

**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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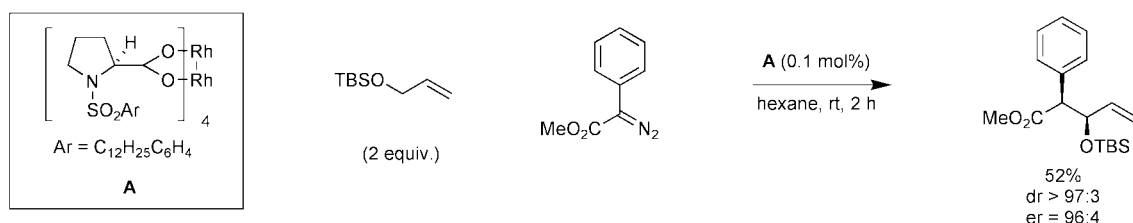
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The journals regularly covered by the abstractors are:

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

Synthesis of silyl-protected  $\beta$ -hydroxy esters via a catalytic, asymmetric C-H insertion.  
 Davies, H. M. L.; Beckwith, R. E. J.; Antoulinakis, E. G.; Jin, Q. *J. Org. Chem.* **2003**, *68*, 6126.

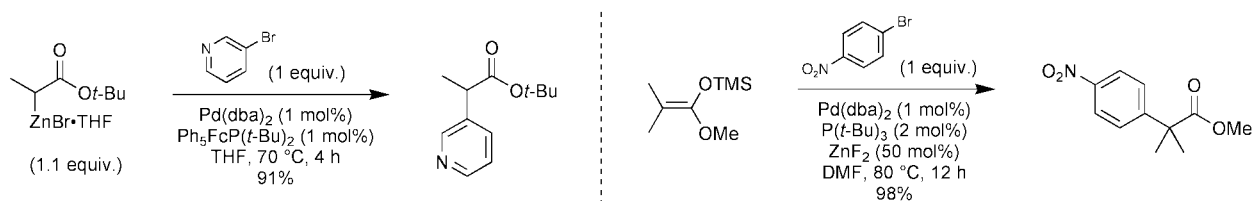
C-H Insertion



39 examples (yields 23-98%, %de 40-98%, %ee 62-96%). The use of allyl and alkyl silyl ethers is reported.

Pd-catalyzed  $\alpha$ -arylation of esters and amides under neutral conditions.  
 Hama, T.; Liu, X.; Culkin, D. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 11176.

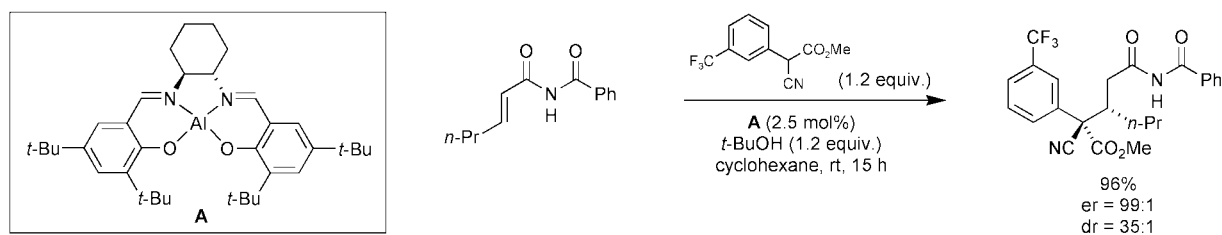
sp<sup>3</sup>-sp<sup>2</sup> Coupling



Reformatsky reagents: 29 examples (yields 66-97%). Silyl ketene acetals: 12 examples (yields 67-99%). Fc = ferrocenyl.

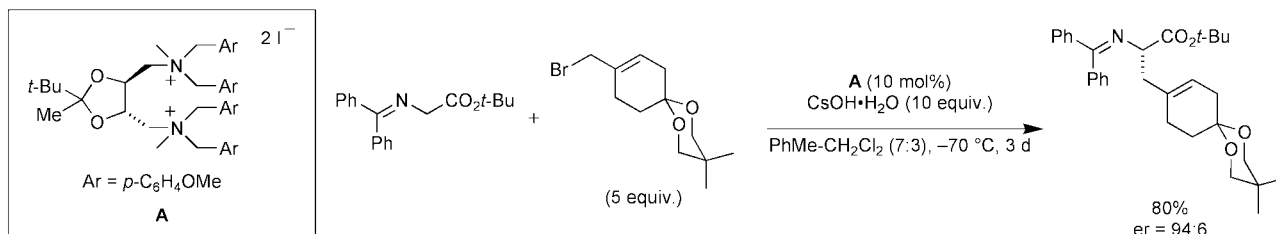
Enantioselective Michael additions to  $\alpha,\beta$ -unsaturated imides.  
 Taylor, M. S.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2003**, *125*, 11204.

