

**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:

John Cooksey, Victoria Coombes, Axel Jansen, Stephen McAteer, Bernard Otto, Joanne Peach and Josephine Yuen, Department of Chemistry, Leeds University, Leeds, LS2 9JT, UK.

Georg Thieme Verlag does not accept responsibility for the accuracy, content, or selection of the data.

**SYNTHESIS** 2004, No. 7, pp 1119–1126

Advanced online publication: 26.04.2004

Art ID: X00704SS

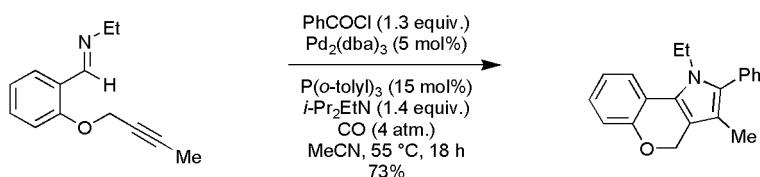
© Georg Thieme Verlag Stuttgart · New York

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.

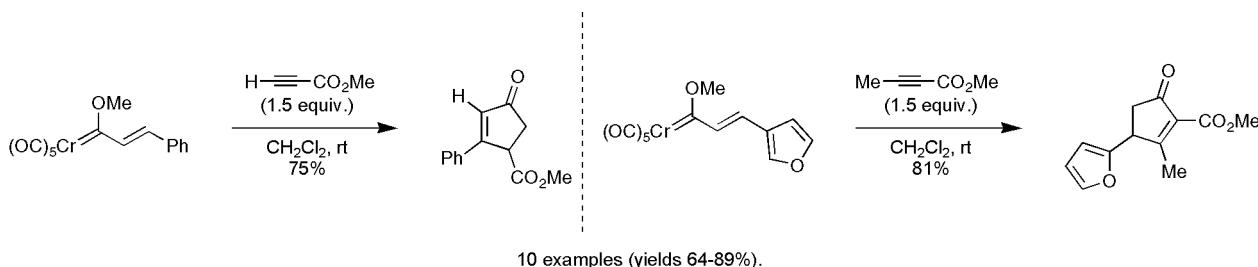
Annulation



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

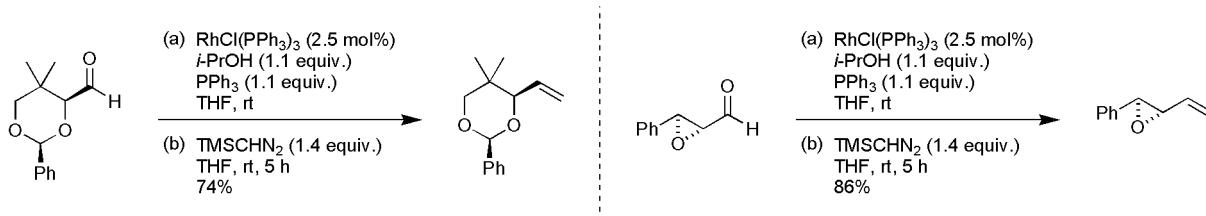
Preparation of 2-cyclopentenones using Fischer carbene complexes of Rh(I).  
Barluenga, J.; Vicente, R.; Lopez, L. A.; Rubio, E.; Tomas, M.; Alvarez-Rua, A. *J. Am. Chem. Soc.* **2004**, 126, 470.

[3+2] Cycloaddition



Rhodium-catalyzed methylenation of aldehydes.  
Lebel, H.; Paquet, V. *J. Am. Chem. Soc.* **2004**, 126, 320.

