

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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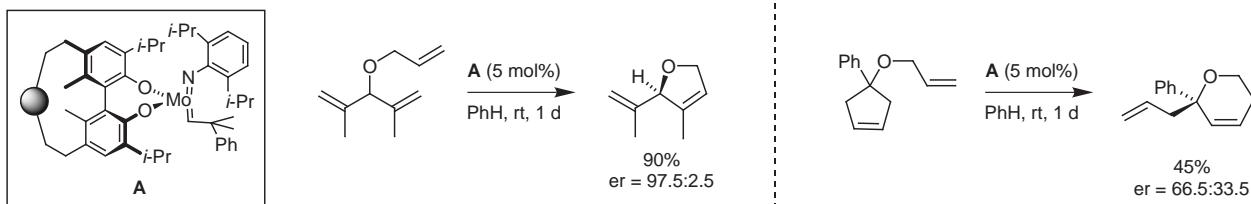
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The journals regularly covered by the abstractors are:

Advanced Synthesis and Catalysis
Angewandte Chemie
Chemical Communications
Chemistry-A European Journal
Collection of Czechoslovak Chemical Communications
European Journal of Organic Chemistry
Helvetica Chimica Acta
Journal of Organic Chemistry
Journal of the American Chemical Society
Organic Letters
Organometallics
Perkin Transactions 1
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry
Tetrahedron Letters

Polymer supported catalytic enantioselective olefin metathesis.
Hultzsch, K. C.; Jernelius, J. A.; Hoveyda, A. H.; Schrock, R. R. *Angew. Chem. Int. Ed.* **2002**, *41*, 589.

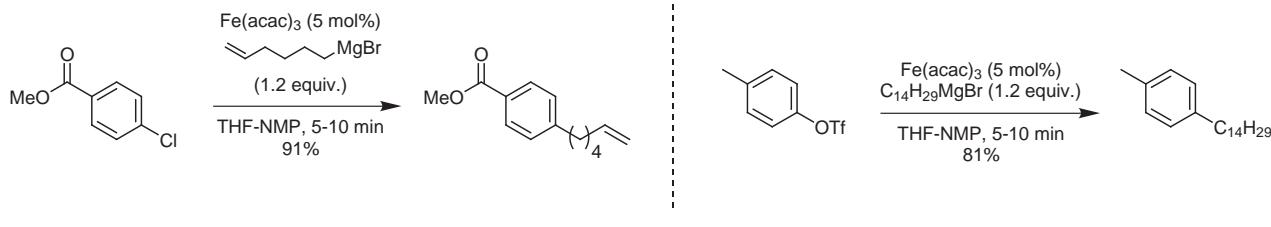
Enantioselective Olefin Metathesis



8 examples (yields 26-92%, %ee 33-98%). Synthesis and recycling of the catalyst are also reported.

Fe-catalysed cross coupling.
Fürstner, A.; Leitner, A. *Angew. Chem. Int. Ed.* **2002**, *41*, 609.

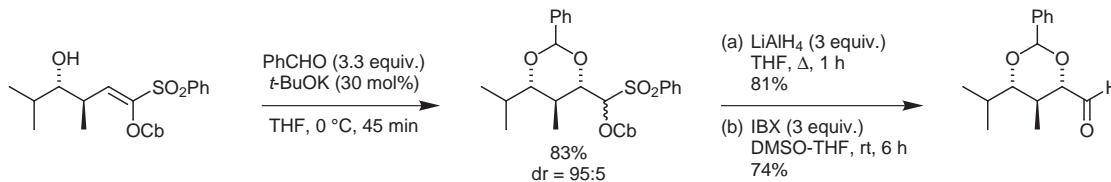
sp²-sp³ Coupling



38 examples (yields 0-96%).

Synthesis of protected syn 1,3-diols.
Grimaud, L.; Mesmay, R.; Prunet, J. *Org. Lett.* **2002**, *4*, 419.

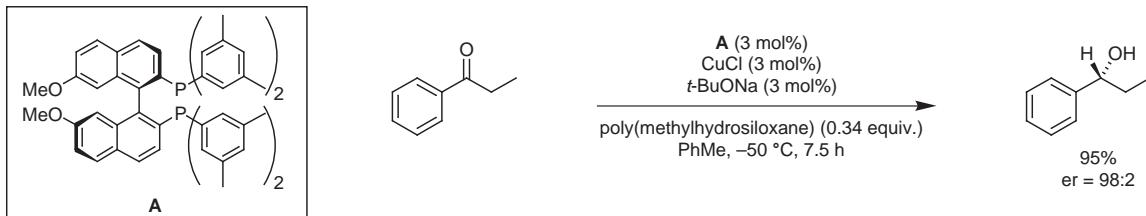
Diastereoselective 1,4-Addition



2 examples of 1,4-addition (yields 83-86%, %de > 90%).

Ligand-accelerated, copper-catalyzed asymmetric hydrosilylations of aryl ketones.
Lipshutz, B. H.; Noson, K.; Chrisman, W. J. *Am. Chem. Soc.* **2001**, 123, 12917.

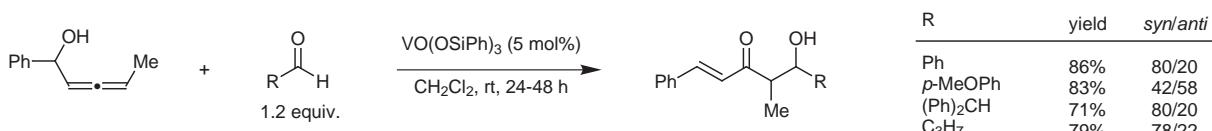
Asymmetric 1,2-Addition



10 Examples (yields 87-99%, %ee 67-97%).

Vanadium-catalyzed aldol reaction of allenic alcohols and aldehydes.
Trost, B. M.; Jonasson, C.; Wuchrer, M. *J. Am. Chem. Soc.* **2001**, 123, 12736.

