

*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.

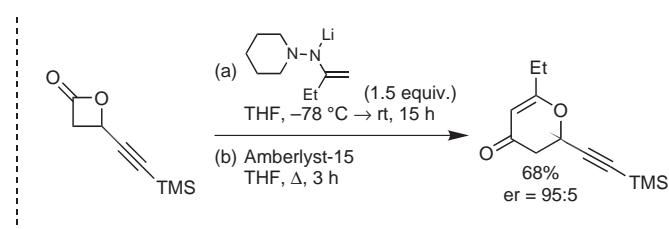
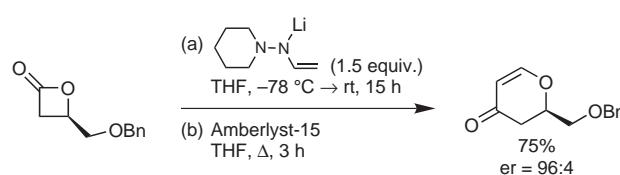
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Synthesis 2002, No. 13, 20 09 2002. Article Identifier: 1437-210X;E;2002;0;13;1937;1944;ftx,en;X01302SS.pdf.  
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The journals regularly covered by the abstractors are:

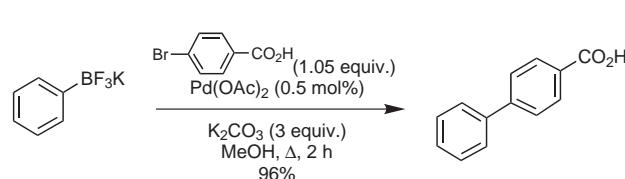
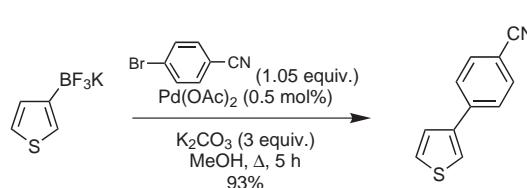
Angewandte Chemie International Edition  
Bulletin of the Chemical Society of Japan  
Chemical Communications  
Chemistry A European Journal  
Chemistry Letters  
Collection Czechoslovak Chemical Communications  
European Journal of Organic Chemistry  
Helvetica Chimica Acta  
Heterocycles  
Journal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

Synthesis of dihydropyrones from  $\beta$ -lactones.  
Zipp, G. G.; Hilfiker, M. A.; Nelson, S. G. *Org. Lett.* **2002**, 4, 1823.



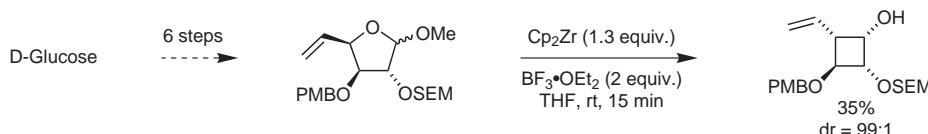
9 Examples (yields 68-81%, %ee 90-91%).

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



23 Examples (yields 52-99%).

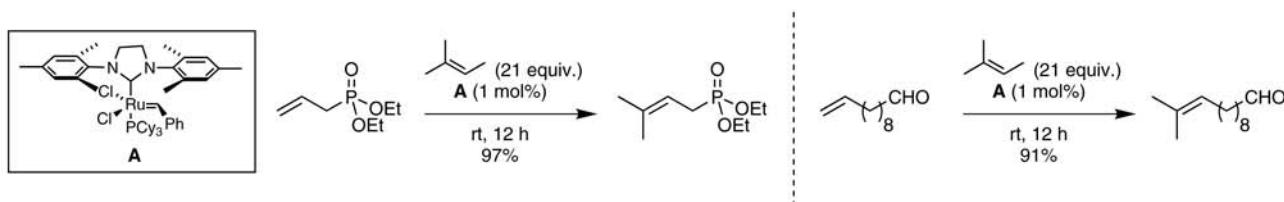
Diastereoselective Zr-mediated ring contraction of 4-vinylfuranosides.  
Paquette, L. A.; Cunière, N. *Org. Lett.* **2002**, 4, 1927.