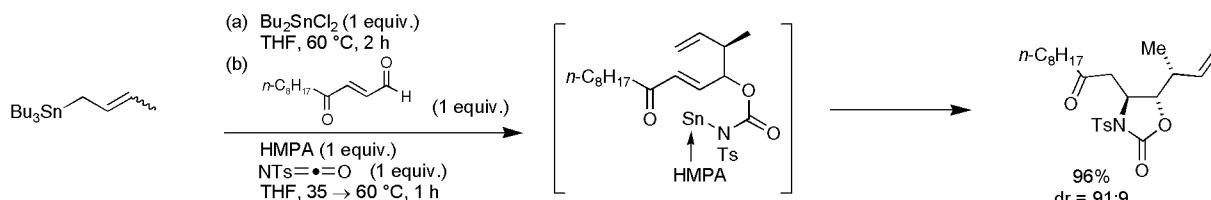
Methylenation



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

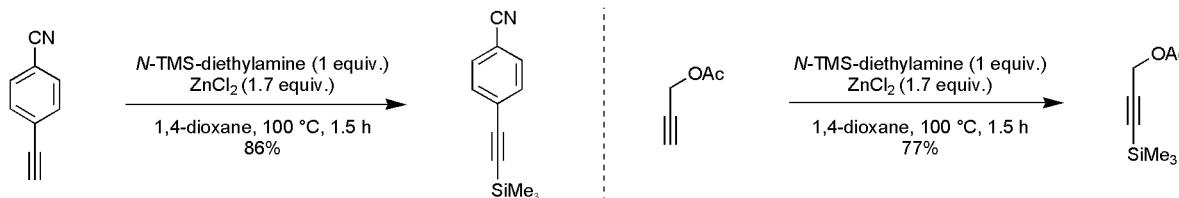


(Z)-Homocrotyl products can be formed instead of 1-methylallyl if the crotyltri-*n*-butyltin,  $\text{Bu}_2\text{SnCl}_2$  and aldehyde are added in one portion.  
8 examples (yields 54–96%, %de 82–100%).

Direct electrophilic silylation of terminal alkynes.

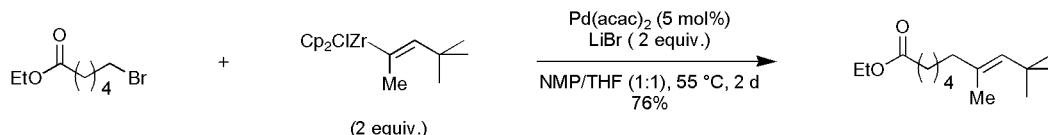
## Silylation

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



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

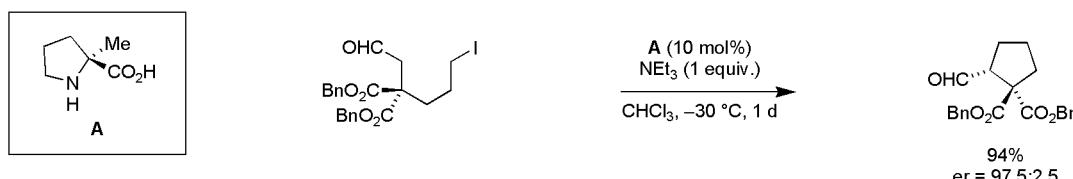
Zirconium-Negishi reactions of alkyl electrophiles under ligandless conditions.  
Wiskur, S. L.; Korte, A.; Fu, G. C. *J. Am. Chem. Soc.*, **2004**, *126*, 82.

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

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

Catalytic, asymmetric intramolecular  $\alpha$ -alkylation of aldehydes.  
Vignola, N.; List, B. *J. Am. Chem. Soc.*, **2004**, *126*, 450.

