

Synthesis Alerts is a monthly feature to help readers of *Synthesis* keep abreast of new reagents, catalysts, ligands, chiral auxiliaries, and protecting groups which have appeared in the recent literature. Emphasis is placed on new developments but established reagents, catalysts etc are also covered if they are used in novel and useful reactions. In each abstract, a specific example of a transformation is given in a concise format designed to aid visual retrieval of information.

Synthesis Alerts is a personal selection by:

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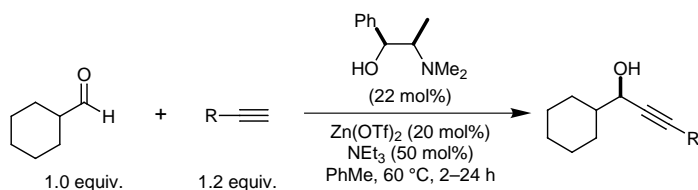
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Chemistry A European Journal
Chemistry Letters
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Heterocycles
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Journal of Organic Chemistry
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Organometallics
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Tetrahedron Asymmetry and Tetrahedron Letters

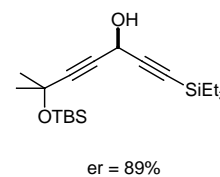
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Catalytic enantioselective addition of terminal alkynes to aldehydes.
Anand, N. K.; Carreira, E. M. *J. Am. Chem. Soc.* **2001**, *123*, 9687.

Enantioselective 1,2-Addition



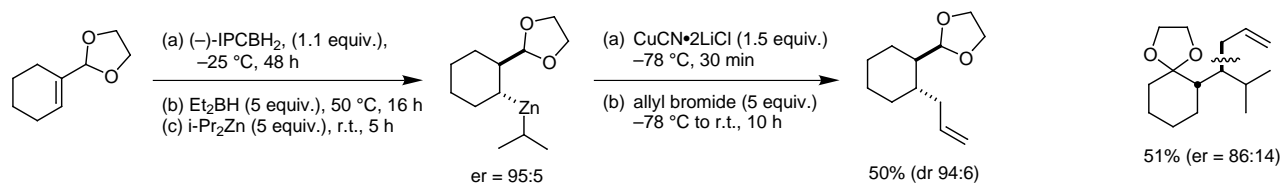
R	Yield	ee
Bn ₂ NCH ₂	91%	97%
Ph(CH ₂) ₂	89%	94%
Ph	94%	86%
(EtO) ₂ CH	88%	94%
n-Bu	81%	93%
TMSOC(Me) ₂	80%	99%
Et ₃ Si	85%	96%



Reaction works best when the aldehyde has an α -branch. Lower yields but useful ee's obtained even with unbranched aldehydes. The reaction can be performed without solvent in which case no aqueous workup is necessary. 10 Aldehydes and 15 different alkynes used: yields typically >80%, ee's >90%.

Enantioselective hydrometallation–alkylation: equivalent to umpolung of a Michael addition.
Hupe, E.; Knochel, P. *Angew. Chem. Int. Ed.* **2001**, *40*, 3022.

