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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The journals regularly covered by the abstractors are:

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Chemical Communications
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European Journal of Organic Chemistry
Helvetica Chimica Acta
Journal of Organic Chemistry
Journal of the American Chemical Society
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Synthesis 2002, No. 2, 01 02 2002. Article Identifier:
1437-210X,E;2002,0,01,292,297,ftx,en;X00202SS.pdf.
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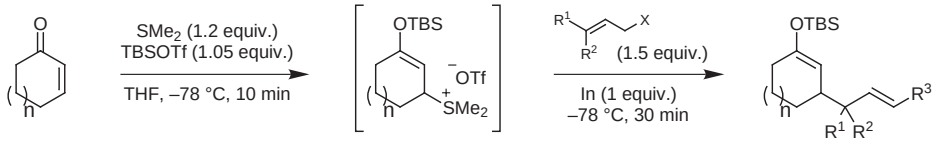
ISSN 0039-7881

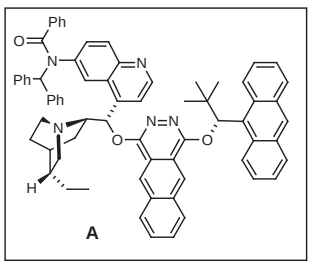
Allylindium addition to α,β-unsaturated enones. **1,4-Addition**
Lee, P. H.; Lee, K.; Kim, S. *Org. Lett.* **2001**, *3*, 3205.

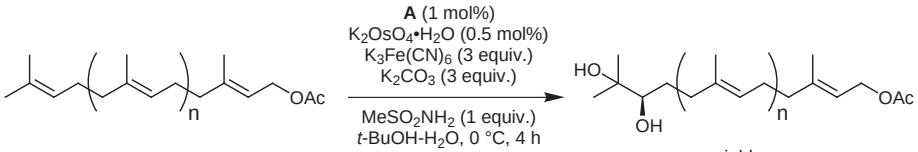


n	R^1	R^2	Yield
0	H	H	62%
1	Me	H	62%
2	Me	Me	66%

12 examples (yields 61-74%). 4 examples of 1,4-addition to hex-4-en-3-one (yields 62-72%), the reaction of the alkylindium reagent generated from ethyl-2-iodoethanoate (4 examples; yields 62-74%), and the use of PPh_3 in place of SMe_2 (1 example; yield 15%) are also reported.

Catalytic enantio- and position-selective dihydroxylation of polyisoprenoids. **Enantioselective Dihydroxylation**
Corey, E. J.; Zhang, J. *Org. Lett.* **2001**, *3*, 3211.

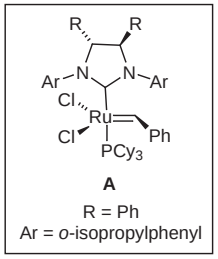


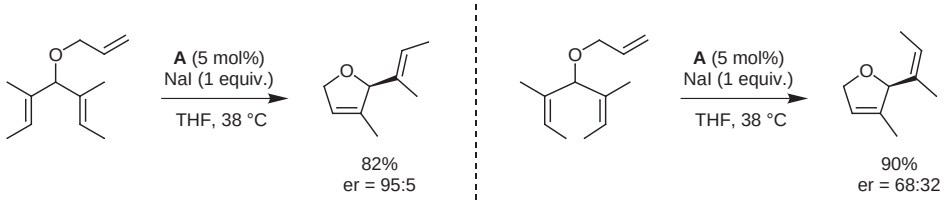


n	yield	er
1	72%	99:1
2	59%	98:2

Dihydroxylation of (*E*)-nerolidol (yield 78%, %ee 94%) and squalene (yield 38%, %ee 90%), and the synthesis of **A** are also reported.

Enantioselective ruthenium-catalysed ring closing metathesis. **Ring Closing Metathesis**
Seiders, T. J.; Ward, D. W.; Grubbs, R. H. *Org. Lett.* **2001**, *3*, 3225.





3 examples (yields 78-96%, %ee 35-90%). Syntheses of the chiral catalysts are also reported.

