

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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SYNTHESIS 2003, No. 12, pp 1920–1927

Advanced online publication: 02 09 2003

Art ID: X01203SS.pdf

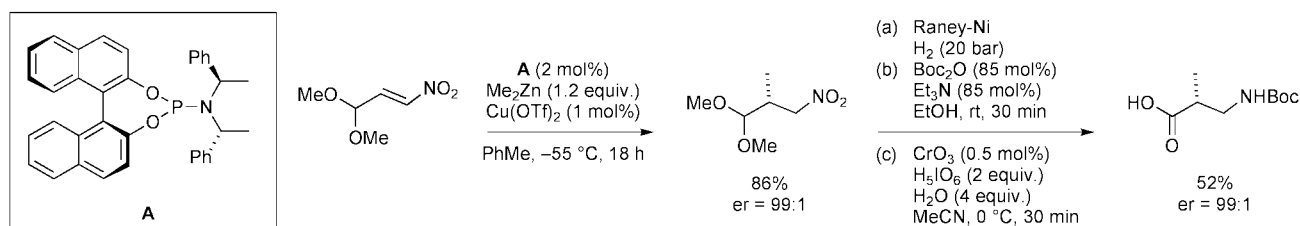
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The journals regularly covered by the abstractors are:

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
 Organic and Biomolecular Chemistry
 Organometallics
 Synlett
 Synthesis
 Tetrahedron
 Tetrahedron Asymmetry and Tetrahedron Letters

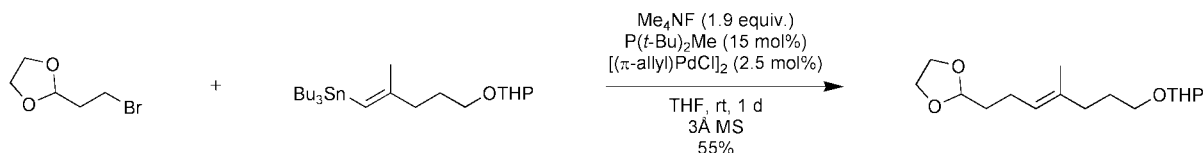
Enantioselective conjugate addition of dialkylzinc reagents to nitroalkenes.
 Duursma, A.; Minaard, A. J.; Feringa, B. L. *J. Am. Chem. Soc.* **2003**, *13*, 3700.

Enantioselective 1,4-Addition



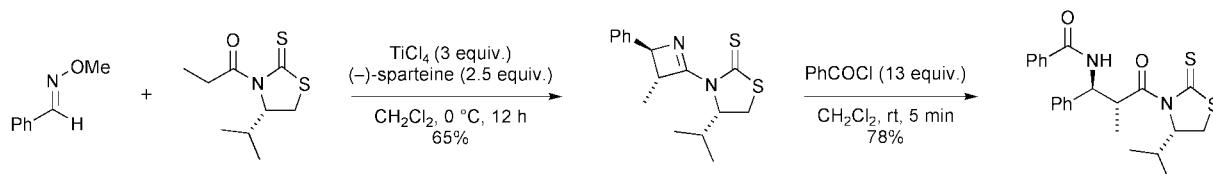
Room temperature Stille cross-couplings of alkenyltin reagents and allyl bromides bearing β -hydrogens.
 Menzel, K.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 3718.

sp^3 - sp^2 Coupling



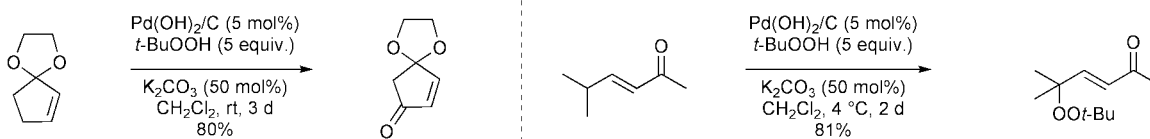
Diastereoselective addition of *N*-acyl thiazolidinethione enolates to *O*-methyl oximes.
 Ambhaikar, N. B.; Snyder, J. P.; Liotta, D. C. *J. Am. Chem. Soc.* **2003**, *13*, 3690.

Nucleophilic Addition/Ring Closure



A mild catalytic method for the oxidation of α,β -enones to 1,4-dienediones.
 Yu, J.-Q.; Corey, E. J. *J. Am. Chem. Soc.* **2003**, *125*, 3232.

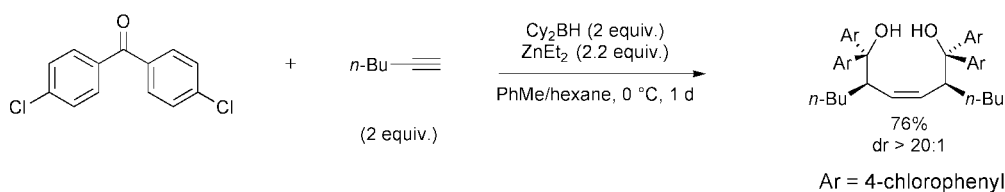
Allylic Oxidation



10 examples (yields 79-90%).

