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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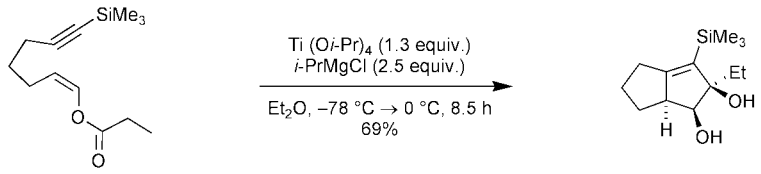
The journals regularly covered by the abstractors are:

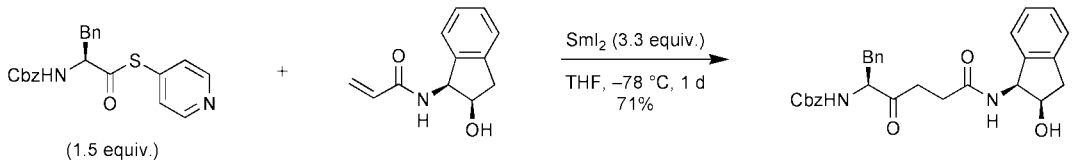
Angewandte Chemie International Edition
Bulletin of the Chemical Society of Japan
Chemical Communications
Chemistry A European Journal
Chemistry Letters
Collection Czechoslovak Chemical Communications
European Journal of Organic Chemistry
Helvetica Chimica Acta
Heterocycles
Journal of the American Chemical Society
Journal of Organic Chemistry
Organic and Biomolecular Chemistry
Organic Letters
Organometallics
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry and Tetrahedron Letters

Titanium-mediated intramolecular tandem cyclization of enol esters and acetylenes. **Annulation**
Urabe, H.; Suzuki, D.; Sasaki, M.; Sato, F. *J. Am. Chem. Soc.* **2003**, 125, 4036.



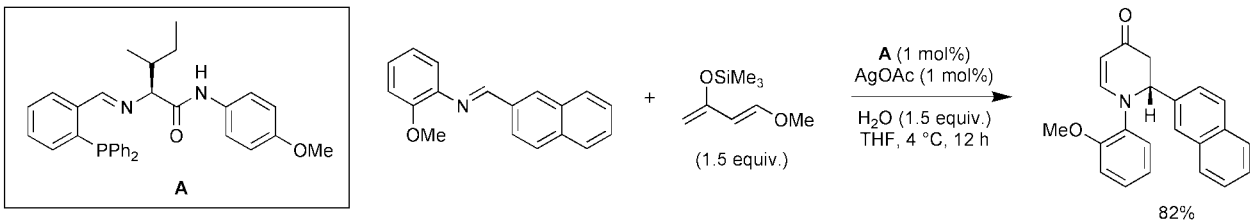
7 examples (yields 62-76%).

SmI_2-promoted addition of amino-acid derived thioesters to α,β-unsaturated amides and esters. **1,4-Addition**
Blakskjær, P.; Høj, B.; Riber, D.; Skrydstrup, T. *J. Am. Chem. Soc.* **2003**, *125*, 4030.



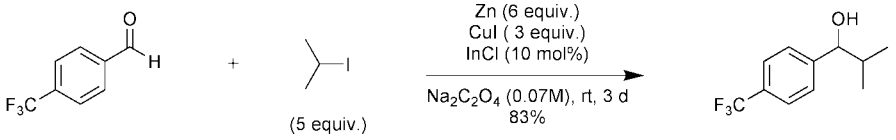
20 examples (yields 7-90%).

Ag-catalyzed cycloadditions between arylimines and Danishefsky's diene. **[4+2]-Cycloaddition**
Josephsohn, N. S.; Snapper, M. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 4018.



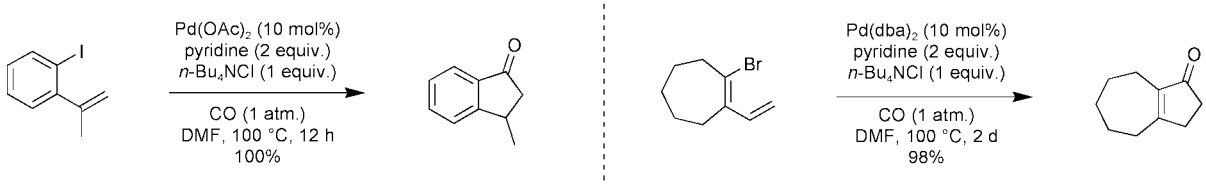
22 examples (yields 52-98%, %ee 20-95%).

Barbier–Grignard type alkylation of aldehydes with unactivated alkyl halides in water. **1,2-Addition**
Keh, C. C. K.; Wei, C.; Li, C-J. *J. Am. Chem. Soc.* **2003**, *125*, 4062.