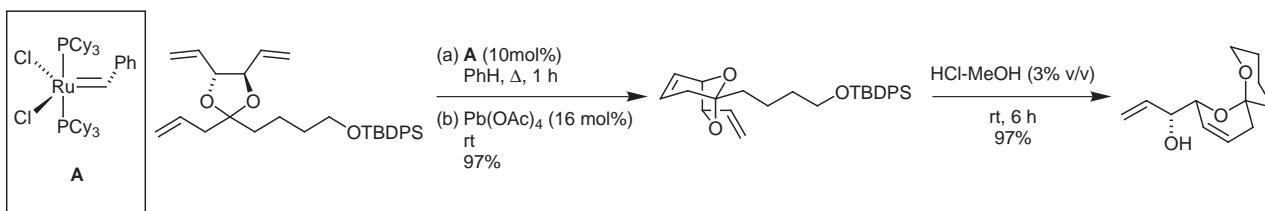
1,2-Addition



15 Examples (yields 57-88%).

Synthesis of 1,7-dioxaspiro[5.5]undecanes.
Keller, V. A.; Martinelli, J. R.; Strieter, E. R.; Burke, S. D. *Org. Lett.* **2002**, 4, 467.

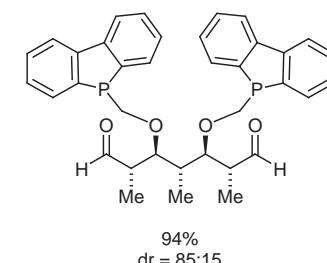
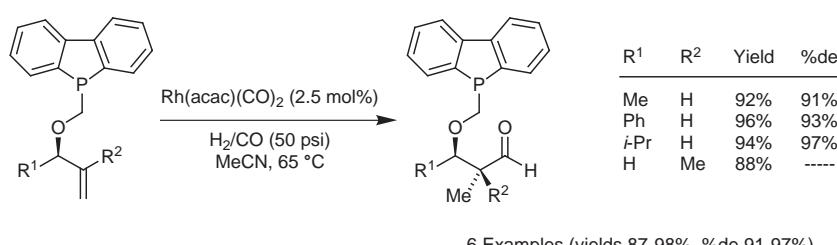
Ring Closing Metathesis/Spiroketalisation



7 examples of acid-catalysed spiroketalisation (yields 71-97%).

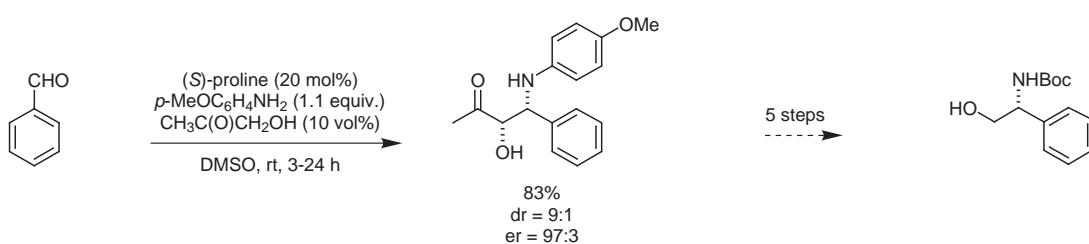
Highly regioselective and diastereoselective directed hydroformylation of allylic ethers.
Krauss, I. J.; Wang, C. C.-Y.; Leighton, J. L. *J. Am. Chem. Soc.* **2001**, 123, 11514.

Hydroformylation



Synthesis of 1,2-amino alcohols via a direct asymmetric three-component Mannich reaction.
List, B.; Pojarliev, P.; Biller, W. T.; Martin, H. J. *J. Am. Chem. Soc.* **2002**, 124, 827.

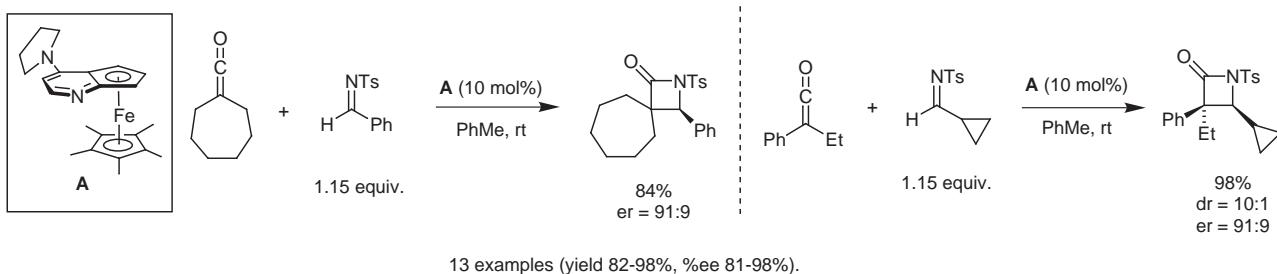
Asymmetric Amination/Alkylation



8 examples (yield 57-92%, %ee 61-99%, dr 3:1 → 20:1). Various ketones and aldehydes were used.

