

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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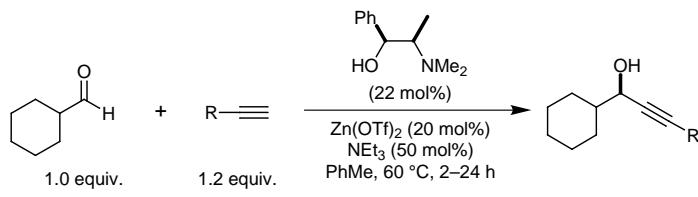
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The journals regularly covered by the abstractors are:

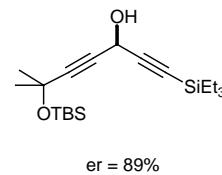
Angewandte Chemie International Edition
Bulletin of the Chemical Society of Japan
Chemical Communications
Chemistry A European Journal
Chemistry Letters
Collection Czechoslovak Chemical Communications
European Journal of Organic Chemistry
Helvetica Chimica Acta
Heterocycles
Journal of the American Chemical Society
Journal of Organic Chemistry
Organic Letters
Organometallics
Perkin Transactions I
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry and Tetrahedron Letters

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



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%

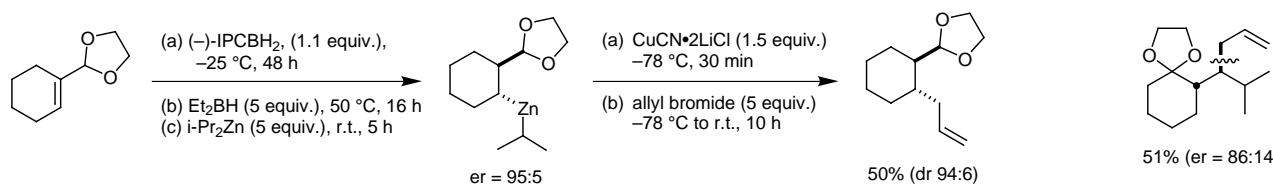
Enantioselective 1,2-Addition



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.

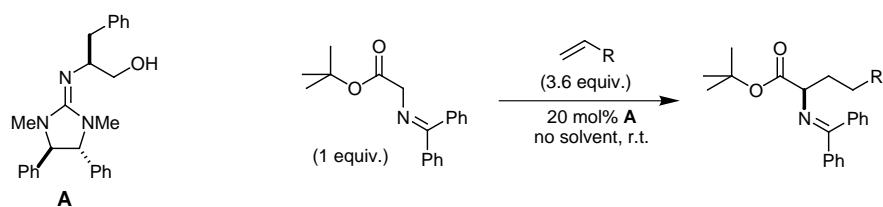
Enantioselective Hydrometallation



alkylation with propargyl bromide and 1-bromoalkynes also reported

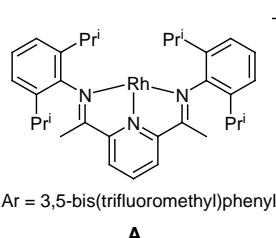
Chiral guanidine base in asymmetric Michael addition reactions of glycine imine.
Ishikawa, T.; Araki, Y.; Kumamoto, T.; Seki, H.; Fukuda, K.; Isobe, T. *Chem. Commun.* **2001**, 245.

Asymmetric 1,4-Addition

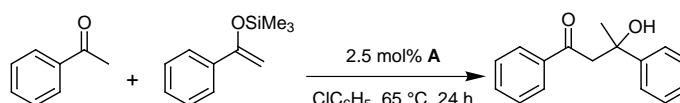
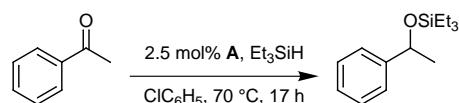


R	time	Yield	ee(%)
CO ₂ E _t	3 d	85%	97
COMe	15 h	90%	80
CN	5 d	79%	55
CO ₂ Me	3 d	98%	93