Enantioselective Hydrometallation

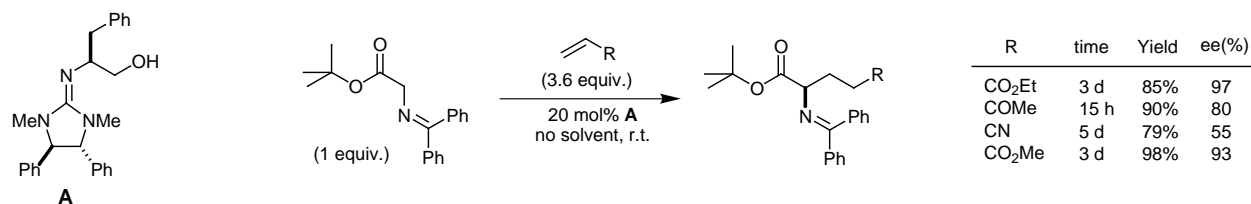


alkylation with propargyl bromide and 1-bromoalkynes also reported

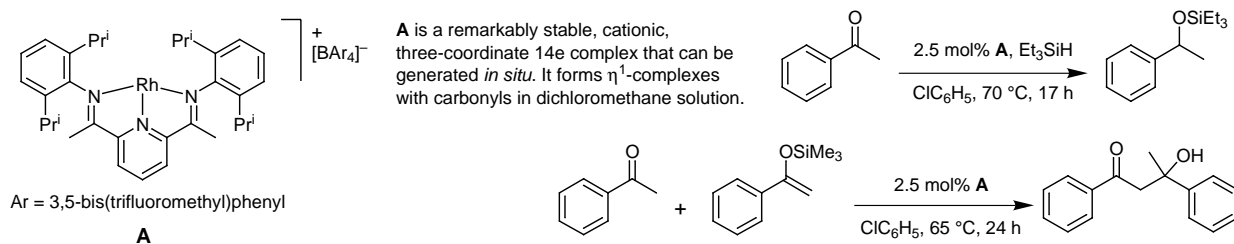
Chiral guanidine base in asymmetric Michael addition reactions of glycine imine.

Ishikawa, T.; Araki, Y.; Kumamoto, T.; Seki, H.; Fukuda, K.; Isobe, T. *Chem. Commun.* **2001**, 245.

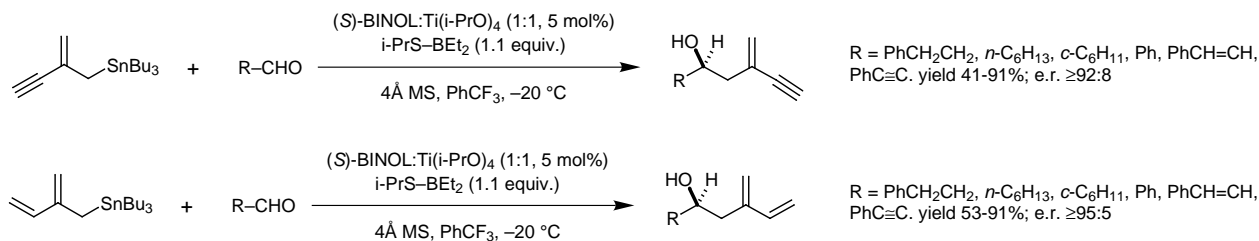
Asymmetric 1,4-Addition



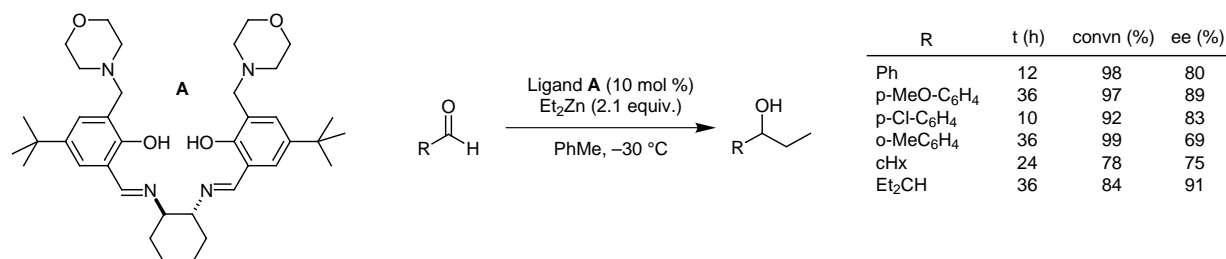
A remarkably stable rhodium Lewis acid catalyst for hydrosilation, Mukaiyama aldol and cyclopropanation reactions. **Novel Lewis Acid**
Dias, E. L.; Brookhart, M.; White, P. S. *Chem. Commun.* **2001**, 423.



