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, Sukhjinder Uppal, Tanya Wildmann and Josephine Yuen, Department of Chemistry, Leeds University, Leeds, LS2 9JT, UK.

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

Synthesis 2002, No. 7, 21 05 2002. Article Identifier:
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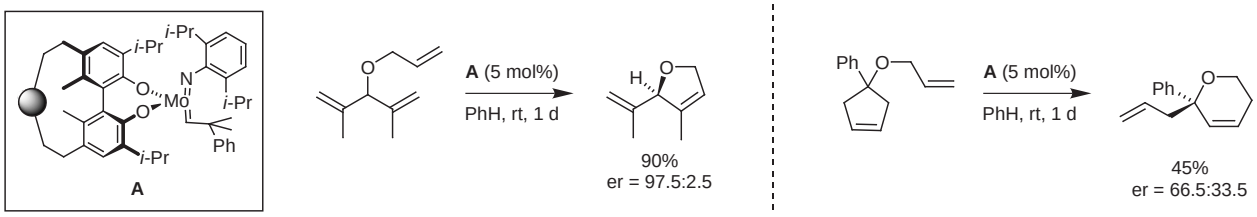
Polymer supported catalytic enantioselective olefin metathesis.
Hultzsch, K. C.; Jernelius, J. A.; Hoveyda, A. H.; Schrock, R. R. *Angew. Chem. Int. Ed.* **2002**, *41*, 589.

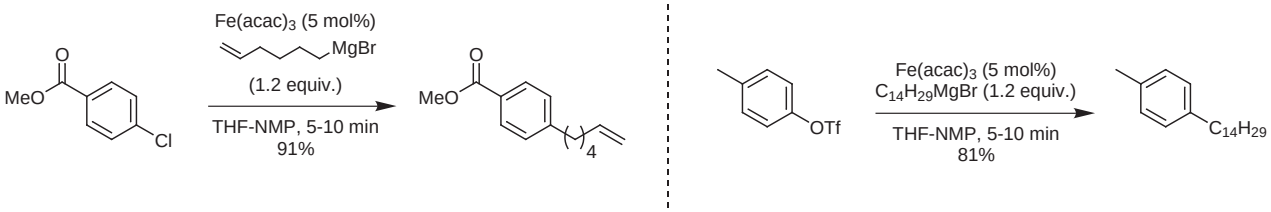
Enantioselective Olefin Metathesis



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.

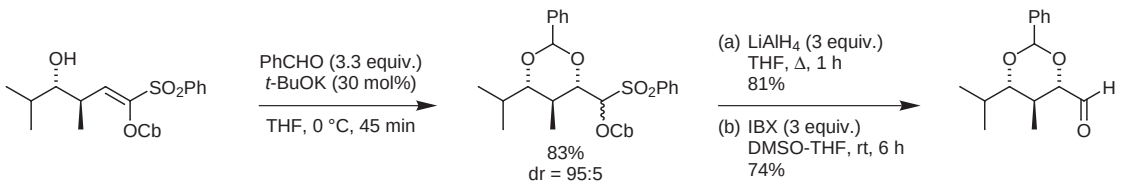
sp^2-sp^3 Coupling



38 examples (yields 0-96%).

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

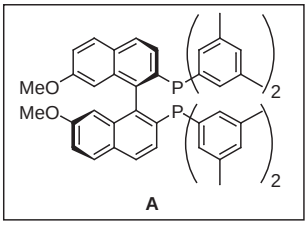
Diastereoselective 1,4-Addition

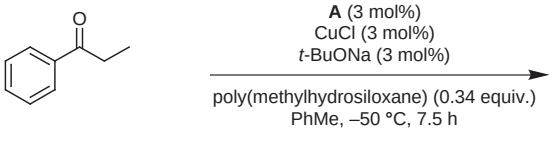


2 examples of 1,4-addition (yields 83-86%, %de > 90%).

