

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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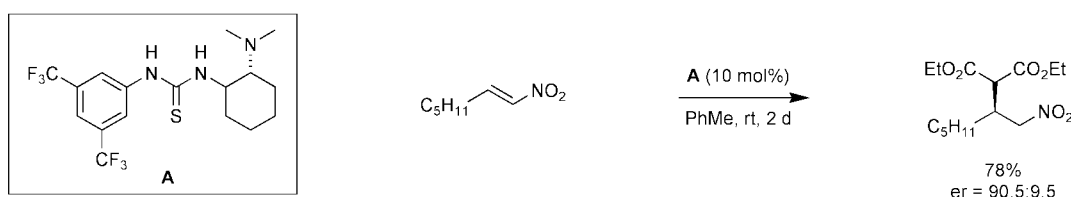
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The journals regularly covered by the abstractors are:

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

Enantioselective Michael reaction of malonate to nitro-olefins.
 Okino, T.; Hoashi, Y.; Takemoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 12672.

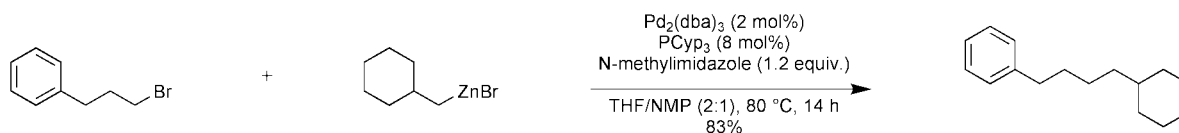
Enantioselective 1,4-Addition



8 examples (yields 74–95%, %ee 81–93%).

Pd-catalyzed Negishi cross-coupling of unactivated alkyl halides and tosylates.
 Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 12527.

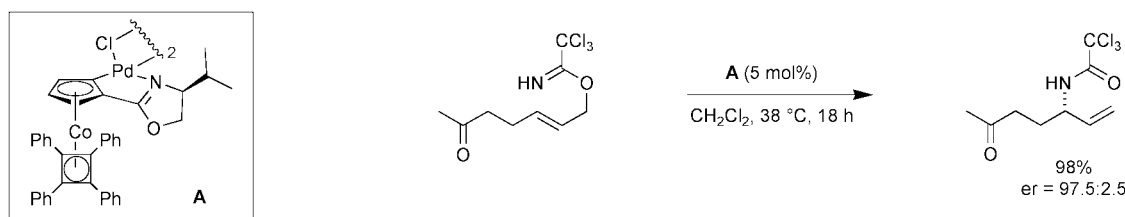
sp²-sp³/sp³-sp³ Coupling



Cyp = cyclopentyl. The same catalyst is effective for coupling alkyl chlorides, bromides, iodides and tosylates to alkyl, alkenyl or arylzincs.
 32 examples (yields 48–93%).

Catalytic asymmetric rearrangement of allylic trichloroacetimidates.
 Anderson, C. E.; Overman, L. E. *J. Am. Chem. Soc.* **2003**, *125*, 12412.

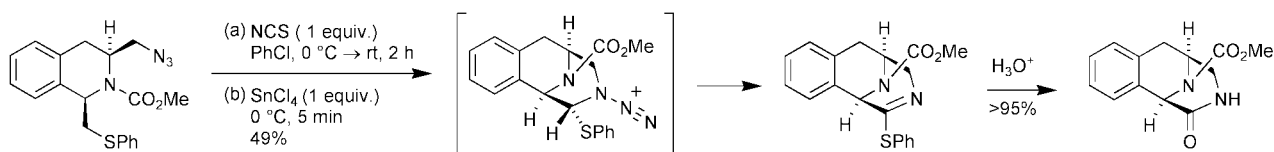
3,3-Sigmatropic Rearrangement



23 examples including *E*- and *Z*-allylic trichloroacetimidates (yields 7–98%, %ee 71–98%).
 Conversions to amino-esters described.

Novel strategy for the synthesis of tetrahydroisoquinoline alkaloids.
Magnus, P.; Matthews, K. S.; Lynch, V. *Org. Lett.* **2003**, *5*, 2181.

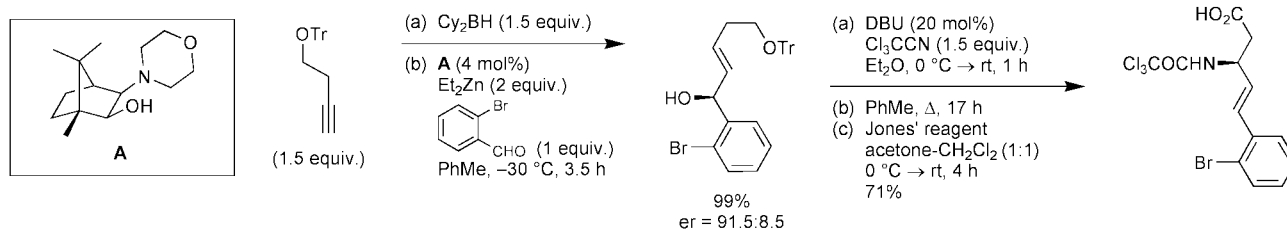
Annulation



Applicable to the synthesis of antitumour antibiotics such as saframycin A, lemomycin and ecteinascidin 743.

