

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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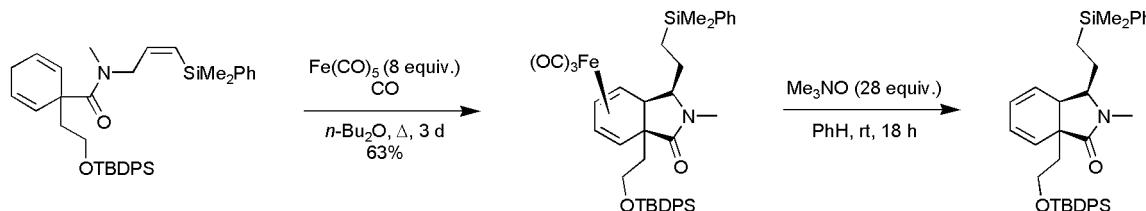
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The journals regularly covered by the abstractors are:

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

Stereospecific iron-carbonyl-mediated [6+2] ene-type cyclizations.
Pearson, A. J.; Wang, X. *J. Am. Chem. Soc.*, **2003**, 125, 13326.

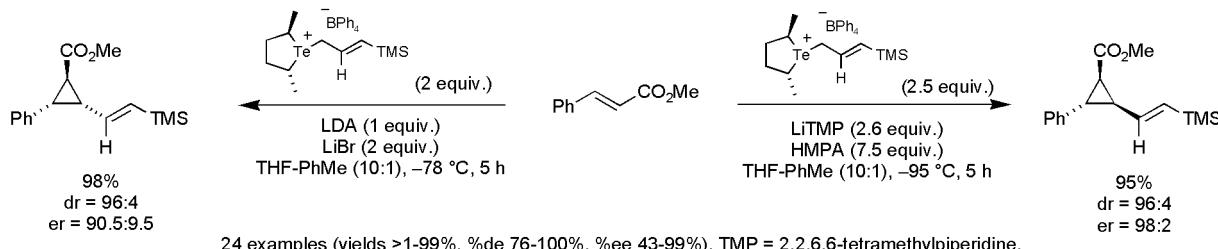
Ene Reaction



7 examples, including an in-situ hydrosilation of alkyne (yields 20–92%).

Enantioselective synthesis of vinyl cyclopropanes using chiral telluronium ylides.
Liao, W. W.; Li, K.; Tang, Y. *J. Am. Chem. Soc.*, **2003**, 125, 13030.

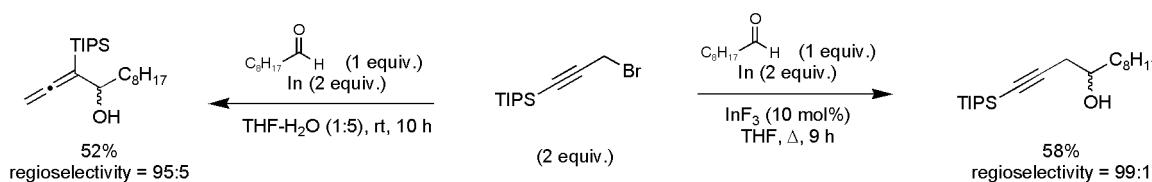
Cyclopropanation



24 examples (yields >1–99%, %de 76–100%, %ee 43–99%). TMP = 2,2,6,6-tetramethylpiperidine.

Regioselective In-mediated synthesis of allenic and homopropargylic alcohols.
Lin, M.-J.; Loh, T.-P. *J. Am. Chem. Soc.*, **2003**, 125, 13042.

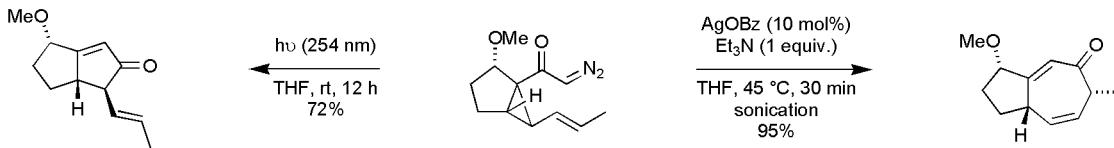
Nucleophilic Addition



32 examples (yields 35–95%, 3:97 \leq regioselectivities \leq 99:1).

Synthesis of fused carbocyclic skeletons via a tandem Wolff–Cope rearrangement.
Sarpong, R.; Su, J. T.; Stoltz, B. M. *J. Am. Chem. Soc.* **2003**, 125, 13624.

Annulation

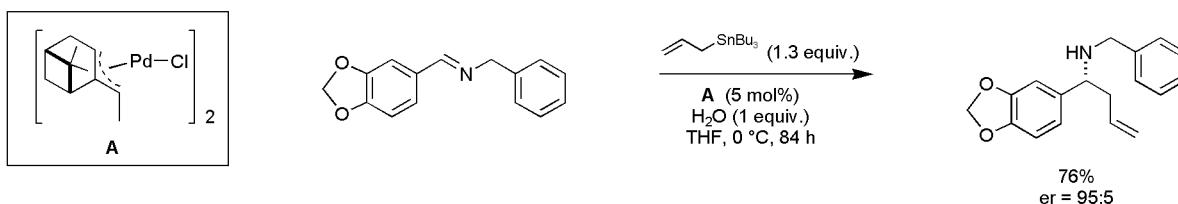


16 examples (yields 55–98%). Single diastereomeric products obtained.

