TSE-LOK HO

Fiesers' Reagents for Organic Synthesis

VOLUME
28

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Reagents for Organic Synthesis

Fiesers'

Reagents for Organic Synthesis

VOLUME TWENTY EIGHT

Tse-Lok Ho

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PREFACE

This volume covers progress of synthetic organic methodologies for the period between the second half of 2011 and the end of 2012, also a few items of yester-years. The major advances have been refinements of reagent applications and expansion of the scope. Although ligands still figure prominently in affecting reactivities of transition metal ions, work aiming at finding ligand-free reactions remains an honorable goal. Fruitful developments concerning oxidative coupling reactions that eschew halogen compounds are also in evidence. It is noted that burgeoning contributions to synthetic methodology are coming from Chinese chemists, perhaps reflecting societal changes from one of most populous nations. Or they are spiritually ingrained in the expostulation of the benevolent Han tribe leader, King Tang of the Shang Dynasty (商湯), who had a bath tub engraved to remind himself to refine his character while cleansing:

REINVIGORATE TODAY　　苟日新
REINVIGORATE EVERY DAY　日日新

Doesn't this maxim somehow coincide with the effort of synthetic organic chemists?

GENERAL ABBREVIATIONS

Ac	acetyl
acac	acetylacetonate
Ad	1-adamantyl
AIBN	2,2′-azobisisobutyronitrile
aq	aqueous
Ar	aryl
9-BBN	9-borabicyclo[3.3.1]nonane
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
BINOL	1,1′-binaphthalene-2,2′-diol
Bn	benzyl
Boc	*t*-butoxycarbonyl
bpy	2,2′-bipyridyl
bpz	2,2′-bipyrazine
BQ	1,4-benzoquinone
Bs	benzenesulfonyl
Bu	*n*-butyl
Bz	benzoyl
18-c-6	18-crown-6
c-	cyclo-
CAN	cerium(IV) ammonium nitrate
cap	caprolactamate
Cbz	benzyloxycarbonyl
cod	1,5-cyclooctadiene
Cp	cyclopentadienyl
*Cp**	1,2,3,4,5-pentamethylcyclopentadienyl
CSA	10-camphorsulfonic acid
Cy	cyclohexyl
DABCO	1,4-diazabicyclo[2.2.2]octane
DAST	(diethylamino)sulfur trifluoride
dba	dibenzylideneacetone
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	1,3-dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DEAD	diethyl azodicarboxylate

DIAD	diisopropyl azodicarboxylate
Dibal-H	diisobutylaluminum hydride
DMA	*N,N*-dimethylacetamide
DMAP	4-dimethylaminopyridine
DMDO	dimethyldioxirane
DME	1,2-dimethoxyethane
DMF	*N,N*-dimethylformamide
DMPU	*N,N′*-dimethylpropyleneurea
DMSO	dimethyl sulfoxide
DPM	dipivaloylmethane
DPPB	1,4-bis(diphenylphosphino)butane
DPPE	1,2-bis(diphenylphosphino)ethane
DPPF	1,1′-bis(diphenylphosphino)ferrocene
DPPP	1,3-bis(diphenylphosphino)propane
DTTB	4,4′-di-*t*-butylbiphenyl
ee	enantiomer excess
Et	ethyl
Fc	ferrocenyl
Fmoc	9-fluorenylmethoxycarbonyl
Fu	2-furyl
HMDS	hexamethyldisilazane
HMPA	hexamethylphosphoric amide
Hx	*n*-hexyl
L	ligand
LAH	lithium aluminum hydride
LDA	lithium diisopropylamide
LHMDS	lithium hexamethyldisilazide
LiDBB	lithium 4,4′-di-*t*-butylbiphenylide
LTMP	lithium, 2,2,6,6-tetramethylpiperidide
LN	lithium naphthalenede
MCPBA	*m*-chloroperbenzoic acid
Me	methyl
MEM	methoxyethoxymethyl
Mes	mesityl
MOM	methoxymethyl
Ms	methanesulfonyl
MS	molecular sieve
MTO	methyltrioxorhenium
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NIS	*N*-iodosuccinimide

NMO	*N*-methylmorpholine *N*-oxide
NMP	*N*-methylpyrrolidone
Np	naphthyl
Ns	*p*-nitrobenzenesulfonyl
Nu	nucleophile
Oc	*n*-octyl
PEG	poly(ethylene glycol)
Ph	phenyl
Phen	1,10-phenanthroline
Pht	phthaloyl
Pin	pinacolato
Piv	pivaloyl
PMB	*p*-methoxybenzyl
PMHS	poly(methylhydrosiloxane)
PMP	*p*-methoxyphenyl
Pr	*n*-propyl
Py	pyridine
RaNi	Raney nickel
RCM	ring-closing metathesis
R^F	perfluoroalkyl
ROMP	ring opening methathesis polymerization
s-	secondary
salen	*N,N′*-ethenebis(salicylideneiminato)
SAMP	(*S*)-1-amino-2-methoxymethylpyrrolidine
SEM	2-(trimethylsilyl)ethoxymethyl
SES	2-[(trimethylsilyl)ethyl]sulfonyl
TBAF	tetrabutylammonium fluoride
TBDPS	*t*-butyldiphenylsilyl
TBS	*t*-butyldimethylsilyl
TEMPO	2,2,6,6-tetramethylpiperidinoxy
TES	triethylsilyl
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid
TFAA	trifluoroacetic anhydride
THF	tetrahydrofuran
THP	tetrahydropyranyl
TIPS	triisopropylsilyl
TMEDA	*N,N,N′,N′*-tetramethylethanediamine
TMS	trimethylsilyl
Tol	*p*-tolyl
tpp	tetraphenylporphyrin

Ts	*p*-toluenesulfonyl
TSE	2-(trimethylsilyl)ethyl
Z	benzyloxycarbonyl
Δ	heat
))))	ultrasound

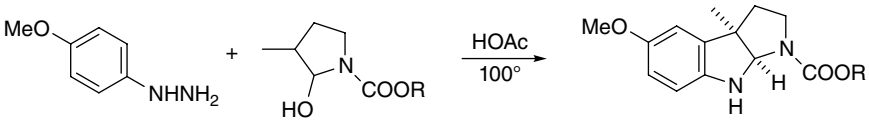
REFERENCE ABBREVIATIONS

ACIE	Angew. Chem. Inter. Ed.
ASC	Adv. Synth. Catal.
CAJ	Chem. Asian J.
CC	Chem. Commun.
CEJ	Chem. Eur. J.
ChJC	Chinese. J. Chem.
CL	Chem. Lett.
CO	ChemistryOpen
CS	Chem. Science
CSR	Chem. Soc. Rev.
EJOC	Eur. J. Org. Chem.
HCA	Helv. Chim. Acta
JACS	J. Am. Chem. Soc.
JCCS	J. Chinese Chem. Soc.
JOC	J. Org. Chem.
OBC	Org. Biomol. Chem.
OL	Org. Lett.
S	Synthesis
SL	Synlett
T	Tetrahed.
TL	Tetrahed. Lett.

A

Acetic acid

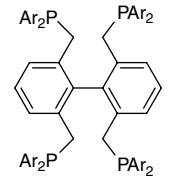
Fischer indole synthesis. The pyrroloindole ring system characterized of the physostigmine alkaloids is formed in the interrupted indolization between an arylhydrazine and *N*-protected 2-hydroxy-3-methylpyrrolidine, and it is accomplished in hot HOAc.[1]



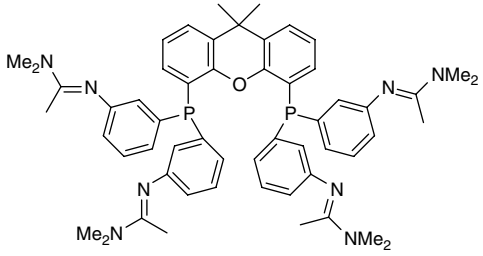
[1] Schammel, A.W., Chiou, G., Garg, N.K. *JOC* **77**, 725 (2012)

Acetylacetonato(dicarbonyl)rhodium(I)

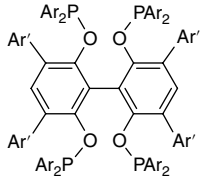
Addition. With ligand **1** hydroformylation of 2-alkenes catalyzed by (acac)Rh(CO)$_2$ proceeds via a double bond shift.[1] In the presence of an amine the reaction becomes a hydroamination process (amino group introduced at the carbon chain terminus).[2]



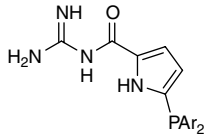
(**1**)



(**2**)



(**3**) Ar = pyrrol-1-yl
Ar′ = 2,4-$F_2C_6H_3$



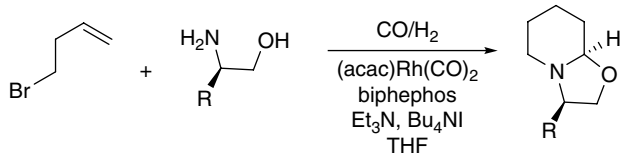
(**4**)

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Ligand **2** is for linear hydroformylation of 1-alkenes, in which the amidate groups bring the catalyst into the aqueous phase as the bicarbonate salt is formed.[3] Developed for highly linear hydroformylation of 1-alkenes, including allyl cyanides, is a ligand series represented by **3**.[4]

When ligands such as **4** for the Rh catalyst are used the aldehyde products undergo reduction to yield primary alcohols.[5] Simpler ligands such as $(4\text{-}FC_6H_4)_3P$ can be used in the hydroacylation of enamides to form 1,4-dicarbonyl compounds.[6]

Homoallylic alcohols form 5-membered cyclic products even if the new CC bond formation is with the internal sp^2-carbon atom.[7] Double trapping of the homologous aldehyde derived from 4-bromo-1-butene with 2-phenyl-2-aminoethanol leads to a bicyclic heterocycle which is amenable to substitution at the α-carbon to the nitrogen atom.[8]



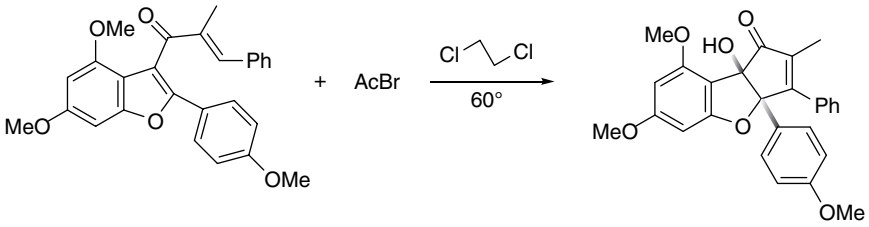
Under normal hydroformylation condition but with addition of a secondary amine and 2,2′,6,6′-tetrakis(diphenylphosphinomethyl)biphenyl to the reaction mixture, Schiff bases are formed and then reduced.[9]

Decarbonylation. The removal of CO from 2-(2-acylaryl)pyridines by heating with $(acac)Rh(CO)_2$ is of synthetic interests because the ketone substrates are generally more readily accessible.[10]

[1] Cai, C., Yu, S., Liu, G., Zhang, X., Zhang, X. *ASC* **353**, 2665 (2011)
[2] Liu, G., Huang, K., Cao, B., Chang, M., Li, S., Yu, S., Zhou, L., Wu, W., Zhang, X. *OL* **14**, 102 (2012)
[3] Mokhadinyana, M., Desset, S.L., Williams, D.B.G., Cole-Hamilton, D.J. *ACIE* **51**, 1648 (2012)
[4] Cai, C., Yu, S., Cao, B., Zhang, X. *CEJ* **18**, 9992 (2012)
[5] Fuchs, D., Rousseau, G., Diab, L., Gellrich, U., Breit, B. *ACIE* **51**, 2178 (2012)
[6] Zhang, H.-J.,Bolm, C. *OL* **13**, 3900 (2011)
[7] Ueki, Y., Ito, H., Usui, I., Breit, B. *CEJ* **17**, 8555 (2011)
[8] Zill, N., Schoenfelder, A., Girard, N., Taddei, M., Mann, A. *JOC* **77**, 2246 (2012)
[9] Liu, G., Huang, K., Cai, C., Cao, B., Chang, M., Wu, W., Zhang, X. *CEJ* **17**, 14559 (2011)
[10] Lei, Z.-Q., Li, H., Li, Y., Zhang, X.-S., Chen, K., Wang, X., Sun, J., Shi, Z.-J. *ACIE* **51**, 2690 (2012)

Acetyl bromide

Nazarov cyclization. Cross-conjugated ketones in which one of the double bonds belongs to a benzofuran nucleus undergo Nazarov cyclization.[1] Enolacetylation to create a highly electrophilic moiety for the reaction to proceed is most likely.



[1] Magnus, P., Freund, W.A., Moorhead, E.J., Rainey, T. *JACS* **134**, 6140 (2012)

1-Acyl-1,5-diazabicyclo[4.3.0]non-5-ene tetraphenylborates

O-Acylation. These reagents are excellent acyl donors to OH-compounds.[1]

[1] Taylor, J.E., Williams, J.M.J., Bull, S.D. *TL* **53**, 4074 (2012)

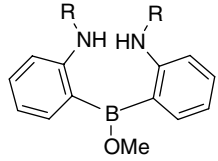
1-Acylpyrazoles

Acylation. A review of the acylating capability of 1-acylpyrazoles has been published.[1]

[1] Goldys, A.M., McErlean, C.S.P. *EJOC* 1877 (2012)

Alkoxybis(2,2′-aminomethylphenyl)boranes

Alcoholysis. Alkoxyboranes **1** are useful catalysts for cleavage of 1,3-dicarbonyl compounds such as β-keto esters and *N*-acylamides by alcohols under essentially neutral conditions. These boranes perform activation on both reactants.[1]

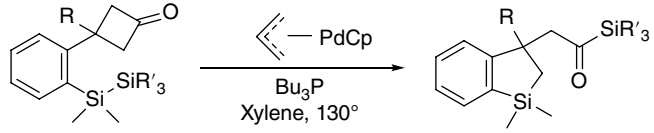


(**1**) R = Me, Cy

[1] Oishi, S., Saito, S. *ACIE* **51**, 5395 (2012)

η^3-Allyl(cyclopentadienyl)palladium

Cyclomutation.[1] Cleavage of the small ring of 3-arylcyclobutanones that is *o*-substituted by a heteroatom group such as disilane is attended by heterocyclization.



Decarboxylation. Benzyl cyanoacetates extrude CO_2 while the remaining parts recombine to afford 3-arylpropanenitriles. In the case of 2-furylmethyl cyanoacetates the choice of the phosphine ligand affects the recombination step. It can be coaxed toward formation of 2-cyanomethyl-5-methylfurans.[2]

[1] Ishida, N., Ikemoto, W., Murakami, M. *OL* **14**, 3230 (2012)
[2] Recio III, A., Heinzman, J.D., Tunge, J.A. *CC* **48**, 142 (2012)

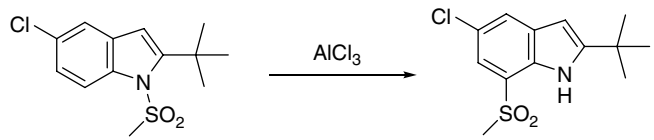
η^3-Allylpalladium molybdosulfide

Allylation.[1] In the presence of $(\eta^3\text{-}C_3H_5)Pd(S_4Mo_3)$ the allylation of arylamines can use allyl alcohol. The allyl group is to be attached to C-3 of an indole nucleus.

[1] Tao, Y., Wang, B., Zhao, J., Song, Y., Qu, L., Qu, J. *JOC* **77**, 2942 (2012)

Aluminum chloride

Group migration. On treatment with $AlCl_3$, the protecting group of *N*-mesylindoles migrates to C-7.[1]



Mannich reaction.[2] Condensation of ArCHO, MeCN and MeCOAr' to afford $ArCH(NHAc)CH_2COAr'$ is observed on treatment with $AlCl_3$ and AcCl. β-Keto esters undergo a similar reaction.

Cyclization. γ,δ–Unsaturated ketones cyclize to form a benzene ring in the presence of $AlCl_3$ in dioxane.[3]

Ether cleavage.[4] Ethers are split by silyldealkylation of ethers using R_3SiCl, with $AlCl_3$ or $FeCl_3$ or $BiCl_3$ as promoter. The other products are RCl.

[1] Prasad, B., Adepu, R., Sandra, S., Rambabu, D., Krishna, G.R., Reddy, C.M., Deora, G.S., Misra, P., Pal, M. *CC* **48**, 10434 (2012)
[2] Ali, Z.M., Ardeshir, K., Mohammad, M., Abdolkarim, Z., Maliheh, S., Fatemeh, D.-P., Hassan, K., Ahmad, A.D.-F., Maria, M. *ChJC* **30**, 345 (2012)
[3] Narender, T., Sarkar, S., Rajendar, K., Tiwari, S. *OL* **13**, 6140 (2011)
[4] Wakabayashi, R., Sugiura, Y., Shibue, T., Kuroda, K. *ACIE* **50**, 10708 (2011)

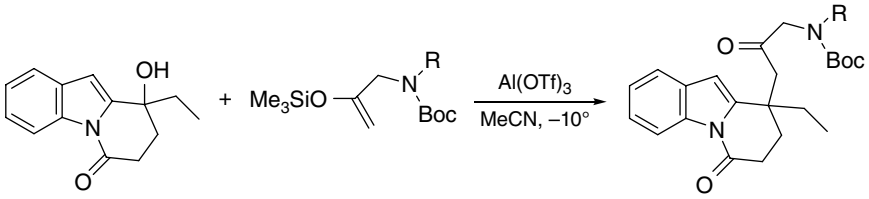
Aluminum fluoride

CH activation. High-surface AlF_3 is able to activate aliphatic C-H bond under very mild conditions (at 40°), and this property can be exploited by deuteration.[1]

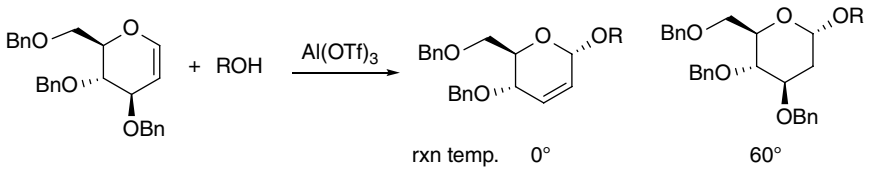
[1] Prechtl, M.H.G., Teltewskoi, M., Dimitrov, A., Kemnitz, E., Braun, T. *CEJ* **17**, 14385 (2011)

Aluminum triflate

Substitution. Benzyl and cinnamyl alcohols are easily converted into the corresponding amines with the aid of $Al(OTf)_3$.[1] Substitution using other nucleophiles are equally smooth, as exemplified in the construction of an intermediate for a synthesis of mersicarpine.[2]



The reaction of tri-*O*-benzylglucal with an alcohol on catalysis by $Al(OTf)_3$ temperature can change the reaction mechanism.[3] At 0° Ferrier rearrangement products are formed but at 60° addition to the double bond is favored.



[1] Ohshima, T., Ipposhi, J., Nakahara, Y., Shibuya, R., Mashima, K. *ASC* **354**, 2447 (2012)
[2] Zhong, X., Li, Y., Han, F.-S. *CEJ* **18**, 9784 (2012)
[3] Williams, D.B.G., Simelane, S.B., Kinfe, H.H. *OBC* **10**, 5636 (2012)

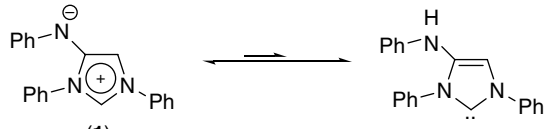
Aluminum tris(2,6-di-β-naphthoxide)

Vinylogous aldol reaction.[1] The title reagent is a more bulky analog of ATPH and perhaps more sensitive to steric effects. Its application as catalyst in site-selective condensation such as reaction between crotonic esters and aldehydes to form 5-hydroxy-2-alkenoates has been demonstrated.

[1] Gazaille, J.A., Sammakia, T. *OL* **14**, 2678 (2012)

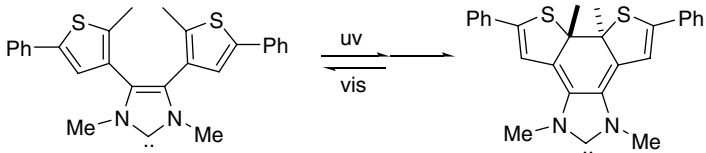
Aminocarbenes

Structural variations. The commercially available mesionic "Nitron" has an *N*-heterocyclic carbene (NHC) tautomer, but its application in directing reactions has yet to be explored.[1] Electron properties and stability of imidazole-based mesionic carbenes (imidazol-5-ylidenes) are found to be inversely correlated.[2]



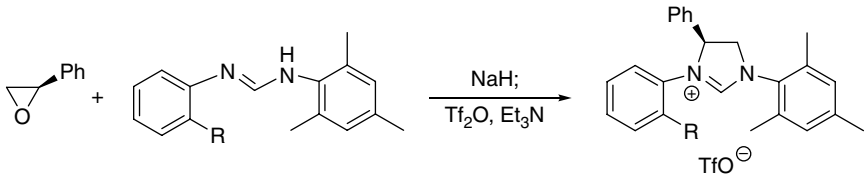
(**1**)

Imidazolium and imidazolinium bicarbonate salts are air-stable precursors of NHC's.[3] 1,3-Bis(2,6-dimethoxyphenyl)imidazol-2-ylidene is a typical electron-rich carbene.[4] A photoswitchable NHC pair is **2A** and **2B**, interconverted by uv and visible lights.[5]

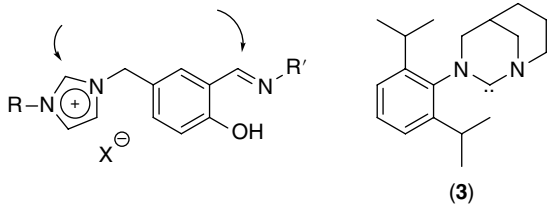


(**2A**) (**2B**)

A convenient method for synthesis of chiral imidazolium salts, precursors of NHC's, is based on reaction of *N,N′*-disubstituted amidines and chiral oxiranes.[6]

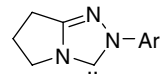


Imidazolium salts that bear an *N*-substituent extended to a salicyldiminato function are versatile precursors of multipurpose and tunable catalysts. Two sites for metal bonding are obvious.[7] A new type of the carbene is represented by **3** which in placing one of the nitrogen atoms at a bridgehead prevents its lone pair electrons to delocalize and therefore increases the electrophilicity of the carbene center while keeping nucleophilicity the same.[8]



(**3**)

Reduction. Transfer reduction of carbonyl compounds by *i*-PrOH is effected with 1,3-diarylimidazolium tetrafluoroborate (each aryl group being 4-substituted) and KOH.[9] Ketones and imines are reduced via hydrosilylation, with **4A** as catalyst.[10] By this procedure the multiple bond of propargylic alcohols and cinnamyl alcohols are reduced, the former class of compounds to be converted into allylic alcohols.[11]

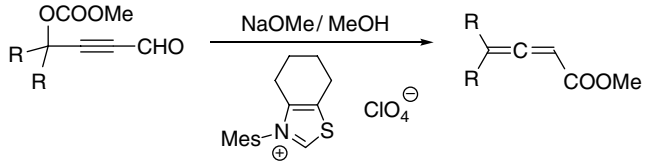


(**4A**) Ar = Ph
(**4B**) Ar = Mes
(**4C**) Ar = C_6F_5

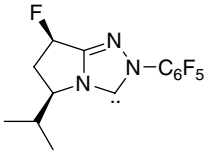
Formation of 3-acyloxy-2-indolinones from isatins and aldehydes is achieved by heating with **4B** and *t*-BuOK in toluene.[12] The aldehydes become the acyl moiety. The effect of **4B** on tri-*O*-benzylfuranoses such as the ribose derivative is that debenzyloxylation occurs at C-2 while oxidation to the γ-lactones is the complementary reaction.[13]

Oxidative functionalization of aldehydes. The most extensive uses of NHC's appear to involve transformation of aldehydes. For example, under oxygen aldehydes and alkyl halides form esters under the influence of the ylide (carbene) derived from 3,4-dimethylthiazole iodide.[14] Type **4** NHC unites aldehydes and thiols to give thioesters,[15] and carboxylic acids are obtained when **4C** exerts its effect.[16] Aldehydes and $ArB(OH)_2$ also combine to yield aryl esters,[17] otherwise anodic oxidation of aldehydes in alcohols to furnish esters is catalyzed by a thiazole carbene.[18]

α-Halocinnamaldehydes lose the halogen substituent during conversion to the cinnamic esters,[19] and an intramolecular redox transformation of 2-alkynals with a carbonato substituent at C-4 leads to 2,3-alkadienoic esters.[20]



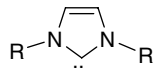
Addition. α-Cyanohydrin ester formation[21] from aldehydes on NHC-catalyzed reaction with acetyl cyanide or ethyl cyanoformate is somewhat unusual. The fluorinated carbene **5** is useful for promoting hydroacylation of cinnamic esters by aldehydes.[22]



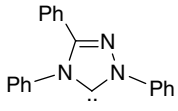
(**5**)

Perhaps the perennial favorite among NHC's, **6A** (often called IPr), helps the union of dimethylamine and CO to form DMF.[23] Actually a general procedure for formylation of amines is that involving a polysiloxane.[24]

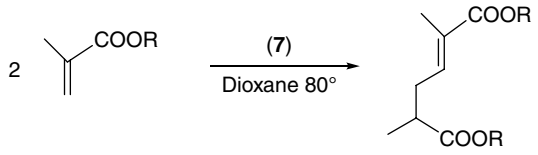
The triazole-based carbene **7** can cause tail-to-tail dimerization of methacrylic esters[25] because it confers the β-carbon of the ester with anionic properties.[26]



(**6A**) R = 2,6-*i*Pr$_2$C$_6$H$_3$
(**6B**) R = 2,4,6-Me$_3$C$_6$H$_2$
(**6C**) R = Cy



(**7**)

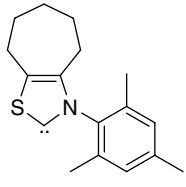


Conjugate addition of aldehydes to vinyl sulfones is akin to the Stetter reaction. A bicyclic thiazole carbene **8** is an active catalyst.[27] However, a carbene can transform α-bromo enals into acylate azolium salts which act as Michael acceptors for β-keto esters.[28]

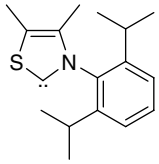
Stable esters can be activated by carbenes to form enolates (not involving ketene intermediates), as shown by a synthesis of 3,4-dihydropyridones from reaction with conjugated imines.[29]

In conjunction with metallic catalysts that fashion and combine a 2-diazo-1,3-diketone and a functionalized alkene ready for Michael addition, an NHC effectively completes the final step leading to a spirolactone or lactam.[30]

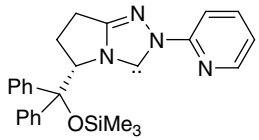
Benzoin condensation and related reactions. Cross-benzoin condensation using **9** which is generated in situ also from a perchlorate salt is successful.[31] As for asymmetric benzoin condensation, **10** has been developed.[32]



(**8**)

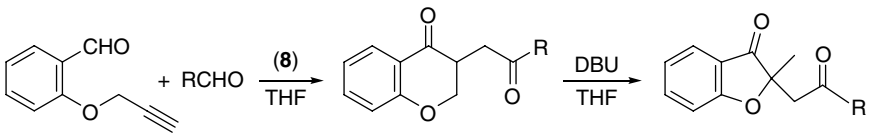


(**9**)

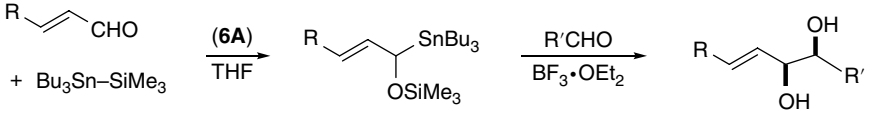


(**10**)

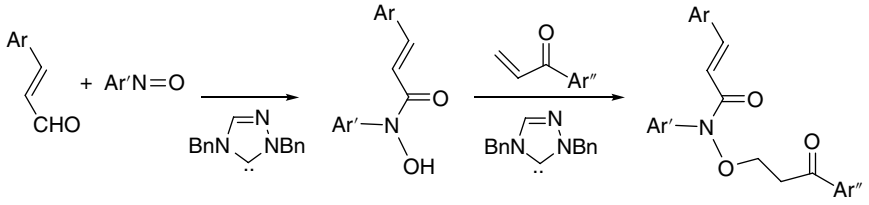
It is quite remarkable that two research groups reported at about the same time the same kind of transformation using the same bicyclic thiazole carbene **8**.[33,34]



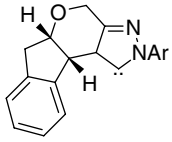
Conjugated aldehydes form 1-tributylstannyl-1-trimethylsiloxy-2-alkenes in a carbene-mediated reaction. The adducts are useful for synthesis of unsaturated diols by further reaction with RCHO in the presence of $BF_3{\cdot}OEt_2$.[35]



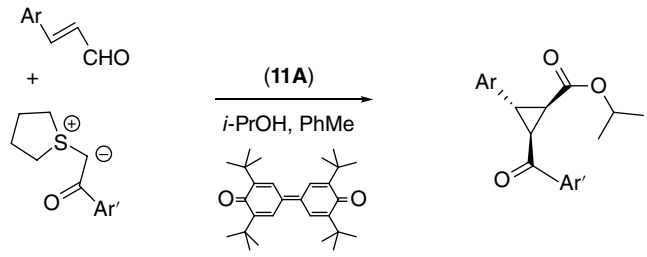
N-(2-Aroylethoxyl) cinnamides are assembled from cinnamaldehydes, nitrosoarenes and aryl vinyl ketones. The first step which forms the hydroxamic acids can be considered as an aza-benzoin condensation.[36]



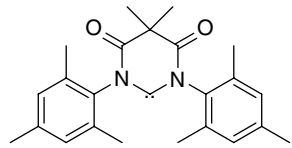
Annulation. The sulfur ylide reaction with electron-deficient alkenes to form cyclopropane derivatives as applied to conjugated aldehydes can give ester products by intervention of carbene **11A**.[37] In the case of spirlactonization of isatin a conjugated aldehyde is transformed into an equivalent of a chiral carboxylic acid β-anion by *ent*-**11B**.[38] Oxindole-3-imines form spirolactams on reaction with conjugated aldehydes.[39]



(**11A**) Ar = Mes
(**11B**) Ar = 2,6-$Et_2C_6H_3$

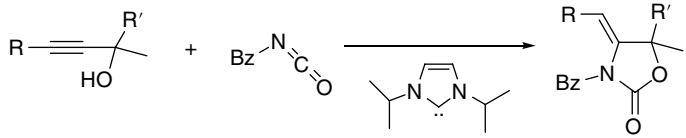


Total consumption of **12** on reaction with alkynes is as expected, adducts of which afford cyclopropenones on hydrolysis.[40] Nitriles also undergo cycloaddition with **12**.



(**12**)

Along with a Lewis acid, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene **6A** or its dihydro derivative is capable of mediating insertion of CO_2 into oxiranes to yield dioxolan-2-ones.[41] A similar transformation is the formation of 4-alkylidene-oxazolidin-2-ones where a carbene serves as a Brønsted base.[42]

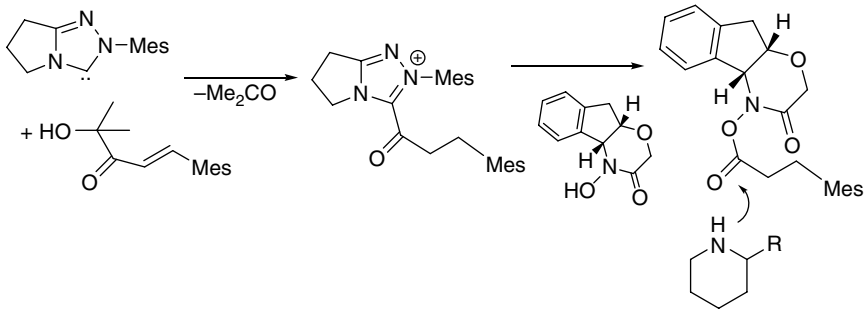


NHC's help unfold the nucleophilicity of saturated aldehydes, as seen in the facile assemblage of 3,4-dihydro-2-pyrones and 2-pyridones.[43] A formal [3+2]cycloaddition between conjugated aldehydes and isatin imines leads to spiroannulated oxindoles, with the formyl group being converted into a lactamic carbonyl by intervention of **6B**.[44]

Decomposition of the Diels-Alder adduct of 1-trimethylsiloxy-1,3-butadiene and acrylyl fluoride to afford 1,3-cyclohexadiene is a favorable reaction, in which Me_3SiF and CO_2 are eliminated.[45] The role of carbene for the two-step process is not clear.

A theoretical study (DFT calculation) indicates the cocatalytic NHC and $Ti(OR)_4$ to develop *cis*-3,4-disubstituted cyclopentenes is due to involvement of a chelated intermediate.[46]

Kinetic resolution. 2-Substituted cyclic amines are resolved via *N*-acylation. The acylating agent is derived from a chiral *O*-acylhydroxamate.[47]



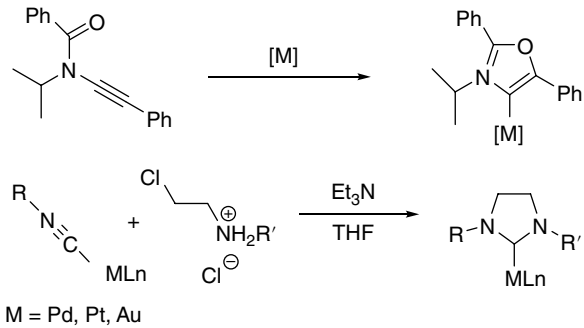
[1] Färber, C., Leibold, M., Bruhn, C., Maurer, M., Siemeling, U. *CC* **48**, 227 (2012)
[2] Ung, G., Bertrand, G. *CEJ* **17**, 8269 (2011)

[3] Fevre, M., Pinaud, J., Leteneur, A., Gnanou, Y., Vignolle, J., Taton, D., Miqueu, K., Sotiropoulos, J.-M. *JACS* **134**, 6776 (2012)
[4] Schedler, M., Fröhlich, R., Daniliuc, C.-G., Glorius, F. *EJOC* 4164 (2012)
[5] Neilson, B.M., Bielawski, C.W. *JACS* **134**, 12693 (2012)
[6] Zhang, J., Su, X., Fu, J., Shi, M. *CC* **47**, 12541 (2011)
[7] Zhong, R., Wang, Y.-N., Guo, X.-Q., Chen, Z.-X., Hou, X.-F. *CEJ* **17**, 11041 (2011)
[8] Martin, D., Lassauque, N., Donnadieu, B., Bertrand, G. *ACIE* **51**, 6172 (2012)
[9] Ikhile, M.I., Nyamori, V.O., Bala, M.D. *TL* **53**, 4925 (2012)
[10] Zhao, Q., Curran, D.P., Malacria, M., Fensterbank, L., Goddard, J.-P., Lacôte, E. *SL* 433 (2012)
[11] Zhao, Q., Curran, D.P., Malacria, M., Fensterbank, L., Goddard, J.-P., Lacôte, E. *CEJ* **17**, 9911 (2011)
[12] Du, D., Lu, Y., Jin, J., Tang, W., Lu, T. *T* **67**, 7557 (2011)
[13] Wendeborn, S., Mondière, R., Keller, I., Nussbaumer, H. *SL* 541 (2012)
[14] Li, Y., Du, W., Deng, Q.-P. *T* **68**, 3611 (2012)
[15] Uno, T., Inokuma, T., Takemoto, Y. *CC* **48**, 1901 (2012)
[16] Kuwano, S., Harada, S., Oriez, R., Yamada, K. *CC* **48**, 145 (2012)
[17] Meng, J.-J., Gao, M., Wei, Y.-P., Zhang, W.-Q. *CAJ* **7**, 872 (2012)
[18] Finney, E.E., Ogawa, K.A., Boydston, A.J. *JACS* **134**, 12374 (2012)
[19] Wang, X.-B., Zou, X.-L., Du, G.-F., Liu, Z.-Y., Dai, B. *T* **68**, 6498 (2012)
[20] Zhao, Y.-M., Tam, Y., Wang, Y.-J., Li, Z., Sun, J. *OL* **14**, 1398 (2012)
[21] Zhang, J., Du, G.F., Xu, Y.K., He, L., Dai, B. *TL* **52**, 7153 (2011)
[22] Sanchez-Larios, E., Thai, K., Bilodeau, F., Gravel, M. *OL* **13**, 4942 (2011)
[23] Li, X., Liu, K., Xu, X., Ma, L., Wang, H., Jiang, D., Zhang, Q., Lu, C. *CC* **47**, 7860 (2011)
[24] Jacquet, O., Gomes, C.D.N., Ephritikhine, M., Cantat, T. *JACS* **134**, 2934 (2012)
[25] Biju, A.T., Padmanaban, M., Wurz, N.E., Glorius, F. *ACIE* **50**, 8412 (2011)
[26] Matsuoka, S., Ota, Y., Washio, A., Katada, A., Ichioka, K., Takagi, K., Suzuki, M. *OL* **13**, 3722 (2011)
[27] Bhunia, A., Yetra, S.R., Bhojgude, S.S., Biju, A.T. *OL* **14**, 2830 (2012)
[28] Yao, C., Wang, D., Lu, J., Li, T., Jiao, W., Yu, C. *CEJ* **18**, 1914 (2012)
[29] Hao, L., Du, Y., Lv, H., Chen, X., Jiang, H., Shao, Y., Chi, Y.R. *OL* **14**, 2154 (2012)
[30] Boddaert, T., Coquerel, Y., Rodriguez, J. *EJOC* 5061 (2011)
[31] Piel, I., Pawelczyk, M.D., Hirano, K., Fröhlich, R., Glorius, F. *EJOC* 5475 (2011)
[32] Soeta, T., Tabatake, Y., Inomata, K., Ukaji, Y. *T* **68**, 894 (2012)
[33] Padmanaban, M., Biju, A.T., Glorius, F. *OL* **13**, 5624 (2011)
[34] Franz, J.F., Fuchs, P.J.W., Zeitler, K. *TL* **52**, 6952 (2011)
[35] Blanc, R., Nava, P., Rajzman, M., Commeiras, L., Parrain, J.-L. *ASC* **354**, 2038 (2012)
[36] Sun, Z.-X., Cheng, Y. *EJOC* 4982 (2012)
[37] Biswas, A., De Sarkar, S., Tebben, L., Studer, A. *CC* **48**, 5190 (2012)
[38] Dugal-Tessier, J., O'Bryan, E.A., Schroeder, T.B.H., Cohen, D.T., Scheidt, K.A. *ACIE* **51**, 4963 (2012)
[39] Lv, H., Tiwari, B., Mo, J., Xing, C., Chi, Y.R. *OL* **14**, 5412 (2012)
[40] Moerdyk, J.P., Bielawski, C.W. *JACS* **134**, 6116 (2012)
[41] Liu, X., Cao, C., Li, Y., Guan, P., Yang, L., Shi, Y. *SL* 1343 (2012)
[42] Jo, K.A., Maheswara, M., Yoon, E., Lee, Y.Y., Yun, H., Kang, E.J. *JOC* **77**, 2924 (2012)
[43] Zhao, X., Ruhl, K.E., Rovis, 2. *ACIE* **51**, 12330 (2012)
[44] Zhang, B., Feng, P., Sun, L.-H., Cui, Y., Ye, S., Jiao, N. *CEJ* **18**, 9198 (2012)
[45] Ryan, S., Candish, L., Lupton, D.W. *SL* 2275 (2011)
[46] Domingo, L.R., Zaragozá, R.J., Arnó, M. *OBC* **9**, 6616 (2011)
[47] Binanzer, M., Hsieh, S.-Y., Bode, J.W. *JACS* **133**, 19698 (2011)

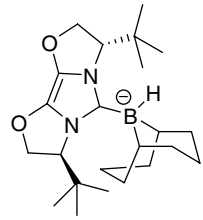
Aminocarbene - metal complexes

The more extensively employed metal-carbene complexes are grouped and discussed individually.

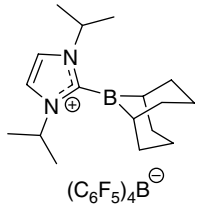
Preparation. Ynamides are useful precursors of unstable NHC's.[1]



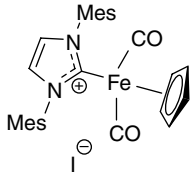
Reduction. Ligand exchange removes Me_2S from borane and the boron atom is linked to a carbene center, the resulting stable solid (to air, water and chromatography) retains power of reducing the carbonyl group with silica promotion.[2] One, two or all three hydrides is transferrable, and no quench or workup is needed. Furthermore, aldehydes can be reduced selectively in the presence of ketones. The use of a more complex entity **12** for asymmetric reduction also has been reported.[3] The salt **13** is a catalyst for hydrogenation of imines and enamines,[4] whereas the iron complex **14A** is active in hydrosilylation of imines under visible light.[5] Complex **14B** is prepared from the imidazolium iodide with an N-substituent bearing a terminal cyclopentadiene unit and $Fe_3(CO)_{12}$, and it serves as a catalyst for sulfoxide reduction.[6]



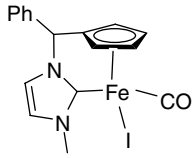
(**12**)



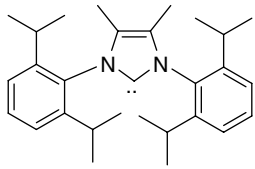
(**13**)



(**14A**)



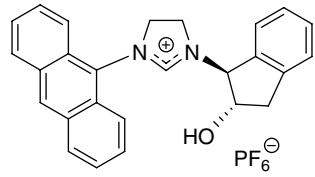
(**14B**)



(**15**)

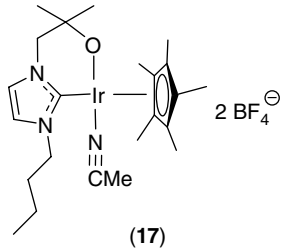
Catalyzing semihydrogenation of alkynes, allenes and dienes with hydrosilane assisted by the complex **15** is a pleasing discovery.[7]

Substitution. Regioselective S_N2' displacement of allyl phosphates with organoboronates is achieved, using the unsymmetrical carbene complex generated from **16** and CuCl.[8] For carboxylation of benzoxazole and benzothiazole the effectiveness of a 1,2, 3-triazol-5-ylidene CuCl is recognized.[9]



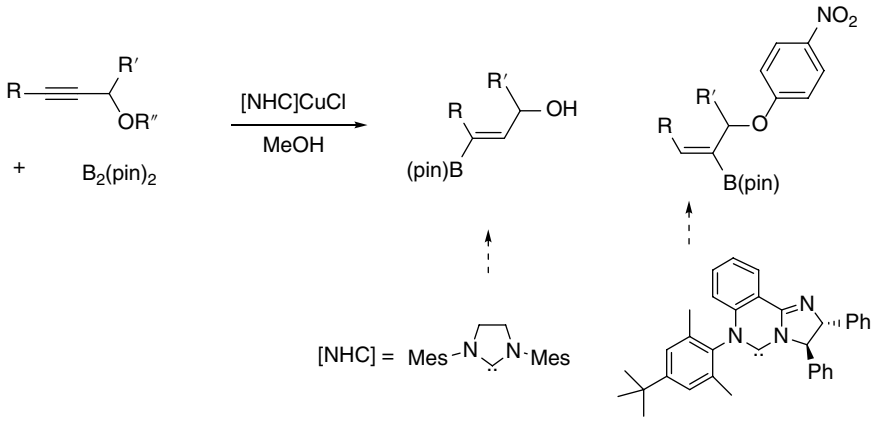
(**16**)

Primary alcohols are viable substrates for *N*-alkylation of amines, when the iridium complex **17** is present in the reaction media.[10]



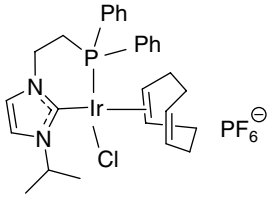
(**17**)

Addition. Hydroboration of propargylic alcohols with (bispinacolato)diboron places the boryl group at the carbon farther from the hydroxyl function, but that of their *p*-nitrophenyl ethers shows an opposite regioselectivity, although different Cu-carbenoids are involved.[11]

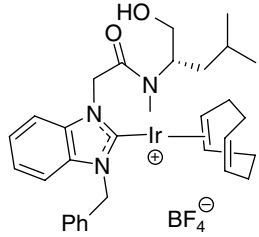


Alkylboranes obtained from hydroboration with 9-BBN deliver 1-aminoalkanes on reaction with hydroxylamine *O*-benzoates in the presence of **5C**-CuCl.[12] Carboxylation is done with CO_2 (catalyst from **6A**-CuCl and MeOLi).[13] Borylcarboxylation of alkynes catalyzed by a copper(I)-carbene provides 4-borato-2-buten-4-olides which are valuable substrates for Suzuki coupling.[14]

An iridium(I) salt in which the metal center is surrounded by **6B**, 1,5-cyclooctadiene, and Bn_3P is serviceable for hydrogenation of alkenes.[15] Another complex (**18**) that one of the imidazoline nitrogen atoms is connected to a phosphinated sidechain is able to catalyze transfer hydrogenation of conjugated ketones (to give saturated alcohols), as well as alkylation of α-arylethanol with primary alcohols [to yield ArCH(OH)CH_2CH_2R],[16] hydrosilylation to produce chiral benzylic alcohols is effected in the presence of **19**.[17]

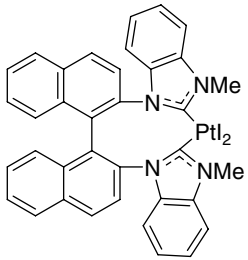


(**18**)

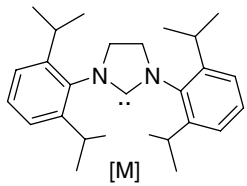


(**19**)

An ionic Pt-complex derived from **20** and $AgBF_4$ is shown to promote intramolecular hydroamination.[18] For accomplishing selective cyclization involving one of two double bonds a lanthanide complex (**21**) proves its value.[19]

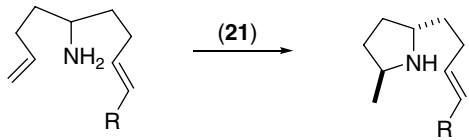


(**20**)



[M] = $Sc(NSiMe_3)_2$, $Y(NSiMe_3)_2$

(**21**)



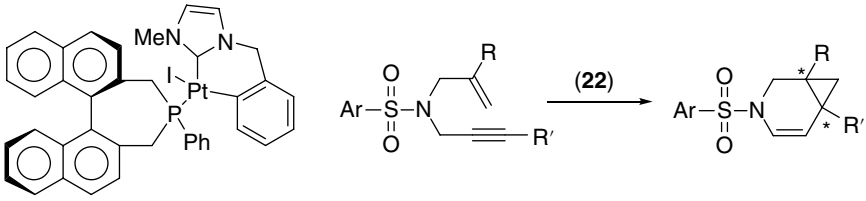
Condensation of RCHO, amines and 1-alkynes to form propargylic amines is also effected by a carbene-AgOAc complex.[20]

(*E*)-3-Chloro-2-alkenoylarenes are adducts of ArCOCl and 1-alkynes, formed in a reaction catalyzed by **6A**-Ir(cod)Cl.[21]

Upon conversion of the type **6** carbene-bound CuCl to CuF·HF by $AgHF_2$ or $Et_3N(HF)_3$ - *t*-BuOK, a catalytic activity for promoting diastereoselective allylation of *N*-*t*-butanesulfinyl aldimines is revealed.[22]

Change of a non-carbene ligand to modify properties of the complex is also the case of **6A**-$GaCl_3$, the replacement of a chlorine atom with a 2,4,6-trifluorophenylcyanide ligand renders the resulting complex more active as a π-Lewis acid with increasing resistance to hydrolysis.[23]

Cycloisomerization. The Pt-carbenoid **22** is the motivator for transforming 1,6-enynes to bicycle[4.1.0]heptenes.[24]



(**22**)

[1] Ung, G., Mendoza-Espinosa, D., Bertrand, G. *CC* **48**, 7088 (2012)
[2] Taniguchi, T., Curran, D.P. *OL* **14**, 4540 (2012)
[3] Curran, D.P., Solovyev, A., Brahmi, M.M., Fensterbank, L., Malacria, M., Lacôte, E. *ACIE* **50**, 10294 (2011)
[4] Farrell, J.M., Hatnean, J.A., Stephan, D.W. *JACS* **134**, 15728 (2012)
[5] Castro, L.C.M., Sortais, J.-B., Darcel, C. *CC* **48**, 151 (2012)
[6] Cardoso, J.M.S., Royo, B. *CC* **48**, 4944 (2012)
[7] Semba, K., Fujihara, T., Xu, T., Terao, J., Tsuji, Y. *ASC* **354**, 1542 (2012)
[8] Shintani, R., Takatsu, K., Takeda, M., Hayashi, T. *ACIE* **50**, 8656 (2011)
[9] Inomata, H., Ogata, K., Fukuzawa, S., Hou, Z. *OL* **14**, 3986 (2012)
[10] Bartoszewicz, A., Marcos, R., Sahoo, S., Inge, A.K., Zou, X., Martin-Matute, B. *CEJ* **18**, 14510 (2012)
[11] Park, J.K., Ondrusek, B.A., McQuade, D.T. *OL* **14**, 4790 (2012)
[12] Rucker, R.P., Whittaker, A.M., Dang, H., Lalic, G. *JACS* **134**, 6571 (2012)
[13] Ohishi, T., Zhang, L., Nishiura, M., Hou, Z. *ACIE* **50**, 8114 (2011)
[14] Zhang, L., Cheng, J., Carry, B., Hou, Z. *JACS* **134**, 14314 (2012)
[15] Bennie, L.S., Fraser, C.J., Irvine, S., Kerr, W.J., Andersson, S., Nilsson, G.N. *CC* **47**, 11653 (2011)
[16] Gong, X., Zhang, H., Li, X. *TL* **52**, 5596 (2011)
[17] Kawabata, S., Tokura, H., Chiyojima, H., Okamoto, M., Sakaguchi, S. *ASC* **354**, 807 (2012)
[18] Zhang, R., Xu, Q., Mei, L., Li, S., Shi, M. *T* **68**, 3172 (2012)
[19] Jiang, T., Livinghouse, T., Lovick, H.M. *CC* **47**, 12861 (2011)
[20] Chen, M.-T., Landers, B., Navarro, O. *OBC* **10**, 2206 (2012)
[21] Iwai, T., Fujihara, T., Terao, J., Tsuji, Y. *JACS* **134**, 1268 (2012)
[22] Vergote, T., Nahra, F., Welle, A., Luhmer, M., Wouters, J., Mager, N., Riant, O., Leyssens, T. *CEJ* **18**, 793 (2012)
[23] Tang, S., Monot, J., El-Hellani, A., Michelet, B., Guillot, R., Bour, C., Gandon, V. *CEJ* **18**, 10239 (2012)
[24] Jullien, H., Brissy, D., Sylvain, R., Retailleau, P., Naubron, J.-V., Gladiali, S., Marinetti, A. *ASC* **353**, 1109 (2011)

O-(2-Aminoethyl)diphenylborinate

Alcohol functionalization. With the title reagent as catalyst, regioselectivity for mono-acylation, sulfonylation and alkylation of diols and sugars is observed.[1] It can also be used in Koenigs-Knorr glycosylation.[2]

[1] Lee, D., Williamson, C.L., Chan, L., Taylor, M.S. *JACS* **134**, 8260 (2012)
[2] Gouliaras, C., Lee, D., Chan, L., Taylor, M.S. *JACS* **133**, 13926 (2011)

Antimony(III) chloride

Benzylation. Friedel-Crafts benzylation with ArCH(OH)R succeeds by using $SbCl_3$ as catalyst.[1]

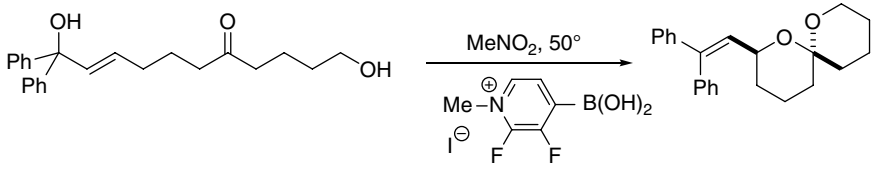
[1] Shukla, P., Choudhary, M.K., Nayak, S.K. *SL* 1585 (2011)

Arylboronic acids

Functionalization. For conversion of $ArB(OH)_2$ into $ArNH_2$, 2,4-dinitrophenoxyamine is an adequate reagent,[1] and phenols are produced by oxidation with tolyldimethylamine oxide.[2]

Condensation. 2-Iodo-5-methoxyphenylboronic acid acts as a stable and recyclable catalyst for the direct amidation of carboxylic acids at room temperature, 4A-MS is also required for the dehydration.[3]

Friedel-Crafts reaction. 2,3-Difluoro-1-methylpyridinium-4-boronic acid iodide is a useful activator of allylic alcohols for cyclization onto an aromatic ring and formation of spiroacetals.[4] Friedel-Crafts alkylation of arenes with propargylic alcohols is catalyzed by $C_6F_5B(OH)_2$.[5]



Suzuki coupling. Coupling procedures using $ArBF_3K$ are now recognized as providing the same results as with $ArB(OH)_2$. It is due to hydrolysis of the aryltrifluoroborate salts.[6]

[1] Zhu, C., Li, G., Ess, D.H., Falck, J.R., Kürti, L. *JACS* **134**, 18253 (2012)
[2] Zhu, C., Wang, R., Falck, J.R. *OL* **14**, 3494 (2012)
[3] Gernigon, N., Al-Zoubi, R.M., Hall, D.G. *JOC* **77**, 8386 (2012)
[4] Zheng, H., Ghanbari, S., Nakamura, S., Hall, D.G. *ACIE* **51**, 6187 (2012)
[5] McCubbin, J.A., Nassar, C., Krokhin, O.V. *S* 3152 (2011)
[6] Butters, M., Harvey, J.N., Jover, J., Lennox, A.J.J., Lloyd-Jones, G.C., Murray, P.M. *ACIE* **49**, 5156 (2010)

2-Azido-1,3-dimethylimidazolinium hexafluorophosphate

Alkyl azides. Alcohols are converted into azides the title phosphate reagent.[1]

[1] Kitamura, M., Koga, T., Yano, M., Okauchi, T. *SL* 1335 (2012)

1-Azidosulfonyl -2,3-dimethylimidazolium triflate

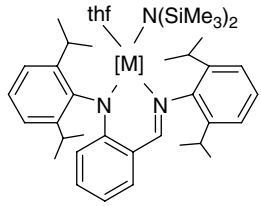
Sulfamoyl azides.[1] The reagent is prepared by methylation of the product of NaN_3, SO_2Cl_2, and 2-methylimidazole. It is used in derivatizing amines.

[1] Culhane, J.C., Fokin, V.V. *OL* **13**, 4578 (2011)

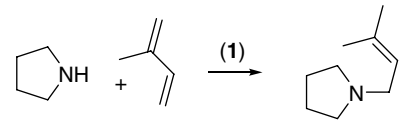
B

Barium iminoanilide

Hydroamination. Preparation from BaI_2, $KN(SiMe_3)_2$, and the N,N-ligand in THF, the amido complex **1** is the most active of a series (Ba > Sr >Ca) of *anti*-Markovnikov hydroamination catalysts for styrenes and conjugated dienes.[1]



(**1**)



[1] Liu, B., Roisnel, T., Carpentier, J.-F., Sarazin, Y. *ACIE* **51**, 4943 (2012)

Barium hydroxide

Baylis-Hillman reaction. For hydroxyalkylation of 2-cycloalkenones in 5:1 aqueous methanol, a promising catalyst system is composed of $Ba(OH)_2$ and *N*-methylpyrrolidine.[1]

[1] Guerra, K.P., Afonso, C.A.M. *T* **67**, 2562 (2011)

***o*-Benzenedisulfonimide**

Substitution. The title reagent is a reusable and mild Brønsted acid that is useful to convert dimethylacetals to homoallylic methyl ethers with allylsilanes.[1] The hydroxyl group of benzyl alcohols is similarly replaced (also by an alkynyl group). Ultimately ArCHO are converted into triarylmethanes by this method.[2]

Condensation. The Mukaiyama aldol reaction can be carried out in the neat with *o*-benzenedisulfonimide as catalyst.[3] Other uses are in bringing about the Pictet-Spengler reaction[4] and the Strecker reaction.[5]

[1] Barbero, M., Bazzi, S., Cadamuro, S., Dughera, S., Piccinini, C. *S* 315 (2010)
[2] Barbero, M., Cadamuro, S., Dughera, S., Magistris, C., Venturello, P. *OBC* **9**, 8393 (2011)

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© 2016 John Wiley & Sons, Inc. Published 2016 by John Wiley & Sons, Inc.

[3] Barbero, M., Bazzi, S., Cadamuro, S., Dughera, S., Magistris, C., Smarra, A., Venturello, P. *OBC* **9**, 2192 (2011)
[4] Barbero, M., Bazzi, S., Cadamuro, S., Dughera, S. *TL* **51**, 6356 (2010)
[5] Barbero, M., Cadamuro, S., Dughera, S., Ghigo, G. *OBC* **10**, 4058 (2012)

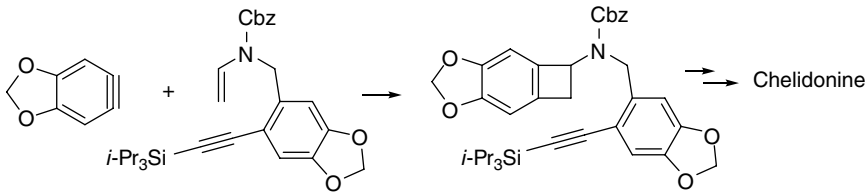
Benzyne

Preparation. A new precursor for the fluoride-induced decomposition is *o*-trimethylsilylphenyl 1-imidazolesulfonate.[1]

Alkenes. Benzyne removes the heteroatoms from 2-thiazolidinethiones to leave behind alkenes.[2] It completes a two-step defunctionalization of *vic*-amino alcohols.

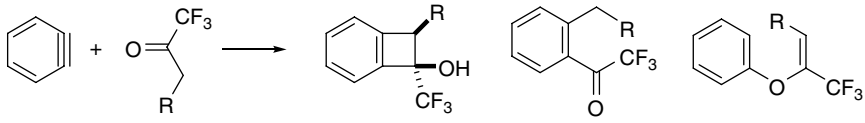
Condensation. Benzyne is trapped by isonitriles and the adducts in turn deprotonate 1-alkynes and cause a union to yield alkynyl arylketimines. An excess of the alkynes can be engaged to form pyridines or isoquinolines.[3]

Access by a [2+2]cycloaddition with enamides, the substituted benzocyclobutenes are valuable precursors of aminoquinodimethanes. A synthesis of chelidonine based on this reactivity is most rewarding.[4]

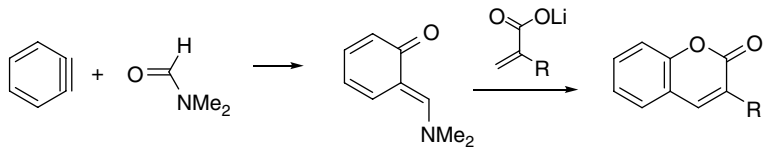


The condensation of benzyne with 2-vinylazetidines leads to 1-benzazocines.[5] An expedient method for preparing aza-bridged benzotropones is by trapping benzyne with pyridinium 3-oxides.[6]

Three different kinds of benzyne adducts with trifluoromethyl ketones CF_3COCH_2R may be isolated, depending on the electronic and steric nature of the CH_2R group.[7]



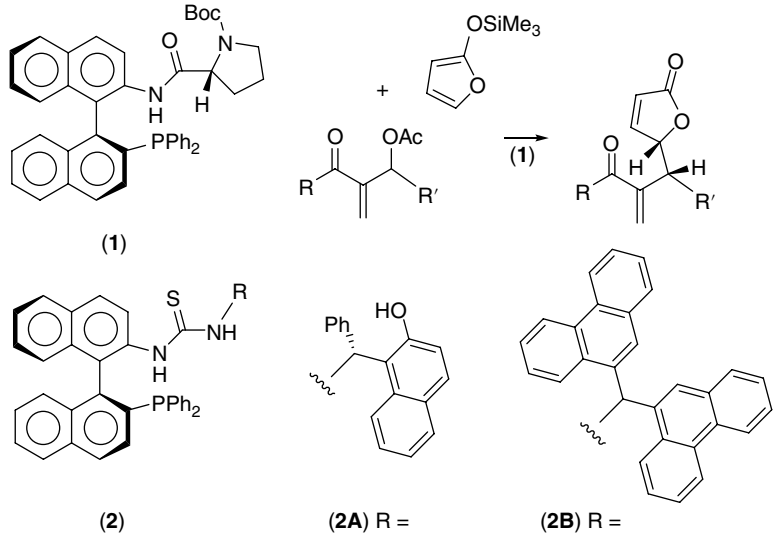
Generation of benzyne in DMF furnishes an *o*-quinomethide which on reaction with ester enolates or ketenimine anions delivers coumarins.[8]



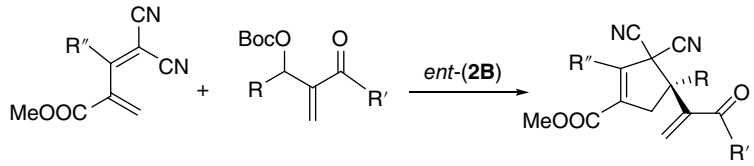
[1] Kovacs, S., Csincsi, A.I., Nagy, T.Z., Boros, S., Timari, G., Novak, Z. *OL* **14**, 2022 (2012)
[2] Hwu, J.R., Hsu, Y.C. *CEJ* **17**, 4727 (2011)
[3] Sha, F., Wu, L., Huang, X. *JOC* **77**, 3754 (2012)
[4] Ma, Z.-X., Feltenberger, J.B., Hsung, R.P. *OL* **14**, 2742 (2012)
[5] Aoki, T., Koya, S., Yamasaki, R., Saito, S. *OL* **14**, 4506 (2012)
[6] Ren, H., Wu, C., Ding, X., Chen, X., Shi, F. *OBC* **10**, 8975 (2012)
[7] Yoshida, H., Ito, Y., Yoshikawa, Y., Ohshita, J., Takaki, K. *CC* **47**, 8664 (2011)
[8] Yoshida, H., Ito, Y., Ohshita, J. *CC* **47**, 8512 (2011)

1,1′-Binaphthalene-2-amine-2′-phosphines

Substitution. The chiral binaphthyl **1** containing both a phosphino group and a prolinamide unit has been used to conduct S_N2 reaction on Baylis-Hillman esters by 2-trimethylsiloxyfuran.[1] Another catalyst is the thiourea **2A**, capable of inducing reaction using as *P*-nucleophile such as secondary phosphine oxides.[2]



Cycloaddition. Baylis-Hillman esters also engage in enantioselective reaction with electron-deficient dienes.[3] A chirality center is created as the cyclopentene adducts are formed.

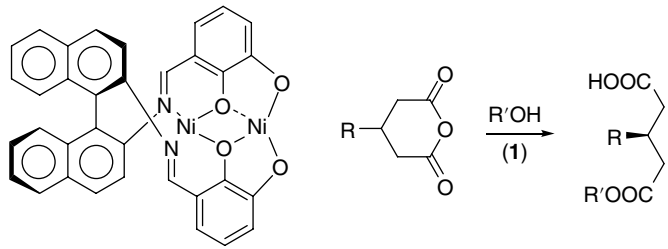


[1] Wei, Y., Ma, C.-N., Shi, M. *EJOC* 5146 (2011)
[2] Deng, H.-P., Shi, M. *EJOC* 183 (2012)
[3] Zhang, X., Deng, H.-P., Huang, L., Wei, Y., Shi, M. *CC* **48**, 8664 (2012)

1,1′-Binaphthalene-2,2′-diamine and derivatives

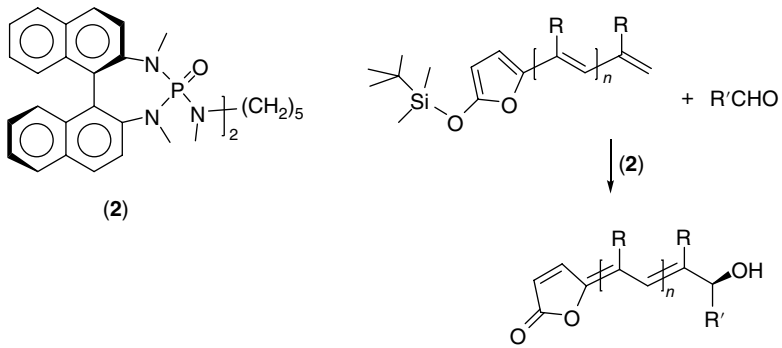
Derivatization. On milling with 3,5-bis(trifluoromethyl)phenyl isothiocyanate, BINAMINE is converted into an adduct containing two thiourea moieties.[1]

Alcoholysis. Desymmetrization of 3-substituted glutaric anhydride by addition of an alcohol furnishes chiral monoesters when conducted in the presence of **1**.[2]



(**1**)

Addition. Deprotonated 2-methyl-3-butenenitrile is nucleophilic toward aldehydes, both saturated and conjugated. An asymmetric carbinol center is established when the reaction is carried out in the presence of **2**. Using the same phosphoramide the condensation of 5-alkenyl-2-trialkylsiloxyfurans with aldehydes leads to 4-alkylidene-2-butenolides with a chiral alcohol sidechain.[3]



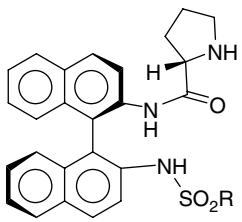
(**2**)

For aldol reaction a reusable catalyst is **3A**.[4] Serving well in a solvent-free synthesis of the Wieland-Miescher ketone and analogs is **3B**.[5] The diamide **4** is employed in the reaction of α-keto esters (acceptor).[6]

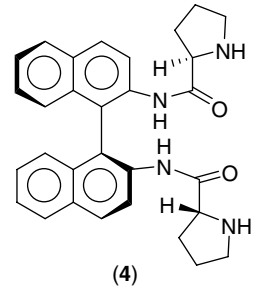
Asymmetric carbonyl-ene reaction involving α-keto esters, formaldehyde *t*-butylhydrazone and the bis-urea adduct of BINAMINE and 3,5-bis(trifluoromethyl)phenyl isocyanate relies on attainment of a multiple H-bonding transition state, one urea unit for each addend.[7]

The cycloalkoxylation initiated by attack of *N*-phenylthiophthalimide on unsaturated alcohols is rendered enantioselective by having the selenophosphoramide **5** present.[8]

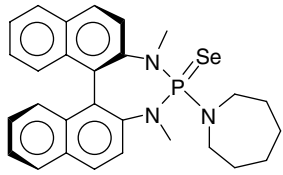
A magnesium complex of (6), an analog to (1), is active for promoting the asymmetric addition of *N*-Boc isoindolinone to *N*-sulfonylimines.[9]



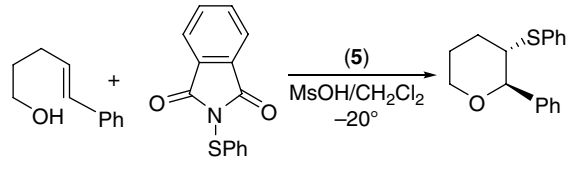
(**3A**) R = polymer
(**3B**) R = Tol

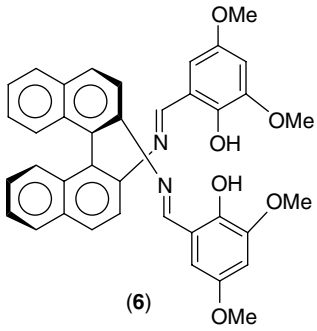


(**4**)

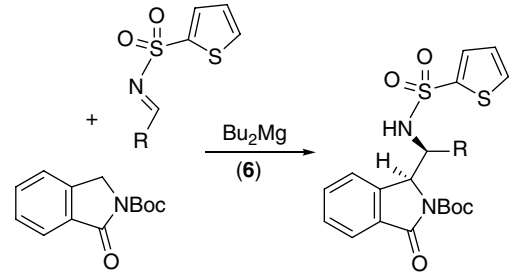


(**5**)





(**6**)



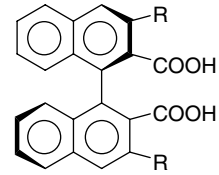
[1] Strukil, V., Irgc, M.D., Eckert-Maksic, M., Friscic, T. *CEJ* **18**, 8464 (2012)
[2] Gopinath, P., Watanabe, T., Shibasaki, M. *OL* **14**, 1358 (2012)
[3] Curti, C., Battistini, L., Sartori, A., Lodola, A., Mor, M., Rassu, G., Pelosi, G., Zanardi, F., Casiraghi, G. *OL* **13**, 4738 (2011)

[4] Bañon,-Caballero, A., Guillena, G., Najera, C. *HCA* **95**, 1831 (2012)
[5] Bradshaw, B., Bonjoch, J. *SL* 337 (2012)
[6] Viozquez, S.F., Bañon-Caballero, A., Guillena, G., Nájera, C., Gómez-Bengoa, E. *OBC* **10**, 4029 (2012)
[7] Crespo-Peña, A., Monge, D., Martin-Zamora, E., Alvarez, E., Fernandez, R., Lassaletta, J.M. *JACS* **134**, 12912 (2012)
[8] Denmark, S.E., Kornfilt, D.J.P., Vogler, T. *JACS* **133**, 15308 (2011)
[9] Suzuki, Y., Kanai, M., Matsunaga, S. *CEJ* **18**, 7654 (2012)

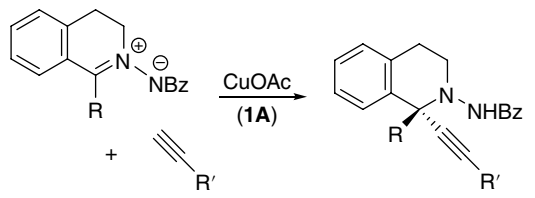
1,1′-Binaphthalene-2,2′-dicarboxylic acids

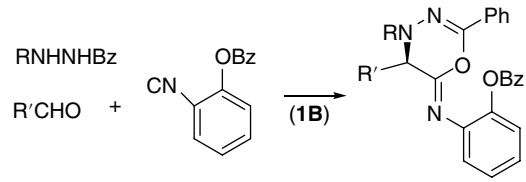
Addition to imines. In the Cu(I)-catalyzed addition of 1-alkynes to *N*-benzoylamino-3, 4-dihydroisoquinoline zwitterions, chiral products are obtained on adding diacid **1A** to the reaction media.[1]

Cycloaddition. The 1,3,4-oxadiazine ring system emerges as aldehydes, benzoylhydrazines, and aryl isonitriles condense in the presence of **1B**.[2]



(**1A**) R = Si(Ph)Me$_2$
(**1B**) R = C$_6$H$_3$[3,5-(NO$_2$)$_2$]





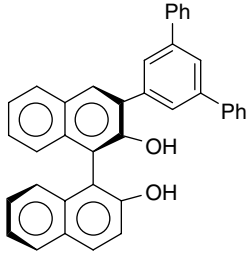
[1] Hashimoto, T., Omote, M., Maruoka, K. *ACIE* **50**, 8952 (2011)
[2] Hashimoto, T., Kimura, H., Kawamata, Y., Maruoka, K. *ACIE* **51**, 7279 (2012)

1,1′-Binaphthalene-2,2′-diol and analogues

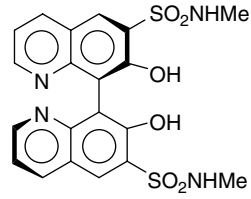
Addition. The BINOL **1**, while displacing two alkoxy groups from (*i*-PrO)$_4$Ti, forms an asymmetric catalyst for the Grignard reaction that forms diarylmethanols.[1] Aryl(triisopropoxy)titanium reagents attack RCHO in a chiral manner as influenced by the complex derived from octahydro-BINOL.[2] Asymmetric induction is also examined in the addition of alkynyl(alkyl)zinc reagents in the presence of BINOL,[3] and to *N*-phosphinoylimines, the 3,3′-dibromo-BINOL.[4]

The dibromo-BINOL also mediates enantioselective propargylation of carbonyl compounds by allenylboronates under microwave irradiation.[5]

The unusual BINOL analog **2** that is actually a 8,8′-Biquinoline-7,7′-diol **1NN** catalyzes the addition of Me_3SiCN to carbonyl compounds and imines.[6] The homocyclic analog itself is inactive.

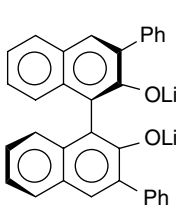


(**1**)

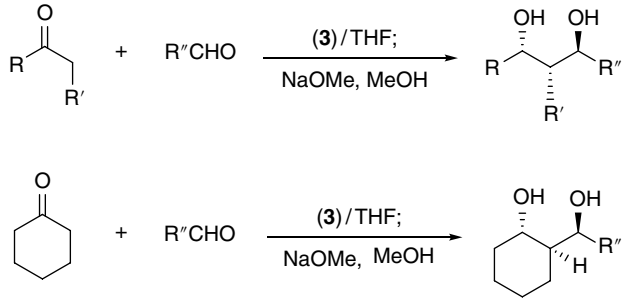


(**2**)

The dilithium salt of a chiral 3,3′-dichloro-BINOL is useful to catalyze the Mukaiyama aldol reaction.[7] *anti*-1,3-Diols are formed from reaction of ketones and aldehydes, as a Tishchenko reaction can be easily realized after an aldol condensation that is promoted by dilithium 3,3′-diphenyl-BINOLate.[8]



(**3**)

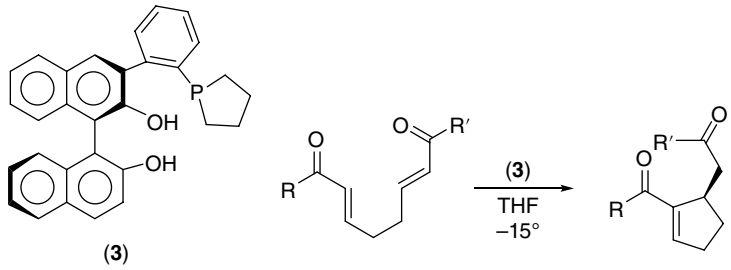


A Zr(IV) complex of 3,3′-bis[3,5-di(trifluoromethyl)phenyl]-BINOL is responsible for asymmetric induction during Friedel-Crafts reaction of pyrrole by α-keto esters.[9]

Many versions of conjugate addition are catalyzed by BINOLs and their metal salts. For example, introduction of a chiral sidechain to C-3 of the indole nucleus is accomplished by addition to enones, catalyzed by zirconium di-*t*-butoxide 3,3′-dibromo-BINOLate.[10] *N*-Acetyltryptophan methyl ester is obtained from the reaction with the α-acetamidoacrylic ester using an analogous dibromo-BINOL complex derived from $SnCl_4$.[11]

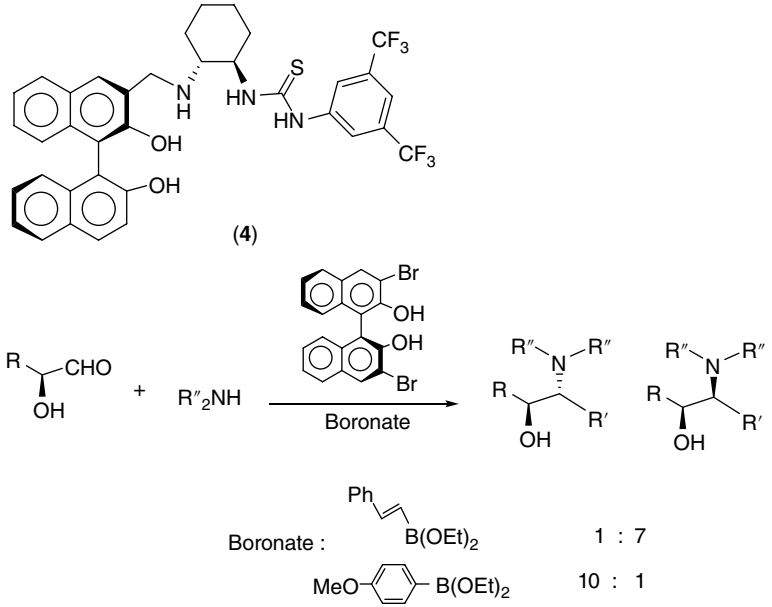
Chain elongation at the γ-position of *N*-acyl 2-butenelactams by conjugate addition is rendered asymmetric by using the Mg salt of a chiral 3,3′-diphenyl-BINOL.[12]

Cyclization involving intramolecular addition of one conjugated carbonyl unit to another is initiated by BINOL **3** which contains a tertiary phosphine.[13]



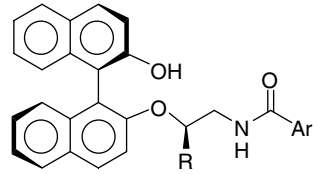
Conjugate addition of organoboronates to enones has been studied employing 3,3′-dichloro-BINOL[14] and 3,3′-bis(pentafluorophenyl)-BINOL.[15] *o*-Quinone methides generated in situ also are serviceable as acceptors for alkenylboronates.[16]

Based on the Petasis reaction of salicylaldehyde for access to chiral benzylamines, BINOL **4** is employed.[17] Interestingly, diastereocontrol for synthesis of β-amino alcohols is obtained on variation of the boronates.[18]

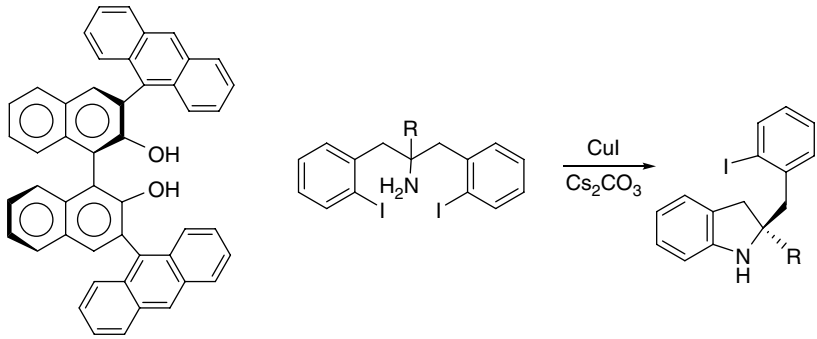


Substitution. In replacement of the sulfonyl group from α-amino sulfones to acquire propargylic amines, chiral products are obtained when the zinc alkynides are associated with an antipodal 3,3′-bis[3,5-di(trifluoromethyl)phenyl]-BINOL.[19]

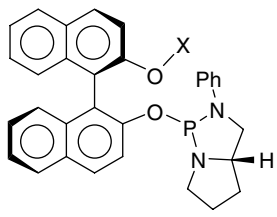
(*R*)-BINOL is used in kinetic resolution of *N*-aroylaziridines.[20]



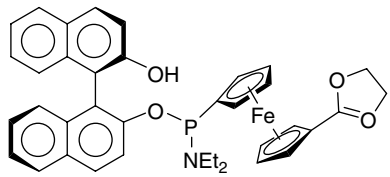
Enantioselective formation of 2-substituted indolines involving desymmetrization directed by (*R*)-3,3′-di(9-anthryl)-BINOL.[21]



A number of BINOL derivatives, represented by **5A** and **5B**, are useful ligands for Pd to promote S_N2' reactions.[22, 23] The complex ligand **5B** which is obtained from (*R*)-BINOL is also employed in a Pd-catalyzed allylation of acylsilanes.[24]



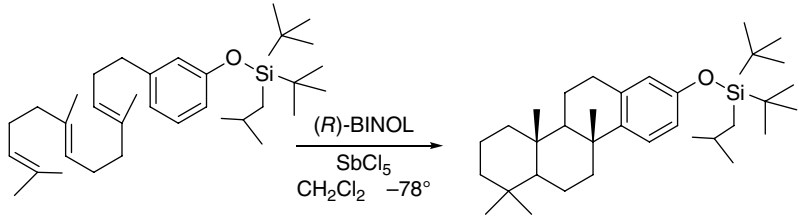
(**5A**) X = Ts, CH_2Py



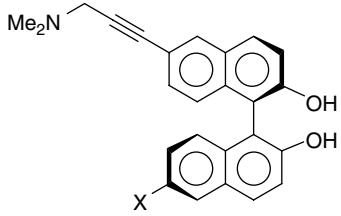
(**5B**)

Cyclization. Transformation of 3-(*N*-acyl-*N*-alkenyl)aminopropanals to 1,2,3, 4-tetrahydropyridin-4-ols is catalyzed by Lewis acids. A chiral diisopropoxytitanium BINOLate is effective.[25]

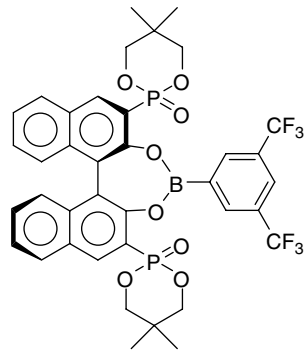
Polyene cyclization that generates four contiguous stereocenters in highly enantioselective manner is very desirable. It can be achieved with a combination of $SbCl_5$ and BINOL.[26]



Cycloaddition. Amphophilic BINOLs such as **6A** and **6B** show catalytic activities for epoxidation of enones.[27] Association of boronate **7** with tris(pentafluorophenyl)borane creates a supramolecular catalyst for directing asymmetric Diels-Alder reaction (e.g., between cyclopentadiene and α-substituted acroleins).[28]



(**6A**) X = H
(**6B**) X = $CCCH_2NMe_2$



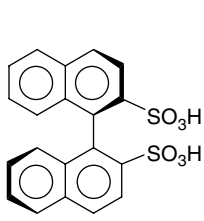
(**7**)

Oxidation. A combination of a chiral BINOL and Bi_2O_3 is used in asymmetric oxidation of sulfides.[29]

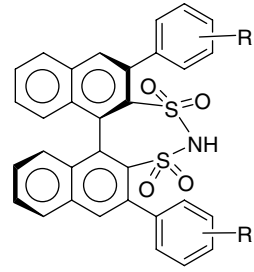
[1] Itakura, D., Harada, T. *SL* 2875 (2011)
[2] Wu, K.-H., Zhou, S., Chen, C.-A., Yang, M.-C., Chiang, R.-T., Chen, C.-R., Gau, H.-M. *CC* **47**, 11668 (2011)
[3] Turington, M., Pu, L. *SL* 649 (2012)
[4] Blay, G., Ceballos, E., Monleon, A., Pedro, J.R. *T* **68**, 2128 (2012)
[5] Barnett, D. S.,Schaus, S. E. *OL* **13**, 4020 (2011)
[6] Sephton, S.M., Wang, C., Zakharov, L.N., Blakemore, P.R. *EJOC* 3249 (2012)
[7] Ichibakase, T., Kaneko, T., Orito, Y., Kotani, S., Nakajima, M. *T* **68**, 4210 (2012)
[8] Ichibakase, T., Nakajima, M. *S* 3145 (2012)
[9] Blay, G., Fernandez, I., Muñoz, M.C., Pedro, J.R., Recuenco, A., Vila, C. *JOC* **76**, 6286 (2011)
[10] Blay, G., Cano, J., Cardona, L., Fernandez, I., Muñoz, M.C., Pedro, J.R., Vila, C. *JOC* **77**, 10545 (2012)
[11] Kieffer, M.E., Repka, L.M., Reisman, S.E. *JACS* **134**, 5131 (2012)
[12] Lin, L., Zhang, J., Ma, X., Fu, X., Wang, R. *OL* **13**, 6410 (2011)
[13] Zhang, X.-N., Shi, M. *EJOC* 6271 (2012)

[14] Turner, H.M., Patel, J., Niljianskul, N., Chong, J.M. *OL* **13**, 5796 (2011)
[15] Lundy, B.J., Jansone-Popova, S., May, J.A. *OL* **13**, 4958 (2011)
[16] Luan, Y., Schaus, S.E. *JACS* **134**, 19965 (2012)
[17] Han, W.-Y., Wu, Z.-J., Zhang, X.-M., Yuan, W.-C. *OL* **14**, 976 (2012)
[18] Muncipinto, G., Moquist, P.N., Schreiber, S.L., Schaus, S.E. *ACIE* **50**, 8172 (2011)
[19] Blay, G., Brines, A., Monleon, A., Pedro, J.R. *CEJ* **18**, 2440 (2012)
[20] Cockrell, J., Wilhelmsen, C., Rubin, H., Martin, A., Morgan, J.B. *ACIE* **51**, 9842 (2012)
[21] Zhou, F., Guo, J., Liu, J., Ding, K., Yu, S., Cai, Q. *JACS* **134**, 14326 (2012)
[22] Gavrilov, K.N., Zheglov, S.V., Rastorguev, E.A., Groshkin, N.N., Maksimova, M.G., Benetsky, E.B., Davankov, V.A., Reetz, M.T. *ASC* **352**, 2599 (2010)
[23] Zheng, B.-H., Ding, C.-H., Hou, X.-L. *SL* 2262 (2011)
[24] Chen, J.-P., Ding, C.-H., Liu, W., Hou, X.-L., Dai, L.-X.. *JACS* **132**, 15493 (2010)
[25] Tong, S., Wang, D.-X., Zhao, L., Zhu, J., Wang, M.-X. *ACIE* **51**, 4417 (2012)
[26] Surendra, K., Corey, E.J. *JACS* **134**, 11992 (2012)
[27] El Kadiri, M.Y., Framery, E., Andrioletti, B. *TL* **53**, 6335 (2012)
[28] Hatano, M., Mizuno, T., Izumiseki, A., Usami, R., Asai, T., Akakura, M., Ishihara, K. *ACIE* **50**, 12189 (2011)
[29] Malik, P., Chakraborty, D. *TL* **53**, 5652 (2012)

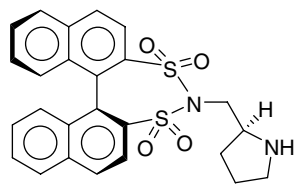
1,1′-Binaphthalene-2,2′-disulfonic acid and imides



(**1**)



(**2A**) R = 3,5-$(CF_3)_2$
(**2B**) R = 3,5-$[(CF_3)_2CF]$
(**2C**) R = 3,5-$(O_2N)_2$-4-Me

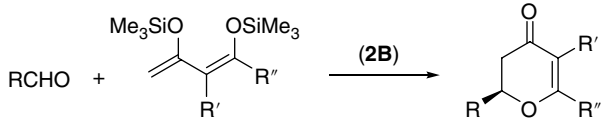


(**3**)

Addition. The Hosomi-Sakurai reaction is affected by a chiral counter-anion as shown by the catalysis of **2C**.[1] Chiral α,α-diaminomethylarenes are acquired by the addition of amides to ArCH=$NCOOCH_2$Ar', using the 2,6-bis(2,4,6-triisopropylphenyl) pyridinium salt of **1** as catalyst.[2] Addition of indole (C-3) to *N*-sulfonylaldimines in the presence of **2A** is enantioselective.[3]

Catalyst **3** possesses two chiral elements and its use in promoting Michael addition to alkylidenemalonic esters has been studied.[4]

Cycloaddition. The pyranone synthesis pioneered by Danishefsky has many applications and numerous catalysts for inducing enantioselectivity are on record. A new catalyst is **2B**.[5]



[1] Mahlau, M., Garcia-Garcia, P., List, B. *CEJ* **18**, 16283 (2012)
[2] Hatano, M., Ozaki, T., Sugiura, Y., Ishihara, K. *CC* **48**, 4986 (2012)
[3] Chen, L.-Y., He, H., Chan, W.-H., Lee, A.W.M. *JOC* **76**, 7141 (2011)
[4] Jia, S., Luo, C., Du, D. *ChJC* **30**, 2676 (2012)
[5] Guin, J., Rabalakos, C., List, B. *ACIE* **51**, 8859 (2012)

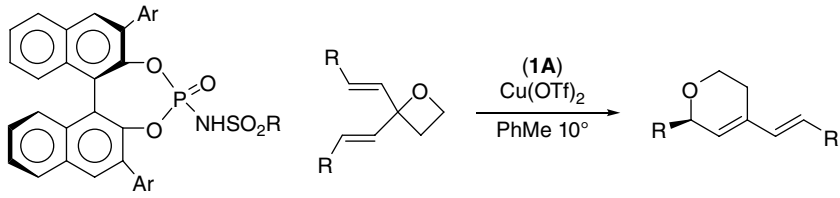
1,1′-Binaphthalene-2,2′-diyl di-*t*-butanesulfinate

Grignard reaction. The title reagent, in either chiral series, is obtained from BINOL on consecutive treatment with BuLi and *t*-BuSOCl. Chiral *t*-butyl sulfoxides can be prepared by a Grignard reaction with the reagent, from which the BINOL is recovered.[1]

[1] Gaggero, N., Albanese, D.C.M. *T* **68**, 7129 (2012)

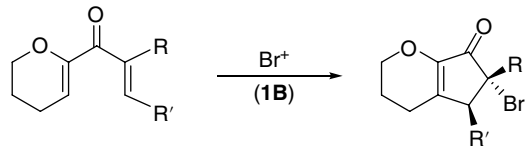
1,1′-Binaphthalene-2,2′-diyl *N*-sulfonylaminophosphates

Ring enlargement. 2,2-Dialkenyloxetanes isomerized by **1A** to 4-alkenyl-5, 6-dihydro-2*H*-pyrans.[1]

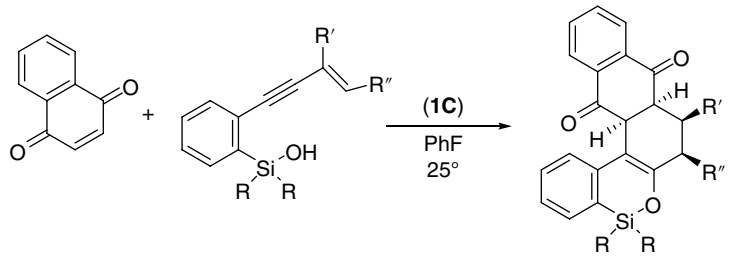


(**1A**) Ar = 9-anthryl, R = Tol
(**1B**) Ar = 9-phenanthryl, R = CF_3
(**1C**) Ar = 1-pyrenyl, R = CF_3

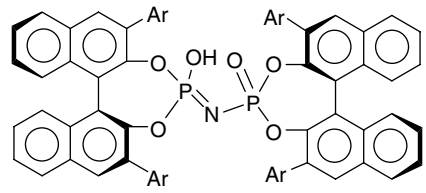
Nazarov cyclization. As chiral Brønsted acids, both **1B** and its octahydro derivative are effective to catalyze cyclization of 2-alkoxy-1,4-alkadien-3-ones.[2] A further modification is to use a Br^+ source to initiate the reaction.[3]



Cycloaddition. Asymmetric Diels-Alder reaction involving *o*-(3-alken-1-ynyl)phenylsilanols as latent dienes has been realized, while employing **1C** to exert chiral guidance.[4]



Oxidation. Enantioselective oxidation of sulfides is accomplished with H_2O_2 and **2**.[5]

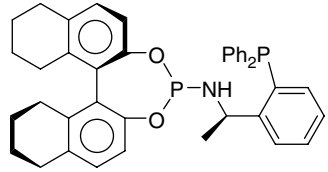


(**2**) Ar = 2,4,6-$Et_3C_6H_2$

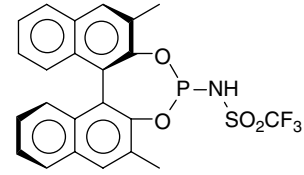
[1] Guo, B., Schwarzwalder, G., Njardarson, J.T. *ACIE* **51**, 5675 (2012)
[2] Raja, S., Ieawsuwan, W., Korotkov, V., Rueping, M. *CAJ* **7**, 2361 (2012)
[3] Rueping, M., Ieawsuwan, W. *CC* **47**, 11450 (2011)
[4] Han, Z.-Y., Chen, D.-F., Wang, Y.-Y., Guo, R., Wang, P.-S., Wang, C., Gong, L.-Z. *JACS* **134**, 6532 (2012)
[5] Liao, S., Coric, I., Wang, Q., List, B. *JACS* **134**, 10765 (2012)

1,1′-Binaphthalene-2,2′-diyl *N*-alkylaminophosphites

Addition. Asymmetric hydrogenation of ketimines based on iridium complexes can rely on aminophosphite **1**[1] or a combination of **2** and $Ph_2PNHSO_2C_6H_4Bu$.[2]



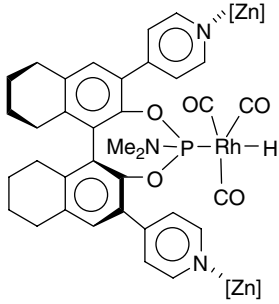
(**1**)



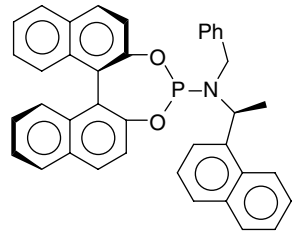
(**2**)

For hydroboration of β,γ-unsaturated Weinreb amides a Rh(I) salt is supported by the BINOL-derived *N*-methylanilinophosphite. The optical yield is highly dependent on the borane used.[3]

Supramolecular axial complexes typified by **3** show excellent activity and selectivity for asymmetric hydroformylation of alkenes.[4] Addition of ethylene to styrenes provides 3-aryl-1-butenes, and this Ni-catalyzed process is subject to chiral manipulation by **4.**[5]

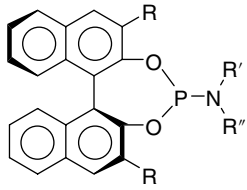


(**3**)

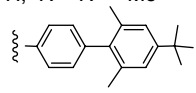


(**4**)

Nickel(0)-mediated gathering of a conjugated diene, an aldehyde and a silylborane serves to construct a carbon chain containing three contiguous stereocenters and a silyl and hydroxyl substituent each. By involving **5D** an enantioselective process is achieved.[6]

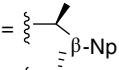


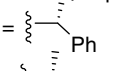
(**5A**) R = H, R′ =R″ = Me

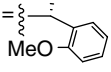
(**5B**) R =  R′ = R″ = Me

(**5C**) R = 9-anthryl, R′ = R″ = Et

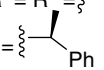
(**5D**) R = $CHPh_2$, R′ = R″ = Bn

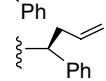
(**5E**) R = H, R′ = R″ = 

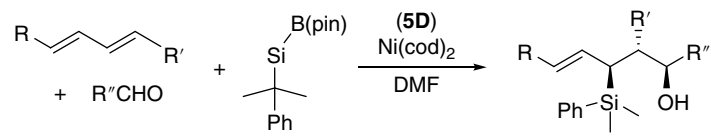
(**5F**) R = H, R′ = R″ = 

(**5G**) R = H, R′ = R″ = 

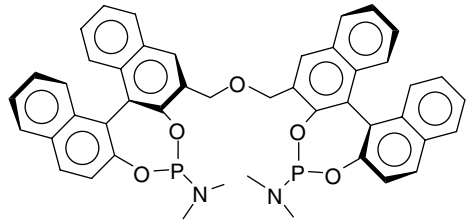
(**5H**) R = 9-anthryl, R′ = R″ = 

(**5I**) R = Me, R′ = R″ = 

(**5J**) R = H, R′ = Bn, R″ = 

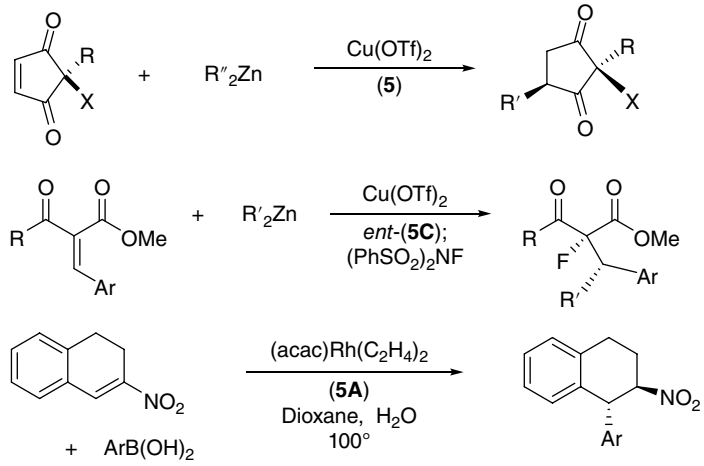


The dimeric BINOL derivative **6** forms with $(Ph_3P)_2RuCl_2$ a catalyst that directs addition of $ArB(OH)_2$ to glyoxylate esters in enantioselective manner.[7]



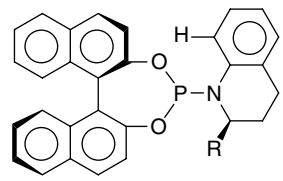
(**6**)

Conjugate addition of R_2Zn and R_3Al to 2,2-disubstituted 4-cyclopentene-1,3-diones is Cu(II)-catalyzed. It favors the *syn* face to the more polar substituent, and enantioselectivity is governed by **5B**.[8]

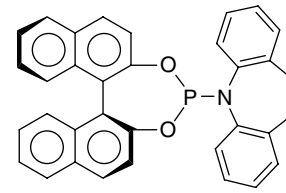


After adding diorganozinc reagents to α-benzylidene-β-keto esters the quenching with $(PhSO_2)_2NF$ establishes two new stereocenters, and the whole process is rendered asymmetric by the presence of *ent*-**5C**.[9] 3-Nitro-1,2-dihydronaphthalene picks up the Ar group from $ArB(OH)_2$ asymmetrically to afford *trans*-1-aryl-2-nitrotetralins when a Rh complex and **5A** are added.[10]

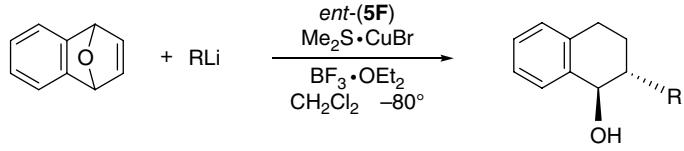
Substitution. The iridium complex with **7** controls the S_N2' reaction of malonate esters and cinnamyl carbonate.[11] An iridacycle is formed in which the metal is covalently bonded to C-8 of the tetrahydroquinoline.



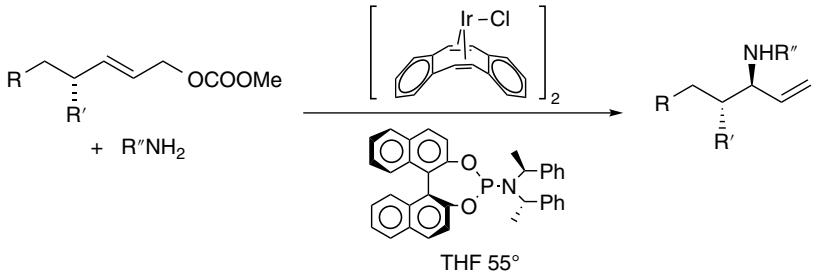
(**7A**) R = H
(**7B**) R = Me



(**8**)

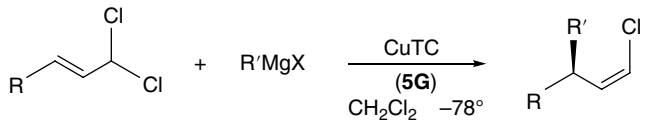


Iridium catalysts always favor bond formation at the secondary allylic center, therefore the reaction can be exploited to access 3-amino-1-alkenes with an additional chirality center at C-4.[12]



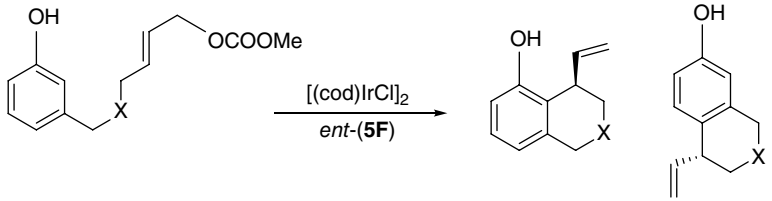
Enantioconvergent access to 3-organothio-1-alkenes is attained in the reaction of allylic alcohols using **8** and $(BuO)_2POOH$.[13] Similarly, chiral 3-aryl-3-aryloxy-1-propenes are synthesized from cinnamyl carbonates and phenols [catalyst: Ir(I) complex + **5E**].[14]

Reaction with RLi opens 1,4-oxa-1,4-dihydronaphthalene in the S_N2' fashion (catalysts: $Me_2S.CuBr$, $BF_3 \cdot OEt_2$), and it is rendered enantioselective by *ent*-**5F**.[15] Attack of Grignard reagents on 1,1-dichloro-2-alkenes can be made regioselective and stereoselective, giving (*Z*)-1-chloro-1-alkenes which are useful for Suzuki coupling.[16] A similar reaction with RLi on 1-alkoxy-2-alkenes[17] or 1-halo-2-alkenes[18] to produce 1-alkenes with a chirality center at C-3 is then a routine extension.



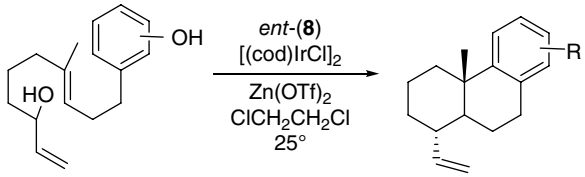
1-Chloro-2-alken-4-ynes are converted by the Cu(I)-catalyzed Grignard reaction into 1-alken-4-ynes while a new chirality center at C-3 is being created.[19]

Further examples of iridium(I)-catalyzed substitution may be mentioned. Thus, using sulfamic acid as nucleophile enables enantioselective replacement of the hydroxyl group of 1-alken-3-ols by NH_2 in the presence of **8**.[20] Cycloallylation of phenols occurs when a *m*-substituent is equipped with the necessary leaving group.[21] Products from substitution at both an *o*- and a *p*-position results have the same absolute configuration at the new chirality center. A similar process serves to form a spirocycle at C-3 of the indole nucleus.[22]



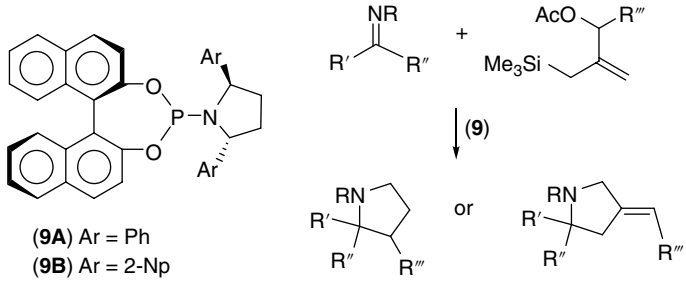
Coupling of 2-vinylaniline with cinnamyl methyl carbonate is interesting, as it produces a 1,4-diene.[23]

A tricyclic structure emerges from exposure of 10-aryl-1,7-decadien-3-ols to a mixture of $[(cod)IrCl]_2$ and $Zn(OTf)_2$, and the products containing three contiguous asymmetric centers are obtained by introducing *ent*-**8** into the reaction media.[24]



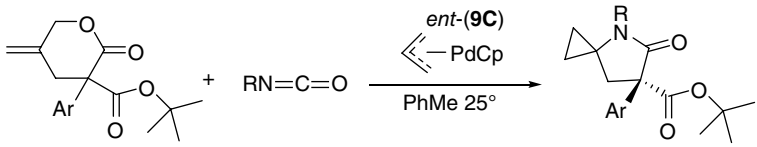
For Pd-catalyzed allylic substitution, **5J** can be employed as a chiral catalyst.[25]

Cycloaddition. [3+2]Cycloaddition involving trimethylenemethanes that are generated from silylated allylic esters is amenable to deliver chiral products on ligating the Pd catalyst with **9A/9B**, as illustrated in the combination with imines[26] and with nitroalkenes.[27]

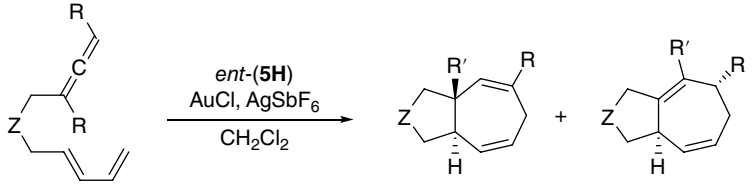


(**9A**) Ar = Ph
(**9B**) Ar = 2-Np
(**9C**) Ar = 3,5-$Me_2C_6H_3$

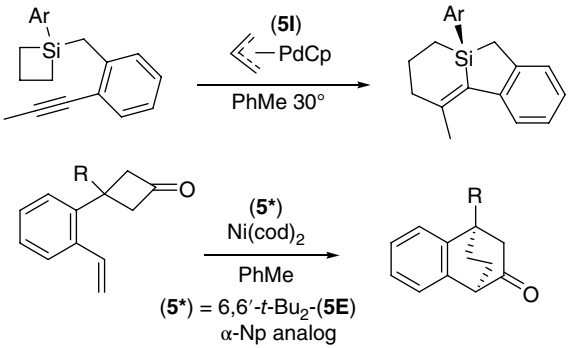
Decarboxylation of γ-methylene-δ-lactones gives rise to more complex trimethylenemethanes, and the capture of which by isocyanates results in the formation of spirolactams. Those with chirality residing in the α-carbon are promptly prepared by ligating the Pd center with **9C**.[28]



Intramolecular [4+3]cycloaddition to unite diene and allene units is induced by Au(I)-activation of the allene. With *ent*-**5H** to ligate the metal center it yields fused cycloheptadienes.[29]



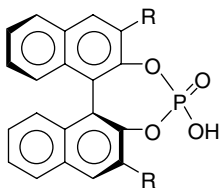
Ring enlargement. Silacyclobutanes insert alkynes to form 1-sila-2-cyclohexenes in a Pd-catalyzed reaction. The ligand H_8-**5I** is useful for asymmetric induction at the silicon atom.[30] A very unusual reaction of 3-(*o*-vinylaryl)cyclobutanones is their conversion into benzonorbornenones. Produced in optically active form is by catalysis of $Ni(cod)_2$ and the 6,6′-di-*t*-butyl derivative of **5E**′.[31]



[1] Hou, C.-J., Wang, Y.-H., Zheng, Z., Xu, J., Hu, X.-P. *OL* **14**, 3554 (2012)
[2] Kluwer, A.M., Detz, R.J., Abiri, Z., van der Burg, A.M., Reek, J.N.H. *ASC* **354**, 89 (2012)

[3] Smith, S.M., Uteuliyev, M., Takacs, J.M. *CC* **47**, 7812 (2011)
[4] Bellini, R., Reek, J.N.H. *CEJ* **18**, 7091 (2012)
[5] Liu, W., Lim, H.J., RajanBabu, T.V. *JACS* **134**, 5496 (2012)
[6] Saito, N., Kobayashi, A., Sato, Y. *ACIE* **51**, 1228 (2012)
[7] Yamamoto, Y., Shirai, T., Miyaura, N. *CC* **48**, 2803 (2012)
[8] Aikawa, K., Okamoto, T., Mikami, K. *JACS* **134**, 10329 (2012)
[9] Wang, L., Meng, W., Zhu, C.-L., Zheng, Y., Nie, J., Ma, J.-A. *ACIE* **50**, 9442 (2011)
[10] Hajra, S., Ghosh, R., Chakrabarti, S., Ghosh, A., Dutta, S., Dey, T.K., Malhotra, R., Asijaa, S., Roy, S., Dutta, S., Basu, S. *ASC* **354**, 2433 (2012)
[11] Liu, W.-B., Zheng, C., Zhuo, C.-X., Dai, L.-X., You, S.-L. *JACS* **134**, 4812 (2012)
[12] Tosatti, P., Campbell, A.J., House, D., Nelson, A., Marsden, S.P. *JOC* **76**, 5495 (2011)
[13] Roggen, M., Carreira, E.M. *ACIE* **51**, 8652 (2012)
[14] He, H., Ye, K.-Y., Wu, Q.-F., Dai, L.-X., You, S.-L. *ASC* **354**, 1084 (2012)
[15] Bos, P.H., Rudolph, A., Perez, M., Fañanas-Mastral, M., Harutyunyan, S.R., Feringa, B.L. *CC* **48**, 1748 (2012)
[16] Giannerini, M., Fananas-Mastral, M., Feringa, B.L. *JACS* **134**, 4108 (2012)
[17] Perez, M., Fañanas-Mastral, M., Hornillos, V., Rudolph, A., Bos, P.H., Harutyunyan, S.R., Feringa, B.L. *CEJ* **18**, 11880 (2012)
[18] Fañanas-Mastral, M., Perez, M., Bos, P.H., Rudolph, A., Harutyunyan, S.R., Feringa, B.L. *ACIE* **51**, 1922 (2012)
[19] Li, H., Alexakis, A. *ACIE* **51**, 1055 (2012)
[20] Lafrance, M., Roggen, M., Carreira, E.M. *ACIE* **51**, 3470 (2012)
[21] Xu, Q.-L., Dai, L.-X., You, S.-L. *OL* **14**, 2579 (2012)
[22] Wu, Q.-F., Zheng, C., You, S.-L. *ACIE* **51**, 1680 (2012)
[23] Ye, K.-Y., He, H., Liu, W.-B., Dai, L.-X., Helmchen, G., You, S.-L. *JACS* **133**, 19006 (2011)
[24] Schafroth, M.A., Sarlah, D., Krautwald, S., Carreira, E.M. *JACS* **134**, 20276 (2012)
[25] Liu, Z., Cao, Z., Du, H. *OBC* **9**, 5369 (2011)
[26] Trost, B.M., Silverman, S.M. *JACS* **134**, 4941 (2012)
[27] Trost, B.M., Bringley, D.A., Seng, P.S. *OL* **14**, 234 (2012)
[28] Shintani, R., Ito, T., Nagamoto, M., Otomo, H., Hayashi, T. *CC* **48**, 9936 (2012)
[29] Alonso, I., Faustino, H., Lopez, F., Mascareñas, J.L. *ACIE* **50**, 11496 (2011)
[30] Shintani, R., Moriya, K., Hayashi, T. *JACS* **133**, 16440 (2011); *OL* **14**, 2902 (2012)
[31] Liu, L., Ishida, N., Murakami, M. *ACIE* **51**, 2485 (2012)

1,1′-Binaphthalene-2,2′-diyl phosphates and 3,3′-diaryl analogs

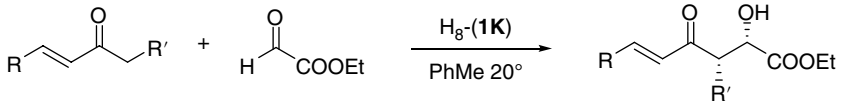


(**1A**) R = H
(**1B**) R = Ph
(**1C**) R = 4-PhC_6H_4
(**1D**) R = 4-(β-Np)C_6H_4
(**1E**) R = 4-$MeOC_6H_4$
(**1F**) R = 4-$O_2NC_6H_4$
(**1G**) R = 4-XC_6H_4
(**1H**) R = 4-FC_6H_4
(**1I**) R = 3,5-$F_2C_6H_4$
(**1J**) R = 3,5-(*i*-Pr)$_2C_6H_3$
(**1K**) R = 2,4,6-$Me_3C_6H_2$
(**1L**) R = 2,4,6-(*i*-Pr)$_3C_6H_2$
(**1M**) R = 2,6-Me_2-4-(*t*-Bu)C_6H_2
(**1N**) R = 3,5-(*i*-Pr)$_2$-4-(MeO)C_6H_2
(**1O**) R = 9-anthryl
(**1P**) R = 9-phenanthryl
(**1Q**) R = β-Np
(**1R**) R = 2-thienyl
(**1S**) R = 3-thienyl
(**1T**) R = Ph_3Si

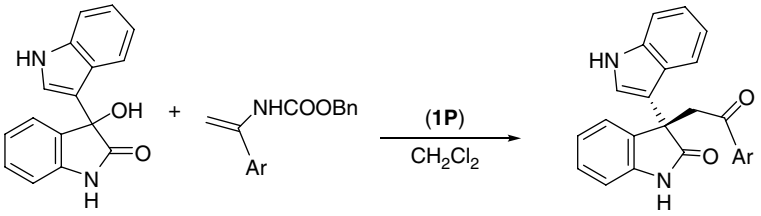
Kinetic resolution. A catalyst composed of **1L** and DABCO is for controlled enantioselective acetylation of secondary alcohols.[1] 1,2-Alkadien-4-ols are half-converted into the (*R*)-2-alkyl-2,5-dihydrofurans, leaving the (*S*)-alcohols alone, on exposure to **1C**.[2]

Selective cyclization of one enantiomer of an unsymmetrically substituted 1,5-diketone is realized by catalysis of **1L**.[3] For kinetic resolution of an *N*-sulfonylated benzylamine, a method is based on desulfonylation of one enantiomer by BnSH, using either **1B** or **1F** as catalyst.[4]

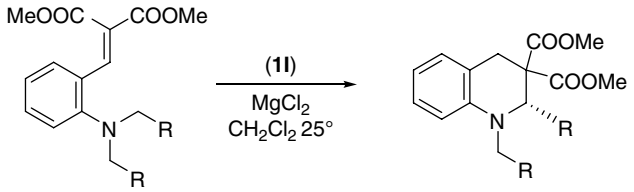
Substitution. Creation of a chiral quaternary benzylic center from allylation of α-substituted arylacetaldehydes is accomplished in a Pd(0)-catalyzed reaction, provided that Brønsted acids such as **1L** and benzhydrylamine are enlisted as participants.[5] Regioselective and enantioselective aldol reaction of conjugated ketones with ethyl glyoxylate occurs at the α′ -position, and in such case H_8-**1K** is of excellent service.[6]



Ketones are alkylated by 3-hydroxy-3-(β-indolyl)oxindole under acidic conditions. It provides chiral products with two contiguous chirality centers when (*ent*)-**1E** is employed.[7] This method was initially developed for a synthesis of (+)-folicanthine using an α-(*N*-benzyloxycarbonyl)aminostyrene as the nucleophile (and **1P** the catalyst).[8]



Cooperative actions from Brønsted acid **1I** and Lewis acid $MgCl_2$ smooth the cyclization of 2-aminoarylidenemalonic esters, which is initiated by a 1,5-hydride shift to create an ion pair.[9]



Addition. For transfer hydrogenation of 2-alkylquinolines to deliver the (*S*)-tetrahydro derivatives, Au(I)-carbene and *ent*-**1L** are a valuable combination, a Hantzsch ester acts as the hydrogen source (>99% yield, 98% ee, turnover up to 10000).[10] A reusable transfer hydrogenation catalyst is prepared from a polymer based on *ent*-**1R**, which has high surface area and shows increased selectivity.[11]

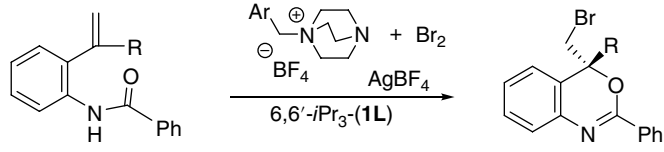
The DMAP salt of *ent*-**1O** effectively mediates the reduction of aryl methyl ketones by catecholborane.[12] Transfer hydrogenation with a Hantzsch ester also converts *N*-protected α-iminoarylacetic esters into the (*S*)-amino esters (catalyst: **1P**).[13] To enentioselectively introduce a deuterium into the α-position of amines one can starts from the corresponding ketimines, which accept the D-atom from 2-aryl-2-deuteriobenzothiazolines in the presence of (*ent*)-**1L**.[14] The same system (but with the ordinary 2-phenylbenzothiazoline as hydrogen source) is effective to conduct asymmetric reductive amination of ketones with *p*-anisidine.[15] Another report describes the use of **1T** and a Hantzsch ester to hydrogenate aryl *o*-hydroxylaryl ketimines.[16]

In the Rh(II)-catalyzed decomposition of α-diazo carbonyl compounds intervention of a proximal carbonyl group offers an opportunity for asymmetric reduction of the latter functionality (through carbonyl ylide). During formation of 1-arylisochroman-4-ones, a Hantzsch ester provides a hydride, while *ent*-**1P** can furnish a proton.[17]

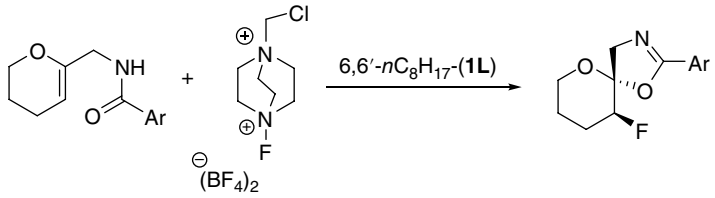
Consecutive hydroamination and asymmetric reduction to access chiral secondary amines employs a phosphine-ligated Au(I) salt for the first step and hydrogenation is catalyzed by a half-sandwich iron complex with **1L** to steer the stereochemical course.[18]

The popularity of **1L** and its enantiomer for asymmetric processes is apparent. Spiroacetalization in its presence is found to be diastereoselective and enantioselective.[19] Internal alkenes with a terminal polar group are coaxed to cyclize on reaction with NBS, and chiral adducts are obtained by furnishing **1L** to the reaction media.[20] Bromosuccinimidation of enecarbamates in the presence of *ent*-**1L** and the calcium salt is stereochemically illuminating, the acid enforces formation of products with the (*1R, 2S*)-configuration, whereas the calcium salt the (*1S, 2R*)-isomers.[21]

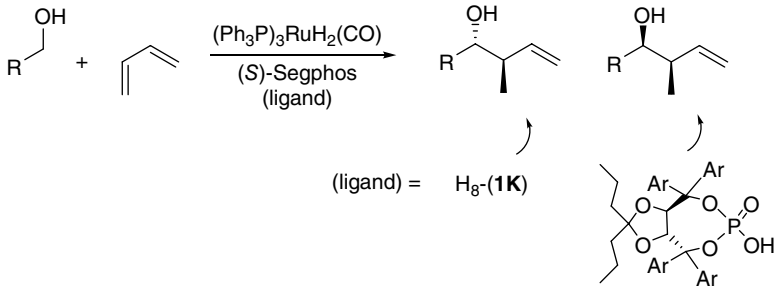
Halocyclization in enantioselective sense is accomplished as shown in the following example.[22] Note that the chiral catalyst is a 6,6′-bis(triisopropylsilyl) derivative of *ent*-**1L**.



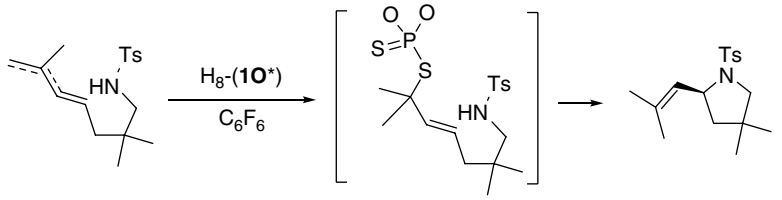
Asymmetric fluorination of enamides with Selectfluor also has been carried out with the 6,6′-dioctyl derivative of **1L**.[23,24]



1,2-Addition to conjugated dienes such as 3-vinylindoles by 2,4-diaryl-5-oxazolinones is found to be highly stereoselective. Two chirality centers appear in the adducts when *ent*-**1C** is employed as the catalyst.[25] Primary alcohols add to 1,3-butadiene under the influence of a Ru hydride complex, which is mainly catalyzed by a chiral Segphos ligand, but the Brønsted acid additive is also of utmost importance to determine the absolute configuration of the carbinolic center.[26]

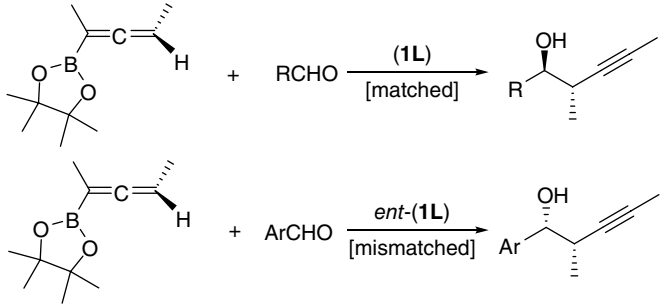


When a conjugated diene undergoes 1,2-addition with a dithiophosphoric acid based on a H_8-BINOL, the addition is able to trigger an intramolecular S_N2' reaction by an N-nucleophile.[27]



(**1O***) : 3,3′-[10-(Mes)An]$_2$-(**1A**)

Propargylation of aldehydes with allenylboronates catalyzed by**1L** proceeds via a matched pairing in the transition state. In switching to *ent*-**1L**, the pairing of the reactants is mismatched therefore it leads to a different diastereomeric series.[28] The same reaction can be conducted with the biphenylphosphoric acid analogous to **1L**.[29]



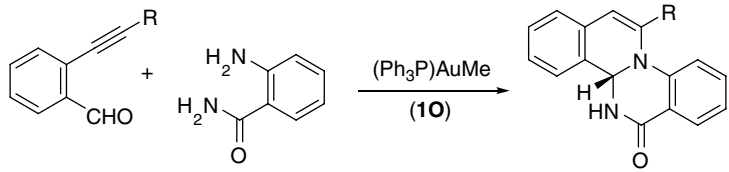
The silver salt of *ent*-**1N** is added to the InCl-catalyzed reaction of 1-methoxy-1-benzaminoalkanes with allylboronates (and allenylboronates). Actually it proceeds by an elimination-addition sequence, to produce the chiral homoallylic amine derivatives (and those of allenyl analogs).[30] Conjugated ketene silyl ethers add to *N*-(*p*-anisyl)aldimines to yield 5-amino-2-alkenoic esters with an *anti*-configuration, *ent*-**1L** is able to exert its effects to make the reaction asymmetric.[31]

N-Boc ketimines derived from isatin have been presented to pyrrole and indole in an asymmetric environment imposed by close association with *ent*-**1C**.[32] Anthranilide and certain aldimines (e.g., *N*-aryl and *N*-sulfonyl derivatives) react via imino exchange and intramolecular addition. The acid *ent*-**1O** can serve as catalyst for both steps.[33] Di-*t*-butyl α-diazomethylphosphonates and *N*-Boc aldimines combine enantioselectively as influenced by *ent*-**1L**,[34] and the same with thiols serving as one group of addends.[35]

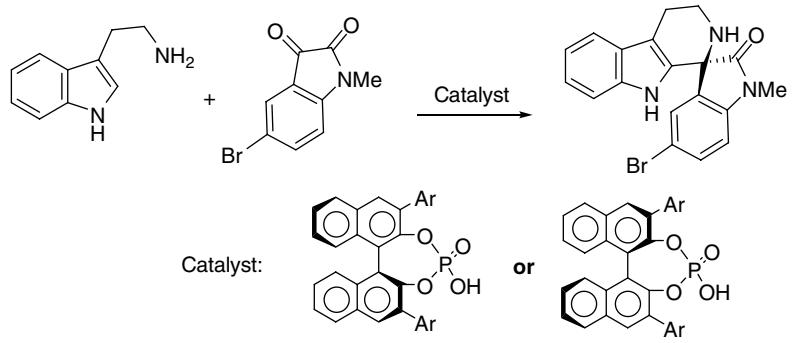
A report on Mannich reaction between oxazolinones and *N*-tosyl imines with the Ag salt of *ent*-**1T** as catalyst is found in recent literature.[36]

The noninterfering dual catalyst system of a phosphine-ligated Au(I) complex and **1L** works well to promote cyclization of 4-pentynol and then alkylation by 2,4-diaryl-5-oxazolinones at C-4, in the second step enantioselectivity is invoked.[37]

A similar strategy is deployed for the synthesis of quinazolinones which are further annulated, from mixtures of anthralinamide and 2-alkynylbenzaldehydes.[38] In this case (Ph_3P)AuMe and **1O** cooperate to deliver an excellent result.



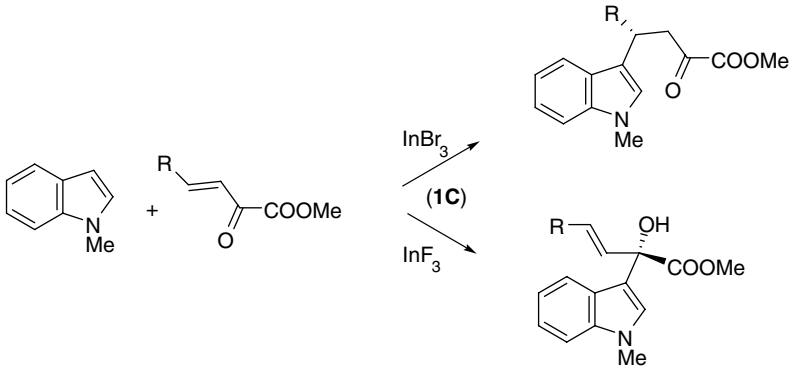
Establishment of the first chirality center in a recent synthesis of corynantheidine enlists H_8-*ent*-**1T** to conduct a Pictet-Spengler reaction.[39] The most remarkable observation is that Pictet-Spengler reaction with tryptamine and an isatin the product of same configuration is obtained from using either a (*R*)- or (*S*)-3,3′-diaryl-1,1′-binaphthalene-2,2′-diyl phosphate.[40]



Asymmetric addition of electron-rich arenes such as indole to ethyl 3,3,3-trifluoro-2-oxopropanoate gives rise to the fluorinated mandelic esters. Calcium salt of an octahydro-3,3′-diaryl-1,1′-binaphthalene-2,2′-diyl phosphate is a useful catalyst.[41]

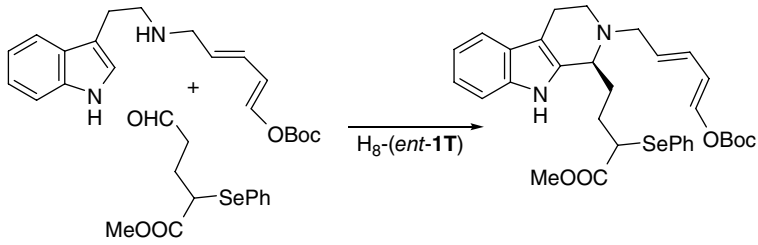
Double Michael addition involving N_b-methoxycarbonyltryptamine and 1-alken-3-ones gives rise to pyrrolo[2,3-*b*]indolines, *ent*-**1L** has shown value of stereoinduction at the ring junction.[42]

The InX_3-catalyzed addition of 1-methylindole to 2-oxo-3-alkenoic esters proceeds in either 1,2- or 1,4-fashion, depending on the halogen atoms associated with indium (F vs. Br).[43] The asymmetric versions are accomplished by adding **1C** and the like.



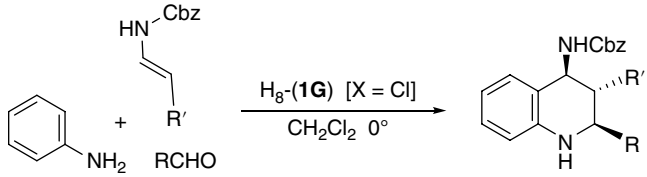
The Friedländer quinoline synthesis from 2-aminobenzaldehyde and 4-substituted cyclohexanones is rendered enantioselective by using *ent*-**1C** as catalyst.[44] Perhaps the Brønsted acid comes into play during enolization.

A synthesis of (+)-yohimbine featuring the C/D-ring construction by an intramolecular Diels-Alder reaction is dependent on enantioselective attachment of the dienophilic chain by a Pictet-Spengler reaction, and this is achievable by using *ent*-H_8-**1T** to catalyze the union.[45]



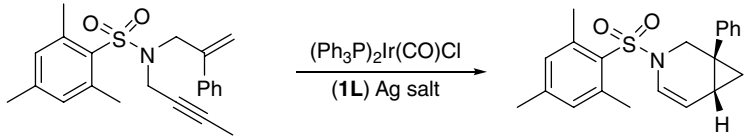
Cycloaddition. The 3,3-oxydimethylene-connected *ent*-**1A** is active in promoting the [3+2]cycloaddition of enones and imines to furnish chiral products.[46] Aldimines formed in situ from α–amino esters and aldehydes also undergo cycloaddition with 1-alkyn-3-ones, and experimentation using catalyst *ent*-**1O** has been reported.[47] Synthesis of pyrazolidines by the cycloaddition employs a catalyst generated from *ent*-**1D** and Ph_2SiCl_2.[48]

The Pavarov reaction has enjoyed much attention in recent years. Tetrahydroisoquinolines in optically active modification are now very readily assembled from anilines, aldehydes and functionalized alkenes that include enamides,[49] *N*-alkenylthioureas,[50] and nuclear hydroxylated styrenes.[51,52] In all these cases the acquisition of chiral products employs various members of **1** [e.g., *ent*-**1L**, **1J**, **1T**, and H_8-**1G** (X= Cl)].

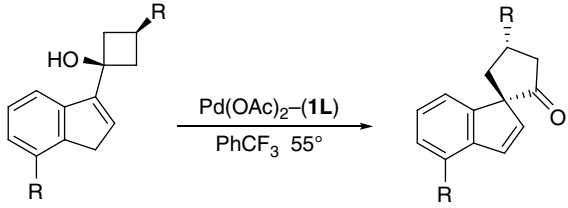


Modification of the Friedländer quinoline synthesis can yield the same type of products as the Pavaro reaction, e.g., by providing a Hantzsch ester to reduce the proper intermediates. Here a catalyst system made up of *ent*-**1L** and $Mg(OTf)_2$ is used to advantage.[53]

As iridium complexes are able to extract an allylcarbenoid activity from an alkyne, intramolecular cyclopropanation of properly distanced ene/yne units is readily practiced, and such reaction is also subject to asymmetric induction (e.g., by the silver salt of **1L**).[54]



Rearrangement. 1-(Inden-3-yl)cyclobutanols undergo rearrangement upon C-H bond activation (at C-1 of the indene nucleus) by a Pd salt to yield spirocyclic ketones under oxidative conditions, and **1L** is for producing chiral products.[55]



Imidates of 2-alkenols are converted into chiral 3-acylamino-1-alkenes. The Claisen rearrangemnt is facilitated by a palladcycle and enantioselectivity is conferred by the 2:2-complex with **1L** (the palladacycle also contains a chiral element).[56]

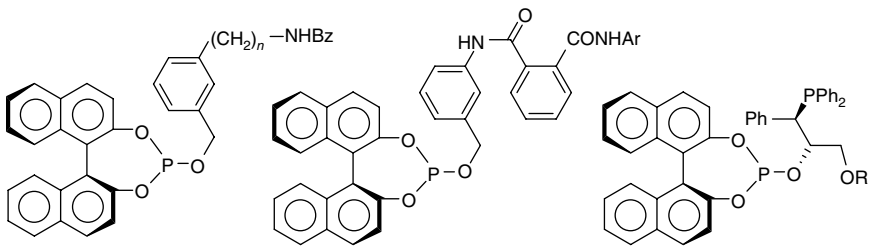
Oxidation. Asymmetric oxidation of sulfides (including 1,3-dithianes) by H_2O_2 is mediated by *ent*-**1Q**.[57] Alternatively, change can be made of the oxidant to PhIO and the catalyst to an iron(III) complex of salicylimine and a 3,3′-di(4-*t*-butylphenyl) derivative of **1A**.[58]

[1] Mandai, H., Murota, K., Mitsudo, K., Suga, S. *OL* **14**, 3486 (2012)
[2] Wang, Y., Zheng, K., Hong, R. *JACS* **134**, 4096 (2012)
[3] Yamanaka, M., Hoshino, M., Katoh, T., Mori, K., Akiyama, T. *EJOC* 4508 (2012)
[4] Wu, X.-S., Tian, S.-K. *CC* **48**, 898 (2012)
[5] Jiang, G., List, B. *ACIE* **50**, 9471 (2011)
[6] Das, J., Le Cavelier, F., Rouden, J., Blanchet, J. *EJOC* 6628 (2011)
[7] Song, L., Guo, Q.-X., Li, X.-C., Tian, J., Peng, Y.-G. *ACIE* **51**, 1899 (2012)
[8] Guo, C., Song, J., Huang, J.-Z., Chen, P.-H., Luo, S.-W., Gong, L.-S. *ACIE* **51**, 1046 (2012)
[9] Chen, L., Zhang, L., Lv, J., Cheng, J.-P., Luo, S. *CEJ* **18**, 8891 (2012)
[10] Tu, X.-F., Gong, L.-Z. *ACIE* **51**, 11346 (2012)
[11] Bleschke, C., Schmidt, J., Kundu, D.S., Blechert, S., Thomas, A. *ASC* **353**, 3101 (2011)
[12] Zhang, Z., Jain, P., Antilla, J.C. *ACIE* **50**, 10961 (2011)
[13] Qian, Y., Jing, C., Zhai, C., Hu, W. *ASC* **354**, 301 (2012)
[14] Sakamoto, T., Mori, K., Akiyama, T. *OL* **14**, 3312 (2012)
[15] Saito, K., Akiyama, T. *CC* **48**, 4573 (2012)
[16] Nguyen, T.B., Wang, Q., Gueritte, F. *CEJ* **17**, 9576 (2011)
[17] Terada, M., Toda, Y. *ACIE* **51**, 2093 (2012)
[18] Fleischer, S., Werkmeister, S., Zhou, S., Junge, K., Beller, M. *CEJ* **18**, 9005 (2012)
[19] Sun, Z., Winschel, G.A., Borovika, A., Nagorny, P. *JACS* **134**, 8074 (2012)
[20] Huang, D., Wang, H., Xue, F., Guan, H., Li, L., Peng, X., Shi, Y. *OL* **13**, 6350 (2011)
[21] Alix, A., Lalli, C., Retailleau, P., Masson, G. *JACS* **134**, 10389 (2012)
[22] Wang, Y.-M., Wu, J., Hoong, C., Rauniyar, V., Toste, F.D. *JACS* **134**, 12928 (2012)
[23] Phipps, R.J., Hiramatsu, K., Toste, F.D. *JACS* **134**, 8376 (2012)
[24] Hennecke, U. *ACIE* **51**, 4532 (2012)
[25] Terada, D., Moriya, K., Kanomata, K., Sorimachi, K. *ACIE* **50**, 12586 (2011)
[26] McInturff, E.L., Yamaguchi, E., Krische, M.J. *JACS* **134**, 20628 (2012)
[27] Shapiro, N.D., Rauniyar, V., Hamilton, G.L., Wu, J., Toste, F.D. *Nature* **470**, 245 (2011)
[28] Chen, M., Roush, W.R. *JACS* **134**, 10947 (2012)
[29] Jain, P., Wang, H., Houk, K.N., Antilla, J.C. *ACIE* **51**, 1391 (2012)
[30] Huang, Y.-Y., Chakrabarti, A., Morita, N., Schneider, U., Kobayashi, S. *ACIE* **50**, 11121 (2011)
[31] Abels, F., Schneider, C. *S* 4050 (2011)
[32] Feng, J., Yan, W., Wang, D., Li, P., Sun, Q., Wang, R. *CC* **48**, 8003 (2012)
[33] Cheng, D.-J., Tian, Y., Tian, S.-K. *ASC* **354**, 995 (2012)

[34] Zhang, H., Wen, X., Gan, L., Peng, Y. *OL* **14**, 2126 (2012)
[35] Ingle, G.K., Mormino, M.G., Wojtas, L., Antilla, J.C. *OL* **13**, 4822 (2011)
[36] Shi, S.-H., Huang, F.-P., Zhu, P., Dong, Z.-W., Hui, X.-P. *OL* **14**, 2010 (2012)
[37] Han, Z.-Y., Guo, R., Wang, P.-S., Chen, D.-F., Xiao, H., Gong, L.-Z. *TL* **52**, 5963 (2011)
[38] Patil, N.T., Mutyala, A.K., Konala, A., Tella, R.B. *CC* **48**, 3094 (2012)
[39] Wanner, M.J., Claveau, E., van Maarseveen, J.H., Hiemstra, H. *CEJ* **17**, 13680 (2011)
[40] Badillo, J.J., Silva-Garcia, A., Shupe, B.H., Fettinger, J.C., Franz, A.K. *TL* **52**, 5550 (2011)
[41] Rueping, M., Bootwicha, T., Kambutong, S., Sugiono, E. *CAJ* **7**, 1195 (2012)
[42] Zhang, Z., Antilla, J.C. *ACIE* **51**, 11778 (2012)
[43] Lv, J., Zhang, L., Zhou, Y., Nie, Z., Luo, S., Cheng, J.-P. *ACIE* **50**, 6610 (2011)
[44] Ren, L., Lei, T., Gong, L.-Z. *CC* **47**, 11683 (2011)
[45] Herlé, B., Wanner, M.J., van Maarseveen, J.H., Hiemstra, H. *JOC* (2011)
[46] He, L., Chen, X.-H., Wang, D.-N., Luo, S.-W., Zhang, W.-Q., Yu, J., Ren, L., Gong, L.-Z. *JACS* **133**, 13504 (2011)
[47] Shi, F., Luo, S.-W., Tao, Z.-L., He, L., Yu, J., Tu, S.-J., Gong, L.-Z. *OL* **13**, 4680 (2011)
[48] Serdyuk, O.V., Zamfir, A., Hampel, F., Tsogoeva, S.B. *ASC* **354**, 3115 (2012)
[49] Dagousset, G., Zhu, J., Masson, G. *JACS* **133**, 14804 (2011)
[50] Dagousset, G., Retailleau, P., Masson, G., Zhu, J. *CEJ* **18**, 5869 (2012)
[51] He, L., Bekkaye, M., Retailleau, P., Masson, G. *OL* **14**, 3158 (2012)
[52] Shi, F., Xing, G.-J., Tao, Z.-L., Luo, S.-W., Tu, S.-J., Gong, L.-Z. *JOC* **77**, 6970 (2012)
[53] Ren, L., Lei, T., Ye, J.-X., Gong, L.-Z. *ACIE* **51**, 771 (2012)
[54] Barbazanges, M., Augé, M., Moussa, J., Amouri, H., Aubert, C., Demarets, C., Fensterbank, L., Gandon, V., Malacria, M., Ollevier, C. *CEJ* **17**, 13789 (2011)
[55] Chai, Z., Rainey, T.J. *JACS* **134**, 3615 (2012)
[56] Jiang, G., Halder, R., Fang, Y., List, B. *ACIE* **50**, 9752 (2011)
[57] Liu, Z.-M., Zhao, H., Li, M.-Q., Lan, Y.-B., Yao, Q.-B., Tao, J.-C., Wang, X.-W. *ASC* **354**, 1012 (2012)
[58] Liao, S., List, B. *ASC* **354**, 2363 (2012)

1,1′-Binaphthalene-2,2′-diyl phosphites

Hydrogenation. Enantioselective hydrogenation of functionalized alkenes is achieved on Rh(I) complexed to BINOL-derived phosphites **1**, **2**, or **3**.[1,2,3]

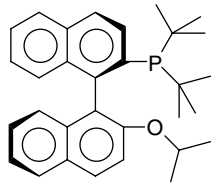


(**1**) (**2**) (**3**)

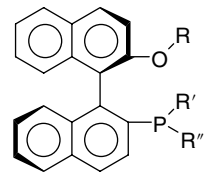
[1] Pignataro, L., Bovio, C., Civera, M., Piarulli, U., Gennari, C. *CEJ* **18**, 10368 (2012)
[2] Pignataro, L., Boghi, M., Civera, M., Carboni, S., Piarulli, U., Gennari, C. *CEJ* **18**, 1383 (2012)
[3] Etayo, P., Nuñez-Rico, J.L., Fernandez-Perez, H., Vidal-Ferran, A. *CEJ* **17**, 13978 (2011)

1,1′-Binaphthalen-2-ol-2′-phosphines and derivatives

Substitution. The binaphthyl-based ether/phosphine **1** has found use as a monodentate ligand for Pd-catalyzed *N*-arylation of $ArNH_2$,[1] and 1,2-bis(*t*-butoxycarbonyl)hydrazine.[2] Different Pd species are used in the two reactions, as the *t*-Boc groups in substrate of second reaction is acid-sensitive.



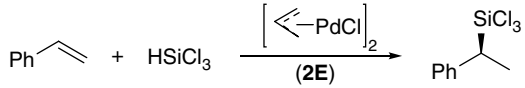
(**1**)



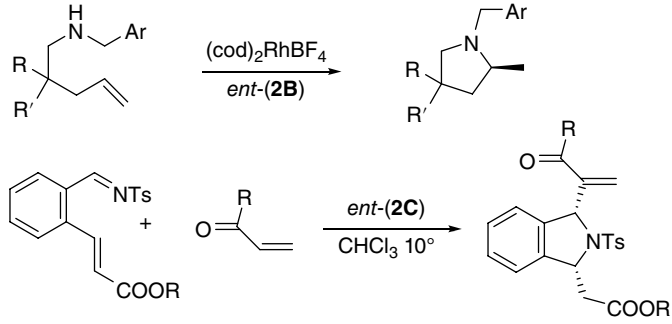
(**2A**) R = CH_2(β-Np), R′ = R″ = Cy
(**2B**) R = $CHPh_2$, R′ = R″ = Cy
(**2C**) R = H, R′ = R″ = Ph
(**2D**) R = *i*-Pr, R′ = R″ = Ph
(**2E**) R = *i*-Pr, R′ = Ph, R″ = *i*-Pr
(**2F**) R = Me, R′ = R″ = Ph

By arylation of ketene silyl ethers to access chiral α–arylalkanoic esters the H_8-derivative of an ether/phosphine **2** may be gainfully employed.[3]

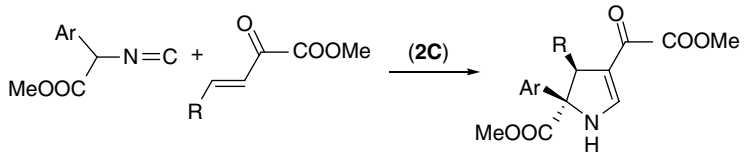
Addition. The ligand **2E**, prepared in five steps from (*R*)-BINOL, can promote enantioselective hydrosilylation of styrenes (with $HSiCl_3$) and thence (*S*)-1-arylethanols.[4]



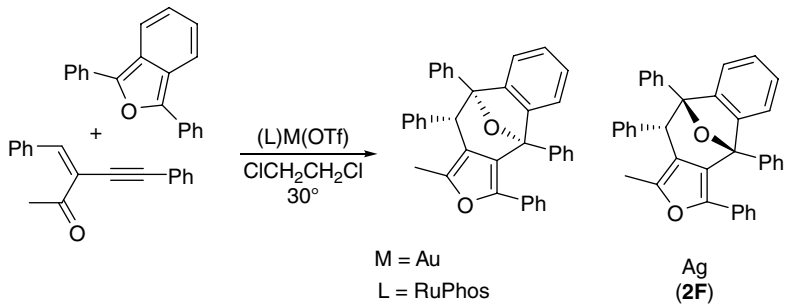
Intramolecular hydroamination in the presence of a Rh(I) salt sequestered by *ent*-**2B** results in the formation of (*S*)-2-methylpyrrolidines.[5] Taking advantage of the ability of tertiary phosphines to catalyze the Baylis-Hillman reaction, an application of *ent*-**2C** to elaborate *cis*-1,3-disubstitited isoindolines in chiral modification is realized.[6]



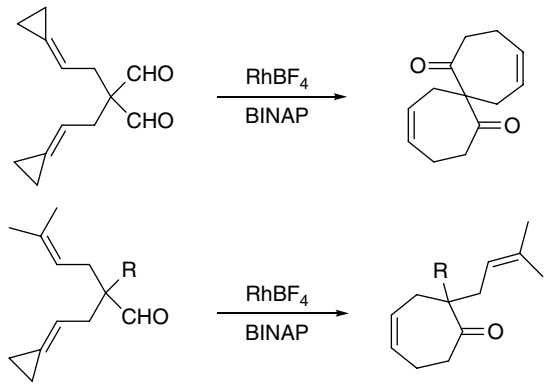
Annulation. An enantioselective route to 2,3-dihydropyrrole-2-carboxylic esters also employs **2C** to catalyze the union of α–isocyano esters and conjugated carbonyl compounds.[7]



Induced by noble metal complexes α-benzylidene-3-alkyn-1-ones are converted into 4-metallo-2-oxoniafulvenes which would actively pursue cycloaddition. In the reaction with isobenzofurans the stereochemical influence by a silver complex of *rac*-**2D** is different from that of a gold complex to RuPhos.[8]



3-Formylpropylidenecyclopropanes undergo intramolecular hydroacylation that breaks up the three-membered ring in a reaction catalyzed by a Rh(I) salt.[9]

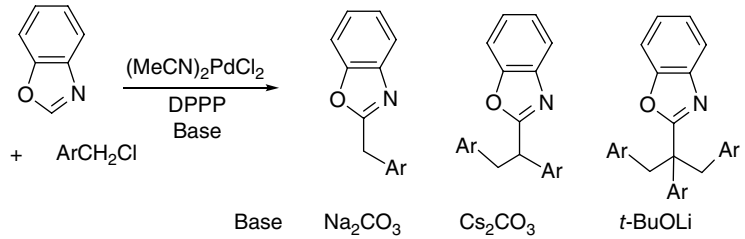


[1] Xie, X., Ni, G., Ma, F., Ding, L., Xu, S., Zhang, Z. *SL* 955 (2011)
[2] Ma, F.-F, Peng, Z.-Y., Li, W.-F., Xie, X.-M., Zhang, Z. *SL* 2555 (2011)
[3] Huang, Z., Liu, Z., Zhou, J. *JACS* **133**, 15882 (2011)
[4] Duclos, M.-C., Singjunla, Y., Petit, C., Favre-Réguillon, A., Jeanneau, E., Popowycz, F., Métay, E., Lemaire, M. *TL* **53**, 5984 (2012)

[5] Shen, X., Buchwald, S.L. *ACIE* **49**, 564 (2010)
[6] Takizawa, S., Inoue, N., Hirata, S., Sasai, H. *ACIE* **49**, 9725 (2010)
[7] Song, J., Guo, C., Chen, P.-H., Yu, J., Luo, S.-W., Gong, L.-Z. *CEJ* **17**, 7786 (2011)
[8] Gao, H., Wu, X., Zhang, J. *CC* **46**, 8764 (2010)
[9] Crépin, D., Tugny, C., Murray, J.H., Aissa, C. *CC* **47**, 10957 (2011)

Bis(acetonitrile)dichloropalladium(II)

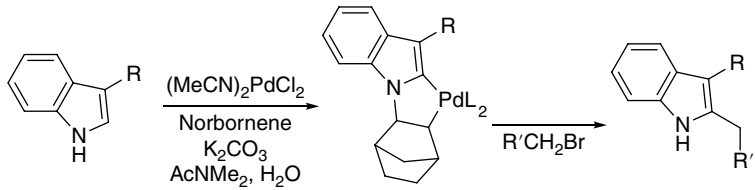
Coupling. Stille coupling for preparation of 3-alkynoic esters and amides starts with tributylstannylalkynes and the α-bromo esters/amides.[1] Arenesulfonyl compounds (chlorides, and sodium salts) are converted to ArCN on reaction with CuCN, the Pd catalyst is assisted by $Cu(acac)_2$.[2] Benzylation at C-2 of benzoxazole can go further at the α-carbon by changing the base from Na_2CO_3 to Cs_2CO_3 and *t*-BuOLi.[3] Hiyama coupling of thiophene occurs selectively at a β-position.[4]



Suzuki coupling of polyfluoroarenes containing a 2-oxazolidinyl group is selective, as expected to occurs at the *o*-position of the heterocyclic substituent.[5]

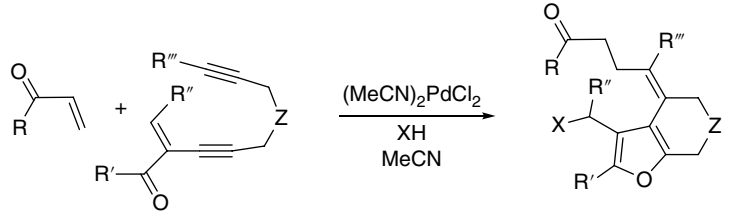
3-Phthalimido-1-alkenes add RZnBr under oxidative conditions [$(MeCN)_2PdCl_2$, $Zn(OTf)_2$, benzoquinone] to afford homologous *N*-alkylphthalimides.[6] Alkyl group transfer to and deoxygenation of isoquinoline-*N*-oxide take place when it is heated with a dialkyl sulfoxide; with $SOCl_2$ chlorination occurs. Besides the Pd(II) catalyst, additives present are Bu_3N, $(Bu_4N)OAc$, and ZnO.[7]

Norbornene is a participant in palladation and then alkylation of indoles at C-2, but its role is transient.[8]



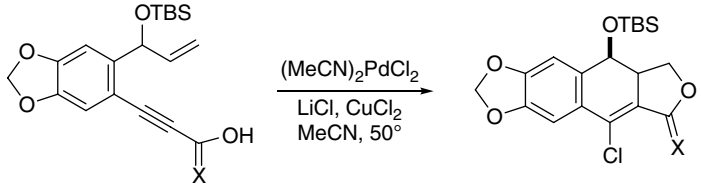
3-Alkylidene-1-isoindolinones are formed in a coupling reaction of *o*-halobenzamides and 1-alkynes. A ligand to assist the metal catalyst is *N,N′*-di(4-pyridinemethylene) hydrazine.[9]

Certain enediynes are susceptible to push-pull bicyclization in the presence of a nucleophile, a Michael acceptor besides the Pd catalyst.[10]



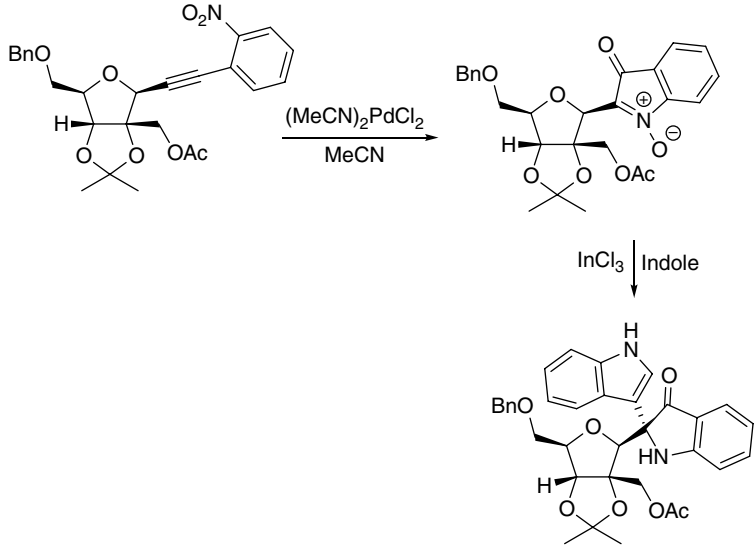
Addition to CC multiple bonds. The passage of styrenes to arylacetaldehydes is >99% regioselective, by oxidative hydration in a reagent system composing of $(MeCN)_2PdCl_2$, benzoquinone, *t*-BuOH and water.[11] The Pd-catalyzed oxidation of 1-alkenes in the presence of pinacol furnishes the aldehyde acetals.[12]

A combination of $(MeCN)_2PdCl_2$ and $CuCl_2$ induces the cycloaddition of *N*-(ω-alkenyl) carbamates with loss of the *O*-alkyl group, to form bicyclic oxazolidinones.[13] An intramolecular cycloaddition is apparently initiated by chloropalladation of a triple bond, in this case sufficient concentration of the chloride ion is provided by LiCl.[14]



X = O; H,H

In a synthesis of (–)-isatisine-A the indolizidinedione unit is constructed in three steps starting from an intramolecular addition.[15]



[1] Kang, J.Y., Connell, B.T. *JOC* **76**, 6856 (2011)
[2] Chen, J., Sun, Y., Liu, B., Liu, D., Cheng, J. *CC* **48**, 449 (2012)
[3] Xie, P., Huang, H., Xie, Y., Guo, S., Xia, C. *ASC* **354**, 1692 (2012)
[4] Funaki, K., Sato, T., Oi, S. *OL* **14**, 6186 (2012)
[5] Yu, D., Shen, Q., Lu, L. *JOC* **77**, 1798 (2012)
[6] DeLuca, R.J., Sigman, M.S. *JACS* **133**, 11454 (2011)
[7] Yao, B., Song, R.-J., Liu, Y., Xie, Y.-X., Li, J.-H., Wang, M.-K., Tang, R.-Y., Zhang, X.-G., Deng, C.-L. *ASC* **354**, 1890 (2012)
[8] Jiao, L., Herdtweck, E., Bach, T. *JACS* **134**, 14563 (2012)
[9] Sarkar, S., Dutta, S., Dey, R., Naskar, S. *TL* **53**, 6789 (2012)
[10] Liu, R., Zhang, J. *CAJ* **7**, 294 (2012)
[11] Teo, P., Wickens, Z.K., Dong, G., Grubbs, R.H. *OL* **14**, 3237 (2012)
[12] Yamamoto, M., Nakaoka, S., Ura, Y., Kataoka, Y. *CC* **48**, 1165 (2012)
[13] Borsini, E., Broggini, G., Fasana, A., Galli, S., Khansaa, M., Piarulli, U., Rigamonti, M. *ASC* **353**, 985 (2011)
[14] Abrams, J.N., Zhao, Q., Minaruzzaman, G. *T* **68**, 423 (2012)
[15] Patel, P., Ramana, C.V. *JOC* **77**, 10509 (2012)

Bis(allyl)calcium

Metallation. 2-Picoline undergoes metallation at the methyl group for reaction with electrophiles.[1]

[1] Jochmann, P., Leich, V., Spaniol, T.P., Okuda, J. *CEJ* **17**, 12115 (2011)

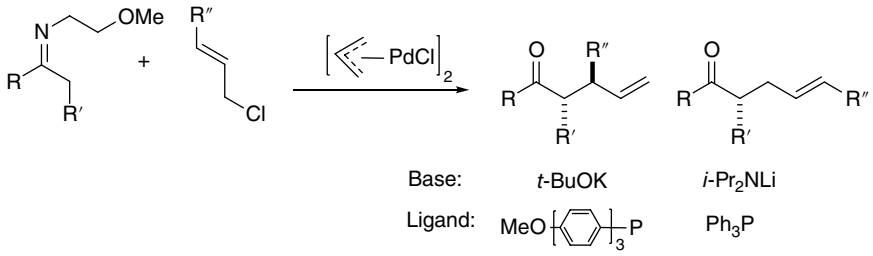
Bis(η³-allyl)dichlorodipalladium

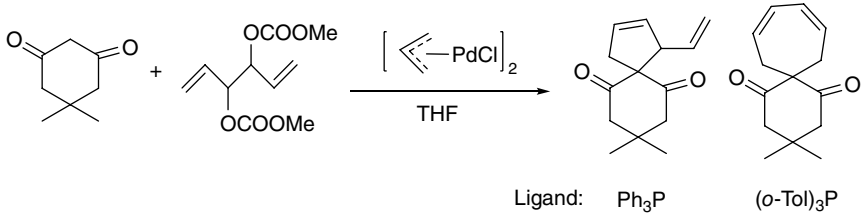
Addition. π-Allylpalladium chloride (dimer) is catalytically active for promotion of hydrohalogenation of 1-haloalkynes by LiX in HOAc, leading to (*Z*)-1,2-dihalo-1-alkenes.[1]

Substitution. The primary carbonate of an (*E*)-2-alkene-1,5-diol can be transformed into *syn*-1-alkene-3-5-diols via Pd-catalyzed hemiacetalization with an added aldehyde, followed by an intramolecular S_N2' reaction. 4-Vinyl-1,3-dioxanes that are formed have an all-*cis* configuration.[2]

In an alkyl aryl ether synthesis from ArX and RR'CHOH it seems that the catalyst is best supported by an encumbered phosphine such as BrettPhos.[3]

Allylation of ketimines by 1-chloro-2-alkenes can follow S_N2 or S_N2' pathway, and a choice of base and ligand becomes the determining factor.[4] A related finding is the double allylation of 5,5-dimethyl-1,3-cyclohexadione by a dicarbonate of 1,5-hexadiene-3,4-diol.[5]





The applicability of allylamines such as *N*-allylpyrrolidine as electrophiles in the reaction with ketones is quite novel.[6] However, the transition of 3-aryl-2-propen-1-ols to amines is straightforward,[7] although whether the ligand, 1,7-bis(diphenylphosphino)indole, has special attributes is unclear.

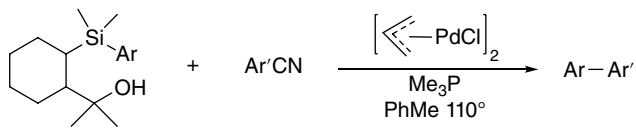
3-Bromo-2,4-pentadienyl acetate undergoes twofold substitution, with the nucleophiles attach themselves at the two terminal carbons in the resulting 2,3-alkadienes.[8]

Amine synthesis based on some substitution/coupling reactions has been extended to using sulfonamides to react with ArX,[9] main purpose seems to be exploration of new catalyst and ligand combinations. More unusual is the substitution of allylic amines to form allyl sulfones on reaction with RSO_2Na.[10]

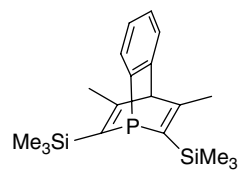
The transformation of ArOTf into ArF is better performed in a microreactor with packed-bed for flow reaction that allows for handling the insoluble CsF, and reaction time control.[11]

The ionic Pd tetrafluoroborate complex containing an allyl and a COD ligand each is active in promoting benzylic displacement by all kinds of nucleophiles, and under such conditions the leaving group selectivity trend is F > OCOOMe >> OAc.[12]

Coupling. Biaryls are formed from coupling reactions. Pairing $(ArSiMe_2)_2O$ with Ar'Br is easily recognized,[13] but that involving Si-C bond cleavage and decyanation is quite unusual.[14] A method for synthesis of $ArCOCH_2CN$ is through coupling of ArI, CO and Me_3SiCH_2CN, here the catalyst system contains bis(η³-methallyl)dichlorodipalladium, $CuBr_2$, and ZnF_2.[15]

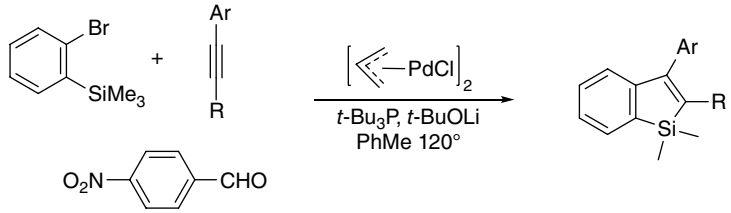


The Negishi coupling can take full advantage of the air-stable phosphabarrelene ligand **1** that forms a catalyst active at room temperature in THF because it allows easy reduction of Pd(II) species to the Pd(0) state.[16]



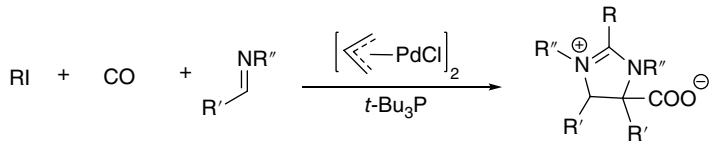
(**1**)

Benzosiloles can be elaborated from 2-bromoaryltrimethylsilanes and alkynes.[17] However, the appropriate Pd catalyst for alkynes having the *sp*-carbons bonded to alkyl groups is $(Ph_3P)_4Pd$.



On converting tertiary amines containing one benzyl group to the tricarbonylchromium complexes, arylation is relatively facile. Thus lithiation on exposure to $LiN(SiMe_3)_2$ is followed by the Pd catalyst, a phosphine ligand and ArOTf to complete the transformation. The use of a chiral ferrocene-based P,N-ligand gives optically active diarylmethylamines.[18]

α-Cyanoalkanoic acid salts (of Na, K) undergo decarboxylative benzylation.[19] In the formation of an imidazolinium salt that bear a carboxylate group at C-4 by coupling of an imine, RI and CO, two equivalents of the imine are consumed.[20]



Many aroylformic acid derivatives can be made in one step from electron-rich ArI, CO and nucleophiles, A base that is preferred is DBU.[21]

[1] Zhu, G., Chen, D., Wang, Y., Zheng, R. *CC* **48**, 5796 (2012)
[2] Wang, L., Menche, D. *ACIE* **51**, 9425 (2012)
[3] Wu, X., Fors, B.P., Buchwald, S.L. *ACIE* **50**, 9943 (2011)
[4] Chen, J.-P., Peng, Q., Lei, B.-L., Hou, X.-L., Wu, Y.-D. *JACS* **133**, 14180 (2011)
[5] Clavier, H., Giordano, L., Tenaglia, A. *ACIE* **51**, 8648 (2012)
[6] Zhao, X., Liu, D., Guo, H., Liu, Y., Zhang, W. *JACS* **133**, 19354 (2011)
[7] Ghosh, R., Sarkar, A. *JOC* **76**, 8508 (2011)
[8] Ogasawara, M., Suzuki, M., Takahashi, T. *JOC* **77**, 5406 (2012)
[9] Rosen, B.R., Ruble, J.C., Beauchamp, T.J., Navarro, A. *OL* **13**, 2564 (2011)
[10] Wu, X.-S., Chen, Y., Li, M.-B., Zhou, M.-G., Tian, S.-K. *JACS* **134**, 14694 (2012)
[11] Noël, T., Maimone, T.J., Buchwald, S.L. *ACIE* **50**, 8900 (2011)
[12] Blessley, G., Holden, P., Walker, M., Brown, J.M., Gouverneur, V. *OL* **14**, 2754 (2012)
[13] Boehner, C.M., Frye, E.C., O'Connor, K.M.G., Galloway, W.R.J.D., Sore, H.F., Dominguez, P.G., Norton, D., Hulcoop, D.G., Owen, M., Turner, G., Crawford, C., Horsley, H., Spring, D.R. *CEJ* **17**, 13230 (2011)
[14] Tang, S., Li, S.-H., Yan, W. *TL* **53**, 6743 (2012)
[15] Park, A., Lee, S. *OL* **14**, 1118 (2012)

[16] Ribagnac, P., Blug, M., Villa-Uribe, J., Le Goff, X.-F., Gosmini, C., Mezailles, N. *CEJ* **17**, 14389 (2012)
[17] Liang, Y., Geng, W., Wei, J., Xi, Z. *ACIE* **51**, 1934 (2012)
[18] McGrew, G.I., Stanciu, J., Carroll, P.J., Dreher, S.D., Walshi, P.J. *ACIE* **51**, 11510 (2012)
[19] Shang, R., Huang, Z., Xiao, X., Lu, X., Fu, Y., Liu, L. *ASC* **354**, 2465 (2012)
[20] Bontemps, S., Quesnel, J.S., Worrall, K., Arndtsen, B.A. *ACIE* **50**, 8948 (2011)
[21] de la Fuente, V., Godard, C., Zangrando, E., Claver, C., Castillon, S. *CC* **48**, 1695 (2012)

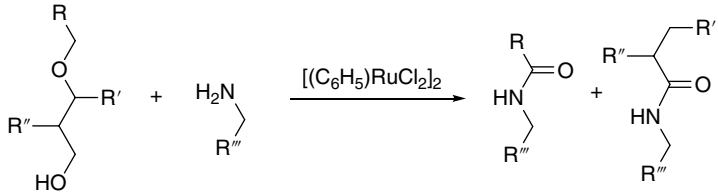
Bis[(η⁶-arene)dichlororuthenium(II)]

Reduction. Under hydrogen the reduction of aroic acid esters to the benzyl alcohols is achieved in the presence of $[(\eta^6\text{-benzene})RuCl_2]_2$ and a 1-methylimidazol-2-ylmethylphosphine ligand (variation of the other *P*-substituents to suit the nature of the ester, ArCOOR or ArCOOAr').[1]

Transfer hydrogenation of nitroarenes and reductive cleavage of azoarenes are readily achieved using $[(\eta^6\text{-cymene})RuCl_2]_2$ as catalyst.[2] The same method is applicable to reduction of sulfinimines [with additive $HOCH_2C(NH_2)Me_2$].[3] A borane complex, $Me_2NH{\cdot}BH_3$, is also a suitable hydrogen source for the reduction of carbonyl compounds, imines, and oximes.[4]

Alkylation of amines by incorporating the carbon chain of allylic alcohols is accomplished by heating the mixtures with HCOOH in toluene at 150° with a modified $[(\eta^6\text{-cymene})RuCl_2]_2$ in which one of the chlorine atom is replaced by an *o*-diphenylphosphinobenzenesulfonate group.[5]

Coupling. 3-Alkoxyalkanols react with primary amines to produce two amides through cleavage of the ethereal carbon bond, each fragment being utilized for oxidative coupling.[6]

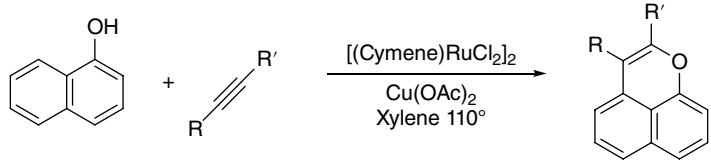


An aroic ester is *o*-hydroxylated on treatment with $[(\eta^6\text{-cymene})RuCl_2]_2$ and an oxidant (e.g., $K_2S_2O_8$) in a mixture of CF_3COOH and $(CF_3CO)_2O$.[7] Amides are similarly *o*-hydroxylated with a slightly different catalyst-oxidant system, $[(\eta^6\text{-cymene})Ru(OCOMes)_2]_2$ and $PhI(OAc)_2$.[8] [Note the dimesylate complex promotes *o*-arylation of functionalized arenes in water by phenols, which are converted into tosylates in situ.[9]]

Phthalides are synthesized by *o*-alkenylation of aroic acids with electron-deficient alkenes, which is followed by lactonization. The oxidant is $Cu(OAc)_2$.[10]

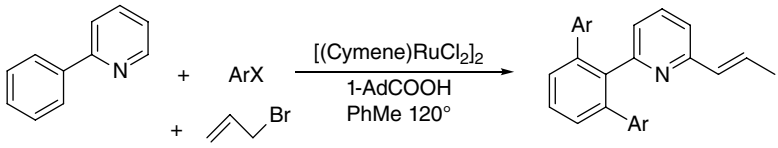
Ring closure via formyl group translocation delivers 3-formylindoles from 2-alkynylformanilines. Heating the substrates with $[(C_{10}H_{14})RuCl_2]_2$ in dichloroethane accomplishes the reaction.[11]

o-Arylation of aromatic amides employs $ArB(OH)_2$, the Ru(II) complex, and Ag_2O – $AgSbF_6$.[12] More extensively investigated is the *o*-alkenylation, involving aroic esters,[13,14] aromatic aldehydes,[15] *O*-aryl carbamates and an acrylic ester in air.[16] In these reactions $Cu(OAc)_2$ and $AgSbF_6$ are essential additives. With alkynes these acids and amides combine to give isocoumarins[17,18] and isoquinolin-1-ones,[19–21] respectively. Tertiary amides furnish *o*-alkenyl derivatives as expected.[22] 1-Naphthol and 4-hydroxycoumarin are annulated across the *peri*-position.[23]



Different results appear in the coupling of aryl ketones with alkynes, as 1-indanols or benzofulvenes are obtained.[24] The latter compounds are the dehydration products produced when larger amounts of $AgSbF_6$ are used.

The familiar activation by the pyridinyl nitrogen atom on a proximal C-H bond of 2-arylpyridines also prevails with the Ru(II) complex. Alkynylation using 1-bromoalkynes[25] and arylation[26] are similarly performed. Interestingly, a 1-propenyl group is selectively introduced to C-6 of the pyridine ring on reaction with allyl bromide.

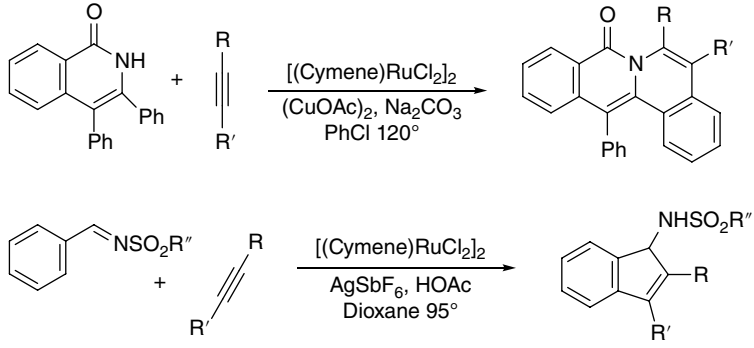


A strategy for *o*-arylation of phenols as developed based on the directive effect of a pyridyl group involves formation of aryl 2-pyridyl ethers. Removal of the pyridyl unit after the arylation completes the transformation.[27]

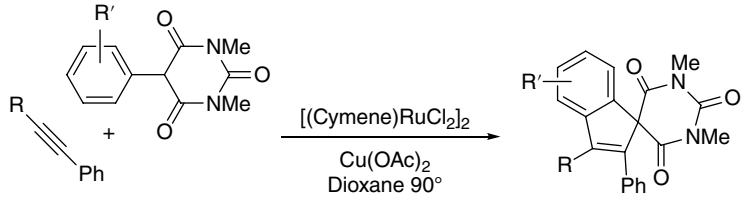
The coupling method is applicable to adding a carbamoyl group, when using RNCO as reactant.[28] *N*-Arylimines of aryl ketones readily undergo *o*-arylation, introduction of the substituent to two open *o*-positions is observed.[29] Similar reactions on oximes and oxime ethers produce substituted isoquinolines.[30]

2-Arylaminopyrimidines form *N*-(2-pyrimidyl)indoles on reaction with alkynes.[31] The *o*-position of the aniline derivatives is activated by the pyrimidyl group.

3-Aryl-1-isoquinolinones offer an opportunity to form a dibenzoquinolizine skeleton.[32] *N*-Sulfonylaldimines derived from araldehydes undergo coupling that ends with addition to the C=N bond.[33]



Activation of a benzylic C-H bond for coupling is exemplified by the method of α-arylation of benzylic amines.[34] On attaching the amino group to C-2 of β-picoline (removable), the pyridyl nitrogen atom can exert its influence on the benzylic position. Spiroannulation of 5-aryl-1,3-dimethylbarbituric acids is quite facile.[35]



Tertiary cyclic amines (pyrrolidines and piperidines) are alkylated by RCHO/HCOOH at a β-carbon in the presence of the slightly modified $[(\eta^6\text{-cymene})RuCl_2]_2$ in which a chlorine atom is replaced by an *o*-phosphinobenzenesulfonato ligand.[36]

N-(α-Diazo-β-oxoalkanoyl)anilines undergo cyclization to furnish 3-acyloxindoles on warming in toluene with $[(\eta^6\text{-cymene})RuCl_2]_2$.[37]

Substitution. *ipso*-Substitution with retention of configuration of cinnamyl acetates/carbonates and their allylomers is a general trend for the Ru(II)-catalyzed reaction. 2-Diphenylphosphinobenzoic acid is a better ligand than Ph_3P. Regarding regioselectivity, the cinnamyl substrates perform poorer than those having the leaving group at the benzylic position.[38]

An unusual arenesulfonylation at a *m*-position of 2-arylpyridine[39] is interpreted as activation of the *p*-position to the metal of a ruthenacycle intermediate. [Note that the *p*-position is *meta* to the pyridyl substituent.]

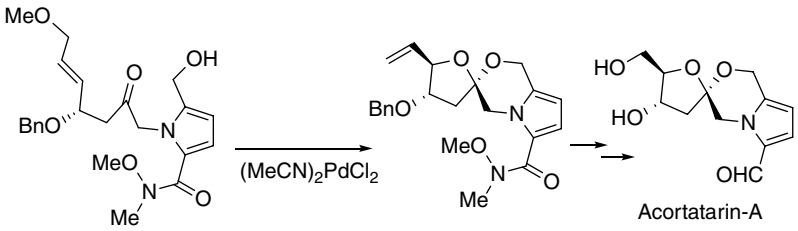
[1] Junge, K., Wendt, B., Westerhaus, F.A., Spannenberg, A., Beller, M. *CEJ* **18**, 9011 (2012)
[2] Jagadeesh, R.V., Wienhöfer, G., Westerhaus, F.A., Surkus, A.-E., Junge, H., Junge, K., Beller, M. *CEJ* **17**, 14375 (2011)

[3] Pablo, O., Guijarro, D., Kovacs, G., Lledos, A., Ujaque, G., Yus, M. *CEJ* **18**, 1969 (2012)
[4] Nixon, T.D., Whittlesey, M.K., Williams, J.M.J. *TL* **52**, 6652 (2011)
[5] Sahli, Z., Sundararaju, B., Achard, M., Bruneau, C. *OL* **13**, 3964 (2011)
[6] Chen, C., Hong, S.H. *OL* **14**, 2992 (2012)
[7] Yang, Y., Lin, Y., Rao, Y. *OL* **14**, 2874 (2012)
[8] Thirunavukkarasu, V.S., Hubrich, J., Ackermann, L. *OL* **14**, 4210 (2012)
[9] Ackermann, L., Pospech, J., Potukuchi, H.K. *OL* **14**, 2146 (2012)
[10] Ackermann, L., Pospech, J. *OL* **13**, 41536 (2011)
[11] Wu, C.-Y., Hu, M., Liu, Y., Song, R.-J., Lei, Y., Tang, B.-X., Li, R.-J., Li, J.-H. *CC* **48**, 3197 (2012)
[12] Chinnagolla, R.K., Jeganmohan, M. *OL* **14**, 5246 (2012)
[13] Graczyk, K., Ma, W., Ackermann, L. *OL* **14**, 4110 (2012)
[14] Padala, K., Pimparkar, S., Madasamy, P., Jeganmohan, M. *CC* **48**, 7140 (2012)
[15] Padala, K., Jeganmohan, M. *OL* **14**, 1134 (2012)
[16] Li, J., Kornhaass, C., Ackermann, L. *CC* **48**, 11343 (2012)
[17] Ackermann, L., Pospech, J., Graczyk, K., Rauch, K. *OL* **14**, 930 (2012)
[18] Chinnagolla, R.K., Jeganmohan, M. *CC* **48**, 2030 (2012)
[19] Ackermann, L., Lygin, A.V., Hofmann, N. *ACIE* **50**, 6379 (2011)
[20] Ackermann, L., Fenner, S. *OL* **13**, 6548 (2011)
[21] Li, B., Feng, H., Xu, S., Wang, B. *CEJ* **17**, 12573 (2011)
[22] Hashimoto, Y., Hirano, K., Satoh, T., Kakiuchi, F., Miura, M. *OL* **14**, 2058 (2012)
[23] Thirunavukkarasu, V.S., Donati, M., Ackermann, L. *OL* **14**, 3416 (2012)
[24] Chinnagolla, R.K., Jeganmohan, M. *EJOC* 417 (2012)
[25] Ano, Y., Tobisu, M., Chatani, N. *SL* 2763 (2012)
[26] Goriya, Y., Ramana, C.V. *CEJ* **18**, 13288 (2012)
[27] Ackermann, L., Diers, E., Manvar, A. *OL* **14**, 1154 (2012)
[28] Muralirajan, K., Parthasarathy, K., Cheng, C.-H. *OL* **14**, 4262 (2012)
[29] Li, B., Devaraj, K., Darcel, C., Dixneuf, P.H. *T* **68**, 5179 (2012)
[30] Chinnagolla, R.K., Pimparkar, S., Jeganmohan, M. *OL* **14**, 3032 (2012)
[31] Ackermann, L., Lygin, A.V. *OL* **14**, 764 (2012)
[32] Li, B., Feng, H., Wang, N., Ma, J., Song, H., Xu, S., Wang, B. *CEJ* **18**, 12873 (2012)
[33] Zhao, P., Wang, F., Han, K., Li, X. *OL* **14**, 5506 (2012)
[34] Dastbaravardeh, N., Schnürch, M., Mihovilovic, M.D. *OL* **14**, 3792 (2012)
[35] Chidipudi, S.R., Khan, I., Lam, H.W. *ACIE* **51**, 12115 (2012)
[36] Sundararaju, B., Achard, M., Sharma, G.V.M., Bruneau, C. *JACS* **133**, 10340 (2011)
[37] Chan, W.-W., Kwong, T.-L., Yu, W.-Y. *OBC* **10**, 3749 (2012)
[38] Kawatsura, M., Sato, M., Tsuji, H., Ata, F., Itoh, T. *JOC* **76**, 5485 (2011)
[39] Saidi, O., Marafie, J., Ledger, A.E.W., Liu, P.M., Mahon, M.F., Kociok-Köhn, G., Whittlesey, M.K., Frost, C.G. *JACS* **133**, 19298 (2011)

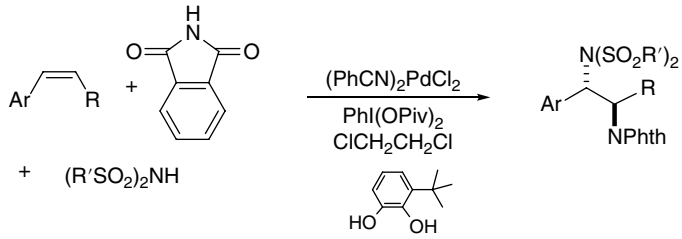
Bis(benzonitrile)dichloropalladium(II)

Coupling. Aryl formates are converted into aroic esters by reaction with ArX, using $(PhCN)_2PdCl_2$ as catalyst (ligand: Xantphos).[1] Unsaturated azacycles undergo C-H arylation at the sp^2-carbon atom adjacent to the nitrogen. The reaction is carried out with RSO_2Na, while the Pd catalyst is supplemented with an oxidant, e.g., $Cu(OAc)_2$.[2]

Substitution. In a synthetic approach to acortatarin-A the spiroketal unit was constructed in a reaction sequence of hemiacetalization and intramolecular S_N2' displacement.[3]



Addition. Functionalization of a double bond by adding two different amino groups is illustrated in the example shown below.[4]

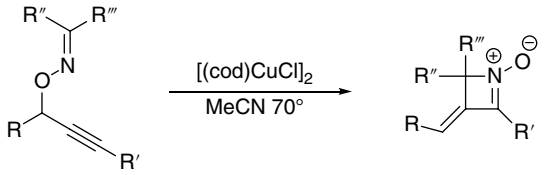


Cyclopentenes are synthesized from a Pd-catalyzed reaction between 1-pinacolatoboryl-1,2-propadiene and doubly activated alkenes.[5]

[1] Fujihara, T., Hosoki, T., Katafuchi, Y., Iwai, T., Terao, J., Tsuji, Y. *CC* **48**, 8012 (2012)
[2] Liu, B., Guo, Q., Cheng, Y., Lan, J., You, J. *CEJ* **17**, 13415 (2011)
[3] Borrero, N.V., Aponick, A. *JOC* **77**, 8410 (2012)
[4] Martinez, C., Muñiz, K. *ACIE* **51**, 7031 (2012)
[5] Kohn, B.L., Jarvo, E.R. *OL* **13**, 4858 (2011)

Bis[chloro(1,5-cyclooctadiene)copper(I)]

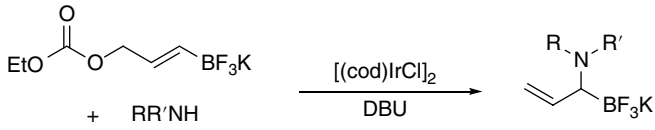
Cycloisomerization. Conversion of oxime propargyl ethers into four-membered nitrones on heating with $[(cod)CuCl]_2$ is a rather unusual reaction.[1]



[1] Nakamura, I., Kudo, Y., Araki, T., Zhang, D., Kwon, E., Terada, M. *S* 1542 (2012)

Bis[chloro(1,5-cyclooctadiene)iridium(I)]

Substitution. Catalyzed by $[(cod)IrCl]_2$, 3-trichloroacetimino-1-alkenes are transformed by $Et_3N{\cdot}3HF$ into the 3-fluoro-1-alkenes.[1] An anionic trifluoroborato group directs the regiochemistry of allylic substitution.[2]

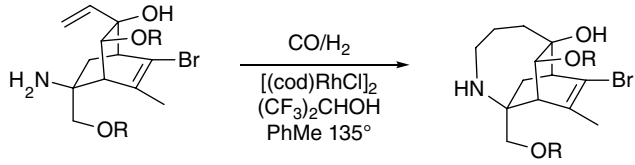


α–Alkylation of nitriles (e.g., MeCN to $ArCH_2CH_2CN$) by primary alcohols is achieved in the presence of a base.[3] Intramolecular reaction is similarly performed.[4]

[1] Topczewski, J.J., Tewson, T.J., Nguyen, H.M. *JACS* **133**, 19318 (2011)
[2] Touchet, S., Carreaux, F., Molander, G.A., Carboni, B., Bouillon, A. *ASC* **353**, 3391 (2011)
[3] Anxionnat, B., Pardo, D.G., Ricci, G.,Cossy, J. *OL* **13**, 4084 (2011)
[4] Anxionnat, B., Pardo, D.G., Ricci, G.,Cossy, J. *EJOC* 4453 (2012)

Bis[chloro(1,5-cyclooctadiene)rhodium(I)]

Addition. Hydroformylation and reduction are accomplished in one operation to transform styrenes into 2-arylpropanols by syngas in the presence of $[(cod)RhCl]_2$ and 1,4-bis(dimethylamino)butane.[1] Linear homologation of a carbon chain and functionalization can lead to cyclization via a Schiff base.[2]

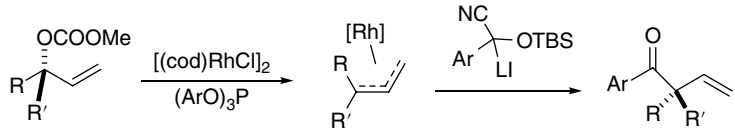


n-Alkenols apparently undergo isomerization to become donors of aldol reaction, and the *syn*-2-alkyl-3-hydroxyalkanals are prepared.[3]

By Rh(I) catalysis, pyridine adds pinacolatoborane to afford *N*-pinacolatoboryl-1, 2-dihydropyridine.[4] A similar reaction is the formation of α-arylamine derivatives from reaction of *N*-sulfinylimines with arylboroxines[5] or (with *S*-chiral imines) sodium tetraarylborates.[6]

Pyridine *N*-oxide and benzannulated azoles add *t*-butyl acrylate at the α-carbon site, when the Rh(I) catalyst supported by a diphosphine is used.[7]

Substitution and coupling. The reaction of cinnamyl halides with triorganoindium reagents is catalyzed by $[(cod)RhCl]_2$.[8] The oxygen function of benzylic acetates is replaced (S_N2') by an allyl group from allylsilanes.[9] However, on reversing the roles of the allylic substrates, the action of the Rh(I) complex on allylic carbonates to render them electrophilic, reaction with masked acyl anions takes place at the internal position.[10]



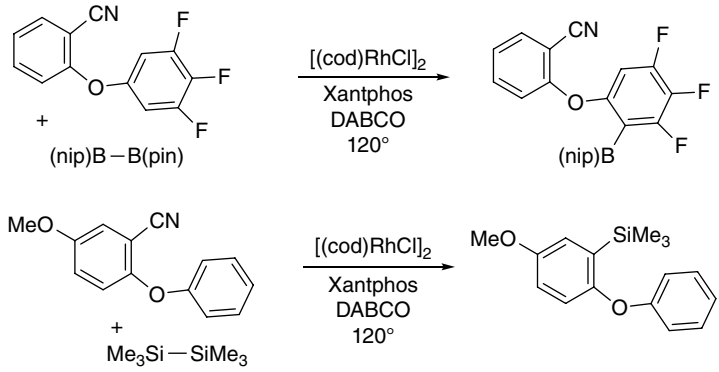
The substitution of 3-(α-sulfonylalkyl)indoles by various nucleophiles usually proceeds by an elimination-addition pathway. It is no exception in the Rh(I)-catalyzed reaction with arylboronic acids under basic conditions.[11] An ester group is introduced at C-3 of the indole nucleus on a carbonylation-trapping sequence promoted by the Rh(I) complex and in the presence of $K_2S_2O_8$.[12]

Substitution (or coupling) of ArI on reaction with Ar'SH in the presence of the Rh complex[13] is of little synthetic significance. Less obvious is the B/CN group exchange from aryl, benzyl and alkenyl cyanides on reaction with cyclic diboronates.[14]

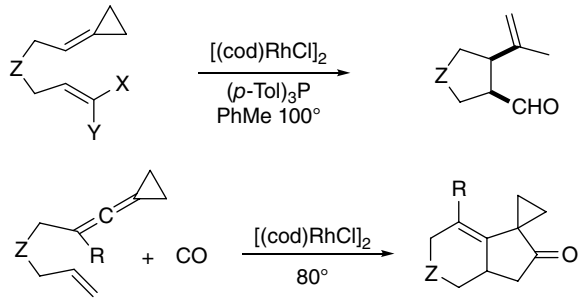
Benzosiloles are synthesized from reaction of *o*-trimethylsilylphenylboronates and alkynes.[15] In the cyclization step loss of a methyl group from the silicon atom occurs.

Bromoarenes couple with acrylic esters at the *m*-position when the Rh(I) complex and $Cu(OAc)_2$ are used as cocatalysts in air. One equivalent of Cl_3CCOOH is also indispensable.[16]

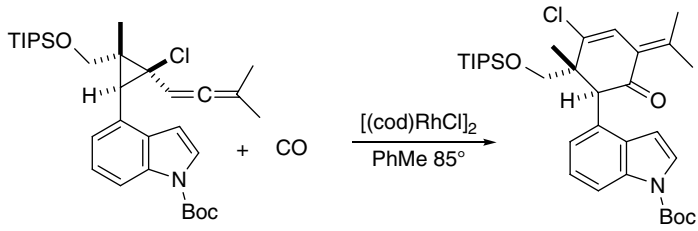
Rhodium insertion into aryl cyanides followed by 1,5-metal migration is featured in certain *o*-cyanodiaryl ethers, and bonding of the coupling partner to the other aryl nucleus is observed.[17]



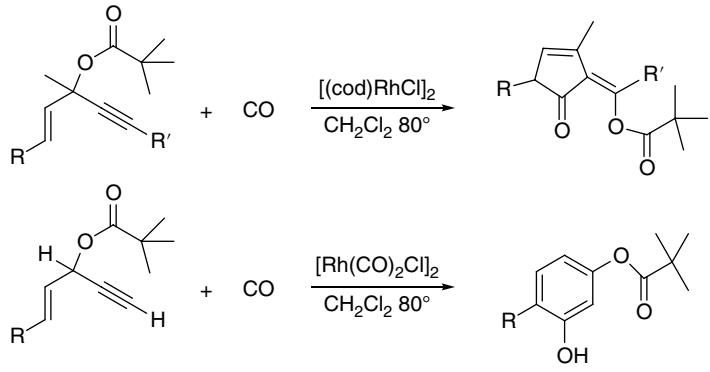
Annulation. An intricate transformation involves ring cleavage of an alkylidenecyclopropane unit while one of the sp^2-carbon atoms participates in the formation of a five-membered ring.[18] Under the Pauson-Khand reaction conditions (presence of CO) the small ring remains unscathed while the π-bond (although as an allenylidenecyclopropane) is normally engaged.[19]



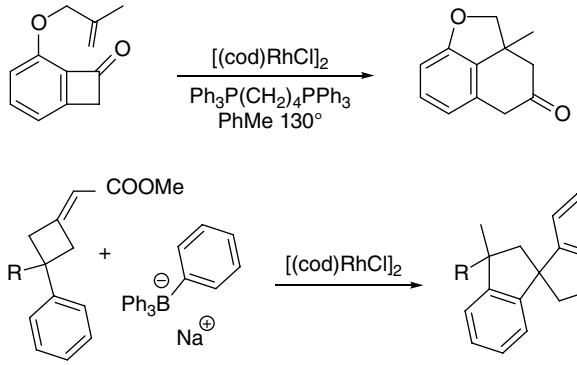
A carbonylative ring enlargement is a critical step toward synthesis of the very interesting indole alkaloid skeleton. Essentially, it is related to addition of CO to an alkenylcyclopropane to form a six-membered ring.[20]



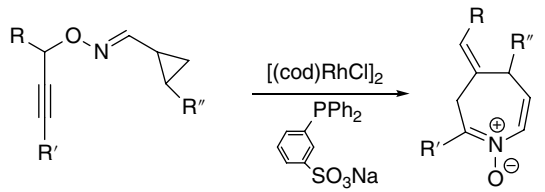
Alkenyl propargyl acetates under similar conditions give 2-acetoxyalkylidenecyclopentenones as the process embodies a 1,3-acetoxy migration.[21,22]



Insertion of Rh in a cyclobutane is responsible for the following molecular reorganizations.[23,24]

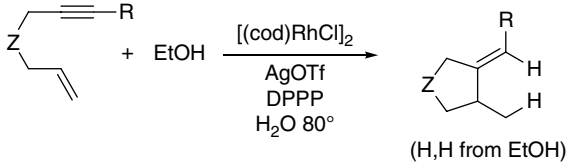


O-Propargylcyclopropylaldehyde oximes undergo rearrangement to give *N*-allenylnitrone intermediates, from which the central carbon of the allenyl group attacks the cyclopropane.[25]



Two Rh(I)-catalyzed processes are used in the synthesis of *N*-tosyl-3-arylisoindolinones from *o*-bromo-*N*-tosylbenzalimine: first an aryl addition, then carbonylative ring closure which is promoted by $[(cod)RhCl]_2$.[26]

1,6-Enynes cyclize when ethanol provides hydrogen atoms (from OH and an α-CH) to the emerging alkylidenecyclopentanes and heterologs.[27]



Pauson-Khand reaction catalyzed by the Rh complex can use 2,2-dimethyl-1, 3-dioxolane-4-carbaldehyde, which is easily obtained from mannitol, as the CO source. [28]

[1] Cheung, L.L.W., Vasapollo, G., Alper, H. *ASC* **354**, 2019 (2012)
[2] Sacher, J.R., Weinreb, S.M. *OL* **14**, 2172 (2012)
[3] Lin, L., Yamamoto, K., Matsunaga, S., Kanai, M. *ACIE* **51**, 10275 (2012)

[4] Oshima, K., Ohmura, T., Suginome, M. *JACS* **134**, 3699 (2012)
[5] Jung, H.H., Buesking, A.W., Ellman, J.A. *JOC* **77**, 9593 (2012)
[6] Reddy, L.R., Gupta, A.P., Villhauer, E., Liu, Y. *JOC* **77**, 1095 (2012)
[7] Ryu, J., Cho, S.H., Chang, S. *ACIE* **51**, 3677 (2012)
[8] Riveiros, R., Tato, R., Sestelo, J.P., Sarandeses, L.A. *EJOC* 3018 (2012)
[9] Onodera, G., Yamamoto, E., Tonegawa, S., Iezumi, M., Takeuchi, R. *ASC* **353**, 2013 (2011)
[10] Evans, P.A., Oliver, S., Chae, J. *JACS* **134**, 19314 (2012)
[11] Gao, L.-L., Ye, Z.-S., Jiang, G.-F., Zhou, Y.-G. *ASC* **353**, 3352 (2011)
[12] Lang, R., Wu, J., Shi, L., Xia, C., Li, F. *CC* **47**, 12553 (2011)
[13] Lai, C.-S., Kao, H.-L., Wang, Y.-J., Lee, C.-F. *TL* **53**, 4365 (2012)
[14] Tobisu, M., Kinuta, H., Kita, Y., Remond, E., Chatani, N. *JACS* **134**, 115 (2012)
[15] Onoe, M., Baba, K., Kim, Y., Kita, Y., Tobisu, M., Chatani, N. *JACS* **134**, 19477 (2012)
[16] Zheng, L., Wang, J. *CEJ* **18**, 9699 (2012)
[17] Tobisu, M., Hasegawa, J., Kita, Y., Kinuta, H., Chatani, N. *CC* **48**, 11437 (2012)
[18] Evans, P.A., Inglesby, P.A. *JACS* **134**, 3635 (2012)
[19] Yuan, W., Dong, X., Shi, M., McDowell, P., Li, G. *OL* **14**, 5582 (2012)
[20] Zhang, M., Tang, W. *OL* **14**, 3756 (2012)
[21] Li, X., Huang, S., Schienebeck, C.M., Shu, D., Tang, W. *OL* **14**, 1584 (2012)
[22] Fukuyama, T., Ohta, Y., Brancour, C., Miyagawa, K., Ryu, I., Dhimane, A.-L., Fensterbank, L., Malacria, M. *CEJ* **18**, 7243 (2012)
[23] Xu, T., Dong, G. *ACIE* **51**, 7567 (2012)
[24] Matsuda, T., Suda, Y., Takahashi, A. *CC* **48**, 2988 (2012)
[25] Nakamura, I., Okamoto, M., Sato, Y., Terada, M. *ACIE* **51**, 10816 (2012)
[26] Fujioka, M., Morimoto, T., Tsumagari, T., Tanimoto, H., Nishiyama, Y., Kakiuchi, K. *JOC* **77**, 2911 (2012)
[27] Park, J.H., Kim, S.M., Chung, Y.K. *CEJ* **17**, 10852 (2011)
[28] Ikeda, K., Morimoto, T., Tsumagari, T., Tanimoto, H., Nishiyama, Y., Kakiuchi, K. *SL* 393 (2012)

Bis[chloro(dicyclooctene)iridium(I)]

Reduction. Esters are reduced via hydrosilylation of the C=O bond which is directed by $[(coe)_2IrCl]_2$, hydrolytic workup yields aldehydes.[1] It is claimed that due to low catalyst loading, mild reaction conditions, high conversions, and broad substrate scope this method becomes a superior alternative to ester reduction using DibalH. Amides are similarly reduced, the amounts of Et_2SiH_2 present determine the type of products that can be isolated: imines are obtained with 2 equiv., amines with 4 equivalents.[2]

Addition. Head-to-tail dimerization of vinylsilanes occurs in the presence of the Ir(I) complex, affording 2,4-bis(triorganosilyl)-1-butenes.[3]

Isomerization. The susceptibility of allyl ethers to isomerization is capitalized in a synthesis of 3-silyl-4-alkenals from 1-silyl-1-alken-3-ols. Thus *O*-allylation followed by treatment of the resulting ethers with $[(coe)IrCl]_2$, Cy_3P and $NaBPh_4$ unveils the structural profile for Claisen rearrangement.[4]

[1] Cheng, C., Brookhart, M. *ACIE* **51**, 9422 (2012)
[2] Cheng, C., Brookhart, M. *JACS* **134**, 11304 (2012)
[3] Park, J.-W., Park, S.J., Jun, C.-H. *OL* **14**, 1468 (2012)
[4] McLaughlin, M.G., Cook, A.J. *JOC* **77**, 2058 (2012)

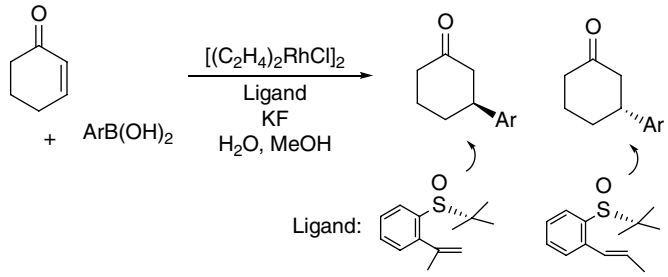
Bis[chloro(dicyclooctene)rhodium(I)]

Cyclization. Intramolecular hydroacylation of the double bond to form common-sized benzocycloalkenones is readily accomplished from aromatic aldehydes that are *o*-substituted with an ω-alkenyl group.[1]

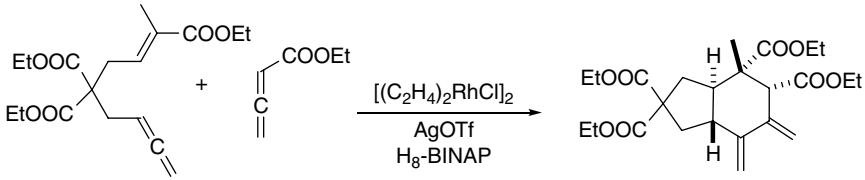
[1] Beletskiy, E.V., Sudheer, C., Douglas, C.J. *JOC* **77**, 5884 (2012)

Bis[chloro(diethene)rhodium(I)]

Addition. The title complex is active in promoting addition of $ArB(OH)_2$ to α-diketones (1:1 adducts),[1] to nitroalkenes[2] and conjugated ketones.[3,4] A remarkable change of stereochemical course by slight variation of a sulfinyl ligand is noted.[4]



Cycloaddition. Cooperation of $[(C_2H_4)_2RhCl]_2$ and AgOTf (and the H_8-BINAP ligand) brings about a [2+2+2]cycloaddition which parleys double bonds from two allene units.[5]



For synthesis of substituted pyridines conjugated oximes and alkynes are condensed.[6]

[1] Feng, X., Nie, Y., Yang, J., Du, H. *OL* **14**, 624 (2012)
[2] Xue, F., Wang, D., Li, X., Wan, B. *JOC* **77**, 3071 (2012)
[3] Shao, C., Yu, H.-J., Feng, C.-G., Wang, R., Lin, G.-Q. *TL* **53**, 2733 (2012)
[4] Chen, G., Gui, J., Li, L., Liao, J. *ACIE* **50**, 7681 (2011)
[5] Brusoe, A.T., Alexanian, E.J. *ACIE* **50**, 6596 (2011)
[6] Martin, R.M., Bergman, R.G., Ellman, J.A. *JOC* **77**, 2501 (2012)

Bis[chloro(norbornadiene)rhodium(I)]

Substitution. *ipso*-Substitution of tertiary allylic trichloroacetimidates by anilines prevails in the presence of $[(nbd)RhCl]_2$ at room temperature.[1]

[1] Arnold, J.S., Cizio, G.T., Nguyen, H.M. *OL* **13**, 5576 (2011)

Bis[(1,5-cyclooctadiene)hydroxyiridium]

Substitution. Primary alcohols are suitable alkylation agents for chain elongation of compounds such as picoline and quinaldine, a base besides $[(cod)IrOH]_2$ and Ph_3P is needed to complete the reaction.[1]

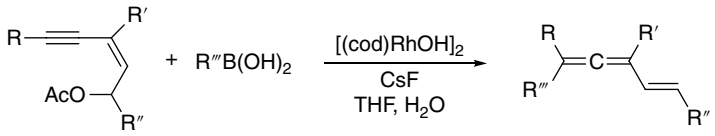
[1] Obora, Y., Ogawa, S., Yamamoto, N. *JOC* **77**, 9429 (2012)

Bis[(1,5-cyclooctadiene)hydroxyrhodium]

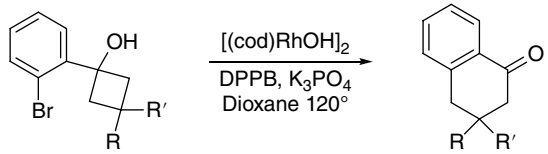
Addition. Hydroarylation of acrylic acid to synthesize 3-arylpropanoic acid in water consumes $ArB(OH)_2$.[1] A route to 3,3-diarylpropanoic esters from a β-aryloxyacrylates is realized due to occurrence of a addition-elimination-addition tandem.[2] However, 3-alkoxy-3-arylpropanoates can be obtained.[3] 3-Aryl-2-propynylamines undergo *cis*-hydroarylation to yield (*E*)-stilbenes.[4]

Substitution and coupling. Replacement of a diazo group (of α-diazo esters) by forming two CC bonds is achieved by the Rh-catalyzed reaction with $ArB(OH)_2$ and subsequent alkylation.[5]

Conjugated enynes that bear at an allylic position a carbonate group are subject to substitution by organoboronic acids to yield 1,2,4-alkatrienes.[6]



1-(*o*-Bromoaryl)cyclobutanols readily undergo a transformation to give α-tetralones, due to favorable insertion of alkoxyrhodium species into the C-Br bond.[7]



Directed borylation. A pinacolatoboryl group can be introduced to an *o*-position of pyrid-2-ylarenes by using Rh catalyst and a silica-supported phosphine ligand.[8]

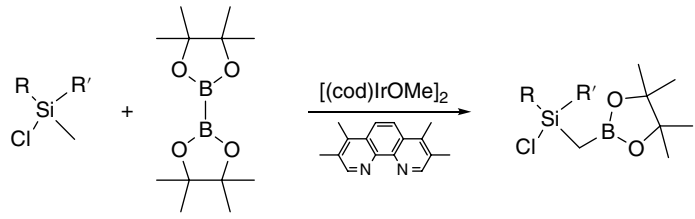
[1] Vautravers, N.R., Breit, B. *SL* 2517 (2011)
[2] Matsuda, T., Shiose, S., Suda, Y. *ASC* **353**, 1923 (2011)
[3] Nishimura, T., Kasai, A., Nagaosa, M., Hayashi, T. *CC* **47**, 10488 (2011)
[4] Panteleev, J., Zhang, L., Lautens, M. *ACIE* **50**, 9089 (2011)
[5] Tsoi, Y.-T., Zhou, Z., Yu, W.-Y. *OL* **13**, 5370 (2011)
[6] Ücüncü, M., Karakus, E., Kus, M., Akpinar, G.E., Aksin-Artok, Ö., Krause, N., Karaca, S., Elmaci, N., Artok, L. *JOC* **76**, 5959 (2011)
[7] Ishida, N., Sawano, S., Murakami, M. *CC* **48**, 1973 (2012)
[8] Kawamorita, S., Miyazaki, T., Ohmiya, H., Iwai, T., Sawamura, M. *JACS* **133**, 19310 (2011)

Bis[(1,5-cyclooctadiene)methoxyiridium(I)]

Substitution. A (cod)iridium complex with a P,N-ligand [(2-pyridylamino) diphenylphosphine] is easily prepared from $[(cod)IrOMe]_2$. It serves as an effective catalyst for *N*-alkylation of anilines by alcohols.[1] 2,6-Divinylpiperidines can be synthesized by a double displacement.[2]

Aryl substituents possessing an n-donor group usually can be used to direct *o*-functionalization via metallocycle intermediates. With $[(cod)IrOMe]_2$ as catalyst *o*-borylation is effective for *N,N*-dimethylbenzylamines,[3] benzaldehyde *N,N*-dimethylhydrazones,[4,5] and pyrid-2-ylarenes.[6]

Activation of a C-H bond adjacent to the silicon atom of chlorosilanes enables borylation to form *gem*-dimetalloid reagents.[7]



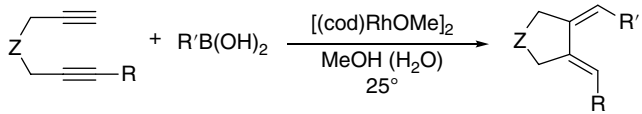
[1] Michlik, S., Hille, T., Kempe, R. *ASC* **354**, 847 (2012)
[2] Brawn, R.A., Guimaraes, C.R.W., McClure, K.F., Liras, S. *OL* **14**, 4802 (2012)
[3] Roering, A.J., Hale, L.V.A., Aquier, P.A., Ringgold, M.A., Wiederspan, E.R., Clark, T.B. *OL* **14**, 3558 (2012)
[4] Ros, A., Lopez-Rodriguez, R., Esyepa, B., Alvarez, E., Fernandez, R., Lassatetta, J.M. *JACS* **134**, 4573 (2012)
[5] Lopez-Rodriguez, R., Ros, A., Fernandez, R., Lassaletta, J.M. *JOC* **77**, 9915 (2012)
[6] Ros, A., Estepa, B., Lopez-Rodriguez, R., Alvarez, E., Fernandez, R., Lassaletta, J.M. *ACIE* **50**, 11724 (2011)
[7] Ohmura, T., Torigoe, T., Suginome, M. *JACS* **134**, 17416 (2012)

Bis[(1,5-cyclooctadiene)methoxyrhodium(I)]

Addition. The hydroxyalkylation of nitriles catalyzed by $[(cod)RhOMe]_2$ – Cy_3P can proceed further to obtain the amides under very mild conditions (Na_2CO_3, H_2O, *i*-PrOH, 25°).[1]

Coupling. Borylation based on activation of an α-CH bond to an amidic or ureido nitrogen atom by the Rh complex and a phosphine ligand has been carried out.[2]

Ring closure of 1,6-diynes is effected in a cross coupling with $RB(OH)_2$.[3] The two neighboring exocyclic double bonds assume the (*E, Z*)-configuration.



[1] Goto, A., Naka, H., Noyori, R., Saito, S. *CAJ* **6**, 1740 (2011)
[2] Kawamorita, S., Miyazaki, T., Iwai, T., Ohmiya, H., Sawamura, M. *JACS* **134**, 12924 (2012)
[3] Artok, L., Kus, M., Ürer, B.N., Türkmen, G., Aksin-Artok, Ö. *OBC* **8**, 2060 (2010)

Bis(η³-cinnamyl)dichlorodipalladium

Substitution. This palladium complex shows catalytic activities for substitution of ArX to form diaryl ethers[1] and alkyl aryl amines.[2,3]

Carbonylative coupling. An extensive array of coupling reaction involving CO is done with the Pd catalyst, for example, synthesis of $ArCONH_2$ from ArOH, CO, and NH_3,[4] ArCOOR from ArOH, CO, and ROH,[5] enol esters (of aromatic carboxylic acids) from ArX, CO, and ketones,[6] ArCOCH=CHCOOBu from ArI, CO, and CH_2=CHOBu,[7] 4-aryl-2-benzylidene-3-buten-4-olides from ArX, CO, and 3-arylpropynes.[8] Often the catalyst requires a bulky phosphine ligand such as *t*-Bu_3P or *n*-$BuP(Ad)_2$. The coupling of ArI, CO, and $(Me_3Si)_2NH$ gives rise to $ArCOSiMe_3$. The ligand is also the less commonly used Ph_3As.[9]

As the reaction conditions are conducive to intramolecular hydroamination, the coupling products of *o*-haloarylalkynes and RNH_2 proceed to furnish indoles.[10]

[1] Salvi, L., Davis, N.R., Ali, S.Z., Buchwald, S.L. *OL* **14**, 170 (2012)
[2] Tardiff, B.J., McDonald, R., Ferguson, M.J., Stradiotto, M. *JOC* **77**, 1056 (2012)
[3] Tardiff, B.J., Stradiotto, M. *EJOC* 3972 (2012)
[4] Wu, X.-F., Neumann, H., Beller, M. *CEJ* **18**, 419 (2012)
[5] Wu, X.-F., Neumann, H., Beller, M. *CEJ* **18**, 3831 (2012)
[6] Schranck, J., Tlili, A., Neumann, H., Alsabeh, P.G., Stradiotto, M., Beller, M. *CEJ* **18**, 15592 (2012)
[7] Gøgsig, T.M., Nielsen, D.U., Lindhardt, A.T., Skrydstrup, T. *OL* **14**, 2536 (2012)
[8] Wu, X.-F., Sundararaju, B., Anbarasan, P., Neumann, H., Dixneuf, P.H., Beller, M. *CEJ* **17**, 8014 (2011)
[9] Wu, X.-F., Neumann, H., Beller, M. *TL* **53**, 582 (2012)
[10] Lavery, C.B., McDonald, R., Stradiotto, M. *CC* **48**, 7277 (2012)

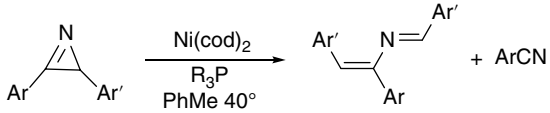
Bis(1,5-cyclooctadiene)iridium hexafluoroantimonate

Addition.[1] Both Mukaiyama aldol and Mannich reactions are catalyzed by $[(cod)_2Ir]SbF_6$.

[1] Onodera, G., Toeda, T., Toda, N., Shibagishi, D., Takeuchi, R. *T* **66**, 9021 (2010)

Bis(1,5-cyclooctadiene)nickel(0)

Redox reaction. An O-C bond of diaryl ethers is cleaved on hydrogenation. For *p*-hydroxyphenyl phenyl ether a selectivity is shown: with $Ni(cod)_2$ and *t*-BuOK it results in the production of only phenol; when an *N*-heterocyclic carbene is added the products are benzene and hydroquinone.[1] 2,3-Diaryl-1-azirenes undergo disproportionation.[2]



Coupling. As an alternative to the Pd(II)-catalyzed synthesis of allylboronate from allyl chloride and (bispinacoltato)diboron, the nickel route involves allyl acetate.[3] Tasking $Ni(cod)_2$ and Zn for conjoining allyl carbonates and alkyl halides a different additive is required to deal with RI (using CuI) and RBr (using $MgCl_2$).[4]

Nickel-catalyzed benzylation and allylation of 1-alkenes is regioselective, the new group becoming attached to C-2 of the alkenes only.[5,6] Conversion of ArX into $ArSCF_3$ is accomplished on reaction with $(Me_4N)SCF_3$, which is catalyzed by $Ni(cod)_2$ – di-*t*-butylbipyridine.[7]

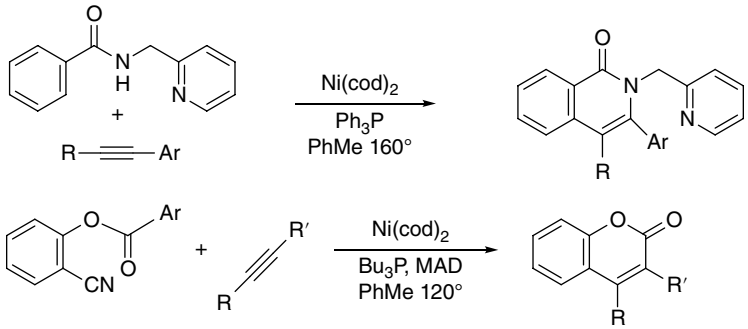
Replacing Pd by Ni to catalyze Heck-type reaction is generally quite successful. For instance, the combination of ArOTf with CH_2=CHOBu furnishes the α-aryl enol ethers.[8] It seems the scope of the Heck reaction is broadened with the change of catalyst, as aryl pivalates are found to be active.[9]

Biaryl synthesis by the Ni-catalyzed Suzuki coupling involving arylboronates has been validated.[10] The general reactivity trend is $ArB(OH)_2 > ArBF_3K > ArB(OR)_2$.[11] Furthermore, in the coupling of $ArB(OR)_2$ with Ar'ONa to provide ArAr', adduct formation results in activation at both the C-B and C-O bonds.[12] To engage ArF as a coupling partner, ZrF_2 and CsF are added to the reaction media.[13]

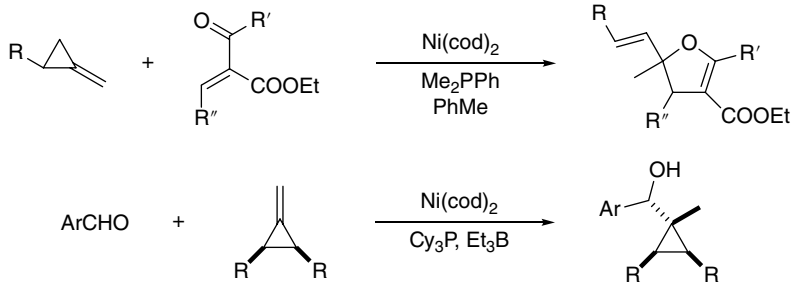
A redox pathway likely is involved in the reaction of styrene oxides with $ArB(OH)_2$ which gives 1,2-diarylethanols.[14]

For Negishi coupling involving $Ar'ZnMe_3Li_2$ the substrates include ArOMe.[15] Heterocycles such as oxazole, quinoline, isoquinoline, and pyrazine that lack any leaving group undergo arylation, e.g., with aryl pivalates[16] and aryl zinc reagents.[17]

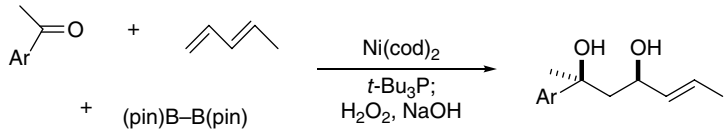
While possessing a bidentate ligand for nickel, *N*-(2-pyridylmethyl)benzamide is able to partake coupling with alkynes to form isoquinolones.[18] Two CC bonds are cleaved during a similar reaction of *o*-cyanoaryl aroates.[19]



Addition. Methylenecyclopropanes are formally transformed into allylic amphophiles by $Ni(cod)_2$. Formation of 2-alkenyl-2,3-dihydrofurans on reaction with enones is illustrative.[20] However, in the presence of Et_3B, the methylene unit is reductively activated without causing ring cleavage.[21]

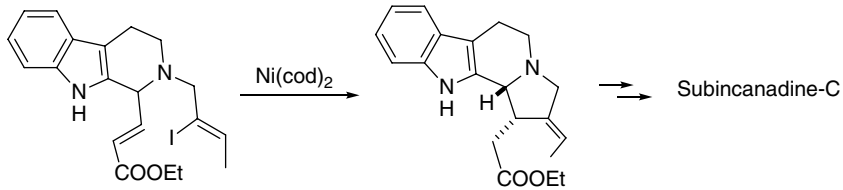


1,3-Pentadiene is converted to a 2-hydroxy-3-pentenyl anion equivalent by $Ni(cod)_2$ and $B_2(pin)_2$.[22] 1,2-Diboration of the terminal double bond is likely the first step, and the reaction proceeds on coordination with the oxygen atom of the carbonyl compound, which is essential for the stereoselectivity. The primary products must be subjected to oxidative workup to give diols.



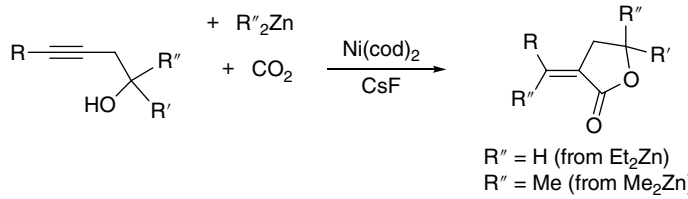
Insertion of alkynes to 3-oxetanone and *N*-substituted azetidinones is achieved.[23,24] The more bulky or electron-negative group on the alkynes ends up in the β-position of the six-membered heterocyclic enones.

Alkenyl iodides form nucleophilic metal derivatives, and such species can be used to effect ring closure on intramolecular addition to a conjugated array.[25] An application is to closure of the D-ring for a synthesis of subincanadine-C.

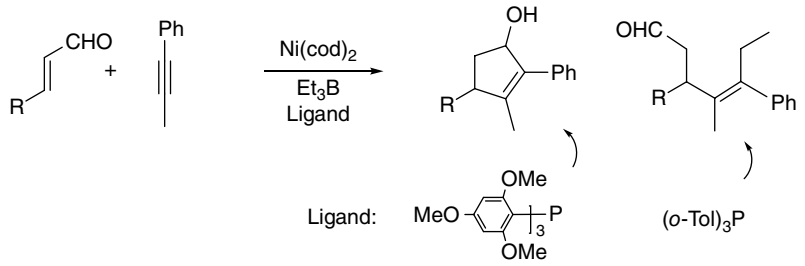


Ketone synthesis from RI and anhydrides is realized by the reagent composed of $Ni(cod)_2$, a diphenylphenanathroline, Zn, and $MgCl_2$.[26]

Cyclization. 1-(*o*-Formyl)aryl-2-alkynes undergo cycloisomerization to afford 2-alkylideneindanones on heating with $Ni(cod)_2$ and *i*-Pr_3P in toluene.[27] α-Alkylidene-γ-butyrolactones are formed when homopropargylic alcohols are treated with R_2Zn, CO_2, $Ni(cod)_2$ and CsF.[28] Difference in using Me_2Zn and Et_2Zn is that a methyl group or a hydrogen atom is introduced.



