

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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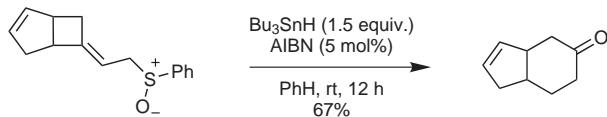
Synthesis 2003, No. 5, 01 04 2003. Article Identifier: 1437-210X,E;2003,0,05,795,802,ftx,en;X00503SS.pdf.
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The journals regularly covered by the abstractors are:

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
Organometallics
Perkin Transactions 1
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry and Tetrahedron Letters

Allyl sulfoxides as precursors for radical two-carbon ring expansion.
Chuard, R.; Giraud, A.; Renaud, P. *Angew. Chem. Int. Ed.* **2002**, *41*, 4323.

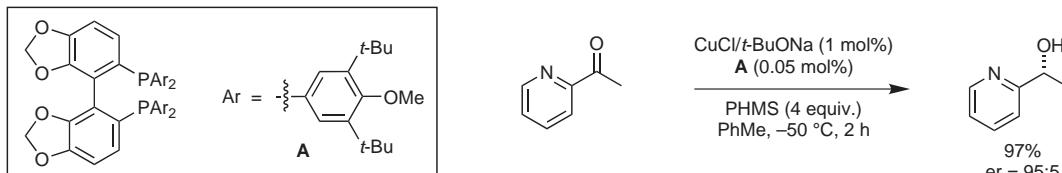
Ring Expansion



8 examples (yields 36-67%).

Enantioselective Cu-catalyzed reduction of heteroaromatic ketones.
Lipshutz, B. H.; Lower, A.; Noson, K. *Org. Lett.* **2002**, *4*, 4045.

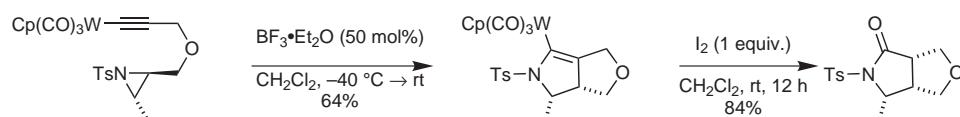
1,2-Addition



8 examples (yields 68-98%, %ee 75-99%).

Synthesis of bicyclic lactams via [3+2] cycloaddition of alkynyltungsten complexes.
Madhushaw, R. J.; Hu, C. C.; Liu, R. S. *Org. Lett.* **2002**, *4*, 4151

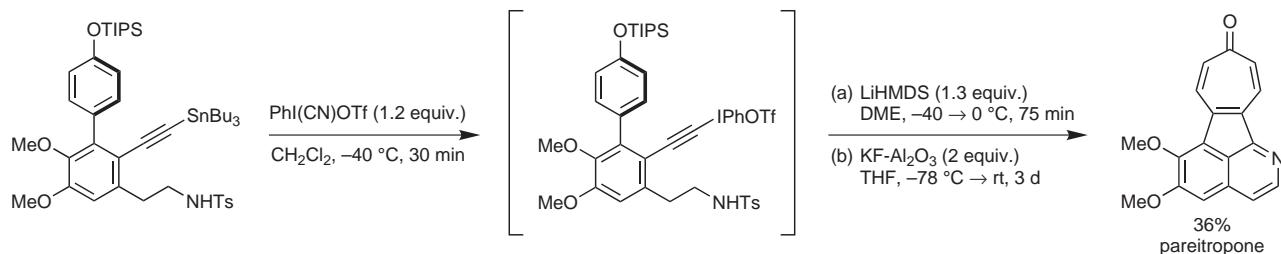
[3+2] Cycloaddition



8 examples (yields 54-90%).

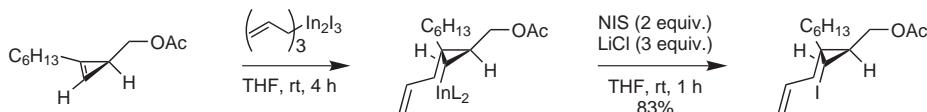
Total synthesis of pareitropone *via* alkynyl iodonium salt chemistry.
Feldman, K. S.; Cutarelli, T. D.; Florio, R. D. *J. Org. Chem.* **2002**, *67*, 8528.