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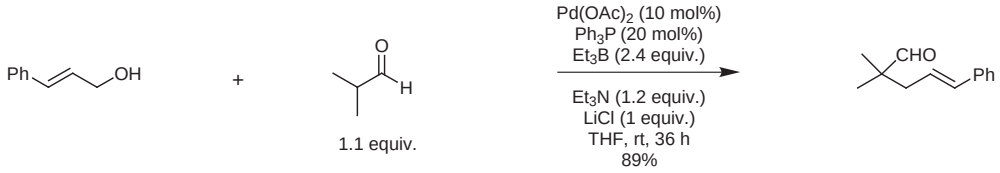
Simple direct α-allylation of aldehydes with allyl alcohols. **α-Allylation**
Kimura, M.; Horino, Y.; Mukai, R.; Tanaka, S.; Tamaru, Y. *J. Am. Chem. Soc.* **2001**, *123*, 10401.



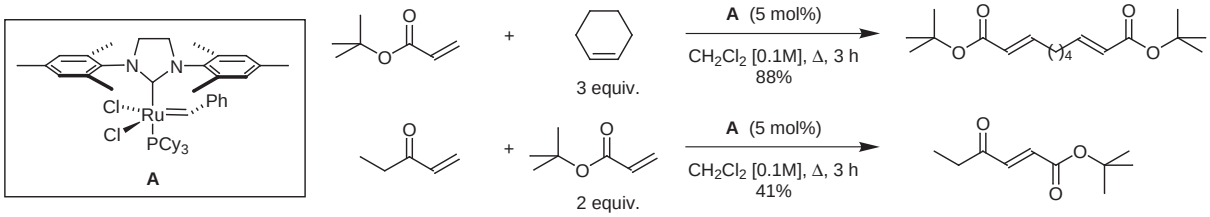
12 examples (yields 63-90%). The allylation works for a variety of 1° and 2° allylic alcohols. 5 Aldehydes and 6 different alcohols used.

Three-component catalytic asymmetric synthesis of aliphatic amines. **Asymmetric 1,2-Addition**
Porter, J. R.; Traverse, J. F.; Hoveyda, A. H.; Snapper M. L. *J. Am. Chem. Soc.* **2001**, *123*, 10409.

R	Yield	%ee
C_4H_9	69%	97%
$Ph(CH_2)_2$	98%	94%
$(CH_3)_2CHCH_2$	58%	95%
$HOCH_2$	48%	98%

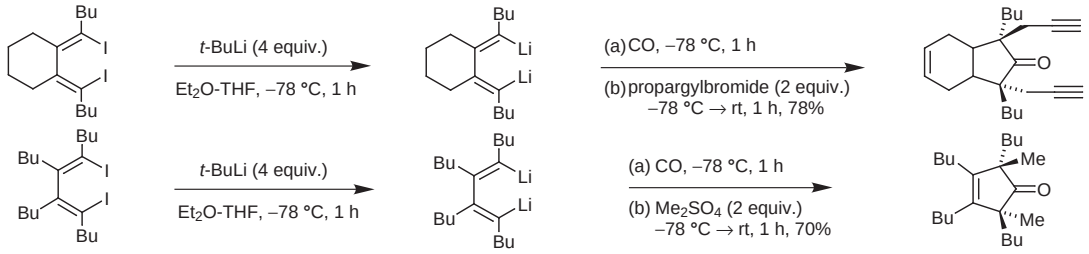
11 examples (yields 48-98%, %ee 94-98%).

Olefin metathesis involving ruthenium enoic carbene complexes. **Metathesis**
Choi, T.-L.; Lee, C. W.; Chatterjee, A. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 10417.