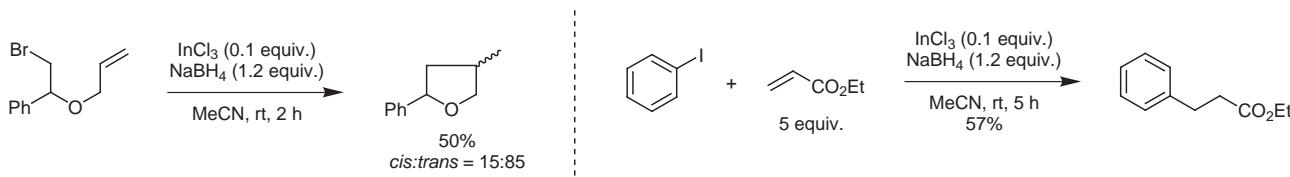
Enantioselective Staudinger synthesis of β -lactams catalyzed by a planar-chiral nucleophile.
Hodous, B. L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 1578.

[2+2] Enantioselective Cycloaddition



Indium(III) chloride-sodium borohydride system as an alternative to tributyltin hydride.
Inoue, K.; Sawada, A.; Shibata, I.; Baba, A. *J. Am. Chem. Soc.* **2002**, *124*, 906.

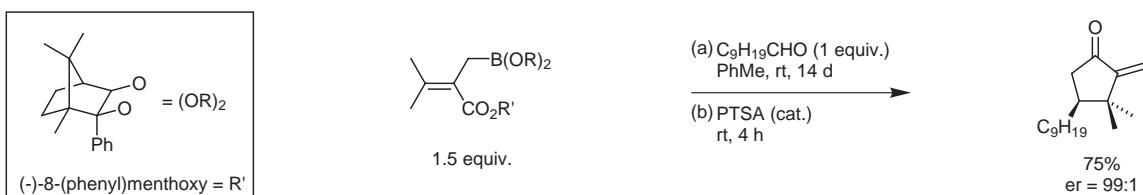
Radical Reduction/Addition



6 examples involving reduction of halides (yield 0-95%), 2 examples of cyclisation (yield 50-62%) and 3 examples of intermolecular addition (yield 45-62%).

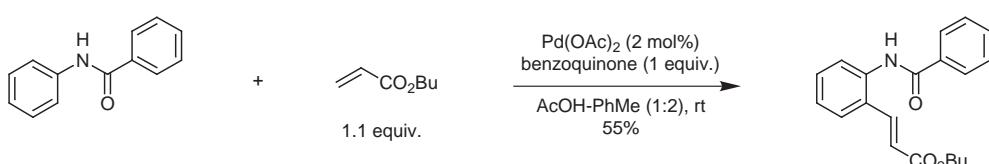
Stereocontrolled synthesis of α -exomethylene γ -lactones with a stereogenic quaternary carbon centre.
Kennedy, J. W. J.; Hall, D. G. *J. Am. Chem. Soc.* **2002**, *124*, 898.

1,2-Addition



9 examples of preparation of tetrasubstituted allylboronates (yield 43-95%, *Z/E* 1.4:1 \rightarrow 20:1) and 18 examples of synthesis of γ -lactones (yield 26-89%, dr 15:1 \rightarrow 20:1).

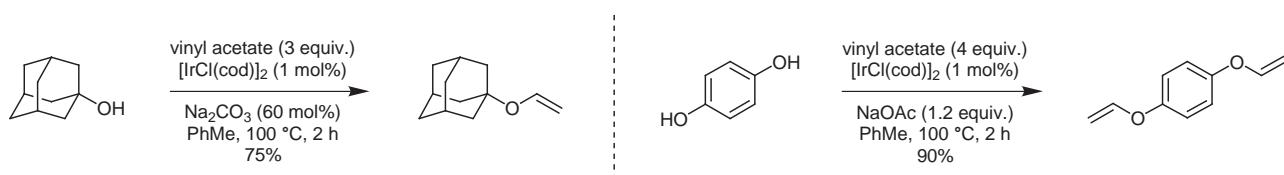
Selective Pd-catalyzed oxidative coupling of anilides with olefins through C-H bond activation.
Boele, M. D. K.; van Strijdonck, G. P. F.; de Vries, A. H. M.; Kamer, P. C. J.; de Vries, J. G.; van Leeuwen, P. W. N. M. *J. Am. Chem. Soc.* **2002**, *124*, 1586.

 sp^2 - sp^2 Coupling

11 examples (yield 0-91%). Various substituted anilide derivatives are reported.

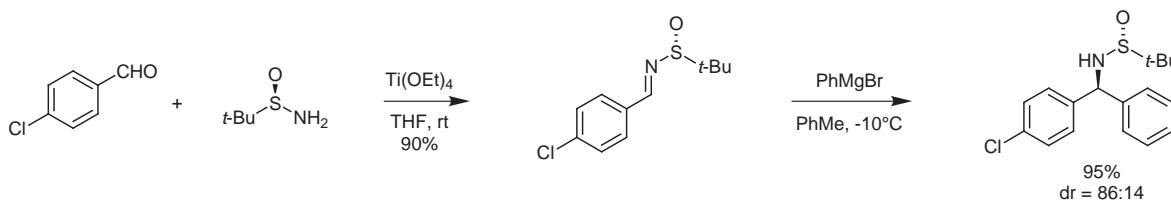
Efficient catalytic synthesis of vinyl ethers.
Okimoto, Y.; Sakaguchi, S.; Ishii, Y. *J. Am. Chem. Soc.* **2002**, *124*, 1590.

Etherification



Asymmetric synthesis of cetirizine dihydrochloride.
Pflum, D. A.; Krishnamurthy, D.; Han, Z.; Wald, S. A.; Senanayake, C. H. *Tetrahedron Lett.* **2002**, *43*, 923.

