

**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, and Stephen McAteer, 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** 2004, No. 17, pp 2934–2941

Advanced online publication: 19.11.2004

Art ID: X01704SS

© Georg Thieme Verlag Stuttgart · New York

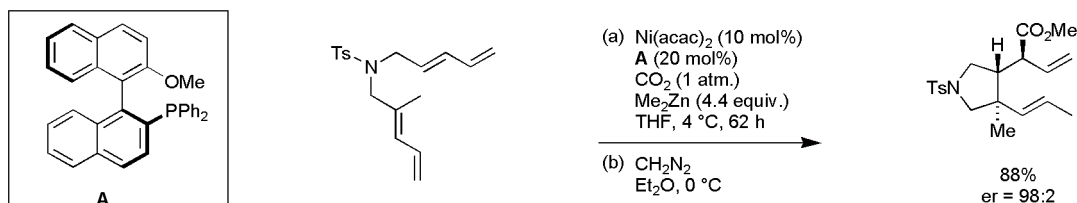
The journals regularly covered by the abstractors are:

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  
Tetrahedron Letters

Ni-catalysed asymmetric carboxylative cyclisation of bis-1,3-dienes.

Takimoto, M.; Nakamura, Y.; Kimura, K.; Mori, M. *J. Am. Chem. Soc.* **2004**, 126, 5956.

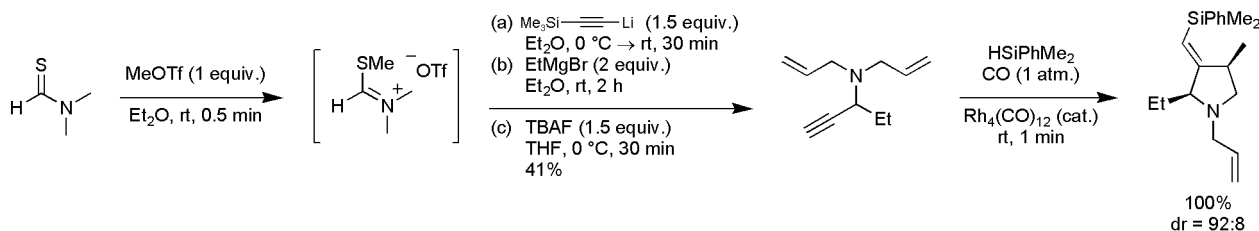
**Annulation**



11 examples (yields 57–100%, %ee 90–96%).

Sequential reactions of *in-situ* generated thioiminium salts with organolithium and Grignard reagents.  
Murai, T.; Mutoh, Y.; Ohta, Y.; Murakami, M. *J. Am. Chem. Soc.* **2004**, 126, 5968.

**C-C Bond Formation**

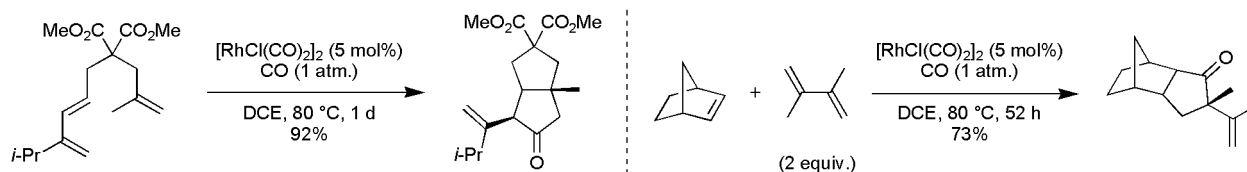


16 examples (yields 41–98%).

Rh(I)-catalyzed [2+2+1] cycloadditions of 1,3-dienes, alkenes and CO.

Wender, P. A.; Croatt, M. P.; Deschamps, N. M. *J. Am. Chem. Soc.* **2004**, 126, 5948.

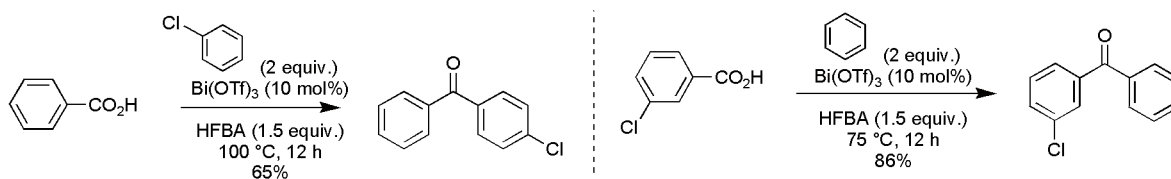
**Annulation**



10 examples (yields 0–94%). Optimization studies are also reported.

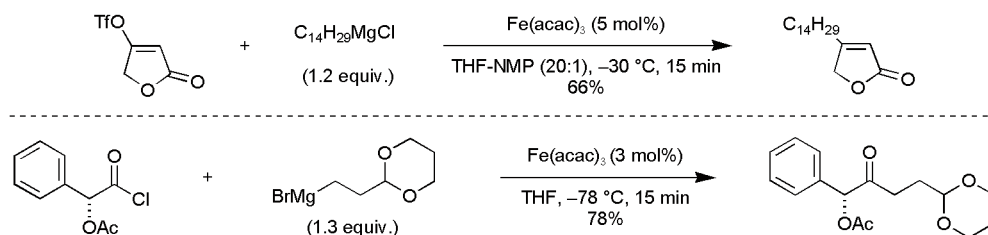
Friedel-Crafts acylation using perfluoroalkanoic anhydride and bismuth or scandium triflate.  
Matsushita, Y.; Sugamoto, K.; Matsui, T. *Tetrahedron Lett.* **2004**, 45, 4723.

