

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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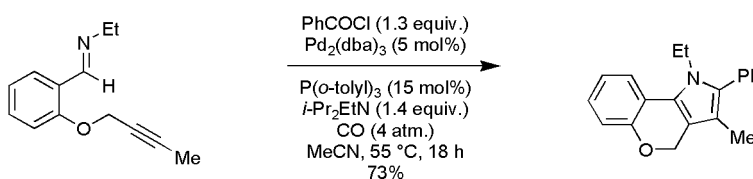
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The journals regularly covered by the abstractors are:

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 and Tetrahedron Letters

Formation of pyrroles using a Pd-catalyzed multicomponent coupling.
 Dhawan, R.; Arndtsen, B. A. *J. Am. Chem. Soc.* **2004**, 126, 468.

Annulation

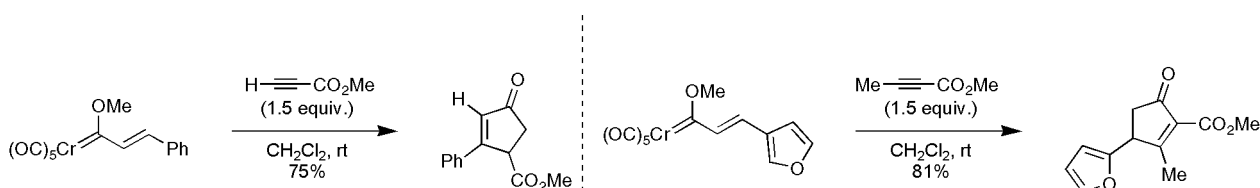


15 examples (yields 56–95%). Mechanistic studies included.

Preparation of 2-cyclopentenones using Fischer carbene complexes of Rh(I).

Barluenga, J.; Vicente, R.; Lopez, L. A.; Rubio, E.; Tomas, M.; Alvarez-Rua, A. *J. Am. Chem. Soc.* **2004**, 126, 470.

[3+2] Cycloaddition

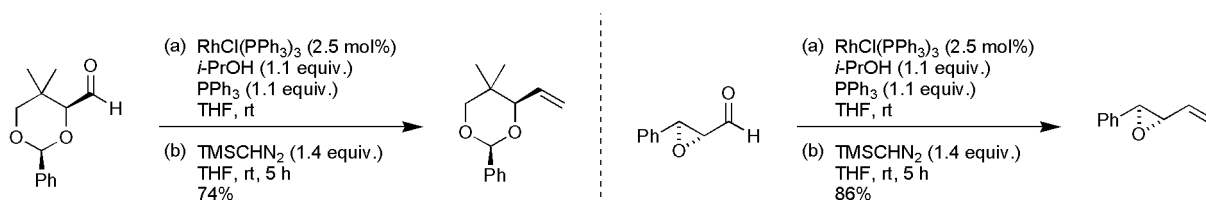


10 examples (yields 64–89%).

Rhodium-catalyzed methylenation of aldehydes.

Lebel, H.; Paquet, V. *J. Am. Chem. Soc.* **2004**, 126, 320.

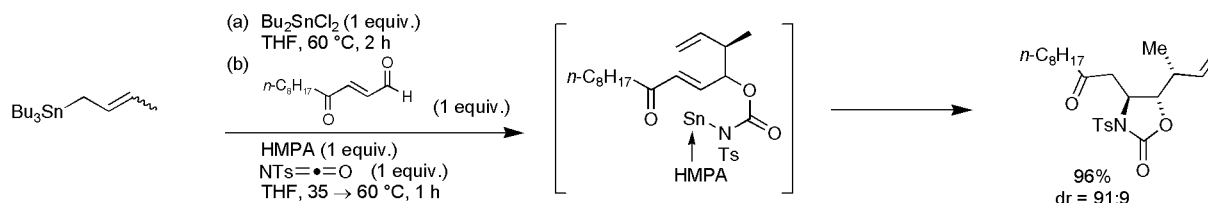
Methylenation



32 examples (yields 63–98%, %ee 79–95%). Mechanistic studies investigated.

One-pot synthesis of oxazolidinones using chemoselective allylation of bifunctional carbonyl compounds. Shibata, I.; Kato, H.; Kanazawa, N.; Yasuda, M.; Baba, A. *J. Am. Chem. Soc.* **2004**, *126*, 466.

Allylation/Crotylation

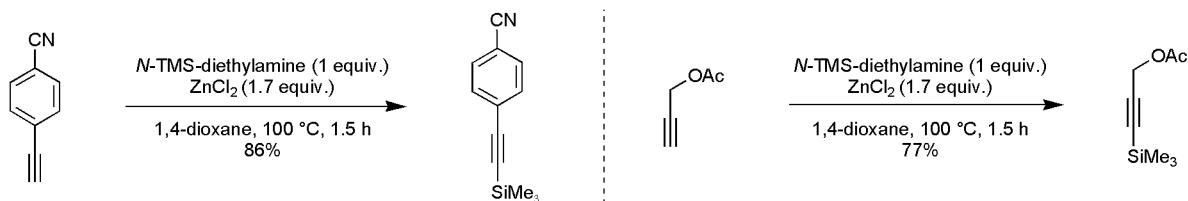


(Z)-Homocrotyl products can be formed instead of 1-methylallyl if the crotyltri-*n*-butyltin, Bu_2SnCl_2 and aldehyde are added in one portion. 8 examples (yields 54-96%, %de 82-100%).

