

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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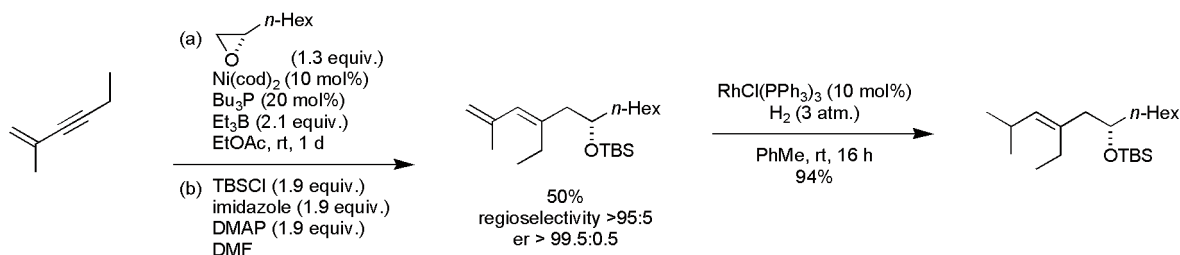
The journals regularly covered by the abstractors are:

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 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.

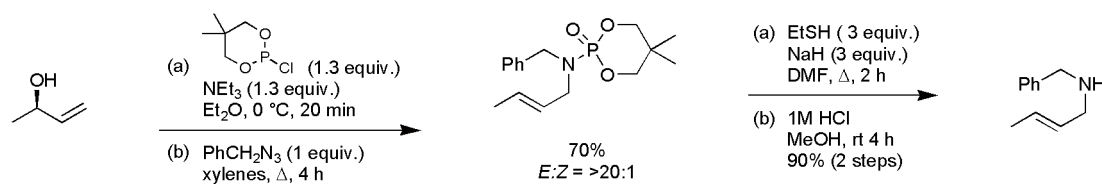
C-C Bond Formation



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

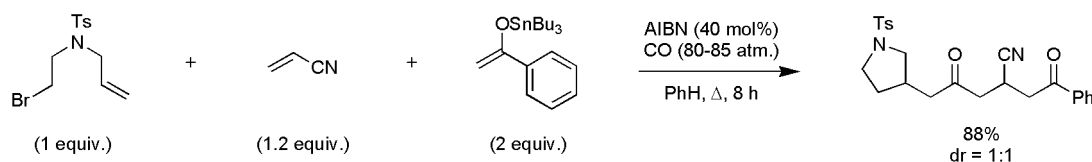
[3,3]-Sigmatropic Rearrangement



11 examples (yields 55–88%).

Synthesis of functionalized β- and δ-diketones via an intermolecular carbonylative cascade reaction.
 Miura, K.; Tojino, M.; Fujisawa, N.; Hosomi, A.; Ryu, I. *Angew. Chem. Int. Ed.* **2004**, *43*, 2423.

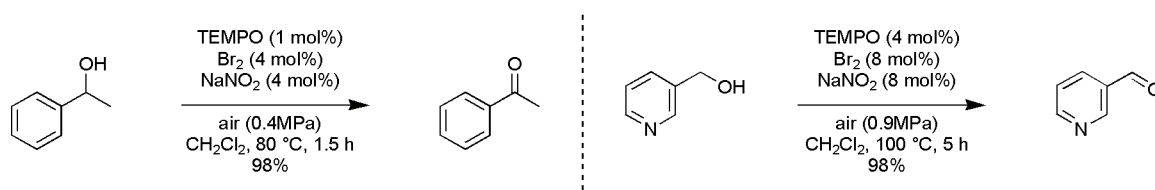
Radical Carbonylation



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.

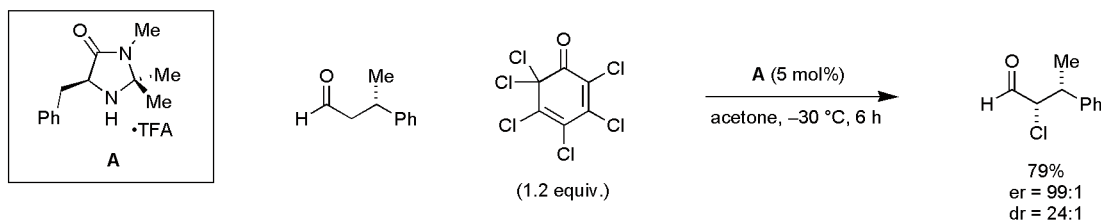
Oxidation



16 examples (yields 0-99%).

