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:

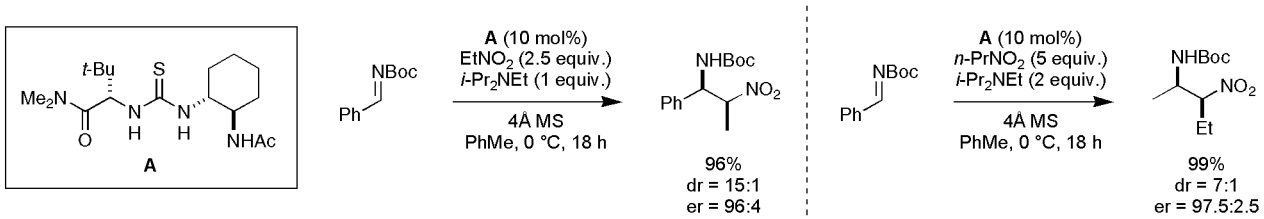
Fiona Black, John Cooksey, Victoria Coombes, Przemyslaw Kubinski, Joanne Peach, and Thomas Snaddon, Department of Chemistry, Leeds University, Leeds, LS2 9JT, UK.

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

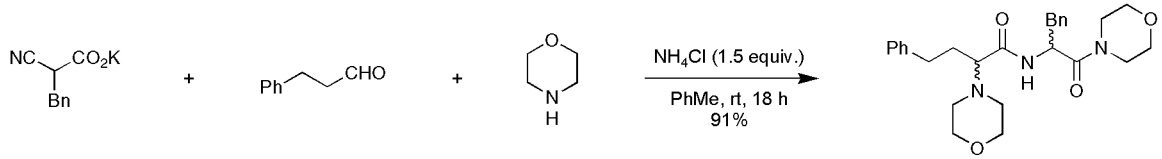
SYNTHESIS 2005, No. 5, pp 843–850
Advanced online publication: 22.03.2005
Art ID: X0505SS

Enantioselective thiourea-catalyzed nitro-Mannich reaction. **Nitro-Mannich**
Yoon, T. P.; Jacobsen, E. N. *Angew. Chem. Int. Ed.* **2005**, *44*, 466.



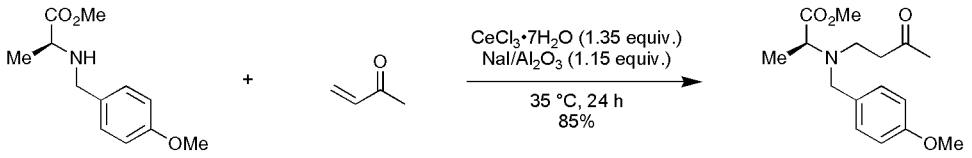
14 examples (yields 79-99%, %de 88-34%, %ee 92-97%).

Ammonium chloride promoted Ugi reaction of α-substituted α-isocyano acetic acid. **Amide Formation**
Bonne, D.; Dekhane, M.; Zhu, J. *Org. Lett.* **2004**, *6*, 4771.



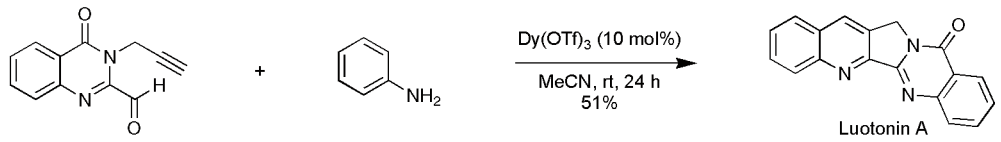
14 examples (yields 70-98%).

Heteroatom nucleophilic addition to electron-poor alkenes promoted by an alumina-supported $CeCl_3 \cdot 7H_2O$/NaI system. **1,4-Addition**
Bartoli, G.; Bartolacci, M.; Giuliani, A.; Marcantoni, E.; Massaccesi, M.; Torregiani, E. *J. Org. Chem.* **2005**, *70*, 169.



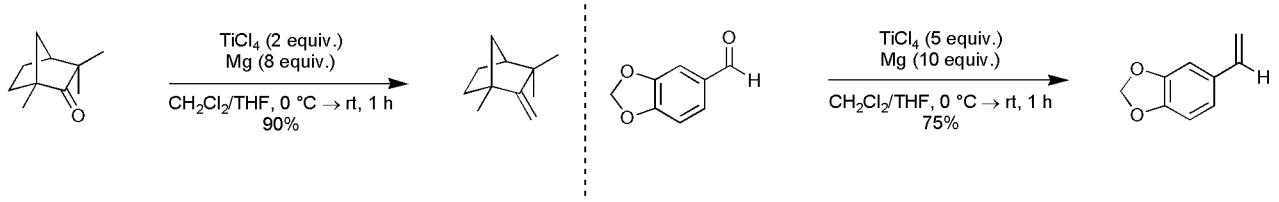
12 examples (yields 70-98%).

Intramolecular hetero Diels–Alder synthesis of the pyrroloquinoline alkaloids. **Hetero Diels–Alder**
Twin, H.; Batey, R. A. *Org. Lett.* **2004**, *6*, 4913.