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

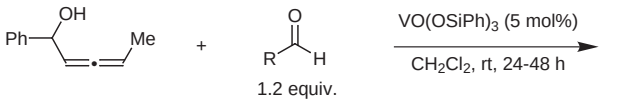




10 Examples (yields 87-99%, %ee 67-97%).

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

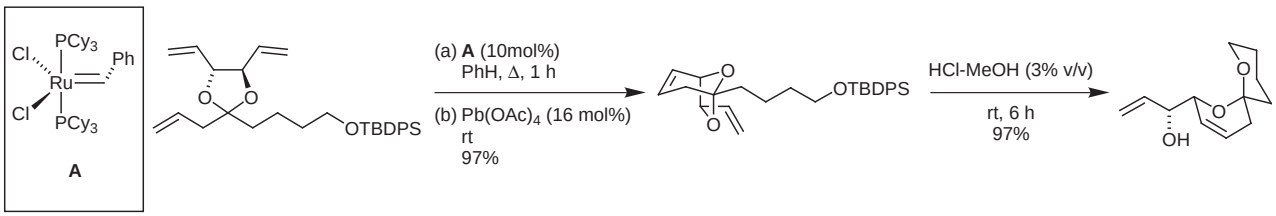


R	yield	*syn*/*anti*
Ph	86%	80/20
p-MeOPh	83%	42/58
$(Ph)_2CH$	71%	80/20
C_3H_7	79%	78/22

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.

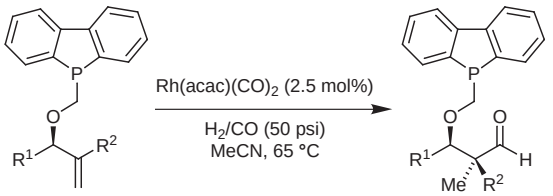
Ring Closing Metathesis/Spiroketalisation



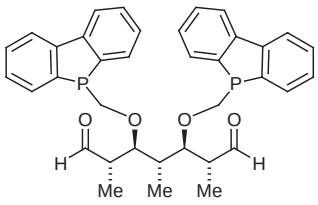
7 examples of acid-catalysed spiroketalisation (yields 71-97%).

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



R^1	R^2	Yield	%de
Me	H	92%	91%
Ph	H	96%	93%
i-Pr	H	94%	97%
H	Me	88%	-----

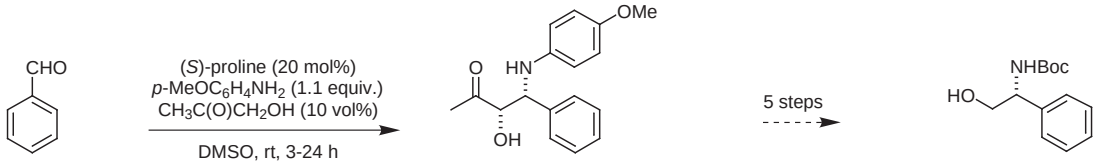


94%
dr = 85:15

6 Examples (yields 87-98%, %de 91-97%).

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.

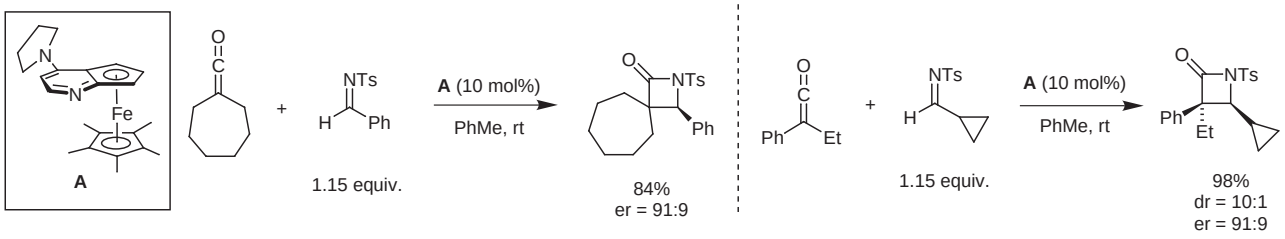
Asymmetric Amination/Alkylation



83%
dr = 9:1
er = 97:3

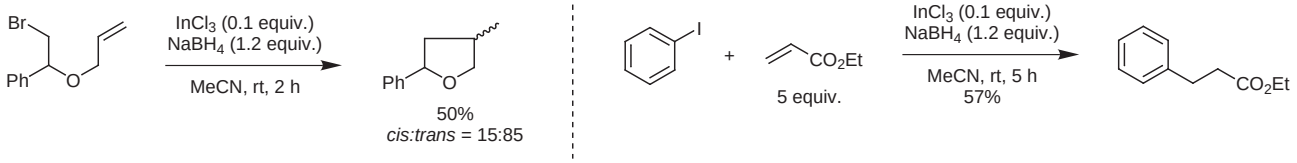
8 examples (yield 57-92%, %ee 61-99%, dr 3:1 → 20:1). Various ketones and aldehydes were used.

Enantioselective Staudinger synthesis of β-lactams catalyzed by a planar-chiral nucleophile. **[2+2] Enantioselective Cycloaddition**
Hodous, B. L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 1578.