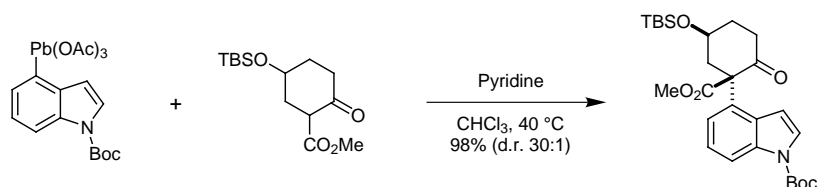
Catalytic asymmetric allyl transfer reactions promoted by a BINOL-Ti complex.
Yu, C.-M.; Jeon, M.; Lee, J.-Y.; Jeon, J. *Eur. J. Org. Chem.* **2001**, 1143.

Asymmetric Addition

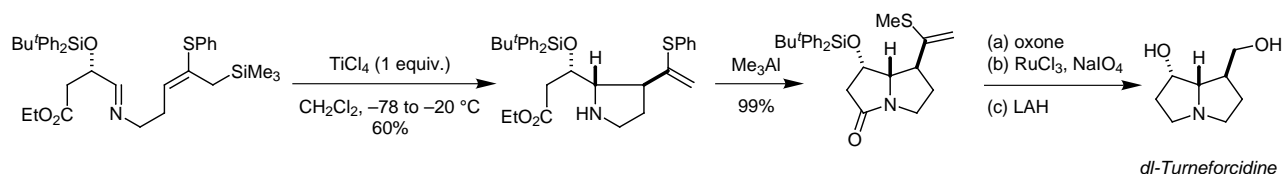
Salen-derived catalysts containing secondary basic groups in the addition of diethylzinc to aldehydes.
DiMauro, E. F.; Kozlowski, M. S. *Org. Lett.* **2001**, 3, 3053.

Asymmetric Addition

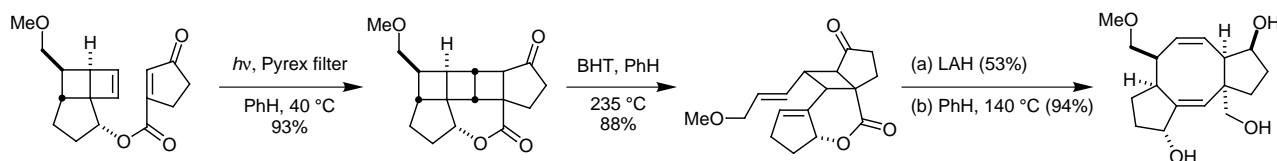
Appendage of a quaternary centre to an indole via arylead(IV) reagents.
Deng, H.; Konopelski, J. P. *Org. Lett.* **2001**, 3, 3001.

sp³-sp² Coupling

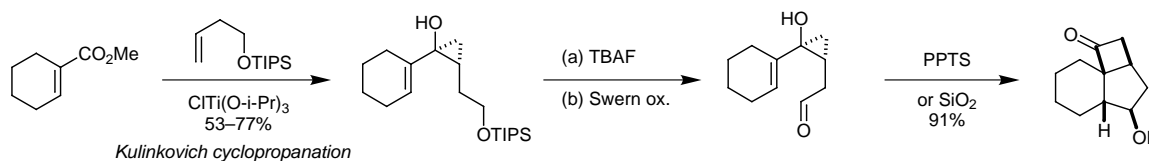
Metalloiminium ion cyclisation terminated by a 2-(methylthio)-3-(trimethylsilyl)-1-propenyl moiety.
An, D. K.; Duncan, D.; Livinghouse, T.; Reid, P. *Org. Lett.* **2001**, 3, 2961.

Heteroannulation

Intramolecular [2+2] photocycloaddition/thermal fragmentation approach toward 5–8–5 ring systems.
Lo, P. C.-K.; Snapper, M. L. *Org. Lett.* **2001**, 3, 2819.

