

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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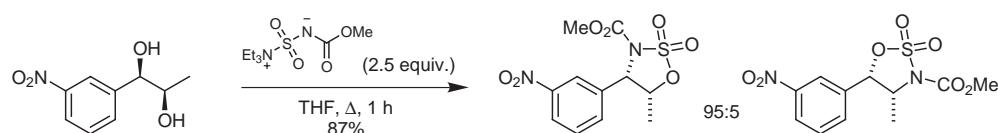
The journals regularly covered by the abstractors are:

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 Letters
Organometallics
Perkin Transactions I
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry and Tetrahedron Letters

Regio- and stereoselective synthesis of sulfamides.

Nicolaou, K. C.; Huang, X.; Snyder, S. A.; Rao, P. B.; Bella, M.; Reddy, M. V. *Angew. Chem. Int. Ed.* **2002**, *41*, 834.

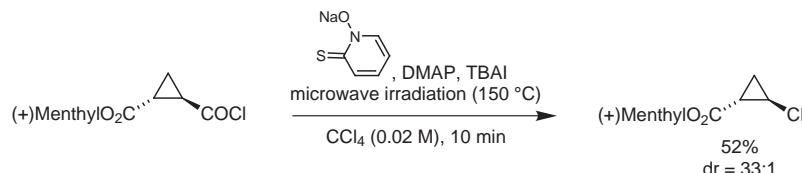
S_N2 Cyclization



22 examples (yields 41-94%). Conversion of the sulfamide products to β-amino alcohols (7 examples, yields 90-95%) is also reported.

Barton–Crich–Motherwell decarboxylation under microwave irradiation.
Trost, B. M.; Dirat, O.; Gunzner, J. L. *Angew. Chem. Int. Ed.* **2002**, *41*, 841.

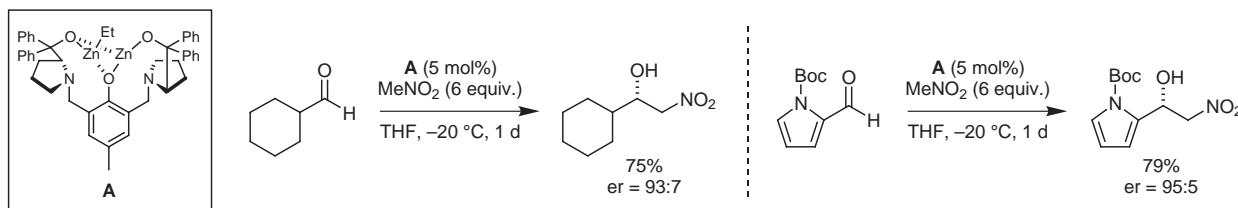
Decarboxylation



A total synthesis of callipeltoside A is also reported.

Asymmetric nitroaldol reaction.
Trost, B. M.; Yeh, V. S. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 861.

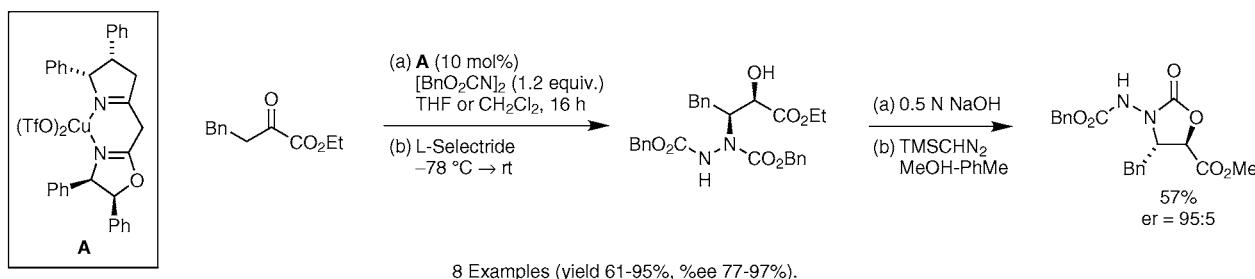
1,2-Addition



13 examples (yields 51-90%, %ee 78-93%).

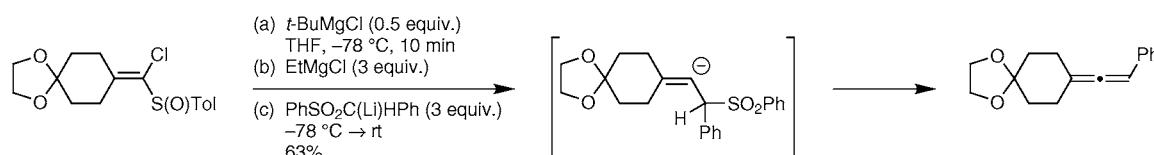
Catalytic asymmetric α -amination reactions of 2-keto esters.
Juhl, K.; Jorgensen, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 2420.

Amination



Synthesis of allenes via alkenylation.
Satoh, T.; Sakamoto, T.; Watanabe, M. *Tetrahedron Lett.* **2002**, *43*, 2043.

