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:

Elyse Bourque, Jennifer Delaney, Andrew Gunn, Stephen McAteer, Marcel de Puit, Stefan Schunk, Sukhjinder Uppal, Tanya Wildmann and Josephine Yuen, Department of Chemistry, Leeds University, Leeds, LS2 9JT, UK.

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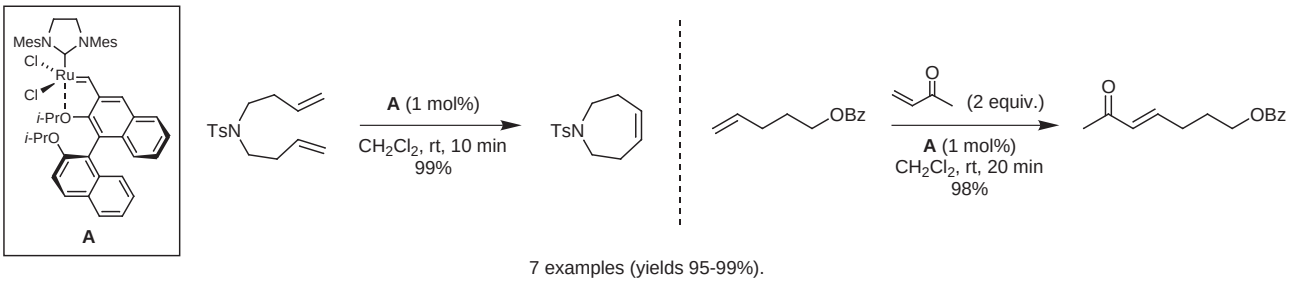
The journals regularly covered by the abstractors are:

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
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry
Tetrahedron Letters

A highly active and air stable ruthenium complex for olefin metathesis.
Wakamatsu, H.; Blechert, S. *Angew. Chem. Int. Ed.* **2002**, *41*, 794.

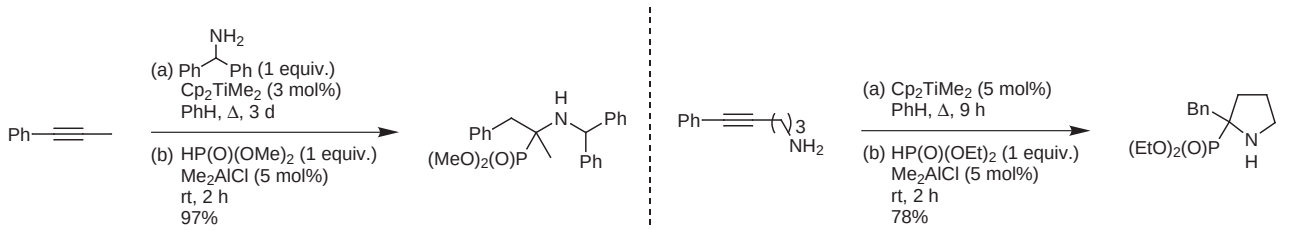
Olefin Metathesis



7 examples (yields 95-99%).

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

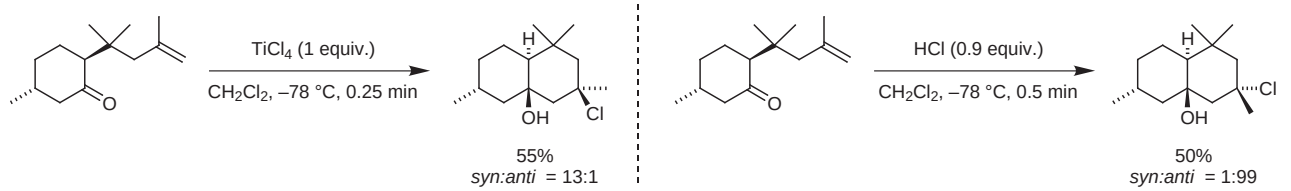
Hydroamination/1,2-Addition



10 examples (yields 52-97%).

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

1,2-Addition



9 examples (yields 50-93%).

