

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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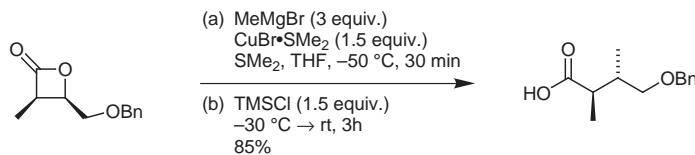
Synthesis 2002, No. 16, 14–11 2002. Article Identifier: 1437-210X;E;2002;0;16;2464;2471;ftx,en;X01602SS.pdf.
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The journals regularly covered by the abstractors are:

Advanced Synthesis & Catalysis
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

Cuprate-mediated ring opening reaction of β -lactones.
Nelson, S. G.; Wan, Z.; Stan, M. A. *J. Org. Chem.* **2002**, 67, 4680.

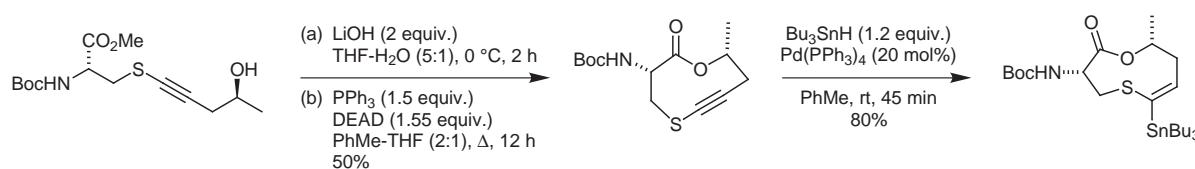
S_N2 Reaction



15 examples (yields 74–94%).

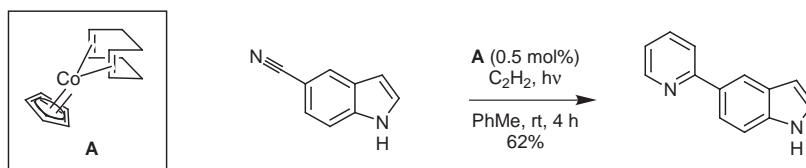
Synthesis of thioethynyl and thiovinyl ether-containing nine membered lactones.
Kugligowski, C.; Bezzanine-Lafollée, S.; Chaume, G.; Mahuteau, J.; Barrière, J.-C.; Bacqué, E.; Pancrazi, A.; Ardisson, J. *J. Org. Chem.* **2002**, 67, 4565.

Macrolactonization/Hydrostannylation



Photocatalyzed [2+2+2]-cycloaddition of nitriles with acetylene.
Heller, B.; Sundermann, B.; Buschmann, H.; Drexler, H.-J.; You, J.; Holzgrabe, U.; Heller, E.; Oehme, G. *J. Org. Chem.* **2002**, 67, 4414.

[2+2+2]-Cycloaddition

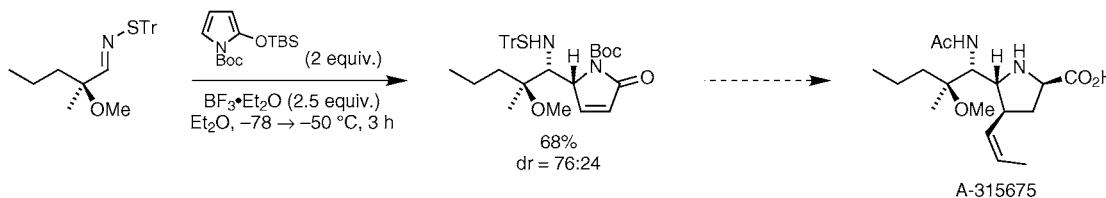


31 examples (yields 10–90%).

Diastereoselective addition of a silyloxypyrrrole to a chiral imine.

DeGoeij, D. A.; Chen, H.-J.; Flosi, W. J.; Grampovnik, D. J.; Yeung, C. M.; Klein, L. L.; Kempf, D. J. *J. Org. Chem.* **2002**, *67*, 5445.

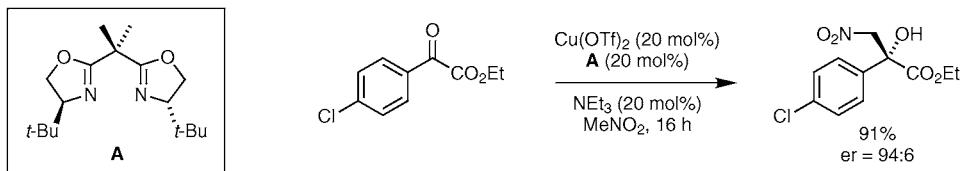
1,2-Addition



Enantioselective Cu-catalyzed Henry reactions of α -keto esters.