Diastereoselective synthesis of *cis*-3-hexene-1,6-diols via a reactive organozinc intermediate.
 Garcia, C.; Libra, E. R.; Carroll, P. J.; Walsh, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 3210.

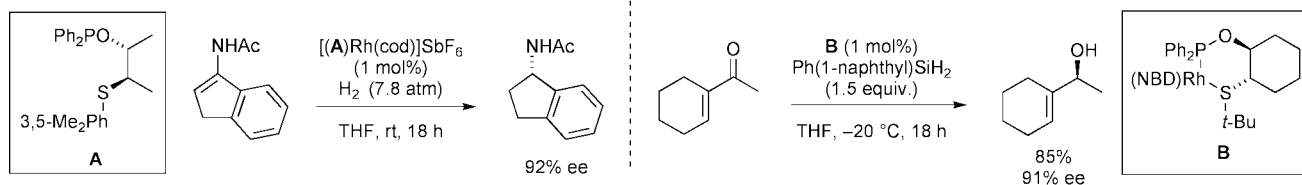
Nucleophilic Addition



15 examples (yields 47-86%, %de 0-90%).

Enantioselective rhodium catalyzed dehydroamino acid hydrogenation and ketone hydrosilylation using mixed phosphorus/sulfur ligands.
 Evans, D. A.; Michael, F. E.; Tedrow, J. S.; Campos, K. R. *J. Am. Chem. Soc.* **2003**, *125*, 3534.

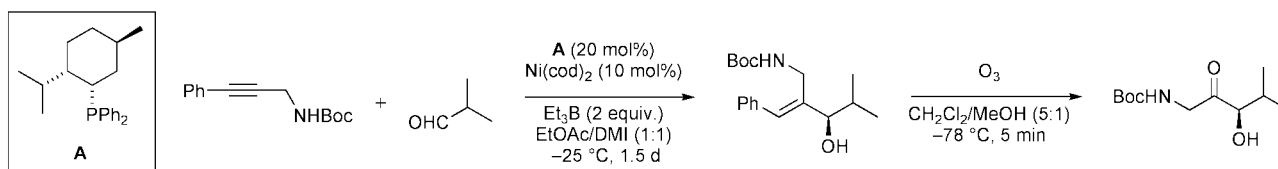
Hydrogenation



75 examples (yields 36-99%, %ee 20-99%). NBD = norbadiene.

Asymmetric catalytic reductive coupling of aldehydes and alkynes.
 Miller, K. M.; Huang, W.-S.; Jamison, T. F. *J. Am. Chem. Soc.* **2003**, *125*, 3442.

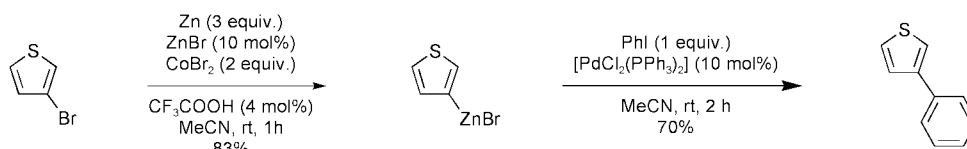
1,2-Addition



DMI = 1,3-dimethylimidazolidinone.

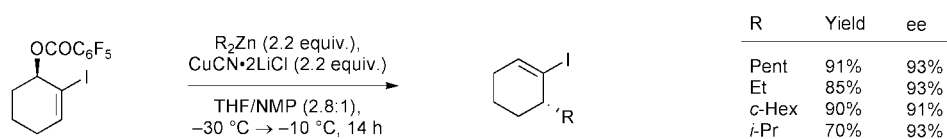
15 examples (yields 35-97%, %ee 42-96%, 95:5<regioselectivities<91:9).

Synthesis of arylzinc compounds from aromatic bromides using CoBr_2 and zinc dust.
 Fillon, H.; Gosmini, C.; Périchon, J. *J. Am. Chem. Soc.* **2003**, *125*, 3867.

Metallation/ sp^2 - sp^2 Coupling

31 examples (yields 3-100%).

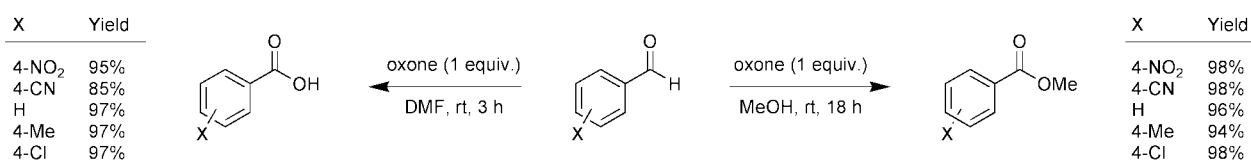
Anti-selective S_N2' reactions of chiral cyclic 2-iodo-allylic alcohol derivatives with mixed zinc-copper reagents.
Calaza, M. I.; Hupe, E.; Knochel, P. *Org. Lett.* **2003**, *5*, 1059.

 S_N2' Reaction

14 examples (yields 62-91%, %ee 91-98%).