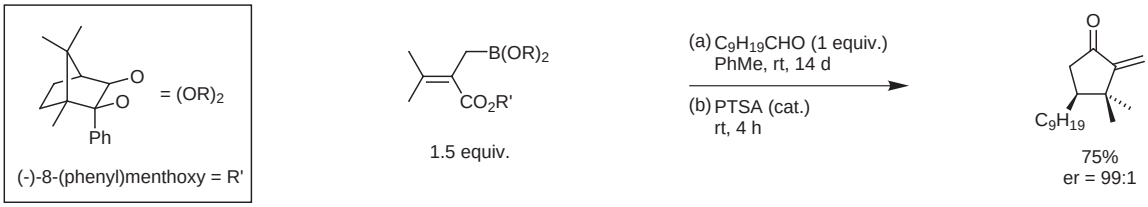
13 examples (yield 82-98%, %ee 81-98%).

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



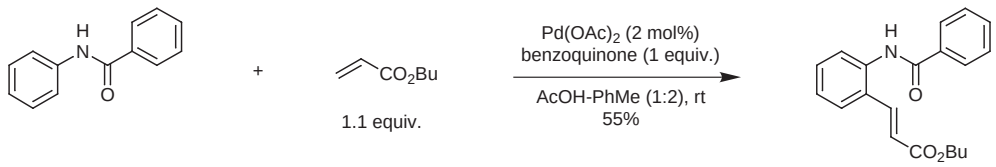
6 examples involving reduction of halides (yield 0-95%), 2 examples of cyclisation (yield 50-62%) and 3 examples of intermolecular addition (yield 45-62%).

Stereocontrolled synthesis of α-exomethylene γ-lactones with a stereogenic quaternary carbon centre. **1,2-Addition**
Kennedy, J. W. J.; Hall, D. G. *J. Am. Chem. Soc.* **2002**, *124*, 898.



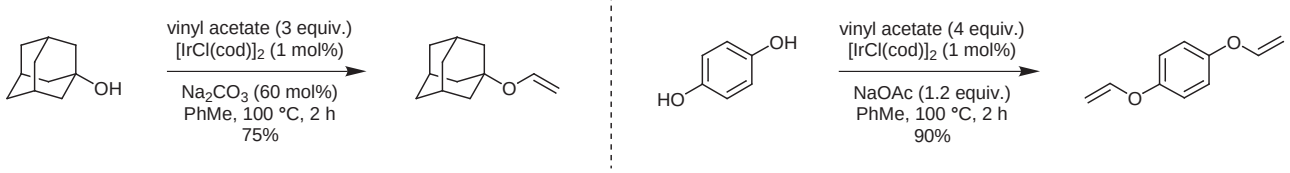
9 examples of preparation of tetrasubtituted allylboronates (yield 43-95%, *Z/E* 1.4:1 → 20:1) and 18 examples of synthesis of γ-lactones (yield 26-89%, dr 15:1 → 20:1).

Selective Pd-catalyzed oxidative coupling of anilides with olefins through C-H bond activation. **sp^2-sp^2 Coupling**
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.



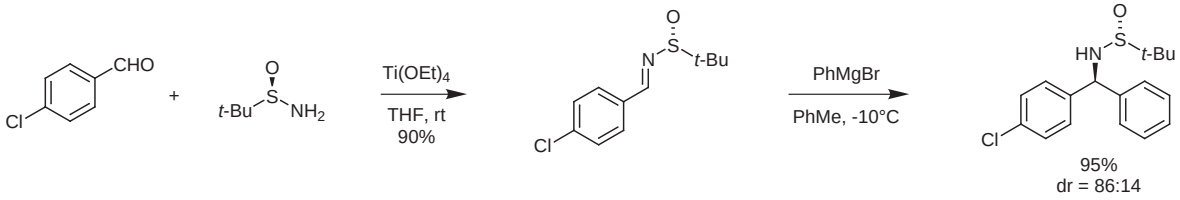
11 examples (yield 0-91%). Various subtitued anilide derivatives are reported.

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



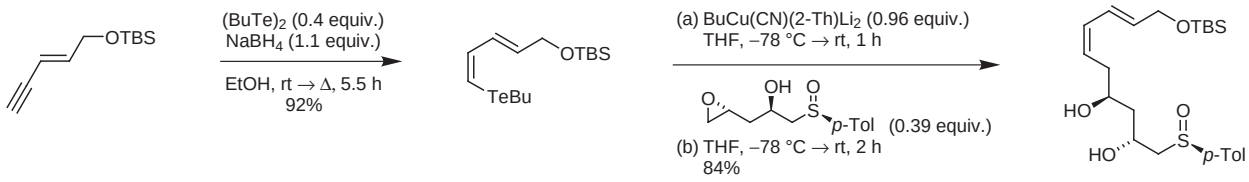
12 examples (yield 63-98%).

