

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:

John Cooksey, Victoria Coombes, Axel Jansen, Stephen McAteer, Bernhard Otto, Joanne Peach, and Josephine Yuen, Department of Chemistry, Leeds University, Leeds, LS2 9JT, UK.

Georg Thieme Verlag does not accept responsibility for the accuracy, content, or selection of the data.

SYNTHESIS 2004, No. 12, pp 2066–2073

Advanced online publication: 10.08.2004

Art ID: X01204SS

© Georg Thieme Verlag Stuttgart · New York

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

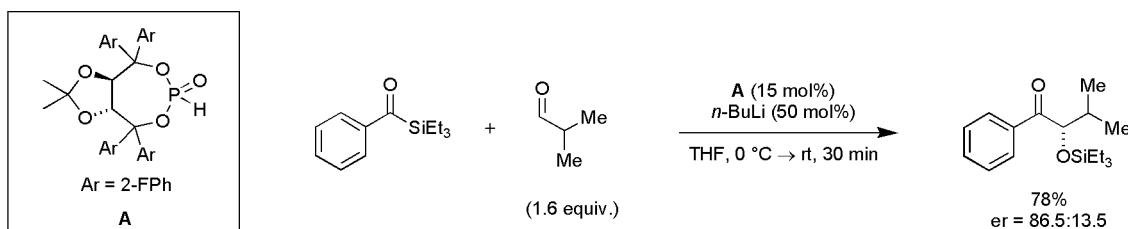
Tetrahedron

Tetrahedron Asymmetry

Tetrahedron Letters

Metallophosphites as umpolung catalysts in an enantioselective cross silyl benzoin reaction.
Linghu, X.; Potnick, J. R.; Johnson, J. S. *J. Am. Chem. Soc.* **2004**, 126, 3070.

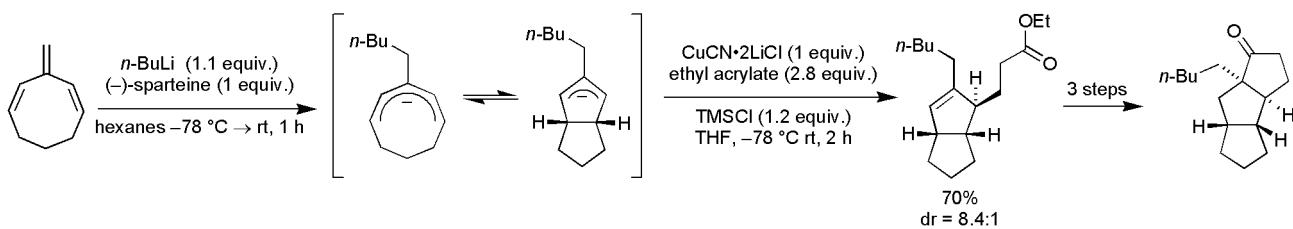
Enantioselective Benzoin



14 examples (yields 65–82%, %ee 41–91%). Catalyst optimization studies are also reported.

Synthesis of functionalized *cis*-bicyclo[3.3.0]octenes via a carbolithiation/electrocyclization/alkylation cascade.
Williams, D. R.; Reeves, J. T. *J. Am. Chem. Soc.* **2004**, 126, 3434.

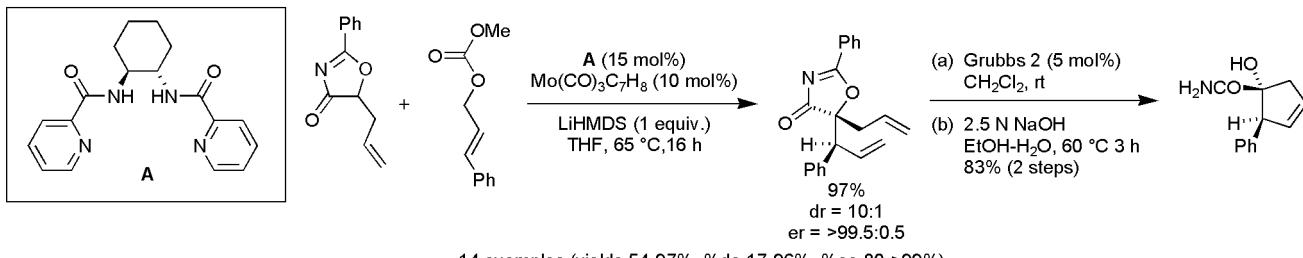
Electrocyclization



12 examples (yields 46–77%, %de 0–>90%).

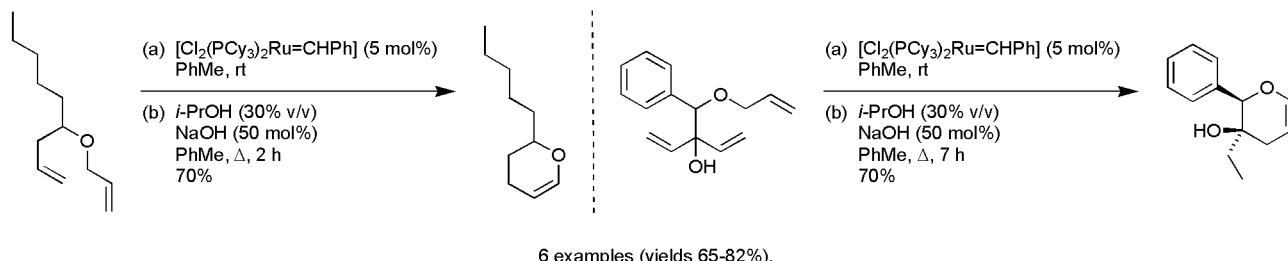
Asymmetric synthesis of tertiary α -hydroxy acids from oxalactims.
Trost, B. M.; Dogra, K.; Franzini, M. *J. Am. Chem. Soc.* **2004**, 126, 1944.

