

**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, Bernard 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** 2003, No. 17, pp 2743–2750

Advanced online publication: 21.11.2003

Art ID: X01703SS.pdf

© 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

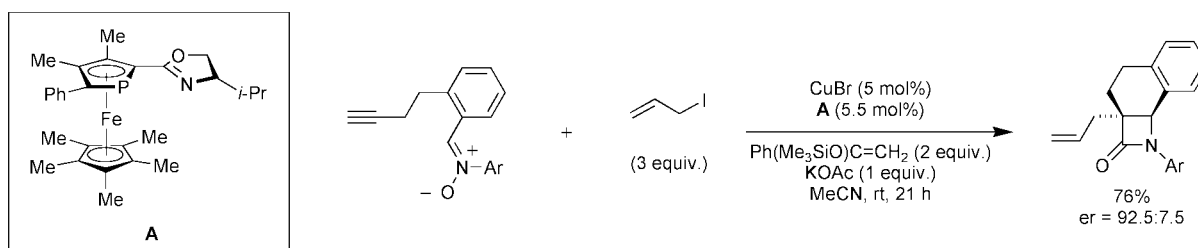
Synthesis

Tetrahedron

Tetrahedron Asymmetry and Tetrahedron Letters

Enantioselective synthesis of  $\beta$ -lactams via an intramolecular Kinugasa reaction.  
Shintani, R.; Fu, G. C. *Angew. Chem. Int. Ed.* **2003**, *42*, 4082.

Annulation

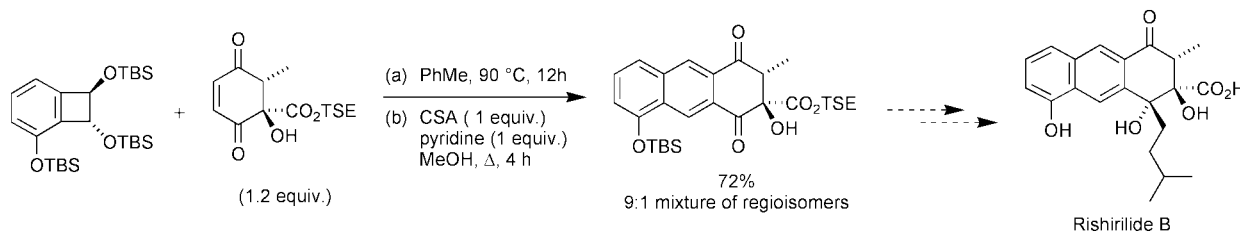


Ar = *p*-carboethoxyphenyl. 12 examples (yields 30–76%, %ee 6–91%).

Total synthesis of Rishirilide B.

Yamamoto, K.; Hentemann, M. F.; Allen, J. G.; Danishefsky, S. J. *Chem.–Eur. J.* **2003**, *9*, 3242.

Diels–Alder

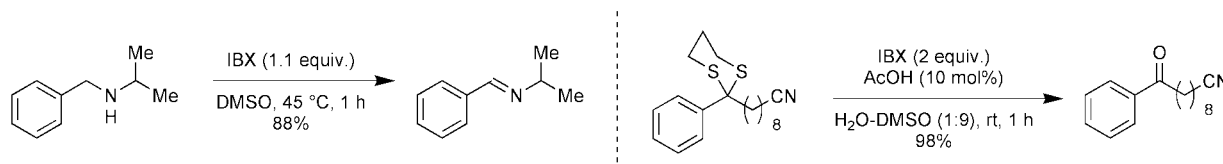


TSE = 2-(trimethylsilyl)ethyl.

IBX oxidation of nitrogen and sulfur-containing substrates.

Nicolaou, K. C.; Mathison, C. J. N.; Montagnon, T. *Angew. Chem. Int. Ed.* **2003**, *42*, 4077.

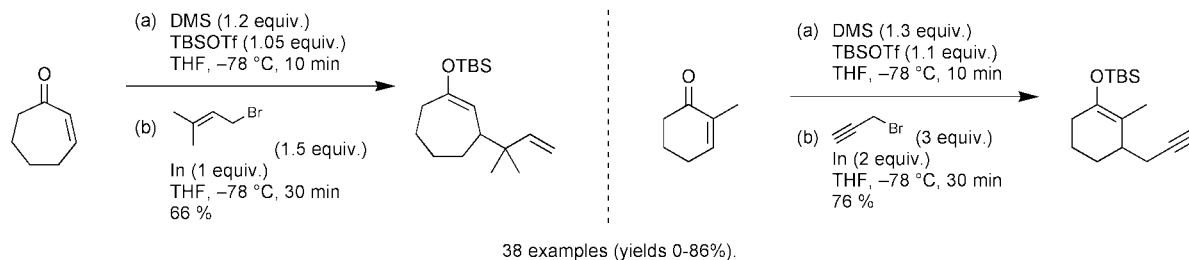
Oxidation



Amines: 19 examples (yields 49–98%). Dithianes: 6 examples (yields 95–99%).