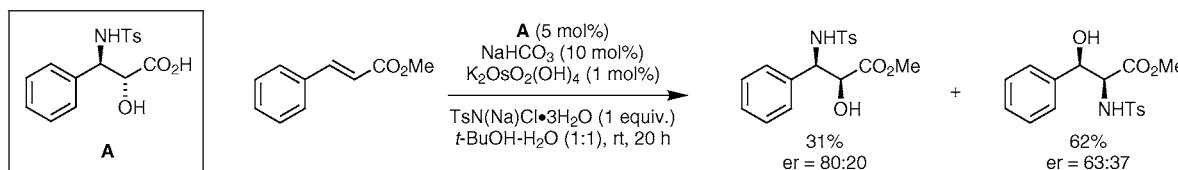
Alkenylation



13 examples (yields 14-65%).

Osmium-catalyzed asymmetric aminohydroxylation of olefins.
Andersson, M. A.; Epple, R.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2002**, *41*, 473.

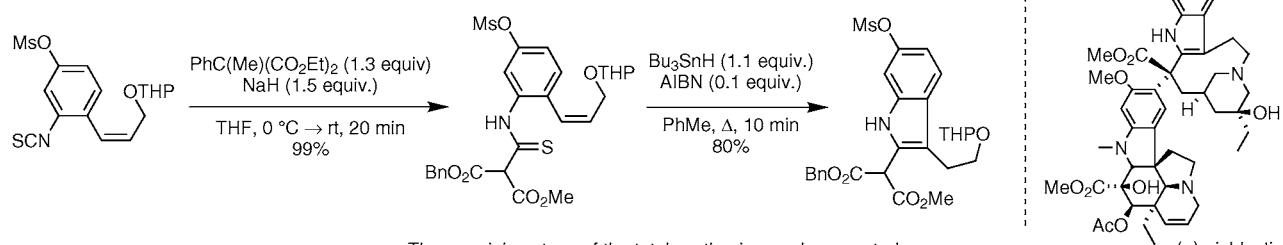
Asymmetric Aminohydroxylation



2 examples (yields 89-93%, %ee 25-60%).

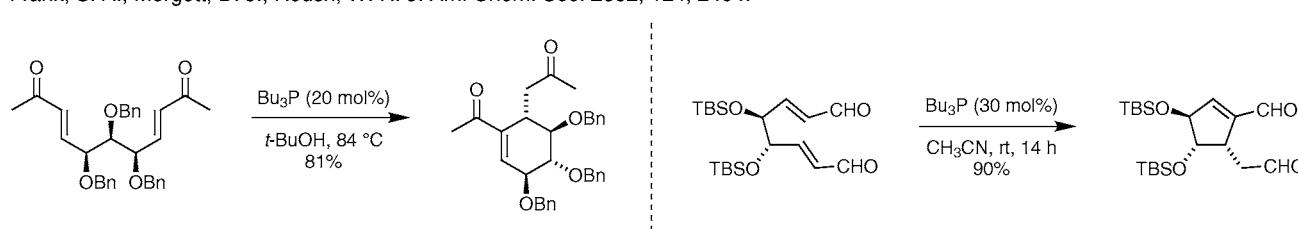
Stereocontrolled total synthesis of (+)-vinblastine.
Yokoshima, S.; Ueda, T.; Kobayashi, S.; Sato, A.; Kuboyama, T.; Tokuyama, H.; Fukuyama, T. *J. Am. Chem. Soc.* **2002**, *124*, 2137.

Radical Cyclization



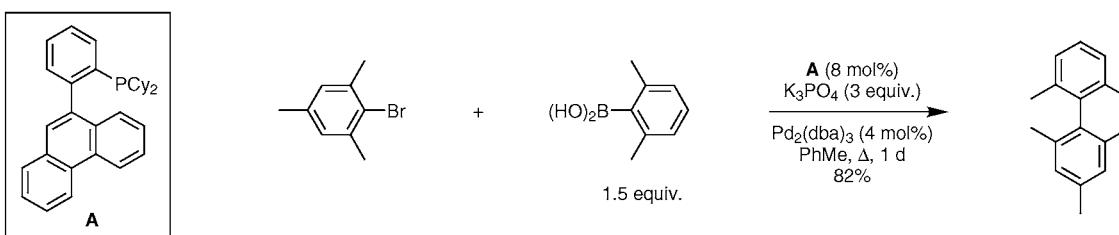
Synthesis of functionalized cyclopentenes/cyclohexenes by Rauhut-Currier or Morita-Baylis-Hillman reaction.
Wang, L.-C.; Luis, A. L.; Agapiou, K.; Jang, H.-Y.; Krische, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 2402.
Frank, S. A.; Mergott, D. J.; Roush, W. R. *J. Am. Chem. Soc.* **2002**, *124*, 2404.

Cyclization



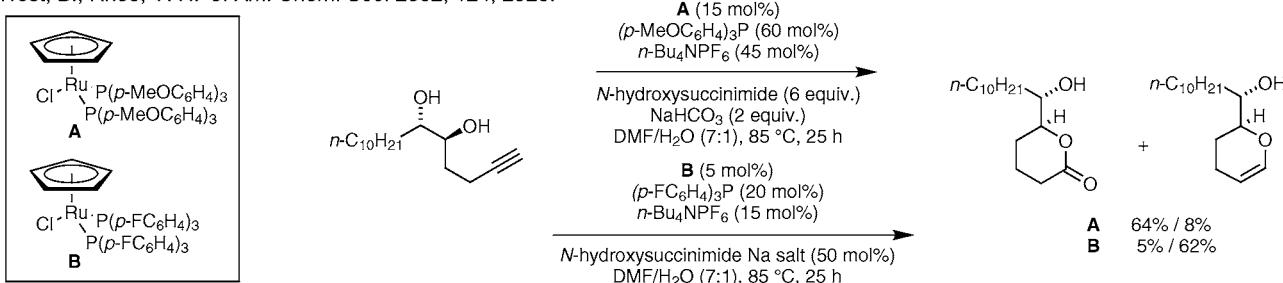
35 examples (yield 32-96%) are reported in both publications.

