

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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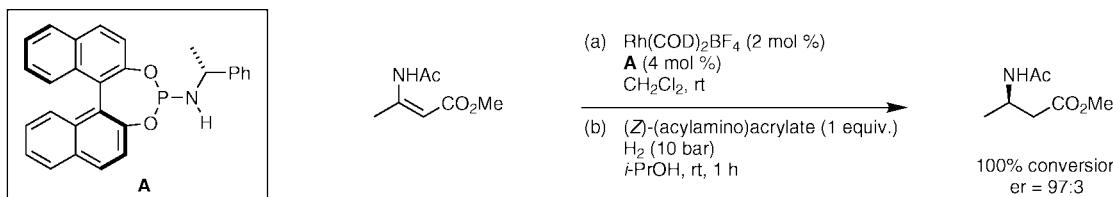
Synthesis 2003, No. 8, 20 05 2003. Article Identifier: 1437-210X;E;2003;0,07,1296,1303,ftx,en;X00803SS.pdf.
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The journals regularly covered by the abstractors are:

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

Enantioselective Rh-catalyzed hydrogenation of β -dehydroamino acid derivates.
Pena, D.; Minnaard, A. J.; de Vries, J. G.; Feringa, L. B. *J. Am. Chem. Soc.* **2002**, *124*, 14552.

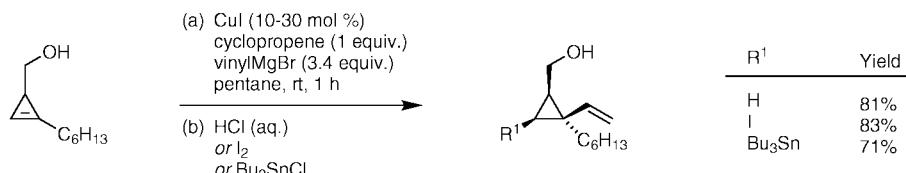
Hydrogenation



24 examples (conversion 49-100%, %ee 92-99%).

Cu-catalyzed facially selective addition of Grignard reagents to cyclopropenes.
Liao, L.; Fox, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 14322.

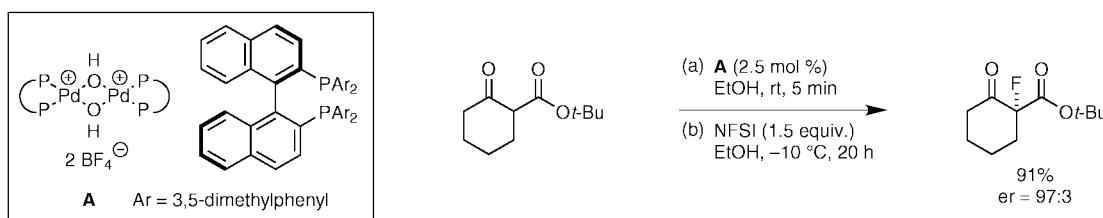
Nucleophilic Addition



15 examples (yields 61-83%).

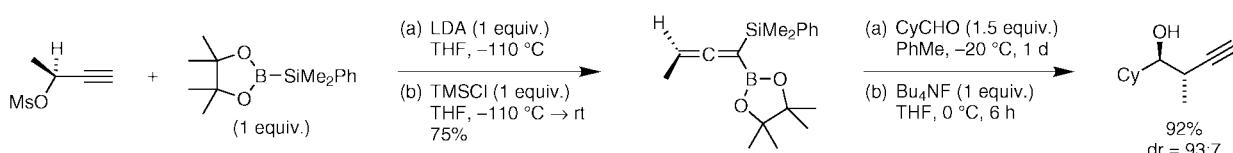
Enantioselective Pd-catalyzed fluorination of β -ketoesters.
Hamashima, Y.; Yagi, K.; Takano, H.; Tamas, L.; Sodeoka, M. *J. Am. Chem. Soc.* **2002**, *124*, 14530.

Fluorination



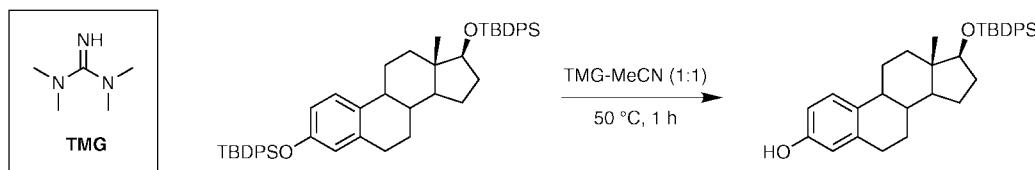
8 examples (yields 49-96%, %ee 93-94%). 6 different catalysts tested.

