

**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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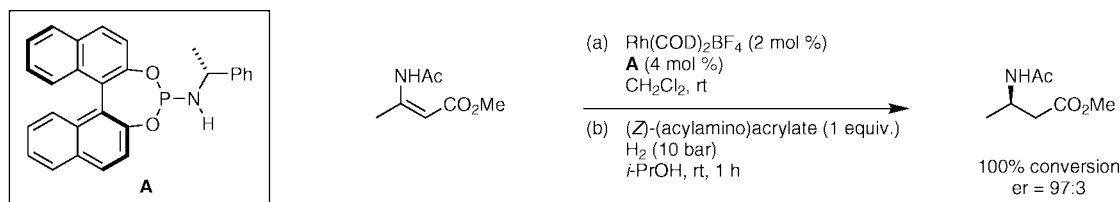
The journals regularly covered by the abstractors are:

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  $\beta$ -dehydroamino acid derivatives.

Pena, D.; Minnaard, A. J.; de Vries, J. G.; Feringa, L. B. *J. Am. Chem. Soc.* **2002**, *124*, 14552.

**Hydrogenation**

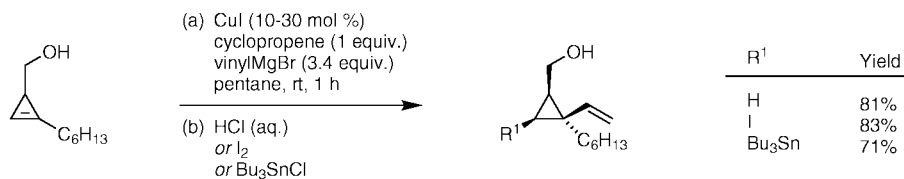


24 examples (conversion 49-100%, %ee 92-99%).

Cu-catalyzed facially selective addition of Grignard reagents to cyclopropenes.

Liao, L.; Fox, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 14322.

**Nucleophilic Addition**

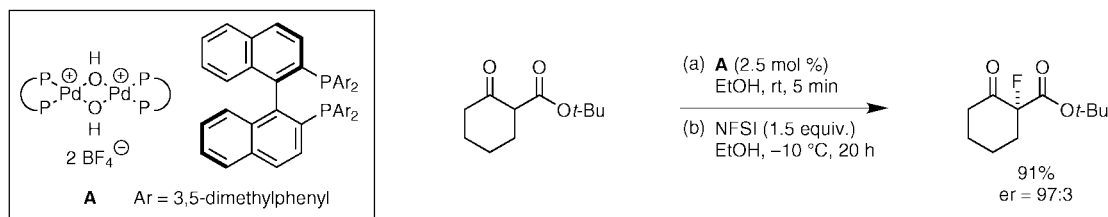


15 examples (yields 61-83%).

Enantioselective Pd-catalyzed fluorination of  $\beta$ -ketoesters.

Hamashima, Y.; Yagi, K.; Takano, H.; Tamas, L.; Sodeoka, M. *J. Am. Chem. Soc.* **2002**, *124*, 14530.

**Fluorination**

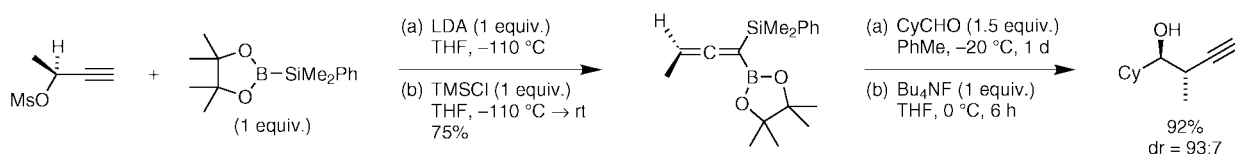


8 examples (yields 49-96%, %ee 93-94%). 6 different catalysts tested.