Asymmetric Allylic Alkylation



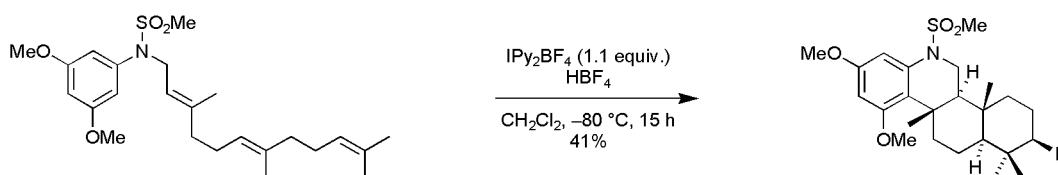
In situ conversion of a Ru metathesis catalyst to an isomerization catalyst.
Schmidt, B. *Chem. Commun.*, **2004**, 742.

Metathesis/Isomerization



Synthesis of chromans and tetrahydroquinolines *via* a metal-free intramolecular arylation of alkenes.
Barluenga, J.; Trincado, M.; Rubio, E.; Gonzalez, J. M. *J. Am. Chem. Soc.* **2004**, 126, 3416.

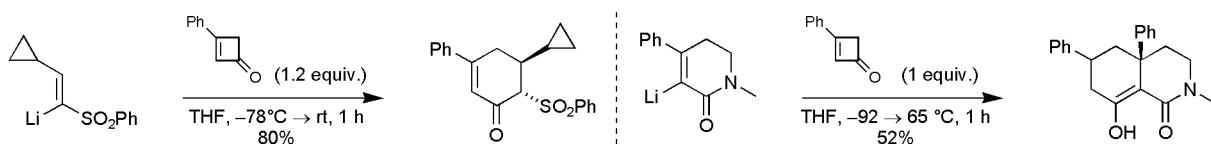
Annulation



15 examples (yields 41–95%).

Synthesis of functionalized cyclohexenones *via* a ring expansion-electrocyclization cascade.
Magomedov, N. A.; Ruggiero, P. L.; Tang, Y. *J. Am. Chem. Soc.* **2004**, 126, 1624.

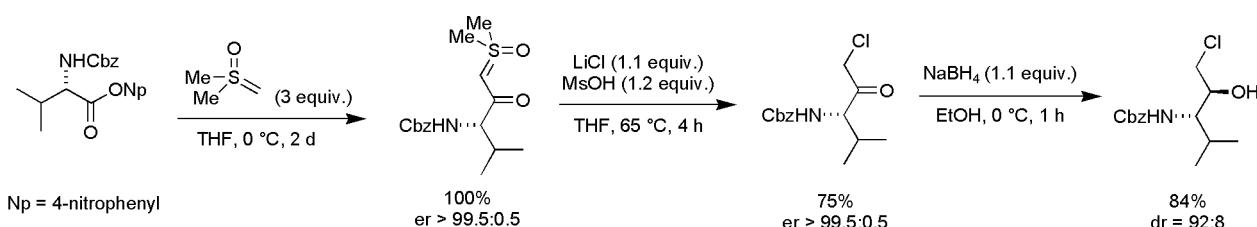
Electrocyclization



10 examples (yields 45–86%).

Chain extension of esters to α-chloroketones avoiding the use of diazomethane.
Wang, D.; Schwinden, M. D.; Radesca, L.; Patel, B.; Kronenthal, D.; Huang, M.-H.; Nugent, W. A. *J. Org. Chem.* **2004**, 69, 1629.

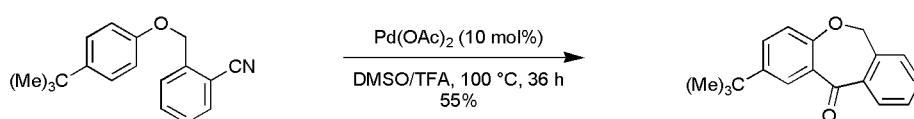
α-Chlorination



Sulfur ylide formation: 11 examples (yields 25–100%, %ee <2->99%); α-Chloroketone formation: 5 examples 70–97%, %ee >99%.

Synthesis of aryl ketones using Pd-catalyzed activation of arenes and carbopalladation of nitriles.
Zhou, C.; Larock, R. C. *J. Am. Chem. Soc.* **2004**, 126, 2302.

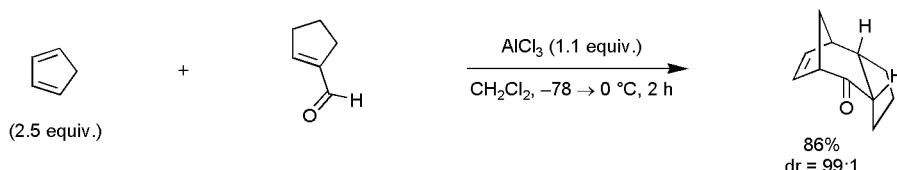
Carbopalladation



10 examples including inter- and intramolecular reactions (yields 55–90%).

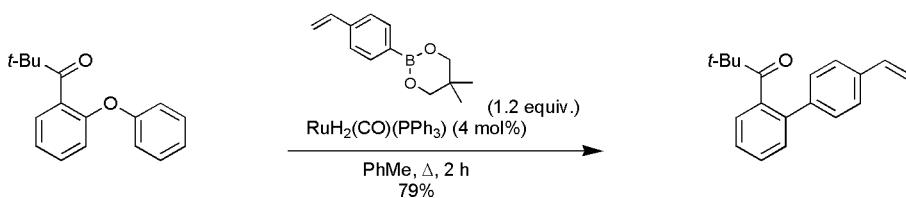
Lewis acid induced tandem Diels-Alder reaction/ring expansion.
Davies, H. M. L.; Dai, X. *J. Am. Chem. Soc.* **2004**, 126, 2692.