Synthesis and reaction of 1-boryl-1-silyllallenenes.
Shimizu, M.; Kurahashi, T.; Kitagawa, H.; Hiyama, T. *Org. Lett.* **2003**, *5*, 225.

1,2-Addition

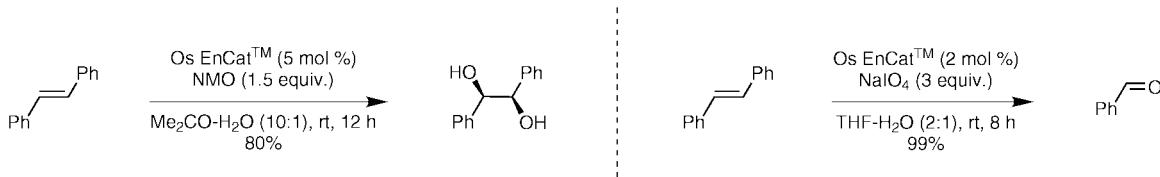
2 examples (yields 67-92%, %de 78-86%). Synthesis of 9 *gem*-silylboryllallenenes (yields 52-83%) is also reported.

Chemosselective 1,1,3,3-tetramethylguanidine-mediated deprotection of both silyl and acetyl groups.
Oyama, K.-I.; Kondo, T. *Org. Lett.* **2003**, *5*, 209.

Deprotection

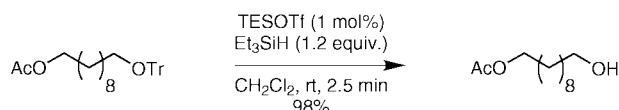
15 examples (yields 71-94%).

Microencapsulation of osmium tetroxide in polyurea.
Ley, S. V.; Ramarao, C.; Lee, A.-L.; Ostergaard, N.; Smith, S. C.; Shirley, I. M. *Org. Lett.* **2003**, *5*, 185.

**Dihydroxylation/
Oxidative Cleavage**

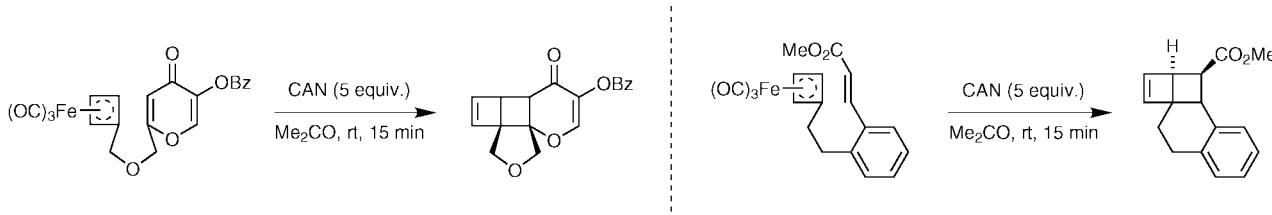
8 examples of dihydroxylation (yields 73-90%) and 8 examples of oxidative cleavage (yields 66-99%).

Trialkylsilyl triflate-catalyzed reductive cleavage of trityl ethers with triethylsilane.
Imagawa, H.; Tsuchihashi, T.; Singh, R. K.; Yamamoto, H.; Sugihara, T.; Nishizawa, M. *Org. Lett.* **2003**, *5*, 153.

Deprotection

16 examples (yields 86-99%).

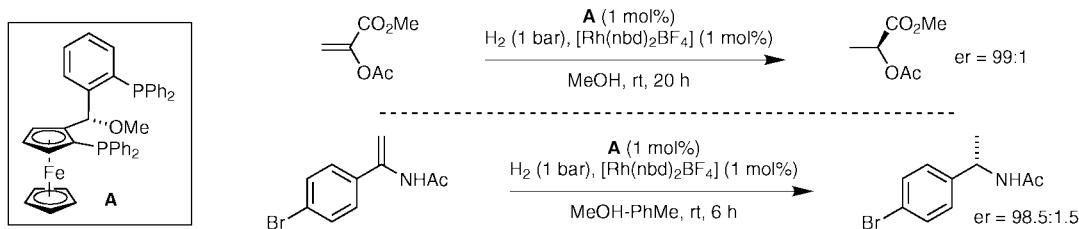
Intramolecular cycloadditions of cyclobutadiene with olefins.
Limato, J.; Tallarico, J. A.; Porter, J. R.; Khuong, K. S.; Houk, K. N.; Snapper, M. L. *J. Am. Chem. Soc.* **2002**, *124*, 14748.

Cycloaddition

37 examples (yields trace-93%).

Application of new ferrocenyl ligands in asymmetric catalytic hydrogenation.
Lotz, M.; Polborn, K.; Knochel, P. *Angew. Chem. Int. Ed.* **2002**, *41*, 4709.

