

**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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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

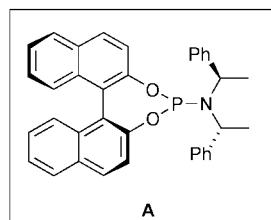
Synlett

Synthesis

Tetrahedron

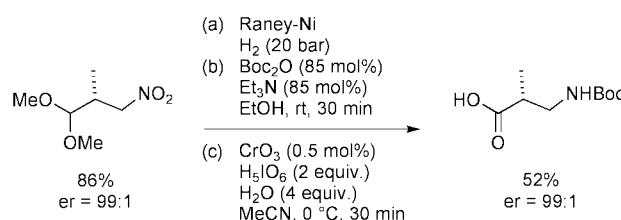
Tetrahedron Asymmetry and Tetrahedron Letters

Enantioselective conjugate addition of dialkylzinc reagents to nitroalkenes.  
Duursma, A.; Minaard, A. J.; Feringa, B. L. *J. Am. Chem. Soc.* **2003**, *125*, 3700.



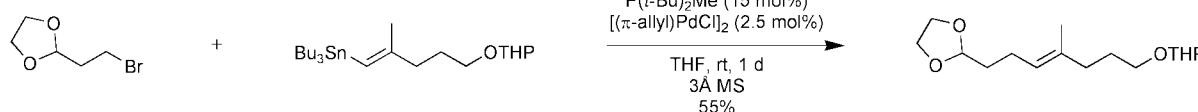
15 examples (yields 25–86%, %ee 4–96%).

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.

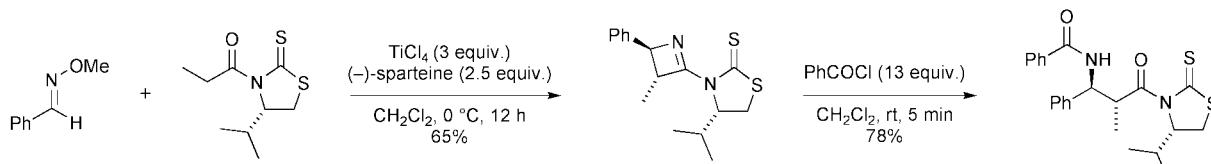
sp<sup>3</sup>-sp<sup>2</sup> Coupling



Various phosphine ligands and additives reported. 30 examples (yields 2–92%).

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**, *125*, 3690.

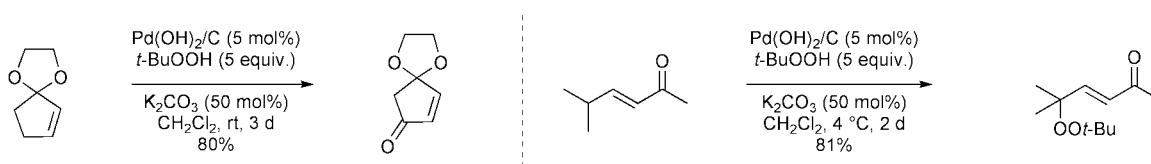
Nucleophilic Addition/Ring Closure



5 examples (yields 31–78%).

A mild catalytic method for the oxidation of  $\alpha,\beta$ -enones to 1,4-enediones.  
Yu, J-Q.; Corey, E. J. *J. Am. Chem. Soc.* **2003**, *125*, 3232.

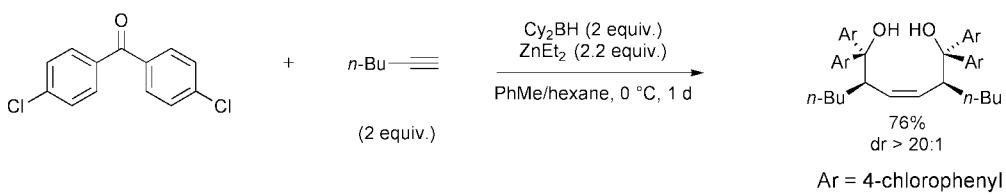
## Allylic Oxidation



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.