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

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

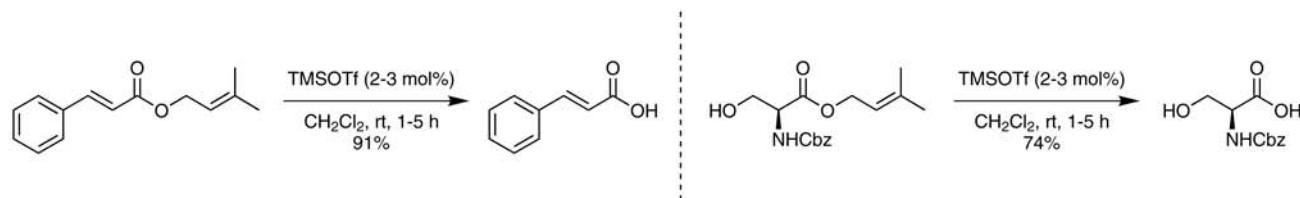
## Cross Metathesis



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.

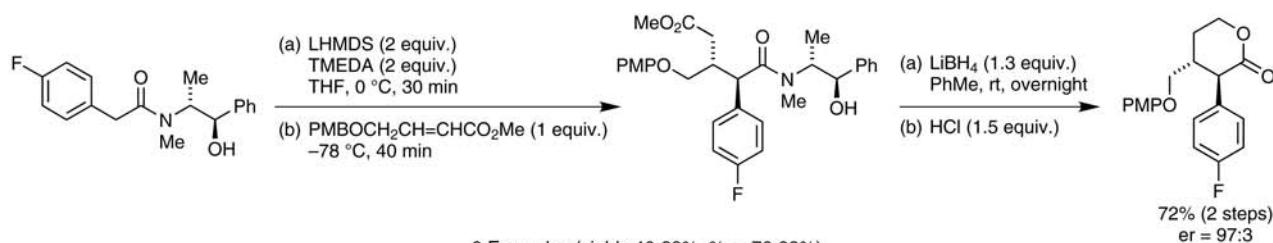
## Electrophilic Heterolysis



15 Examples (yields 15-99%).

Synthesis of 3-aryl- $\delta$ -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.

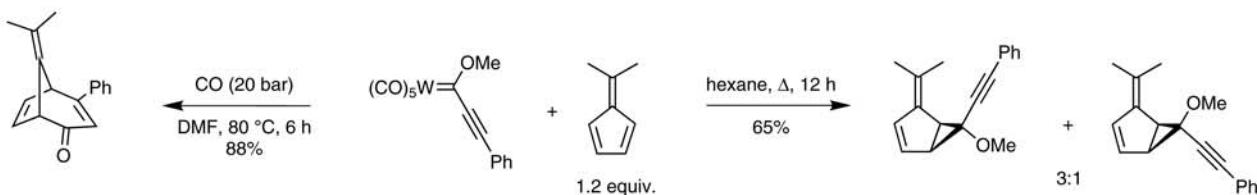
## Asymmetric 1,4-Addition/Lactonization



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.

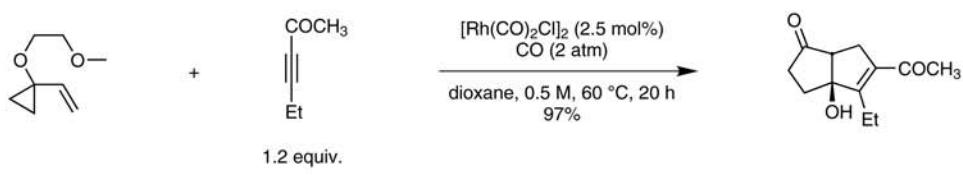
## Cyclization



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.

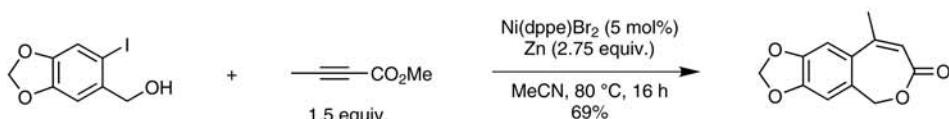
## [5+2+1] Cycloaddition



9 Examples (yield 48-97%).

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

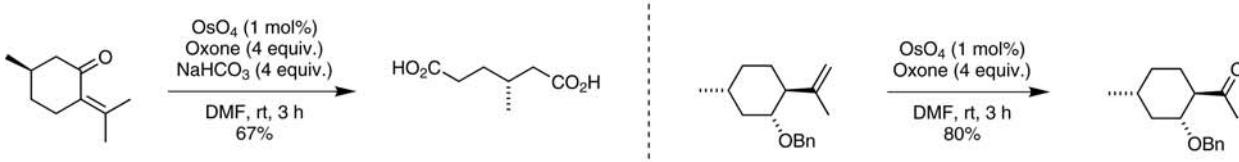
**Conjugate Addition  
Annulation**



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.

