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.

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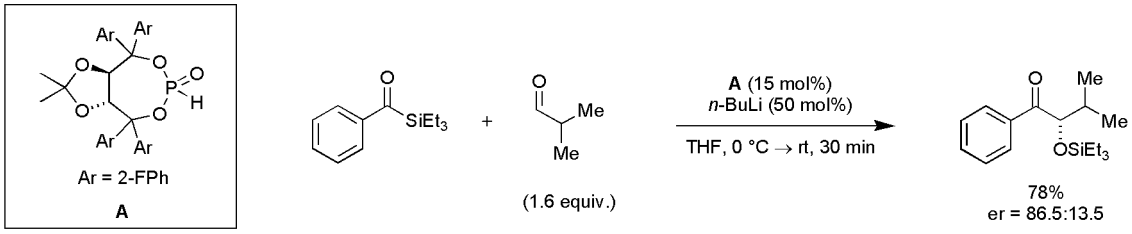
The journals regularly covered by the abstractors are:

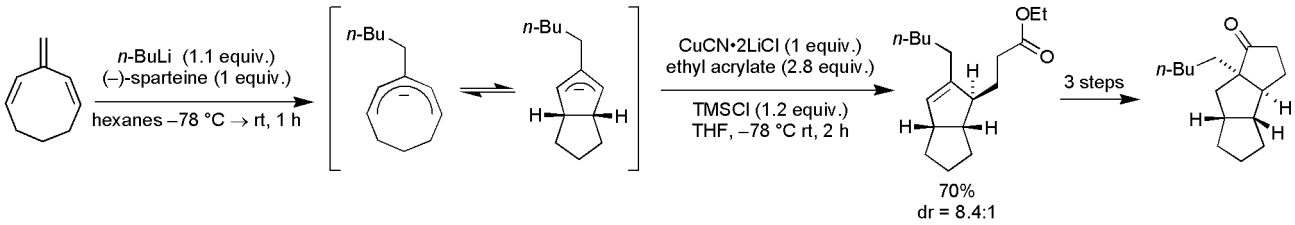
Angewandte Chemie International Edition
Bulletin of the Chemical Society of Japan
Chemical Communications
Chemistry A European Journal
Chemistry Letters
Collection Czechoslovak Chemical Communications
European Journal of Organic Chemistry
Helvetica Chimica Acta
Heterocycles
Journal of the American Chemical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

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



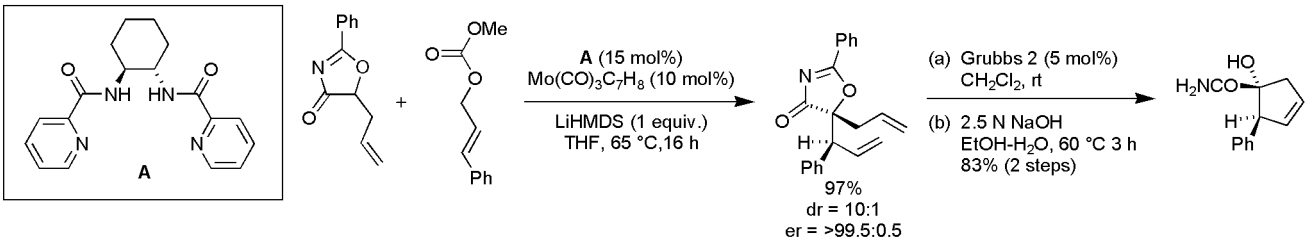
14 examples (yields 65-82%, %ee 41-91%). Catalyst optimization studies are also reported.

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



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

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



14 examples (yields 54-97%, %de 17-96% %ee 80->99%).

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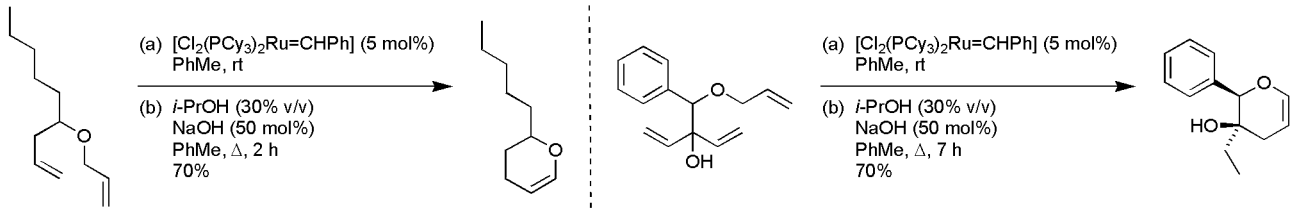
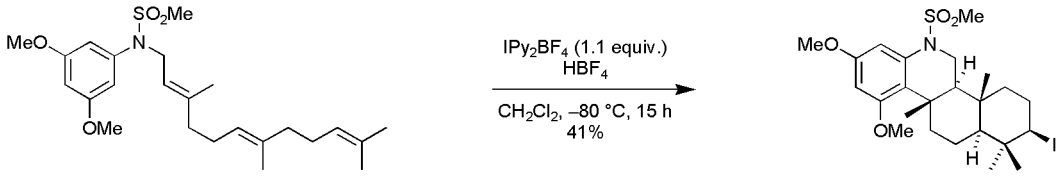
In situ conversion of a Ru metathesis catalyst to an isomerization catalyst. **Metathesis/Isomerization**
Schmidt, B. *Chem. Commun.*, **2004**, 742.



