

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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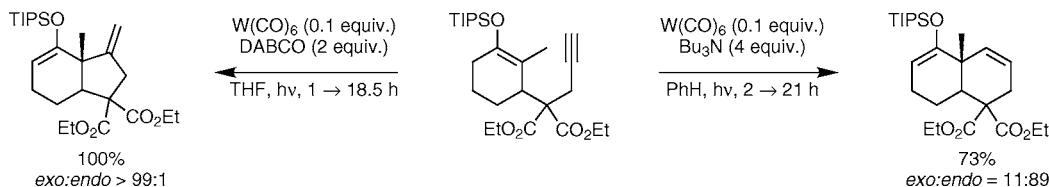
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Chemistry A European Journal
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Heterocycles
Journal of the American Chemical Society
Journal of Organic Chemistry
Organic Letters
Organometallics
Perkin Transactions 1
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry and Tetrahedron Letters

W(CO)₆-amine catalyzed *exo*- and *endo*-selective cyclizations of ω -alkynyl silyl enol ethers.

Cyclization

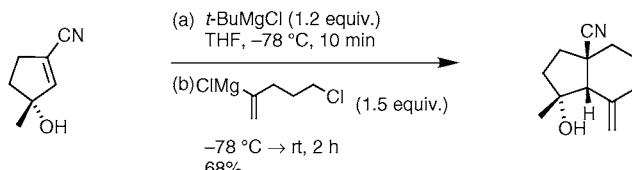


5 examples (yields 73–100%). The tandem cyclization of bis-alkynyl silyl enol ethers is also reported.

Chelation-controlled conjugate addition/annulation of alkenenitriles with ω -chloro Grignard reagents.

1,4-Addition/Annulation

Fleming, F. F.; Zhang, Z.; Wang, Q.; Steward, O. W. *Org. Lett.* 2002, 15, 2493.

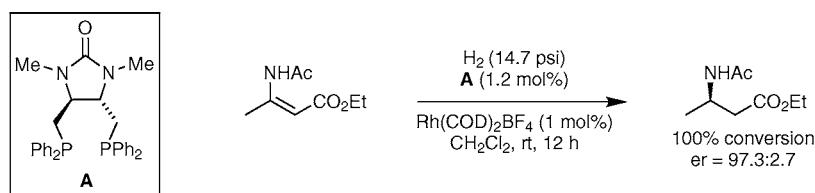


7 examples (yields 56–75%).

Enantioselective Rh-catalyzed hydrogenation of (*E*) and (*Z*)- β -(acylamino)acrylates.

Hydrogenation

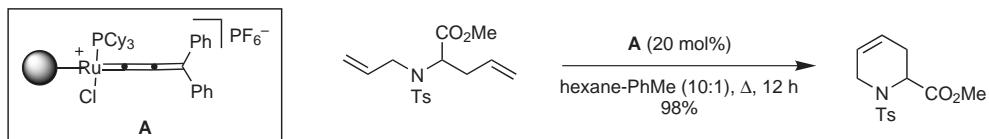
Lee, S-G.; Zhang, J. Y. *Org. Lett.* 2002, 4, 2429.



9 examples (conversion 100%, %ee 75.6–97.4%).

Polymer-supported Ru-catalyzed ring closing olefin metathesis.
Akiyama, R.; Kobayashi, S. *Angew. Chem. Int. Ed.* **2002**, *14*, 2602.

Ring Closing Metathesis

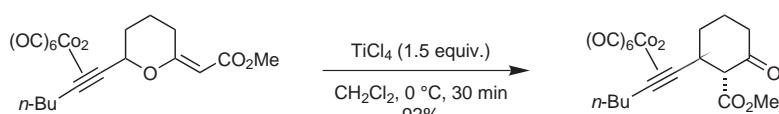


7 examples (yields 57-98%).

Co-mediated rearrangement of cyclic enol ethers.

Carberry, D. R.; Reignier, S.; Myatt, J. W.; Miller, N. D.; Harrity, J. P. A. *Angew. Chem. Int. Ed.* **2002**, *14*, 2584.

Ferrier Rearrangement

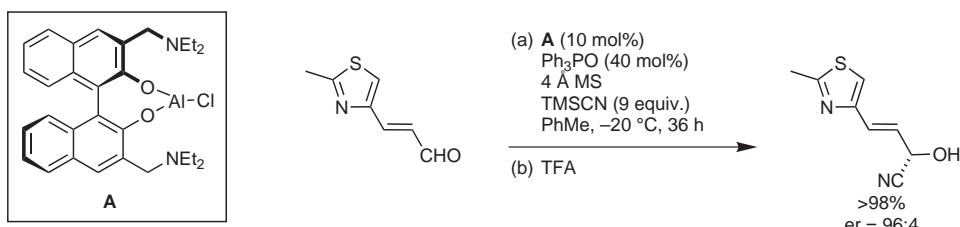


8 examples (yields 70-98%).