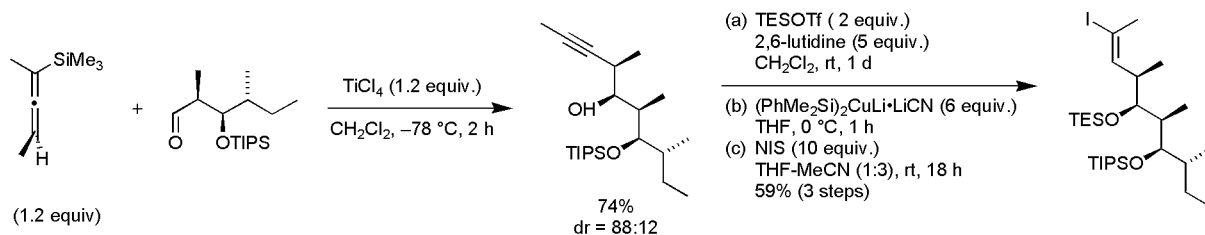
Direct, enantioselective organocatalytic α -chlorination of aldehydes.
Brochu, M. P.; Brown, S. P.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2004**, *126*, 4108.

Asymmetric C-Hal Bond Formation



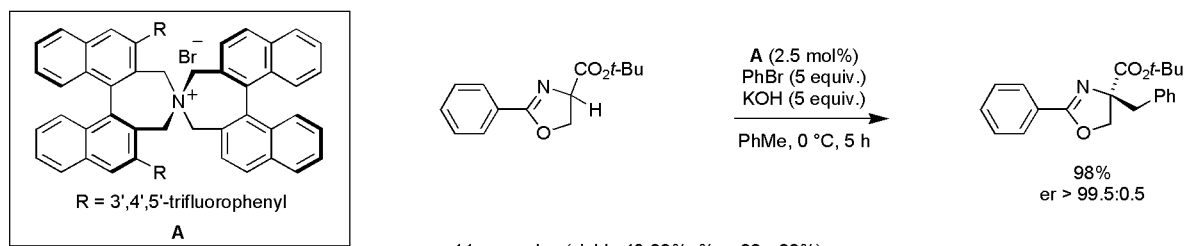
9 examples (yields 71-94%, %ee 80-98%).

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.

 $S_{\text{E}}2'$ Reaction/Silylcupration

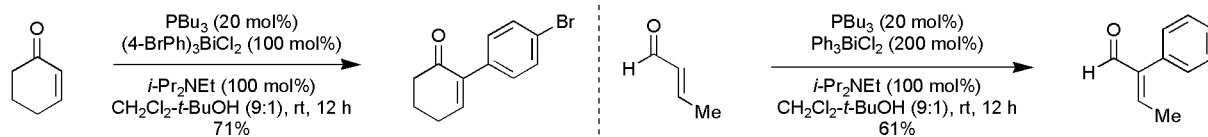
Synthesis of chiral α -alkyl serines via an enantioselective phase-transfer catalysed alkylation.
Jew, S.; Lee, Y.-J.; Lee, J.; Kang, M. J.; Jeong, B.-S.; Lee, J.-H.; Yoo, M.-S.; Kim, M.-J.; Choi, S.; Ku, J.-M.; Park, H. *Angew. Chem. Int. Ed.* **2004**, *43*, 2382.

Asymmetric Alkylation



11 examples (yields 48-99%, %ee 93->99%).

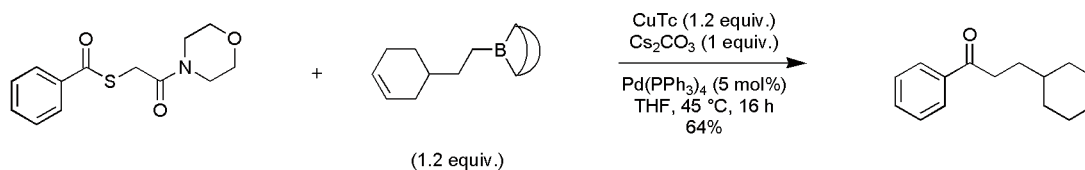
Phosphine catalyzed α -arylation of enones and enals using hypervalent bismuth reagents.
Koech, P. K.; Krische, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 5350.

 sp^2 - sp^2 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.