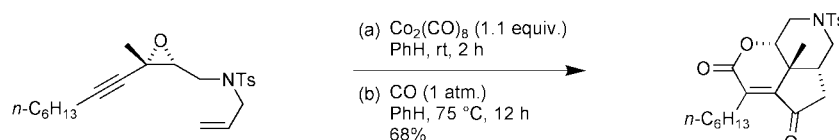
Indium-mediated  $\beta$ -allylation, propargylation and allenylation of  $\alpha,\beta$ -unsaturated ketones. Lee, K.; Kim, H.; Miura, T.; Kiyota, K.; Kusama, H.; Kim, S.; Iwasawa, N.; Lee, P. H. *J. Am. Chem. Soc.* **2003**, *125*, 9682.

1,4-Addition/Substitution



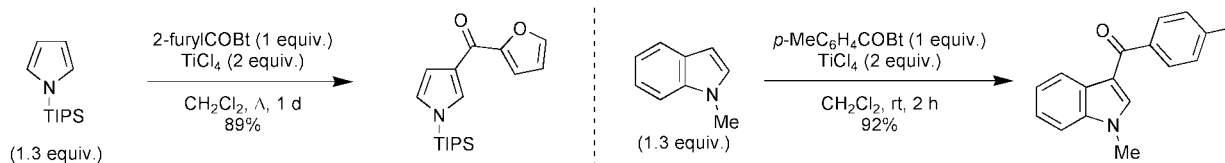
Synthesis of tricyclic  $\delta$ -lactones via a  $\text{Co}_2(\text{CO})_8$ -mediated tandem  $[5+1]/[2+2+1]$  cycloaddition reaction. Odedra, A.; Wu, C.-J.; Madhushaw, R. J.; Wang, S.-L.; Liu, R.-S. *J. Am. Chem. Soc.* **2003**, *125*, 9610.

Annulation

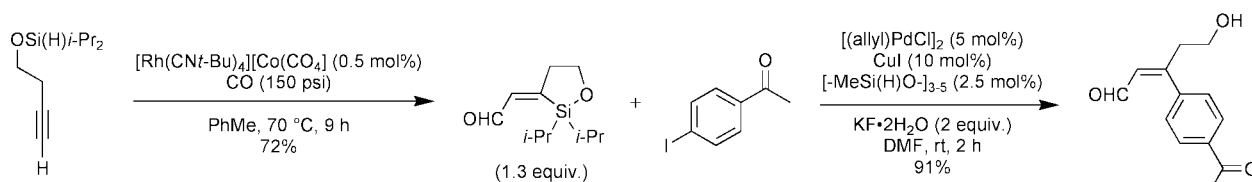


Regiospecific C-acylation of pyrroles and indoles using *N*-acylbenzotriazoles. Katritzky, A. R.; Suzuki, K.; Singh, S. K.; He, H.-Y. *J. Org. Chem.* **2003**, *68*, 5720.

Acylation

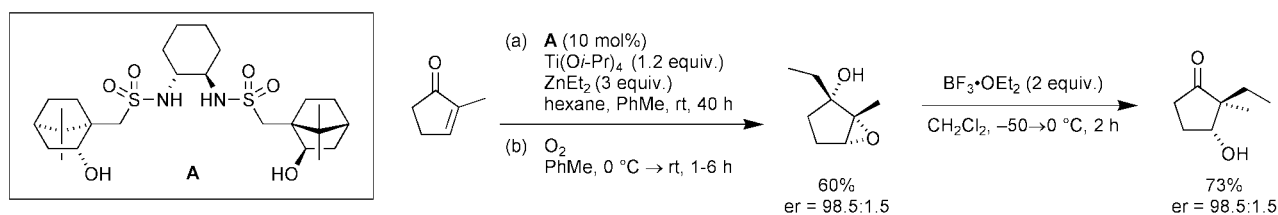


Tandem intramolecular silylformylation and silicon-assisted cross-coupling reactions. Denmark, S. E.; Kobayashi, T. *J. Org. Chem.* **2003**, *68*, 5153.

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

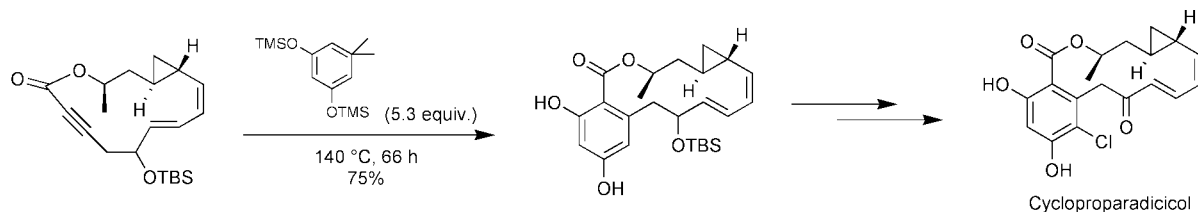
A tandem enantioselective alkylzinc addition to cyclic  $\alpha,\beta$ -unsaturated ketones/diastereoselective epoxidation. Jeon, S.-J.; Walsh, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 9544.