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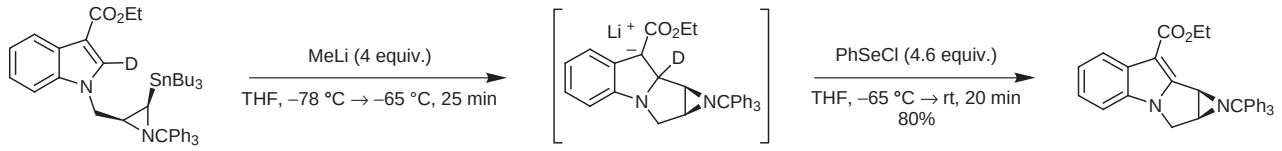
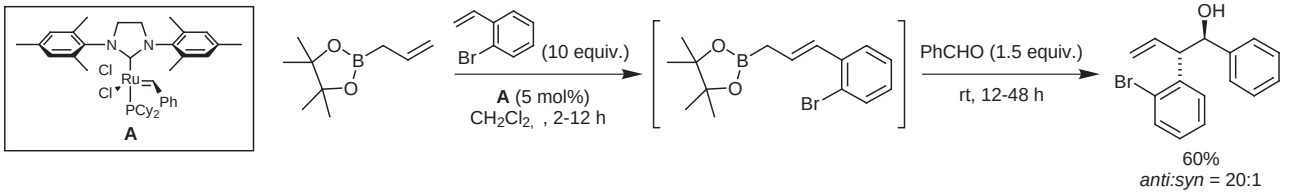
Use of deuterium as a blocking group in the synthesis of aziridinomitosenes by anionic cyclization. **Conjugate Addition**
Vedejs, E.; Little, J. *J. Am. Chem. Soc.* **2002**, *124*, 748.



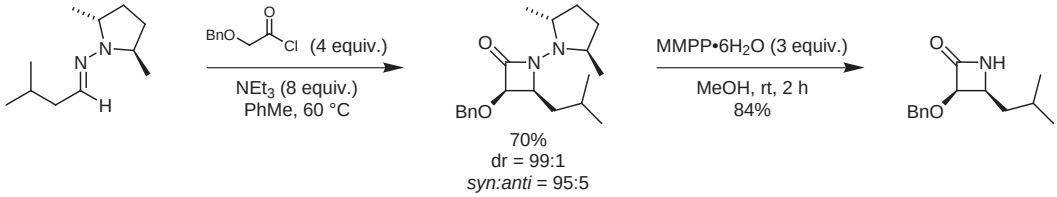
This deuterium serves as a blocking group in the tin-lithium exchange step.

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



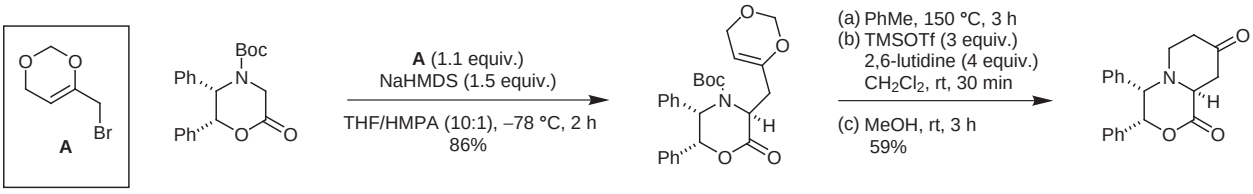
12 examples (yields 25-79%).

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



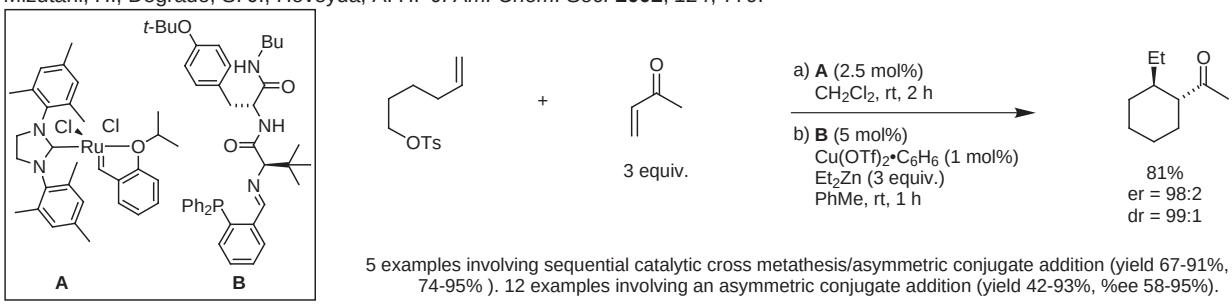
9 examples [yields 56-91% (2 steps), %de 52-98%, *syn:anti* 85:15 → 99:1].

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



11 examples (yield 59-94%).

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



5 examples involving sequential catalytic cross metathesis/asymmetric conjugate addition (yield 67-91%, %ee 74-95%). 12 examples involving an asymmetric conjugate addition (yield 42-93%, %ee 58-95%).

