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:

Elyse Bourque, Jennifer Delaney, Andrew Gunn, Stephen McAteer, Marcel de Puit, Stefan Schunk, Sukhjinder Uppal, Tanya Wildmann and Josephine Yuen, Department of Chemistry, Leeds University, Leeds, LS2 9JT, UK.

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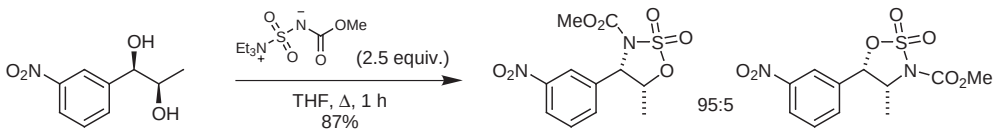
The journals regularly covered by the abstractors are:

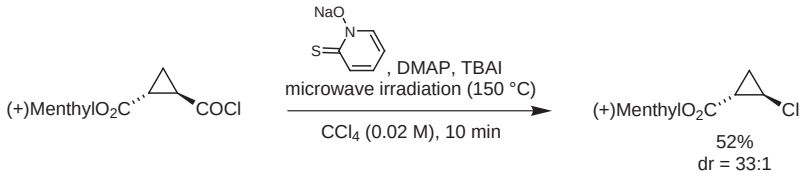
Angewandte Chemie International Edition
Bulletin of the Chemical Society of Japan
Chemical Communications
Chemistry A European Journal
Chemistry Letters
Collection Czechoslovak Chemical Communications
European Journal of Organic Chemistry
Helvetica Chimica Acta
Heterocycles
Journal of the American Chemical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

Regio- and stereoselective synthesis of sulfamidates. **S_N2 Cyclization**
Nicolaou, K. C.; Huang, X.; Snyder, S. A.; Rao, P. B.; Bella, M.; Reddy, M. V. *Angew. Chem. Int. Ed.* **2002**, *41*, 834.



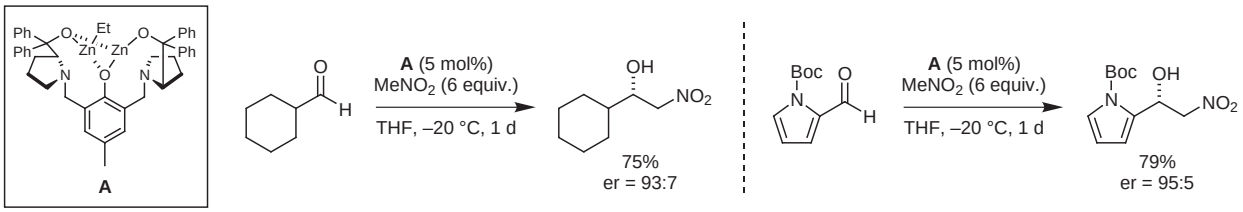
22 examples (yields 41-94%). Conversion of the sulfamidate products to β-amino alcohols (7 examples, yields 90-95%) is also reported.

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



A total synthesis of callipeltoside A is also reported.

Asymmetric nitroaldol reaction. **1,2-Addition**
Trost, B. M.; Yeh, V. S. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 861.



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

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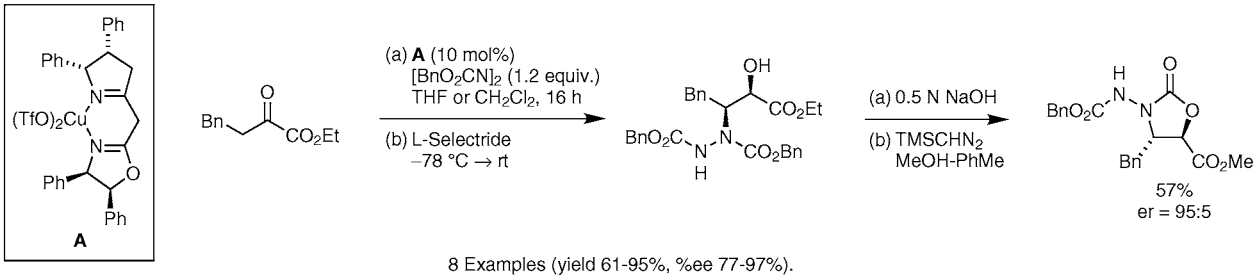
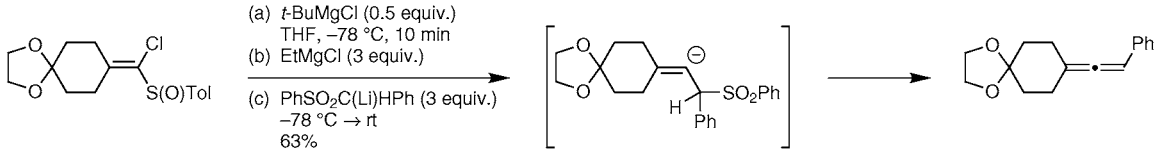
Catalytic asymmetric α-amination reactions of 2-keto esters. **Amination**
Juhl, K.; Jorgensen, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 2420.