Suzuki catalyst for the synthesis of sterically hindered biaryls.
Yin, J.; Rainka, M. P.; Zhang, X-X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1162.

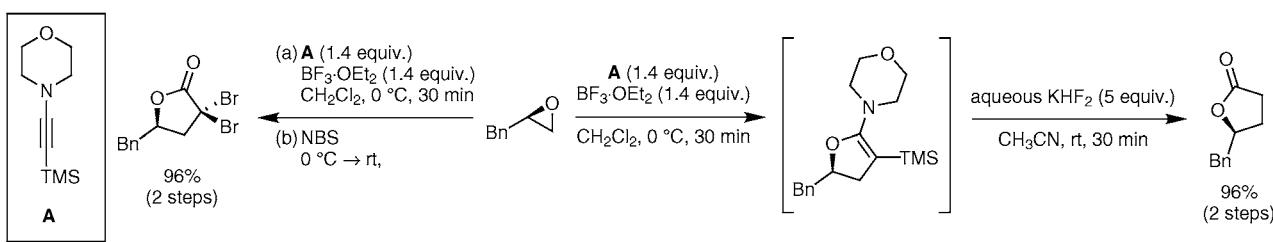
sp²-sp² Coupling

6 examples (yield 58-98%). Other ligands were also studied (8 examples).

Oxidative cyclization vs cycloisomerization of bis-homopropargylic alcohols.
Trost, B.; Rhee, Y. H. *J. Am. Chem. Soc.* **2002**, *124*, 2528.

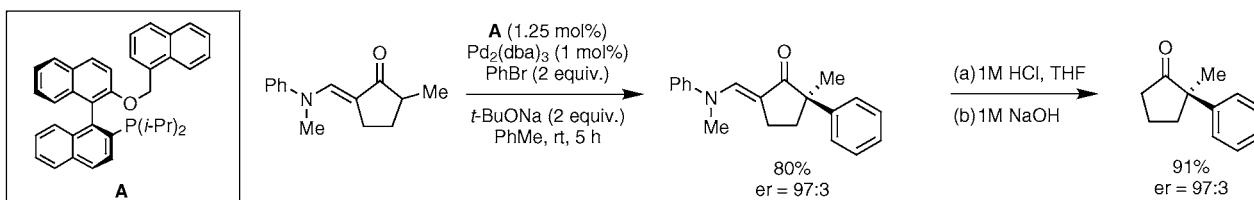
Oxidative Cyclization

Conversion of terminal epoxides into γ -butanolides.
Movassaghi, M.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 2456.

Alkylation

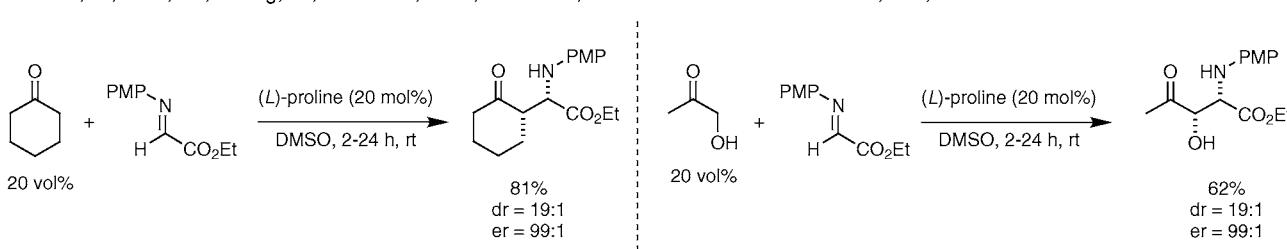
14 Examples (yield 65-96%).

An improved catalyst for the asymmetric arylation of ketone enolates.
Hamada, T.; Chieffi, A.; Ahman, J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1261.

Asymmetric Arylation

10 examples (yield 43-85%, %ee 22-94%). Substituted aryl derivatives were also used.

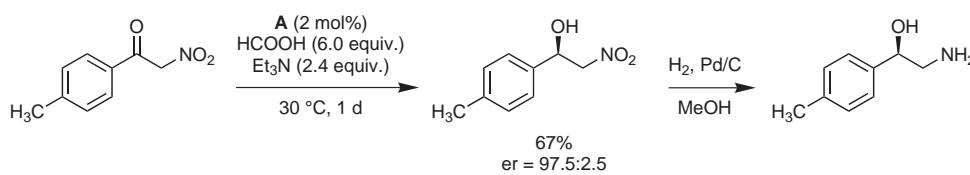
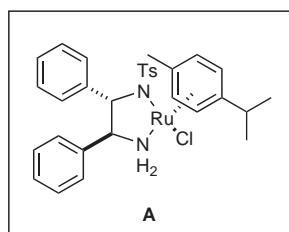
Enantioselective amino acid-catalyzed functionalization of α -amino acids.
Cordova, A.; Notz, W.; Zhong, G.; Betancort, J. M.; Barbas III, C. F. *J. Am. Chem. Soc.* **2002**, *124*, 1842.