1,2-Addition/Epoxidation



Synthesis of benzo-fused macrolactones via ynohides.  
 Yang, Z.-Q.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 9602.

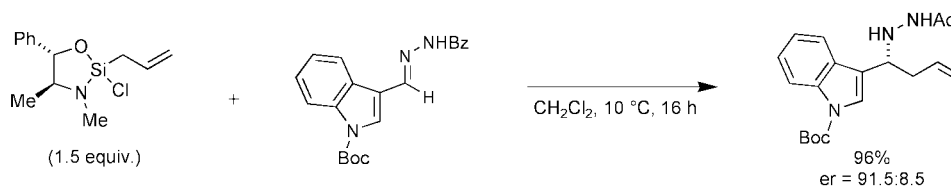
Diels–Alder



A total synthesis of cycloproparadicicol is also reported.

Enantioselective allylation of acylhydrazones using strained silacycles.  
 Berger, R.; Rabbatt, P. M. A.; Leighton, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 9596.

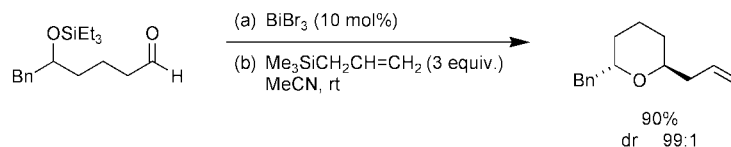
Allylation/Crotylation



17 examples of allylations and 2 examples of crotylations (yields 49–96%, %ee 23–99%, %de 90–92%).

Stereoselective formation of *cis*- and *trans*-2,6-substituted tetrahydropyran rings catalyzed by bismuth tribromide.  
 Evans, P. A.; Cui, J.; Gharpure, S. J.; Hinkle, R. J. *J. Am. Chem. Soc.* **2003**, *125*, 11456.

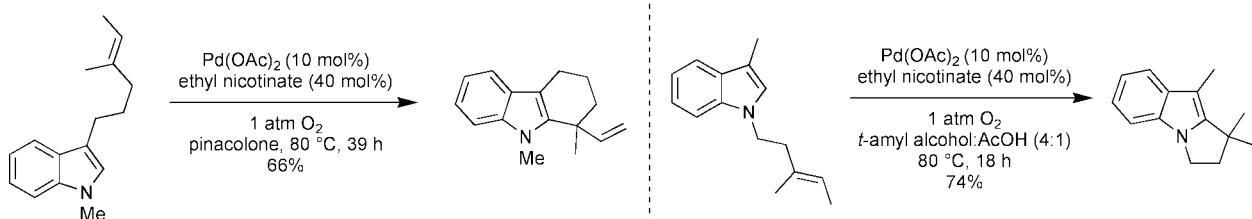
Annulation



The coupling reactions with carbon nucleophiles give *trans*-diastereomers, whilst the reductive coupling gives *cis*-diastereomers.  
 10 examples (yields 72–95%, %de 90–98%).

Palladium(II)-catalyzed oxidative annulation of indoles.  
 Ferreira, E. M.; Stoltz, B. M. *J. Am. Chem. Soc.* **2003**, *125*, 9578.

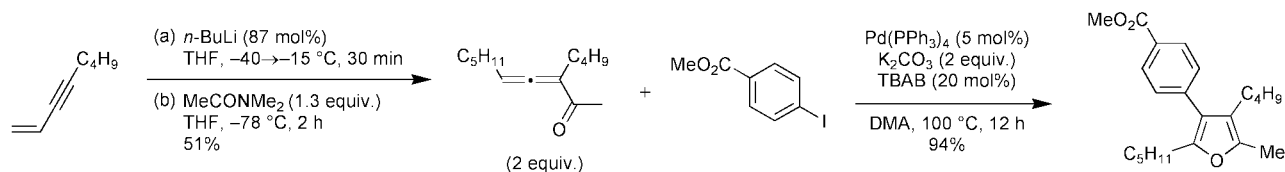
Annulation



13 examples (yields 60–82%).

Synthesis of 2,3,4-, 2,3,5- and 2,3,4,5-substituted furans via a Pd(0)-catalyzed coupling cyclization.  
 Ma, S.; Zhang, J.; Lu, L. *Chem.–Eur. J.* **2003**, *9*, 2447.