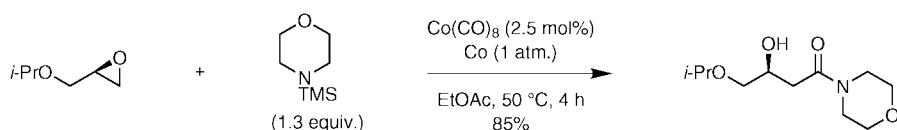
Hydrogenation



8 examples (%ee 95->99%). 5 different ferrocenyl ligands were screened.

Carbonylation of enantiopure terminal epoxides.
Goodman, S. N.; Jacobsen, E. N. *Angew. Chem. Int. Ed.* **2002**, *41*, 4703.

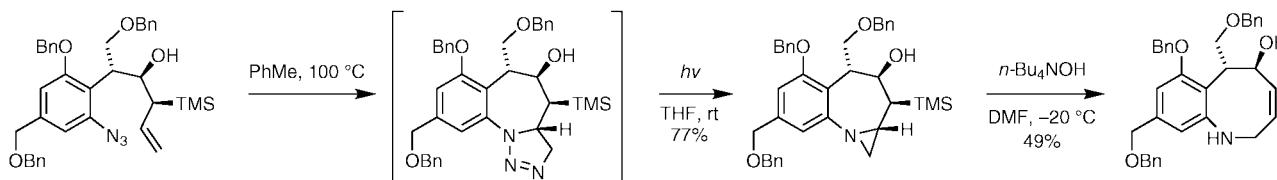
1,2-Addition/Carbonylation



11 examples (yields 56-85%).

Total synthesis of (\pm) -FR-66979.
Ducray, R.; Ciufolini, M. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 4688.

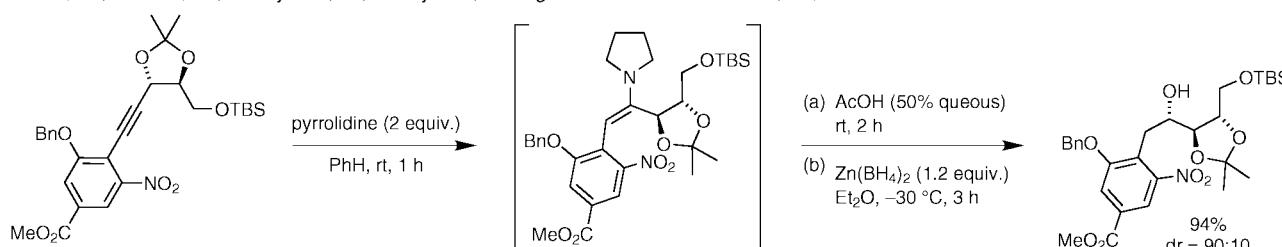
[3+2] Cycloaddition/Photolysis/Fragmentation



Application to the total synthesis of $(+)$ -FR-66979.

Total synthesis of $(+)$ -FR-900482.
Suzuki, M.; Kambe, M.; Tokuyama, H.; Fukuyama, T. *Angew. Chem. Int. Ed.* **2002**, *41*, 4686.

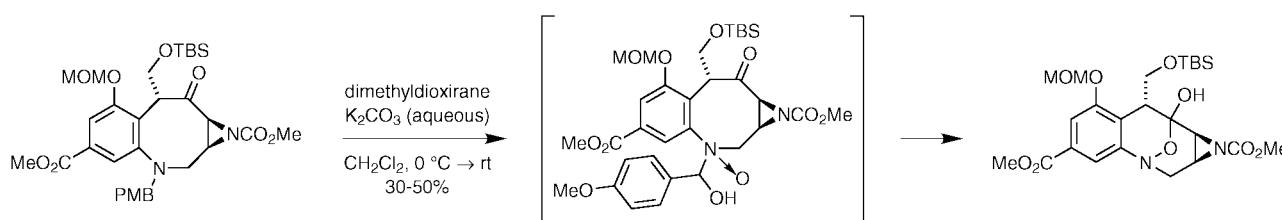
1,6-Addition/Hydrolysis/1,2-Addition



Application to the total synthesis of $(+)$ -FR-900482.

Dimethyldioxirane-mediated construction of hydroxylamine hemiketals.
Judd, T. C.; Williams, R. M. *Angew. Chem. Int. Ed.* **2002**, *41*, 4683.