Palladium-catalyzed asymmetric allylation of imines.

Fernandes, R. A.; Stimac, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, 125, 14133.

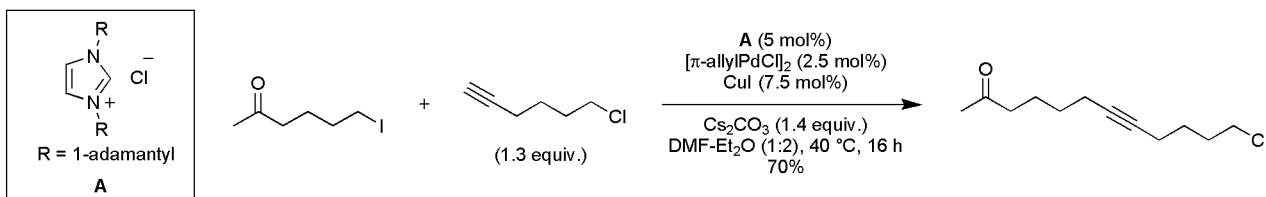
Asymmetric Addition



28 examples (yields 10–94%, %ee 2–91%).

Sonogashira reaction of unactivated alkyl bromides and iodides.
Eckhardt, M.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, 125, 13642.

sp-sp³ Coupling

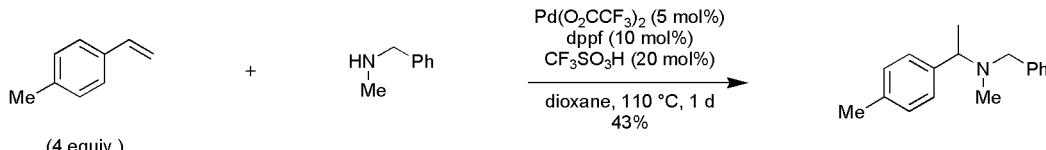


16 examples (yields 50–81%). Ligand optimization is also reported.

Markovnikov hydroamination of vinylarenes with alkylamines.

Utsunomiya, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, 125, 14286.

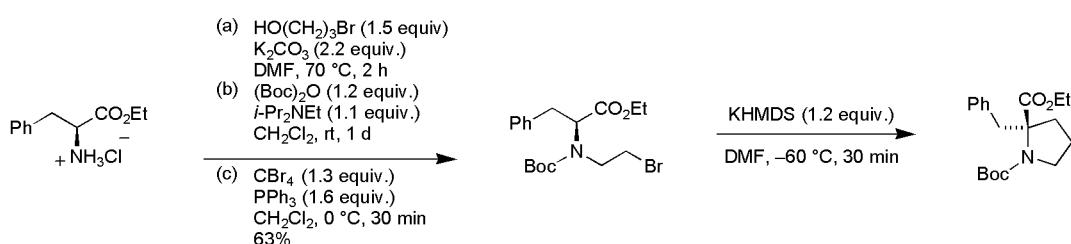
Hydroamination



15 examples (yields 36–79%) including an enantioselective hydroamination. Mechanistic studies investigated.

Synthesis of cyclic amino acids with a quaternary centre via asymmetric cyclization.
Kawabata, T.; Kawakami, S.; Majumdar, S. *J. Am. Chem. Soc.* **2003**, 125, 13012.

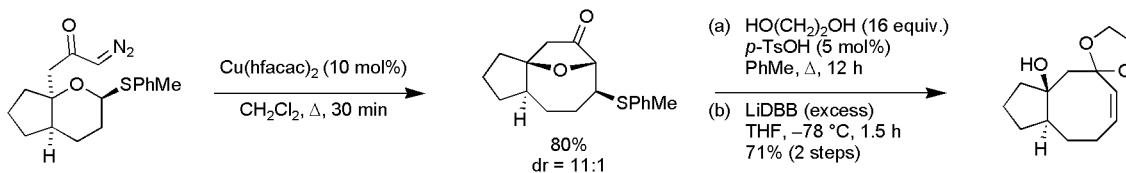
Asymmetric Alkylation



9 examples including synthesis of 4,5 and 6 membered rings (yields 31–95%, %ee 72–98%).

Cyclooctanoid ring systems from mixed acetals via heteroatom-assisted [1,2]-shift of oxonium ylides.
Marmsaeter, F. P.; Murphy, G. K.; West, F. G., *J. Am. Chem. Soc.* **2003**, 125, 14724.

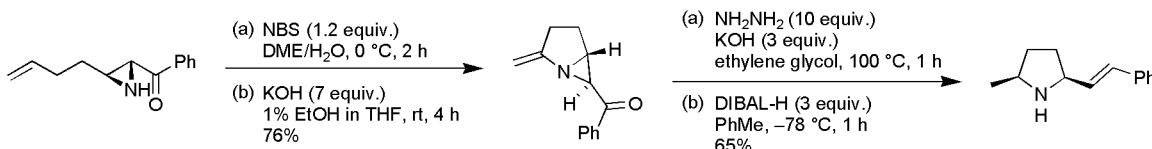
Annulation



hfacac = hexafluoroacetylacetone.
The [1,2]-shift followed by a complementary base-induced elimination route is also described.

