

**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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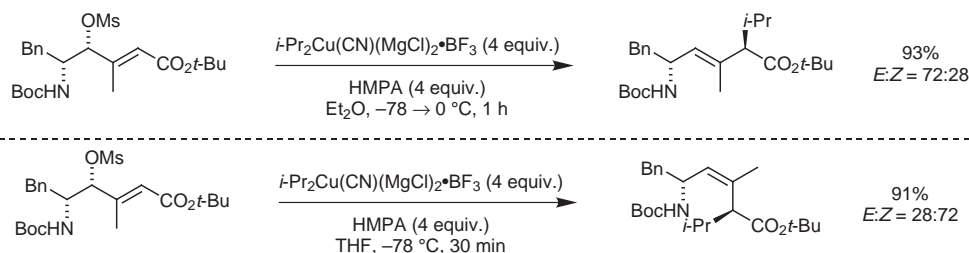
The journals regularly covered by the abstractors are:

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-addition.

Oishi, S.; Kamano, T.; Niida, A.; Odagaki, Y.; Tamamura, H.; Otaka, A.; Hamanaka, N.; Fujii, N. *Org. Lett.* **2002**, *4*, 1051.

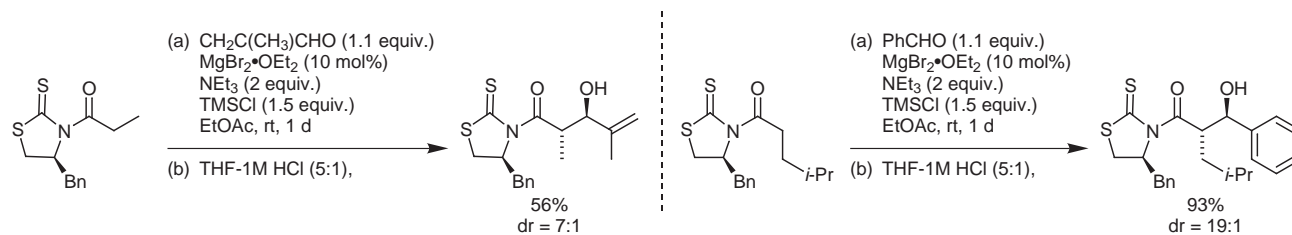
1,4-Addition



Magnesium halide-catalysed anti-aldol reactions of chiral *N*-acylthiazolidinethiones.

Evans, D. A.; Downey, C. W.; Shaw, J. T.; Tedrow, J. S. *Org. Lett.* **2002**, *4*, 1127.

Stereoselective 1,2-Addition

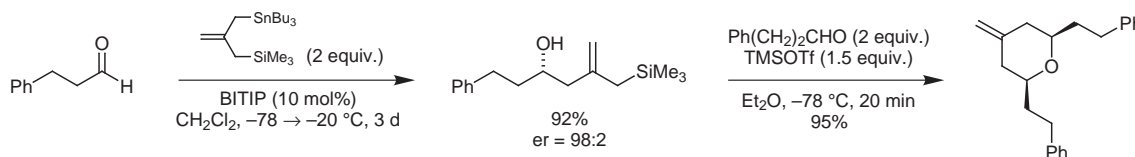


11 examples (yields 56-93%, %de 75-90%).

Stereoselective synthesis of 2,6-disubstituted-4-methylene tetrahydropyrans.

Keck, G. E.; Covell, J. A.; Schiff, T.; Yu, T. *Org. Lett.* **2002**, *4*, 1189.

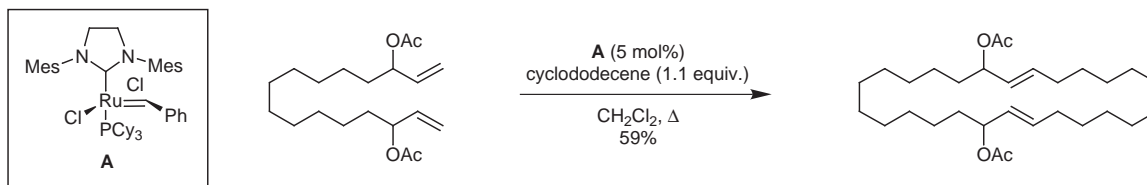
1,2-Addition/Annulation



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

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

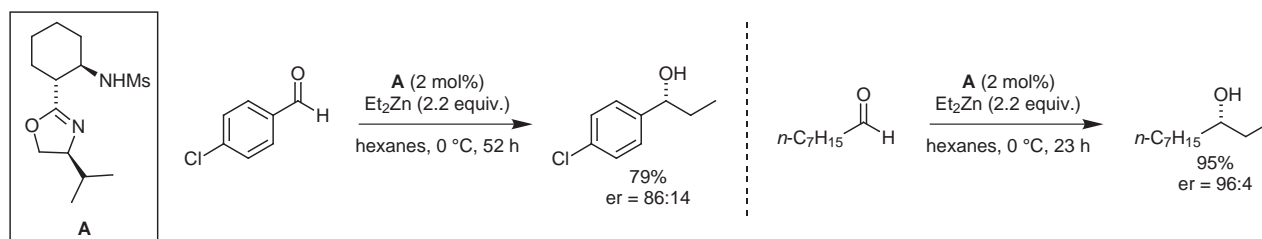
Metathesis



18 Examples (yield 23-63%).

Stereoselective addition of  $\text{Et}_2\text{Zn}$  to aldehydes.Wipf, P.; Wang, X. *Org. Lett.* **2002**, *4*, 1197.