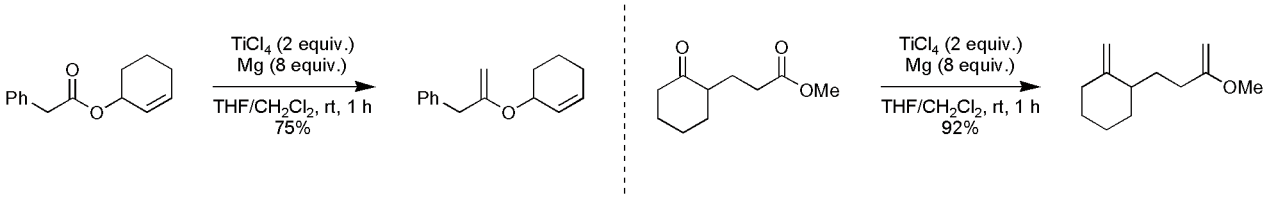
Formal synthesis of Camptothecin also described. 3 examples (yields 51-71%).

Direct methylenation of ketones and aldehydes with CH_2Cl_2 promoted by Mg/$TiCl_4$/THF. **Methylenation**
Yan, T-H.; Tsai, C-C.; Chien, C-T.; Cho, C-C.; Huang, P-C. *Org. Lett.* **2004**, *6*, 4961.



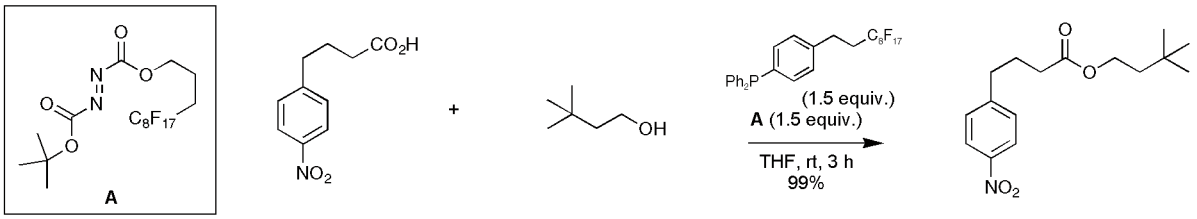
16 examples (yields 61-95%).

Nucleophilic and selective Ti-methylene complexes for ester methylenation. **Methylenation**
Yan, T-H.; Chien, C-T.; Tsai, C-C.; Lin, K-W.; Wu, Y-H. *Org. Lett.* **2004**, *6*, 4965.



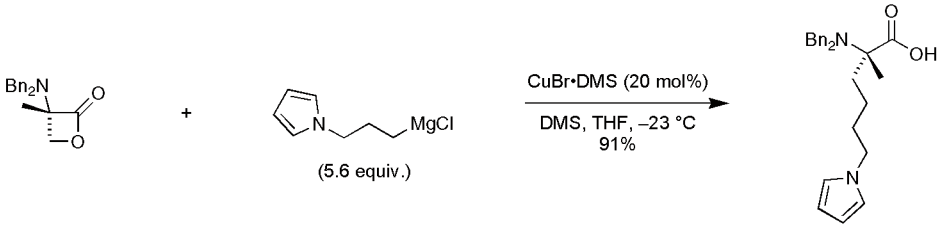
18 examples (yields 0-92%).

Second generation fluorous DEAD reagents in the Mitsunobu reaction. **Fluorous Reagents/Mitsunobu**
Dandapani, S.; Curran, D. P. *J. Org. Chem.* **2004**, *69*, 8751.



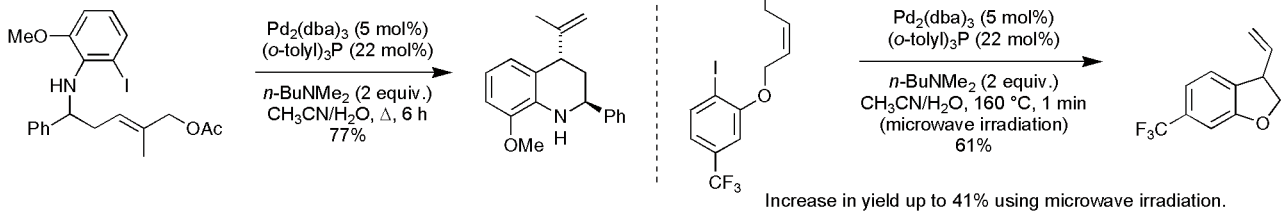
Comparison of fluorous and classical protocols is reported. 21 examples (yields 54-100%).

Enantio-controlled synthesis of α-methyl amino acids. **Nucleophilic Substitution**
Smith, N. D.; Wohlrab, A. M.; Goodman, M. *Org. Lett.* **2005**, *7*, 255.



13 examples (yields 0-98%).