Oxidation/Deprotection/1,2-Addition

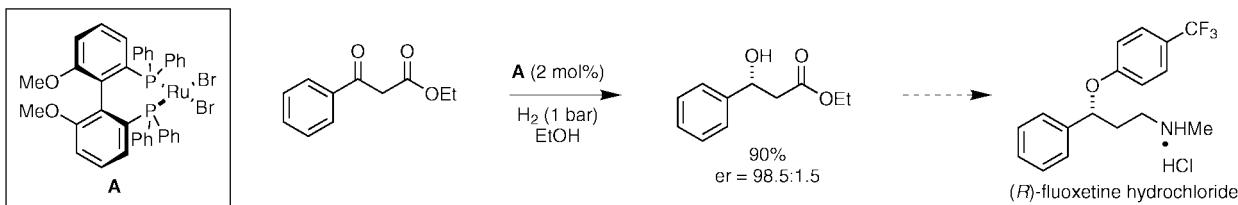


Application to the total synthesis of $(+)$ -FR-66979 and $(+)$ -FR-900482.

Enantioselective Ru-catalyzed hydrogenation of β -keto esters.

Ratovelomanana-Vidal, V.; Girard, C.; Touati, R.; Tranchier, J. P.; Ben-Hassine, B.; Genêt, J. P. *Adv. Synth. Catal.* **2003**, 345.

Hydrogenation

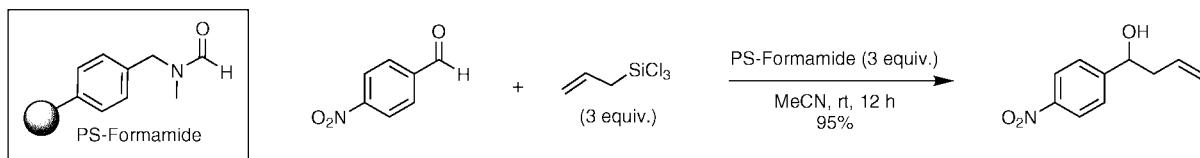


11 examples (yields 75-100%, %ee 77-99%). Syntheses of (+)-(2*R*,3*R*)-corynomycolic acid and duloxetine are also reported.

Polymer-supported formamides as reusable organocatalysts for allylation of aldehydes with allyltrichlorosilane.

Ogawa, C.; Sugiure, M.; Kobayashi, S. *Chem. Commun.* **2003**, 192.

1,2-Addition

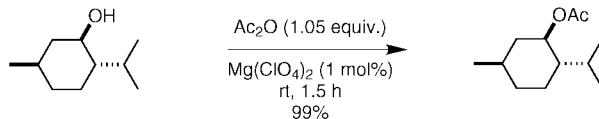


6 examples (yields 66-95%).

$\text{Mg}(\text{ClO}_4)_2$ as a powerful catalyst for the acylation of alcohols under solvent-free conditions.

Bartoli, G.; Bosco, M.; Dalpozzo, R.; Marcantonio, E.; Massaccesi, M.; Rinaldi, S.; Sambri, L. *Synlett*, **2003**, 1, 39.

Acylation

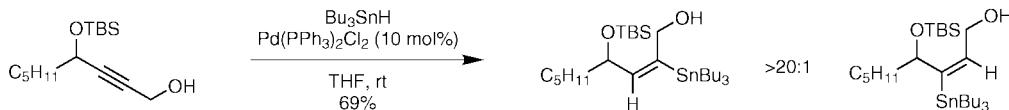


16 examples (yields 92-99%).

Pd-catalyzed hydrostannylation of internal alkynes.

Marshall, J. A.; Bourbeau, M. P. *Tetrahedron Lett.* **2003**, 44, 1087.

Stannylation

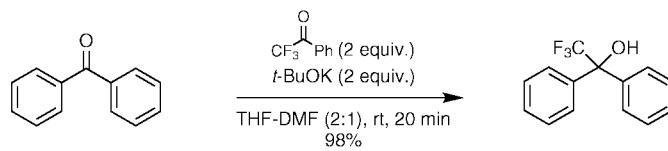


14 examples (yields 58-93%, 2.9:1 regioselectivity 20:1).

Nucleophilic trifluoromethylation of non-enolizable ketones.

Jablonski, L.; Billard, T.; Langlois, B. R. *Tetrahedron Lett.* **2003**, 44, 1055.

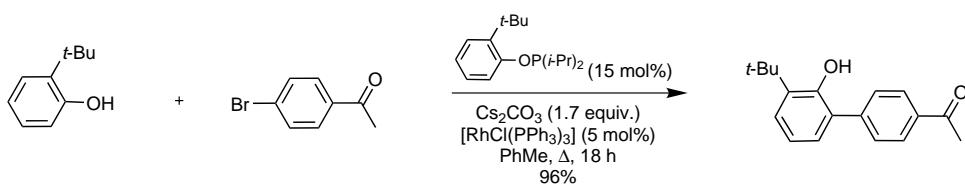
Trifluoromethylation



4 examples (yields 50-99%).