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



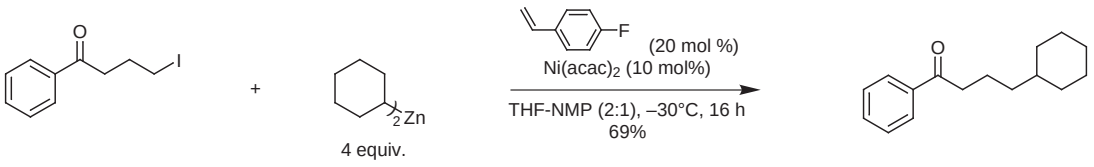
The opposite enantiomer can be synthesised as the major product by starting with benzaldehyde and adding 4-chlorophenylmagnesium bromide. The remaining steps in the synthesis of cetirizine dihydrochloride are also reported.

Stereocontrolled synthesis of (–)-macrolactin A. **Hydrometalation/Alkylation**
Marino, J. P.; McClure, M. S.; Holub, D. P.; Comasseto, J. V.; Tucci, F. C. *J. Am. Chem. Soc.* **2002**, *124*, 1664.



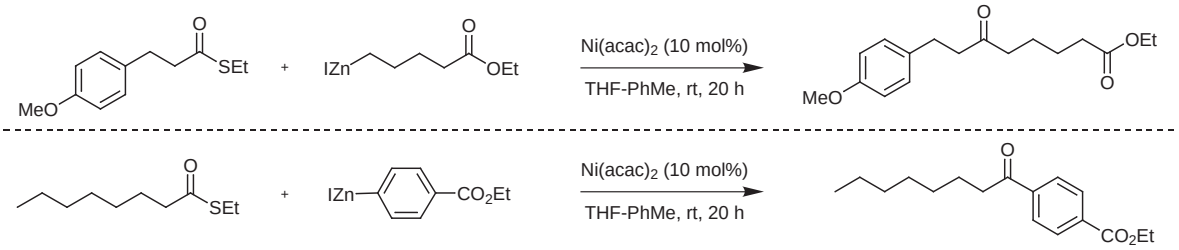
This is the first reported use of vinyl tellurides in the synthesis of a natural product.

Nickel-catalyzed cross-coupling of alkylzinc halides and alkyl halides. **sp^3-sp^3 Coupling**
Jensen, A. E.; Knochel, P. *J. Org. Chem.* **2002**, *67*, 79.



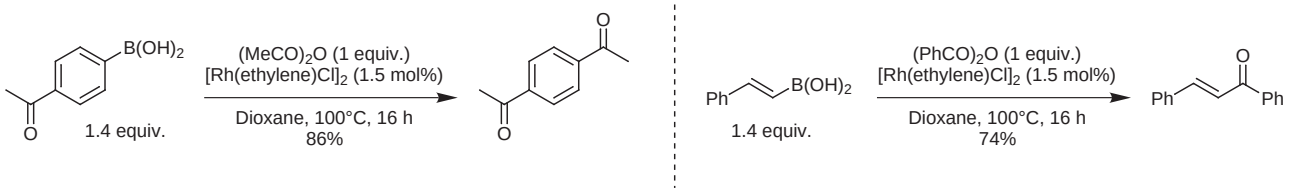
25 examples (yields 48-82%).

Nickel-catalyzed coupling of organozinc reagents with thiolesters to give functionalized ketones. **sp^2-sp^3 Coupling**
Shimizu, T.; Seki, M. *Tetrahedron Lett.* **2002**, *43*, 1039.



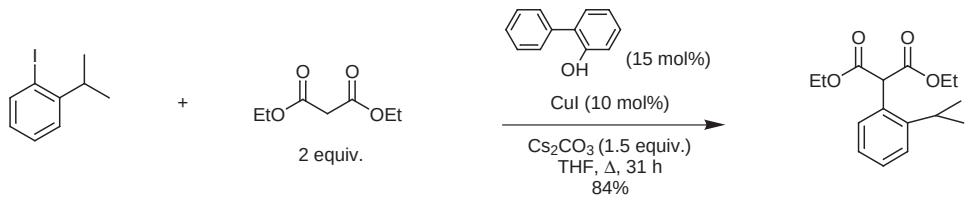
11 examples (yields 39-89%).