Christensen, C.; Juhl, K.; Hazell, R. G.; Jorgensen, K. A. *J. Org. Chem.* **2002**, *67*, 4875.

1,2-Addition

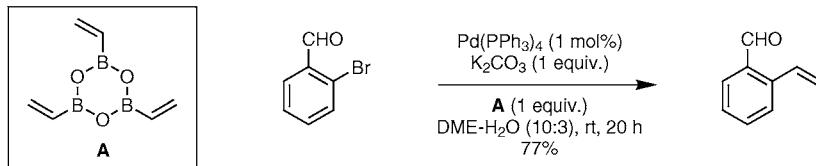


15 examples (yields 46-99%, %ee 30-94%).

Suzuki cross-coupling of aryl halides with 2,4,6-trivinylcyclotriboroxane.

Kerins, F.; O'Shea, D. F. *J. Org. Chem.* **2002**, *67*, 4968.

sp²-sp²-Coupling

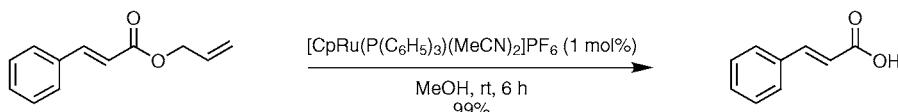


11 examples (yields 68-84%).

Ru-catalyzed deprotection of allyl carboxylic esters.

Kitamura, M.; Tanaka, S.; Yoshimura, M. *J. Org. Chem.* **2002**, *67*, 4975.

Deprotection

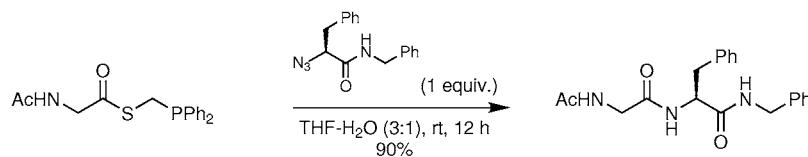


12 examples (yields 20-99%).

Staudinger ligation of α -azido acids.

Soellner, M. B.; Nilsson, B. L.; Raines, R. T. *J. Org. Chem.* **2002**, *67*, 4993.

Amidation

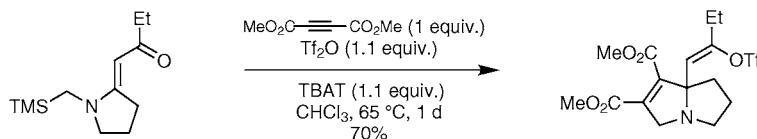


6 examples (yields 90-99%).

1,3-Dipolar cycloaddition of azomethine ylides.

Epperson, M. T.; Gin, D. Y. *Angew. Chem. Int. Ed.* **2002**, *41*, 1778.

Cycloaddition

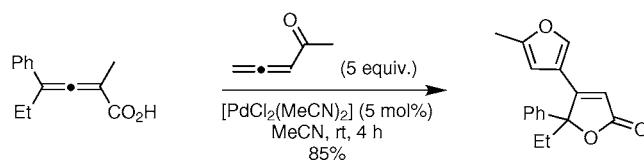


9 examples (yields 51–75%). TBAT = tetrabutylammonium triphenyldifluor osilicate.

Pd-catalyzed cyclization/dimerization reaction of 2,3-allenoic acids and 1,2-allenyl ketones.

Ma, S.; Yu, Z. *Angew. Chem. Int. Ed.* **2002**, *41*, 1775.

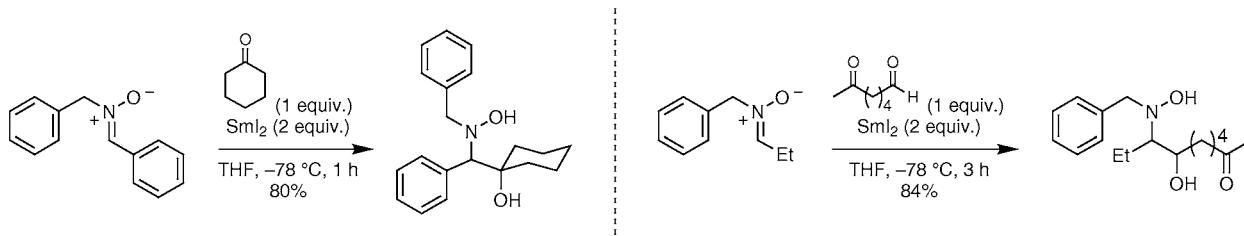
Cyclization/Dimerization



13 examples (yields 61–92%).

SmI₂-mediated cross coupling of nitrones with aldehydes and ketones.Masson, G.; Py, S.; Vallée, Y. *Angew. Chem. Int. Ed.* **2002**, *41*, 1772.

