

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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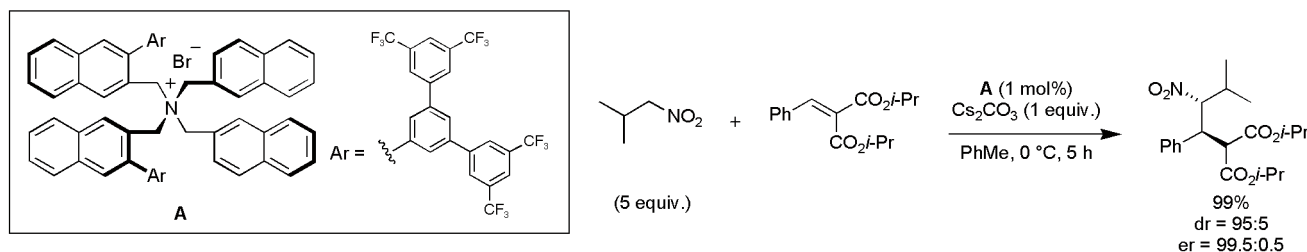
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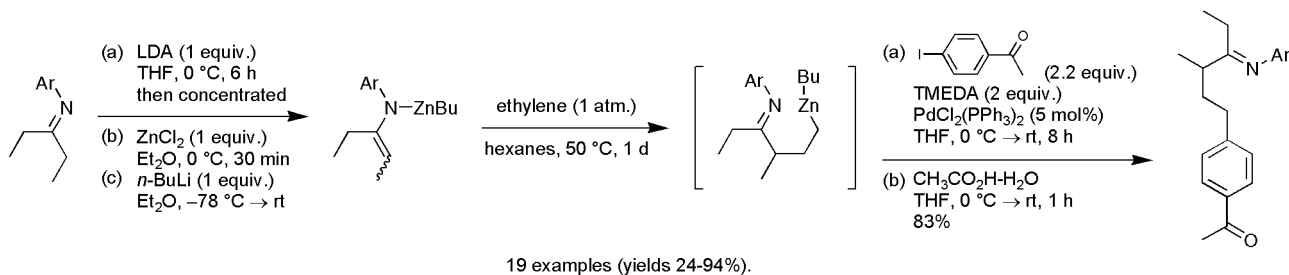
The journals regularly covered by the abstractors are:

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
 Tetrahedron Letters

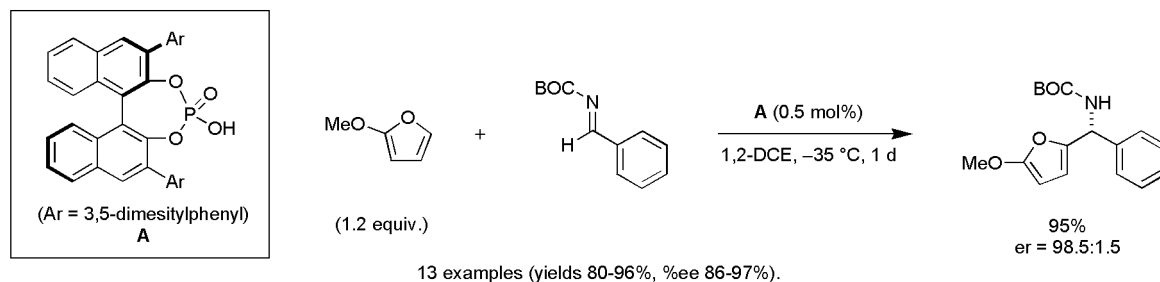
Enantioselective conjugate addition of nitroalkanes to alkylidenemalonates using phase-transfer catalysis. **Asymmetric 1,4-Addition**
 Ooi, T.; Fujioka, S.; Maruoka, K. *J. Am. Chem. Soc.* **2004**, *126*, 11790.



α -Alkylation of ketones by addition of zinc enamides to unactivated olefins. **C-C Bond Formation**
 Nakamura, M.; Hatakeyama, T.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 11820.

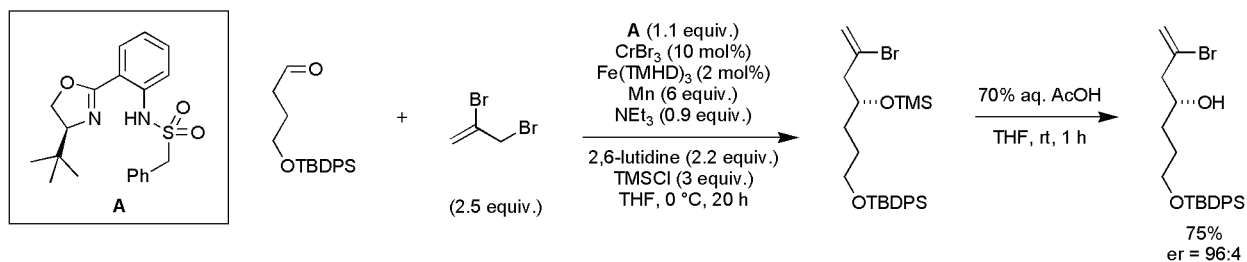


Organocatalytic asymmetric aza-Friedel-Crafts alkylation of furan. **Asymmetric 1,2-Addition**
 Uruguchi, D.; Sorimachi, K.; Terada, M. *J. Am. Chem. Soc.* **2004**, *126*, 11804.