Oxidative cycloamination of olefins with aziridines.
Sasaki, M.; Yudin, A. K. *J. Am. Chem. Soc.* **2003**, 125, 14242.

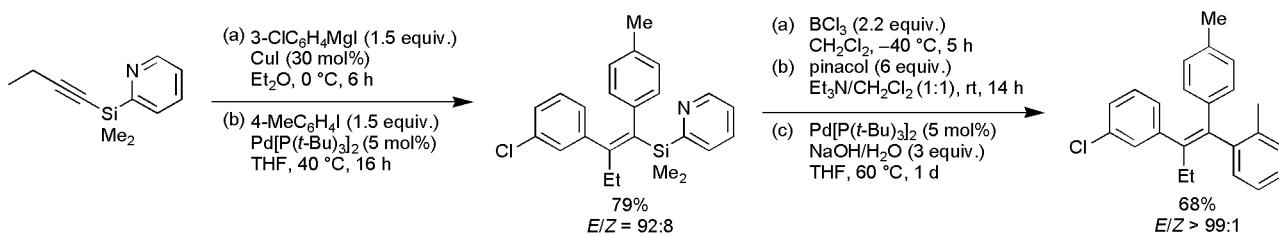
Cycloamination



5 examples of bicyclic aziridine formation (yields 51–76%) and 7 alternative methods of aziridine ring-opening (yields 30–99%).

Copper-catalyzed carbomagnesation across alkynyl(2-pyridyl)silane.
Itami, K.; Kamei, T.; Yoshida, J.-i. *J. Am. Chem. Soc.* **2003**, 125, 14670.

Carbomagnesation

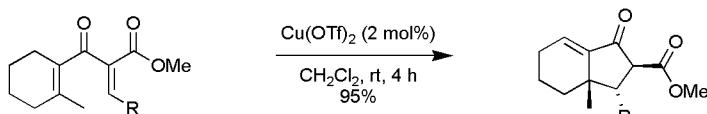


Applicable to the synthesis of Tamoxifen and its derivatives. 8 examples (yields 55–99%, 88:12 < regioselectivities < 95:5).

Polarized Nazarov cyclization.

He, W.; Sun, X.; Frontier, A. J. *J. Am. Chem. Soc.* **2003**, 125, 14278.

4π-Electrocyclization



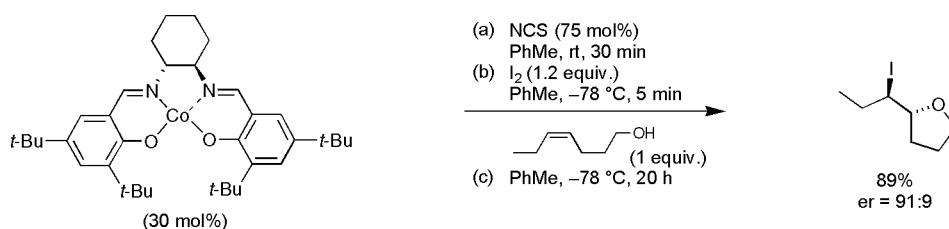
20 examples (yields 30–>99%). R = 2,4,6-trimethoxyphenyl.

Use of polar substituents on the divinyl ketone facilitates the Nazarov cyclization allowing very mild conditions and improved regioselectivity.

Enantioselective iodocyclization of γ-hydroxy-cis-alkenes.

Kang, S. H.; Lee, S. B.; Park, C. M. *J. Am. Chem. Soc.* **2003**, 125, 15748.

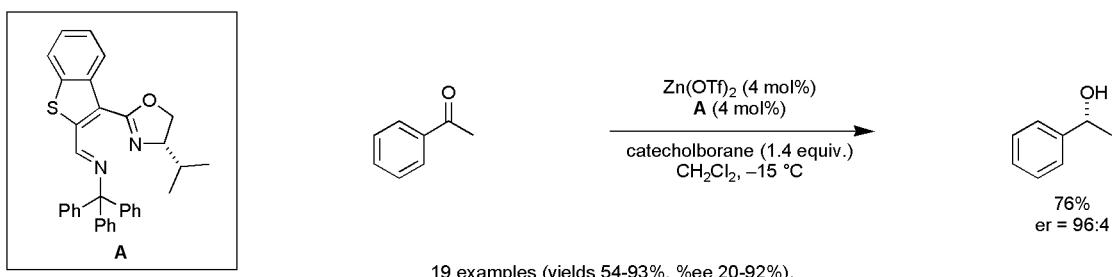
Enantioselective Iodoetherification



12 examples (yields 79–96%, %ee 40–90%). Catalyst design studies included.

[Zn(iminooxazoline)]-promoted enantioselective reduction of ketones by catecholborane.
Locatelli, M.; Cozzi, P. G. *Angew. Chem. Int. Ed.* **2003**, *42*, 4928.

