

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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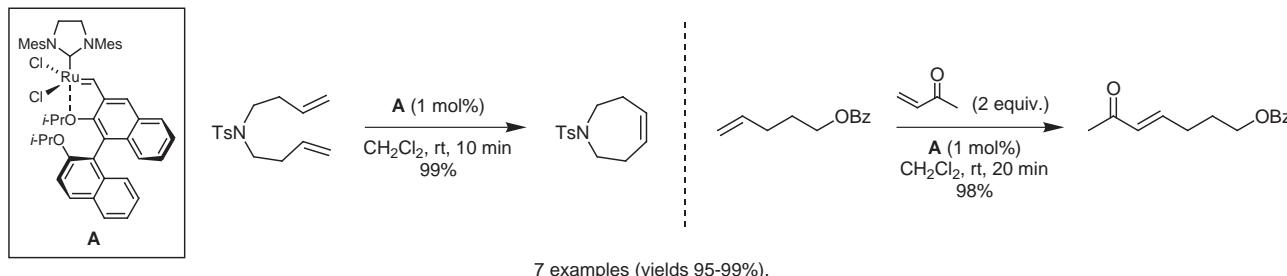
Synthesis 2002, No. 8, 04 06 2002. Article Identifier:
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The journals regularly covered by the abstractors are:

Advanced Synthesis and Catalysis
Angewandte Chemie
Chemical Communications
Chemistry-A European Journal
Collection of Czechoslovak Chemical Communications
European Journal of Organic Chemistry
Helvetica Chimica Acta
Journal of Organic Chemistry
Journal of the American Chemical Society
Organic Letters
Organometallics
Perkin Transactions 1
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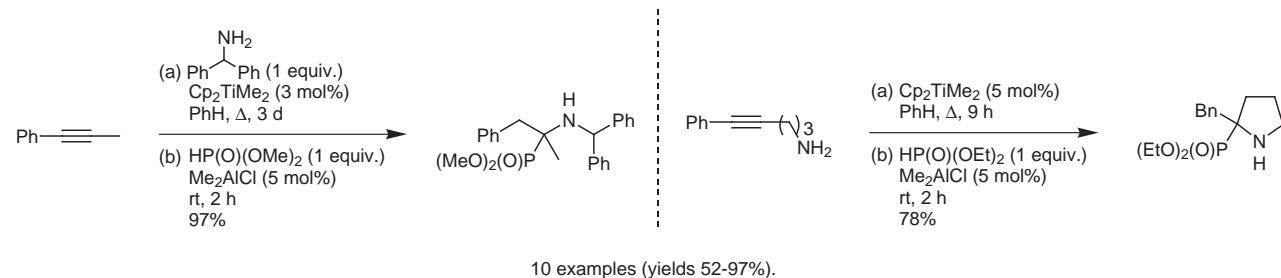
A highly active and air stable ruthenium complex for olefin metathesis.
Wakamatsu, H.; Blechert, S. *Angew. Chem. Int. Ed.* **2002**, *41*, 794.

Olefin Metathesis



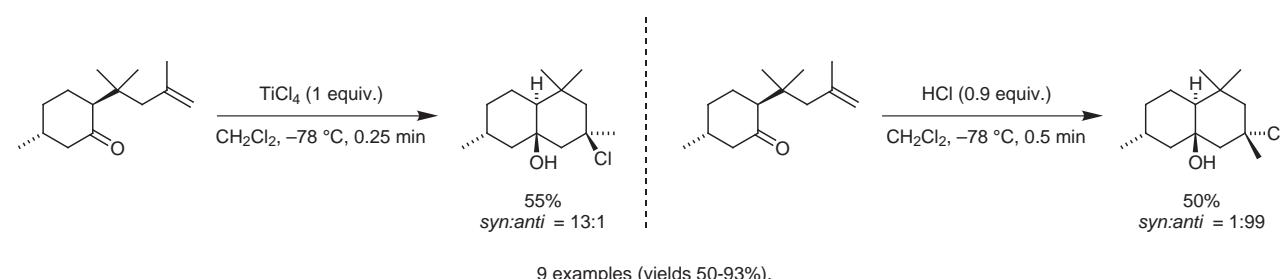
Synthesis of α -amino phosphonates from alkynes.
Haak, E.; Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2002**, 457.

Hydroamination/1,2-Addition



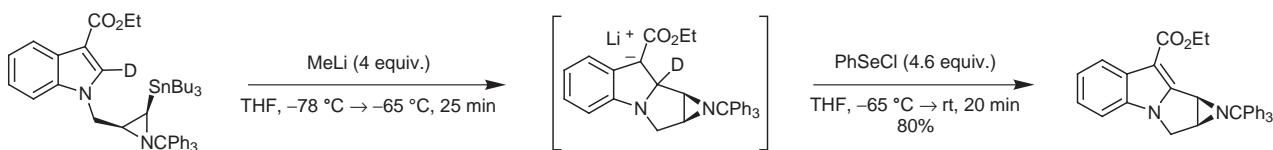
Synthesis of 3-chlorocyclohexanols.
Davis, C. E.; Coates, R. M. *Angew. Chem. Int. Ed.* **2002**, *41*, 491.

1,2-Addition



Use of deuterium as a blocking group in the synthesis of aziridinomitosenes by anionic cyclization.
Vedejs, E.; Little, J. *J. Am. Chem. Soc.* **2002**, *124*, 748.