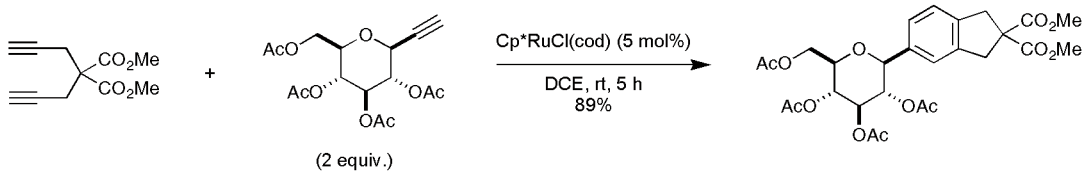
Thermal and microwave assisted Pd-catalyzed intramolecular coupling between aryl iodides and allyl moieties. **Annulation**
Lautens, M.; Tayama, E.; Herse, C. *J. Am. Chem. Soc.* **2005**, *127*, 72.



8 examples (yields 73-88%).

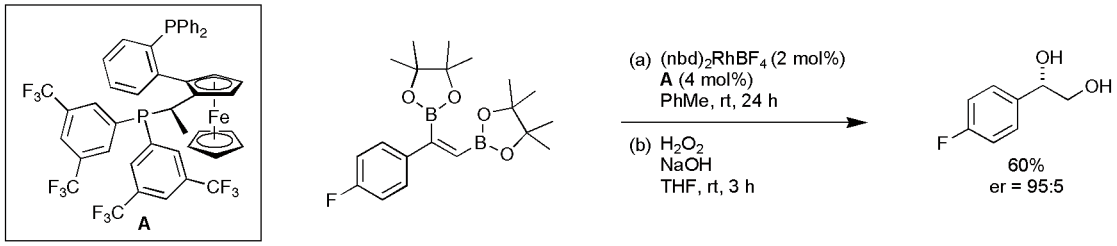
Increase in yield up to 41% using microwave irradiation.
9 examples (yields 56-74%).

C-Arylglycosides *via* Ru(II)-catalyzed [2+2+2]-cyclocaddition. **[2+2+2]-Cycloaddition**
Yamamoto, Y.; Saigoku, T.; Ohgai, T.; Nishiyama, H.; Itoh, K. *Chem. Commun*. **2004**, 2702.



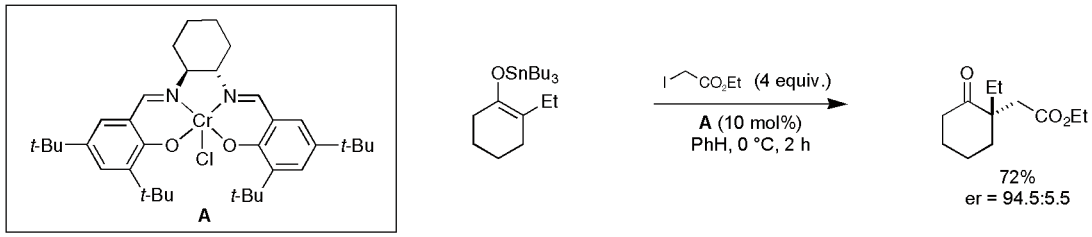
Applicable to 1,6 and 1,7 diynes. 11 examples (yields 46-93%).

Enantioselective hydrogenation of vinyl bis(boronates). **Enantioselective Hydrogenation**
Morgan, J. B.; Morken, J. P. *J. Am. Chem. Soc.* **2004**, *126*, 15338.



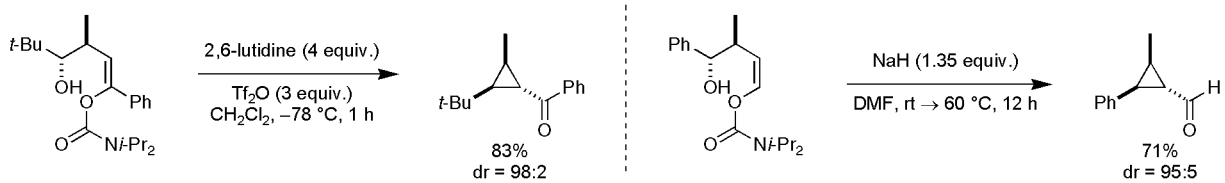
6 examples (yields 60-92%, %ee 77-93%).

Enantioselective alkylation of tributyltin enolates. **Enantioselective α-Alkylation**
Doyle, A. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2005**, *127*, 62.



9 examples (yields 43-91%, %ee 85-96%).

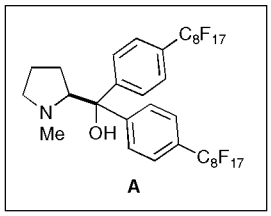
Synthesis of stereohomogeneous cyclopropanecarbaldehydes and cyclopropyl ketones. **Cyclopropanation**
Kalkofen, R.; Brandau, S.; Wibbeling, B.; Hoppe, D. *Angew. Chem. Int. Ed.* **2004**, *43*, 6667.

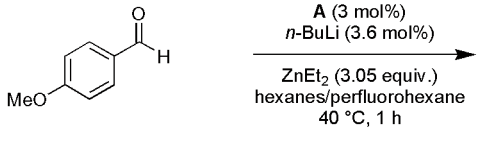


9 examples (yields 39->99%, %de 76-96%).

13 examples (yields 58-98%, %de 90-96%).