## Acylation



HFBA = heptafluorobutyric anhydride. 9 examples (yields 12-99%).

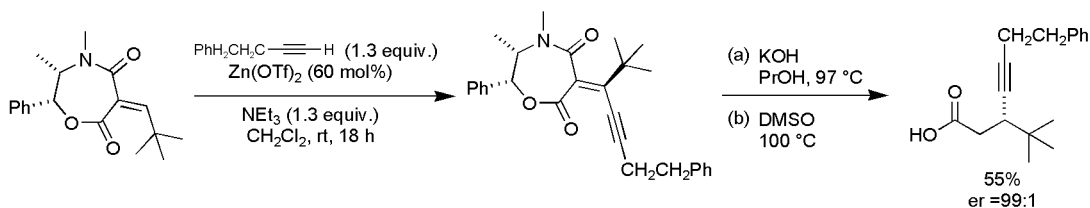
Selective iron-catalyzed cross-coupling reactions of Grignard reagents with enol triflates and acid chlorides.  
Scheiper, B.; Bonnekessel, M.; Krause, H.; Fürstner, A. *J. Org. Chem.* **2004**, 69, 3943.

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

Enol triflates (41 examples, yields 45-98%), acid chlorides (28 examples, yields 43-99%), and monoalkylation of dichloroarenes (8 examples, yields 39-83%).

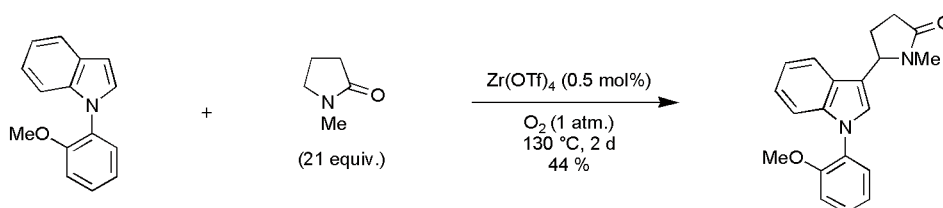
Zinc-catalysed conjugate addition of alkynes.  
Knopf, T. F.; Boyall, D.; Carreira, E. M. *Org. Lett.* **2004**, 6, 2281.

## Asymmetric 1,4-Addition



5 examples (yields 55-82%, %ee 68->98%).

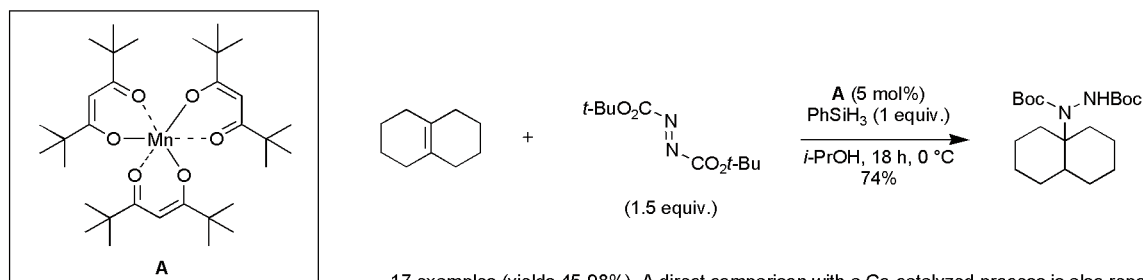
Zr(OTf)<sub>4</sub>-catalysed oxidative coupling of lactams with heterocyclic arenes.  
Tsuchimoto, T.; Ozawa, Y.; Negoro, R.; Shirakawa, E.; Kawakami, Y. *Angew. Chem. Int. Ed.* **2004**, 43, 4231.

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

12 examples (yields <1-99%).

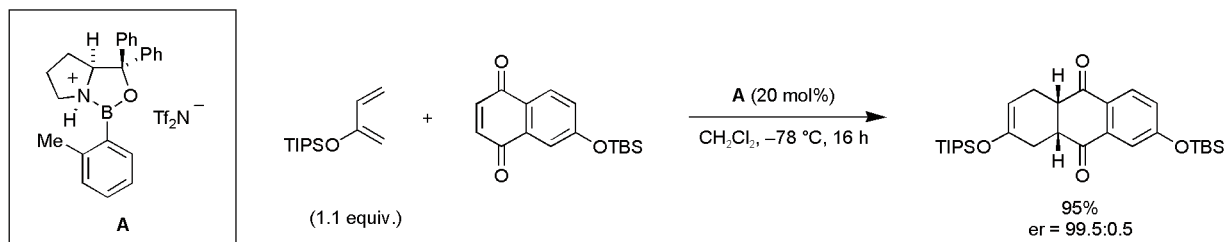
Catalytic hydrohydrazination of alkenes using a simple Mn complex.  
Waser, J.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2004**, 43, 4099.

## C-N Bond Formation



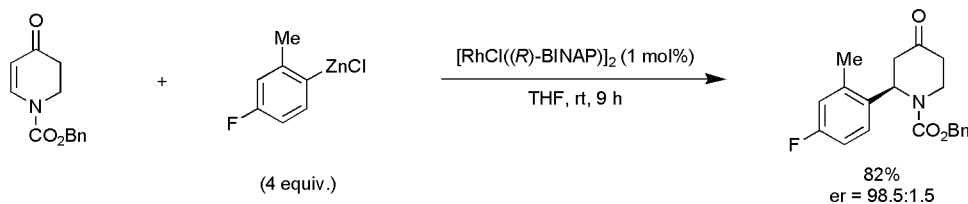
17 examples (yields 45-98%). A direct comparison with a Co-catalyzed process is also reported.