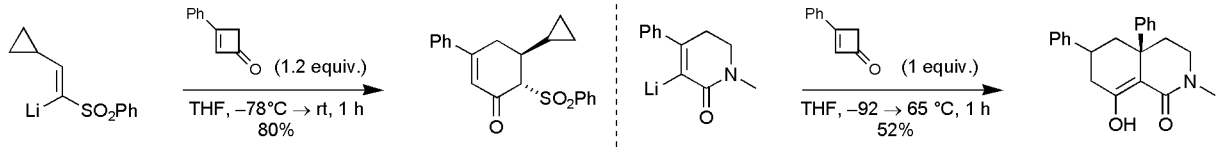
6 examples (yields 65-82%).

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



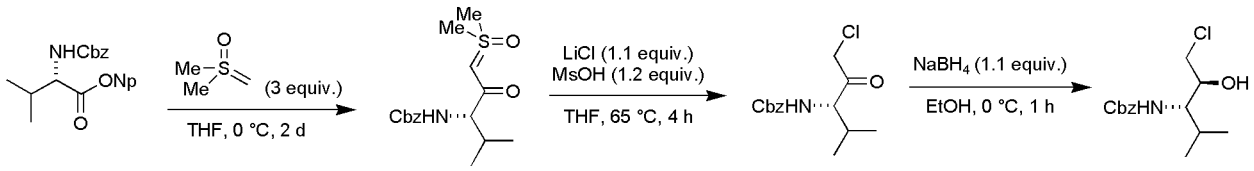
15 examples (yields 41-95%).

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



10 examples (yields 45-86%).

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



Np = 4-nitrophenyl

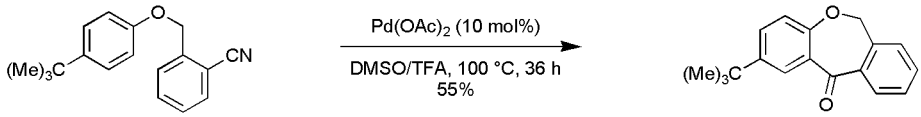
100%
er > 99.5:0.5

75%
er > 99.5:0.5

84%
dr = 92:8

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. **Carbopalladation**
Zhou, C.; Larock, R. C. *J. Am. Chem. Soc.* **2004**, *126*, 2302.



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

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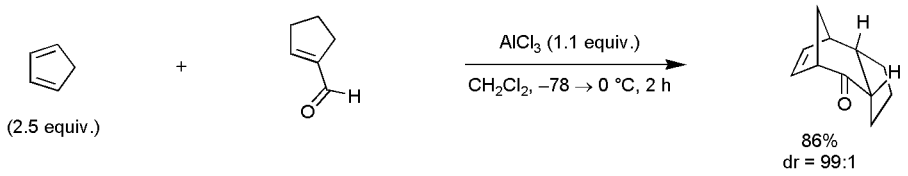
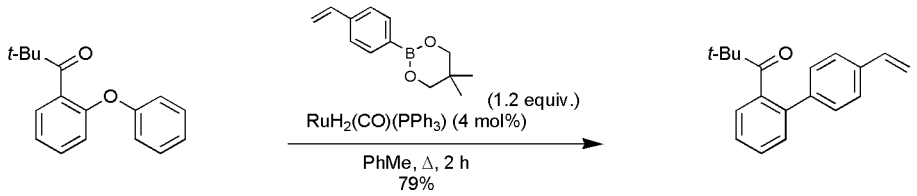
Lewis acid induced tandem Diels-Alder reaction/ring expansion. **[4+3] Cycloaddition**
Davies, H. M. L.; Dai, X. *J. Am. Chem. Soc.* **2004**, *126*, 2692.