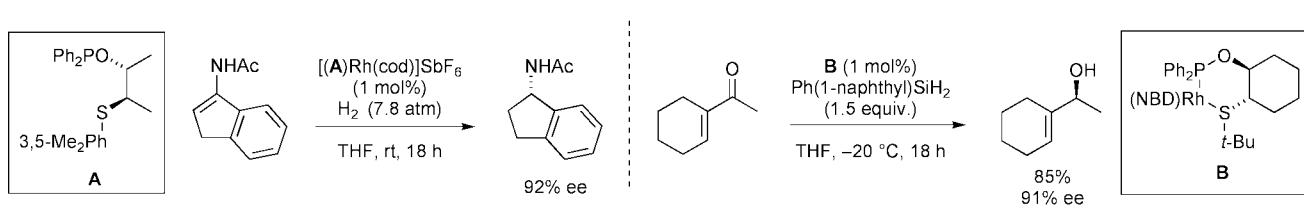
## Nucleophilic Addition



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.

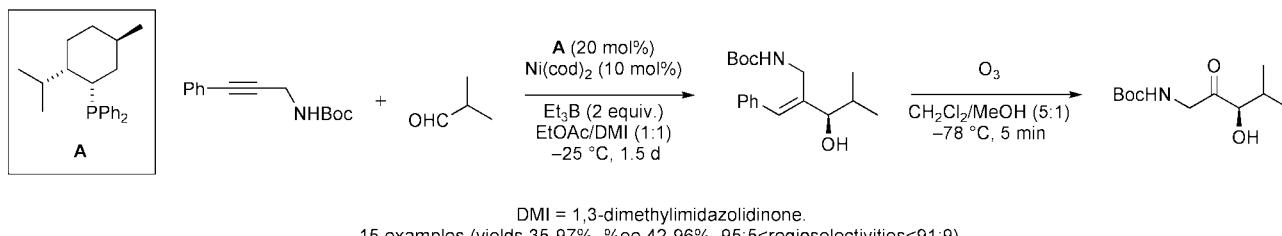
## Hydrogenation



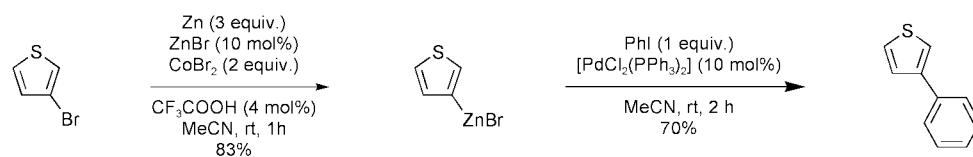
75 examples (yields 36-99%, %ee 20-99%). NBD = norbadiene.

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

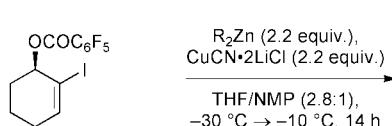
DMI = 1,3-dimethylimidazolidinone  
15 examples (yields 35-97%, %ee 42-96%, 95:5<regioselectivities<91:9).

Synthesis of arylzinc compounds from aromatic bromides using CoBr2 and zinc dust.  
Fillon, H.; Gosmini, C.; Péridon, J. *J. Am. Chem. Soc.* **2003**, *125*, 3867.

Metallation/sp<sup>2</sup>-sp<sup>2</sup> Coupling

31 examples (yields 3-100%).

*Anti-selective S<sub>N</sub>2' 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<sub>N</sub>2' Reaction**

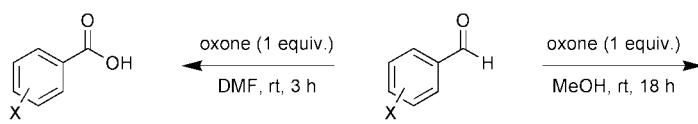
R	Yield	ee
Pent	91%	93%
Et	85%	93%
c-Hex	90%	91%
i-Pr	70%	93%

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**

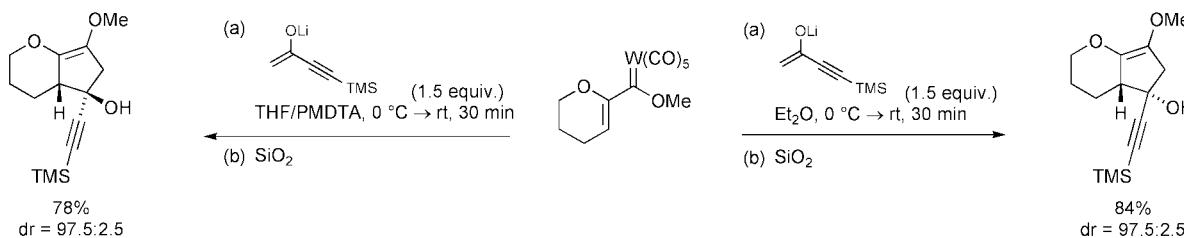
X	Yield
4-NO <sub>2</sub>	95%
4-CN	85%
H	97%
4-Me	97%
4-Cl	97%