Catalytic asymmetric synthesis of γ -unsaturated β -amino acid derivatives.
Lurain, A. E.; Walsh, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 10677.

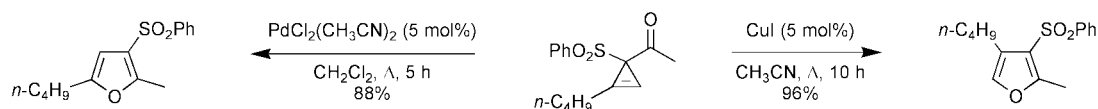
Enantioselective 1,2-Addition



9 examples (yields 54-76%, %ee 78-99%).

Synthesis of tri-substituted furans via a ring-opening cycloisomerization of cyclopropyl ketones.
Ma, S.; Zhang, J. *J. Am. Chem. Soc.* **2003**, *125*, 12386.

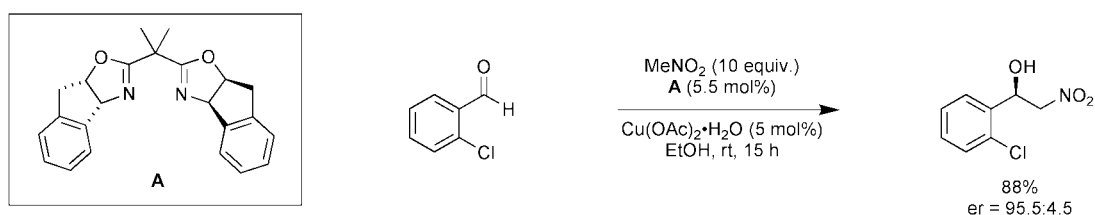
Cycloisomerization



14 examples (yields 50-96%).

Catalytic enantioselective Henry reaction.
Evans, D. A.; Siedel, D.; Rueping, M.; Lam, H. W.; Shaw, J. T.; Downey, C. W. *J. Am. Chem. Soc.* **2003**, *125*, 12692.

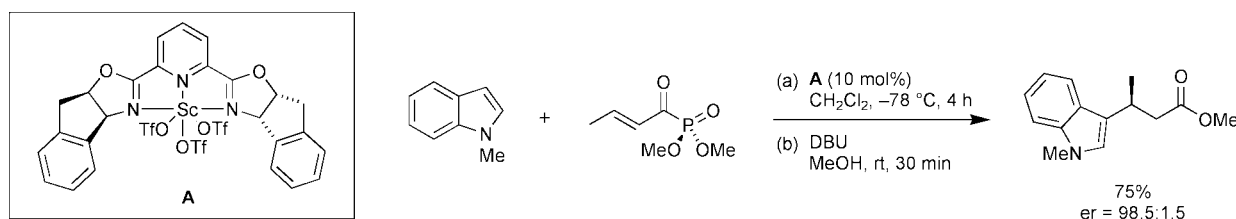
Enantioselective 1,2-Addition



15 examples (yields 66-95%, %ee 87-94%).

Enantioselective indole Friedel-Crafts alkylations.
Evans, D. A.; Scheidt, K. A.; Fandrick, K. R.; Lam, H. W.; Wu, J. *J. Am. Chem. Soc.* **2003**, *125*, 10780.

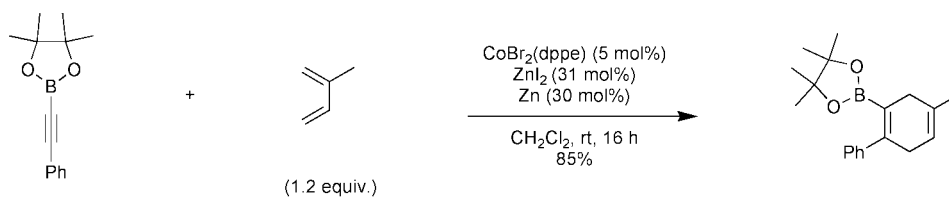
Friedel-Crafts



18 examples (yields 51-88%, %ee 80->99%). A modified quench to isolate amides is also reported.

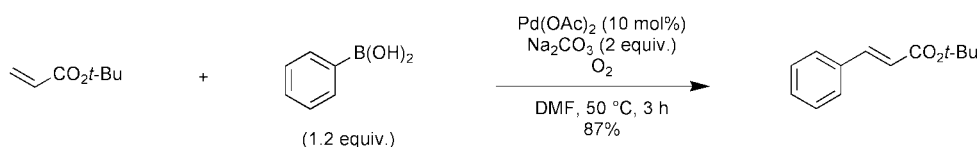
Alkynylboronic esters as dienophiles in cobalt-catalyzed Diels–Alder reactions.
Hilt, G.; Smolko, K. I. *Angew. Chem. Int. Ed.* **2003**, *42*, 2795.