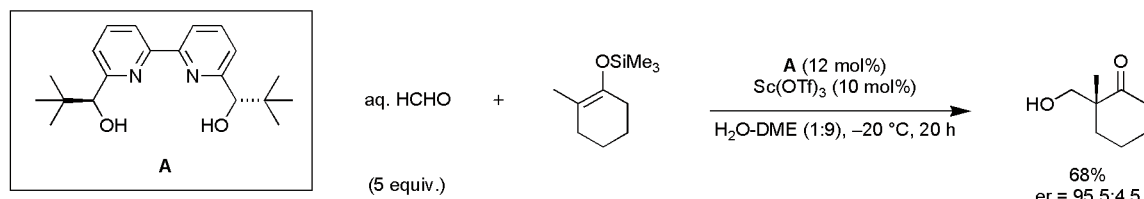
Fe/Cr and Co/Cr-mediated catalytic asymmetric 2-haloallylations of aldehydes.
Kurosa, M.; Lin, M.-H.; Kishi, Y. *J. Am. Chem. Soc.* **2004**, *126*, 12248.

Asymmetric 1,2-Addition



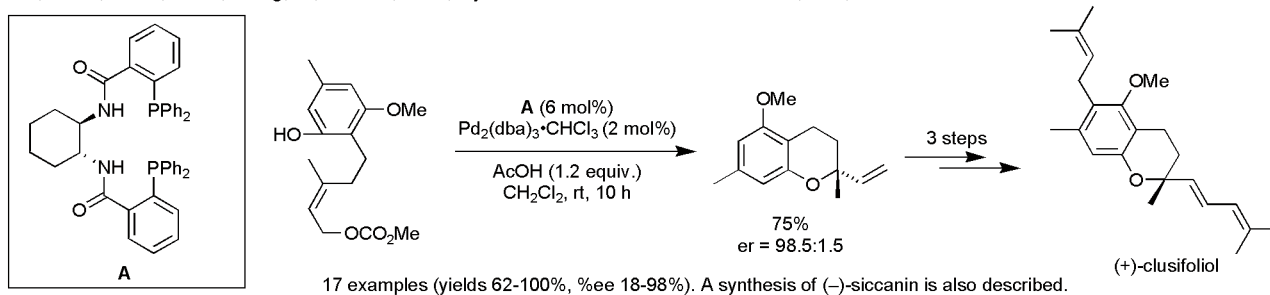
Catalytic asymmetric hydroxymethylation of silicon enolates.
Ishikawa, S.; Hamada, T.; Manabe, K.; Kobayashi, S. *J. Am. Chem. Soc.* **2004**, *126*, 12236.

Asymmetric Hydroxymethylation



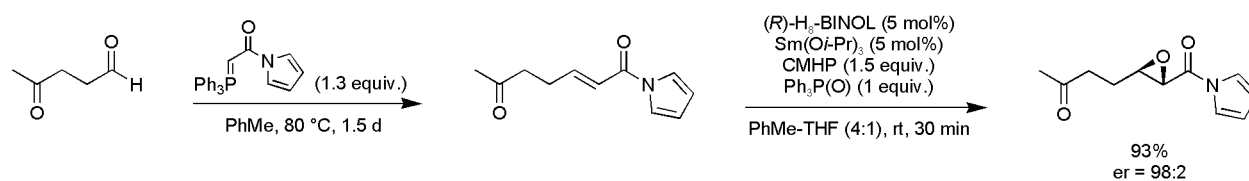
Synthesis of chiral chromans by a Pd-catalysed asymmetric allylic alkylation.
Trost, B. M.; Shen, H. C.; Dong, L.; Surivet, J.-P.; Sylvain, C. *J. Am. Chem. Soc.* **2004**, *126*, 11966.

Asymmetric Allylic Alkylation



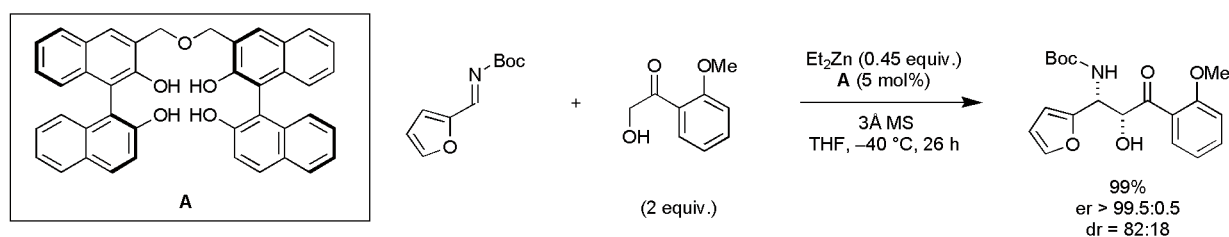
Catalytic asymmetric 1,4-addition reactions using α,β -unsaturated *N*-acylpyrroles.
Matsunaga, S.; Kinoshita, T.; Okada, S.; Harada, S.; Shibasaki, M. *J. Am. Chem. Soc.* **2004**, *126*, 7559.

Asymmetric 1,4-Addition



Direct, catalytic, asymmetric Mannich-type reaction of hydroxyketones using a Et_2Zn /linked-BINOL complex.
Matsunaga, S.; Yoshida, T.; Morimoto, H.; Kumagai, N.; Shibasaki, M. *J. Am. Chem. Soc.* **2004**, *126*, 8777.