Predictive selection rules for Diels-Alder reactions of unsymmetrical quinones catalysed by a chiral oxazaborolidinium cation. **Diels-Alder**  
 Ryu, D. H.; Zhou, G.; Corey, E. J. *J. Am. Chem. Soc.* **2004**, 126, 4800.



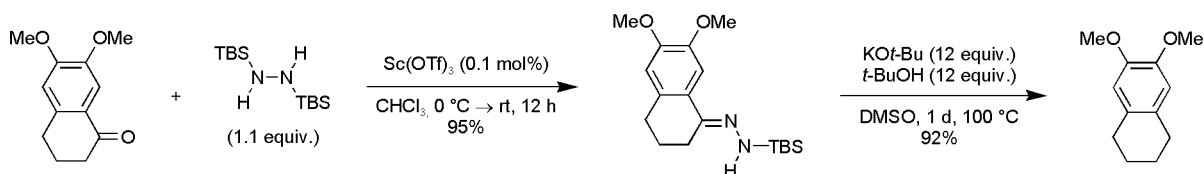
A mechanistic model and selection rules for the reaction of mono-, di- and trisubstituted quinones are presented. 15 examples (yields 84-99%, %ee 88-99%).

Rhodium-catalysed asymmetric 1,4-addition of organozinc reagents for the synthesis of 2-aryl-4-piperidones. **1,4-Addition**  
 Shintani, R.; Tokunaga, N.; Doi, H.; Hayashi, T. *J. Am. Chem. Soc.* **2004**, 126, 6240.



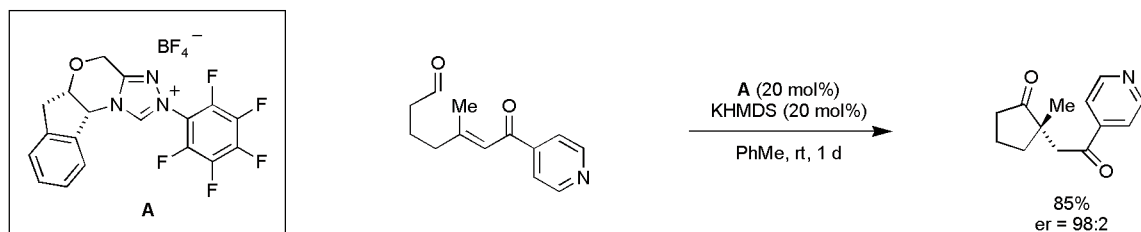
8 examples (yields 87-99%, %ee 94-99%).

Preparation of *N*-tert-butyldimethylsilylhydrazones and their application in synthesis. **C-N Bond Formation**  
 Furrow, M. E.; Myers, A. G. *J. Am. Chem. Soc.* **2004**, 126, 5436.



Synthesis (15 examples, yields 85-95%) and application in reductions, synthesis of vinyl halides and gem-dihalides (25 examples, yields 44-99%).

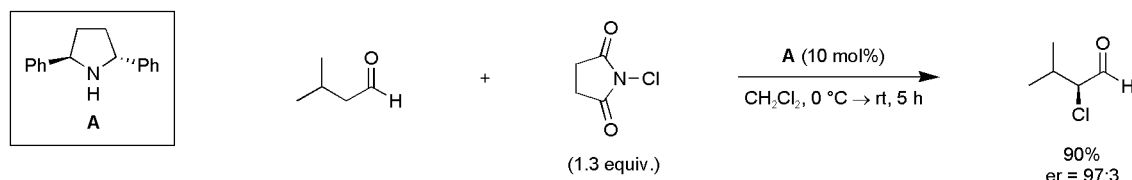
Enantioselective synthesis of quarternary stereocentres via a catalytic asymmetric Stetter reaction. **C-C Bond Formation**  
 Kerr, M. S.; Rovis, T. *J. Am. Chem. Soc.* **2004**, 126, 8876.



18 examples (yields 45-96%, %ee 56-99%).

Direct organocatalytic asymmetric  $\alpha$ -chlorination of aldehydes. **Asymmetric Chlorination**

Halland, N.; Braunton, A.; Bachmann, S.; Marigo, M.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2004**, 126, 4790.

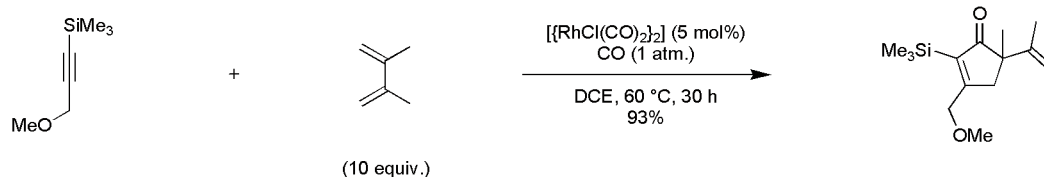


32 examples (yields 30-99%, %ee 5-97%).

An intermolecular dienylyl Pauson-Khand reaction.