1,4-Addition

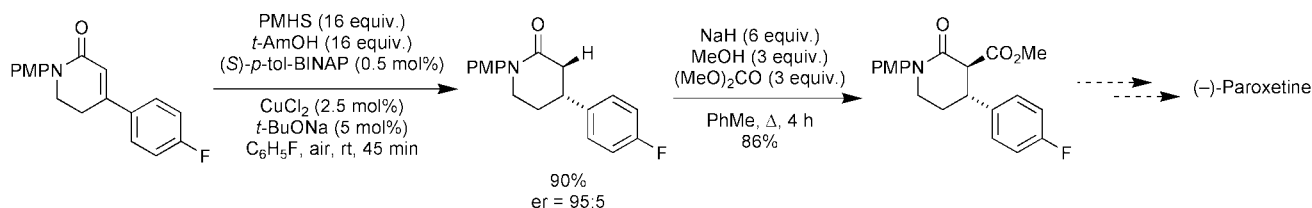


22 examples (yields 68-99%, %ee 86-98%).

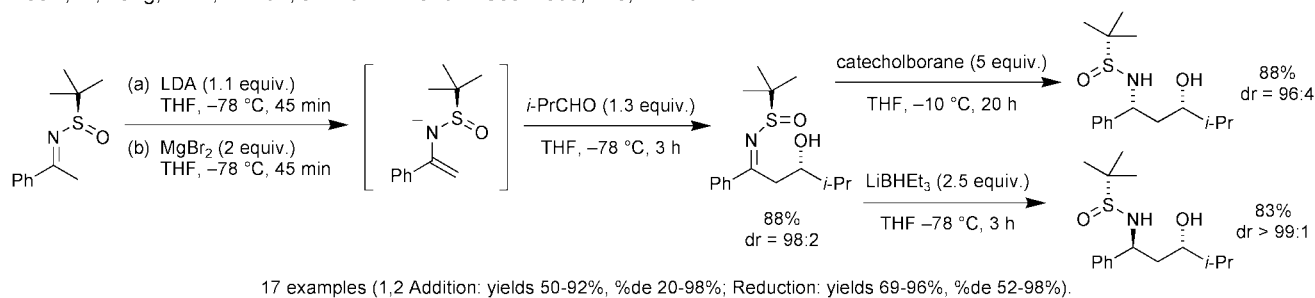
Synthesis of Aeruginosin 298-A utilising a catalytic asymmetric phase-transfer alkylation. Ohshima, T.; Gnanadesikan, V.; Shibuguchi, T.; Fukuta, Y.; Nemoto, T.; Shibasaki, M. *J. Am. Chem. Soc.* **2003**, *125*, 11206. **Asymmetric Alkylation**



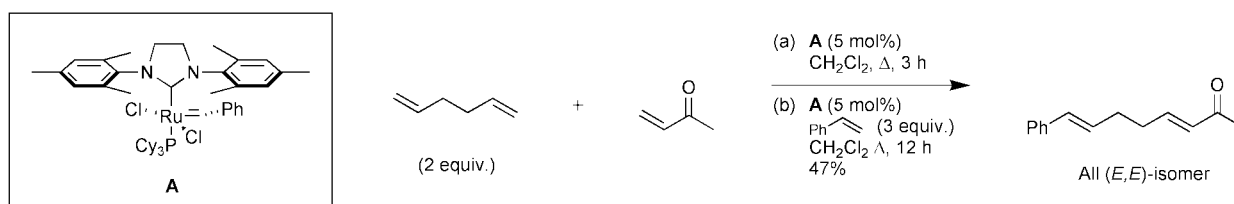
Catalytic enantioselective conjugate reduction of lactones and lactams. Hughes, G.; Kimura, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 11253. **Conjugate Reduction**



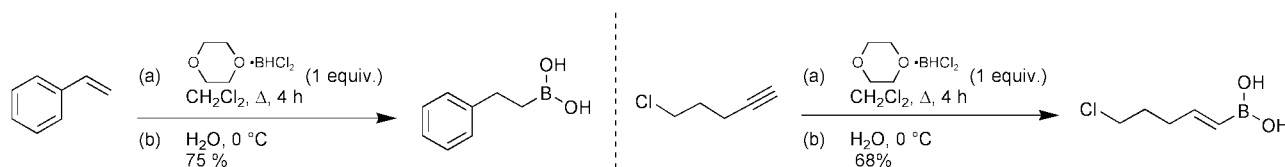
Asymmetric synthesis of *syn* and *anti*-1,3-amino alcohols. Kochi, T.; Tang, T. P.; Ellman, J. A. *J. Am. Chem. Soc.* **2003**, *125*, 11276. **Diastereoselective 1, 2-Addition/Reduction**