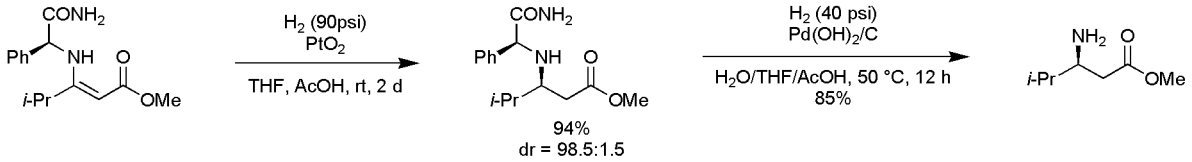
7 examples including one enantioselective reaction using a chiral Lewis acid for the Diels-Alder step (yields 21-90%, %de 37-98%, %ee 85%).

Ruthenium catalyzed coupling of aromatic ethers with organoboron compounds. **sp^2-sp^2 Coupling**
Kakiuchi, F.; Usui, M.; Ueno, S.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* **2004**, *126*, 2706.



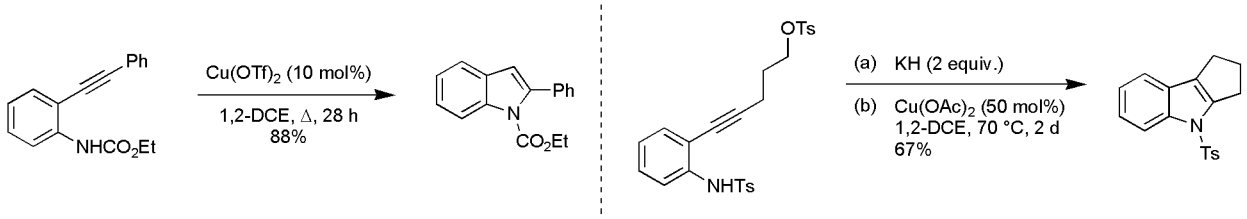
The ortho-carbonyl group is necessary for co-ordination to the ruthenium. 20 examples (yields 50-96%).

Diastereoselective hydrogenation of enamines for the synthesis of chiral β-amino acid derivatives. **Diastereoselective Hydrogenation**
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.



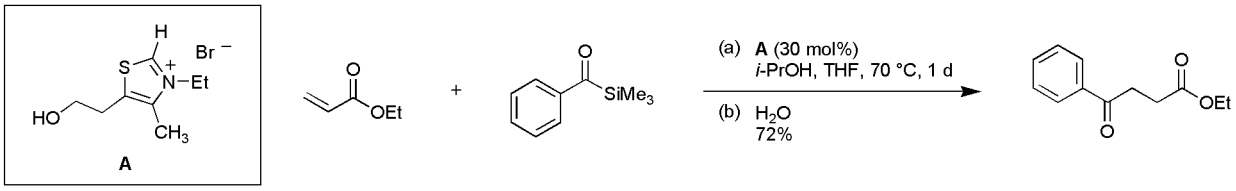
16 examples (yields 12-100%, %de 70-99%).

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



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. **1,4-Addition**
Mattson, A. E.; Bharadwaj, A. R.; Scheidt, K. A. *J. Am Chem. Soc.* **2004**, *126*, 2314.



31 examples (yields 0-84%).

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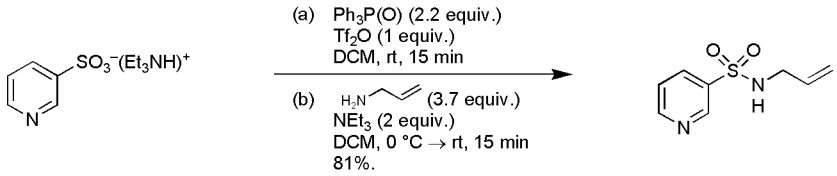
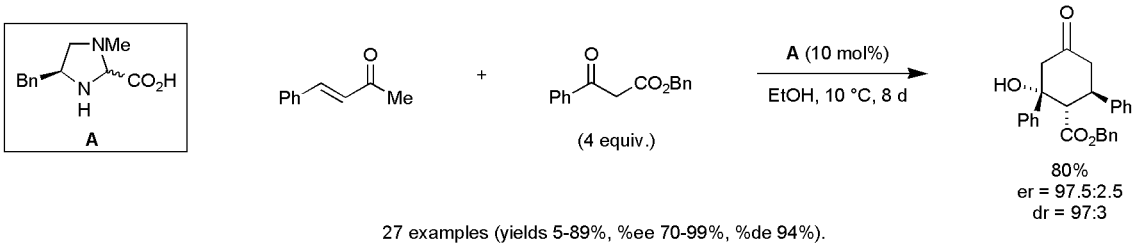
Direct synthesis of sulfonamides and activated sulfonate esters from sulfonic acids. **Nucleophilic Substitution**
Caddick, S.; Wilden, J. D.; Judd, D. B. *J. Am. Chem. Soc.* **2004**, *126*, 1024.