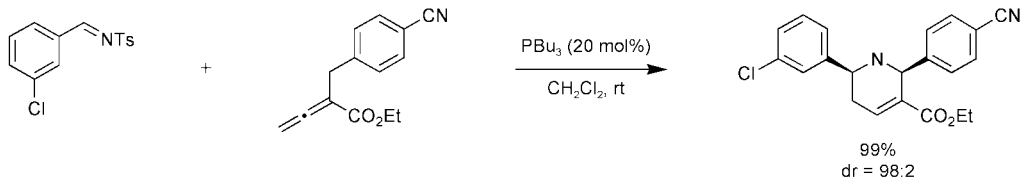
24 examples (yields 14-88%).

Synthesis of indanones and 2-cyclopentenones *via* Pd-catalyzed carbonylative cyclization. **Carbonylative Cyclization**
Gagnier, S. V.; Larock, R. C. *J. Am. Chem. Soc.* **2003**, *125*, 4804.



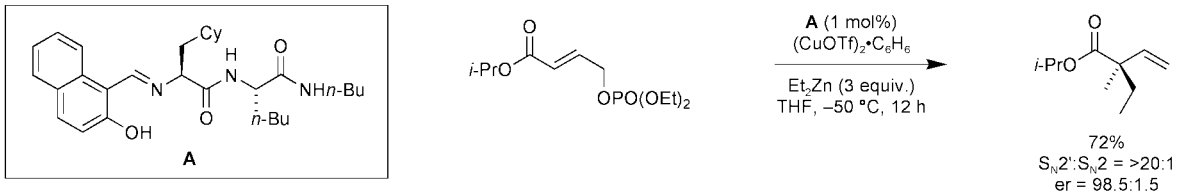
5,5-fused ring products could not be obtained. 14 examples (yields 45-100%).

Synthesis of highly functionalized tetrahydropyridines using a [4+2]-annulation. **[4+2]-Cycloaddition**
Zhu, X-F.; Lan, J.; Kwon, O. *J. Am. Chem. Soc.* **2003**, *125*, 4716.



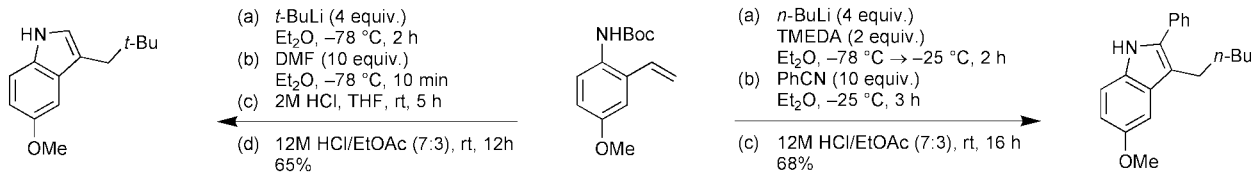
27 examples (yields 80-99%, %de 66-96%).

Enantioselective synthesis of α-alkyl-β,γ-unsaturated esters using Cu-catalyzed allylic alkylations. **Asymmetric Allylic Alkylation**
Murphy, K. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 4690.



12 examples (yields 47-93%, %ee 87-97%, 7:1 < regioselectivities < 20:1).

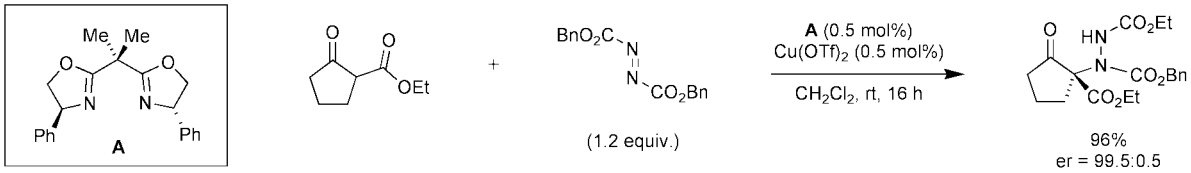
Synthesis of functionalized indoles *via* an organolithium addition-cyclization sequence. **Annulation**
Coleman, C. M.; O'Shea, D. F. *J. Am. Chem. Soc.* **2003**, *125*, 4054.



16 examples (yields 30-81%).

Highly enantioselective, catalytic amination of β-ketoesters.
Marigo, M.; Juhl, K.; Jorgensen, K. A. *Angew. Chem. Int. Ed.* **2003**, *42*, 1367.