Catalytic intermolecular orthoarylation of phenols.
Bedford, R. B.; Coles, S. J.; Hursthouse, M. B.; Limmert, M. E. *Angew. Chem. Int. Ed.* **2003**, *42*, 112.

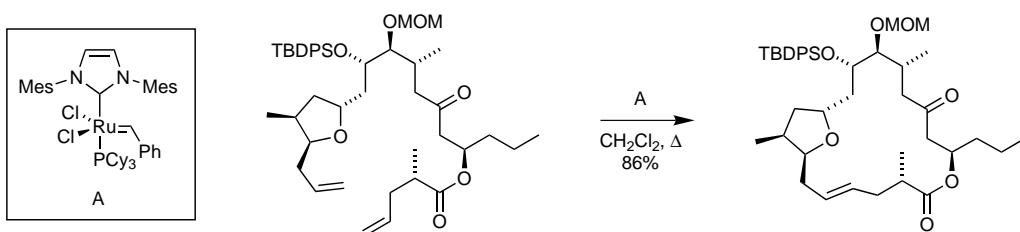
C-C Bond Formation



13 examples (6-96%).

Total synthesis of Amphidinolide T4.
Fürstner, A.; Aissa, C.; Riveiros, R.; Ragot, J. *Angew. Chem. Int. Ed.* **2002**, *41*, 4763.

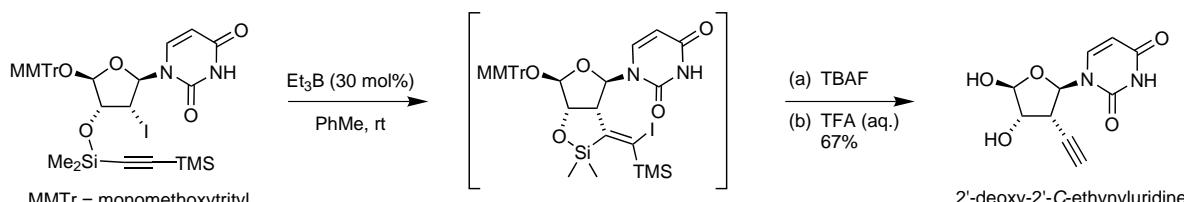
Ring Closing Metathesis



Application to the total synthesis of amphidinolide T4.

Stereoselective introduction of an ethynyl group via a radical reaction
Sukeda, M.; Ichikawa, S.; Matsuda, A.; Shuto, S. *Angew. Chem. Int. Ed.* **2002**, *41*, 4748.

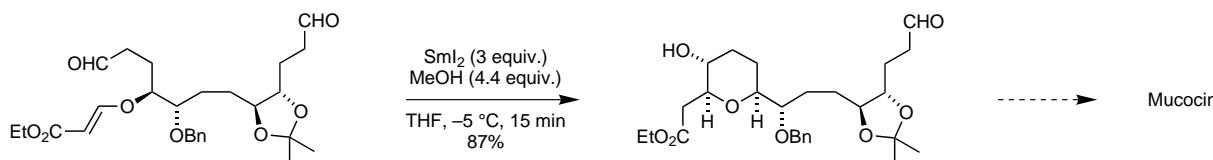
Atom Transfer



18 examples (yields 33-100%).

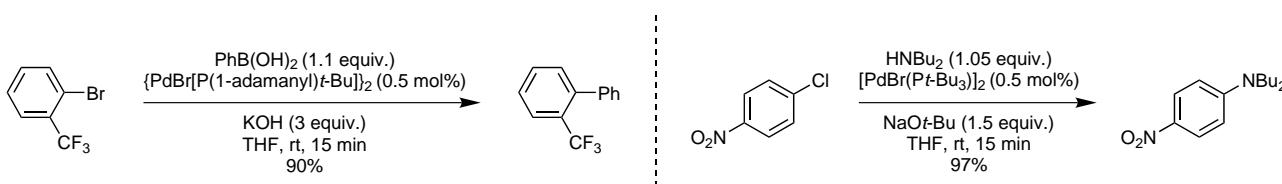
Stereoselective total synthesis of Mucocin.
Takahashi, S.; Kubota, A.; Nakata, T. *Angew. Chem. Int. Ed.* **2002**, *41*, 4751.

1,4-Addition



Pd-catalyzed coupling with amines and boronic acids.
Stambuli, J. P.; Kuwano, R.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2002**, *41*, 4747.