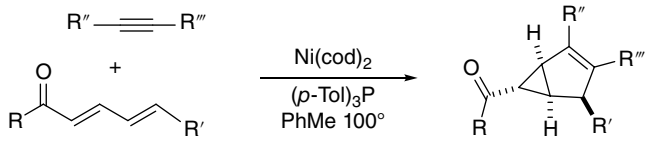
Conjugated aldehydes and phenyl 2-alkenoates combine with alkynes to afford 2-cyclopentenols and 2-cyclopentenones, respectively.[29,30] Ligand effects have also been observed.[31]



A remarkable dehydrogenative cyclization is that which converts a 2-aminophenyl ethyl ketone into a quinolin-4-one.[32] Trapping benzyne by Ni(0) species allows its reaction with an enyne to form a dihydronaphthalene.[33]

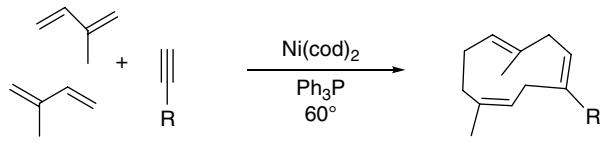
N-Benzoylaminals lose the alkoxy group and thereby are transformed into isoindolones. Besides $Ni(cod)_2$ and DPPF, a Lewis acid (e.g., $MgBr_2$) in stoichiometric quantity is required.[34]

Cycloaddition. Cyclopropyl ketones participate in the [3+2]cycloaddition with alkynes when catalyzed by $Ni(cod)_2$ and in the presence of Me_2AlCl.[35] Contrarily, a cyclopropyl ketone unit is created from dienones and alkynes, hence a synthesis of 6-acyl bicycle[3.1.0]hex-2-ones is realized.[36]



Unactivated diynes and nitriles readily combine to form pyridines.[37] For cyanamides to give 2-aminopyridines it calls for supporting the Ni catalyst with an azacyclic carbene.[38] Dehydrogenation follows the condensation of conjugated dienes with nitriles.[39]

Formation of a 1,4,7-cyclodecatriene from two molecules of isoprene and an 1-alkyne is a unique synthetic process with implication to elaboration of sesquiterpenes.[40]

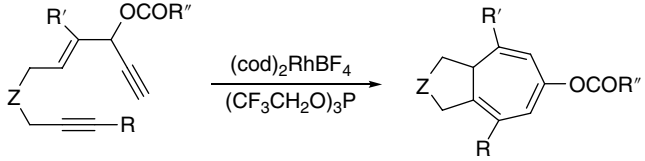


[1] Sergeev, A.G., Webb, J.D., Hartwig, J.F. *JACS* **134**, 20226 (2012)
[2] Okamoto, K., Mashida, A., Watanabe, M., Ohe, K. *CC* **48**, 3554 (2012)
[3] Zhang, P., Roundtree, I.A., Morken, J.P. *OL* **14**, 1416 (2012)
[4] Dai, Y., Wu, F., Zang, Z., You, H., Gong, H. *CEJ* **18**, 808 (2012)
[5] Matsubara, R., Gutierrez, A.C., Jamison, T.F. *JACS* **133**, 19020 (2011)
[6] Matsubara, R., Jamison, T.F. *CAJ* **6**, 1860 (2011)
[7] Zhang, C.-P., Vicic, D.A. *JACS* **134**, 183 (2012)
[8] Gøgsig, T.M., Kleimark, J., Lill, S.O.N., Korsager, S., Lindhardt, A.T., Norrby, P.-O., Skrydstrup, T. *JACS* **134**, 443 (2012)
[9] Ehle, A.R., Zhou, Q., Watson, M.P. *OL* **14**, 1202 (2012)
[10] Leowanawat, P., Zhang, N., Resmerita, A.-M., Rosen, B.M., Percec, V. *JOC* **76**, 9946 (2011)
[11] Yu, D.-G., Shi, Z.-J. *ACIE* **50**, 7097 (2011)
[12] Zhang, N., Hoffman, D.J., Gutsche, N., Gupta, J., Percec, V. *JOC* **77**, 5956 (2012)
[13] Tobisu, M., Xu, T., Shimasaki, T., Chatani, N. *JACS* **133**, 19505 (2011)
[14] Nielsen, D.K., Doyle, A.G. *ACIE* **50**, 6056 (2011)
[15] Wang, C., Ozaki, T., Takita, R., Uchiyama, M. *CEJ* **18**, 3482 (2012)
[16] Muto, K., Yamaguchi, J., Itami, K. *JACS* **134**, 169 (2012)
[17] Hyodo, I., Tobisu, M., Chatani, N. *CAJ* **7**, 1357 (2012)
[18] Shiota, H., Ano, Y., Aihara, Y., Fukumoto, Y., Chatani, N. *JACS* **133**, 14952 (2011)
[19] Nakai, K., Kurahashi, T., Matsubara, S. *JACS* **133**, 11066 (2011)
[20] Inami, T., Sako, S., Kurahashi, T., Matsubara, S. *OL* **13**, 3837 (2011)
[21] Ogata, K., Shimada, D., Fukuzawa, S. *CEJ* **18**, 6142 (2012)
[22] Cho, H.Y., Yu, Z., Morken, J.P. *OL* **13**, 5267 (2011)
[23] Ho, K.Y.T., Aissa, C. *CEJ* **18**, 3486 (2012)
[24] Kumar, P., Louie, J. *OL* **14**, 2026 (2012)
[25] Yu, F., Cheng, B., Zhai, H. *OL* **13**, 5782 (2011)
[26] Yin, H., Zhao, C., You, H., Lin, K., Gong, H. *CC* **48**, 7034 (2012)
[27] Yang, F., Jin, T., Yamamoto, Y. *T* **68**, 5223 (2012)
[28] Li, S., Ma, S. *OL* **13**, 6046 (2011); *CAJ* **7**, 2411 (2012)
[29] Jenkins, A.D., Herath, A., Song, M., Montgomery, J. *JACS* **133**, 14460 (2011)
[30] Ohashi, M., Taniguchi, T., Ogoshi, S. *JACS* **133**, 14900 (2011)
[31] Li, W., Montgomery, J. *CC* **48**, 1114 (2012)
[32] Ueno, S., Shimizu, R., Maeda, R., Kuwano, RQ. *SL* 1639 (2012)
[33] Candito, D.A., Lautens, M. *SL* 1987 (2011)
[34] Shacklady-McAtee, D. M., Dasgupta, S., Watson, M. P. *OL* **13**, 3490 (2011)
[35] Tamaki, T., Ohashi, M., Ogoshi, S. *ACIE* **50**, 12067 (2011)
[36] Horie, H., Kurahashi, T., Matsubara, S. *ACIE* **50**, 8956 (2011)

[37] Kumar, P., Prescher, S., Louie, J. *ACIE* **50**, 10694 (2011)
[38] Stolley, R.M., Maczka, M.T., Louie, J. *EJOC* 3815 (2011)
[39] Ohashi, M., Takeda, I., Ikawa, M., Ogoshi, S. *JACS* **133**, 18018 (2011)
[40] Holte, D., Götz, D.C.G., Baran, P.S. *JOC* **77**, 825 (2012)

Bis(1,5-cyclooctadiene)rhodium tetrafluorborate

Cycloaddition.[1] 4-Alken-1,9-diynes undergo cycloaddition to yield bicycle[5.3.0] decatrienes.

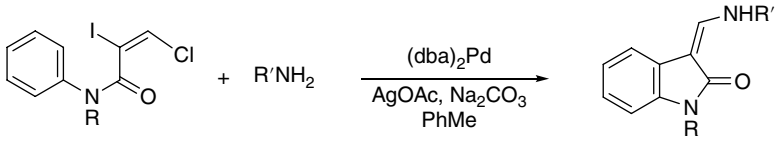


[1] Shu, X., Huang, S., Shu, D., Guzei, I.A., Tang, W. *ACIE* **50**, 8153 (2011)

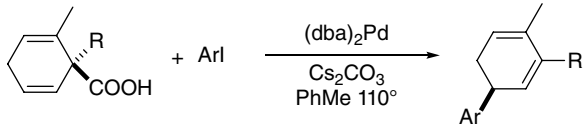
Bis(dibenzylideneacetone)palladium(0)

Coupling. Many catalytic activities exhibited by $(dba)_2Pd$ are similar to those of other Pd(0) species. Thus it can be used to convert alkenyl fluoroalkanesulfonates into trifluoromethylalkenes,[1] ArBr to ArCN,[2] with Me_3SiCF_3 and $K_4[Fe(CN)_6]$ and certain phosphine ligand, respectively.

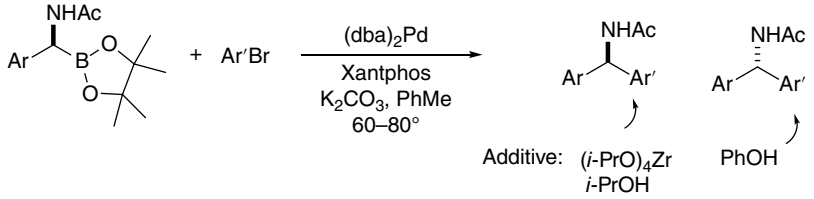
Upon dehydration on heating with a heteropoly acid, α-arylethanols are dehydrated and then enter Heck reaction in situ to afford stilbenes.[3] A highly regioselective coupling of ArOTf with 1-alkenes to provide 2-aryl-1-alkenes is observed with $(dba)_2Pd$, hexamethylenetetramine, and 1,1′-bis(di-1-naphthylphosphino)ferrocene.[4] A dual (CC and CN) coupling is involved in a convenient access to 3-aminomethylene-2-indolinones.[5]



Allenylmethyl esters of β-ketoacids undergo chain contraction (loss of CO_2) but without other skeletal changes on exposure to $(dba)_2Pd$ – DPEphos.[6] Perhaps it represents a convenient method to access γ,δ;δ,ε-doubly unsaturated ketones. Decarboxylative coupling of 2,5-cyclohexadiene-1-carboxylic acids is regio- and stereoselective.[7] Trapping benzyne with *o*-iodoanilides leads to the formation of *N*-acylcarbazoles.[8]



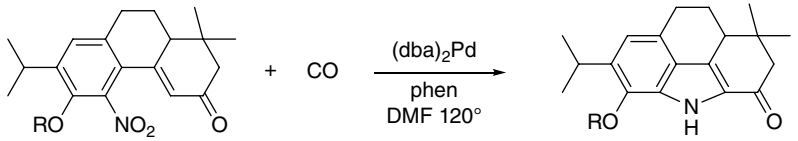
Suzuki coupling based on potassium organotrifluoroborates is now well established. Besides variation in Pd salts and complexes, many phosphine ligands are equally effective. Among the newer ligands is 1-methyl-2-[(*o*-dicyclohexylphosphino)phenyl]benzimidazole.[9] For homologation of ArX (to synthesize $ArCH_2OH$) the coupling with $AcOCH_2BF_3K$ is an option.[10] Replacement of the boryl group from α-acetamino-α-pinacolatoboryltoluenes with an aryl group, the Suzuki coupling is subject to stereochemical regulation by some additives.[11]



Negishi coupling between ArCOSEt and Ar'ZnCl catalyzed by $(dba)_2Pd$ proceeds at room temperature, phosphine ligand is not required.[12] Hiyama coupling employing a sodium crotylsilanoate involves γ-selective transfer of the crotyl group to the arene, while the phsophine ligand for $(dba)_2Pd$ is generated in situ from the air-stable borane complex of *t*-$BuPCy_2$.[13]

Carbonylative coupling gathers ArBr, CO and *t*-BuONa to give *t*-butyl aroates.[14] On replacing the butoxide with ketone enolates the reaction leads to β-diketones.[15] For such carbonylative coupling a CO source is 9-chloroformyl-9-methylfluorene.[16] *N*-Aroylureas of the type ArCONHCONHR are also accessed from $H_2NCONHR$, ArX and CO by the Pd(0)-catalyzed process.[17]

A reductive intramolecular C-N coupling is the critical step in a synthesis of salviadione.[18]



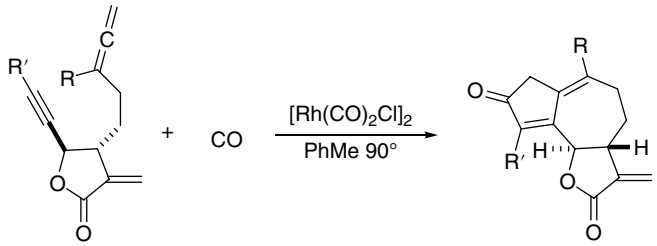
In the preparation of ArCN from ArBr and NaCN the employment of $(dba)_2Pd$, *t*-Bu_3P, Zn or CaH_2 is perhaps overly complicated.[19]

[1] Cho, E.J., Buchwald, S.L. *OL* **13**, 6552 (2011)
[2] Yeung, P.Y., Tsang, C.P., Kwong, F.Y. *TL* **52**, 7038 (2011)
[3] Colbon, P., Barnard, J.H., Purdie, M., Mulholland, K., Kozhevnikov, I., Xiao, J. *ASC* **354**, 1395 (2012)
[4] Qin, L., Ren, X., Lu, Y., Li, Y., Zhou, J. *ACIE* **51**, 5919 (2012)
[5] Deng, G.-B., Wang, Z.-Q., Song, R.-J., Zhou, M.-B., Wei, W.-T., Xie, P., Li, J.-H. *CC* **47**, 8151 (2011)
[6] Wan, B., Jia, G., Ma, S. *OL* **14**, 46 (2012)
[7] Chou, C.-M., Chatterjee, I., Studer, A. *ACIE* **50**, 8614 (2011)

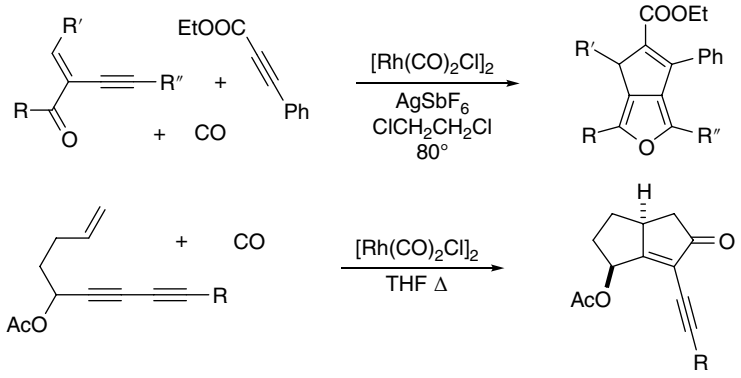
[8] Lu, C., Markina, N.A., Larock, R.C. *JOC* **77**, 11153 (2012)
[9] Wong, S.M., So, C.M., Chung, K.H., Luk, C.H., Lau, C.P., Kwong, F.Y. *TL* **53**, 3754 (2012)
[10] Murai, N., Yonaga, M., Tanaka, K. *OL* **14**, 1278 (2012)
[11] Awano, T., Ohmura, T., Suginome, M. *JACS* **133**, 20738 (2011)
[12] Kunchithapatham, K., Eichman, C.C., Stambuli, J.P. *CC* **47**, 12679 (2011)
[13] Denmark, S.E., Werner, N.S. *OL* **13**, 4596 (2011)
[14] Xin, Z., GØgsig, T.M., Lindhardt, A.T., Skrydstrup, T. *OL* **14**, 284 (2012)
[15] GØgsig, T.M., Taaning, R.H., Lindhardt, A.T., Skrydstrup, T. *ACIE* **51**, 798 (2012)
[16] Nielsen, D.U., Taaning, R.H., Lindhardt, A.T., GØgsig, T.M., Skrydstrup, T. *OL* **13**, 4454 (2011)
[17] Bjerglund, K., Lindhardt, A.T., Skrydstrup, T. *JOC* **77**, 3793 (2012)
[18] Cummings, M.M., Clawson Jr, R.W., Sharma, S.B., Byerly, R.A., Akhmedov, N.G., Söderberg, B.C.G. *T* **67**, 4753 (2011)
[19] Ushkov, A.V., Grushin, V.V. *JACS* **133**, 10999 (2011)

Bis[dicarbonylchlororhodium(I)]

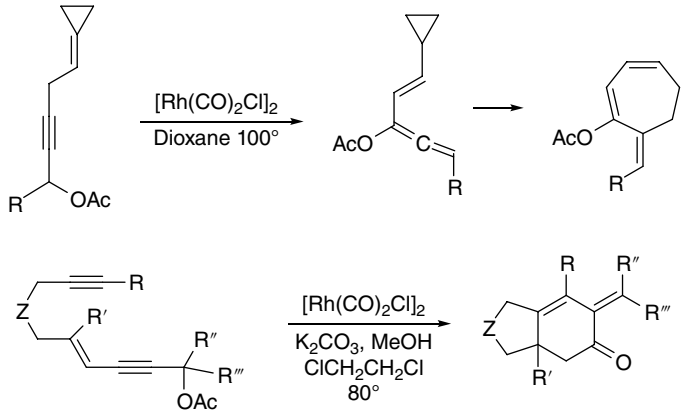
Annulation. 1,3-Acetoxy migration from 1-alken-3-yn-5-yl acetates precedes incorporation of CO which ultimately delivers α–alkylidene-β-acetoxy-α,β-unsaturated γ-lactones.[1] An intramolecular Pauson-Khand reaction involving allene and alkyne linkages paves an expedient route to the framework of guaianolide sesquiterpenes.[2]



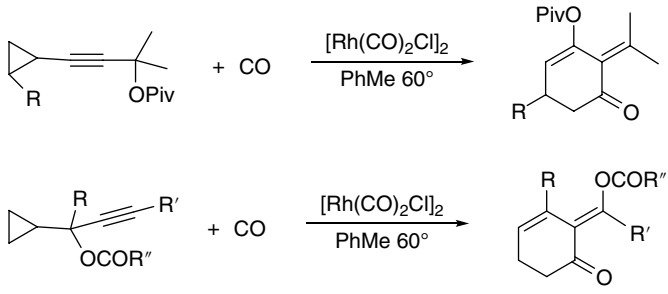
A tandem sequence of heterocyclization and [3+2]cycloaddition is realized from mixtures of 2-acyl-1,3-enynes, electron-deficient alkynes and CO when they are heated with $[Rh(CO)_2Cl]_2$ and $AgSbF_6$ in dichloroethane.[3] The Pauson-Khand reaction using $[Rh(CO)_2Cl]_2$ as catalyst is subject to diastereocontrol by certain functional group present in the substrate.[4]



With cycloisomerization following 1,3-acetoxy group migration from 5-acetoxy-1-cyclopropyl-1-alken-3-ynes, formation of alkylidenecycloheptadienes is the result.[5] This migration also precedes a [4+2]cycloaddition of enediynes.[6]



Carbonylative conditions applied to cyclopropanes that bear a propargyl ester sidechain transform them into 2-alkylidene-3-cyclohexenones.[7]



Acylation. Desilylative acylation of β-trimethylsilylstyrenes on reaction with $(RCO)_2O$ is catalyzed by the Rh complex.[8]

[1] Chen, W., Tay, J.-H., Yu, X.-Q., Pu, L. *JOC* **77**, 6215 (2012)
[2] Grillet, F., Huang, C., Brummond, K.M. *OL* **13**, 6304 (2011)
[3] Gao, H., Zhang, J. *CEJ* **18**, 2777 (2012)
[4] Turlington, M., Pu, L. *OL* **13**, 4332 (2011)
[5] Li, X., Zhang, M., Shu, D., Robichaux, P.J., Huang, S., Tang, W. *ACIE* **50**, 10421 (2011)
[6] Huang, S., Li, X., Lin, C.L., Guzei, I.A., Tang, W. *CC* **48**, 2204 (2012)
[7] Shu, D., Li, X., Zhang, M., Robichaux, P.J., Guzei, I.A., Tang, W. *JOC* **77**, 6463 (2012)
[8] Pawluc, P., Szudkowska, J., Hreczycho, G., Marciniec, B. *JOC* **76**, 6438 (2011)

Bis[dicarbonyl(hydroxytetraphenylcyclopentadienyl)ruthenium], (Shvo complex)

N-C bond formation. The Shvo complex catalyzes the reaction of NH_4X with primary alcohols to form tertiary amines.[1] A Cp*Ir complexed to a nitrogen atom of *N,N*-dimesitylformamidine has the same catalytic activity. *N*-Acylation of lactams, oxazolidinones, and imidazolidines is accomplished with aldehydes.[2]

Various *N*-protected 4-aminobutanols are converted into the γ-lactams by aerial oxidation. Besides Shvo complex, a Salen-Co(II) chelate and 2,6-dimethoxy-1,4-benzoquinone are used as electron-transfer mediators.[3]

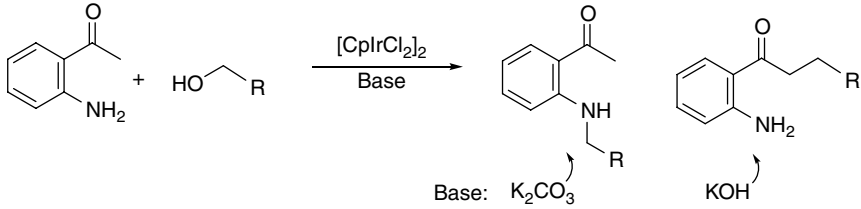
Reductive hydration. Primary alcohols are created on treatment of 1-alkynes with Shvo complex in H_2O/ *i*-PrOH at 70°. On the other hand, reverse regioselectivity is observed in the hydration catalyzed by an Au-carbene complex.[4]

Dehydrogenation. Alcohols and amines are respectively converted into carbonyl compounds and imines by the Shvo complex in hot mesitylene.[5]

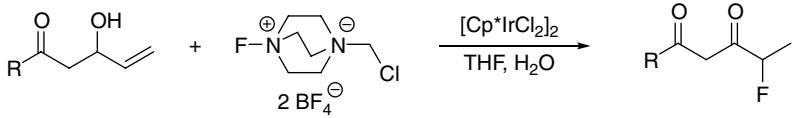
[1] Segarra, C., Mas-Marza, E., Mata, J.A., Peris, E. *ASC* **353**, 2078 (2011)
[2] Zhang, J., Hong, S.H. *OL* **14**, 4646 (2012)
[3] Babu, B.P., Endo, Y., Bäckvall, J.-E. *CEJ* **18**, 11524 (2012)
[4] Li, L., Herzon, S.B. *JACS* **134**, 17376 (2012)
[5] Muthaiah, S., Hong, S.H. *ASC* **354**, 3045 (2012)

Bis[dichloro(pentamethylcyclopentadienyl)iridium(III)]

Substitution. The iridium complex is a catalyst for *N*-alkylation of aminoazoles by primary alcohols.[1] The base is important when other nucleophilic centers are available for competing reaction, as in the case of *o*-aminoacetophenone.[2] As the metal complex can handle redox transformations the condensation of *o*-aminobenzamide with alcohols lead to quinazolinones.[3]



α-Alkylation of ketones is achieved by heating with the catalyst, an alcohol and KOH at 110°.[4] Advantage can be taken to prepare functionalized ketones by trapping the isomerization products of allylic alcohols. Thus α−fluoro ketones are readily obtained.[5]

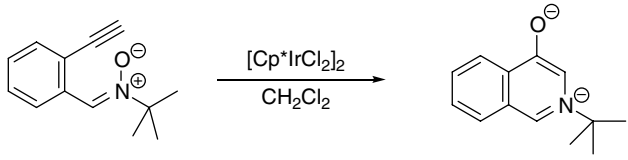


Coupling. ω-Arylalkanols with (n+1) methylene groups are converted into linear diarylalkanes in which the two aryl termini are joined by a (2n+1) methylene chain. This transformation is the result of oxidation, aldol reaction, reduction and decarbonylation.[6]

Cyclization. α-(3-Acetylphenoxy) ketones undergo cyclization to deliver 4-acetylbenzofurans, the catalyst system contains $[Cp^*IrCl_2]_2$, $AgSbF_6$, and $Cu(OAc)_2$.[7]

2-Propargyl-1,3-propanediols are turned into bridgehead-substituted 2,6-dioxabicyclo[2.2.1]heptanes; from 1,6-enynes the treatment with $[Cp^*IrCl_2]_2$ furnishes bicycle[4.1.0]hept-2-enes.[8]

The Ir(III) complex and a Au(I)-carbenoid have different effects on 2-ethynylbenzaldehyde *N*-*t*-butylnitrone, here a redox cyclization gives the zwitterionic isoquinolinium 4-oxide.[9]



[1] Li, F., Shan, H., Chen, L., Kang, Q., Zou, P. *CC* **48**, 603 (2012)
[2] Bhat, S., Sridharan, V. *CC* **48**, 4701 (2012)
[3] Zhou, J., Fang, J. *JOC* **76**, 7730 (2011)
[4] Li, J., Zhang, W., Wang, F., Jiang, M., Dong, X., Zhao, W. *ChJC* **30**, 2363 (2012)
[5] Ahlsten, N., Bartoszewicz, A., Agrawal, S., Martin-Matute, B. *S* 2600 (2011)
[6] Obora, Y., Anno, Y., Okamoto, R., Matsu-ura, T., Ishii, Y. *ACIE* **50**, 8616 (2011)
[7] Shibata, T., Hashimoto, Y., Otsuka, M., Tsuchikama, K., Endo, K. *SL* 2075 (2011)
[8] Benedetti, E., Simonneau, A., Hours, A., Amouri, H., Penoni, A., Palmisano, G., Malacria, M., Goddard, J.-P., Fensterbank, L. *ASC* **353**, 1908 (2011)
[9] Song, G., Chen, D., Su, Y., Han, K., Pan, C.-L., Jia, A., Li, X. *ACIE* **50**, 7791 (2011)

Bis[dichloro(pentamethylcyclopentadienyl)rhodium(III)]

Coupling. The title complex, often accompanied by a silver salt, is one of the most popular catalyst for chelation-directed functionalization. Aryl methyl ketoxime *O*-methyl ethers[1] and benzamides[2,3] undergo *o*-acylation by RCHO. An auxiliary oxidant such as Ag_2CO_3 is a requisite. Phthalides are obtained from a union of PhCOOH and RCHO, the aldehyde unit does not alter its oxidation state.[4]

Aromatic ketoxime ethers, acids, and benzylamines are alkylated with diazomalonic esters in MeOH (EtOH and *t*-BuOH unsuitable).[5] Chloramines serve as aminating agents,[6,7] as do aryl azides[8] and sulfonyl azides.[9]

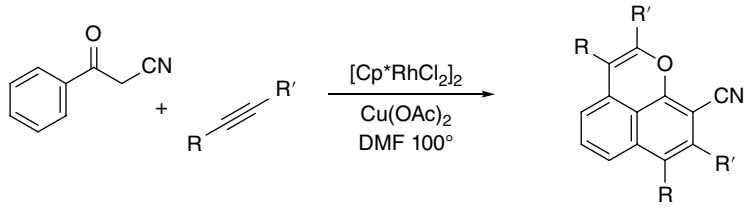
Trimetallic (Rh-Ag-Cu) catalyst system performs performs β-arylation of acrylic esters by aryl carbamates[10] and 1-aryltriazenes.[11]

N-Substituted isoquinolin-1-ones undergo alkenylation at C-8.[12] These substrates are also alkenylated at the same site by alkynes using $[(cymene)RuCl_2]_2$ as catalyst.

When 2-(2-pyridyl)benzyl alcohols are subjected to the alkenylation conditions (Rh-Ag catalyst system) the hydroxyalkyl group is removed and replaced.[13] The alkenylation of *N*-tosylbenzamides is terminated at formation of isoindolinones as a result of intramolecular hydroamination after the coupling.[14]

Heteroarylbenzenes and enones form adducts as if they engage in a Michael reaction.[15] Acetic acid is a good solvent. *N*-Methoxybenzamide also adds to allenes to give the *o*-allylated products, and no Ag salt additive is present.[16]

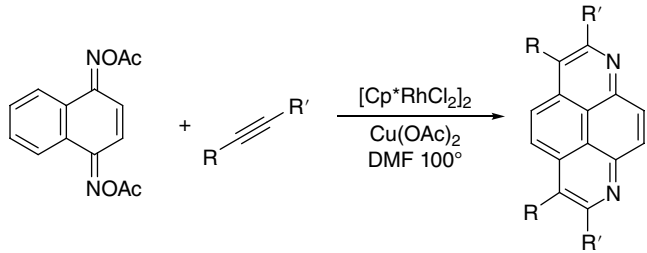
The addition pattern is followed by *N*-(4-pentyn-1-oxy)benzamide which forms 3-(3-hydroxypropyl)isoquinolone.[17] Two equivalents of an alkyne are incorporated into aroylacetonitriles.[18]



The reaction conditions for coupling of $ArB(OH)_2$ are the reaction conditions are conducive to oxidative cyclization, thus *N*-methoxyphenanthridones are readily acquired.[19]

Numerous benzannulated heterocycles can be prepared based on the dehydrogenative coupling strategy [oxidant: $Cu(OAc)_2$]. They include iminophthalimides by reaction of *N*-tosylbenzamide with isonitriles,[20] and aurones from salicylaldehyde and alkenes.[21] Condensation of *N*-pivaloyloxybenzamide with ethynylboronate furnishes a 3-boryl-1-isoquinolone,[22] and with 1,2-alkadienes to afford 4-alkylidene-3,4-dihydro-1-isoquinolones.[23] In the same manner 4-aryl-1,2-dihydrophthalazines are prepared from hydrazones of diaryl ketones and 1-alkenes.[24]

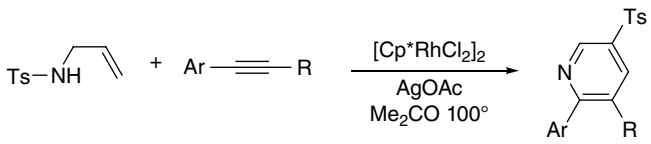
The reaction of aryl ketoxime acetates with diarylethynes to generate 3,4-diarylquinolines is favored by having the easily eliminable *N*-acetoxy group,[25] the same reaction pattern is shown in the case of 1,4-naphthoquinone oxime acetate which forms 1,8-diazapyrenes by engaging the two *peri*-positions,[26] although isoquinolinium salts are obtainable when ArCHO, RNH_2 and alkynes are heated with a Rh-Ag-Cu catalytic triad.[27]



Bridging C-2 of 1-arylimidazoles to an *o*-position of the arene moiety by uniting with an alkyne is relatively facile,[28] also is the ring closure of 2-aryl-3-alkynylpyridines to 9-alkylidene-4-azafluorenes.[29]

Unlike the Pd-catalyzed Heck reaction, bromoarenes do not sacrifice the halogen atom in alkenylation which takes place mainly at an *m*-position to the brominated site in the process handled by Rh-Ag-Cu salts.[30]

Annulation. In the following examples are several versions of pyridine synthesis that feature aromatization after cycloaddition. With conjugated oximes and alkynes a dehydration completes the formation.[31,32] The reaction between allylamine and an alkyne must involve two stages of dehydrogenation.[33] As for *N*-(tosyl)allylamine a group migration occurs to afford 3-tosylpyridines.[34]



A straightforward extension of the reaction for preparation of substituted pyridines is from conjugated carbonyl compounds, NH_4OAc (or NH_3) and alkynes.[35]

A Rh-Ag-Cu triad catalyst is active in promoting cross-coupling of five-membered heterocycles.[36] With slight modification of the cyclopentadienyl ligand on Rh, it also inveigles decarboxylation and *o,o′*-coupling of 2,2-diarylalkanoic acids.[37]

Substitution. Benzamides are *o*-(α-amino)benzylated by reaction with ArCH=NTs, the catalyst $[Cp^*RhCl_2]_2$ is activated by $AgB(C_6F_5)_3$.[38] Dehydrogenative cross-coupling of benzamides with certain electron-deficient arenes[39] and with aldehydes[3] have also been accomplished. In the former case the combination of $Cu(OAc)_2$ and C_6Br_6 plays a unique role, and the latter constitutes a method for *o*-acylation.

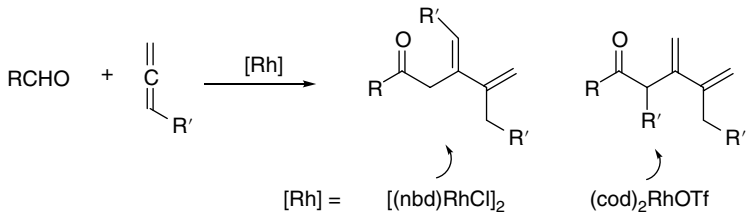
Hydrogenation. On conversion of $[Cp^*RhCl_2]_2$ to the anionic $[Cp^*RhI_2H]$ by KI it delivers a catalyst for transfer hydrogenation (HCOOH, Et_3N) to quinolines and related heterocycles.[40]

[1] Yang, Y., Zhou, B., Li, Y. *ASC* **354**, 2916 (2012)
[2] Park, J., Park, E., Kim, A., Lee, Y., Chi, K.-W., Kwak, J.H., Jung, Y.H., Kim, I.S. *OL* **13**, 4390 (2011)
[3] Sharma, S., Park, E., Park, J., Kim, I.S. *OL* **14**, 906 (2012)
[4] Shi, X., Li, C.-J. *ASC* **354**, 2933 (2012)
[5] Chan, W.-W., Lo, S.-F., Zhou, Z., Yu, W.-Y. *JACS* **134**, 13565 (2012)
[6] Ng, K.-H., Zhou, Z., Yu, W.-Y. *OL* **14**, 272 (2012)
[7] Grohmann, C., Wang, H., Glorius, F. *OL* **14**, 656 (2012)
[8] Ryu, J., Shin, K., Park, S.H., Kim, J.Y., Chang, S. *ACIE* **51**, 9904 (2012)
[9] Kim, J.Y., Park, S.H., Ryu, J., Cho, S.H., Kim, S.H., Chang, S. *JACS* **134**, 9110 (2012)
[10] Feng, C., Loh, T.-P. *CC* **47**, 10458 (2011)
[11] Wang, C., Chen, H., Wang, Z., Chen, J., Huang, Y. *ACIE* **51**, 7242 (2012)
[12] Zhao, P., Niu, R., Wang, F., Han, K., Li, X. *OL* **14**, 4166 (2012)
[13] Li, H., Li, Y., Zhang, X.-S., Chen, K., Wang, X., Shi, Z.-J. *JACS* **133**, 15244 (2011)
[14] Zhu, C., Falck, J.R. *CC* **48**, 1674 (2012)
[15] Yang, L., Qian, B., Huang, H. *CEJ* **18**, 9511 (2012)
[16] Zeng, R., Fu, C., Ma, S. *JACS* **134**, 9597 (2012)
[17] Xu, X., Liu, Y., Park, C.-M. *ACIE* **51**, 9372 (2012)
[18] Tan, X., Liu, B., Li, X., Xu, S., Song, H., Wang, B. *JACS* **134**, 16163 (2012)
[19] Karthikeyan, J., Haridharan, R., Cheng, C.-H. *ACIE* **51**, 12343 (2012)
[20] Zhu, C., Xie, W., Falck, J.R. *CEJ* **17**, 12591 (2011)

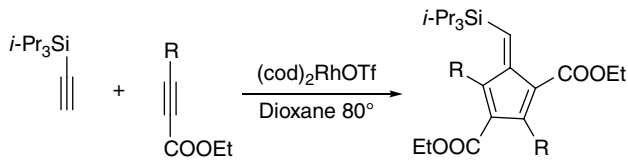
[21] Shi, Z., Schröder, N., Glorius, F. *ACIE* **51**, 8092 (2012)
[22] Wang, H., Grohmann, C., Nimphius, C., Glorius, F. *JACS* **134**, 19592 (2012)
[23] Wang, H., Glorius, F. *ACIE* **51**, 7318 (2012)
[24] Li, G., Ding, Z., Xu, B. *OL* **14**, 5338 (2012)
[25] Too, P.C., Chua, S.H., Wong, S.H., Chiba, S. *JOC* **76**, 6159 (2011)
[26] He, T., Too, P.C., Chen, R., Chiba, S., Sun, H. *CAJ* **7**, 2090 (2012)
[27] Jayakumar, J., Parthasarathy, K., Cheng, C.-H. *ACIE* **51**, 197 (2012)
[28] Huang, J.-R., Dong, L., Han, B., Peng, C., Chen, Y.-C. *CEJ* **18**, 8896 (2012)
[29] Shibata, T., Takayasu, S., Yuzawa, S., Otani, T. *OL* **14**, 5106 (2012)
[30] Wencel-Delord, J., Nimphius, C., Patureau, F.W., Glorius, F. *CAJ* **7**, 1208 (2012)
[31] Too, P.C., Noji, T., Lim, Y.J., Li, X., Chiba, S. *SL* 2789 (2011)
[32] Hyster, T.K., Rovis, T. *CC* **47**, 11846 (2011)
[33] Kim, D.-S., Park, J.-W., Jun, C.-H. *CC* **48**, 11334 (2012)
[34] Wang, D., Wang, F., Song, G., Li, X. *ACIE* **51**, 12348 (2012)
[35] Sim, Y.-K., Lee, H., Park, J.-W., Kim, D.-S., Jun, C.-H. *CC* **48**, 11787 (2012)
[36] Kuhl, N., Hopkinson, M.N., Glorius, F. *ACIE* **51**, 8230 (2012)
[37] Morimoto, K., Itoh, M., Hirano, K., Satoh, T., Shibata, Y., Tanaka, K., Miura, M. *ACIE* **51**, 5359 (2012)
[38] Hesp, K.D., Bergman, R.G., Ellman, J.A. *OL* **14**, 2304 (2012)
[39] Wencel-Delord, J., Nimphius, C., Wang, H., Glorius, F. *ACIE* **51**, 13001 (2012)
[40] Wu, J., Wang, C., Tang, W., Pettman, A., Xiao, J. *CEJ* **18**, 9525 (2012)

Bis(1,5-cyclooctadiene)rhodium(I) salts

Addition. Hydroformylation of alkenes with syngas in an alcohol leads to acetals.[1] Adducts of aldehydes and allenes in the 1:2 stoichiometry are formed with the complexed Rh(I) salt. The π-ligand on the metal has great influence on the regiochemistry regarding the bonding to the carbonyl.[2]



Silylethyne-ketene adducts are nucleophilic, their further reaction leads to 3-acyloxy-1-silyl-1-alkyn-3-enes.[3] By a three-component addition with a 2-alkynoic ester as the linchpin molecule and an electrophile, 5-silylpent-2-en-4-ynoic esters bearing a functional chain at C-2 are obtained.[4] Without the active electrophile the reaction proceeds to capture a second molecule of the alkynoic ester and a fulvene is produced.[5]

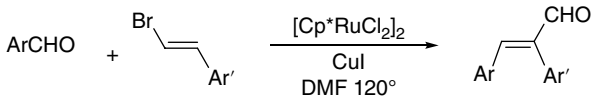


Cycloaddition. Intramolecular [5+2]cycloaddition occurs when 1,9-dialkyn-4-en-3-yl esters (and 7-heterologs) are treated with $(cod)_2RhBF_4$. The formation of bicycle[5.3.0] decatrienes is preceded by migration of the ester group.[6]

[1] Diebolt, O., Cruzeuil, C., Müller, C., Vogt, D. *ASC* **354**, 670 (2012)
[2] Toyoshima, T., Miura, T., Murakami, M. *ACIE* **50**, 10436 (2011)
[3] Ogata, K., Ohashi, I., Fukuzawa, S. *OL* **14**, 4214 (2012)
[4] Hoshino, Y., Shibata, Y., Tanaka, K. *ACIE* **51**, 9407 (2012)
[5] Shibata, Y., Tanaka, K. *ACIE* **50**, 10917 (2011)
[6] Shu, X.-Z., Li, X., Shu, D., Huang, S., Schienebeck, C.M., Zhou, X., Robichaux, P.J., Tang, W. *JACS* **134**, 5211 (2012)

Bis[dichloro(pentamethylcyclopentadienyl)ruthenium(III)]

Substitution. A very unusual reaction between ArCHO and β-bromostyrenes brought about by the couple of $[Cp^*RuCl_2]_2$ and CuI is the formation of α,β-diarylacroleins.[1] It appears that the formyl group is split from the aromatic ring and the two residues are separately attached to the double bond and there is a net loss of HBr.



[1] Wang, P., Rao, H., Zhou, F., Hua, R., Li, C.-J. *JACS* **134**, 16468 (2012).

Bis(dimethylaluminum) selenide

Selenoisocyanates. The $(Me_2Al)_2Se$ reagent is useful to convert RN=C=O into RN=C=Se.[1]

[1] Maeda, H., Takashima, M., Sakata, K., Watanabe, T., Honda, M., Segi, M. *TL* **52**, 415 (2011).

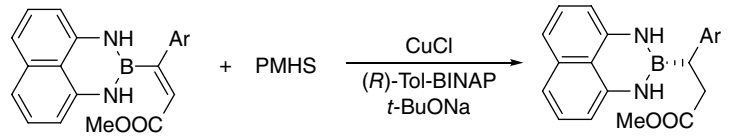
2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl and analogues

Preparation.[1] A general procedure for the preparation of various BINAP's is based on the Grignard reaction of 1,1′-binaphthalene-2,2′-bis(magnesium bromide) with bromodiarylphosphines [e.g., bromobis{3,5-di(trifluoromethyl)phenyl}phosphine]. The corresponding chlorophosphines are much inferior reactants (yields 5% vs. 70% in one case).

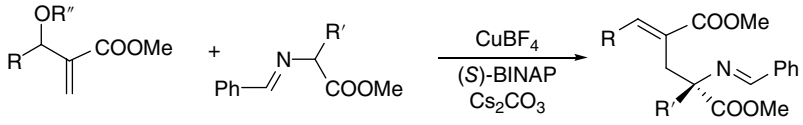
[1] Liu, L., Wu, H.-C., Yu, J.-Q. *CEJ* **17**, 10828 (2011).

Copper complexes

Reduction. The CuCl complex of a chiral Tol-BINAP is responsible for directing the enantioselective reduction of β-borylcinnamic esters.[1]

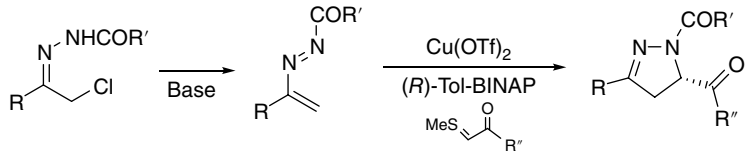


Substitution. An S_N2' reaction of *N*-benzylidene-α-amino esters on derivatives of Baylis-Hillman adducts furnishes chiral glutaric diesters containing at C-2 an amino group and at C-4 an alkylidene unit.[2]



Addition. Asymmetric propargylation of carbonyl compounds is achieved using 1-pinacolatoboryl-2-alkynes. On activation by lithium *t*-butoxide, the stereochemical course of the nucleophilic attack is steered by the complex derived from copper(II) pivalate and (*R*)-BINAP.[3] Enantioselective conjugate addition of Me_3Al to 2-oxo-3-alkenoic esters also benefits from the involvement of a chiral binap-Cu(I) complex.[4]

Cycloaddition. A [4+1]cycloaddition to elaborate pyrazolines starts from generation of alkenylazo compounds from acylhydrazones of chloromethyl ketones. The crucial step is the reaction with α-ketosulfonium ylides which is rendered enantioselective by a chiral BINAP-ligated Cu(II) salt.[5]



By a [3+2]cycloaddition between the 2-deprotonated 1-alkylidenepyrazolidin-3-ones and alkynes, 5:5-fused 1,5-diazabicyclo[3.3.0]oct-7-en-2-ones are obtained. The use of a catalyst composed of $(Me_3Si)_2NCu$ and a chiral BINAP leads to chiral products.[6]

[1] Ding, J., Lee, J.C.H., Hall, D.G. *OL* **14**, 4462 (2012).
[2] Teng, H.-L., Luo, F.-L., Tao, H.-Y., Wang, C.-J. *OL* **13**, 5600 (2011).
[3] Fandrick, K.R., Fandrick, D.R., Reeves, J.T., Gao, J., Ma, S., Li, W., Lee, H., Grinberg, N., Lu, B., Senanayake, C.H. *JACS* **133**, 10332 (2011).
[4] Gremaud, L., Alexakis, A. *ACIE* **51**, 794 (2012).
[5] Chen, J.-R., Dong, W.-R., Candy, M., Pan, F.-F., Jörres, M., Bolm, C. *JACS* **134**, 6924 (2012).
[6] Imaizumi, T., Yamashita, Y., Kobayashi, S. *JACS* **134**, 20049 (2012).

Gold-silver complexes

Protonation. Exposure of enol silyl ethers of cyclic ketones to (*R*)-binap$(AuCl)_2$ and $AgBF_4$ in a mixture of EtOH and CH_2Cl_2 furnishes chiral ketones.[1]

Cycloaddition. Formation of chiral methyl 1-aryl-2-cyclopropene-1-carboxylates is observed from diazo ester decomposition in alkynes, as catalyzed by (*S*)-xylyl-BINAP-AuCl and $AgSbF_6$.[2]

An *endo*-selective [3+2]cycloaddition between *N*-benzylidene-α-amino esters and electron-deficient alkenes is also subject to enantioselection through interaction with a chiral BINAP which complexes to $Au(OCOCF_3)_2$ and $Ag(OCOCF_3)$. Chiral pyrrolidinecarboxylic esters are produced.[3] Azlactones can serve as the 3-atom component in the cycloaddition.[4]

[1] Cheon, C.H., Kanno, O., Toste, F.D. *JACS* **133**, 13248 (2011)
[2] Briones, J.F., Davies, H.M.L. *JACS* **134**, 11916 (2012)
[3] Martin-Rodriguez, M., Najera, C., Sansano, J.M., de Cozar, A., Cossio, F.P. *CEJ* **17**, 14224 (2011)
[4] Martin-Rodriguez, M., Najera, C., Sansano, J.M. *SL* 62 (2012)

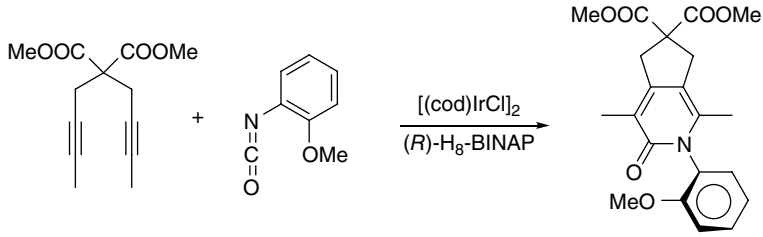
Iridium complexes

Substitution. Enantioselective opening of 1,4-oxa-1,4-dihydronaphthalene with phenols gives chiral *trans*-1-hydroxy-2-aryloxy-1,2-dihydronaphthalenes using a catalyst system that contains a Tol-BINAP (chiral), $[(cod)IrCl]_2$, AgOTf, and Bu_4NI.[1]

Degradation. Removal of the hydroxyl group and its associated methylene group from primary alcohols is an uncommon transformation, as performed by $[(coe)IrCl]_2$ which is ligated to BINAP.[2] A dehydrogenation - decarbonylation sequence is implicated.

Addition. An α-C-H group of 2-alkylaminopyridines is activated by an iridium(I) salt. Homologation by addition to alkenes and alkynes of the metallated species creates a stereocenter which can be manipulated enantioselectively by a chiral Tol-BINAP.[3]

A [4+2]cycloaddition of diynes with *N*-(*o*-anisyl)isocyanate furnishes stereo-defined atropisomers when the $[(cod)IrCl]_2$ catalyst is modified by (*R*)-H_8-BINAP.[4]



[1] Cheng, H., Yang, D. *JOC* **77**, 9756 (2012)
[2] Olsen, E.P.K., Madsen, R. *CEJ* **18**, 16023 (2012)
[3] Pan, S., Matsuo, Y., Endo, K., Shibata, T. *T* **68**, 9009 (2012)
[4] Onodera, G., Suto, M., Takeuchi, R. *JOC* **77**, 908 (2012)

Nickel complexes

Substitution. The complex derived from $Ni(cod)_2$ and (*R*)-BINAP catalyzes asymmetric arylation of ketones (e.g., α-tetralone), better results with respect to enantioselectivity are obtained from reaction with ArCl than ArBr.[1] (For reaction involving heteroaryl halides, (*R*)-difluorphos is a superior ligand.)

Asymmetric benzylic chlorination of *N*-arylacetyl-2-oxazolidinones by CF_3SO_2Cl is accomplished via the (*R*)-BINAP complex of $NiCl_2$ and further assisted by Et_3SiOTf and a tertiary amine.[2]

[1] Ge, S., Hartwig, J.F. *JACS* **133**, 16330 (2011).
[2] Hamashima, Y., Nagi, T., Shimizu, R., Tsuchimoto, T., Sodeoka, M. *EJOC* 3675 (2011).

Palladium complexes

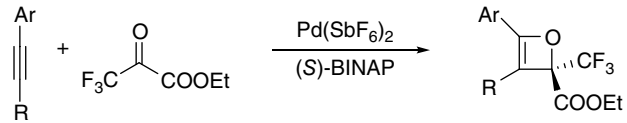
Substitution. α-Hydroxylation of ketones is rendered enantioselective using a (binap)Pd complex. The reaction is tasked by $CuCl_2$ in oxygen.[1] Attack of *N*-tosylaziridines by *o*-bromoarylacetonitriles under basic conditions is followed by an intramolecular arylation of the tosylamines. In this way chiral 2,3-disubstituted 4-cyanotetrahydroquinolines are accessed.[2]

Coupling. An atroposelective intramolecular Heck reaction calls for employment of a (binap)Pd complex.[3]

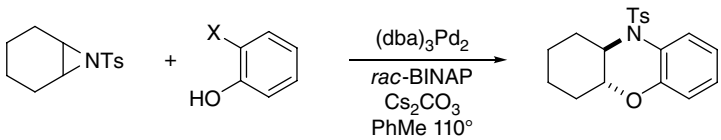
Addition. 4-Aryl-4-pentenoic acids cyclize on inducement of a Br^+ source in trifluoroethanol, and the 4-bromomethyl-4-butanolides are produced in an optically active form if a chiral (binap)$Pd(SbF_6)_2$ is present.[4]

Allyl cyanoacetate extrudes CO_2 on contact with a Pd(0) species and the remaining fragments can be used as addends to Michael acceptors. Furthermore, chiral adducts are accessible by binding the Pd atom to a chiral BINAP.[5]

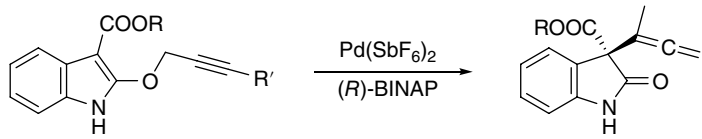
Cycloaddition. Chiral oxetanes and oxetenes are formed in the [2+2]cycloaddition of ethyl 3,3,3-trifluoro-2-oxopropanoate with vinyl esters and alkynes, respectively.[6,7]



An enantioselective route to benzo-1,4-oxazines which are *trans*-annulated on the opposite side of the aromatic ring consists of aziridine ring opening and intramolecular *N*-arylation.[8]



Rearrangement. 2-Propargyloxyindole-3-carboxylic esters undergo enantioselective rearrangement to afford 3-allenyl-2-indolinones, precursors of spiroannulated oxindoles.[9]



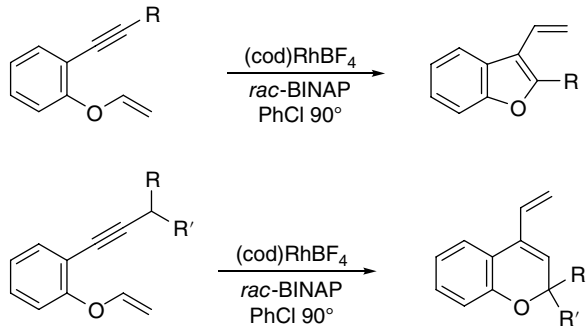
[1] Hamed, O.A., El-Qisairi, A., Qaseer, H., Hamed, E.M., Henry, P.M., Becker, D.P. *TL* **53**, 2699 (2012)
[2] Ghorai, M.K., Nanaji, Y., Yadav, A.K. *OL* **13**, 4256 (2011)
[3] Groh, M., Meidlinger, D., Bringmann, G., Speicher, A. *OL* **14**, 4548 (2012)
[4] Lee, H.J., Kim, D.Y. *TL* **53**, 6984 (2012)
[5] Lu, S., Jin, T., Bao, M., Asiri, A.M., Yamamoto, Y. *TL* **53**, 1210 (2012)
[6] Mikami, K., Aikawa, K., Aida, J. *SL* 2719 (2011).
[7] Aikawa, K., Hioki, Y., Shimizu, N., Mikami, K. *JACS* **133**, 20092 (2011)
[8] Rao, R.K., Kathikeyan, I., Sekar, G. *T* **68**, 9090 (2012)
[9] Cao, T., Deitch, J., Linton, E.C., Kozlowski, M.C. *ACIE* **51**, 2448 (2012)

Rhodium complexes

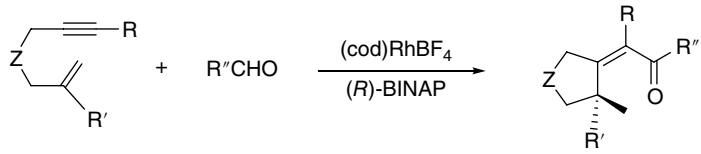
Addition. A Rh(I)-BINAP catalyst system directs addition of $ArB(OH)_2$ to 1-aryl-1-alkyn-3-ol such that the products are stilbenes with a 1-hydroxyalkyl substituent on the double bond.[1] A BINAP ligand modified by linking at C-6 to a group containing both lipophilic and hydrophilic moieties is used to assist the Rh complex in the conjugate addition to enones.[2]

Enantioselective attack on 2-cyclohexenones by Me_3Al is at the carbonyl group, but arylzinc and boron reagents add in the Michael fashion.[3] A similar reactivity profile is presented in the reaction of $ArB(OH)_2$ and vinyl sulfonamides.[4] Of course *rac*-BINAP is employed in the latter situation as no stereocenter is created.

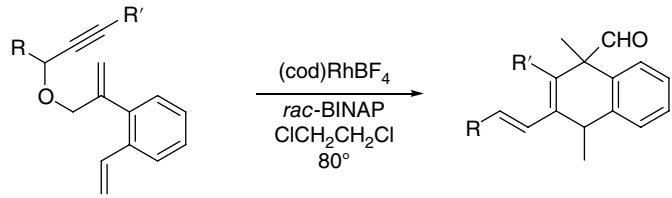
The vinyl moiety of *o*-alkynylaryl vinyl ethers is split off but subsequently adds back onto the triple bond while cyclization involving the oxygen atom occurs. Depending on the substitution pattern at the propargylic position of the substrate, 3-vinylbenzofurans or 4-vinyl-2*H*-chromenes may emerge.[5]



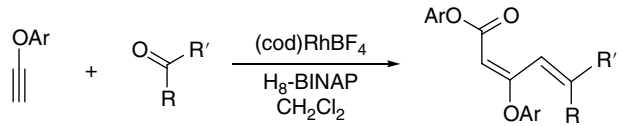
1,6-Enynes and aldehydes combine in quite a remarkable manner. A five-membered ring with extension of an exocyclic enone system is created.[6] Cycloisomerization of 1,6-enynes is also promoted by [RhCl] ligated to a 5,5′-disubstitued BINAP that is linked to a polymer backbone. The catalyst is reusable.[7]



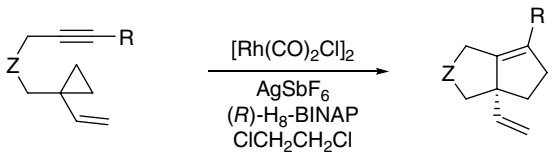
o-Alkynylaryl allyl ethers cyclize to afford 2-alkenyl-3-alkylidene-2,3-dihydrobenzofurans.[8] Double bond migration also enables Claisen rearrangement to intervene prior to cyclization that delivers a dihydronaphthalene aldehyde.[9]



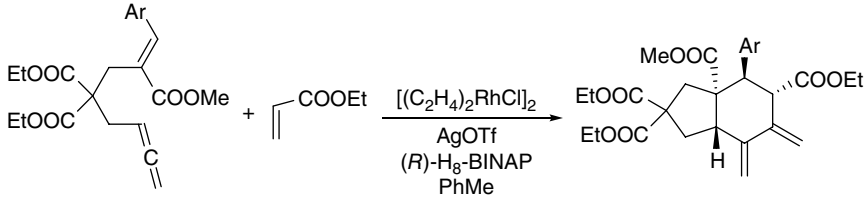
Alkynyl aryl ethers and carbonyl compounds combine in a 2:1 stoichiometry with total retention of all atoms. Octahydro-BINAP is the ligand to supported $(cod)_2RhBF_4$ catalyst for promoting the reaction.[10]



Annulation. A cyclopropane ring is selected for cycloaddition with a triple bond, even if there is a vinyl group only one CC bond away in the molecule.[11]



[2+2+2]Cycloaddition of 1,6-enynes and acrylamides affords bicyclic products in very high regioselectivity and diastereoselectivity.[12] Also an unusual version is that depicted in the following equation, one double bond each of two allene units is engaged in the ring formation.[13]

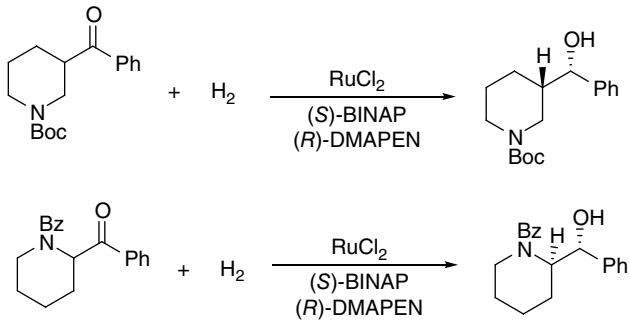


[1] Panteleev, J., Huang, R.Y., Lui, E.K.J., Lautens, M. *OL* **13**, 5314 (2011)
[2] Lipshutz, B.H., Isley, N.A., Moser, R., Ghorai, S., Leuser, H., Taft, B.R. *ASC* **354**, 3175 (2012)
[3] Kolb, A., Hirner, S., Harms, K., von Zezschwitz, P. *OL* **14**, 1978 (2012)
[4] Zilaout, H., van den Hoogenband, A., de Vries, J., Lange, J.H.M., Terpstra, J.W. *TL* **52**, 5934 (2011)
[5] Sakiyama, N., Noguchi, K., Tanaka, K. *ACIE* **51**, 5976 (2012)
[6] Ishida, M., Shibata, Y., Noguchi, K., Tanaka, K. *CEJ* **17**, 12578 (2011)
[7] Corkurn, E.G., Hass, M.J., Sullivan, A.D., Bergens, S.H. *OL* **13**, 3522 (2011)
[8] Okamoto, R., Okazaki, E., Noguchi, K., Tanaka, K. *OL* **13**, 4894 (2011)
[9] Okazaki, E., Okamoto, R., Shibata, Y., Noguchi, K., Tanaka, K. *ACIE* **51**, 6722 (2012)
[10] Miyauchi, Y., Kobayashi, M., Tanaka, K. *ACIE* **50**, 10922 (2011)
[11] Lin, M., Kang, G.-Y., Guo, Y.-A., Yu, Z.-X. *JACS* **134**, 398 (2012)
[12] Masutomi, K., Sakiyama, N., Noguchi, K., Tanaka, K. *ACIE* **51**, 13031 (2012)
[13] Brusoe, A.T., Edwankar, R.V., Alexanian, E.J. *OL* **14**, 6096 (2012)

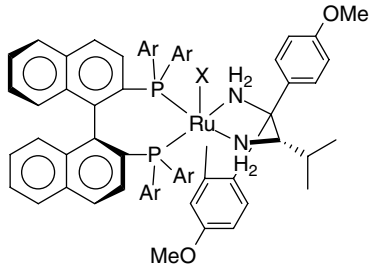
Ruthenium complexes

Asymmetric hydrogenation. Mechanistic insights can be of enormous value for new designs of the hydrogenation catalyst.[1] Upon application to transfer hydrogenation (KOH, *i*-PrOH) of geraniol the involvement of enantiomer isomerization is noted.[2]

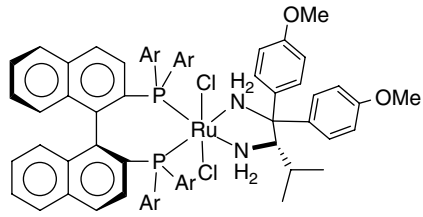
Hydrogenation of phenyl piperidinyl ketones reveals diastereoselectivity differences due to variation of connectivity between the carbonyl group and the nitrogen atom, although the absolute configuration of the carbinolic center remains constant.[3]



A modified catalyst for asymmetric hydrogenation of $ArCOCH_3$ is the ruthenacycle **1**.[4] Using complex **2** the hydrogenation of β-amino enones gives chiral γ-amino alcohols.[5]

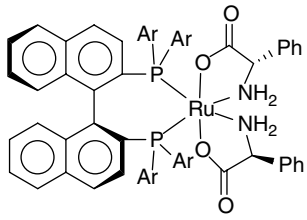


(**1**) Ar = *m*-xylyl

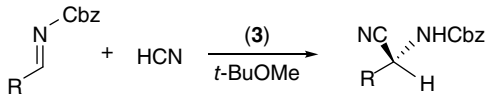


(**2**)

Addition. The well-known catalyst **3** along with LiX (e.g., X = OPh) is useful for conducting addition of HCN to *N*-benzyloxycarbonylaldimines,[6] as well as the addition of Me_3SiCN to ketones.[7]



(**3**)



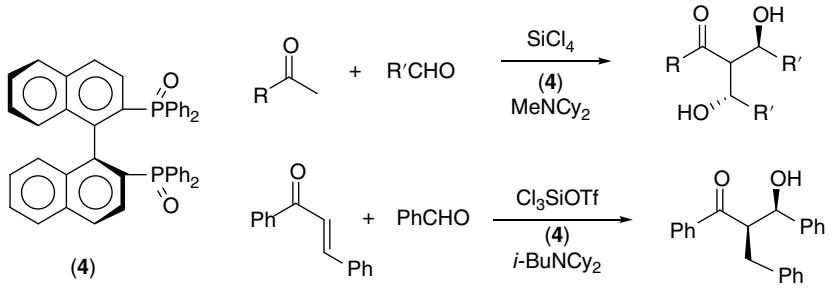
[1] Kitamura, M., Nakatsuka, H. *CC* **47**, 842 (2011)
[2] Wu, R., Beauchamps, M.G., Laquidara, J.M., Sowa Jr, J.R. *ACIE* **51**, 2106 (2012)
[3] Akashi, M., Arai, N., Inoue, T., Ohkuma, T. *ASC* **353**, 1955 (2011)
[4] Matsumura, K., Arai, N., Hori, K., Saito, T., Sayo, N., Ohkuma, T. *JACS* **133**, 10696 (2011)
[5] Geng, H., Zhang, X., Chang, M., Zhou, L., Wu, W., Zhang, X. *ASC* **353**, 3039 (2011)
[6] Uemura, M., Kurono, N., Ohkuma, T. *OL* **14**, 882 (2012)
[7] Uemura, M., Kurono, N., Sakai, Y., Ohkuma, T. *ASC* **354**, 2023 (2012)

2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl P-oxide and P,P′-dioxide

Resolution and other transformations. The dioxide forms inclusion complexes with a chiral BINOL and this phenomenon has been exploited for optical resolution.[1]

Reaction of the dioxide with NBS occurs at C-4 and C-4′, the product is amenable to coupling and other manipulations.[2]

Aldol reaction. Methyl ketones condense with two equivalents of aldehydes to give keto diols,[3] aldol reaction is also conducted from conjugated ketones which undergo reduction in situ (an amine as source of hydride).[4]



Coupling. The Heck reaction of 2,3-dihydrofuran with PhOTf affords 1-phenyl-2, 5-dihydrofuran in 92% ee, with the monoxide of (*R*)-BINAP, comparing to giving 1-phenyl-1,2-dihydrofuran in 66% ee with the parent (*R*)-BINAP.[5]

[1] Hatano, B., Hashimoto, K., Katagiri, H., Kijima, T., Murakami, S., Matsuba, S., Kusakari, M. *JOC* **77**, 3595 (2012)
[2] Dayoub, W., Favre-Réguillon, A., Berthod, M., Jeanneau, E., Mignani, G., Lemaire, M. *EJOC* 3074 (2012)
[3] Shimoda, Y., Kotani, S., Sugiura, M., Nakajima, M. *CEJ* **17**, 7992 (2011)
[4] Osakama, K., Sugiura, M., Nakajima, M., Kotani, S. *TL* **53**, 4199 (2012)
[5] Wöste, T.H., Oestreich, M. *CEJ* **17**, 11914 (2011)

Bismuth(III) bromide

Cycloaddition. The Lewis acidity of $BiBr_3$ is sufficiently high for ionization of allylic acetates for trapping with 1-alkynes. It is easy to conceive a route to fluorenes from acetoxyalkenynes and alkynes.[1]



Carbobismuthination. 1-Alkynes are also activated by $BiBr_3$, and the loose complexes are attacked antarafacially by ketene silyl acetals.[2]

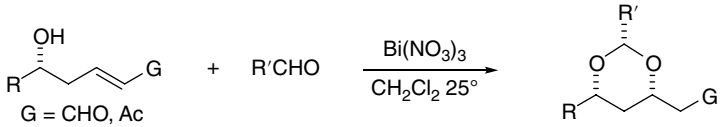


[1] Wang, X.-C., Yan, R.-L., Zhong, M.-J., Liang, Y.-M. *JOC* **77**, 2064 (2012)
[2] Nishimoto, Y., Takeuchi, M., Yasuda, M., Baba, A. *ACIE* **51**, 1051 (2012)

Bismuth(III) nitrate

Nitroarenes. Addition of $K_2S_2O_8$ enables oxidative transformation of $ArB(OH)_2$ to $ArNO_2$, while $Bi(NO_3)_3$ supplies the nitro group.[1]

Directed hydration. Hemiacetal formation is catalyzed by $Bi(NO_3)_3$, from mixtures of homoallylic alcohols and aldehydes. When the double bond is conjugated to an electron-withdrawing group cyclization of the hemiacetal follows.[2]



[1] Manna, S., Maity, S., Rana, S., Agasti, S., Maiti, D. *OL* **14**, 1736 (2012)
[2] Evans, P.A., Grisin, A., Lawler, M.J. *JACS* **134**, 2856 (2012)

Bismuth(III) triflate

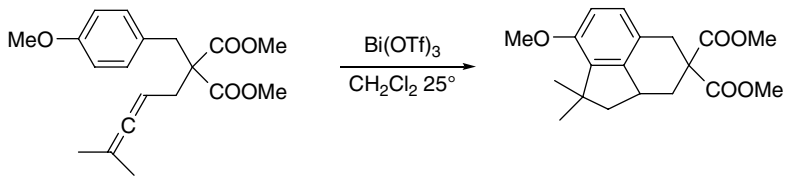
Nitriles. From aldehydes the condensation with acetohydroxamic acid and subsequent elimination to deliver nitriles are catalyzed by $Bi(OTf)_3$.[1]

Substitution. Intramolecular S_N2' reaction of allylic alcohols enabled by $Bi(OTf)_3$ is the basis of the route to 1-alkenyltetrahydroisoquinolines from *o*-substituted arylethylamine derivatives.[2]

Friedel-Crafts reaction between acyl halides and arenes is accomplished in the presence of $Bi(OTf)_3$ and an ionic liquid under microwave irradiation.[3] The catalyst system is well suited for the replacement of OH group in an activated position by silicon reagents (allyl-, alkynyl-, and hydrosilanes).[4]

Cyclization of certain alkenylarenes is also brought about on exposure to $Bi(OTf)_3$.[5] Although prenylation of aryl methyl ethers is observed on reaction with isoprene, the reaction of phenols leads to 2,2-dimethylchromans.[6]

Formation of two rings from arenes containing an allenyl group in a sidechain of an arene is particularly valuable.[7]

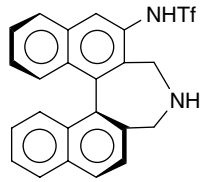


Hydroamination. The ability of $Bi(OTf)_3$ to promote the addition is illustrated by the ring closure of *N*-(4-pentenyl)sulfonamides to the 2-methylpyrrolidine derivatives.[8]

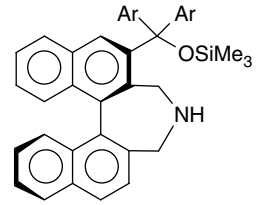
[1] Sridhar, M., Reddy, M.K.K., Sairam, V.V., Raveendra, J., Godala, K.R., Narsaiah, C., Ramaiah, B.V., Reddy, C.S. *TL* **53**, 3421 (2012)
[2] Kawai, N., Matsuda, M., Uenishi, J. *T* **67**, 8648 (2011)
[3] Tran, P.H., Duus, F., Le, T.N. *TL* **53**, 222 (2012)
[4] Kumar, G.G.K.S.N., Laali, K.K. *OBC* **10**, 7347 (2012)
[5] Caciuttolo, B., Poulain-Martini, S., Duñach, E. *EJOC* 3710 (2011)
[6] Judd, K.E., Caggiano, L. *OBC* **9**, 5201 (2011)
[7] Lemiere, G., Cacciuttolo, B., Belhassen, E., Duñach, E. *OL* **14**, 2750 (2012)
[8] Mathia, F., Szolcsanyi, P. *OBC* **10**, 2830 (2012)

Bis(naphtho[2,1-*c*])azepines

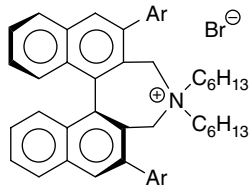
Aldol reaction. The unsymmetrical azepine **1**is used as catalyst for aldol reaction involving *t*-butyl glyoxylate as the acceptor.[1]



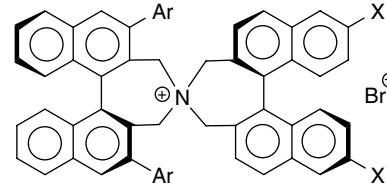
(**1**)



(**2**)



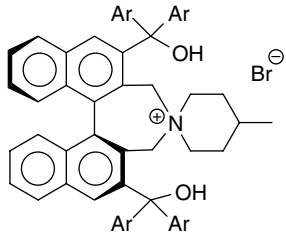
(**3**) Ar = 3,5-(3,5-*t*Bu$_2$C$_6$H$_3$)$_2$C$_6$H$_3$



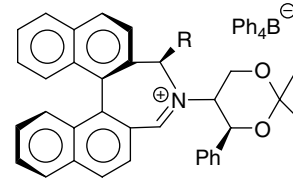
(**4**)

Alkylation. The very bulky salt **3** is a phase-transfer catalyst for *N*-alkylation of *o*-iodoanilides, thereby axially chiral products are formed.[2] The spirocyclic quaternary ammonium bromide **4** is shown to be suitable for catalyzing alkylation of 1-cyanoisoquinoline and its addition to phenyl vinyl sulfone.[3]

Conjugate addition. Asymmetric addition of aldehydes to nitroalkenes is accomplished in the presence of **2**,[4] and one use for **5** is the asymmetric addition of α-nitroalkanoic esters to maleimide.[5]



(**5**) Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$



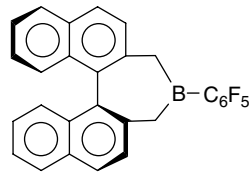
(**6**)

Epoxidation. To render epoxidation of alkenes by Oxone enantioselective, **6** is gainfully employed.[6]

[1] Kano, T., Noishiki, A., Sakamoto, R., Maruoka, K. *CC* **47**, 10626 (2011)
[2] Shirakawa, S., Liu, K., Maruoka, K. *JACS* **134**, 916 (2012)
[3] Shirakawa, S., Liu, K., Ito, H., Le, T.N., Maruoka, K. *ASC* **353**, 2614 (2011)
[4] Liang, D.-C., Luo, R.-S., Yin, L.-H., Chan, A.S.C., Lu, G. *OBC* **10**, 3071 (2012)
[5] Shirakawa, S., Terao, S.J., He, R., Maruoka, K. *CC* **47**, 10557 (2011)
[6] Page, P.C.B., Bartlett, C.J., Chan, Y., Day, D., Parker, P., Buckley, B.R., Rassias, G.A., Slawin, A.M.Z., Allin, S.M., Lacour, J., Pinto, A. *JOC* **77**, 6128 (2012)

Bis(naphtho[2,1-*c*])borepins

Lewis acidity. The Lewis acidity of compound **1** is about 85% that of $(C_6F_5)_3B$. Accordingly its proper applications for certain reactions can be determined.[1]

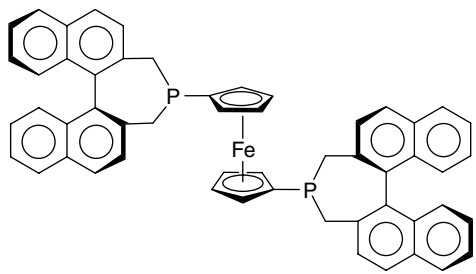


(**1**)

[1] Mewald, M., Fröhlich, R., Oestreich, M. *CEJ* **17**, 9406 (2011).

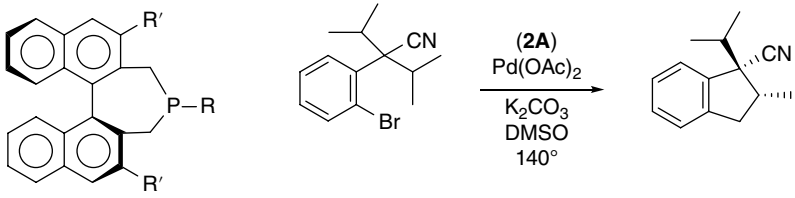
Bis(naphtho[2,1-*c*])phosphepins

Reduction. Hydrogenation of 1-substitued 3,4-dihydroisoquinolines based on asymmetric induction by the ferrocenyldiphosphine **1** that is to compex an iridium compound has been further studied employing an iodine-bridged dimeric iridium species.[1]



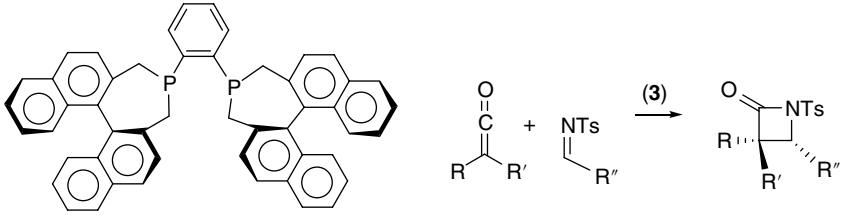
(**1**)

Coupling. Based on C-H activation by Pd catalyst the dehydrobrominative ring closure of *o*-bromoarylalkanes that bear two identical alkyl branches at the benzylic position is enantiodiscriminated by using **2A**.[2]



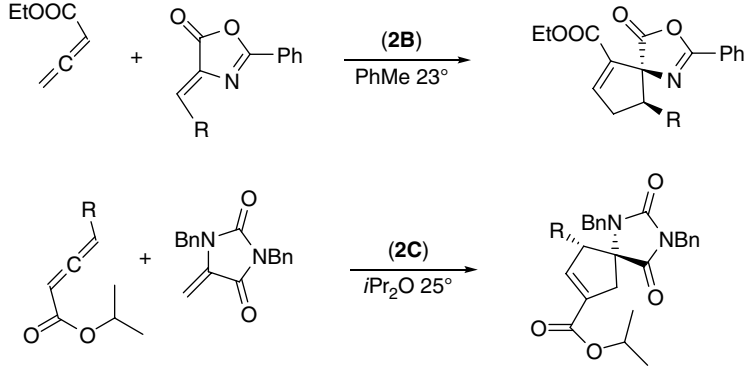
(**2A**) R = *t*-Bu, R′ = H
(**2B**) R = Ph, R′ = H
(**2C**) R = R′ = Ph

Cycloaddition. Access to chiral β-lactams from ketenes and *N*-tosylaldimines can take advantage of the stereochemical direction from **3**.[3]



(**3**)

Enantioselective spiroannulation results when allenes and alkylideneoxazolinones[4] or imidazolidinediones[5] are combined in the presence of **2B**/**2C**.

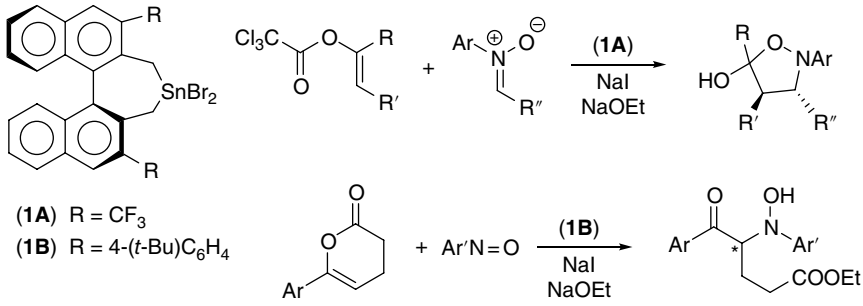


[1] Chang, M., Li, W., Zhang, X. *ACIE* **50**, 10679 (2011)
[2] Martin, N., Pierre, C., Davi, M., Jazzar, R., Baudoin, O. *CEJ* **18**, 4480 (2012)

[3] Chen, S., Salo, E.C., Wheeler, K.A., Kerrigan, N.J. *OL* **14**, 1784 (2012)
[4] Steurer, M., Jensen, K.L., Worgull, D., Jørgensen, K.A. *CEJ* **18**, 76 (2012)
[5] Fujiwara, Y., Fu, G.C. *JACS* **133**, 12293 (2011)

Bis(naphtho[2,1-*c*])stannepins

Stetter reaction. Stannepin **1A** provides chiroptical information to guide the cycloaddition of nitrones with enol trichloroacetates.[1] But only moderate ee is observed in the adducts.

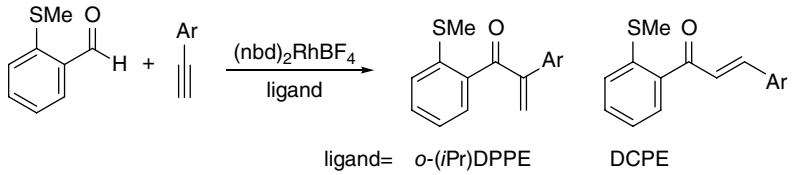


Hydroxyamination. Enolates generated from opening of enollactones react with nitrosoarenes to form a new C-N bond which is subject to asymmetric induction by **1B**.[2]

[1] Yanagisawa, A., Izumiseki, A., Sugita, T., Kushihara, N., Yoshida, K. *SL* 107 (2012)
[2] Yanagisawa, A., Fujinami, T., Oyokawa, Y., Sugita, T., Yoshida, K. *OL* **14**, 2434 (2012)

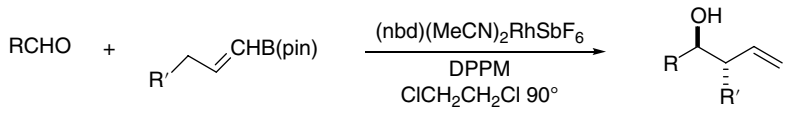
Bis(norbornadiene)rhodium(I) tetrafluoroborate

Addition. Hydroacylation of alkynes is controllable by choosing the proper phosphine ligand.[1,2] When propargyl alcohols are chosen as addends, γ-hydroxy-α,β-unsaturated ketones are produced.[3]



Transfer of a 2-furyl group to conjugated ketones from the lithium salt of a bridged triolatoborate is successful using the $(nbd)_2RhBF_4$ catalyst.[4]

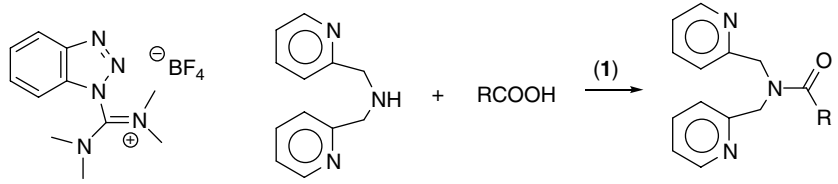
The mixed-ligand Rh salt (nbd)$(MeCN)_2RhSbF_6$ is an allylation catalyst for alkenylboronates. The reaction is preceded by double bond migration therefore both (*E*)- and (*Z*)-boronates converge to provide the same reagent.[5]



[1] Gonzalez-Rodriguez, C., Pawley, R.J., Chaplin, A.B., Thompson, A.L., Weller, A.S., Willis, M.C. *ACIE* **50**, 5134 (2011)
[2] Poingdestre, S.-J., Goodacre, J.D., Weller, A.S., Willis, M.C. *CC* **48**, 6354 (2012)
[3] Lenden, P., Entwistle, D.A., Willis, M.C. *ACIE* **50**, 10657 (2011)
[4] Yu, X.-Q., Shuai, T., Yamamoto, T., Miyaura, N. *CAJ* **6**, 932 (2011)
[5] Shimizu, H., Igarashi, T., Miura, T., Murakami, M. *ACIE* **50**, 11465 (2011)

Bis(picolyl)amine

Carboxyl protection.[1] Carboxylic acids form amides with the title compound in the presence of **1.** These amides are cleaved by either methanolysis [$Cu(OTf)_2$, MeOH] or hydrolysis [$Cu(OTf)_2$, $Ba(OH)_2{\cdot}8H_2O$].



[1] Bröhmer, M.C., Mundinger, S., Bräse, S., Bannwarth, W. *ACIE* **50**, 6175 (2011)

Bis(pinacolato)diboron

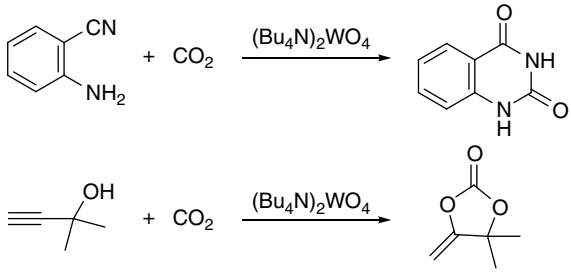
Cyclic boronates. *B*-Substituted pinacolatoboranes are prepared from (pin)BB(pin): for aryl derivatives by a radical process involving in situ diazotization of $ArNH_2$ with *t*-BuONO and promotion by $(PhCOO)_2$;[1] and for alkyl derivatives a reaction with tosylhydrazones under basic conditions (NaOMe, PhMe, 90°).[2]

In the presence of an iridium-$B(pin)_3$ complex saturated heterocycles are borylated by (pin)BB(pin) at an α-carbon.[3]

[1] Mo, F., Jiang, Y., Qiu, D., Zhang, Y., Wang, J. *ACIE* **49**, 1846 (2010)
[2] Li, H., Wang, L., Zhang, Y., Wang, J. *ACIE* **51**, 2943 (2012)
[3] Liskey, C.W., Hartwig, J.F. *JACS* **134**, 12422 (2012)

Bis(tetrabutylammonium) tungstate

Carbonylative cyclization.[1] Incorporation of CO_2 into propargylic alcohols, *o*-phenylenediamine and *o*-cyanoaniline to form heterocycles is catalyzed by $(Bu_4N)_2WO_4$.

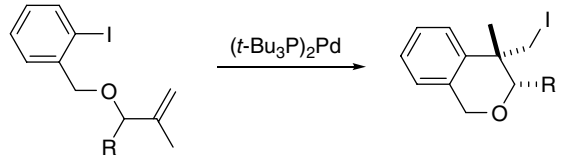


[1] Kimura, T., Kamata, K., Mizuno, N. *ACIE* **51**, 6700 (2012)

Bis(tri-*t*-butylphosphine)palladium(0)

Elimination. 1-Bromoalkanes undergo dehydrobromination in the presence of $(t\text{-}Bu_3P)_2Pd$ and a base at room temperature.[1] (*E,E*)-2,4-Alkadienoic esters are obtained from either the (*E*)- or (*Z*)-isomer of 3-triflyloxy-2-alkenoic esters.[2]

Coupling. Ring closure with halogen atom transposition is observed on treatment of *o*-iodobenzyl methallyl ethers with $(t\text{-}Bu_2P)_2Pd$.[3] The process is diastereoselective.



A method for the preparation of *B*-benzylpinacolatoboron consists of coupling between ArBr and methylenedi(pinacolatoboron).[4]

[1] Bissember, A.C., Levina, A., Fu, G.C. *JACS* **134**, 14232 (2012)
[2] Crouch, I.T., Dreier, T., Frantz, D.E. *ACIE* **50**, 6128 (2011)
[3] Petrone, D.A., Malik, H.A., Clemenceau, A., Lautens, M. *OL* **14**, 4806 (2012)
[4] Endo, K., Ohkubo, T., Shibata, T. *OL* **13**, 3368 (2011)

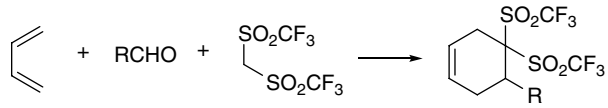
Bis[tricarbonyldichlororuthenium(II)]

Ketone synthesis. Reaction of RCHO with $R'B(OH)_2$ furnishes RCOR' directly.[1]

[1] Li, H., Xu, Y., Shi, E., Wei, W., Suo, X., Wan, X. *CC* **47**, 7880 (2011)

Bis(trifluoromethylsulfonyl)methane

1,1- Bis(trifluoromethylsulfonyl)alkenes. On formation of the reactive dienophile with aldehydes, a range of Diels-Alder reaction products can be made. Those from aliphatic dienes are readily transformed into aryl trifluoromethyl sulfones.[1]



[1] Yanai, H., Fujita, M., Taguchi, T. *CC* **47**, 7245 (2011)

Bis(triorganosilyl)propenes

1,3-Alkadienes. Deoxygenative chain elongation of aldehydes to afford dienes with three more carbons is achieved on reaction with $R_3SiCH{=}CHCH_2SiR_3$ in the presence of a Lewis acid.[1]

[1] Borg, T., Tuzina, P., Somfai, P. *JOC* **76**, 8070 (2011)

9-Borabicyclo[3.3.1]nonane, (9-BBN)

Isomerization. A 1:1-mixture of (*Z*)- and (*E*)-stilbenes is converted into essentially pure (>95%) (*E*)-isomer by the 9-BBN-THF complex under microwave irradiation (20 min.) and then treatment with *t*-BuONO.[1]

[1] Gray, E.E., Rabenold, L.E., Goess, B.C. *TL* **52**, 6177 (2011)

Borane – lithium amide

Reduction. 1,2-Reduction of conjugated carbonyl compounds is the preferred course for the borane – $LiNH_2$ complex.[1]

[1] Xu, W., Zhou, Y., Wang, R., Wu, G., Chen, P. *OBC* **10**, 367 (2012)

Borane-sulfides

New reagents. Poly(propylene sulfide) forms coordination adduct with BH_3 and such is as useful as $Me_2S{\cdot}BH_3$.[1]

Cyclization. As an alternative to intramolecular hydroamination, amines containing a distant double bond are converted into the cyclic isomers via hydroboration-oxidation and Mitsunobu reaction, as demonstrated in a synthesis of the indolizidine alkaloids.[2]

[1] Smith, K., Balakit, A.A., El-Hiti, G.A. *T* **68**, 7834 (2012)
[2] Pronin, S.V., Tabor, M.G., Jansen, D.J., Shenvi, R.A. *JACS* **134**, 2012 (2012)

Boric acid

Transamination. Tertiary amides exchange their amino groups by heating with other amines in the presence of H_3BO_3 and water (1-2 equiv.).[1]

Addition. The boric acid-catalyzed addition of Bu_3SnH in air to propargyl ethers is regio- and stereoselective.[2] The (*Z*)-isomers of $RCH{=}C(SnBr_3)CH_2OR$ are obtained.

[1] Nguyen, T.B., Sorres, J., Tran, M.Q., Ermolenko, L., Al-Mourabit, A. *OL* **14**, 3202 (2012)
[2] Oderinde, M.S., Hunter, H.N., Froese, R.D.J., Organ, M.G. *CEJ* **18**, 10821 (2012)

Boron trichloride

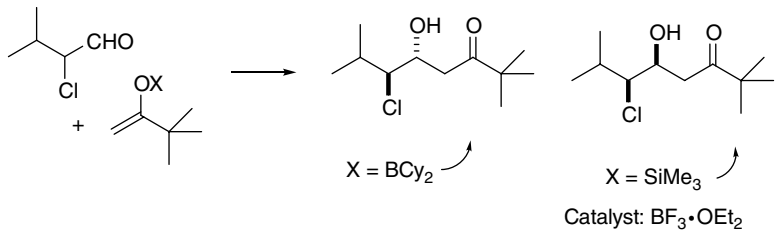
Borylation. Complexation to 2,6-lutidine to give a reagent for electrophilic borylation of arenes, BCl_3 is assisted by $AlCl_3$.[1] Products are readily converted into the conventional ArB(pin).

Allylation. When supramolar quantities of BX_3 (X = Cl, Br) are used to promote the addition of allylmetals to ArCHO the products are homoallyl halides as the oxyfunctionality at benzylic position is further transformed.[2] With dehydrohalogenation to follow the reaction can be included as part of diene synthesis.

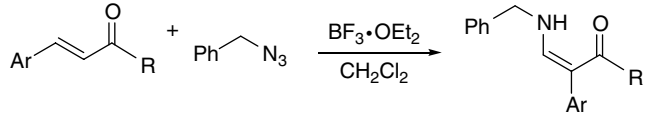
[1] Del Grosso, A., Helm, M.D., Solomon, S.A., Caras-Quinter, D., Ingleson, M.J. *CC* **47**, 12459 (2011)
[2] Quinn, M.P., Yao, M.-L., Yong, L., Kabalka, G.W. *S* 3815 (2011)

Boron trifluoride etherate

Aldol reaction. With $BF_3{\cdot}OEt_2$ to catalyze reaction of enol ethers with α-chloro aldehydes the diastereoselectivity is found to be affected by the nature of the heteroatom attached to the oxygen atom of the enol ether.[1]



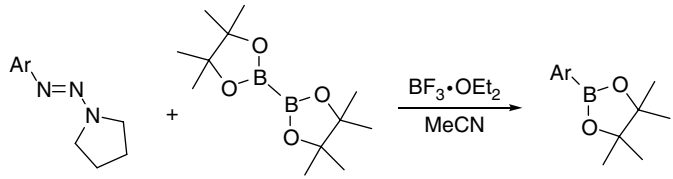
Substitution. A 3-indolyl group is introduced to the β-position of enones in a reaction catalyzed by $BF_3{\cdot}OEt_2$. Presence of DDQ is essential to maintain the oxidation state.[2] When benzyl azides, β-styryl ketones and $BF_3{\cdot}OEt_2$ are brought together the organic compounds combine (with loss of N_2) to furnish α-aryl (*Z*)-enaminones as the major product, due to incurrence of a 1,2-aryl migration.[3]



A carboxamidoxy group in a mixed acetal is replaceable on reaction with RBF_3K.[4] Diarylmethanes are obtained from benzyl hydroxamates $ArCH_2ON(Ac)Me$ and various arenes, even those deactivated.[5]

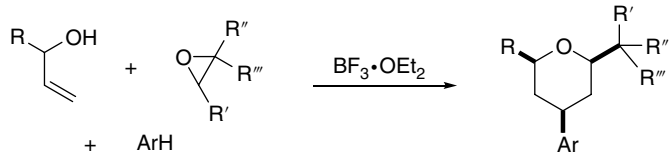
Cyanation at C-3 of the indole nucleus is accomplished using PhN(Ts)CN.[6]

Triphenylenes are generated from 1,2-diarylarenes which carry an *o*-triazeno group in one of the aryl substituents. For the transformation $BF_3 \cdot OEt_2$ is a suitable catalyst.[7] Aryltriazenes are also readily converted into arylboronates.[8]



Alcohols are activated by $BF_3 \cdot OEt_2$ to react with glycosyl trichloroacetimidates.[9]

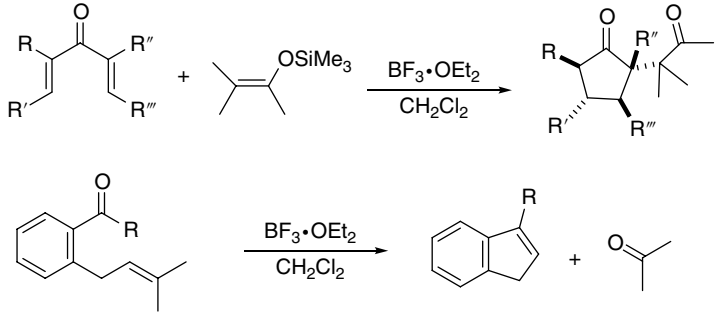
Ring formation. 2,4,6-Trisubstituted tetrahydropyrans with an all-*cis* stereochemistry are elaborated from homoallylic alcohols, epoxides, and arenes.[10] Isomerization of the epoxide component to an aldehyde precedes condensation with the alcohol and ring closure. The final step is the attack by a nucleophilic arene.



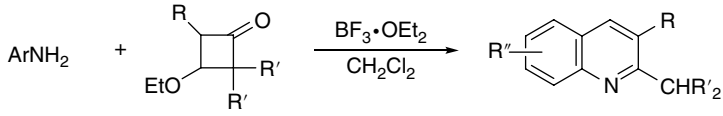
4-Alkenethiols similarly undergo Prins cyclization in the reaction with aldehydes. In this case the reaction is terminated by deprotonation at an allylic position, therefore the products are tetrahydrothiopyrans that contain an alkenyl substituent..[11]

The reaction of 5-arylpentanals react with $TsNH_2$ to yield 2-arylpiperidines as a result of a 1,5-hydride shift to enable cyclization.[12] Necessarily the aryl group is electron-rich (e.g., anisyl) to support creation of a benzyl cation.

When Nazarov cyclization is carried out in the presence of enol silyl ethers, the cationic intermediates are captured.[13] On the other hand, splitting off acetone as a ring is being formed from aryl ketones is observed when the latter compounds are *o*-substituted with a sidechain terminated at a propylidene group.[14]

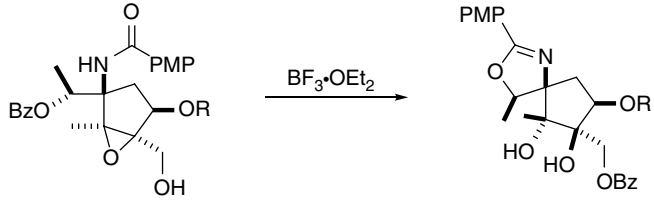


3-Alkoxycyclobutanones are cleaved in the presence of $BF_3 \cdot OEt_2$ and the oxonium ions can be trapped by anilines. Further events then lead to formation of quinolines.[15]

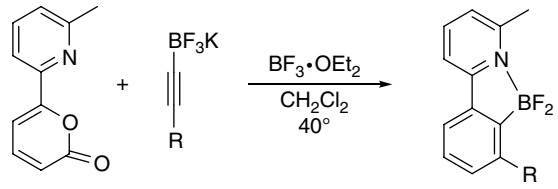


Ionization of propargylic alcohols followed by trapping with *N*-sulfonylhydrazones leads to the formation of pyrazolines.[16] Migration of the sulfonyl group is noted.

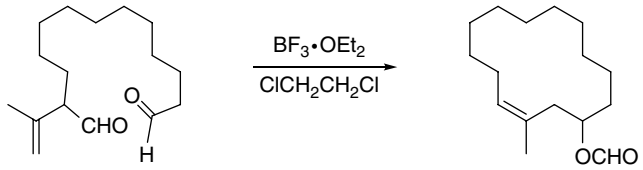
A densely substituted cyclopentene oxide offers unique opportunity for neighboring group participation that is triggered by opening of the epoxide, an oxazoline ring is formed.[17]



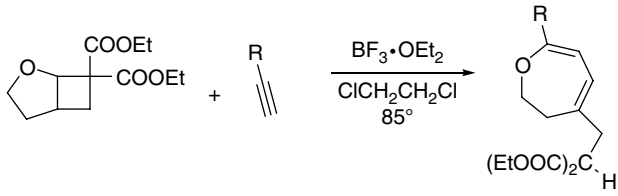
Regioselective [4+2]cycloaddition between 2-pyrones bearing a pyridyl or amide substituent at C-6 and potassium alkynyltrifluoroborates occurs.[18]



Condensation. Formation of homoallylic formate from a β,γ-unsaturated aldehyde when reacting with another aldehyde proceeds via an oxonia-Cope rearrangement.[19] It is significant that some macrocyclic compounds can be erected by the method.[20]



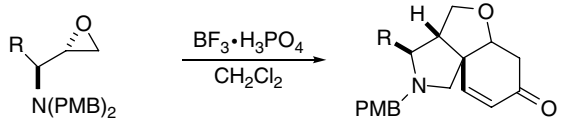
A cyclobutane-1,1-dicarboxylic ester fused to a tetrahydrofuran ring is prone to fragmentation on exposure to $BF_3 \cdot OEt_2$, and the resulting oxonium species can be trapped by a terminal alkyne to form a propargyl ether. Further ionization and ring cleavage is also favorable, and the fate of the propargyl cation is formation of a 2,3-dihydrooxepine.[21]



[1] Borg, T., Danielsson, J., Somfai, P. *CC* **46**, 1281 (2010)
[2] Xiang, S.-K., Wu, G., Zhang, B., Cui, Y., Jiao, N. *TL* **53**, 3802 (2012)
[3] Cunha, S., Gomes, A.T. *TL* **53**, 6710 (2012)
[4] Vo, C.-V.T., Mitchell, T.A., Bode, J.W. *JACS* **133**, 14082 (2011)
[5] Schäfer, G., Bode, J.W. *ACIE* **50**, 10913 (2011)
[6] Yang, Y., Zhang, Y., Wang, J. *OL* **13**, 5608 (2011)
[7] Zhou, J., Yang, W., Wang, B., Ren, H. *ACIE* **51**, 12293 (2012)
[8] Zhu, C., Yamane, M. *OL* **14**, 4560 (2012)
[9] Kumar, A., Kumar, V., Dere, R.T., Schmidt, R.R *OL* **13**, 3612 (2011)
[10] Indukuri, K., Bondalapati, S., Kotipalli, T., Gogoi, P., Saikia, A.K. *SL* 233 (2012)
[11] Bondalapati, S., Gogoi, P., Indukuri, K., Saikia, A.K. *JOC* **77**, 2508 (2012)
[12] Vadola, P.A., Carrera, I., Sames, D. *JOC* **77**, 6689 (2012)
[13] Wu, Y.-K., McDonald, R., West, F.G. *OL* **13**, 3584 (2011)
[14] Soicke, A., Slavov, N., Neudörfl, J.-M., Schmalz, H.-G. *SL* 2487 (2011)
[15] Shan, G., Sun, X., Xia, Q., Rao, Y. *OL* **13**, 5770 (2011)
[16] Zhu, Y., Wen, S., Yin, G., Hong, D., Lu, P., Wang, Y. *OL* **13**, 3553 (2011)
[17] Haussener, T.J., Looper, R.E. *OL* **14**, 3632 (2012)
[18] Kirkham, J.D., Butlin, R.J., Harrity, J.P.A. *ACIE* **51**, 6402 (2012)
[19] Zou, Y., Ding, C., Zhou, L., Li, Z., Wang, Q., Schoenebeck, F., Goecke, A. *ACIE* **51**, 5647 (2012)
[20] Zou, Y., Mouhib, H., Stahl, W., Goeke, A., Wang, Q., Kraft, P. *CEJ* **18**, 7010 (2012)
[21] Machin, B.P., Pagenkopf, B.L. *SL* 2799 (2011)

Boron trifluoride – phosphoric acid

Annulation. *N,N*-Di(*p*-methoxybenzyl)amines that are α-substituted with an epoxy moiety undergo stereoselective intramolecular alkylation and Michael addition on treatment with $BF_3{\cdot}H_3PO_4$.[1] One of the aryl groups is transformed into a cyclohexenone.



[1] Rodriguez-Solla, H., Concellon, C., Tuya, P., Garcia-Granda, S., Diaz, M.R. *ASC* **354**, 295 (2012)

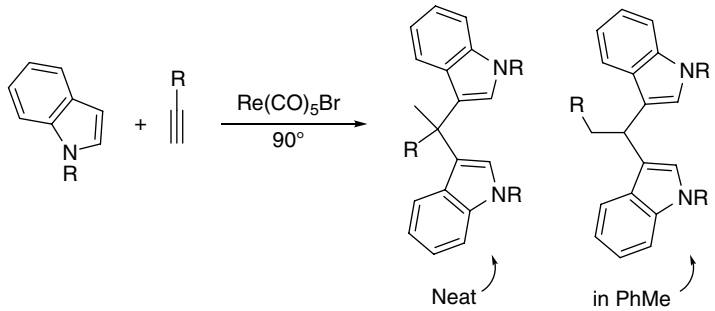
Bromine trifluoride - pyridine complex

Fluorination.[1] The C=S group in aryl thiones and aryl thionoesters is replaced by the *gem*-difluoro residue on treatment with py.BrF_3. Imino analogs (C=N instead of C=S bond present) also undergo the same transformation.

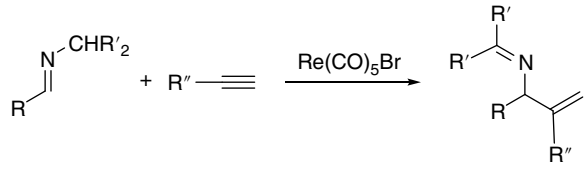
[1] Hagooly, Y., Rozen, S. *OL* **14**, 1114 (2012)

Bromopentacarbonylrhenium

Alkylation of indole. 1-Alkynes are captured by indoles in the presence of $Re(CO)_5Br$. Two different types of the 2:1-adducts appear, depending on the reaction conditions (neat or in toluene).[1]



N-(Alkylidene)allylamines. 1-Alkynes form organometallic reagents with $Re(CO)_5Br$ which add to imines at the sp^2-carbon.[2]



[1] Xia, D., Wang, Y., Du, Z., Zheng, Q.-Y., Wang, C. *OL* **14**, 588 (2012)
[2] Fukumoto, Y., Daijo, M., Chatani, N. *JACS* **134**, 8762 (2012)

Bromopentafluorosulfur

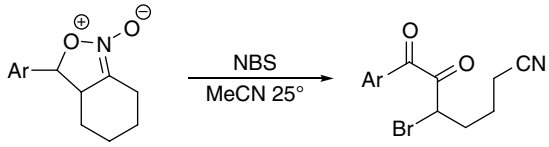
Addition. A preparation of the unique pentafluorothioacetaldehyde (F_5SCH_2CHO) involves addition of $BrSF_5$ to vinyl acetate followed by hydrolysis.[1]

[1] Ngo, S.C., Lin, J.-H., Savoie, P.R., Hines, E.M., Pugliese, K.M., Welch, J.T. *EJOC* 4902 (2012)

N-Bromosuccinimide (NBS)

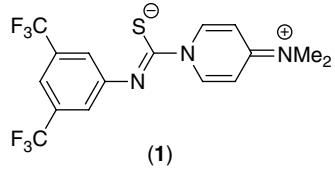
Bromination. Alkyl *p*-tolyl ketones can be brominated at two sites with NBS, when $SiCl_4$ is also added.[1] A method for 3-arylthiolation of indole employs NBS and ArSSAr in DMF.[2]

Oxidation. A selective oxidation of secondary benzylic alcohols by NBS and *N.N′*-bis[3,5-bis(trifluoromethyl)phenyl]thiourea is observed. Thus α-(*p*-hydroxymethylphenyl) ethanol is converted into *p*-acetylbenzyl alcohol.[3] A redox cleavage of bicyclic isoxazoline *N*-oxides provides α-diketones.[4]



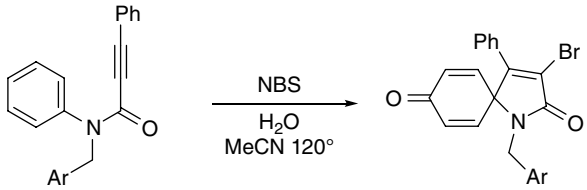
Thiosulfates are formed by NBS oxidation of RSO_2Na in the presence of disulfides.[5]

Addition. Conjugated ketones undergo addition (NBS, $TsNH_2$) to yield *anti*-α-amino-β-bromo ketones with (+)-tartaric acid serving as catalyst. An exception is the β-(*p*-anisyl) enones which give the α-bromo-β-amino isomers.[6] Bromolactonization initiated by NBS to deliver mesocyclic products is catalyzed by the zwitterionic thiourea **1**.[7]

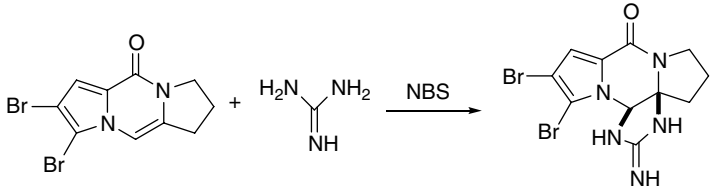


(**1**)

The spiroannulation of *N*-alkynoylanilines is quite remarkable as the benzene ring is oxygenated.[8]



A guanidine synthesis from alkenes, amines and R_2NCN is mediated by NBS.[9] Guanidines also participate in addition to form 2-iminoimidazolidines.[10]



Cyclization and ring expansion. The adduct of NBS and $(PhO)_3P$ is effective to induce Nazarov cyclization.[11] Spirocyclic imidazolidines derived from diamines and cyclobutanone are subject to ring expansion via *N*-bromination.[12]

With NBS to oxidize NH_4OH in the presence of an Ir(II)-corrole, insertion of a nitrogen atom into a CC bond occurs and a *meso*-azaporphyrin is produced.[13]

[1] Salama, T.A., Novak, Z. *TL* **52**, 4026 (2011)
[2] Huang, D., Chen, J., Dan, W., Ding, J., Liu, M., Wu, H. *ASC* **354**, 2123 (2012)
[3] Tripathi, C.B., Mukherjee, S. *JOC* **77**, 1592 (2012)
[4] Raihan, M.J., Kavala, V., Guan, Q.-Z., Kuo, C.-W., Kataria, S., Shishodia, S., Janreddy, D., Habib, P.M., Yao, C.-F. *ASC* **354**, 2251 (2012)
[5] Liang, G., Liu, M., Chen, J., Ding, J., Gao, W., Wu, H. *ChJC* **30**, 1611 (2012)
[6] Chen, Z., Wei, J., Li, W., Wang, Y., Zhao, P., Shi, X. *ChJC* **29**, 1689 (2011)
[7] Cheng, Y.A., Chen, T., Tan, C.K., Heng, J.J., Yeung, Y.-Y. *JACS* **134**, 16492 (2012)
[8] Tang, B.-X., Zhang, Y.-H., Song, R.-J., Tang, D.-J., Deng, G.-B., Wang, Z.-Q., Xie, Y.-X., Xia, Y.-Z., Li, J.-H. *JOC* **77**, 2837 (2012)
[9] Zhou, L., Chen, J., Zhou, J., Yeung, Y.-Y. *OL* **13**, 5804 (2011)
[10] Hewlett, N.M., Tepe, J.J. *OL* **13**, 4550 (2011)
[11] Guo, F., Wang, L., Mao, S., Zhang, C., Yu, J., Han, J. *T* **68**, 8367 (2012)
[12] Murai, K., Komatsu, H., Nagao, R., Fujioka, H. *OL* **14**, 772 (2012)
[13] Palmer, J.H., Brock-Nannestad, T., Mahammed, A., Durell, A.C., VanderVelde, D., Virgil, S., Gross, Z., Gray, H.B. *ACIE* **50**, 9433 (2011)

t-Butyl arenediazocarboxylates

Electrophiles and radical source. The *p*-substituted arenediazo compounds can serve as electrophiles and radicals are then generated on cleaving the C-N bond.[1]

[1] Hofling, S.B., Bartus, A.L., Heinrich, M.R. *ACIE* **49**, 9769 (2010)

t-Butyl hydroperoxide

Oxidation. When mixtures of ArCHO and Ar′Me are heated with *t*-BuOOH and Bu_4NI there produces $ArCOOCH_2Ar'$.[1] Benzyl esters are obtained from oxidation of ArCHRR′ in the presence of alkanoic acids.[2] The latter technique is applicable to gaining access to allyl esters of the type $RCOOCH(R')CHCH{=}CH_2$.[3]

An unactivated C-H bond of cycloalkyl acetates and acetamides can be oxidized by *t*-BuOOH – $PhI(OAc)_2$ to afford ketones at the 3-position in moderate yields. In this oxidation AcOBu exerts an unusual effect.[4]

The oxidation system composed of *t*-BuOOH and KI converts primary alkyl azides into nitriles.[5]

Oxidative coupling. A convenient route to *t*-butyl esters consists of oxidation of RCHO with *t*-BuOOH. If the reaction mixture is further treated with CuBr and cyclohexene then 2-cyclohexen-1-yl carboxylates are generated.[6] Several types of esters and amides are prepared from RCHO and R′XH, with the latter including disulfonimides, *N*-hydroxyimides.[7] Amides are also formed in the co-oxidation of RCHO or RCH_2OH and *N*-substituted formamides, due to union of the acyl and aminyl radical intermediates.[8-10] Slight variation of experimental conditions has been presented for such transformations (e.g., Bu_4NI or I_2 as additive). Aryl methyl ketones are converted into aroylformamides in the same manner.[11]

Oxidative activation of formamides enables them to condense with sulfonamides to generate $RSO_2N{=}CHNR'_2$.[12]

α-CH unit to an amino nitrogen atom is subject to oxidative activation and thence functionalization. Thus, *N,N*-dimethylcarbamides are readily converted into $RCON(Me)CH_2SR'$ by reaction with *t*-BuOOH and R′SSR′.[13]

Amination at C-2 of the oxazole and benzoxazole nuclei is accomplished with assistance of *t*-BuOOH.[14,15]

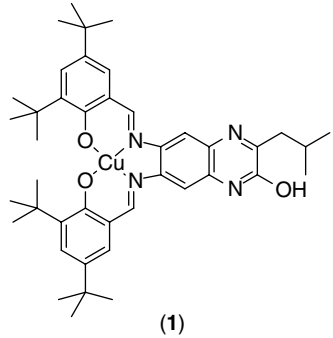
Substitution. Tosylhydrazide submits the Ts group to α-alkylstyrenes to form $ArC(=CH_2R)CH_2Ts$.[16]

[1] Huang, J., Li, L.-T., Li, H.-Y., Husan, E., Wang, P., Wang, B. *CC* **48**, 10204 (2012)
[2] Feng, J., Liang, S., Chen, S.-Y., Zhang, J., Fu, S.-S., Yu, X.-Q. *ASC* **354**, 1287 (2012)
[3] Shi, E., Shao, Y., Chen, S., Hu, N., Liu, Z., Zhang, J., Wan, X. *OL* **14**, 3384 (2012)
[4] Zhao, Y., Yim, W.-L., Tan, C.K., Yeung, Y.-Y. *OL* **13**, 4308 (2011)
[5] Lamani, M., Devadig, P., Prabhu, K.R. *OBC* **10**, 2753 (2012)
[6] Wei, W., Zhang, C., Xu, Y., Wan, X. *CC* **47**, 10827 (2011)
[7] Tan, B., Toda, N., Barbas III, C.F. *ACIE* **51**, 12538 (2012)
[8] Liu, Z., Zhang, J., Chen, S., Shi, E., Xu, Y., Wan, X. *ACIE* **51**, 3231 (2012)
[9] Li, H., Xie, J., Xue, Q., Cheng, Y., Zhu, C. *TL* **53**, 6479 (2012)
[10] Xu, K., Hu, Y., Zhang, S., Zha, Z., Wang, Z. *CEJ* **18**, 9793 (2012)
[11] Mai, W.-P., Wang, H.-H., Li, Z.-C., Yuan, J.-W., Xiao, Y.-M., Yang, L.-R., Mao, P., Qu, L.-B. *CC* **48**, 10117 (2012)
[12] Chen, S., Xu, Y., Wan, X. *OL* **13**, 6152 (2011)
[13] Tang, R.-Y., Xie, Y.-X., Xie, Y.-L., Xiang, J.-N., Li, J.-H. *CC* **47**, 12867 (2011)
[14] Kloeckner, U., Weckenmann, N.M., Nachtsheim, B.J. *SL* 97 (2012)
[15] Lamani, M., Prabhu, K.R. *JOC* **76**, 7938 (2011)
[16] Li, X., Xu, X., Zhou, C. *CC* **48**, 12240 (2012)

t-Butyl hydroperoxide - metal salts

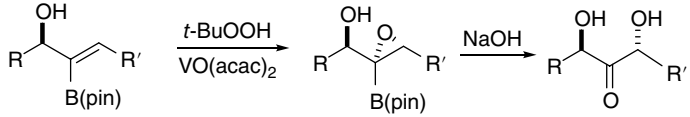
Oxidation. Almost any metal salt is useful to catalyze oxidation of organic compounds by *t*-BuOOH. Propargylic alcohols are oxidized with nano-Cu and a bipyridine ligand.[1] CAN serves as a catalyst for the oxidation of alcohols and aldehydes, primary alcohols to carboxylic acids and secondary alcohols to ketones.[2]

Ethers of the allylic, propargylic and benzylic classes are *t*-butylperoxylated to form special acetals. The iron complex $Fe(acac)_3$ plays the catalytic role in this reaction.[3] A more valuable transformation concerns with oxidation of alkenes to conjugated ketones, and it can be achieved in more than one way --- with copper complex **1** [4] or $PhI(OAc)_2$ [5] to accompany *t*-BuOOH.



(**1**)

Through epoxidation an alkenylboronate moiety of the functionalized allyl alcohols are transformed into α,α′-dihydroxy ketones on treatment of the epoxides with NaOH.[6]

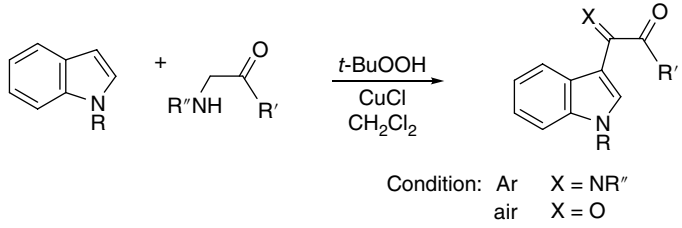


Benzylic oxidation by *t*-BuOOH is catalyzed by dirhodium(II) tetrakis(2-methanesulfonaminopyrrolidinate),[7] or vanadium compounds such as Cp_2VCl_2.[8] Oxidation of diarylmethanes to diaryl ketones is expected to proceed more readily, nano-MnO_2 is one of the catalysts.[9]

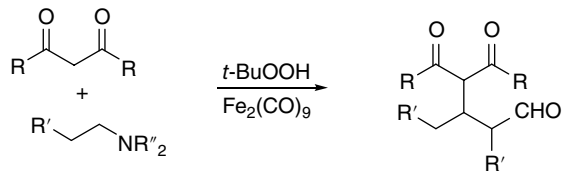
As expected, with a metal catalyst the oxidation of benzylic amines is more efficient. Benzamides are acquired with either $ZnBr_2$ or $FeCl_3$ playing the catalytic role.[10] By catalysis of $Cu(NO_3)_2$ or $Fe(NO_3)_3$ the oxidation of tetrahydroisoquinolines and isochroman in the presence of an electron-rich arene (polyalkoxybenzene, indole, etc.) introduces a substituent at C-1.[11]

Co-oxidation of RCHO and $ArCH_3$, also employing a Cu(II) salt as catalyst, furnishes $RCOOCH_2Ar$.[12] Either a Fe(II) or Cu(II) salt is useful to trap the oxidation intermediate from RCHO to provide amides.[13,14] For access to primary amides, NH_4Cl is the nitrogen source and Cu_2O is the catalyst. The same kind of metal salts [i.e., Cu(II) and Fe(III)] are used to bring about amide synthesis that employs R_2NCl.[15,16]

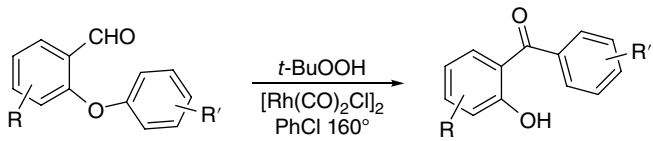
The oxidation of 1-amino-2-alkanones in the presence of an indole leads to substitution of the heterocycle at C-3. It gives products containing an α-iminoketone or α-diketone sidechain.[17]



The Cu(II)-catalyzed oxidation of formamides produces acylating species which can be trapped by β-keto esters to yield enol carbamates, and also by *o*-hydroxyaryl ketones.[18] Interestingly, substitution at C-2 of 1,3-dicarbonyl compounds is observed when tertiary amines are oxidized in their presence.[19]



By catalysis of a Rh(I) complex, the oxidation of *o*-aryloxybenzaldehydes affords diaryl ketones.[20]



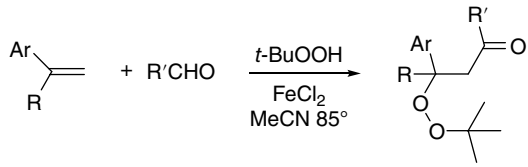
2,2-Disubstituted *N*-arylethanolamines can be prepared in one step from $ArNH_2$, ketones and MeOH, by an oxidative coupling using $TiCl_4$ – Zn for catalyst.[21] Apparently ketimines are formed and they undergo free radical hydroxymethylation.

Functionalization of arenes. *p*-Substituted phenols form 4-*t*-butylperoxy-2,5-cyclohexadienones on treatment with *t*-BuOOH and $(Ph_3P)_3RuCl_2$.[22] Such products undergo decomposition on contact with an acid to furnish 2-substituted 1,4-benzoquinones. The $Ru_3(CO)_{12}$ cluster along with DPPB forms a catalyst to alkylate arenes under oxidative conditions, using cycloalkanes. The alicyclic moiety usually enters at the *p*-position of the substituted arene.[23]

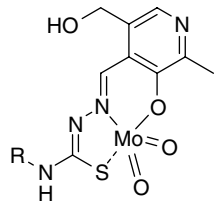
o-Azidoanilines are formed by mixing the amines with Me_3SiN_3, CuBr and *t*-BuOOH in MeCN at room temperature.[24] Acetanilides undergo alkoxycarbonylation with glyoxylate esters, but in this reaction a Pd catalyst is used.[25]

By means of cooxidation (in the presence of CuCl), $ArB(OH)_2$ and CF_3SO_2Na are defunctionalized and combine to form $ArCF_3$.[26]

Addition. It is found that *t*-BuOOH serves as both an oxidant and an addend for the reaction of styrenes and aldehydes, under catalysis of $FeCl_2$.[27] The adducts are precursors of epoxy ketones (formed on inducement by DBU).



The molybdyl complex **2** is active for catalyzing epoxidation of alkenes with *t*-BuOOH in aqueous media.[28]

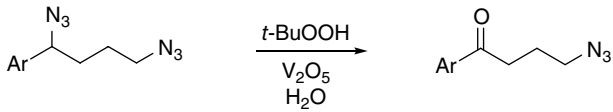


(**2**)

Benzylidenehydrazinoarenes and 1,2-alkanediols form 5-substituted 1,3-diarylpyrazoles in a Fe(III)-catalyzed oxidative condensation.[29]

Oxidation of nitrogen compounds. *t*-Butyl *N*-hydroxycarbamate is oxidized to the unstable nitroso compound (to be captured in situ by conjugated dienes) on oxidation catalyzed by $Rh_2(cap)_4$,[30] or vanadyl isopropoxide.[31]

It is possible to oxidize benzylic azides while retaining a primary azido group.[32] α-Anilino carboxamides are obtained from mixtures of *N*-methylanilines and isonitriles on carrying out the oxidation in the presence of CuCl and Ph_3P in aqueous MeCN.[23]



[1] Han, C., Yu, M., Sun, W., Yao, X. *SL* 2363 (2011)
[2] Gowda, R.R., Chakraborty, D. *ChJC* **29**, 2379 (2011)
[3] Iwata, S., Hata, T., Urabe, H. *ASC* **354**, 3480 (2012)
[4] Li, Y., Lee, T.B., Wang, T., Gamble, A.V., Gordon, A.E.V. *JOC* **77**, 4628 (2012)
[5] Zhao, Y., Yeung, Y.-Y. *OL* **12**, 2128 (2010)
[6] Hussain, M.M., Toribio, J.H., Carroll, P.J., Walsh, P.J. *ACIE* **50**, 6337 (2011)

[7] Wusiman, A., Tusun, X., Lu, C.-D. *EJOC* 3088 (2012)
[8] Xia, J.-B., Cormier, K.W., Chen, C. *CS* **3**, 2240 (2012)
[9] Burange, A.S., Kale, S.R., Jayaram, R.V. *TL* **53**, 2989 (2012)
[10] Wu, X.-F., Bheeter, C.B., Neumann, H., Dixneuf, P.H., Beller, M. *CC* **48**, 12237 (2012)
[11] Ghobrial, M., Schnürch, M., Mihovilovic, M.D. *JOC* **76**, 8781 (2011)
[12] Rout, S.K., Guin, S., Ghara, K.K., Banerjee, A., Patel, B.K. *OL* **14**, 3982 (2012)
[13] Ghosh, S.C., Ngiam, J.S.Y., Seayad, A.M., Tuan, D.T., Chai, C.L.L., Chen, A. *JOC* **77**, 8007 (2012)
[14] Ghosh, S.C., Ngiam, J.S.Y., Chai, C.L.L., Seayad, A.M., Dang, T.T., Chen, A. *ASC* **354**, 1407 (2012)
[15] Cadoni, R., Porcheddu, A., Giacomelli, G., De Luca, L. *OL* **14**, 5014 (2012)
[16] Porcheddu, A., De Luca, L. *ASC* **354**, 2949 (2012)
[17] Wu, J.-C., Song, R.-J., Wang, Z.-Q., Huang, X.-C., Xie, Y.-X., Li, J.-H. *ACIE* **51**, 3453 (2012)
[18] Kumar, G.S., Maheswari, C.U., Kumar, R.A., Kantam, M.L., Reddy, K.R. *ACIE* **50**, 11748 (2011)
[19] Liu, W., Liu, J., Ogawa, D., Nishihara, Y., Guo, X., Li, Z. *OL* **13**, 6272 (2011)
[20] Rao, H., Li, C.-J. *ACIE* **50**, 8936 (2011)
[21] Rossi, B., Pastori, N., Clerici, A., Punta, C. *T* **68**, 10151 (2012)
[22] Murahashi, S.-I., Miyaguchi, N., Noda, S., Naota, T., Fujii, A., Inubushi, Y., Komiya, N. *EJOC* 5355 (2011)
[23] Guo, X., Li, C.-J. *OL* **13**, 4977 (2011)
[24] Tang, C., Jiao, N. *JACS* **134**, 18924 (2012)
[25] Wang, S., Yang, Z., Liu, J., Xie, K., Wang, A., Chen, X., Tan, Z. *CC* **48**, 9924 (2012)
[26] Ye, Y., Künzi, S.A., Sanford, M.S. *OL* **14**, 4979 (2012)
[27] Liu, W., Li, Y., Liu, K., Li, Z. *JACS* **133**, 10756 (2011)
[28] Pisk, J., Agustin, D., Vrdoljak, V., Poli, R. *ASC* **353**, 2910 (2011)
[29] Panda, N., Jena, A.K. *JOC* **77**, 9401 (2012)
[30] Tusun, X., Lu, C.-D. *SL* 1801 (2012)
[31] Hoshino, Y., Suzuki, K., Honda, KD. *SL* 2375 (2012)
[32] Alagiri, K., Prabhu, K.R. *T* **67**, 8544 (2011)
[23] Ye, X., Xie, C., Huang, R., Liu, J. *SL* 409 (2012)

t-Butyl perbenzoate

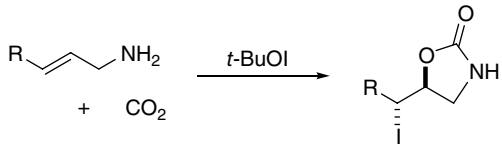
Acylation. Indole is formylated at C-3 while *N*-methylaniline is being oxidized by *t*-BuOOBz to furnish the reagent.[1] On the other hand, azoles are carbamoylated at C-2 by formamides.[2]

[1] Li, L.-T., Huang, J., Li, H.-Y., Wen, L.-J., Wang, P., Wang, B. *CC* **48**, 5187 (2012)
[2] He, T., Li, H., Li, P., Wang, L. *CC* **47**, 8946 (2011)

t-Butyl hypoiodite

Nitrile oxides. Aldoximes are rapidly dehydrogenated by *t*-BuOI.[1]

Addition. Allylic and propargylic amines form 2-oxazolidinones with a 5-iodinated sidechain, on treatment with *t*-BuOI under CO_2.[2]

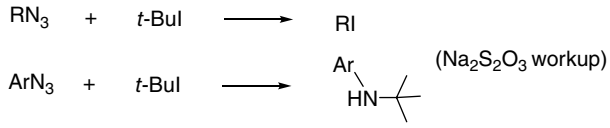


Oxidative coupling. A mixture of two anilines can be induced by *t*-BuOI to couple, affording unsymmetrical azoarenes.[3]

[1] Minakata, S., Okumura, S., Nagamachi, T., Takeda, Y. *OL* **13**, 2966 (2011)
[2] Takeda, Y., Okumura, S., Tone, S., Sasaki, I., Minakata, S. *OL* **14**, 4874 (2012)
[3] Takeda, Y., Okumura, S., Minakata, S. *ACIE* **51**, 7804 (2012)

t-Butyl iodide

Reaction with azides. Different fates are encountered by aliphatic and aromatic azides on reaction with *t*-BuI, each being transformed into alkyl iodides and *N*-*t*-butylanilines, respectively.[1]



[1] Maury, J., Feray, L., Bertrand, M.P., Kapat, A., Renaud, P. *T* **68**, 9606 (2012)

t-Butyl nitrite

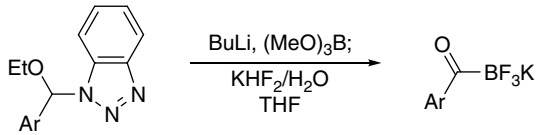
Oxidation. Primary and secondary benzyl alcohols are oxidized to the carbonyl compounds by *t*-BuONO.[1]

Nitroarenes. The dihydroxyboryl group of $ArB(OH)_2$ is exchanged for a nitro group on treatment with *t*-BuONO in air.[2]

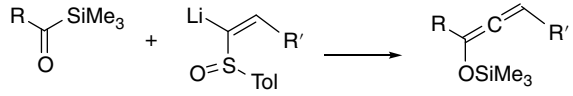
[1] Hamasaki, A., Kuwada, H., Tokunaga, M. *TL* **53**, 811 (2012)
[2] Wu, X.-F., Schranck, J., Neumann, H., Beller, M. *CC* **47**, 12462 (2011)

Butyllithium

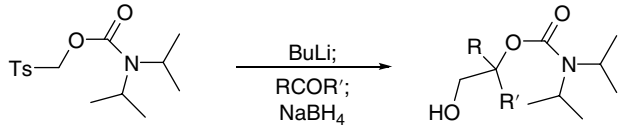
Lithiation. Borane complexes of imidazol-2-ylidenes are lithiated by BuLi at an sp^2-carbon.[1] In a synthesis of acyltrifluoroborates starting from 1-alkoxymethylbenzotriazoles, lithiation is repeated after alkylation and then a reaction with $(MeO)_3B$. The final step is hydrolytic fluorination with KHF_2.[2]



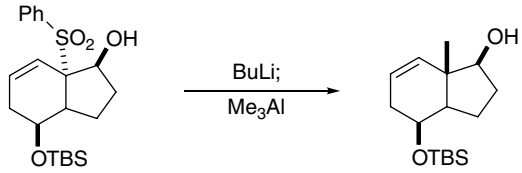
α-Lithio sulfoxides react with acylsilanes to form enol silyl ethers. More interesting is a route developed for the allenyloxy analogs.[3]



Lithiation of *N,N*-diisopropylcarbamoyloxymethyl *p*-tolyl sulfone is involved in a synthesis of 1,2-alkanediol derivatives.[4] Addition to carbonyl compounds is followed by carbamoyl group transfer and release of a sulfinate ion to generate the α-carbamoyloxy aldehydes.

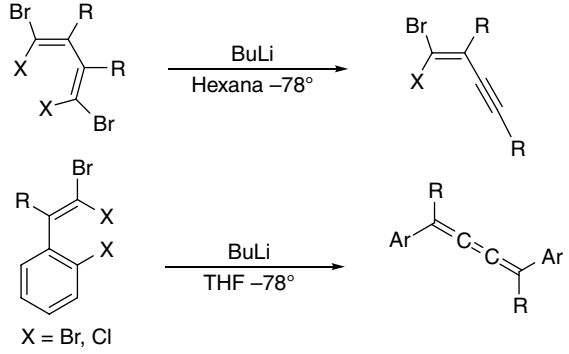


X/Li group exchange. *ipso*-Alkylation from a hydroindan bearing an angular sulfonyl group proceeds via the lithio species. Stereocontrol can be gained if the subangular position is hydroxylated. Thus, quenching the O,C-dilithiated compound with Me_3Al delivers a product with the C-methyl group *cis* to the hydroxyl.[5]



Benzyllithium is generated from *o*-(benzyldimethylsilyl)benzyl alcohol on treatment with BuLi.[6] A new approach to amines from alkylpinacolatoboron compounds consists of lithiation and reaction with $MeONH_2$. The products have the same configuration.[7]

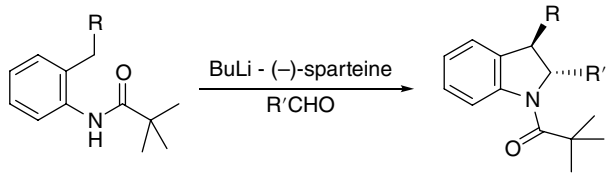
1,1-Dihaloalkenes are prone to rearrangement upon X/Li exchange.[8]



[1] Solovyev, A., Lacôte, E., Curran, D.P. *OL* **13**, 6042 (2011)
[2] Dumas, A.M., Bode, J.W. *OL* **14**, 2138 (2012)
[3] Honda, M., Nakajima, T., Okada, M., Yamaguchi, K., Suda, M., Kunimoto, K.-K., Segi, M. *TL* **52**, 3740 (2011)
[4] Ma, L., Zhao, D., Chen, L., Wang, X., Chen, Y.-L., Shen, J. *T* **68**, 8704 (2012)
[5] Sikervar, V., Fuchs, P.L. *OL* **14**, 2922 (2012)
[6] Hudrlik, P.F., Hudrlik, A.M., Jeilani, Y.A. *T* **67**, 10089 (2011)
[7] Mlynarski, S.N., Karns, A.S., Morken, J.P. *JACS* **134**, 16449 (2012)
[8] Meng, T., Zhang, H.-J., Xi, Z. *TL* **53**, 4555 (2012)

Butyllithium - (–)-sparteine

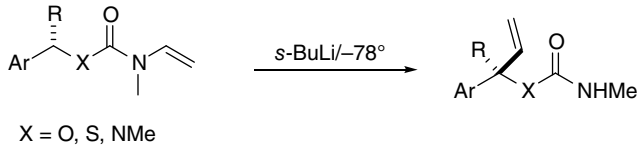
Indoline synthesis. *o*-Alkyl-*N*-pivaloylanilines upon lithiation react with aldehydes to form optically active indolines.[1]



[1] Kang, K.H., Do, J., Park, Y.S. *JOC* **77**, 808 (2012)

s-Butyllithium

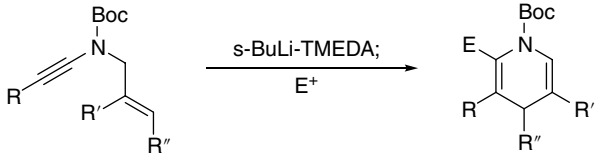
Deprotonation. Ureas, thioureas and carbamates in which the heteroatom is bonded to a benzyl group are deprotonated by *s*-BuLi at −78°, and a vinyl group on the other nitrogen atom can be moved. Accordingly on the basis of this action a stereoselective construction of allylarenes functionalized at the benzylic position is developed.[1]



N-Substituted tetrahydroisoquinolines are deprotonated by *s*-BuLi at C-4 instead of C-1.[2] 2-Aryloxetanes form 2-lithio derivatives,[3] but since the benzylic carbon of 2-aryl-2-alkyloxetanes is quaternary lithiation necessarily is diverted toward an open *o*-position.[4]

N-Boc indoline undergoes lithiation at C-7 by *s*-BuLi in the presence of TMEDA, but changes location to C-2 if the *N*-protecting group is *t*-butyliminomethyl (using *t*-BuLi).[5] A tertiary carbamoyl or sulfamoyl group at C-3 of indole serves to direct lithiation C-4 (not C-2).[6]

Cyclization of *N*-Boc-*N*-alkynyl-*N*-allylamines is initiated by deprotonation at the α-CH_2 group and an electrophile can be introduced at the emerging double bond.[7]



[1] Lefranc, J., Fournier, A.M., Mingat, G., Horbert, S., Marcelli, T., Clayden, J. *JACS* **134**, 7286 (2012)
[2] Singh, K.N., Singh, P., Singh, P., Deol, Y.S. *OL* **14**, 2202 (2012)
[3] Coppi, D.I., Salomone, A., Perna, F.M., Capriati, V. *CC* **47**, 9918 (2011)
[4] Coppi, D.I., Salomone, A., Perna, F.M., Capriati, V. *ACIE* **51**, 7532 (2012)
[5] Cheng, L., Liu, L., Li, C., Jia, H., Wang, D., Chen, Y.-J. *TL* **53**, 4004 (2012)
[6] Schneider, C., David, E., Toutov, A.A., Snieckus, V. *ACIE* **51**, 2722 (2012)
[7] Gati, W., Rammah, M.M., Rammah, M.B., Couty, F., Evano, G. *JACS* **134**, 9078 (2012)

N-(4-*t*-Butylphenyl)-*N*,*N*-ditriflylaniline

Enoltriflylation.[1] This triflimide can be sublimed and therefore is easier to keep anhydrous. The byproducts from which after donating the Tf group are much more readily separated from the enol triflates.

[1] Benson, S., Collin, M.-P., Arlt, A., Gabor, B., Goddard, R., Fürstner, A. *ACIE* **50**, 8739 (2011)

C

Calcium triflimide

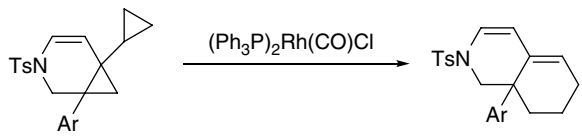
Cyclization. Unsaturated alcohols are converted by $Ca(NTf_2)_2$ (additive: Bu_4NPF_6) into cyclic ethers.[1]

Substitution. Replacement of the hydroxyl group of secondary, tertiary and activated alcohols is observed on reaction with silyl compounds (allylsilanes, alkenylsilanes, arylsilanes,…) at room temperature, employing the same combination of catalysts as above.[2]

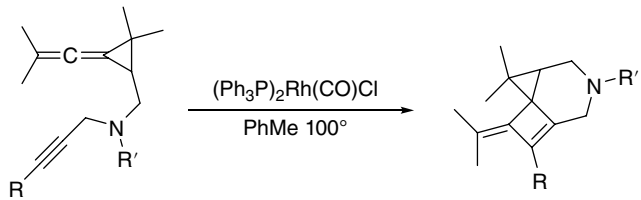
[1] Diba, A.K., Begouin, J.-M., Niggemann, M. *TL* **53**, 6629 (2012)
[2] Meyer, V.J., Niggemann, M. *EJOC* 3671 (2011)

Carbonyl(chloro)bis(triphenylphosphine)rhodium(I)

Rearrangement. Certain 1-cyclopropylbicyclo[4.1.0]hept-2-enes are found to break both 3-membered rings and recombine them into a cyclohexene unit on treatment with $(Ph_3P)_2Rh(CO)Cl$ and $AgBF_4$.[1]



Cycloaddition. A highly strained tricyclic system is elaborated by an intramolecular [2+2]cycloaddition that combines an alkyne and a double bond of an allene unit.[2]



[1] Son, S., Kim, S.Y., Chung, Y.K. *CO* **1**, 169 (2012)
[2] Lu, B.-L., Shi, M. *ACIE* **50**, 12027 (2011)

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Carbonyl(chloro)hydridotris(triphenylarsine)ruthenium(II)

Reduction. With pyridazine the complex constitutes a new catalyst for reduction of ketones, with the hydride source coming from isopropanol.[1]

[1] Raja, N., Ramesh, R. *TL* **53**, 4770 (2012)

Carbonyl(chloro)hydridotris(triphenylphosphine)ruthenium(II)

Substitution. The OH to NH_2 functional group exchange is realized by the exertion of the Ru catalyst under an ammonia atmosphere, primary and secondary alcohols included.[1] Silylation of styrenes at the β-carbon is catalyzed by the Ru complex while the silyl group is provided by vinyltrimethylsilane.[2]

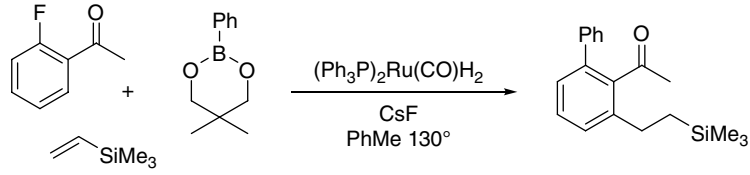
Methyl ketones are alkylated by primary alcohols via a series of redox reactions.[3]

[1] Imm, S., Bähn, S., Zhang, M., Neubert, L., Neumann, D., Klasovsky, F., Pfeffer, J., Haas, T., Beller, M. *ACIE* **50**, 7599 (2011)
[2] Pawluc, P., Szudkowska, J., Hreczycho, G., Marciniec, B. *JOC* **76**, 6438 (2011)
[3] Kuwahara, T., Fukuyama, T., Ryu, I. *OL* **14**, 4703 (2012)

Carbonyldihydridotris(triphenylphosphine)ruthenium(II)

Cycloaddition. An alternative catalyst (other than Cu and salts) for the "click reaction" to prepare 1,2,3-triazoles from organoazides and alkynes is the complex $(Ph_3P)_3Ru(CO)H_2$.[1]

Coupling. Double coupling of *o*-fluoroacetophenone demonstrates the ordered substitution and directed addition by arylboronates and vinylsilanes, respectively, yet achieved with the same catalyst.[2]

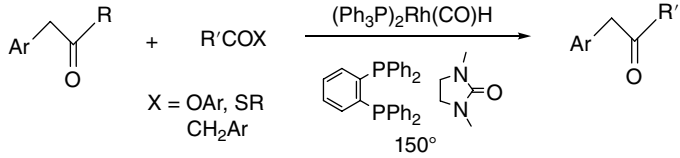


By virtue of carbonyl direction the reaction of anthraquinone with 1-alkenes, four alkyl groups are attached to C-1, C-4, C-5, and C-8.[3]

[1] Liu, P.N., Siyang, H.X., Zhang, L., Tse, S.K.S., Jia, G. *JOC* **77**, 5844 (2012)
[2] Kawamoto, K., Kochi, T., Sato, M., Mizushima, E., Kakiuchi, F. *TL* **52**, 5888 (2011)
[3] Matsumura, D., Kitazawa, K., Terai, S., Kochi, T., Ie, Y., Nitani, M., Aso, Y., Kakiuchi, F. *OL* **14**, 3882 (2012)

Carbonylhydridotris(triphenylphosphine)rhodium(I)

Group exchange. The acyl group of a benzyl ketone can be exchanged by reaction with aryl carboxylates or thioesters.[1] Aromatic thioesters are also converted into ArCOOAr′ in a reaction with Ar′OMe.[2]



[1] Arisawa, M., Kuwajima, M., Toriyama, F., Li, G., Yamaguchi, M. *OL* **14**, 3804 (2012)
[2] Arisawa, M., Nihei, Y., Suzuki, T., Yamaguchi, M. *OL* **14**, 855 (2012)

Cellulose sulfuric acid

Acetalization. The biodegradable acid functions as a catalyst for acetalization of carbonyl compounds, e.g., with pentaerythritol.[1]

[1] Shaterian, H.R., Rigi, F. *ChJC* **30**, 695 (2012)

Cerium

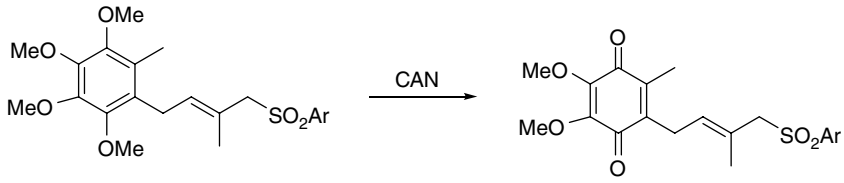
Reformatsky reaction. Cerium is another metal to convert α–bromoalkanoic esters into nucleophilic enolates that can attack carbonyl compounds, and the procedure has been applied to synthesis of γ-substituted paraconic acid derivatives.[1]

[1] Rodrigues, S.M.M., Nardini, V., Constantino, M.G., da Silva, G.V.J. *TL* **53**, 6136 (2012)

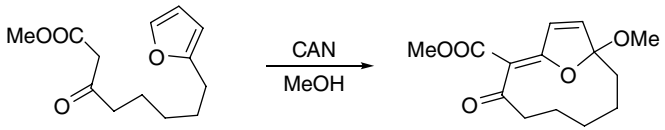
Cerium(IV) ammonium nitrate, (CAN)

Functionalization. Benzylic nitroxylation by CAN is catalyzed with *N*-hydroxyphthalimide.[1] Dehydrogenation of 3-acylpropanals is also realized.[2]

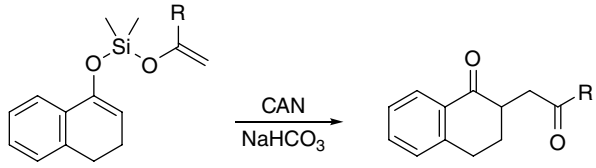
Oxidation. The oxidation of methoxyarenes to quinones by CAN is well established, its application to the preparation of a ubiquinone (coenzyme Q) synthon is now presented.[3]



By intramolecular oxidative coupling of furans substituted with a long sidechain terminated by a β-keto ester unit succeeds in the elaboration of macroheterocycles.[4]



1,4-Diketones are obtained from CAN oxidation of bis(alkenoxy)silanes.[5]



[1] Kamijo, S., Amaoka, Y., Inoue, M. *TL* **52**, 4654 (2011)
[2] Zhu, J., Yu, S., Lu, W., Deng, J., Li, J., Wang, W. *TL* **53**, 1207 (2012)
[3] Oh, E.-T., Kim, H.J., Oh, J.T., Su, L., Yun, I., Nam, K., Min, J.-H., Kim, J.W., Koo, S. *EJOC* 4954 (2012)
[4] Nicolaou, K.C., Hale, C.R.H., Ebner, C., Nilewski, C., Ahles, C.F., Rhoades, D. *ACIE* **51**, 4726 (2012)
[5] Clift, M.D., Taylor, C.T., Thomson, R.J. *OL* **9**, 4667 (2007)

Cerium(IV) oxide

Hydration. A use of CeO_2 is as a recoverable catalyst for the hydration of nitriles (particularly heteroaryl cyanides) to yield amides.[1]

[1] Tamura, M., Wakasugi, H., Shimizu, K., Satsuma, A. *CEJ* **17**, 11428 (2011)

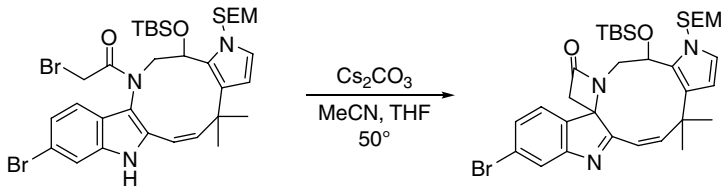
Cerium(III) triflate

Substitution. Electron-rich arenes including indole and furan undergo propargylation (with the alcohols) in the presence of $Ce(OTf)_3$.[1]

[1] Silveira, C.C., Mendes, S.R., Martins, G.M. *TL* **53**, 1567 (2012)

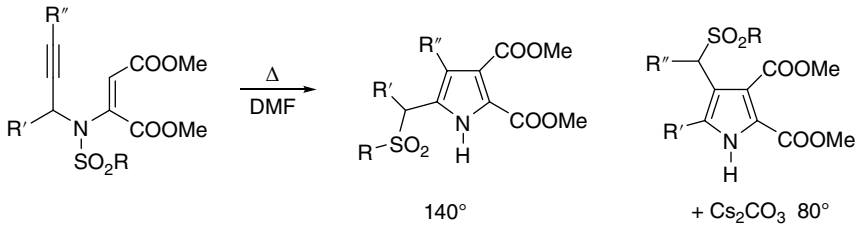
Cesium carbonate

Alkylation. Closure of a β-lactam ring by intramolecular alkylation is a critical operation in a construction of the skeleton of chartelline-C, the achievement in high yield involves Cs_2CO_3 as the base.[1]



Thiolation. Serving both as dehydrobromination and deprotonation agents, Cs_2CO_3 plays valuable roles in the reaction of β,β-dibromostyrenes with ArSH.[2]

Cyclization. Sulfonamides with both propargyl and alkenyl substituents on the nitrogen atom undergo thermal cyclization to afford pyrroles. Different products are obtained when the substrates are heated with Cs_2CO_3 at a lower temperature.[3]



Indoles are produced from intramolecular hydroamination of 2-alkynylanilides on heating with Cs_2CO_3 in toluene at 150°. Iron(III) chloride is a beneficial additive. Carboxamides and sulfonamides add to ethynylarenes to give terminal enamides.[4]

[1] Iwasaki, K., Kanno, R., Morimoto, T., Yamashita, T., Yokoshima, S., Fukuyama, T. *ACIE* **51**, 9160 (2012)
[2] Ni, Z., Wang, S., Mao, H., Pan, Y. *TL* **53**, 3907 (2012)
[3] Xin, X., Wang, D., Li, X., Wan, B. *ACIE* **51**, 1693 (2012)
[4] Herrero, M.T., de Sarralde, J.D., SanMartin, R., Bravo, L., Dominguez, E. *ASC* **354**, 3054 (2012)

Cesium fluoride

Benzyne generation. The currently preferred method for benzyne generation is from 2-triorganosilylphenyl triflate by treatment with either CsF or Bu_4NF. A great number of addends have been employed to intercept benzyne, e.g., nitrones to form benzisoxazolines,[1] tosylhydrazones of aldehydes to give benzopyrazoles.[2] In the case of ketone tosylhydrazones, *N*-phenylation occurs.[3] *N*-Tritylanilines undergo *o*-phenylation.[4]

Fulvenes are said to trap benzyne by a Diels-Alder reaction.[5]

Coupling. Tosylhydrazones and alkenylboronic acids condense to give alkenes under the influence of CsF.[6] Nature of the boronic acid determines the position of the double bond in the products (styrylboronic acids prefer deconjugated products).

A tributylstannyl group germinal to an NBoc or OAc group is replaced by COOH by the CsF-mediated carboxylation.[7]

Aryl fluorides. A method for the conversion of ArOH to ArF uses CsF and is catalyzed by 2,2-difluoro-1,3-bis(2,6-diisopropylphenyl)imidazoline.[8]

Desilylation. CsF can be used to deprotect amides that are *N*-substituted by a 4-(*t*-butyldimethylsiloxy)-2-methoxybenzyl group.[9]

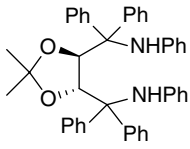
[1] Lu, C., Dubrovskiy, A.V., Larock, R.C. *JOC* **77**, 2279 (2012)
[2] Li, P., Zhao, J., Wu, C., Larock, R.C., Shi, F. *OL* **13**, 3340 (2011)
[3] McAusland, D., Seo, S., Pintori, D.G., Finlayson, J., Greaney, M.F. *OL* **13**, 3667 (2011)

[4] Pirali, T., Zhang, F., Miller, A.H., Head, J.L., McAusland, D., Greaney, M.F. *ACIE* **51**, 1006 (2012)
[5] Bhojgude, S.S., Kaicharla, T., Bhunia, A., Biju, A.T. *OL* **14**, 4098 (2012)
[6] Perez-Aguilar, M.C., Valdes, C. *ACIE* **51**, 5953 (2012)
[7] Mita, T., Sugawara, M., Hasegawa, H., Sato, Y. *JOC* **77**, 2159 (2012)
[8] Tang, P., Wang, W., Ritter, T. *JACS* **133**, 11482 (2011)
[9] Muranaka, K., Ichikawa, S., Matsuda, A. *JOC* **76**, 9278 (2011)

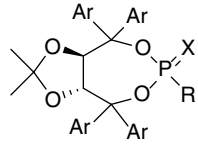
Chiral auxiliaries and catalysts

General aspects. Chiral catalysts contribute to weaving a vast portion of the synthetic tapestry, as witnessed by the amount of work described in this section and somewhere else (BINOL, BINAP, proline derivatives, etc.). A comprehensive review on the development of sustainable asymmetric organocatalysts deals with solvent-free conditions, reactions in water, ionic liquids and organic carbonates, effects of microwave irradiation, ultrasound, and high pressure, solid supported versions, and one-pot reactions.[1] Other important summaries include multicatalyst systems,[2] reactions using alkaline earth metal complexes with diverse ligands,[3] nonlinear effects exhibited in catalysis by amino acids with proposal of cooperative catalytic pathways,[4] regioselectivity controlled by chiral catalysts,[5] and asymmetric dearomatization.[6]

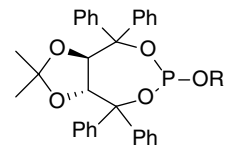
New tartaric acid-derived chiral ligands/catalysts have been synthesized,[7,8] and the variegated applications are expected.



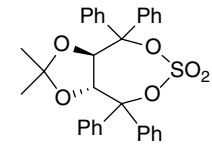
(**1**)



(**2A**) X = :
(**2B**) Ar = Ph, R = NHTf
X = O
(**2C**) Ar = 3,5-$R_2C_6H_3$,
R = NMe_2, X = :

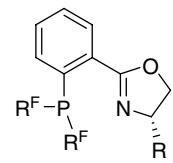


(**3A**) R = Me
(**3B**) R = (2-Ph_2P)(6-Ph)C_6H_3



(**4**)

Also available is a series of air- and moisture-stable, easy to prepare ligands **5**, which are strong π-acceptors and tunable with respect to steric hindrance.[9]



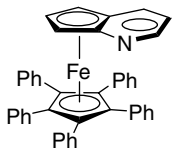
(**5**)

Many catalysts/ligands are available in both enantiomeric forms therefore synthetic targets are accessible in the desired absolute configuration. For the sake of simplified representation in the following summary an indicated ligand might actually be the optical antipode to the original report, but the validity of the chemistry is solid.

[1] Hernandez, J.G., Juaristi, E. *CC* **48**, 5396 (2012)
[2] Piovesana, S., Schietroma, D.M.S., Bella, M. *ACIE* **50**, 6216 (2011)
[3] Kobayashi, S., Yamashita, Y. *ACR* **44**, 58 (2011)
[4] Rios, R., Schyman, P., Sunden, H., Zhao, G.-L., Ullah, F., Chen, L.-J., Laaksonen, A., Cordova, A. *CEJ* **16**, 13935 (2010)
[5] Kumar, R.R., Kagan, H.B. *ASC* **352**, 231(2010)
[6] Zhuo, C.-X., Zhang, W., You, S.-L. *ACIE* **51**, 12665 (2012)
[7] Pichota, A., Gramlich, V., Bichsel, H.-U., Styner, T., Knöpfel, T., Wünsch, R., Hintermann, T., Schweizer, W.B., Beck, A.K., Seebach, D. *HCA* **95**, 1273 (2012)
[8] Seebach, D., Beck, A.K., Bichsel, H.-U., Pichota, A., Sparr, C., Wünsch, R., Schweizer, W.B. *HCA* **95**, 1303 (2012)
[9] Hu, Z., Li, Y., Liu, K., Shen, Q. *JOC* **77**, 7957 (2012)

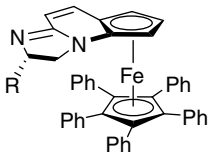
Kinetic resolution and desymmetrizaion. Review has been written for dynamic kinetic resolution by enzymatic and nonenzymatic methods,[1] as well as one devoted to only employing chemicals.[2]

For dynamic kinetic resolution of secondary alcohols by acetylation, a Ru catalyst supported by **6** has been demonstrated.[3] Another ferrocene ligand **7A** is used in acylation of aryl 2-alkenyl carbinols[4] and hindered secondary alcohols.[5]

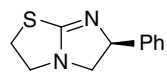


(**6**)

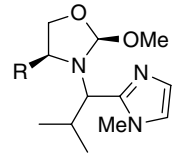
Silylation is another reaction amenable to kinetic resolution of secondary alcohols, and **8** serves such a purpose.[6] *meso*-1,2-Cycloalkanols are monosilylated by assistance of **9A**[7] and **10.**[8]



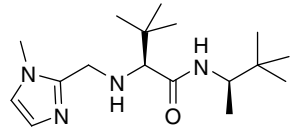
(**7A**) R = Ph
(**7B**) R = C(OH)Ph$_2$



(**8**)

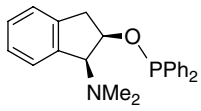


(**9A**) R = *i*-Pr
(**9B**) R = *c*-C$_5$H$_9$

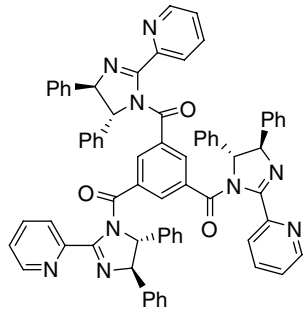


(**10**)

Monoaroylation of *meso*-1,2-diols in the presence of **11**[9] and **12** [+ $Cu(BF_4)_2$][10] has also been reported. A review of desymmetrization reactions of *meso*-diols using organocatalysts is available.[11] Enantioselective acylation of *meso*-1,3-diols is achieved with a chiral sulfonamide **13** derived from histidine.[12]

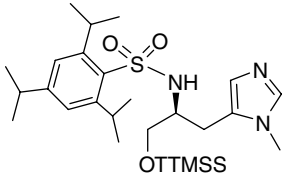


(**11**)

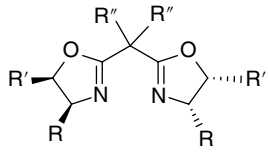


(**12**)

Monotosylation of 2-acylamino-1,2-alkanediols in the presence of **14A** produces oxazoline-4-methanols.[13]

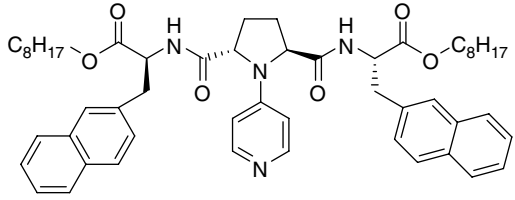


(**13**)



(**14A**) R = Ph, R′ = H, R″ = Me
(**14B**) R = Bn, R′ = H, R″ = Me
(**14C**) R = *t*-Bu, R′ = H, R″ = Me
(**14D**) R = Ph, R′ = H, R″ = 4-*t*-$BuC_6H_4CH_2$
(**14E**) R = R′ = α-Np, R″ = Me

Selective acylation of 2-alkylidene-1,3-propanediols is dependent of different substituents on the two branches, while employing C_2- symmetric **15** to catalyze the reaction.[14]

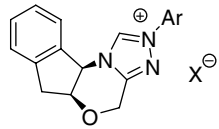


(**15**)

On examining the benzolog of **8**, it was found that the (*S*)-form (enantiomeric to the configuration shown in **8**) is the privileged catalyst for high rates, and this phenomenon is useful for determination of the absolute configuration of a chiral alcohol.[15] When a diastereomer of **15** (enantiomeric at α-C of the ester groups) catalyzes acetylation and

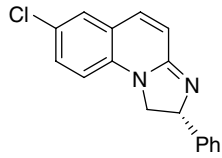
it commands selective reaction on a secondary hydroxy group in the presence of a primary alcohol that constitutes a *vic*-amino alcohol unit.[16] When 1,2-alkanediols are allowed to undergo monosilylation (catalyst: **9B**) the primary silyl ethers are produced in only moderate ee (chiral at the carbonyl center) but high enantioselectivity for forming the secondaryl alkyl silyl ethers is high.[17]

Acylating agents are generated in situ by oxidation of aldehydes to perform kinetic resolution of alcohols and desymmetrization of *meso*-diols, the system consists of a carbene precursor **16A** and a flavin and it operates under oxygen.[18] Utility of a modified tetrapeptide catalyst for asymmetric *O*-acylation is based on its tendency to assume the β-hairpin conformation.[19]



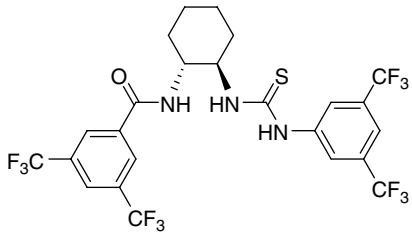
(**16A**) Ar = C_6F_5, X = BF_4
(**16B**) Ar = Mes, X = Cl
(**16C**) Ar = 2,6-$Cl_2C_6H_3$, X = BF_4
(**16D**)Ar = Ph, X = Cl

α-Substituted alkanoic acids can be resolved kinetically via alcoholysis of their anhydrides in the presence of the benzolog of *ent*-**8**.[20] Relatively new developments are concerned with *N*-acylation of lactams and thiolactams (including β-lactams) catalyzed by **17** or enantiomer,[21] and also the utility of the benzolog of **8** for selective methanolysis of *N*-acyl-β–lactams.[22]



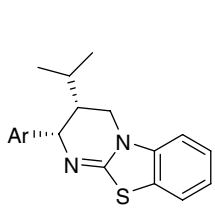
(**17**)

anti-1,2-Diarylethane diamines are resolved by benzoylation (catalyst: **18**).[23]

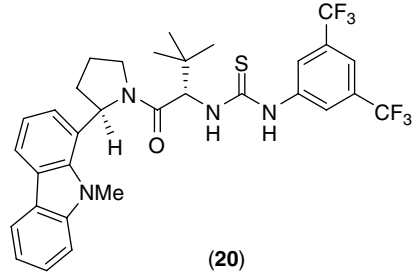


(**18**)

The cyclic isothiourea **19** and thiourea **20** have found service in acylation of silyl ketene acetals.[24,25]

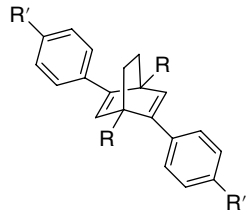


(**19**)



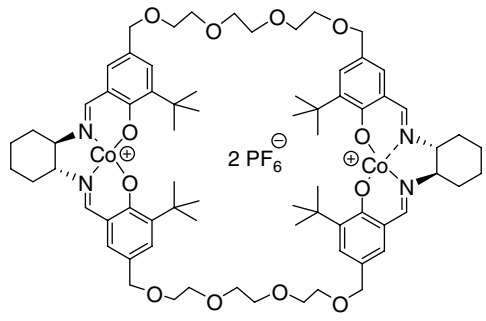
(**20**)

The Rh(I)-catalyzed substitution of allylic trichloroacetimidates by an aniline can be exploited as a method for kinetic resolution.[26] The chiral ligand to bind to the metal ion is **21A**.

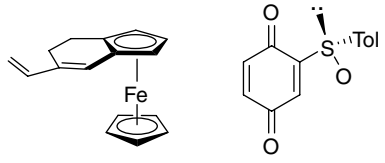


(**21A**) R = H, R′ = F
(**21B**) R = H, R′ = CF_3
(**21C**) R = Me, R′ = H

Hydrolytic opening of *meso*-epoxides to *vic*-diols employing **22** has been executed.[27] The planar diene **23** is resolvable by a chiral sulfinyl quinone **24**.[28]



(**22**)

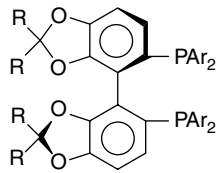


(**23**)

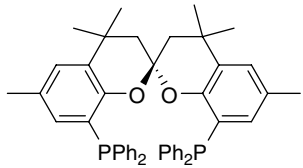
(**24**)

[1] Ahmed, M., Kelly, T., Ghanem, A. *T* **68**, 6781 (2012)
[2] Pellissier, H. *ASC* **353**, 1613 (2011)
[3] Lee, S.Y., Murphy, J.M., Ukai, A., Fu, G.C. *JACS* **134**, 15149 (2012)
[4] Hu, B., Meng, M., Jiang, S., Deng, W. *ChJC* **30**, 1289 (2012)
[5] Hu, B., Meng, M., Fossey, J.S., Mo, W., Hu, X., Deng, W.-P. *CC* **47**, 10632 (2011)
[6] Sheppard, C.I., Taylor, J.L., Wiskur, S.L. *OL* **13**, 3794 (2011)
[7] Sun, X., Worthy, A.D., Tan, K.L. *ACIE* **50**, 8167 (2011)
[8] Rodrigo, J.M., Zhao, Y., Hoveyda, A.H., Snapper, M.L. *OL* **13**, 3778 (2011)
[9] Aida, H., Mori, K., Yamaguchi, Y., Mizuta, S., Moriyama, T., Yamamoto, I., Fujimoto, T. *OL* **14**, 812 (2012)
[10] Arai, T., Sakagami, K. *EJOC* 1097 (2012)
[11] Diaz-de-Villegas, M.D., Galvez, J.A., Badorrey, R., Lopez-Ram-de-Viu, M.P. *CEJ* **18**, 13920 (2012)
[12] Sakakura, A., Umemura, S., Ishihara, K. *ASC* **353**, 1938 (2011)
[13] Tsuda, Y., Kuriyama, M., Onomura, O. *CEJ* **18**, 2481 (2012)
[14] Yoshida, K., Mishiro, K., Ueda, Y., Shigeta, T., Furuta, T., Kawabata, Y. *ASC* **354**, 3291 (2012)
[15] Wagner, A.J., David, J.G., Rychnovsky, S.D. *OL* **13**, 4470 (2011)
[16] Yoshida, K., Shigeta, T., Furuta, T., Kawabata, T. *CC* **48**, 6981 (2012)
[17] Worthy, A.D., Sun, X., Tan, K.L. *JACS* **134**, 7321 (2012)
[18] Iwahana, S., Iida, H., Yashima, E. *CEJ* **17**, 8009 (2011)
[19] Chen, P., Qu, J. *JOC* **76**, 2994 (2011)
[20] Yang, X., Birman, V.B. *CEJ* **17**, 11296 (2011)
[21] Yang, X., Bumbu, V.D., Liu, P., Li, X., Jiang, H., Uffman, E.W., Guo, L., Zhang, W., Jiang, X., Houk, K.N., Birman, V.B. *JACS* **134**, 17605 (2012)
[22] Bumbu, V.D., Birman, V.B. *JACS* **133**, 13902 (2011)
[23] Min, C., Mittal, N., De, C.K., Seidel, D. *CC* **48**, 10853 (2012)
[24] Woods, P.A., Morrill, L.C., Bragg, R.A., Smith, A.D. *CEJ* **17**, 11060 (2011)
[25] Birrell, J.A., Desrosiers, J.-N., Jacobsen, E.N. *JACS* **133**, 13872 (2011)
[26] Arnold, J.S., Nguyen, H.M. *JACS* **134**, 8380 (2012)
[27] Sadhukhan, A., Khan, N.H., Roy, T., Kireshy, R.I., Abdi, S.H.R., Bajaj, H.C. *CEJ* **18**, 5256 (2012)
[28] Latorre, A., Urbano, A., Carreno, M.C. *CC* **47**, 8103 (2011)

Substitution. Among C-X bond-forming processes, asymmetric fluorination has attracted considerable efforts. Fluorination of β-keto acid derivatives on reaction with Selectfluor is catalyzed by Ti(IV) complexes of TADDOLate,[1] whereas $(PhSO_2)_2NF$ is the electrophilic species in reaction with α-ketoacid *t*-butyl esters, the Pd catalyst is accompanied by ligand **25A**.[2] Another Pd-catalyzed process is benzylic fluorination of α-arylcyanoacetic esters to established a chiral quaternary center (ligand: **26A**).[3]

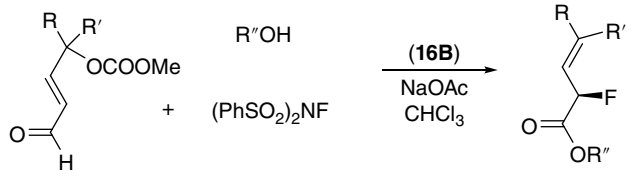


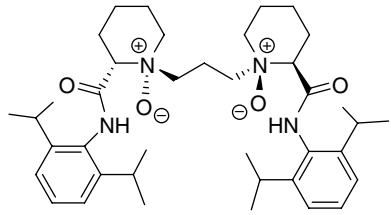
(**25A**) R = H, Ar = 3,5-$Me_2C_6H_3$
(**25B**) R = H, Ar = 3,5-*t*-Bu_2-4-$MeOC_6H_3$
(**25C**) R = F, Ar = Ph
(**25D**) R = Me, Ar = Ph



(**26A**)

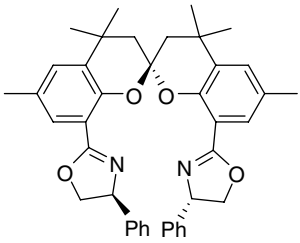
The carbene-mediated elimination of conjugated aldehydes containing a γ-leaving group is well suited to generate enols. With **16B** to attach itself close to the nucleophilic site fluorination is enantioselective.[4] 3-Substituted oxindoles undergo fluorination with yet another asymmetric system, that is $Sc(OTf)_3$ and **27**.[5] Application of the same complex to phenylsulfenylation is successful.[6]



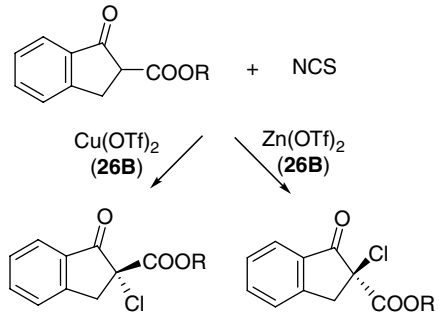


(**27**)

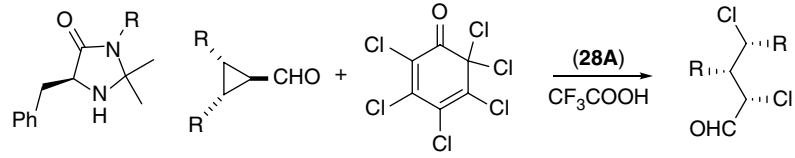
A single ligand **26B** can determine chlorination of indanone-2-carboxylic esters in the absolute sense of chirality, and it is most felicitous to be able to switch production of one enantiomer or the other by changing the metal salt (Cu to Zn).[7]



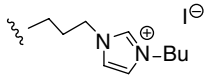
(**26B**)

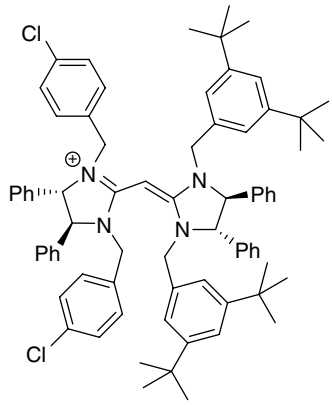


Ring opening precedes chlorination of cyclopropanecarbaldehydes, and **28** ensures the devolvement of chiral products.[8]



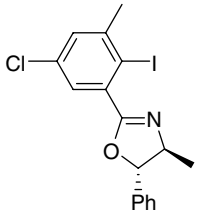
(**28A**) R = Me

(**28B**) R = 



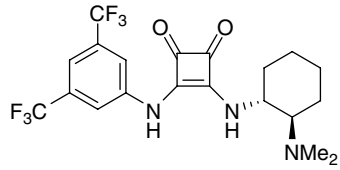
(**29**)

Oxindoles incorporate oxygen to form 3-hydroxyoxindoles enantioselectively, one induction source of chirality is **29**.[9] To achieve α-tosyloxylation of ketones, the method employing MCPBA and TsOH is rendered asymmetric by **30**, as the electrophile is a chiral tosyloxyiodine(III) compound.[10]



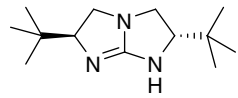
(**30**)

With catalysis of PhBox (cf. **14**) ligated $Cu(OTf)_2$, cyclic β-keto thioesters are aminoxygenated by nascent nitroso compounds.[11] Phenylsulfenylation of *N*-Boc oxindole finds in **31** an adequate catalyst.[12]

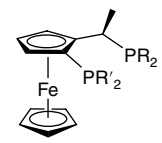


(**31**)

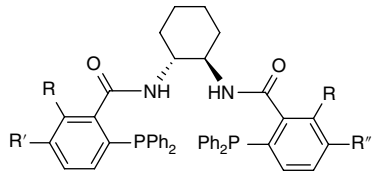
(*E*)–β,γ-Unsaturated thioesters combine with *t*-butyl azodicarboxylate to form γ-aminated α,β-unsaturated isomers. The bicyclic guanidine directs creation of an (*S*)-configuration in the adducts [double bond is (*E*)]. The enantiomeric series is reached by using (*Z*)–β,γ-Unsaturated thioesters.[13]



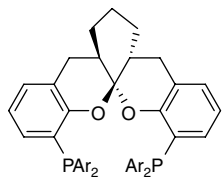
Many reactions involving heteronucleophiles and carbon electrophiles are subject to asymmetric induction. Opening of 1,4-oxa-1,4-dihydronaphthalene by a Rh-catalyzed reaction with a hydrogen fluoride complex follows an enantioselective S_N2' pathway in the presence of **32A**.[14] Silver fluoride is the nucleophiles for transforming 1-bromo- or 1-chloro-2-alkenes into 3-fluoro-1-alkenes, here a Pd complex of **33B** is the chosen ligand.[15]



(**32A**) R = *t*-Bu, R′ = Ph
(**32B**) R = Cy, R′ = Ph
(**32C**) R = R′ = Cy
(**32D**) R = Ph, R′ = Cy

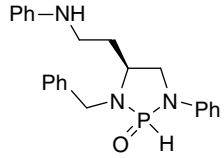


(**33A**) R = R′ = H
(**33B**) R+R′ = $(CH{=}CH)_2$

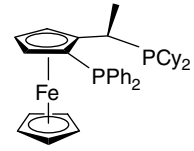


(**34**)

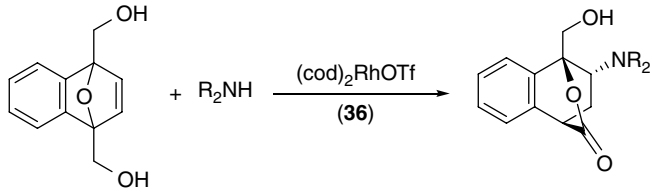
Allylic amination can be made to yield chiral adducts, and again many metal-ligand combinations are effective: S_N2 displacement to convert some Baylis-Hillman acetates into benzylic amines is accomplished with a Pd(II) complex and **34**,[16] pairing Pd with **35** is another option.[17] The S_N2' reaction on an oxabicyclic substrate is followed by allylic alcohol isomerization, hemiacetalization and oxidation because those reactions are within the capability of a Rh(I) salt. Furthermore, the presence of Josiphos (**36**) enables preparation of the chiral product.[18]



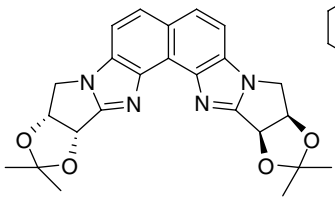
(**35**)



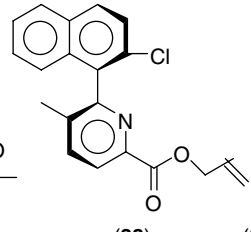
(**36**)



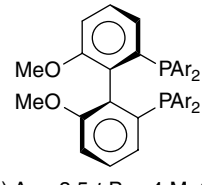
The CpRu(I) salt, further associated with a naphthalenebiimidazole ligand **37** or **38** has proven value in conducting S_N2'cyclization, while an allylic alcohol under acidic conditions acting as electrophile to submit to attack by nucleophile.[19,20] The same type of transformation is also realized using AuCl, and for a chiral version, ligand **39A** is useful.[21]



(**37**)

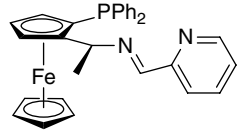


(**38**)



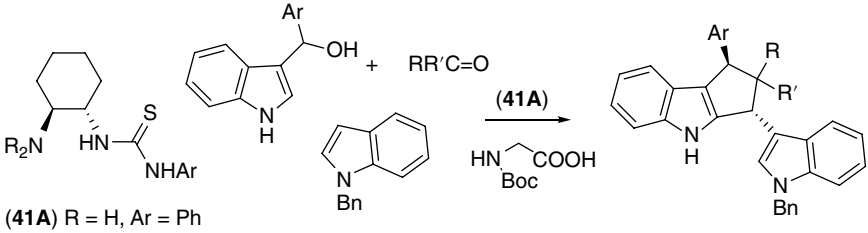
(**39A**) Ar = 3,5-*t*-Bu_2-4-$MeOC_6H_2$
(**39B**) Ar = 3,5-*i*-Pr_2-4-$Me_2NC_6H_2$

Catalysis by CuI is proper for substitution of propargylic acetates by amines, the ferrocene-based tridentate ligand **40** satisfies an enantioselective operation.[22]



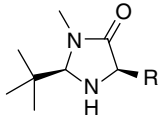
(**40**)

The imidazolidinone **28** is responsible for asymmetric induction in alkylation of aldehydes by a benzodithiazolium salt,[23,24] as well as by xanthenes (while being oxidized in situ).[25] Aldehydes serve as the linchpin to connect two indole units by an initial alkylation (mechanistically likely to be an elimination –vinylogous Mannich reaction sequence) and the first CC bond-forming step is subject to chiral regulation by a Brønsted acid and **41A**.[26]

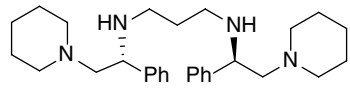


(**41A**) R = H, Ar = Ph
(**41B**) R+R = $(CH_2)_4$, Ar = Ph
(**41C**) R = H, Ar = 4-$C_8F_{17}C_6H_4$
(**41D**) R = H, Ar = 2,6-$Ph_2C_6H_3$

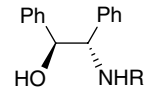
The simplest way to access β,γ-unsaturated aldehydes chiral at the α-position is by enantioselective alkenylation. This can be achieved as alkenyl aryl iodonium triflates are now readily prepared, and promotion of the reaction by CuBr and the TFA salt of **42A** is established.[27]



(**42A**) R = Ph
(**42B**) R = Bn
(**42C**) R = *t*-Bu



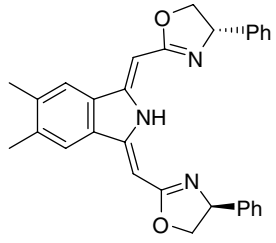
(**43**)



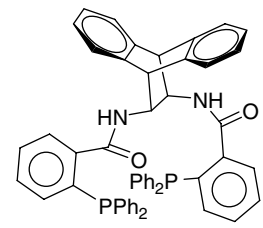
(**44A**) R = Me
(**44B**) R = Bn

Arylacetic acid undergo enantioselective alkylation with the help of the amine ligand **43**.[28] (−)-Pseudoephenamine (**44A**) is now proposed to replace pseudoephedrine for use in acylation and asymmetric alkylation because it is not a regulated substance.[29]

Gainful trifluoromethylation of β-keto esters is accomplished with the CuOTf complex of **45**.[30] A convenient route to α-trifluoromethylalkanoic acid derivatives involves reaction of the zirconium enolates of a chiral 3-acyl-4-benzyl-5,5-dimethyl-2-oxazolidinones. By virtue of steric shielding on the face occupied by the benzyl group stereofacial discrimination for the approaching CF_3I is attained, and the absolute configuration of the emerging chirality center correlates with that of the heterocycle.[31] Enol carbonates prepared from 2-acyl-1-phenylimidazoles decompose on treatment with $(dba)_3Pd_2{\cdot}CHCl_3$ and ligand **46**.[32] Alternatively, enol carbonates of 3-acylbenzoxazolin-2-ones are used to the same effect [ligand is a **48A** analog without di(o-tolyl)phosphino groups].[33] The products, obtained in practically quantitative yields and optical purity, readily react with nucleophiles to provide chiral acid derivatives.



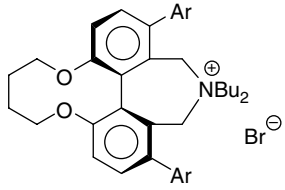
(**45**)



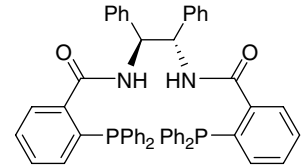
(**46**)

Activation of allenyl benzyl ether by Pd sets up reaction with a 3-indolyloxindole, which furnishes a product adorned with two contiguous stereocenters. Ligand **33A** makes the product chiral.[34]

Alkylation of *N*-arylidene α-amino esters mediated by a phase transfer catalyst is of certain advantages, and **47** is useful in situation where chiral discrimination is desired.[35] Benzylation of azlactones employing a Pd catalyst bound to **48A** gives good results.[36]

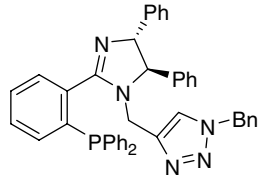


(**47**) Ar = 3,4,5-$F_3C_6H_2$

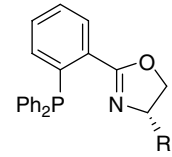


(**48**)

The CuOTf – **45** pairing is well suited for asymmetric allylation of cyclic β-keto esters.[37] Electrophiles contained in a 9-membered Pd-chelate derived from **49** delivers higher ee in allylic substitution.[38] In allylation of ketones by allyl carbonates or through a decomposition-trapping route of allyl alkenyl carbonates ligand **50A** proves pivotal in assisting the Pd(0) species.[39]

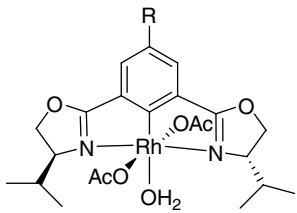


(**49**)

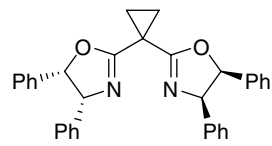


(**50A**) R = *t*-Bu
(**50B**) R = Ph

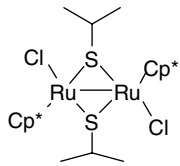
The rhodacycle **51** (R = H) is a privileged catalyst for alkynylation of ethyl 3,3,3-trifluoro-2-oxopropanoate.[40] Quite different is the situation for propargylation of β-keto esters that employs the alcohols as electrophiles: besides a Cu chelate of **52**, the dinuclear ruthenium complex **53** is a synergistic catalyst.[41]



(**51**)

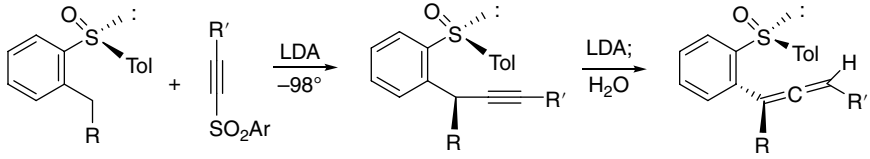


(**52**)



(**53**)

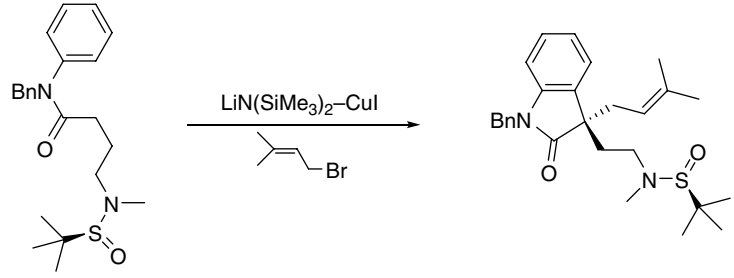
1,4-Asymmetric induction by a chiral sulfinyl group is witnessed in benzylic alkynylation, as well as isomerization of the products into chiral allenes.[42]



C-Arylation serves to establish a new benzylic stereocenter. There is a discussion of the challenges involved in asymmetric α–arylation of aldehydes by transition metal catalysis.[43]

In the cyclization of *N*-(*o*-haloaryl)-*N*-(α-aryl)alkanamides to form oxindoles the enantioselectivity displayed in a fenchol-based Pd-catalyzed process depends on the electronegativity of the halogen (F > Cl > Br).[44]

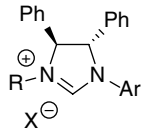
1,5-Asymmetric induction from a chiral sulfur atom is exploited in a prenylation after oxidative cyclization that forms the oxindole nucleus.[45]



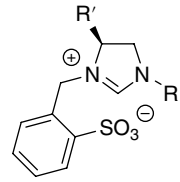
Aryliodonium salts supply the electrophile to arylation of a silyl enol ether derived from *N*-acyl-2-oxazolidinone. The (*R*)-isomer is obtained if *ent*-**14A** is used to modify the steric environment surrounding the Cu ion.[46] Asymmetric arylation of indoles (at C-3) is achieved by a similar method.[47]

Establishment of chirality in the electrophiles is also managed by using the proper catalyst. 1-Alkynylisochromans are synthesized from 1-methoxyisochroman by a substitution reaction, a Cu(I) salt complexed to **14B** gives good results.[48]

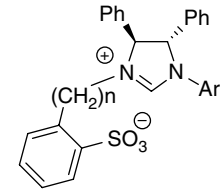
The carbene from imidazolinium salt **54A** must be closely associated with the Grignard reagent to guide the enantioselective attack on allylic bromides containing a fluoroalkyl group on the double bond, to generate alkenes with a quaternary carbon center.[49] In the Grignard reaction with cinnamyl bromides, **55** exerts an asymmetric induction (up to 82% ee).[50]



(**54A**) R = [(2-HO-5-Ph)C_6H_3]CH_2
Ar = 2-Et-6-MeC_6H_3, X = Cl
(**54B**) R = Mes
Ar = 2-MesC_6H_4, X = BF_4

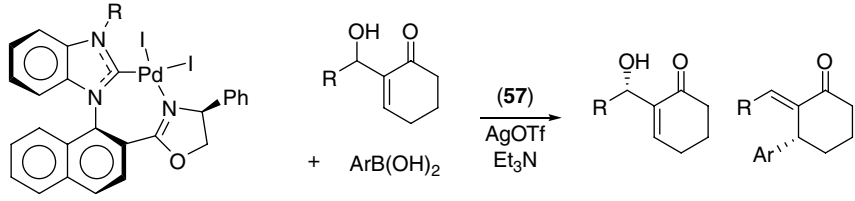


(**55**)



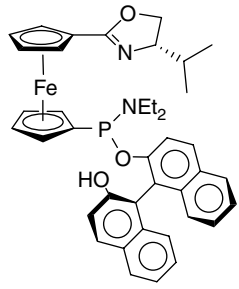
(**56A**) Ar = 3,5-(2,4,6-i$Pr_3C_6H_2$)$_2C_6H_3$
n = 1
(**56B**) Ar = 2-Ph-6-MeC_6H_3, n = 0

Allenylboronates attack allyl phosphates as led by CuCl- **56A** gives 1,2,5-hexatrienes branched at C-4. The products are subject to selective hydration via hydroboration with the same catalyst, the overall process is thus for preparation of chiral 5-hexen-2-ones.[51] Other S_N2' displacement reaction by organoboron reagents to produce chiral alkenes often depend on Segphos ligands (e.g., **25B**) to complement Cu salts or Rh complexes.[52,53] The palladacycle **57** in conjunction with AgOTf enables asymmetric addition of the aryl group from $ArB(OH)_2$ to C-3 of 2-(α-hydroxyalkyl)-2-cyclohexenones with concurrent removal of the hydroxyl group. This reaction can be applied to kinetic resolution.[54]

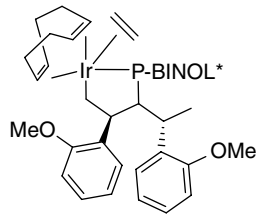


(**57**)

In allylic substitution by nitromethane, the ligand exchange with **58** in $(dba)_3Pd_2{\cdot}CHCl_3$ modifies the reaction in the chiral sense.[55] Racemic allyl acetates react with 2-trimethylsiloxyfuran and they can be kinetically resolved under controlled conditions [catalyst: $(dba)_3Pd_2{\cdot}CHCl_3$ – **33A**].[56] Another catalyst for the reaction is ZnF_2-(**59**).[57]

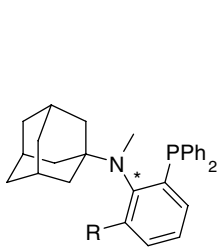


(**58**)

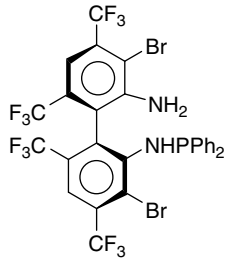


(**59**)

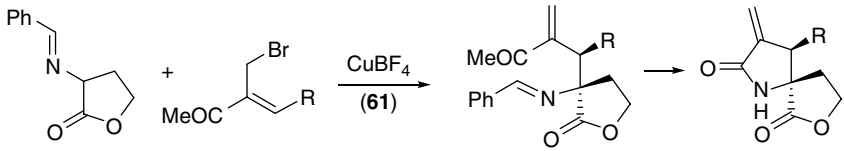
A resolved atropisomeric **60** is used in Pd-catalyzed allylation,[58] whereas $CuBF_4$ and **61** forms a complex to perform an S_N2' substitution of α-benzalamino-γ-butyrolactone.[59]



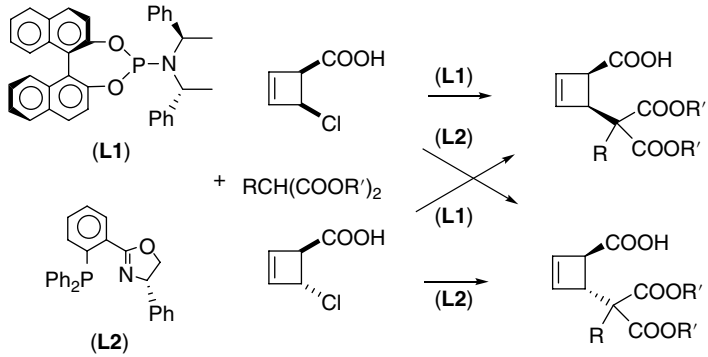
(**60**)



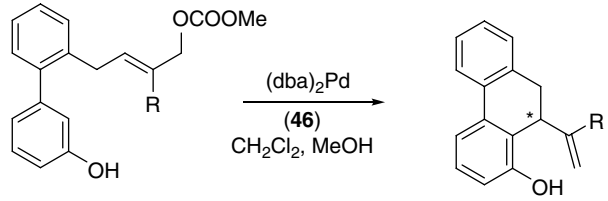
(**61**)



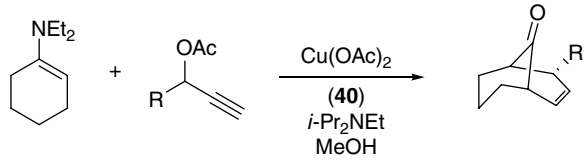
The reaction of 4-chloro-2-cyclobutenecarboxylic acid, both the *cis*- and *trans*-isomers, and the bicyclic β-lactone, with malonic esters manifests the possibility of guiding towards diastereodivergent routes by ligands.[60,61]



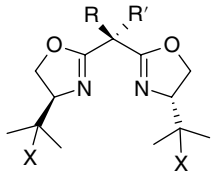
BOX ligands **62A** in which the *meso*-position carries a sidechain with a phosphite have been employed to ensnare Pd for allylic substitution in CH_2Cl_2 or ionic liquids.[62] Actually, all sorts of chiral ligands are effective and that include **25B** for substitution on 1,2-alkadien-3-yl acetates.[63] Chiral 9,10-dihydrophenanthrenes are obtained by a ring-closing substitution, in which ligand **46** is employed to render the reaction enantioselective.[64]



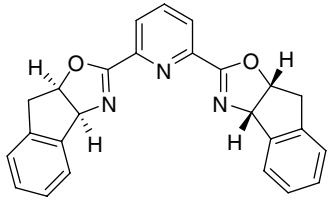
Coaxing cyclic enamines to engage in nucleophilic substitution in two consecutive steps, such as in reaction with propargylic acetates, creates a bridged ring system. To obtain chiral products a Cu(II)-catalyzed reaction is warranted by **40**.[65]



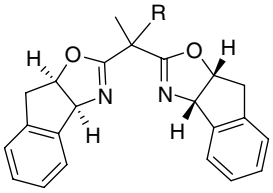
Negishi coupling based on nickel catalysis to replace a propargylic ester group with an aromatic nucleus is effectively guided by **63**.[66] A similar ligand (**64**) for $Ni(ClO_4)_2$ serves in the opening of prochiral 1,1- cyclopropanedicarboxylic esters by amines.[67]



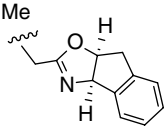
(**62A**) R = Me, Bn
R′ = $CHOPR'_2$, X = H
(**62B**) R = Bn
R′ = Me, X = H
(**62C**) R = 3,5-$Me_2C_6H_3CH_2$
R′ = Me, X = H
(**62D**) R = R′ = X = Me

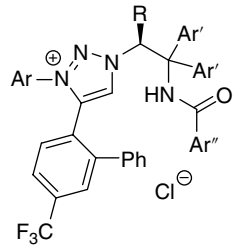


(**63**)



(**64A**) R = Me
(**64B**) R =

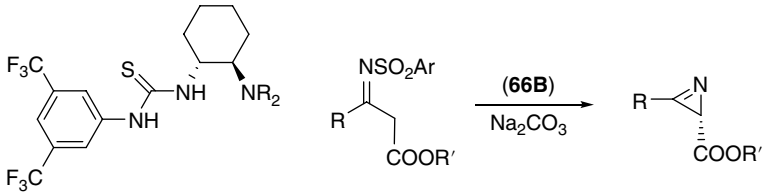




(**65**)

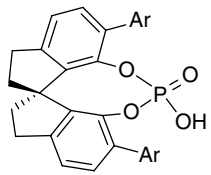
In cleaving *N*-arenesulfonylaziridines with Me_3SiCl, the triazolium salt **65** acts as a chiral catalyst.[68] The chromium(III) chelate of 3,5-di-*t*-butylsalicylaldimine derived from chiral 1,2-diaminocyclohexane assists transformation of oxiranes to β-lactones by insertion of CO.[69]

Chiral azirene-3-carboxylic esters are obtained by treatment of β-arenesulfonyliminoalkanoic esters with a mild base in the presence of **66B**.[70]

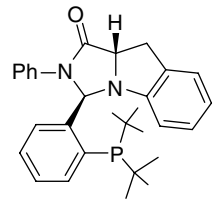


(**66A**) R = H
(**66B**) R = Me
(**66C**) R + R = $(CH_2)_5$

α-Diazoalkanoic esters as electrophiles offer two bonding opportunities. They can be converted into α-amino acid derivatives by amines. A demonstration of advantages for using Rh(II) catalysts is related to chiral modification (e.g., with ligand **67C**).[71] Insertion of Cu-carbenoids into an O-H bond giving rise to α–alkoxyalkanoic esters is also subject to asymmetric induction by a ligand, as shown by reaction involving **68**.[72]

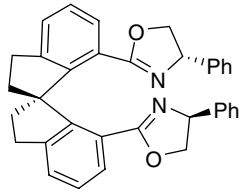


(**67A**) Ar = 2,4,6-$iPr_3C_6H_2$
(**67B**) Ar = 1-Np
(**67C**) Ar = 2-Np
(**67D**) Ar = Ph

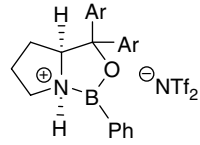


(**68**)

Examples for enantioselective C-H bond insertion by carbenoids generated from the diazo compounds include reaction at C-3 of an indole, accomplished by catalysis of $Fe(ClO_4)_2$ -**69**.[73] To assemble β-keto esters from diazoesters and aldehydes, a bicyclic oxazaborolidinium salt (**70**) is enlisted to direct the reaction path.[74]



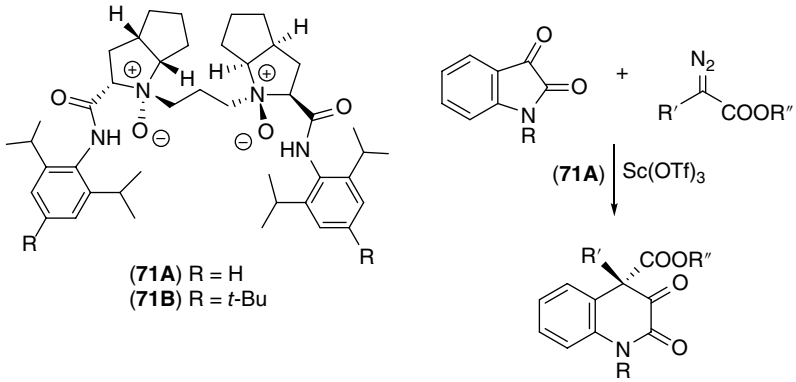
(**69**)



(**70**) R = 3,5-$Me_2C_6H_3$

Cyclic ketones undergo ring expansion through carbene insertion into the CC bond connecting the carbonyl group and the α-carbon readily. As the process is subject to catalysis by Lewis acids, modification of the acids by chiral ligands enables homologation of prochiral ketones to furnish optically active products. Combining $Sc(OTf)_3$ with either a BOX ligand or **71A** can attain the goal.[75,76]

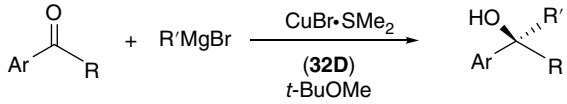
It is noteworthy that the reaction pathway can be diverted toward a C-H bond insertion by the terminal nitrogen atom.[77]



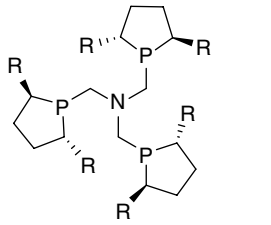
[1] Bertogg, A., Hintermann, L., Huber, D.P., Perseghini, M., Sanna, M., Togni, A. *HCA* **95**, 353 (2012)
[2] Suzuki, S., Kitamura, Y., Lectard, S., Hamashima, Y., Sodeoka, M. *ACIE* **51**, 4581 (2012)
[3] Jacquet, O., Clement, N.D., Blanco, C., Belmonte, M.M., Benet-Buchholz, J., van Leeuwen, P.W.N.M. *EJOC* 4844 (2012)
[4] Zhao, Y.-M., Cheung, M.S., Lin, Z., Sun, J. *ACIE* **51**, 10359 (2012)
[5] Li, J., Cai, Y., Chen, W., Liu, X., Lin, L., Feng, X. *JOC* **77**, 9148 (2012)
[6] Cai, Y., Li, J., Chen, W., Xie, M., Liu, X., Lin, L., Feng, X. *OL* **14**, 2726 (2012)
[7] Li, J., Pan, W., Wang, Z., Zhang, X., Ding, K. *ASC* **354**, 1980 (2012)
[8] Sparr, C., Gilmour, R. *ACIE* **50**, 8391 (2011)
[9] Yang, Y., Moinodeen, F., Chin, W., Ma, T., Jiang, Z., Tan, C.-H. *OL* **14**, 4762 (2012)
[10] Guilbault, A.-A., Basdevant, B., Wanie, V., Legault, C.Y. *JOC* **77**, 11283 (2012)
[11] Baidya, M., Griffin, K.A., Yamamoto, H. *JACS* **134**, 18566 (2012)
[12] Wang, C., Yang, X., Loh, C.C.J., Raabe, G., Enders, D. *CEJ* **18**, 11531 (2012)
[13] Wang, J., Chen, J., Kee, C.W., Tan, C.-H. *ACIE* **51**, 2382 (2012)
[14] Zhu, J., Tsui, G.C., Lautens, M. *ACIE* **51**, 12353 (2012)
[15] Katcher, M.H., Sha, A., Doyle, A.G. *JACS* **133**, 15902 (2011)
[16] Wang, X., Meng, F., Wang, Y., Han, Z., Chen, Y.-J., Liu, L., Wang, Z., Ding, K. *ACIE* **51**, 9276 (2012)
[17] Kakugawa, K., Nemoto, T., Kohno, Y., Hamada, Y. *S* 2540 (2011)
[18] Boyer, A., Lautens, M. *ACIE* **50**, 7346 (2011)
[19] Miyata, K., Kitamura, M. *S* 2138 (2012)
[20] Seki, T., Tanaka, S., Kitamura, M. *OL* **14**, 608 (2012)
[21] Mukherjee, P., Widenhoefer, R.A. *ACIE* **51**, 1405 (2012)
[22] Zhang, C., Wang, Y.-H., Hu, X.-H., Zheng, Z., Hu, X.-P. *ASC* **354**, 2854 (2012)
[23] Gualandi, A., Emer, E., Capdevila, M.G., Cozzi, P.G. *ACIE* **50**, 7842 (2011)
[24] Tak-Tak, L., Dhimane, H., Dalko, P.I. *ACIE* **50**, 12146 (2011)
[25] Zhang, B., Xiang, S.-K., Zhang, L.-H., Cui, Y., Jiao, N. *OL* **13**, 5212 (2011)
[26] Xu, B., Guo, Z.-L., Jin, W.-Y., Wang, Z.-P., Peng, Y.-G., Guo, Q.-X. *ACIE* **51**, 1059 (2012)
[27] Skucas, E., MacMillan, D.W.C. *JACS* **134**, 9090 (2012)
[28] Stivala, C.E., Zakarian, A. *JACS* **133**, 11936 (2011)
[29] Morales, M.R., Mellem, K.T., Myers, A.G. *ACIE* **51**, 4568 (2012)
[30] Deng, Q.-H., Wadepohl, H., Gade, L.H. *JACS* **134**, 10769 (2012)
[31] Herrmann, A.T., Smith, L.L., Zakarian, A. *JACS* **134**, 6976 (2012)

[32] Trost, B.M., Lehr, K., Michaelis, D.J., Xu, J., Buckl, A.K. *JACS* **132**, 8915 (2010)
[33] Trost, B.M., Michaelis, D.J., Charpentier, J., Xu, J. *ACIE* **51**, 204 (2012)
[34] Trost, B.M., Xie, J., Sieber, J.D. *JACS* **133**, 20611 (2011)
[35] Kubota, Y., Shirakawa, S., Inoue, T., Maruoka, K. *TL* **53**, 3739 (2012)
[36] Trost, B.M., Czabaniuk, L.C. *JACS* **134**, 5778 (2012)
[37] Deng, Q.-H., Wadepohl, H., Gade, L.H. *JACS* **134**, 2946 (2012)
[38] de la Fuente, V., Marcos, R., Cambeiro, X.C., Castillon, S., Claver, C., Pericas, M.A. *ASC* **353**, 3255 (2011)
[39] Behenna, D.C., Mohr, J.T., Sherden, N.H., Marinescu, S.C., Harned, A.M., Tani, K., Seto, M., Ma, S., Novak, Z., Krout, M.R., McFadden, R.M., Roizen, J.L., Enquist Jr, J.A., White, D.E., Levine, S.R., Petrova, K.V., Iwashita, A., Virgil, S.C., Stoltz, B.M. *CEJ* **17**, 14199 (2011)
[40] Ohshima, T., Kawabata, T., Takeuchi, Y., Kakinuma, T., Iwasaki, T., Yonezawa, T., Murakami, H., Nishiyama, H., Mashima, K. *ACIE* **50**, 6296 (2011)
[41] Ikeda, M., Miyake, Y., Nishibayashi, Y. *CEJ* **18**, 3321 (2012)
[42] Ruano, J.L.G., Marzo, L., Marcos, V., Alvarado, C., Aleman, J. *CEJ* **18**, 9775 (2012)
[43] Mazet, C. *SL* 1999 (2012)
[44] Trillo, R.B., Leven, M., Neudörfl, J.M., Goldfuss, B. *ASC* **354**, 1451 (2012)
[45] Zhou, Y., Xi, Y., Zhao, J., Sheng, X., Zhang, S., Zhang, H. *OL* **14**, 3116 (2012)
[46] Bigot, A., Williamson, A.E., Gaunt, M.J. *JACS* **133**, 13778 (2011)
[47] Zhu, S., MacMillan, D.W.C. *JACS* **134**, 10815 (2012)
[48] Maity, P., Srinivas, H.D., Watson, M.P. *JACS* **133**, 17142 (2011)
[49] Grassi, D., Li, H., Alexakis, A. *CC* **48**, 11404 (2012)
[50] Latham, C.M., Blake, A.J., Lewis, W., Lawrence, M., Woodward, S. *EJOC* 699 (2012)
[51] Jung, B., Hoveyda, A.H. *JACS* **134**, 1490 (2012)
[52] Shido, Y., Yoshida, M., Tanabe, M., Ohmiya, H., Sawamura, M. *JACS* **134**, 18573 (2012)
[53] Kiuchi, H., Takahashi, D., Funaki, K., Sato, T., Oi, S. *OL* **14**, 4502 (2012)
[54] Wang, F., Li, S., Qu, M., Zhao, M.-X., Liu, L.-J., Shi, M. *CC* **47**, 12813 (2011)
[55] Yang, X.-F., Ding, C.-H., Li, X.-H., Huang, J.-Q., Hou, X.-L., Dai, L.-X. *JOC* **77**, 8980 (2012)
[56] Mao, B., Ji, Y., Fañanas-Mastral, M., Caroli, G., Meetsma, A., Feringa, B.L. *ACIE* **51**, 3168 (2012)
[57] Chen, W., Hartwig, J.F. *JACS* **134**, 15249 (2012)
[58] Mino, T., Yamada, H., Komatsu, S., Kasai, M., Sakamoto, M., Fujita, T. *EJOC* 4540 (2011)
[59] Teng, H.-L., Huang, H., Wang, C.-J. *CEJ* **18**, 12614 (2012)
[60] Audisio, D., Luparia, M., Oliveira, M.T., Klütt, D., Maulide, N. *ACIE* **51**, 7314 (2012)
[61] Luparia, M., Oliveira, M.T., Audisio, D., Frebault, F., Goddard, R., Maulide, N. *ACIE* **50**, 12631 (2011)
[62] Castillo, M.R., Castillon, S., Claver, C., Fraile, J.M., Gual, A., Martin, M., Mayoral, J.A., Sola, E. *T* **67**, 5402 (2011)
[63] Li, Q., Fu, C., Ma, S. *ACIE* **51**, 11783 (2012)
[64] Suzuki, Y., Nemoto, T., Kakugawa, K., Hamajima, A., Hamada, Y. *OL* **14**, 2350 (2012)
[65] Zhang, C., Hu, X.-H., Wang, Y.-H., Zheng, C., Xu, J., Hu, X.-P. *JACS* **134**, 9585 (2012)
[66] Oelke, A.J., Sun, J., Fu, G.C. *JACS* **134**, 2966 (2012)
[67] Zhou, Y.-Y., Wang, L.-J., Li, J., Sun, X.-L., Tang, Y. *JACS* **134**, 9066 (2012)
[68] Ohmatsu, K., Hamajima, Y., Ooi, T. *JACS* **134**, 8794 (2012)
[69] Ganji, P., Ibrahim, H. *CC* **48**, 10138 (2012)
[70] Sakamoto, S., Inokuma, T., Takemoto, Y. *OL* **13**, 6374 (2011)
[71] Xu, B., Zhu, S.-F., Xie, X.-L., Shen, J.-J., Zhou, Q.-L. *ACIE* **50**, 11483 (2011)
[72] Osako, T., Panichakul, D., Uozumi, Y. *OL* **14**, 194 (2012)
[73] Cai, Y., Zhu, S.-F., Wang, G.-P., Zhou, Q.-L. *ASC* **353**, 2939 (2011)
[74] Gao, L., Kang, B.C., Hwang, G.-S., Ryu, D.H. *ACIE* **51**, 8322 (2012)
[75] Rendina, V.L., Kaplan, H.Z., Kingsbury, J.S. *S* 686 (2012)
[76] Li, W., Liu, X., Hao, X., Cai, Y., Lin, L., Feng, X. *ACIE* **51**, 8644 (2012)
[77] Li, W., Liu, X., Hao, X., Hu, X., Chu, Y., Cao, W., Qin, S., Hu, C., Lin, L., Feng, X. *JACS* **133**, 15268 (2011)

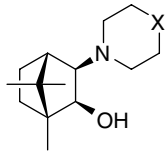
Addition to C=O bond. Whereas Grignard reaction to aryl ketones rendered asymmetric by a copper catalyst[1] including ligand **32D** is unquestionable, it seems odd that enones are also under 1,2-attack[2] Using the Li-Mg bimetallic reagent chelate containing a (*R,R*)-TADDOLate portion in metallation of heteroaryl bromides a subsequent reaction with aldehydes generates chiral alcohols.[3]



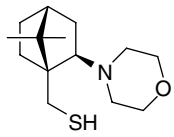
Production of chiral secondary alcohols by organozinc addition to aldehydes is a well-researched subject. It is now understood that reagents prepared from RLi and $ZnCl_2$ are unsuitable because LiCl is detrimental to enantioselective attack, therefore scavengers such as TMEDA are necessary, and using R_2Zn is recommended. Several isoborneol/fenchol-based (**73A**, **74**, **75**)[4,5,6] and menthol-based (**76A**, **76B**) ligands are viable.[7,8] An analog of **73A**, i.e., with a piperazine instead of morpholine group to link up to polystyrene[9] and the isoborneol **77** in which C-10 carries a sulfonamide group[10] also have been developed. The glucosamine derivative **78** promotes Ti(IV)-catalyzed addition of alkynylzinc reagents.[11]



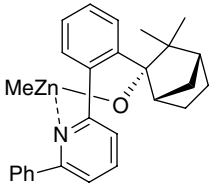
(**72**)



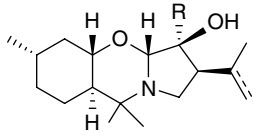
(**73A**) X = O
(**73B**) X = NCH_2-polymer



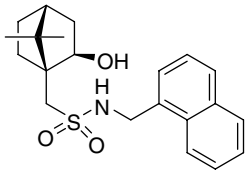
(**74**)



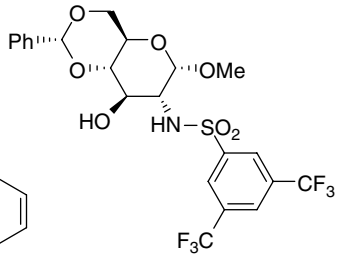
(**75**)



(**76A**) R = Ph, dihydro
(**76B**) R = *i*-Pr

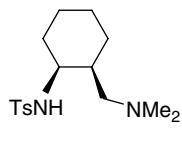


(**77**)

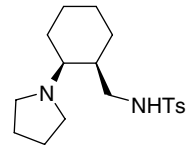


(**78**)

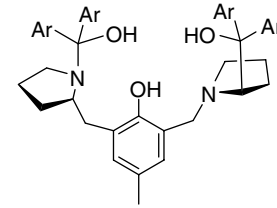
Two ligands **79** and **80** in which the major difference is the location of the tosyl substituent guide the addition of diethylzinc to aldehydes in opposite sense enantioselection.[12]



(**79**)

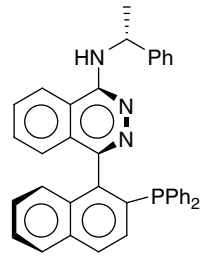


(**80**)

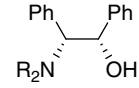


(**81A**) Ar = Ph
(**81B**) Ar = 2-Th
(**81C**) Ar = 2-Np

To economize the reagent Me_2Zn which is used to form alkynlzincs by group exchange for synthesis of chiral propargylic alcohols (ligand: **81A**) triphenylphosphine oxide is added to the reaction media.[13] Propargyl alcohols condense with aldehydes to provide allenyl carbinols (allene chirality) by employing a copper-catalyzed reaction (ligand: **82**).[14]



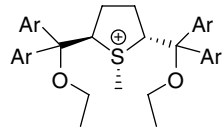
(**82**)



(**83A**) R = H
(**83B**) R = Me

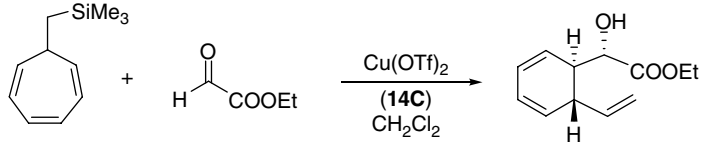
To perform enantioselective Barbier reaction from a mixture of indium, propargyl bromide, a carbonyl compound the simple aminoethanol **83A** suffices.[15] Another simple chiral catalyst is (*R*)- *N*-(*t*-butanesulfinyl)cinnamylamine that modifies the Rh complex for catalyzing addition of $ArB(OH)_2$ to α-diketones and α-keto esters.[16] A variation of this theme is the intramolecular attack of boronate on a ketone.[17]

Intramolecular addition resulting in 3-hydroxyoxindoles is initiated by palladation of *N*-(2-oxoalkanoyl)-*o*-triflyloxyanilides, the enantioselective version being enabled by DifluoPhos **25C**.[18] Sulfonium methylide derived from **84** is useful for transforming aromatic aldehydes into chiral styrene oxides.[19] Total sacrifice of a chiral sulfinylimine group for asymmetric addition of a difluoromethyl residue to C=O is the crux of a strategy,[20] and the method is viable only if the chiral reagent is readily prepared.



(**84**) Ar = 3,5-$Ph_2C_6H_3$

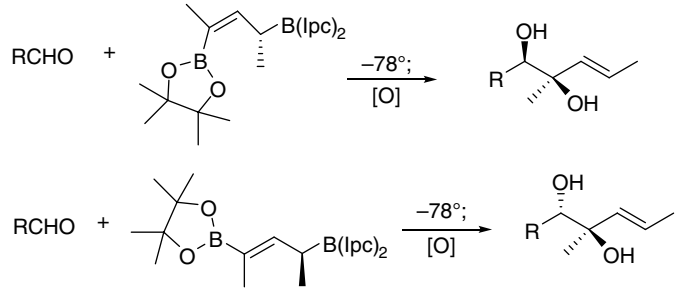
The reaction between 7-trimethylsilylmethyl-1,3,5-cycloheptatriene and ethyl glyoxylate generates a product with a vinylcyclohexadiene skeleton,[21] as the nucleophilic species is the 7-trimethylsilylmethylbicycle[4.1.0]cyclohepta-2,4-diene tautomer.



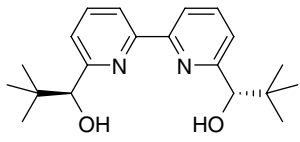
Adducts from reaction of magnesium α-diazo esters that are placed in a chiral environment presented by **81A** with aldehydes is highly enantioselective,[22] and such products can be oxidized and then an additional carbon chain introduced with complete stereocontrol, due to maneuverability via participation of the neighboring hydroxyl group.

Allylboron and silicon derivatives are popular nucleophiles, their reactions are catalyzed by protic or Lewis acids. The phosphoric acid **67A** is a catalyst by itself,[23] but **85** forms a chelate with the Zn(II) ion to activate the aldehydes and directs the enantioselective attack.[24]

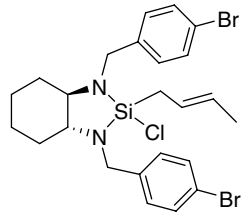
The γ-attack of 3,3-difluoroallyl(2-pinanyl)borane on aldehydes gives (*R*)-3,3-difluoro-1-alken-4-ols.[25] With acquisition of 4,5-diborylated 2-pentene from enantioselective borylation of 1,3-pentadiene (Pt-catalyst with type **2A** ligand), the reaction with aldehydes generates secondary alcohols bearing two adjacent asymmetric centers and one allylic boronate functionality.[26] On hydroboration of an optically active 2-pinacolatoboryl-2,3-pentadiene, e.g., with diisopinocampheylborane, provides a diborylalkene that is a synthetic equivalent of a C-2 anion of 3-penten-2-ol.[27] From a similar hydroboration of 1-tributylstannyl-1,2-propadiene a chiral *gem*-B/Sn disubstituted allylating agent is obtained (a 1,3-boratropic shift occurs after the initial addition).[28]



An allylsilane derived from the chiral *trans*-1,2-diaminocyclohexane (cf. **86**) endows spatial information as to selectively transfer the allyl group in a predictive manner.[29,30] For crotylation the method is quite practical as a mixture of (*E/Z*) –isomers can be used to afford a homogeneous product.

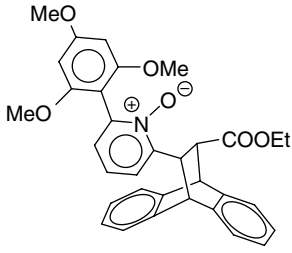


(**85**)

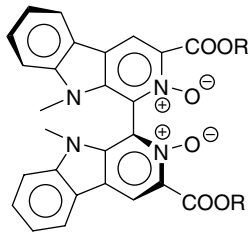


(**86**)

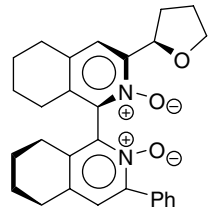
On complexation to **63**, $Sc(OTf)_3$ encourages allyl transfer from an allylsilane to isatin which is activated by Me_3SiCl.[31] When allyltrichlorosilane is enlisted as the allylating agent, heteroaromatic *N*-oxides are ideal catalysts. Of proven value are **87**,[32] **88**,[33] **89**,[34] and **90**.[35]



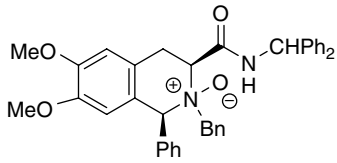
(**87**)



(**88**)

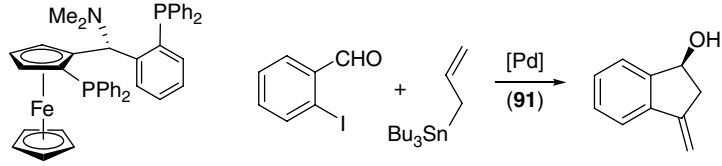


(**89**)



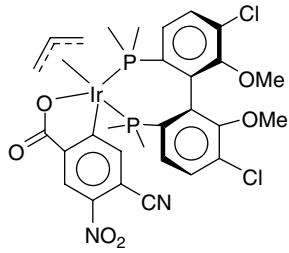
(**90**)

Less in use are allylstannanes, but one report describes a reaction relying on the complex of $Bi(OTf)_3$ to **81A**.[36] A more interesting result is the route to 3-methyleneindanol which consists of a Heck reaction and intramolecular destannylative allylation.[37] It is speculated that in Taniaphos **91** the chiral amino portion would be intimately involved in the second reaction.



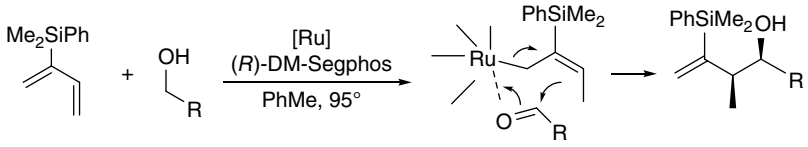
(**91**)

The benefit of redox CC bond formation is the simplification of reactants, and iridium complexes are especially adept in such maneuver. Thus in the presence of iridium complex **92** or a Segphos-ligated analog **93**, primary alcohols are genuine surrogates of aldehydes,[38,39,40] Propargylation employing an iridium complex follows a similar pattern.[41]

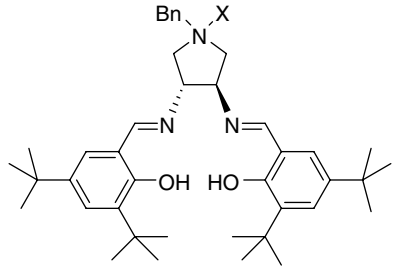


(**92**) [two Ph groups on each P]

The reactivity of certain hydridoruthenium complexes to promote redox condensation is also much appreciated. A 2-silyl-1,3-butadiene is turned into an allyl anion equivalent for attack of the aldehyde equivalents.[42] The regiochemistry is a synthetically exploitable issue.



A titanium(IV) complex of **94** is a catalyst for silylcyanation of aldehydes. The derived pyrrolidine *N*-oxide maintains the catalytic activity but the adducts it serves to produce are enantiomerically opposite.[43]

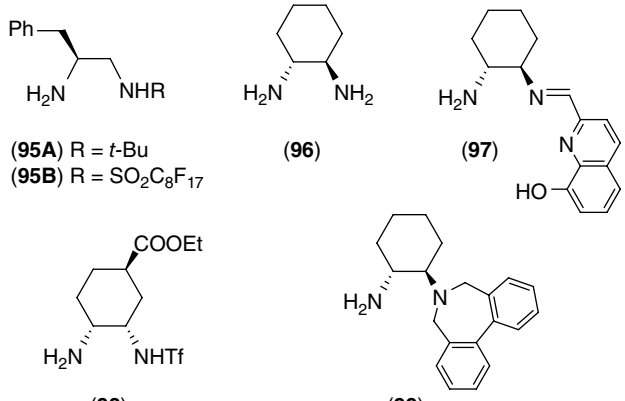


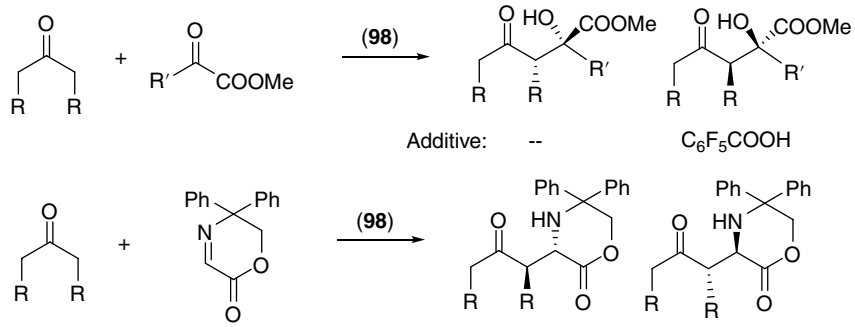
(**94**) X = O; lone pair

[1] Madduri, A.V.R., Harutyunyan, S.R., Minnaard, A.J. *ACIE* **51**, 3164 (2012)
[2] Madduri, A.V.R., Minnaard, A.J., Harutyunyan, S.R. *CC* **48**, 1478 (2012)
[3] Catel, D., Chevallier, F., Mongin, F., Gros, P.C. *EJOC* 53 (2012)
[4] Salvi, L., Kim, J.G., Walsh, P.J. *JACS* **131**, 12483 (2009)
[5] Cheng, Y.-N., Wu, H.-L., Wu, P.-Y., Shen, Y.-Y., Uang, B.-J. *CAJ* **7**, 2921 (2012)
[6] Leven, M., Schlrer, N.E., Neudörfl, J.M., Goldfuss, B. *CEJ* **16**, 13443 (2010)
[7] Infante, R., Nieto, J., Andrés, C. *S* 1343 (2012)
[8] Infante, R., Nieto, J., Andrés, C. *CEJ* **18**, 4375 (2012)
[9] Osorio-Planes, L., Rodriguez-Escrich, C., Pericas, M.A. *OL* **14**, 1816 (2012)
[10] Liu, T.-L., Ma, H., Zhang, F.-G., Zheng, Y., Nie, J., Ma, J.-A. *CC* **47**, 12873 (2011)
[11] Bauer, T., Smolinski, S., Gawel, P., Jurczak, J. *TL* **52**, 4882 (2011)
[12] Hirose, T., Sugawara, K., Kodama, K. *JOC* **76**, 5413 (2011)
[13] Trost, B.M., Bartlett, M.J., Weiss, A.H., von Wangelin, A.J., Chan, V.S. *CEJ* **18**, 16498 (2012)
[14] Ye, J., Li, S., Chen, B., Fan, W., Kuang, J., Liu, J., Liu, Y., Miao, B., Wan, B., Wang, Y., Xie, X., Yu, Q., Yuan, W., Ma, S. *OL* **14**, 1346 (2012)
[15] Haddad, T.D., Hirayama, L.C., Buckley, J.J., Singaram, B. *JOC* **77**, 889 (2012)
[16] Zhu, T.-S., Jin, S.-S., Xu, M.-H. *ACIE* **51**, 780 (2012)
[17] Low, D.W., Pattison, G., Wieczysty, M.D., Churchill, G.H., Lam, H.W. *OL* **14**, 2548 (2012)
[18] Yin, L., Kanai, M., Shibasaki, M. *ACIE* **50**, 7620 (2011)
[19] Piccinini, A., Kavanagh, S.A., Connon, S.J. *CC* **48**, 7814 (2012)
[20] Shen, X., Zhang, W., Ni, C., Gu, Y., Hu, J. *JACS* **134**, 16999 (2012)
[21] Beniazza, R., Desvergnes, V., Girard, E., Kauffmann, B., Berlande, M., Landais, Y. *CEJ* **18**, 11976 (2012)
[22] Trost, B.M., Malhotra, S., Koschker, P., Ellerbrock, P. *JACS* **134**, 2075 (2012)
[23] Xing, C.-H., Liao, Y.-X., Zhang, Y., Sabarova, D., Bassous, M., Hu, Q.-S. *EJOC* 1115 (2012)
[24] Kobayashi, S., Endo, T., Ueno, M. *ACIE* **50**, 12262 (2011)
[25] Ramachandran, P.V., Tafelska-Kaczmarek, A., Chatterjee, A. *JOC* **77**, 9329 (2012)
[26] Kliman, L.T., Mlynarski, S.N., Ferris, G.E., Morken, J.P. *ACIE* **51**, 521 (2012)
[27] Han, J.-L., Chen, M., Roush, W.R. *OL* **14**, 3028 (2012)
[28] Chen, M., Ess, D.H., Roush, W.R. *JACS* **132**, 7881 (2010)
[29] McCubbin, J.A., Maddess, M.L., Lautens, M. *SL* 2857 (2011)
[30] Kim, H., Ho, S., Leighton, J.L. *JACS* **133**, 6517 (2011)
[31] Hanhan, N.V., Tang, Y.C., Tran, N.T., Franz, A.K. *OL* **14**, 2218 (2012)
[32] Gnanamani, E., Someshwar, N., Ramanathan, C.R. *ASC* **354**, 2101 (2012)
[33] Bai, B., Zhu, H.-J., Pan, W. *T* **68**, 6829 (2012)
[34] Kadlcikova, A., Valterova, I., Duchackova, L., Roithova, J., Kotora, M. *CEJ* **16**, 94 42 (2010)
[35] Naicker, T., Arvidsson, P.I., Kruger, H.G., Maguire, G.E.M., Govender, T. *EJOC* 6923 (2011)
[36] Li, Z., Plancq, B., Ollevier, T. *CEJ* **18**, 3144 (2012)
[37] Schütte, J., Ye, S., Schmalz, H.-G. *SL* 2725 (2011)
[38] Hassan, A., Townsend, I.A., Krische, M.J. *CC* **47**, 10028 (2011)
[39] Gao, X., Han, H., Krische, M.J. *JACS* **133**, 12795 (2011)
[40] Zhang, Y.J., Yang, J.H., Kim, S.H., Krische, M.J. *JACS* **132**, 4562 (2010)
[41] Woo, S.K., Geary, L.M., Krische, M.J. *ACIE* **51**, 7830 (2012)
[42] Zbieg, J.R., Moran, J., Krische, M.J. *JACS* **133**, 10582 (2011)
[43] Lv, C., Cheng, Q., Xu, D., Wang, S., Xia, C., Sun, W. *EJOC* 3407 (2011)

The enantioselective aldol reaction conducted in the presence of organocatalysts has been reviewed.[1] More attention is being paid to the utility of α-amino acids as aldol reaction catalyst. For example, histidine for enolizable aldehydes,[2] L-His and L-Ile for access to diastereomeric products,[3] the β-methylvaline for reaction involving chloromethyl ketones.[4] Particularly advantageous is the combination of an acyclic amino acid and a H-bond donor (e.g., thioureas).[5]

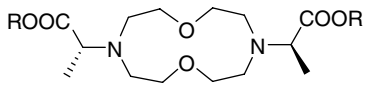
Many aldol catalysts are 1,2-diamine derivatives. Examples include the acyclic **95B**[6] and cyclohexanediamines **96**,[7] **97**,[8] **98**,[9] and **99**.[10] Both **97** and **98** were developed for reaction with α-keto esters as acceptors, and it is important to note the catalytic effect of **98** being influenced by an additive (C_6F_5COOH).