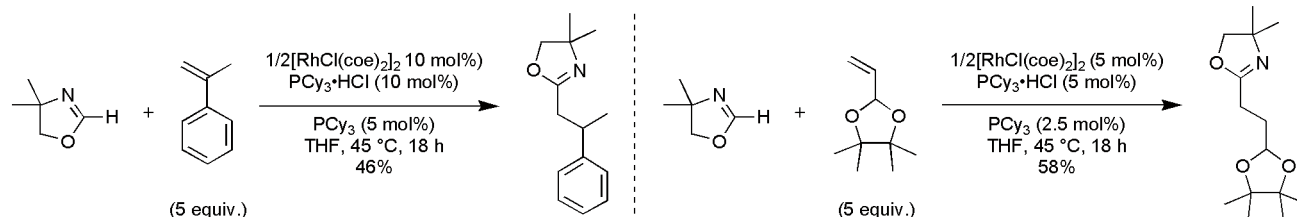
sp²-sp³ Coupling



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.

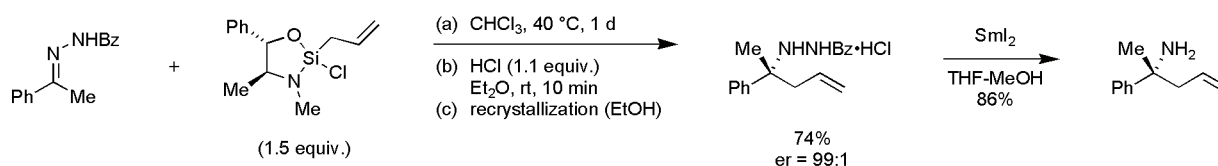
C-H Addition



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

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

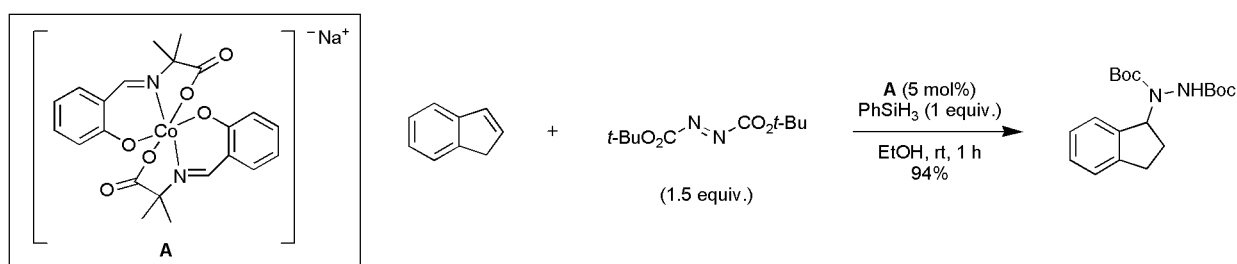
Asymmetric Allylation



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

Synthesis of alkyhydrazides 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

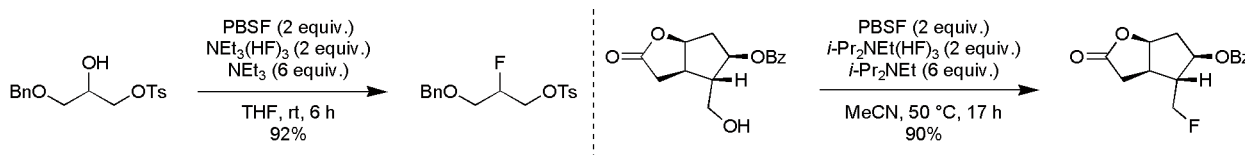


22 examples (yields 62-94%).

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

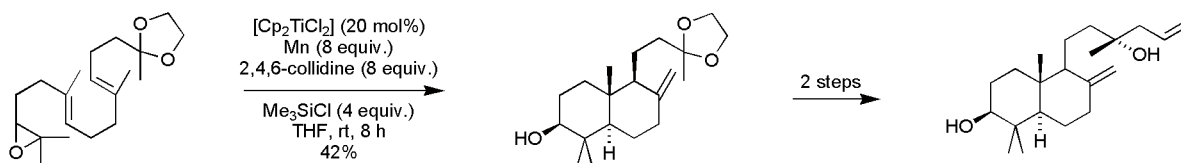


PBSF = perfluoro-1-butanefluoride. 17 examples (yields 65-96%).