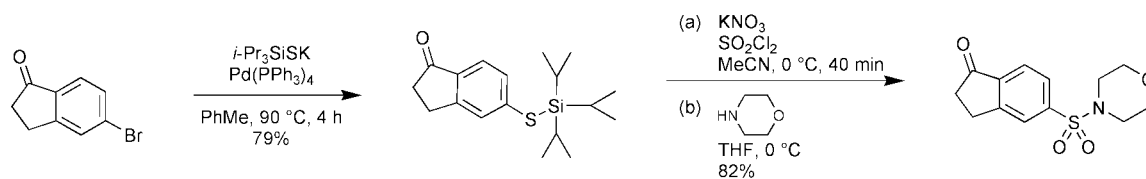
A general model for selectivity in olefin cross-metathesis. Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360. **Cross-Metathesis**



Preparation of alkenyl- and alkylboronic acids using a dichloroborane-dioxane reagent. Josyula, K. V. B.; Gao, P.; Hewitt, C. *Tetrahedron Lett.* **2003**, *44*, 7789. **Hydroboration**

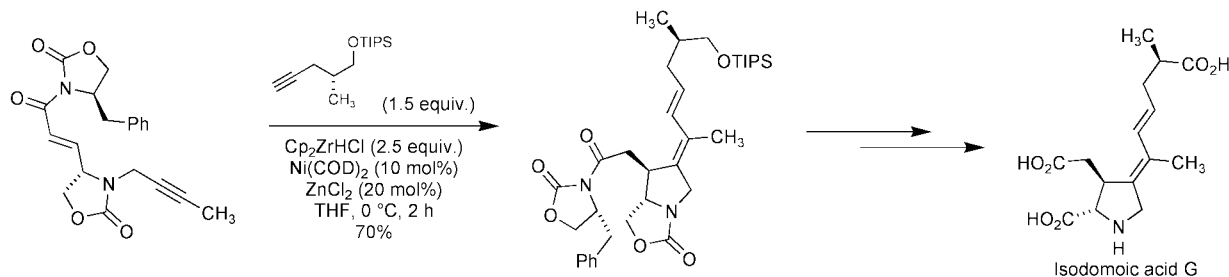


Synthesis of sulfonamides from triisopropylsilylanyl sulfanyl.

Gareau, Y.; Pellicelli, J.; Laliberte, S.; Gauvreau, D. *Tetrahedron Lett.* **2003**, *44*, 7821.sp<sup>3</sup>-sp<sup>2</sup> Coupling

18 examples (yields 9-71%).

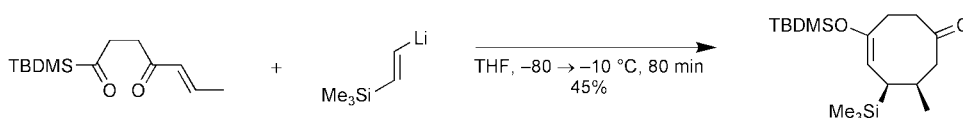
First total synthesis and stereochemical definition of Isodomoic acid G.

Ni, Y.; Amarasinghe, K. K. D.; Ksebati, B.; Montgomery, J. *Org. Lett.* **2003**, *5*, 3771.sp-sp<sup>2</sup> Coupling/1,4-Addition

Synthesis of eight-membered carbocycles by Brook rearrangement mediated annulation.

Takeda, K.; Haraguchi, H.; Okamoto, Y. *Org. Lett.* **2003**, *5*, 3705.

Annulation

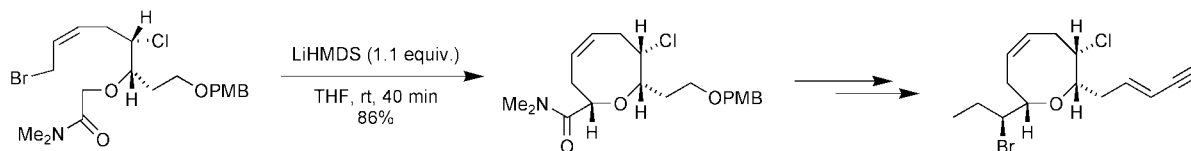


4 examples (yields 42-45%).

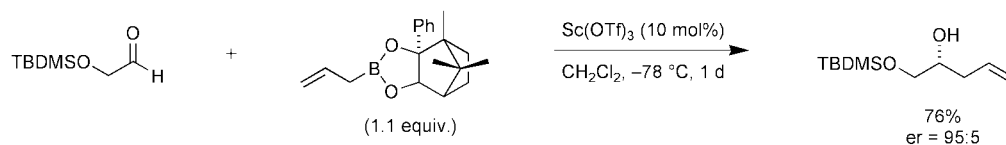
Olefin-geometry dependent internal alkylation: asymmetric total synthesis of (+)-3-(E)- and (+)-3-(Z)-Pinnatidienyne.