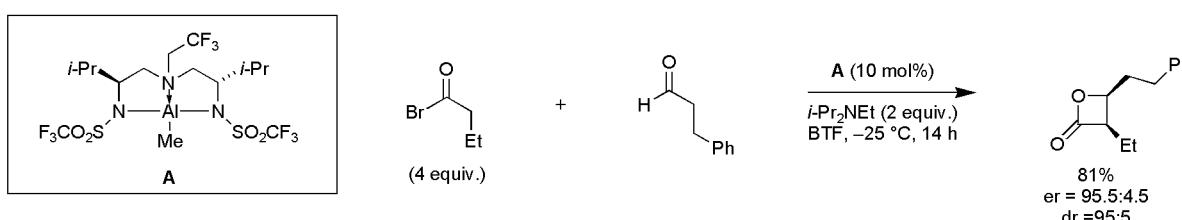
## Enantioselective Alkylation



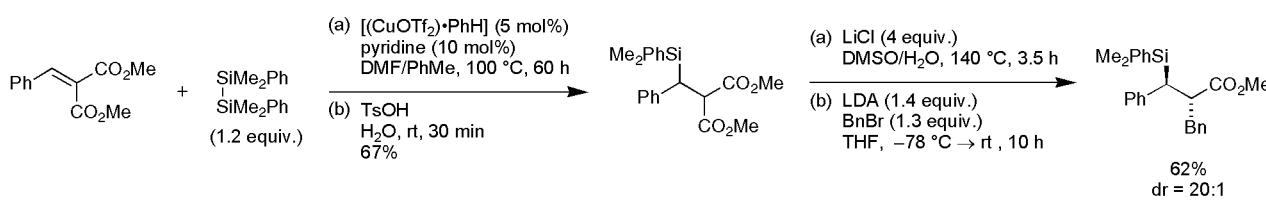
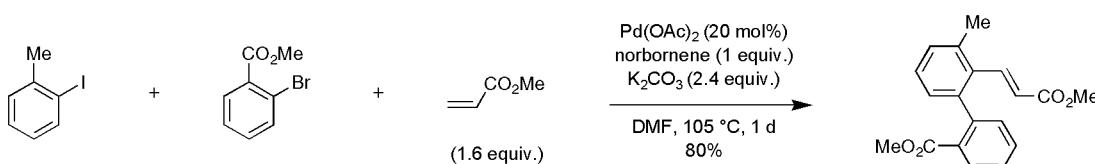
8 examples (yields 20–93%, %ee 84–96%). Substituted, chiral pyrrolidines and cyclopropanes are also reported.

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

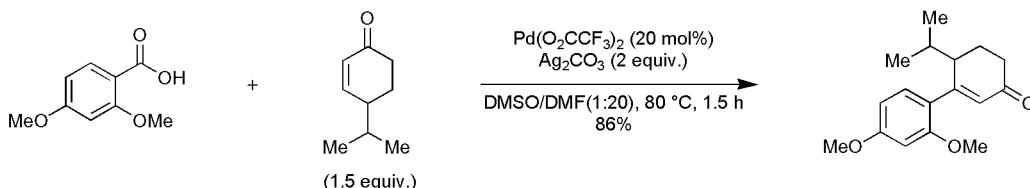


13 examples (yields 71–88%, %ee 88–96%, %de 72–>96%). BTF = benzotrifluoride.

**Copper(I)-catalyzed disilylation of alkylidene malonates.**Clark, C. T.; Lake, J. F.; Scheidt, K. A. *J. Am. Chem. Soc.*, **2004**, *126*, 84.**Disilylation****Palladium-catalyzed unsymmetrical aryl couplings.**Faccini, F.; Motti, E.; Catellani, M. *J. Am. Chem. Soc.*, **2004**, *126*, 78. **$sp^2$ - $sp^2$  Coupling**

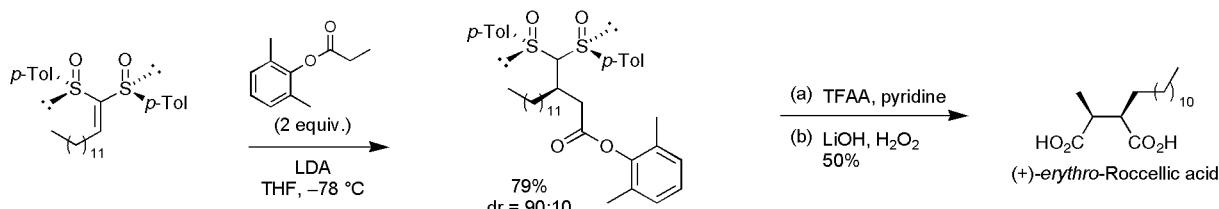
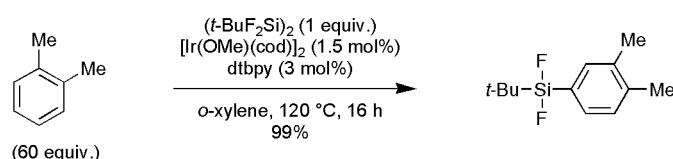
22 examples (yields 0-83%).

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

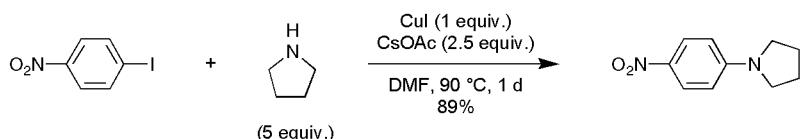
**Heck-type decarboxylative arylation of 2-cycloalken-1-ones.**Tanaka, D.; Myers, A. G. *Org. Lett.* **2004**, *6*, 433. **$sp^2$ - $sp^2$  Coupling**

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%).

