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, Stefan Schunk and Josephine Yuen, Department of Chemistry, Leeds University, Leeds, LS2 9JT, UK.

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Bulletin of the Chemical Society of Japan
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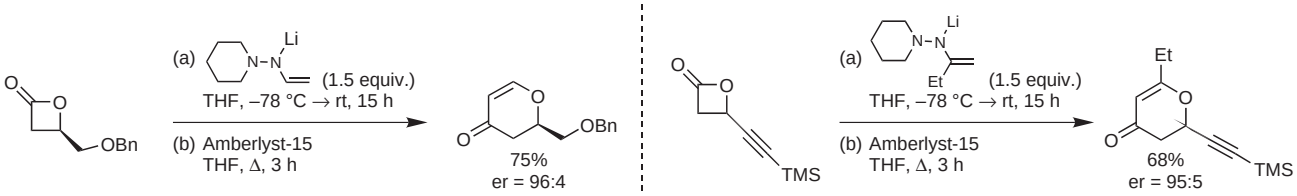
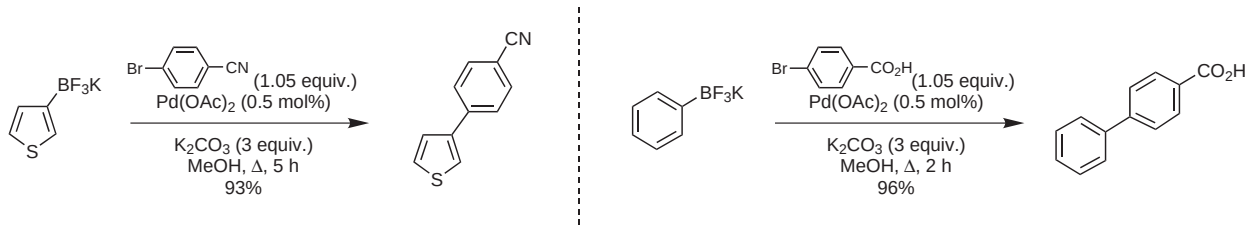
Journal of the American Chemical Society
Journal of Organic Chemistry
Organic Letters
Organometallics
Perkin Transactions 1
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry and Tetrahedron Letters

Synthesis of dihydropyrones from β-lactones. **1,2-Addition/Cyclization**
Zipp, G. G.; Hilfiker, M. A.; Nelson, S. G. *Org. Lett.* **2002**, *4*, 1823.



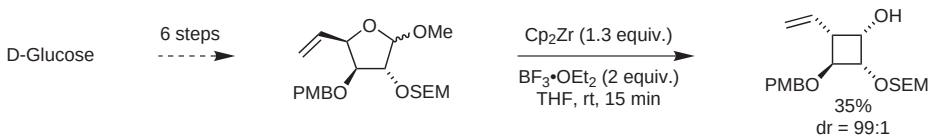
9 Examples (yields 68-81%, %ee 90-91%).

Ligandless Pd-catalyzed Suzuki reaction. **sp^2-sp^2 Coupling**
Molander, G. A.; Biolatto, B. *Org. Lett.* **2002**, *4*, 1867.



23 Examples (yields 52-99%).

Diastereoselective Zr-mediated ring contraction of 4-vinylfuranosides. **Ring Contraction**
Paquette, L. A.; Cunière, N. *Org. Lett.* **2002**, *4*, 1927.



5 Examples (yields 35-88%, %de 10-98%).

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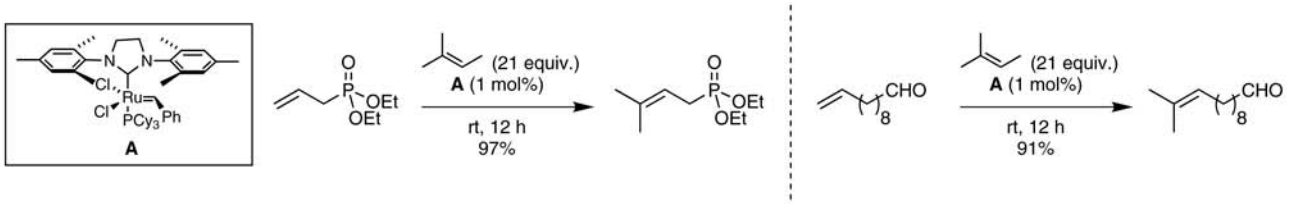
Synthesis of trisubstituted olefins *via* cross metathesis.
Chattarjee, A. K.; Sanders, D. P.; Grubbs, R. H. *Org. Lett.* **2002**, *4*, 1939.

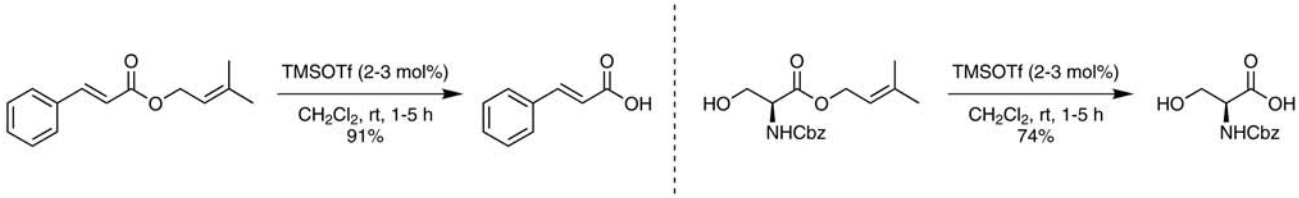
Cross Metathesis



13 Examples (yields 48-99%).

TMSOTf-catalyzed cleavage of 3-methylbut-2-enyl ester.
Nishizawa, M.; Yamamoto, H.; Seo, K.; Imagawa, H.; Sugihara, T. *Org. Lett.* **2002**, *4*, 1947.