1,2-Addition

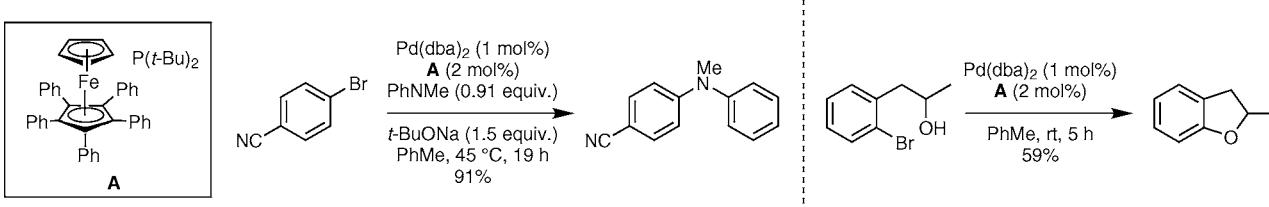


15 examples (yields 69–99%).

Pd-catalyzed C-C, C-N and C-O bond forming cross coupling reactions.

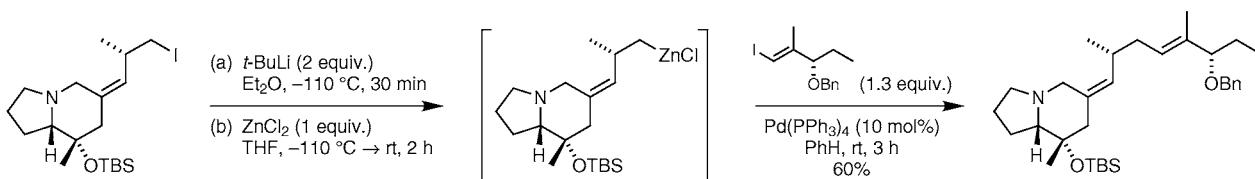
Kataoka, N.; Shelby, Q.; Stambuli, J. P.; Hartwig, J. F. *J. Org. Chem.* **2002**, *67*, 5553.

Cross Coupling



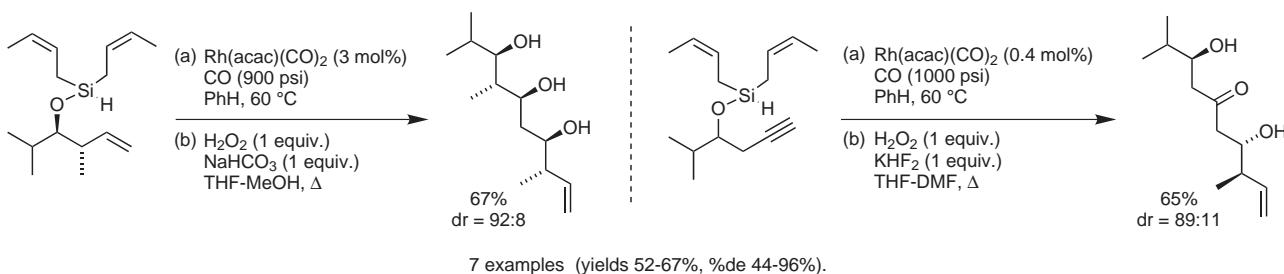
54 examples of C-N cross coupling (yields 37–99%), 41 examples of Suzuki C-C cross coupling (yields 55–99%) and 19 examples of C-O cross coupling (yields 58–99%).

Pd-catalyzed cross coupling of a homoallylic organozinc and a vinyl iodide.

Aoyagi, S.; Hirashima, S.; Saito, K.; Kibayashi, C. *J. Org. Chem.* **2002**, *67*, 5517.sp²-sp³-Coupling

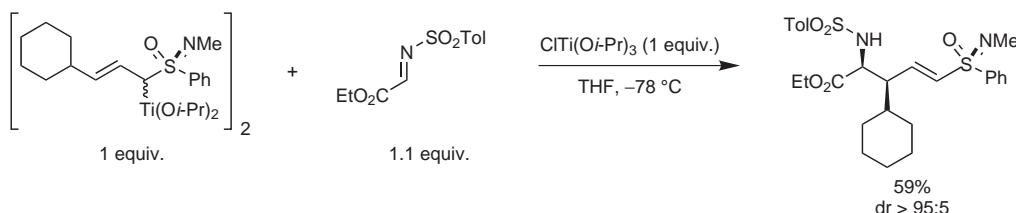
Synthesis of polyketide fragments via tandem intramolecular silylformylation/crotylsilylation.
Zacuto, M. J.; O'Malley, S. J.; Leighton, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 7890.