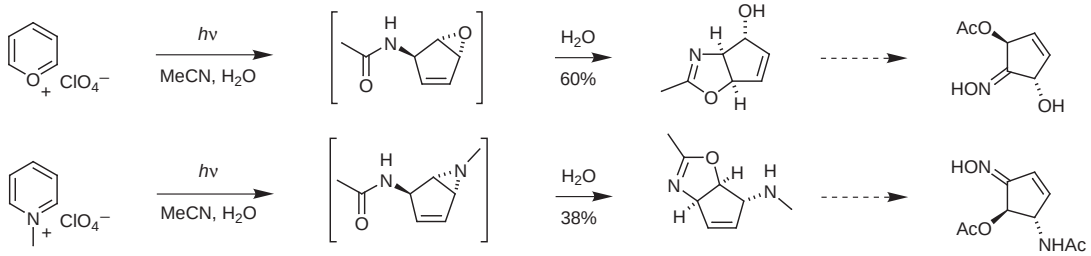
11 examples of cross metathesis (yield 41-99%) and 7 examples involving dimerisation of the substrate (yield 75-95%).

Highly regio- and stereoselective 1,1-cycloaddition of carbon monoxide with 1,4-dilithio-1,3-dienes. **Annulation; 1,1-Cycloaddition**
Song, Q.; Chen, J.; Jin, X.; Xi, Z. *J. Am. Chem. Soc.* **2001**, *123*, 10419.



13 examples (yield 58-91%). Benzyl bromide, allyl bromide and methyl iodide were also used as electrophiles.

Photohydrations and photoamidations of heterocycles leading to bicyclic oxazolines and functionalized cyclopentenes. **Ring Contraction**
Clark, M. A.; Schoenfeld, R. C.; Ganem, B. *J. Am. Chem. Soc.* **2001**, *123*, 10425.



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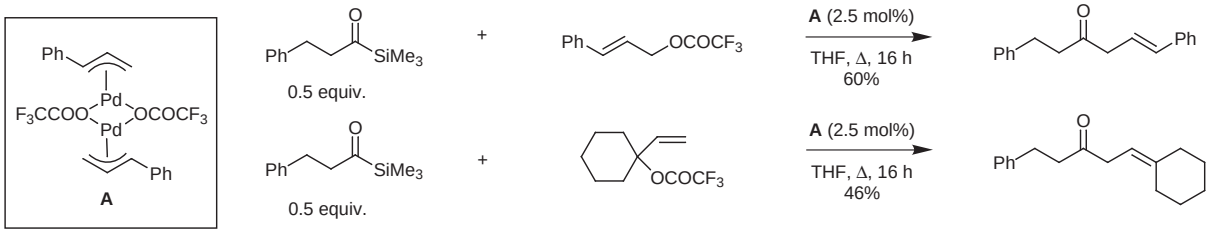
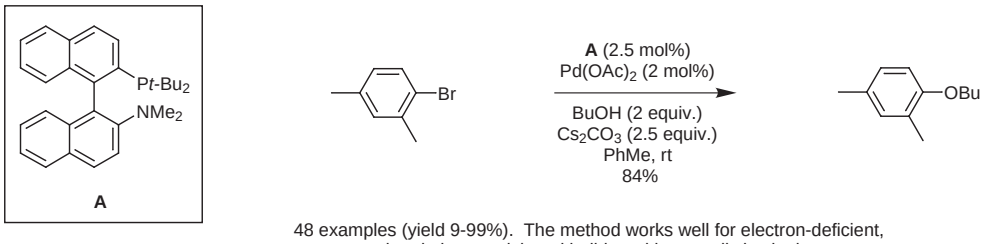
Palladium-catalyzed acylation of allylic esters with acylsilanes. **Acylation**
Obora, Y.; Ogawa, Y.; Imai, Y.; Kawamura, T.; Tsuji, Y. *J. Am. Chem. Soc.* **2001**, *123*, 10489.



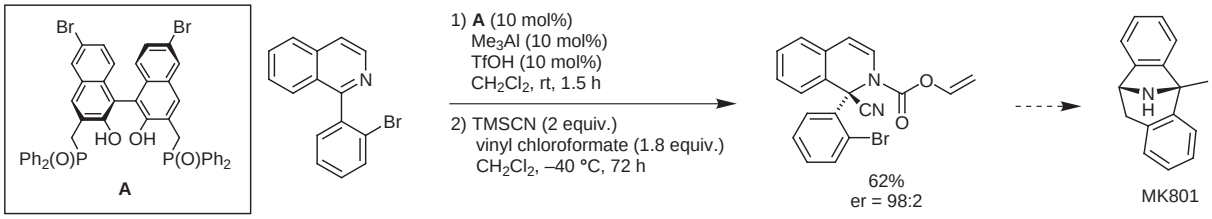
10 examples (yield 43-63%). Best results achieved with trifluoroacetate derivatives.