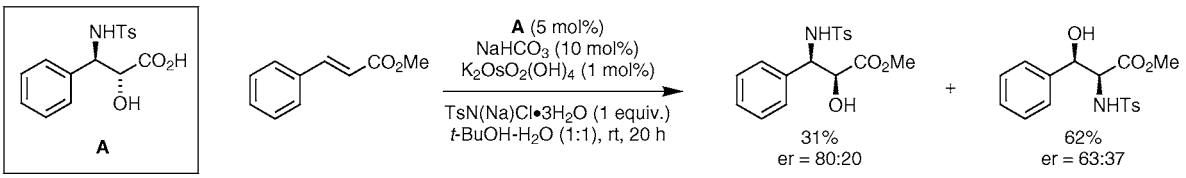
8 Examples (yield 61-95%, %ee 77-97%).

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



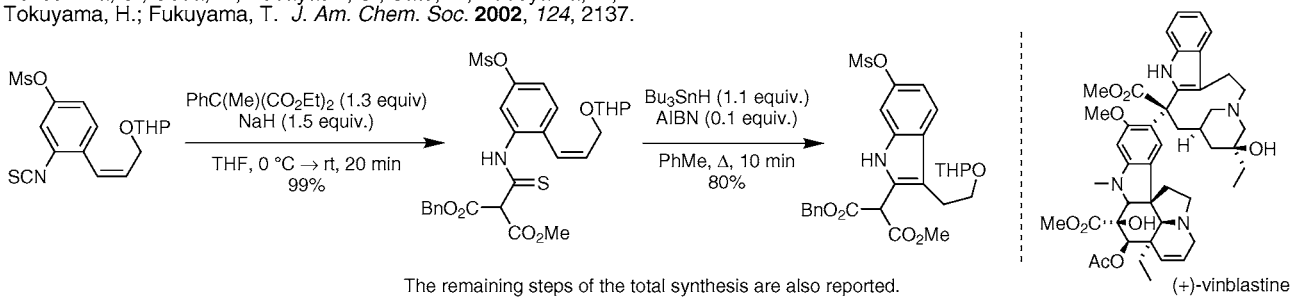
13 examples (yields 14-65%).

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



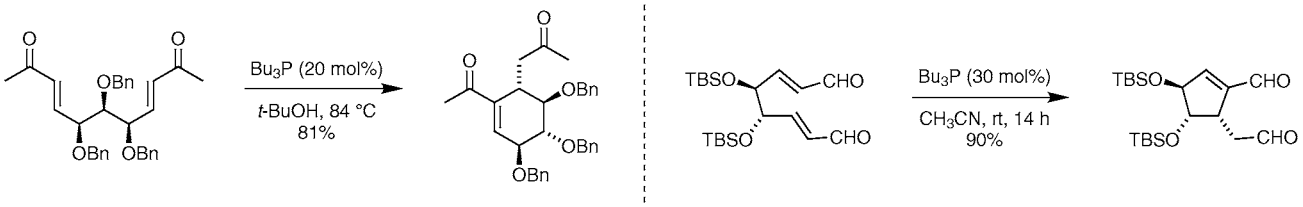
2 examples (yields 89-93%, %ee 25-60%).

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



The remaining steps of the total synthesis are also reported.

Synthesis of functionalized cyclopentenes/cyclohexenes by Rauhut–Currier or Morita–Baylis–Hillman reaction. **Cyclization**
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.



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

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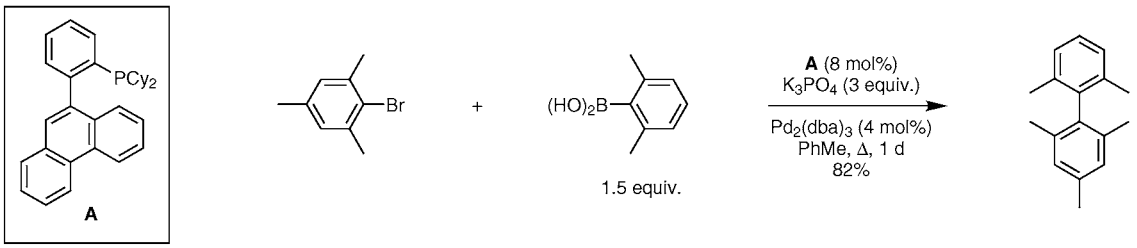
Suzuki catalyst for the synthesis of sterically hindered biaryls.
Yin, J.; Rainka, M. P.; Zhang, X-X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1162.

