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.

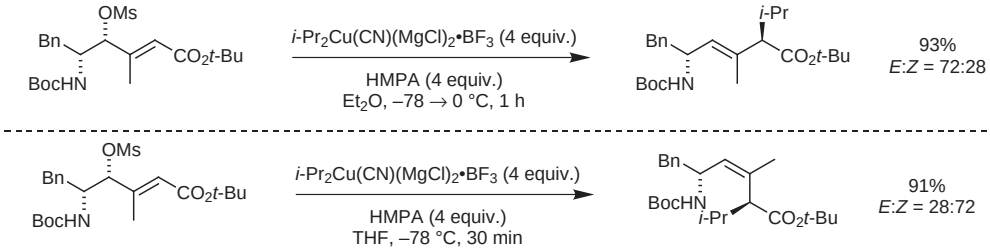
Synthesis 2002, No. 11, 22 08 2002. Article Identifier:
1437-210X,E;2002,0,11,1615,1622,ftx,en;X00602SS.pdf.

ISSN 0039-7881

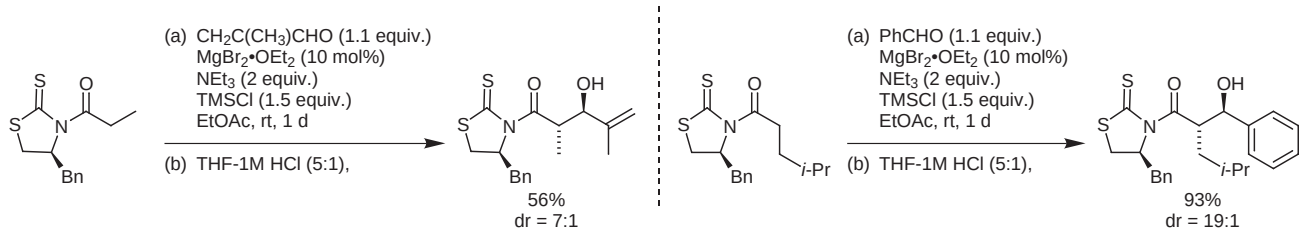
The journals regularly covered by the abstractors are:

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

Cu-mediated stereoselective 1,4-additon. **1,4-Addition**
Oishi, S.; Kamano, T.; Niida, A.; Odagaki, Y.; Tamamura, H.; Otaka, A.; Hamanaka, N.; Fujii, N. *Org. Lett.* **2002**, *4*, 1051.

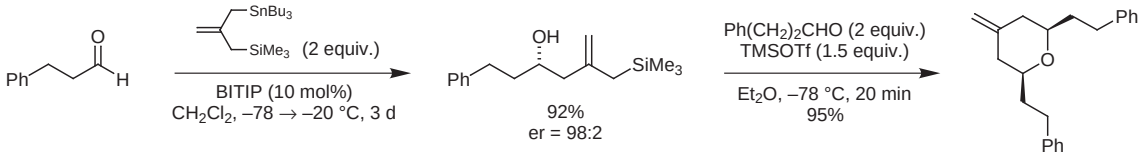


Magnesium halide-catalysed anti-aldol reactions of chiral *N*-acylthiazolidinethiones. **Stereoselective 1,2-Addition**
Evans, D. A.; Downey, C. W.; Shaw, J. T.; Tedrow, J. S. *Org. Lett.* **2002**, *4*, 1127.



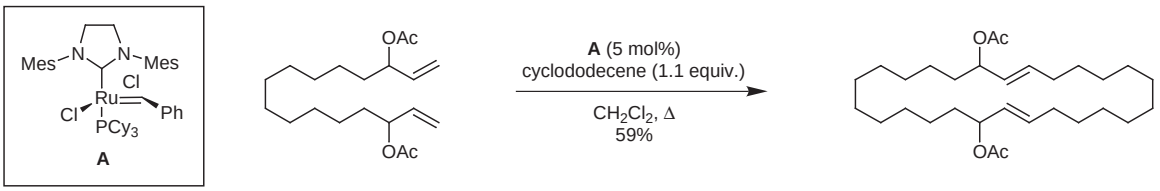
11 examples (yields 56-93%, %de 75-90%).

Stereoselective synthesis of 2,6-disubstituted-4-methylene tetrahydropyrans. **1,2-Addition/Annulation**
Keck, G. E.; Covel, J. A.; Schiff, T.; Yu, T. *Org. Lett.* **2002**, *4*, 1189.



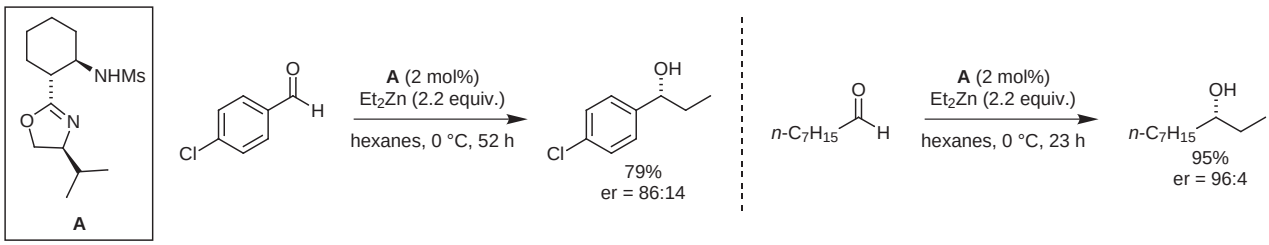
6 examples [yields 71-91% (2 steps), %ee 90-96%].