Kim, H.; Choi, W. J.; Jung, J.; Kim, S.; Kim, D. *J. Am. Chem. Soc.* **2003**, *125*, 10238.

Alkylation

The *trans* allylic halide gave exclusively S<sub>N</sub>2' product, whilst the *cis* allylic halide gave predominantly the S<sub>N</sub>2 product.Sc(OTf)<sub>3</sub> catalyzed enantioselective allylboration.Lachance, H.; Lu, X.; Gravel, M.; Hall, D. G. *J. Am. Chem. Soc.* **2003**, *125*, 10160.

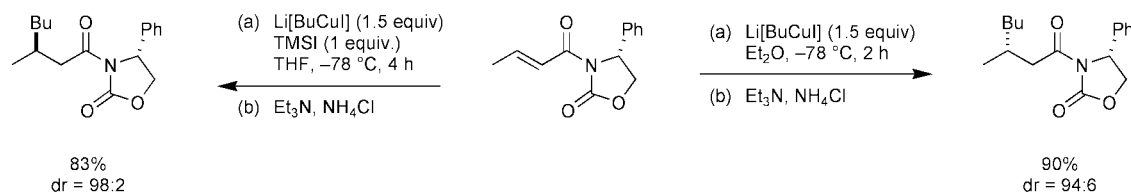
Asymmetric Allylation



12 examples of allylations (yields 62-90%, %ee 77-98%). 8 examples of crotylations (yields 52-74%, %ee 94-97%, %de &gt;98%).

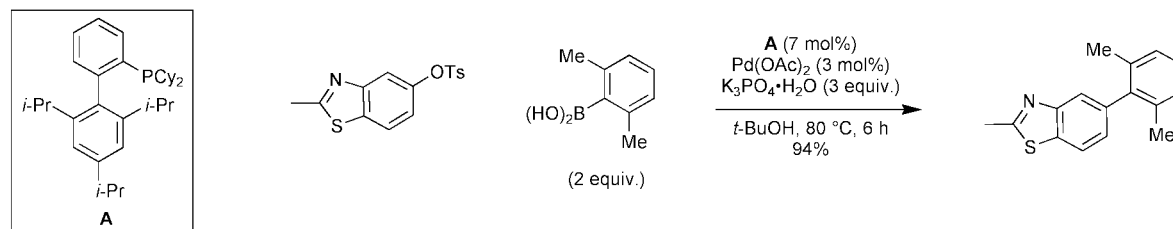
Reversal of the stereoselectivity in the conjugate addition of Li[BuCu] to a chiral *N*-crotyl-2-oxazolidinone.  
Dambacher, J.; Bergdahl, M. *Org. Lett.* **2003**, *5*, 3539.

1,4-Addition



Optimization studies investigated.

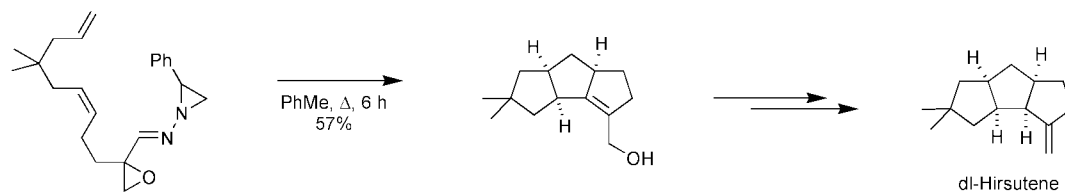
Pd-catalyzed Suzuki-Miyaura and carbonyl enolate coupling of aryl sulfonates.  
Nguyen, H. N.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 11818.

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

10 examples of Suzuki-Miyaura couplings and 6 examples of carbonyl enolate couplings with aryl sulfonates (yields 75-95%).

Triquinanes from alkylidene carbenes via trimethylene diyls.  
Lee, H.-Y.; Kim, Y. *J. Am. Chem. Soc.* **2003**, *125*, 10156.

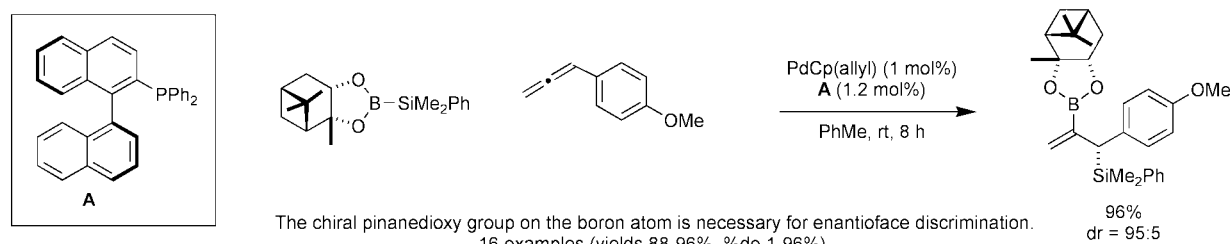
Carbene Insertion/Radical Cyclization



7 examples of cyclization step (yields 35-68%).