An efficient intermolecular palladium-catalyzed synthesis of aryl ethers. **C–O sp^2-sp^3 Coupling**
Torraca, K. E.; Huang, X.; Parrish, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2001**, *123*, 10770.



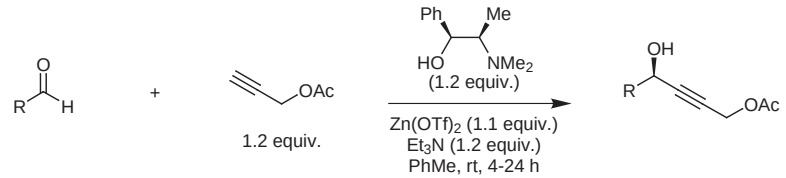
48 examples (yield 9-99%). The method works well for electron-deficient, neutral and electron-rich aryl halides with an *o*-alkyl substituent.

Enantioselective construction of a quaternary stereocentre *via* a Reissert-type reaction catalyzed by an electronically tuned bifunctional catalyst. **Enantioselective Addition**
Funabashi, K.; Ratni, H.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2001**, *123*, 10784.



11 examples (yields 59-98%, %ee 73-95%). MK801 was synthesized in six steps from the Reissert product.

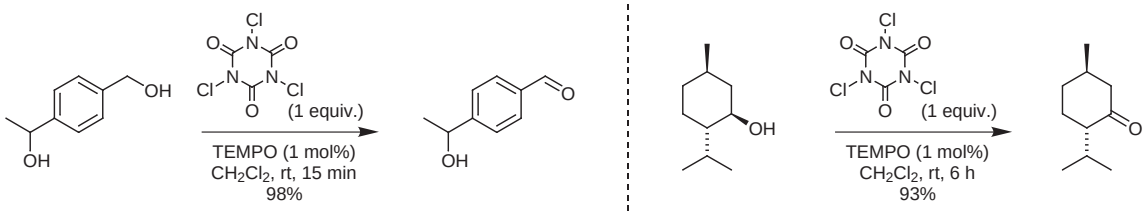
Enantioselective direct addition of propargyl acetate to aldehydes. **Enantioselective 1,2-Addition**
El-Sayed, E.; Anand, N. K.; Carreira, E. M. *Org. Lett.* **2001**, *3*, 3017.



R	Yield	%ee
i-Pr	95%	96%
c-C_6H_{11}	88%	97%
t-$BuCH_2$	68%	97%
(*S*)-CH_3CH(OTBS)	70%	93% de
Ph	57%	97%
$TBSOCH_2$	54%	88%

Subsequent O-silyl protection, palladium-catalyzed isomerisation, AcOH addition and hydrolysis leads to optically active γ-hydroxy α,β-unsaturated aldehydes.

Mild and chemoselective oxidation of alcohols to carbonyl compounds. **Oxidation**
De Luca, L.; Giacomelli, G.; Porcheddu, A. *Org. Lett.* **2001**, *3*, 3041.



14 examples of oxidation of primary alcohols to aldehydes (yields 70-99%), 6 examples of oxidation of secondary alcohols to ketones (yields 75-98%) and 3 examples of chemoselective oxidation of diols to hydroxyaldehydes (yields 95-98%).

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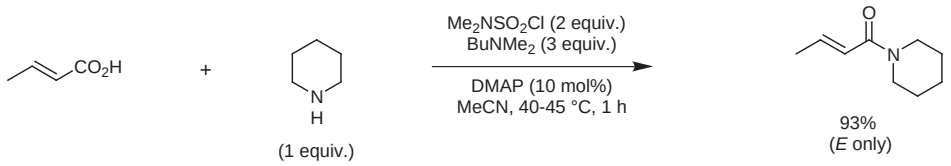
Esterification and amidation using dimethylsulfamoylchloride and *N*,*N*-dimethylamines.
Nakasugi, K.; Nakamura, A.; Tanabe, Y. *Tetrahedron Lett*. **2001**, *42*, 7427.