Ring expansion *via* olefin metathesis. **Metathesis**
Lee, C. W.; Choi, T-L.; Grubbs, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 3224.



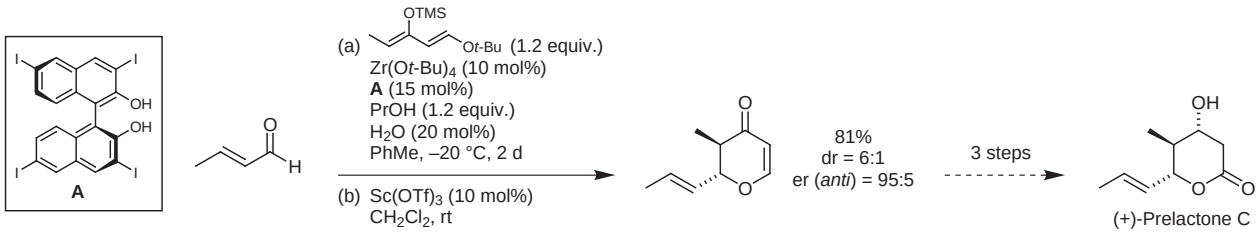
18 Examples (yield 23-63%).

Stereoselective addition of Et_2Zn to aldehydes. **1,2-Addition**
Wipf, P.; Wang, X. *Org. Lett.* **2002**, *4*, 1197.



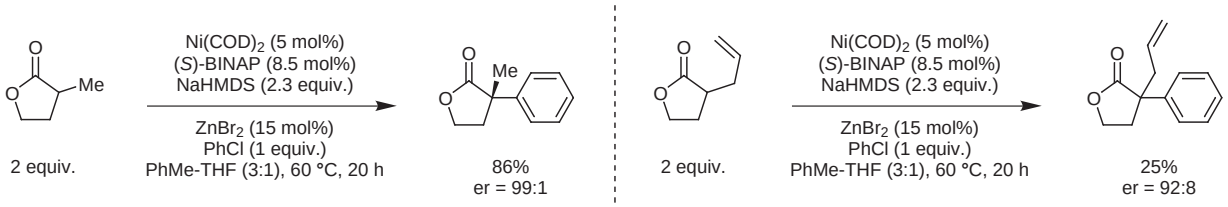
10 examples (yields 47-97%, %ee 11->98%).

Catalytic asymmetric hetero Diels–Alder reaction. **Hetero Diels–Alder**
Yamashita, Y.; Saito, S.; Ishitani, H.; Kobayashi, S. *Org. Lett.* **2002**, *4*, 1221.



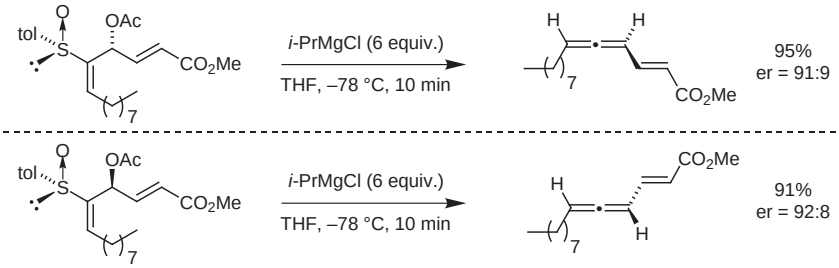
13 examples (yields 39-100%, %ee 22-98%).

Nickel-BINAP catalyzed enantioselective α-arylation of α-substituted γ-butyrolactones. **Arylation**
Buchwald, S. L.; Spielvogel, D. J. *J. Am. Chem. Soc.* **2002**, *124*, 3500.



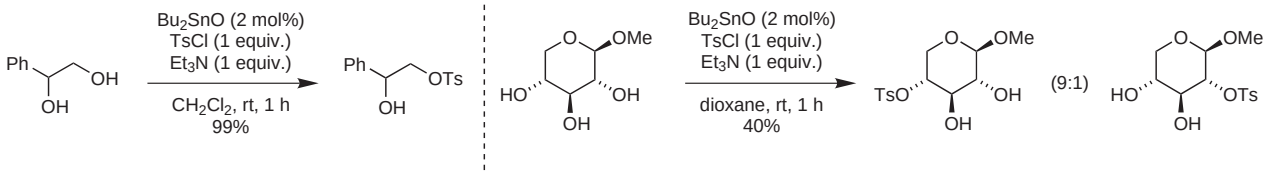
16 Examples (yield 25-95%, %ee 83-99%).

Synthesis of allenes from alkenyl aryl sulfoxides. **Metallation**
Satoh, T.; Hanaki, N.; Kuramochi, J.; Inoue, Y.; Hosoya, K.; Saki, K. *Tetrahedron* **2002**, *13*, 2533.