Ring Expansion



Stereoselective synthesis of halocyclopropanes *via* halogenation of cyclopropylindium reagents.
Araki, S.; Kenji, O.; Shiraki, F.; Hirashita, T. *Tetrahedron Lett.* **2002**, *43*, 8033.

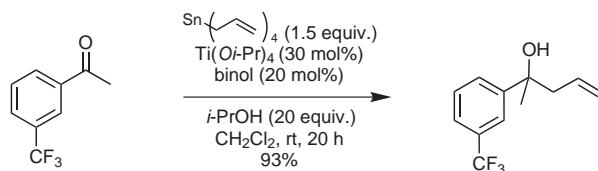
Carbometallation



4 examples (yields 41-83%).

Ti-catalyzed allylation of ketones
Waltz, K. M.; Gavenonis, J.; Walsh, P. J. *Angew. Chem. Int. Ed.* **2002**, *41*, 3697.

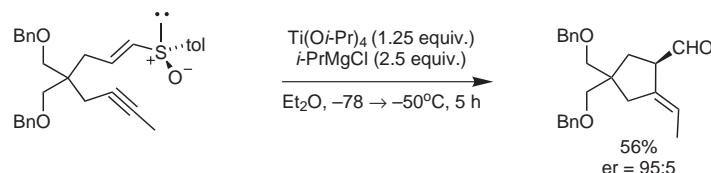
1,2-Addition



10 examples (yields 67-99%, %ee 76-96%).

Sulfur-functionalized olefins for titanacycle formation.
Narita, M.; Urabe, H.; Sato, F. *Angew. Chem. Int. Ed.* **2002**, *41*, 3671.

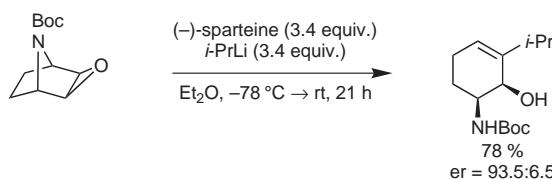
Cyclization



10 examples (yields 30-98%, %ee 77-99%).

Enantioselective alkylative double ring opening of epoxides.
Hodgson, D. M.; Maxwell, C. R.; Miles, T. J.; Paruch, E.; Stent, M. A. H.; Matthews, I. R.; Wilson, F. X.; Withington, J. *Angew. Chem. Int. Ed.* **2002**, *41*, 4313.

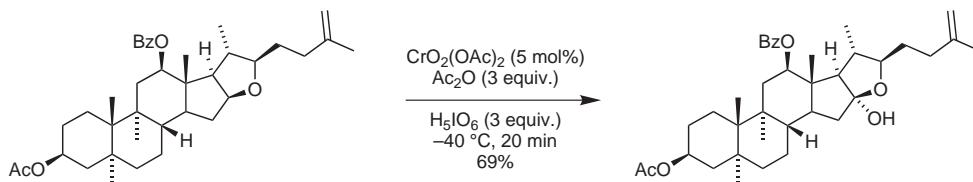
Enantioselective Metallation



17 examples (yields 25-85%).

Chemoselective Cr-catalyzed oxidation of C-H bonds.
Lee, S.; Fuchs, P. L. *J. Am. Chem. Soc.* **2002**, *124*, 13978.

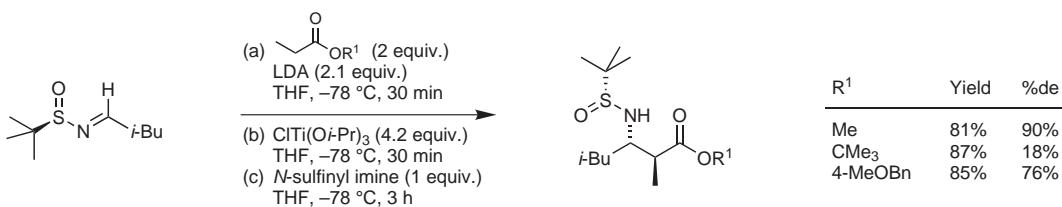
Oxidation



16 examples (yields 23-97%).

Stereoselective synthesis of β -amino acid derivatives.
Tang, T. P.; Ellman, J. A. *J. Org. Chem.* **2002**, *67*, 7819.