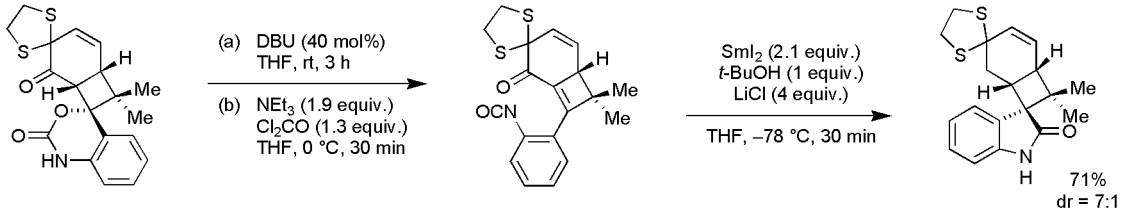
22 examples (yields 48-98%) and investigation towards a solid-supported phosphine oxide.

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



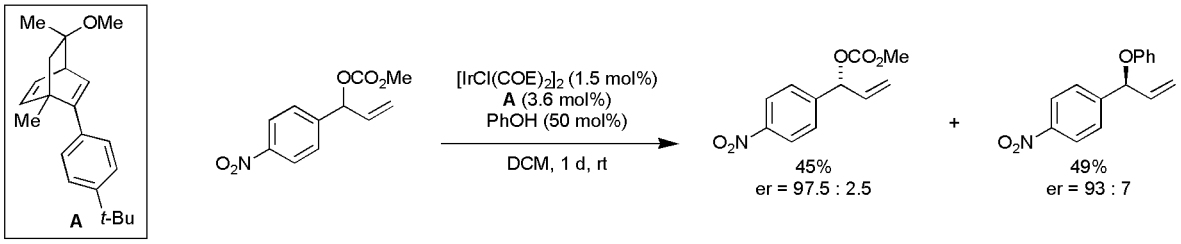
27 examples (yields 5-89%, %ee 70-99%, %de 94%).

A mild and efficient synthesis of oxindoles: Progress towards the synthesis of Welwitindolinone A isonitrile. **Reductive Coupling**
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.



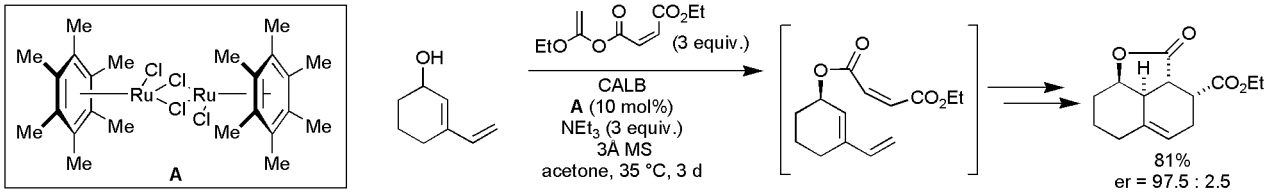
Application of a novel SmI_2-mediated synthesis of spiro-oxindoles: 6 examples (yields 5-88%).

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



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. **Esterification/ Diels-Alder**
Akai, S.; Tanimoto, K.; Kita, Y. *Angew. Chem. Int. Ed.* **2004**, *43*, 1407.



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

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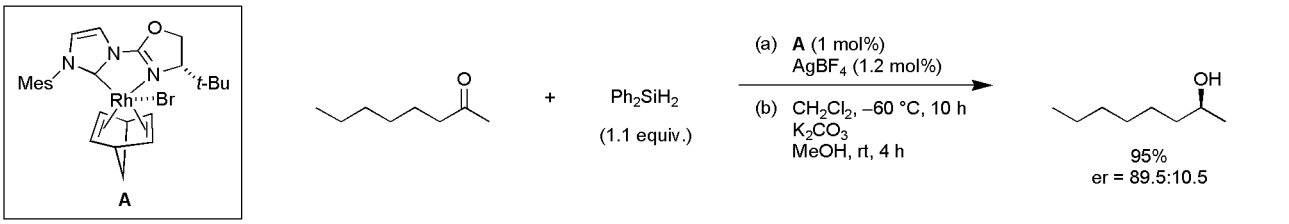
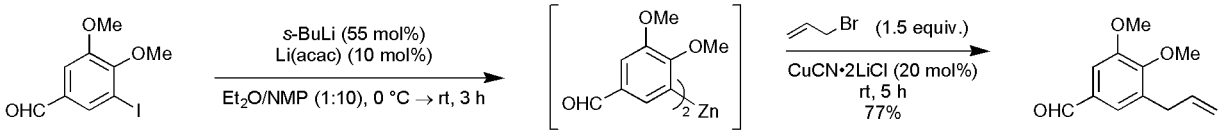
Efficient phosphane free catalysts for the asymmetric hydrosilylation of dialkylketones. **Enantioselective Hydrosilylation**
Gade, L. H.; Cesar, V.; Bellemin-Laponnaz, S. *Angew. Chem. Int. Ed.* **2004**, *43*, 1014.