[4+3] Cycloaddition



7 examples including one enantioselective reaction using a chiral Lewis acid for the Diels-Alder step (yields 21-90%, %de 37-98%, %ee 85%).

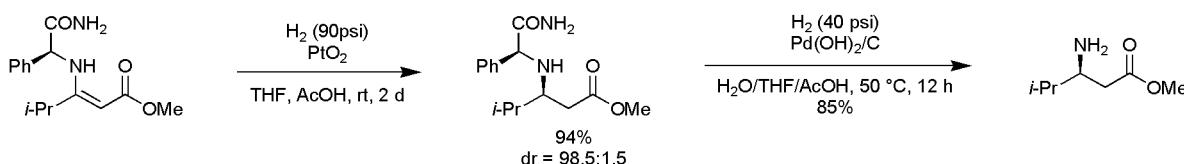
Ruthenium catalyzed coupling of aromatic ethers with organoboron compounds.
Kakiuchi, F.; Usui, M.; Ueno, S.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* **2004**, 126, 2706.

 $\text{sp}^2\text{-sp}^2$ Coupling

The ortho-carbonyl group is necessary for co-ordination to the ruthenium. 20 examples (yields 50-96%).

Diastereoselective hydrogenation of enamines for the synthesis of chiral β -amino acid derivatives.
Ikemoto, N.; Tellers, D. M.; Dreher, S. D.; Liu, J.; Huang, A.; Rivera, N. R.; Njolito, E.; Hsiao, Y.; McWilliams, J. C.; Williams, J. M.; Armstrong III, J. D.; Sun, Y.; Mathre, D. J.; Grabowski, E. J. J. Tillyer, R. D. *J. Am. Chem. Soc.* **2004**, 126, 3048.

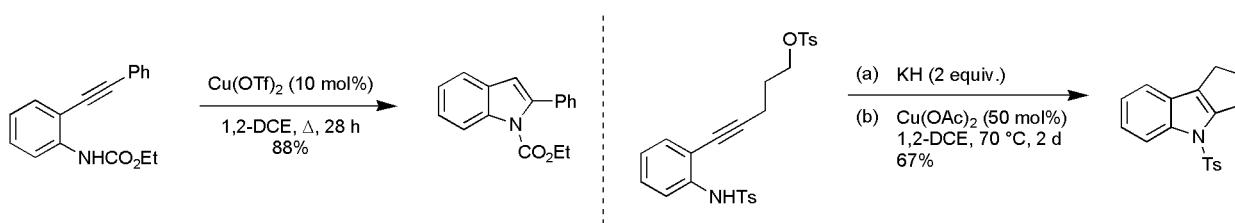
Diastereoselective Hydrogenation



16 examples (yields 12-100%, %de 70-99%).

Copper-catalyzed indole synthesis using 2-ethynylaniline.
Hiroya, K.; Itoh, S.; Sakamoto, T. *J. Org. Chem.* **2004**, 69, 1126.

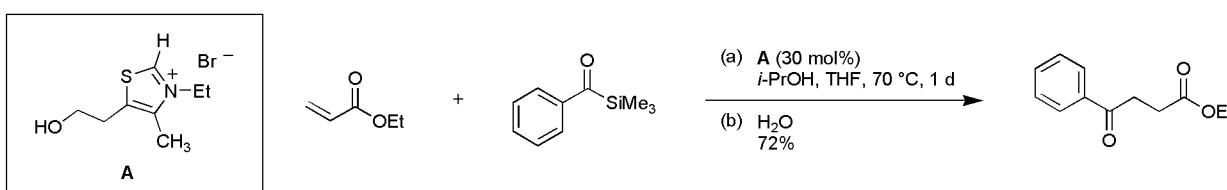
Annulation



Reaction can also be performed on the free amine. 76 examples (yields 0-100%). Applied to the formal synthesis of Hippadine.

Thiazolium-catalyzed sila-Stetter reaction: conjugate addition of acylsilanes to unsaturated esters and ketones.
Mattson, A. E.; Bharadwaj, A. R.; Scheidt, K. A. *J. Am. Chem. Soc.* **2004**, 126, 2314.

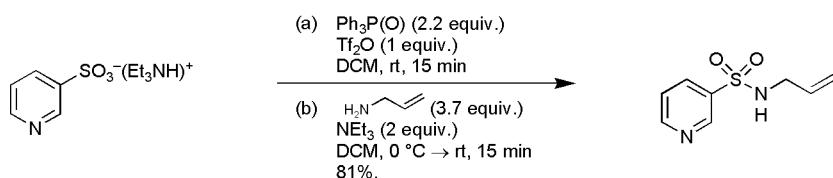
1,4-Addition



31 examples (yields 0-84%).

Direct synthesis of sulfonamides and activated sulfonate esters from sulfonic acids.
Caddick, S.; Wilden, J. D.; Judd, D. B. *J. Am. Chem. Soc.* **2004**, *126*, 1024.