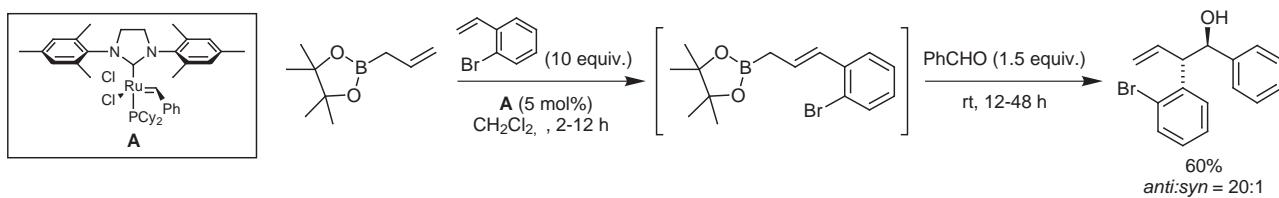
Conjugate Addition



This deuterium serves as a blocking group in the tin-lithium exchange step.

One-pot cross metathesis/allylboration reaction.
Goldberg, S. D.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2002**, *41*, 807.

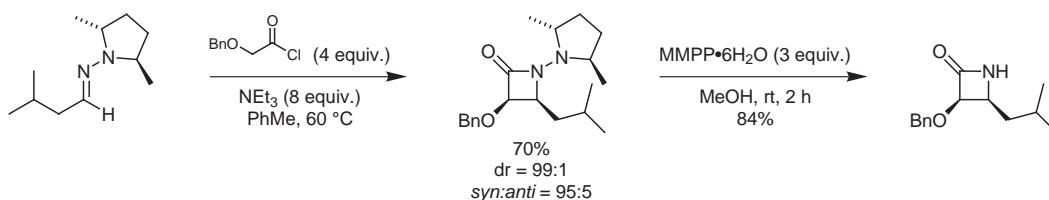
Cross Metathesis/Allylboration



12 examples (yields 25-79%).

[2+2] Cycloadditions of *N,N*-dialkylhydrazones to benzyloxyketene.
Fernández, R.; Ferrete, A.; Lassalleta, J. M.; Llera, J. M.; Martín-Zamora, E. *Angew. Chem. Int. Ed.* **2002**, *41*, 831.

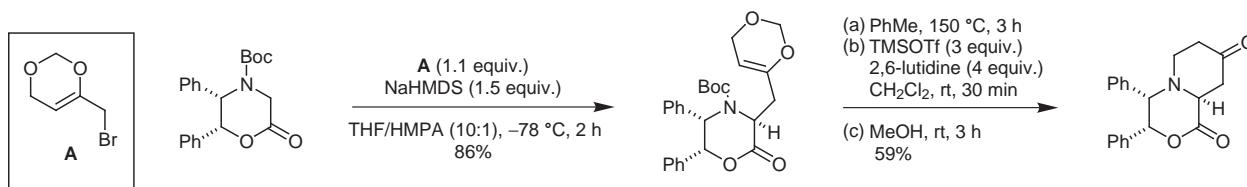
[2+2] Cycloaddition



9 examples [yields 56-91% (2 steps), %de 52-98%, *syn:anti* 85:15 → 99:1].

6-Bromomethyl-4*H*-1,3-dioxin as a vinyl ketone equivalent for heterocycle and carbocycle construction.
Greshock, T. J.; Funk, R. L. *J. Am. Chem. Soc.* **2002**, *124*, 754.

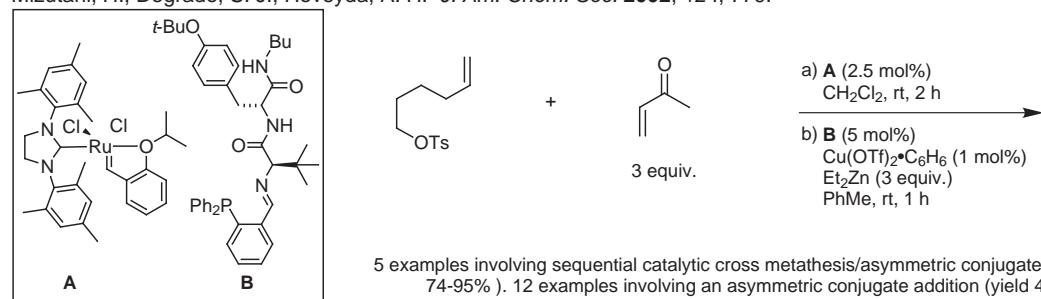
Annulation



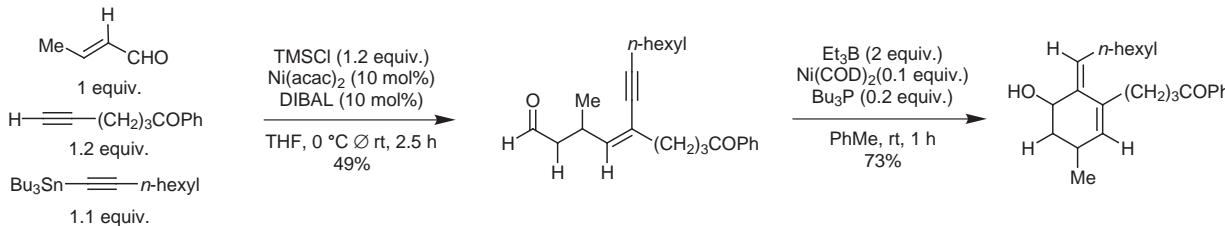
11 examples (yield 59-94%).