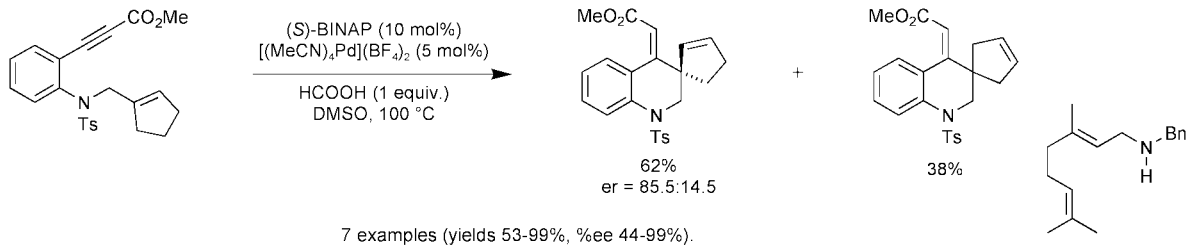
Asymmetic Amination



17 examples (yields 65-98%, %ee = 55-99%).

Enantioselective tetrahydroquinoline synthesis *via* an ene-type cyclization.
Hatano, M.; Mikami, K. *J. Am. Chem. Soc.* **2003**, *125*, 4704.

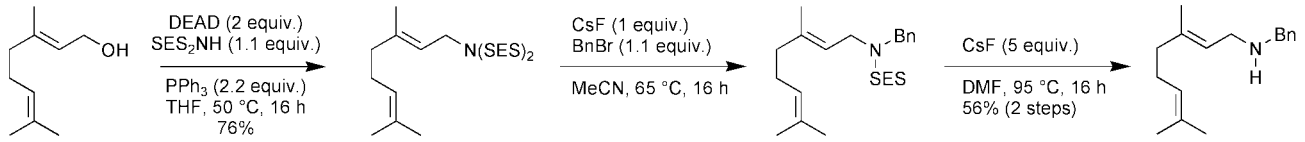
Ene cyclization



7 examples (yields 53-99%, %ee 44-99%).

One-pot monodeprotection of bis-SES imides/N-alkylation.
Dastrup, D. M.; VanBrunt, M. P.; Weinreb, S. M. *J. Org. Chem.* **2003**, *68*, 4112.

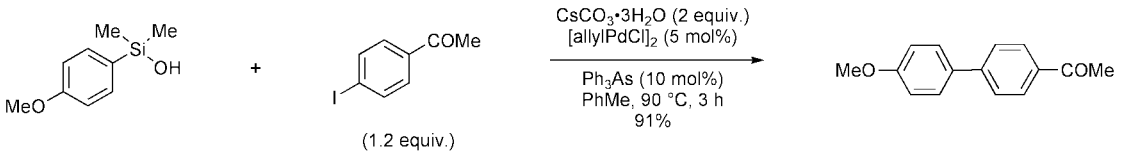
N-Alkylation



SES = 2-trimethylsilylethylsulfonyl. 9 examples including primary and secondary alcohols (yields 59-93%).

Cross-coupling reactions of arylsilanols with substituted aryl halides.
Denmark, S. E.; Ober, M. H. *Org. Lett.* **2003**, 5, 1357.

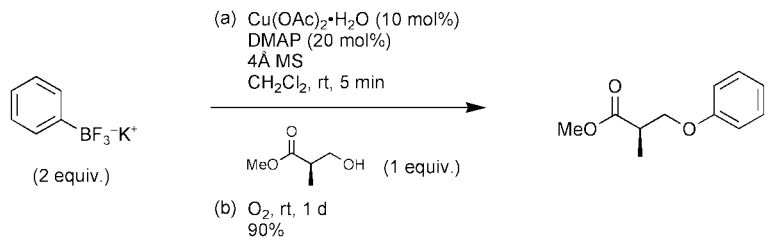
sp^2-sp^2 Coupling



18 examples (yields 79-92%).

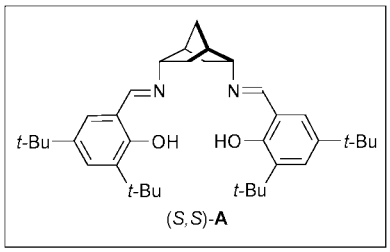
Copper(II)-catalyzed ether synthesis using aliphatic alcohols and potassium organotrifluoroborate salts.
Quach, T. D.; Batey, R. A. *Org. Lett.* **2003**, 5, 1381.

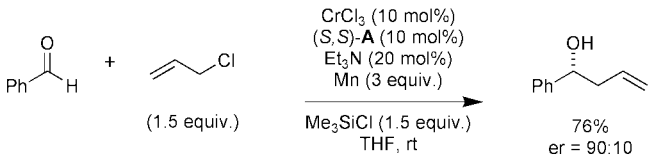
Etherification



31 examples (yields 48-100%) including primary and secondary aromatic, aliphatic, allylic and propargylic alcohols.