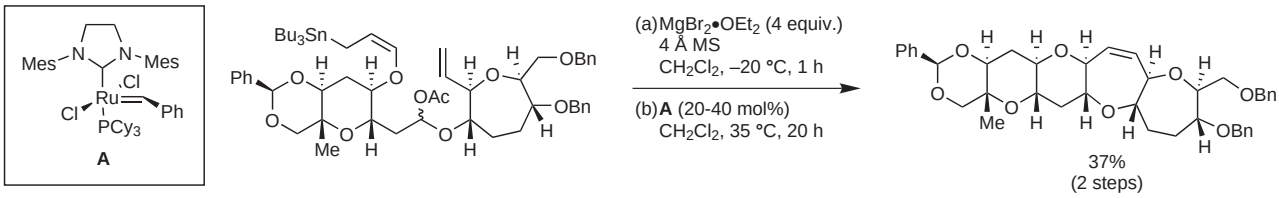
22 examples of metallation-allenation (yields 47-99%).

Catalytic regioselective sulfonylation of α-chelatable alcohols. **Sulfonylation**
Martinelli, M. J.; Vaidyanathan, R.; Pawlak, J. M.; Nayar, N. K.; Dhokte , U. P.; Doecke, C. W.; Zollars, L. M. H.; Moher, E. D.; Khau, V. V.; Kosmrlj, B. *J. Am. Chem. Soc.* **2002**, *124*, 3578.



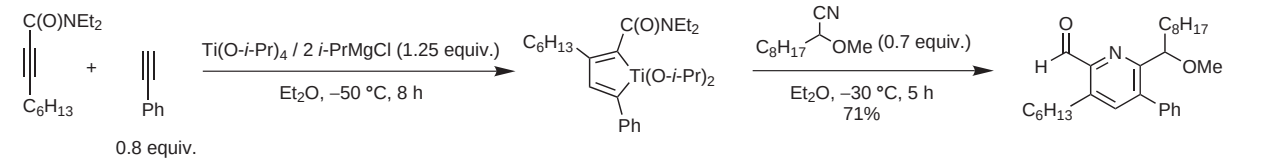
16 examples (yields 32-99%).

Synthesis of polycyclic ethers *via* the intramolecular allylation of α-acetoxy ethers and ring-closing metathesis. **Allylation/ Metathesis**
Kadota, I.; Ohno, A.; Matsuda, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 3562.



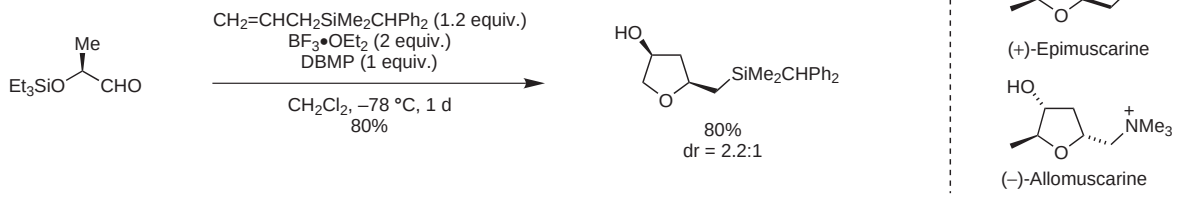
7 examples (yields 37-80%, 2 steps).

Synthesis of metalated pyridines. **Arylation**
Suzuki, D.; Tanaka, R.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **2002**, *124*, 3518.



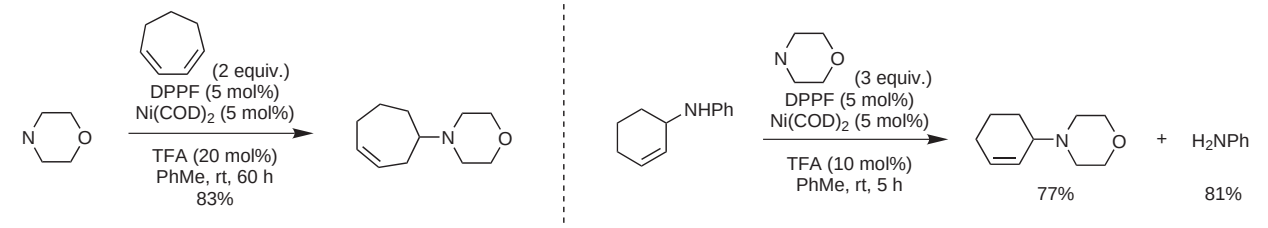
13 Examples (yield 51-99%).

Stereoselective synthesis of tetrahydrofurans *via* formal [3+2]-cycloaddition of aldehydes and allylsilanes. **[3+2]-Cycloaddition**
Angle, S. R.; El-Said, N. A. *J. Am. Chem. Soc.* **2002**, *124*, 3608.



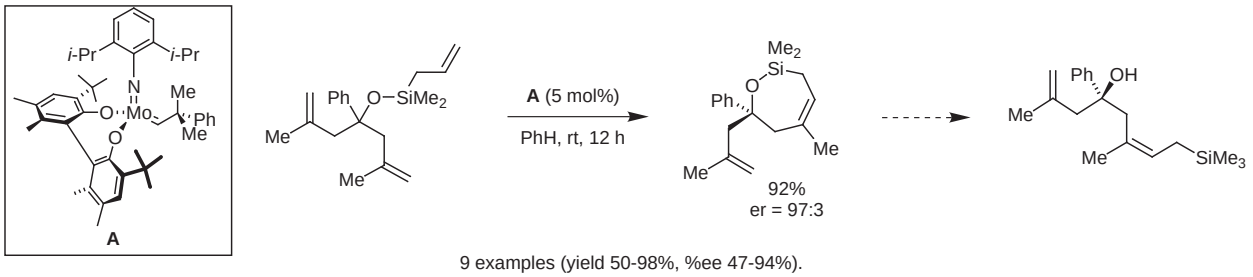
13 examples (yields 41-96%). Formal syntheses of (+)-epimuscarine and (–)-allomuscarine are also reported.