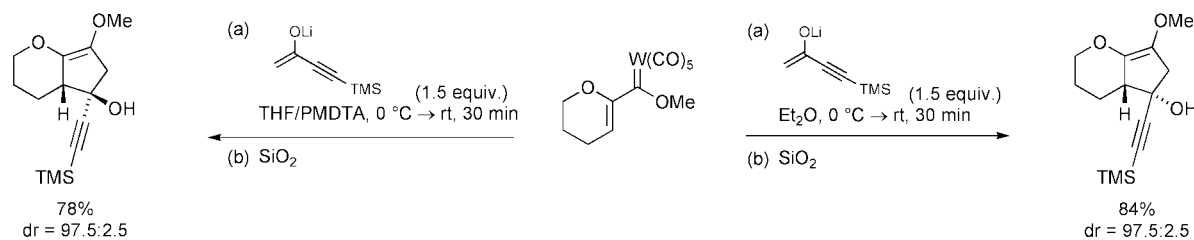
Facile oxidation of aldehydes to acids and esters with oxone.

Travis, B. R.; Sivakumar, M.; Hollist, G. O.; Borhan, B. *Org. Lett.* **2003**, *5*, 1031.

Oxidation

43 examples (yields 0-98%).

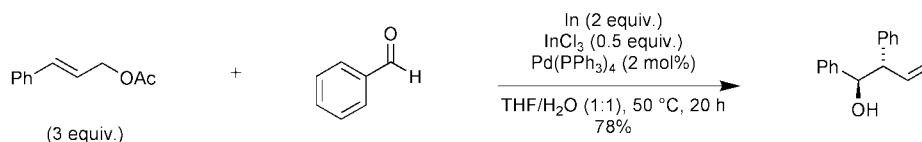
[3+2] Cycloaddition of α,β -disubstituted (alkenyl)(methoxy)carbene complexes with lithium enolates.
Barluenga, J.; Alonso, J.; Fananas, F. J. *J. Am. Chem. Soc.* **2003**, *125*, 2610.

[3+2] Cycloaddition

PMDTA = *N,N,N',N',N''*-pentamethyldiethylenetriamine. 45 examples (yields 68-95%, %de 0-95%).

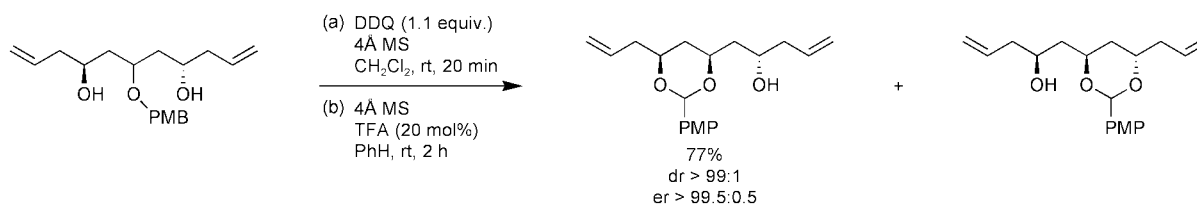
Palladium catalyzed allylation of carbonyl compounds using In-InCl₃.

Jang, T.-S.; Keum, G.; Kang, S. B.; Chung, B. Y.; Kim, Y. *Synthesis*, **2003**, 775.

Allylmetalation

50 examples (yields 5-100%).

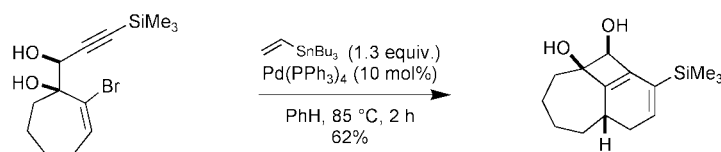
Synthesis of polyketides via diastereoselective acetalization.
Shepherd, J. N.; Myles, D. C. *Org. Lett.* **2003**, *5*, 1027.

Diastereoselective Acetalization

Syn-acetal favoured under both kinetic and thermodynamic conditions.

Formation of bicyclic 1,2-cyclobutanediols via a rare 4-exo-dig cyclocarbopalladation.
Salem, B.; Klotz, P.; Suffert, J. *Org. Lett.* **2003**, *5*, 845.

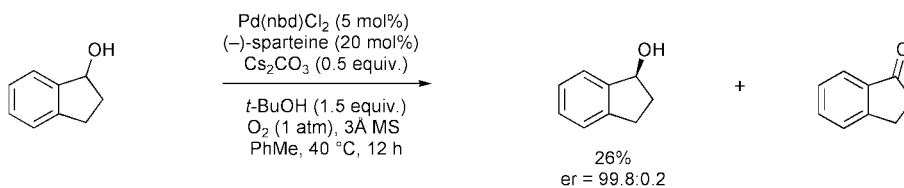
Cyclization



21 examples (yields 12-71%).

Palladium-catalysed enantioselective oxidation of alcohols.
Bagdanoff, J. T.; Ferreira, E. M.; Stoltz, B. M. *Org. Lett.* **2003**, *6*, 835.