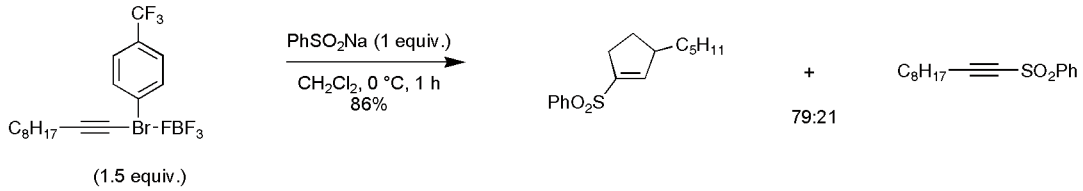
Asymmetric diethyl and diphenylzinc additions to aldehydes. **Enantioselective 1,2-Addition**
Park, J. K.; Lee, H. G.; Bolm, C.; Kim, B. M. *Chem. Eur. J.* **2005**, *11*, 945.





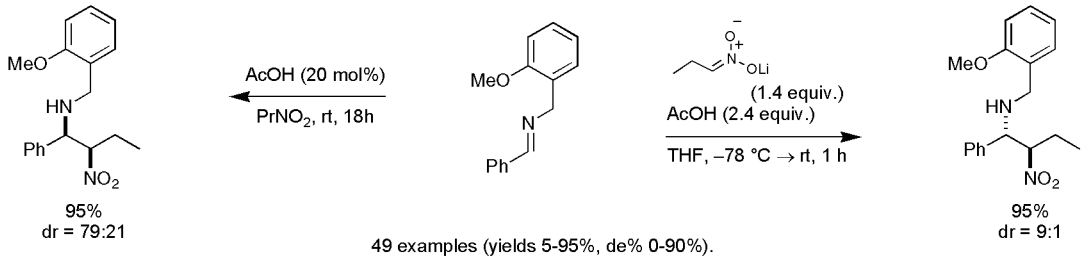
Addition of diphenyl zinc also reported. 4 examples (yields 80-90%, %ee 78-90%).

Tandem Michael addition-carbene insertion reaction of 1-alkynyl(aryl)(tetrafluoroborato)-λ^3-bromanes. **Annulation**
Ochiai, M.; Tada, N.; Nishi, Y.; Murai, K. *Chem. Commun.* **2004**, 2894.



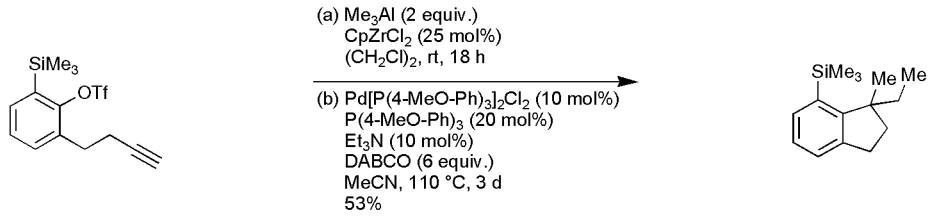
6 examples (yields 84-95%, pentene:alkyne 67:33-96:4).

Nitro-Mannich reaction for the stereoselective synthesis of 1,2-diamines. **Nitro-Mannich**
Anderson, J. C.; Blake, A. J.; Howell, G. P.; Wilson, C. *J. Org. Chem.* **2005**, *70*, 549.



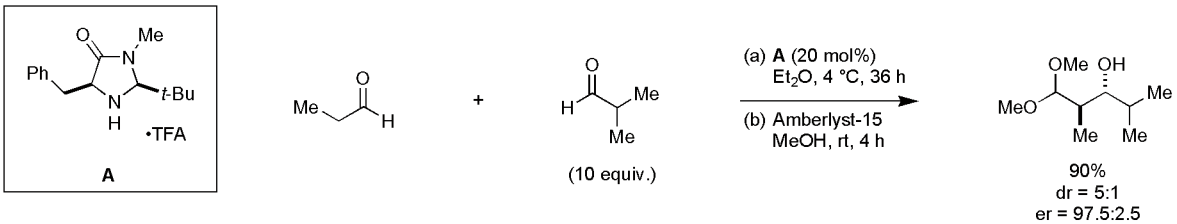
49 examples (yields 5-95%, de% 0-90%).

Pd-Catalyzed C-C bond forming 1,2-ligand migration of organoalanes. **C-C Bond Formation**
Fillion, E.; Carson, R. J.; Trépanier, V. E.; Goll. J. M.; Remorova, A. A. *J. Am. Chem. Soc.* **2004**, *126*, 15354.



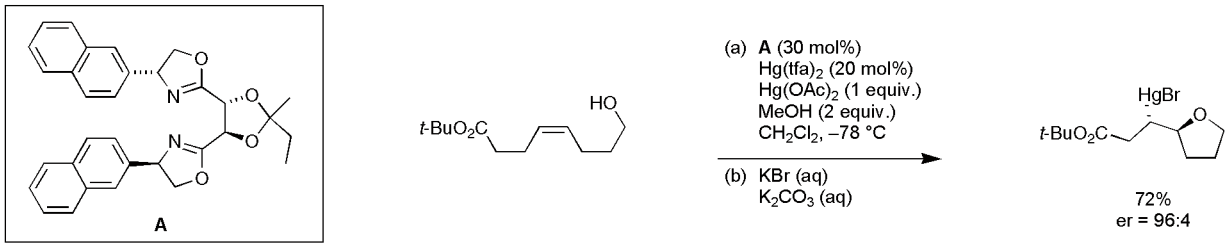
10 examples (yields 6-67%).

