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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1437-210X,E;2002,0,15,1937,1944,ftx,en;X01502SS.pdf.

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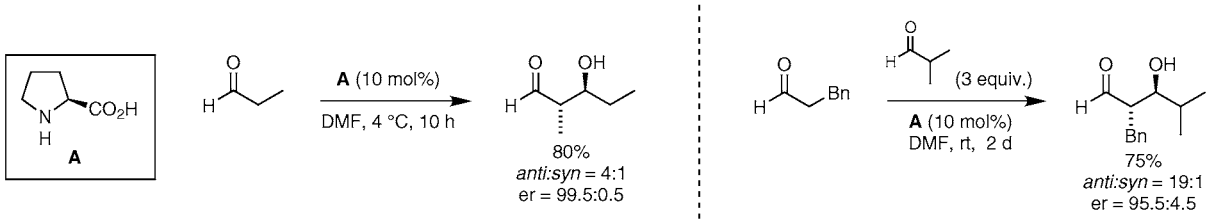
The journals regularly covered by the abstractors are:

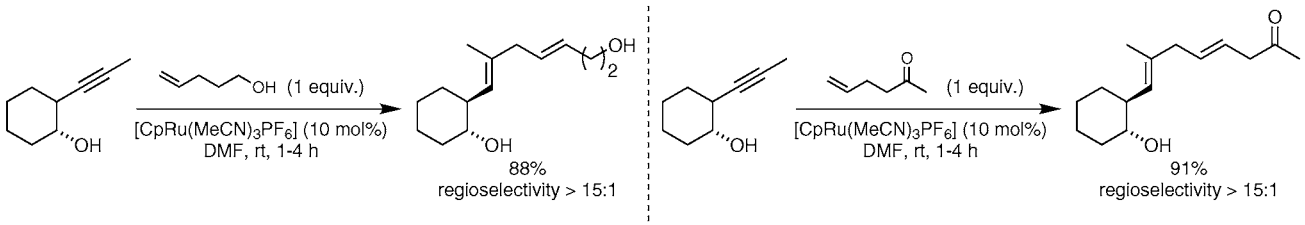
Angewandte Chemie International Edition
Bulletin of the Chemical Society of Japan
Chemical Communications
Chemistry A European Journal
Chemistry Letters
Collection Czechoslovak Chemical Communications
European Journal of Organic Chemistry
Helvetica Chimica Acta
Heterocycles
Journal of the American Chemical Society
Journal of Organic Chemistry
Organic Letters
Organometallics
Perkin Transactions 1
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry and Tetrahedron Letters

Enantioselective cross-aldol reaction of aldehydes. **1,2-Addition**
Northrup, A. B.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2002**, *124*, 6799.



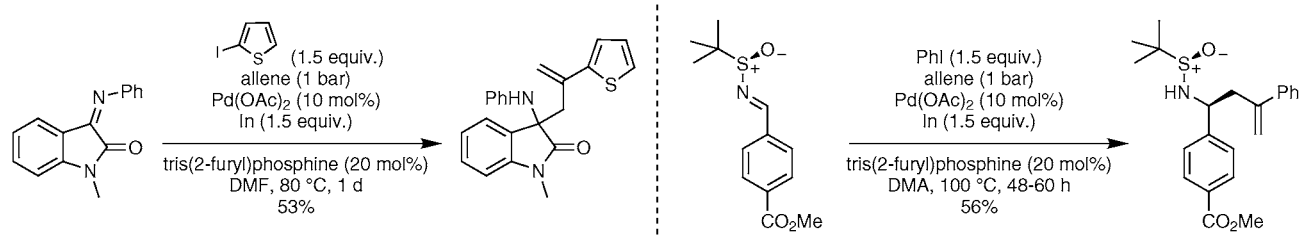
7 examples (yields 75-80%, 3:1 ≥ *anti:syn* ≥ 24:1, %ee 91->99%).

Ru-catalyzed Alder-ene reaction of alkenes and alkynes. **Alder-ene Reaction**
Trost, B. M.; Shen, H. C.; Pinkerton, A. B. *Chem.–Eur. J.* **2002**, *8*, 2341.



25 examples (yields 52-91%, 1.3:1 ≥ regioselectivity ≥ 20:1)

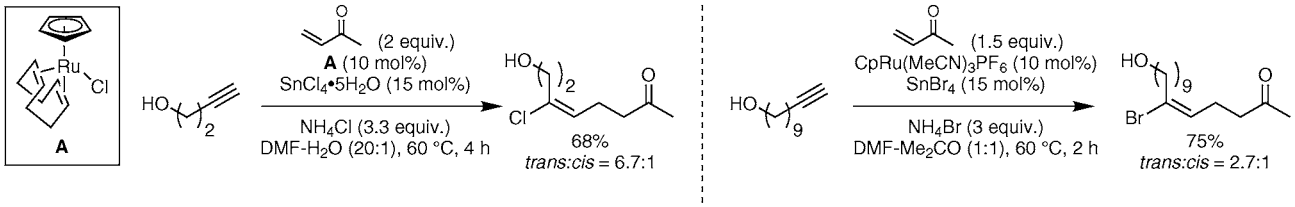
3-Component Pd/In-mediated allylation of imines with allenes and aryl iodides. **1,2-Addition**
Cooper, I. R.; Grigg, R.; MacLachlan, W. S.; Thornton-Pett, M.; Sridhara n, V. *Chem. Commun.* **2002**, 1372.



14 examples (yields 45-61%)

Ru-catalyzed formation of vinyl halides from alkynes and enones.
Trost, B. M.; Pinkerton, A. B. *J. Am. Chem. Soc.* **2002**, *124*, 7376.