Enantioselective 1,2-Addition

8 examples (yield 47-85%, %ee 61-99%, %de 90%).

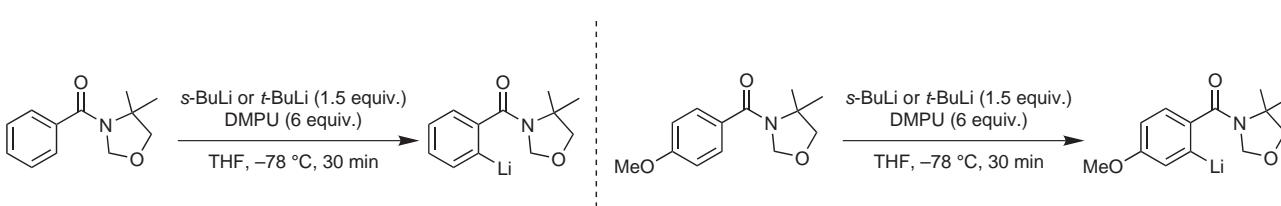
Synthesis of optically active amino alcohols.
Watanabe, M.; Murata K.; Ikariya, T. *J. Org. Chem.* **2002**, *67*, 1712.

Asymmetric Transfer Hydrogenation



6 examples (yields 65-100%, %ee 92-99%).

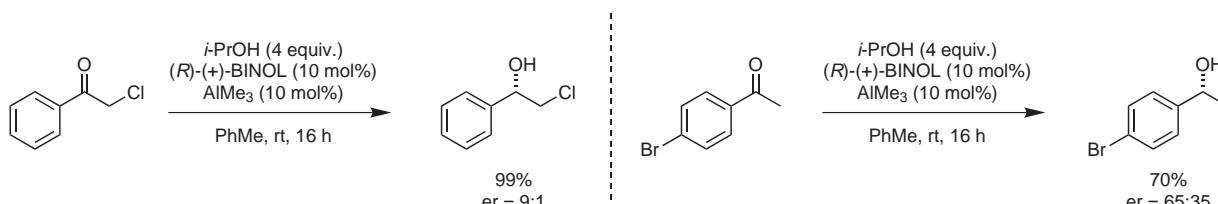
Lithiated *N*-Benzoyloxazolines.
Clayden, J.; Purewal, S.; Helliwell, M.; Mantell, S. *J. Angew. Chem. Int. Ed.* **2002**, *41*, 1049.

o-Metallation

The anion rearranges with time, leading to dearomatization and trapping with an electrophile.

Meerwein–Schmidt–Ponndorf–Verley reduction of prochiral ketones.
Campbell, E. J.; Zhou, H.; Nguyen, S. T. *J. Angew. Chem. Int. Ed.* **2002**, *41*, 1020.

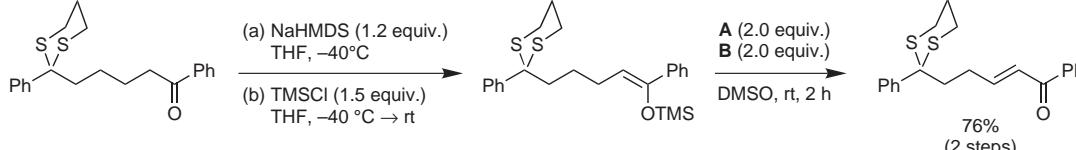
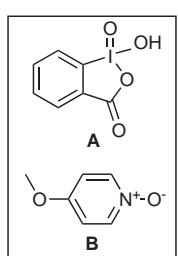
Asymmetric Reduction



12 examples (yields 20-99%, %ee 8-83%).

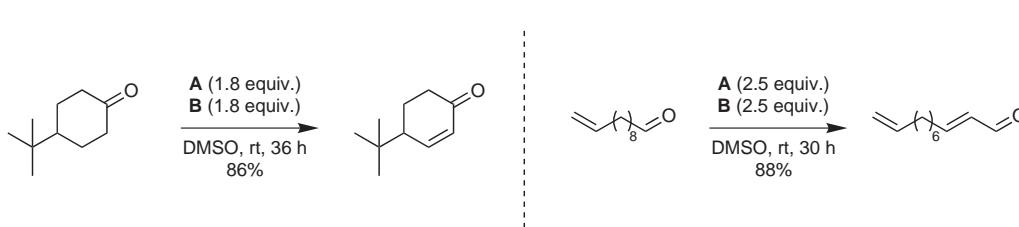
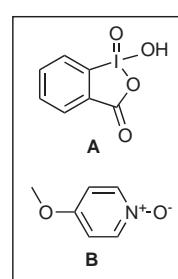
Oxidation of silyl enol ethers.
Nicolaou, K. C.; Gray, D. L. F.; Montagnon, T.; Harrison, S. T. *J. Angew. Chem. Int. Ed.* **2002**, *41*, 996.

Oxidation

13 examples of oxidation of silyl enol ethers formed *in situ* (yields 43-96%) and 7 examples of conjugate addition followed by oxidation (yields 47-98%).