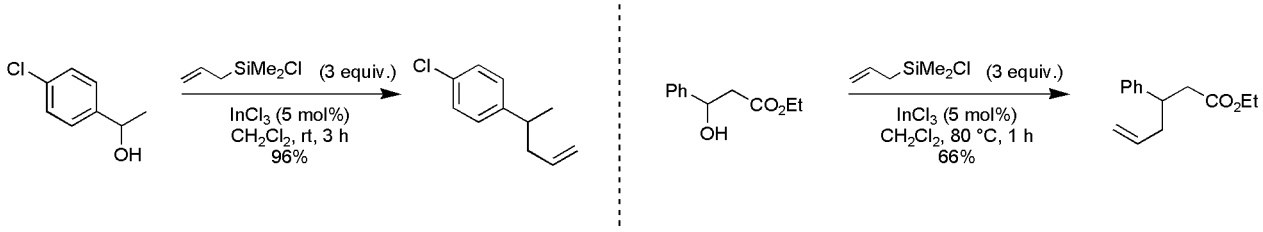
11 examples (yields 53-99%, %ee 77-95%).

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



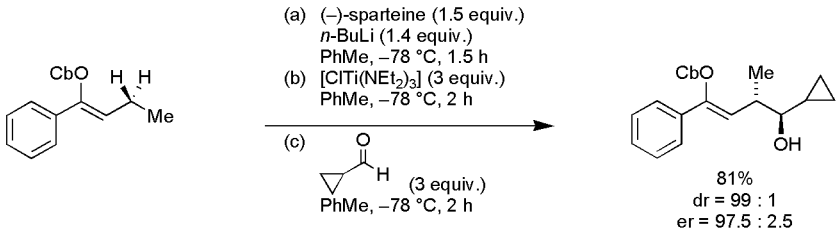
17 examples (yields 52-87%). NMP = N-methyl-2-pyrrolidinone.

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



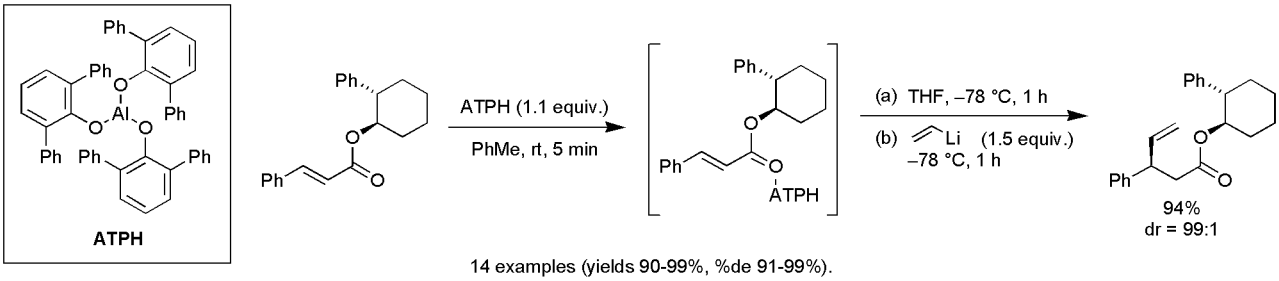
28 examples (yields 0-100%).

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



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-diphenylphenoxide) in an asymmetric 1,4-addition. **Diastereoselective 1,4-Addition**
Ito, H.; Nagahara, T.; Ishihara, K.; Saito, S.; Yamamoto, H. *Angew. Chem. Int. Ed.* **2004**, *43*, 994.



14 examples (yields 90-99%, %de 91-99%).