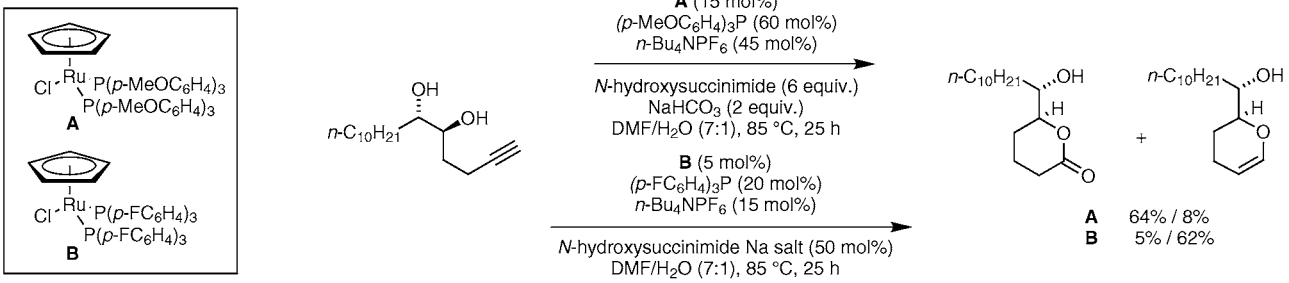
sp^2-sp^2 Coupling



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

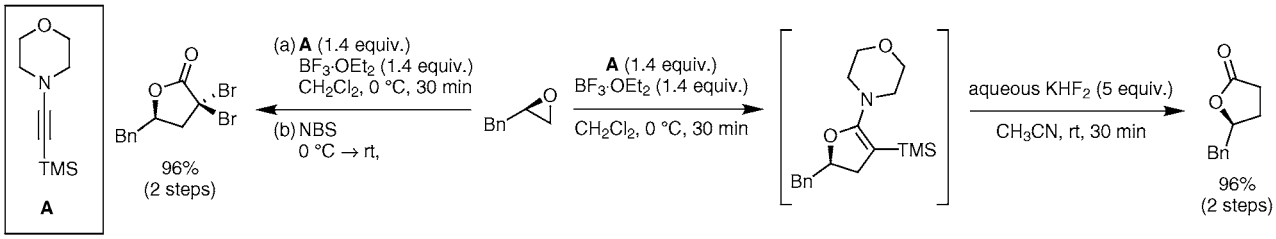
Oxidative cyclization vs cycloisomerization of bis-homopropargylic alcohols.
Trost, B.; Rhee, Y. H. *J. Am. Chem. Soc.* **2002**, *124*, 2528.

Oxidative Cyclization



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

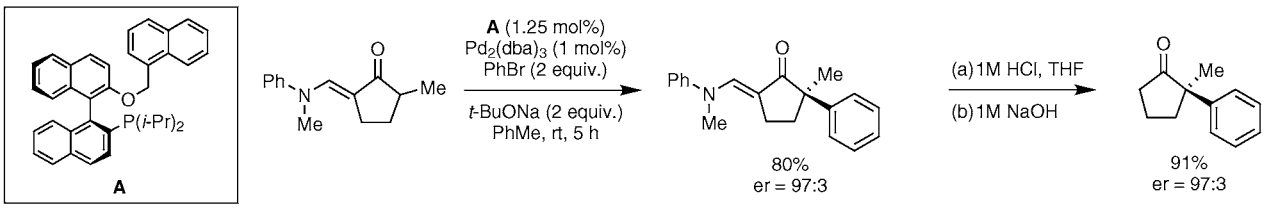
Alkylation



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.

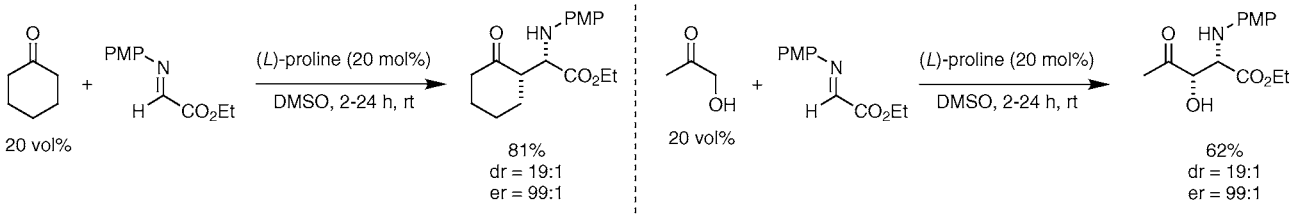
Asymmetric Arylation



10 examples (yield 43-85%, %ee 22-94%). Substituted aryl derivatives w ere 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%).