Diels–Alder



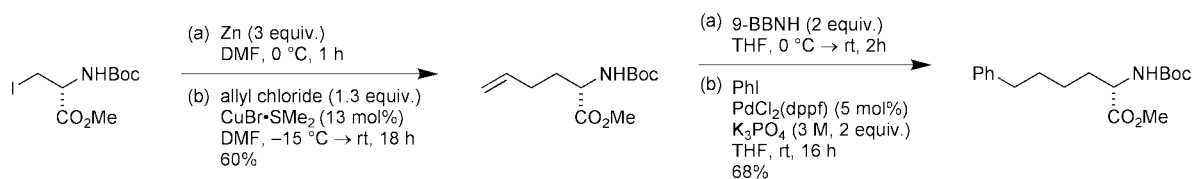
9 examples (yields 61–91%).

Oxygen-promoted Pd(II)-catalysis for the coupling of organoboron compounds and olefins.
Jung, Y. C.; Mishra, R. K.; Yoon, C. H.; Jung, K. W. *Org. Lett.* **2003**, *5*, 2231.

 sp^2 – sp^2 -Cross-Coupling

22 examples (yields 48–92%).

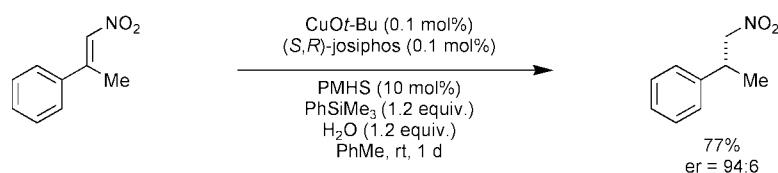
Synthesis of amino acids *via* a one-pot hydroboration–Suzuki coupling.
Rodriguez, A.; Miller, D. D.; Jackson, R. F. W. *Org. Biomol. Chem.* **2003**, *1*, 973.

 sp^3 – sp^2 -Cross-Coupling

13 examples (yields 26–93%).

Catalytic enantioselective conjugate reduction of β,β -disubstituted nitroalkenes.
Czekelius C.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2003**, *42*, 4793.

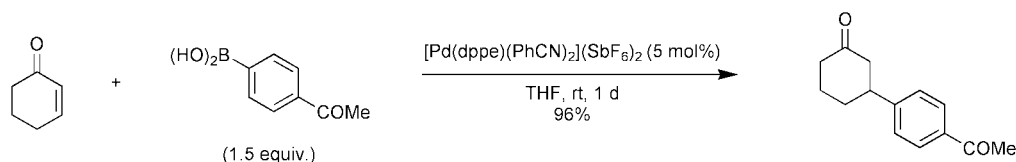
Enantioselective Reduction



11 examples (yields 55–94%, %ee 66–94%). PMHS = poly(methylhydrosiloxane).

Palladium-catalyzed conjugate addition of aryl boronic acids to enones.
Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Angew. Chem. Int. Ed.* **2003**, *42*, 2768.

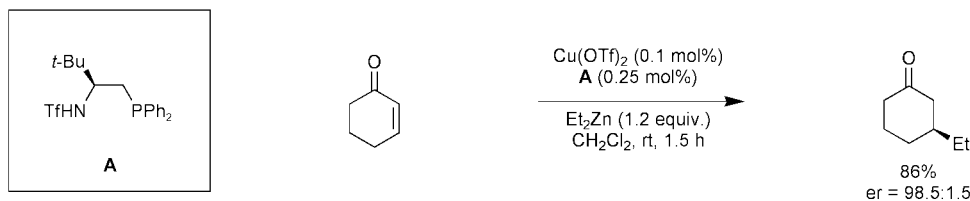
1,4-Addition



37 examples (yields 0–97%). Optimisation studies are also reported.

Enantioselective Cu-catalyzed conjugate addition of alkylzinc reagents to cyclic enones.
 Krauss, I. J.; Leighton, J. I. *Org Lett.* **2003**, *5*, 3201.

Enantioselective 1,4-Addition

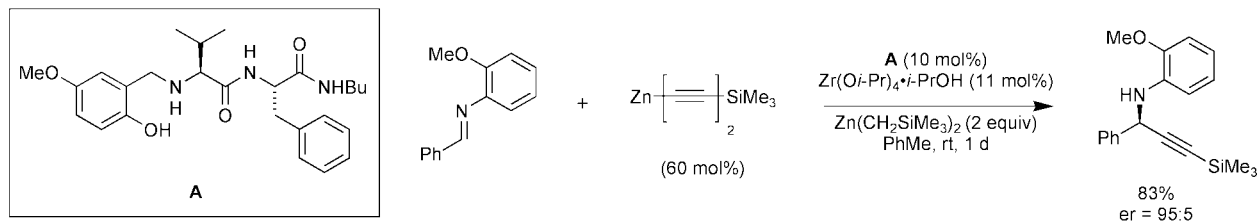


8 examples (yields 52-90%, %ee 84-97%). Optimization of ligand design and reaction conditions is also described.