Rhodium-catalyzed addition of boronic acids to anhydrides. **sp^2-sp^2Coupling**
Frost, C. G.; Wadsworth, K. J. *Chem. Commun.* **2001**, 2316.



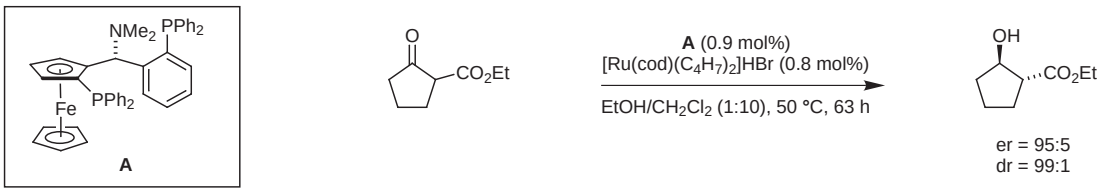
10 examples (yields 54-88%). Optimization of the reaction conditons is also reported.

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



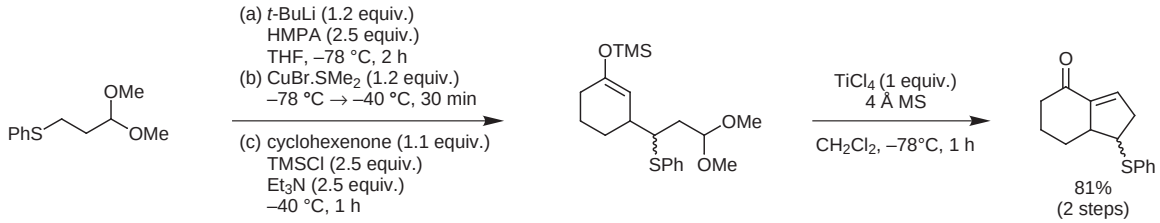
16 examples (yields 61-98%)

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



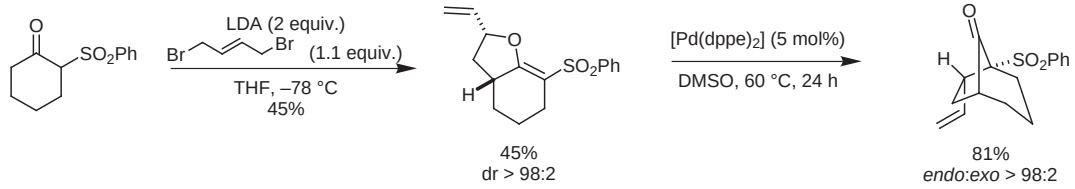
Examples of hydrogenation of α-(acylamino)acrylic acids, enol esters, enamides, 1,3-diketones and hydrazones using Rh- or Ru-catalysts with ferrocenylphosphanes.

Cyclopentannulation of enones with acetal or orthoester organocuprates **1,4-Addition/Cyclization**
Ding, P.; Ghosez, L. *Tetrahedron*, **2002**, *58*, 1565.



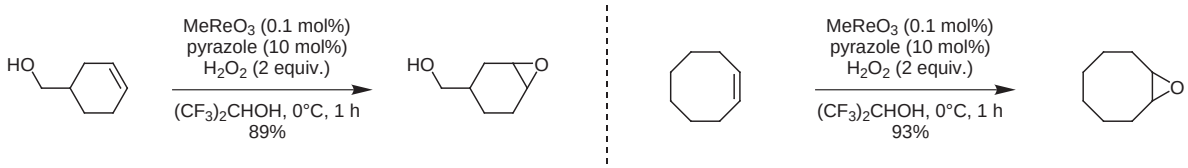
5 examples of acetal organocuprates (yields 40-93%) and 1 example of an orthoester organocuprate.

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



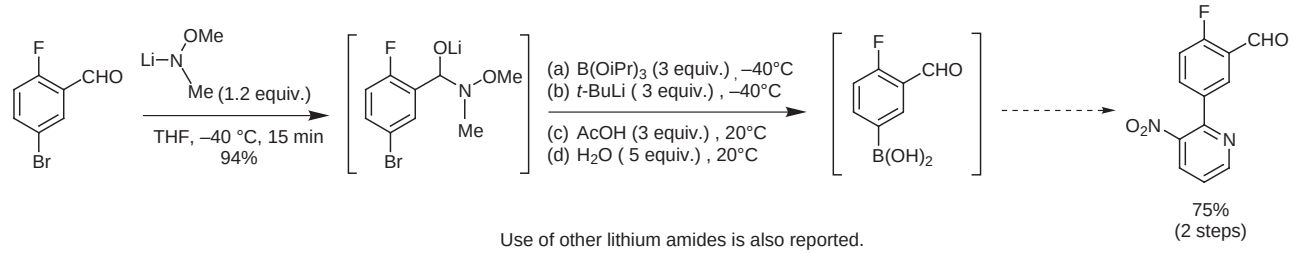
10 examples of bicyclo[3.2.1]octan-8-ones. High *endo*:*exo* selectivity obtained for the Pd-catalysed rearrangement with β-ketosulfones, but poor stereoselectivity for β-ketoesters.