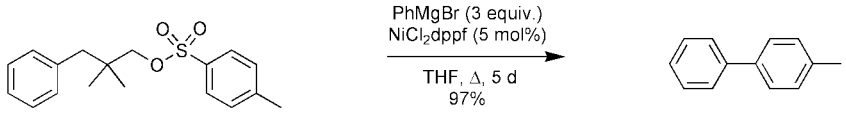
Asymmetric, catalytic Nozaki–Hiyama–Kishi reaction of allylic and vinylic halides. **Enantioselective 1,2-Addition**
Berkessel, A.; Menche, D.; Sklorz, C. A.; Schröder, M.; Paterson, I. *Angew. Chem. Int. Ed.* **2003**, 42, 1032.





8 examples (yields 54-76%, %ee 31-92%).

Ni(0)-catalyzed cross-coupling of alkyl arenesulfonates with aryl Grignard reagents. **Cross-Coupling**
Cho, C.-H.; Yun, H.-S.; Park, K. *J. Org. Chem.* **2003**, *68*, 3017.

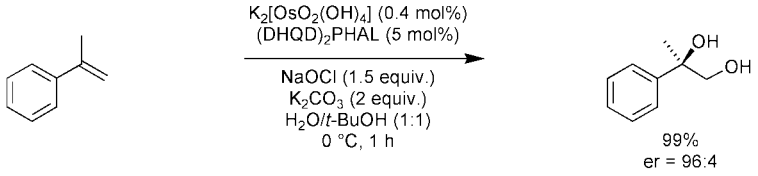


39 examples (yields 7-97%). C-S bond *vs* C-O bond cleavage investigated.

Orthoacylimines as chiral auxiliaries for nucleophilic addition of organolithium reagents to imines. **1,2-Addition**
Boezio, A. A.; Solberghe, G.; Lauzon, C.; Charette, A. B. *J. Org. Chem.* **2003**, *68*, 3241.

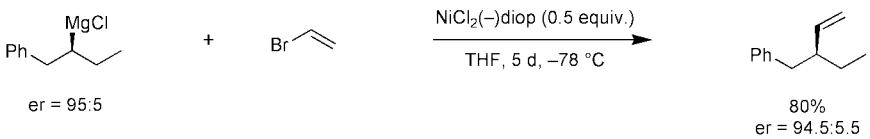
11 examples (yields 54->98%, %ee 70-98%). Application to the synthesis of *tert*-Leucine is also reported.

Os-catalyzed dihydroxylation of olefins using bleach as the terminal oxidant. **Dihydroxylation**
Mehltretter, G. M.; Bhor, S.; Klawonn, M.; Döbler, C.; Sundermeier, U.; Eckert, M.; Militzer, H. C.; Beller, M. *Synthesis*, **2003**, 295.



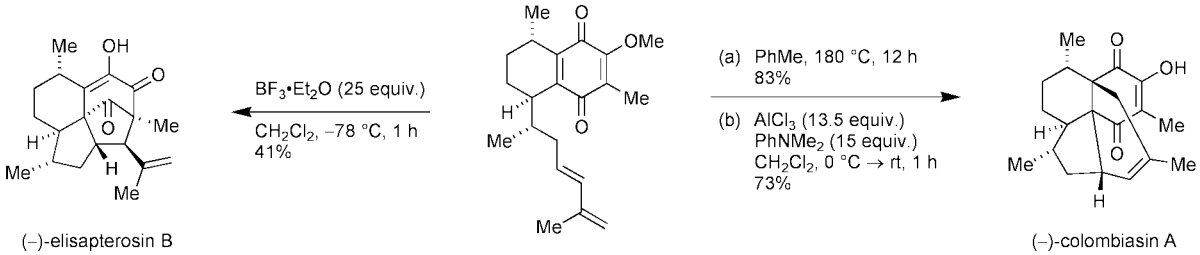
10 examples (yields 84-99%, %ee 34-95%).

Kumada-Corriu coupling of a chiral Grignard reagent under Pd(0) or Ni(0)-catalysis. **sp^2-sp^3 Coupling**
Hölzer, B.; Hoffmann, R. W. *Chem. Commun.* **2003**, 732.



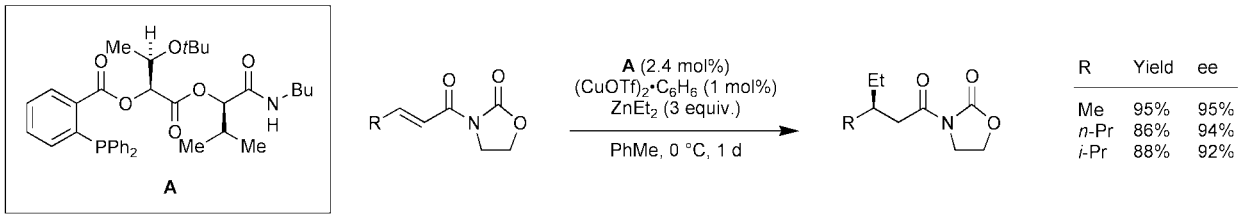
4 examples (yields 55-80%, %ee 88-89%). diop = (–)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.

