

**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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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

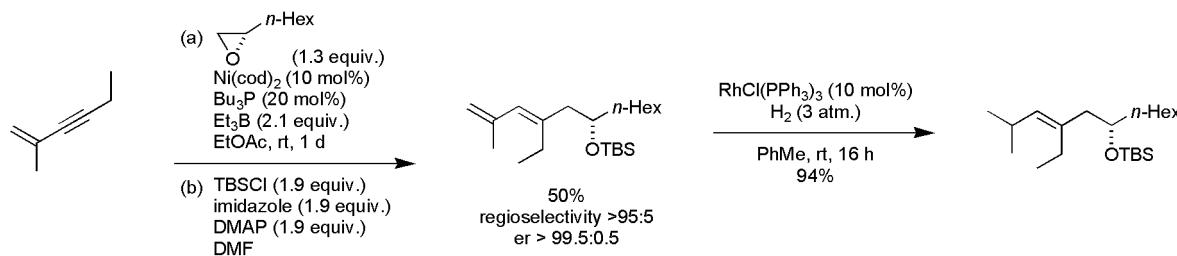
Tetrahedron Asymmetry

Tetrahedron Letters

Alkene-directed, Ni-catalyzed alkyne coupling reactions.

Miller, K. M.; Luanphaisarnnont, T.; Molinaro, C.; Jamison, T. F. *J. Am. Chem. Soc.* **2004**, *126*, 4130.

C-C Bond Formation

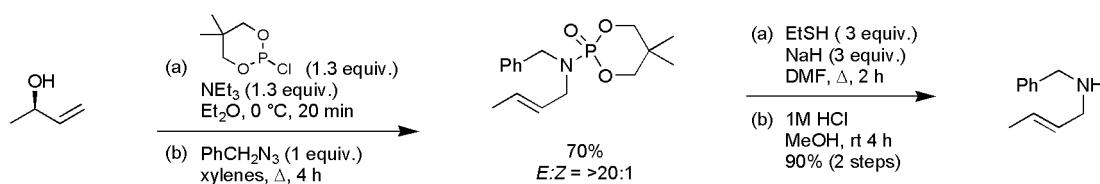


Nickel coupling reactions: 11 examples (yields 50–89%, 90:10 > regioselectivities > 95:5); Hydrogenation: 8 examples (yields 76–96%).

Synthesis of allylic amines via a phosphoramide rearrangement.

Chen, B.; Mapp, A. K. *J. Am. Chem. Soc.* **2004**, *126*, 5364.

[3,3]-Sigmatropic Rearrangement

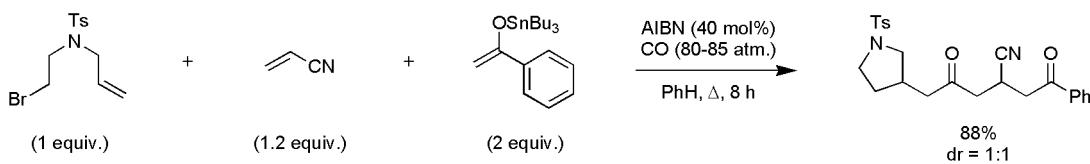


11 examples (yields 55–88%).

Synthesis of functionalized  $\beta$ - and  $\delta$ -diketones via an intermolecular carbonylative cascade reaction.

Miura, K.; Tojino, M.; Fujisawa, N.; Hosomi, A.; Ryu, I. *Angew. Chem. Int. Ed.* **2004**, *43*, 2423.

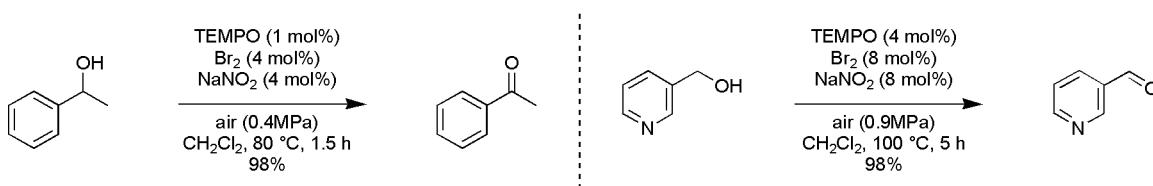
Radical Carbonylation



15 examples (yields 56–92%, %de 0–20%).

Transition-metal free aerobic oxidation of alcohols.  
Liu, R.; Liang, X.; Dong, C.; Hu, X. *J. Am. Chem. Soc.* **2004**, *126*, 4112.

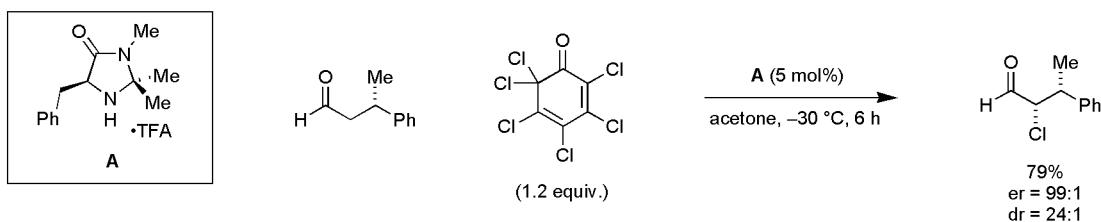
## Oxidation



16 examples (yields 0-99%).