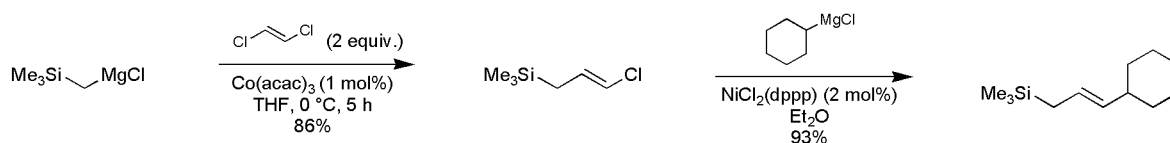
Wender, P. A.; Deschamps, N. M.; Williams, T. J. *Angew. Chem. Int. Ed.* **2004**, 43, 3076.

Annulation



DCE = 1,2-dichloroethane. 31 examples (yields 11-99%).

Synthesis of  $\gamma$ -substituted (*E*)-allylsilanes *via* a Co-catalysed coupling of  $R_3SiCH_2MgCl$  with 1,2-dihaloethene. **C-C Bond Formation**  
 Kamachi, T.; Kuno, A.; Matsuno, C.; Okamoto, S. *Tetrahedron. Lett.* **2004**, 45, 4677.

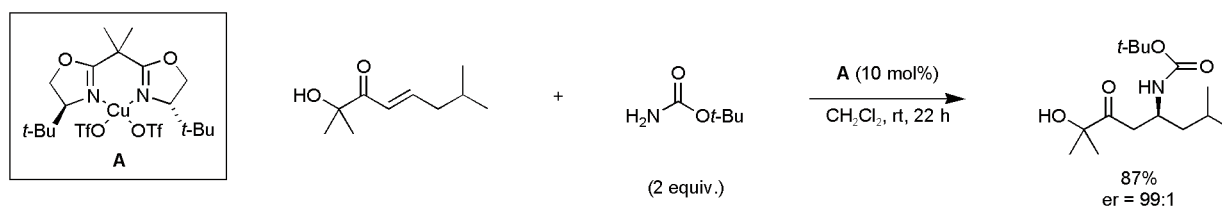


dppp = 1,3-bis(diphenylphosphino)propane. 19 examples (yields 5-95%).

Catalytic enantioselective conjugate addition of carbamates.

Palomo, C.; Oiarbide, M.; Rajkumar, H.; Kelso, M.; Gómez-Bengoia, E.; García, J. M. *J. Am. Chem. Soc.* **2004**, 126, 9188.

Asymmetric 1,4-Addition

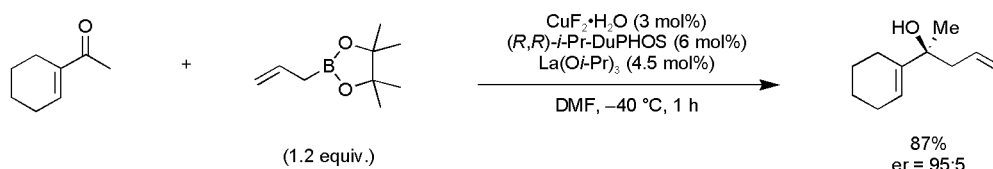


15 examples (yields 49-92%, %ee 83-99%).

Catalytic enantioselective allylboration of ketones.

Wada, R.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2004**, 126, 8910.

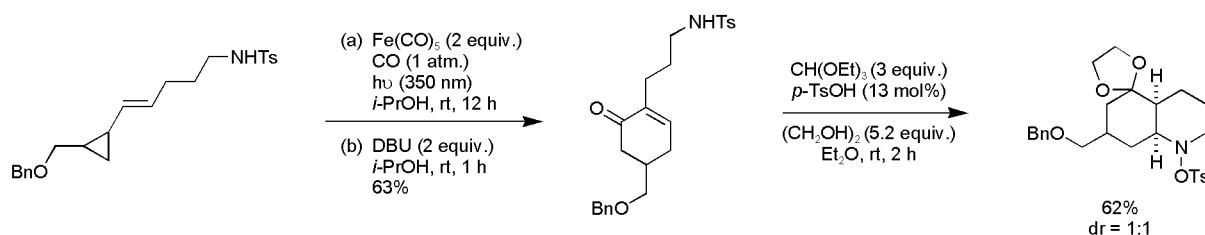
Asymmetric Allylation



14 examples (yields 42-99%, %ee 67-91%). 4 examples for catalytic enantioselective crotylations of ketones (yields 73-94%, %ee 75-93%, %de 24-68%).

Functional group compatibility in  $Fe(CO)_5$ -mediated carbonylations of alkenyl cyclopropanes.Taber, D. F.; Joshi, P. V.; Kanai, K. *J. Org. Chem.* **2004**, 69, 2268.

Carbonylation

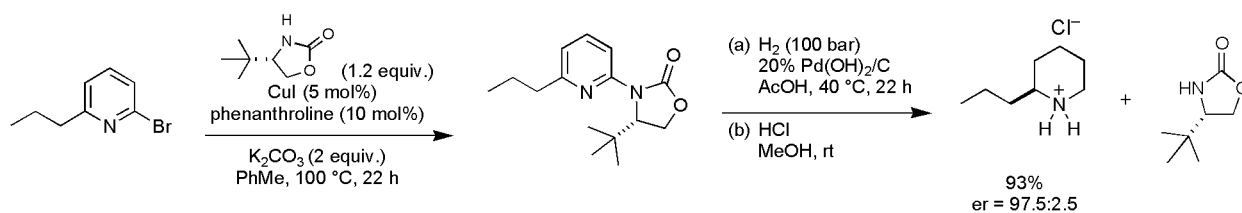


11 examples (yields 21-80%).