General Nickel-catalyzed hydroamination of 1,3-dienes by alkylamines. **Hydroamination**
Pawlas, J.; Nakao, Y.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 3669.



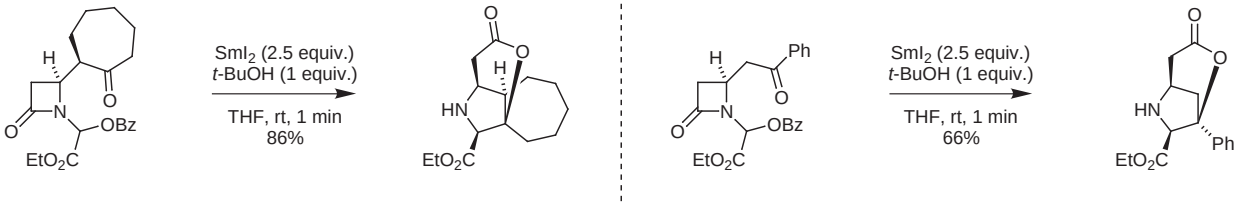
16 examples (yields 38-94%). 10 examples of Nickel-catalyzed exchange of amines with allylic amines.

Enantioselective synthesis of medium-ring heterocycles, tertiary ethers and tertiary alcohols. **Enantioselective Metathesis**
Kiely, A. F.; Jernelius, J. A.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 2868.



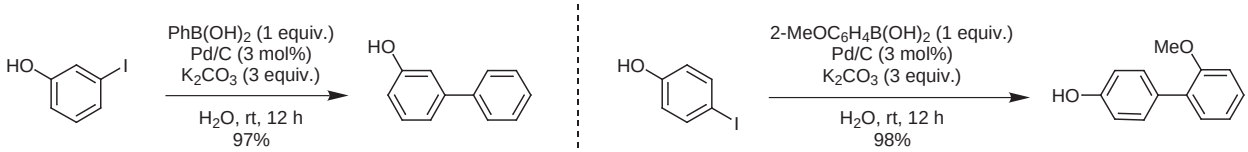
9 examples (yield 50-98%, %ee 47-94%).

SmI_2-mediated cyclization of β-lactams. **Diastereoselective Cyclization**
Jacobsen, M. F.; Turks, M.; Hazell, R.; Skrydstrup, T. *J. Org. Chem.* **2002**, *67*, 2411.



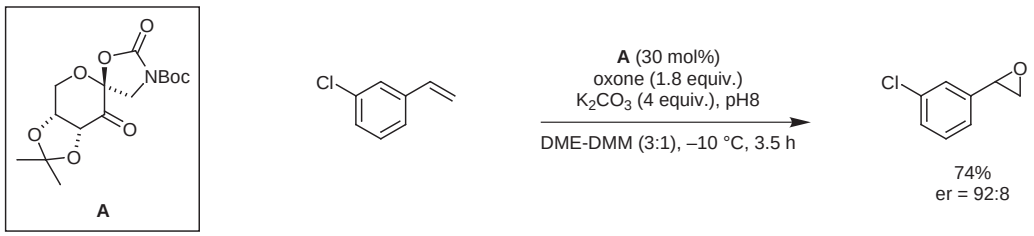
9 examples (yields 42-86%).

Pd/C-catalyzed coupling of halophenols and arylboronic acids in aqueous media. **sp^2-sp^2 Coupling**
Sakurai, H.; Tsukuda, T.; Hirao, T. *J. Org. Chem.* **2002**, *67*, 2721.



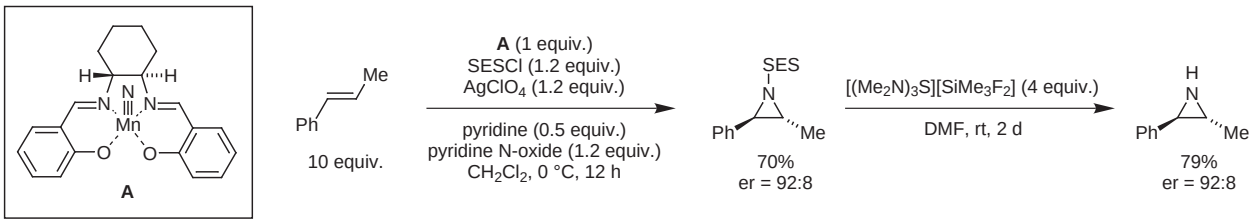
9 examples (yields 76-99%).

Asymmetric epoxidation of *cis* and terminal olefins. **Asymmetric Epoxidation**
Tian, H.; She, X.; Yu, H.; Shu, L.; Shi, Y. *J. Org. Chem.* **2002**, *67*, 2435.



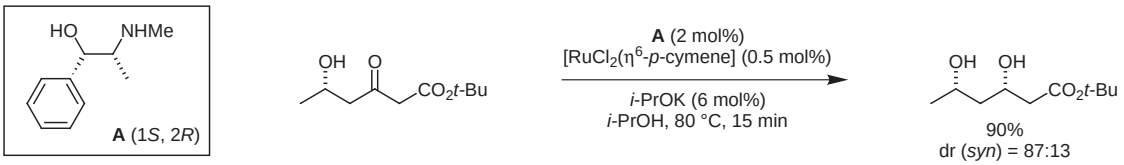
28 examples (yields 47-93%, %ee = 30-97%). Synthesis of the chiral ketone catalyst is also reported.