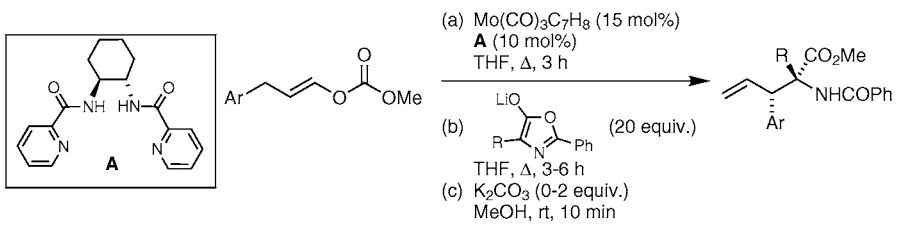
1,4-Addition/Halogenation

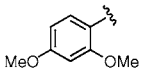


17 examples of vinyl chlorides (yields 42-83%) and 27 examples of vinyl bromides (yields <5-92%). The use of LiCl and LiBr is also reported.

Mo-catalyzed asymmetric allylic alkylation.
Trost, B. M.; Dogra, K. *J. Am. Chem. Soc.* **2002**, *124*, 7256.

Asymmetric Substitution

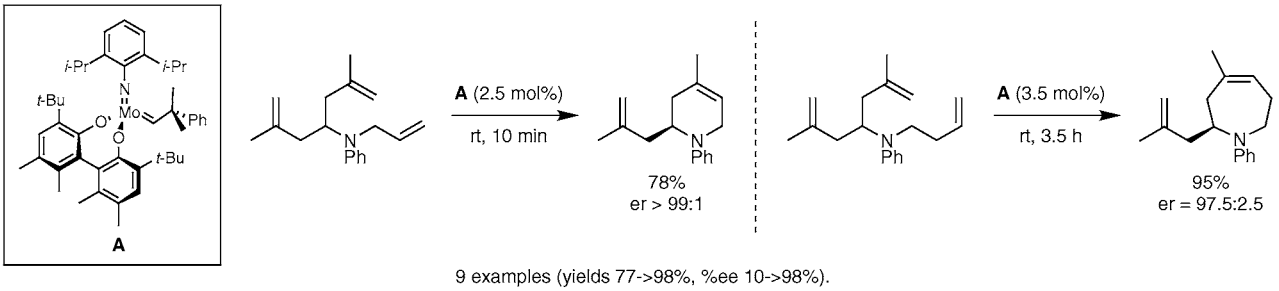


Ar	R	Yield	%ee	%de
Ph	Me	92%	99%	94%
	$PhCH_2$	86%	94%	>96%
	$PhCH_2$	90%	94%	>96%

12 examples (yields 84-92%, %ee 85-99%, %de 92-96%).

Enantioselective Mo-catalyzed ring closing metathesis.
Dolman, S. J.; Sattely, E. S.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 6991.

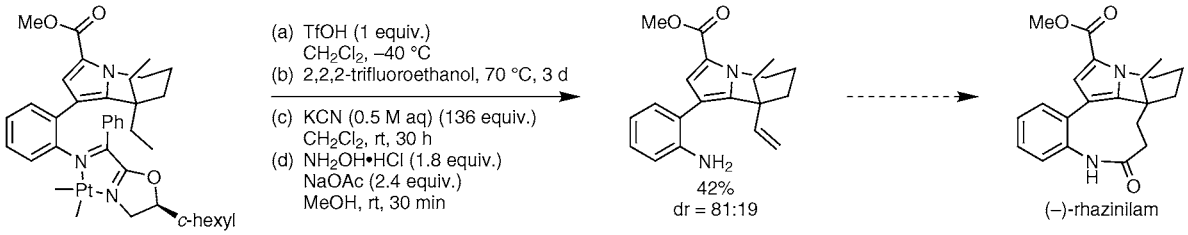
Ring Closing Metathesis



9 examples (yields 77->98%, %ee 10->98%).

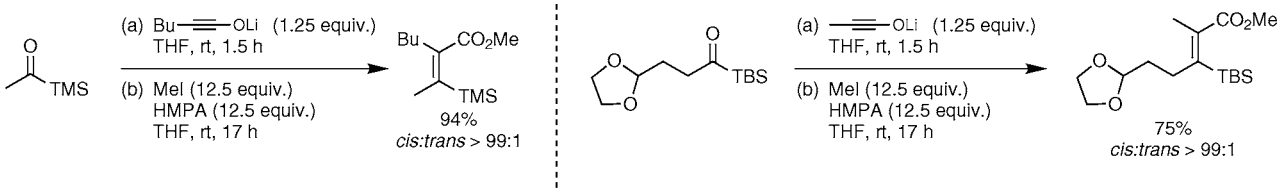
Stereoselective dehydrogenation: application to (–)-rhazinilam.
Johnson, J. A.; Li, N.; Sames, D. *J. Am. Chem. Soc.* **2002**, *124*, 6900.

Dehydrogenation



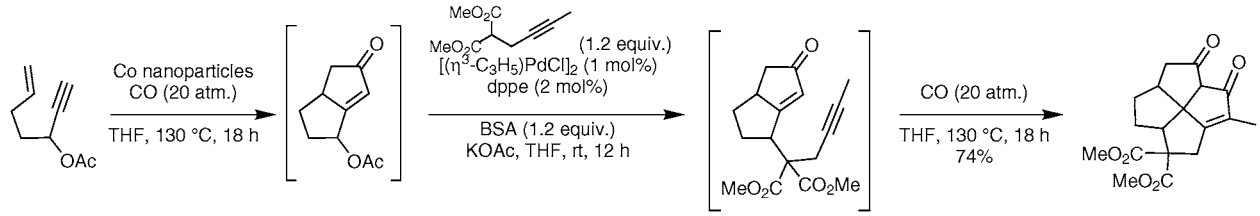
Z-Selective olefination of acylsilanes *via* ynolate anions.
Shindo, M.; Matsumoto, K.; Mori, S.; Shishido, K. *J. Am. Chem. Soc.* **2002**, *124*, 6841.