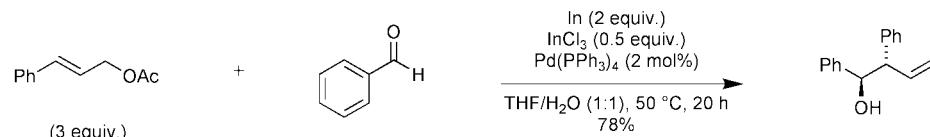
X	Yield
4-NO <sub>2</sub>	98%
4-CN	98%
H	96%
4-Me	94%
4-Cl	98%

43 examples (yields 0-98%).

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

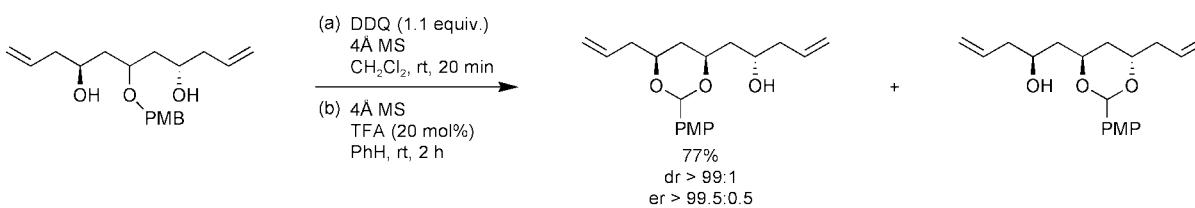
**[3+2] Cycloaddition**PMDTA = *N,N,N',N',N''*-pentamethyldiethylenetriamine. 45 examples (yields 68-95%, %de 0-95%).

Palladium catalyzed allylation of carbonyl compounds using In-InCl<sub>3</sub>.  
Jang, T-S.; Keum, G.; Kang, S. B.; Chung, B. Y.; Kim, Y. *Synthesis*, **2003**, 775.

**Allylmetallation**

50 examples (yields 5-100%).

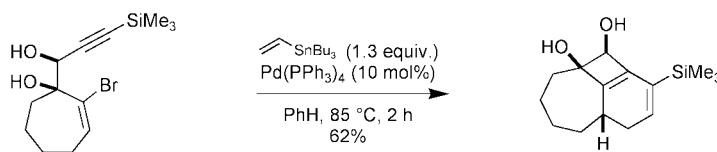
Synthesis of polyketides via diastereoselective acetalization.  
Shepherd, J. N.; Myles, D. C. *Org. Lett.* **2003**, *5*, 1027.

**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.

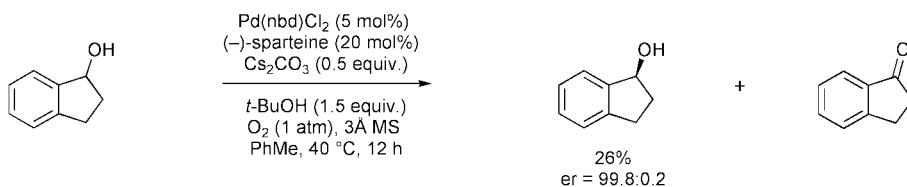
Cyclization



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.

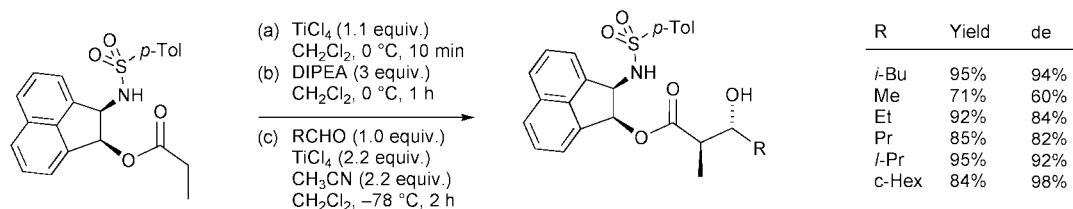
Kinetic Resolution: Oxidation



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

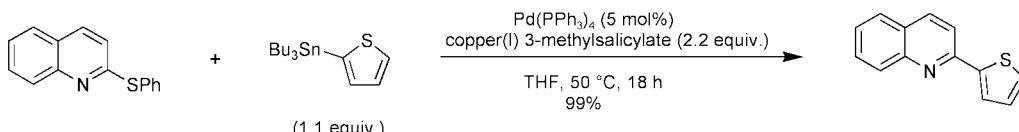
Diastereoselective anti-aldol reactions of cis-2-arylsulfonamido-1-acenaphthenyl propionate.  
Ghosh, A. K.; Kim, J.-H. *Org. Lett.* **2003**, 5, 1063.