Cu-catalyzed asymmetric conjugate additions of alkylzinc reagents to acyclic aliphatic enones.
Mizutani, H.; Degrado, S. J.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 779.

Conjugate Addition



A two-step four-component synthesis of highly functionalized cyclohexenols by sequential Nickel-catalyzed couplings. **sp²-sp² Coupling**
 Lozanov, M.; Montgomery, J. *J. Am. Chem. Soc.* **2002**, *124*, 2106.



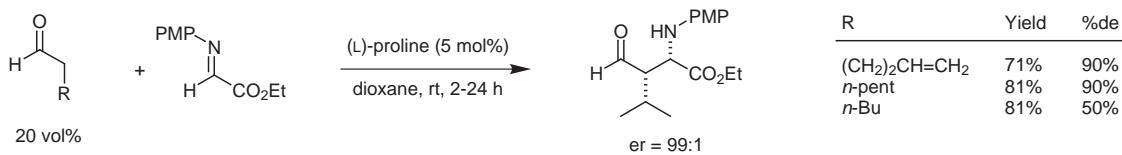
8 examples (yield 41-74% for the first step, 71-86% for the cyclization).

Intramolecular silicon-assisted cross-coupling reactions.
 Denmark, S. E.; Yang, S.-M. *J. Am. Chem. Soc.* **2002**, *124*, 2102.

sp²-sp² Coupling

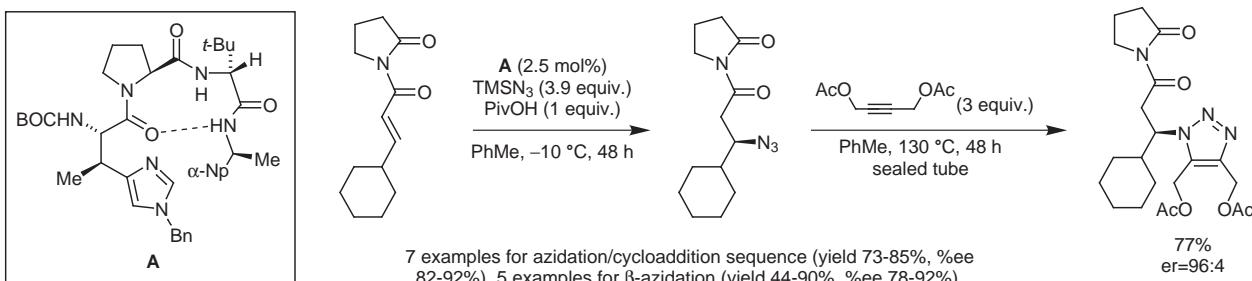

8 examples (yield 55-77%).

A route to either enantiomer of α - and β -amino acid derivatives.
 Cordova, A.; Watanabe, S.-i.; Tanaka, F.; Notz, W.; Barbas III, C. F. *J. Am. Chem. Soc.* **2002**, *124*, 1866.

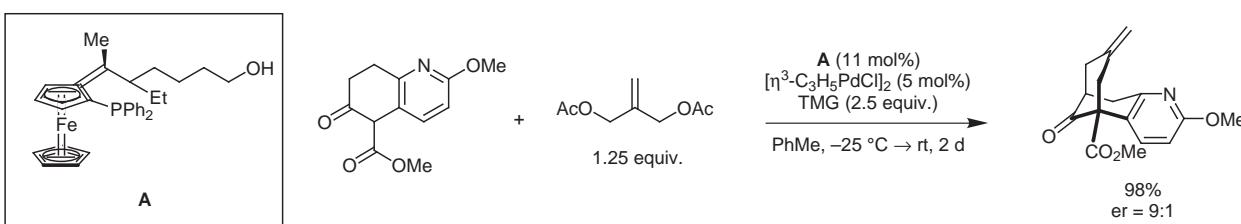
Enantioselective 1,2-Addition


7 examples (yield 57-89%, %ee 93-99%, %de 5-90%).

Asymmetric azidation-cycloaddition with open-chain peptide-based catalysts.
 Guerin, D. J.; Miller, S. J. *J. Am. Chem. Soc.* **2002**, *124*, 2134.

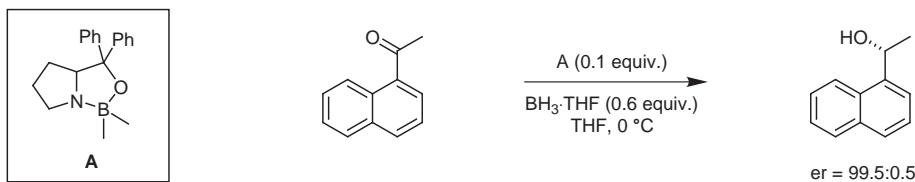
Asymmetric Azidation-Cycloaddition


Asymmetric synthesis of huperzine A via enantioselective palladium-catalyzed bicycloannulation reaction.
 He, X. C.; Wang, B.; Yu, G.; Bai, D. *Tetrahedron: Asymmetry* **2001**, *12*, 3213.

Bicycloannulation


The reaction is a key step in the synthesis of huperzine A. 11 different ligands and 3 different allylic agents were used during optimization (yields 13-98%, %ee 6-90%).