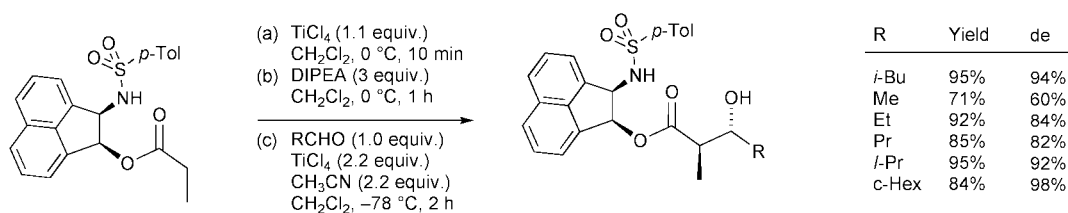
Kinetic Resolution:Oxidation



10 examples (yields 26-44%, %ee 88-100%). nbd = norbornadiene.

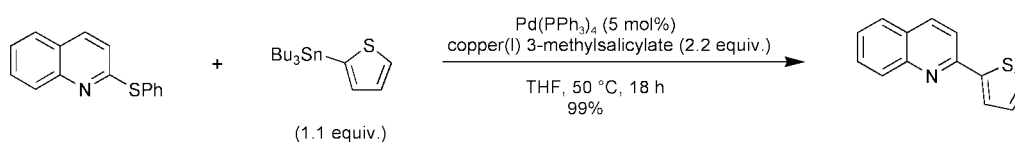
Diastereoselective *anti*-aldol reactions of *cis*-2-arylsulfonamido-1-acenaphthenyl propionate.
Ghosh, A. K.; Kim, J.-H. *Org. Lett.* **2003**, *5*, 1063.

Aldol Reaction



9 examples (yields 71-97%, %de 60-98%). The synthesis of *cis*-2-amino-1-acenaphthenol is also reported (8 steps).

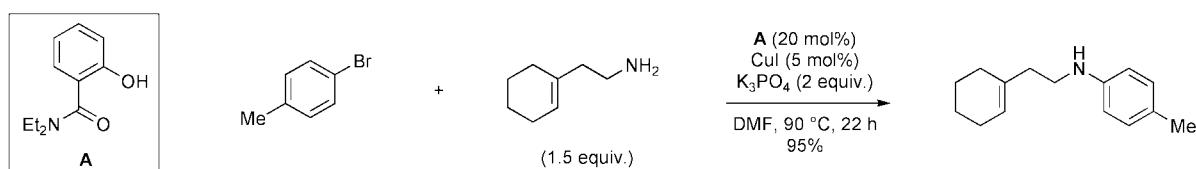
Heteroaromatic thioether-organostannane cross-coupling.
Egi, M.; Liebeskind, L. S. *Org. Lett.* **2003**, *5*, 801.

sp²-sp²Cross-Coupling

12 examples (yields 36-100%).

Copper-catalysed amination of aryl bromides with primary alkylamines.
Kwong, F. Y.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 793.

Amination

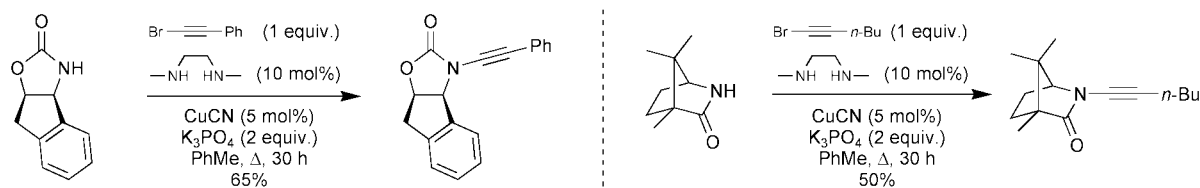


23 examples including intramolecular aminations (yields 71-95%).

Synthesis of chiral ynamides via a copper-catalyzed N-alkynylation of amides.

Frederick, M. O.; Mulder, J. A.; Tracey, M. R.; Hsung, R. P.; Huang, J.; Kurtz, K. C. M.; Shen, L.; Douglas, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 2368.

sp-sp³ Coupling

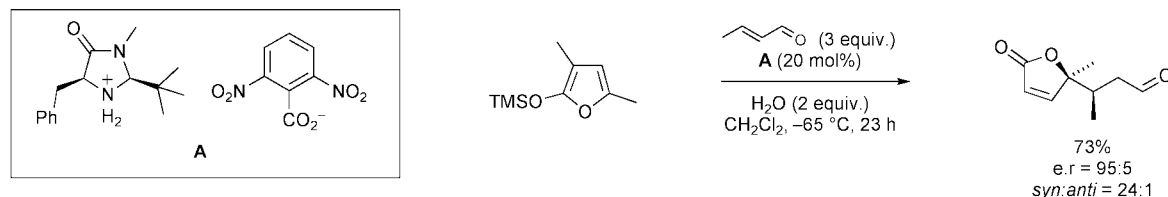


23 examples (yields 10-85%).

Enantioselective organocatalytic Mukaiyama–Michael reaction.

Brown, S. P.; Goodwin, N. C.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2003**, *125*, 1192.