Unified strategy for the synthesis of (–)-Elisapterosin B and (–)-Colombiasin A. **Cycloaddition**
Kim, A. I.; Rychnovsky, S. D. *Angew. Chem. Int. Ed.* **2003**, *42*, 1267.



(–)-elisapterosin B (–)-colombiasin A

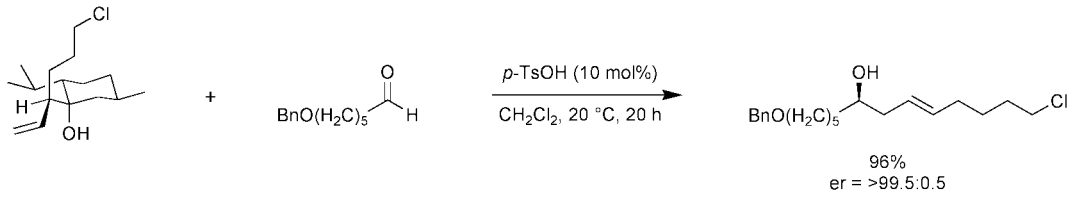
Cu-catalyzed enantioselective conjugate additions of alkyl zinc reagents to unsaturated *N*-acyloxazolidinones. **1,4-Addition**
Nokami, J.; Nomiyama, K.; Matsuda, S.; Imai, N.; Kataoka, K. *Angew. Chem. Int. Ed.* **2003**, *42*, 1273.



R	Yield	ee
Me	95%	95%
n-Pr	86%	94%
i-Pr	88%	92%

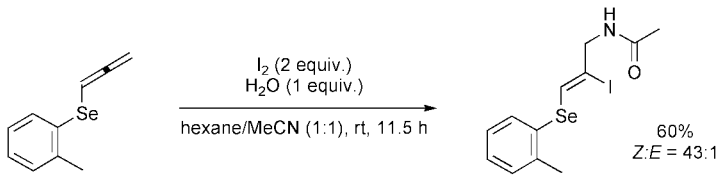
8 examples including $ZnMe_2$, $Zn(i\text{-}Pr)_2$ and $Zn\{i\text{-}Pr(CH_2)_3\}_2$ (yields 61-95%, %ee 76-98%).

Highly enantioselective alkyl-2-enylation of aldehydes through an allyl-transfer reaction. **Allyl Transfer**
Nokami, J.; Nomiyama, K.; Matsuda, S.; Imai, N.; Kataoka, K. *Angew. Chem. Int. Ed.* **2003**, *42*, 1273.



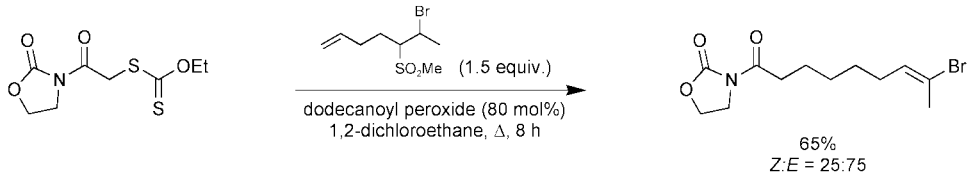
19 examples (yields 63-96%, %ee > 99%).

Synthesis of *N*-(3-organoseleno-2-iodo-2(*Z*)-propenyl) acetamides *via* iodoamination of selenium substituted allenes. **Iodoamination**
Ma, S.; Hao, X.; Huang, X. *Chem. Commun.* **2003**, 1082.



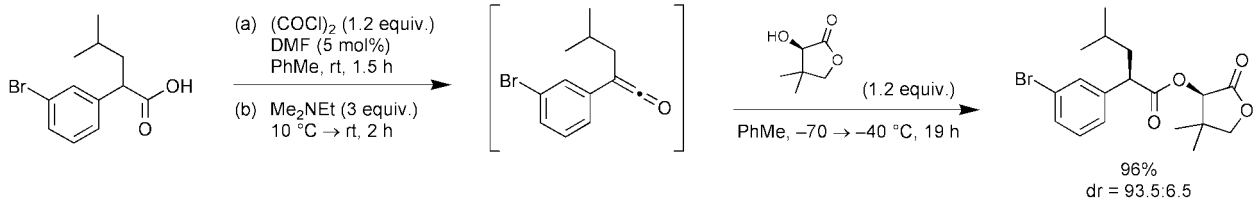
13 examples (yields 15-64%, 18:1 ≤ *Z*:*E* ≤ 65 :1).

Xanthate-mediated radical addition/intramolecular hydrogen atom transfer. **Radical Addition/Hydrogen Transfer**
Ouvry, G.; Zard, S. Z. *Chem. Commun.* **2003**, 778.