Olefination



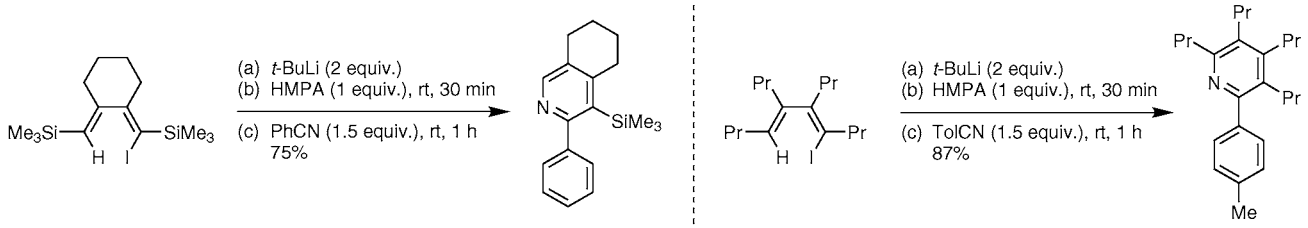
15 examples (yields 74-99%, *cis:trans* > 99:1).

One-pot synthesis of fenestranes from an enyne and an alkyne diester. **Pauson-Khand Cyclizations**
Son, S. U.; Park, K. H.; Chung, Y. K. *J. Am. Chem. Soc.* **2002**, *124*, 6839.



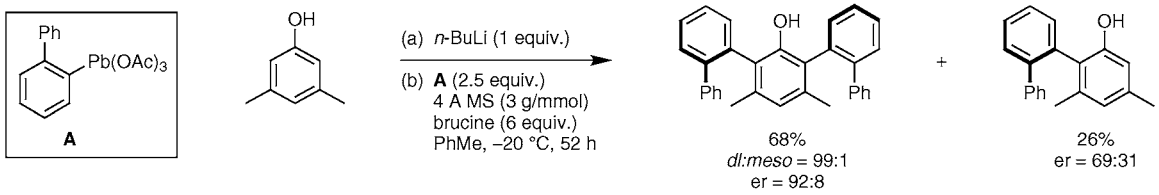
6 examples (yields 50-84%).

Cycloaddition of nitriles with monolithio-and dilithiobutadienes generates pyridines. **Cycloaddition**
Chen, J.; Song, Q.; Wang, C.; Xi, Z. *J. Am. Chem. Soc.* **2002**, *124*, 6238.



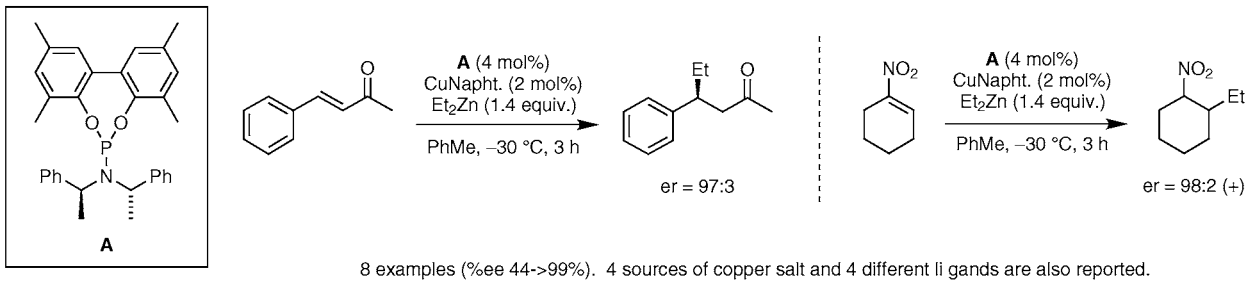
5 examples (yields 75-87%).

Asymmetric carbon-carbon coupling of phenols or anilines with aryllead triacetates. **sp²-sp² Coupling**
Kano, T.; Ohyabu, Y.; Saito, S.; Yamamoto, H. *J. Am. Chem. Soc.* **2002**, *124*, 5365.



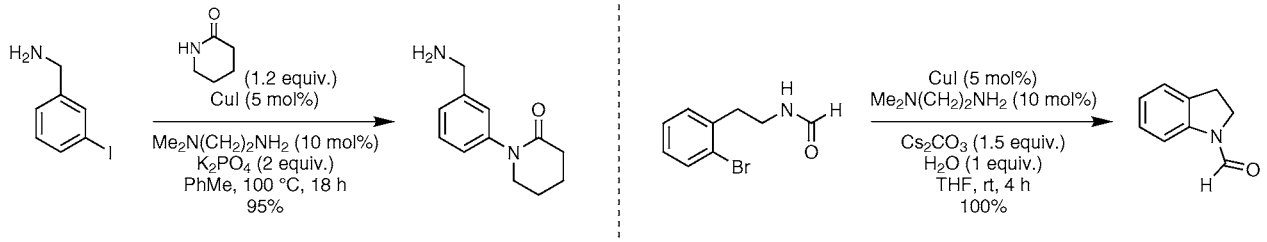
4 examples (yields 55-83%, %ee 83-93%). 6 phenols were studied with 3 different arylleads. 5 anilines were studied with 6 different arylleads.

Asymmetric conjugate addition reaction with phosphoramidites as chiral adjuvants. **1,4-Addition**
Alexakis, A.; Benhaim, C.; Rosset, S.; Humam, M. *J. Am. Chem. Soc.* **2002**, *124*, 5262.