Novel stereoselective synthesis of aziridines and oxazolines. **N1 Transfer**
Nishimura, M.; Satoshi, M.; Takahashi, T.; Oderaotoshi, Y.; Komatsu, M. *J. Org. Chem.* **2002**, *67*, 2101.



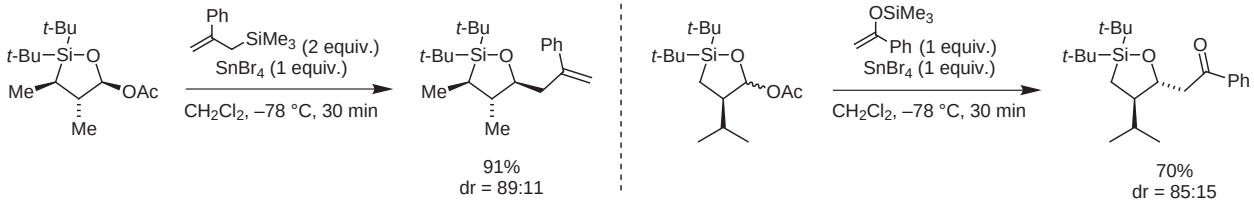
6 examples of aziridine formation (yields 37-70%, %ee = 24-93%) and 12 examples of oxazoline formation (yields 45-88%, %ee = 9-90%).

Ruthenium-catalyzed asymmetric transfer hydrogenation of chiral 5-hydroxy-3-ketoesters. **Asymmetric Hydrogenation**
Everere, K; Franceschini, N; Morteux, A; Carpentier, J-F. *Tetrahedron Lett*. **2002**, *43*, 2569.



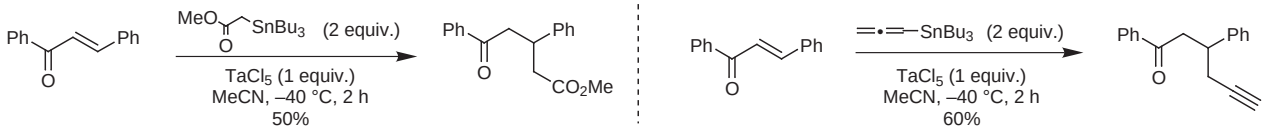
5 different arenes and chiral ligands used (conversion 29-100%, %de 12-79%).

Diastereoselective nucleophilic substitution reactions of oxasilacyclopentane acetals. **Nucleophilic Substitution**
Bear, T.J.; Shaw, J. T.; Woerpel, K. A. *J. Org. Chem.* **2002**, *67*, 2056.



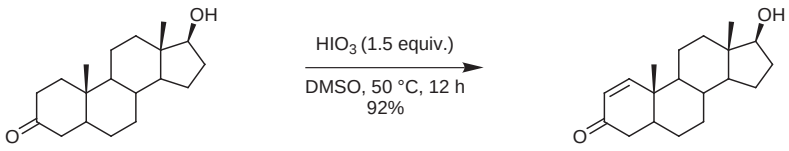
20 examples (yields 52-97%).

Conjugate addition of organotantalum reagents to enones. **1,4-Addition**
Shibata, I; Kano, T; Kanazaw, N; Fukuoka, S; Baba, A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1389.



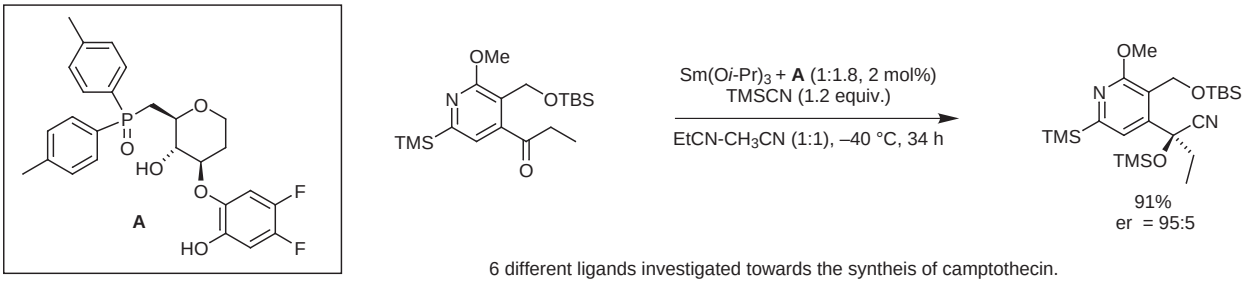
23 examples (yields <1-99%). Catalytic use of $TaCl_5$ (20 mol %) is possible with the addition of Me_3SiCl (1 equiv.). The use of allylic, benzyl and alkynyl tributyltin reagents is also reported.

Dehydrogenation of aldehydes and ketones using HIO_3 and I_2O_5. **Dehydrogenation**
Nicolaou, K. C; Montagnon, T; Bara, P. S. *Angew. Chem. Int. Ed*. **2002**, *41*, 1386.



10 examples (yields 74-95%). Highly chemoselective and safer to use than IBX.