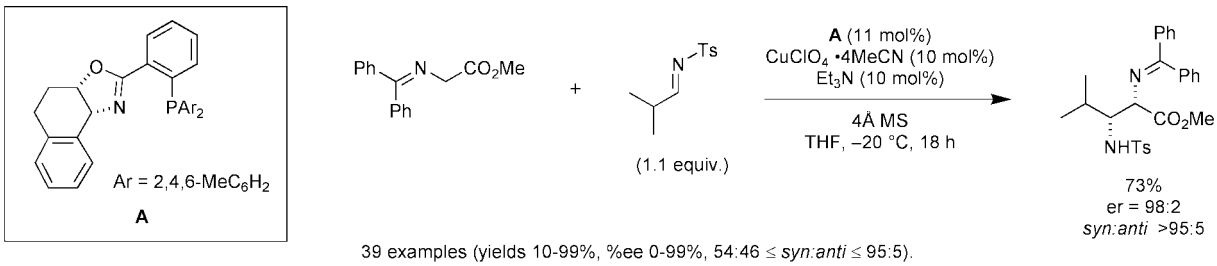
8 examples (yields 38-81%).

De-racemization *via* addition of a chiral alcohol to an *in situ*-generated ketene. **Asymmetric Protonation**
Chen, C-Y, Dagneau, P.; Grabowski, E. J. J.; Oballa, R.; O'Shea, P.; Prasit, P.; Robichaud, J.; Tillyer, R.; Wang, X. *J. Am. Chem. Soc.* **2003**, *125*, 2633.



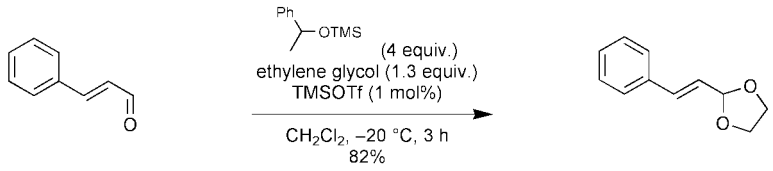
Applied to a large scale, chromatography-free synthesis of a cathepsin K inhibitor.

Catalytic, asymmetric Mannich reactions of glycine derivatives with imines. **Mannich Reaction**
Bernardi, L.; Gothelf, A. S.; Hazell, R. G.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2003**, *125*, 2583.



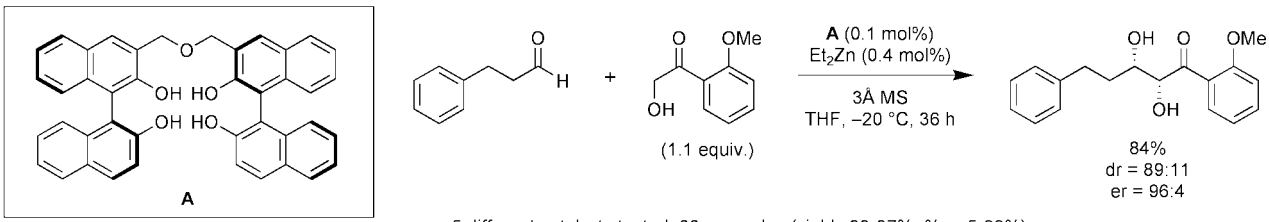
39 examples (yields 10-99%, %ee 0-99%, 54:46 ≤ *syn:anti* ≤ 95:5).

A mild preparation of cyclic acetals. **Acetal Formation**
Kurihara, M.; Hakamata, W. *J. Org. Chem.* **2003**, *68*, 3413.



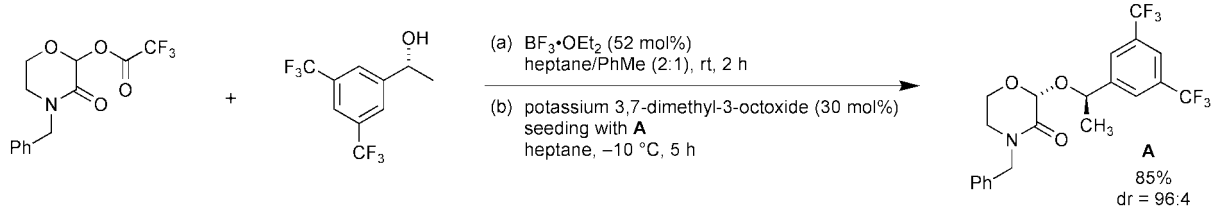
24 examples (yields 70-99%). Alternative TMS sources to alkoxysilanes were also reported, including a solid-supported reagent.

Asymmetric aldol reaction using a Et_2Zn/linked-BINOL complex. **Enantioselective Aldol**
Kumagai, N.; Matsunaga, S.; Kinoshita, T.; Harada, S.; Okada, S.; Sakamoto, S.; Yamaguchi, K.; Shibasaki, M. *J. Am. Chem. Soc.* **2003**, *125*, 2169.