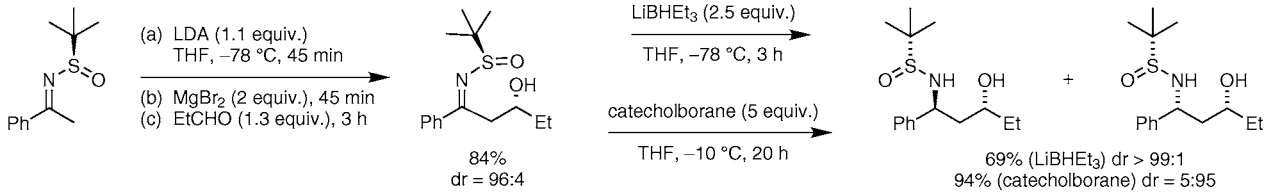
8 examples (%ee 44->99%). 4 sources of copper salt and 4 different li gands are also reported.

Cu-catalyzed amidation of aryl halides. **Amidation**
Klapars, A.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 7421.



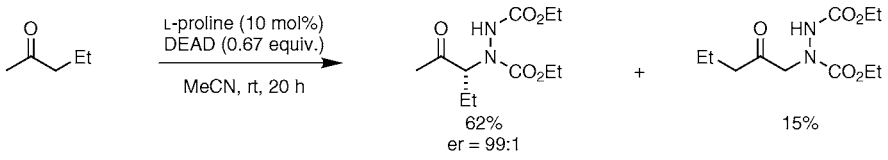
43 examples (yields 49-100%).

Asymmetric synthesis of *syn*- and *anti*-1,3-amino alcohols. **1,2-Addition/Reduction**
Kochi, T.; Tang, T. P.; Ellman, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 6508.



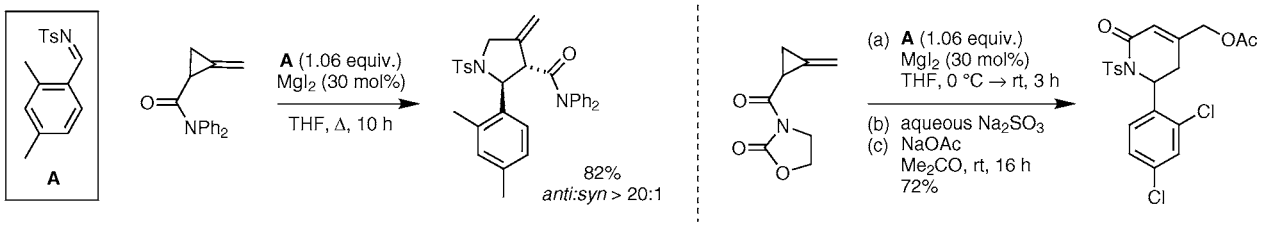
10 examples (yields 48-77% over 2 steps, %de 52->98%).

Asymmetric L-proline-catalyzed α-amination of ketones. **α-Amination**
Kumaragurubaran, N.; Juhl, K.; Zhuang, W.; Bogevig, A.; Jorgensen, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 6254.



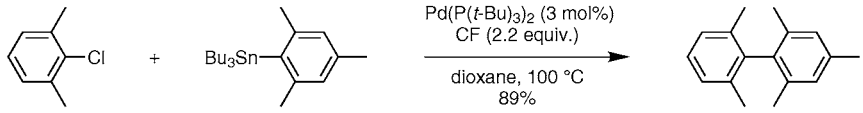
6 examples (yields 67-92%, %ee 84-99%).

Divergent selectivity in MgI_2-mediated ring expansions of methylenecyclopropyl amides and imides. **Ring Expansion**
Lautens, M.; Han, W. *J. Am. Chem. Soc.* **2002**, *124*, 6312.



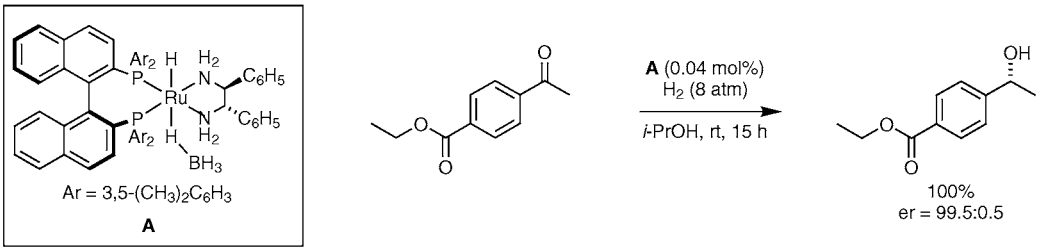
20 examples (yields 57-88%).

Pd/P(*t*-Bu)$_3$: a mild and general catalyst for Stille reactions of aryl chlorides and aryl bromides. **sp^2-sp^2 Coupling**
Littke, A. F.; Schwarz, L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 6343.



14 examples with aryl chlorides (yields 47-98%). 21 examples with aryl bromides (yields 66-97%).

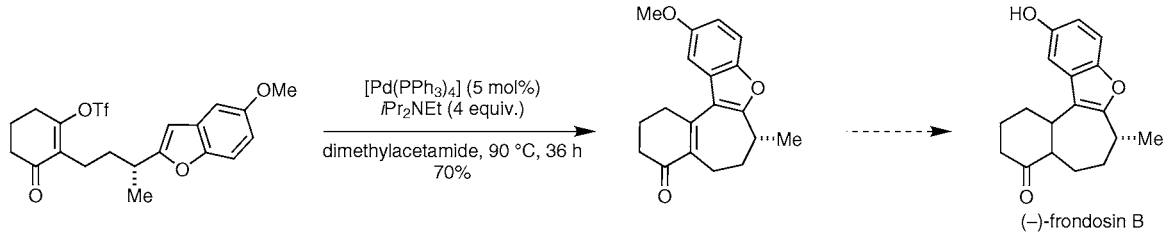
Asymmetric hydrogenation of ketones under base-free conditions. **Hydrogenation**
Ohkuma, T.; Koizumi, M.; Muniz, Kilian, Hilt, G.; Kabuto, C.; Noyori, R. *J. Am. Chem. Soc.* **2002**, *124*, 6508.