Direct electrophilic silylation of terminal alkynes.

Andreev, A. A.; Konshin, V. V.; Komarov, N. V.; Rubin, M.; Brouwer, C.; Gevorgyan, V. *Org. Lett.*, **2004**, *6*, 421.

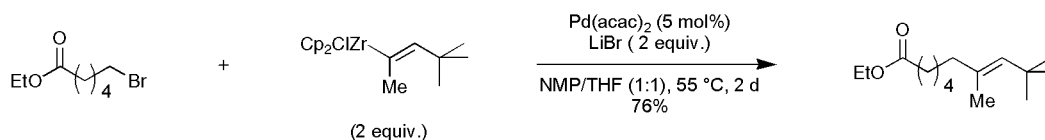
Silylation



15 examples (yields 68-97%). Optimization of reaction conditions and mechanistic studies are also reported.

Zirconium-Negishi reactions of alkyl electrophiles under ligandless conditions.

Wiskur, S. L.; Korte, A.; Fu, G. C. *J. Am. Chem. Soc.*, **2004**, *126*, 82.

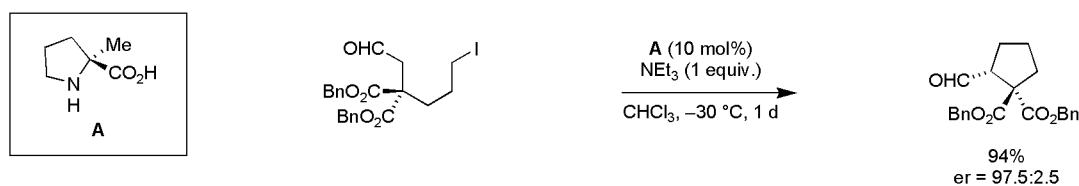
 $\text{sp}^2\text{-sp}^3$ Coupling

18 examples (yields 46-99%). Reaction of alkyl chlorides, iodides and tosylates are also reported.

Catalytic, asymmetric intramolecular α -alkylation of aldehydes.

Vignola, N.; List, B. *J. Am. Chem. Soc.*, **2004**, *125*, 450.

Enantioselective Alkylation

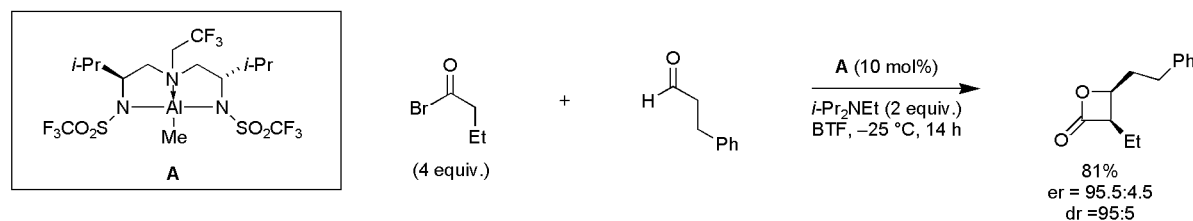


8 examples (yields 20-93%, %ee 84-96%). Substituted, chiral pyrrolidines and cyclopropanes are also reported.

Catalytic, asymmetric acyl halide-aldehyde cyclocondensations of substituted ketenes.

Nelson, S. G.; Zhu, C.; Shen, X. *J. Am. Chem. Soc.*, **2003**, *126*, 14.

[2+2] Cycloaddition

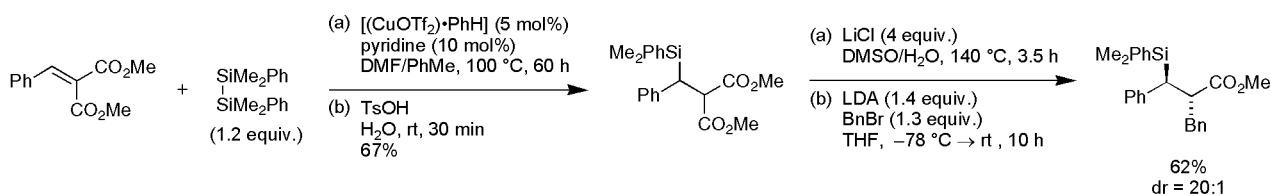


13 examples (yields 71-88%, %ee 88-96%, %de 72->96%). BTF = benzotrifluoride.

Copper(I)-catalyzed disilylation of alkylidene malonates.