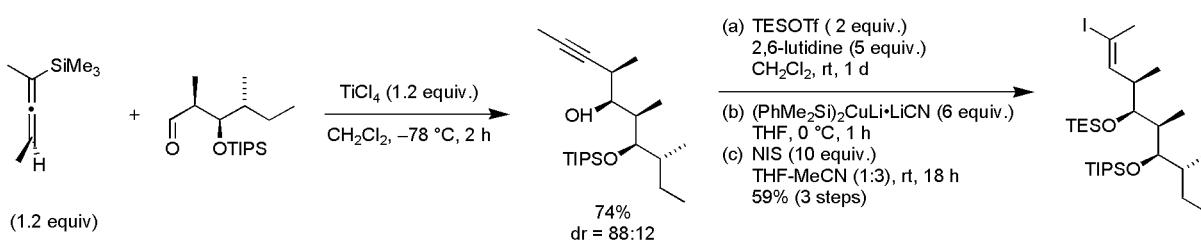
Direct, enantioselective organocatalytic  $\alpha$ -chlorination of aldehydes.Brochu, M. P.; Brown, S. P.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2004**, *126*, 4108.

## Asymmetric C-Hal Bond Formation

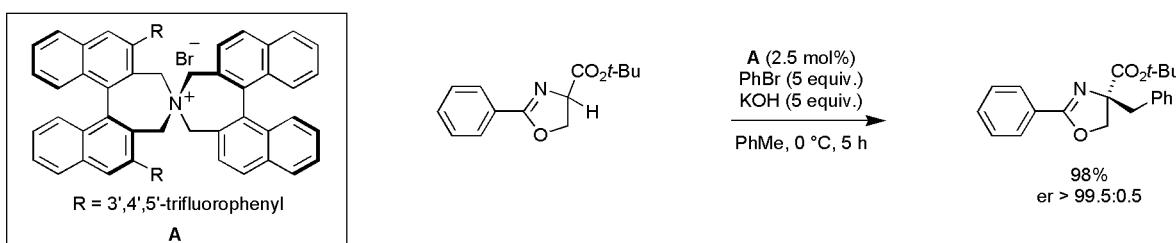


9 examples (yields 71-94%, %ee 80-98%).

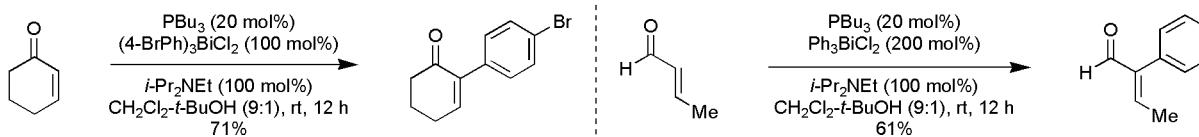
Stereocontrolled approach towards ebelactone A using organosilicon chemistry.

Archibald, S. C.; Barden, D. J.; Bazin, J. F. Y.; Fleming, I.; Foster, C. F.; Mandal, A. K.; Mandal A. K.; Parker, D.; Takaki, K.; Ware, A. C.; Williams, A. R. B.; Zwicky, A. B. *Org. Biomol. Chem.* **2004**, *2*, 1051.S<sub>E</sub>2' Reaction/SilylcuprationSynthesis of chiral  $\alpha$ -alkyl serines via an enantioselective phase-transfer catalysed alkylation.Jew, S.; Lee, Y.-J.; Lee, J.; Kang, M. J.; Jeong, B.-S.; Lee, J.-H.; Yoo, M.-S.; Kim, M.-J.; Choi, S.; Ku, J.-M.; Park, H. *Angew. Chem. Int. Ed.* **2004**, *43*, 2382.

## Asymmetric Alkylation

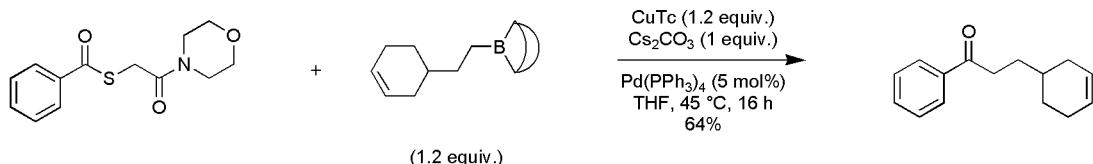


11 examples (yields 48-99%, %ee 93-&gt;99%).

Phosphine catalyzed  $\alpha$ -arylation of enones and enals using hypervalent bismuth reagents.Koech, P. K.; Krische, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 5350.sp<sup>2</sup>-sp<sup>2</sup> Coupling

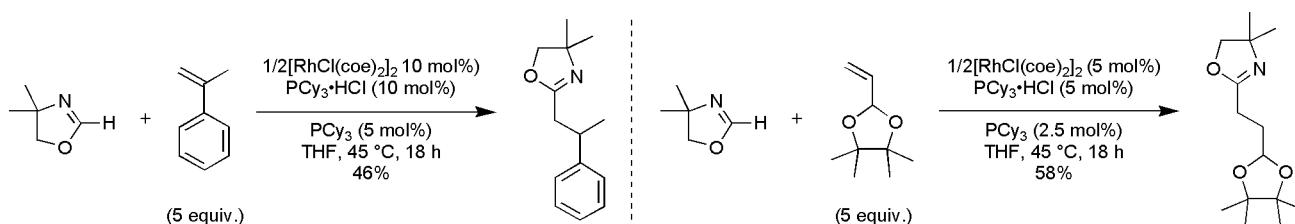
22 examples (yields 44-93%).