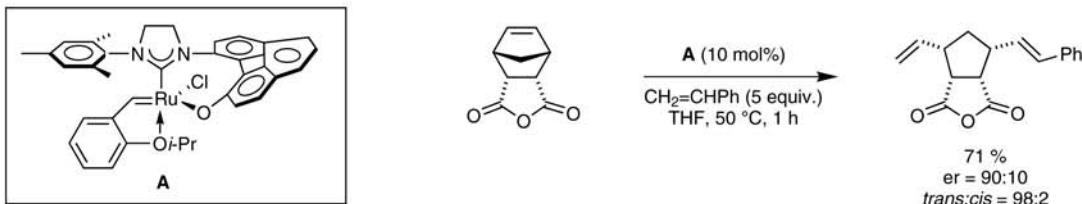
**Oxidative Cleavage**



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.

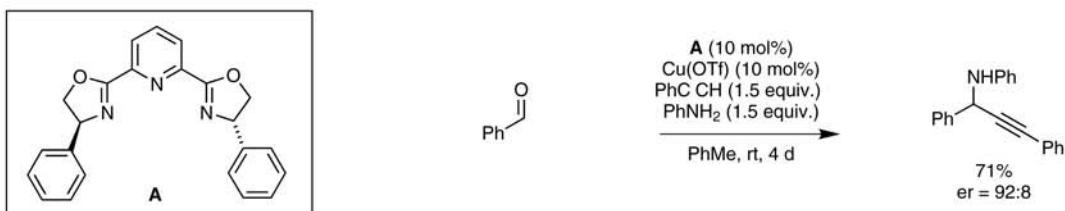
**Metathesis**



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.

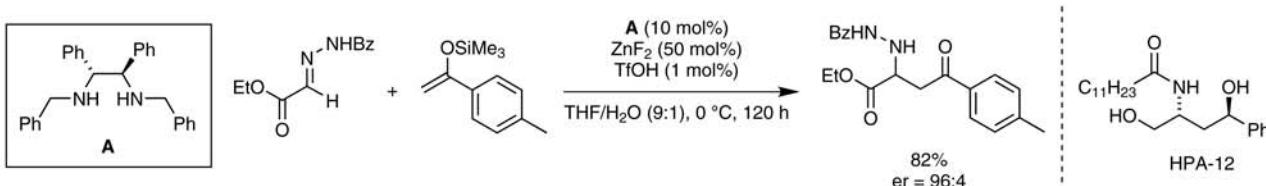
**Asymmetric 1,2-Addition**



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

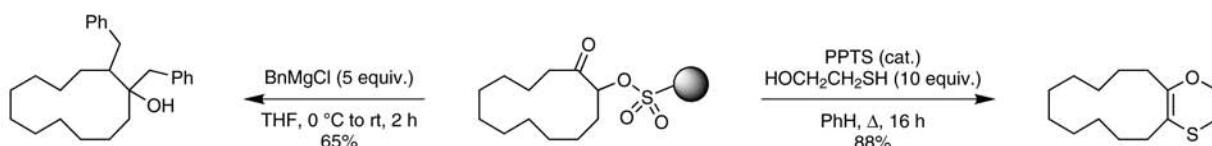
Catalytic asymmetric Mannich-type reactions in aqueous media.  
Kobayashi, S.; Hamada, T.; Manabe, K. *J. Am. Chem. Soc.* **2002**, *124*, 5640.

**Asymmetric 1,2-Addition**



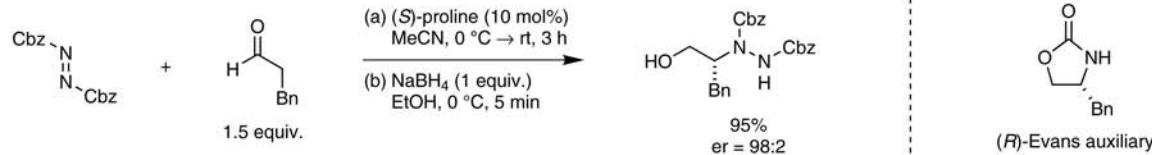
6 Examples (yield 30-91%, %ee 88-99%). The synthesis of sphingomyelin inhibitor HPA-12 is reported.