## Asymmetric hydrogenation of pyridines.

Glorius, F.; Spielkamp, N.; Holle, S.; Goddard, R.; Lehmann, C. W. *Angew. Chem. Int. Ed.* **2004**, 43, 2850.

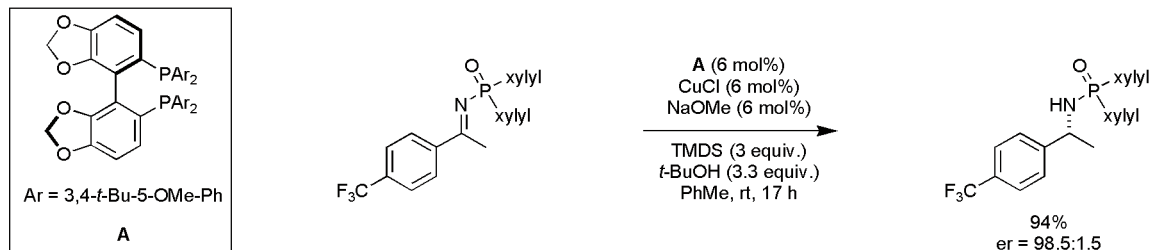
## Asymmetric Hydrogenation



## Cu(I)-catalysed asymmetric hydrosilylations of imines at ambient temperatures.

Lipshutz, B. H.; Shimizu, H. *Angew. Chem. Int. Ed.* **2004**, 43, 2228.

## Asymmetric Hydrosilylation

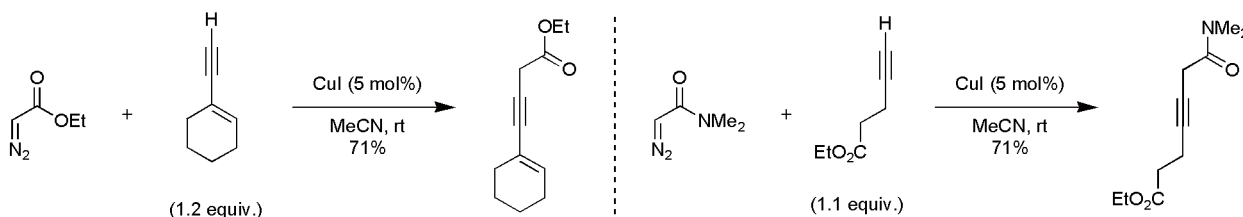


TMSD = tetramethyldisiloxane, xylyl = 3,4-Me-Ph.

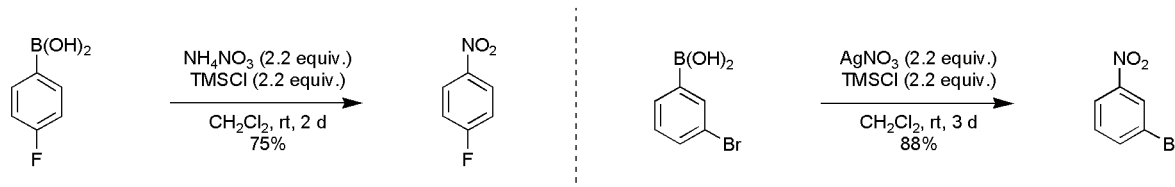
## Synthesis of functionalised 3-alkynoates.

Suárez, A.; Fu, G. C. *Angew. Chem. Int. Ed.* **2004**, 43, 3580.

## C-C Bond Formation

*ipso*-Nitration of arylboronic acids with chlorotrimethylsilane-nitrate salts.Surya Prakash, G. K.; Panja, C.; Mathew, T.; Surampudi, V.; Petasis, N. A.; Olah, G. A. *Org. Lett.* **2004**, 13, 2205.