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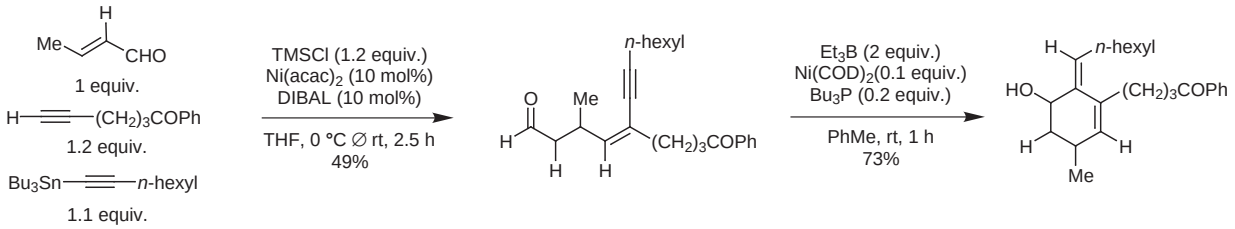
A two-step four-component synthesis of highly functionalized cyclohexenols by sequential Nickel-catalyzed couplings.
Lozanov, M.; Montgomery, J. *J. Am. Chem. Soc.* **2002**, *124*, 2106.

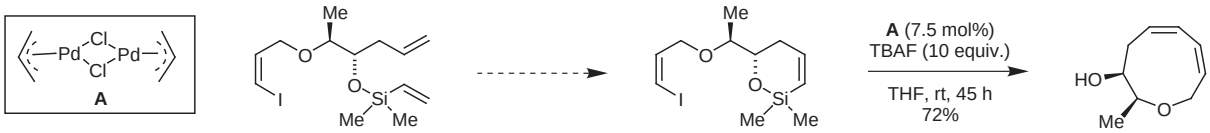
sp^2-sp^2 Coupling



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.

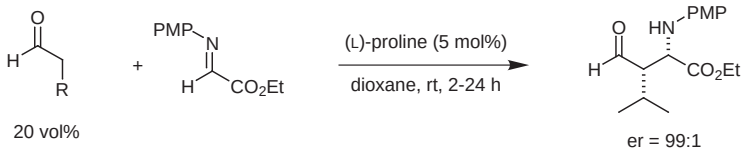
sp^2-sp^2 Coupling



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

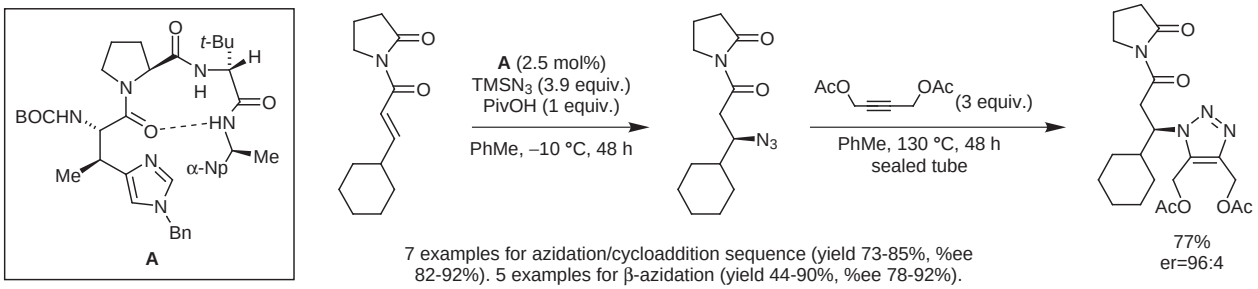


R	Yield	%de
$(CH_2)_2CH=CH_2$	71%	90%
n-pent	81%	90%
n-Bu	81%	50%

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.

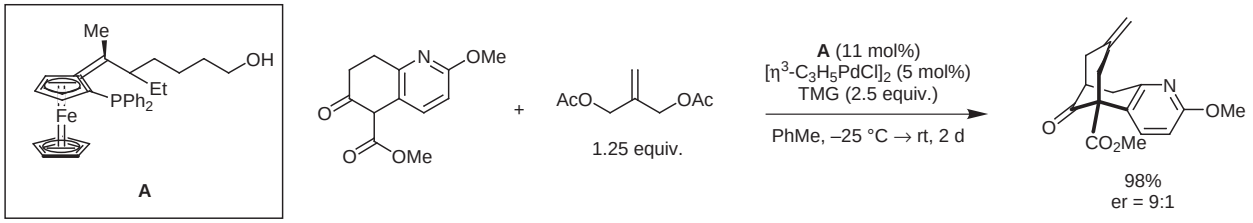
Asymmetric Azidation-Cycloaddition



7 examples for azidation/cycloaddition sequence (yield 73-85%, %ee 82-92%). 5 examples for β-azidation (yield 44-90%, %ee 78-92%).

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%).