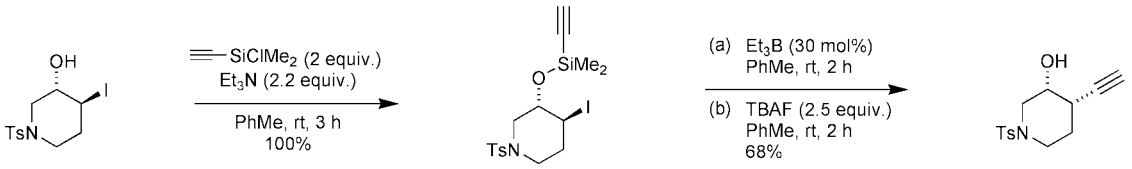


5 different catalysts tested. 33 examples (yields 39-97%, %ee 5-99%).

A novel crystallization-induced diastereoselective glycosidation. **Diastereoselective *O,O*-Acetal Formation**
Brands, K. M. J.; Payack, J. F.; Rosen, J. D.; Nelson, T. D.; Candelario, A.; Huffman, M. A.; Zhao, M. M.; Li, j.; Craig, B.; Song, Z. J.; Tschaen, D. M.; Hansen, K.; Devine, P. N.; Pye, P. J.; Rossen, K.; Dormer, P. G.; Reamer, R. A.; Welch, C. J.; Mathre, D. J.; Tsou, N. N.; McNamara, J. M.; Reider, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 2129.

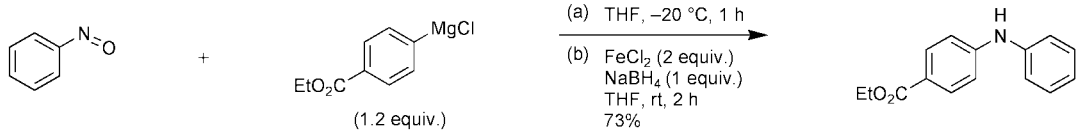


Introduction of an ethynyl group using a silicon tether *via* a radical method. **Radical Cyclization/Elimination**
Sukeda, M.; Ichikawa, A.; Shuto, S. *J. Org. Chem.* **2003**, *68*, 3465.



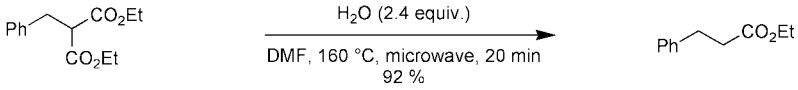
11 examples (yields 18-86%). Applied towards the synthesis of 2'-deoxy-2'-*C*-ethynylnucleosides.

Synthesis of polyfunctional amines by the addition of arylmagnesium reagents to nitrosoarenes. **Amination**
Kopp, F.; Sapountzis, I.; Knochel, P. *Synlett* **2003**, 743.



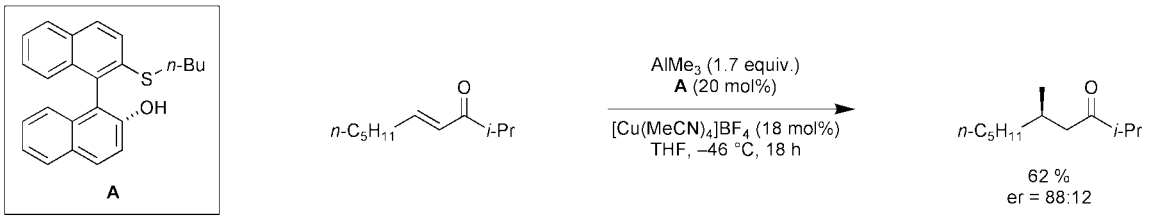
11 examples (yields 42-74%).

Microwave-assisted decarboalkoxylation of mono-alkylated malonates and β-ketoesters. **Decarboalkoxylation**
Curran, D. P.; Zhang, Q.; *Adv. Synth. Catal.* **2003**, *345*, 329.



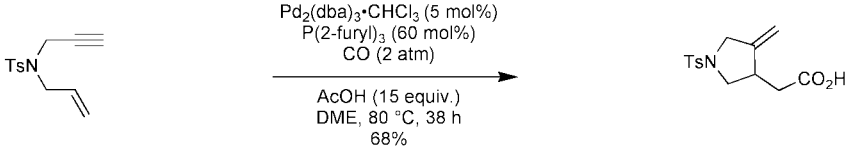
9 examples (yields 0-96%).

Enantioselective conjugate addition of $AlMe_3$ to linear aliphatic enones. **1,4-Addition**
Fraser, P. K.; Woodward, S. *Chem.–Eur. J.* **2003**, *9*, 776.