Iminium geometry control in enamine catalysis: a new catalyst for aldehyde-aldehyde couplings. **Asymmetric Aldol**
Mangion, I. K.; Northrup, A. B.; MacMillan, D. W. C. *Angew. Chem. Int. Ed.* **2004**, *43*, 6722.



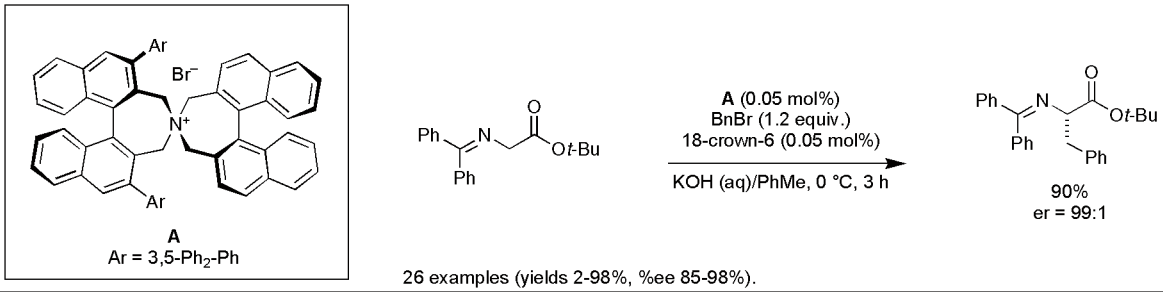
10 examples (yields 58-90%, %de 60-83%, %ee 90-97%).

Catalytic asymmetric mercuriocyclization of γ-hydroxy-*cis*-alkenes. **Annulation**
Kang, S. H.; Kim, M.; Kang, S. Y. *Angew. Chem. Int. Ed.* **2004**, *43*, 6177.



18 examples (yields 42-93%, %ee 22-95%).

Rate enhancement of asymmetric phase-transfer-catalyzed alkylations. **Enantioselective Alkylation**
Shirakawa, S.; Yamamoto, K.; Kitamura, M.; Ooi, T.; Maruoka, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 625.

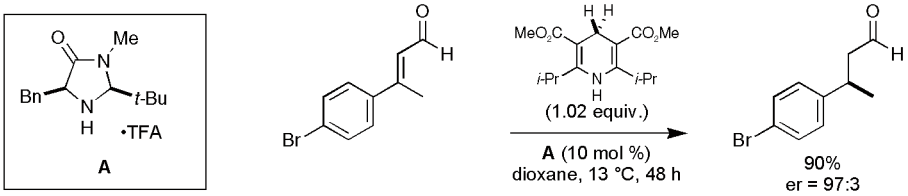


26 examples (yields 2-98%, %ee 85-98%).

Hydrocarbon oxidation verses C-C bond forming approaches for efficient syntheses of oxygenated molecules. **Oxidation**
Fraunhoffer, K. J.; Bachovchin, D. A.; White, M. C. *Org. Lett.* **2005**, *7*, 223.

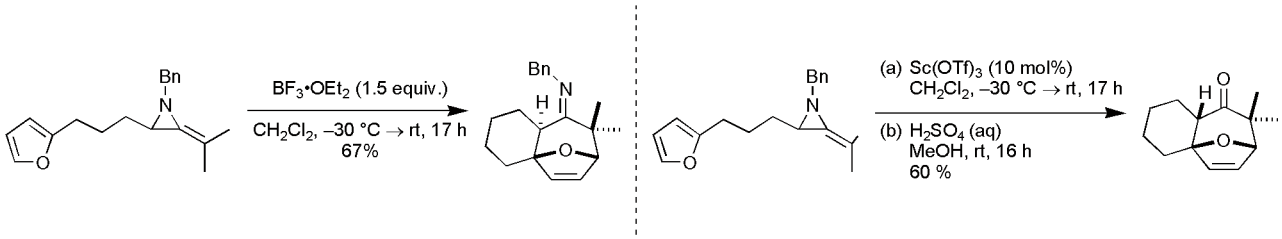
BQ = Benzoquinone. 6 examples (yields 58-91%).

Metal-free, organocatalytic asymmetric transfer hydrogenation of α,β-unsaturated aldehydes. **Enantioselective 1,4-Addition**
Yang, J. W.; Hechavarria Fonseca, M. T.; Vignola. N.; List, B. *Angew. Chem. Int. Ed.* **2005**, *44*, 108.



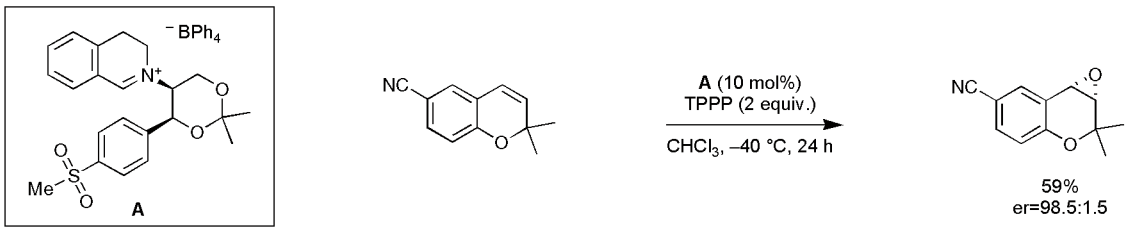
8 examples (yields 77-90%, %ee 90-96%).