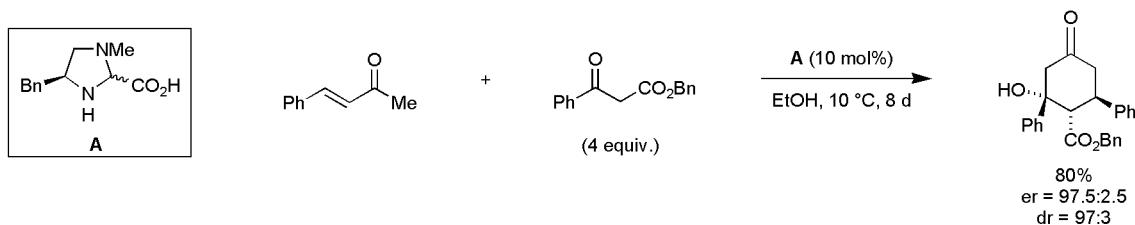
Nucleophilic Substitution



22 examples (yields 48–98%) and investigation towards a solid-supported phosphine oxide.

Highly stereoselective organocatalytic domino Michael-aldol reaction.
Halland, N.; Aburel, P. S.; Jørgensen, K. A. *Angew. Chem. Int. Ed.* **2004**, *43*, 1272.

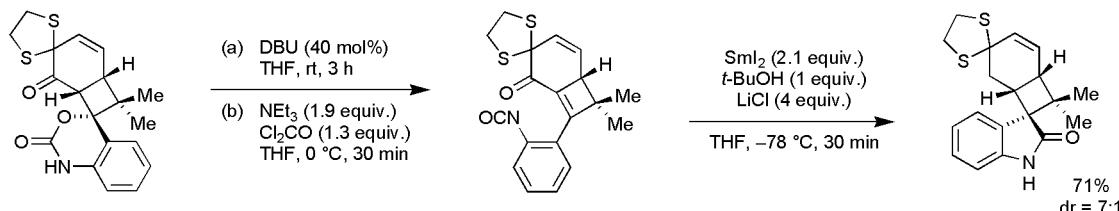
Asymmetric Robinson Annulation



27 examples (yields 5–89%, %ee 70–99%, %de 94%).

A mild and efficient synthesis of oxindoles: Progress towards the synthesis of Welwitindolinone A isonitrile.
Ready, J. M.; Reisman, S. E.; Hirata, M.; Weiss, M. M.; Tamaki, K.; Ovaska, T. V.; Wood, J. L. *Angew. Chem. Int. Ed.* **2004**, *43*, 1270.

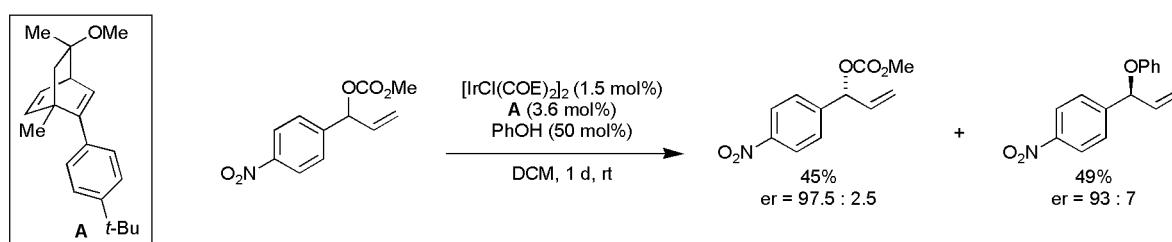
Reductive Coupling



Application of a novel SmI_2 -mediated synthesis of spiro-oxindoles: 6 examples (yields 5–88%).

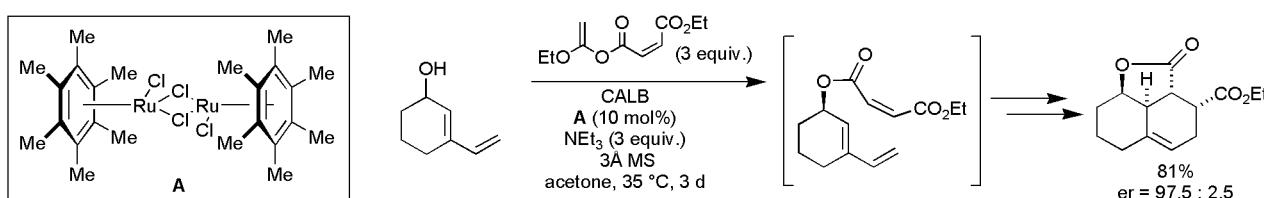
Catalytic, kinetic resolution of allyl carbonates using [2.2.2]-bicyclooctadienes as new chiral ligands for Ir(I).
Fischer, C.; Defieber, C.; Suzuki, T.; Carreira, E. M. *J. Am. Chem. Soc.* **2004**, *126*, 1628.

Kinetic Resolution



A is synthesised from (-)-carvone (31%, 4 steps). COE = cyclooctene. 19 examples (yields 28–46%, %ee 80–97%).

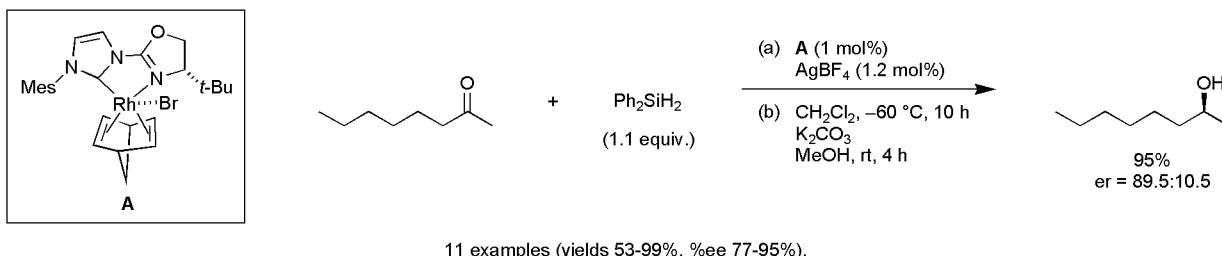
Synthesis of optically active decalins via a domino dynamic kinetic resolution / intramolecular Diels-Alder reaction.
Akai, S.; Tanimoto, K.; Kita, Y. *Angew. Chem. Int. Ed.* **2004**, *43*, 1407.