Mukaiyama/1,4-Addition

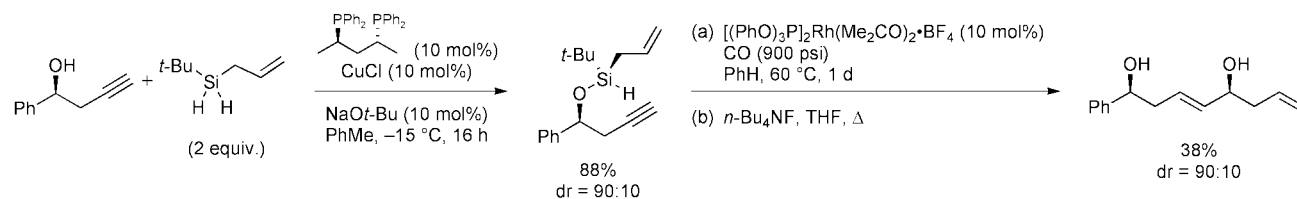


13 examples (yields 73-87%, %ee 84-99%, *syn:anti* 7:1-33:1).

Catalytic, asymmetric silane alcoholysis: Access to chiral silanes.

Schmidt, D. R.; O'Malley, S. J.; Leighton, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 1190.

Hydroformylation/Allylmethylation

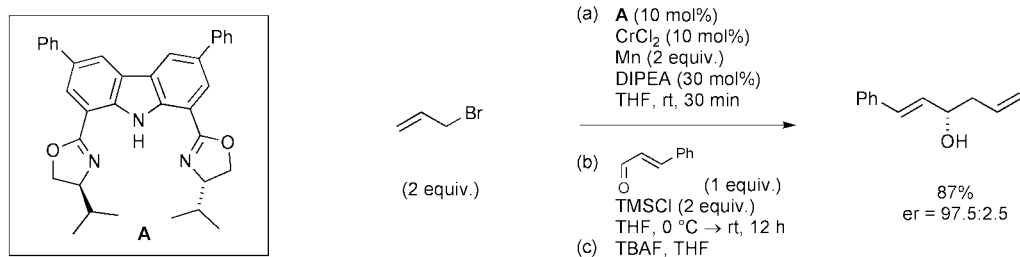


13 examples (yields 54-99%, %de 30-94%). Optimisation of the chiral ligand is also reported.

Asymmetric catalysis of Nozaki–Hiyama allylation.

Inoue, M.; Suzuki, T.; Nakada, M. *J. Am. Chem. Soc.* **2003**, *125*, 1140.

Allylmethylation

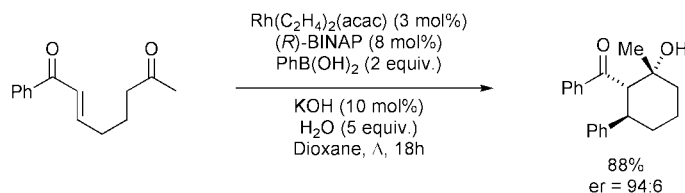


10 examples (yields 50-98%, %ee 86-96%). Synthesis of ligand **A** is also reported.

Catalytic, asymmetric carbometallative aldol cycloreduction.

Cauble, D. F.; Gipson, J. D.; Krische, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 1110.

1,4-Addition/Aldol Reaction

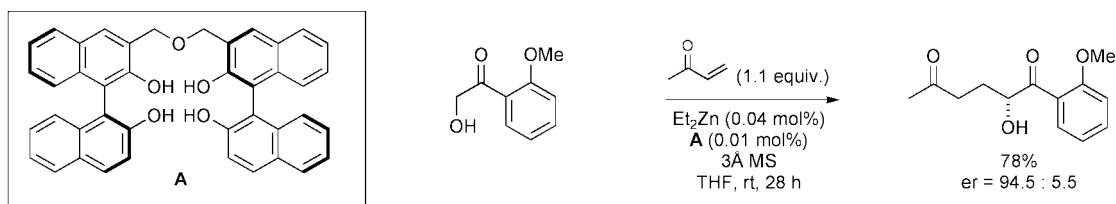


24 examples (yields 0-94%, %ee 0-95%). Optimization of chiral ligand is also reported.

Asymmetric, catalytic Michael reaction of hydroxyketones.

Harada, S.; Kumagai, N.; Kinoshita, T.; Matsunaga, S.; Shibasaki, M. *J. Am. Chem. Soc.* **2003**, *125*, 2582.

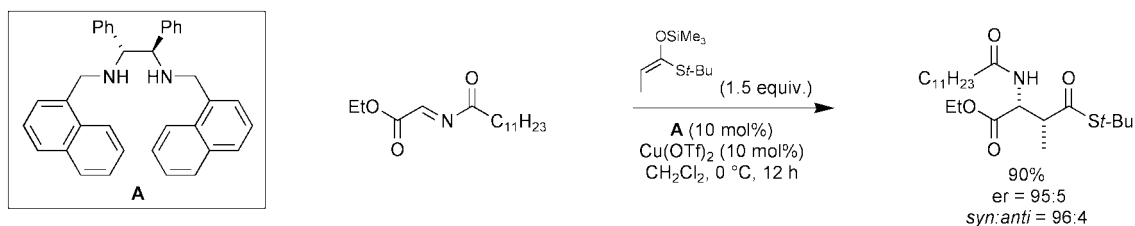
Enantioselective 1,4-Addition



32 examples (yields 39-99%, %ee 74-99%).