Metal complexes of bis(oxazolines) have also found widespread utility as chiral catalysts for CC bond forming reactions, the Mukaiyama aldol reaction included. Imbobilization of the catalyst in supported ionic liquids is beneficial in attaining much high optical yields.[11] The Ni(II) chelate of BOX ligand **14C** promotes aldol reaction of 3-acyl-2-thiazolidinethiones without having to form metal enolates.[12]

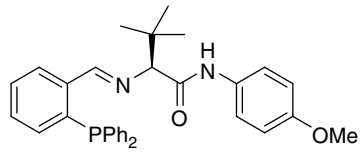
A polydentate ligand **100** constructed from alanine binds to lanthanide ions (e.g., europium) and the chelates are effective promoters of the Mukaiyama aldol reaction in water, which displays high *syn/anti* ratios.[13]



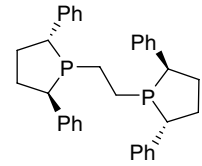
(**100**)

The great variety of chiral catalysts and ligands to support metal ions to perform asymmetric Mukaiyama aldol reactions is impressive, new additions now include iron(II) perchlorate coordinated to **85**,[14] a bicyclic oxazoborolidinium salt,[15] as well as a combination of AgOAc and **101**.[16]

Diposphine ligands that support copper species to catalyze the aldol reaction are also numerous and effective, among which are **102**,[17] **25C**,[18] and **91**.[19]

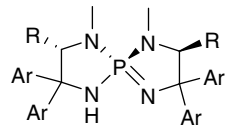


(**101**)



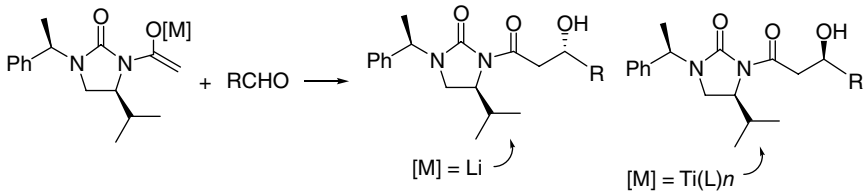
(**102**)

While the CuOAc-Taniaphos system helps creating chiral nucleophile from decarboxylation of α-cyanoalkanoic acids, glycolate enolates are generated from 2-hydroxy-2-phosphonylalkanoic esters via a C-to-O phosphoryl group shift. Adding **103A** renders the aldol reaction enantioselective.[20]



(**103A**) Ar = Ph, R = *i*-Pr
(**103B**) Ar = 4-FC_6H_4, R = *i*-Bu

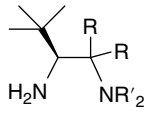
A most felicitous fact is that different metal enolates favor specific diastereomer production, as shown in the following equation.[21]



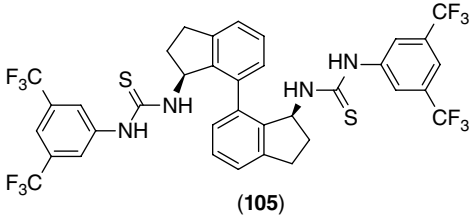
Selective aldol reaction of 2-(3-oxobutyl)-1,3-cycloalkanediones is crucial to the elaboration of chiral bicyclic diketones such as the Wieland-Miescher ketone. A new catalyst is the TfOH salt of **104A** which must engage in enamination of the sidechain ketone to initiate the reaction.[22]

Hydroxyalkylation of 2-cyclohexenones by the Baylis-Hillman reaction to furnish adducts with an asymmetric carbonyl center is accomplished with **105**.[23] Better chiral induction is seen for the reaction with aliphatic aldehydes than aromatic aldehydes.

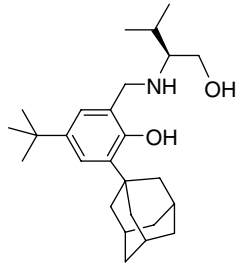
An aluminum chelate derived from **106** directs the addition of dimethyl phosphonate to trifluoromethyl ketones.[24]



(**104A**) R = H, R′ = Et
(**104B**) R = Ph, R′ = H

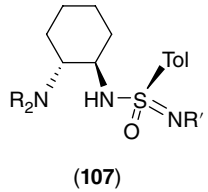


(**105**)

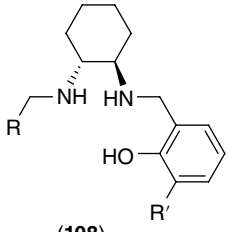


(**106**)

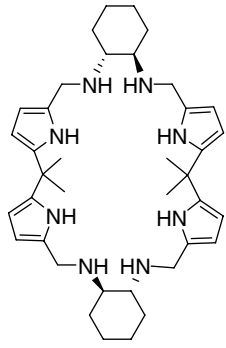
The Henry reaction, similar to the aldol reaction, is amenable to chiral intervention by catalysts, which contain a copper ion. Chiral bidentate ligands belonging to *N,O*- and *N,N*-classes are the most frequently encountered: **83B** in the first,[25] **107**,[26] **108**,[27] **109**,[28] **110**,[29] and a diamine related to **79**[30]. Certain 1,3-diamines also are serviceable,[31] of course they include complexes of the BOX ligands **64B**,[32] **112**,[33] and **113**.[34]



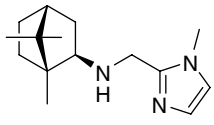
(**107**)



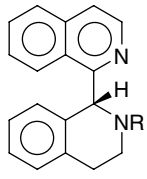
(**108**)



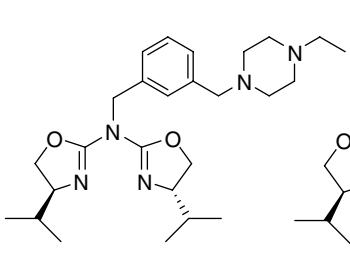
(**109**)



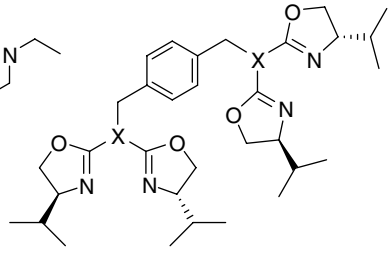
(**110**)



(**111**)



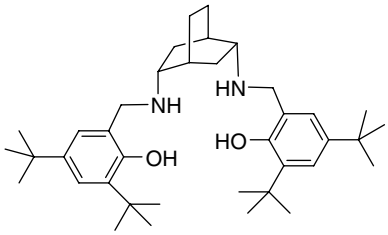
(**112**)



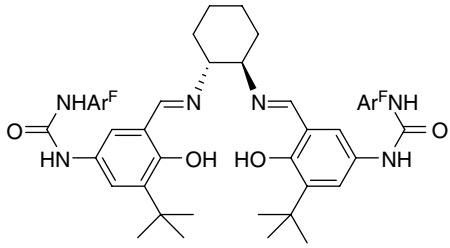
(**113**) X = N; CH

Tetradentate ligands for the Cu ion to use in Henry reaction are **114**[35] and the imine from condensation of 3-aminoisoborneol and 6-methylsalicylaldehyde.[36]

By considering H-bonding to the nitronate ion with a urea unit and the formyl group of the aldehyde to occupy an axial coordination site of the metal ion (cobalt) results in the design of catalyst **115**.[37]



(**114**)



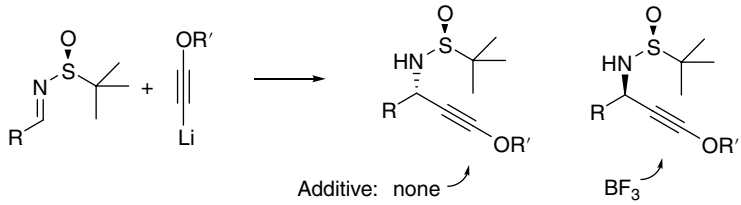
(**115**) $Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$

Friedel-Crafts addition of pyrrole to isatin goes asymmetric with the $In(OTf)_3$ complex of **63**.[38]

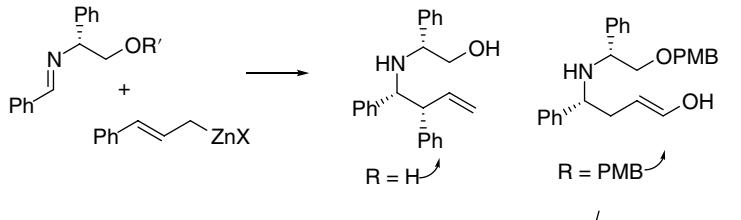
[1] Bisai, V., Bisai, A., Singh, V.K. *T* **68**, 4541 (2012)
[2] Scheffler, U., Mahrwald, R. *JOC* **77**, 2310 (2012)
[3] Rohr, K., Mahrwald, R. *OL* **14**, 2180 (2012)
[4] Umehara, A., Kanemitsu, T., Nagata, K., Itoh, T. *SL* 453 (2012)
[5] Ma, G., Bartoszewicz, A., Ibrahim, I., Cordova, A. *ASC* **353**, 3114 (2011)
[6] Miura, T., Imai, K., Kasuga, H., Ina, M., Tada, W., Imai, N., Itoh, A. *T* **67**, 6340 (2011)
[7] Liu, Y., Wang, J., Sun, Q., Li, R. *TL* **52**, 3584 (2011)
[8] Zhu, X., Lin, A., Fang, L., Li, W., Zhu, C., Cheng, Y. *CEJ* **17**, 8281 (2011)
[9] Moteki, S.A., Han, J., Arimitsu, S., Akakura, M., Nakayama, K., Maruoka, K. *ACIE* **51**, 1187 (2012)
[10] Lygo, B., Davison, C., Evans, T., Gilks, J.A.R., Leonard, J., Roy, C.-E. *T* **67**, 10164 (2011)
[11] Goodrich, P., Hardacre, C. Paun, C., Ribeiro, A., Kennedy, S., Lourenço, M.J.V., Manyar, H., de Castro, C.A.N., Besnea, M., Parvulescu, V.I. *ASC* **353**, 995 (2011)
[12] Evans, D.A., Downey, C.W., Hubbs, J.L. *JACS* **125**, 8706 (2003)
[13] Mei, Y., Averill, D.J., Allen, M.J. *JOC* **77**, 5624 (2012)
[14] Ollevier, T., Plancq, B. *CC* **48**, 2289 (2012)
[15] Senapati, B.K., Gao, L., Lee, S.I., Hwang, G.-S., Ryu, D.H. *OL* **12**, 5088 (2010)
[16] Curti, C., Battistini, L., Ranieri, B., Pelosi, G., Rassu, G., Casiraghi, G., Zanardi, F. *JOC* **76**, 2248 (2011)
[17] Kawato, Y., Iwata, M., Yazaki, R., Kumagai, N., Shibasaki, M. *T* **67**, 6539 (2011)
[18] Shi, S.-L., Kanai, M., Shibasaki, M. *ACIE* **51**, 3932 (2012)
[19] Yin, L., Karrai, M., Shibasaki, M. *T* **68**, 3497 (2012)
[20] Corbett, M.T., Uraguchi, D., Ooi, T., Johnson, J.S. *ACIE* **51**, 4685 (2012)
[21] Khatik, G.L., Kumar, V., Nair, V.A. *OL* **14**, 2442 (2012)
[22] Zhou, P., Zhang, L., Luo, S., Cheng, J.-P. *JOC* **77**, 2526 (2012)
[23] Nakayama, Y., Gotanda, T., Ito, K. *TL* **52**, 6234 (2011)
[24] Zhou, X., Zhang, Q., Hui, Y., Chen, W., Jiang, J., Lin, L., Liu, X., Feng, X. *OL* **12**, 4296 (2010)
[25] Qin, D.-D., Lai, W.-H., HU, D., Chen, Z., Wu, A.-A., Ruan, Y.-P., Zhou, Z.-H., Chen, H.-B. *CEJ* **18**, 10515 (2012)
[26] Steurer, M., Bolm, C. *JOC* **75**, 3301 (2010)

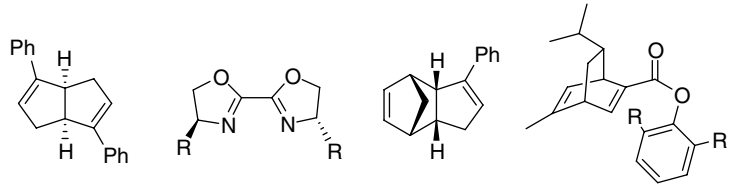
[27] Chougnet, A., Zhang, G., Liu, K., Häussinger, D., Kägi, A., Allmendingen, T., Woggon, W.-D. *ASC* **353**, 1797 (2011)
[28] Gualandi, A., Cerisoli, L., Stoeckli-Evans, H., Savoia, D. *JOC* **76**, 3399 (2011)
[29] Zhou, Y., Gong, Y. *EJOC* 6092 (2011)
[30] Kodama, K., Sugawara, K., Hirose, T. *CEJ* **17**, 13584 (2011)
[31] Yao, Q., Gao, Q., Judeh, Z.M.A. *EJOC* 4892 (2011)
[32] Didier, D., Magnier-Bouvier, C., Schulz, E. *ASC* **353**, 1087 (2011)
[33] Lang, K., Park, J., Hong, S. *JOC* **75**, 6424 (2010)
[34] Angulo, B., Garcia, J.I., Harrerias, C.I., Mayoral, J.A., Miñana, A.C. *JOC* **77**, 5525 (2012)
[35] White, J.D., Shaw, S. *OL* **14**, 6270 (2012)
[36] Boobalan, R., Lee, G.-H., Chen, C. *ASC* **354**, 2511 (2012)
[37] Lang, K., Park, J., Hong, S. *ACIE* **51**, 1620 (2012)
[38] Gutierrez, E.G., Wong, C.J., Sahin, A.H., Franz, A.K. *OL* **13**, 5754 (2011)

Addition to C=N bond. 1,3-Stereoinduction of (*S*)-*N*-(*t*-butanesulfinyl)aldimines in the reaction with lithiated alkoxyethynes is completely switched when BF_3 is added to the reaction medium.[1] One such imine is a valuable precursor to α-amino acids based on its reaction with $RZnX{\cdot}MgCl_2{\cdot}LiCl$.[2]



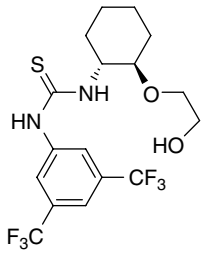
Reaction of aldimines derived from a chiral 2-phenyl-2-aminoethanol with cinnamylzinc halide is γ-selective with respect to the organozinc reagent, the PMB ether of the aldimine furnishes a linear product.[3]





(**116**) (**117A**) R = *i*-Pr (**117B**) R = Bn (**118**) (**119A**) R = Me (**119B**) R = *i*-Pr

Organoboron reagents for transfer of allyl, propargyl, aryl groups to various *N*-substituted imines have been employed. These reagents can be boronates,[4,5] trifluoroborates,[6] boronic acids,[7,8,9] boroxins,[10] and tetraarylborates,[11,12] whereas the *N*-protecting group can be phosphonyl, sulfonyl, or aryl (in the case of aryliminoacetic esters and amides). Copper and rhodium complexes are most frequently employed together with ligands as diversified as **54B**,[4,5] *ent*-**21C**,[6] **116**,[7] **117A**,[8] **118**,[9]**119B**,[10] *ent*-**21B**,[11a] and **119A**.[11b] Enantioselective Petasis reaction to form β,γ-unsaturated α-amino amides reaps benefit from participation of **120**.[12]

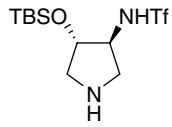


(**120**)



After extension of an isobutyl group at the end of the exocyclic double bond, a chiral ligand for Pd is created from (–)-β-pinene. The complex shows utility in allyl transfer from $Bu_3SnCH_2CH{=}CH_2$ to imines.[13]

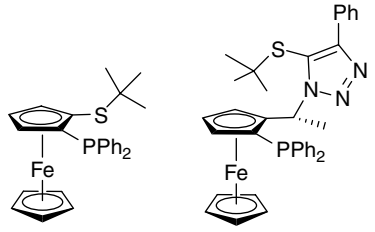
To modify the traditional Mannich reaction into a version to produce chiral products many catalysts have been developed. Thus the simple amino acid derivative threonine *t*-butyl ether in conjunction with DMAP and a thiourea is able to achieve the desired effect.[14] Besides enantioselectivity, diastereoselectivity in favor of generating isomers of the *anti*-configuration is observed for reaction catalyzed by **121**.[15] Also *anti*-selective is found in the decarboxylative addition of half-thioester of an α-substituted malonic acid, catalyzed by a C_2-symmetric di-*t*-butyl bicyclic guanidine.[16]



(**121**)

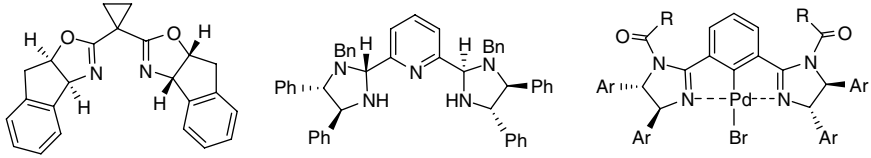
The copper-catalyzed Mannich reaction concedes to dominance by chiral phosphine ligands ranging from the Segphos (**25**) type[17] to the ferrocene-based Fesuphos (**122**).[18]

A cognate **123** is for chelation of Ag(I) and the proline-derived **81B** to combine with Et_2Zn to catalyze the Mannich reaction.[19,20]

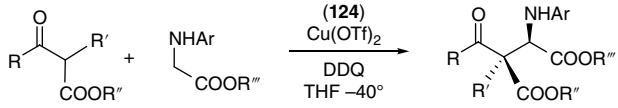


(**122**) (**123**)

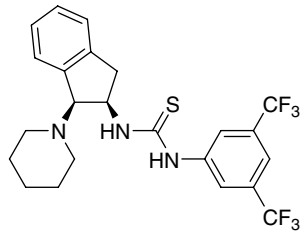
The BOX ligand **124** forms with $Cu(OTf)_2$ a valuable catalyst and it can be used to combine β-keto esters with *N*-arylglycine esters, the latter species being dehydrogenated by DDQ in situ.[21] Predominantly 2*S*,3*R*-diamino esters are obtained from a reaction between an *N*-diphenylmethyleneglycine ester and an *N*-(4-nitrobenzenesulfonyl)aldimine when it is under charge of **125**.[22] Both the pincer complex **126A** and AgOAc play an important role in the condensation of alkyl cyanides and *N*-tosylaldimines.[23]



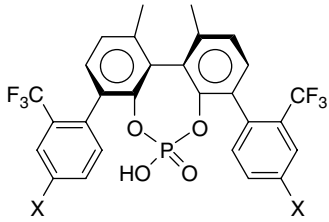
(**124**) (**125**) (**126A**) Ar = Mes, R = Ph
(**126B**) Ar = 1-Np, R = Me



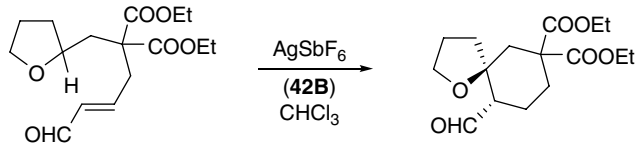
Malonitrile adds to both an enone and an imine unit of β-(*o*-alkylideneaminoaryl) ketones to afford tetrahydroquinolines, the tandem Michael and Mannich reaction sequence is efficient and subject to enantiocontrol by catalysts such as **127**.[24] The tetrahydroquinoline synthesis depending on a 1,5-hydride shift to create an ion pair for completing a Mannich reaction is also biased by initiating the reaction with a chiral Brønsted acid (e.g., **128**).[25] [The hydride shift is also featured in spiroannulation of a tetrahydrofuran derivative containing an enal unit in a C-2 sidechain, as catalyzed by $AgSbF_6$ and the hydrochloride of **42C**.[26]]



(**127**)

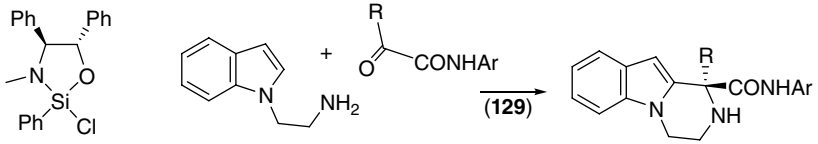


(**128**) X = CF_3, NO_2

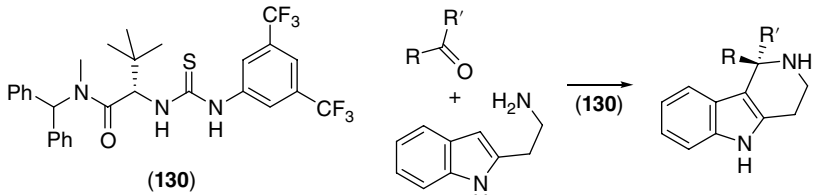


Access to 4-quinazolinones from condensation of *o*-aminobenzamide and aldehydes is easily conceived, as ring closure after the Schiff bases are formed by addition of the amide is analogous to the Mannich reaction indicated earlier. However, a new set of catalyst, i.e., the Sc(III) complex of **63** can be employed to set the stereochemical pathway.[27]

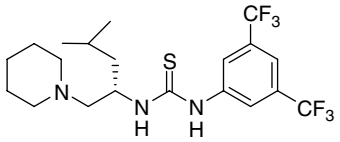
Since the Pictet-Spengler cyclization is acid-catalyzed, it is not surprising that the chiral Brønsted acid *ent*-**67B**[28] as well as chlorosilane **129**[29] prove effective for directing the enantioselective courses. By virtue of H-bonding characteristics **130** exerts chiral influences also to make itself a valuable catalyst.[30]



(**129**)



(**130**)



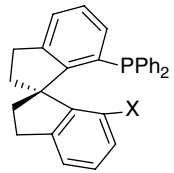
(**131**)

Aminobenzylation of arenes greatly benefits from involvement of **131**.[31] In the case of 2-trimethylsiloxypyrrole, a Ag(I)-catalyzed, *anti*-selective reaction is rendered asymmetric by **101**.[32]

Hydroacylation of aldimines on carbene-catalyzed reaction with aldehydes is placed under enantiocontrol by selecting a chiral carbene (e.g., from *ent*-**16C**).[33]

Oxidative addition of aryl triflate to Pd followed by intramolecular addition to a C=N bond successfully converts the *N*-(α-iminoalkanoyl)arylamines into 3-aminooxindoles. As a ligand for the Pd species **25C** also makes possible the acquisition of chiral products.[34]

Two different ways to promote an aza-Baylis-Hillman reaction concern with activation of the donor or the accetor. Tertiary phosphines can be used as catalysts because they perform conjugate addition to the donors and are readily eliminated after adduct formation, therefore a practice involving the chiral phosphine **132B** is reasonable.[35] The second choice of activating the acceptors is exemplified by the effect of AgOAc and **126A**.[36]



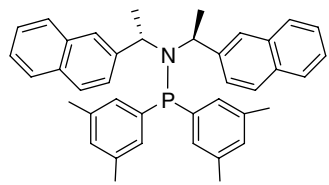
(**132A**) X = PPh_2
(**132B**) X = OH

Adduct of 3,4-dihydroisoquinoline and nitromethane is formed by catalysis of **66B**, the ee is moderate.[37]

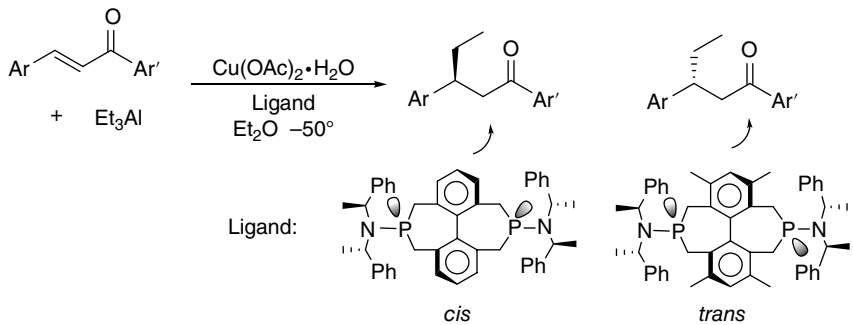
[1] Verrier, C., Carret, S., Poisson, J.-F. *OL* **14**, 5122 (2012)
[2] Lin, L., Fu, X., Ma, X., Zhang, J., Wang, R. *SL* 2559 (2012)
[3] Delaye, P.-O., Vasse, J.-L., Szymoniak, J. *OL* **14**, 3004 (2012)
[4] Vieira, E.M., Snapper, M.L., Hoveyda, A.H. *JACS* **133**, 3332 (2011)
[5] Vieira, E.M., Haeffner, F., Snapper, M.L., Hoveyda, A.H. *ACTE* **51**, 6618 (2012)
[6] Luo, Y., Hepburn, H.B., Chotsaeng, N., Lam, H.W. *ACIE* **51**, 8309 (2012)
[7] Cui, Z., Yu, H.-J., Yang, R.-F., Gao, W.-Y., Feng, C.-G., Lin, G.-Q. *JACS* **133**, 12394 (2011)
[8] Chen, J., Lu, X., Lou, W., Ye, Y., Jiang, H., Zeng, W. *JOC* **77**, 8541 (2012)
[9] Shao, C., Yu, H.-J., Wu, N.-Y., Feng, C.-G., Lin, G.-Q. *OL* **12**, 3820 (2010)
[10] Nishimura, T., Noishiki, A., Tsui, G.C., Hayashi, T. *JACS* **134**, 5056 (2012)
[11a] Shintani, R., Takeda, M., Tsuji, T., Hayashi, T. *JACS* **132**, 13168 (2010)
[11b] Shintani, R., Soh, Y.-T., Hayashi, T. *OL* **12**, 4106 (2010)
[12] Inokuma, T., Suzuki, Y., Sakaeda, T., Takemoto, Y. *CAJ* **6**, 2902 (2011)
[13] Fernandes, R.A., Nallasivam, J.L. *OBC* **10**, 7789 (2012)
[14] Nugent, T.C., Sadiq, A., Bibi, A., Heine, T., Zeonjuk, L.L., Venkova, N., Bassil, B.S. *CEJ* **18**, 4088 (2012)
[15] Martin-Rapun, R., Fan, X., Sayalero, S., Bahramnejad, M., Cuervas, F., Pericas, M.A. *CEJ* **17**, 8780 (2011)
[16] Pan, Y., Kee, C.W., Jiang, Z., Ma, T., Zhao, Y., Yang, Y., Xue, H., Tan, C.-H. *CEJ* **17**, 8363 (2011)
[17] Shi, S.-L., Wei, X.-F., Shimizu, Y., Kanai, M. *JACS* **134**, 17019 (2012)
[18] Hernando, E., Arrayas, R.G., Carretero, J.C. *CC* **48**, 9622 (2012)
[19] Imae, K., Shimizu, K., Ogata, K., Fukuzawa, S. *JOC* **76**, 3604 (2011)
[20] Zhao, D., Wang, L., Yang, D., Zhang, Y., Wang, R. *ACIE* **51**, 7523 (2012)
[21] Zhang, G., Zhang, Y., Wang, R. *ACIE* **50**, 10429 (2011)

[22] Arai, T., Mishiro, A., Matsumura, E., Awata, A., Shirasugi, M. *CEJ* **18**, 11219 (2012)
[23] Hyodo, K., Nakamura, S., Tsuji, K., Ogawa, T., Funahashi, Y., Shibata, N. *ASC* **353**, 3385 (2011)
[24] Tan, H.R., Ng, H.F., Chang, J., Wang, J. *CEJ* **18**, 3865 (2012)
[25] Mori, K., Ehara, K., Kurihara, K., Akiyama, T. *JACS* **133**, 6166 (2011)
[26] Jiao, Z.-W., Zhang, S.-Y., He, C., Tu, Y.-Q., Wang, S.-H., Zhang, F.-M., Zhang, Y.-Q., Li, H. *ACIE* **51**, 8811 (2012)
[27] Prakash, M., Kesavan, V. *OL* **14**, 1896 (2012)
[28] Huang, D., Xu, F., Lin, X., Wang, Y. *CEJ* **18**, 3148 (2012)
[29] Schönherr, H., Leighton, J.L. *OL* **14**, 2610 (2012)
[30] Lee, Y., Klausen, R.S., Jacobsen, E.N. *OL* **13**, 5564 (2011)
[31] Li, G.-X., Qu, J. *CC* **48**, 5518 (2012)
[32] Ranieri, B., Curti, C., Battistini, L., Sartori, A., Pinna, L., Casiraghi, G., Zanardi, F. *JOC* **76**, 10291 (2011)
[33] DiRocco, D.A., Rovis, T. *ACIE* **51**, 5904 (2012)
[34] Tolstoy, P., Lee, S.X.Y., Sparr, C., Ley, S.V. *OL* **14**, 4810 (2012)
[35] Takizawa, S., Kiriyama, K., Ieki, K., Sasai, H. *CC* **47**, 9227 (2011)
[36] Hyodo, K., Nakamura, S., Shibata, N. *ACIE* **51**, 10337 (2012)
[37] Amarasinghe, N.R., Turner, P., Todd, M.H. *ASC* **354**, 2954 (2012)

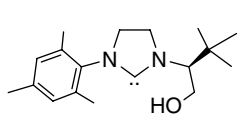
Conjugate additions. A vast body of literature concerning conjugate addition of organometallic reagents has accumulated. Alkenylaluminums add to dihydro-1-acyl- 4-pyridones to follow a 1,4-mode by intervention of copper naphthenate, with chirality direction from **133**.[1] With a demonstration using Et_3Al, the pursuit of a Cu(II)-catalyzed addition to conjugated ketones can be regulated by a subtle change of ligand structure, i.e., in the relative configuration among the pair of phosphorus atoms which lie far apart. Steric repulsion between the substrate and ligand within two alternative copper-organized transition states is the determinant.[2]



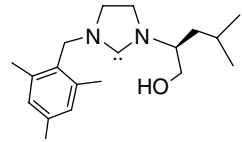
(**133**)



A ligand analogous to **3** (OMe replaced by an *o*-diphenylphosphinophenoxy moiety) guides an enantioselective 1,4-addition of Grignard reagents to 2-cyclohexenone.[3] The same regioselectivity is observed in the reaction of 3-alkenyl- and 3-alkynyl-2-cyclohexenones, using copper-carbene **134** complex (nucleophilic attack occurs at the fully substituted carbon and not at the sidechain).[4] Carbene derived from **135** seems best to pair with $Cu(OTf)_2$ to catalyze the addition. It features an optimal combination of *N*-substituents, one being 2,4,6-trimethylbenzyl and the other a primary alcohol created from leucine.[5]



(**134**)



(**135**)

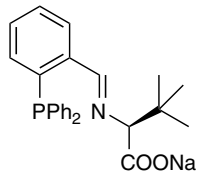
A series of C_2- and C_1-symmetric analogs of TADDOL with one or two sulfur substituents to coordinate the copper ion to catalyze conjugate addition of Grignard reagents are now available.[6]

A sequence of conjugate addition and trapping, the latter step with *N*-Boc isopropoxymethylamine, serves to establish two new stereocenters, as shown by reaction with RMgBr together with a copper salt and **91**.[7]

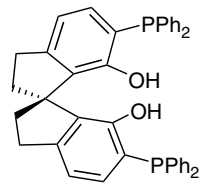
Introduction of an alkynyl group to conjugated thioamides also relies on copper catalysis and lithium 4-methoxyphenoxide. The effective chiral ligand for the addition is **39B**.[8] It operates on the action of a soft Lewis acid and a hard Brønsted base.

Also with a copper catalyst, diorganozincs undergo addition to conjugated ketones. In the system of an extended conjugation that 2-cyclohexenone is substituted at C-3 with a propenyl group, 1,6-addition proceeds, and asymmetric amplification (nonlinear effect) is observed (ligand: **136**).[9]

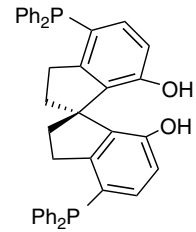
Very interesting variations of ligands to manipulate enantioselectivity (opposite enantiomers to be formed) in conjugate addition of diorganozincs are the following: **137** vs. **138**,[10] **139A** vs. **139B**.[11]



(**136**)

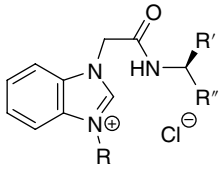


(**137**)

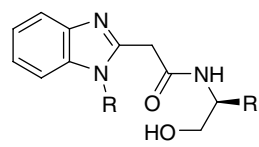


(**138**)

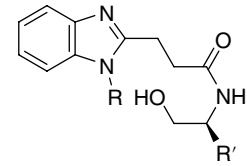
Due to differences in ligand exchange the nature of the copper precatalyst [$Cu(OTf)_2$ vs. $Cu(acac)_2$] in combination with either ligand **140** or **141** has dramatic consequences.[12]



(**139A**) R″ = CH_2OH
(**139B**) R″ = COOR‴

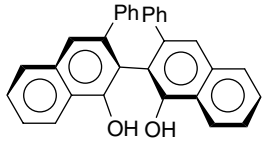


(**140**)

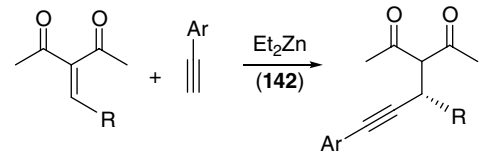


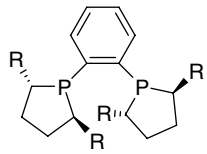
(**141**)

Preparation of chiral 5-alkyn-2-ones with branching at C-4 can be achieved via alkyne addition to 3-alkylidene-2,4-pentanediones in the presence of **142**, and deacetylation afterwards.[13] Similarly, 1,6-addition to 2,4-alkadienoic acid derivatives (esters, amides) affords the 2-en-6-yne adducts chiral at C-5; in this case $Co(OAc)_2$ and **143** form a chiral catalyst.[14]

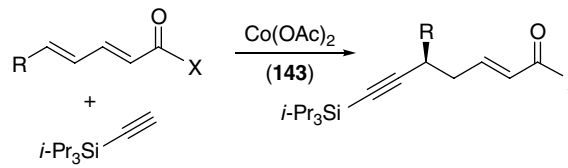


(**142**)



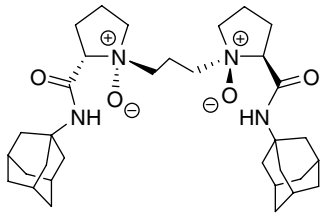


(**143**) R = Me, Et

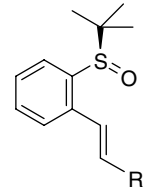


A Cu-Yb bimetallic triflate catalyzes allyl group transfer from an allylstannane to the coumarin ring. The hard Lewis acid and ligand **144** must be responsible for the stereoinduction.[15]

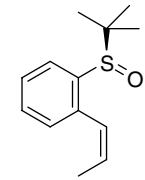
Rh(I)-based chiral catalysts for promoting reaction of $ArB(OH)_2$ with conjugated ketones can be assembled in numerous ways, with stilbenes **145A/145B**[16,17] and styrenes **145C** and **146**,[18] diphosphine **33B**,[19] **147**,[20] and **25C**.[21] The (*E/Z*)-isomeric pair of **145C** and **146** prompt the generation of products with (*S*)- and (*R*)-configuration, respectively.



(**144**)



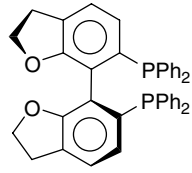
(**145A**) R = Ph
(**145B**) R = 4-FC_6H_4
(**145C**) R = Me



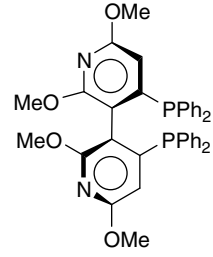
(**146**)

The benzyl bromide salt of a 3-pyridinecarboxylic ester exposes itself to attack by $ArB(OH)_2$ at C-6 because the position is less hindered. This addition can be considered as of 1,2- or 1,6-mode, but in any case it is subject to asymmetric induction by **148** [with a Rh(I) salt].[22]

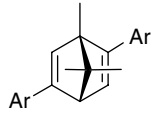
Bridged bicyclic dienes to complement Rh(I) has gained some popularity also. For conjugate addition **149A** and **149B** have been employed.[23,24] The Rh(I) complex of **150A** is serviceable in an addition to alkenyl sulfones.[25] As the coordination chemistry of iridium and rhodium ions is quite similar, these chiral dienes are suitable for iridium. A pairing (e.g., with **150B**) for catalyzing conjugate addition is well within expectation.[26]



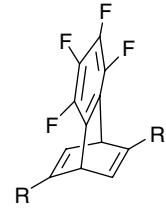
(**147**)



(**148**)

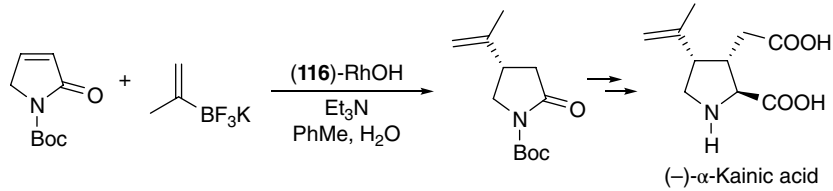


(**149A**) Ar = 4-$O_2NC_6F_4$
(**149B**) Ar = 1-Np

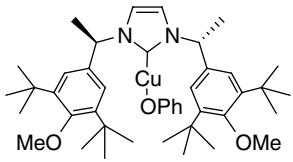


(**150A**) R = Ferrocenyl
(**150B**) R = COO(2-Np)

With diene **116** to form a catalyst with RhOH to effect the addition of potassium 2-propenyltrifluoroborate on *N*-Boc 3-pyrrolin-2-one at the starting point, a synthesis of (–)-α-kainic acid is completed in 7 steps (40% yield).[27]



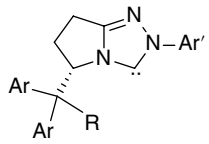
β-Substituted cyclohexenones undergo enantioselective hydroarylation, besides **14A**-complexed $PdCl_2$, a supplementary catalyst is $AgSbF_6$.[28] In the addition of an alkyl-BBN to conjugated ketones, the copper phenoxide adduct **151** has passed the test for effectiveness.[29]

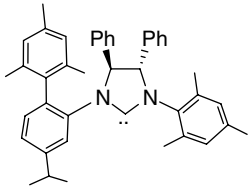


(**151**)

Hydroboration of conjugated ketones and esters is realized by reaction with $B_2(pin)_2$. The copper-catalyzed version can take advantage of chiral induction by **85**,[30] or **32B**.[31] If a 2-alkynoic ester is used as the substrate the copper-catalyzed hydroboration can still give chiral β-boryl carboxylates via further hydrosilylation, as the ligand **36** being still influential.[32]

Asymmetric delivery of the boryl group to *N*-(2-alkenoyl)-2-oxazolidinones can be accomplished in the presence of Cu_2O and carbene **152C**.[33] or only the carbene **153** without metal ion (and for many conjugated systems).[34]





(**153**)

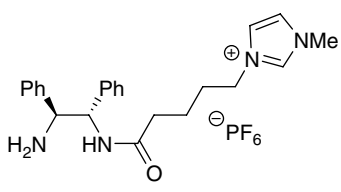
(**152A**) Ar = Ph, Ar′ = 2,6-$(MeO)_2C_6H_3$, R = H
(**152B**) Ar = 3,5-$(F3C)_2C_6H_3$, Ar′ = Bn, R = OH
(**152C**) Ar = Ph, Ar′ = [2.2]paracyclophane, R = OH
(**152D**) Ar = Ph, Ar′ = 2-(iPr)C_6H_4, R = OTBS

Conjugate hydrophosphonylation by $Ar_2P(=O)H$ is catalyzed by a chelate derived from **81B** and diethylzinc.[35]

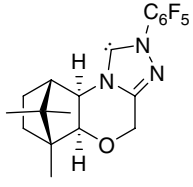
[1] Müller, D., Alexakis, A. *OL* **14**, 1842 (2012)
[2] Yu, H., Xie, F., Ma, Z., Liu, Y., Zhang, W. *ASC* **354**, 1941 (2012)
[3] Naeemi, Q., Dindaroglu, M., Kranz, D.P., Velder, J., Schmalz, H.-G. *EJOC* 1179 (2012)
[4] Tissot, M., Poggiali, D., Henon, H., Müller, D., Guenée, L., Maudit, M., Alexakis, A. *CEJ* **18**, 8731 (2012)

[5] Germain, N., Magrez, M., Kehrli, S., Mauduit, M., Alexakis, A. *EJOC* 5301 (2012)
[6] Pichota, A., Gramlich, V., Beck, A.K., Seebach, D. *HCA* **95**, 1239 (2012)
[7] Bilcik, F., Drusan, M., Marak, J., Sebesta, R. *JOC* **77**, 760 (2012)
[8] Yazaki, R., Kumagai, N., Shibasaki, M. *CAJ* **6**, 1778 (2011)
[9] Magrez, M., Wencel-Delord, J., Alexakis, A., Crevisy, C., Mauduit, M. *OL* **14**, 3576 (2012)
[10] Endo, K., Hamada, D., Yakeishi, S., Ogawa, M., Shibata, T. *OL* **14**, 2342 (2012)
[11] Yoshimura, M., Shibata, N., Kawakami, M., Sakaguchi, S. *T* **68**, 3512 (2012)
[12] Shibata, N., Yoshimura, M., Yamada, H., Arakawa, R., Sakaguchi, S. *JOC* **77**, 4079 (2012)
[13] Blay, G., Cardona, L., Pedro, J.R., Sanz-Marco, A. *CEJ* **18**, 12966 (2012)
[14] Sawano, T., Ashouri, A., Nishimura, T., Hayashi, T. *JACS* **134**, 18936 (2012)
[15] Kuang, Y., Liu, X., Chang, L., Wang, M., Lin, L., Feng, X. *OL* **13**, 3814 (2011)
[16] Qi, W.-Y., Zhu, T.-S., Xu, M.-H. *OL* **13**, 3410 (2011)
[17] Xue, F., Li, X., Wan, B. *JOC* **76**, 7256 (2011)
[18] Chen, G., Gui, J., Cao, P., Liao, J. *T* **68**, 3220 (2012)
[19] Trost, B.M., Burns, A.C., Tautz, T. *OL* **13**, 4566 (2011)
[20] Mino, T., Hashimoto, M., Uehara, K., Naruse, Y., Kobayashi, S., Sakamoto, M., Fujita, T. *TL* **53**, 4562 (2012)
[21] Berhal, F., Wu, Z., Gênet, J.-P., Ayad, T., Ratovelomanana-Vidal, V. *JOC* **76**, 6320 (2011)
[22] Nadeau, C., Aly, S., Belyk, K. *JACS* **133**, 2878 (2011)
[23] Liu, C.-C., Janmanchi, D., Chen, C.-C., Wu, H.-L. *EJOC* 2503 (2012)
[24] Wei, W.-T., Yeh, J.-Y., Kuo, T.-S., Wu, H.-L. *CEJ* **17**, 11405 (2011)
[25] Nishimura, T., Takiguchi, Y., Hayashi, T. *JACS* **134**, 9086 (2012)
[26] Nishimura, T., Noishiki, A., Hayashi, T. *CC* **48**, 973 (2012)
[27] Yu, H.-J., Shao, C., Cui, Z., Feng, C.-G., Lin, G.-Q. *CEJ* **18**, 13274 (2012)
[28] Gottumukkala, A.L., Matcha, K., Lutz, M., de Vries, J.G., Minnaard, A.J. *CEJ* **18**, 6907 (2012)
[29] Yoshida, M., Ohmiya, H., Sawamura, M. *JACS* **134**, 11896 (2012)
[30] Kobayashi, S., Xu, P., Endo, T., Ueno, M., Kitanosono, T. *ACIE* **51**, 12763 (2012)
[31] Sole, C., Tatla, A., Mata, J.A., Whiting, A., Gulyas, H., Fernandez, E. *CEJ* **17**, 14248 (2011)
[32] Jung, H.-Y., Feng, X., Kim, H., Yun, J. *T* **68**, 3444 (2012)
[33] Zhao, L., Ma, Y., Duan, W., He, F., Chen, J., Song, C. *OL* **14**, 5780 (2012)
[34] Wu, H., Radomkit, S., O'Brien, J.M., Hoveyda, A.H. *JACS* **134**, 8277 (2012)
[35] Zhao, D., Wang, L., Yang, D., Zhang, Y., Wang, R. *CAJ* **7**, 881 (2012)

The traditional Michael addition involves stabilized and semi-stabilized carbanionic species. The monoamide of a C_2-symmetric diamine with an ionic liquid tether (**154**) has been examined for its ability to catalyze asymmetric conjugate addition toward synthesis of (*S*)-warfarin from 4-hydroxycoumarin, a 80% ee of the adduct was observed.[1] Prepared from *exo*-3-aminoisoborneol the carbene **155** unites β-dicarbonyl compounds and conjugated aldehydes to create 5-acyl-3,4-dihydro-2-pyrones.[2]



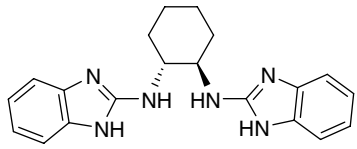
(**154**)



(**155**)

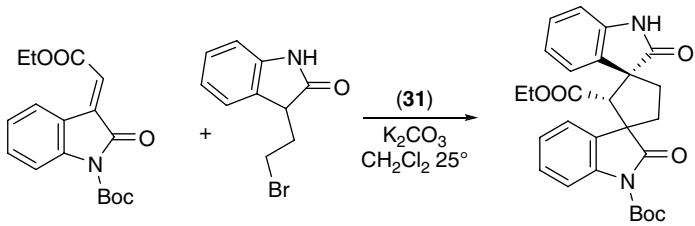
At the conclusion of the addition that combines α-nitro ketones with 2-oxo-3-alkenoic esters, an acyl group transfer occurs on catalysis by **66C**.[3] A union of α-isocyano esters and maleimides is set to absolute order of chirality by the *cis*-isomer of **66C**.[4]

Different members of the **66** series serve well in the conjugate addition of malonic esters[5,6] and α-cyano esters.[7] Favorable cross-coordination of the Michael acceptor to a metal chelate is evident in 2-alkenoylpyridine *N*-oxides, therefore the complex constituting $Zn(OTf)_2$ and *ent*-**124** is useful for catalyzing their reaction with malonate.[8] Presence of multiple NH groups in **156** apparently is critical to organizing the transition state that malonate and maleimide adopt for their union.[9] For bringing oxindole and maleimide into formation of an adduct in diastereoselective and enantioselective manner, **31** a C_2-symmetric bicyclic guanidine ligand has the required attributes.[10]



(**156**)

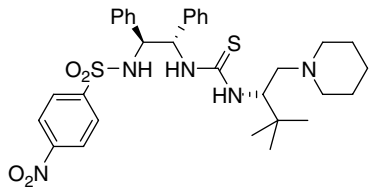
Thanks to intervention of *ent* **31** the linking of two oxindole systems together by spiroannulation via a tandem Michael addition-intramolecular alkylation sequence is rendered asymmetric.[11]



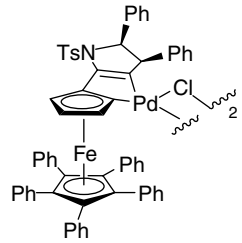
3-Hydroxyoxindole combines with phenyl 2-alkenoates, under the influence of the Et_2Zn chelate of **81A** realizes a spirolactonization.[12]

Carbonylated 5-membered heterocycles such as 2-phenyl-4-oxazolinones, 4-aryl-3-buten-4-olides, 5-pyrazolinones, and the azlactones are genuine Michael donors, and their reactions are subject to stereocontrol. Thus thiourea **157** derived from *t*-leucine shows its ability as an organocatalyst for the Michael addition,[13] and **103B** directs a 1,8-addition of the butenolides to *N*-(2,4,6-alkatrienoyl)pyrroles.[14] The identification of palladacycle **158** as catalyst for azlactones is quite remarkable.[15]

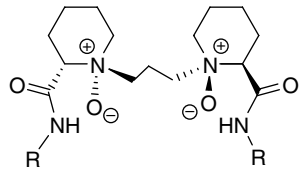
Chelate of $Sc(OTf)_3$ and **144** is found to catalyze the addition of 1-phenyl-5-pyrazolinones to aryl ethynyl ketones. The double bond of the chiral adducts has a (*Z*)-configuration.[16] The complex of the much simpler ligand **159A** with $Gd(OTf)_3$ is the catalyst to be used to conduct the similar addition of pyrazolinones to azodicarboxylates.[17]



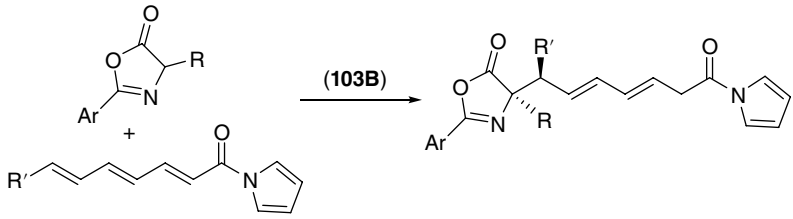
(**157**)



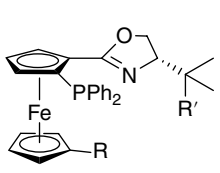
(**158**)



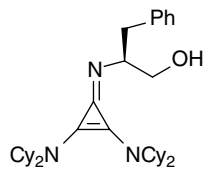
(**159A**) R = Ph
(**159B**) R = 2,6-(*i*Pr)$_2$C$_6$H$_3$
(**159C**) R = CH_2CH_2Ph
(**159D**) R = $CHPh_2$
(**159E**) R = (*S*)-CH(Me)Ph



An obvious synthetic approach to chiral α-amino acids starts from asymmetric alkylation or Michael addition of an NH-masked glycine ester such as the Schiff base with benzophenone. Suitable for copper-catalyzed processes are ligands **160** and **7B**.[18,19] Among organocatalysts the cyclopropenone imine **161** is structurally distinguished.[20]



(**160A**) R = R′ = H
(**160B**) R = P(3,5-Me$_2$C$_6$H$_3$)$_2$
R′ = Me



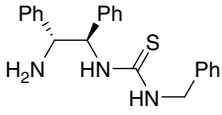
(**161**)

A method for 3,4-dihydropyridone synthesis in a chiral form from arylacetic acids and conjugated imines is via activation of the acids as mixed anhydrides to acylate the benzolog of **8** (or *ent*-**8**), and engaging the derived enolates in the addition.[21] The enolate of 3-butenenitrile adds to conjugated thioamides with its terminal carbon. As these reactions are catalyzed by copper salts, the use of diphosphine ligands such as **25B** to

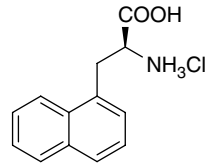
generate chiral adducts (double bond moved into conjugation with the cyano group) is quite natural, although the (*Z*)-configuration of the double bond probably is not easily predicted.[22]

For aldehydes and ketones, C_2-symmetric 1,2-diamine-derived thioureas (**41C**,**162**) are found to be excellent catalysts.[23,24] The former compound with a long fluorous appendage makes it readily recyclable. The HCl salt of amino acid **163** helps α-methylalkanals to form chiral adducts with azodicarboxylic esters.[25]

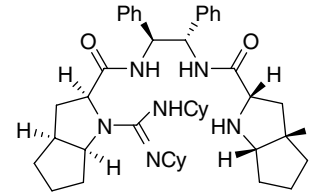
By incorporating one of the pyrrolidinyl unit of a C_2-symmetric 1,2-diamine into a guanidine the resulting compound **164** performs superbly in assembling *N*-Boc pyrrolinone and alkylidenemalonic esters in a highly enantioselective and diastereoselective (*syn*-) manner.[26]



(**162**)

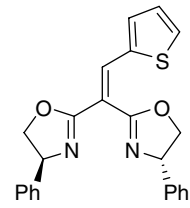


(**163**)



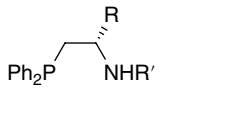
(**164**)

A carbon chain is quite easily stitched onto C-3 of indole and derivatives by Michael addition. To establish a chirality center at the new "benzylic" position several options of catalyst are available, recent examples being the $Y(OTf)_{23}$– **159B**[27] and $Cu(OTf)_2$ – **165**[28] combinations. Adding an *o*-hydroxyaryl group by using a phenol follows the similar pattern and the $Sc(OTf)_3$ chelate of **144** is a serviceable catalyst.[29]

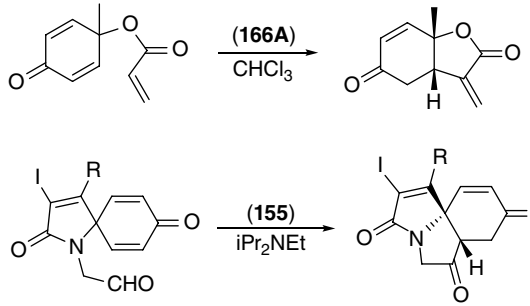


(**165**)

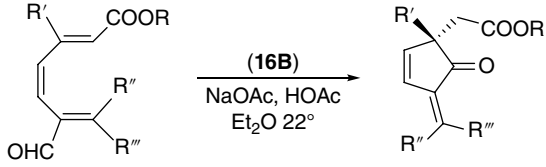
A double Michael addition initiated by aminophosphine **166A** is to engage the acrylate moiety of a 4-acryloxy-2,5-cyclohexadienone as the donor group, and the chirality of the catalyst is transmitted at the selection of one double bond.[30] Intramolecular hydroacylation by a Stetter reaction catalyzed by **155**[31] or **16A**[32] is based on the intimate intervention of carbene catalysts which perform umpolung.



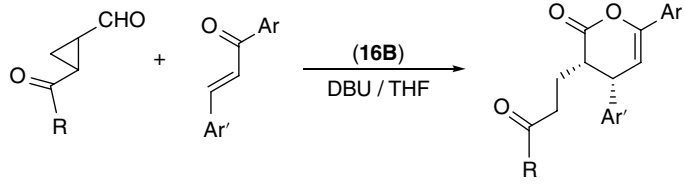
(**166A**) R = *i*-Pr, R′ = Ts
(**166B**) R = Bn,
R′ = C(=S)NHCHPh$_2$



Another mode of intramolecular 1,4-hydroacylation converts 6-formyl-2,4,6-alkatrienoic esters into 2-alkylidene-3-cyclopentenone-5-acetic esters in the presence of **16B**.[33]



Whereas all the above examples deal with acceptors possessing at least one β-substituent, it is possible to synthesize γ-oxoalkanoic esters with an α-asymmetric carbon by the same method (e.g. using catalyst **152A**).[34] Spirolactonization of isatin by reaction with conjugated aldehydes is enabled by **152B**.[35] 5-Acyl-3,4-dihydro-2-pyrone synthesis from β-dicarbonyl compounds and 2-alkynals is dependent on oxidative transformation of the formyl group by a carbene (e.g., **16B**), the same results can be obtained using enals if a mild oxidant (such as a 4,4′-bibenzoquinone) is provided.[36] 2-Acylcyclopropanecarbaldehydes form reactive adducts with carbenes via ring opening, and such species can be intercepted by conjugated ketones.[37]



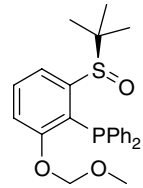
Sulfonimides also react with enals to form the *N*-sulfonyl-2,3-dihydropyridones.[38] The allylic carbon of the imines is involved in the CC bond formation.

The enantioselective addition of nitroalkanes to conjugated ketones has been investigated with the catalyst composed of Boc-L-Phe and the Phe-derived diamine in which the terminal amino group is *exo*-linked to C-2 of the bornyl framework.[39]

[1] Kucherenko, A.S., Sigutkin, D.E., Nigmatov, A.G., Chizhov, A.O., Zlotin, S.G. *ASC* **354**, 3078 (2012)
[2] Rong, Z.-Q., Jia, M.-Q., You, S.-L. *OL* **13**, 4080 (2011)
[3] Lu, R., Yan, Y., Wang, J., Du, Q., Nie, S., Yan, M. *JOC* **76**, 6230 (2011)
[4] Bai, J.-F., Wang, L.-L., Peng, L., Guo, Y.-L., Jia, L.-N., Tian, F., He, G.-Y., Xu, X.-Y., Wang, L.-X. *JOC* **77**, 2947 (2012)
[5] Moritaka, M., Miyamae, N., Nakano, K., Ichikawa, Y., Kotsuki, H. *SL* 2554 (2012)
[6] Dudzinski, K., Pakulska, A.M., Kwiatkowski, P. *OL* **14**, 4222 (2012)
[7] Liao, Y.-H., Liu, X.-L., Wu, Z.-J., Du, X.-L., Zhang, X.-M., Yuan, W.-C. *ASC* **353**, 1720 (2011)
[8] Ray, S.K., Singh, P.K., Singh, V.K. *OL* **13**, 5812 (2011)
[9] Gomez-Torres, E., Alonso, D.A., Gomez-Bengoa, E., Najera, C. *OL* **13**, 6106 (2011)
[10] Li, L., Chen, W., Yang, W., Pan, Y., Liu, H., Tan, C.-H., Jiang, Z. *CC* **48**, 5124 (2012)
[11] Sun, W., Zhu, G., Wu, C., Hong, L., Wang, R. *CEJ* **18**, 6737 (2012)
[12] Trost, B.M., Hirano, K. *OL* **14**, 2446 (2012)
[13] Huang, H., Zhu, K., Wu, W., Jin, Z., Ye, J. *CC* **48**, 461 (2012)
[14] Uraguchi, D., Yoshioka, K., Ueki, Y., Ooi, T. *JACS* **134**, 19370 (2012)
[15] Weber, M., Peters, R. *JOC* **77**, 10846 (2012)
[16] Wang, Z., Chen, Z., Bai, S., Li, W., Liu, X., Lin, L., Feng, X. *ACIE* **51**, 2776 (2012)
[17] Yang, Z., Wang, Z., Bai, S., Liu, X., Lin, L., Feng, X. *OL* **13**, 596 (2011)
[18] Strohmeier, M., Leach, K., Zajac, M.A. *ACIE* **50**, 12335 (2011)
[19] Shi, Y.-H., Wang, Z., Hu, B., Wang, M., Fossey, J.S., Deng, W.-P. *OL* **13**, 6010 (2011)
[20] Bandar, J.S., Lambert, T.H. *JACS* **134**, 5552 (2012)
[21] Simal, C., Lebl, T., Slawin, A.M.Z., Smith, A.D. *ACIE* **51**, 3653 (2012)
[22] Yanagida, Y., Yazaki, R., Kumagai, N., Shibasaki, M. *ACIE* **50**, 7910 (2011)
[23] Miura, T., Nishida, S., Masuda, A., Tada, N., Itoh, A. *TL* **52**, 4158 (2011)
[24] Kang, J.Y., Carter, R.G. *OL* **14**, 3178 (2012)
[25] Fu, J.-Y., Yang, Q.-C., Wang, Q.-L., Ming, J.-N., Wang, F.-Y., Xu, X.-Y., Wang, L.-X. *JOC* **76**, 4661 (2011)
[26] Yang, Y., Dong, S., Liu, X., Lin, L., Feng, X. *CC* **48**, 5040 (2012)
[27] Wang, W., Lian, X., Chen, D., Liu, X., Lin, L., Feng, X. *CC* **47**, 7821 (2011)
[28] Liu, L., Ma, H., Xiao, Y., Du, F., Qin, Z., Li, N., Fu, B. *CC* **48**, 9281 (2012)
[29] Bai, S., Liu, X., Wang, Z., Cao, W., Lin, L., Feng, X. *ASC* **354**, 2096 (2012)
[30] Takizawa, S., Nguyen, T.M.-N., Grossmann, A., Enders, D., Sasai, H. *ACIE* **51**, 5423 (2012)
[31] Jia, M.-Q., You, S.-L. *CC* **48**, 6363 (2012)
[32] Jia, M.-Q., Liu, C., You, S.-L. *JOC* **77**, 10996 (2012)
[33] Liu, G., Wilkerson, P.D., Toth, C.A., Xu, H. *OL* **14**, 858 (2012)
[34] Wurz, N.E., Daniliuc, C.G., Glorius, F. *CEJ* **18**, 16297 (2012)
[35] Sun, L.-H., Shen, L.-T., Ye, S. *CC* **47**, 10136 (2011)
[36] Zhu, Z.-Q., Zheng, X.-L., Jiang, N.-F., Wan, X., Xiao, J.-C. *CC* **47**, 8670 (2011)
[37] Lv, H., Mo, J., Fang, X., Chi, Y.R. *OL* **13**, 5366 (2011)
[38] Kravina, A.G., Mahatthananchai, J., Bode, J.W. *ACIE* **51**, 9433 (2012)
[39] Zhou, Y., Liu, Q., Gong, Y. *OBC* **10**, 7618 (2012)

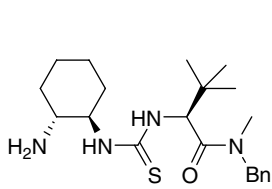
On development of synthetic methods the model addition to nitroalkenes, especially β-nitrostyrene, is much investigated. In general, catalyst systems that work for conjugated carbonyl compounds are also valid, therefore many reports are mere repetition with changing of the substrates.

Metal chelates are used for alkyl/aryl group transfer from organoboron and related compounds to nitroalkenes. Examples are Rh(I) complexes with **167**.[1] The Et_2Zn – **81C** chelate has been identified for the reaction with 4-oxazolinones.[2]

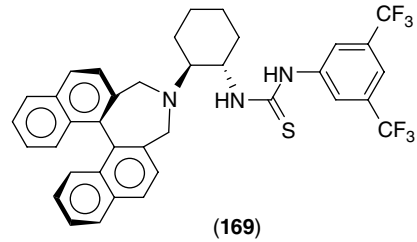


(**167**)

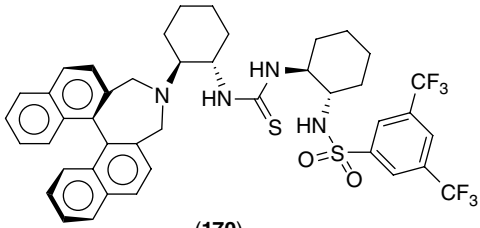
The **66** series of thioureas are popular catalysts for conjugate addition to nitroalkenes with various donors,[3,4,5] even in a reaction in liquid CO_2.[6] Catalysts with an additional chiral element are **168**,[7] **169**,[8] and **170**.[9] There is also **171** which is derived from aspartic acid di-*t*-butyl ester.[10]



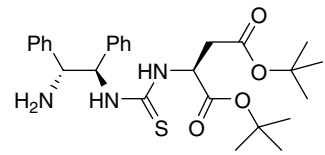
(**168**)



(**169**)



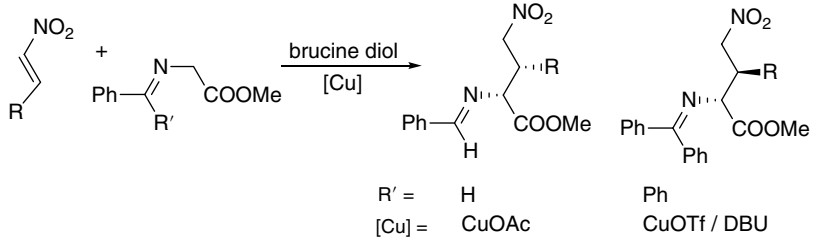
(**170**)



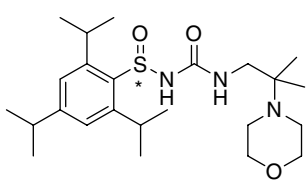
(**171**)

Catalyst **172** for addition to 2-nitro-1-alkenes, the chiral sulfoxide determines enantioselective protonation of the nitronate intermediates.[11]

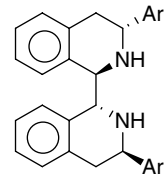
Options for enantioselective addition of *N*-alkylideneglycine esters to nitroalkenes are several with respect to useful catalysts. For example, the AgOAc – **123** pairing[12] and a Cu(I) salt with brucine diol.[13] In the latter reaction the *syn/anti*-diastereoselectivity issue is happily resolved, as slight change of the donor structure and the copper salt can lead to one of the desired isomers.



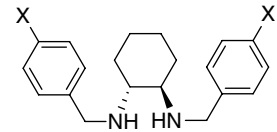
Nickel salts have also been evaluated as catalysts. With $NiBr_2$ and ligand **173**[14] or **174 (A+B)**[15] asymmetric addition of malonic esters and β-keto esters can be accomplished. In the latter ligand pair one half of the otherwise identical bidentate ligands is linked to mesoporous silica so that easy recovery is achieved.



(**172**)

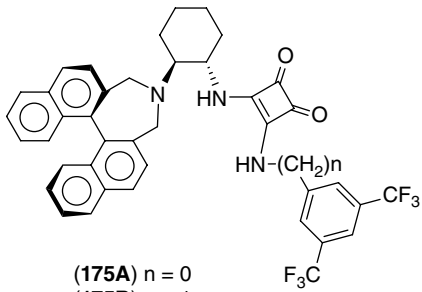


(**173**)

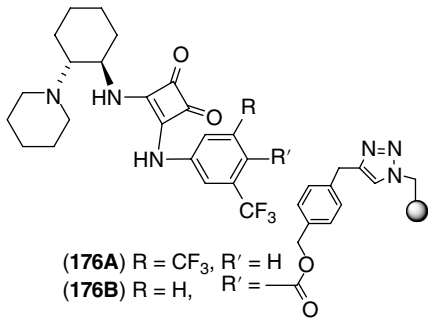


(**174A**) X = H
(**174B**) X = $Si(Me)_2O$-silica

Both **175** and **176** contain structural motifs established for maximal catalytic activities, i.e., a trifluorophenylamine and a chiral 1,2-cyclohexanediamine unit. With **175** the β-keto acid donor undergoes decarboxylation before the products are isolated;[16] **176B** is quite easy to prepare using a click reaction as the immobilization step.[17]

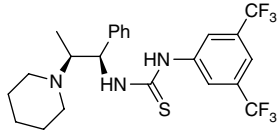


(**175A**) n = 0
(**175B**) n = 1

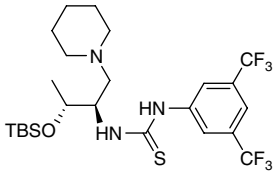


(**176A**) R = CF_3, R′ = H
(**176B**) R = H, R′ =

Besides C_2-symmetric 1,2-diamines many others have been derivatized into the monothiourea products and tested for asymmetric synthesis. In the present context **177**,[18] **178**,[19] and **179**[20] are such examples. These thioureas are versatile catalysts, as shown by a synthesis of a multifunctional cyclohexane (six contiguous stereocenters established in one operation) from a β-keto ester, an enal, and a nitroalkene (catalyst: **177**).

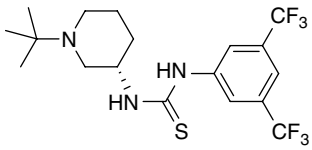


(**177**)

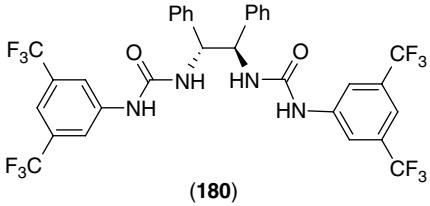


(**178**)

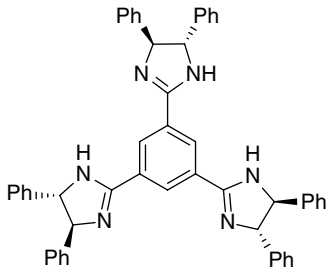
α-Keto sulfonium ylides and nitroalkenes combine to afford 5-acyl-2-oxazolidinones as a result of sulfide extrusion and rearrangement. The chiral version of this transformation is realized in the presence of **180**.[21] The C_3-symmetric tris(imidazoline) **181** performs better than the bis(imidazoline) analog as catalyst.[22]



(**179**)

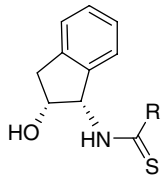


(**180**)

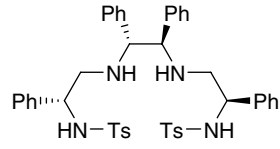


(**181**)

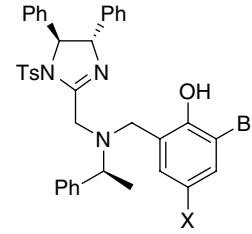
Addition of indole to nitroalkenes can use organocatalysts alone or metal chelates. Thus **182A**[23] and *ent*-**182B**[24,25] are in the former category and their effects are related to strong H-bondings to put the substrates in order, and $Cu(OTf)_2$ ligated to **183**[26] or **184A**[27] exerts influences in the metal's coordination sphere.



(**182A**) R = 3,5-$(CF_3)_2C_6H_3NH$
(**182B**) R = 2-quinolinyl

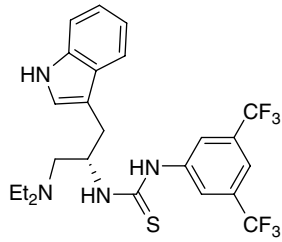


(**183**)

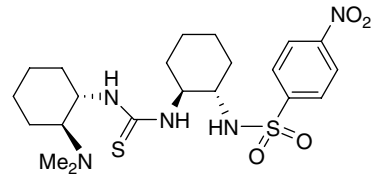


(**184A**) X = NO_2
(**184B**) X = Br

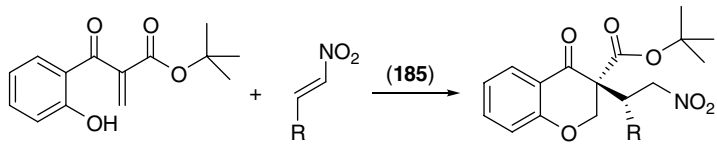
Two more thiourea catalysts are **185**[28] and **186**.[29] Their application to chroman synthesis starts from addition of *o*-substituted phenols.



(**185**)

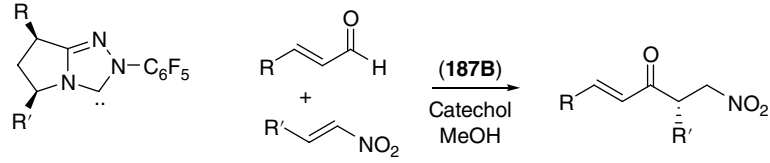


(**186**)

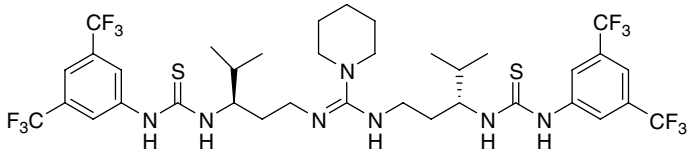


The fluorine-containing carbene **187B** converts aldehydes into Michael donors, thus it is easy to synthesize 1-nitro-3-alkanones with a chirality center at C-2.[30] Alkenals react to give the corresponding nitroalkenones.[31] During the reaction, monoionized catechol is able to enhance the catalytic efficiency, as perhaps by maintaining the sp^3 character of the carbinolate in the aldehyde-carbene adducts. The less delocalized state does not react as a homoenolate, otherwise an enal would behave as ester β-carbanion (involving a more electron-rich carbene).[32]

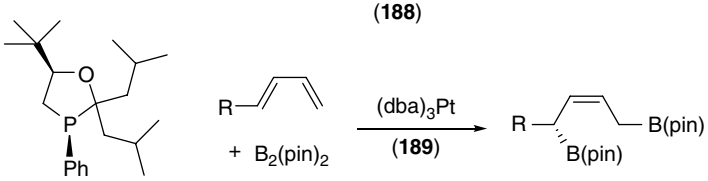
A study of the addition of diphenyl phosphite to nitroalkenes using an organocatalyst (**188**) containing guanidine and thiourea fragments shows the possibility of tuning by the reaction media. Different catalyst assembly is indicated for reaction in toluene-water (2:1) and toluene alone. Both guanidine and thiourea units are essential for obtaining high yields and ee.[33]



(**187A**) R = H, R′ = C_6H_{11}
(**187B**) R = F, R′ = *i*-Pr



(**188**)



(**189**)

That 1,1-bis(benzenesulfonyl)ethene is an excellent Michael acceptor is well known. The adducts with α-branched aldehydes are versatile synthetic intermediates because they possess two valuable functionalities. The chiral addicts are acquired by conducting the Michael reaction in the presence of the primary nonafluorobutanesulfonamide of valine-derived diamine.[34] Another combination is that which involves addition of oxindole (catalyst: **175**).[35]

Synthesis of β,γ-disubstituted γ-lactams from conjugated imines and enals benefits from a cooperative maneuver of Brønsted acid and carbene (e.g., **187A**).[36] As for addition to azodicarboxylates, useful catalysts are **176A**[37] and $Cu(OTf)_2$ - **71**.[38]

Bromoamination of chalcones via aziridinium intermediates gives rise to α-amino-β-bromo adducts, to reverse the regioselectivity it requires formation of bromonium ions. This can be achieved by using $Sc(OTf)_3$, **159C** and 4Å-molecular sieves to promote the proper events.[39]

Various rhodacycles derived from C_2-symmetric benzene-1,3-dioxazolines are catalysts for hydrosilylation of 3,3-diarylacrylic esters.[40] Asymmetric 1,4-reduction by copper hydrides is achieved with Josiphos, but the reaction switches to the 1,2-reduction modes in changing to a Segphos ligand.[41]

cis-1,4-Dihydroxylation of 1,3-cyclohexadienes is accomplished via the diboration, an asymmetric version is managed by a TADDOL-based phenylphosphine.[42] Similarly, 1,3-alkadienes yield (*Z*)-1,3-diboryl-2-alkenes, although the ligand (**189**) is different.[43]

For intramolecular hydroamination of 7-arenesulfonylamino-1,3-heptadienes by catalysis of $AgBF_4$ and **25B** complex of AuCl it also needs 2 equivalents of (–)-menthol to attain

a high level of ee (95%). The effect is attributed to a coordination to Au(I) to generate an essential Brønsted acid.[44] Without menthol there is no asymmetric induction.

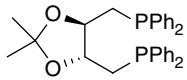
[1] Xing, J., Chen, G., Cao, P., Liao, J. *EJOC* 1230 (2012)
[2] Trost, B.M., Hirano, K. *ACIE* **51**, 6480 (2012)
[3] Yang, G., Luo, C., Mu, X., Wang, T., Liu, X.-Y. *CC* **48**, 5880 (2012)
[4] Sun, Z.-W., Peng, F.-Z., Li, Z.-Q., Zou, L.-W., Zhang, S.-X., Li, X., Shao, Z.-H. *JOC* **77**, 4103 (2012)
[5] Raimondi, W., Basle, O., Constantieux, T., Bonne, D., Rodriguez, J. *ASC* **354**, 563 (2012)
[6] Nigmatov, A.G., Kuchurov, I.V., Siyutkin, D.E., Zlotin, S.G. *TL* **53**, 3502 (2012)
[7] Retini, M., Bergonzini, G., Melchiorre, P. *CC* **48**, 3336 (2012)
[8] Li, X., Li, Y.-M., Peng, F.-Z., Wu, S.-T., Li, Z.-Q., Sun, Z.-W., Zhang, H.-B., Shao, Z.-H. *OL* **13**, 6160, 6200 (2011)
[9] Lee, H.J., Woo, S.B., Kim, D.Y. *TL* **53**, 3374 (2012)
[10] Tsakos, M., Kokotos, C.G., Kokotos, G. *ASC* **354**, 740 (2012)
[11] Kimmel, K.L., Weaver, J.D., Lee, M., Ellman, J.A. *JACS* **134**, 9058 (2012)
[12] Imae, K., Konno, T., Ogata, K., Fukuzawa, S. *OL* **14**, 4410 (2012)
[13] Kim, H.Y., Li, J.-Y., Kim, S., Oh, K. *JACS* **133**, 20750 (2011)
[14] Wilckens, K., Duhs, M.-A., Lentz, D., Czekelius, C. *EJOC* 5441 (2011)
[15] Jin, R., Liu, K., Xia, D., Qian, Q., Liu, G., Li, H. *ASC* **354**, 3265 (2012)
[16] Moon, H.W., Kim, D.Y. *TL* **53**, 6569 (2012)
[17] Kasapar, P., Riente, P., Hartmann, C., Pericas, M.A. *ASC* **354**, 2905 (2012)
[18] Enders, D., Urbanietz, G., Cassens-Sasse, E., Keess, S., Raabe, G. *ASC* **354**, 1481 (2012)
[19] Dou, X., Han, X., Lu, Y. *CEJ* **18**, 85 (2012)
[20] Jörres, M., Schiffers, I., Atodiresei, I., Bolm, C. *OL* **14**, 4518 (2012)
[21] Lu, L.-Q., Li, F., An, J., Cheng, Y., Chen, J.-R., Xiao, W.-J. *CEJ* **18**, 4073 (2012)
[22] Murai, K., Fukushima, S., Nakamura, A., Shimura, M., Fujioka, H. *T* **67**, 4862 (2011)
[23] Marques-Lopez, E., Alcaine, A., Tejero, T., Herrera, R.P. *EJOC* 3700 (2011)
[24] Loh, C.C.J., Badorrek, J., Raabe, G., Enders, D. *CEJ* **17**, 13409 (2011)
[25] Loh, C.C.J., Raabe, G., Enders, D. *CEJ* **18**, 13250 (2012)
[26] Wu, J., Li, X., Wu, F., Wan, B. *OL* **13**, 4834 (2011)
[27] Arai, T., Awata, A., Wasai, M., Yokoyama, N., Masu, H. *JOC* **76**, 5450 (2011)
[28] Wang, H., Luo, J., Han, X., Lu, Y. *ASC* **353**, 2971 (2011)
[29] Hou, W., Zheng, B., Chen, J., Peng, Y. *OL* **14**, 2378 (2012)
[30] DiRocco, D.A., Noey, E.L., Houk, K.N., Rovis, T. *ACIE* **51**, 2391 (2012)
[31] DiRocco, D.A., Rovis, T. *JACS* **133**, 104020 (2011)
[32] Maji, B., Ji, L., Wang, S., Vedachalam, S., Ganguly, R., Liu, X.-W. *ACIE* **51**, 8276 (2012)
[33] Sohtome, Y., Horitsuge, N., Takagi, R., Nagasawa, K. *ASC* **353**, 2631 (2011)
[34] Miura, T., Yuasa, H., Murahashi, M., Ina, M., Nakashima, K., Tada, N., Itoh, A. *SL* 2385 (2012)
[35] Lee, H.J., Kang, S.H., Kim, D.Y. *SL* 1559 (2011)
[36] Zhao, X., DiRocco, D.A., Rovis, T. *JACS* **133**, 12466 (2011)
[37] Konishi, H., Lam, T.Y., Malerich, J.P., Rawal, V.H. *OL* **12**, 2028 (2010)
[38] Chang, L., Kuang, Y., Qin, B., Zhou, X., Liu, X., Lin, L., Feng, X. *OL* **12**, 2214 (2010)
[39] Cai, Y.F., Liu, X.H., Hui, Y.H., Liang, J., Wang, W.T., Chen, W.L., Lin, L.L., Feng, X.M. *ACIE* **49**, 6160 (2010)
[40] Itoh, K., Tsuruta, A., Ito, J., Yamamoto, Y., Nishiyama, H. *JOC* **77**, 10914 (2012)
[41] Voigtritter, K.R., Isley, N.A., Moser, R., Aue, D.H., Lipshutz, B.H. *T* **68**, 3410 (2012)
[42] Hong, K., Morken, J.P. *JOC* **76**, 9102 (2011)
[43] Schuster, C.H., Li, B., Morken, J.P. *ACIE* **50**, 7906 (2011)
[44] Kanno, O., Kuriyama, W., Wang, Z.J., Toste, F.D. *ACIE* **50**, 9919 (2011)

Addition to unactivated double bonds. Optically active 3-acyloxy-1-alkenes are the adducts of terminal allenes and carboxylic acids generated by Rh(I) catalyst modified by a chiral DIOP ligand (e.g., **190**).[1]

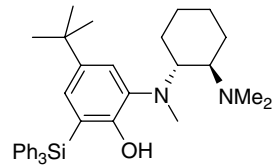
Numerous catalyst systems are available to hydroamination of alkenes. Thus addition of anilines to 1,2-alkadienes is also performed by a Rh(I) complex and another ligand (**32C**) may be employed.[2] The same regioselectivity is observed in hydroamination of alkoxyallenes which produces N,O-acetals of acrolein.[3] It being a Pd(II) catalyzed reaction and a chiral hydroamination is realized by adding ligand **33A**.

Chiral α-methyl cinnamylamines are obtained in a reaction mediated by Au-Ag catalyst and **39A** to coordinate the gold center.[4] 1-Tosylamino-4,5-alkadienes give pyrrolidine derivatives on cyclohydroamination, and higher ee of the products as occupation of the P-ligand **72** is increased from 1 to 2 to 3 by AuCl.[5]

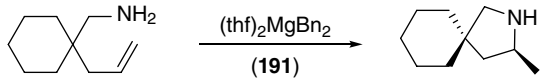
Addition of aromatic amides $ArCONH_2$ to unactivated 1-alkenes in the Markovnikov sense, catalyzed by $[(coe)_2IrCl]_2$ – (*S*)-**25B**, is carried out at 140°.[6] In the presence of the magnesium phenoxide derived from **190**, 1-allylcyclohexylmethylamine undergoes intramolecular addition to afford a spirocyclic amine in good ee value.[7]



(**190**)



(**191**)

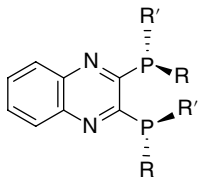


Hydroboration of alkenylarenes by pinacolborane delivers (*S*)-benzylboranes.[8] However, 2-arylalkenes furnish (*S*)-2-arylboranes on reaction with $B_2(pin)_2$ [catalyst: CuCl, **56B**, *t*-BuONa].[9] In Rh(I)-catalyzed asymmetric hydroboration with pinacolatoborane, optimization can be achieved by changing the catalyst scaffold and then the ligating groups.[10]

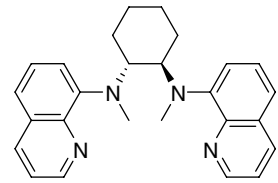
Hydrosilylation of styrenes falls into the same pattern as hydroboration, and with the rhodacycle **51** as catalyst the reaction leads to benzylsilanes of the (*S*)-configuration.[11] Alkenylhydrosilanes arise from addition of dihydrosilanes to alkynes, it changes the silicon atom into a chirality center on adding a cyclic dialkoxyphosphine of the **2A** series.[12]

A cobalt salt complexed to **192B** and zinc in DMSO constitute a system useful for mediating enantioselective addition of silylalkynes to benzannulated 1,4-oxa and azanorbornadienes.[13]

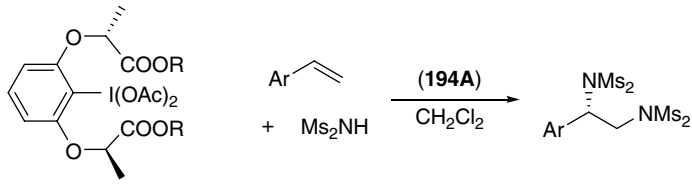
cis-Dihydroxylation of electron-deficient alkenes on reaction with Oxone becomes enantioselective by the direction of the $MnCl_2$ – **193** complex.[14] The hypervalent iodine reagent **194A** is responsible for converting styrenes and Ms_2NH into the chiral arylethanediamines.[15]



(**192A**) R = *t*-Bu, R′ = Me
(**192B**) R = Me, R′ = *t*-Bu



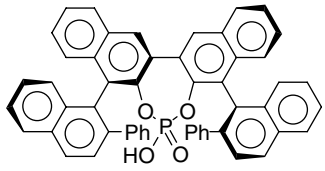
(**193**)



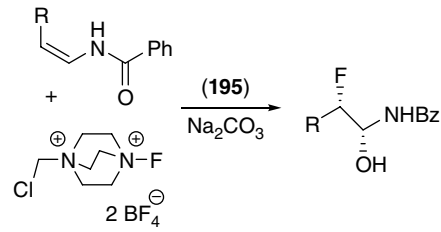
(**194A**) R = Me
(**194B**) R = (*S*)-CH(Ph)COOEt

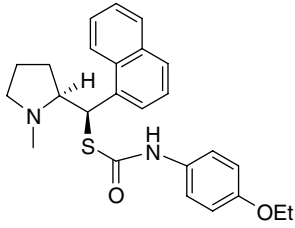
Sulfonaminoalkenes are further functionalized stereoselectively by PhI=NNs and alcohols such that α-aminocarbaldehyde O,N-acetals are created.[16] The phosphoric acid **195** motivates enamides to undergo *cis*-fluorohydrination that places the fluorine atom at C-2 of the (1*R*, 2*S*)-N,O-hemiacetal products.[17] Asymmetric halogenation of alkenes has been reviewed.[18]

Enantioselective bromolactonization of alkenoic acids has found useful catalysts such as **181**[19] and **196**,[20] whereas iodolactonization is achieved by NIS and the Brønsted base **197**.[21]

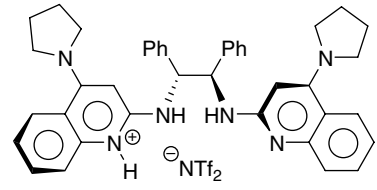


(**195**)



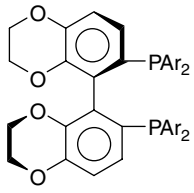


(**196**)

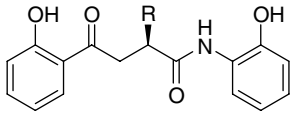


(**197**)

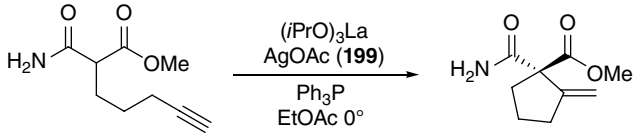
A synphos ligand (**198A**) renders the iridium(I)-catalyzed hydroalkynylation of norbornadienes enantioselective.[22] Cyclization of 2-(3-alkynyl)-1,3-dicarbonyl compounds is promoted by bimetallic systems, either $Zn(OAc)_2/Yb(OTf)_3$, **14A**, and hexafluoroisopropanol[23] or $(i\text{-PrO})_3La/AgOAc\text{-}Ph_3P$ and **199**.[24] In the former case it is thought that π–π-interaction between the aroylacetic esters and a phenyl group of the BOX ligand is at play, and in the latter circumstance specific utility of the two kinds of metal ions is to activate the respective hard and soft base sites (carbonyls and alkyne).



(**198A**) Ar = Ph
(**198B**) Ar = 3,5-$Me_2C_6H_3$

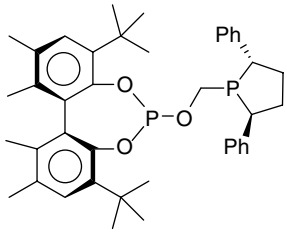


(**199**)

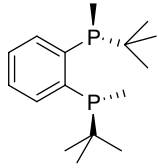


An enol silyl ether attacks intramolecularly on a metal-activated triple bond in an analogous manner. Accordingly 2-methylenecyclopentyl ketones with a chirality center at C-1 are readily acquired, e.g., by subjecting the substrates to $Pd(OTf)_2$ and **25B**.[25]

Selective formation of branched chiral aldehydes by hydroformylation of 1-alkenes is controlled by a ligand (**200**, bobphos) for the Rh(I) complex.[26] Applying the protocol that generating linear aldehydes is preferred to α-branched acrylic esters, chiral products are obtainable if diphosphines such as **201** are added.[27]

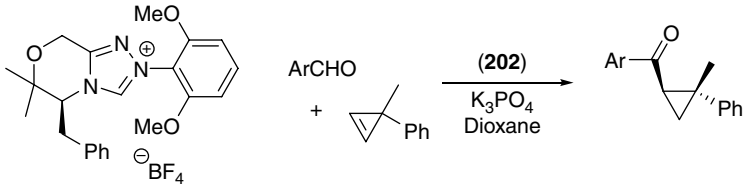


(**200**)

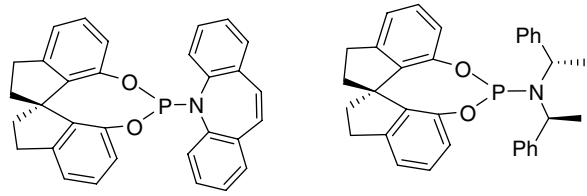


(**201**)

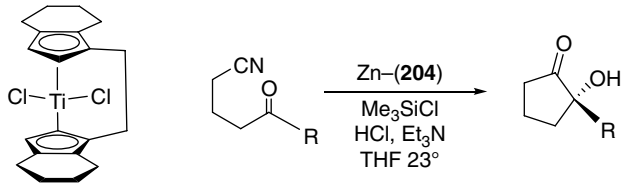
Cyclopropenes are receptive to addition under certain conditions. Asymmetric hydroacylation by ArCHO is now established.[28] The intramolecular hydroacylation to convert 4-substituted 4-pentenals is also rendered asymmetric by using a chiral ligand (e.g., **203A**) to form the Rh(I) catalyst.[29]



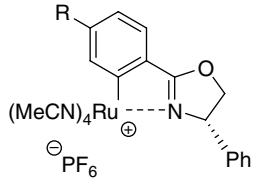
(**202**)



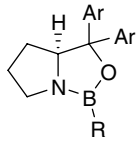
(**203A**) (**203B**)



(**204**)



(**205A**) R = H
(**205B**) R = CH_2OH



(**206A**) Ar = 3,5-$Me_2C_6H_3$, R = α-Np
(**206B**) Ar = 3,5-$Me_2C_6H_3$, R = *o*-$CF_3C_6H_4$
(**206C**) Ar = Ph, R = Me

The titanocene-zinc combination for ketyl generation has been modified to furnish chiral intermediates for intramolecular attack on a cyano group. Thus **204** is valuable for synthesis of (*R*)-2-hydroxycyclopentanones.[30]

vic-Diboration of alkenes by $B_2(pin)_2$ is conveniently rendered asymmetric by adding a chiral alcohol to the reaction medium.[31]

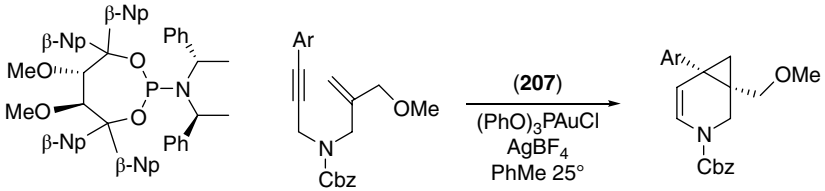
[1] Koschker, P., Lumbroso, A., Breit, B. *JACS* **133**, 20746 (2011)
[2] Cooke, M.L., Xu, K., Breit, B. *ACIE* **51**, 10876 (2012)
[3] Kim, H., Rhee, Y.H. *JACS* **134**, 4011 (2012)
[4] Butler, K.L., Tragni, M., Widenhoefer, R.A. *ACIE* **51**, 5175 (2012)
[5] Rodriguez, L.-I., Roth, T., Lloret-Fillol, J., Wadepohl, H., Gade, L.H. *CEJ* **18**, 3721 (2012)
[6] Sevov, C.S., Zhou, J., Hartwig, J.F. *JACS* **134**, 11960 (2012)

[7] Zhang, X., Emge, T.J., Hultzsch, K.C. *ACIE* **51**, 394 (2012)
[8] Noh, D., Yoon, S.K., Won, J., Lee, J.Y., Yun, J. *CAJ* **6**, 1967 (2011)
[9] Corberan, R., Mszar, N.W., Hoveyda, A.H. *ACIE* **50**, 7079 (2011)
[10] Moteki, S.A., Toyama, K., Liu, Z., Ma, J., Holmes, A.E., Takacs, J.M. *CC* **48**, 263 (2012)
[11] Naito, T., Yoneda, T., Ito, J., Nishiyama, H. *SL* 2957 (2012)
[12] Igawa, K., Yoshihiro, D., Ichikawa, N., Kokan, N., Tomooka, K. *ACIE* **51**, 12745 (2012)
[13] Sawano, T., Ou, K., Nishimura, T., Hayashi, T. *CC* **48**, 6106 (2012)
[14] Chow, T.W.-S., Liu, Y., Che, C.-M. *CC* **47**, 11204 (2011)
[15] Röben, C., Souto, J.A., Gonzalez, Y., Lishchynskyi, A., Muñiz, K. *ACIE* **50**, 9478 (2011)
[16] Nakanishi, M., Minard, C., Retailleau, P., Cariou, K., Dodd, R.H. *OL* **13**, 5792 (2011)
[17] Honjo, T., Phipps, R.J., Rauniyar, V., Toste, F.D. *ACIE* **51**, 9684 (2012)
[18] Hennecke, U. *CAJ* **7**, 456 (2012)
[19] Murai, K., Nakamura, A., Matsushita, T., Shimura, M., Fujioka, H. *CEJ* **18**, 8448 (2012)
[20] Jiang, X., Tan, C.K., Zhou, L., Yeung, Y.-Y. *ACIE* **51**, 7771 (2012)
[21] Dobish, M.C., Johnston, J.N. *JACS* **134**, 6068 (2012)
[22] Fan, B.-M., Yang, Q., Hu, J., Fan, C., Li, S., Yu, L., Huang, C., Tsang, W.W., Kwong, F.Y. *ACIE* **51**, 7821 (2012)
[23] Suzuki, S., Tokunaga, E., Reddy, D.S., Matsumoto, T., Shiro, M., Shibata, N. *ACIE* **51**, 4131 (2012)
[24] Matsuzawa, A., Mashiko, T., Kumagai, N., Shibasaki, M. *ACIE* **50**, 7616 (2011)
[25] Brazeau, J.-F., Zhang, S., Colomer, I., Corkey, B.K., Toste, F.D. *JACS* **134**, 2742 (2012)
[26] Noonan, G.M., Fuentes, J.A., Cobley, C.J., Clarke, M.L. *ACIE* **51**, 2477 (2012)
[27] Wang, X., Buchwald, S.L. *JACS* **133**, 19080 (2011)
[28] Liu, F., Bugaut, X., Schedler, M., Fröhlich, R., Glorius, F. *ACIE* **50**, 12626 (2011)
[29] Hoffman, T.J., Carreira, E.M. *ACIE* **50**, 10670 (2011)
[30] Streuff, J., Feurer, M., Bichovski, P., Frey, G., Gellrich, U. *ACIE* **51**, 8661 (2012)
[31] Bonet, A., Sole, C., Gulyas, H., Fernandez, E. *OBC* **10**, 6621 (2012)

Cycloadditions. Asymmetric organocatalytic cycloaddition reactions have been reviewed.[1] Cyclopropanation of alkenes using a copper complex of **62B** (loading 0.05 mol%) is accomplished under very mild conditions.[2] For cyclopropanation of *N*-Boc indoles the utility of a CuOTf complex to a BOX ligand constructed from peracetylglucose is moderately successful in terms of ee.[3] Ruthenacycles **205A/B** are reusable and water soluble catalysts.[4,5] The triflate salt of oxazaborolidine **206A** effects reaction of diazoacetic esters and conjugated aldehydes.[6]

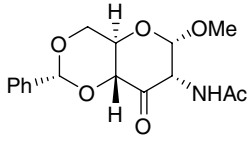
Besides diazo compounds, iodonium ylides can also serve as carbene source, and chiral copper-carbenoids are readily formed by introducing ligand **14D** to the reaction.[7]

Allylcarbenoids of gold(I) species or the like are generated into situ from alkynes, and intramolecular trapping results in the formation of bicyclic structures containing a cyclopropane unit.[8]

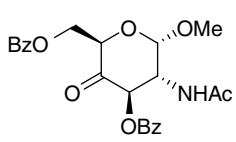


(**207**)

Two ketones (**208**, **209**) prepared from *N*-acetylglucosamine show catalytic activities of directing alkene epoxidation from opposite π-faces.[9]

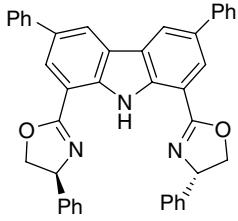


(**208**)

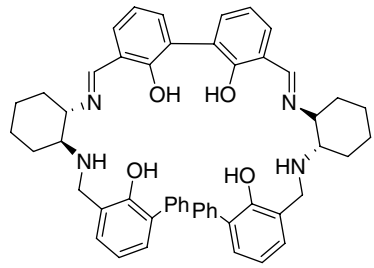


(**209**)

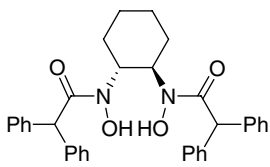
Oxoiron(IV) species are generated from complex of $FeCl_2$ with **210** and a cyclic carbene, on picking the oxygen atom from PhIO. The oxygen atom is to be transferred asymmetrically to alkenes.[10] The three-nitrogen ribbon that is constituted from the two oxazoline groups and the carbazole is a mimic of a porphyrin segment of heme. Other elaborate metal chelates used in epoxidation are the titanium complex of **211**[11] and the hafnium(IV) hydroxamate derived from **212**.[12] The latter system achieves epoxidation of *N*-alkenyl sulfonamides and *N*-tosylimines.



(**210**)

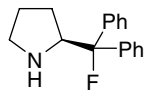


(**211**)

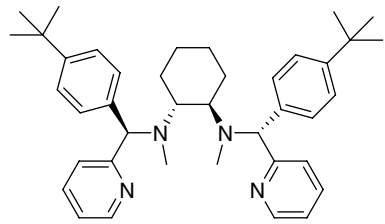


(**212**)

Enantioselective epoxidation of conjugated carbonyl compounds in the presence of **213** is an exploitation of fluorine atom's gauche effect.[13] A salt of the simpler diamine **95A** is also effective,[14] as well as the $Fe(OTf)_2$ complex of **214** for chalcones (moderate ee).[15]



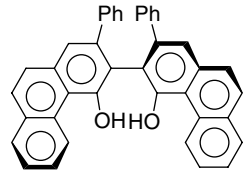
(**213**)



(**214**)

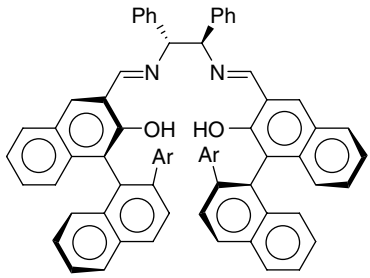
By incorporating a chiral oxazolidinone unit as mixed urea with 1,2-dihydroquinoline, a 1,6-asymetric induction is realized during epoxidation.[16]

Recent developments of asymmetric aziridine synthesis from imines and ethyl diazoacetate include catalysis by boroxinates associated with (*S*)-Vapol (**215**)[17] and (*S*)-Vanol (*ent*-**142**).[18]

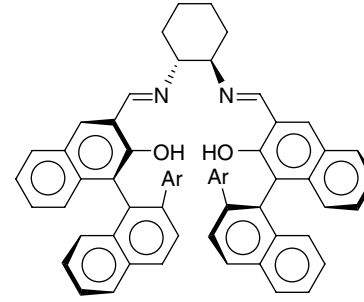


(**215**)

Organoazides and PhI=NNs also serve as nitrene sources for aziridination of alkenes. Ruthenium chelates of **216/217**[19,20] and $Cu(OTf)_2$ complex of **64A**[21] are useful catalysts for the reaction.



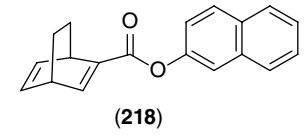
(**216**) Ar = 3,5-$(CF_3)_2C_6H_3$



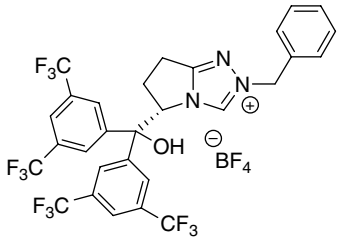
(**217**) Ar = 3,5-Cl_2-4-$(Me_3Si)C_6H_2$

The $AlBr_3$ salt of **206B** affects the intramolecular [2+2]cycloaddition of 4-(4-pentenyl) coumarin in the absolute stereochemical sense.[22] Head-to-head [2+2]cycloaddition between styrenes and allenylamine tosylates is chirally directed by AuCl, $AgNTf_2$ and a (*R*)-Vanol-derived dioxoaminophosphine.[23]

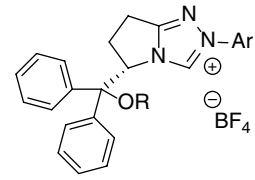
Substituted cyclobutanes are prepared from cycloaddition of nitroalkenes and ynamides, using a **218**-ligated Rh salt as catalyst.[24] Isomerization of conjugated aldehydes by carbene to furnish ketene equivalents offers opportunity for intramolecular trapping by a carbonyl group and hence leading to β-lactones. Asymmetric induction by a chiral carbene has been demonstrated.[25] Ketenes and isothiocyanates form 1:1 or 2:1 cycloadducts, depending on the carbene employed (e.g., **219** vs **220A**).[26] Also interesting is the acquisition of either enantiomer of the 1,2-thiazetidin-3-one oxide from cycloaddition of a ketene and an *N*-sulfinylaniline (catalysts: **152D**, *ent*-**16D**).[27]



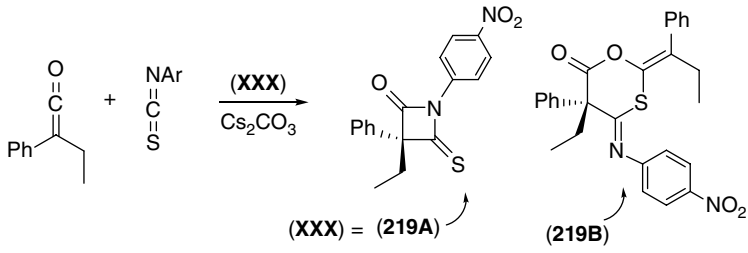
(**218**)

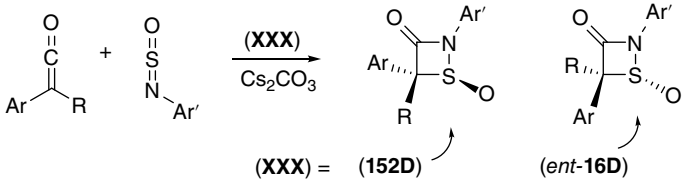


(**219A**)



(**219B**) R = TBS, Ar = 2-*i*PrC$_6$H$_4$
(**219C**) R = TMS, Ar = C$_6$F$_5$





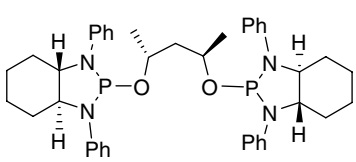
(**XXX**) = (**152D**) (*ent*-**16D**)

The **152** series of catalysts also promote the [2+2+2]cycloaddition to assemble 1,3-oxathian-6-ones from two equivalents of ketenes and one equivalent of CS_2.[28]

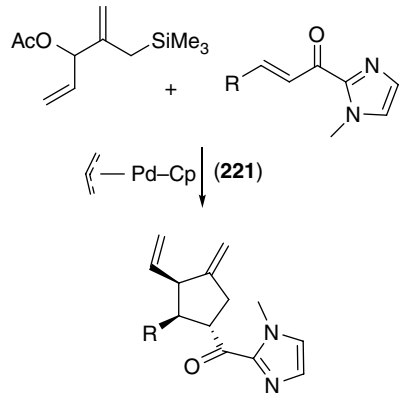
Pyridine formation by stitching two alkyne segments and a nitrile is a well-studied process. As iridium(I) catalysts are readily modified by chiral diphosphines (e.g., Segphos) their value in synthesis of optically active α-branched 2-alkylpyridines is appreciated.[29]

For synthesis of cyclopentenes by [3+2]cycloaddition, with the 1,3-dipolar segments generated from ionization of allyl carbonates, N,P-bidentate organocatalysts such as **166B**

(from Phe) or a Val-Thr derivative are recognized as useful.[30,31] A more elaborate trimethylene synthon is for assembling the somewhat unusual 2-vinyl-1-methylenecyclopentanes.[32] The ease of π-allylpalladium complex formation by cleaving highly polarizable vinylcyclopropanes makes them viable dipolar addends and therefore many types of vinylcyclopentanes becomes accessible. Again, chiral products are obtained on augmenting the Pd catalyst with a chiral ligand (e.g., *ent*-**48A**).[33]



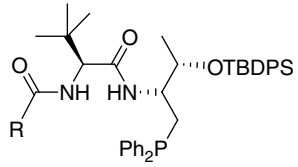
(**221**)



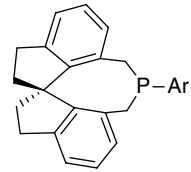
Conjugate addition of tertiary phosphines to allenyl ketones and esters generates enolate/vinylphosphonium species and paves a way to yet another class of cyclopentenes. Naturally a chiral phosphine (e.g., **222A**,[34] **223A**[35]) can induce the [3+2]cycloaddition asymmetrically.

Five-membered heterocycles are most amenable to assembly by the [3+2]cycloaddition.The list includes tetrahydrofurans, pyrrolidines, oxazolidines and isoxazolidines. Starting from a Pd(0)-induced ring cleavage of vinyl epoxides a rapid reaction with nitroalkenes affords 3-nitro-4-vinyltetrahydrofurans which contain an additional stereocenter at C-2; using ligand **160B** to modify $(dba)_3Pd_2{\cdot}CHCl_3$ the reaction adopts a chiral transition state.[36] An allylsilane behaves as the 3-carbon addend to engage the ketonic function of isatin in spiroannulation; as the process is catalyzed by a Lewis acid asymmetric induction by a Sc(III) complex of **63** can be designed.[37] 2-Oxa-1,3-dipolar species can be trapped to form the tetrahydrofuran nucleus. Double activation by enamination with *ent*-**41D** and assisted ionization of the ester group by a nonchiral thiourea are most effective.[38]

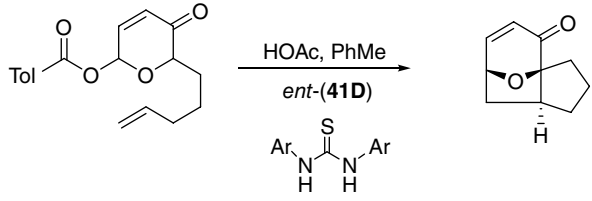
N-Alkylidene-α-amino esters are the frequently employed precursors of azomethine ylides for [3+2]cycloaddition because of their availability. Many pyrrolidine derivatives are acquired through such a route. Copper salts and chiral ligands form the most popular catalytic systems, thus ligands like **25B**,[39] **61**,[40] **224**[42] play their assigned roles.



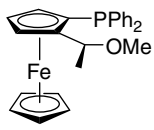
(**222A**) R = $OC(CCl_3)Me_2$
(**222B**) R = *t*-Bu



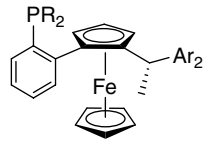
(**223A**) Ar = Ph
(**223B**) Ar = 3,5-$t Bu_2$-4-$MeOC_6H_2$



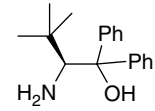
[Ar = 3,5-$(CF_3)_2C_6H_3$]



(**224**)



(**225A**) R = Ph, Ar = 3,5-$(CF_3)_2C_6H_3$
(**225B**) R = Cy, Ar = 3,5-$(CF_3)_2C_6H_3$



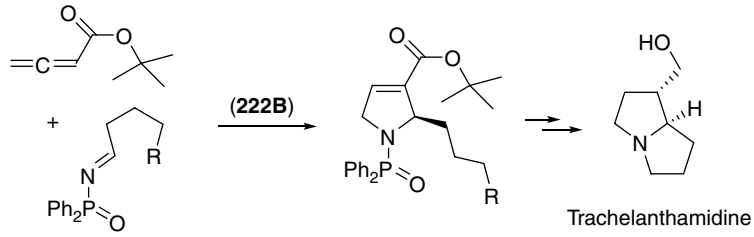
(**226**)

It should be emphasized that the α-amino esters are not employed because of their chirality is destroyed during the transition into the active addends (thus explaining the requirement of a chiral ligand). Actually, for the preparation of proline derivatives without any substituent at C-5, α-imino esters derived from α-keto esters and trimethylsilylmethylamine are the most expedient precursors.

Nickel(II) and Ag salts are also useful for catalyzing the [3+2]cycloaddition involving azomethine ylides, particularly in conjunction with chiral ligands **184B**[43] and **61**,[44] **25B**[45] respectively.

Organocatalysts that rely on H-bonding to set up transition states can be exploited, as for example the addition of azomethine ylides to maleimides using **41B**.[46] An alternative bonding scheme (N-C2 and C3-C4) to assemble pyrrolidines is based on umpolung of a formyl group from a 3-sulfonylaminopropanal by **42B** [and a Fe(III) salt in this case].[47]

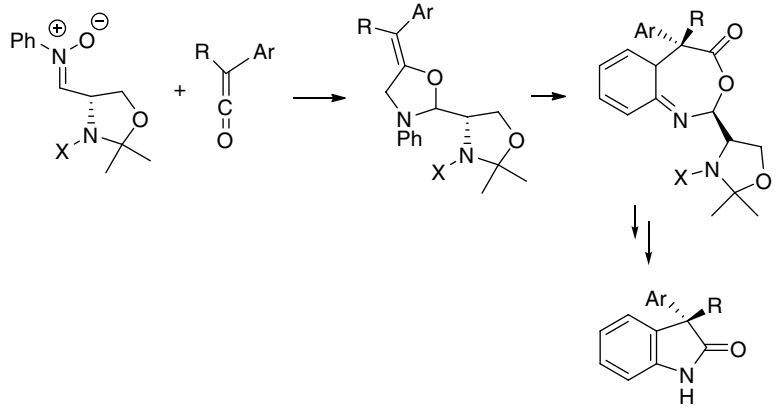
In the above the 1,3-dipolar species generated from allenecarboxylic esters and construction of chiral cyclopentenes have been mentioned. A variant of the [3+2]cycloaddition is the assembly of 3-pyrroline-3-carboxylic esters which can be applied to a synthesis of trachelanthamidine based on chiral induction by **222B**.[48]



2-Nitrosopyridine is a dipolarophile for allylstannanes, the Cu(I)-catalyzed combination to furnish tin-containing isoxazolidines is rendered chiral by **225**.[49] A recyclable catalyst for conducting addition of nitrones to conjugated aldehydes is the ionic liquid **28B**.[50] No diastereoselectivity needs concern the addition to 2-alkynals, but 4-isoxazolines of a single enantiomeric series are produced on adding **213** to the reactants.[51]

Again there are two alternative pathways for the construction of oxazolidines by [3+2] cycloaddition: one involving oxiranes and imines, the other, oxaziridines and alkenes. Both of these seem to require metal complexes and they offer opportunities for chiral manipulations. In the former case Rh(I) and Ag salts help activate the two addends, respectively, and favorable ligands are those capable of intimate association with the rhodium center to influence the approach of the dipolar intermediate. The iron(II) complex to **14E** is for enantioselectively presenting the O-N bond-severed heterocycles to the alkene addends.[52]

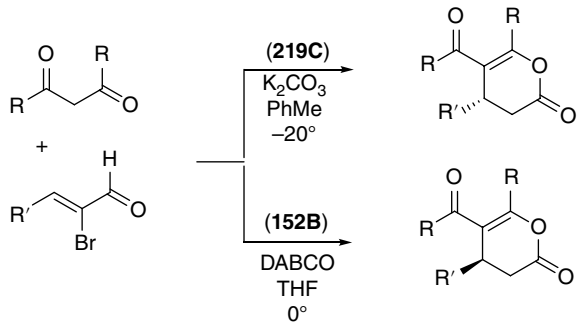
The asymmetric synthesis of oxindoles from nitrones derived from anilines with ketenes is now considered as proceeding via a [3+2]cycloaddition and then a [3,3]sigmatropic rearrangement.[53]



Nitrones can undergo a [3+2+2]cycloaddition and with a 1,6-enyne activated by a gold(I) complex. The products are cyclopentano-dihydro-1,2-oxazepines. Of course diphosphines

such as **39A** have great effects on the metal center and thence the stereochemical outcome.[54]

Reactivity modulation of aldehydes by carbenes is most prominent. It is interesting that 2-bromo-2-alkenals behaves as 1,3-dications (one being the acylium ion) toward β-dicarbonyl compounds. Particularly significant is the finding of such [3+3] cycloaddition should give enantiomers by changing the carbene catalyst only moderately.[55]

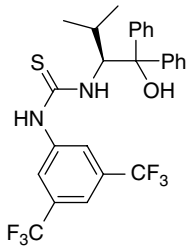


The **62C**-ligated copper-carbenoids formed through decomposition of aryl diazoacetates are trapped by α-ethoxycarbonylchalcone to give 2,3-dihydrofuran-2,4-dicarboxylic esters. Undoubtedly the chiral **62C** would exert its effect in the chiral sense.[56] Noteworthy is the profound ligand control for transition state because in that a Cu(I)-dihydroacenaphthylenediimine complex catalyzes the formation of dihydrobenzoxepines, a [6+1]cycloaddition instead of the [4+1]cycloaddition.

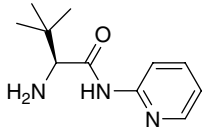
Intramolecular Diels-Alder reaction of some 1,3,8-trienes can be made asymmetric by the intervention of a Rh(I) complex along with **3B**, although the optical yields are only moderate.[57] *N*-Acyl-1,2-dihydropyridines and 2-alkenals are brought together chirally by the TFA salt of **226**.[58] By this process a synthetic intermediate for the antiviral drug oseltamivir is readily accessed.

In the presence of CoI_2, Zn and $ZnCl_2$, the combination of 2-cycloalkenones with alkynes to yields 1-hydroxybicyclo[n.2.1]alkenes. It is remarkable that the conjugated ketones participate in the reaction in the enol form, and furthermore, are subject to asymmetric induction by a phosphine ligand such as Duanphos.[59]

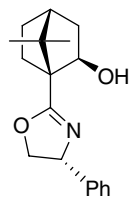
Binding $In(OTf)_3$ to the bidentate **159D** by ligand exchange leaves one triflyloxy group to engage an aldehyde. Accordingly aldehydes are activated toward hetero-Diels-Alder reaction with electron-rich dienes (e.g., Danishefsky diene), and 5,6-disubstituted 5,6-dihydro-2-pyrones are synthesized in ciral form.[60] Under high pressure the ketone group of isatin behaves as dienophile in the [4+2]cycloaddition catalyzed by **227**.[61] Also developed for hetero-Diels-Alder reaction of 2-oxo-3-alkenoic esters and ketones is the Y(III) complex of **228**,[62] and for components with inverse electron demand, $Cu(OTf)_2$ and **229**.[63]



(**227**)



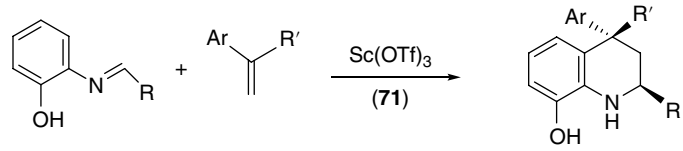
(**228**)

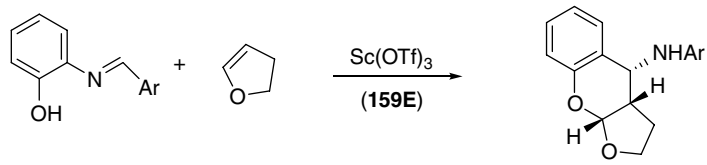


(**229**)

Quick access to tetrahydropyridines is through the [4+2]cycloaddition of conjugated imines. An example of the intramolecular version is the formation of a 1,2,3,4-tetrahydropyridin[3,4-*c*]coumarin from 2-acrylyloxybenzalacetone *N*-tosylimine, on catalysis by **166A**.[64] Catalysis by the phosphine derived from threonine for the condensation of 3-buten-2-one with conjugated imines follows the mechanism of the Baylis-Hillman reaction, the important feature is that the chirality of the catalyst is readily experienced by the two addends.[65]

Two different dienophilic profiles are exhibited by salicylaldehyde imines: one leading to 8-hydroxy-1,2,3,4-tetrahydroquinolines,[66] while the other to 4-aminobenzopyrans.[67]

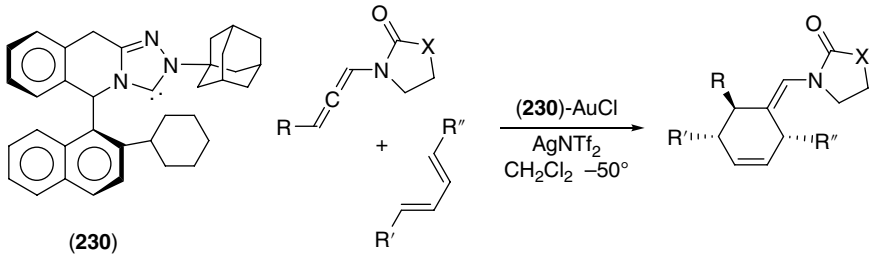




Allenylidenesuccinic esters are conferred with special reactivities in that the adducts with a tertiary phosphine act initially as nucleophilic 1,3-dipolar reagents. After addition to imines a subsequent deprotonation to generate allylidene phosphoranes sets up the cyclization.[68]

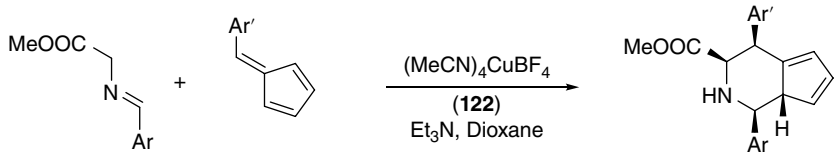
Ketenes are not dienophilic, but the masked ketene equivalents generated from α-halo aldehydes by carbenes can undergo the formal [4+2]cycloaddition, and in chiral version too.[69] 2-Alkenoyl chlorides that are 3-methylated are transformed into conjugated ketenes that engage into cycloaddition with a carbonyl group such as that of the trifluoromethyl ketones. Carbene **152D** is capable to turning out chiral dihydro-2-pyrones.[70] Practically the same results are obtained using conjugated aldehydes instead of the acid chlorides if an oxidant (2,6-di-*t*-butylbenzoquinone) is present.[71] A Lewis acid such as $Sc(OTf)_3$ or $Mg(OTf)_2$ is an essential additive for attaining high ee values.

Chiral helicenes which feature a terminal 2-aminopyridine nucleus can direct asymmetric Diels-Alder reactions of the dienophilc nitroethene, due to their ability to form suitable H-bonds.[72] Allene activation by Au(I) catalysts enables the asymmetric synthesis of some unusual cyclohexenes.[73]



(**230**)

6-Arylfulvenes and an *N*-benzylideneglycine methyl ester combine in the [6+2] mode which is amenable to asymmetric induction by the Cu(I) complex of **122**.[74]



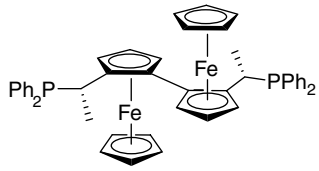
[1] Pellissier, H. *T* **68**, 2197 (2012)
[2] Li, J., Liao, S.-H., Xiong, H., Zhou, Y.-Y., Sun, X.-L., Zhang, Y., Zhou, X.-G., Tang, Y. *ACIE* **51**, 8838 (2012)
[3] Özüduru, G., Schubach, T., Boysen, M.M.K. *OL* **14**, 4990 (2012)
[4] Chanthamath, S., Phomkeona, K., Shibatomi, K., Iwasa, S. *CC* **48**, 7750 (2012)
[5] Abu-Elfotoh, A.-B., Nguyen, D.P.T., Chanthamath, S., Phomkeona, K., Shibatomi, K., Iwasa, S. *ASC* **354**, 3435 (2012)
[6] Gao, L., Hwang, G.-S., Ryu, D.H. *JACS* **133**, 20708 (2011)
[7] Deng, C., Wang, L.-J., Zhu, J., Tang, Y. *ACIE* **51**, 11620 (2012)
[8] Teller, H., Fürstner, A. *CEJ* **17**, 7764 (2011)
[9] Schöberl, C., Jäger, V. *ASC* **354**, 790 (2012)
[10] Niwa, T., Nakada, M. *JACS* **134**, 13538 (2012)
[11] Xiong, D., Hu, X., Wang, S., Miao, C.-X., Xia, C., Sun, W. *EJOC* 4289 (2011)
[12] Olivares-Romero, J.L., Li, Z., Yamamoto, H. *JACS* **134**, 5440 (2012)
[13] Tanzer, E.-M., Zimmer, L.E., Schweizer, W.B., Gilmour, R. *CEJ* **18**, 11334 (2012)
[14] Lu, Y., Zheng, C., Yang, Y., Zhao, G., Zou, G. *ASC* **353**, 3129 (2011)
[15] Wu, M., Miao, C.-X., Wang, S., Hu, X., Xia, C., Kühn, F.E., Sun, W. *ASC* **353**, 3014 (2011)
[16] Jean-Gérard, L., Macé, F., Ngo, A.N., Pauvert, M., Dentel, H., Evain, M., Collet, S., Guingant, A. *EJOC* 4240 (2012)
[17] Gupta, A.K., Mukherjee, M., Hu, G., Wulff, W.D. *JOC* **77**, 7932 (2012)
[18] Huang, L., Zhang, Y., Staples, R.J., Huang, R.H., Wulff, W.D. *CEJ* **18**, 5302 (2012)
[19] Kim, C., Uchida, T., Katsuki, T. *CC* **48**, 7188 (2012)

[20] Fukunaga, Y., Uchida, T., Ito, Y., Matsumoto, K., Katsuki, T. *OL* **14**, 4658 (2012)
[21] Hajra, S., Sinha, D. *JOC* **76**, 7334 (2011)
[22] Brimioulle, R., Guo, H., Bach, T. *CEJ* **18**, 7552 (2012)
[23] Suarez-Pantiga, S., Hernandez-Diaz, C., Rubio, E., Gonzalez, J.M. *ACIE* **51**, 11552 (2012)
[24] Smith, D.L., Chidipudi, S.R., Goundry, W.R., Lam, H.W. *OL* **14**, 4934 (2012)
[25] Cohen, D.T., Eichman, C.C., Phillips, E.M., Zarefsky, E.R., Scheidt, K.A. *ACIE* **51**, 7309 (2012)
[26] Wang, X.-N., Shen, L.-T., Ye, S. *OL* **13**, 6382 (2011)
[27] Jian, T.-Y., He, L., Tang, C., Ye, S. *ACIE* **50**, 9104 (2011)
[28] Wang, X.-N., Shen, L.-T., Ye, S. *CC* **47**, 8388 (2011)
[29] Onodera, G., Shimizu, Y., Kimura, J., Kobayashi, J., Ebihara, Y., Kondo, K., Sakata, K., Takeuchi, R. *JACS* **134**, 10515 (2012)
[30] Deng, H.-P., Shi, M. *ASC* **354**, 783 (2012)
[31] Zhong, F., Chen, G.-Y., Han, X., Yao, W., Lu, Y. *OL* **14**, 3764 (2012)
[32] Trost, B.M., Lam, T.M. *JACS* **134**, 11319 (2012)
[33] Trost, B.M., Morris, P.J., Sprague, S.J. *JACS* **134**, 17823 (2012)
[34] Zhao, Q., Han, X., Wei, Y., Shi, M., Lu, Y. *CC* **48**, 970 (2012)
[35] Wang, D., Wei, Y., Shi, M. *CC* **48**, 2764 (2012)
[36] Wu, W.-Q., Ding, C.-H., Hou, X.-L. *SL* 1035 (2012)
[37] Hanhan, N.V., Ball-Jones, N.R., Tran, N.T., Franz, A.K. *ACIE* **51**, 989 (2012)
[38] Burns, N.Z., Witten, M.R., Jacobsen, E.N. *JACS* **133**, 14578 (2011)
[39] Hernandez-Toribio, J., Padilla, S., Adrio, J., Carretero, J.C. *ACIE* **51**, 8854 (2012)
[40] Liu, T.-L., He, Z.-L., Wang, C.-J. *CC* **47**, 9600 (2011) Liu, T.-L., He, Z.-L., Tao, H.-Y., Wang, C.-J. *CEJ* **18**, 8042 (2012)
[41] Zhong, F., Han, X., Wang, Y., Lu, Y. *ACIE* **50**, 7837 (2011)
[42] He, Z., Liu, T., Tao, H., Wang, C.J. *OL* **14**, 6230 (2012)
[43] Awata, A., Arai, T. *CEJ* **18**, 8278 (2012)
[44] Liu, T.-L., He, Z.-L., Li, Q.-H., Tao, H.-Y., Wang, C.-J. *ASC* **353**, 1713 (2011)
[45] Yamashita, Y., Imaizumi, T., Guo, X.-X., Kobayashi, S. *CAJ* **6**, 2550 (2011)
[46] Bai, J.-F., Wang, L.-L., Peng, L., Guo, Y.-L., Ming, J.-N., Wang, F.-Y., Xu, X.-Y., Wang, L.-X. *EJOC* 4472 (2011)
[47] Jui, N.T., Garber, J.A.O., Finelli, F.G., MacMillan, D.W.C. *JACS* **134**, 11400 (2012)
[48] Han, X., Zhong, F., Wang, Y., Lu, Y. *ACIE* **51**, 767 (2012)
[49] Chatterjee, I., Fröhlich, R., Studer, A. *ACIE* **50**, 11257 (2011)
[50] Shen, Z.-L., Goh, K.K.K., Wong, C.H.A., Loo, W.-Y., Yang, Y.-S., Lu, J., Loh, T.-P. *CC* **48**, 5856 (2012)
[51] Aleman, J., Fraile, A., Marzo, L., Ruano, J.L.G., Izquierdo, C., Diaz-Tendero, S. *ASC* **354**, 1665 (2012)
[52] Williamson, K.S., Yoon, T.P. *JACS* **134**, 12370 (2012)
[53] Çelebi-Ölçüm, N., Lam, Y., Richmond, E., Ling, K.B., Smith, A.D., Houk, K.N. *ACIE* **50**, 11478 (2011)
[54] Gawade, S.A., Bhunia, S., Liu, R.-S. *ACIE* **51**, 7835 (2012)
[55] Sun, F.-G., Sun, L.-H., Ye, S. *ASC* **353**, 3134 (2011)
[56] Zhou, J.-L., Liang, Y., Deng, C., Zhou, H., Wang, Z., Sun, X.-L., Zheng, J.-C., Yu, Z.-X., Tang, Y. *ACIE* **50**, 7874 (2011)
[57] Falk, A., Fiebig, L., Neudörfl, J.-M., Adler, A., Schmalz, H.-G. *ASC* **353**, 3357 (2011)
[58] Suttibut, C., Kohari, Y., Igarashi, K., Nakano, H., Hirama, M., Seki, C., Matsuyama, H., Uwai, K., Takano, N., Okuyama, Y., Osone, K., Takeshita, M., Kwon, E. *TL* **52**, 4745 (2011)
[59] Wei, C.-H., Mannathan, S., Cheng, C.-H. *ACIE* **51**, 10592 (2012)
[60] Lin, L., Kuang, Y., Liu, X., Feng, X. *OL* **13**, 3868 (2011)
[61] Mori, K., Yamauchi, T., Maddaluno, J., Nakano, K., Ichikawa, Y., Kotsuki, H. *SL* 2080 (2011)
[62] Xu, Z., Wang, H. *SL* 2907 (2011)

[63] Barba, A., Barroso, S., Blay, G., Cardona, L., Melegari, M., Pedro, J.R. *SL* 1592 (2011)
[64] Jin, Z., Yang, R., Du, Y., Tiwari, B., Ganguly, R., Chi, Y.R. *OL* **14**, 3226 (2012)
[65] Shi, Z., Yu, P., Loh, T.-P., Zhong, G. *ACIE* **51**, 7825 (2012)
[66] Xie, M., Liu, X., Zhu, Y., Zhao, X., Xia, Y., Lin, L., Feng, X. *CEJ* **17**, 13800 (2011)
[67] Zhang, Y., Dong, S., Liu, X., Xie, M., Zhu, Y., Lin, L., Feng, X. *CEJ* **17**, 13684 (2011)
[68] Xiao, H., Chai, Z., Wang, H.-F., Wang, X.-W., Cao, D.-D., Liu, W., Lu, Y.-P., Yang, Y.-Q., Zhao, G. *CEJ* **17**, 10562 (2011)
[69] Jian, T.-Y., Sun, L.-H., Ye, S. *CC* **48**, 10907 (2012)
[70] Shen, L.-T., Shao, P.-L., Ye, S. *ASC* **353**, 1943 (2011)
[71] Mo, J., Chen, X., Chi, Y.R. *JACS* **134**, 8810 (2012)
[72] Narcis, M.J., Sprague, D.J., Captain, B., Takenaka, N. *OBC* **10**, 9134 (2012)
[73] Francos, J., Grande-Carmona, F., Faustino, H., Iglesias-Sigüenza, J., Diez, E., Alonso, I., Fermandez, R., Lassaletta, J.M., López, F., Mascareñas, J.M. *JACS* **134**, 14322 (2012)
[74] Potowski, M., Bauer, J.O., Strohmann, C., Antonchick, A.P., Waldmann, H. *ACIE* **51**, 9512 (2012)

Hydrogenation and reductions

C=C Bond reduction. An important discovery is the partial hydrogenation of 2,6- and 2,7-disubstituted naphthalenes to tetralins, that chirality is conferred to the emerging sp^3-carbon atom. This goal has been accomplished by using a ruthenium catalyst associated with ligand **231**.[1]

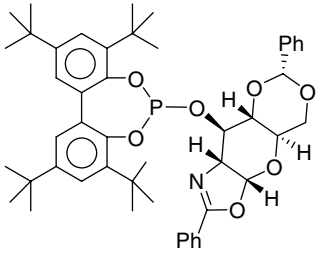


(**231**)

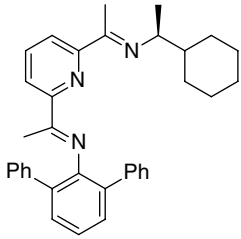
A series of C_3-symmetric trisphospholanes (**72**) is readily prepared from 1,1-bis(hydroxymethyl)phospholanium chloride and NH_4Cl in a 3:1 ratio. On adding these ligands to Rh(I) complexes they form catalysts for hydrogenation of prochiral alkenes.[2] Diphosphines with one chiral phosphorus such as **192A/192B** and the benzolog also make up useful Rh catalysts.[3,4]

A useful ligand to enable iridium(I) complexes to exert chiral control in alkene hydrogenation is obtained from a L-furanose derivative containing sulfide and phosphate groups.[5] Available from glucosamine the scaffold **232** also serves to support the iridium(I) complexes for the same purpose.[6]

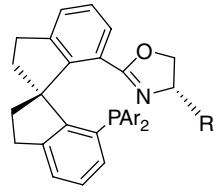
A cobalt complex to the pyridinediimine **233** is the arbiter of chirality in the hydrogenation of α-branched styrenes.[7] Hydrogenation of 4-aryl-3-alkenoic acids can use an iridium catalyst that contains the P,N-ligand **234**.[8] Iridium catalysts are applicable to hydrogenation of a wide range of unsaturated compounds, for α-substituted acrylic acids it is composed of the spirobiindan-based P,N-ligand **235A**,[9] and for β,β-disubstituted and α,β-disubstituted acrylic acids, **236D** and **236B,** respectively.[10] In the case of cyclic sulfones containing a double bond the saturated products [from H_2, Ir(I), **236D**] can be fashioned into cycloalkenes by a Ramberg-Bäcklund reaction.[11]



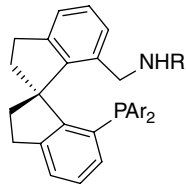
(**232**)



(**233**)



(**234**) Ar = 3,5-$Me_2C_6H_3$

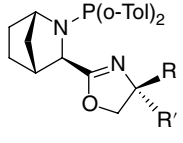


Ar = 3,5-*t*-$Bu_2C_6H_3$

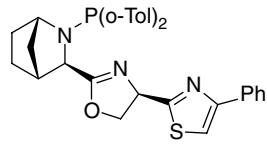
(**235A**) R = H

(**235B**) R =





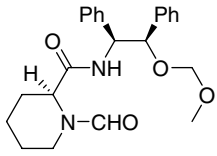
(**236A**) R = *i*-Pr, R′ = H
(**236B**) R = R′ = Ph
(**236C**) R = *t*-Bu, R′ = H



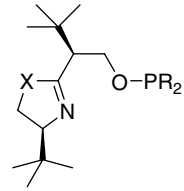
(**236D**)

Asymmetric hydrogenation of 1-ethyl-3-fluoro-4-benzoylamino-1,2,5,6-tetrahydropyridine in kilogram scale is achieved with a Ru(II) catalyst that is composed of **32A**.[12] A Ru-carbene **220** complex is of service to enantioselective hydrogenation of 5-membered heterocycles, e.g., conversion of 2-substituted benzofurans to the dihydro derivatives,[13] and various substituted thiophenes to sulfolanes.[14] Chiral indolines are obtained via hydrosilylation ($HSiCl_3$, **237**).[15]

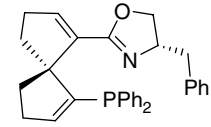
Rhodium(I) salts bounded to a **32A** analog[16] as well as Ir(I) to **238A**[17] and **239**[18] are used in asymmetric hydrogenation of conjugated ketones.



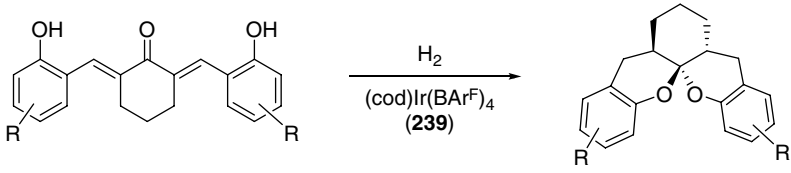
(**237**)



(**238A**) R = Ph, X = O
(**238B**) R = Cy, X = NPh



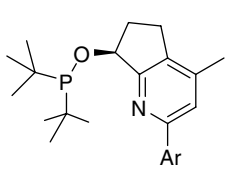
(**239**)



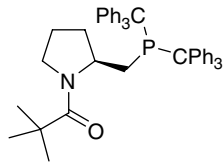
By having a carboxyl group on each of the benzene rings in the phosphine units of **39**, the resulting ligand makes possible hydrogenation of unsaturated acids in water.[19]

After *O*-arylation of ethyl acetoacetate, hydrogenation [Rh(I), **225B**] gives the (*R*)-3-aryloxypropanoates.[20] Two crowded ligands for Ir(I)-catalyzed hydrogenation of conjugated esters are **240B**[21] and **241**.[22] Less so are the P,N-ligands **242**[23] and **243**,[24] the latter forming a catalyst system for hydrogenation of 3-arylideneoxindoles. For hydrogenation of β,β-disubstituted acrylamides of the Weinreb class, the iridium catalyst composed of a 2-(2-oxazolinyl)-2′-diphenylphosphinospiro[4.4]nona-2,2′-diene can be employed.[25]

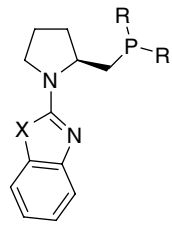
The mixed P,P-ligand **244A** and phosphoric acid **245B** support rhodium(I) tetrafluoroborate to hydrogenate unsaturated phosphonates.[26,27]



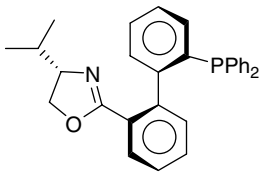
(**240A**) Ar = Ph
(**240B**) Ar = 2,4,6-$Me_3C_6H_2$



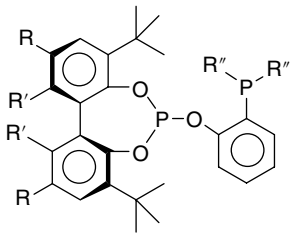
(**241**)



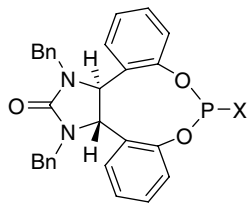
(**242**) X = O, S



(**243**)



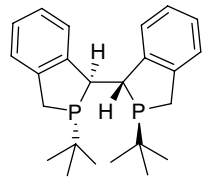
(**244A**) R = R′ = Me, R″ = *i*-Pr
(**244B**) R = *t*-Bu, R′ = H, R″ = *p*-Tol



(**245A**) X = NHR
(**245B**) X = O + OH

More challenging is finding the best conditions for hydrogenation of alkenes containing directly attached heterofunctionalities. Until the present not too much effort has been devoted to hydrogenation of α-acetoxy-α,β-unsaturated ketones, but it is now established that such compounds are smoothly reduced with a Rh salt complexed to **246** (Duanphos).[28] Simpler enol esters are saturated with amino(diphenoxy)phosphine **245A** to occupy the coordination sphere for chiral transfer of hydrogen.[29]

P-ligands of the spirobiindan series for Rh(I) salts enable enantioselective delivery of hydrogen to the double bond of β-methylstyrene-β-enamides.[30] Most remarkably, same products are obtained from both (*Z*)- and (*E*)-enamides by selecting ligands of opposite optical series to control the course of hydrogenation.

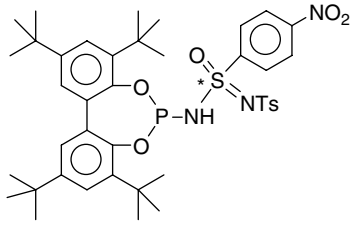


(**246**)

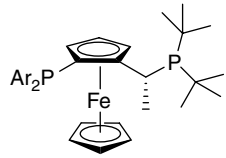
(*S*)-3-Acylaminochromans are procured by asymmetric hydrogenation [(cymene)$RuCl_2$, Synphos] of the 2*H*-chromenes.[31]

Hindered cyclic enamides undergo asymmetric hydrogenation with the aid of an iridium(I) catalyst bounded to a sulfonimidamide **247** which is chiral at the sulfur atom.[32] Hydrogenation of imines, β-enamino esters and indoles is facilitated by protonation.[33] As for saturation of the double bond of α-methyl-β-nitrostyrenes, **248** is used to ligate the Rh(I) center,[34] and the hydrosilylation method ($HSiCl_3$, catalyst **249**) accomplishes reduction of β-anilino-α,β-unsaturated nitroalkanes).[35] It is also found that chiral Lewis base **250** is an excellent catalyst for hydrosilylation of α-acetoxy-β-enamino esters in a highly diastereoselective and enantioselective manner, applicable to synthesis of the taxol sidechain.[36]

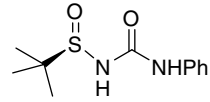
Asymmetric hydrogenation of alkenylboranes is alternative to hydroboration of alkenes, and it can be achieved with iridium catalysts containing proper P,N-ligands. For 2-boryl-1-alkenes a useful ligand is **238B**, and trisubstituted alkenes (two alkyl groups and one boryl group) **240A** is preferred.[37] Alkenes possessing the *gem*-B,Cl disubstituted pattern can be hydrogenated enantioselectively by using iridium complex of **251**.[38]



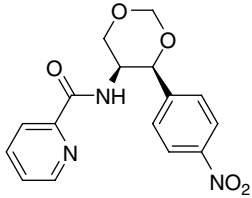
(**247**)



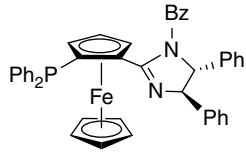
(**248**) Ar = 4-$CF_3C_6H_4$



(**249**)

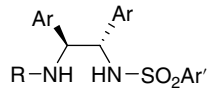


(**250**)

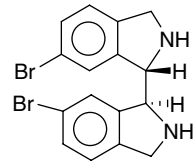


(**251**)

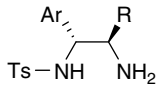
C=O Bond reduction. Ruthenium- chiral diamine complexes are the most versatile catalysts for transfer hydrogenation of ketones. Newly employed ligands are **252A**[39] and **253** together with DPPF.[40] A crucial structural characteristic of **254** which are used to form a complexes with $(cymene)_2RuCl_2$ is that a R must be bulky.[41]



(**252A**) Ar = Ph, Ar′ = Tol,
R = CH_2-(1-Bn-1,2,3-triazol-4-yl)
(**252B**) Ar = 1-Np, Ar′ = 2,6-$Ph_2C_6H_3$
R = H

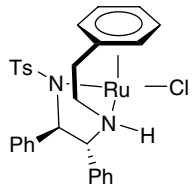


(**253**)

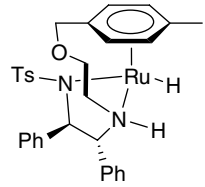


(**254**)

Two complexes (**255**,[42] **256** [43]) have compact structures for they feature a tether that connects the benzene ring to one of the nitrogen atoms. The former catalyst can conduct transfer hydrogenation to a ketone group adjacent to a quaternary carbon center.



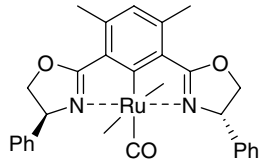
(**255**)



(**256**)

The effectiveness of ruthenacycle **257** as asymmetric hydrogenation catalyst is greatly increased by a chiral alcohol additive such as (*S*)-1-(9-anthryl)ethanol.[44] By slight modification of the now well-known (cymene)Ru(TsDPEN)Cl_2 complex to the bis(triflate) the hydrogenation of 1,2-diarylethanediones to the chiral diols is highly successful.[45]

Constructed from cooperative binding of a spirobiindan-based diphosphine **132A** and 1,2-diphenylethanediamine the $RuCl_2$ complex mediates hydrogenation of aryl ketones without affecting a conjugated ester.[46] Iridium complex of P,N-ligand **235B** with the same spirocyclic skeleton is applicable to conversion of conjugated ketones into the corresponding allyl alcohols.[47]



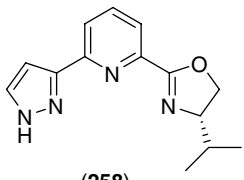
(**257**)

Two adjacent stereocenters are established during hydrogenation of β-keto phosphonates, thus diastereoselectivity emerges as depending on the enantioselective reaction which is controlled by ligand *ent*-**25D** in association with a ruthenium ion.[48]

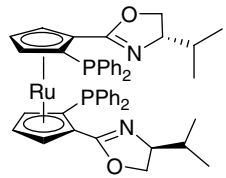
Five-membered metallacycles derived from chiral benzylamines, including Ir, Rh, and Ru species, are also active in the prootion of transfer hydrogenation of C=O and C=N bonds.[49]

The great variety of chiral ligands suitable for pairing with Ru(II) species to accomplish asymmetric hydrogenation of ketones is further illustrated by the following list: **258**,[50] **259**,[51] **252B**.[52] Also dynamic kinetic resolution of 2-aroyl-1-tetralones[53] and α-amino-β-keto esters[54] is accomplished by transfer hydrogenation in the presence of a chiral Ru(II) catalyst, the latter performed with *ent*-**44B** in an emulsion.

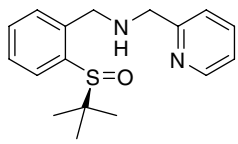
Chiral iridium(I) complexes are slightly less popular, still they encompass those with ligands of 1,2-diphenylethanediamine monosulfonates,[55] spirobiindan P,N-ligand **235B**,[56] the S,N-ligand **260** with a chirality element at the sulfur atom,[57] and the carbenoid **261**.[58]



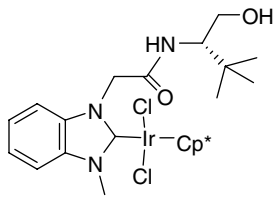
(**258**)



(**259**)



(**260**)



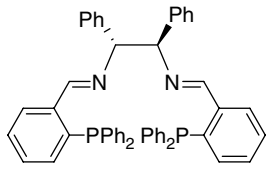
(**261**)

Interests in devising recoverable Rh catalysts and their use in micellar systems are shown in a *trans*-1,2-cyclohexanediamine monoarenesulfonate in which the linking to

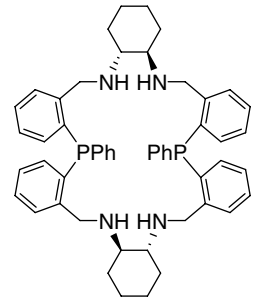
a polymer backbone is easily achieved.[59] With a Cp*Rh(TsDPEN) catalyst both the carbonyl group and the double bond of chromenone are reduced.[60] Oxazoline ligands for Rh are readily generated in situ from chiral 2-amino alcohols and imino ethers.[61]

Recent research has touched on te utility of Fe(0) complexes for hydrogenation of ketones. Examples are those containing **262**[62] and **263**.[63]

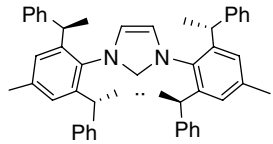
Copper catalysts are active in hydrosilylation, and there are many ligands to ensure the reaction to pursue a stereochemically defined course. Among such ligands, **148**[64] and carbene **264**[65] may be mentioned. Without metal ions the picolinic acid amide **250** alone is sufficient to bring about the conversion of 2-acetoxy-3-amino-2-alkenoic esters into the saturated 2,3-*syn*-disubstituted esters.[66]



(**262**)



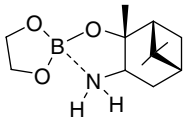
(**263**)



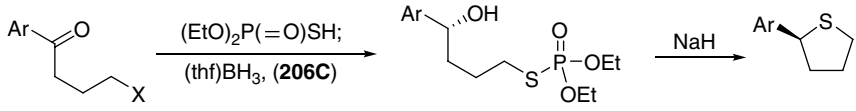
(**264**)

Reduction of ketones by the borane-dimethylsulfide complex is made asymmetric by **265**.[67] In using KBH_4 as the reducing agent, the $Sc(OTf)_3$ complex of **71B** is of service.[68]

A synthesis of (*S*)-2-arylsulfolanes from aryl 3-halopropyl ketones involves an S_N2 reaction with phosphrothioic acid and borane reduction in the presence of **206C**.[69] There is an S-to-O transphosphorylation prior to ring closure.

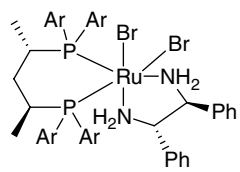


(**265**)

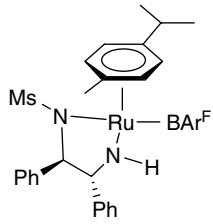


Asymmetric hydrosilylation of a benzylic C=X bond with $HSiCl_3$ is participated by a chiral (*R*)-5-phenyl-2-(1-isoquinolinyl)oxazoline.[70]

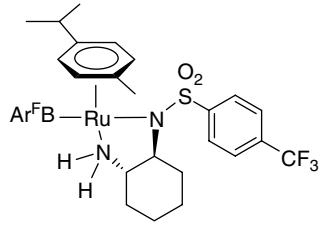
C=N Bond reduction. Hydrosilylation of C=N compounds with $HSiCl_3$ and chiral organocatalysts is summarized.[71] *N*-Arylimines are hydrogenated in the presence of $RuBr_2$ in which the metal center is also bound to diphosphine and diamine ligands, i.e., **266**.[72] Further modification of [(S,S)-DPEN]$RuCl_2$ by mixing with **244B** leads to another catalyst,[73] but without phosphorus ligands arene-complexed Ru(II) teraarylborate salts (e.g., **267**, **268**) are also capable catalysts.[74]



(**266**) Ar = 3,5-$Me_2C_6H_3$

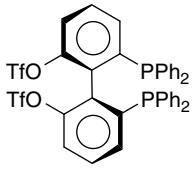


(**267**)

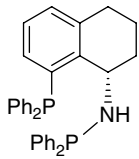


(**268**)

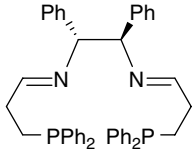
The development of a model for evolutionary screening of iridium catalysts for asymmetric hydrogenation of cyclic imines starts from optimization of initial leads by ligand identification.[75] Practical demonstrations are shown in the use of **25** and **198** series of P,P-ligands for hydrogenation of pyridinium salts,[76] quinolines,[77] isoquinolines,[78] 1-aryl-3, 4-dihydroisoquinolines,[79] quinoxalines,[80] and 2*H*-1,4-benzoxazines.[81] Two other ligands for the asymmetric induction are **269**[82] and **270**.[83]



(**269**)



(**270**)



(**271**)

Iron complexes of **271** are used to make the hydrogen transfer from *i*-PrOH to imines enantioselective.[84] The catalyzed reduction of 3-hydroxy-1-isoindolones with a Hantzsch ester by the **215**-derived phosphoric acid obviously proceeds via dehydration.[85]

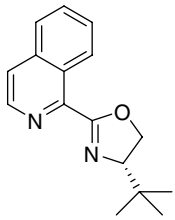
[1] Kuwano, R., Morioka, R., Kashiwabara, M., Kameyama, N. *ACIE* **51**, 4136 (2012)
[2] Lloret-Fillol, J., Kruckenberg, A., Scherl, P., Wadepohl, H., Gade, L.H. *CEJ* **17**, 14047 (2012)
[3] Zhang, Z., Tamura, K., Mayama, D., Sugiya, M., Imamoto, T. *JOC* **77**, 4184 (2012)
[4] Imamoto, T., Tamura, K., Zhang, Z., Horiuchi, Y., Sugiya, M., Yoshida, K., Yanagisawa, A., Gridnev, I.D. *JACS* **134**, 1754 (2012)
[5] Coll, M., Pàmies, O., Diéguez, M. *CC* **47**, 9215 (2011)

[6] Mazuela, J., Norrby, P.-O., Andersson, P.G., Pamies, O., Dieguez, M. *JACS* **133**, 13634 (2011)
[7] Monfette, S., Turner, Z.R., Semproni, S.P., Chirik, P.J. *JACS* **134**, 4561 (2012)
[8] Song, S., Zhu, S.-F., Yang, S., Li, S., Zhou, Q.-L. *ACIE* **51**, 2708 (2012)
[9] Zhu, S.-F., Yu, Y.-B., Li, S., Wang, L.-X., Zhou, Q.-L. *ACIE* **51**, 8872 (2012)
[10] Li, J.-Q., Quan, X., Andersson, P.G. *CEJ* **18**, 10609 (2012)
[11] Zhou, T., Peters, B., Maldonado, M.F., Govender, T., Andersson, P.G. *JACS* **134**, 13592 (2012)
[12] Stumpf, A., Reynolds, M., Sutherlin, D., Babu, S., Bappert, E., Spindler, F., Welch, M., Gaudino, J. *ASC* **353**, 3367 (2011)
[13] Ortega, N., Urban, S., Beiring, B., Glorius, F. *ACIE* **51**, 1710 (2012)
[14] Urban, S., Beiring, B., Ortega, N., Paul, D., Glorius, F. *JACS* **134**, 15241 (2012)
[15] Xiao, Y.-C., Wang, C., Yao, Y., Sun, J., Chen, Y.-C. *ACIE* **50**, 10661 (2011)
[16] Calvin, J.R., Frederick, M.O., Laird, D.L.T., Remacle, J.R., May, S.A. *OL* **14**, 1038 (2012)
[17] Maurer, F., Huch, V., Ullrich, A., Kazmaier, U. *JOC* **77**, 5139 (2012)
[18] Wang, X., Han, Z., Wang, Z., Ding, K. *ACIE* **51**, 936 (2012)
[19] Leseurre, L., Püntener, K., Gênet, J.-P., Scalone, M., Michelet, V. *ASC* **353**, 3269 (2011)
[20] Stewart, G.W., Shevlin, M., Yamagata, A.D.G., Gibson, A.W., Keen, S.P., Scott, J.P. *OL* **14**, 5440 (2012)
[21] Woodmansee, D.H., Müller, M.-A., Tröndlin, L., Hörmann, E., Pfaltz, A. *CEJ* **18**, 13780 (2012)
[22] Rageot, G., Woodmansee, D.H., Pugin, B., Pfaltz, A. *ACIE* **50**, 9598 (2011)
[23] Rageot, D., Pfaltz, A. *HCA* **95**, 2176 (2012)
[24] Liu, Y., Yao, D., Li, K., Tian, F., Xie, F., Zhang, W. *T* **67**, 8445 (2011)
[25] Shang, J., Han, Z., Li, Y., Wang, Z., Ding, K. *CC* **48**, 5172 (2012)
[26] Chavez, M.A., Vargas, S., Suarez, A., Alvarez, E., Pizzano, A. *ASC* **353**, 2775 (2011)
[27] Dong, K., Wang, Z., Ding, K. *JACS* **134**, 12474 (2012)
[28] Sun, T., Zhang, X. *ASC* **354**, 3211 (2012)
[29] Liu, Y., Wang, Z., Ding, K. *T* **68**, 7581 (2012)
[30] Zhu, S.-F., Liu, T., Yang, S., Song, S., Zhou, Q.-L. *T* **68**, 7685 (2012)
[31] Wu, Z., Ayad, T., Ratovelomanana-Vidal, V. *OL* **13**, 3782 (2011)
[32] Patureau, F.W., Worch, C., Siegler, M.A., Spek, A.L., Bolm, C., Reek, J.N.H. *ASC* **354**, 59 (2012)
[33] Yu, Z., Jin, W., Jiang, Q. *ACIE* **51**, 6060 (2012)
[34] Li, S., Huang, K., Cao, B., Zhang, J., Wu, W., Zhang, X. *ACIE* **51**, 8573 (2012)
[35] Liu, X.-W., Yan, Y., Wang, Y.-Q., Wang, C., Sun, J. *CEJ* **18**, 9204 (2012)
[36] Jiang, Y., Chen, X., Zheng, Y., Xue, Z., Shu, C., Yuan, W., Zhang, X. *ACIE* **50**, 7304 (2011)
[37] Ganic, A., Pfaltz, A. *CEJ* **18**, 6724 (2012)
[38] Smilovic, I.G., Casas-Arce, E., Roseblade, S.J., Nettekoven, U., Zanotti-Gerosa, A., Kovacevic, M. *ACIE* **51**, 1014 (2012)
[39] Johnson, T.C., Totty, W.G., Wills, M. *OL* **14**, 5230 (2012)
[40] Zhu, Q., Shi, D., Xia, C., Huang, H. *CEJ* **17**, 7760 (2011)
[41] Zhang, B., Wang, H., Lin, G.-Q., Xu, M.-H. *EJOC* 4205 (2011)
[42] Soni, R., Collinson, J.-M., Clarkson, G.C., Wills, M. *OL* **13**, 4304 (2011)
[43] Touge, T., Hakamata, T., Nara, H., Kobayashi, T., Sayo, N., Saito, T., Kayaki, Y., Ikariya, T. *JACS* **133**, 14960 (2011)
[44] Ito, J., Teshima, T., Nishiyama, H. *CC* **48**, 1105 (2012)
[45] Huang, X., Li, N., Geng, Z., Pan, F., Wang, X. *ChJC* **30**, 2657 (2012)
[46] Xie, J.-H., Guo, L.-C., Yang, X.-H., Wang, L.-X., Zhou, Q.-L. *OL* **14**, 4758 (2012)
[47] Zhang, Q.-Q., Xie, J.-H., Yang, X.-H., Xie, J.-B., Zhou, Q.-L. *OL* **14**, 6158 (2012)
[48] Tao, X., Li, W., Ma, X., Li, X., Fan, W., Zhu, L., Xie, X., Zhang, Z. *JOC* **77**, 8401 (2012)
[49] Pannetier, N., Sortais, J.-B., Issenhuth, J.-T., Barloy, L., Sirlin, C., Holuigue, A., Lefort, L., Panella, L., de Vries, J.G., Pfeffer, M. *ASC* **353**, 2844 (2011)
[50] Ye, W., Zhao, M., Yu, Z. *CEJ* **18**, 10843 (2012)
[51] Guo, H., Liu, D., Butt, N.A., Liu, Y., Zhang, W. *T* **68**, 3295 (2012)

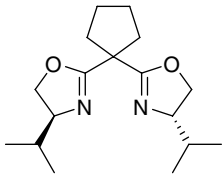
[52] Steward, K.M., Gentry, E.C., Johnson, J.S. *JACS* **134**, 7329 (2012)
[53] Wu, Y., Geng, Z., Bai, J., Zhang, Y. *ChJC* **29**, 1467 (2011)
[54] Seashore-Ludlow, B., Villo, P., Somfai, P. *CEJ* **18**, 7219 (2012)
[55] Ariger, M.A., Carreira, E.M. *OL* **14**, 4522 (2012)
[56] Xie, J.-H., Liu, X.-Y., Yang, X.-H., Xie, J.-B., Wang, L.-X., Zhou, Q.-L. *ACIE* **51**, 201 (2012)
[57] Tang, L., Wang, Q., Wang, J., Lin, Z., Wang, X., Cun, L., Yuan, W., Zhu, J., Liao, J., Deng, J. *TL* **53**, 3839 (2012)
[58] Chiyojima, H., Sakaguchi, S. *TL* **52**, 6788 (2011)
[59] Elias, S., Goren, K., Vigalok, A. *SL* 2619 (2012)
[60] Tang, L., Lin, Z., Wang, Q., Wang, X. Cun, L., Yuan, W., Zhu, J., Deng, J. *TL* **53**, 3828 (2012)
[61] Frauenlob, R., McCormack, M.M., Walsh, C.M., Bergin, E. *OBC* **9**, 6934 (2011)
[62] Sonnenberg, J.F., Coombs, N., Dube, P.A., Morris, R.H. *JACS* **134**, 5893 (2012)
[63] Yu, S., Shen, W., Li, Y., Dong, Z., Xu, Y., Li, Q., Zhang, J., Gao, J. *ASC* **354**, 818 (2012)
[64] Yu, F., Zhou, J.-N., Zhang, X.-C., Sui, Y.-Z., Wu, F.-F., Xie, L.-J., Chan, A.S.C., Wu, J. *CEJ* **17**, 14234 (2011)
[65] Albright, A., Gawley, R.E. *JACS* **133**, 19680 (2011)
[66] Jiang, Y., Chen, X., Zheng, Y., Xue, Z., Shu, C., Yuan, W., Zhang, X. *ACIE* **50**, 7304 (2011)
[67] Krzeminski, M.P., Cwiklinska, M. *TL* **52**, 3919 (2011)
[68] He, P., Liu, X., Zheng, H., Li, W., Lin, L., Feng, X. *OL* **14**, 5134 (2012)
[69] Robertson, F.J., Wu, J. *JACS* **134**, 2775 (2012)
[70] Malkov, A.V., Stewart-Liddon, A.J.P., McGeoch, G.D., Ramirez-López, P., Kocovsky, P. *OBC* **10**, 4864 (2012)
[71] Jones, S., Warner, C.J.A. *OBC* **10**, 2189 (2012)
[72] Arai, N., Utsumi, N., Matsumoto, Y., Murata, K., Tsutsumi, K., Ohkuma, T. *ASC* **354**, 2089 (2012)
[73] Vaquero, M., Suarez, A., Vargas, S., Bottari, G., Alvarez, E., Pizzano, A. *CEJ* **18**, 15586 (2012)
[74] Qin, J., Chen, F., Ding, Z., He, Y.-M., Xu, L., Fan, Q.-H. *OL* **13**, 6568 (2011)
[75] Kluwer, A.M., Detz, R.J., Abiri, Z., van der Burg, A.M., Reek, J.N.H. *ASC* **354**, 89 (2012)
[76] Ye, Z.-S., Chen, M.-W., Chen, Q.-A., Shi, L., Duan, Y., Zhou, Y.-G. *ACIE* **51**, 10181 (2012)
[77] Maj, A.M., Suisse, I., Méliet, C., Hardouin, C., Agbossou-Niedercorn, F. *TL* **53**, 4747 (2012)
[78] Shi, L., Ye, Z.-S., Cao, L.-L., Guo, R.-N., Hu, Y., Zhou, Y.-G. *ACIE* **51**, 8286 (2012)
[79] Berhal, F., Wu, Z., Zhang, Z., Ayad, T., Ratovelomanana-Vidal, V. *OL* **14**, 3308 (2012)
[80] Cartigny, D., Berhal, F., Nagano, T., Phansavath, P., Ayad, T., Gênet, J.-P., Ohshima, T., Mashima, K., Ratovelomanana-Vidal, V. *JOC* **77**, 4544 (2012)
[81] Gao, K., Yu, C.-B., Wang, D.-S., Zhou, Y.-G. *ASC* **354**, 483 (2012)
[82] Zhang, D.-Y., Wang, D.-S., Wang, M.-C., Yu, C.-B., Gao, K., Zhou, Y.-G. *S* 2796 (2011)
[83] Hu, J., Wang, D., Zheng, Z., Hu, X. *ChJC* **30**, 2664 (2012)
[84] Mikhailine, A.A., Maishan, M.I., Morris, R.H. *OL* **14**, 4638 (2012)
[85] Chen, M.-W., Chen, Q.-A., Duan, Y., Ye, Z.-S., Zhou, Y.-G. *CC* **48**, 1698 (2012)

Coupling reactions. In recent years more attention has been directed toward synthesis of chiral substances by coupling reactions. The Negishi coupling is considered as most amenable to development because organozinc reagents are relatively reactive, stable, and readily subject to Ni-catalysis which can be regulated by ligands. Indeed alkylation of secondary benzylic bromides and 2-bromoalkanitriles are successful by this method using **272** and **273**, respectively to modify the nickel halide catalyst.[1,2]

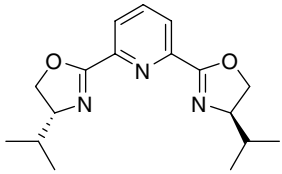
Nickel bromide also mediates Suzuki coupling of functionalized alkyl halides and 9-alkyl-BBN. A chiral version is driven by (1*R*,2*R*)-(*N*,*N*′-dimethyl)diphenyldiamine.[3,4] Other effective ligands include **274** for replacing the halogen by a B(pin) group.[5]



(**272**)

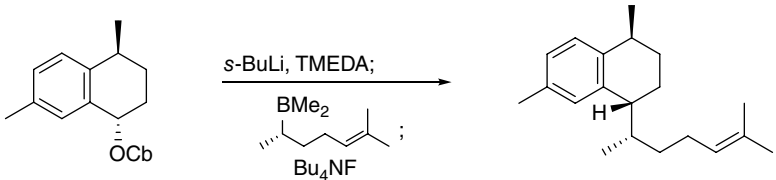


(**273**)



(**274**)

Configurationally stable organolithium and organoborane reagents are coupled to furnish products of defined stereochemistry, and this strategy is embodied in a synthesis of erogorgiane.[6]



In a chiral route to binaphthyls by Pd-catalyzed Suzuki cross-coupling polyquinoxaline-based phosphines are employed.[7] The P,N-ligand **275** is still effective in the coupling leading to 2-acylbiphenyls despite its chirality element is further removed.[8]

An application of the Suzuki coupling is for kinetic resolution of 2-(α-hydroxybenzyl) cyclopentenones. Chiral 1-(*t*-butanesulfinylamino)-1,3-diphenyl-2-propene **276** is used for the purpose.[9]

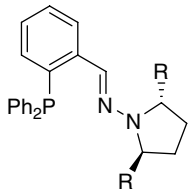
A synthetic approach to chiral diarylsilanes is that which involves Hiyama coupling of $ArSiMeH_2$ and Ar′I. A Pd-complex containing **2D** is rewarding.[10]

Alkylation of *N*-acylindoles at C-2 by 1-alkenes is accomplished under catalysis of an iridium(I) salt and a diphosphine ligand. With BINAP a linear alkyl group is introduced therefore the racemic phosphine suffices, but **132A** changes the course to producing branched 2-alkylindoles.[11]

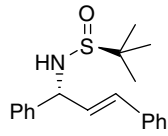
A catalyst system consisting of $[(C_2H_4)_2RhCl]_2$ and ligand **277** promotes coupling of $RB(OH)_2$ with 5,6-dihydro-2-pyrone, but asymmetric 1,4-addition to *N*-Boc 3-pyrrolinone.[12]

The combination of $Pd(OCOCF_3)_2$ and **117B** is stable to air and moisture, and it promotes enantioselective Heck reaction of cycloalkenes.[13] *N*-Branched alkylated *o*-haloanilines cyclize to chiral indolines when $Pd(OAc)_2$ is modified by **143**.[14] This process is found to be facilitated by a bulky acid (as cooperative catalyst to phosphine such as **278**).[15]

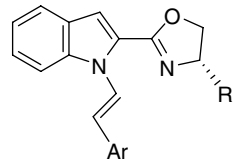
A very bulky Pd-carbenoid derived from **279** and cinnamylpalladium chloride is useful for the dehydrobrominative cyclization of *N*-(α-fluoroarylacetyl)-*o*-bromoanilines in the chiral sense.[16]



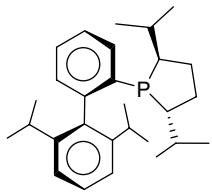
(**275**)



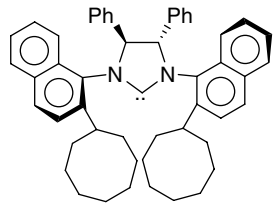
(**276**)



(**277**)



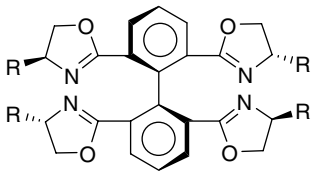
(**278**)



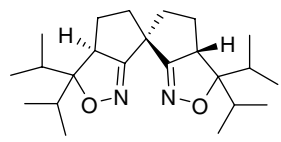
(**279**)

Diaryl(*o*-triflyloxyphenyl)silanes in which the two aryl groups are identical undergo desymmetrization on cyclization. It is achieved by using $Pd(OAc)_2$ and **32B** as catalyst.[17]

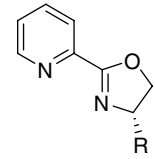
Unsaturated alcohols, acids, and amines form 2-alkenyl heterocycles under oxidative coupling conditions, and Pd catalysts can be modified by chiral ligands, e.g., **280**[18] **281**,[19] **282A/B**,[20,21] to attain enantioselective results.



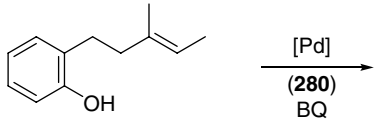
(**280**) R = Ph, *i*-Pr, *t*-Bu



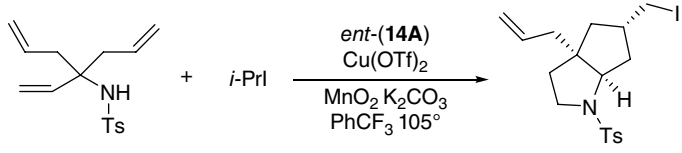
(**281**)

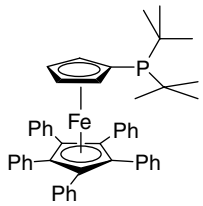


(**282A**) R = *t*-Bu
(**282B**) R = Ph



o-Bromobenzamides bearing an α-styryl and a methallyl groups on the nitrogen atom are converted into benzannulated pyrrolizidinones, as a result of a tandem Heck reaction and iodination as the terminal step. Pd ligated to Q-Phos **283** is a good catalyst.[22] Interestingly, **14A**-$Cu(OTf)_2$ is able to deliver the same results.[23]





(**283**)

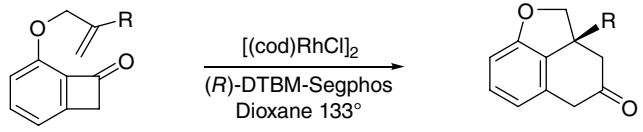
A direct synthesis of 4-benzyl-2-imidazolidinones from *N*-allylureas is to conduct Heck reaction and intramolecular hydroamination. The chiral process uses **203B** to enable the Pd species.[24] The same strategy is applicable to the elaboration of *N*-tosyl-2-cinnamylpyrrolidines, and a Cu(II)- Ph-box catalyst system is applicable.[25]

By introduction of an aryl group to the triple bond of 6-alkyn-1-enyl ketones simultaneously to cyclization leads to 2-arylidenecyclopentylmethyl ketones. It creates an asymmetric carbon atom when a Segphos-supportede Pd(II) salt is used.[26]

Intramolecular arylation of cyclopropane is observed and the result is an enantioselective formation of a fused tetrahydroquinoline system [catalyst: $(dba)_2Pd$, ligand **2D**]. It is proposed that 7-membered palladacycles are the intermediates.[27]

Cycloisomerization of *N*-(4-chloro-2*Z*-butenyl)-2-alkynamides involves return of the chlorine atom to the β-carbon of the amide unit while establishing a vinyl group in the pyrrolidone ring. This reaction is catalyzed by a Rh complex and subject to asymmetric command by a phosphine ligand such as **198A**.[28] Dihydronaphthobenzofuran has been acquired in a two-step coupling, initiated by a Rh-catalyzed (ligand: **32A**) S_N2' reaction of a 2-chlorophenylboronate on 1,4-oxa-1,4-dihydronaphthalene.[29]

The ring strain of benzocyclobutenone apparently facilitates insertion of Rh. A conveniently located double then participates in reorganization of the cyclic array.[30]

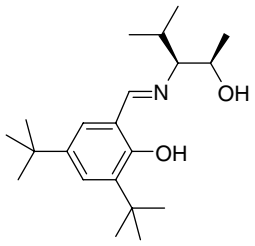


[1] Binder, J.T., Cordier, C.J., Fu, G.C. *JACS* **134**, 17003 (2012)
[2] Choi, J., Fu, G.C. *JACS* **134**, 9102 (2012)
[3] Zultanski, S.L., Fu, G.C. *JACS* **133**, 15362 (2011)
[4] Wilsily, A., Tramutola, F., Owston, N.A., Fu, G.C. *JACS* **134**, 5794 (2012)
[5] Dudnik, A.S., Fu, G.C. *JACS* **134**, 10693 (2012)
[6] Elford, T.G., Nave, S., Sonawane, R.P., Aggarwal, V.K. *JACS* **133**, 16798 (2011)

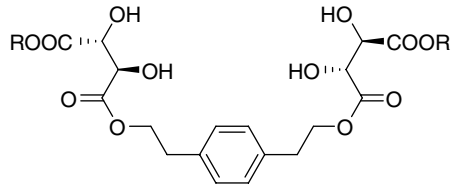
[7] Yamamoto, T., Akai, Y., Nagata, Y., Suginome, M. *ACIE* **50**, 8844 (2011)
[8] Ros, A., Estepa, B., Bermejo, A., Alvarez, E., Fernandez, R., Lassaletta, J.M. *JOC* **77**, 4740 (2012)
[9] Wang, Y., Feng, X., Du, H. *OL* **13**, 4954 (2011)
[10] Kurihara, Y., Nishikawa, M., Yamanoi, Y., Nishihara, H. *CC* **48**, 11564 (2012)
[11] Pan, S., Ryu, N., Shibata, T. *JACS* **134**, 17474 (2012)
[12] Kuuloja, N., Vaismaa, M., Franzen, R. *T* **68**, 2313 (2012)
[13] Correia, C.R.D., Oliveira, C.C., Salles Jr, A.G., Santos, E.A.F. *TL* **53**, 3325 (2012)
[14] Anas, S., Cordi, A., Kagan, H.B. *CC* **47**, 11483 (2011)
[15] Saget, T., Lemouzy, S.J., Cramer, N. *ACIE* **51**, 2238 (2012)
[16] Wu, L., Falivene, L., Drinkel, E., Grant, S., Linden, A., Cavallo, L., Dorta, R. *ACIE* **51**, 2870 (2012)
[17] Shintani, R., Otomo, H., Ota, K., Hayashi, T. *JACS* **134**, 7305 (2012)
[18] Liu, Q., Wen, K., Zhang, Z., Wu, Z., Zhang, Y.J., Zhang, W. *T* **68**, 5209 (2012)
[19] Takenaka, K., Akita, M., Tanigaki, Y., Takizawa, S., Sasai, H. *OL* **13**, 3506 (2011)
[20] Yang, G., Shen, C., Zhang, W. *ACIE* **51**, 9141 (2012)
[21] Weinstein, A.B., Stahl, S.S. *ACIE* **51**, 11505 (2012)
[22] Newman, S.G., Howell, J.K., Nicolaus, N., Lautens, M. *JACS* **133**, 14916 (2011)
[23] Bovino, M.T., Chemler, S.R. *ACIE* **51**, 3923 (2012)
[24] Hopkins, B.A., Wolfe, J.P. *ACIE* **51**, 9886 (2012)
[25] Liwosz, T.W., Chemler, S.R. *JACS* **134**, 2020 (2012)
[26] Shen, K., Han, X., Lu, X. *OL* **14**, 1756 (2012)
[27] Saget, T., Cramer, N. *ACIE* **51**, 12842 (2012)
[28] Jackowski, O., Wang, J., Xie, X., Ayad, T., Zhang, Z., Ratovelomanana-Vidal, V. *OL* **14**, 4006 (2012)
[29] Tsui, G.C., Tsoung, J., Dougan, P., Lautens, M. *OL* **14**, 5542 (2012)
[30] Xu, T., Ko, H.M., Savage, N.A., Dong, G. *JACS* **134**, 20005 (2012)

Oxidation reactions. In the presence of $Sc(OTf)_3$ the regioselectivity of Baeyer-Villiger oxidation of 2-substituted cyclohexanones is overthrown. A procedure for the acquisition of chiral 6-hexanolides is therefore developed by adding the Sc salt, **71B,** and $(i\text{-PrO})_3Al$, besides MCPBA.[1]

Oxidation of 1,3-dithianes to the chiral mono-sulfoxides is based on the established method using $VO(acac)_2$ and H_2O_2, but adding **284** to exert stereocontrol during delivery of the oxygen atom.[2] The other method using titanium(IV) tartrate chelates is modified by joining two ligands. In other words, **285** instead of normal tartrate esters is used.[3]



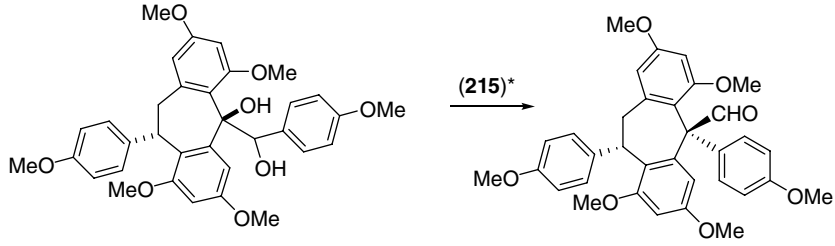
(**284**)



(**285**)

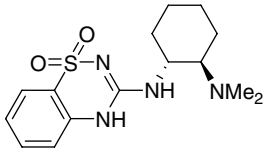
[1] Zhou, L., Liu, X., Ji, J., Zhang, Y., Hu, X., Lin, L., Feng, X. *JACS* **134**, 17023 (2012)
[2] Wu, Y., Mao, F., Meng, F., Li, X. *ASC* **353**, 1707 (2011)
[3] Newhouse, T.R., Li, X., Blewett, M.M., Whitehead, C.M.C., Corey, E.J. *JACS* **134**, 17354 (2012)

Isomerization and rearrangements. A key intermediate for a hopeanol synthesis is a dibenzocycloheptadiene with chirality at the benzhydryl position. The goal was achieved by a pinacol rearrangement and the most remarkable observation is that both (*R*)- and (*S*)-**215** can be used.[1]

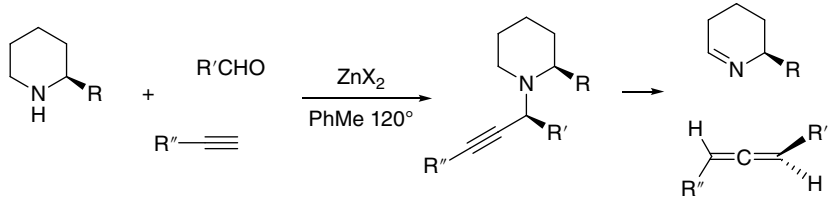


(**215**)*, either (*R*)- or (*S*)-

To acquire β-branched chiral aldehydes by isomerization of allylic alcohols an iridium complex of **236C** is found valuable.[2] For conversion of 3-alkynoic esters into the 2,3-alkadienoic ester isomers in chiral modification the cyclohexanediamine derivative **285** has been employed as catalyst.[3] Chiral allenes are synthesized from aldehydes and 1-alkynes via propargylic amines, chirality transfer from a 2-substituted piperidine is the crux of the transformation.[4]



(**285**)

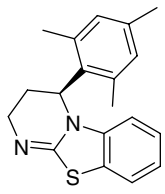


Hydration followed by a 1,5-hydride migration converts 1.4-oxa-1,4-dihydronaphthalene into (*R*)-2-hydroxy-1-tetralone. The chiral information comes from **32A** via complexation to the Rh center of the catalyst.[5]

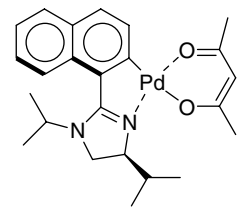
Treatment with **286** changes oxazol-5-yl acetates and carbonates into chiral 4-acyl-5-oxazolinones.[6]

Claisen rearrangement of 2-allyloxy- and 2-propargyloxyindole-3-carboxylic esters can be effected by Pd(II) or Cu(II) hexafluoroantimonates, ligation of the Pd center ligated by a BINAP or Cu(II) by **64A** gains access to the enantiomers.[7] Ring contraction and functional group transformation from Claisen rearrangement of macrocyclic alkenyl/allyl ethers are also amenable to chiral manipulation such as catalysis by $Cu(SbF_6)_2$ and **62D**.[8] Complementary to $Cu(OTf)_2$ by the diphenyl analog of **62D** the rearrangement of α-allyloxyalkenylphosphonates leads to acylphosphonates containing an asymmetric carbon atom at the β-position.[9] With the same ligand to bind $Pd(OCOCF_3)_2$ enantioselective sigmatropic rearrangement of the ene reaction products from 1-alkenes and sulfodiimides, hence a synthesis of (*S*)- 3- amino-1-alkenes is realized.[10]

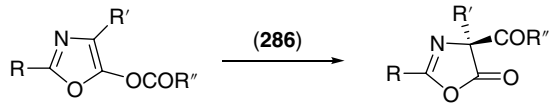
Palladacycle **287** is developed for catalyzing rearrangement of allyl trichloroacetimidates.[11] Chloropalladium species linking to a ferrocene is oxidized by AgX to the Pd(III) state that is active in catalyzing aza-Claisen rearrangement.[12]



(**286**)

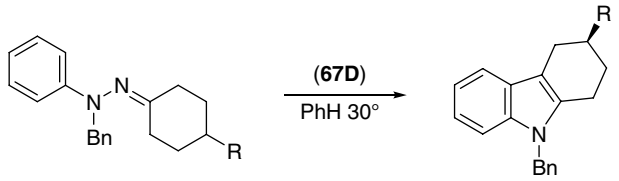


(**287**)



R″ = Me, OR

Phosphoric acid **67D** effectively mediates the Fischer indolization of 4-substituted cyclohexanone *N*-benzyl-*N*-phenylhydrazones. The tetrahydrocarbazole products are chiral.[13]

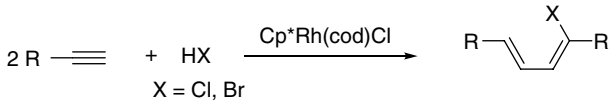


[1] Snyder, S.A., Thomas, S.B., Mayer, A.C., Breazzano, S.P. *ACIE* **51**, 4080 (2012)
[2] Li, J.-Q., Peters, B., Andersson, P.G. *CEJ* **17**, 11143 (2011)
[3] Inokuma, T., Furukawa, M., Uno, T., Suzuki, Y., Yoshida, K., Yano, Y., Matsizaki, K., Takemoto, Y. *CEJ* **17**, 10470 (2011)

[4] Periasamy, M., Sanjeevakumar, N., Dalai, M., Gurubrahamam, R., Reddy, P.O. *OL* **14**, 2932 (2012)
[5] Tsui, G.C., Lautens, M. *ACIE* **51**, 5400 (2012)
[6] Viswambharan, B., Okimura, T., Suzuki, S., Okamoto, S. *JOC* **76**, 6678 (2011)
[7] Cao, T., Linton, E.C., Deitch, J., Berritt, S., Kozlowski, M.C. *JOC* **77**, 11034 (2012)
[8] Jaschinski, T., Hiersemann, M. *OL* **14**, 4114 (2012)
[9] Tan, J., Cheon, C.-H., Yamamoto, H. *ACIE* **51**, 8264 (2012)
[10] Bao, H., Tambar, U.K. *JACS* **134**, 18495 (2012)
[11] Cannon, J.S., Frederich, J.H., Overman, L.E. *JOC* **77**, 1939 (2012)
[12] Eitel, S.H., Bauer, M., Schweinfurth, D., Deibel, N., Sarkar, B., Kelm, H., Krüger, H.-J., Frey, W., Peters, R. *JACS* **134**, 4683 (2012)
[13] Müller, S., Webber, M.J., List, B. *JACS* **133**, 18534 (2011)

Chloro(1,5-cyclooctadiene)pentamethylcyclopentadienylrhodium(II)

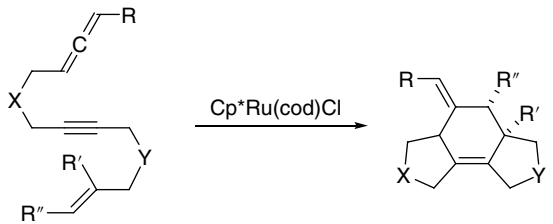
Additive dimerization. Head-to-head dimerization of 1-alkynes is accompanied by addition of HX.[1]



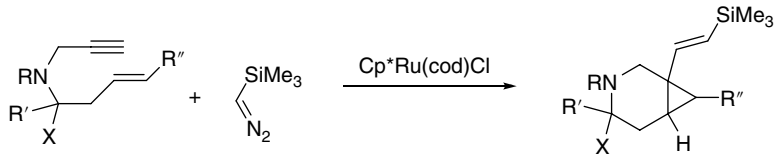
[1] Klein, H., Roisnel, T., Bruneau, C., Dérien, S. *CC* **48**, 11032 (2012)

Chloro(1,5-cyclooctadiene)pentamethylcyclopentadienylruthenium(II)

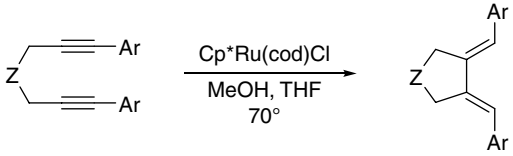
Annulation. The title complex can gather molecules containing two double bonds and a triple bond (properly distanced) and coax them into tricyclic systems.[1]



Another mode of cycloaddition involves an enyne unit and a diazo compound.[2]



1,6-Diynes cyclize to give 1,2-dialkylidenecyclopentanes, the source of the two hydrogen atoms is MeOH.[3]

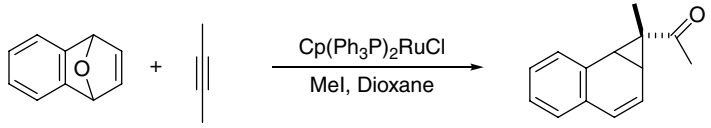


[1] Saito, N., Ichimaru, T., Sato, Y. *CAJ* **7**, 1521 (2012)
[2] Vovard-Le Bray, C., Klein, H., Dixneuf, P.H., Mace, A., Berree, F., Carboni, B., Derien, S. *ASC* **354**,1919 (2012)
[3] Yamashita, K., Nagashima, Y., Yamamoto, Y., Nishiyama, H. *CC* **47**, 11552 (2011)

Chloro(cyclopentadienyl)bis(triphenylphosphine)ruthenium(II)

Cyclization. *N*-Tosyl-*o*-propargylaniline undergoes intramolecular hydroamination on heating with $(Ph_3P)_2Ru(Cp)Cl$ and pyridine to afford the 1,4-dihydroquinoline derivative. The method is also applicable to synthesis of indoles and dihydroisoquinolines.[1]

Reaction of alkynes with 1,4-oxa-1,4-dihydronaphthalene yields cyclopropanonaphthalenes,[2] oxygen transfer is involved and the alkynes react as if they were α-acylcarbenes.



[1] Varela-Fernandez, A., Varela, J.A., Saá, C. *ASC* **353**, 1933 (2011)
[2] Tenaglia, A., Marc, S., Giordano, L., De Riggi, I. *ACIE* **50**, 9062 (2011)

1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate), (Selectfluor®).

Fluorination. Direct fluorination of ketones by Selecfluor proceeds in MeCN containing 0.1 equivalent H_2SO_4 [1] along with $[Cp^*IrCl_2]_2$ as catalyst in aq. THF, it transforms allylic alcohols into α-fluoroketones.[2]

3,3-Difluorination of indole at C-3 is accomplished; *N*-substituted indoles afford the 3,3-difluoro-2-hydroxyindolines.[3] Three catalysts, $Sn(OTf)_2$, $KB(C_6F_5)_4$, and pyridine, are used in α,α-difluorination of acid chlorides.[4] Decarboxylative fluorination of carboxylic acids is executed in the presence of $AgNO_3$,[5] or in the case of $ArOCH_2COOH$, photo-assisted.[6]

Facilitators for monofluorination of saturated cycloalkanes such as cyclododecane with Selecfluor are CuI, *N,N′*-dibenzalethanediamine, *N*-hydroxyphthalimide, and $KB(C_6F_5)_4$.[7]

Carboxylic acids and tosylamines which feature an allene in the carbon chain cyclize on fluorination, the products contain two allylic fluorine atoms.[8]

Desilylfluorination of aryltrialkoxysilanes is achieved on heating with Selecfluor and Ag_2O–BaO.[9]

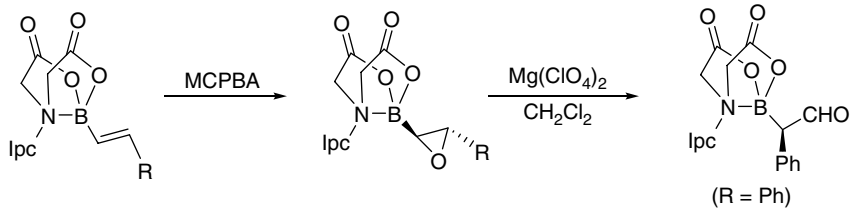
Coupling. In the reaction of arylboronic acids and arylstannanes with tris(dimethylamino)sulfonium trifluoromethoxide to give $ArOCF_3$, mediation by a silver salt and Selectfluor is indicated.[10] By the same token, Selectfluor enables allylation of α-amino esters with allylsilanes and potassium allyltrifluoroborate.[11]

In another capacity that Selectfluor serves is the cinnamylation of *N*-tosylcarbamates, allylarenes are activated for palladation or the $Pd(OAc)_2$ catalyst is recycled in situ.[12] The Au-catalyzed coupling-cyclization of 4-penten-1-ylamines with $RB(OH)_2$ also requires formation of bimetallic Au(II)-Au(II) complexes and Selectfluor is responsible for promotion of such key intermediates.[13]

[1] Liu, J., Chan, J., Bryant, C.M., Duspara, P.A., Lee, E.E., Powell, D., Yang, H., Liu, Z., Walpole, C., Roberts, E., Batey, R.A. *TL* **53**, 2971 (2012)
[2] Ahlsten, N., Martin-Matute, B. *CC* **47**, 8331 (2011)
[3] Lin, R., Ding, S., Shi, Z., Jiao, N. *OL* **13**, 4498 (2011)
[4] Bloom, S., Scerba, M.T., Erb, J., Lectka, T. *OL* **13**, 5068 (2011)
[5] Yin, F., Wang, Z., Li, Z., Li, C. *JACS* **134**, 10401 (2012)
[6] Leung, J.C.T., Chatalova-Sazepin, C., West, J.G., Rueda-Becerril, M., Paquin, J.-F., Sammis, G.M. *ACIE* **51**, 10804 (2012)
[7] Bloom, S., Pitts, C.R., Miller, D.C., Haselton, N., Holl, M.G., Urheim, E., Lectka, T. *ACIE* **51**, 10580 (2012)
[8] Cui, J., Chai, Z., Lu, Y., Li, P., Zhao, G., Zhu, S. *ChJC* **29**, 2744 (2011)
[9] Tang, P., Ritter, T. *T* **67**, 4449 (2011)
[10] Huang, C., Liang, T., Harada, S., Lee, E., Ritter, T. *JACS* **133**, 13308 (2011)
[11] Daniels, M.H., Hubbs, J. *TL* **52**, 3543 (2011)
[12] Xiong, T., Li, Y., Mao, L., Zhang, Q., Zhang, Q. *CC* **48**, 2246 (2012)
[13] Tkatchouk, E., Mankad, N.P., Benitez, D., Goddard III, W.A., Toste, F.D. *JACS* **133**, 14293 (2011)

m-Chloroperoxybenzoic acid, (MCPBA)

Epoxidation. Upon epoxidation by MCPBA and subsequent exposure to a Lewis acid, alkenylboronates are transformed into α-boryl carbonyl compounds.[1] Although alkenes undergo epoxidation by MCPBA alone, a report indicates the use of cobalt perchlorate to catalyze the reaction with 1-alkenes.[2]

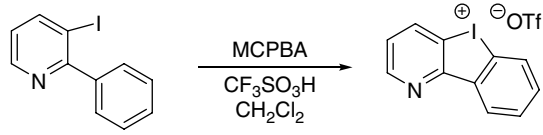


N-Silyloxaziridines have been acquired by epoxidation. Further treatment with amines leads to hydrazones.[3]

Oxidation of iodine reagents. *N*-Phthaloylaziridines are prepared from *N*-amino phthalimide by oxidation with HIO, which is generated from Bu_4NI (catalytic) and MCPBA.[4]

Whereas $ArI(OAc)_2$ are generated from iodoarenes by treatment with MCPBA in acetic acid,[5] their stoichiometric use in most circumstances can be circumvented catalytically. For example, it requires small quantities of PhI to perform Hofmann rearrangement of primary amides as long as sufficient MCPBA and HBF_4 are added.[6]

3-Iodo-2-phenylpyridine is oxidized by MCPBA to the tricyclic iodonium ion.[7] On a Pd-catalyzed coupling with $BnNH_2$ a δ-carboline is obtained.



A convenient preparation of alkynyl(aryl)iodonium salts from ArI consists of oxidation and coupling with alkynylboronic acids.[8] When NaI is oxidized in the presence of propargylic alcohols, it transforms the latter compounds into α-iodoalkenones (oxygen-site transposed).[9]

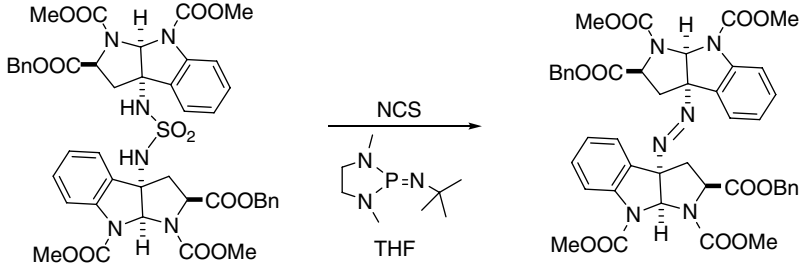
Heterocycle cleavage. 1,3-Diarylbenzo[*c*]furans undergo oxidative cleavage to give 1,2-diaroylarenes. The corresponding thiophenes and selenophenes are similarly oxidized (with loss of the heteroatoms).[10]

Alkylation. Indoles can be alkylated by *N.N*-disubstituted glycine esters under oxidative conditions.[11] It is likely that *N*-oxides and iminium species are the intermediates. (The MeCN solvent might play an important role to allow a Polonovski reaction to proceed.)

[1] Li, J., Burke, M.D. *JACS* **133**, 13774 (2011)
[2] Hyun, M.Y., Kim, S.H., Song, Y.J., Lee, H.G., Jo, Y.D., Kim, J.H., Hwang, I.H., Noh, Y.Y., Kang, J., Kim, C. *JOC* **77**, 7307 (2012)
[3] Richy, N., Ghoraf, M., Vidal, J. *JOC* **77**, 10972 (2012)
[4] Yoshimura, A., Middleton, K.R., Zhu, C., Nemykin, V.N., Zhdankin, V.V. *ACIE* **51**, 8059 (2012)
[5] Iinuma, M., Moriyama, K., Togo, H. *SL* 2663 (2012)
[6] Miyamoto, K., Sakai, Y., Goda, S., Ochiai, M. *CC* **48**, 982 (2012)
[7] Letessier, J., Detert, H. *S* 290 (2012)
[8] Bouma, M.J., Olofsson, B. *CEJ* **18**, 14242 (2012)
[9] Moran, W.J., Rodriguez, A. *OBC* **10**, 8590 (2012)
[10] Nandakumar, M., Sivasakthikumaran, R., Mohanakrishnan, A.K. *EJOC* 3647 (2012)
[11] Xu, Z., Yu, X., Feng, X., Bao, M. *JOC* **77**, 7114 (2012)

N-Chlorosuccinimide

N-Oxidation. Removal of SO_2 from *N,N′*-disubstituted sulfuric diamides via *N*-chlorination is analogous to the Ramberg-Bäcklund reaction.[1]



Synthesis of sulfondiimides from aminosulfonium salts is easily carried out with NCS then reaction with amines.[2]

[1] Movassaghi, M., Ahmad, O.K., Lathrop, S.P. *JACS* **133**, 13002 (2011)
[2] Candy, M., Guyon, C., Mersmann, S., Chen, J.-R., Bolm, C. *ACIE* **51**, 4440 (2012)

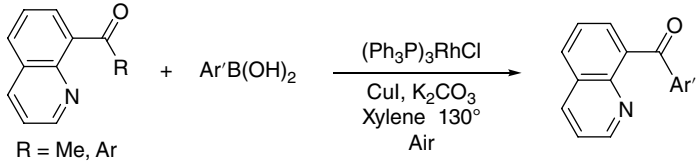
Chlorotris(triphenylphosphine)rhodium(I)

Reduction. A new application of $(Ph_3P)_3RhCl$ is as catalyst for transfer hydrogenation from *i*-PrOH to carbonyl compounds.[1]

Reductive acylation. Conjugated esters are transformed into α–substituted β-keto esters by reaction with acid chlorides in the presence of Et_2Zn and $(Ph_3P)_3RhCl$.[2]

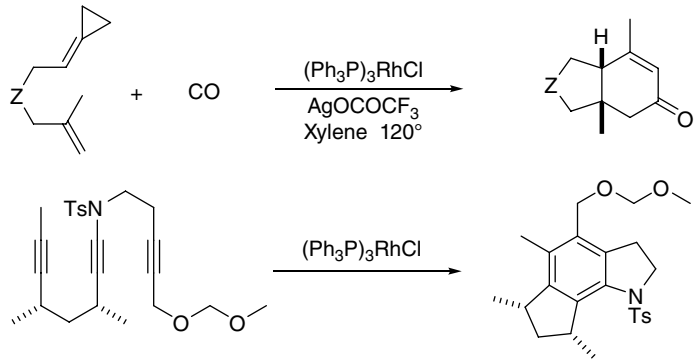
Alkylation. Enolizable α-diketones are alkylated by alkenes via formation of enamino-rhodium hydrides, an essential but recyclable additive is 2-aminopyridine.[3]

Group exchange. 8-Quinolinyl ketones (methyl and phenyl) can shed the methyl or phenyl group and form new mixed aryl ketones on reaction with $ArB(OH)_2$. The reaction goes through stabilized rhodacycle intermediates initiated by Rh insertion into a CC bond.[4]

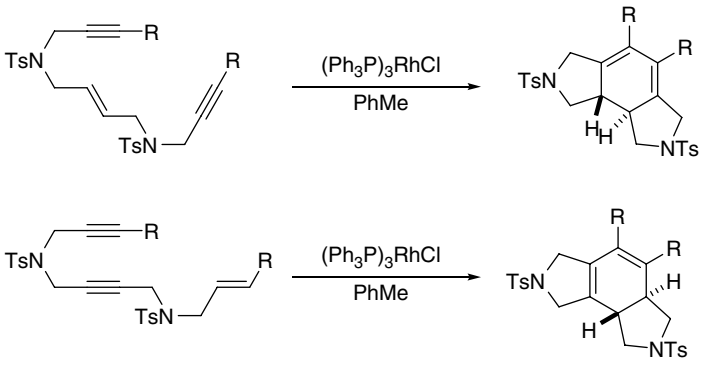


Cycloaddition. The ability of the rhodium chloride to promote double bond migration transforms *N*-allylproline esters into reactants of [3+2]cycloaddition with electron-deficient alkenes.[5]

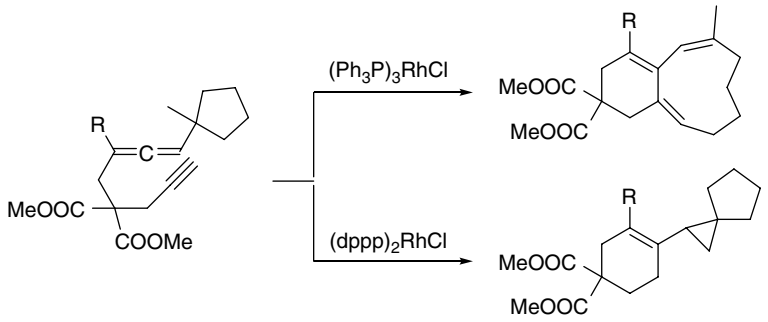
Several cycloaddition modes participated by selected alkenes, allenes, alkynes, and alkylidenecyclopropanes have been unraveled. It can also incorporate CO to form cyclic ketones,[6] and elaborate a *cis*-trikentrin intermediate.[7]



Carbon chains containing two triple bonds and one double bond in different relations undergo [2+2+2]cycloaddition to give tricyclic systems of distinct stereochemistry and location of the diene unit.[8]



Perhaps the most unusual case is the ring cleavage of an allenylcyclopentane to furnish a 7-carbon unit for cycloaddition with an alkyne.[9] It is also noteworthy that the RhCl with bidentate phosphine ligands commands a remarkably diverse pathway due to preferential C-H bond activation instead of acting on a C-C bond.

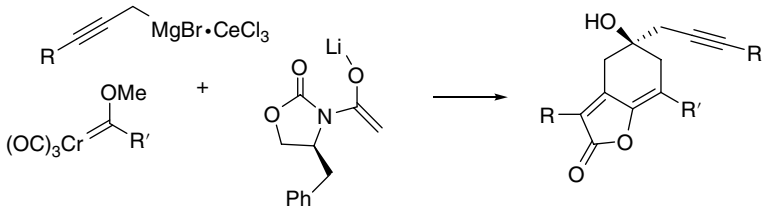


[1] Bogar, K., Krumlinde, P., Bacsik, Z., Hedin, N., Bäckvall, J.-E. *EJOC* 4409 (2011)
[2] Sato, K., Isoda, M., Ohata, S., Morita, S., Tarui, A., Omote, M., Kumadaki, I., Ando, A. *ASC* **354**, 510 (2012)
[3] Wang, Z., Reinus, B.J., Dong, G. *JACS* **134**, 13954 (2012)
[4] Wang, J., Chen, W., Zuo, S., Liu, L., Zhang, X., Wang, J. *ACIE* **51**, 12334 (2012)
[5] Gorman, R.M., Little, M.A., Morris, J.A., Sridharan, V. *CC* **48**, 9537 (2012)
[6] Mazumder, S., Shang, D., Negru, D.E., Baik, M.-H. *JACS* **134**, 20569 (2012)
[7] Saito, N., Ichimaru, T., Sato, Y. *OL* **14**, 1914 (2012)
[8] Dachs, A., Pla-Quintana, A., Parella, T., Sola, M., Roglans, A. *CEJ* **17**, 14493 (2011)
[9] Mukai, C., Ohta, Y., Oura, Y., Kawaguchi, Y., Inagaki, F. *JACS* **134**, 19580 (2012)

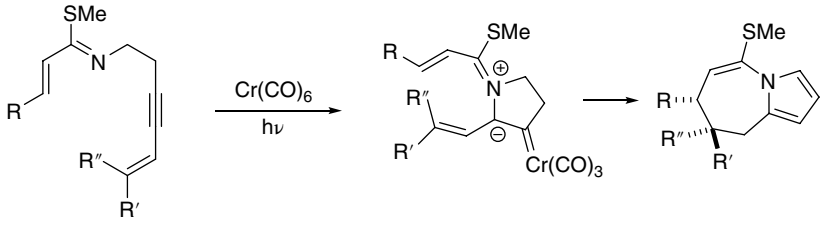
Chromium – carbene complexes

Annulation. Fischer carbene complexes with a conjugated triple bond are found to be 1,3-dipolarophiles.[1] The metal-carbenoid remains intact in the cycloadducts and can be employed for other reactions.

That three different organometallic compounds combine to yield bicyclic lactones[2] must be considered a rare event.



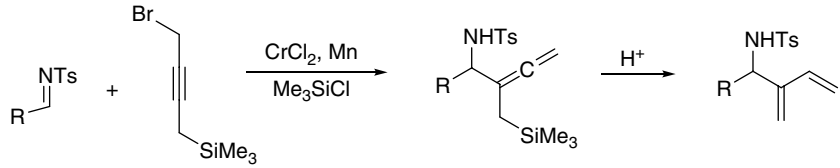
The in situ generation of Cr-carbenoid from an alkyne also sets up an electronically complimentary allyl carbanion and a conjugated iminium ion for electrocyclization.[3]



[1] Luo, N., Zheng, Z., Yu, Z. *OL* **13**, 3384 (2011)
[2] Suero, M.G., De la Campa, R., Torre-Fernandez, L., Garcia-Granda, S., Florez, J. *CEJ* **18**, 7287 (2012)
[3] Karibe, Y., Kusama, H., Iwasawa, N. *ACIE* **51**, 6214 (2012)

Chromium(II) chloride

Allenylation. Generated from propargyl bromides and $CrCl_2$ - Mn, the resulting organometallic reagents attack imines by the γ-carbon, therefore they behave as allenylating agents.[1]

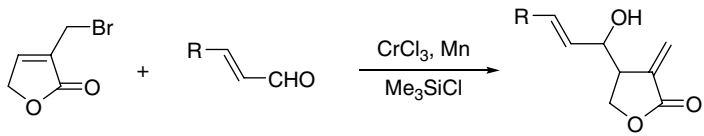


Alkenylsilanes. Dihalomethylsilanes are converted into silylmethylenating agents for aldehydes by $CrCl_2$.[2]

[1] Duran-Galvan, M., Connell, B.T. *T* **67**, 7901 (2011)
[2] Lim, D.S.W., Anderson, E.A. *OL* **13**, 4806 (2011).

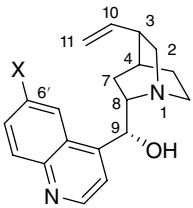
Chromium(III) chloride

Allylchromium reagents. 2-Bromomethyl-2-buten-4-olide is converted by $CrCl_3$ – Mn to an organochromium reagent, which adds to aldehydes to give α-methylene-γ-butyrolactones.[1]

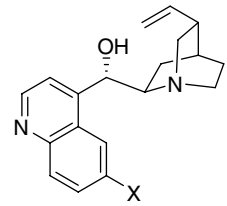


[1] Hodgson, D.M., Talbot, E.P.A., Clark, B.P. *CC* **48**, 6349 (2012)

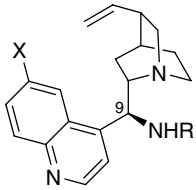
Cinchona alkaloid derivatives



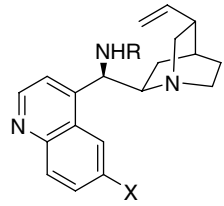
(**1A**) X = OMe quinine
(**1B**) X = H cinchonidine



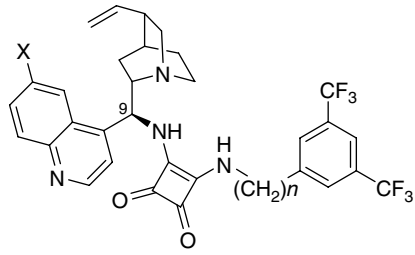
(**2A**) X = OMe quinidine
(**2B**) X = H cinchonine



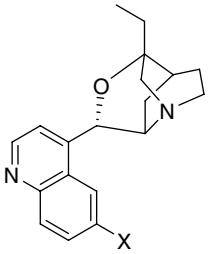
(**3A**) X = OMe, R = H
(**3B**) X = R = H
(**3C**) X = OMe,
R = C(S)NH[3,5-$(CF_3)_2C_6H_3$]
(**3D**) X = OMe,
R = C(S)NH[4-$MeOC_6H_4$]
(**3E**) X = OMe,
R = C(S)NH[2,6-Cl_2-4-$CF_3C_6H_2$]
(**3F**) X = OMe,
R = C(S)NHC*H(CH_2Ph)CH_2OH
(**3G**) X = OMe,
R = C(S)NH[2,6-*i*$Pr_2C_6H_3$]
(**3H**) X = OMe,
R = C(O)NHTs
(**3I**) X = OMe,
R = C(O)NH[3,5-$(CF_3)_2C_6H_3$]



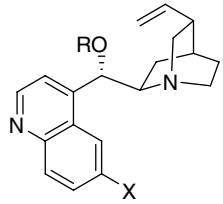
(**4A**) X = OMe, R = H
(**4B**) X = R = H
(**4C**) X = OMe,
R = C(S)NH[3,5-$(CF_3)_2C_6H_3$]



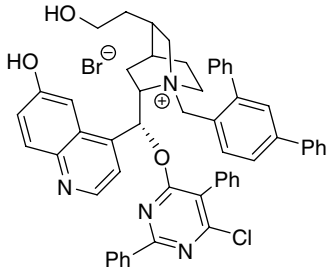
(**5A**) X = OMe, *n* = 0
(**5B**) X = R = H, *n* = 0
(**5C**) X = OMe, *n* = 1



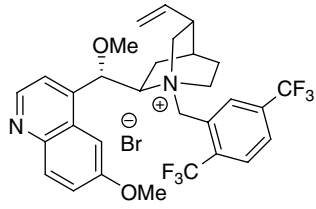
(**6A**) X = OMe
(**6B**) X = R = H
(**6C**) X = OH
(**6D**) X = OCONHCOCCl_3
(**6E**) X = CONH(*o*-$MeOC_6H_4$)



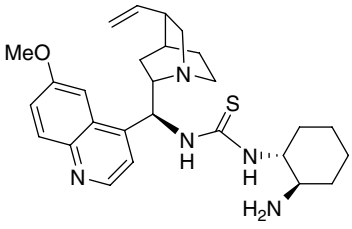
(**7A**) R = CH_2(α-Np), X = OMe
(**7B**) R = Bn,
X = C(S)NH[3,5-$(CF_3)_2C_6H_3$]



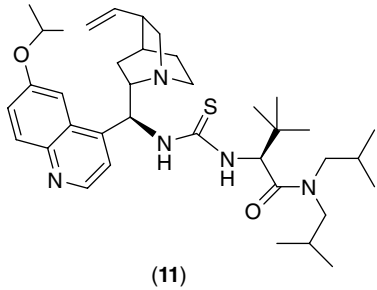
(**8**)



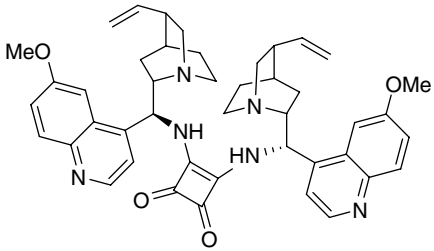
(**9**)



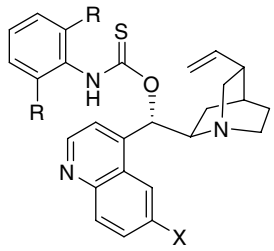
(**10**)



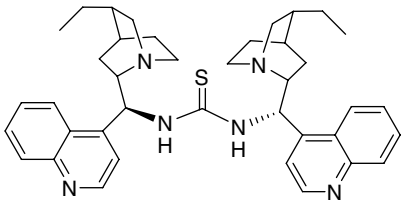
(**11**)



(**12**)



(**13A**) X = H, R = OEt
(**13B**) X = *i*-Am, R = Et



(**14**)

General aspects. Applications of cinchona alkaloids and preparation of new derivatives thereof for asymmetric synthesis are a flourishing subject of research. Various uses of the primary amines (C-9) are summarized.[1] The valuable (*R*)-*t*-butanesulfinamide is obtained from (−)-quinine in three steps: reaction with $SOCl_2$, then *t*-BuMgCl, and Li in liquid ammonia.[2] In the last step quinine is recovered.

Protonation. Isomerization of 3,4-disubstituted 3-cyclohexenones to the chiral 2-cyclohexenones is accomplished by treatment with the 2-chloropropanoic acid salt of **4C**.[3] 4-Substituted 3-buten-4-olides are transformed into the conjugated (4*S*)-butenolides by the catalytic action of *N*′-oxido-6′-hydroxycinchonine (obtained from dihydroquinidine).[4]

2′-Chloro-10,11-dihydroquinine promotes double bond migration of trifluoromethyl ketone benzylimines to afford (*R*)-2-benzylideneamino-1,1,1-trifluoroalkanes.[5] By changing the methoxy group of quinine into an arenesulfonamido group (for H-bonding) and the 9-hydroxyl into a 3-mesitylpropyl ether (steric sensor) a catalyst for enantioselective transamination of α-keto esters by *o*-chlorobenzylamine is carried out.[6]

A 9(*S*)-aryl-9-deoxydihydroquinine is useful for catalyzing alcoholysis of azlactones by allyl alcohol.[7] Mild hydrolysis of 3-trifluoroacetoxybenzofuran and allied heterocycles in the presence of $(DHQ)_2AQN$ {anthraquinone-1,4-diyl diether of dihydroquinine} provides the (*R*)-ketones.[8] Using $(DHQD)_2AQN$ as catalyst the Boc derivatives of methyl 2-(α−hydroxyalkyl)acrylates are hydrolyzed to give the (*S*)-alcohols.[9] In hydrolysis of 2-substituted 3-trifluoroacetoxybenzofuran and other heterocyclic analogs by $KHCO_3$ in DMSO, protonation is enantioselective as also directed by $(DHQ)_2AQN$.[9a]

Substitution. It is known that certain ammonium salts derived from cinchona alkaloids serve well as phase transfer agents. Another example of such application is in the alkylation of *N*-diphenylmethylideneglycine esters, employing *O*-allyl-1-(9-anthrylmethyl) cinchonidinium bromide.[10] This reaction is applicable to a synthesis of a tryptophan precursor [electrophile being a (3-indolylmethyl)ammonium bromide].[11]

Alkylation of aldehydes by 1,3-benzodithiolium tetrafluoroborate is enantioselective as rendered by the (-)camphor-10-sulfonate of 9-epiamino-9-deoxyquinidine (**4A**).[12] The salicylate of the dihydro base serves to guide the enantioselective α-benzoylation of ketones.[13] A similar catalyst [the (9*R*)-amine **3A**, which is prepared from quinine] is employed for benzoyloxylation of carbonyl compounds by $(PhCOO)_2$.[14] Cyclic ketones undergo Pd-catalyzed α-arylation, quinine can turn the process into asymmetric.[15]

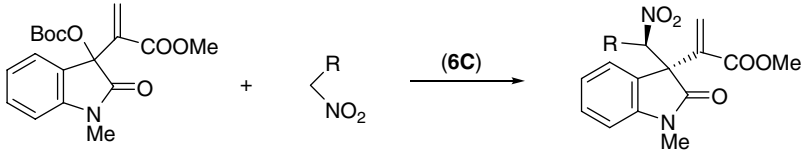
More uses of **3A** and derivatives have been discovered. Thus **3A** catalyzes asymmetric amination of aldehydes with BocN=NBoc,[16] the mixed thiourea derived from **3A** and substituted at the other nitrogen atom with a 3,5-bis(trifluoromethyl)phenyl group for that of 3-alkyl and 3-aryloxindoles.[17] A more complex derivative, **5A**, performs hydroxyamination (with PhN=O) on β-keto esters.[18] Asymmetric α-hydroxylation of β-keto esters is readily carried out with $Me_2C(Ph)OOH$ and the 1-adamantylcarboxylate of **2B**.[19] An alternative method for acquiring chiral 3-hydroxyoxindoles is by an S_N2 reaction of the halo compounds with ArCH=NOH (and K_2CO_3), followed by hydrogenative cleavage of the resulting oxime ethers. The chiral route is mediated by the 1-naphthylmethyl ether of de-*O*-methylquinidine.[20]

Sulfenylation of oxindoles has choice of quinidine[21] or the 1,4-phthalazinediyl diether pair $(DHQ)_2PHAL$/$(DHQD)_2PHAL$,[22] the latter two derivatives generate enantiomerically opposite products.

Another mixed thiourea **3D** is catalytic for fluorination of cyclic β-keto esters.[23]

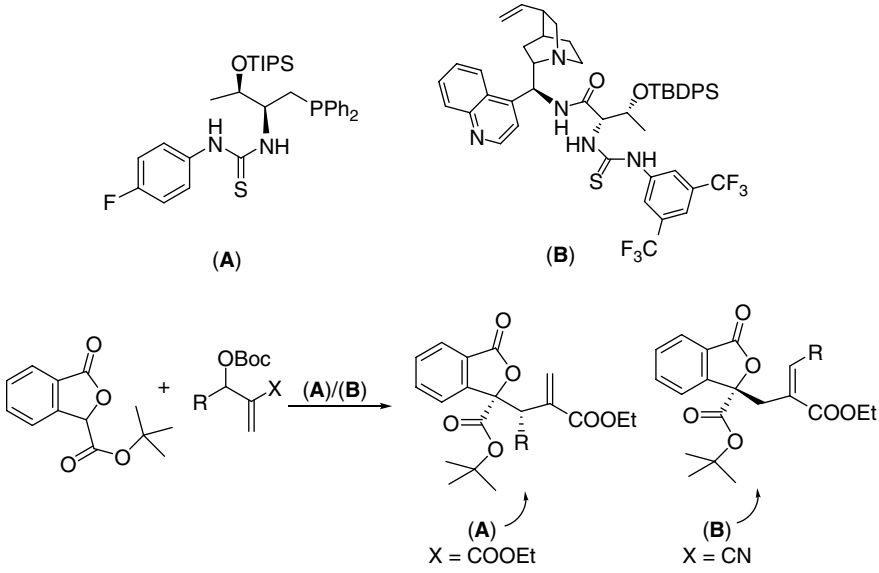
The hydroxyl group of Baylis-Hillman adducts is readily replaced after acylation. Enantioselective S_N2 reactions with benzophenone imine,[24] *N*-tosylallylamines,[25] and *N*-tosylcarbamates[26] are some of the N-nucleophiles that are used successfully, catalyzed by $(DHQD)_2AQN$, quinidine, and the cyclic ether **6B**, respectively.

Reaction of carbonates derived from Baylis-Hillman adducts with C-nucleophiles has also been scrutinized. These include 3-substituted 2(3*H*)-benzofuranones,[27] indene,[28] and bis(benzenesulfonyl)methane,[29] each employing $(DHQD)_2AQN$, and included in the last case also $FeCl_2$ or $(i\text{-PrO})_4Ti$. It is somewhat surprising that the new CC bond is formed at the quaternary carbon center in the reaction of a 3-alkenyl-3-hydroxyoxindole carbonate in the reaction with either nitroalkanes[30] or 4-methyl-3-buten-4-olide,[31] while **6C** serves as the catalyst.