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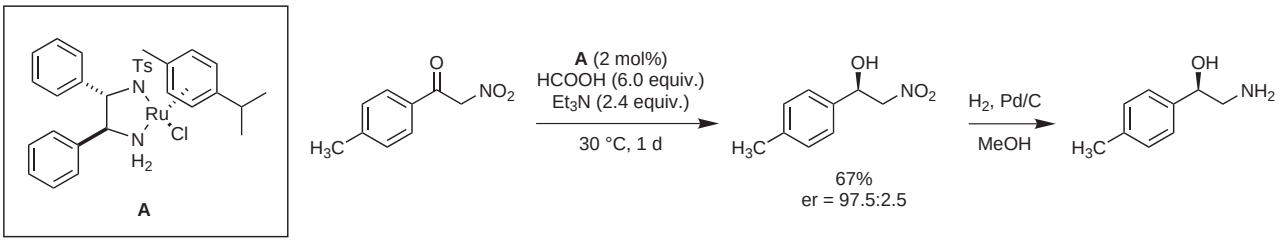
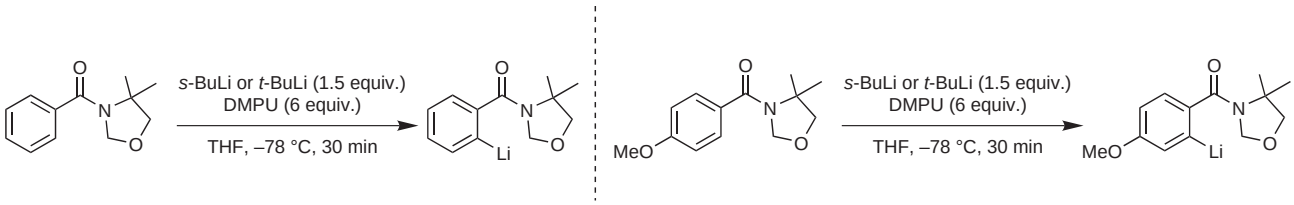
Synthesis of optically active amino alcohols. **Asymmetric Transfer Hydrogenation**
Watanabe, M.; Murata K.; Ikariya, T. *J. Org. Chem.* **2002**, *67*, 1712.



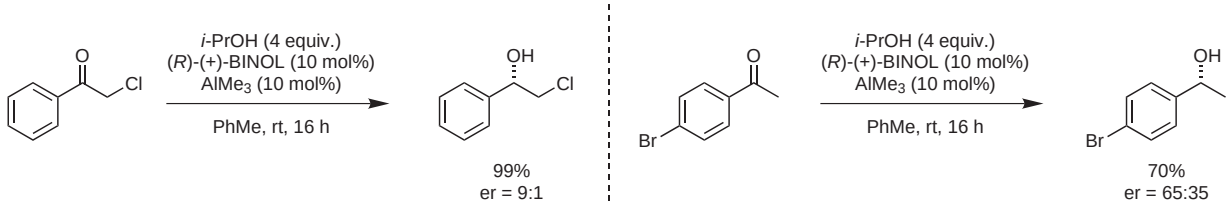
6 examples (yields 65-100%, %ee 92-99%).

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



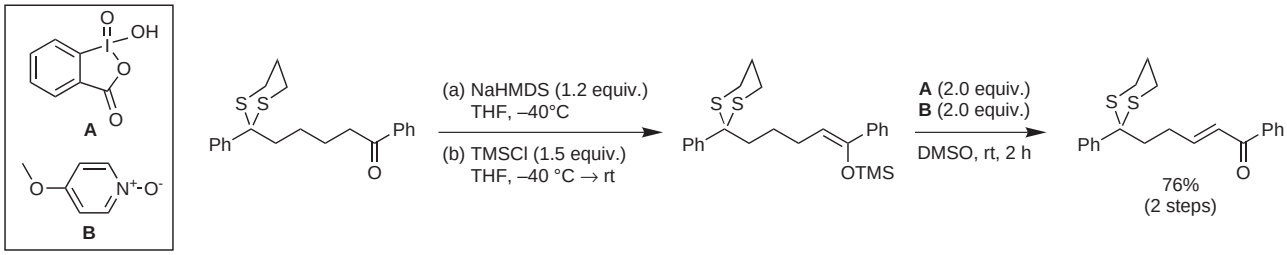
The anion rearranges with time, leading to dearomatization and trapping with an electrophile.

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



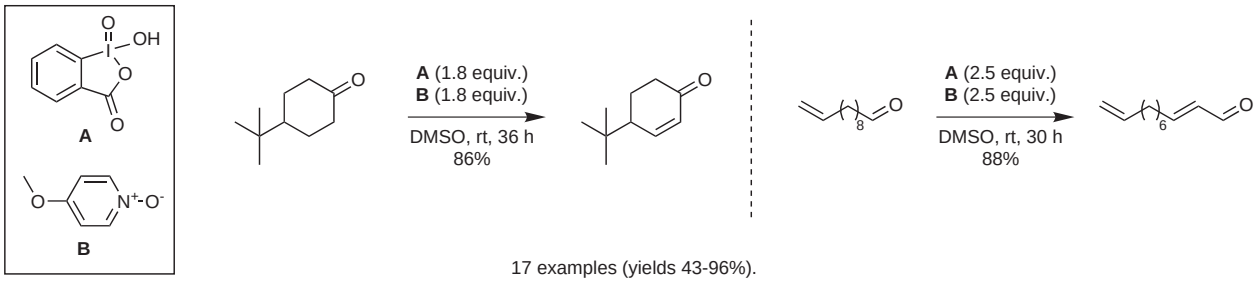
12 examples (yields 20-99%, %ee 8-83%).