6 examples (yields 95-100%, %ee 97-99%).

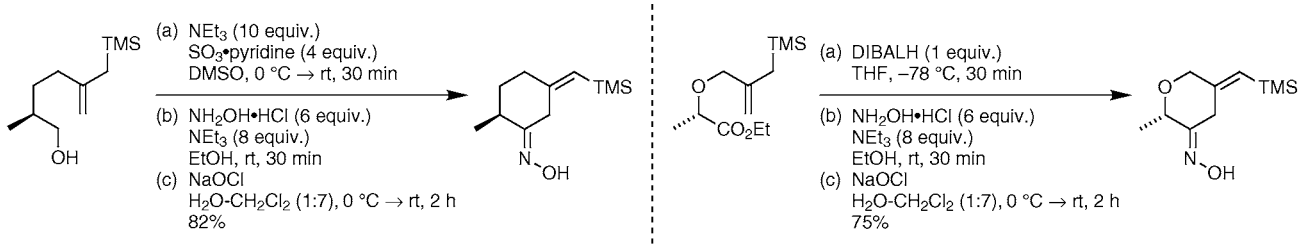
Synthesis of (–)-frondosin B *via* a Pd-catalyzed cyclization.
Hughes, C. C.; Trauner, D. *Angew. Chem. Int. Ed.* **2002**, *9*, 1569.

sp^2-sp^2 Coupling



Cycloisomerization reaction of nitrile oxides with a tethered allyltrime thylsilyl group.
Ishikawa, T.; Urano, J.; Ikeda, S.; Kobayashi, Y.; Saito, S. *Angew. Chem. Int. Ed.* **2002**, *9*, 1586.

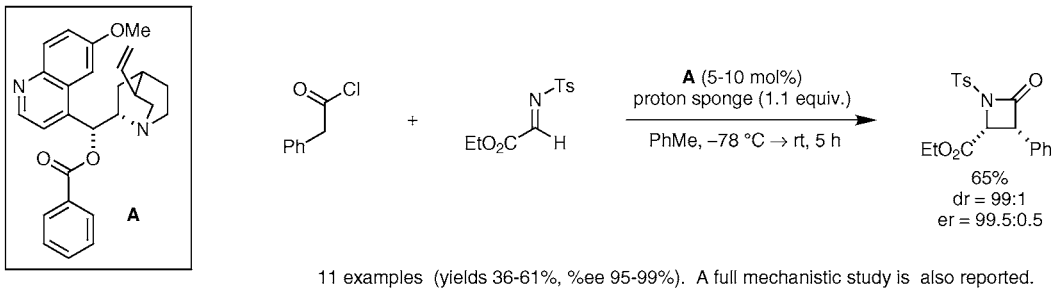
Cycloisomerization



9 examples (yields 33-82%).

Catalytic, asymmetric synthesis of β-lactams from ketenes and imides.
Taggi, A. E.; Hafez, A. M.; Wack, H.; Young, B.; Ferraris, D.; Lectka, T . *J. Am. Chem. Soc.* **2002**, *124*, 6626.

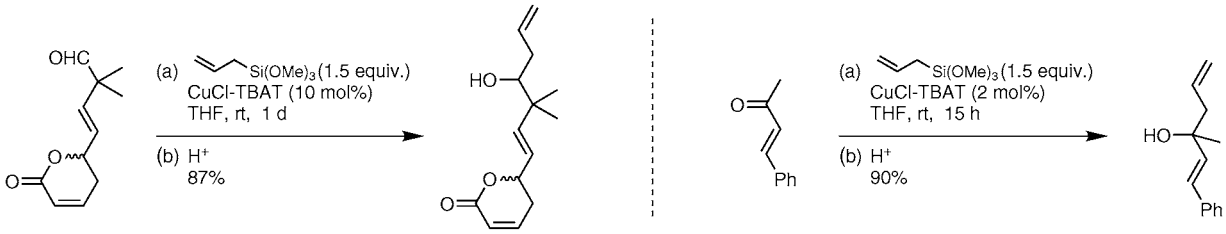
1,2-Addition/Cyclization



11 examples (yields 36-61%, %ee 95-99%). A full mechanistic study is also reported.

A general catalytic allylation using allyltrimethoxysilane.
Yamasaki, S.; Fujii, K.; Wada, R.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2002**, *124*, 6536.

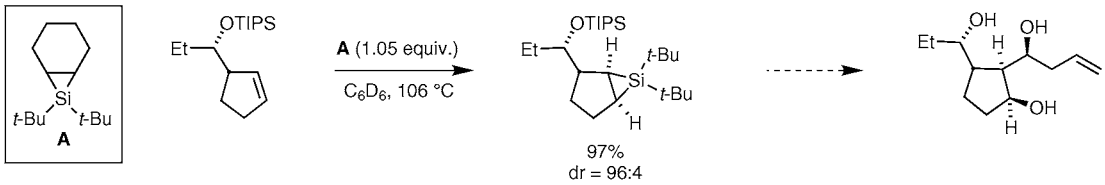
Allylation



8 examples with aldehydes (yields 79-97%). 8 examples with ketones (yields 76-95%). 4 examples with imines (yields 68-96%). TBAT = tetrabutylammonium difluorotriphenylsilicate.

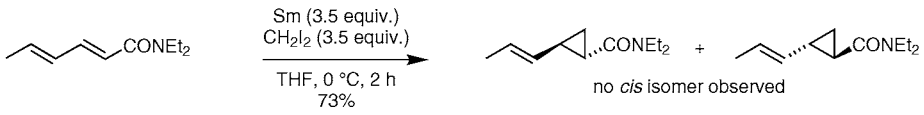
Diastereoselective silacyclopropanations of functionalized chiral alkenes.
Driver, T. G.; Franz, A. K.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 6524.