Exchange of an allylic OBoc group by CF_3 is similarly performed, the nucleophile is generated from Me_3SiCF_3 by attack of KF and its course is guided by $(DHQD)_2PHAL$[32,33]

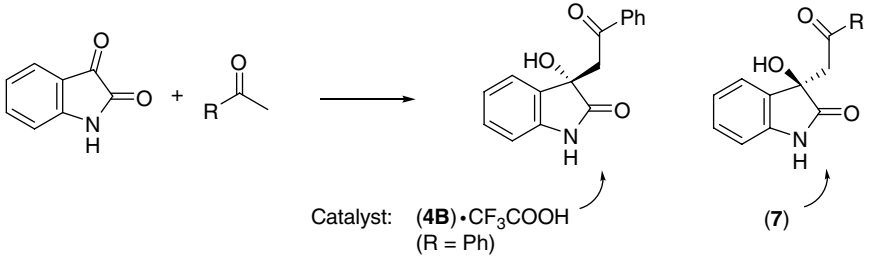
There are reports indicating an S_N2' course for the substitution, one using a mixed thiourea **4C** to conduct reaction with nitroalkanes,[34] and a second one involving allylation of *t*-butyl phthalide-3-carboxylate, which either S_N2 or S_N2' pathway can be chosen by varying the organocatalyst.[35]



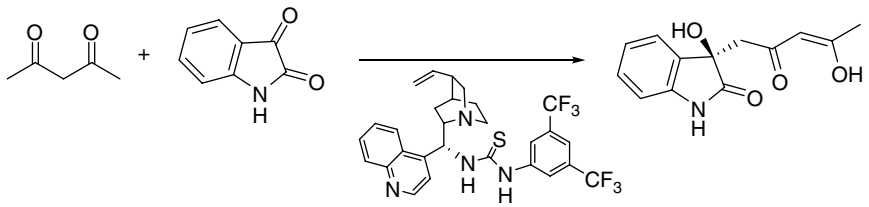
Addition to C=O. Silyl cyanation of the carbonyl group in acylphosphonates gives rise to adducts possessing a quaternary carbon center surrounded by very different functional groups and such compounds should find some unique synthetic applications. The thiourea derived from **3A** and tetraacetyl-β-glucosylamine is used in the addition.[36] Diisopropyl acetylphosphonate is an aldol donor and the products can undergo alcoholysis to yield 3-hydroxyalkanoic esters. For an access to the chiral hydroxyl compounds, mixed thiourea of **4D** is quite competent.[37]

The more popular mixed thiourea **4C** again (together with L-Phe) is recognized for its catalysis to generate *syn*-aldol products.[38] Reaction of homophthalic anhydride with aldehydes affords 3-substituted dihydroisocoumarin-4-carboxylic acids, and by using **5A** as catalyst the products have a (3*S*, 4*S*)-configuration.[39] An arylsuccinic anhydride adds to an aldehyde and the adduct turns up to be a 3-carboxyl-4-butanolide, with the aryl group and the carbon chain of the original aldehyde *cis*-related. A 2′-phenylated analog of **5A** carries the chirality mandate.[40]

Hydroxyacetone adds to 2-keto-3-alkenoic esters at room temperature to form adducts with two adjacent stereocenters. The reaction shows high enantioselectivity (99% ee) when catalyzed by the TFA salt of **4B**.[41] Linear aldol products emerge from reaction of methyl ketones and isatin. While the (*S*)-aldols are obtained in the reaction catalyzed by the TFA salt of **4B**, the enantiomeric (*R*)-isomers are produced by changing the catalyst to its ureido derivative.[42] The (*R*)-aldols are also assembled from isatin and β-keto acids using thiourea **3C**.[43]



The aldol reaction between oxindoles and ethyl glyoxylates proceeds well in the presence of $(DHQ)_2PHAL$[44] The mixed thiourea containing a 3,5-bis(trifluoromethyl) aniline group and (9*S*)-amino-(9*S*)-deoxycinchonidine imposes 1,3-dicarbonyl compounds like acetoacetic esters to perform aldol reaction at the chain terminus.[45]

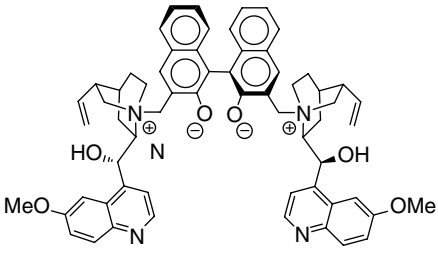


Cyclic ether **6D** is a catalyst for the asymmetric Baylis-Hillman reaction.[46] The imine derived from **3A** and 4,6-di-*t*-butylsalicylaldehyde forms a chelate with $Cu(OTf)_2$ to promote the Henry reaction, affording diastereomeric mixtures of nitro alcohols which have the carbinolic center in (*S*)-configuration.[47]

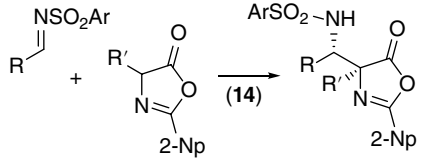
Addition to C=N. The nucleophilic addition to imines is well within the sphere of influence of cinchona alkaloid-derived catalysts. In some cases very subtle electronic interactions become a dominant factor, as for example a urea of epidihydro **4A** catalyzes addition of Me_3SiCN to imine of trifluoroacetophenone and *p*-anisidine, but it has no control over the steric course of an analogous reaction on the simple acetophenone imine (0% ee).[48]

Ethyl cyanoacetate is found to be a cyanide ion donor for 3,4-dihydroisoquinoline. The cyano group transfer to give the (*R*)-amino nitrile is catalyzed by **3C**, and its enantiomer can be obtained using the thiourea derived from quinidine.[49] A cinchona alkaloid is able to direct the chiral attachment of an acrolein unit to C-1 of *N*-aryltetrahydroisoquinolines under oxygen and by catalysis of $Cu(OTf)_2$, obviously through an aza-Baylis-Hillman reaction of nascent iminium species.[50]

A route to chiral β-amino acids starts from malonate addition to imines of 2-aminobenzothiazole, which is catalyzed by **3E**.[51] An α,β–diamino acid synthesis is also based on the Mannich reaction, that between azlactones and *N*-sulfonylaldimines. A 2:1 quinidine-BINOL salt mediates the task.[52]



(**14**)

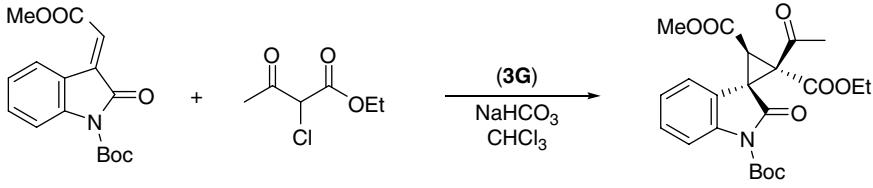


The quinine-catalyzed Mannich reaction of 2,3-dihalo-2-butenolides with aldimines is *syn*-selective and enantioselective.[53] The condensation products of isatin and carbamic esters are receptive to asymmetric attack by 1,3-dicarbonyl compounds using the 9-epimer of **3D** as catalyst.[54] Dihydro-**3C** guides the addition of nitroalkanes to 3-indolones.[55]

One of the expedient methods for access to *vic*-diaminoalkanes involves addition of nitroalkanes to aldimines. For this purpose, catalyst screening has identified **3F** to be useful,[56] and when *N*-protected α–benzenesulfonylamines are more readily available, in situ elimination prior to the reaction with nitroalkanes can be achieved equally well. A benzyl bromide salt of the urea analog of **4C** is serviceable under such conditions.[57]

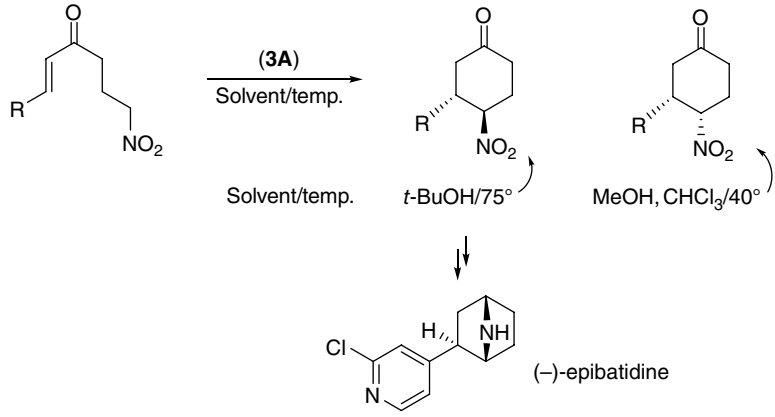
Conjugate addition. Acetone cyanohydrins donates the cyano group to conjugate carbonyl compounds to furnish chiral bifunctional products under the influence of a salt such as **8**[58] or **9**.[59]

A **4B**-derived mixed urea catalyzes the asymmetric addition of malonitrile to 2-alkenoylpyridines,[60] while the addition to chalcones employs an analog of **5A** in which the aniline portion bears only a single CF_3 group at the *p*-position.[60a] Cyclopropanation of 3-alkylideneoxindoles is achieved by reaction with ethyl 2-chloroacetoacetate (catalyst: **3G**).[61]

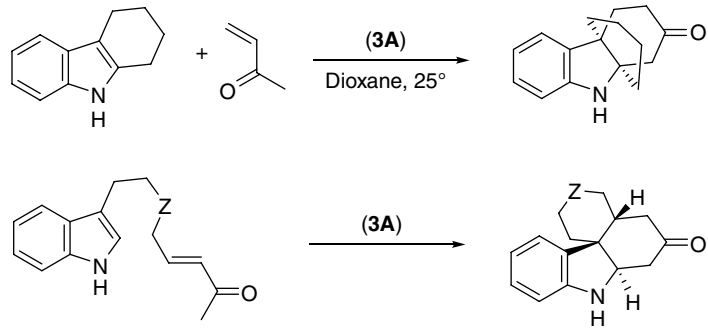


Studies of conjugate addition of nitroalkanes to enones have extended to the effects high pressure using the benzoic acid salt of **4B**.[62] Amines and thioureas belonging to the **3** and **4** series are quite effective catalysts.[63,64,65]

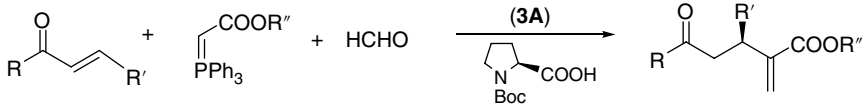
Alkenyl 3-nitropropyl ketones undergo intramolecular 1,4-addition, resulting in 4-nitrocyclohexanones. Remarkable solvent and temperature effects have been discovered that enable generation of either the *cis*- or *trans*-isomers are obtained.[66]



4-[3-bis(benzenesulfonyl)propyl]-2,5-cyclohexadienones undergo desymmetrizative cyclization by catalysis of **4C**.[67] High pressure has a rate enhancement effect on the conjugate addition (catalyst: **4B** salt) of indole to α,β-unsaturated ketones,[68] and tetrahydrocarbazole is annulated by 3-buten-2-one to afford a tetracyclic propellane.[69] A further development is the bisannulation of an indole bearing at C-3 a sidechain that is terminated at an enone moiety.[70]

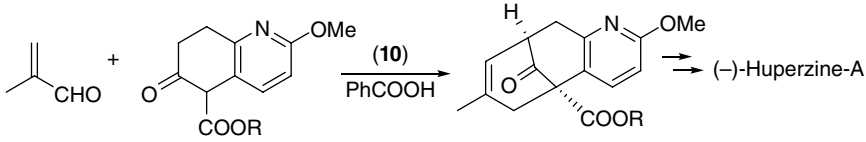


Stabilized Wittig reagents serve as normal Michael donors to conjugate carbonyl compounds and the reaction is subject to asymmetric induction by Boc-prolinate of **3A**.[71] Further alkenation of the adducts proceeds without any difficulties.



Regio- and enantioselective hydration of 4-oxo-2-alken-1-ols proceeds via hemiacetalization which is followed by an intramolecular addition. Suitable for helping establish a new (2*S*)-oxygenated pattern is **4C**.[72,73] Ring closure of 6-oxo-4-alken-1-ols to form (*R*)-2-(2-oxoalkyl)tetrahydrofurans is also effected by the same thiourea.[74] The 9-anthrylmethyl bromide salt of cinchonine is used in the formation of (*R*)-flavanones from 2′-hydroxychalcones.[75]

In a synthesis of (−)-huperzine-A the bridged ring system is constructed by a sequence of Michael addition, aldol reaction and dehydration. The presence of **10** (as benzoic acid salt) is crucial to produce the correct enantiomeric intermediate.[76]

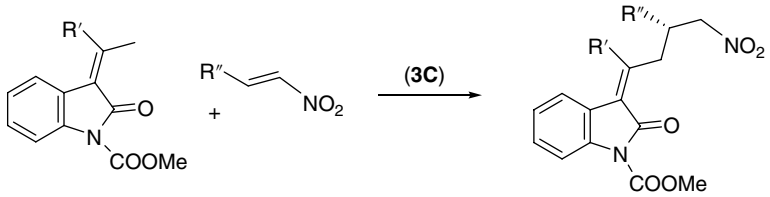


The point of nucleophilic attack on dicyanomethyleneoxindoles by ketones is C-3, which is directed by the salt of epi-**3A** and BINOL-phosphoric acid.[77,78]

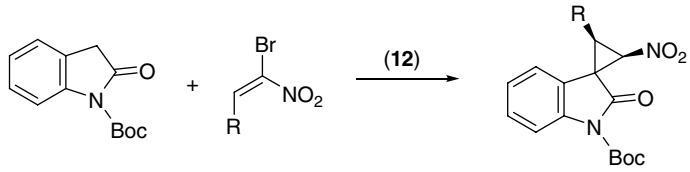
Great interests are annexed to asymmetric conjugate addition to nitroalkenes. Besides **5A** and **5C**,[79,80] a trimeric **5C** in which all three substituents on the benzene ring

are identical (i.e., each trifluoromethyl group is replaced by the aminomethyl unit) has been enlisted to realize the process.[81] Simpler catalysts are the 9-OBn derivatives of de-*O*-methylquinine and quinidine, which guide β-keto esters to pursue 1,4-addition on 1-nitro-1,3-alkadienes.[82] For turning the γ-carbon of 3-butenolides into a chiral quaternary center by addition to nitroalkenes the cinchona alkaloid-derived catalyst **11** was introduced.[83]

The adducts of oxindole-3-carboxylic esters and nitroalkenes have an (*S*)-configuration at C-3 and a (*R*)-configuration in the sidechain, when the addition is conducted in the presence of **3C**.[84] The same catalyst also enables chain elongation of 3-alkylideneoxindoles.[85]

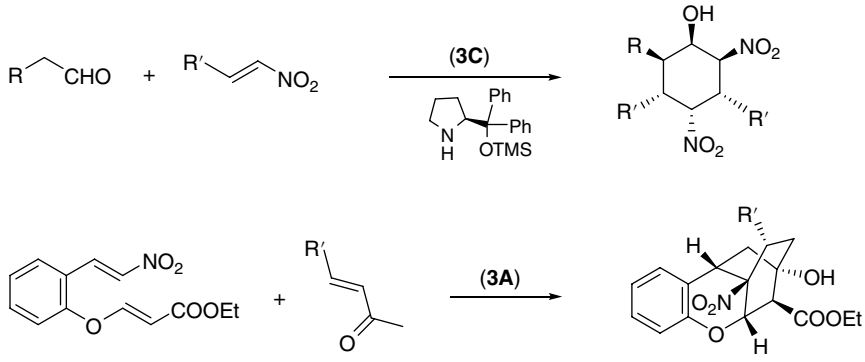


By modification of either the oxindole or the nitroalkene spiroannulation can be accomplished in one step.[86,87]



As donors in the addition to nitroalkenes *N*-acylpyrazoles have been developed. These compounds are ester equivalents and they have additional attributes in directing and activation. The unsymmetrical urea dihydro-**3I** is a valuable organocatalyst for use in the relevant conjugate addition.[88]

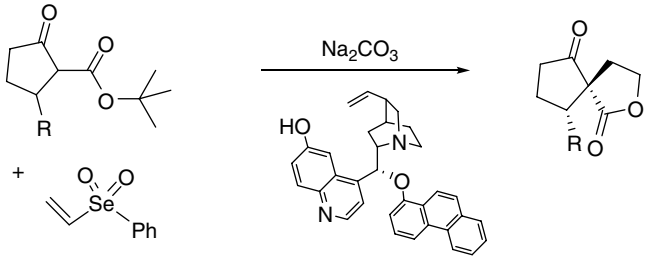
Tandem reactions are powerful tools for synthesis, of which the underlying principle is chemical selectivity. In the context of the present discussion the elaboration of 2,4-dinitrocyclohexanols from aldehydes and two equivalents of conjugated nitroalkenes in a highly enantioselective manner is exemplified.[89] Another distinct case is the formation of polyfunctional bridged ring system initiated from 1,4-addition to a β-nitrostyrene unit by an enone which is followed by two intramolecular Michael reactions.[90]



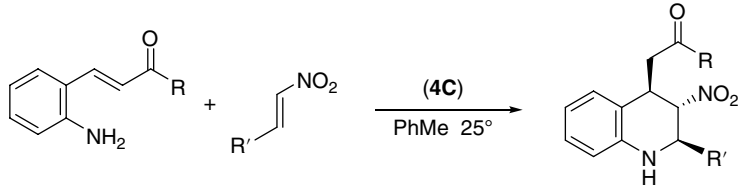
Adducts from nitroalkanes and conjugated nitroalkenes are 1,3-dinitroalkanes; two adjacent stereocenters arising from the reaction can be controlled, for example by the organocatalyst **12**.[91]

A formal Friedel-Crafts reaction of phenol and 2-cyclohexenone imines involves conjugate addition catalyzed by **3A**.[92]

A rare example of Baylis-Hillman reaction with respect to reactants and catalyst is the addition of allenyl carbonyl compounds (ketones and esters) to maleimides. The chiral catalyst is **6C**.[93] Equally unusual is the employment of phenyl vinyl selenone as the Michael acceptor, to fulfill the synthetic goal of rapid annulations of spirolactones. It is accomplished with the aid of 6′-de-*O*-methylquinine 9-phenanthryl ether.[94]



The copious attention paid to asymmetric conjugate addition of N-nucleophiles to α,β-unsaturated carbonyl compounds is due to importance of such products per se and as synthetic intermediates. A report shows the addition of aniline to chalcones catalyzed by cinchonine is aided by Me_3SiX,[95] and *N*′-Boc *N*-benzylhydrazine is useful for the addition to enones (catalysts: **3A/4A** and PhCOOH) in a mixture of toluene and dichloroethane.[96] Also studied are intramolecular addition,[97,98] and a relay process for synthesis of 3-nitro-4-(2-oxoalkyl)-tetrahydroquinolines.[99]

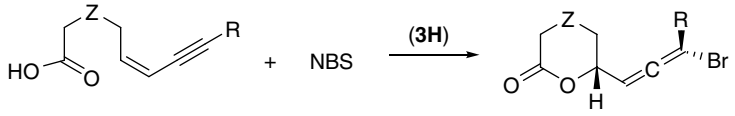


Addition of sodium *N*-chlorocarbamates to conjugated carbonyl compounds promoted by the 9-anthrylmethyl salt of cinchonidine *epi*-9-allyl ether provides aziridines.[100]

Dihydro-**3C** catalyzes the reaction of $NaHSO_3$ with chalcones, generating (*R*)-3-sulfo-1,3-diarylpropanones.[101] Thiols pursue a course of 1,6-addition to 3-alkenyl-2-cyclohexenones, in which chirality is induced by 2′-phenyl-**3A**.[102] The use of **5B** to foster the addition of thiols to α-substituted *N*-benzoylacrylamides is quite rewarding.[103]

Asymmetric bromoamination of *N*-sulfonyl-4-butenamines on reaction with *N*-bromophthalimide occurs in the presence of **13A**. The bromine-bearing carbon of the resulting pyrrolidine derivatives has an (*R*)-configuration.[104]

Annulation. Modified at both oxyfunctionalities of quinidine, **13B** is found suitable for mediating bromolactonization of 4-alkenoic acids by NBS.[105] Either **3H** or its dihydro derivative can be used to direct bromolactonization of 5-alken-7-ynoic acids and analogs with an intervening heteroatom between the two functionalities.[106]

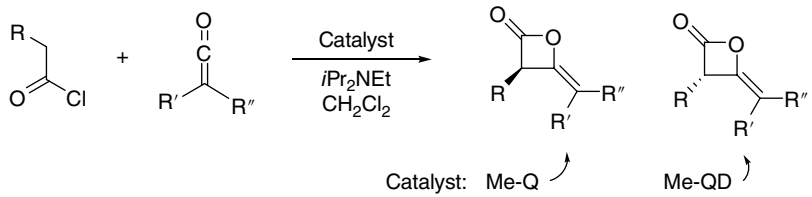


An expedient access to *N*-amino-3-pyrroline-3-aldehydes starts from α-amination of 2,2--disubstituted aldehydes, which is catalyzed by **3A** –TFA. Upon removing one Boc group from the adducts by TFA, the reaction is concluded by the Michael addition-aldol reaction sequence.[107] The *N*-Boc (*R*)-phenylglycine salt of **3A** is an effective catalyst to conduct spiroannulation of oxindole on reaction with cross-conjugated dienones.[108]

De-*O*-methyldihydroquinidine 9-(9-anthrylmethyl) ether provides chiral guidance to epoxidation of *N*-tosylaldimines.[109] For epoxidation of a conjugated enone double bond the (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoic acid salt of **3A** seems to be a useful chiral catalyst.[110] An alternative catalyst is **3C** (for epoxidation of 2-methylene-1,3-dicarbonyl compounds).[111]

Perfluoroalkyl ketones and 2,3-butadienoic esters undergo [2+2]cycloaddition under the aegis of **6C** to furnish 4,4-disubstituted oxetanylideneacetic esters of the (*R*)-configuration.[112] A mixed ketene dimer is formed enantiomerically when the one partner reactant

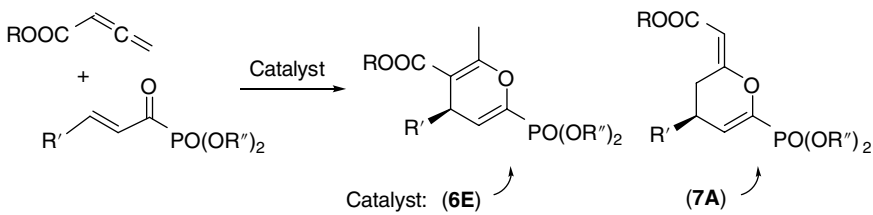
(donor) is generated in situ from an acyl chloride. Either the (*R*)- or (*S*)-β-alkylidene-β-lactone which differs in the α-carbon configuration can be prepared, on choosing the methyl ether of quinine or quinidine to intercede in the transition stater.[113]



α-Isocyano(arylacetic) esters[114] and 1-(isothiocyanatoacetyl)-3,5-dimethylpyrazole[115] are used as 1,3-dipoles in [3+2]cycloaddition. Maximal hydrogen bondings are of great importance to arrange the proper transition state motifs, as corroborated by the effectiveness of epi-**4C** in the latter reaction series.

The Diels-Alder reaction of 5-hydroxy-2-pyrones and β-nitrostyrenes in the presence of **3C** is *exo*-selective and products are obtained with excellent ee values.[116] By virtue of enamination with **3A**, conjugated dienones are activated to become engage in the Diels-Alder reaction, i.e., through deconjugation, and the derivatization sets the dienes in spatially biased conformation.[117]

Two different types of hetero-Diels-Alder reaction between β,γ-unsarurated α-ketophosphonates and 2,3-butadienoic esters are achieved. The selected transition state is consequential of a cinchona alkaloid-derived catalyst which dominates by steric interactions (**7A**) or H-bonding (**6E**).[118]



Conjugated ketenes and BocN=NBoc combine in the presence of quinidine trimethylsilyl ether enantioselectively.[119] The cycloadducts are potential precursors of chiral γ-amino acids.

Aza-Claisen rearrangement. Quinine methyl ether along with dichlorodimethylhydantoin promotes [3,3]sigmatropic rearrangement of 2-alken-1-yl trichloroacetimidates, but the chiral induction it brings about is low.[120]

Kinetic dynamic resolution. An *N*-aroyl-α-amino acid can be resolved via esterification (ROH, DCC) by means of **14**.[121] The reaction mixture contains the (*S*)-ester and (*R*)-acid.

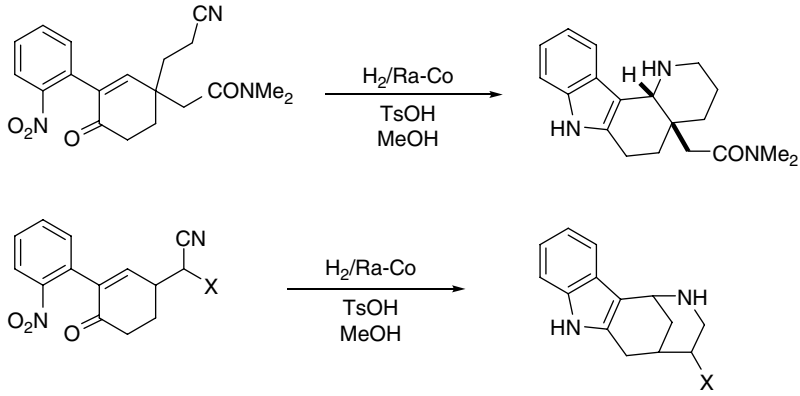
[1] Melchiorre, P. *ACIE* **51**, 9748 (2012)
[2] Zhang, Y., Chitale, S., Gogal, N., Li, G., Han, Z.S., Shen, S., Ma, S., Grinberg, N., Lee, H., Lu, B.Z.,Senanayake, C.H. *JOC* **77**, 690 (2012)
[3] Lee, J.H., Deng, L. *JACS* **134**, 18209 (2012)
[4] Wu, Y., Singh, R.P., Deng, L. *JACS* **133**, 12458 (2011)
[5] Wu, Y., Deng, L. *JACS* **134**, 14334 (2012)
[6] Xiao, X., Liu, M., Rong, C., Xue, F., Li, S., Xie, Y., Shi, Y. *OL* **14**, 5270 (2012)
[7] Quigley, C., Rodriguez-Docampo, Z., Connon, S.J. *CC* **48**, 1443 (2012)
[8] Claraz, A., Leroy, J., Oudeyer, S., Lavacher, V. *JOC* **76**, 6457 (2011)
[9] Zhu, B., Yan, L., Pan, Y., Lee, R., Liu, H., Han, Z., Huang, K.-W., Tan, C.-H., Jiang, Z. *JOC* **76**, 6894 (2011)
[9a] Claraz, A., Leroy, J., Oudeyer, S., Levacher, V. *JOC* **77**, 10773 (2012)
[10] Nun, P., Perez, V., Calmes, M., Martinez, J., Lamaty, F. *CEJ* **18**, 3773 (2012)
[11] Todd, R., Huisman, M., Uddin, N., Oehm, S., Hossain, M.M. *SL* 2687 (2012)
[12] Gualandi, A., Petruzziello, D., Emer, E., Cozzi, P.G. *CC* **48**, 3614 (2012)
[13] Jadhav, M.S., Righi, P., Mercantoni, E., Bencivenni, G. *JOC* **77**, 2667 (2012)
[14] Demoulin, N., Lifchits, O., List, B. *T* **68**, 7568 (2012)
[15] Richter, C., Ranganath, K.V.S., Glorius, F. *ASC* **354**, 377 (2012)
[16] Desmarchelier, A., Yalgin, H., Coeffard, V., Moreau, X., Greck, C. *TL* **52**, 4430 (2011)
[17] Zhou, F., Ding, M., Liu, Y.-L., Wang, C.-H., Ji, C.-B., Zhang, Y.-Y., Zhou, J. *ASC* **353**, 2945 (2011)
[18] Yang, H.-J., Dai, L., Yang, S.-Q., Chen, F.-E. *SL* 948 (2012)
[19] Yao, H., Lian, M., Li, Z., Wang, Y., Meng, Q. *JOC* **77**, 9601 (2012)
[20] Liao, Y.-H., Wu, Z.-J., Han, W.-Y., Zhang, X.-M., Yuan, W.-C. *CEJ* **18**, 8916 (2012)
[21] Li, X., Liu, C., Xue, X.-S., Cheng, J.-P. *OL* **14**, 4374 (2012)
[22] Han, Z., Chen, W., Dong, S., Yang, C., Liu, H., Pan, Y., Yan, L., Jiang, Z. *OL* **14**, 4670 (2012)
[23] Xu, J., Hu, Y., Huang, D., Wang, K.-H., Xu, C., Niu, T. *ASC* **354**, 515 (2012)
[24] Lin, A., Mao, H., Zhu, X., Ge, H., Tan, R., Zhu, C., Cheng, Y. *CEJ* **17**, 13676 (2011)
[25] Sun, W., Ma, X., Hong, L., Wang, R. *JOC* **76**, 7826 (2011)
[26] Pei, C.-K., Zhang, X.-C., Shi, M. *EJOC* 4479 (2011)
[27] Liu, C., Tan, B.-X., Jin, J.-L., Zhang, Y.-Y., Dong, N., Li, X., Cheng, J.-P. *JOC* **76**, 5838 (2011)
[28] Cui, H.-L., Sun, X.-H., Jiang, L., Dong, L., Chen, Y.-C. *EJOC* 7366 (2011)
[29] Furukawa, T., Kawazoe, J., Zhang, W., Nishimine, T., Tokunaga, E., Matsumoto, T., Shiro, M., Shibata, N. *ACIE* **50**, 9684 (2011); Companyó, X., Valero, G., Ceban, V., Calvet, T., Font-Bardia, M., Moyano, A., Rios, R. *OBC* **9**, 7986 (2011)
[30] Chen, G.-Y., Zhong, F., Lu, Y. *OL* **14**, 3955 (2012)
[31] Huang, X., Peng, J., Dong, L., Chen, Y.-C. *CC* **48**, 2439 (2012)
[32] Li, Y., Liang, F., Li, Q., Xu, Y., Wang, Q.-R., Jiang, L. *OL* **13**, 6082 (2011)
[33] Furukawa, T., Nishimine, T., Tokunaga, E., Hasegawa, K.,Shiro, M., Shibata, N. *OL* **13**, 3972 (2011)
[34] Chen, G.-Y., Zhong, F., Lu, Y. *OL* **13**, 6070 (2011)
[35] Zhong, F., Luo, J., Chen, G.-Y., Dou, X., Lu, Y. *JACS* **134**, 10222 (2012)
[36] Kong, S., Fan, W., Wu, G., Miao, Z. *ACIE* **51**, 8864 (2012)
[37] Guang, J., Guo, Q., Zhao, J.C.-G.. *OL* **14**, 3174 (2012)
[38] Sinha, D., Mandal, T., Gogoi, S., Goldman, J.J., Zhao, J.C. *ChJC* **30**, 2624 (2012)
[39] Cornaggia, C., Manoni, F., Torrente, E., Tallon, S., Connon, S.J. *OL* **14**, 1850 (2012)
[40] Manoni, F., Cornaggia, C., Murray, J., Tallon, Connon, S.J. *CC* **48**, 6502 (2012)
[41] Liu, C., Dou, X., Lu, Y. *OL* **13**, 5248 (2011)
[42] Allu, S., Molleti, N., Panem, R., Singh, V.K. *TL* **52**, 4080 (2011)
[43] Zhong, F., Yao, W., Dou, X., Lu, Y. *OL* **14**, 4018 (2012)

[44] Pesciaioli, F., Righi, P., Mazzanti, A., Gianelli, C., Mancinelli, M., Bartoli, G., Bencivenni, G. *ASC* **353**, 2953 (2011)
[45] Liu, H., Wu, H., Luo, Z., Shen, J., Kang, G., Liu, B., Wan, Z., Jiang, J. *CEJ* **18**, 11899 (2012)
[46] Martelli, G., Orena, M., Rinaldi, S. *EJOC* 4140 (2012)
[47] Yao, L., Wei, Y., Wang, P., He, W., Zhang, S. *T* **68**, 9119 (2012)
[48] Liu, Y.-L., Shi, T.-D., Zhou, F., Zhao, X.-L., Wang, X., Zhou, J. *OL* **13**, 3826 (2011)
[49] Shao, Y.-D., Tian, S.-K. *CC* **48**, 4899 (2012)
[50] Zhang, G., Ma, Y., Wang, S., Zhang, Y., Wang, R. *JACS* **134**, 12334 (2012)
[51] Li, L., Song, B.-A., Bhadury, P.S., Zhang, Y.-P., Hu, D.-Y., Yang, S. *EJOC* 4743 (2011)
[52] Zhang, W.-Q., Cheng, L.-F., Yu, J., Gong, L.-Z. *ACIE* **51**, 4085 (2012)
[53] Guo, Y.-L., Bai, J.-F., Peng, L., Wang, L.-L., Jia, L.-N., Luo, X.-Y., Tian, F., Xu, X.-Y., Wang, L.-X. *JOC* **77**, 8338 (2012)
[54] Yan, W., Wang, D., Feng, J., Li, P., Zhao, D., Wang, R. *OL* **14**, 2512 (2012)
[55] Parra, A., Alfaro, R., Marzo, L., Moreno-Carrasco, A., Ruano, J.L.G., Alemán, J. *CC* **48**, 9759 (2012)
[56] Li, H., Zhang, X., Shi, X., Ji, N., He, W., Zhang, S., Zhang, B. *ASC* **354**, 2264 (2012)
[57] Johnson, K.M., Rattley, M.S., Sladojevich, F., Barber, D.M., Nuñez, M.G., Goldys, A.M., Dixon, D.J. *OL* **14**, 2492 (2012)
[58] Provencher, B.A., Bartelson, K.J., Liu, Y., Foxman, B.M., Deng, L. *ACIE* **50**, 10565 (2011)
[59] Kawai, H., Okusu, S., Tokunaga, E., Sato, H., Shiro, M., Shibata, N. *ACIE* **51**, 4959 (2012)
[60] Molleti, N., Rana, N.K., Singh, V.K. *OL* **14**, 4322 (2012)
[60a] Yang, W., Du, D.-M. *OBC* **10**, 332 (2012)
[61] Noole, A., Sucman, N.S., Kabeshov, M.A., Kanger, T., Macaev, F.Z., Malkov, A.V. *CEJ* **18**, 14929 (2012)
[62] Kwiatkowski, P., Dudzinski, K., Lyzwa, D. *OL* **13**, 3624 (2011)
[63] Chiarucci, M., Lombardo, M., Trombini, C., Quintavalla, A. *ASC* **354**, 364 (2012)
[64] Prakash, G.K.S., Wang, F., Zhang, Z., Ni, C., Harges, R., Olah, G.A. *OL* **14**, 3260 (2012)
[65] Kawai, H., Kitayama, T., Tokunaga, E., Matsumoto, T., Sato, H., Shiro, M., Shibata, N. *CC* **48**, 4067 (2012)
[66] Jensen, K.L., Weise, C.F., Dickmeiss, G., Morana, F., Davis, R.L., J Ørgensen, K.A. *CEJ* **18**, 11913 (2012)
[67] Gu, Q., You, S.-L. *OL* **13**, 5192 (2011)
[68] Lyzwa, D., Dudzinski, K., Kwiatkowski, P. *OL* **14**, 1540 (2012)
[69] Cai, Q., You, S.-L. *OL* **14**, 3040 (2012)
[70] Cai, Q., Zheng, C., Zhang, J.-W., You, S.-L. *ACIE* **50**, 8665 (2011)
[71] Lin, A., Wang, J., Mao, H., Ge, H., Tan, R., Zhu, C., Cheng, Y. *OL* **13**, 4176 (2011)
[72] Asano, K., Matsubara, S. *OL* **14**, 1620 (2012)
[73] Okamura, T., Asano, K., Matsubara, S. *CC* **48**, 5076 (2012)
[74] Asano, K., Matsubara, S. *JACS* **133**, 16711 (2011)
[75] Hintermann, L., Dittmer, C. *EJOC* 5573 (2012)
[76] Ding, X.-H., Li, X., Liu, D., Cui, W.-C., Ju, X., Wang, S., Yao, Z.-J. *T* **68**, 6240 (2012)
[77] Liu, L., Wu, D., Li, X., Wang, S., Li, H., Li, J., Wang, W. *CC* **48**, 1692 (2012)
[78] Lan, Y.-B., Zhao, H., Liu, Z.-M., Liu, G.-G., Tao, J.-C., Wang, X.-W. *OL* **13**, 4866 (2011)
[79] Bae, H.Y., Some, S., Lee, J.H., Kim, J.-Y., Song, M.J., Lee, S., Zhang, Y.J., Song, C.E. *ASC* **353**, 3196 (2011)
[80] Yong, H., Some, S., Oh, J.S., Lee, Y.S., Song, C.E. *CC* **47**, 9621 (2011)
[81] Min, C., Han, X., Liao, Z., Wu, X., Zhou, H.-B., Dong, C. *ASC* **353**, 2715 (2011)
[82] Chauhan, P., Chimni, S.S. *ASC* **353**, 3203 (2011)
[83] Manna, M.S., Kumar, V., Mukherjee, S. *CC* **48**, 5193 (2012)

[84] Chen, X., Zhu, W., Qian, W., Feng, E., Zhou, Y., Wang, J., Jiang, H., Yao, Z.-J., Liu, H. *ASC* **354**, 2151 (2012)
[85] Curti, C., Rassu, G., Zambrano, V., Pinna, L., Pelosi, G., Sartori, A., Battistini, L., Zanardi, F., Casiraghi, G. *ACIE* **51**, 6200 (2012)
[86] Albertshofer, K., Tan, B., Barbas III, C.F. *OL* **14**, 1834 (2012)
[87] Dou, X., Lu, Y. *CEJ* **18**, 8315 (2012)
[88] Tan, B., Hernandez-Torres, G., Barbas III, C.F. *ACIE* **51**, 5381 (2012)
[89] Mao, Z., Jia, Y., Xu, Z., Wang, R. *ASC* **354**, 1401 (2012)
[90] Yu, D.-F., Wang, Y., Xu, P.-F. *ASC* **353**, 2960 (2011)
[91] Yang, W., Du, D.-M. *CC* **47**, 12706 (2011)
[92] Paradisi, E., Righi, P., Mazzanti, A., Ranieri, S., Bencivenni, G. *CC* **48**, 11178 (2012)
[93] Zhao, Q.-Y., Pei, C.-K., Guan, X.-Y., Shi, M. *ASC* **353**, 1973 (2011)
[94] Sternativo, S., Calandriello, A., Costantino, F., Testaferri, L., Tiecco, M., Marini, F. *ACIE* **50**, 9382 (2011)
[95] Yang, H.-M., Li, L., Li, F., Jiang, K.-Z., Shang, J.-Y., Lai, G.-Q., Xu, L.-W. *OL* **13**, 6508 (2011)
[96] Campbell, N.R., Sun, B., Singh, R.P., Deng, L. *ASC* **353**, 3123 (2011)
[97] Liu, J.-D., Chen, Y.-C., Zhang, G.-B., Li, Z.-Q., Chen, P., Du, J.-Y., Tu, Y.-Q., Fan, C.-A. *ASC* **353**, 2721 (2011)
[98] Fustero, S., del Pozo, C., Mulet, C., Lazaro, R., Sanchez-Rosello, M. *CEJ* **17**, 14267 (2011)
[99] Jia, Z.-X., Luo, Y.-C., Wang, Y., Chen, L., Xu, P.-F., Wang, B. *CEJ* **18**, 12958 (2012)
[100] Murakami, Y., Takeda, Y., Minakata, S. *JOC* **76**, 6277 (2011)
[101] Moccia, M., Fini, F., Scagnetti, M., Adamo, M.F.A. *ACIE* **50**, 6893 (2011)
[102] Tian, X., Liu, Y., Melchiorre, P. *ACIE* **51**, 6439 (2012)
[103] Dai, L., Yang, H., Niu, J., Chen, F. *SL* 314 (2012)
[104] Chen, J., Zhou, L., Yeung, Y.-Y. *OBC* **10**, 3808 (2012)
[105] Tan, C.K., Le, C., Yeung, Y.-Y. *CC* **48**, 5793 (2012)
[106] Zhang, W., Liu, N., Schienebeck, C.M., Decloux, K., Zheng, S., Werness, J.B., Tang, W. *CEJ* **18**, 7296 (2012)
[107] Desmarchelier, A., Coeffard, V., Moreau, X., Greck, C. *CEJ* **18**, 13222 (2012)
[108] Wu, B., Chen, J., Li, M.-Q., Zhang, J.-X., Xu, X.-P., Ji, S.-J., Wang, X.-W. *EJOC* 1318 (2012)
[109] Lykke, L., Rodriguez-Escrich, C., JØrgensen, K.A. *JACS* **133**, 14932 (2011)
[110] Lee, A., Reisinger, C.M., List, B. *ASC* **354**, 1701 (2012)
[111] Russo, A., Galdi, G., Croce, G., Lattanzi, A. *CEJ* **18**, 6152 (2012)
[112] Zhao, Q.-Y., Huang, L., Wei, Y., Shi, M. *ASC* **354**, 1926 (2012)
[113] Ibrahim, A.A., Nalla, D., Van Raaphorst, M., Kerrigan, N.J. *JACS* **134**, 2942 (2012)
[114] Zhou, M.-X., Wei, D.-K., Ji, F.-H., Zhao, X.-L., Shi, M. *CAJ* **7**, 2777 (2012)
[115] Tan, B., Zeng, X., Leong, W.W.Y., Shi, Z., Barbas III, C.F., Zhong, G. *CEJ* **18**, 63 (2012)
[116] Wu, W., Min, L., Zhu, L., Lee, C.-S. *ASC* **353**, 1135 (2011)
[117] Xiong, X.-F., Zhou, Q., Gu, J., Dong, L., Liu, T.-Y., Chen, Y.-C. *ACIE* **51**, 4401 (2012)
[118] Pei, C.-K., Jiang, Y., Wei, Y., Shi, M. *ACIE* **51**, 11328 (2012)
[119] Shen, L.-T., Sun, L.-H., Ye, S. *JACS* **133**, 15894 (2011)
[120] Liu, N., Schienebeck, C.M., Collier, M.D., Tang, W. *TL* **52**, 6217 (2011)
[121] Oh, J.-S., Lee, J.-W., Ryu, T.H., Lee, J.H., Song, C.E. *OBC* **10**, 1052 (2012)

Cobalt, Raney

Hydrogenation. Hydrogenation of both nitro and cyano groups on catalysis by Raney cobalt facilitates the elaboration of tetrahydrocarbazole derivatives characteristic of some indole alkaloids.[1,2]



[1] Tan, S.H., Banwell, M.G., Willis, A.C., Reekie, T.A. *OL* **14**, 5621 (2012)
[2] Reekie, T.A., Banwell, M.G., Willis, A.C. *JOC* **76**, 6457 (2011)

Cobalt(II) bromide

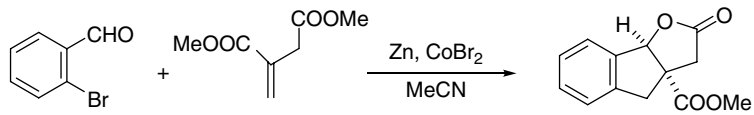
Coupling. The coupling of allyl acetates and carbonates with RX by means of $CoBr_2$ has a wide scope.[1] Using $CoBr_2$ as catalyst and in the presence of DBU, 1-alkynes are converted into propargylic amines on reaction with CH_2X_2 and RNH_2 in MeCN.[2]

Alkylation of 5-aryloxazoles and benzothiazole can be accomplished with tosylhydrazones using $CoBr_2$ – phenanthroline as catalyst.[3] Directed alkenylation of various 3-substituted acetophenone *N*-arylimines occurs at C-2 by alkynes.[4] As an alternative to the Pd-catalyzed process aminobenzylation of 2-arylpyridines (reaction with imines) can be accomplished using $CoBr_2$ and a carbene ligand.[5]

[1] Qian, X., Auffrant, A., Felouat, A., Gosmini, C. *ACIE* **50**, 10402 (2011)
[2] Tang, Y., Xiao, T., Zhou, L. *TL* **53**, 6199 (2012)
[3] Yao, T., Hirano, K., Satoh, T., Miura, M. *ACIE* **51**, 775 (2012)
[4] Lee, P.-S., Fujita, T., Yoshikai, N. *JACS* **133**, 17283 (2011)
[5] Gao, K., Yoshikai, N. *CC* **48**, 4305 (2012)

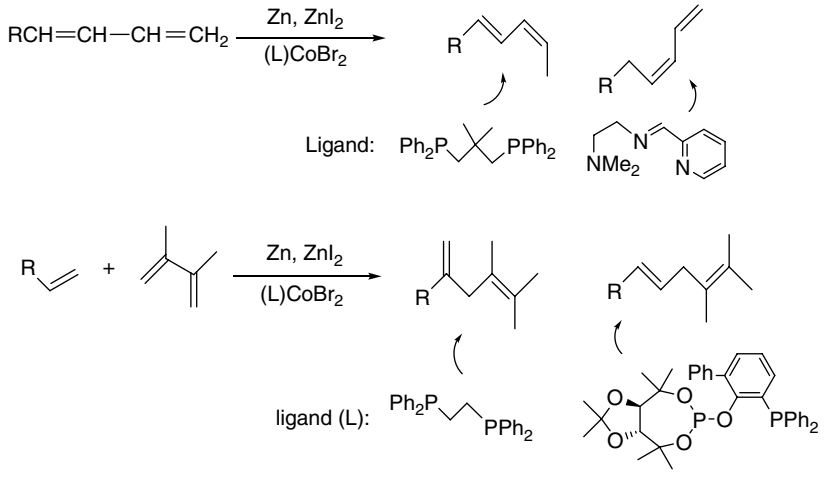
Cobalt(II) bromide – zinc – zinc iodide

Zincation. After β-halo-α,β-unsaturated aldehydes are transformed into organozinc reagents by Zn-$CoBr_2$, reaction with dimethyl itaconate starts with conjugate addition and it is followed by aldol condensation and lactonization.[1]



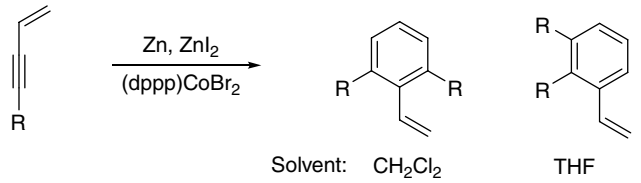
syn-Arylzincation of alkynes creates styrenic nucleophiles.[2]

Reaction of conjugated dienes. 1,3-Alkadienes undergo isomerization on exposure to $CoBr_2$ – Zn –ZnI_2. The ligand present determines the course of whether configurational change of the internal double bond or inward migration of the whole diene unit by one carbon to take place.[3] Ligand control is also manifested in the addition of 1-alkenes to 2,3-dimethyl-1,3-butadiene.[4]



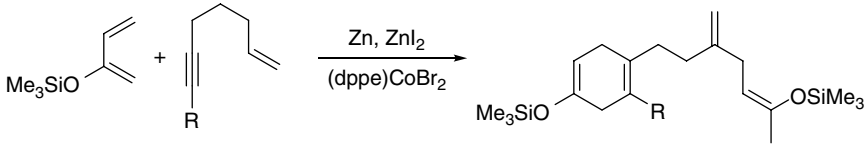
For synthetic applications it is valuable to determine that 1,4-addition of 1-alkenes to 2-trimethylsiloxy-1,3-butadiene furnishes (4*E*)-2-alkyl-5-trimethylsiloxy-1,4-hexadienes.[5] 1-Aryl-1,3-butadienes add to 2,3-dimethyl-1,3-butadiene to give 1,3,6-octatriene adducts.[6]

Annulation. The course for cyclodimerization of 1-alken-3-ynes is solvent dependent, either 2,3-dialkylstyrenes or 2,6-dialkylstyrenes can be obtained as the major products.[7]

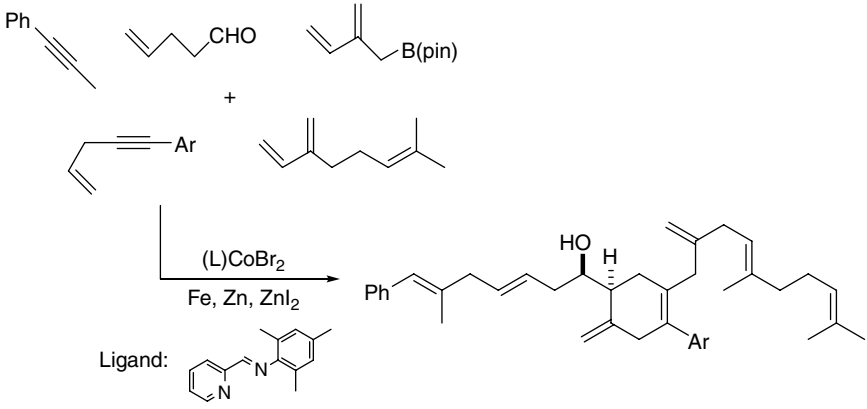


A new set of conditions for the Pauson-Khand reaction employs $CoBr_2$ – Zn - TMTU in toluene under CO.[8]

Deconjugated enynes engage in reaction with 2-siloxy-1,3-butadiene with both unsaturated sites, 1,4-addition of closed and open options for the diene are exercised.[9]



A 5-component one-pot synthesis from reactions between alkynes and alkenes/dienes is a significant contribution to methodological advancement.[10]



[1] Le Froch, C., Laymand, K., Le Gall, E., Leonel, E. *ASC* **354**, 823 (2012)
[2] Corpet, M., Gosmini, C. *CC* **48**, 11561 (2012)
[3] Pünner, F., Schmidt, A., Hilt, G. *ACIE* **51**, 1270 (2012)
[4] Arndt, M., Dindaroglu, M., Schmalz, H.-G., Hilt, G. *OL* **13**, 6236 (2011)
[5] Kersten, L., Hilt, G. *ASC* **354**, 863 (2012)
[6] Bohn, M.A., Schmidt, A., Hilt, G., Dindaroglu, M., Schmalz, H.-G. *ACIE* **50**, 9689 (2011)
[7] Pünner, F., Hilt, G. *CC* **48**, 3617 (2012)
[8] Wang, Y., Xu, L., Yu, R., Chen, J., Yang, Z. *CC* **48**, 8183 (2012)
[9] Erver, F., Kuttner, J.R., Hilt, G. *JOC* **77**, 8375 (2012)
[10] Erver, F., Hilt, G. *OL* **14**, 1884 (2012)

Cobalt(II) chloride

Addition. Arylzinc reagents add to unactivated alkynes via arylcobalt species formed in the presence of $CoCl_2$ –Xantphos, and it is followed by 1,4-cobalt migration (vinyl-to-aryl) and transmetallation. The ZnX group ends up in the *o*-position (to its original site).[1]

Conjugate addition involving $ArB(OH)_2$ is performed by catalysis of $(dppe)CoCl_2$ and $ZnCl_2$.[2] Reductive addition of 1-alkynes to electron-deficient alkenes CH_2=CHX (acrylic esters, acrylonitrile, 1-alken-3-ones) is observed to provide $RCH=CHCH_2CH_2X$

when the mixtures of the unsaturated compounds are treated with $CoCl_2$, $(MeO)_3P$, and zinc metal.[3]

Coupling. A route to diaryl ketones involves the $CoCl_2$-catalyzed reaction of ArCHO and $Ar'B(OH)_2$.[4]

Cycloaddition. Cyclotrimerization of alkynes to afford benzene derivatives is effected by $CoCl_2 \cdot 6H_2O$, Zn, and an imine of 2-pyridinecarbaldehyde. Dimethyl phthalate is an essential additive (0% yield of products if absent).[5]

[1] Tan, B.-H., Dong, J., Yoshikai, N. *ACIE* **51**, 9610 (2012)
[2] Chen, M.-H., Mannathan, S., Lin, P.-S. Cheng, C.-H. *CEJ* **18**, 14918 (2012)
[3] Mannathan, S., Cheng, C.-H. *CEJ* **18**, 11771 (2012)
[4] Karthikeyan, J., Parthasarathy, K., Cheng, C.-H. *CC* **47**, 10461 (2011)
[5] Sugiyama, Y., Kariwa, T., Sakurada, T., Okamoto, S. *SL* 2549 (2012)

Copper

Coupling. Copper powder alone is capable of effecting arylation of benzannulated azoles.[1] Many electron transfer reactions are carried out with copper on magnesium surface, the C-F bonds in aryl chlorides bearing polyfluoroalkyl groups are not affected when the chlorine atom undergoes replacement.[2]

Cross coupling methods are generally applied to synthesis of $ArCF_3$, for example by pairing $ArB(OH)_2$ with $CF_3SPh_2(OTf)$,[3] or ArI with $NaOCOCF_3$,[4] both based on promotion by Cu, but in the latter case also Ag_2O. 2-Aryl-1,1,1-trifluoroethanes are similarly prepared from benzyl bromides and $CF_3SPh_2(OTf)$.[5]

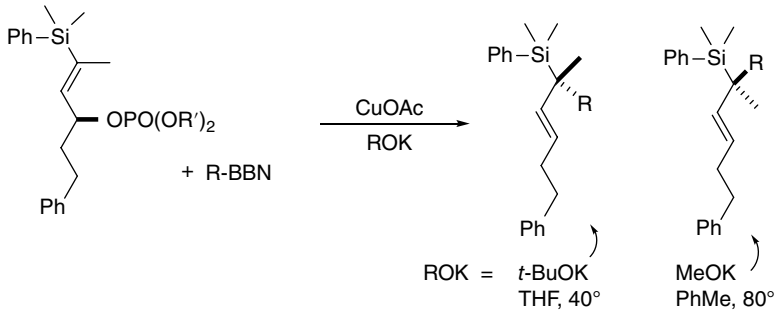
For condensation of aldehydes, amines and 1-alkynes to form propargylic amines a reusable catalyst is copper nanoparticles on titania.[6]

Reduction. Added to the numerous protocols for the reduction of aryl azides to anilines is that employing nano-Cu and $HCOONH_4$ in water.[7]

[1] Han, Y., Wang, X., Wang, X., Lv, L., Diao, G., Yuan, Y. *S* 3027 (2012)
[2] Utsumi, S., Katagiri, T., Uneyama, K. *T* **68**, 1085 (2012)
[3] Zhang, C.-P., Cai, J., Zhou, C.-B., Wang, X.-P., Zheng, X., Gu, Y.-C., Xiao, J.-C. *CC* **47**, 9516 (2011)
[4] Li, Y., Chen, T., Wang, H., Zhang, R., Jin, K., Wang, X., Duan, C. *SL* 1713 (2011)
[5] Kawai, H., Furukawa, T., Nomura, Y., Tokunaga, E., Shibata, N. *OL* **13**, 3596 (2011)
[6] Albaladejo, M.J., Alonso, F., Moglie, Y., Yus, M. *EJOC* 3093 (2012)
[7] Ahammed, S., Saha, A., Ranu, B.C. *JOC* **76**, 7235 (2011)

Copper(I) acetate

Substitution. In S_N2' substitution of an allylic phosphate group in silylalkenes by organoboranes very slight change of base and solvent has enormous effects on the steric course.[1]



Arylation of *N*-(*p*-anisylmethyl)guanidine is catalyzed by CuOAc-proline.[2]

[1] Nagao, K., Yokobori, U., Makida, Y., Ohmiya, H., Sawamura, M. *JACS* **134**, 8982 (2012)
[2] Hammoud, H., Schmitt, M., Bihel, F., Antheaume, C., Bourguignon, J.-J. *JOC* **77**, 417 (2012)

Copper(II) acetate

Amides. Aldoximes undergo rearrangement to primary amides on heating with catalytic amounts of $Cu(OAc)_2$ in toluene at 80°.[1] A direct synthesis of amides from aldehydes and hydroxylamine in water is also reported.[2]

Primary amides exchange the NH_2 group for NHR on heating with $Cu(OAc)_2$ and primary amines. Monosubstituted ureas are similarly transformed into RNHCONHR′.[3]

Condensation. Henry reaction can be conducted with catalysis of $Cu(OAc)_2$ in *t*-BuOH.[4]

Substitution and coupling. *O*-Benzoylhydroxylamines serve as aminating agents for ketene silyl acetals[5] and organoboronic acids,[6] and $Cu(OAc)_2$ is an enabler.

In catalyzing arylation of amines, $Cu(OAc)_2$ is reduced to the Cu(I) state in situ by $PhNHNH_2$.[7] Among the recently developed methods for cyanoarene synthesis that employing an ammonium salt and DMF to provide, respectively, the nitrogen and carbon atoms (from a methyl group) is most remarkable.[8] Other CN sources are malonitrile[9] and acetonitrile,[10] but each reaction requires different additives (1,10-phenanthroline, KF, *t*-BuONa in the former instance, and Ag_2O/Ph_3PO in the latter).

The thio groups of ketene dithioacetals can be replaced on reaction with organoboronic acids.[11]

A Ritter reaction is observed when $ArCH_2BF_3K$ and RCN are treated with $Cu(OAc)_2$ and $BF_3{\cdot}OEt_2$.[12] As expected from the nature of such reaction secondary and tertiary but not primary alkyltrifluoroborate salts are useful substrates.

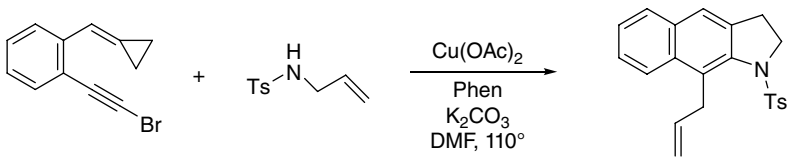
While $Cu(OAc)_2$ is recognized to play a supporting role in certain Pd-catalyzed coupling processes, it is definitely essential for the best results. An example is the synthesis of 2-arylpyridines by Suzuki coupling of a privileged 2-pyridineboronate with ArX.[13]

N-Formylindoles are synthesized from adducts of *N*-formyl-*o*-haloanilines and alkynes by an intramolecular Heck reaction which can be effected with $Cu(OAc)_2$.[14]

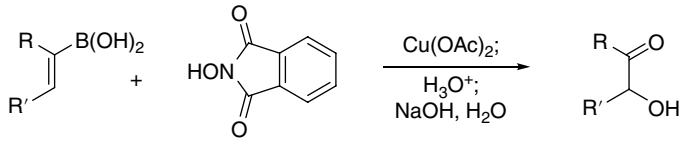
The same catalyst is responsible for access to 3-indolecarboxylic esters from *o*-pinacolatoborylaniline and β-keto esters under oxygen.[15] For synthesis of 3-indolecarboxylic acids an alternative carboxylative route involves metalloamination of *o*-alkynylanilines.[16]

Cross-coupling of 2-alkylpyridines and cinnamic acids leads to 2-arylindolizines, as decarboxylation also occurs during the reaction.[17] Amination with azodicarboxylic esters is carried out similarly.[18]

An intriguing route to benzoindolines on combining *N*-tosylallylamine and *o*-bromoethynylbenzylidenecyclopropanes is rationalized as the result of *N*-alkynylation, aza-Claisen rearrangement, electrocyclization, and cyclopropylcarbimine rearrangement.[19]



Oxidation of alkenylboronic acids by *N*-hydroxyphthalimide proceeds from C-O coupling and [3,3]sigmatropic rearrangement.[20]



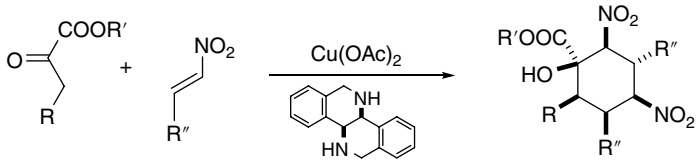
Addition. Alkynes add $B_2(pin)_2$ to afford (*Z*)-dipinacolatoborylalkenes,[21] a propargylic methoxy group is replaced also under the reaction conditions [catalyst: $Cu(OAc)_2$, Cy_3P]. If Bu_3SnOR is also present the reaction yields *vic*-stannyl/borylalkenes.[22]

N-Allylamidines are converted into 4-acetoxymethylimidazolines in a reaction with $PhI(OAc)_2$,which is catalyzed by $Cu(OAc)_2$.[23]

Allylboronates add to alkynoic esters, amides and also alkynyl nitriles and sulfones to deliver functionalized 1,4-dienes.[24] To maximize reactivity and regioselectivity of conjugate addition of RZnX to 2-cycloalkenones in aqueous media, a bimetallic Au(Ag)/Cu catalyst system to activate the hard terminus of the acceptor and softening of the nucleophile, respectively, is adapted by adding a surfactant.[25]

Annulation. Anthranilic esters are assembled from β-aminocrotonic esters and α, β-unsaturated carbonyl compounds via a Michael addition and aldol reaction sequence.[26] 5-Substituted 1*H*-tetrazoles are constructed by the reaction of NaN_3 with aldoximes.[27]

From α-keto esters and conjugated nitroalkenes the formation of 1:2-cycloadducts is a neat display of efficiency of tandem reactions.[28]



[1] Sharma, S.K., Bishopp, S.D., Allen, C.L., Lawrence, R., Bamford, M.J., Lapkin, A.A., Plucinski, P., Watson, R.J., Williams, J.M.J. *TL* **52**, 4252 (2011)
[2] Martinez-Asencio, A., Yus, M., Ramon, D.J. *T* **68**, 3948 (2012)
[3] Zhang, M., Imm, S., Bähn, S., Neubert, L., Neumann, H., Beller, M. *ACIE* **51**, 3905 (2012)
[4] Cheng, H.-G., Lu, L.-Q., Wang, T., Chen, J.-R., Xiao, W.-J. *CC* **48**, 5596 (2012)
[5] Matsuda, N., Hirano, K., Satoh, T., Miura, M. *ACIE* **51**, 11827 (2012)
[6] Matsuda, N., Hirano, K., Satoh, T., Miura, M. *ACIE* **51**, 3642 (2012)
[7] Komori, T., Satoh, N., Yokoshima, S., Fukuyama, T. *SL* 1859 (2011)
[8] Zhang, G., Ren, X., Chen, J., Hu, M., Cheng, J. *OL* **13**, 5004 (2011)
[9] Jiang, Z., Huang, Q., Chen, S., Long, L., Zhou, X. *ASC* **354**, 589 (2012)
[10] Sun, R.-J., Wu, J.-C., Liu, Y., Deng, G.-B., Wu, C.-Y., Wei, W.-T., Li, J.-H. *SL* 2491 (2012)
[11] Dong, Y., Wang, M., Liu, J., Ma, W., Liu, Q. *CC* **47**, 7380 (2011)
[12] Cazorla, C., Métay, E., Lemaire, M. *T* **67**, 8615 (2011)
[13] Dick, G.R., Woerly, E.M., Burke, M.D. *ACIE* **51**, 2667 (2012)
[14] Gao, D., Back, T.G. *CEJ* **18**, 14828 (2012)
[15] Bunescu, A., Wang, Q., Zhu, J. *S* 3811 (2012)
[16] Li, S., Ma, S. *ASC* **354**, 2387 (2012)
[17] Yang, Y., Xie, C., Xie, Y., Zhang, Y. *OL* **14**, 957 (2012)
[18] Liu, J.-Y., Niu, H.-Y., Wu, S., Qu, G.-R., Guo, H.-M. *CC* **48**, 9723 (2012)
[19] Li, S., Li, Z., Wu, J. *ASC* **354**, 3087 (2012)
[20] Patil, A.S., Mo, D.-L., Wang, H.-Y., Mueller, D.S., Anderson, L.L. *ACIE* **51**, 7799 (2012)
[21] Yoshida, H., Kawashima., S., Takemoto, Y., Okada, K., Ohshita, J., Takaki, K. *ACIE* **51**, 235 (2012)
[22] Takemoto, Y., Yoshida, H., Takaki, K. *CEJ* **18**, 14841 (2012)
[23] Sanjaya, S., Chiba, S. *OL* **14**, 5342 (2012)
[24] Yamamoto, Y., Yamada, S., Nishiyama, H. *CEJ* **18**, 3153 (2012)
[25] Lipshutz, B.H., Huang, S., Leong, W.W.Y., Zhong, G., Isley, N.A. *JACS* **134**, 19985 (2012)
[26] Li, L., Zhao, M.-N., Ren, Z.-H., Li, J.-L., Guan, Z.-H. *OL* **14**, 3506 (2012)
[27] Patil, U.B., Kumthekar, K.R., Nagarkar, J.M. *TL* **53**, 3706 (2012)
[28] Shi, D., Xie, Y., Zhou, H., Xia, C., Huang, H. *ACIE* **51**, 1248 (2012)

Copper(II) acetylacetonate

Condensation. In the presence of $Cu(acac)_2$ dehydrative union of aryl propargyl ethers and trimethylamine oxide to give 1,4-*N,O*-difunctionalized 2-butynes is observed.[1]

Tosylhydrazones are reductively defunctionalized and transformed to amines on reaction with RR′NH.[2]

Addition. Regioselective addition of RN(Ts)Cl to ethynylarenes forms (*E*)-α-chloro-β-tosylaminostyrenes.[3]

[1] Xu, Z., Yu, X., Feng, X., Bao, M. *JOC* **76**, 6901 (2011)
[2] Hamze, A., Tréguier, B., Brion, J.-D., Alami, M. *OBC* **9**, 6200 (2011)
[3] Liu, X.-Y., Gao, P., Shen, Y.-W., Liang, Y.-M. *ASC* **353**, 3157 (2011)

Copper(I) bromide

Condensation. Propargylic amines can be assembled from aldehydes, *N*-substituted hydroxylamines and 1-alkynes with CuBr as the catalyst.[1] An alternative protocol employs α-keto acids (instead of aldehydes), amines and alkynes with microwave heating.[2] A similar reaction involving potassium salt of α-keto acids, amines and ArX yields aryl ketone imines.[3] However, a cocatalyst of palladium hexafluoroacetylacetonate and a phosphine ligand are required.

Synthesis of α-aminoarylacetic esters from ethyl glyoxylate, amines and $ArB(OH)_2$ by CuBr catalysis has the advantage over the original Petasis reaction conditions in the flexibility of choice of reagents.[4]

Oxidative functionalization of ArCOMe to give ArCOCONRR′ involves reaction with the amine in the presence of CuBr and NIS in air.[5]

Coupling. Sulfoximines are arylated (at N) by Ar_2IX in aqueous PEG-400 with ultrasound irradiation, while CuBr serving as catalyst.[6] Coupling of arenediazonium salts with $B_2(pin)_2$ offers an alternative method of access to arylboron compounds.[7]

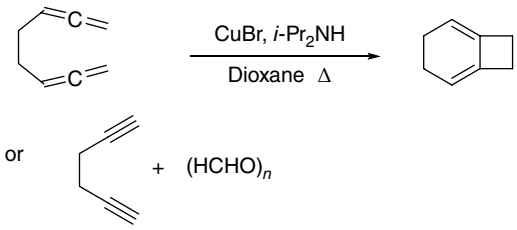
2-Alkynoic acids undergo decarboxylation prior to coupling with ArX. This reaction is catalyzed by CuBr and it requires additive to activate the aryl halides ($NaNO_2$ for ArI, and $PdCl_2$ for ArBr).[8] The coupling of 1-alkynes with $RB(OH)_2$ employing CuBr as catalyst is greatly accelerated by 2,6-lutidine.[9]

Diarylation of acetic esters is accomplished in hot DMF using CuBr ligated to Ph_3P and 1,10-phenanthroline.[10]

A method for *N*-alkynylation of imides consists of CuBr-catalyzed coupling with alkynyl(triaryl)bismuthonium salts.[11]

Annulation. Oxidative cyclization to form oxazolines from *N*-alkylamidines is observed. It is achieved by catalysis of $CuBrSMe_2$ in DMSO-$PhCF_3$ under an oxygen atmosphere.[12]

A remarkable catalytic effect of CuBr is the induction of [2+2]cycloaddition between the terminal double bonds of 1,2,6,7-octatetraene. The same result can be achieved starting from a mixture of 1,5-hexadiynes and paraformaldehyde.[13]

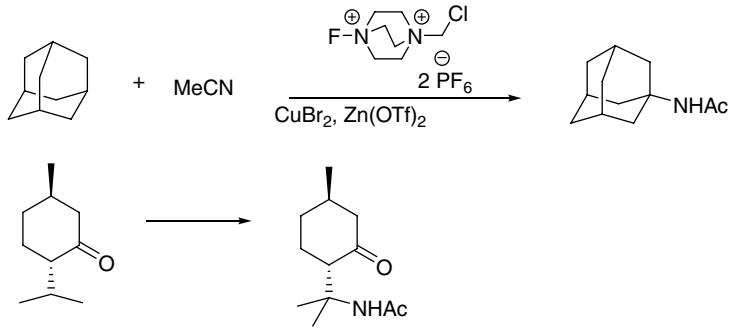


[1] Guo, N., Ji, J.-X. *TL* **53**, 4797 (2012)
[2] Feng, H., Ermolat'ev, D.S., Song, G., Van der Eycken, E.V. *JOC* **76**, 7608 (2011)
[3] Collet, F., Song, B., Rudolpji, F., Goossen, L.J. *EJOC* 6486 (2011)
[4] Frauenlob, R., Garcia, C., Bradshaw, G.A., Burke, H.M., Bergin, E. *JOC* **77**, 4445 (2012)
[5] Zhang, J., Wei, Y., Lin, S., Liang, F., Liu, P. *OBC* **10**, 9237 (2012)
[6] Vaddula, B., Leazer, J., Varma, R.S. *ASC* **354**, 986 (2012)
[7] Zhang, J., Wang, X., Yu, H., Ye, J. *SL* 1394 (2012)
[8] Pan, D., Zhang, C., Ding, S., Jiao, N. *EJOC* 4751 (2011)

[9] Yasukawa, T., Miyamura, H., Kobayashi, S. *OBC* **9**, 6208 (2011)
[10] Song, B., Himmler, T., Goossen, L.J. *ASC* **353**, 1688 (2011)
[11] Sueda, T.,Oshima, A.,Teno, N. *OL* **13**, 3996 (2011)
[12] Wang, Y.-F., Chen, H., Zhu, X., Chiba, S. *JACS* **134**, 11980 (2012)
[13] Kitagaki, S., Kajita, M., Narita, S., Mukai, C. *OL* **14**, 1366 (2012)

Copper(II) bromide

C-H amination. Unactivated C-H bonds such as those of cyclooctane and adamantane are converted into C-N bonds by a catalytic process using $CuBr_2$ and $Zn(OTf)_2$, in the presence of an oxidant (e.g., Selectfluor).[1]



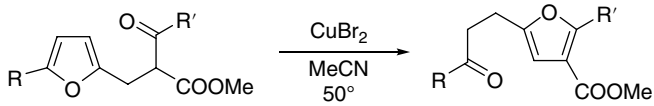
Coupling. A procedure for preparation of *N,N*-diarylcarbamides from the *N*-monoaryl amides calls for heating with ArX, $CuBr_2$, Cs_2CO_3, and DMEDA in toluene.[2] *N*-Arylcarbamates are obtained by the coupling reaction of $ArB(OH)_2$, KOSCN and an alcohol catalyzed by $CuBr_2$.[3]

A new method for etherification of di-(*p*-anisyl)methanol involves mixing it with a triorganosilyl ether in the presence of $CuBr_2$.[4]

Intramolecular *N*-arylation succeeds in the synthesis of *N*-alkoxyoxindoles.[5] Coupling with involvement of Schiff base and a triple bond leads to formation of the pyridine ring.[6]

The enamide-to-oxazole transformation consists of an oxidation process, but the essential activation is provided by catalysis by $CuBr_2$.[7]

Friedel-Crafts reaction. The mild Lewis acidity of $CuBr_2$ is responsible for cyclization of α-(2-furylmethyl)-β-keto esters which is followed by skeletal reorganization to generate a new furan ring.[8]



[1] Michaudel, Q., Thevenet, D., Baran, P.S. *JACS* **134**, 2547 (2012)
[2] Wang, M., Yu, H., You, X., Wu, J., Zhang, Z. *ChJC* **30**, 2356 (2012)
[3] Kianmehr, E., Baghersad, M.H. *ASC* **353**, 2599 (2011)

[4] Specklin, S., Gallier, F., Mezaache, R., Harkat, H., Dembelé, Y.A., Weibel, J.-M., Blanc, A., Pale, P. *TL* **52**, 5820 (2011)
[5] Kukosha, T., Trufilkina, N., Katkevics, M. *SL* 2525 (2011)
[6] Sakai, N., Tamura, K., Shimamura, K., Ikeda, R., Konakahara, T. *OL* **14**, 836 (2012)
[7] Cheung, C.W., Buchwald, S.L. *JOC* **77**, 7526 (2012)
[8] Yin, B., Yu, H., Li, Z., Zhong, W., Gu, W. *S* 3735 (2012)

Copper(I) *t*-butoxide

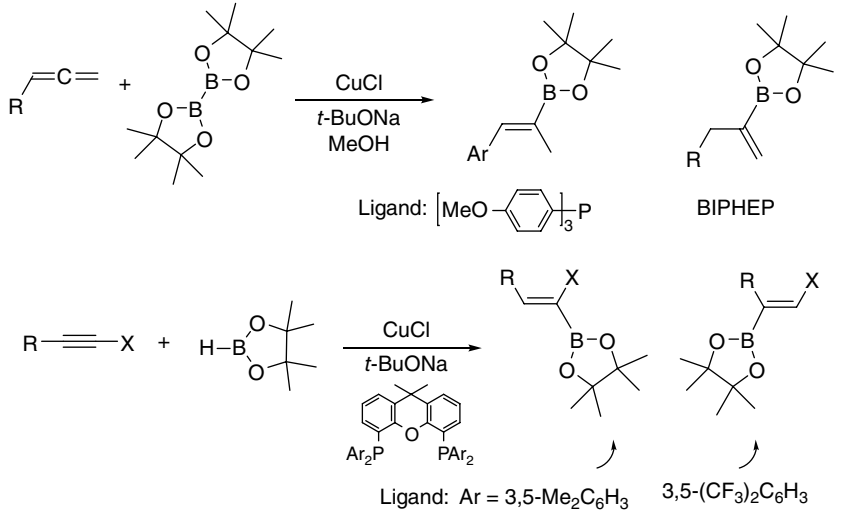
Coupling. Hindered arylamines such as 1-(*o*-tolyl)-2,2,6,6-tetramethylpiperidine can be elaborated by coupling of the arylboronate and the *N*-benzoyloxy derivative of the piperidine.[1]

[1] Rucker, R.P., Whittaker, A.M., Dang, H., Lalic, G. *ACIE* **51**, 3953 (2012)

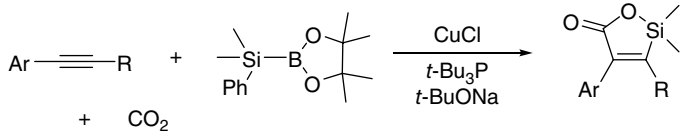
Copper(I) chloride

Addition. An extensive body of work concerning addition of organoboron compounds to unsaturated CC and CX bonds exists, and most of the reactions are catalyzed by CuCl. Thus arylboroxines add to aldehydes, *N*-tosylimines, and conjugated carbonyl compounds with ease.[1] Benzylic boronates are generated from reaction of alkenylarenes with (pin)BH,[2] and they are precursors of benzyl anions.

Regiocontrol by ligand in the hydroboration of 1,2-alkadienes[3] and to certain alkynes[4] is a valuable result. Also of synthetic significance is the twofold hydroboration of 1-trimethylsilylalkynes leading to *syn*-1,2-diboryl derivatives.[5] Alkynes in which a propargylic position bears a heterosubstituent tend to be borylated at the far end of the triple bond.[6]



The apparent hydroboration using $B_2(pin)_2$ is due to protonation, and if other electrophiles are present the reaction can lead to adducts with other substituents. For example ethynylbenzene is converted into (*E*)-α-methyl-β-borylstyrene when the reaction is conducted in the presence of MeI.[7] A route to silalactones is delineated from silylboration and carboxylation in situ.[8]



N,N-Dipropargylation of α-amino acids occurs from treatment with formaldehyde, 1-alkynes and CuCl.[9]

Substitution. For synthesis of enamines from alkenylzirconocene alkoxides the CuCl-catalyzed reaction with hydroxylamine benzoates is adequate.[10] The heterocycle of benzoxazole is opened by reaction with amines which affords *N*-(*o*-hydroxyphenyl) formamidines.[11]

1-Alkynes also undergo trifluoromethylation successfully by intervention of CuCl.[12] The Sonogashira coupling of 1-alkynes with ArI at room temperature is under catalysis of CuCl and photoinduced by a blue LED.[13]

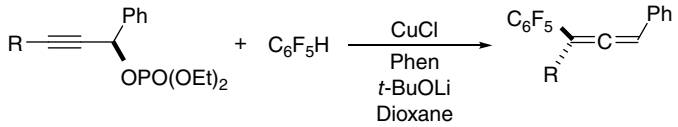
Complexation of CuCl to 2,9-di(*p*-anisyl)-1,10-phenanthroline gives rise to a photoredox catalyst sensitive to green LED emission. It initiates atom-transfer radical allylation of α-halo ketones (reaction with allylstannanes).[14]

Suzuki coupling replaces an aryl bromine atom by a B(pin) group; *o*-bromostyrenes under such reaction conditions (CuCl, $Cy_2PCH_2CH_2PCy_2$, *t*-BuOK/THF) also incorporate HBr (bromine at the benzylic position).[15] Both epimers of a 3-halo-*p*-menthane give the thermodynamically stable menthyl-B(pin) from reaction with $B_2(pin)_2$.[16]

Allylic trifluoromethylation is accompanied by double bond shift.[17] That based on desilylation is of course γ-selective.[18] *N*-Hydroxycarbamates are oxidized to the nitroso compounds in air prior to condensation with an α-alkylstyrene (ene reaction),[19] but in allylic amination by PhNHOH there is dehydration.[20]

Stoichiometric quantities of *t*-BuOK favor substitution on allylic carbonates by $B_2(pins)_2$ as reaction time is shortened.[21] The reaction with disilanes is sensitive to steric hindrance, the silicon atom would be attached to the carbon atom adjacent to a smaller group.[22]

Copper(I) chloride enables allenylation of pentafluorobenzene with propargylic phosphates, i.e., γ-selective substitution.[23]

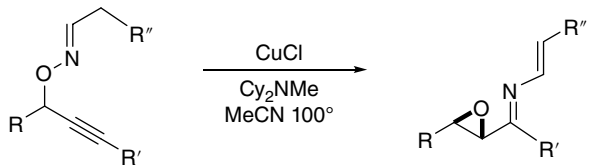


Coupling. With an oxidant and *t*-BuOLi present, coupling of C_6F_5H with benzthiazole is also a process made feasible by CuCl (or CuI).[24] Formation of 3-arylindenes by combining 2-alkylphenylalkynes and $ArSO_2Cl$ perhaps is initiated by desulfonylative cupration which then attack the triple bond.[25]

Cyclization of β-halo-α,β-unsaturated ketones to furans requires CuCl as well as a base such as Et_3N which performs dehydrohalogenation.[26] Mixtures of *o*-haloanilines, aldehydes and NaN_3 are sources of benzimidazoles, the formation of which involves azide ion addition to the emerging imines and an intramolecular coupling with loss of dinitrogen, or in the order of coupling as the first step.[27]

Imines are activated on *N*-acylation, and they become receptive to coupling with organoborates which is catalyzed by CuCl – pyridine.[28]

The replacement of an ethynyl residue in 3-amino-1-alkynes by another alkynyl group is a very unusual transformation enabled by CuCl.[29] Another remarkable reaction is the conversion of *O*-propargyl oximes into α-epoxy imines[30] or azete oxides.[31]



[1] Liao, Y.-X., Hu, Q.-S. *JOC* **76**, 7602 (2011)
[2] Grigg, R.D., Rigoli, J.W., Van Houeln, R., Neale, S., Schomaker, J.M. *CEJ* **18**, 9391 (2012)
[3] Yuan, W., Ma, S. *ASC* **354**, 1867 (2012)
[4] Semba, K., Fujihara, T., Terao, J., Tsuji, Y. *CEJ* **18**, 4179 (2012)
[5] Jung, H.-Y., Yun, J. *OL* **14**, 2606 (2012)
[6] Moure, A.L., Arrayas, R.G., Cardenas, D.J., Alonso, I., Carretero, J.C. *JACS* **134**, 7219 (2012)
[7] Alfaro, R., Parra, A., Aleman, J., Ruano, J.L.G., Tortosa, M. *JACS* **134**, 15165 (2012)
[8] Fujihara, T., Tani, Y., Semba, K., Terao, J., Tsuji, Y. *ACIE* **51**, 11487 (2012)
[9] Uhlig, N., Li, C.-J. *OL* **14**, 3000 (2012)
[10] Yan, X., Chen, C., Zhou, Y., Xi, C. *OL* **14**, 4750 (2012)
[11] Yu, D., Lee, S., Sum, Y.N., Zhang, Y. *ASC* **354**, 1672 (2012)
[12] Luo, D.-F., Xu, J., Fu, Y., Guo, Q.-X. *TL* **53**, 2769 (2012)
[13] Sagadevan, A., Hwang, K.C. *ASC* **354**, 3421 (2012)
[14] Pirtsch, M., Paria, S., Matsuno, T., Isobe, H., Reiser, O. *CEJ* **18**, 7336 (2012)
[15] Grigg, R.D., Van Hoveln, R., Schomaker, J.M. *JACS* **134**, 16131 (2012)
[16] Ito, H., Kubota, K. *OL* **14**, 890 (2012)
[17] Wang, X., Ye, Y., Zhang, S., Feng, J., Xu, Y., Zhang, Y., Wang, J. *JACS* **133**, 16410 (2011)
[18] Mizuta, S., Galicia-Lopez, O., Engle, K.M., Verhoog, S., Wheelhouse, K., Rassias, G., Gouverneur, V. *CEJ* **18**, 8583 (2012)
[19] Frazier, C.P., Engelking, J.R., de Alaniz, J.R. *JACS* **133**, 10430 (2011)
[20] Srivastava, R.S., Bertrand III, R., Gallo, A.A., Nicholas, K.M. *TL* **52**, 3478 (2011)
[21] Ito, H., Miya, T., Sawamura, M. *T* **68**, 3423 (2012)
[22] Ito, H., Horita, Y., Sawamura, M. *ASC* **354**, 813 (2012)
[23] Nakatani, A., Hirano, K., Satoh, T., Miura, M. *OL* **14**, 2586 (2012)

[24] Fan, S., Chen, Z., Zhang, X. *OL* **14**, 4950 (2012)
[25] Zeng, X., Ilies, L., Nakamura, E. *JACS* **133**, 17638 (2011)
[26] Kim, H.Y., Li, J.-Y., Oh, K. *JOC* **77**, 11132 (2012)
[27] Kim, Y., Kumar, M.R., Park, N., Heo, Y., Lee, S. *JOC* **76**, 9577 (2011)
[28] Morin, M.S.T., Lu, Y., Black, D.A., Arndtsen, B.A. *JOC* **77**, 2013 (2012)
[29] Kim, Y., Nakamura, H. *SL* 1686 (2012)
[30] Nakamura, I., Iwata, T., Zhang, D., Terada, M. *OL* **14**, 206 (2012)
[31] Nakamura, I., Araki, T., Zhang, D., Kudo, Y., Kwon, E., Terada, M. *OL* **13**, 3616 (2011)

Copper(II) chloride

Substitution. A highly *p*-selective bromination of anisole and thioanisole is performed by LiBr with $CuCl_2$ as catalyst under O_2 and CO_2 in EtOH.[1] It is speculated that the adduct of EtOH and CO_2 might play some role.

Sugar hydrazides are transformed into α-glycosyl phosphates in a reaction with H_3PO_4 catalyzed by $CuCl_2$.[2] S_N2' displacement of propargylic phosphates by organoboronates[3] is also catalyzed by $CuCl_2$ (cf. CuCl above).

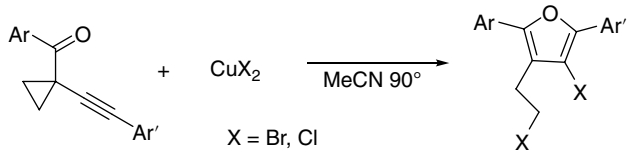
Redox reactions. The virtue of $CuCl_2$ for catalyzing hydrolysis of imines without further complication such as dehydration of β–hydroxy carbonyl compounds makes it desirable to act in consort with aluminum to cleave Δ^2-isoazolines.[4]

A method to assemble 2-hydroxybenzophenones from phenols and benzaldehydes consists of heating the mixtures with $CuCl_2$ and Ph_3P in toluene.[5] Certain aromatic and heteroaromatic compounds are oxidized by molecular oxygen when in the presence of $CuCl_2$ and *t*-BuONa,[6] for example 1,2,4,5-tetrachlorobenzene to the corresponding phenol, and benzthiazole to 2- benzthiazolinone, respectively.

Addition. 5-*endo*-Cyclization of 2-(α-hydroxyalkyl)-2,3-butadienoic esters is engendered by $CuCl_2$.[7] In assembling 1-alkynes, amines and carbonyl compounds into propargylic amines the function of $(EtO)_4Ti$ is to facilitate the Schiff base formation while $CuCl_2$ aids the subsequent addition by the alkynes.[8] The ring closure of 2-(*N*-propagylamino)-1,4-naphthoquinones to 3-chloro-1-azaanthraquinones is promoted by $CuCl_2$.[9]

Annulation. Condensation of *o*-iodoaniline with ArCHO and sulfur to form 2-arylbenzothiazoles can be effectuated by $CuCl_2$ –phenanthroline.[10] The ability of $CuCl_2$ to trigger *N*-oxidation has found an application to elaboration of tetrahydroquinolines from *N*-methylanilines, the strategy involves trapping of transient iminium salts by dienophiles.[11]

The small ring of 1-alkynylcyclopropyl ketones opens upon attack by a chloride ion from $CuCl_2$ as the salt activates the triple bond for the formation of a furan nucleus.[12]



[1] Liu, A.-H., He, L.-N., Hua, F., Yang, Z.-Z., Huang, C.-B., Yu, B., Li, B. *ASC* **353**, 3187 (2011)
[2] Edgar, L.J.G., Dasgupta, S., Nite, M. *OL* **14**, 4226 (2012)
[3] Yang, M., Yokokawa, N., Ohmiya, H., Sawamura, M. *OL* **14**, 816 (2012)
[4] Karpaviciene, I., Lapinskaite, R., Brukstus, A., Cikotiene, I. *SL* 381 (2012)
[5] Hu, J., Adogla, E.A., Ju, Y., Fan, D., Wang, Q. *CC* **48**, 11256 (2012)
[6] Liu, Q., Wu, P., Yang, Y., Zeng, Z., Liu, J., Lei, H.Y.A. *ACIE* **51**, 4666 (2012)
[7] Kim, S., Lee, P.H. *JOC* **77**, 215 (2012)
[8] Pierce, C.J., Nguyen, M., Larsen, C.H. *ACIE* **51**, 12289 (2012)
[9] Fei, H., Yin, H., Wang, S., Wang, H., Yao, Z.-J. *OL* **13**, 4208 (2011)
[10] Deng, H., Li, Z., Ke, F., Zhou, X. *CEJ* **18**, 4840 (2012)
[11] Nishino, M., Hirano, K., Satoh, T., Miura, M. *JOC* **76**, 6447 (2011)
[12] Zhu, M., Fu, W.-J., Xu, C., Zou, G.-L., Wang, Z.-Q., Ji, B.-M. *EJOC* 4609 (2012)

Copper(I) cyanide

Substitution. Borylsilanes are activated by CuCN - NaOMe (to release nucleophilic silylcopper species) to attack propargyl phosphates in the S_N2' reaction manner.[1]

[1] Vyas, D.J., Hazra, C.K., Oestreich, M. *OL* **13**, 4462 (2011)

Copper(II) fluoride

Polyfluoroalkylation. Transfer of a polyfluoroalkyl group from hypervalent iodine reagents by catalysis of CuF_2 has the advantage that 2-alkenoic acids react simultaneously to decarboxylation.[1]

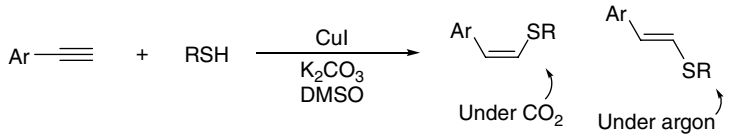
The air-stable reagent, $(Ph_3P)_3CuCF_3$, for replacing the iodine atom of ArI with a CF_3 group, $(Ph_3P)_3CuCF_3$, is obtained in two step: refluxing the rehydrate of CuF_2 and Ph_3P in MeOH, and treatment with Me_3SiCF_3.[2]

[1] He, Z., Luo, T., Hu, M., Cao, Y., Hu, J. *ACIE* **51**, 3944 (2012)
[2] Tomashenko, O.A., Escudero-Adan, E.C., Belmonte, M.M., Grushin, V.V. *ACIE* **50**, 7655 (2011)

Copper(I) iodide

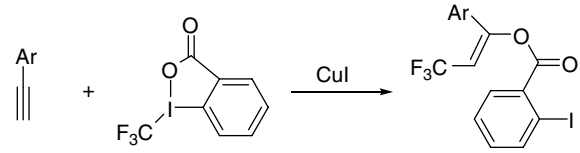
Addition. Hydration of nitriles affords amides can be carried out with CuI in water at 100°.[1] Under oxidative conditions, CuI catalyzes the addition of amines to aldehydes to furnish amides.[2]

Preparation of alkenyl sulfides by addition of RSH to alkynes is subject to variation of solvent, with respect to the adduct configuration.Thus in DMF or THF the *cis*-isomer predominates, in ethanediol or *i*-AmOH, the *trans*-isomer.[3] It is even more remarkable that, in the addition of RSH to ethynylarenes the atmosphere under which the reaction is carried out has a decisive effect.[4]

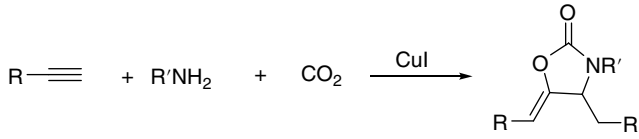


Homologation of 1-alkynes to give allenes involves addition to iminium species that are formed in situ from aldehydes (including paraformaldehyde) and *i*-Bu_2NH. Both this step and the subsequent elimination are catalyzed by CuI.[5]

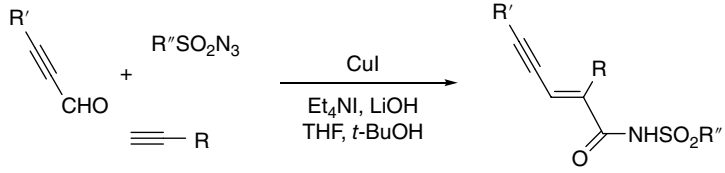
The benzannulated trifluoromethyliodonio-γ-lactone adds to styrenes and ethynylarenes to give adducts terminated by a trifluoromethyl group.[6]



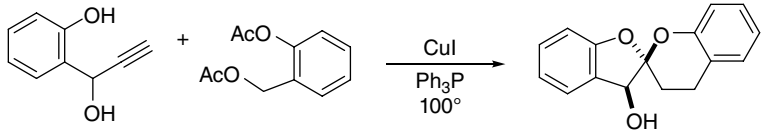
Under CO_2, alkynes and amines are combined under the influence of CuI, forming 5-alkylidene-2-oxazolidinones.[7] The same type of compounds (but with different groups attached to C-4 and the double bond) are assembled from 2-alkynoic acids, aldehydes and amines, via decarboxylation and carboxylative cyclization.[8]



The metallated species derived from coupling of 1-alkynes with sulfonyl azides add to 2-alkynals which eventually yield (*E*)-2-alken-4-ynecarboxamides.[9] On replacing 2-alkynals with nitrones for the reaction the products are 4-imidazolidinones.[10]



Formation of dibenzospiroacetals from 1-(*o*-hydroxyaryl)-2-propynols and *o*-hydroxybenzyl acetates probably proceeds via a hetero-Diels-Alder reaction. The dieneophiles are 2-methylene-3-hydroxydihydrobenzofurans and the dienes are *o*-quinomethanes, generated separately by CuI-catalyzed cyloetherification and 1,4-elimination.[11]



Substitution and coupling. It is better to use $K_4[Fe(CN)6]$ instead of the toxic alkali metal cyanides in converting benzyl halides into arylacetonitriles. However, a catalyst such as CuI is required.[12]

α-Arylation of diarylethanones is achieved by direct reaction with ArI. For best results either 1,10-phenanthroline or 2-acetylcyclohexanone is used as ligand for CuI, depending on whether the ArI is electron-rich or electron-deficient.[13] Amination of ketene silyl acetals derived from arylacetic esters by R_2NCl is similarly catalyzed.[14]

Heating 1-(*o*-haloaryl)-1,3-alkanediones with CuI and picolinic acid in toluene gives 3-substituted isocoumarins.[15] It is not known whether benzocyclobutenones are the intermediates.

The Pd-catalyzed arylation (coupling) of *N,N′*-dibenzyluracil is switched from C-5 to C-6 on adding CuI to the reaction media.[16] Oxidative cross coupling of two arenes is achieved via in situ iodination (of the more electron-rich component).[17]

Arylation at heteroatoms has expanded in scope and choice of reaction conditions. Primary arylamines are prepared with aq.NH_3 in PEG-400.[18] While using $LiNH_2$ as the nucleophile the reaction can proceed further to produce diarylamines and even triarylamines, either symmetrical or unsymmetrical.[19] Another preparation of $ArNH_2$ specifies the use of CuI, Cs_2CO_3 in DMSO with quinaldinic acid *N*-oxide as a ligand.[20]

N-Arylcarbamates are also accessed from reaction of ArX with KOCN and ROH, while the CuI catalyst is ligated to potassium *N*-(2,4-dimethylphenyl)oxamate.[21] Monoaryl and *N,N′*-diarylguanidines are synthesized by arylation, in which *N*-methylglycine serves to preserve the catalytic activity of CuI.[22] Cyclization of 2-(*N*-arylamino)benzophenones is done in DMSO at 120° in air.[23]

Diaryl ethers and aryl benzyl ethers are concocted out of ArI and alcohols, facilitated by CuI – hexamethylenetetramine.[24] A more useful information concerns with the difference between phenolic and alcoholic nucleophiles: ligand free CuI (with *t*-BuONa) favors arylation of aliphatic oxygen, and in the presence of picolinic acid, diaryl ether formation dominates.[25] Reaction of ArI with KSCN (catalyzed by CuI) in PEG-400 at 150° generates diaryl sulfides.[26]

As organoboron compounds gain prominence for synthetic processes, expedient synthesis of such compounds is always in demand. Coupling of $B_2(pin)_2$ with various halides and tosylates meets the important criterion of simplicity in access.[27] Carboxylation of $ArB(OH)_2$ has been applied to a synthesis of isotope-labeled acids.[28]

Sonogashira coupling requires both a Pd salt and CuI as cocatalysts, but only recently a study delineates the electronic nature of the substrates and phosphine ligands.[29] In fact many methods for alkyne synthesis rely on copper catalysts alone. Prior dehydrobromination of 1,1-dibromoalkenes to coupling with organoboronic acids[30] and that of 1,2-dibromo-1-alkenes for alkynylation of *N*-tosylamines[31] are based on the same logic.

On occasion that avoidance of 1-alkynes to partake the Sonogashira coupling is desired, protection by phosphonylation (phosphinylation by Ph_2PCl in the presence of CuI, then oxidation by H_2O_2) is an option.[32]

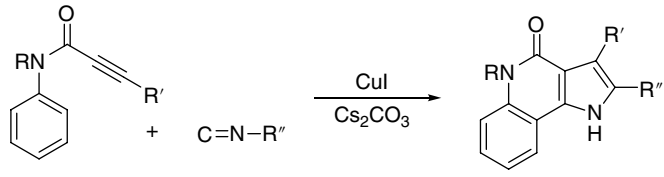
The ability of copper catalysts to promote decarboxylation enables coupling with 2-alkynoic acids,[33,34] although sometimes an adjunct such as $Fe(acac)_3$ is introduced. Unconventional coupling partners are tosylhydrazones which are decomposed in situ by a base (*t*-BuOLi).[35]

1-Alkynylation of 2-methyltetrahydroisoquinoline is performed with ethynylarenes in the presence of CuI and DEAD, the latter acting as a proton abstractor.[36]

Straightforward cross coupling is the most direct method for synthesis of conjugate enynes.[37] In partial response to the contemporary intensity of research into acquisition of polyfluorinated compounds is the development of a coupling approach, which includes trifluoromethylation of different substrates by Sonogashira coupling,[38] Hiyama coupling,[39,40] Stille coupling,[41] and Heck reaction.[42] The difluoromethyl group is similarly introduced with slight modification of the reaction conditions which all employ CuI.[43,44] Attachment of a phosphoryldifluoromethyl substituent to 1-alkynes is also successful.[45]

Decomposition of diazoalkanes by CuI in the presence of Me_3SiCF_3 leads to trifluoromethylated products.[46] Water is a promoter because protonation is required before the products emerge.

Annulation. *N*-(Alkynoyl)anilines and isonitriles are united to yield pyrrolo[3,2-*c*]quinolin-4-ones.[47] Secondary amines add to 1,4-diaryl-1,3-butadiynes and the adducts cyclize to give 1-aryl-2,4-diaminonaphthalenes.[48]



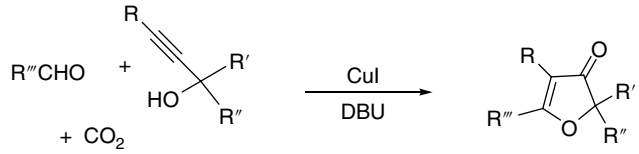
α-Arylation of alkyl cyanides is featured in the CuI-catalyzed reaction with methyl *N*-(*o*-halobenzoyl)anthranilates. It is followed by intramolecular addition and lactamization.[49] Glycine esters and *o*-halobenzaldehydes condense to give 2*H*-isoindole-1-carboxylic esters.[50]

The *N*-arylation of an aliphatic primary amide by *o*-halobenzamides sets the stage for ring closure to assemble quinazolinones.[51] Upon *N*′-arylation of *N*′-(aryl)benzohydrazides by *o*-bromoaryl carbonyl compounds the products would undergo debenzoylation and then cyclization, provided that a mild base is added to release the hydrazine.[52]

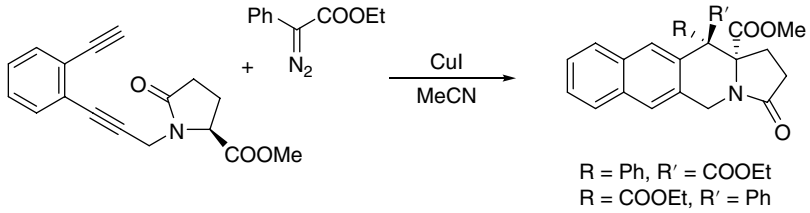
o,β-Dihalostyrenes and diethyl hydrazine-1,2-dicarboxylate react to give 1,2-dihydrocinnolinedicarboxylic esters.[53] Pyrrole and indole are another type of divalent nucleophiles with which tricyclic heterocycles are formed [in this case the catalyst system consists of CuI and $Pd(OAc)_2$].[54]

The reaction of (*E*)-ethyl α-bromomethylcinnamate with ethynylarenes furnishes 4-benzyl-2-naphthoic esters due to activation of the triple bond of the 1,4-enynes by CuI toward a 6-*exo* cyclization.[55]

Propargyl alcohols and aldehydes are combined to furnish 3(2*H*)-furanones.[56] Quite unexpectedly, the ketonic oxygen atom of the products comes from CO_2 under which the reaction is conducted.



Formation of 2-alkoxyfurans during decomposition of α-diazoalkanoic esters in the presence of alkynes[57] must be due to facilitation of ring-expanding rearrangement by CuI (coordination to the cyclopropene double bond?). The intriguing passage to naphtho-fused indolizidinones from reaction of diazo esters with a 1,2-benzenediyne has been documented.[58]



Piperidin-2-ylideneacetic esters are prepared from 4-pentynylamines and Cu(I)-carbenoids of acetic esters.[59]

It is likely that CuI is the initiator of the intramolecular hetero-Diels-Alder reaction of 3-(*o*-propargyloxy)benzylideneoxindoles, by way of coordination to the triple bond.[60]

[1] Li, Z., Wang, L., Zhou, X. *ASC* **354**, 584 (2012)
[2] Zhu, M., Fujita, K., Yamaguchi, R. *JOC* **77**, 9102 (2012)
[3] Trostyanskaya, I.G., Beletskaya, I.P. *SL* 535 (2012)
[4] Riduan, S.N., Ying, J.Y., Zhang, Y. *OL* **14**, 1780 (2012)
[5] Kuang, J., Luo, H., Ma, S. *ASC* **354**, 933 (2012)
[6] Janson, P.G., Ghoneim, I., Ilchenko, N.O., Szabo, K.J. *OL* **14**, 2882 (2012)
[7] Zhao, J., Jiang, H. *TL* **53**, 6999 (2012)
[8] Feng, H., Emolat'ev, D.S., Song, G., Van der Eycken, E.V. *ASC* **354**, 505 (2012)
[9] Cheng, D., Ling, F., Li, Z., Yao, W., Ma, C. *OL* **14**, 3146 (2012)
[10] Namitharan, K., Pitchumani, K. *OL* **13**, 5728 (2011)
[11] Li, X., Xue, J., Huang, C., Li, Y. *CAJ* **7**, 903 (2012)
[12] Ren, Y., Dong, C., Zhao, S., Sun, Y., Wang, J., Ma, J., Hou, C. *TL* **53**, 2825 (2012)
[13] Danoun, G., Tlili, A., Monnier, F., Taillefer, M. *ACIE* **51**, 12815 (2012)
[14] Miura, T., Morimoto, M., Murakami, M. *OL* **14**, 5214 (2012)
[15] Ge, Z.-Y., Fei, X.-D., Tang, T., Zhu, Y.-M., Shen, J.-K. *JOC* **77**, 5736 (2012)
[16] Cernova, M., Cerna, I., Pohl, R., Hocek, M. *JOC* **76**, 5309 (2011)
[17] Do, H.-Q., Daugulis, O. *JACS* **133**, 13577 (2011)
[18] Chen, J., Yuan, T., Hao, W., Cai, M. *TL* **52**, 3710 (2011)
[19] Tlili, A., Monnier, F., Taillefer, M. *CC* **48**, 6408 (2012)
[20] Zeng, X., Huang, W., Qiu, Y., Jiang, S. *OBC* **9**, 8224 (2011)
[21] Yang, X., Zhang, Y., Ma, D. *ASC* **354**, 2443 (2012)

[22] Xing, H., Zhang, Y., Lai, Y., Jiang, Y., Ma, D. *JOC* **77**, 5449 (2012)
[23] Zhou, W., Liu, Y., Yang, Y., Deng, G.-J. *CC* **48**, 10678 (2012)
[24] Qian, C., Zong, Q., Fang, D. *ChJC* **30**, 199 (2012)
[25] Maiti, D. *CC* **47**, 8340 (2011)
[26] Li, X., Yuan, T., Chen, J. *ChJC* **30**, 651 (2012)
[27] Yang, C.-T., Zhang, Z.-Q., Tajuddin, H., Wu, C.-C., Liang, J., Liu, J.-H., Fu, Y., Czyzewska, M., Steel, P.G., Marder, T.B., Liu, L. *ACIE* **51**, 528 (2012)
[28] Riss, P.J., Lu, S., Telu, S., Aigbirhio, F.I., Pike, V.W. *ACIE* **51**, 2698 (2012)
[29] Schilz, M., Plenio, H. *JOC* **77**, 2798 (2012)
[30] Liu, J., Dai, F., Yang, Z., Wang, S., Xie, K., Wang, A., Chen, X., Tan, Z. *TL* **53**, 5678 (2012)
[31] Yang, Y., Zhang, X., Liang, Y. *TL* **53**, 6557 (2012)
[32] Yang, X., Matsuo, D., Suzuma, Y., Fang, J.-K., Xu, F., Orita, A., Otera, J., Kajiyama, S., Koumura, N., Hara, K. *SL* 2402 (2011)
[33] Li, T., Sun, P., Yang, H., Zhu, Y., Yan, H., Lu, L., Mao, J. *T* **68**, 6413 (2012)
[34] Li, T., Qu, X., Zhu, Y., Sun, P., Yang, H., Shan, Y., Zhang, H., Liu, D., Zhang, X., Mao, J. *ASC* **353**, 2731 (2011)
[35] Ye, F., Ma, X., Xiao, Q., Li, H., Zhang, Y., Wang, J. *JACS* **134**, 5742 (2012)
[36] Singh, K.N., Singh, P., Kaur, A., Singh, P. *SL* 760 (2012)
[37] Lin, Y.-Y., Wang, Y.-J., Cheng, J.-H., Lee, C.-F. *SL* 930 (2012)
[38] Weng, Z., Li, H., He, W., Yao, L.-F., Tan, J., Chen, J., Yuan, Y., Huang, K.-W. *T* **68**, 2527 (2012)
[39] Xu, J., Xiao, B., Xie, C.-Q., Luo, D.-F., Liu, L., Fu, Y. *ACIE* **51**, 12551 (2012)
[40] Hafner, A., Bräse, S. *ASC* **353**, 3044 (2011)
[41] Sanhueza, I.A., Nielsen, M.C., Ottiger, M., Schoenebeck, F. *HCA* **95**, 2231 (2012)
[42] Egami, H., Shimizu, R., Sodeoka, M. *TL* **53**, 5503 (2012)
[43] Fier, P.S., Hartwig, J.F. *JACS* **134**, 5524 (2012)
[44] Prakash, G.K.S., Ganesh, S.K., Jones, J.-P., Kulkarni, A., Masood, K., Swabeck, J.K., Olah, G.A. *ACIE* **51**, 12090 (2012)
[45] Jiang, X., Chu, L., Qing, F.-L. *OL* **14**, 2870 (2012)
[46] Hu, M., Ni, C., Hu, J. *JACS* **134**, 15257 (2012)
[47] Zhou, F., Liu, J., Ding, K., Liu, J., Cai, Q. *JOC* **76**, 5346 (2011)
[48] Sun, H., Wu, X., Hua, R. *TL* **52**, 4408 (2011)
[49] Liu, T., Zhu, C., Yang, H., Fu, H. *ASC* **354**, 1579 (2012)
[50] Biswas, S., Nayak, M., Kanojiya, S., Batra, S. *ASC* **353**, 3330 (2011)
[51] Xu, L., Jiang, Y., Ma, D. *OL* **14**, 1150 (2012)
[52] Xiong, X., Jiang, Y., Ma, D. *OL* **14**, 2552 (2012)
[53] Ball, C.J., Gilmore, J., Willis, M.C. *ACIE* **51**, 5718 (2012)
[54] Sun, L.-L., Loao, Z.-Y., Tang, R.-Y., Deng, C.-L., Zhang, X.-G. *JOC* **77**, 2850 (2012)
[55] Lim, J.W., Kim, K.H., Kim, S.H., Kim, J.N. *TL* **53**, 5449 (2012)
[56] Qi, C., Jiang, H., Huang, L., Yuan, G., Ren, Y. *OL* **13**, 5520 (2011)
[57] Zhou, L., Ma, J., Zhang, Y., Wang, J. *TL* **52**, 5484 (2011)
[58] Mondal, S., Nechab, M., Campolo, D., Vanthuyne, N., Bertrand, M.P. *ASC* **354**, 1987 (2012)
[59] Kumaraswamy, G., Jayaprakash, N., Balakishan, G. *OBC* **9**, 7913 (2011)
[60] Jha, M., Guy, S., Chou, T.-Y. *TL* **52**, 4337 (2011)

Copper(II) 4-methoxysalicylate

Alcoholysis. The copper salt catalyzes the conversion of the dithioesters of malonic acid into the *S,O*-esters under neutral conditions.[1]

[1] Matsuo, K., Shindo, M. *OL* **13**, 4406 (2011)

Copper(I) oxide

Substitution. Copper(I) oxide functions as a catalyst for the reaction of ArI with KSCN to produce Ar_2S.[1] With L-proline as ligand it catalyzes the conversion of ArBr into ArCl by reaction with Me_4NCl.[2]

The BBr_3 complexes of 2-arylpyridines are susceptible to nucleophilic attack in the presence of Cu_2O, and accordingly various functionalities (e.g., halogen, azide, amine, sulfonyl) can be introduced into the *o*-position of the aryl substituent.[3]

[1] Kelly, C.B., Lee, C., Leadbeater, N.E. *TL* **52**, 4587 (2011)
[2] Feng, X., Qu, Y., Han, Y., Yu, X., Bao, M., Yamamoto, Y. *CC* **48**, 9468 (2012)
[3] Niu, L., Yang, H., Yang, D., Fu, H. *ASC* **354**, 2211 (2012)

Copper(II) oxide

Oxidation. An expedient preparation of methyl vinyl ketone (in about 15% yield) from levulinic acid consists of decomposition by CuO on either CeO_2 of Al_2O_3 under UV.[1] With CuO alone the reaction produces 2-butanone.

Mixtures of benzylic alcohols and primary amines are transformed into benzylideneamines on exposure to CuO/Fe_3O_4.[2]

Substitution. Copper(II) oxide on mesoporous silica forms a catalyst for converting ArI into phenols on reaction with CsOH.[3] A one-pot synthesis of ArSR employs nano-CuO to effect substitution of ArX by KSC(=S)OEt and *S*-alkylation.[4]

For synthesis of anilines from ArX and amines or ammonia in water, the CuO catalyst is modified by oxamic acid hydrazide.[5,6] Ynamides are obtained by a CuO-catalyzed *N*-alkynylation.[7]

Addition. Hydration of ArCN is readily carried out in the presence of CuO and $CH_3CH{=}NOH$ in aq. MeOH.[8]

[1] Gong, Y., Lin, L., Zhang, B. *ChJC* **30**, 327 (2012)
[2] Perez, J.M., Cano, R., Yus, M., Ramon, D.J. *EJOC* 4548 (2012)
[3] Chan, C.-C., Chen, Y.-W., Su, C.-S., Lin, H.-P., Lee, C.-F. *EJOC* 7288 (2011)
[4] Akkilagunta, V.K., Kakulapati, R.R. *JOC* **76**, 6819 (2011)
[5] Huang, M., Lin, X., Zhu, X., Peng, W., Xie, J., Wan, Y. *EJOC* 4523 (2011)
[6] Li, Y., Zhu, X., Meng, F., Wan, Y. *T* **67**, 5450 (2011)
[7] Tong, X., Ni, G., Deng, X., Xia, C. *SL* 2497 (2012)
[8] Ma, X.-Y., He, Y., Hu, Y.-L., Lu, M. *TL* **53**, 449 (2012)

Copper(II) perchlorate

5-Iodo-1,2,3-triazoles. Redox reaction between $Cu(ClO_4)_2$ and NaI generates Cu(I) and I_3^- species which collectively catalyze the cycloaddition of organoazides to alkynes and then the adducts are iodinated.[1]

[1] Brotherton, W.S., Clark, R.J., Zhu, L. *JOC* **77**, 6443 (2012)

Copper(II) sulfate

Coupling. Anilines are formed when potassium aryltrifluoroborates are treated at room temperature with NH_4OH, NaOH and $CuSO_4$.[1] Another catalyst is derived from $CuSO_4$, sucrose in PEG-200 which can operate in water to convert ArX into anilines.[2]

Addition. A method for transfer of the phenyldimethylsilyl group from the substituted pinacolboryl derivative to conjugated carbonyl compounds involves catalysis by $CuSO_4$ and 4-picoline.[3]

[1] Liesen, A.P., Silva, A.T., Sousa, J.C., Menezes, P.H., Oliveira, R.A. *TL* **53**, 4240 (2012)
[2] Huang, M., Wang, L., Zhu, X., Mao, Z., Kuang, D., Wan, Y. *EJOC* 4897 (2011)
[3] Calderone, J.A., Santos, W.L. *OL* **14**, 2090 (2012)

Copper(I) 2-thienylcarboxylate, (CuTC)

Trifluromethylation. Chain elongation of 1-alkenes by one carbon to give $RCH{=}CHCH_2CF_3$ can be accomplished on reaction catalyzed by CuTC, with either 9-trifluoromethyldibenzothiophene triflate or Me_3SiCF_3 as the CF_3 group donor.[1,2] In the latter instance an oxidant is also required.

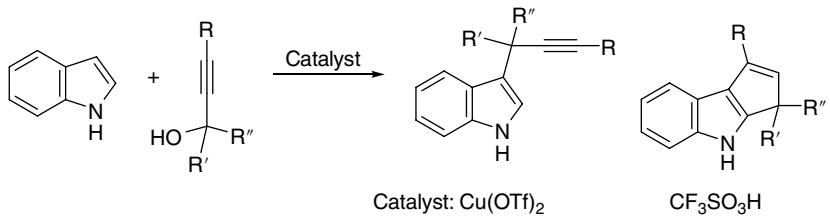
[1] Xu, J., Fu, Y., Luo, D.-F., Jiang, Y.-Y., Xiao, B., Liu, Z.-J., Gong, T.-J., Liu, L. *JACS* **133**, 15300 (2011)
[2] Chu, L., Qing, F.-L. *OL* **14**, 2106 (2012)

Copper(II) triflate

Acetalization. Owing to its being a relatively mild Lewis acid the aspiration of $Cu(OTf)_2$ for a wide catalytic reach is implicit. It is easy to conceive the utility in acetalization of diols (e.g., sugars) with $ArCH(OMe)_2$,[1] and promoting the Prins reaction of alkenols with aldehydes.[2]

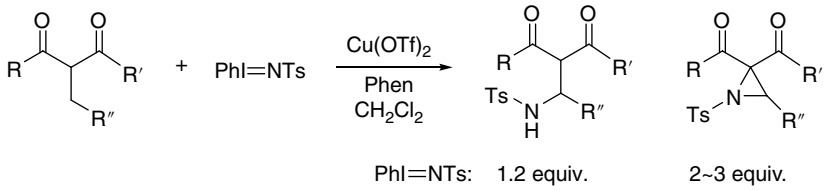
Substitution. Monoarylation of diols with $Ar_2I(OTf)$ can be achieved by heating with $Cu(OTf)_2$ and Na_3PO_4 in toluene.[3] *C*-Arylation of alkenes is effected by the same reagents, thus methylenecyclohexane gives 1-benzylcyclohexenes.[4]

Propargylation of indole proceeds as expected in the presence of $Cu(OTf)_2$, whereas a different result is observed with TfOH.[5]



Isochroman is oxidized by the *N*-oxoammonium salt derived from TEMPO in situ to condense with aldehydes, using $Cu(OTf)_2$ as catalyst. 2-Alkenals are benzylated at the γ-position.[6]

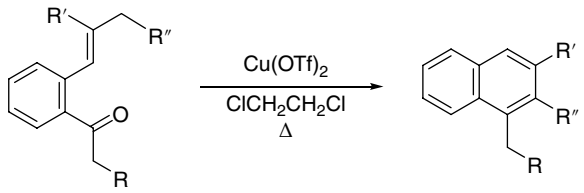
A method for hydroxyamination of 1,3-dicarbonyl compounds employs two different copper salts: CuCl to generate the electrophilic nitrosoformates from *N*-hydroxycarbamates, and $Cu(OTf)_2$ for the substitution step.[7] Sulfonylamination by $PhI{=}NSO_2Ar$ is straightforward,[8] however, for α-monoalkylated substrates the amination occurs at the α-carbon of the sidechain, or aziridination when excess iodonium imine is used.[9]



Complementary to traditional electrophilic nitration, conversion of ArX to nitroarenes is also practical by the Cu-catalyzed reaction with KNO_2.[10] Trifluoromethyl sulfides are available by a coupling route with $RB(OH)_2$ and Me_4NSCF_3.[11]

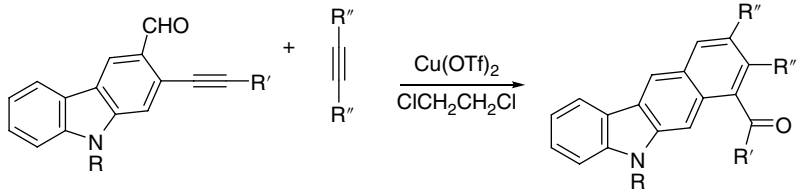
Condensation. Diaryl ketones are obtained from reaction of ArCHO and $Ar'B(OH)_2$.[12] Both Schiff base formation and addition of 1-alkynes to the resultant imines are promoted by $Cu(OTf)_2$.[13]

On heating with $Cu(OTf)_2$ in dichloroethane alkyl *o*-(1-alkenyl)aryl ketones undergo cyclodehydration to furnish substituted naphthalenes.[14]



Addition. A more extensive variety of conjugated systems has been subjected to addition of a silyl group from disilanes.[15] 6-Alkynals and analogs containing a heteroatom inside the carbon chain undergo intramolecular addition, on activation by enamination (with $CyNH_2$) at one side and complexation with Cu(I) species [from $Cu(OTf)_2$ + Ph_3P] at the other.[16]

The annulations of 2-alkynylbenzaldehydes on reaction with alkynes, catalyzed by $Cu(OTf)_2$,[17] likely involves pyrylium intermediates which are trapped by way of a hetero-Diels-Alder reaction.



[1] Tran, A.-T., Jones, R.A., Pastor, J., Boisson, J., Smith, N., Galan, C. *ASC* **353**, 2593 (2011)
[2] Ghosh, A.K., Kass, J., Nicponski, D.R., Keyes, C. *S* 3579 (2012)
[3] Kuriyama, M., Hamaguchi, N., Onomura, O. *CEJ* **18**, 1591 (2012)
[4] Phipps, R.J., McMurray, L., Ritter, S., Duong, H.A., Gaunt, M.J. *JACS* **134**, 10773 (2012)
[5] Zhang, L., Zhu, Y., Yin, G., Lu, P., Wang, Y. *JOC* **77**, 9510 (2012)
[6] Richter, H., Rohlmann, R., Mancheño, O.G. *CEJ* **17**, 11622 (2011)
[7] Sandoval, D., Frazier, C.P., Bugarin, A., de Alaniz, J.R. *JACS* **134**, 18948 (2012)
[8] Ton, T.M.U., Himawan, F., Chang, J.W.W., Chan, P.W.H. *CEJ* **18**, 12020 (2012)
[9] Ton, T.M.U., Tejo, C., Tiong, D.L.Y., Chan, P.W.H. *JACS* **134**, 7344 (2012)
[10] Joseph, P.J.A., Priyadarshini, S., Kantam, M.L., Maheswaran, H. *TL* **53**, 1511 (2012)
[11] Zhang, C.-P., Vicic, D.A. *CAJ* **7**, 1756 (2012)
[12] Zheng, H., Ding, J., Chen, J., Liu, M., Gao, W., Wu, H. *SL* 1626 (2011)
[13] Meyet, C.E., Pierce, C.J., Larsen, C.H. *OL* **14**, 964 (2012)
[14] Liu, W.-M., Tnay, Y.L., Gan, K.P., Liu, Z.-H., Tyan, W.H., Narasaka, K. *HCA* **95**, 1953 (2012)
[15] Iannazzo, L., Molander, G.A. *EJOC* 4923 (2012)
[16] Montaignac, B., Vitale, M.R., Ratovelomanana-Vidal, V., Michelet, V. *EJOC* 3723 (2011)
[17] Prakash, K.S., Nagarajan, R. *ASC* **354**, 1566 (2012)

Copper(II) trifluoroacetate

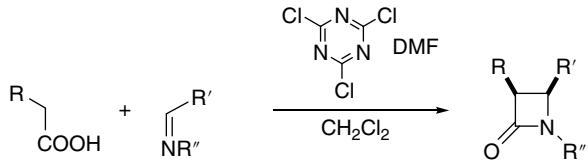
Coupling. A synthesis of $ArCF_3$ from $ArBF_3K$ and 1-trifluoromethyl-1-iodonio-3, 3-dimethyl-1,3-dihydroisobenzofuran employs $Cu(OCOCF_3)_2$ as catalyst.[1]

For the transformation of ArX into $ArNH_2$ on reaction with aqueous ammonia a promoter is derived from $Cu(OCOCF_3)_2$ and 2,7-di(2-pyridyl)-1,8-naphthyridine.[2]

[1] Huang, Y., Fang, X., Lin, X., Li, H., He, W., Huang, K.-W., Yuan, Y., Weng, Z. *T* **68**, 9949 (2012)
[2] Liao, B.-S., Liu, S.-T. *JOC* **77**, 6653 (2012)

Cyanuric chloride

β-Lactams. An expedient synthesis of β-lactams from carboxylic acids and imines uses cyanuric chloride as the condensation agent.[1]

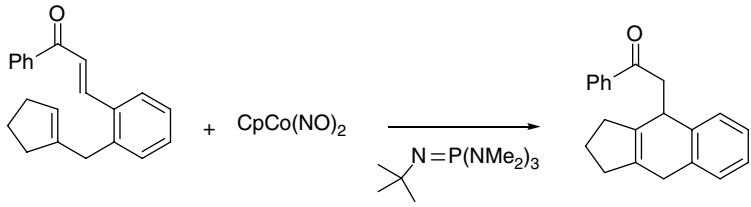


Beckmann rearrangement. Cyanuric chloride in a biodegradable ionic liquid has been proposed as reagent to promote the Beckmann rearrangement of ketoximes.[2]

[1] Zarei, M., Jarrahpour, A. *SL* 2572 (2011)
[2] Maia, A., Albanese, D.C.M., Landini, D. *T* **68**, 1947 (2012)

Cyclopentadienyl(dinitroso)cobalt

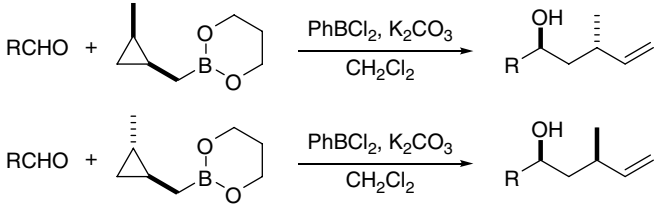
Michael reaction. The $CpCo(NO)_2$ complex forms cycloadducts with alkenes (esp. cyclopentene) and thereby activates the originally unactivated alkenyl hydrogen atom (for deprotonation). Such activation is demonstrated by an intramolecular Michael reaction.[1]



[1] Zhao, C., Toste, F.D., Bergman, R.GQ. *JACS* **133**, 10787 (2011)

Cycloproylmethylboronic esters

Homoallylation. By a deborylative ring opening the boronates are converted into homoallylation reagents for carbonyl compounds. The value of the reagents is illustrated by the access to 3-methyl-1-alken-5-ols.[1]



[1] Pei, W., Krauss, I.J. *JACS* **133**, 18514 (2011)

D

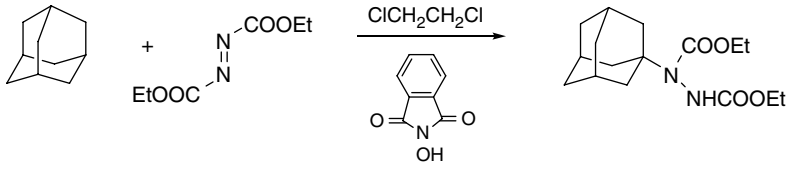
Dess-Martin periodinane

Oxidation. A method for α-trichloromethylation of alcohols involve treatment with the Dess-Martin reagent in the presence of $CHCl_3$ and then a bicyclic guanidine base.[1] The aldehydes formed in situ incorporate chloroform.

[1] Gupta, M.K., Li, Z., Snowden, T.S. *JOC* **77**, 4854 (2012)

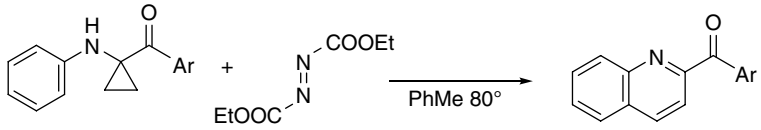
Dialkyl azodicarboxylates

Hydrazines. Reductive coupling of azodicarboxylic esters with ArX is mediated by Ph_3P and catalyzed by CuI to provide ArN(COOR)NHCOOR. Slighly different reaction conditions (solvent, temperature) are applied to using ArBr from ArI.[1] Radical amination by breaking a benzylic, propagyl or cyclic C-H bond induced by *N*-hydroxyphthalimide is readily accomplished.[2]



(Z)-β-Enaminones. 1-Amino-2-alkynes are transformed into (*Z*)-β-enaminones on reaction with water in the presence of diethyl azodicarboxylate (DEAD).[3]

2-Aroylquinolines. Aryl 1-arylamino-1-cyclopropyl ketones on heating with DEAD in toluene undergo dehydrogenative cyclization.[4]



Fiesers' Reagents for Organic Synthesis, First Edition. Tse-Lok Ho.
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[1] Yavari, I., Ghazanfarpour-Darjani, M., Solgi, Y., Ahmadian, S. *SL* 1745 (2011)
[2] Amaoka, Y., Kamijo, S., Hoshikawa, T., Inoue, M. *JOC* **77**, 9959 (2012)
[3] Xu, X., Du, P., Cheng, D., Wang, H., Li, X. *CC* **48**, 1811 (2012)
[4] Mao, Z., Qu, H., Zhao, Y., Lin, X. *CC* **48**, 9927 (2012)

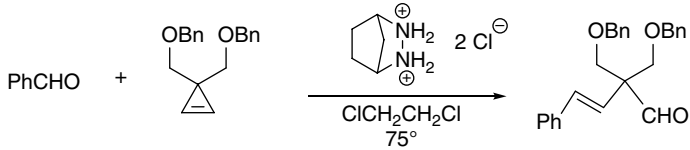
Diaryliodonium salts

Aryl esters. Heating potassium carboxylates with Ar_2IX in toluene comples the esterification.[1]

[1] Petersen, T.B., Khan, R., Olofsson, B. *OL* **13**, 3462 (2011)

2,3-Diazabicyclo[2.2.1]heptane

Alkenals. Condensation of aldehydes and cycloalkenes with ring scission and redistribution of functionalities is effected by the title reagent (as HCl salt). [3+2]Cycloaddition of alkylidenehydrazine zwitterions with the cycloalkenes is followed by fragmentation to generate the products after hydrolytic workup.[1]



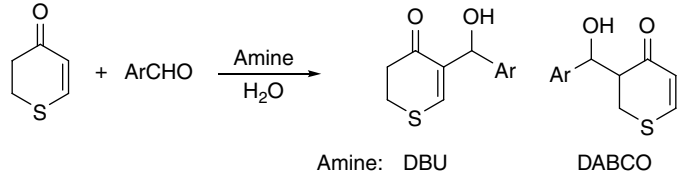
[1] Griffith, A.K., Vanos, C.M., Lambert, T.H. *JACS* **134**, 18581 (2012)

1,4-Diazabicyclo[2.2.2]octane, (DABCO)

Substitution. DABCO is an excellent base to remove proton from pronucleophiles such as phenol and *N*-heterocycles in their reaction with 3-iodoacrylic esters in DMF at room temperature, the products have the double bond configuration retained.[1]

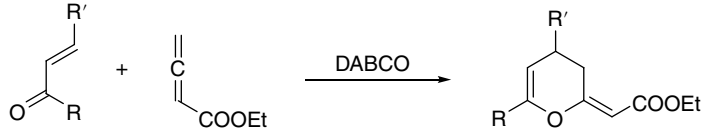
The internal salt *t*-BuOCONSO$_2$(DABCO) is an excellent reagent for sulfamoylation of alcohols, the products are readily hydrolyzed to alkyl sulfamates.[2]

Addition. The subtle difference between DABCO and DBU is illustrated in the catalyzed reaction between 2,3-dihydrothiapyran-4-one and ArCHO, one favors aldol reaction and the other, the Baylis-Hillman reaction.[3]



1-Alkyn-3-ones combine with carbonyl compounds via an aldol reaction and intramolecular hydroalkoxylation to give 2,3-dihydropyran-4-ones.[4]

Cycloaddition. A formal hetero-Diels-Alder reaction between conjugated carbonyl compounds and a 2,3-butadienoic ester occurs when the mixtures are treated with DABCO.[5]



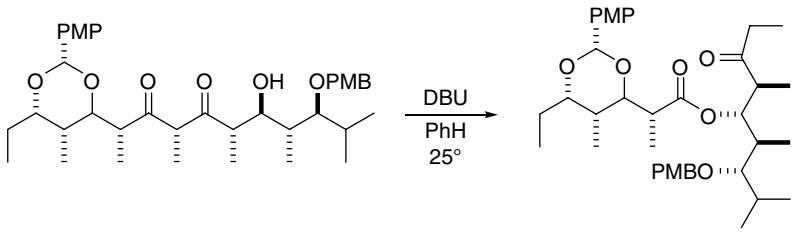
[1] Kabir, M.S., Namjoshi, O.A., Verma, R., Lorenz, M., Tiruveedhula, V.V.N.P.B., Monte, A., Bertz, S.H., Schwabacher, A.W., Cook, J.M. *JOC* **77**, 300 (2012)
[2] Armitage, I., Berne, A.M., Elliott, E.L., Fu, M., Hicks, F., McCubbin, Q., Zhu, L. *OL* **14**, 2626 (2012)
[3] Abaee, M.S., Mojtahedi, M.M., Pasha, G.F., Akbarzadeh, E., Shockravi, A., Mesbah, A.W., Massa, W. *OL* **13**, 5282 (2011)
[4] Lian, Z., Zhao, Q.-Y., Wei, Y., Shi, M. *EJOC* 3338 (2012)
[5] Ashtekar, K.D., Staples, R.J., Borhan, B. *OL* **13**, 5732 (2011)

1,8-Diazabicyclo[5.4.0]undec-7-ene, (DBU)

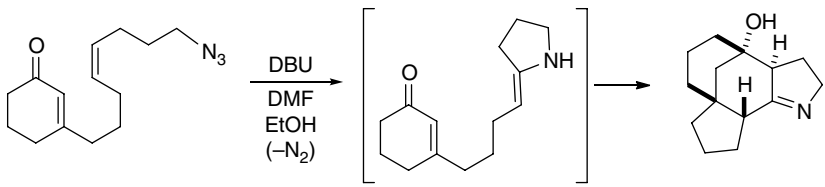
Depivaloylation. 1-Pivaloylindoles are deprotected in aqueous THF in the presence of DBU, it is far less vigorous than using LDA in warm THF (40-45°).[1]

Substitution. β,β-Dibromostyrenes have the two bromine atoms replaced by thio groups upon reaction with RSH in DMSO, the base used is DBU.[2]

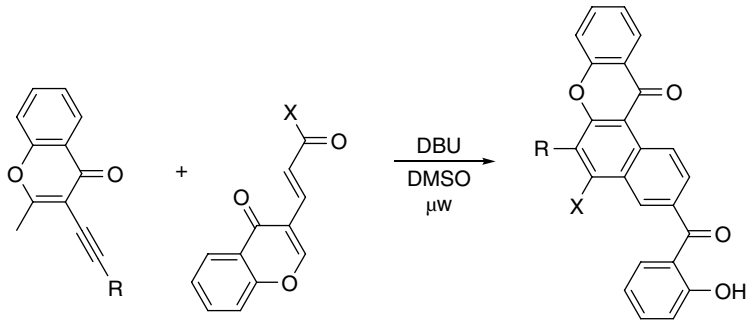
Retro-Claisen rearrangement. Intramolecular attack of the hydroxyl group in a 5-hydroxy-1,3-diketone is a key step for a synthesis of (−)-dolabriferol, the CC bond cleavage is initiated by DBU.[3]



Annulation. The function of DBU in a transformation of 3-[8-azido-(4*Z*)-octenyl]-2-cyclohexenone to a tetracyclic alcohol is apparently the decomposition of a fused 1,2,3-dihydrotriazole that is the product of an intramolecular [3+2]cycloaddition, as well as isomerization of an imine to an enamine for the final addition to the ketone.[4]



A very intriguing condensation between two chromen-4-ones results in the formation of a xanthone.[5]



[1] Ruiz, M., Sanchez, J.D., Lopez-Alvaredo, P., Menendez, J.C. *T* **68**, 705 (2012)
[2] Jin, H., Yang, Y., Kuang, C., Yang, Q. *SL* 28865 (2011)
[3] Currie, R.H., Goodman, J.M. *ACIE* **51**, 4695 (2012)
[4] de Miguel, I., Herradon, B., Mann, E. *ASC* **354**, 1731 (2012)
[5] Gong, J., Xie, F., Chen, H., Hu, Y. *OL* **12**, 3848 (2010)

Diazomethane

Safe generation.[1] A method for generation of CH_2N_2 involves decomposition of sodium 3-(*N*-nitroso-*N*-methylaminosulfonyl)benzoate in water. On transfer to an organic phase, diazomethane is ready to be used, e.g, for cyclopropanation.

[1] Kaschel, J., Schneider, T.F., Werz, D.B. *ACIE* **51**, 7085 (2012)

1,3-Dibromo-5,5-dimethylhydantoin

Bromination.[1] The reagent delivers bromine atoms to alkenes when a mild base, $Me_2NCH_2CH_2NHC(=S)NHAr$ where Ar = 3,5-$(CF_3)_2C_6H_3$, is also introduced.

[1] Hernandez-Torres, G., Tan, B., Barbas III, C.F. *OL* **14**, 1858 (2012)

N,N-Dibromo-*p*-toluenesulfonamide

Hofmann rearrangement.[1] Along with DBU in MeOH, the conversion of amides by $TsNBr_2$ into methyl carbamates is not complicated.

N-Benzyl-N-tosylamides. On treatment with K_2CO_3 in EtOAc, $TsNBr_2$ generates the nitrene TsN: which inserts into a benzylic N-H bond readily.[2]

[1] Borah, A.J., Phukan, P. *TL* **53**, 3035 (2012)
[2] Borah, A.J., Phukan, P. *CC* **48**, 5491 (2012)

Di-*t*-butyl peroxide

Redox condensation.[1] Treatment of $ArCH_2OH$ and $Ar'NO_2$ with *t*-Bu_2O_2 and KOH in PhCl at 140° leads to formation of $ArCONHAr'$.

Oxidative coupling of adenine with cycloalkanes by *t*-Bu_2O_2 occurs at C-8. When CuI is present the reaction is switched to the primary amino group.[2] Generally, C-H amination with anilines and *N*-alkylanilines are readily accomplished using a β-diketiminato Cu(I) complex as catalyst.[3]

A reagent system consisting of *t*-Bu_2O_2 and CuO promotes decarboxylation of cinnamic acid, the styrenic species prepared couple with a cogenerated benzyl radical.[4]

[1] Xiao, F., Liu, Y., Tang, C., Deng, G.-J. *OL* **14**, 984 (2012)
[2] Xia, R., Niu, H.-Y., Qu, G.-R., Guo, H.-M. *OL* **14**, 5546 (2012)
[3] Gephart III, R.T., Huang, D.L., Aguila, M.J.B., Schmidt, G., Shahu, A., Warren, T.H. *ACIE* **51**, 6488 (2012)
[4] Yang, H., Sun, P., Zhu, Y., Yan, H., Lu, L., Qu, X., Li, T., Mao, J. *CC* **48**, 7847 (2012)

Dichlorotris(triphenylphosphine)ruthenium(II)

Isomerization.[1] Suprafacial 1,3-hydrogen shift from the carbinolic center of an allylic alcohol is effected by $(Ph_3P)_3RuCl_2$.

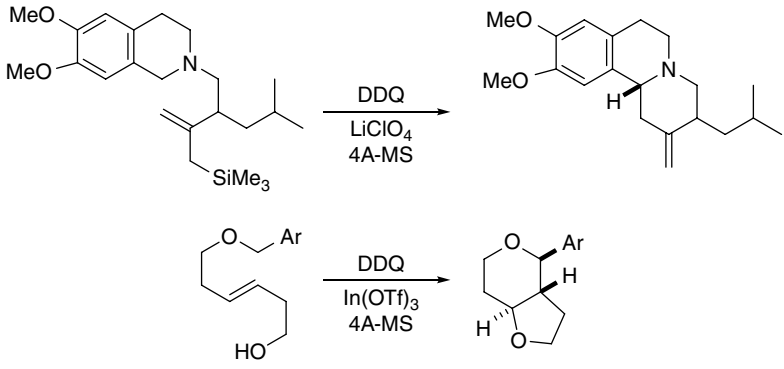
Substitution.[2] Titanium enolates of *N*-acyl-2-oxazolidinones undergo trichloromethylation by a Ru(II)-catalyzed reaction with $BrCCl_3$. An enantioselective course is followed when the heterocycle contains a chirality center at C-4.

[1] Bizet, V., Pannecoucke, X., Renaud, J.-L., Cahard, D. *ACIE* **51**, 6467 (2012)
[2] Gu, Z., Herrmann, A.T., Zakarian, A. *ACIE* **50**, 7136 (2011)

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone, (DDQ)

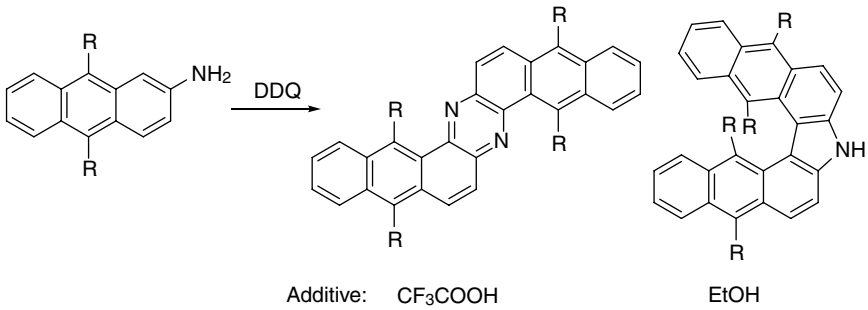
Oxidation. Alcohols are oxidized with DDQ – $NaNO_2$ in the air in CH_2Cl_2 containing 10% v/v of HOAc.[1]

Benzylic and allylic activation. Abstraction of a benzylic C-H of isochroman and tetrahydroisoquinoline systems by DDQ is exploitable for CC bond formation, in both intermolecular and intramolecular manners.[2,3] 2*H*-Chromene is similarly activated.[4] Biheterocyclic systems can be prepared based on the initiative.[5]



Amination of 1,3-diarylpropenes through hydride abstraction is easily conceived.[6] 2-Aryl-1,3-dithiolanes are alkoxylated on treatment with DDQ in an alcohol.[7] The products can be converted into esters of aromatic acids.

Aromatization. To provide a driving force to encourage condensation of styrenes with juglone, DDQ takes away hydrogen from the adducts.[8] 2-Aminoanthracenes form bisnaphthophenazines or carbazoles upon treatment with DDQ.[9]



Aryl cyanides. A very rare application of DDQ is in providing the cyano group for coupling with $ArB(OH)_2$, as catalyzed by $Cu(OTf)_2$ and Ag_2CO_3.[10]

[1] Wang, L., Li, J., Yang, H., Lv, Y., Gao, S. *JOC* **77**, 790 (2012)
[2] Park, S.J., Price, J.R., Todd, M.H. *JOC* **77**, 949 (2012)
[3] Son, Y.W., Kwon, T.H., Lee, J.K., Pae, A.N., Lee, J.Y., Cho, Y.S., Min, S.-J. *OL* **13**, 6500 (2011)
[4] Clausen, D.J., Floreancig, P.E. *JOC* **77**, 6574 (2012)
[5] Reddy, B.V.S., Borkar, P., Yadav, J.S., Reddy, P.P., Kunwar, A.C., Sridhar, B., Grée, R. *OBC* **10**, 1349 (2012)
[6] Wang, Z., Mo, H., Cheng, D., Bao, W. *OBC* **10**, 4249 (2012)
[7] Fu, L., Yao, C.-J., Chang, N.-J., Chen, J.-R., Lu, L.-Q., Xiao, W.-J. *OBC* **10**, 506 (2012)
[8] Hsu, D.-S., Huang, J.-Y. *JOC* **77**, 2659 (2012)
[9] Goto, K., Yamaguchi, R., Hiroto, S., Ueno, H., Kawai, T., Shinokubo, H. *ACIE* **51**, 10333 (2012)
[10] Zhang, G., Chen, S., Fei, H., Cheng, J., Chen, F. *SL* 2247 (2012)

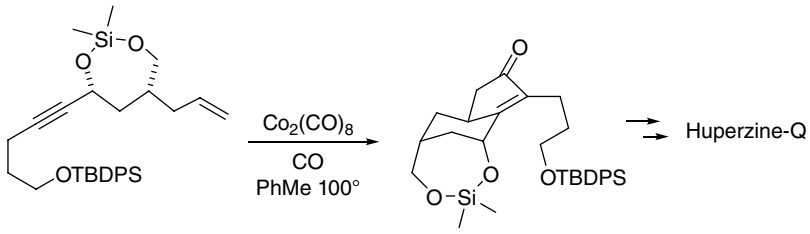
Dicobalt octacarbonyl

Debenzylation. Benzyl ethers are converted into silyl ethers by a hydrosilane with $Co_2(CO)_8$ under CO.[1]

N-Alkylation. Amides undergo *N*-alkylation while the condensation products with carbonyl compounds are hydrogenated in situ, $Co_2(CO)_8$ and R_3Sb constitute the catalytic system.[2]

Enone synthesis. Complexes derived from alkynes and $Co_2(CO)_8$ react with alkenes in HOAc and pyridine. Enacylcobalt species are generated and the further reaction gives acyclic enones instead of the Pauson-Khand reaction products.[3]

Pauson-Khand reaction. A synthesis of huperzine-Q involves a Pauson-Khand reaction to build up a cyclopentenone intermediate. In this case it is essential to form a cyclic siloxane to ensure the proper conformation.[4]



[1] Wang, B., Yin, Z., Li, Y., Yang, T.-X., Meng, X.-B., Li, Z.-J. *JOC* **76**, 9531 (2011)
[2] Rubio-Perez, L., Sharma, P., Perez-Flores, F.J., Velasco, L., Arias, J.L., Cabrera, A. *T* **68**, 2342 (2012)
[3] Ooi, I., Sakurai, T., Takaya, J., Iwasawa, N. *CEJ* **18**, 14618 (2012)
[4] Nakayama, A., Kogure, N., Kitajima, M., Takayama, H. *ACIE* **50**, 8025 (2011)

Diethylaluminum phenylthiolate

Addition to C=O. Aldehydes can be protected as the adducts, $RCH(OAlEt_2)SPh$, and further treatment of the adducts from ketones with *i*-Bu_2AlH constitutes an indirect reduction.[1]

[1] Bastug, G., Dierick, S., Lebreux, F., Marko, I.E. *OL* **14**, 1306 (2012)

Diethylaminodifluorosulfur tetrafluoroborate

Alkyl halides. The title compound is able to activate alcohols to have their OH group replaced by a halogen atom provided by Et_4NX.[1]

Cyclodehydration. The reagent can be used to convert 1,2-diacylhydrazines into 1,3,4-oxadiazoles.[2]

[1] Pouliot, M.-F., Mahé, O., Hamel, J.-D., Desroches, J., Paquin, J.-F. *OL* **14**, 5428 (2012)
[2] Pouliot, M.-F., Angers, L., Hamel, J.-D., Paquin, J.-F. *OBC* **10**, 988 (2012)

Difluoromethyl 2-pyridyl sulfone

Addition to C=O. Carbonyl compounds form halodifluoroalkoxypyridines on reaction with the title reagent and NXS under basic conditions.[1]

[1] Zhao, Y., Gao, B., Hu, J. *JACS* **134**, 5790 (2012)

Difluoromethyltributylammonium chloride

Difluorocarbene. The title reagent is a source of :CF_2, which shows normal reactivity toward *O-, S-, N-*, and *C*-nucleophiles.[1]

[1] Wang, F., Huang, W., Hu, J. *ChJC* **29**, 2717 (2011)

Difluoro(4-trifluoromethylphenyl)bromane

Oxidative fluorination.[1] Aldehydes react with (4-$CF_3C_6H_4$)BrF_2 to give either RCOF or $ArOCHF_2$, the latter being formed from a Baeyer-Villiger oxidation and deoxydifluorination.

Diacetoxybromane. On reaction with Ac_2O – HOAc the difluorobromane is transformed into $ArBr(OAc)_2$ which can be used to activate triflimide to react with alkenes.[2]

[1] Ochiai, M., Yoshimura, A., Hoque, M.M., Okubo, T., Saito, M., Miyamoto, K. *OL* **13**, 5568 (2011)
[2] Hoque, M.M., Miyamoto, K., Tada, N., Shiro, M., Ochiai, M. *OL* **13**, 5428 (2011)

Dihydridotetrakis(triphenylphosphine)ruthenium(II)

Amides. Carboxamides are formed when mixtures of primary alcohols and RN_3 are treated with NaH and then heated with $(Ph_3P)_4RuH_2$ in toluene.[1]

[1] Fu, Z., Lee, J., Kang, B., Hong, S.H. *OL* **14**, 6028 (2012)

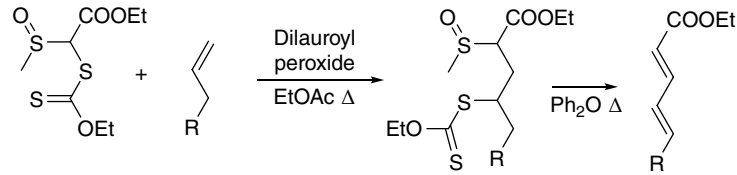
Diisobutylaluminum hydride

Reduction.[1] The double bond of an *N*-(2-alkenoyl)-2-oxazolidinone is saturated on treatment with CuI, MeLi, *i*-Bu_2AlH, HMPA in THF at -78°. Other hydride agents (K selectride, superhydride) and SmI_2 are totally ineffective.

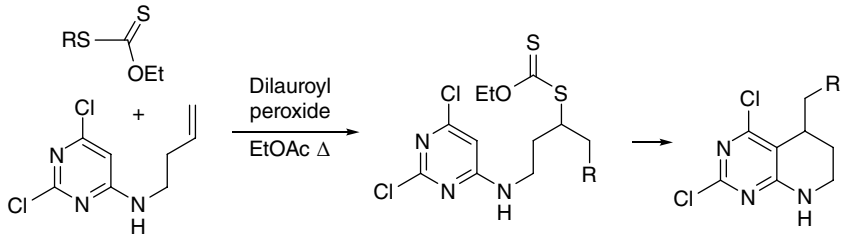
[1] Li, S.-G., Jin, J.-W., Wu, Y. *T* **68**, 846 (2012)

Dilauroyl peroxide

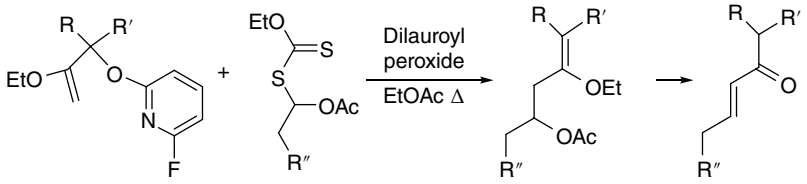
Addition. Fragments from S-C bond homolysis of dithiocarbonates add to 1-alkenes. Adducts readily undergo thermal decomposition to generate conjugated dienes.[1]



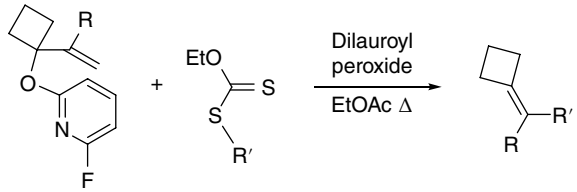
Under oxygen *N*-hydroxycarbamates add to alkenes to afford 1,2-diols that are *O*-aminated at the primary site.[2] Both homologation of ω-[*N*-(2,4-dichloropyrimidin-6-yl)amino-1-alkenes and cyclization are processed by dilauroyl peroxide with no need to protect the NH.[3]



Substitution. A route to enones based on radical substitution exploits the reactivity of 6-fluoro-2-allyloxypyridines.[4,5] A heterosubstituent at the allyl group extends the scope and variety of the products.



A new route to alkylidenecyclobutanes is based on transpositional radical substitution.[6]

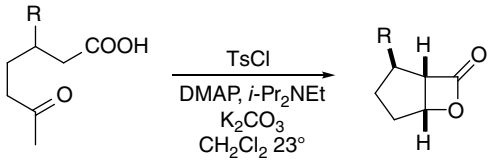


[1] Hawkins, B., Paddock, V.L., Tölle, N., Zard, S.Z. *OL* **14**, 1020 (2012)
[2] Giglio, B.C., Schmidt, V.A., Alexanian, E.J. *JACS* **133**, 13320 (2011)
[3] Liu, Z., Qin, L., Zard, S.Z. *OL* **14**, 5976 (2012)
[4] Debien, L., Quiclet-Sire, B., Zard, S.Z. *OL* **13**, 5676 (2011)
[5] Braun, M.-G., Quiclet-Sire, B., Zard, S.Z. *JACS* **133**, 15954 (2011)
[6] Brioche, J., Michalak, M., Quiclet-Sire, B., Zard, S.Z. *OL* **13**, 6296 (2011)

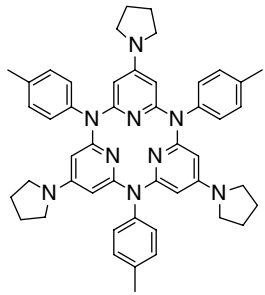
4-Dimethylaminopyridine, (DMAP)

Modification. A robust and recyclable form of DMAP which retains its catalytic activities is obtained by embedding it in a nanoporous conjugated polymer.[1] The combination of DMAP and saccharin also constitutes a recyclable acylation catalyst.[2]

Ketene formation. Ketenes are generated from carboxylic acids by treatment with TsCl, DMAP and auxiliary bases. Such ketenes are subject to intramolecular capture by a carbonyl group to form β-lactones.[3]



Henry and Michael reactions. The DMAP analog **1** is a superbase useful for catalyzing the addition of nitroalkanes to ArCHO and enones.[4]

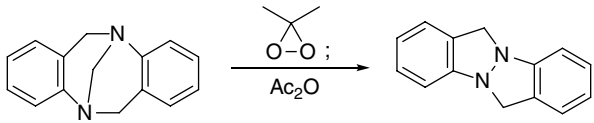


(**1**)

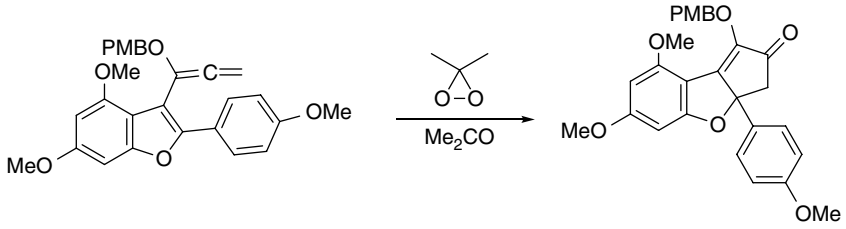
[1] Zhang, Y., Zhang, Y., Sun, Y.L., Du, X., Shi, J.Y., Wang, W.D., Wang, WE. *CEJ* **18**, 6328 (2012)
[2] Lu, N., Chang, W.-H., Tu, W.-H., Li, C.-K. *CC* **47**, 7227 (2011)
[3] Liu, G., Shirley, M.E., Romo, D. *JOC* **77**, 2496 (2012)
[4] Uchida, N., Kuwabara, J., Taketoshi, A., Kanbara, T. *JOC* **77**, 10631 (2012)

Dimethyldioxirane, (DMDO)

Degradation of Tröger's bases. A loss of the methylene group connecting the two nitrogen atoms of Tröger's bases has been observed, on treatment with DMDO.[1]



Oxidative cyclization. Oxidation of an oxygenated allene by DMDO to initiate Nazarov cyclization is a significant step toward synthesis of some complex natural products.[2]



[1] Gao, X., Hampton, C.S., Harmata, M. *EJOC* 7053 (2012)
[2] Malona, J.A., Cariou, K., Spender III, W.T., Frontier, A.J. *JOC* **77**, 1891 (2012)

N,N-Dimethylformamide

As reagent. Besides the common use as a polar solvent, DMF has found many new uses as reagent to furnish structural subunits such as CHO, CN, NMe_2, etc. A review for the development has been written.[1]

[1] Ding, S., Jiao, N. *ACIE* **51**, 9226 (2012)

1,3-Dimethylimidazolidine

Mannich reaction. The heterocyclic compound serves as a formaldehyde surrogate in the Mannich reaction.[1]

[1] Guo, Y., An, J., Lu, Z., Peng, M. *ChJC* **30**, 1561 (2012)

Dimethylsulfonium methylide

Ester cleavage. The ylide cleaves esters at room temperature.[1]

[1] Leggio, A., De Marco, R., Perri, F., Spinella, M., Liguori, A. *EJOC* 114 (2012)

N-(2,6-Diphenyl)phenyl-*N*-[(2,4,6-triisopropylphenyl)ammonium pyrosulfate

Hydrolysis. The ammonium salt is a catalyst of the reverse micelle-type, useful for hydrolysis of esters.[1]

[1] Koshikari, Y., Sakakura, A., Ishihara, K. *OL* **14**, 3194 (2012)

Diphenylphosphinyl chloride

Amidation. Phosphinimines of the type $Ph_2P{=}NR$ are formed on mixing Ph_2PCl and RN_3, and they react with RCOOH (+ a base) to give amides.[1]

[1] Kosal, A.D., Wilson, E.E., Ashfeld, B.L. *CEJ* **18**, 14444 (2012)

O-(Diphenylphosphinyl)hydroxylamine

Nitriles. After derivatization aldehydes with $Ph_2P(=O)ONH_2$, heating in toluene at 85° induces elimination of $Ph_2P(=O)OH$ to leave the nitriles.[1]

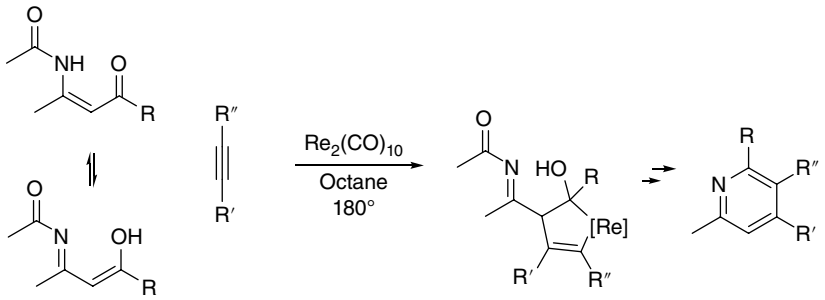
[1] Laulhe, S., Gori, S.S., Nantz, M.H. *JOC* **77**, 9334 (2012)

Dirhenium decacarbonyl

Allylation.[1] Aromatic carboxylic acids undergo *o*-allylation with allyl acetate when catalyzed by $Re_2(CO)_{10}$.

Cyclopentenones.[2] Ketones and two equivalents of an aldehyde combine to give cyclopentenones that have identical substituents at C-3 and C-4.

Pyridine synthesis.[3] β-Acylenamides attack Re-activated alkynes to form 5-membered metallocycles. The subsequent reductive elimination gives rise to cyclobutenols which are prone to undergo electrocyclic opening. Cyclodehydraton concludes the ring-forming process.



[1] Kuninobu, Y., Ohta, K., Takai, K. *CC* **47**, 10791 (2011)
[2] Nishina, Y., Tatsuzaki, T., Tsubakihara, A., Kuninobu, Y., Takai, K. *SL* 2585 (2011)
[3] Yamamoto, S., Okamoto, K., Murakoso, M., Kuninobu, Y., Takai, K. *OL* **14**, 3182 (2012)

E

Europium(III) triflate

Pyrrole synthesis. With $Eu(OTf)_3$ as catalyst the condensation of ketoximes with alkynes (e.g., acetylenedicarboxylic esters) yields polysubstituted pyrroles — Trofimov synthesis.[1]

[1] Madabhushi, S., Vangipuram, V.S., Mallu, K.K.R., Chinthala, N., Beeram, C.R. *ASC* **354**, 1413 (2012)

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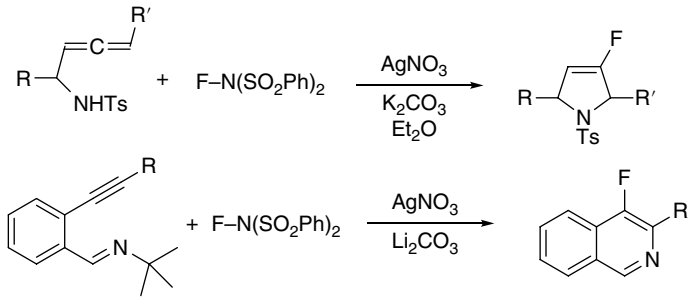
F

_N_-Fluoro-(_o_-benzenedisulfonimide)

Fluorination. Radical fluorination can employ the title reagent.[1] For fluorination of alkenes with the reagent a good catalyst is $AgNO_3$.[2] 3,3-Difluorooxindoles are obtained on carrying out fluorination of oxindoles under oxidative conditions (e.g., + _t_-BuOOH).[3] Terminal alkynes are fluorinated after lithiation.[4]

Amination. With CuCl ligated to 1,10-phenanthroline to catalyze the reaction with alkylarenes at the benzylic position, C-N bond formation dominates.[5]

Cyclization. Several types of fluorinated heterocycles are formed with involvement of the _N_-fluorinated reagent which is catalyzed by $AgNO_3$.[6,7]



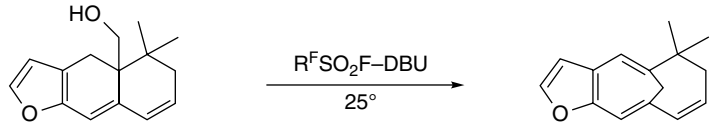
[1] Rueda-Becerril, M., Sazepin, C.C., Leung, J.C.T., Okbinoglu, T., Kennepohl, P., Paquin, J.-F., Sammis, G.M. *JACS* **134**, 4026 (2012)
[2] Xu, T., Liu, G. *SL* 955 (2012)
[3] Lim, Y.H., Ong, Q., Duong, H.A., Nguyen, T.M., Johannes, C.W. *OL* **14**, 5676 (2012)
[4] Liu, C., Ma, H., Nie, J., Ma, J. *ChJC* **30**, 47 (2012)
[5] Ni, Z., Zhang, Q., Xiong, T., Zheng, Y., Li, Y., Zhang, H., Zhang, J., Liu, Q. *ACIE* **51**, 1244 (2012)
[6] Xu, T., Mu, X., Peng, H., Liu, G. *ACIE* **50**, 8176 (2011)
[7] Xu, T., Liu, G. *OL* **14**, 5416 (2012)

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Fluorous reagents and ligands

Acylation and sulfonylation. DMAP salts of perfluoroalkanoic acids are useful catalysts for acylation of alcohols with anhydrides, these insoluble salts release DMAP to perform and they are recovered by filtration.[1] Also as a useful amidation agent is the 2-chloropyridinium triflate which carries the *N*-$CH_2CH_2C_{10}F_{21}$ substituent, the pyridine sideproduct is a readily recoverable solid.[2]

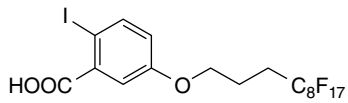
A perfluoroalkanesulfonyl fluoride has been applied to advantage in the final step of a synthesis of spiniferin-1.[3] The neopentyl sulfonate is liable to rearrangement.



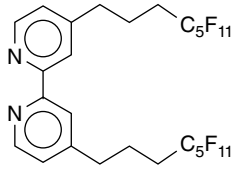
Spiniferin-1

Oxidation. The benzoic acid **1** with a polyfluoroalkyl chain serves as a recoverable catalyst for the oxidation of alcohols (to acids and ketones) by Oxone.[4]

Epoxidation of alkenes is achieved with hydrogen peroxide in the presence of **2**.[5]



(**1**)

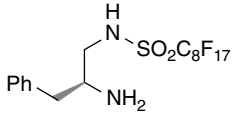


(**2**)

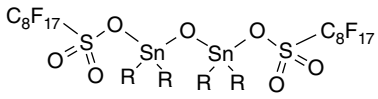
Perfluoroalkylation. Perfluoroalkyl sulfones R^FSO_2R are ready to submit the R^F group to carbonyl and imino compounds (*t*-BuOK as promoter).[6] Perfluoroalkyltitanates add to nitriles to form imines, which can be hydrogenated to afford chiral $RCH(R^F)NH_2$.[7]

A preparation of perfluoroalkylarenes involves coupling of ArI with phenanthroline-ligated R^FCu in DMF. Many functional groups attached to the aromatic nucleus (e.g., Br, NO_2, CN, NHCOOMe, CH_2OH, CHO, COOMe) are tolerated.[8]

Aldol reaction. The mono(perfluorooctanesulfonyl) derivative **3** of a chiral diamine in the trifluoromethylacetate form is a catalyst for aldol reaction.[9] For catalyzing the Mukaiyama aldol reaction the surface-active tin compounds **4** have proven useful.[10]



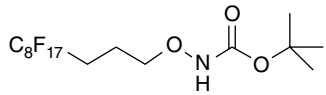
(**3**)



(**4**)

A chiral monotriflyldiamine prepared from (*S*)-tyrosine in which the phenolic hydroxyl group is also etherified by the $(CH_2)_3C_8F_{17}$ group serves as catalyst for aldol reaction performed in brine.[11]

Amine synthesis. As ammonia equivalent, **5** serves as a precursor of secondary amines[12] and anilines.[13] After *N*-alkylation/arylation, reductive cleavage of the N-O bond completes the process.



(**5**)

Diazo group transfer. Nonafluorobutanesulfonyl azide is shelf-stable, it reacts with amines to give azides,[14] and is useful in the synthesis of α-diazo carbonyl compounds.[15]

Protection of phosphates. The free OH group of phosphoric acid diesters can be protected when derivatized into $C_8F_{17}CH(Br)CH_2OPO(OR)_2$. The original diesters are recovered by treatment with zinc and ammonium formate.[16]

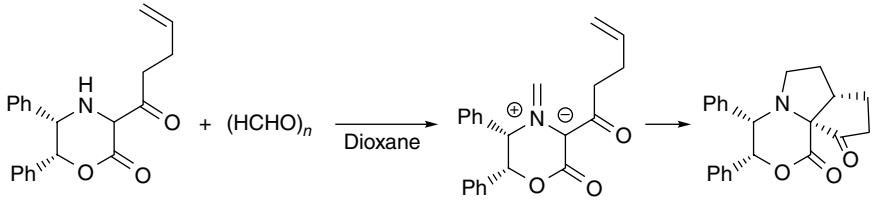
[1] Vuluga, D., Legros, J., Crouse, B., Bonnet-Delpon, D. *CEJ* **16**, 1776 (2010)
[2] Sugiyama, Y., Kurata, Y., Kunda, Y., Miyazaki, A., Matsui, J., Nakamura, S., Hamamoto, H., Shioiri, T., Matsugi, M. *T* **68**, 3885 (2012)
[3] Ding, K.,Sun, Y., Tian, W.-S. *JOC* **76**, 1495 (2011)
[4] Miura, T., Nakashima, K., Tada, N., Itoh, A. *CC* **47**, 1875 (2011)
[5] Saladino, R., Ginnasi, M.C., Collalto, D., Bernini, R., Crestini, C. *ASC* **352**, 1284 (2010)
[6] Prakash, G.K.S., Wang, Y., Mogi, R., Hu, J., Mathew, T., Olah, G.A. *OL* **12**, 2932 (2010)
[7] Mikami, K., Murase, T., Zhai, L., Kawauchi, S., Itoh, Y., Ito, S. *TL* **51**, 1371 (2010)
[8] Morimoto, H., Tsubogo, T., Litvinas, N.D., Hartwig, J.F. *ACIE* **50**, 3793 (2011)
[9] Miura, T., Imai, K., Ina, M., Tada, N., Imai, N., Itoh, A. *OL* **12**, 1620 (2010)
[10] Orita, A., Tanabe, S., Ono, T., Otera, J. *ASC* **352**, 1419 (2010)
[11] Miura, T., Kasuga, H., Imai, K., Ina, M., Tada, N., Imai, N., Itoh, A. *OBC* **10**, 2209 (2012)
[12] Nielsen, S.D., Smith, G., Begtrup, M., Kristensen, J.L. *CEJ* **16**, 4557 (2010)
[13] Nielsen, S.D., Smith, G., Begtrup, M., Kristensen, J.L. *EJOC* 3704 (2010)
[14] Suarez, J.R., Trastoy, B., Perez-Ojeda, M.E., Marin-Barrios, R., Chiara, J.L. *ASC* **352**, 2515 (2010)
[15] Chiara, J.L., Suarez, J.R. *ASC* **353**, 575 (2011)
[16] Liu, L., Pohl, N.L.B. *OL* **13**, 1824 (2011)

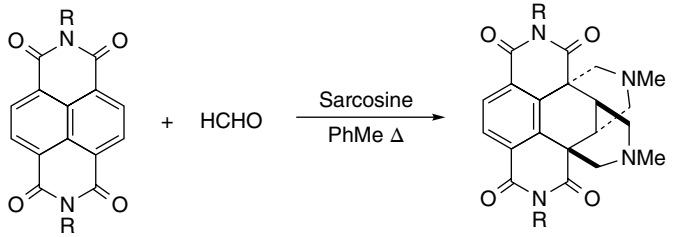
Formaldehyde

Hydroformylation. A novel use of HCHO is as syngas substitute in the Rh(I)-catalyzed hydroformylation of alkenes to deliver linear aldehydes.[1]

α-Methylenation.[2] On heating with paraformaldehyde in the presence of isopropylamine-trifluoroacetic acid (and a slight excess of either the amine or the acid) in THF, ketones undergo α-methylenation.

Annulation. Transforming amines into azomethine ylides by paraformaldehyde to set up cycloaddition is synthetically expedient, as shown by examples below.[3,4]





[1] Makado, G., Morimoto, T., Sugimoto, Y., Tsutsumi, K., Kagawa, N., Kakiuchi, K. *ASC* **352**, 299 (2010)
[2] Bugarin, A., Jones, K.D., Connell, B.T. *CC* **46**, 1715 (2010)
[3] Namba, K., Inai, M., Sundermeier, U., Greshock, T.J., Williams, R.M. *TL* **51**, 6557 (2010)
[4] Gryko, D.T., Rogacki, M.K., Klajn, J., Galezowski, M., Stepien, D.K., Cyranski, M.K. *OL* **12**, 2020 (2010)

N-Formylsaccharin

N-Formylation. The saccharin derivative readily submits its formyl group to amines at room temperature.[1]

[1] Cochet, T., Bellosta, V., Greiner, A., Roche, D., Cossy, J. *SL* 1920 (2011)

G

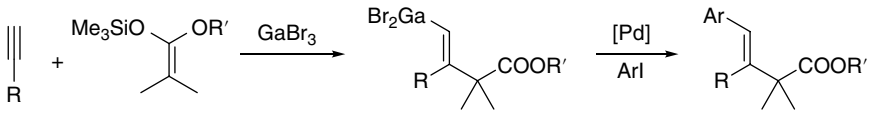
Gallium

Barbier reaction.[1] Gallium and allyl bromide in an ionic liquid performs addition to the carbonyl group.

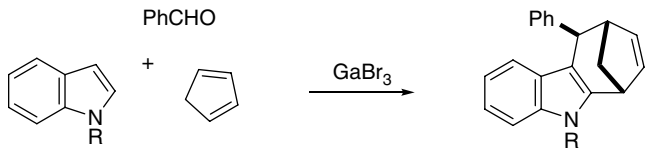
[1] Goswami, D., Chattopadhyay, A., Sharma, A., Chattopadhyay, S. *JOC* **77**, 11064 (2012)

Gallium(III) bromide

Addition. Vicinal addition to 1-alkynes initiated by bromogallation and trapping with ketene silyl acetals provides opportunities for further coupling.[1]



Condensation. Related to the reaction above is the formal substitution on alkenyl ethers, resulting in 3-butenoic esters.[2] The Lewis acid nature of $GaBr_3$ enables reaction of indole with aldehydes and further ionization to generate allyl cations which can participate in a [4+3]cycloaddition.[3]



[1] Nishimoto, Y., Ueda, H., Yasuda, M., Baba, A. *CEJ* **17**, 11135 (2011)
[2] Nishimoto, Y., Ueda, H., Yasuda, M., Baba, A. *ACIE* **51**, 8073 (2012)
[3] Han, X., Li, H., Hughes, R.P., Wu, J. *ACIE* **51**, 10390 (2012)

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Gallium(III) chloride

Addition.[1] Hydroamination of alkynes catalyzed by $GaCl_3$ proceeds in the Markovnikov sense.

Cyanation. Arenes are transformed into ArCN on reaction with BrCN in the presence of $GaCl_3$.[2]

[1] Li, L., Huang, G., Chen, Z., Liu, W., Wang, X., Chen, Y., Yang, L., Li, W., Li, Y. *EJOC* 5564 (2012)
[2] Okamoto, K., Watanabe, M., Murai, M., Hatano, R., Ohe, K. *CC* **48**, 3127 (2012)

Gallium(III) perchlorate

Quinoxaline synthesis.[1] With $Ga(ClO_4)_3$ as catalyst, condensation of *o*-phenylenediamine with 1-hydroxy-2-alkanones furnishes 2-substituted quinoxalines.

[1] Pan, F., Chen, T.-M., Cao, J.-J., Zou, J.-P., Zhang, W. *TL* **53**, 2508 (2012)

Gallium(III) tetraflate

Halogenation.[1] The title reagent serves as a catalyst for halogenation of arenes with NXS, but the most likely active species is tetraflic acid ($HCF_2CF_2SO_3H$), a hydrolytic product. (Activity for isomerization of tetrahydrodicyclopentadiene to adamantane is similarly attributed.)

[1] Prakash, G.K.S., Mathew, T., Panja, C., Kulkarni, A., Olah, G.A., Harmer, M.A. *ASC* **354**, 2163 (2012)

Gallium(III) triflate

Cyclization.[1] 2-Aminomethyl-1-alken-3-ynes undergo cyclization to give pyrroles on instigation by $Ga(OTf)_3$, notwithstanding the terminal *sp*-carbon carrying an electron-withdrawing group (that the addition goes against the Michael mode).

[1] Zhu, D., Zhao, J., Wei, Y., Zhou, H. *SL* 2185 (2011)

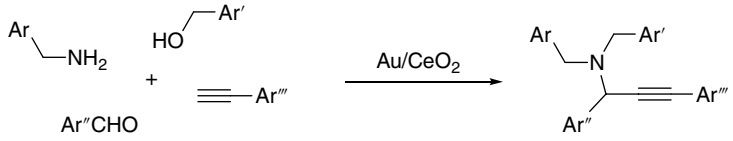
Gold

Reduction. Semihydrogenation of alkynes with a nanoporous Au catalyst is observed.[1] The thiol-complexed gold cluster monolayer (grown by adding $NaBH_4$) is a useful catalyst for the reduction of $ArNO_2$ to $ArNH_2$.[2] Gold nanoparticles deposited over hydrotalcite have been employed in the conversion of allyl carbonates to 1-alkenes.[3] The specimen on ZrO_2 catalyzes reduction of levulinic acids by formic acid to afford the γ-lactone.[4] Deoxygenation of benzylic alcohols is achieved by a reaction with $Me_3SiSiMe_3$ (catalyzed by Au/TiO_2 and involving oxygen insertion into the Si-Si bond).[5]

Coupling. There are several reports on using nano-Au clusters[6] to effect coupling of ArI, including those supported on organosilica[7] and with additives of glucose and Bu_4NOH.[8]

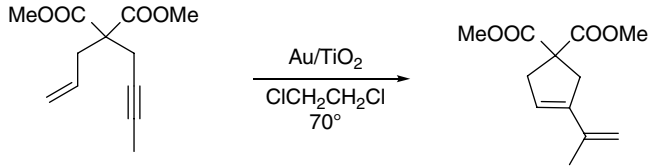
Homologation of oxiranes to provide 3-hydroxyalkanoic esters by reaction with syngas, traditionally performed with $Co_2(CO)_8$, is also effected with nano-Au/Co_3O_4.[9]

Assemblage of *N,N*-dibenzylpropargylamines from four components is an impressive accomplishment catalyzed by nano-Au/CeO_2.[10]



Dehydrogenative coupling of RCH_2OH and R'_2NH to furnish amides is a result of the action of Au on hydrotalcite (*t*-BuOK also present).[11]

Ring formation. Nanoporous Au is capable of conducting condensation between 2-alkynylaraldehydes with 1-alkynes to form 1-acylnaphthalenes.[12] 1,6-Enynes undergo cycloisomerization, and interestingly, leading to structurally different products when either Au/TiO_2 or Au(I) catalyst is employed.[13]



Aryl propynyl ethers undergo cycloisomerization to give 2*H*-chromenes and their 3,3′-dimers on contact with nano-gold particles that are deposited on titania.[14]

Tetramethyldisiloxane undergoes dehydrogenation on contact with nano-Au/TiO_2 and the active species are trapped by alkynes to furnish 1,2,5-oxadisila-3-cyclopentenes.[15]

[1] Yan, M., Jin, T., Ishikawa, Y., Minato, T., Fujita, T., Chen, L.-Y., Bao, M., Asao, N., Chen, M.-W., Yamamoto, Y. *JACS* **134**, 17536 (2012)
[2] Dasog, M., Hou, W., Scott, R.W.J. *CC* **47**, 8569 (2011)
[3] Noujima, A., Mitsudome, T., Mizugaki, T., Jitsukawa, K., Kaneda, K. *CC* **48**, 6723 (2012)
[4] Du, X.-L., He, L., Zhao, S., Liu, Y.-M., Cao, Y., He, H.-Y., Fan, K.-N. *ACIE* **50**, 7815 (2011)
[5] Gryparis, C., Stratakis, M. *CC* **48**, 10751 (2012)
[6] Li, G., Liu, C., Lei, Y., Jin, R. *CC* **48**, 12005 (2012)
[7] Karimi, B., Esfahani, F.K. *CC* **47**, 10452 (2011)
[8] Monopoli, A., Cotugno, P., Palazzo, G., Ditaranto, N., Mariano, B., Cioffi, N., Ciminale, F., Nacci, A. *ASC* **354**, 2777 (2012)
[9] Hamasaki, A., Muto, A., Haraguchi, S., Liu, X., Sakakibara, T., Yokoyama, T., Tokunaga, M. *TL* **52**, 6869 (2011)
[10] Corma, A., Navas, J., Sabater, M.J. *CEJ* **18**, 14150 (2012)
[11] Zhu, J., Zhang, Y., Shi, F., Deng, Y. *TL* **53**, 3178 (2012)

[12] Asao, N., Menggenbateer, Seya, Y., Yamamoto, Y., Chen, M., Zhang, W., Inoue, A. *SL* 66 (2012)
[13] Gryparis, C., Efe, C., Raptis, C., Lykakis, I.N., Stratakis, M. *OL* **14**, 2956 (2012)
[14] Efe, C., Lykakis, I.N., Stratakis, M. *CC* **47**, 803 (2011)
[15] Lykakis, I.N., Psyllaki, A., Stratakis, M. *JACS* **133**, 10426 (2011)

Gold(I) bromide, phosphine-ligated

Cyclization. For inducing cycloisomerization of 4,5-alkadienols $(Me_3P)AuBr$ encapsulated in a supramolecular host shows greatly increased (by 8-fold) reactivity.[1] Unsaturated amines such as 4-pentenylamines undergo coupling with $RB(OH)_2$ to form 2-alkyl substituted *N*-heterocycles. The catalyst is $(dppm)(AuBr)_2$ and an oxidant such as Selectfluor is present.[2]

Addition. 1-Alkenes CH_2=$CHCH_2X$ add an aryl group from $ArB(OH)_2$ and an alkoxy group to give $ArCH_2CH(OR)CH_2X$ when exposed to $(dppm)(AuBr)_2$ and Selectfluor.[3,4]

[1] Wang, Z.J., Brown, C.J., Bergman, R.G., Raymomd, K.N., Toste, F.D. *JACS* **133**, 7358 (2011)
[2] Brenzovich Jr, W.E., Benitez, D., Lackner, A.D., Shunatona, H.P., Tkatchouk, E., Goddard III, W.A., Toste, F.D. *ACIE* **49**, 5519 (2011)
[3] Melhado, A.D., Brenzovich Jr, W.E., Benitez, D., Lackner, A.D., Toste, F.D. *JACS* **132**, 8885 (2010)
[4] Brenzovich Jr, W.E., Brazeau, J.-F., Toste, F.D. *OL* **12**, 4728 (2010)

Gold(III) bromide

Addition. (*N*-Acetoacetyl-*N*-allenyl)methylamines form 3-acetyl-4-alkenyl-2-pyrrolidinones as a result of the catalytic action by $AuBr_3$ and Bu_4NOH.[1] It is a formal intramolecular addition initiated by interaction of Au(III) species with an allenyl double bond.

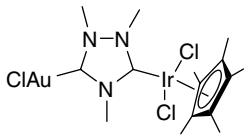
Cycloisomerization of allenyl carbinols to give 2,5-dihydrofurans is promoted by the air-stable $AuBr_3$ solution in a micellar system,[2] which is accelerated by aq. NaCl (forming larger micelles). A further advantage is recyclability of the catalyst.

[1] Boutier, A., Kammerer-Pentier, C., Krause, N., Prestat, G., Poli, G. *CEJ* **18**, 3840 (2012)
[2] Minkler, S.R.K., Lipshutz, B.H., Krause, N. *ACIE* **50**, 7820 (2011)

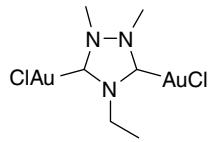
Gold-carbene complexes

Preparation. A simple and practical route to carbene-ligated $AuCl_3$ is to mix imidazolium/imidazolinium chlorides with a tetrachloroaurate salt.[1]

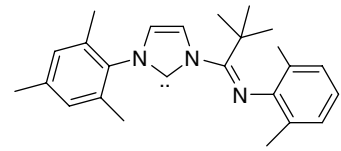
Aldimines. The involvement of both oxidation and reduction is clear in the transformation of a mixture of $PhNO_2$ and $PhCH_2OH$ into PhN=CHPh, which is catalyzed by a distinguished bimetallic carbenoid **1**. The species containing two gold centers (**2**) effects reduction of nitrobenzene to phenylhydroxylamine while benzyl alcohol is the hydrogen donor.[2]



(**1**)

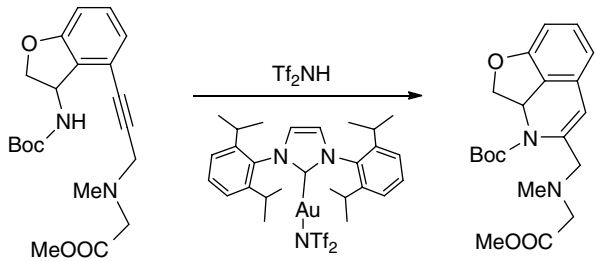


(**2**)

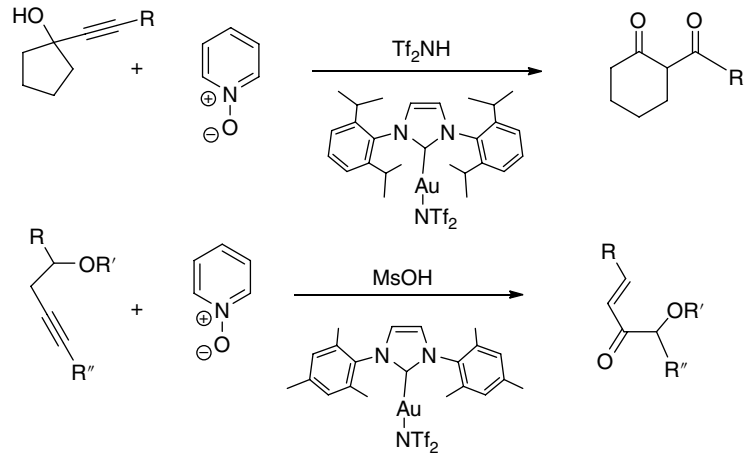


(**3**)

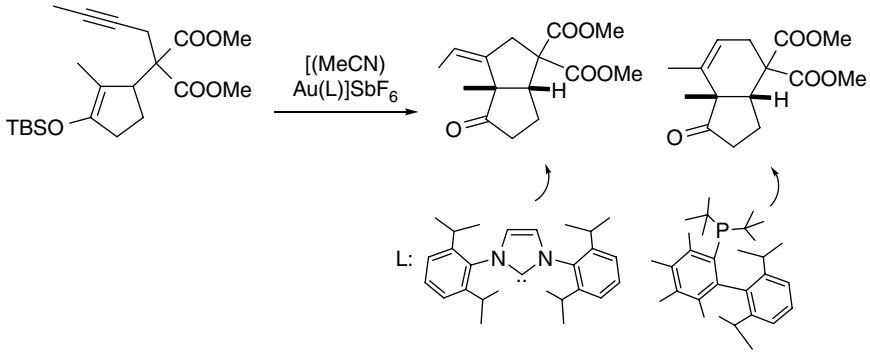
Hydroamination. Addition of $ArNH_2$ to phenylacetylene in the Markovnikov fashion is conducted with AuCl which is also ligated to Me_2S and **3**.[3] Intramolecular hydroamination of a triple bond is subject to steric constraints, a desirable regioselective *5-endo* cyclization can be realized.[4]



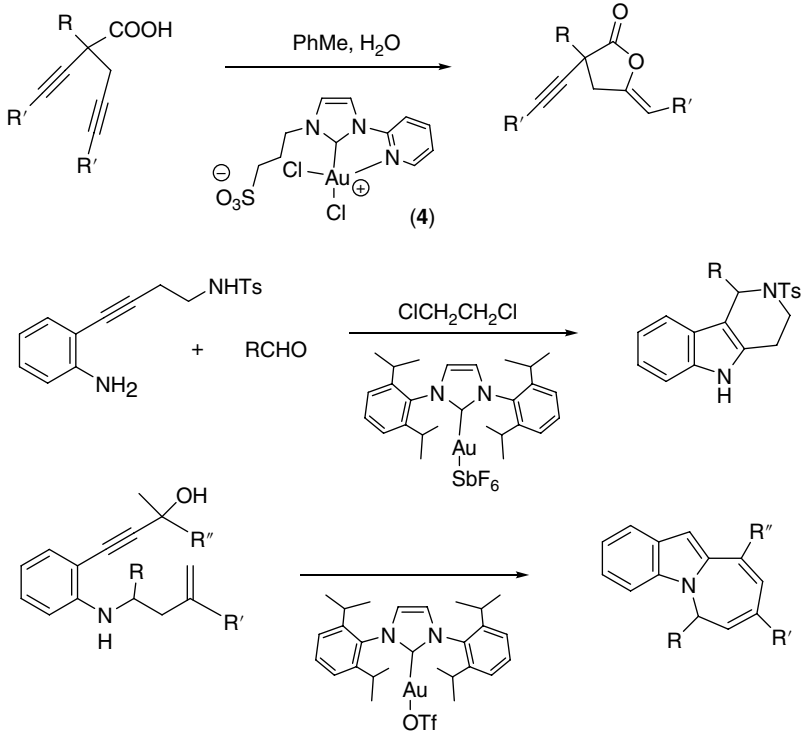
Oxidation. Gold-carbenoids effectively functionalize alkynes by catalyzing oxygen atom transfer from a pyridine *N*-oxide. Thus, propargylic alcohols are transformed into β-diketones,[5] and α′-alkoxy-α,β-unsaturated ketones are obtained from homopropagyl ethers.[6]



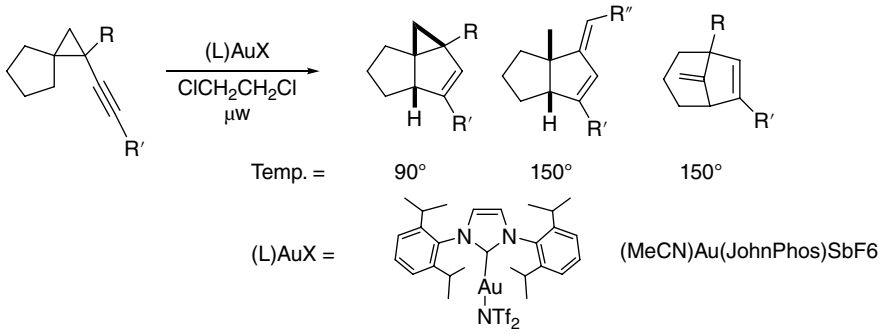
Cyclization. Intramolecular alkenylation catalyzed by a gold(I) salt is influenced by a ligand.[7]



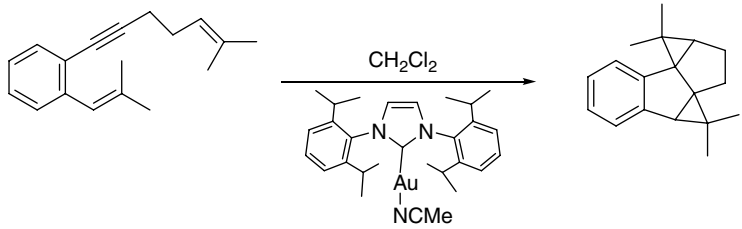
γ–Lactonization is observed from 4-alkynoic acids using catalyst **4**, the double bond of the products assumes a (*Z*)-configuration.[8] Tetrahydro-γ-carbolines are assembled by the cyclization process that is terminated with a Pictet-Spengler reaction.[9] After formation of the indole nucleus, coupling of the alkenylgold intermediate with a conveniently distanced carbonyl group leads to formation of a new ring.[10]



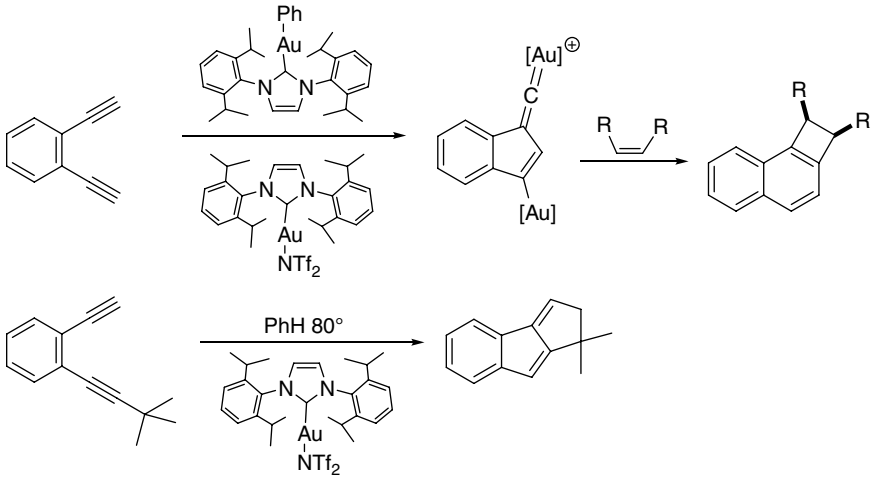
Cyclization mode can further be regulated by reaction temperature besides ligand effects.[11]



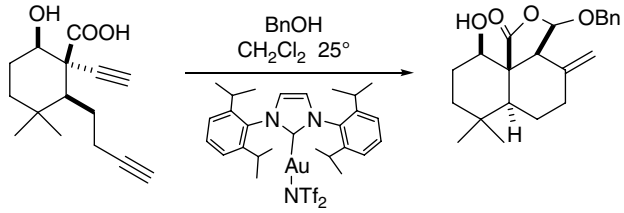
3-Tosylaminoindenes are the products of an imino-Nazarov cyclization of 1-aryl-1-tosylamino-1,2-propenes.[12] Intramolecular addition of a styrene moiety to an *o*-propargyloxy triple bond paves a way to benzoxocines (an 8-*endo-dig* cyclization).[13] An *endo-dig* cyclization also occurs when a 1,5-enynes is exposed to a Au-carbene complex, and by intramolecular trapping a rather complex ring system is assembled.[14]



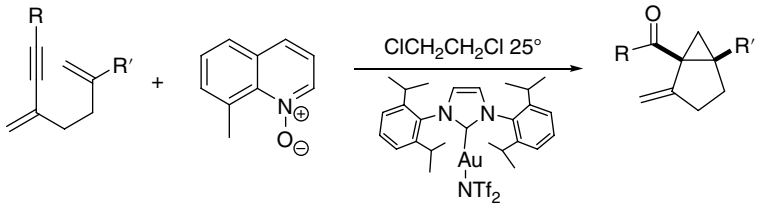
1,2-Bisethynylarenes form indenemethylene-gold species which can serve as cyclopropanation agents. Usually the adducts are further transformed into naphthalene derivatives.[15,16] Insertion of the carbenoid intermediates into a neighboring C-H bond is also a possibility.[17,18]



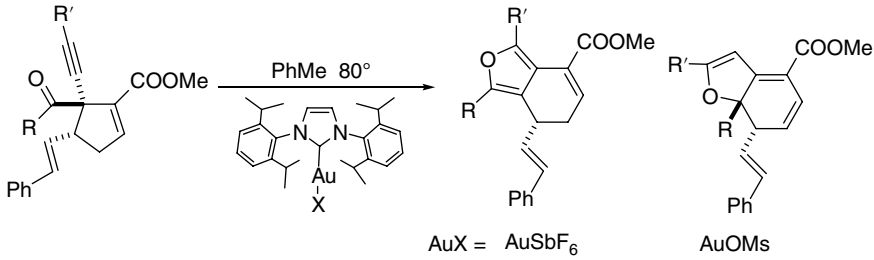
An application of the cyclization involving two triple bonds concerns with elaboration of the tricyclic skeleton of antrocin.[19] Several new bonds (one CC, two CX, two CH), two rings and two stereocenters are erected in one step.



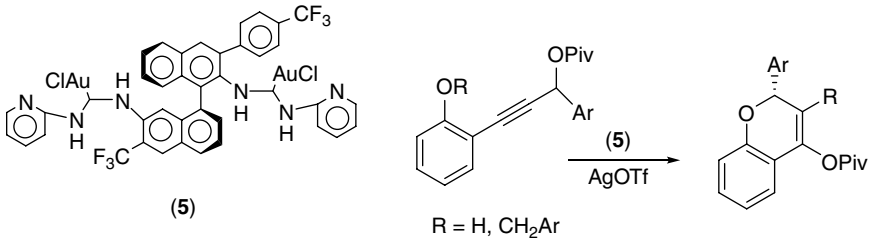
Under oxidative conditions an alkyne behaves as if it were an acylcarbene by intervention of a gold catalyst. Accordingly, enynes can be converted into acylcyclopropanes.[20,21] Indanone formation from *o*-ethynyltoluene shows a C-H insertion reactivity.[22]



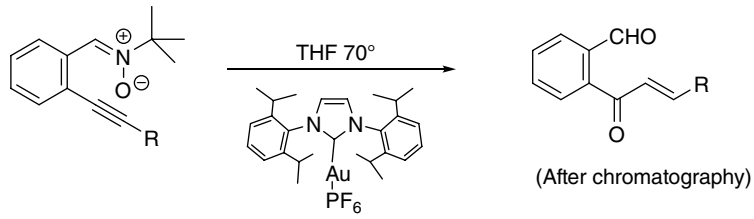
Conversion of 2,2-disubstituted 3-alkynones to furans necessarily requires an alkyl shift. In the following equations the intriguing aspect is that different molecular frameworks evolve on changing the anion of the auxiliary silver salt.[23]



The complex **5** further modified by AgOTf is responsible for transforming diarylpropynyl pivalates into chiral 2-aryl-4-pivaloyloxy-2*H*-chromenes.[24]

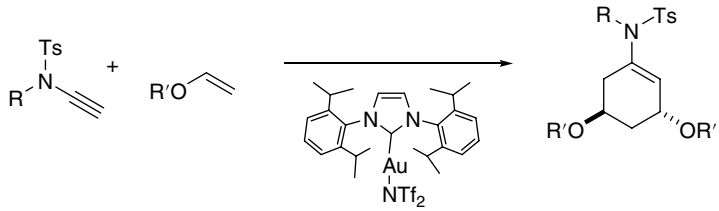


Cyclization to afford an imino ester is featured in the 2-ethynylbenzylidene *t*-butylnitrone. Through an Au-induced intramolecular attack of the triple bond and dissociation of the intermediates into nitrilium ion/gold-enolate pairs, reclosure to a five-membered heterocycle terminates the reaction. With higher alkynyl homologs the reaction leads to alkenyl 2-formylphenyl ketones (on chromatographic workup).[25]



2-Alkynylaryl azides are converted into indoles with incorporation of a nucleophile at C-3, when they are treated with an Au-carbenoid.[26,27]

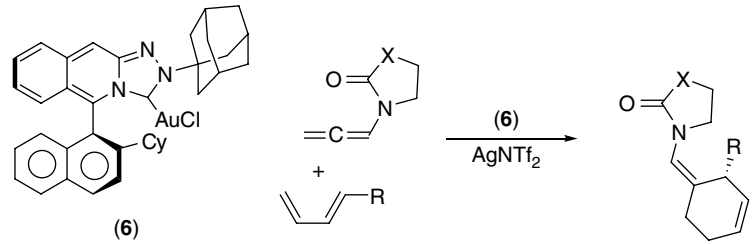
Cycloaddition. *N*-Sulfonylaminoethynes combine with two equivalents of vinyl ethers to form cyclohexenylamine derivatives. With a phenyl group at the other *sp*-carbon the aromatic ring can participate in CC bonding.[28]



It is proposed that gold-linked keteniminium species are involved in the reaction. They insert into oxiranes to produce larger oxacycles.[29]

2-Acyloxy-1,3-butadienylgold species are likely generated from 3-acyloxy-1-alkynes, the reactive intermediates then engage in a [4+2]cycloaddition with nitrosoarenes. An arylamino group is also incorporated into the products.[30]

The Au-carbenoid **6** is specially designed for enantioselective Diels-Alder reaction between dienes and a 3-allenyl-2-oxazolidinone.[31]



Rearrangement. Very effective Claisen rearrangement of 4-vinyloxy-1,2-alkadienes are mediated by a gold-carbene complex. By this method 1,3-alkadienes bearing an acetaldehyde chain at C-2 are readily available.[32]

[1] Zhu, S., Liang, R., Chen, L., Wang, C., Ren, Y., Jiang, H. *TL* **53**, 815 (2012)
[2] Sabater, S., Mata, J.A., Peris, E. *CEJ* **18**, 6380 (2012)
[3] Alvarado, E., Badaj, A.C., Larocque, T.G., Lavoie, G.G. *CEJ* **18**, 12112 (2012)
[4] Chiba, H., Oishi, S., Fujii, N., Ohno, H. *ACIE* **51**, 9169 (2012)
[5] Hashmi, A.S.K., Wang, T., Shi, S., Rudolph, M. *JOC* **77**, 7761 (2012)
[6] Xu, M., Ren, T.-T., Li, C.-Y. *OL* **14**, 4902 (2012)
[7] Barabe, F., Levesque, P., Korobkov, I., Barriault, L. *OL* **13**, 5580 (2011)
[8] Tomas-Mendivil, E., Toullec, P.Y., Diez, J., Conejero, S., Michelet, V., Cadierno, V. *OL* **14**, 2520 (2012)
[9] Reddy, B.V.S., Swain, M., Reddy, S.M., Yadav, J.S., Sridhar, B. *JOC* **77**, 11355 (2012)
[10] Cera, G., Piscitelli, S., Chiarucci, M., Fabrizi, G., Goggiamani, A., Ramon, R.S., Nolan, S.P., Bandini, M. *ACIE* **51**, 9891(2012)
[11] Barluenga, J., Sigüeiro, R., Vicente, R., Ballesteros, A., Tomas, M., Rodriguez, M.A. *ACIE* **51**, 10377 (2012)
[12] Ma, Z.-X., He, S., Song, W., Hsung, R.P. *OL* **14**, 5736 (2012)
[13] Wittstein, K., Kumar, K., Waldmann, H. *ACIE* **50**, 9076 (2011)
[14] Lopez-Carrillo, V., Huguet, N., Mosquera, A., Echavarren, A.M. *CEJ* **17**, 10972 (2011)
[15] Hashmi, A.S.K., Wieteck, M., Braun, I., Rudolph, M., Rominger, F. *ACIE* **51**, 10633 (2012)
[16] Naoe, S., Suzuki, Y., Hirano, K., Inaba, Y., Oishi, S., Fujii, N., Ohno, H. *JOC* **77**, 4907 (2012)
[17] Hashmi, A.S.K., Braun, I., Nösel, P., Schädlich, J., Wieteck, M., Rudolph, M., Rominger, F. *ACIE* **51**, 4456 (2012)
[18] Hashmi, A.S.K., Wieteck, M., Braun, I., Nösel, P., Jongbloed, L., Rudolph, M., Rominger, F. *ASC* **354**, 555 (2012)

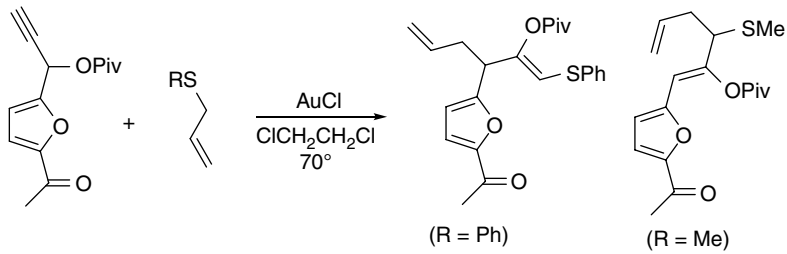
[19] Shi, H., Fang, L., Tan, C., Shi, L., Zhang, W., Li, C., Luo, T., Yang, Z. *JACS* **133**, 14944 (2011)
[20] Vasu, D., Hung, H.-H., Bhunia, S., Gawade, S.A., Das, A., Liu, R.-S. *ACIE* **50**, 6911 (2011)
[21] Qian, D., Zhang, J. *CC* **47**, 11152 (2011)
[22] Bhunia, S., Ghorpade, S., Huple, D.B., Liu, R.-S. *ACIE* **51**, 2939 (2012)
[23] Li, W., Li, Y., Zhou, G., Wu, X., Zhang, J. *CEJ* **18**, 15113 (2012)
[24] Denmark, S.E., Kornfilt, D.J.P., Vogler, T. *JACS* **133**, 15308 (2011)
[25] Chen, D., Song, G., Jia, A., Li, X. *JOC* **76**, 8488 (2011)
[26] Wetzel, A., Gagosz, F. *ACIE* **50**, 7354 (2011)
[27] Lu, B., Luo, Y., Liu, L., Ye, L., Wang, Y., Zhang, L. *ACIE* **50**, 8358 (2011)
[28] Dateer, R.B., Shaibu, B.S., Liu, R.-S. *ACIE* **51**, 113 (2012)
[29] Karad, S.N., Bhunia, S., Liu, R.-S. *ACIE* **51**, 8722 (2012)
[30] Pagar, V.V., Jadhav, A.M., Liu, R.-S. *JACS* **133**, 20728 (2011)
[31] Francos, J., Grande-Carmona, F., Faustino, H., Iglesias-Sigüenza, J., Diez, E., Alonso, I., Fermandez, R., Lassaletta, J.M., López, F., Mascareñas, J.M. *JACS* **134**, 14322 (2012)
[32] Krafft, M.E., Hallal, K.M., Vidhani, D.V., Cran, J.W. *OBC* **9**, 7535 (2011)

Gold(I) chloride

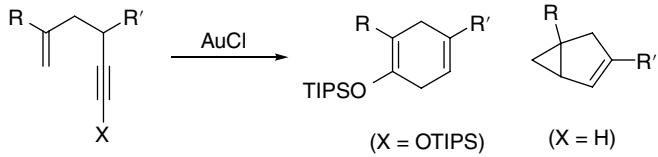
Coupling. Various areneboron compounds are coupled by AuCl and a mild base.[1] Introduction of an alkynyl group to heteroaromatic compounds[2] or the *p*-position of an aniline[3] is through the AuCl-catalyzed reaction with an alkynyliodine(III) reagent.

Addition to alkynes and allenes. Propargylic alcohols add ArSH in the presence of AuCl. The products are α-arenesulfenyl ketones which are formed via Au-activation of the triple bond, and after the addition of ArSH, isomerization.[4]

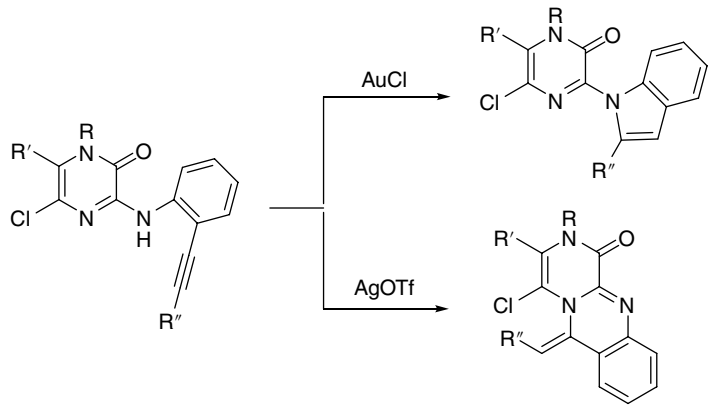
As propargyl esters are now known to undergo group shift upon Au-coordination of the triple bond, addition to such substrates often leads to rearranged products. A more unusual observation is that involving a reaction with allyl sulfides --- a reactivity switch from the second *S*-substituent (Ph vs. Me).[5] Rearrangement accompanied the Au-coordination and intramolecular addition to an enone enable the elaboration of cyclic structures containing two functional sidechains.[6]



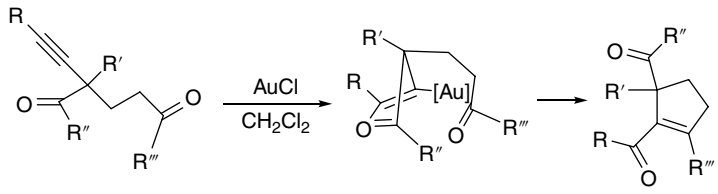
Formation of different cyclic products from 1,5-enynes, as influenced by the presence of a *sp*-bound siloxy group, is significant.[7]



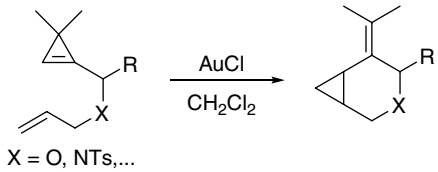
Variation in the cyclization mode is noted in the 3-[*N*-(2-alkynlaryl)amino]-2-pyrazinones, between catalysis by AgOTf and AuCl.[8]



The adducts of indole-2-carbaldehydes and 1-lithio-1-methoxyallene are transformed into 2-methoxycarbazoles by AuCl.[9] Cyclopentenes are evolved from 2-alkynyl-1,5-alkanediones.[10]



Cyclopropenes are also susceptible to attack by Au(I) species. An interesting transformation initiated by such a process is the generation of allylcarbenoids and intramolecular trapping to form a new alkenylcyclopropane system.[11]

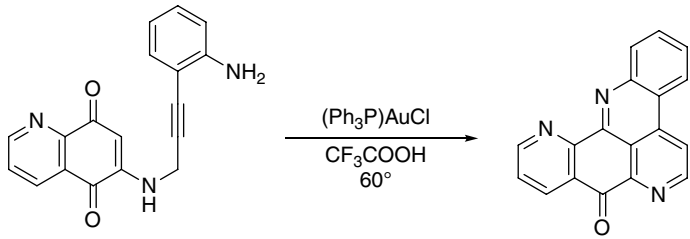


[1] Matsuda, T., Asai, T., Shiose, S., Kato, K. *TL* **52**, 4779 (2011)
[2] Brand, J.P., Chevalley, C., Scopelliti, R., Waser, J. *CEJ* **18**, 5655 (2012)
[3] Brand, J.P., Waser, J. *OL* **14**, 744 (2012)
[4] Biswas, S., Samec, J.S.M. *CC* **48**, 6586 (2012)
[5] Davies, P.W., Albrecht, S.J.-C. *SL* 70 (2012)
[6] Cran, J.W., Krafft, M.E. *ACIE* **51**, 9398 (2012)
[7] Soriano, E., Marco-Contelles, J. *JOC* **77**, 6231 (2012)
[8] Vachhani, D.D., Mehta, V.P., Modha, S.G., Van Hecke, K., VanMeervelt, L., Van der Eycken, E.V. *ASC* **354**, 1593 (2012)
[9] Kong, W., Fu, C., Ma, S. *CEJ* **17**, 13134 (2011)
[10] Liu, L.-P., Malhotra, D., Jin, Z., Paton, R.S., Houk, K.N., Hammond, G.B. *CEJ* **17**, 10690 (2011)
[11] Miege, F., Meyer, C., Cossy, J. *CEJ* **18**, 7810 (2012)

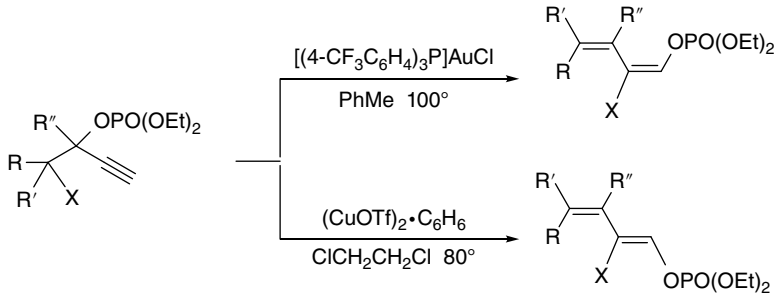
Gold(I) chloride -phosphine

Addition. Carbomethoxylation of alkenes employing $ArSiMe_3$ and MeOH involves oxidative removal of the Me_3Si group, the reaction being conducted with $(Ph_3P)AuCl$ and an oxidant (IBX) in $PhCF_3$,[1] *cis*-1,2-Borauration of 1-alkynes forms very useful products which are susceptible to systematic coupling reactions (e.g., Pd-catalyzed processes).[2]

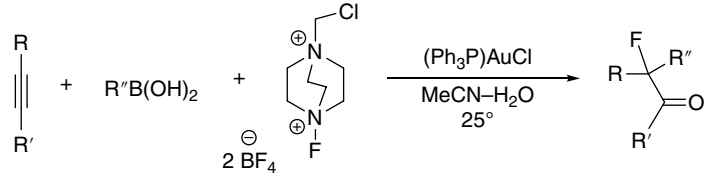
A pleasing annulation is that starts from the intramolecular addition of an enamine segment to a triple bond of a propargylamine (same amino group bonded to the two unsaturated units).[3]



A propargyl phosphate in which the vicinal sp^3-carbon is halogenated is transformed into a dienyl phosphate. Both functional groups migrate during the catalyzed reaction, and by proper choice of catalyst either the (*E*)-isomer or the (*Z*)-isomer can be obtained as major product.[4]



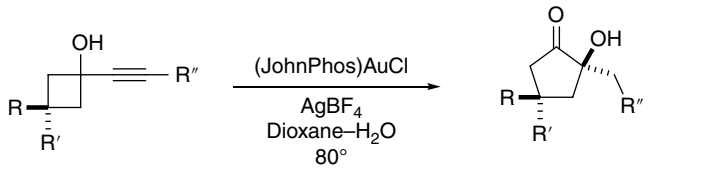
Selectfluor activates $(Ph_3P)AuCl$ to engage alkynes in hydration and CC bond formation with $RB(OH)_2$ as well as submitting a fluorine atom.[5]



Coupling. Alkynylation of electron-rich arenes by ethyne substituted with an electron-withdrawing group is accomplished by oxidative coupling [$(Ph_3P)AuCl$, $PhI(OAc)_2$].[6] The same oxidant add two acetoxy groups to benzylidenecyclopropanes to afford 2-benzylidene-1,3-diacetoxypropanes [catalyst: $(Me_3P)AuCl$].[7]

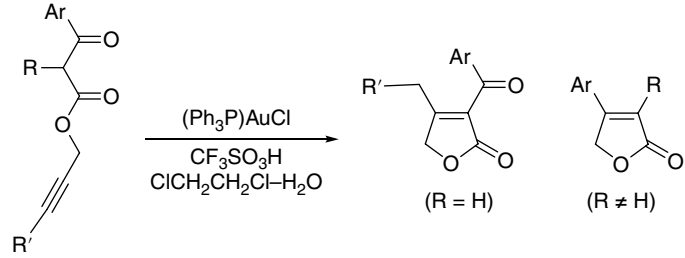
The Au(I) version of Suzuki and Hiyama couplings following oxidative cyclization of certain ω-hydroxy and aminoalkenes in the presence of Selectfluor is established, providing another route to 2-benzyl heterocycles.[8,9]

Hydration and ring expansion are experienced by 1-alkynylcyclobutanols.[10]

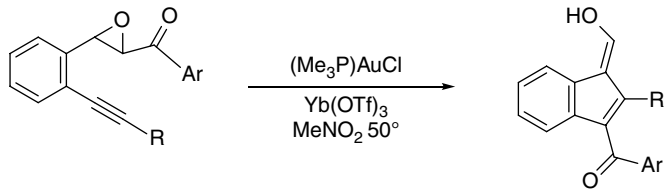


(R = Ph, R′ = H, R″ = COOEt)

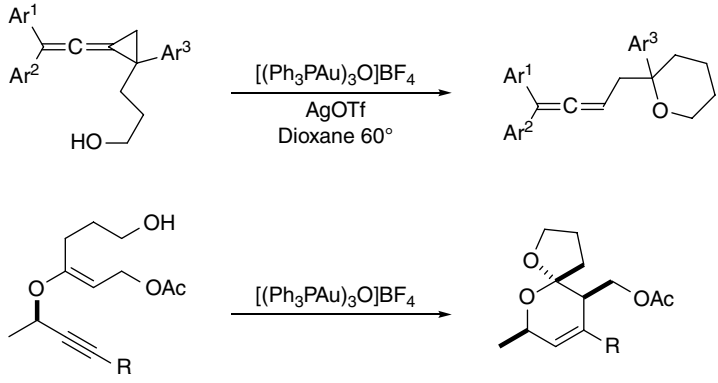
Cyclization. Propargylic esters of 2-aroylalkanoic acids are transformed into 2-butenolides. Products of different substitution patterns emerge from esters having one substituent at C-2 or none.[11]



With a Lewis acid to convert an epoxy ketone unit into the nucleophilic α-hydroxymethylene ketone while a triple bond is being activated by an Au(I) catalyst, cyclization is a natural consequence.[12]



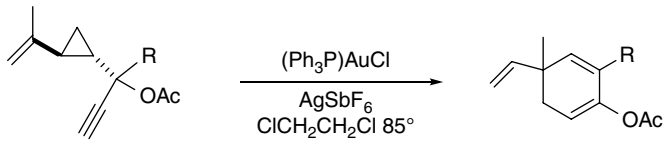
The $[(Ph_3P)Au]OBF_4$ salt is obtained from treatment of $[(Ph_3P)Au]BF_4$ with NaOH.[13] There have been several reports on its application to promote intramolecular addition: in the formation of 2-borylbenzofuran and indole,[14] cycloisomerization of aryl propargyl ethers into 2*H*-chromenes,[15] opening of alkylidenecyclopropanes,[16] and spiroacetalization/carbocyclization.[17]



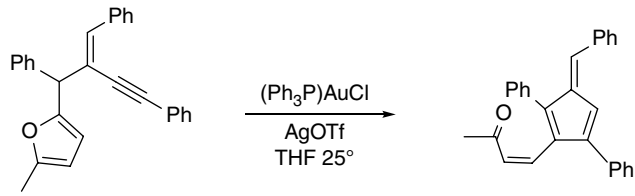
[1] Ball, L.T., Llyod-Jones, G.C., Russell, C.A. *CEJ* **18**, 2931 (2012)
[2] Ye, H., Lu, Z., You, D., Chen, Z., Li, Z.H., Wang, H. *ACIE* **51**, 12047 (2012)
[3] Yin, H., Kong, F., Wang, S., Yao, Z.-J. *TL* **53**, 7078 (2012)
[4] Shiroodi, R.K., Dudnik, A.S., Gevorgyan, V. *JACS* **134**, 6928 (2012)
[5] Wang, W., Jasinski, J., Hammond, G.B., Xu, B. *ACIE* **49**, 7247 (2010)
[6] de Haro, T., Nevado, C. *JACS* **132**, 1512 (2010)
[7] Zhang, D.-H., Dai, L.-Z., Shi, M. *EJOC* 5454 (2010)
[8] Zhang, G., Cui, L., Wang, Y., Zhang, L. *JACS* **132**, 1474 (2010)
[9] Ball, L.T., Green, M., Lloyd-Jones, G.C., Russell, C.A. *OL* **12**, 4724 (2010)
[10] Kim, K.-D., Yeom, H.-S., Shin, S., Shin, S. *T* **68**, 5241 (2012)
[11] Sun, H., Huang, H., Zhang, D., Feng, E., Qian, W., Zhang, L., Chen, K., Liu, H. *ASC* **353**, 1412 (2011)
[12] Dai, L.-Z., Shi, M. *CEJ* **16**, 2496 (2010)
[13] Yang, Y., Ramamoorthy, V., Sharp, P.R. *Inorg. Chem.* **32**, 1946 (1993)
[14] Chan, J.M.W., Amarante, G.W., Toste, F.D. *T* **67**, 4396 (2011)
[15] Karageorge, G.N., Macor, J.E. *TL* **52**, 1013 (2011)
[16] Li, W., Yuan, W., Pindi, S., Shi, M., Li, G. *OL* **12**, 920 (2011)
[17] Sherry, B.D., Marus, L., Lafortezza, B.N., Toste, F.D. *JACS* **128**, 8132 (2006)

Gold(I) chloride –silver salt

Cyclization. The AuCl-$AgClO_4$ couple (effectively $AuClO_4$) causes cyclization of *N′*-(propargyl)tosylhydrazides to furnish pyrazoles.[1] An intriguing transformation of an α-cyclopropylpropargyl acetate to cyclohexadiene is executed by $(Ph_3P)AuCl - AgSbF_6$.[2] It is proposed that migration of the acetoxy group and Au(I)-carbenoid formations are followed by skeletal rearrangement involving the three-membered ring.