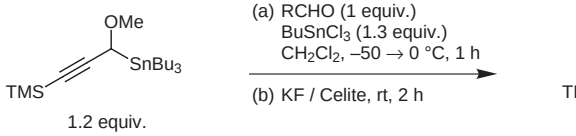
Esterification and Amidation



15 examples of esterification (yields 71-94%) and 7 examples of amidation (yields 92-94%).

Diastereoselective synthesis of propagylic 1,2-*anti*-diol derivatives.
Savall, B. M.; Powell, N. A.; Roush, W. R. *Org. Lett.* **2001**, *3*, 3057.

Stereoselective 1,2-Addition

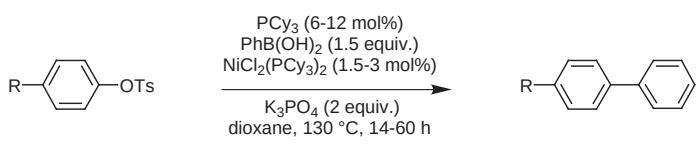


RCHO	yield	*anti* :*syn*
isobutyraldehyde	96%	97:3
benzaldehyde	96%	97:3
crotonaldehyde	96%	96:4
hydrocinnamaldehyde	98%	97:3
pivaldehyde	96%	98:2

Reaction of the MOM-protected α-hydroxy propargylstannanes with the same aldehydes gave the corresponding products in 90-98% yield. The synthesis of a key intermediate towards the synthesis of formamicin is also reported.

$NiCl_2(PCy_3)_2$-catalyzed cross-coupling of aryl tosylates and arylboronic acids.
Zim, D.; Lando V. R.; Dupont, J.; Monteiro, A. L. *Org. Lett.* **2001**, *3*, 3049.

sp^2–sp^2 Coupling

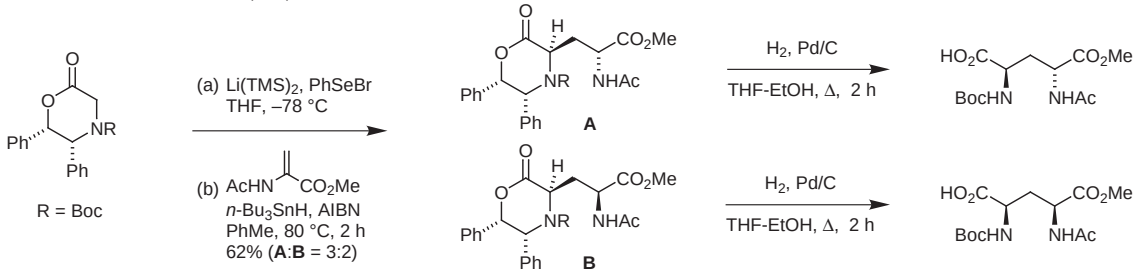


R	Yield
COMe	94%
CN	96%
OMe	89%
t-Bu	83%
Me	79%

11 examples (yields 47-99%).

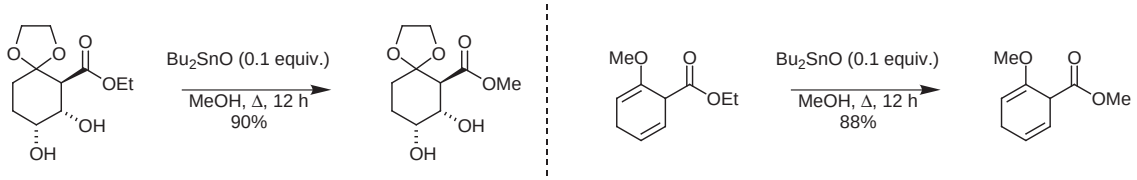
Radical addition of Williams' glycinate auxiliaries to α-amidoacrylates.
Kabat, M. *Tetrahedron Lett*. **2001**, *42*, 7521.