Esterification/
Diels-Alder

8 examples (yields 69–86%, %ee 82–97%). CALB = Candida antarctica lipase.

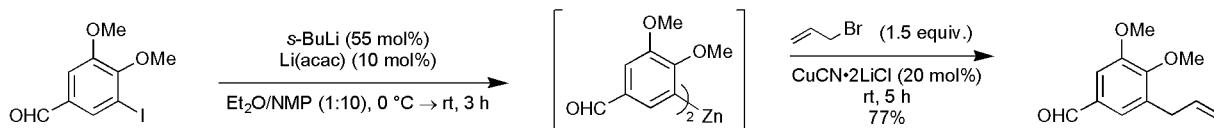
Efficient phosphane free catalysts for the asymmetric hydrosilylation of dialkylketones.
Gade, L. H.; Cesar, V.; Bellemain-Laponnaz, S. *Angew. Chem. Int. Ed.* **2004**, *43*, 1014.

Enantioselective Hydrosilylation



Preparation of highly functionalized diaryl zinc compounds using nucleophilic catalysis.
Kneisel, F. F.; Dochnahal, M.; Knochel, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 1017.

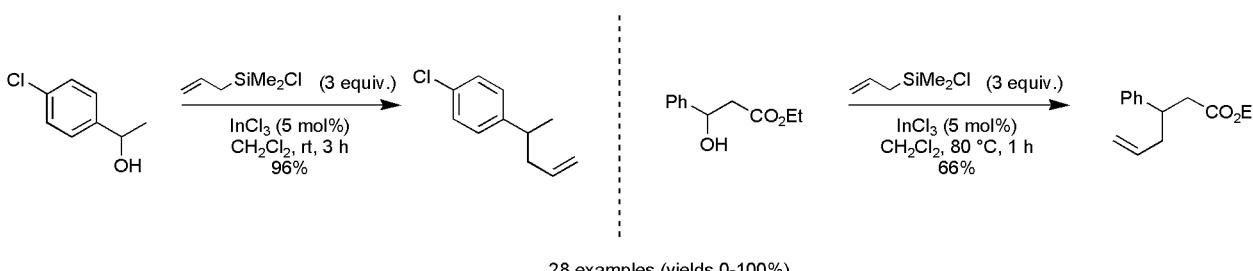
Metallation



17 examples (yields 52-87%). NMP = N-methyl-2-pyrrolidinone.

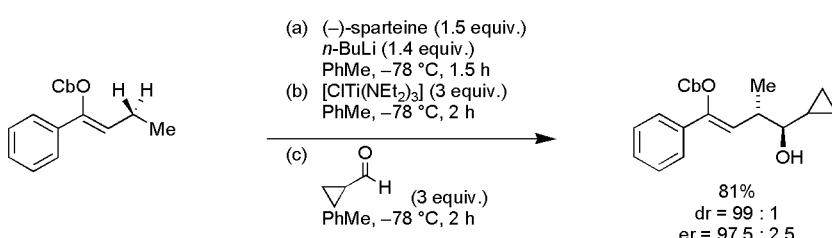
Indium trichloride catalyzed direct substitution of the hydroxy group in alcohols with silyl nucleophiles.
Yasuda, M.; Saito, T.; Ueba, M.; Baba, A. *Angew. Chem. Int. Ed.* **2004**, *43*, 1414.

Nucleophilic Substitution



Synthesis of ketone homoenolate reagents *via* γ -deprotonation of 1-alkenyl carbamates.
Seppi, M.; Kalkofen, R.; Reupohl, J.; Fröhlich, R.; Hoppe, D. *Angew. Chem. Int. Ed.* **2004**, *43*, 1423.

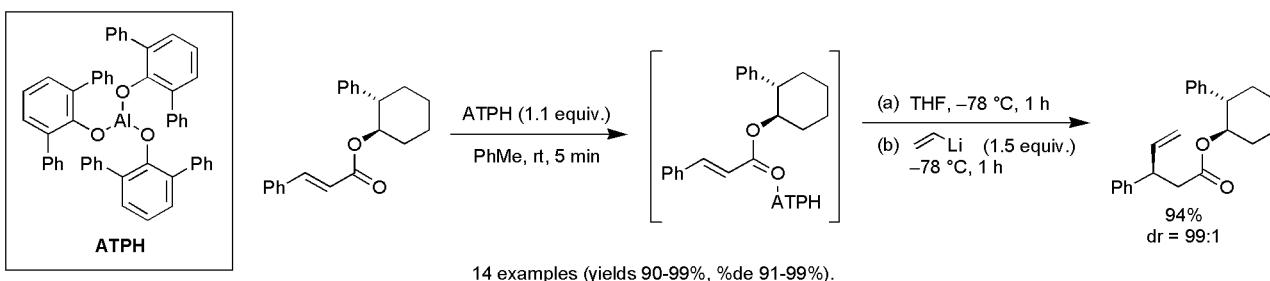
Enantioselective Deprotonation/Aldol



Enantioselective deprotonation: 18 examples (yields 50-97%, %ee 77-97%). Homoaldol: 9 examples (yields 49-82%, %ee 93-97%).