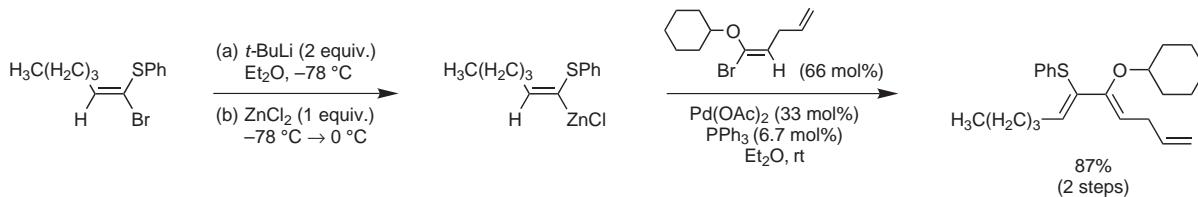
Dehydrogenation of aldehydes and ketones to α,β -unsaturated carbonyl compounds.
Nicolaou, K. C.; Montagnon, T.; Baran, P. S. *J. Angew. Chem. Int. Ed.* **2002**, *41*, 993.

Dehydrogenation



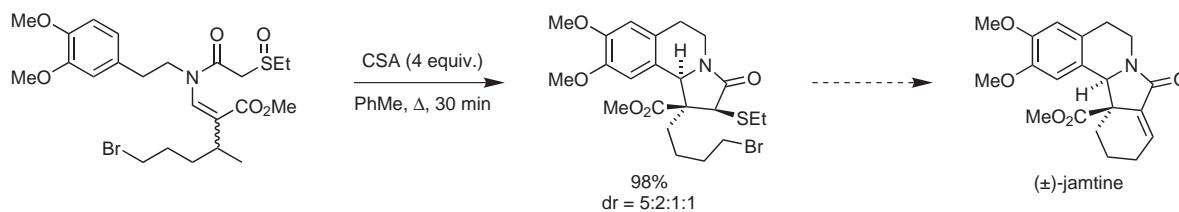
17 examples (yields 43-96%).

Negishi coupling between α -allyl(aryl)thiovinylzinc chloride and α -bromo vinyl ether.
Su, M.; Kang, Y.; Yu, W.; Hua, Z.; Jin, Z. *Org. Lett.* **2002**, 4, 691.

sp²-sp² Coupling

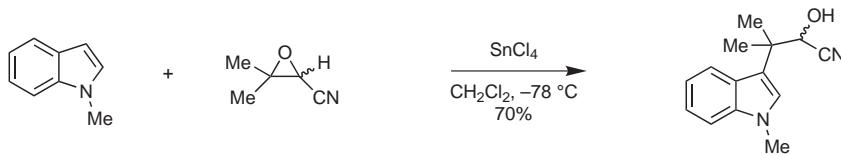
10 examples (yields 70-91%).

Tandem thionium/N-acyliminium cyclization.
Padwa, A.; Danca, M. D. *Org. Lett.* **2002**, 4, 715.

Cyclization

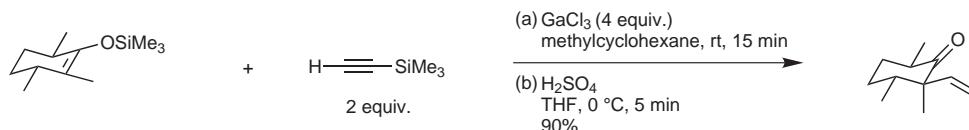
The desired diastereomer for jamantine was the major product and could be separated from the mixture.

SnCl₄-mediated ring opening of epoxynitriles by *N*-methylindole.
Reddy, R.; Jaquith, J. B.; Neelagiri, V. R.; Saleh-Hanna, S.; Durst, T. *Org. Lett.* **2002**, 4, 695.

Alkylation

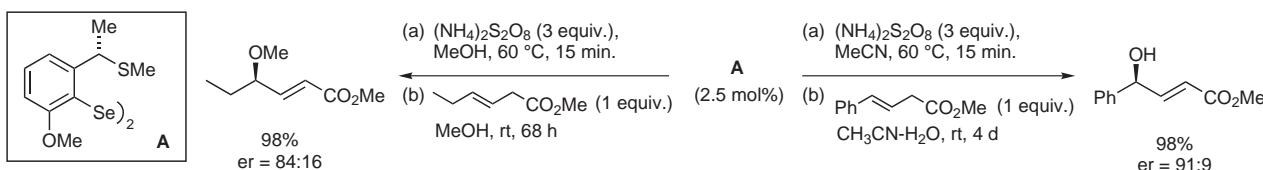
5 examples (yields 69-70%).

GaCl₃-promoted equatorial ethenylation of cyclic ketones.
Ansawa, M.; Miyagawa, C.; Yamaguchi, M. *Synthesis*, **2002**, 138.

sp²-sp² Coupling

13 examples (yields 36-90%). All showed preference for the equatorial ethenylation.