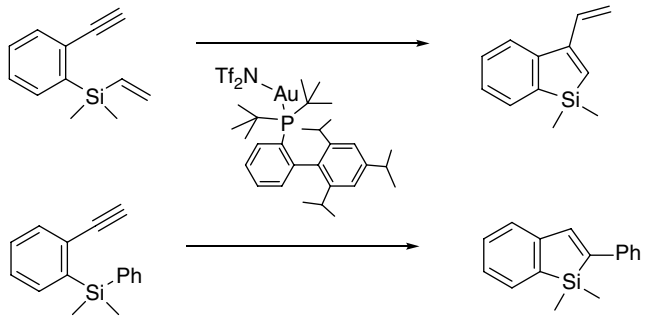


Ring-for-ring exchange is seen in the breaking of a furan to form a fulvene system that is initiated by activation of a triple bond.[3]

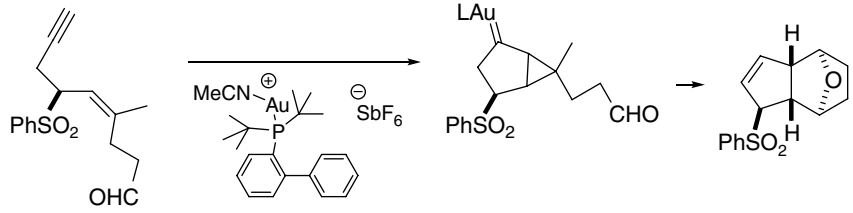


Cycloisomerization of 1,2-alkadien-5-ylsulfamates that forms six-memebred sulfamidates, an intramolecular hydroamination, is a regioselective functionalization mediated by $(Ph_3P)AuCl - AgNTf_2$.[4]

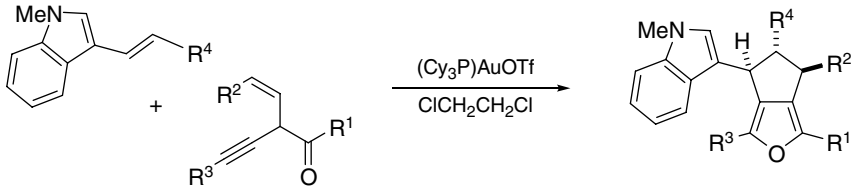
During reaction of 2-ethynylphenylsilanes with a phosphine-ligated $AuNTf_2$ two different types of products emerge that are concerned with the destination for migration of an unsaturated substituent from Si to C.[5]



N-(2,3-Butadienyl) amides cyclize (O-C bond formation) to create a six-membered heterocycle on exposure to $(Ph_3P)AuCl$ – AgOTs.[6] A linear nonenynal chain undergoes oxabicyclization via an initial generation of a bicyclo[3.1.0]hexane.[7]



Other examples of cyclization involving double bond-triple bond pairs include the indene ring formation from *o*-alkenylaryl alkynes.[8] From 2-alken-3-yn-1-ones it results in the generation of 1,3-dipolar species and a furan ring.[9]

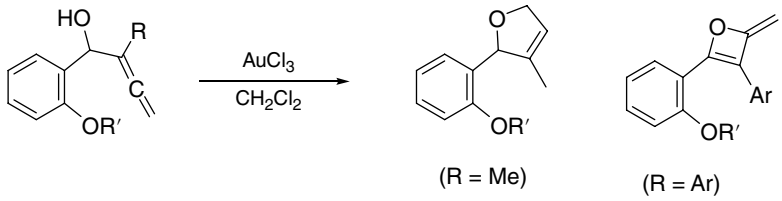


Alkyne functionalization. The transformation of 1-alkynes into 1-halo-2-alkanones is perfomed in the presence of $(Ph_3P)AuCl$ – $AgNTf_2$ and 8-methylquinoline *N*-oxide. The 1,2-dihaloethane solvent contributes the halogen atom.[10]

[1] Yoshimatsu, M., Ohta, K., Takahashi, N. *CEJ* **18**, 15602 (2012)
[2] Wang, G., Zou, Y., Li, Z., Wang, Q., Goeke, A. *JOC* **76**, 5825 (2011)
[3] Chen, Y., Liu, Y. *JOC* **76**, 5274 (2011)
[4] Higinbothom, M.C.M., Bebbington, M.W.P. *CC* **48**, 7565 (2012)
[5] Matsuda, T., Yamaguchi, Y., Shigeno, M., Sato, S., Murakami, M. *CC* **47**, 8697 (2011)
[6] Hashmi, A.S.K., Schuster, A.M., Litters, S., Rominger, F., Pernpointer, M. *CEJ* **17**, 5661 (2011)
[7] Huguet, N., Echavarren, A.M. *SL* 49 (2012)
[8] Martinez, A., Garcia-Garcia, P., Fernandez-Rodriguez, M.A., Rodriguez, F., Sanz, R. *ACIE* **49**, 4633 (2010)
[9] Gao, H., Wu, X., Zhang, J. *CEJ* **17**, 2838 (2011)
[10] He, W., Xie, L., Xu, Y., Xiang, J., Zhang, L. *OBC* **10**, 3168 (2012)

Gold(III) chloride

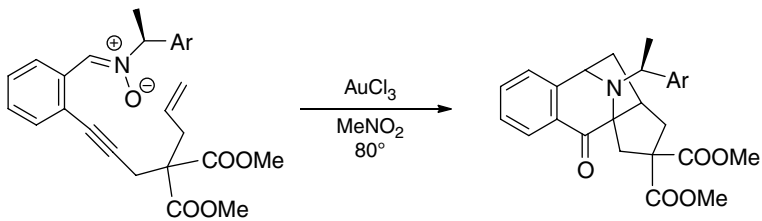
Cyclization. Certain allenyl carbinols cyclize to afford either dihydrofurans or 4-methylene-2-oxetenes, as catalyzed by $AuCl_3$.[1]



Conversion of 1-bromoalkyn-4-ols to butyrolactones is due to a straightforward cycloetherification followed by hydration.[2] Formation of carbazoles from 2-(α-hydroxy-3-alkynyl) indoles is similarly envisioned as a result of cyclization and dehydrative aromatization.[3]

The bimetallic catalyst duo $AuCl_3$-AgOTf serves to effect annulations of 4-hydroxy-2-pyrone via Michael reaction with conjugated carbonyl compounds, then cyclodehydration.[4] It also effects ring closure of 4-penten-1-ylarenes[4] and heterologs (homoallyl aryl ethers and *N*-homoallylanilines).[5]

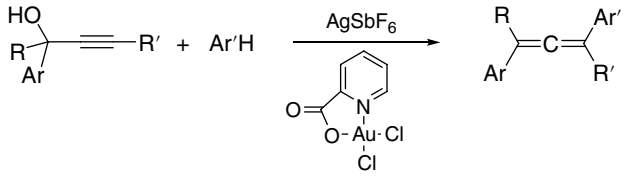
Cycloaddition. Nitriles and ω-azido-1-alkynes form amidines and the ensuing [3+2] cycloaddition leads to bicyclic imidazoles.[6] Complex ring systems can be elaborated in a single step through a cycloaddition sequence after Au-activation (of a triple bond).[7]



N-(Acylamino)pyridinium zwitterions cycloadd to ynamines with elimination of pyridine. The reaction catalyzed by dichlorogold picolinate (derived from $AuCl_3$) leads to 4-aminooxazoles.[8]

Isomerization. Allene-to-conjugated diene isomerization occurs when nucleophiles are excluded from the reaction system.[9] The previously reported formation of furans from 2-alkynyloxiranes is not extendable to tetrasubstituted oxiranes. The coordination of Au(III) ion to both the oxygen atom and the triple bond is followed by rearrangement to carbonyl compounds, when reaction is performed in a nonalcoholic solvent (e.g., dichloroethane).[10] Simpler oxiranes do isomerize to give carbonyl compounds on treatment with $AuCl_3$ and $AgSbF_6$.[11]

Substitution. Either $AuCl_3$ or $Cu(OTf)_2$ renders $MeNO_2$ electrophilic and to behave as equivalent of $[CH_2]^{++}$ toward substances such as 1,3-dicarbonyl compounds.[12] Dichlorogold picolinate together with $AgNTf_2$ causes ionization of acetals and reaction with alkenes, which produces 1,3-dialkoxyalkanes.[13] With a similar reagent/catalyst system allenylation of arenes with propargylic alcohols is accomplished.[14]



Under oxidative conditions (*t*-BuOOH) the (bpy)$AuCl_3$ complex catalyzes α-cyanation of amines using Me_3SiCN.[15] Amination at a benzylic carbon of benzocycloalkanes is similarly performed (NBS as oxidant).[16]

Condensation. A three-component synthesis of propargylic amines from 1-alkynes, aldehydes and secondary amines using $AuCl_3$ suffers from catalyst decomposition [generation of inactive Au(0) species], but a remedy consisting of $CuCl_2$ – TEMPO is found.[17]

[1] Alcaide, B., Almendros, P., del Campo, T.M., Fernandez, I. *CC* **47**, 9054 (2011)
[2] Reddy, M.S., Kumar, Y.K., Thirupathi, N. *OL* **14**, 824 (2012)
[3] Qiu, Y., Kong, W., Fu, C., Ma, S. *OL* **14**, 6198 (2012)
[4] Liu, Y., Zhu, J., Qian, J., Jiang, B., Xu, Z. *JOC* **76**, 9096 (2011)
[5] Jean, M., van de Weghe, P. *TL* **52**, 3509 (2011)
[6] Xiao, Y., Zhang, L. *OL* **14**, 4662 (2012)
[7] Jeong, J., Yeom, H.-S., Kwon, O., Shin, S. *CAJ* **6**, 1977 (2011)
[8] Davies, P.W., Cremonesi, A., Dumitrescu, L. *ACIE* **50**, 8931 (2011)
[9] Ting, C.-M., Hsu, Y.-L., Liu, R.-S. *CC* **48**, 6577 (2012)
[10] Gonzalez, M.J., Gonzalez, J., Vicente, R. *EJOC* 6140 (2012)
[11] Gudla, V., Balamurugan, R. *TL* **53**, 5243 (2012)
[12] Balamurugan, R., Manojveer, S. *CC* **47**, 11143 (2011)
[13] Dong, W., Zhang, M., Xiao, F., Wang, Y., Liu, W., Hu, X., Yuan, Q., Zhang, S. *SL* 2799 (2012)

[14] Xu, C.-F., Xu, M., Yang, L.-Q., Li, C.-Y. *JOC* **77**, 3010 (2012)
[15] Zhang, Y., Peng, H., Zhang, M., Cheng, Y., Zhu, C. *CC* **47**, 2354 (2011)
[16] Zhang, Y., Feng, B., Zhu, C. *OBC* **10**, 9137 (2012)
[17] Graf, T.A., Anderson, T.K., Bowden, N.B. *ASC* **353**, 1033 (2011)

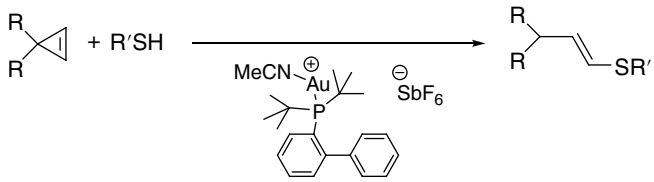
Gold(I) chloride (tertiary phosphine) – silver hexafluoroantimonate

Some variations of the ionic gold complexes for catalysis are concerned with the silver salt used (most often are the hexafluoroantimonate, tosylate, and triflimide) to exchange the chloride, the phosphine (Ph_3P, JohnPhos, and cognate biaryldi-*t*-butylphosphines), and the other ligand to the metal (e.g., MeCN, and 1-substituted benzotriazolyl group, the latter can be further linked to a polymer skeleton.[1])

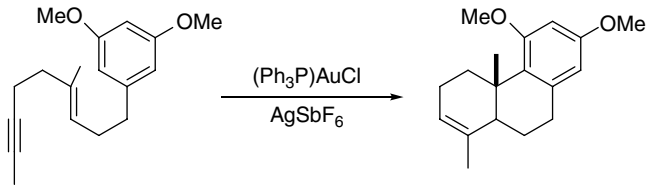
Substitution. Formation of indenes from alkenyl benzyl carbinols by the action of the Au(I) catalyst[2] only demonstrates its Lewis acidity, although there is no complication for being devoid of nucleophiles.

Rearrangement. The conversion of 1-(3-alkoxy-3-aryl)prop-1-enyl-1-cycloalkanols into 2-styrylcycloalkanones is also a Lewis acid-catalyzed reaction (In comparision the formation of 2-aryl-5-spiroannulated 3-dihydrofuran in the reaction catalyzed by $ZnBr_2$ is noteworthy).[3] Vinylidenecyclopropanes undergo oxygenative ring expansion to afford 2-alkylidenecyclobutanones, using a pyridine oxide as the oxygen atom source.[4]

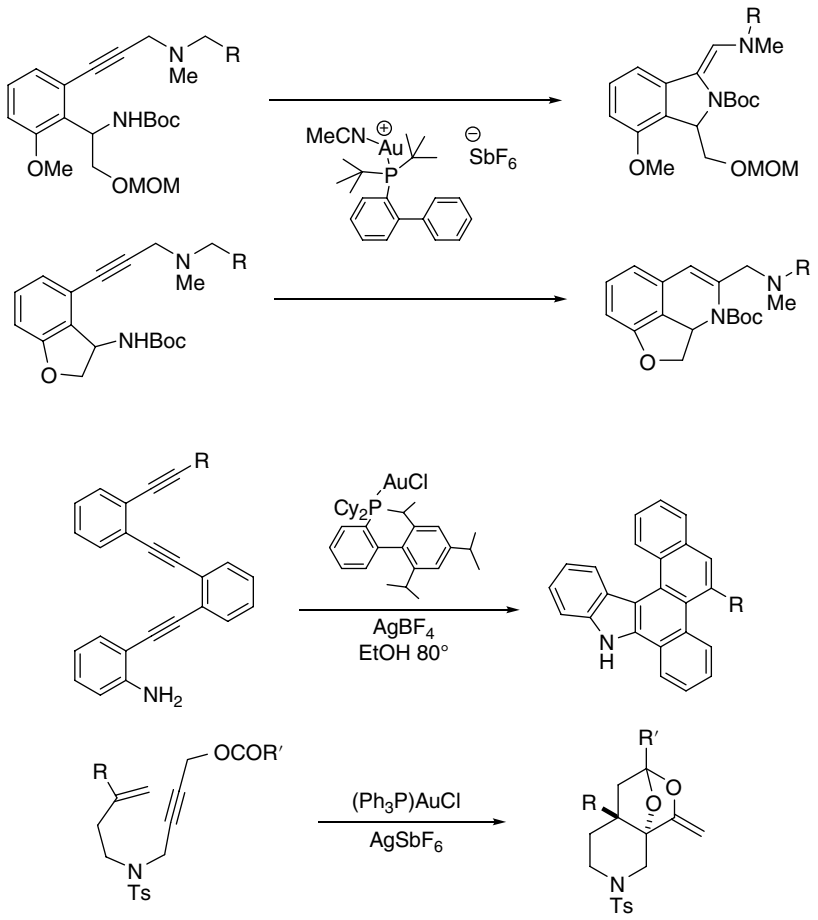
Addition. Cyclopropenes are attacked by nucleophiles such as RSH and indole in a process resulting in ring opening.[5,6]



1,5-Enynes are induced to form a cyclohexene unit, and by installment of properly situated structural elements in the substrate further transformations are possible, e.g., creation of a tricyclic system.[7]



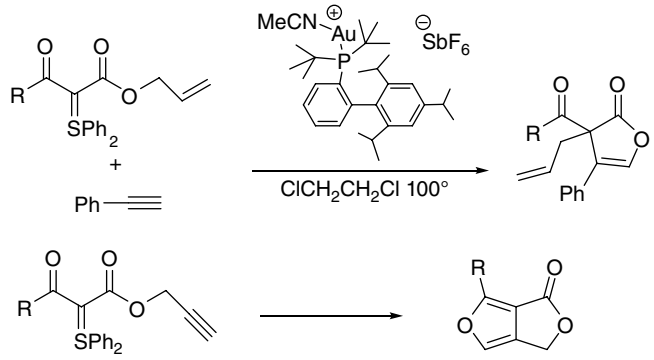
Intramolecular hydroamination to form 1-alkylideneisoindolines and 1,2-dihydroisoquinolines is determined by the molecular strain of the products.[8] A relay process is shown in the creation of the bisannulated carbazoles.[9]



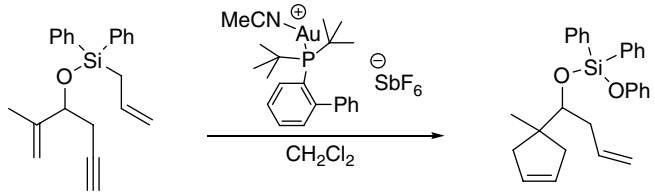
Different patterns for oxyamination. Thus ynamides emerge from reactions with ArNO and nitrones.[10]

The involvement of propargylic rearrangement and intramolecular trapping by a double bond is embodied in the formation of bridged cyclic acetals shown in the following.[11]

A dual CC bond-forming process ensues during addition of a stabilized sulfur ylides to an Au-coordinated alkyne.[12]

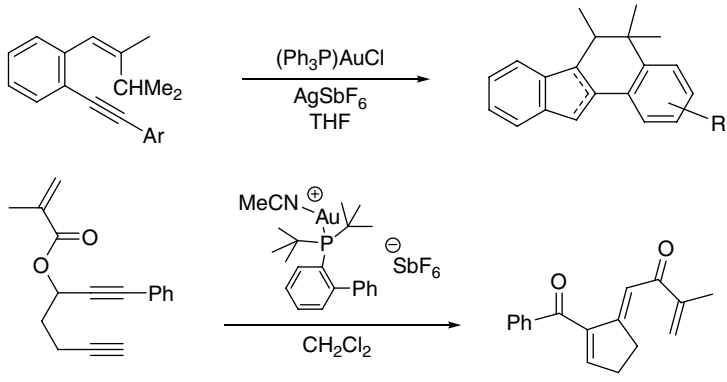


4-Oxy-hex-5-en-1-ynes deliver cyclopentenes, while involving cyclization and 1,2-CC bond migration.[13]



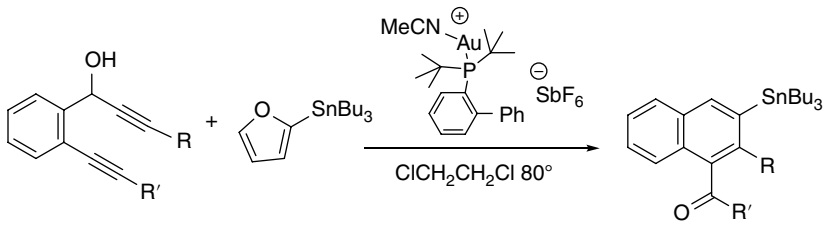
2-Propynoic acid is susceptible to attack by alkenes when activated by the Au complex, 5,6-dihydro-2-pyrones are produced. Interestingly, the reaction with cyclooctene leads to 1,9-cyclodecadien-1-carboxylic acid (apparently from electrocyclic opening of the [2+2] cycloadduct).[14]

Cycloaddition. Two rings are attached to an indole nucleus that bears at C-3 a sidechain terminated by a propargylic alcohol unit, while involving C-2 and C-3 of the indole nucleus to form the C-C and C-O bonds.[15] Propargylic rearrangement (1,3-acyloxy shift) attends the cyclization of 3-acyloxy-1,6-heptadiynes to furnish 2-acyl-2-cyclopentenylidenyl ketones.[16]

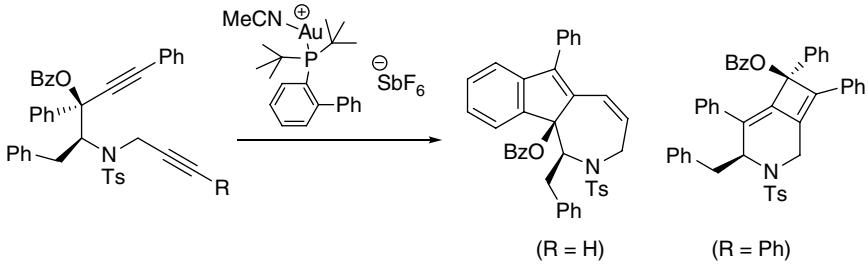


Diarylethynes that are substituted by an alkenyl group at one of the *o*-positions are liable to annulations on activation of the triple bond.[17] Indano[*b*]naphthalenes are the products of Au(I)-catalyzed reaction of *o*-arylethynylbenzyl propagyl carbinol carbonates.[18]

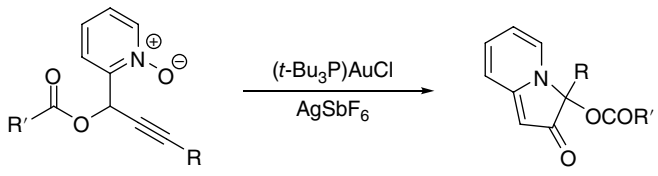
Involvement of a furan nucleus in intramolecular alkenylation necessarily opens the heterocyclic unit, as exemplified by the transformation of 2-alkynylbenzyl α-furyl carbinol silyl ethers.[19] 2-Tributylstannylfuran acts as an Sn-transfer agent (during Au/Sn transmetallation) in the cycloisomerization of α-(2-alkynylbenzyl)propargyl alcohols.[20]



Initiated by propargylic shift of a benzyloxy group, cycloaddition involving a 1,7-diyne can pursue different courses in dependence of substitution on one *sp*-terminus.[21] (Enynes give bicyclic products containing a four-membered ring.[22]) However, incorporation of an aldehyde takes precedence to the cyclobutene formation from enynes.[23]



Oxygen atom shift of 2-(*o*-Alkynylaryl)oxiranes is instigated by activation of the triple bond, and further oxidation of the α-oxoalkylidene-gold species (by Ph_2SO) to an α-dione is followed by a carbonyl-ene cyclization.[24] Allenyl ester resulting from propargylic ester migration can coordinate to Au(I) to precipitate attack of a pyridine oxide, and eventually the generation of indolizinone results.[25]



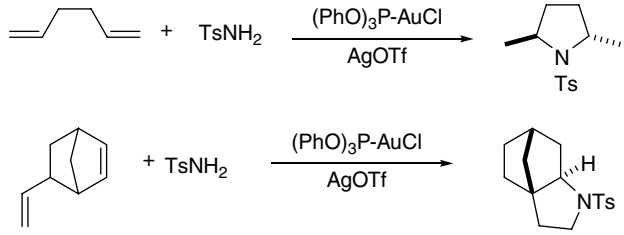
Often appeared is the exhibition of an allylcarbenoid reactivity by an alkyne, as attested by cyclopropane formation.[26,27] [2+2]Cycloaddition of allenylamine derivatives with alkenes to give iminocyclobutanes is observed in an Au(I)-catalyzed reaction.[28,29]

[1] Cao, W., Yu, B. *ASC* **353**, 1903 (2011)
[2] Usanov, D.L., Yamamoto, H. *OL* **14**, 414 (2012)
[3] Zhu, L.-L., Li, X.-X., Zhou, W., Li, X., Chen, Z. *JOC* **76**, 8814 (2011)
[4] Yuan, W., Dong, X., Wei, Y., Shi, M. *CEJ* **18**, 10501 (2012)
[5] Mudd, R.J., Young, P.C., Jordan-Hore, J.A., Rosair, G.M., Lee, A.-L. *JOC* **77**, 7633 (2012)
[6] Young, P.C., Hadfield, M.S., Arrowsmith, L., Macleod, K.M., Mudd, R.J., Jordan-Hore, J.A., Lee, A.-L. *OL* **14**, 898 (2012)
[7] Pradal, A., Chen, Q., Faudot dit Bel, P., Toullec, P.Y., Michelet, V. *SL* 74 (2012)
[8] Chiba, H., Oishi, S., Fujii, N., Ohno, H. *ACIE* **51**, 9169 (2012)
[9] Hirano, K., Inaba, Y., Takasu, K., Oishi, S., Takemoto, Y., Fujii, N., Ohno, H. *JOC* **76**, 9068 (2011)
[10] Mukherjee, A., Dateer, R.B., Chaudhuri, R., Bhunia, S., Karad, S.N., Liu, R.-S. *JACS* **133**, 15372 (2011)
[11] Zheng, H., Huo, X., Zhao, C., Jing, P., Yang, J., Fang, B., She, X. *OL* **13**, 6448 (2011)
[12] Huang, X., Peng, B., Luparia, M., Gomes, L.F.R., Veiros, L.F., Maulide, N. *ACIE* **51**, 8886 (2012)
[13] Li, J., Liu, X., Lee, D. *OL* **14**, 410 (2012)
[14] Yeom, H.-S., Koo, J., Park, H.-S., Wang, Y., Liang, Y., Yu, Z.-X., Shin, S. *JACS* **134**, 208 (2012)
[15] Cera, G., Chiarucci, M., Mazzanti, A., Mancinelli, M., Bandini, M. *OL* **14**, 1350 (2012)
[16] Leboeuf, D., Simonneau, A., Aubert, C., Malacria, M., Gandon, V., Fensterbank, L. *ACIE* **50**, 6868 (2011)
[17] Garcia-Garcia, P., Rashid, M.A., Sanjuan, A.M., Fernandez-Rodriguez, M.A., Sanz, R. *OL* **14**, 4778 (2012)
[18] Chen, Y., Chen, M., Liu, Y. *ACIE* **51**, 6493 (2012)
[19] Wang, C., Chen, Y., Xie, X., Liu, J., Liu, Y. *JOC* **77**, 1915 (2012)
[20] Chen, Y., Chen, M., Liu, Y. *ACIE* **51**, 6181 (2012)
[21] Rao, W., Koh, M.J., Kothandaraman, P., Chan, P.W.H. *JACS* **134**, 10811 (2012)
[22] Rao, W., Susanti, D., Chan, P.W.H. *JACS* **133**, 15248 (2011)
[23] Huple, D.B., Liu, R.-S. *CC* **48**, 10975 (2012)
[24] Chaudhuri, R., Liu, R.-S. *ASC* **353**, 2589 (2011)
[25] Murai, M., Kitabata, S., Okamoto, K., Ohe, K. *CC* **48**, 7622 (2012)
[26] Sperger, C.A., Tungen, J.E., Fiksdahl, A. *EJOC* 3719 (2011)
[27] Zhang, D.-H., Wei, Y., Shi, M. *CEJ* **18**, 7026 (2012)
[28] Li, X.-X., Zhu, L.-L., Zhou, W., Chen, Z. *OL* **14**, 436 (2012)
[29] Faustino, H., Bernal, P., Castedo, L., Lopez, F., Mascareñas, J.L. *ASC* **354**, 1658 (2012)

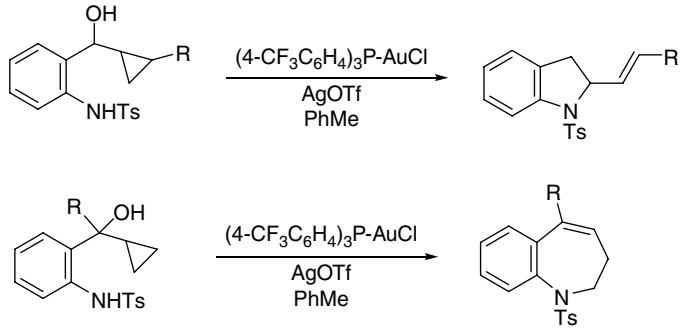
Gold(I) chloride (phosphine-ligated) – silver tosylate

Addition. Hydration of the triple bond of 2-alkynylaryl ketones is regioselective due to participation of the carbonyl oxygen.[1] Involvement of the acetonide unit in the functionalization of the triple bond of protected 6-alkyne-1,2-diols is evident in their transformation into bridged dioxoabicyclic products.[2]

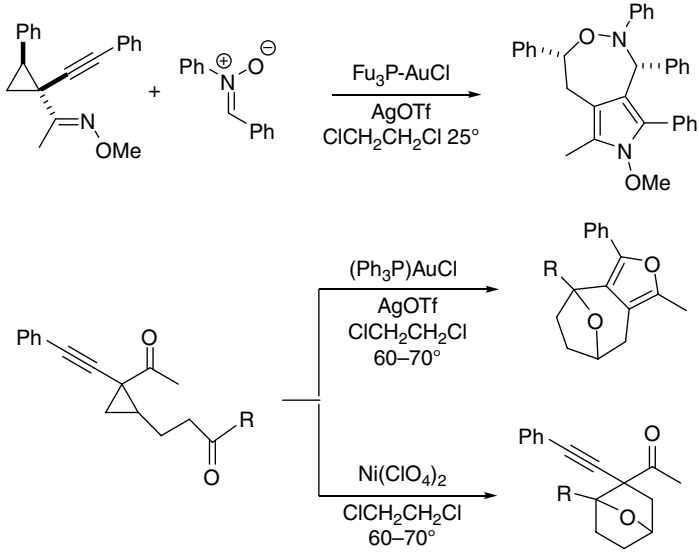
1-Iodo-1-alkynes add phosphoric diesters to provide (*Z*)-1-iodo-2-alkenyl phosphates.[3] The products are useful for synthetic modification of the carbon chain via two different CC couplings. Acquisition of *N*-tosylpyrrolidines from 1,5-dienes and $TsNH_2$ by a Au(I)-catalyzed process is quite general.[4]



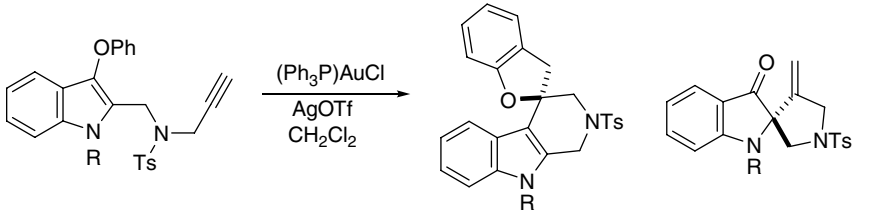
Substitution. Propargylic alcohols and acetates in wet MeOH are converted into transposed enones (the catalyst has Au bonded to a benzotriazolyl unit).[5] Moderate yields of 3-(2-oxoalkylidene)oxindoles are obtained from hydration of 3-alkynyl-3-benzyloxyoxindoles.[6] Importance of substitution patterns for supporting cationic sites is evident for the transformation of *o*-aminoaryl cyclopropyl carbinols into either 2-alkenylindolines or benzoazepines.[7]



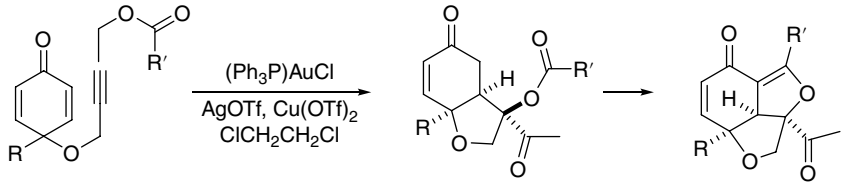
Oxime ethers of 1-alkynyl-1-cyclopropylcarbonyl compounds are found to undergo carbocycle opening and pyrrole formation, a nucleophile enters at the new sidechain.[8] Particularly interesting is the reaction involving a nitrone, an additional CC bond is formed with the aurated carbon from the emerging pyrrole unit.[9] Similarly, furans emerge from alkynylcyclopropyl ketones.[10]



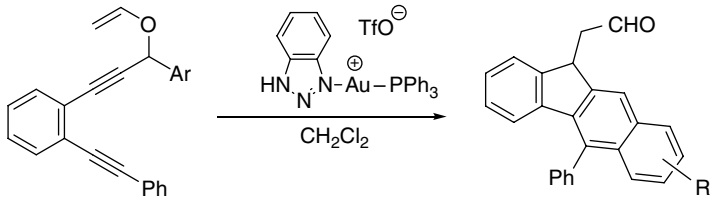
Cyclization. Indoles with an ynone sidechain cyclize readily, and such a reaction has been applied to a synthesis of azocino[5,4-*b*]indoles,[11] and 2-hydroxycarbazoles.[12] A significant selection of cyclization modes that results in either tetrahydro-β-carbolines or 2-spiroannulated pseudoindoxyl products is shown to be governed by the indolic *N*-substituent.[13]



An ester group shift from propargyl to allenyl carbon prior to intramolecular 1,4-addition and then a Claisen condensation starts annulation of a 2,5-cyclohexadienone.[14] The route to quinolin-3-yl ketones by combination of 2-acylanilines and ynones is more straightforward.[15]

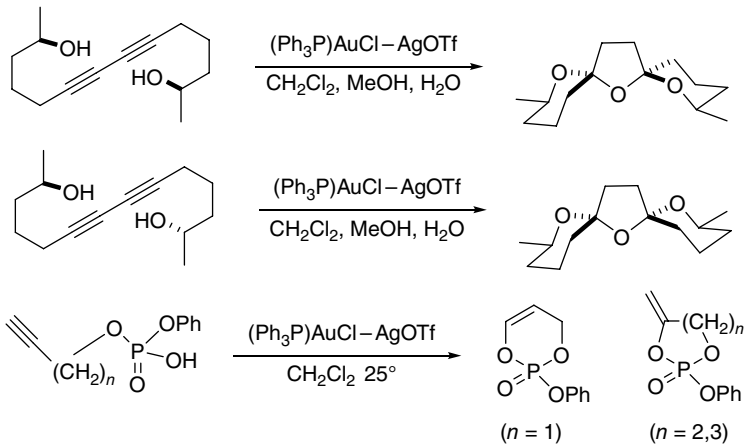


Au(I) species may play a role in Claisen rearrangement and also to keep the resulting allenyl residue activated for intramolecular attack by another triple bond in the transformation into a benzannulated fluorene system.[16]

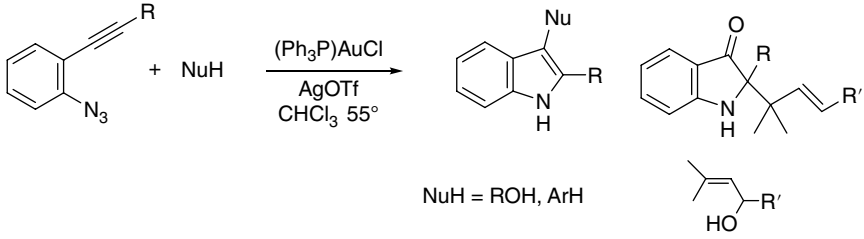


It is reasonable to assume that for an unsymmetrical allene, coordination with Au(I) takes place at the more electron-rich π-bond, and closure of a cyclopentene unit proceeds smoothly from 3-(allenyl)indoles that bear an electron-withdrawing group at the sp^2-carbon germinal to the indole nucleus.[17]

In whatever order the hydration and intramolecular hydroalkoxylation sequence of certain alkynols is subject to stereocontrol.[18] The chain length is crucial in determining the cyclization mode (*exo* vs. *endo*) of ω-alkynyl phosphates.[19] By activation of conjugated dienes with Au(I), 1,3-alkadien-n-ols that can form 5- and 6-membered oxacycles react to furnish products containing a 2-(1-propenyl) group.[20]



o-Azidoarylalkynes lose N_2 to form indoles, and a nucleophile becomes attached to C-3. When allylic alcohols are used as the nucleophile, 2-(2-alkenyl)pseudoindoxyls are obtained (Claisen rearrangement products).[21]



[1] Jeong, J., Ray, D., Oh, C.H. *SL* 897 (2012)
[2] Alcaide, B., Almendros, P., Carrascosa, R. *T* **68**, 9391 (2012)
[3] Chary, B.C., Kim, S., Shin, D., Lee, P.H. *CC* **47**, 7851 (2011)
[4] Giner, X., Najera, C., Kovacs, G., Lledos, A., Ujaque, G. *ASC* **353**, 3451 (2011)
[5] Wang, D., Zhang, Y., Harris, A., Gautam, L.N.S., Chen, Y., Shi, X. *ASC* **353**, 2584 (2011)
[6] Zhang, D.-H., Shi, M. *CO* **1**, 215 (2012)
[7] Kothandaraman, P., Huang, C., Susanti, D., Rao, W., Chan, P.W.H. *CEJ* **17**, 10081 (2011)
[8] Zhang, Y., Zhang, J. *SL* 1389 (2012)
[9] Zhang, Y., Zhang, J. *ASC* **354**, 2556 (2012)
[10] Bai, Y., Tao, W., Ren, J., Wang, Z. *ACIE* **51**, 4112 (2012)
[11] Peshkov, V.A., Pereshivko, O.P., Van der Eycken, E.V. *ASC* **354**, 2841 (2012)
[12] Wang, L., Li, G., Liu, Y. *OL* **13**, 3786 (2011)
[13] Zhang, Y.-Q., Zhu, D.-Y., Jiao, Z.-W., Li, B.-S., Zhang, F.-M., Tu, Y.-Q., Bi, Z. *OL* **13**, 3458 (2011)
[14] Cai, S., Liu, Z., Zhang, W., Zhao, X., Wang, D.Z. *ACIE* **50**, 11133 (2011)
[15] Cai, S., Zeng, J., Bai, Y., Liu, X.-W. *JOC* **77**, 801 (2012)
[16] Wang, Q., Aparaj, S., Akhmedov, N.G., Petersen, J.L., Shi, X. *OL* **14**, 1334 (2012)
[17] Chen, B., Fan, W., Chai, G., Ma, S. *OL* **14**, 3616 (2012)
[18] Volchkov, I., Sharma, K., Cho, E.J., Lee, D. *CAJ* **6**, 1961 (2011)
[19] Chary, B.C., Low, W.S., Kim, S., Kim, H., Lee, P.H. *CAJ* **6**, 1970 (2011)
[20] Chandrasekhar, B., Ryu, J.-S. *T* **68**, 4805 (2012)
[21] Wetzel, A., Gagosz, F. *ACIE* **50**, 7354 (2011)

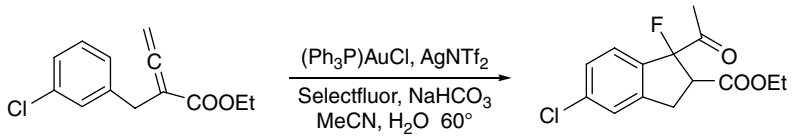
Gold(I) chloride (phosphine-ligated) – silver triflimide

Isomerization. Meyer-Schuster rearrangement of propargylic alcohols is induced by $(Ph_3P)AuNTf_2$, in contrast to substitution that occurs when AgNTf is used as the catalyst.[1]

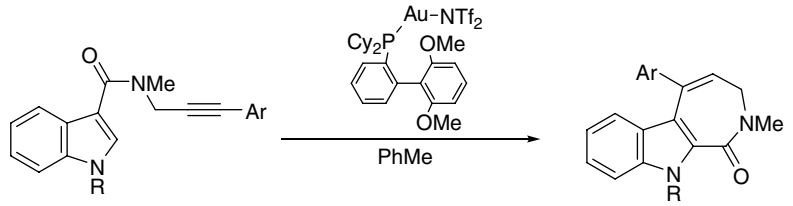
Addition. A phosphine-ligated $AuNTf_2$ is found to dimerize 1-alkynes in a head-to-tail addition reaction to supply conjugated enynes.[2] Generation of β-alkoxy ketones from mixtures of aldehydes, alcohols and 1-alkynes indicates that the Au(I) catalyst can promote oxonium ion formation, addition and hydration.[3,4]

In a cycloiodination of the triple bond of *o*-(*N*-tosylaminoaryl) ethynyl carbinols with NIS in acetone, 2-iodomethyleneindolin-3-ols are obtained. At a somewhat higher (than ambient) temperature the products are indole-2-carbaldehydes.[5] *N*-(2-Alkynoyl)anilines undergo oxidative cyclization that results in the formation of 3-acyloxindoles (in enolic form), provided an oxygen atom source (e.g., 2-bromopyridine oxide) is present.[6] Arylhydroxylamines and 1-alkynes combine regioselectively to give 2-substituted indoles.[7]

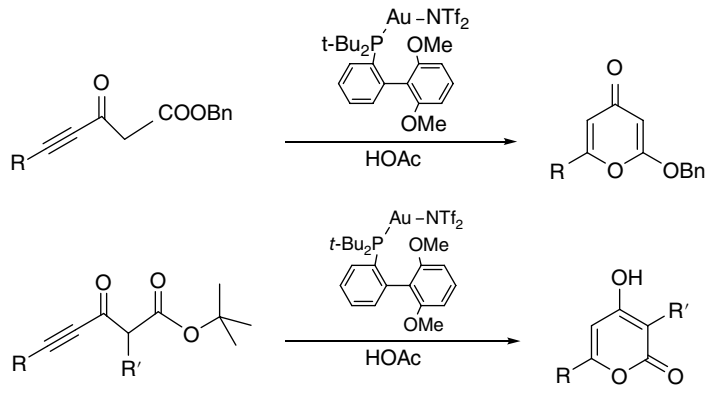
2-Benzylallenoic esters form indan products with Selectfluor, a C-F bond being made at the ring closure site while the neighboring carbon is oxygenated.[8]



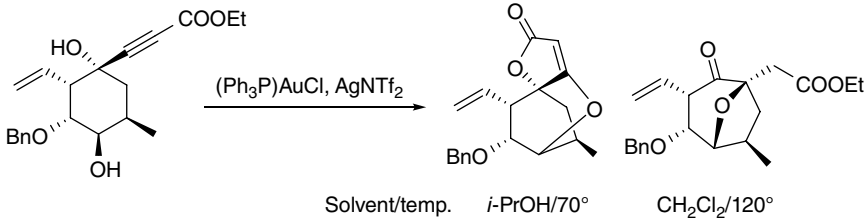
Two rings are closed in one operation from *N*-formyl-*N*-homopropargyltryptamine, with perfect atom economy.[9] It appears that spirocyclic products are formed from *N*-propargyl-3-indolecarbamides which are then stabilized via a rearrangement.[10]



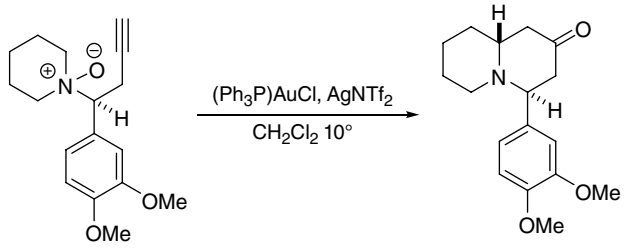
The ester group of benzyl 3-oxo-4-alkynoates is masked in their transformation into 2-benzyloxy-4-pyrones, however, the *t*-butyl esters suffer a loss of isobutene under the same reaction condition.[11]



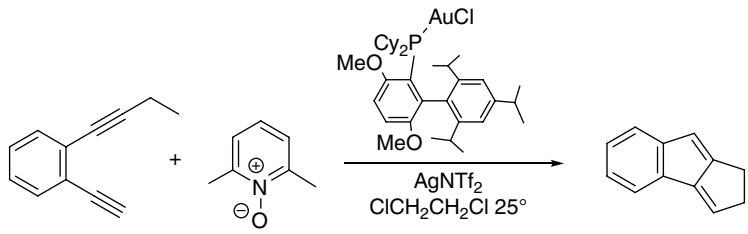
In the following example, a simple transannular addition of a hydroxyl group to a triple bond is preceded by a rearrangement (ring expansion) when the reaction is conducted in a different solvent and at a higher temperature.[12]



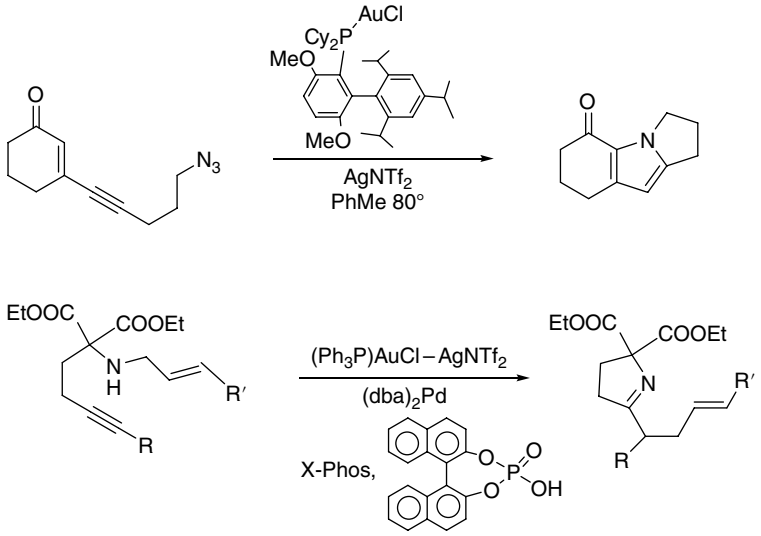
Oxidative cyclization of alkynes is effected by the Au(I) catalyst in conjunction with an oxidant. Thus, 3-butyn-1-ol gives γ-butyrolactone,[13] phenyl propargyl ether affords 3-chromanone,[14] and *N*-homopropargylpiperidines furnish quinolizidinones.[15]



A quite intriguing generation of a dihydrobenzopentalene involves activation of two triple bonds.[16]

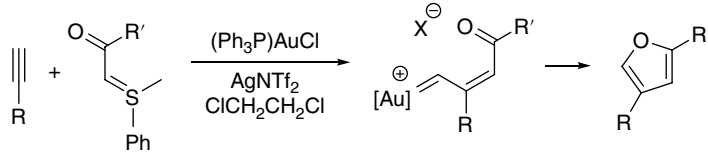


Amphiphilic characters of the C-linked nitrogen atom of an azido group are witnessed in the formal [4+1]cycloaddition with an enyne system.[17] An Au(I)- Pd(0) cocatalyst can promote intramolecular addition of an *N*-allylamino group to an alkyne and subsequent allyl shift to yield cyclic imine bearing a more complex sidechain at the α-carbon.[18]



Alkenyl(*o*-ethynylphenyl)dimethylsilanes are subject to intramolecular 1,1-addition, furnishing 2-alkenylbenzosiloles.[19] Group migration is also featured in the transformation of conjugated dienynes into substituted benzenes,[20] where the triple bond temporarily behaves as an α-aurio carbene to engage in cyclopropanation. The three-membered ring is then severed and the group migration follows.

Cycloaddition. The types of cycloaddition catalyzed by the Au(I) catalyst are [2+2] version between allenyl silyl ethers and allenylamides with enol ethers,[21] [3+2] version of diaziridines with alkynes to create 3-pyrazolines,[22] α-oxosulfonium ylides with alkynes to form furans.[23] *N*-Oxides of quinoline-4-carboxylic esters are formed via a cycloaddition of nitrosoarenes and 2-diazo-3-butenoic esters.[24]



[1] Pennell, M.N., Turner, P.G., Sheppard, T.D. *CEJ* **18**, 4748 (2012)
[2] Sun, S., Kroll, J., Luo, Y., Zhang, L. *SL* 54 (2012)
[3] Schultz, D.M., Babij, N.R., Wolfe, J.P. *ASC* **354**, 3451 (2012)
[4] Zhang, M., Wang, Y., Yang, Y., Hu, X. *ASC* **354**, 981 (2012)
[5] Kothandaraman, P., Mothe, S.R., Toh, S.S.M., Chan, P.W.H. *JOC* **76**, 7633 (2011)
[6] Qian, D., Zhang, J. *CC* **48**, 7082 (2012)
[7] Wang, Y., Ye, L., Zhang, L. *CC* **47**, 7815 (2011)

[8] Liu, Y., Zhu, J., Qian, J., Xu, Z. *JOC* **77**, 5411 (2012)
[9] Liu, L., Zhang, L. *ACIE* **51**, 7301 (2012)
[10] Hashmi, A.S.K., Yang, W., Rominger, F. *ASC* **354**, 1273 (2012)
[11] Chaladaj, W., Corbet, M., Fürstner, A. *ACIE* **51**, 6929 (2012)
[12] Bihelovic, F., Saicic, R.N. *ACIE* **51**, 5687 (2012)
[13] Shu, C., Liu, M.-Q., Sun, Y.-Z., Ye, L.-W. *OL* **14**, 4958 (2012)
[14] Wang, Y., Ji, K., Lan, S., Zhang, L. *ACIE* **51**, 1915 (2012)
[15] Shan, Z.-H., Liu, J., Xu, L.-M., Tang, Y.-F., Chen, J.-H., Yang, Z. *OL* **14**, 3712 (2012)
[16] Ye, L., Wang, Y., Aue, D.H., Zhang, L. *JACS* **134**, 31 (2012)
[17] Yan, Z.-Y., Xiao, Y., Zhang, L. *ACIE* **51**, 8624 (2012)
[18] Wu, H., He, Y.-P., Gong, L.-Z. *ASC* **354**, 975 (2012)
[19] Matsuda, T., Yamaguchi, Y., Shigeno, M., Sato, S., Murakami, M. *CC* **47**, 8697 (2011)
[20] Garcia-Garcia, P., Martinez, A., Sanjuan, A.M., Fernandez-Rodriguez, M.A., Sanz, R. *OL* **13**, 4970 (2011)
[21] Suarez-Pantiga, S., Hernandez-Diaz, C., Piedrafita, M., Rubio, E., Gonzalez, J.M. *ASC* **354**, 1651 (2012)
[22] Capretto, D.A., Brouwer, C., Poor, C.B., He, C. *OL* **13**, 5842 (2011)
[23] Kramer, S., Skrydstrup, T. *ACIE* **51**, 4681 (2012)
[24] Pagar, V.V., Jadhav, A.M., Liu, R.-S. *JACS* **133**, 20728 (2011)

Graphite oxide

Dehydrogenation and oxidation. Graphite oxide has found use in oxidation of alcohols to carbonyl compounds under ultrasonication.[1] Aromatization of tetrahydroquinoline, dihydrobenzofuran, arylcyclohexanes, 1,2,3,6-tetrahydrobenzaldehyde, and the like is accomplished on treatment with graphite oxide and 4Å-molecular sieves.[2]

A sequential condensation and aromatization converts 2-acylanilines and benzylamines into 2-arylquinazolines. The reaction employs graphite oxide and *t*-BuOOH.[3]

Rapid conversion of thiols to disulfides and sulfides to sulfoxides by graphite oxide has been observed.[4]

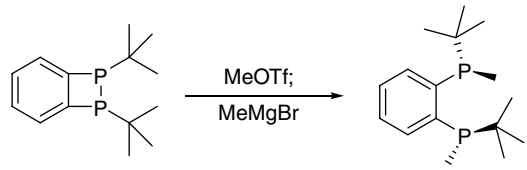
[1] Mirza-Aghayan, M., Kashef-Azar, E., Boukherroub, R. *TL* **53**, 4962 (2012)
[2] Zhang, X., Xu, L., Wang, X., Ma, N., Sun, F. *ChJC* **30**, 1525 (2012)
[3] Karnakar, K., Kumar, A.V., Murthy, S.N., Ramesh, K., Nageswar, Y.V.D. *TL* **53**, 4613 (2012)
[4] Dreyer, D.R., Jia, H.-P., Todd, A.D., Geng, J., Bielawski, C.W. *OBC* **9**, 7292 (2011)

Grignard reagents

Preparation. Arylmagnesium chloride-lithium complexes are obtained by the exchange reaction of ArX with *i*-PrMgCl·LiCl, the relative rates of exchange are 10^{11} (for X=I): 10^6 (for X=Br): 1 (for X=Cl).[1] One new way to prepare RCH_2CH_2MgX starts from hydroboration of 1-alkenes and followed by B/Mg exchange using $XMg(CH_2)_nMgX$.[2]

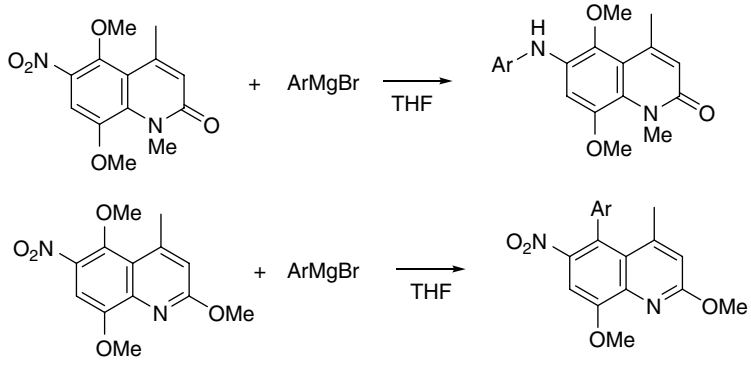
For access to 2-pyridylmagnesium halides the exchange agent is prepared from *n*-BuMgCl, TADDOL and then adding BuLi.[3] The direct method (2-PyCl + Mg in THF) is benefited by irradiation with microwaves of low field strength (high field strength microwaves tend to suppress Mg insertion).[4]

Substitution. Large scale preparation of important phosphine ligands such as BrettPhos and RockPhos safely is through reaction of the biaryls with Mg and then with R_2PCl in the presence of catalytic CuCl.[5] It is definitely more advantageous than the procedure employing *t*-BuLi and stoichiometric copper salt. The following equation depicts a route to another diphosphine ligand using a Grignard reagent.[6]



α-Alkoxyphosphonium salts and ArMgBr react under dry oxygen.[7] A C-P bond is replaced by a C-C bond. However, C-heteroatom bonds can also be created in reactions with Grignard reagents: organoboronate formation from dioxaborolanes or dioxaborinanes,[8] Aryl sulfides from RSCl,[9] but particularly $RSCF_3$ from $PhN(SCF_3)Me$.[10]

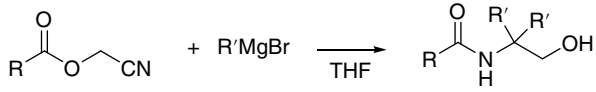
The nitro group of 2-nitropyridine *N*-oxide is replaced on reaction with RMgX.[11] A change of chemoselectivity as influenced by the nature of a neighboring heterocycle is evident in the following equations.[12]



The hydroxyl group of 2-(α-hydroxyalkyl)acrylonitriles directs its own departure, as a cyclic transition state is adopted in the displacement.[13]

Addition. It has been shown that ArMgBr attacks isocyanides in preference to a carbonyl group.[14] By employment of a Grignard reaction to acquire hindered amides is illustrated by the addition of mesitylmagnesium bromide to *t*-butyl isocyanate.[15]

Cyanomethyl carboxylates are attacked at the CN group, formation of amide products indicates an O-to-N transacylation after the addition.[16]

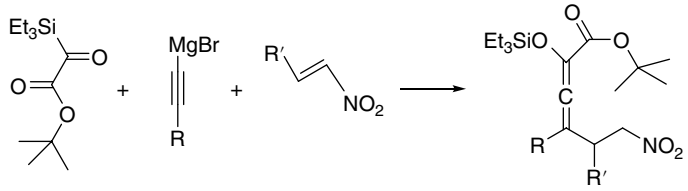


Grignard reagents add twice to the nitrogen atom of α-alkoxyimino esters, resulting in the formation of *N,N*-disubstituted α-amino esters.[17] From imino esters a two-stage addition, first by $PhMe_2SiLi$ and then RMgX, gives rise to α-silyl amines.[18] *N*-(*t*-Butyl) nitrones are alkynylated by alkynylmagnesium chlorides such that the functional group is retained when the reaction is carried out in the presence of TEMPO under oxygen.[19]

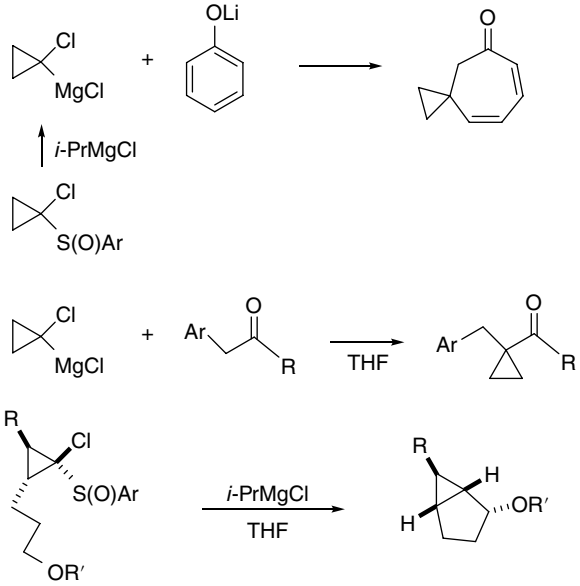
A stable solid 1:2-adduct of DABCO and SO_2 can be employed for synthesis of sulfonamides. It is more expedient to mix RMgX with DABCO and SO_2Cl_2 at low temperatures, then quench the reaction mixture with amines.[20]

Oxazole-3-carboxylic esters behave in the same manner as the imidazole analogs, because the tetrahedral adducts are stabilized (Mg atom coordinated to the nuclear nitrogen atom), ketones are obtained on workup.[21] The addition of RMgX to C-2 of 3-acylindoles[22] perhaps is due to rapid generation of the imino enolates.

Silyloxalic esters condense with alkynylmagnesium bromides and nitroalkenes to form 2-siloxy-2,3-alkadienoic esters substituted at C-4 with a nitroalkyl chain.[23] The result is rationalized in terms of addition to the C=O and a Brook rearrangement that is followed by a conjugate addition.

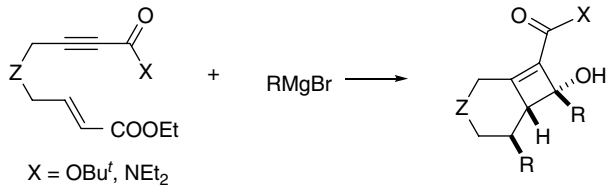


It is said that Grignard reaction on a furyl ketone facilitates an intramolecular Diels-Alder reaction (of the furan nucleus) with an alkyne due to chelation of the Mg alkoxide unit.[24] Unusual results are found in the reaction of 1-chlorocycloalkylmagnesium chlorides with lithium phenolate.[25] Insertion reactions of a cyclopropyl unit into benzyl ketones[26] and an α-CH bond of an ether[27] are also remarkable.



The adducts of allyl- and cinnamylmagnesium bromides with α-halo carbonyl compounds the adducts do not survive. An ensuing intramolecular S_N2 reaction turns them into epoxides.[28] A similar transformation is witnessed from the corresponding reaction with the organozinc reagents.[29]

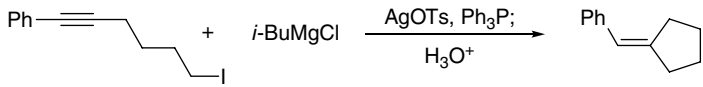
3,4-Dialkoxy-1,2-cyclobutenones add two equivalents of vinylmagnesium bromide, highly functionalized 1,2-cyclopentanediones are produced.[30] A 1,6-alkenyne with each unsaturated terminus bearing an electron-withdrawing group (e.g., ester) suffers Michael attack by RMgX. In turn the ester enolate adds across the triple bond and it continues a course of Dieckmann cyclization (cyclobutenone formation). Finally another Grignard reaction occurs.[31]



The addition of ArMgCl to *t*-butyl azodicarboxylate translates to a new approach to Fischer indole synthesis.[32]

Coupling. Without added transition metal catalysts, ArMgBr and Ar′X (X = Br, I) couple in hot toluene containing a small amount of THF.[33] It is speculated that the reaction proceeds via an $S_{RN}1$ mechanism.

Ethynylarenes and triorganosilylethynes are carbomagnesiated by a mixture of RX, *i*-BuMgCl and the AgOTs – Ph_3P catalyst to generate internal alkenylmagnesium chlorides, which can be trapped by electrophiles. 1-Phenyl-6-iodo-1-hexyne undergoes cyclization.[34]



The Grignard reaction on acid chlorides can be stopped at producing ketones when DMF or *N*-methylpyrrolidone is added to the reaction medium.[35]

[1] Shi, L., Chu, Y., Knochel, P., Mayr, H. *OL* **14**, 2602 (2012)
[2] Reichle, M.A., Breit, B. *ACIE* **51**, 5730 (2012)
[3] Catel, D., Chevallier, F., Mongin, F., Gros, P.C. *EJOC* 53 (2012)
[4] Gutmann, B., Schwan, A.M., Reichart, B., Gspan, C., Hofer, F., Kappe, C.O. *ACIE* **50**, 7636 (2011)
[5] Hoshiya, N., Buchwald, S.L. *ASC* **354**, 2031 (2012)
[6] Reynolds, S.C., Hughes, R.P., Glueck, D.S., Rheingold, A.L. *OL* **14**, 4238 (2012)
[7] Fujioka, H., Goto, A., Otake, K., Kubo, O., Sawama, Y., Maegawa, T. *CC* **47**, 9894 (2011)
[8] Myslinska, M., Heise, G.L., Walsh, D.J. *TL* **53**, 2937 (2012)
[9] Cheng, J.-H., Ramesh, C., Kao, H.-L., Wang, Y.-J., Chan, C.-C., Lee, C.-F. *JOC* **77**, 10369 (2012)
[10] Baert, F., Colomb, J., Billard, T. *ACIE* **51**, 10382 (2012)
[11] Wang, L., Shao, Y., Liu, Y. *OL* **14**, 3978 (2012)
[12] Sanchez, J.D., Egris, R., Perumal, S., Villacampa, M., Menendez, J.C. *EJOC* 2375 (2012)
[13] Fleming, F.F., Liu, W., Yao, L., Pitta, B., Purzycki, M., Ravikumar, P.C. *EJOC* 6843 (2011)

[14] Kobayashi, K., Kozuki, T., Konishi, M., Suzuki, T., Tanmatsu, M., Konishi, H. *HCA* **95**, 1234 (2012)
[15] Schäfer, G., Matthey, C., Bode, J.W. *ACIE* **51**, 9173 (2012)
[16] Boukattaya, F., Stanovych, A., Setzer, P., Abid, S., Ammar, H., Pearson-Long, M.S.M., Bertus, P. *CC* **48**, 8655 (2012)
[17] Mizutani, Y., Tanimoto, H., Morimoto, T., Nishiyama, Y., Kakiuchi, K. *TL* **53**, 5903 (2012)
[18] Han, X.-J., Yao, M., Lu, C.-D. *OL* **14**, 2906 (2012)
[19] Murarka, S., Studer, A. *ASC* **353**, 2708 (2011)
[20] Woolven, H., Gonzalez-Rodriguez, C., Marco, I., Thompson, A.L., Willis, M.C. *OL* **13**, 4876 (2011)
[21] Murai, K., Miyazaki, S., Fujioka, H. *TL* **53**, 3746 (2012)
[23] Boyce, G.R., Liu, S., Johnson, J.S. *OL* **14**, 652 (2012)
[24] Chen, Y., Wang, L., Liu, Y., Li, Y. *CEJ* **17**, 12582 (2011)
[25] Satoh, T., Kimura, T., Sasaki, Y., Nagamoto, S. *S* 2091 (2012)
[26] Satoh, T., Kashiwamura, G., Nagamoto, S., Sasaki, Y., Suginome, S. *TL* **52**, 4468 (2011)
[27] Satoh, T., Tsuru, T., Ikeda, S., Miyagawa, T., Momochi, H., Kimura, T. *T* **68**, 1071 (2012)
[28] Fan, L., Zhang, M., Zhang, S. *OBC* **10**, 3182 (2012)
[29] Pan, J., Zhang, M., Zhang, S. *OBC* **10**, 1060 (2012)
[30] Varea, T., Alcalde, A., de Dicastillo, C.L., de Arellano, C.R., Cossio, F.P., Asensio, G. *JOC* **77**, 6327(2012)
[31] Hata, T., Imade, H., Urabe, H. *OL* **14**, 2450 (2012)
[32] Inman, M., Carbone, A., Moody, C.J. *JOC* **77**, 1217 (2012)
[33] Shirakawa, E., Hayashi, Y., Itoh, K., Watabe, R., Uchiyama, N., Konagaya, W., Masui, S., Hayashi, T. *ACIE* **51**, 218 (2012)
[34] Kambe, N., Moriwaki, Y., Fujii, Y., Iwasaki, T., Terao, J. *OL* **13**, 4656 (2011)
[35] Gowda, M.S., Panda, S.S., Ramakrishna, R.A., Prabhu, K.R. *OBC* **9**, 5365 (2011)

Grignard reagents/cobalt(II) salts

Alkylation and alkenylation. *o*-Alkylation of aryl ketones by 1-alkenes is enabled by conversion of the ketone group into an imine and then the reaction is carried out with Me_3SiCH_2MgBr – $CoBr_2$, and a phenanthroline ligand.[1]

Introduction of an alkenyl sidechain to C-2 of indoles requires NH protection. A method involves the *N*-(pyramid-2-yl) derivatives (the protecting group is eventualy removed from the products is by treatment with NaOEt in DMSO), and the reaction with alkynes is promoted by *t*-$BuCH_2MgBr$ – $CoBr_2$ and a *P,N*-ligand.[2]

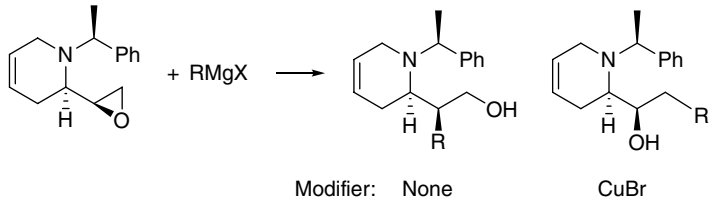
[1] Gao, K., Yoshikai, N. *ACIE* **50**, 6888 (2011)
[2] Ding, Z., Yoshikai, N. *ACIE* **51**, 4698 (2012)

Grignard reagents/copper salts

Substitution. Secondary and tertiary alkylmagnesium halides couple with RX in the presence of CuCl.[1] Assistance of CuI (and butadiene or TMEDA) maximizes the efficiency of coupling with secondary alkyl halides,[2,3] and the displacement of an *N*-tosylamino group from an alkyl residue by RMgX also benefits from CuI additive.[4]

N-Methylation facilitates aziridine opening by RMgX – CuI, the regioselectivity of which is strongly dependent on the existing substituent at C-2.[5]

Regiochemical switch in opening an epoxide by RMgX on addition of CuBr is noteworthy.[6]

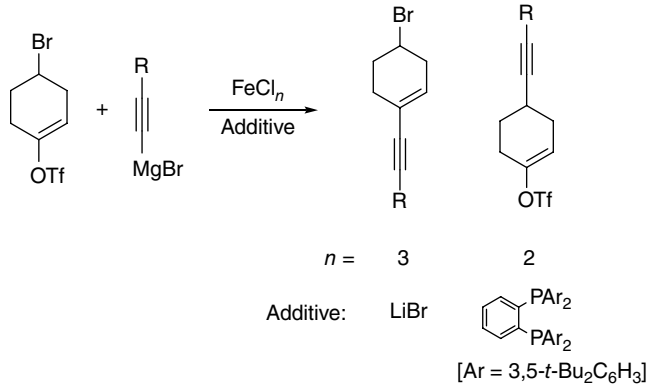


Conjugate addition. With CuCl as catalyst, RMgCl adds to 2,3-butadienoic esters at C-3.[7]

[1] Ren, P., Stern, L.-A., Hu, X. *ACIE* **51**, 9110 (2012)
[2] Shen, R., Iwasaki, T., Terao, J., Kambe, N. *CC* **48**, 9313 (2012)
[3] Yang, C.-T., Zhang, Z.-Q., Liang, J., Liu, J.-H., Lu, X.-Y., Chen, H.-H., Liu, L. *JACS* **134**, 11124 (2012)
[4] Li, M.-B., Tang, X.-L., Tian, S.-K. *ASC* **353**, 1980 (2011)
[5] Yoon, D.-H., Kang, P., Lee, W.K., Kim, Y., Ha, H.-J. *OL* **14**, 429 (2012)
[6] Gálvez, J.A., de Villegas, M.D.D., Badorrey, R., López-Ram-de-Viu, P. *OBC* **9**, 8155 (2011)
[7] He, J., Lu, Z., Chai, G., Fu, C., Ma, S. *T* **68**, 2719 (2012)

Grignard reagents/iron salts

Substitution. All sorts of aliphatic chlorides (including 1-chloroadamantane) couple with ArMgBr, and of ArCl with RCH_2MgCl using $FeCl_3$ (and an imidazolium chloride) as catalyst.[1,2] Besides the sp^3-sp^3 version, RMgX and alkenyl halides combine to make alkenes, although iron(II) naphthalene-2-thiolate[3] or the $FeCl_3$-Cu(I) 2-thiophenecarboxylate cocatalyst system[4] for promotion is indicated. Option for sp-sp^2 or sp-sp^3 coupling is left open, achievable by tuning the iron catalyst.[5] Of course there is no problem in derivatizing 2-chloroquinoline into 2-arylquinolines.[6]

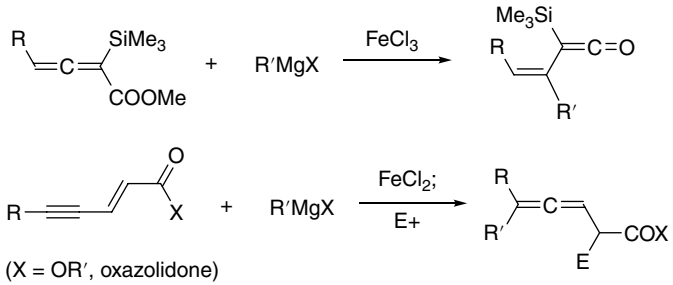


The scope of coupling is extended further by demonstrating the viability of $ArOSO_2NMe_2$ and $ArOCONEt_2$ in the reaction with RMgCl.[7] Coupling between ArMgBr and Ar′NHZnCl proceeds by catalysis of $Fe(acac)_3$ and in the presence of $Me_2C(Cl)CH_2Cl$.[8]

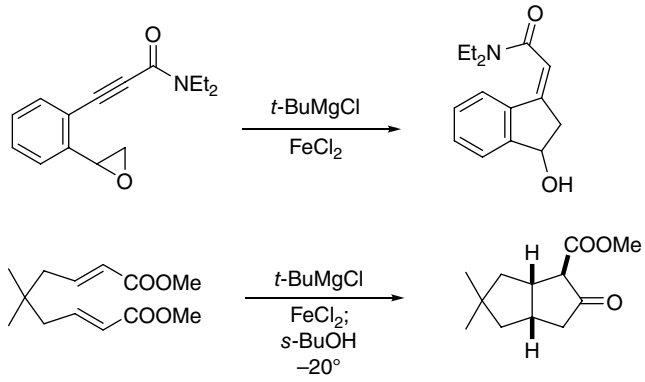
Chain elongation from 1-haloalkenes with saturation of the double bond is executed by Grignard reagents, Me_2NBH_3Li, and $FeCl_2$ that is ligated by a tetradentate imine ligand.[9]

Addition. Stilbenylmagnesium halides are available from hydromagnesiation of diarylethynes (EtMgX, $FeCl_2$),[10] whereas primary alkylmagnesium bromides are obtained from 1-alkenes using cyclopentylmagnesium bromide and the dual catalyst $FeCl_3$-CuBr with the ligand Bu_3P.[11] The conversion of electron-rich styrenes into α-methylarylacetic acids may actually proceed via hydromagnesiation and carboxylation.[12]

Addition of RMgX to 2-(1,3-alkadienyl)pyridines (catalyst: $FeCl_2$) changes the sidechain to the allyl-type with the R group entered at the far end of the original diene unit.[13] Conjugate addition to methyl 2-trimethylsilyl-2,3-alkadienoates is attended by elimination to form ketenes.[14] However, elimination is not observed in a similar addition to 2-alken-4-ynoic esters.[15]



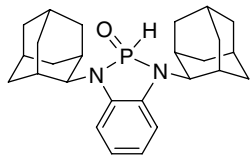
In the presence of $Fe(acac)_3$, 1,10-phenanthroline and $Me_2C(Cl)CH_2Cl$, two equivalents of diphenylethyne are taken up in the reaction with PhMgBr, and the adduct cyclizes to yield 1,2,3,4-tetraphenylnaphthalene.[16] The combination of *t*-BuMgCl and $FeCl_2$ effects hydrometallation of activated multiple bond, carbocyclization follows in molecules that are equipped with interactive functionalities.[17]



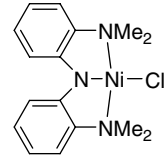
[1] Ghorai, S.K., Jin, M., Hatakeyama, T., Nakamura, M. *OL* **14**, 1066 (2012)
[2] Perry, M.C., Gillett, A.N., Law, T.C. *TL* **53**, 4436 (2012)
[3] Cahiez, G., Gager, O., Buendia, J., Patinote, C. *CEJ* **18**, 5860 (2012)
[4] Hamze, A., Brion, J.-D., Alami, M. *OL* **14**, 2782 (2012)
[5] Hatakeyama, T., Okada, Y., Yoshimoto, Y., Nakamura, M. *ACIE* **50**, 10973 (2011)
[6] Kuzmina, O.M., Steib, A.K., Flubacher, D., Knochel, P. *OL* **14**, 4818 (2012)
[7] Silberstein, A.L., Ramgren, S.D., Garg, N.K. *OL* **14**, 3796 (2012)
[8] Nakamura, Y., Ilies, L., Nakamura, E. *OL* **13**, 5998 (2011)
[9] Le Bailly, B.A.F., Greenhalgh, M.D., Thomas, S.P. *CC* **48**, 1580 (2012)
[10] Ilies, L., Yoshida, T., Nakamura, E. *JACS* **134**, 16951 (2012)
[11] Shirakawa, E., Ikeda, D., Masui, S., Yoshida, M., Hayashi, T. *JACS* **134**, 272 (2012)
[12] Greenhalgh, M.D., Thomas, S.P. *JACS* **134**, 11900 (2012)
[13] Roscales, S., Salado, I.G., Csaky, A.G. *SL* 2234 (2011)
[14] Chai, G., Fu, C., Ma, S. *OL* **14**, 4058 (2012)
[15] Hata, T., Iwata, S., Seto, S., Urabe, H. *ASC* **354**, 1885 (2012)
[16] Ilies, L., Matsumoto, A., Kobayashi, M., Yoshikai, N., Nakamura, E. *SL* 2381 (2012)
[17] Hata, T., Sujaku, S., Hirone, N., Nakano, K., Imoto, J., Imade, H., Urabe, H. *CEJ* **17**, 14593 (2011)

Grignard reagents/nickel complexes

Coupling. Many combinations of reactants (Grignard reagent and organohalides with respect to the hybridization status of the carbon atoms bonding to either the Mg or X atom) are successfully coupled: ArMgX + Ar′X with $NiCl_2$ and the diaminophosphine oxide **1**,[1] and those involving alkynyl or alkylmagnesium halides in the presence of **2**.[2,3]



(**1**)



(**2**)

Certain phosphine-ligated $NiCl_2$ (or $FeCl_2$) species are capable of inducing coupling of RMgX with $ArCH_2OH$ (involving C-O bond activation).[4]

The coupling of RMgBr with ArF, conducted in the presence of (tmeda)$ZnCl_2$,[5] likely proceeds via Mg/Zn exchange prior to intervention of the Ni(II) species. *N*-Arylation of anilines by PhMgBr and catalyzed by $Ni(acac)_2$ in DMPU seems to require the additive $Me_2C(Cl)CH_2Cl$.[6]

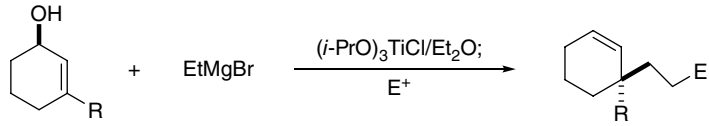
Substitution. The Ni(II)-mediated reaction of RMgBr with 1-bromo-2-alkynes furnishes 1,1-disubstituted 1,2-propadienes, evidently the result of a S_N2' process.[7] A dramatic solvent effect is noted in the NiI_2-catalyzed reaction of RMgBr with α-methyl benzyl tolyl sulfones, and with $ArCOCH_2Ts$, in that THF causes formation of styrenes in the former case and substitution of the Ts group (instead of attacking the carbonyl group).[8]

Oxidative coupling is observed in the Grignard reaction of certain heterocycles (purines, imidazole, thiazole) while catalyzed by (dppp)$NiCl_2$.[9,10]

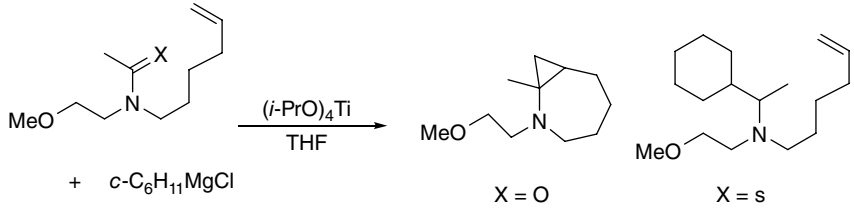
[1] Jin, Z., Li, Y.-J., Ma, Y.-Q., Qiu, L.-L., Fang, J.-X. *CEJ* **18**, 446 (2012)
[2] Vechorkin, O., Godinat, A., Scopelliti, R., Hu, X. *ACIE* **50**, 11777 (2011)
[3] Garcia, P.M.P., Di Franco, T., Orsino, A., Ren, P., Hu, X. *OL* **14**, 4286 (2012)
[4] Yu, D.-G., Wang, X., Zhu, R.-Y., Luo, S., Zhang, X.-B., Wang, B.-Q., Wang, L., Shi, Z.-J. *JACS* **134**, 14638 (2012)
[5] Nakamura, Y., Yoshikai, N., Ilies, L., Nakamura, E. *OL* **14**, 3316 (2012)
[6] Ilies, L., Matsubara, T., Nakamura, E. *OL* **14**, 5570 (2012)
[7] Li, Q., Gau, H. *SL* 747 (2012)
[8] Wu, J.-C., Gong, L.-B., Xia, Y., Song, R.-J., Xie, Y.-X., Li, J.-H. *ACIE* **51**, 9909 (2012)
[9] Qu, G.-R., Xin, P.-Y., Niu, H.-Y., Wang, D.-C., Ding, R.-F., Guo, H.-M. *CC* **47**, 11140 (2011)
[10] Xin, P.-Y., Niu, H.-Y., Qu, G.-R., Ding, R.-F., Guo, H.-M. *CC* **48**, 6717 (2012)

Grignard reagents/titanium(IV) compounds

Substitution. After *N*-chlorination, amines are arylated by ArMgX in the presence of $(i\text{-PrO})_4Ti$.[1] Allylic alcohols undergo formal S_N2' reaction, and furthermore, using EtMgBr and $(i\text{-PrO})_3TiCl$ the terminus of the newly introduced two-carbon unit can be functionalized (with an electrophile).[2]



Cross coupling between a carbonyl compound and an imine is a way to obtain β-amino alcohols, it can be done with *c*-C_5H_9MgCl and $(i\text{-PrO})_4Ti$.[3] Intramolecular cyclopropanation involving an amidic carbonyl group and an alkene is of obvious synthetic interests.[4] However, the C=S linkage of a thioamide behaves differently (desufurative coupling with the Grignard reagent being preferred).



[1] Barker, T.J., Jarvo, E.R. *ACIE* **50**, 8325 (2011)
[2] Das, P.P., Lysenko, I.L., Cha, J.K. *ACIE* **50**, 9459 (2011)
[3] Fan, G., Liu, Y. *TL* **53**, 5084 (2012)
[4] Augustowska, E., Boiron, A., Deffit, J., Six, Y. *CC* **48**, 5031 (2012)

Grignard reagents/zinc halides

Mg-Zn hybrids. Formation of metallic hybrids is noted in admixture of RMgCl and $ZnCl_2$.[1] With such species the addition to sensitive trifluoroacetophenone presents no problem.

[1] Armstrong, D.R., Clegg, W., Garcia-Alvarez, P., Kennedy, A.R., McCall, M.D., Russo, L., Hevia, E. *CEJ* **17**, 8333 (2011)

Guanidinium nitrate

Diimide. Oxidation of hydrazine in the air is catalyzed by guanidinium nitrate.[1]

[1] Lamani, M., Guralamata, R.S., Prabhu, K.RQ. *CC* **48**, 6583 (2012)

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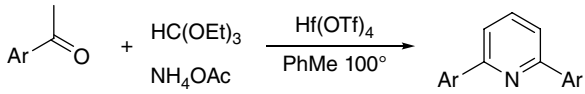
Hafnium chloride

Tetrabenzylhafnium. Prepared from $HfCl_4$, the organohafnium reagent adds to imines.[1]

[1] Mei, H., Ji, X., Han, J., Pan, Y. *EJOC* 5783 (2011)

Hafnium triflate

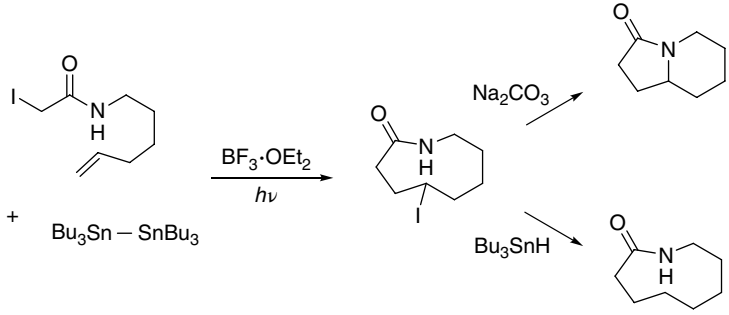
2,6-Diarylpyridines.[1] Formation of pyridine derivatives by condensation of three components has been carried out in the presence of $Hf(OTf)_4$.



[1] Sasada, T., Kobayashi, F., Moriuchi, M., Sakai, N., Konakahara, T. *SL* 2029 (2011)

Hexabutylditin

Cyclization. *N*-(ω-Alkenyl) iodoacetamides undergo atom-transfer cyclization which is mediated by $Bu_3SnSnBu_3$ under uv and catalyzed by $BF_3{\cdot}OEt_2$. The mesocyclic lactams can be deiodinated or further transformed into bicyclic products.[1]



[1] Song, L., Liu, K., Li, C. *OL* **13**, 3434 (2011)

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Hexachlorodisilane

Reduction. Different courses for reduction of P=O and P=S groups, inversion and retention of configuration, respectively, is featured.[1]

[1] Krenske, E.H. *JOC* **77**, 1 (2012)

2,2,4,4,6,6-Hexachlorophosphazene

Alkylidenation. *N,N*-Disubstituted alkanamides react with aldehydes on heating with the chlorinated heterocycle and sulfuric acid to give he conjugated amides.[1]

[1] Foo, S.W., Oishi, S., Saito, S. *TL* **53**, 5445 (2012)

Hexakis[hydrido(triphenylphosphine)copper]

Reduction. Solvent effects are unraveled for selective reduction of the conjugated double bond in 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic esters by $[(Ph_3P)CuH]_6$.[1] While a 86% conversion is observed in THF, only 26% in toluene.

[1] Sass, D.C., Heleno, V.C.G., Cavalcante, S., dBarbosa, J.d.S., Soares, A.C.F., Constantino, M.G. *JOC* **77**, 9374 (2012)

Hexamethylphosphoramide

Modified version. With one of the methyl group of HMPA replaced by a dendritic framework of hyperbranched poly(glycerol), the macromolecular species shows superior activity in promoting allylation of aldehydes with allyltrichlorosilane and the Mukaiyama aldol reaction. Thus, HMPA is practical inactive for bringing about the allylation reaction, a 99% yield of a product is obtained while employing the dendritic version.[1]

[1] Mummy, F., Haag, R. *SL* 2672 (2012)

Hydrogen fluoride

Hydrofluorination. Ynamides are converted to (*E*)-α-fluoroenamides as a result of *cis*-addition of anhydrous HF.[1]

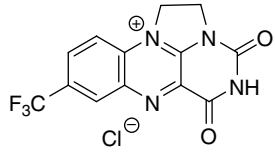
Desilylation. The *O*-silyl group from a piperitol derivative is removed using Bu_4NF and some other reagents proved unsatisfactory, the problem was solved by treatment with the HF-pyridine complex.[2]

β-Fluoro amines. Aziridines are opened by HF complexed to DBN, which is prepared from PhCOF, ROH and DBN.[3]

[1] Compain, G., Jouvin, K., Martin-Mingot, A., Evano, G., Marrot, J., Thibaudeau, S. *CC* **48**, 5196 (2012)
[2] Kreis, L.M., Carreira, E.M. *ACIE* **51**, 3436 (2012)
[3] Kalow, J.A., Schmitt, D.E., Doyle, A.G. *JOC* **77**, 4177 (2012)

Hydrogen peroxide

Oxidation. Activated carbon promotes oxidation of benzylic alcohols by H_2O_2.[1] Aldehydes are converted to carboxylic acids by H_2O_2 in the presence of the flavinium salt **1**.[2]



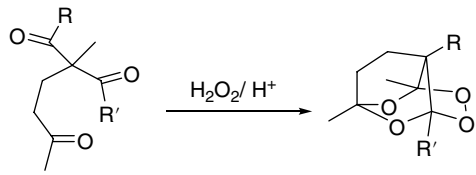
(**1**)

Baeyer-Villiger oxidation of ketones using H_2O_2 depends on the activation of certain quaternarized *N*-heteroaromatics such as 1-ethyl-3-cyanopyrazinium tetrafluoroborate[3] or *N*-methylacridinium perchlorate under uv light.[4] Dakin oxidation that converts ArCHO into ArOH is achieved by H_2O_2 and flavin under weakly basic conditions ($NaHCO_3$, aq. MeOH).[5]

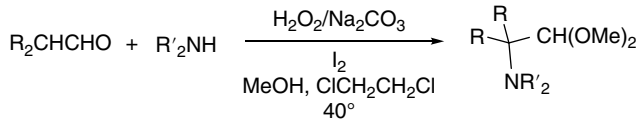
Reaction conditions for *cis*-dihydroxylation with H_2O_2 and TsOH are mild enough to keep groups such as OBz, OTs, OSEM, NBoc, NBz, NFmoc intact.[6] Dihydroxylation of alkenes also can be accomplished with H_2O_2 and catalytic ArI in HOAc.[7] Another method involves selenium as a catalyst.[8] A cyclic seleninate ester is featured in epoxidation and *S*-oxidation.[9]

To avoid fluoride for oxidative desilylation of $ArSiMe_2H$ (to acquire ArOH), H_2O_2 buffered by $KHCO_3$ can be employed.[10] A combination of H_2O_2 and iodine converts $ArB(OH)_2$ into ArOH.[11]

Reasonably good yields of bridged diperoxides are obtained from triketones in acidic solutions.[12]



Amination. Aldehydes undergo oxidative α-amination quite readily, when iodine is converted into the catalytically active HIO. The formyl group is also acetalized by MeOH.[13]



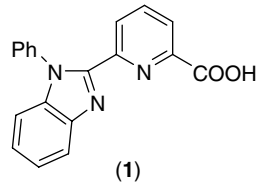
[1] Nishida, S., Hayashi, M. *SL* 1683 (2012)
[2] Murray, A.T., Matton, P., Fairhurst, N.W.G., John, M.P., Carbery, D.R. *OL* **14**, 3656 (2012)
[3] Menova, P., Kafka, F., Dvorakova, H., Gunnoo, S., Sanda, M., Cibulka, R. *ASC* **353**, 865 (2011)
[4] Xu, H.-J., Zhu, F.-F., Shen, Y.-Y., Wan, X., Feng, Y.-S. *T* **68**, 4145 (2012)
[5] Chen, S., Hossain, M.S., Foss Jr, F.W. *OL* **14**, 2806 (2012)
[6] Rosatella, A.A., Afonso, A.M., *ASC* **353**, 2920 (2011)
[7] Zhong, W., Liu, S., Yang, J., Meng, X., Li, Z. *OL* **14**, 3336 (2012)
[8] Santi, C., Di Lorenzo, R., Tidei, C., Bagnoli, L., Wirth, T. *T* **68**, 10530 (2012)
[9] Mercier, E.A., Smith, C.D., Parvez, M., Back, T.G. *JOC* **77**, 3508 (2012)

[10] Rayment, E.J., Summerhill, N., Anderson, E.A. *JOC* **77**, 7052 (2012)
[11] Gogoi, A., Bora, U. *SL* 1079 (2012)
[12] Terent'ev, A.O., Yaremenko, I.A., Chernyshev, V.V., Dembitsky, V.M., Nikishin, G.I. *JOC* **77**, 1833 (2012)
[13] Tian, J.-S., Ng, K.W.J., Wong, J.-R., Loj, T.-P. *ACIE* **51**, 9105 (2012)

Hydrogen peroxide - metal catalysts

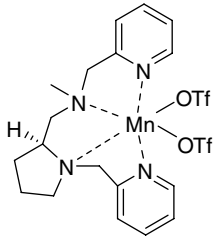
gem-Dihydroperoxides. Both $ZnCl_2$ and $Bi(OTf)_3$ are effective for catalyzing the conversion of ketones to dihydroperoxides.[1,2]

Oxidation. New variants of procedures for the oxidation of benzylic alcohols by H_2O_2 include $FeCl_2$ ligated to **1**.[3] On employing $ZnBr_2$ and CF_3COOH, there is an option of extending the oxidation further to give esters by carrying the reaction in MeOH instead of THF. [4]

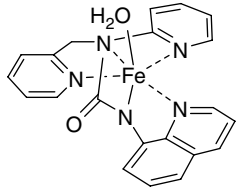


(**1**)

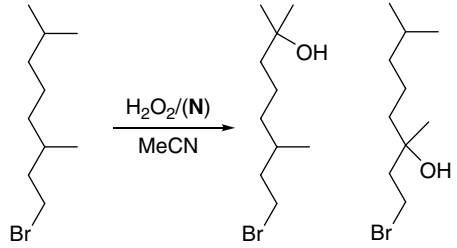
Oxidation at a C-H bond is represented by converting $ArCH_2R$ to ArCOR. The system containing H_2O_2, $ZnBr_2$, CF_3COOH in dioxane is effective.[5] Less common is the direct oxidation of arenes to phenols, but with $VO(acac)_2$ embedded in mesoporous organosilica as catalyst the reaction is realized.[6] However, far more interesting is the hydroxylation of tertiary aliphatic C-H bonds, especially with high regioselectivity.[7,8]



(**2**)



(**3**)



(**2**) (97 : 1)
(**3**) (15 : 1)

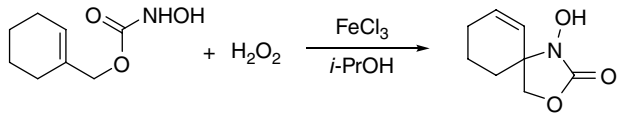
Epoxidation of alkenes with H_2O_2 has the option of choosing several metal salts and complexes: Iron with the *N,N′*-(bis-2-pyridyl) -2,2′- bipiperidine ligand,[9] a tetranuclear peroxotungstate which exerts a dramatically enhanced activity,[10] and a simple Na_2WO_4 in combination with an ammonium surfactant and phosphonic acid,[11] whereas in the epoxidation of terpenes a salt effect has been noted. Homoallylic alcohols are epoxidized by H_2O_2 catalyzed by methyltrioxorhenium ligated with 3-methylpyrazole.[12]

1,2-Dihydroxylation with catalytic Os(III) complex which contains the tris(2-pyridylmethyl)amine ligand shows high turnover.[13] This method does away the volatile and toxic OsO_4.

Conditions for double bond cleavage by catalytic OsO_4 (0.01 equiv.) and 50% H_2O_2 have been established.[14]

Oxidation at heteroatoms. For catalytic oxidation of sulfides to sulfoxides using H_2O_2, nano-Fe_2O_3 supported on SBA-15 has been evaluated.[15] Cleavage of dithioacetals via *S*-oxidation, metal catalyst $NbCl_5$ or $TaCl_5$ is active.[16]

N-Hydroxy carbamates are susceptible to oxidation into the alkoxylated nitroso compounds. Setting up such an unstable functionality for an intramolecular nitroso-ene reaction accomplishes an allylic amination.[17]



Introduction of a CF_3 group into 1,3-dicarbonyl compounds succeeds under an oxidative condition (H_2O_2, $FeSO_4$, DMSO).[18] It seems possible that oxidation at the iodine activates CF_3I toward participating in the reaction.

The oxidation catalyst system composed of nano-RuO_2 and H_2O_2 mimics the reactivity of catalases and peroxidases. For example, it promotes oxidation of 4,4'-diaminobiaryls to the biquinonediimines.[19]

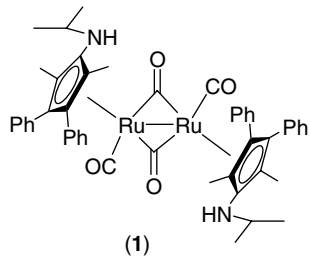
Tungsten and zinc oxides on SnO_2 constitute a reusable catalyst for oxidation of a wide range of compounds that include alkenes, sulfides and amines.[20]

[1] Khosravi, K., Kazemi, S. *JCCS* **59**, 641 (2012)
[2] Sashidhara, K.V., Avula, S.R., Singh, L.R., Palnati, G.R. *TL* **53**, 4880 (2012)
[3] Join, B., Möller, K., Ziebart, C., Schröder, K., Gördes, D., Thurow, K., Spannenberg, A., Junge, K., Beller, M. *ASC* **353**, 3023 (2011)
[4] Wu, X.-F. *CEJ* **18**, 8912 (2012)
[5] Wu, X.-F. *TL* **53**, 6123 (2012)
[6] Borah, P., Ma, X., Nguyen, K.T., Zhao, Y. *ACIE* **51**, 7756 (2012)
[7] Ottenbacher, R.V., Samsonenko, D.G., Talsi, E.P., Bryliakov, K.P. *OL* **14**, 4310 (2012)
[8] Hitomi, Y., Arakawa, K., Funabiki, T., Kodera, M. *ACIE* **51**, 3448 (2012)
[9] Mikhalyova, E.A., Makhlynets, O.V., Palluccio, T.D., Filatov, A.S., Rybak-Akimova, E.V. *CC* **48**, 687 (2012)
[10] Ishimoto, R., Kamata, K., Mizuno, N. *ACIE* **51**, 4662 (2012)

[11] Hachiya, H., Kon, Y., Ono, Y., Takumi, K., Sasagawa, N., Ezaki, Y., Sato, K. *SL* 2819 (2011)
[12] Yamazaki, S. *JOC* **77**, 9884 (2012)
[13] Sugimoto, H., Kitayama, K., Mori, S., Itoh, S. *JACS* **134**, 19270 (2012)
[14] Hart, S.R., Whitehead, D.C., Travis, B.R., Borhan, B. *OBC* **9**, 4741 (2011)
[15] Rajabi, F., Naserian, S., Primo, A., Luque, R. *ASC* **353**, 2060 (2011)
[16] Kirihara, M., Noguchi, T., Okajima, N., Naito, S., Ishizaka, Y., Harano, A., Tsukiji, H., Takizawa, R. *T* **68**, 1515 (2012)
[17] Atkinson, D., Kabeshov, M.A., Edgar, M., Malkov, A.V. *ASC* **353**, 3347 (2011)
[18] Ohtsuka, Y., Uraguchi, D., Yamamoto, K., Tokuhisa, K., Yamakawa, T. *T* **68**, 2636 (2012)
[19] Deng, H., Shen, W., Peng, Y., Chen, X., Yi, G., Gao, Z. *CEJ* **18**, 8906 (2012)
[20] Kamata, K., Yonehara, K., Sumida, Y., Hirata, K., Nojima, S., Mizuno, N. *ACIE* **50**, 12062 (2011)

Hydrosilanes

Reduction and hydrosilylation. More catalyst systems have been examined for hydrosilylation of carbonyl compounds: with poly(methylhydrosilane), $Bu_4N[Fe(CO)_3(NO)]$ and Cy_3P,[1] Pd-on-magnetite,[2] as well as $Fe(OAc)_2$ – BuLi in an ionic liquid.[3] Selective hydrosilylation of keto aldehydes to yield keto silyl ethers is achieved with Et_3SiH in the presence of the dinuclear Ru complex **1** under irradiation (30 W lamp).[4]

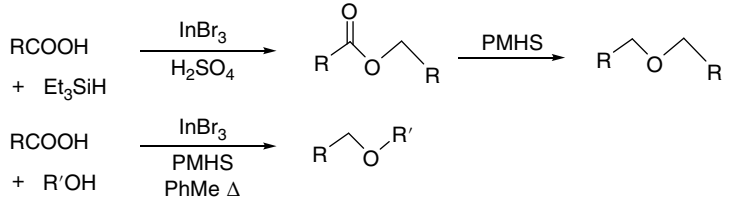


(**1**)

There have been attempts at acquiring chiral secondary silyl ethers from aryl ketones [$PhSiH_3$, $Fe(acac)_2$], but using a chiral diamine ligand led to rather poor (37% ee) results.[5]

By adjustment of reaction conditions a carboxylic acid can be reduced to either the aldehyde [$(Me_2SiH)_2O$, PhCH=CHCOMe/$Fe(CO)_3$] or the alcohol stage [$PhSiH_3$/(cod)$Fe(CO)_3$,[6] or $Me_2SiH)_2O$ / $Cu(OTf)_2$[7]] Succinic and glutaric acids furnish tetrahydrofuran and tetrahydropyran derivatives, respectively, on being subjected to treatment with [$(Me_2SiH)_2O$ (catalyst: $InBr_3$)].[8] With $(dba)_2Pd$ and Mes_3P as catalyst the reduction of RCOCl by Et_3SiH is straightforward.[9] The catalyst system that includes $(Ph_3P)_2PdCl_2$ promotes reduction of alkenes and defunctionalization of ArCOCl.[10]

Ester reduction to primary alcohols can be carried out with $(Me_2SiH)_2O$ / $MoO_2(acac)_2$,[11] or without solvent $PhSiH_3$/$[CpFe(CO)_2PCy_3]BF_4$.[12] From other conditions , ethers are produced: $(Me_2SiH)_2O/Fe_3(CO)_{12}$,[13]. Actually both symmetrical and unsymmetrical ethers from carboxylic acids are prepared in two consecutive reactions.[14,15]

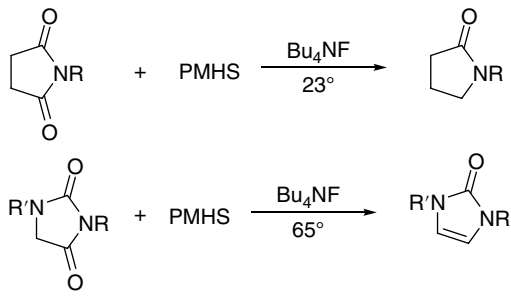


The stereoselective conversion of *cis*-1,7-diphenylheptane-3,5-diol-1,7-dione to diospongin-A relies on hydride delivery directed by an axial hydroxyl group to an incipient oxonium ion.[16]

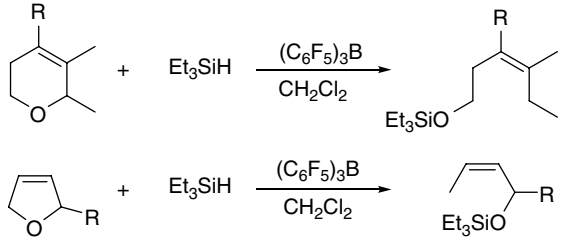
Hydrosilylation of 1-alkynes catalyzed by nano-Au/TiO_2 furnishes (*E*)-1-silylalkenes and some 1,2-disilylated products.[17]

Amide formation and reduction. Carboxylic acids and organoazides combine to yield secondary amides through a Staudinger reaction, in which Ph_3P is recycled in situ with the aid of $PhSiH_3$.[18]

Carboxamides usually undergo reduction to the corresponding amines, e.g., with $(EtO)_2Si(Me)H/Zn(OAc)_2$,[19] $(EtO)_2Si(Me)H/Fe(OAc)_2$ – $(Et_3NH)[HFe_3(CO)_{11}]$ and a phenanthroline,[20] or poly(methylhydrosilane)/$(i\text{-PrO})_4Ti$.[21] One of the carbonyl groups of succinimides suffer deoxygenation, but imidazolidine-2,4-diones furnish imidazolinones.[22]



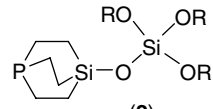
Other deoxygenation motifs. Allylic and propargylic alcohols are deoxygenated by Et_3SiH in the presence of a heteropoly acid catalyst,[23] or $Ca(NTf_2)_2$ and $Bu_4N(PF_6)$,[24] benzylic deoxygenation with PMHS is catalyzed by $FeCl_3$.[25] Reductive cleavage of cyclic allyl ethers is rather intriguing as the two examples shown below show different chemoselectivity.[26]



The ROH to RBr transformation based on reaction with a mixture of Ph_2SiH_2, *P*-phenyldibenzophosphole, and $BrCH(COOEt)_2$ is probably of little synthetic value.[27] On the other hand, transformation of carboxylic acids into RCH_2X (X= Br, SR′) with reagents such as Me_3SiBr[28] and R′SH[29] and indium(III) halide promotion has also been demonstrated. For direct preparation of ethers, thioethers, sulfonamides, etc. from carbonyl compounds, hydrosilylation is followed by in situ trapping under acidic conditions (Et_3SiH, TfOH, $MeNO_2$).[30]

Carbonyl compounds are found to undergo cross-coupling with diazoalkanes under the influence of PMHS, (tcp)FeCl, and a polyethylene-supported arsine.[31] Formation of the (*E*)-isomers is strongly favored.

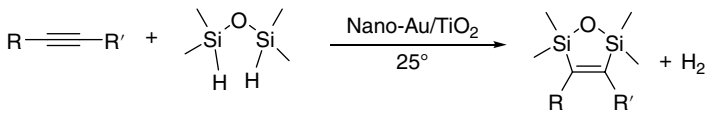
Addition. For saturation of an enone double bond (via conjugate hydrosilylation) with PMHS as catalyzed by $Cu(OAc)_2$, the metal ion is stabilized by the silica-supported phosphine **2**.[32] Alternatively, the catalyst system consists of $Bi(OTf)_3$ and malonitrile.[33]



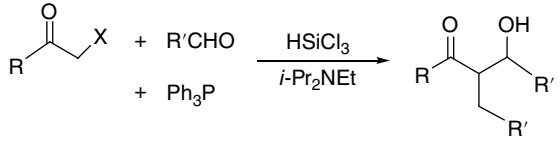
(**2**)

anti-Markovnikov hydration of 1-alkenes via a free-radical process enlists $HSiCl_3$ and Et_3B, and after the addition it requires workup with KF and H_2O_2.[34] Hydrosulfenylation of alkenes with $ArSO_2SR$ and $PhSiH_3$ proceeds in the Markovnikov sense, a Co(II) complex is also involved.[35]

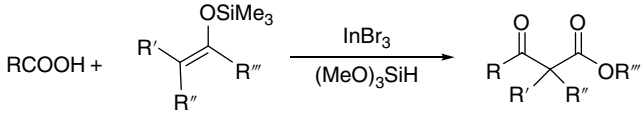
Quite remarkable is the dehydrogenative cycloaddition between $(Me_2SiH)_2O$ and alkynes catalyzed by nano-Au/TiO_2.[36]



Condensation. 1-Halo-2-alkanones and aldehydes furnish aldol products in which one aldehyde molecule is completely reduced.[37] Actually a Wittig reaction is involved, which is followed by reduction and aldol reaction. It is pleasing to observe that Ph_3PO generated in situ acts as a catalyst for the last step.

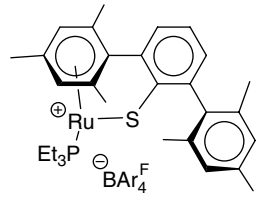


Acylation with carboxylic acids[38] and the formation of aldols from esters and enol silyl ethers[39] are new developments.



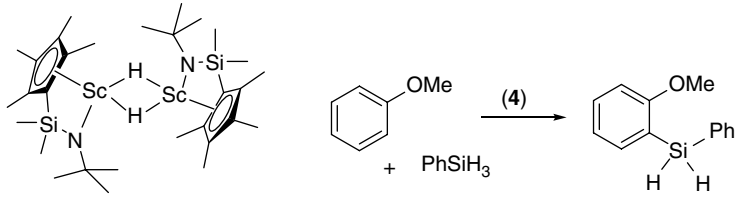
Silylation. Dehydrosilylation of indoles (at the nitrogen atom) and 1-alkynes are carried out with a hydrosilane in a nitrile solvent. Pyridine accelerates the reaction catalyzed by $Zn(OTf)_2$.[40] It is also found that $Rh_2(OAc)_4$ is catalytically active.[41] Formation of silylamines $R_2NSi(Ar)H_2$ is also catalyzed by a bis(silyl)ytterbium complex (azolecarbene).[42]

Enolsilylation of ketones by $PhSi(Me_2)H$ proceeds without base when the Ru complex **3** is used as catalyst.[43] Reductive enolization of ArCH=CHCOCOOEt with Et_3SiH, $InCl_3$, CF_3COOH in toluene affords $ArCH_2CH=C(OSiEt_3)COOEt$ at room temperature.[44]



(**3**)

Aryl ethers are *o*-silylated with a hydrosilane and a scandium complex (**1**) as catalyst.[45]



(**4**)

Reductive cleavage. Deoxygenation of phosphine oxide by hydrosilanes is facile [e.g., employing $(Me_2SiH)_2O$ / $InBr_3$[46] or $Cu(OTf)_2$[47]]. The use of a hydrosilane to recycle

the phosphine in the Staudinger reaction of RN_3 is advantageous as production of stoichiometric quantities of a phosphine oxide is avoided.[48]

Sulfides suffer C-S bond cleavage in a Ni(0)-catalyzed process. Both dialkyl sulfides and aryl sulfides are affected (e.g., ArSMe to ArH and $ArCH_2SMe$ to $ArCH_3$).[49] For partial defluorination of polyfluoroarenes with a hydrosilane, xantphos-ligated AuCl plays a catalytic role.[50]

[1] Dieskau, A.P., Begouin, J.-M., Plietker, B. *EJOC* 5291 (2011)
[2] Cano, R., Yus, M., Ramon, D.J. *T* **67**, 8079 (2011)
[3] Buitrago, E., Tinnis, F., Adolfsson, H. *ASC* **354**, 217 (2012)
[4] Do, Y., Han, J., Rhee, Y.H., Park, J. *ASC* **353**, 3363 (2011)
[5] Flückiger, M., Togni, A. *EJOC* 4353 (2011)
[6] Castro, L.C.M., Li, H., Sortais, J.-B., Darcel, C. *CC* **48**, 10514 (2012)
[7] Zhang, Y.-J., Dayoub, W., Chen, G.-R., Lemaire, M. *T* **68**, 7400 (2012)
[8] Pehlivan, L., Métay, E., Delbrayelle, D., Mignani, G., Lemaire, M. *EJOC* 4689 (2012)
[9] Fujihara, T., Cong, C., Iwai, T., Terao, J., Tsuji, Y. *SL* 2389 (2012)
[10] Bai, X.-F., Xu, L.-W., Zheng, L.-S., Jiang, J.-X., Lai, G.-Q., Shang, J.-Y. *CEJ* **18**, 8174 (2012)
[11] Pehlivan, L., Métay, E., Laval, S., Dayoub, W., Delbrayelle, D., Mignani, G., Lemaire, M. *EJOC* 7400 (2011)
[12] Bezier, D., Venkanna, G.T., Castro, L.C.M., Zheng, J., Roisnel, T., Sortais, J.-B., Darcel, C. *ASC* **354**, 1879 (2012)
[13] Das, S., Li, Y., Junge, K., Beller, M. *CC* **48**, 10742 (2012)
[14] Sakai, N., Usui, Y., Ikeda, R., Konakahara, T. *ASC* **353**, 3397 (2011)
[15] Sakai, N., Usui, Y., Moriya, T., Ikeda, R., Konakahara, T. *EJOC* 4603 (2012)
[16] Ho, T.-L., Tang, B., Ma, G., Xu, P. *JCCS(Taipei)* **59**, 455 (2012)
[17] Psyllaki, A., Lykakis, I.N., Stratakis, M. *T* **68**, 8724 (2012)
[18] Kosal, A.D., Wilson, E.E., Ashfeld, B.L. *ACIE* **51**, 12036 (2012)
[19] Das, S., Addis, D., Junge, K., Beller, M. *CEJ* **17**, 12186 (2011)
[20] Das, S., Wendt, B., Möller, K., Junge, K., Beller, M. *ACIE* **51**, 1662 (2012)
[21] Laval, S., Dayoub, W., Pehlivan, L., Métay, E., Favre-Réguillon, A., Delbrayelle, D., Mignani, G., Lemaire, M. *TL* **52**, 4072 (2011)
[22] Das, S., Addis, D., Knöpke, L.R., Bentrup, U., Junge, K., Brückner, A., Beller, M. *ACIE* **50**, 9180 (2011)
[23] Egi, M., Kawai, T., Umemura, M., Akai, S. *JOC* **77**, 7092 (2012)
[24] Meyer, V.J., Niggemann, M. *CEJ* **18**, 4687 (2012)
[25] Chan, L.Y., Lim, J.S.K., Kim, S. *SL* 2862 (2011)
[26] Mack, D.J., Guo, B., Njardarson, J.T. *CC* **48**, 7844 (2012)
[27] van Kalkeren, H.A., Bruins, J.J., Rutjes, F.P.J.T., van Delft, F.L. *ASC* **354**, 1417 (2012)
[28] Moriya, T., Yoneda, S., Kawana, K., Ikeda, R., Konakahara, T., Sakai, N. *OL* **14**, 4842 (2012)
[29] Sakai, N., Miyazaki, T., Sakamoto, T., Yatsuda, T., Moriya, T., Ikeda, R., Konakahara, T. *OL* **14**, 4366 (2012)
[30] Gellert, B.A., Kahlcke, N., Feurer, M., Roth, S. *CEJ* **17**, 12203 (2011)
[31] Wang, P., Liu, C.-R., Sun, X.-L., Chen, S.-S., Li, J.-F., Xie, Z., Tang, Y. *CC* **48**, 290 (2012)
[32] Kawamorita, S., Yamazaki, K., Ohmiya, H. Iwai, T., Sawamura, M. *ASC* **354**, 3440 (2012)
[33] Shang, J.-Y., Li, F., Bai, X.-F., Jiang, J.-X., Yang, K.-F., Lai, G.-Q., Xu, L.-W. *EJOC* 2809 (2012)
[34] Palframan, M.J., Parsons, A.F., Johnson, P. *SL* 2811 (2011)
[35] Girijavallabhan, V., Alvarez, C., Njoroge, F.G. *JOC* **76**, 6442 (2011)
[36] Lykakis, I.N., Psyllaki, A., Stratakis, M. *JACS* **133**, 10426 (2011)
[37] Lu, J., Toy, P.H. *CAJ* **6**, 2251 (2011)

[38] Nishimoto, Y., Okita, A., Yasuda, M., Baba, A. *ACIE* **50**, 8623 (2011)
[39] Inamoto, Y., Nishimoto, Y., Yasuda, M., Baba, A. *OL* **14**, 1168 (2012)
[40] Tsuchimoto, T., Iketani, Y., Sekine, M. *CEJ* **18**, 9500 (2012);Tsuchimoto, T., Fujii, M., Iketani, Y., Sekine, M. *ASC* **354**, 2959 (2012)
[41] Itagaki, S., Kamata, K., Yamaguchi, K., Mizuno, N. *CC* **48**, 9269 (2012)
[42] Xie, W., Hu, H., Cui, C. *ACIE* **51**, 11141 (2012)
[43] Königs, C.D.F., Klare, H.F.T., Ohki, Y., Tatsumi, K., Oestreich, M. *OL* **14**, 2842 (2012)
[44] Xing, P., Zang, W., Huang, Z., Zhan, Y., Zhu, C., Jiang, B. *SL* 2269 (2012)
[45] Oyamada, J., Nishiura, M., Hou, Z. *ACIE* **50**, 10720 (2011)
[46] Pehlivan, L., Métay, E., Delbrayelle, D., Mignani, G., Lemaire, M. *T* **68**, 3151 (2012)
[47] Li, Y., Das, S., Zhou, S., Junge, K., Beller, M. *JACS* **134**, 9727 (2012)
[48] van Kalkeren, H.A., Bruins, J.J., Rutjes, F.P.J.T., van Delft, F.L. *ASC* **354**, 1417 (2012)
[49] Barbero, N., Martin, R. *OL* **14**, 796 (2012)
[50] Zhan, J.-H., Lv, H., Yu, Y., Zhang, J.-L. *ASC* **354**, 1529 (2012)

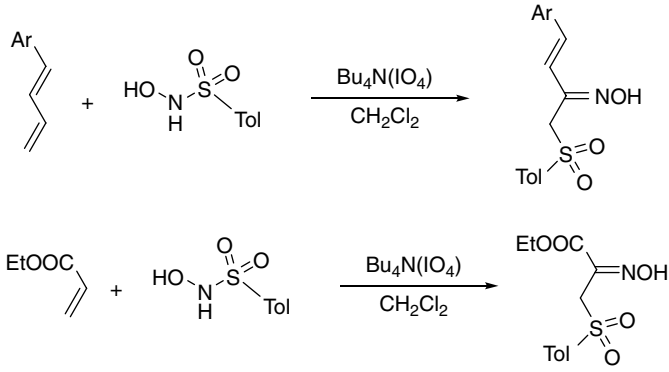
[(2-Hydroxy-5-methoxy)phenyl]diphenylmethanol

Oxidation. Primary alcohols and their ether and ester derivatives form 1,3-benzodioxanes on treatment with the title reagent (catalyst: H_2SO_4).[1]

[1] Yang, H., Mu, F., Wang, P. *JOC* **76**, 8955 (2011)

N-Hydroxy-*p*-toluenesulfonamide

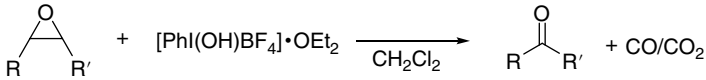
Addition. The title compound is oxidized by $Bu_4N(IO_4)$ and the ensuing TsN=O undergoes rapid homolysis. An alkene present in the reaction medium is attacked and an α-tosyl sulfone is produced.[1]



[1] Liu, N., Yin, P., Chen, Y., Deng, Y., He, L. *EJOC* 2711 (2012)

Hydroxyiodobenzene tetrafluoroborate-etherate

Degradation of epoxides. Oxidative removal of one carbon unit from an epoxide by $[PhI(OH)]BF_4 \cdot OEt_2$ is observed. PhI(OH)OTs.[1] When some water is present, cleavage to two aldehydes ensues.



[1] Havare, N., Plattner, D.A. *HCA* **95**, 2036 (2012)

Hydroxy(tosyloxy)iodobenzene

Diaryliodonium salts. Specifically aimed at derivatizing aryl halides that contain boron substituents, diaryliodonium salts are accessed on reaction with PhI(OH)OTs in trifluoroethanol, so that they can be functionalized at the halogen-attached sites without affecting the boron substituents.[1]

Species generated from $PhI(OAc)_2$ is further transformed into various diaryliodonium tosylates by reaction with electron-rich arenes or organostannanes.[2]

Coupling. Thiophenes undergo oxidative dimerization at C-2 with PhI(OH)OTs and Me_3SiBr.[3]

Cycloetherification. 4-Hydroxy-2-cycloheptenone affords 8-oxabicyclo[3.2.1]oct-3-en-2-one on treatment with PhI(OH)OTs in 65% yield.[4]

[1] Ito, M., Itani, I., Toyoda, Y., Morimoto, K., Dohi, T., Kita, Y. *ACIE* **51**, 12555 (2012)
[2] Chun, J.-H., Pike, V.W. *JOC* **77**, 1931 (2012)
[3] Morimoto, K., Nakae, T., Yamaoka, N., Dohi, T., Kita, Y. *EJOC* **6326** (2011)
[4] Kawasumi, M., Kanoh, N., Iwabuchi, Y. *OL* **13**, 3620 (2011)

Hypofluorous acid

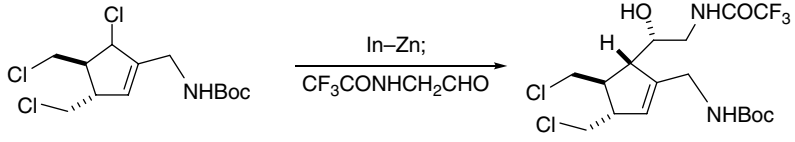
Oxidation. The HOF·MeCN complex is generated from reaction of fluorine with water. It is stabilized to some extent by MeCN, and the reagent oxidizes thiophene to the sulfone. Applications include a synthesis of star oligothiophene *S,S*-dioxide.[1]

[1] Potash, S., Rosen, S. *JOC* **76**, 7245 (2011)

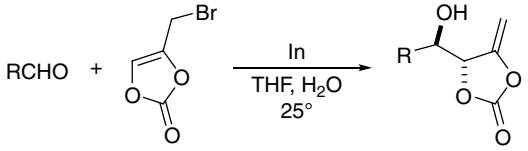
I

Indium

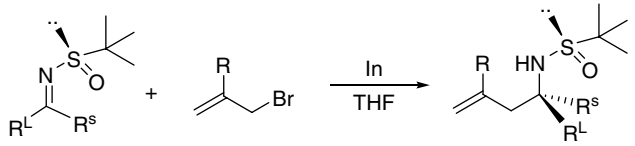
Barbier reaction. In a synthetic approach to the axinellamines a tetrasubstituted cyclopentene intermediate was constructed by a Barbier reaction, both indium and zinc were required to form the proper allylmetal species.[1]



Condensation of 4-bromomethyl-1,3-dioxol-4-en-2-one with aldehydes in the presence of indium occurs at C-5.[2]



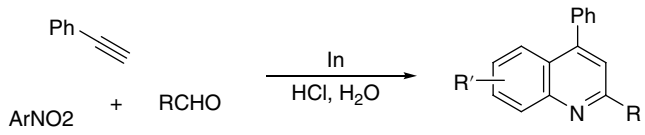
Preparation of homoallylamine derivatives from imines is completed by an indium-mediated allylation.[3] Aza-Henry reaction is also smoothly conducted by generating the nucleophilic α-nitroalkylindium species from *gem*-bromonitroalkanes under ultrasonic agitation.[4]



Perfluoroalkylindium reagents. These nucleophilic reagents add to carbonyl compounds to form perfluoroalkyl carbinols. They can be prepared from $C_nF_{2n+1}I$, using one equivalent of indium metal, ferrocene, LiCl or NaI in DMF.[5]

Fiesers' Reagents for Organic Synthesis, First Edition. Tse-Lok Ho.
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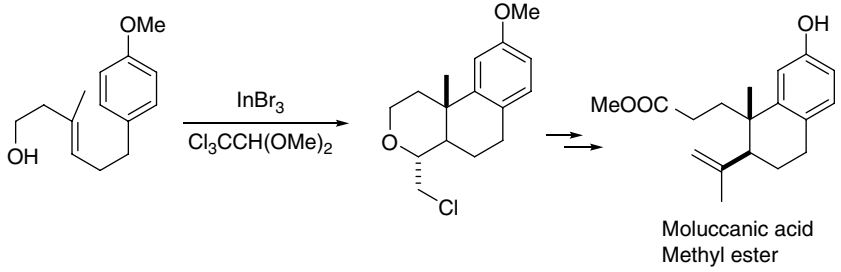
Quinoline synthesis.[6] A route to 2,4-disubstituted quinolines involves reduction of $ArNO_2$ and subsequent condensation, as promoted by indium.



[1] Su, S., Rodriguez, R.A., Baran, P.S. *JACS* **133**, 13922 (2011)
[2] Bigovic, M., Maslak, V., Tokic-Vujosevic, Z., Divjakovic, V., Saicic, R.N. *OL* **13**, 4720 (2011)
[3] Sirvent, J.A., Foubelo, F., Yus, M. *CC* **48**, 2543 (2012)
[4] Soengas, R.G., Silva, S., Estévez, A.M., Estévez, J.C., Estévez, R.J., Rodríguez-Solla, H. *EJOC* 4339 (2012)
[5] Fujiu, M., Nakamura, Y., Serizawa, H., Aikawa, K., Ito, S., Mikami, K. *EJOC* 7043 (2012)
[6] Das, B., Jangili, P., Kashanna, J., Kumar, R.A. *S* 3267 (2011)

Indium(III) bromide

Cyclization + reduction. An efficient construction of a tricyclic intermediate for a synthesis of moluccanic acid involves transacetalization, generation of oxocarbenium species to initiate bicyclization, all processes being instigated by $InBr_3$.[1] There is a partial dechlorination also.



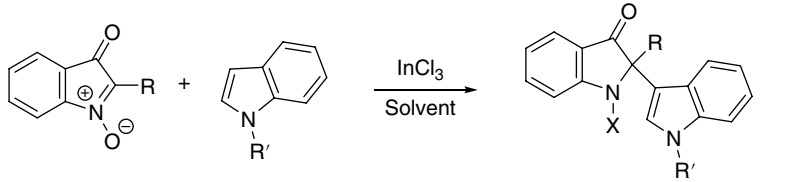
[1] Li, B., Lai, Y.-C., Zhao, Y., Wong, Y.-H., Shen, Z.-L., Loh, T.-P. *ACIE* **51**, 10619 (2012)

Indium(III) chloride

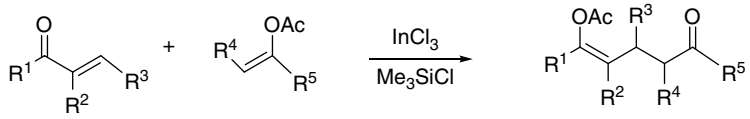
Review. Recent development of synthetic aspects of $InCl_3$ is under review.[1]

Metallation. *o*-Dibromoarenes containing various nuclear substituents are derivatized into bis(halozincio) and bis(haloalumino) compounds by insertion of the respective metal, under the influence of $InCl_3$.[2]

Addition. With $InCl_3$ as catalyst, indoles and isatogens add to 3-indolone *N*-oxides. The adducts suffer *N*-deoxygenation when an excess of $InCl_3$ is used.[3]

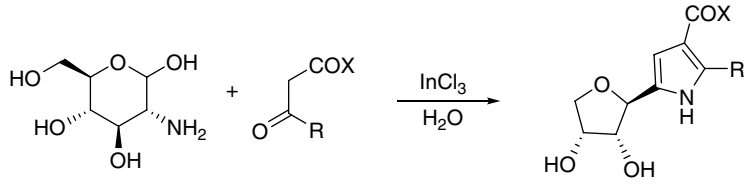


Aryl iodides form $ArInCl_2$ on reaction with $InCl_3$, and these undergo conjugate addition to enones in the presence of a BINAP-ligated Rh species.[4] Other catalytic activities of $InCl_3$ for conjugate addition are those involving desilylative addition of 1-trimethylsilylalkynes to acrylic esters to form 4-alkynoic esters,[5] and the use of enolacetates as nucleophiles in that the acetyl group is duly transferred.[6]

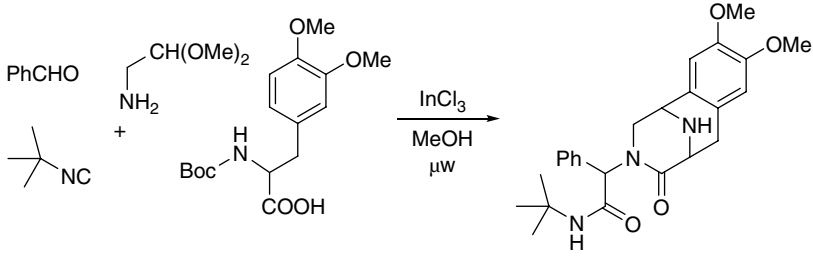


Ring formation. Cyclotrimerization of 1-alkynes by action of $InCl_3$ (additive: 2-iodophenol) is found to furnish 1,3,5-trialkyl benzenes.[7] A pyridine ring is formed from 2-arylanilines upon condensation with ArCHO, via a reaction induced by $InCl_3$.[8]

Condensation of glucosamine with β-keto carboxylic acid derivatives gives rise to pyrrole products;[9] enamination and subsequent condensation involving the open aldehyde form of glucosamine precipitate the overall transformation.



A four-component Ugi reaction employing RCOOH, R′NC, ArCHO, and an amine delivers α-acylamino amides,[10] but an apparently more synthetically useful example is that represented by the access to a tricyclic compound.[11]

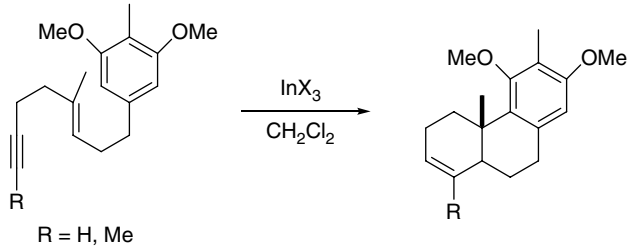


[1] Singh, M.S., Raghuvanshi, K. *T* **68**, 8683 (2012)
[2] Blümke, T.D., Klatt, T., Koszinowski, K., Knochel, P. *ACIE* **51**, 9926 (2012)
[3] Kumar, C.V.S., Puranik, V.G., Ramana, C.V. *CEJ* **18**, 9601 (2012)
[4] Tato, R., Riveiros, R., Sestelo, J.P., Sarandeses, L.A. *T* **68**, 1606 (2012)
[5] Xu, Y., Pan, Y., Liu, P., Wang, H., Tian, X., Su, G. *JOC* **77**, 3557 (2012)
[6] Onishi, Y., Yoneda, Y., Nishimoto, Y., Yasuda, M., Baba, A. *OL* **14**, 5788 (2012)
[7] Xu, Y., Pan, Y., Wu, Q., Wang, H., Liu, P. *JOC* **76**, 8472 (2011)
[8] Majumdar, K.C., Nandi, R.K., Ponra, S. *SL* 113 (2012)
[9] Li, B., Wang, G., Li, Z., Meng, X. *TL* **52**, 3891 (2011)
[10] Polindara-Garcia, L.A., Miranda, L.D. *OL* **14**, 5408 (2012)
[11] Cano-Herrera, M.-A., Miranda, L.D. *CC* **47**, 10770 (2011)

Indium(III) iodide

Substitution. Using InI_3 as catalyst ROAc is converted into RSR′ by Me_3SiSR'.[1]

Polycyclization. Involving an internal triple bond in polycyclization is an extension of a previously reported process, the substrates and products necessarily have distinctly different structural features.[2]



[1] Nishimoto, Y., Okita, A., Yasuda, M., Baba, A. *OL* **14**, 1846 (2012)
[2] Qiu, W.-W., Surendra, K., Yin, L., Corey, E.J. *OL* **13**, 5893 (2011)

Indium(III) oxide

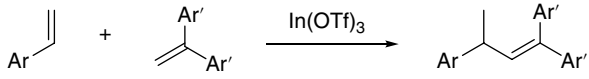
Propargylamines. Aminomethylation of 1-alkynes with CH_2Cl_2 and R_2NH in a procedure that employs nano-In_2O_3 and DABCO in DMSO has been reported.[1]

[1] Rahman, M., Bagdi, A.K., Majee, A., Hajra, A. *TL* **52**, 4437 (2011)

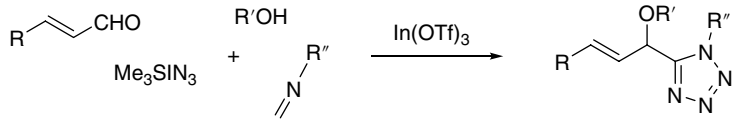
Indium(III) triflate

Transacetalization. In the presence of $In(OTf)_3$ functional group exchange that replaces two alkoxy groups by those from a diol is accomplished.[1]

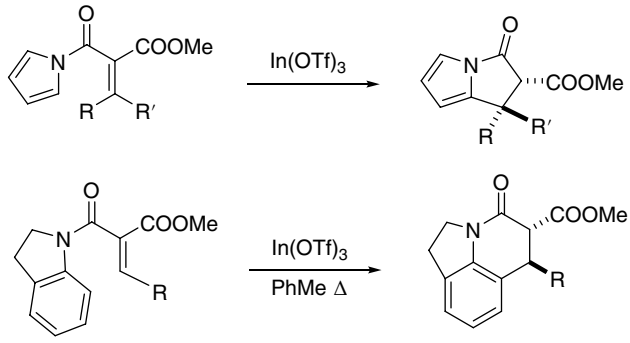
Addition. 1,1-Diarylethenes add to styrenes to form 1,1,3-triaryl-1-butenes.[2]



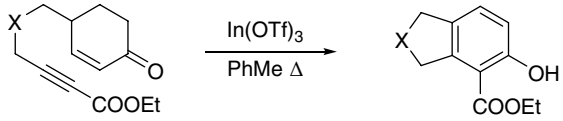
Chiral arylglycine derivatives are synthesized from an $In(OTf)_3$-catalyzed reaction of arenes with the sulfinimine of a glyoxylic ester.[3] When an aldehyde, Me_3SiN_3, R′OH, and R″NC are mixed with $In(OTf)_3$, cycloaddition (to form a tetrazoyl nucleophile) and then addition to the carbonyl group ensues.[4]



Annulation. 2-Benzylaryl ketones undergo intramolecular acylation and dehydration, substituted anthracenes are obtained.[5] Pyrrolizine[6] and 1,8-benzo hydroindolizine derivatives[7] have been assembled by intramolecular cyclization.



A quite intriguing transformation is that of the formation of bicyclic phenols from 4-substituted 2-cyclohexenones in which the sidechain carries a 2-alkynoic ester unit.[8]



The hetero-Diels-Alder reaction between Brassard-type dienes and aldehydes is facilitated by $In(OTf)_3$.[9]

[1] Smith, B.M., Kubczyk, T.M., Graham, A.E. *T* **68**, 7775 (2012)
[2] Dai, J., Wu, J., Zhao, G., Dai, W.-M. *CEJ* **17**, 8290 (2011)
[3] Li, Y., Ji, D.-M., Xu, M.-H. *OBC* **9**, 8452 (2011)
[4] Yanai, H., Sakiyama, T., Oguchi, T., Taguchi, T. *TL* **53**, 3161 (2012)
[5] Kuninobu, Y., Tatsuzaki, T., Matsuki, T., Takai, K. *JOC* **76**, 7005 (2011)
[6] Patil, D.V., Cavitt, M.A., France, S. *OL* **13**, 5820 (2011)
[7] Patil, D.V., Cavitt, M.A., Grzybowski, P., France, S. *CC* **48**, 10337 (2012)
[8] Kinbara, A., Yamagishi, T., Hanzawa, N., Kawashima, E., Miyaoka, H. *JOC* **77**, 8999 (2012)
[9] Lin, L., Kuang, Y., Liu, X., Feng, X. *OL* **13**, 3868 (2011)

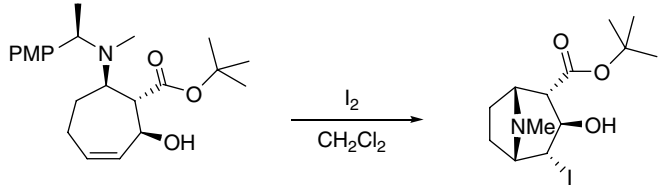
Indium triisopropoxide

Reduction. As belonging to the family as aluminum, the effectiveness of the indium analog $(i\text{-PrO})_3\text{In}$ for catalyzing the Meerwein-Ponndorf-Verley reduction of aldehydes is well anticipated.[1]

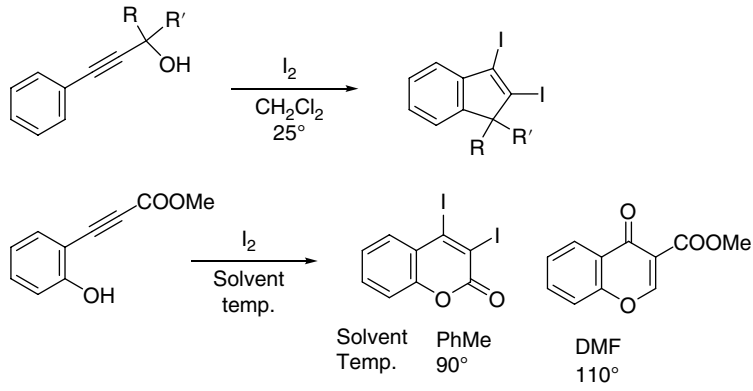
[1] Lee, J., Ryu, T., Park, S., Lee, P.H. *JOC* **77**, 4821 (2012)

Iodine

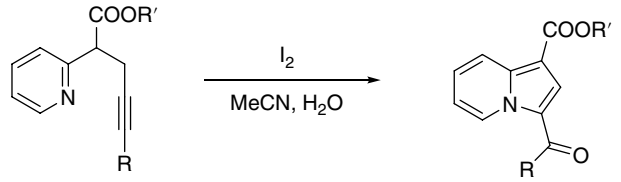
Addition. Markovnikov hydriodination of 1-alkynes (and triorganosiyl derivatives) occurs on exposure to I_2 and diphenylphosphine oxide.[1] An azabridged product (tropane skeleton) emerges as transannular addition is initiated by iodine from a cycloheptenylamine.[2] Noteworthy is an *N*-debenzylation that accompanies the reaction.



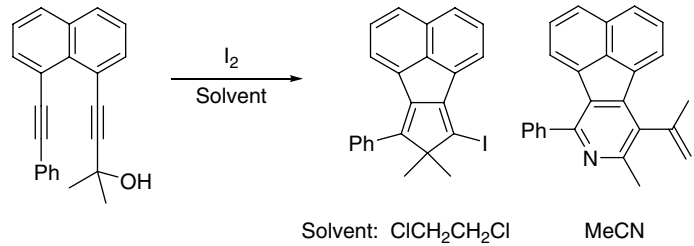
Through Iodination of a triple bond enables indene formation from arylalkynyl carbinols.[3] Similarly, either chromen-2-ones or chromen-4-ones are prepared from a 2-hydroxyphenylpropynoic ester.[4]



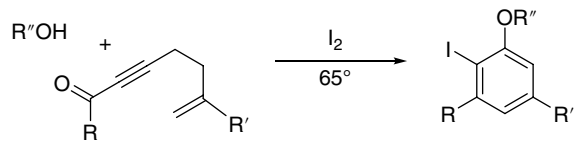
2-Alkynylbenzyl alcohols yield indenones on treatment with iodine in an aqueous medium,[5] whereas 2-(3-alkynyl)pyridines cyclize to indolizinyl ketones.[6]



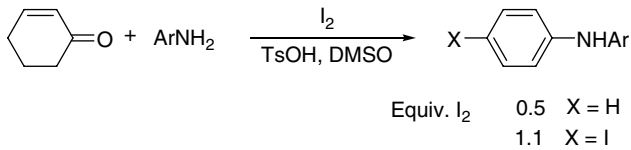
From the reaction of benzyne and iodine, 1,2-diiodobenzene is formed.[7] 1,8-Dialkynylnaphthalenes give annulated acenaphthylene products.[8]



Iodoalkoxylation of 2-alkyn-6-en-1-ones is followed by aromatization.[9]



Substitution. Aminoalkylation of arenes from a mixture of ArH, RCHO, and H_2NCOOR' to deliver $ArCH(NHCOOR')R$ is catalyzed by iodine, which likely proceeds via imine intermediates.[10] Unsymmetrical diarylamines are synthesized from 2-cyclohexenone and $ArNH_2$, in a reaction which iodine serves as condensing and aromatizing agents, and iodinating agent if being used in stoichiometrically.[11] Primary alcohols can be converted directly into mixed aulfides on reaction with RSSR – I_2 in *N*-methylpyrrolidone with microwave irradiation.[12]



Aryl bis(3-indolyl)methyl ketones are formed in an iodine-catalyzed reaction between ArCOMe and indole.[13] Perhaps the acetyl group is iodinated prior to indolylation. An indoloquinoline system is assembled from indoles and 2-acyl-*N*-tosylanilines, the condensation is followed by aromatizing elimination of TsOH.[14]

Iodine pairing with TfOH becomes a powerful promoter of diarylation of $ArCOCH_3$ by dimethylaniline (at the *p*-position).[15] It turns $K_3[Fe(CN)_6]$ into an electrophilic agent to perform cyanation of electron-rich arenes (e.g., anisole) by catalysis of $Cu(NO_3)_2$.[16]

Amide formation. Oxidative amination of ArCHO is carried out at room temperature, utilizing iodine as the active catalyst.[17] A system consisting of I_2, $(MeO)_3P$ and Et_3N is also useful for amidation where alcohols and thiols do not interfere (ester and thiol esters are not formed).[18]

Oxidative functionalization. α-Tosyloxylation of ketones can be carried out with TsOH in that activation by I_2/MCPBA is crucial.[19] After a Vilsmeier-Haack reaction, the immediate exposure to I_2 in aqueous ammonia enables the attainment of ArCN from arenes.[20] Another method for ArCN synthesis is via functional group modification, i.e., that of ArCOOEt, which is reduced by Dibal-H and similarly the treatment with I_2/aq. NH_3.[21]

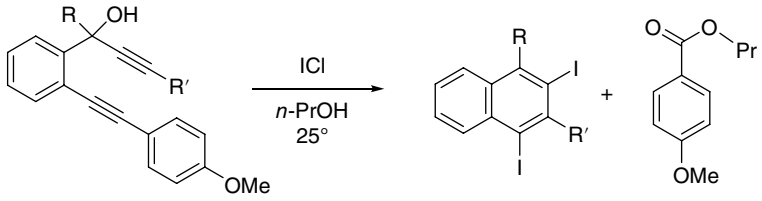
Degradation of cyclopropyl methyl ketones to the carboxylic acid derivatives (esters, amides) is simply carried out with iodine and ROH or NH_4OH.[22] Perhaps an iodoform reaction is involved.

Condensation. An expedient synthesis of flavanone[23] from *o*-hydroxyacetophenone and PhCHO consists of adding the reactants and iodine to an amine. The reaction can be considered to proceed by aldol reaction, dehydration and intramolecular Michael addition.

[1] Kawaguchi, S., Masuno, H., Sonoda, M., Nomoto, A., Ogawa, A. *T* **68**, 9818 (2012)
[2] Brock, E.A., Davies, S.G., Lee, J.A., Roberts, P.M., Thomson, J.E. *OL* **14**, 4278 (2012)
[3] Zhou, C., Chen, X., Lu, P., Wang, Y. *T* **68**, 2844 (2012)
[4] Cai, S., Shen, Y., Lu, P., Wang, Y. *TL* **52**, 4164 (2011)
[5] Wang, C., Yang, J., Cheng, X., Li, E., Li, Y. *TL* **53**, 4402 (2012)
[6] Jung, Y., Kim, I. *T* **68**, 8198 (2012)
[7] Rodriguez-Lojo, D., Cobas, A., Peña, D., Perez, D., Guitian, E. *OL* **14**, 1363 (2012)
[8] Chen, X., Lu, P., Wang, Y. *CEJ* **17**, 8105 (2011)
[9] Yang, F., Qiu, Y.-F., Ji, K.-G., Niu, Y.-N., Ali, S., Liang, Y.-M. *JOC* **77**, 9029 (2012)
[10] Jaratjaroonphong, J., Krajangsri, S., Reutrakul, V. *TL* **53**, 2476 (2012)
[11] Barros, M.T., Dey, S.S., Maycock, C.D., Rodrigues, P. *CC* **48**, 10901 (2012)
[12] Hu, B., Hu, H., Sun, L., Tang, R. *ChJC* **30**, 2556 (2012)
[13] Zhu, Y., Liu, M., Jia, F., Yuan, J., Gao, Q., Lian, M., Wu, A. *OL* **14**, 3392 (2012)
[14] Ali, S., Li, Y.-X., Anwar, S., Yang, F., Chen, Z.-S., Liang, Y.-M. *JOC* **77**, 424 (2012)
[15] Zhu, Y., Jia, F., Liu, M., Wu, L., Cai, Q., Gao, Q., Wu, A. *OL* **14**, 5378 (2012)
[16] Ren, Y., Yan, M., Zhao, S., Wang, J., Ma, J., Tian, X., Yin, W. *ASC* **354**, 2301 (2012)
[17] Baba, H., Moriyama, K., Togo, H. *SL* 1175 (2012)
[18] Luo, Q.-L., Lv, L., Li, Y., Tan, J.-P., Nan, W., Hui, Q. *EJOC* 6916 (2011)
[19] Tanaka, A., Moriyama, K., Togo, H. *SL* 1853 (2011)
[20] Ushijima, S., Moriyama, K., Togo, H. *T* **68**, 4588 (2012)
[21] Suzuki, Y., Moriyama, K., Togo, H. *T* **67**, 7956 (2011)
[22] Zhang, D., Zhang, R., Xiang, D., Zhang, N., Liang, Y., Dong, D. *S* 705 (2012)
[23] Kavala, V., Lin, C., Kuo, C.-W., Fang, H., Yao, C.-F. *T* **68**, 1321 (2012)

Iodine(I) chloride

Ring formation. Cycloisomerization of 2-alkynyl nitroarenes gives benz[*c*]isoxazol-5-yl ketones. The use of ICl gives better results than $AuBr_3$ in some cases.[1] Two iodine atoms are incorporated into the new ring when 2-alkynylaryl alkynyl carbinols are treated with ICl.[2]



[1] Cikotiene, I. *EJOC* 2766 (2012)
[2] Wang, L.-J., Zhu, H.-T., Lu, L., Yang, F., Liu, X.-Y., Liang, Y.-M. *OL* **14**, 1990 (2012)

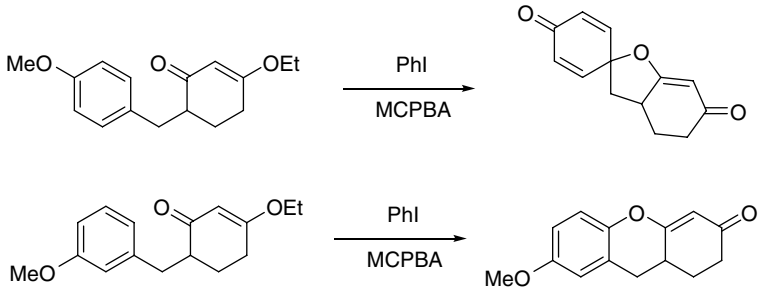
Iodine(V) fluoride

Fluorination. The IF_5-Py.HF complex is stable to air and moisture therefore a superior reagent for fluorination. Application to the transformation of $Ar_2C(SPh)_2$ to Ar_2CF_2 and the fluorination of RCH(SAr)X [X is an electron-withdrawing group] to give RCF(SAr)X is now established.[1]

[1] Hara, S., Monoi, M., Umemura, R., Fuse, C. *T* **68**, 10145 (2012)

Iodobenzene - oxidant

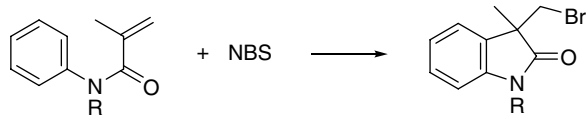
Oxidation. In situ generation of iodosylbenzene from catalytic amounts of PhI and stoichiometric oxidant such as a peracid is frequently a preferable option for oxidation as exemplified by the creation of oxacycles.[1]



Modification at the benzene ring of PhI renders the oxidant more versatile. A water-soluble *N*-(4-iodophenyl)pyridinium salt in conjunction with peracetic acid constitutes a useful system for the oxidation of alcohols.[2]

Hofmann rearrangement. The amide-to-carbamate conversion is readily achieved with PhI and Oxone in a mixture of $(CF_3)_2CHOH$ and aqueous MeOH.[3] Similarly, the 3-aminopropanoic ester derivative is acquired from succinimide (MCPBA being used as the oxidant).[4] Noteworthy is that *O*-methylhydroxamic acids do not undergo Lossen rearrangement, instead oxidation produces electrophilic species that attack arenes. In other words, *N*-arylation is the main reaction course (the report specifies reagents of peracetic acid and 2,2′-diiodo-4,6,4′,6′-tetramethylbiphenyl).[5]

Brominative cyclization of *N*-methacrylanilines by reaction with NBS is assisted by *N*-(2-iodobenzoyl)glycine.[6] Apparently, a much more reactive brominating agent is formed in situ.



[1] Ngatimin, M., Frey, R., Andrews, C., Lupton, D.W., Hutt, O.E. *CC* **47**, 11778 (2011)
[2] Zhu, C., Yoshimura, A., Wei, Y., Nemykin, V.N., Zhdankin, V.V. *TL* **53**, 1438 (2012)
[3] Yoshimura, A., Middleton, K.R., Luedtke, M.W., Zhu, C., Zhdankin, V.V. *JOC* **77**, 11399 (2012)
[4] Moriyama, K., Ishida, K., Togo, H. *OL* **14**, 946 (2012)
[5] Samanta, R., Bauer, J.O., Strohmann, C., Antonchick, A.P. *OL* **14**, 5518 (2012)
[6] Fabry, D.C., Stodulski, M., Hoerner, S., Gulder, T. *CEJ* **18**, 10834 (2012)

Iododiphenylphosphine

Alkyldiphenylphosphines.[1] The title reagents are generated in situ from R_2PCl in an analogous Finkelstein reaction, with NaI in MeCN at 80°. In the presence of ArCHO a follow-up reaction and oxidation with H_2O_2 give benzyldialkylphosphine oxides.

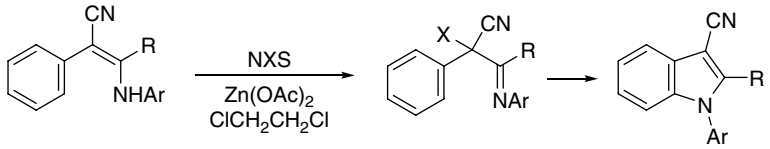
[1] Wang, F., Qu, M., Chen, F., Xu, Q., Shi, M. *CC* **48**, 8580 (2012)

N-Iodosuccinimide, (NIS)

Iodination. Solvent effects are observed in iodination of anilines with NIS: overwhelming *p*-iodination in DMSO, but it reverts to *o*-iodination in PhH-HOAc (selectivity >99% in each instance).[1] Iodination of 1-alkynes by NIS that requires $(Ph_3P)AuNTf_2$ is perhaps overly involved.[2]

BINOL dimethyl ether is iodinated at C-6 and C-6′ with NIS using $Sc(OTf)_3$ as catalyst.[3]

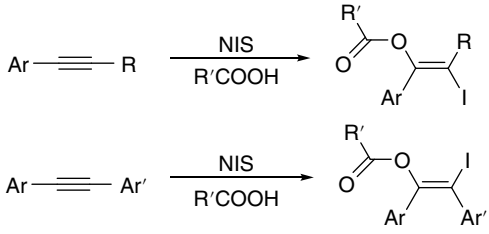
Cyclization of α–aryl-β-arylamino-α,β-unsaturated nitriles is effected via halogenations with NXS and dehydrohalogenation in the presence of $Zn(OAc)_2$.[4]



Alkenylsilanes are converted rapidly into the iodoalkenes with retention of configuration by NIS – Ag_2CO_3 in hexafluoroisopropanol at 0°.[5]

Hydroxy protection.[6] Alcohols are transformed into *N*-alkoxymethylphthalimides by reaction with *N*-phenylselenylmethylphthalimide in the presence of of NIS and Me_3SiOTf. For the O-C bond cleavage, it is initiated by treatment with ethylenediamine.

Addition. Iodocarboxylation of arylalkynes and diarylethynes yields different adducts.[7]



[1] Shen, H., Vollhardt, K.P.C. *SL* 208 (2012)
[2] Starkov, P., Rota, F., D'Oyley, J.M., Sheppard, T.D. *ASC* **354**, 3217 (2012)
[3] Kamei, T., Shibaguchi, H., Sako, M., Toribatake, K., Shimada, T. *TL* **53**, 3894 (2012)
[4] Yan, Q., Luo, J., Zhang-Negrerie, D., Li, H., Qi, X., Zhao, K. *JOC* **76**, 8690 (2011)
[5] Sidera, M., Costa, A. M., Vilarrasa, J. *OL* **13**, 4934 (2011)
[6] Temperini, A., Minuti, L. *TL* **53**, 2709 (2012)
[7] Okamoto, N., Miwa, Y., Minami, H., Takeda, K., Yanada, R. *JOC* **76**, 9133 (2011)

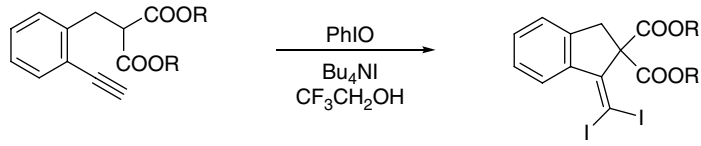
Iodosylbenzene

Oxidative cleavage. α-Branched arylacetaldehydes are degraded to aryl ketones by PhIO and $BF_3{\cdot}OEt_2$.[1]

Functionalization. Using PhIO to generate chlorine in situ from conc. HCl, chlorination of alkenes and 1,3-dicarbonyl compounds can be performed.[2] Oxidative activation of $TsNH_2$ makes it an *N*-electrophile, and a successful reaction with 1,3-dicarbonyl compounds is catalyzed by $Zn(ClO_4)_2$.[3]

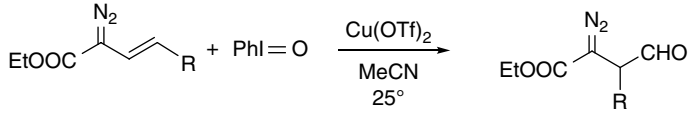
1-Alkenes are converted to aldehydes in a reaction with PhIO in the presence of $Fe(BF_4)_2$.[4]

Positive iodine species generated from Bu_4NI is capable of initiating iodinative cyclization, and one example is the formation of a 1-diiodomethyleneindane-2,2-dicarboxylic ester.[5]



Carboxylic acids and β-aminoalkenoic esters (and nitriles,…) undergo oxidative coupling that results in α-carboxylation of the latter compounds.[6]

Rearrangement. *N*-Boc-*N*-allylhydrazines are subject to oxidation which is followed by a rapid [2,3]sigmatropic rearrangement of the ensuing nitrenes to give 3-(*N*′-Boc-azo)-1-alkenes.[7] α-Diazo-β,γ-unsaturated esters yield β-formylalkanoic esters with one less carbon unit in the main chain.[8]

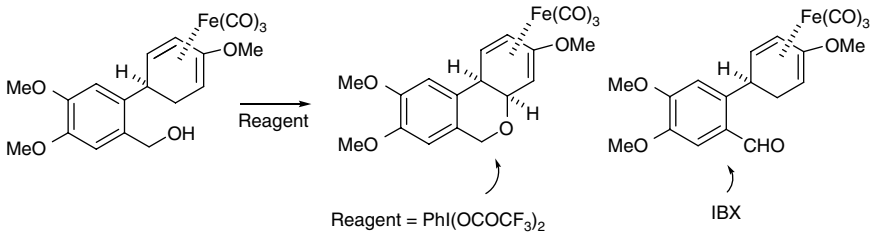


Hofmann rearrangement of carboxamides instigated by PhIO can use alcohol solvents or amines, if carbamates and ureas are the desired products, respectively.[9]

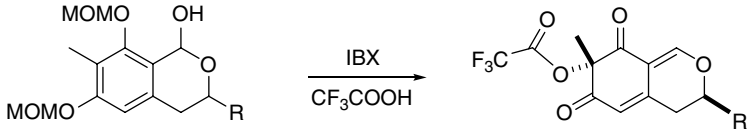
[1] Havare, N., Plattner, D.A. *OL* **14**, 5078 (2012)
[2] Kitamura, T., Tazawa, Y., Morshed, M.H., Kobayashi, S. *S* 1159 (2012)
[3] Yu, J., Liu, S.-S., Cui, J., Hou, X.-S., Zhang, C. *OL* **14**, 832 (2012)
[4] Chowdhury, A.D., Ray, R., Lahiri, G.K. *CC* **48**, 5497 (2012)
[5] Zheng, C., Fan, R. *CC* **47**, 12221 (2011)
[6] Liu, X., Cheng, R., Zhao, F., Zhang-Negrerie, D., Du, Y., Zhao, K. *OL* **14**, 5480 (2012)
[7] Strick, B.F., Mundal, D.A., Thomson, R.J. *JACS* **133**, 14252 (2011)
[8] Barluenga, J., Lonzi, G., Riesgo, L., Tomas, M., Lopez, L.A. *JACS* **133**, 18138 (2011)
[9] Liu, P., Wang, Z., Hu, X. *EJOC* 1994 (2012)

o-Iodylbenzoic acid, (IBX)

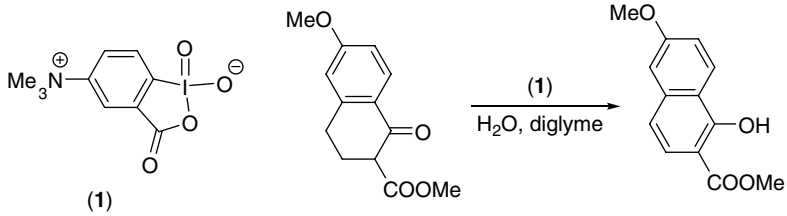
Oxidation. In further examination of the oxidation power of IBX the finding of its use in converting aldols into 1,3-diketones comes to no surprise.[1] While the normal oxidation of certain benzylic alcohols by IBX to furnish aldehydes, the contrasting oxidative cyclization by $PhI(OOCCF_3)_2$ shown in the following equation is noteworthy.[2]



Perhaps unexpected is the behavior of a bicyclic lactol towards IBX, dearomatization taking precedence to simple transformation into the lactone.[3]



Dehydrogenation. The ammonium salt **1** is a water-soluble IBX-analog. It is used in aromatization of α-tetralonecarboxylic esters.[4]

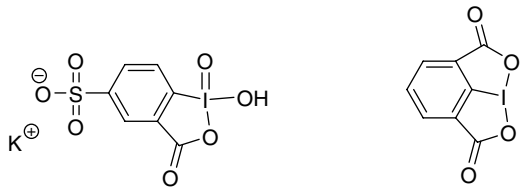


(**1**)

Pyrrolidines suffer dehydrogenation (to give pyrroles) on exposure to IBX in the presence of β-cyclodextrin in water.[5]

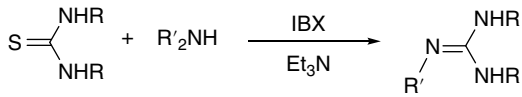
Functional group transformation. Secondary and tertiary amines undergo *N*-nitrosation when they are treated with IBX, Bu_4NF in $MeNO_2$.[6] Azidation of 1,3-dicarbonyl compounds is observed while employing **2** (and catalytic NaI) to generate the reactive species from NaN_3.[7]

Esterification (including lactonization) and amidation from the reaction components are performed by **3**, with assistance of DMAP (or pyridine) and Ph_3P.[8]



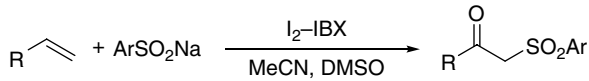
(**2**) (**3**)

Thiono compounds such as thioamides and thioureas are readily desulfurated by IBX, and synthetic values of the oxidation lie in trapping to furnish other products,[9] one example being the synthesis of guanidines.[10]



Degradative cyanation of epoxides in the presence of aqueous ammonia furnishes nitriles with one carbon short.[11]

Addition. A mixture of IBX, I_2, and $ArSO_2Na$ in DMSO-MeCN converts alkenes into α-sulfonyl ketones.[12]

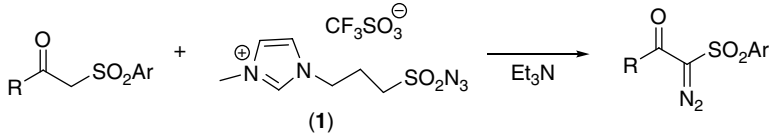


[1] Bartlett, S.L., Beaudry, C.M. *JOC* **76**, 9852 (2011)
[2] Stephenson, G.R., Roe, C., Anson, C.E. *JOC* **77**, 9684 (2012)
[3] Boulange, A., Peixoto, P.A., Franck, X. *CEJ* **17**, 10241 (2011)
[4] Cui, L.-Q., Dong, Z.-L., Liu, K., Zhang, C. *OL* **13**, 6488 (2011)
[5] Murthy, S.N., Nageswar, Y.V.D. *TL* **52**, 4481 (2011)
[6] Potturi, H.K., Gurung, R.K., Hou, Y. *JOC* **77**, 626 (2012)
[7] Harschneck, T., Hummel, S., Kirsch, S.F., Klahn, P. *CEJ* **18**, 1187 (2012)
[8] Tian, J., Gao, W.-C., Zhou, D.-M., Zhang, C. *OL* **14**, 3020 (2012)
[9] Chaudhari, P.S., Pathare, S.P., Akamanchi, K.G. *JOC* **77**, 3716 (2012)
[10] Dangate, P.S., Akamanchi, K.G. *TL* **53**, 6765 (2012)
[11] Deshmukh, S.S., Huddar, S.N., Jadhav, R.R., Akamanchi, K.G. *TL* **52**, 4533 (2011)
[12] Samakkanad, N., Katrun, P., Techajaroonjit, T., Hlekhlai, S., Pohmakotr, M., Reutrakul, V., Jaipetch, T., Soorukram, D., Kuhakam, C. *S* 1693 (2012)

Ionic liquids

Assorted applications. The catalytic activities of acidic ionic liquids have been summarized.[1] 1-Methyl-3-(4-nitrobenzyl)imidazolium hexafluorophosphate is safe, non-volatile, and recyclable, a suitable replacement for nitromethane and nitrobenzene as solvent.[2]

Replacement of a sulfonyloxy group (by halogen, acetoxy, thiocyanate, etc.) under solvent free conditions is achieved with [bmim]X-MX, a salt MX supplies the nucleophilic anion.[3] *N*-Alkylation catalyzed by CuI with microwave irradiation has been carried out in an imidazolium ionic liquid in which a nuclear nitrogen atom is linked to a hydrophobic calix[4]arene moiety.[4] The ionic liquid **1** acts as diazo group transfer agent for 1,3-dicarbonyl compounds, α-sulfonyl ketones, and the like.[5]



(**1**)

Benzyl alcohols are dehydrated (to styrenes or dibenzyl ethers) in phosphonium ionic liquids.[6] In many other transformations the routine solvents are successfully replaced with ionic liquids, examples are nitration of arenes with $Bi(NO_3)_3$,[7] preparation of aryl

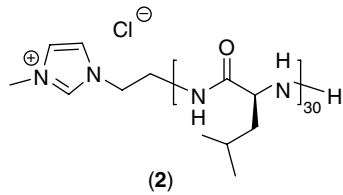
2-benzoxazolyl ketones from arylethynyl bromides and 2-aminophenol ($FeCl_3$-catalyzed);[8] chloroaluminate ionic liquids used in the acylchlorination of ethyne to give RCOCH=CHCl.[9]

An analog of the Vilsmeier reagent is that one of the methyl groups of $(Me_2N{=}CHCl)Cl$ is replaced by an 1-ethyl-3-methylimidazolium moiety. The reagent retains reactivities such as inducing Beckmann rearrangement of ketoximes.[10]

A recently developed ionic liquid has a DABCO skeleton; each nitrogen atom is quaternized by a propanesulfonic acid. This ionic liquid has been used as solvent for [3+2]cycloaddition to form pyrazolines.[11] Diels-Alder reactions are said to proceed with significantly enhanced rates in ionic liquid/aqueous micellar solutions (imidazolium salts with an *N*-dodecyl group).[12] Ionic liquids containing an $AuCl_4$ anion actively promote reactions of alkynes, and it induces formation of polycyclic compounds from seemingly inactive substrates (except the alkyne unit).[13] 1,6-Heptadiynes give 3-methyl-2-cyclohexenones on treatment with $(Ph_3P)AuNO_3$, MsOH, $[bmim]BF_4$ in MeOH containing some water.[14]

A modification of the oxidation protocols developed by Swern and Corey-Kim consists of replacing DMSO with imidazolium tosylates that contain an *N*-(ω-methylsulfinylalkyl) group.[15]

A report is concerned with epoxidation of chalcones in a polymeric imidazolium chloride (**2**).[16]



(**2**)

Other applications of ionic liquids as reaction media are deoximation with $FeCl_3$[17] and the degradation of carbohydrates with hexachlorotriphosphazene to give 5-hydroxymethylfurfural.[18]

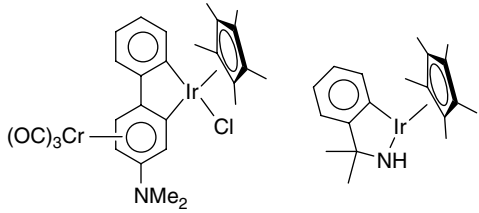
Ionic liquids can act simultaneously as nucleophilic and electrophilic catalysts. This issue has been addressed.[19]

[1] Chiappe, C., Rajamani, S. *EJOC* 5517 (2011)
[2] Ren, Y., Li, M., Yang, J., Peng, J., Gu, Y. *ASC* **353**, 3473 (2011)
[3] Liu, Y., Xu, Y., Jung, S.H., Chae, J. S*L* 2692 (2012)
[4] Huang, L., Jin, C., Su, W. *ChJC* **30**, 2394 (2012)
[5] Muthyala, M.K., Chaudhary, S., Kumar, A. *JOC* **77**, 8787 (2012)
[6] Kalviri, H.A., Kerton, F.M. *ASC* **353**, 3178 (2011)
[7] Jacoway, J., Kumar, G.K.S.N., Laali, K.K. *TL* **53**, 6782 (2012)
[8] Cui, L., He, Y., Fan, X. *ChJC* **30**, 992 (2012)
[9] Snelders, D.J.M., Dyson, P.J. *OL* **13**, 4048 (2011)
[10] Hullio, A.A., Mastoi, G.M. *ChJC* **30**, 1647 (2012)
[11] Safaeli, S., Mohammadpoor-Baltork, I., Khosropour, A.R., Moghadam, M., Tangestaninejad, S., Mirkhani, V. *ASC* **354**, 3095 (2012)

[12] Bica, K., Gärtner, P., Gritsch, P.J., Ressmann, A.K., Schröder, C., Zirbs, R. *CC* **48**, 5013 (2012)
[13] Song, X.-R., Xia, X.-F., Song, Q.-B., Yang, F., Li, Y.-X., Liu, X.-Y., Liang, Y.-M. *OL* **14**, 3344 (2012)
[14] Cui, D.-M., Ke, Y.-N., Zhuang, D.-W., Wang, Q., Zhang, C. *TL* **51**, 980 (2010)
[15] Tsuchiya, D., Tabata, M., Moriyama, K., Togo, H. *T* **68**, 6849 (2012)
[16] Luo, W., Yu, Z., Qiu, W., Yang, F., Liu, X., Tang, J. *T* **67**, 5289 (2011)
[17] Zhang, X., Lu, B., Wang, X., Zhao, J., Cai, Q. *ChJC* **29**, 1846 (2011)
[18] Song, J., Zhang, B., Shi, J., Ma, J., Yang, G., Han, B. *ChJC* **30**, 2079 (2012)
[19] Lucchini, V., Noc, M., Selva, M., Fabris, M., Perosa, A. *CC* **48**, 5178 (2012)

Iridacycles

Hydroamination.[1] A reaction sequence of hydroamination and reduction for converting 1-alkynes into 2-aminoalkanes is accomplished by the iridacycle **1** and the reduction is by a hydrosilane.



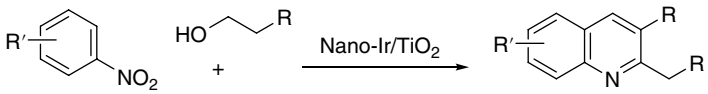
(**1**) (**2**)

Chiral benzylic acetates are obtained through a reaction conducted in a chemoenzymatic system, in which iridacycle **2** catalyzes the redox process and the enzyme CALB performs an asymmetric transacetylation.[2]

[1] Iali, W., LaPaglia, F., Le Goff, X.-F., Sredojevic, D., Pfeffer, M., Djukic, J.-P. *CC* **48**, 10310 (2012)
[2] Sato, Y., Kayaki, Y., Ikariya, T. *CC* **48**, 3635 (2012)

Iridium

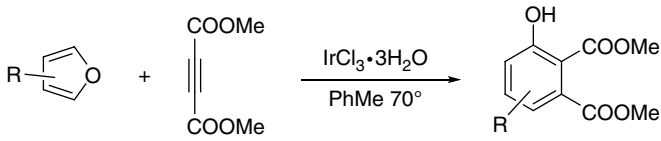
Quinoline synthesis.[1] Heating of $ArNO_2$ and alkanols with subnano-Ir on titania at 120° gives quinolines. The metal catalyst serves both as reducing (for $ArNO_2$) and oxidizing (for alcohols) agents. Two molecules of the alcohols are consumed to build the heterocyclic portion of the products.



[1] He, L., Wang, J.-Q., Gong, Y., Liu, Y.-M., Cao, Y., He, H.-Y. *ACIE* **50**, 10216 (2011)

Iridium(III) chloride

Phenol synthesis.[1] The Diels-Alder reaction of furans and dimethyl acetylenedicarboxylate is followed by aromatization when $IrCl_3$ is present. (The far less expensive $FeCl_3$ seems to be effective also.)



[1] Shinohara, H., Sonoda, M., Atobe, S., Masuno, H., Ogawa, A. *TL* **52**, 6238 (2011)

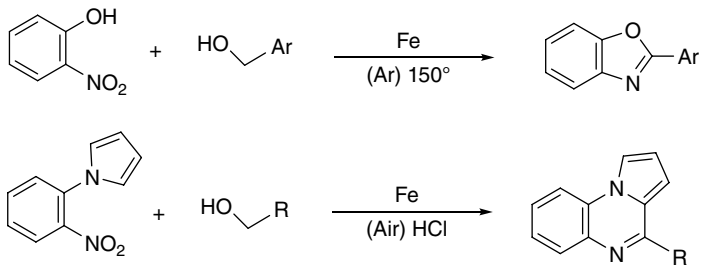
Iridium(IV) oxide

Dehydrative condensation.[1] The ability of iridium compounds to mediate redox reactions is further exploitable in converting a mixture of RCH_2CH_2OH and $ArCH_2OH$ into $RCH(CH_2Ar)CH_2OH$ by heating it with IrO_2/Fe_3O_4 and KOH in toluene. The catalyst is reusable.

[1] Cano, R., Yus, M., Ramón, D.J. *CC* **48**, 7628 (2012)

Iron

Cyclocondensation. Heterocyclic systems such as benzoxazole and quinoxaline are accessible from properly *o*-substituted nitroarenes and primary alcohols.[1,2]

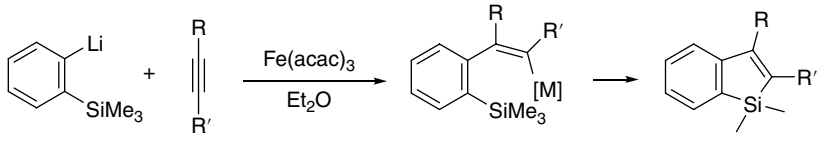


[1] Wu, M., Hu, X., Liu, J., Liao, Y., Deng, G.-J. *OL* **14**, 2722 (2012)
[2] Pereira, M.deF., Thiery, V. *OL* **14**, 4754 (2012)

Iron(II/III) acetylacetonate

Coupling reactions. Extension of a carbon chain of a bromoalkane is realizable on coupling with tetraorganoboratomagnesium chlorides, using $Fe(acac)_3$ as catalyst.[1]

Addition. 1-Alkynes undergo sulfonylchlorination in a $Fe(acac)_2$-catalyzed reaction with $ArSO_2Cl$ to produce, aryl (*E*)-2-chloro-1-alkenyl sulfones.[2] Benzosiloles are elaborated by an addition process involving 2-triorganosilylaryllithiums and alkynes.[3]

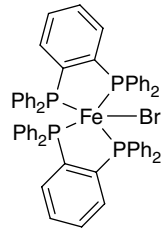


[1] Hatakeyama, T., Hashimoto, T., Kathriarachchi, K.K.A.D.S., Zenmyo, T., Seike, H., Nakamura, M. *ACIE* **51**, 8834 (2012)
[2] Zeng, X., Ilies, L., Nakamura, E. *OL* **14**, 954 (2012)
[3] Shirakawa, E., Masui, S., Narui, R., Watabe, R., Ikeda, D., Hayashi, T. *CC* **47**, 9714 (2011)

Iron(II) bromide

Metallation. A combination of lithium tetramethylpiperidide and $FeBr_2$ is useful for nuclear metallation of certain aromatic compounds, e.g., at C-3 of 2-methoxypyridine.[1]

Negishi coupling. A highly unusual Fe(I) complex that is active in promoting Negishi coupling is **1**.[2] It is available by treating the 1,2-bis(diphenylphosphino)benzene-$FeBr_2$ complex with $MgBr_2$.



(**1**)

[1] Nagaradja, E., Chevallier, F., Roisnel, T., Jouikov, V., Mongin, F. *T* **68**, 3063 (2012)
[2] Adams, C.J., Bedford, R.B., Carter, E., Gower, N.J., Haddow, M.F., Harvey, J.N., Huwe, M., Cartes, M.A., Mansell, S.M., Mendoza, C., Murphy, D.M., Neeve, E.C., Nunn, J. *JACS* **134**, 10333 (2012)

Iron(III) bromide

Diarylmethanes. Benzyl thiocyanates behave as benzylating agents in the presence of $FeBr_3$.[1]

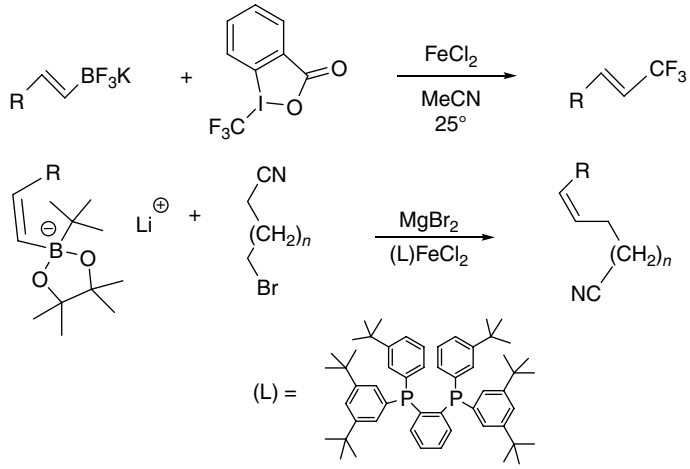
[1] Guo, X.-K., Zhao, D.-Y., Li, J.-H., Zhang, X.-G., Deng, C.-L., Tang, R.-Y. *SL* 627 (2012)

Iron(II) chloride

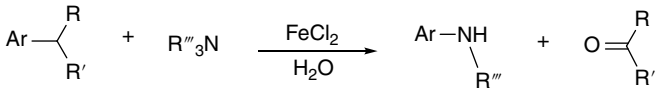
Dehydration. The presence of $FeCl_2$ is indicated in the dehydration of $ArCONH_2$ by $CF_3CON(SiMe_3)Me$.[1]

Substitution. To catalyze opening of aziridines with ArNHR a cocatalyst system of $FeCl_2$ and $AgSbF_6$ is found.[2] A far less expensive catalyst system for *N*-arylation (e.g., in comparison with Pd species) for ArN(R)MgBr is $FeCl_2$ – LiBr.[3]

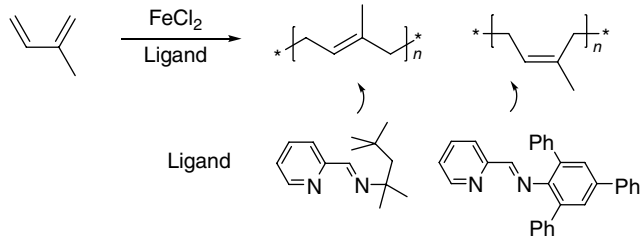
Another service of $FeCl_2$ is found in the coupling of alkenylboron reagents couple with halogen compounds.[4,5]



Homocoupling of arenediazonium salts to form biaryls is also readily catalyzed by $FeCl_2$.[6] More unusual is the report of a dealkylative arylation of amines.[7]

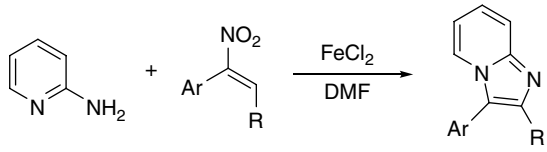


Addition and cycloaddition. Stereoselective polymerization of isoprene catalyzed by $FeCl_2$ is intimately associated with the ligand for the metal.[8]



Free radicals are generated from iodoalkanes on exposure to $(dppe)_2FeCl_2$ – $NaBH_4$, and the intramolecular addition of such species to a proximal double bond can be achieved.[9]

Imidazo[1,2-*a*]pyridines are assembled from 2-aminopyridine and nitroalkenes on treatment with $FeCl_2$ in DMF.[10]



N-Cyanoamines participate in cycloaddition with two alkyne molecules to form 2-aminopyridines. A catalytic system for this reaction is composed of $FeCl_2$, Zn and pyridine-2,6-bis(methylidene)dimesitylamine.[11]

Degradation. Carboxylic acids are degraded to alkenes (loss of CO and water) on heating with $FeCl_2$, KI and Ac_2O at 250° under N_2 or CO. Macrocyclic acids such as cyclododecanecarboxylic acids are similarly converted.[12] The reaction is not affected by free radical scavengers.

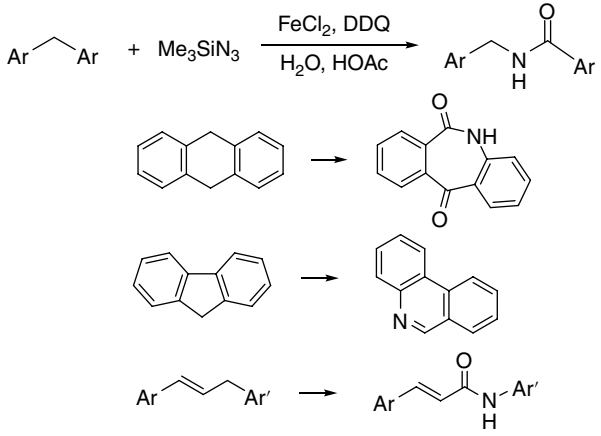
[1] Enthaler, S. *EJOC* 4760 (2011)
[2] Marti, A., Richter, L., Schneider, C. *SL* 2513 (2011)
[3] Hatakeyama, T., Imayoshi, R., Yoshimoto, Y., Ghorai, S.K., Jin, M., Takaya, K., Norisuje, K., Sohrin, Y., Nakamura, M. *JACS* **134**, 20262 (2012)
[4] Parsons, A.T., Senecal, T.D., Buchwald, S.L. *ACIE* **51**, 2947 (2012)
[5] Hashimoto, T., Hatakeyama, T., Nakamura, M. *JOC* **77**, 1168 (2012)
[6] Ding, Y., Cheng, K., Qi, C., Song, Q. *TL* **53**, 6269 (2012)
[7] Qin, C., Shen, T., Tang, C., Jiao, N. *ACIE* **51**, 6971 (2012)
[8] Raynaud, J., Wu, J.Y., Ritter, T. *ACIE* **51**, 11805 (2012)
[9] Ekomie, A., Lefevre, G., Fensterbank, L., Lacôte, E., Malacria, M., Ollivier, C., Jutand, A. *ACIE* **51**, 6942 (2012)
[10] Yan, H., Yang, S., Gao, X., Zhou, K., Ma, C., Yan, R., Huang, G. *SL* 2961 (2012)
[11] Lane, T.K., D'Souza, B.R., Louie, J. *JOC* **77**, 7555 (2012)
[12] Maetani, S., Fukuyama, T., Suzuki, N., Ishihara, D., Ryu, I. *CC* **48**, 2552 (2012)

Iron(II) chloride - oxidants

Substitution. It is expedient to generate electrophilic agents by oxidation in situ for nucleophilic substitution. Thus, propargyl ethers/esters are activated by $FeCl_2$-DDQ to be used to introduce an α-alkoxypropargyl group to 1,3-dicarbonyl compounds.[1] Under similar conditions, acyloxylation of propargylic azides provides bifunctional alkynes.[2]

Oxidative activation at a benzylic position and the α-carbon site of an amine is achieved with di-*t*-butyl peroxide, and the active species have been intercepted by azoles.[3,4]

A quite remarkable reaction sequence is that of transforming diarylmethanes into *N*-aryl arenecarboxamides with Me_3SiN_3.[5]

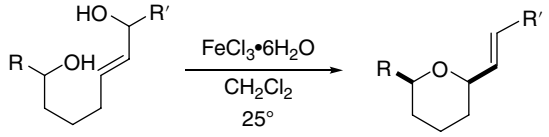


[1] Xie, Y., Yu, M., Zhang, Y. *S* 2803 (2011)
[2] Wang, T., Zhou, W., Yin, H., Ma, J.-A., Jiao, N. *ACIE* **51**, 10823 (2012)
[3] Xia, Q., Chen, W., Qiu, H. *JOC* **76**, 7577 (2011)
[4] Xia, Q., Chen, W. *JOC* **77**, 9366 (2012)
[5] Qin, C., Zhou, W., Chen, F., Ou, Y., Jiao, N. *ACIE* **50**, 12595 (2011)

Iron(III) chloride

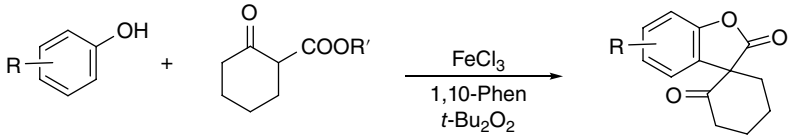
Dehydration.[1] Dehydration of propargylic alcohols to provide conjugated enynes, accomplished by catalysis of $FeCl_3$ proceeds in high yields only when a particular ligand [2-(1-benzotriazolyl)ethanol] is used. (The 95% yield observed in one case is decreased to <5% when the ligand is changed to 2-(2-pyridyl)ethanol.

Substitution. Several traditional Lewis acid-catalyzed substitution reactions are found to be equally well performed in the presence of $FeCl_3$. These include benzoins to benzoin ethers (with ROH),[2] and benzyl silyl ethers to benzyl azides (with Me_3SiN_3).[3] Also the substitution that changes a halogen atom attached to an sp^2-carbon atom to a thio group,[4] and the intramolecular S_N2' process leading to 2-alkenyl oxacycles.[5]



Double substitution on CH_2Cl_2 occurs in its incorporation into propargylic amines, in an assemblage with 1-alkynes and amines.[6] (*Z*)- 3-chloro-2-alken-1-ones are the products from reaction of RCOCl and 1-alkynes which is catalyzed by $FeCl_3$. Interestingly, alkynones are obtained by changing the alkynes to the 1-trimethylsilylalkynes.[7]

Electron-rich arenes including phenol, furan and thiophene, combine with *N*-acetylindoles to give the 3-arylindolines under the influence of $FeCl_3$,[8] the reaction can be considered as an electrophilic aromatic substitution. Phenols form a new CC bond at an *o*-position with cyclic β-keto esters to deliver spirocyclic products.[9] In this reaction an oxidant (*t*-Bu_2O_2) activates the β-keto esters.



Oxidative allylic substitution by *O*- and *N*-nucleophiles R′XH_n transforms $RCH_2C(Ar)$=CHR into RCH(XR′)C(Ar)=CHR, when carried out with $FeCl_3$, NaI, PrSSPr in air.[10] Decarboxylation accompanies alkylation of 3-oxoalkanoic acids with secondary tosylamines.[11]

1-Trimethylsilyl-1-alkyn-3-ols react with $TsNHNH_2$, which affords conjugated nitriles.[12] The role $FeCl_3$ plays is to help ionization of the hydroxy group.

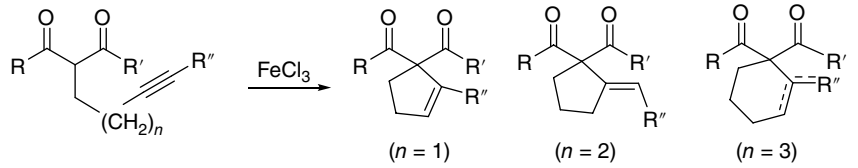
α-Oximation of aldehydes can be carried out with pyrrolidine, $NaNO_2$, and $FeCl_3$.[13] Apparently pyrrolidine plays a double role of enamination and formation of the nitrosating agent, *N*-nitrosopyrrolidine.

Addition. Both hydrothiolation of styrenes and hydration of 1-alkynes (both in the Markovnikov sense) are catalyzed by a combination of $FeCl_3$ and $AgNTf_2$ in dioxane at 80°.[14,15] With $FeCl_3$ present the reaction of alkynes with an *N*-halosuccinimide changes course to deliver α,α-dihaloketones in aq.THF (in anhydrous THF only dihaloalkenes are produced), arylethynes undergo this transformation (into $ArCOCHX_2$) without catalyst.[16]

N-Substituted cyanamides add ROH in the presene of $FeCl_3$.[17] The 1,3-disubstituted ureas obtained from the reaction apparently are the rearrangement products (from the isoureas).

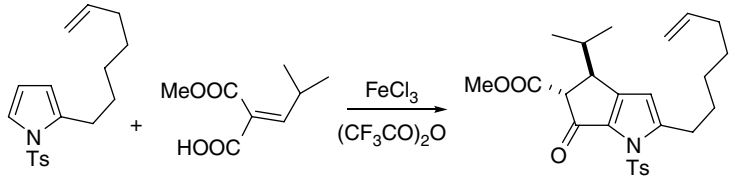
Insertion of CO_2 into small oxacycles (oxiranes, oxetanes) forms homologous cyclic carbonates, apparently both reactants being interacted with $FeCl_3$ (a special tertiary benzylamine ligand is employed in the reaction).[18]

Cyclization. 2-Alkynyl-1,3-dicarbonyl compounds are transformed into 1,1-diacylcycloalkanes or cyloalkenes.[19] In the $FeCl_3$-catalyzed cyclization there is some correlation of ring size and double bond position of the products with respect to the distance between the triple bond and the carbonyl group(s) in the substrates.

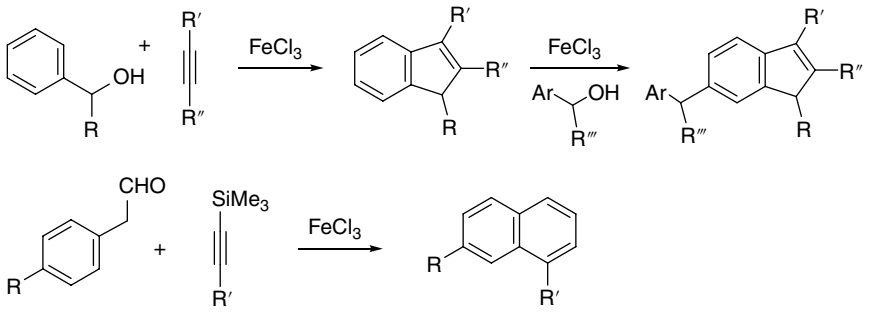


The cyclization of 2-(2-oxoalkoxy)maleic esters to yield furan-2,3-dicarboxylic esters is a well-anticipated result from catalysis by a Lewis acid, and hence the effectiveness of

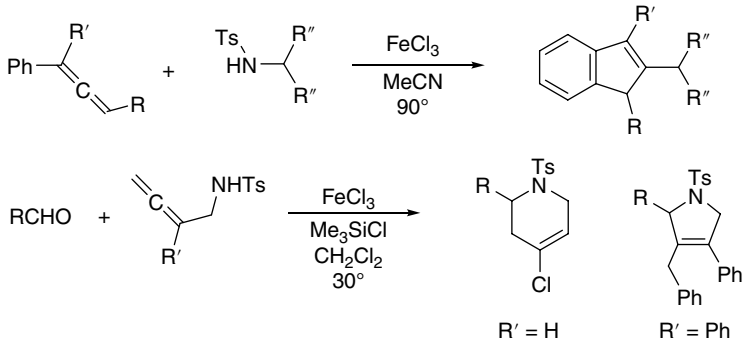
$FeCl_3$.[20] Friedel-Crafts annulation of 2-substituted *N*-tosylpyrroles in a single step definitely smoothed a synthetic pathway toward roseophilin.[21]



4-Alkynones and RNH_2 condense in the presence of $FeCl_3$ to provide pyrroles.[22] Cyclization of *N*-arylthioamides to afford benzothiazoles requires the combination of a Lewis acid (e.g., $FeCl_3$) and an oxidant (e.g., $Na_2S_2O_8$).[23] Activation of a triple bond or an oxygenated carbon site by $FeCl_3$ is implicated in the formation of isocoumarins from 2-alkynylbenzoic esters,[24] indenes from mixtures of benzyl alcohols and alkynes,[25] and naphthalenes from arylacetaldehydes and 1-trimethylsilylalkynes.[26]



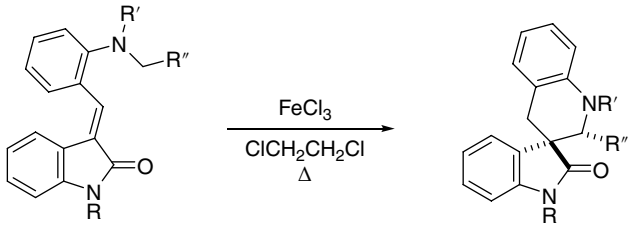
Indene formation is also initiated by alkylation of arylallenes, which forms allylic cations to be trapped on cyclization.[27] Heterocyclization results from allenylmethyl amines on reaction with aldehydes.[28]



The elaboration of 3-arylquinolines from aniline and styrene oxides involves two equivalents of the latter molecule, there is a net loss of an [ArCO] fragment.[29] Cyclization of *N*-(3-aryl-2-propynyl)-*N*-tosylanilines to provide 4-arylquinolines is straightforward,[30] so is the dehydrative process via ionization of allylic/benzylic alcohols with intramolecular trapping by an *o*-amino function in an aromatic ring, leading to 1,2-dihydroquinolines.[31]

Still further examples of annulation involving alkynes are those assembled with arylindium halides, after transmetallation (with Me_3SiCH_2MgCl) of the latter species (ultimately producing naphthalenes).[32] 2-Acyl-2′-alkynylbiaryls undergo cyclization to give 9-acylphenanthrenes.[33]

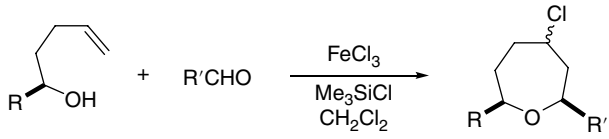
When 3-alkylidene oxindoles interact with Lewis acids, the β-position is rendered nucleophilic. This mechanistic understanding has been exploited for design of a reaction sequence that consists of 1,5-hydride shift and spiroannulation.[34]



Again, provision of *N*-oxidation to eventually render an α-carbon to an arylamino nitrogen atom electrophilic and the presence of alkenes or alkynes, it is possible to synthesize quinolines from the proper components.[35,36] Necessarily, in addition to $FeCl_3$, an oxidizing agent [e.g., *t*-Bu_2O_2, $(TEMPO)^+(BF_4)^-$] must be added.

Several reactions are integrated into the elaboration of 2-aroylbenzoxazoles and benzothiazoles from bromoethynylarenes and *o*-aminophenols/thiophenols. There are a twofold coupling and oxygenation.[37]

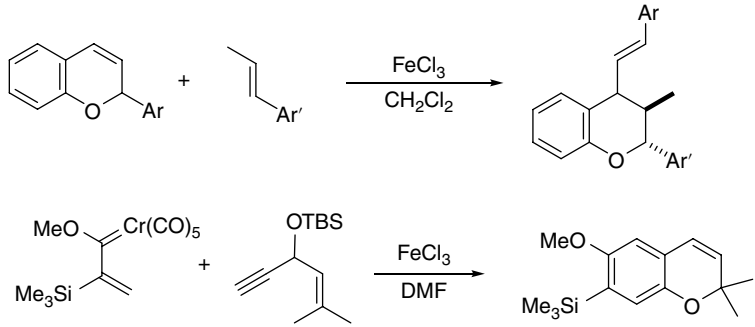
To create oxacycles from alkenols and aldehydes by the Prins reaction requires acidic conditions. Predominant generation of 2,7-*cis*-disubstituted oxepanes in the $FeCl_3$-mediated process[38] are of some synthetic significance.



Cycloaddition. Cyclopropanation of alkenes using a mixture of CH_2Br_2 and *i*-Bu_3Al is catalyzed by $FeCl_3$.[39] Push-pull cyclopropane derivatives readily undergo ring opening in the presence of a Lewis acid ($FeCl_3$), and their participation in regioselective [3+2] cycloaddition, e.g., with RCHO is anticipated (and realized).[40] Certain (easily oxidizable)

stilbenes and styrenes combine to afford 1,3-diarylnaphthalenes when exposed to $FeCl_3$ and DDQ.[41]

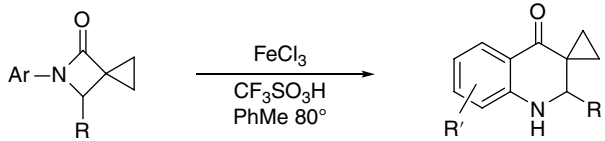
Formation of *o*-quinonemethides from 2-aryl-2H-chromenes is followed by trapping to form chromanes.[42] More intriguingly is the combination of Fischer-type carbenoids with alkenyl alkynyl carbinol silyl ethers,[43] in which $FeCl_3$ apparently serves to oxidize the metal carbenoids to initiate a nucleophilic attack.



Oxidation. Potassium organotrifluoroborates are susceptible to oxidation by $FeCl_3$ in aqueous THF, giving rise to $RB(OH)_2$.[44] An unusual transformation of a methyl group at C-2 of a quinoxaline ring to a vinyl substituent is observed under the influence of $FeCl_3$ and $K_2S_2O_8$, the extra carbon atom comes from an *N*-methyl group of the solvent $AcNMe_2$.[45]

1-Aryl-1,alkanediones lose the active methylene group to form α-diketones on treatment with $FeCl_3$ and *t*-BuONO at 30°.[46] It is likely that oximation (nitrosation) and further oxidation precipitate the event.

Rearrangement. α,α-Polymethylene *N*-aryl-β-lactams undergo ring expansion into spirocyclic tetrahydroquinolin-4-ones on treatment with $FeCl_3$ and CF_3SO_3H in toluene.[47]



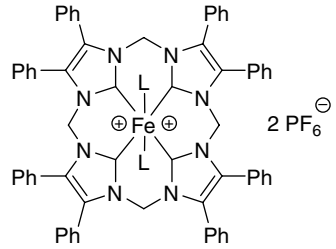
[1] Yan, W., Ye, X., Akhmedov, N.G., Petersen, J.L., Shi, X. *OL* **14**, 2358 (2012)
[2] Mirzaei, A., Biswas, S., Samec, J.S.M. *S* 1213 (2012)
[3] Sawama, Y., Nagata, S., Yabe, Y., Morita, K., Monguchi, Y., Sajiki, H. *CEJ* **18**, 16608 (2012)
[4] Lin, Y.-Y., Wang, Y.-J., Lin, C.-H., Cheng, J.-H., Lee, C.-F. *JOC* **77**, 6100 (2012)
[5] Guerinot, A., Serra-Muns, A., Bensoussan, C., Reymond, S., Cossy, J. *T* **67**, 5024 (2011)
[6] Gao, J., Song, Q.-W., He, L.-N., Yang, Z.-Z., Dou, X.-Y. *CC* **48**, 2024 (2012)
[7] Gandeepan, P., Parthasarathy, K., Su, T.-H., Cheng, C.-H. *ASC* **354**, 457 (2012)
[8] Beaud, R., Guillot, R., Kouklovsky, C., Vincent, G. *ACIE* **51**, 12546 (2012)

[9] Parnes, R., Kshirsagar, U.A., Werbeloff, A., Regev, C., Pappo, D. *OL* **14**, 3324 (2012)
[10] Huang, D., Wang, H., Xue, F., Shi, Y. *JOC* **76**, 7269 (2011)
[11] Yang, C.-F., Wang, J.-Y., Tian, S.-K. *CC* **47**, 8343 (2011)
[12] Hao, L., Wu, F., Ding, Z.-C., Xu, S.-X., Ma, Y.-L., Chen, L., Zhan, Z.-P. *CEJ* **18**, 6453 (2012)
[13] Gentili, P., Pedetti, S. *CC* **48**, 5358 (2012)
[14] Cabrero-Antonino, J.R., Leyva-Perez, A., Corma, A. *ASC* **354**, 678 (2012)
[15] Cabrero-Antonino, J.R., Leyva-Perez, A., Corma, A. *CEJ* **18**, 11107 (2012)
[16] Liu, J., Li, W., Wang, C., Li, Y., Li, Z. *TL* **52**, 4320 (2011)
[17] Basavaprabhu, H., Sreshbabu, V.V. *OBC* **10**, 2528 (2012)
[18] Whiteoak, C.J., Martin, E., Belmonte, M.M., Benet-Buchholz, J., Kleij, A.W. *ASC* **354**, 469 (2012)
[19] Chan, L.Y., Kim, S., Park, Y., Lee, P.H. *JOC* **77**, 5239 (2012)
[20] Cao, H., Zhan, H., Wu, J., Zhong, H., Lin, Y., Zhang, H. *EJOC* 2318 (2012)
[21] Song, C., Liu, H., Hong, M., Liu, Y., Jia, F., Sun, L., Pan, Z., Chang, J. *JOC* **77**, 704 (2012)
[22] Wang, Y., Bi, X., Li, D., Liao, P., Wang, Y., Yang, J., Zhang, Q., Liu, Q. *CC* **47**, 809 (2011)
[23] Wang, H., Wang, L., Shang, J., Li, X., Wang, H., Gui, J., Lei, A. *CC* **48**, 76 (2012)
[24] Speranca, A., Godoi, B., Pinton, S., Back, D.F., Menezes, P.H., Zeni, G. *JOC* **76**, 6789 (2011)
[25] Bu, X., Hong, J., Zhou, X. *ASC* **353**, 2111 (2011)
[26] Bu, X., Hong, L., Liu, R., Hong, J., Zhang, Z., Zhou, X. *T* **68**, 7960 (2012)
[27] Liu, C.-R., Wang, T.-T., Qi, Q.-B., Tian, S.-K. *CC* **48**, 10913 (2012)
[28] Cheng, J., Tang, X., Yu, Y., Ma, S. *CC* **48**, 12074 (2012)
[29] Zhang, Y., Wang, M., Li, P., Wang, L. *OL* **14**, 2206 (2012)
[30] Roy, B., Ansary, I., Samanta, S., Majumdar, K.C. *TL* **53**, 5119 (2012)
[31] Wang, Z., Li, S., Yu, B., Wu, H., Wang, Y., Sun, X. *JOC* **77**, 8615 (2012)
[32] Adak, L., Yoshikai, N. *T* **68**, 5167 (2012)
[33] Bera, K., Sarkar, S., Jalal, S., Jana, U. *JOC* **77**, 8780 (2012)
[34] Han, Y.-Y., Han, W.-Y., Hou, X., Zhang, X.-M., Yuan, W.-C. *OL* **14**, 4054 (2012)
[35] Liu, P., Li, Y., Wang, H., Wang, Z., Hu, X. *TL* **53**, 6654 (2012)
[36] Richter, H., Mancheño, O.G. *OL* **13**, 6066 (2011)
[37] Cui, L., He, Y., Fan, X. *ChJC* **30**, 992 (2012)
[38] Purino, M.A., Ramirez, M.A., Daranas, A.H., Martin, V.S., Padron, J.I. *OL* **14**, 5904 (2012)
[39] Brunner, G., Elmer, S., Schröder, F. *EJOC* 4623 (2011)
[40] Benfatti, F., de Nanteuil, F., Waser, J. *OL* **14**, 386 (2012)
[41] Liu, H., Cao, L., Sun, J., Fossey, J.S., Deng, W.-P. *CC* **48**, 2674 (2012)
[42] Luan, Y., Sun, H., Schaus, S.E. *OL* **13**, 6480 (2011)
[43] Majumdar, N., Korthals, K.A., Wulff, W.D. *JACS* **134**, 1357 (2012)
[44] Blevins, D.W., Yao, M.-L., Yong, L., Kabalka, G.W. *TL* **52**, 6534 (2011)
[45] Lou, S.-J., Xu, D.-Q., Shen, D.-F., Wang, Y.-F., Liu, Y.-K., Xu, Z.-Y. *CC* **48**, 11993 (2012)
[46] Huang, L., Cheng, K., Yao, B., Xie, Y., Zhang, Y. *JOC* **76**, 5732 (2011)
[47] Hu, Y., Fu, X., Barry, B.-D., Bi, X., Dong, D. *CC* **48**, 690 (2012)

Iron(II) iodide

Cyanation.[1] Arenes are converted into ArCN by reaction with CuCN in DMF at 130°, an oxidant [air or $PhI(OAc)_2$] besides the catalyst FeI_2 is required.

Cycloaddition. The catalytic system consisting of FeI_2, DPPP, and zinc promotes formation of the pyridine ring from a diyne and RCN.[2] The Fe(II) complex **1** that can bring about aziridine formation from alkenes and ArN_3 is prepared from FeI_2.[3]



(**1**) L = MeCN

[1] Zhang, G., Lv, G., Pan, C., Cheng, J., Chen, F. *SL* 2991 (2011)
[2] Wang, C., Li, X., Wu, F., Wan, B. *ACIE* **50**, 7162 (2011)
[3] Cramer, S.A., Jenkins, D.M. *JACS* **133**, 19342 (2011)

Iron(III) nitrate

Oxidation.[1] Oxidation of alcohols to carbonyl compounds by 4-hydroxy-TEMPO in air is catalyzed by $Fe(NO_3)_3$. The reaction is accelerated by NaCl.

Hydrofluorination.[2] Markovnikov addition of HF to unactivated alkenes is accomplished with Selectfluor, $NaBH_4$, and $Fe(NO_3)_3$ in aqueous MeCN at 0°. This is a free-radical reaction.

[1] Tamura, N., Aoyama, T., Takido, T., Kodomari, M. *SL* 1397 (2012)
[2] Barker, T.J., Boger, D.L. *JACS* **134**, 13588 (2012)

Iron(II) oxalate

Hydroazidation.[1] Alkenes are transformed into alkyl azides by reaction with NaN_3 in an aqueous medium, the other reagents are Fe(II) oxalate and $NaBH_4$.

[1] Leggans, E.K., Barker, T.J., Duncan, K.K., Boger, D.L. *OL* **14**, 1428 (2012)

Iron oxides

N-Arylation.[1] The use of Fe_2O_3 and *t*-BuOK in DMSO to effect arylation of diarylamines is less costly than a Pd catalyst.

Redox reactions. Reduction of $ArNO_2$ using reusable magnetite (Fe_3O_4) is convenient.[2] On the other hand, oxidative cleavage of styrenes occurs on supported nano-Fe_2O_3.[3]

Annulation. Synthesis of imidazo[1,2-*a*]pyridines from 2-aminopyridine, RCHO, and 1-alkynes is accomplished on heating the mixture with nano-Fe_3O_4, $KHSO_4$ on silica in toluene.[4]

Caveat. Employing magnetite as a core to attach catalytic components has become popular because recovery of the catalyst is greatly facilitated. However, one should be aware that magnetite is not always inert.[5]

[1] Alakonda, L., Periasamy, M. *S* 1063 (2012)
[2] Kim, S., Kim, E., Kim, B.M. *CAJ* **6**, 1921 (2011)
[3] Rajabi, F., Karimi, N., Saidi, M.R., Primo, A., Varma, R.S., Luque, R. *ASC* **354**, 1707 (2012)
[4] Guntreddi, T., Allam, B.K., Singh, K.N. *SL* 2635 (2012)
[5] Gleeson,O., Davies, G.-L., Peschiulli, A., Tekoriute, R., Gun'ko, Y.K., Connon, S.J. *OBC* **9**, 7929 (2011)

Iron(II) sulfate

Carbonitrosation.[1] 1-Alkenes combine with arenediazonium salts and nitric oxide (from waste gas) to form ketoximes of the constitution $ArCH_2C(=NOH)R$ when mixed with $FeSO_4$ in DMSO and an acetate buffer.

[1] de Salas, C., Blank, O., Heinrich, M.R. *CEJ* **17**, 9306 (2011)

Iron(II) sulfide

Arylation.[1] Under oxidative conditions ($K_2S_2O_8$) and catalysis of FeS, pyridines and benzoquinones are arylated by $ArB(OH)_2$.

[1] Wang, J., Wang, S., Wang, G., Zhang, J., Yu, X.-Q. *CC* **48**, 11769 (2012)

Iron(II) tetrafluoroborate

Hydrogenation.[1] A new method for semihydrogenation of alkynes involves $Fe(BF_4)_2$ [ligand: $(Ph_2PCH_2CH_2)_3P$] to catalyze hydrogen transfer from HCOOH.

Cycloaddition. A tetraphenylporphyrin-coordinated $Fe(BF_4)$ promotes condensation of conjugated aldehydes (and ArCHO) with simple dienes to give dihydropyrans,[2] The adducts are mainly *cis*-substituted at C-2 and C-6. [A cognate reagent, the porphyrin-iron complex with chloride anion is found to promote cyclopropanation with the carbene derived from ethyl glycinate.[3]]

[1] Wienhöfer, G., Westerhaus, F.A., Jagadeesh, R.V., Junge, K., Junge, H., Beller, M. *CC* **48**, 4827 (2012)
[2] Fujiwara, K., Kurahashi, T., Matsubara, S. *JACS* **134**, 5512 (2012)
[3] Morandi, B., Dolva, A., Carreira, E.M. *OL* **14**, 2162 (2012)

Iron(III) tosylate

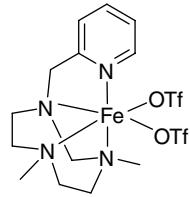
Esterification.[1] Esterification of alcohols by carboxylic anhydrides is said to be catalyzed by $Fe(OTs)_3$, although the advantage is questionable except the conversion of aldehydes into $RCH(OAc)_2$.

Ether cleavage.[2] Tetrahydropyranyl ethers are cleaved in MeOH in the presence of $Fe(OTs)_3$.

[1] Baldwin, N.J., Nord, A.N., O'Donnell, B.D., Mohan, R.S. *TL* **53**, 6946 (2012)
[2] Bockman, M.R., Angeles, V.V., Martino, J.M., Vagadia, P.P., Mohan, R.S. *TL* **52**, 6939 (2011)

Iron(II) triflate

Oxidation. The complex **1** is converted into a reagent for hydroxylation of alkanes and cis-1,2-dihydroxylation of alkenes by CAN in water.[1]



(**1**)

[1] Garcia-Bosch, I., Codola, Z., Prat, I., Ribas, X., Lloret-Fillol, J., Costas, M. *CCEJ* **18**, 13269 (2012)

Iron(III) triflate

Biaryls. A method for synthesizing unsymmetrical biaryls from ArH and Ar′B(OH)$_2$ involves oxidative cleavage of the arylboronic acids to give aryl radicals. The reagent system contains Fe(OTf)$_3$, *t*-Bu$_2$O$_2$, and a phenanthroline ligand.[1]

[1] Uchiyama, N., Shirakawa, E., Nishikawa, R., Hayashi, T. *CC* **47**, 11671 (2011)

L

Lanthanum chloride

Friedländer synthesis.[1] The employment of $LaCl_3$ in HOAc to conduct Friedländer synthesis of 3-acylquinolines from 1,3-dicarbonyl compounds is described in a report.

[1] Chen, Y., Huang, J., Hwang, T.-L., Li, T.J., Cui, S., Chen, J., Bio, M. *TL* **53**, 3237 (2012)

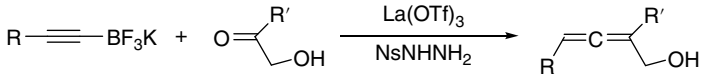
Lanthanum nitrate

Transesterification.[1] In situ generation of $La(NO_3)_n(OR)_{3-n}$ probably occurs when $La(NO_3)_3$ is used as a catalyst for transesterification.

[1] Hatano, M., Kamiya, S., Ishihara, K. *CC* **48**, 9465 (2012)

Lanthanum triflate

Allene synthesis. A three-component assemblage of allenes involves condensation of carbonyl compounds with $NsNHNH_2$ and reaction with potassium alkynyltrifluoroborates. A suitable catalyst is $La(OTf)_3$.[1]

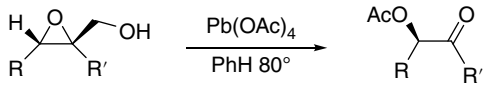


[1] Mundal, D.A., Lutz, K.E., Thomson, R.J. *JACS* **134**, 5782 (2012)

Lead(IV) acetate

2-Formylaryl ketones.[1] Oxidation with $Pb(OAc)_4$ the acylhydrazones derived from salicylaldehyde and $RCONHNH_2$ are transformed into 2-formylaryl ketones.

α-Acetoxy carbonyl compounds. Degradation of oxirane-2-methanols by $Pb(OAc)_4$ is preceded by *O*-acetylation and an internal S_N2 reaction, which unveils the α-glycol unit.[2]



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[1] Augner, D., Gerbino, D.C., Slavov, N., Neudörfl, J.-M., Schmalz, H.-G. *OL* **13**, 5374 (2011)
[2] Alvarez-Manzaneda, E., Chahboun, R., Alvarez, E., Alvarez-Manzaneda, R., Munoz, P.E., Jimenez, F., Bouanou, H. *TL* **52**, 4017 (2011)

Lithium aluminum hydride

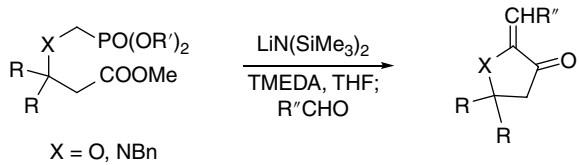
Reductive dephosphonylation. When β-phosphonyl esters are reduced by $LiAlH_4$ the phosphorus residue is completely removed.[1]

[1] Zhu, J.-L., Bau, J.-S., Shih, Y.-C. *SL* 863 (2012)

Lithium diisopropylamide (LDA)

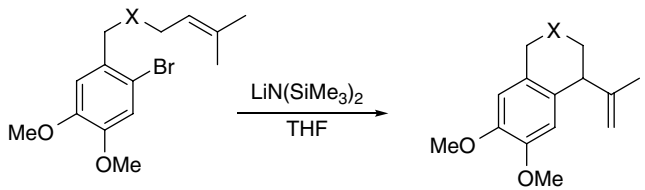
Isomerization. 2-triflyloxyindoles on treatment with LDA undergo isomerization to afford 3-(triflyl)oxindoles.[1]

2-Alkylidene-3-oxo heterocycles. Esters bearing an ω-dialkoxyphosphonylmethyloxy or amino substituent (at some proper distance) cyclize to β-oxophosphonates, Alkylidenation (Horner-Wadsworth-Emmons reaction) occurs on further addition of RCHO.[2]

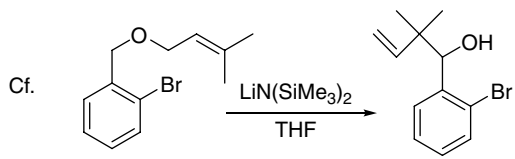


X = O, NBn

Benzyne generation. Dehydrobromination of certain aryl bromides by LDA is not always in high priority unless some nuclear substituents facilitate the deprotonation.[3]



X = O, NMe



[1] Xu, X.-H., Wang, X., Liu, G., Tokunaga, E., Shibata, N. *OL* **14**, 2544 (2012)
[2] Maegawa, T., Otake, K., Hirosawa, K., Goto, A., Fujioka, H. *OL* **14**, 4798 (2012)
[3] Candito, D.A., Panteleev, J., Lautens, M. *JACS* **133**, 14200 (2011)

Lithium hexamethyldisilazide (LiHMDS)

Allylation. Benzylic allylation is readily accomplished via deprotonation of the arene-$Cr(CO)_3$ complexes by LiHMDS.[1]

Difluoromethylation.[2] Lithium enolates (from ketones) react with HCF_3, a rather unusual expulsion of a fluoride ion in an S_N2 process.

[1] Zhang, J., Stanciu, C., Wang, B., Hussain, M.M., Da, C.-S., Carroll, P.J., Dreher, S.D., Walsh, P.J. *JACS* **133**, 20552 (2011)
[2] Iida, T., Hashimoto, R., Aikawa, K., Ito, S., Mikami, K. *ACIE* **51**, 9535 (2012)

Lithium iodide

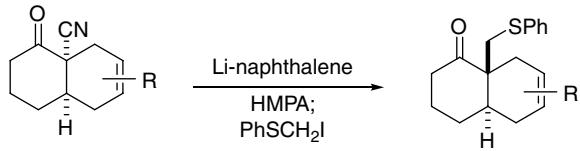
Rearrangement. 2-Alkoxypyridines (primary alkyl) on heating with LiI afford *N*-alkyl 2-pyridones.[1]

[1] Tasker, S.Z., Bosscher, M.A., Shandro, C.A., Lanni, E.L., Ryu, K.A., Snapper, G.S., Utter, J.M., Ellsworth, B.A., Andersson, C.E. *JOC* **77**, 8220 (2012)

Lithium naphthalenide (LN)

Reductive amination. On admixture RCHO and $R'NH_2$ combine in the presence of lithium and catalytic arene in THF to produce RCH_2NHR'.[1]

Alkylation. Angular alkylation of keto enolates regioselectively generated from the α-cyano ketones is a versatile method. Furthermore, from a *cis*-fused substrate products with a *trans*-juncture are obtained.[2]



Aryllithiums. Sterically hindered aryllithiums can be prepared by Cl/Li exchange using LN (Li spherules, $C_{10}H_8$) in ether.[3]

[1] Nador, F., Moglie, Y., Ciolino, A., Pierini, A., Dorn, V., Yus, M., Alonso, F., Radivoy, G. *TL* **53**, 3156 (2012)
[2] Peng, F., Grote, R.E., Danishefsky, S.J. *TL* **52**, 3957 (2011)
[3] Screttas, C.G., Steele, B.R., Micha-Screttas, M., Heropoulos, G.A. *OL* **14**, 5680 (2012)

Lithium tetrakis(pentafluorophenyl)borate

Baeyer-Villger oxidation.[1] Ketones are oxidized by H_2O_2 in the presence of $LiB(C_6F_5)_4$ or $Ca[B(C_6F_5)_4]_2$.

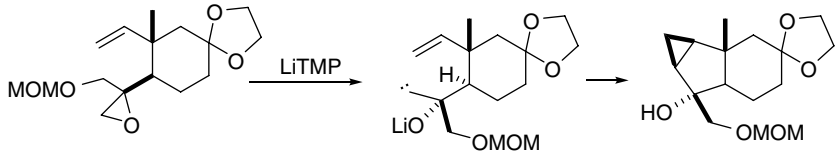
[1] Uyanik, M., Nakashima, D., Ishihara, K. *ACIE* **51**, 9093 (2012)

Lithium 2,2,6,6-tetramethylpiperidide (LiTMP)

Deacetalization. A new method for deprotection of carbonyl compounds from ethyleneacetals employs LiTMP.[1]

Substitution. Arylation at an *sp*-carbon (e.g., of 1-alkyn-3-ols) is accomplished with LiTMP, no transition metal catalysts are required.[2] In silylation of monosubstituted oxiranes usually the *trans*-products are formed.[3]

After lithiation oxiranes may devolve into carbenes, an exploitation of such transformation is intramolecular cyclopropanation.[4]



Benzyne is generated from PhCl by dehydrochlorination with LiTMP. 1,2,3, 4-Tetrahydroquinoline undergoes phenylation at C-8.[5]

[1] Yuan, C., Yang, L., Yue, G., Yu, T., Zhong, W., Liu, B. *TL* **53**, 6972 (2012)
[2] Truong, T., Daugulis, O. *OL* **13**, 4172 (2011)
[3] Hodgson, D.M., Salik, S. *OL* **14**, 4402 (2012)
[4] Yue, G., Yang, L., Yuan, C., Jiang, X., Liu, B. *OL* **13**, 5406 (2011)
[5] Truong, T., Daugulis, O. *OL* **14**, 5964 (2011)

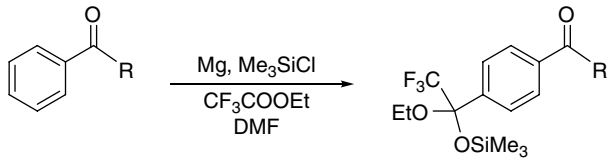
M

Magnesium

Reductive cleavage. The facile cleavage of the O-C bond of pyridine-4-methyl esters with Mg in MeOH or water at room temperature may render such esters as protected carboxylic acids.[1]

Enol ethers. Ethyleneacetals of α-bromo ketones are transformed regioselectively into enoxyethoxymagnesium bromides, which can be derivatized into silyl ethers, benzoates, etc.[2]

Substitution. A trifluoroacetyl group in the form of mixed acetals enters at the *p*-position of an aryl ketone when Mg, Me_3SiCl, and CF_3COOEt are added.[3]



B-Alkylation of pinacolborane involves magnesiation and quenching with organobromides.[4] Defluorosilylation of trifluoroacetic esters proceeds via magnesioenolate formation (Mg, CuCl, LiCl in dimethylimidazolidinone) which is followed by Me_3SiCl quench.[5]

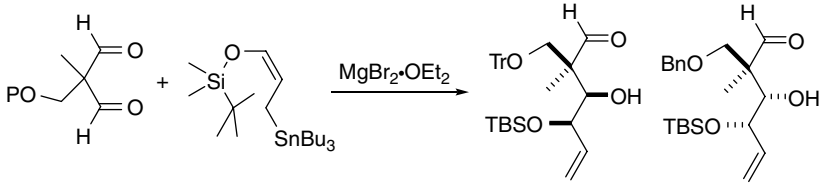
Benzo[*h*]quinoline is arylated at C-10 by ArBr, when mixing with Mg, $Fe(acac)_3$, 4,4′-di-*t*-butyl-2,2′-bipyridyl, and $Me_2C(Cl)CH_2Cl$.[6]

[1] Zhu, J., Miao, W., Bao, L., Ji, T., Tang, G., Xu, P., Zhao, Y. *SL* 142 (2012)
[2] André, M., Letribot, B., Bayle, M., Mounetou, E., Chezal, J.-M. *TL* **53**, 6107 (2012)
[3] Maekawa, H., Ozaki, T., Zulkeflee, D., Murakami, T., Kihara, S., Nishiguchi, I. *SL* 401 (2012)
[4] Clary, J.W., Rettenmaier, T.J., Snelling, R., Bryks, W., Banwell, J., Wipke, W.T., Singaram, B. *JOC* **76**, 9602 (2011)
[5] Utsumi, S., Katagiri, T., Uneyama, K. *T* **68**, 580 (2012)
[6] Ilies, L., Kobayashi, M., Matsumoto, A., Yoshikai, N., Nakamura, E. *ASC* **354**, 593 (2012)

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Magnesium bromide etherate

Allylation.[1] α-Alkoxymethylmalonaldehydes react with allylstannanes diastereoselectively, depending on the nature of the alkoxy group.



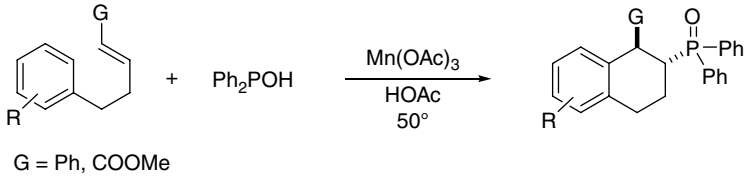
[1] Linclau, B., Cini, E., Oakes, C.S., Josse, S., Light, M., Ironmonger, V. *ACIE* **51**, 1232 (2012)

Manganese(III) acetate

Formamides.[1] Amines are formylated by RCH_2CHO in the presence of $Mn(OAc)_3$ in the air.

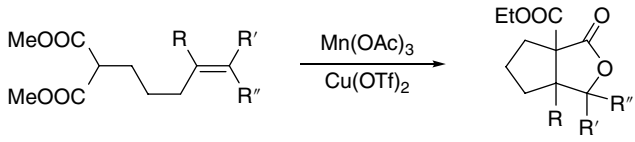
Addition. Conjugated ketones are chlorinated (to α,β-dichloro ketones) using aq. HCl with assistance of $Mn(OAc)_3$.[2] Functionalization of cycloalkenes (5- to 7-membered demonstrated) by adding a chlorine atom and a β-dicarbonyl unit is realized in aq. HCl, but it requires suprastoichiometric $Mn(OAc)_3$.[3]

Cyclization. Tetralins phosphonylated at C-2 are formed from certain 3-alkenylarenes and $Ph_2P(O)H$, in a reaction mediated by $Mn(OAc)_3$.[4]

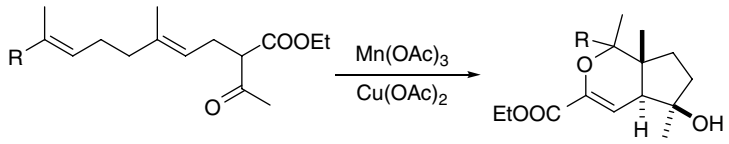


N-Alkynylaminomalonic esters in which the triple bond is 3 or 4 bonds away from the nitrogen atom undergo cyclization to afford azacycles with a (*Z*)-configured exocyclic double bond.[5]

4-Alkenylmalonic esters are transformed into bicyclic lactones under the consorted influence of $Mn(OAc)_3$ and $Cu(OTf)_2$.[6]



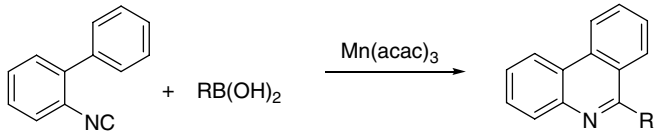
A more complex reaction involves oxidative loss of an acetyl group prior to cyclization.[7]



[1] Zhang, C., Xu, Z., Shen, T., Wu, G., Zhang, L., Jiao, N. *OL* **14**, 2362 (2012)
[2] Liu, X., Wang, L., Zou, J. *ChJC* **29**, 2097 (2011)
[3] Dengiz, C., Caliskan, R., Balci, M. *TL* **53**, 550 (2012)
[4] Pan, X.-Q., Wang, L., Zou, J.-P., Zhang, W. *CC* **47**, 7875 (2011)
[5] Keane, H.A., Hess, W., Burton, J.W. *CC* **48**, 6496 (2012)
[6] Logan, A.W.J., Parker, J.S., Hallside, M.S., Burton, J.W. *OL* **14**, 2940 (2012)
[7] Li, Z., Jung, H., Park, M., Lah, M.S., Koo, S. *ASC* **353**, 1913 (2011)

Manganese(III) acetylacetonate

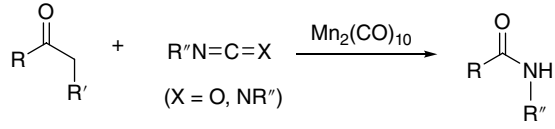
Benz[c]quinolines.[1] 2-Isocyanobiphenyl and organoboronic acids react in the presence of $Mn(acac)_3$ to deliver the benzoquinolines.



[1] Tobisu, M., Koh, K., Furukawa, T., Chatani, N. *ACIE* **51**, 11363 (2012)

Manganese carbonyls

Amides.[1] Metathetic transformation among ketones and carbodiimides or isocyanates catalyzed by $Mn_2(CO)_{10}$ or $[HMn(CO)_4]_3$ is quite unusual.



[1] Kuninobu, Y., Uesugi, T., Kawata, A., Takai, K. *ACIE* **50**, 10406 (2011)

Manganese(II) chloride

Secondary alkyl chlorides.[1] It is found that conversion of secondary alkyl mesylates into the corresponding chlorides by reaction with LiCl is accelerated by $MnCl_2$.

Cross-coupling. Replacing a BuTe group on a double bond is performed with ArMgCl in the presence of $MnCl_2$ and CuI.[2]

[1] Cahiez, G., Gager, O., Moyeux, A., Delacroix, T. *ASC* **354**, 1519 (2012)
[2] Silva, M.S., Ferrarini, R.S., Sousa, B.A., Toledo, F.T., Comasseto, J.V., Gariani, R.A. *TL* **53**, 3556 (2012)

Manganese(II) fluoride

N-Arylation.[1] A condition for arylation of azoles consists of a catalytic system of MnF_2, CuI, KOH, 1,2-diaminocyclohexane in water.

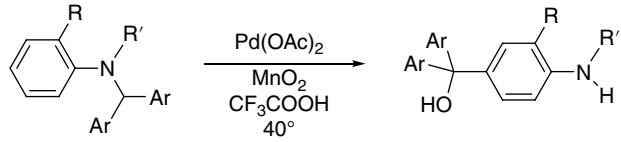
[1] Teo, Y.-C., Yong, F.-F., Lim, G.-S. *TL* **52**, 7171 (2011)

Manganese dioxide

Nitriles. MnO_2 is effective for converting thioamides into nitriles.[1]

Arylation. With MnO_2 to oxidize arylhydrazines to form free radicals, anilines are *o*-arylated in situ.[2]

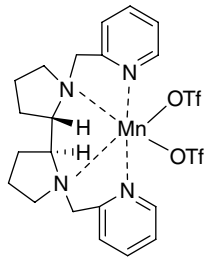
Oxidative cleavage. On treatment with MnO_2 and $Pd(OAc)_2$ in CF_3COOH, *N*-alkyl-*N*-benzhydrylanilines undergo oxidation and cleavage to release the benzhydryl unit, apparently as diaryl ketone which is re-incorporated into the *p*-position of the amino group.[3]



[1] Yamaguchi, K., Yajima, K., Mizuno, N. *CC* **48**, 11247 (2012)
[2] Jasch, H., Scheumann, J., Heinrich, M.R. *JOC* **77**, 10699 (2012)
[3] Tian, Y., Sui, Y., Gu, Y., Tian, S.-K. *ASC* **354**, 3475 (2012)

Manganese(II) triflate

Epoxidation. Complexing to *N.N′*-bis(2-pyridylmethyl)-2,2′-bipyrrolidine the manganese salt acts as a catalyst for alkene epoxidation (with peracetic acid). With the ligand in chiral modification (**1**) the best ee value observed is 89%.[1]



(**1**)

[1] Ottenbacher, R.V., Bryliakov, K.P., Talsi, E.P. *ASC* **353**, 885 (2011)

Meerwein reagents

Fluorosilanes. Trialkyloxonium tetrafluoroborates convert alkoxysilanes which also contain allyl groups into the corresponding fluorosilanes.[1]

[1] Jorapur, Y.R., Shimada, T. *SL* 1064 (2012)

Mercury(II) perchlorate

Allylation. Addition of allylsilanes to isatins and their ketimines is promoted by $Hg(ClO_4)_2$.[1]

Substitution. In the presence of $Hg(ClO_4)_2$ 3-hydroxyoxindoles react with ArH to give 3-aryloxindoles.[2]

[1] Cao, Z.-Y., Zhang, Y., Ji, C.-B., Zhou, J. *OL* **13**, 6398 (2011)
[2] Zhou, F., Cao, Z.-Y., Zhang, J., Yang, H.-B., Zhou, J. *CAJ* **7**, 233 (2012)

Mercury(II) triflate

Substitution. Allyl silyl ethers are subject to reaction with $AcN(Ts)NH_2$, as catalyzed by $Hg(OTf)_2$.[1]

[1] Yamamoto, H., Yamasaki, N., Yoshidome, S., Sasaki, I., Namba, K., Imagawa, H., Nishizawa, M. *SL* 1069 (2012)

Methyl 2,2-difluoro-2-(fluorosulfonyl)acetate

Difluorocarbene source.[1] This ester has activity comparable to the more labile trimethylsilyl ester. Generation of $:CF_2$ by KI is demonstrated.

[1] Eusterwiemann, S., Martinez, H., Dolbier Jr, W.R. *JOC* **77**, 5461 (2012)

Methyltrichlorosilane

Double Mannich reaction.[1] Condensation of ketones with dioxazepanes derived from ethanediol, paraformaldehyde and amines proceeds to form piperidine-4-ones. This reaction is mediated by $MeSiCl_3$ in CH_2Cl_2 and it shows promise in the construction of the bridged azabicyclic portion of diterpene alkaloids from certain cyclohexanone.