1,2-Addition

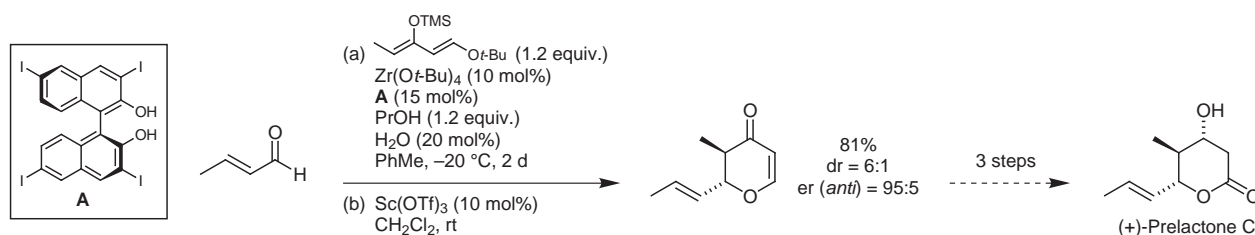


10 examples (yields 47-97%, %ee 11-&gt;98%).

Catalytic asymmetric hetero Diels-Alder reaction.

Yamashita, Y.; Saito, S.; Ishitani, H.; Kobayashi, S. *Org. Lett.* **2002**, *4*, 1221.

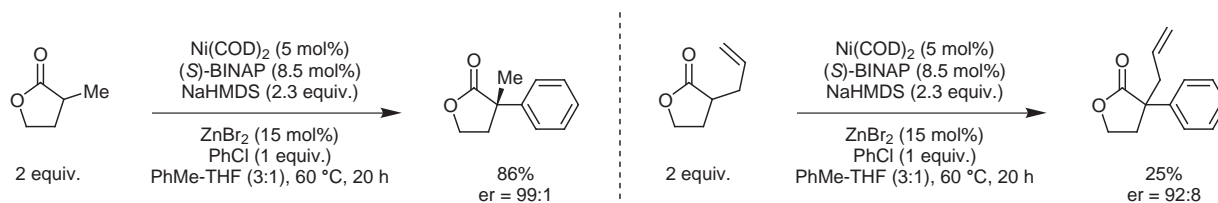
Hetero Diels-Alder



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

Nickel-BINAP catalyzed enantioselective  $\alpha$ -arylation of  $\alpha$ -substituted  $\gamma$ -butyrolactones.Buchwald, S. L.; Spielvogel, D. J. *J. Am. Chem. Soc.* **2002**, *124*, 3500.

Arylation

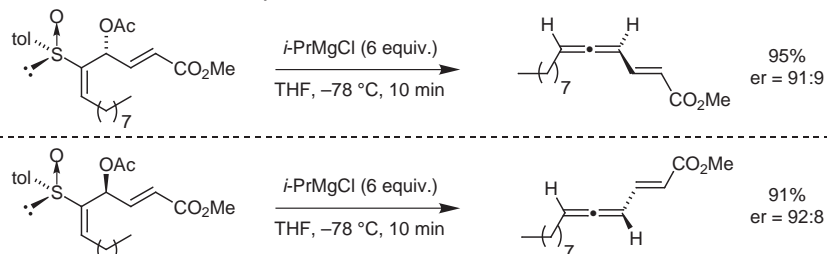


16 Examples (yield 25-95%, %ee 83-99%).

Synthesis of allenes from alkenyl aryl sulfoxides.

Satoh, T.; Hanaki, N.; Kuramochi, J.; Inoue, Y.; Hosoya, K.; Saki, K. *Tetrahedron* **2002**, *13*, 2533.