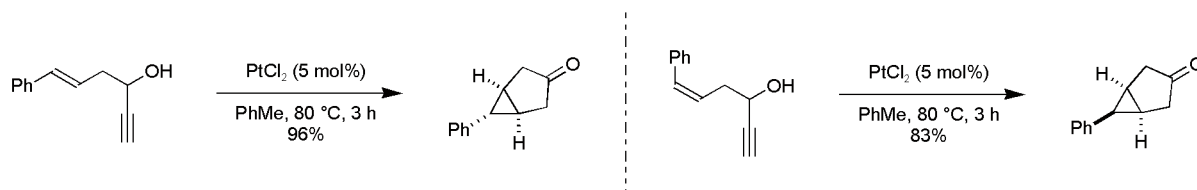
Asymmetric 1,2-Addition



PtCl₂-catalysed cycloisomerisations of 5-en-1-yn-3-ol systems.

Harrak, Y.; Blaszykowski, C.; Bernard, M.; Cariou, K.; Mainetti, E.; Mouriers, V.; Dhimane, A.-L.; Fensterbank, L.; Malacria, M. *J. Am. Chem. Soc.* **2004**, *126*, 8656.

Annulation

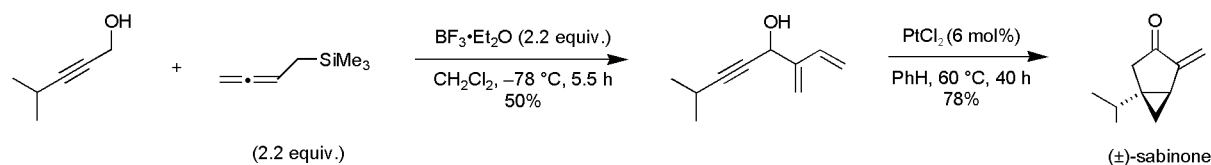


15 examples (yields 42-96%). Application to the synthesis of sabinone (2 steps, 83% yield).

Pt and Au-catalysed cycloisomerisation reactions of hydroxylated enynes.

Mamane, V.; Gress, T.; Krause, H.; Fürstner, A. *J. Am. Chem. Soc.* **2004**, *126*, 8654.

Annulation

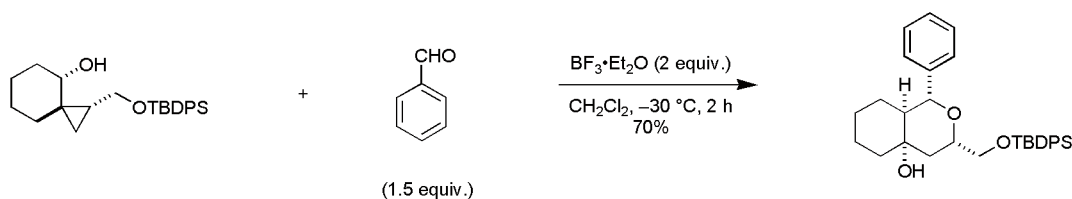


(PPh₃)AuCl/AgSbF₆ also catalyzes the cycloisomerization. 16 examples (yields 52-94%).

Stereoselective Prins cyclization of silylmethyl-substituted cyclopropyl carbinols.

Yadav, V. K.; Kumar, N. V. *J. Am. Chem. Soc.* **2004**, *126*, 8652.

Heteroannulation

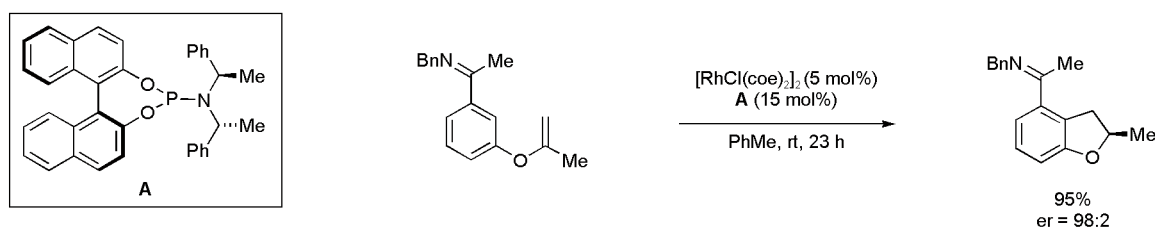


13 examples (yields 20-78%).

Enantioselective cyclisation of aromatic imines via direct C-H bond activation.

Thalji, R. K.; Ellman, J. A.; Bergman, R. G. *J. Am. Chem. Soc.* **2004**, *126*, 7192.

Annulation

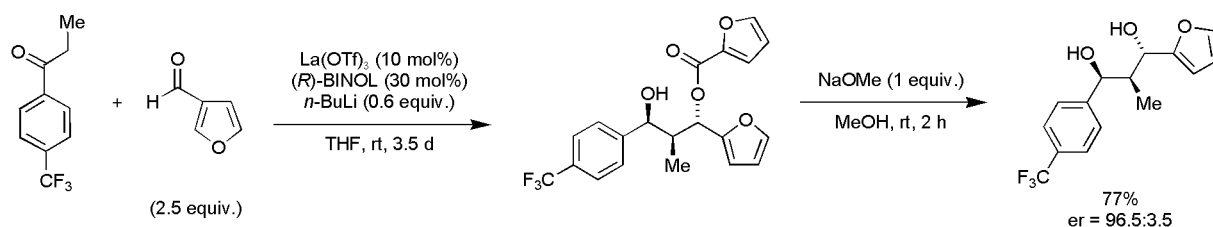


45 examples (yields 5-100%, %ee 8-96%).

Direct, catalytic, asymmetric Aldol-Tishchenko reaction.

Gnanadesikan, V.; Horiuchi, Y.; Ohshima, T.; Shibasaki, M. *J. Am. Chem. Soc.* **2004**, *126*, 7782.