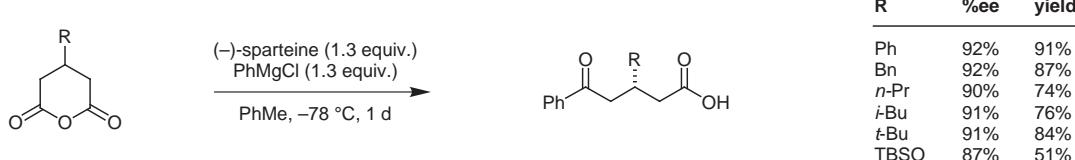
Enantioselective reducing agent from $(-)\alpha,\alpha$ -diphenylpyrrolidinemethanol and 9-borabicyclo[3.3.1]nonane. **Enantioselective Reduction**
Kanth, J. V. B.; Brown, H. C. *Tetrahedron*, **2002**, *58*, 1069.



Works best for hindered aralkyl ketones and aralkyl ketones having electron-withdrawing groups either on the aromatic ring or side chain. 15 ketone examples, 9 different reducing agents and 5 catalysts from different aminoalcohols.

Desymmetrization of anhydrides by addition of Grignard reagents.
Shintani, R.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 1057.

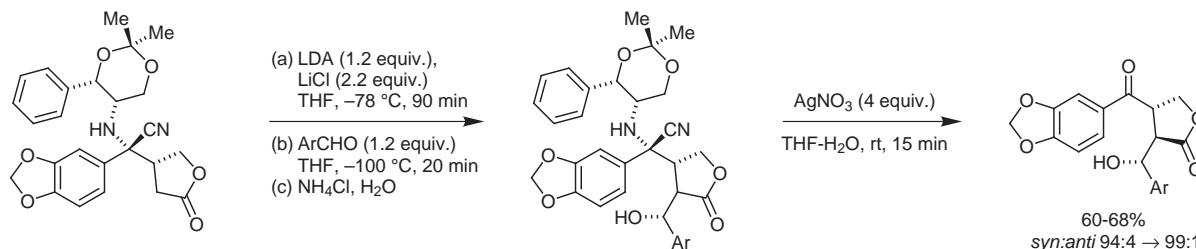
Enantioselective Desymmetrization



9 examples (yields 51-91%, %ee 97-92%)

Asymmetric synthesis of lignans.
Enders, D.; Lausberg, V.; Del Signore, G.; Berner, O. M. *Synthesis*, **2002**, 515.

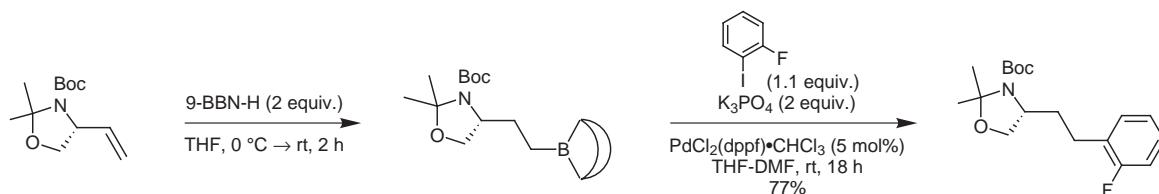
Asymmetric 1,2-Addition



3 examples (yields as above). The products were then transformed to lignan natural products following a literature procedure.

Enantiomerically pure α -amino acids via hydroboration-Suzuki cross-coupling.
Collier, P. N.; Campbell, A. D.; Patel, I.; Raynham, T. M.; Taylor, R. J. K. *J. Org. Chem.* **2002**, *67*, 1802.

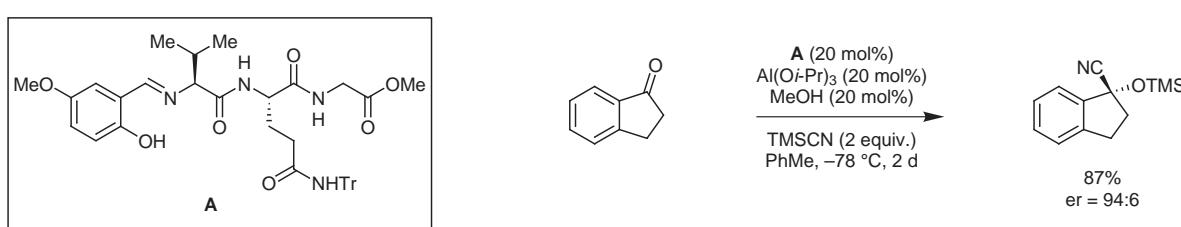
$\text{sp}^2\text{-sp}^3$ coupling



16 examples (yields 47-84%). The products are then converted into *N*-protected α -amino acids via a one-pot cleavage-oxidation.

Aluminium-catalyzed addition of TMSCN to ketones.
Deng, H.; Isler, M. P.; Snapper, M. L.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2002**, *41*, 1009.

Asymmetric 1,2-Addition

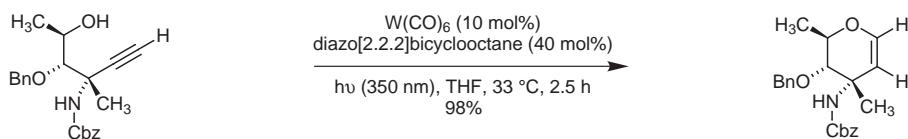


15 examples (yields 66-98%, %ee 80-95%).

Tungsten-catalyzed cycloisomerization.

Cutchins, W. W.; McDonald, F. E. *Org. Lett.* **2002**, *4*, 749.