Cu-mediated, Pd-catalyzed coupling of thiol esters with aliphatic organoboron reagents.  
Yu, Y.; Liebeskind, L. S. *J. Org. Chem.* **2004**, 69, 3554.

**sp<sup>2</sup>-sp<sup>3</sup> Coupling**

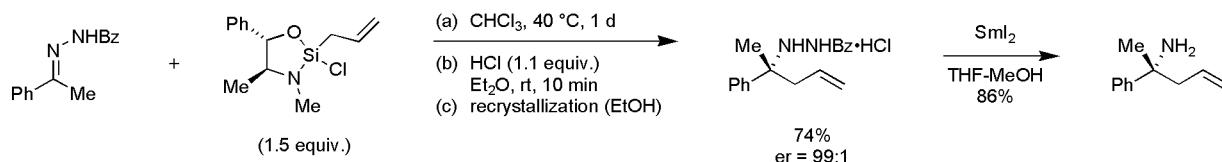
CuTc = Cu(I)-thiophene-2-carboxylate. 15 examples (yields 21-90%).

Rh-catalyzed direct C-H addition of 4,4-dimethyl-2-oxazoline to alkenes.  
Wiedemann, S. H.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2004**, 6, 1685.

**C-H Addition**

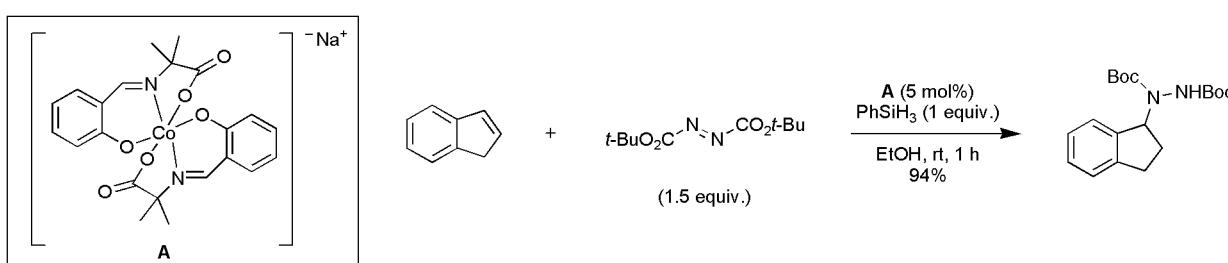
coe - *cis*-*s*-cyclooctene. 11 examples (yields 37-86%).

Synthesis of tertiary carbinamines via an enantioselective allylation of ketone-derived benzoylhyrazones.  
Berger, R.; Duff, K.; Leighton, J. L. *J. Am. Chem. Soc.* **2004**, 126, 5686.

**Asymmetric Allylation**

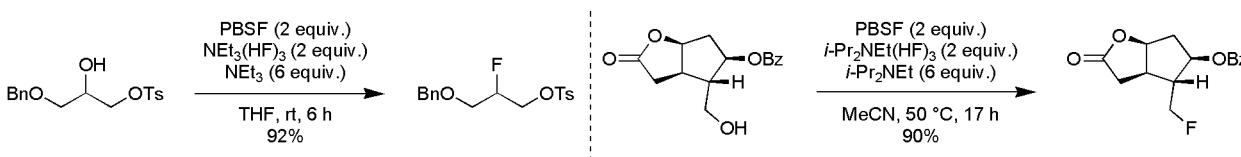
15 examples (yields 46-95%, %ee 84-98%).

Synthesis of alkylhydrazides via a Co-catalyzed hydrohydrazination reaction of olefins and azodicarboxylates.  
Waser, J.; Carreira, E. M. *J. Am. Chem. Soc.* **2004**, 126, 5676.

**C-N Bond Formation**

22 examples (yields 62-94%).

Direct conversion of alcohols to fluorides.  
Yin, J.; Zarkowsky, D. S.; Thomas, D. W.; Zhao, M. M.; Huffman, M. A. *Org. Lett.* **2004**, 6, 1465.

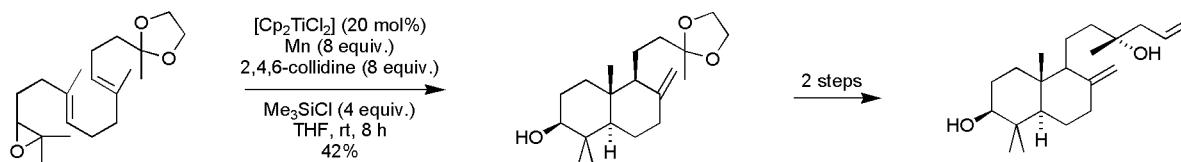
**C-F Bond Formation**

PBSF = perfluoro-1-butanesulfonylfluoride. 17 examples (yields 65-96%).