Aldol Reaction



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

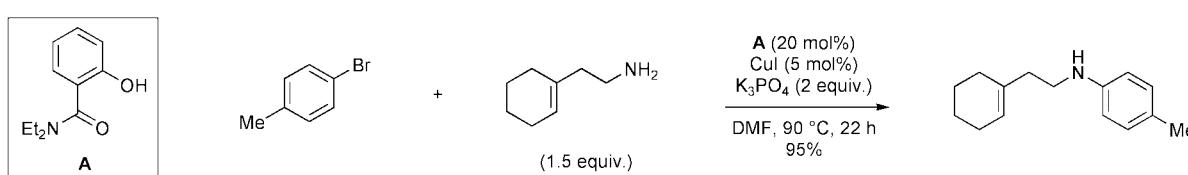
Heteroaromatic thioether-organostannane cross-coupling.  
Egi, M.; Liebeskind, L. S. *Org. Lett.* **2003**, 5, 801.

sp<sup>2</sup>-sp<sup>2</sup> Cross-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.

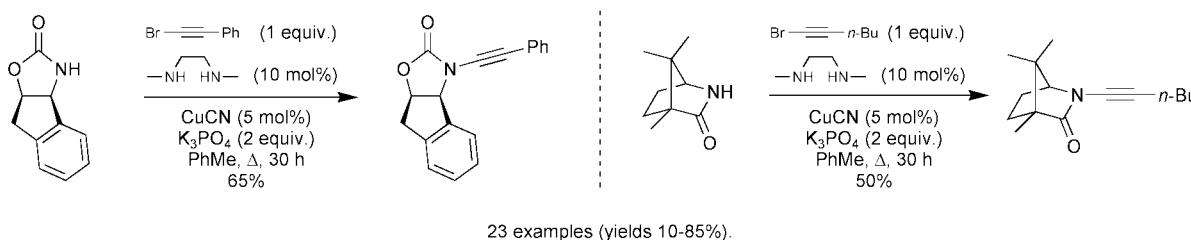
Amination



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

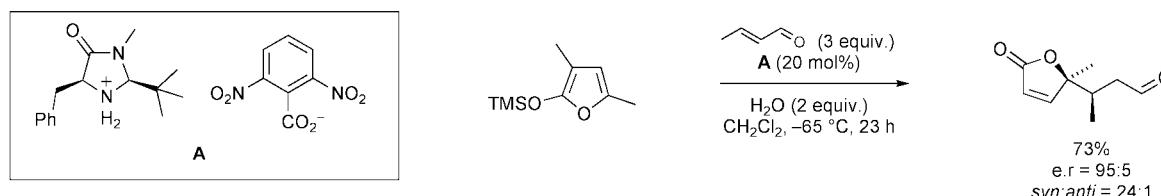
## Synthesis of chiral ynamides via a copper-catalyzed N-alkynylation of amides.

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-sp<sup>3</sup> Coupling**

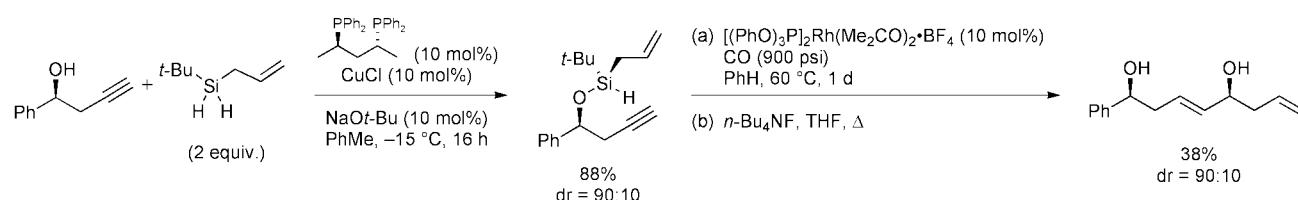
## Enantioselective organocatalytic Mukaiyama–Michael reaction.