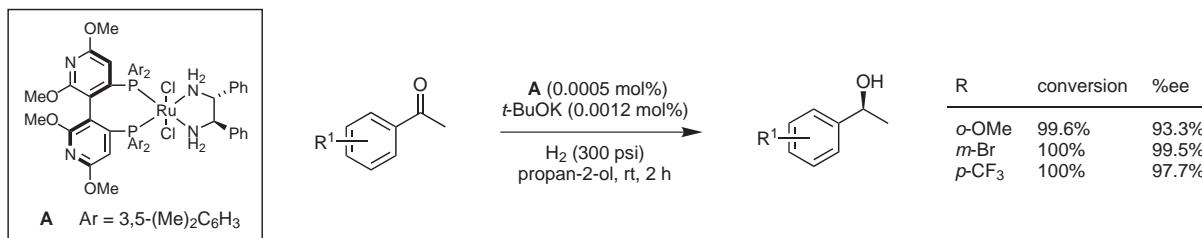
1,2-Addition



17 examples (yields 65-94%).

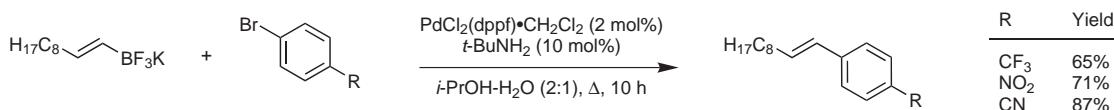
Enantioselective Ru-catalyzed hydrogenation of aromatic ketones.
Wu, J.; Chen, H.; Kwok, W.; Guo, R.; Zhou, Z.; Yeung, C.; Chan, A. S. C. *J. Org. Chem.* **2002**, *67*, 7908.

Hydrogenation



27 examples, (conversions 93.4-100%, %ee 78-99.9%).

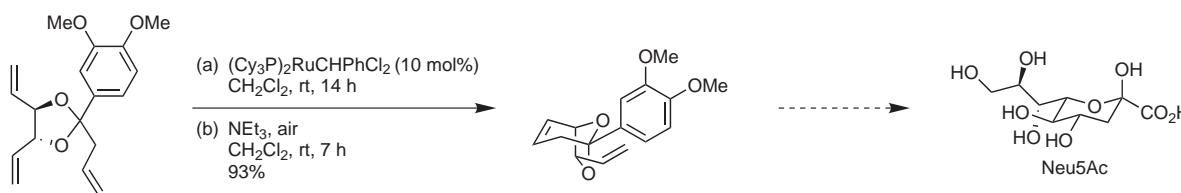
Suzuki-Miyaura cross coupling reactions of potassium alkenyltrifluoroborates.
Molander, G. A.; Bernardi, C. R. *J. Org. Chem.* **2002**, *67*, 8424.

sp²-sp² Coupling

37 examples (yields 59-91%).

Synthesis of sialic acids via desymmetrization by ring closing metathesis.
Voight, E. A.; Rein, C.; Burke, S. D. *J. Org. Chem.* **2002**, *67*, 8489.

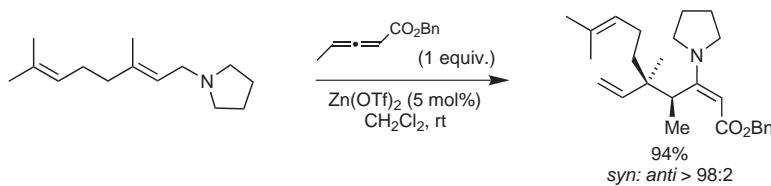
Metathesis



Formal total syntheses of sialic acids KDN and Neu5Ac.

Zn-catalyzed [3,3]-sigmatropic allenoate-Claisen rearrangement.
Lambert, T. H.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2002**, *124*, 13646.

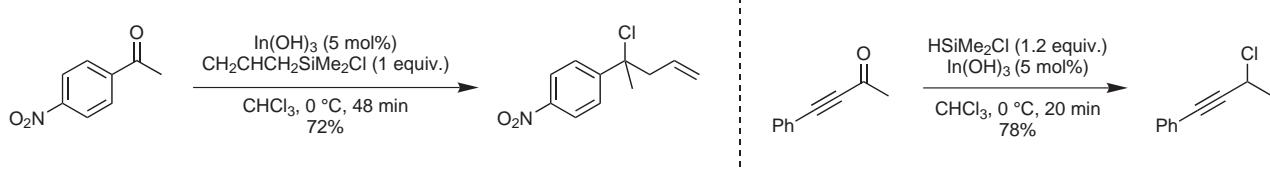
[3,3]-Sigmatropic Rearrangement



14 examples (yields 75-97%, %de 82-86%).