Enantioselective synthesis of propargylamines via Zr-catalyzed addition of alkynylzinc reagents to arylimines.

Enantioselective 1,2-Addition

Traverse, J. F.; Hoveyda, A. H.; Snapper, M. L. *Org Lett.* **2003**, *5*, 3273.

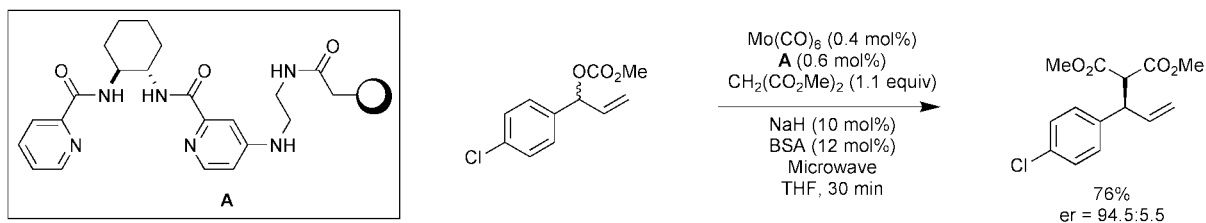


7 examples (yields 69-90%, %ee 69-90%).

Microwave-accelerated molybdenum-catalyzed asymmetric allylic alkylations.

Asymmetric Allylic Alkylation

Belda, O.; Lundgren, S.; Moberg, C. *Org Lett.* **2003**, *5*, 2275.

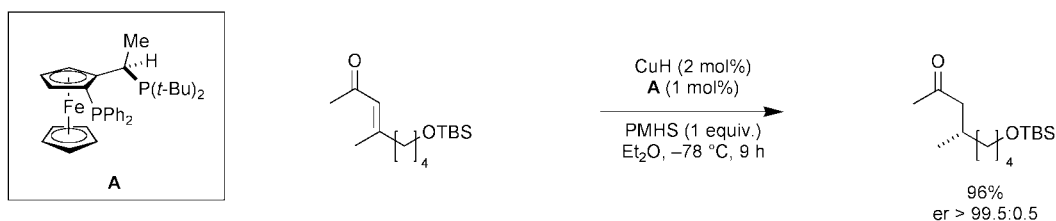


BSA = *N,O*-Bis(trimethylsilyl)acetamide. 12 examples (yields 76-90%, %ee 48-99%).
 A synthesis of (*R*)-baclofen with recycling of **A** is also described.

CuH-catalyzed asymmetric conjugate reductions of acyclic enones.

Asymmetric Conjugate Reduction

Lipshutz, B. H.; Servesko, J. M. *Angew. Chem. Int. Ed.* **2003**, *42*, 4789.

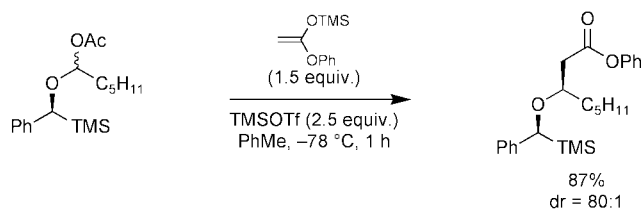


20 examples (yields 88-97%, %ee 35-99%). PMHS = poly(methylhydrosiloxane).

Diastereoselective additions of nucleophiles to α -acetoxy ethers using an α -(trimethylsilyl)benzyl auxiliary.

Nucleophilic Addition

Rychnovsky, S. D.; Cossrow, J. *Org. Lett.* **2003**, *5*, 2367.

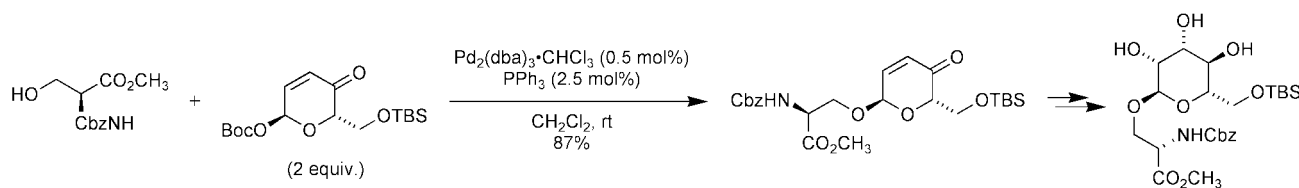


24 examples (yields 61-100%, %de 33-98%).