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

**Mukaiyama/1,4-Addition**

## Catalytic, asymmetric silane alcoholysis: Access to chiral silanes.

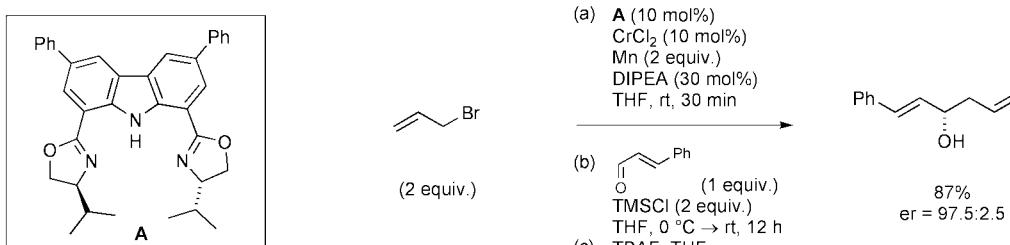
Schmidt, D. R.; O’Malley, S. J.; Leighton, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 1190.

**Hydroformylation/Allylmetallation**

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

## Asymmetric catalysis of Nozaki-Hiyama allylation.

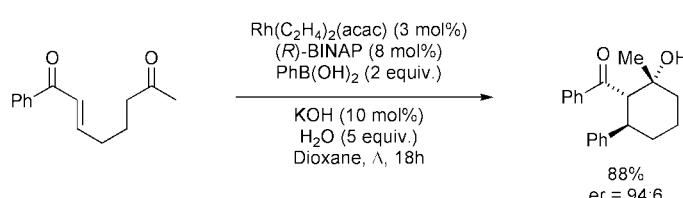
Inoue, M.; Suzuki, T.; Nakada, M. *J. Am. Chem. Soc.* **2003**, *125*, 1140.

**Allylmetallation**

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

## Catalytic, asymmetric carbometallative aldol cycloreduction.

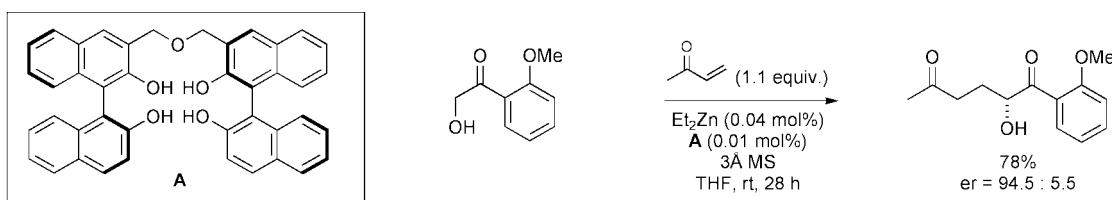
Cable, D. F.; Gipson, J. D.; Krische, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 1110.

**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.

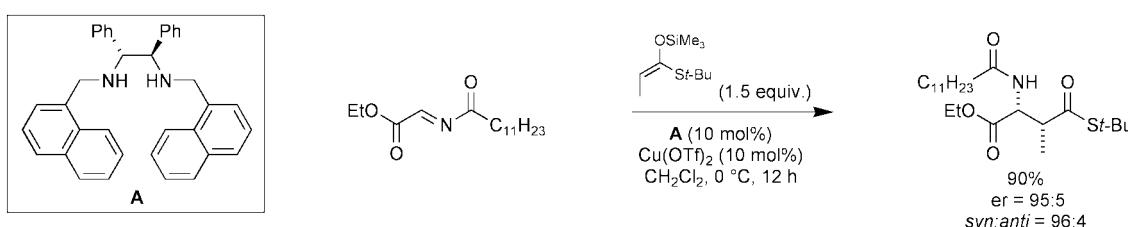
## Enantioselective 1,4-Addition



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.