Enantioselective Al-catalyzed synthesis of cyanohydrins.

Casas, J.; Nájera, C.; Sansano, J. M.; Saá, J. M. *Org. Lett.* **2002**, *15*, 2589.

1,2-Addition

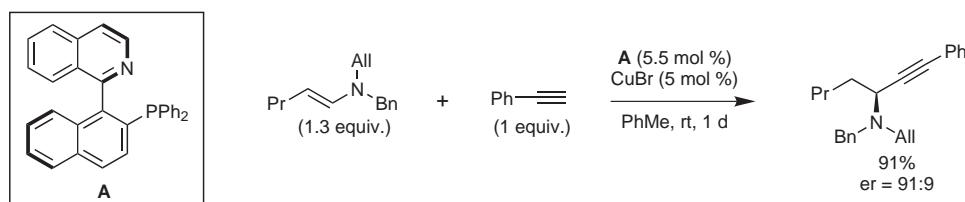


13 examples (yields 70-99%, %ee 66->99%).

Enantioselective Cu-catalyzed addition of alkynes to enamines.

Koradin, C.; Polborn, K.; Knochel, P. *Angew. Chem. Int. Ed.* **2002**, *14*, 2535.

1,2-Addition

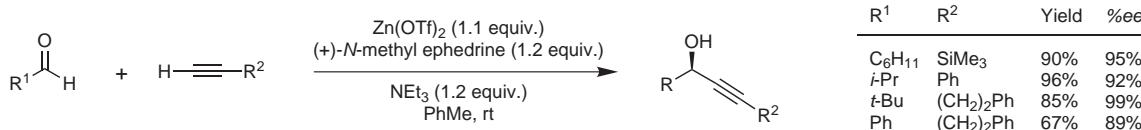


13 examples (yields 50-99%, %ee 54-90%).

Enantioselective Zn-catalyzed addition of terminal alkynes to aldehydes.

Byoall, D.; Frantz, D. E.; Carreira, E. M. *Org. Lett.* **2002**, *15*, 2605.

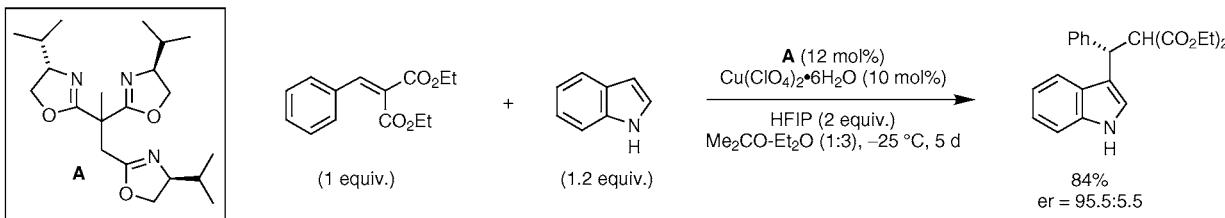
1,2-Addition



14 examples (yields 67-96%, %ee 80-99%).

Improvement of the enantiomeric excess in the asymmetric Michael addition of indoles to alkylidene malonates.
Zhou, J.; Tang, Y. *J. Am. Chem. Soc.* **2002**, 124, 9030.

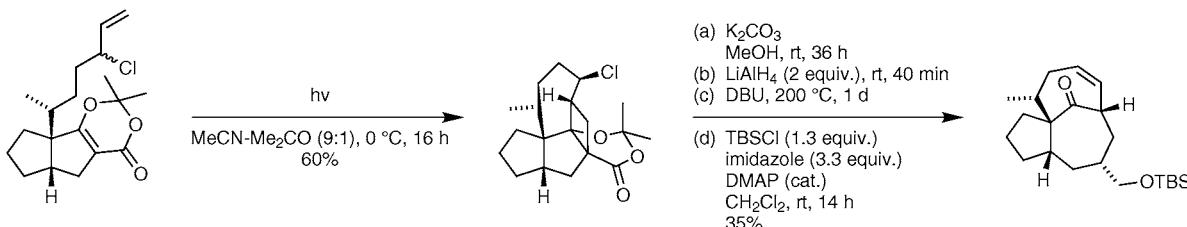
1,4-Addition



13 examples (yields 73-99%, %ee 60-92%).

Total synthesis of (\pm)-ingenol.Winkler, J. D.; Rouse, M. B.; Greaney, M. F.; Harrison, S. J.; Jeon, Y. T. *J. Am. Chem. Soc.* **2002**, 124, 9727.