Titanocene-catalyzed cascade cyclization of epoxydipolyrenes.

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.

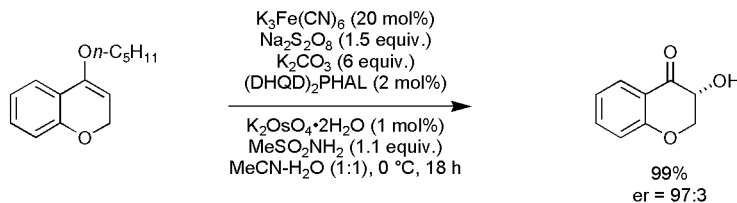
C–C Bond Formation



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.

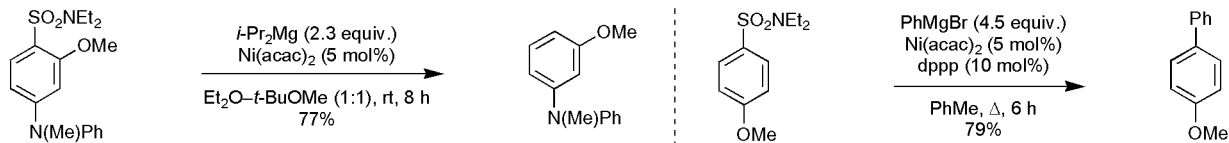


25 examples (yields 23-99%, %ee 20-95%).

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/sp²-sp² Coupling**

Milburn, R. R.; Snieckus, V. *Angew. Chem. Int. Ed.* **2004**, *43*, 888.



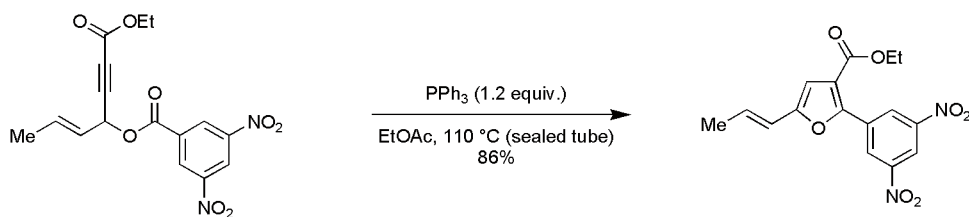
Reductive cleavage: 26 examples (yields 10-97%).

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

Synthesis of substituted furans via a phosphine-mediated reductive condensation of γ -acyloxy butynoates.

Jung, C.-K.; Wang, J.-C.; Krische, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 4118.

Heteroannulation

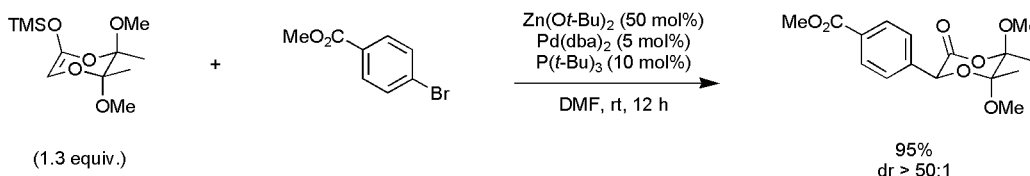


16 examples (yields 60-91%).

Palladium-catalyzed arylation of trimethylsilyl enolates of esters and imides.

Liu, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 5182.

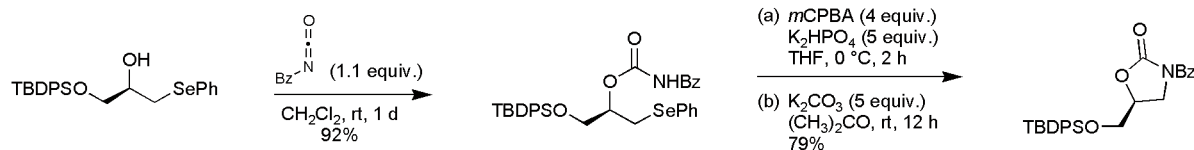
C–C Bond Formation



52 examples (yields 0-100%, %de 54->99%).