Lewis acid catalyzed intramolecular [4+3]-cycloaddition. **[4+3]-Cycloaddition**
Prié, G., Prévost, N., Twin, H.; Fernandes, A.; Hayes, J. F.; Shipman, M. *Angew. Chem. Int. Ed.* **2004**, *43*, 6517.



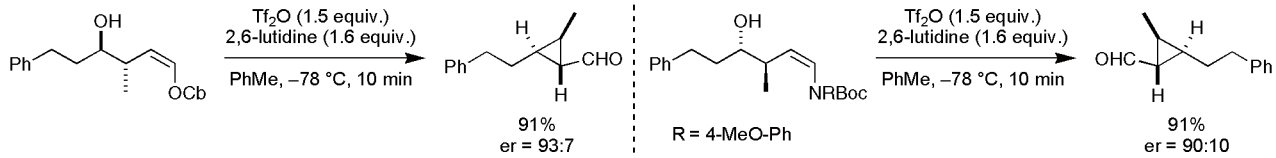
10 examples (yields 45-72%, %de 2-99%).

Asymmetric epoxidation of *cis*-alkenes mediated by iminium salts: highly enantioselective synthesis of Levcromakalim. **Epoxidation**
Page, P. C. B.; Buckley, B. R.; Heaney, H.; Blacker, A. J. *Org. Lett.* **2005**, *7*, 375.



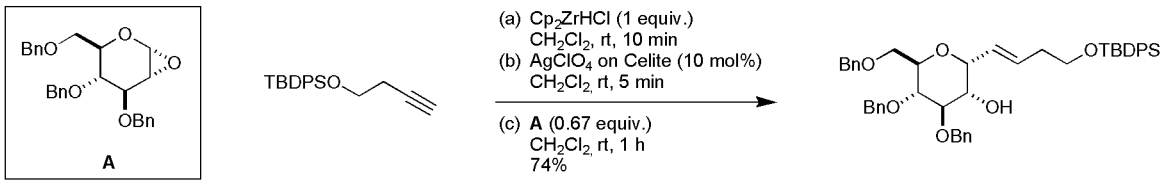
TPPP = Tetraphenyl phosphonium monoperoxysulfate. 6 examples (yields 59-89%, %ee 61-97%).

Enantioselective synthesis of cyclopropanes by aldehyde homologation. **Cyclopropanation**
Risatti, C. A.; Taylor, R. E. *Angew. Chem. Int. Ed.* **2004**, *43*, 6671.



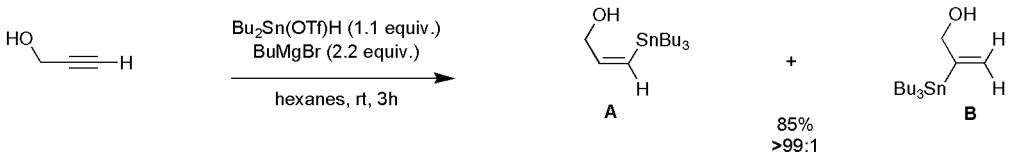
5 examples (yields 73-96%, %ee 66-86%). 5 examples (yields 70-96%, %ee 80-88%).

Ag(I)-catalyzed addition of zirconocenes to glycal epoxides. **Hydrozirconation/Addition**
Wipf, P.; Pierce, J. G.; Zhuang, N. *Org. Lett.* **2005**, *7*, 483.



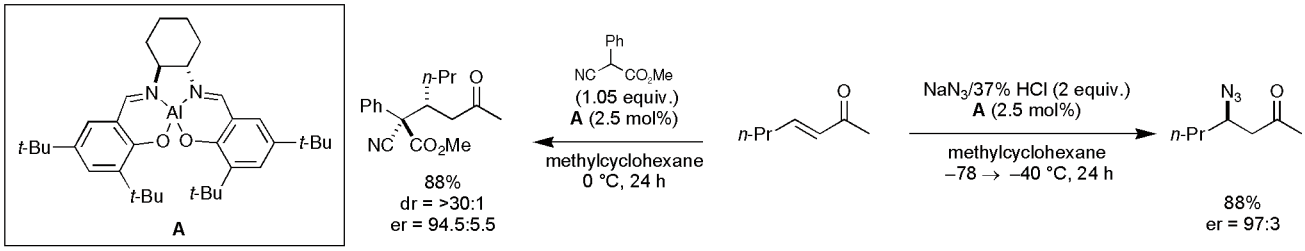
9 examples (yields 0-76%).

Regio- and stereoselective hydrostannylation of alkynols. **Hydrostannylation**
Miura, K.; Wang, D.; Matsumoto, Y.; Hosomi, A. *Org. Lett.* **2005**, *7*, 503.