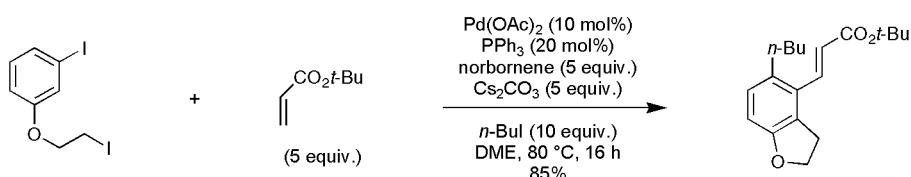
**Diastereoselective conjugate addition to alkylidene bis(sulfoxides) and application to (+)-erythro-Roccellic acid.**Brebion, F.; Delouvre, B.; Najera, F.; Fensterbank, L.; Malacia, M.; Vaissermann, J. *Angew. Chem. Int. Ed.* **2003**, *42*, 5342.**1,4-Addition**Application to the synthesis of (*R*)-Fenoprofen 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.

***sp*<sup>2</sup>-*sp*<sup>3</sup> Coupling**

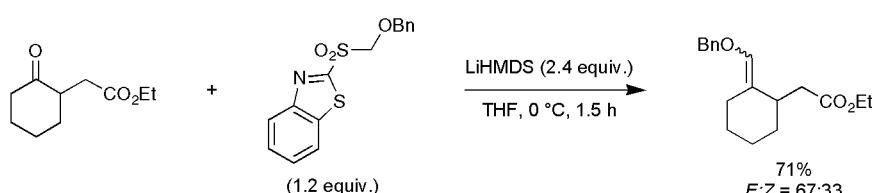
23 examples (yields 8-96%).

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

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

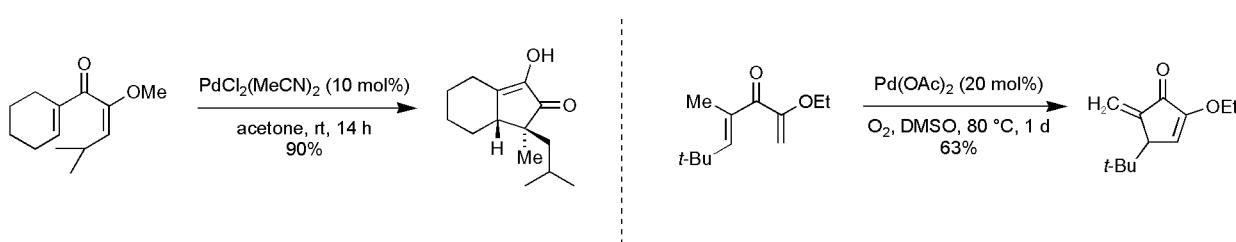
19 examples (yields 0-86%).

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).

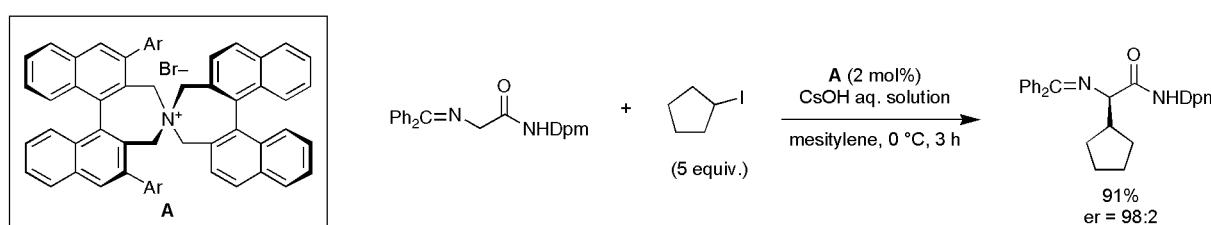
Pd(II)-catalyzed Nazarov reaction.  
Bee, C.; Leclerc, E.; Tius, M. A. *Org. Lett.* **2003**, 5, 4927.

**Annulation**

13 examples (yields 41-92%).

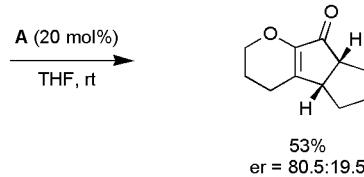
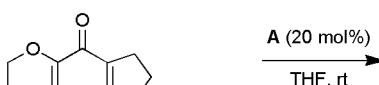
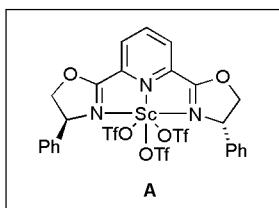
5 examples (yields 32-63%).