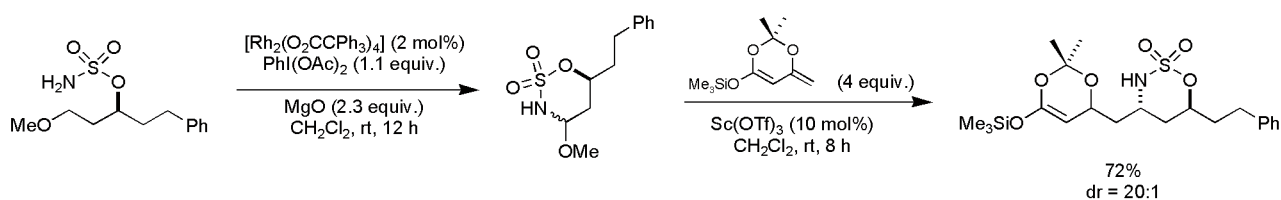
Asymmetric 1,2-Addition/Reduction



22 examples (yields 65-96%, %ee 64-95%).

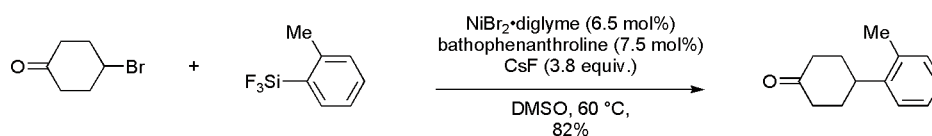
Synthesis of complex amines *via* a Rh-catalysed amination of etheral C^α-H bonds.
Williams-Fiori, K.; Fleming, J. J.; Du Bois, J. *Angew. Chem. Int. Ed.* **2004**, *43*, 4349.

Asymmetric 1,2-Addition



21 examples (yields 60-89%, %de 20-91%).

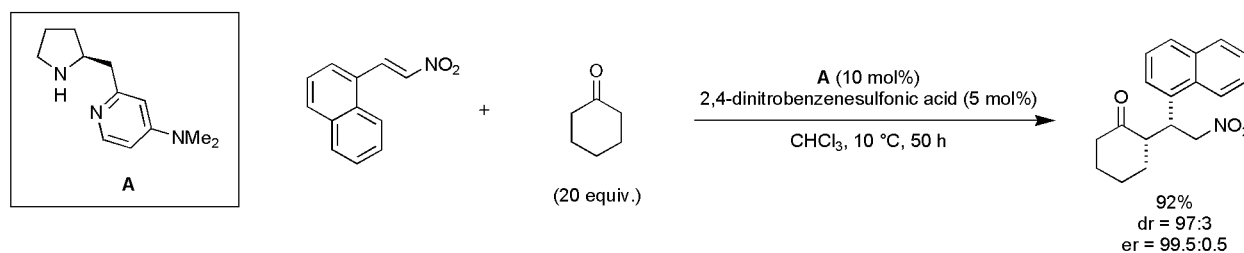
Ni-catalysed cross-coupling of organosilicon reagents with unactivated secondary alkyl bromides.
Powell, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 7788.

sp²-sp³ Coupling

bathophenanthroline = 4,7-diphenyl-1,10-phenanthroline. 16 examples (yields 60-82%).

Chiral pyrrolidine-pyridine conjugate catalyst for asymmetric Michael addition reactions.
Ishii, T.; Fujioka, S.; Sekiguchi, T. Kotsuki, H. *J. Am. Chem. Soc.* **2004**, *126*, 9558.

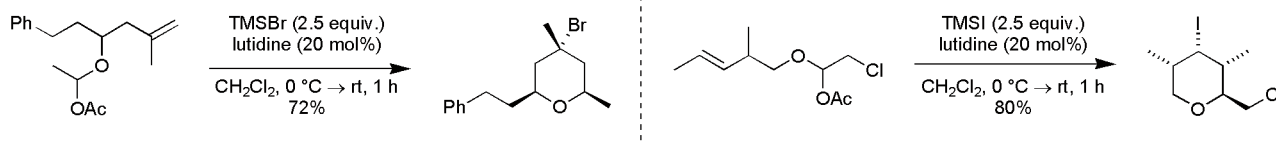
Asymmetric 1,4-Addition



15 examples (yields 42-100%, %de 86-98%, %ee 7-98%).

Axial-selective Prins cyclisations by solvolysis of α -bromo ethers.
Jasti, R.; Vitale, J.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **2004**, *126*, 9904.

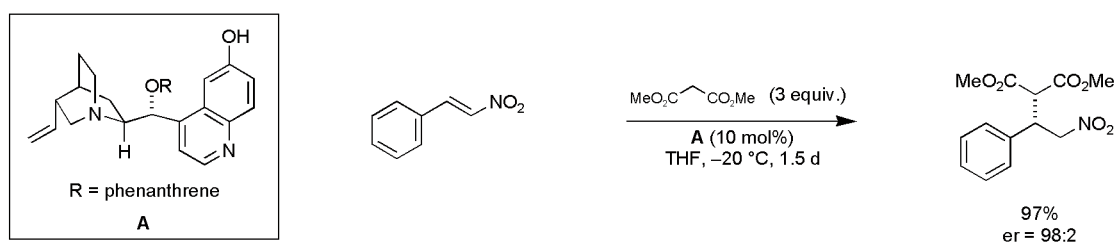
Heteroannulation



12 examples (yields 64-98%).

Enantioselective conjugate addition of malonate and β -ketoesters to nitroalkenes.
Li, H.; Wang, Y.; Tang, L.; Deng, L. *J. Am. Chem. Soc.* **2004**, *126*, 9906.