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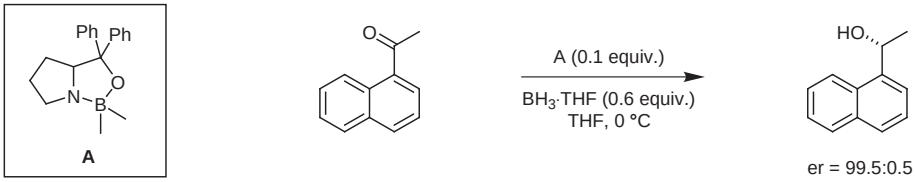
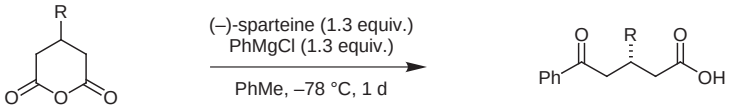
Enantioselective reducing agent from (-)-α,α-diphenylpyrrolidinemethanol and 9-borabicyclo[3.3.1]nonane. **Enantioselective Reduction**
Kanth, J. V. B.; Brown, H. C. *Tetrahedron*, **2002**, *58*, 1069.



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.

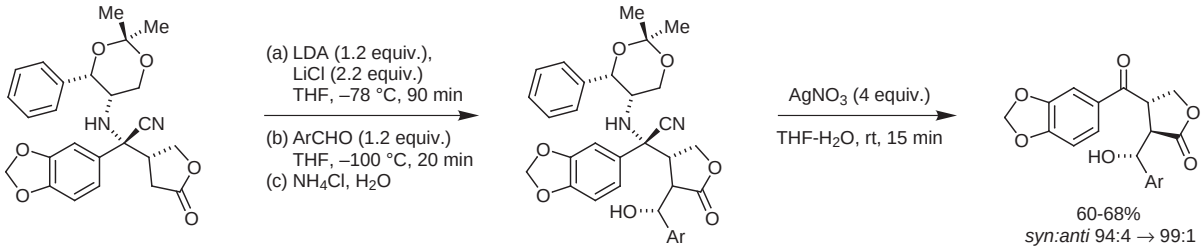
Desymmetrization of anhydrides by addition of Grignard reagents. **Enantioselective Desymmetrization**
Shintani, R.; Fu, G. C. *Angew. Chem. Int. Ed*. **2002**, *41*, 1057.



R	%ee	yield
Ph	92%	91%
Bn	92%	87%
n-Pr	90%	74%
i-Bu	91%	76%
t-Bu	91%	84%
TBSO	87%	51%

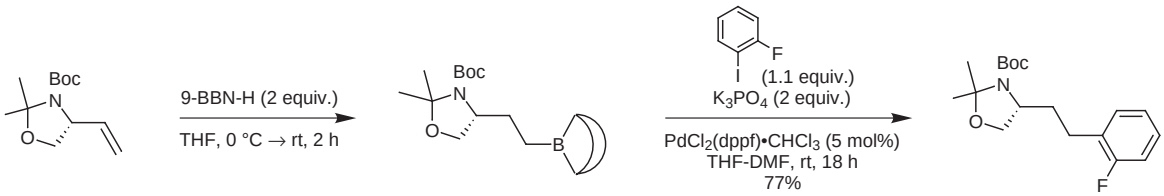
9 examples (yields 51-91%, %ee 97-92%)

Asymmetric synthesis of lignans. **Asymmetric 1,2-Addition**
Enders, D.; Lausberg, V.; Del Signore, G.; Berner, O. M. *Synthesis*, **2002**, 515.



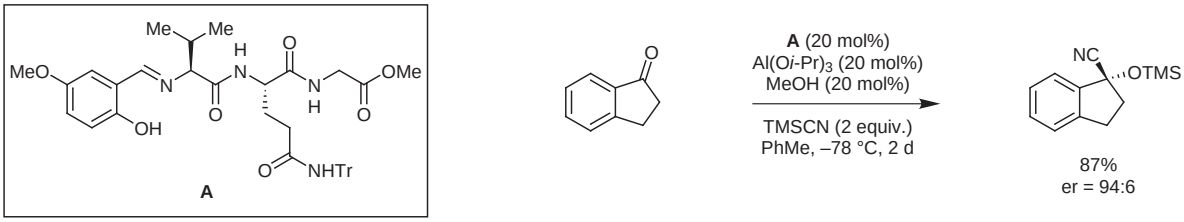
3 examples (yields as above). The products were then transformed to lignan natural products following a literature procedure.

Enantiomerically pure α-amino acids *via* hybroboration-Suzuki cross-coupling. **sp^2-sp^3 coupling**
Collier, P. N.; Campbell, A. D.; Patel, I.; Raynham, T. M.; Taylor, R. J. K. *J. Org. Chem.* **2002**, *67*, 1802.