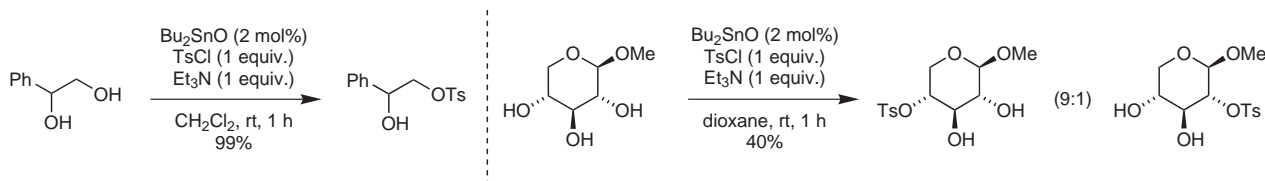
Metallation



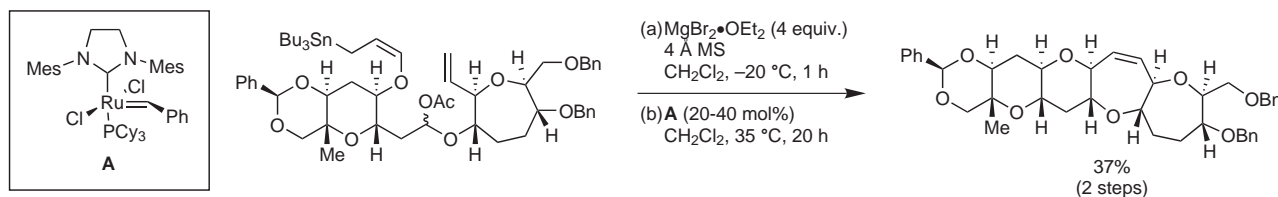
22 examples of metallation-allenation (yields 47-99%).

Catalytic regioselective sulfonylation of  $\alpha$ -chelatable alcohols.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.

Sulfonylation



16 examples (yields 32-99%).

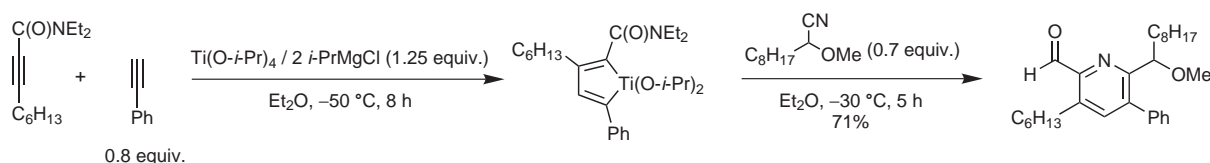
Synthesis of polycyclic ethers *via* the intramolecular allylation of  $\alpha$ -acetoxy ethers and ring-closing metathesis.Kadota, I.; Ohno, A.; Matsuda, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 3562.Allylation/  
Metathesis

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

Synthesis of metalated pyridines.

Suzuki, D.; Tanaka, R.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **2002**, *124*, 3518.

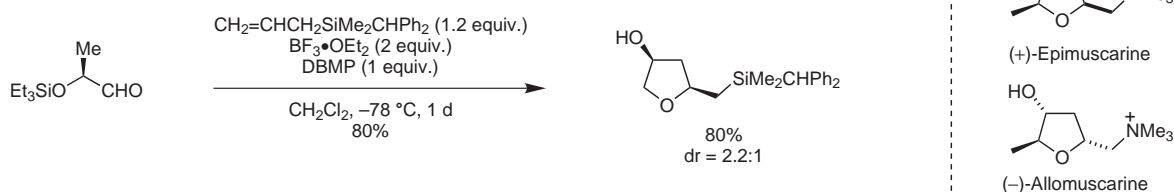
Arylation



13 Examples (yield 51-99%).

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

[3+2]-Cycloaddition

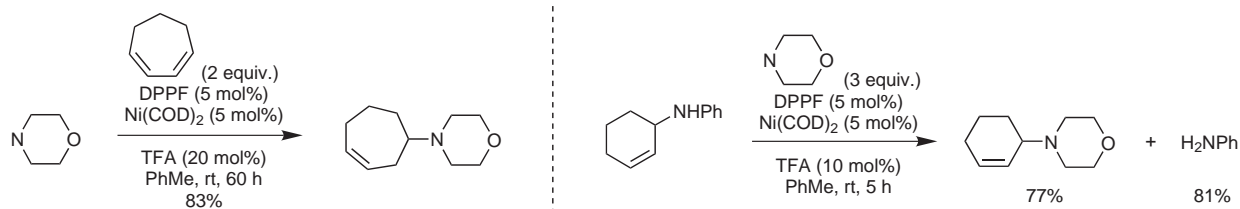


13 examples (yields 41-96%). Formal syntheses of (+)-epimuscarine and (-)-allomuscarine are also reported.

General Nickel-catalyzed hydroamination of 1,3-dienes by alkylamines.

Pawlas, J.; Nakao, Y.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 3669.

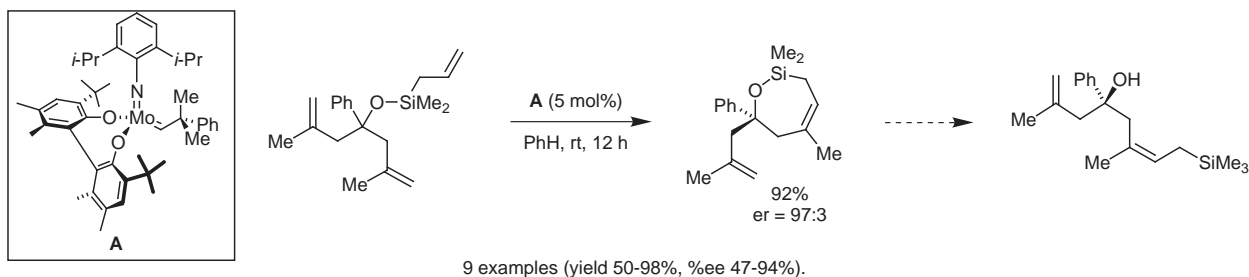
Hydroamination



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.  
Kiely, A. F.; Jemelius, J. A.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 2868.