Cycloisomerization

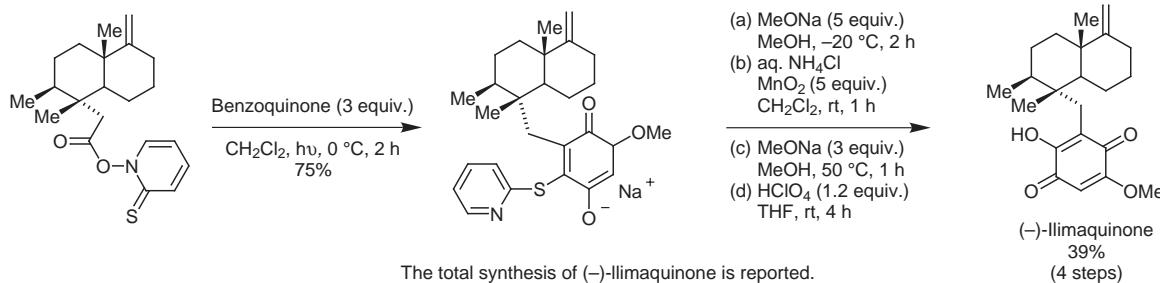


2 examples (yield 98%). Used towards the synthesis of vancoamine and saccharosamine.

Photochemical radical decarboxylation with quinone trapping.

Ling, T.; Poupon, E.; Rueden, E. J.; Theodorakis, E. A. *Org. Lett.* **2001**, *4*, 819.

Decarboxylation/Addition

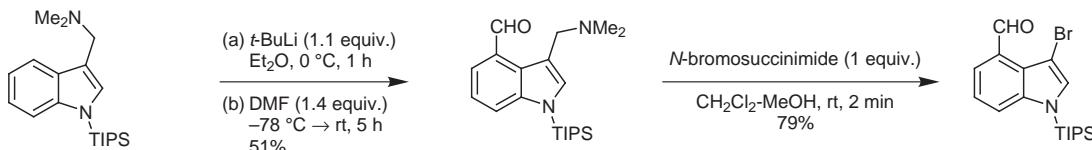


The total synthesis of (-)-Ilimaquinone is reported.

Directed ortho metallation and retro-Mannich approach to 3,4-substituted indoles.

Chauder, B.; Larkin, A.; Snieckus, V. *Org. Lett.* **2002**, *4*, 815.

Metallation/Retro-Mannich

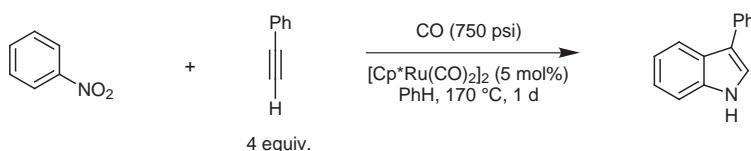


8 examples (yields 21-51%).

Reductive annulation of nitrosoarenes with alkynes.

Penoni, A.; Volkmann, J.; Nicholas, K. M. *Org. Lett.* **2002**, *4*, 699.

Reductive Annulation

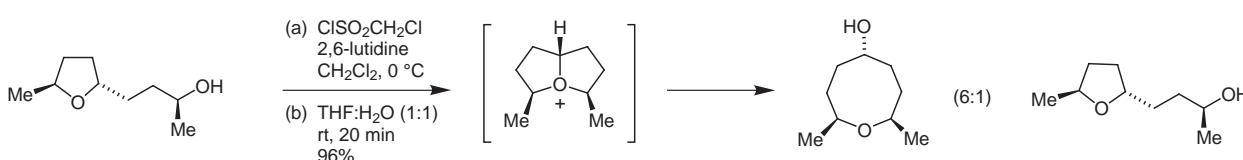


4 examples (yields 21-53%) and 10 examples using an alternative 2 step route (yields 29-64%).

Stereoselective ring expansion via bicyclooxonium ion.

Sakamoto, Y.; Tamegai, K.; Nakata, T. *Org. Lett.* **2002**, *4*, 675.

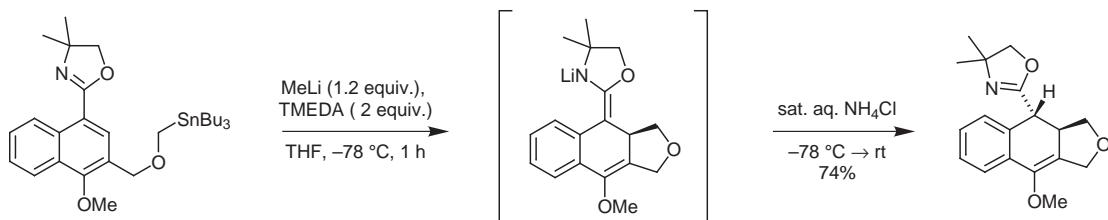
Ring Expansion



7 examples (combined yields 48-96%).

Dearomatizing annulation of five-membered rings to naphthalenes by organolithium cyclization.
Clayden, J.; Kenworthy, M. N. *Org. Lett.* **2002**, *4*, 787.

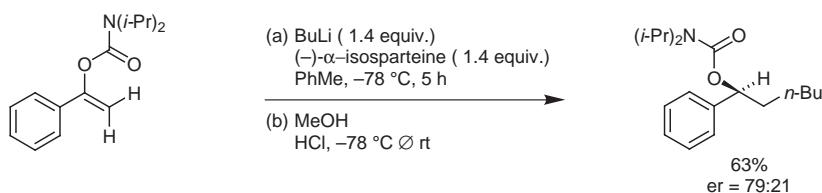
Annulation



3 further examples (Yields 41-79%). Lower yields were obtained in absence of TMEDA.