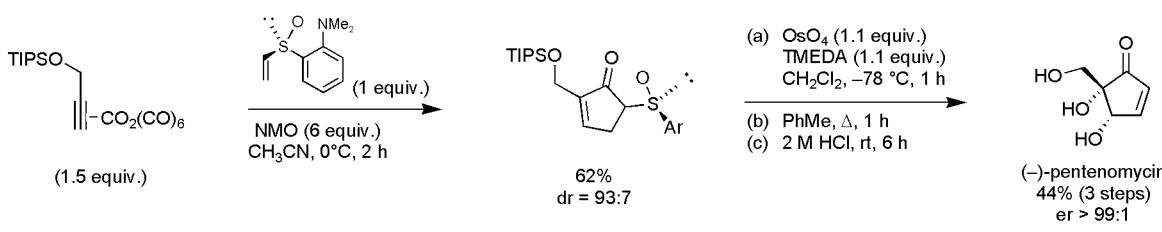
Enantioselective Reduction



Asymmetric intermolecular Pauson–Khand reactions of unstrained olefins.

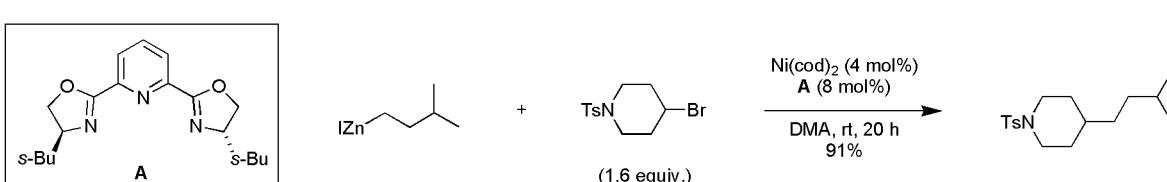
Rivero, M. R.; de la Rosa, J. C.; Carretero, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 14992.

Pauson–Khand



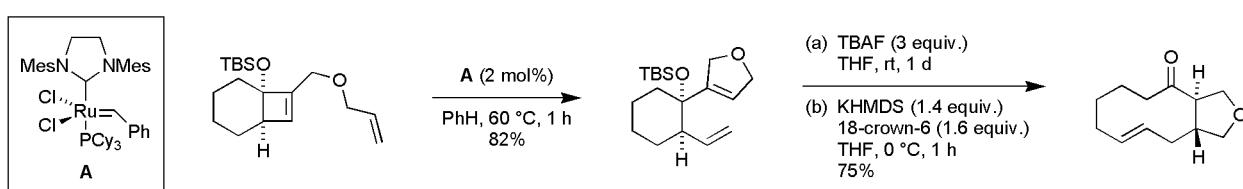
Nickel-catalyzed Negishi reactions of unactivated secondary alkyl halides.
Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 14726.

$\text{sp}^3\text{-sp}^3$ Coupling



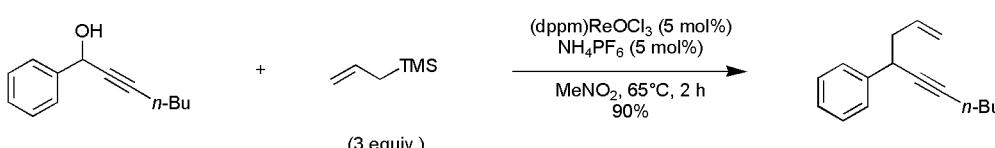
Ring-opening metathesis/oxy-Cope rearrangement strategy towards bicyclic medium-ring synthesis.
White, B. H.; Snapper, M. L. *J. Am. Chem. Soc.* **2003**, *125*, 14901.

Metathesis/ Rearrangement



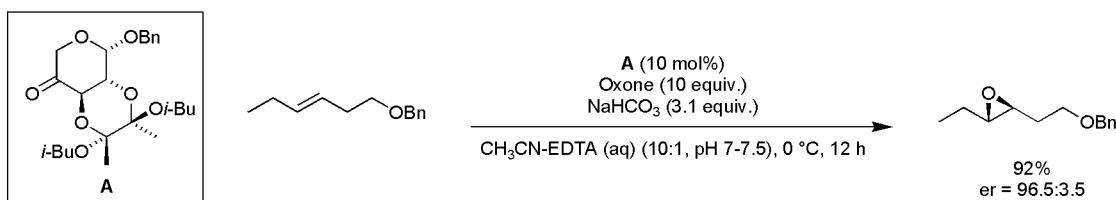
Rhenium-catalyzed coupling of propargyl alcohols and allyl silanes.
Luzung, M. R.; Toste, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 15760.

$\text{S}_{\text{N}}2$ Reaction



Catalytic enantioselective epoxidation with arabinose-derived uloses.
Shing, T. K. M.; Leung, G. Y. C.; Yeung, K. W. *Tetrahedron Lett.* **2003**, 44, 9225.

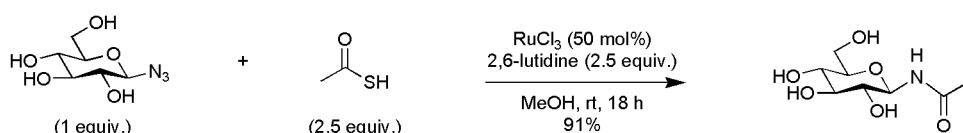
Epoxidation



23 examples (yields 80-99%, %ee 42-93%).

RuCl₃-promoted amide formation from azides and thioacids.
Fazio, F.; Wong, C.-H. *Tetrahedron Lett.* **2003**, 44, 9083.