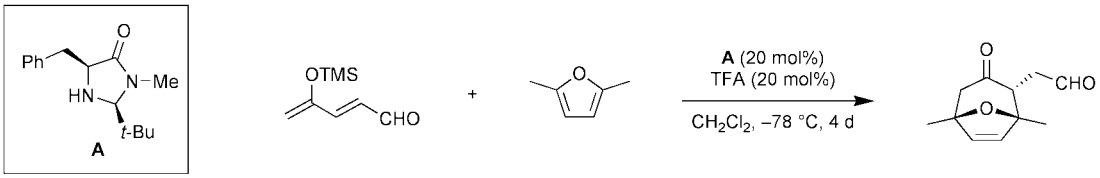
10 examples (yields 46-64%, %ee 76-93%).

Palladium-catalyzed cyclization-carbonylation of enynes to cyclic γ,δ -unsaturated acids. **Annulation**
Aggarwal, V. K.; Butters, M.; Davies, P. W. *Chem. Commun.* **2003**, 1046.



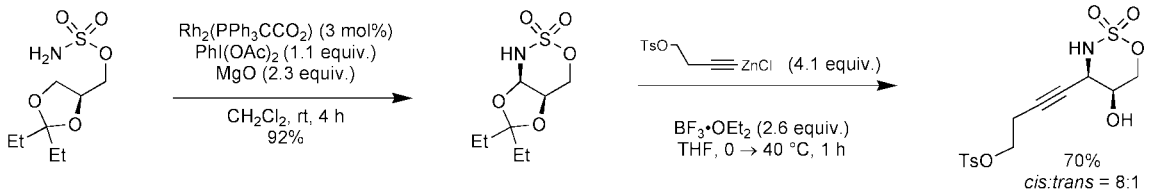
7 examples (yields 0-77%).

Asymmetric organocatalysis of [4 + 3] cycloaddition reactions. **[4+3]-Cycloaddition**
Harmata, M.; Ghosh, S. K.; Hong, X.; Wacharasindhu, S.; Kirchhoefer, P. *J. Am. Chem. Soc.* **2003**, *125*, 2058.



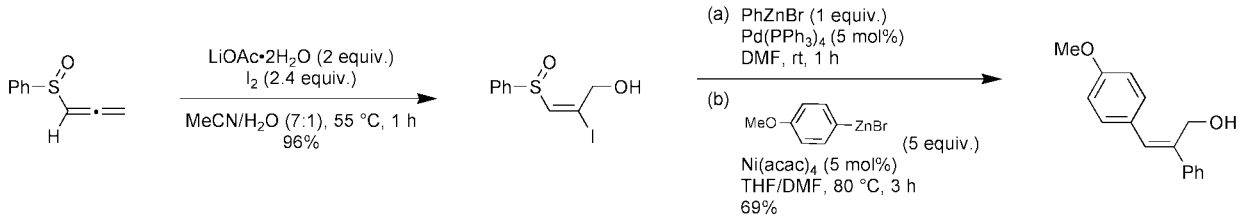
14 examples (yields 8-74%, %ee 50-90%).

Novel iminium ion equivalents prepared through C-H oxidation for the stereocontrolled synthesis of propargylic amines. **Substitution**
Fleming, J. J.; Fiori, K. W.; Du Bois, J. *J. Am. Chem. Soc.* **2003**, *125*, 2028.



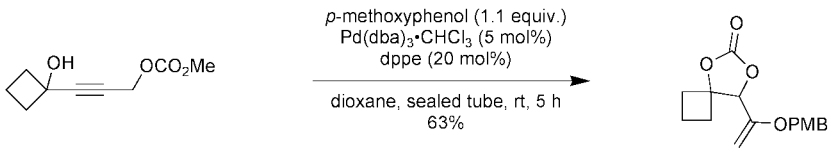
6 examples (yields 63-85%, %de 72-90%).

Halohydroxylation of 1,2-allenyl phenyl sulfoxides and Pd/Ni-catalyzed selective coupling reactions. **Halohydroxylation/Cross-Coupling**
Ma, S.; Ren, H.; Wei, Q. *J. Am. Chem. Soc.* **2003**, *125*, 4817.



31 halohydroxylation examples (yields 51-98%), 10 Pd(0) catalyzed couplings (yields 71-94%), 16 Ni(0) catalyzed couplings (yields 57-84%).

Palladium-catalyzed cascade reaction of 4-methoxycarbonyloxy-2-butyn-1-ols with phenols. **CO_2 Elimination-Fixation**
Yoshida, M.; Fujita, M.; Ishii, T.; Ihara, M. *J. Am. Chem. Soc.* **2003**, *125*, 4874.



32 examples (yields 36-97%).

Binding and activation of aromatic molecules by a molybdenum π-base. **Asymmetric Allylic Alkylation**
Meiere, S. H.; Keane, J. M.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2003**, *125*, 2024.