16 examples (yields 64-91%, A:B 100:0-59:41).

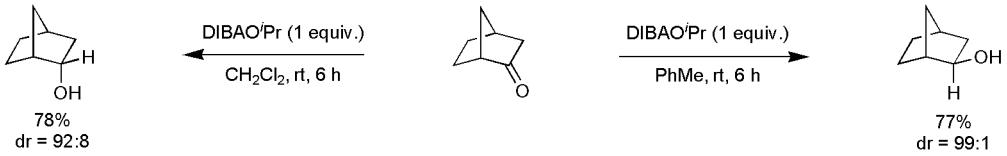
Highly enantioselective conjugate additions to α,β-unsaturated ketones catalyzed by a (Salen)Al complex. **Enantioselective 1,4-Addition**
Taylor, M. S.; Zalatan, D. N.; Lerchner, A. M.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2005**,*127*, 1313.



25 examples (yields 70-97%, %ee 75-96%)

Effect of solvent on the stereoselective reduction of cyclic ketones.
Bahia, P. S.; Jones, M. A.; Snaith, J. S. *J. Org. Chem.* **2004**, *69*, 9289.

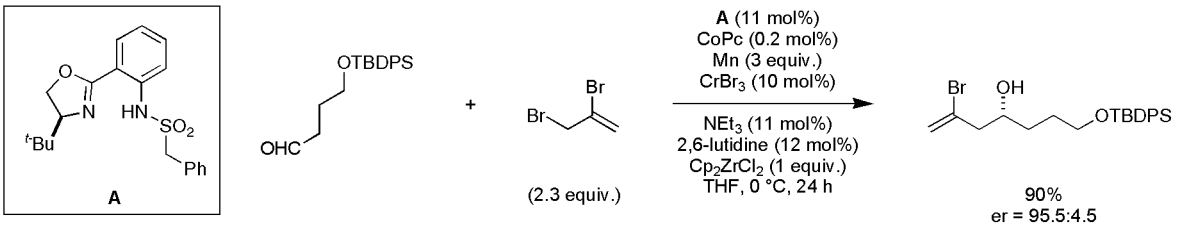
Reduction



29 examples (yield 50-97%, %de 0-98%).

New catalytic cycle for couplings of aldehydes with organochromium reagents.
Namba, K.; Kishi, Y. *Org. Lett.* **2004**, *6*, 5031.

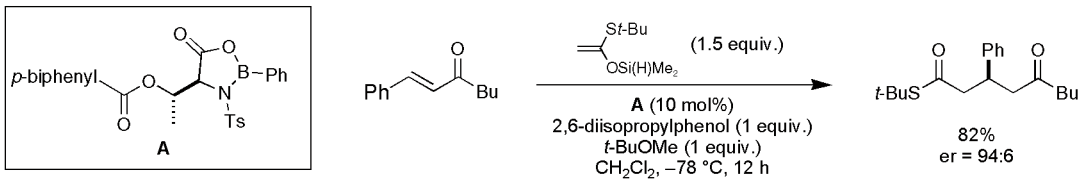
Enantioselective 1,2-Addition



15 examples (yields 79-98%, %ee 82-91%).

Asymmetric Michael reaction using dimethylsilyl ketene acetals.
Harada, T.; Adachi, S.; Wang, X. *Org. Lett.* **2004**, *6*, 4877.

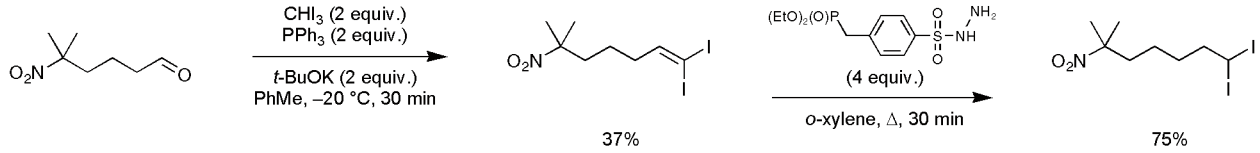
Enantioselective 1,4-Addition



13 examples (yields 54-85%, %ee 84-98%).

Synthesis of C-sp^3-centered geminal diiodides.
Cloarec, J. M.; Charette, A. B. *Org. Lett.* **2004**, *6*, 4731.

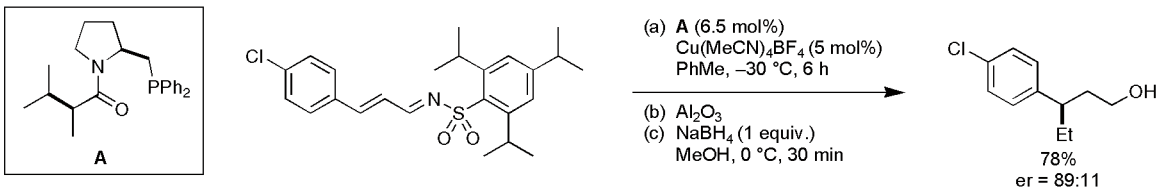
Reduction



20 examples (yields 61-91% for second step).