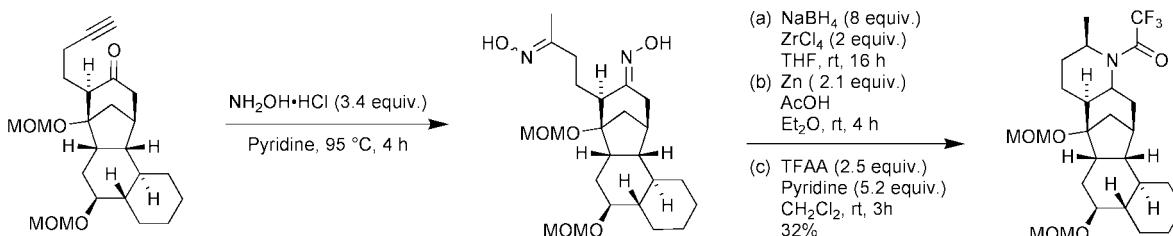
## Mannich Reaction



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.

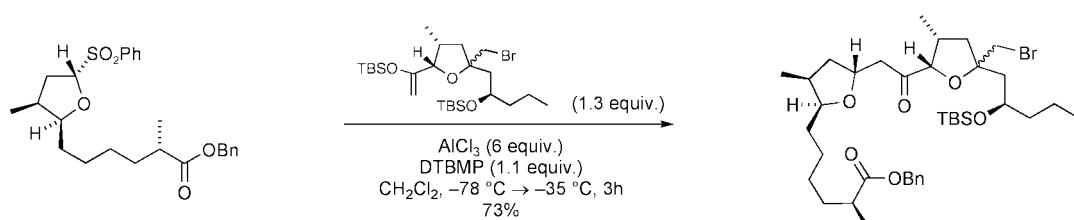
## Annulation



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.

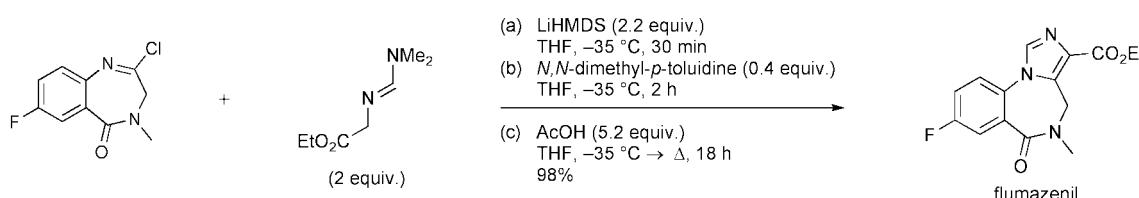
## Alkylation



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

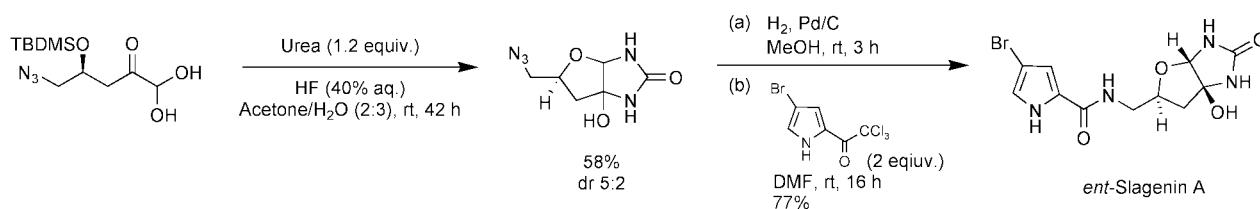
Synthesis of flumazenil *via* an isolated benzodiazepine iminochloride.  
Rogers-Evans, M.; Spurr, P.; Hennig, M. *Tetrahedron Lett.* **2003**, *44*, 2425.

## Annulation

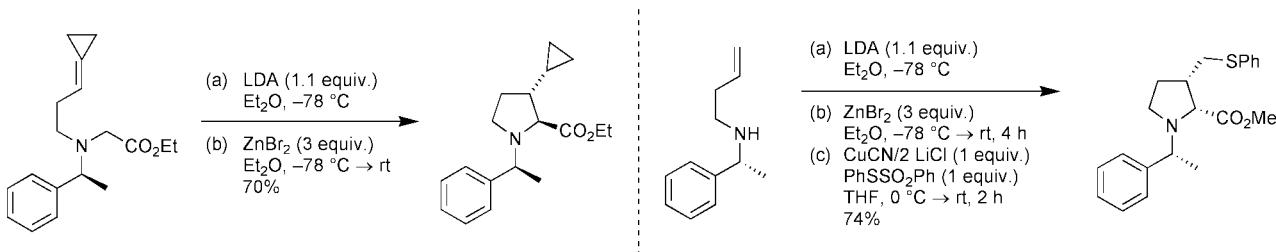


Enantioselective total syntheses of slagenins A-C and their antipodes.  
Jiang, B.; Liu, J. F.; Zhao, S. Y. *J. Org. Chem.* **2003**, *68*, 2376.