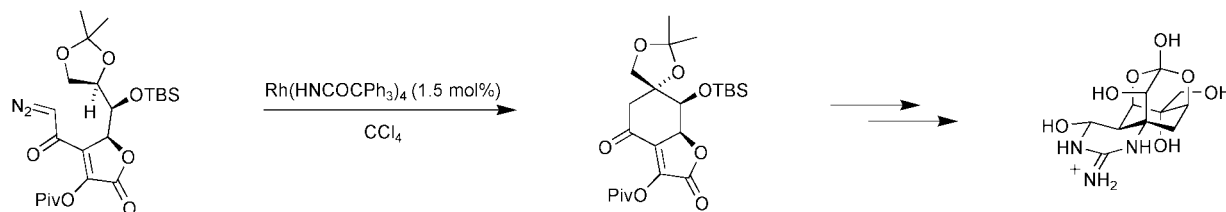
Annulation



Mechanistic studies investigated. 29 examples (yields 51–97%).

Stereoselective synthesis of (-)-Tetrodotoxin.  
Hinman, A.; Du Bois, J. *J. Am. Chem. Soc.* **2003**, *125*, 11510.

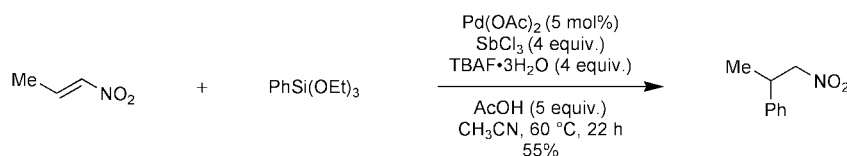
Stereospecific Carbene C-H Insertion



A stereospecific Rh-nitrene C-H insertion is also applied in the total synthesis.

Pd-catalyzed conjugate addition of organosiloxanes to  $\alpha,\beta$ -unsaturated carbonyl compounds and nitroalkenes.  
Denmark, S. E.; Amishiro, N. *J. Org. Chem.* **2003**, *68*, 6997.

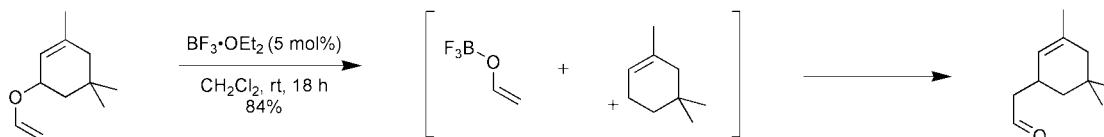
1,4-Addition



29 examples (0-93%).

Lewis acid-catalyzed cleavage and subsequent alkylation of enol ethers.  
Gansauer, A.; Fielenbach, D.; Stock, C.; Geich-Gimbel, D. *Adv. Synth. Catal.* **2003**, *345*, 1017.

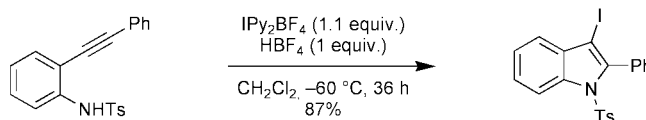
[1,3]-Rearrangement



Mechanistic studies were included. 32 examples (yields 32-87%).

Intramolecular addition of anilines to alkynes promoted by IPy<sub>2</sub>BF<sub>4</sub>.  
Barluenga, J.; Trincado, M.; Rubio, E.; Gonzalez, J. M. *Angew. Chem. Int. Ed.* **2003**, *42*, 2406.

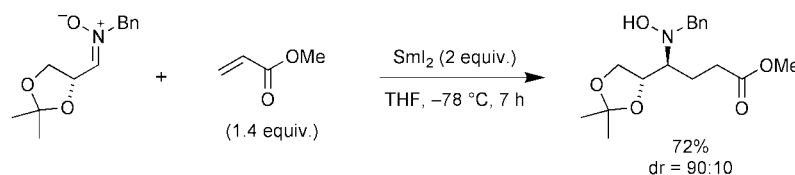
Annulation



12 examples (yields 10-87%). A solid-supported version is also reported.

Reductive conjugate addition of nitrones to  $\alpha,\beta$ -unsaturated esters using Sml<sub>2</sub>.  
Masson, G.; Cividino, P.; Py, S.; Vallee, Y. *Angew. Chem. Int. Ed.* **2003**, *42*, 2265.

1,4-Addition

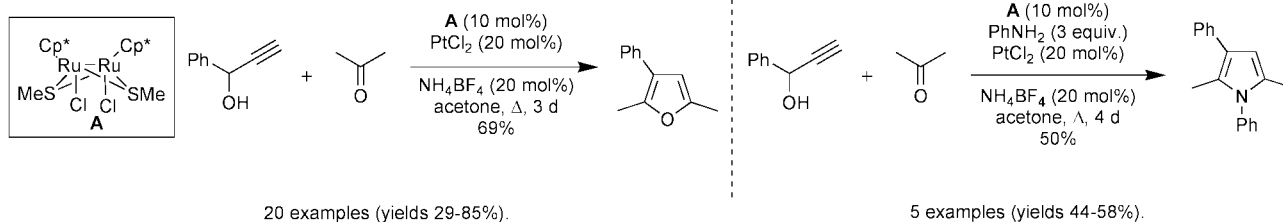


25 examples (yields 10-96%, %de 20-90%) including enantioselective 1,4-additions by use of chiral auxiliaries at the nitrogen centre.