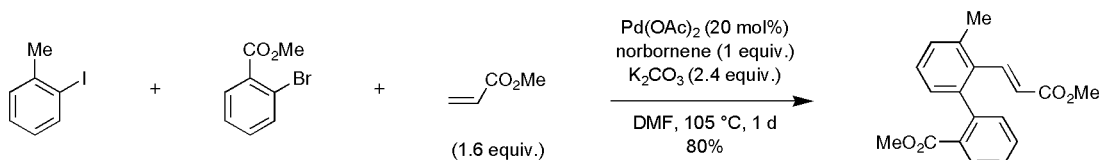
Clark, C. T.; Lake, J. F.; Scheidt, K. A. *J. Am. Chem. Soc.*, **2004**, *126*, 84.

Disilylation



14 examples (yields 0-87%).

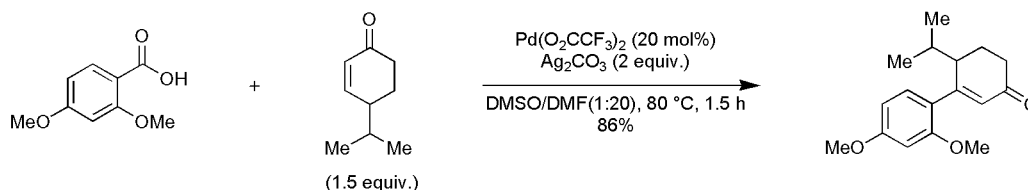
Palladium-catalyzed unsymmetrical aryl couplings.

Faccini, F.; Motti, E.; Catellani, M. *J. Am. Chem. Soc.*, **2004**, *126*, 78.sp²-sp² Coupling

22 examples (yields 0-83%).

Selective unsymmetric aryl coupling is postulated to arise from the different reactivity of bromo- and iodo-derivatives with Pd(0) and Pd(II) complexes.

Heck-type decarboxylative arylation of 2-cycloalken-1-ones.

Tanaka, D.; Myers, A. G. *Org. Lett.* **2004**, *6*, 433.sp²-sp² Coupling

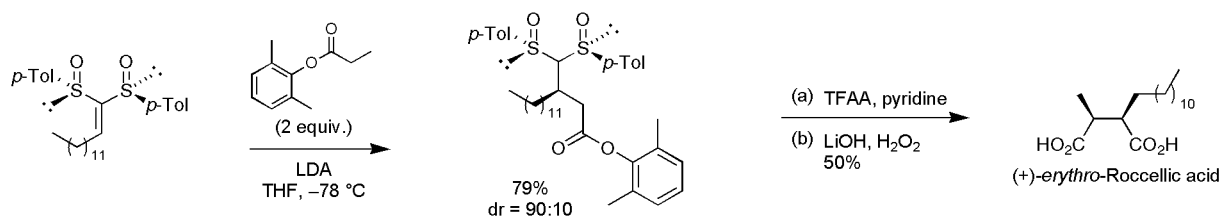
14 examples (yields 30-92%).

A comparison with conventional Heck-type couplings under optimized phosphine-free conditions was also reported. 7 examples (yields 3-100%).

Diastereoselective conjugate addition to alkylidene bis(sulfoxides) and application to (+)-erythro-Roccellic acid.

Brebion, F.; Delouvie, B.; Najera, F.; Fensterbank, L.; Malacria, M.; Vaissermann, J. *Angew. Chem. Int. Ed.* **2003**, *42*, 5342.

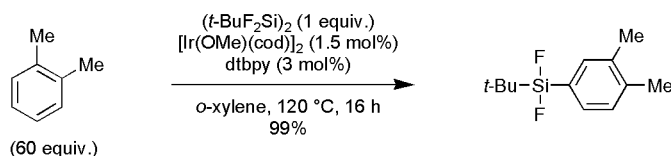
1,4-Addition

Application to the synthesis of (*R*)-Fenoprofen also reported.

Ir(I)-catalyzed aromatic C-H silylation by disilanes.

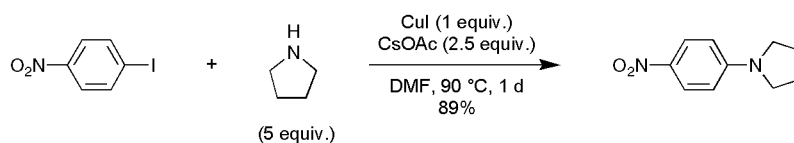
Ishiyama, T.; Sato, K.; Nishio, Y.; Miyaura, N. *Angew. Chem. Int. Ed.* **2003**, *42*, 5346.

Silylation

dtbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine. 10 examples (yields 46-99%).

Synthesis of secondary arylamines through Cu-mediated intermolecular aryl amination.
Okano, K.; Tokuyama, H.; Fukuyama, T. *Org. Lett.* **2003**, *5*, 4987.

sp²-sp³ Coupling



23 examples (yields 8-96%).

Pd-catalyzed sequential alkylation-alkenylation leading to oxacycles.
Pache, S.; Lautens, M. *Org. Lett.* **2003**, *5*, 4827.