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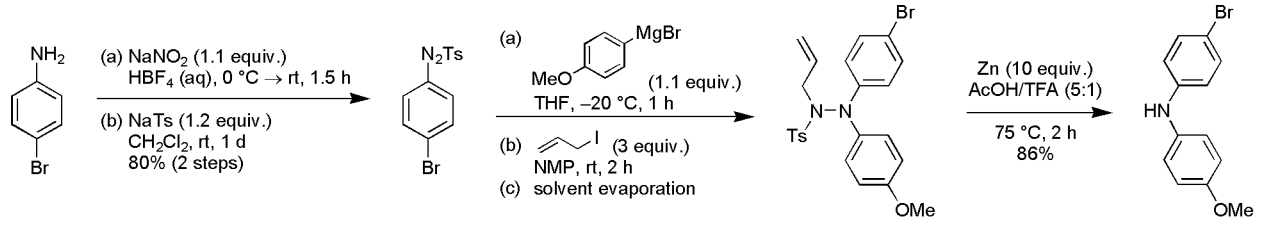
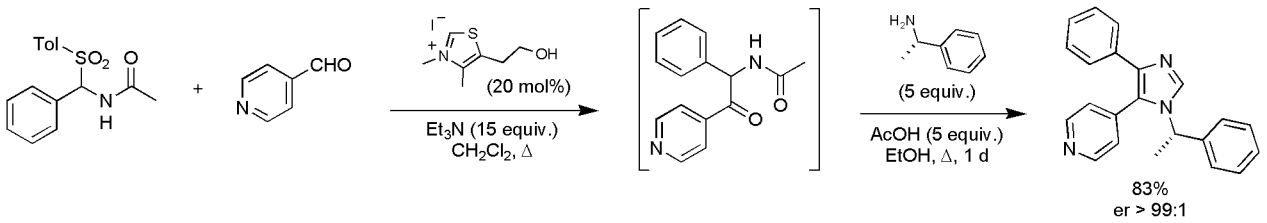
Amination *via* addition of polyfunctional arylmagnesium reagents to functionalised arylazo tosylates. **Amination**
Sapountzis, I.; Knochel, P. *Angew. Chem. Int. Ed.* **2004**, *43*, 897.



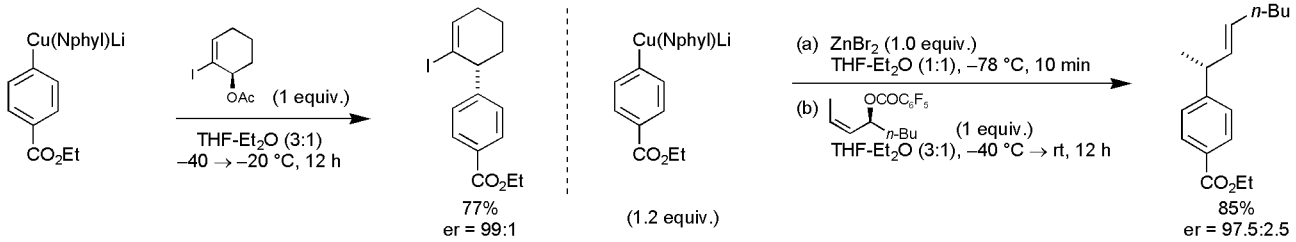
17 examples (yields 58-86%). NMP = *N*-methylpyrrolidinone.

Synthesis of substituted imidazoles *via* organocatalysis. **Imidazole Synthesis**
Frantz, D. E.; Morency, L.; Soheili, A.; Murry, J. A.; Grabowski, E. J. J.; Tillyer, R. D. *Org. Lett.* **2004**, *6*, 843.



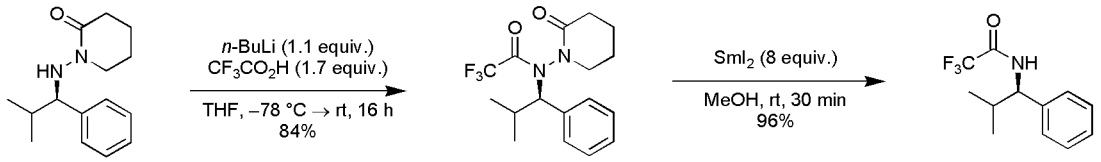
12 examples of di-, tri- and tetrasubstiuted imidazoles (yields 22-83%).

Stereoselective S_N2-substitutions using polyfunctional lithium arylcuprates. **Nucleophilic Substitution**
Calaza, M. I.; Yang, X.; Soorukram, D.; Knochel, P. *Org. Lett.* **2004**, *6*, 529.



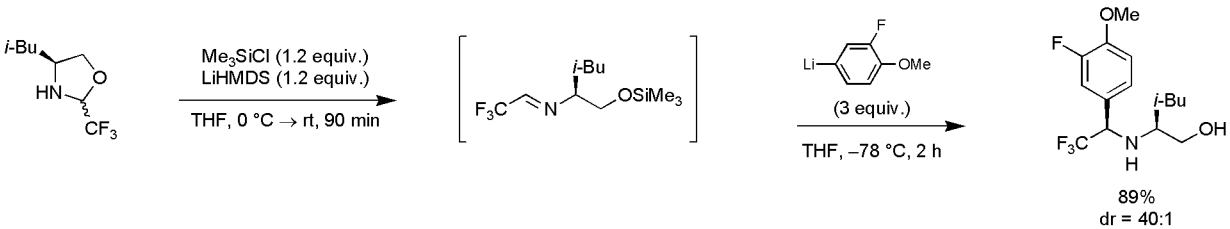
Nphyl = $PhMe_2CCH_2$. 10 examples (yields 50-89%, %ee 89-98%).