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

**Cleavage**

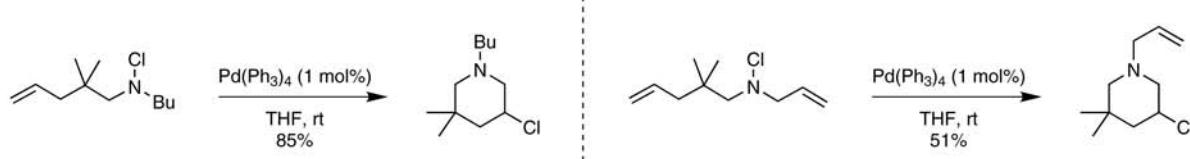
20 Examples of functionalizing-cleavage options (yields 38-95%). 4 Examples of functionalizing-cleavage options involving carbon-carbon bond-forming (yields 65-85%).

Catalytic asymmetric  $\alpha$ -amination of aldehydes.  
List, B. *J. Am. Chem. Soc.* **2002**, *124*, 5656.

**Asymmetric 1,2-Addition  
 $\alpha$ -Amination**

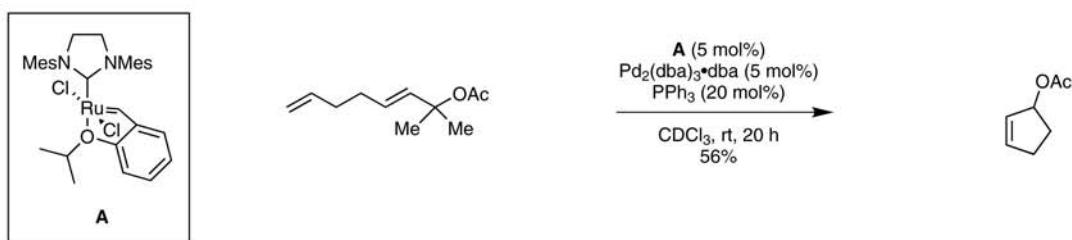
5 Examples (yield 93-99%, %ee 95-97%). The synthesis of Evans auxiliary is presented.

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

**Cyclization**

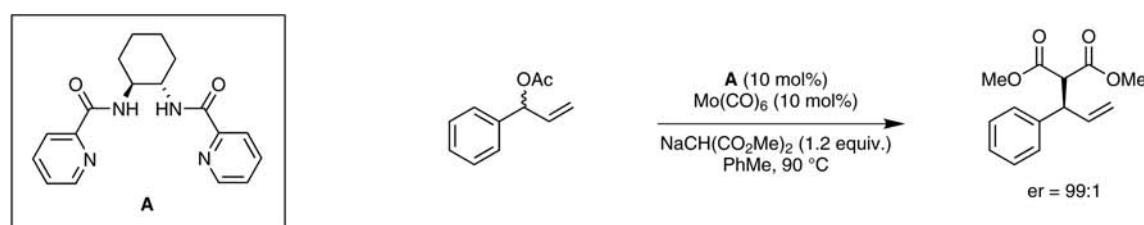
8 Examples (yields 43-86%).

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

**Isomerisation / Metathesis**

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

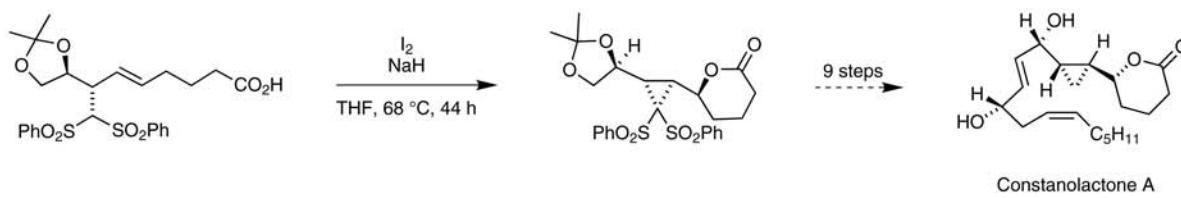
Dynamic kinetic asymmetric transformation / kinetic resolution.  
Hughes, D. L.; Palucki, M.; Yasuda, N.; Reamer, R. A.; Reider, P. J. *J. Org. Chem.* **2002**, *67*, 2762.

**Asymmetric Allylic Alkylation**

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

Iodolactonization and cyclopropanation applied to the synthesis of Constanolactones A and B.  
 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.

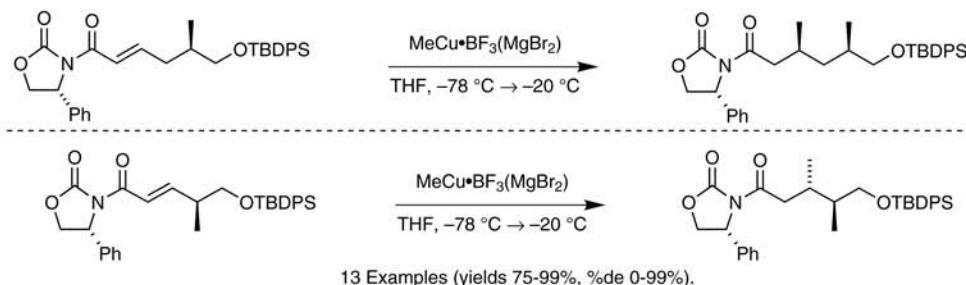
## Iodolactonization/Alkylation



Constanolactone B was also prepared using the same method.