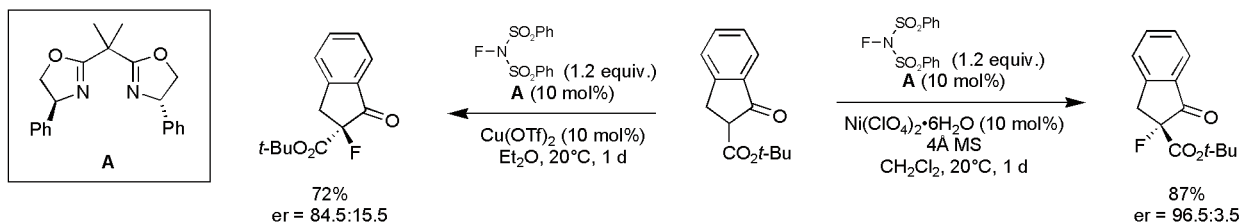
Asymmetric 1,4-Addition



18 examples (yields 71-99%, %ee 94-98%).

The first enantioselective fluorination reaction using metal-bis(oxazoline) complexes.
Shibata, N.; Ishimaru, T.; Nagai, T.; Kohno, J.; Toru, T. *Synlett*. **2004**, 10, 1703.

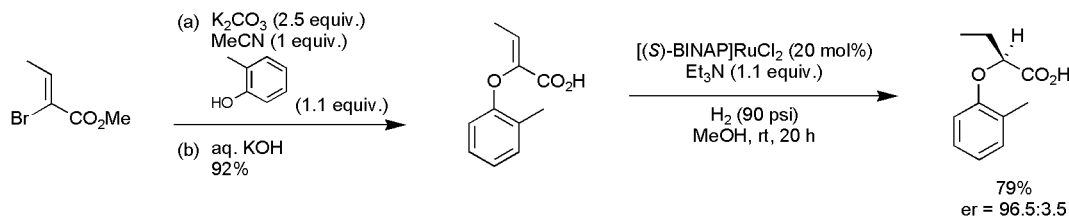
Enantioselective Fluorination



24 examples (yields 50-99%, %ee 1-93%).

Enantioselective hydrogenation of α -aryloxy α,β -unsaturated acids.
Maligres, P.; Krska, S.W.; Humphrey, G.R. *Org. Lett.* **2004**, 18, 3147.

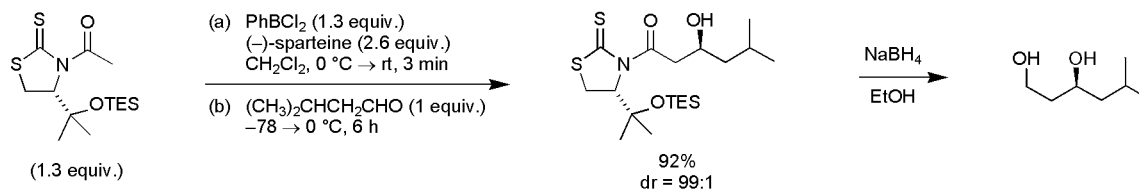
Asymmetric Hydrogenation



13 examples (yields 65-99%, %ee 32-95%).

Application of a new *N*-acetyl thiazolidinethione reagent in an asymmetric acetate Aldol reaction.
Zhang, Y.; Sammakia, T. *Org. Lett.* **2004**, 18, 3139.

Asymmetric Aldol

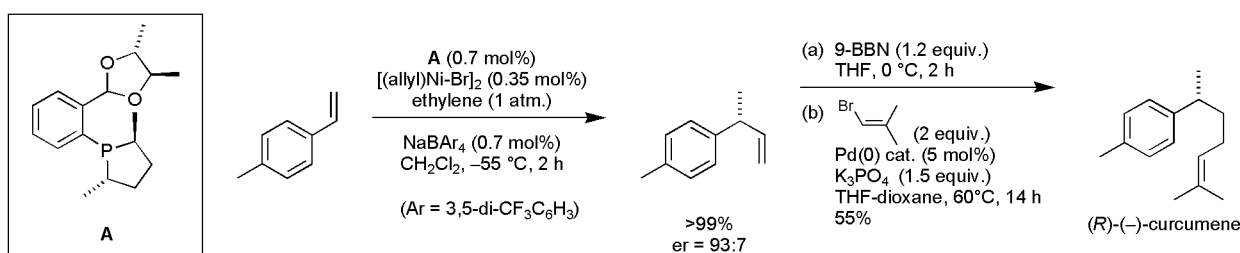


8 examples (yields 63-92%, %de 81-98%).

Thiazolidinethione auxiliary synthesised in 4 steps (62% yield).

Synthesis of (*R*)-(-)- α -curcumene via an asymmetric hydrovinylation.
Zhang, A.; RajanBabu, T.V. *Org. Lett.* **2004**, 18, 3159.

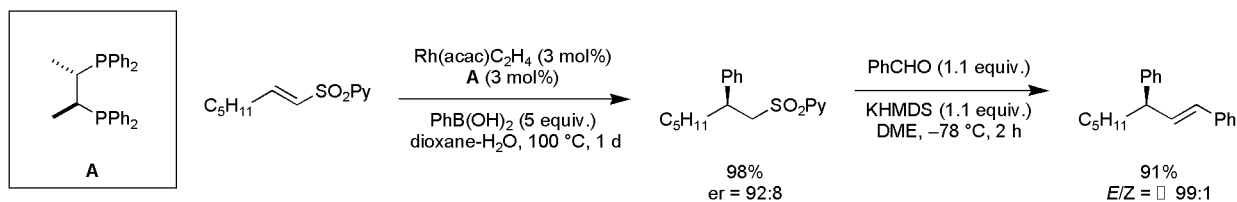
Asymmetric C-C Bond Formation



A synthesis of (-)-(*R*)-ar-Turmerone is also described.