Silylformylation/Crotylsilylation



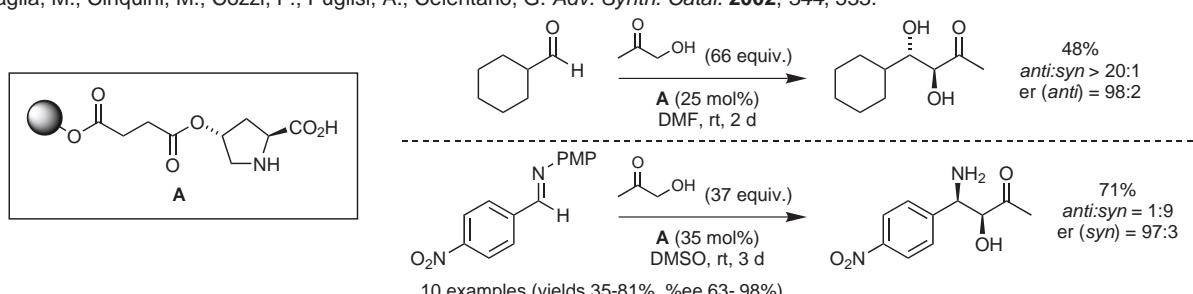
Asymmetric synthesis of a γ,δ -unsaturated α -amino acid bearing a chiral nucleofuge at the δ -position.
Schleusner, M.; Gais, H.-J.; Koep, S.; Raabe, G. *J. Am. Chem. Soc.* **2002**, *124*, 7789.

1,2-Addition



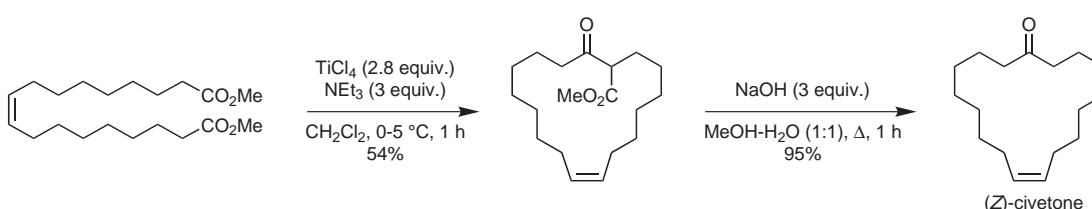
Enantioselective aldol and iminoaldol reactions catalyzed by polymer-supported proline.
Benaglia, M.; Cinquini, M.; Cozzi, F.; Puglisi, A.; Celentano, G. *Adv. Synth. Catal.* **2002**, *344*, 533.

1,2-Addition



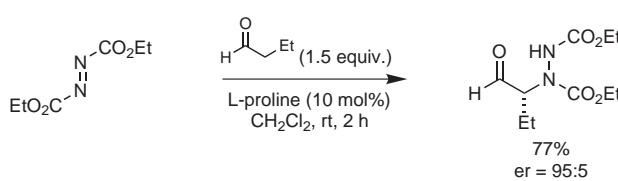
Ti-mediated Dieckmann condensation.
Tanabe, Y.; Makita, A.; Funakoshi, S.; Hamasaki, R.; Kawakusu, T. *Adv. Synth. Catal.* **2002**, *344*, 507.

Condensation Reaction

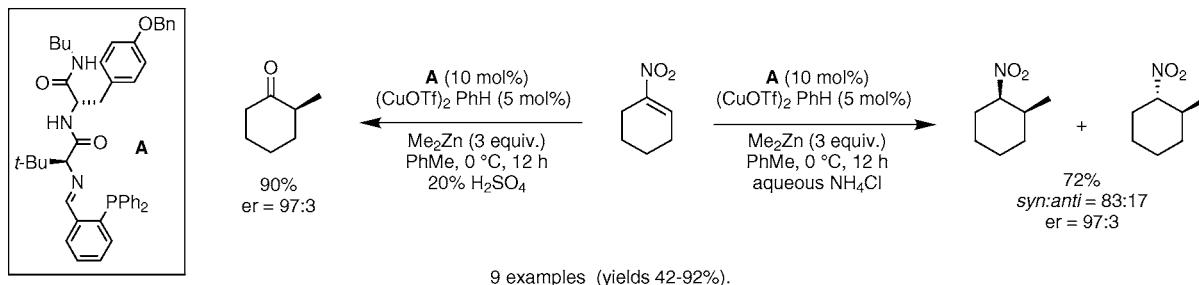


Asymmetric α -amination of aldehydes.
Bøgevig, A.; Juhl, K.; Kumaragurubaran, N.; Zhuang, W.; Jørgensen, K. *Angew. Chem. Int. Ed.* **2002**, *41*, 1791.