## Synthesis and reaction of 1-boryl-1-silyllallenes.

Shimizu, M.; Kurahashi, T.; Kitagawa, H.; Hiyama, T. *Org. Lett.* **2003**, *5*, 225.

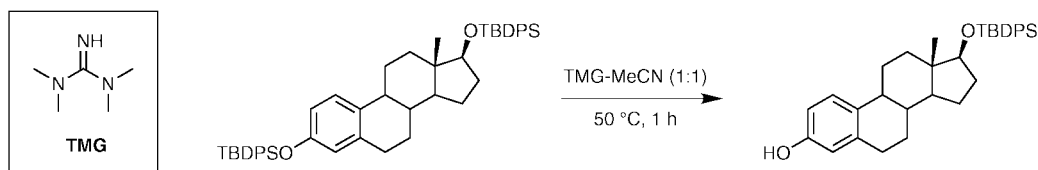
## 1,2-Addition

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

## Chemoselective 1,1,3,3-tetramethylguanidine-mediated deprotection of both silyl and acetyl groups.

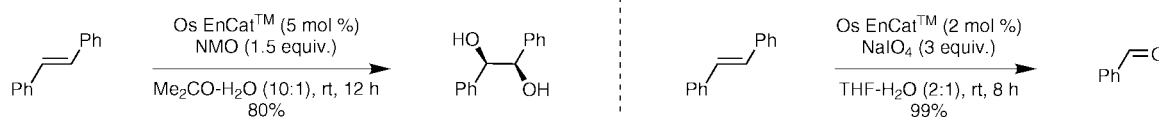
Oyama, K. -I.; Kondo, T. *Org. Lett.* **2003**, *5*, 209.

## Deprotection



15 examples (yields 71-94%).

## Microencapsulation of osmium tetroxide in polyurea.

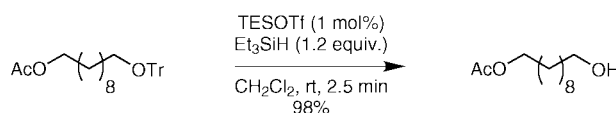
Ley, S. V.; Ramarao, C.; Lee, A. -L.; Ostergaard, N.; Smith, S. C.; Shirley, I. M. *Org. Lett.* **2003**, *5*, 185.Dihydroxylation/  
Oxidative Cleavage

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

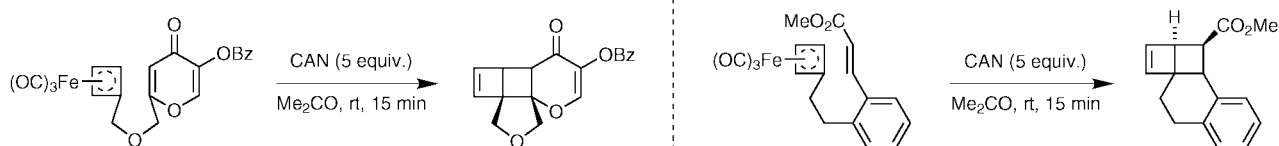


16 examples (yields 86-99%).

## 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.

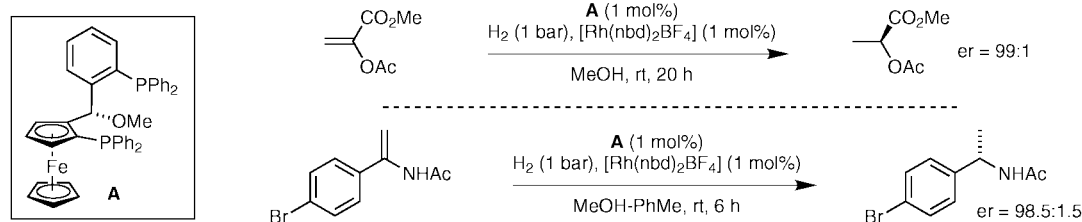
## Cycloaddition



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

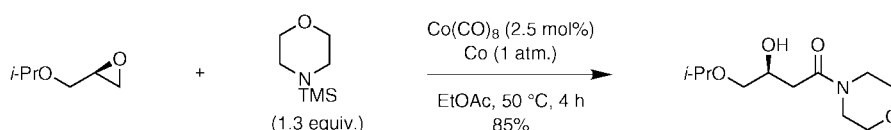


8 examples (%ee 95->99%). 5 different ferrocenyl ligands were screened.