Asymmetric Addition

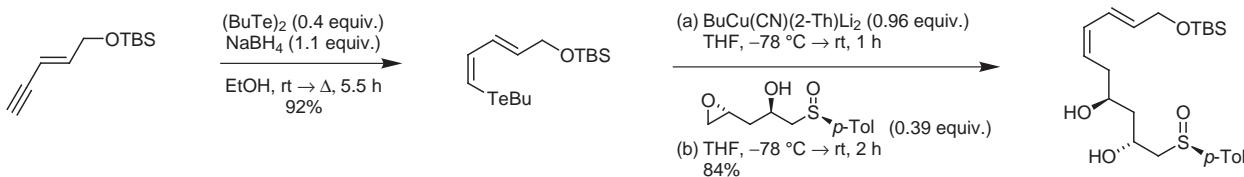


The opposite enantiomer can be synthesised as the major product by starting with benzaldehyde and adding 4-chlorophenylmagnesium bromide. The remaining steps in the synthesis of cetirizine dihydrochloride are also reported.

Stereocontrolled synthesis of (–)-macrolactin A.

Marino, J. P.; McClure, M. S.; Holub, D. P.; Comasseto, J. V.; Tucci, F. C. *J. Am. Chem. Soc.* **2002**, *124*, 1664.

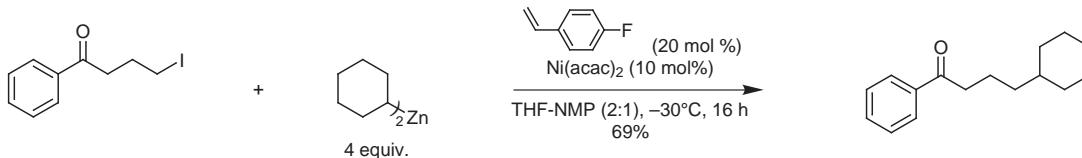
Hydrometalation/Alkylation



This is the first reported use of vinyl tellurides in the synthesis of a natural product.

Nickel-catalyzed cross-coupling of alkylzinc halides and alkyl halides.
Jensen, A. E.; Knochel, P. *J. Org. Chem.* **2002**, *67*, 79.

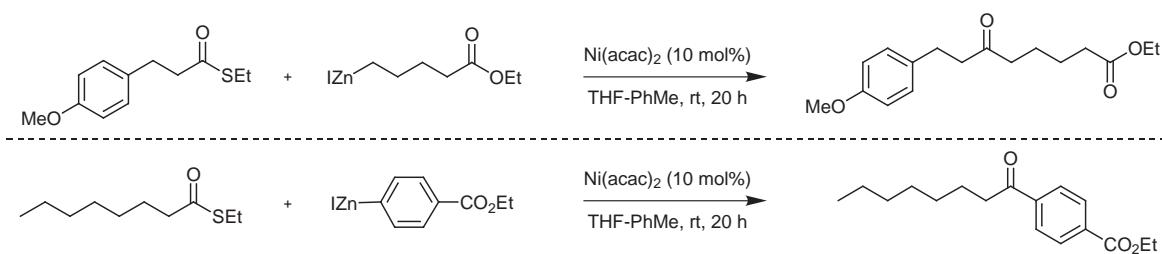
sp^3-sp^3 Coupling



25 examples (yields 48-82%).

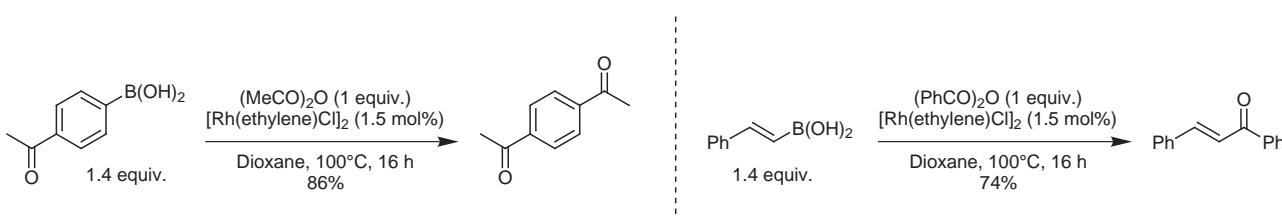
Nickel-catalyzed coupling of organozinc reagents with thioesters to give functionalized ketones.
Shimizu, T.; Seki, M. *Tetrahedron Lett.* **2002**, *43*, 1039.

sp^2-sp^3 Coupling



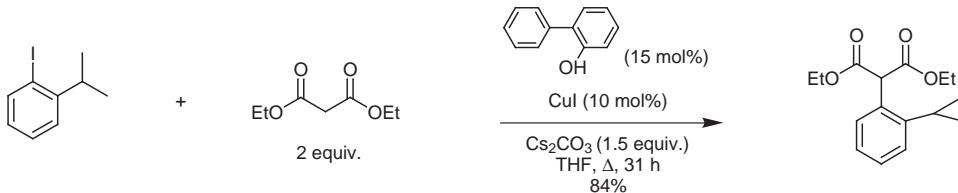
Rhodium-catalyzed addition of boronic acids to anhydrides.
Frost, C. G.; Wadsworth, K. *J. Chem. Commun.* **2001**, 2316.

sp^2-sp^2 Coupling



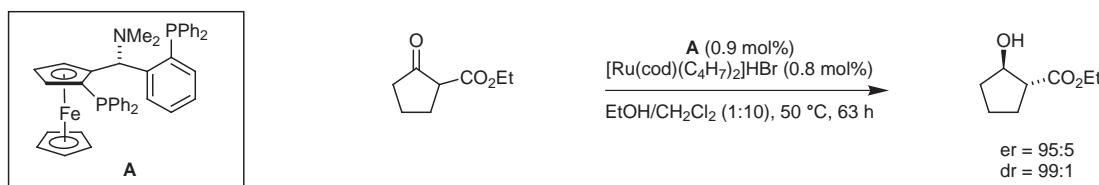
A mild copper-catalyzed arylation of diethyl malonate
Hennessy, E. J.; Buchwald, S. L. *Org. Lett.* **2002**, *4*, 269.