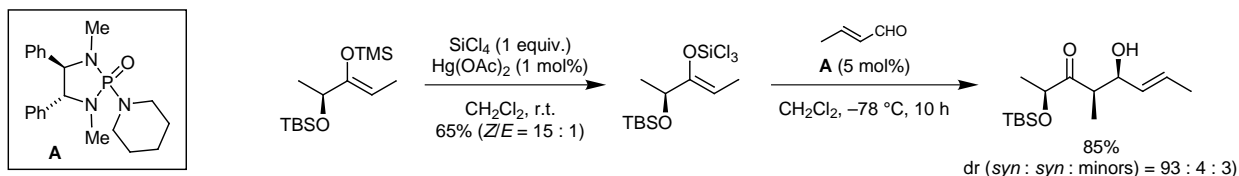
[2+2] Cycloaddition

Electrophilic cyclisations of vinylcyclopropanols to tethered aldehydes.
Yon, J.-H.; Lee, J.; Cha, J. K. *Org. Lett.* **2001**, 3, 2935.

Prins-Pinacol Annulation

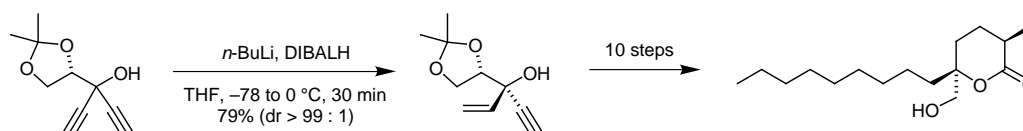
4 examples. Cyclisation to form 5- and 6-membered rings was successful but closure to a 7-membered ring failed.

Highly diastereoselective aldol additions of a chiral ethyl ketone enolate under Lewis base catalysis.
Denmark, S. E.; Pham, S. M. *Org. Lett.* **2001**, 3, 2201.

Asymmetric Aldol

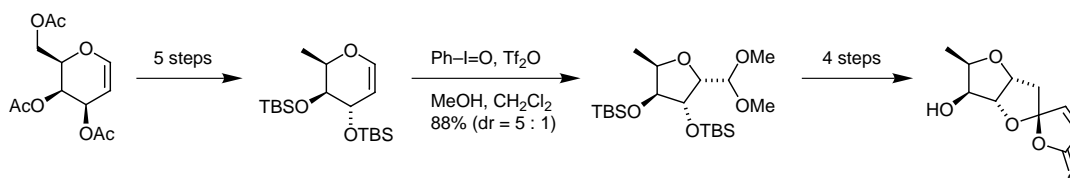
7 examples (unsaturated aldehydes); yields 71–88%

Group-selective hydroalumination of bis-alkynyl carbinols: application to malyngolide.
Suzuki, T.; Ohmori, K.; Suzuki, K. *Org. Lett.* **2001**, 3, 1741.

Hydrometallation

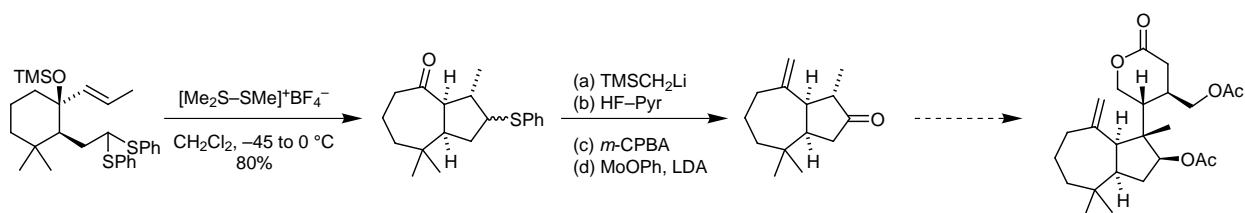
Hydroalumination also works with LAH in better yield (84%) but the dr is only 92:8.