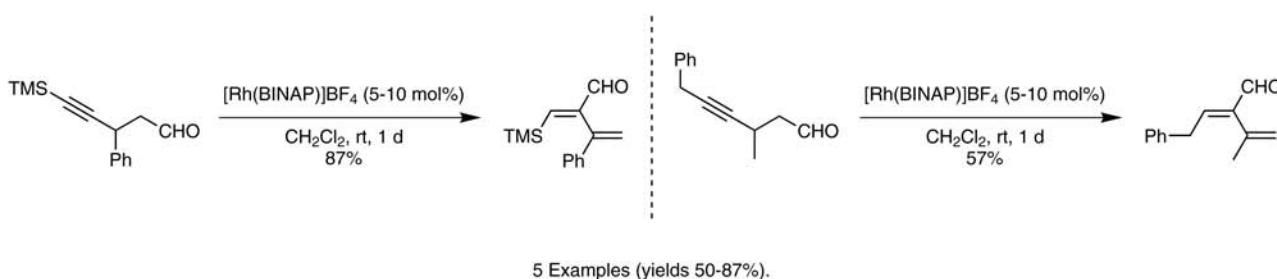
Stereoselective synthesis of *syn*- and *anti*-1,3- and 1,2-dimethyl arrays.  
 Williams, D. R.; Kissel, W. S.; Li, J. J.; Mullins, R. J. *Tetrahedron Lett.* **2002**, *43*, 3723.

## Asymmetric 1,4-Addition



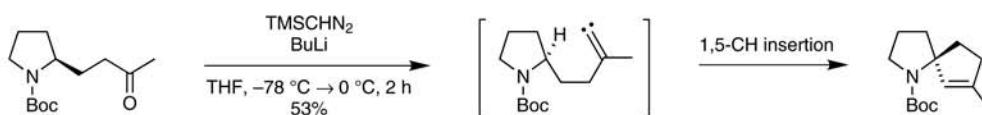
Rh-catalyzed isomerization of 4-alkynals to dienals.  
 Tanaka, K.; Fu, G. C. *Chem. Commun.* **2002**, 684.

## Isomerization



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

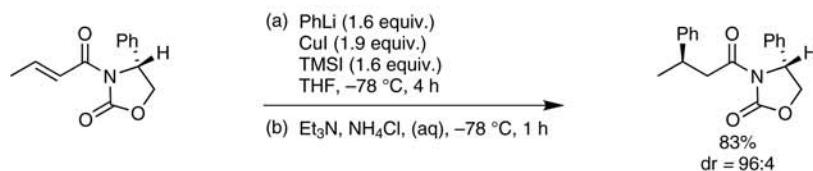
## CH Insertion



5 Examples (yields 10-53%).

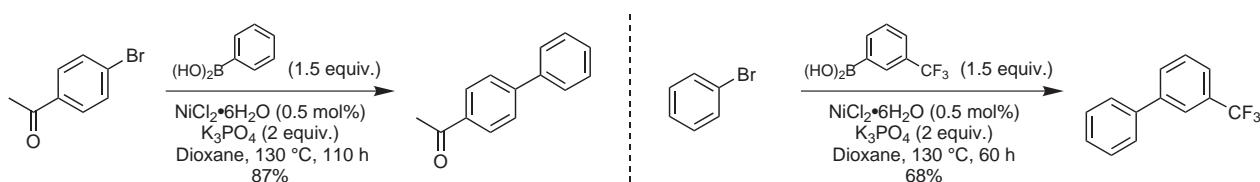
Asymmetric conjugate addition of Li[RCuI]/TMSI to *N*-enoyl oxazolidinones.  
 Pollock, P.; Dambacher, J.; Anness, R.; Bergdahl, M. *Tetrahedron Lett.* **2002**, *43*, 3693.