In-catalyzed conversion of carbonyl compounds to organic halides.
Onishi, Y.; Ogawa, D.; Yasuda, M.; Baba, A. *J. Am. Chem. Soc.* **2002**, *124*, 13690.

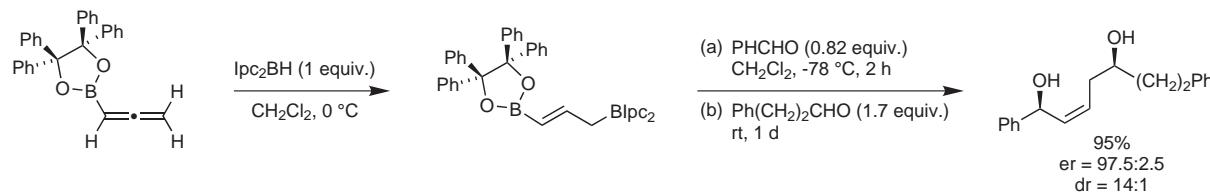
Deoxygenative Halogenation



16 examples (yields 46-90%).

Enantioselective synthesis of 1,5-*anti*- and 1,5-*syn*-diols using a double allylboration sequence.
Flamme, E. M.; Roush, W. R. *J. Am. Chem. Soc.* **2002**, *124*, 13644.

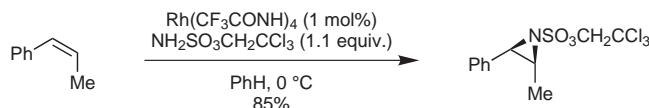
1,2-Addition



19 examples (yields 34-95%, %ee 82-96%).

Rh-catalyzed olefin aziridination.
Guthikonda, K.; Du Bois, J. *J. Am. Chem. Soc.* **2002**, *124*, 13672.

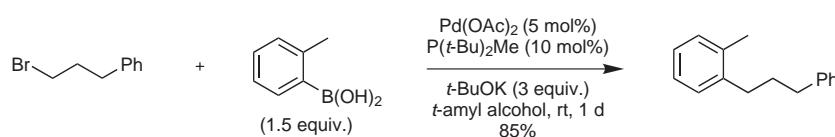
Aziridination



12 examples (yields 57-95%).

Suzuki reactions of unactivated alkyl bromides.
Kirchoff, J. H.; Netherton, M. R.; Hills, I. D.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 13662.

sp²-sp³/sp³-sp³ Coupling

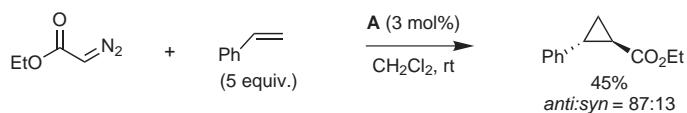
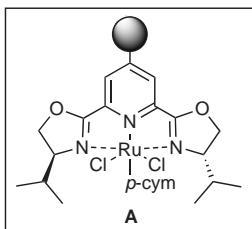


19 examples (yields 2-94%).

The first immobilization of pyridine-bis(oxazoline) chiral ligands.

Cornejo A, Fraile, J. M.; Garcia, J. I.; Garcia-Verdugo, E.; Gil, M. J.; Legarreta, G.; Luis, S. V.; Martinez-Merino, V.; Mayoral, J. A. *Org. Lett.* **2002**, 22, 3927.

Cyclopropanation

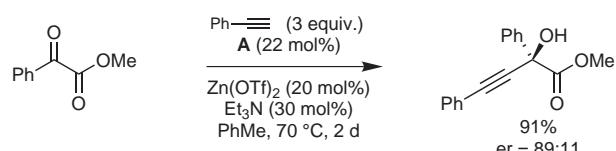
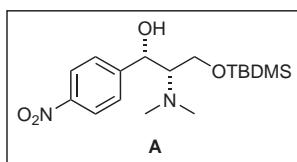


12 examples (yields 9-39%).

Enantioselective Zn-catalyzed alkynylation of α -keto esters.

Jiang, B.; Chen, Z.; Tang, X. *Org. Lett.* **2002**, 4, 3451.