Trifluoroacetyl-activated nitrogen-nitrogen bond cleavage of hydrazines by samarium(II) iodide. **N-N Bond Cleavage**
Ding, H.; Friestad, G. K. *Org. Lett.* **2004**, *6*, 637.



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

Oxazolidine ring opening and isomerization to (*E*)-imines. **Ring Opening/Addition**
Gosselin, F.; Roy, A.; O' Shea, P. D.; Chen, C.; Volante, R. P. *Org. Lett.* **2004**, *6*, 641.



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

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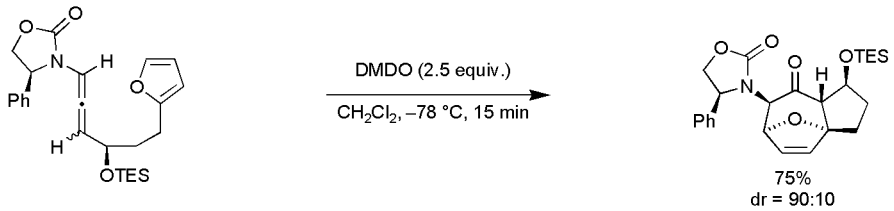
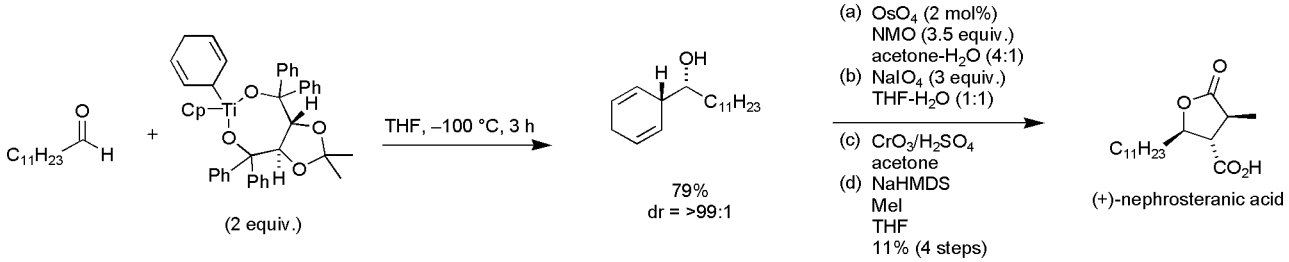
Tandem epoxidation/intramolecular [4+3] cycloaddition of γ-tethered allenamides. **Epoxidation/ [4+3] Cycloaddition**
Rameshkumar, C.; Hsung, R. P. *Angew. Chem. Int. Ed.* **2004**, *43*, 615.



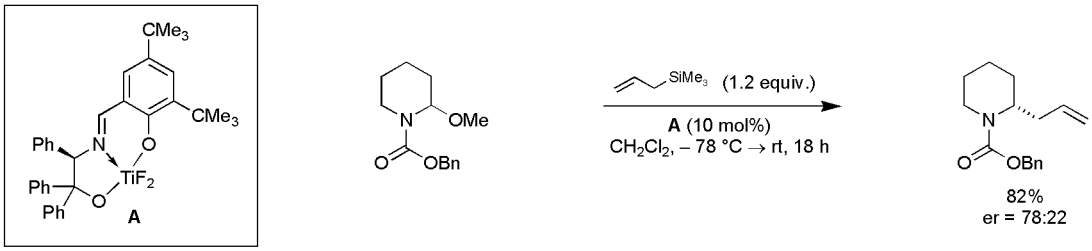
12 examples (yields 34-83%, %de 42->90%).
Chirality of allene does not impact on stereoselectivity.

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



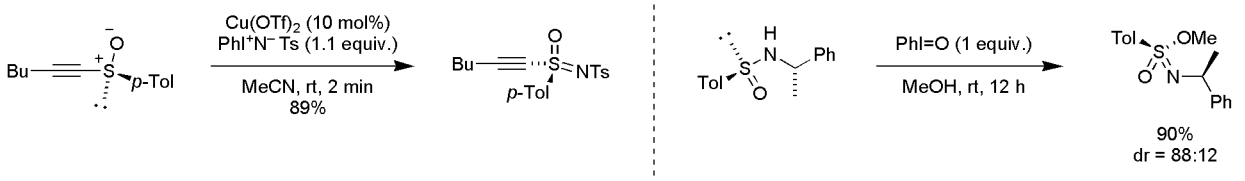
15 examples (yields 40-96%, %de 96-98%, %ee 80-98%).

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



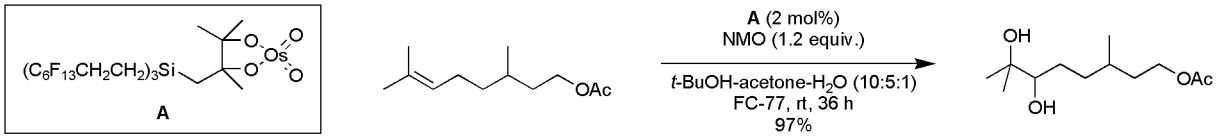
7 examples (yields 62-96%, %ee 54-99%).