Enantioselective palladium-catalyzed silaboration of allenes.  
Suginome, M.; Ohmura, T.; Miyake, Y.; Mitani, S.; Ito, Y.; Murakami, M. *J. Am. Chem. Soc.* **2003**, *125*, 11174.

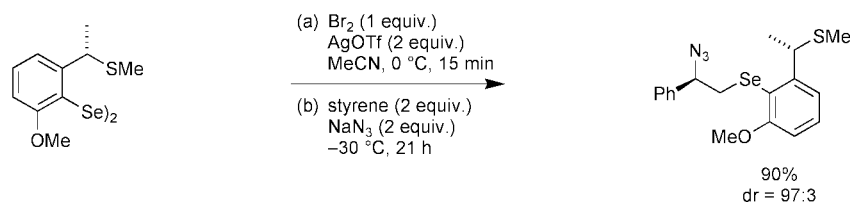
Silaboration



The chiral pinanedioxy group on the boron atom is necessary for enantioface discrimination.  
16 examples (yields 88-96%, %de 1-96%).

Asymmetric azidoselenenylation of alkenes.  
Tiecco, M.; Testaferri, L.; Santi, C.; Tomassini, C.; Marini, F.; Bagnoli, L. *Angew. Chem. Int. Ed.* **2003**, *42*, 3131.

Asymmetric Addition

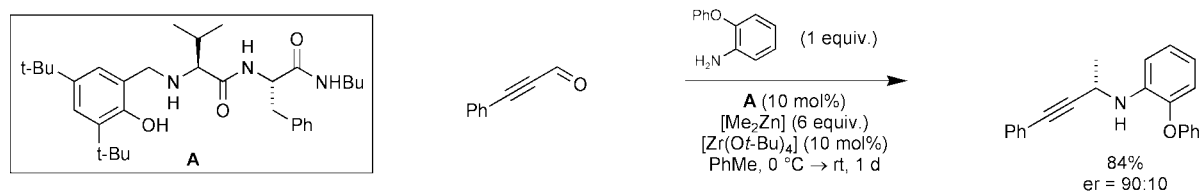


6 examples (yields 70-90%, %de 90-98%).

Conversion of azidoselenenides into optically active oxazolines, aziridines and triazoles is described.

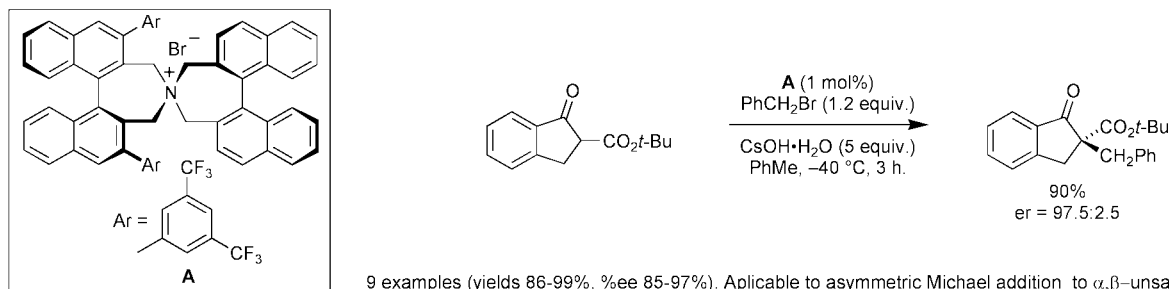
Enantioselective Zr-catalyzed addition of alkylzinc reagents to alkynylimines.  
Akullian, L. C.; Snapper, M. L.; Hoveyda, A. M. *Angew. Chem. Int. Ed.* **2003**, *42*, 4244.

## Asymmetric Addition



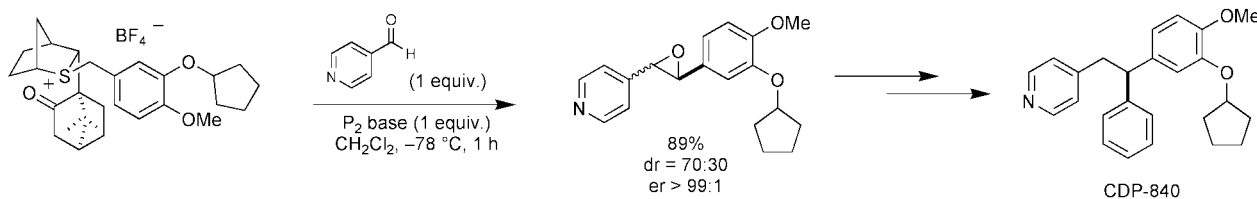
Phase-transfer catalytic asymmetric alkylation and Michael reaction on  $\beta$ -keto esters.  
Ooi, T.; Miki, T.; Taniguchi, M.; Shiraishi, M.; Takeuchi, M.; Maruoka, K. *Angew. Chem. Int. Ed.* **2003**, *42*, 3796.