Oxidative ring contraction of a glycal derivative: application to the synthesis of (+)-pyrenolide D.
Engstrom, K. M.; Mendoza, M. R.; Navarro-Villalobos, M.; Gin, D. Y. *Angew. Chem. Int. Ed.* **2001**, 40, 1128.

Ring Contraction

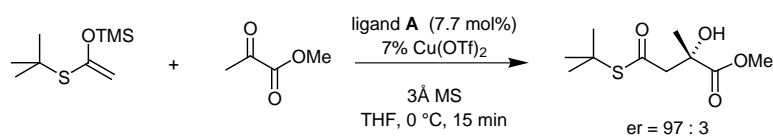
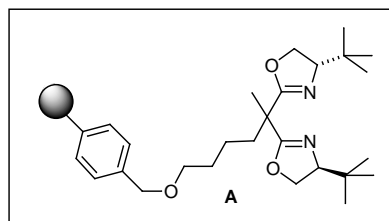
Prins-pinacol annulation reaction initiated by an α -thiacarbenium ion: application to Shahamin K.
Lebsack, A. D.; Overman, L. E.; Valentekovich, R. V. *J. Am. Chem. Soc.* **2001**, *123*, 4851.

Prins-Pinacol



Polymer-bound bis-oxazoline copper(II) complex: a catalyst for the enantioselective Mukaiyama aldol reaction.
Orlandi, S.; Mandoli, A.; Pini, D.; Salvadori, P. *Angew. Chem. Int. Ed.* **2001**, *40*, 2519.

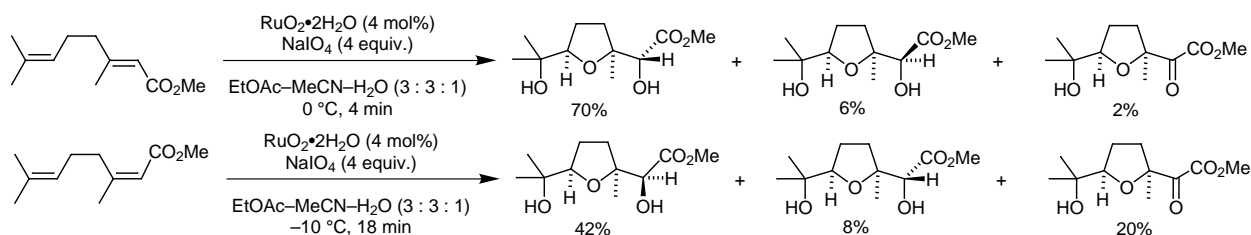
Asymmetric Aldol



only one example; the ligand can be recovered

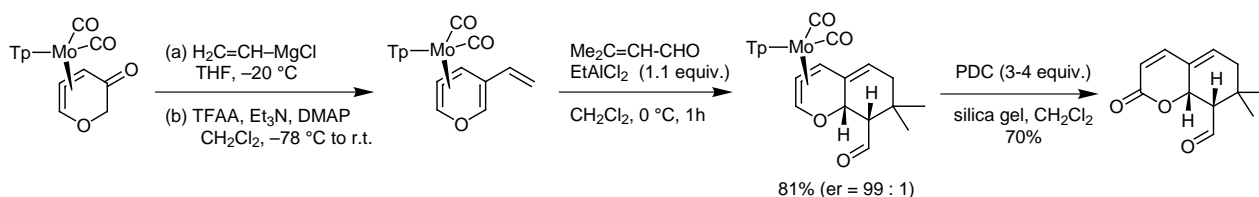
RuO_4 -catalysed oxidative cyclisation of 1,5-dienes to *cis*-2,5-bis(hydroxymethyl)tetrahydrofuranlydiols.
Piccilli, V.; Cavallo, N. *Tetrahedron Lett.* **2001**, *42*, 4695.