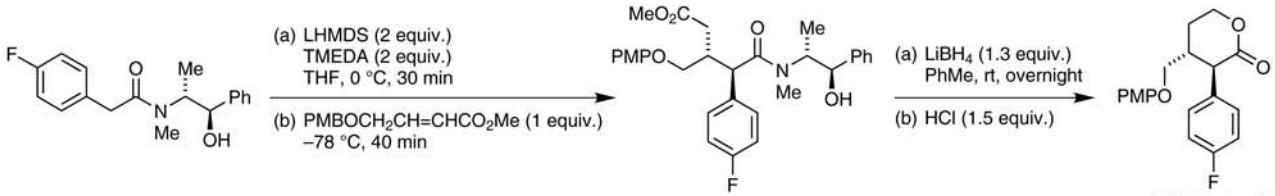
Electrophilic Heterolysis



15 Examples (yields 15-99%).

Synthesis of 3-aryl-δ-lactones *via* asymmetric Michael reactions.
Smitrovich, J. H.; Boice, G. N.; Qu, C.; DiMichele, L.; Nelson, T. D.; Huffman, M. A.; Murry, J.; McNamara, J.; Reider, P. J. *Org. Lett.* **2002**, *4*, 1963.

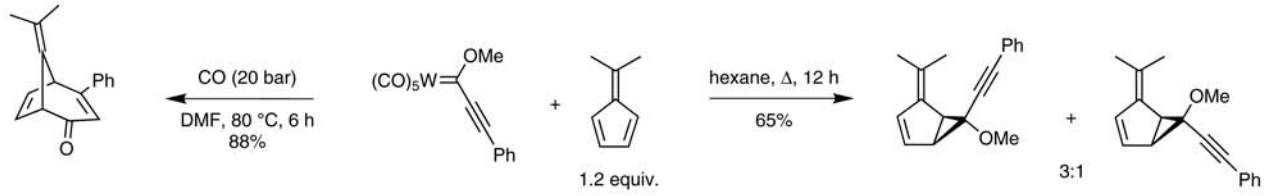
Asymmetric 1,4-Addition/Lactonization



9 Examples (yields 46-89%, %ee 76-93%).

The [2+1] and [4+3] cyclization reactions of fulvenes with Fisher carbene complexes.
Barluenga, J.; Martinez, S.; Suarez-Sobrino, A. L.; Tomas, M. *J. Am. Chem. Soc.* **2002**, *124*, 5948.

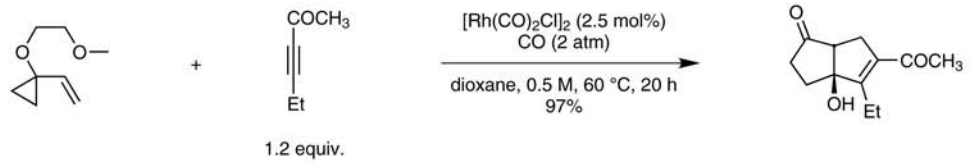
Cyclization



5 Examples of [4+3] cyclization (yields 50-88%). 4 Examples of [2+1] cyclization (yields 65-73%).

Three-component cycloadditions: the first transition metal-catalyzed [5+ 2+1] cycloaddition reactions.
Wender, P. A.; Gamber, G. G.; Hubbard, R. D.; Zhang, L. *J. Am. Chem. Soc.* **2002**, *124*, 2876.

[5+2+1] Cycloaddition



9 Examples (yield 48-97%).

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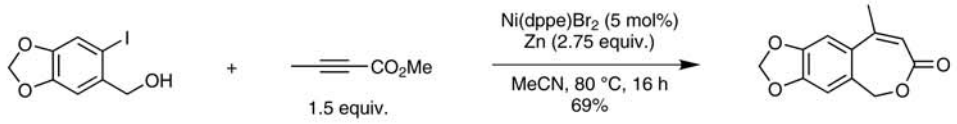
Ni- and Zn-catalyzed reaction of 2-iodobenzyl alcohols with propiolates.
Rayabarapu, D. K.; Cheng, C.-H. *J. Am. Chem. Soc.* **2002**, *124*, 5630.

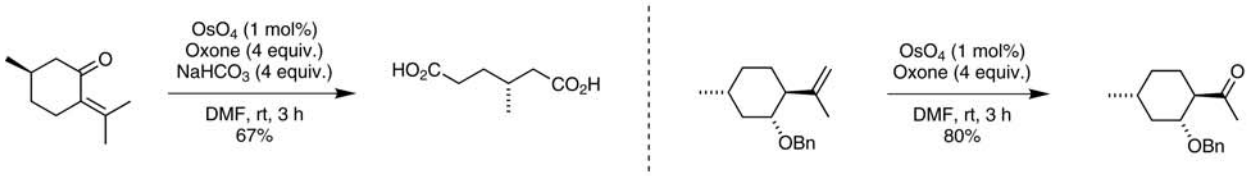
Conjugate Addition
Annulation



13 Examples (yield 56-81%).

Osmium tetroxide catalyzed oxidative cleavage of olefins.
Travis, B. R.; Narayan, R. S.; Borhan, B. *J. Am. Chem. Soc.* **2002**, *124*, 3824.