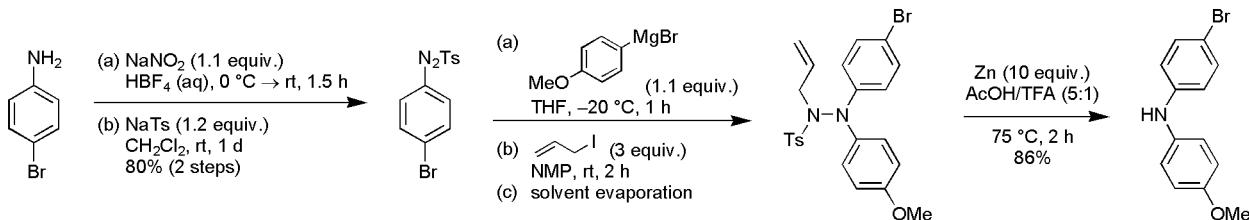
Chiral molecular recognition by aluminium tris(2,6-diphenylphenoxyde) in an asymmetric 1,4-addition.
Ito, H.; Nagahara, T.; Ishihara, K.; Saito, S.; Yamamoto, H. *Angew. Chem. Int. Ed.* **2004**, *43*, 994.

Diastereoselective 1,4-Addition



Amination via addition of polyfunctional arylmagnesium reagents to functionalised arylazo tosylates.
Sapountzis, I.; Knochel, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 897.

Amination

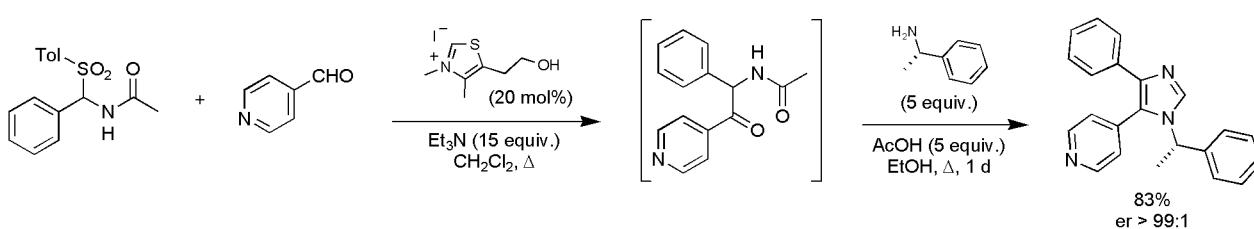


17 examples (yields 58–86%). NMP = *N*-methylpyrrolidinone.

Synthesis of substituted imidazoles via organocatalysis.

Frantz, D. E.; Morency, L.; Soheili, A.; Murry, J. A.; Grabowski, E. J. J.; Tillyer, R. D. *Org. Lett.* **2004**, *6*, 843.

Imidazole Synthesis

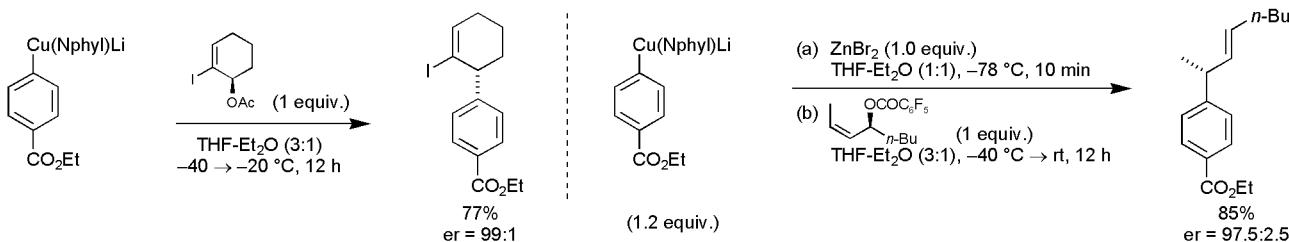


12 examples of di-, tri- and tetrasubstituted imidazoles (yields 22–83%).

Stereoselective $\text{S}_{\text{N}}2$ -substitutions using polyfunctional lithium arylcuprates.

Calaza, M. I.; Yang, X.; Soorukram, D.; Knochel, P. *Org. Lett.* **2004**, *6*, 529.

Nucleophilic Substitution



Nphenyl = $\text{PhMe}_2\text{CCH}_2$. 10 examples (yields 50–89%, %ee 89–98%).

Trifluoroacetyl-activated nitrogen-nitrogen bond cleavage of hydrazines by samarium(II) iodide.

Ding, H.; Friestad, G. K. *Org. Lett.* **2004**, *6*, 637.

N-N Bond Cleavage

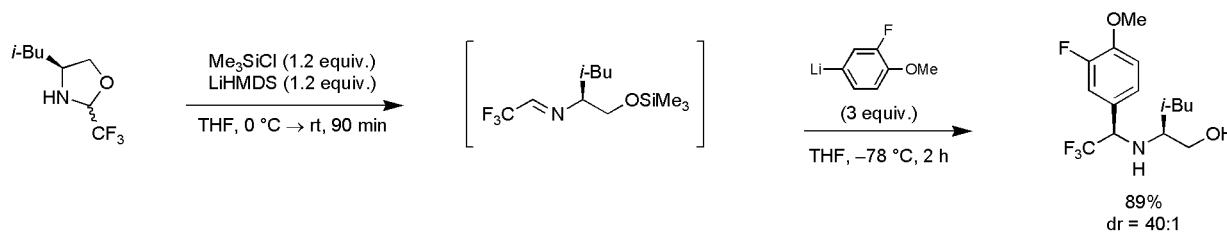


8 examples of N-N bond cleavage (yields 70–96%). No racemization observed.

Oxazolidine ring opening and isomerization to (*E*)-imines.

Gosselin, F.; Roy, A.; O'Shea, P. D.; Chen, C.; Volante, R. P. *Org. Lett.* **2004**, *6*, 641.