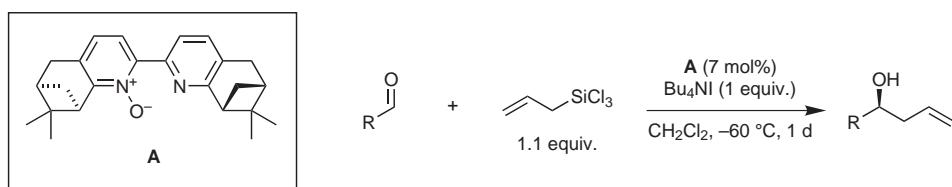
Catalytic one-pot selenenylation-deselenenylation using a chiral, sulfur-containing diselenide.
Tiecco, M.; Testaferri, L.; Santi, C.; Tomassini, C.; Marini, F.; Bagnoli, L.; Temperini, A. *Chem.-Eur. J.* **2002**, 8, 1118.

Allylic Oxidation

4 examples (yields 85-98%, %ee 55-82%). Synthesis of A is also reported.

Catalytic enantioselective allylation of aldehydes with allyltrichlorosilane.
Malkov, A. V.; Orsini, M.; Pernazza, D.; Muir, K. W.; Langer, V.; Meghan, P.; Kocovsky, P. *Org Lett.* **2002**, *4*, 1047.

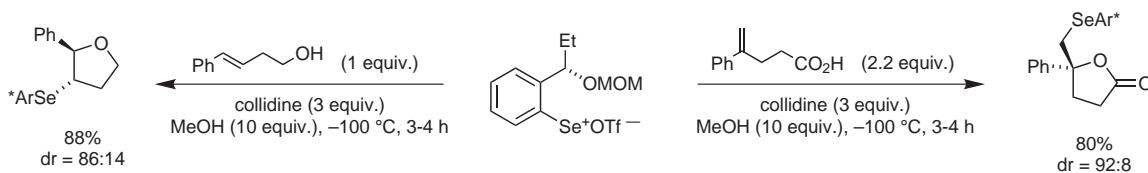
Allylation



11 examples (yields 10-85%, %ee 4-92%).

Stereoselective functionalization of alkenes utilising a series of new chiral selenium electrophiles.
Uehlin, L.; Fragale, G.; Wirth, T. *Chem.-Eur. J.* **2002**, *8*, 1125.

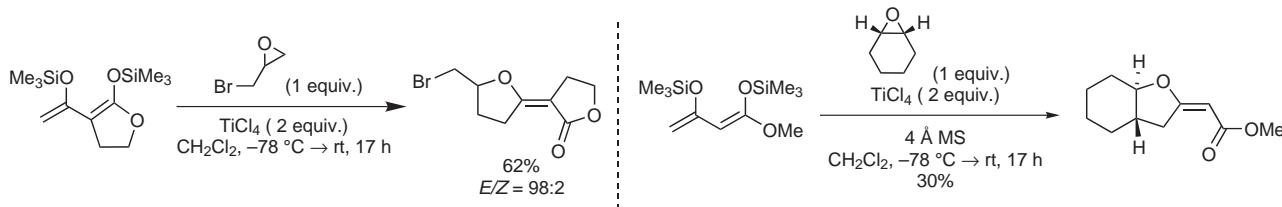
Selenocyclization



10 examples (yields 41-92%, %de 68-95%).

Chemo-, regio- and diastereoselective synthesis of functionalized 2-alkylidenetetrahydrofurans.
Langer, P.; Armbrust, H.; Eckardt, T.; Magull, J. *Chem.-Eur. J.* **2002**, *8*, 1443.

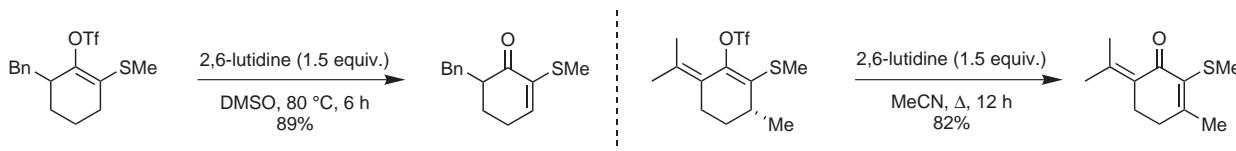
Heteroannulation



A purification procedure for these compounds utilising an ion-exchange resin to scavenge by-products is also reported.

Preparation of α -sulphenyl enones by thermal fragmentation of β -sulphenyl enol triflates.
Hynes, J.; Nasser, T.; Overman, L. E.; Watson, D. A. *Org. Lett.* **2002**, *4*, 929.

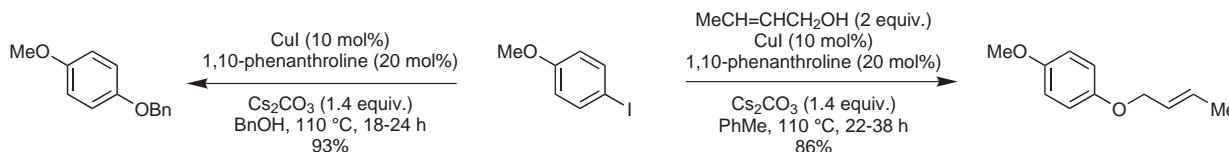
Oxidation



10 examples (yields 37-89%).

Copper-catalyzed coupling of aryl iodides with aliphatic alcohols.
Wolter, M.; Nordmann, G.; Job, G. E.; Buchwald, S. L. *Org. Lett.* **2002**, *4*, 973.