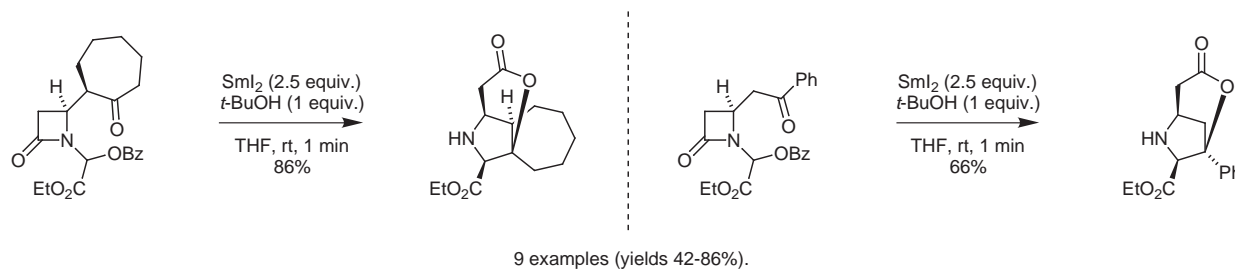
## Enantioselective Metathesis



Sml<sub>2</sub>-mediated cyclization of β-lactams.

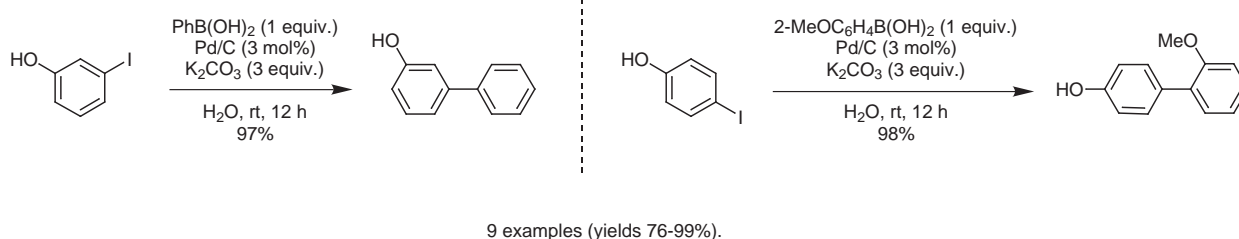
Jacobsen, M. F.; Turks, M.; Hazell, R.; Skrydstrup, T. *J. Org. Chem.* **2002**, *67*, 2411.

## Diastereoselective Cyclization



Pd/C-catalyzed coupling of halophenols and arylboronic acids in aqueous media.

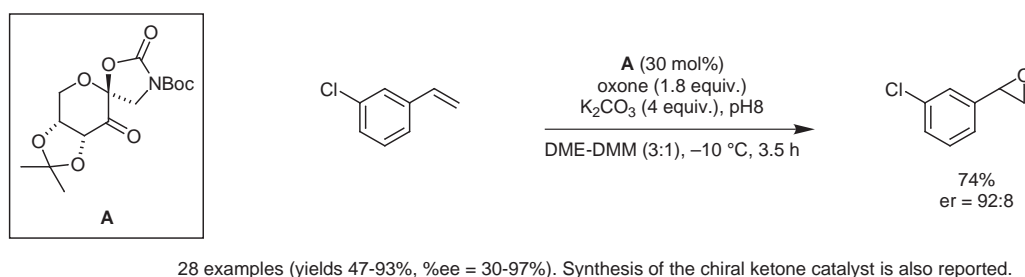
Sakurai, H.; Tsukuda, T.; Hirao, T. *J. Org. Chem.* **2002**, *67*, 2721.

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

Asymmetric epoxidation of *cis* and terminal olefins.

Tian, H.; She, X.; Yu, H.; Shu, L.; Shi, Y. *J. Org. Chem.* **2002**, *67*, 2435.

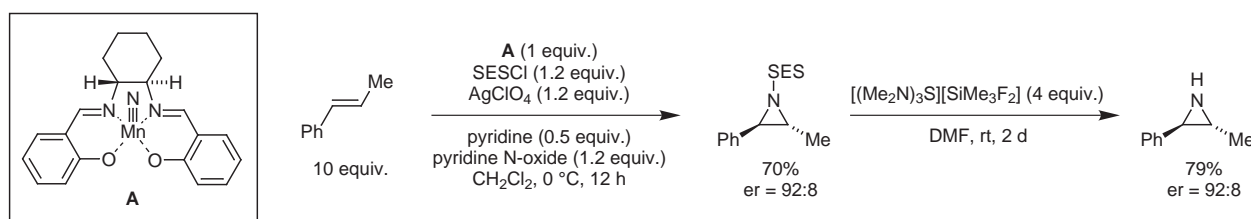
## Asymmetric Epoxidation



Novel stereoselective synthesis of aziridines and oxazolines.