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. **Asymmetric 1,2-Addition**
Deng, H.; Isler, M. P.; Snapper, M. L.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2002**, *41*, 1009.



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

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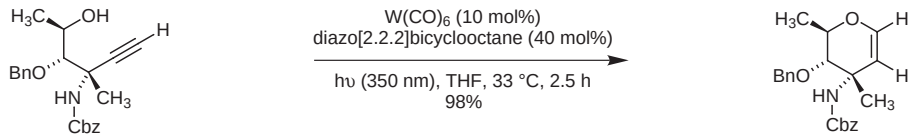
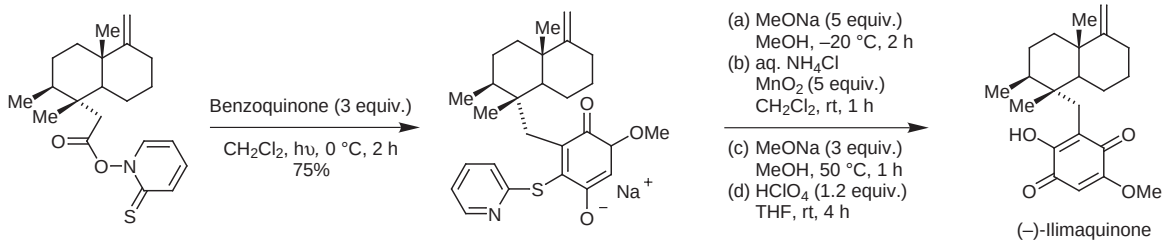
Tungsten-catalyzed cycloisomerization. **Cycloisomerization**
Cutchins, W, W; McDonald, F, E. *Org, Lett*. **2002**, *4*, 749.



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

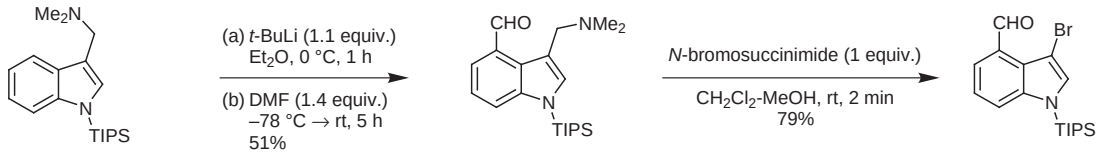
Photochemical radical decarboxylation with quinone trapping. **Decarboxylation/Addition**
Ling, T.; Poupon, E.; Rueden, E. J.; Theodorakis, E. A. *Org. Lett.* **2001**, *4*, 819.



(–)-Ilimaquinone
39%
(4 steps)

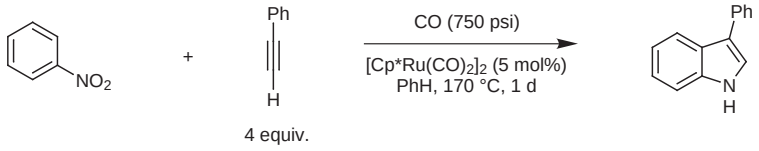
The total synthesis of (–)-Ilimaquinone is reported.

Directed ortho metallation and retro-Mannich approach to 3,4-substituted indoles. **Metallation/Retro-Mannich**
Chauder, B.; Larkin, A.; Snieckus, V. *Org. Lett.* **2002**, *4*, 815.



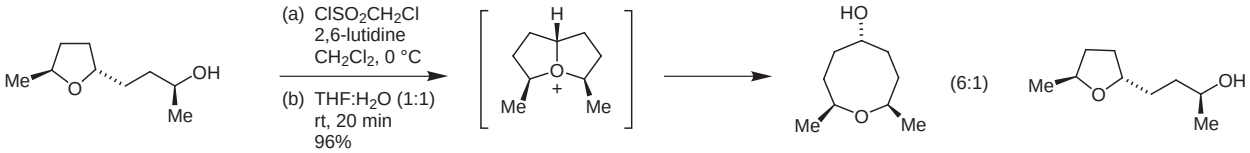
8 examples (yields 21-51%).

Reductive annulation of nitrosoarenes with alkynes. **Reductive Annulation**
Penoni, A; Volkmann, J; Nicholas, K, M. *Org. Lett*. **2002**, *4,* 699.



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

Stereoselective ring expansion via bicyclooxonium ion. **Ring Expansion**
Sakamoto, Y; Tamegai, K; Nakata, T. *Org. Lett*. **2002**, *4*, 675.



7 examples (combined yields 48-96%).