1,2-Addition

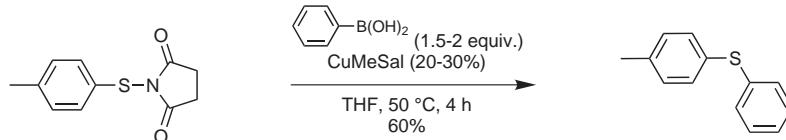


12 examples (yields 11-95%, %ee 73-94%).

Cu-catalyzed coupling of boronic acids with *N*-thioimide derivatives.

Savarin, C.; Srogl, J.; Liebeskind, L. S. *Org. Lett.* **2002**, 4, 4309.

C-S Cross Coupling

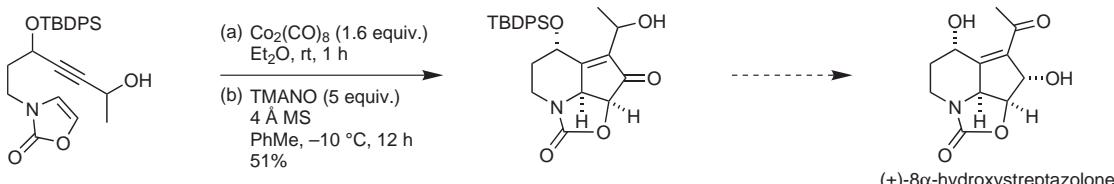


12 examples (yields 51-83%).

Total synthesis of (\pm)-8 α -hydroxystreptazolone.

Nomura, I.; Mukai, C. *Org. Lett.* **2002**, 24, 4301.

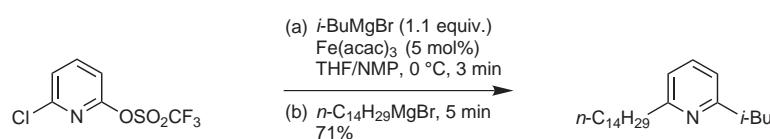
Pauson-Khand



Fe-catalyzed cross coupling reactions.

Furstner, A.; Leitner, A.; Mendez, M.; Krause, H. *J. Am. Chem. Soc.* **2002**, 124, 13856.

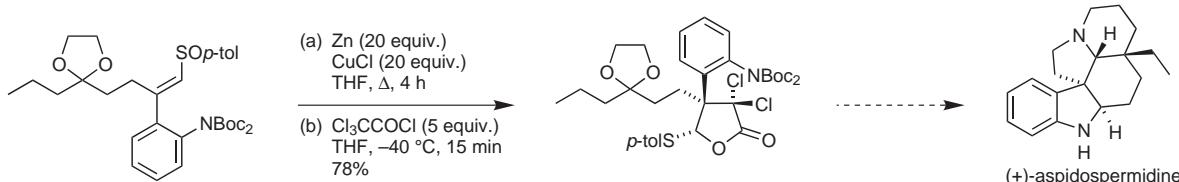
$\text{sp}^2\text{-sp}^3$ Coupling



51 examples (yields 27-98%).

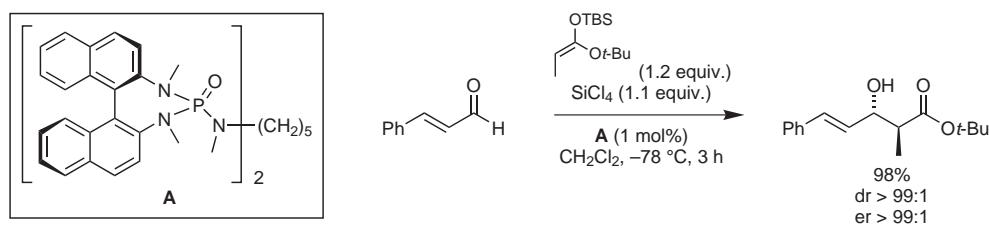
Total synthesis of (+)-aspidospermidine via Cu-Zn-catalyzed lactonization.
Marino, J. P.; Rubio, M. B.; Cao, G.; de Dios, A. *J. Am. Chem. Soc.* **2002**, *124*, 13398.

Lactonization



Enantioselective addition of silyl ketene acetals to aldehydes.
Denmark, S. E.; Wynn, T.; Beutner, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 13405.