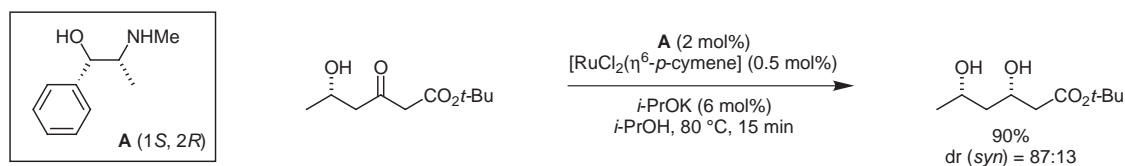
Nishimura, M.; Satoshi, M.; Takahashi, T.; Oderaotoshi, Y.; Komatsu, M. *J. Org. Chem.* **2002**, *67*, 2101.

## N1 Transfer



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

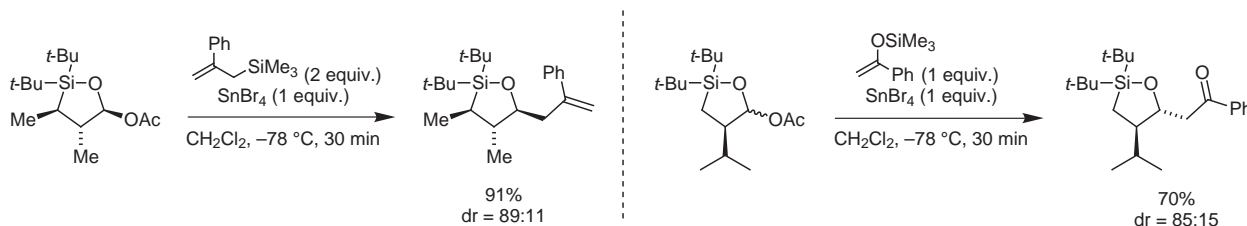
## Asymmetric Hydrogenation



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

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

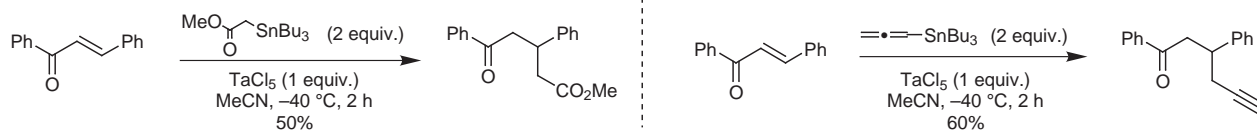
## Nucleophilic Substitution



20 examples (yields 52-97%).

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

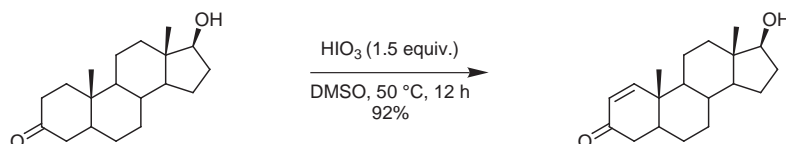
## 1,4-Addition



23 examples (yields <1-99%). Catalytic use of TaCl<sub>5</sub> (20 mol %) is possible with the addition of Me<sub>3</sub>SiCl (1 equiv.). The use of allylic, benzyl and alkynyl tributyltin reagents is also reported.

Dehydrogenation of aldehydes and ketones using HIO<sub>3</sub> and I<sub>2</sub>O<sub>5</sub>.  
 Nicolaou, K. C; Montagnon, T; Bara, P. S. *Angew. Chem. Int. Ed.* **2002**, 41, 1386.