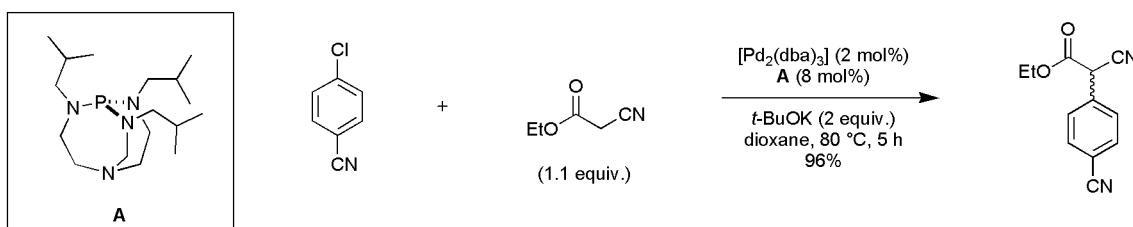
Amide Formation



6 examples (yields 78-91%).

Direct α -arylation of nitriles with aryl chlorides.
Yoi, J.; Verkade, J. G. *Angew. Chem. Int. Ed.* **2003**, 42, 5051.

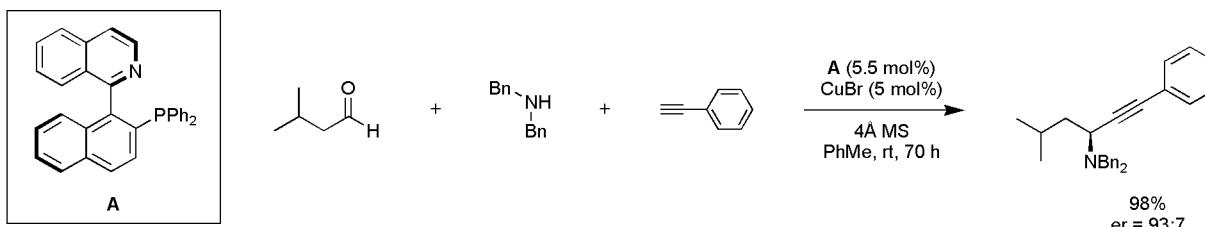
Arylation



26 examples (yields 10-96%).

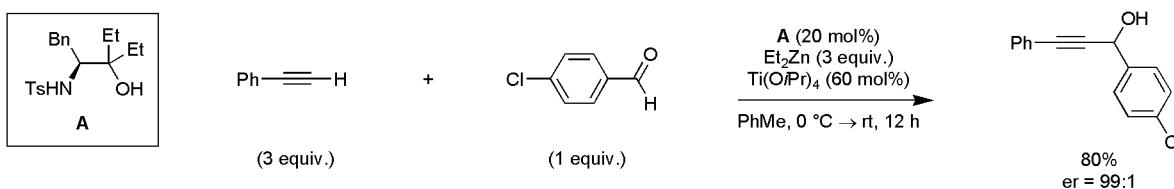
Copper(I)-catalyzed synthesis of propargylamines.
Gommermann, N.; Koradin, C.; Polborn, K.; Knochel, P. *Angew. Chem. Int. Ed.* **2003**, 42, 5763.

Asymmetric 1,2-Addition



17 examples (yields 43-99%, %ee 32-96%). Reaction is diastereoselective if chiral amine or aldehyde used.

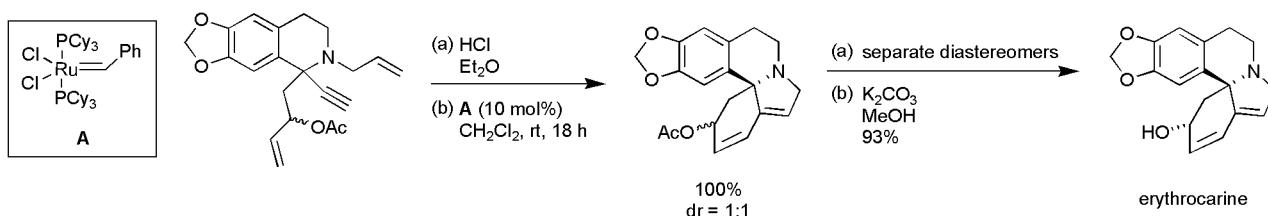
Catalytic enantioselective addition of phenylacetylene to aldehydes using a β -sulfonamide alcohol-Ti complex. **Asymmetric 1,2-Addition**
Xu, Z.; Wang, R.; Xu, J.; Da, C.; Yan, W.; Chen, C. *Angew. Chem. Int. Ed.* **2003**, 42, 5747.



9 examples (yields 70-92%, %ee 90-98%).

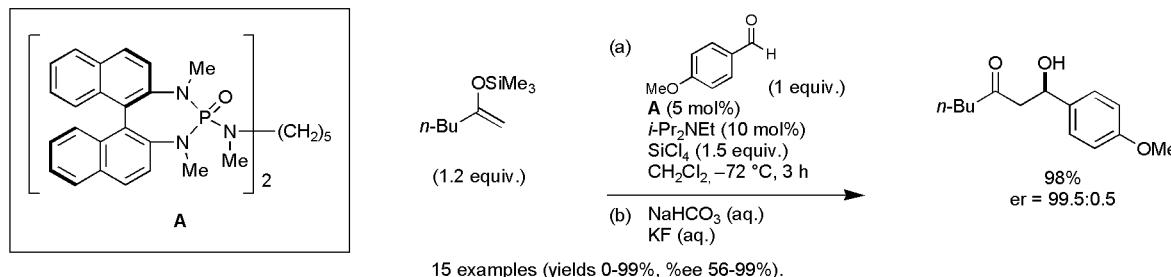
Total synthesis of erythrocarine.
Shimizu, K.; Takimoto, M.; Mori, M. *Org. Lett.* **2003**, 5, 2323.