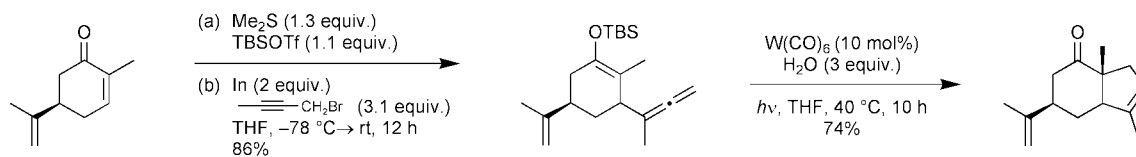
Ruthenium- and platinum catalyzed-synthesis of tri- and tetra-substituted furans and pyrroles.

Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; Milton, M. D.; Hidai, M.; Uemura, S. *Angew. Chem. Int. Ed.* **2003**, *42*, 2681.

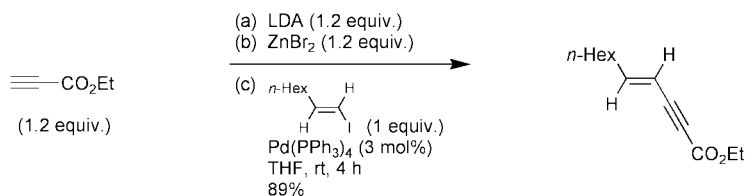
Annulation

 $W(CO)_5(L)$ -catalyzed cyclization of allenyl silyl enol ethers.Miura, T.; Kiyota, K.; Kusama, H.; Lee, K.; Kim, H.; Kim, S.; Lee, P. H.; Iwasawa, N. *Org. Lett.* **2003**, *5*, 1725.

Annulation



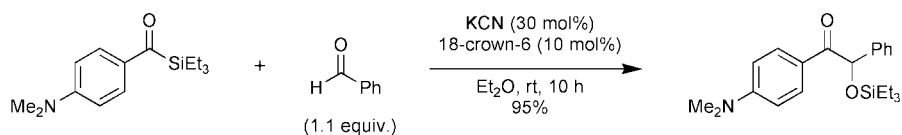
Pd-catalyzed cross-coupling of alkynylzincs with alkenyl halides.

Negishi, E.; Qian, M.; Zeng, F.; Anastasia, L.; Babinski, D. *Org. Lett.* **2003**, *5*, 1597.sp-sp<sup>2</sup> Coupling

Regiospecific cyanide-catalyzed cross silyl benzoin reaction.

Linghu, X.; Johnson, J. S. *Angew. Chem. Int. Ed.* **2003**, *42*, 2534.

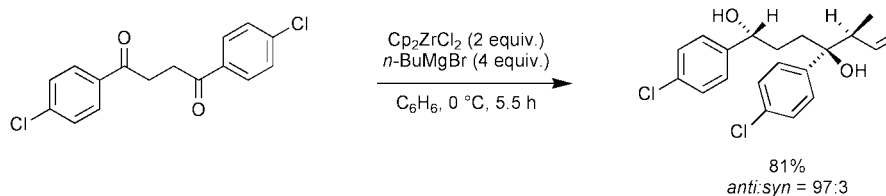
Nucleophilic Addition



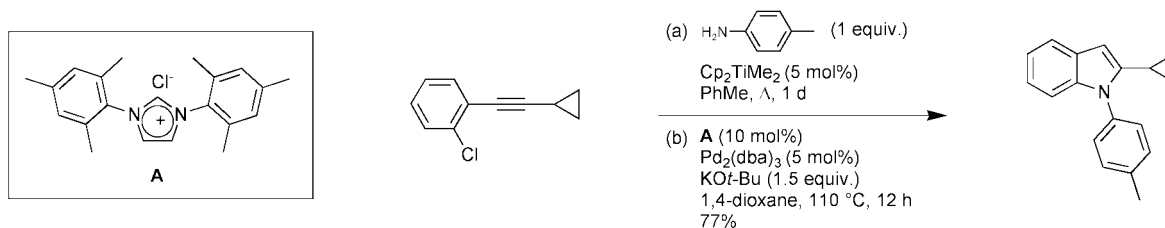
Highly diastereoselective tandem reduction-allylation reactions of 1,4-diketones.

Fujita, K.; Shinokubo, H.; Oshima, K. *Angew. Chem. Int. Ed.* **2003**, *42*, 2550.

Reduction/Allylation



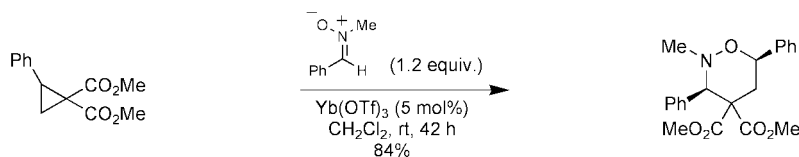
Catalytic one-pot synthesis of indoles.  
Siebeneicher, H.; Bytschkov, I.; Doye, S. *Angew. Chem. Int. Ed.* **2003**, *42*, 3042.