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



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

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



17 examples (yields 43-96%).

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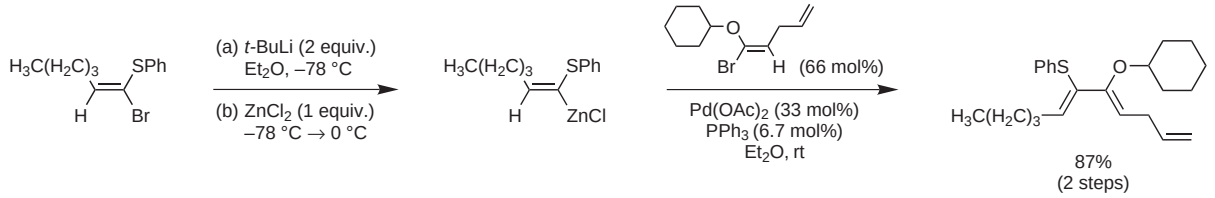
Negishi coupling between α-allyl(aryl)thiovinylzinc chloride and α-bromo vinyl ether.
Su, M.; Kang, Y.; Yu, W.; Hua, Z.; Jin, Z. *Org. Lett*. **2002**, *4*, 691.

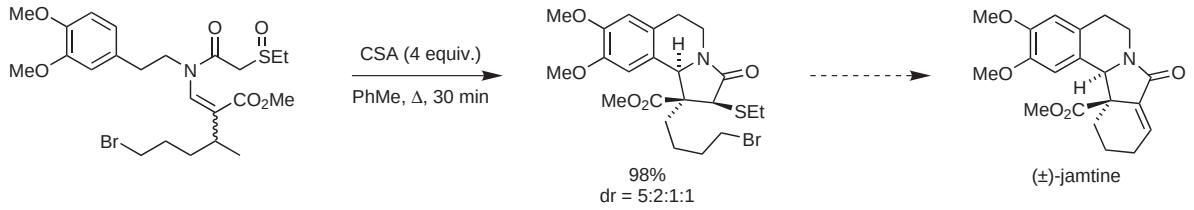
sp^2-sp^2 Coupling



10 examples (yields 70-91%).

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

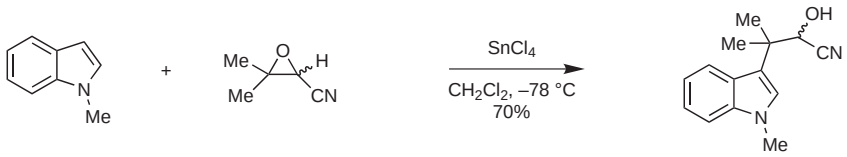
Cyclization



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

$SnCl_4$-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.

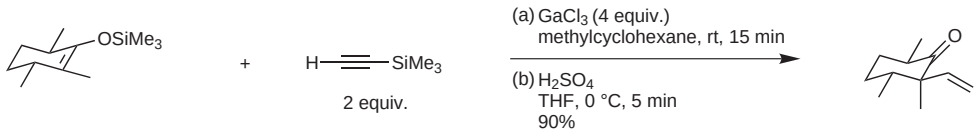
Alkylation



5 examples (yields 69-70%).

$GaCl_3$-promoted equatorial ethenylation of cyclic ketones.
Ansawa, M.; Miyagawa, C.; Yamaguchi, M. *Synthesis*, **2002**, 138.

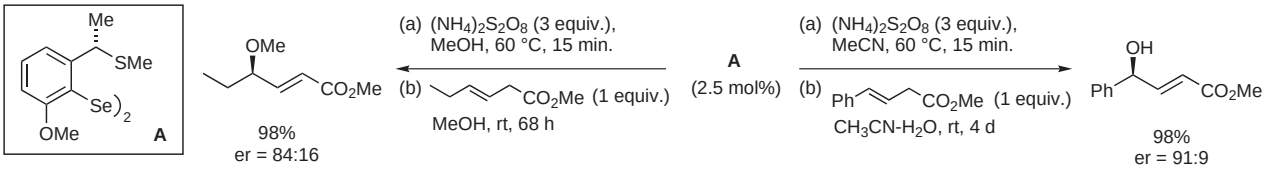
sp^2-sp^2 Coupling



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.; Bagnol i, 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.