[2+2]-Cycloaddition/Fragmentation

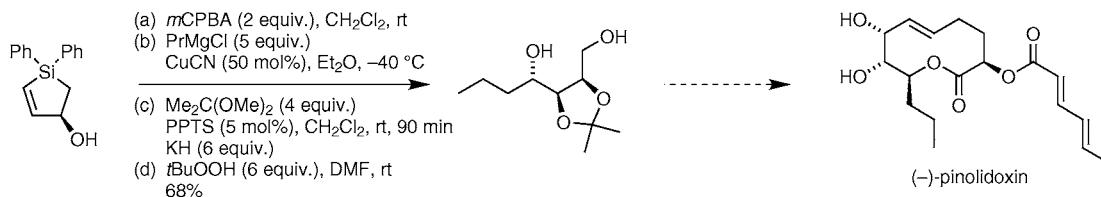


Application to the total synthesis of (+/-)-ingenol.

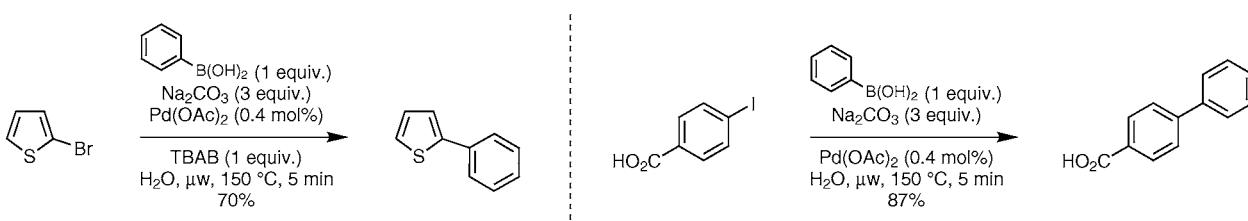
Synthesis of (-)-pinolidoxin from a common silacyclic precursor.

Liu, D.; Kozmin, S. A. *Org. Lett.* **2002**, 4, 3005.

Nucleophilic Addition



Both enantiomers are employed in the synthesis.

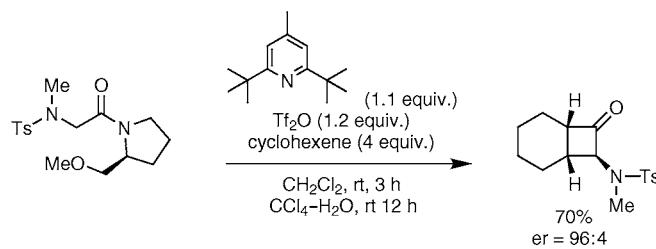
Microwave-accelerated Pd-catalyzed Suzuki reaction in water.
Leadbetter, N. E.; Marco, M. *Org. Lett.* **2002**, 4, 2973.sp²-sp² Coupling

25 examples (yields 45-96%).

Enantioselective synthesis of cyclobutanones.

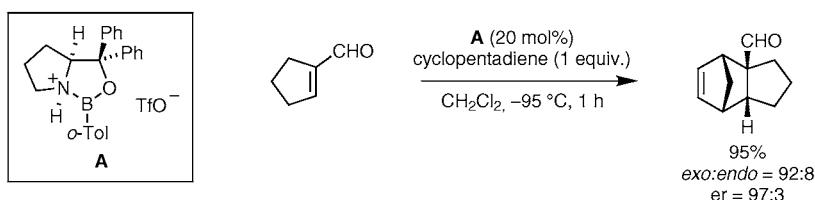
Ghosez, L.; Mahuteau-Betzer, F.; Genicot, C.; Vallribera, A.; Cordier, J. F. *Chem.-Eur. J.* **2002**, 8, 3411.

[2+2] Cycloaddition



Enantioselective cationic oxazaborolidine-catalyzed Diels-Alder reaction.
Ryu, D. H.; Lee, T. W.; Corey, E. J. *J. Am. Chem. Soc.* **2002**, *124*, 9992.

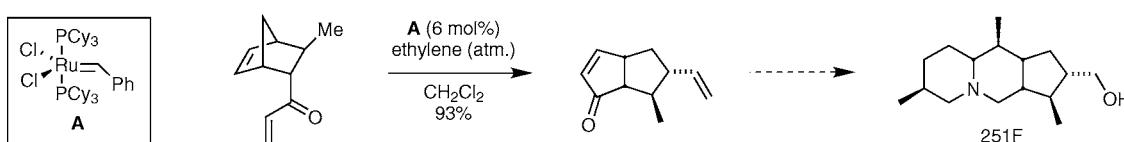
[4+2]-Cycloaddition



15 examples (yields 33-99%, %ee 69-99%).

Total synthesis of dendrobatid alkaloid 251F via Ru-catalyzed ring closing metathesis
Wroblewski, A.; Sahasrabudhe, K.; Aubé, J. *J. Am. Chem. Soc.* **2002**, *124*, 9974.