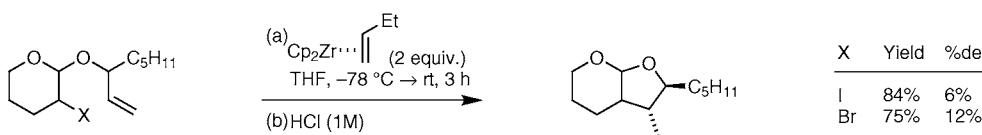
C–O Coupling



15 examples (yields 40-97%) of primary alcohols, 4 examples (yields 67-92%) of secondary alcohols and 5 examples (yields 54-96%) of aliphatic alcohols.

Zirconocene-olefin complex mediated radical cyclization reactions.
Fujita, K.; Yorimitsu, H.; Oshima, K. *Synlett* 2002, 337.

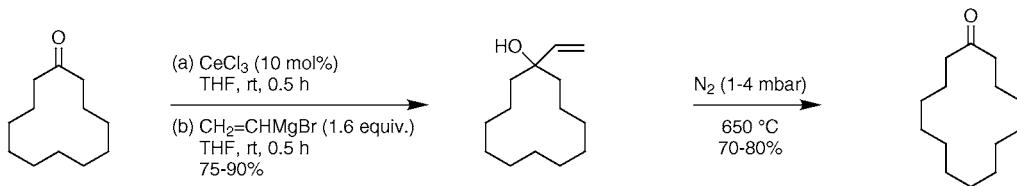
Radical Cyclization



13 examples (yields 34-97%, combined yields for saturated and unsaturated cyclic products).

Two-carbon ring expansion of cyclic ketones.
Nagel, M.; Hansen, H.-J.; Frater, G. *Synlett* 2002, 275.

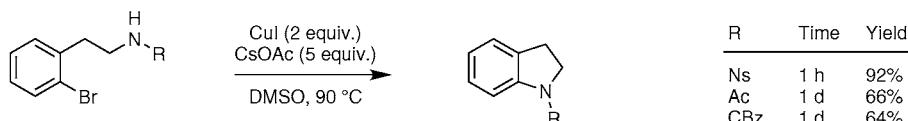
Ring Expansion



7 examples (yields 65-90%). A quartz tube reactor was used for the isomerisation.

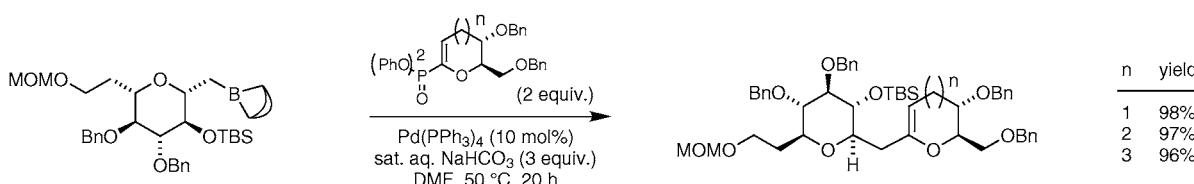
Copper-mediated intramolecular amination of aryl halides.
Yamada, K.; Kubo, T.; Tokuyama, H.; Fukuyama, T. *Synlett* 2002, 231.

C,N-Coupling



11 examples (yields 44-96%) of 5-membered rings, 6 examples (yields 54-99%) of 6-membered rings and 1 example of a 7-membered ring (yield 39%).

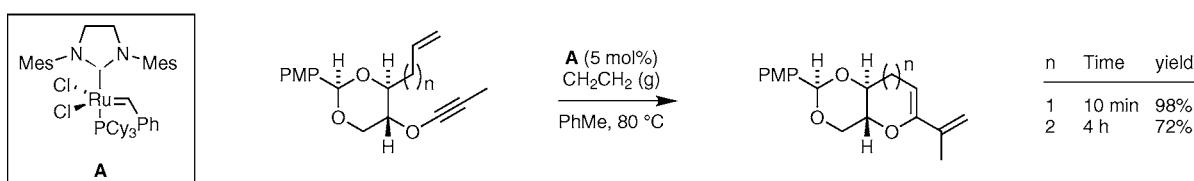
A general strategy for the convergent synthesis of fused polycyclic ethers via β -alkyl Suzuki coupling.
Sasaki, M.; Ishikawa, M.; Fuwa, H.; Tachibana, K. *Tetrahedron* 2002, 53, 1889.

 sp^3-sp^2 Coupling

5 examples (yields 94-98%) using 6-9 membered ring enol phosphates. Synthesis of the ABCD ring fragment of ciguatoxin analogues is also reported.

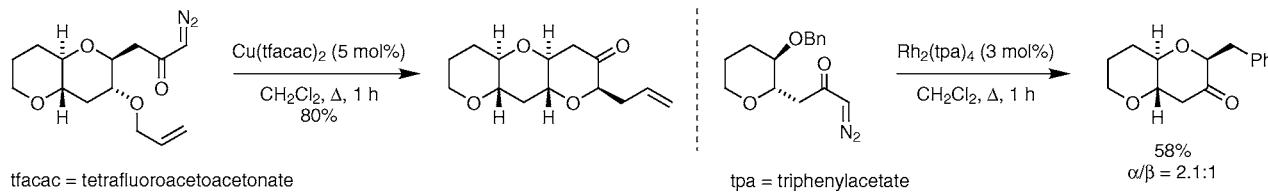
Preparation of cyclic enol ethers by catalytic ring-closing metathesis of alkynyl ethers.
Clark, J. S.; Elustondo, F.; Trevitt, G. P.; Boyall, D.; Robertson, J.; Blake, A. J.; Wilson, C.; Stammen, B. *Tetrahedron* 2002, 58, 1973.