Metathesis



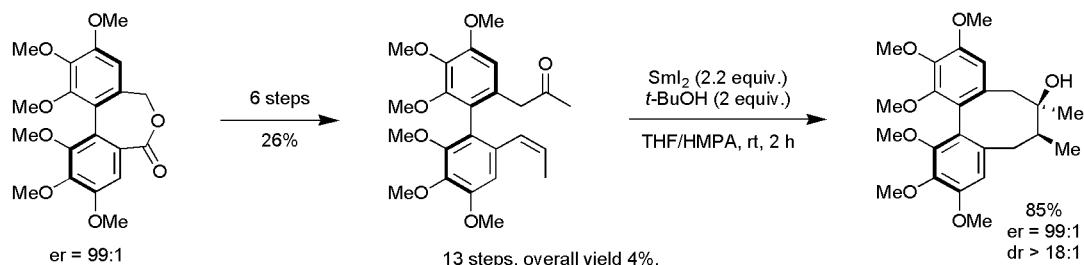
Catalytic enantioselective addition of silyl enol ethers of achiral methyl ketones to aldehydes.
Denmark, S. E.; Heemstra Jr., J. R. *Org. Lett.* **2003**, 5, 2303.

Enantioselective Aldol

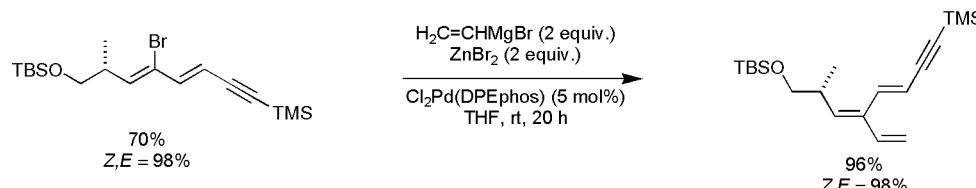


Total synthesis of (+)-Isoschizandrin utilizing a samarium(II) iodide-promoted 8-ketyl-olefin cyclization.
Molander, G. A.; George, K. M.; Monovich, L. G. *J. Org. Chem.* **2003**, 68, 9533.

Radical Cyclization



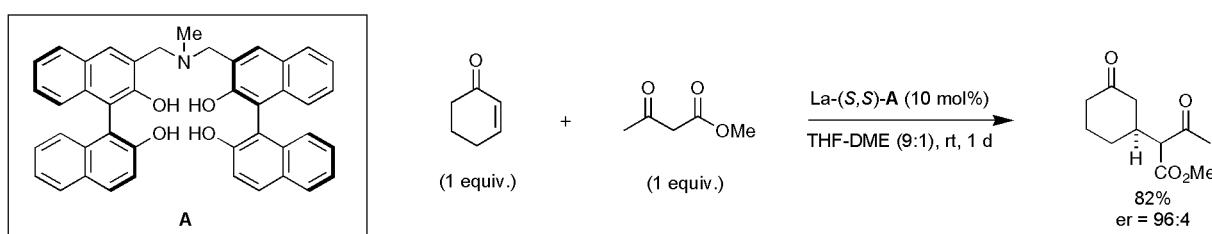
Inversion of configuration in Pd-catalyzed cross-coupling of 2-bromo-1,3-dienes.
Zeng, X.; Hu, Q.; Qian, M.; Negishi, E. *J. Am. Chem. Soc.* **2003**, 125, 13636.

sp²-sp² Coupling

20 examples (yields 61-96%, 1 ≥ Z,E ≥ 98%).

Catalytic, asymmetric Michael reaction of β-keto esters.
Majima, K.; Takita, R.; Okada, A.; Ohshima, T.; Shibasaki, M. *J. Am. Chem. Soc.* **2003**, 125, 15837.

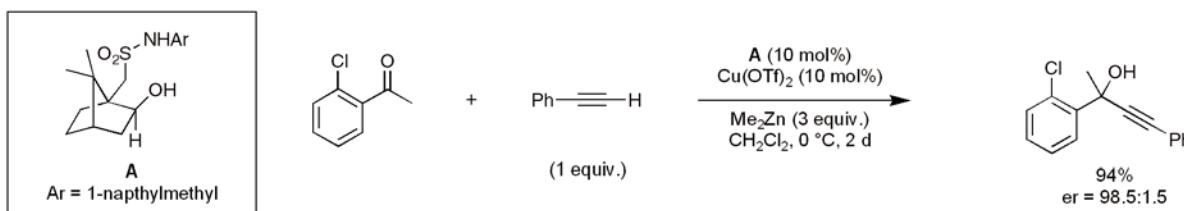
Asymmetric 1,4-Addition



Synthesis of a key intermediate of (-)-Tubifolidine and (-)-19,20-Dihydroakuammicine and mechanistic studies are also reported.

Enantioselective alkynylation of aromatic ketones catalyzed by chiral camphorsulfonamide ligands.
Lu, G.; Li, X.; Jia, X.; Chan, W. L.; Chan, A. S. C. *Angew. Chem. Int. Ed.* **2003**, *42*, 5057.