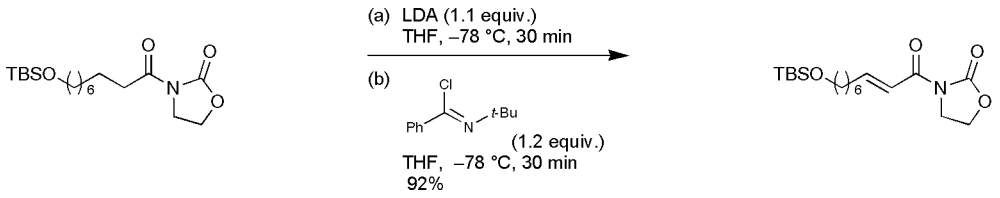
Catalytic asymmetric conjugate addition of dialkylzinc reagents to phenylsulfonylaldimines.
Soeta, T.; Kuriyama, M.; Tomioka, K. *J. Org. Chem.* **2005**, *70*, 297.

Enantioselective 1,4-Addition



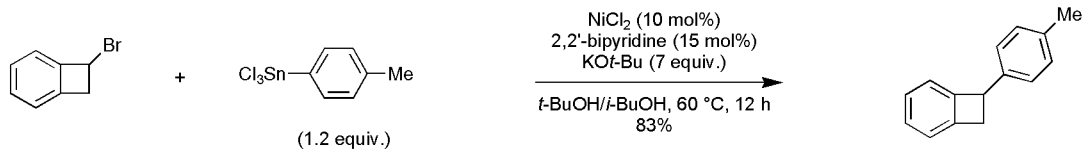
11 examples (yields 72-85%, %ee 67-91%).

One-pot dehydrogenation of carboxylic acid derivatives to α,β-unsaturated carbonyl compounds under mild conditions. **Dehydrogenation**
Matsuo, J-I.; Aizawa, Y. *Tetrahedron Lett.* **2005**, *46*, 407.



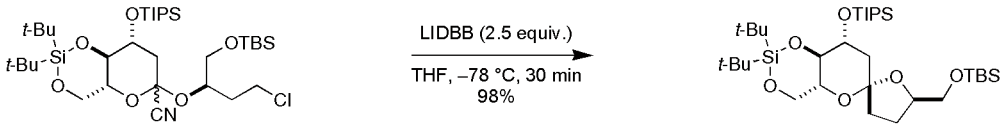
22 examples (yields 15-92%).

Stille cross-coupling of unactivated secondary alkyl halides using monoorganotin reagents. **sp^3-sp^2 Coupling**
Powell, D. A.; Maki, T.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 510.



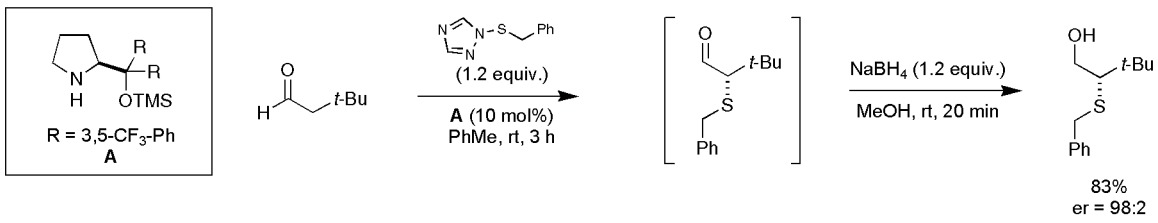
14 examples (yields 47-83%).

Rational synthesis of contra-thermodynamic spiroacetals by reductive cyclizations. **Reductive Cyclization**
Takaota, L. R.; Buckmelter, A. J.; LaCruz, T. E.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **2005**, *127*, 528.



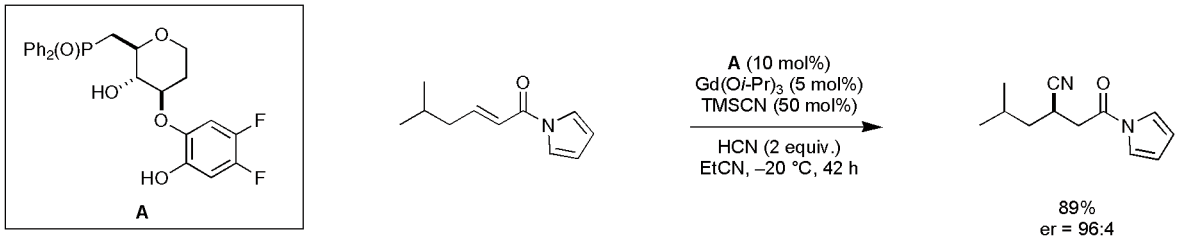
6 examples (yields 63-98%).

Enantioselective organocatalyzed α-sulfenylation of aldehydes. **Enantioselective C-S Bond Formation**
Marigo, M.; Wabnitz, T. C.; Fielenbach, D.; Jørgensen, K. A. *Angew. Chem. Int. Ed.* **2005**, *44*, 794.



7 examples (yields 60-94%, %ee 61-98%).

Catalytic enantioselective conjugate addition of cyanide to α,β-unsaturated *N*-acylpyrroles. **Enantioselective 1,4-Addition**
Mita, T.; Sasaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2005**, *127*, 514.



9 examples (yields 78-99%, %ee 89-98%).