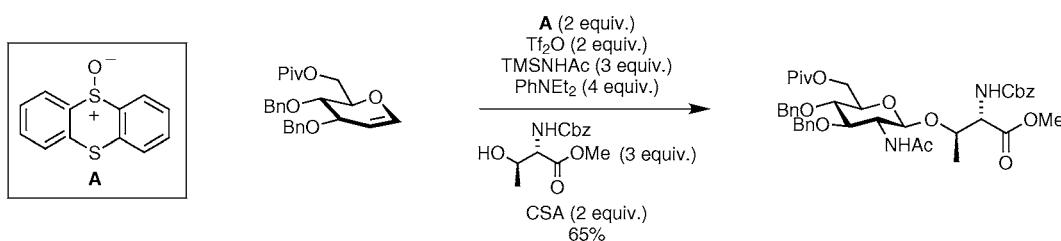
Ring Closing Metathesis



Total synthesis of alkaloid 251F (13 steps, overall yield 5-8%).

C2-Amidoglycosylation: the scope and mechanism of nitrogen transfer.
Liu, J.; Gin, D. Y. *J. Am. Chem. Soc.* **2002**, *124*, 9789.

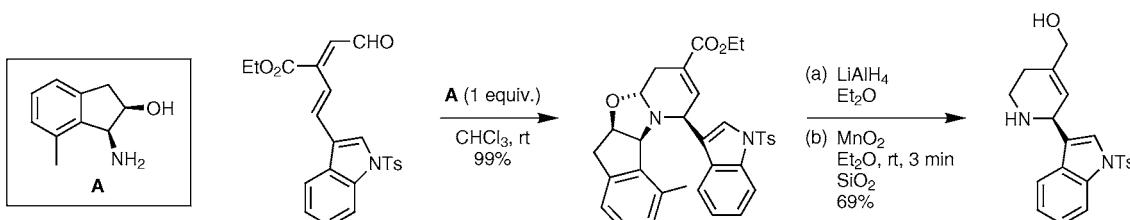
Amidoglycosylation



12 examples (yields 51-77%).

Asymmetric 6π-azaelectrocyclization.
Tanaka, K.; Katsumura, S. *J. Am. Chem. Soc.* **2002**, *124*, 9660.

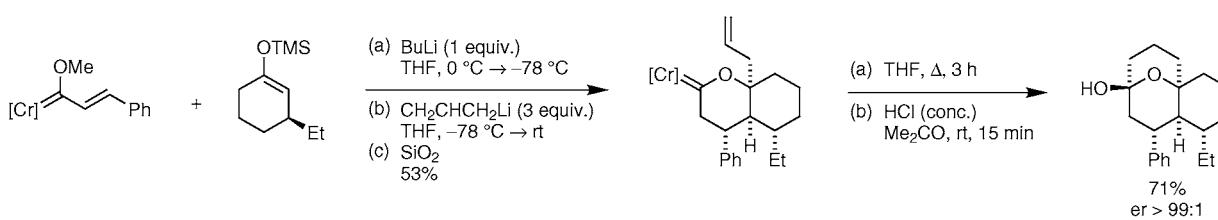
Electrocyclization



Application to a formal synthesis of 20-epiuleine is reported.

Enantioselective formation of eight-membered rings from alkenyl Fischer carbene and ketone enolates.
Barluenga, J.; Diéguez, A.; Rodríguez, F.; Florez, J.; Fananas, F. J. *J. Am. Chem. Soc.* **2002**, *124*, 9056.

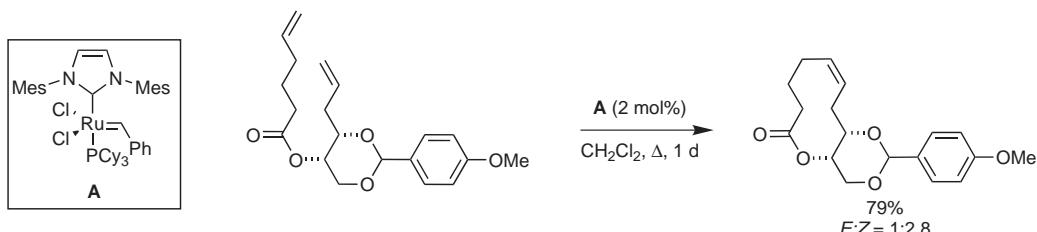
Cyclization



6 examples (yields 69-82%, %ee >98%).

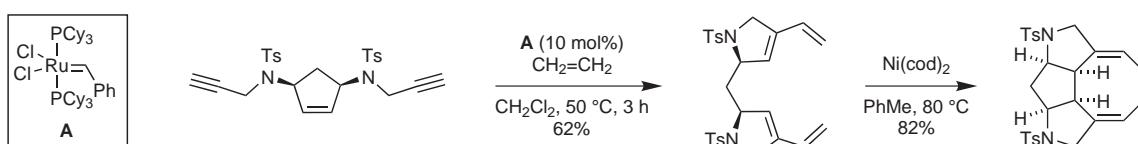
Formal total synthesis of ascidiatrienolide A and the didemnolactones.
Fürstner, A.; Schlede, M. *Adv. Synth. Catal.* **2002**, 344, 657.