Palladium-catalyzed glycosylation reaction.

Anderson, C. E.; Overman, L. E. *J. Am. Chem. Soc.* **2003**, *125*, 12412.

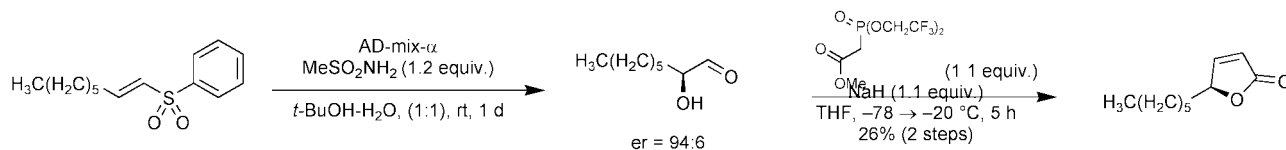
Glycosylation



A range of alcohol nucleophiles investigated including menthol, amino acids and sugars. 26 examples (yields 52-90%).

Asymmetric dihydroxylation of vinyl sulfones to α -hydroxyaldehydes.Evans, P.; Leffray, M. *Tetrahedron*, **2003**, *59*, 7973.

Asymmetric Dihydroxylation

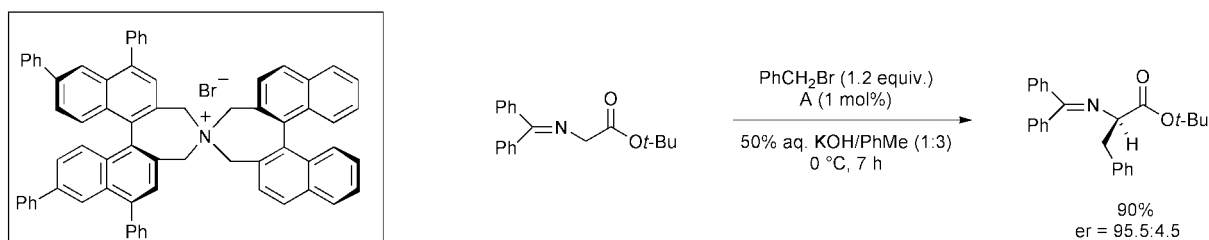


6 examples (yields 20-52%, %ee 88-95%).

Substituent effect of binaphthyl-modified phase-transfer catalysts.

Hashimoto, T.; Maruoka, K. *Tetrahedron Lett.* **2003**, *44*, 3313.

Asymmetric Alkylation



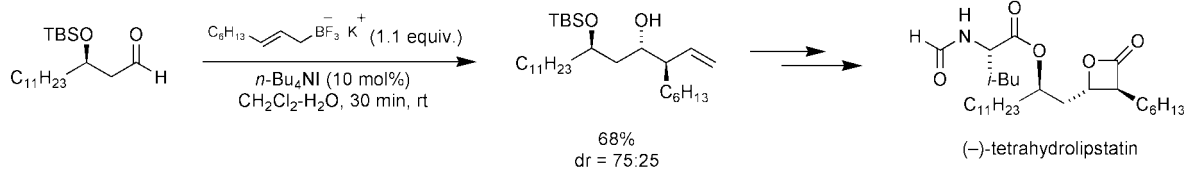
12 examples (yields 18-93%, %ee 71-96%).

Synthesis and optimization studies towards ligand A is also reported.

Diastereoselective allylations and crotylations under phase-transfer conditions using trifluoroborate salts.

Thadani, A. N.; Batey, R. A. *Tetrahedron Lett.* **2003**, *44*, 8051.

Diastereoselective Allylation

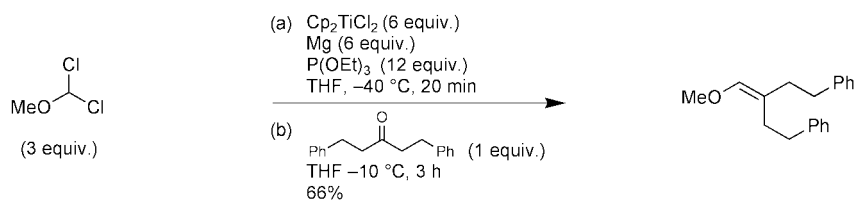


11 examples (yields 68-99%).

Preparation of enol ethers by titanocene(II)-promoted alkoxylation of carbonyl compounds.

Takeda, T.; Shono, T.; Ito, K.; Sasaki, H.; Tsubouchi, A. *Tetrahedron Lett.*, **2003**, *44*, 7897.