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



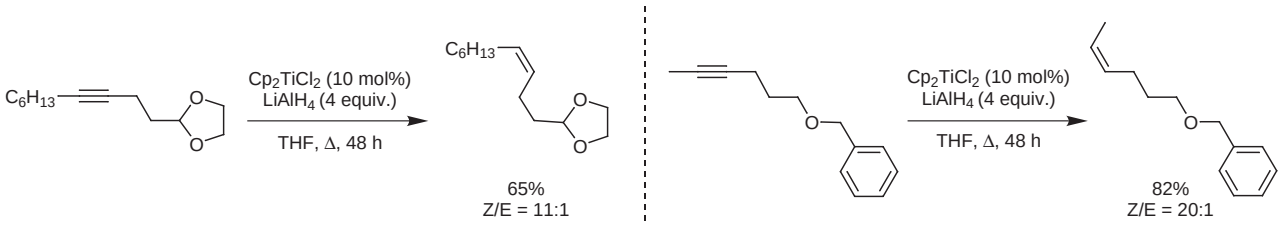
7 examples (yields 80-93%).

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



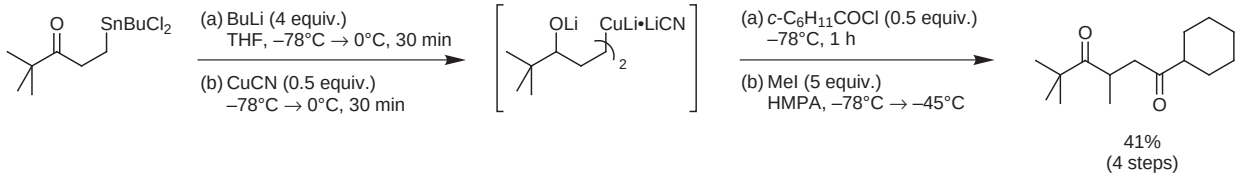
Use of other lithium amides is also reported.

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



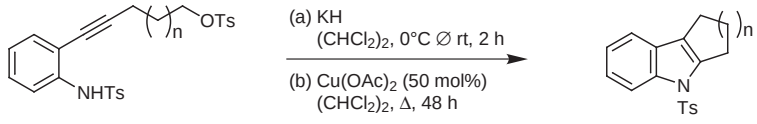
6 examples (Yields 52-82%, 9:1 *Z/E* 20 : 1).

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



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

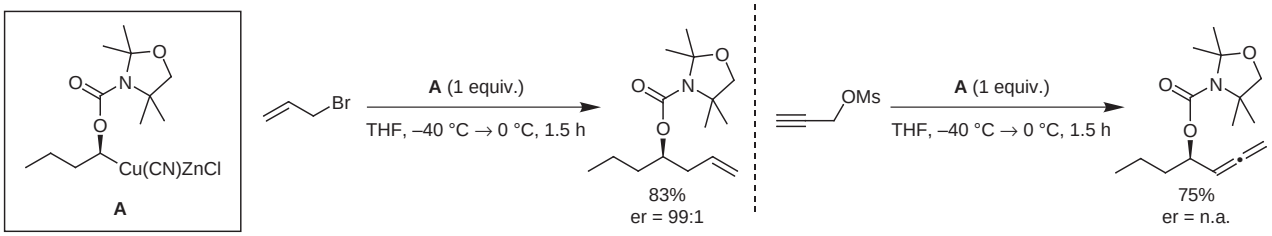
Copper-catalyzed indole formation from 2-ethynylaniline derivatives. **Heteroannulation**
Hiroya, K.; Itoh, S.; Ozawa, M.; Kanamori, Y.; Sakamoto, T. *Tetrahedron Lett.* **2002**, *43,* 1277.



n	Yield
1	67%
2	64%

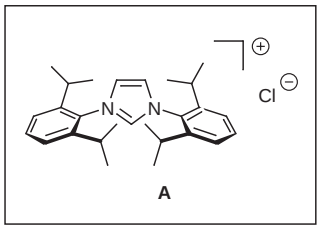
16 examples of indole cyclisation (Yields 9-95%)