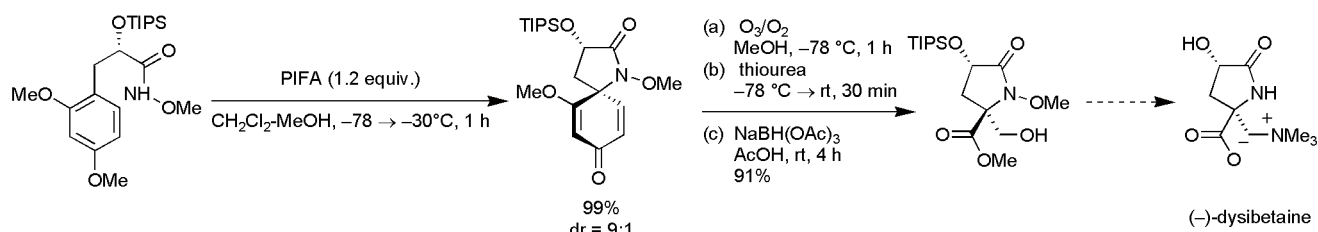
## C-N Bond Formation



## Total synthesis of (–)-dysibetaine via a nitrenium ion cyclisation-dienone cleavage strategy.

Wardrop, D. J.; Burge, M. S. *Chem. Comm.* **2004**, 10, 1230

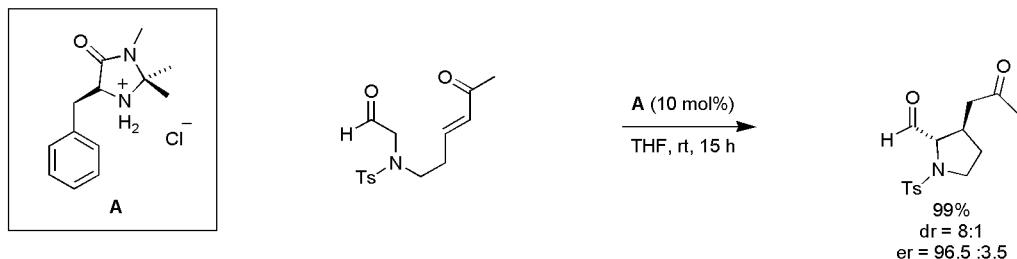
## Annulation



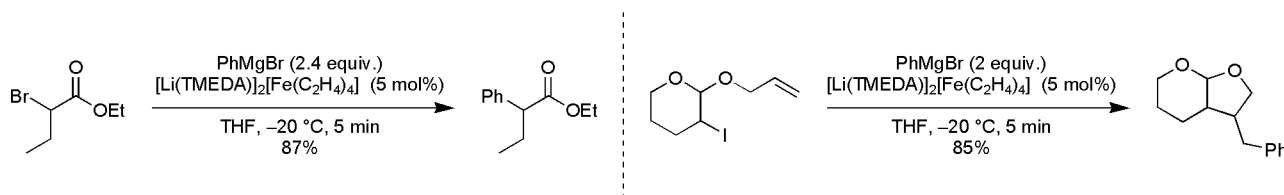
## Asymmetric intramolecular Michael reaction.

Hechavarria Fonseca, M. T.; List, B. *Angew. Chem. Int. Ed.* **2004**, 43, 3958.

## Asymmetric 1,4-Addition



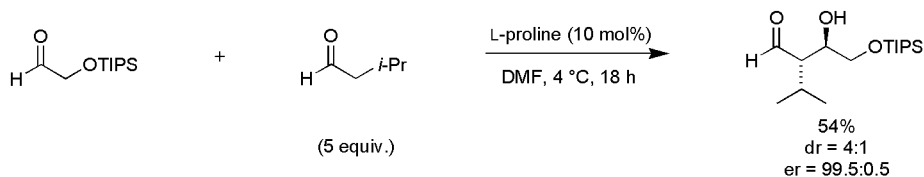
## Cross-coupling of alkyl halides with aryl Grignard reagents.

Martin, R.; Furstner, A. *Angew. Chem. Int. Ed.* **2004**, 43, 3955.sp<sup>2</sup>-sp<sup>3</sup> Coupling

## Enantioselective organocatalytic Aldol reactions of α-oxyaldehydes.

Northrup, A. D.; Mangion, I. K.; Hettche, F.; MacMillan, D. W. C. *Angew. Chem. Int. Ed.* **2004**, 43, 2152.

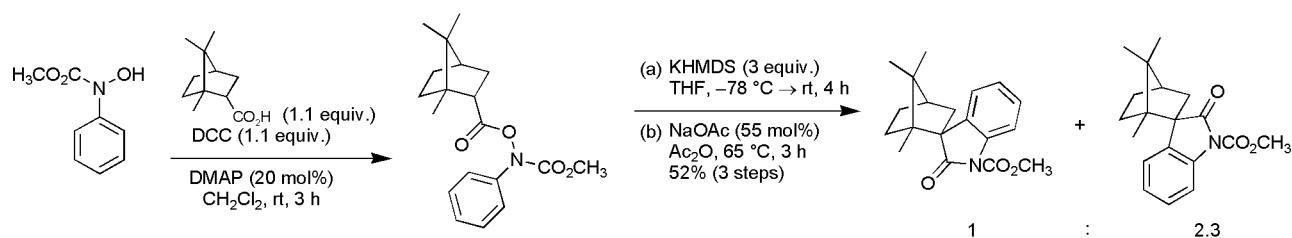
## Aldol Reaction



## Spirocyclic oxindole synthesis via a hetero-Claisen rearrangement.

Mao, Z.; Baldwin, S. W. *Org. Lett.* **2004**, 6, 2425.

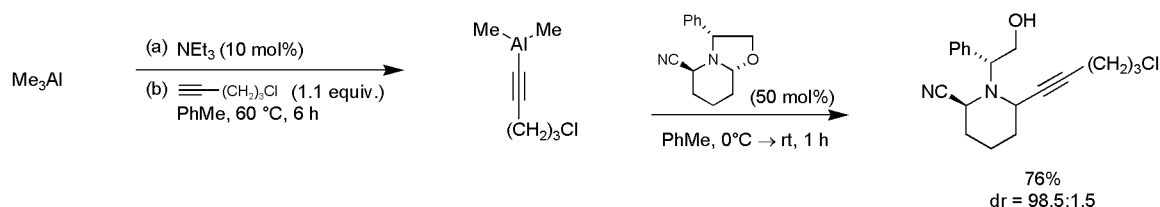
## [3,3]-Sigmatropic Rearrangement



## Direct triethylamine-catalysed alumination of terminal alkynes.

Feuvrie, C.; Blanchet, J.; Bonin, M.; Micouin, L. *Org. Lett.* **2004**, 6, 2333.