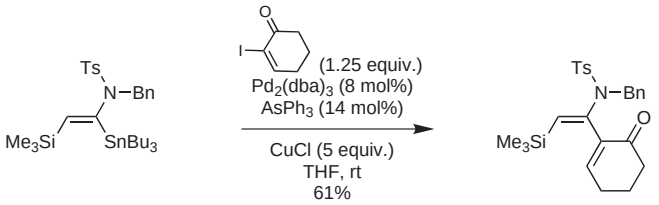
Catalytic enantioselective cyanosilylation of ketones. **Nucleophilic Addition**
Yabu, K; Masumoto, S; Kanai, M; Curran, D. P; Shibasaki, M. *Tetrahedron Lett*. **2002**, *43*, 2923.



6 different ligands investigated towards the syntheis of camptothecin.

Synthesis of 1,2-bis-substituted enamides *via* a modified Stille coupling procedure.
Timbart, L.; Cintrat, J.-C. *Chem.–Eur. J.* **2002**, *8*, 1637.

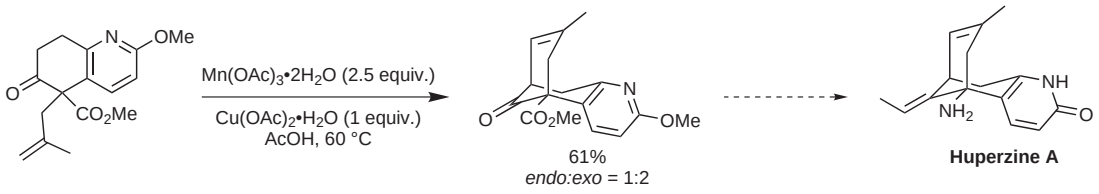
sp²-sp² Coupling



11 examples (yields 28-80%). Iododesilylation of vinylsilanes with ICl (3 examples, yields 32-56%) was also reported.

Mn(III)-mediated oxidative radical cyclization of cyclic β-ketoesters.
Lee, I. Y. C.; Jung, M. H.; Lee, H. W.; Yang, J. Y. *Tetrahedron Lett.* **2002**, *43*, 2407.

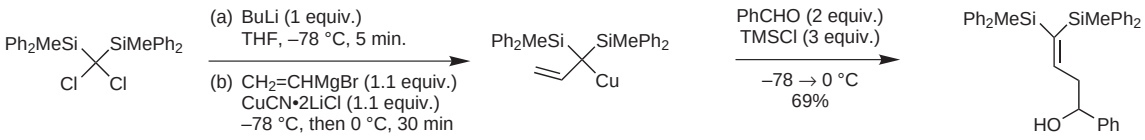
Radical Cyclization



5 examples (yields 21-84%). *Exo* to *endo* conversion was performed with CF_3SO_3H.

Synthesis and regioselective reactions of α,α-bis(silyl)-substituted allylcopper reagents.
Kondo, J.; Inoue, A.; Shinokubo, H.; Oshima, K. *Tetrahedron Lett.* **2002**, *43*, 2399.

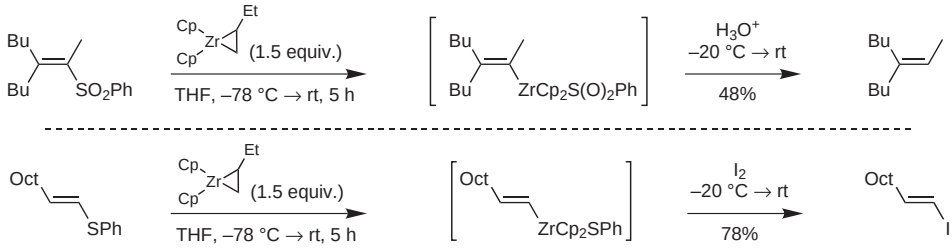
Nucleophilic Addition



Vinyl (13 examples, yields 52-86%); isopropenyl, α-styryl and β-styryl (10 examples, yields 55-83%).

Preparation of vinylic organozirconium derivatives from vinyl sulfides, sulfoxides, and sulfones.
Farhat, S.; Marek, I. *Angew. Chem. Int. Ed.* **2002**, *41*, 1410.

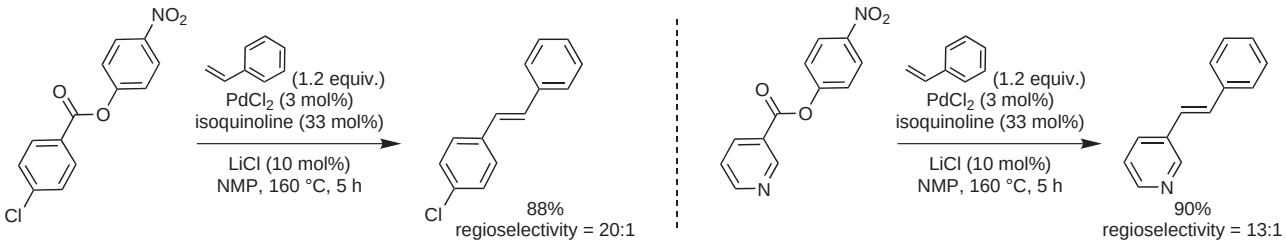
Metallation



10 examples (yields 48-90%). Transmetallation of the vinyl zirconium species is also reported.