Arylation



Chiral 1,5-diphosphorylferrocene ligands for enantioselective hydrogenation
Ireland, T.; Tappe, K.; Grossheimann, G.; Knochel, P. *Chem. Eur. J.* **2002**, *8*, 843.

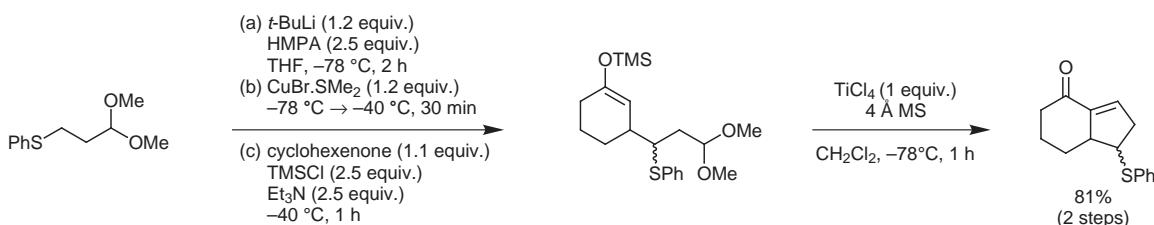
Enantioselective Hydrogenation



Examples of hydrogenation of α -(acylamino)acrylic acids, enol esters, enamides, 1,3-diketones and hydrazones using Rh- or Ru-catalysts with ferrocenylphosphanes.

Cyclopentannulation of enones with acetal or orthoester organocuprates
Ding, P.; Ghosez, L. *Tetrahedron*, **2002**, *58*, 1565.

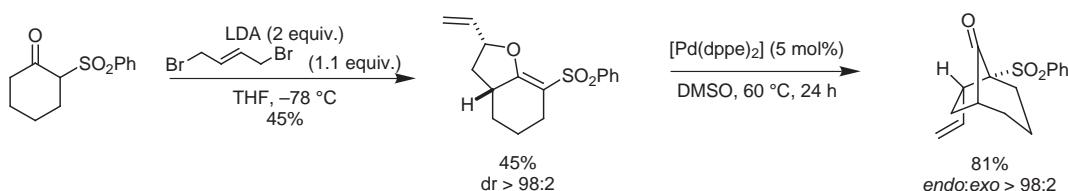
1,4-Addition/Cyclization



5 examples of acetal organocuprates (yields 40-93%) and 1 example of an orthoester organocuprate.

Bicyclo[3.2.1]octan-8-ones by Pd-catalysed isomerisation of 2-vinyl-hexahydro-2,3-benzofurans.
Langer, P.; Holtz, E.; Saleh, N. N. R. *Chem.-Eur. J.* **2002**, *8*, 917.

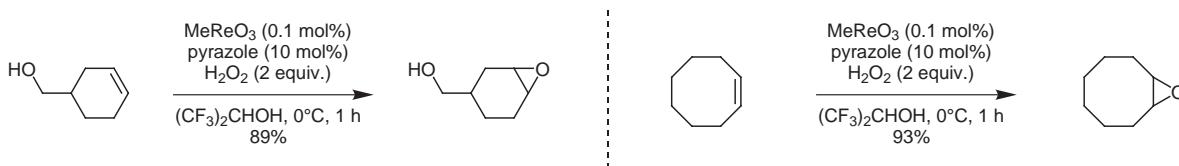
Isomerization



10 examples of bicyclo[3.2.1]octan-8-ones. High *endo*:*exo* selectivity obtained for the Pd-catalysed rearrangement with β -ketosulfones, but poor stereoselectivity for β -ketoesters.

Enhancement of methyltrioxorhenium-catalyzed epoxidation of alkenes by hexafluoro-2-propanol.
Iskra, J.; Bonnet-Deplon, D.; Bégué, J. P. *Tetrahedron Lett.* **2002**, *43*, 1001.

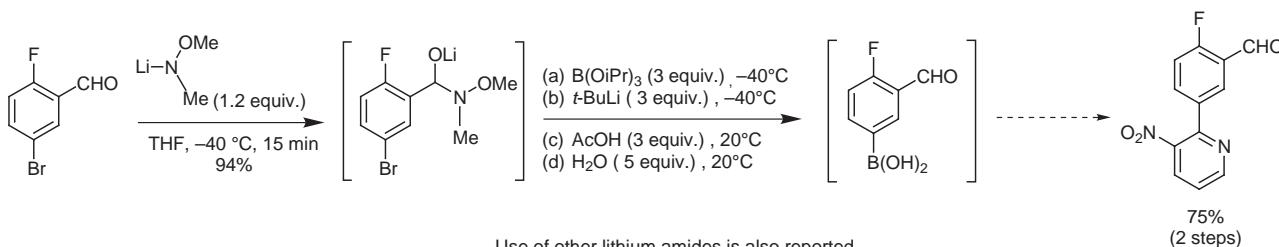
Epoxidation



7 examples (yields 80-93%).