Stereoselective intermolecular carbolithiation of 1-aryl, 1-alkenyl carbamates.
Peters, J. G.; Seppi, M.; Frohlich, R.; Wibbeling, B.; Hoppe, D. *Synthesis* **2002**, *3*, 381.

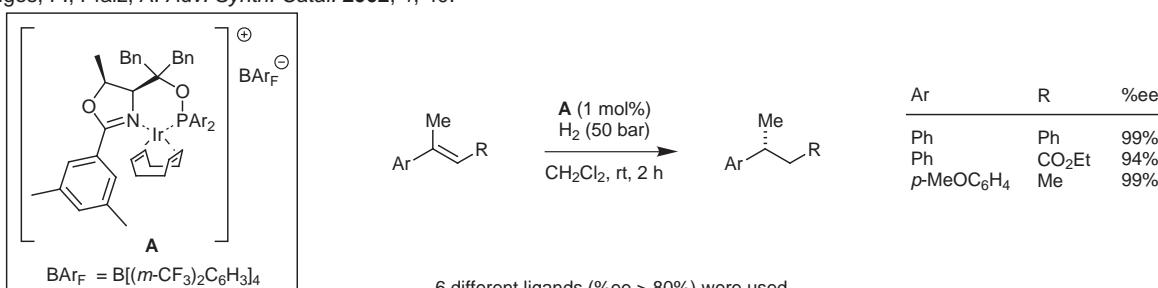
Carbolithiation



Configurationally stable lithiated intermediates have been trapped with a range of electrophiles.

P,N ligands for enantioselective iridium-catalyzed hydrogenation.
Menges, F.; Pfalz, A. *Adv. Synth. Catal.* **2002**, *1*, 40.

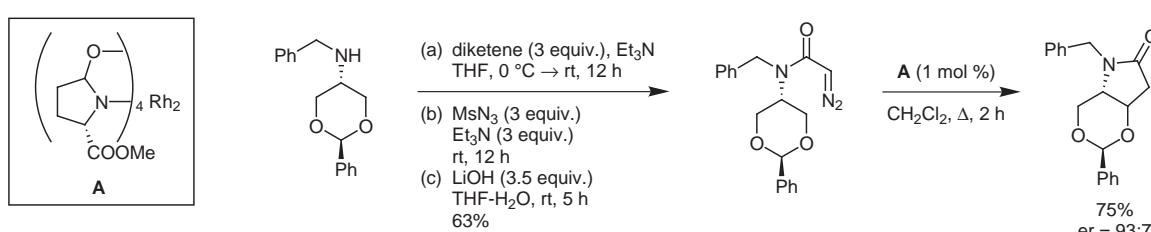
Hydrogenation



6 different ligands (%ee > 80%) were used.

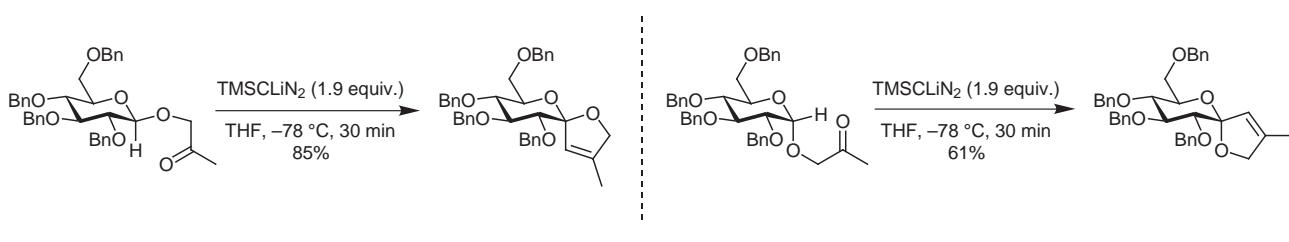
2-deoxyxylonolactams via enantioselective carbon-hydrogen insertion
Doyle, M. P.; Yan, M.; Phillips, I. M.; Timmons, D. J. *Adv. Synth. Catal.* **2002**, *1*, 91.

C-H Insertion



Stereospecific preparation of [4,5]-spiroketals.
Wardrop, D. J.; Zhang, W.; Fritz, J. *J. Org. Lett.* **2002**, *4*, 489.

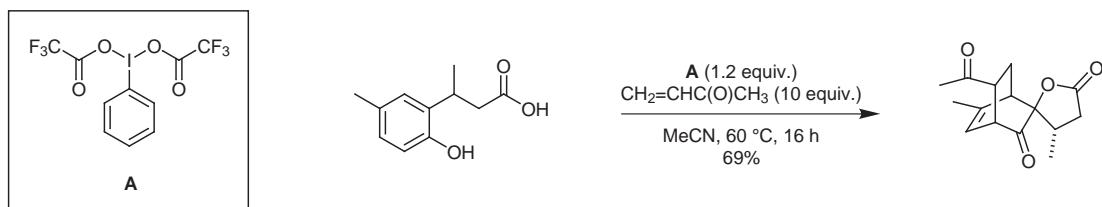
Insertion



6 examples (yields 59-89%).