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

Nucleophilic Substitution

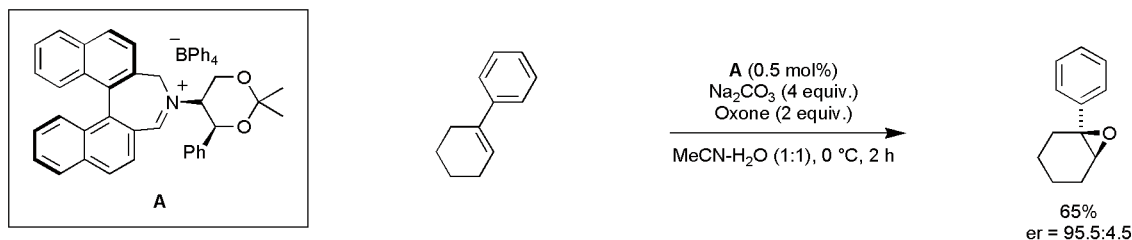


32 examples (yields 44-89%).

Iminium salt catalysts for asymmetric epoxidation.

Bulman Page, P. C.; Buckley, B. R.; Blacker, A. J. *Org. Lett.* **2004**, *6*, 1543.

Asymmetric Epoxidation

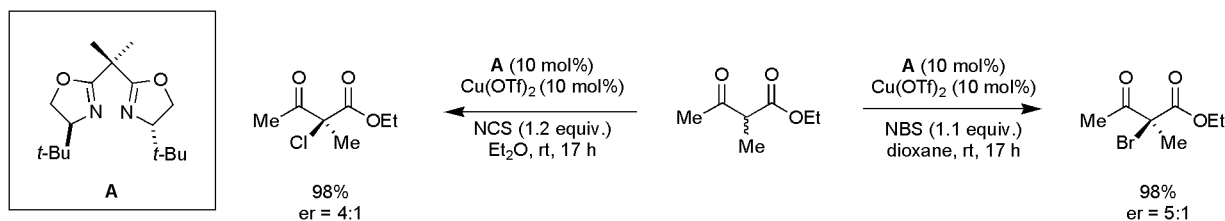


26 examples (yields 0-70%, %ee 0-95%).

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

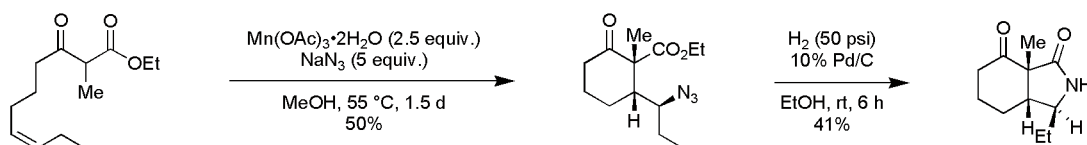


22 examples (yields 93-99%, %ee 30-82%).

Termination of Mn(II)-based oxidative cyclizations by trapping azides.

Snider, B. B.; Duvall, J. R. *Org. Lett.* **2004**, *6*, 1265.

Radical Cyclization

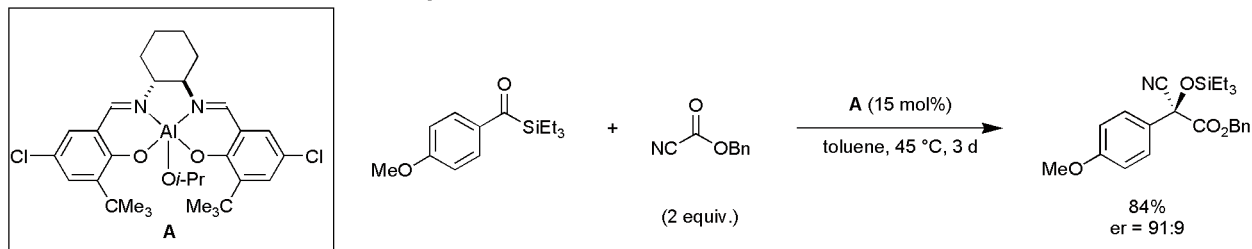


9 examples (yields 8-78%).

Catalytic asymmetric acylation of (siloxy)nitrile anions.

Nicewicz, D. A.; Yates, C. M.; Johnson, J. S. *Angew. Chem. Int. Ed.* **2004**, *43*, 2652.