Ring Closing Metathesis

4 examples (yields 43-83%, $1:2.8 \geq E:Z \geq 8.4:1$).

Ru-catalysed enyne metathesis.
Randl, S.; Lucas, N.; Connon, S. J.; Blechert, S. *Adv. Synth. Catal.* **2002**, 344, 631.

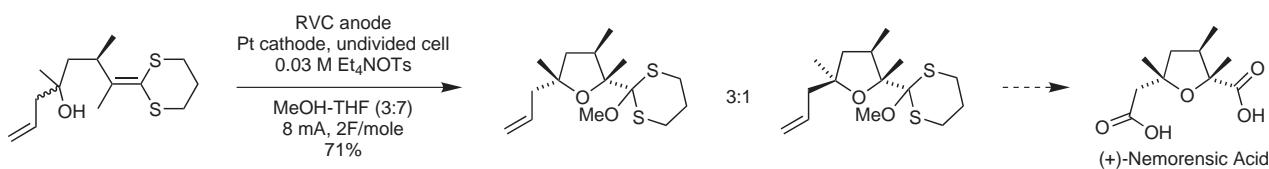
Metathesis



9 examples of enyne metathesis (yields 49-99%).

Oxidative cyclization based on reversing the polarity of enol ethers and ketene dithioacetals.
Liu, B.; Duan, S.; Sutterer, A. C.; Moeller, K. D. *J. Am. Chem. Soc.* **2002**, 124, 10101.

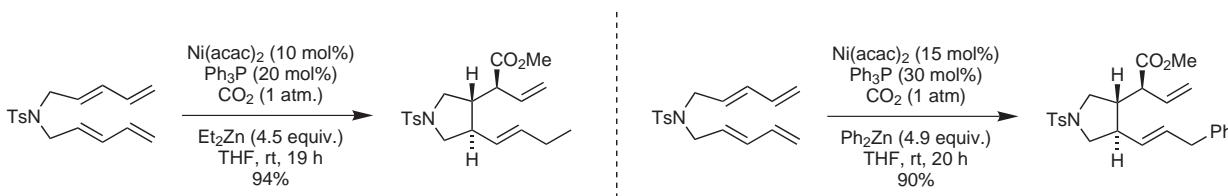
Oxidative Cyclization



29 examples (yields 20-96%).

Regio- and stereoselective Ni-catalyzed ring-closing carboxylation of bis-1,3-dienes.
Takimoto, M.; Mori, M. *J. Am. Chem. Soc.* **2002**, 124, 10008.

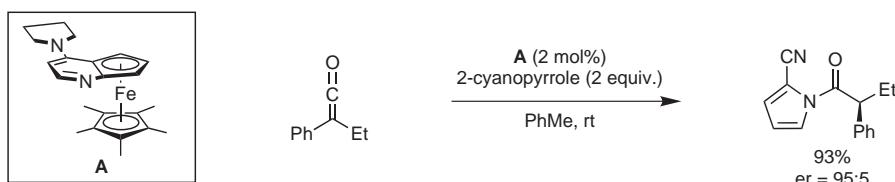
Ring Closing Carboxylation



9 examples (yields 56-95%).

Enantioselective Fe-catalyzed addition of amines to ketenes.
Hodous, B. L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, 124, 10006.

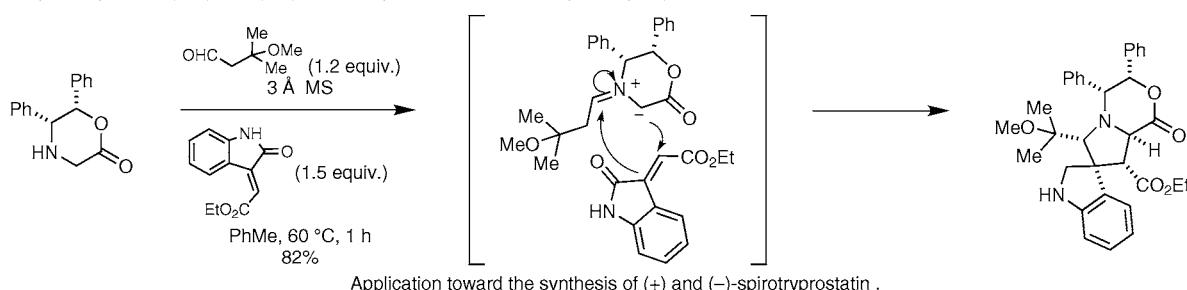
1,2-Addition



7 examples (yields 80-96%, %ee 81-98%).