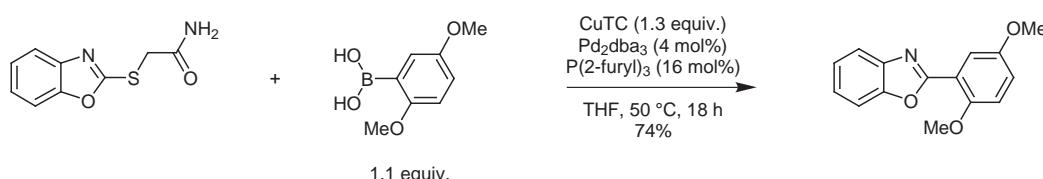
Intramolecular aromatic oxidation of 3-(2-hydroxyphenyl)-propionic acids.
Drutu, I.; Njardarson, J. T.; Wood, J. L. *Org Lett.* **2002**, *4*, 493.

Oxidation



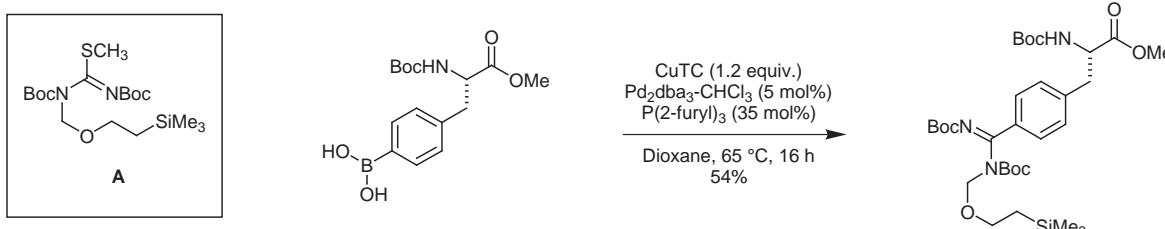
27 examples (yields 0-91%).

Copper(I) thiophene-2-carboxylate-mediated Pd-catalyzed heteroaromatic thioether-boronic acid cross-coupling.
Liebeskind, L. S.; Srogl, J. *Org Lett.* **2002**, *4*, 979.

*sp*²-*sp*² Coupling

12 examples (yields 53-87%).

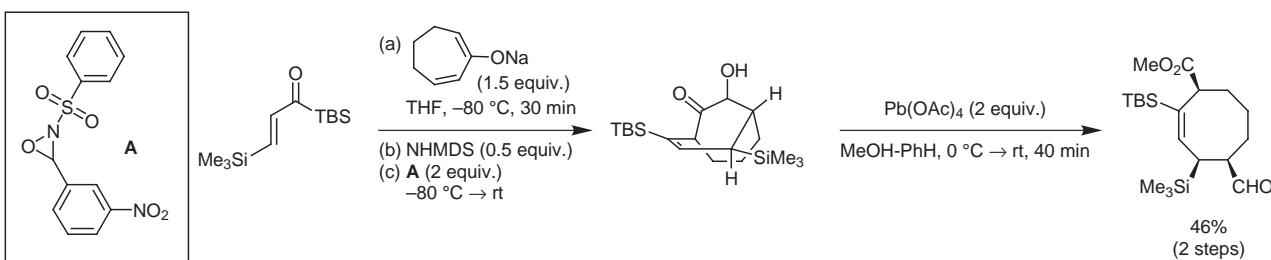
Synthesis of protected aryl and heteroaryl amines.
Kusturin, C. L.; Liebeskind, L. S.; Neumann, W. L. *Org Lett.* **2002**, *4*, 983.

*sp*²-*sp*² Coupling

13 examples (yields 41-91%).

Brook rearrangement-mediated [3+4] annulation.
Takeda, K.; Sawada, Y.; Sumi, K. *Org Lett.* **2002**, *4*, 1031.

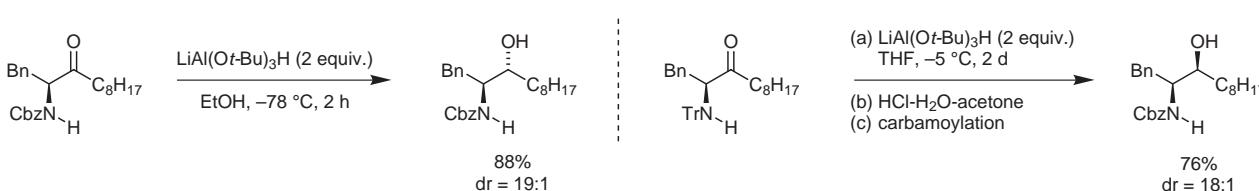
Annulation



5 examples (yields 46-69%).

Stereoselective syntheses of *syn*- and *anti*-1,2-amino alcohols.
Hoffmann, R. V.; Maslouh, N.; Cervantes-Lee, F. *J. Org. Chem.* **2002**, *67*, *4*, 1045.

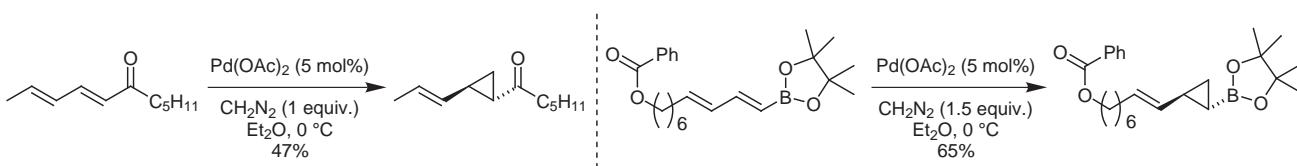
Stereoselective Reduction



8 examples of *anti*-selective reduction of carbamate-protected amino ketones (yields 80-89%, %de 90%) and 3 examples of *syn*-selective reduction of trityl-protected amino ketones (yields 88-91%, dr 4:1 → 18:1) are reported.