Hydroamination/sp<sup>2</sup>-sp<sup>3</sup> Coupling

18 examples (yields 0-81%).

Homo [3+2] dipolar cycloaddition of nitrones with cyclopropanes.  
Young, I. S.; Kerr, M. A. *Angew. Chem. Int. Ed.* **2003**, *42*, 3023.

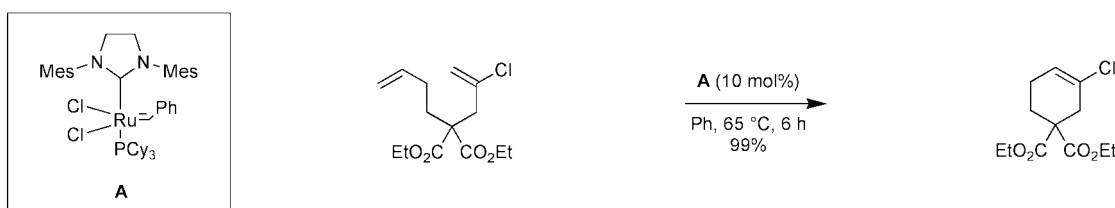
## [3+2] Cycloaddition



11 examples (yields 50-96%). Application towards the formal synthesis of antitumour antibiotic FR-900482.

Ring-closing olefin metathesis of vinyl chlorides.  
Chao, W.; Weinreb, S. M. *Org. Lett.* **2003**, *5*, 2505.

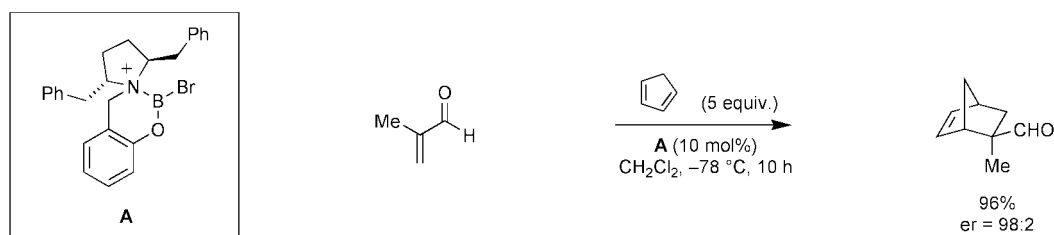
## Metathesis



Synthesis of 5, 6 and 7 membered rings are described. 10 examples (yields 84-99%).

Cationic Lewis acid catalysis of enantioselective Diels–Alder reactions.  
Spratt, K. T.; Corey, E. J. *Org. Lett.* **2003**, *5*, 2465.

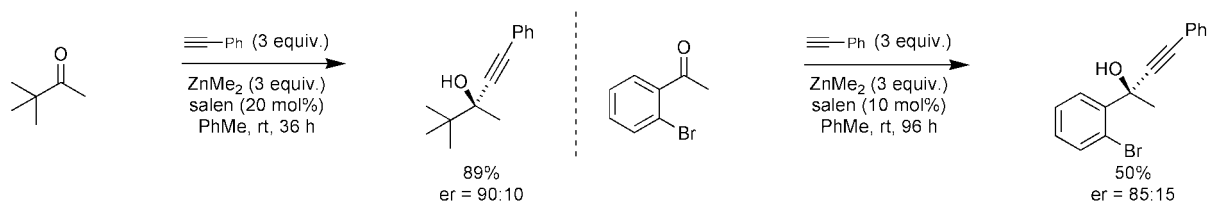
## Diels–Alder



5 examples (yields 76-96%, %ee 86-96%). Synthesis of catalyst **A** is also described.

Enantioselective alkylation of ketones catalyzed by Zn(salen) complexes.  
Cozzi, P. G. *Angew. Chem. Int. Ed.* **2003**, *42*, 2895.

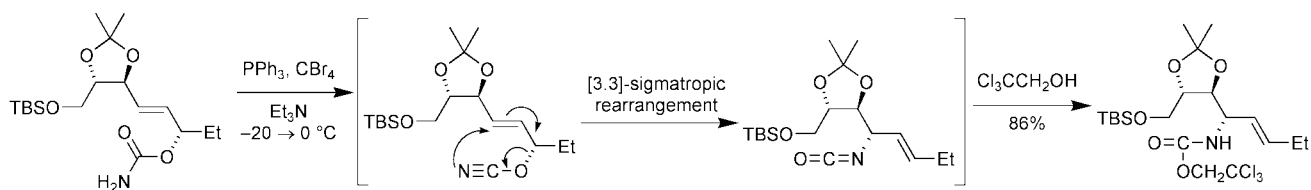
## Alkylation



17 examples (yields 40-89%, %ee 32-81%).