## Asymmetric 1,4-Addition



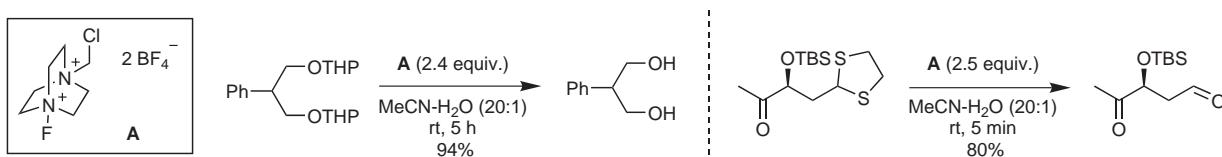
24 Examples (yields 0-96%, %de 0-96%). The use of valine and phenylalanine-derived oxazolidinones is also reported.

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

**sp<sup>2</sup>-sp<sup>2</sup> Coupling**

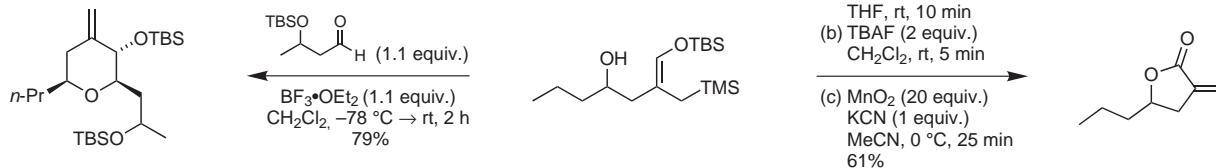
11 Examples (yields 6-87%).

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

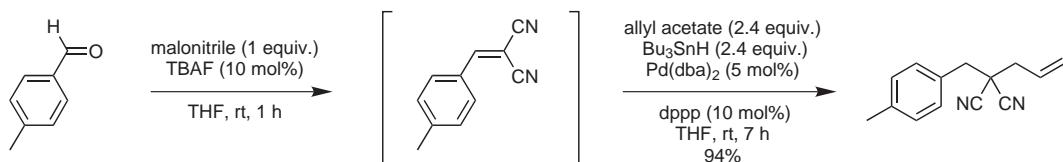
**Deprotection**

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%).

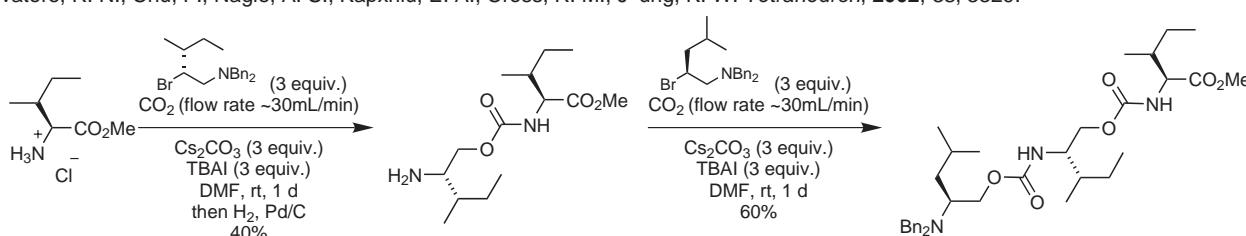
Tandem ene-reaction/intramolecular Sakurai cyclization.  
Marko, I. E.; Dumeunier, R.; Leclercq, C.; Leroy, B.; Plancher, J.-M.; Melkhalfia, A.; Bayston, D. J. *Synthesis*, **2002**, 958.

**Heteroannulation**Ene adducts (8 examples, yields 51-79%), tetrahydropyrans (5 examples, yields 57-85%),  $\gamma$ -butyrolactones (9 examples, yields 57-99%).

Regiospecific Pd-catalyzed hydrocarbonation at  $\alpha$ -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 also reported.

$\text{Cs}_2\text{CO}_3$ -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.; Jung, K. W. *Tetrahedron*, **2002**, *58*, 3329.

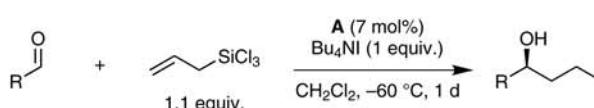
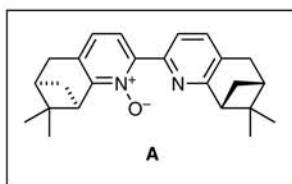
**3 Component Coupling**

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%).

Catalytic enantioselective allylation of aldehydes with allyltrichlorosilane.

## Allylation

Malkov, A. V.; Orsini, M.; Pernazza, D.; Muir, K. W.; Langer, V.; Meghan I., P.; Kocovsky, P. *Org. Lett.* **2002**, *4*, 1047.