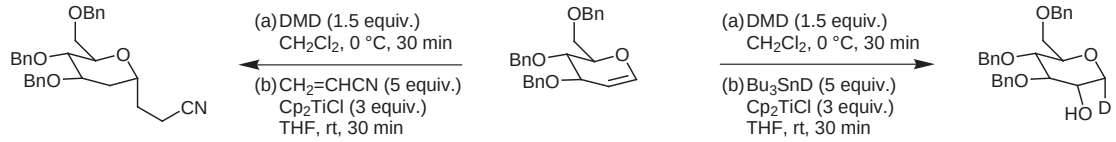
Pd-catalyzed decarbonylative olefination of aryl esters
Gooßen, L. J.; Paetzold, J. *Angew. Chem. Int. Ed.* **2002**, *7*, 1237.

sp²-sp² Coupling



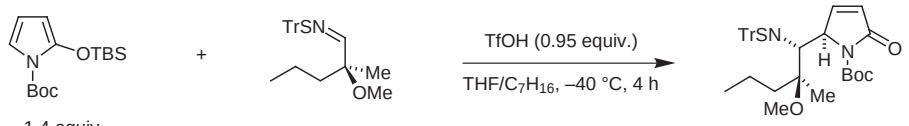
20 examples (yields 40-95%, 4:1 > regioselectivity < 20:1).

Preparation of α-*C*-glycosides from glycals. **Reductive Ring Opening/Trapping**
Parrish, J. D.; Little, R. D. *Org. Lett.* **2002**, *4*, 1439.



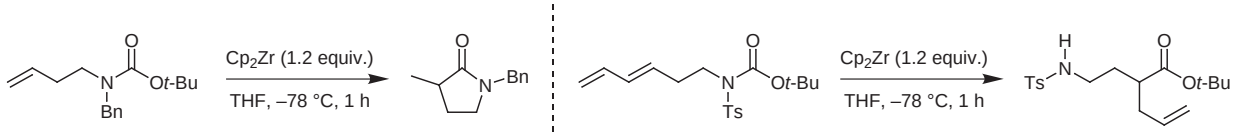
9 examples (yields 10, 47-61%).

Highly diastereoselective coupling reaction. **1,2-Addition**
Barnes, D. M.; McLaughlin, M. A.; Oie, T.; Rasmussen, M. W.; Stewart, K. D.; Wittenberger, S. J. *Org. Lett.* **2002**, *4*, 1427.



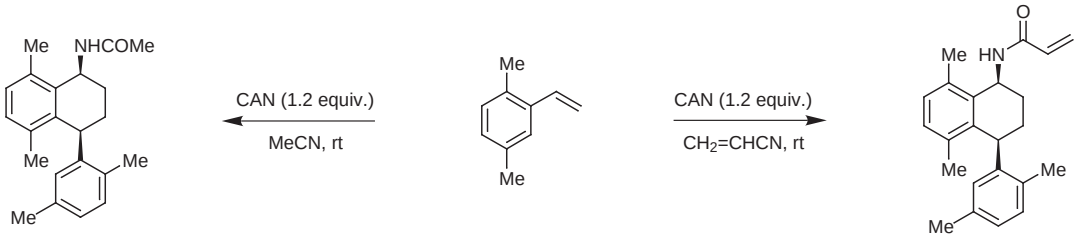
Attempts using BF_3•OEt_2 and TMSOTf resulted with diminished diastereoselectivity.

Zirconium-mediated intramolecular ester transfer reaction. **Ester Transfer**
Ito, H.; Omodera, K.; Takigawa, Y.; Taguchi, T. *Org. Lett.* **2002**, *4*, 1499.



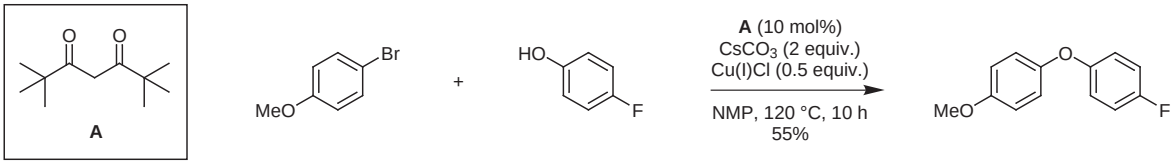
10 examples (yields 41-95%).

One-pot synthesis of 1-amino-4-aryltetralins from styrenes. **Cyclodimerization**
Nair, V.; Rajan, R.; Rath, N. P.; Taguchi, T. *Org. Lett.* **2002**, *4*, 1575.



12 examples (yields 40-82%, %de 9-83%).

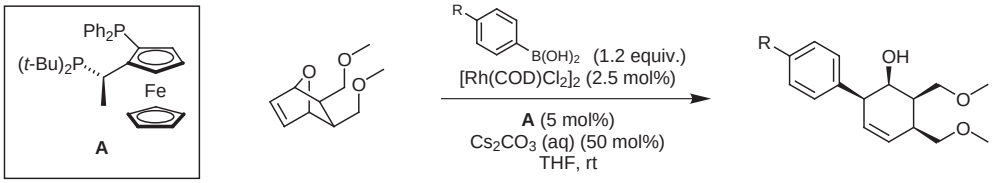
Ullmann diaryl ether synthesis. **Ullmann Coupling**
Buck, E.; Song, Z. J.; Tschaen, D.; Dormer, P. G.; Volante, R. P.; Reider, P. J. *Org. Lett.* **2002**, *4*, 1623.



13 examples (yields 51-85%).