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.

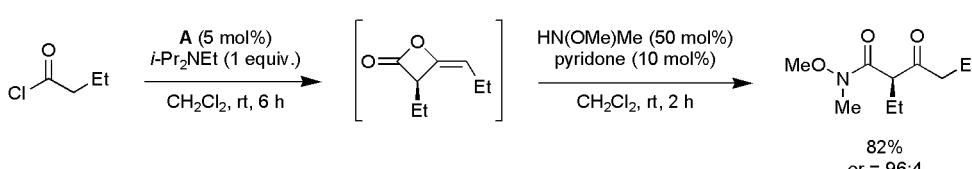
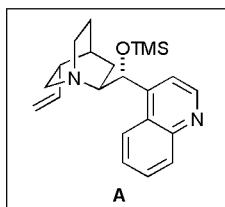
## 4-II Electrocyclization



20 examples (yields 40-93%).

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

## C-C Bond Formation

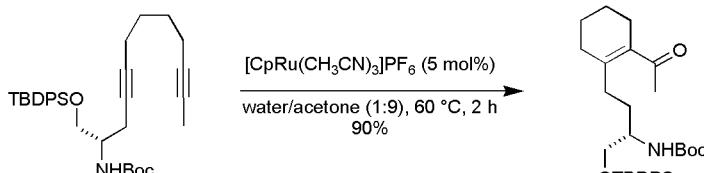


5 examples (yields 58-88%, %ee 91-96%).

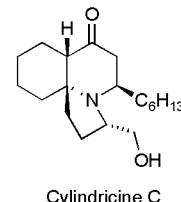
Optimization of reaction conditions and mechanistic studies are also reported.

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

## Annulation

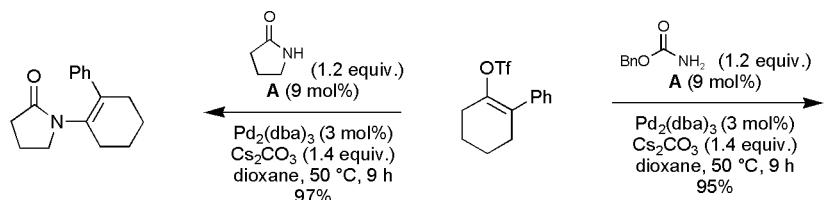
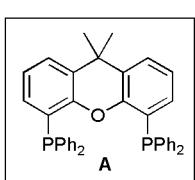


- (a) LDA (3 equiv.) heptane, -78 °C → rt, 4 h
- (b) MsCl (5 equiv.) NEt<sub>3</sub> (10 equiv.) CH<sub>2</sub>Cl<sub>2</sub>, 0 °C → rt, 20 h
- (c) TFA (120 equiv.) CH<sub>2</sub>Cl<sub>2</sub>, rt, 1 h
- (d) K<sub>2</sub>CO<sub>3</sub> (16 equiv.) PhMe, Δ, 68 h
- (e) TBAF (3 equiv.) THF, rt, 4 h  
74% (5 steps)



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

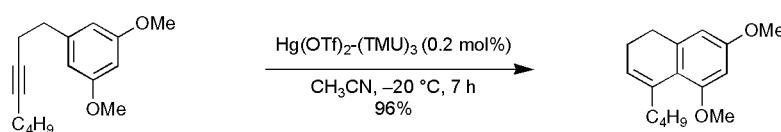
Palladium catalyzed amidation of enol triflates.  
Wallace, D. J.; Klauber, D. J.; Chen, C.; Volante, R. P. *Org. Lett.* **2003**, 5, 4749.