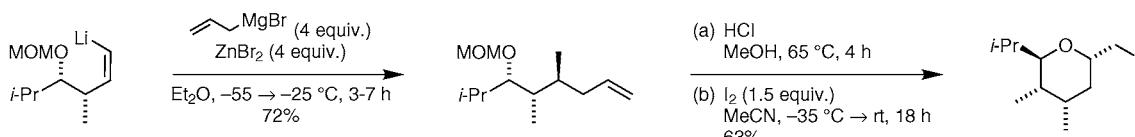
Diastereoselective azomethine ylide [1,3]-dipolar cycloaddition.
Sebahar, P. R.; Osada, H.; Usui, T.; Williams, R. M. *Tetrahedron*, **2002**, *58*, 6311.

[1,3]-Cycloaddition



Addition of allylzinc reagents to δ -alkoxy- γ,δ -disubstituted alkenyllithium compounds.
Bernard, N.; Chemla, F.; Ferreira, F.; Mostefai, N.; Normant, J. F. *Chem.-Eur. J.* **2002**, *8*, 3139.

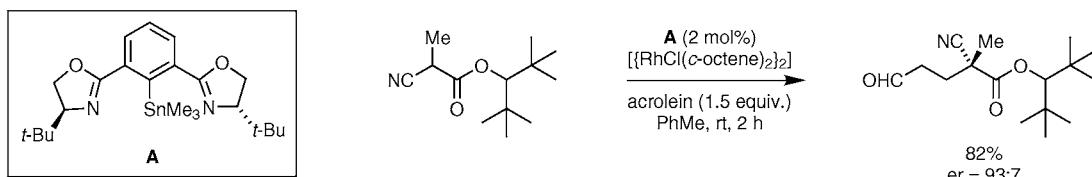
Carbometallation



11 examples of carbometallation (yields 52-79%).

Asymmetric Rh-catalyzed Michael addition of α -cyanopropionates to acrolein.
Motoyama, Y.; Koga, Y.; Kobayashi, K.; Aoki, K.; Nishiyama, H. *Chem.-Eur. J.* **2002**, *8*, 2968.

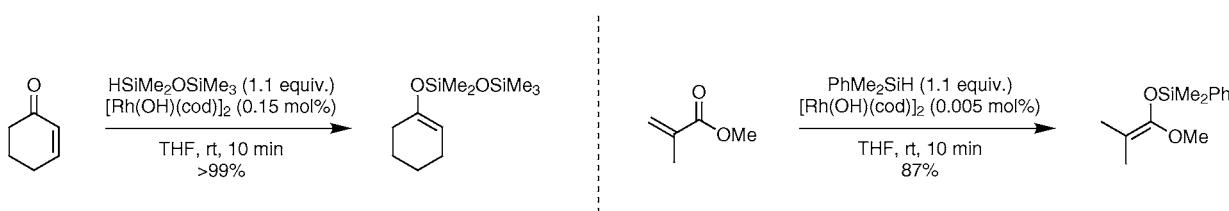
1,4-Addition



7 examples (yields 92-97%, %ee 69-86%).

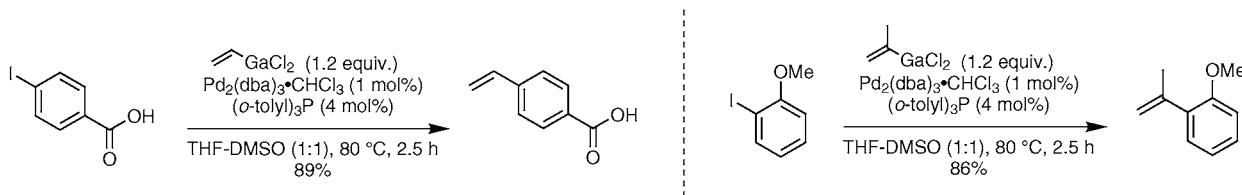
1,4-Hydrosilylation of α,β -unsaturated carbonyl compounds.
Mori, A.; Kato, T. *Synlett* **2002**, 1167.

1,4-Addition



13 examples (yields 82->99%).