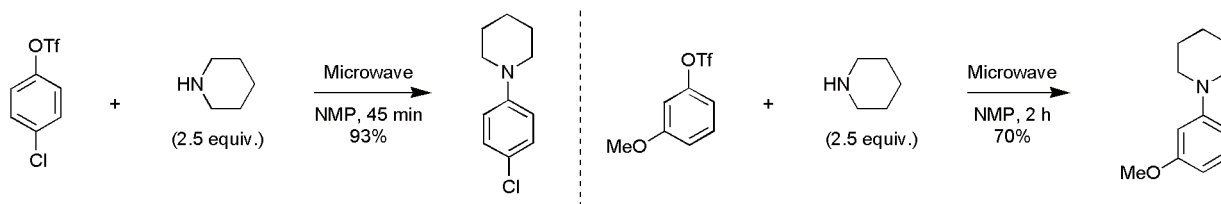
Asymmetric Acylation



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.

sp²-Nsp³ Coupling

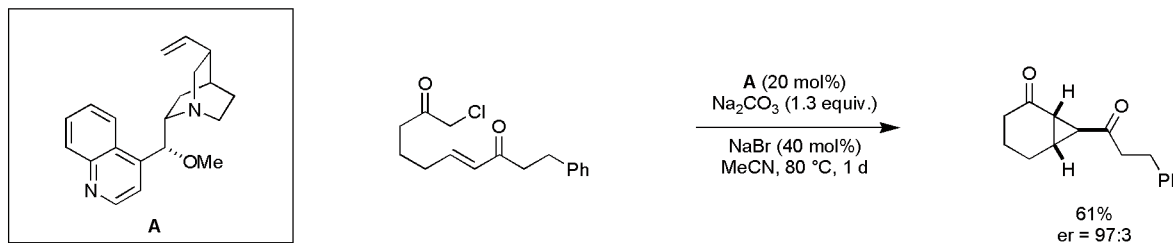


27 examples (yields <1-98%).

An intramolecular organocatalytic cyclopropanation reaction.

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

Cyclopropanation

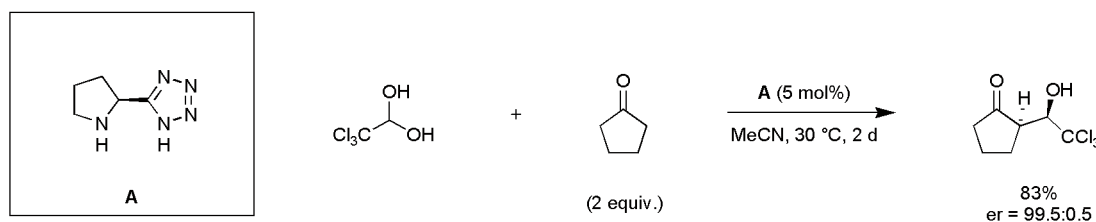


18 examples (yields 10-95%, %ee 64-95%).

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

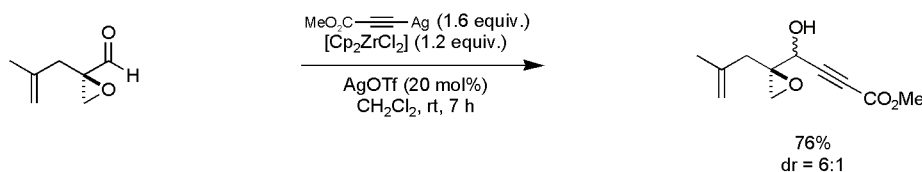


16 examples (yields 39-93%, %ee 67-99%).

A mild method for the preparation of γ -hydroxy- α,β -acetylenic esters.

Shahi, S. P.; Koide, K. *Angew. Chem. Int. Ed.* **2004**, *43*, 2525.

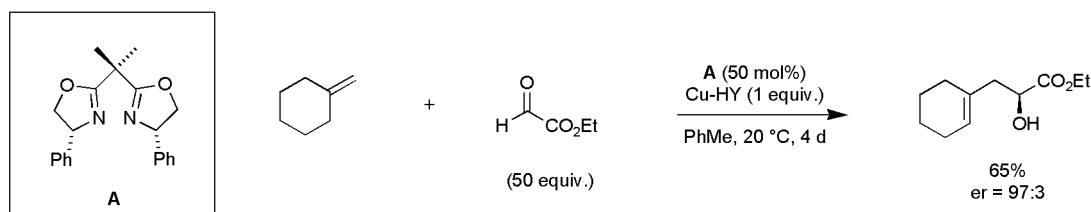
1,2-Addition



18 examples (yields 0-95%).