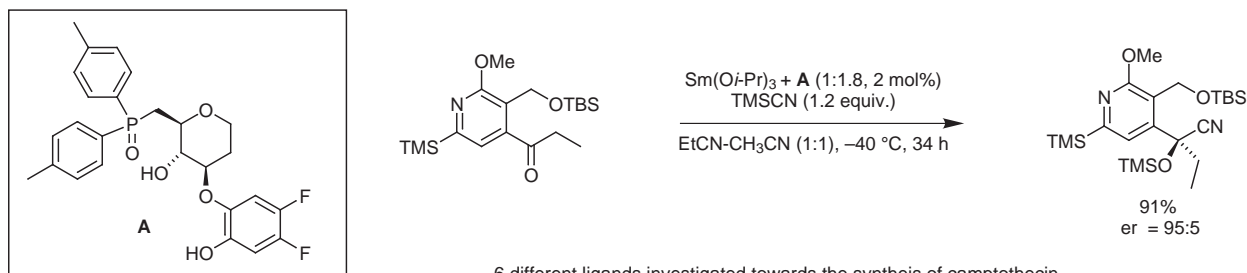
## Dehydrogenation



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

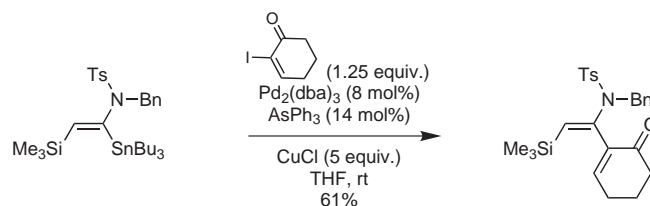
Catalytic enantioselective cyanosilylation of ketones.  
 Yabu, K; Masumoto, S; Kanai, M; Curran, D. P; Shibasaki, M. *Tetrahedron Lett.* **2002**, 43, 2923.

## Nucleophilic Addition



6 different ligands investigated towards the synthesis 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.

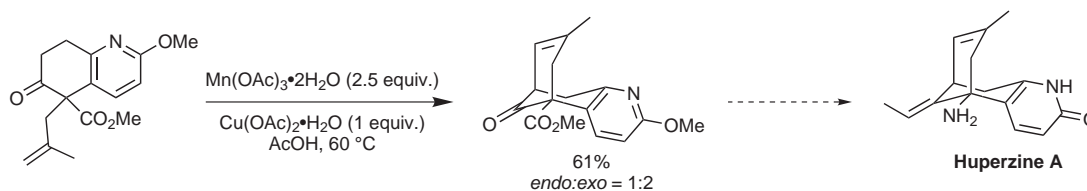
sp<sup>2</sup>-sp<sup>2</sup> Coupling

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  $\beta$ -ketoesters.

Lee, I. Y. C.; Jung, M. H.; Lee, H. W.; Yang, J. Y. *Tetrahedron Lett.* **2002**, *43*, 2407.

Radical Cyclization

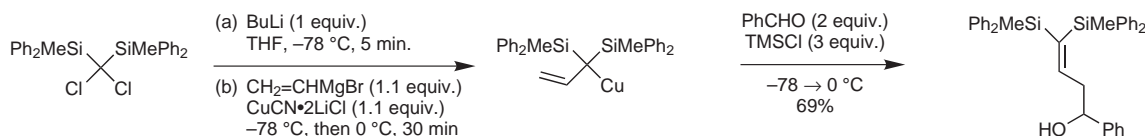


5 examples (yields 21-84%). *Exo* to *endo* conversion was performed with CF<sub>3</sub>SO<sub>3</sub>H.

Synthesis and regioselective reactions of  $\alpha,\alpha$ -bis(silyl)-substituted allylcopper reagents.

Kondo, J.; Inoue, A.; Shinokubo, H.; Oshima, K. *Tetrahedron Lett.* **2002**, *43*, 2399.

Nucleophilic Addition

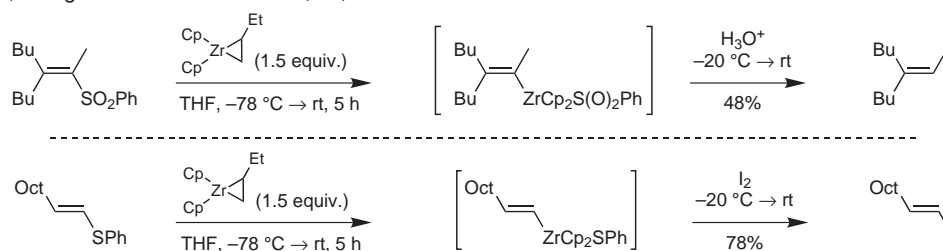


Vinyl (13 examples, yields 52-86%); isopropenyl,  $\alpha$ -styryl and  $\beta$ -styryl (10 examples, yields 55-83%).

Preparation of vinylic organozirconium derivatives from vinyl sulfides, sulfoxides, and sulfones.

Farhat, S.; Marek, I. *Angew. Chem. Int. Ed.* **2002**, *41*, 1410.