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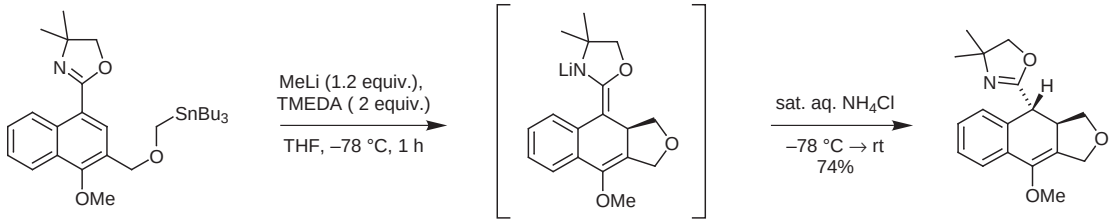
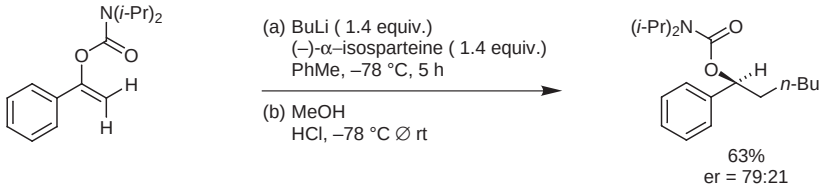
Dearomatizing annulation of five-membered rings to naphthalenes by organolithium cyclization. **Annulation**
Clayden, J.; Kenworthy, M. N. *Org. Lett.* **2002**, *4*, 787.



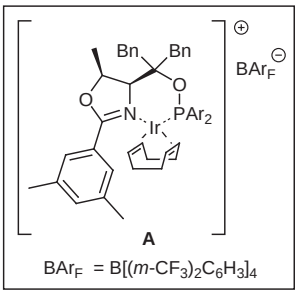
3 further examples (Yields 41-79%). Lower yields were obtained in absence of TMEDA.

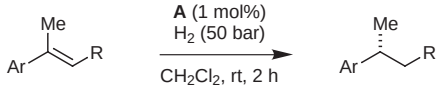
Stereoselective intermolecular carbolithiation of 1-aryl, 1-alkenyl carbamates. **Carbolithiation**
Peters, J. G.; Seppi, M.; Frohlich, R.; Wibbeling, B.; Hoppe, D. *Synthesis* **2002**, *3*, 381.



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

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

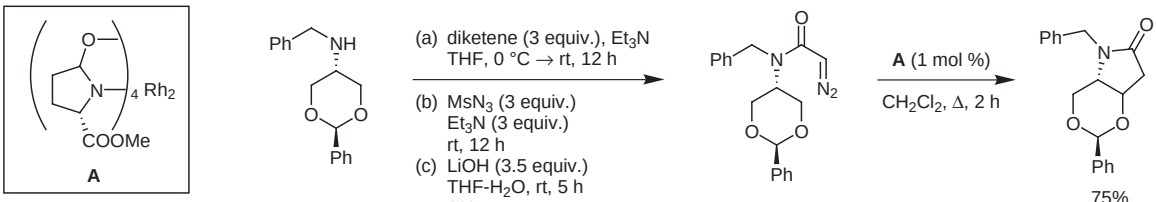




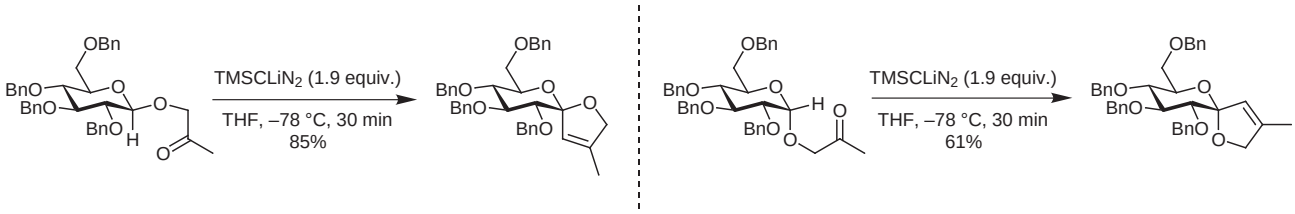
Ar	R	%ee
Ph	Ph	99%
Ph	CO_2Et	94%
p-$MeOC_6H_4$	Me	99%

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

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



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



6 examples (yields 59-89%).