## Alkylation/1,4-Addition



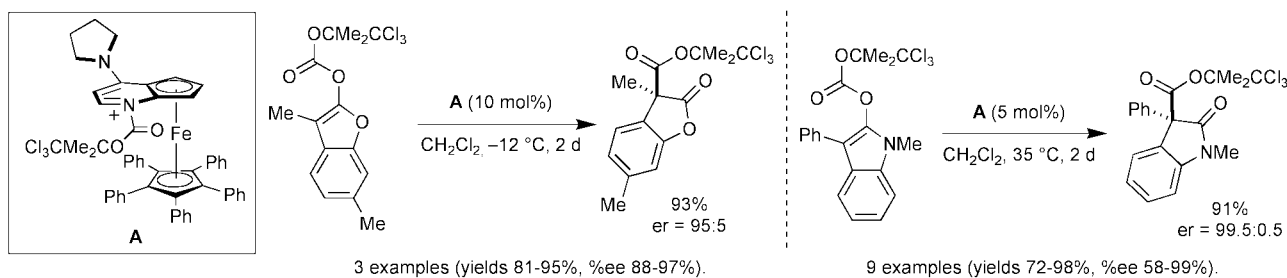
Sulfur-ylide mediated synthesis of epoxides.  
Aggarwal, V. K.; Bae, I.; Lee, H. Y.; Richardson, J.; Williams, D. T. *Angew. Chem. Int. Ed.* **2003**, *42*, 3274.

## Asymmetric Epoxidation



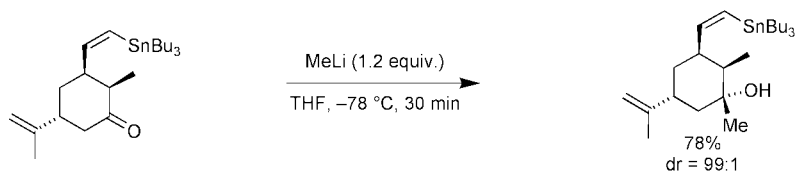
Enantioselective synthesis of oxindoles and benzofuranones.  
Hills, I. D.; Fu, G. C. *Angew. Chem. Int. Ed.* **2003**, *42*, 3921.

## O-C Rearrangement



Diastereoselective addition of organometallic compounds to tin containing cyclic ketones.  
Barbero, A.; Pulido, F. J.; Rincon, J. A. *J. Am. Chem. Soc.* **2003**, *125*, 12049.

## Diastereoselective Nucleophilic Addition

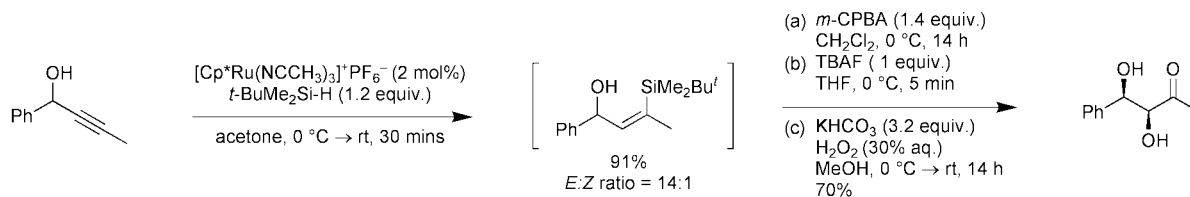


Proposed mechanism is *via* a chelation controlled intramolecular nucleophile transfer, with an optimum Sn/CO distance of 5 bonds.  
27 examples (yields 71-96%, %de 50-98%).



Regioselective hydrosilylation of propargylic alcohols as an aldol surrogate.  
Trost, B. M.; Ball, Z. T.; Jöge, T. *Angew. Chem. Int. Ed.* **2003**, *42*, 3145.

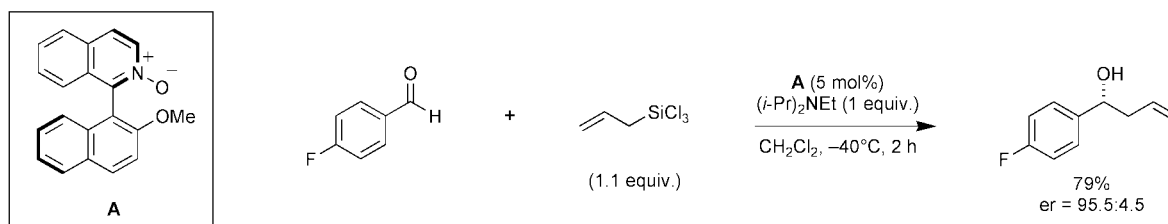
## Hydrosilylation



13 hydrosilylation examples (yields 8-99%, *E:Z* ratio 5:1->20:1).