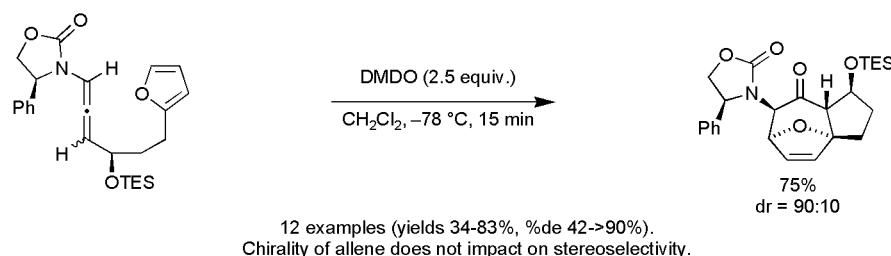
Ring Opening/Addition



20 examples (yields 64–97%, %de 94–>99%).

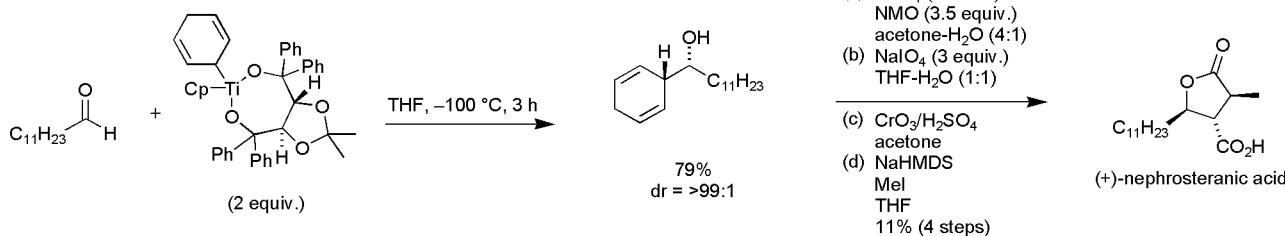
Tandem epoxidation/intramolecular [4+3] cycloaddition of γ -tethered allenamides.
Rameshkumar, C.; Hsung, R. P. *Angew. Chem. Int. Ed.* **2004**, *43*, 615.

Epoxidation/ [4+3] Cycloaddition



Desymmetrization of metallated cyclohexadienes.
Schleith, F.; Studer, A. *Angew. Chem. Int. Ed.* **2004**, *43*, 313.

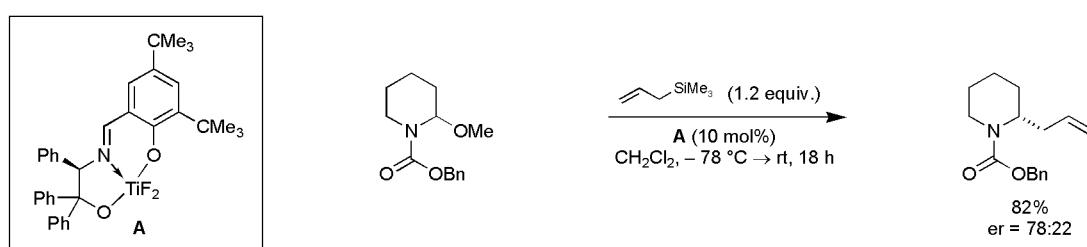
Asymmetric Allylation



15 examples (yields 40-96%, %de 96-98%, %ee 80-98%).

Titanium (IV) catalyzed dynamic kinetic asymmetric allylation.
Braun, M.; Kotter, W. *Angew. Chem. Int. Ed.* **2004**, *43*, 514.

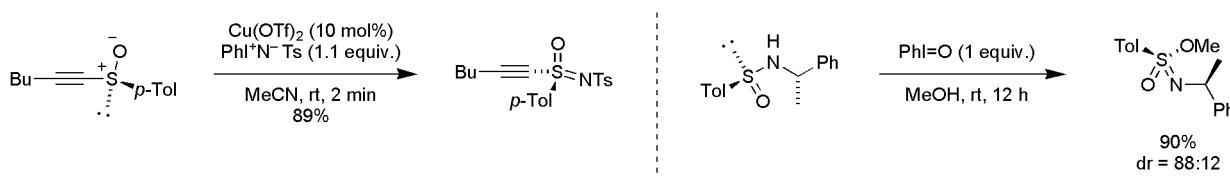
Asymmetric Allylation



7 examples (yields 62-96%, %ee 54-99%).

Iodine(III)-mediated preparation of nitrogen-containing sulfur derivatives.
Leca, D.; Song, K.; Amatore, M.; Fensterbank, L.; Lacote, E.; Malacia, M. *Chem. Eur. J.* **2004**, *10*, 906.

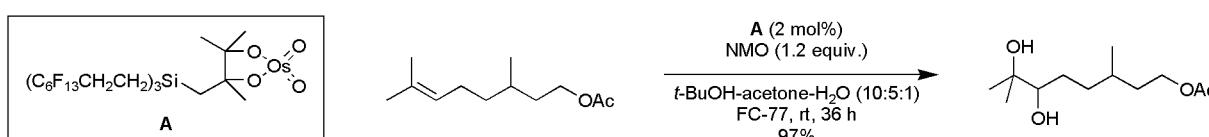
Oxidation



Sulfoximines: 21 examples (yields 0-96%); Sulfonimidates: 27 examples (yields 0-100%, %de 55-76%).
Oxidation of sulfinamides to sulfonamides is also reported: 7 examples (yields 78-84%).

Fluorous osmium tetroxide: a recoverable and reusable catalyst for dihydroxylation of olefins.
Huang, Y.; Meng, W.-D.; Qing, F.-L. *Tetrahedron Lett.* **2004**, *45*, 1965.