Carbonylation of enantiopure terminal epoxides.

Goodman, S. N.; Jacobsen, E. N. *Angew. Chem. Int. Ed.* **2002**, *41*, 4703.

1,2-Addition/Carbonylation

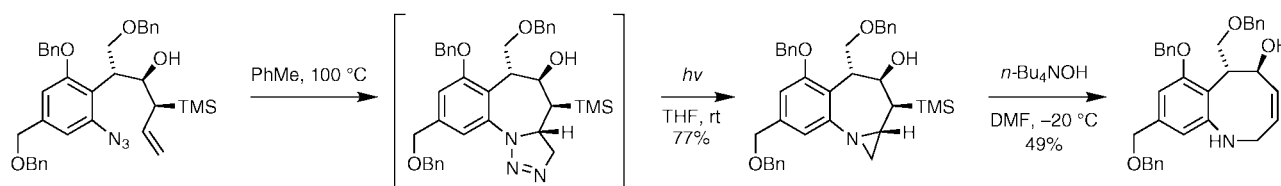


11 examples (yields 56-85%).

Total synthesis of (±)-FR-66979.

Ducray, R.; Ciufolini, M. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 4688.

[3+2] Cycloaddition/Photolysis/Fragmentation

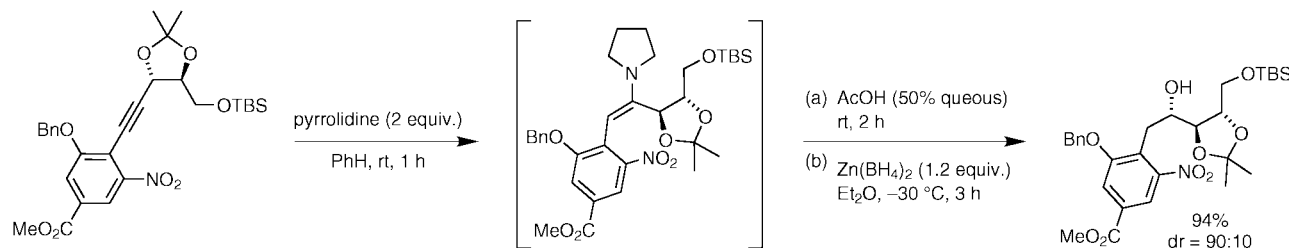


Application to the total synthesis of (+)-FR66979.

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

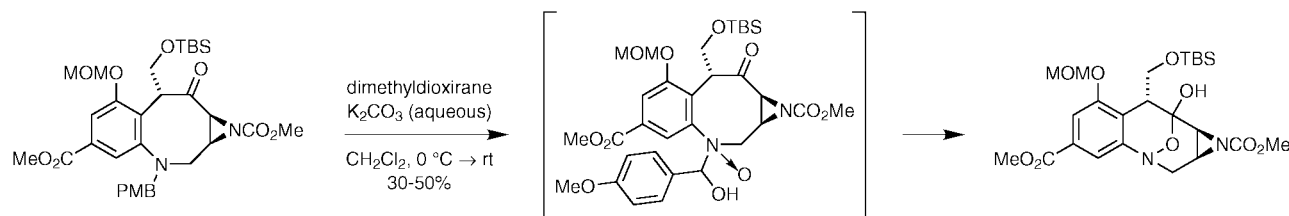


Application to the total synthesis of (+)-FR900482.

Dimethyldioxirane-mediated construction of hydroxylamine hemiketals.

Judd, T. C.; Williams, R. M. *Angew. Chem. Int. Ed.* **2002**, *41*, 4683.