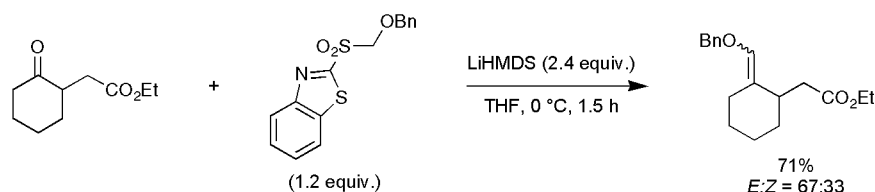
sp²-spⁿ Coupling



19 examples (yields 0-86%).

Efficient synthesis of substituted vinyl ethers using the Julia-Kocienski olefination.
Surprenant, S.; Chan, W. Y.; Berthelette, C. *Org. Lett.* **2003**, *5*, 4851.

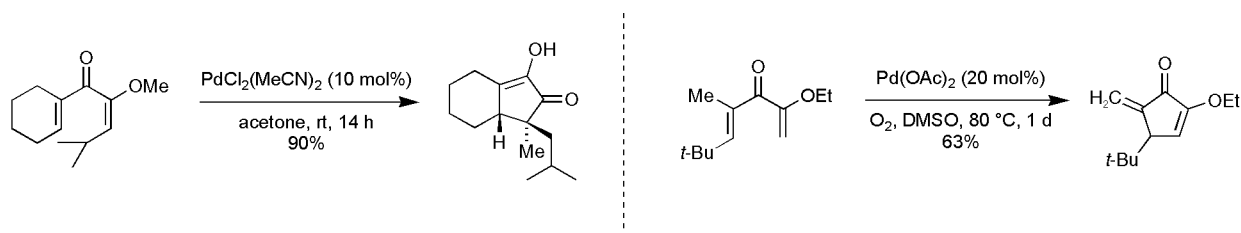
Olefination



21 examples (yields 46-90%, E:Z = 50:50-74:26).

Pd(II)-catalyzed Nazarov reaction.
Bee, C.; Leclerc, E.; Tius, M. A. *Org. Lett.* **2003**, *5*, 4927.

Annulation

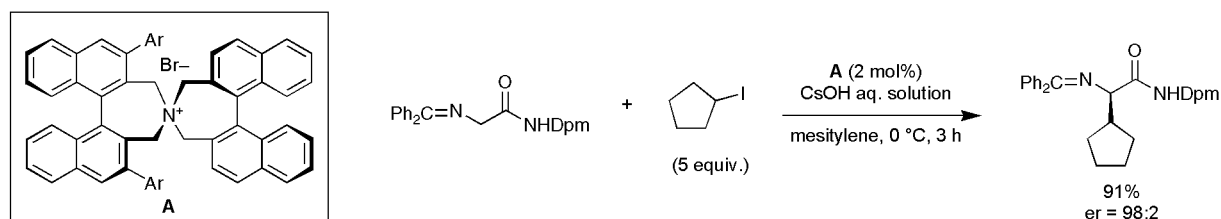


13 examples (yields 41-92%).

5 examples (yields 32-63%).

Synthesis of vicinal diamines through catalytic enantioselective alkylation of glycine amide derivatives.
Ooi, T.; Sakai, D.; Takeuchi, M.; Tayama, E.; Maruoka, K. *Angew. Chem. Int. Ed.* **2003**, *42*, 5868.

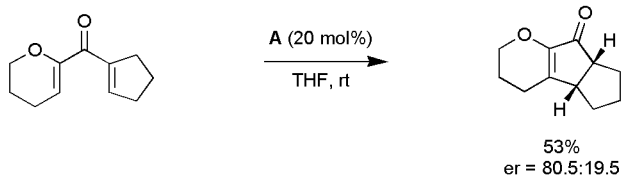
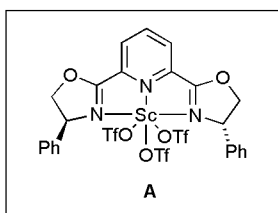
Enantioselective Alkylation



Ar = 3,5-bis(3,5-di-*tert*-butylphenyl)phenyl, Dpm = diphenylmethyl. 10 examples (yields 71-99%, %ee 82-98%).

Nazarov cyclizations of 2-alkoxy-1,4-pentadien-3-ones.
Liang, G.; Gradl, S. N.; Trauner, D. *Org. Lett.* **2003**, 5, 4931.

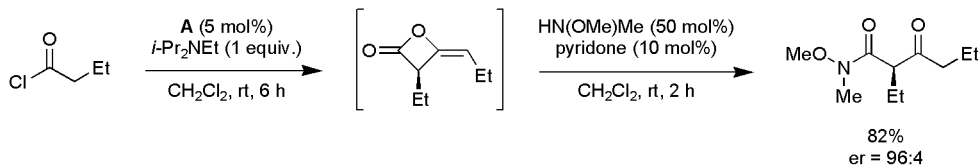
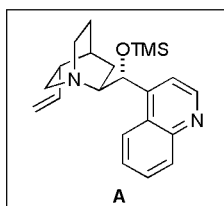
4-II Electrocyclization



20 examples (yields 40-93%).