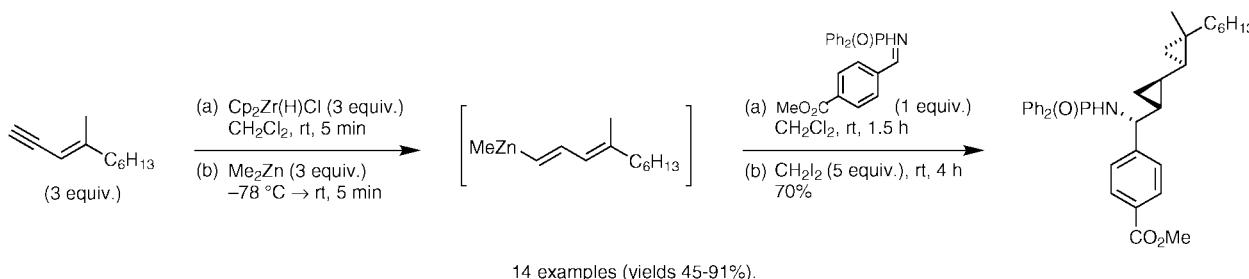
C-C/C-N Coupling



18 examples (yields 68-99%).

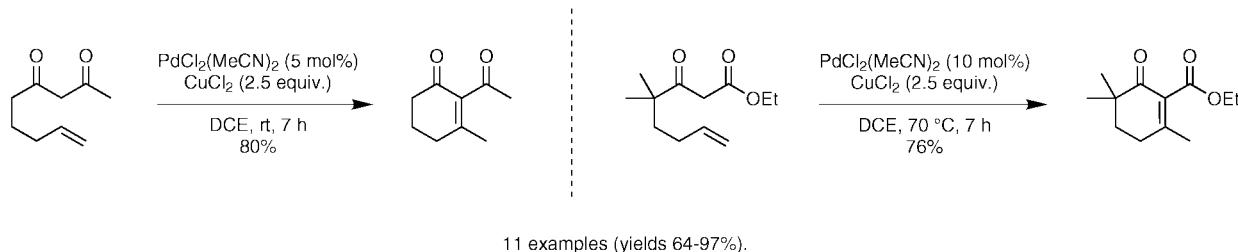
Dimethylzinc-mediated addition of alkenylzirconocenes to aldimines.
Wipf, P.; Kendall, C.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2003**, *125*, 761.

1,2-Addition/Cyclopropanation



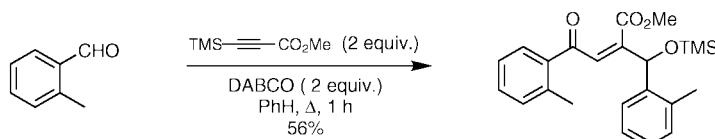
Pd-catalyzed intramolecular oxidative alkylation of unactivated olefins.
Pei, T.; Wang, X.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 648.

Oxidative Alkylation



A modified Baylis–Hillman reaction of propiolate.
Matsuya, Y.; Hayashi, K.; Nemoto, H. *J. Am. Chem. Soc.* **2003**, *125*, 646.

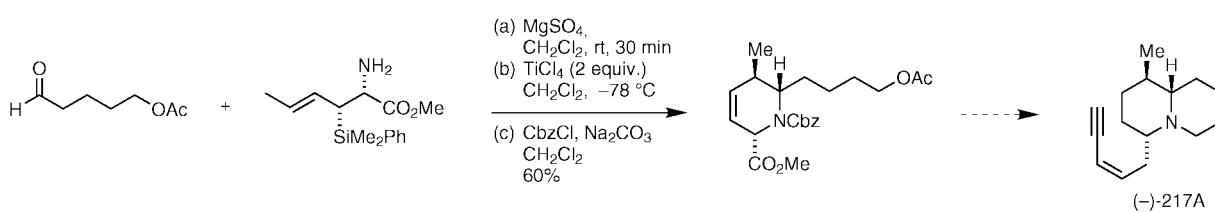
Baylis–Hillman Reaction



11 examples (yields 43-100%). Mechanistic studies are also reported.

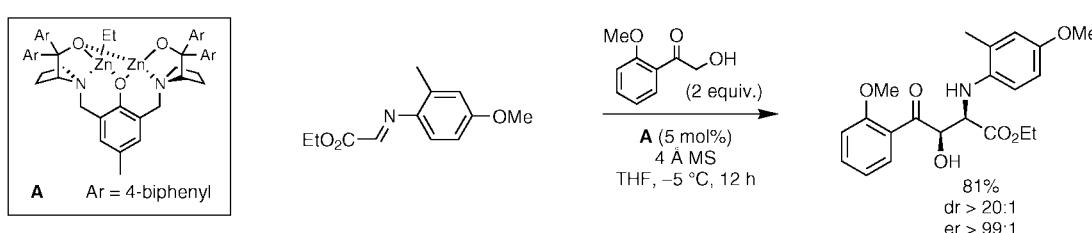
Synthesis of tetrahydropyridines from chiral organosilanes *via* imine crotylation.
Huang, H.; Spande, T. F.; Panek, J. S. *J. Am. Chem. Soc.* **2003**, *125*, 626.