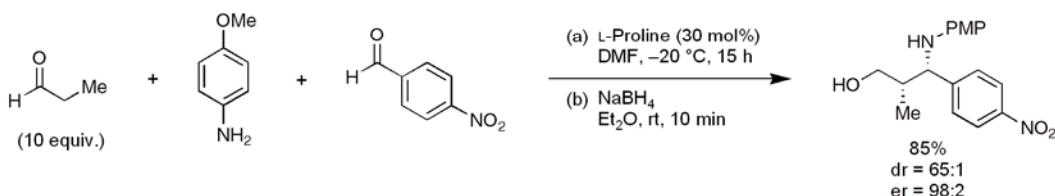
Asymmetric 1,2-Addition



24 examples (yields 39-94%, %ee 13-97%).

Direct organocatalytic asymmetric Mannich reaction.
Notz, W.; Tanaka, S.-i. W.; Chowdari, N. S.; Turner, J. M.; Thayumanavan, Barbas, C. F. III. *J. Org. Chem.* **2003**, *68*, 9624.

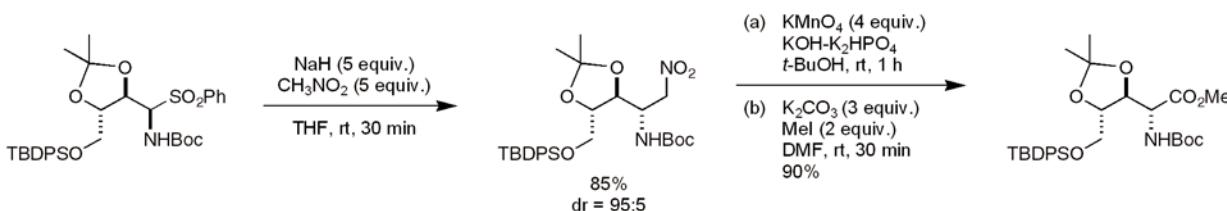
Asymmetric Mannich Reaction



7 examples (yields 65-92%, %de 60-99%, %ee 75-99%).

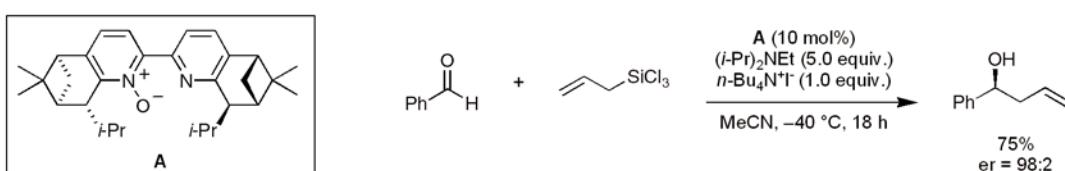
Diastereoselective addition of nitromethane anion to chiral α -amidoalkylphenyl sulfones.
Foresti, E.; Palmieri, G.; Petrini, M.; Profeta, R. *Org. Biomol. Chem.* **2003**, *1*, 4275.

Nucleophilic Addition

Stereoselective synthesis of α -amino acid derivatives, 6 examples (yields 55-85%, %de 46-90%).

Lewis-basic *N*-oxides as chiral organocatalysts in asymmetric allylation of aldehydes.
Malkov, A. V.; Bell, M.; Orsini, M.; Pernazza, D.; Massa, A.; Herrmann, P.; Meghani, P.; Kocovsky, P. *J. Org. Chem.* **2003**, *68*, 9659.

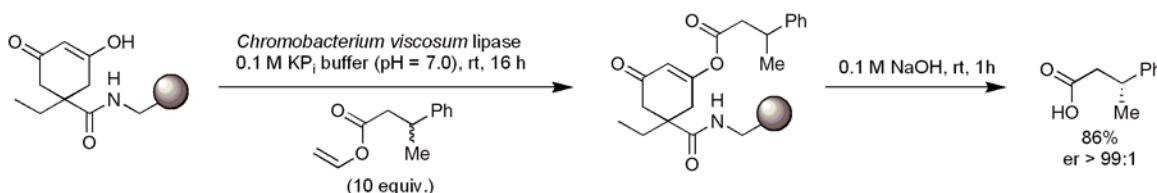
Asymmetric 1,2-Addition

Synthesis and application of various *N*-Oxide ligands reported. 46 examples (yields 15-95%, %ee 10-97%, %de 80-96%).

Lipase-catalyzed kinetic resolution on solid-phase.

Humphrey, C. E.; Turner, N. J.; Easson, M. A. M.; Flitsch, S. L.; Ulijn, R. V. *J. Am. Chem. Soc.* **2003**, *125*, 13952.

Kinetic Resolution

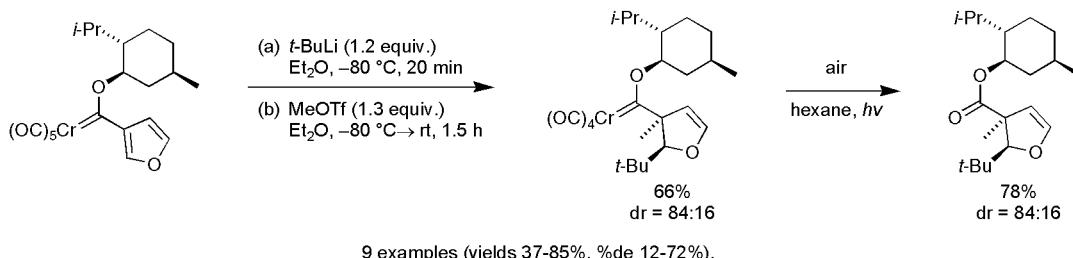


8 examples (yields 7-92%, %ee 59-99%).