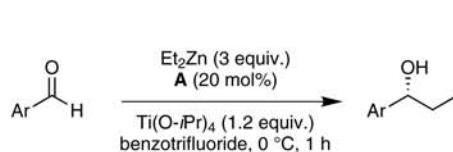
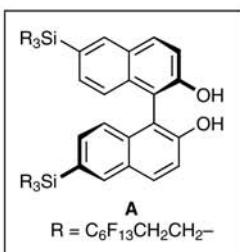
R	Yield	%ee
Ph	78%	90%
p-MePh	71%	87%
p-ClPh	62%	89%
p-NO <sub>2</sub> Ph	58%	65%

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

Asymmetric addition of diethylzinc to aromatic aldehydes catalyzed by fluorous BINOL-Ti complexes.

Nakamura, Y.; Takeuchi, S.; Okumura, K.; Ohgo, Y.; Curran, D. P. *Tetrahedron* **2002**, *58*, 3963.

## Asymmetric 1,2-Addition



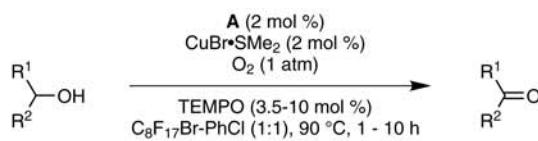
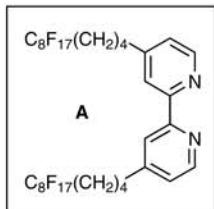
Ar	Yield	%ee
Ph	92%	84%
3-MeO-C <sub>6</sub> H <sub>4</sub>	95%	85%
4-Me-C <sub>6</sub> H <sub>4</sub>	91%	81%
1-Naphthyl	98%	91%
4-Cl-C <sub>6</sub> H <sub>4</sub>	93%	82%

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.

Ragagnin, G.; Betzmeier, B.; Quici, S.; Knochel, P. *Tetrahedron* **2002**, *58*, 3985.

## Oxidation



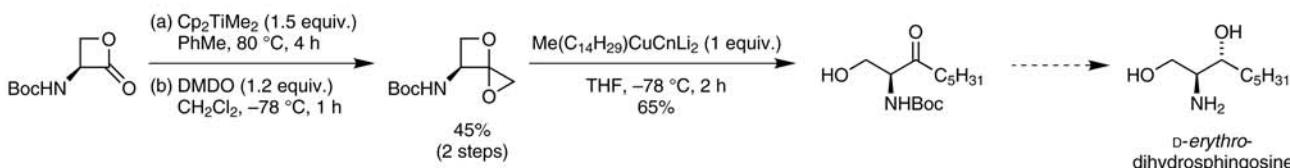
R <sup>1</sup>	R <sup>2</sup>	Yield
p-NO <sub>2</sub> Ph	H	93%
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub>	H	73%
p-NCPh	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	95%
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub>	CH <sub>3</sub>	88%

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-*o*-phytosphingosine.

Ndakala, A. J.; Hashemzadeh, M.; So, R. C.; Howell, A. R. *Org. Lett.* **2002**, *4*, 1719.

## Methylenation/Oxidation/Cuprate Addition

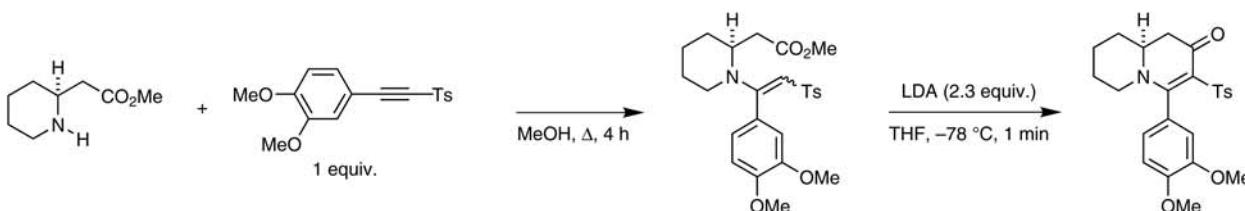


The total syntheses of D-erythro-dihydrosphingosine and D-xylo-*o*-phytosphingosine are reported.

Conjugate addition and intramolecular acylation of an amino ester with an acetylinic sulfone.

Back, T. G.; Hamilton, M. D. *Org. Lett.* **2002**, *4*, 1779.