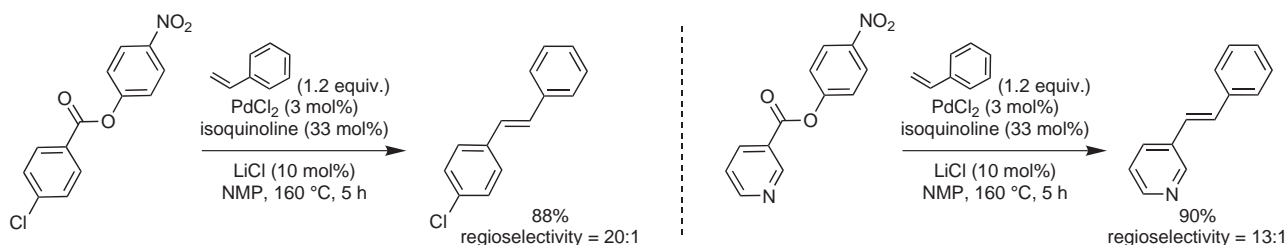
Metallation



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

Pd-catalyzed decarbonylative olefination of aryl esters

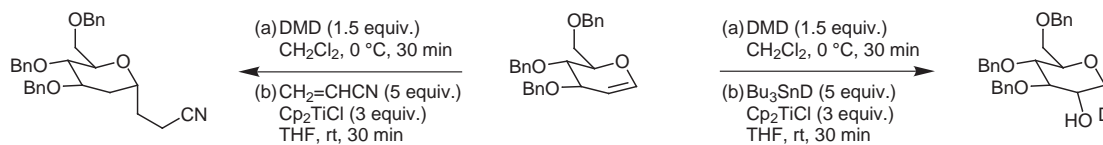
Gooßen, L. J.; Paetzold, J. *Angew. Chem. Int. Ed.* **2002**, *7*, 1237.

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

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

Preparation of  $\alpha$ -C-glycosides from glycals.  
Parrish, J. D.; Little, R. D. *Org. Lett.* **2002**, *4*, 1439.

## Reductive Ring Opening/Trapping

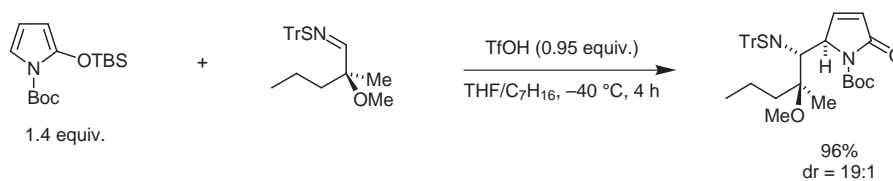


9 examples (yields 10, 47-61%).

Highly diastereoselective coupling reaction.

Barnes, D. M.; McLaughlin, M. A.; Oie, T.; Rasmussen, M. W.; Stewart, K. D.; Wittenberger, S. J. *Org. Lett.* **2002**, *4*, 1427.

## 1,2-Addition

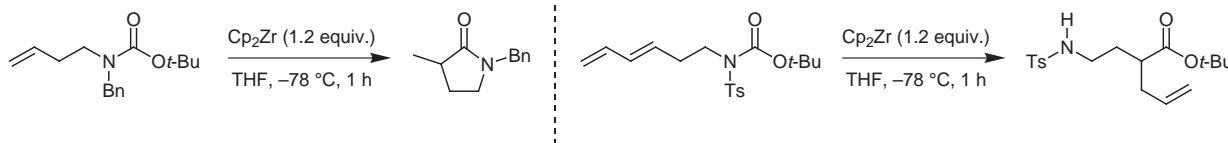


Attempts using  $\text{BF}_3 \cdot \text{OEt}_2$  and TMSOTf resulted with diminished diastereoselectivity.

Zirconium-mediated intramolecular ester transfer reaction.

Ito, H.; Omodera, K.; Takigawa, Y.; Taguchi, T. *Org. Lett.* **2002**, *4*, 1499.

## Ester Transfer

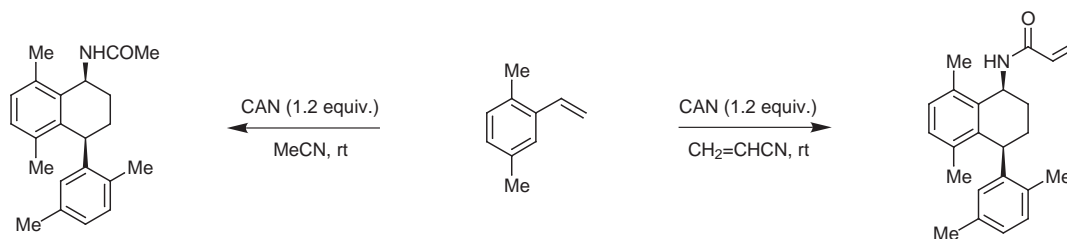


10 examples (yields 41-95%).

One-pot synthesis of 1-amino-4-aryltetralins from styrenes.

Nair, V.; Rajan, R.; Rath, N. P.; Taguchi, T. *Org. Lett.* **2002**, *4*, 1575.

## Cyclodimerization

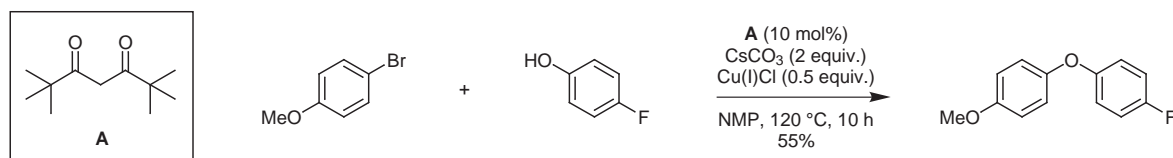


12 examples (yields 40-82%, %de 9-83%).

Ullmann diaryl ether synthesis.