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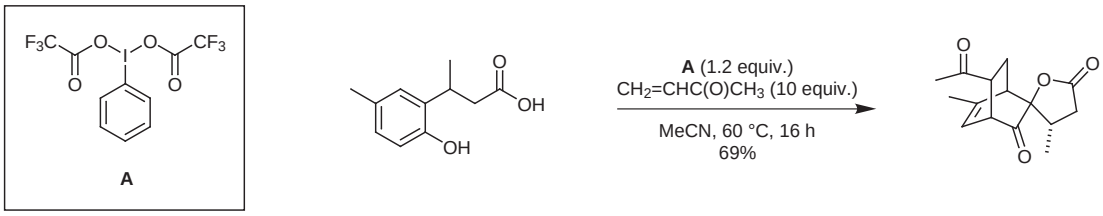
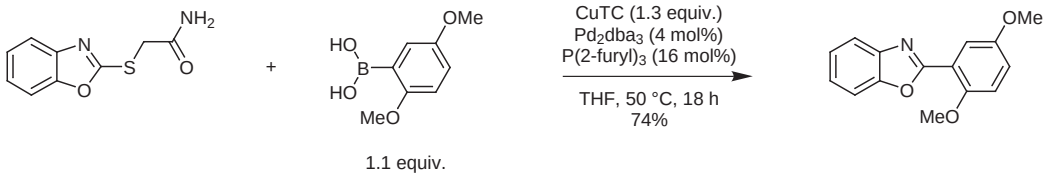
Intramolecular aromatic oxidation of 3-(2-hydroxyphenyl)-propionic acids. **Oxidation**
Drutu, I.; Njardarson, J. T.; Wood, J. L. *Org Lett.* **2002**, *4*, 493.



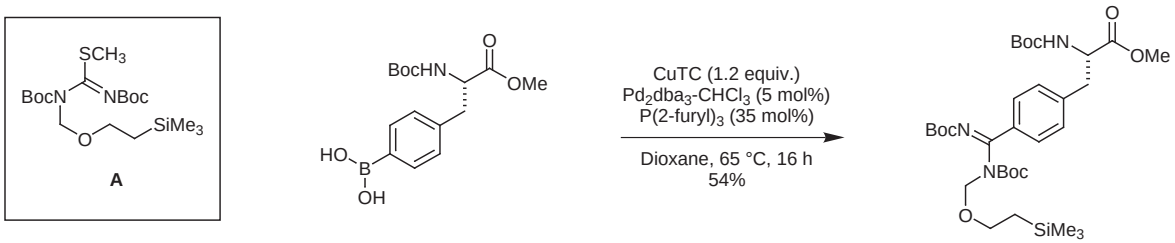
27 examples (yields 0-91%).

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



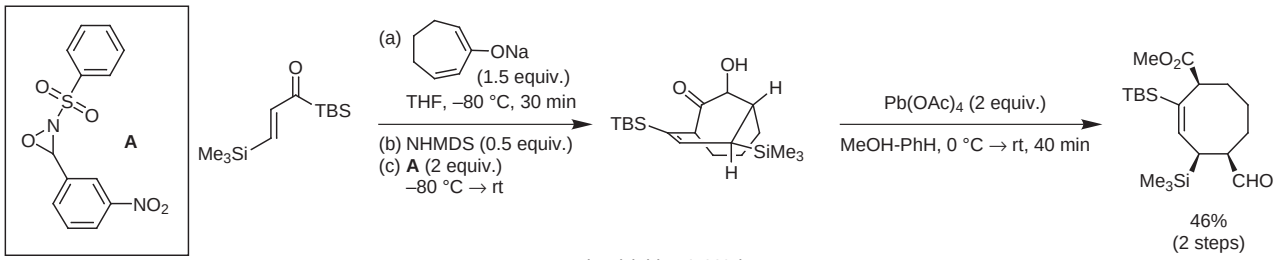
12 examples (yields 53-87%).

Synthesis of protected aryl and heteroaryl amines. **sp^2-sp^2 Coupling**
Kusturin, C. L.; Liebeskind, L. S.; Neumann, W. L. *Org Lett.* **2002**, *4*, 983.



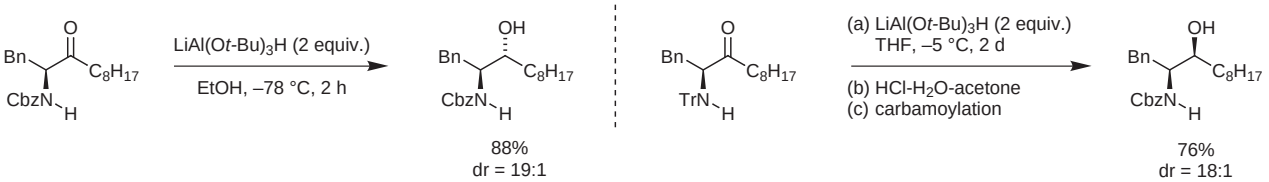
13 examples (yields 41-91%).