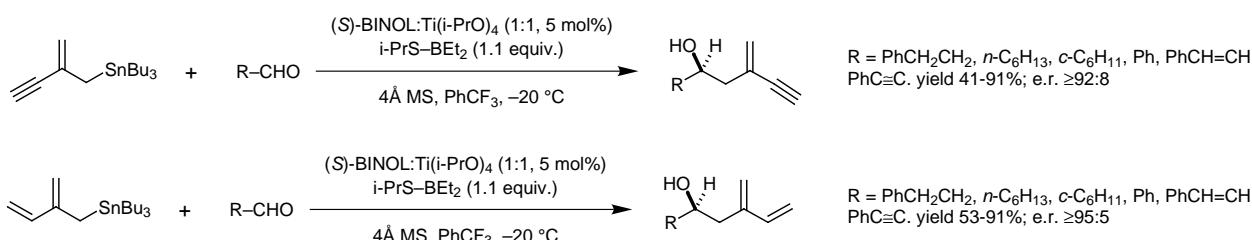
A remarkably stable rhodium Lewis acid catalyst for hydrosilation, Mukaiyama aldol and cyclopropanation reactions. **Novel Lewis Acid**
Dias, E. L.; Brookhart, M.; White, P. S. *Chem. Commun.* **2001**, 423.



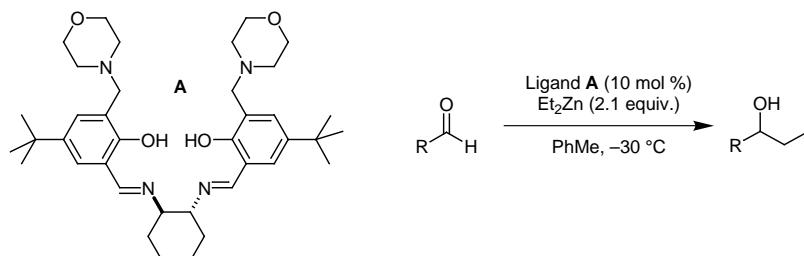
A is a remarkably stable, cationic, three-coordinate 14e complex that can be generated *in situ*. It forms η^1 -complexes with carbonyls in dichloromethane solution.



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

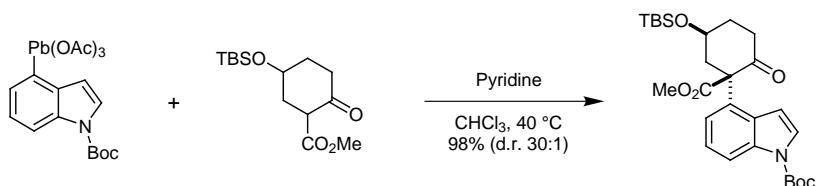


Salen-derived catalysts containing secondary basic groups in the addition of diethylzinc to aldehydes. **Asymmetric Addition**
DiMauro, E. F.; Kozlowski, M. S. *Org. Lett.* **2001**, 3, 3053.

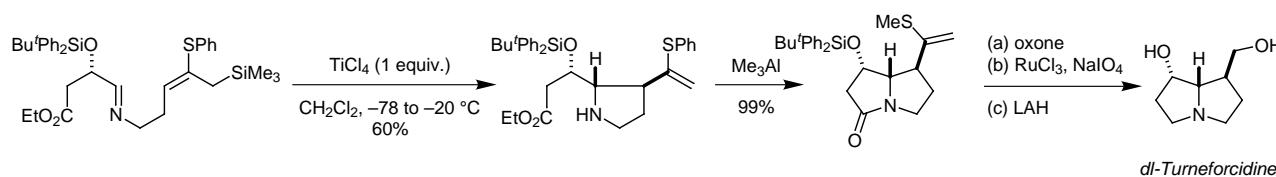


R	t (h)	convn (%)	ee (%)
Ph	12	98	80
p-MeO-C ₆ H ₄	36	97	89
p-Cl-C ₆ H ₄	10	92	83
o-MeC ₆ H ₄	36	99	69
cHx	24	78	75
Et ₂ CH	36	84	91

Appendage of a quaternary centre to an indole via arylead(IV) reagents. **sp³-sp² Coupling**
Deng, H.; Konopelski, J. P. *Org. Lett.* **2001**, 3, 3001.