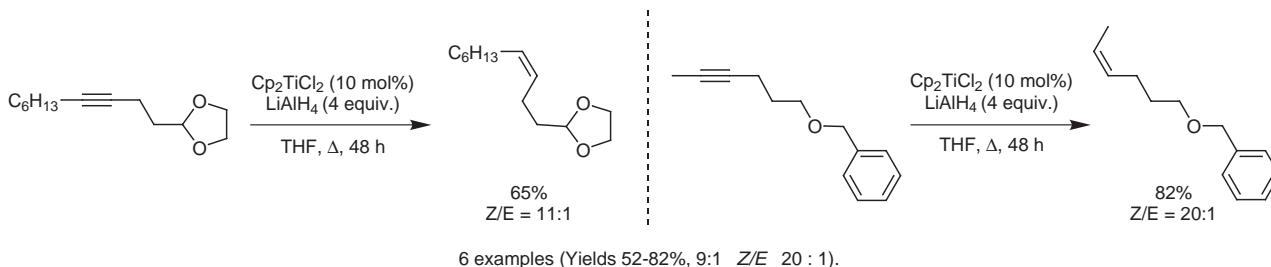
Lithium *N,O*-dimethylhydroxyamide (LDHA) as an *in situ* protecting group for aromatic aldehydes.
Roschangar, F.; Brown, J. C.; Cooley Jr., B. E.; Sharp, M. J.; Matsuoka, R. T. *Tetrahedron* **2002**, *58*, 1657.

Protecting Group



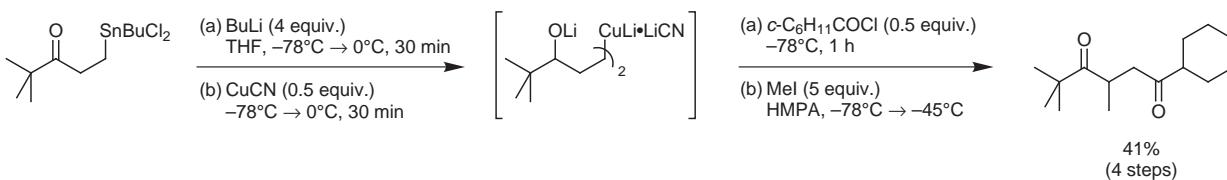
Stereoselective titanium-catalyzed hydroalumination of internal alkynes.
Parenty, A.; Campagne, J. M. *Tetrahedron Lett.* **2002**, *43*, 1231.

Stereoselective Reduction



Cross-coupling reaction of dianion cuprates with acid chlorides.
Ryu, I.; Ibeke, M.; Sonoda, N.; Yamato, S.-Y.; Yamamura, G.-H.; Komatsu, M. *Tetrahedron Lett.* **2002**, *43*, 1257.

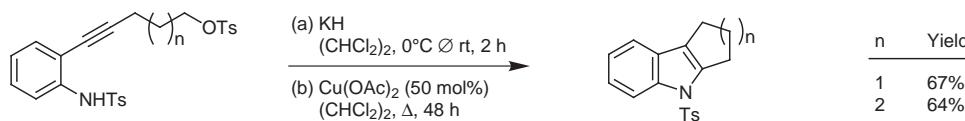
Acylation



11 examples of 1,4 unsymmetrical diketones (Yields 40-76%), including 2 examples of three-component coupling (Yields 41-59%).

Copper-catalyzed indole formation from 2-ethynylaniline derivatives.
Hiroya, K.; Itoh, S.; Ozawa, M.; Kanamori, Y.; Sakamoto, T. *Tetrahedron Lett.* **2002**, *43*, 1277.

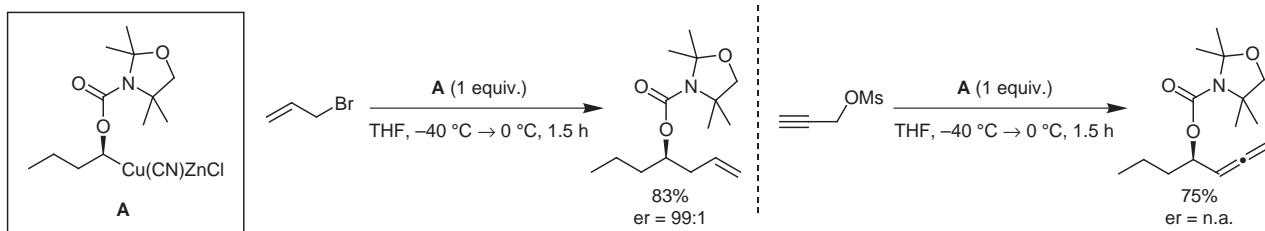
Heteroannulation



16 examples of indole cyclisation (Yields 9-95%)

Preparation and utilization of nonracemic secondary α -(carbamoyloxy)alkylzinc and copper reagents.
Papillon, J. P.; Taylor, R. J. K. *Org Lett.* **2002**, *4*, 119.

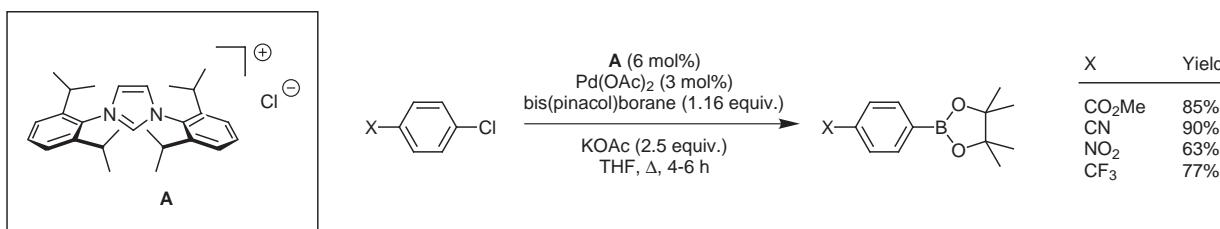
C-C Coupling



11 examples (yields 0-83%) are reported as well as the synthesis of A.