Stereoselective allyl amine synthesis.  
Ichikawa, Y.; Ito, T.; Nishiyama, T.; Isobe, M. *Synlett*. **2003**, 1034.

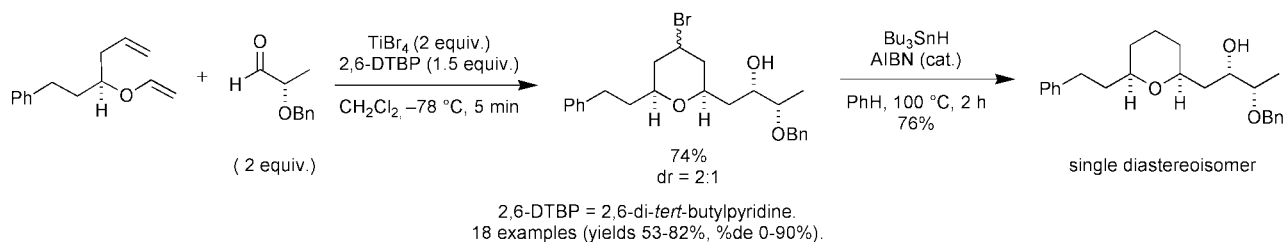
## [3,3] Sigmatropic Rearrangement



Application to the synthesis of Lentiginosine is also reported.

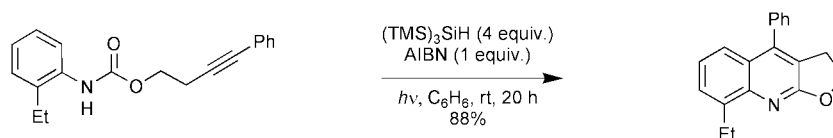
Titanium(IV)-promoted Mukaiyama aldol-Prins cyclizations.  
Patterson, B.; Marumoto, S.; Rychnovsky, S. D. *Org. Lett.* **2003**, 5, 3163.

## Annulation



Synthesis of carbocyclic and heterocyclic fused quinolines by cascade radical annulations.  
Du, W.; Curran, D. P. *Org. Lett.* **2003**, 5, 1765.

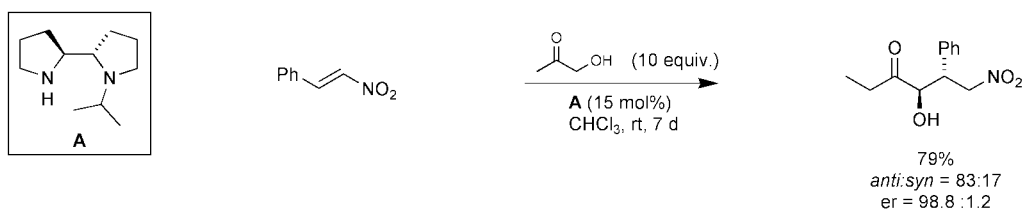
## Annulation



Cyclizations of *N*-aryl thiocarbamates, thioamides and thioureas are described. 15 examples (yields 0-88%).

Asymmetric Michael addition of  $\alpha$ -hydroxyketones to nitroolefins.  
Andrey, O.; Alexakis, A.; Bernardinelli, G. *Org. Lett.* **2003**, 5, 2559.

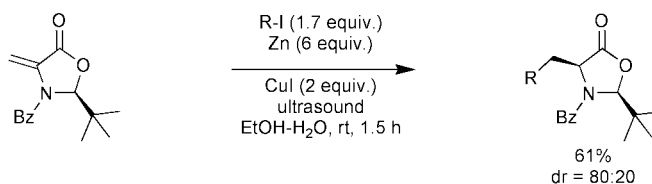
## 1,4-Addition



19 examples (yields 21-85%, 17:83  $\leq$  *anti:syn*  $\leq$  95:5, %ee 11-99%).

Ultrasonically-induced zinc-copper conjugate addition to  $\alpha,\beta$ -unsaturated carbonyl systems.  
Suarez, R. M.; Sestelo, J. P.; Sarandeses, L. A. *Chem.-Eur. J.* **2003**, 9, 4179.

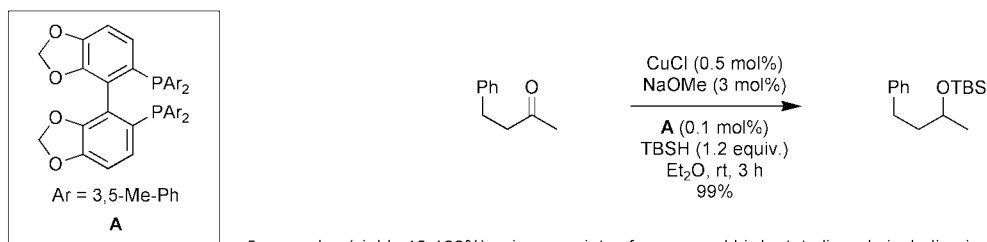
## 1,4-Addition



R-I = (*S*)-MeO<sub>2</sub>CCH(NHBoc)CH<sub>2</sub>-. 21 examples (yields 38-95%, %de 4-92%).