Silacyclopropanation



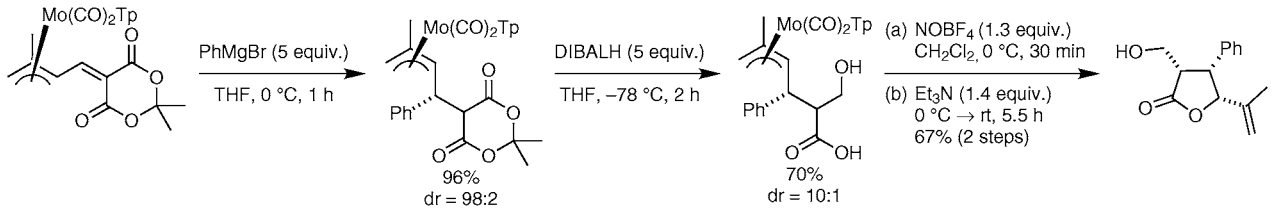
10 examples (yields 43-98%, %de 76->98%).

Stereospecific cyclopropanation of α,β-unsaturated amides using Sm/CH_2I_2. **Cyclopropanation**
Concellon, J. M.; Rodriguez-Solla, H.; Gomez, C. *Angew. Chem. Int. Ed.* **2002**, *41*, 1917.



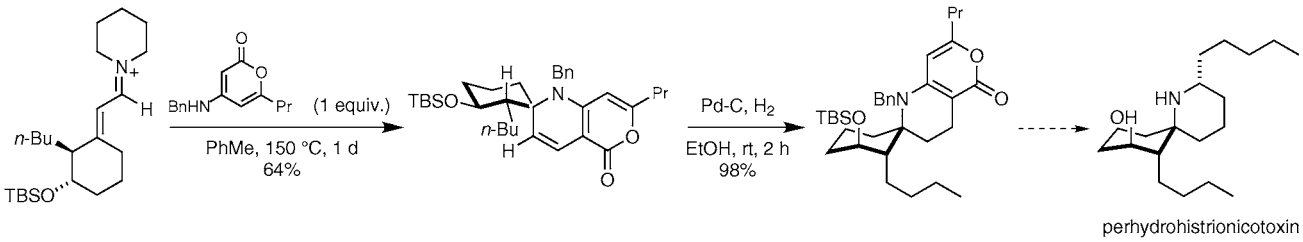
14 examples (yields 66-85%) with di-, tri- and tetrasubstituted double bonds. *Trans* and *cis* cyclopropanamides are obtained from (*E*)- and (*Z*)-α,β-unsaturated amides respectively.

Diastereoselective conjugate additions to π-allylmolybdenum complexes. **1,4-Addition**
Pearson, A. J.; Mesaros, E. F. *Org. Lett.* **2002**, *4*, 2001.



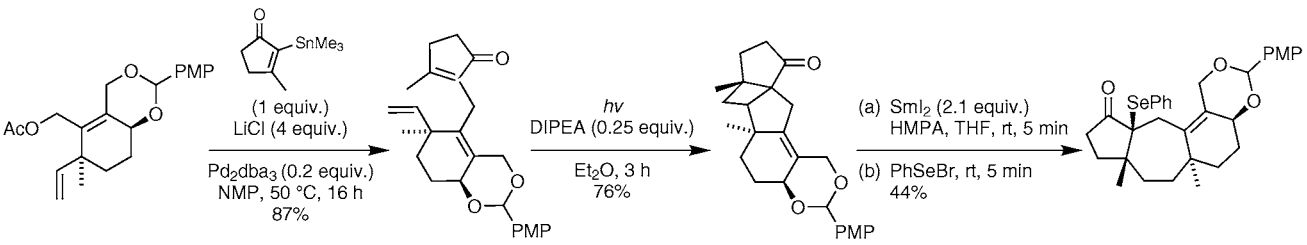
6 examples of 1,4-addition to π-allylmolybdenum complexes (yields 74-97%, %de > 96%).

Synthesis of 2-*epi*-(±)-perhydrohistrionicotoxin *via* a stereoselective [3+3]-cycloaddition. **Spirocycloaddition**
McLaughlin, M. J.; Hsung, R. P.; Cole, K. P.; Hahn, J. M.; Wang, J. *Org. Lett.* **2002**, *4*, 2017.

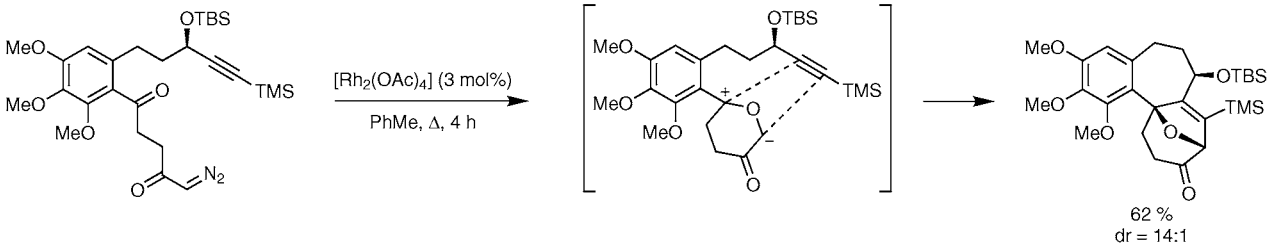


11 examples of spirocycloaddition (yields 40-85%).