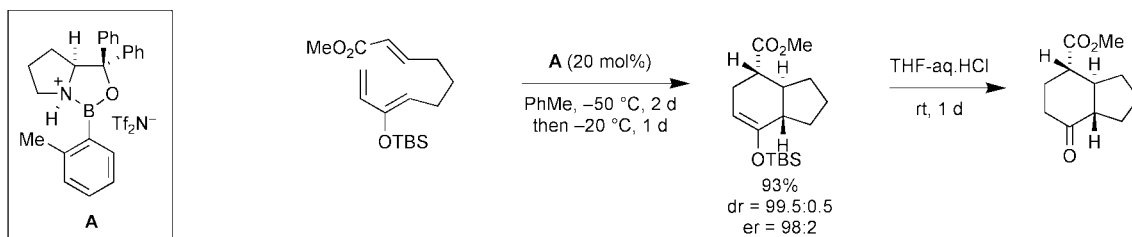
Alkoxylation



15 examples (yields 49-85%).

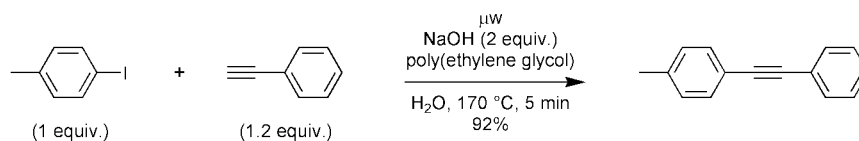
Enantioselective bicyclization reactions using an *N*-protected chiral oxazaborolidine as catalyst.
Zhou, G.; Hu, Q. Y.; Corey, E. J. *Org. Lett.* **2003**, *5*, 3979.

[4+2] Cycloaddition



Transition-metal free Sonogashira-type couplings.

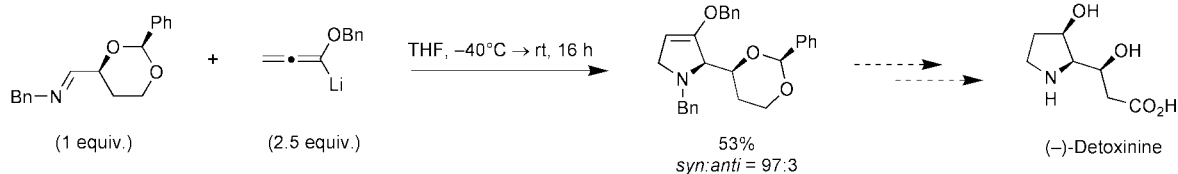
Leadbeater, N. E.; Marco, M.; Tominack, B. J. *Org. Lett.* **2003**, *5*, 3919.

sp²-sp Coupling

Stereoselective synthesis of dihydropyrrole derivatives from lithiated alkoxyallenes.

Flogel, O.; Ghislaine, M.; Amombo, O.; Reißig, H. U.; Zahn, G.; Brudgam, I.; Hartl, H. *Chem. Eur. J.* **2003**, *9*, 1405.

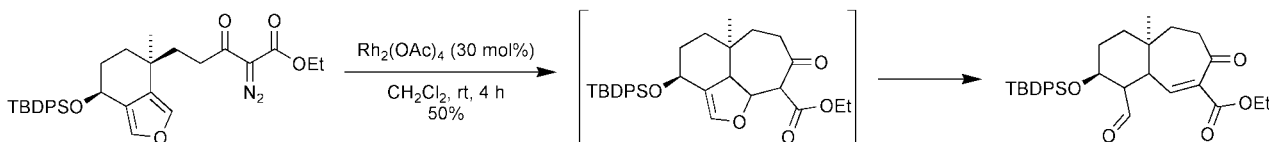
1,2-Addition



Studies towards guanacastepenes.

Hughes, C. C.; Kennedy-Smith, J. J.; Trauner, D. *Org. Lett.* **2003**, *22*, 4113.

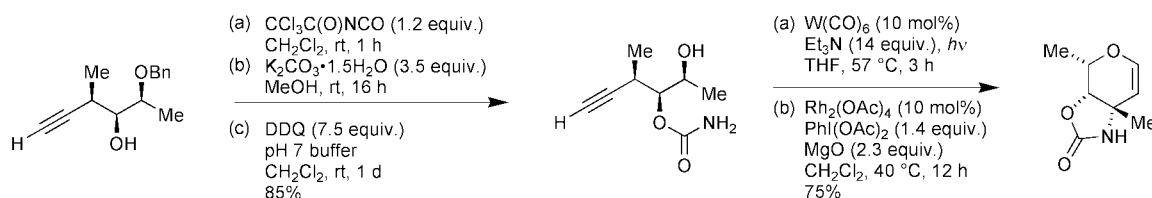
Annulation



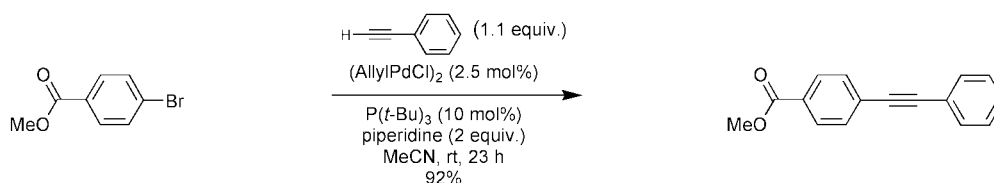
L-Vancosamine derivatives from non-carbohydrate precursors.