## Condensation

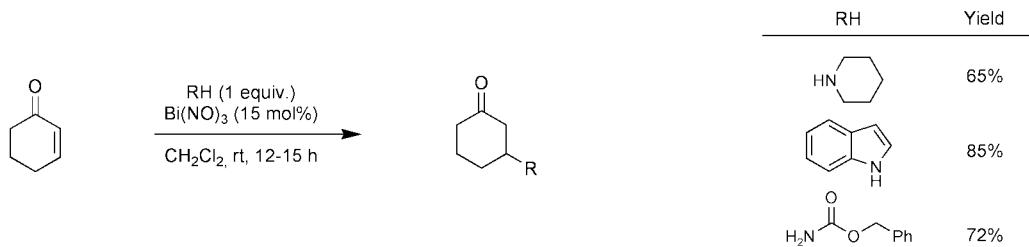


Amino-zinc-enolate carbometallation reactions: Application towards the synthesis of *cis*- and *trans*-3-prolinoleucine. *Carbometallation*  
Karoyan, P.; Quancard, J.; Vaissermann, J.; Chassaing, G. *J. Org. Chem.* **2003**, *68*, 2256.

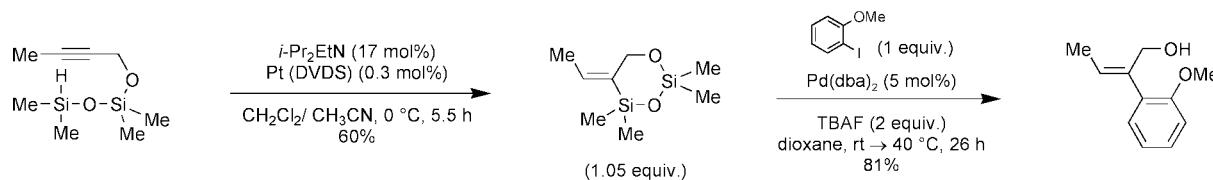


Bismuth nitrate-catalyzed Michael reactions.  
Srivastava, N.; Banik, B. K. *J. Org. Chem.* **2003**, *68*, 2109.

## 1,4-Addition



Intramolecular *syn* and *anti* hydrosilylation of propargylic alcohols and silicon assisted cross-coupling. *Hydrosilylation/sp<sup>2</sup>-sp<sup>2</sup> Coupling*  
Denmark, S. E.; Pan, W. *Org. Lett.* **2003**, *5*, 1119.

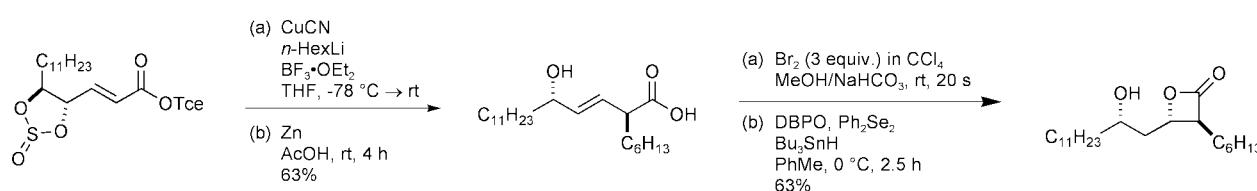


DVDS = 1,3-divinyl-1,1,3,3-tetramethylidisiloxane.

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

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

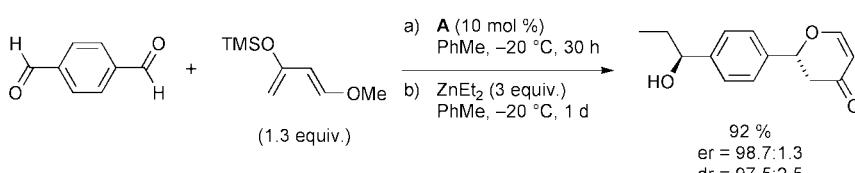
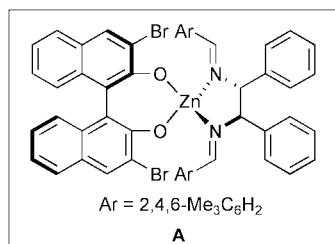
## Bromolactonisation/Radical Debromination



DBPO = Di-*tert*-butylperoxyxalate. Application towards the total synthesis of (-)-Tetrahydrolipstatin.