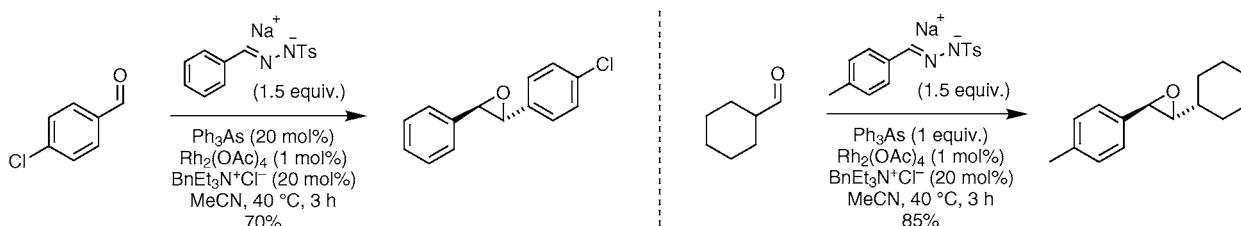
Pd-catalyzed coupling reaction of alkenylgalliums with aryl halides.
Mikami, S.; Yorimitsu, H.; Oshima, K. *Synlett* **2002**, 1137.

sp²-sp² Coupling

18 examples (yields 33-97%).

Rh-catalyzed synthesis of epoxides from aldehydes and tosylhydrazone salts.
Aggarwal, V. K.; Patel, M.; Studley, J. *Chem. Commun.* **2002**, 1514.

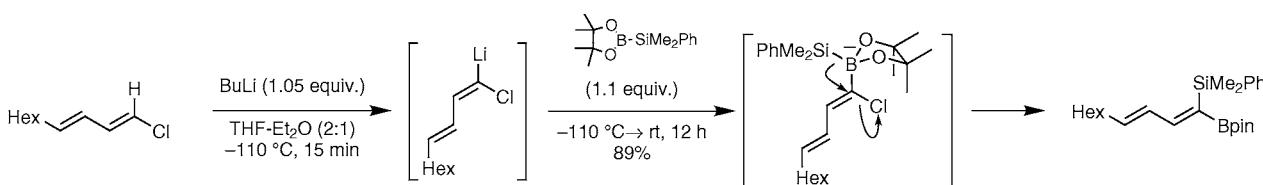
Epoxidation



18 examples (yields 10-98%). Complete *trans* selectivity in all cases.

Geminal dimetallation of alkylidene-type carbenoids with silylboranes and diborons.
Kurashiki, T.; Hata, T.; Masai, H.; Kitagawa, H.; Shimizu, M.; Hiyama, T. *Tetrahedron*, **2002**, 58, 6381.

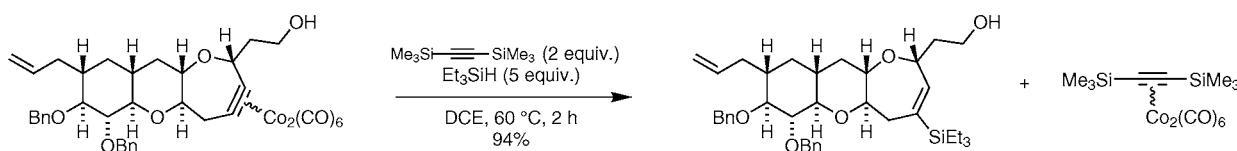
Metallation



23 examples (yields <1->99%).

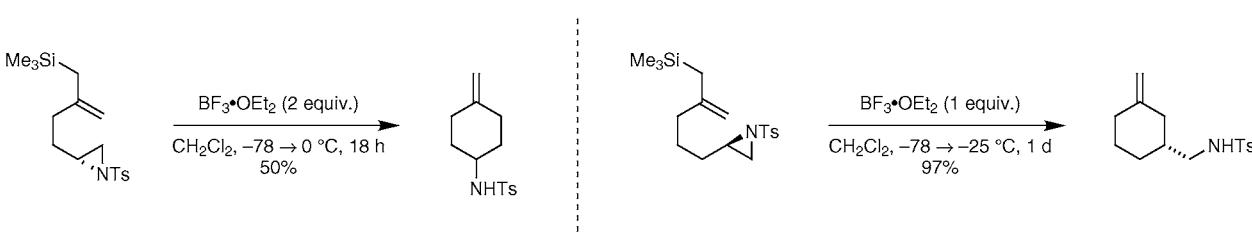
Hydrosilylation of an acetylene cobalt complex.
Kira, K.; Tanda, H.; Hamajima, A.; Baba, T.; Takai, S.; Isobe, M. *Tetrahedron*, **2002**, 58, 6485.

Hydrosilylation



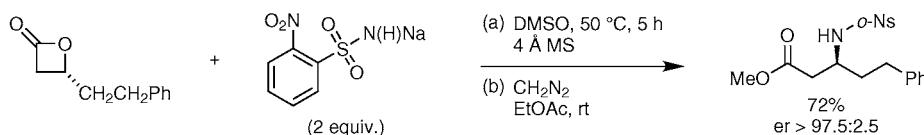
Intramolecular addition of allylsilanes to aziridines.
Lapinsky, D. J.; Bergmeier, S. C. *Tetrahedron*, **2002**, 58, 7109.

Cyclization



3 examples (yields 50-97%).