Rh-catalysed enantioselective conjugate addition of organoboronic acids to α,β -unsaturated sulfones.
Mauleón, P.; Carretero, J. C. *Org. Lett.* **2004**, 6, 3195.

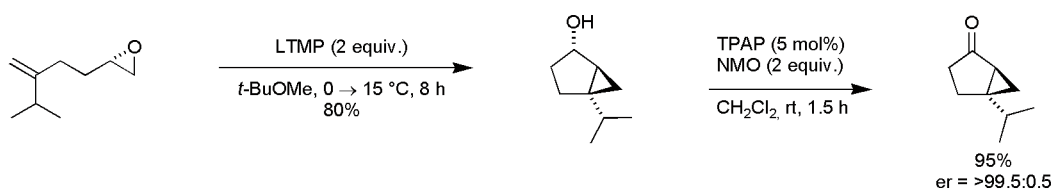
Asymmetric 1,4-Addition



13 examples (yields 84-98%, %ee 76-92%).

Cyclopropanation of unsaturated terminal epoxides.
Hodgson, D. M.; Chung, Y. K.; Paris, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 8664.

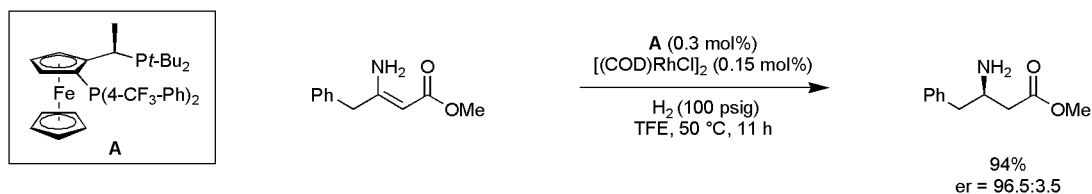
Cyclopropanation



LTMP = 2,2,6,6-tetramethylpiperidine. 13 examples (yield 65-82%).

Synthesis of β -amino acid derivatives *via* an asymmetric hydrogenation of unprotected enamines.
Hisao, Y.; Rivera, N. R.; Rosner, T.; Krska, S. W.; Njolito, E.; Wang, F.; Sun, Y.; Armstrong, J.; Grabowski, E. J. J.; Tillyer, R. D.; Spindler, F.; Malan, C. *J. Am. Chem. Soc.* **2004**, *126*, 9918.

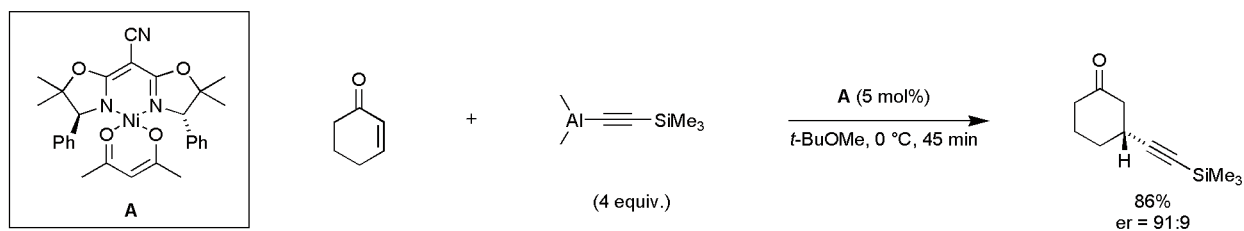
Asymmetric Hydrogenation



TFE = 2,2,2-trifluoroethanol. 10 examples (yields 74-98%, %ee 82-97%).

Catalytic, enantioselective conjugate addition of trimethylsilylacetylene to 2-cyclohexen-1-one.
Kwak, Y.; Corey, E. J. *Org. Lett.* **2004**, *6*, 3385.

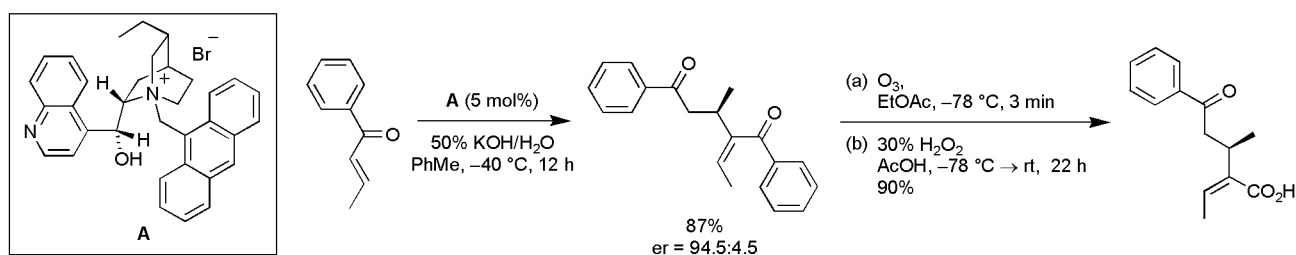
Asymmetric 1,4-Addition



13 examples (yields 33-86%, %ee 0-88%).

Highly enantioselective dimerization of α,β -enones catalysed by a rigid quaternary ammonium salt.
Zhang, F.; Corey, E. J. *Org. Lett.* **2004**, *6*, 3399.