Catalytic, asymmetric Mannich-type reactions of *N*-acylimino esters.Kobayashi, S.; Matsubara, R.; Nakamura, Y.; Kitagawa, H.; Sugiura, M. *J. Am. Chem. Soc.* **2003**, *125*, 2507.

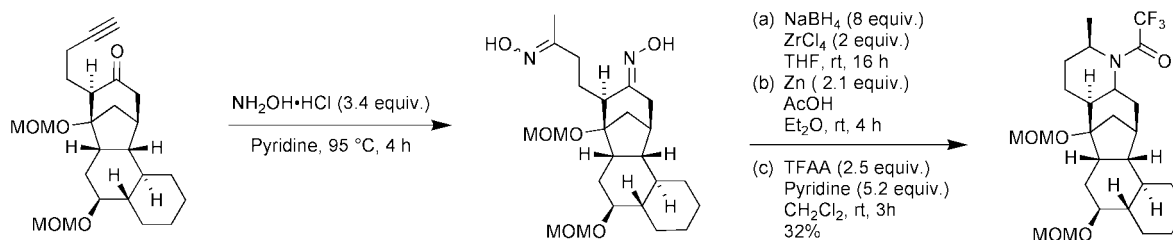
Mannich Reaction



47 examples (yields 44-97%, %ee 6-97%). Application to the synthesis of HPA-12 is also reported.

Total synthesis of Galbulimima alkaloid (\pm)-GB 13.Mander, L. N.; McLachlan, M. M. *J. Am. Chem. Soc.* **2003**, *125*, 2400.

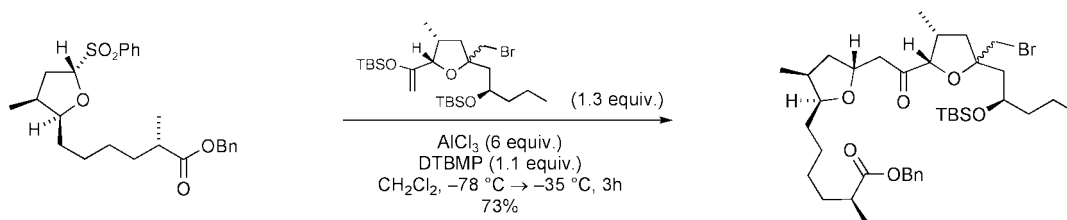
Annulation

Application to the total synthesis of Galbulimima alkaloid (\pm)-GB 13.

Fragment assembly via an oxocarbenium ion-mediated alkylation.

Ghosh, A. K.; Liu, C. *J. Am. Chem. Soc.* **2003**, *125*, 2374.

Alkylation

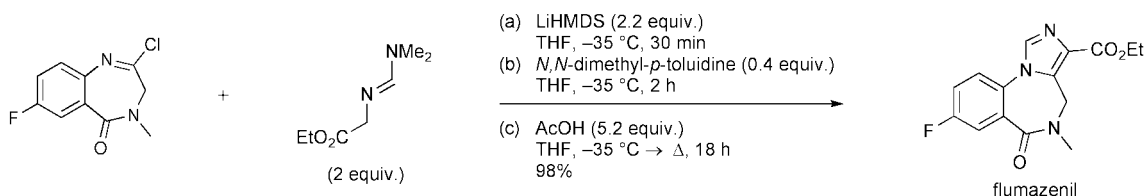


Applied towards the total synthesis of (+)-Amphidinolide T1.

Synthesis of flumazenil via an isolated benzodiazepine iminochloride.

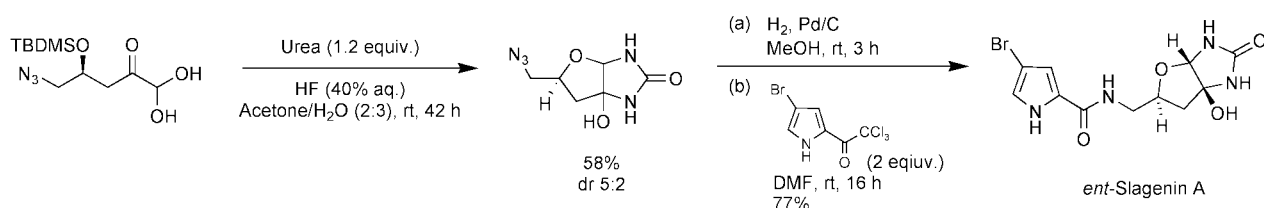
Rogers-Evans, M.; Spurr, P.; Hennig, M. *Tetrahedron Lett.* **2003**, *44*, 2425.