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

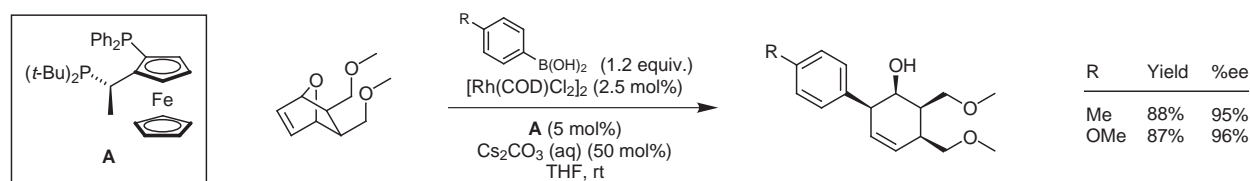
## Ullmann Coupling



13 examples (yields 51-85%).

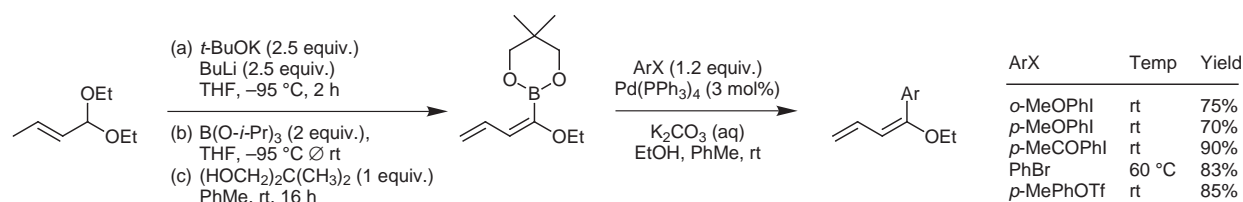
Rhodium-catalyzed asymmetric ring opening of oxabicyclic alkenes with organoboronic acids.  
Lautens, M.; Dockendorff, C.; Fagnou, K.; Malicki, A. *Org. Lett.* **2002**, *4*, 1311.

## Asymmetric Ring-Opening



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.

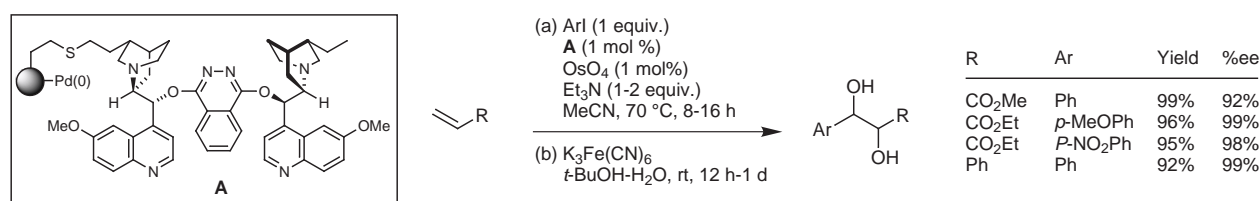
sp<sup>2</sup>-sp<sup>2</sup> Coupling

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.

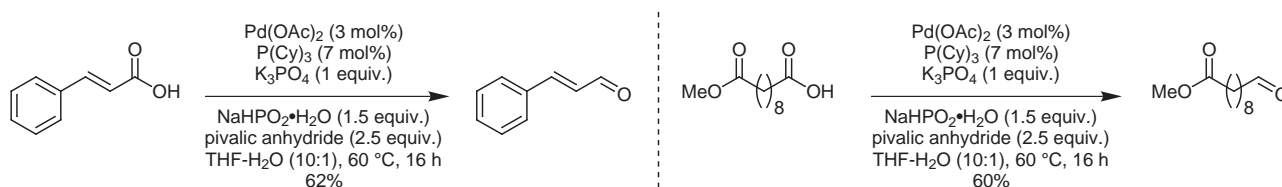
## Heck/Asymmetric Dihydroxylation



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.

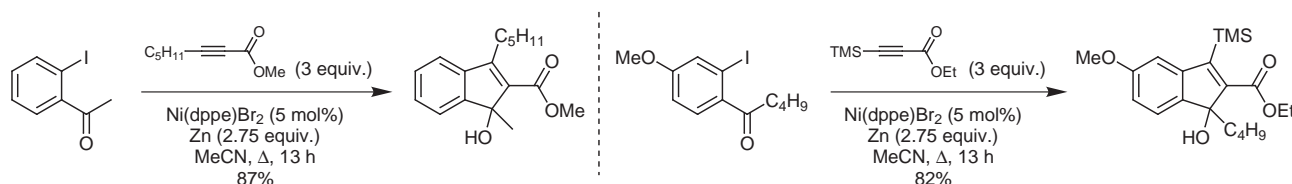
## Reduction



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.  
Rayabharapu, D. K.; Cheng C.-H. *Chem. Commun.* **2002**, 942.

## Carbocyclization



16 examples (46-88%).