Asymmetric allylation of aromatic aldehydes catalyzed by an isoquinoline N-oxide derivative.  
Malkov, A. V.; Dufková, L.; Farrugia, L.; Kocovsky, P. *Angew. Chem. Int. Ed.* **2003**, *42*, 3674.

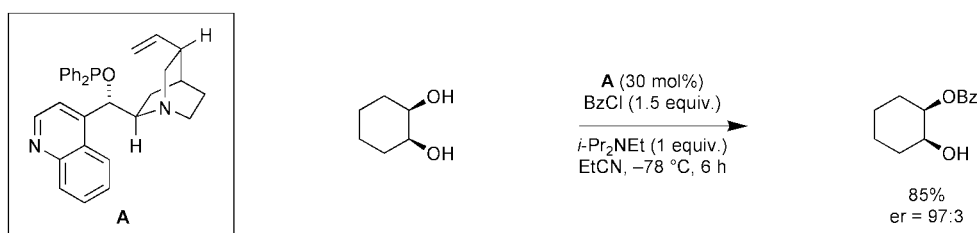
## Asymmetric Allylation



16 examples (yields 25-86%, %ee 5-96%).

Asymmetric desymmetrization of *meso*-1,2-diols by phosphinite derivatives of Cinchona alkaloids.  
Mizuta, S.; Sadamori, M.; Fujimoto, T.; Yamamoto, I. *Angew. Chem. Int. Ed.* **2003**, *42*, 3383.

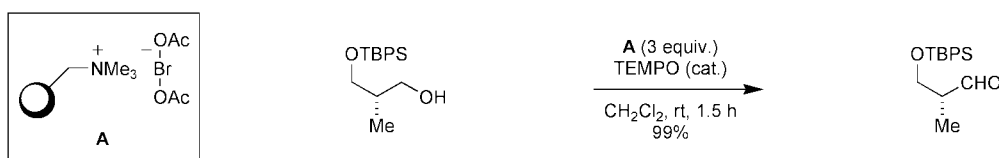
## Desymmetrization



5 examples (yields 80-99%, %ee 76-94%).

TEMPO-mediated oxidations of primary and secondary alcohols assisted by a polymer-bound bromate complex.  
Brünjes, M.; Sourkouni-Argirusi, G.; Kirschning, A. *Adv. Synth. Catal.* **2003**, 635.

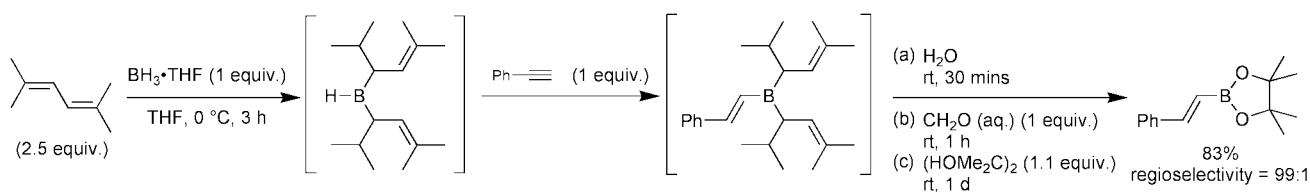
## Oxidation



20 examples (yields 56-99 %).

A new hydroboration reagent for the synthesis of alkyl and alkenyl boronic acids.  
Kalinin, A. V.; Scherer, S.; Snieckus, V. *Angew. Chem. Int. Ed.* **2003**, *42*, 3399.

## Hydroboration

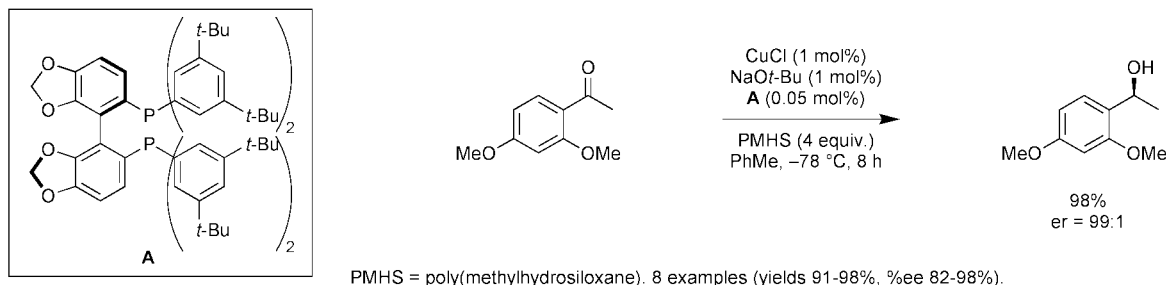


38 examples (yields 41-86%, regioselectivities 83:17-100).