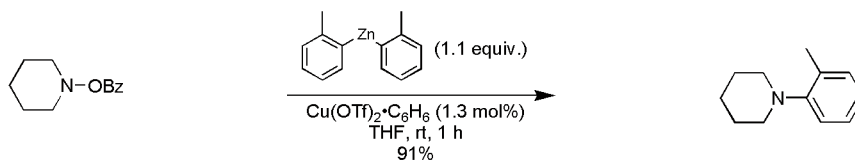
Catalytic, heterogeneous, enantioselective carbonyl- and imino-ene reactions using copper bis(oxazoline) zeolite Y. **C-C Bond Formation**

Caplan, N. A.; Hancock, F. A.; Bulman Page, P. C.; Hutchings, G. J. *Angew. Chem. Int. Ed.* **2004**, *43*, 1685.



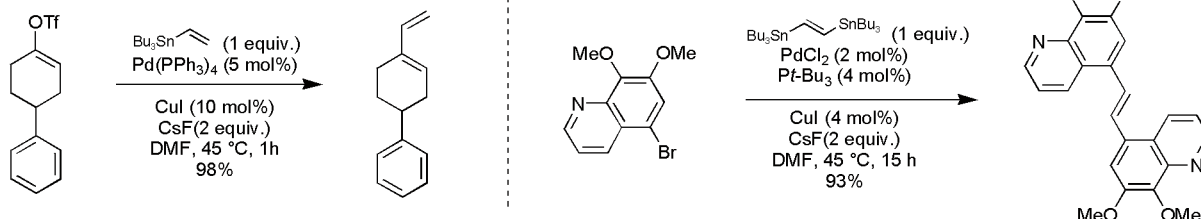
Cu-HY = Immobilized copper-zeolite Y catalyst. 14 examples (yields 23-92%, %ee 57-99%).

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

sp²-Nsp³ Coupling

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

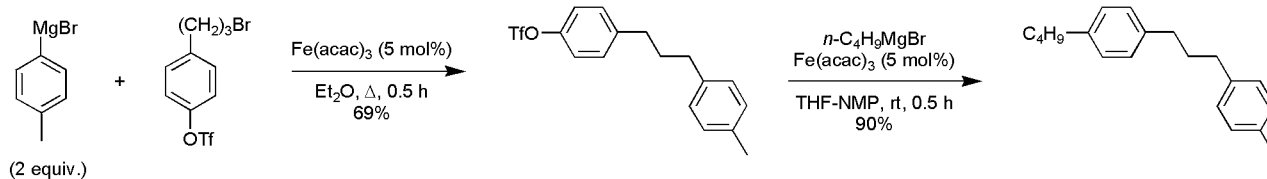
Synergic effect of copper(I) salts and fluoride ion in the Stille coupling.
Mee, S. P. H.; Lee, V.; Baldwin, J. E. *Angew. Chem. Int. Ed.* **2004**, *43*, 1132.

sp²-sp² Coupling

5 examples (yields 92-98%).

5 examples (yields 40-97%).

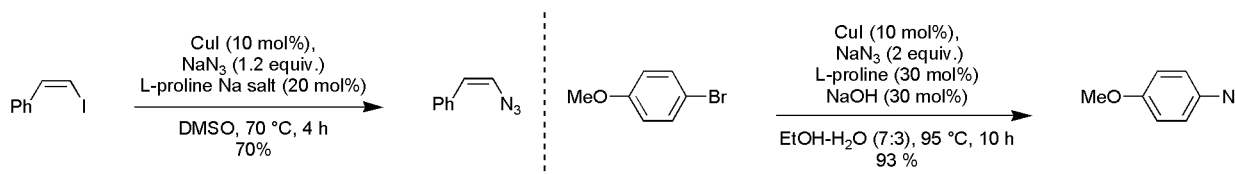
Fe-catalyzed Grignard cross-coupling with alkyl halides possessing β-hydrogens.
Nagano, T.; Hayashi, T.; *Org. Lett.* **2004**, *6*, 1297.

sp²-sp³ Coupling

13 examples (yields 0-73%).