Parker, K. A.; Chang, W. *Org. Lett.* **2003**, *5*, 3891.

Cycloisomerization/Insertion



Copper-free Sonogashira coupling of aryl bromides with acetylenes.

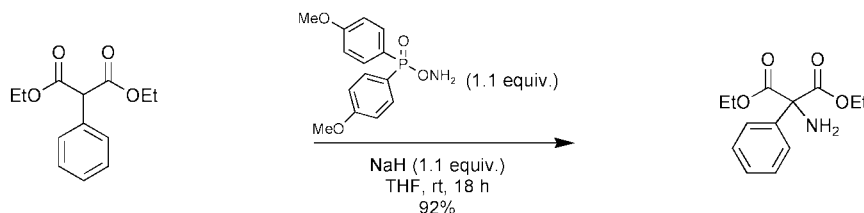
Soheili, A.; Albaneze-Walker, J.; Murry, J. A.; Dormer, P. G.; Hughes, D. L. *Org. Lett.*, **2003**, *5*, 4191.sp-sp² coupling

15 examples (yields 50-99%).

Electrophilic amination of stabilised carbanions.

Smulik, J. A.; Vedejs, E. *Org. Lett.*, **2003**, *5*, 4187.

Amination

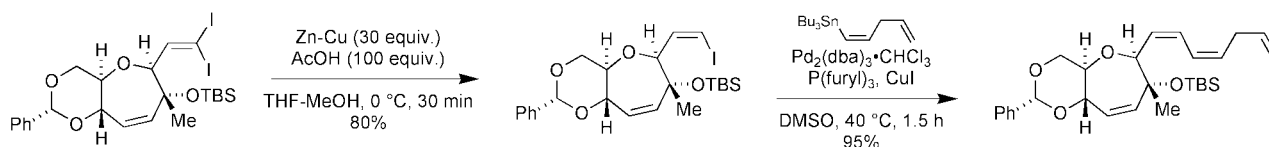


7 examples (yields <2-99%).

Stereoselective synthesis of (Z)-1-iodo alkenes from 1,1-diiodo-1-alkenes.

Kadota, I.; Ueno, H.; Ohno, A.; Yamamoto, Y. *Tetrahedron Lett.* **2003**, *44*, 8645.

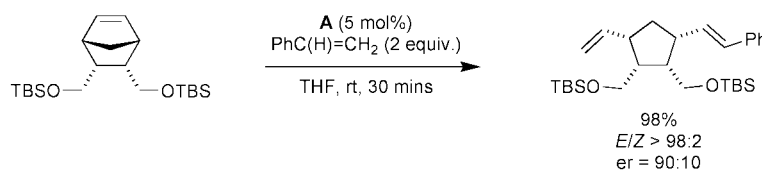
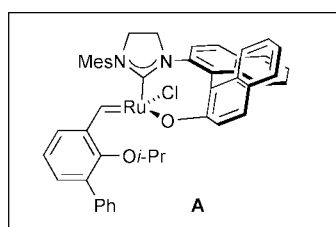
Reduction

Application to total synthesis of Gambierol. 7 examples (74-95%, 75:25 *E/Z* 0:100).

Chiral Ru-complexes for asymmetric ring-opening and ring closing metathesis.

Van Veldhuizen, J. J.; Gillingham, D. G.; Garber, S. B.; Katoaka, O.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 12502.

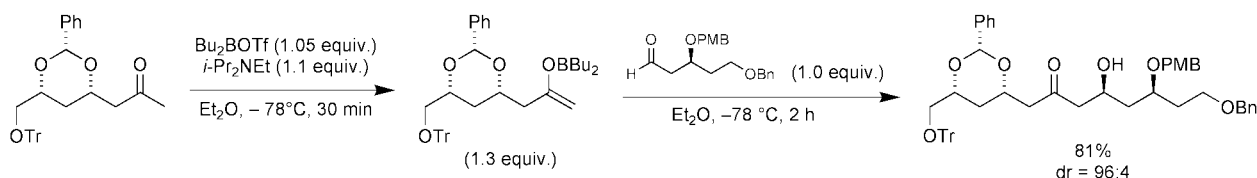
Asymmetric Olefin Metathesis



Although the efficiency of catalyst A is greater than previous analogues, the catalyst recovery is significantly lower.

20 examples (yields 0-98%, %ee 10-91%, *E/Z* 81:19 - 98:2).1,5-Asymmetric induction in boron-mediated β -alkoxymethyl ketone aldol reactions.Evans, D. A.; Côté, B.; Coleman, P. J.; Connell, B. T. *J. Am. Chem. Soc.* **2003**, *125*, 10893.