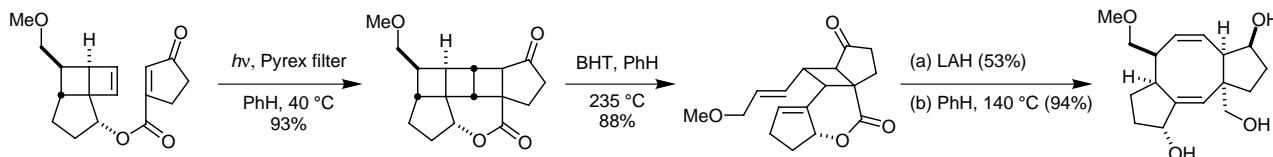


Metallocinium ion cyclisation terminated by a 2-(methylthio)-3-(trimethylsilyl)-1-propenyl moiety. **Heteroannulation**
An, D. K.; Duncan, D.; Livinghouse, T.; Reid, P. *Org. Lett.* **2001**, 3, 2961.



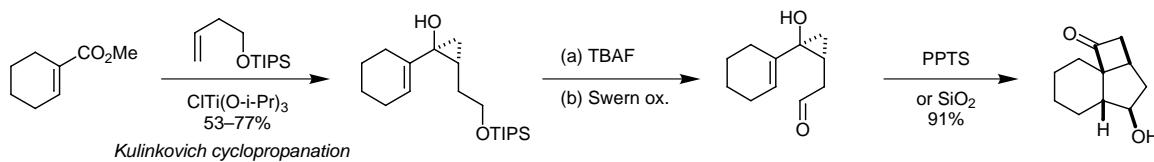
Intramolecular [2+2] photocycloaddition/thermal fragmentation approach toward 5–8–5 ring systems.
Lo, P. C.-K.; Snapper, M. L. *Org. Lett.* **2001**, 3, 2819.

[2+2] Cycloaddition



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

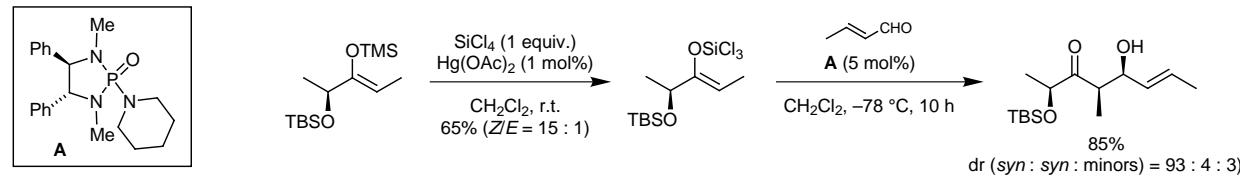
Prins-Pinacol Annulation



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.

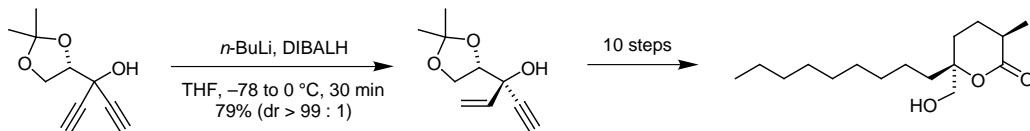
Asymmetric Aldol



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.