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

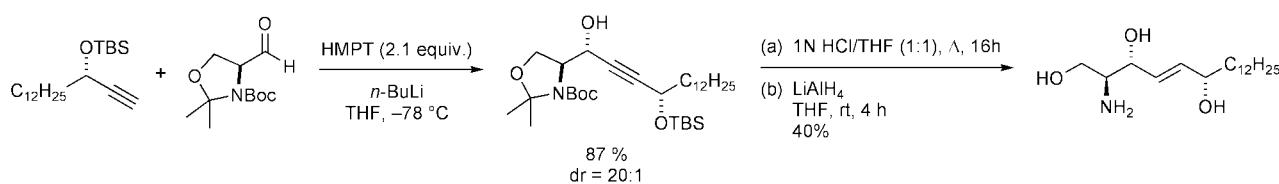


2 examples (yields 82–92%, %ee = 96–97%, %de = 95%).

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

## 1,2-Addition

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

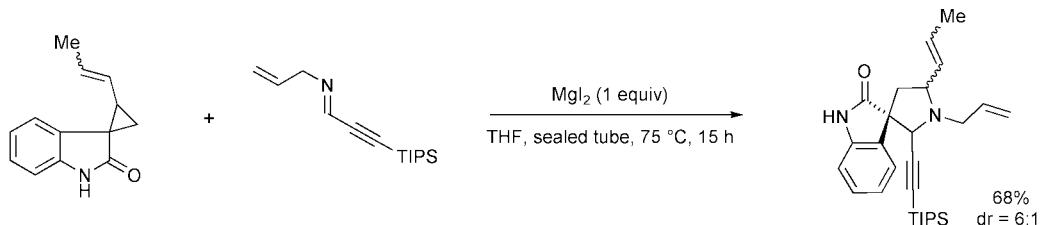


Synthesis of the other diastereomer was also reported.

Total synthesis of (–)-spirotryprostatin B.

## Annulation

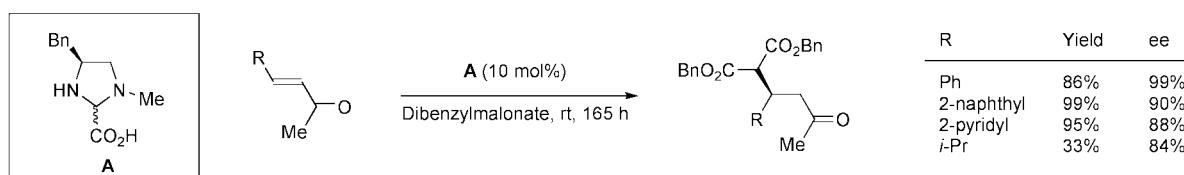
Meyers, C.; Carreira, E. *Angew. Chem. Int. Ed.* **2003**, *42*, 694.



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

Enantioselective organocatalytic conjugate addition of malonates to acyclic  $\alpha,\beta$ -unsaturated enones.  
Halland, N., Aburel, P. S., Jorgensen, K. A. *Angew. Chem. Int. Ed.* **2003**, *42*, 661.

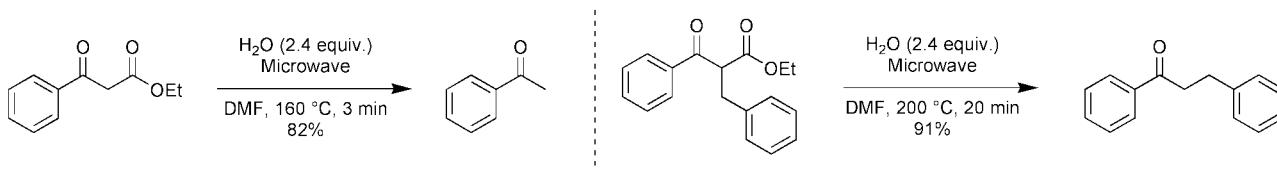
## Enantioselective 1,4-Addition



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

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

## Decarboalkylation



9 examples (yields 82–96%)