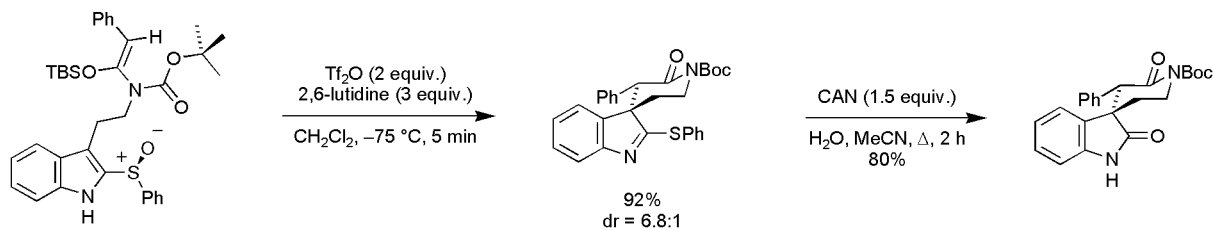
## C-C Bond Formation



## Oxidative cyclisation of indole derivatives.

Feldman, K. S.; Vidulova, D. B. *Org. Lett.* **2004**, 6, 1869.

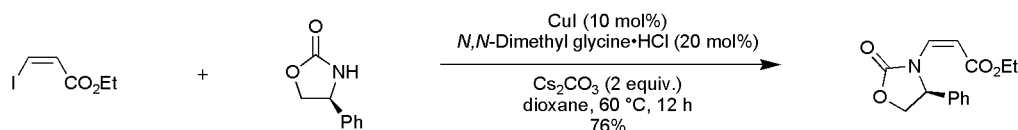
## Annulation



CAN = cerium (IV) ammonium nitrate. 5 examples (yields 64-93%).

CuI/*N,N*-Dimethylglycine-catalysed coupling of vinyl halides with amides or carbamates.Pan, X.; Cai, Q.; Ma, D. *Org. Lett.* **2004**, 6, 1809.

## C-N Bond Formation

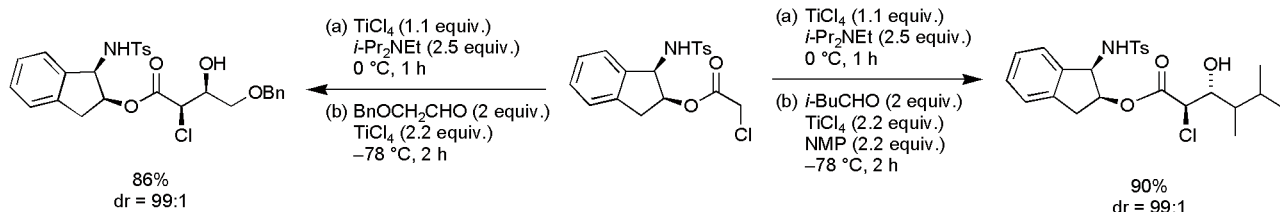


32 examples (yields 10-85%).

## Stereoselective chloroacetate Aldol reactions.

Ghosh, A. K.; Kim, J. *Org. Lett.* **2004**, 6, 2725.

## Asymmetric C-C Bond Formation

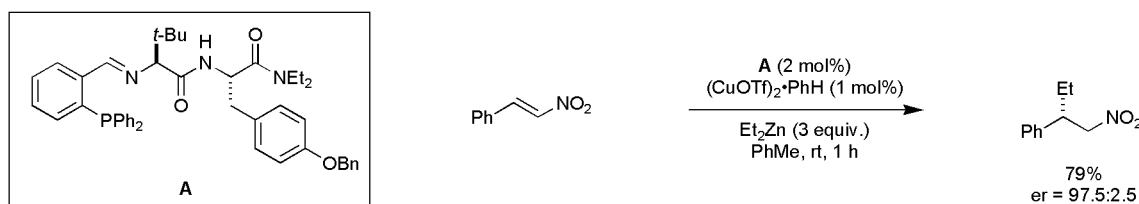


27 examples (yields 15-97%, %de = 48-98%).

## Cu-catalysed asymmetric conjugate addition of alkylzinc reagents to aromatic and aliphatic acyclic nitroalkenes.

Mampreian, D. M.; Hoveyda, A. H. *Org. Lett.* **2004**, 6, 2829.

## Asymmetric 1,4-Addition

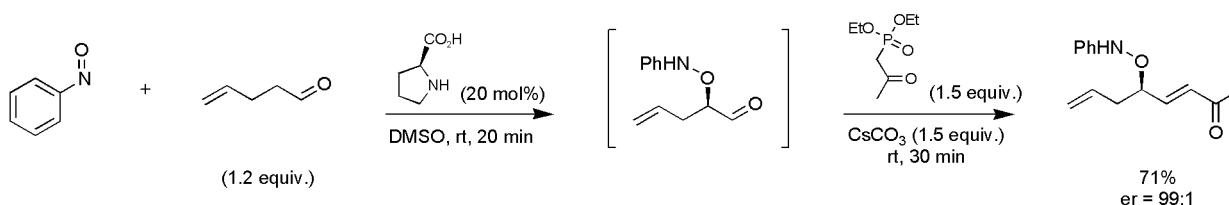


30 examples (yields 52-84%, %ee 77-95%).

## Enantioselective synthesis of allylic alcohols via a sequential aminooxylation-olefination of aldehydes.

Zhong, G.; Yu, Y. *Org. Lett.* **2004**, 6, 1637.