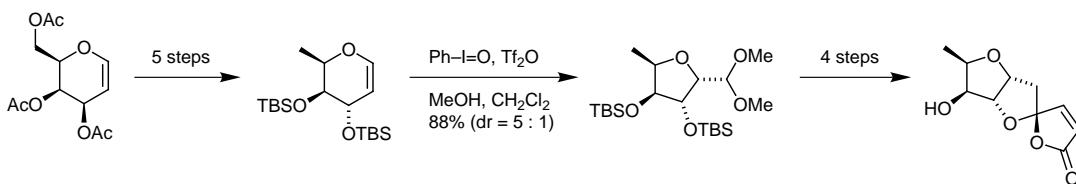
Hydrometallation



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

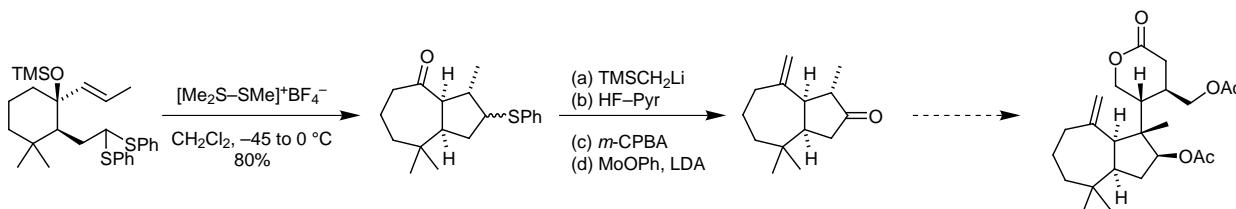
Oxidative ring contraction of a glycal derivative: application to the synthesis of (+)-pyrenolide D.
Engstrom, K. M.; Mendoza, M. R.; Navarro-Villalobos, M.; Gin, D. Y. *Angew. Chem. Int. Ed.* **2001**, 40, 1128.

Ring Contraction



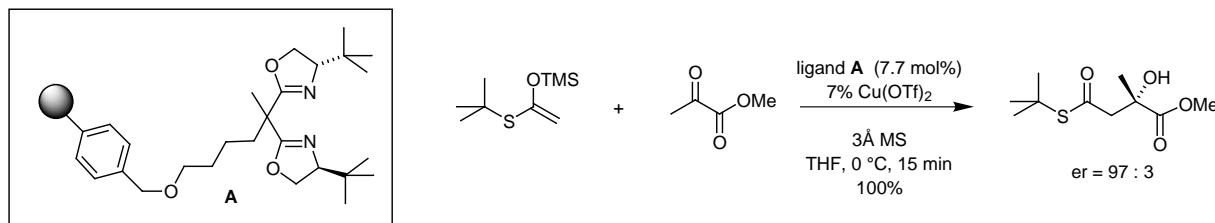
Prins-pinacol annulation reaction initiated by an α -thiacarbenium ion: application to Shahamin K. Lebsack, A. D.; Overman, L. E.; Valenteckovich, R. V. *J. Am. Chem. Soc.* **2001**, 123, 4851.

Prins-Pinacol



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

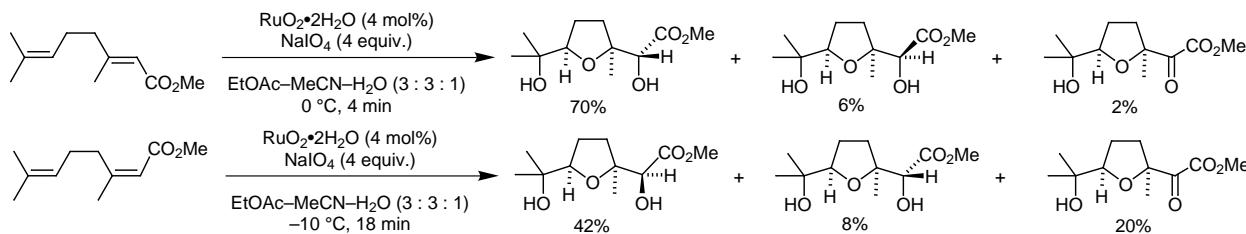
Asymmetric Aldol



only one example; the ligand can be recovered

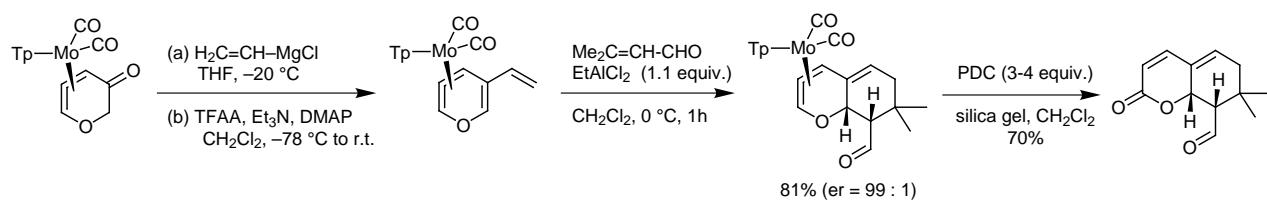
RuO₄-catalysed oxidative cyclisation of 1,5-dienes to *cis*-2,5-bis(hydroxymethyl)tetrahydrofuranyldiols. Piccialli, V.; Cavallo, N. *Tetrahedron Lett.* **2001**, 42, 4695.