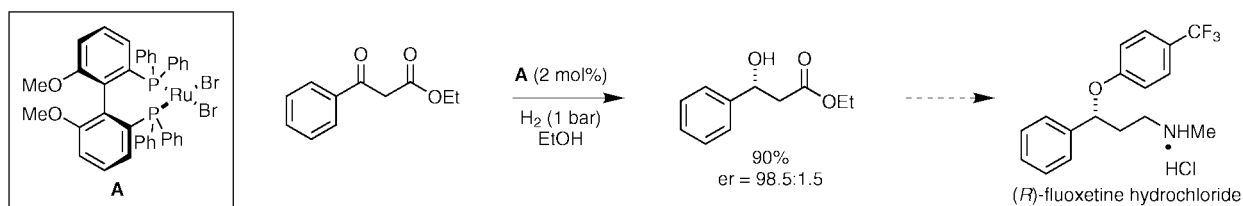
Oxidation/Deprotection/1,2-Addition



Application to the total synthesis of (+)-FR66979 and (+)-FR900482.

Enantioselective Ru-catalyzed hydrogenation of  $\beta$ -keto esters.Ratovelomanana-Vidal, V.; Girard, C.; Touati, R.; Tranchier, J. P.; Ben-Hassine, B.; Genêt, J. P. *Adv. Synth. Catal.* **2003**, 345.

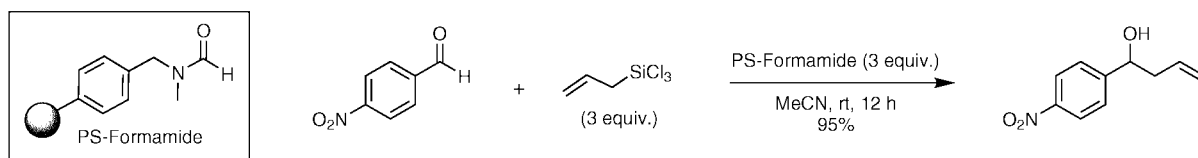
## Hydrogenation



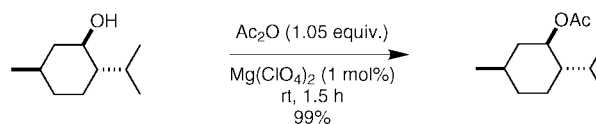
Polymer-supported formamides as reusable organocatalysts for allylation of aldehydes with allyltrichlorosilane.

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

## 1,2-Addition

 $Mg(ClO_4)_2$  as a powerful catalyst for the acylation of alcohols under solvent-free conditions.Bartoli, G.; Bosco, M.; Dalpozzo, R.; Marcantoni, E.; Massaccesi, M.; Ri naldi, S.; Sambri, L. *Synlett*, **2003**, 1, 39.

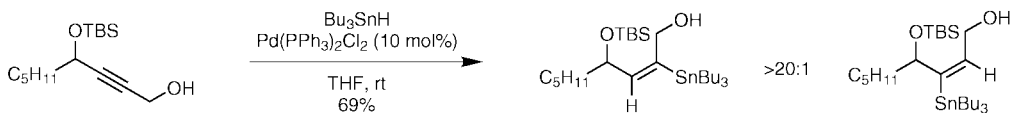
## Acylation



Pd-catalyzed hydrostannylation of internal alkynes.

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

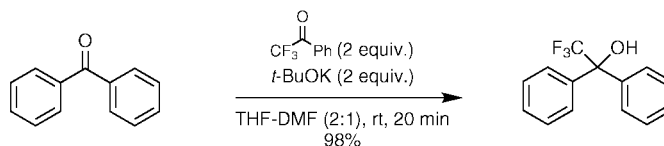
## Stannylation



Nucleophilic trifluoromethylation of non-enolizable ketones.