1,2-Addition



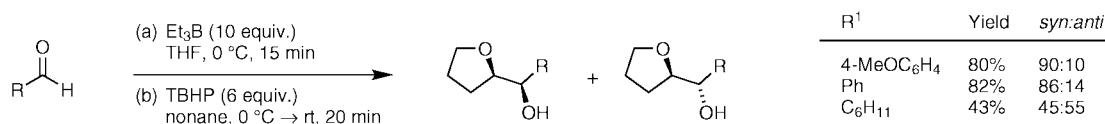
Asymmetric Zn-catalyzed Mannich-type reaction of *syn*-amino alcohols.
Trost, B. M.; Terrell, L. R. *J. Am. Chem. Soc.* **2003**, *125*, 338.

1,2-Addition



Hydroxyalkylation of tetrahydrofuran.
Yoshimitsu, T.; Arano, Y.; Nagaoka, H. *J. Org. Chem.* **2003**, *68*, 625.

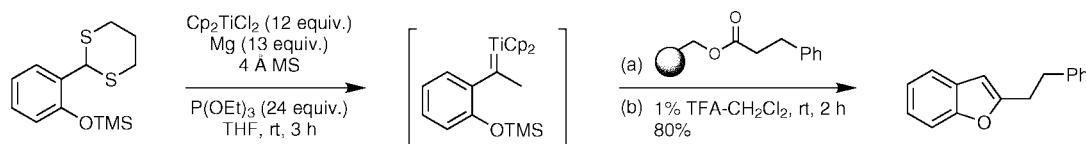
Hydroxyalkylation

6 examples (yields 43-82%, 55:45 *syn:anti* 90:10).

Synthesis of 2-substituted benzofurans and indoles.

MacLeod, C.; McKiernan, G. J.; Guthrie, E. J.; Farrugia, L. J.; Hamprecht, D. W.; Macritchie, J.; Hartley, R. C. *J. Org. Chem.* **2003**, *68*, 387.

Olefination

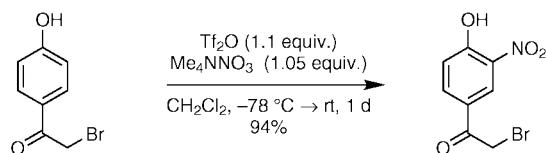


30 examples (yields 33-91%).

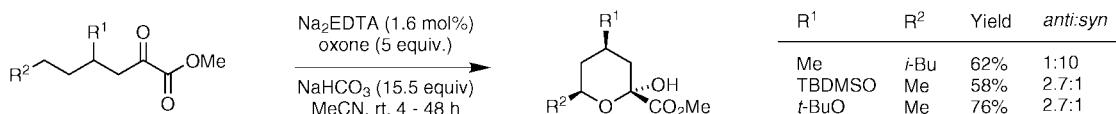
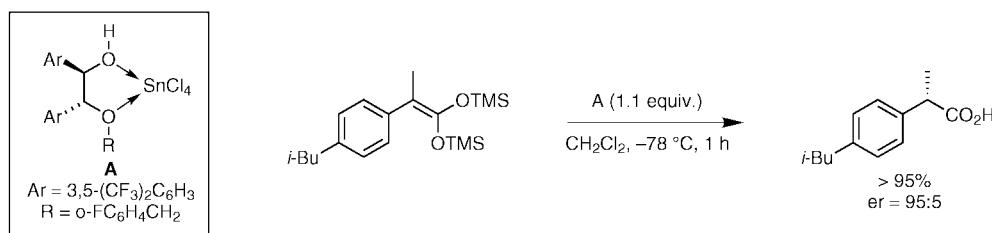
Electrophilic tetraalkylammonium nitrate-mediated nitration.

Shackelford, S. A.; Anderson, M. B.; Christie, L. C.; Goetzen, T.; Guzman, M. C.; Hananel, M. A.; Kornreich, W. D.; Li, H.; Pathak, V. P.; Rabinovich, A. K.; Rajapakse, R. J.; Truesdale, L. K.; Tsank, S. M.; Vaznir, H. N. *J. Org. Chem.* **2003**, *68*, 267.