Catalytic, asymmetric preparation of ketene dimers from acid chlorides.
Calter, M. A.; Orr, R. K.; Song, W. *Org. Lett.* **2003**, 5, 4745.

C-C Bond Formation

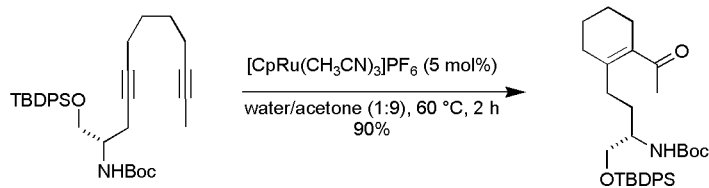


5 examples (yields 58-88%, %ee 91-96%).

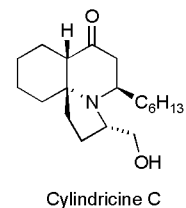
Optimization of reaction conditions and mechanistic studies are also reported.

Ruthenium-catalyzed hydrative diyne cyclization.
Trost, B. M.; Rudd, M. T. *Org. Lett.* **2003**, 5, 4599.

Annulation

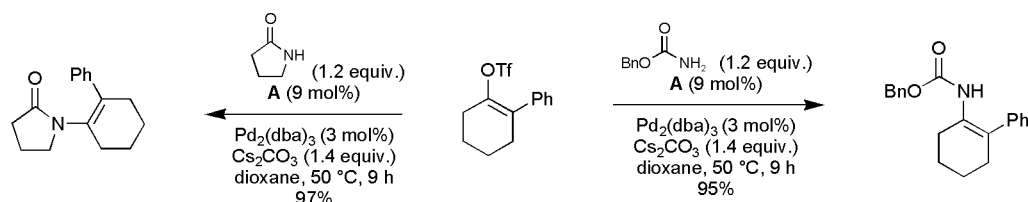
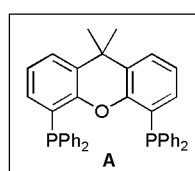


- (a) LDA (3 equiv.)
heptanal, -78 °C → rt, 4 h
 - (b) MsCl (5 equiv.)
NEt₃ (10 equiv.)
CH₂Cl₂, 0 °C → rt, 20 h
 - (c) TFA (120 equiv.)
CH₂Cl₂, rt, 1 h
 - (d) K₂CO₃ (16 equiv.)
PhMe, Δ, 68 h
 - (e) TBAF (3 equiv.)
THF, rt, 4 h
- 74% (5 steps)



Application to total synthesis of Cyllindricine C, D and E.

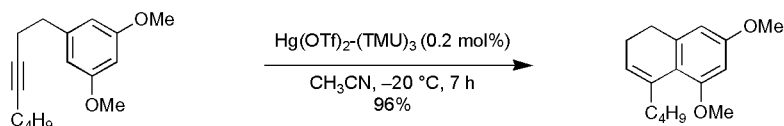
Palladium catalyzed amidation of enol triflates.
Wallace, D. J.; Klauber, D. J.; Chen, C.; Volante, R. P. *Org. Lett.* **2003**, 5, 4749.

Nsp³-sp² Coupling

16 examples (yields 10-97%). Optimization of conditions reported.

Synthesis of dihydronaphthalenes via a mercuric triflate-(TMU)₃-catalyzed cyclization of an arylalkyne.
Nishizawa, M.; Takao, H.; Yadav, V. K.; Imagawa, H.; Sugihara, T. *Org. Lett.* **2003**, 5, 4563.

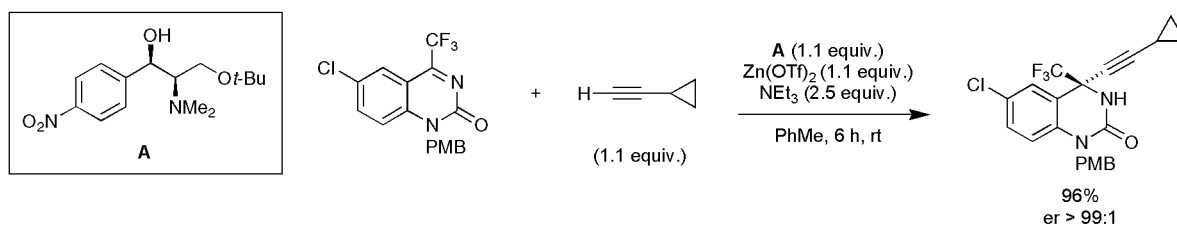
Annulation



TMU = trimethylurea. 7 examples (yields 25-96%).