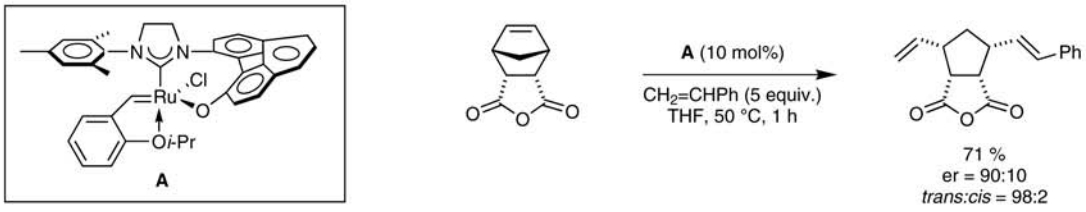
Oxidative Cleavage



24 Examples (yield 50-97%).

A recyclable Ru catalyst for enantioselective olefin metathesis in air.
Van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954.

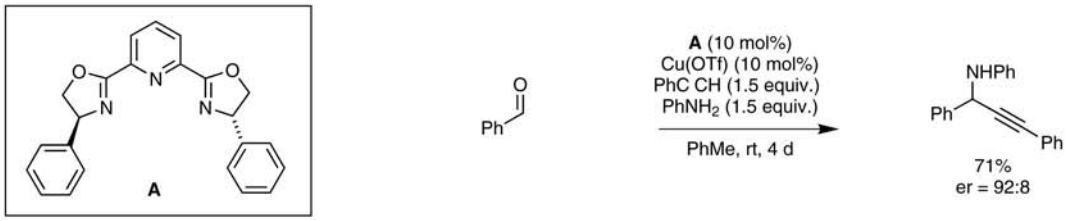
Metathesis



4 Examples (yield 57-76%, %ee 80-98%).

Enantioselective addition of terminal alkynes to imines catalyzed by copper(I)pybox complex.
Wei, C.; Li, C.-J. *J. Am. Chem. Soc.* **2002**, *124*, 5638.

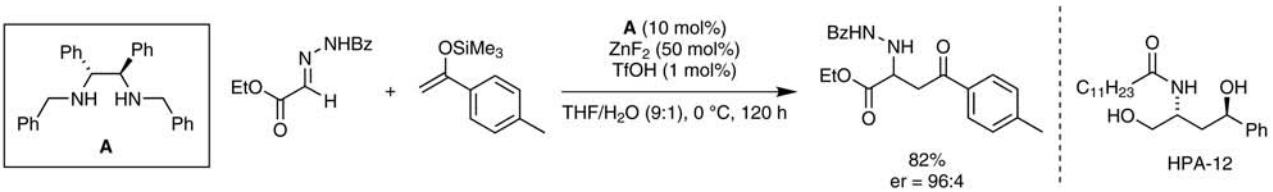
Asymmetric 1,2-Addition



11 Examples (yield 63-93%, %ee 82-96%). Water can also be used as solvent.

Catalytic asymmetric Mannich-type reactions in aqueous media.
Kobayashi, S.; Hamada, T.; Manabe, K. *J. Am. Chem. Soc.* **2002**, *124*, 5640.

Asymmetric 1,2-Addition



6 Examples (yield 30-91%, %ee 88-99%). The synthesis of sphingomyelin inhibitor HPA-12 is reported.

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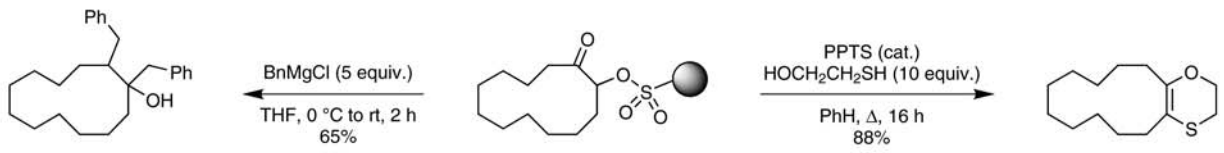
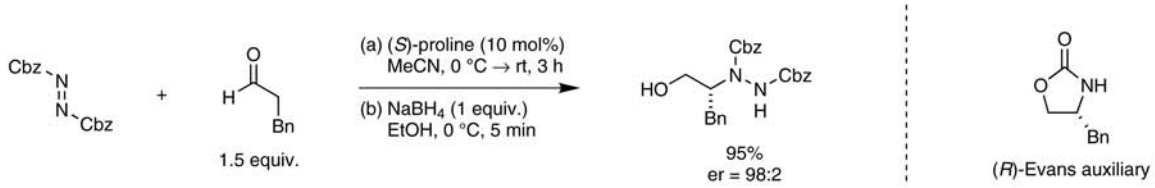
Solution- and solid-phase synthesis of heterocycle and enediyne libraries. **Cleavage**
Nicolaou, K. C.; Montagnon, T.; Ulven, T.; Baran, P. S.; Zhong, Y.-L.; Sarabia, F. *J. Am. Chem. Soc.* **2002**, *124*, 5718.