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



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



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.

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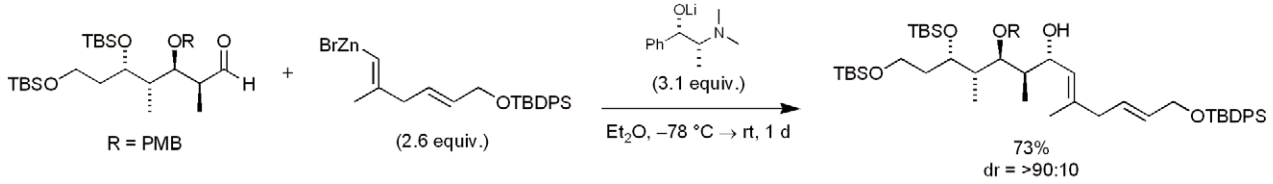
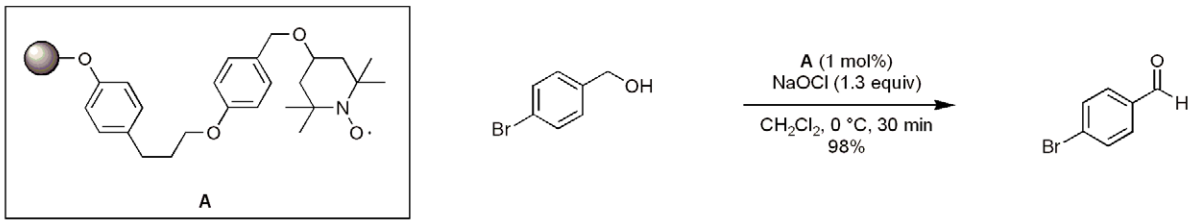
Diastereoselective addition of chiral vinylzinc reagents to α-chiral aldehydes. **Diastereoselective 1,2-Addition**
Marshall, J. A.; Eidam, P. *Org. Lett.* **2004**, *6*, 445.



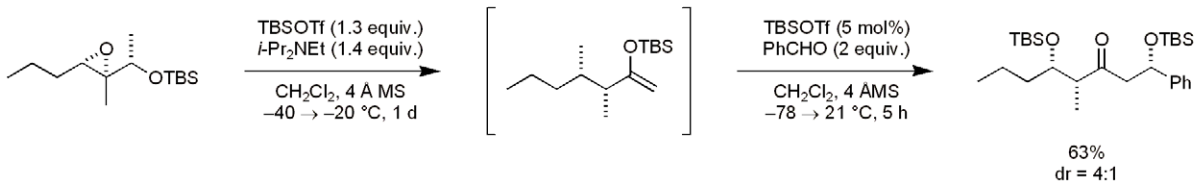
19 examples (yields 60-82%, %de 0->80%).

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



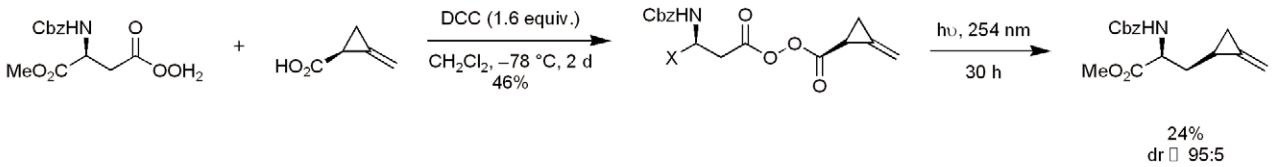
Preparation of the poly(ethylene glycol)-supported TEMPO and optimization studies is described.
10 examples (yields 78-98%).

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



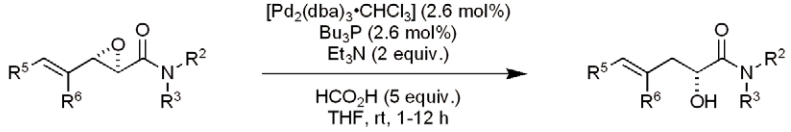
16 examples (yields 21-70%, %de 0-60%).

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



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. **Nucleophilic Substitution**
Kakei, H.; Nemoto, T.; Ohshima, T.; Shibasaki, M. *Angew. Chem. Int. Ed.* **2004**, *43*, 317.



R^2NR^3	R^5	R^6	Yield(%)
MeNH	Ph	H	91
BnNH	Ph	H	90
MeNMe	Ph	H	87
c-HexNH	Ph	H	94
BnNH	Me	H	94
BnNH	$-(CH_2)_4-$		94

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

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