1,2-Addition

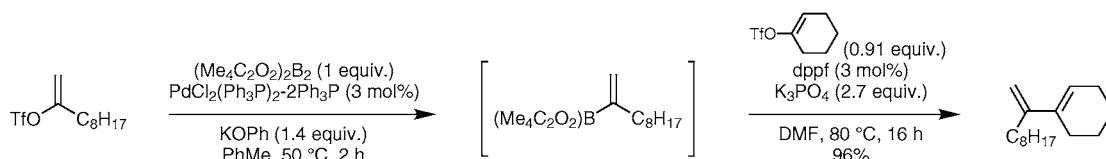


Enantioselective Cu-catalyzed conjugate addition of alkylzincs to cyclic nitroalkenes.
Luchaco-Cullis C. A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 8192.

1,4-Addition

Synthesis of unsymmetrical 1,3-dienes via Pd-catalyzed cross-coupling.

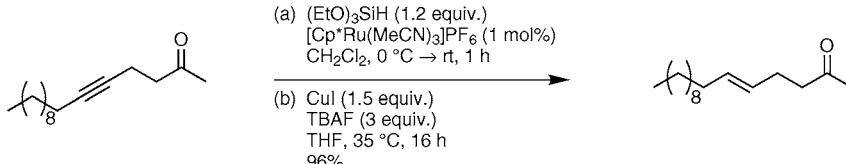
Takagi, J.; Takahashi, K.; Ishiyama, T.; Miyaura, N. *J. Am. Chem. Soc.* **2002**, *124*, 8001.

sp²-sp²-Coupling

9 examples (yields 62-99%).

Chemoselective reduction of alkynes to (*E*)-alkenes.

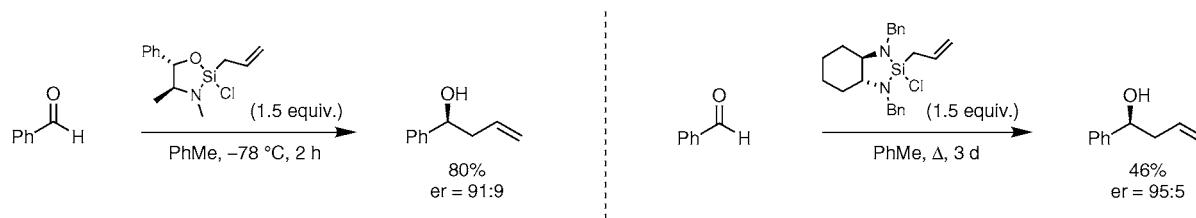
Trost, B. M.; Ball, Z. T.; Jöge, T. *J. Am. Chem. Soc.* **2002**, *124*, 7922.

Hydrosilylation/Protodesilylation

8 examples (yields 59-96%).

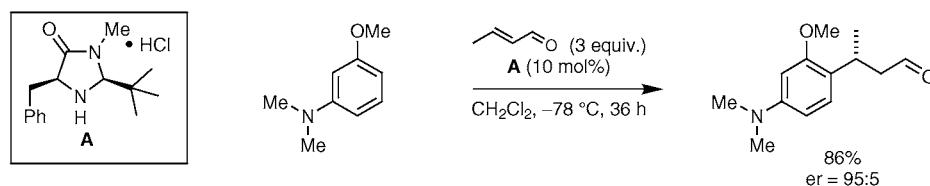
Strained silacycles for the enantioselective allylation of aldehydes.

Kinnaird, J. W. A.; Ng, P. Y.; Kubota, K.; Wang, X.; Leighton, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 7920.

1,2-Addition

10 examples (yields 46-85%, %ee 78-96%).

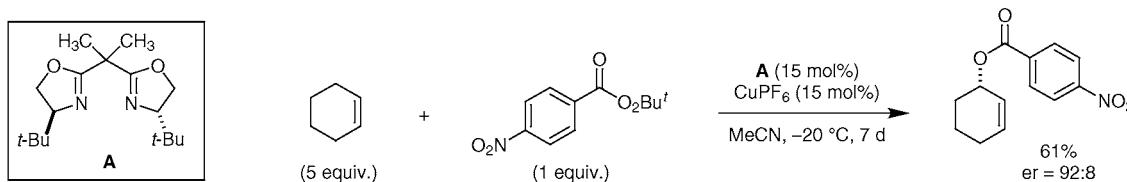
Enantioselective organocatalytic 1,4-addition of electron-rich benzenes to α,β-unsaturated aldehydes.
Paras, N. A.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2002**, *124*, 7894.

1,4-Addition

24 examples (yields 65-97%, %ee 84-99%).

Enantioselective Cu-catalyzed allylic oxidation of cyclic olefins with *t*-butyl *p*-nitroperoxybenzoate.
Andrus, M. B.; Zhou, Z. *J. Am. Chem. Soc.* **2002**, *124*, 8806.