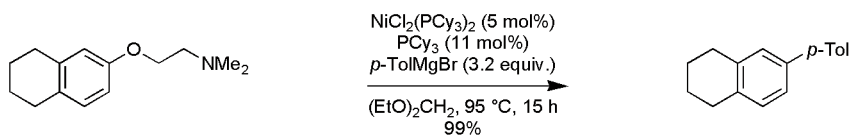
Synthesis of aryl and vinyl azides *via* proline-promoted CuI-catalyzed coupling reactions.
Zhu, W.; Ma, D.; *Chem. Commun.* **2004**, 888.

C-N Bond Formation



30 examples (yields 9-93%).

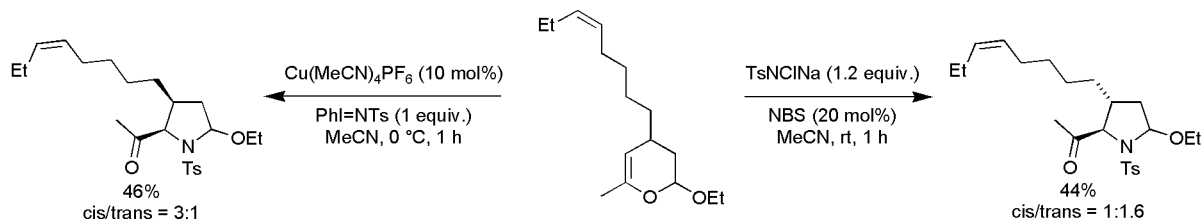
Ni-catalyzed cross-coupling of aryl Grignard reagents with aromatic alkyl ethers.
Dankwardt, J. W.; *Angew. Chem. Int. Ed.* **2004**, *43*, 2428.

sp²-sp² 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.

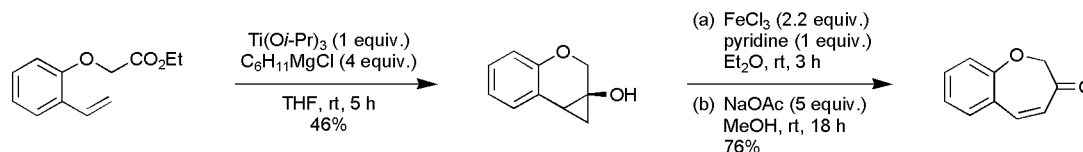
Aziridination/ Rearrangement



9 examples (yields 42-99%).

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

Annulation

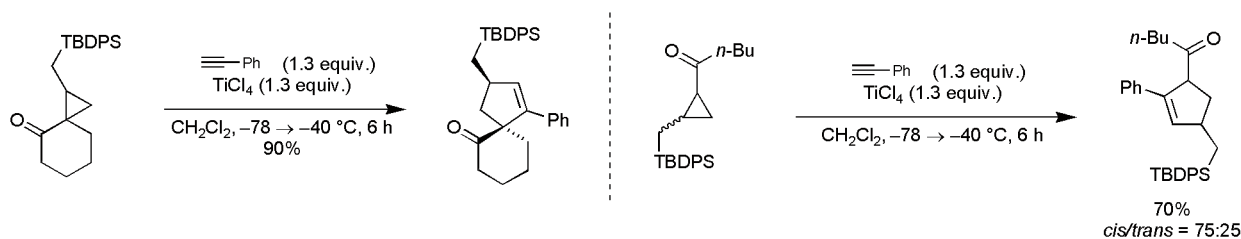


7 examples (yields 9-62%).

7 examples (yields 25-76%).

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

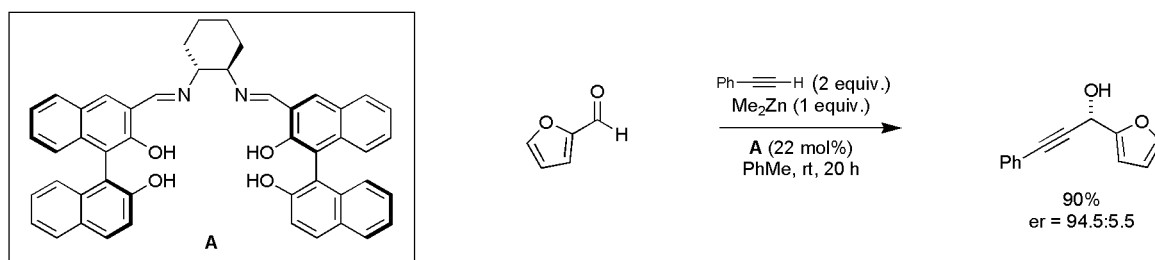
Annulation



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 β -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