Oxidative Annulation



Enantio- and regio-controlled [4+2] cycloaddition to 3-alkenyl- η^3 -pyranylmolybdenum complexes.
Gómez, R.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2001**, *123*, 6185.

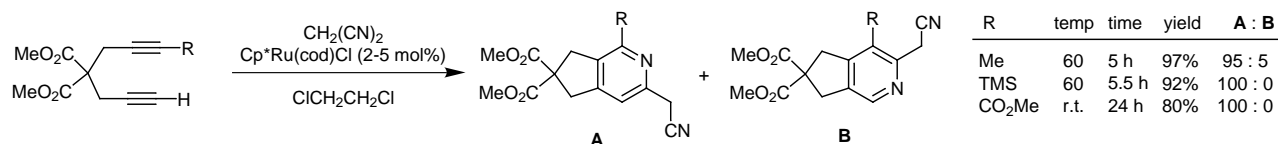
[4+2] Cycloaddition



9 examples; yields typically >80%

Chemo- and regioselective Ru(II)-catalysed [2+2+2] cycloaddition of 1,6-diynes with dicyanides.
Yamamoto, Y.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2001**, *123*, 6189.

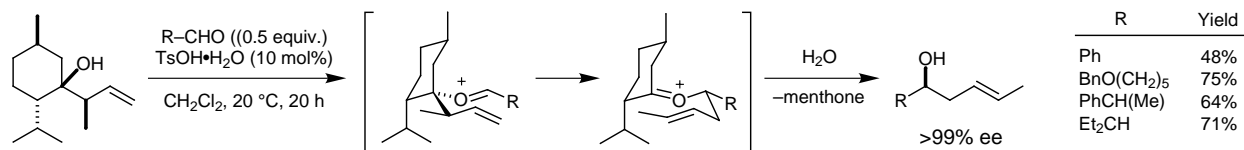
[2+2+2] Cycloaddition



8 diynes and 5 dicyanides used

Enantioselective crotylation of aldehydes via an allyl transfer reaction from a chiral crotyl donor.
Nokami, J.; Ohga, M.; Nakamoto, H.; Matsubara, T.; Hussain, I.; Kataoka, K.
J. Am. Chem. Soc. **2001**, *123*, 9168.

Asymmetric 1,2-Addition

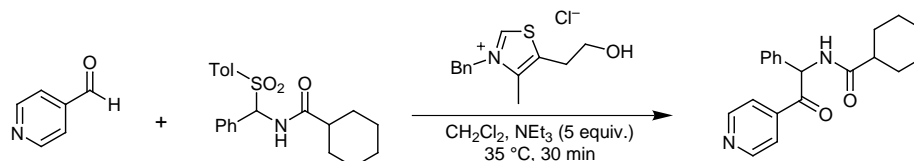


9 examples; 2 failed: citronellal and 2-octenal. The corresponding asymmetric allylation reaction gave lower ee.

Thiazolium-catalysed cross-coupling of aldehydes with acylimines.

Murry, J. A.; Frantz, D. E.; Soheila, A.; Tillyer, R.; Grabowski, E. J. J.; Reider, P. J.
J. Am. Chem. Soc. **2001**, *123*, 9696.

1,2-Addition

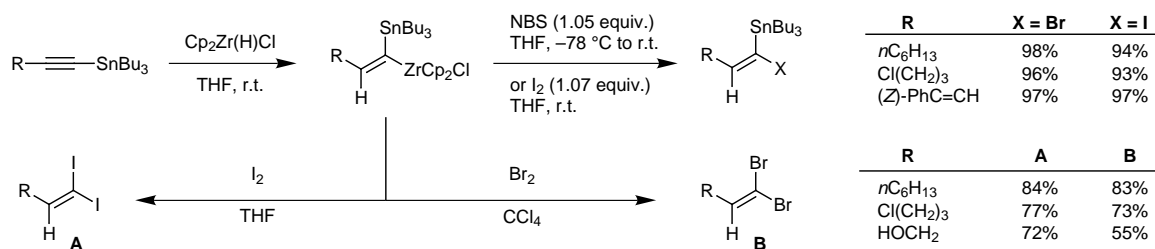


21 examples; yields typically >70%

Hydrozirconation of stannylalkynes. Synthesis of 1,1-dibromo- and 1,1-diiodo alkynes.