[1] Sparrow, K., Barker, D., Brimble, M.A. *T* **68**, 1017 (2012)

Methyltrioctylphosphonium carbonates

Henry reaction. The use of the title reagent as a catalyst for the Henry reaction is on record.[1]

[1] Fabris, M., Noe, M., Perosa, A., Selva, M., Ballini, R. *JOC* **77**, 1805 (2012)

Microwaves

Methylthiomethyl esters. A simplified method for the preparation of $RCOOCH_2SMe$ from carboxylic acids is to subject them to microwave irradiation in DMSO.[1]

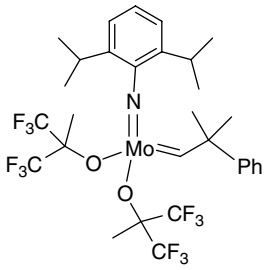
Grignard reagents. Electric field strength in a microwave figures prominently in Grignard reagent formation from Mg metal and aryl halide. At low field strength the initiation step is accelerated, but a high field strength at the same temperature favors solvent decomposition and passivation of the Mg metal, and it suppresses Mg insertion.[2]

Cycloaddition. Direct use of dicyclopentadiene as the diene component in the Diels-Alder reaction is possible by microwave heating it with dienophiles.[3] The cobalt-catalyzed cycloaddition of diynes with nitriles to form pyridines benefits from microwave irradiation, one of the reasons is that it lowers the induction period.[4]

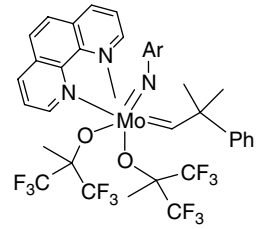
[1] McCarthy, A., Spatney, R., Manpadi, M., Myers, B.J., Zimmerman, J.R. *TL* **53**, 4782 (2012)
[2] Gutmann, B., Schwan, A.M., Reichart, B., Gspan, C., Hofer, F., Kappe, C.O. *ACIE* **50**, 7636 (2011)
[3] Dejmek, M., Hrebabecky, H., Sala, M., Dracinsky, M., Nencka, R. *S* 4077 (2011)
[4] Rodriguez, A.M., Cebrian, C., Prieto, P., Garcia, J.I., de la Hoz, A., Diaz-Ortiz, A. *CEJ* **18**, 6217 (2012)

Molybdenum-carbyne complexes

Metathesis. An active catalyst **1** for alkene metathesis is generated on demand from the bench-stable **2** by treatment with $ZnCl_2$ in toluene.[1]

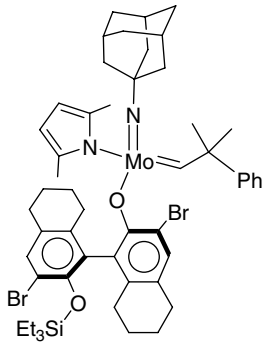


(**1**)

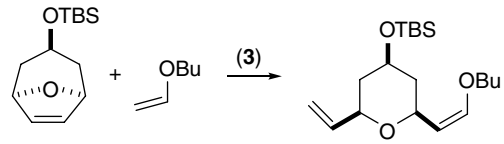


(**2**)

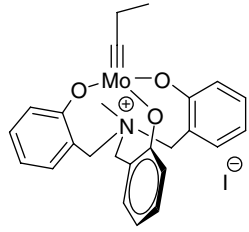
Ring opening and cross-metathesis exemplified by the following take full advantage of the activity of complex **3**.[2]



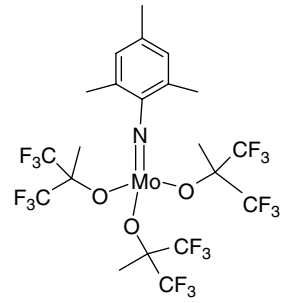
(**3**)



The carbyne complex **4** containing a quaternary ammonium ion for alkyne metathesis is rendered inactive when the nitrogen is basic.[3] Ring-closing metathesis of diynes (terminal and internal) into cycloalkynes proceeds at room temperature when **5** is present.[4]

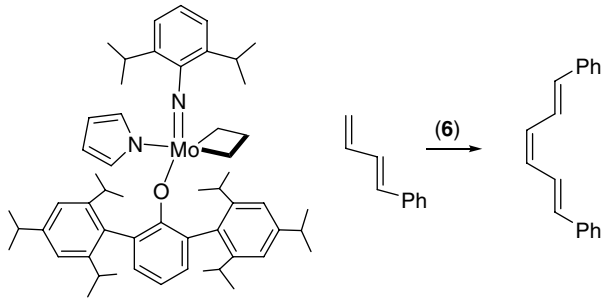


(**4**)



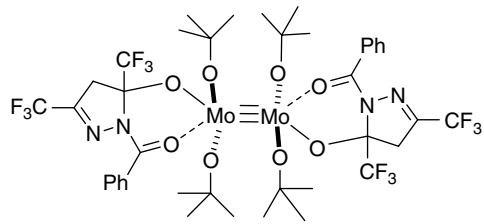
(**5**)

The complex **6** featuring a molybdacycle accomplishes (*Z*)-selective metathetic coupling of 1,3-dienes.[5]



(**6**)

The dimolybdenum complex **7** derived from $(t\text{-}BuO)_6Mo_2$ catalyzes reductive cleavage of tertiary amides into primary alcohols and amines with a hydrosilane.[6]



(**7**)

[1] Heppekausen, J., Fürstner, A. *ACIE* **50**, 7829 (2011)
[2] Yu, M., Ibrahem, I., Hasegawa, M., Schrock, R.S., Hoveyda, A.H. *JACS* **134**, 2788 (2012)
[3] Jyothish, K., Wang, Q., Zhang, W. *ASC* **354**, 2073 (2012)
[4] Haberlag, B., Freytag, M., Daniliuc, C.G., Jones, P.G., Tamm, M. *ACIE* **51**, 13019 (2012)
[5] Townsend, E.M., Schrock, R.R., Hoveyda, A.H. *JACS* **134**, 11334 (2012)
[6] Krackl, S., Someya, C.I., Enthaler, S. *CEJ* **18**, 15267 (2012)

Molybdenum(V) chloride

Oxidative coupling. Cross-coupling of arenes is realized on treatment with $MoCl_5$.[1]

[1] Waldvogel, S.R., Trosien, S. *CC* **48**, 9109 (2012)

Molybdenum hexacarbonyl

Carbon monoxide surrogate. In situ generation of CO from $Mo(CO)_6$ makes carbonylation more easily manageable.[1] For example, aminocarbonylation of ArX employs a system of $Mo(CO)_6$ and DBU,[2] and a similar operation converts ArX into ArCOOR.[3]

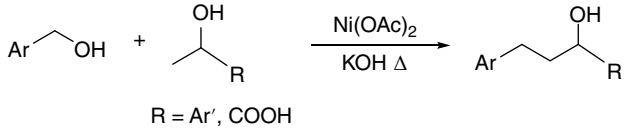
A synthesis of $ArCOCH_2CN$ from ArI and Me_3SiCH_2CN is catalyzed by $(Ph_3P)_2PdCl_2$, with $Mo(CO)_6$ to provide the CO unit (also present is CuF_2).[4]

[1] Odell, L.R., Russo, F., Larhed, M. *SL* 685 (2012)
[2] Nordman, P., Odell, L.R., Larhed, M. *JOC* **77**, 11393 (2012)
[3] Ren, W., Emi, A., Yamane, M. *S* 2303 (2011)
[4] Pyo, A., Park, A., Jung, H.M., Lee, S. *S* 2885 (2012)

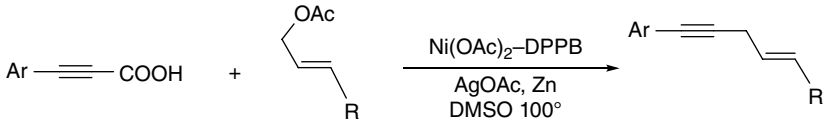
N

Nickel(II) acetate

Coupling reactions. A novel synthesis of γ-arylalkanols from benzyl alcohols and secondary alcohols involves catalysis of $Ni(OAc)_2$. The process is applicable to the preparation of 4-aryl-2-hydroxycarboxylic acids (from lactic acid).[1]



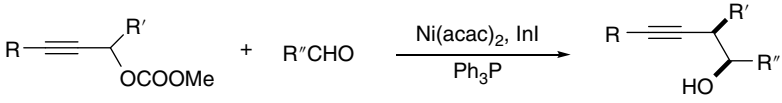
Decarboxylative coupling of 2-alkynoic acids with allyl acetates furnishes skipped enynes.[2]



[1] Tang, G., Cheng, C.-H. *ASC* **353**, 1918 (2011)
[2] Choe, J., Yang, J., Park, K., Palani, T., Lee, S. *TL* **53**, 6908 (2012)

Nickel(II) acetylacetonate

Coupling reactions. A modification of aryl ketone synthesis calls for use of ArCOCl and RR′CHX, apparently involving organozinc species that are generated on reaction of the alkyl halides with zinc in the presence of $MgCl_2$.[1] Propargylic carbonates condense with aldehydes diastereoselectively, under the influence of indium(I) iodide and catalyzed by $Ni(acac)_2$-Ph_3P. [2]



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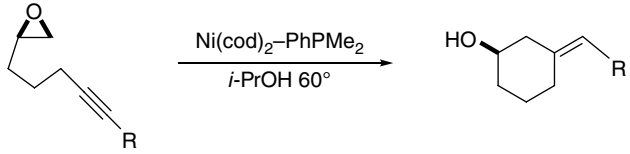
With $Ni(acac)_2$ as catalyst, the coupling of polyfluoroarenes with $ArB(OH)_2$ under oxygen affords mixed diaryl ethers.[3]

[1] Wu, F., Lu, W., Qian, Q., Ren, Q., Gong, H. *OL* **14**, 3044 (2012)
[2] Hirashita, T., Suzuki, Y., Tsuji, H., Sato, Y., Naito, K., Araki, S. *EJOC* 5668 (2012)
[3] Zhang, J., Wu, J., Xiong, Y., Cao, S. *CC* **48**, 8553 (2012)

Nickel(II) bromide

Cross-coupling. The $(Cy_3P)_2NiBr_2$ is used in coupling of $ArB(OH)_2$ with aryl and alkenyl tosylates.[1]

Addition. β-Oxynickel species are generated from epoxides via oxidative addition, and they add onto a triple bond intramolecularly.[2]

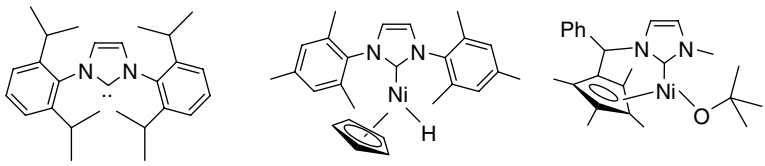


[1] Xing, C.-H., Lee, J.-R., Tang, Z.-Y., Zheng, J.R., Hu, Q.-S. *ASC* **353**, 2051 (2011)
[2] Beaver, M. G., Jamison, T. F. *OL* **13**, 4140 (2011)

Nickel-carbene complexes

Redox reaction. Chemoselective Tishchenko reaction of RCHO and ArCHO leading to benzyl alkanoates is instigated by $Ni(cod)_2$ associated with (**1**).[1] Nickel-carbenoids are active in *C*-arylation of primary and secondary alcohols by arylboronates in the presence of CsF and PhCl, carbinols containing two different aryl groups can be synthesized in one pot, there being a sequence of oxidation and addition reactions.[2,3]

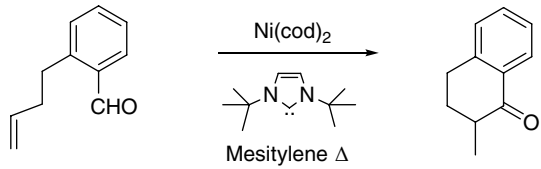
In the reduction of carbonyl compounds via hydrosilylation, **2** and **3** can be employed as catalyst.[4,5]



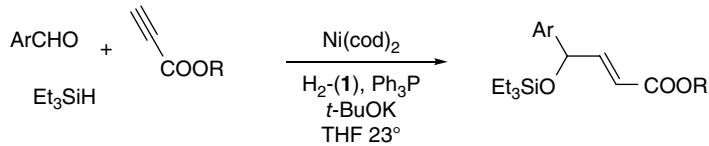
Substitution. Conversion of haloarenes into aryl sulfides is easily catalyzed by a nickel-carbenoid.[6] A similar displacement by R_2NH gives access to arylamines from $ArOCONMe_2$ and $ArOSO_2NMe_2$ under basic conditions.[7] Triarylamines are produced when the nucleophiles are changed to Ar_2NMgBr.[8]

The complex (**1**)NiCl(η^3-C_3H_5) is useful for coupling of ArMgBr with Ar′OMe.[9]

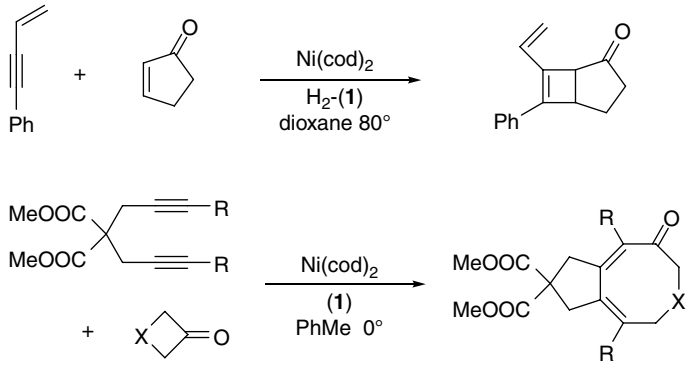
Addition. Benzocycloalkanones are formed from *o*-(ω-alkenyl)benzaldehydes,the result of an intramolecular hydroacylation.[10]



A synthesis of 4-aryl-4-triethylsiloxy-2-butenoic esters is based on a three-component association edified by a nickel-carbenoid.[11]



Cycloaddition. Chemoselective [2+2]cycloaddition of activated alkenes and conjugated enynes involves the triple bond.[12] Very unusual is the ring cleavage of 4-membered heterocyclic ketones and their participation in cycloaddition with diynes.[13]



Combination of two equivalents of an isocyanate with an acrylic ester forms 1,3,5-trisubstituted hydantoins.[14]

[1] Dzik, W.I., Goossen, L.J. *ACIE* **50**, 11047 (2011)
[2] Maekawa, T., Sekizawa, H., Itami, K. *ACIE* **50**, 7022 (2011)
[3] Berini, C., Navarro, O. *CC* **48**, 1538 (2012)
[4] Bheeter, L.P., Henrion, M., Brelot, L., Darcel, C., Chetcuti, M.J., Sortais, J.-B., Ritleng, V. *ASC* **354**, 2619 (2012)
[5] Postigo, L., Royo, B. *ASC* **354**, 2613 (2012)
[6] Guan, P., Cao, C., Liu, Y., Li, Y., He, P., Chen, Q., Liu, G., Shi, Y. *TL* **53**, 5987 (2012)
[7] He, L., Ramgren, S.D., Mesganaw, T., Garg, N.K. *OL* **14**, 4182 (2012)
[8] Tadaoka, H., Yamakawa, T. *TL* **53**, 5531 (2012)
[9] Iglesias, M.J., Prieto, A., Nicasio, N.C. *OL* **14**, 4318 (2012)
[10] Hoshimoto, Y., Hayashi, Y., Suzuki, H., Ohashi, M., Ogoshi, S. *ACIE* **51**, 10812 (2012)
[11] Rodrigo, S.K., Guan, H. *JOC* **77**, 8303 (2012)
[12] Nishimura, A., Ohashi, M., Ogoshi, S. *JACS* **134**, 15692 (2012)
[13] Kumar, P., Zhang, K., Louie, J. *ACIE* **51**, 8602 (2012)
[14] Miura, T., Mikano, Y., Murakami, M. *OL* **13**, 3560 (2011)

Nickel chloride

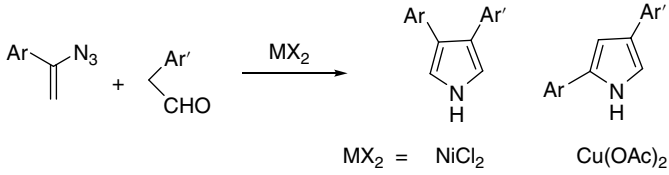
Dehydration. Aldoximes undergo dehydration to afford nitriles on heating with $NiCl_2$ and molecular sieves in MeCN.[1]

Coupling reactions. The (dme)$NiCl_2$ complex with di-*t*-butylbipyridine and a reducing metal (Zn or Mn) cross-couples RCOX and R′X into ketones RCOR′.[2] Defunctionalized cross coupling of allyl acetates with ArX and secondary alkyl bromides favors formation of linear products, even from 3-acetoxy-1-alkenes.[3]

Amines are *N*-arylated on microwave treatment of ArX, $NiCl_2$, and Et_3N.[4] Arylation of amides by $ArB(OH)_2$ employs a similar catalytic system ($NiCl_2$, bipyridyl, DBU).[5]

Ring formation. 1-Alkylidenebenzocycloalkanes and certain heterologs are formed by reacting 2-iodoarylalkynes with (bpy)$NiCl_2$ and Mn in DMF. The metallated alkenes derived from *cis*-addition can be functionalized with various electrophiles.[6]

Isomeric diarylpyrroles are obtained from reaction of α-azidostyrenes with arylacetaldehydes, regioselectivity of the process depends on whether $Cu(OAc)_2$ or $NiCl_2$ is used.[7]



Wurtz-type reaction of 2-iodoaryloxypropyl bromide as effected by $NiCl_2$ and Zn in the presence of pyridine delivers benzopyrans (also analogously, the tetrahydroquinolines). An important additive is ethyl crotonate which serves as a π-ligand for Ni.[8]

Aziridine opening. 2-Aryl-*N*-tosylaziridines are attacked by RZnBr at the benzylic position in the presence of (glyme)$NiCl_2$, and a fumarate ester to support the nickel.[9]

[1] Li, Y.-T., Liao, B.-S., Chen, H.-P., Liu, S.-T. *S* 2639 (2011)
[2] Wotal, A.C., Weix, D.J. *OL* **14**, 1476 (2012)
[3] Anka-Lufford, L.L., Prinsell, M.R., Weix, D.J. *JOC* **77**, 9989 (2012)
[4] Gupta, A.K., Rao, G.T., Singh, K.N. *TL* **53**, 2218 (2012)
[5] Raghuvanshi, D.S., Gupta, A.K., Singh, K.N. *OL* **14**, 4326 (2012)
[6] Durandetti, M., Hardou, L., Lhermet, R., Rouen, M., Maddaluno, J. *CEJ* **17**, 12773 (2011)
[7] Chen, F., Shen, T., Cui, Y., Jiao, N. *OL* **14**, 4926 (2012)
[8] Yan, C.-S., Peng, Y., Xu, X.-B., Wang, Y.-W. *CEJ* **18**, 6039 (2012)
[9] Huang, C.-Y., Doyle, A.G. *JACS* **134**, 9541 (2012)

Nickel chloride – tertiary phosphines

Hydrodefluorination. With $NiCl_2$ and $(Cy_3P)_2NiCl_2$ as catalyst, ArF and $ArCF_3$ are reduced by $LiBHEt_3$ in refluxing THF to ArH and $ArCH_3$, respectively.[1]

Aryl ketones. The Ni-catalyzed reaction of ArI and Zn with RCN results in the formation of ArCOR. A phosphine (DPPP) is used to coordinate the nickel species.[2]

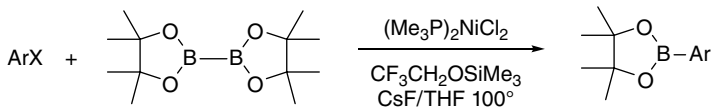
Carboxylation. Alkenyl and aryl chlorides are carboxylated when subjected to $(Ph_3P)_2NiCl_2$, Ph_3P, Mn, Et_4NI in dimethylimidazolidone under carbon dioxide.[3]

Coupling. An alternative to the Sonogashira coupling to prepare aryl and arylmethylalkynes involves a Ni-catalyzed reaction of the bromides with alkynyldiethylaluminum reagents.[4] Diarylzincs couple with ArX under the influence of $NiCl_2$ and tris(pyrrolidinyl) phosphine as the ligand.[5]

Aryl pivaloyloxymethyl ketones are active towards coupling with $ArB(OH)_2$, 1,2-diarylethanones are produced.[6] Access to biaryls from nickel-mediated Suzuki coupling between $ArB(OH)_2$ and $Ar'OSO_2NMe_2$,[7] and that between aryl boronates and aryl sulfonates[8] is readily managed. Reaction of benzyl halides with alkenylaluminum reagents in the presence of $(Ph_3P)_2NiCl_2$ leads to allylarenes.[9]

The cyano group of ArCN is lost in Ni-catalyzed coupling reaction with $Ar'MnCl$[10] and Ph_2PSiMe_3[11] the latter process giving rise to $ArPPh_2$. Mixed tertiary arylphosphines can also be prepared from ArX and R_2PH or $R_2P(O)H$,[12] whereas arylphosphones are obtained from an analogous reaction between ArOH and $R_2P(O)H$.[13]

Arylboronates are similarly synthesized.[14]



[1] Zhao, W., Wu, J., Cao, S. *ASC* **354**, 574 (2012)
[2] Hsieh, J.-C., Chen, Y.-C., Cheng, A.-Y., Tseng, H.-C. *OL* **14**, 1282 (2012)
[3] Fujihara, T., Nogi, K., Xu, T., Terao, J., Tsuji, Y. *JACS* **134**, 9106 (2012)
[4] Biradar, D.B., Gau, H.-M. *CC* **47**, 10467 (2011)
[5] Gerber, R., Frech, C.M. *CEJ* **17**, 11893 (2011)

[6] Huang, K., Li, G., Huang, W.-P., Yu, D.-G., Shi, Z.-J. *CC* **47**, 7224 (2011)
[7] Chen, G.-J., Han, F.-S. *EJOC* 3575 (2012)
[8] Leowanawat, P., Zhang, N., Safi, M., Hoffman, D.J., Fryberger, M.C., George, A., Percec, V. *JOC* **77**, 2885 (2012)
[9] Biradar, D.B., Gau, H.-M. *OBC* **10**, 4243 (2012)
[10] Liu, N., Wang, Z.-X. *ASC* **354**, 1641 (2012)
[11] Sun, M., Zhang, H.-Y., Han, Q., Yang, K., Yang, S.-D. *CEJ* **17**, 9566 (2011)
[12] Zhao, Y.-L., Wu, C.-J., Li, Y., Gao, L.-X., Han, F.-S. *CEJ* **18**, 9622 (2012)
[13] Zhao, Y.-L., Wu, G.-J., Han, F.-S. *CC* **48**, 5868 (2012)
[14] Yamamoto, T., Morita, T., Takagi, J., Yamakawa, T. *OL* **13**, 5766 (2011)

Nickel fluoride

β-Fluoroalkylamines. The opening of aziridines by Bu_4NF is catalyzed by NiF_2.[1]

[1] Zhang, W.X., Su, L., Hu, W.G., Zhou, J. *SL* 2413 (2012)

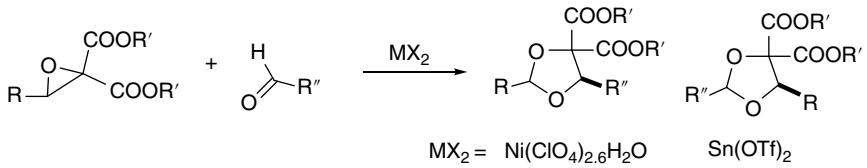
Nickel iodide

Coupling. The coupling of ArX with RBr proceeds in the presence of NiI_2 and zinc metal.[1,2] A bipyridyl or phenanthroline is useful ligand. Using allyl acetate instead of the bromide leads to allylarenes.[2]

[1] Everson, D.A., Jones, B.A., Weix, D.J. *JACS* **134**, 6146 (2012)
[2] Wang, S., Qian, Q., Gong, H. *OL* **14**, 3352 (2012)

Nickel perchlorate

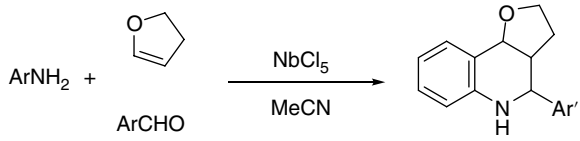
Cycloaddition. A [3+2]cycloaddition occurs when activated epoxides and aziridines are mixed with dipolarophiles in the presence of $Ni(ClO_4)_2$. Thus, heteroannulation of indoles,[1] formation of oxazolidines[2] and dioxolanes,[3] respectively, from the three-membered heterocycles and aldehydes, are accomplished. Interestingly, the dioxolanes arising via C-C bond cleavage of the oxirane ring are isomeric to those generated from a reaction catalyzed from $Sn(OTf)_2$, which features a CO bond scission.



[1] Zhang, J., Chen, Z., Wu, H.-H., Zhang, J. *CC* **48**, 1817 (2012)
[2] Wu, X., Li, L., Zhang, J. *CC* **47**, 7824 (2011)
[3] Chen, Z., Tian, Z., Zhang, J., Ma, J., Zhang, J. *CEJ* **18**, 8591 (2012)

Niobium(V) chloride

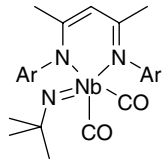
Condensation.[1] Admixture of $ArNH_2$, Ar′CHO, and 2,3-dehydro oxacycles with $NbCl_5$ in MeCN gives rise to tetrahydroquinolines that are fused to an oxacyclic moiety.



[1] da Silva, B.H.S.T., Martins, L.M., da Silva-Filho, L.C. *SL* 1973 (2012)

Niobium- imine complexes

Semihydrogenation.[1] The complex **1** catalyzes semihydrogenation of alkynes by syngas. The CO in syngas serves to stabilize the complex and renders it a high activity and selectivity.

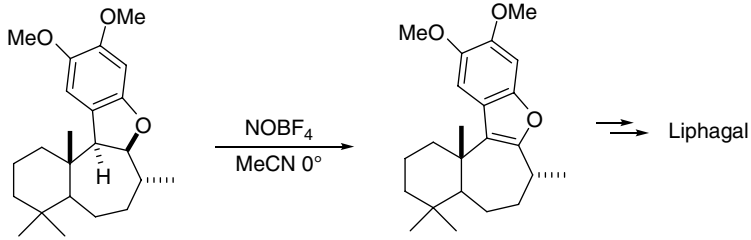


(**1**)

[1] Gianetti, T.L., Tomson, N.C., Arnold, J., Bergman, R.G. *JACS* **133**, 14904 (2011).

Nitrosonium tetrafluoroborate

Dehydrogenation.[1] During a synthesis of liphagal, dehydrogenation of a dihydrofuran moiety was accomplished by using $NOBF_4$. Many other reagents and conditions were found unsatisfactory.



Nitrosoarenes.[2] Conversion of $ArBF_3K$ into ArNO by $NOBF_4$ is quite straightforward.

Glycosylation.[3] A method for replacing the trichloroacetimido group at the anomeric position is to treat the sugar derivatives with $NOBF_4$ and an alcohol.

[1] Day, J.J., McFadden, R.M., Virgil, S.C., Kolding, H., Alleva, J.L., Stoltz, B.M. *ACIE* **50**, 6814 (2011)
[2] Molander, G.A., Cavalcanti, L.N. *JOC* **77**, 4402 (2012)
[3] Sau, A., Santra, A., Misra, A.K. *SL* 2341 (2012)

Nonafluorobutanesulfonyl fluoride

Enol nonaflylation.[1] It is possible to selectively convert the formyl group of a keto aldehyde into a =CHONf unit while leaving a ketone alone. Thus it is quite easy to prepare ketoalkynes from $RCO(CH_2)nCH_2CHO$, while applying a strong base such as $(C_4H_8N)_3P{=}NCMe_3$ to perform elimination on the enol derivatives.

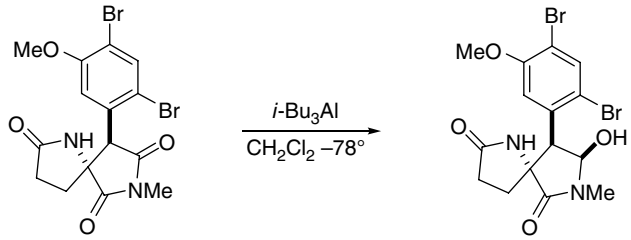
[1] Boltukhina, E.V., Sheshenev, A.E., Lyapkalo, I.M. *T* **67**, 5382 (2011)

O

Organoaluminum reagents

Preparation. Arylaluminum halides are prepared from ArBr and Al with additives $PbCl_2$ and LiCl in THF, the resulting reagents can be used for Pd-catalyzed coupling to form biaryls.[1] To obtain benzylaluminum chlorides metallation by Al is promoted by $InCl_3$, and the conversion of such products to organozinc derivatives with $Zn(OAc)_2$ renders them properly reactive towards various electrophiles.[2]

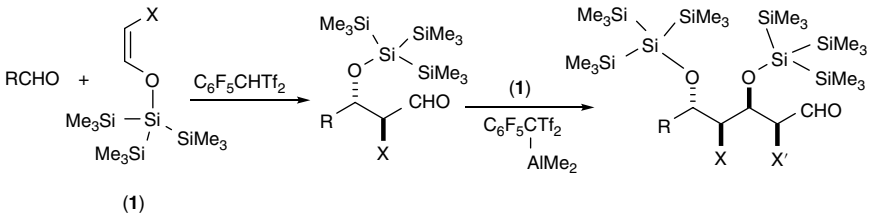
Reduction. Triisobutylaluminum reduces succinimides and the regioselectivity may be complementary to that shown by $NaBH_4$, $NaBH_4$-$CeCl_3$, $LiAlH_4$, and L-Selectride.[3]



Arylation. Arylaluminum reagents of the type $Ar_4Al(MgBr)$ react with alkyl halides including chlorohydrins under the influence of $FeCl_2$ to form CC bond.[4] Ketones undergo α-arylation with Ar_3Al (prepared from ArMgCl and $AlCl_3$) in the presence of isoxazolidine.[5]

Amidation. Trimethylaluminum promotes direct union of carboxylic acids and amines to form amides.[6,7]

Aldol and Baylis-Hillman reactions. The highly fluorinated benzyldimethylaluminum reagent $C_6F_5C(SO_2CF_3)_2AlMe_2$ is a potent catalyst for aldol reaction.[8]

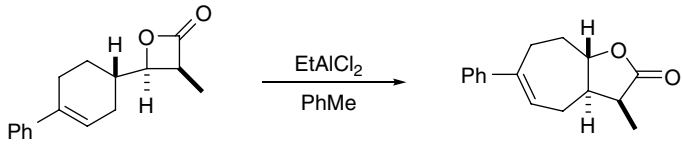


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Very mild conditions (at −78°~−55°) are required for conducting the Baylis-Hillman reaction on cyclopentenones when promoted by Et_2AlI.[9]

Diels-Alder reaction. 3-Methyl-2-cyclohexenone is activated to undergo cycloaddition with dienophiles such as 2-siloxy-4-methyl-1,3-pentadienes by $MeAl(NTf_2)_2$ or Me_2AlNTf_2.[10]

Dyotropic rearrangement. Dual ring expansion of a β-cycloalkyl β-lactone is readily catalyzed by $EtAlCl_2$.[11]



[1] Groll, K., Blümke, T.D., Unsinn, A., Haas, D., Knochel, P. *ACIE* **51**, 11157 (2012)
[2] Blümke, T.D., Groll, K., Karaghiosoff, K., Knochel, P. *OL* **13**, 6440 (2011)
[3] Chiyoda, K., Shimokawa, J., Fukuyama, T. *ACIE* **51**, 2505 (2012)
[4] Kawamura, S., Kawabata, T., Ishizuka, K., Nakamura, M. *CC* **48**, 9376 (2012)
[5] Miyoshi, T., Sato, S., Tanaka, H., Hasegawa, C., Ueda, M., Miyata, O. *TL* **53**, 4188 (2012)
[6] Chung, S., Uccello, D.P., Choi, H., Montgomery, J.I., Chen, J. *SL* 2072 (2011)
[7] Li, J., Subramaniam, K., Smith, D., Qiao, J.X., Li, J.J., Qian-Cutrone, J., Kadow, J.F., Vite, G.D., Chen, B.-C. *OL* **14**, 214 (2012)
[8] Saadi, J., Akakura, M., Yamamoto, H. *JACS* **133**, 14248 (2011)
[9] Ghosal, P., Ajay, S., Bajpai, V., Kumar, B., Shaw, A.K. *EJOC* 4906 (2012)
[10] Jung, M.E., Guzaev, M. *OL* **14**, 5169 (2012)
[11] Ren, W., Bian, Y., Zhang, Z., Shang, H., Zhang, P., Chen, Y., Yang, Z., Luo, T., Tang, Y. *ACIE* **51**, 6984 (2012)

Organocerium reagents

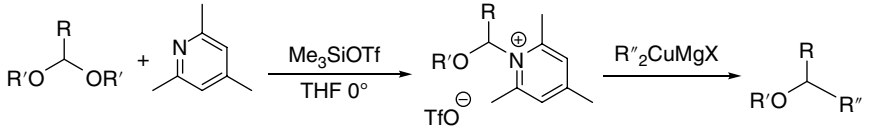
Reaction with imino esters.[1] Imino triflates prepared in situ from secondary amides and Tf_2O are attacked by RM-$CeCl_3$ reagents, such that further quenching with $NaBH_4$ leads to α-branched secondary amines.

[1] Xiao, K.-J., Wang, A.-E., Huang, P.-Q. *ACIE* **51**, 8314 (2012)

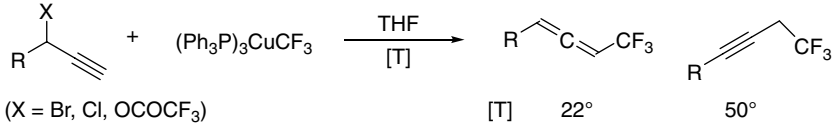
Organocopper reagents

Substitution. Unstabilized tertiary alkyl cyanides RCN are converted into $RCuL_n$ on consecutive treatment with LiDBB and $Me_3SiCH_2Cu(CN)Li$, and the *t*-alkylcopper species are reactive towards C-electrophiles.[1]

The chlorine atom of RR′C(Cl)CH=NOH is replaced by an aryl group on reaction with ArCu(CN)Li.[2] On mediation with RCu and Et_3SiOTf one of the methoxy groups of a dimethylacetal can be replaced by *C*-nucleophiles (enamines, enol silyl ethers, Me_3SiCN, RNC).[3] Organocopper reagents also can act as nucleophiles for monosubstitution on acetals via the *N*-alkoxyalkylpyridinium salts.[4]



3-Halo-1-alkynes react at room temperature with $(Ph_3P)_3CuCF_3$ to give allene products. However, at a higher temperature isomerization to afford the 3-alkynes occurs.[5]



Coupling. Quite unexpectedly, direct conversion of carboxylic acids into ketones is accomplished using RCuLi·LiCN.[6] α-Haloketones undergo chain extension to give 1,1, 1-trifluoro-3-alkanones on coupling with CF_3Cu, which is prepared from CuCl, *t*-BuOK and HCF_3 in DMF.[7] The CF_3Cu reagent has found use in the synthesis of $ArCF_3$.[8,9,10] [The last report indicates a preparation of $(Ph_3P)_3CuCF_3$ as the reagent from CuF_2, Ph_3P and Me_3SiCF_3 in MeOH.] A slight variation employs R^FCu ligated to phenanthroline.[11]

Trifluoromethylation of 1-alkynes are similarly accessible by an improved method: reaction of alkynylcoppers with CF_3SiMe_3.[12]

Addition. Mediated by MesCu – DPPP in DMSO, ketones add to styrenes to furnish γ-aryl ketones.[13] In Michael addition to alkylidene(bissulfinyl)methanes, RCu reagents show different diastereoselectivity from other nucleophiles.[14]

Aldol reaction. Mesitylcopper promotes aldol reaction of an *N*-protected pyrrolidine-2-thione with aldehydes, and an anti-selectivity is manifested.[15]

[1] Schnermann, M.J., Untiedt, N.L., Jimenez-Oses, G., Houk, K.N., Overman, L.E. *ACIE* **51**, 9581 (2012)
[2] Sengupta, R., Weinreb, S.M. *S* 2933 (2012)
[3] Fujioka, H., Yahata, K., Hamada, T., Kubo, O., Okitsu, T., Sawama, Y., Ohnaka, T., Maegawa, T., Kita, Y. *CAJ* **7**, 367 (2012)
[4] Minamitsuji, Y., Kawaguchi, A., Kubo, O., Ueyama, Y., Maegawa, T., Fujioka, H. *ASC* **354**, 1861 (2012)
[5] Zhao, T.S.N., Szabo, K.J. *OL* **14**, 3966 (2012)
[6] Genna, D.T., Posner, G.H. *OL* **13**, 5358 (2011)
[7] Novak, P., Lishchynskyi, A., Grushin, V.V. *JACS* **134**, 16167 (2012)
[8] Zanardi, A., Novikov, M.A., Martin, E., Benet-Buchholz, J., Grushin, V.V. *JACS* **133**, 20901 (2011)
[9] Novak, P., Lishchynskyi, A., Grushin, V.V. *ACIE* **51**, 7767 (2012)
[10] Tomashenko, O.A., Escudero-Adan, E.C., Belmonte, M.M., Grushin, V.V. *ACIE* **50**, 7655 (2011)
[11] Litvinas, N.D., Fier, P.S., Hartwig, J.F. *ACIE* **51**, 536 (2012)
[12] Zhang, K., Qiu, X.-L., Huang, Y., Qing, F.-L. *EJOC* 58 (2012)
[13] Majima, S., Shimizu, Y., Kanai, M. *TL* **53**, 4381 (2012)
[14] Brebion, F., Vincent, G., Chelli, S., Kwasnieski, O., Najera, F., Delouvrie, B., Marek, I., Derat, E., Goddard, J.-P., Malacria, M., Fensterbank, L. *CAJ* **6**, 1825 (2011)
[15] Sureshkumar, D., Kawato, Y., Iwata, M., Kumagai, N., Shibasaki, M. *OL* **14**, 3108 (2012)

Organogallium reagents

Addition. There is a report on the use of Me_3Ga to initiate addition of arylethynes to α-keto esters.[1]

[1] Jiang, H., Lin, A., Peng, H., Zhu, Y., Pan, Y., Zhu, C., Cheng, Y. *SL* 2039 (2011)

Organoiodine reagents

O-Arylation. Diaryliodonium salts convert phenols and carboxylic acids (upon deprotonation with *t*-BuOK) into diaryl ethers and aryl esters, respectively.[1]

[1] Jalalian, N., Petersen, T.B., Olofsson, B. *CEJ* **18**, 14140 (2012)

Organolithium reagents

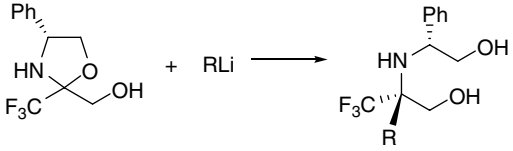
General aspects. An article delineates many aspects of RLi.[1]

Elimination. Alkynyllithiums catalyze benzyne generation from 2-iodophenyl triflate. In the presence of nucleophiles an apparent substitution of the triflate group is observed (iodine atom retained).[2]

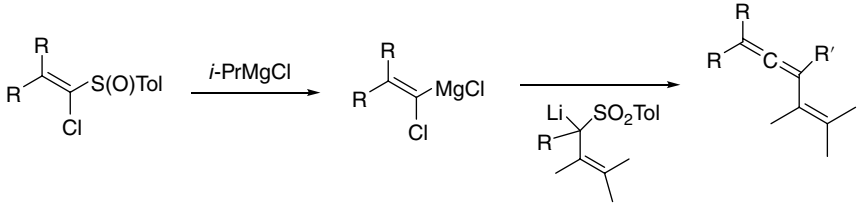
Dimethylaminoethylbenzene is converted to styrene by RLi. When *t*-BuOK is also present, benzylic kaliation is observed.[3]

Substitution. Organolithiums (and Grignard reagents) effect replacement of the methoxy group at C-1 or C-3 of 2-naphthoic acid derivatives.[4] Chain elongation at the terminal carbon of 1-alkynes is achieved when alkynyl sulfones are available --- a simple reaction with RLi suffices.[5]

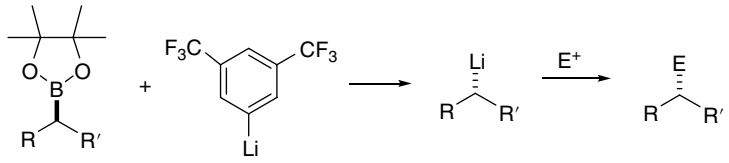
An S_N2' process occurs when 2,2-difluoro-1-methylenetetralin is exposed to RLi.[6] An apparent 1,3-asymmetric induction operates in the reaction of 4-phenyl-2-trifluoromethyloxazolidine-2-methanol with organolithiums.[7]



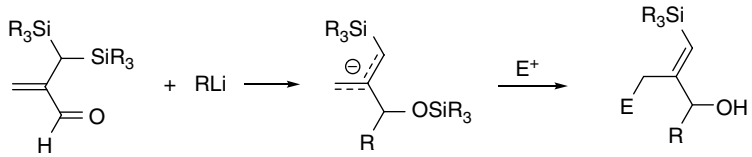
A method for elaborating 1,2,4-alkatrienes involves reaction of α-lithio allylsulfones with 1-chloroalkenylmagnesium chlorides, which are accessible from the chloroalkenyl tolyl sulfoxides (+ *i*-PrMgCl).[8]



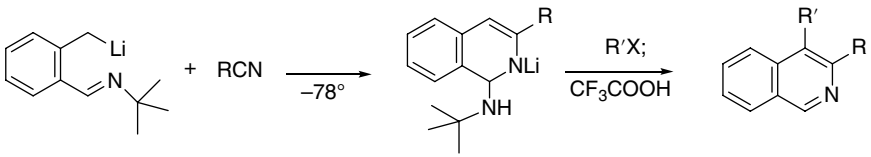
Addition. The *B*-substituent on 9-BBN is activated by metal methoxides during Suzuki coupling, and alternative approach involves addition of RLi to *B*-methoxy-BBN.[9] Replacement of a secondary pinacolatoboryl group with inversion is achieved by treatment with 3,5-bis(trifluoromethyl)phenyllithium and then an electrophile.[10]



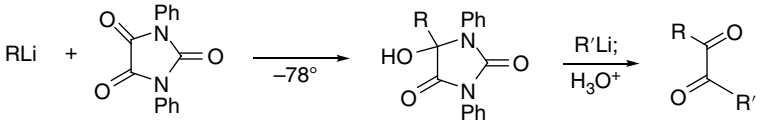
A 1,4-Brook rearrangement intervenes during addition of RLi to 2-bis(triorganosilyl) methyl acroleins. On quenching the reaction with electrophiles various β-silyl allylic alcohols are produced.[11]



A synthesis of *cis*-2-iodo-3-arylaziridines from reaction of *N*-Boc α-tosylbenzylamines with $LiCHI_2$ involves imine intermediates.[12] 3,4-Disubstituted isoquinolines are obtained from reaction of 2-*t*-butyliminomethylbenzyllithium with RCN, with subsequent addition of an alkyl halide and CF_3COOH.[13]



While excess quantities of RLi attack both non-ureido carbonyl groups of diphenylparabanic acid, symmetrical α-diketones are generated on hydrolytic workup. Controlled addition of one equivalent of the reagent at −78° is possible. Accordingly unsymmetrical α-diketones can be acquired.[14]



Aroic esters. Aryllithium reagents react with either HCOOEt or $HCONMe_2$, mediated by iodine and under slightly different conditions (presence of MeOH in the latter case), to afford ArCOOR.[15]

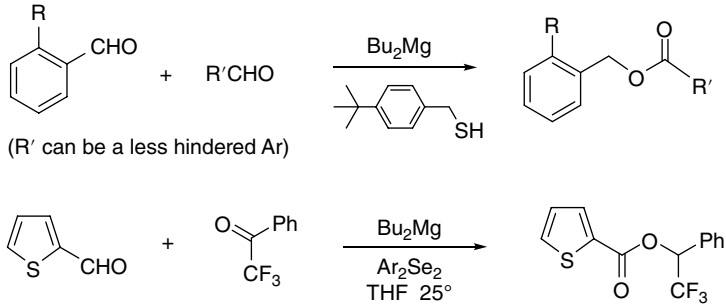
[1] Reich, H.J. *JOC* **77**, 5471 (2012)
[2] Hamura, T., Chuda, Y., Nakatsuji, Y., Suzuki, K. *ACIE* **51**, 3368 (2012)
[3] Unkelbach, C., Rosenbaum, H.S., Strohmann, C. *CC* **48**, 10612 (2012)
[4] Aissaoui, R., Nourry, A., Coquel, A., Dao, T.T.H., Derdour, A., Helesbeux, J.-J., Duval, O., Castanet, S.-S., Mortier, J. *JOC* **77**, 718 (2012)
[5] Ruano, J.L.G., Aleman, J., Marzo, L., Alvarado, C., Tortosa, M., Diaz-Tendero, S., Fraile, A. *ACIE* **51**, 2712 (2012)
[6] Bergeron, M., Johnson, T., Paquin, J.-F. *ACIE* **50**, 11112 (2011)
[7] Simon, J., Chelain, E., Brigaud, T. *OL* **14**, 604 (2012)
[8] Kimura, T., Kobayashi, G., Ishigaki, M., Inumaru, M., Sakurada, J., Satoh, T. *S* 3623 (2012)
[9] Seidel, G., Fürstner, A. *CC* **48**, 2055 (2012)
[10] Larouche-Gauthier, R., Elford, T.G., Aggarwal, V.K. *JACS* **133**, 16794 (2011)
[11] Gao, L., Lin, X., Lei, J., Song, Z., Lin, Z. *OL* **14**, 158 (2012)
[12] Bull, J.A., Boultwood, T., Taylor, T.A. *CC* **48**, 12246 (2012)
[13] Si, C., Myers, A.G. *ACIE* **50**, 10409 (2011)
[14] Watanabe, N., Hamano, M., Todaka, S., Asaeda, T., Ijuin, H.K., Matsumoto, M. *JOC* **77**, 632 (2012)
[15] Ushijima, S., Moriyama, K., Togo, H. *T* **68**, 4701 (2012)

Organomagnesium reagents

Modified Shapiro reaction. Magnesioalkenes are generated from tosylhydrazones on treatment with the dimesitylmagnesium-LiCl complex, a subsequent reaction with electrophiles enables access to functionalized alkenes.[1]

Coupling. A more elaborate way to accomplish the Suzuki coupling is to form arylborates in situ from ArBr and $(BuO)_3B$ with assistance of Mg and LiCl.[2]

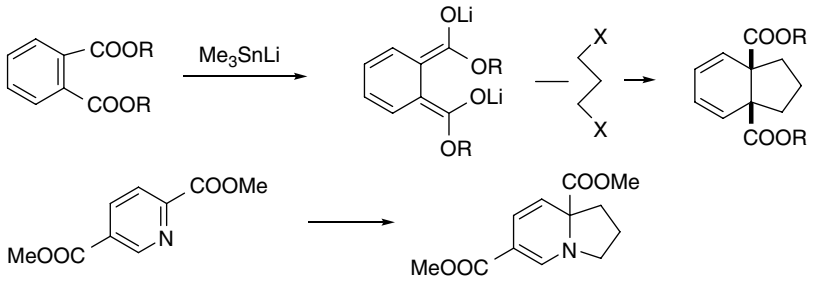
Tishchenko reaction. Bu_2Mg mediates condensation of 2-substituted araldehydes with less hindered aldehydes (aliphatic or aromatic) in the presence of 4-*t*-butyltoluenethiol.[3] Trifluoromethyl ketones undergo reductive acylation.[4]



[1] Kerr, W.J., Morrison, A.J., Pazicky, M., Weber, T. *OL* **14**, 2250 (2012)
[2] Haag, B.A., Sämann, C., Jana, A., Knochel, P. *ACIE* **50**, 7290 (2011)
[3] Curran, S.P., Connon, S.J. *ACIE* **51**, 10866 (2012)
[4] Curran, S.P., Connon, S.J. *OL* **14**, 1074 (2012)

Organotin reagents

Dearomatizative alkylation.[1] Phthalate esters form *o*-quinonedimethide dioxide salts, which can be annulated via alkylation. Picolinate esters behave analogously.

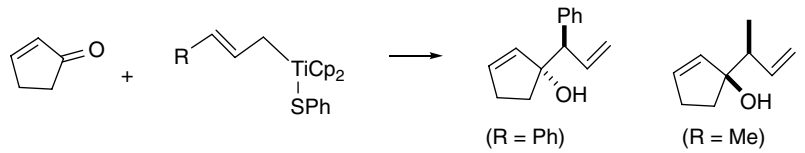


Selective benzylation.[2] *meso*-1,2- and 1,3-diols are liable to monobenzylation. The reaction is carried out with Me_2SnCl_2 in water.

[1] Perez-Vazquez, J., Veiga, A.X., Prado, G., Sardina, F.J., Paleo, M.R. *EJOC* 975 (2012)
[2] Muramatsu, W., William, J.M., Onomura, O. *JOC* **77**, 754 (2012)

Organotitanium reagents

Addition. Contrasting diastereoselective addition of crotyl(phenylthio)titanocene and of cinnamyl(phenylthio)titanocene to 2-cyclopentenone has been reported.[1]



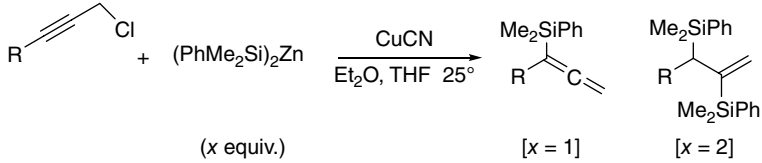
[1] Takeda, T., Nishimura, T., Yoshida, S., Saiki, F., Tajima, Y., Tsubouchi, A. *OL* **14**, 2042 (2012)

Organozinc reagents

Preparation. Allylzinc hexamethyldisilazide arises on mixing an allylboronate with $[(Me_3Si)_2N]_2Zn$, and such is used in catalytic allylation.[1] Benzyl halides are converted into bis(arylmethyl)zinc compounds by Mg, ZnX_2 and catalytic $Cu(acac)_2$.[2] Metathesis between ArMgCl·LiCl and $Zn(OPiv)_2$ leads to easily handled ArZnOPiv.[3] Compounds such as methyl 5-nitrofuran-2-carboxylate are zincated by the tetramethylpiperidinylzinc chloride-lithium chloride complex (at C-3);[4] Negishi coupling can then be conducted.

Catalyzed by AIBN, hydrosilanes are zincated. Lithium silylzincates are obtained from such species.[5] Zincation of *N*-heterocycles is executed with di-*t*-butylzinc complexed to (thf)LiTMP.[6]

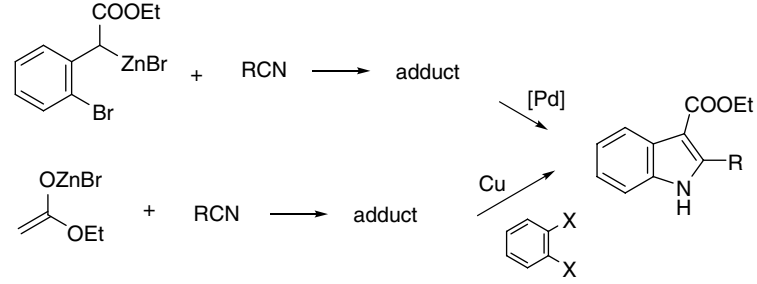
Substitution. Propargylic chlorides undergo S_N2' reaction with disilylzinc reagents. With excess (2 equiv.) reagents, further addition to allene linkage occurs.[7]



Two complementary methods for the preparation of 4-substituted 2-pyrones from 4-bromo-2-pyrones are: zincation and reaction with RX, and direct reaction with RZnX.[8] Formation of amides from RZnX and ClCONR′R″ is catalyzed by Pd(II) salts.[9] Also known is the CuCl-catalyzed reaction of ArZnCl ($ArMgCl{\cdot}LiCl + ZnCl_2$) with $ClCOCH_2OAc$.[10]

Addition. Phosphonium salts show catalytic activity for the addition of R_2Zn to aldehydes.[11] Pinacolatoborylallene is converted into an allenylating agent for carbonyl compounds by Et_2Zn.[12] Addition of R_2Zn or RZnBr to α-chloro *N*-tosylaldimines is under chelation control to furnish the *syn*-isomers.[13]

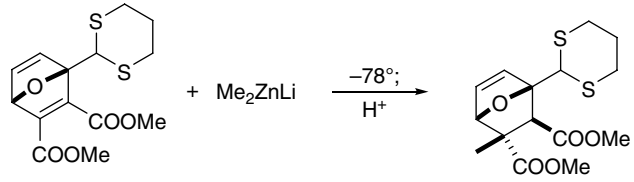
Two routes to 2-substituted indoles are based on organozinc addition to nitriles.[14] The adducts are liable to coupling reaction to complete the synthesis.



Interesting regioselectivity is exhibited in the reaction of diarylzincs with acridine --- at C-4 under Ni(0) catalysis, and at C-9 in the presence of Rh(I) salts or complexes.[15]

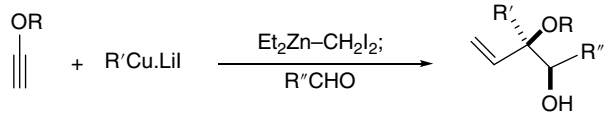
The Cu-catalyzed conjugate addition of R_2Zn to enones is well established. However, the resulting zinc enolates failed to be alkylated. The unreactivity is overcome by changing the solvent to toluene.[16]

The oxabridge in a dimethyl 7-oxabicycl[2.2.1]hepta-2,5-diene-2,3-dicarboxylate exerts a directing effect on the steric course of attack by Me_2ZnLi.[17] Such a result is favorable to elaboration of the ring-A portion of the gibberellins.

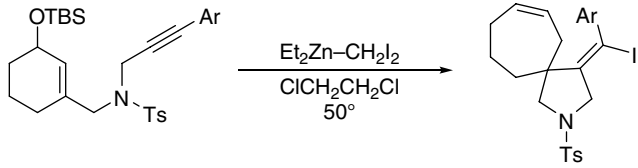


In the presence of $(PhO)_2P(O)H$ the addition of organozinc reagents to carbonyl compounds leads directly to alkene products.[18]

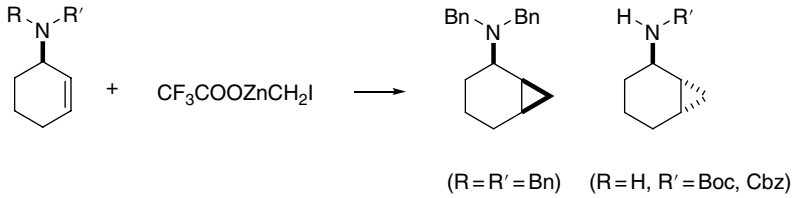
Allylation. 3-Oxoalkylzinc compounds are generated in situ from cyclopropanols and they undergo Cu-catalyzed S_N2' allylation.[19] A more interesting carbon chain construction involves cyclopropanation and unraveling to generate alkoxyallyl nucleophiles.[20]



Ring formation. A general method for securing the useful series of reagents $RXZnCH_2I$ starts from Et_2Zn: reaction with CH_2I_2 to afford $Zn(CH_2I)_2$ then reaction with RXH.[21] The alternative sequence is also viable. For halocyclopropanation (of allylic alcohols) XCHI(ZnX) is a suitable reagent.[22] The spiroannulation shown below proceeds via cyclopropanation, addition across the triple bond (attendant ring formation) and elimination.[23]



Iodomethylzinc trifluoroacetate serves as a cyclopropanation agent. Remarkably, the reaction of allylic amines shows diastereoselectivities depending on certain *N*-substituents.[24]



Prepared from Et_2Zn, CH_2I_2 and $(BuO)_2P(=O)OH$, the stable reagent (several days at −20°) $(BuO)_2P(=O)OZnCH_2I$ also exhibits activity for cyclopropanation, insertion into β-diketones, and promoting [2,3]sigmatropic rearrangement of sulfonium ylides.[25]

Rearrangement. Ethylzinc trifluoroacetate is an effective catalyst for the transformation of bromohydrins into aldehydes.[26]

[1] Cui, Y., Yamashita, Y., Kobayashi, S. *CC* **48**, 10319 (2012)
[2] Fu, Y., Hu, X., Chen, Y., Yang, Y., Hou, H., Hu, Y. *S* 1030 (2012)
[3] Stathakis, C.I., Bernhardt, S., Quint, V., Knochel, P. *ACIE* **51**, 9428 (2012)
[4] Haag, B., Mosrin, M., Ila, H., Malakhov, V., Knochel, P. *ACIE* **50**, 9794 (2011)
[5] Dobrovetsky, R., Kratish, Y., Tumanskii, B., Botoshansky, M., Bravo-Zhivotovskii, D., Apeloig, Y. *ACIE* **1**, 4671 (2012)

[6] Blair, V.L., Blakemore, D.C., Hay, D., Hevia, E., Pryde, D.C. *TL* **52**, 4690(2011)
[7] Hazra, C.K., Oestreich, M. *OL* **14**, 4010 (2012)
[8] Rieke, R.D., Kim, S.-H. *SL* 2867 (2012)
[9] Rieke, R.D., Kim, S.-H. *TL* **53**, 3478 (2012)
[10] McLaughlin, M., Belyk, K.M., Qian, G., Reamer, R.A., Chen, C. *JOC* **77**, 5144 (2012)
[11] Werner, T., Riahi, A.M., Schramm, H. *S* 3482 (2011)
[12] Fandrick, D.R., Saha, J., Fandrick, K.R., Sanyal, S., Ogikubo, J., Lee, H., Roschangar, F., Song, J.J., Senanayake, C.H. *OL* **13**, 5616 (2011)
[13] Stanton, G.R., Norrby, P.-O., Carroll, P.J., Walsh, P.J. *JACS* **134**, 17599 (2012)
[14] Kim, J.H., Lee, S. *S* 1464 (2012)
[15] Hyodo, I., Tobisu, M., Chatani, N. *CC* **48**, 308 (2012)
[16] Jarugumilli, G.K., Zhu, C., Cook, S.P. *EJOC* 1712 (2012)
[17] Isobe, M., Chiang, C.-T., Tsao, K.-W., Cheng, C.-Y., Breunig, R. *EJOC* 2109 (2012)
[18] Cui, H., Li, Y., Zhang, S. *OBC* **10**, 2862 (2012)
[19] Das, P.P., Belmore, K., Cha, J.K. *ACIE* **51**, 9517 (2012)
[20] Mejuch, T., Botoshansky, M., Marek, I. *OL* **13**, 3604 (2011)
[21] Cornwall, R.G., Wong, O.A., Du, H., Ramirez, T.A., Shi, Y. *OBC* **10**, 5498 (2012)
[22] Beaulieu, L.-P.B., Zimmer, L.E., Gagnon, A., Charette, A.B. *CEJ* **18**, 14784 (2012)
[23] Yeh, M.-C.P., Liang, C.-J., Fan, C.-W., Chiu, W.-H., Lo, J.-Y. *JOC* **77**, 9707 (2012)
[24] Csatayova, K., Davies, S.G., Lee, J.A., Ling, K.B., Roberts, P.M., Russell, A.J., Thomson, J.E. *T* **66**, 8420 (2010)
[25] Voituriez, A., Zimmer, L.E., Charette, A.B. *JOC* **75**, 1244 (2010)
[26] Wang, Z., Li, M., Zhang, W., Jia, J., Wang, F., Xue, S. *TL* **52**, 5968 (2011)

Osmium tetroxide

gem-Aminohydroxylation. In the addition to hindered alkenes 4-$ClC_6H_4COONHCbz$ in conjunction with OsO_4 serves adequately.[1] Another aminohydroxylation system involves $K_2OsO_2(OH)_4$ and ROCONHOTs.[2]

[1] Ma, Z., Naylor, B.C., Loertscher, B.M., Hafen, D.D., Li, J.M., Castle, S.L. *JOC* **77**, 1208 (2012)
[2] Masruri, Willis, A.C., McLeod, M.D. *JOC* **77**, 8480 (2012)

Oxabis(triphenylphosphonium) triflate

Dehydration and cyclodehydration. The salt $[(Ph_3P)_2O](OTf)_2$ is a powerful oxaphilic agent, it converts 2-acylaminobiaryls into phenanthridines at room temperature or below.[1]

The heterocyclic analog, i.e., the diphosphonium salt with an oxygen atom bridging the two phosphorous atoms of 1,2-bis(diphenylphosphino)benzene, shows similar reactivity, for example, in dehydration of aldoximes.[2]

[1] Xi, J., Dong, Q.-L., Liu, G.-S., Wang, S., Chen, L., Yao, Z.-J. *SL* 1674 (2012)
[2] Moussa, Z. *S* 460 (2012)

Oxygen

Oxidation. The Cu-catalyzed C-H functionalization under aerobic conditions has been reviewed.[1] A practical oxidation of primary alcohols to aldehydes at room temperature is said to employ (bpy)CuCl, 1-methylimidazole, TEMPO in MeCN.[2] Use of TEMPO

in oxidation of alcohols by oxygen features cobaloxime as a platform where activation takes place, and nitric oxide to pick up one oxygen atom.[3] Other reports indicate addition of either $Fe(NO_3)_3$ and NaCl,[4] or CuCl, 4,7-diphenyl-1,10-phenanthroline, and di-*t*-butyl azodicarboxylate.[5]

Aerobic oxidation of alcohols is also accomplished on nanoparticles of gold[6] and that dispersed through periodic mesoporous organosilica.[7] Nano-Mn_3O_4 species shows selectivity that favors oxidation of primary alcohols.[8]

For oxidation of allylic alcohols, *t*-butyl 2-methyl-6-trifluoromethyl-1-hydroxyindole-3-carboxylate serves as a ligand for the CuCl catalyst.[9] (*Z*)-Allylic alcohols undergo oxidation to give the conjugated aldehydes, and in the presence of DMAP, isomerization into the (*E*)-isomers also takes place.[10]

An iron salt [$Fe(NO_3)_3$] in conjunction with TEMPO constitutes a system for aerobic oxidation of secondary propargylic alcohols.[11] The more exotic nano-composite of MoS_2 and Ta_3N_5 appears to have a broader catalytic power, e.g., for oxidation of alcohols, epoxidation of alkenes, oxidation of sulfides (to sulfoxides), and conversion of primary amines to azoalkanes.[12] A ruthenium salt with the metal complex to both a bipyridyl and a terpyridyl ligand is used in aerial oxidation of benzyl alcohols.[13] A nonmetallic catalytic system for alcohol oxidation consists of DDQ and *t*-BuONO.[14]

An epoxidizing agent for alkenes is generated from oxidation of Me_2CHCHO in the presence of $Mn(OAc)_2$.[15]

N-Substituted 3-methylindoles are subject to oxidation (O_2, $CuBr{\cdot}SMe_2$, DABCO, DMSO, 100°) to furnish the aldehydes.[16] 2-Arylmethylpyridines and pyrimidines are converted into oxo derivatives, and various copper salts or $FeCl_2$ can serve as catalyst.[17] Oxidation of arylacetamides to ArCOCONHR does not require metal catalysts.[18]

Furthermore, RCH_2NH_2 give primary amides in a MnO_2-catalyzed oxidation by air, nitriles being the intermediates.[19] A similar reaction of $ArCH_2NH_2$ to afford $ArCONH_2$ is reported, although it is under catalysis by CuBr.[20] Cyclic amines give lactams on aerial oxidation in the presence of PVP-stabilized nano-Au.[21]

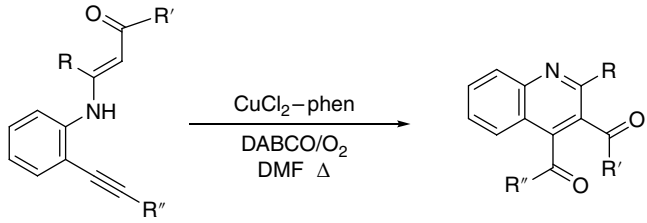
N-Substituted hydroxylamines are oxidized to nitroso compounds (CuCl, pyridine, air), and the reaction is usually carried out in trapping dienes.[22] Aerial oxidation of hydrazine catalyzed by $FeCl_2$ or a flavinium chloride generates diimide, and accordingly alkenes (e.g., enamides) present in the reaction medium are hydrogenated.[23,24] No catalyst is needed for generating diimide for the hydrogenation of enamides in aqueous solution.[25]

Although convolute, under oxidative conditions indole is iodinated by NH_4I in the presence of $Cu(OCOCF_3)_2$ and the product can be further transformed into 3-cyanoindole. The carbon atom is supplied by DMF.[26]

Oxidative coupling. Several articles describe the transformation of primary amines RCH_2NH_2 into imines $RCH_2N{=}CHR$ by air, and usually a copper salt is the catalyst: CuCl,[27] Cu(I) 3-methylsalicylate,[28] CuI, bipyridine, and TEMPO.[29] Mixtures of $ArCH_2NH_2$ and RNH_2 give ArCH=NR, and in this case in the presence of 5-*t*-butyl-2-hydroxy-1,4-benzoquinone.[30] Primary amines are dehydrogenated to nitriles at room temperature by a nano-Ru oxide composite of pyrochlore Nafion.[31]

Direct conversion of methylarenes into $ArCONH_2$ involves incorporation of oxygen and ammonia in the presence of amorphous and reusable MnO_2.[32] Combining $ArCH_2CHO$ and Ar′NHR to give ArCOCON(Ar)R is also readily accomplished (CuBr, O_2),[33] and 2-oxoacetamidines RCOC(NHR′)=NR″ can also be obtained from RCH_2CHO and two amines.[34]

It is also relatively facile to oxygenate a triple bond attached to an aryl moiety. α-Diketones are produced (e.g., with CAN, O_2),[35] and such functionality may then participate in cyclization.[36,37,38]



An oxidation-condensation tandem in a Cu-catalyzed reaction between 1-alkynes and amines furnishes amides.[39]

Several other variants of amide synthesis based on aerial oxidation involve: RCHO, R'_2NH with $Co(OAc)_2$, *N*-hydroxysuccinimide,[40] nano-gold stabilized by DNA, LiOH.[41] Oxidation of benzylamines can take advantage of the reactivity of $Cu(OTf)_2$ to catalyze *N*-arylation, thereby accomplishing an elaboration of ArCONHAr′ from $ArCH_2NH_2$ and Ar′I in one pot.[42]

Interestingly, under certain reaction conditions *N*-alkylation of primary amines with RCH_2OH can be effected.[43]

Cu(II)-catalyzed oxidation of 2-cyclohexenones in the presence of ROH gives rise to alkyl aryl ethers. From 1,3-cyclohexanedione, it generates resorcinyl ethers.[44]

Under acidic conditions functionalization with nucleophiles during the oxidation at a benzylic position has been demonstrated.[45] Whether the specified high pressure oxygen (10 bar) is necessary must be clarified. The C-1 of *N*-aryltetrahydroisoquinolines is readily oxidized [O_2, $(bpy)AuCl_3$] to engage in CC bond formation with nitroalkanes.[46]

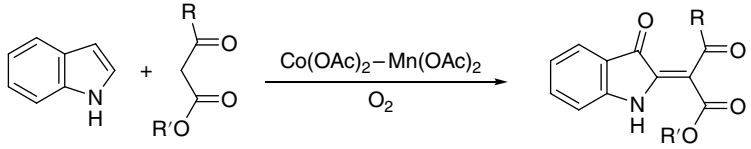
Aryl ketones are obtained from RCHO and $ArSO_2Na$ when subjected to aerial oxidation in the presence of $[(cod)RhCl]_2$.[47]

The oxidizability of C-H bond(s) germinal to an amino nitrogen atom has been exploited in that TMEDA is used as a formyl source. Thus, formylation of the indole nucleus (at C-3) is accomplished in a reaction with $CuCl_2$, TMEDA, DMSO, H_2O at 120°.[48] Under somewhat different reaction conditions anilines are transformed into bis(4-aminoaryl)methanes.[49] Also in a route to arylbis(3-indolyl)methanes, $ArCH_2OH$ and indole are cooxidized (catalyst: I_2).[50]

Trapping by Me_3SiCN in an aerial oxidation of $ArNMe_2$ (in the presence of AIBN) produces $ArN(Me)CH_2CN$.[51]

Oxidative coupling between amides and 1-alkynes [O_2, $Cu(OH)_2$] without further transformation of the triple bond furnishes a method for ynamide synthesis.[52] From imines such as $Ar_2C{=}NH$, 1-iminoalkynes are formed,[53] and the reaction can be followed by noting a color change.[54] Benzalamines undergo *o*-cyanation in a reaction with phenylacetonitrile catalyzed by CuBr in the air.[55]

The well-known Glaser coupling of 1-alkynes is shown to proceed in poly(ethylene glycol).[56] Coupling involving azoles has received much attention in recent years, various metal catalysts being examined. New examples include the cross-coupling of 3-cyano-1-(pyrimidin-2-yl)indole with benzoxazole as catalyzed by $Cu(OAc)_2$,[57] indole with β-dicarbonyl compounds that results in 2-alkylidene-3-indolinones with bimetallic catalysts.[58] A photoredox CC coupling reaction mediated by $(bpy)_3RuCl_2$ combines 3-unsubstituted indoles and 1-amino carbonyl compounds.[59]



Benzannulated oxazoles, thiazoles, and imidazoles are aminated on reaction with amines in the presence of $Cu(acac)_2$ under oxygen (but no base).[60]

Nano-Mn_3O_4 on diatomite effects oxidative coupling of alkenylarenes and THF (and 1,3-dioxolane) to afford aryl α-heterocycl-2-ylalkyl ketones.[61]

Oxidative transformation of boronic acids. Two procedures have been worked out for converting $ArB(OH)_2$ into phenols under oxygen: $CuCl_2$ and a surfactant in water,[62] under visible light irradiation with $(bpy)_3RuCl_2$ and *i*-Pr_2NEt in DMF.[63]

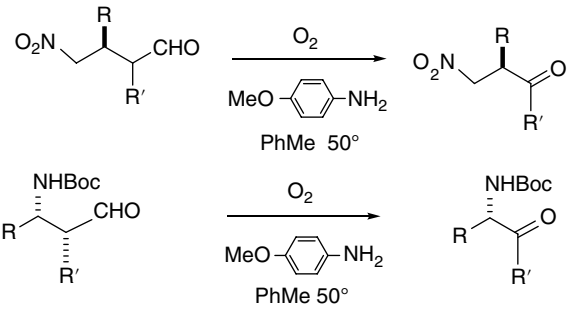
A Suzuki-type coupling involving polyfluoroalkyl iodides is conducted with Cu in the air at room temperature, in a solvent system of DMSO-DMF (5:1).[64] The stable salt of $K[B(CF_3)(OMe)_3]$ is a convenient source for introducing a trifluoromethyl group to arenes via the Suzuki-type coupling [but using $Cu(OAc)_2$, under O_2].[65] A more prosaic transformation is the preparation of ArSAr′.[66] Homocoupling of $ArB(OH)_2$ also succeeds with nano-Au on Mg-Al oxides.[67]

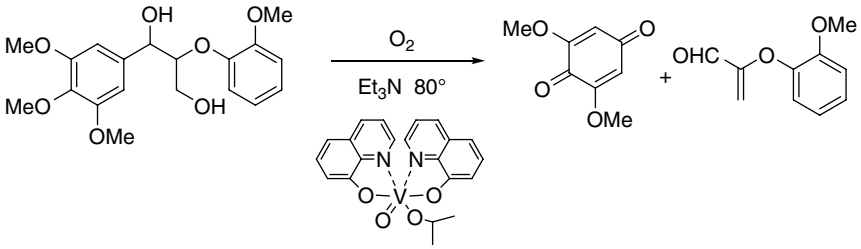
The solvent DMF is the carbon source of the cyano group in the reaction that converts $ArB(OH)_2$ into ArCN in the presence of NH_4I and $Cu(NO_3)_2$ under oxygen.[68] The process is thought to involve ArI as intermediates.

By Pd-catalysis under oxygen, RCOCl and $ArB(OH)_2$ combine to give RCOAr.[69]

Bond cleavage processes. Alkenes are cleaved under oxygen with *N*-hydroxyphthalimide.[70] Conversion of carboxylic acids into $RCOOCH_2O(CH_2)_2OCHO$ is observed in the reaction in 1,4-dioxane (Cu_2O, K_2CO_3, 110°).[71] Potassium aroates undergo decarboxylative alkoxylation by $(RO)_4Si$, upon exposure to $Cu(OAc)_2$ and Ag_2CO_3 under oxygen.[72]

Oxidative deformylation of certain α-branched aldehydes occurs with assistance of 4-methoxyaniline, probably via enamine intermediates.[73] A vanadyl complex is capable of catalyzing cleavage of certain 4-alkoxybenzyl alcohols.[74]

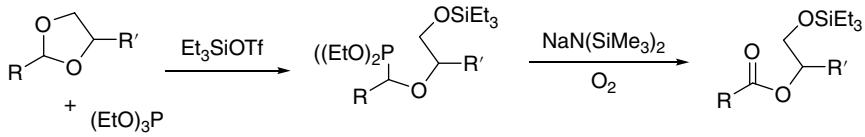




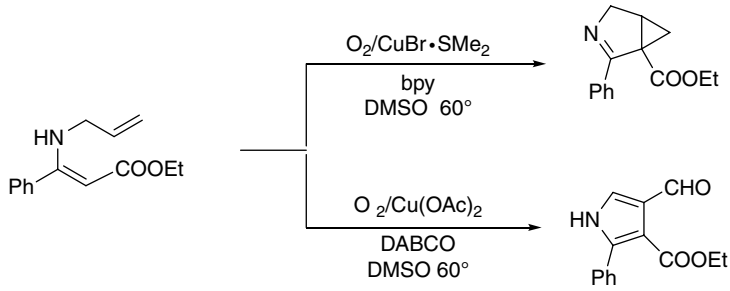
1,3-Diaryl-1,3-propanediones are degraded to give benzils upon treatment with I_2 in hot DMSO in the air.[75]

The transformation of ArX into $ArSO_2Me$ by DMSO consists of C-S bond cleavage/formation as well as *S*-oxidation, using a catalytic system of Cu_2O, *t*-BuOK and acetylacetone.[76]

Oxidative cleavage of 2,4-disubstituted 1,3-dioxolanes via open-chain O,P-acetals affords esters.[77]

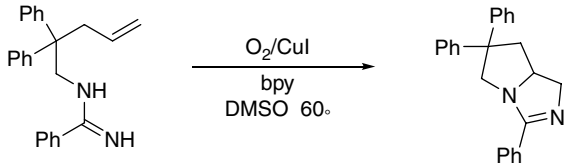


Annulation. (*Z*)-β-(*N*-Allylamino)cinnamic esters undergo oxidative cyclization; variation of reaction conditions, e.g., with different Cu-salts, can have profound effects on the course.[78]



Several benzannulated heterocycles are accessed from oxidative cyclization: cinnolines,[79] brominated isoquinolones,[80] quinazolines.[81] In the last case the oxidant 4-hydroxy-TEMPO is maintained active by oxygen.

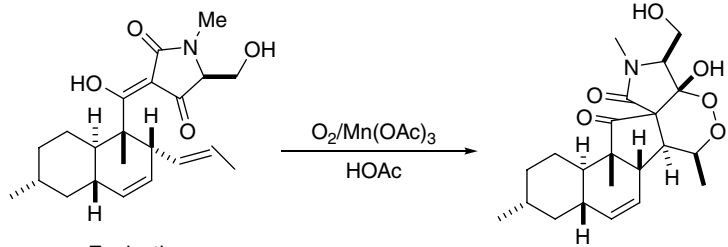
In the following it is shown that an amidine moiety is oxidized and participates in an intramolecular [3+2]cycloaddition.[82]



Examples showing the contribution of a nitrogen atom from an azido group for ring formation include the preparation of 5-formylpyrazin-2-ones from *N*-allyl α-azidoalkanamides,[83] and the Ru-catalyzed cyclization-oxidation sequence of 2′-alkyl-2-azidobiaryls which affords benz[*c*]quinolines.[84] 2-Hydroxy-3′-acylaminobiaryls cyclize to afford dibenzofuran derivatives, in which the heteroatoms are *o*-related.[85]

A mixture of $ArCH_2CHO$ and $R'CH_2NH_2$ is prompted (by $CuBr_2$) to generate substituted oxazoles, the oxygen atom of the heterocycle comes from molecular oxygen.[86] α-Methylene-γ-butyrolactones are obtained by a Pd(II)-catalyzed condensation of acrylic acid and 1-alkenes in oxygen.[87]

In the Au-catalyzed cycloisomerization of *N*-propargyl carboxamides, further oxygenation to give oxazole-5-methyl hydroperoxides are produced.[88] Conversion of equisetin to peroxyfusarisetin is quite facile.[89]



Equisetin

Aromatization. Dehydrogenation of dihydropyrimidines and their oxo compounds under oxygen [$Co(OAc)_2$, *N*-hydroxyphthalimide] is accomplished in hot dichloroethane.[90] Polymethoxystilbenes give phenanthrenes in the oxidative cyclization using $NaNO_2$ as catalyst and CF_3COOH as an additive.[91]

Addition. Sodium organosulfonates are found to add to alkynes, *cis*-addition is favored.[92] Methyl cyanoacetate acts as a glyoxylate anion equivalent in its addition to conjugate carbonyl compounds, under the influence of CuI in the air.[93] The cyano group is lost in the process.

Intramolecular hydroamination involving an unactivated double bond occurs when the substrates are exposed to nano-Au clusters under aerobic conditions.[94] Oxophosphorylation of alkenes reaction with $HP(O)(OR)_2$ and oxygen to furnish β–keto phosphonates is enabled by a Cu-Fe bimetallic catalyst.[95]

2′-Hydroxychalcones are converted into flavones on warming with CuI and an ionic liquid under oxygen.[96]

[1] Wendlandt, A.E., Suess, A.M., Stahl, S.S. *ACIE* **50**, 11062 (2011)
[2] Hoover, J.M., Stahl, S.S. *JACS* **133**, 16901 (2011)
[3] Jing, Y., Jiang, J., Yan, B., Lu, S., Jiao, J., Xue, H., Yang, G., Zheng, G. *ASC* **353**, 1146 (2011)
[4] Ma, S., Liu, J., Li, S., Chen, B., Cheng, J., Kuang, J., Liu, Y., Wan, B., Wang, Y., Ye, J., Yu, Q., Yuan, W., Yu, S. *ASC* **353**, 1005 (2011)
[5] Nishii, T., Ouchi, T., Matsuda, A., Matsubara, Y., Haraguchi, Y., Kawano, T., Kaku, H., Horikawa, M., Tsunoda, T. *TL* **53**, 5880 (2012)
[6] Asao, N., Hatakeyama, N., Menggenbateer, Minato, T., Ito, E., Hara, M., Kim, Y., Yamamoto, Y., Chen,M., Zhang, W., Inoue, A. *CC* **48**, 4540 (2012)
[7] Karimi, B., Esfahani, F.K. *ASC* **354**, 1319 (2012)
[8] Sun, H., Hua, Q., Guo, F., Wang, Z., Huang, W. *ASC* **354**, 569 (2012)
[9] Shen, S.-S., Kartika, V., Tan, Y.S., Webster, R.D., Narasaka, K. *TL* **53**, 986 (2012)
[10] Könning, D., Hiller, W., Christmann, M. *OL* **14**, 5258 (2012)
[11] Liu, J., Xie, X., Ma, S. *S* 1569 (2012)
[12] Gao, Q., Giordano, C., Antonietti, M. *ACIE* **51**, 11740 (2012)
[13] Taketoshi, A., Beh, X.N., Kuwabara, J., Koizumi, T., Kanbara, T. *TL* **53**, 3573 (2012)
[14] Shen, Z., Dai, J., Xiong, J., He, X., Mo, W., Hu, B., Sun, N., Hu, X. *ASC* **353**, 3031 (2011)
[15] Serra, A.C., Gonsalves, A.M. d'A. *TL* **52**, 3489 (2011)
[16] Wang, Y.-F., Zhang, F.-L., Chiba, S. *S* 1526 (2012)
[17] De Houwer, J., Tehrani, K.A., Maes, B.U.W. *ACIE* **51**, 2745 (2012)
[18] Shao, J., Huang, X., Wang, S., Liu, B., Xu, B. *T* **68**, 573 (2012)
[19] Wang, Y., Kobayashi, H., Yamaguchi, K., Mizuno, N. *CC* **48**, 2642 (2012)
[20] Xu, W., Jiang, Y., Fu, H. *SL* 801 (2012)
[21] Preedasuriyachai, P., Chavasiri, W., Sakurai, H. *SL* 1121 (2011)
[22] Frazier, C.P., Bugarin, A., Engelking, J.R., de Alaniz, J.R. *OL* **14**, 3620 (2012)
[23] Lamani, M., Ravikumara, G.S., Prabhu, K.R. *ASC* **354**, 1437 (2012)
[24] Imada, Y., Kitagawa, T., Ohno, T., Iida, H., Naota, T. *OL* **12**, 32 (2010)
[25] Marsh, B.J., Heath, E.L., Carberg, D.R. *CC* **47**, 280 (2011)
[26] Kim, J., Kim, H., Chang, S. *OL* **14**, 3924 (2012)
[27] Patil, R.D., Adimurthy, S. *ASC* **353**, 1695 (2011)
[28] Largeron, M., Fleury, M.-B. *ACIE* **51**, 5409 (2012)
[29] Tian, H., Yu, X., Li, Q., Wang, J., Xu, Q. *ASC* **354**, 2671 (2012)

[30] Wendlandt, A.E., Stahl, S.S. *OL* **14**, 2850 (2012)
[31] Venkatesan, S., Kumar, A.S., Lee, J.-F., Chan, T.-S., Zen, J.-M. *CEJ* **18**, 6147 (2012)
[32] Wang, Y., Yamaguchi, K., Mizuno, N. *ACIE* **51**, 7250 (2012)
[33] Zhang, C., Xu, Z., Zhang, L., Jiao, N. *ACIE* **50**, 11088 (2011)
[34] Zhang, C., Zhang, L., Jiao, N. *ASC* **354**, 1293 (2012)
[35] Su, C.-F., Hu, W.-P., Vandavasi, J.K., Liao, C.-C., Hung, C.-Y., Wang, J.-J. *SL* 2132 (2012)
[36] Xia, X.-F., Zhang, L.-L., Song, X.-R., Liu, X.-Y., Liang, Y.-M. *OL* **14**, 2480 (2012)
[37] Toh, K.K., Sanjaya, S., Sahnoun, S., Chong, S.Y., Chiba, S. *OL* **14**, 2290 (2012)
[38] Wang, Z.-Q., Zhang, W.-W., Gong, L.-B., Tang, R.-Y., Yang, X.-H., Liu, Y., Li, J.-H. *ACIE* **50**, 8968 (2011)
[39] Wei, W., Hu, X.-Y., Yan, X.-W., Zhang, Q., Cheng, M., Ji, J.-X. *CC* **48**, 305 (2012)
[40] Yao, H., Yamamoto, K. *CAJ* **7**, 1542 (2012)
[41] Wang, Y., Zhu, D., Tang, L., Wang, S., Wang, Z. *ACIE* **50**, 8917 (2011)
[42] Xu, M., Zhang, X.-H., Shao, Y.-L., Han, J.-S., Zhong, P. *ASC* **354**, 2665 (2012)
[43] Yu, X., Liu, C., Jiang, L., Xu, Q. *OL* **13**, 6184 (2011)
[44] Simon, M.-O., Girard, S.A., Li, C.-J. *ACIE* **51**, 7537 (2012)
[45] Pinter, A., Klussmann, M. *ASC* **354**, 701 (2012)
[46] Xie, J., Li, H., Zhou, J., Cheng, Y., Zhu, C. *ACIE* **51**, 1252 (2012)
[47] Rao, H., Yang, L., Shuai, Q., Li, C.-J. *ASC* **353**, 1701 (2011)
[48] Chen, J., Liu, B., Liu, D., Liu, S., Cheng, J. *ASC* **354**, 2438 (2012)
[49] Zhang, L., Peng, C., Zhao, D., Wang, Y., Fu, H.-J., Shen, Q., Li, J.-X. *CC* **48**, 5928 (2012)
[50] Nobuta, T., Fujiya, A., Tada, N., Miura, T., Itoh, A. *SL* 2975 (2012)
[51] Liu, L., Wang, Z., Fu, X., Yan, C.-H. *OL* **14**, 5692 (2012)
[52] Jin, X., Yamaguchi, K., Mizuno, N. *CC* **48**, 4974 (2012)
[53] Laouiti, A., Rammah, M.M., Rammah, M.B., Marrot, J., Couty, F., Evano, G. *OL* **14**, 6 (2012)
[54] Laouiti, A., Jouvin, K., Bourdreux, F., Rammah, M.M., Rammah, M.B., Evano, G. *S* 1491 (2012)
[55] Jin, J., Qen, Q., Lu, P., Wang, Y. *CC* **48**, 9933 (2012)
[56] Li, Y.N., Wang, J.-L., He, L.-N. *TL* **52**, 3485 (2011)
[57] Nishino, M., Hirano, K., Satoh, T., Miura, M. *ACIE* **51**, 6993 (2012)
[58] Wu, W., Xu, J., Huang, S., Su, W *CC* **47**, 9660 (2011)
[59] Wang, Z.-Q., Hu, M., Huang, X.-C., Gong, N.-B., Xie, Y.-X., Li, J.-H. *JOC* **77**, 8705 (2012)
[60] Wagh, Y.S., Bhanage, B.M. *TL* **53**, 6500 (2012)
[61] Sun, H., Zhang, Y., Guo, F., Zha, Z., Wang, Z. *JOC* **77**, 3563 (2012)
[62] Inamoto, K., Nozawa, K., Yonemoto, M., Kondo, Y. *CC* **47**, 11775 (2011)
[63] Zou, Y.-Q., Chen, J.-R., Liu, X.-P., Lu, L.-Q., Davis, R.L., J Ørgensen, K.A., Xiao, W.-J. *ACIE* **51**, 784 (2012)
[64] Qi, Q., Shen, Q., Lu, L. *JACS* **134**, 6548 (2012)
[65] Khan, B.A., Buba, A.E., Goossen, L.J. *CEJ* **18**, 1577 (2012)
[66] Xu, H.-J., Zhao, Y.-Q., Feng, T., Feng, Y.-S. *JOC* **77**, 2878 (2012)
[67] Wang, L., Zhang, W., Su, D.S., Meng, X., Xiao, F.-S. *CC* **48**, 5476 (2012)
[68] Kim, J., Choi, J., Shin, K., Chang, S. *JACS* **134**, 2528 (2012)
[69] Chen, J., Peng, Y., Liu, M., Ding, J., Su, W., Wu, H. *ASC* **354**, 2117 (2012)
[70] Lin, R., Chen, F., Jiao, N. *OL* **14**, 4158 (2012)
[71] Liu, Z.-Q., Zhao, L., Shang, X., Cui, Z. *OL* **14**, 3218 (2012)
[72] Bhadra, S., Dzik, W.I., Goossen, L.J. *JACS* **134**, 9938 (2012)
[73] Tiwari, B., Zhang, J., Chi, Y.R. *ACIE* **51**, 1911 (2012)
[74] Hanson, S.K., Wu, R., Silks, L.A. *ACIE* **51**, 3410 (2012)
[75] Yuan, Y., Zhu, H. *EJOC* 329 (2012)
[76] Yuan, G., Zheng, J., Gao, X., Li, X., Huang, L., Chen, H., Jiang, H. *CC* **48**, 7513 (2012)
[77] Maegawa, T., Otake, K., Goto, A., Fujioka, H. *OBC* **9**, 5648 (2011)

[78] Toh, K.K., Wang, Y.-F., Ng, E.P.J., Chiba, S. *JACS* **133**, 13942 (2011)
[79] Zhang, G., Miao, J., Zhao, Y., Ge, H. *ACIE* **51**, 8318 (2012)
[80] Too, P.C., Chiba, S. *CC* **48**, 7634 (2012)
[81] Han, B., Wang, C., Han, R.-F., Yu, W., Duan, X.-Y., Fang, R., Yang, X.-L. *CC* **47**, 7818 (2011)
[82] Wang, Y.-F., Zhu, X., Chiba, S. *JACS* **134**, 3679 (2012)
[83] Zhang, L., Lee, J.-Y., Yamazaki, N., Chiba, S. *SL* 2167 (2011)
[84] Intrieri, D., Mariani, M., Caselli, A., Ragaini, F., Gallo, E. *CEJ* **18**, 10487 (2012)
[85] Zhao, J., Wang, Y., Zhu, Q. *S* 1551 (2012)
[86] Xu, Z., Zhang, C., Jiao, N. *ACIE* **51**, 11367 (2012)
[87] Yonehara, K., Miyoshi, Y., Tsukajima, A., Akatsuka, T., Saito, M. *ASC* **353**, 1071 (2011)
[88] Hashmi, A.S.K., Jaimes, M.C.B., Schuster, A.M., Rominger, F. *JOC* **77**, 6394 (2012)
[89] Yin, J., Wang, C., Kong, L., Cai, S., Gao, S. *ACIE* **51**, 7786 (2012)
[90] Han, B., Han, R.-F., Ren, Y.-W., Duan, X.-Y., Xu, Y.-C., Zhang, W. *T* **67**, 5615 (2011)
[91] Su, B., Li, L., Hu, Y., Liu, Y., Wang, Q. *ASC* **354**, 383 (2012)
[92] Taniguchi, N. *SL* 1245 (2012)
[93] Kim, S.H., Kim, K.H., Kim, J.N. *ASC* **353**, 3335 (2011)
[94] Kitahara, H., Sakurai, H. *CL* **39**, 46 (2010)
[95] Wei, W., Ji, J.-X. *ACIE* **50**, 9097 (2011)
[96] Du, Z., Ng, H., Zhang, K., Zeng, H., Wang, J. *OBC* **9**, 6930 (2011)

Oxygen, singlet

CC Bond cleavage. Singlet oxygen (O_2, hν, 2-chloroanthraquinone) cleaves 1,2-diols.[1] From 1-aryl-1,3-alkanediones the aroic acids are produced from a singlet oxygen reaction in the presence of iodine.[2]

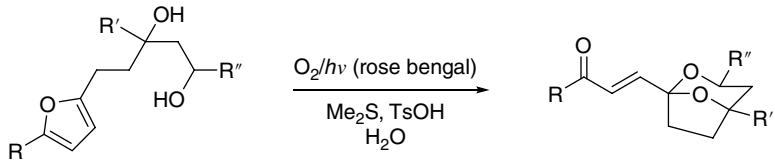
Oxidation. Co-oxidation of a benzylic alcohol and an aliphatic alcohol by singlet oxygen gives rise to the ester ArCOOR.[3] Ethylarenes are converted into dibromacetophenones $ArCOCHBr_2$ when 48% HBr and CBr_4 are co-oxidized.[4]

On TiO_2 the oxidation of benzylamine gives benzaldehyde which rapidly forms the Schiff base $PhCH{=}NCH_2Ph$.[5] Dibenzylamine and tribenzylamine yield the same product. The tertiary amine splits off toluene in the process.

The oxidation of α-ketols on mesoporous carbon nitride to α-diketones by oxygen is carried out in MeCN at 100° and under visible light.[6] It is not clear whether singlet oxygen is generated under such conditions.

Ring formation. Indoles are obtained from 2-alkenylanilines on being subjected to irradiation in air in the presence of a bpz-complexed $Ru(PF_6)_2$.[7]

In situ acetalization of a ketone of the enedione unit generated from furan occurs when the substrate contains two hydroxyl groups in favorable positions.[8]



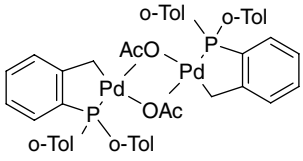
Rearrangement. 3-(α-hydroxyalkyl)furans are converted into 2-alkyl-3-furaldehydes upon treatment with singlet oxygen, then Me_2S.[9]

[1] Matsusaki, Y., Yamaguchi, T., Tada, N., Miura, T., Itoh, A. *SL* 2059 (2012)
[2] Tada, N., Shomura, M., Cui, L., Nobuta, T., Miura, T., Itoh, A. *SL* 2896 (2011)
[3] Nobuta, T., Fujiya, A., Hirashima, S., Tada, N., Miura, T., Itoh, A. *TL* **53**, 5306 (2012)
[4] Tada, N., Ban, K., Ishigami, T., Nobuta, T., Miura, T., Itoh, A. *TL* **52**, 3821 (2011)
[5] Liang, X., Ma, W., Zhao, Y., Chen, C., Ji, H., Zhao, J. *CEJ* **18**, 2624 (2012)
[6] Zheng, Z., Zhou, X. *ChJC* **30**, 1683 (2012)
[7] Maity, S., Zheng, N. *ACIE* **51**, 9562 (2012)
[8] Kouridaki, A., Montagnon, T., Tofi, M., Vassilikogiannakis, G. *OL* **14**, 2374 (2012)
[9] Charbonnet, N., Riguet, E., Bochet, C.G. *SL* 2231 (2011)

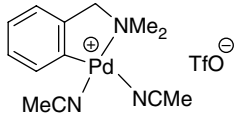
P

Palladacycles

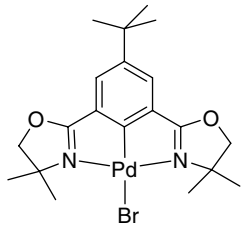
Substitution and coupling. Hydrolysis of ArCl to access phenols by microwave irradiation in aqueous DMF is mediated by **1** and *t*-BuXPhos.[1] To *o*-allylate anilines using allylic alcohol, **2** is serviceable for its realization.[2]



(**1**)

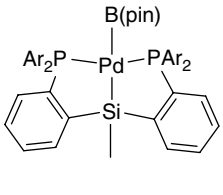


(**2**)

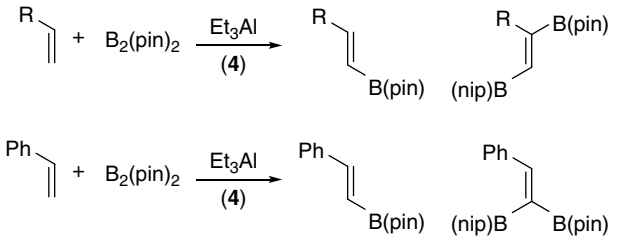


(**3**)

The pincer pallacycle **3** is obtained from reaction of $(dba)_3Pd_2$ with the 4-*t*-butyl-2, 6-dioxazolino-1-bromobenzene, and its use for catalyzing arylation of ketones has been demonstrated.[3] Another pincer-type compound **4** promotes boration of 1-alkenes at the C-1. With two equivalents of (pinacolato)diboron the reaction leads to (*E*)-1,2-diboryl-1-alkenes, but from styrenes both boryl groups enter the β-position. Cycloalkenes such as cyclooctene yield 1,2-diborylcycloalkenes.[4]



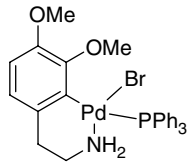
(**4**)



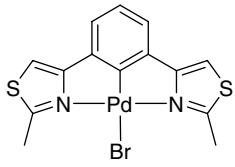
(1 equiv. $B_2(pin)_2$) (2 equiv. $B_2(pin)_2$)

Fiesers' Reagents for Organic Synthesis, First Edition. Tse-Lok Ho.
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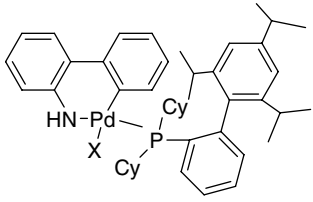
A thermally stable and oxygen-insensitive monomeric palladcycle **5** is well-suited for conducting the Heck reaction.[5] Many palladcycles are useful for conducting Suzuki coupling: **6**[6] and **7**[7] are representative. Actually **7** is used in a method for preparing $ArB(OR)_2$ from ArX and $B_2(NMe_2)_4$,[8] or $B_2(OH)_4$.[9] The coupling between RBF_3K and aryl imidazol-1-ylsulfonates can be performed with **8**, and there is no need for a phosphine ligand.[10]



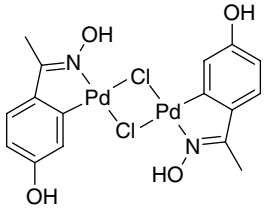
(**5**)



(**6**)

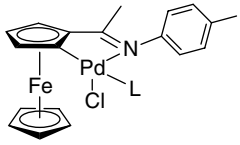


(**7**)

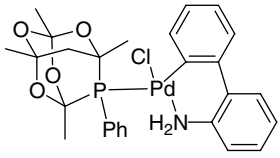


(**8**)

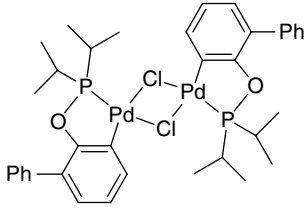
More elaborate pallacycle catalysts include the ferrocene-based **9A**, with which the Suzuki coupling involving ArCOX or anhydrides gives diaryl ketones;[11] the Hayashi-type coupling is extended to $ArCOSiMe_3$, and it is plied by **10**.[12] For Sonogashira coupling the palladacycle **11** is benefited by having an internal phosphine ligand.[13]



(**9A**) L = PPh_3
(**9B**) L = S-Phos



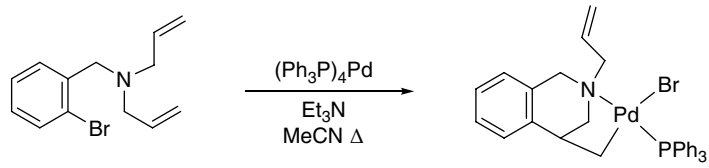
(**10**)



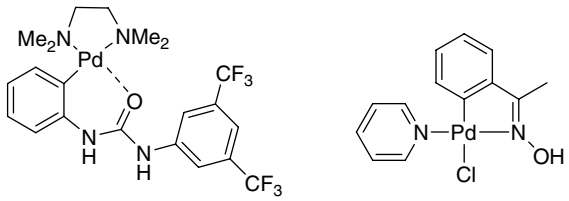
(**11**)

Stable palladacycle intermediates containing a σ-alkyl-palladium bond are formed during Heck reaction of *N*-(*o*-halobenzyl)allylamines. These can be isolated and are

precatalysts for Heck, Suzuki and Stille reactions.[14] The ferrocene-based palladacycle **9B** is suitable for catalyzing of ArX with cyclopropaneboronic acid.[15]

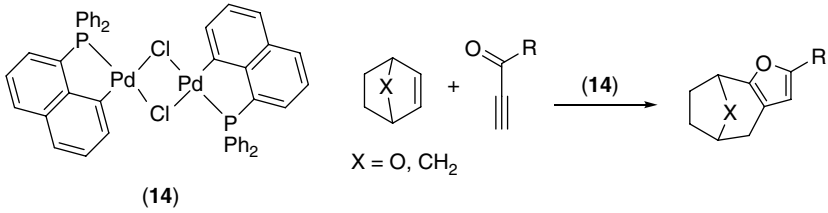


Addition and cycloaddition. Michael addition of indole and alkylidenemalonic esters is induced by **12**.[16] A Pd-variant of the Pauson-Khand reaction is demonstrated with the employment of **13**.[17]



(**12**) (**13**)

Mediated by **14** the reaction of norbornene and 7-oxanorbornene with 1-alkyn-3-ones, yields furans.[18]



(**14**)

[1] Yu, C.-W., Chen, G.S., Huang, C.-W., Chern, J.-W. *OL* **14**, 3688 (2012)
[2] Chen, K., Li, Y., Pullarkat, S.A., Leung, P.-H. *ASC* **354**, 83 (2012)
[3] Bugarin, A., Connell, B.T. *CC* **47**, 7218 (2011)
[4] Takaya, J., Kirai, N., Iwasawa, N. *JACS* **133**, 12980 (2011)
[5] Hajipour, A.R., Rafiee, F., Rouho, A.E. *TL* **52**, 4782 (2011)
[6] Luo, Q.-L., Tan, J.-P., Li, Z.-F., Nan, W.-H., Xiao, D.-R. *JOC* **77**, 8332 (2012)
[7] Oberli, M.A., Buchwald, S.L. *OL* **14**, 4606 (2012)
[8] Molander, G.A., Trice, S.L.J., Kennedy, S.M. *OL* **14**, 4814 (2012)
[9] Molander, G.A., Trice, S.L.J., Kennedy, S.M. *JOC* **77**, 8678 (2012)
[10] Civicos, J.F., Alonso, D.A., Najera, C. *ASC* **354**, 2771 (2012)
[11] Yu, A., Shen, L., Cui, X., Peng, D., Wu, Y. *T* **68**, 2283 (2012)
[12] Schmink, J.R., Krska, S.W. *JACS* **133**, 19574 (2011)
[13] Marziale, A.N., Schlüter, J., Eppinger, J. *TL* **52**, 6355 (2011)

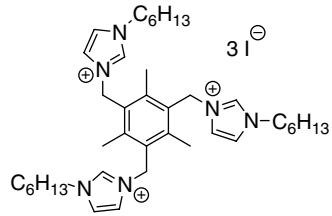
[14] Beccalli, E.M., Borsini, E., Brenna, S., Galli, S., Rigamonti, M., Broggini, G. *CEJ* **16**, 1670 (2010)
[15] Zhang, M., Cui, X., Chen, X., Wang, L., Li, J., Wu, Y., Hou, L., Wu, Y. *T* **68**, 900 (2012)
[16] Nickerson, D.M., Mattson, A.E. *CEJ* **18**, 8310 (2012)
[17] Wang, X.-R., Lu, F.-H., Song, Y., Lu, Z.-L. *TL* **53**, 589 (2012)
[18] Ge, G.-C., Mo, D.-L., Ding, C.-H., Dai, L.-X., Hou, X.-L. *OL* **14**, 5756 (2012)

Palladium, nanosized

Hydrogenation. Nanosized palladium on MIL-101 (a chromium terephthalate framework) is a water-compatible catalyst for hydrogenation of phenols in water at room temperature to furnish cyclohexanones in high selectivity and the conversion is complete.[1]

Coupling reactions. Nano-Pd promotes Heck reaction without ligand.[2,3]

Because of its popularity the Suzuki coupling has drawn a large share of attention with respect to finding new conditions for its achievement. On the use of nano-Pd deposition thermoresponsive hydrogels to carry out reaction in water is described in one report.[4] In porous form the activity is quite independent with the catalyst size, but more active than Pd/C.[5] Palladium on nanosized mesoporous silica has been employed.[6] Nano-Pd is also effective for reaction involving in situ generation of arenediazonium salts from $ArNH_2$.[7] A salt (**1**) containing three imidazolium units that form branches from a central benzene ring has stabilizing effect on nano-Pd for Suzuki coupling.[8] Another method for stabilization is to generate the particles by reduction of Pd(II) salts in the presence of diazodendrons.[9]



(**1**)

Palladium nanoparticles supported on fluorous silica gel are reusable for catalyzing arylation of indole at C-2.[10] It is noted that monodisperse nanoparticles of palladium can be prepared at lower temperatures when $(C_8H_{17})_3PO$ is added to a mixture of $Pd(acac)_2$ and $C_{16}H_{33}NH_2$.[11]

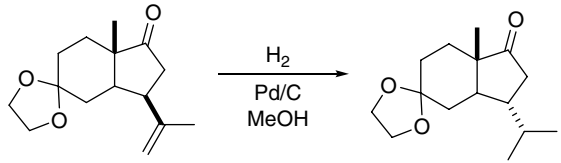
Oxidation. Nano-Pd particles confined in the core of ferritin cages are robust catalyst for aerobic oxidation of alcohols.[12]

[1] Liu, H., Li, Y., Luque, R., Jiang, H. *ASC* **353**, 3107 (2011)
[2] Kaneko, T., Tanaka, S., Asao, N., Yamamoto, Y., Chen, M., Zhang, W., Inoue, A. *ASC* **353**, 2927 (2011)
[3] Sharma, D., Kumar, S., Shil, A.K., Guha, N.R., Bandna, Das, P. *TL* **53**, 7044 (2012)
[4] Hong, M.C., Choi, M.C., Chang, Y.W., Lee, Y., Kim, J., Rhee, H. *ASC* **354**, 1257 (2012)
[5] Wang, F., Li, C., Sun, L.-D., Xu, C.-H., Wang, J., Yu, J.C., Yan, C.-H. *ACIE* **51**, 4872 (2012)
[6] Okada, S., Urata, T., Kamegawa, T., Mori, K., Yamashita, H. *CL* **40**, 609 (2011)

[7] Zong, Y., Hu, J., Sun, P., Jiang, X. *SL* 2393 (2012)
[8] Planellas, M., Pleixats, R., Shafir, A. *ASC* **354**, 651 (2012)
[9] Kumar, V.K.R., Krishnakumar, S., Gopidas, K.R. *EJOC* 3447 (2012)
[10] Wang, L., Yi, W., Cai, C. *CC* **47**, 806 (2011)
[11] Man, R.W.Y., Brown, A.R.C., Wolf, M.O. *ACIE* **51**, 11350 (2012)
[12] Kanbak-Aksu, S., Hasan, M.N., Hagan, W.R., Hollmann, F., Sordi, D., Sheldon, R.A., Arends, I.W.C.E. *CC* **48**, 5745 (2012)

Palladium/carbon

Hydrogenation. Production of a perhydroindanone with an inverted configuration at the carbon bearing an isopropenyl group that undergoes hydrogenation is observed. This abnormal result could be due to rapid shift of the double bond before taking up hydrogen.[1] This complication can be avoided by a change of the Pd/C catalyst to PtO_2.



In hexafluoroisopropanol the hydrogenation of indoles can give different products --- indolines, cyclohexanopyrroles, or perhydroindoles --- according to the substitution pattern of the substrate.[2]

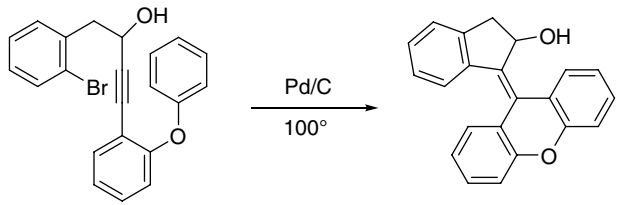
In the hydrogenation of the C=O unit of aryl methyl ketones the activity of Pd/C is said to be enhanced by water and CO_2.[3] Reduction of nitriles in a system of Pd/C and $HCOONH_4$, tertiary amines of the structure $(RCH_2)_3N$ are formed.[4] Hydrogenation of aryl azides (H_2, Pd/C) without solvent is reported.[5]

Hydrogenation of β-(*o*-nitroaryl)-α,β-unsaturated carbonyl compounds delivers quinolines. A Hantzsch ester provides hydrogen to reduce the nitro group.[6]

Quinoline is partially saturated (to 1,2,3,4-tetrahydroquinoline) on heating with Pd/C, Zn and aqueous ROH at 150°.[7] When water is excluded *N*-alkylation also occurs.

Substitution and coupling. Synthesis of water-soluble phosphine oxides from halobenzoic acids and diphenylphosphine oxide is accomplished in the presence of Pd/C with microwave iradiation.[8]

A Heck reaction with Baylis-Hillman adducts produces β-aryl ketones bearing an electron-withdrawing group at the α-position.[9] A relay Heck reaction forms two rings and involves participation of a triple bond.[10]



New coupling partners for biaryl synthesis are the triarylbismuths, the solvent-free reaction uses Pd/C and Bu_4NF3H_2O.[11]

2-Substituted benzoxazoles and benzimidazoles are forged from primary amines and *o*-aminophenols/*o*-phenylenediamine.[12] Dehydrogenation of the primary amines must take place prior to becoming active reaction partners. Another report specifies using $(RCH_2)_3N$ for the same reaction while an alkene acts as hydrogen acceptor.[13]

Since it is recognized that Pd/C exhibits activity typical of Pd(0) complexes, its subrogation in carbonylative coupling is not surprising, and only the reaction conditions need to be defined. Thus, in functionalization of 1-alkynes to form 2-alkynamides on reaction with CO and amines, Pd/C is assisted by Bu_4NI under oxygen.[14] Similarly the synthesis of phthalimides starts from 1,2-diiodoarenes or 1-bromo-2-iodoarenes.[15]

[1] Hog, D.T., Mayer, P., Trauner, D. *JOC* **77**, 5838 (2012)
[2] Clarisse, D., Fenet, B., Fache, F. *OBC* **10**, 6587 (2012)
[3] Hiyoshi, N., Sato, O., Yamaguchi, A., Shirai, M. *CC* **47**, 11546 (2011)
[4] Shares, J., Yehl, J., Kowalsick, A., Byers, P., Haaf, M.P. *TL* **53**, 4426 (2012)
[5] Monguchi, Y., Fujita, Y., Hashimoto, S., Ina, M., Takahashi, T., Ito, R., Nozaki, K., Maegawa, T., Sajiki, H. *T* **67**, 8628 (2011)
[6] Xing, R.-G., Ni, Y.-N., Liu, Q., Han, Y.-F., Wei, X., Li, J., Zhou, B. *S* 2066 (2011)
[7] Abarca, B., Adam, R., Ballesteros, R. *OBC* **10**, 1826 (2012)
[8] Rummelt, S.M., Ranocchiari, M., van Bokhoven, J.A. *OL* **14**, 2188 (2012)
[9] Kim, H.-S., Lee, S.-J., Choi, B., Yoon, C.M. *S* 3161 (2012)
[10] Tietze, L.F., Hungerland, T., Depken, C., Maass, C., Stalke, D. *SL* 2516 (2012)
[11] Monguchi, Y., Hattori, T., Miyamoto, Y., Yanase, T., Sawama, Y., Sajiki, H. *ASC* **354**, 2561 (2012)
[12] Pizzetti, M., De Luca, E., Petricci, E., Porcheddu, A., Taddei, M. *ASC* **354**, 2453 (2012)
[13] De Luca, L., Porcheddu, A. *EJOC* 5791 (2011)
[14] Gadge, S.T., Khedkar, M.V., Lanke, S.R., Bhanage, B.M. *ASC* **354**, 2049 (2012)
[15] Khedhar, M.V., Khan, S.R., Sawant, D.N., Bagal, D.B., Bhanage, B.B. *ASC* **353**, 3415 (2011)

Palladium/inorganic supports

Hydrogenation. A catalyst for alkene hydrogenation is Pd on mixed oxides of Mg and La.[1] Molecular sieves (3A and 5A) are also suitable supports for Pd in the formation of hydrogenation catalysts, such can be used to reduce alkenes, alkynes and azides, but not nitro compounds.[2] With 0.3% Pd on boron nitride and a bis(aminoethyl)amine ligand, semihydrogenation of alkynes is achieved in MeOH.[3]

For reduction of $ArNO_2$ to $ArNH_2$ a solid-supported Pd is effective to complement reducing agents such as Et_3SiH, $NaBH_4$, or N_2H_4.[4]

[1] Kantam, M.L., Kishore, R., Yadav, J., Sudhakar, M., Venugopal, A. *ASC* **354**, 663 (2012)
[2] Takahashi, T., Yoshimura, M., Suzuka, H., Maegawa, T., Sawama, Y., Monguchi, Y., Sajiki, H. *T* **68**, 8293 (2012)
[3] Yabe, Y., Yamada, T., Nagata, S., Sawama, Y., Monguchi, Y., Sajiki, H. *ASC* **354**, 1264 (2012)
[4] Shil, A.K., Sharma, D., Guha, N.R., Das, P. *TL* **53**, 4858 (2012)

Palladium(II) acetate

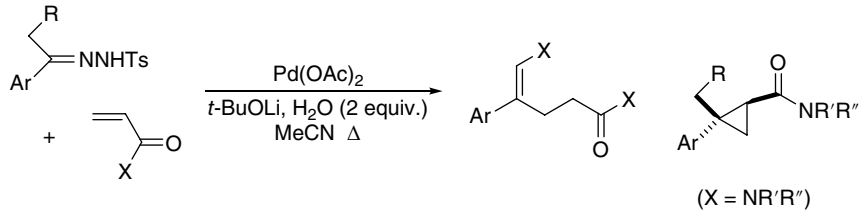
Substitution. *N*-Alkylation of amines by primary alcohols is impelled by $Pd(OAc)_2$.[1] It is also a catalyst for *o*-bromination of $ArOCONMe_2$ with NBS.[2]

C-H activation. *o*-Toluic acid is oxidized to form phthalide by $Pd(OAc)_2$ in the presence of an *N*-acetyl-α-amino acid.[3]Thermal decarbonylation of aldehydes is reported using $Pd(OAc)_2$ and molecular sieves as catalyst.[4]

Addition. Formation of aryl ketones from $ArSO_2H$ and RCN in isobutanol involves expulsion of SO_2 and addition of the aryl group to the nitrile. Besides the Pd(II) catalyst which is protected by 2,2′-bipyridyl the reaction medium also contains H_2SO_4 (2 equiv.) and water (1 equiv.).[5] Similar conditions are applicable to hydroarylation of cycloalkenones by $ArSO_2H$.[6] Hindered 2-cyclohexenones (e.g., 3,4,4-trisubstituted) become viable Michael acceptors for the aryl group of $(ArBO)_3$ when proper additives (TfOH, $NaNO_3$, air) are present.[7]

(*Z*)-Enamides can be prepared by a Pd-catalyzed reaction between $RCONH_2$ and 1-alkyn-3-ones.[8] Addition of RCOOH to ynamides gives ketene-*O,N*-diesters.[9]

Under basic conditions and in the presence of $Pd(OAc)_2$, tosylhydrazones decompose to carbenoids and they can be captured by electron-deficient alkenes. Remarkably, trapping by acrylamides and enones leads to different types of products (cyclopropanation and interrupted Shapiro reaction).[10]



Substitution and coupling. Reaction of MesONHCOOEt with ArCOOLi gives *o*-ethoxycarbonylaminobenzoic acids.[11] Coupling of (ArIPh)OTf with $K_4[Fe(CN)_6]$ exhibits chemoselectivity that favors formation of ArCN.[12]

Ullmann coupling can use $Pd(OAc)_2$ as catalyst. With additives of norbornene and CsOPiv the coupling between ArI and *o*-bromobenzyl alcohol affords 2-formylbiaryls, as a dehydrogenation also occurs.[13]

One set of conditions for Heck reaction catalyzed by $Pd(OAc)_2$ needs Bu_4NF and K_2CO_3 but no ligand.[14] Conversion of phenols to $ArOSi(t\text{-}Bu)_2OH$ ensures alkenylation by acrylic esters at an *o*-position.[15]

3-Iodo-1,1,1-trifluoropropane can be used in coupling with ArI, it only needs a base to perform dehydroiodination in situ, prior to the Heck raction.[16] Arylation of 1,3-bis(trifluoromethyl) benzene occurs at C-5, as electron-deficient arenes undergo *meta*-selective coupling preferably.[17] The arylation site of 2-alkenylated furan and thiophene varies according to certain additives. Previously, attack at the α-position (proximal to the heteroatom) had been reported (KF, R_3N as additive), a switch to C-5 by adding KOAc is now found.[18]

Arenediazonium salts have become popular reactants for Heck reaction. Addition of carbon to $Pd(OAc)_2$ constitutes a new catalyst system that garners advantages of both

heterogeneous and homogeneous conditions.[19] An additive for such Heck reaction is 1-benzyl-3-(2-hydroxy-2-phenyl)ethylimidazonium chloride.[20] The intramolecular coupling of either a diazonium salt derived from 2-benzyloxyaniline or 2-phenoxymethylaniline leads to 6*H*-benzo[*c*]chromene.[21] Double arylation at the β-position of methyl acrylate is readily performed with ArN_2BF_4.[22] The suitability of ArN_2BF_4 for Hiyama coupling is now assured experimentally.[23]

Coupling of ArN_2BF_4 with crotonaldehyde in methanol furnishes $ArCH{=}CHCH_2CH(OMe)_2$.[24]

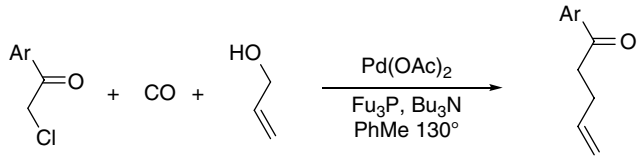
New findings related to the Heck reaction are the usefulness of arylhydrazines,[25] and the synthesis of 2,4-alkadienoic esters from allylic and homoallylic alcohols upon their reaction with acrylic esters.[26]

3-Arylation of pyridine is catalyzed by $Pd(OAc)_2$ complexed to 1,10-phenanthroline.[27] The flavone synthesis[28] from *o*-hydroxyacetophenone, CO and ArBr can proceed via carbonylation and condensation , although a Heck reaction of a chromone cannot be ruled out.

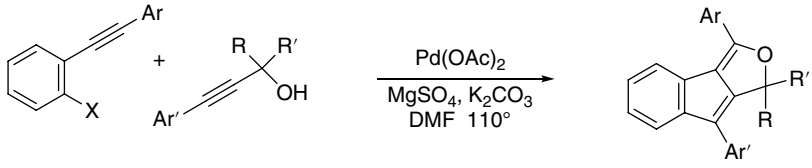
Suzuki coupling now encompasses the pyridine complexes of triarylboranes.[29] Catalyst modification by mixing $Pd(OAc)_2$ with $[bmim]PF_6$ on silica or alumina and then polystyrene is a new assay.[30] The access to $BocNHCH_2BF_3K$ from $ClCH_2B(pin)$ offers a route towards $ArCH_2NHBoc$ by a Suzuki coupling with ArX.[31]

The Sonogashira coupling of 8-aroylaminoquinolines is directed at an *o*-position of the aroyl group, evidently by the quinoline moiety.[32]

An oblique substitution of chloromethyl ketones to extend the carbon chain by an allyl group involves carbonylation, esterification and decarboxylative allylation.[33]

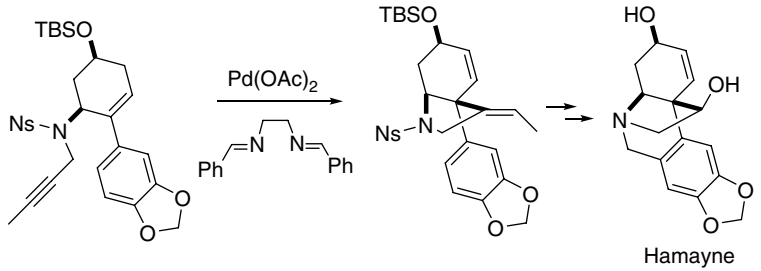


Addition to triple bond. Diarylethynes in which one of the *o*-position is halogenated are capable of initiating a tandem addition with an external alkyne molecule. Benzofulvenes are produced.[34]

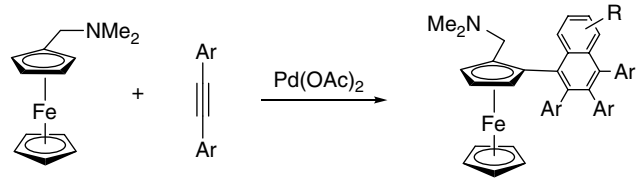


A synthesis of hamayne features cycloisomerization which is essentially an intramolecular addition on a triple bond.[35] Co-addition of allyl and acetoxy groups (by splitting allyl

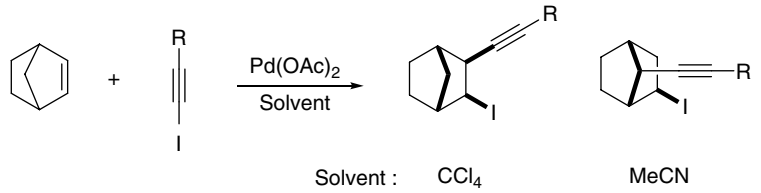
acetate) to alkynyl halides is regioselective in that (*Z*)-4-halo-5-acetoxy-1,4-alkadienes are obtained.[36] With benzyl chlorides and electron-deficient alkenes as co-addends to furnish benzyl and alkenyl groups to alkynes the products are conjugated dienes.[37]



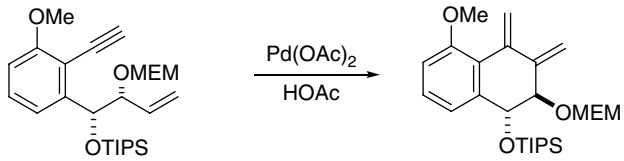
N,N-Dimethylaminomethylferrocene engages in a [1+2] addition with diarylethynes, which essentially affords naphthalenes bearing three aryl group and the ferrocenyl residue.[38]



Alkynylarenes are acceptors of $ArB(OH)_2$ and benzylzinc reagents. The reaction affords alkenes bearing two aryl groups at C-1 and one at C-4.[39] The Pd-catalyzed reaction between alkynyl halides and norbornene has been studied.[40,41] A polar solvent favors formation of rearrangement products.



Cycloisomerization of arenes that are *o*-disubstituted with an ethynyl group and a functionalized 3-butenyl chain by $Pd(OAc)_2$ is of obvious synthetic potential as it generates addends for Diels-Alder annulations.[42]



o,o′-Disubstituted diarylethynes in which one of the substituents being a dimethylamino group and the other a secondary amide cyclize on warming with $Pd(OAc)_2$, Bu_4NI and HOAc in DMSO.[43] Formation of indolo[3,2-*c*]isoquinolinones involves demethylation, obviously by iodide ion (regenerated continuously from MeI and HOAc).



To facilitate the participation in the 1,2-diamination of the triple bond, the dimethylamino group is demethylated by the iodide ion (regenerated from MeI when HOAc is present). The bimolecular reaction of 1-(*o*-dimethylamino)aryl-2-arylethynes with arylethynes under the same conditions produces 2-aryl-3-arylethynyl-*N*-methylindoles.[44]

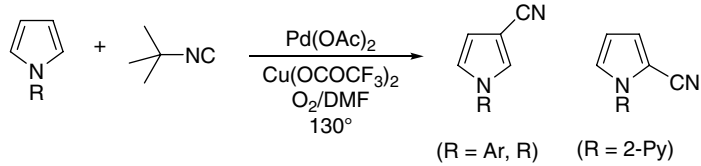
[1] Martinez-Asencio, A., Yus, M., Ramon, D.J. *S* 3730 (2011)
[2] John, A., Nicholas, K.M. *JOC* **77**, 5600 (2012)
[3] Novak, P., Correa, A., Gallardo-Donaire, J., Martin, R. *ACIE* **50**, 12236 (2011)
[4] Modak, A., Deb, A., Patra, T., Rana, S., Maity, S., Maiti, D. *CC* **48**, 4253 (2012)
[5] Miao, T., Wang, G.-W. *CC* **47**, 9501 (2011)
[6] Wang, H., Li, Y., Zhang, R., Jin, K., Zhao, D., Duan, C. *JOC* **77**, 4849 (2012)
[7] Jordan-Hore, J.A., Sanderson, J.N., Lee, A.-L. *OL* **14**, 2508 (2012)
[8] Panda, N., Mothkuri, R. *JOC* **77**, 9407 (2012)
[9] Smith, D.L., Goundry, W.R.F., Lam, H.W. *CC* **48**, 1505 (2012)
[10] Jiang, H., Fu, W., Chen, H. *CEJ* **18**, 11884 (2012)
[11] Ng, K.-H., Ng, F.-N., Yu, W.-Y. *CC* **48**, 11680 (2012)
[12] Liu, L., Li, J., Xu, J., Sun, J. *TL* **53**, 6954 (2012)
[13] Motti, E., Della Ca′, N., Xu, D., Piersimoni, A., Bedogni, E., Zhou, Z.-M., Catellani, M. *OL* **14**, 5792 (2012)
[14] Sun, P., Qu, X., Li, T., Zhu, Y., Yang, H., Xing, Z., Mao, J. *SL* 150 (2012)
[15] Huang, C., Chattopadhyay, B., Gevorgyan, V. *JACS* **133**, 12406 (2011)
[16] Prakash, G.K.S., Krishnan, H.S., Jog, P.V., Iyer, A.P., Olah, G.A. *OL* **14**, 1146 (2012)
[17] Wang, Y.-N., Guo, X.-Q., Zhu, X.-H., Zhong, R., Cai, L.-H., Hou, X.-F. *CC* **48**, 10437 (2012)
[18] Chen, L., Roger, J., Bruneau, C., Dixneuf, P.H., Doucet, H. *ASC* **353**, 2749 (2011)
[19] Rossy, C., Fouquet, E., Felpin, F.-X. *S* 37 (2012)
[20] Penafiel, I., Pastor, I.M., Yus, M. *EJOC* 3151 (2012)
[21] Zhou, J., Huang, L.-Z., Li, Y.-Q., Du, Z.-T. *TL* **53**, 7036 (2012)
[22] Taylor, J.G., Robeiro, R.da S., Correira, C.R.D, . *TL* **52**, 3861 (2011)
[23] Cheng, K., Wang, C., Ding, Y., Song, Q., Qi, C., Zhang, X.-M. *JOC* **76**, 9261 (2011)
[24] Zaragoza, F., Heinze, V. *TL* **52**, 4678 (2011)
[25] Zhu, M.-K., Zhao, J.-F., Loh, T.-P. *OL* **13**, 6308 (2011)
[26] Wen, Z.-K., Xu, Y.-H., Loh, T.-P. *CEJ* **18**, 13284 (2012)
[27] Ye, M., Gao, G.-L., Edmunds, A.J.F., Worthington, P.A., Morris, J.A., Yu, J.-Q. *JACS* **133**, 19090 (2011)
[28] Wu, X.-F., Neumann, H., Beller, M. *CEJ* **18**, 12595 (2012)
[29] Yang, M., Gu, Y., Wang, Y., Zhao, X., Yan, G. *ChJC* **30**, 2581 (2012)

[30] Hagiwara, H., Sato, K., Hoshi, T., Suzuki, T. *SL* 2545 (2011)
[31] Molander, G.A., Shin, I. *OL* **13**, 3956 (2011)
[32] Ano, Y., Tobisu, M., Chatani, N. *OL* **14**, 354 (2012)
[33] Giboulot, S., Liron, F., Prestat, G., Wahl, B., Sauthier, M., Castanet, Y., Mortreux, A., Poli, G. *CC* **48**, 5889 (2012)
[34] Jin, J., Luo, Y., Zhou, C., Chen, X., Wen, Q., Lu, P., Wang, Y. *JOC* **77**, 11368 (2012)
[35] Petit, L., Banwell, M.G., Willis, A.C. *OL* **13**, 5800 (2011)
[36] Chen, X., Chen, D., Lu, Z., Kong, L., Zhu, G. *JOC* **76**, 6338 (2011)
[37] Wen, Y., Huang, L., Jiang, H. *JOC* **77**, 5418 (2012)
[38] Zhang, H., Cui, X., Yao, X., Wang, H., Zhang, J., Wu, Y. *OL* **14**, 3012 (2012)
[39] Miesch, A., Hilt, G. *CEJ* **18**, 9798 (2012)
[40] Liu, H., Chen, C., Wang, L., Tong, X. *OL* **13**, 5072 (2011)
[41] Li, Y., Liu, X., Jiang, H., Liu, B., Chen, Z., Zhou, P. *ACIE* **50**, 6341 (2011)
[42] Zilke, L., Hall, D.G. *EJOC* 4153 (2012)
[43] Yao, B., Wang, Q., Zhu, J. *ACIE* **51**, 5170 (2012)
[44] Yao, B., Wang, Q., Zhu, J. *ACIE* **51**, 12311 (2012)

Palladium(II) acetate – copper salts

Oxidation. 1-Alkynylarenes are readily oxygenated to give α-diketones when heated with $Pd(OAc)_2$ and $CuBr_2$ in DMSO in air.[1]

Cyanation. Among improvements in cyanation of arenes, a combination of $Pd(OAc)_2$ and $Cu(OCOCF_3)_2$ forms a catalyst system to smooth the transfer of the CN group from a tertiary alkyl isonitrile.[2,3] For nuclear cyanation of *N*-substituted pyrroles the substitution usually takes place at the β-carbon. However, a 2-pyridyl or 3-pyrimidyl substituent on the nitrogen atom exerts a directing effect to place the cyano group at the α-carbon. Benzofuran and *N*-methylindole prefer cyanation at C-3 (unless the position is blocked) using $HCONMe_2$ as the CN source.[4] A small amount of $FeCl_2$ and equivalent $CuBr_2$ accompany the Pd salt.



Substitution. Indoles are aminated [reaction with TsN(Cl)R] at C-2 or also chlorinated at C-3.[5] Formation of the different reaction products is due to variation of the Cu salt and other additives: $Cu(acac)_2$ - bipy and Na_2CO_3 in the former case, whereas CuCl, LiCl and Ag_2CO_3 in the latter.

Coupling. Under oxidative conditions the homocoupling of arylacetamides leads to biaryls bearing sidechains at C-2 and C-2′.[6] Conversion of α-acetaminostyrenes into the acetaminostilbenes is accomplished by coupling with arenes in HOAc. Introduction of another aryl group is possible if CF_3COOH is added after the first reaction.[7] For Heck reaction of anilides, additives include $Cu(OAc)_2$, TsOH, HOAc and *t*-butyl perbenzoate.[8]

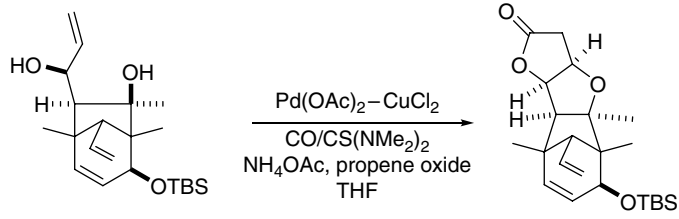
β-Aryl ketones are obtained from Suzuki coupling between $ArB(OH)_2$ and allylic alcohols under oxygen, provided that CuX is also present.[9] Both oxidative Suzuki and Hiyama coupling reactions[10,11] are applicable to the arylation of enaminones (e.g., 2,3-dihydro-4-pyridones), the only major difference is that CuF_2 is used in the Hiyama coupling.

By oxidative coupling to introduce a carbon substituent to C-2 of azoles, sulfonyl compounds such as RSO_2Cl and $ArSO_2NHNH_2$ prove adequate in the role of furnishing the organic component.[12,13] (Note in the reaction involving arenesulfonylhydrazides a phosphine ligand is present.)

A limitation for Heck reaction on enamides has been that substrates with only unsubstituted vinyl group are viable. By changing to the oxidative conditions [$Pd(OAc)_2$, $Cu(OAc)_2$, phosphine, O_2] the problem is solved.[14]

Coupling while incorporating CO can change arylamines into *N,N′*-diaryl ureas, or in the presence of an alcohol, *N*-arylcarbamates.[15] The method is applicable to the ring closure of *N*-arylamidines to quinazolinones.[16]

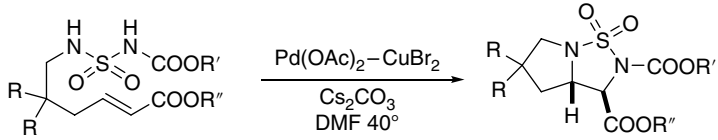
A critical step in a synthesis of pallambin-C/D is the construction of two five-membered oxacycles that are fused to one another, from an allylic alcohol and a tertiary hydroxyl group three bonds away.[17]



N-Methylbenzo[*a*]carbazoles are obtained in an oxidative coupling between *o*-dimethylaminodiarylethynes and diarylethynes.[18]

Glycals and activated alkenes are coupled by $Pd(OAc)_2$ - $Cu(OTf)_2$, to form a push-pull conjugated diene system.[19]

Addition. Both nitrogen atoms of *gem*-diaminosulfones are employed in the intramolecular addition to a double bond.[20]



[1] Gao, A., Yang, F., Li, J., Wu, Y. *T* **68**, 4950 (2012)
[2] Xu, S., Huang, X., Hong, X., Xu, B. *OL* **14**, 4614 (2012)
[3] Peng, J., Zhao, J., Hu, Z., Liang, D., Huang, J., Zhu, Q. *OL* **14**, 4966 (2012)
[4] Ding, S., Jiao, N. *JACS* **133**, 12374 (2011)
[5] Liu, X.-Y., Gao, P., Shen, Y.-W., Liang, Y.-M. *OL* **13**, 4196 (2011)
[6] Pintori, D.G., Greaney, M.F. *OL* **13**, 5713 (2011)
[7] Pankajakshan, S., Xu, Y.-H., Cheng, J.K., Low, M.T., Loh, T.-P. *ACIE* **51**, 5701 (2012)
[8] Liu, X., Hii, K.K. *JOC* **76**, 8022 (2011)
[9] Chen, M., Wang, J., Chai, Z., You, C., Lei, A. *ASC* **354**, 341 (2012)
[10] Kim, Y.W., Niphakis, M.J., Georg, G.I. *JOC* **77**, 9496 (2012)
[11] Bi, L., Georg, G.I. *OL* **13**, 5413 (2011)
[12] Zhang, M., Zhang, S., Liu, M., Cheng, J. *CC* **47**, 11522 (2011)
[13] Liu, B., Li, J., Song, F., You, J. *CEJ* **18**, 10830 (2012)
[14] Liu, Y., Li, D., Park, C.-M. *ACIE* **50**, 7333 (2011)
[15] Guan, Z.-H., Lei, H., Chen, M., Ren, Z.-H., Bai, Y., Wang, Y.-Y. *ASC* **354**, 489 (2012)
[16] Ma, B., Wang, Y., Peng, J., Zhu, Q. *JOC* **76**, 6362 (2011)
[17] Xu, X.-S., Li, Z.-W., Zhang, Y.-J., Peng, X.-S., Wong, H.N.C. *CC* **48**, 8517 (2012)
[18] Xia, X.-F., Wang, N., Zhang, L.-L., Song, X.-R., Liu, X.-Y., Liang, Y.-M. *JOC* **77**, 9163 (2012)
[19] Bai, Y., Zeng, J., Cai, S., Liu, X.-W. *OL* **13**, 4394 (2011)
[20] Chavez, P., Kirsch, J., Streuff, J., Muñiz, K. *JOC* **77**, 1922 (2012)

Palladium(II) acetate – copper/silver salts

Coupling. Anilides are *o*-activated toward coupling with alkynes by a mixture of $Pd(OAc)_2$ [10 mol%], $Cu(OTf)_2$ [1 equiv.], and Ag_2O [1.5 equiv.], indoles derivatives are obtained.[1]

[1] Zhou, F., Han, X., Lu, X. *TL* **52**, 4681 (2011)

Palladium(II) acetate – oxidants

Oxidation. The derivatization of cyclohexanones into *N*-alkylanilines involves admixture with RNH_2 in the presence of $Pd(OAc)_2$, Bu_4NBr under oxygen.[1] More unusual is the addition-oxidation sequence that combines styrenes and nitroalkanes (RCH_2NO_2) to give α-diketones of the type $ArCOCOCH_2R$. It is a free radical process as AIBN is required.[2]

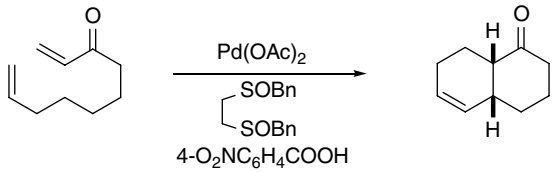
CH activation. For some years it has been known that a conjugated double bond can be introduced to carbonyl compounds via dehydrogenation of their enol ethers by Pd(II) species. The metal ion is kept active by adding an oxidant. It is found that 1-alkoxy-1-alkenes may be converted into enals by catalytic $Pd(OAc)_2$, along with benzoquinone and some water as additive, but if Ph_3P (additive) is used the products are 2-alkoxy-2,5-dihydrofurans.[3]

In rendering alkenes electrophilic (instead of employing allylic esters) for alkylation reactions a complex of $Pd(OAc)_2$ with a 1,2-disulfinylated ethane and benzoquinone, a further requirement of DMSO in the functionalization step is recognized.[4] (*Z*)-1-Triethylsilyl-1-alkenes are acetoxylated at C-3 on treatment with $Pd(OAc)_2$ in HOAc.

While employing $PhI(OAc)_2$ as oxidant the products retain the (*Z*)-configuration; the benzoquinone additive engenders isomerization to the (*E*)-isomer.[5] Cyclohexenes carrying a substituent at C-4 undergo trifluoroacetoxylation to furnish *trans*-1,4-disubstituted 2-cyclohexenes.[6]

Arylation of 2-oxocyclopentane-1-carboxylic esters by very reactive arenes (phenol, 1,3,5-trimethoxybenzene, etc.) at the β-carbon to both functionalities can be considered to proceed via dehydrogenation of the enols and electrophilic aromatic substitution.[7]

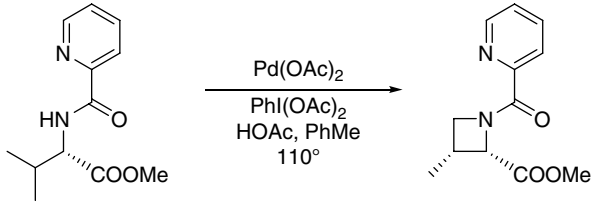
Simple 1-alkenes undergo dehydrogenation to afford conjugated dienes with $Pd(OAc)_2$ and $BnS(O)CH_2CH_2S(O)Bn$ and 4-nitrobenzoic acid. Under such conditions 1,9-decadien-3-one is transformed into an octalone as an intramolecular Diels-Alder reaction rapidly following the dehydrogenation.[8]



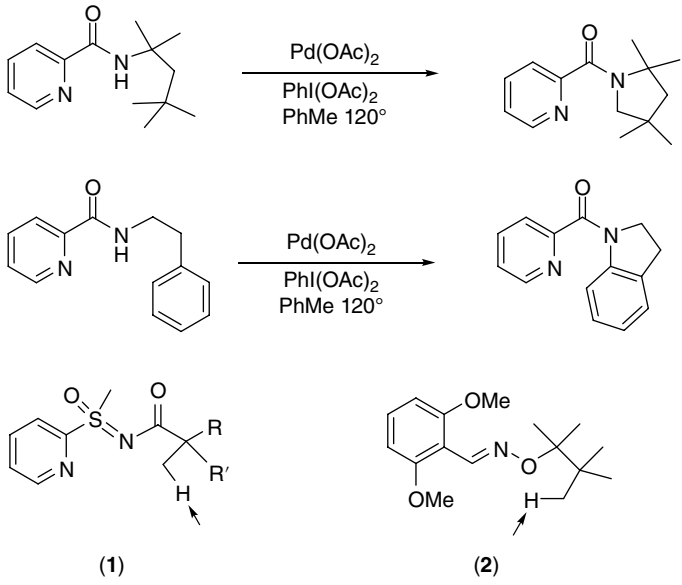
Nondirected acetoxylation of arenes is performed with $Pd(OAc)_2$ and $ArI(OAc)_2$. Addition of pyridine in equimolar ratio to $Pd(OAc)_2$ (2mol% each) enhances the catalytic activity and regioselectivity.[9]

Directed functionalization. While there have been numerous research reports on regioselective functionalization of aromatic rings directed by polar substituents, it is generally assumed that to achieve similar results at saturated CH bond is far more difficult. Perhaps time is ripe for much more efforts to unravel the intricacy of such processes.

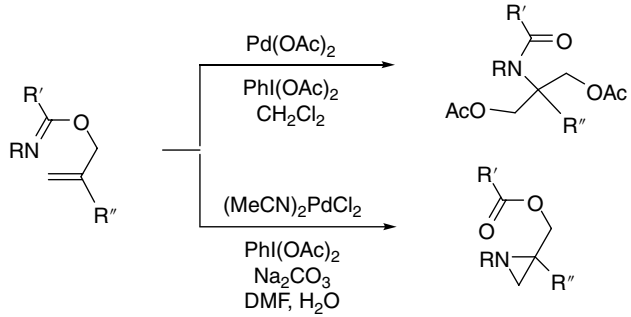
Azetidine formation from *N*-(picolinoyl)valine methyl ester is achieved.[10] On having some MeOH in the solvent system the ring closure is stopped and instead the two terminal methyl groups are methoxylated.[11] When structural limitation leaves the choice for generating either *N*-acylaziridines or pyrrolidines, the five-membered ring wins out.[12]



An imino nitrogen atom can direct activation of a hydrogen four bonds apart. Oxycarbonylation at the said position (see **1** and **2**) is observed.[13,14]



Acetoxylation following a [3,3]sigmatropic rearrangement of *O*-allylimino ethers[15] is also significant. Noteworthy is the change of reaction pathway on switching the Pd catalyst from $Pd(OAc)_2$ to $(MeCN)_2PdCl_2$, with the latter a nitrenoid transfer pathway dominates.



That certain aromatic substituents activate an *o*-position is well known. For reactions catalyzed by $Pd(OAc)_2$ and facilitated by an oxidant, new results are those concerning oxygenation (eventually to phenols via trifluoroacetoxylation) of a great variety of carbonyl compounds, sulfonamides,[16] and alkoxylation of anilides,[17] aryl cyanides[18] and *O*-methylbenzohydroxamic acids[19] by alcohols. A more convolute method for *o*-acetoxylation of aroic acids involves transition through *N*-aroylsulfoximines.[20]

Arylsilanes change their silyl substituent on undergoing electrophilic *ipso*-substitution, and accordingly phenyl(2-pyrimidyl)diisopropylsilane is a valuable precursor of certain

o-disubstituted arenes given the directing effect of a pyrimidine nitrogen atom. This notion has been confirmed with the Pd-catalyzed *o*-pivaloxylation [using $PhI(OCOCMe_3)_2$].[21]

Both anilides and *N*-arylbenzamides are susceptible to Pd-catalyzed borylation by $B_2(pin)_2$ under oxidative conditions.[22,23] The most frequently used oxidant for all the above reactions is an alkali metal persulfate, and it is applicable to arylation and Heck reaction of arylguanidines also,[24] despite employment of benzoquinone in alkenylation of *N*-arylureas,[25] and *N*-fluorocollidinium triflate, of *N*-aryl-2-pyridylsulfonamides.[26]

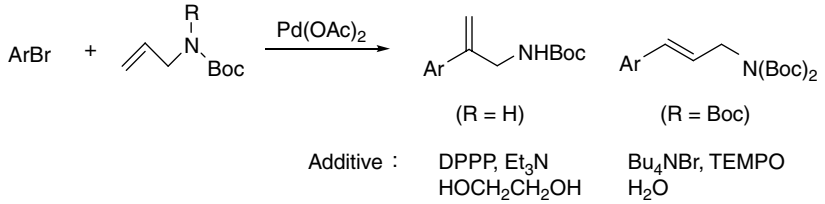
o-Alkylation of benzylamines is smoothed by picolinoylation, and molecular oxygen is for recycling the active Pd species.[27] Similar reaction conditions are prescribed for the Heck reaction in the reverse sense (i.e., arene + alkenyl iodides).[28]

o-Acylation of anilides [$Pd(OAc)_2$, *t*-BuOOH] can use RCHO,[29] $ArCH_2OH$,[30] and even $ArCH_3$.[31] The viability of benzyl alcohols and methylarenes as substrates is due to their oxidizability under the reaction conditions. Similarly, an $ArCH_3$ furnishes the aroyl group to be attached to an *o*-position of 2-pyridylarenes.[32]

2-Pyridylarenes and benz[*h*]quinoline are acylated by α-diketones while the latter compounds undergo cleavage. From an unsymmetrical α-diketone two products are obtained.[33] A nuclear C-H bond can be activated in functionalized methylcyclopropanes.[34]

Coupling. In addition to the few mentioned earlier, $ArI(OCOR)_2$ serve as both substrates and oxidants in Heck reaction.[35] Regarding the effectiveness of alkenylation at C-3 of indole to be carried out in DMSO under oxygen,[36] there is hardly any surprise.

The Heck reaction with *N*-Boc allylamine introduces an aryl group to the internal sp^2-carbon atom; with the *N,N*-diBoc amine the coupling in the presence of TEMPO leads to cinnamylamine derivatives.[37]



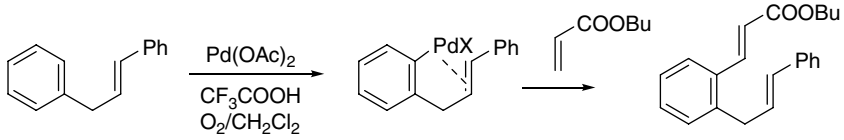
As lithioalkenes can be generated from tosylhydrazones with *t*-BuOLi in an anhydrous medium, an expedient route to the regioselective synthesis of γ,δ-unsaturated ketones on Heck reaction with allylic alcohols, via transmetallation [and catalytic amounts of $Pd(OAc)_2$ plus benzoquinone], opens up.[38]

Arenesulfonhydrazides decompose to generate arylpalladium reagents suitable for the Heck reaction, and it needs an oxidant to recycle the metal species in an active form.[39]

The first arylation of methyl acrylate by $ArB(OH)_2$ in the presence of nitroxide and KF is impelled by $Pd(acac)_2$, for further arylation of (*E*)-cinnamic esters, $Pd(OAc)_2$ seems to be the better catalyst. It can continue to introduce a third aryl group at the α-carbon.[40] In general, Heck reaction involving conjugated esters [with $Pd(OAc)_2$ and *t*-BuOOCOPh] is promoted by pyridine.[41]

Coumarin and chromone are each arylated at the β-position of the carbonyl group.[42,43]

Regioselective Heck reaction of 1,3-diphenylpropene occurs at the nonconjugated benzene ring.[44] It is suggested that the styrenic double bond provides coordinative stabilization to the arylpalladium species.

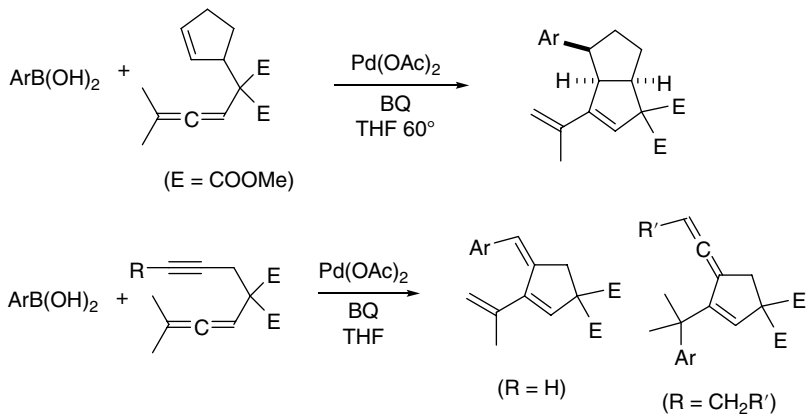


Cross-coupling of benzamides with monosubstituted benzenes furnishes 4′-substituted biphenyl-2-carboxamides,[45] the regioselectivity is most agreeable. Coupling reactions addressing substitution of oxazole, thiazole and their benzologs are a well-researched topic in recent years, therefore appearance of reports[46,47] on the oxidant assistance to minimize Pd(II) catalyst is anticipated. Arylgold(I) complexes can untake Sonogashira coupling under oxygen.[48]

Carbonylative coupling is convenient for synthesizing β,γ-unsaturated esters[49] and indole-3-carboxylic esters,[50] iodine being the oxidant in the latter process. In assembling arenesulfonhydrazides, the DABCO complex of SO_2 is the linchpin for connecting components from $ArB(OH)_2$ and hydrazines.[51]

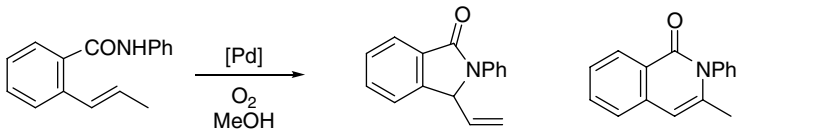
Annulative coupling. Lactone formation is effected from unsaturated carboxylic acids by intramolecular trapping of an oxidized allylic site.[52] 3-Carboxymethoxy-1-alkenes furnish 6-vinyl-1,4-dioxan-2-ones.[53]

A well-placed double bond would participate in cyclization induced by a coupling at some distance in the same molecule. Such a process can be induced under oxidative Pd-catalyzed conditions.[54,55]



β-Keto esters have a high tendency to couple with a double bond in a sidechain, the oxidative version is applicable to a synthesis of α-skytanthine.[56] A tandem pallada-amination and Heck reaction operated on *N*-acryloyl-2-anilines gives an α-methylenated benzoindolizidinone.[57]

From *N*-phenyl-2-(1-propenyl)benzamide the oxidative cyclization can proceed in two different ways. Either a 3-vinylisoindolin-1-one or an isoquinolin-1-one is obtainable.[58]



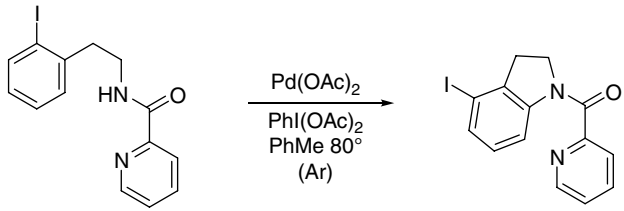
[Pd] = $Pd(OAc)_2$ phen. $(MeCN)_2PdCl_2$, $CuCl_2$ Et_3N

3-Alkylidene-2-methoxyisoindolin-1-ones are prepared by oxidative coupling between *O*-methylbenzohydroxamate and 1-alkenes.[59,60] Combination of *N*-arylamidines and isonitriles under oxygen affords 1-aminoquinazolines.[61]

Two CC bonds are formed when *N*-acryloylanilines and Me_3SiCF_3 are combined, and 3-(2,2,2-trifluoroethyl)oxindoles result.[62] This process needs $Pd(OAc)_2$ and $Yb(OTf)_3$ in catalytic amounts and sufficient quantities of $PhI(OAc)_2$ and CsF.

N-Arylimines act as precursors of indoles based on their cyclizability under the influence of $Pd(OAc)_2$ under oxygen, which is added in catalytic quantities.[63] This method has a broad scope and does not require an activator in the aliphatic moiety.

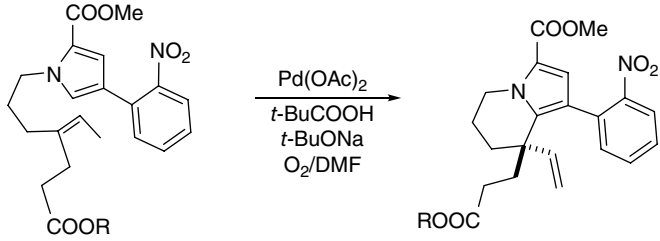
It is remarkable that there is preferential dehydrogenative palladation of the *N*-picolinoyl-*o*-iodophenethylamine (rather than formation of arylpalladium iodide) when it is treated with $Pd(OAc)_2$ and $PhI(OAc)_2$.[64] This observation manifests the advantage of oxidative conditions for coupling with substrates containing "sensitive" functionalities.



Dehydrogenative intramolecular coupling is quite facile, given the presence of an appropriate oxidant. Examples are *N*-tosylcarbazole formation from 2-tosylaminobiaryls (oxidant: Oxone)[65] and the reaction of 3-benzoylindole to form indenoindolone.[66] Such a step

also concludes the oxidative coupling between benzaldoxime *O*-methyl ether and an arene, hydrolysis of the product engenders a fluorenone.[67]

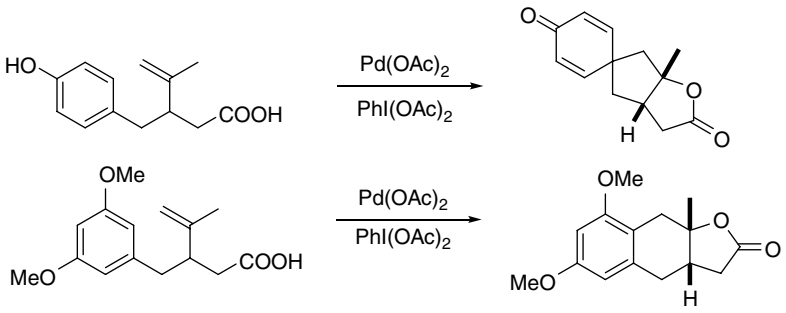
In a synthetic approach to the alkaloid rhazinilam the establishment of an indolizidine intermediate involves ring closure onto a pyrrole nucleus.[68]



Consecutive inter/intramolecular coupling steps serve to transform mixtures of arenes and benzohydroxamic acid *O*-methyl ether into phenanthridinones.[69] From arenes and arenesulfonic acids it leads to biaryl-2,2′-sultones.[70]

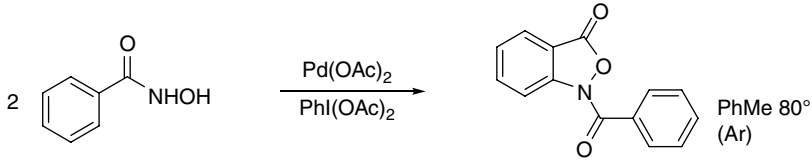
Incorporation of an electron-deficient alkene into 2-tosylaminobiaryls gives rise to 6-substituted 5,6-dihydrophenanthridines, as a result of directed alkenylation and hydroamination.[71]

Bicyclization involving an electron-rich aryl group with a sidechain containing properly disposed double bond and carboxyl residue[72] seems to be inevitable. Analogous reaction profile is established with an ordinary aromatic ring (phenyl, pyridyl) and the carboxy group can be replaced with an alcohol.[73]



1-Arylcyclopropyl silyl ethers undergo ring opening then recyclization to afford indanones, in a process initiated by desilylation with Bu_4NF.[74] Union of *o*-phenylenediamine and isonitriles delivers 2-aminobenzimidazoles.[75]

Benzohydroxamic acids are susceptible to oxidation and the ensuing acylnitroso compounds can serve as electrophile for attack on another hydroxamic acid molecule. Cyclization to the 1-aroylbenzo-2,1-oxazol-3-ones concludes the process.[76]



Benzylsilanols form a new five-membered heterocycle under oxidative coupling conditions,[77] the products can be used in a Hiyama coupling to introduce a carbon chain at the benzylic position.

Carbonylative coupling is the simple way to convert diaryl ethers into xanthones.[78] Also five-membered cyclic carbonates are readily made from 1,2-diols on incorporating CO (oxidant: NCS).[79]

Ring closure of 5-tosylamino-1-alkenes in the reaction induced by $Pd(OAc)_2$ in the presence of H_2O_2, $CaCl_2$, and HOAc leads to 3-chloro-*N*-tosylpiperidines.[80] Hydrogen peroxide has the dual duty of oxidizing the spent Pd as well as generating a positive chlorine species from $CaCl_2$.

[1] Hajra, A., Wei, Y., Yoshikai, N. *OL* **14**, 5488 (2012)
[2] Wang, A., Jiang, H., Li, X. *JOC* **76**, 6958 (2011)
[3] Lauer, M.G., Henderson, W.H., Awad, A., Stambuli, J.P. *OL* **14**, 6000 (2012)
[4] Young, A.J., White, M.C. *ACIE* **50**, 6824 (2011)
[5] Check, C.T., Henderson, W.H., Wray, B.C., Vanden Eycken, M.J., Stambuli, J.P. *JACS* **133**, 18503 (2011)
[6] Alam, R., Pilarski, L.T., Pershagen, E., Szabo, K.J. *JACS* **134**, 8778 (2012)
[7] Yip, K.-T., Nimje, R.Y., Leskinen, M.V., Pihko, P.M. *CEJ* **18**, 12590 (2012)
[8] Stang, E.M., White, M.C. *JACS* **133**, 14892 (2011)
[9] Emmert, M.H., Cook, A.K., Xie, Y.J., Sanford, M.S. *ACIE* **50**, 9409 (2011)
[10] He, G., Zhao, Y., Zhang, S., Lu, C., Chen, G. *JACS* **134**, 3 (2012)
[11] Zhang, S.-Y., He, G., Zhao, Y., Wright, K., Nack, W.A., Chen, G. *JACS* **134**, 7313 (2012)
[12] Nadres, E.T., Daugulis, O. *JACS* **134**, 7 (2012)
[13] Rit, R.K., Yadav, M.R., Sahoo, A.K. *OL* **14**, 3724 (2012)
[14] Ren, Z., Mo, F., Dong, G. *JACS* **134**, 16991 (2012)
[15] Cui, S., Wojtas, L., Antilla, J.C. *ACIE* **50**, 8927 (2011)
[16] Shan, G., Yang, X., Ma, L., Rao, Y. *ACIE* **51**, 13070 (2012)
[17] Jiang, T.-S., Wang, G.-W. *JOC* **77**, 9504 (2012)
[18] Li, W., Sun, P. *JOC* **77**, 8362 (2012)
[19] Anand, M., Sunoj, R.B. *OL* **13**, 4802 (2011)
[20] Yadav, M.R., Rit, R.K., Sahoo, A.K. *CEJ* **18**, 5541 (2012)
[21] Gulevich, A.V., Melkonyan, F.S., Sarkar, D., Gevorgyan, V. *JACS* **134**, 5528 (2012)
[22] Xiao, B., Li, Y.-M., Liu, Z.-J., Yang, H.-Y., Fu, Y. *CC* **48**, 4854 (2012)
[23] Dai, H.-X., Yu, J.-Q. *JACS* **134**, 134 (2012)
[24] Shao, J., Chen, W., Giulianotti, M.A., Houghton, R.A., Yu, Y. *OL* **14**, 5452 (2012)
[25] Wang, L., Liu, S., Li, Z., Yu, Y. *OL* **13**, 6137 (2011)
[26] Garcia-Rubia, A., Urones, B., Arrayas, R.G., Carretero, J.C. *ACIE* **50**, 10927 (2011)
[27] Zhao, Y., Chen, G. *OL* **13**, 4850 (2011)
[28] Zhao, Y., He, G., Nack, W.A., Chen, G. *OL* **14**, 2948 (2012)
[29] Chan, C.-W., Zhou, Z., Y, W.-Y. *ASC* **353**, 2999 (2011)
[30] Yuan, Y., Chen, D., Wang, X. *ASC* **353**, 3373 (2011)

[31] Yin, Z., Sun, P. *JOC* **77**, 11339 (2012)
[32] Guin, S., Rout, S.K., Banerjee, A., Nandi, S., Patel, B.K. *OL* **14**, 5294 (2012)
[33] Zhou, W., Li, H., Wang, L. *OL* **14**, 4594 (2012)
[34] Kubota, A., Sanford, M.S. *S* 2579 (2011)
[35] Qu, X., Sun, P., Li, T., Mao, J. *ASC* **353**, 1061 (2011)
[36] Chen, W.-L., Gao, Y.-R., Mao, S., Zhang, Y.-L., Wang, Y.-F., Wang, Y.-Q. *OL* **14**, 5920 (2012)
[37] Deng, Y., Jiang, Z., Yao, M., Xu, D., Zhang, L., Li, H., Tang, W., Xu, L. *ASC* **354**, 899 (2012)
[38] Chen, H., Huang, L., Fu, W., Liu, X., Jiang, H. *CEJ* **18**, 10497 (2012)
[39] Yang, F.-L., Ma, X.-T., Tian, S.-K. *CEJ* **18**, 1582 (2012)
[40] He, Z., Kirchberg, S., Fröhlich, R., Studer, A. *ACIE* **51**, 3699 (2012)
[41] Kubota, A., Emmert, M.H., Sanford, M.S. *OL* **14**, 1760 (2012)
[42] Li, Y., Qi, Z., Wang, H., Fu, X., Duan, C. *JOC* **77**, 2053 (2012)
[43] Khoobi, M., Alipour, M., Zarei, S., Jafarpour, F., Shafiee, A. *CC* **48**, 2985 (2012)
[44] Gandeepan, P., Cheng, C.-H. *JACS* **134**, 5738 (2012)
[45] Wang, X., Leow, D., Yu, J.-Q. *JACS* **133**, 13864 (2011)
[46] Li, C., Li, P., Yang, J., Wang, L. *CC* **48**, 4214 (2012)
[47] Yu, P., Zhang, G., Chen, F., Cheng, J. *TL* **53**, 4588 (2012)
[48] Pankajakshan, S., Loh, T.-P. *CAJ* **6**, 2291 (2011)
[49] Chen, H., Cai, C., Liu, X., Li, X., Jiang, H. *CC* **47**, 12224 (2011)
[50] Lang, R., Shi, L., Li, D., Xia, C., Li, F. *OL* **14**, 4130 (2012)
[51] Ye, S., Wu, J. *CC* **48**, 7753 (2012)
[52] Bishop, M., Pietruszka, J. *SL* 2689 (2011)
[53] Gormisky, P.E., White, M.C. *JACS* **133**, 12584 (2011)
[54] Jiang, T., Persson, A.K.A., Bäckvall, J.-E. *OL* **13**, 5838 (2011)
[55] Deng, Y., Bartholomeyzik, T., Persson, A.K.A., Sun, J., Bäckvall, J.-E. *ACIE* **51**, 2703 (2012)
[56] Takeda, K., Toyota, M. *TL* **52**, 5872 (2011)
[57] Yip, K.-T., Yang, D. *CAJ* **6**, 2166 (2011)
[58] Yang, G., Zhang, W. *OL* **14**, 268 (2012)
[59] Wrigglesworth, J.W., Cox, B., Lloyd-Jones, G.C., Booker-Milburn, K.I. *OL* **13**, 5326 (2011)
[60] Li, D.-D., Yuan, T.-T., Wang, G.-W. *CC* **47**, 12789 (2011)
[61] Wang, Y., Wang, H., Peng, J., Zhu, Q. *OL* **13**, 4604 (2011)
[62] Mu, X., Wu, T., Wang, H., Guo, Y., Liu, G. *JACS* **134**, 878 (2012)
[63] Wei, Y., Deb, I., Yoshikai, N. *JACS* **134**, 9098 (2012)
[64] He, G., Lu, C., Zhao, Y., Nack, W.A., Chen, G. *OL* **14**, 2944 (2012)
[65] Youn, S.W., Bihn, J.H., Kim, B.S. *OL* **13**, 3738 (2011)
[66] Guchhait, S.K., Kashyap, M., Kandekar, S. *TL* **53**, 3919 (2012)
[67] Thirunavukkarasu, V.S., Cheng, C.-H. *CEJ* **17**, 14723 (2011)
[68] McMurray, L., Beck, E.M., Gaunt, M.J. *ACIE* **51**, 9288 (2012)
[69] Karthikeyan, J., Cheng, C.-H. *ACIE* **50**, 9880 (2011)
[70] Li, F., Jiang, T., Cai, H., Wang, G. *ChJC* **30**, 2041 (2012)
[71] Kim, B.S., Lee, S.Y., Youn, S.W. *CAJ* **6**, 1952 (2011)
[72] Matsuura, B.S., Condie, A.G., Buff, R.C., Karahalis, G.J., Stephenson, C.R.J. *OL* **13**, 6320 (2011)
[73] Zhu, R., Buchwald, S.L. *ACIE* **51**, 1926 (2012)
[74] Rosa, D., Orellana, A. *CC* **48**, 1922 (2012)
[75] Vlaar, T., Cioc, R.C., Mampuys, P., Maes, B.U.W., Orru, R.V.A., Ruijter, E. *ACIE* **51**, 13058 (2012)
[76] Gao, X.-A., Yan, R.-L., Wang, X.-X., Yan, H., Li, J., Guo, H., Huang, G.-S. *JOC* **77**, 7700 (2012)
[77] Huang, C., Ghavtadze, N., Godoi, B., Gevorgyan, V. *CEJ* **18**, 9789 (2012)
[78] Zhang, H., Shi, R., Gan, P., Liu, C., Ding, A., Wang, Q., Lei, A. *ACIE* **51**, 5204 (2012)
[79] Pearson, D.M., Conley, N.R., Waymouth, R.M. *ASC* **353**, 3007 (2011)
[80] Yin, G., Wu, T., Liu, G. *CEJ* **18**, 451 (2012)

Palladium(II) acetate – silver salts

Coupling. Arylation of arenes[1] with ArX catalyzed by $Pd(OAc)_2$ using one equivalent of $AgNO_3$ at 110° is probably too uneconomical. The same comment is applicable to 1,1-diarylation of 1-alkenes (requiring 2.1 equivalents of AgOAc)[2] as well as the intramolecular Heck reaction of *N*-(2-halobenzoyl)indoles.[3]

1-Alkenes and styrenes couple with allylic esters afford dienes while the carboxylato functionality remains intact, as it is a bimolecular dehydrogenative reaction.[4] Involving a formal intermolecular dehydroiodination is the coupling of alkenyl iodides with allylic alcohols to furnish hydroxylated conjugated polyenes, the configuration of the iodoalkenes is retained in the products.[5]

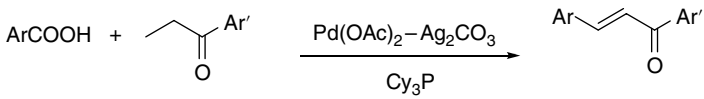
Cinnamyl esters/ethers are assembled from arenes and 3-oxy-1-alkenes,[6] and a one-pot synthesis of 1,3-diarylpropenes is developed taking advantage of the capability of the Pd species to conduct a follow-up coupling of the cinnamyl esters with $ArB(OH)_2$.[7]

With polyfluoroarenes the nuclear fluorinated cinnamyl esters are obtained.[8] Coupling of $C_6F_nH_{(6-n)}$ with ArI is essentially a Heck reaction,[9] and when involving dihydro-4-pyranone and dihydropyridones it occurs at the α-position.[10]

A synthesis of 2-alkenylpyridines based on coupling in the presence of $Pd(OAc)_2$ and AgOAc takes advantage of the regioselectivity.[11] Heck reaction employing $ArI(OAc)_2$ is quite complicated regarding the catalyst-promoter system that contains $Pd(OAc)_2$, Ag_2CO_3, TEMPO, and $CaCO_3$.[12]

The coupling between arylsilicon compounds and alkenes employs AgF to activate the C-Si bond.[13]

Substituted benzoic acids are arylated by *o*-direction, but Ag-catalyzed decarboxylation renders the reaction more interesting.[14] The carboxyl group is also lost during dehydrogenative condensation with propiophenones.[15]



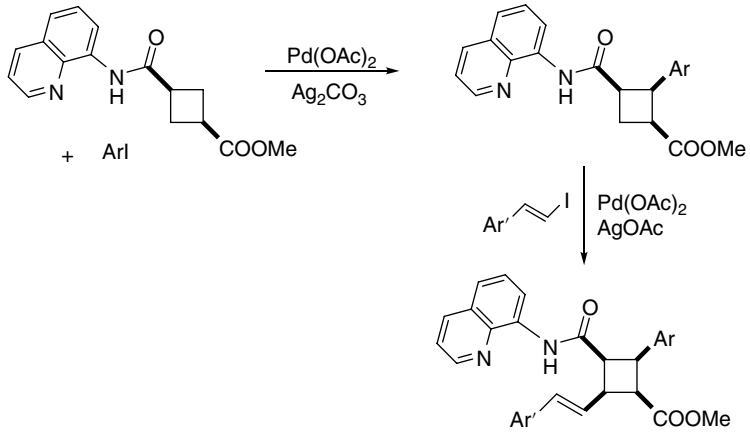
α-Arylalkanoic acids undergo *o*-arylation by reaction with $ArBF_3K$. It is found that besides $Pd(OAc)_2$, Ag_2CO_3, and benzoquinone, an important additive (ligand) is *N*-acetylisoleucine, as in its presence the yields of the products in some cases are increased from 5% to 99%.[16]

Silver salts often exhibit similar effects as oxidants in Pd(II) catalyzed coupling, accordingly many directed reactions can be carried out by replacing one additive with the other. Such are the case for *o*-arylation of benzamides[17,18] and *N*-tosylbenzamides.[19]

The sulfur atom of a sulfenylbenzyl substituent on an aromatic ring can direct *o*-alkenylation by alkenes in the presence of $AgOCOCF_3$.[20] A methylthio group can also serve the same purpose in assorted coupling processes.[21]

The well-known direction of 2-pyridyl group for coupling works according to expectation, including reaction with $ArSi(OMe)_3$ which is served by AgF.[22] Alkenylation of benzylsilanols is another example exploiting the same feature.[23] However, a newer directing device is the 2-pyridylsulfinyl group which enjoys the advantage of being detachable after its service.[24]

Site-specific functionalization at an aliphatic or alicyclic carbon has also been developed. For example, a carboxylic acid on derivatization into an amide bearing an *N*-quinolin-8-yl substituent is palladized at the β-carbon.[25] Furthermore, the β-CH of specially designed cyclopropanecarboxamides can be arylated,[26] and also cyclobutanecarboxamides carrying an *N*-quinolin-8-yl group[27] or a 2-methylthioanilino group.[28]

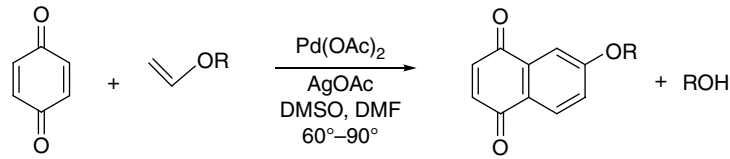


In three steps *o*-toluidine is converted into *o*-aroylanilines: derivatization into the picolinamide, oxidation-coupling in whichever order with ArI, $Pd(OAc)_2$, AgOAc under oxygen, and removal of the picolinoyl group.[29]

Double C-H bond activation is required for creating fluorenones from diaryl ketones, a combination of Ag_2O and CF_3COOH is conducive to the Pd-mediated cyclization.[30,31] The transition of *N*-acetyldiarylamines to carbazole derivatives is straightly analogous,[32] but the elaboration of *N*-(2-pyridyl)carbazoles from *N*-(2-pyridyl)anilines and $Ar'BF_3K$ is sometimes more flexible as a great variety of the substrates for the cyclization step can be prepared (still in the same operation).[33]

Oxindoles bearing a cyanoethyl chain at C-3 are obtained in an oxidative coupling between *N*-arylacrylamides and acetonitrile, the latter compound is being oxidized to participate in the reaction.[34]

A novel annulation of *p*-benzoquinone consists of gathering two equivalents of a vinyl ether.[35] One molecule of alcohol is eliminated during the reaction.



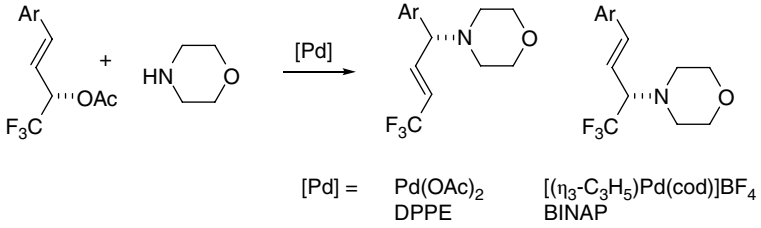
[1] Hong, W.K., Qiu, Y., Yao, Z., Wang, Z., Jiang, S. *TL* **52**, 4916 (2011)
[2] Xu, D., Lu, C., Chen, W. *T* **68**, 1466 (2012)
[3] Zhao, L., Li, Z., Chang, L., Xu, J., Yao, H., Wu, X. *OL* **14**, 2066 (2012)
[4] Zhang, Y., Cui, Z., Li, Z., Liu, Z.-Q. *OL* **14**, 1838 (2012)
[5] Brandt, D., Bellosta, V., Cossy, J. *OL* **14**, 5594 (2012)
[6] Shang, X., Xiong, Y., Zhang, Y., Zhang, L., Liu, Z. *SL* 259 (2012)
[7] Mino, T., Koizumi, T., Suzuki, S., Hirai, K., Kajiwara, K., Sakamoto, M., Fujita, T. *EJOC* 678 (2012)
[8] Li, Z., Zhang, Y., Liu, Z.-Q. *OL* **14**, 74 (2012)
[9] Chen, F., Min, Q.-Q., Zhang, X. *JOC* **77**, 2992 (2012)
[10] Chen, F., Feng, Z., He, C.-Y., Wang, H.-Y., Guo, Y., Zhang, X. *OL* **14**, 1176 (2012)
[11] Wen, P., Li, Y., Zhou, K., Ma, C., Lan, X., Ma, C., Huang, G. *ASC* **354**, 2135 (2012)
[12] Evdokimov, N.M., Kornienko, A., Magedov, I.V. *TL* **52**, 4327 (2011)
[13] Mino, T., Shibuya, M., Suzuki, S., Hirai, K., Sakamoto, M., Fujita, T. *T* **68**, 429 (2012)
[14] Cornella, J., Righi, M., Larrosa, I. *ACIE* **50**, 9429 (2011)
[15] Zhou, J., Wu, G., Zhang, M., Jie, X., Su, W. *CEJ* **18**, 8032 (2012)
[16] Engle, K.M., Thuy-Boun, P.S., Dang, M., Yu, J.-Q. *JACS* **133**, 18183 (2011)
[17] Li, D.-D., Yuan, T.-T., Wang, G.-W. *JOC* **77**, 3341 (2012)
[18] Reddy, B.V.S., Revathi, G., Reddy, A.S., Yadav, J.S. *SL* 2374 (2011)
[19] Peron, F., Fossey, C., Cailly, T., Fabis, F. *OL* **14**, 1827 (2012)
[20] Yu, M., Xie, Y., Xie, C., Zhang, Y. *OL* **14**, 2164 (2012)
[21] Yao, J., Yu, M., Zhang, Y. *ASC* **354**, 3205 (2012)
[22] Li, W., Yin, Z., Jiang, X., Sun, P. *JOC* **76**, 8543 (2011)
[23] Wang, C., Ge, H. *CEJ* **17**, 14371 (2011)
[24] Romero-Revilla, J.A., Garcia-Rubia, A., Arrayas, R.G., Fernandez-Ibanez, M.A., Carretero, J.C. *JOC* **76**, 9525 (2011)
[25] Ano, Y., Tobisu, M., Chatani, N. *JACS* **133**, 12984 (2011)
[26] Wasa, M., Engle, K.M., Lin, D.W., Yoo, E.J., Yu, J.-Q. *JACS* **133**, 19598 (2011)
[27] Gutekunst, W.R., Gianatassio, R., Baran, P.S. *ACIE* **51**, 7507 (2012)
[28] Frebault, F., Maulide, N. *ACIE* **51**, 2815 (2012)
[29] Xie, Y., Yang, Y., Huang, L., Zhang, X., Zhang, Y. *OL* **14**, 1238 (2012)
[30] Li, H., Zhu, R.-Y., Shi, W.-J., He, K.-H., Shi, Z.-J. *OL* **14**, 4850 (2012)
[31] Gandeepan, P., Hung, C.-H., Cheng, C.-H. *CC* **48**, 9379 (2012)
[32] Wang, S., Mao, H., Ni, Z., Pan, Y. *TL* **53**, 505 (2012)
[33] Chu, J.-H., Lin, P.-S., Lee, Y.-M., Shen, W.-T., Wu, M.-J. *CEJ* **17**, 13613 (2011)
[34] Wu, T., Mu, X., Liu, G. *ACIE* **50**, 12578 (2011)

Palladium(II) acetate – tertiary phosphine

Condensation. A redox sequence of reaction between $ArNO_2$ and cyclohexanones leads to diarylamines.[1] The nitroarenes must undergo reduction first, and subsequently formation of the Schiff bases and dehydrogenation follow.

During oxidation of RCHO [$Pd(OAc)_2$, DPPE, *t*-BuOOH] in the presence of a picolinic ester a transesterification is involved.[2]

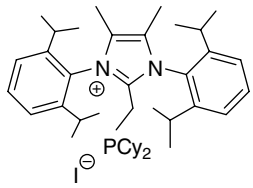
Substitution. When diols undergo mono-*O*-allylation by a Pd(II)-catalyzed reaction with allyl acetate, Me_2SnCl_2 is a crucial mediator.[3] Allylation of amines with 1,1,1-trifluoro-4-aryl-3-buten-2-yl acetates can occur at either the *ipso*- or the allylic position, and it is realizable by the proper choice of a Pd catalyst.[4] However, the reaction of 2-oxazolidinone, 1-*t*-butylimidazolidinone or phthalimide always gives 1-amino-2-alkenes when either 1-alken-3-ols or 2-alken-1-ols are the electrophile.[5]



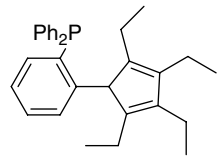
Whereas cyano group transfer from a cyanoacetic ester in the reaction with ArX (planned for arylation at the methylene site?)[6] is perhaps unexpected, the displacement involving $ArCH_2Cl$ and $K_4[Fe(CN)_6]$ to form $ArCH_2CN$ [7] is not unusual, although the scope is somewhat limited such that secondary benzyl chlorides and 1-naphthylmethyl chloride do not fare well.

Benzylation of pyridine-*N*-oxide at C-2 is accomplished on using *t*-Bu_3P as a ligand for $Pd(OAc)_2$.[8] In the reaction of anthranilic acid with benzyl alcohols in water , sodium *m*-diphenylphosphinobenzenesulfonate is a valuable ligand.[9] The products are the *N*-(1,2-diarylethyl) derivatives.

N-Arylation has many choices of ligands to entertain $Pd(OAc)_2$, usually highly hindered phosphines (e.g., **1**) are used.[10] For twofold amination of 1,4-dibromo-1,3-dienes and β,*o*-dibromostyrenes to afford pyrroles and indoles, respectively, **2** and t-BuOLi are added to the reaction medium.[11]

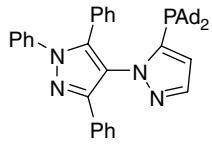


(**1**)



(**2**)

Ligand **3** is involved in the Pd-catalyzed conversion of ArX to ArOMe.[12] A micellar system is developed for the elaboration of ArSR from ArX, thiourea, and RBr, with the presence of the hindered XPhos.[13] The similar biarylphosphine ligand RuPhos serves the Pd catalyst in constituting arylselenides.[14] To assemble arenesulfonhydrazides from ArX, hydrazines and potassium metabisulfite the catalyst system contains $Pd(OAc)_2$, *t*-Bu_3P. HBF_4 and Bu_4NBr.[15]



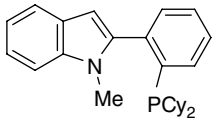
(**3**)

Very hindered arylboronates are synthesized from ArCl and $B_2(pin)_2$. A choice ligand is a silica-supported siloxane terminated by a 1-sila-4-phosphabicyclo[2.2.2] octane unit.[16]

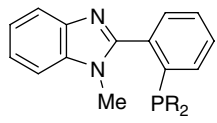
Xantphos is employed in the arylation of ketones,[17] and of diarylmethanes.[18] Nickel is also involved in the latter process, although it is not in the arylation of fluorine.[19]

Coupling. To the Pd-catalyzed Ullmann homocoupling of ArBr the addition of benzoin which acts as reducing agent increases the product yield.[20] Cross-coupling of ArOTf and $Ar'SO_2Na$ involves elimination of SO_2.[21]

Continuing efforts to modify catalysts for various coupling reactions to test their effectiveness are being made. Examples include oxysilylalkyl(diphenyl)phosphines supported on magnetite to form complexes with Pd.[22] A quick mix of a $Pd(OAc)_2$ solution with equimolar *t*-Bu_3P and immediate transfer (within 0.65 sec.) to a flow microreactor for Suzuki coupling is to avoid palladacycle formation.[23] Pairing $Pd(OAc)_2$ with **4** or **5** has been proposed.[24,25]



(**4**)

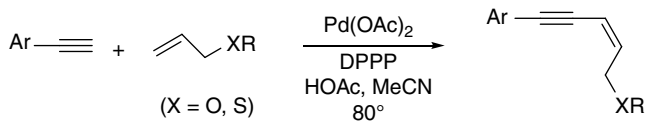


(**5**)

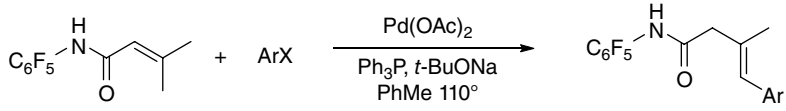
Suzuki coupling of heteroaryl boronic acids and alkenyl halides with minimal protodeboronation can be carried out in the presence of SPhos, CsF in isopropanol.[26] The same ligand is of service in the coupling of sodium phthalimidomethyltrifluoroborate and ArOTs or ArOMs.[27] It is noted that $(dba)_2Pd$ is better than $Pd(OAc)_2$ for the coupling with ArOTf.

Sonogashira coupling can use an $ArNH_2$ which is diazotized in situ, trifurylphosphine is an appropriate ligand.[28] Couping of azoles with 1,1-dichloroalkenes proceeds in the presence of *t*-BuOLi to yield alkynyl derivatives.[29] Benzazoles are arylated on treatment with $ArSO_2NHNH_2$, and it is necessary to include $Cu(OAc)_2$ and air in the reaction media.[30] Success in employing $ArSiF_3$for Hiyama coupling[31] is no surprise.

1,4-Alkadienes are alkylating agents when a quinone is added to the reaction media.[32] Dehydrogenative coupling joins alkynes and alkenes to form (*Z*)-enynes.[33]



Ring closure is achieved by coupling of aryl sulfonates *o*-substituted by an ω-arylalkyl group.[34] It is an intramolecular aryl version of the Heck reaction. The α-selective Heck reaction of alkyl vinyl ethers is also applicable to the silyl ethers as a way to aryl methyl ketones.[35] Improvement in the Heck reaction of ArCl is to use DavePhos and TBAE.[36] β,β-Disubstituted acrylic acid derivatives are rather poor substrates for the Heck reaction, however, the *N*-pentafluorophenylamide of 3,3-dimethylacrylic acid would undergo double bond shift to become reactive.[37]



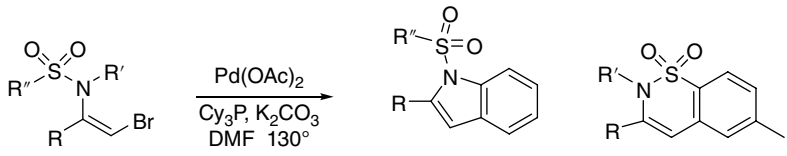
2-Bromo-1-alkenes are more reactive toward cross coupling with $ArB(OH)_2$ that replaces the bromine atom with an aryl group, rather than following a Heck reaction pathway.[38]

Cyclobutanols are active coupling partners, but their reaction occurs only upon ring cleavage.[39]

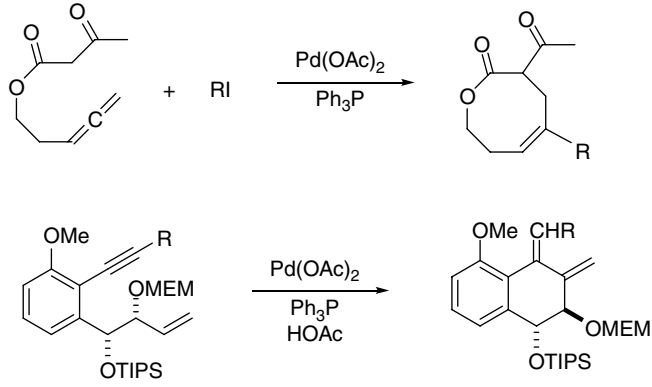
Coupling of aryl formates serves to elongate the carboxylic group (e.g., with alkenyl halides, sulfonates, and also ArX).[40] 2,4,6-Trichlorphenyl formate is a crystalline compound and it shows excellent reactivity to be transformed into higher carboxylates.[41] The products are good acylating agents.

Aromatic amides can be synthesized from ArX without using CO. Thus condensation employs instead *N*-substituted formamides and $POCl_3$ in which Vilsmeier-type intermediates play a major role.

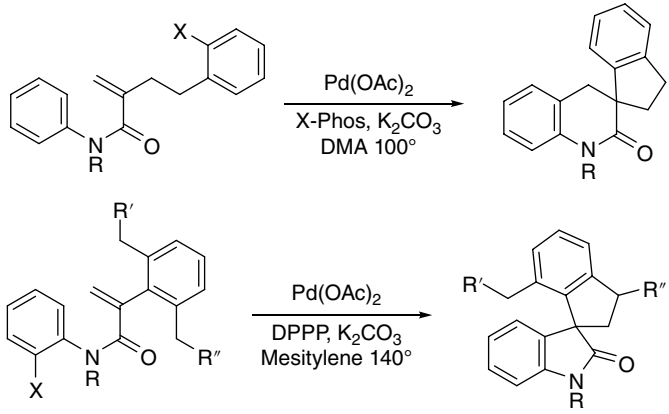
Annulative coupling. Dehydrohalogenative intramolecular coupling is readily achieved. Examples include 2-(*o*-bromoaryl)pyrroles[43] and (*Z*)-1-bromo-2-sulfonylamino-1-alkenes.[44] Cyclization also occurs with compounds containing two aryl groups tethered by one or two atoms and one of the aryl groups is *o*-brominated and the other carries a carboxyl substituent.[45] Decarboxylation accompanies the CC bond formation.



γ,δ-Unsaturated α-acyl mesolactones with a γ-substituent are assembled from acetoacetyl esters of ω-allenylalkyl alcohols.[46] Cyclization and introduction of the γ-substituent are accomplished practically simultaneously. Intramolecular hydrovinylation of alkynes is a way to construct cyclic compounds with adjacent exocyclic double bonds.[47]



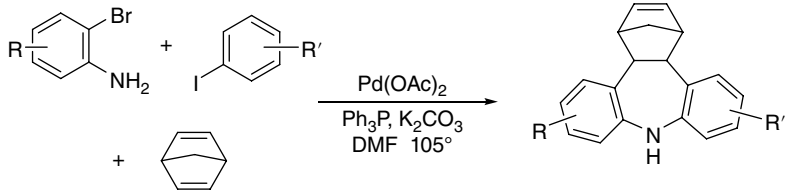
Spirobicyclization initiated by a Heck reaction is also dependent on a subsequent C-H bond (aryl or benzyl) activation to close the second ring, $Pd(OAc)_2$ with a phosphine ligand satisfies the requirement for catalyzing both steps.[48,49]



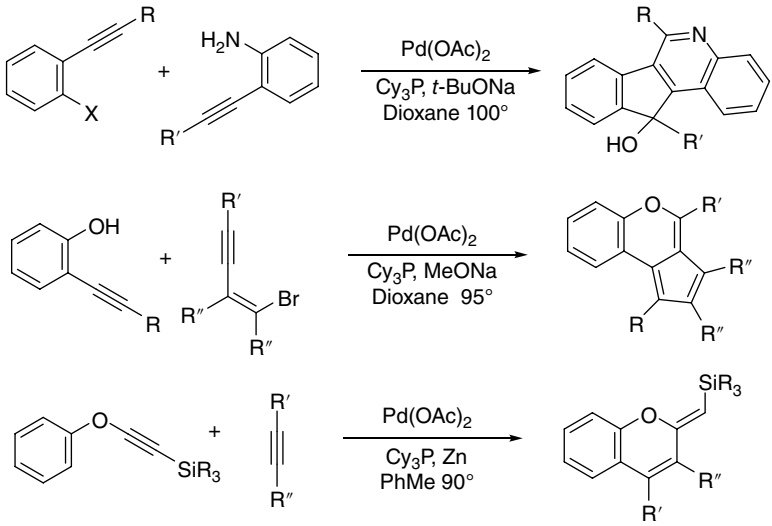
Pyrroles and indoles *N*-substitued by an *o*-(2,2-dibromovinyl)phenyl group are susceptible to dehydrobrominative cyclization. The reaction conditions are conducive to further coupling with a polyfluorobenzene.[50] β,β-Dibromostyrenes bearing OH or SH group in an *o*-position readily undergo cyclization and coupling, e.g., with $ArSi(OR)_3$.[51] *o*-Allenylaryl halides form indoles via reaction with amines and then intramolecular hydroamination to deliver indoles.[52] Different Pd catalysts are employed to gain best results according the electronic nature of a substituent on the terminus of the allenic double bond [$Pd(OAc)_2$ for electron-withdrawing group, $(dba)_2Pd$ for electron-donating substituent or simply a hydrogen atom].

The carbon atom of an isonitrile is capable of forming two new bonds, accordingly aryl isonitriles can be fashioned into indoles or more complex heterocyclic systems when they contain carbon chains at the *o*-position(s).[53] Benzyne offers amphiphilic sites for bonding and the coupling with *o*-halobenzamides leads to phenanthridinones.[54]

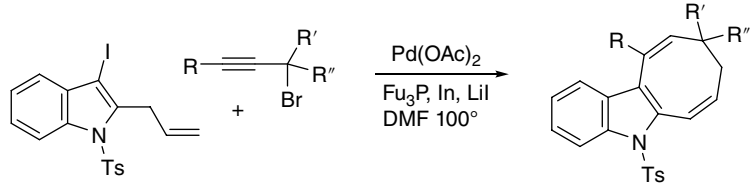
Dibenzoazepines are generated by pyrolytic decomposition (retro-Diels-Alder reaction) of the three-compnent coupling products. The reactants are *o*-bromoaniline, iodoarenes and norbornadiene.[55]



Functionalized alkynes are sources of complex quinolines[56] and chromenes,[57,58] at some stage of the reaction a triple bond of one alkyne interacts with that of the reaction partner.[59]

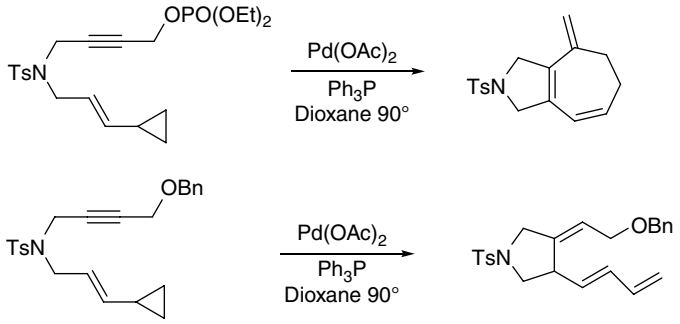


An eight-membered ring is created in the reaction between 2-allyl-3-iodoindole derivatives and propargylic bromides. The process is initiated by formation of organoindium reagents which attack the propargylic bromides in an S_N2' fashion. The allene linkage is then engaged in coupling with the terminal double bond.



Palladium insertion of acyl chlorides and alkenyl bromides is the key to cyclization involving a tetrahedral carbon at some distance, e.g., in a reaction that creates oxindoles[60] and tetrahydroindolines.[61]

By an intramolecular [5+2] process a seven-membered ring is formed with cleavage of the 3-membered ring of alkenylcyclopropane subunit. A nucleofugal group at the propargylic site plays a critical role for the occurrence of the transformation.[62]



Addition. Upon coupling with ArI, quenching of the allylpalladium species derived from 1,2-alkadienes with added NaOAc gives allyl acetates.[63] Both primary and secondary acetates are formed, and the process is formally an addition.

[1] Xie, Y., Liu, S., Wen, Y., Deng, G.-J. *OL* **14**, 1692 (2012)
[2] Bao, Y.-S., Chen, C.-Y., Huang, Z.-Z. *JOC* **77**, 8344 (2012)
[3] Kuriyama, M., Takeichi, T., Ito, M., Yamasaki, N., Yamamura, R., Demizu, Y., Onomura, O. *CEJ* **18**, 2477 (2012)
[4] Hirakawa, T., Ikeda, K., Ikeda, D., Tanaka, T., Ogasa, H., Kawatsura, M., Itoh, T. *T* **67**, 8238 (2011)
[5] Banerjee, D., Jayadeesh, R.V., Junge, K., Beller, M. *ACIE* **51**, 11556 (2012)
[6] Zheng, S., Yu, C., Shen, Z. *OL* **14**, 3644 (2012)
[7] Ren, Y., Yan, M., Zhao, S., Sun, Y., Wang, J., Yin, W., Liu, Z. *TL* **52**, 5107 (2011)
[8] Mai, W., Yuan, J., Li, Z., Yang, L., Xiao, Y., Mao, P., Qu, L. *SL* 938 (2012)
[9] Hikawa, H., Yokoyama, Y. *OL* **13**, 6512 (2011)
[10] Dumrath, A., Lübbe, C., Neumann, H., Jackstell, R., Beller, M. *CEJ* **17**, 9599 (2011)
[11] Geng, W., Zhang, W.-X., Hao, W., Xi, Z. *JACS* **134**, 20230 (2012)
[12] Gowrisankar, S., Neumann, H., Beller, M. *CEJ* **18**, 2498 (2012)
[13] Wang, L., Zhou, W.-Y., Chen, S.-C., He, M.-Y., Chen, Q. *ASC* **354**, 839 (2012)
[14] Grenader, K., Schüpbach, B., Peters, A., Kümmel, O., Halter, O., Terfort, A. *ASC* **354**, 2653 (2012)

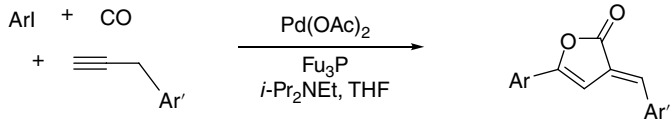
[15] Ye, S., Wu, J. *CC* **48**, 10037 (2012)
[16] Kawamorita, S., Ohmiya, H., Iwai, T., Sawamura, M. *ACIE* **50**, 8363 (2011)
[17] Ackermann, L., Mehta, V.P. *CEJ* **18**, 10230 (2012)
[18] Zhang, J., Bellomo, A., Creamer, A.D., Dreher, S.D., Walsh, P.J. *JACS* **134**, 13765 (2012)
[19] Chen, J.-J., Onogi, S., Hsieh, Y.-C., Hsioa, C.-C., Higashibayashi, S., Sakurai, H., Wu, Y.-T. *ASC* **354**, 1551 (2012)
[20] Park, B.R., Kim, K.H., Kim, T.H., Kim, J.N. *TL* **52**, 4405 (2011)
[21] Zhou, C., Liu, Q., Li, Y., Zhang, R., Fu, X., Duan, C. *JOC* **77**, 10468 (2012)
[22] Li, P., Wang, L., Zhang, L., Wang, G.-W. *ASC* **354**, 1307 (2012)
[23] Nagaki, A., Takabayashi, N., Moriwaki, Y., Yoshida, J. *CEJ* **18**, 11871 (2012)
[24] Wong, P.Y., Chow, W.K., Chung, K.H., So, C.M., Lau, C.P., Kwong, F.Y. *CC* **47**, 8328 (2011)
[25] Wong, S.M., So, C.M., Chung, K.H., Lau, C.P., Kwong, F.Y. *EJOC* 4172 (2012)
[26] Thakur, A., Zhang, K., Louie, J. *CC* **48**, 203 (2012)
[27] Murai, N., Miyano, M., Yonaga, M., Tanaka, K. *OL* **14**, 2818 (2012)
[28] Wu, X.-F., Neumann, H., Beller, M. *CC* **47**, 7959 (2011)
[29] Ackermann, L., Kornhaass, C., Zhu, Y. *OL* **14**, 1824 (2012)
[30] Yuen, O.Y., So, C.M., Wong, W.T., Kwong, F.Y. *SL* 2714 (2012)
[31] Molander, G.A., Iannazzo, L. *JOC* **76**, 9182 (2011)
[32] Trost, B.M., Hansmann, M.M., Thaisrivongs, D.A. *ACIE* **51**, 4950 (2012)
[33] Shao, Y.-L., Zhang, X.-H., Han, J.-S., Zhong, P. *OL* **14**, 5242 (2012)
[34] Nervig, C.S., Waller, P.J., Kalyani, D. *OL* **14**, 4838 (2012)
[35] Qian, W., Zhang, L., Sun, H., Jiang, H., Liu, H. *ASC* **354**, 3231 (2012)
[36] Xu, H.-J., Zhao, Y.-Q., Zhou, X.-F. *JOC* **76**, 8036 (2011)
[37] Yu, M., Xie, Y., Li, J., Zhang, Y. *ASC* **353**, 2933 (2011)
[38] Guo, B., Fu, C., Ma, S. *EJOC* 4034 (2012)
[39] Ziadi, A., Martin, R. *OL* **14**, 1266 (2012)
[40] Ueda, T., Konishi, H., Manabe, K. *OL* **14**, 5171 (2012)
[41] Ueda, T., Konishi, H., Manabe, K. *OL* **14**, 5370 (2012)
[42] Sawant, D.N., Wagh, Y.S., Bhatte, K.D., Bhanage, B.M. *JOC* **76**, 5489 (2011)
[43] Chang, J., Sun, L., Dong, J., Shen, Z., Zhang, Y., Wu, J., Wang, R., Wang, J., Song, C. *SL* 2704 (2012)
[44] Yamagishi, M., Nishigai, K., Ishii, A., Hata, T., Urabe, H. *ACIE* **51**, 6471 (2012)
[45] Shen, Z., Ni, Z., Mo, S., Wang, J., Zhu, Y. *CEJ* **18**, 4859 (2012)
[46] Wan, B., Jia, G., Ma, S. *ASC* **353**, 1763 (2011)
[47] Zilke, L., Hall, D.G. *EJOC* 4153 (2012)
[48] Piou, T., Neuville, L., Zhu, J. *OL* **14**, 3760 (2012)
[49] Piou, T., Neuville, L., Zhu, J. *ACIE* **51**, 11561 (2012)
[50] Ye, S., Liu, J., Wu, J. *CC* **48**, 5028 (2012)
[51] Liu, J., Chen, W., Ji, Y., Wang, L. *ASC* **354**, 1585 (2012)
[52] Liu, B., Hong, X., Yan, D., Xu, S., Huang, X., Xu, B. *OL* **14**, 4398 (2012)
[53] Nanjo, T., Tsukano, C., Takemoto, Y. *OL* **14**, 4270 (2012)
[54] Lu, C., Dubrovskiy, A.V., Larock, R.C. *JOC* **77**, 8648 (2012)
[55] Della Ca′, N., Maestri, G., Malacria, M., Derat, E., Catellani, M. *ACIE* **50**, 12257 (2011)
[56] Pan, X., Luo, Y., Wu, J. *CC* **47**, 8967 (2011)
[57] Wang, H., Luo, Y., Zhu, B., Wu, J. *CC* **48**, 5581 (2012)
[58] Minami, Y., Shiraishi, Y., Yamada, K., Hiyama, T. *JACS* **134**, 6124 (2012)
[59] Zhu, C., Zhang, X., Lian, X., Ma, S. *ACIE* **51**, 7817 (2012)
[60] Tsukano, C., Okuno, M., Takemoto, Y. *ACIE* **51**, 2763 (2012)
[61] Sofack-Kreutzer, J., Martin, N., Renaudat, A., Jazaar, R., Baudoin, O. *ACIE* **51**, 10399 (2012)
[62] Oh, H.M., Sim, S.H., Lee, S.I., Kim, J., Chung, Y.K. *SL* 2657 (2012)
[63] Husinec, S., Petkovic, M., Savic, V., Simic, M. *S* 399 (2012)

Palladium(II) acetate – tertiary phosphine – carbon monoxide

Carbonylative coupling. Transformation of ArBr into ArCHO with syngas is catalyzed by $Pd(OAc)_2$ and a bulky monodentate phosphine.[1] However, in diarylethanone synthesis from ArI, CO and $Ar'CH_2Cl$, the bidentate DPPB is used to assist the Pd catalyst.[2] Members of the chalcone family of compounds are assembled from $ArB(OH)_2$, CO and CH_2=CHAr′, in a reaction conducted under oxygen.[3] When two different styrenes and CO are condensed, $ArCH_2CH_2COCH$=CHAr′ can be obtained.[4]

Aroylation of anilines is observed in a reaction which some anilines are diazotized to undergo coupling with CO to form the active acylating agent.[5] Capture of the aroylpalladium species derived from diazotized anilines and CO by arylethynes gives diarylpropynones.[6] Trapping with 2-chloroethylamine or 3-chloropropylamine completes the reaction in forming the cyclic iminoethers.[7]

From condensation of *o*-bromobenzaldehyde and hydrazines with CO, phthalizinones are produced.[8] A more intriguing annulation is that two equivalents of CO are consumed to bind with ArI and 3-aryl-1-propynes.[9]

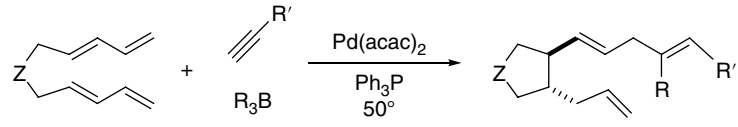


Under oxidative conditions *o*-hydroxystyrenes pick up CO to form coumarins.[10]

[1] Neumann, H., Kadyrov, R., Wu, X.-F., Beller, M. *CAJ* **7**, 2213 (2012)
[2] Wu, X.-F., Schranck, J., Neumann, H., Beller, M. *CAJ* **7**, 40 (2012)
[3] Wu, X.-F., Neumann, H., Beller, M. *CAJ* **7**, 282 (2012)
[4] Wu, X.-F., Neumann, H., Beller, M. *CAJ* **7**, 1199 (2012)
[5] Wu, X.-F., Schranck, J., Neumann, H., Beller, M. *TL* **52**, 3702 (2011)
[6] Wu, X.-F., Neumann, H., Beller, M. *ACIE* **50**, 11142 (2011)
[7] Wu, X.-F., Neumann, H., Beller, M. *CEJ* **18**, 13619 (2012)
[8] Wu, X.-F., Neumann, H., Beller, M. *CEJ* **18**, 8596 (2012)
[9] Wu, X.-F., Jiao, H., Neumann, H., Beller, M. *CEJ* **18**, 16177 (2012)
[10] Ferguson, J., Zeng, F., Alper, H. *OL* **14**, 5602 (2012)

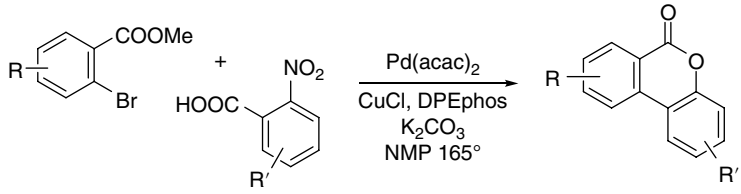
Palladium(II) acetylacetonate

Coupling. 1,3,8,10-Undecatetraenes are able to couple at the two innermost sp^2-carbon atoms to form bis-π-allylpalladium complexes, and such species are liable to coupling with alkynes and organoboron reagents.[1]



(Z = O, NTs, $C(COOR)_2$)

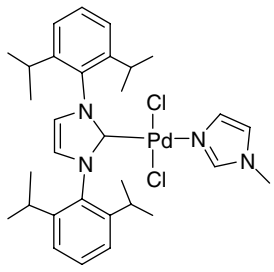
Bimetallic catalyst system in which a copper salt induces decarboxylation is useful to present aromatic carboxylic acids as coupling partners to aryl halides.[2] An example is shown in the following equation.



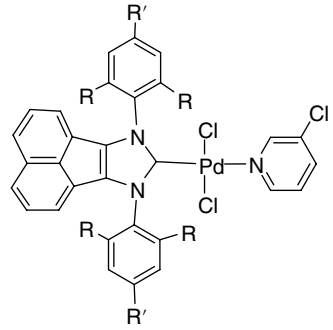
[1] Fukushima, M., Takushima, D., Satomura, H., Onodera, G., Kimura, M. *CEJ* **18**, 8019 (2012)
[2] Luo, J., Lu, Y., Liu, S., Deng, G.-J. *ASC* **353**, 2604 (2011)

Palladium – aminocarbene complexes

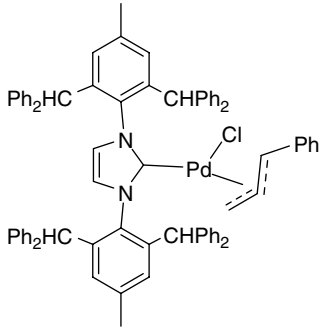
Substitution and coupling. Carbene-ligated palladium complexes share with many other catalysts in conducting reactions. Thus, for arylation of amines, **1, 2A** and **3** are quite effective.[1,2,3] The use of **1** to both arylate and deacylate amides is noted.[4]



(**1**)

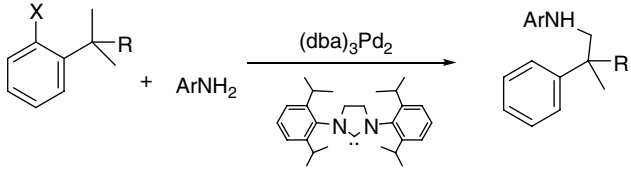


(**2A**) R = *i*-Pr, R′ = H
(**2B**) R = R′ = Me

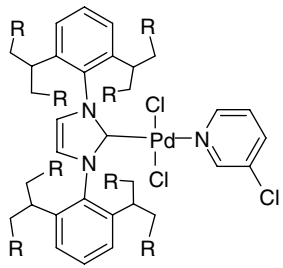


(**3**)

The reaction of arylamines with aryl halides bearing a tertiary alkyl group at an *o*-position gives products in which a benzylic methyl group becomes attached to the amine.[5]



The complex **4B**, with somewhat bulkier *N*-substituents of the imidazoline moiety, is catalytic in the substitution reaction of ArX and RSH,[6] whereas $Pd(OAc)_2$ complexed to *N,N′*-bis(2,6-diisopropylphenyl)imidazolinylidene guides the oxidative coupling of $ArCH_2OH$ with Ar′OH in furnishing ArCOOAr′.[7]



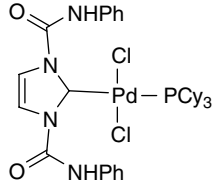
(**4A**) R = H
(**4B**) R = Me

Alkyl aryl ketones are α-arylated using **1** as catalyst.[8] A far more significant contribution to synthetic methodology is the dehydrochlorination of *o*-chloroarylacetaldehydes leading to benzocyclobutenones.[9] The carbene unit in the Pd catalyst is *N,N′*-bis(1-adamantyl) imidazolylidene and an additive is diallyl ether.[9]

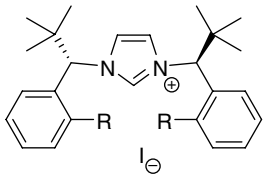
With **1** a biaryl synthesis proceeds by Suzuki coupling.[10] Carbene ligands derived from triazoles and tetrazoles have been scrutinized,[11,12] as well as more *N*-substituent variants from imidazolium salts or their dihydro congeners, including the unsymmetrical *N*-benzyl-*N′*-[(2-hydroxy-2-phenyl)]ethylimidazolium chloride for Hiyama coupling,[13] the symmetrical salts bearing two 2,6-bis(diphenylmethyl)-4-methylphenyl groups,[14] and two 1-(2,7-biscyclooctyl)naphthyl substituents[15] are said to work wonders on very hindered substrates.

Among Pd complexes useful for Suzuki coupling of are **2B**[16] and one partnered with *N,N′*-bis[2,6-di(3,3,3-trifluoropropylphenyl)imidazolinylidene.[17]

For arylation of five-membered heterocycles by ArCl, a different precatalyst is **5**.[18] 1,4-Disubstituted 1,2,3-triazoles are arylated at C-5.[19] Chiral imidazolium iodide **6** is the precursor of the carbene ligand for ring closure to erect *trans*-fused indolines from *N*-cycloalkylaniline derivatives via intramolecular C-H insertion at high temperatures.[20]



(**5**)



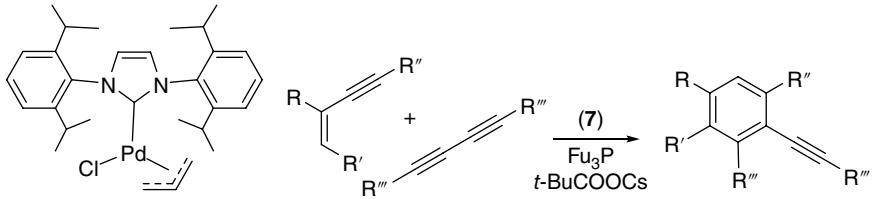
(**6**)

Complex **4B** has been selected for conducting the coupling of ArX with allylic pinacolatoboranes,[21] as well as Negishi coupling with organozinc compounds.[22,23] Of bis(pinacolato) methane one boryl group is eligible for elimination to prepare homoallylboryl and benzylboryl reagents through coupling catalyzed by **4A**.[24]

Immobilization strategy to ease catalyst recovery has also been applied to the Pd-carbene series. One modification is changing one of the *N*-substituents on the imidazolylidene ring to an oxasilylpropyl group, which is in turn attached to silica.[25]

Another use for a Pd-carbene complex is the insertion of CO_2 into the carbon-heteroatom bond of allyltin compounds and allylboronates.[26]

Addition and cycloaddition. A 2:1-carbene/Pd complex mediates the head-to-head dimerization of 1-alkenes to afford conjugated (*E*)-enynes.[27] [4+2]Cycloaddition of conjugated enynes with alkynes occurs in much higher turnover number if a Pd-carbene is employed as catalyst.[28]



(**7**)

Another dicarbene-Pd complex with an *N*-substituent linked to a polymer assists the dehalocarbonylation of *o*-halobenzyl alcohol to acquire phthalide, and the three-component coupling involving *o*-halobenzoic esters, CO and amines in a synthesis of phthalimides.[29]

[1] Zhu, L., Gao, T.-T., Shao, L.-X. *T* **67**, 5150 (2011)
[2] Tu, T., Fang, W., Jiang, J. *CC* **47**, 12358 (2011)
[3] Chartoire, A., Frogneux, X., Nolan, S.P. *ASC* **354**, 1897 (2012)
[4] Chen, W.-X., Shao, L.-X. *JOC* **77**, 9236 (2012)
[5] Pan, J., Su, M., Buchwald, S.L. *ACIE* **50**, 8647 (2011)
[6] Sayah, M., Organ, M.G. *CEJ* **17**, 11719 (2011)
[7] Luo, F., Pan, C., Cheng, J., Chen, F. *T* **67**, 5878 (2011)
[8] Xiao, Z.-K., Shao, L.-X. *S* 711 (2012)

[9] Flores-Gaspar, A., Gutierrez-Bonnet, A., Martin, R. *OL* **14**, 5234 (2012)
[10] Zhou, X.-X., Shao, L.-X. *S* 3138 (2011)
[11] Huang, J., Hong, J.-T., Hong, S.H. *EJOC* 6630 (2012)
[12] Inomata, S., Hiroki, H., Terashima, T., Ogata, K., Fukuzawa, S. *T* **67**, 7263 (2011)
[13] Penafiel, I., Pastor, I.M., Yus, M., Esteruelas, M.A., Olivan, M., Onate, E. *EJOC* 7174 (2011)
[14] Chartoire, A., Lesieur, M., Falivene, L., Slawin, A.M.Z., Cavallo, L., Cazin, C.S.J., Nolan, S.P. *CEJ* **18**, 4517 (2012)
[15] Wu, L., Drinkel, E., Gaggia, F., Capolicchio, S., Linden, A., Falivene, L., Cavallo, L., Dorta, R. *CEJ* **17**, 12886 (2011)
[16] Tu, T., Sun, Z., Fang, W., Xu, M., Zhou, Y. *OL* **14**, 4250 (2012)
[17] Liu, T., Zhao, X., Shen, Q., Lu, L. *T* **68**, 6535 (2012)
[18] Ghosh, D., Lee, H.M. *OL* **14**, 5534 (2012)
[19] He, T., Wang, M., Li, P., Wang, L. *ChJC* **30**, 979 (2012)
[20] Nakanishi, M., Katayev, D., Besnard, C., Kündig, E.P. *ACIE* **50**, 7438 (2011)
[21] Farmer, J.L., Hunter, H.N., Organ, M.G. *JACS* **134**, 17470 (2012)
[22] McCann, L.C., Hunter, H.N., Clyburne, J.A.C., Organ, M.G. *ACIE* **51**, 7024 (2012)
[23] Pompeo, M., Froese, R.D.J., Hadei, N., Organ, M.G. *ACIE* **51**, 11354 (2012)
[24] Endo, K., Ohkubo, T., Ishioka, T., Shibata, T. *JOC* **77**, 4826 (2012)
[25] Borja, G., Monge-Marcet, A., Pleixats, R., Parella, T., Gattoen, X., Wong, M.C.M. *EJOC* 3625 (2012)
[26] Hazari, N., Hruszkewycz, D.P., Wu, J. *SL* 1793 (2011)
[27] Jahier, C., Zatolochnaya, O.V., Zvyagintsev, N.V., Ananikov, V.P., Gevorgyan, V. *OL* **14**, 2846 (2012)
[28] Zatolochnaya, O.V., Galenko, A.V., Gevorgyan, V. *ASC* **354**, 1149 (2012)
[29] Khedkar, M.V., Khan, S.R., Dhake, K.P., Bhanage, B.M. *S* 2623 (2012)

Palladium(II) bis(trifluoroacetate)

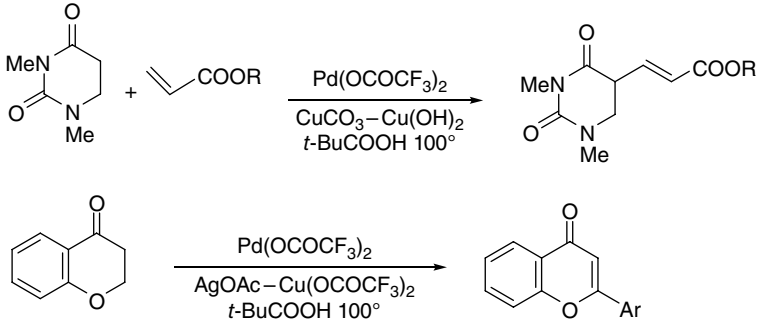
Arylpalladium trifluoroacetates. Certain $ArPd(OCOCF_3)$ can be prepared and stored. The general method is mixing of ArCOOH, $Pd(OCOCF_3)_2$ and Na_2CO_3 in DMSO.[1]

Dehydrogenation. Cyclic ketones are dehydrogenated by the DMSO complex of $Pd(OCOCF_3)_2$ under oxygen. Cyclohexenones thus obtained are not further converted into phenols.[2]

Functionalization of aromatics. Nuclear hydroxylation of aryl ketones is fulfilled by palladation and oxidation, the oxidant can be either $K_2S_2O_8$ or $PhI(OAc)_2$.[3] Anilides are converted into *o*-acylaminoaryl ketones on reaction with aldehydes, by heating with $Pd(OCOCF_3)_2$ and *t*-BuOOH in toluene.[4]

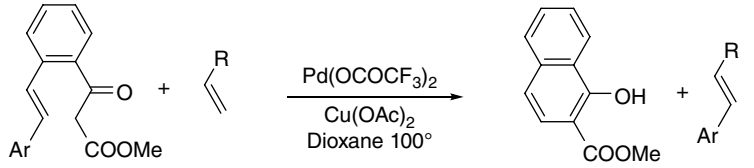
Coupling. Unsymmetrical biaryls can be prepared from mixtures of two different ArCOOH, with Ag_2CO_3 to promote decarboxylation.[5] The balance of rates for decarboxylation is critical as the transmetallation (ArAg to $ArPdL_n$ then ArPdAr′) and reductive elimination steps are fast. The oxidative Heck reaction can use $ArBF_3K$, and as catalyst, $Pd(OCOCF_3)_2$ - DPPP, while oxygen or benzoquinone supplies the oxidative power.[6]

The location of dehydrogenative coupling of 4-chromanone is dependent on the substrate and some variation of catalyst constitution.[7]



1,3-Disubstitued conjugated dienes are assembled by coupling of 1-alkenes with alkenylboronic acids under oxygen.[8] The alkenes participate in the coupling at C-2.