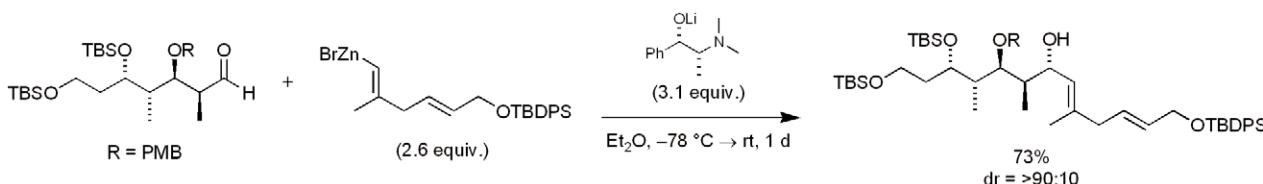
Dihydroxylation



FC-77 = perfluoroalkane primarily with eight carbons. 7 examples (yields 58-100%).
The recoverable catalyst can be used at least 5 times with excellent yields.

Diastereoselective addition of chiral vinylzinc reagents to α -chiral aldehydes.
Marshall, J. A.; Eidam, P. *Org. Lett.* **2004**, 6, 445.

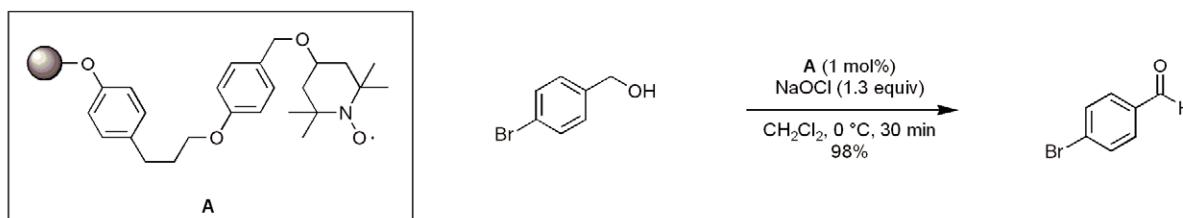
Diastereoselective 1,2-Addition



19 examples (yields 60-82%, %de 0->80%).

Poly(ethylene glycol)-supported TEMPO: a recoverable catalyst for the selective oxidation of alcohols.
Pozzi, G.; Cavazzini, M.; Quici, S.; Benaglia, M.; Dell'Anna, G. *Org. Lett.* **2004**, 6, 441.

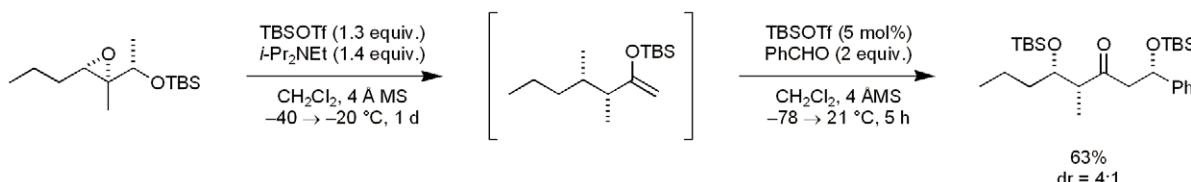
Oxidation



Preparation of the poly(ethylene glycol)-supported TEMPO and optimization studies is described.
10 examples (yields 78-98%).

A tandem non-aldol aldol/Mukaiyama-aldo reaction.
Jung, M. E.; van der Heuvel, A. *Org. Lett.* **2003**, 5, 4705.

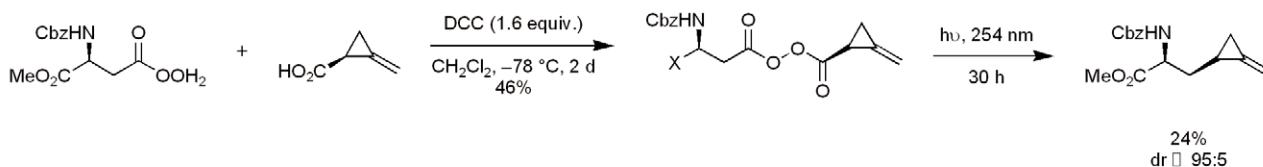
C-C Bond Formation



16 examples (yields 21-70%, %de 0-60%).

Synthesis of β -cyclopropylalanines by photolysis of diacyl peroxides.
Jain, R. P.; Vedera, J. C. *Org. Lett.* **2003**, 5, 4669.

Photolysis

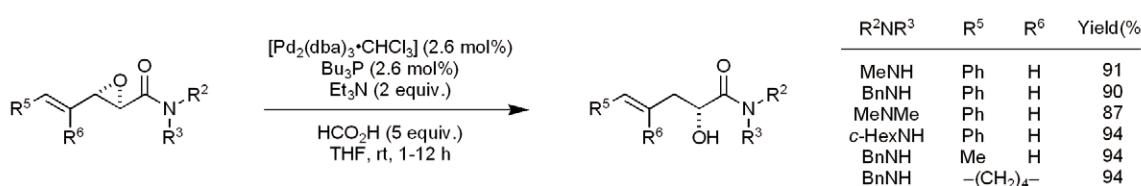


7 examples (yields 24-58%).

Studies towards the synthesis of hypoglycan A and belactosin A are described.

Regioselective epoxide-opening of α - β epoxyamides to give α and β hydroxy amides.
Kakei, H.; Nemoto, T.; Ohshima, T.; Shibasaki, M. *Angew. Chem. Int. Ed.* **2004**, 43, 317.

Nucleophilic Substitution

29 examples (yields 48-95%, %ee 33->99%). Application to the synthesis of (*R*)-fluoxetine.