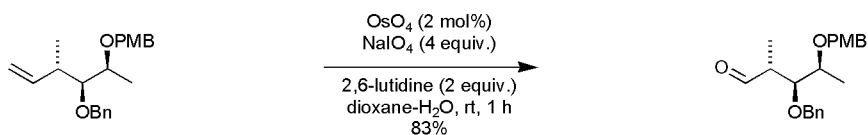
Asymmetric C-C Bond Formation



9 examples (yields 79-97%, %ee 83-97%).

Improved procedure for the oxidative cleavage of olefins by $\text{OsO}_4\text{-NaIO}_4$.
Yu, W.; Mei, Y.; Kang, Y.; Hua, Jin, Z. *Org. Lett.* **2004**, *6*, 3217.

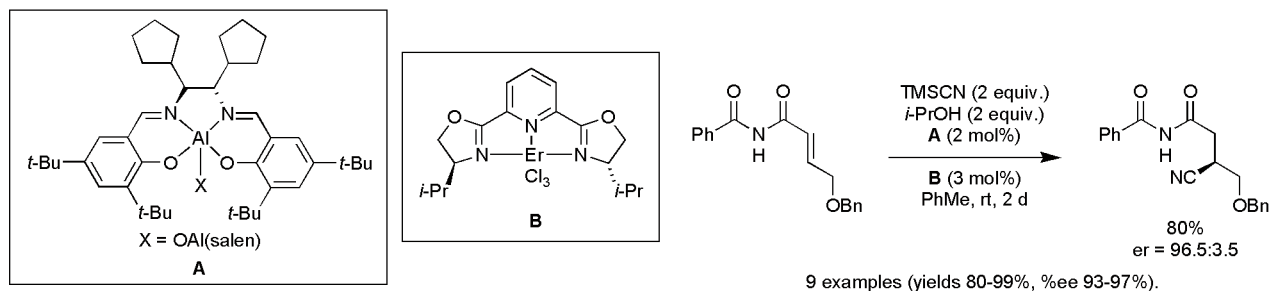
Oxidation



11 examples (yields 60-99%).

Enantioselective conjugate cyanation of unsaturated imides using co-operative dual catalysis.
Sammis, G. M.; Danjo, H.; Jacobsen. *J. Am. Chem. Soc.* **2004**, *126*, 9928.

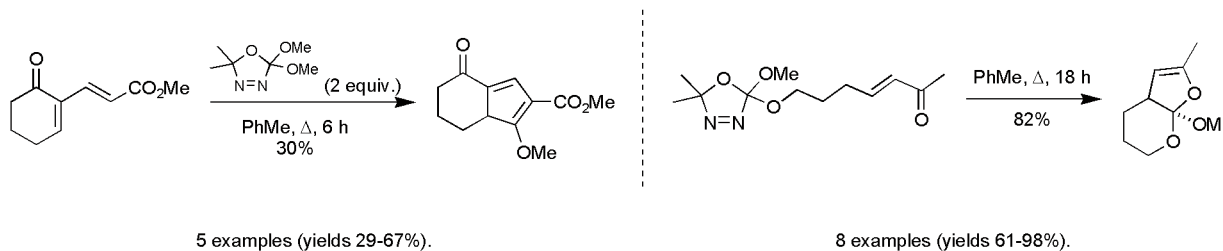
Asymmetric 1,4-Addition



Inter- and intramolecular [4+1]-cycloadditions.

Spino, C.; Rezaei, H.; Dupont-Gaudet, K.; Belanger, F. *J. Am. Chem. Soc.* **2004**, *126*, 9926.

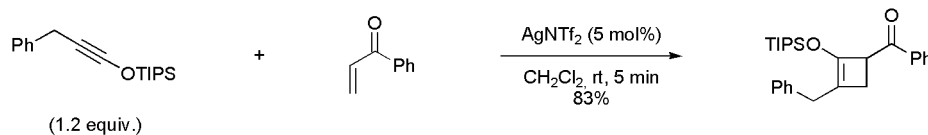
Annulation



Ag-catalysed [2+2] cycloadditions of siloxyalkynes.

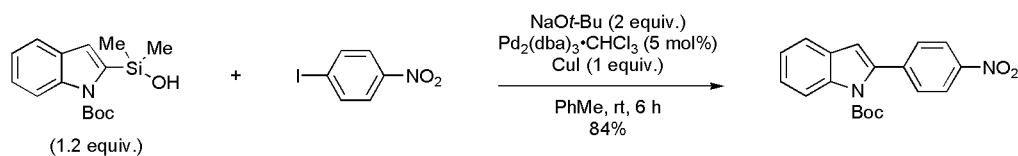
Sweis, R. F.; Schramm, M. P.; Kozmin, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 7442.

Annulation



Pd-catalysed cross-coupling of 2-indolyl(dimethyl)silanols with substituted aryl halides.

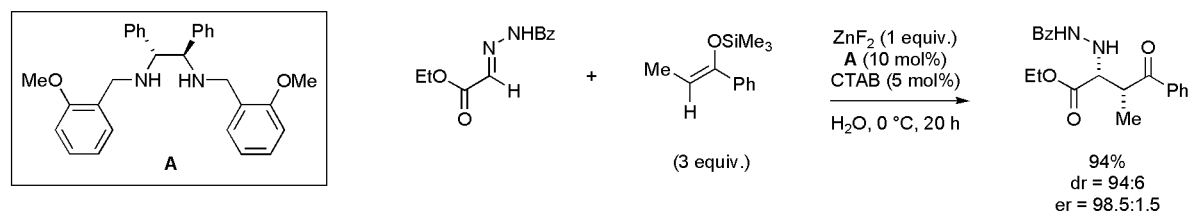
Denmark, S. E.; Baird, J. D. *Org. Lett.* **2004**, *6*, 3649.

sp²-sp² Coupling

Enantio- and diastereoselective, stereospecific Mannich-type reactions in water.