## Titanocene-catalyzed cascade cyclization of epoxypolypropenes.

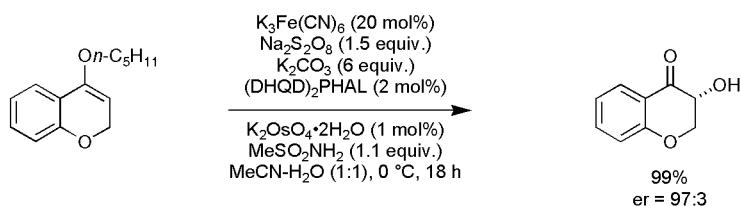
Justicia, J.; Rosales, A.; Buñuel, E.; Oller-López, J. L.; Valdivia, M.; Haïdour, A.; Oltra, J. E.; Barrero, A. F.; Cárdenas, D. J.; Cuerva, J. M. *Chem. Eur. J.* **2004**, *10*, 1778.

## C–C Bond Formation



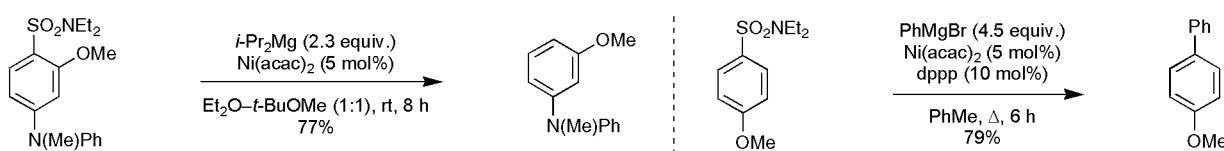
The synthesis of natural occurring terpenoids with various carboxylic skeletons is described. 6 examples (yields 31–61%).

Synthesis of cyclic hydroxy ketones derived from enol ethers via a Sharpless asymmetric dihydroxylation. **Asymmetric Dihydroxylation**  
Marcune, B. F.; Karady, S.; Reider, P. J.; Miller, R. A.; Biba, M.; DiMichele, L.; Reamer, R. A. *J. Org. Chem.* **2003**, *68*, 8088.



The correlation of the enol ether chain length and enantioselectivity in hydroxychromanone synthesis is outlined.

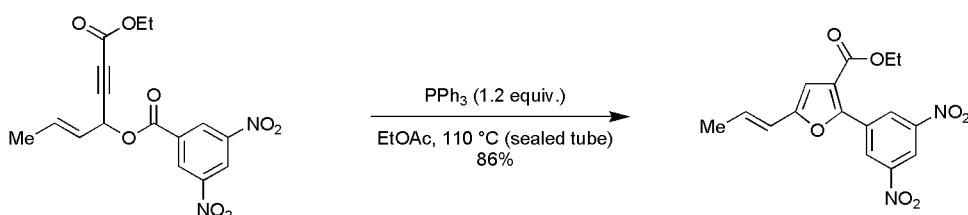
Ni-catalyzed reductive cleavage and cross-coupling reactions of aryl sulfonamides with Grignard reagents. **Reduction/sp<sup>2</sup>-sp<sup>2</sup> Coupling**  
Milburn, R. R.; Snieckus, V. *Angew. Chem. Int. Ed.* **2004**, *43*, 888.



Reductive cleavage: 26 examples (yields 10–97%).

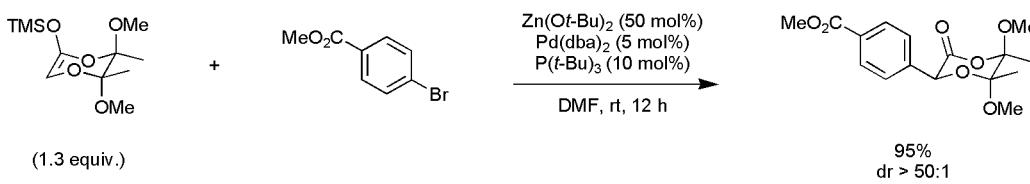
Cross-coupling: 11 examples (yields 52–84%).

Synthesis of substituted furans via a phosphine-mediated reductive condensation of γ-acyloxy butynoates. **Heteroannulation**  
Jung, C.-K.; Wang, J.-C.; Krische, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 4118.



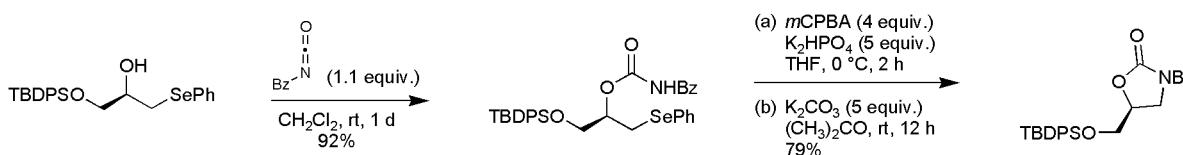
16 examples (yields 60–91%).

Palladium-catalyzed arylation of trimethylsilyl enolates of esters and imides. **C–C Bond Formation**  
Liu, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 5182.



**Ring-closure reactions via intramolecular displacement of a phenylselenoyl group by nitrogen nucleophiles.**  
Tiecco, M.; Testaferri, L.; Temperini, A.; Bagnoli, L.; Marini, F.; Santui, C. *Chem. Eur. J.* **2004**, *10*, 1752.