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

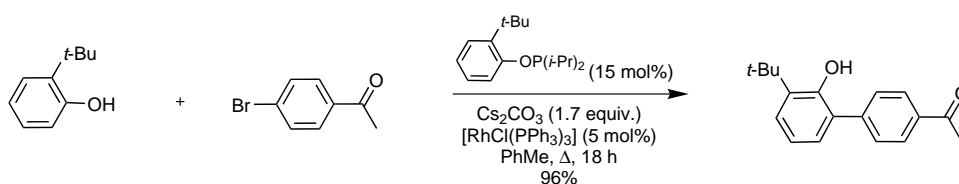
## Trifluoromethylation



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

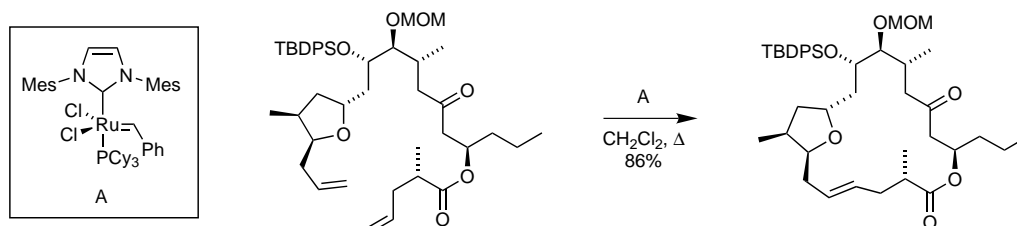


13 examples (6-96%).

Total synthesis of Amphidinolide T4.

Fürstner, A.; Aissa, C.; Riveiros, R.; Ragot, J. *Angew. Chem. Int. Ed.* **2002**, *41*, 4763.

Ring Closing Metathesis

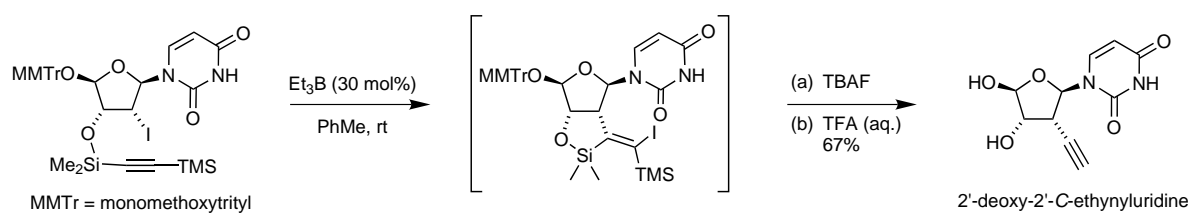


Application to the total synthesis of amphidinolide T4.

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

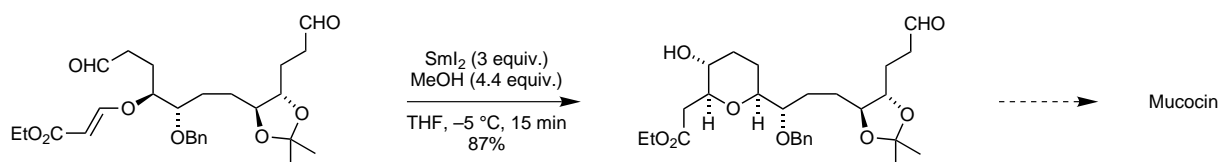


18 examples (yields 33-100%).

Stereoselective total synthesis of Mucocin.

Takahashi, S.; Kubota, A.; Nakata, T. *Angew. Chem. Int. Ed.* **2002**, *41*, 4751.

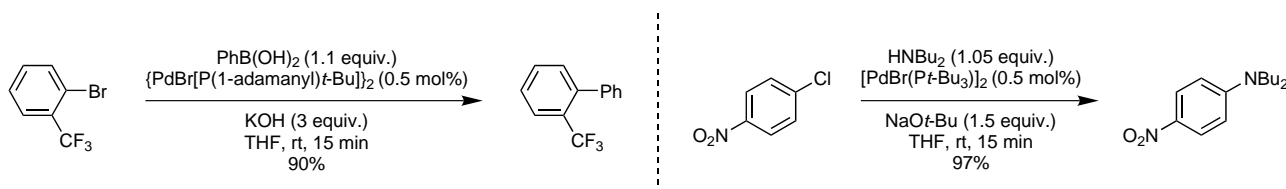
1,4-Addition



Pd-catalyzed coupling with amines and boronic acids.