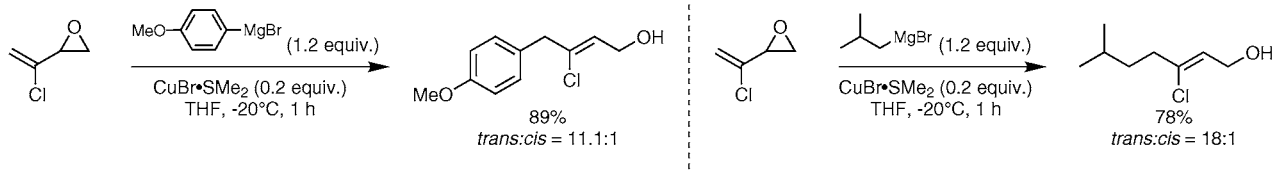
Synthesis of the [5-7-6] tricyclic system of the guanacastepenes. **Fragmentation**
Shipe, W. D.; Sorensen, E. J. *Org. Lett.* **2002**, *4*, 2063.



Construction of the colchicine skeleton by a Rh-catalyzed cyclization/cycloaddition cascade reaction. **Cyclization/Cycloaddition**
Graening, T.; Friedrichsen, W.; Lex, J.; Schmalz, H. G. *Angew. Chem. Int. Ed.* **2002**, *9*, 1524.

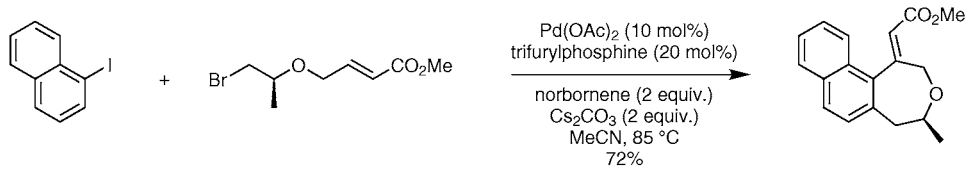


Synthesis of (*Z*)-3-chloroallylic alcohols *via* Cu-catalyzed nucleophilic addition to 2-chloro-3,4-epoxy-1-butene. **S_N2'-Addition**
Taber, D. F.; Mitten, J. V. *J. Org. Chem.* **2002**, *67*, 3847.



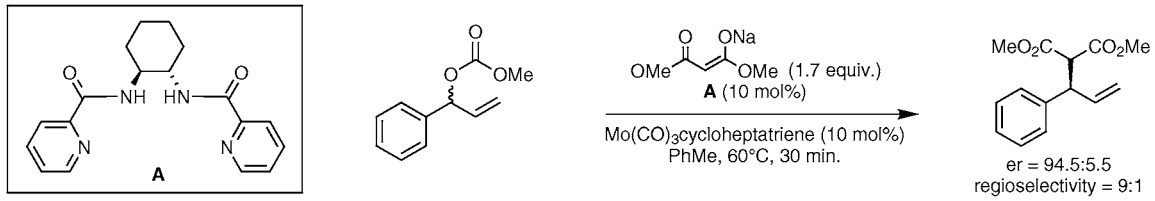
11 examples (yields 72-89%, 6.5:1 ≥ *trans:cis* ≥ 23.5:1).

Pd-catalyzed sequential alkylation-alkenylation reactions. **Alkylation/Alkenylation**
Lautens, M.; Paquin, J. F.; Piguel, S. *J. Org. Chem.* **2002**, *67*, 3972.



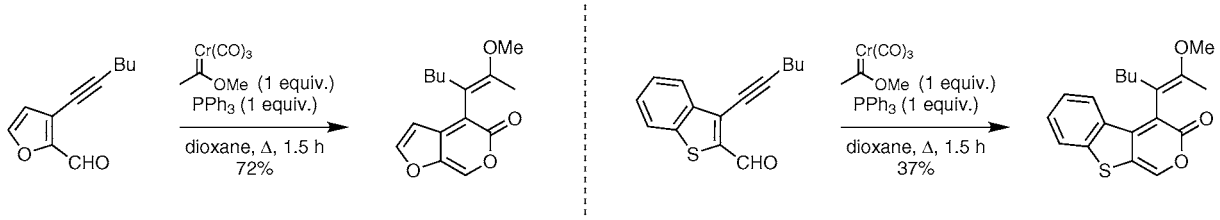
10 examples (yields 23-85%).

Mo-catalyzed asymmetric allylic alkylations. **Allylic Alkylation**
Hughes, D. L.; Palucki, M.; Yasuda, N.; Reamer, R. A.; Reider, P. J. *J. Org. Chem.* **2002**, *67*, 2762.



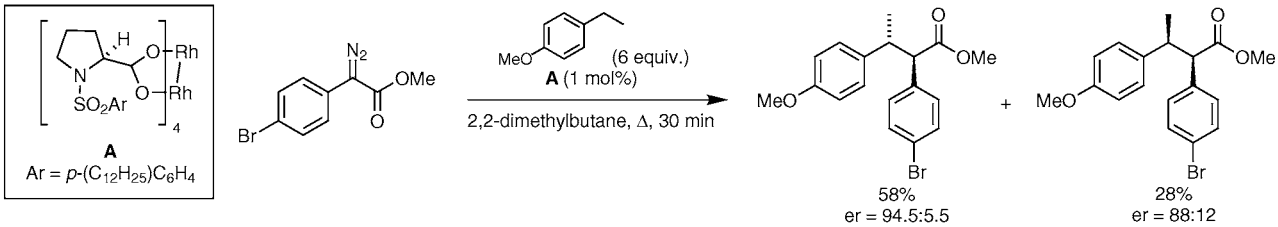
Minimal stereochemical memory effect using toluene and 1,2-dichloroethan e as solvent, resulting in higher product %ee than with THF, THP, *i*PrOAc and MeCN.

Coupling of 3-alkynyl-2-heteroaromatic carboxaldehydes with Fischer carbene complexes. **Carbene Insertion/Cyclization**
Zhang, Y.; Herndon, J. W. *J. Org. Chem.* **2002**, *67*, 4177.