Ring-Closing Metathesis



9 examples (yields 0-98%). A second, similar catalyst is also examined (8 examples, yields 20-84%).

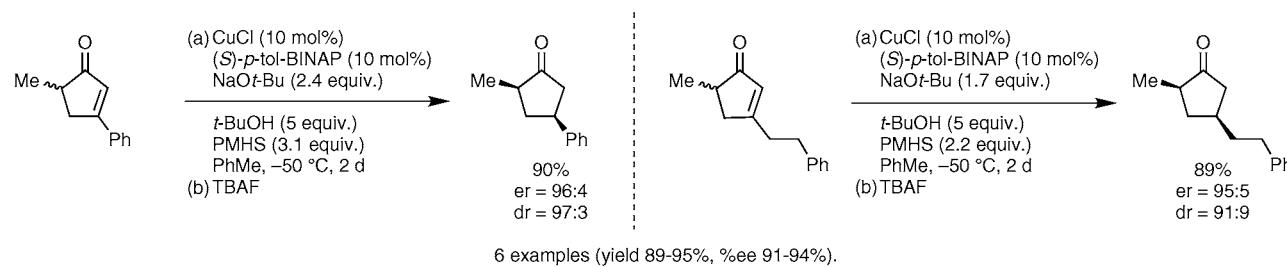
Cyclic oxonium ylides: building blocks for iterative synthesis of polycyclic ethers.
Marmsäter, F. P.; Vancko, J. A.; West, F. G. *Tetrahedron* **2002**, *58*, 2027.



Cyclic oxonium ylide formation followed by a [2,3]-shift (3 examples, yields 45–80%, de 25–98%) or [1,2] and [1,4]-shifts (1 example, yield 70%) are reported.

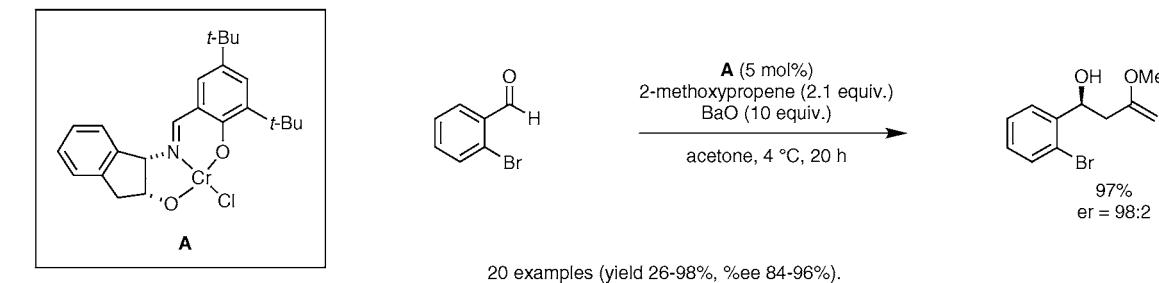
Enantio- and diastereoselective synthesis of 2,4-dialkyl cyclopentanones.
Jurkauskas, V.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 2892.

Asymmetric Reduction



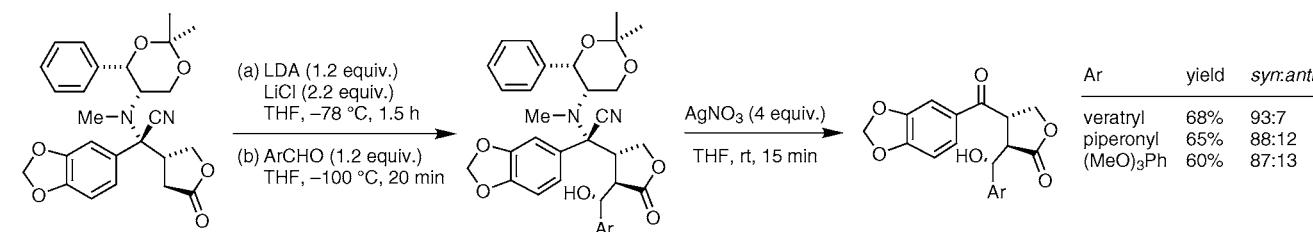
Asymmetric catalysis of hetero-ene reactions with tridentate Schiff base chromium(III) complexes.
Jacobsen, E. N.; Ruck, R. T. *J. Am. Chem. Soc.* **2002**, *124*, 2882.

Asymmetric-Ene Reaction



Asymmetric synthesis of lignans.
Enders, D.; Lausberg, V.; Del Signore, G.; Berner, O. M. *Synthesis* **2002**, *515*.

Diastereoselective Aldol



Conversion of the product γ -butyrolactones into a variety of lignans is also reported.

Immobilization of TADDOLs on silica gel and their use in enantioselective heterogeneous catalysis.
Heckel, A.; Seebach, D. *Chem.–Eur. J.* **2002**, *8*, 560.

Dipolar Cycloaddition