Copper-catalyzed one-pot hydrosilylation of dialkylketones to trialkylsilyl ethers.  
Lipshutz, B. H.; Caires, C. C.; Kuipers, P.; Chrisman, W. *Org. Lett.* **2003**, *5*, 3085.

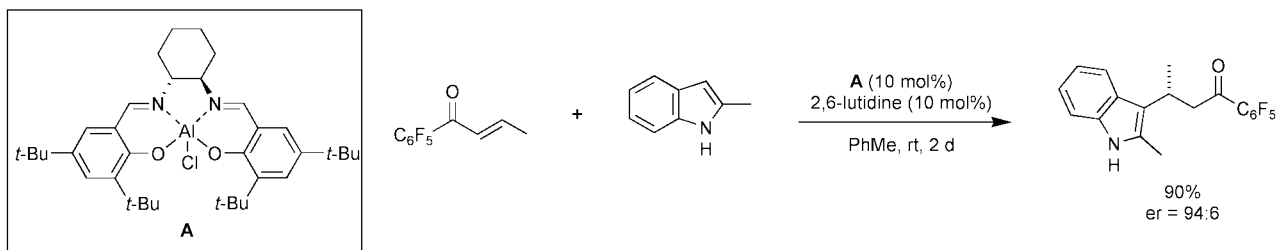
Hydrosilylation



5 examples (yields 10-100%) using a variety of mono- and bi-dentate ligands including investigations on asymmetric hydrosilylation and the impact of microwave irradiation on reaction rate.

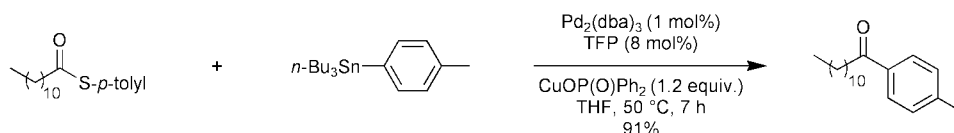
Catalytic enantioselective conjugate addition of indoles to  $\alpha,\beta$ -unsaturated ketones.  
Bandini, M.; Fagioli, M.; Melchiorre P.; Melloni A.; Umani-Ronchi A. *Tetrahedron Lett.* **2003**, *44*, 5843.

1,4-Addition



16 examples (yields 35-98%, %ee 11-89%).

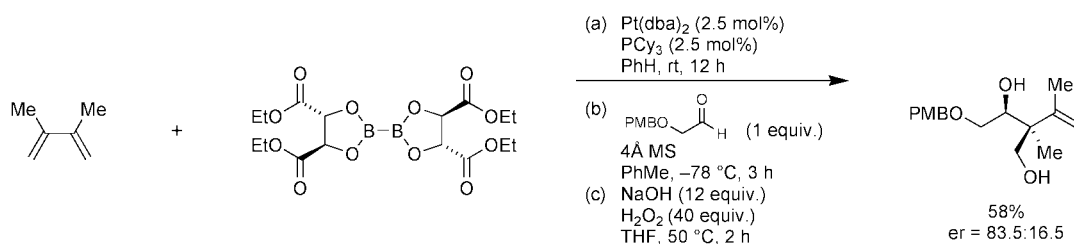
Palladium-catalyzed coupling of thiol esters and organostannanes.  
Wittenberg, R.; Srogl, J.; Egi, M.; Liebeskind, L. S. *Org. Lett.* **2003**, *5*, 3033.

 $sp^2$ - $sp^2$  Coupling

TFP = tri-2-furylphosphine. 17 examples (yields 61-97%).

Platinum-catalyzed tandem diboration/asymmetric allylboration.  
Morgan, J. B.; Morken, J. P. *Org. Lett.* **2003**, *5*, 2573.

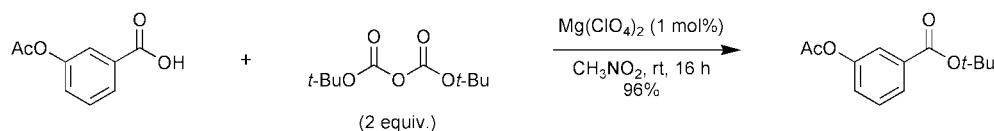
Stereoselective Dimetallation/Allylation



6 examples (yields 58-72%, *syn:anti* ratio >19:1, %ee 33-74%).

Lewis acid catalyzed decarboxylative esterification.  
Gooßen, L.; Döhring, A. *Adv. Synth. Catal.* **2003**, *345*, 943.

Decarboxylative Esterification



The formation of methyl and benzyl esters is also described. 36 examples (yields <5-99%).