Annulation



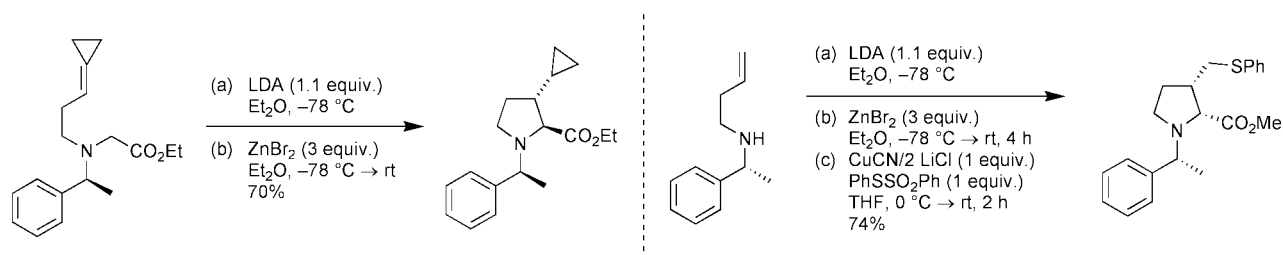
Enantioselective total syntheses of slagenins A-C and their antipodes.
Jiang, B.; Liu, J. F.; Zhao, S. Y. *J. Org. Chem.* **2003**, *68*, 2376.

Condensation



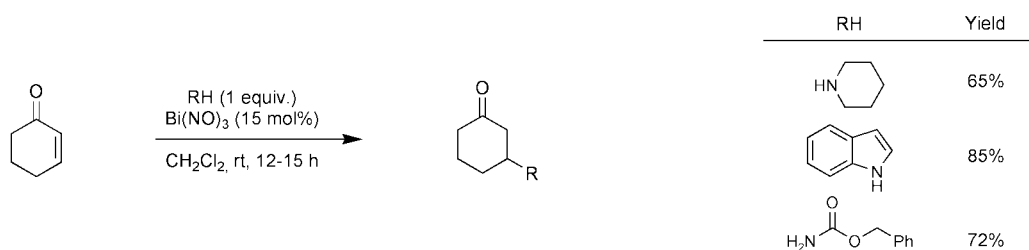
Amino-zinc-enolate carbometallation reactions: Application towards the synthesis of *cis*- and *trans*-3-prolinoleucine.
Karoyan, P.; Quancard, J.; Vaissermann, J.; Chassaing, G. *J. Org. Chem.* **2003**, *68*, 2256.

Carbometallation



Bismuth nitrate-catalyzed Michael reactions.
Srivastava, N.; Banik, B. K. *J. Org. Chem.* **2003**, *68*, 2109.

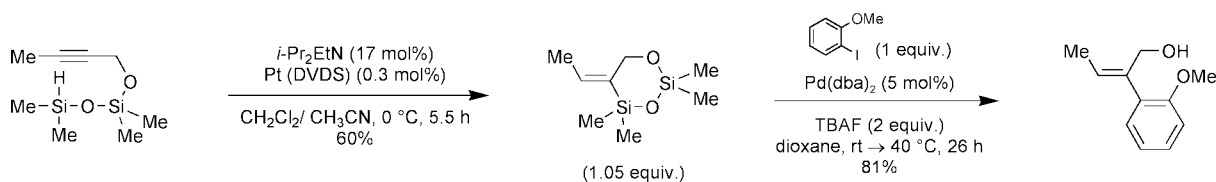
1,4-Addition



28 examples (yields 45-85%).

Intramolecular *syn* and *anti* hydrosilylation of propargylic alcohols and silicon assisted cross-coupling.
Denmark, S. E.; Pan, W. *Org. Lett.* **2003**, *5*, 1119.

Hydrosilylation/sp²-sp² Coupling

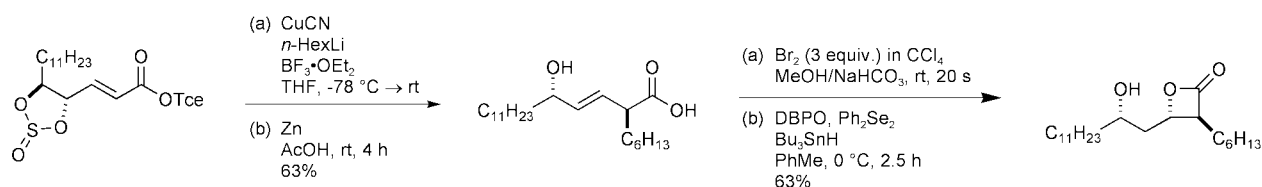


DVDS = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane.

9 examples (yields 50-82%). *Anti*-hydrosilylation product also reported using a ruthenium catalyst instead of platinum.

Bromolactonisation of α,β -unsaturated acid/radical debromination.
Bodkin, J. A.; Humphries, E. J.; McLeod, M. D. *Tetrahedron Lett.* **2003**, *44*, 2869.