Stambuli, J. P.; Kuwano, R.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2002**, *41*, 4747.

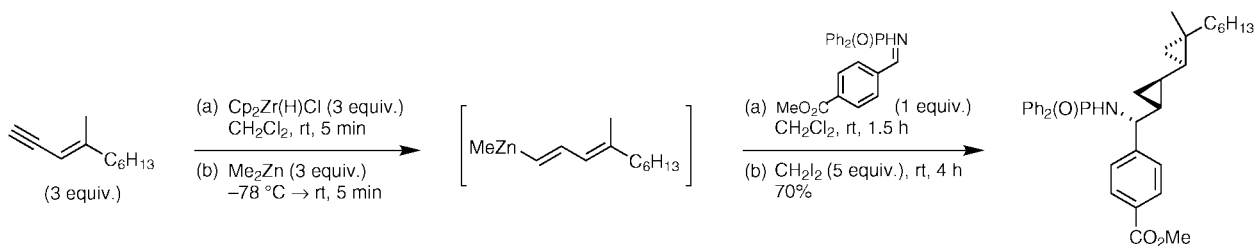
C-C/C-N Coupling



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.

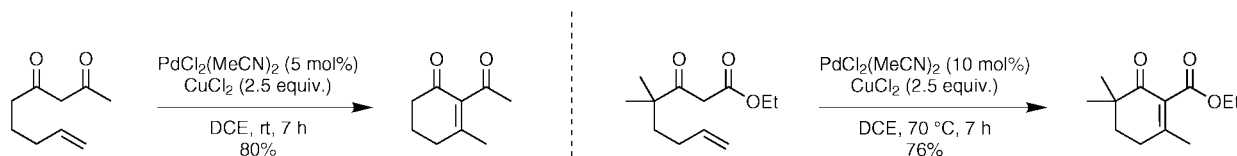
## 1,2-Addition/Cyclopropanation



14 examples (yields 45-91%).

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

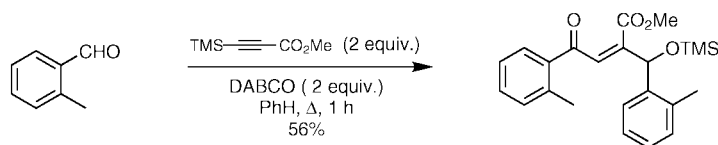
## Oxidative Alkylation



11 examples (yields 64-97%).

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

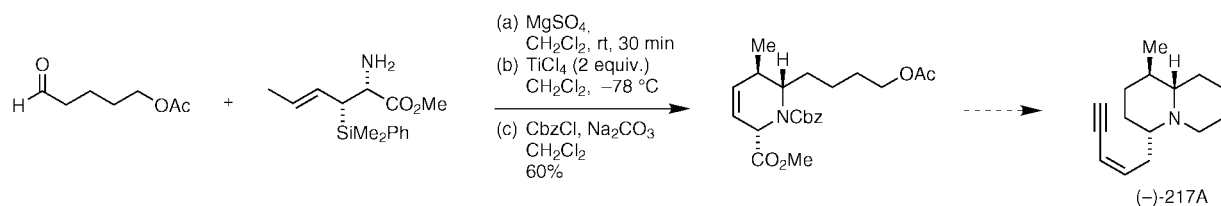
## Baylis–Hillman Reaction



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.