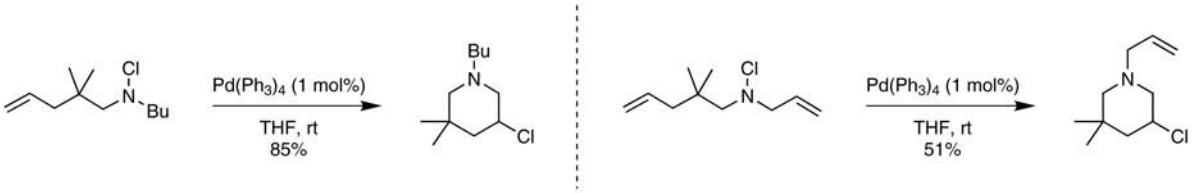
20 Examples of functionalizing-cleavage options (yields 38-95%). 4 Examples of functionalizing-cleavage options involving carbon-carbon bond-forming (yields 65-85%).

Catalytic asymmetric α-amination of aldehydes. **Asymmetric 1,2-Addition α-Amination**
List, B. *J. Am. Chem. Soc.* **2002**, *124*, 5656.



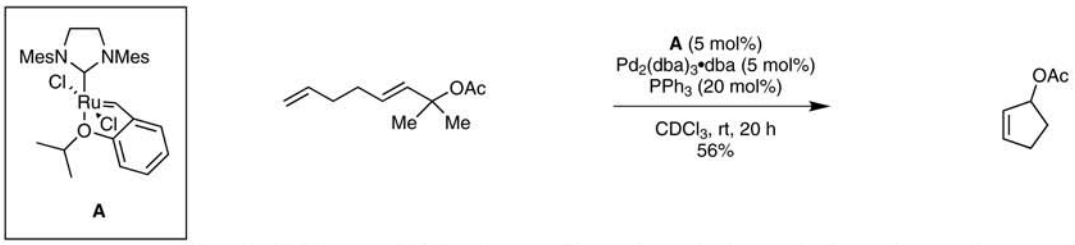
5 Examples (yield 93-99%, %ee 95-97%). The synthesis of Evans auxiliary is presented.

Catalytic hetero-Heck type reaction. **Cyclization**
Helaja, J.; Göttlich, R. *Chem. Commun.* **2002**, 720.



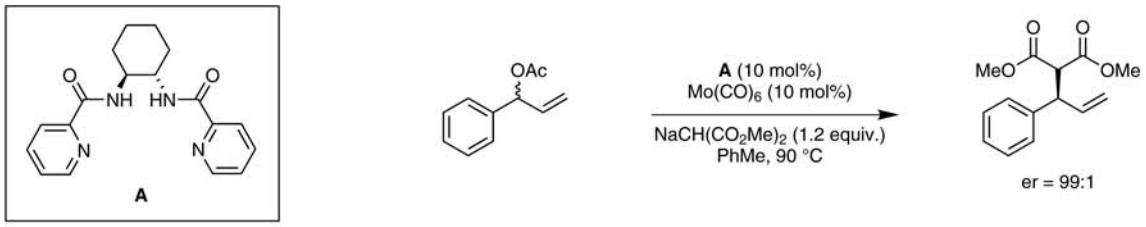
8 Examples (yields 43-86%).

Tandem allylic acetate isomerisation-ring closing metathesis. **Isomerisation / Metathesis**
Braddock, D. C.; Matsuno, A. *Tetrahedron Lett.* **2002**, *43*, 3305.



3 Examples (yields trace-56%). Development of the catalyst and other metathesis reactions are also reported.

Dynamic kinetic asymmetric transformation / kinetic resolution. **Asymmetric Allylic Alkylation**
Hughes, D. L.; Palucki, M.; Yasuda, N.; Reamer, R. A.; Reider, P. J. *J. Org. Chem.* **2002**, *67*, 2762.



3 Examples. Effect of solvent and temperature upon the reaction kinetics was also investigated.

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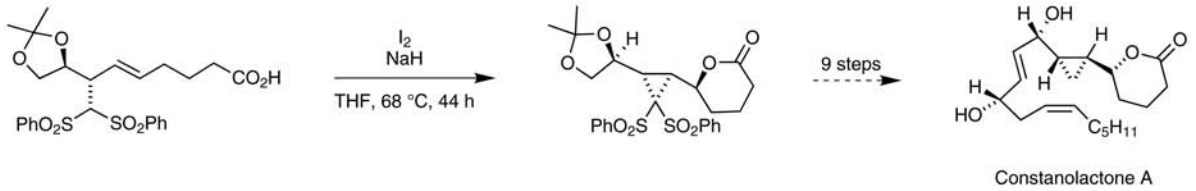
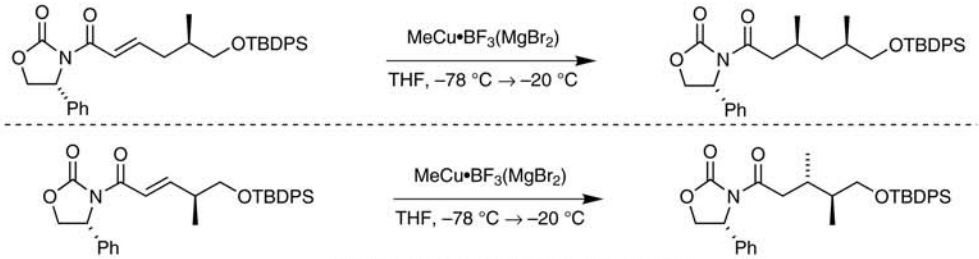
Iodolactonization and cyclopropanation applied to the synthesis of Constanolactones A and B. **Iodolactonization/Alkylation**
Yu, J.; Lai, J.-Y.; Ye, J.; Balu, N.; Reddy, L. M.; Duan, W.; Fogel, E. R.; Capdevila, J. H.; Falck, J. R. *Tetrahedron Lett.* **2002**, *43*, 3939.