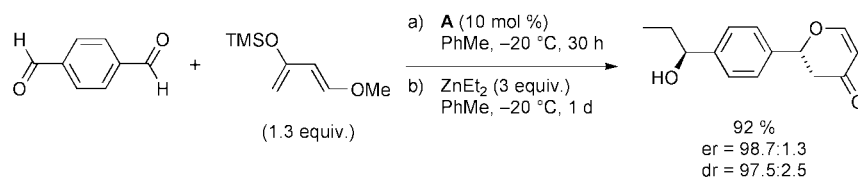
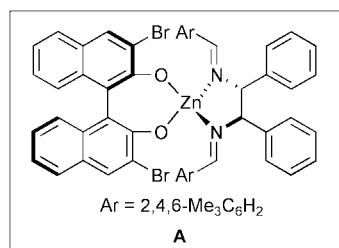
Bromolactonisation/Radical Debromination



DBPO = Di-*tert*-butylperoxyoxalate. Application towards the total synthesis of (-)-Tetrahydropipstatin.

One-pot hetero Diels–Alder reaction/diethylzinc addition using a single enantioselective catalyst.
Du, H.; Ding, K. *Org. Lett.* **2003**, *5*, 1091.

Hetero Diels–Alder/1,2-Addition

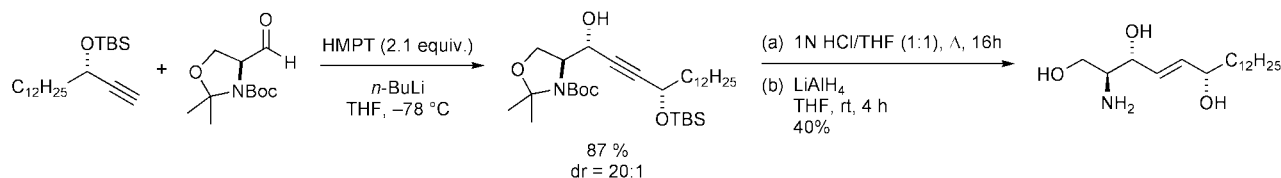


2 examples (yields 82–92%, %ee = 96–97%, %de = 95%).

Total synthesis of 6-hydroxy-4*E*-sphingenes.

1,2-Addition

Yadav, J. S.; Geetha, V.; Krishnam Raju, A.; Gnaneshwar, D.; Chandrasekhar, S. *Tetrahedron Lett.* **2003**, *44*, 2983.

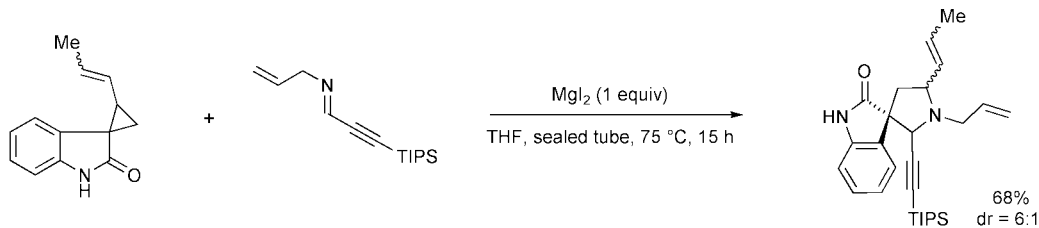


Synthesis of the other diastereomer was also reported.

Total synthesis of (–)-spirotryprostatin B.

Annulation

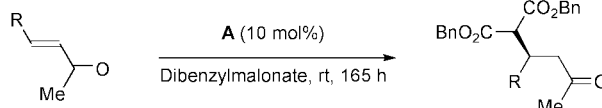
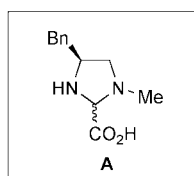
Meyers, C.; Carreira, E. *Angew. Chem. Int. Ed.* **2003**, *6*, 694.



Application towards the total synthesis of (–)-spirotryprostatin B.

Enantioselective organocatalytic conjugate addition of malonates to acyclic α,β-unsaturated enones.
Halland, N.; Aburel, P. S.; Jorgensen, K. A. *Angew. Chem. Int. Ed.* **2003**, *6*, 661.

Enantioselective 1,4-Addition

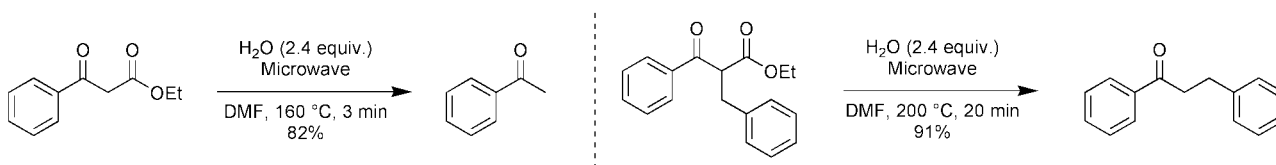


R	Yield	ee
Ph	86%	99%
2-naphthyl	99%	90%
2-pyridyl	95%	88%
<i>i</i> -Pr	33%	84%

16 examples (yields 33–99%, %ee 77–99%).

Microwave-assisted decarboalkoxylation of mono-alkylated malonates and β-ketoesters.
Curran, D. P.; Zhang, Q. *Adv. Synth. Catal.* **2003**, *3*, 329.

Decarboalkoxylation



9 examples (yields 82–96%)