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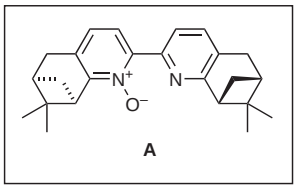
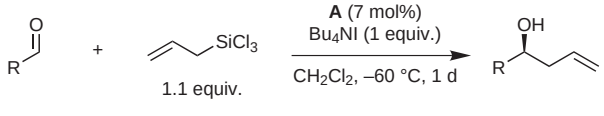
Catalytic enantioselective allylation of aldehydes with allyltrichlorosilane. **Allylation**
Malkov, A. V.; Orsini, M.; Pernazza, D.; Muir, K. W.; Langer, V.; Meghan i, P.; Kocovsky, P. *Org Lett.* **2002**, *4*, 1047.

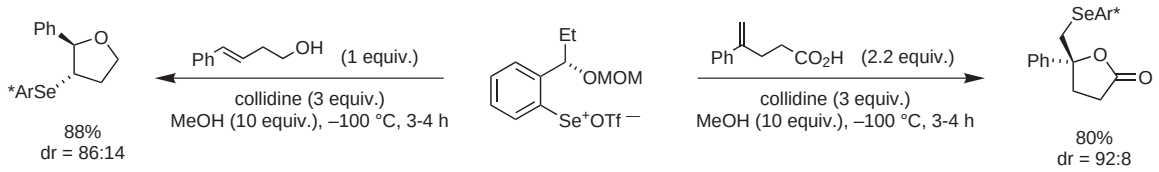




R	Yield	%ee
Ph	78%	90%
p-MePh	71%	87%
p-ClPh	62%	89%
p-NO_2Ph	58%	65%

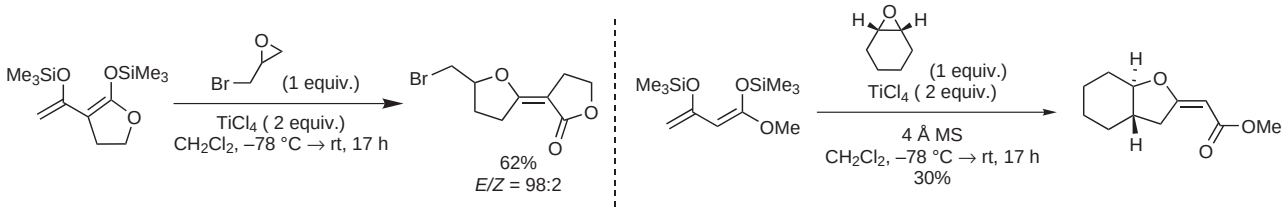
11 examples (yields 10-85%, %ee 4-92%).

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



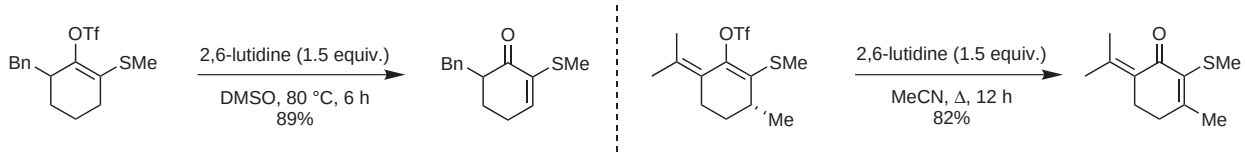
10 examples (yields 41-92%, %de 68-95%).

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



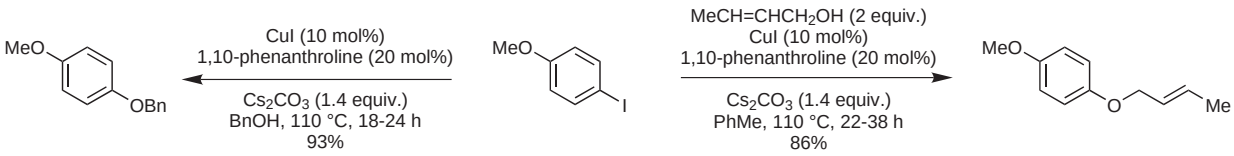
A purification procedure for these compounds utilising an ion-exchange r esin to scavenge by-products is also reported.

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



10 examples (yields 37-89%).

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



15 examples (yields 40-97%) of primary alcohols, 4 examples (yields 6 7-92%) of secondary alcohols and 5 examples (yields 54-96%) of aliphat ic alcohols.

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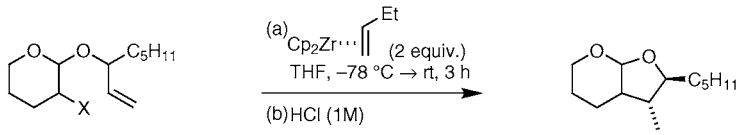
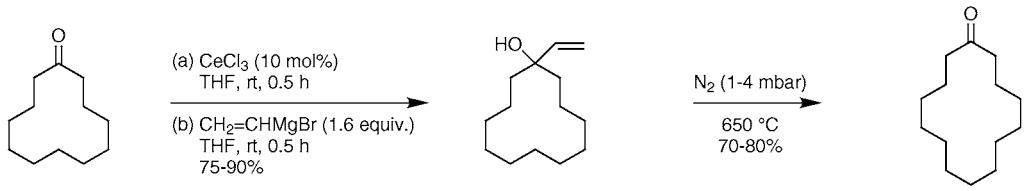
Zirconene-olefin complex mediated radical cyclization reactions. **Radical Cyclization**
Fujita, K.; Yorimitsu, H.; Oshima, K. *Synlett* **2002**, 337.