Pinacol boronate synthesis catalyzed by a palladium/imidazolium salt system.
Fürstner, A.; Seidel, G. *Org Lett.* **2002**, *4*, 541.

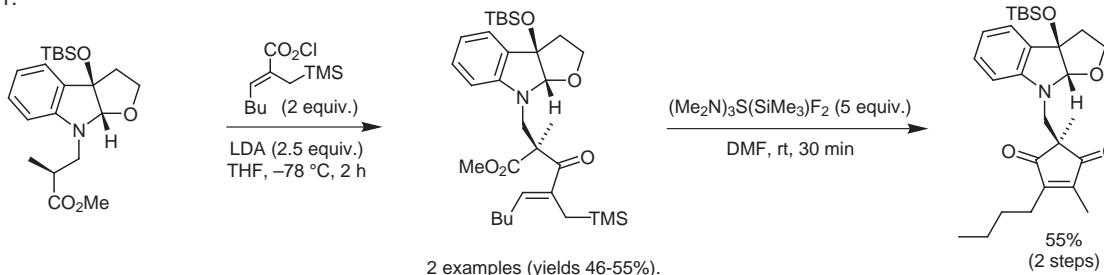
Borylation



8 examples (yields 53–90%).

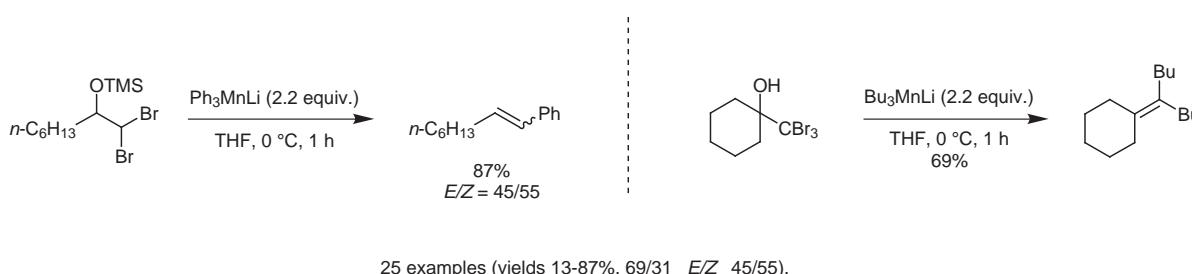
Chelation-controlled 1,4-diastereoselective acylation/intramolecular acylation sequence.
Hirose, T.; Sunazuka, T.; Shirahata, T.; Yamamoto, D.; Harigaya, Y.; Kuwajima, I.; Omura, S. *Org Lett.* **2002**, *4*, 501.

Diastereoselective Acylation



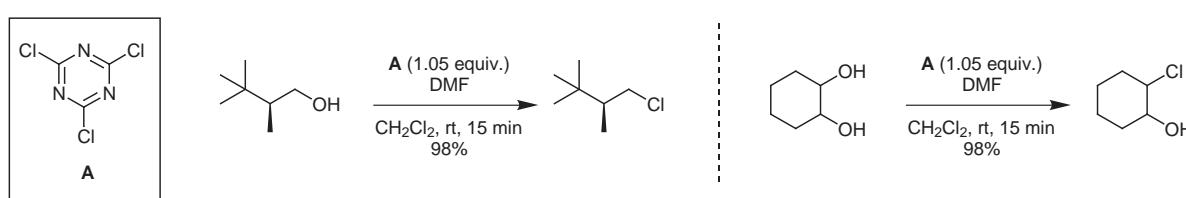
Substituted alkenes via migration-elimination reaction.
Kakiya, H.; Shinokubo, H.; Oshima, K. *Tetrahedron* **2001**, *57*, 10063.

Migration-Elimination



Alkyl chlorides from alcohols using 2,4,6-trichloro[1,3,5]triazine and DMF.
De Luca, L.; Giacomelli, G.; Porcheddu, A. *Org Lett.* **2002**, *4*, 553.

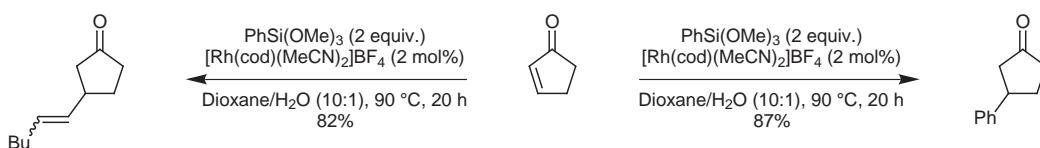
Chlorination



12 examples of aliphatic alcohols (yields 96–99%), 3 examples of diols (yields 95–98%), 2 examples of unsaturated alcohols (yields 92–98%) and 6 examples of β-amino alcohols (yields 83–97%).

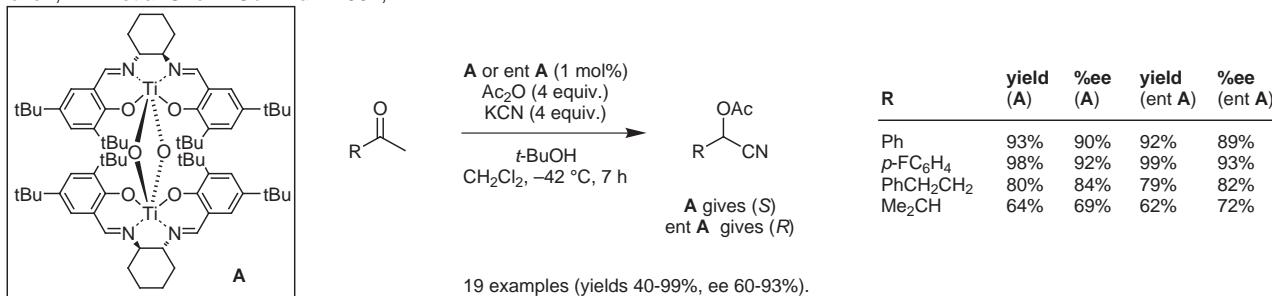
Rh-catalyzed conjugate addition of organosiloxanes to α,β-unsaturated carbonyl compounds.
Oi, S.; Honma, Y.; Inoue, Y. *Org Lett.* **2002**, *4*, 667.