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



5 examples (yields 46-69%).

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



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.

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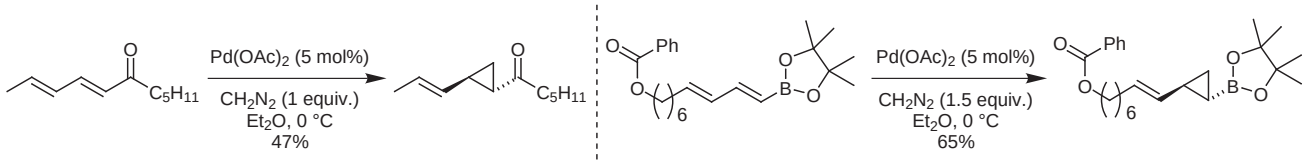
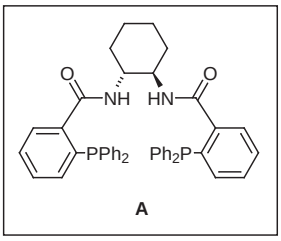
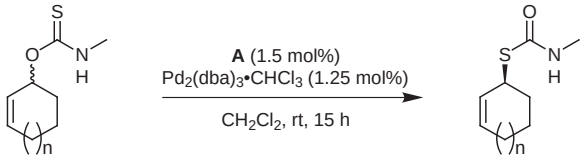
Regio- and stereoselective cyclopropanation of functionalized dienes. **Selective Cyclopropanation**
Markó, I. E.; Giard, T.; Sumida, S.; Gies, A.-E. *Tetrahedron Lett*. **2002**, *43*, 2317.



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

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

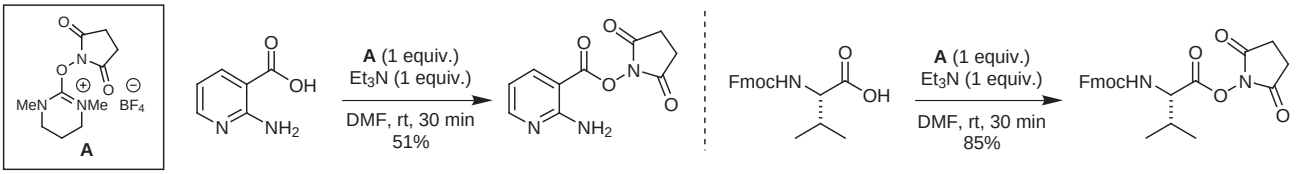




n	yield	%ee
1	94%	97%
2	94%	92%

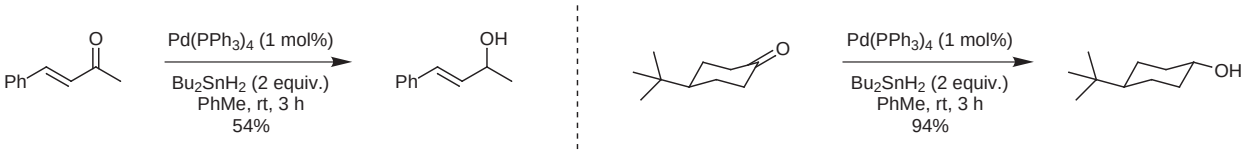
17 examples (yields 76%, %ee 64-99%) with variation of the *N*-substituent. Preparation of the *O*-allylic thiocarbamates; further derivitisation of the products and application to the solid-phase are also reported.

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



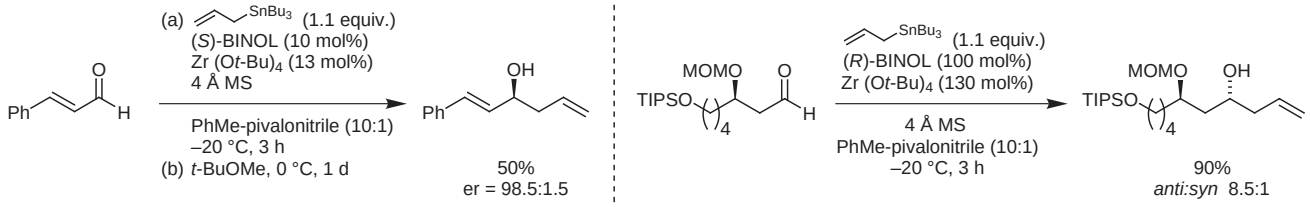
15 examples (yields 51-89%) and preparation of **A** are reported.

Palladium-catalyzed reduction of ketones with Bu_2SnH_2. **Ketone Reduction**
Kamiya, I.; Ogawa, A. *Tetrahedron Lett*. **2002**, *43*, 1701.



13 examples (yields 31-100%).

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



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

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