Oxidative Annulation



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

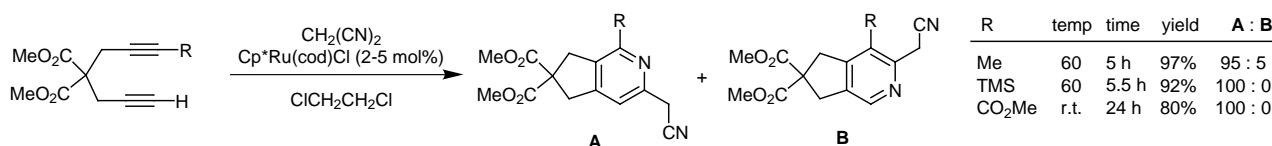
[4+2] Cycloaddition



9 examples; yields typically >80%

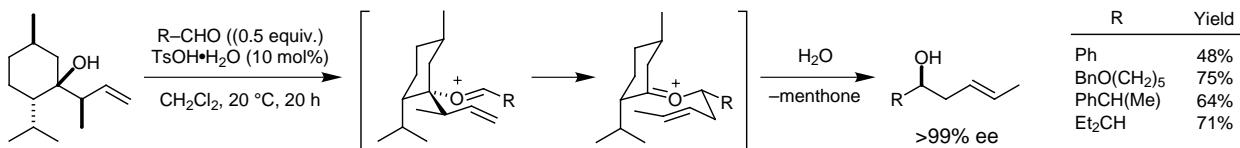
Chemo- and regioselective Ru(II)-catalysed [2+2+2] cycloaddition of 1,6-diyne with dicyanides. Yamamoto, Y.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2001**, 123, 6189.

[2+2+2] Cycloaddition



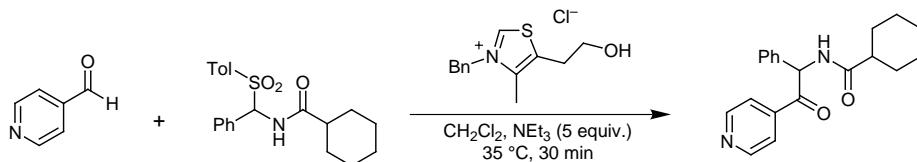
8 diynes and 5 dicyanides used

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

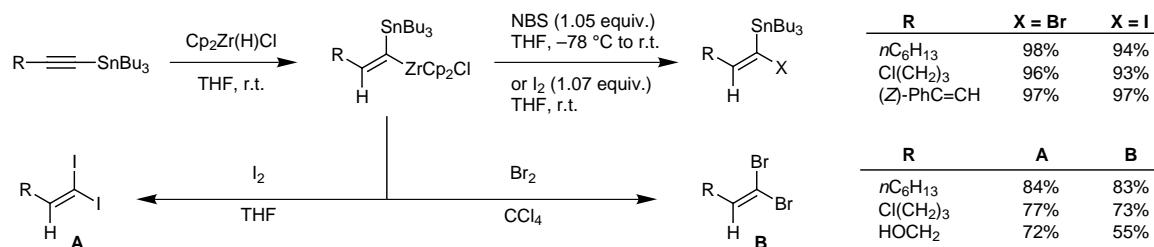
9 examples; 2 failed: citronellal and 2-octenal. The corresponding asymmetric allylation reaction gave lower ee.

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.

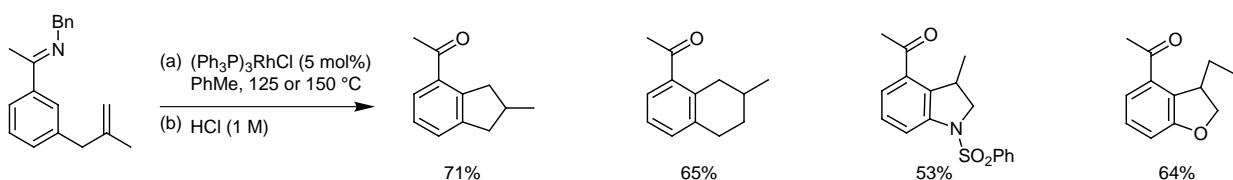
1,2-Addition

21 examples; yields typically >70%

Hydrozirconation of stannyllalkynes. 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.