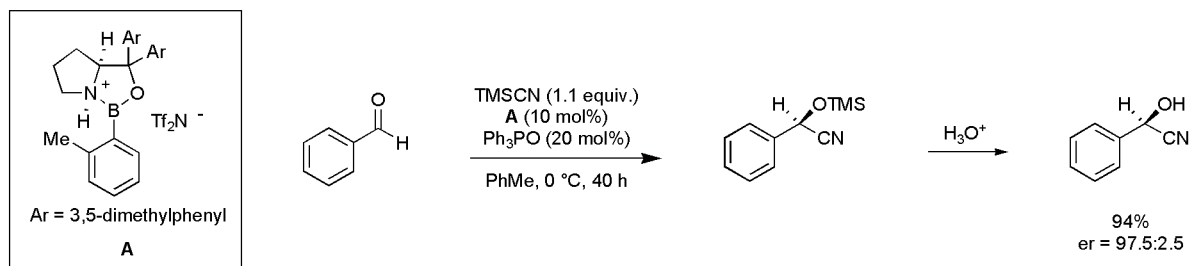
Hamada, T.; Manabe, K.; Kobayashi, S. *J. Am. Chem. Soc.* **2004**, *126*, 7768.

Asymmetric 1,2-Addition



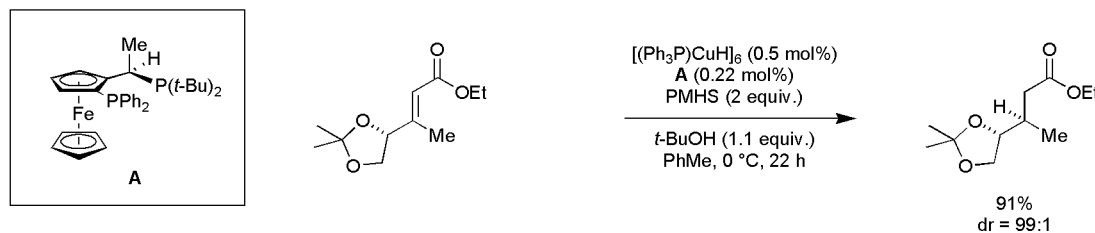
Enantioselective cyanosilylation of aldehydes catalysed by a chiral oxazaborolidinium ion.
Ryu, D. H.; Corey, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 8106.

Asymmetric 1,2-Addition



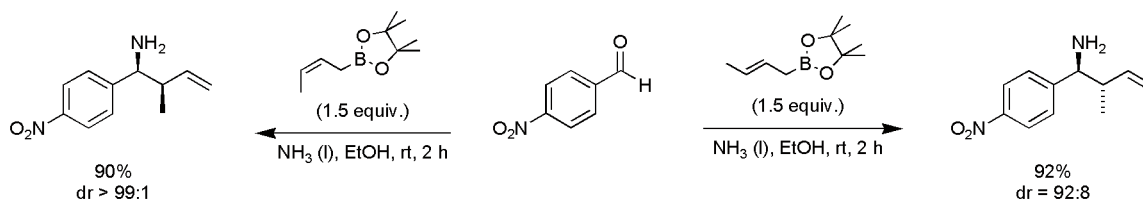
Asymmetric 1,4-hydrosilylations of α,β -unsaturated esters.
Lipshutz, B. H.; Servesko, J. M.; Taft, B. R. *J. Am. Chem. Soc.* **2004**, *126*, 8352.

Asymmetric 1,4-Reduction



Stereoselective synthesis of homoallylic primary amines via α -aminoallylation of aldehydes with ammonia.
Sugiura, M.; Hirano, K.; Kobayashi, S. *J. Am. Chem. Soc.* **2004**, *126*, 7182.

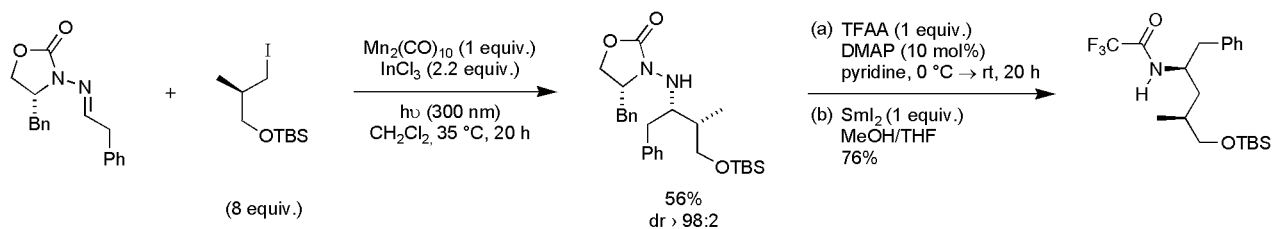
Asymmetric Allylation



21 examples (yields 67-100%).

Stereoselective Mn-mediated coupling of functionalised iodides and hydrazones.
Friestad, G. K.; Marie, J.-C.; Deveau, A. M. *Org. Lett.* **2004**, *6*, 3249.

Asymmetric C-C Bond Formation



3 examples (yields 56-77%, %de 90-96%). Application towards the tubulysin γ -amino acids.

Synthesis of 6,7-dehydrostipiamide via a Zr-catalysed asymmetric carboalumination and Pd-catalysed cross-coupling of organozincs.
Zeng, X.; Zeng, F.; Negishi, E. *Org. Lett.* **2004**, *6*, 3245.

Asymmetric 1,2-Addition
sp²-sp² Coupling