Nsp<sup>3</sup>-sp<sup>2</sup> Coupling

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

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

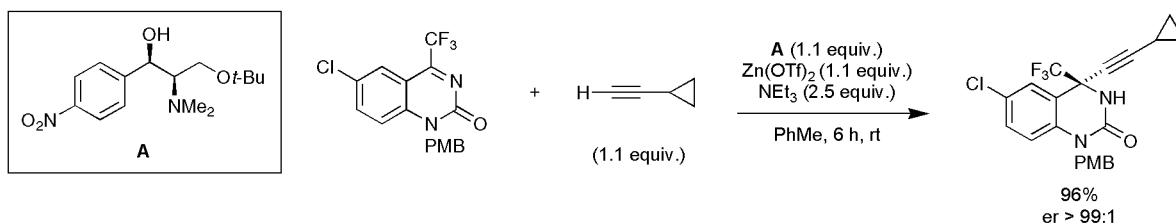
## Annulation



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

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

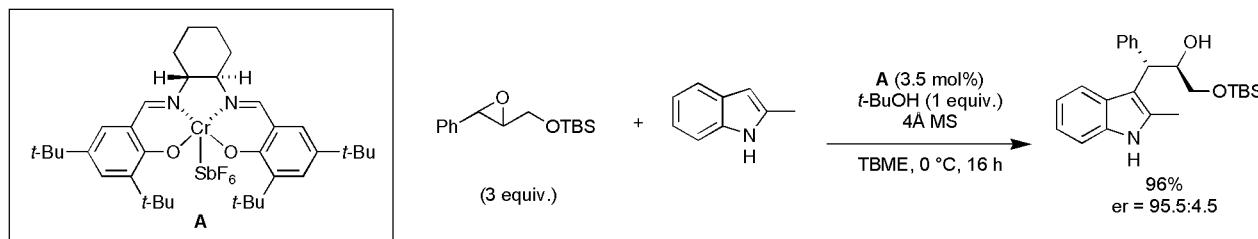
### Enantioselective 1,2-Addition



17 examples (yields 24–96%, %ee 24–99%).

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

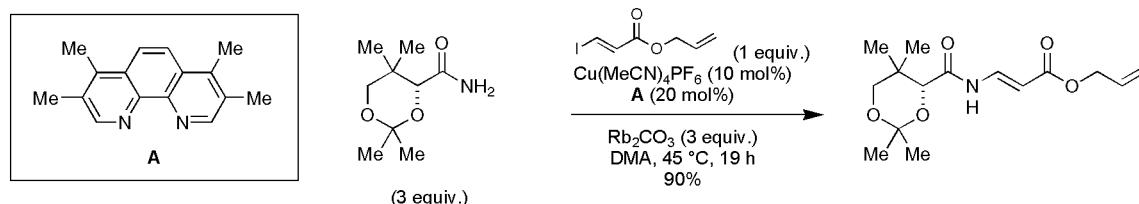


TBME = *tert*-butyl methyl ether.

Reactions with 1,2-disubstituted *cis*, *trans* and *meso* epoxides are reported. 17 examples (yields 24–99%, %ee 80–99%).

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.

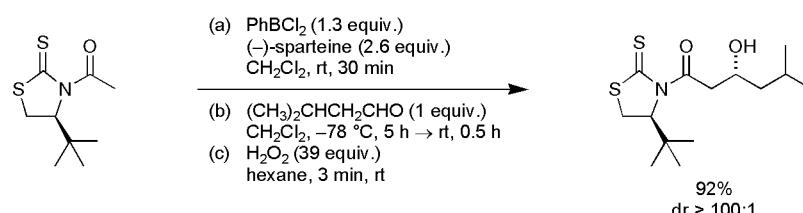
### C–N Bond Formation



13 examples (yields 6–92%). A synthesis of the antibiotic CJ-15,801 is also described.

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

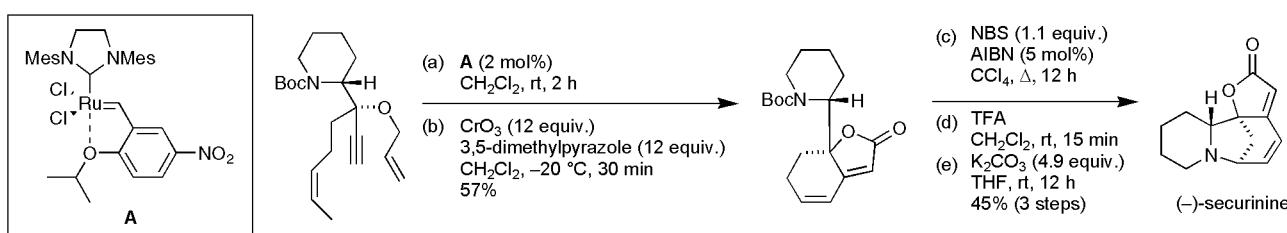
### Asymmetric Aldol



8 examples (yields 65–92%, %de 81–>99%).