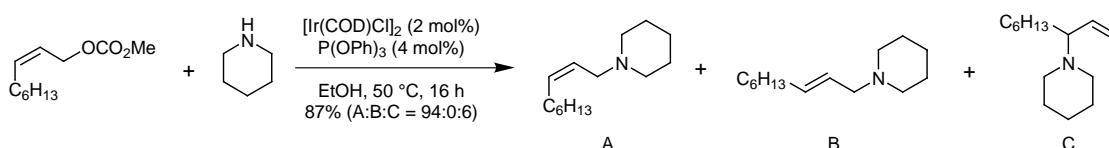
Hydrometallation

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.

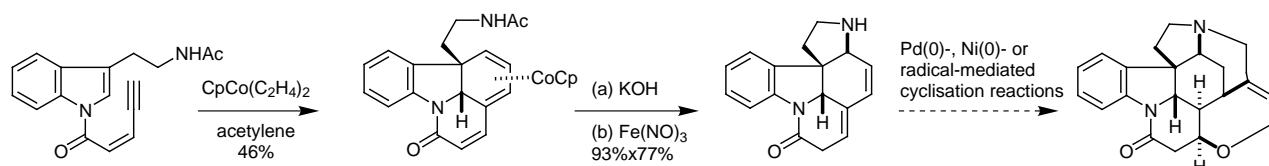
N–C sp³ Coupling

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

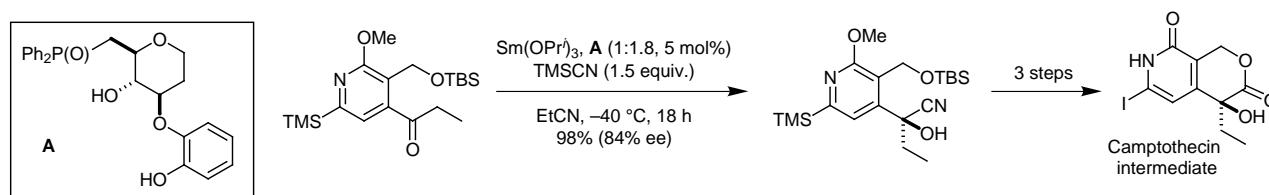


(\pm)-Strychnine synthesised in 1.9% overall yield in 14 steps (longest linear sequence).

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

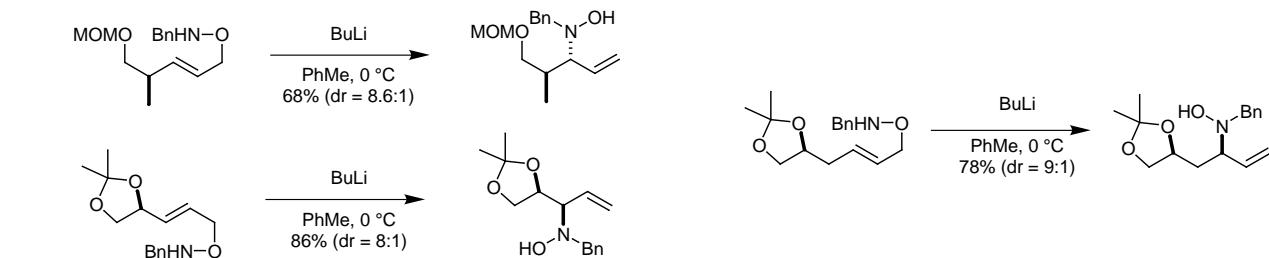


7 additional examples using $\text{Gd}(\text{OPr})_3$ as Lewis acid; yields typically $\geq 90\%$. Aromatic methyl ketones give the best ee's (89–97%) followed by enones (80–89%). Phenethyl methyl ketone gave 90% yield but only 62% ee.

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.

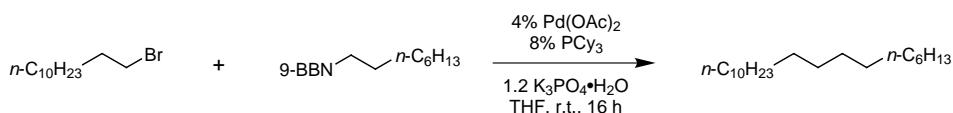
[2,3]-Sigmatropic Rearrangement



Alkyl–alkyl Suzuki cross-coupling of bromoalkanes.

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

sp^3 - sp^3 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