An intriguing reaction is that the result appears to indicate involvement of alkene metathesis and oxidative cyclization.[9]



Ynamides in which a nitrogen substituent is Boc lose isobutene on treatment with $Pd(OCOCF_3)_2$. 2-Oxazolinones are formed.[10] Ring formation accompanies coupling of 1,n-enynes (n = 6, 7) with organoboron compounds, and the products are characterized by the presence of an exocyclic double bond.[11,12]

When an oxidant is supplied two $ArB(OH)_2$ molecules are incorporated into the product,[11] and this stoichiometry is also observed in the 1,2-diarylation of allyl ethers.[13] A reaction of $ArBF_3K$ with cyanamides delivers arylamidines.[14]

Certain alkanes are useful in dehydrogenative coupling with arenes. For example, β-keto esters for the alkylation of indole the C-H bond involved is β to both the ketone and the ester carbonyl groups.[15] The β-CH of *N*-(*p*-trifluoromethylphenyl)alkanamides is also activated toward arylation by ArI.[16]

[1] Simmons, R.L., Yu, R.T., Myers, A.G. *JACS* **133**, 15870 (2011)
[2] Diao, T., Stahl, S.S. *JACS* **133**, 14566 (2011)
[3] Mo, F., Trzepkowski, L.J., Dong, G. *ACIE* **51**, 13075 (2012)
[4] Li, C., Wang, L., Li, P., Zhou, W. *CEJ* **17**, 10208 (2011)
[5] Hu, P., Shang, Y., Su, W. *ACIE* **51**, 5945 (2012)
[6] Sävmarker, J., Lindh, J., Nilsson, P., Sjöberg, P.J.R., Larhed, M. *CO* **1**, 140 (2012)
[7] Moon, Y., Kwon, D., Hong, S. *ACIE* **51**, 11333 (2012)
[8] Zheng, C., Wang, D., Stahl, S.S. *JACS* **134**, 16496 (2012)

[9] Youn, S.W., Kim, B.S., Jagdale, A.R. *JACS* **134**, 11308 (2012)
[10] Lu, Z., Xu, X., Yang, Z., Kong, L., Zhu, G. *TL* **53**, 3433 (2012)
[11] Jiang, M., Jiang, T., Bäckvall, J.-E. *OL* **14**, 3538 (2012)
[12] Pardo-Rodriguez, V., Buñuel, E., Collado-Sanz, D., Cardenas, D.J. *CC* **48**, 10517 (2012)
[13] Trejos, A., Odell, L.R., Larhed, M. *CO* **1**, 49 (2012)
[14] Sävmarker, J., Rydfjord, J., Gising, J., Odell, L.R., Larhed, M. *OL* **14**, 2394 (2012)
[15] Leskinen, M.V., Yip, K.-T., Valkonen, A., Pihko, P.M. *JACS* **134**, 5750 (2012)
[16] Wasa, M., Chan, K.S.L., Zhang, X.-G., He, J., Miura, M., Yu, J.-Q. *JACS* **134**, 18570 (2012)

Palladium(II) bromide

Coupling. A catalyst for Suzuki coupling is constituted of $PdBr_2$ and a polymer-bound ligand.[1] A less explored carbonylative coupling is that which employs vinyl ethers, but a successful synthesis of ArCOCH=CHOR from ArBr, CO and CH_2=CHOR is now on record, a rarer ligand, *N*-(*o*-anisyl)-2-dicyclohexylphosphinopyrrole, is also used.[2]

Substitution. Vinylepoxide is attacked by carboxylic acids in the S_N2' fashion, the enlisted catalyst is $(MeCN)_2PdBr_2$.[3]

Isomerization. The double bond of an allylic ester is shifted on treatment with $(t\text{-}Bu_3P)PdBr_2$, providing alkenyl esters.[4]

[1] Karimi, B., Akhavan, P.F. *CC* **47**, 7686 (2011)
[2] Schranck, J., Wu, X.-F., Neumann, H., Beller, M. *CEJ* **18**, 4827 (2012)
[3] Hamasaki, A., Maruta, S., Nakamura, A., Tokunaga, M. *ASC* **354**, 2129 (2012)
[4] Mamone, P., Grünberg, M.F., Fromm, A., Khan, B.A., Goossen, L.J. *OL* **14**, 3716 (2012)

Palladium(II) chloride

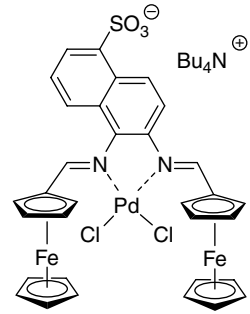
Reduction. Reduction of aryl ketones to the benzylic alcohols is selective (not affecting aliphatic ketones) by using an ionic liquid with a formate anion, and as catalyst, $PdCl_2$.[1] Removal of the thiol group from ArSR by reaction with a hydrosilane can be performed with catalytic $PdCl_2$.[2]

Substitution. A silica-bound $PdCl_2$ catalyst is suitable for allylation of β-keto esters. This species has a link terminated at an ethylenediamine to chelate Pd, and also tertiary amine units on the solid surface for promoting enolization.[3] Mixing a solution of $PdCl_2$ and cellulose and treatment with $NaBH_4$ give a reusable catalyst for allylation of amines by allylic acetates.[4]

Oxidation probably follows CC bond formation between 1,3-dicarbonyl compounds and allylic alcohols, and that accounts for the generation of alkylidenated products.[5]

Coupling. Modification of $PdCl_2$ by a crown ether salt $[(18\text{-c-}6)K]_3PO_4$ yields a Heck reaction catalyst.[6] Another additive is 2,2-bis(hydroxymethyl)-1,3-propylenebis(3-methylimidazolium) dicyanomethide.[7] Additives can play important roles to increase the efficiency of catalysis in coupling, thus a tertiary amine is used to moderate $PdCl_2$ which is ligated to a polymer-bound ligand of dithiocarbohydrazide. Triethylamine is good for the Heck reaction, whereas pyridine for Sonogashira coupling.[8] Rapid cross coupling of $ArB(OH)_2$ with Ar′Cl in water is observed in the presence of **1**.[9] However, fancy ligands are superfluous as

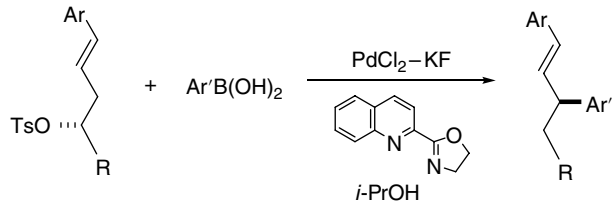
a report indicates the production of biaryls at room temperature under the influence of $PdCl_2$ and K_2CO_3 in 50% ethanol[10] or in water containing PEG-400.[11]



(**1**)

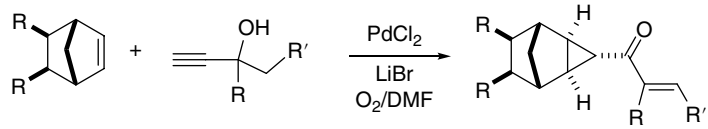
A new result in the directed coupling of 2-pyridylarenes is ethoxycarbonylation. Diethyl *N*-(*t*-butyl)oxaziridine-3,3-dicarboxylate would furnish the functional group.[12]

Homocinnamyl tosylates are found to be arylated at the allylic position. After palladation, metal migration precedes the Suzuki coupling.[13] There is a report of using bis(2-pyridylmethyl) amine to render the Suzuki coupling catalyst air-stable and water-soluble.[14]

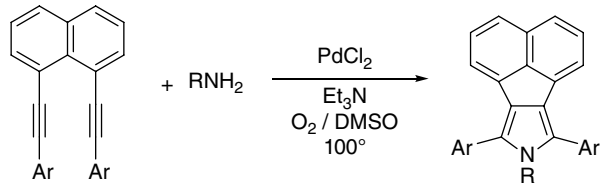


Addition. Functionalized alkynes such as alkoxyalkynes and ynamides undergo *cis*-addition with allyl chloride in that the chlorine is germinal to the polar group.[15,16]

Propargylic alcohols exhibit the behavior of conjugated acylcarbenes by several metal salts under specified conditions, $PdCl_2$ is identified as one of them. Acylcyclopropanation of alkenes results.[17]

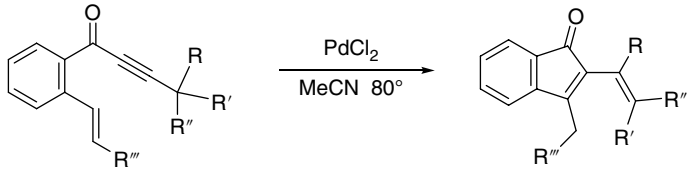


Diarylethynes are assembled into tetraarylfurans in a Pd-catalyzed reaction in which the oxygen atom comes from water.[18] With amines the analogous reaction is shown by an intramolecular case that furnishes 7,9-diaryl-8*H*-acenaptho[1,2-*c*]pyrroles.[19]



Cyclization. Allenyl 2-indolyl carbinols are susceptible to cyclodehydration to afford carbazoles in the presence of $PdCl_2$.[20] When an allylic bromide is present coupling at the central carbon of the allene also occurs during the cyclization.[21] Coupling of isonitriles with *N*-trifluoroacetyl-*o*-alkynylanilines at room temperature in air is a way to prepare indole-3-carboxamides.[22]

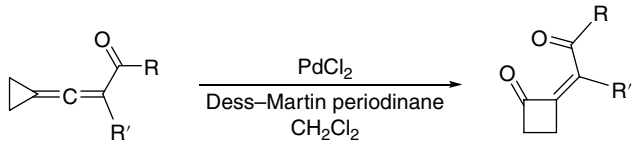
Indenones are formed in an intramolecular coupling of *o*-alkenylaryl alkynyl ketones in which a 1,2-migration of a group from the propargylic position accompanies the cyclization.[23]



R = H, Me

(*Z*)-Allyl acetates with extended conjugation to a triple bond react with *N*-methylindole to form a cyclopentadiene moiety which is attached to C-3.[24]

Rearrangement. Acylallenylidenecyclopropanes undergo oxidative ring expansion which is instigated by $PdCl_2$ and the Dess-Martin periodinane (oxidant).[25]



[1] Suzuki, H., Nishioka, H., Takeuchi, Y. *TL* **53**, 3686 (2012)
[2] Matsumura, T., Niwa, T., Nakada, M. *TL* **53**, 4318 (2012)
[3] Noda, H., Motokura, K., Miyaji, A., Baba, T. *ACIE* **51**, 8017 (2012)
[4] Vaddula, B.R., Saha, A., Varma, R.S., Leazer, J. *EJOC* 6707 (2012)
[5] Yuan, F.-Q., Han, F.-S. *OL* **14**, 1218 (2012)
[6] Song, Y., Jing, H., Li, B., Bai, D. *CEJ* **17**, 8731 (2011)
[7] Cai, Y., Song, G., Zhou, X. *ChJC* **30**, 2819 (2012)
[8] Bakherad, M., Keivanloo, A., Samangooei, S. *TL* **53**, 5773 (2012)

[9] Hanhan, M.E., Martinez-Mañez, R., Ros-Lis, J.V. *TL* **53**, 2388 (2012)
[10] Qiu, J., Wang, L., Liu, M., Shen, Q., Tang, J. *TL* **52**, 6489 (2011)
[11] Du, Z., Zhou, W., Wang, F., Wang, J.-X. *T* **67**, 4914 (2011)
[12] Peng, X., Zhu, Y., Ramirez, T.A., Zhao, B., Shi, Y. *OL* **13**, 5244 (2011)
[13] Stokes, B.J., Opra, S.M., Sigman, M.S. *JACS* **134**, 11408 (2012)
[14] Yu, J., Wang, L., Liu, M., Qiu, J., Shen, Q., Fang, L., Tang, J. *ChJC* **30**, 1114 (2012)
[15] Cai, H., Yuan, Z., Zhu, W., Zhu, G. *CC* **47**, 8682 (2011)
[16] Lu, Z., Kong, W., Yuan, Z., Zhao, X., Zhu, G. *JOC* **76**, 8524 (2011)
[17] Wu, W., Jiang, H., Gao, Y., Huang, H., Zeng, W., Cao, D. *CC* **48**, 10340 (2012)
[18] Wang, L., Li, J., Lv, Y., Zhao, G., Gao, S. *SL* 1074 (2012)
[19] Chen, X., Jin, J., Wang, Y., Lu, P. *CEJ* **17**, 9920 (2011)
[20] Alcaide, B., Almendros, P., Alonso, J.M., Fernandez, I. *CC* **48**, 6604 (2012)
[21] Alcaide, B., Almendros, P., Alonso, J.M., Quiros, M.T., Gadzinski, P. *ASC* **353**, 1871 (2011)
[22] Hu, Z., Liang, D., Zhao, J., Huang, J., Zhu, Q. *CC* **48**, 7371 (2012)
[23] Wu, N., Messinis, A., Batsanov, A.S., Yang, Z., Whiting, A., Marder, T.B. *CC* **48**, 9986 (2012)
[24] Zhong, M.-J., Wang, X.-C., Zhu, H.-T., Hu, J., Liu, L., Liu, X.-Y., Liang, Y.-M. *JOC* **77**, 10955 (2012)
[25] Miao, M., Cao, J., Zhang, J., Huang, X., Wu, L. *OL* **14**, 2718 (2012)

Palladium(II) chloride –copper salts

Coupling. Active aryl species are generated from $ArSO_2Na$ for arylation of indole (at C-2), the necessary catalyst system is composed of (cod)$PdCl_2$, and $CuCl_2$.[1]

Either phenanthridines or 6-substituted phenanthridines are accessible, starting from directed coupling of 2-aminobiaryls. If the reaction employs *N*-tosylamines and butyl acrylate and executed under oxygen, it is terminated by aromatization with splitting off butyl glyoxylate,[2] but when primary amines are the coupling partners intramolecular hydroamination follows the coupling.[3]

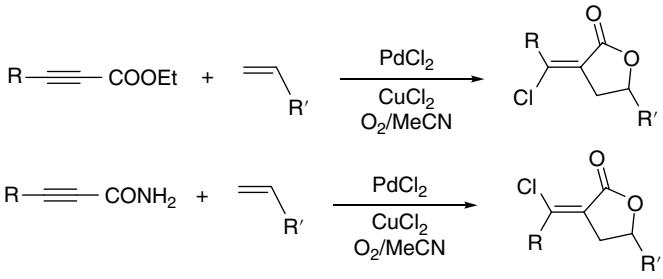
Since so many methods have been developed for amination of benzoxazole and analogs, the coupling with R_2NSO_2Cl via in situ desulfonylation by CuCN to generate active reagents[4] is probably not competitive.

Silylmethylation at the β-carbon of α,β–unsaturated esters involves C-H activation of a methyl group attached to silicon of 2-[dimethyl(*t*-butyl)silyl]pyridine.[5]

To enable coupling of ArLi (or alkenyllithiums) with bromoalkenes, a 2,1-benzoxasilole is used as a relay to canvass attack from the organolithium reagents, thereby turning the reaction into a Hiyama coupling. This method requires $PdCl_2$, CuI, and a tertiary phosphine ligand.[6]

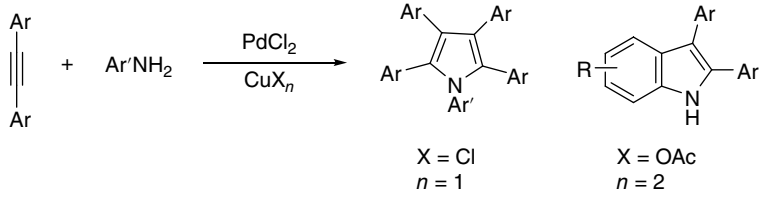
Addition. *trans*-Bromopalladation of alkynes is obviously effected by a mixture of $PdCl_2$ and $CuBr_2$. The intermediates then undergo Heck reaction with allylic alcohols. It constitutes a synthesis of δ-bromo-γ,δ-unsaturated ketones.[7] Five-membered heterocycles act as if they are Michael addends for enones.[8]

Under the typical Wacker oxidation condition, but with 1-alkenes added, 2-alkynoic acid derivatives are converted into halogenated α-alkylidene-γ-lactones.[9] Most remarkably, esters and amides furnish adducts in which the steric disposition of the halogen atom is different.



Mechanistically intriguing is the transformation of 2-allylbenzaldehydes into isocoumarins.[10] The catalyst system is conducive to Wacker oxidation (either direct or after double bond migration) and the simultaneous formation of acylpalladium species from the formyl group.

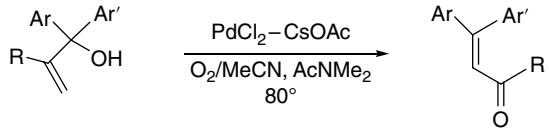
Arylamines can combine with one or two equivalents of diarylethynes.[11] The reaction conditions, particularly the copper salt being used, are critical in determining the reaction pathway.



[1] Wu, M., Luo, J., Xiao, F., Zhang, S., Deng, G.-J., Luo, H.-A. *ASC* **354**, 335 (2012)
[2] Liu, Y.-Y., Song, R.-J., Wu, C.-Y., Gong, L.-B., Hu, M., Wang, Z.-Q., Xie, Y.-X., Li, J.-H. *ASC* **354**, 347 (2012)
[3] Liang, Z., Ju, L., Xie, Y., Huang, L., Zhang, Y. *CEJ* **18**, 15816 (2012)
[4] Chen, S., Zheng, K., Chen, F. *TL* **53**, 6297 (2012)
[5] Wang, C., Ge, H. *S* 2590 (2011)
[6] Smith III, A.B., Hoye, A.T., Martinez-Solario, D., Kim, W.-S., Tong, R. *JACS* **134**, 4533 (2012)
[7] Wen, Y., Huang, L., Jiang, H., Chen, H. *JOC* **77**, 2029 (2012)
[8] Zhang, X., Yu, X., Feng, X., Bao, M. *SL* 1605 (2012)
[9] Huang, L., Wang, Q., Liu, X., Jiang, H. *ACIE* **51**, 5696 (2012)
[10] Chen, P.-Y., Huang, K.-S., Tsai, C.-C., Wang, T.-P., Wang, E.-C. *OL* **14**, 4930 (2012)
[11] Chen, X., Li, X., Wang, N., Jin, J., Lu, P., Wang, Y. *EJOC* 4380 (2012)

Palladium(II) chloride – oxidant

Oxidative rearrangement. Under oxygen the reaction of diaryl alkenyl carbinols with $PdCl_2$ furnishes β,β-diaryl-α,β-unsaturated carbonyl compounds.[1]

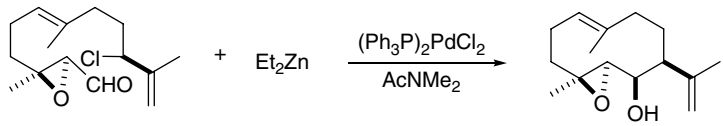


[1] Rosa, D., Orellana, A. *OL* **13**, 3648 (2011)

Palladium(II) chloride – tertiary phosphine

Addition. The ability of $PdCl_2$ along with an aminophosphine ligand to perform *trans*-additions of thiols to arylethynes has been reported.[1] Schiff base formation is the first step toward aromatization to acquire anilines from cyclohexenones.[2]

Substitution and coupling. A synthesis of epoxygermacrenol proceeds by macrocyclization involving an allyl chloride and a formyl group under the influence of Et_2Zn and $(Ph_3P)_2PdCl_2$.[3]



Alkylation of β-styrenolzinc chlorides with α-chlorobenzyl ketones is a method for building 2,3-diaryl-1,4-diones.[4] It requires (dppf) $PdCl_2$ as a catalyst. An unusual aspect in the oxidative coupling of RCHO with alcohols to form RCOOR' is that $PhCH_2Cl$ acts as the oxidant.[5]

Many procedures are already known for acquisition of diarylamines by arylation of arylamines, yet another is being added to the list that features $(Ph_3P)_2PdCl_2$ and a salicylimine.[6]

Biaryl synthesis from two ArI with better control is to derive one of them to a borylarene on treatment with R_2NBH_2, with subsequent addition of the other ArI and Cs_2CO_3 to perform Suzuki coupling [$PdCl_2$ and DPPP already present].[7] A catalyst for 2-arylation of indoles (at C-2) is composed of $PdCl_2$, Amphos [*p*-dimethylaminophenyldi-*t*-butylphosphine] and tetrachlorophthalic anhydride.[8] The same system is applicable to Negishi coupling, but the ligand influences the double bond configuration of the products when starting from (*Z*)-alkenyl halides, and TMEDA is beneficial to help maintain of configuration.[9]

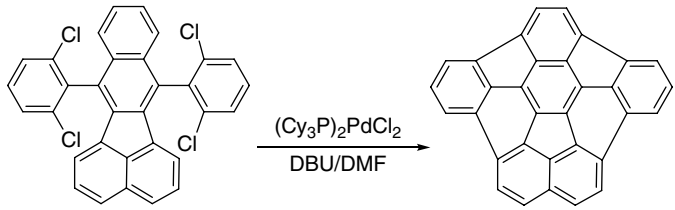
A Pd-catalyzed synthesis of 2-aryloxazolines is achieved from 2-aminoethanol, ArX and *t*-BuNC.[10]

A normal coupling course is pursued with triarylbismuths and 2-bromomethyl- or 2-acetoxymethylacrylic esters (or the acrylonitriles).[11]

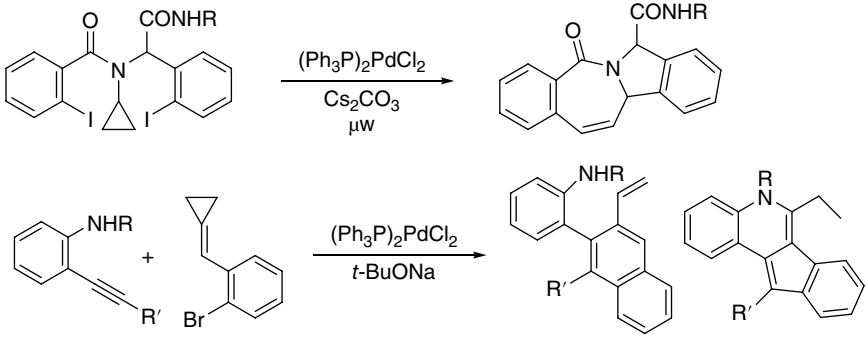
By Suzuki coupling the preparation of benzyl ethers and amines from ArOMs is accomplished in one step at the availability of XCH_2BF_3K (X= OR, NHBoc).[12,13]

For Sonogashira coupling to form diarylethynes a Pd-Au duo (the latter in the form of AuI) has been studied.[14] Those involving propynoic acid to furnish the 3-arylated acids can be caused to decarboxylate if $Cu(acac)_2$ is also present.[15] The actual Heck catalyst derived from aminophosphine-ligated $PdCl_2$ is identified as nanoparticles.[16]

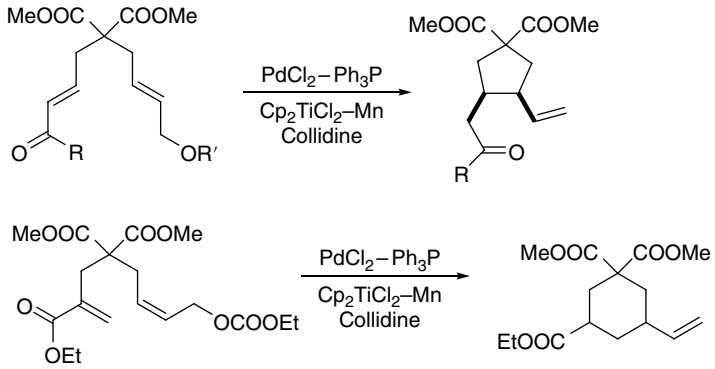
Shapiro reaction intermediates from decomposition of tosylhydrazones are useful Heck reaction partners, therefore α-alkylstyrenes are readily synthesized.[17] A fourfold intramolecular coupling (dehydrochlorination) of a naphtha[1,2-*b*]acenaphthylene is an expedient way to construct an eleven-ring polyaromatic hydrocarbon.[18]



In dimerizative coupling of *o*-bromobenzamides to provide phenanthridones whether one amide group is lost depends on solvent (retention in dioxane, loss in DMF).[19] A cyclopropyl group attached to the amidic nitrogen atom of an *o*-iodobenzamide can break open to participate in a coupling reaction and another iodoarene unit present can be involved in concert, to create two rings in one step.[20] In a different situation a cyclopropane opens to utilize its base carbon atom in CC or CN bond formation.[21]



Quinoline synthesis from anilines and (*Z*)-1-bromo-1-alken-3-ynes probably proceeds via *N*-alkenylation then cyclization.[22] Reductive cyclization of 2,7-nonadienyl carbonyl compounds bearing an oxygenated function at C-9 is initiated by an action of Cp_2TiCl.[23] Isomeric substrates with the electron-deficient group shifted to the internal sp^2-carbon generate 6-membered ring products.



Oxidative decarboxylation. Carboxylic acids RCH_2CH_2COOH are degraded to $RCH{=}CH_2$ on heating with $PdCl_2$, Ph_3P and Ac_2O ($T > 200^o$).[24]

[1] Gerber, R., Frech, C.M. *CEJ* **18**, 8901 (2012)
[2] Girard, S.A., Hu, X., Knauber, T., Zhou, F., Simon, M.-O., Deng, G.-J., Li, C.-J. *OL* **14**, 5606 (2012)
[3] Foo, K., Usui, I., Götz, D.C.G., Werner, E.W., Holte, D., Baran, P.S. *ACIE* **51**, 11491 (2012)
[4] Liu, C., Deng, Y., Wang, J., Yang, Y., Tang, S., Lei, A. *ACIE* **50**, 7337 (2011)
[5] Liu, C., Tang, S., Zheng, L., Liu, D., Zhang, H., Lei, A. *ACIE* **51**, 5662 (2012)
[6] Liu, T.-P., Cheng, Q., Song, W.-J., Cai, L.-Z., Tao, X.-C. *SL* 2333 (2012)
[7] Marciasini, L., Richy, N., Vaultier, M., Pucheault, M. *CC* **48**, 1553 (2012)
[8] Lu, G., Cai, C. *SL* 2992 (2012)
[9] Krasovskiy, A., Lipshutz, B.H. *OL* **13**, 3818 (2011)
[10] Boissarie, P.J., Hamilton, Z.E., Lang, S., Murphy, J.A., Suckling, C.J. *OL* **13**, 6256 (2011)
[11] Rao, M.L.N., Giri, S. *EJOC* 4580 (2012)
[12] Molander, G.A., Beaumard, F. *OL* **13**, 3948 (2011)
[13] Molander, G.A., Shin, I. *OL* **14**, 3138 (2012)
[14] Lauterbach, T., Livendahl, M., Rosellon, A., Espinet, P., Echavarren, A.M. *OL* **12**, 3006 (2010)
[15] Park, K., Palani, T., Pyo, A., Lee, S. *TL* **53**, 733 (2012)
[16] Oberholzer, M., Gerber, R., Frech, C.M. *ASC* **354**, 627 (2012)
[17] Ojha, D.P., Prabhu, K.R. *JOC* **77**, 11027 (2012)
[18] Wu, T.-C., Hsin, H.-J., Kuo, M.-Y., Li, C.-H., Wu, Y.-T. *JACS* **133**, 16319 (2011)
[19] Donati, L., Leproux, P., Prost, E., Michel, S., Tillequin, F., Gandon, V., Poree, F.-H. *CEJ* **17**, 12809 (2011)
[20] Dos Santos, A., ElKaim, L., Grimaud, L., Ramozzi, R. *SL* 438 (2012)
[21] Li, S., Luo, Y., Wang, X., Guo, M., Wu, J. *CAJ* **7**, 1691 (2012)
[22] Wang, Y., Liao, Q., Zhao, P., Xi, C. *ASC* **353**, 2659 (2011)
[23] Millan, A., Martin-Lasanta, A., Miguel, D., de Cienfuegos, L.A., Cuerva, J.M. *CC* **47**, 10470 (2011)
[24] Kraus, G.A., Riley, S. *S* 3003 (2012)

Palladium(II) chloride – tertiary phosphine – carbon monoxide

Carbonylative coupling. Introduction of an ester group to indole by reaction with CO and ROH, by catalysis of $(Ph_3P)_2PdCl_2$, occurs at the nitrogen atom, and to *N*-substituted indoles, at C-3. Thiophene is functionalized at C-2.[1]

A benzylic position is alkoxycarbonylated when $(t\text{-BuO})_2$ is added to exert the proper activation.[2] Carbonylation of α-chloro ketones to synthesize α-substituted β-keto esters is carried out with $(Ph_3P)_2PdCl_2$ and Xantphos under CO.[3]

[1] Zhang, H., Liu, D., Chen, C., Liu, C., Lei, A. *CEJ* **17**, 9581 (2011)
[2] Xie, P., Xie, Y., Qian, B., Zhou, H., Xia, C., Huang, H. *JACS* **134**, 9902 (2012)
[3] Wahl, B., Bonin, H., Montreux, A., Giboulot, S., Liron, F., Poli, G., Sauthier, M. *ASC* **354**, 3105 (2012)

Palladium(II) chloride – tertiary phosphine – copper salts

Coupling. The Heck reaction between ArX and 5-aryl-1-alkyn-2-en-3-ols furnishes cross-conjugated dienones carrying two aryl groups at the chain termini.[1] Organozinc chlorides couple with Ar_2Te by $(dppf)PdCl_2{\cdot}CH_2Cl_2$ and CuI in THF.[2]

Annulative coupling. An efficient synthetic application of *o*-functionalized β,β-dibromostyrenes is to exploit both intramolecular and intramolecular coupling reactions, which is enabled by a combination of Pd(II) and Cu(I) salts.[3]

Sonogashira coupling of *o*-bromobenzaldehyde in the presence of $t\text{-BuNH}_2$ leads to 3-substituted isoquinolines as de-*t*-butylation is driven by aromatization after an intramolecular addition of the derived imines.[4] Tricyclic compounds are readily formed with an initial Sonogashira coupling involving ethyl oct-2-ene-7-ynoate and an *o*-iodobenzamide, due to a terminating Heck reaction.[5]

[1] Gendron, T., Davioud-Charvet, E., Müller, T.J.J. *S* 3829 (2012)
[2] Stefani, H.A., Pena, J.M., Manarin, F., Ando, R.A., Leal, D.M., Petragnanai, N. *TL* **52**, 4398 (2011)
[3] Chen, W., Wang, M., Li, P., Wang, L. *T* **67**, 5913 (2011)
[4] Lin, L., Wu, Q., Huang, S., Yang, G. *ChJC* **30**, 1075 (2012)
[5] Martinez, C., Aurrecoechea, J.M., Madich, Y., Denis, J.G., de Lera, A.R., Alvarez, R. *EJOC* 99 (2012)

Palladium(II) hydroxide

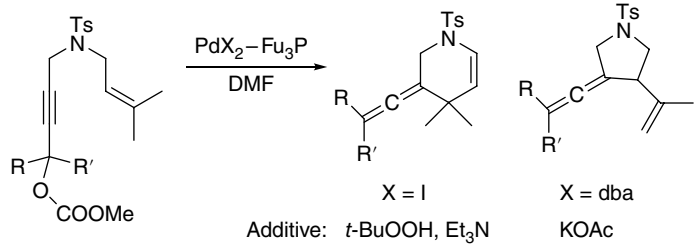
Hydrogenation.[1] In comparison with Pd/C, the more powerful $Pd(OH)_2/C$ effects hydrogenation of ArCN to yield $ArCH_3$.

Coupling. Deposition of $Pd(OH)_2$ on magnetite gives rise to a ligand-free and readily recoverable catalyst for Suzuki coupling.[2] Heating a mixture of $ArSO_2Na$ and RCN in the presence of $Pd(OH)_2$ and 1,10-phenanthroline in aqueous dioxane furnishes ArCOR.[3]

[1] Ouellet, E., Poirier, D. *SL* 2025 (2011)
[2] Cano, R., Ramon, D.J., Yus, M. *T* **67**, 5432 (2011)
[3] Liu, J., Zhou, X., Rao, H., Xiao, F., Li, C.-J., Deng, G.-J. *CEJ* **17**, 7996 (2011)

Palladium(II) iodide

Substitution. 2-Alkyn-7-en-1-yl carbonates undergo cyclization to 6-membered ring products containing an exocyclic allene linkage. However, changing the catalyst from PdI_2 (and $t\text{-BuOOH}$) to $(dba)_2Pd$ a new pathway leading to 5-membered ring compounds is adopted.[1]

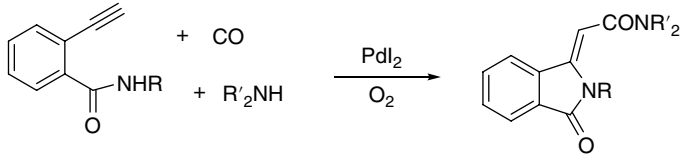


[1] Zhao, S.-C., Ji, K.-G., Lu, L., He, T., Zhou, A.-X., Yan, R.-L., Ali, S., Liu, X.-Y., Liang, Y.-M. *JOC* **77**, 2763 (2012)

Palladium(II) iodide – carbon monoxide

Heterocycle synthesis. 3-Alkyne-1,2-diols are subject to cyclizative coupling to incorporate CO and an alcohol, and dehydration to yield furan-3-carboxylic esters or, if C-1 is a quaternary carbon, the 4-methylene-4,5-dihydrofuran derivatives.[1] The *N*-Boc aminoalcohols are similarly transformed into pyrrolecarboxylic esters.[2]

Two equivalents of CO are consumed to react with *o*-ethynylbenzamides and amines under oxygen. Isoindolinone-3-ylideneacetamides are obtained.[3]

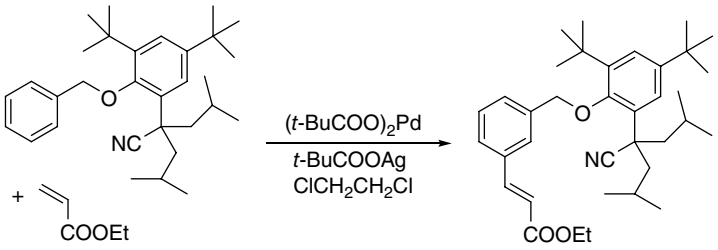


[1] Gabriele, B., Mancuso, R., Maltese, V., Veltri, L., Salerno, G. *JOC* **77**, 8657 (2012)
[2] Gabriele, B., Veltri, L., Mancuso, R., Salerno, G., Maggi, S., Aresta, B.M. *JOC* **77**, 4005 (2012)
[3] Gabriele, B., Mancuso, R., Ziccarelli, I., Slarno, G. *TL* **53**, 6694 (2012)

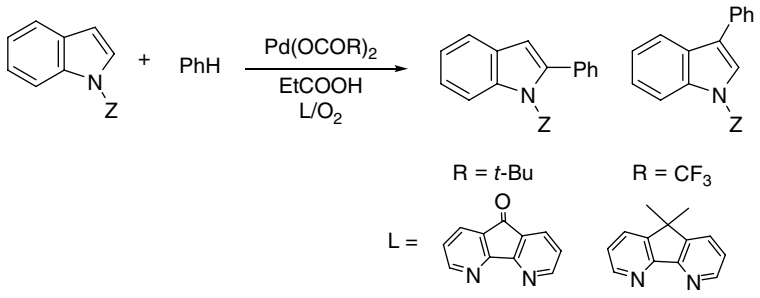
Palladium(II) pivalate

Directed functionalization. Catechols are made from phenols via the hydroxydi-*t*-butylsilyl ethers. Dehydrogenation is then effected by $Pd(OPiv)_2$ and $PhI(OAc)_2$, and finally, decomposition by fluoride ion.[1]

A cyano group-directed Heck reaction has been designed such that an alkenyl substituent is selectively introduced into a *m*-position of benzyl alcohols.[2]



Ligand and counterion of Pd(II) are determining factors to control arylation of *N*-protected indoles, at C-2 or C-3.[3]



[1] Huang, C., Ghavtadze, N., Chattopadhyay, B., Gevorgyan, V. *JACS* **133**, 17630 (2011)
[2] Truong, T., Daugulis, O. *ACIE* **51**, 11677 (2012)
[3] Campbell, A.N., Meyer, E.B., Stahl, S.S. *CC* **47**, 10257 (2011)

Palladium(II) tetrafluoroborate

Coupling. Access to allylboronic acids is enabled by coupling of allylic alcohols with $B_2(OH)_4$, the $(MeCN)_4Pd(BF_4)_2$ complex or H_2PdCl_4 can serve as catalyst, and suitable solvents are MeOH and aqueous DMSO.[1]

Phenylboronic acids *o*-substituted by an *N*-*t*-butanesulfinylaminomethylene group undergo coupling with alkynes to furnish 1-aminoindene derivatives.[2]

[1] Raducan, M., Alam, R., Szabo, K.J. *ACIE* **51**, 13050 (2012)
[2] Yu, X., Lu, X. *ASC* **353**, 2805 (2011)

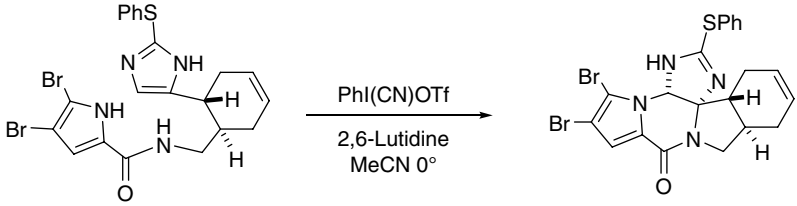
Palladium(II) triflate

Coupling. Formation of cinnamylamines is observed when styrene and $CH_2(NR_2)_2$ are treated with $(MeCN)_2Pd(OTf)_2$ and Xantphos in isopropanol.[1]

[1] Xie, Y., Hu, J., Wang, Y., Xia, C., Huang, H. *JACS* **134**, 20613 (2012)

Phenyl(cyano)iodine(III) triflate

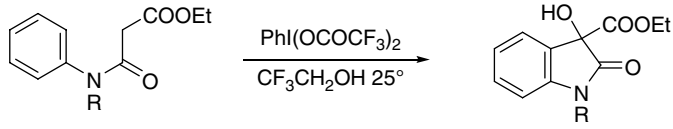
Cyclization. Intramolecular addition of pyrrolyl and amidic groups to an imidazole ring (formation of two NC bonds) is initiated by oxidation of a thio residue by PhI(CN)OTf.[1]



[1] Feldman, K.S., Nuriye, A.Y. *OL* **12**, 4532 (2010)

Phenyliodine(III) bis(trifluoroacetate), (PIFA)

Oxidation-cyclization. Malonanilide-esters are oxidized and cyclize to afford α-hydroxyoxindolecarboxylic esters on exposure to $PhI(OCOCF_3)_2$ at room temperature.[1] 3-Acylindoles are produced from 2-aryl-3-amino-2-alkenones.[2]



Tosyloxylation. Anilides are tosyloxylated at the *p*-position. The reagent package includes 1.5 equivalents each of $PhI(OCOCF_3)_2$ and BF_3OEt_2, 3 equivalents of $TsOH{\cdot}H_2O$.[3]

Oxidative cycloisomerization. In trifluoroacetic acid and CH_2Cl_2, 2-propargyl-1,3-dicarbonyl compounds give furfuryl alcohols as a result of cyclization and oxidation at the terminal carbon (originally the *sp*-terminus) and hydrolytic workup. Excess PIFA would further oxidize the alcohols into aldehydes.[4]

[1] Wang, J., Yuan, Y., Xiong, R., Zhang-Negrerie, D., Du, Y., Zhao, K. *OL* **14**, 2210 (2012)
[2] Ban, X., Pan, Y., Lin, Y., Wang, S., Du, Y., Zhao, K. *OBC* **10**, 3606 (2012)
[3] Liu, H., Xie, Y., Gu, Y. *TL* **52**, 4324 (2011)
[4] Saito, A., Anzai, T., Matsumoto, A., Hanzawa, Y. *TL* **52**, 4658 (2011)

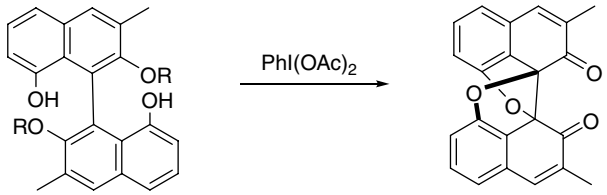
Phenyliodine(III) diacetate

Oxidation. A modified $PhI(OAc)_2$ in which the *p*-position is connected through a three-carbon chain to a pyrrolidinium moiety has been prepared and used in conjunction with TEMPO to oxidize alcohols.[1] The combination of $PhI(OAc)_2$ and TEMPO releases HOAc which is helpful for exchange of a hydroxyl group to amines.[2]

Oxidation of benzylamines by $PhI(OAc)_2$ furnishes aldehydes.[3] Another procedure indicates oxidative condensation of aldehydes and amines to form amides with or without catalysis by *N*-hydroxysuccinimide.[4,5]

Along with an azaadamantane *N*-oxy, the TEMPO analog, the hypervalent iodine compound effects glycol cleavage that results in production of carboxylic acids.[6]

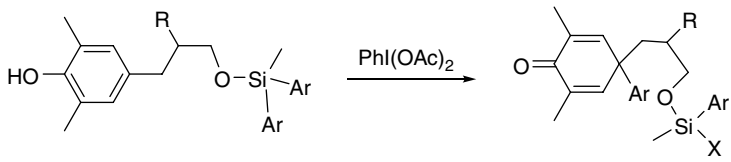
Selective oxidation and OC-coupling is observed on treatment of 1,1′-binaphthalene-2, 2′,8,8′-tetrols with $PhI(OAc)_2$.[7] High yields of spirocyclic products is generated.



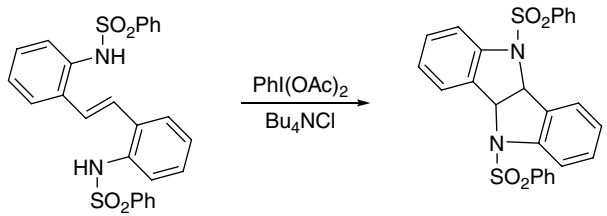
Benzylic acetoxylation is performed with I_2 and $TsNH_2$ as catalyst.[8] *N*-Boc tetrahydrocarbazole is acetoxylated at C-1, and when that position is substituted (e.g., monomethylated), the reaction site is switched to C-4.[9]

Substitution. Nuclear imidation of aromatics such as *p*-xylene is observed.[10,11] Electrophilic imidoiodine(III) intermediates are proposed. Interestingly, reaction with $(PhSO_2)_2NH$ takes place at a benzylic position.

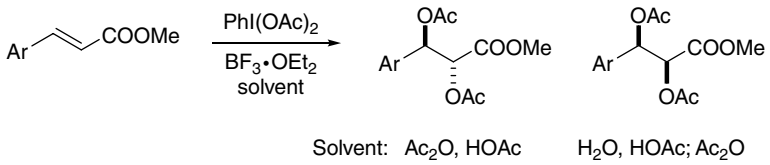
Aryl group transfer from a silicon atom in a sidechain of 4-substituted phenols accomplishes dearomatization.[12]



Addition. 1,2-Diamination of alkenes with Ts_2NH, as promoted by $PhI(OAc)_2$, is quite general, as enones, styrenes as well as common alkenes undergo the addition.[13] 1,4-Diamaination occurs with 1,3-butadiene, but for 1-aryl-1,3-butadiene only the terminal double bond is attacked.[14] Fused head-to-tail biindolines are readily constructed from 2,2′-bisphenylsulfonylstilbenes.[15]



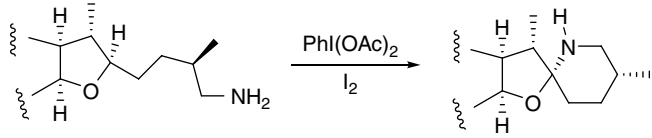
Both electron-rich and electron-poor alkenes can be dicarboxylated. The reaction on cinnamic esters is enlightening as by slight variation of the procedure either *syn*- or *anti*-adducts can be acquired.[16] Different kinds of 2,3-dicarboxylatoindolines are generated at will with added RCOOH.[17]



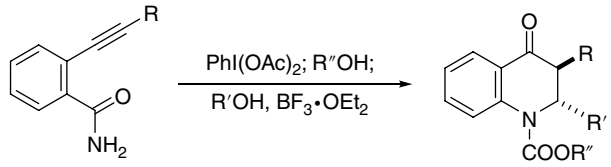
α-Acetoxy-β-amino esters are prepared from 2-alkynoic esters by reaction with amines and $PhI(OAc)_2$.[18]

Annulation. The oxidative cyclization of *N*-tosyl-4-pentynylamines with C-2 quaternized still leads to 2-acetoxymethylpyrroles because aromatization is a strong driving force for group migration.[19] For cyclization of enamides (to oxazoles)[20] and of *N*-arylamidines (to benzimidazoles),[21] quite different additives ($BF_3{\cdot}OEt_2$ and Cs_2CO_3, respectively) are used.

2-Acetaminobiphenyl undergoes dehydrogenation to yield *N*-acetylcarbazole.[22] Generation of simple nonstabilized aminyl radicals and their successful cyclization has been realized.[23]



A synthesis of tetrahydroquinolin-4-ones from *o*-alkynylbenzamides and aldehydes starts from Hofmann rearrangement. Then trapping of the aryl isocyanates by an alcohol, imination, hydration of the triple bond and Mannich reaction follow.[24]



Cross-coupling of arenesulfonic acids and arenes in the presence of $(NH_4)_2S_2O_8$ leads to formation of sultones with the heteroatom bridge joining two *o*-carbon atoms of the biaryl system.[25]

A facile access to 1,4-benzoxazine derivatives is by oxidation of *o*-aminophenol to *o*-quinone monoimine and in situ trapping by vinyl ethers and vinyl sulfides.[26]

o-Alkoxyphenyliodine(III) diacetates are readily obtained. These compounds form iodonium ylides on reaction with dimethyl malonate that show good solubility in common organic solvents (CH_2Cl_2, acetone, etc.) and superior reactivity in the Rh-catalyzed cyclopropanation.[27]

Degradation. Aroic acids possessing an electron-rich nucleus are degraded to aryl iodides by a mixture of $PhI(OAc)_2$ and LiI in hexafluoroisopropanol.[28] 2-Oxazolidinone-4-carboxylic acids apparently generate acyliminium species through decarboxylation, and such compounds readily react with nucleophiles including enol silyl ethers, allylsilanes and furan.[29]

[1] Suzuki, Y., Iinuma, M., Moriyama, K., Togo, H. *SL* 1250 (2012)
[2] Guerin, C., Bellosta, V., Guillamot, G., Cossy, J. *OL* **13**, 3534 (2011)
[3] Desjardins, S., Jacquemot, G., Canesi, S. *SL* 1497 (2012)
[4] Yao, H., Tang, Y., Yamamoto, K. *TL* **53**, 5094 (2012)
[5] Prasad, V., Kale, R.R., Mishra, B.B., Kumar, D., Tiwari, V.K. *OL* **14**, 2936 (2012)
[6] Shibuya, M., Shibuta, T., Fukuda, H., Iwabuchi, Y. *OL* **14**, 5010 (2012)
[7] Podlesny, E.E., Carroll, P.J., Kozlowski, M.C. *OL* **14**, 4862 (2012)
[8] Baba, H., Moriyama, K., Togo, H. *TL* **52**, 4303 (2011)
[9] Zaimoku, H., Hatta, T., Taniguchi, T., Ishibashi, H. *OL* **14**, 6088 (2012)
[10] Kim, H.J., Kim, J., Cho, S.H., Chang, S. *JACS* **133**, 16382 (2011)
[11] Kantak, A.A., Potavathri, S., Barham, R.A., Romano, K.A., DeBoef, B. *JACS* **133**, 19960 (2011)
[12] Jacquemot, G., Canesi, S. *JOC* **77**, 7588 (2012)
[13] Souto, J.A., Gonzalez, Y., Iglesias, A., Zian, D., Lishchynskyi, A., Muñiz, K. *CAJ* **7**, 1103 (2012)
[14] Lishchynskyi, A., Muñiz, K. *CEJ* **18**, 2212 (2012)
[15] Kim, H.J., Cho, S.H., Chang, S. *OL* **14**, 1424 (2012)
[16] Zhong, W., Yang, J., Meng, X., Li, Z. *JOC* **76**, 9997 (2011)
[17] Liu, Q., Zhao, Q.Y., Liu, J., Wu, P., Yi, H., Lei, A. *CC* **48**, 3239 (2012)
[18] Liu, W., Chen, C., Zhang, Q. *OBC* **9**, 6484 (2011)
[19] Mo, D.-L., Ding, C.-H., Dai, L.-X., Hou, X.-L. *CAJ* **6**, 3200 (2011)
[20] Zheng, Y., Li, X., Ren, C., Zhang-Negrerie, D., Du, Y., Zhao, K. *JOC* **77**, 10353 (2012)
[21] Huang, J., He, Y., Wang, Y., Zhu, Q. *CEJ* **18**, 13964 (2012)
[22] Antonchick, A.P., Samanta, R., Kulikov, K., Lategahn, J. *ACIE* **50**, 8605 (2011)
[23] Kong, M., Lee, S. *OL* **13**, 4766 (2011)
[24] Okamoto, N., Takeda, K., Ishikura, M., Yanada, R. *JOC* **76**, 9139 (2011)
[25] Li, F., Jiang, T., Cai, H., Wang, G. *ChJC* **30**, 2041 (2012)
[26] Bodipati, N., Peddinti, R.K. *OBC* **10**, 1958 (2012)
[27] Zhu, C., Yoshimura, A., Ji, L., Wei, Y., Nemykin, V.N., Zhdankin, V.V. *OL* **14**, 3170 (2012)
[28] Hamamoto, H., Hattori, S., Takemaru, K., Miki, Y. *SL* 1563 (2011)
[29] Boto, A., Romero-Estudillo, I. *OL* **13**, 3426 (2011)

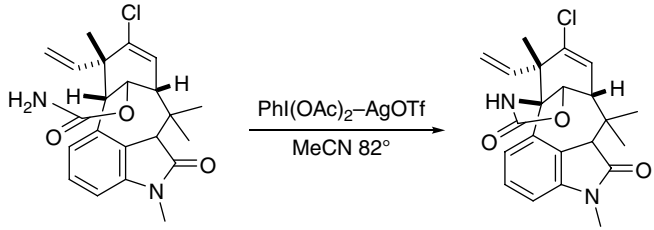
Phenyliodine(III) diacetate – heavy metal salts

Acetoxylation. Arenes are acetoxylated by $PhI(OAc)_2$ with $AuCl_3$ or $(Ph_3P)AuCl$ as catalyst,[1,2] and it results in polysubstitution with the iodine compound in suprastoichiometric quantities.

Coupling. Demetallative alkoxylation of Ar_3Bi by tertiary alcohols is carried out with the hypervalent iodine reagent and $Cu(OAc)_2$ under oxygen.[3]

As coupling partners to conjugate with alkenes, the reaction of $ArI(OAc)_2$ is executed by a mixture of $Pd(OAc)_2$ and Ag_2CO_3 while TEMPO is employed to the requisite oxidation state of the reactant.[4]

CH functionalization. Primary amides are oxidized to nitrenes. Given a favorable C-H bond to insert, lactam formation can be quite selective. Advantage of this aspect has been taken in a synthesis of the welwitindolinones.[5]



[1] Qiu, D., Zheng, Z., Mo, F., Xiao, Q., Tian, Y., Zhang, Y., Wang, J. *OL* **13**, 4988 (2011)
[2] Pradal, A., Faudot dit Bel, P., Toullec, P.Y., Michelet, V. *S* 2463 (2012)
[3] Harada, S., Hayashi, D., Sato, I., Hirama, M. *SL* 405 (2012)
[4] Evdokimov, N.M., Kornienko, A., Magedov, I.V. *TL* **52**, 4327 (2011)
[5] Quasdorf, K.W., Huters, A.D., Lodewyk, M.W., Tantillo, D.J. *JACS* **134**, 1369 (2012)

Phenyliodine(III) *t*-butylperoxide

Oxidation. The reagent is prepared from $PhI(OAc)_2$ and *t*-BuOOH. It is used to oxidize an unactivated methylene group as directed by a distant C=O.[1] Benzylic azides are transformed into ArCN or ArCOR, depending on the substitution pattern.[2]

[1] Zhao, Y., Yim, W.-L., Tan, C.K., Yeung, Y.-Y. *OL* **13**, 4308 (2011)
[2] Zhao, Y., Chew, X., Leung, G.Y.C., Yeung, Y.-Y. *TL* **53**, 4766 (2012)

Phenyliodine(III) dichloride

Isocyanates. The reagent causes oxidation of alcohols, condensation with NaN_3 and Curtius rearrangement, thereby completing the transforming of RCH_2OH into RN=C=O.[1]

[1] Zhang, C., Wang, W.-K., He, T. *S* 3006 (2012)

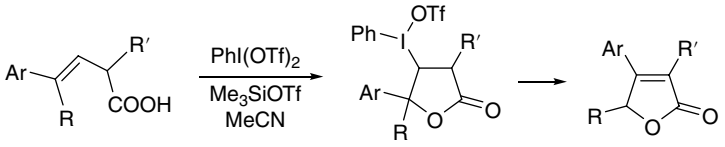
Phenyliodine(III) tosylimide

Tosylamination.[1] Analogs in which an alkoxy group is placed in an *o*-position to the iodine atom are more soluble in organic solvents. These reagents have been used in tosylamination of enol silyl ethers, adamantane (at C-1), and aziridination of alkenes, each reaction with a different catalyst.

[1] Yoshimura, A., Nemykin, V.N., Zhdankin, V.V. *CEJ* **17**, 10538 (2011)

Phenyliodine(III) triflate

Oxidative cyclization. Treatment of homocinnamic acids with $PhI(OTf)_2$ and Me_3SiOTf causes them to cyclize with aryl group migration.[1]



[1] Singh, F.V., Rehbein, J., Wirth, T. *CO* **1**, 245 (2012)

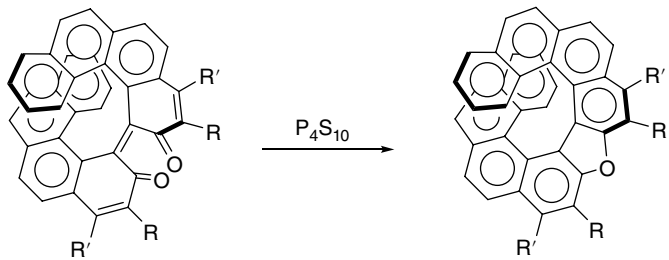
Phenyltrifluorosilane

Glycosylation. The reagent mediates the anomeric substitution of a glycosyl trichloroacetimidate by the alkoxy group of an alcohol.[1]

[1] Kumar, A., Geng, Y., Schmidt, R.R. *ASC* **354**, 1489 (2012)

Phosphorus(V) sulfide

Oxa[9]helicenes.[1] The enedione unit in the dimers of benzophenanthrenones are condensed to form a furan ring on treatment with P_4S_{10} or Lawesson's reagent.

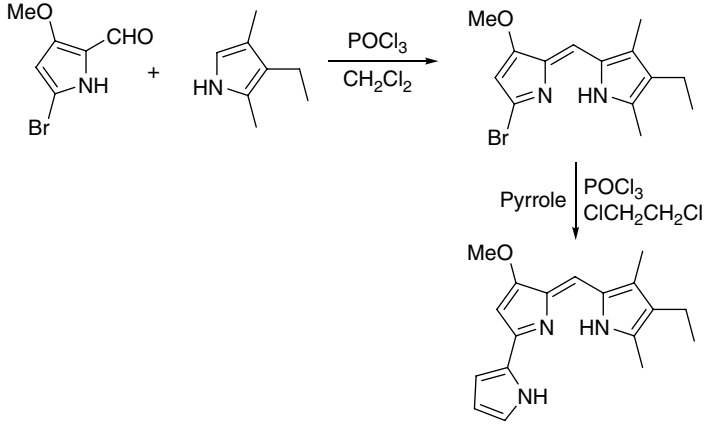


Thioamides.[2] Beckmann rearrangement of ketoximes with P_4S_{10} in hot benzene yields thioamides. The reaction of benzaldoxime leads to primary thiobenzamide.

[1] Salim, M., Akutsu, A., Kimura, T., Minabe, M., Karikomi, M. *TL* **52**, 4518 (2011)
[2] Li, J., Cheng, C., Zhang, X., Li, Z., Cai, F., Xue, Y., Liu, W. *ChJC* **30**, 1687 (2012)

Phosphoryl chloride

Condensation.[1] Dipyrromethenes are assembled. Further condensation of bromopyrroles is mediated by $POCl_3$.



[1] Yu, C., Jiao, L., Tan, X., Wang, J., Xu, Y., Wu, Y., Yang, G., Wang, Z., Hao, E. *ACIE* **51**, 7688 (2012)

Pinacol

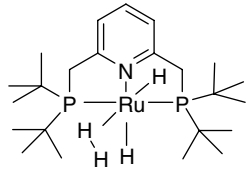
Reduction. Pinacol acts as a reducing agent for Mo(VI)-catalyzed reactions: $ArNO_2$ to $ArNH_2$, and R_2SO to R_2S. The byproducts are acetone and water.[1]

[1] Garcia, N., Garcia-Garcia, P., Fernandez-Rodriguez, M.A., Rubio, R., Pedrosa, M.R., Arnaiz, F.J., Sanz, R. *ASC* **354**, 321 (2012)

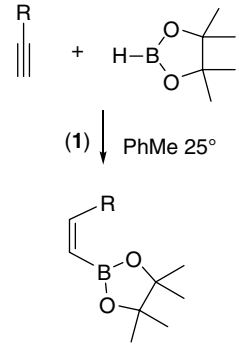
Pinacolborane

Reduction. Pinacolborane is activated by *t*-BuONa to deliver the hydride to ketones.[1]

Hydroboration. (*Z*)-1-pinacolborylalkenes are obtained by hydroboration of 1-alkynes using the Ru complex **1** as catalyst.[2]



(**1**)



[1] Query, I.P., Squier, P.A., Larsen, E.M., Isley, N.A., Clark, T.B. *JOC* **76**, 6452 (2011)
[2] Gunanathan, C., Hölscher, M., Pan, F., Leitner, W. *JACS* **134**, 14349 (2012)

Platinum

Reduction. The Pt/C catalyst is suitable for hydrogenation of indoles in water to provide indolines, and an acid additive is beneficial.[1]

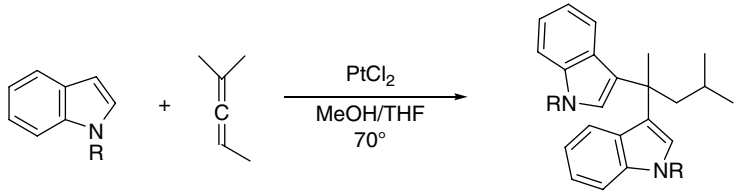
Hydrodechlorination of 1,1,1-trichloroalkanes affords $RCHCl_2$,[2] whereas the ease of hydrodehalogenation of ArX by Pt/C (and with Na_2CO_3 to neutralize the acid liberated) in aqueous isopropanol follows the trend of X = F > Cl > Br >> I.[3]

Over Pt/Fe_3O_4 the hydrogenation of chloronitrobenzenes furnishes chloroanilines.[4] Platinum nanowires are catalytic in reductive amination of carbonyl compounds with ammonia or NH_4OAc.[5] The bimetallic Pt-Sn species deposited on γ-Al_2O_3 is useful for the conversion of 1,ω-diols to the corresponding diamines.[6]

[1] Kulkarni, A., Zhou, W., Török, B. *OL* **13**, 5124 (2011)
[2] Imanishi, T., Fujiwara, Y., Sawama, Y., Monguchi, Y., Sajiki, H. *ASC* **354**, 771 (2012)
[3] Sawama, Y., Yabe, Y., Shigetsura, M., Yamada, T., Nagata, S., Fujiwara, Y., Maegawa, T., Monguchi, Y., Sajiki, H. *ASC* **354**, 777 (2012)
[4] Lian, C., Liu, H., Xiao, C., Yang, W., Zhang, K., Liu, Y., Wang, Y. *CC* **48**, 3124 (2012)
[5] Qi, F., Hu, L., Lu, S., Cao, X., Gu, H. *CC* **48**, 9631 (2012)
[6] Wang, L., He, W., Wu, K., He, S., Sun, C., Yu, Z. *TL* **52**, 7103 (2011)

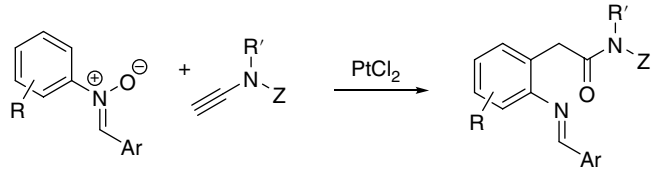
Platinum(II) chloride

Addition. Hydrosilanes and diorganoboranes add to 1-alkyn-3-ols in the Markovnikov sense under the influence of $PtCl_2$ and XPhos.[1] *N*-Protected indoles and allenes combine to form 2:1 adducts.[2]

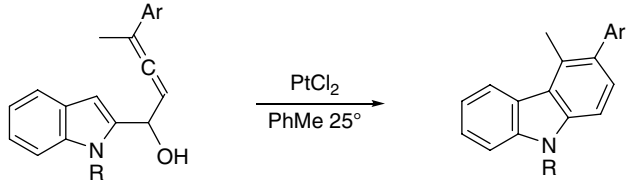


Formation of pyrroloazepinones from *N*-alkynoylaminomethylpyrroles as catalyzed by $PtCl_2$ is in contrast to the Au(I)-catalyzed cyclization (that leads to pyrrolopyridones).[3]

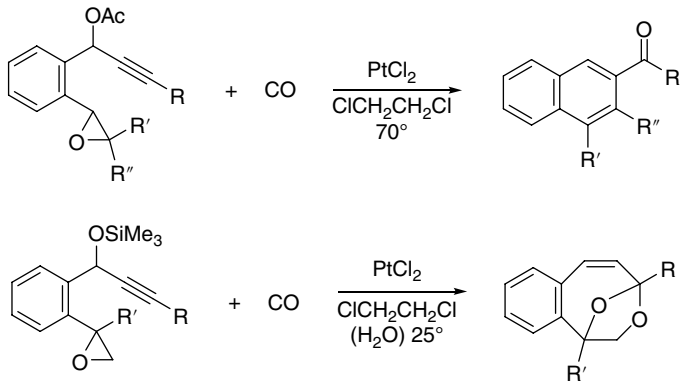
Ynamides activated by $PtCl_2$ are attacked by nitrones and those derived from anilines follow a coupling pathway that leads to arylacetamides.[4]



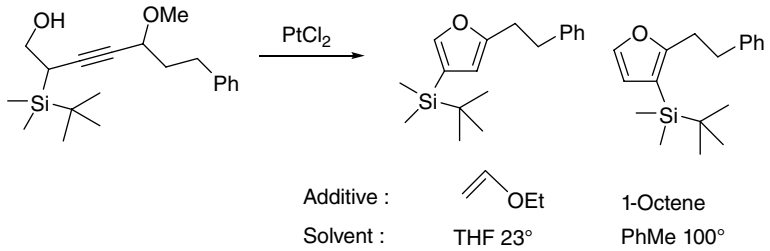
Substitution. Catalytic activity of $PtCl_2$ (with a phosphine ligand) in promoting the conversion of allylic alcohols into amines is established.[5] The dehydrative cyclization of allenyl 2-indolyl carbinols involves group migration.[6]



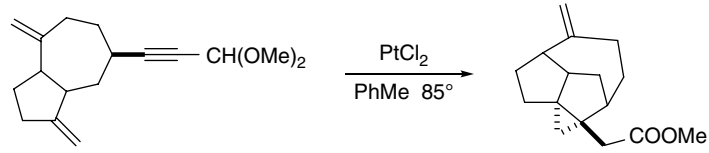
Cyclization. The dual effect of $PtCl_2$ on propargyl acetate and epoxide functionalities causes molecules containing such in proximity to engage in 1,3-acyloxy shift and isomerization to carbonyl compounds, respectively. Subsequent aldol reaction can lead to ring closure.[7]



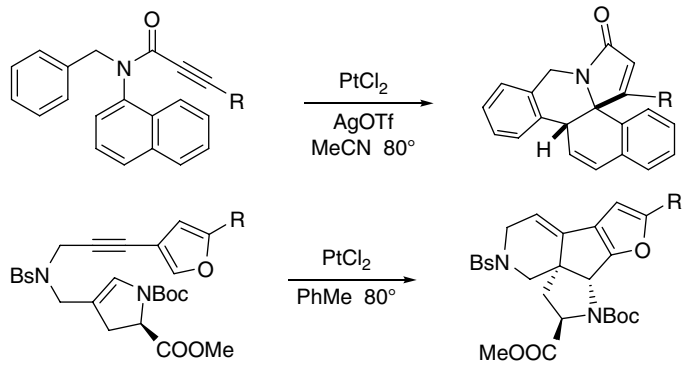
The interesting aspect of furan formation by elimination of a propagylic methoxy group (as MeOH) depicted in the following equation is that an additive can influence group migration (H vs. Si) during aromatization.[8]



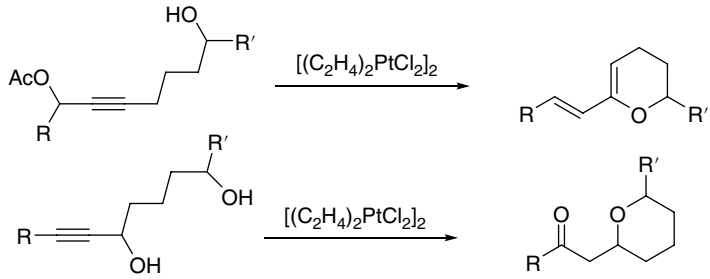
1,6-Enynes are directed by $PtCl_2$ to cyclize, giving bicycle[4.1.0]hept-2-enes.[9,10] A most intriguing example of the cyclization is shown by the elaboration of echinopine-B.[11]



Activation of the triple bond of the 2-alkynamides of *N*-benzyl-α-naphthylamine triggers cyclization that a ring of the naphthalene moiety is dearomatized.[12] A more facile process is involved with participation of polarizable cyclic enamide and furan segments.[13]

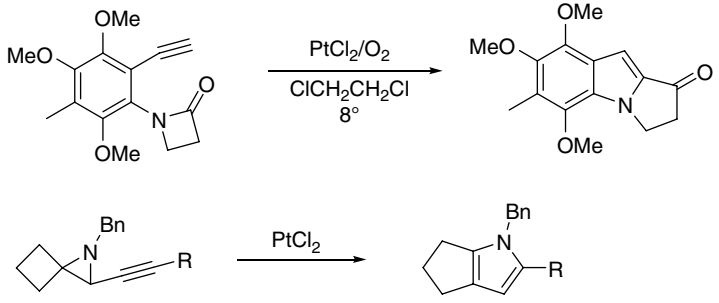


The Zeise dimer, $[(CH_2{=}CH_2)PtCl_2]_2$, effects cycloetherification of alkynols, and the formation of cyclic ethers with an α-acylmethyl chain is observed from certain alkynediols.[14]



Indenes are formed from 2-alkynylarenes on treatment with the same complex.[15]

Isomerization. An *N*-(*o*-ethynylaryl)-2-azetidinone undergoes cyclization and ring expansion in one step, to arrive at the tricyclic core of the mitomycins.[16] Also interesting is the isomerization of spiroannulated alkynylaziridines that is attended by ring enlargement.[17]



Ring-opening isomerization of 1-trimethylsilylcyclopropenes affords 3-trimethylsilyl-1, 2-alkadienes.[18] It is now shown the isomerization of propargylic esters via [1,2]- and [1.3]-acyloxy group migration ($PtCl_2$, CO, PhMe) is temperature dependent, lower temperatures favor the [1,3]-migration and higher temperatures the [1,2]-version.[19]

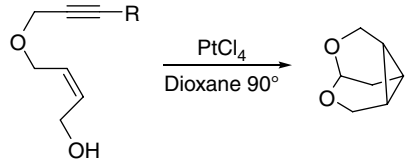
[1] McLaughlin, M.G., Cook, M.J. *CC* **47**, 11104 (2011)
[2] Muñoz, M.P., de la Torre, M.C., Sierra, M.A. *CEJ* **18**, 4499 (2012)
[3] Modha, S.G., Kumar, A., Vachhani, D.D., Sharma, S.K., Parmar, V.S., Van der Eycken, E.V. *CC* **48**, 10916 (2012)
[4] Bhunia, S., Chang, C.-J., Liu, R.-S. *OL* **14**, 5522 (2012)
[5] Das, K., Shibuya, R., Nakahara, Y., Germain, N., Ohshima, T., Mashima, K. *ACIE* **51**, 150 (2012)
[6] Kong, W., Qiu, Y., Zhang, X., Fu, C., Ma, S. *ASC* **354**, 2339 (2012)
[7] Chaudhuri, R., Pawar, S.K., Pati, K., Liu, R.-S. *ASC* **354**, 2241 (2012)
[8] Allegretti, P.A., Ferreira, E.M. *OL* **13**, 5924 (2011)
[9] Elitzin, V., Liu, B., Sharp, M., Tabet, E. *TL* **52**, 3518 (2011)
[10] Kim, S.Y., Park, Y., Son, S., Chung, Y.K. *ASC* **354**, 179 (2012)
[11] Michels, T.D., Dowling, M.S., Vanderwal, C.D. *ACIE* **51**, 7572 (2012)
[12] Shibuya, T., Noguchi, K., Tamaka, K. *ACIE* **51**, 6219 (2012)
[13] Cheng, B., Wu, F., Yang, X., Zhou, Y., Wan, X., Zhai, H. *CEJ* **17**, 12569 (2011)
[14] Liang, Q., Qian, M., Razzak, M., De Brander, J.K. *CAJ* **6**, 1958 (2011)
[15] Sato, T., Onuma, T., Nakamura, I., Terada, M. *OL* **13**, 4992 (2011)
[16] Liu, L., Wang, Y., Zhang, L. *OL* **14**, 3736 (2012)
[17] Yoshida, M., Maeyama, Y., Al-Amin, M., Shishido, K. *JOC* **76**, 5813 (2011)
[18] Li, J., Sun, C., Demerzhan, S., Lee, D. *JACS* **133**, 12964 (2011)
[19] Cho, E.J. *CEJ* **18**, 4495 (2012)

Platinum(IV) chloride

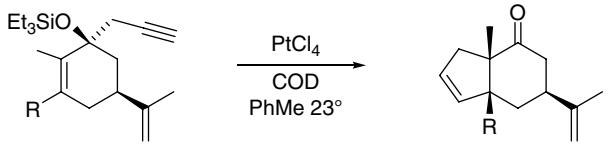
1,4-Diiodo-1,3-butadiene. Iodinative dimerization of ethyne occurs on treatment with I_2 – NaI and catalytic $PtCl_4$ in acetone.[1]

Cyclization. The ring closure of α-alkynylcinnamic esters to give 2-naphthoic esters is a straightforward result of triple bond activation and Friedel-Crafts-type reaction.[2]

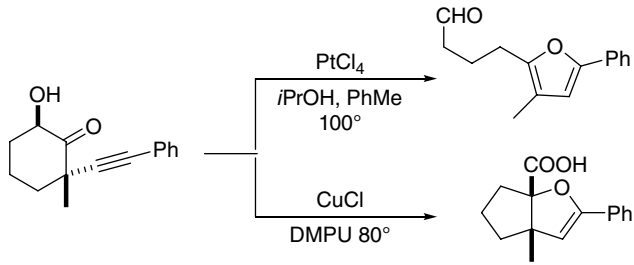
Isomerization of a triple bond to form the allene isomer is evidently precedent to cyclization of certain 1,6-enynes to tricycle[3.3.1.$0^{2,8}$]nonanes.[3]



The following example of annulation with apparent double CC bond shift proceeds via bridged ring intermediates.[4]



6-Alkynyl-2-hydroxycyclohexanones suffer from fragmentation after OC bond formation induced by $PtCl_4$ and ring contraction.[5] The adopted reaction mode is different from that elicited by CuCl.[5]



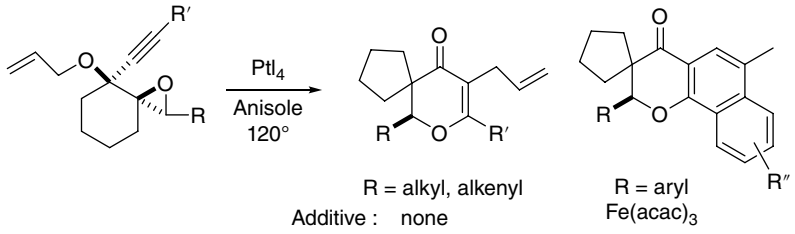
Alkyne hydration is the dominant event for 4-hydroxy-1-alken-8-ynes when exposed to $PtCl_4$ in THF containing water. It is followed by the formation of a 6-membered ring with involvement of the double bond.[6]

A study on intramolecular hydroarylation of aryl 2-alkynoates has revealed the complementary utility of $PtCl_4$ and Au-Ag catalysts.[7]

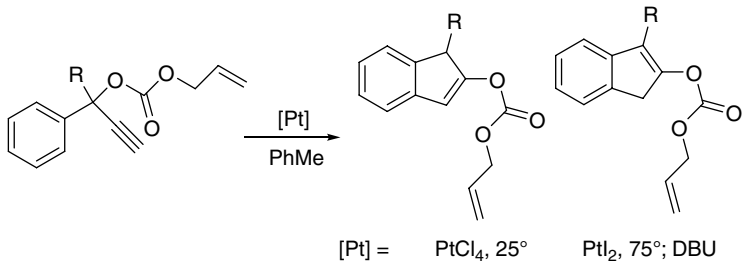
[1] Ananikov, V.P., Kashin, A.S., Hazipov, O.V., Beletskaya, I.P., Starikova, Z.A. *SL* 2021 (2011)
[2] Kang, D., Kim, J., Oh, S., Lee, P.H. *OL* **14**, 5636 (2012)
[3] Sim, S.H., Park, Y., Chung, Y.K. *SL* 473 (2012)
[4] Klahn, P., Duschek, A., Liebert, C., Kirsch, S.F. *OL* **14**, 1250 (2012)
[5] Umland, K.-D., Palisse, A., Haug, T.T., Kirsch, S.F. *ACIE* **50**, 9965 (2011)
[6] Pardo, P., Fernandez, A., Fañanas, F.J., Rodriguez, F. *ASC* **354**, 2141 (2012)
[7] Vadola, P.A., Sames, D. *JOC* **77**, 7804 (2012)

Platinum(II) iodide

Cyclization. An epoxy group appended to the α-carbon atom of propargyl allyl ethers is prone to participate as nucleophile toward bonding with the Pt-activated triple bond. It can be followed by group migration to create new molecular frameworks.[1]



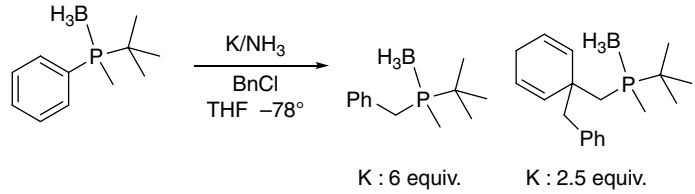
Allyl carbonate group migration without decomposition distinguishes Pt from Pd catalysts. A simultaneous cyclization to indene derivatives by Pt halides shows subtle differences between actions of $PtCl_4$ and PtI_2.[2,3]



[1] Yang, Y.-F., Shu, X.-Z., Luo, J.-Y., Ali, S., Liang, Y.-M. *CEJ* **18**, 8600 (2012)
[2] Zhao, J., Clark, D.A. *OL* **14**, 1668 (2012)
[3] Zheng, H., Xie, X., Yang, J., Zhao, C., Jing, P., Fang, B., She, X. *OBC* **9**, 7755 (2011)

Potassium

Benzylation.[1] Phenylphosphine-BH_3 complexes shed the phenyl substituent while picking a benzyl group on reaction with BnCl in liquid ammonia-THF. It requires large amounts (6 equiv.) of potassium to bring about the reaction, for lesser quantities leads to reductive benzylation at the benzene ring.



[1] Stankevic, M., Wojcik, K., Jaklinska, M., Pietrusiewicz, K.M. *EJOC* 2521 (2012)

Potassium *t*-butoxide.

Carboxylation.[1] *t*-Butyl aroates are synthesized from ArX and CO, using *t*-BuOK as base and trapping agent, 1,10-phenanthroline is a useful additive.

Styrenation. Ketones are enolized (*t*-BuOK, DMSO) and add to arylethynes.[2]

[1] Zhang, H., Shi, R., Ding, A., Lu, L., Chen, B., Lei, A. *ACIE* **51**, 12542 (2012)
[2] Trofimov, B.A., Schmidt, E.Yu., Zorina, N.V., Ivanova, E.V., Ushakov, I.A. *JOC* **77**, 6880 (2012)

Potassium ferrocyanide

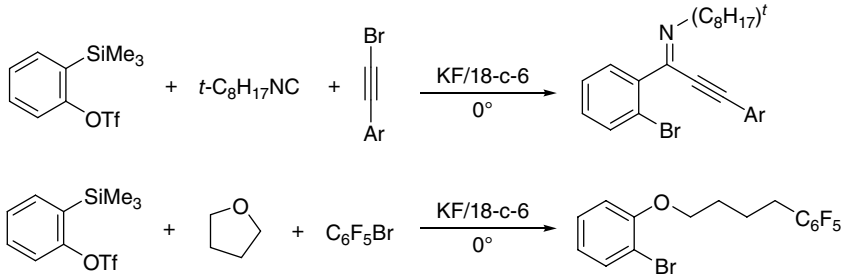
Cyanation. The nontoxic $K_4Fe(CN)_6$ is a source of cyanide ion for conjugate addition to chalcones.[1]

[1] Li, Z., Liu, C., Zhang, Y., Li, R., Ma, B., Yang, J. *SL* 2567 (2012)

Potassium fluoride

Amide hydrolysis. A method involves microwave irradiation of the substrates with KF-on-alumina.[1]

Benzyne generation. Either Bu_4NF or KF (the latter often accompanied by a crown ether) is used routinely to generate benzynes from *o*-trimethylsilylaryl triflates, with suitable trapping agents present. Two more examples[2] are depicted in the following:



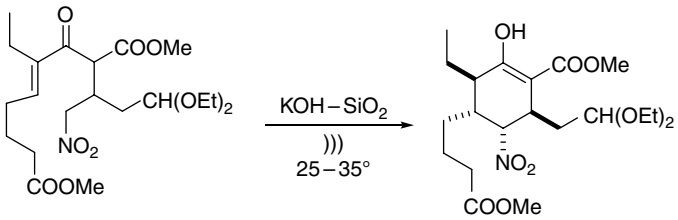
o-Quinones are shown to be able to act as dienes in Diels-Alder reactions.[3]

[1] Zhang, X., Luo, K., Chen, W., Wang, L. *ChJC* **29**, 2209 (2011)
[2] Yoshida, H., Asatsu, Y., Mimura, Y., Ito, Y., Ohshita, J., Takaki, K. *ACIE* **50**, 9676 (2011)
[3] Kaicharla, T., Bhojgude, S.S., Biju, A.T. *OL* **14**, 6238 (2012)

Potassium hydroxide

Base. 1,1,2,2-Tetrachloro-1,2-dibromoethane provides positive halogen to react with sulfones in Ramberg-Bäcklund reaction that also employs the KOH-on-alumina base.[1]

Deprotonation of a nitroalkane by KOH/SiO_2 under microwave irradiation is found to give the best result for intramolecular conjugate addition.[2]



A convenient preparation of a superbase involves dissolving KOH in a mixture of *t*-BuOH and DMSO.[3]

[1] Söderman, S.C., Schwan, A.LQ. *JOC* **77**, 10978 (2012)
[2] Chen, J., Chen, J., Xie, Y., Zhang, H. *ACIE* **51**, 1024 (2012)
[3] Trofimov, B.A., Schmidt, Yu.E., Zorina, N.V., Ivanova, E.V., Ushakov, I.A., Mikhaleva, A.I. *ASC* **354**, 1813 (2012)

Potassium monoperoxysulfate, (Oxone®)

Oxidation. Oxidation of $ArCH_2R$ to aryl ketones is accomplished by Oxone ($KHSO_5$) and KBr in MeCN or CH_2Cl_2 containing water.[1,2] Lesser amounts (1.2 equiv.) of the oxidant are required when the reaction is irradiated with visible light. The positive bromine species so produced is utilizable in bromoamination.[3]

Dioxiranes. A special dioxirane (useful for epoxidation of alkenes) is derived from a trifluoromethyl ketone in which the other alkyl group is linked through a siloxane unit to silica.[4]

The dioxirane generated in situ from 1,1,1-trifluoroacetone performs oxygen atom insertion into tertiary aliphatic C-H bonds. Generally, a site close to the chain terminus is preferred, and the selectivity is further increased in the presence of β-cyclodextrin.[5]

Water-soluble iodylarenes. A thermally stable iodylarene is obtained in high yield from reaction of *p*-iodobenzenesulfonic acid with Oxone in water.[6]

[1] Yin, L., Wu, J., Xiao, J., Cao, S. *TL* **53**, 4418 (2012)
[2] Moriyama, K., Takemura, M., Togo, H. *OL* **14**, 2414 (2012)
[3] Moriyama, K., Izumisawa, Y., Togo, H. *JOC* **76**, 7249 (2011)
[4] D'Accolti, L., Annese, C., De Riccardis, A., De Giglio, E., Cafagna, D., Fanelli, F., Fusco, C. *EJOC* 4616 (2012)
[5] Fung, Y.-S., Yan, S.-C., Wong, M.-K. *OBC* **10**, 3122 (2012)
[6] Yusubov, M.S., Yusubova, R.Y., Nemykin, V.N., Maskaev, A.V., Geraskina, M.R., Kirschning, A., Zhdankin, V.V. *EJOC* 5935 (2012)

Potassium permanganate

Oxidation. Various Lewis acids (e.g., BF_3) in MeCN are found to greatly accelerate oxidation of alcohols by $KMnO_4$.[1] A more lipophilic oxidizing agent is created by mixing $KMnO_4$ with Bu_4NI and $(PhNMe_3)I$ in MeCN.[2] Smooth oxidation of primary alcohols to aldehydes, anilines to azoarenes, and arenthiols to the disulfides is noted.

[1] Du, H., Lo, P.-K., Hu, Z., Liang, H., Lau, K.-C., Wang, Y.-N., Lam, W.W.Y., Lau, T.-C. *CC* **47**, 7143 (2011)
[2] Ellis, R., Lee, K.-H., Ainsworth, M., Kerr, A., Viseux, E.M.E. *SL* 1371 (2012)

Potassium tetrachloroaurate

Amides. Condensation of aldehydes with amines by $KAuCl_4$ in aq. MeCN leads to amides.[1]

[1] Li, G.-L., Kung, K.K.-Y., Wong, M.-K. *CC* **48**, 4112 (2012)

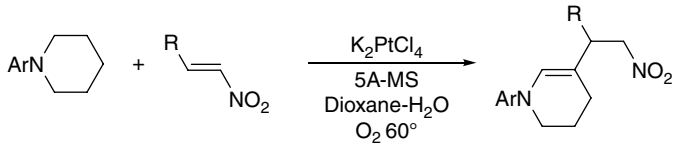
Potassium tetrachloropalladate

2-Alkylbenzoxazinones. The palladate salt is a catalyst for carbonylation and the combination of *o*-bromoaniline with CO and carboxylic anhydrides in its presence furnishes the bicyclic heterocycle.[1]

[1] Wu, X.-F., Neumann, H., Beller, M. *CEJ* **18**, 12599 (2012)

Potassium tetrachloroplatinate

Dehydrogenation-conjugate addition. Through interaction of K_2PtCl_4 under oxygen certain cyclic amines undergo transformation into enamines and then capture Michael receptors.[1]

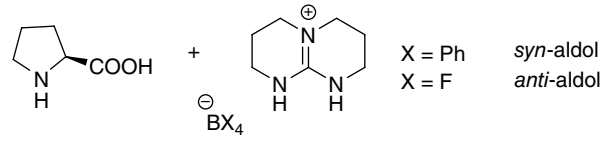


[1] Xia, X.-F., Zhu, X.-Z., Ji, K.-G., Yang, Y.-F., Shaukat, A., Liu, X.-Y., Liang, Y.-M. *JOC* **75**, 2893 (2010)

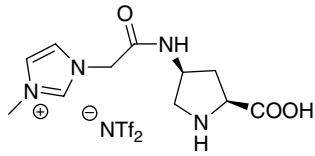
(*S/R*)-Proline and 4-hydroxyproline

Aldol rection. Together, (*S*)-proline and $CoCl_2$ in 2:1 ratio are proposed as a new combination to catalyze asymmetric aldol reaction, its advantage being of broad scope, capable of high yields, enantioselectivity (>99%) and diastereoselectivity (*anti/syn* 45:1).[1]

The bicyclic guanidinium salts depicted by formula **1** are remarkable additives that can determine the sense of diastereoselection of proline-mediated aldol reaction. A change of the borate anion switches the *syn-/anti-* selectivity.[2] Thus a chloromethyl ketone and ArCHO condense in the neat with the tetrafluoroborate salt to provide the *anti*-isomer.[3]



(**1**)

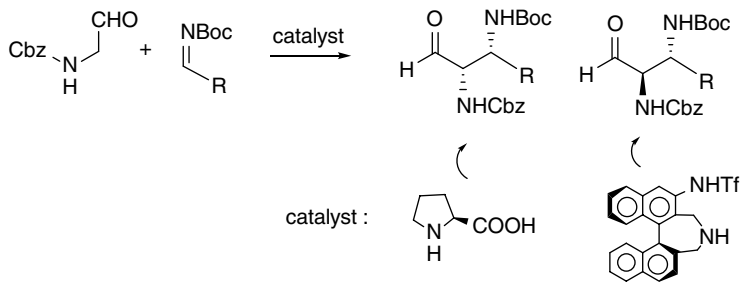


(**2**)

Linking (2*S*,4*R*)-4-hydroxyproline to magnetic nanoparticles renders them recoverable after aldol reaction.[4] The (4*S*)-amido derivative **2** is also effective.[5] Another variant for the purpose is to attach a proline derivative to β-cyclodextrin.[6]

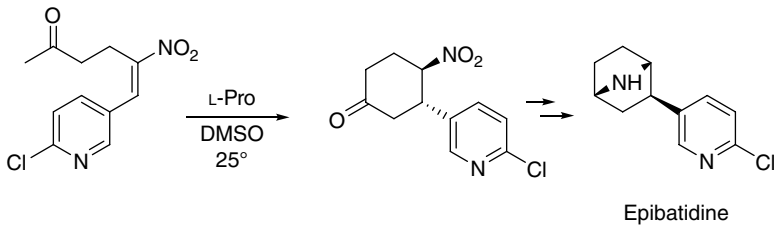
The synthesis of $ArCOCH{=}CHNMe_2$ from ArCOMe and $(MeO)_2CHNMe_2$ by proline catalysis of course does not exploit any enantioselective benefit.[7]

Mannich reaction. A enantioselective approach to 2-substituted piperidine alkaloids is based on the addition of ketones to cyclic imines.[8] An *N*-Protected aminoacetaldehyde and aldimines give the *syn*- (2*S*,3*R*)-diaminoalkanals, and when the *anti*- (2*R*,3*R*)-isomers are needed, replacing (*S*)-proline with an (*S*)-bisnaphthoazepine shall meet the demand.[9] [see ref. 10 for related cases.][10]



Asymmetric Mannich reaction has been performed on 2-substituted indol-3-ones.[11] Chiral 2,3-disubstituted pyrrolidines are accessible from an initial Mannich reaction of imines with succindialdehyde.[12]

Michael reaction. An intramolecular Michael addition for synthesis of 3-aryl-4-nitrocyclohexanones as catalyzed by proline is adaptable to a synthesis of epibatidine.[13]



Epibatidine

A bicyclic analog of proline, (2*R*, 3a*S*, 7a*S*)-octahydroindole-2-carboxylic acid, has been used in catalyzing the Michael reaction.[14]

Assorted reactions. Arylation of unactivated arenes to form biaryls is promoted by *t*-BuOK and additive proline (20 mol%), but the reaction is conducted at a relatively high temperature (150°).[15] Ketones condense with aryl azides to provide 1-aryl-1,2,3-triazoles on microwave irradiation with proline.[16]

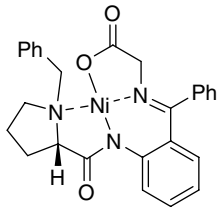
The reaction of stabilized Wittig reagents and ArCHO can be carried out with proline as catalyst to form cinnamic esters.[17] An *N*-picolylproline ligand for Fe(III) salts to catalyze *cis*-dihydroxylation of alkenes is mainly to mimic non-heme iron oxidase.[18]

[1] Karmakar, A., Maji, T., Wittmann, S., Reiser, O. *CEJ* **17**, 11024 (2011)
[2] Martinez-Castañeda, A., Rodriguez-Solla, H., Concellon, C., del Amo, V. *JOC* **77**, 10375 (2012)
[3] Martinez-Castaneda, A., Poladura, B., Rodriguez-Solla, H., Concellon, C., del Amo, V. *CEJ* **18**, 5188 (2012)
[4] Yacob, Z., Nan, A., Liebscher, J. *ASC* **354**, 3259 (2012)
[5] Montroni, E., Sanap, S.P., Lombardo, M., Quintavalla, A., Trombini, C., Dhavale, D.D. *ASC* **353**, 3234 (2011)
[6] Shen, H.-M., Ji, H.-B. *TL* **53**, 3541 (2012)
[7] Kumar, D., Kummi, D.N., Chopra, P., Ansari, M.I., Chakraborti, A.K. *EJOC* 6407 (2012)
[8] Monaco, M.R., Renzi, P., Schietroma, D.M.S., Bella, M. *OL* **13**, 4546 (2011)
[9] Kano, T., Sakamoto, R., Akakura, M., Maruoka, K. *JACS* **134**, 7516 (2012)
[10] Kano, T., Song, S., Kubota, Y., Maruoka, K. *ACIE* **51**, 1191 (2012)
[11] Li, L., Han, M., Xiao, M., Xie, Z. *SL* 1727 (2011)
[12] Kumar, I., Mir, N.A., Gupta, V.K., Rajnikant. *CC* **48**, 6975 (2012)
[13] Reddy, C.R., Reddy, M.D., Haribabu, K. *EJOC* 6414 (2012)
[14] Shen, J., Liu, D., An, Q., Liu, Y., Zhang, W. *ASC* **354**, 3311 (2012)
[15] Tanimoro, K., Ueno, M., Takeda, K., Kirihata, M., Tanimori, S. *JOC* **77**, 7844 (2012)
[16] Belkheira, M., El Abed, D., Pons, J.-M., Bressy, C. *CEJ* **17**, 12917 (2011)
[17] McNulty, J., McLeod, D. *CEJ* **17**, 8794 (2011)
[18] Dungan, V.J., Wong, S.M., Barry, S.M., Rutledge, P.J. *T* **68**, 3231 (2012)

(*S*)-Proline amides

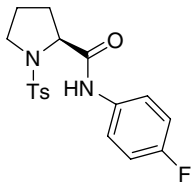
Reduction. A method for hydrosilylation of imines employs *N*-(1-pivaloylprolyl) aniline.[1]

Alkylation. A Ni(II) complex **1** derived from an *N*-benzylprolylaniline and glycine is capable of enantioselective alkylation.[2]

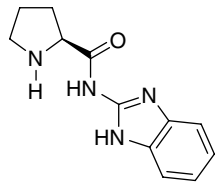


(**1**)

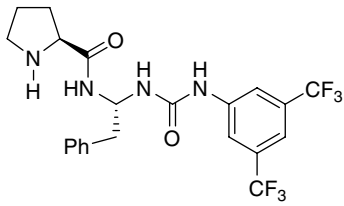
Aldol reaction. Identified as aldol reaction catalyst are the following proline amide derivatives: **2**,[3] **3**,[4] **4**,[5] and **5**.[6]



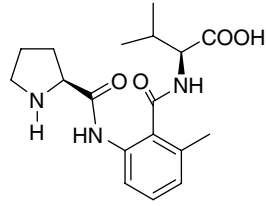
(**2**)



(**3**)



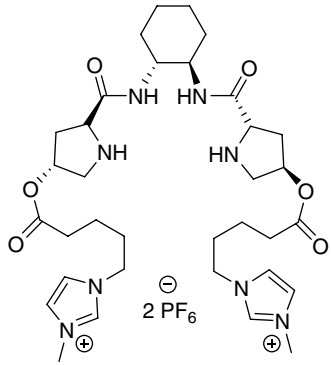
(**4**)



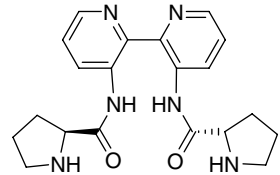
(**5**)

A general approach for the preparation of prolinamides involves reaction of the anhydride of prolinecarbamic acid with lithium amides (and sulfonamides).[7]

Additional aldol reaction catalysts are those based on 4-hydroxyproline. The sulfate associated with a [bmim] cation can be used in an ionic liquid.[8] Other amides are from the simple 1,6-hexanediamine[9] or a chiral 1,2-cyclohexanediamine (**6**).[10]



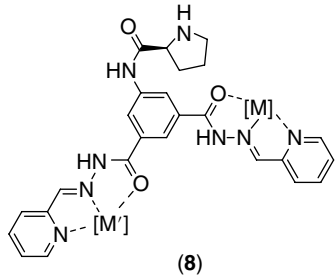
(**6**)



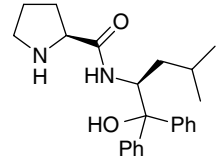
(**7**)

Catalytic systems that include a metal salt are represented by the simple primary prolinamide [with Zn(II) to enhance reaction rates and stereoselectivity],[11] whereas the prolyl derivative of (*R,R*)-1,2-diphenylethanamine[12] is said to be inspired by natural aldolases.

Amide **7** is used in conjuction with $Yb(OTf)_3$ to conduct *anti*-selective aldol reaction.[13] A size-selective asymmetric aldol reaction catalyst **8** contains a L-Pro unit.[14]



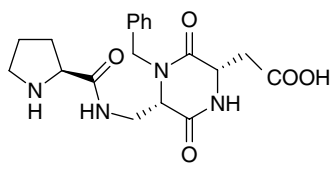
(**8**)



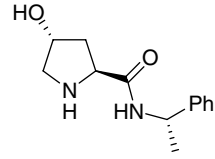
(**9**)

A careful study on the effect of catalyst loading on aldol reaction with **9** shows that high ee production (93%) is afforded by kinetic control (with 0.5 mol% catalyst) and the thermodynamically controlled reaction (10 mol% catalyst) gives racemates.[15]

Conjugate addition. A typical test for asymmetric Michael reaction is set by aldehydes and β-nitrostyrene, and prolinamides **10**,[16] **11**,[17] and an enzyme with a Pro terminus[18] have been evaluated.

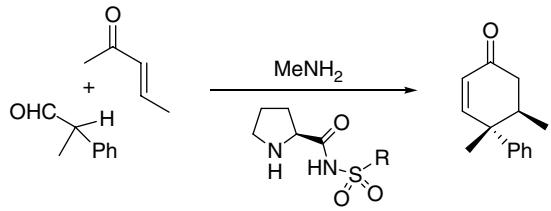


(**10**)

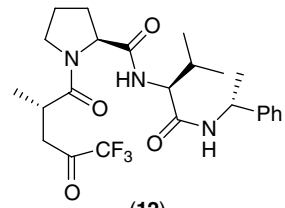


(**11**)

N-Sulfonylprolinamides are also useful to conduct the synthesis of cyclohexenones from aldehydes and conjugated ketones.[19,20]



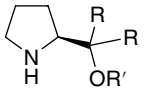
Epoxidation. Dipeptide **12** is found to direct the enantioselective epoxidation of alkenes by H_2O_2.[21]



(**12**)

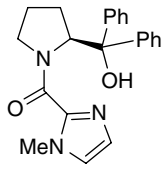
[1] Kanemitsu, T., Umehara, A., Haneji, R., Nagata, K., Itoh, T. *T* **68**, 3893 (2012)
[2] Wang, J., Zhou, S., Lin, D., Ding, X., Jiang, H., Liu, H. *CC* **47**, 8355 (2011)
[3] Thorat, P.B., Goswami, S.V., Khade, B.C., Bhusare, S.R. *TL* **53**, 6083 (2012)
[4] Tang, G., Gün, U., Altenbach, H.-J. *T* **68**, 10230 (2012)
[5] Revelou, P., Kokotos, C.G., Moutevelis-Minakakis, P. *T* **68**, 8732 (2012)
[6] Pearson, A.J., Panda, S. *OL* **13**, 5548 (2011)
[7] Tang, G., Hu, X., Altenbach, H.J. *TL* **52**, 7034 (2011)
[8] Gauchot, V., Schmitzer, A.R. *JOC* **77**, 4917 (2012)
[9] Delaney, J.P., Henderson, L.C. *ASC* **354**, 197 (2012)
[10] Kochetkov, S.V., Kucherenko, A.S., Zlotin, S.G. *EJOC* 6128 (2011)
[11] Andreu, C., Asensio, G. *T* **67**, 7050 (2011); Andreu, C., Sanz, F., Asensio, G. *EJOC* 4185 (2012)
[12] Paradowska, J., Pasternak, M., Gut, B., Gryzlo, B., Mlynarski, J. *JOC* **77**, 173 (2012)
[13] Zhao, H.-W., Li, H.-L., Yue, Y.-Y., Qin, X., Sheng, Z.-H., Cui, J., Su, S., Song, X.-Q., Yan, H., Zhong, R.-G. *SL* 1990 (2012)
[14] Wu, X., He, C., Wu, X., Qu, S., Duan, C. *CC* **47**, 8415 (2011)
[15] Rulli, G., Duangdee, N., Baer, K., Hummel, W., Berkessel, A., Gröger, H. *ACIE* **50**, 7944 (2011)
[16] Durini, M., Sahr, F.A., Kuhn, M., Civera, M., Gennari, C., Piarulli, U. *EJOC* 5599 (2011)
[17] Watts, J., Luu, L., McKee, V., Carey, E., Kelleher, F. *ASC* **354**, 1035 (2012)
[18] Zandvoort, E., Geertsema, E.M., Baas, B.-J., Quax, W.J., Poelarends, G.-J. *ACIE* **51**, 1240 (2012)
[19] Pierce, M.D., Johnston, R.C., Mahapatra, S., Yang, H., Carter, R.G., Cheong, P.H.-Y. *JACS* **134**, 13624 (2012)
[20] Yang, H., Banerjee, S., Carter, R.G. *OBC* **10**, 4851 (2012)
[21] Romney, D.K., Miller, S.J. *OL* **14**, 1138 (2012)

(*S/R*)-Prolinol derivatives

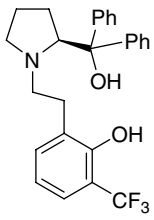


(**1**) R = Ph
(**2**) R = 3,5-$(CF_3)_2C_6H_3$
(**3**) R = 4-$(Me_2NCH_2)C_6H_4$
(**4**) R = 2-Np
(**5**) R = *n*-C_6H_{13}
(**6**) R = *n*-$C_{12}H_{25}$

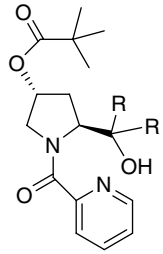
(**A**) R′ = H
(**B**) R′ = $SiMe_3$
(**C**) R′ = $SiEt_3$
(**D**) R′ = $Si(Ph)_2Me$
(**E**) R′ = $SiPh_3$
(**F**) R′ = Si(*i*-Pr)$_3$
(**G**) R′ = Si(*t*-Bu)Me_2



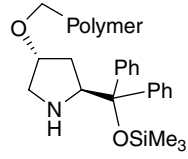
(**7**)



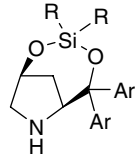
(**8**)



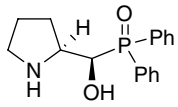
(**9A**) R = Ph
(**9B**) R = Tol



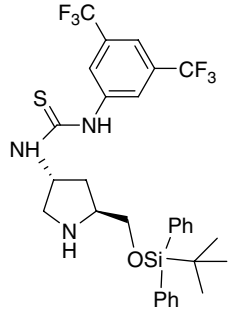
(**10**)



(**11**) R = Me, Ar = Ph
(**12**) R = Ph, Ar = 3,5-$(CF_3)_2C_6H_3$



(**13**)



(**14**)

Reduction. β-Amino-α,β-unsaturated esters get reduced enantioselectively via hydrosilylation using **7** as catalyst.[1] The hydroxyproline derived **9A** is employed in hydrosilylation of cyclic imines,[2,3] **9B** in the case of γ-imino esters.[4]

Alkylation. Secondary alcohols that have a greater tendency to ionize than usual are prompted by $InBr_3$ to act as alkylating agents for aldehydes, and the reaction is rendered enantioselective and diastereoselective by **2B**.[5] Although Brønsted acids such as TfOH and 2,3,4-trihydroxybenzoic acid are good promoters,[6] in trifluoroethanol no acid is needed to accomplish the alkylation.[7] Working together with a Rh(II) carboxylate that catalyzes

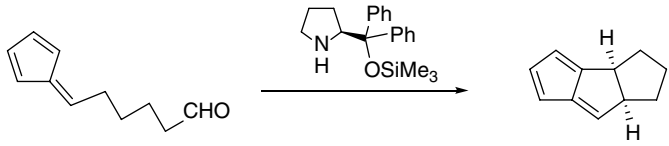
hydroformylation, **1B** can complete the transformation of mixtures of $RCH{=}CH_2$ and Ar_2CHOH into $RCH_2CH(CHO)CHAr_2$.[8]

α,β-Unsaturated aldehydes are diarylmethylated selectively at the γ-position (catalyst: **1D** + saccharin).[9]

An S_N2' pathway is pursued in the reaction of aldehydes with phenyl 2-bromomethyl-2-alkenoates. The reaction involving lipophilic catalyst **5E** delivers (3*R*, 4*R*)-4-formyl-2-methylenecarboxylic esters.[10] The same reaction (catalyst: **1B**) is applicable to kinetic resolution of 2-acetoxy-3-nitro-4-aryl-3-butenoic esters, the nucleophile is 3-indoleacetaldehyde which is formed in situ from indole and acrolein.[11] α–Branched 4-alkenals are obtained in the Pd(0)-catalyzed allylation, and with **1B** present the products are chiral.[12]

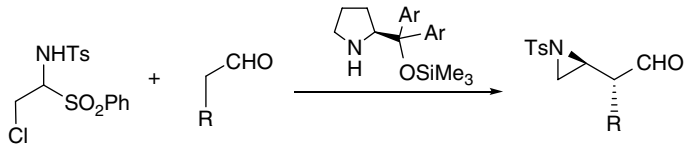
Addition. An allene linkage activated by $Pd(OAc)_2$ is receptive to intramolecular attack of an aldehyde. Cyclization of 6,7-octadienals is rendered enantioselective by **2F** (but only up to 82% ee in the present report).[13]

6-(3-Formylbutyl)fulvene undergoes intramolecular addition to form a chiral cyclopentanecarbaldehyde imine ontreatment with **1B**, and a return attack of the cyclopentadienide closes a second five-membered ring.[14]



Pyruvaldehyde hydrate is found to behave as acceptor in aldol reaction. Chiral 3-hydroxy-4-pentanon-1-als are prepared with assistance of **2A.**[15]

Mannich reaction of aldehydes with cryptoaldimines (α-sulfonylamines) as catalyzed by **2B** furnishes the *anti*-isomers, (2*S*, 3*R*)-3-tosylaminoalkanals.[16] When applying the reaction to the 2-chloroethanamine derivative, chiral aziridines are produced.[17]

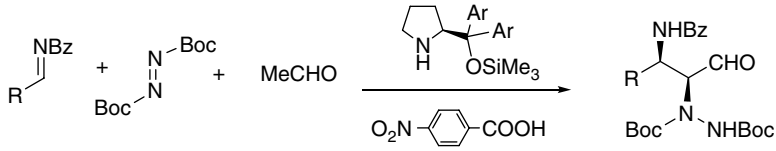


The development of **14** for catalyzing Mannich reaction[17a] is evidently an empirical pursuit, as the thiourea unit containing the bistrifluoromethylphenyl substituent has conferred on numerous occasions very beneficial effects.

In situ activation of an α-CH bond to an amino nitrogen atom is most expedient for accessing β-aminoaldehydes. A reagent system comprising catalytic **2B**, $CuBr_2$, and the oxidant *t*-BuOOH is serviceable.[18]

A tandem addition sequence for 2,3-diaminoalkanal synthesis is accomplished by agency of **2B** and 4-nitrobenzoic acid, the aldehyde adds to an azodicarboxylic ester preferably and regeneration of the same nucleophilic site through proton transfer allows for

further reaction with an imine.[19] Addition of aldehydes to acridinium salts also has been investigated, e.g., using **2B**.[20]



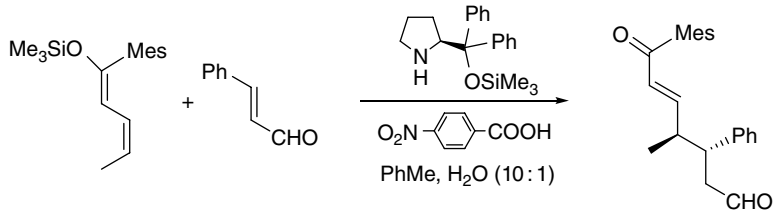
An *anti*-selective asymmetric Henry reaction has been established while utilizing $CuBr_2$ and **8**.[21]

The Cu-catalyzed conjugate addition of diorganozincs to enals is enantioselective due to the presence of **1B**.[22] Cyclic siloxanes **11** show excellent stability toward hydrolysis and good catalytic activities not only for Michael reaction, but also for cyclopropanation and Diels-Alder reaction.[23]

In catalyzing addition of arylacetic esters to enals, **1B** is the motivator for enantioselectivity, Bu_4NBr is a valuable additive because Bu_4NOH generated therefrom is a needed base.[24] 1-(2-Pyridinesulfonyl)-2-alkanones are valuable Michael donors in view of the removable activating group, 3-substituted 5-oxoalkanals are synthesized enantioselectively in a reaction conducted in the presence of **1G**.[25]

Aldehyde hydrazones also engage in conjugate addition to enals, and the reaction gives ketoaldehydes in a semi-masked state and **2G** is responsible for chirality at C-3.[26] When carrying out the addition of nitromethane to enals in MeOH containing NBS, chiral esters are obtained with involvement of **1B**.[27] 2-Nitroethyl phenyl sulfone is a synthetic equivalent of a vinyl anion, as its adducts with enals are liable to elimination.[28]

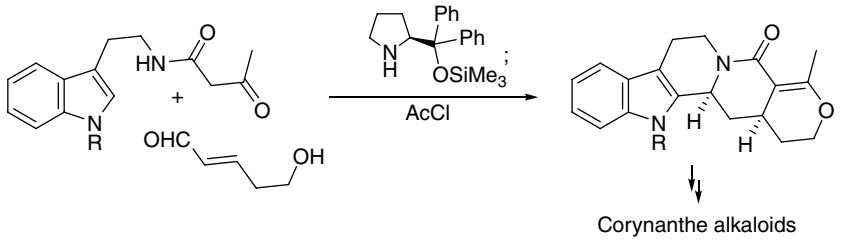
That the enol silyl ether of 1-butenyl mesityl ketone prefers utilizing its γ-carbon to add to cinnamaldehyde must be due to steric hindrance around the α-site. Still, asymmetric induction by **1B** is not impeded.[29]



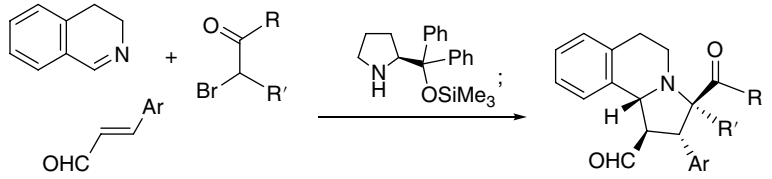
Conjugate addition with concurrent oxygenation at the α-position of the aldehydes further increases the synthetic potential of the reaction. This can be achieved by adding TEMPO to the reaction media.[30] Since allylic alcohols are oxidized by copper under oxygen, they can be used instead of enals.[31]

For catalyzing the addition of *N*-Boc oxindoles to maleimides, a report indicates that the use of **6B** is advantageous.[32]

Annulation. The adduct of N_b-acetoacetyltryptamine and 5-hydroxy-2-pentenal formed by catalysis of *ent*-**1B** is ready to cyclize (Pictet-Spengler reaction) to furnish a pentacyclic precursor of corynanthe alkaloids with two new chirality centers [in (*S,S*)-configuration].[33] The use of β-tryptaminoacrylic esters also succeeds in the preparation of tetracyclic congeners (catalyst: **2B**).[34] Simpler enamino ketones and enals proceed to give 5-acyl-1,2,3,4-tetrahydropyridin-2-ols (catalyst: **1B**).[35]



In elaboration of polysubstituted hexahydropyrrolo-isoquinolines enantioselectively, 3,4-dihydroisoquinoline undergoes quaternization with α-bromoketones, and the involvement of **1B** in the following step of Michael addition to enals is chirogenic.[36]



While the extensive utility of **1B** and **2B** in enantioselective conjugate addition is already evident, more examples attest to their great value. Thus two different enals may be combined to form 3,4-disubstituted benzaldehydes without capitalizing the chiral induction ability of **1B**.[37]

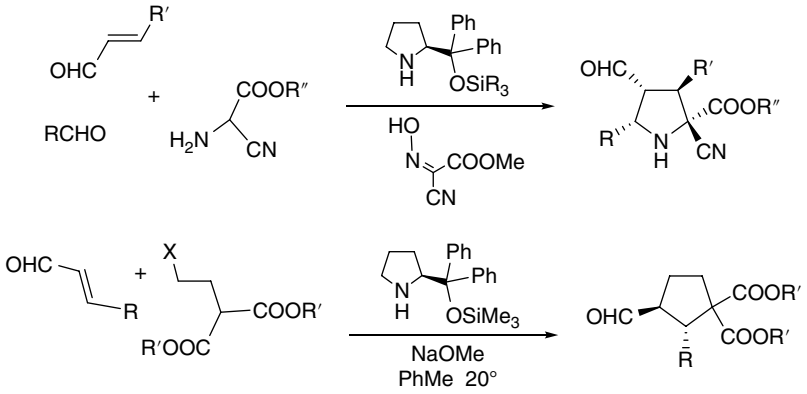
As δ-keto aldehydes are readily assembled, their susceptibility to undergo cyclization under the influence of a carbene can be exploited.In other words, a dual catalyst system comprising **2B** and a triazolecarbene should be able to convert addends of Michael reaction directly into cyclopentanolones or cyclopentenones.[38,39] A Michael-aldol reaction tandem impelled by **1B** on 3-acylmethyloxindoles and 2-alkenals delivers spirocyclic products with two adjacent chirality centers.[40]

3-Keto-4-alkenoic esters are capable of reflexive Michael reaction tandem, thus with enals they form six-membered aldehydoketo esters in one step. Furthermore, access to products with at least three asymmetric centers (with **1B** as catalyst) is quite facile.[41]

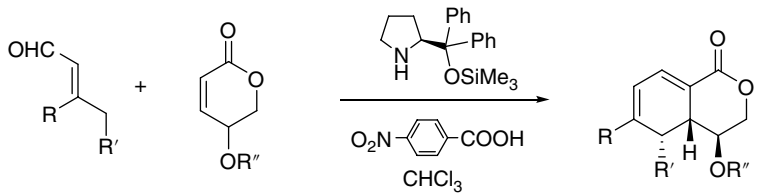
Stabilized Wittig reagents can be added to the conjugate addition reaction media to trap the adducts without interfering with the initial process.[42] On the other hand, phosphorylacetic esters as Michael donors toward enals retain an active alkenylating moiety (for Horner-Wadsworth-Emmons reaction) in the adducts and the derived δ-lactones or lactams.[43]

Asymmetric addition of 3-propargyloxindole to cinnamaldehyde in the presence of **1B** and $PdCl_2$ completes a spiroannulation as the Pd catalyst enables cyclization of the adduct. Two contiguous asymmetric carbon centers are created in the first step.[44]

Two other tandem reaction sequences leading to five-membered ring structures are Michael-Mannich reactions involving α-aminocyanoacetic esters, aldehydes and enals to construct chiral pyrrolidines,[45] and the use of dialkyl 2-haloethylmalonates to react with enals.[46]



On playing the donor role (as dienamine) to condense with 5-alkoxy-5,6-dihydropyrones a conjugated aldehyde is also involved in an aldol reaction.[47]



Propargylic amines represent heterodonors to form cyclic products with enals, provided that a Pd catalyst is available to complete the addition step.[48] *N,O*-Diacylhydroxylamines are aziridination agents for enals and the chiral products are obtained when reaction is carried out with **1B** or **2B**.[49,50]

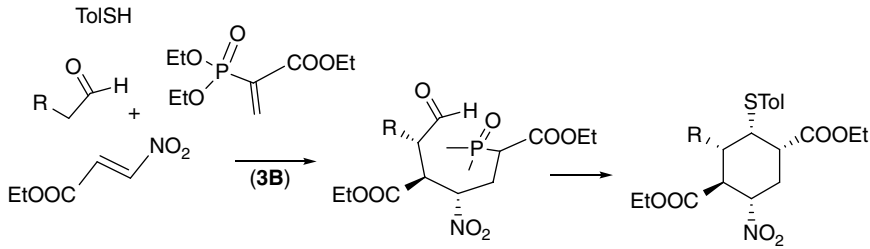
Many exploratory works that aim at screening proline-derived catalysts and other aspects for asymmetric Michael addition employ β-nitrostyrene as the acceptor. Thus the

addition of β-keto esters to nitroalkenes employing **4A** as the catalyst reveals that the C_6F_6 solvent can have a dramatic effect on stereoselectivity.[51] For the addition that uses *N*-Boc oxindole as donor the highly lipophilic **6B** is called to service.[52] Kinetic resolution of 7-hydroxy-2-alkenals is based on ring closure to tetrahydropyran that generates the *C*-nucleophiles. Cyclization is facilitated by **1B** due to formation of the more electrophilic conjugated iminium species. It also enforces enantioselectivity.[53]

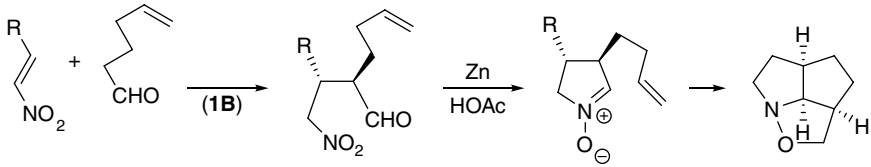
Conjugated iminium ions present two sites for attack, one mode being addition leading to *N,O*-acetals, as in the reaction of *o*-hydroxy-β-nitrostyrene with an enal. The product is a 3-alkenyl-4-nitromethyl-2-chromanol.[54]

A dimethylaminomethyl substituent in each of the phenyl ring of **1B** must have some effects on the catalytic properties, and **3B** is found to useful to catalyze Michael addition in brine.[55] The elaboration of 2-substituted 4-hydroxy-3-nitrocyclohexanecarbaldehydes that contain four contiguous stereocenters from glutaraldehyde is an efficient synthetic operation.[56]

Even more impressive achievement is implicative of cyclohexane construction with diverse substituents from a four-component reaction, i.e., the tandem Michael-Michael-Wittig-Michael sequence in which each Michael addition involves a different donor/acceptor pair.[57]



A well-designed synthetic process comprising addition of 5-hexenal to nitroalkenes and a follow-up treatment with Zn –HOAc, which converts the γ-nitroaldehydes into cyclic nitrones. Trapping by the double bond affords tricyclic isoxazolidines.[58]



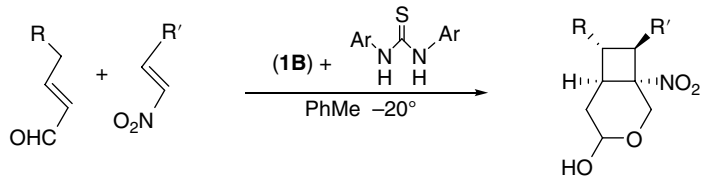
For *syn*-selective and enatioselective addition of ketones to nitroalkenes a novel catalyst is **13**.[59]

Cycloaddition. Epoxidation of 3-ethoxycarbonylmethyleneoxindoles by *t*-BuOOH is rendered enantioselective (ee up to 88%) by **1A**.[60] Epoxidation of enals by H_2O_2 and

catalyzed by **2B** is to provide chiral electrophilic substrates for synthesis of chiral 5-(α–hydroxyalkyl)azoles, i.e., condensation with amides, thioamides,and amidines.[61] These epoxides are also useful for synthesis of 2,3-disubstituted benzofurans.[62]

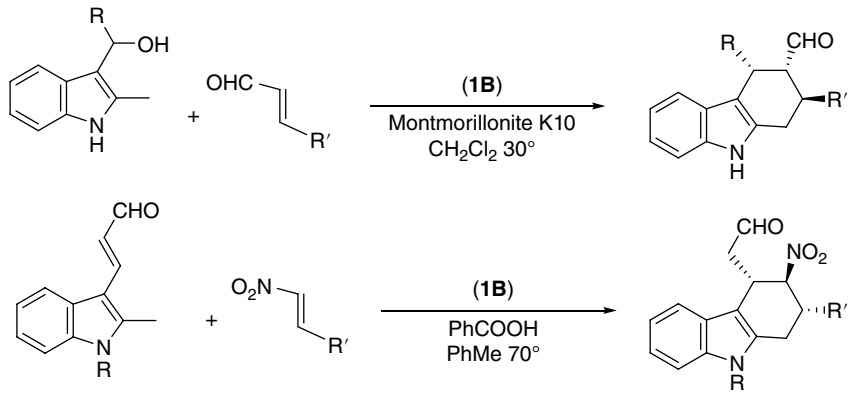
A similar epoxidation system for enals is constituted from a sulfur-containing analog of **1B**, i.e., each of the benzene ring carries a SC_5H_{11} chain at the *p*-position.[63]

In a formal [2+2]cycloaddition (actually involving two consecutive Michael reactions) that combines enals and nitroalkenes, an *N,N′*-diarylthiourea serves as a cocatalyst to **1B**.[64]



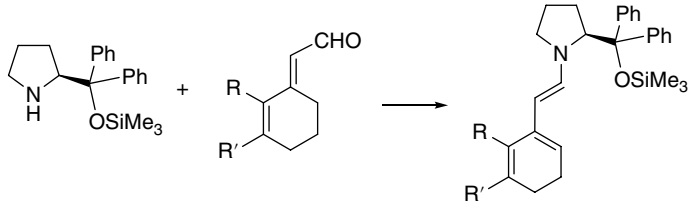
Chiral 3-substituted isoxazoline-4-carbaldehydes are the cycloadducts of nitrones and 2-alkynals formed by participation of **2A**.[65] Preparation of 5-alkenylpyrrolidines which are capable of many transformations is based on employing 2-alkenylideneaminomalonic esters to generate azomethine ylides for the cycloaddition with enals.[66]

A prolinol derivative can influence the Diels-Alder reaction of *o*-quinodimethane analogs based on the indole nucleus as shown later. Using **1B** to derivatize enal addends[67] or β-(3-indolyl)acroleins.[68]

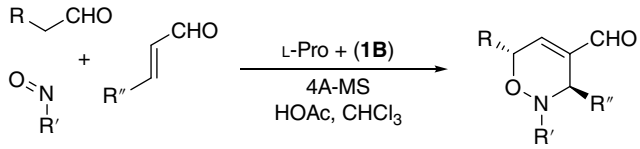


R = Me, Boc

2-Cyclohexen-1-ylideneacetaldehydes form cross-trienamines on condensation with prolinols such as **1B**. Two modes of Diels-Alder reaction are open to these compounds, and the consequence is dependent of the dienophile.[69]



The efficient synthesis of 1,2-oxazine aldehydes, which involves sequential aminoxylation of saturated aldehydes by nitroso compounds, conjugate addition to enals, and intramolecular aldol reaction, is the result of a cooperative action from L-proline and **1B**.[70]



An analysis of the nucleophilic reactivity of enamines derived from cyclic amines indicates a correlation with pyramidalizability of the nitrogen atom. Thus prolinol derivatives such as **1B** form better nucleophiles than imidazolidinones.[71]

[1] Jones, S., Li, X. *T* **68**, 5522 (2012)
[2] Chen, X., Zheng, Y., Shu, C., Yuan, W., Liu, B., Zhang, X. *JOC* **76**, 9109 (2011)
[3] Jiang, Y., Liu, L.-X., Yuan, W.-C., Zhang, X.-M. *SL* 1797 (2012)
[4] Xue, Z.-Y., Liu, L.-X., Jiang, Y., Yuan, W.-C., Zhang, X.-M. *EJOC* 251 (2012)
[5] Xiao, J. *OL* **14**, 1716 (2012)
[6] Xiao, J., Zhao, K., Loh, T.-P. *CAJ* **6**, 2890 (2011)
[7] Xiao, J., Zhao, K., Loh, T.-P. *CC* **48**, 3548 (2012)
[8] Stiller, J., Vorholt, A.J., Ostrowski, K.A., Behr, A., Christmann, M. *CEJ* **18**, 9496 (2012)
[9] Silvi, M., Cassani, C., Moran, A., Melchiorre, P. *HCA* **95**, 1985 (2012)
[10] Jimenez, J., Landa, A., Lizarraga, A., Maestro, M., Mielgo, A., Oiarbide, M., Velilla, I., Palomo, C. *JOC* **77**, 747 (2012)
[11] Roy, S., Chen, K. *OL* **14**, 2496 (2012)
[12] Afewerki, S., Ibrahem, I., Rydfjord, J., Breistein, P., Cordova, A. *CEJ* **18**, 2972 (2012)
[13] Li, M., Datta, S., Barber, D.M., Dixon, D.J. *OL* **14**, 6350 (2012)
[14] Hayashi, Y., Gotoh, H., Honma, M., Sankar, K., Kumar, I., Ishikawa, H., Konno, K., Yui, H., Tsuzuki, S., Uchimaru, T. *JACS* **133**, 20175 (2011)
[15] Hayashi, Y., Yasui, Y., Kojima, M., Kawamura, T., Ishikawa, H. *CC* **48**, 4570 (2012)
[16] Urushima, T., Ishikawa, H., Hayashi, Y. *CEJ* **17**, 8273 (2011)
[17] Hayashi, Y., Urushima, T., Sakamoto, D., Torii, K., Ishikawa, H. *CEJ* **17**, 11715 (2011)
[17a] Gao, J., Chuan, Y., Li, J., Xie, F., Peng, Y. *OBC* **10**, 3730 (2012)
[18] Zhang, J., Tiwari, B., Xing, C., Chen, X., Chi, Y.R. *ACIE* **51**, 3649 (2012)
[19] Coeffard, V., Desmarchelier, A., Morel, B., Moreau, X., Greck, C. *OL* **13**, 5778 (2011)
[20] Liang, T., Xiao, J., Xiong, Z., Li, X. *JOC* **77**, 3583 (2012)
[21] Xu, K., Lai, G., Zha, Z., Pan, S., Chen, H., Wang, Z. *CEJ* **18**, 12357 (2012)

[22] Afewerki, S., Breistein, P., Pirtilä, Deriana, L., Dziedzic, P., Ibrahem, I., Cordova, A. *CEJ* **17**, 8784 (2011)
[23] Lombardo, M., Montroni, E., Quintavalla, A., Trombini, C. *ASC* **354**, 3428 (2012)
[24] Duce, S., Mateo, A., Alonso, I., Ruano, J.L.G., Cid, M.B. *CC* **48**, 5184 (2012)
[25] Deng, J., Wang, F., Yan, W., Zhu, J., Jiang, H., Wang, W., Li, J. *CC* **48**, 148 (2012)
[26] Fernandez, M., Uria, U., Vicario, J.L., Reyes, E., Carrilli, L. *JACS* **134**, 11872 (2012)
[27] Jensen, K.L., Poulsen, P.H., Donslund, B.S., Morana, F., Jørgensen, K.A. *OL* **14**, 1516 (2012)
[28] Gianelli, C., Lopez, R., Puente, A., Zalacain, M., Palomo, C. *EJOC* 2774 (2012)
[29] Gupta, V., Sudhir, V., Mandal, T., Schneider, C. *ACIE* **51**, 12609 (2012)
[30] Yoon, H.-S., Ho, X.-H., Jang, J., Lee, H.-J., Kim, S.-J., Jang, H.-Y. *OL* **14**, 3272 (2012)
[31] Ho, X.-H., Oh, H.-J., Jang, H.-Y. *EJOC* 5655 (2012)
[32] Yang, X., Wang, C., Ni, Q., Enders, D. *S* 2601 (2012)
[33] Zhang, W., Bah, J., Wohlfarth, A., Franzen, J. *CEJ* **17**, 13814 (2011)
[34] Wu, X., Dai, X., Fang, H., Nie, L., Chen, J., Cao, W., Zhao, G. *CEJ* **17**, 10510 (2011)
[35] Wan, J.-P., Loh, C.C.J., Pan, F., Enders, D. *CC* **48**, 10049 (2012)
[36] Fraile, A., Schietroma, D.M.S., Albrecht, A., Davis, R.L., Jørgensen, K.A. *CEJ* **18**, 2773 (2012)
[37] Song, X., Zhang, X., Zhang, S., Li, H., Wang, W. *CEJ* **18**, 9770 (2012)
[38] Enders, D., Grossmann, A., Huang, H., Raabe, G. *EJOC* 4298 (2011)
[39] Jacobsen, C.B., Jensen, K.L., Udmark, J., Jørgensen, K.A. *OL* **13**, 4790 (2011)
[40] Albertshofer, K., Anderson, K.E., Barbas III, C.F. *OL* **14**, 5968 (2012)
[41] McGarraugh, P.G., Jones, J.H., Brenner-Moyer, S.E. *JOC* **76**, 6309 (2011)
[42] Enders, D., Grossmann, A., Gieraths, B., Düzdemir, M., Merkens, C. *OL* **14**, 4254 (2012)
[43] Albrecht, A., Morana, F., Fraile, A., Jørgensen, K.A. *CEJ* **18**, 10348 (2012)
[44] Sun, W., Zhu, G., Wu, C., Hong, L., Wang, R. *CEJ* **18**, 13959 (2012)
[45] Lin, S., Deiana, L., Zhao, G.-L., Sun, J., Cordova, A. *ACIE* **50**, 7624 (2011)
[46] Remes, M., Vesely, J. *EJOC* 3747 (2012)
[47] Orue, A., Reyes, E., Vicario, J.L., Carrillo, L., Uria, U. *OL* **14**, 3740 (2012)
[48] Sun, W., Zhu, G., Hong, L., Wang, R. *CEJ* **17**, 13958 (2011)
[49] Deiana, L., Dziedzic, P., Zhao, G.-L., Vesely, J., Ibrahem, I., Rios, R., Sun, J., Cordova, A. *CEJ* **17**, 7904 (2011)
[50] Desmarchelier, A., de Sant'Ana, D.P., Terrasson, V., Campagne, J.M., Moreau, X., Greck, C., de Figueiredo, R.M. *EJOC* 4046 (2011)
[51] Lattanzi, A., De Fusco, C., Russo, A., Poater, A., Cavallo, L. *CC* **48**, 1650 (2012)
[52] Wang, C., Yang, X., Enders, D. *CEJ* **18**, 4832 (2012)
[53] McGarraugh, P.G., Brenner-Moyer, S.E. *OL* **13**, 6460 (2011)
[54] Enders, D., Yang, X., Wang, C., Raabe, G., Runsik, J. *CAJ* **6**, 2255 (2011)
[55] Qiao, Y., He, J., Ni, B., Headley, A.D. *ASC* **354**, 2849 (2012)
[56] Chintala, P., Ghosh, S.K., Long, E., Headley, A.D., Ni, B. *ASC* **353**, 2905 (2011)
[57] Shen, H., Yang, K.-F., Shi, Z.-H., Jiang, J.-X., Lai, G.-Q., Xu, L.-W. *EJOC* 5031 (2011)
[58] Sadaba, D., Delso, I., Tejero, T., Merino, P. *TL* **52**, 5976 (2011)
[59] Zeng, Z., Luo, P., Jiang, Y., Liu, Y., Tang, G., Xu, P., Zhao, Y., Blackburn, G.M. *OBC* **9**, 6973 (2011)
[60] Palumbo, C., Mazzeo, G., Mazziotta, A., Gambacorta, A., Loreto, M.A., Migliorini, A., Superchi, S., Tofani, D., Gasperi, T. *OL* **13**, 6248 (2011)
[61] Albrecht, L., Ransborg, L.K., Albrecht, A., Lykke, L., Jørgensen, K.A. *CEJ* **17**, 13240 (2011)
[62] Albrecht, L., Ransborg, L.K., Lauridsen, V., Overgaard, M., Zweifel, T., Jørgensen, K.A. *ACIE* **50**, 12496 (2011)
[63] Deobald, A.M., Corrêa, A.G., Rivera, D.G., Paixao, M.W. *OBC* **10**, 7681 (2012)
[64] Talavera, G., Reyes, E., Vicario, J.L., Carrillo, L. *ACIE* **51**, 4104 (2012)
[65] Cai, X., Wang, C., Sun, J. *ASC* **354**, 359 (2012)
[66] Roboredo, S., Reyes, E., Vicario, J.L., Badia, D., Carrillo, L., de Cozar, A., Cossio, F.P. *CEJ* **18**, 7179 (2012)
[67] Xiao, Y.-C., Zhou, Q.-Q., Dong, L., Liu, T.-Y., Chen, Y.-C. *OL* **14**, 5940 (2012)

[68] Liu, Y., Nappi, M., Arceo, E., Vera, S., Melchiorre, P. *JACS* **133**, 15212 (2011)
[69] Halskov, K.S., Johansen, T.K., Davis, R.L., Steurer, M., Jensen, F., Jørgensen, K.A. *JACS* **134**, 12943 (2012)
[70] Lin, H., Tam, Y., Sun, X.-W., Lin, G.-Q. *OL* **14**, 3818 (2012)
[71] Lakhdar, S., Maji, B., Mayr, H. *ACIE* **51**, 5739 (2012)

Propylphosphonic anhydride

Condensation. The heterocyclic reagent is a dehydrating agent for acetalization and thioacetalization.[1]

[1] Augustine, J.K., Bombrun, A., Sauer, W.H.B., Vijaykumar, P. *TL* **53**, 5030 (2012)

Pyridine

Decomposition of ozonides. A new and convenient method for the decomposition of ozonides to carbonyl compounds is by treatment with pyridine.[1]

[1] Willand-Charnley, R., Fisher, T.J., Johnson, B.M., Dussault, P.H. *OL* **14**, 2242 (2012)

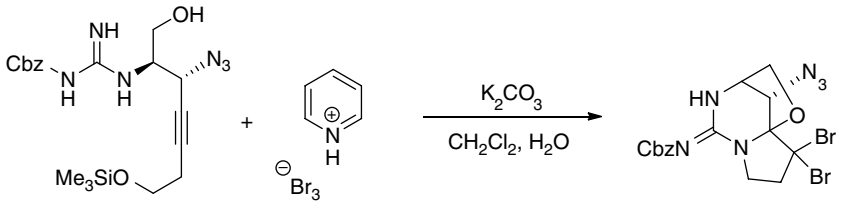
Pyridinium chlorochromate, (PCC)

Oxidative cleavage. Using PCC in catalytic quantities together with periodic acid the oxidation of substituted tetrahydrofurans results in ring cleavage, either to provide 1,4-diketones (from 2,5-disubstituted THF's) or β-acyloxy carboxylic acids (from 2,2,5-trisubstituted THF's).[1]

[1] Piccialli, V., Zaccaria, S., Oliviero, G., D'Errico, S., D'Altri, V., Borbone, N. *EJOC* 4293 (2012)

Pyridinium tribromide

Cyclization. Bromination of the triple bond of a complex guanidine triggers formation of three interlocking rings on way to a synthesis of a natural saxitoxin analog.[1]

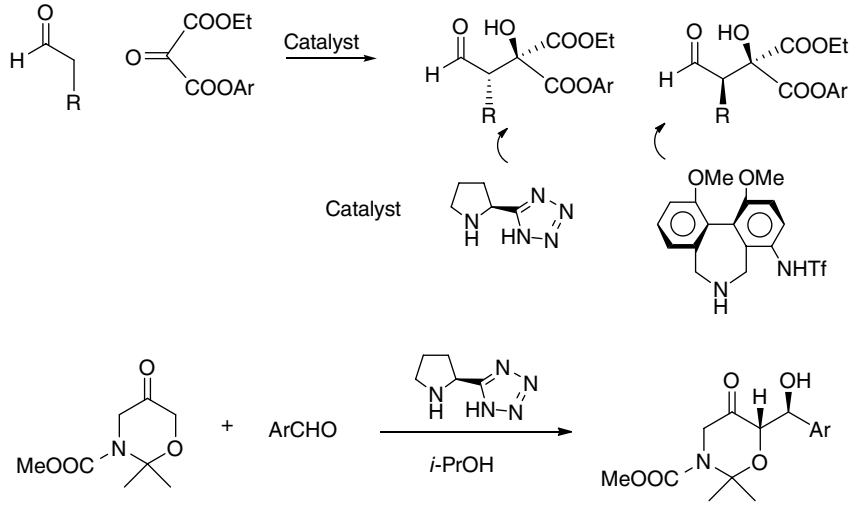


[1] Sawayama, Y., Nishikawa, T. *ACIE* **50**, 7176 (2011)

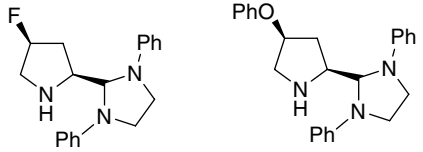
(*S*)-(2-Pyrrolidinyl)azoles

Aldol reaction. Aldol reaction featuring aldehydes, unsymmetrical oxomalonic esters and **1** as catalyst is enantioselective and *anti*-selective.[1] It is possible to acquire the *syn*-series by a switch of catalyst.

Regioselectivity is observed in the aldol reaction of *N*-protected 2,2-dimethyl-1,3-oxazin-5-ones with ArCHO. The favored site is C-6.[2]

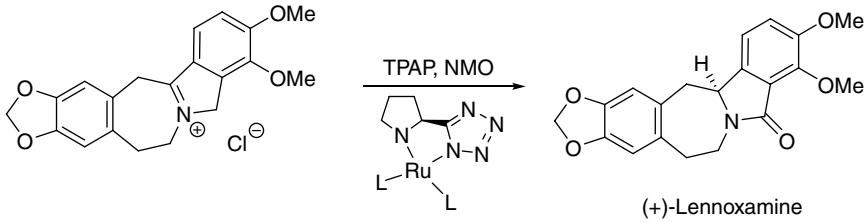


Conjugate addition. Studies have shown that a fluorine atom on the pyrrolidine ring of proline-like catalysts (e.g., **2**) has conformation- stabilizing effects and notable improvement in enantioselectivity for conjugate addition.[3] The use of **3** to mediate addition with various *O*-, *N*-, *S*-, and *C*-nucleophiles to enals and trapping by the very reactive 1,1-bis(phenylsulfonyl)ethane serves to establish polyfunctional molecules in chiral modification.[4]



(**2**) (**3**)

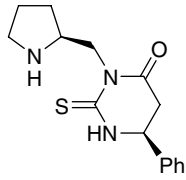
Redox transformations. The Ru complex of **1** is capable of mediating the transformation of a tetracyclic iminium salt into lennoxamine, there being reduction as well as oxidation in the process.[5]



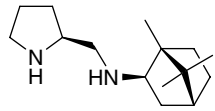
[1] Kano, T., Song, S., Maruoka, K. *CC* **48**, 7037 (2012)
[2] Komatsu, Y., Watanabe, R., Ikishima, H., Nakano, K., Ichikawa, Y., Kotsuki, H. *OBC* **10**, 2993 (2012)
[3] Quintard, A., Langlois, J.-B., Emery, D., Mareda, J., Guenée, L., Alexakis, A. *CEJ* **17**, 13433 (2011)
[4] Quintard, A., Alexakis, A. *CC* **47**, 7212 (2011)
[5] Mirabal-Gallardo, Y., Piérola, J., Shankaraiah, N., Santos, L.S. *TL* **53**, 3672 (2012)

(*S*)-2-Pyrrolidinylmethylamines

Alkylation. Enamination of ketones with **1** generates nucleophiles that can discriminate stereochemical attack by diarylmethanols, although the optical purity of the products is not sufficiently high (only up to 80%).[1]



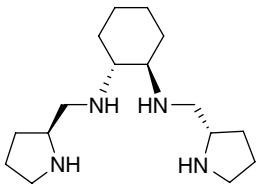
(**1**)



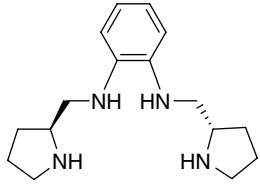
(**2**)

Henry reaction. Complexation of $Cu(OAc)_2$ by **2** forms a catalyst that mediates condensation of $MeNO_2$ with ArCHO.[2]

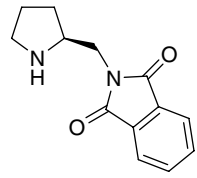
Conjugate addition. Besides **1**,[3] other catalysts of this class showing ability to induce enantioselective conjugate addition are **3**,[4] **4**,[5] as well as the cyclic imides **5** and **6**.[6,7]



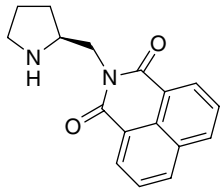
(**3**)



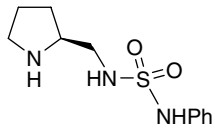
(**4**)



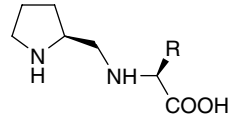
(**5**)



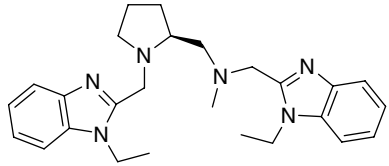
(**6**)



(**7**)



(**8**)

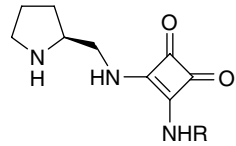


(**9**)

For the addition of ketones to nitroalkenes, sulfamide **7**[8] and amino acid **8** are useful.[9]

Cycloaddition. On complexing to $Fe(OTf)_2$ the tetradentate ligand **9** creates a chiral environment for epoxidation of enones (H_2O_2 supplying the oxidant).[10]

A versatile catalyst for both [2+2] and [4+2] modes of cycloaddition involving nitroalkenes is **10**, due to its being a multi-H-bond donor, presenting two sites to bind the nitro group in the transition states to dictate region- and stereoselectivity.[11,12]

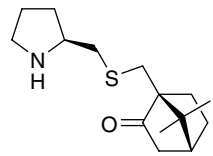


(**10**)

[1] Trifonidou, M., Kokotos, C.G. *EJOC* 1563 (2012)
[2] Lu, D., Zhou, Y., Li, Y., Yan, S., Gong, Y. *JOC* **76**, 8869 (2011)
[3] Tsakos, M., Trifonidou, M., Kokotos, C.G. *T* **68**, 8630 (2012)
[4] Ma, S., Wu, L., Liu, M., Wang, Y. *ChJC* **30**, 2707 (2012)
[5] Ma, S., Wu, L., Liu, M., Wang, Y. *OBC* **10**, 3721 (2012)
[6] Ban, S., Xie, H., Zhu, X., Li, Q. *EJOC* 6413 (2011)
[7] Xie, H.-Y., Ban, S.-R., Liu, J.-N., Li, Q.-S. *TL* **53**, 3865 (2012)
[8] Chen, J.-R., Fu, L., Zou, Y.-Q., Chang, N.-J., Rong, J., Xiao, W.-J. *OBC* **9**, 5280 (2011)
[9] Cao, X., Wang, G., Zhang, R., Wei, Y., Wang, W., Sun, H., Chen, L. *OBC* **9**, 6487 (2011)
[10] Wang, B., Wang, S., Xia, C., Sun, W. *CEJ* **18**, 7332 (2012)
[11] Albrecht, L., Dickmeiss, G., Acosta, F.C., Rodriguez-Escrich, R., Davis, R.L., Jørgensen, K.A. *JACS* **134**, 2543 (2012)
[12] Jiang, H., Rodriguez-Escrich, C., Johansen, T.K., Davis, R.L., Jørgensen, K.A. *ACIE* **51**, 10271 (2012)

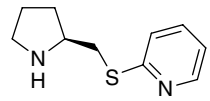
(*S*)-2-Pyrrolidinylmethyl sulfide\es

S_N2' reaction. A method for kinetic resolution of α-acetoxy-β-nitro-β,γ-unsaturated esters is to use them as alkylating agents for cyclohexanone or aldehydes.[1]



(**1**)

Cycloaddition. Sulfide **2** in poly(alkene glycol)s exerts great enantioselective influences in the unusual Diels-Alder reaction between nitrodienes and cyclohexenones.[2]



(**2**)

[1] Reddy, R.J., Lee, P.-H., Magar, D.R., Chen, J.-H., Chen, K. *EJOC* **353** (2012)
[2] Xia, A.-B., Xu, D.-Q., Wu, C., Zhao, L., Xu, Z.-Y. *CEJ* **18**, 1055 (2012)

R

Rhenium(VII) oxide

Amines. Replacement of the hydroxyl group of benzylic and propargylic alcohols by the amino group (in protected form) is mediated by Re_2O_7.[1] By adding Et_3SiH to the reaction medium reductive amination of carbonyl compounds can be accomplished.[2]

The initially formed imines are trapped by allyltrimethylsilane.[3]

Ring contraction. 1-Oxa-2-sila-3,6-cyclo octadienes are converted into the six-membered heterocycles with an alkenyl group protruding from the α-carbon to the oxygen atom.[4]

[1] Das, B.G., Nallagonda, R., Ghorai, P. *JOC* **77**, 5577 (2012)
[2] Das, B.G., Ghorai, P. *CC* **48**, 8276 (2012)
[3] Pramanik, S., Ghorai, P. *CC* **48**, 1820 (2012)
[4] Volchkov, I., Park, S., Lee, D. *OL* **13**, 3530 (2011)

Rhenyl trichloride

Reduction. Sulfoxides are deoxygenated by heating with 10 mol% $(Ph_3P)_2ReOCl_3$ in chloroform.[1] No other reducing agent is needed.

Rearrangement. The complex $(Me_2S)(Ph_3PO)ReOCl_3$ is useful for conducting the Meyer-Schuster rearrangement of secondary and tertiary propargyl alcohols.[2] The reaction likely proceeds by a [3,3]sigmatropic rearrangement of metal-alkoxide intermediates.

[1] Sousa, S.C.A., Bernardo, J.R., Ramão, C.C., Fernandes, A.C. *T* **68**, 8194 (2012)
[2] Stefanoni, M., Luparia, M., Porta, A., Zanoni, G., Vidari, G. *CEJ* **15**, 3940 (2009)

Rhodium

Hydrogenation. Nanoparticles of Rh serve as hydrogenation catalyst for converting nitrostyrene into nitroarylethane.[1] With hydrazine as hydrogen source the chemoselectivity switches to production of the aminostyrene.

Rhodium-on-alumina promotes complete hydrogenation of benzene, however, in water containing an ionic liquid, cyclohexene is obtained.[2] In the reductive monoalkylation of amines in which an alkyl nitrile RCN provides the RCH_2 group, Rh/C is the preferred catalyst over Pd/C as the latter causes formation of tertiary amines.[3] (Monobenzylation can be carried out with ArCN using the Pd/C catalyst.)

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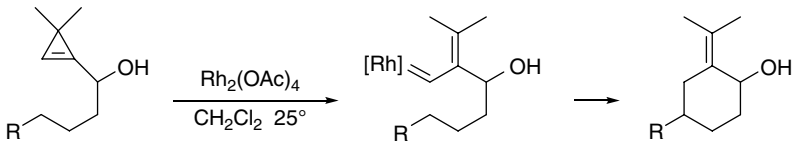
Hydroformylation. Nano-Rh is active in lengthening of the carbon chain of1-alkenes to form the homologous aldehydes.[4]

Coupling. Suzuki coupling can be executed with nano-Rh on PEG-400; an additive for the reaction is KF.[5]

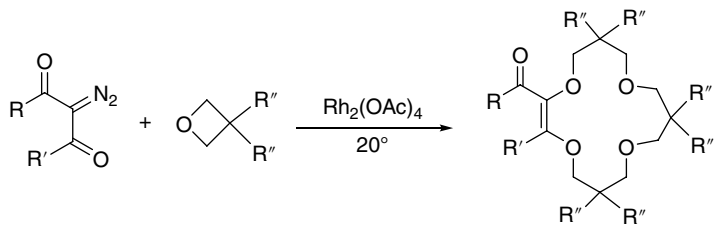
[1] Huang, L., Luo, P., Pei, W., Liu, X., Wang, Y., Wang, J.J., Xing, W., Huang, J. *ASC* **354**, 2689 (2012)
[2] Schwab, F., Lucas, M., Claus, P. *ACIE* **50**, 10453 (2011)
[3] Ikawa, T., Fujita, Y., Mizusaki, T., Betsuin, S., Takamatsu, H., Maegawa, T. *OBC* **10**, 293 (2012)
[4] Behr, A., Brunsch, Y., Lux, A. *TL* **53**, 2680 (2012)
[5] Guha, N.R., Reddy, C.B., Aggarwal, N., Sharma, D., Shil, A.K., Bandna, Das, P. *ASC* **354**, 2911 (2012)

Rhodium(II) acetate

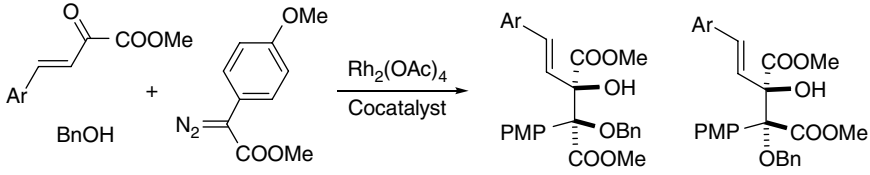
C-H bond insertion. Formation of conjugated carbenoids by cyclopropene cleavage, then intramolecular C-H insertion gives rise to new ring systems.[1] Decomposition of methyl 3′-methoxy-2-biaryldiazoacetate results in a regioselective insertion to form a new CC bond with the carbon atom para to the nuclear methoxy substituent.[2]



Oxonium ylide cascade. Oxonium ylides are the first intermediates in the reaction of carbenoids with carbonyl compounds. Reaction of 2-diazo-1-naphthalenone with Ac_2O results in the formation of 1,2-diacetoxynaphthalene.[3] From 2-diazo-1,3-dicarbonyl compounds and oxetanes the formation of the 1:3 cyclo adducts seems to be preferred.[4]



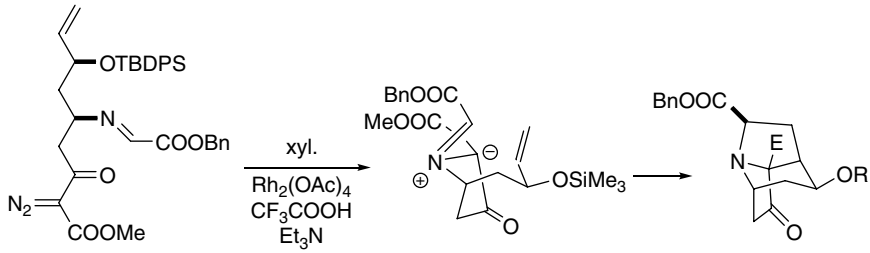
A metal cocatalyst is very influential on the stereochemical course of the insertion of stabilized Rh-carbenoids into the keto group of α-keto esters.[5] Michael acceptors can be used to trap oxonium ylides (derived from α-diazo esters and ROH), and the process is shown to be diastereoselective.[6]



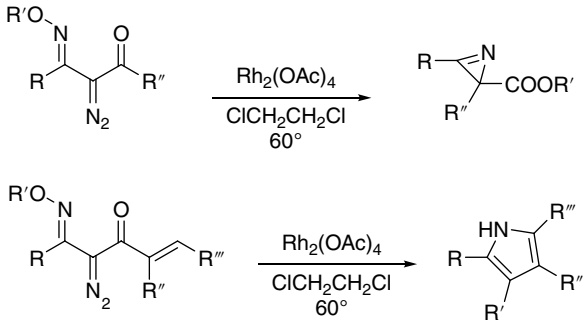
Cocatalyst: $AgBF_4$ 96 : 4
$InBr_3$ 4 : 96

Homologation of aromatic aldehydes including ferrocenecarbaldehyde with α-diazo esters[7] is an alternative to the Knoevenagel method.

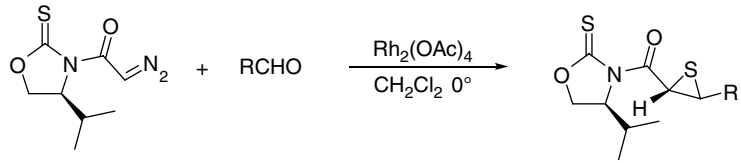
Ammonium ylide cascade. A bridged tricycle is elaborated from a diazo compound that contains imine and alkene linkages at convenient distances.[8] With such an example the synthetic potential of the Rh-catalyzed is well displayed.



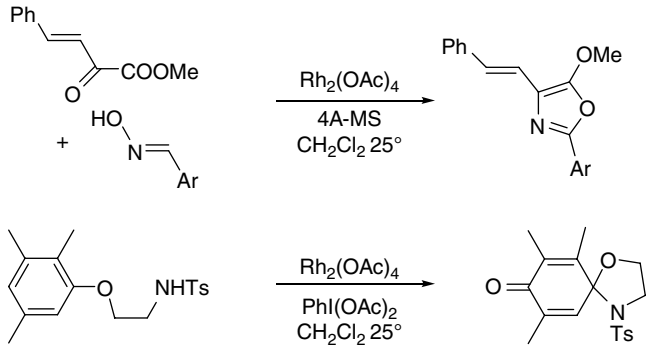
Ring closure to generate azirenes and pyrroles are other possibilities of carbenoid trapping by an imino nitrogen atom.[9]



Sulfonium ylide cascade. Carbenoids derived from decomposition of *N*-tosyl benzalhydrazones are trapped by propargylic sulfides. It gives rise to α-allenyl benzyl sulfides.[10] Participation of the thiono group of *N*-diazoacetyl-1,3-oxazolidine-2-thiones is noted when the Rh-catalyzed reaction with aldehydes is performed.[11] Oxathia-bridged internediates are obviously involved.



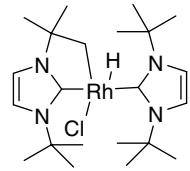
Ring formation. Dicarbenoids generated from 2,2′-bis(tosylhydrazonoalkyl)biaryls promptly undergo intramolecular coupling to afford phenanthrenes.[12] Some other heterocycles (e.g., oxazoles[13]) are created with the help of $Rh_2(OAc)_4$, and under oxidative conditions.[14]



[1] Archambeau, A., Miege, F., Meyer, C., Cossy, J. *ACIE* **51**, 11540 (2012)
[2] Kim, J., Ohk, Y., Park, S.H., Jung, Y., Chang, S. *CAJ* **6**, 2040 (2011)
[3] Kitamura, M., Kisanuki, M., Okauchi, T. *EJOC* 905 (2012)
[4] Rix, D., Ballesteros-Garrido, R., Zeghida, W., Besnard, C., Lacour, J. *ACIE* **50**, 7308 (2011)
[5] Ji, J., Zhang, X., Zhu, Y., Qian, Y., Zhou, J., Yang, L., Hu, W. *JOC* **76**, 5821 (2011)
[6] Han, X., Gan, M., Qiu, H., Ji, J., Zhang, X., Jiang, L., Hu, W. *SL* 1717 (2011)
[7] Chen, S., Zhang, L., Du, Y., Li, B. *SL* 943 (2012)
[8] Fang, C., Shanahan, C.S., Paull, D.H., Martin, S.F. *ACIE* **51**, 10596 (2012)
[9] Jiang, Y., Chan, W.C., Park, C.-M. *JACS* **134**, 4104 (2012)
[10] Li, Y., Huang, Z., Wu, X., Xu, P.-F., Jin, J., Zhang, Y., Wang, J. *T* **68**, 5234 (2012)
[11] Cano, I., Gomez-Bengoa, E., Landa, A., Maestro, M., Mielgo, A., Olaizola, I., Oiarbide, M., Palomo, C. *ACIE* **51**, 10856 (2012)
[12] Xia, Y., Liu, Z., Xiao, Q., Qu, P., Ge, R., Zhang, Y., Wang, J. *ACIE* **51**, 5714 (2012)
[13] Xu, X., Zavalij, P.Y., Hu, W., Doyle, M.P. *CC* **48**, 11522 (2012)
[14] Deng, Y.-X., Xie, J.-P., Zhang, W.-W., Yin, P., Yu, J., He, L. *CEJ* **18**, 1077 (2012)

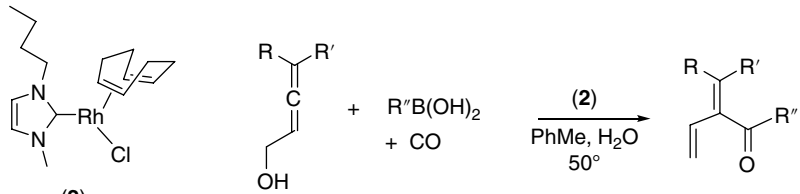
Rhodium-carbene complexes

Hydrosilylation. The complex **1** is a promoter for hydrosilylation of carbonyl compounds and imines.[1]



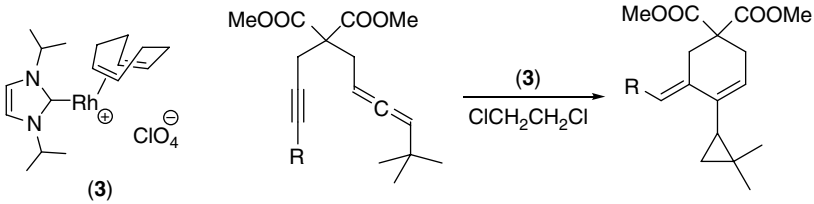
(**1**)

Coupling. A three-component coupling unites 2,3-alkadienols, CO and organoboronic acids is mediated by **2**. It produces 2-acyl-1,3-alkadienes.[2]



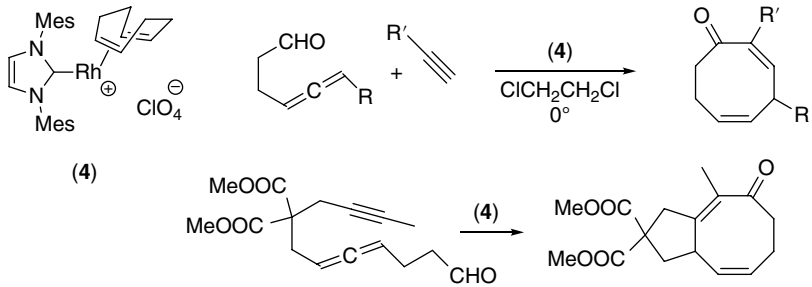
(**2**)

Cycloaddition. Molecules with allene and alkyne units placed in a suitably interactive distance can be brought to form rhodacycle intermediates, and the demetallative denouement of which can result in some remarkable structures.[3]



(**3**)

A synthetic method for 2,5-cyclooctadienones is based on the combination of alkynes and 4,5-alkadienals.[4,5]

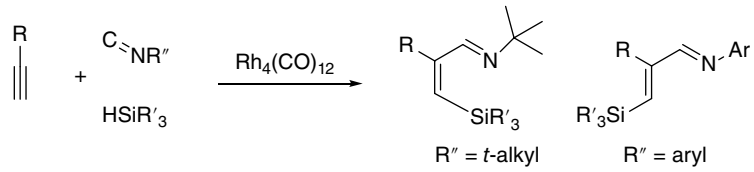


(**4**)

[1] Egbert, J.D., Nolan, S.P. *CC* **48**, 2794 (2012)
[2] Choi, S.Y., Chung, Y.K. *ASC* **353**, 2609 (2011)
[3] Oonishi, Y., Kitano, Y., Sato, Y. *ACIE* **51**, 7305 (2012)
[4] Oonishi, Y., Hosotani, A., Sato, Y. *ACIE* **51**, 11548 (2012)
[5] Oonishi, Y., Hosotani, A., Sato, Y. *JACS* **133**, 10386 (2011)

Rhodium carbonyl clusters

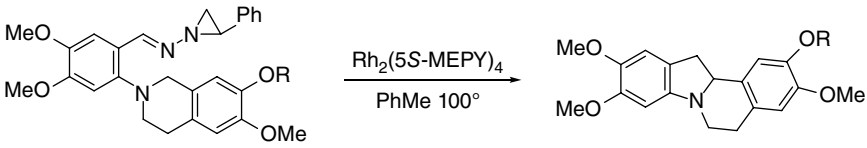
Three-component condensation. Silylimination of alkynes catalyzed by $Rh_4(CO)_{12}$ Shows switch in stereoselectivity according to the sionitrile structure.[1]



[1] Fukumoto, Y., Hagihara, M., Kinashi, F., Chatani, N. *JACS* **133**, 10014 (2011)

Rhodium(II) carboxamidates

C-H bond insertion. Carbenoids generated from *N*-(benzylideneamino)-2-phenylaziridines are able to insert into a C-H bond intramolecularly to form a five-membered ring. An application of the method is demonstrated in a synthesis of cryptaustoline.[1]



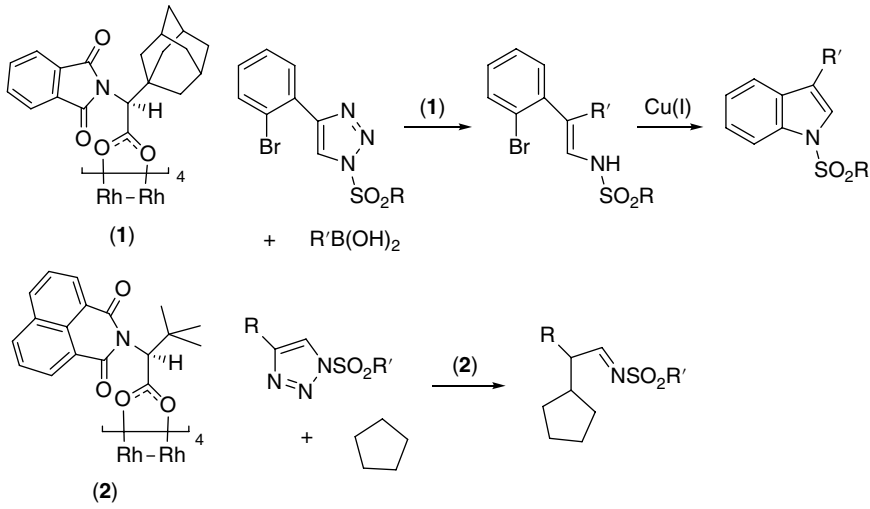
[1] Mahoney, S.J., Fillion, E. *CEJ* **18**, 68 (2012)

Rhodium(II) carboxylates

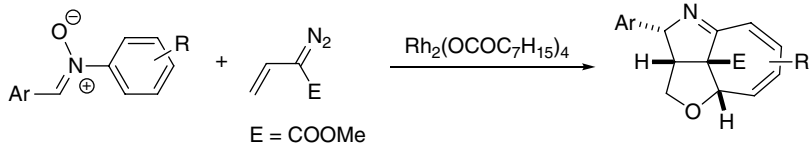
C-H bond insertion. Modification of $Rh_2(OAc)_4$ by replacing two acetoxy group with amino acid residues empowers the catalyst with asymmetric guidance.[1]

Reactions of 1,2,3-triazoles. Hydrolytic extrusion of N_2 from 4-substituted 1-tosyl-1,2,3-triazoles, which gives rise to 1-tosylamino-2-alkanones, is accomplished in the presence of rhodium(II) octanoate.[2] The α-iminocarbene-rhodium intermediates can be trapped by alkynes (silver salt present) to furnish 2,4-disubstituted *N*-tosylpyrroles.[3] In the case of a (1-tosyl-1,2,3-triazol-4-yl)-1-cycloalkanols, ring enlargement of the carbocycle to yield the 2-tosylaminomethylenecycloalkanone is observed.[4]

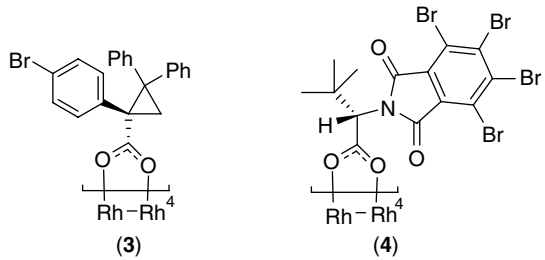
Coupling with $RB(OH)_2$ during the removal of N_2 is effected by **1** [Rh_2(*S*-PTAD)$_4$].[5] However, a more remarkable demonstration is the C-H (from cycloalkanes, adamantane, etc.) insertion reactivity of such intermediates [using **2**, i.e. Rh_2(*S*-NTIL)$_4$].[6]



Annulation. *N*-Arylnitrones react with methyl 2-diazo-3-butenoate to give a tricyclic product.[7] This transformation involves a sequence of several reactions: [3+2]cycloaddition, Buchner reaction, and [1,7]migration of an oxy group (with N-O bond cleavage).

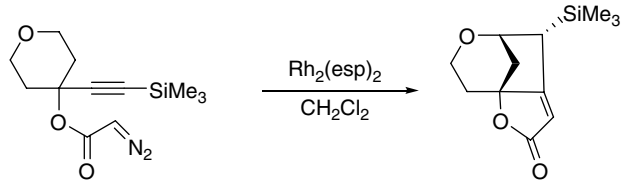


Complex **3** is easily available from 1,1-diphenylethene and the methyl α-diazoarylacetate [with Rh_2(*R*-DOSP)$_4$]. It catalyzes asymmetric cycloaddition.[8] Also **4**, an analog of **2**, is employable for synthesizing chiral 2-cyclopropene-1-carboxylic esters.[9]



(**3**) (**4**)

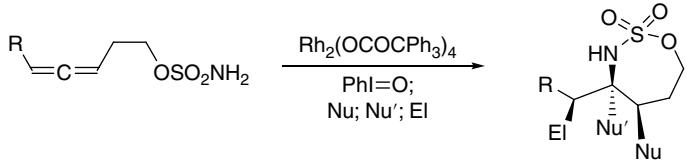
The Rh_2(esp)$_2$ complex [esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropanoate] has found application in an intramolecular addition and C-H bond insertion sequence leading to a tricyclic product.[10]



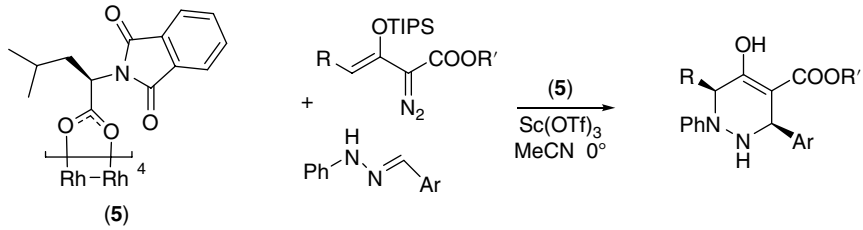
n-(2-Azidophenyl)pyridinium salts undergo intramolecular C-H bond insertion on treatment with $Rh_2(esp)_2$, producing a carbolinium salt.[11] As expected, insertion into a C(sp^3)-H bond proceeds analogously.[12]

Under oxidative conditions [$Rh_2(esp)_2$- $PhI(OAc)_2$], 4-alkynyl-2-oxazolidinones are formed from carbamides of homopropargyl alcohols, and it represents an access to 2-amino-3-alkyn-1-ols.[13] From aminosulfonates of hydroxylamines the reaction furnishes cyclic derivatives of 1,2-diaminoalkane.[14]

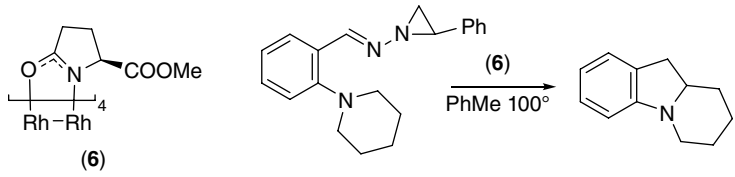
All three carbon atoms of the allenyl group of 3,4-alkadienols can be functionalized via the sulfamates.[15]



Siloxycyclopropenes emerged from decomposition of enolsilane derivatives of α-diazo-β-keto esters are trapped by nitrile oxides via cycloaddition which is followed by a Lossen rearrangement. The products are stabilized by cyclization into β,γ-unsaturated γ-amino-γ-lactones with loss of the silyl group.[16] A [3+3]cycloaddition between unsaturated diazoesters and hydrazones has been realized, the ring formation is a stepwise process which involves both $Rh_2(PTL)_4$ (**5**) and $Sc(OTf)_3$.[17] 2-Azido-1-alkenes enter into cyclopropanation with α-diazo esters without disturbing the azido function.[18]

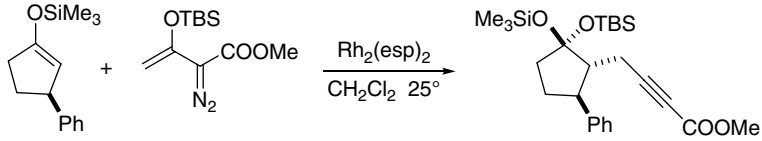


(**5**)



Functionalization. The reagent system $Rh_2(esp)_2$-$PhI(OAc)_2$ is also useful for diastereoselective amination at a benzylic position.[19] *N*-Protected cyclic enamines undergo oxyamidation in the presence of $Cl_3CCH_2OSO_2NH_2$ and ROH (or RCOOH).[20]

For 2-(3-methoxcarbonyl)propargylation of silyl enol ethers, methyl 2-diazo-3-siloxy-3-butenoate emerges as the electrophile.[21]

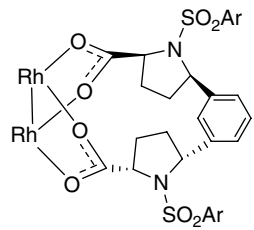


An analog of $Rh_2(esp)_2$ is prepared from the corresponding diamide, and its reaction product with NCS, $Rh_2(espn)_2Cl$ is a stable catalyst capable of inducing intramolecular C-H amination.[22]

Chain elongation and functionalization to assemble 2-hydroxy-4-alkenoic esters is readily accomplished by the reaction of α-diazo esters with allylic alcohols.[23] A [2,3] sigmatropic rearrangement following formation of oxonium ylides delivers the products.

Related processes are the double transpositional assemblage of 2-diazo-3-alkenoic esters and 1-methoxy-1-alkenes to provide 5-methoxy-2-6-alkadienoic esters.[24]

A dimeric (*S*-DOSP) ligand for Rh has been developed and it finds use in asymmetric allylation of indole (at C-3).[25]



[1] Candeias, N.R., Carias, C., Gomes, L.F.R., Andre, V., Duarte, M.T., Gois, P.M.P., Afonso, C.A.M. *ASC* **354**, 2921 (2012)
[2] Miura, T., Biyajima, T., Fujii, T., Murakami, M. *JACS* **134**, 194 (2012)
[3] Chattopadhyay, B., Gevorgyan, V. *OL* **13**, 3746 (2011)
[4] Miura, T., Funakoshi, Y., Morimoto, M., Biyajima, T., Murakami, M. *JACS* **134**, 17440 (2012)
[5] Selander, N., Worrell, B.T., Chuprakov, S., Velaparthi, S., Fokin, V.V. *JACS* **134**, 14670 (2012)
[6] Chuprakov, S., Malik, J.A., Zibinsky, M., Fokin, V.V. *JACS* **133**, 10352 (2011)

[7] Wang, X., Abrahams, Q.M., Zavalij, P.Y., Doyle, M.P. *ACIE* **51**, 5907 (2012)
[8] Qin, C., Boyarskikh, V., Hansen, J.H., Hardcastle, K.I., Musaev, D.G., Davies, H.M.L. *JACS* **133**, 19198 (2011)
[9] Goto, T., Takeda, K., Shimada, N., Nambu, H., Anada, M., Shiro, M., Ando, K., Hashimoto, S. *ACIE* **50**, 6803 (2011)
[10] Jansone-Popova, S., May, J.A. *JACS* **134**, 17877 (2012)
[11] Pumphrey, A.L., Dong, H., Driver, T.G. *ACIE* **51**, 5920 (2012)
[12] Nguyen, Q., Sun, K., Driver, T.G. *JACS* **134**, 7262 (2012)
[13] Grigg, R.D., Rigoli, J.W., Pearce, S.D., Schomaker, J.M. *OL* **14**, 280 (2012)
[14] Olson, D.E., Roberts, D.A., Du Bois, J. *OL* **14**, 6174 (2012)
[15] Adams, C.A., Boralsky, L.A., Guzei, I.A., Schomaker, J.M. *JACS* **134**, 10807 (2012)
[16] Xu, X., Shabashov, D., Zavalij, P.Y., Doyle, M.P. *OL* **14**, 800 (2012)
[17] Xu, X., Zavalij, P.Y., Doyle, M.P. *ACIE* **51**, 9829 (2012)
[18] Gu, P., Su, Y., Wu, X.-P., Sun, J., Liu, W., Xue, P., Li, R. *OL* **14**, 2246 (2012)
[19] Nörder, A., Warren, S.A., Herdtweck, E., Huber, S.M., Bach, T. *JACS* **134**, 13524 (2012)
[20] Gigant, N., Dequirez, G., Retailleau, P., Gillaizeau, I., Dauban, P. *CEJ* **18**, 90 (2012)
[21] Valette, D., Lian, Y., Haydek, J.P., Hardcastle, K.I., Davies, H.M.L. *ACIE* **51**, 8636 (2012)
[22] Kornecki, K.P., Berry, J.F. *CC* **48**, 12097 (2012)
[23] Li, Z., Parr, B.T., Davies, H.M.L. *JACS* **134**, 10942 (2012)
[24] Lian, Y., Davies, H.M.L. *JACS* **133**, 11940 (2011)
[25] Lian, Y., Davies, H.M.L. *OL* **14**, 1934 (2012)

Rhodium porphyrins

CC Bond cleavage. [2.2]Paracyclophane is split to give 1,2-di(*p*-tolyl)ethane by the mediation of a Rh porphyrin.[1]

[1] To, C.T., Choi, K.S., Chan, K.S. *JACS* **134**, 11388 (2012)

Ruthenium

Redox reactions. Nano-Ru prepared by reduction of $RuCl_3$with $NaBH_4$ is stabilized by poly(vinylpyrrolidone). It catalyzes dehydrogenation of alcohols in water and an ionic liquid.[1] For use in hydrogenation of alkenes, a supramolecular hydrogel catalyst made from nano-Ru and a pyridinium salt *N*-substituted with a long carbon chain embedded in two α-cyclodextrin units shows a very high turnover frequency.[2]

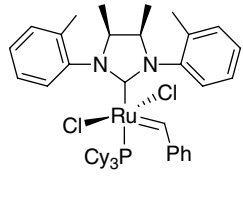
Stabilization of Ru nanoparticles by *N*-heterocyclic carbenes has also been observed.[3]

[1] Feng, B., Chen, C., Yang, H., Zhao, X., Hua, L., Yu, Y., Cao, T., Shi, Y., Hou, Z. *ASC* **354**, 1559 (2012)
[2] Leger, B., Menuel, S., Ponchel, A., Hapiot, F., Monflier, E. *ASC* **354**, 1269 (2012)
[3] Lara, P., Rivada-Wheelaghan, O., Conjero, S., Poteau, R., Philippot, K., Chaudret, B. *ACIE* **50**, 12080 (2011)

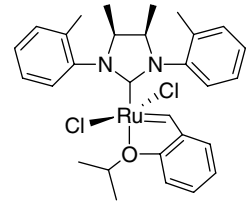
Ruthenium-carbene complexes

Modified metathesis catalysts. Various ways for removal of Ru residues after metathesis reaction has been summarized.[1] When the catalyst is deposited on thermomorphic polyethylene, its use has the advantage of easy separation from toluene at the end of reaction by cooling.[2] The Grubbs II precatalyst is rendered more active by using a hydrophilic

phosphine ligand (e.g., Cy_2PNR_3Cl) while reaction is carried out in CH_2Cl_2 – H_2O.[3] Complexes **1** and **2** are very active.[4]

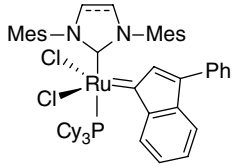


(**1**)

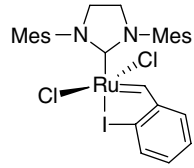


(**2**)

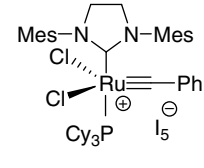
Favorable to olefin metathesis in a fluorinated solvent is conducted in the presence of complex **3** (and beneficially under microwave irradiation).[5] With excellent stability and reactivity for promoting metathesis **4** offers a new option.[6] The alkynylidene complex **5** is thermoendurable.[7]



(**3**)

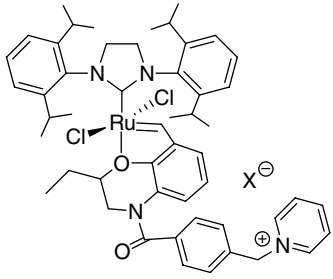


(**4**)

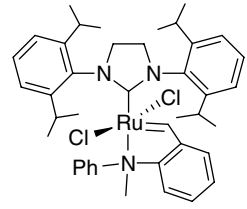


(**5**)

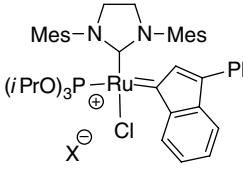
Fast initiation of metathesis is achieved with a complex (**6**, in homogeneous and heterogeneous versions) modified in the benzylidene portion of the ligand.[8] A more drastic change is to have an *o*-amino group (as in **7**) instead of ethereal oxygen.[9]



(**6**) X = PF_6 homogeneous
X = O_3S-polymer heterogeneous



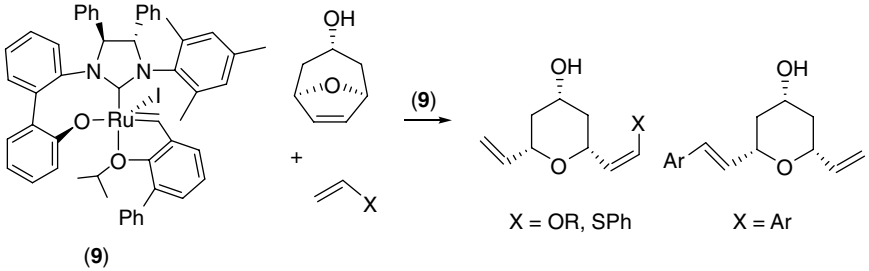
(**7**)



(**8**)

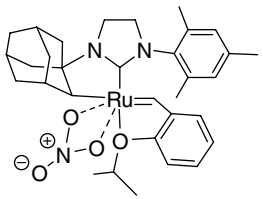
There is also a preparation of catalysts having chlorine ligands replaced by the trifluoroacetoxy groups.[10] The complex containing a phosphite ligand besides the cyclic carbene unit, two chlorine atoms and benzylidene, is easily available and shown to be highly efficient for olefin metathesis.[11] On further removal of a chlorine ligand by a silver salt, cationic Ru complexes including **8** become available. This latter species can be used at high temperatures.[12]

In the presence of **9**, the cross-metathesis of an 8-oxabicyclo[3.2.1]oct-6-en-3-ol with vinyl ethers and vinyl sulfides shows (*Z*)-selectivity, contrary to that involving styrene.[13]



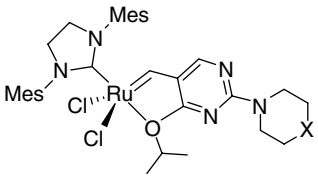
(**9**)

The complex **10** with the Ru atom ligated to a nitrate anion and C-bonded to adamantane is a (*Z*)-selective catalyst.[14,15]



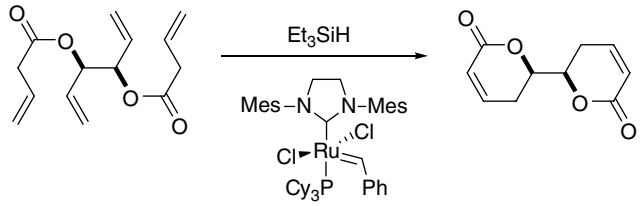
(**10**)

Off-coordination site modifications are represented by the complexes **11** and **12**, as well as dimeric species linked by a piperazine unit.[16]



(**11**) X = O
(**12**) X = CH_2

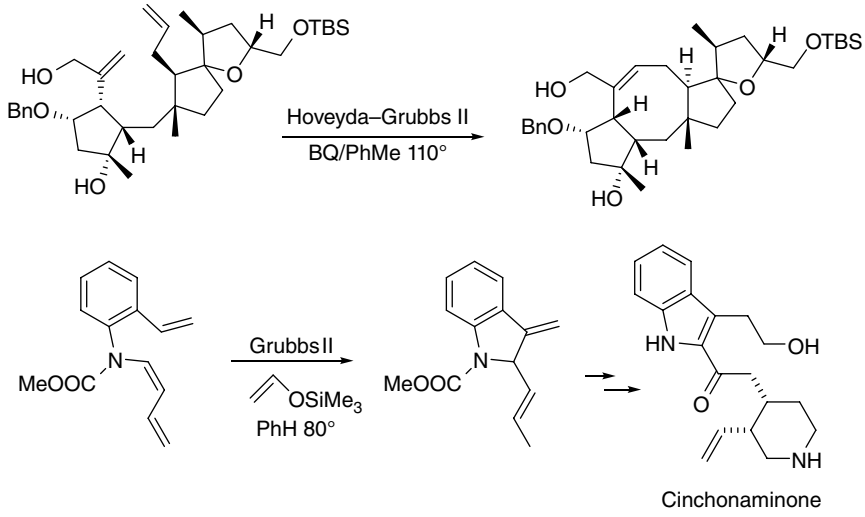
Metathesis applications. 2-Substituted 1,3-butadienes are formed from 1-alkynes in situ for Diels-Alder reaction when the easily available 1,7-octadiene is employed as an ethylene source.[18] Lactone formation from a 1,5-hexadiene-3,4-diol bis(3-butenoate) is triggered by Et_3SiH, and due to action of Ru hydride the double bonds of primary product move into conjugation with the carbonyl groups.[19]



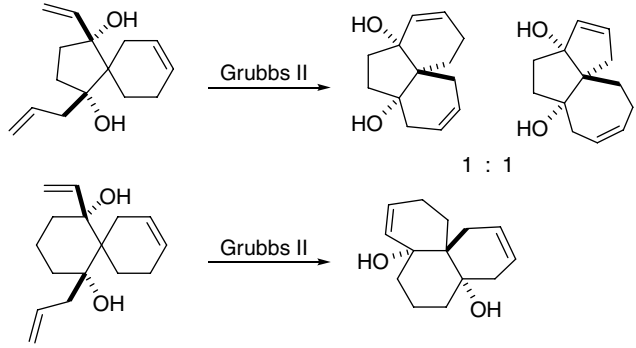
The Δ^{12} double bond of retinol acetate participates in cross-metathesis with many alkenes;[20] the selectivity is remarkable. During conversion of allyl ethers and esters into 1,4-dioxygenated 2-butenes by metathesis, contents of the (*E*)-isomer increase with time due to isomerization.[21]

It is noted that in ring-closing metathesis (RCM) involving alkyne and alkene units, the substitution pattern at the propargylic center exerts some influence. In the case of an unhindered alkyne there is need for ethylene to suppress catalyst (Grubbs I, II) deactivation, but for substrates possessing a quaternary propargylic carbon no such need arises.[22]

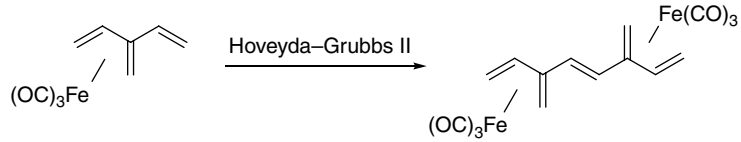
For solving synthetic problems, RCM plays a crucial role in the elaboration of indoloquinones,[23] formation of the 8-membered ring en route to (+)-ophiobolin-A,[24] an indoline precursor for cinchonaminone,[25] and particularly septulene.[26]



Interesting pairing selectivities for ring opening/ring closing metathesis are evident from reaction of the following compounds.[27]

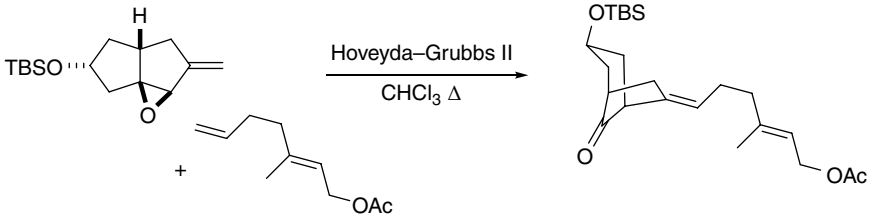


A synthetic approach to certain dendralenes by cross-metathesis is successful only when the designed nonparticipating diene is protected by complexation to a $Fe(CO)_3$ unit.[28]

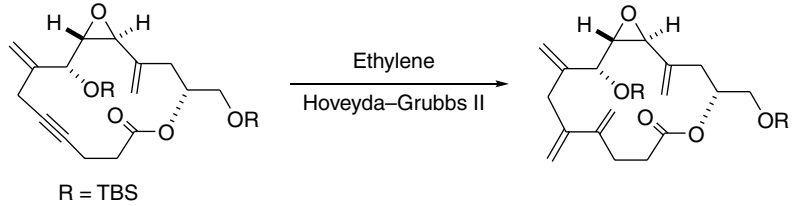


Cross-metathesis involving a 1-alkyne and an unsymmetrical diallyl ether gives the interesting result that the more highly substituted double bond of the ether is retained in the diene product, due to splitting off 2,5-dihydrofuran.[29]

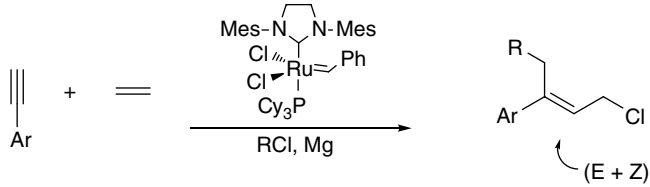
The Lewis acidity of the Ru species is responsible for a semipinacol rearrangement after cross-metathesis involving an epoxide.[30]



The great strength of the metathesis method is further illustrated by two key steps in the synthesis of the rare marine marolide amphidinolide-V.[31] An intramolecular diyne ring closure employing a Mo-based complex is followed by the Ru-carbene catalyzed *vic*-dimethylenation.

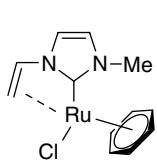


N-Trichloroacetyldiallylamine cyclizes to give the *N*-acyl-3-pyrroline. In the presence of styrene a transfer radical addition to follow the metathesis becomes possible.[32]

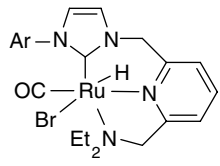


At completing the RCM of *o*-(*N*-allylamino)styrenes the addition of *t*-BuOOH causes oxidation to give 2-quinolones.[33]

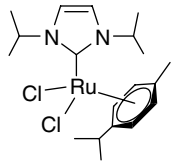
Redox reactions. The carbene complex **13** has served as catalyst for transfer hydrogenation of alkenes,[34] and the pincer complex **14** helps cleavage of esters into alcohols by hydrogen.[35] Promotion by **15** is observed of oxidative condensation of primary alcohols and amines to yield amides.[36]



(**13**)

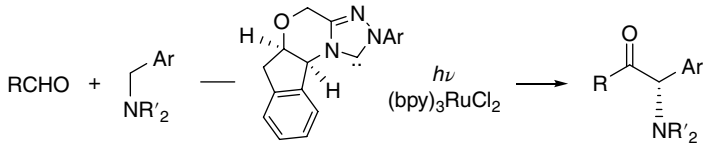


(**14**)



(**15**)

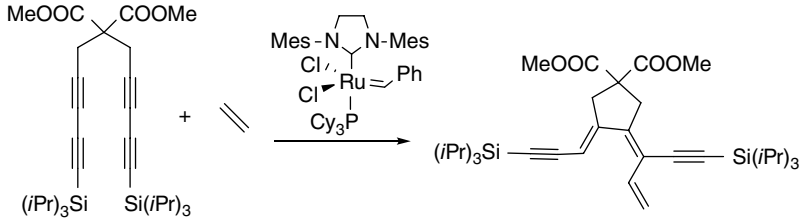
Benzylamines are *C*-acylated by RCHO under visible light and the influence of a Ru-carbene.[37]



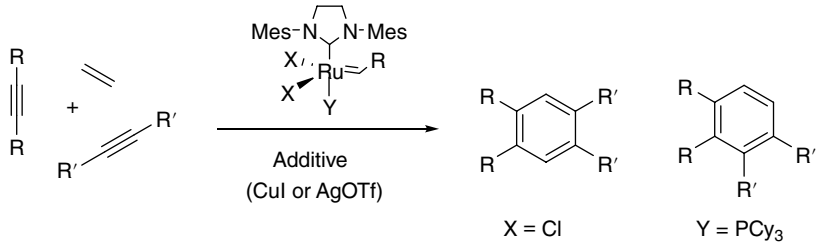
The Grubbs II complex also catalyzes cleavage of diols by NaOCl, selectively for those with one OH group allylic.[38] During synthesis of meayamycin-B an alkene to be subjected to cross-metathesis contains a hydroxyl group freshly unveiled from the TES ether by Bu_4NF, and it is necessary to scavenge any residual fluoride ion by $(Me_3Si)_2O$.[39] Without this additive, metathesis failed.

Addition. Catalysis on addition of thiols to alkynes is subject to regiochemical control by ligands surrounding the Ru center.[40] Interplay of electronic and steric factors is recognized.

Cycloaddition. Terminally silylated 1,3,8,10-undecatetraynes are converted into monocyclic trienynes bearing an ethynyl group in cross conjugation.[41] In these cases the Grubbs II complex does not catalyze metathesis.



Ligand effects from the catalyst are also displayed in the [2+2+2]cycloaddition involving two alkynes and ethylene.[42] And the catalyst is tuned by an additive (CuI or AgOTf).



Grubbs-Hoveyda II precatalyst is active in promoting the cycloaddition of two alkynes and a nitrile to produce pyridines.[43]

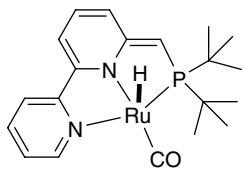
Coupling. An uneconomical way to couple thioamides with 2-diazo-1,3-dicarbonyl compounds is that utilizing the Grubbs I complex.[44]

[1] Vougioukalakis, G.C. *CEJ* **18**, 8868 (2012)
[2] Hobbs, C., Yang, Y.-C., Ling, J., Nicola, S., Su, H.-L., Bazzi, H.S., Bergbreiter, D.E. *OL* **13**, 3904 (2011)
[3] Xi, Z., Bazzi, H.S., Gladysz, J.A. *OL* **13**, 6188 (2011)
[4] Costabile, C., Mariconda, A., Cavallo, L., Longo, P., Bertolasi, V., Ragone, F., Grisi, F. *CEJ* **17**, 8618 (2011)
[5] Samojlowicz, C., Borre, E., Maudit, M., Grela, K. *ASC* **353**, 1993 (2011); Samojlowicz, C., Bieniek, M., Pazio, A., Makal, A.,Wozniak, K., Poater, A., Cavallo, L., Wojcik, J., Zdanowski, K., Grela, K. *CEJ* **17**, 12981 (2011)
[6] Barbasiewicz, M., Michalak, M., Grela, K. *CEJ* **18**, 14237 (2012)
[7] Shao, M., Zheng, L., Qiao, W., Wang, J., Wang, J. *ASC* **354**, 2743 (2012)
[8] Borre, E., Rouen, M., Laurent, I., Magrez, M., Caijo, F., Crevisy, C., Solodenko, W., Toupet, L., Frankfurter, R., Vogt, C., Kirschning, A., Maudit, M. *CEJ* **18**, 16369 (2012)
[9] Peeck, L.H., Savka, R.D., Plenio, H. *CEJ* **18**, 12845 (2012)
[10] Anderson, E.B., Buchmeiser, M.R. *SL* 185 (2012)
[11] Schmid, T.E., Bantreil, X., Citadelle, C.A., Slawin, A.M.Z., Cazin, C.S.J. *CC* **47**, 7060 (2011)
[12] Songis, O., Slawin, A.M.Z., Cazin, C.S.J. *CC* **48**, 1266 (2012)
[13] Khan, R.K.M., O'Brien, R.V., Torker, S., Li, B., Hoveyda, A.H. *JACS* **134**, 12774 (2012)
[14] Keitz, B.K., Endo, K., Patel, P.R., Herbert, M.B., Grubbs, R.H. *JACS* **134**, 693 (2012)
[15] Keitz, B.K., Fedorov, A., Grubbs, R.H. *JACS* **134**, 2040 (2012)
[16] Wu, G.-L., Cao, S.-L., Chen, J., Chen, Z. *EJOC* 6777 (2012)

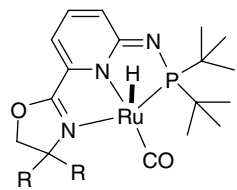
[17] Fustero, S., Bello, P., Miro, J., Simon, A., del Pozo, C. *CEJ* **18**, 10991 (2012)
[18] Schmidt, B., Kunz, O. *SL* 851 (2012)
[19] Wojtkielewicz, A., Maj, J., Dzieszkowska, A., Morzycki, J.W. *T* **67**, 6868 (2011)
[20] Moulins, J.R., Burnell, D.J. *TL* **52**, 3992 (2011)
[21] Grotevendt, A.G.D., Lummiss, J.A.M., Mastronardi, M.L., Fogg, D.E *JACS* **133**, 15918 (2011)
[22] Nishiyama, T., Choshi, T., Kitano, K., Hibino, S. *TL* **52**, 3876 (2011)
[23] Tsuna, K., Noguchi, N., Nakada, M. *ACIE* **50**, 9452 (2011)
[24] Ogawa, T., Nakamura, T., Araki, T., Yamamoto, K., Shuto, S., Arisawa, M. *EJOC* 3084 (2012)
[25] Kumar, B., Viboh, R.L., Bonifacio, M.C., Thompson, W.B., Buttrick, J.C., Westlake, B.C., Kim, M.-S., Zoellner, R.W., Varganov, S.A., Mrschel, P., Teteruk, J., Schmidt, M.U., King, B.T. *ACIE* **51**, 12795 (2012)
[26] Gao, F., Stamp, C.T.M., Thornton, P.D., Cameron, T.S., Doyle, L.E., Miller, D.O., Burnell, D.J. *CC* **48**, 233 (2012)
[27] Toombs-Ruane, H., Osinski, N., Fallon, T., Wills, C., Willis, A.C., Paddon-Row, M.N., Sherburn, M.S. *CAJ* **6**, 3243 (2011)
[28] Clark, J.R., French, J.M., Jecs, E., Diver, S.T. *OL* **14**, 4178 (2012)
[29] Plummer, C.W., Soheili, A., Leighton, J.L. *OL* **14**, 2462 (2012)
[30] Fürstner, A., Flügge, S., Larionov, O., Takahashi, Y., Kubota, T., Kobayashi, J. *CEJ* **15**, 4011 (2009)
[31] Kiefer, G., Ruiz, J., Solari, E., Hilt, G., Severin, K. *EJOC* 93 (2012)
[32] Kato, H., Ishigame, T., Oshima, N., Hoshiya, N., Shimawaki, K., Arisawa, M., Shuto, S. *ASC* **353**, 2676 (2011)
[33] Horn, S., Albrecht, M. *CC* **47**, 8802 (2011)
[34] Sun, Y., Koehler, C., Tan, R., Annibale, V.T., Song, D. *CC* **47**, 8349 (2011)
[35] Markarov, I.S., Fristrup, P., Madsen, R. *CEJ* **18**, 15683 (2012)
[36] DiRocco, D.A., Rovis, T. *JACS* **134**, 8094 (2012)
[37] Han, C., Yamano, Y., Kakichi, F., Nakamura, K., Uemura, D. *T* **67**, 9622 (2011)
[38] Osman, S., Koide, K. *TL* **53**, 6637 (2012)
[39] Di Giuseppe, A., Castarelenas, R., Perez-Torrente, J.J., Crucianelli, M., Polo, V., Sancho, R., Lahoz, F.J., Oro, L.A. *JACS* **134**, 8171 (2012)
[40] Yun, S.Y., Wang, K.-P., Kim, M., Lee, D. *JACS* **134**, 10783 (2012)
[41] Feng, C., Wang, X., Wang, B.-Q., Zhao, K.-Q., Hu, P., Shi, Z.-J. *CC* **48**, 356 (2012)
[42] Medina, S., Dominguez, G., Perez-Castells, J. *OL* **14**, 4982 (2012)
[43] Koduri, N.D., Scott, H., Hileman, B., Cox, J.D., Coffin, M., Glicksberg, L., Hussaini, S.R. *OL* **14**, 440 (2012)

Ruthenium bipyridine complexes

Redox reactions. The bipyridylmethylphosphine-Ru complex **1** is a catalyst for reductive condensation of nitriles with primary amines under hydrogen that furnishes aldimines.[1] The same complex, however, promotes ester formation from mixtures of primary and secondary alcohols.[2]



(**1**)



(**2**)

Complex **2**, an analog of **1** in which one of the pyridine ring is replaced by an oxazoline unit, catalyzes transfer hydrogenation of carbonyl compounds with isopropanol.[3]

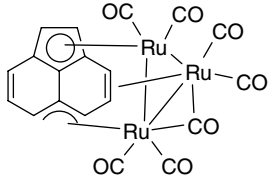
With $(bpy)_3Ru(BF_4)_2$ acting as catalyst to induce photochemical fragmentation, *t*-carboxylic acid esters of *N*-hydroxyphthalide provide *t*-alkyl radicals as addends to conjugated ketones.[4]

Three 2,2′-bipyrazine molecules form a closely related complex with the Ru(II) ion. Such a salt is useful for promoting Diels-Alder reactions under visible light at room temperature. Substrates are converted into active radical cations.[5]

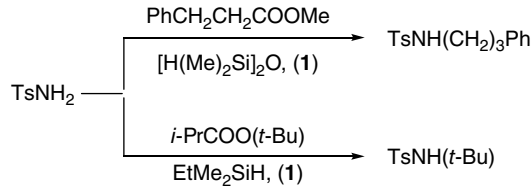
[1] Srimani, D., Feller, M., Ben-David, Y., Milstein, D. *CC* **48**, 11853 (2012)
[2] Srimani, D., Balaraman, E., Gnanaprakasam, B., Ben-David, Y., Milstein, D. *ASC* **354**, 2403 (2012)
[3] Chen, T., He, L.-P., Gong, D., Yang, L., Miao, X., Eppinger, J., Huang, H.-W. *TL* **53**, 4409 (2012)
[4] Schnermann, M.J., Overman, L.E. *ACIE* **51**, 9576 (2012)
[5] Lin, S., Ischay, M.A., Fry, C.G., Yoon, T.P. *JACS* **133**, 19350 (2011)

Ruthenium carbonyl complexes

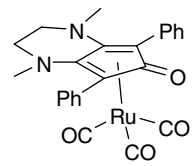
Alkylation. Alkylation of arenes via acylation and reduction performed with ester and hydrosilane mixtures is enabled by the Ru complex **1**.[1] When *N*-alkylation of tosylamines is accomplished the option of attaching a primary or tertiary alkyl group is easily exercised.[2]



(**1**)



2-(2-Pyrrolyl)ethyl ketones are obtained by the condensation of pyrrole with 1-alkyn-3-ols under the influence of the complex **2**. The reaction involving 4-penten-1-yn-3-ols leads to the formation of indoles.[3]



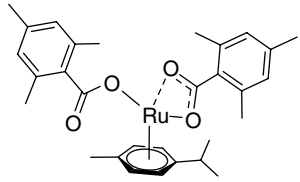
(**2**)

Pentenynols behave as synthetic equivalent of cross-conjugated dienones in the presence of **2**, thus enabling spiroannulation of 1,3-cyclohexanedione.[4]

[1] Nagashima, H., Kubo, Y., Kawamura, M., Nishikata, T., Motoyama, Y. *T* **67**, 7667 (2011)
[2] Nishikata, T., Nagashima, H. *ACIE* **51**, 5363 (2012)
[3] Thies, N., Hrib, C.G., Haak, E. *CEJ* **18**, 6302 (2012)
[4] Jonek, A., Berger, S., Haak, E. *CEJ* **18**, 15504 (2012)

Ruthenium(II) carboxylates

Aryl ketone o-hydroxylation. This reaction is performed in the presence of **1** and $PhI(OAc)_2$ in CF_3COOH – $(CF_3CO)_2O$.[1]



(**1**)

[1] Thirunavukkarasu, V.S., Ackermann, L. *OL* **14**, 6206 (2012)

Ruthenium(III) chloride

Acylation. With *N*-alkylanilines $ArNHCH_2R$ to supply the COR group, indole is acylated at C-3. The reagent system contains $RuCl_3$, *t*-BuOOH, and pivalic acid.[1]

Oxidation. The ruthenium salt complexed to silica which is further functionalized with amidine and *o*-iodobenzamide is paired with Oxone to oxidize alcohols and also $ArCH_2R$ (to ArCOR).[2]

[1] Wu, W., Su, W. *JACS* **133**, 11924 (2011)
[2] Zeng, X.-M., Chen, J.-M., Middleton, K., Zhdankin, V.V. *TL* **52**, 5652 (2011)

Ruthenium(III) hydroxide

N-Alkylation. Anilines, sulfinamides and sulfonamides are alkylated by RCH_2OH using the easily recoverable $Ru(OH)_3/Fe_3O_4$ as catalyst.[1]

Hydration of nitriles.[2] A similar Ru catalyst on magnetite-silica converts ArCN into $ArCONH_2$ in water (100°).

[1] Cano, R., Ramon, D.J., Yus, M. *JOC* **76**, 5547 (2011)
[2] Baig, R.B.N., Varma, R.S. *CC* **48**, 6220 (2012)

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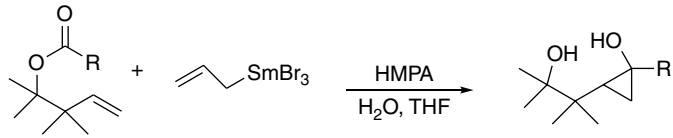
Salicylaldehyde

Amine protection. Schiff base formation with RNH_2 allows *N*-alkylation of secondary amines[1].

[1] Culf, A.S., Melanson, J.A., Ouellette, R.J., Briand, G.-G. *TL* **53**, 3301 (2012)

Samarium

Group transfer. Certain homoallylic esters are transformed into cyclopropanols while involving the double bond and the ester acyl group. Allylsamarium bromide derived from Sm effects this reaction.[1]



[1] Tu, Y., Zhou, L., Yin, R., Lv, X., Flowers II, R.A., Choquette, K.A., Liu, H., Niu, Q., Wang, X. *CC* **48**, 11026 (2012)

Samarium(II) bromide

Preparation. In application $SmBr_2$ is totally eclipsed by SmI_2. However, owing to the differing reduction potentials of various lanthanide halides their synthetic uses should be carefully evaluated.[1] As for preparation of $SmBr_2$, several methods are available: $SmBr_3$ + Li,[2] SmI_2 + LiBr,[3] Sm + CBr_4.[4]

[1] Szostak, M., Procter, D.J. *ACIE* **51**, 9238 (2012)
[2] Lebrun, A., Namy, J.-L., Kagan, H.B. *TL* **34**, 2311 (1993)
[3] Fuchs, J.R., Mitchell, M.L., Shabangi, M., Flowers II, R.A. *TL* **38**, 8157 (1997)
[4] Hølion, F., Lannou, M.I., Namy, J.-L. *TL* **44**, 5507 (2003)

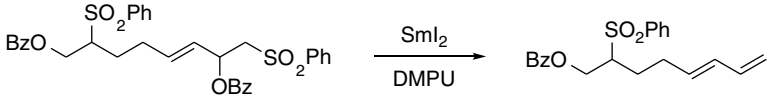
Samarium(II) iodide

Preparation. In formation of SmI_2 from Sm, ICH_2CH_2I, I_2 and an oxidant in THF, effects of water, oxygen and peroxide have been evaluated.[1]

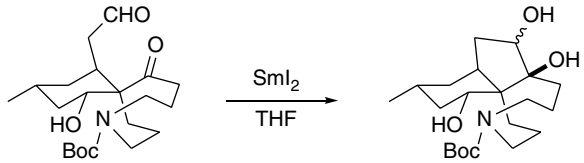
Fiesers' Reagents for Organic Synthesis, First Edition. Tse-Lok Ho.
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Reduction. A review has been written on the selective reductions using SmI_2 in the presence of water.[2] The SmI_2/H_2O and Et_3N system is good for reduction of acids and esters to primary alcohols.[3,4] With SmI_2-ROH, PhC=NPh is reduced faster than PhN=NPh,[5] and the reduction of RCN to primary amines is promoted by visible light.[6]

Elimination. Selectivity in the elimination of β-acyloxy sulfones is achievable. Preference is accorded to those leading to conjugated dienes.[7]



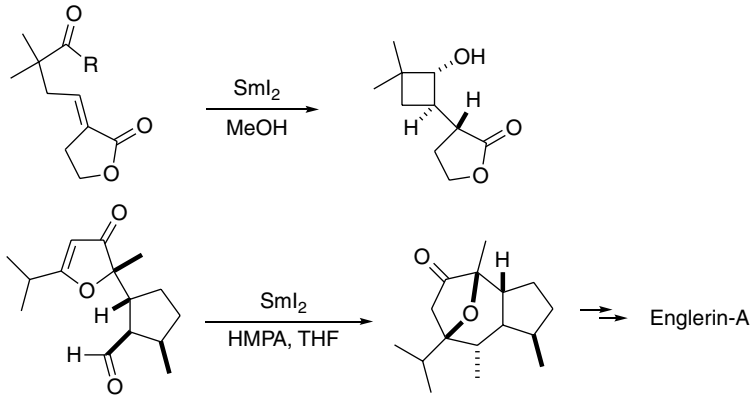
Carbonyl coupling. The course for the formation of a 1,2-cyclopentanediol unit in a spirocyclic system is greatly influenced by a hydroxyl in the vicinity (multi-site complexability), and also the presence of HMPA affects the stereochemical outcome (diol configuration).[8]



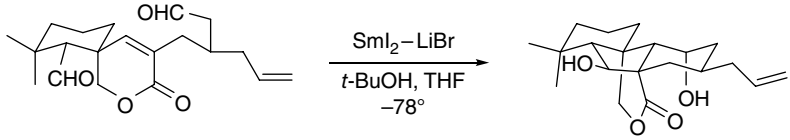
4-Acyl-1,3-dioxolanes are transformed into 3-alkene-1,2-diols through a sequence of reductive elimination to release an enone and a ketone that engage in 1,2-coupling.[9]

Addition. Alkyl bromides are rendered nucleophilic by the action of SmI_2, and accordingly bromonitromethane becomes a nitromethylating agent for aldehydes.[10] From *N*-(α-bromoalkanoyl)-α-amino esters a Barbier reaction is readily accomplished.[11] Also an aldol-Tishchenko reaction sequence between a 3-amino-1-chloro-2-alkanone and an aldehyde leads to a *syn,anti*-amino diol monoester stereoselectively.[12]

It is now well known that carbonyl compounds generate ketyls and such active species are trapped by an activated double bond. Further examples show the possibility of cyclobutanol synthesis,[13] and the closure of the oxabicyclic core of englerin-A.[14]



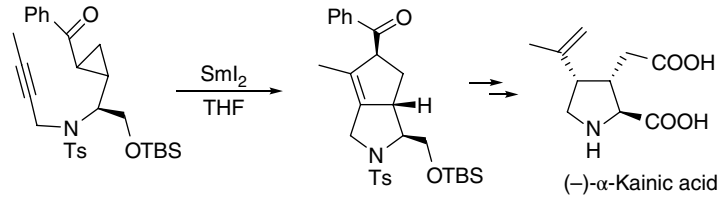
The involvement of two formyl groups and an intervening double bond of a dihydropyrone to form two rings in one step shows the power of the method.[15]



Disubstituted Meldrum acids in which carbon chains terminated in styryl groups are shown to form bicyclic compounds containing at the ring juncture a hydroxyl and a carboxyl groups.[16] α-(3-Butenyl)-δ-allenyl-δ-lactones undergo cyclization to furnish perhydroazulenediols.[17]

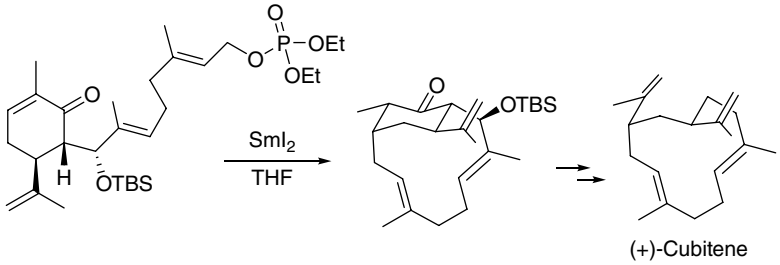
Most unusual is the dearomatizative intramolecular addition of 1-(4-oxo)pentylnaphthalene onto C-2 to form a hydroxyhexahydrophenanthrene.[18] Most importantly, this report describes the use of tripyrrolidinopphosphoramide to replace the carcinogenic HMPA.

Ketyls generated from conjugated carbonyl compounds also actively pursue addition reactions, and the involvement of a triple bond as receptor is witnessed.[19,20]



2,3-Butadienoic esters and imine derivatives are combined to afford 3-(α-aminoalkyl)-3-butenoic esters.[21] The union of nitrones with conjugated esters appears to involve reductive transformation of the nitrogenated functionality, the products are γ-hydroxylamino esters.[22,23] 2-Pyridyl tetrahydropyran-2-yl sulfones and acrylic acid derivatives are transformed into β-tetrahydropyran-2-ylpropanoic esters and cognate compounds, but NaI_2 is needed.[24]

Reductive allylation. Macrocyclization by an intramolecular allylation is the crucial step in a synthesis of (+)-cubitene.[25]



[1] Szostak, M., Spain, M., Procter, D.J. *JOC* **77**, 3049 (2012)
[2] Szostak, M., Spain, M., Parmar, D., Procter, D.J. *CC* **48**, 330 (2012)
[3] Szostak, M., Spain, M., Procter, D.J. *OL* **14**, 840 (2012)
[4] Szostak, M., Spain, M., Procter, D.J. *CC* **47**, 10254 (2011)
[5] Rao, C.N., Hoz, S. *JOC* **76**, 9438 (2011)
[6] Rao, C.N., Hoz, S. *JOC* **77**, 4029 (2012)
[7] Volz, E.O., O'Neil, G.W. *JOC* **76**, 8428 (2011)
[8] Li, H., Wang, X., Lei, X. *ACIE* **51**, 491 (2012)
[9] Zhao, Y.-H., Ma, R.-L., Sun, X.-W., Lin, G.-Q. *S* 2763 (2012)
[11] Bai, W.-J., Jackson, S.K., Pettus, T.R.R. *OL* **14**, 3862 (2012)
[12] Rodriguez-Solla, H., Concellon, C., Tuya, P., Garcia-Granda, S., Diaz, M.R. *ASC* **354**, 1679 (2012)
[13] Harb, H.Y., Procter, D.J. *SL* **6** (2012)
[14] Li, Z., Nakashige, M., Chain, W.J. *JACS* **133**, 6553 (2011)
[15] Cha, Z., Teoman, J.T.S., Reisman, S.E. *JACS* **133**, 14965 (2011)
[16] Sautier, B., Lyons, S.E., Webb, M.R., Procter, D.J. *OL* **14**, 146 (2012)
[17] Parmar, D., Matsubara, H., Price, K., Spain, M., Procter, D.J. *JACS* **134**, 12751 (2012)
[18] Berndt, M., Hölemann, A., Niermann, A., Bentz, C., Zimmer, R., Reissig, H.-U. *EJOC* 1299 (2012)
[19] Takahashi, K., Morita, H., Honda, T. *TL* **53**, 3342 (2012)
[20] Luo, Z., Zhou, B., Li, Y. *OL* **14**, 2540 (2012)
[21] Xu, C.-P., Huang, P.-Q., Py, S. *OL* **14**, 2034 (2012)
[22] Rehak, J., Fisera, L., Kozisek, J., Bellovicova, L. *T* **67**, 5762 (2011)
[23] Gilles, P., Py, S. *OL* **14**, 1042 (2012)
[24] Li, G., Xiong, D.-C., Ye, X.-S. *SL* 2410 (2011)
[25] Simon, K., Wefer, J., Schöttner, E., Lindel, T. *ACIE* **51**, 10889 (2012)

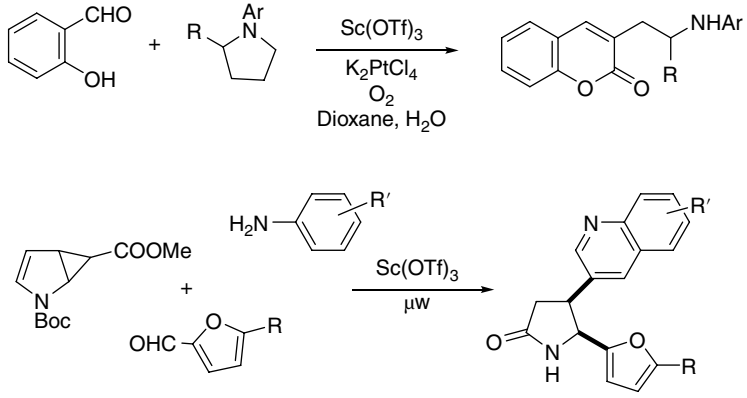
Scandium(III) triflate

Esterification. Use of $Sc(OTf)_3$ as catalyst primary alcohols are selectively esterified without affecting secondary alcohols.[1] Thiosulfinates are formed when RSO_2Na and *N*-sulfenylsuccinimides are brought into contact with $Sc(OTf)_3$ in [bmim] PF_6 and water.[2]

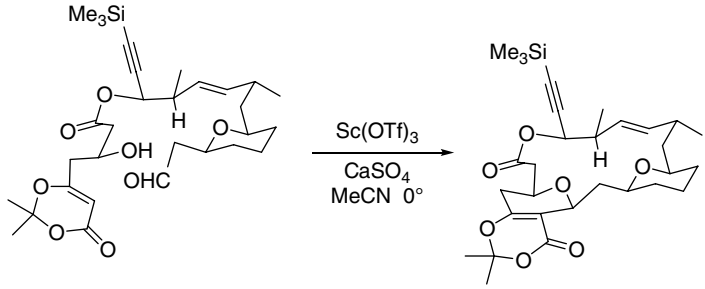
Condensation. *N*-Methoxy homoallylamines are acquired from a three-component condensation: ketone, BnNHOMe and allyltributylstannane in the presence of $Sc(OTf)_3$.[3] 6-Aryl-3-alken-1-ols and the sulfur and nitrogen congeners condense with RCHO to give tricyclic products.[4] Friedel-Crafts reaction of *N*-aryl-1-amino-2-alkyn-4-ones results in 3-(2-oxoalkyl)indoles.[5] It is apparent that $Sc(OTf)_3$ is a stronger Lewis acid than $SnCl_4$, the latter only submits a chlorine atom to the triple bond (hydrochlorination).

2-(4-Methoxyphenylethyl)benzaldehyde and $TsNH_2$ condense to give 3-(4-methoxyphenyl)-*N*-tosyl-1,2,3,4-tetrahydroisoquinoline,[6] as a result of the intervention of a 1,5-hydride shift to enable cyclization.

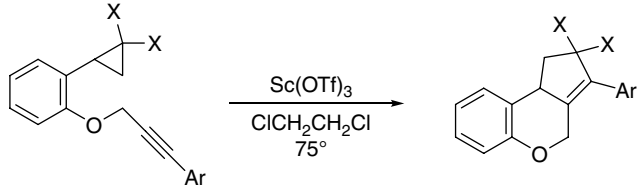
Cyclic *N*-arylamines suffer oxidation and the enamines condense with salicylaldehyde. A method for synthesis of 3-(ω-aminoalkyl)coumarins is based on the reaction.[7] A more intriguing process is that which combines anilines, furaldehydes, and cyclopropanopyrrolines.[8]



An efficient macrocyclization involving hemiacetal formation is achieved via intervention of $Sc(OTf)_3$, although an unusually large amount of which seems necessary.[9]



Cycloaddition. Polarization of 2,2-diacyloxiranes by $Sc(OTf)_3$unveils their reactivity as 1,3-dipolarophiles.[10] Some 2-aryl-1,1-diacylcyclopropanes behave similarly.[11]



Isobenzofuran obtained from phthalaldehyde on reduction with Et_3SiH [catalyzed by $Sc(OTf)_3$] is trapped by dienophiles.[12] Doping zeolite with $Sc(OTf)_3$ gives an even better catalyst for the hetero-Diels-Alder reaction between the Danishefsky diene and imines, because it can be recovered and reused.[13]

Coupling. Amination of 1,3,4-oxadiazoles at C-2 is accomplished using $Sc(OTf)_3$,TfOH and the oxidant $(TEMPO)BF_4$.[14] A procedure for arylation at the methyl

group of α-picoline involves zincation and *N*-complexation with $Sc(OTf)_3$ prior to palladation. Without the $Sc(OTf)_3$ coupling is not observed.[15]

Iodination. 2,2′-Dimethoxy-1,1′-binaphthyl is iodinated at C-6 and C-6′. The reaction is catalyzed by $Sc(OTf)_3$ and 1,3-diiodo-5,5-dimethylhydantoin furnishes the positive iodine species. NIS is not suitable (yield 4% vs. 98%).[16]

[1] McClure, M.S., Berry, M.B., Caine, D., Crawford, C., Crump, B.C., Glover, B.N., Kedia, S.B., Miller, A., Mitchell, M.B., Nichols, C.J., Patterson, D.E., Powers, J. *EJOC* 3561 (2012)
[2] Liang, G., Chen, J., Li, W., Chen, J., Wu, H. *TL* **53**, 6768 (2012)
[3] Kurosaki, Y., Shirokane, K., Oishi, T., Sato, T., Chida, N. *OL* **14**, 2098 (2012)
[4] Reddy, B.V.S., Borkar, P., Yadav, J.S., Sridhar, B., Grée, R. *JOC* **76**, 7677 (2011)
[5] Yang, F., Ji, K.-G., Ali, S., Liang, Y.-M. *JOC* **76**, 8329 (2011)
[6] Mori, K., Kawasaki, T., Akiyama, T. *OL* **14**, 1436 (2012)
[7] Xia, X.-F., Shu, X.-Z., Ji, K.-G., Shaukat, A., Liu, X.-Y., Liang, Y.-M. *JOC* **76**, 342 (2011)
[8] Roy, S., Reisser, O. *ACIE* **51**, 4722 (2012)
[9] Crane, E.A., Zabawa, T.P., Farmer, R.L., Scheidt, K.A. *ACIE* **50**, 9112 (2011)
[10] Liu, R., Zhang, M., Zhang, J. *CC* **47**, 12870 (2011)
[11] Xia, X.-F., Song, X.-R., Liu, X.-Y., Liang, Y.-M. *CAJ* **7**, 1538 (2012)
[12] Nishina, Y., Kida, T., Ureshino, T. *OL* **13**, 3960 (2011)
[13] Olmos, A., Louis, B., Pale, P. *CEJ* **18**, 4894 (2012)
[14] Wertz, S., Kodama, S., Studer, A. *ACIE* **50**, 11511 (2011)
[15] Duez, S., Steib, A.K., Manolikakes, S.M., Knochel, P. *ACIE* **50**, 7686 (2011)
[16] Kamei, T., Shibaguchi, H., Sako, M., Toribatake, K., Shimada, T. *TL* **53**, 3894 (2012)

Selenium

Aldol reaction. As an alternative but noncatalytic Baylis-Hillman reaction to functionalize conjugated carbonyl compounds, the adducts with BuSeLi (BuLi + Se) are treated with RCHO, and regeneration of the unsaturation by oxidation (H_2O_2) and elimination.[1]

[1] Sousa, B.A., Dos Santos, A.A. *EJOC* 3431 (2012)

Selenium dioxide

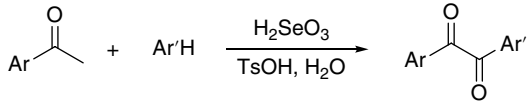
α-Keto amides. In situ oxidation of the condensation products of amines and α-keto aldehydes with SeO_2 under microwave irradiation results in keto amides.[1]

Diarylation. Methyl ketones and arenes combine in 1:2 ratio when they are exposed to SeO_2 and $BF_3{\cdot}OEt_2$ at room temperature.[2]

[1] Shaw, A.Y., Denning, C.R., Hulme, C. *TL* **53**, 4151 (2012)
[2] Laloo, B.M., Mecadon, H., Rohman, M.R., Kharbangar, I., Kharkongor, I., Rajbangshi, M., Nongkhlaw, R., Myrboh, B. *JOC* **77**, 707 (2012)

Selenious acid

Benzils. Acetophenones undergo oxidation, and when the keto aldehyde stage is reached a Friedel-Crafts reaction with active arenes can follow. Ultimately, benzils (symmetrical or unsymmetrical) are obtained.[1]



[1] Kharkongor, I., Rohman, M.R., Myrboh, B. *TL* **53**, 2837 (2012)

Silver

Addition. Nano-Ag/TiO_2 promotes addition of arylethynes to ArCHO in water at 60° (Ph_3P and Et_3N also present).[1]

[1] Yu, M., Wang, Y., Sun, W., Yao, X. *ASC* **354**, 71 (2012)

Silver acetate

Decarboxylation. Arenecarboxylic acids decarboxylate on heating with AgOAc and K_2CO_3. This reaction can be adapted to the synthesis of ArD from ArCOOD.[1] In a different report an oxidant ($K_2S_2O_8$) is included in the reagent system,[2] and from 2-aroylbenzoic acids it produces fluorenones.[3]

Coupling. A method for deborative carboxylation of areneboronic esters consists of the catalyst AgOAc-Ph_3P and a base (*t*-BuOK).[4] Suzuki coupling can be performed by AgOAc.[5]

Addition and cycloaddition. Intramolecular iodoamination of an alkene (I_2-AgOAc) is a prominent step in a synthesis of (+)-saxitoxin.[6] In this case the amino group is actually a Boc-protected guanidine.

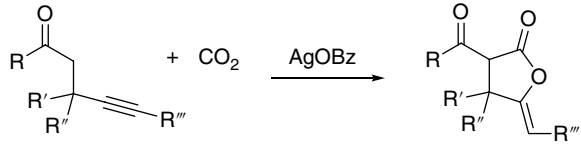
A new route to 5-arylpyrrole-2-carboxylic esters is based on the [3+2]cycloaddition of *N*-benzylideneglycine esters with 1-bromoethenyl phenyl sulfone.[7]

As an alternative to the copper catalysts the "click reaction" (alkyne + azide) is also catalyzed by the AgOAc complex of *N,N*-diisoproyl *o*-diphenylphosphinobenzamide.[8]

[1] Rudzki, M., Alcaide-Aragonés, A., Dzik, W.I, Rodriguez, N., Goossen, L.J. *S* **184** (2012)
[2] Seo, S., Taylor, J.B., Greaney, M.F. *CC* **48**, 8270 (2012)
[3] Seo, S., Slater, M., Greaney, M.F. *OL* **14**, 2650 (2012)
[4] Zhang, X., Zhang, W.-Z., Shi, L.-L., Guo, C.-X., Zhang, L.-L., Lu, X.-B. *CC* **48**, 6292 (2012)
[5] Das, R., Chakraborty, D. *TL* **53**, 7023 (2012)
[6] Bhonde, V.R., Looper, R.E. *JACS* **133**, 20172 (2011)
[7] Kudryavtsev, K.V., Ivantcova, P.M., Churakov, A.V., Vasin, V.A. *TL* **53**, 4300 (2012)
[8] McNulty, J., Keskar, K., Vemula, R. *CEJ* **17**, 14727 (2011)

Silver benzoate

Carboxylation. 4-Alkyn-1-ones incorporate CO_2 to form α-acyl-γ-alkylidene-γ-butyrolactones.[1]



[1] Kikuchi, S., Sekine, K., Ishida, T., Yamada, T. *ACIE* **51**, 6989 (2012)

Silver carbonate

3-Acylfurans. The oxidative coupling of, 1,3-dicarbonyl compounds with 1-alkynes is terminated in ring closure to afford 3-acylfurans.[1]

[1] He, C., Guo, S., Ke, J., Hao, J., Xu, H., Chen, H., Lei, A. *JACS* **134**, 5766 (2012)

Silver fluoride

Glycosyl fluorides. Thioglycosides react with I_2 in the presence of AgF, iodine(I) fluoride that is generated in situ transforms the substrates into fluorides.[1]

o-Trifluoromethylation. 1-Aryltriazenes undergo *o*-trifluoromethylation on reaction with Me_3SiCF_3 in the presence of AgF.[2] The active reagent could be $AgCF_3$.