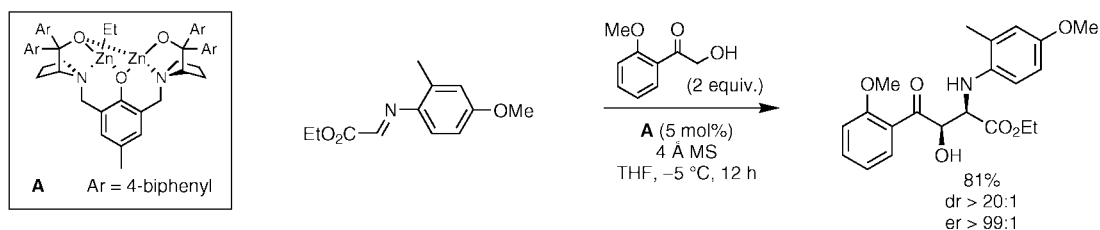
## 1,2-Addition



7 examples (yields 64-90%).

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

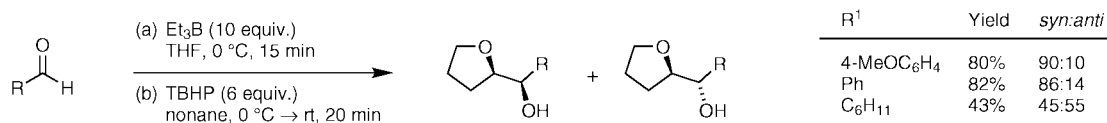


7 examples of glyoxalate imines (yields 59-97%, %de 33-90%, %ee 95-99%).  
5 examples of aldimines (yields 64-90%, %de 62-88%, %ee 98-99%).

## Hydroxyalkylation of tetrahydrofuran.

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

## Hydroxyalkylation

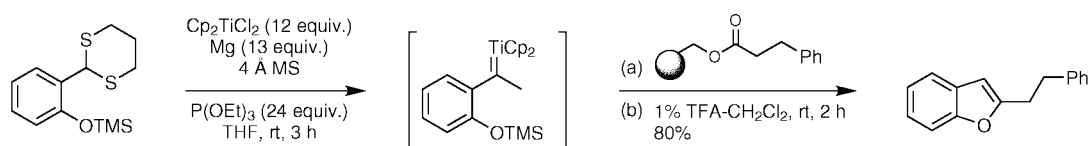


6 examples (yields 43-82%, 55:45 syn:anti 90:10).

## 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

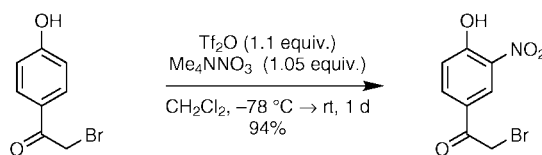


30 examples (yields 33-91%).

## 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

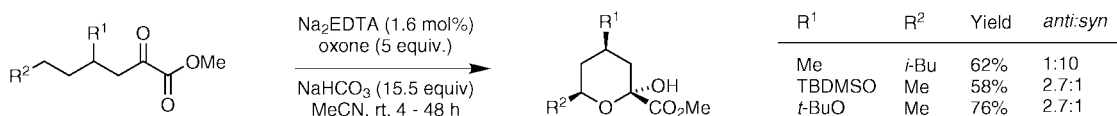


14 examples (yields 52-100%).

## Stereoselective synthesis of substituted tetrahydropyrans via regioselective oxidation of unactivated C-H bonds.

Wong, M. K.; Chung, N. W.; He, L.; Yang, D. *J. Am. Chem. Soc.* **2003**, *125*, 158.

## Oxidation/1,2-Addition

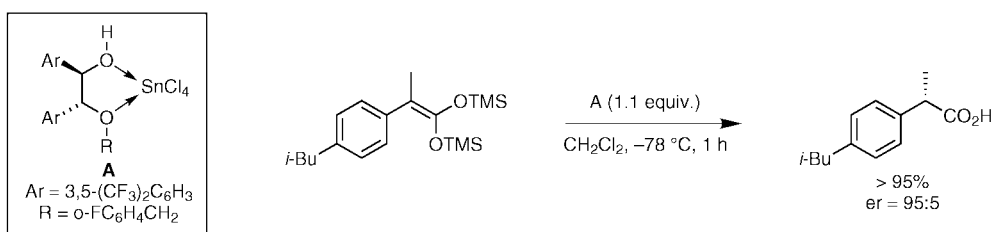


13 examples (yields 9-85%, 3.1:1 anti:syn 1:4.7).