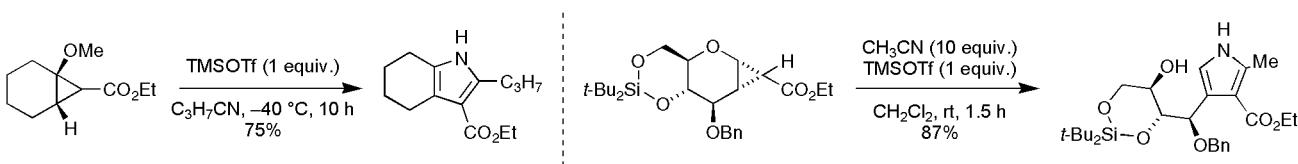
Total synthesis of (–)-securinine.  
Honda, T.; Namiki, H.; Kaneda, K.; Mizutani, H. *Org. Lett.* **2004**, *6*, 87.

### Metathesis



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

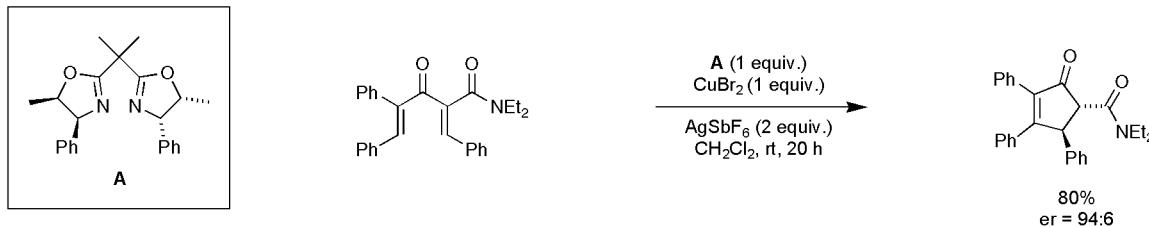
## [3+2] Cycloaddition



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.

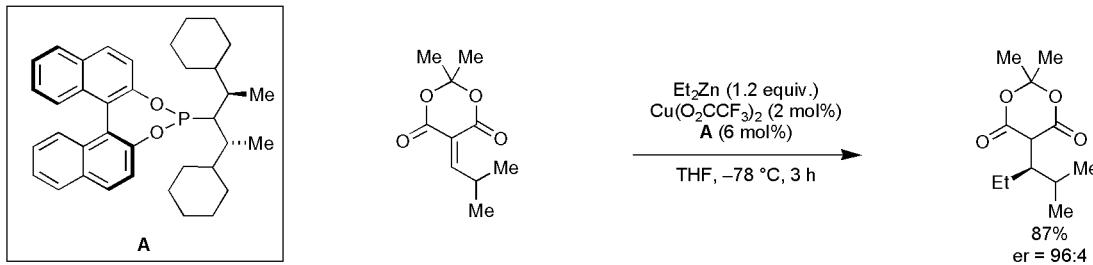
## 4III-Electrocyclization



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.

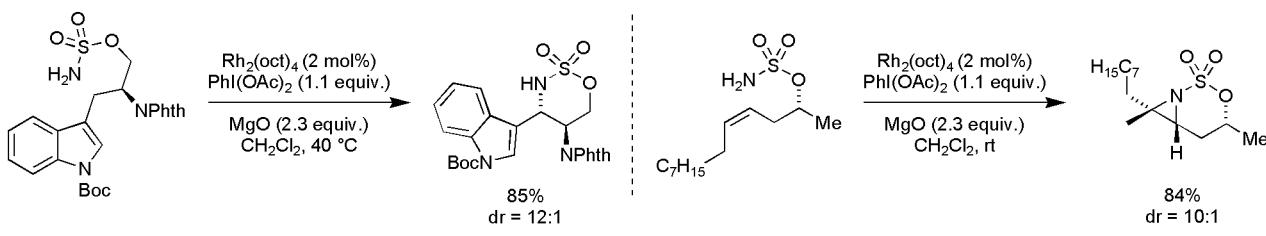
## Enantioselective 1,4-Addition



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

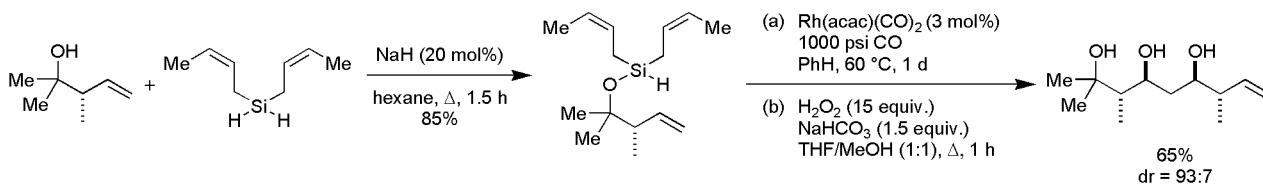


Phth = phthalimide.