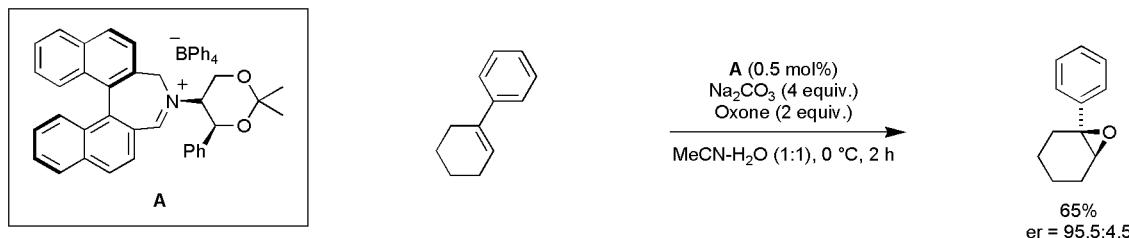
### Nucleophilic Substitution



32 examples (yields 44-89%).

**Iminium salt catalysts for asymmetric epoxidation.**  
Bulman Page, P. C.; Buckley, B. R.; Blacker, A. *J. Org. Lett.* **2004**, *6*, 1543.

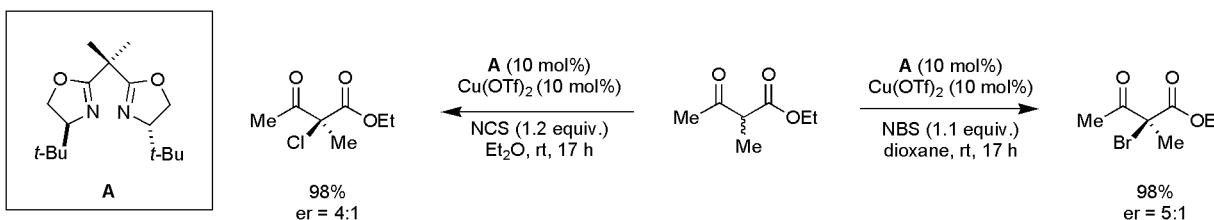
### Asymmetric Epoxidation



26 examples (yields 0-70%, %ee 0-95%).

**Catalytic, asymmetric bromination and chlorination of β-keto esters.**  
Marigo, M.; Kumaragurubaran, N.; Jorgensen, K. A. *Chem. Eur. J.* **2004**, *10*, 2133.

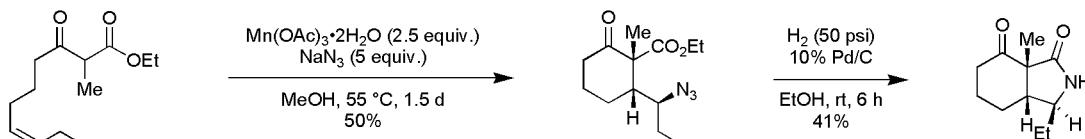
### Asymmetric C–Hal Bond Formation



22 examples (yields 93-99%, %ee 30-82%).

**Termination of Mn(II)-based oxidative cyclizations by trapping azides.**  
Snider, B. B.; Duvall, J. R. *Org. Lett.* **2004**, *6*, 1265.

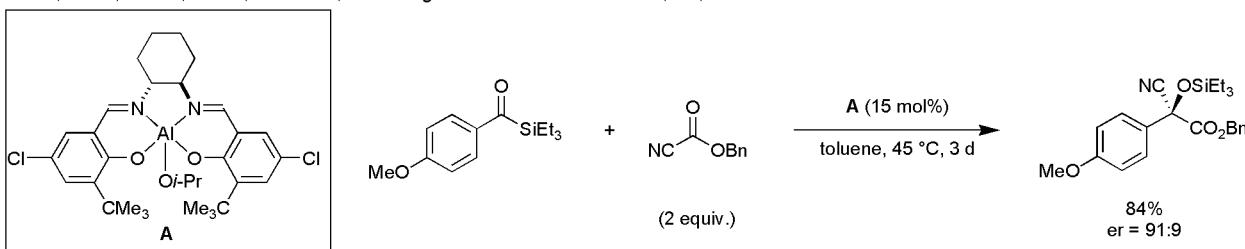
### Radical Cyclization



9 examples (yields 8-78%).

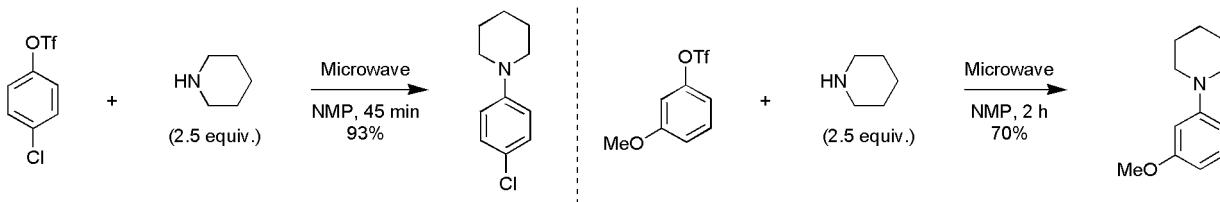
**Catalytic asymmetric acylation of (siloxy)nitrile anions.**  
Nicewicz, D. A.; Yates, C. M.; Johnson, J. S. *Angew. Chem. Int. Ed.* **2004**, *43*, 2652.