Stereoselective Radical Addition



Chemoselective dibutyltin oxide-mediated transesterification.
Baumhof, P; Mazitschek, R; Giannis, A. *Angew. Chem. Int. Ed.* **2001**, *40*, 3672.

Transesterification



16 examples (yields 77-96%). *tert*-Butyl alcohol cannot be used for transesterification.

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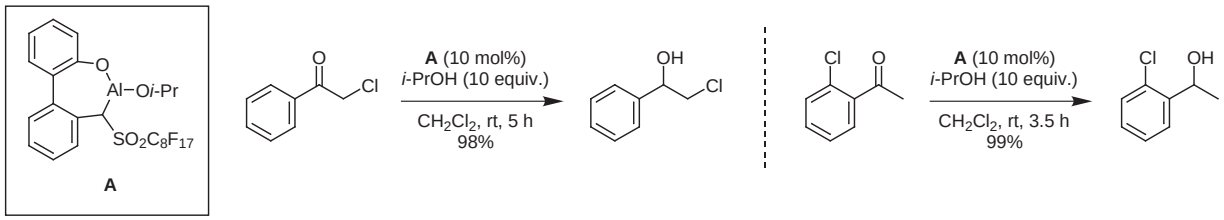
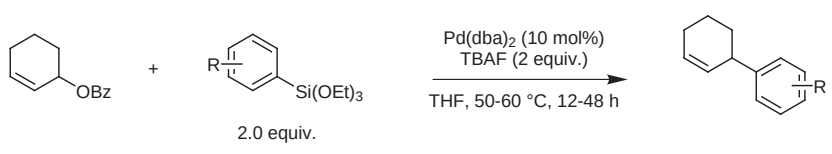
Meerwein–Ponndorf–Verley reduction with new aluminium catalysts. **Reduction**
Ooi, T.; Ichikawa, H.; Maruoka, K. *Angew. Chem. Int. Ed.* **2001**, *40*, 3610.



7 examples (yields 82-99%). All examples have been repeated with 5 g of starting ketones. Synthesis of **A** is also reported.

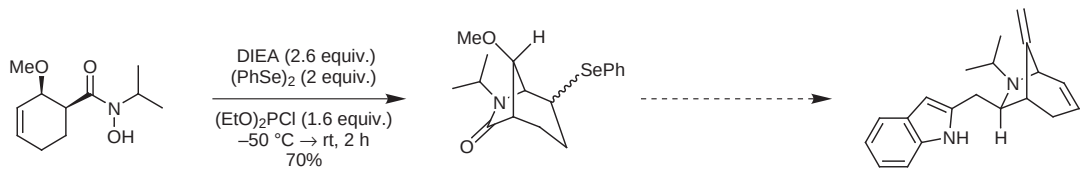
Palladium-catalyzed arylation of cyclic allylic benzoates. **sp^3–sp^2 Coupling**
Correia, R.; DeShong, P. *J. Org. Chem.* **2001**, *66*, 7159.



R	Yield
p-Me	87%
m-Me	86%
o-Me	77%
p-OMe	88%
m-OMe	88%

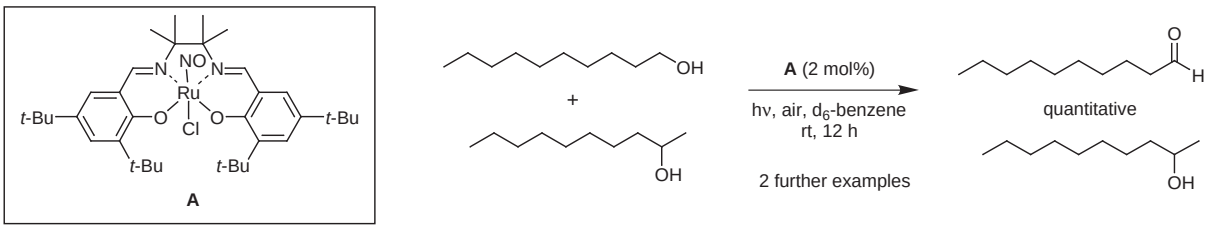
12 examples (yields 9-88%).