1,4-Addition



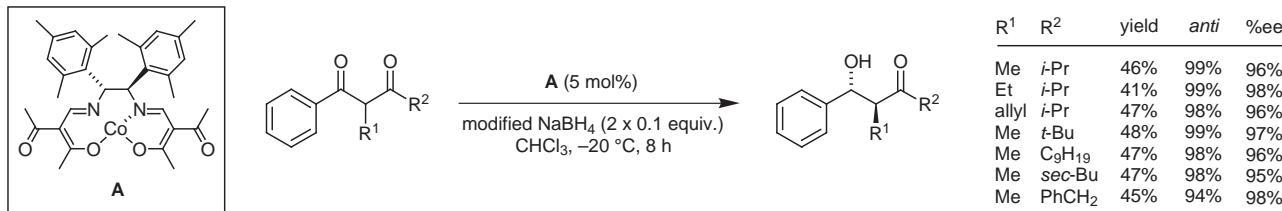
14 examples (yields 72–97%).

Catalytic asymmetric synthesis of O-acetyl cyanohydrins from potassium cyanide, acetic anhydride and aldehydes. **Asymmetric Addition**
Belokon, Y. N. et al *Chem. Commun.* **2002**, 244.



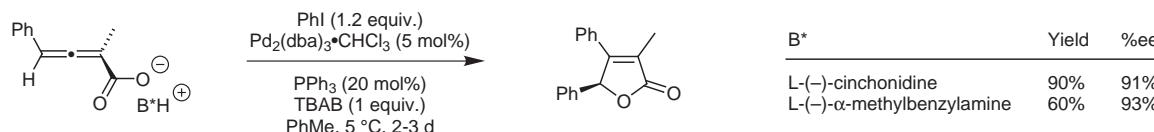
Chemo-, diastereo-, and enantioselective reduction of 1,2-dialkyl-3-aryl-1,3-diketones.
Ohtsuka, Y.; Koyasu, K.; Miyazaki, D.; Ikeno, T.; Yamada, T. *Org. Lett.* **2001**, 3, 3421.

Enantioselective Reduction



Chirality transfer in Pd(0)-catalyzed coupling-cyclization of aryl iodides.
Ma, S.; Shi, Z. *Chem. Commun.* **2002**, 540.

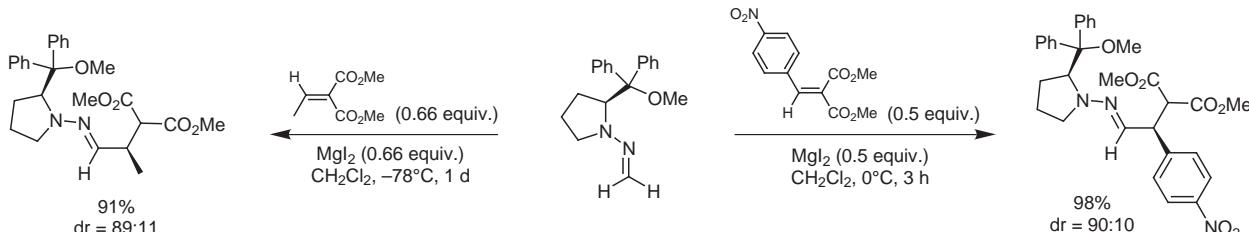
Enantioselective Coupling-Cyclization



11 examples (yields 55-90%, ee 91-98%).

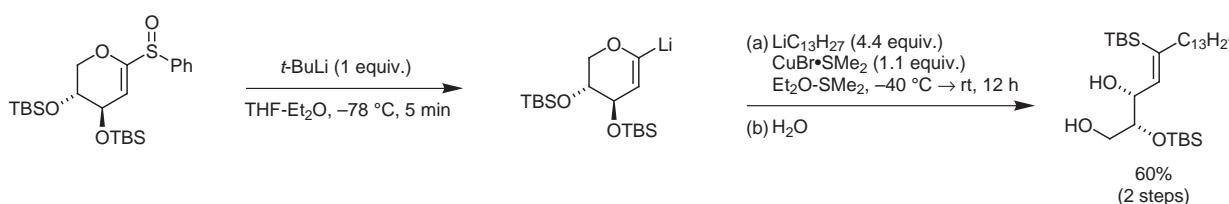
Asymmetric Michael addition of formaldehyde N,N-dialkylhydrazones to alkylidene malonates.
Vázquez, J.; Prieto, A.; Fernández, R.; Enders, D.; Lassalleta, J. M. *Chem. Commun.* **2002**, 498.

Asymmetric Michael Addition



1,2-Metallate rearrangement in the synthesis of D-erythro-sphingosine and D-erythro-ceramide.
Milne, J. E.; Jarowicki, K.; Kocienski, P. J.; Alonso, J. *Chem. Commun.* **2002**, 426.

1,2-Metallate Rearrangement



The remaining steps in the total synthesis of D-erythro-sphingosine are also reported.