Nitration



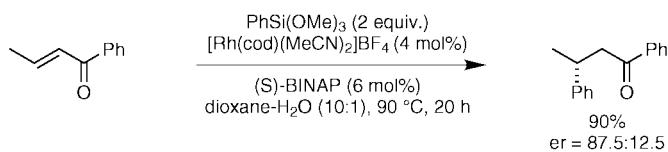
14 examples (yields 52-100%).

Stereoselective synthesis of substituted tetrahydropyrans via regioselective oxidation of unactivated C-H bonds. **Oxidation/1,2-Addition**
Wong, M. K.; Chung, N. W.; He, L.; Yang, D. *J. Am. Chem. Soc.* **2003**, *125*, 158.13 examples (yields 9-85%, 3.1:1 *anti:syn* 1:4.7).Lewis acid-assisted chiral Bronsted acid as an enantioselective protonation reagent for silyl enol ethers. **Protonation**
Ishihara, K.; Nakashima, D.; Hiraiwa, Y.; Yamamoto, H. *J. Am. Chem. Soc.* **2003**, *125*, 25.

7 examples (yields > 95%, %ee 76-90%).

Enantioselective Rh-catalyzed 1,4-addition of organosiloxanes to α,β -unsaturated carbonyl compounds
Oi, S.; Taira, A.; Honma, Y.; Inoue, Y. *Org. Lett.* **2003**, *5*, 97.

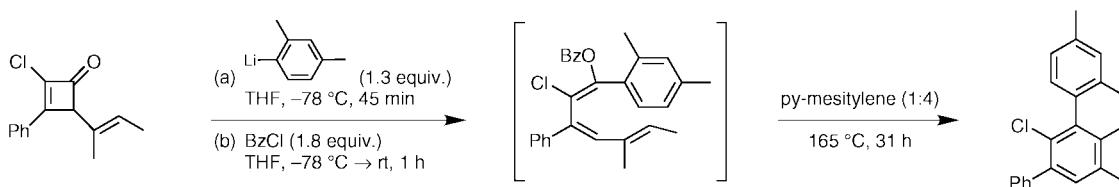
1,4-Addition



13 examples (yields 54-93%, %ee 75-98%).

Synthesis of functionalized biaryl compounds via ring expansion of alkenylcyclobutenones
Hamura, T.; Morita, M.; Matsumoto, T.; Suzuki, K. *Tetrahedron Lett.* **2003**, *44*, 167.

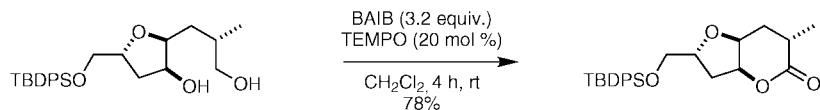
Ring Expansion



9 examples (yields 22-90%).

Chemoselective oxidation of 1,5-diols to δ -lactones with TEMPO/BAIB.
Hansen, T. M.; Florence, G. J.; Lugo-Mas, P.; Chen, J.; Abrams, J. N.; Forsyth, C. J. *Tetrahedron Lett.* **2003**, *44*, 57.

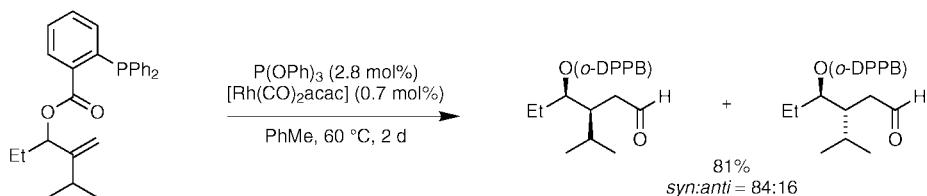
Oxidation



7 examples (yields 77-96%).

Hydroformylation of 2-substituted allylic o-DPPB-ester
Breit, B.; Heckmann, G.; Zahn, S. K. *Chem.-Eur. J.* **2003**, *9*, 425.

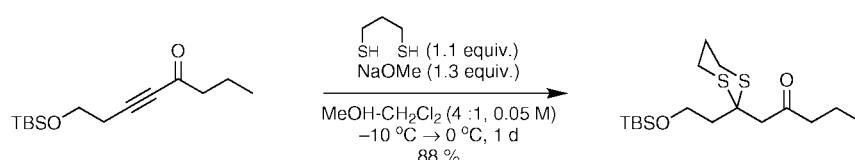
Hydroformylation



9 examples (yields 71-99%, %de 20-98%). DPPB = diphenylphosphanylbenzoyl.

Synthesis of β -keto 1,3-dithianes.
Gaunt, M. J.; Sneddon, H. F.; Hewitt, P. R.; Orsini, P.; Hook, D. F.; Ley, S. V. *Org. Biomol. Chem.* **2003**, *1*, 15.

Conjugate Addition



11 examples (yields 48-95%).