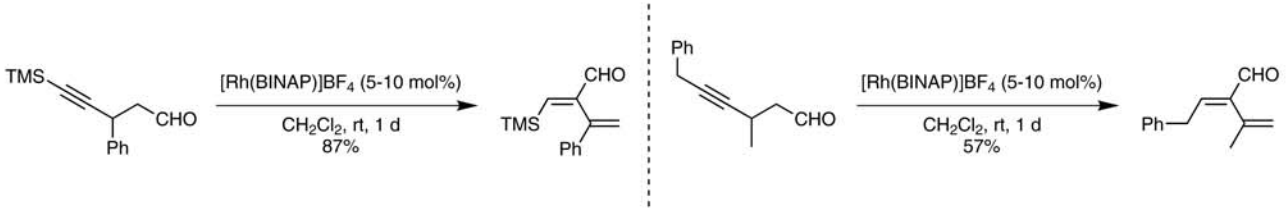
Constanolactone B was also prepared using the same method.

Stereoselective synthesis of *syn*- and *anti*-1,3- and 1,2-dimethyl arrays. **Asymmetric 1,4-Addition**
Williams, D. R.; Kissel, W. S.; Li, J. J.; Mullins, R. J. *Tetrahedron Lett.* **2002**, *43*, 3723.



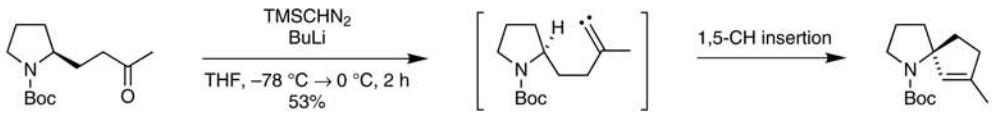
13 Examples (yields 75-99%, %de 0-99%).

Rh-catalyzed isomerization of 4-alkynals to dienals. **Isomerization**
Tanaka, K.; Fu, G. C. *Chem. Commun.* **2002**, 684.



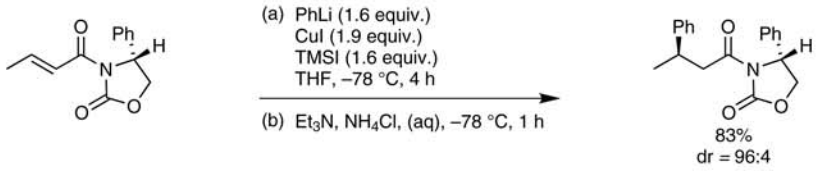
5 Examples (yields 50-87%).

Alkylidene carbene 1,5-CH insertion reactions of α-amino acid derived substrates. **CH Insertion**
Mapitse, R.; Hayes, C. J., *Tetrahedron Lett.* **2002**, *43*, 3541.



5 Examples (yields 10-53%).

Asymmetric conjugate addition of Li[RCuI]/TMSI to *N*-enoyl oxazolidinones. **Asymmetric 1,4-Addition**
Pollock, P.; Dambacher, J.; Anness, R.; Bergdahl, M. *Tetrahedron Lett.* **2002**, *43*, 3693.



24 Examples (yields 0-96%, %de 0-96%). The use of valine and phenylala nine-derived oxazolidinones is also reported.

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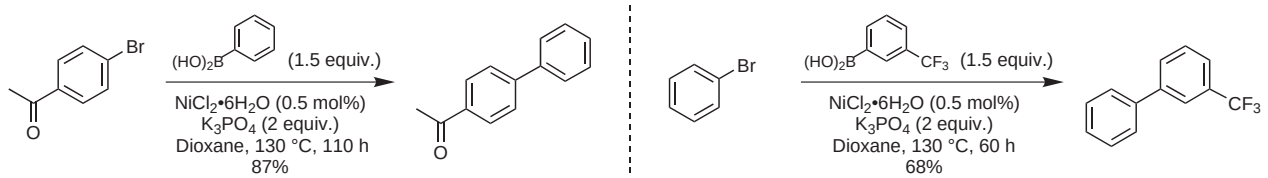
Suzuki cross-coupling catalyzed by a phosphine-free nickel catalyst.
Zim, D.; Monteiro, A. L. *Tetrahedron Lett.* **2002**, *43*, 4009.

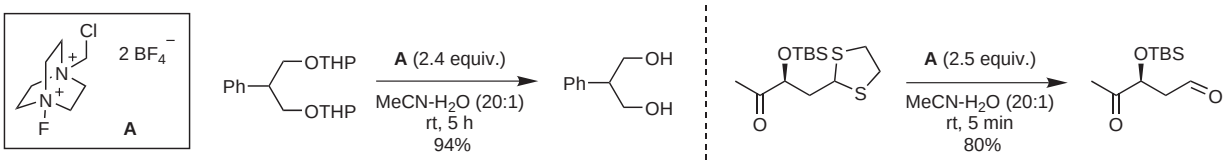
sp^2–sp^2 Coupling



11 Examples (yields 6-87%).

Cleavage of PMP, THP and 1,3-dithiane protecting groups by Selectfluor™.
Liu, J.; Wong, C.-H. *Tetrahedron Lett.* **2002**, *43*, 4037.