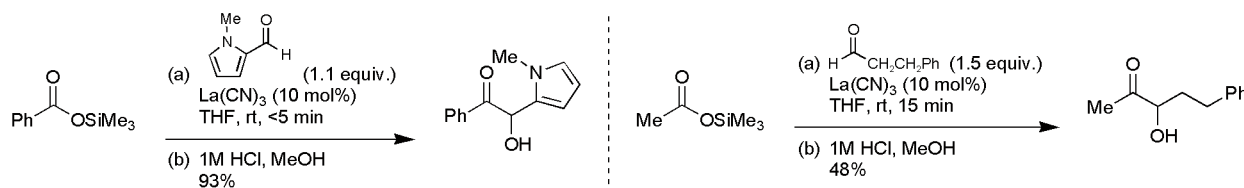
## Asymmetric C-O Bond Formation



8 examples (yields 52-81%, %ee 95-99%).

Lanthanum-catalysed cross silyl benzoin additions.  
Bausch, C. C.; Johnson, J. S. *J. Org. Chem.* **2004**, *69*, 4283.

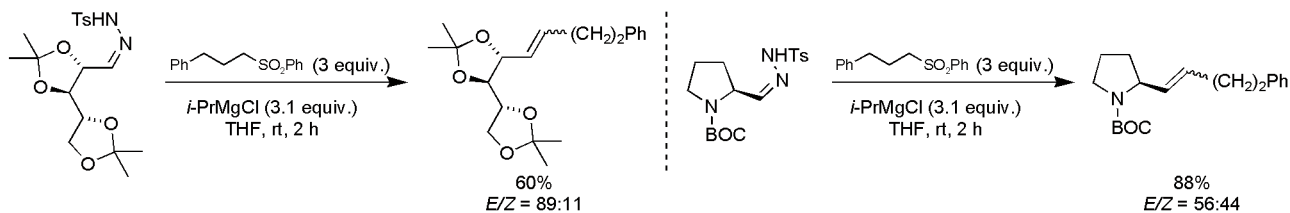
## 1,2-Addition/Rearrangement



11 examples (yields 48-93%).

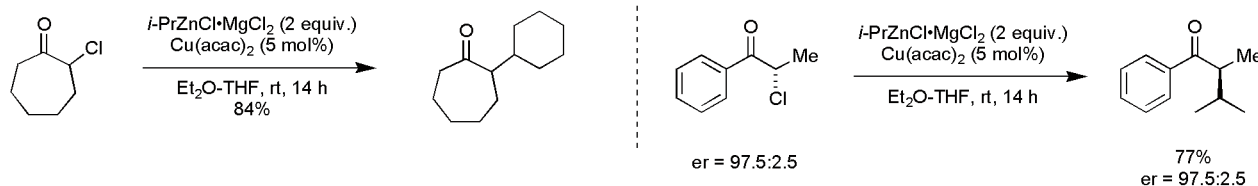
Olefination of  $\alpha$ -hydroxy and  $\alpha$ -amino aldehyde derivatives.  
Wicha, J.; Zarecki, A. *J. Org. Chem.* **2004**, *69*, 5810.

## C-C Bond Formation



8 examples (yields 21-88%, 48:52  $\square$  E/Z  $\square$  89:11).

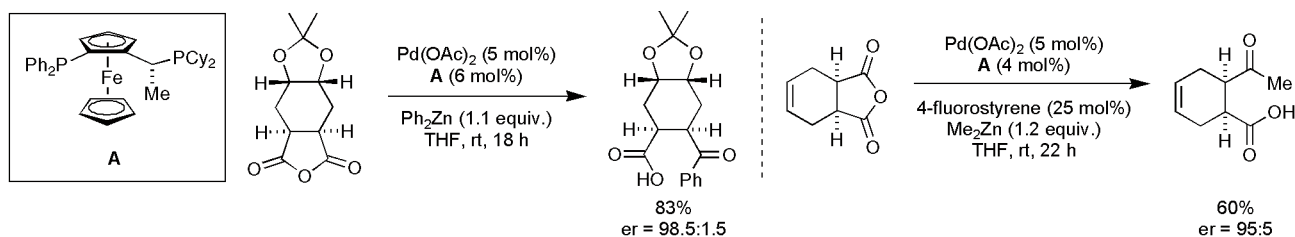
Catalytic cross-coupling of alkylzinc halides with  $\alpha$ -chloroketones.  
Malosh, C. F.; Ready, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 10204.

 $sp^3$ - $sp^3$  Coupling

23 examples (yields 45-96%).

Pd-catalyzed enantioselective alkylative desymmetrisation of *meso*-succinic anhydrides.  
Bercot, E. A.; Rovis, T. *J. Am. Chem. Soc.* **2004**, *126*, 10248.

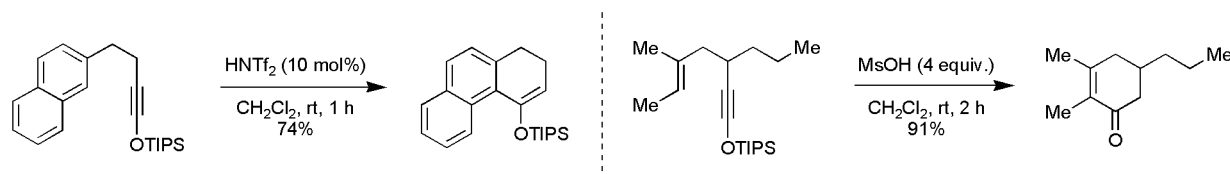
## Desymmetrisation



13 examples (yields 0-89%, %ee 64-97%).

Bronsted acid-promoted cyclisations of siloxyalkynes with arenes and alkenes.  
Zhang, L.; Kozmin, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 10204.

## Annulation



Arene cyclisations: 6 examples (yields 40-92%); Alkene cyclisations: 5 examples (yields 76-91%).