### Asymmetric Acylation



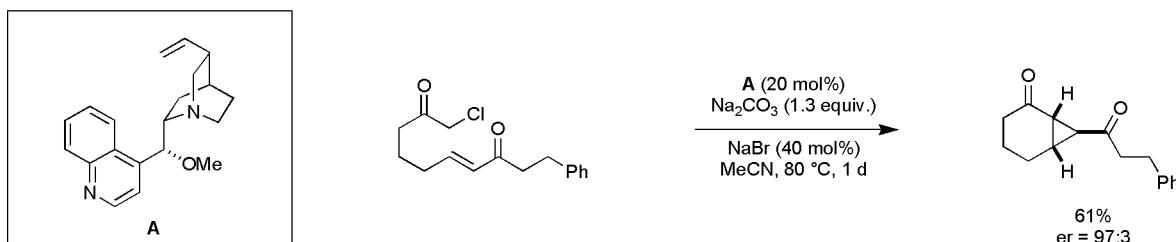
10 examples (yields 70-93%, %ee 61-84%).

Microwave-assisted amination from aryl triflates without base or catalyst.  
Xu, G.; Wang, Y.-G.; *Org. Lett.* **2004**, *6*, 985.

**sp<sup>2</sup>-Nsp<sup>3</sup> Coupling**

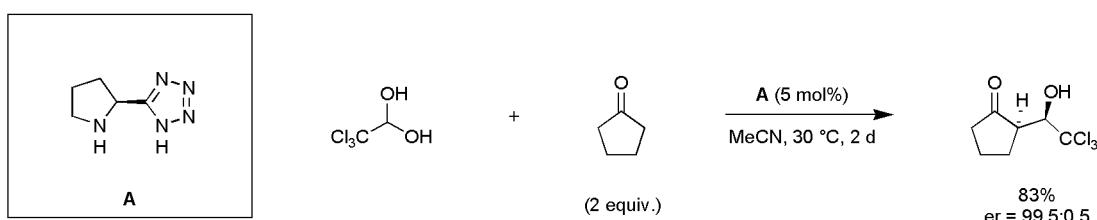
27 examples (yields <1-98%).

An intramolecular organocatalytic cyclopropanation reaction.  
Bremeyer, N.; Smith, S. C.; Ley, S. V.; Gaunt, M. J. *Angew. Chem. Int. Ed.* **2004**, *43*, 2681.

**Cyclopropanation**

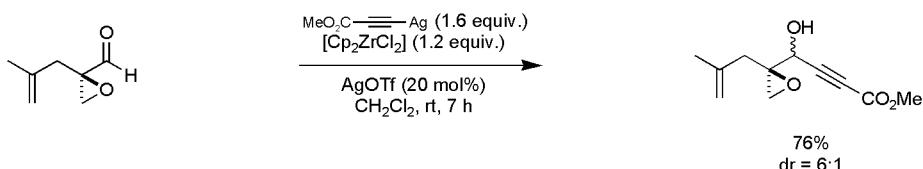
18 examples (yields 10-95%, %ee 64-95%).

Asymmetric direct Aldol reaction assisted by water and a proline-derived tetrazole catalyst.  
Torii, H.; Nakadai, M.; Ishihara, K.; Saito, S.; Yamamoto, H. *Angew. Chem. Int. Ed.* **2004**, *43*, 1983.

**Aldol Reaction**

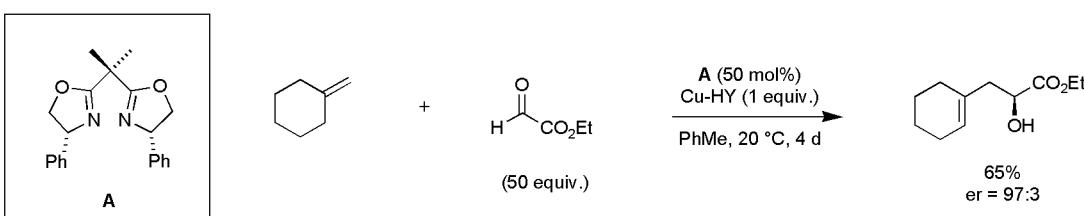
16 examples (yields 39-93%, %ee 67-99%).

A mild method for the preparation of  $\gamma$ -hydroxy- $\alpha,\beta$ -acetylenic esters.  
Shahi, S. P.; Koide, K. *Angew. Chem. Int. Ed.* **2004**, *43*, 2525.

**1,2-Addition**

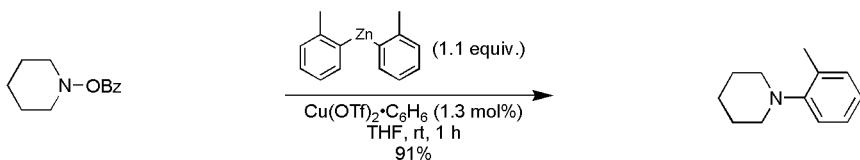
18 examples (yields 0-95%).

Catalytic, heterogeneous, enantioselective carbonyl- and imino-ene reactions using copper bis(oxazoline) zeolite Y. **C-C Bond Formation**  
Caplan, N. A.; Hancock, F. A.; Bulman Page, P. C.; Hutchings, G. J. *Angew. Chem. Int. Ed.* **2004**, *43*, 1685.