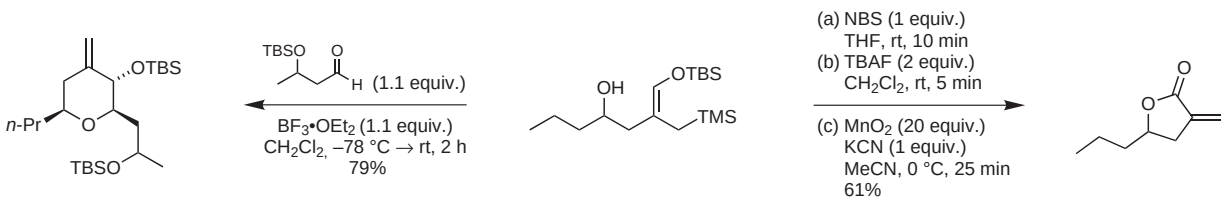
Deprotection



4 Examples of PMP removal (yields 87-92%), 5 examples of THP removal (yields 89-95%) and 5 examples of 1,3-dithiane (yields 80-95%).

Tandem ene-reaction/intramolecular Sakurai cyclization.
Marko, I. E.; Dumeunier, R.; Leclercq, C.; Leroy, B.; Plancher, J.-M.; M ekhalfia, A.; Bayston, D. J. *Synthesis*, **2002**, 958.

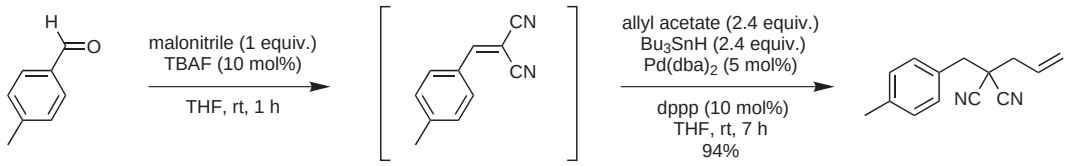
Heteroannulation



Ene adducts (8 examples, yields 51-79%), tetrahydropyrans (5 examples, yields 57-85%), γ-butyrolactones (9 examples, yields 57-99%).

Regiospecific Pd-catalyzed hydrocarbonation at α-position of a Michael acceptor.
Shim, J.-G.; Park, J. C.; Cho, C. S.; Shim, S. C.; Yamamoto, Y. *Chem. Commun.* **2002**, 852.

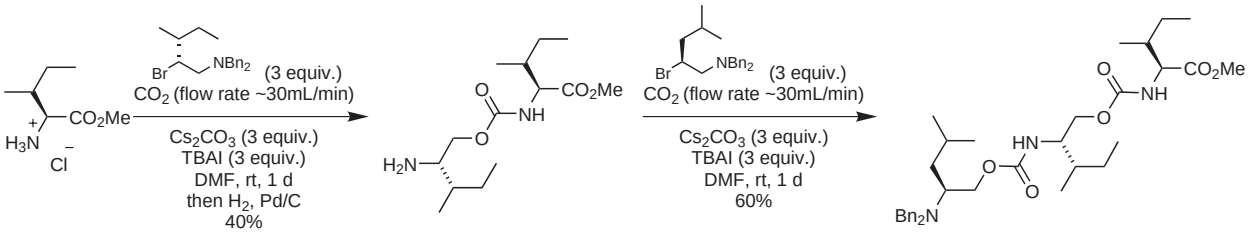
Hydrocarbonation



11 Examples (yields 72-97%). A one-pot variant *via in situ* generation of the Michael acceptor (4 examples, yields 70-94%) is als o reported.

Cs_2CO_3-Promoted synthesis of carbonates and carbamates *via* a 3 component coupling.
Salvatore, R. N.; Chu, F.; Nagle, A. S.; Kapxhiu, E. A.; Cross, R. M.; J ung, K. W. *Tetrahedron*, **2002**, *58*, 3329.

3 Component Coupling



Solution phase: carbonates (16 examples, yields 65-98%), carbamates (44 examples, yields 47-98%).
Solid phase: carbonates (14 examples, yields 63-99%), carbamates (30 examples, yields 21-97%).

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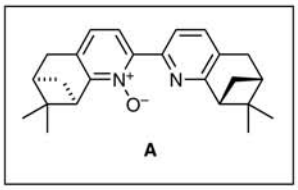
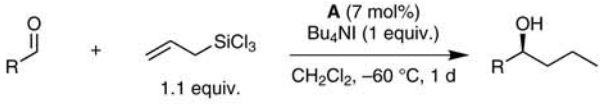
Catalytic enantioselective allylation of aldehydes with allyltrichlorosi lane. **Allylation**
Malkov, A. V.; Orsini, M.; Pernazza, D.; Muir, K. W.; Langer, V.; Meghan i, P.; Kocovsky, P. *Org. Lett.* **2002**, *4*, 1047.