1,2-Addition



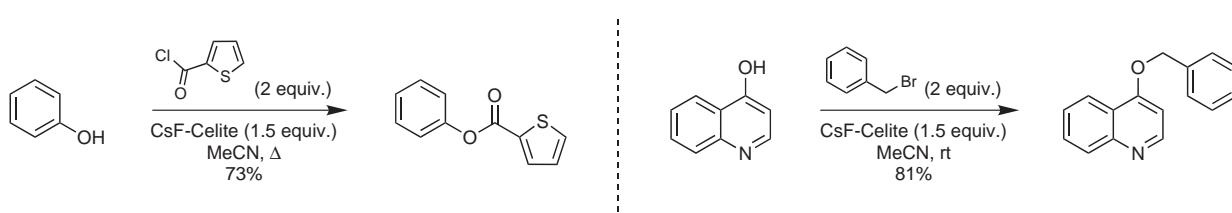
Total synthesis of (S)-oxybutynin via enantioselective cyanosilylation.
Masumoto, S.; Suzuki, M.; Kanai, M.; Shibasaki, M. *Tetrahedron Lett.* **2002**, *43*, 8647.

1,2-Addition



Synthesis of ethers and esters using CsF-Celite as a solid base.
Shah, S. T. A.; Khan, K. M.; Heinrich, A. M.; Choudhary, M. I.; Voelter, W. *Tetrahedron Lett.* **2002**, *43*, 8603.

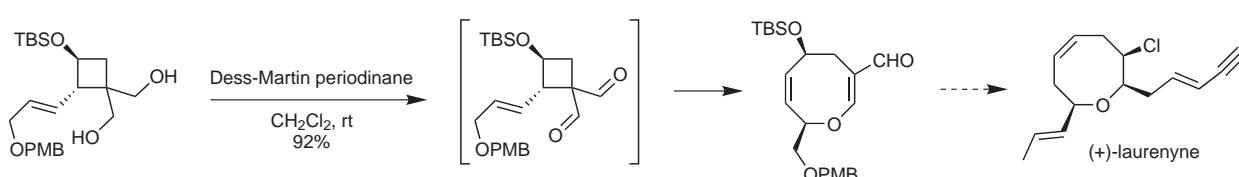
O-Acylation/Alkylation



24 examples (yields 54-91%).

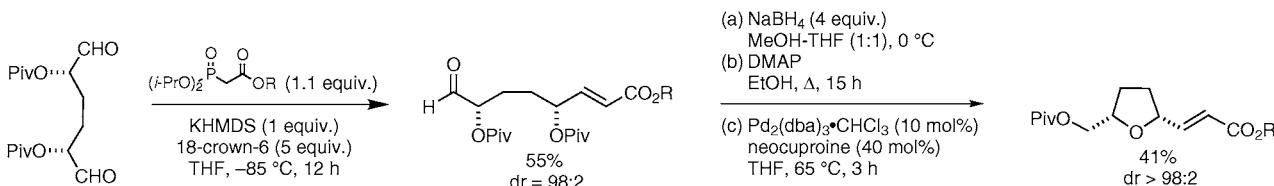
Total synthesis of (+)-laurenyne via a retro-Claisen rearrangement.
Boeckman, R. K.; Zhang, J.; Reeder, M. R. *Org. Lett.* **2002**, *22*, 3891.

Retro-Claisen Rearrangement



Horner–Wadsworth–Emmons/ring closure approach to chiral tetrahydrofurans and tetrahydropyrans.
Vares, L.; Rein, T. *J. Org. Chem.* **2002**, *65*, 7226.

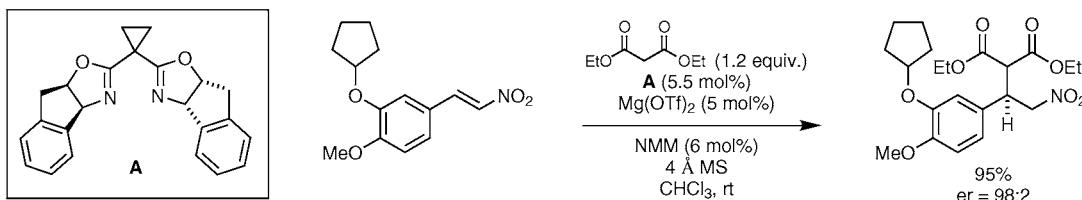
Deymmetralization



R = (*1R,2S,5R*)-8-phenylmenthyl. Application to chiral tetrahydropyrans is also reported.