Imidyl and amidyl radical cyclisations: application to (±)-peduncularine. **N-Radical Cyclisations**
Lin, X.; Artman, III, G. D.; Stien, D.; Weinreb, S. M. *Tetrahedron* **2001**, *57*, 8779.



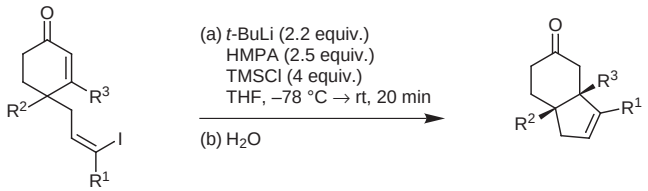
7 further amidyl examples (yields 59-84%) and 5 imidyl examples (yields 49-86%) are reported.

Chemoselective aerobic oxidation of primary alcohols catalysed by Ru complex. **Oxidation**
Miyata, A.; Murakami, M.; Irie, R.; Katsuki, T. *Tetrahedron Lett.* **2001**, *42*, 7067.



Functionalised primary alcohols (3 examples) were also oxidised in quantitative yield.

Intramolecular conjugate addition of alkenyl and aryl functions to enones initiated by Li-I exchange. **Conjugate Addition**
Piers, E.; Harrison, C. L.; Zetina-Rocha, C. *Org. Lett.* **2001**, *3*, 3245.



R^1	R^2	R^3	Yield
Me	H	H	91%
Me	H	Me	72%
Me	Me	H	85%
Me	Bn	H	81%

8 examples using alkenyl functions (yields 72-91%) and 3 examples using aryl functions (yields 75-90%).

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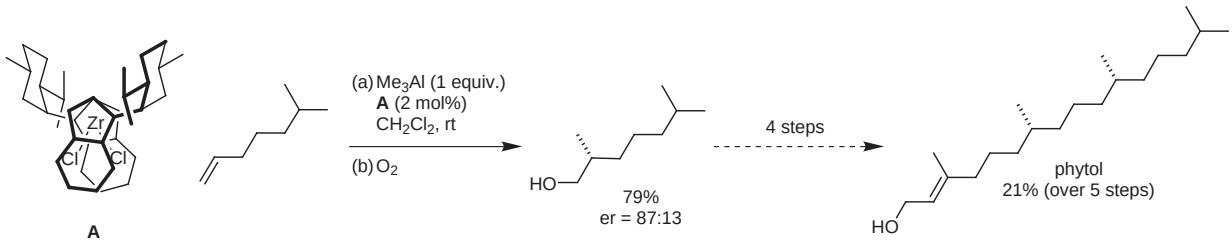
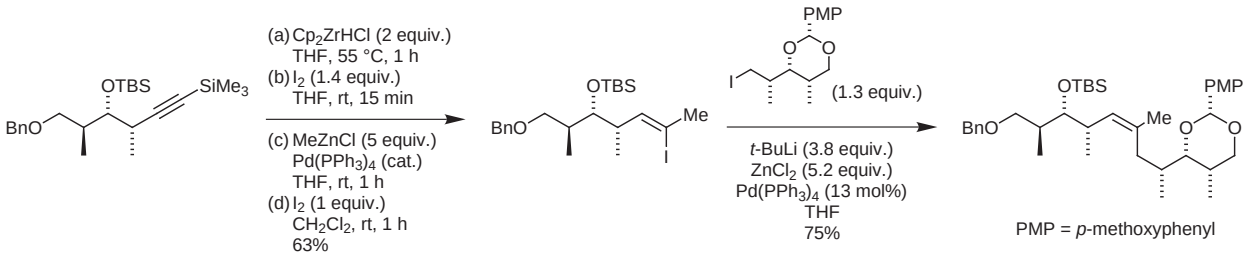
Zirconium-catalyzed asymmetric carboalumination of alkenes towards the synthesis of chiral oligoisoprenoids. **Carboalumination**
Huo, S.; Negishi, E. *Org. Lett.* **2001**, *3*, 3253.