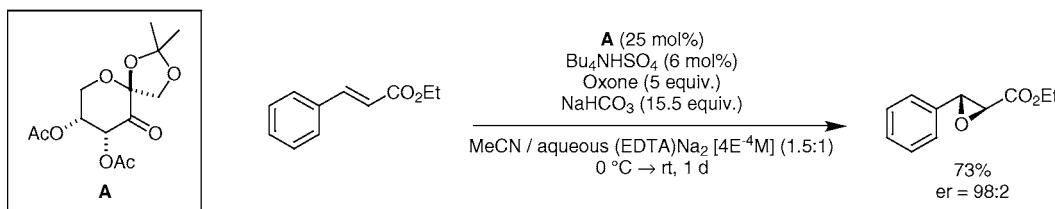
Oxidation



4 examples (yields 3-61%, %ee 79-95%). The effect of the substituents on the bisoxazoline is also reported.

Enantioselective epoxidation of α - β -unsaturated esters by chiral dioxirane.
Wu, X-Y.; She, X.; Shi, Y. *J. Am. Chem. Soc.* **2002**, *124*, 8792.

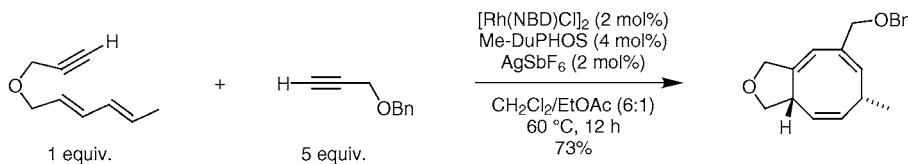
Epoxidation



17 examples (yields 40-96%, %ee 44-98%).

Rh-catalyzed [4+2+2]-cycloaddition and alkyne insertion.
Gilbertson, S. R.; Deboef, B. *J. Am. Chem. Soc.* **2002**, *124*, 8784.

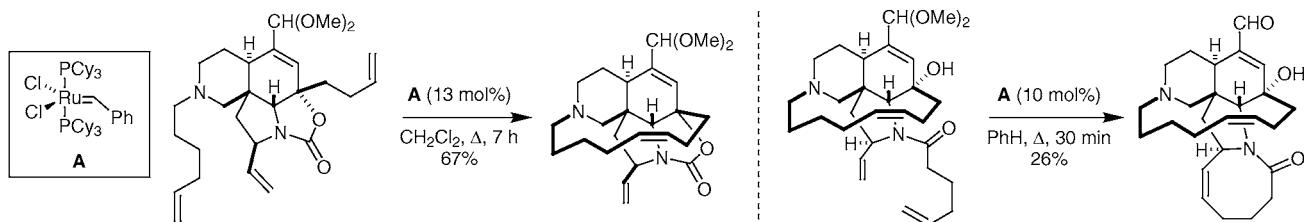
Cyclization



9 examples (yields 36-73%). Dimer formation (4 examples, yields 44-80%) is also reported.

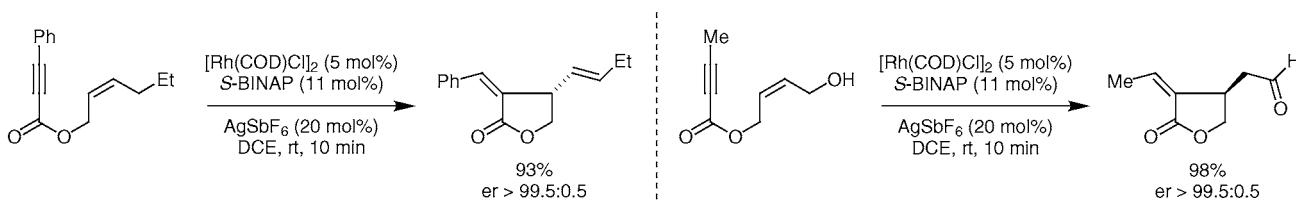
Enantioselective total syntheses of manzamine A and related alkaloids via ring-closing metathesis.
Humphrey, J. M.; Liao, Y.; Ali, A.; Rein, T.; Wong, Y-L.; Chen, H-J.; Courtney, A. K.; Martin, S. F. *J. Am. Chem. Soc.* **2002**, *124*, 8584.

Metathesis



Enantioselective Rh(I)-catalyzed intramolecular Alder ene reaction.
Lei, A.; He, M.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 8198.

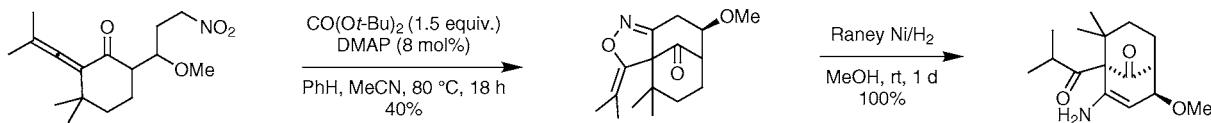
Cyclization



20 examples (yields 90-99%). Application to the formal synthesis of (+)-pilocarpine is also reported.