Asymmetric dearomatization of the furan ring.

Barluenga, J.; Nandy, S. K.; Laxmi, Y. R. S.; Suarez, J. R.; Merino, I.; Florez, J.; Garcia-Granda, S.; Montejo-Bernardo, J. *Chem.-Eur. J.* **2003**, 9, 5725.

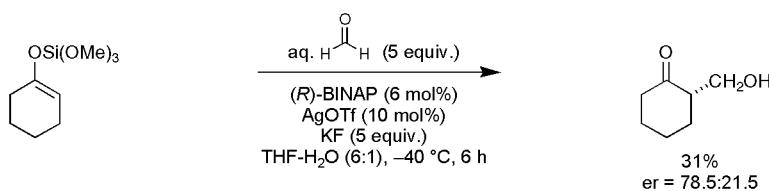
Nucleophilic Addition



Aldol synthesis with aqueous solution of formalin.

Ozasa, N.; Wadamoto, M.; Ishihara, K.; Yamamoto, H. *Synlett* **2003**, 2216.

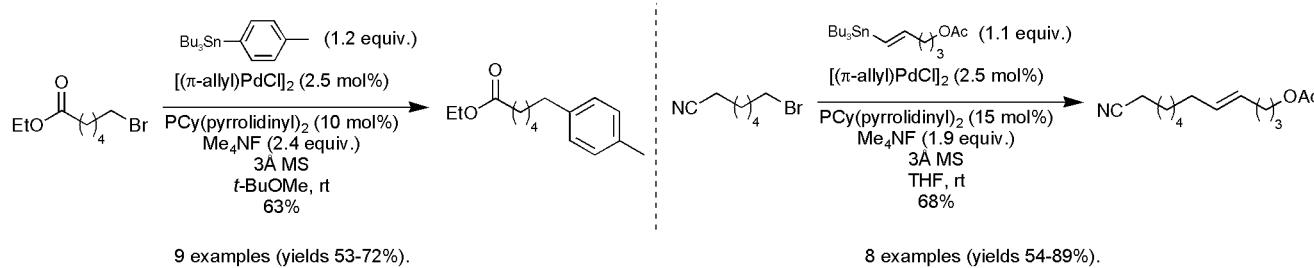
Asymmetric Aldol



8 examples including 2 enantiocontrolled reactions (yields 18-89%, %ee 57%).

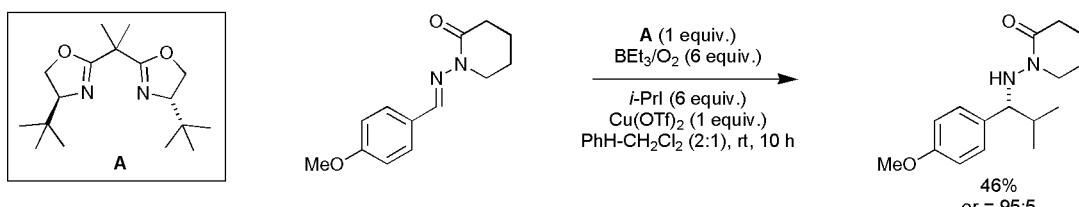
Palladium-catalyzed cross-coupling of alkyl halides.

Tang, H.; Menzel, K.; Fu, G. C. *Angew. Chem. Int. Ed.* **2003**, 42, 5079.

 $\text{sp}^2\text{-sp}^3$ CouplingRadical addition to *N*-acyl hydrazones.

Friestad, G. K.; Shen, Y.; Ruggles, E. L. *Angew. Chem. Int. Ed.* **2003**, 42, 5061.

Radical Addition

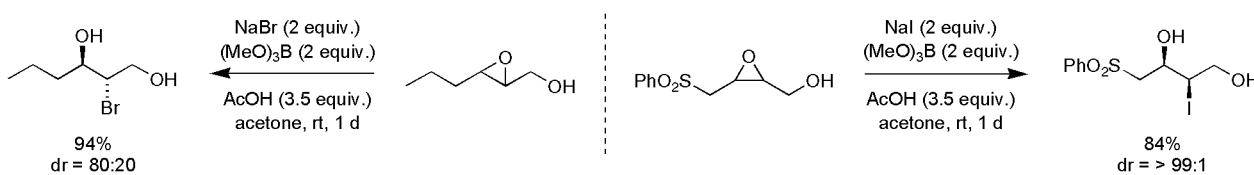


8 examples (yields 44-88%, %ee 46-95%). Optimization of reaction described.

Selective halide substitution of 2,3-epoxy alcohols.

Tomata, Y.; Sasaki, M.; Tanino, K.; Miyashita, M. *Tetrahedron Lett.* **2003**, 44, 8975.

Nucleophilic Substitution



13 examples (yields 84-100%, %de 44->98%).