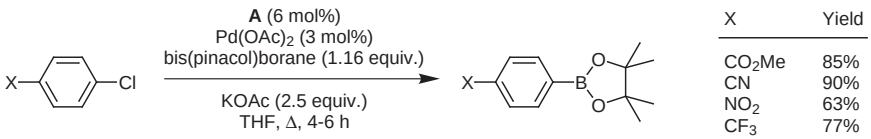
Preparation and utilization of nonracemic secondary α-(carbamoyloxy)alkylzinc and copper reagents. **C-C Coupling**
Papillon, J. P.; Taylor, R. J. K. *Org Lett.* **2002**, *4*, 119.



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

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

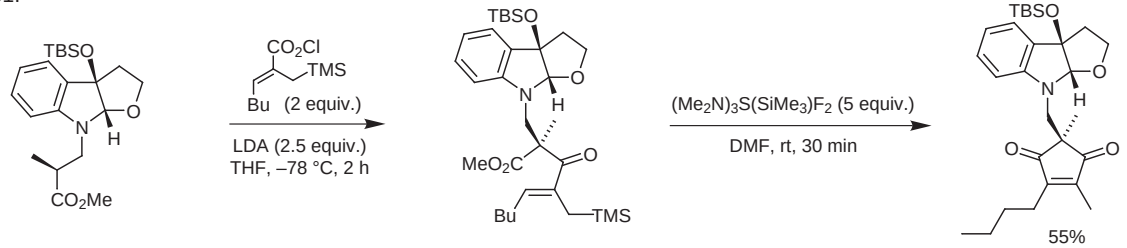




X	Yield
CO_2Me	85%
CN	90%
NO_2	63%
CF_3	77%

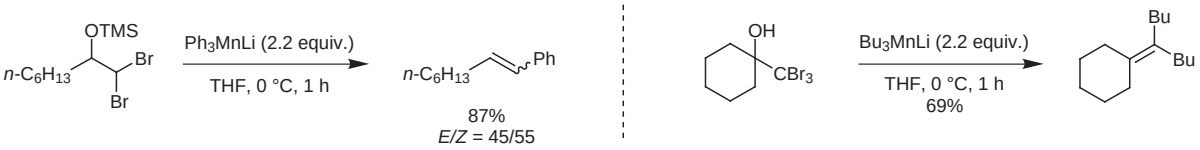
8 examples (yields 53-90%).

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



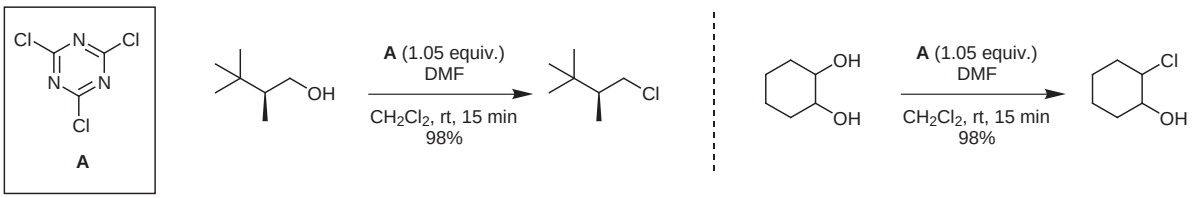
2 examples (yields 46-55%).

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



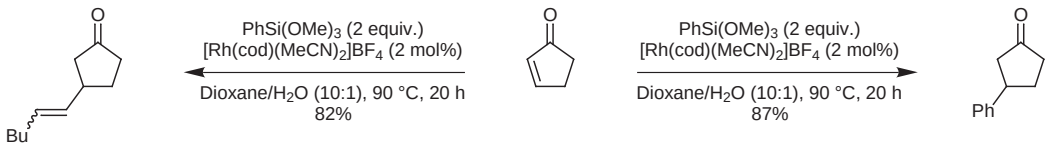
25 examples (yields 13-87%, 69/31 *E/Z* 45/55).

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



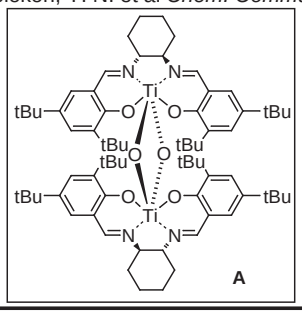
12 examples of aliphatic alcohols (yields 96-99%), 3 examples of diols (yields 95-98%), 2 examples of unsaturated alcohols (yields 92-98%) and 6 examples of β-amino alcohols (yields 83-97%).