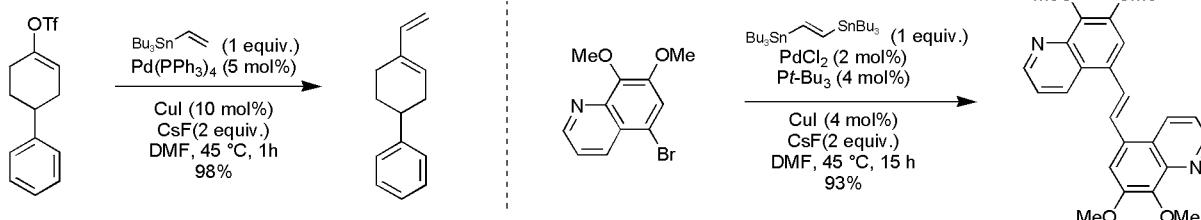
Cu-HY = Immobilized copper-zeolite Y catalyst. 14 examples (yields 23-92%, %ee 57-99%).

Cu-catalyzed electrophilic amination of diorganozinc reagents.  
Berman, A. W.; Johnson, J. S. *J. Am. Chem. Soc.* **2004**, 126, 5680.

**sp<sup>2</sup>-Nsp<sup>3</sup> Coupling**

15 examples (yields 69–98%). Use of alternative copper salts is also reported.

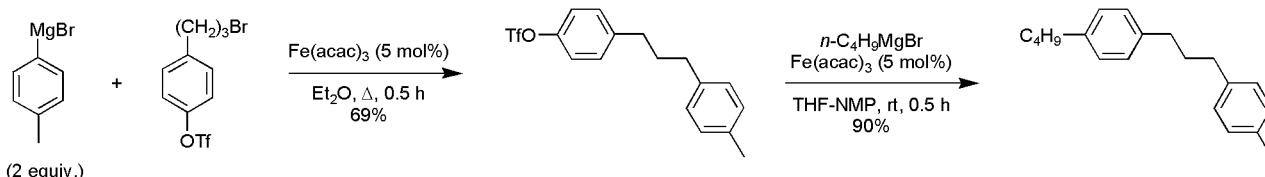
Synergic effect of copper(I) salts and fluoride ion in the Stille coupling.  
Mee, S. P. H.; Lee, V.; Baldwin, J. E. *Angew. Chem. Int. Ed.* **2004**, 43, 1132.

**sp<sup>2</sup>-sp<sup>2</sup> Coupling**

5 examples (yields 92–98%).

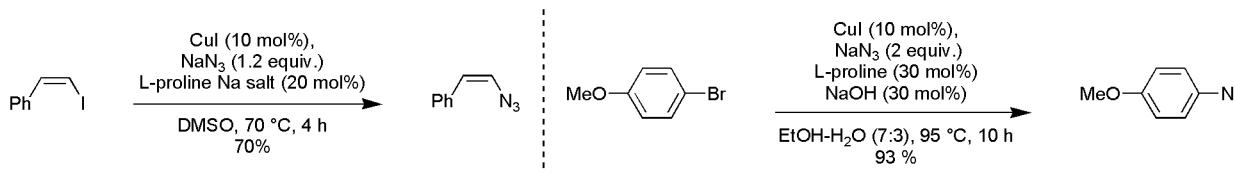
5 examples (yields 40–97%).

Fe-catalyzed Grignard cross-coupling with alkyl halides possessing  $\beta$ -hydrogens.  
Nagano, T.; Hayashi, T.; *Org. Lett.* **2004**, 6, 1297.

**sp<sup>2</sup>-sp<sup>3</sup> Coupling**

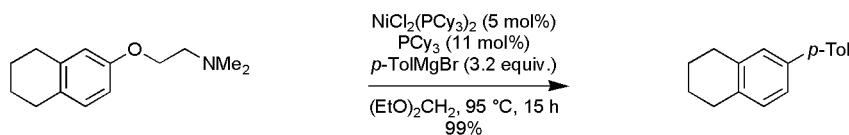
13 examples (yields 0–73%).

Synthesis of aryl and vinyl azides via proline-promoted Cul-catalyzed coupling reactions.  
Zhu, W.; Ma, D.; *Chem. Commun.* **2004**, 888.

**C–N Bond Formation**

30 examples (yields 9–93%).

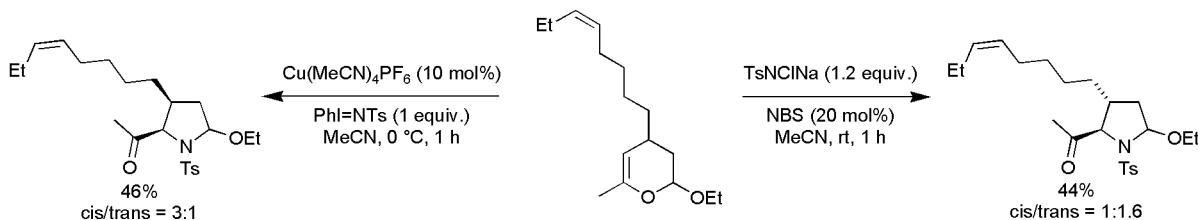
Ni-catalyzed cross-coupling of aryl Grignard reagents with aromatic alkyl ethers.  
Dankwardt, J. W.; *Angew. Chem. Int. Ed.* **2004**, 43, 2428.