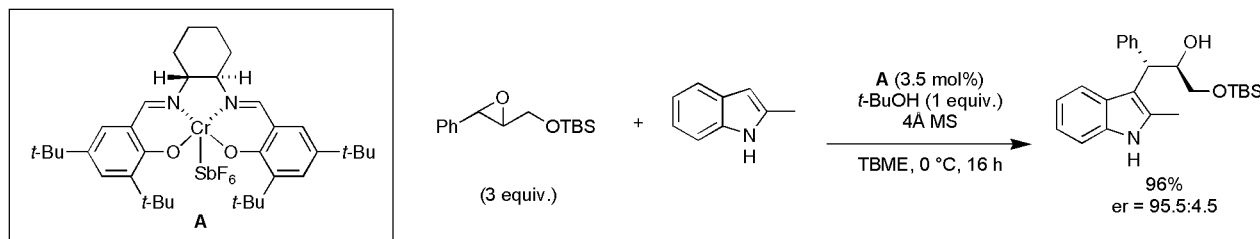
Enantioselective alkylation of a cyclic *N*-acyl ketimine.
Jiang, B.; Si, Y.-G. *Angew. Chem. Int. Ed.* **2004**, *43*, 216.

Enantioselective 1,2-Addition



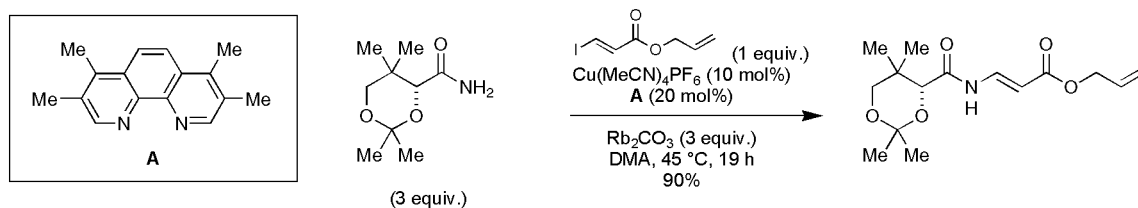
Kinetic resolution of epoxides by Cr-catalyzed enantioselective addition of indoles.
Bandini, M.; Cozzi, P. G.; Melchiorre, P.; Umani-Ronchi, A. *Angew. Chem. Int. Ed.* **2004**, *43*, 84.

Kinetic Resolution



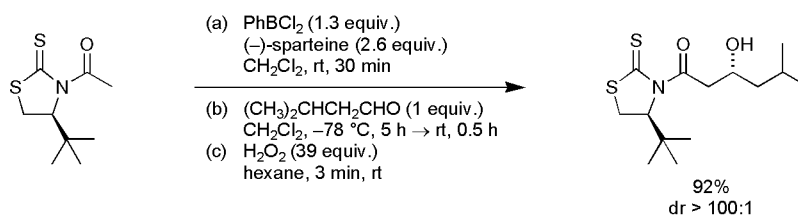
Copper-mediated synthesis of *N*-acyl vinylogous carbamic acids and derivatives.
Han, C.; Shen, R.; Su, S.; Porco Jr., J. A. *Org. Lett.* **2004**, *6*, 27.

C-N Bond Formation



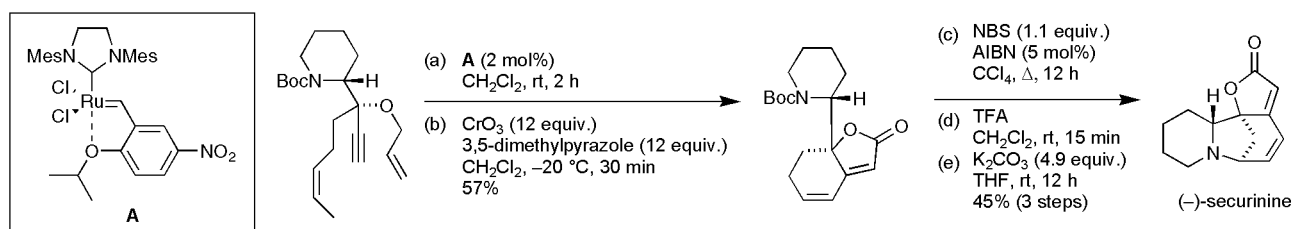
Asymmetric acetate aldol reaction of an *N*-acetyl thiazolidinethione reagent.
Zhang, Y.; Phillips, A. J.; Sammakia, T. *Org. Lett.* **2004**, *6*, 23.

Asymmetric Aldol

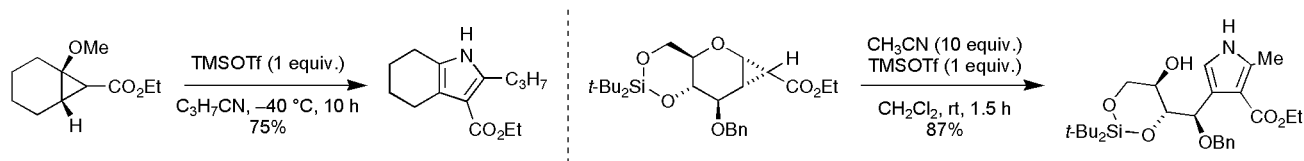


Total synthesis of (-)-securinine.
Honda, T.; Namiki, H.; Kaneda, K.; Mizutani, H. *Org. Lett.* **2004**, *6*, 87.