## Lewis acid-assisted chiral Bronsted acid as an enantioselective protonation reagent for silyl enol ethers.

Ishihara, K.; Nakashima, D.; Hiraiwa, Y.; Yamamoto, H. *J. Am. Chem. Soc.* **2003**, *125*, 25.

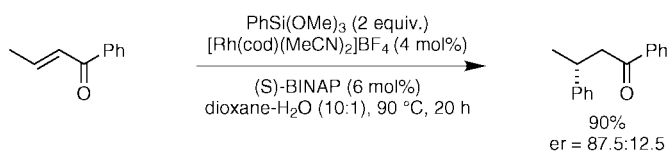
## Protonation



7 examples (yields &gt; 95%, %ee 76-90%).

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

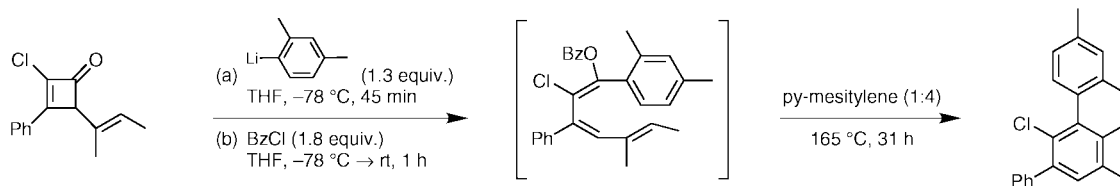
1,4-Addition



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

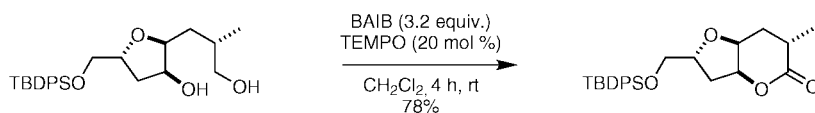


9 examples (yields 22-90%).

Chemoselective oxidation of 1,5-diols to  $\delta$ -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

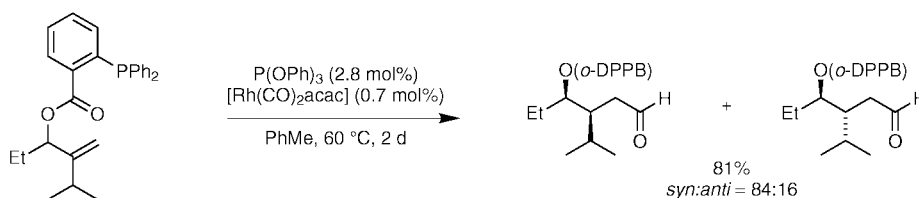


7 examples (yields 77-96%).

Hydroformylation of 2-substituted allylic  $\alpha$ -DPPB-ester

Breit, B.; Heckmann, G.; Zahn, S. K. *Chem.-Eur. J.* **2003**, *9*, 425.

Hydroformylation

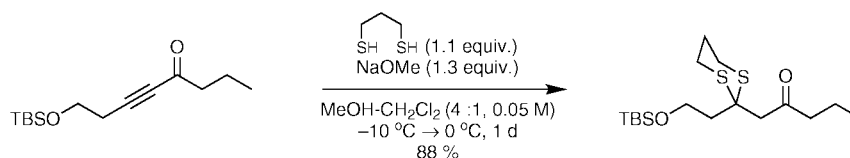


9 examples (yields 71-99%, %de 20-98%). DPPB = diphenylphosphanylbenzoyl.

Synthesis of  $\beta$ -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%).