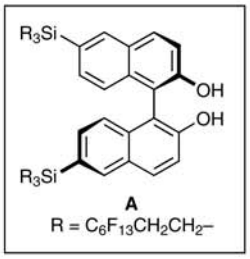


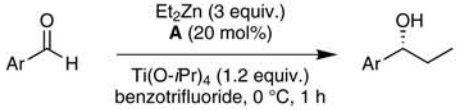


R	Yield	%ee
Ph	78%	90%
p-MePh	71%	87%
p-ClPh	62%	89%
p-NO_2Ph	58%	65%

11 Examples (yields 10-85%, %ee 4-92%).

Asymmetric addition of diethylzinc to aromatic aldehydes catalyzed by fluorous BINOL-Ti complexes. **Asymmetric 1,2-Addition**
Nakamura, Y.; Takeuchi, S.; Okumura, K.; Ohgo, Y.; Curran, D. P. *Tetrahedron* **2002**, *58*, 3963.

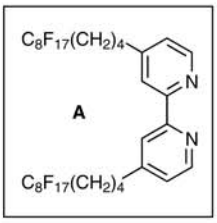


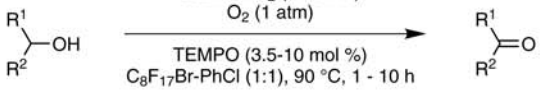


Ar	Yield	%ee
Ph	92%	84%
3-MeO-C_6H_4	95%	85%
4-Me-C_6H_4	91%	81%
1-Naphthyl	98%	91%
4-Cl-C_6H_4	93%	82%

9 Examples (yields 91-98%, %ee 78-91%). Almost complete recovery of catalyst after reaction.

Cu-catalyzed aerobic oxidation of alcohols using fluorous biphasic catalysis. **Oxidation**
Ragagnin, G.; Betzmeier, B.; Quici, S.; Knochel, P. *Tetrahedron* **2002**, *58*, 3985.

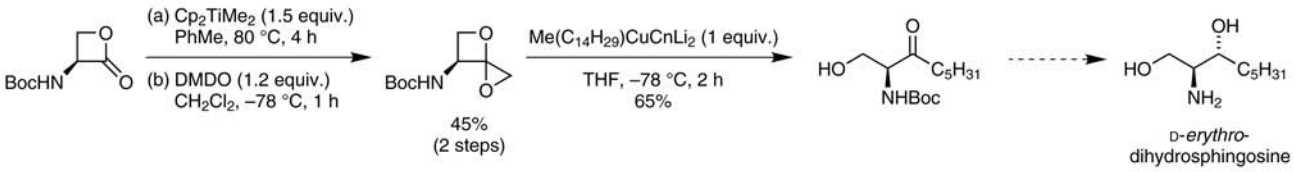




R^1	R^2	Yield
p-NO_2Ph	H	93%
$CH_3(CH_2)_8$	H	73%
p-NCPh	$CH_3(CH_2)_3$	95%
$CH_3(CH_2)_7$	CH_3	88%

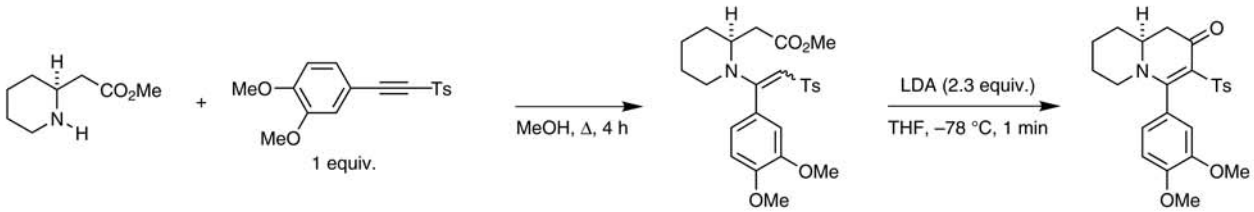
21 Examples (yields 31-97%). Selective oxidation of *cis:trans* mixtures of substituted cyclohexanols (6 examples) is also reported.

Synthesis of D-*erythro*-dihydrosphingosine and D-*xylo*-phytosphingosine. **Methylenation/Oxidation/Cuprate Addition**
Ndakala, A. J.; Hashemzadeh, M.; So, R. C.; Howell, A. R. *Org. Lett.* **2002**, *4*, 1719.



The total syntheses of D-*erythro*-dihydrosphingosine and D-*xylo*-phytosphingosine are reported.

Conjugate addition and intramolecular acylation of an amino ester with an acetylinic sulfone. **Conjugate Addition/ Intramolecular Acylation**
Back, T. G.; Hamilton, M. D. *Org. Lett.* **2002**, *4*, 1779.



The remaining steps towards the synthesis of lasubine II are reported.