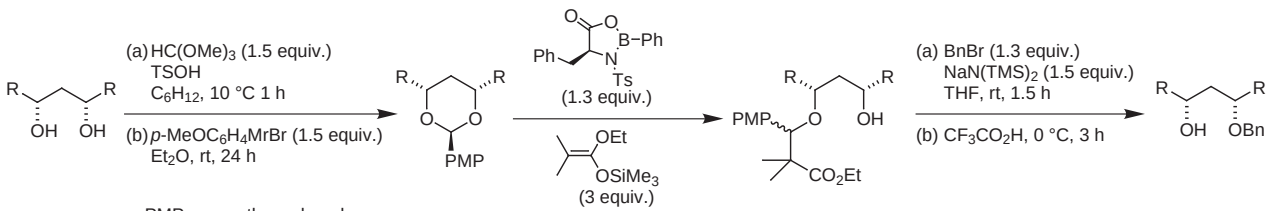
7 examples (yields 65-86%, %ee 72-74%).

Stereoselective synthesis of functionalized trisubstituted olefins via palladium(0)-catalyzed cross-coupling. **sp^3–sp^2 Coupling**
Arefolov, A.; Langille, N. F.; Panek, J. S. *Org. Lett.* **2001**, *3*, 3281.



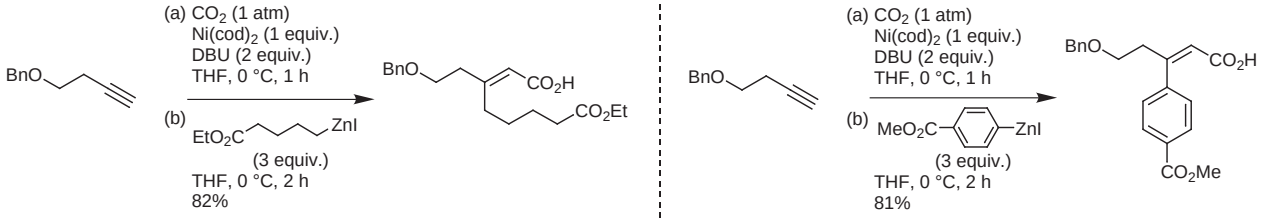
2 examples of (+)-discodermolide models and 2 examples of callystatin A models.

Enantioselective ring cleavage of dioxane acetals: Application to desymmetrization of *meso*-1,3-diols. **Enantioselective Ring Cleavage**
Harada, T.; Sekiguchi, K.; Nakamura, T.; Suzuki, J.; Oku, A. *Org. Lett.* **2001**, *3*, 3281.



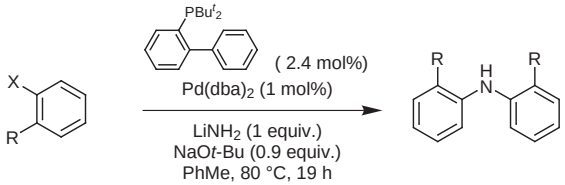
4 examples (yields 26-38%, %ee 86-94%).

Nickel-promoted alkylative or arylative carboxylation of alkynes. **sp^3–sp^2 Coupling: Carboxylation**
Takimoto, M.; Shimizu, K.; Miwako, M. *Org. Lett.* **2001**, *3*, 3345.



11 examples (yields 33-100%) using both aliphatic and aromatic terminal alkynes in combination with a variety of organozincs, including functionalised aryl- and alkylzinc reagents. β-Hydride elimination only occurred when Et_2Zn was employed.

New ammonia equivalents for the Pd-catalysed amination of aryl halides. **Amination**
Huang, X.; Buchwald, S. L. *Org. Lett.* **2001**, *3*, 3417.



X	R	T	Yield
Cl	OMe	80 °C	95%
Cl	Me	80 °C	94%
Br	*i*-Pr	100 °C	86%
Br	Ph	100 °C	91%

8 Examples of di- and triarylamine preparation (yields 64-95%). The amination of *m*- and *p*-substituted aryl halides using LHMDS (5 examples; yields 94-96%) and *o*-substituted aryl halides using aminotriphenylsilane (5 examples; yields 85-98%) are also reported.

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