C-H Amination: 15 examples (yields &lt;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.

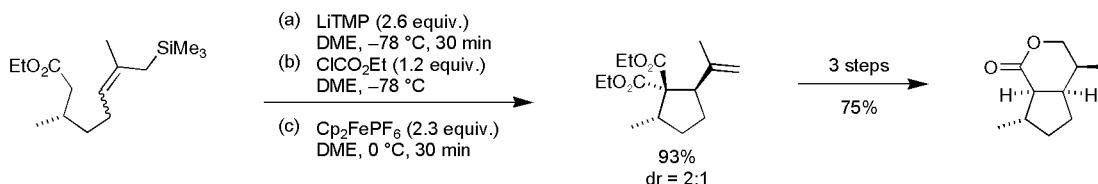
## Silylation



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.

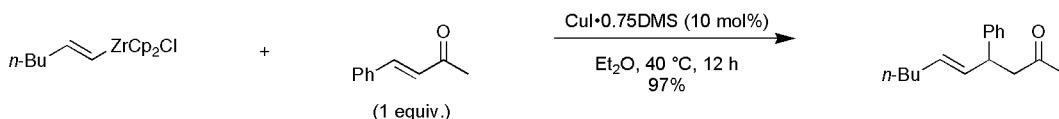
## Radical Cyclization



6 examples (yields 53-98%).

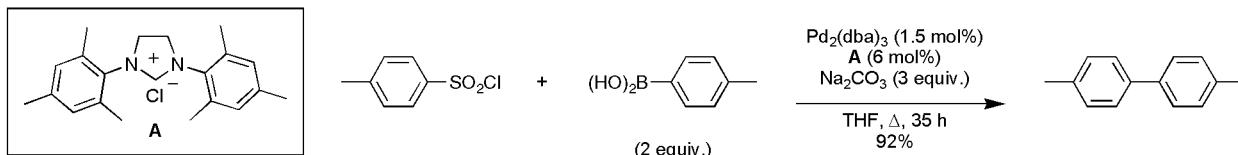
Cu(I)-catalyzed conjugate addition of alkenyl groups from vinylzirconocene reagents.  
El-Batta, A.; Hage, T. R.; Plotkin, S.; Bergdahl, M., *Org. Lett.* **2004**, 6, 107.

## 1,4-Addition



10 examples (yields 54-97%).

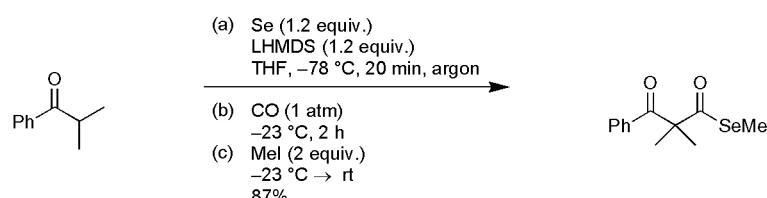
Palladium-catalyzed Suzuki-Miyaura cross-coupling of sulfonyl chlorides and boronic acids.  
Dubbaka, S. R.; Vogel, P., *Org. Lett.* **2004**, 6, 95.

sp<sup>2</sup>-sp<sup>2</sup> 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.

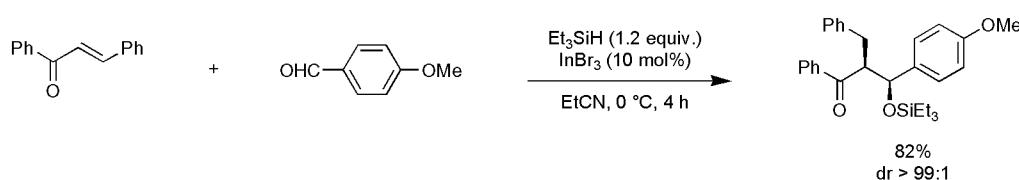
## Carbonylation



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-&gt;98%).