Aldol Reaction

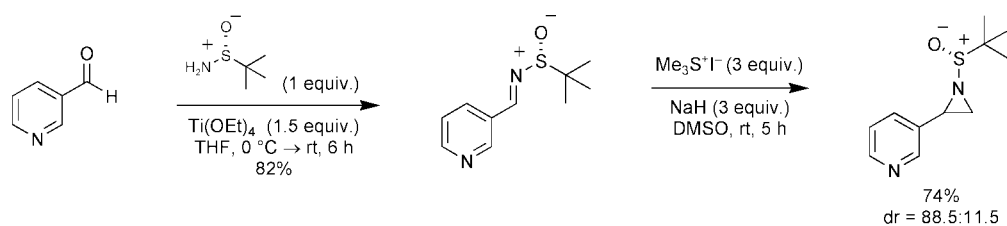


27 examples (yields 52-89%, %de 20-96%).

Synthesis of chiral aziridines from sulfinyl imines.

Morton, D.; Pearson, D.; Field, R. A.; Stockman, R. A. *Synlett*. **2003**, *13*, 1985.

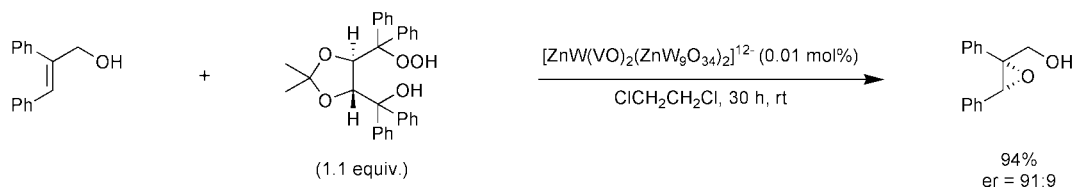
Aziridination



Catalytic stereoselective epoxidation of allylic alcohols by sandwich-type polyoxometallates.

Adam, W.; Alsters, P. L.; Neumann, R.; Saha-Moeller, C. R.; Seebach, D.; Beck, A. K.; Zhang, R. J. *Org. Chem.* **2003**, *68*, 8222.

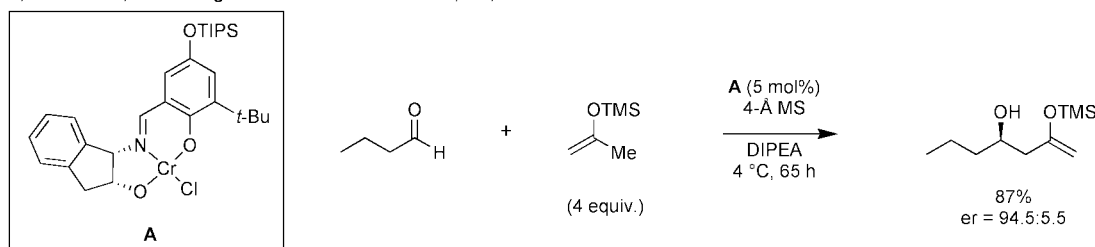
Epoxidation



Chromium(III)-catalyzed hetero-ene reactions of trimethylsilyl enol ethers.

Ruck, R. T.; Jacobsen, E. N. *Angew. Chem. Int. Ed.* **2003**, *42*, 4771.

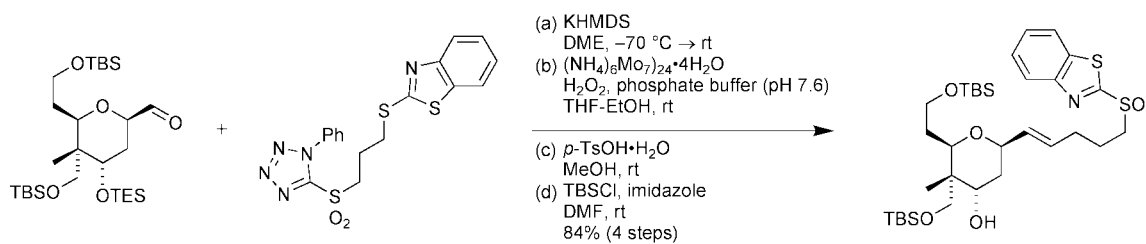
Hetero-Ene-Reaction



Total synthesis of (+)-Lasonoilde A.

Kang, S. H.; Kang, S. Y.; Kim, C. M.; Choi, H.-W.; Jun, H.-S.; Lee, B. M.; Park, C. M.; Jeong, J. W. *Angew. Chem. Int. Ed.* **2003**, *42*, 4779.

Stereoselective Olefination

Samarium-catalyzed semipinacol rearrangement/Tishchenko reduction of secondary α -hydroxy epoxides.Fan, C. A.; Hu, X. D.; Tu, Y. Q.; Wang, B. M.; Song, Z. L. *Chem.-Eur. J.* **2003**, *9*, 4301.

Rearrangement/Reduction