Regio- and stereoselective cyclopropanation of functionalized dienes.
Markó, I. E.; Giard, T.; Sumida, S.; Gies, A.-E. *Tetrahedron Lett.* **2002**, *43*, 2317.

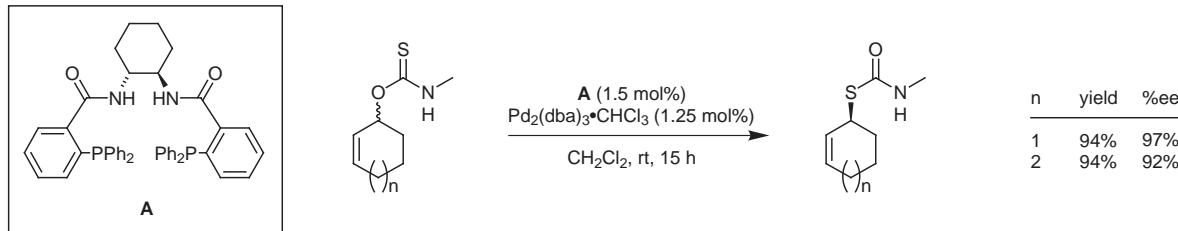
Selective Cyclopropanation



7 examples (yields 61-70%) of cyclopropanation of dienylboronates.

Palladium(0)-catalyzed enantioselective O,S-rearrangement of racemic O-allylic thiocarbamates.
Gais, H. -J.; Böhme, A. J. *Org. Chem.* **2002**, *67*, 4, 1153.

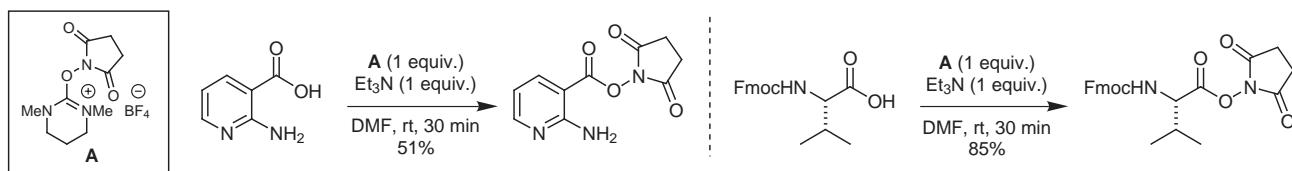
Enantioselective O,S-Rearrangement



17 examples (yields 76%, %ee 64-99%) with variation of the N-substituent. Preparation of the O-allylic thiocarbamates; further derivitisation of the products and application to the solid-phase are also reported.

O-Succinimidyl-1,3-dimethyl-1,3-trimethylenuronium salts as efficient reagents in active ester synthesis.
Bailén, M. A.; Chinchilla, R.; Dodsworth, D. J.; Nájera, C. *Tetrahedron Lett.* **2002**, *43*, 1661.

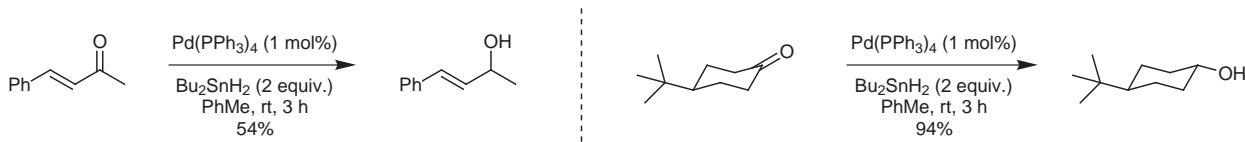
Esterification



15 examples (yields 51-89%) and preparation of A are reported.

Palladium-catalyzed reduction of ketones with Bu2SnH2.
Kamiya, I.; Ogawa, A. *Tetrahedron Lett.* **2002**, *43*, 1701.

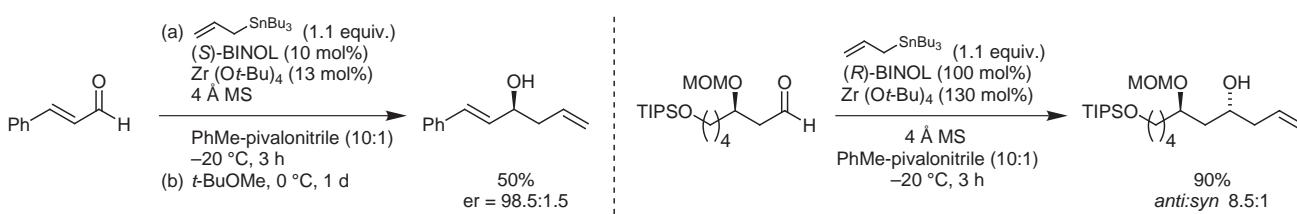
Ketone Reduction



13 examples (yields 31-100%).

Catalytic asymmetric allylations of achiral and chiral aldehydes via BINOL-Zr complex.
Kurosu, M.; Lorca, M. *Tetrahedron Lett.* **2002**, *43*, 1765.

Asymmetric Allylation



24 examples (yields 45-90%, %ee 85-98%). Diastereoselectivity of protected chiral β-hydroxy aldehydes was influenced by choice of protecting group.