Catalytic enantioselective conjugate addition of 1,3-dicarbonyl compound s to nitroalkenes.
Barnes, D. M.; Ji, J.; Fickes, M. G.; Fitzgerald, M. A.; King, S. A.; Morton, H. E.; Plagge, F. A.; Preskill, M.; Wagaw, S. H.; Wittenberger, S. J.; Zhang, J. *J. Am. Chem. Soc.* **2002**, *124*, 13097.

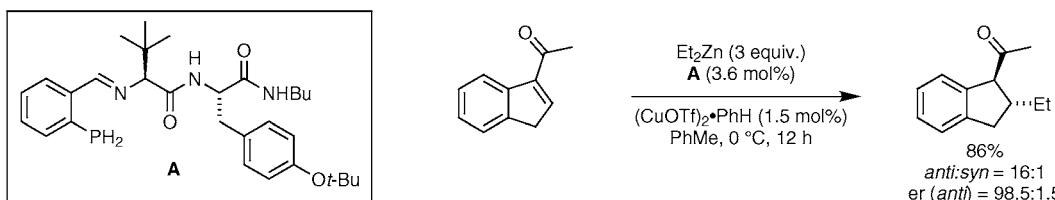
1,4-Addition



26 examples (yields 50-99%, %de 29-97%).

Stereoselective Cu-catalyzed conjugate addition of alkylzincs to cyclic enones.
Degrado, S. J.; Mizutani, H.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 13362.

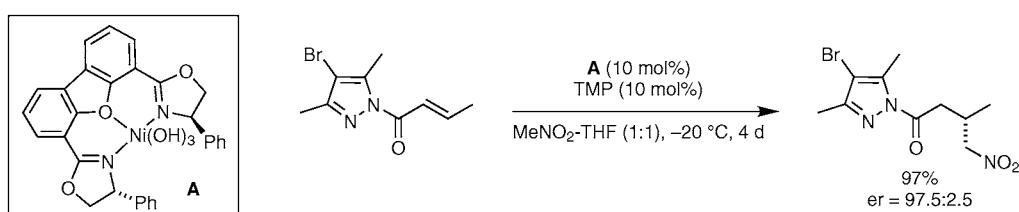
1,4-Addition



12 examples (yields 42-86%, 3:1 \geq anti:syn \geq 25:1, %ee 94->98%).

Enantioselective Ni-catalyzed conjugate addition of nitromethane.
Itoh, K.; Kanemasa, S. *J. Am. Chem. Soc.* **2002**, *124*, 13394.

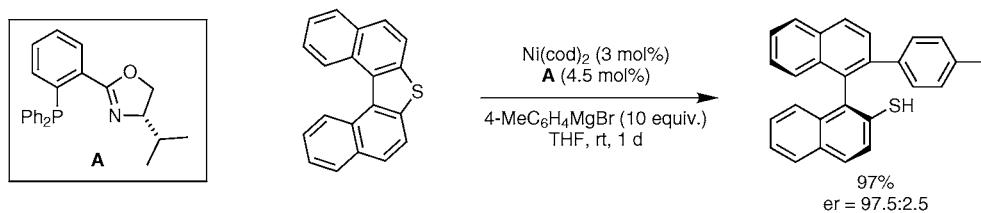
1,4-Addition



15 examples (yields 39-97%, %ee 77-98%).

Ni-catalyzed cross coupling of Grignard reagents and dinaphthothiophene.
Shimada, T.; Cho, Y.-H.; Hayashi, T. *J. Am. Chem. Soc.* **2002**, *124*, 13396.

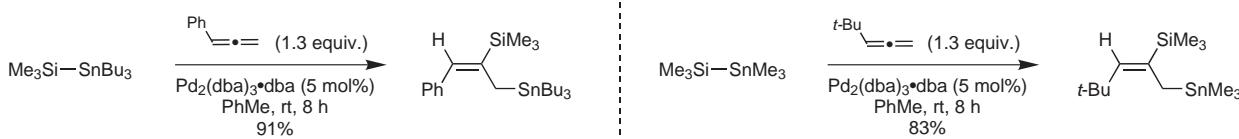
Cross Coupling



5 examples (yields 90-97%, %ee 68-95%).