Addition. Silver fluoride along with NBS performs *cis*-bromofluorination of alkynes in aqueous MeCN.[3] The same reagent pair is used in converting ω-hydroxy-1-triorganosilyl-1-alkynes into (*Z*)-2-bromomethylene oxacycles.[4]

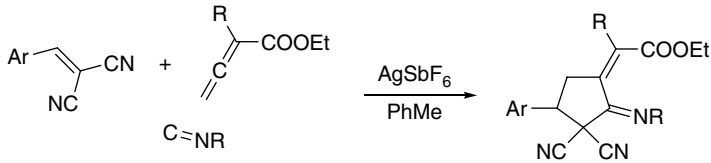
[1] Mugunthan, G., Kartha, K.P.R. *TL* **53**, 5631 (2012)
[2] Hafner, A., Bräse, S. *ACIE* **51**, 3713 (2012)
[3] Li, Y., Liu, X., Ma, D., Liu, B., Jiang, H. *ASC* **354**, 2683 (2012)
[4] Lee, H.-J., Lim, C., Hwang, S., Jeong, B.-S., Kim, S. *CAJ* **6**, 1943 (2011)

Silver hexafluoroantimonate

Ether cleavage. 4-Methoxybenzyl ethers are cleaved in the presence of $AgSbF_6$ and trimethylphloroglucinol.[1]

Hydration. In aqueous MeOH, conversion of 1-alkynes to methyl ketones is catalyzed by $AgSbF_6$.[2]

Cycloaddition. 2-Trifluoromethyl-*N*-tosylaziridine and aldehydes form 4-trifluoromethyloxazolidines in which the substituents at C-2 and C-4 are *cis*-related.[3] Doubly activated alkenes, allenes and isonitriles combine to afford polyfunctionalized cyclopentanes.[4]



[1] Kern, N., Dombray, T., Blanc, A., Weibel, J.-M., Pale, P. *JOC* **77**, 9227 (2012)
[2] Thuong, M.B.T., Mann, A., Wagner, A. *CC* **48**, 434 (2012)
[3] Maeda, R., Ishibashi, R., Kamaishi, R., Hirotaki, K., Furuno, H., Hanamoto, T. *OL* **13**, 6240 (2011)
[4] Li, J., Liu, Y., Li, C., Jia, X. *ASC* **353**, 913 (2011)

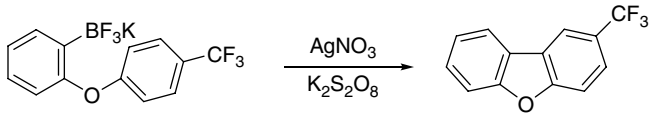
Silver iodide

Carboxylation+esterification.[1] As an extension of the 2011 report concerning carboxylation of 1-alkynes with CO_2, the presence of RCH_2Cl besides AgI and Cs_2CO_3 causes formation of esters.

[1] Zhang, X., Zhang, W.-Z., Shi, L.-L., Zhu, C., Jiang, J.-L. *T* **68**, 9085 (2012)

Silver nitrate

Substitution. Decarboxylative alkynylation by *o*-carboxylatobenzeneiodonium alkynides is effected with $AgNO_3/K_2S_2O_8$. It is a radical-mediated coupling.[1] Pyridine *N*-oxide undergoes arylation at C-2 on reaction with $ArB(OH)_2$ using the same catalyst-reagent pair.[2] An intramolecular version is that leading to dibenzofurans.[3] Substitution at C-3 of 1,2-naphthoquinone is also observed [the change of oxidant to $(NH_4)_2S_2O_8$ is of little consequence].[4]



(28S-15)

Nitration of arenes occurs on reaction with $AgNO_3$-NBS.[5] It avoids strongly acidic conditions, but the reagent cost is too high to be of practical value. Also reported is the directed nitration of 2-arylpyridines in the aryl portion. With a bimetallic system of $AgNO_3$ and $Cu(OAc)_2$ under O_2 the reaction is found to be highly depending on solvent: 1,2,3-trichloropropane seems to be crucial to attend a high conversion.[6]

Addition and cycloaddition. Propargylamines incorporate CO_2 from air to form 5-alkylidene-2-oxazolidinones under the influence of $AgNO_3$ and DBU in DMSO.[7]

A cooperative catalyst for [3+2]cycloaddition of α-isocyano esters with conjugated carbonyl compounds consists of $AgNO_3$ and cupreine.[8]

[1] Liu, X., Wang, Z., Cheng, X., Li, C. *JACS* **134**, 14330 (2012)
[2] Mai, W., Yuan, J., Li, Z., Sun, G., Qu, L. *SL* **145** (2012)
[3] Lockner, J.W., Dixon, D.D., Risgaard, R., Baran, P.S. *OL* **13**, 5628 (2011)
[4] York, M. *TL* **53**, 2226 (2012)
[5] Nowrouzi, N., Mehranpour, A.M., Bashiri, E., Shayan, Z. *TL* **53**, 4841 (2012)
[6] Zhang, L., Liu, Z., Li, H., Fang, G., Barry, B.-D., Belay, T.A., Bi, X., Liu, Q. *OL* **13**, 6536 (2011)
[7] Yoshida, M., Mizuguchi, T., Shishido, K. *CEJ* **18**, 15578 (2012)
[8] Arroniz, C., Gil-Gonzalez, A., Semak, V., Escolano, C., Bosch, J., Amat, M. *EJOC* 3755 (2011)

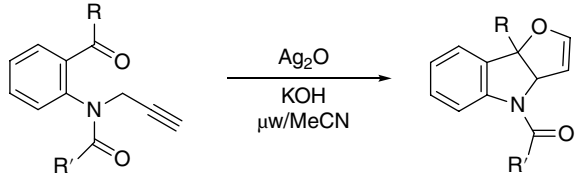
Silver nitrite

Nitrosation. Regioselective introduction of a nitroso group to a silyl enol ether by $AgNO_2$ – *i*-Pr_3SiCl is attended by desilylation. The original substitution pattern at the α-carbon determines whether the product would tautomerize to give the α-oximino carbonyl compound.[1]

[1] Baidya, M., Yamamoto, H. *JACS* **133**, 13880 (2011)

Silver(I) oxide

Cycloaddition. A novel route to furo[3,2-*b*]indoles is based on the transformation of *N*-protected *o*-acyl-*N*-propargylanilines by Ag_2O.[1]



[1] Zhang, Z., Fang, S., Liu, Q., Zhang, G. *ASC* **354**, 927 (2012)

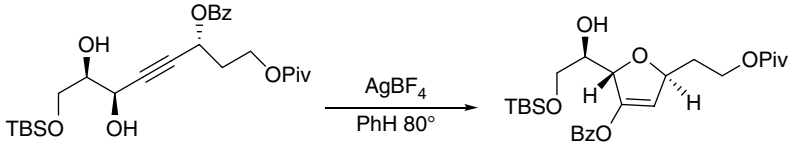
Silver phosphomolybdate

Isomerization.[1] α-Alkynyl benzyl alcohols give (*Z*)-β-aryl enones when treated with $Ag_3[PMo_{12}O_{40}]$ in acetone. The (*E*)-isomers are obtained in the reaction with $H_3[PMo_{12}O_{40}]$.

[1] Egi, M., Umemura, M., Kawai, T., Akai, S. *ACIE* **50**, 12197 (2011)

Silver tetrafluoroborate

Cyclization. Certain ynediol mono esters undergo 1,3-ester migration to induce cyclization. The Ag salt is useful while Au catalysts fail in the following example.[1]



[1] Mahapatra, S., Carter, R.G. *ACIE* **51**, 7948 (2012)

Silver trifluoromethylsulfenate

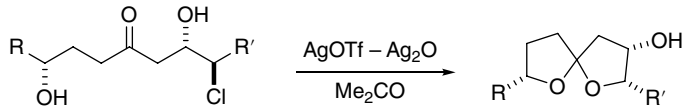
Substitution. Bromoarenes are converted into $ArSCF_3$ on reaction with $AgSCF_3$ in a Pd-catalyzed reaction.[1]

[1] Teverovsky, G., Surry, D.S., Buchwald, S.L. *ACIE* **50**, 7312 (2011)

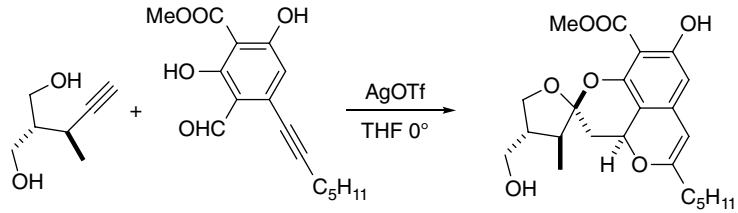
Silver triflate

Substitution. Friedel-Crafts alkylation of phenols is found to be catalyzed by AgOTf –*t*-BuCl.[1] However, the true catalyst might be TfOH. Allylation[2] and trifluoromethylation[3] of arenes with allyl alcohols and Me_3SiCF_3, respectively, is similarly conducted, although in the latter reaction KF is an additive.

α-Bromobenzyl ketones react with various nucleophiles (e.g., allylsilanes, electron-rich arenes) with the help of AgOTf (for ionization).[4] Ionization of an alkyl chloride with participation of a carbonyl group and further triggering spiroacetalization is shown below.[5]

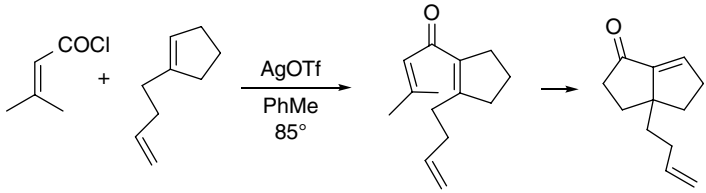


Intermolecular assemblage of alkyne units with aldehyde and hydroxyl groups is featured in the synthesis of the core structure of berkelic acid.[6]



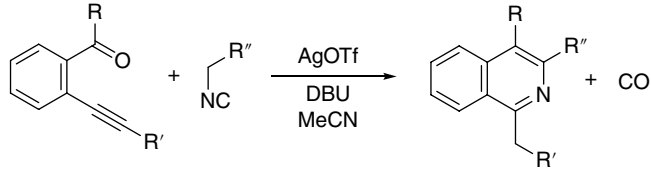
Alkanoic acids, regardless whether the α-carbon atom is primary, secondary, or tertiary, are degraded to RCl by reaction with *t*-BuOCl while being catalyzed by AgOTf.[7]

Acylation of alkenes by RCOCl is readily promoted by AgOTf, and in some ensuing structures further transformation (e.g., Nazarov cyclization) may take place.[8]

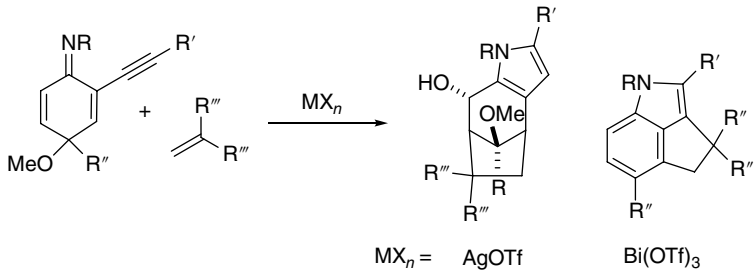


Cyclization. To obtain 3-chloro-3-pyrrolines from 4-amino-1,2-alkadienes a reaction with NCS is induced by AgOTf/1,10-phenanthroline.[9]

Ynediols substituted at one carbinolic center by an *o*-tosylaminoaryl group cyclize to give 2-alkynylindoles.[10] Isoquinolines are formed from *o*-alkynylbenzylideneamine derivatives (oximes, hydrazones).[11,12] Another mode of cyclization leading to isoquinolines is that which is preceded by condensation.[13]



Isomerization of an oxirane (to allylic alcohol) is involved prior to intramolecular addition to a triple bond.[14] An interesting variation of cyclization mode is that induced by AgOTf on one hand, and by $Bi(OTf)_3$ on the other.[15]

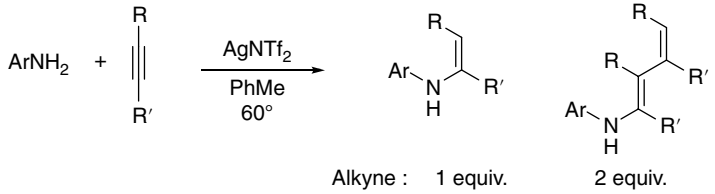


Activation of a triple bond by AgOTf triggers intramolecular attack by a tosylhydrazono nitrogen atom, thereby generating azomethine imine dipolar species for cycloaddition to create pyrazoles.[16]

[1] Dang, T.T., Boeck, F., Hintermann, L. *JOC* **76**, 9353 (2011)
[2] Chen, G.-Q., Xu, Z.-J., Chan, S.L.-F., Zhou, C.-Y., Che, C.-M. *SL* 2713 (2011)
[3] Ye, Y., Lee, S.H., Sanford, M.S. *OL* **13**, 5464 (2011)
[4] Lai, P.-S., Dubland, J.A., Sarwar, M.G., Chudzinski, M.G., Taylor, M.S. *T* **67**, 7586 (2011)
[5] Chang, S., Britton, R. *OL* **14**, 5844 (2012)
[6] Fañanas, F.J., Mendoza, A., Arto, T., Temelli, B., Rodriguez, F. *ACIE* **51**, 4930 (2012)
[7] Wang, Z., Zhu, L., Yin, F., Su, Z., Li, Z., Li, C. *JACS* **134**, 4258 (2012)
[8] Barczak, N.T., Jarvo, E.R. *CEJ* **17**, 12912 (2011)
[9] Sai, M., Matsubara, S. *OL* **13**, 4676 (2011)
[10] Mothe, S.R., Kothandaraman, P., Lauw, S.J.L., Chin, S.M.W., Chan, P.W.H. *CEJ* **18**, 6133 (2012)
[11] Zheng, D., Wang, Z., Wu, J. *S* 2810 (2011)
[12] Peshkov, V.A., Pereshivko, O.P., Van Hove, S., Ermolat'ev, D.S., Van der Eycken, E.V. *S* 3371 (2011)
[13] Zheng, D., Li, S., Wu, J. *OL* **14**, 2655 (2012)
[14] Maheswara, M., Lee, Y.Y., Kang, E.J. *SL* 2481 (2012)
[15] Wang, L., Fan, R. *OL* **14**, 3596 (2012)
[16] Huple, D.B., Chen, C.-H., Das, A., Liu, R.-S. *ASC* **353**, 1877 (2011)

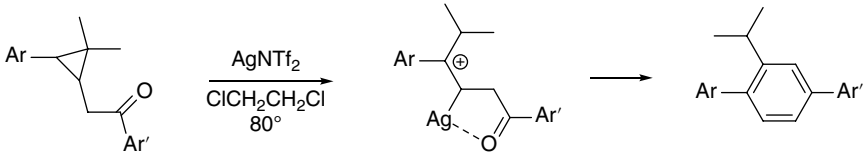
Silver triflimide

Addition. The stereoselective addition of anilines to alkynes can be controlled to yield 1:1 or 1:2 adducts.[1]

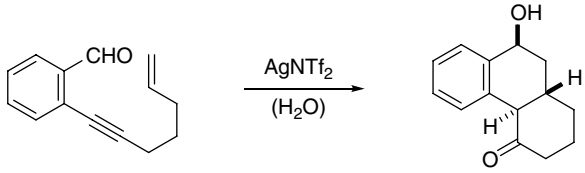


Treatment of 2-(4-pentyn-1-yl)cycloalkyl silyl ethers with $AgNTf_2$ causes desilylative spirocyclization. If NIS is present the exocyclic double bond of the ensuing cyclopentane unit is iodinated.[2]

Isomerization. 2-(2-Aryl-3,3-dimethylcyclopropyl)ethanones are converted into biaryls via ring cleavage and recyclization.[3]



Cycloaddition. Diels-Alder reaction with inverse electron demand occurs readily between phthalazine and siloxyalkynes by catalysis of $AgNTf_2$ and 2,2′-bipyridyl, with subsequent extrusion of N_2.[4] A formal cycloaddition involves alkyne hydration.[5]

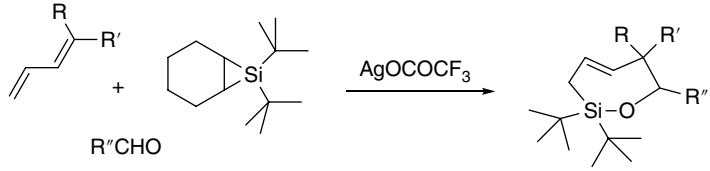


The addition of alkynylsilver species to *N*-aryliminium salts eventually elaborates quinolines in a process requiring both $AgNTf_2$ and TfOH.[6]

[1] Zhang, X., Yang, B., Li, G., Shu, X., Mungra, D.C., Zhu, J. *SL* **622** (2012)
[2] Schäfer, C., Miesch, M., Miesch, L. *CEJ* **18**, 8028 (2012)
[3] Pati, K., Liu, R.-S. *CC* **48**, 6049 (2012)
[4] Türkmen, Y.E., Montavon, T.J., Kozmin, S.A., Rawal, J.H. *JACS* **134**, 9062 (2012)
[5] Zhu, S., Liang, R., Jiang, H., Wu, W. *ACIE* **51**, 10861 (2012)
[6] Zhang, X., Liu, B., Shu, X., Gao, Y., Lv, H., Zhu, J. *JOC* **77**, 501 (2012)

Silver trifluoroacetate

Heterocycles. Seven-membered heterocycles containing O and Si atoms and a trans double bond are condensation products of dienes, aldehydes and di-*t*-butylsilylene, the last component being generated in situ. The reaction occurs in the presence of $AgOCOCF_3$.[1]



[1] Greene, M.A., Prevost, M., Tolopilo, J., Woerpel, K.A. *JACS* **134**, 12482 (2012)

Sodium – liquid ammonia

Birch reduction. Phosphoryl-substituted arenes undergo 1,4-reduction , the influence on regioselectivity is similar to other electron-withdrawing groups.[1]

[1] Stankevic, M., Bazan, J. *JOC* **77**, 8244 (2012)

Sodium aminoborohydride

Reduction. $Na(HNBH_3)$ is a reducing agent for ketones and imines.[1]

[1] Xu, W., Wu, G., Yao, W., Fan, H., Wu, J., Chen, P. *CEJ* **18**, 13885 (2012)

Sodium arenesulfinates

Stilbenes. An $ArSO_2Na$ can be used to mediate (E)-stilbene synthesis from two benzyl halides via a Lythgoe-Julia reaction.[1]

[1] Zhao, F., Luo, J., Tan, Q., Liao, Y., Peng, S. Deng, G.-J. *ASC* **354**, 1914 (2012)

Sodium azide

Reduction. Selective reduction of the *o*-nitro group in a 2,4-dinitrostilbene by NaN_3 is observed.[1]

Substitution. High yield of 2,4,6-triazidopyridine is obtained from reaction of the trifluoropyridine with NaN_3 in DMSO at room temperature.[2] Alkyl aryl ketones undergo α,α-diazidation, but NaN_3 must be made electrophilic by an oxidant (e.g., $NaIO_4$).[3]

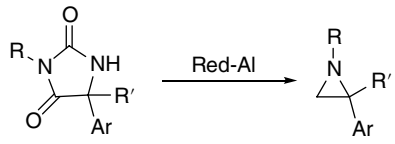
Addition. Nucleophilic attack of NaN_3 on cyclopropane-1,1-dicarboxylic esters proceeds in cleavage of the more highly substituted CC bond.[4]

[1] Janowska, K., Matczak, R., Zakrzewski, J., Krawczyk, H. *TL* **53**, 6504 (2012)
[2] Chapyshev, S.V., Chernyak, A.V. *S* 3158 (2012)
[3] Kamble, D.A., Karabal, P.U., Chouthaiwale, P.V., Sudalai, A. *TL* **53**, 4195 (2012)
[4] Emmett, M.R., Grover, H.K., Kerr, M.A. *JOC* **77**, 6634 (2012)

Sodium bis(2-methoxyethoxy)aluminum hydride, (Red-Al)

N-Detriflylation. *N*-Triflylaziridines release the free amines on treatment with Red-Al in toluene.[1]

Aziridines. An unexpected result for the reduction of hydantoins is the formation of aziridines.[2]

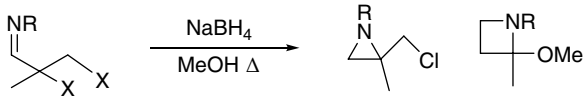


[1] Miyamoto, K., Hoque, M.M., Ogasa, S. *JOC* **77**, 8317 (2012)
[2] von Kieseritzky, F., Lindström, J. *TL* **52**, 4558 (2011)

Sodium borohydride

Reduction. α-Amino acids are reduced by $NaBH_4$ in the presence of H_2SO_4 in ether.[1] A general reduction of carboxylic acids is via the mixed anhydrides with 1-propanephosphonic acid.[2]

Reduction of 2,3-dihalo-2-methylpropanal imines gives either aziridines or azetidines, depending on whether the halogen atoms are chlorine or bromine.[3]



(X = Cl) (X = Br)

For reduction of C=N compounds such as imines, oximes, and hydrazones to amines by $NaBH_4$ in MeOH, enhanced reaction rates are observed by adding amorphous nickel powder.[4]

[1] Pinaka, A., Vougioukalakis, G.C., Dimotikali, D., Psyharis, V., Papadopoulos, K. *S* 1057 (2012)
[2] Nagendra, G., Madhu, C., Vishwanatha, T.M., Sureshbabu, V.V. *TL* **53**, 5059 (2012)
[3] Stankovic, S., D'hooghe, M., Dewulf, J., Bogaert, P., Jolie, R., De Kimpe, N. *TL* **52**, 4529 (2011)
[4] Liu, S., Yang, Y., Zhen, X., Li, J., He, H., Feng, J., Whiting, A. *OBC* **10**, 663 (2012)

Sodium borohydride – metal salts

Reduction. In the presence of $InCl_3$, $NaBH_4$ is able to reduce RCN to give primary amines.[1] More remarkably, $NaBH_4$- $NiCl_2$ effects 1,4-reduction of electron-rich dienes (e.g., siloxydienes), and the removal of the allylic ester group from a glycal derivative.[2]

[1] Saavedra, J.Z., Resendez, A., Rovira, A., Eagon, S., Haddenham, D., Singaram, B. *JOC* **77**, 221 (2012)
[2] Yin, B.-L., Cai, C.-B., Lai, J.-Q., Zhang, Z.-R., Huang, L., Xu, L.-W., Jiang, H.-F. *ASC* **353**, 3319 (2011)

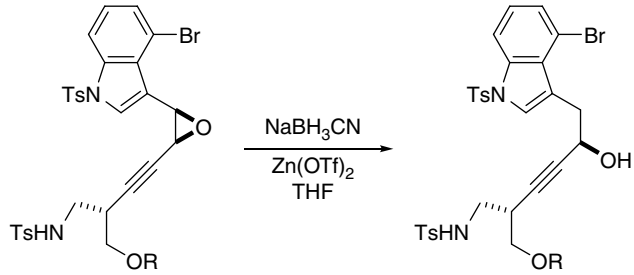
Sodium chlorite

Oxidation. Saturated heterocycles containing a [*c*]fused benzene ring are oxidized by $NaClO_2$ in $MeCCl_3$ – H_2O, to afford lactones and lactams.[1] Allylamines are converted into α,β-epoxy amides.[2]

[1] Song, A.-R., Yu, J., Zhang, C. *S* 2903 (2012)
[2] Fuentes, L., Osorio, U., Quintero, L., Höpfl, H., Vazquez-Cabrera, N., Sartillo-Piscil, F. *JOC* **77**, 5515 (2012)

Sodium cyanoborohydride

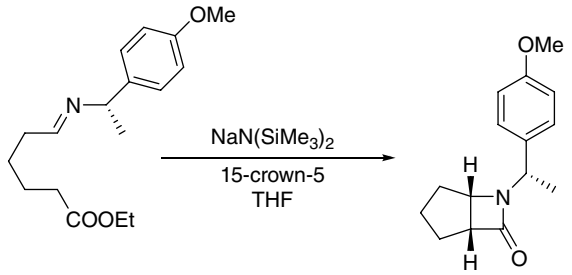
Reductive cleavage of epoxides. Regioselective cleavage of 3-indolyloxiranes by $NaBH_3CN$ is achieved by catalysis of $Zn(OTf)_2$.[1]



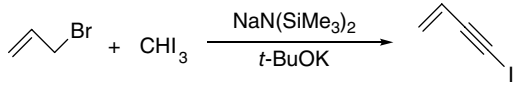
[1] Iwata, A., Inuki, S., Oishi, S., Fujii, N., Ohno, H. *JOC* **76**, 5506 (2011)

Sodium hexamethyldisilazide, (NaHMDS)

Deprotonation. To generate 1,3-diamino-1,3-dienes for Diels –Alder reaction,[1] ketiminium salts of 4-amino-3-buten-2-one are treated with $NaN(SiMe_3)_2$. ω-Iminoalkanoic esters with the main chain of 6 or 7 carbon atoms are deprotonated and the end result is formation of fused β-lactams.[2]



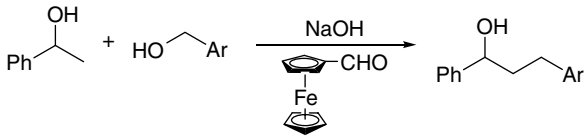
Homologation. The triiodomethide ion is formed on deprotonation of iodoform, and it is readily alkylated by allyl bromide and benzyl bromides. The products give iodoalkynes on further dehydroiodination (with *t*-BuOK).[3]



[1] Zhou, S., Sanchez-Larios, E., Gravel, M. *JOC* **77**, 3576 (2012)
[2] Evans, C.D., Mahon, M.F., Andrews, P.C., Muir, J., Bull, S.D. *OL* **13**, 6276 (2011)
[3] Pelletier, G., Lie, S., Mousseau, J.J., Charette, A.B. *OL* **14**, 5464 (2012)

Sodium hydroxide

Benzylation.[1] α-Arylethanols and benzyl alcohols combine to afford 1,3-diarylpropanols via a series of redox reactions catalyzed by NaOH and ferrocenecarbaldehyde.



[1] Yang, J., Liu, X., Meng, D.-L., Chen, H.-Y., Zong, Z.-H., Feng, T.-T., Sun, K. *ASC* **354**, 328 (2012)

Sodium hypohalite

Halogenation.[1] Hydrogen atoms at the α-carbon of sulfones are readily converted into halogen by NaOX. For example, $ArSO_2Me$ to $ArSO_2CX_3$.

[1] Borys, K.M., Korzynski, M.D., Ochal, Z. *TL* **53**, 6606 (2012)

Sodium iodide

Aminoalkylation.[1] Employment of catalytic NaI instead of a strong base for the addition of bromonitromethane to imines is obviously advantageous.

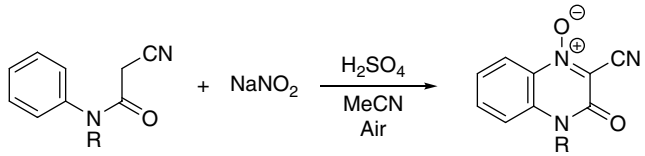
Difluorocyclopropanation.[2] The cycloaddition to alkenes is accomplished with a mixture of Me_3SiCF_3 and an initiator. At lower temperature F^- is adequate but at higher temperature NaI is effective (i.e., reaction on alkynes).

Alkyldiphenylphosphine oxides. A method for synthesis of mixed phosphine oxides is to combine Ph_2PCl and RCHO with NaI, taking advantage of the reductive power of NaI to remove the iodine atom from the α-iodoalkylphosphine oxide products.[3]

[1] Rodriguez-Solla, H., Concellon, C., Alvaredo, N., Soengas, R.G. *T* **68**, 1736 (2012)
[2] Wang, F., Luo, T., Hu, J., Wang, Y., Krishnan, H.S., Jog, P.V., Ganesh, S.K., Prakash, G.K.S., Olah, G.A. *ACIE* **50**, 7153 (2011)
[3] Wang, F., Qu, M., Chen, F., Xu, Q., Shi, M. *CC* **48**, 8580 (2012)

Sodium nitrite

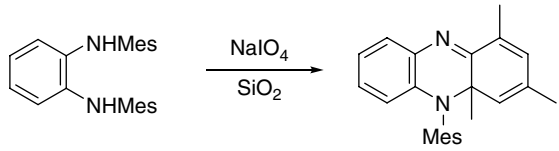
Cyclonitrosation. *N*-Cyanomethylanilines undergo cyclization with incorporation of an NO group on reaction with $NaNO_2 - H_2SO_4$ in air.[1]



[1] Kobayashi, Y., Kuroda, M., Toba, N., Okada, M., Tanaka, R., Kimachi, T. *OL* **13**, 6280 (2011)

Sodium periodate

Oxidation. A method for oxidation of alcohols employs $NaIO_4$ and $NH_2OH{\cdot}HCl$ in dichloromethane.[1] A highly unusual oxidative cyclization promoted by $NaIO_4$ is a transformation of *N,N′*-dimesityl-1,2-diaminobenzene into a dihydrophenazine.[2]



N-Formylation. Under CO and the intervention of $NaIO_4$ and NaI, amines are converted into formamides.[3]

Sulfonylation. Alkenes are functionalized (to give alkenyl sulfones) upon treatment with $ArSO_2Na$, $NaIO_4$, and a catalytic amount of HOAc in MeCN.[4]

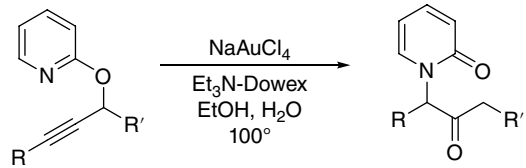
[1] Majee, A., Kundu, S.K., Santra, S., Hajra, A. *TL* **53**, 4433 (2012)
[2] Borguet, Y., Zaragozi, G., Demonceau, A., Delaude, L. *ASC* **354**, 1356 (2012)
[3] Gerack, C.J., McElwee-White, L. *CC* **48**, 11310 (2012)
[4] Das, B., Lingaiah, M., Damodar, K., Bhunia, N. *S* 2941 (2011)

Sodium tetrachloroaurate

Substitution. The hydroxyl group of allylic and benzylic alcohols is directly replaced by amines, amides, sulfonamides under the influence of $NaAuCl_4$. The method is especially valuable for the preparation of acid-sensitive compounds.[1]

Cross-coupling. Along with an oxidant (*t*-BuOOH), a cross-coupling between indole and an *N*-aryltetrahydroisoquinoline is achieved by $NaAuCl_4$.[2]

Rearrangement. 2-Propargyloxypyridines are susceptible to oxidative rearrangement to yield *N*-(2-oxoalkyl)-2-pyridones, using $NaAuCl_4$ as a catalyst.[3]



Heterocycle synthesis. Reaction of aniline with 1-bromo-2-alkynes furnishes quinolines readily, if $NaAuCl_4$ is employed as catalyst.[4] Activation of the triple bond of a propargylamine enables alkenylation of β-keto esters, and the cyclization to 2,5-dihydropyridine-5-carboxylic esters follows.[5]

[1] Ohshima, T., Nakahara, Y., Ipposhi, J., Miyamoto, Y., Mashima, K. *CC* **47**, 8322 (2011)
[2] Zhang, Y., Luo, S., Feng, B., Zhu, C. *ChJC* **30**, 2741 (2012)
[3] Romero, N.A., Klepser, B.M., Anderson, C.E. *OL* **14**, 874 (2012)
[4] Alfonsi, M., Arcadi, A., Chiarini, M., Marinelli, F. *TL* **52**, 5145 (2011)
[5] Fañanas, F.J., Arto, T., Mendoza, A., Rodriguez, F. *OL* **13**, 4184 (2011)

Sodium 2,2,6,6-tetramethyl-*N*-oxidopiperidine

Addition. In $PhCF_3$ alkenes react with an $ArN_2(BF_4)$ and the title reagent to form adducts in which the aryl group becomes attached to the less substituted sp^2-carbon site and a new C-O bond with the neighboring atom.[1]

[1] Hartmann, M., Li, Y., Studer, A. *JACS* **134**, 16516 (2012)

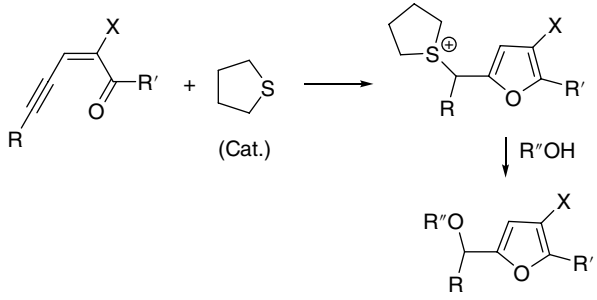
Sodium 2,2,6,6-tetramethylpiperidinozincate

Zincation. The title reagent is useful for zincation of *N*-(*t*-butoxycarbonyl)pyrrolidine at room temperature. Hexane is the solvent of choice, and toluene is unsuitable as it causes formation of *N*-phenylacetylpyrrolidine.[1]

[1] Garden, J.A., Kennedy, A.R., Mulvey, R.E., Robertson, S.D. *CC* **48**, 5265 (2012)

Sulfolane

Cyclofunctionalization. 2-Alken-4-yn-1-ones cyclize and incorporate a nucleophile to form furan derivatives. Sulfolane plays an important role.[1]



[1] Clark, J.S., Boyer, A., Aimon, A., Garcia, P.E., Lindsay, D.M., Symington, A.D.F., Danoy, Y. *ACIE* **51**, 12128 (2012)

Sulfur

Thioamides. Sulfurative condensation is observed from amines on heating with sulfur. Thus a mixture of $PhCH_2NH_2$ and $BnCH_2NH_2$ combines to afford PhC(=S) $NHCH_2Bn$.[1]

Sulfenylation. *N*-Substituted diketopiperazines are *C*-sulfenylated on deprotonation with $NaN(SiMe_3)_2$ or LDA and treatment with sulfur. The protocol generally involves reduction of the crude products by $NaBH_4$ and further process by oxidation to the disulfides or methylation.[2,3]

[1] Nguyen, T.B., Ermolenko, L., Al-Mourabit, A. *OL* **14**, 4274 (2012)
[2] Nicolaou, K.C., Giguere, D., Totokotsopoulos, S., Sun, Y.-P. *ACIE* **51**, 728 (2012)
[3] Ruff, B.M., Zhong, S., Nieger, M., Bräse, S. *OBC* **10**, 935 (2012)

Sulfuric acid

Ritter reaction. *N*-(*t*-Butyl)carboxamides are produced from admixture of RCN and *t*-BuOMe with H_2SO_4 at room temperature.[1]

[1] Dawar, P., Raju, M.B., Ramakrishna, R.A. *TL* **52**, 4262 (2011)

T

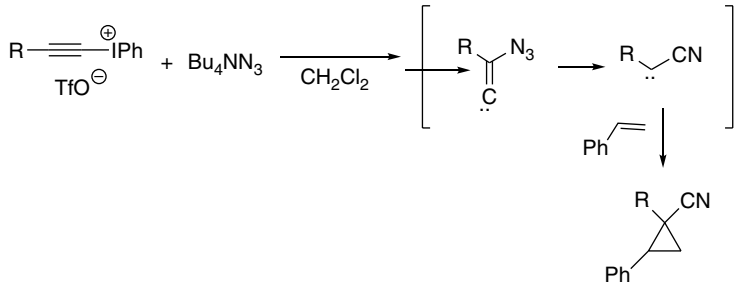
N,N,N′N′-Tetrabromo-1,3-benzenedisulfonamide

Bromination. The title reagent is useful for bromination of electron-deficient arenes in the presence of 98% sulfuric acid.[1]

[1] Ghorbani-Vaghei, R., Shahbazi, H., Veisi, H. *TL* **53**, 2325 (2012)

Tetrabutylammonium azide

α-Cyanocarbenes. The quaternary ammonium azide reacts with alkynyliodonium salts to give azidovinylidenecarbenes which rapidly isomerizes to α-cyanocarbenes.[1]



Organoazides.[2] The mixture of NaN_3 and Bu_4NBr used in the conversion of tosylhydrazones into organoazides in dioxane likely forms Bu_4NN_3 in situ.

[1] Hyatt, I.F.D., Croatt, M.P. *ACIE* **51**, 7511 (2012)
[2] Barluenga, J., Tomas-Gamasa, M., Valdes, C. *ACIE* **51**, 5950 (2012)

Tetrabutylammonium chloride

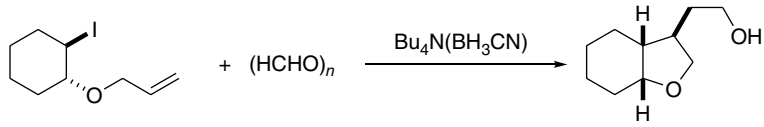
Reaction medium. As an ionic liquid, Bu_4NCl has seen applications as a reaction medium for chlorination of RCH_2COCl (to yield $RCCl_2COCl$),[1] and N-alkylation of anilines.[2]

[1] Bellesia, F., D'Anna, F., Felluga, F., Frenna, V., Ghelfi, F., Parsons, A.F., Reverberi, F., Spinelli, D. *S* 605 (2012)
[2] Monopoli, A., Cotugno, P., Cortese, M., Calvano, C.D., Ciminale, F., Nacci, A. *EJOC* 3105 (2012)

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Tetrabutylammonium cyanoborohydride

Hydroxymethylation. Trapping of carbon radicals by paraformaldehyde to furnish homologated primary alcohols is completed by reducing the oxy radical with $Bu_4N(BH_3CN)$.[1]



[1] Kawamoto, T., Fukuyama, T., Ryu, I. *JACS* **134**, 875 (2012)

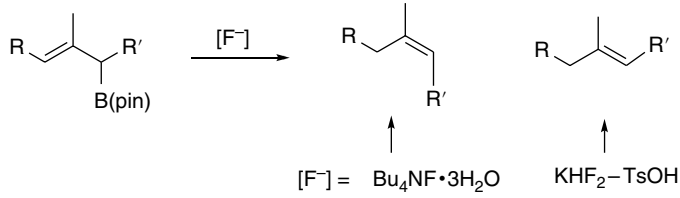
Tetrabutylammonium decatungstate

Radical addition.[1] Hydroacylation of conjugated sulfones by RCHO, and HCONHR is performed with the aid of $(Bu_4N)_4W_{10}O_{32}$ and light. It is an alternative to using tin compounds.

[1] Ravelli, D., Montanaro, S., Zema, M., Fagnoni, M., Albini, A. *ASC* **353**, 3295 (2011)

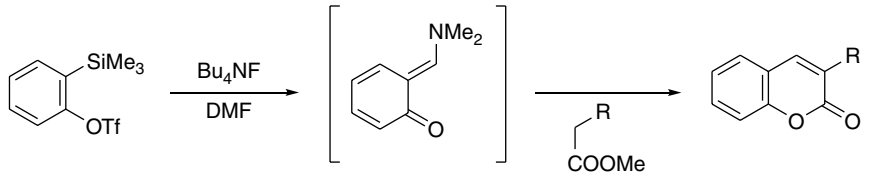
Tetrabutylammonium fluoride, (TBAF)

Elimination. Propargylboronates have been defunctionalized to give allenes on exposure to $Bu_4NF{\cdot}3H_2O$.[1] Allylboranes are similarly hydrodeborated with the double bond transposed. Interestingly, configuration of the double bond of the products is different from that obtained in the reaction with KHF_2-TsOH.[2]

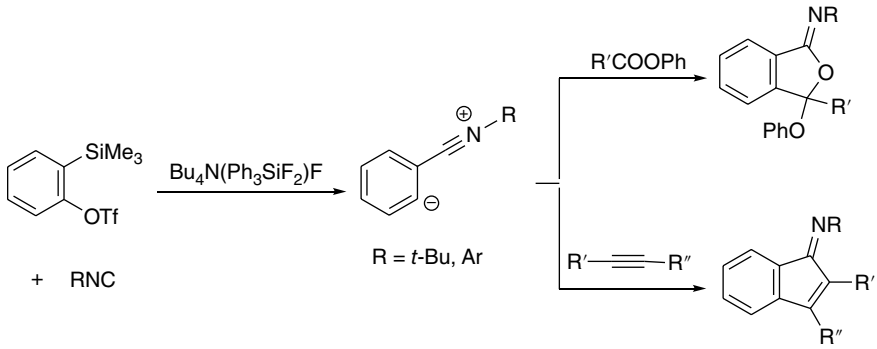


1,2-Dibromo-3-alkoxyalkanes undergo dehydrobromination. If a large excess (5 equiv.) of Bu_4NF is used a double elimination ensues (leading to 1-alkynes).[3]

Benzyne generation from reaction of 2-trimethylsilylphenyl triflate is now well established, a new twist is the insitu trapping by DMF and subsequent condensation with esters to form coumarins.[4] Actually, direct hydrolysis of the benzyne-DMF adducts gives rise to salicylaldehydes, and a further use of the adducts is based on reaction with diorganozinc reagents.[5]

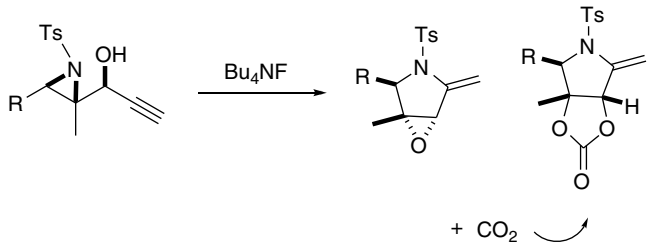


Parenthetically, for the purpose of benzyne generation TBAF and $Bu_4N(Ph_3SiF_2)$ are practically interchangeable, an example is the trapping with an isonitrile and an electrophile.[6]



Cyclization. β,β-Dihalostyrenes which bear hydroxyl or thiol group at an *o*-position cyclize on treatment with Bu_4NF.[7] Obviously the remaining halogen atom at C-2 of the resulting benzofurans and benzothiophenes is useful for coupling.

N-Tosylaziridines containing an α-hydroxy-2-propynyl group are converted into pyrrolidines by Bu_4NF.[8] The transformation is initiated by deprotonation of the OH group which is followed by opening of the aziridine ring and intramolecular hydroamination.



Condensation. 2-Halo-1-cycloalkenecarbaldehydes (5- and 6-membered) are found to condense with ArCHO at the allylic position away from the halogenated site.[9]

[1] Partridge, B.M., Chausset-Boissarie, L., Burns, M., Pulis, A.P., Aggarwal, V.K. *ACIE* **51**, 11795 (2012)

[2] Hesse, M.J., Butts, C.P., Willis, C.L., Aggarwal, V.K. *ACIE* **51**, 12444 (2012)
[3] Kutsumura, N., Kubokawa, K., Saito, T. *S* 2377 (2011)
[4] Yoshioka, E., Kohtani, S., Miyabe, H. *ACIE* **50**, 6638 (2011)
[5] Cui, P., Xu, L., Cheng, H., Gan, L. *T* **68**, 152 (2012)
[6] Allan, K.M., Gilmore, C.D., Stoltz, B.M. *ACIE* **50**, 4488 (2011)
[7] Chen, W., Zhang, Y., Zhang, L., Wang, M., Wang, L. *CC* **47**, 10476 (2011)
[8] Kulshrestha, A., Marzijarani, N.S., Ashtekar, K.D., Staples, R., Borhan, B. *OL* **14**, 3592 (2012)
[9] Zhang, J., Gu, L., Gong, Y. *SL* 468 (2012)

Tetrabutylammonium peroxydisulfate

Addition. A free radical is generated from 1,3-dioxolane by action of $(Bu_4N)_2S_2O_8$ for conjugate addition to electron-deficient alkenes. Thus a masked formyl group is introduced.[1]

[1] Jung, J.C., Kim, Y.H., Lee, K. *TL* **52**, 4662 (2011)

Tetrabutylammonium tribromide

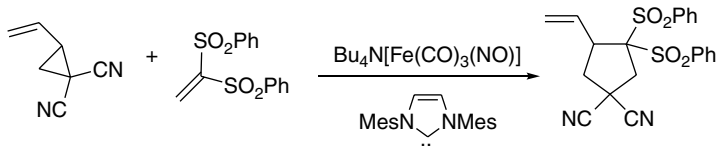
Aryl bromides.[1] To convert $ArBF_3K$ into ArBr it simply requires reaction with Bu_4NBr_3 in aqueous THF at room temperature.

[1] Yao, M.-L., Kabalka, G.W., Blevins, D.W., Reddy, M.S., Yong, L. *T* **68**, 3738 (2012)

Tetrabutylammonium (tricarbonyl)nitrosoferrate

Substitution. Functional group exchange such as formation of thioesters from aryl esters,[1] replacement of an allylic carbonate by a sulfonyl group (e.g., from 3-sulfonyl-*N*-phenylsuccinimides),[2] and carbene transfer from diazoacetic esters to amines, allylic sulfides, etc.[3] may take advantage of the catalytic activity of the salt under essentially neutral conditions.

Cycloaddition. Cyclopropanes exemplified by 2-vinyl-1,1-bis(phenylsulfonyl) cyclopropane undergo [3+2]cycloaddition with electron-deficient alkenes, as catalyzed by $Bu_4N[Fe(CO)_3NO]$ and an *N*-heterocyclic carbene ligand.[4]



[1] Magens, S., Plietker, B. *CEJ* **17**, 8807 (2011)
[2] Jegelka, M., Plietker, B. *CEJ* **17**, 10417 (2011)
[3] Holzwarth, M.S., Alt, I., Plietker, B. *ACIE* **51**, 5351 (2012)
[4] Dieskau, A.P., Holzwarth, M.S., Plietker, B. *JACS* **134**, 5048 (2012)

Tetrachloroauric acid

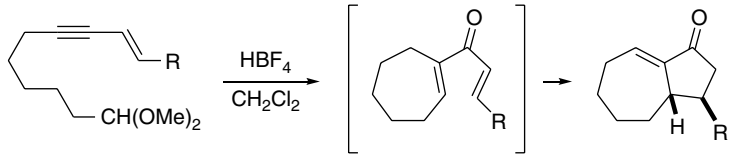
Hydration. (2*H*)-2-Arylchromenes suffer ring scission to give 1-aryl-3-(*o*-hydroxyphenyl)-1-propanones.[1] The catalyst is $HAuCl_4$.

[1] Maiti, G., Kayal, U., Karmakar, R., Bhattacharya, R.N. *TL* **53**, 6321 (2012)

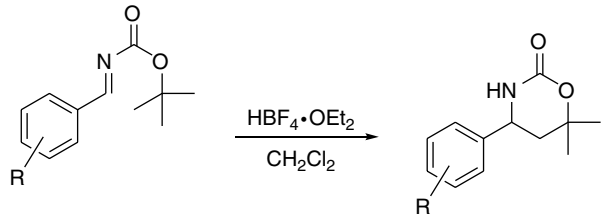
Tetrafluoroboric acid

Fluorination. An easy access to α-fluoro-β-keto esters from α-diazo-β-keto esters is to react with $HBF_4{\cdot}OEt_2$ in ether at room temperature.[1]

Cyclization. Exposure of alk-7-yn-9-enal acetals to HBF_4 causes a sequence of transformations (hydration, aldol reaction, and Nazarov cyclization) that results in the formation of hydroazulenones.[2]



Mild conditions are needed for the cycloisomerization of *N*-Boc aldimines to give oxazinones.[3]



[1] Pasceri, R., Bartrum, H.E., Hayes, C.J., Moody, C.J. *CC* **48**, 12077 (2012)
[2] Escalante, L., Gonzalez-Rodriguez, C., Varela, J.A., Saá, C. *ACIE* **51**, 12316 (2012)
[3] Uddin, N., Ulicki, J.S., Foersterling, F.H., Hossain, M.M. *TL* **52**, 4353 (2011)

Tetrafluoroethanesulfonic acid, (tetraflic acid)

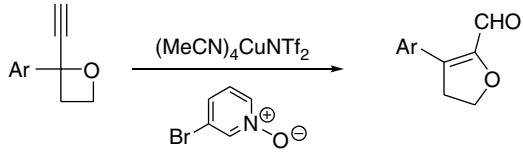
Isomerization. This strong acid can be used to isomerize cycloalkanes, e.g., methylcyclopentane to cyclohexane and tetrahydrodicyclopentadiene to adamantane. Also it is a good catalyst for catalyzing arene halogenations with NXS.[1]

[1] Prakash, G.K.S., Mathew, T., Panja, C., Kulkarni, A., Olah, G.A., Harmer, M.A. *ASC* **354**, 2163 (2012)

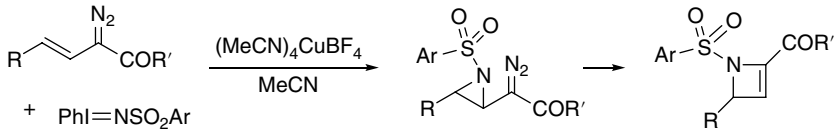
Tetrakis(acetonitrile)copper(I) salts

Halogen exchange. Aryl halides can switch the halogen atom by a Cu(I)-catalyzed reaction. For example, with AgF in MeCN to access ArF (or KF in MeCN-DMSO).[1]

Ring expansion. Alkynyl oxiranes and oxetanes undergo oxidation with ring expansion[2] when react with a pyridine *N*-oxide in the presence of $(MeCN)_4CuNTf_2$.



Cycloaddition-rearrangement. A Cu(I) species catalyzes aziridination of conjugated diazo compounds, but it also causes ring expansion of the adducts.[3]

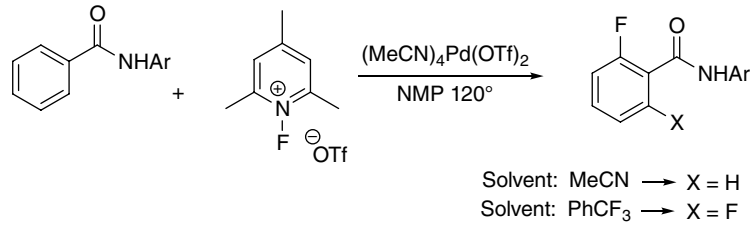


[1] Casitas, A., Canta, M., Sola, M., Costas, M., Ribas, X. *JACS* **133**, 19386 (2011)
[2] Gronnier, C., Kramer, S., Odabachian, Y., Gagosz, F. *JACS* **134**, 828 (2012)
[3] Barluenga, J., Riesgo, L., Lonzi, G., Tomas, M., Lopez, L.A. *CEJ* **18**, 9221 (2012)

Tetrakis(acetonitrile)palladium(II) salts

Suzuki coupling. By using a MeCN-ligated Pd salt and a proper phosphine ligand, it is possible to carry out Suzuki coupling of benzoyloxyquinolines.[1]

Substitution. One of two fluorine atoms can be introduced to free *o*-position(s) of benzamides by reaction with *N*-fluoro-*s*-collidinium triflate. Solvent and reaction temperature determine the extent of fluorination.[2]



Ureas of the type $ArNHCONMe_2$ are arylated by Ar_4Sn using $(MeCN)_4Pd(OTs)_2$ as catalyst. Benzoquinone is also added and the reaction occurs at an *o*-position.[3]

[1] Li, W., Gao, J.J., Zhang, Y., Tang, W., Lee, H., Fandrick, K.R., Lu, B., Senanayake, C.H. *ASC* **353**, 1671 (2011)
[2] Chan, K.S.L., Wasa, M., Wang, X., Yu, J.-Q. *ACIE* **50**, 9081 (2011)
[3] Xue, D., Li, J., Liu, Y.-X., Han, W.-Y., Zhang, Z.-T., Wang, C., Xiao, J. *SL* 1941 (2012)

1,1,2,2-Tetrakis(dimethylamino)diboron

Tetraoxydiboranes. On treatment with a diol and base, $(Me_2N)_2B\text{-}B(NMe_2)_2$ is converted to boronates, which are useful for borylation of arenes.[1]

[1] Bello, C.S., Schmidt-Leithoff, J. *TL* **53**, 6230 (2012)

1,1,3,3-Tetrakis(trifluoromethanesulfonyl)propane

Substitution. The title reagent splits off bis(trifluoromethanesulfonyl)methane in MeCN to generate $Tf_2C{=}CH_2$ which is an excellent electrophile for arenes (to be converted into $ArCH_2Tf_2$).[1]

[1] Yanai, H., Ogura, H., Fukaya, H., Kotani, A., Kusu, F., Taguchi, T. *CEJ* **17**, 11747 (2011)

Tetrakis(triphenylphosphine)nickel(0)

Substitution. Serving as a catalyst for homolytic aromatic substitution $(Ph_3P)_4Ni$ induces cyclization of some ω-iodoalkylarenes.[1] Naturally, annulation of heterocycles proceeds as readily.

1-Triorganosilyl-1,5-alkadienes are synthesized from allyl alcohols and α–silyl allyl boronates in the presence of $(Ph_3P)_4Ni$. Less than 1% of the branched isomers is produced.[2]

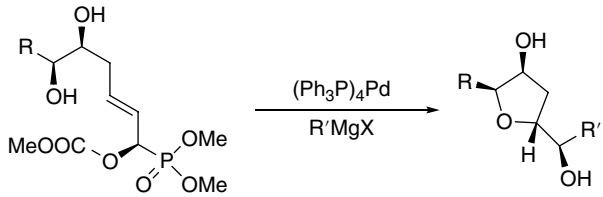
Heck reaction. Styrenes are homologated with bromoalkanes containing an electron-withdrawing group at the α-carbon, by catalysis with $(Ph_3P)_4Ni$ and DPPP.[3]

[1] Beaulieu, L.-P.B., Roman, D.S., Vallée, F., Charette, A.B. *CC* **48**, 8249 (2012)
[2] Jiménez-Aquino, A., Flegeau, E.F., Schneider, U., Kobayashi, S. *CC* **47**, 9456 (2011)
[3] Liu, C., Tang, S., Liu, D., Yuan, J., Zheng, L., Meng, L., Lei, A. *ACIE* **51**, 3638 (2012)

Tetrakis(triphenylphosphine)palladium(0)

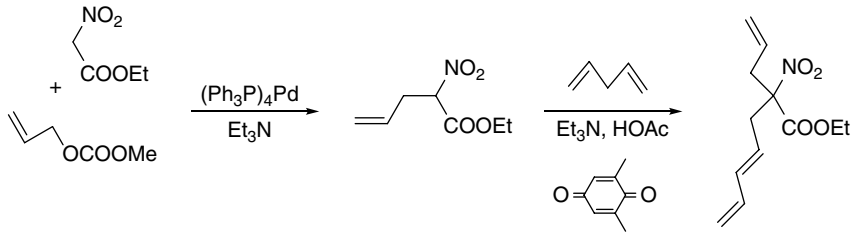
Oxidation. A rather unusual reaction is the transformation of RCHO into RCOOEt by $(Ph_3P)_4Pd$ in EtOH containing BnX (1 equiv.) and with microwave irradiation.[1]

Substitution. The Pd(0)-catalyzed allylic substitution is well known, but to the synthetic expediency of combining a Grignard reaction is a worthy of note.[2]



Seven-membered cyclic carbonates substituted with an alkynyl residue at an α-carbon to an oxygen atom is susceptible to C-O bond cleavage. Decarboxylation is aided by having a boronic acid in the reaction mixture and it enables the cyclization to afford the

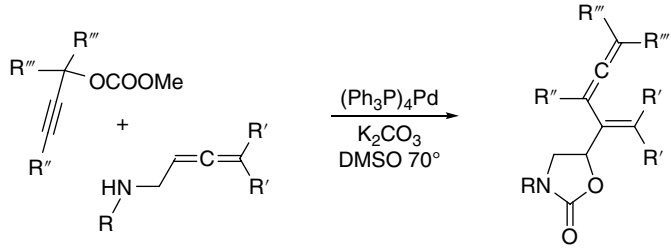
α-alkynyltetrahydrofurans.[3] Double allylation by adding 1,4-pentadiene in the second step under oxidative conditions (with the same catalyst) is recognized as involving Pd(0) and Pd(II) species, respectively.[4]



Allylic substitution via deacylative generation of the nucleophile (e.g., from β-diketones, α-nitro ketones) needs only allyl alcohols,[5] as the alcohols are activated (for the formation of π-allyl-Pd complexes) on esterification. In the allylation of arylacetaldehydes with allyl alcohol, the procedure calls for addition of PhCOOH.[6] It may act as a catalyst for acetalization and elimination, and a Claisen rearrangement is the key for the transformation.

α-Keto acids and allyl carbonate are combined, while decarboxylation precedes allylation and double bond migration. (The products are 2-alken-4-ones.)[7]

Propargylic carbonates enter into a substitution reaction with homoallenylamines. Carbon dioxide released during the reaction is reincorporated into the oxazolidinone products.[8]



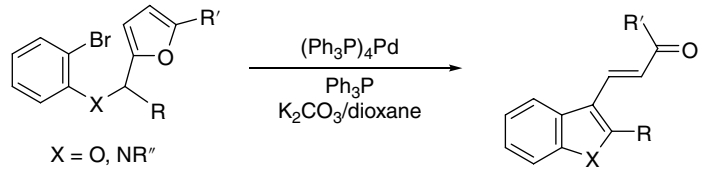
A synthetic precursor of α-kainic acid has been elaborated from a benzylamine carrying two other allyl groups, one disubstituted and terminated by an acetoxy residue. Ionization of the acetoxylated allyl moiety triggers attack by the other double bond and eventually Et_2Zn.[9]

Coupling. A prosaic synthesis of ArCN is from ArBr and $K_4[Fe(CN)_6]$.[10] Somewhat more elaborate structures are those accessed from coupling between $RB(OH)_2$ and MeSC(OMe)=NCOOMe[11] and dehydroiodinative reaction between 1-iodoalkynyltributylstannanes and 1-alkynes (to furnish stannylenynes),[12] both require a Cu(I) cocatalyst.

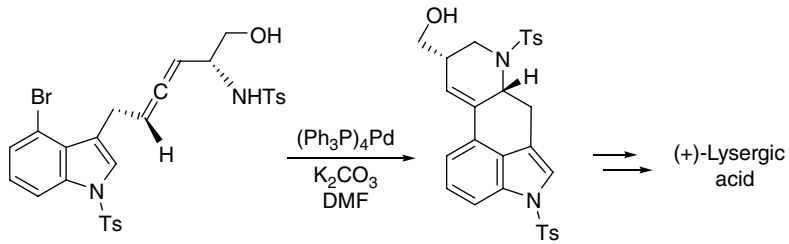
1-(1-Chloroalkyl)naphthalenes undergo substitution with amines in an unexpected way. 4-Alkyl-1-aminonaphthalenes emerge as the products. (9-chloroalkylanthracenes behave analogously.)[13]

1,2,7,8-Nonatetraene, a diallene, couples with RNH_2 and R′I to form 10-membered cyclic amines.[14] The bimetallic catalytic system is composed of $(Ph_3P)_4Pd$ and Ag_3PO_4.

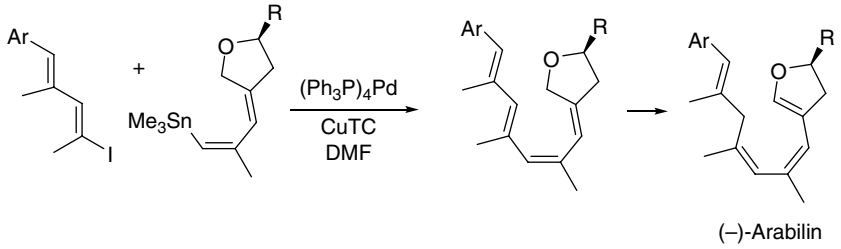
By an intramolecular Heck reaction the heterocycle of 2-[α-(*o*-bromophenoxyalkyl)] furans is severed while a new furan ring is created. Indole derivatives are formed from the bromoanilino analogs.[15]



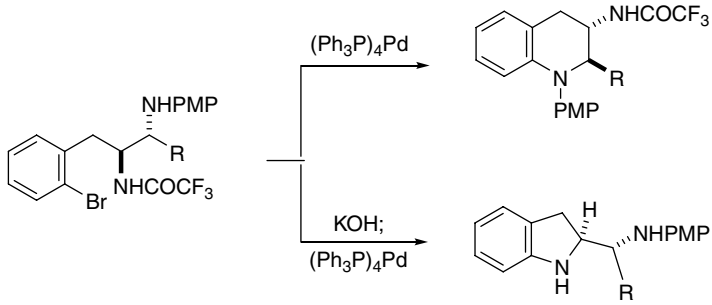
An intramolecular Heck reaction features prominently in a synthetic approach to (+)-lysergic acid.[16]



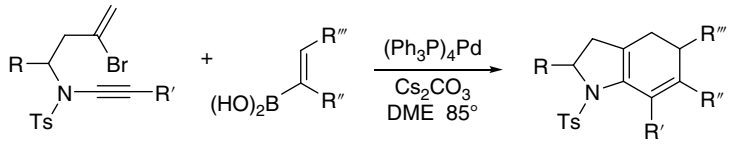
Nonaromatic version of the Heck reaction has been realized using hybrid organometal and radical catalysts.[17] A Stille coupling that furnishes a tetraene is automatically deconjugated by a [1,7]hydrogen shift.[18] Perhaps the last transformation is exactly how (-)-arabilin arises in nature.



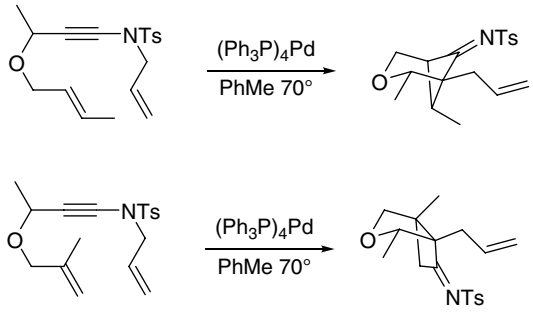
Selective intramolecular *N*-arylation is shown in the following equations.[19] The different reactivities of the nucleophilic *N*-atoms are consistent with the respective protection.



The cyclization products of bromoenynamides are susceptible to depalladation in the presence of an alcohol (e.g., EtOH).[20] However, by adding a boronic acid to the reaction mixture an opportunity for another coupling event becomes available.[21]

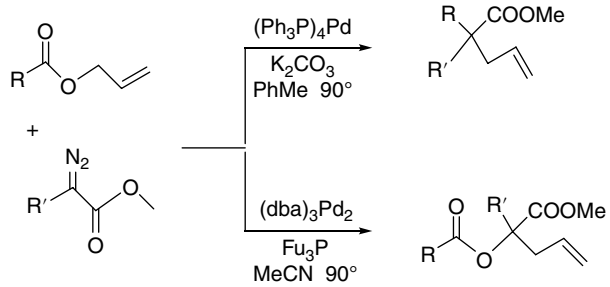


Quite a remarkable transformation of *N*-alkynyl-*N*-allylamines that also contain another double bond further along the alkynyl chain is the formation of bicyclic imines which starts from departure of the *N*-allyl group and return to create ketenimine for the concluding [2+2]cycloaddition.[22]

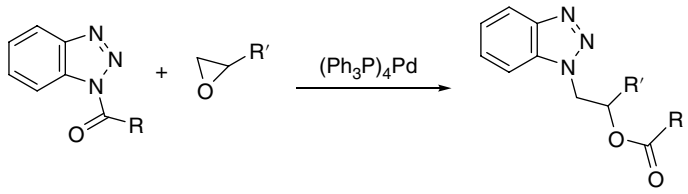


Steric and electronic effects account for the regiochemical differences arising from Suzuki coupling between ArI and secondary allylboronic esters.[23] Construction of 8- to 10-membered cyclic ketones from *S*-(*t*-butyl) ω-alkenethioates involves hydroboration prior to coupling catalyzed by $(Ph_3P)_4Pd$ and Cu(I) thienate.[24]

Coupling of tosylhydrazones with RNC leads to homologous amides (extension by one carbon unit).[25] Insertion of the carbene unit from a diazo ester to allyl esters proceeds in different ways for allyl aroates and others.[26] Variation of the Pd catalyst should not be the determining factor.



Insertion of an oxirane unit into the amidic bond of 1-acylbenzotriazoles has been observed.[27]



2-Bromo-2′-trialkylsilylbiaryls which contain at least one methyl substituent at the silicon atom undergo dehydrobromination on heating with $(Ph_3P)_4Pd$, *t*-Bu_3P, *t*-BuONa, and Bu_4NBr in toluene.[28]

[1] Heropoulos, G.A., Villalonga-Barber, C. *TL* **52**, 5319 (2011)
[2] Roy, S., Spilling, C.D. *OL* **14**, 2230 (2012)
[3] Daniels, D.S.B., Thompson, A.L., Anderson, E.A. *ACIE* **50**, 11506 (2011)
[4] Trost, B.M., Thaisrivongs, D.A., Hansmann, M.M. *ACIE* **51**, 11522 (2012)
[5] Grenning, A.J., Tunge, J.A. *JACS* **133**, 14785 (2011)
[6] Jiang, G., List, B. *ASC* **353**, 1667 (2011)
[7] Manjolinho, F., Grünberg, M.F., Rodriguez, N., Goossen, L.J. *EJOC* 4680 (2012)
[8] Ye, J., Li, S., Ma, S. *OL* **14**, 2312 (2012)
[9] Wei, G., Chalker, J.M., Cohen, T. *JOC* **76**, 7912 (2011)
[10] Zhang, D., Sun, H., Zhang, L., Zhou, Y., Li, C., Jiang, H., Chen, L., Liu, H. *CC* **48**, 2909 (2012)
[11] Tomizawa, T., Orimoto, K., Niwa, T., Nakada, M. *OL* **14**, 6294 (2012)
[12] Nazario, C.E.D., Santana, A.S., Kawasoko, C.Y., Carollo, C.A., Hurtado, G.R., Viana, L.H., Barbosa, S.L., Guerro Jr, P.G., Marques, F.A., Dabdoub, V.B., Dabdoub, M.J., Baroni, A.C.M. *TL* **52**, 4177 (2011)
[13] Zhang, S., Wang, Y., Feng, X., Bao, M. *JACS* **134**, 5492 (2012)
[14] Cheng, J., Jiang, X., Ma, S. *OL* **13**, 5200 (2011)
[15] Yin, B., Cai, C., Zeng, G., Zhang, R., Li, X., Jiang, X. *OL* **14**, 1098 (2012)
[16] Iwata, A., Inuki, S., Oishi, S., Fujii, N., Ohno, H. *JOC* **76**, 5506 (2011)
[17] Bloome, K.S., McMahen, R.L., Alexanian, E.J. *JACS* **133**, 20146 (2011)
[18] Lim, H.N., Parker, K.A. *JACS* **133**, 20149 (2011)
[19] Anderson, J.C., Noble, A., Tocher, D.A. *JOC* **77**, 6703 (2012)
[20] Greenaway, R.L., Campbell, C.D., Chapman, H.A., Anderson, E.A. *ASC* **354**, 3187 (2012)
[21] Greenaway, R.L., Campbell, C.D., Holton, O.T., Russell, C.A., Anderson, E.A. *CEJ* **17**, 14366 (2011)

[22] DeKorver, K.A., Hsung, R.P., Song, W.-Z., Wang, X.-N., Walton, M.C. *OL* **14**, 3214 (2012)
[23] Glasspoole, B.W., Ghozati, K., Moir, J.W., Crudden, C.M. *CC* **48**, 1230 (2012)
[24] Tsuna, K., Noguchi, N., Nakada, M. *TL* **52**, 7202 (2011)
[25] Zhou, F., Ding, K., Cai, Q. *CEJ* **17**, 12268 (2011)
[26] Chen, Z.-S., Duan, X.-H., Zhou, P.-X., Ali, S., Luo, J.-Y., Liang, Y.-M. *ACIE* **51**, 1370 (2012)
[27] El Khatib, M., Elagawany, M., Todadze, E., Khelashvili, L., Said, A., Katritzky, A.R. *SL* 1384 (2012)
[28] Liang, Y., Geng, W., Wei, J., Ouyang, K., Xi, Z. *OBC* **10**, 1537 (2012)

Tetramethylfluoroformamidinium hexafluorophosphate

Fluorination. The amidinium salt acts as a catalyst for synthesis of alkyl fluorides from alcohols in the reaction with $Et_3N{\cdot}3HF$.[1]

[1] Bellavance, G., Dubé, P., Nguyen, B. *SL* 569 (2012)

Tetramethylguanidine

Mannich reaction. Using $(Me_2N)_2C{=}NH$ as catalyst Mannich reaction shows *syn*-selectivity.[1]

[1] Guo, Q., Zhou, J.C.-G., Arman, H. *TL* **53**, 4866 (2012)

2,2,6,6-Tetramethylpiperidine 1-oxyl, (TEMPO)

Functionalization.[1] The TEMPO group is introduced to an α-position of ketones on reaction with the title compound and *B*-chlorocatecholborane (additive: 2,6-di-*t*-butylpyridine). The same reagent pair effects addition to conjugated ketones, besides the TEMPO group a chlorine atom is bonded to the β-carbon.

α–Hydroxylation of ketones, acids, esters, amides and nitriles involves a single-electron transfer process with TEMPO and the catalyst $Cp_2Fe(PF_6)$, followed by treatment with zinc in HOAc to cleavage the N-O bond of the products.[2]

Oxidation. Photoxidation of alcohols by TEMPO can be carried out in the presence of the dye-sensitive ZnO and $AgNO_3$.[3] The TEMPO complexes of certain metal chlorides ($AlCl_3$, $FeCl_3$) are able to oxidize ArCHOHR to give ArCOR.[4]

Primary alcohols RCH_2OH are converted into $RCOOCH_2R$ by TEMPO, which is being continuously regenerated by *t*-BuOCl.[5] A method for the conversion of bromides into oxime ethers is by reaction with $RCONH_2$ in the presence of TEMPO and Et_3N.[6]

A few structural analogs of TEMPO have been scrutinized for their chemical applications. The azanoradamantane *N*-oxyl is a good catalyst for alcohol oxidation based on hydrogen transfer to diisopropyl azodicarboxylate,[7] and in conjunction with a peracid and $LiBF_4$, to convert silyl ethers into α-diketones.[8] The 1-methyl-2-azaadamantane *N*-oxyl serves as a cocatalyst (together with NaOCl) for cleavage of 1,2-diols.[9]

[1] Li, Y., Puliot, M., Vogler, T., Renaud, P., Studer, A. *OL* **14**, 4474 (2012)
[2] Dinca, E., Hartmann, P., Smrcek, J., Dix, I., Jones, P.G., Jahn, U. *EJOC* 4461 (2012)
[3] Jeena, V., Robinson, R.S. *CC* **48**, 299 (2012)
[4] Scepaniak, J.J., Wright, A.M., Lewis, R.A., Wu, G., Hayton, T.W. *JACS* **134**, 19350 (2012)

[5] Abramovich, A., Toledo, H., Pisarevsky, E., Szpilman, A.M. *SL* 2261 (2012)
[6] Wertz, S., Studer, A . *HCA* **95**, 1758 (2012)
[7] Hayashi, M., Shibuya, M., Iwabuchi, Y. *JOC* **77**, 3005 (2012)
[8] Hayashi, M., Shibuya, M., Iwabuchi, Y. *SL* 1025 (2012)
[9] Shibuya, M., Doi, R., Shibuta, T., Uesugi, S., Iwabuchi, Y. *OL* **14**, 5006 (2012)

2,2,6,6-Tetramethylpiperidinylzinc chloride

Zincation. Regioselective zincation of 4-chromenone occurs at C-3 with the (TMP)ZnCl·LiCl complex.[1] However, changing to $(TMP)_2Zn·(MgCl.LiCl)_2$ at lower temperature (−30° vs. 25°) causes a dramatic switch to C-2.

[1] Klier, L., Bresser, T., Nigst, T.A., Karaghiosoff, K., Knochel, P. *JACS* **134**, 13584 (2012)

Tetranitromethane

2-Amino nitrates. *N*-Tosylaziridines are opened by $C(NO_2)_4$.[1]

[1] Volkova, Y.A., Averina, E.B., Kuznatsova, T.S., Zefirov, N.S. *TL* **51**, 2254 (2010)

Tetrapropylammonium perruthenate

Oxidation. Catalytic amounts of the perruthenate salt as supplanted by *N*-methylmorpholine *N*-oxide perform oxidative cleavage of 1,2-diols to carboxylic acids.[1] Primary alcohols are oxidized to carboxylic acids under the same conditions.[2]

[1] Schmidt, A.-K.C., Stark, C.B.W. *OL* **13**, 5788 (2011)
[2] Schmidt, A.-K.C., Stark, C.B.W. *OL* **13**, 4164 (2011)

Tin

Allylation. Barbier reaction is accomplished with tin and allyl bromide in an ionic liquid at room temperature.[1] Homoallylic alcohols are obtained from aldoximes on reaction with allyl bromide and tin in aqueous THF, with$TiCl_3$ to convert the oximino group to the carbonyl in situ.[2] An alternative method uses $SnCl_2$-KI.

[1] Slaton, R., Petrone, A., Manchanayakage, R. *TL* **52**, 5073 (2011)
[2] Lin, M.-H., Lin, L.-Z., Chuang, T.-H., Liu, H.-J. *T* **68**, 2631 (2012)

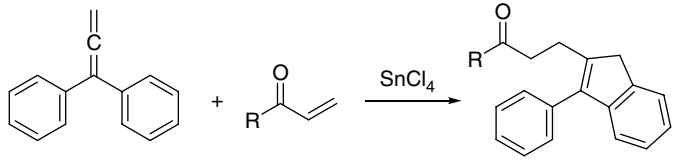
Tin(II) chloride

Allylation. γ-Attack from an allylic bromide to HCHO is witnessed using $SnCl_2$-KI in water to conduct the reaction.[1]

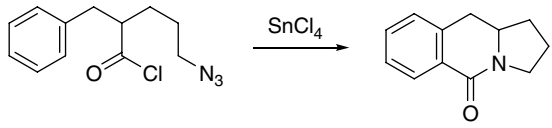
[1] Lin, M.-H., Lin, L.-Z., Chuang, T.-H. *SL* 1871 (2011)

Tin(IV) chloride

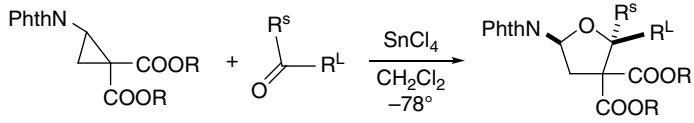
Annulation. Condensation of 1,1-diarylethylenes and 1-alken-3-ones promoted by $SnCl_4$ gives 3-aryl-2-(3-oxoalkyl)indenes.[1]



From 3,3-bis(methylthio)acrylic esters and congeners (nitrile, ketones) the replacement of a thio group by attack from the carbonyl end of 4,4-dimethoxy-2,5-cyclohexadienone is followed by the formation of a benzofuran skeleton.[2] A modified Curtius-Schmidt reaction sequence generates an activated isocyanate, and it allows for further cyclization.[3]

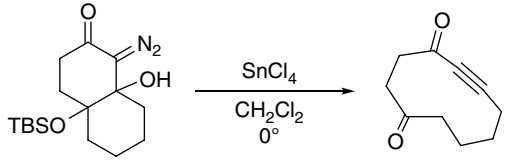


Occurrence of [3+2]cycloaddition between cyclopropanes and carbonyl compounds depends on activation of the latter components by a Lewis acid (here, $SnCl_4$). Of both mechanistic and synthetic interests is the stereochemical outcome.[4,5]



Enol ethers and push-pull cyclopropanes react at -78° in the presence of $SnCl_4$ to yield functionalized cyclopentanes.[6]

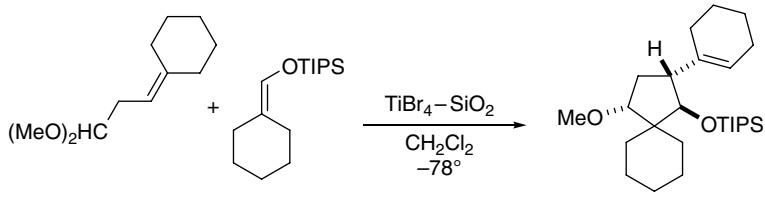
Fragmentation. A route to macrocyclic ynediones is based on the $SnCl_4$-catalyzed transformation of bicyclic β-hydroxy-α-diazo ketones that place the hydroxyl at a ring juncture and another oxy substituent at the other.[7]



[1] Yamazaki, S., Fukushima, Y., Ukai, T., Tatsumi, K., Akiya, A. *S* 2155 (2012)
[2] Liu, Y., Liu, J., Wang, M., Liu, J., Liu, Q. *ASC* **354**, 2678 (2012)
[3] Gu, P., Kang, X.-Y., Sun, J., Wang, B.-J., Yi, M., Li, X.-Q., Xue, P., Li, R. *OL* **14**, 5796 (2012)
[4] Dunn, J., Motevalli, M., Dobbs, A.P. *TL* **52**, 6974 (2011)
[5] Benfatti, F., de Nanteuil, F., Waser, J. *CEJ* **18**, 4844 (2012)
[6] de Nanteuil, F., Waser, J. *ACIE* **50**, 12075 (2011)
[7] Tsvetkov, N.P., Bayir, A., Schneider, S., Brewer, M. *OL* **14**, 264 (2012)

Titanium(IV) bromide

Annulation. Siloxyalkenes and allyl acetals are condensed in a Mukaiyama aldol reaction. With structural implement in the substrates to enable an intramolecular ene reaction, functionalized spirocyles are accessed.[1]



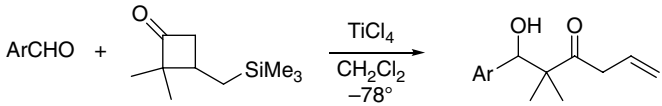
[1] Li, H., Loh, T.-P. *CAJ* **6**, 1948 (2011)

Titanium(IV) chloride

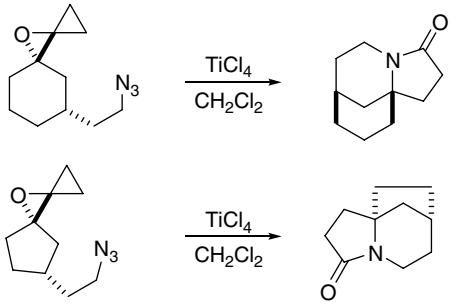
Substitution. *N*-Alkylation of sulfonamides by ethers is catalyzed by $TiCl_4$ in dichloroethane at 120°.[1]

Enamide formation. An expedient route to (*E*)-enamides is through reaction of RCONHR′ with ketones in the presence of $TiCl_4$ and Et_3N.[2]

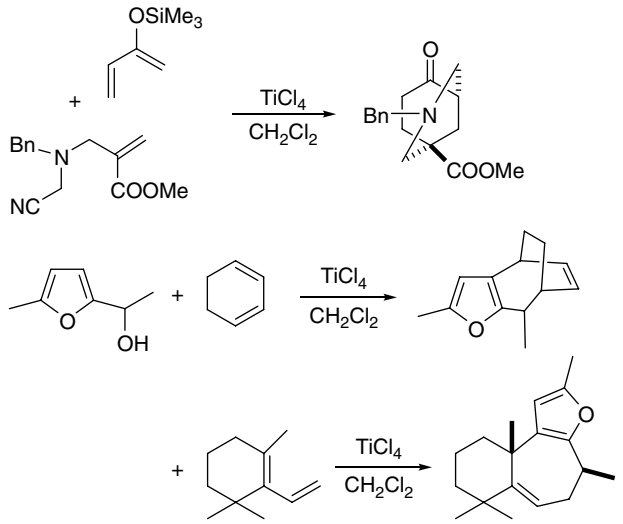
Condensation. A (*Z*)-selective condensation of ArCHO with 3,3,3-trifluoropropanoic acid is mediated by $TiCl_4$.[3] Generation of titanium(IV) enolates by fragmentation of 3-trimethylsilylmethylcyclobutanones paves way to a synthesis of 5-hydroxy-1-alken-4-ones.[4]



Indolizidinones. Spirotricyclic epoxides in which a larger ring bears an azidoalkyl chain are liable to transformation that results in the formation of bridged indolizidinones, through a reaction sequence including semipinacol rearrangement and Schmidt reaction.[5]

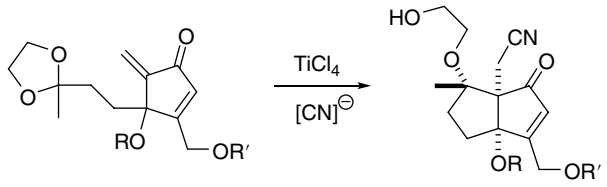


Cycloaddition. Two useful cycloaddition processes have been carried out: a [4+2] version for building the azabicyclic portion of many diterpene alkaloids,[6] and the [4+3] reaction employing dienes and furfuryl carbinols.[7]



Cyclization. 2*H*-Indazoles are made from *o*-nitrobenzylamines by the action of $TiCl_4$ – Zn, in the presence of Et_3N.[8] It is apparent that reduction of the nitro group by a low-valent titanium species the intermediate is trapped by the existing amino group on the sidechain.

In a formal synthesis of merrilactone[9] conjugate addition to an enone by nucleophile such as a cyanide ion while polarizing a dioxolane unit by $TiCl_4$ promotes ring closure to establish a properly functionalized diquinane intermediate.

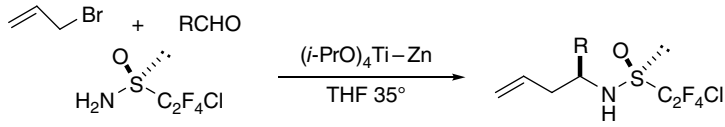


[1] Chen, J., Dang, L., Li, Q., Ye, Y., Fu, S., Zeng, W. *SL* 595 (2012)
[2] Genovino, J., Lagu, B., Wang, Y., Touré, B.B. *CC* **48**, 6735 (2012)
[3] Liu, Y., Lai, H., Rong, B., Zhou, T., Hong, J., Yuan, C., Zhao, S., Zhao, X., Jiang, B., Fang, Q. *ASC* **353**, 3161 (2011)
[4] Matsuo, J., Harada, K., Kawano, M., Okuno, R., Ishibashi, H. *OL* **13**, 5986 (2011)
[5] Puppala, M., Murali, A., Baskaran, S. *CC* **48**, 5778 (2012)
[6] Goodall, K.J., Brimble, M.A., Barker, D. *T* **68**, 5759 (2012)

[7] Winne, J.M., Catak, S., Waroquier, M., Van Speybroeck, V. *ACIE* **50**, 11990 (2011)
[8] Sun, F., Feng, X., Zhao, X., Huang, Z.-B., Shi, D.-Q. *T* **68**, 3851 (2012)
[9] Nazef, N., Davies, R.D.M., Greaney, M.F. *OL* **14**, 3720 (2012)

Titanium tetraisopropoxide

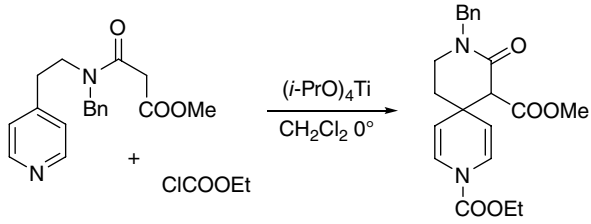
Condensation. A catalytic amount of $(i\text{-PrO})_4\text{Ti}$ serves to condense carboxylic acids with amines.[1] A three-component condensation leading to *N*-sulfinyl homoallylamines involves RCHO, allyl bromide, and a sulfonamide in the presence of $(i\text{-PrO})_4\text{Ti}$ and zinc.[2] It gives better results than the protocol using indium.



Imination of carbonyl compounds by chiral *t*-butanesulfinamide under microwave irradiation does not affect the chiral purity of the products.[3]

Enamides. 2-Acetamido-1-alkenes are obtained from methyl ketones in a two-step reaction sequence, first with ammonia in methanol and $(i\text{-PrO})_4\text{Ti}$ in toluene, then with Ac_2O and Et_3N.[4]

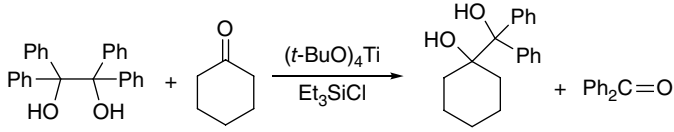
Cyclization. *N*-Ethoxycarbonylation of pyridines prompts attack by nucleophiles, in the case that a C-4 sidechain with an active methylene group present, an intramolecular cyclization leading to spirocyclic product is expected. The reaction is facilitated by $(i\text{-PrO})_4\text{Ti}$.[5]



[1] Lundberg, H., Tinnis, F., Adolfsson, H. *SL* 2201 (2012)
[2] Liu, L., Liu, J. *ChJC* **29**, 2722 (2011)
[3] Collados, J.F., Toledano, E., Guijarro, D., Yus, M. *JOC* **77**, 5744 (2012)
[4] Reeves, J.T., Tan, Z., Han, Z.S., Li, G., Zhang, Y., Xu, Y., Reeves, D.C., Gonnella, N.C., Ma, S., Lee, H., Lu, B.Z., Senanayake, C.H. *ACIE* **51**, 1400 (2012)
[5] Parameswarappa, S.G., Pigge, F.C. *TL* **52**, 4357 (2011)

Titanium tetra(*t*-butoxide)

Pinacol exchange.[1] When tetraphenylethanediol and a carbonyl compound are treated with $(t\text{-BuO})_4\text{Ti}$ and Et_3SiCl, a mixed pinacol is formed.



[1] Scheffler, U., Stösser, R., Mahrwald, R. *ASC* **354**, 2648 (2012)

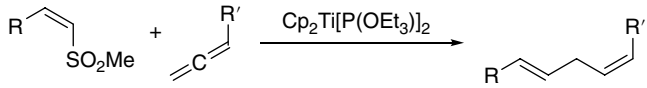
Titanocene bis(perfluorooctanesulfonate)

CC-bond forming ractions.[1] Both $Cp_2Ti(OSO_2C_8F_{17})_2$ and $Cp_2Zr(OSO_2C_8F_{17})_2$ are reusable, air-stable, efficient catalysts for Mukaiyama aldol reaction, Mannich reaction, Friedel-Crafts acylation of ArOR, allylation of RCHO, and cycloisomerization of ketones.

[1] Qiu, R., Xu, X., Peng, L., Zhao, Y., Li, N., Yin, S. *CEJ* **18**, 6172 (2012)

Titanocene bis(triethyl phosphite)

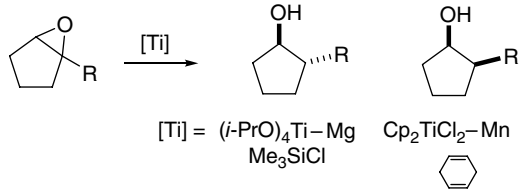
Substitution. 1,4-Dienes are obtained from reaction of 1,2-alkadienes and alkenyl sulfones in a regioselective and stereoselective manner.[1]



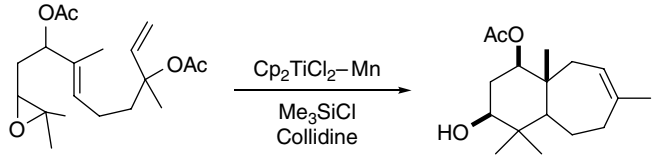
[1] Oishi, S., Hatano, K., Tsubouchi, A., Takeda, T. *CC* **47**, 11639 (2011)

Titanocene dichloride - manganese

Reduction of epoxides. Cleavage of the heterocycle resulting in alcohols can be controlled stereochemically.[1]



Trapping of the radical generated from an epoxide by a proximal double bond leads to carbocyclic products, and even more complex structures can be constructed.[2]



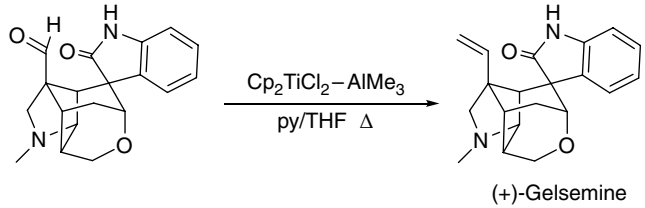
Addition. Transfer of an allyl group to carbonyl compounds can use allyl carbonates as reagent, the catalytic system is somewhat complex it being consisting of Cp_2TiCl_2, Mn, $(Ph_3P)_2NiCl_2$, Me_3SiCl, and collidine.[3]

Ozonides are decomposed to perform radical addition to conjugated carbonyl compounds when catalyzed by Cp_2TiCl, it means generation of R· from $RCH{=}CH_2$.[4] Using the same reagent it is possible to achieve Barbier reaction: propargylation of ketones and allenylation of aldehydes with propargyl halides in THF at room temperature.[5]

[1] Kawaji, T., Shohji, N., Miyashita, K., Okamoto, S. *CC* **47**, 7857 (2011)
[2] Jimenez, T., Morcillo, S.P., Martin-Lasanta, A., Collado-Sanz, D., Cardenas, D.J., Gansäuer, A., Justicia, J., Cuerva, J.M. *CEJ* **18**, 12825 (2012)
[3] Martinez-Peragon, A., Millan, A., Campana, A.G., Rodriguez-Marquez, I., Resa, S., Miguel, D., de Cienfuegos, L.A., Cuerva, J.M. *EJOC* 1499 (2012)
[4] Rosales, A., Muñoz-Bascon, J., Lopez-Sanchez, C., Alvarez-Corral, M., Muñoz-Dorado, M., Rodriguez-Garcia, I., Oltra, J.E. \ *JOC* **77**, 4171 (2012)
[5] Muñoz-Bascon, J., Sancho-Sanz, I., Alvarez-Manzaneda, E., Rosales, A., Oltra, J.E. *CEJ* **18**, 14479 (2012)

Titanocene dichloride - trimethylaluminum

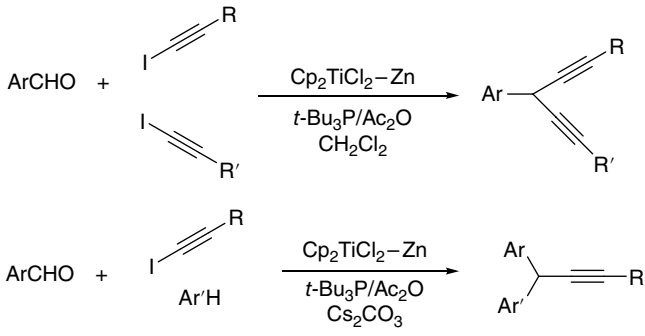
Methylenation. The Tebbe reagent generated from Cp_2TiCl_2 and Me_3Al becomes a methylenating agent in the presence of a Lewis base. The Tebbe reagent brought a synthesis of (+)-gelsemine to a successful conclusion, whereas Wittig reaction failed.[1]



[1] Zhou, X., Xiao, T., Iwama, Y., Qin, Y. *ACIE* **51**, 4909 (2012)

Titanocene dichloride - zinc

1-Aryl-2-alkynes. The Cp_2TiCl_2 – Zn combination together with a phosphine induces addition of 1-iodoalkynes to ArCHO, and the resulting benzylic/propargylic alcohols are susceptible to further substitution, either by another iodoalkyne[1] or an electron-rich arene.[2]

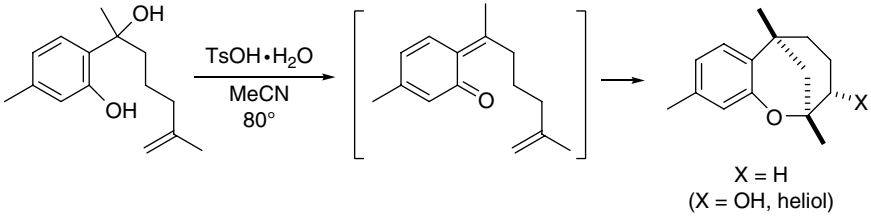


Homoallylamines. The reagent mediates addition of allyl bromide to imines.[3]

[1] Campos, C.A., Gianino, J.B., Pinkerton, D.M., Ashfeld, B.L. *OL* **13**, 5680 (2011)
[2] Gianino, J.B., Ashfeld, B.L. *JACS* **134**, 18217 (2012)
[3] Saha, S., Roy, S.C. *JOC* **76**, 7229 (2011)

p-Toluenesulfonic acid

Cyclization. Ionization of an *o*-hydroxybenzyl alcohol by protonation with TsOH is embodied in a synthesis of the heliol skeleton.[1]



[1] Green, J.C., Brown, E.R., Pettus, T.R.R. *OL* **14**, 2929 (2012)

p-Toluenesulfonylimino iodobenzene

Hofmann rearrangement. The hypervalent iodine reagent causes rearrangement of primary amides into isocyanates.[1]

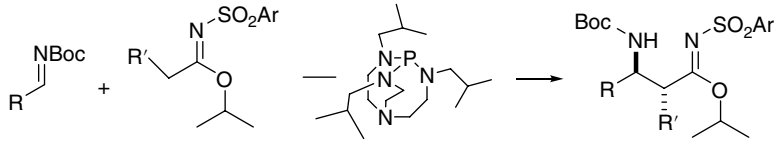
[1] Yoshimura, A., Luedtke, M.W., Zhdankin, V.V. *JOC* **77**, 2087 (2012)

2,8,9-Trialkyl-1-phospha-2,5,8,9-tetraazabicyclo[3.3.3]undecanes

As base. These cage molecules have special uses.[1] The 2,8,9-trimethyl base can be used to deprotonate MeOH to activate $(RO)_2BB(OR)_2$ for conjugate addition.[2]

Transesterification. By linking to a polymer backbone through an imido group at the phosphorus atom a recyclable catalyst for transesterification (and amidation) is obtained.[3]

Addition. *anti*-Selective addition of sulfonylimidates to *N*-Boc aldimines proceeds in the presence of the 2,8,9-triisobutyl derivative.[4]

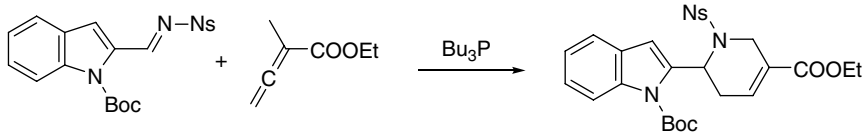


[1] Zablocka, M., Hameau, A., Caminade, A.-M., Majoral, J.-P. *ASC* **352**, 2341 (2010)
[2] Pubill-Ulldemolins, C., Bonet, A., Bo, C., Gulgas, H., Fernandez, E. *CEJ* **18**, 1121 (2012)
[3] Chintareddy, V.R., Ho, H.-A., Sadow, A.D., Verkade, J.G. *TL* **52**, 6523 (2011)
[4] Nakano, J., Masuda, K., Yamashita, Y., Kobayashi, S. *ACIE* **51**, 9525 (2012)

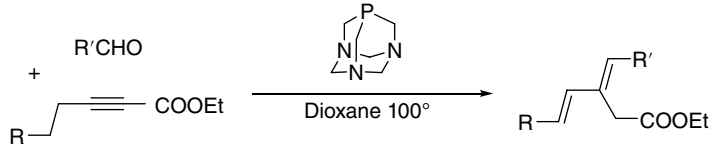
Trialkylphosphines

Preparation. From PCl_3 the HBF_4 salt of *t*-Bu_3P is obtained without isolation of sensitive intermediates.[1]

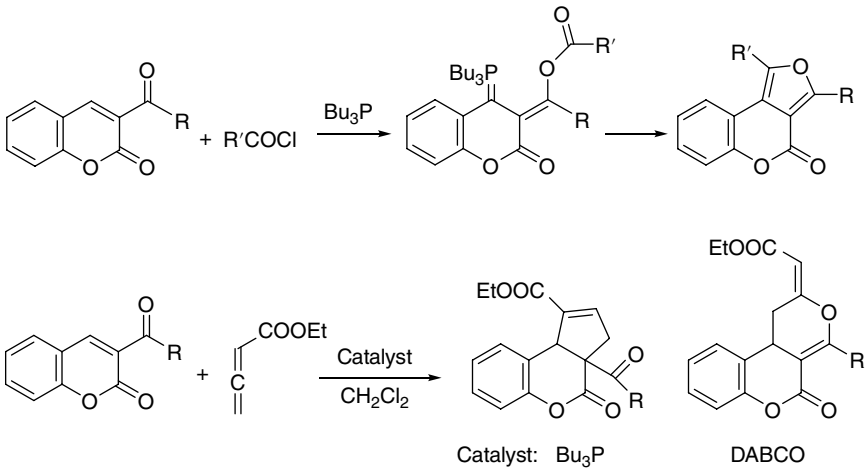
Cycloaddition. On converting propargylic bromides to allenyl cyanides by CuCN-KCN, 3-pyrrolines are formed on further reaction with *N*-sulfonylimines when catalyzed by a phosphine (Bu_3P or Ph_3P).[2] In situ isomerization of ethyl 2-methyl-2,3-butadienoate into the less directly accessible conjugated diene enables a synthesis of functionalized tetrahydropyridines.[3]



Condensation. Conjugate addition of 1,3,5-triaza-7-phosphaadamantane to a 2-alkynoic ester initiates a transformation into a 3-phosphoranyl-4-alkenoic ester, which can undergo Wittig reaction with aldehydes.[4]



3-Acylcoumarins undergo annulation by an acyl chloride in the presence of Bu_3P and Et_3N. A furan ring is attached to C-3/C-4.[5] A cyclopentene unit is introduced on reaction with a 2,3-butadienoic ester, in a markedly different manner from using DABCO as promoter.[6]

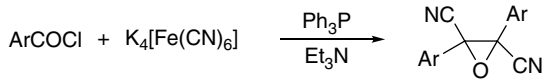


[1] Saget, T., Cramer, N. *S* 2369 (2011)
[2] Kinderman, S.S., van Maarseveen, J.H., Hiemstra, H. *SL* 1693 (2011)
[3] Villa, R.A., Xu, Q., Kwon, O. *OL* **14**, 4634 (2012)
[4] Jacobsen, M.J., Funder, E.D., Cramer, J.R., Gothelf, K.V. *OL* **13**, 3418 (2011)
[5] Jang, Y.-J., Syu, S., Chen, Y.-J., Yang, M.-C., Lin, W. *OBC* **10**, 843 (2012)
[6] Wang, Y., Yu, Z.-H., Zheng, H.-F., Shi, D.-Q. *OBC* **10**, 7739 (2012)

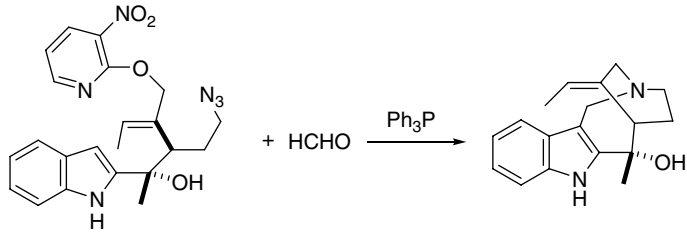
Triarylphosphines

2,2′-Bis(diphenylphosphino)biaryls.[1] These important ligands are readily prepared from the corresponding dihalobiaryls via a Pd-catalyzed process. Due to high reaction rates the undesirable formation of phosphafluorenes is avoided.

Substitution. The usefulness of Ph_3P to induce reaction of electron-rich ArH with $Ar'SO_2Cl$ is probably due to its reducing power.[2] In the presence of Ph_3P, the reaction of ArCOCl with $K_4[Fe(CN)_6]$ does not stop at the formation of ArCOCN.[3]



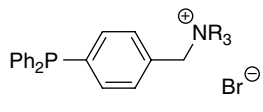
By removing N_2 from the azido group and rendering it nucleophilic, cyclization to give a bridged ring system demonstrates a well-designed synthetic development.[4]



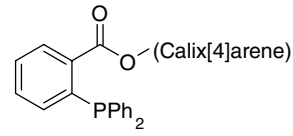
Allyl carbonate cleavage. Light facilitates the release of alcohols ROH from $ROCOOCH_2CH{=}CH_2$ by decomposition on treatment with $Pd(OAc)_2$ and the ligand sodium 4′-diphenylphosphinoazobenzene-4-sulfonates, which effects isomerization of the azo linkage (to *cis*).[5]

Addition. For temporary masking of the formyl group in a keto aldehyde to reverse the relative carbonyl reactivity, the Ph_3P-Me_3SiOTf pair is useful, as the α-trimethylsiloxyphosphonium salt is selectively formed.[6]

For conducting aza-Baylis-Hillman reaction the water-soluble phosphine **1**[7] and the air-stable calix[4]arene-based **2**[8] have shown their efficiency.



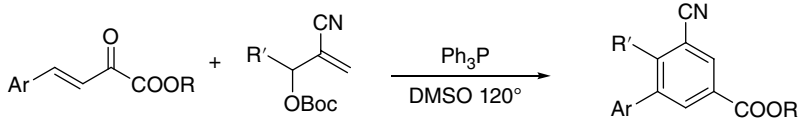
(**1**)



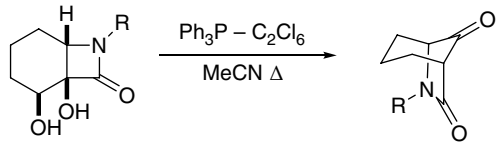
(**2**)

Activation of 2(α–tosylaminoalkyl)-2,3-butadienoic esters by Ph_3P initiates cyclization to afford 3-pyrrolines.[9] 3-Acylquinolines are assembled from *o*-tosylaminoaryl ketones and 1-alkyn-3-ones with the help of Ph_3P.[10]

Cycloaddition. Annulation of 3-dicyanomethyleneoxindole with esters of Baylis-Hillman adducts is induced by Ph_3P.[11] Those involving 2-oxo-3-alkenoic esters deliver benzene derivatives.[12]



Rearrangement. 2-Alkynyl-2-hydroxytetrahydrofurans undergo ring expansion on treatment with Ph_3P, producing 2-alkylidene-3-oxotetrahydropyrans.[13] By forming a phosphonium salt the Ph_3P and C_2Cl_6 pairing is able to convert a diol unit in a fused β-lactam to a ketone, while releasing the ring strain.[14]



[1] Bonnafoux, L., Gramage-Doria, R., Colobert, F., Leroux, F.R. *CEJ* **17**, 11008 (2011)
[2] Wu, Q., Zhao, D., Qin, X., Lan, J., You, J. *CC* **47**, 9188 (2011)
[3] Li, Z., Xu, J., Niu, P., Liu, C., Yang, J. *T* **68**, 8880 (2012)
[4] Noguchi, Y., Hirose, T., Furuya, Y., Ishiyama, A., Otoguro, K., Omura, S., Sunazuka, T. *TL* **53**, 1802 (2012)
[5] Bricout, H., Banaszak, E., Len, C., Hapiot, F., Monflier, E. *CC* **46**, 7813 (2010)
[6] Fujioka, H., Yahata, K., Kubo, O., Sawama, Y., Hamada, T., Maegawa, T. *ACIE* **50**, 12232 (2011)
[7] Imura, Y., Shimojuh, N., Moriyama, K., Togo, H. *T* **68**, 2319 (2012)
[8] Shen, Y., Tang, Q., Zhang, C., Zhong, W. *SL* 741 (2012)
[9] Andrews, I.P., Blank, B.R., Kwon, O. *CC* **48**, 5373 (2012)
[10] Khong, S., Kwon, O. *JOC* **77**, 8257 (2012)
[11] Deng, H.-P., Wei, Y., Shi, M. *OL* **13**, 3348 (2011)
[12] Xie, P., Huang, Y., Chen, R. *CEJ* **18**, 7362 (2012)
[13] Saha, J., Lorenc, C., Surana, B., Peczuh, M.W. *JOC* **77**, 3846 (2012)
[14] Grainger, R.S., Betou, M., Male, L., Pitak, M.B., Coles, S.J. *OL* **14**, 2234 (2012)

Triarylphosphines – azo compounds

Substitution. Disulfides are elaborated from alcohols by reaction with NH_4SCN, activation is provided by Ph_3P and 4,4′-azopyridine.[1]

[1] Iranpoor, N., Firouzabadi, H., Khalili, D. *TL* **53**, 6913 (2012)

Tribromocarbenium bromoaluminate

Acylation. The strong electrophile $Br_3C[Al_2Br_7]$ is formed from bromoform, HBr, and Al_2Br_6. It promotes ionization of halides such as adamantyl bromide and converts them into acyl derivatives under CO and participation of nucleophiles.[1]

[1] Akhrem, I.S., Avetisyan, D.V., Afanas'eva, L.V. *TL* **53**, 3493 (2012)

Tributylstannyltrimethylsilane

α-Amido stannanes. Replacement of the sulfonyl group of $RCH(SO_2Ar)NHCOOR'$ by an $SnBu_3$ unit is accomplished by a fluoride-mediated generation of the required nucleophile from $Me_3SiSnBu_3$.[1] The main purpose of the transformation is to obtain substrates for the Stille coupling.

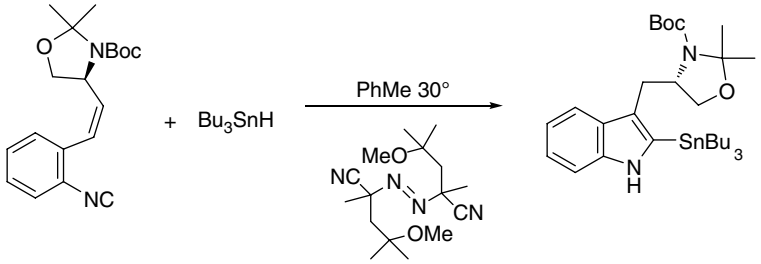
[1] Mita, T., Higuchi, Y., Sato, Y. *S* 194 (2012)

Tributyltin hydride

Reduction. Selective reduction of the double bond of an alkenyl aryl ketone by Bu_3SnH in preference to alkenyl alkyl ketone is readily achieved.[1]

Hydrostannylation. Catalyzed by $(Ph_3P)_4Pd$, 3-alkyn-1-enyl sulfones add Bu_3SnH to give dienes in which the stannyl group is situated at C-3 and with the new double bond in an (*E*)-configuration.[2] On the other hand, the reaction with propargylic alcohols catalyzed by $(C_6F_5)_3B$ furnishes selectively (*Z*)-2-tributylstannyl-2-alkenols.[3]

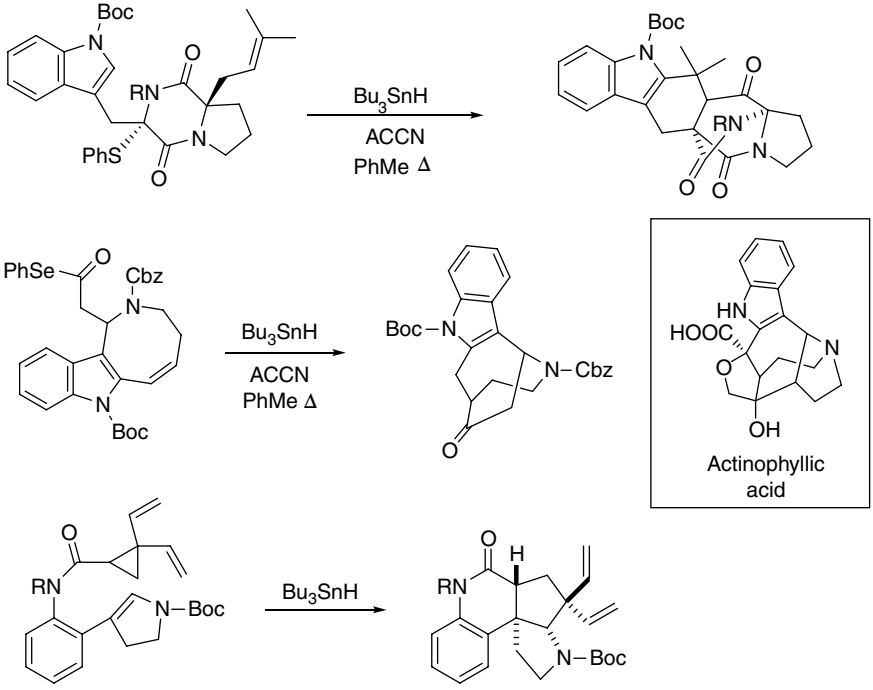
o-Isocyanostyrenes are converted into 2-tributylstannylindole derivatives, suitable to be used in Stille coupling.[4]



In the addition to propargyl silyl ethers, (*Z*)-selectivity is noted when catalytic amounts of Et_3B are added (AIBN has no such effect).[5]

Radical reactions. In a method for functionalization at C-2 of cyclic 1,3-diamines one of the nitrogen atoms is attached to an *o*-iodobenzyl group and involved in a reaction with Bu_3SnH, BnSH, AIBN, and a radical acceptor.[6] A rapid intramolecular radical transfer occurs prior to trapping by the last reagent.

Radical cyclization is featured in examples depicted by the following equations, all being initiated by the action of Bu_3SnH.[7,8,9]



[1] Krafft, M.E., Vidhani, D.V., Cran, J.W. *SL* 2355 (2011)
[2] Zhao, H., Yang, W., Xie, S., Cai, M. *EJOC* 831 (2012)
[3] Oderinde, M.S., Organ, M.G. *ACIE* **51**, 9834 (2012)
[4] Yamakawa, T., Ideue, E., Iwaki, Y., Sato, A., Tokuyama, H., Shimokawa, J., Fukuyama, T. *T* **67**, 6547 (2011)
[5] Oderinde, M.S., Hunter, H.N., Organ, M.G. *CEJ* **18**, 10817 (2012)
[6] Schiedler, D.A., Vellucci, J.K., Beaudry, C.M. *OL* **14**, 6092 (2012)
[7] Simpkins, N., Pavlakos, I., Male, L. *CC* **48**, 1958 (2012)
[8] Zaimoku, H., Taniguchi, T., Ishibashi, H. *OL* **14**, 1656 (2012)
[9] Zhang, H., Curran, D.P. *JACS* **133**, 10376 (2011)

Trichlorosilyl triflate

Reduction. Conjugated ketones are reduced to saturated ketones in a mixture of Cl_3SiOTf and dicyclohexyl(isobutyl)amine.[1]

[1] Kotani, S., Osakama, K., Sugiura, M., Nakajima, M. *OL* **13**, 3968 (2011)

Triethylammonium formate

Homologation. Chain elongation of RCHO by two carbon units to RCH_2CH_2COOH is readily accomplished in one step: condensation with Meldrum acid in the presence of

$Et_3NH(HCOO)$ [or a mixture of Et_3N and HCOOH].[1] Advantage is taken of the reducing power of the formate ion.

[1] Mudhar, H., Witty, A. *TL* **51**, 4972 (2010)

Triethylborane

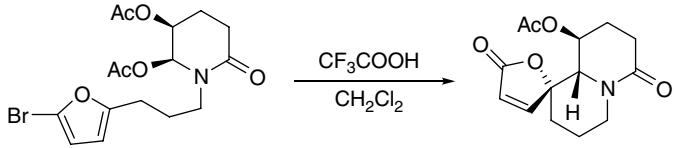
Radical reactions. Toluene forms benzyl radical by the action of Et_3B, to convert fumaric esters into 2-benzylsuccinic esters.[1] Radical is also generated from the hypophosphite anion of quaternary ammonium salts by heating with Et_3B under oxygen. Such P-radical is capable of abstracting an iodine atom and removal of the OC(=S)SMe group from a carbon skeleton.[2]

Other uses of Et_3B (often with oxygen) pertain to reaction of iodoalkanes with imine derivatives.[3,4]

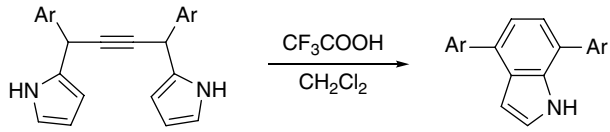
[1] Ueda, M., Kondoh, E., Ito, Y., Shono, H., Kakiuchi, M., Ichii, Y., Kimura, T., Miyoshi, T., Naito, T., Miyata, *O. OBC* **9**, 2062 (2011)
[2] Lee, E.H., Cho, D.H., Satyender, A., Jang, D.O. *TL* **52**, 6927 (2011)
[3] Yamada, K., Konishi, T., Nakano, M., Fujii, S., Cadou, R., Yamamoto, Y., Tomioka, K. *JOC* **77**, 1547 (2012)
[4] Kim, J.-G., Mishra, M.K., Jang, D.O. *TL* **53**, 3527 (2012)

Trifluoroacetic acid, (TFA)

Mannich reaction. Generation of acyliminium ions from α-acetoxy amides/lactams on exposure to TFA readies capture by an internal nucleophile such as a furan ring. While the reaction of a substrate can lead to dimeric macroheterocycle, blocking at C-5 by a bromine substituent diverts the nucleophilic site.[1]



4,7-Diarylindoles. 1,4-Diaryl-1,4-di(2-pyrrolyl)-2-butynes undergo an intramolecular Friedel-Crafts cyclization on expulsion of a pyrrole unit.[2]

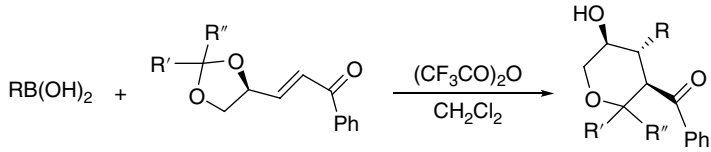


[1] Shengule, S.R., Willis, A., Pyne, S.G. *T* **68**, 1207 (2012)
[2] Nojman, E., Latos-Grazynski, L., Szterenberg, L. *EJOC* 4115 (2012)

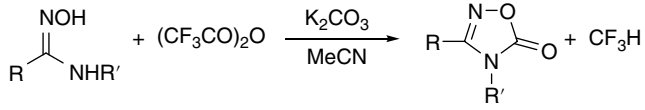
Trifluoroacetic anhydride, (TFAA)

Nitrating agent. A powerful nitrating agent for arenes is the mixed anhydride CF_3COONO_2, available from mixing TFAA with HNO_3 and $EtNH_2$.[1] (using triflic anhydride instead of TFAA in the reaction gives an even stronger reagent.)

Ring enlargement. 1,3-Dioxolanes substituted at C-4 with an enone sidechain react with $RB(OH)_2$ on activation by TFAA. Polysubstituted tetrahydropyrans are produced.[2]



Carbonylation. Formation of 1,2,4-oxadiazol-5-ones from amidoximes on exposure to TFAA (or C_6F_5COCl) is the result of condensation with expulsion of HCF_3.[3]



Ionization. 1,4-Bi(trisdimethylamino)-2-butyne is transformed by exposure to TFAA in THF at -50° into $[(Me_2N)_2CCCC(NMe_2)_2](CF_3COO)_2$ which can be isolated after anion exchange into the tetrafluoroborate salt. The dicationic species shows dienophilic characters.[4]

[1] Aridoss, G., Laali, K.K. *JOC* **76**, 8088 (2011)
[2] Roscales, S., Csaky, A.G. *OL* **14**, 1187 (2012)
[3] Gerfaud, T., Wei, H.-L., Neuville, L., Zhu, J. *OL* **13**, 6172 (2011)
[4] Drandarov, K., Tiritiris, I., Wassiljew, O., Siehl, H.-U., Kantlehner, W. *CEJ* **18**, 7224 (2012)

2,2,2-Trifluorodiazoethane

Aziridination. The reagent is generated in situ by diazotization of the salt $CF_3CH_2NH_3Cl$.[1] It engages in cycloaddition with imines and from imines of α-ketoaldehydes the *cis*-2,3-disubstituted aziridines can be prepared.

[1] Künzi, S.A., Morandi, B., Carreira, E.M. *OL* **14**, 1900 (2012)

Trifluoromethanesulfonic acid

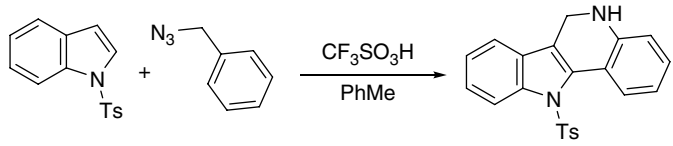
Metal triflates. Anhydrous metal triflates can be prepared using CF_3SO_3H.[1] For example, ultrasonicate zinc powder with TfOH in MeCN at 0°.

Bisacetoxylation. Triflic acid is a good catalyst for generating [AcO^+] from peracetic acid to initiate addition of two acetoxy groups to a double bond, HOAc and Ac_2O supply the nucleophilic species.[2]

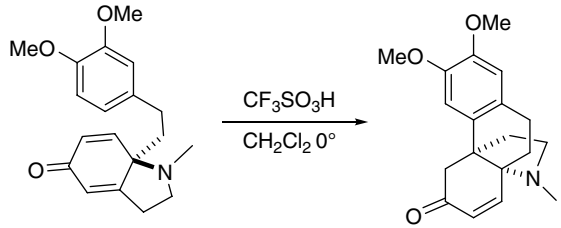
Substitution. The cyclic trimer of *O*-benzyl trichloroacetimidate, i.e., tribenzyloxy-1,3,5-triazine, submits benzyl residues to alcohols when CF_3SO_3H is employed as catalyst.[3]

With CF_3SO_3H to help ionization of secondary alcohols, alkylation of alkenes is achieved.[4] Allylic alcohols are similarly activated for conversion into amines.[5]

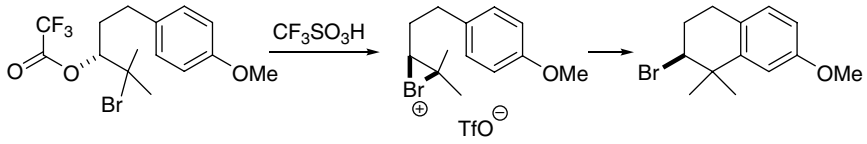
A Schmidt reaction between ArCHO and NaN_3 to furnish ArCN as catalyzed by CF_3SO_3H does not affect ketones and carboxylic acids.[6] Anilinomethylation of arenes is observed after mixing $ArCH_2N_3$ and Ar′H with CF_3SO_3H at room temperature.[7] By this method a benzannulated hydro-γ-carboline has been constructed.[8]



The high activity of CF_3SO_3H renders it valuable for protonation of an *o*-nitroaniline moiety that is part of an *N,N′*-disubstituted urea, thus enabling acylation to form lactams.[9] Protonation of a 2,5-cyclohexadienone is a prelude to Friedel-Crafts alkylation, the regioselectivity of which is governed by the preference in forming a more stable hydroxyallyl cation.[10]

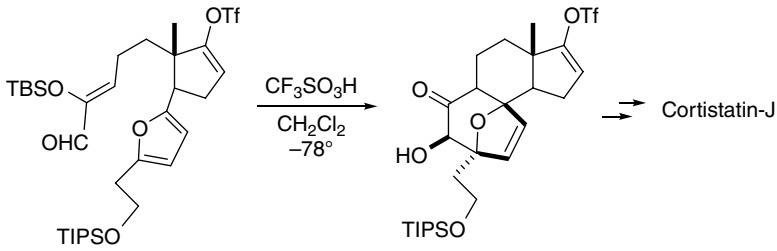


Other applications of CF_3SO_3H include assemblage of coumarins from phenols and 2,3-alkadienoic esters,[11] the cyclization of a bromohydrin ester terminated at a *p*-anisyl group via a bromonium ion,[12] and Friedel-Crafts acetylation with 4-nitroacetanilide.[13]



Cycloaddition. The enforced protonation of the sulfonyl group of an aldehyde tosylhydrazone induces attack of 1-alkynes, and it results in the formation of 3,5-disubstituted pyrazoles.[14] Similarly, enol formation from an α-siloxy enal system conveniently creates

a species with potential 1,3-dipolarophilic activity, and its exploitation in a synthesis of cortistatin-J has been successful.[15]



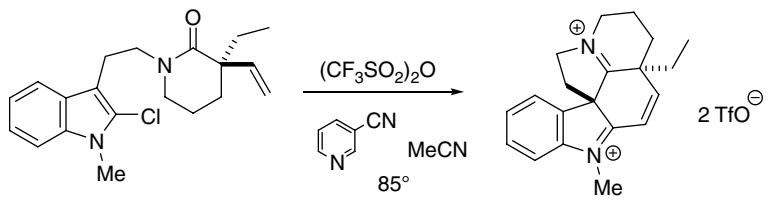
N-Arylaldimines are protonated to facilitate condensation with conjugated diazoalkenes.[16]

[1] Legrave, N., Couhert, A., Olivero, S., Desmurs, J.-R., Duñach, E. *EJOC* 901 (2012)
[2] Kang, Y.-B., Gade, L.H. *JOC* **77**, 1610 (2012)
[3] Yamada, K., Fujita, H., Kunishima, M. *OL* **14**, 5026 (2012)
[4] Yue, H.-L., Wei, W., Li, M.-M., Yang, Y.-R., Ji, J.-X. *ASC* **353**, 3139 (2011)
[5] Trillo, P., Baeza, A., Najera, C. *EJOC* 2929 (2012)
[6] Rokade, B.V., Prabhu, K.R. *JOC* **77**, 5364 (2012)
[7] Tummatorn, J., Thongsornkleeb, C., Ruchirawat, S. *T* **68**, 4732 (2012)
[8] Song, Z., Zhao, Y.-M., Zhai, H. *OL* **13**, 6331 (2011)
[9] Raja, E.K., Lill, S.O.N., Klumpp, D.A. *CC* **48**, 8141 (2012)
[10] Chuang, K.V., Navarro, R., Reisman, S.E. *ACIE* **50**, 9447 (2011)
[11] Kim, S., Kang, D., Lee, C.-H., Lee, P.H. *JOC* **77**, 6530 (2012)
[12] Braddock, D.C., Marklew, J.S., Thomas, A.J.F. *CC* **47**, 9051 (2011)
[13] Raja, E.K., DeSchepper, D.J., Lill, S.O.N., Klumpp, D.A. *JOC* **77**, 5788 (2012)
[14] Liu, P., Xu, Q.-Q., Dong, C., Lei, X., Lin, G. *SL* 2087 (2012)
[15] Nilson, M.G., Funk, R.L. *JACS* **133**, 12451 (2011)
[16] Jadhav, A.M., Pagar, V.V., Liu, R.-S. *ACIE* **51**, 11809 (2012)

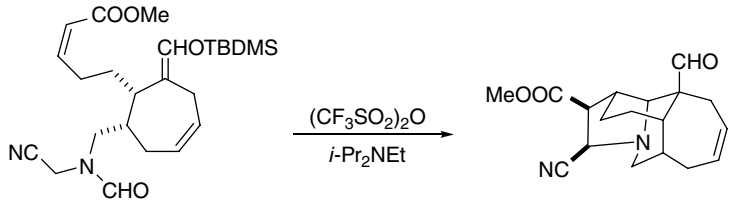
Trifluoromethanesulfonic anhydride

Imide synthesis. Mixed anhydrides derived from ammonium carboxylates and Tf_2O are highly electrophilic and they can be used as acylating agents even for nitriles (extension of the Ritter reaction). Products from this reaction are imides.[1]

Cyclization. The complete skeleton of the aspidosperma alkaloids is forged on treatment of an *N*-(3-indolyl)-α-vinyl-δ-lactam with Tf_2O.[2]



Activation of a formamide by Tf_2O preludes cyclization by attack of an enol silyl ether as the first step for constructing an intricate tetracycle (the following reaction being a [3+2] cycloaddition).[3]



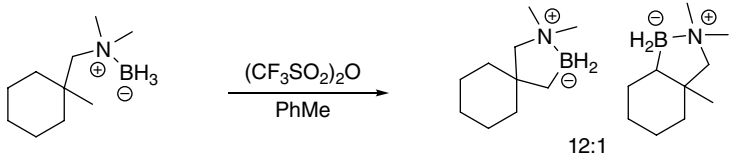
Benzylation. Secondary benzylic alcohols are ionized by the reagent formed from Ph_3PO and Tf_2O, and 1,1-diarylalkanes are readily prepared.[4]

Deoxyallylation. Aryl sulfoxides are allylated at an *o*-position while losing the *S*-bonded oxygen atom, when they react with an allylsilane in Tf_2O.[5]

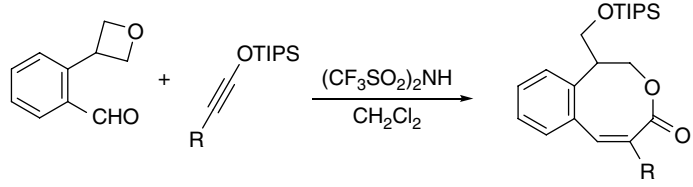
[1] Khodaei, M.M., Nazari, E. *TL* **53**, 2881 (2012)
[2] Medley, J.W., Movassaghi, M. *ACIE* **51**, 4572 (2012)
[3] Belanger, G., Boudreault, J., Levesque, F. *OL* **13**, 6204 (2011)
[4] Khodaei, M.M., Nazari, E. *TL* **53**, 5131 (2012)
[5] Eberhart, A.J., Imbriglio, J.E., Procter, D.J. *OL* **13**, 5882 (2011)

Trifluoromethanesulfonimide

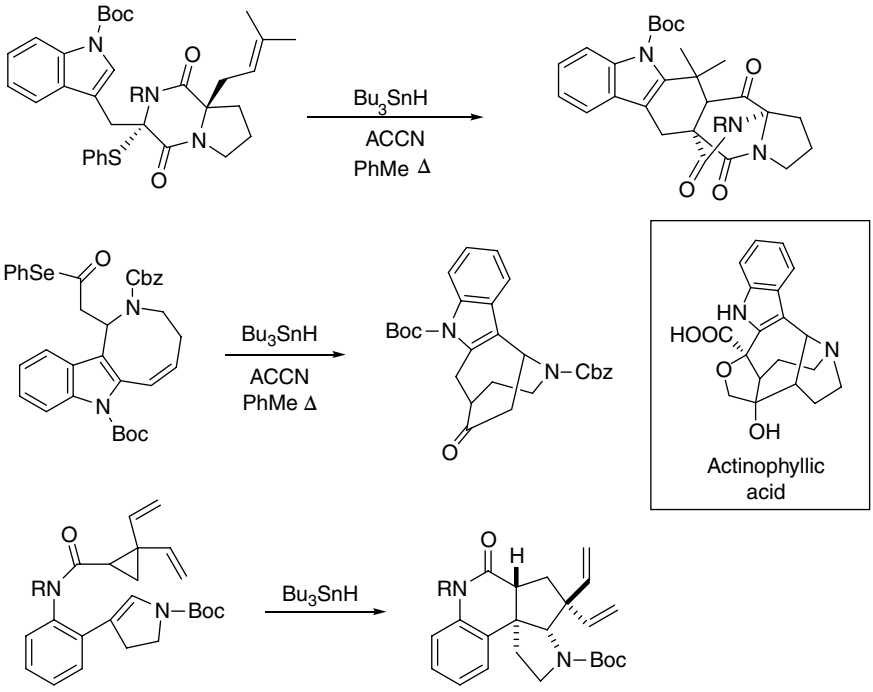
Dehydrogenation. A rather surprising Tf_2NH-mediated transformation of ammonioborates is dehydrogenative cyclization to give five-membered heterocycles.[1] The new C-B bond can involve sp^3- or sp^2 -carbon.



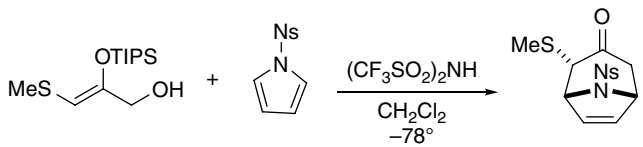
Substitution. Allyl acetates and allylsilanes combine in a head-to-head manner to provide 1,5-dienes.[2] Protonation of oxetanes makes them electrophilic and the ring opening with participating of a formyl group can trigger condensation of the latter functionality with alkynyl silyl ethers.[3]



Condensation. The Mukaiyama aldol reaction with two different bulky enol silyl ethers can be performed in sequence under steric control, Tf_2NH and Me_2AlNTf_2 are the different catalysts being used.[4]



Cycloaddition. An expeditious approach to tropine alkaloids is based on a [4+3] cycloaddition of *N*-substituted pyrroles with 2-siloxy-2-propen-1-ols.[5]



[1] Prokofjevs, A., Vedejs, E. *JACS* **133**, 20056 (2011)
[2] Ding, F., William, R., Wang, F., Liu, X.-W. *CC* **48**, 8709 (2012)
[3] Zhao, W., Wang, Z., Sun, J. *ACIE* **51**, 6209 (2012)
[4] Brady, P.B., Yamamoto, H. *ACIE* **51**, 1942 (2012)
[5] Fuchigami, R., Namba, K., Tanino, K. *TL* **53**, 5725 (2012)

Trifluoromethanesulfonimino(4-trifluoromethylphenyl)-λ^3-bromane

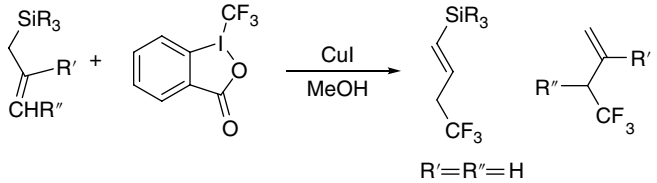
Nitrene source.[1] The reagent, prepared from $ArBrF_2$ and $TfNH_2$ in MeCN at 0°, is useful for C-H bond insertion into ethers, e.g., to functionalize THF at C-2.

Group transfer. The TfN group is readily transferred from the reagent to sulfides and sulfoxides.[2]

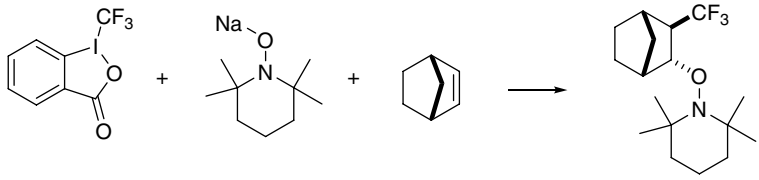
[1] Ochiai, M., Yamane, S., Hoque, M.M., Saito, M., Miyamoto, K. *CC* **48**, 5280 (2012)
[2] Ochiai, M., Naito, M., Miyamoto, K., Hayashi, S., Nakanishi, W. *CEJ* **16**, 8713 (2010)

2-(Trifluoromethyliodonio)benzoate

Trifluoromethylation. Conversion of 1-alkenes to 1,1,1-trifluoro-3-alkenes in a Cu(I)-catalyzed reaction leads to predominantly the (*E*)-isomer.[1] The reaction on allylsilanes proceeds with loss of the silyl group if the double bond is di- or trisubstituted.[2]



Addition. Functionalization of a double bond initiated by trifluoromethylation can be terminated using sodium 2,2,6,6-tetramethylpiperidinoxide.[3]



[1] Parsons, A.T., Buchwald, S.L. *ACIE* **50**, 9120 (2011)
[2] Shimizu, R., Egami, H., Hamashima, Y., Sodeoka, M. *ACIE* **51**, 4577 (2012)
[3] Li, Y., Studer, A.. *ACIE* **51**, 8221 (2012)

2-(Trifluoromethyliodonio)-α,α-dimethylbenzyloxide

Trifluoromethylation. The Togni reagent is also a CF_3 donor for azoles.[1]

[1] Niedermann, K., Früh, N., Senn, R., Czarniecki, B., Verel, R., Togni, A. *ACIE* **51**, 6511 (2012)

Trifluoromethyltrimethylsilane

Substitution. Alkenyl halides, both activated and unactivated, are susceptible to replacement of their halogen atom by a CF_3 group on reaction with Me_3SiCF_3, KF, CuI or Cu(I) 2-thienylcarboxylate.[1,2]

Arylboronic acids have similarly the boron residue replaced, when $Cu(OTf)_2$ and Ag_2CO_3 are called for their the manipulation.[3] For synthesis of $ArSCF_3$, sulfur is added as a reactant (changing the catalyst to CuSCN as indicated should be of little consequence).[4]

Also to functionalize the terminal carbon atom of 1-alkynes by an SCF_3 group it requires simple admixture of S_8 and Me_3SiCF_3 in DMF at room temperature.[5]

Synthesis of trifluoroacetylarenes from Weinreb amides is to form adducts with Me_3SiCF_3 (catalyst: CsF), and then decompose them with Bu_4NF in water.[6]

Addition. 4-Nitroisoxazoles are susceptible to nucleophilic attack by Me_3SiCF_3 to form 4-nitro-5-trifluoromethylisoxazolines. Only a mild base (NaOAc) and a surfactant ammonium bromide are additives for the reaction.[7]

[1] Hafner, A., Bräse, S. *ASC* **353**, 3044 (2011)
[2] Miyake, Y., Ota, S., Nishibayashi, Y. *CEJ* **18**, 13255 (2012)
[3] Jiang, X., Chu, L., Qing, F.-L. *JOC* **77**, 1251 (2012)
[4] Chen, C., Xie, Y., Chu, L., Wang, R.-W., Zhang, X., Qing, F.-L. *ACIE* **51**, 2492 (2012)
[5] Chen, C., Chu, L., Qing, F.-L. *JACS* **134**, 12454 (2012)
[6] Rudzinski, D.M., Kelly, C.B., Leadbeater, N.E. *CC* **48**, 9610 (2012)
[7] Kawai, H., Tachi, K., Tokunaga, E., Shiro, M., Shibata, N. *ACIE* **50**, 7803 (2011)

Triiodocyanuric acid

Iodination.[1] This reagent is powerful enough to iodinate deactivated arenes in acidic media.

[1] de Ribeiro, R.S., Esteves, P.M., de Mattos, M.C.S. *S* 739 (2011)

Triiron dodecacarbonyl

Reductive amination.[1] *N*-Alkylanilines are isolated from hydrogenated mixtures of carbonyl compounds, $ArNH_2$ and $Fe_3(CO)_{12}$.

Alkenamides.[2] By catatysis of $Fe_3(CO)_{12}$ [ligand: *N,N′*-(2,6-diisopropylphenyl) oximine] mixtures of 1-alkynes, CO and amines give RCH=CHCONR′R″.

[1] Fleischer, S., Zhou, S., Junge, K., Beller, M. *CAJ* **6**, 2240 (2011)
[2] Driller, K.M., Prateeptongkum, S., Jackstell, R., Beller, M. *ACIE* **50**, 537 (2011)

3-Trimethylammoniophenoxide

1,3-Dioxolan-2-ones.[1] The title internal salt is an activator for the insertion of CO_2 into a C-O bond of oxiranes.

[1] Tsutsumi, Y., Yamakawa, K., Yoshida, M., Ema, T., Sakai, T. *OL* **12**, 5728 (2010)

Trimethylsilyl azide

Azido compounds. Direct substitution of allyl alcohols is accomplished in a reaction with Me_3SiN_3 that is catalyzed by AgOTf.[1] 2-Alkenyloxiranes and *N*-substituted aziridines undergo electrophilic attack by Me_3SiN_3 predominantly at the allylic position.[2]

For hydroazidation of acrylic acid with Me_3SiN_3 a polystyrene-linked quaternized DABCO with fluoride counterion can be used to liberate the azide ion.[3]

Nitrile synthesis. Benzyl and cinnamyl alcohols are converted into aryl cyanides and β-arylacrylonitriles, respectively, on a Cu(II)-catalyzed reaction with Me_3SiN_3 in the presence of DDQ.[4]

Tetrazoles. Both diarylmethanes and 1,3-diarylpropenes are converted into 1,5-disubstituted tetrazoles on reaction with Me_3SiN_3 under the influence of CuI and DDQ.[5] The reaction proceeds via free radical formation, trapping by the azide group, rearrangement to nitrilium ions, and cycloaddition with another azide ion.



[1] Rueping, M., Vila, C., Uria, U. *OL* **14**, 768 (2012)
[2] Righi, G., Bovicelli, P., Marucci, C., Ilaria, I. *S* 3202 (2012)
[3] Angelini, T., Bonollo, S., Lanari, D., Pizzo, F., Vaccaro, L. *OL* **14**, 4610 (2012)
[4] Rokade, B.V., Malekar, S.K., Prabhu, K.R. *CC* **48**, 5506 (2012)
[5] Chen, F., Qin, C., Cui, Y., Jiao, N. *ACIE* **50**, 11487 (2011)

Trimethylsilyl chloride

Activation. Allylic alcohols are activated with Me_3SiCl to undergo substitution by various nucleophiles including amines, 1,3-dicarbonyl compounds, and arenes, while a fluorinated alcohol [CF_3CH_2OH or $(CF_3)_2CHOH$] is added as promoter.[1]

Formation of *N*-benzyloxycarbonyl-*N′*-trimethylsilylcarbodiimide from the potassium salt of Cbz-cyanamide is a crucial step for attack by amines to assemble guanidines.[2] In the addition of RZnX to nitrones, Me_3SiCl serves an important promoter.[3]

A method for the preparation of trichloromethylcarbinol silyl ethers involves trimethylsilylation of lithiated chloroform and then addition to carbonyl compounds.[4]

[1] Trillo, P., Baeza, A., Najera, C. *JOC* **77**, 7344 (2012)
[2] Looper, R.E., Haussener, T.J., Mack, J.B.C. *JOC* **76**, 6967 (2011)
[3] Fu, Y., Liu, Y., Chen, Y., Hügel, H.M., Wang, M., Huang, D., Hu, Y. *OBC* **10**, 7669 (2012)
[4] Henegar, K.E., Lira, R. *JOC* **77**, 2999 (2012)

Trimethylsilyl cyanide

Substitution. Benzyl cyanides are obtained from the alcohols on reaction with Me_3SiCN, using $Zn(OTf)_2$ as catalyst.[1] On the other hand, isonitriles are formed when alcohols are treated consecutively with Me_3SiCN, Et_3N, and TsCl-pyridine.[2]

Addition. In the formation of α-cyanohydrin trimethylsilyl ethers from carbonyl compounds, a new catalyst is the salt $[Ph_3P{=}N{=}PPh_3]Cl$.[3] A summary describes cyanopalladation of nonactivated alkynes [Pd(II) catalyst, Me_3SiCN] and C-C bond forming processes it triggers.[4]

Difluorocyanomethylation. The reagent Me_3SiCF_2CN, reactive toward C=O and C=N bonds, is created by insertion of difluorocarbene into the Si-C bond of Me_3SiCN.[5]

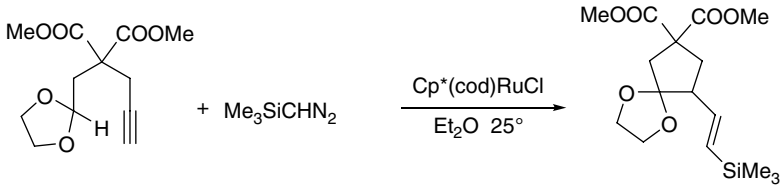
Cycloalkenyl cyanides. Enynes separated at a convenient distance and bearing at each chain terminus an electron-withdrawing group are induced to cyclize and incorporate a cyano residue, while a tertiary phosphine serves as the catalyst.[6]



[1] Theerthagiri, P., Lalitha, A. *TL* **53**, 5535 (2012)
[2] Okada, I., Kitano, Y. *S* 3997 (2011)
[3] Lacour, M.-A., Rahier, N.J., Taillefer, M. *CEJ* **17**, 12276 (2011)
[4] Arai, S., Nishida, A. *SL* 2880 (2012)
[5] Kosobokov, M.D., Dilman, A.D., Levin, V.V., Struchkova, M.I. *JOC* **77**, 5850 (2012)
[6] MacKay, J.A., Landis, Z.C., Motika, S.E., Kench, M.H. *JOC* **77**, 7768 (2012)

Trimethylsilyldiazomethane

Homologative cyclization. A Ru(I) complex mediates homologation of an alkyne with Me_3SiCHN_2 which is also attended by 1,5-hydride shift and cyclization.[1]



[1] Cambeiro, F., Lopez, S., Varela, J.A., Saa, C. *ACIE* **51**, 723 (2012)

Trimethylsilyl iodide

Silylation. Styrenes are silylated at the β-carbon, but 1-alkenes furnish 1-trimethylsilyl-2-alkenes. A $(cod)Pd(CH_2SiMe_3)_2$ complex is maintained active as the catalyst by the electron-rich and suitably bulky *t*-$BuPPh_2$ ligand and an amine base drive the reaction with Me_3SiI.[1]

α-Iodostyrenes. These iodides are formed when aryltrimethylsilylethynes are exposed to Me_3SiI, followed by a hydrolytic workup.[2]

γ-Lactones. Epoxymalonic esters are activated toward intramolecular attack by Me_3SiI to form β-hydroxy-γ-lactones.[3]

[1] McAtlee, J.R., Martin, S.E.S., Ahneman, D.T., Johnson, K.A., Watson, D.A. *ACIE* **51**, 3663 (2012)
[2] Sato, A.H., Mihara, S., Iwasawa, T. *TL* **53**, 3585 (2012)
[3] Pehlivan, L., Jacolot, M., Coia, N., Monteiro, N., Bouyssi, D., Balm, G. *TL* **52**, 4716 (2011)

Trimethylsilylmethylphosphonic esters

Conjugated ketones.[1] Serving as a one-carbon connector to join RCOF and R′CHO in a one-step synthesis of RCOCH=CHR′, the versatility of $Me_3SiCH_2PO(OR'')_2$ owes to a high affinity to fluorine as well as capacity for the Horner-Wadsworth-Emmons reaction.

[1] Umezawa, T., Seino, T., Matsuda, F. *OL* **14**, 4206 (2012)

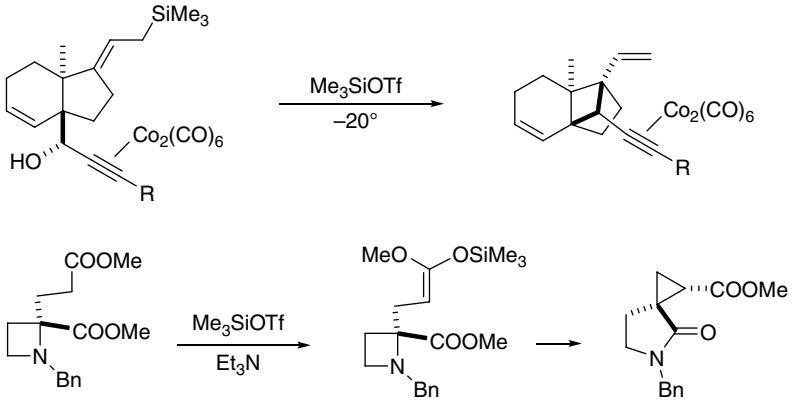
Trimethylsilyl trifluoromethanesulfonate

Alcoholysis.[1] To mediate transformation of RCN into RCOOR′ by reaction with R′OH, the requirement of 2 equivalents of Me_3SiOTf makes the method impractical (uneconomical).

Cyclization. The Prins reaction of aldehydes with 3-buten-ols bearing a bis(trimethylsilyl)methyl substituent at C-3 yielding 4-trimethylsilylmethylenetetrahydropyrans is stereoselective.[2] Intramolecular reaction of 5-alkenals generated in situ from epoxides leads to cyclopentanols (here *i*-Pr_3SiOTf is responsible for both reactions).[3]



Formation of a cyclobutane involving a cobalt-coordinated propargyl alcohol and an allylsilane has been realized.[4] Also of synthetic interest is the ring mutation sequence initiated by cyclopropanation that opens an azetidine unit for eventual lactamization.[5]



Cycloaddition. The rearrangement of alkenyloxiranes on contact with a silyl triflates may be slower due to stability of the allyl cations. Accordingly, trapping by cyclic dienes is viable.[6]

The Lewis acid-catalyzed [3+2]cycloaddition involving *N*-acylhydrazones and cyclopentadiene leads to bicyclic pyrazolidines.[7]

[1] Pfaff, D., Nemecek, G., Podlech, J. *HCA* **95**, 1851 (2012)
[2] Lu, J., Song, Z., Zhang, Y., Gan, Z., Li, H. *ACIE* **51**, 5367 (2012)
[3] Kodama, T., Harada, S., Tanaka, T., Tachi, Y., Morimoto, Y. *SL* 458 (2012)
[4] Tsao, K.-W., Cheng, C.-Y., Isobe, M. *OL* **14**, 5274 (2012)
[5] Nocquet, P.-A., Hazelard, D., Compain, P. *EJOC* 6619 (2011)
[6] Lo, B., Lam, S., Wong, W.-T., Chiu, P. *ACIE* **51**, 12120 (2012)
[7] Zamfir, A., Schenker, S., Bauer, W., Clark, T., Tsogoeva, S.B. *EJOC* 3706 (2011)

Triphosgene

Alkyl chlorides. Primary alcohols react with $O{=}C(OCCl_3)_2$ to yield RCH_2Cl.[1]

[1] Ayala, C.E., Villalpando, A., Nguyen, A.L., McCandless, G.T., Kartika, R. *OL* **14**, 3676 (2012)

Tripyrrolidinylbromophosphonium hexafluorophosphate

Substitution. The title reagent promotes attack of a variety of nucleophiles on C-2 of pyridine *N*-oxide, the oxygen atom being transferred to phosphorus.[1]

[1] Londregan, A.T., Jennings, S., Wei, L. *OL* **13**, 1840 (2011)

Tripyrrolidinylphosphine *t*-butylimide

As base. Known also as P_1-base, the nitrogenated phosphorane is used in occasions where a strong non-nucleophilic base is required. Chemoselective enol-nonaflation of aldehydes while sparing the keto group is performed and elimination to give a terminal alkyne is realizable.[1]

[1] Boltukhina, E.V., Sheshenev, A.E., Lyapkalo, I.M. *T* **67**, 5382 (2011)

Triruthenium dodecacarbonyl

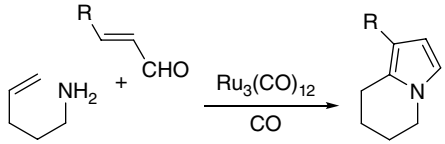
Addition. Reduction of an alkyne to the alkene occurs with $Ru_3(CO)_{12}$, Ph_3P, water (2 equiv.) and an acid at 145°.[1] The acid has great influence on the stereochemical outcome, HOAc favoring the (*Z*)-isomer, whereas CF_3COOH, the (*E*)-isomer.

1-Alkenes pick up HCOOR to form the homologous saturated esters, the catalytic system consists of $Ru_3(CO)_{12}$ and an N-substituted imidazole.[2]

The ruthenium carbonyl promotes 1,4-addition of an α-hydroxycarboxylic ester to 2-substituted 1,3-butadienes, and accordingly the carbon chain is elongated as exemplified by prenylation and geranylation.[3] Cyclic amines are activated toward alkylation at an α-carbon, in this reaction two different additives are beneficial: RCOOH to activate the catalyst and prolongs its lifetime, and disopropyl carbinol reduces side reactions.[4]

Substitution. During the change of α-hydroxycarbamides into the aminocarbamides by reaction with amines (including NH_3), $Ru_3(CO)_{12}$ is protected by the ligand $Cy_2PCH_2CH_2PCy_2$.[5]

Coupling. Arylation at the sp^3-carbon of 2-benzylaminopyridines with arylboronates is conducted with $Ru_3(CO)_{12}$ and added pinacolone.[6] It requires stepwise orchestration of bond-forming processes to direct the condensation leading to an indolizine skeleton shown below.[7]

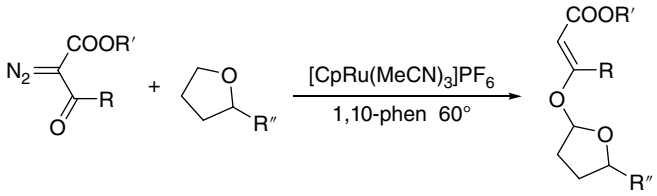


Indole synthesis from arylhydrazines and alcohols obviously proceeds via oxidation of the alcohols by the Ru catalyst and the formation of hydrazones. The added Lewis acid ($ZnCl_2$) is responsible for bringing about the ring closure.[8]

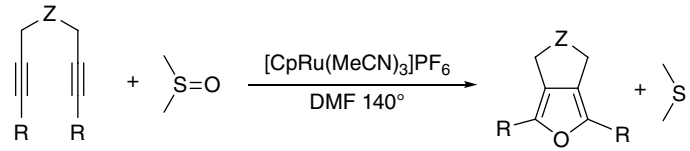
[1] Li, J., Hua, R. *CEJ* **17**, 8462 (2011)
[2] Konishi, H., Ueda, T., Muto, T., Manabe, K. *OL* **14**, 4722 (2012)
[3] Leung, J.C., Geary, L.M., Chen, T.-Y., Zbieg, J.R., Krische, M.J. *JACS* **134**, 15700 (2012)
[4] Bergman, S.D., Storr, T.E., Prokopcova, H., Aelvoet, K., Diels, G., Meerpoel, L., Maes, B.U.W. *CEJ* **18**, 10393 (2012)
[5] Zhang, M., Imm, S., Bähn, S., Neumann, H., Beller, M. *ACIE* **50**, 11197 (2011)
[6] Dastbaravardeh, N., Schnürch, M., Mihovilovic, M.D. *OL* **14**, 1930 (2012)
[7] Biletzki, T., Imhof, W. *EJOC* 6513 (2012)
[8] Porcheddu, A., Mura, M.G., De Luca, L., Pizzetti, M., Taddei, M. *OL* **14**, 6112 (2012)

Tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate

C-H bond insertion. α-Diazo-β-keto esters are decomposed by the Ru salt and insert into the α-CH bond of THF in their enol form.[1]



Cycloaddition. Dimethyl sulfoxide contributes an oxygen atom to a [2+2+1]cycloaddition with 1,6-diynes to create 3,4-annulated furans.[2]

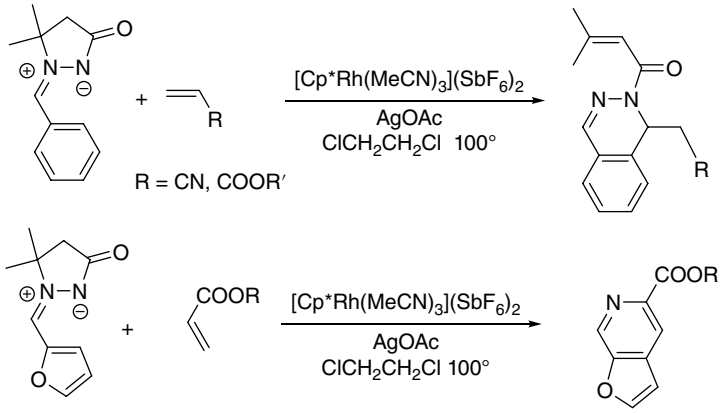


[1] Tortoreto, C., Achard, T., Zeghida, W., Austeri, M., Guenée, L., Lacour, J. *ACIE* **51**, 5847 (2012)
[2] Yamashita, K., Yamamoto, Y., Nishiyama, H. *JACS* **134**, 7660 (2012)

Tris(acetonitrile)pentamethylcyclopentadienylrhodium(II) hexafluoroantimonate

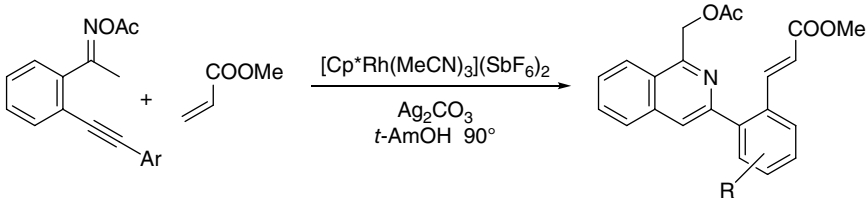
Addition. Functionalization of 2-vinylpyridine at the terminal sp^2-carbon atom on reaction with aldehydes and aldimines with catalysis by $[Cp^*Rh(MeCN)_3](SbF_6)_2$ provides (Z)-allylic alcohols and amines.[1] In a Friedel-Crafts-type reaction a carbamoyl group is introduced into the *o*-position of an anilide using RNCO. Enamides are similarly homologated.[2]

Coupling. That zwitterionic 1-benzylidenepyrazolidin-3-ones and alkenes react in the presence of $[Cp^*Rh(MeCN)_3](SbF_6)_2$ to create heterocycles is of some synthetic value.[3]



Oxidative cyclization of ω-tosylamino-1-alkenes serves to elaborate 2-vinylazacyclic compounds. The Rh(III) catalyst is assisted by $Cu(OAc)_2$, an oxidant.[4] A similar pairing of catalyst and oxidant proves effective in an indenone synthesis from *N*-aroyloxazolidin-2-ones and alkynes.[5]

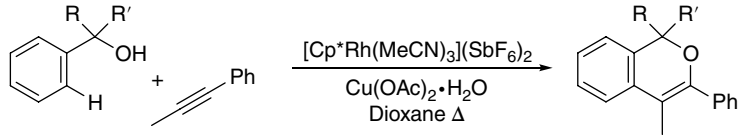
N-Carbamoylindoles are acylated at C-2 in the reaction with aldehydes, the oxidant used is Ag_2CO_3.[6] A much more involved coupling between an *o*-arylethynylacetophenone oxime *O*-acetate and an electron-deficient ethylene results in the formation of a 3-arylisoquinoline.[7]



While many methods have been developed for the directed substitution of 2-arylpyridines and related compounds. It is interesting that the Rh(III) salt catalyzes the reductive cleavage of the same C-C bond in the hydroxylbenzyl derivatives.[8]

By using the perchlorate salt of the same cationic Rh(III) complex and Ag_2CO_3 as cocatalysts, incorporation of CO into benzamides leads to formation of phthalimides.[9]

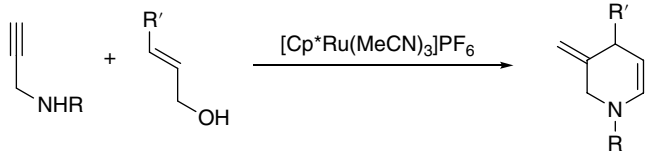
Benzyl alcohols are transformed into 2*H*-benzo[*c*]pyrans by reaction with alkynes.[10]



[1] Li, Y., Zhang, X.-S., Zhu, Q.-L., Shi, Z.-J. *OL* **14**, 4498 (2012)
[2] Hesp, K.D., Bergman, R.G., Ellman, J.A. *JACS* **133**, 11430 (2011)
[3] Zhen, W., Wang, F., Zhao, M., Du, Z., Li, X. *ACIE* **51**, 11819 (2012)
[4] Cochet, T., Bellosta, V., Roche, D., Ortholand, J.-Y., Greiner, A., Cossy, J. *CC* **48**, 10745 (2012)
[5] Li, B.-J., Wang, H.-Y., Zhu, Q.-L., Shi, Z.-J. *ACIE* **51**, 3948 (2012)
[6] Zhou, B., Yang, Y., Li, Y. *CC* **48**, 5163 (2012)
[7] Zhao, P., Wang, F., Han, K., Li, X. *OL* **14**, 3400 (2012)
[8] Chen, K., Li, H., Lei, Z.-Q., Li, Y., Ye, W.-H., Zhang, L.-S., Sun, J., Shi, Z.-J. *ACIE* **51**, 9851 (2012)
[9] Du, Y., Hyster, T.K., Rovis, T. *CC* **47**, 12074 (2011)
[10] Morimoto, K., Hirano, K., Satoh, T., Miura, M. *JOC* **76**, 9548 (2011)

Tris(acetonitrile)pentamethylcyclopentadienylruthenium(II) hexafluorophosphate

Annulation. The Ru(II) salt can be used to combine propargyl amines with allyl alcohols to form 3-methylene-1,2,3,4-tetrahydropyridines through a reaction sequence of N-allylation and cycloisomerization.[1]



[1] Murugesan, S., Jiang, F., Achard, M., Bruneau, C., Dérien, S. *CC* **48**, 6589 (2012)

Tris(4-bromophenyl)aminium hexachloroantimonate

Annulation. A Pavarov isoquinoline synthesis is based on the condensation of *N*-arylaldimines with *N*-vinyl-ε-caprolactam which serves an ethylene equivalent. The process is induced by the radical cation aminium salt.[1]

The ring of β-aryl-α,β-epoxy ketones is broken by interaction with the title reagent to form carbocation-oxy radical species, and such are trapped by β-naphthol.[2]

[1] Jia, X., Qing, C., Huo, C., Peng, F., Wang, X. *TL* **53**, 7140 (2012)
[2] Huo, C., Xu, X., An, J., Jia, X., Wang, X., Wang, C. *JOC* **77**, 8310 (2012)

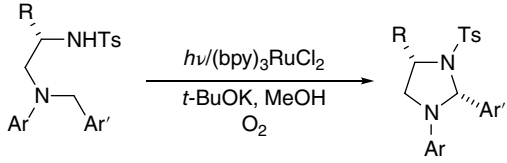
Tris(bipyridine)dichlororuthenium(II)

Substitution. The title complex is a photosensitizer to mediate photoredox reactions. Electron-rich arenes are derivatized on reaction with dibenzoyl peroxide to aryl benzoates.[1] Replacement of the boron substituent in an $ArB(OH)_2$ by a trifluoromethyl group is accomplished on reaction with CF_3I, the reaction being conducted with assistance of $(bpy)_3RuCl_2$ and $Cu(OAc)_2$ under visible light.[2] A similar trifluoromethylation of 1-alkenes to afford (*E*)-1,1,1-trifluoro-2-alkenes is reported to use $(phen)_3RuCl_2$.[3]

Photoinduced, Ru(II)-directed arylation of 2-acetoxy-1-alkenes but not internal enol acetates with ArN_2BF_4 proceeds well.[4]

Annulation. 3-Arylindenes are acquired from reaction of alkynylarenes that contain an *o*-alkyl chain with $ArSO_2Cl$. This Ru-catalyzed, photoinduced reaction liberates SO_2 and HCl (therefore Na_2CO_3 is added).[5]

A benzylamine is oxidizable and the resulting iminium ion can be trapped by an internal nucleophile that is present. This is the rationale behind the development of a route to 2-arylimidazolidines.[6]



α-Oxidation of *N*-alkylanilines enables reaction with dienophiles to form 3,4-disubstituted tetrahydroquinolines.[7]

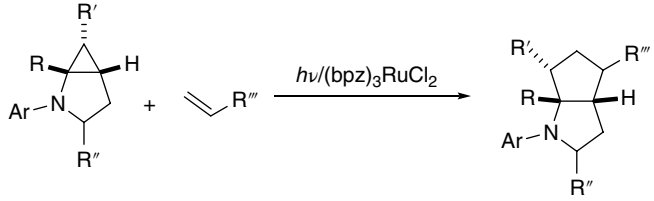
Vilsmeier-Haack reagent. Formation of the V-H reagent from DMF and CBr_4 by irradiation with the Ru complex is shown by the conversion of carboxylic acids into anhydrides.[8]

[1] Rao, H., Wang, P., Li, C.-J. *EJOC* 6503 (2012)
[2] Ye, Y., Sanford, M.S. *JACS* **134**, 9034 (2012)
[3] Iqbal, N., Choi, S., Kim, E., Cho, E.J. *JOC* **77**, 11383 (2012)
[4] Hering, T., Hari, D.P., König, B. *JOC* **77**, 10347 (2012)
[5] Xia, J.-D., Deng, G.-B., Zhou, M.-B., Liu, W., Xie, P., Li, J.-H. *SL* 2707 (2012)
[6] Xuan, J., Cheng, Y., An, J., Lu, L.-Q., Zhang, X.-X., Xiao, W.-J. *CC* **47**, 8337 (2011)
[7] Ju, X., Li, D., Li, W., Yu, W., Bian, F. *ASC* **354**, 3561 (2012)
[8] Konieczynska, M.D., Dai, C., Stephenson, C.R.J. *OBC* **10**, 4509 (2012)

Tris(bipyridine)ruthenium(II) hexafluorophosphate

Substitution. Arylsulfenylation of *N*-substituted indoles at C-3 by $ArSO_2Cl$ has been observed.[1]

Cycloaddition. The 2,2′-bipyrazine congener of the title complex is gainfully employed in the insertion of a two-carbon unit into a cyclopropane ring by alkenes.[2]

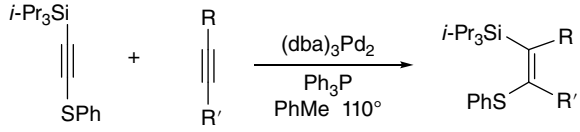


[1] Chen, M., Huang, Z.-T., Zheng, Q.-Y. *CC* **48**, 11686 (2012)
[2] Maity, S., Zhu, M., Shinabery, R.S., Zheng, N. *ACIE* **51**, 222 (2012)

Tris(dibenzylideneacetone)dipalladium

Addition. There are marked catalytic activity differences between $(Ph_3P)_4Pd$ and $(dba)_3Pd_2$ regarding hydrogenation of alkynes using HCOOH as hydrogen source: semihydrogenation is performed by the former complex [to (*Z*)-alkenes, and with aq. HCOOH to (*E*)-alkenes], but complete saturation is observed with $(dba)_3Pd_2$ and Cy_3P.[1]

Alkynes undergo *cis*-addition on heating with silylethynyl sulfides and $(dba)_3Pd_2$.[2] The adducts from 1-alkynes have the sulfenyl group attached to C-2. 1-Alkynes act as nucleophiles toward conjugated ketones to form 4-alkyn-1-ones.[3]



The adducts of 1-alkynes and Bu_3SnH are (*E*)-1-tributylstannylalkenes, easily employed for Stille coupling or converted by iodine into the alkenyl iodides.[4]

Substitution. Cinnamylation of polyfluorobenzenes is a bimolecular dehydrochlorination catalyzed by $(dba)_3Pd_2$ with pivalic acid and Cs_2CO_3 additives.[5] The conversion of ArX to *N*-arylureas on reaction with NaOCN and R_2NH is facilitated by phenol because of its role in delivering the carbamate intermediates for the coupling.[6]

An NH_2 group of allylic amines is directly replaced (S_N2 reaction) by the Ar group of $ArB(OH)_2$.[7] Also shown is the S_N2 reaction between propargylic acetates and allylpinacolatoboron when *rac*-BINAP is present.[8] A ligand change to Ph_3P favors the formation of 1,4,5-alkatrienes (from attack of the allylborate at the chain terminus). Allylic sulfonimides undergo displacement on exposure to RZnX in the presence of $(dba)_3Pd_2$.[9]

Methyl 2-dibenzylaminoalkanoates can be arylated at the unactivated carbon chain terminus by ArBr, with Cy_2NLi, $(dba)_3Pd_2$ and DavePhos present in toluene.[10]

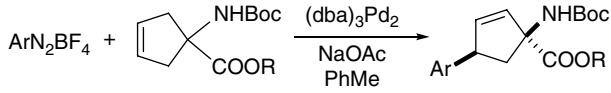
A method for arylation of alcohols (including tertiary members) performed by $(dba)_3Pd_2$ is probably a demonstration and is of limited practicality, considering the rather elaborate diphosphine ligand used.[11] Biaryl synthesis by Suzuki coupling involving a prior activation of phenols by nonaflylation is quite a different matter.[12]

N-C Coupling. Pd-catalyzed arylation of amines can now be done with a great variety of reaction conditions, particularly the selection of hindered phosphine ligands. Such a reaction is extended to amidines,[13] sulfinamides,[14] sulfoximines,[15] and sulfondiimines.[16] For 2-aminobenzimidazole it is noted that the Pd-catalyzed extranuclear *N*-arylation is shifted to arylation at position 1 by using CuI as catalyst.[17]

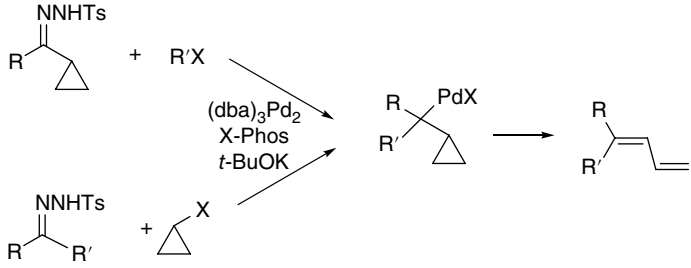
Other coupling reactions. Useful processes are the replacement of the silyl group of $Me_3SiCH{=}CHCF_3$ to gain access to various β-trifluoromethylstyrenes,[18] preparation of arylphosphones from R_2POH and ArI,[19] and the deallylation of allyl aryl sulfones for subsequent coupling to obtain unsymmetrical diaryl sulfones.[20]

As for Stille coupling involving (*Z*)-alkenyl halides, the ligand plays an important role on determining the configuration of double bond.[21] Using *o*-Tol_3P formation of the (*Z*)-alkenes is favored. By Negishi coupling it is quite easy to synthesize tryptophan derivatives, reaction components are *N*-protected 3-bromoindoles and chiral alanyl-3-zinc iodides.[22]

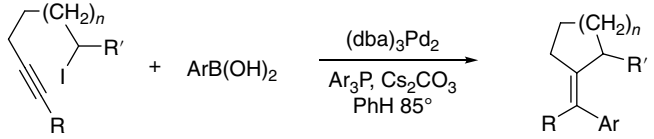
By a Heck reaction to prepare *N*-cinnamylcarboxamides from the *N*-allyl congeners is quite strightforward,[23] the diastereoselectivity exhibited in the attachment of an aryl group to 1-(*N*-Boc-amino)-3-cyclopentenecarboxylates is perhaps less than expected.[24]

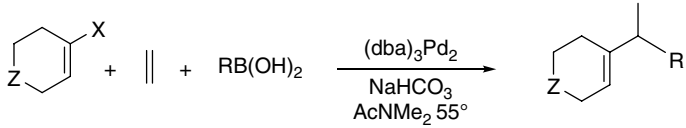


Two complementary routes to 1,1-disubstituted 1,3-butadienes mechanistically akin to the Heck reaction involves reaction of tosylhydrazones.[25] *o*-(3-Butenyl)phenol acts as a precursor of 2-substituted chromans based on the Heck reaction.[26]



Various aryl bromides are converted into $ArCF{=}CF_2$ on coupling with the stable and crystalline lithium trimethoxy(trifluorovinyl)borate.[27] β,β-Cycloalkylidenestyrenes have been obtained from Suzuki coupling of $ArB(OH)_2$ with alkynes containing a distant iodine substituent.[28] By ethylene relay organoboronic acids and alkenyl halides can be stitched together.[29]

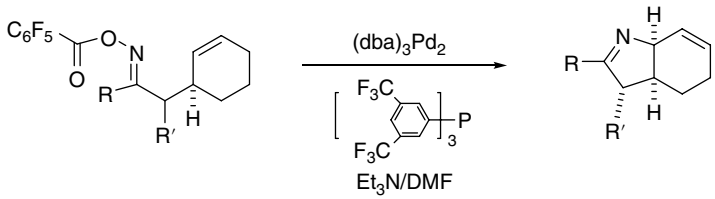




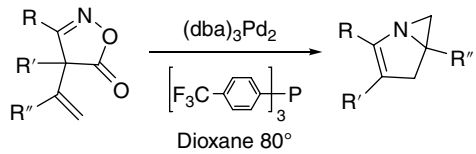
4-Substituted 1-arylcyclohexenes are obtained from Diels-Alder reaction of a 2-boryl-1,3-butadiene and in situ Suzuki coupling.[30]

Alkenylsulfonium salts are reactive toward coupling with organoboron compounds. Accordingly, a method for the synthesis of 3,3,3-trifluoro-1-propenylarenes employing ($CF_3CH{=}CHSPh_2$)OTf takes advantage of the selective activation of an alkenyl C-S bond over the aryl C-S bond.[31] A number of aliphatic boronates are accessible by Suzuki coupling of (bispinacolato)diboron.[32,33]

Iminoxy esters capable of having the C=N double bond shifted out are subject to ionization in the presence of Pd(0) species, and the interaction with a well-situated C=C bond can lead to cyclic products.[34]

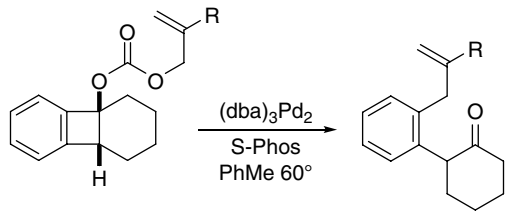


An isoxazolin-5-one ring is also susceptible to open and decarboxylate, the 4-allyl derivatives of such heterocycle are convertible to 1-azabicyclo[3.1.0]hex-2-enes.[35]



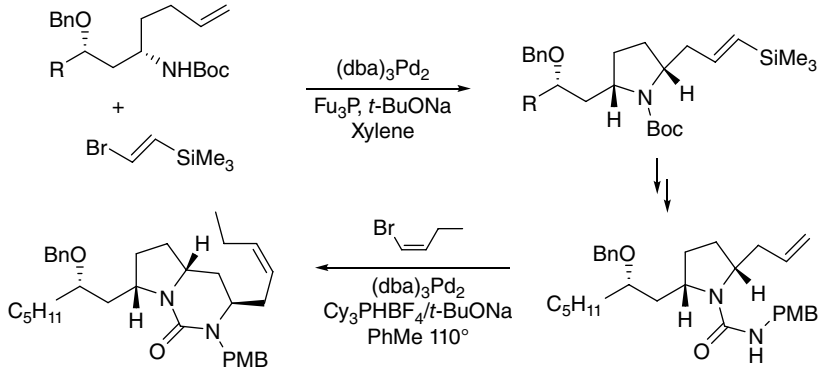
Allyl esters of α-keto acids are transformed into unsaturated ketones through ionization, decarboxylation, and recombination.[36] A more intricate reaction sequence is

pursued by certain allyl benzocyclubutenyl carbonates in which one of the oxygen atoms is linked to a benzylic position. There is a rapid fragmentation of the four-membered ring.[37]



Aryl cyanates in which an *o*-position carries an alkenyl chain undergo cycloisomerization, i.e., on severance fragments of the cyanato unit are redistributed while closing the 2-cyanomethyl oxacycles.[38]

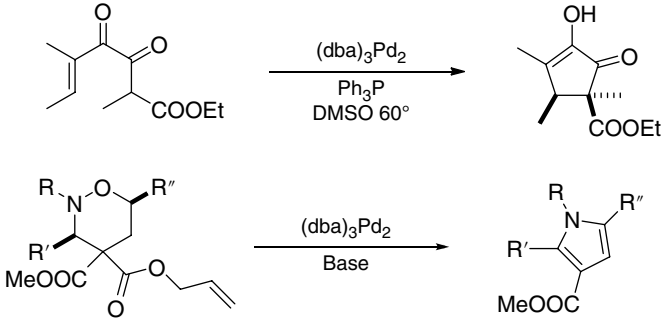
Two intermolecular coupling reactions figure prominently in a synthesis of merobatzelladine-B.[39] They involve a nitrogen atom in each ring formation.



The α-carbon of cyclic nitrones can be arylated.[40]

Cyclization. Allylation in tandem with cycloisomerization of 4-alkynones builds up furan derivatives with an unsaturated carbon chain at an α-position.[41] The indole synthesis from 1,2-dihaloarenes, amines and carbonyl compounds obviously proceeds from *N*-arylation and enamine formation either before or after Pd-insertion into the remaining C-X bond.[42]

The Nazarov reaction of 3,4-dioxo-5-alkenoic esters under neutral conditions is performed with $(dba)_3Pd_2$- Ph_3P in DMSO.[43] Oxidation is implicit in the deoxygenative ring contraction of perhydro-1,2-oxazines containing an allyl ester.[44]



Solvent and ligand effects are observed in polyene cyclization catalyzed by dba_3Pd_2.[45]

Carbonylation. Synthesis of benzamides from ArI (but not ArBr and ArCl), amines, and CO is well established, the only novel feature in a report describing the process is the bulky, electron-rich bidentate ligand: *cis*-1,2-bis(di-*t*-butylphosphinomethyl)cyclohexane,[46] the combination of ArI, CO, and NaN_3 to synthesize $ArCON_3$ is more interesting.[47]

Tetrahydroquinolin-4-one-2,3,3-tricarboxylic esters are obtained from *o*-iodoaniline, ethyenetricarboxylic esters and CO.[48]

Group exchange.[49] To employ a relatively expensive catalyst-reagent system of $(dba)_3Pd_2$, *i*-Bu_3Al, BrettPhos, and KX to achieve the conversion of ArOTf to ArX is perhaps of little synthetic value.

[1] Shen, R., Chen, T., Zhao, Y., Qiu, R., Zhou, Y., Yin, S., Wang, X., Goto, M., Han, L.-B. *JACS* **133**, 17037 (2011)
[2] Iwasaki, M., Fujino, D., Wada, T., Kondoh, A., Yorimitsu, H., Oshima, K. *CAJ* **6**, 3190 (2011)
[3] Villarino, L., Garcia-Fandiño, R., Lopez, F., Mascareñas, J.L. *OL* **14**, 2996 (2012)
[4] Darwish, A., Chong, J.M. *T* **68**, 654 (2012)
[5] Yu, Y.-B., Fan, S., Zhang, X. *CEJ* **18**, 14643 (2012)
[6] Vinogradova, E.V., Fors, B.P., Buchwald, S.L. *JACS* **134**, 11132 (2012)
[7] Li, M.-B., Wang, Y., Tian, S.-K. *ACIE* **51**, 2968 (2012)
[8] Ardolino, M.J., Morken, J.P. *JACS* **134**, 8770 (2012)
[9] Tang, X.-L., Wu, Z., Li, M.-B., Gu, Y., Tian, S.-K. *EJOC* 4107 (2012)
[10] Aspin, S., Goutierre, A.S., Larini, P., Jazzar, R., Baudoin, O. *ACIE* **51**, 10808 (2012)
[11] Maligres, P.E., Li, J., Krska, S.W., Schreier, J.D., Raheem, I.T. *ACIE* **51**, 9071 (2012)
[12] Ikawa, T., Saito, K., Akai, S. *SL* 2241 (2012)
[13] McGowan, M.A., McAvoy, C.Z., Buchwald, S.L. *OL* **14**, 3800 (2012)
[14] Sun, X., Tu, X., Dai, C., Zhang, X., Zhang, B., Zeng, Q. *JOC* **77**, 4454 (2012)
[15] Yongpruksa, N., Calkins, N.L., Harmata, M. *CC* **47**, 7665 (2011)
[16] Candy, M., Bohmann, R.A., Bolm, C. *ASC* **354**, 2928 (2012)
[17] Ueda, S., Buchwald, S.L. *ACIE* **51**, 10364 (2012)
[18] Omote, M., Tanaka, M., Ikeda, A., Nomura, S., Tarui, A., Sato, K., Ando, A. *OL* **14**, 2286 (2012)
[19] Bloomfield, A.J., Herzon, S.B. *OL* **14**, 4370 (2012)
[20] Le Duc, G., Bernoud, E., Prestat, G., Cacchi, S., Fabrizi, G., Iazzetti, A., Madec, D., Poli, G. *SL* 2943 (2011)
[21] Lu, G., Voigtritter, K.R., Cai, C., Lipshutz, B.H. *CC* **48**, 8661 (2012)

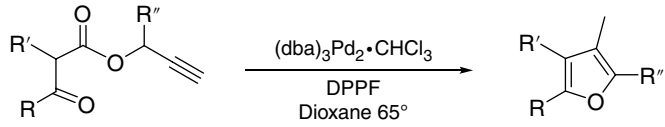
[22] Tanaka, M., Hikawa, H., Yokoyama, Y. *T* **67**, 5897 (2011)
[23] Prediger, P., Barbosa, L.F., Genisson, Y., Correia, C.R.D. *JOC* **76**, 7737 (2011)
[24] Oliveira, C.C., dos Santos, E.A.F., Nunes, J.H.B., Correia, C.R.D. *JOC* **77**, 8182 (2012)
[25] Zhou, L., Ye, F., Zhang, Y., Wang, J. *OL* **14**, 922 (2012)
[26] Ward, A.F., Xu, Y., Wolfe, J.P. *CC* **48**, 609 (2012)
[27] Duric, S., Schmidt, B.M., Ninnemann, N.M., Lentz, D., Tzschucke, C.C. *CEJ* **18**, 437 (2012)
[28] Monks, B.M., Cook, S.P. *JACS* **134**, 15297 (2012)
[29] Saini, V., Sigman, M.S. *JACS* **134**, 11372 (2012)
[30] Wang, L., Welker, M.E. *JOC* **77**, 8280 (2012)
[31] Lin, H., Dong, X., Li, X., Shen, Q., Lu, L. *EJOC* 4675 (2012)
[32] Yi, J., Liu, J.-H., Liang, J., Dai, J.-J., Yang, C.-T., Fu, Y., Liu, L. *ASC* **354**, 1685 (2012)
[33] Joshi-Pangu, A., Ma, X., Diane, M., Iqbal, S., Kribs, R.J., Huang, R., Wang, C.-Y., Biscoe, M.R. *JOC* **77**, 6629 (2012)
[34] Faulkner, A., Bower, J.F. *ACIE* **51**, 1675 (2012)
[35] Okamoto, K., Oda, T., Kohigashi, S., Ohe, K. *ACIE* **50**, 11470 (2011)
[36] Rodriguez, N., Manjolinho, F., Grünberg, M.F., Goossen, L.J. *CEJ* **17**, 13688 (2011)
[37] Rosa, D., Chtchemelinine, A., Orellana, A. *S* 1885 (2012)
[38] Koester, D.C., Kobayashi, M., Werz, D.B., Nakao, Y. *JACS* **134**, 6544 (2012)
[39] Babij, N.R., Wolfe, J.P. *ACIE* **51**, 4128 (2012)
[40] Demory, E., Farran, D., Baptiste, B., Chavant, P.Y., Blandin, V. *JOC* **77**, 7901 (2012)
[41] Saito, A., Enomoto, Y., Hanzawa, Y. *TL* **52**, 4299 (2011)
[42] Knapp, J.M., Zhu, J.S., Tantillo, D.J., Kurth, M.J. *ACIE* **51**, 10588 (2012)
[43] Shimada, N., Stewart, C., Bow, W.F., Jolit, A., Wong, K., Zhou, Z., Tius, M.A. *ACIE* **51**, 5727 (2012)
[44] Humenny, W.J., Kyriacou, P., Sapeta, K., Karadeolian, A., Kerr, M.A. *ACIE* **51**, 11088 (2012)
[45] Lucciola, D., Keay, B.A. *SL* 1618 (2011)
[46] de la Fuente, V., Goddard, C., Claver, C., Castillon, S. *ASC* **354**, 1971 (2012)
[47] Miloserdov, F.M., Grushin, V.V. *ACIE* **51**, 3668(2012)
[48] Okuro, K., Alper, H. *JOC* **77**, 4420 (2012)
[49] Shen, X., Hyde, A.M., Buchwald, S.L. *JACS* **132**, 14076 (2010)

Tris(dibenzylideneacetone)dipalladium - chloroform

Substitution. When allylindium reagents generated in situ react with alkynyl/aryl halides in the presence of $(dba)_3Pd_2{\cdot}CHCl_3$, LiCl in DMF at 100°, 1,4-enynes/allylarenes are produced.[1]

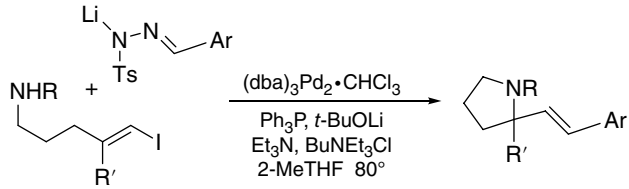
The S_N2 reaction is observed for allyl carbonates, either with an *N,N*-dialkylglycine ester or carboxylic acid enolates as nucleophile.[2,3] In arylation of nitroacetic esters it does not require any phosphine ligands.[4]

Propargyl esters of β-keto carboxylates also undergo skeletal detachment. After decarboxylation two fragements recombine to afford furans.[5]

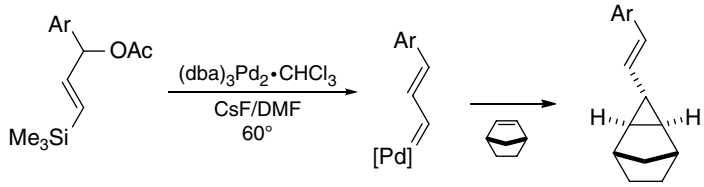


Coupling. Suzuki coupling is applicable to the preparation of 2,2,2-trifluoroethylarenes and 1,1,1-trifluoro-3-alkenes from CF_3CH_2I.[6] A synthesis of 2-(β-styryl)pyrrolidines

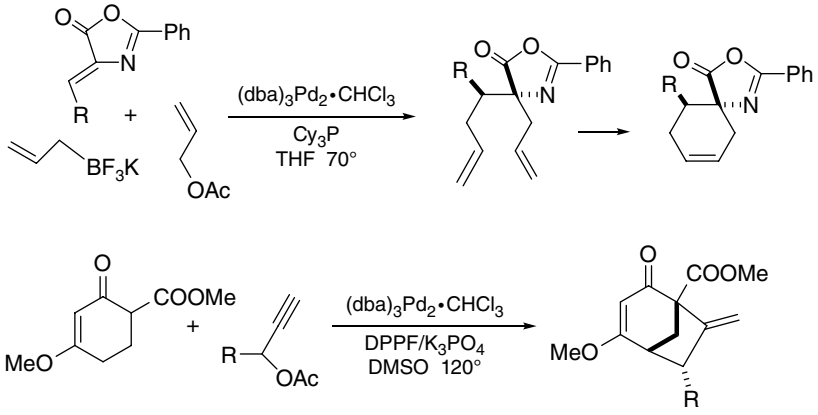
based on coupling of 5-iodo-4-pentenylamines and lithiated araldehyde hydrazones has been realized.[7]



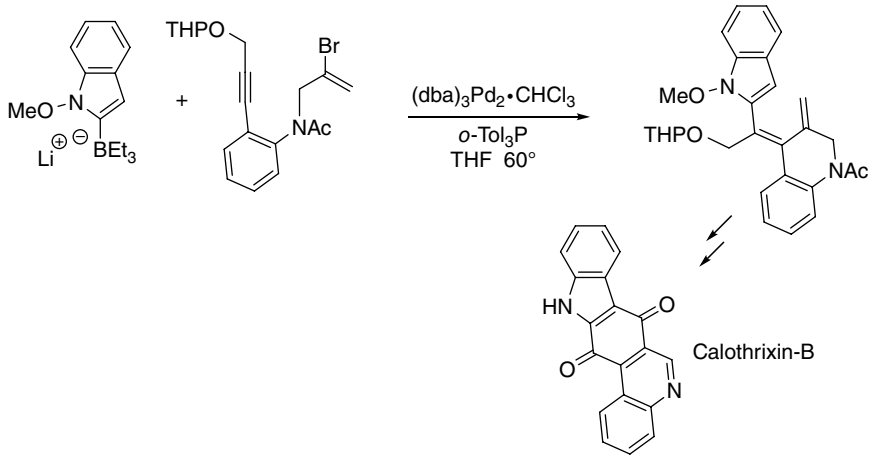
Cinnamylcarbene- palladium complexes are implicated as intermediates in the reaction of 3-acetoxy-3-aryl-1-trimethylsilyl-1-propenes with norbornene.[8] The isomeric 3-aryl-3-trimethylsilylallyl acetates are not useful for the cycloaddition.



An adroit attachment of two allyl groups to a conjugated double bond is demonstrated.[9] Bridged annulations of 2-cyclohexenone-6-carboxylic esters on reaction with propargyl acetates occurs in the presence of the Pd complex and DPPF.[10]

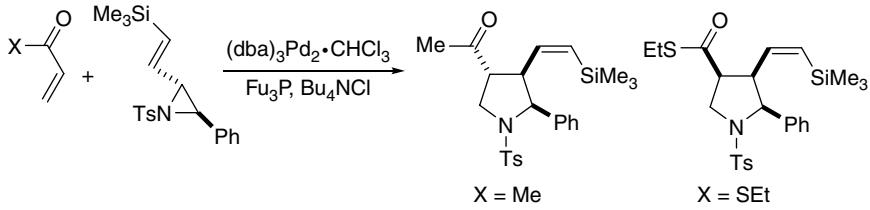


An indol-2-ylborate is used in the construction of a tetracyclic precursor of calothrixin-B.[11]



2-Alkenylaziridines are converted into 2-oxazolidinones by incorporating CO_2, via ring opening to give π-allylpalladium intermediates.[12]

Cycloaddition. Cleavage of 2-alkenylaziridines generates 1,3-dipoles for [3+2] cycloaddition. An interesting diastereoselection due to change of the dipolarophile from MVK to a thioacrylate has been observed.[13]

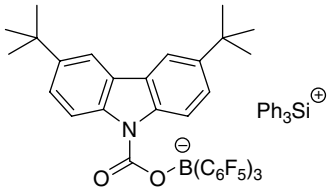


[1] Lee, K., Kim, H., Lee, P.H. *CAJ* **6**, 2147 (2011)
[2] Soheili, A., Tambar, U.K. *JACS* **133**, 12956 (2011)
[3] Braun, M., Meletis, P., Visse, R. *ASC* **353**, 3380 (2011)
[4] Metz, A.E., Berritt, S., Dreher, S.D., Kozlowski, M.C. *OL* **14**, 760 (2012)
[5] Yoshida, M., Ohno, S., Shishido, K. *CEJ* **18**, 1604 (2012)
[6] Zhao, Y., Hu, J. *ACIE* **51**, 1033 (2012)
[7] Khanna, A., Maung, C., Johnson, K.R., Luong, T.T., Van Vranken, D.L. *OL* **14**, 3233 (2012)
[8] Horino, Y., Homura, N., Inoue, K., Yoshikawa, S. *ASC* **354**, 828 (2012)
[9] Genady, A.R., Nakamura, H. *OBC* **9**, 7180 (2011)
[10] Yoshida, M., Sugimura, C., Shishido, K. *OL* **13**, 3482 (2011)
[11] Abe, T., Ikeda, T., Choshi, T., Hibino, S., Hatae, N., Toyata, E., Yanada, R., Ishikura, M. *EJOC* 5018 (2012)
[12] Fontana, F., Chen, C.C., Aggarwal, V.K. *OL* **13**, 3454 (2011)

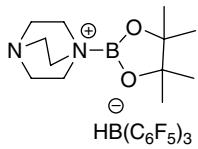
[13] Lowe, M.A., Ostovar, M., Ferrini, S., Chen, C.C., Lawrence, P.G., Fontana, F., Calabrese, A.A., Aggarwal, V.K. *ACIE* **50**, 6370 (2011)

Tris(pentafluorophenyl)borane

Generation. Photolysis of the salt **1** results in a controlled release of $(C_6F_5)_3B$.[1]



(**1**)



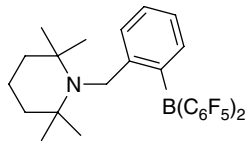
(**2**)

Reduction. Hydrogenation of polyaromatic hydrocarbons with $(C_6F_5)_3B$ and $C_6F_5PPh_2$ has been examined. Anthracene is converted to 9,10-dihydroanthracene.[2]

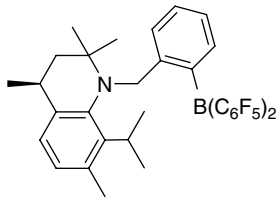
A catalyst for fast reduction of imines with boranes is the salt **2**, prepared by mixing DABCO and $(C_6F_5)_3B$ and then treatment with pinacolborane.[3] The action of this reducing system on acridine gives the dihydro derivative.

The catalyst with a mesityl group attached to boron and two tetrafluorophenyl rings shows very high selectivity for hydrogenation of quinolines. The heterocyclic portion is saturated and the double bond of a 5-styryl group is preserved (but not the 6-styryl substituent).[4]

Ansa-catalysts are arylbis(pentafluorophenyl)boranes possessing an *o*-aminomethyl unit. A member of the first generation, depicted by formula **3**, has been improved upon (see **4**) by reducing the basicity of the amino group and providing steric crowding in certain quarter of the molecules to direct the placement of nonbulky imines.[5]



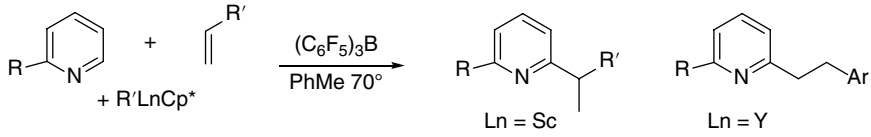
(**3**)



(**4**)

The earlier developed frustrated Lewis pair $(C_6F_5)_2BCH_2CH_2P(Mes)_2$ used in semihydrogenation of conjugated alkynones to alkenones is replaceable by $(C_6F_5)_3B$ – t-Bu_3P.[6] Alternatively, the salt of protonated DABCO and hydridotris(pentafluorophenyl)boron is active in catalyzing reduction of electron-poor alkenes such as the conjugated double bond of allenic esters.[7]

Alkylation. Using 1-alkenes to alkylate pyridines with an open C-2 position, both a lanthanide complex and $(C_6F_5)_3B$ seem to be necessary, and there are some variation of regiochemistry in the addition.[8]



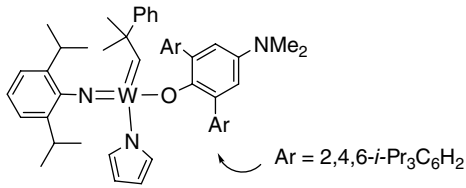
O-Phosphorylation. In reaction of alcohols with $(PhO)_2POCl$, an effective catalyst is $(C_6F_5)_3B$.[9]

[1] Khalimon, A.Y., Piers, W.E., Blackwell, J.M., Michalak, D.J., Parvez, M. *JACS* **134**, 9601 (2012)
[2] Segawa, Y., Stephan, D.W. *CC* **48**, 11963 (2012)
[3] Eisenberger, P., Bailey, A.M., Crudden, C.M. *JACS* **134**, 17384 (2012)
[4] Erös, G., Nagy, K., Mehdi, H., Papai, I., Nagy, P., Kiraly, P., Tarkanyi, G., Soos, T. *CEJ* **18**, 574 (2012)
[5] Sumerin, V., Chernichenko, K., Nieger, M., Leskelä, M., Rieger, B., Repo, T. *ASC* **353**, 2093 (2011)
[6] Xu, B.-H., Kehr, G., Fröhlich, R., Wibbeling, B., Schirmer, B., Grimme, S., Erker, G. *ACIE* **50**, 7183 (2011)
[7] Ines, B., Palomas, D., Holle, S., Steinberg, S., Nicasio, J.A., Alcarazo, M. *ACIE* **51**, 12367 (2012)
[8] Guan, B.-T., Hou, Z. *JACS* **133**, 18086 (2011)
[9] Xue, W., Zhang, L. *ChJC* **30**, 1797 (2012)

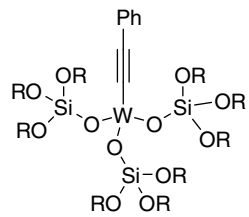
Tungsten carbene and carbyne complexes

Catalyst library. Siloxy-based tungsten-centered alkyne metathesis catalysts become air-stable by adding 1,10-phenanthroline or 2,2′-bipyridyl. A catalyst library is built to provide an application profile.[1]

Catalyst **1**on calcined alumina is a highly selective for (*Z*)-homocoupling metathesis of 1-alkenes.[2] The effectiveness of **2** to bring about ring closure is evident.[3]



(**1**)



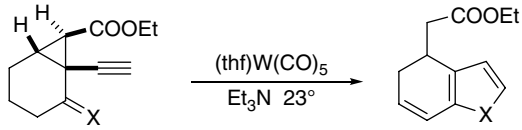
(**2**) R = *t*-Bu

[1] Heppekausen, J., Stade, R., Kondoh, A., Seidel, G., Goddard, R., Fürstner, A. *CEJ* **18**, 10281 (2012)
[2] Yuan, J., Townsend, E.M., Schrock, R.R., Goldman, A.S., Müller, P., Takase, M.K. *ASC* **353**, 1985 (2011)
[3] Lysenko, S., Volbeda, J., Jones, P.G., Tamm, M. *ACIE* **51**, 6757 (2012)

Tungsten hexacarbonyl

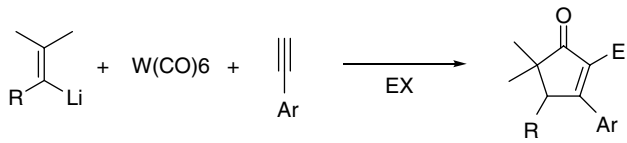
N.N′-Diarylureas. Carbonylative transformation of anilines is done with $W(CO)_6$, I_2, and DMAP under CO.[1]

Cyclomutation. The solvent-modified (thf)$W(CO)_5$ has found a new use in catalyzing the reorganization of 1-ethynylbicyclo[4.1.0]heptan-2-ones and the derived oxime ethers, that is to produce 4,5-dihydrobenzo[*b*]furans and indoles.[2]



X = O, NOR

Cyclopentenones. A one-step multicomponent synthesis of 2-cyclopentenones starts from generation of Fischer carbenes and alkenyllithiums which combine. It is terminated by reaction with an electrophile.[3]



EX = NBX, $CH_2{=}CHCH_2I$,...

[1] Zhang, L., Darko, A.K., Johns, J.I., McElwee-White, L. *EJOC* 6261 (2011)
[2] Fisher, E.L., Wilkerson-Hill, S.M., Sarpong, R. *JACS* **134**, 9946 (2012)
[3] Barluenga, J., Alvarez-Fernandez, A., Suarez-Sobrino, A.L., Tomas, M. *ACIE* **51**, 183 (2012)

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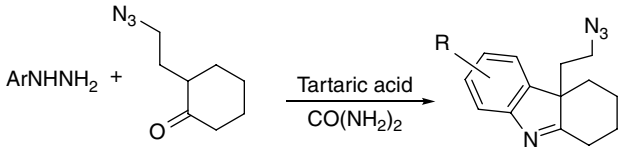
Uranyl nitrate

Nitriles.[1] Primary amides are dehydrated on treatment with $UO_2(NO_3)_2 \cdot 6H_2O$ and $CF_3CON(SiMe_3)Me$ in DME.

[1] Enthaler, S. *CEJ* **17**, 9316 (2011)

Urea-tartaric acid

Fischer indole synthesis.[1] The eutectic mixture induces indole formation from $ArNHNH_2$ and carbonyl compounds.



[1] Gore, S., Baskaran, S., König, B. *OL* **14**, 4568 (2012)

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V

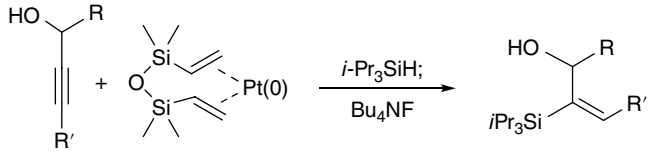
Vanadium(IV) chloride

Aryllithium coupling.[1] Biaryls are readily formed from ArLi on exposure of VCl_4 at room temperature.

[1] Lu, F. *TL* **53**, 2444 (2012)

(Vinyldimethylsiloxane)platinum(0). Karlstedt catalyst

Hydrosilylation.[1] Propargyl alcohols undergo regioselective *cis*-hydrosilylation with a hydrosilane to afford allylic alcohols (after treatment with Bu_4NF) in which the silyl group is vicinal to the hydroxyl.



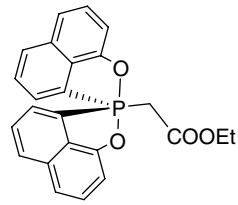
[1] Kawasaki, Y., Ishikawa, Y., Igawa, K., Tomooka, K. *JACS* **133**, 20712 (2011)

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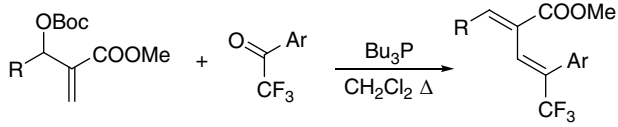
Wittig reagents

(Z)-selective alkenylation. The pentavekent organophosphorus reagent (**1**) is useful for synthesizing (*Z*)-2-alkenoic esters.[1]

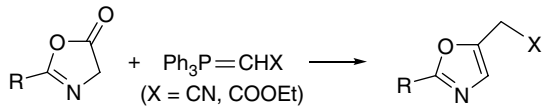


(**1**)

o-Substituted benzaldehydes also give *cis*-styrenes on reaction with stabilized phosphoranes.[2] Conjugated phosphonium ylides that carry an electron-deficient group at the α-position are accessed from esters of Baylis-Hillman adducts.[3]



5-Substituted oxazoles. Upon cyclization of α-amino acids using a carbodiimide the nascent oxazolinones can engage in reaction with stabilized Wittig reagents.[4]



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Product separation.[5] A solution to the often tedious isolation of Wittig reaction products is through treatment of the reaction mixture with oxalyl chloride. Phosphine oxides are converted into the ionic chlorophosphonium chlorides and such solids can be removed by filtration (then reduced back to the phosphines).

[1] Kojima, S., Arimura, J., Kajiyama, K. *CL* **39**, 1138 (2010)
[2] Byrne, P.A., Higham, L.J., McGovern, P., Gilheany, D.G. *TL* **53**, 6701 (2012)
[3] Wang, T., Shen, L.-T., Ye, S. *S* 3359 (2011)
[4] Huang, W., Dong, G., Mijiti, Z. *T* **68**, 977 (2012)
[5] Byrne, P.A., Rajendran, K.V., Muldoon, J., Gilheany, D.G. *OBC* **10**, 3531 (2012)

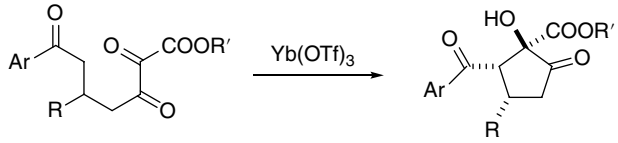
Y

Ytterbium(III) triflate

Reduction. By catalysis of $Yb(OTf)_3$ ketones and aliphatic aldehydes are reduced to alcohols by isopropanol.[1]

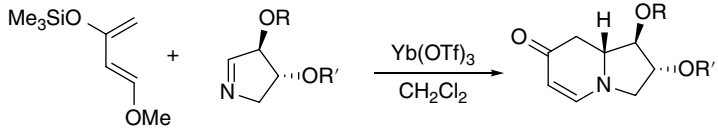
Alkylation. *N*-Tosyl derivatives of some amines (e.g., benzylamines) behave as alkylating agents for 1,3-dicarbonyl compounds in the presence of $Yb(OTf)_3$.[2]

Aldol reaction and Michael reaction. The intramolecular aldol reaction shown below[3] pursues a different steric course from that conducted in the presence of a sulfonic acid catalyst.



Addition of 2-alkylpyridines to alkylidenmalonitriles is achieved by heating the mixtures with $Yb(OTf)_3$ in dioxane.[4]

Ring formation. The catalytic capability of $Yb(OTf)_3$ for uniting aziridines with imines,[5] and activated dienes with imines,[6,7] is excellent.

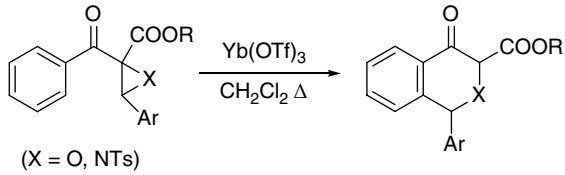


Heating a mixture of $ArNH_2$, RCHO and $(EtO)_2CHCH_2COOEt$ with $Yb(OTf)_3$ in dioxane leads to the formation of *N*-aryl-1,4-dihydropyridine-3,5-dicarboxylic esters.[8]

Skraup synthesis of quinolines from 2-acylanilines and ketones proceeds at room temperature on catalysis of $Yb(OTf)_3$.[9] 2,4-Disubstituted quinolines are obtained from the $Yb(OTf)_3$-catalyzed reaction of $ArNH_2$, RCHO, and 1-alkynes in an ionic liquid.[10]

2-Aryl-3-aroyloxiranes and –aziridines undergo ring cleavage and ring formation sequence in a reaction catalyzed by Yb(OTf).[11]

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(X = O, NTs)

[1] Mollica, A., Genovese, S., Pinnen, F., Stefanucci, A., Curini, M., Epifano, F. *TL* **53**, 890 (2012)
[2] Liu, J., Wang, L., Zheng, X., Wang, A., Zhu, M., Yu, J., Shen, Q. *TL* **53**, 1843 (2012)
[3] Truong, P., Shanahan, C.S., Doyle, M.P. *OL* **14**, 3608 (2012)
[4] Qian, B., Shi, D., Yang, L., Huang, H. *ASC* **354**, 2146 (2012)
[5] Wu, X., Zhang, J. *S* 2147 (2012)
[6] Shao, J., Yang, J.-S. *JOC* **77**, 7891 (2012)
[7] Boomhoff, M., Schneider, C. *CEJ* **18**, 4185 (2012)
[8] Sueki, S., Takei, R., Abe, J., Shimizu, I. *TL* **52**, 4473 (2011)
[9] Genovese, S., Epifano, F., Marcotullio, M.C., Pellucchini, C., Curini, M. *TL* **52**, 3474 (2011)
[10] Kumar, A., Rao, V.K. *SL* 2157 (2011)
[11] Wei, L., Zhang, J. *CC* **48**, 2636 (2012)

Z

Zinc

Reduction. 2-Alkynylindoles are reduced by zinc in methanolic HCl to afford (*Z*)-2-alkenyl products.[1] Protecting groups such as *O*-TBS, *N*-SEM are untouched.

Dehalogenation. 1,2-Dihalo-2-alkenes undergo elimination to give allenes. Either Zn or In can be used.[2]

Addition. 1-Nitro-2-alkanols are prepared from reaction of bromonitromethane with aldehydes, using zinc metal and catalytic quantitites of indium and ultrasonication.[3] α-Selective crotylation of carbonyl compounds employs zinc in 1,3-dimethylpropyleneurea.[4] Prenylation of imines is accomplished with a similar reagent system.[5]

Coupling. Benzaldiamines afford 1,2-diaryl-1,2-ethanediamines by treatment with Zn – Me_3SiCl in CH_2Cl_2 at room temperature.[6]

[1] Iwasaki, K., Kanno, R., Morimoto, T., Yamashita, T., Yokoshima, S., Fukuyama, T. *ACIE* **51**, 9160 (2012)
[2] Lin, M.-H., Tsai, W.-S., Lin, L.-Z., Hung, S.-F., Chuang, T.-H., Su, Y.-J. *JOC* **76**, 8518 (2011)
[3] Soengas, R.G., Silva, A.M.S. *SL* 873 (2012)
[4] Zhao, L.-M., Wan, L.-J., Jin, H.-S., Zhang, S.-Q. *EJOC* 2579 (2012)
[5] Zhao, L.-M., Zhang, S.-Q., Jin, H.-S., Wan, L.-J., Dou, F. *OL* **14**, 886 (2012)
[6] Hatano, B., Tachikawa, T., Mori, T., Nagahashi, K., Kajima, T. *TL* **52**, 3467 (2011)

Zinc acetate

Cyclization. α–Aryl-β-aminoacrylonitriles are converted into indole-3-nitriles[1] on consecutive treatment with NBS and zinc acetate.

[1] Yan, Q., Luo, J., Zhang-Negrerie, D., Li, H., Qi, X., Zhao, K. *JOC* **76**, 8690 (2011)

Zinc acetylacetonate

Nitriles.[1] Oximation and subsequent dehydration of aldehydes to provides nitriles are performed in the presence of $Zn(acac)_2$ in toluene at 100°.

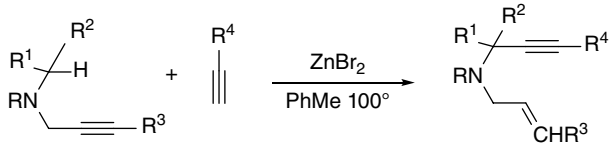
[1] Enthaler, S., Weidauer, M., Schröder, F. *TL* **53**, 882 (2012)

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Zinc bromide

Coupling. Alkynyltin compounds are obtained on transfer of the organostannyl group from a methoxide (e.g., Bu_3SnOMe) to 1-alkynes at room temperature, employing $ZnBr_2$ as catalyst.[1] Formation of $Zn(OMe)_2$ through Sn/Zn transmetallation is the key.

A synthetic approach to 1,6-enynes is realized from redox cross-dehydrogenative coupling of propargylamines and 1-alkynes, mediated by $ZnBr_2$.[2]

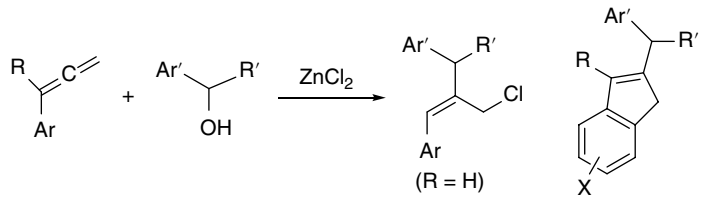


[1] Kiyokawa, K., Tachikake, N., Yasuda, M., Baba, A. *ACIE* **50**, 10393 (2011)
[2] Sugiishi, T., Nakamura, H. *JACS* **134**, 2504 (2012)

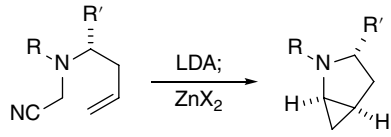
Zinc chloride

Reduction.[1] The reduction of 2,2-difluoroalkanoic esters and amides by $LiAlH_4$ is assisted by $ZnCl_2$, which involves hydrodefluorination.

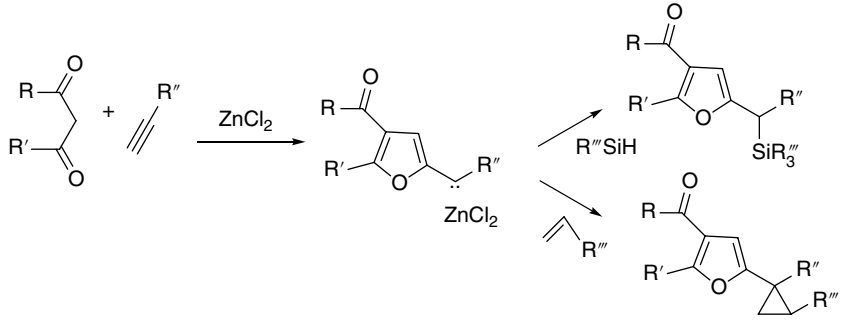
Addition.[2] In the presence of $ZnCl_2$, 3-arylallenes and benzylic alcohols combine to afford allylic chlorides or indenes.



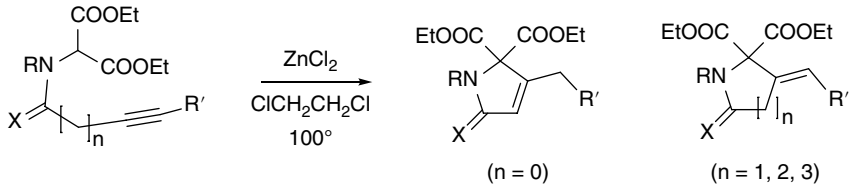
Cyclization and cycloaddition. 2,3-Cyclopropanopyrrolidines are made from *N*-homoallyl *N*-cyanomethylamines via deprotonation and $ZnCl_2$-induced cycloaddition.[3]



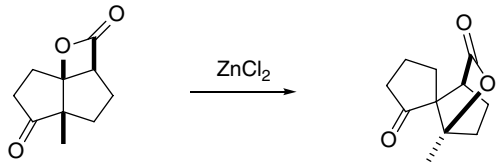
Formation of 4-acetyl-2-furylalkylidene-coordinated zinc species is facile when 1,3-dicarbonyl compounds and 2-alkynals are exposed to $ZnCl_2$. The zinc-carbenoids can be trapped with alkenes and hydrosilanes.[4]



Azacycle synthesis from *N*-alkynyl-aminomalonates by the action of $ZnCl_2$ is observed.[5] It is a type of Conia-ene reaction.



Rearrangement. Ring strain of β-lactone drives a dyotropic rearrangement which is induced by $ZnCl_2$.[6]



[1] Cheng, J., Wu, J., Cao, S. *TL* **52**, 3481 (2011)
[2] Meng, B., Ma, S. *OL* **14**, 2674 (2012)
[3] Ouizem, S., Chemla, F., Ferreira, F., Perez-Luna, A. *SL* 1374 (2012)
[4] Vicente, R., Gonzalez, J., Riesgo, L., Gonzalez, J., Lopez, L.A. *ACIE* **51**, 8063 (2012)
[5] Hess, W., Burton, J.W. *ASC* **353**, 2966 (2011)
[6] Davis, R.L., Leverett, C.A., Romo, D., Tantillo, D.J. *JOC* **76**, 7167 (2011)

Zinc difluoromethanesulfonate

Difluoromethylation.[1] Chemoselective and regioselective introduction of a CHF_2 group to heterocycles in gram quantitites is conveniently performed with $Zn(SO_2CF_2H)_2$ in an open flask in water at room temperature.

[1] Fujiwara, Y., Dixon, J.A., Rodriguez, R.A., Baxter, R.D., Dixon, D.D., Collins, M.R., Blackmond, D.G., Baran, P.S. *JACS* **134**, 1494 (2012)

Zinc iodide

Arylmethanephosphonic esters.[1] Benzyl alcohols are converted into $ArCH_2PO(OR)_2$ on reaction with $P(OR)_3$ and ZnI_2.

Hydroamination.[2] On heating certain alkenylamines with ZnI_2 in dioxane delivers azacycles, including pyrrolidines.

[1] Richardson, R.M., Barney, R.J., Wiemer, D.F. *TL* **53**, 6682 (2012)
[2] Liu, G.-Q., Li, W., Wang, Y.-M., Ding, Z.-Y., Li, Y.-M. *TL* **53**, 4393 (2012)

Zinc oxide

Enamination. Nanoparticles of ZnO are said to promote enamination of 1,3-dicarbonyl compounds by anilines at 80° without solvent.[1]

[1] Indulkar, U.U., Kale, S.R., Gawande, M.B., Jayaram, R.V. *TL* **53**, 3857 (2012)

Zinc perchlorate

Conjugate addition. $Zn(ClO_4)_2$ combined with thiourea forms a mild catalyst for the addition of indole to nitroalkenes.[1]

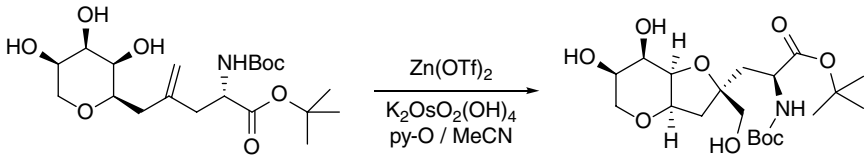
[1] Wan, N., Hui, Y., Xie, Z., Wang, J. *ChJC* **30**, 311 (2012)

Zinc triflate

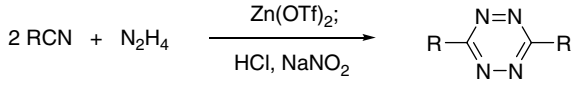
Transformation of amides. Action of $Zn(OTf)_2$ and $CF_3CON(SiMe_3)Me$ on $ArCONH_2$ achieves dehydration to furnish ArCN.[1] *N*-Acylethanolamines are converted into esters by heating with $Zn(OTf)_2$, $CO(OEt)_2$ and an alcohol.[2]

Propargyl alcohols. Addition of 1-alkynes (including conjugated polyynes) to aldehydes are catalyzed by $Zn(OTf)_2$,in the presence of *N*-methylephedrine.[3]

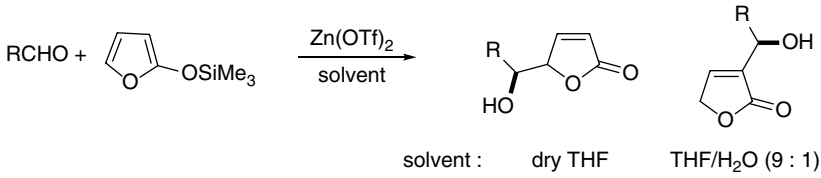
Cyclization. Upon dihydroxylation of an alkene, $Zn(OTf)_2$ provokes cyclization that involves a proximal hydroxyl group.[4]



Tetrazines.[5] Hydrazine and two molecules of nitriles are combined under the influence of $Zn(OTf)_2$ [or $Ni(OTf)_2$]. Two different nitriles can be employed.



Aldol reaction. Catalyzed by $Zn(OTf)_2$, regioselectivity for the reaction of 2-trimethylsiloxyfuran with aldehydes is influenced by water.[6]



[1] Enthaler, S., Inoue, S. *CAJ* **7**, 169 (2012)
[2] Kita, Y., Nishii, Y., Higuchi, T., Mashima, K. *ACIE* **51**, 5723 (2012)
[3] Graham, E.R., Tykwinski, R.R. *JOC* **76**, 6574 (2011)
[4] Donohoe, T.J., Winship, P.C.M., Tatton, M.R., Szeto, P. *ACIE* **50**, 7604 (2011)
[5] Yang, J., Karver, M.R., Li, W., Sahu, S., Devaraj, N.K. *ACIE* **51**, 5222 (2012)
[6] Woyciechowska, M., Forcher, G., Buda, S., Mlynarski, J. *CC* **48**, 11029 (2012)

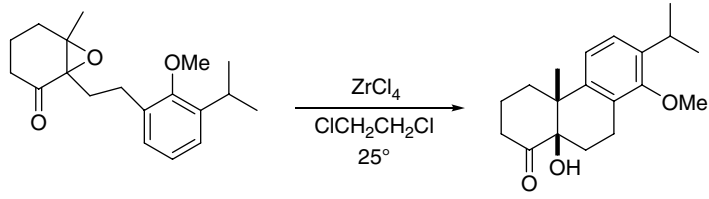
Zinc trifluoroacetate cluster

Transesterification. The tetranuclear zinc cluster $Zn_4(OCOCF_3)_6O$ is useful for converting α-amino methyl esters into other esters.[1]

[1] Maegawa, Y., Agura, K., Hayashi, Y., Oshima, T., Mashima, K. *SL* **137** (2012)

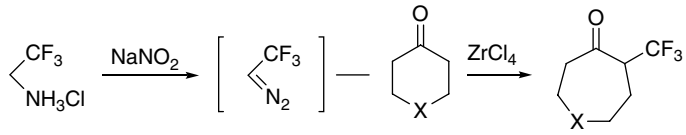
Zirconium (IV) chloride

Friedel-Crafts cyclization.[1] Intramolecular attack on an epoxy ketone by an aryl group leads to formation of a six-membered ring is accomplished by exposure to $ZrCl_4$ which appears to be superior to other Lewis acids, because the competing isomerization (2-acylcyclopentanone formation) is less favored.



Amidation. Secondary and tertiary amides are prepared from carboxylic acids and amines with $ZrCl_4$ as catalyst.[2,3] The amines can be replaced by the salts $[R_2NH_2^+ (R'_2NHCOO)^-]$.[4]

1,1,1-Trifluoro-3-alkanones.[5] Diazotized 2,2,2-trifluoroethylamine reacts with RCHO in the presence of $ZrCl_4$, and CF_3CH_2COR results. With cycloalkanones, ring expansion is observed.



Aza-Henry reaction. Using $ZrCl_4$ as catalyst nitroalkanes add to $CF_3CH{=}NR$ in the neat state. The *anti*-isomer generally predominates.[6]

[1] Goncalves, S., Nicolas, M., Maillos, P., Baati, R. *T* **67**, 8373 (2011)
[2] Lundberg, H., Tinnis, F., Adolfsson, H. *CEJ* **18**, 3822 (2012)
[3] Allen, C.L., Chhatwal, A.R., Williams, J.M.J. *CC* **48**, 666 (2012)
[4] Tinnis, F., Lundberg, H., Adolfsson, H. *ASC* **354**, 2531 (2012)
[5] Morandi, B., Carreira, E.M. *ACIE* **50**, 9085 (2011)
[6] Fioravanti, S., Pellacani, L., Vergari, M.C *OBC* **10**, 8207 (2012)

Zirconium(IV) dimethylamide

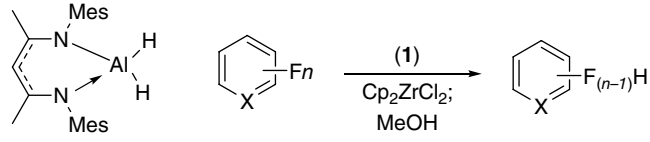
Hydroamination. Hydroamination of alkynes is achieved in the presence of $(Me_2N)_4Zr$ and $ArSO_2NH\ CMe_3$.[1]

[1] Born, K., Doye, S. *EJOC* 764 (2012)

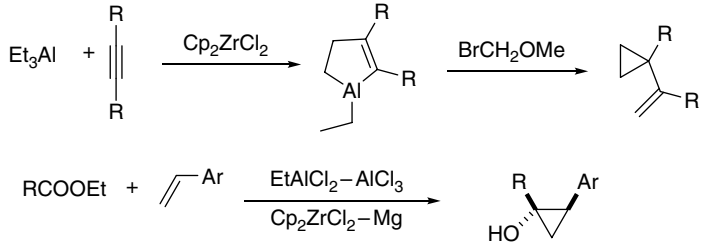
Zirconocene dichloride

Transamidation.[1] Conversion of primary amides to secondary amides is achieved on their treatment with amines in the presence of Cp_2ZrCl_2.

Hydrodefluorination.[2] Polyfluoroarenes undergo partial defluorination in a Zr-catalyzed reduction with amine-complexed aluminum hydride **1**.



Cyclopropanes. The synthetic utility of a previously established synthesis of aluminacyclopentenes is expanded by treatment with simple alkylating agents to provide cyclopropanes.[3] Cyclopropanols are also obtained from esters, aluminum chlorides, and alkenes.[4]



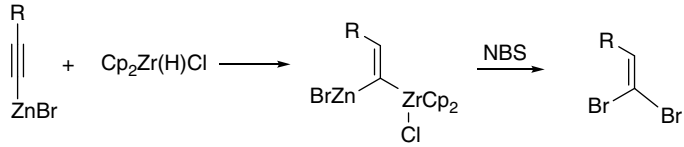
[1] Atkinson, B.N., Chhatwal, A.R., Lomax, H.V., Walton, J.W., Williams, J.M.J. *CC* **48**, 11626 (2012)
[2] Yow, S., Gates, S.J., White, A.J.P., Crimmin, M.R. *ACIE* **51**, 12559 (2012)
[3] D'yakonov, V.A., Tuktarova, R.A., Khalilov, L.M., Dzhemilev, U.M. *TL* **52**, 4602 (2011)
[4] Khafizova, L.O., Gubaidullin, R.R., Dzhemilev, U.M. *T* **67**, 9142 (2011)

Zirconocene hydrochloride

Reduction. Amides are reduced to aldehydes by $Cp_2Zr(H)Cl$, and *N*-Boc lactams may be converted into cyclic enamides.[1] The carbonyl group of tertiary amides is deoxygenated and replaced by the allyl/H pair on sequential reaction with $Cp_2Zr(H)Cl$ and an allylstannane in the presence of CF_3COOH.[2]

Diene synthesis. A simple method for deoxygenative chain lengthening of aldehydes by three carbon atoms involves reaction with propargyltrimethylsilane. The catalytic system consists of $Cp_2Zr(H)Cl$ and $AgClO_4$.[3]

1,1-Dihaloalkenes. Hydrozirconation of alkynylzinc bromides followed by reaction with a positive halogen source completes transformation of 1-alkynes to 1,1-dihaloalkenes.[4]



[1] Piperno, A., Carnovale, C., Giofrè, S.V., Iannazzo, D. *TL* **52**, 6880 (2011)
[2] Oda, Y., Sato, T., Chida, N. *OL* **14**, 950 (2012)
[3] Maeng, J.-H., Yang, Z., Manning, D.D., Masih, L., Cao, Y., Pattamana, K., Bois, F., Molino, B.F. *S* **63** (2012)
[4] Guerrero Jr, P.G., de Oliveira, P.R., Baroni, A.C.M., Marques, F.A., Labes, R., Dabdoub, M.J. *TL* **53**, 1582 (2012)

Zirconyl chloride

Amidation.[1] Carboxylic acids are converted into amides on reaction with ureas in the presence of the reusable and water-tolerant $ZrOCl_2$ catalyst.

[1] Talukdar, D., Saikia, L., Thakur, A.J. *SL* 1597 (2011)

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