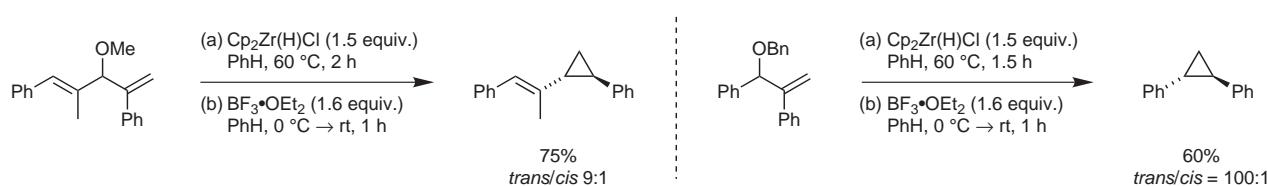
## Conjugate Addition/Intramolecular Acylation



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

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

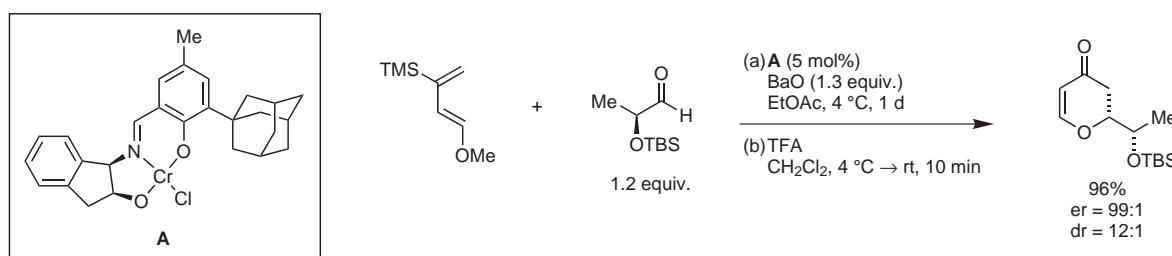
### Cyclopropanation



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

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

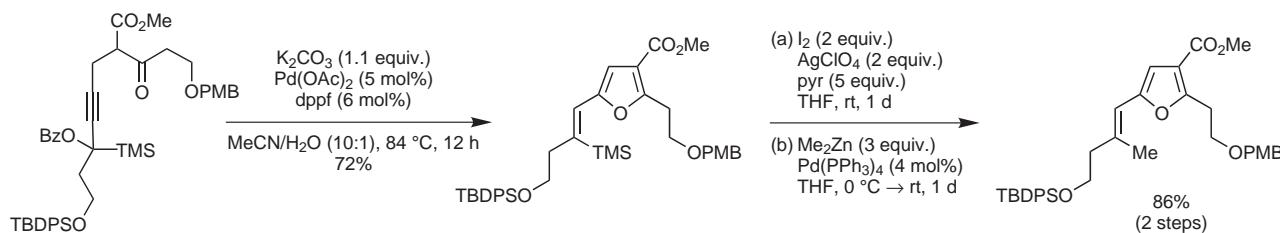
### [4 + 2] - Cycloaddition



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

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

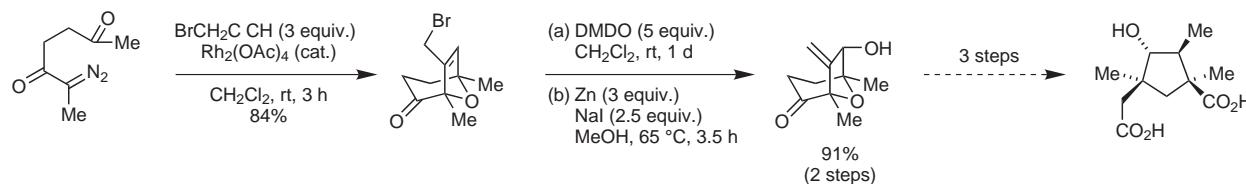
### Heteroannulation



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

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

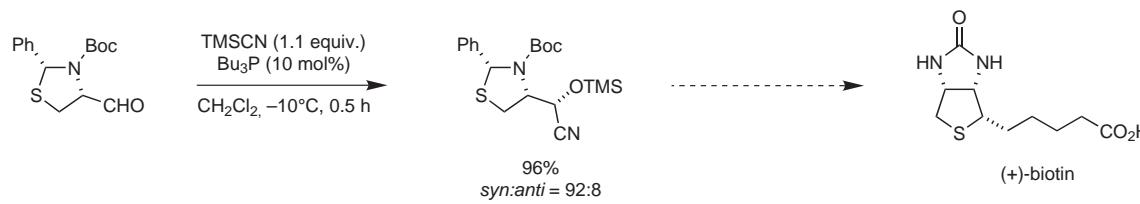
### Dipolar Cycloaddition



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

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

### Cyanosilylation



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