X	Yield	%de
I	84%	6%
Br	75%	12%

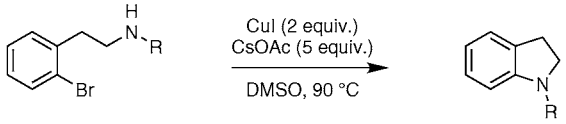
13 examples (yields 34-97%, combined yields for saturated and unsaturated cyclic products).

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



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

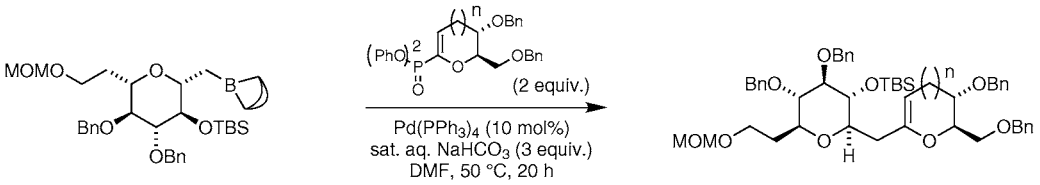
Copper-mediated intramolecular amination of aryl halides. **C,N-Coupling**
Yamada, K.; Kubo, T.; Tokuyama, H.; Fukuyama, T. *Synlett* **2002**, 231.



R	Time	Yield
Ns	1 h	92%
Ac	1 d	66%
CBz	1 d	64%

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%).

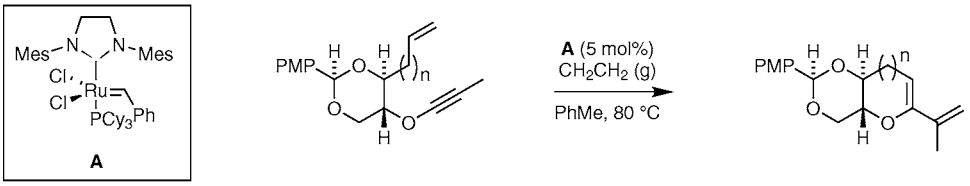
A general strategy for the convergent synthesis of fused polycyclic ethers *via* β-alkyl Suzuki coupling. **sp^3-sp^2 Coupling**
Sasaki, M.; Ishikawa, M.; Fuwa, H.; Tachibana, K. *Tetrahedron* **2002**, *53*, 1889.



n	yield
1	98%
2	97%
3	96%

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 enyne metathesis of alkynyl ethers. **Ring-Closing Metathesis**
Clark, J. S.; Elustondo, F.; Trevitt, G. P.; Boyall, D.; Robertson, J.; Blake, A. J.; Wilson, C.; Stammen, B.
Tetrahedron **2002**, *58*, 1973.



n	Time	yield
1	10 min	98%
2	4 h	72%

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

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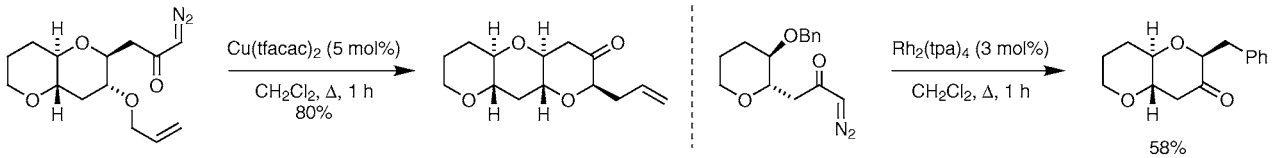
Cyclic oxonium ylides: building blocks for iterative synthesis of polycyclic ethers. **Heteroannulation / [2,3]-Sigmatropic Shift**
Marmsäter, F. P.; Vanecko, J. A.; West, F. G. *Tetrahedron* **2002**, *58*, 2027.