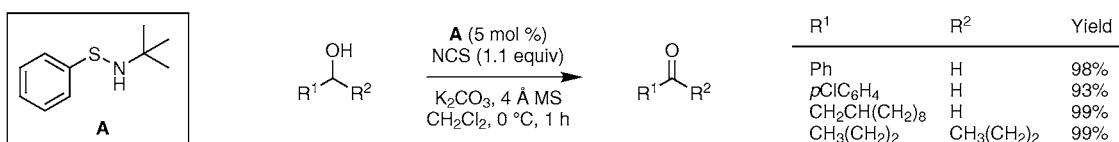
Nucleophilic β-lactone ring opening.
Nelson, S. G.; Spencer, K. L.; Cheung, W. S.; Mamie, J. *Tetrahedron*, **2002**, 58, 7081.

S_N2 Ring Opening

5 examples (yields 43-83%, %ee 93->95%). Ring opening with NaN₃ (8 examples, yields 78-95%, %ee 92-97%) is also reported.

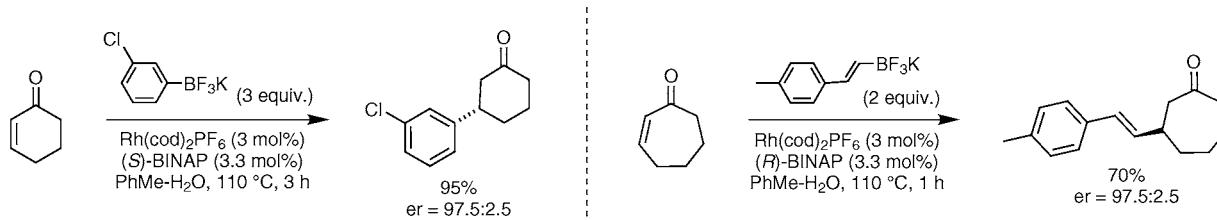
Catalytic oxidation of alcohols.
Mukaiyama, T.; Matsuo, D.; Iida, D.; Kitagawa, H. *Chem. Lett.* **2001**, 864.

Oxidation

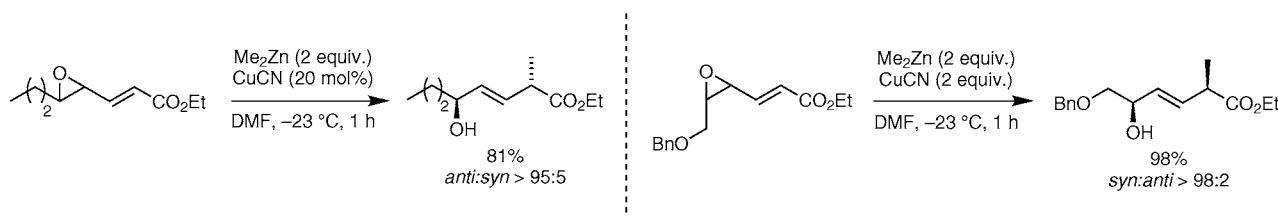


Enantioselective Rh-catalyzed conjugate additions to enones using potassium organotrifluoroborates.
Pucheaule, M.; Darses, S.; Genet, J.-P. *Tetrahedron Lett.* **2002**, 43, 6155.

1,4-Addition

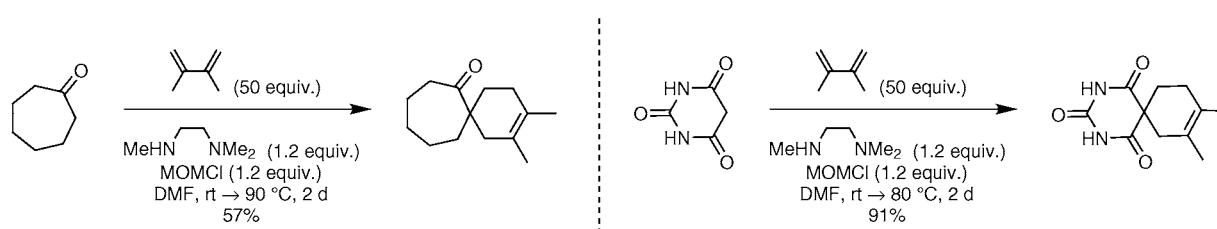


Regio- and stereoselective α -methylation of γ,δ -epoxy- α,β -unsaturated esters.
Hirai, A.; Matsui, A.; Komatsu, K.; Tanino, K.; Miyashita, M. *Chem. Commun.* **2002**, 1970.

 S_N^2' Reaction

Synthesis of spiranones via a tandem α -methyleneation/Diels–Alder reaction.
Nakamura, H.; Yamamoto, H. *Chem. Commun.* **2002**, 1648.

Diels–Alder



Enantioselective alkynylation of aldehydes.
Jiang, B.; Chen, Z.; Xiong, W. *Chem. Commun.* **2002**, 1524.

1,2-Addition