Pd-catalyzed silylstannylation of allenes.
Jeganmohan, M.; Shanmugasundaram, M.; Chang, K.-J.; Cheng, C.-H. *Chem. Commun.* **2002**, 2552

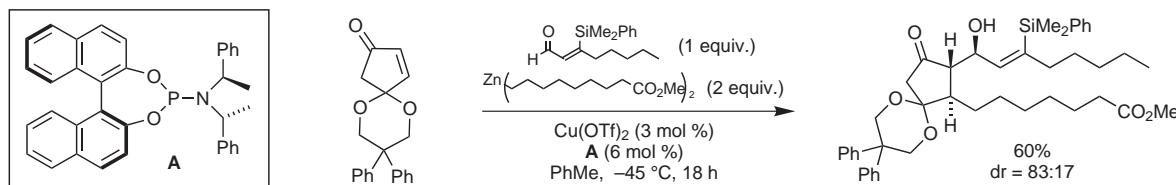
Silylstannylation



15 examples (yields 80–91%). Only (*E*)-alkenylsilanes are generated.

Enantioselective Cu-catalyzed tandem 1,4-addition/aldol reaction.
Arnold, L. A.; Naasz, R.; Minnaard, A. J.; Feringa, B. L. *J. Org. Chem.* **2002**, 67, 7244.

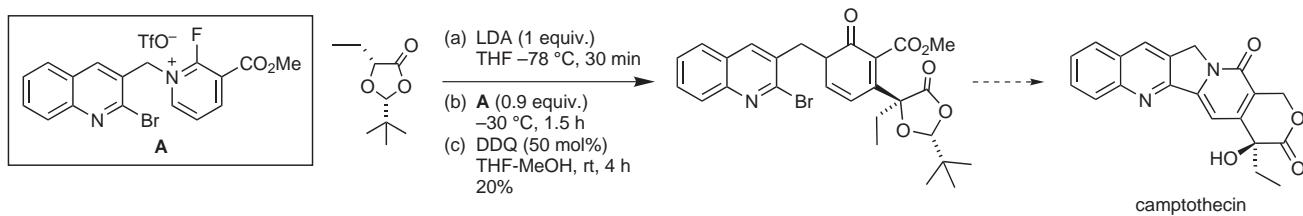
1,4-Addition



Total synthesis of (−)-prostaglandin E₁ methyl ester is also reported.

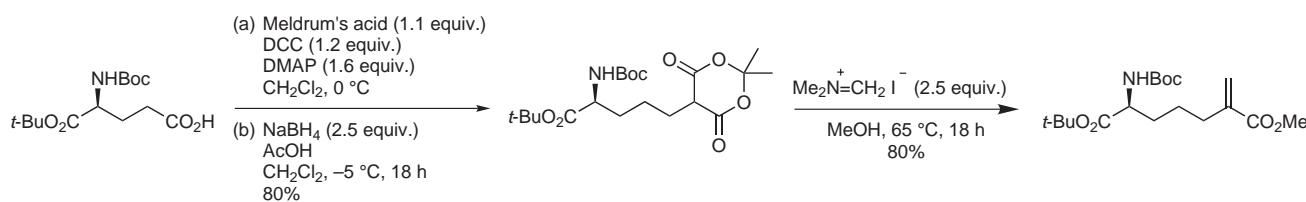
Total synthesis of (+)-camptothecin *via* addition of ester enolates to *N*-alkyl-2-fluoropyridinium salts.
Bennasar, M.-L.; Zulaica, E.; Juan, C.; Alonso, Y.; Bosch, J. *J. Org. Chem.* **2002**, 67, 7465.

Nucleophilic Addition



Synthesis of α-substituted acrylate esters.
Hin, B.; Majer, P.; Tsukamoto, T. *J. Org. Chem.* **2002**, 67, 7365.

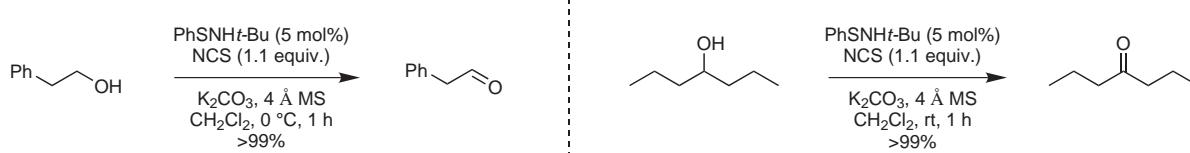
Mannich Reaction



11 examples (yields 57–86%, 3 steps).

Organocatalyzed oxidation of alcohols.
Mukaiyama, T.; Matsuo, J.; Iida, D.; Kitagawa, H. *Chem. Lett.* **2002**, 286.

Oxidation



4 examples (yields 93–>99%).