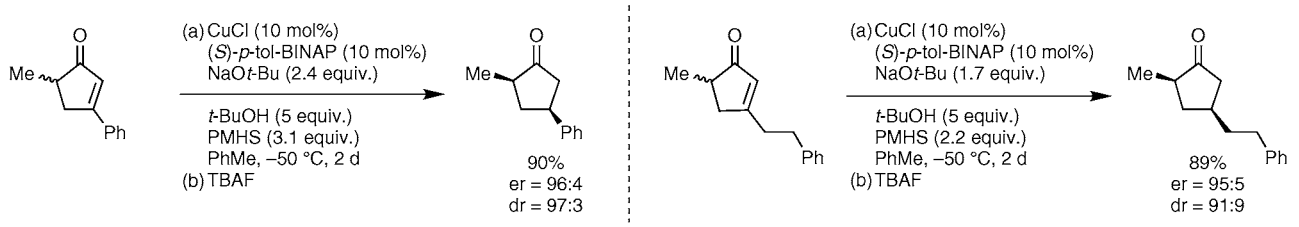
tfacac = tetrafluoroacetoacetonate

tpa = triphenylacetate

58%
α/β = 2.1:1

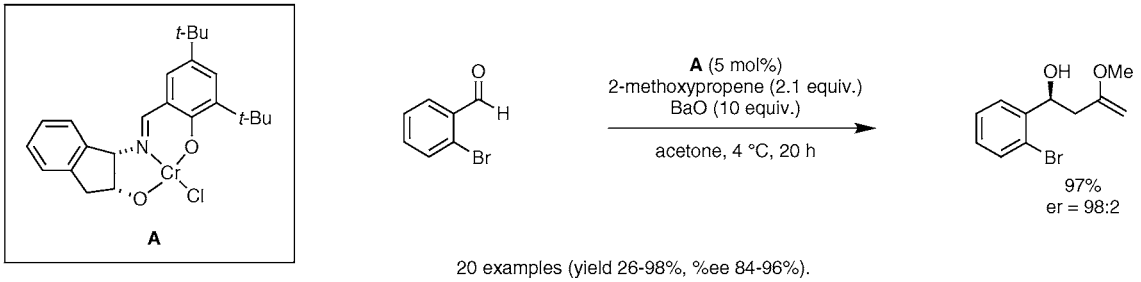
Cyclic oxonium ylide formation followed by a [2,3]-shift (3 examples, yields 45-80%, de 25-98%) or [1,2] and [1,4]-shifts (1 exa mple, yield 70%) are reported.

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



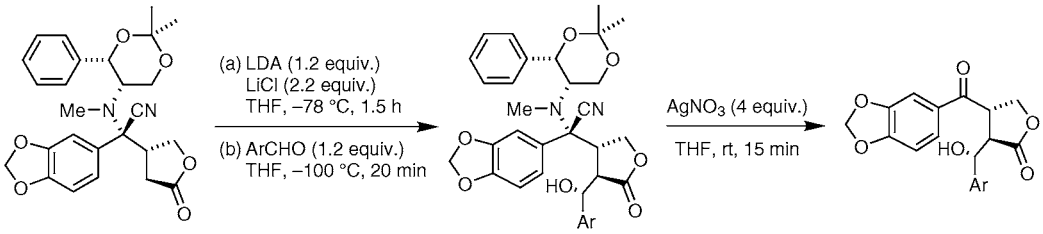
6 examples (yield 89-95%, %ee 91-94%).

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



20 examples (yield 26-98%, %ee 84-96%).

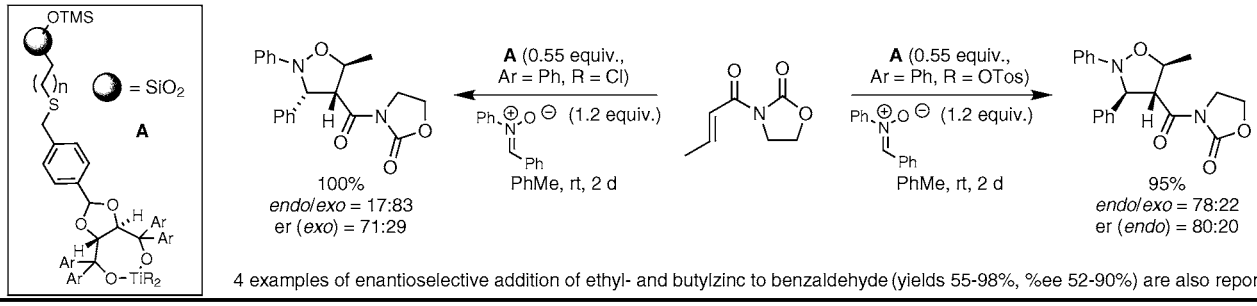
Asymmetric synthesis of lignans. **Diastereoselective Aldol**
Enders, D.; Lausberg, V.; Del Signore, G.; Berner, O. M. *Synthesis* **2002**, 515.



Ar	yield	*syn*:*anti*
veratryl	68%	93:7
piperonyl	65%	88:12
$(MeO)_3Ph$	60%	87:13

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

Immobilization of TADDOLS on silica gel and their use in enantioselectiv e heterogeneous catalysis. **Dipolar Cycloaddition**
Heckel, A.; Seebach, D. *Chem.–Eur. J.* **2002**, *8*, 560.



4 examples of enantioselective addition of ethyl- and butylzinc to benzaldehyde (yields 55-98%, %ee 52-90%) are also reported.

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