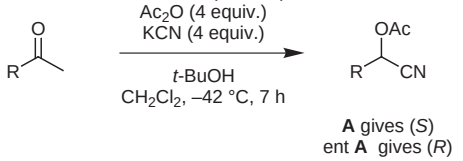
Rh-catalyzed conjugate addition of organosiloxanes to α,β-unsaturated carbonyl compounds. **1,4-Addition**
Oi, S.; Honma, Y.; Inoue, Y. *Org Lett.* **2002**, *4*, 667.



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.

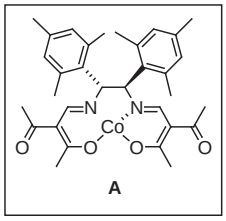


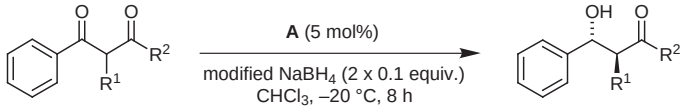


R	yield (**A**)	%ee (**A**)	yield (ent **A**)	%ee (ent **A**)
Ph	93%	90%	92%	89%
p-FC_6H_4	98%	92%	99%	93%
$PhCH_2CH_2$	80%	84%	79%	82%
Me_2CH	64%	69%	62%	72%

19 examples (yields 40-99%, ee 60-93%).

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

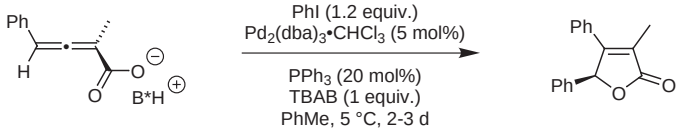




R^1	R^2	yield	*anti*	%ee
Me	*i*-Pr	46%	99%	96%
Et	*i*-Pr	41%	99%	98%
allyl	*i*-Pr	47%	98%	96%
Me	*t*-Bu	48%	99%	97%
Me	C_9H_{19}	47%	98%	96%
Me	*sec*-Bu	47%	98%	95%
Me	$PhCH_2$	45%	94%	98%

Sodium borohydride is modified using ethanol and tetrahydrofurfuryl alcohol.

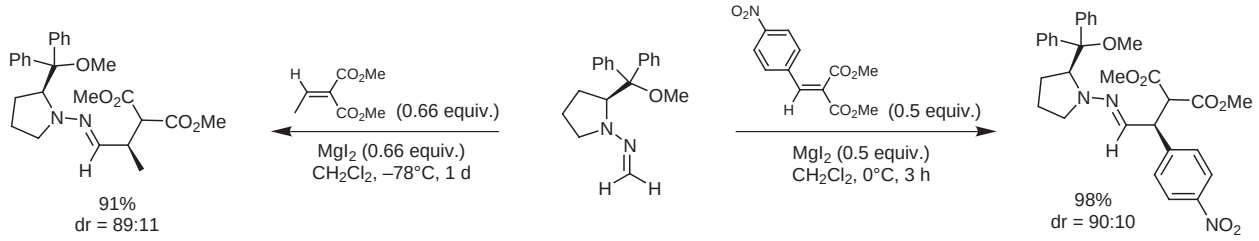
Chirality transfer in Pd(0)-catalyzed coupling-cyclization of aryl iodides. **Enantioselective Coupling-Cyclization**
Ma, S.; Shi, Z. *Chem. Commun*. **2002**, 540.



B*	Yield	%ee
L-(–)-cinchonidine	90%	91%
L-(–)-α-methylbenzylamine	60%	93%

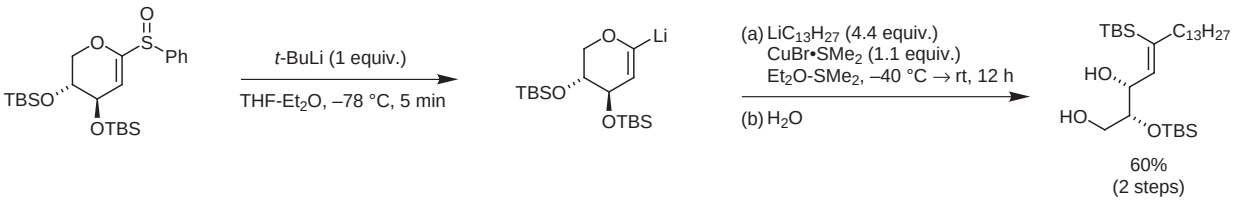
11 examples (yields 55-90%, ee 91-98%).

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



7 examples (yields 70-98%, %de 68-90%).

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



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