Metathesis

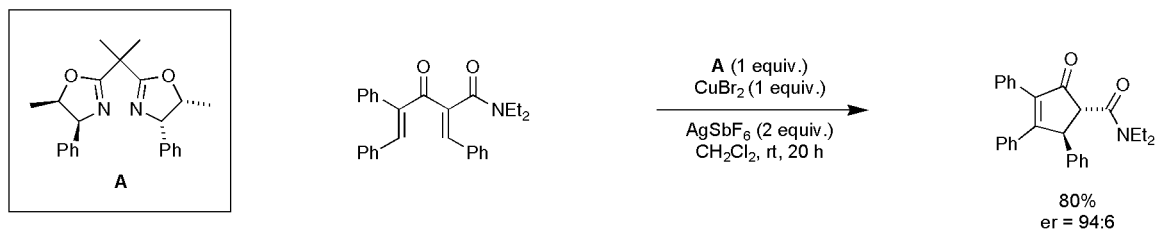


Diversity-orientated synthesis of pyrroles from donor-acceptor cyclopropanes and nitriles.
Yu, M.; Pagenkopf, B. L. *Org. Lett.* **2003**, *5*, 5099.

[3+2] Cycloaddition

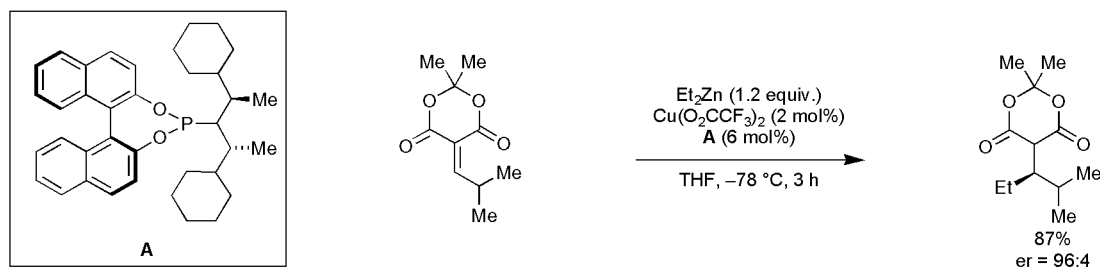
32 examples (yields 25-98%).

Catalytic, asymmetric Nazarov reactions promoted by chiral Lewis acid complexes.
Aggarwal, V. K.; Belfield, A. J. *Org. Lett.* **2003**, *5*, 5075.

4π-Electrocyclization

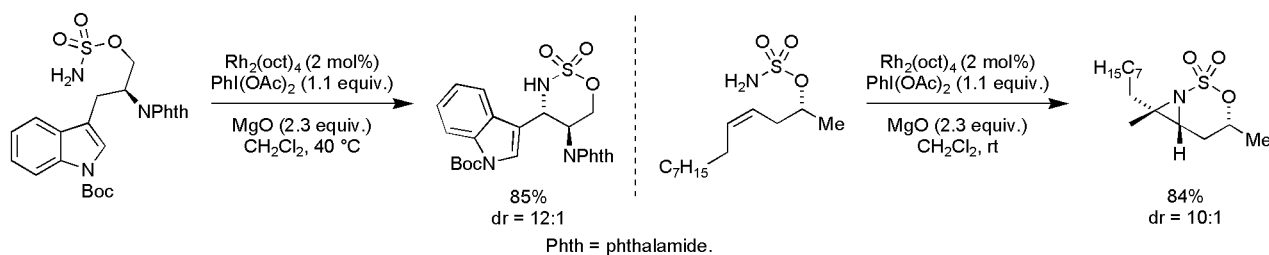
24 examples (yields 17-96%, %ee 1-88%).

Asymmetric conjugate addition reactions of Meldrum's acid derived acceptors.
Watanabe, T.; Knopfel, T. F.; Carreira, E. M. *Org. Lett.* **2003**, *5*, 4557.

Enantioselective 1,4-Addition

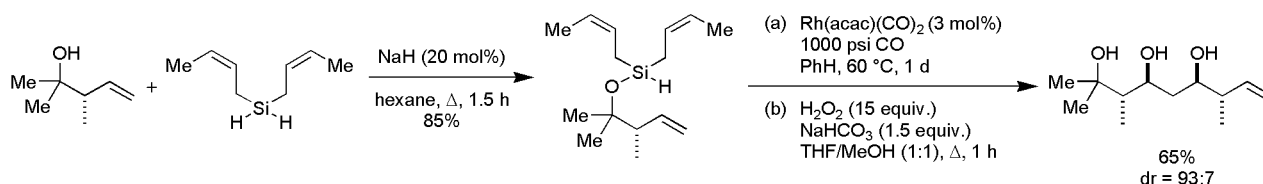
A variety of phosphoramidite ligands screened. 19 examples (yields 52-94%, %ee 24-94%).

Rh-catalyzed amination reactions of chiral sulfamates.
Wehn, P. M.; Lee, J.; Du Bois, J. *Org. Lett.* **2003**, *5*, 4823.