21 examples (yields 6-75%). If the carbene complex contains a remote alkene substituent, a subsequent Diels-Alder reaction is observed.

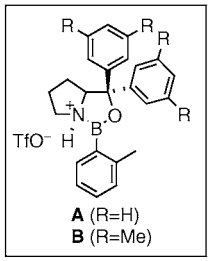
Rh-carbenoid benzylic C-H insertion. **C-H Insertion**
Davies, H. M. L.; Jin, Q.; Ren. P.; Kovalevsky, A. Y. *J. Org. Chem.* **2002**, *67*, 4165.



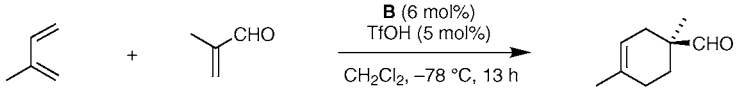
20 examples (yields 38-86%).

Asymmetric Diels-Alder reactions catalyzed by a triflic acid-activated chiral oxazaborolidine.
Corey, E. J.; Shibata, T.; Lee, T. W. *J. Am. Chem. Soc.* **2002**, *124*, 3808.

Diels-Alder Reaction



A (R=H)
B (R=Me)

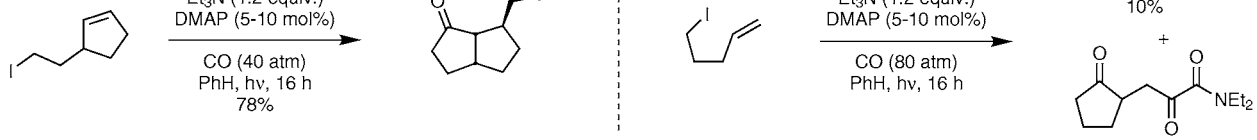


98%
er = 99:1

13 examples (yield 58-99%, %ee 91-97%).

Cascade radical reactions catalyzed by a Pd/light system.
Ryu, I.; Kreimerman, S.; Araki, F.; Nishitani, S.; Oderaotoshi, Y.; Minakata, S.; Komatsu, M.
J. Am. Chem. Soc. **2002**, *124*, 3812.

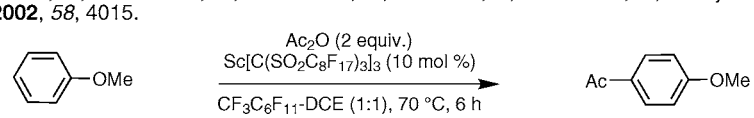
Carbonylation



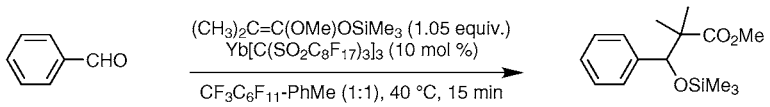
15 examples (yield 49-83%).

Recyclable Lewis acid catalysts in fluorous phase or as solids.
Mikami, K.; Mikami, Y.; Matsuzawa, H.; Matsumoto, Y.; Nishikido, J.; Yamamoto, F.; Nakajima, H.
Tetrahedron **2002**, *58*, 4015.

Lewis Acid Catalysis



Cycle	Yield
1	94%
2	93%
3	93%

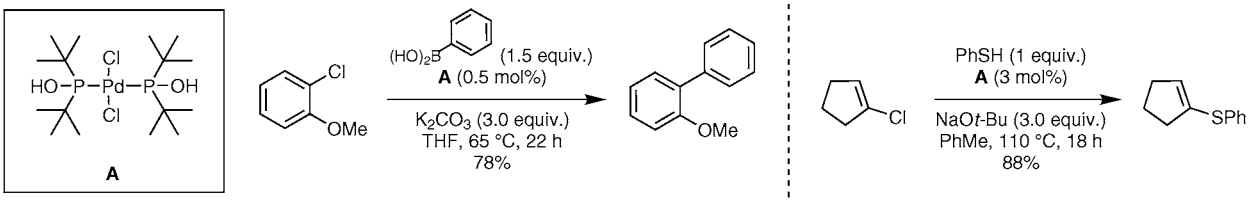


Cycle	Yield
1	84%
2	85%
3	83%

Various examples of Lewis acid catalysed reactions are also reported.

Air stable Pd-catalyzed C-C and C-S bond-forming reactions of vinyl and aryl chlorides.
Li, G. Y. *J. Org. Chem.* **2002**, *67*, 3643.

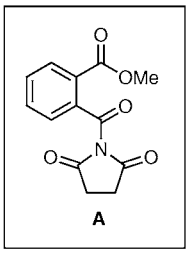
sp^2-sp^2 Coupling/C-S Bond Formation

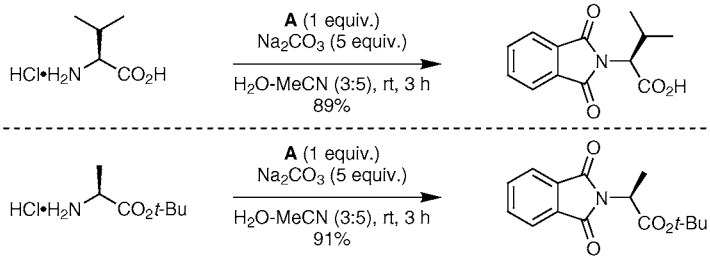


9 examples of Suzuki cross-coupling (yields 73-99%), 2 examples with vinyl chlorides (yields 53-92%), 6 examples of Negishi cross-coupling (yields 40-83%) and 2 examples of C-S bond form ation (yields 38-97%).

N-Phthaloylation of amino acid and peptide derivatives.
Casimir, J. R.; Guichard, G.; Briand, J. P. *J. Org. Chem.* **2002**, *67*, 3764.

***N*-Phthaloylation**





14 examples (yields 65-100%).