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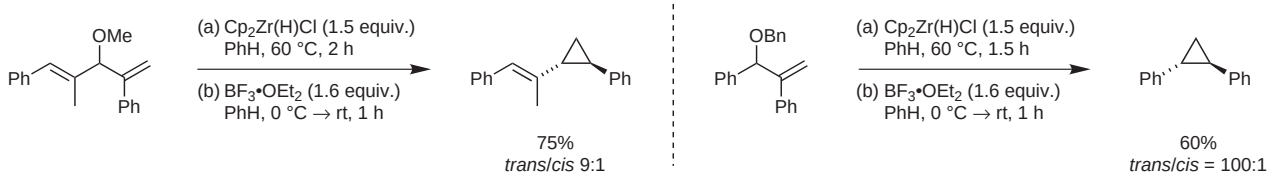
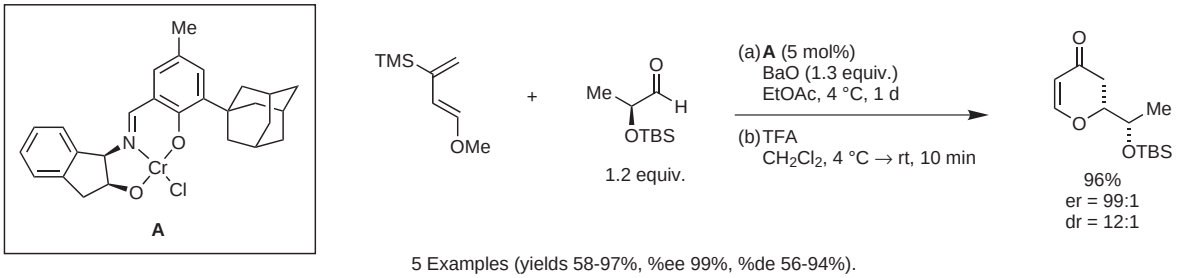
A one-pot access to cyclopropanes from allylic ethers *via* hydrozirconation-deoxygenative ring formation. **Cyclopropanation**
Gandon, V.; Szymoniak, J. *Chem. Commun*. **2002**, 1308.



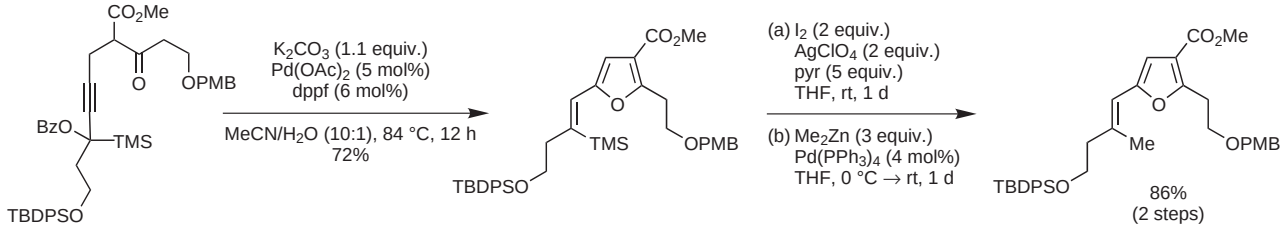
11 Examples (yields 42-92%, 71:29 *trans*/*cis* 100:1).

Diastereoselective hetero-Diels–Alder reactions. **[4 + 2] - Cycloaddition**
Joly, G. D.; Jacobsen, E. N. *Org. Lett.* **2002**, *4*, 1795.



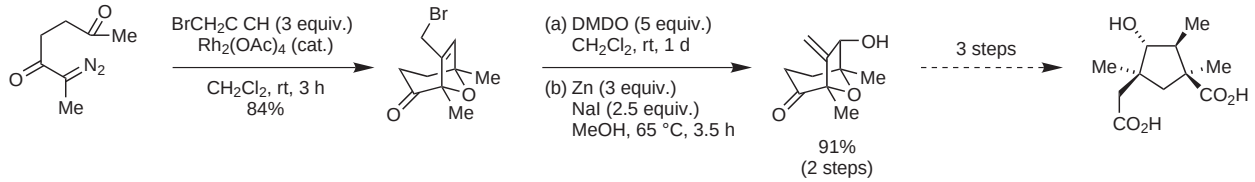
5 Examples (yields 58-97%, %ee 99%, %de 56-94%).

Control of 2-alkenylfuran (*E*/*Z*)-configuration. **Heteroannulation**
Wipf, P.; Soth, M. J. *Org. Lett.* **2002**, *4*, 1787.



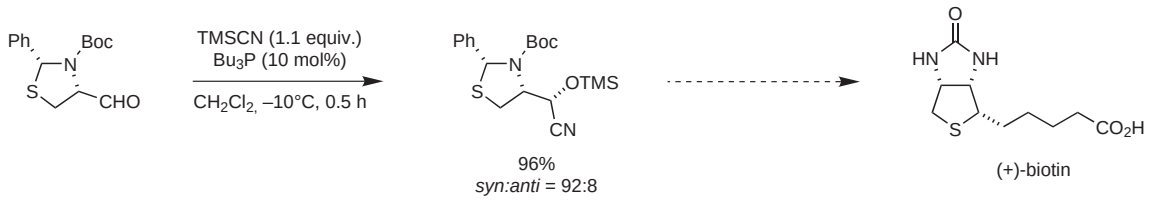
2 Examples are reported including the synthesis of the C1-C18 segment of lophotoxin and pukalide.

Tandem carbonyl ylide formation-cycloaddition. **Dipolar Cycloaddition**
Hodgson, D. M.; Avery, T. D.; Donohue, A. C. *Org. Lett.* **2002**, *4*, 1809.



The stereoselective synthesis of *cis*-nemorensic acid is also reported.

Stereocontrolled synthesis of (+)-biotin from L-cysteine. **Cyanosilylation**
Seki, M.; Hatsuda, M.; Mori, Y.; Yamada, S. *Tetrahedron Lett.*, **2002**, *43*, 3269.



1 Example.The product is an intermediate in the synthesis of the natural product (+)-biotin.

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