Rhodium-catalyzed asymmetric ring opening of oxabicyclic alkenes with organoboronic acids.
Lautens, M.; Dockendorff, C.; Fagnou, K.; Malicki, A. *Org. Lett*. **2002**, *4*, 1311.

Asymmetric Ring-Opening

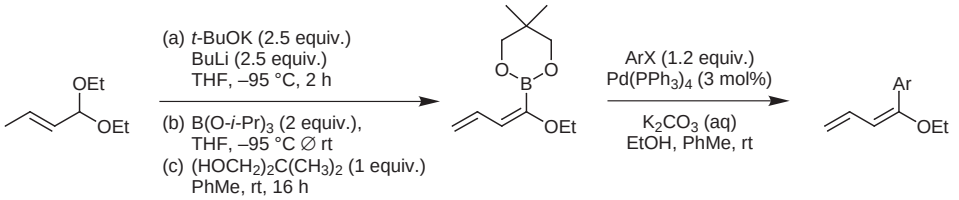


R	Yield	%ee
Me	88%	95%
OMe	87%	96%

12 examples (yields 60-95%, %ee 88-99%). 3 examples using aromatic-fused oxabicyclic alkenes (3 examples, yields 60-93%, %ee 88-92%) with organoboronic esters used instead of acids.

Synthesis and subsequent Suzuki cross-coupling of butadienyl- and styrylboronic esters.
Tivola, P. B.; Deagostino, A.; Prandi, C.; Venturello, P. *Org. Lett*. **2002**, *4*, 1275.

sp²-sp² Coupling

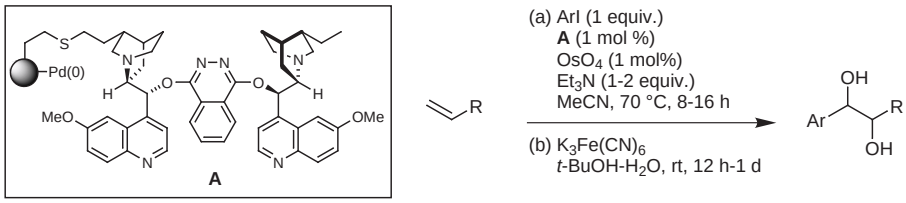


ArX	Temp	Yield
o-MeOPhI	rt	75%
p-MeOPhI	rt	70%
p-MeCOPhI	rt	90%
PhBr	60 °C	83%
p-MePhOTf	rt	85%

16 examples (yields 10-90%) and 4 examples involving the preparation and coupling of styrylboronic esters (yields 65-92%).

A bifunctional catalyst for tandem Heck-asymmetric dihydroxylation of olefins.
Choudary, B. M.; Chowdari, N. S.; Jyothi, K.; Kumar, N. S.; Kantam, M. L. *Chem. Commun*. **2002**, 586.

Heck/Asymmetric Dihydroxylation

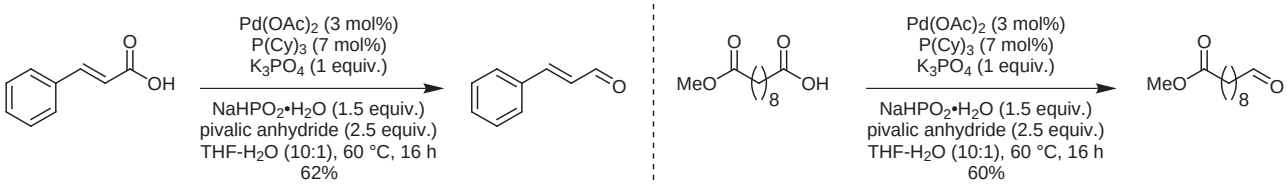


R	Ar	Yield	%ee
CO_2Me	Ph	99%	92%
CO_2Et	*p*-MeOPh	96%	99%
CO_2Et	*P*-NO_2Ph	95%	98%
Ph	Ph	92%	99%

NMO also used as the co-oxidant (yields 90-94%, %ee 88-99%).

Palladium-catalyzed selective reduction of carboxylic acids to aldehydes.
Gooßen, L. J.; Ghosh, K. *Chem. Commun*. **2002**, 836.

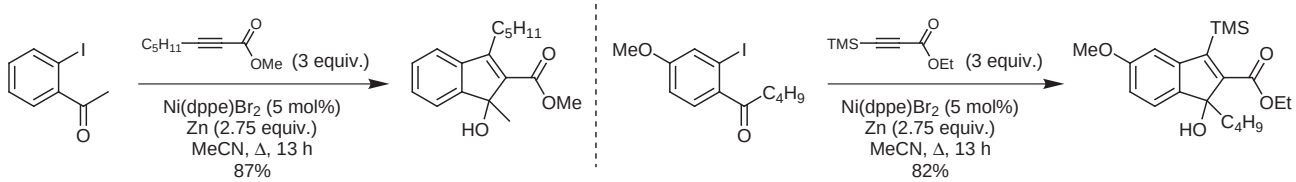
Reduction



15 examples (yields 53-75%). Alkoxy, keto, cyano, hydroxyl and protected amino groups are tolerated.

Nickel-catalyzed regioselective carbocyclization of *ortho*-halophenyl ketones with propiolates.
Rayabarapu, D. K.; Cheng C.-H. *Chem. Commun*. **2002**, 942.

Carbocyclization



16 examples (46-88%).