**sp<sup>2</sup>-sp<sup>2</sup> Coupling**

39 examples (yields 30–99%).

Aminative rearrangement of 2-alkoxy-3,4-dihydro-2H-pyrans.  
Armstrong, A.; Cumming, G. R.; Pike, K. *Chem. Commun.* **2004**, 812.

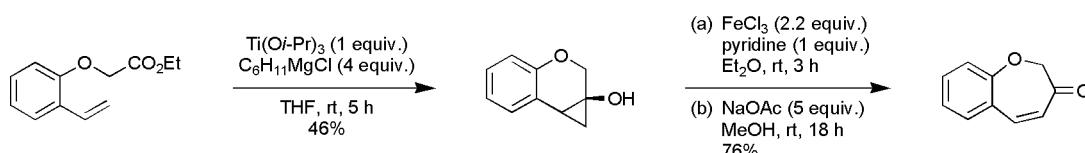
## Aziridination/ Rearrangement



9 examples (yields 42-99%).

Construction of medium-ring oxacycloalkenones.  
Lecornue, F.; Ollivier, J. *Org. Biomol. Chem.* **2003**, 1, 3600.

## Annulation

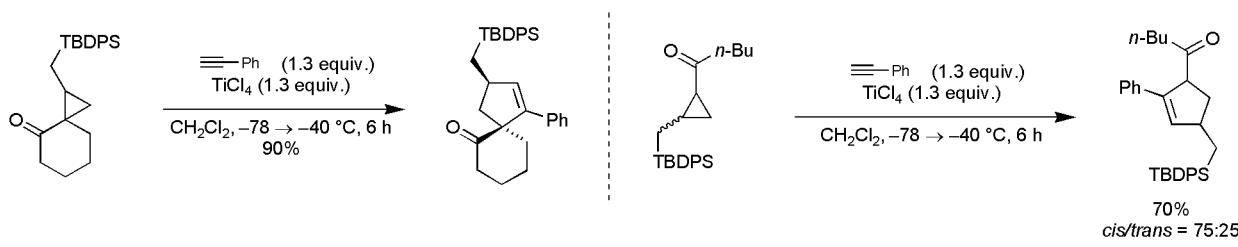


7 examples (yields 9-62%).

7 examples (yields 25-76%).

Formal [3 + 2] addition of cyclopropylmethyilsilanes with aryl acetylenes.  
Yadav, V. K.; Sriramurthy, V. *Angew. Chem. Int. Ed.* **2004**, 43, 2669.

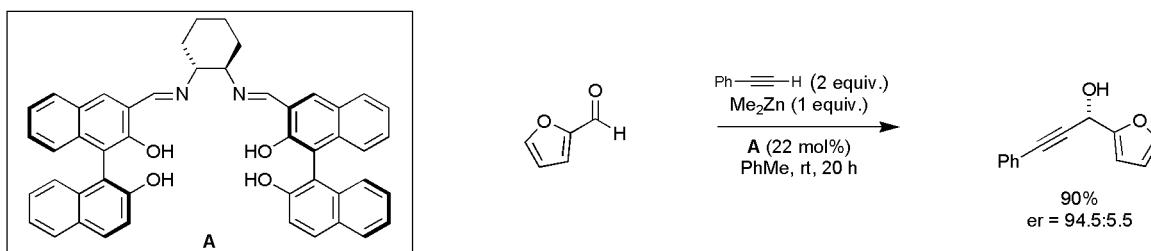
## Annulation



9 examples (yields 55-90%, cis/trans 57:43-95:5).

Enantioselective alkyne addition to aromatic aldehydes.  
Li, Z. B.; Pu, L. *Org. Lett.* **2004**, 6, 1065.

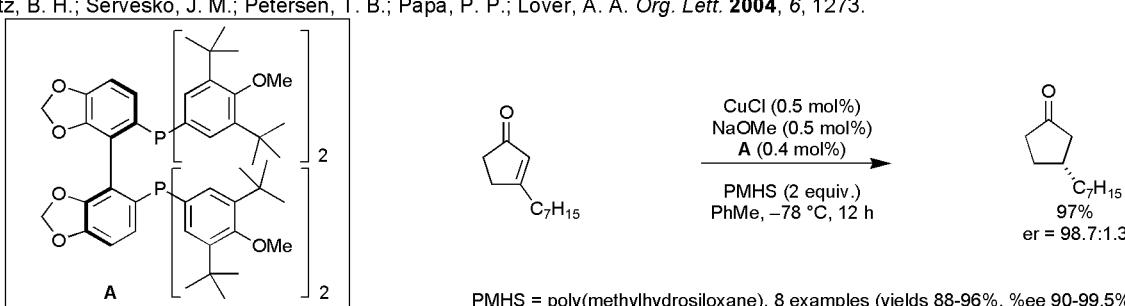
## Asymmetric 1,2-Addition



19 examples (yields 61-90%, %ee 86-97%).

Asymmetric reduction of  $\beta$ -substituted cycloalkenones.  
Lipshutz, B. H.; Servesko, J. M.; Petersen, T. B.; Papa, P. P.; Lover, A. A. *Org. Lett.* **2004**, 6, 1273.

## Asymmetric 1,4-Reduction



PMHS = poly(methylhydrosiloxane). 8 examples (yields 88-96%, %ee 90-99.5%).