Amination

C-H Amination: 15 examples (yields <5-92%, %de 50-100%). Azridination: 4 examples (yields 84-92%, %de 43-82%).

Tandem silylformylation-allyl(crotyl)silylation.
Zacuto, M. J.; O'Malley, S. J.; Leighton, J. L. *Tetrahedron*, **2003**, *59*, 8889.

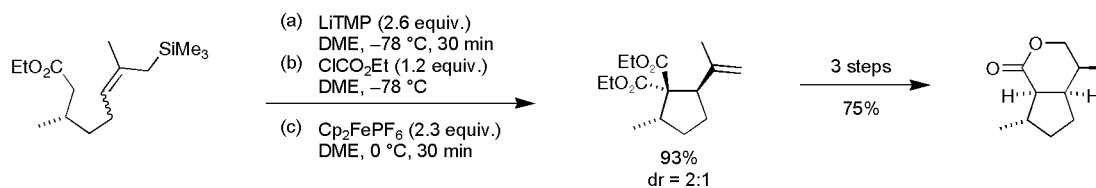
Silylation

13 examples (yields 45-83%, %de 38-92%).

Efficient oxidative radical cyclizations of ester enolates.

Jahn, U.; Hartmann, P.; Kaasalainen, E., M., *Org. Lett.* **2004**, *6*, 257.

Radical Cyclization

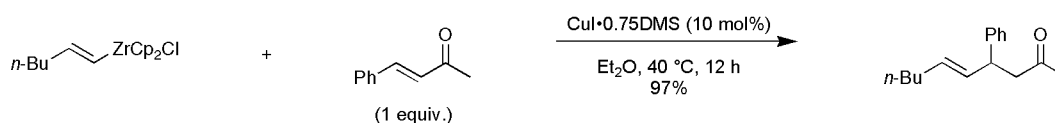


6 examples (yields 53-98%).

Cu(I)-catalyzed conjugate addition of alkenyl groups from vinylzirconocene reagents.

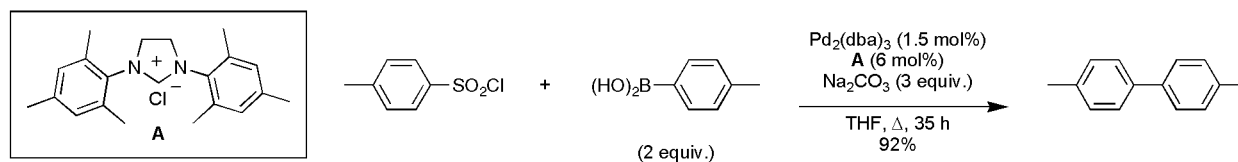
El-Batta, A.; Hage, T. R.; Plotkin, S.; Bergdahl, M., *Org. Lett.* **2004**, *6*, 107.

1,4-Addition



10 examples (yields 54-97%).

Palladium-catalyzed Suzuki-Miyaura cross-coupling of sulfonyl chlorides and boronic acids.

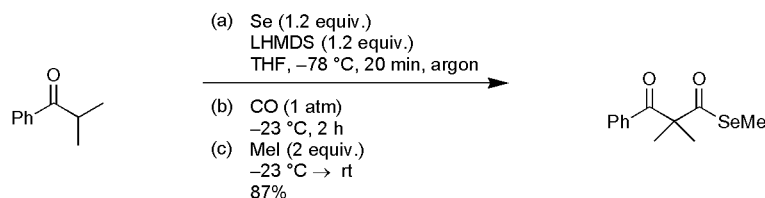
Dubbaka, S. R.; Vogel, P., *Org. Lett.* **2004**, *6*, 95.sp²-sp² Coupling

34 examples (yields 14-92%).

Carbonylation of lithium enolates with carbon monoxide mediated selenium.

Fujiwara, S.; Nishiyama, A.; Shin-ike, T.; Kambe, N.; Sonoda, N., *Org. Lett.* **2004**, *6*, 453.

Carbonylation

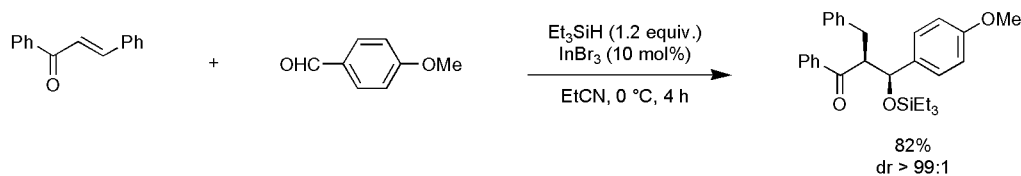


6 examples (yields 41-87%).

Catalytic generation of indium hydride in a highly diastereoselective reductive aldol reaction.

Shibata, I.; Kato, H.; Ishida, T.; Yasuda, M.; Baba, A., *Angew. Chem. Int. Ed.* **2004**, *43*, 711.

Reductive Aldol Reaction



12 examples (yields 33-87%, %de 56->98%).