A sequential one-pot hydroboration/Suzuki-Miyaura cross coupling is also reported.

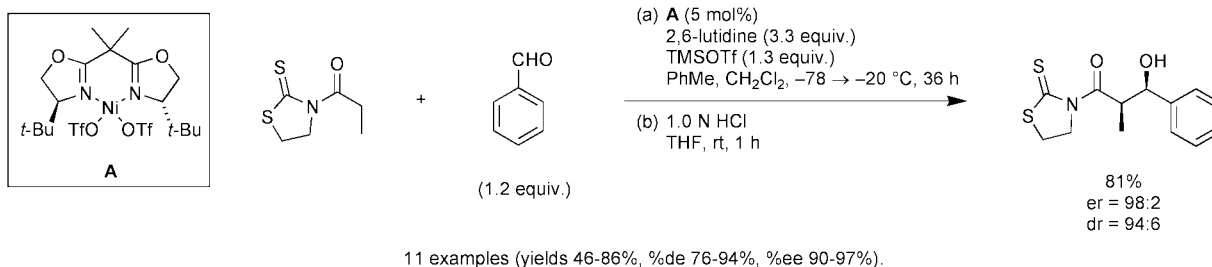
Asymmetric hydrosilylation of aryl ketones catalyzed by copper hydride.  
Lipshutz, B. H.; Noson, K.; Chrisman, W.; Lower, A. *J. Am. Chem. Soc.* **2003**, *125*, 8779.

## Asymmetric Hydrosilylation



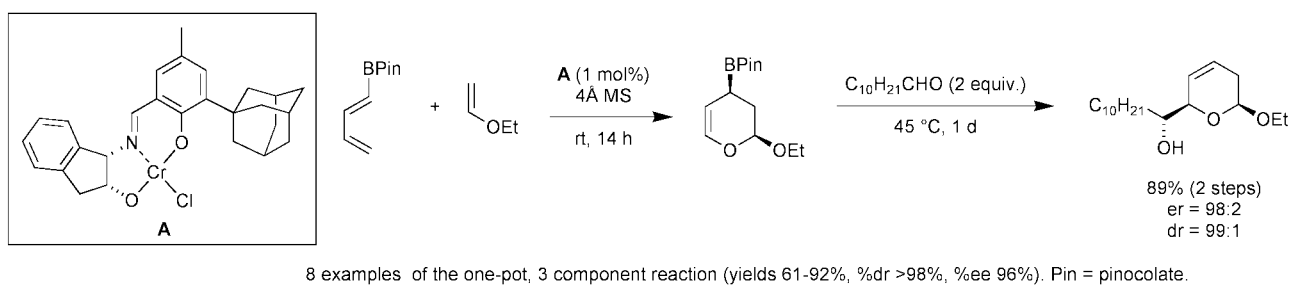
Enantioselective *syn*-Aldol reaction in the presence of silyl triflates.  
Evans, D. A.; Downey, C.W.; Hubbs, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 8706.

## Catalytic Asymmetric Aldol



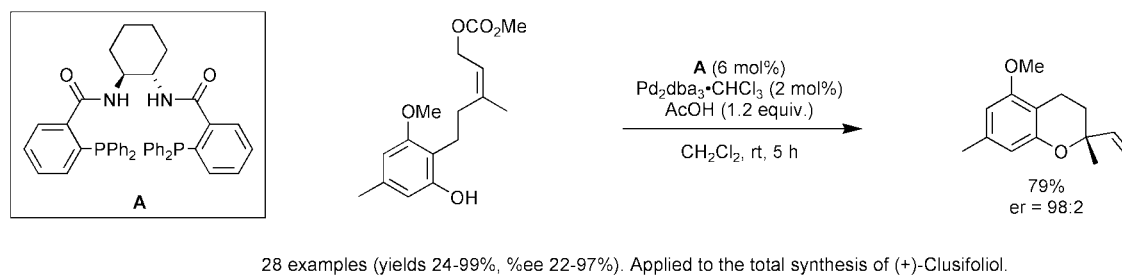
Enantio- and diastereoselective Cr(III)-catalyzed three-component [4+2]/allylboration.  
Gao, X.; Hall, D. G., A. *J. Am. Chem. Soc.* **2003**, *125*, 9308.

## Hetero[4+2]/Allylboration



Synthesis of chiral chromans.  
Trost, B. M.; Shen, H. C.; Dong, L.; Surivet, J.-P., A. *J. Am. Chem. Soc.* **2003**, *125*, 9276.

## Asymmetric Allylic Alkylation



Suzuki cross-coupling of sterically hindered aryl chlorides with a new *N*-heterocyclic carbene ligand.  
Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *Angew. Chem. Int. Ed.* **2003**, *42*, 3690.

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