Dabdoub, M. J.; Dabdoub, V. B.; Baroni, A. C. M. *J. Am. Chem. Soc.* **2001**, *123*, 9694.

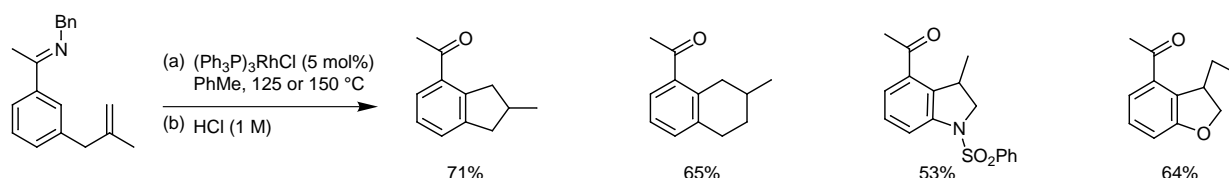
Hydrometallation



Annulation of aromatic imines via directed C–H activation with Wilkinson's catalyst.

Thalji, R. K.; Ahrendt, K. A.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2001**, *123*, 9692.

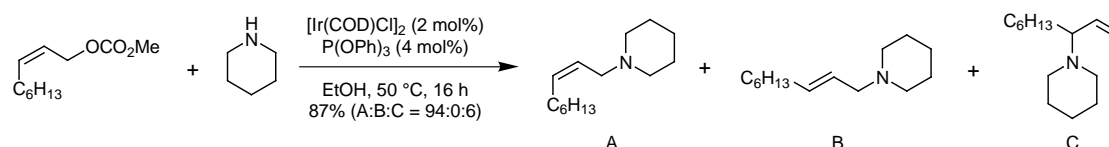
Annulation



11 examples; yields typically 50–65%. The ketimine group is necessary; the ketone does not cyclise. An aldimine also works (1 example).

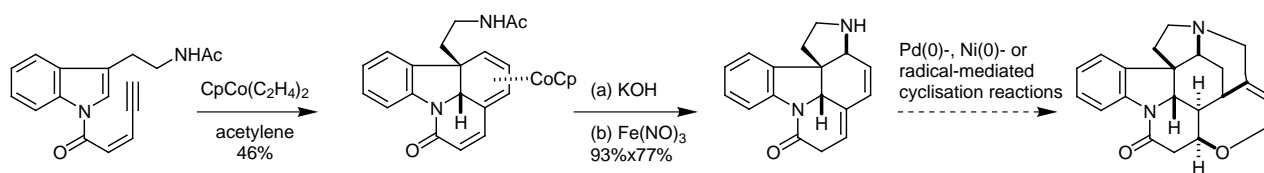
Iridium-catalysed allylic amination of allylic esters.

Takeuchi, R.; Ue, N.; Tanabe, K.; Yamashita, K.; Shiga, N. *J. Am. Chem. Soc.* **2001**, *123*, 9525.