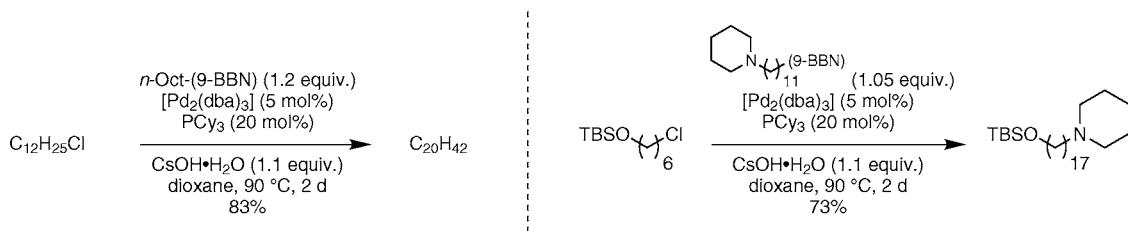
Intramolecular nitrile oxide-allene [3+3]-cycloaddition.
Young, D. G. J.; Zeng, D. *J. Org. Chem.* **2002**, *67*, 3134.

Cycloaddition



Contains requisite vicinal quaternary centres and functionality at appropriate positions for hyperevolutin A.

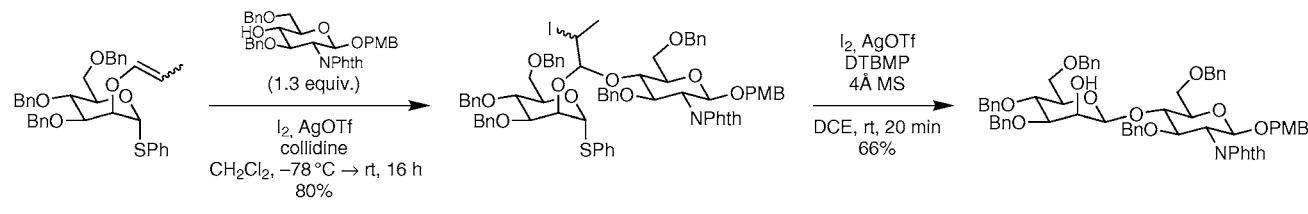
Pd-catalyzed cross-coupling of alkyl chlorides.
Kirchoff, J. H.; Dai, C.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 1945.

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

22 examples (yields 2-84%). The use of various ligands, alkyl chlorides and alkyl boranes is also reported.

Stereoselective 1,2-syn glycosylation of 2-O-allyl protected thioglycosides.
Aloui, M.; Chambers, D. J.; Cumpstey, I.; Fairbanks, A. J.; Redgrave, A. J.; Seward, C. M. P. *Chem.-Eur. J.* **2002**, *8*, 2608.

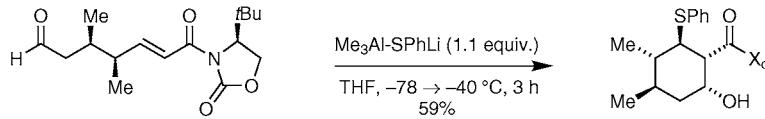
Glycosylation



13 examples (yields 53-89%).

Stereoselective synthesis of functionalised cyclohexanes.
Schneider, C.; Reese, O. *Chem.-Eur. J.* **2002**, *8*, 2585.

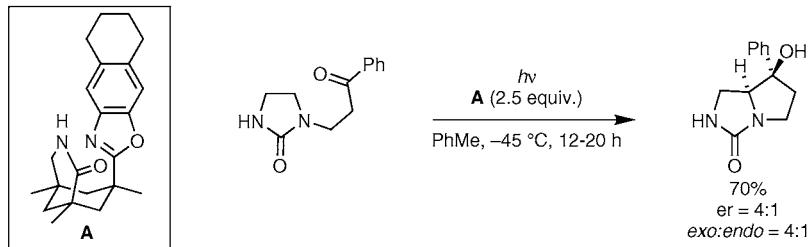
1,4-Addition/1,2-Addition



26 examples (yields 41-83%).

Enantioselective Norrish-Yang cyclization reactions.
Bach, T.; Aechtner, T.; Neumüller, B. *Chem.-Eur. J.* **2002**, *8*, 2464.

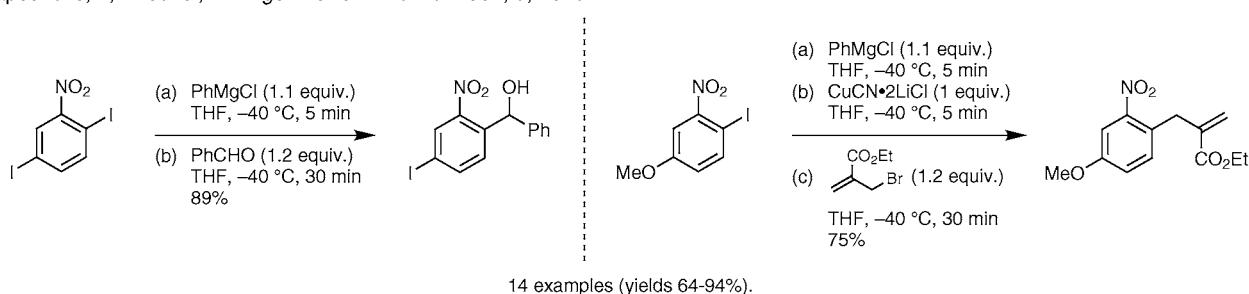
Radical Cyclization



4 examples (yields 70-86%, %ee 5-60%, 77:23 ≥ exo:endo ≥ 88:12). Control solution phase and solid phase reactions are also reported.

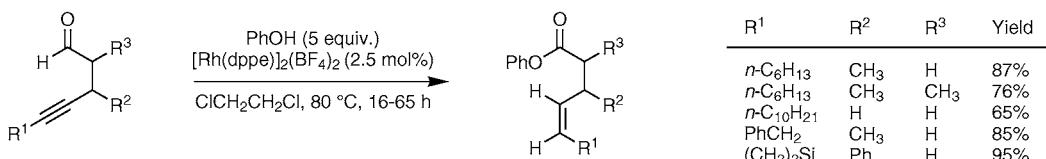
Preparation and reaction of functionalized *o*-nitroaryl magnesium halides.
Sapountzis, I.; Knochel, P. *Angew. Chem. Int. Ed.* **2002**, *9*, 1610.

Nucleophilic Addition



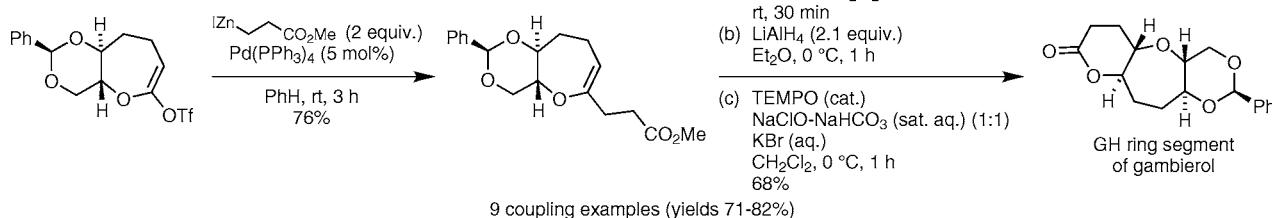
Rh-catalyzed reaction of 4-alkynals with phenol: synthesis of *cis*-4-alkenoates.
Tanaka, K.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *9*, 1607.

Oxidation/Reduction



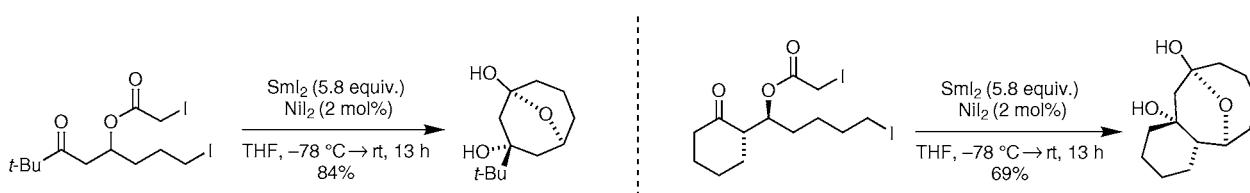
7 examples (yields 65-95%).

Pd-catalyzed coupling of ketene acetal triflates with zinc homoenolates.
Kadota, I.; Takamura, H.; Sato, K.; Yamamoto, Y. *J. Org. Chem.* **2002**, *67*, 3494.

sp²-sp³-Coupling

Sequential SmI₂-promoted Reformatsky/nucleophilic acyl substitution.
Molander, G. A.; Brown, G. A.; Storch de Gracia, I. *J. Org. Chem.* **2002**, *67*, 3459.

Cyclization



Intramolecular radical cyclization of the oxepane ring in the (E)FGH ring system of ciguatoxin.
Sasaki, M.; Noguchi, T.; Tachibana, K. *J. Org. Chem.* **2002**, *67*, 3301.

7-exo Radical Cyclization