N–C sp³ Coupling

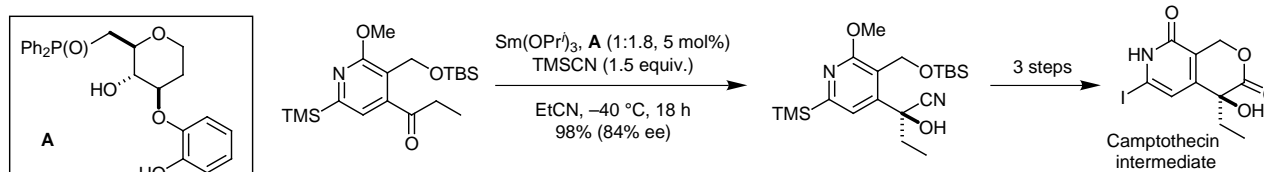
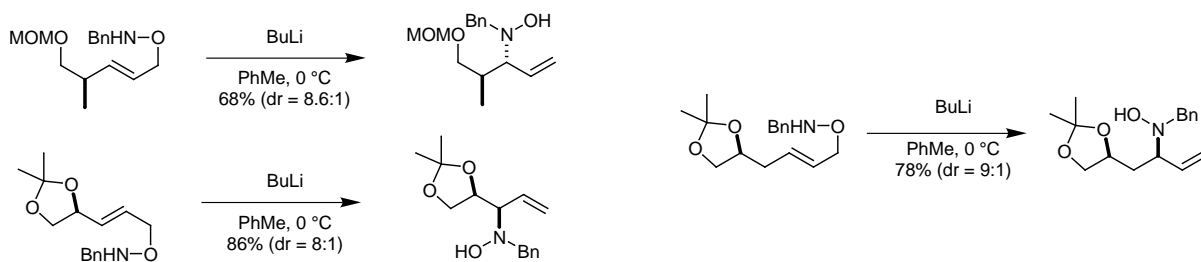
Terminal (*E*)- and (*Z*)-allylic carbonates and acetates only. 1° and 2° amines used include pyrrolidine, morpholine, cyclopentylamine, *n*-butylamine, *tert*-butylamine and benzylamine.

Strychnine via cobalt-mediated [2+2+2] cycloaddition.

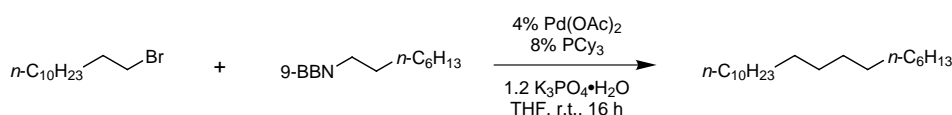
Eichberg, M. J.; Dorta, R. L.; Grotjahn, D. B.; Lamottke, K.; Schmidt, M.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **2001**, 123, 9324.**[2+2+2] Cycloaddition**

(±)-Strychnine synthesised in 1.9% overall yield in 14 steps (longest linear sequence).

Catalytic enantioselective cyanosilylation of ketones.

Yabu, K.; Masumoto, S.; Yamasaki, S.; Hamashima, Y.; Kanai, M.; Du, W.; Curran, D. P.; Shibasaki, M. *J. Am. Chem. Soc.* **2001**, 123, 9908.**Enantioselective 1,2-Addition**7 additional examples using Gd(OPr)₃ as Lewis acid; yields typically ≥90%. Aromatic methyl ketones give the best ee's (89–97%) followed by enones (80–89%). Phenethyl methyl ketone gave 90% yield but only 62% ee.Diastereoselective [2,3]-sigmatropic rearrangement of metallated *O*-allylic-(*N*-benzyl)hydroxylamines.Ishikawa, T.; Kawakami, M.; Fukui, M.; Yamashita, A.; Urano, J.; Saito, S. *J. Am. Chem. Soc.* **2001**, 123, 7734.**[2,3]-Sigmatropic Rearrangement**

Alkyl-alkyl Suzuki cross-coupling of bromoalkanes.

Netherton, M. R.; Dai, C.; Neuschütz, K.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, 123, 10099.**sp³-sp³ Coupling**

10 examples; yields 66-93%. Tricyclohexylphosphane is uniquely effective. With other phosphanes, β-elimination competes or predominates.

Polymer-bound *tert*-butanesulfonamide.Dragoli, D. R.; Burdett, M. T.; Ellman, J. A. *J. Am. Chem. Soc.* **2001**, 123, 10127.**Asymmetric 1,2-Addition**