**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, Steven McAteer, Marcel de Puit, Sukhjinder Uppal, Tanya Wildmann and Josephine Yuen, Department of Chemistry, Leeds University, Leeds, LS2 9JT, UK.

The journals regularly covered by the abstractors are:

- 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
- Organic Letters
- Organometallics
- Perkin Transactions 1
- Synlett
- Synthesis
- Tetrahedron
- Tetrahedron Asymmetry
- Tetrahedron Letters

Georg Thieme Verlag does not accept responsibility for the accuracy, content, or selection of the data.

---

**Allylindium addition to α,β-unsaturated enones.**


![Chemical Structure](image1)

1,4-Addition

<table>
<thead>
<tr>
<th>n</th>
<th>R₁</th>
<th>R₂</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>H</td>
<td>H</td>
<td>62%</td>
</tr>
<tr>
<td>1</td>
<td>Me</td>
<td>H</td>
<td>62%</td>
</tr>
<tr>
<td>2</td>
<td>Me</td>
<td>Me</td>
<td>66%</td>
</tr>
</tbody>
</table>

12 examples (yields 61-74%). 4 examples of 1,4-addition to hex-4-en-3-one (yields 62-72%), the reaction of the allylindium reagent generated from ethyl-2-iodoethanoate (4 examples; yields 62-74%), and the use of PPh₃ in place of SMₑ₂ (1 example; yield 15%) are also reported.

**Catalytic enantio- and position-selective dihydroxylation of polyisoprenoids.**


![Chemical Structure](image2)

**Enantioselective Dihydroxylation**

<table>
<thead>
<tr>
<th>n</th>
<th>Yield</th>
<th>er</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>72%</td>
<td>99:1</td>
</tr>
<tr>
<td>2</td>
<td>59%</td>
<td>98:2</td>
</tr>
</tbody>
</table>

Dihydroxylation of (E)-nerolidol (yield 76%, %ee 94%) and squalene (yield 38%, %ee 90%), and the synthesis of **A** are also reported.

**Enantioselective ruthenium-catalysed ring closing metathesis.**


![Chemical Structure](image3)

**Ring Closing Metathesis**

<table>
<thead>
<tr>
<th>R</th>
<th>Ar</th>
<th>Ar'</th>
<th>Ph</th>
<th>Cl</th>
<th>PCy₃</th>
<th>R₁</th>
<th>R₂</th>
<th>Yield</th>
<th>er</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td>Ph</td>
<td>o-isopropylphenyl</td>
<td></td>
<td></td>
<td></td>
<td>82%</td>
<td>99:5</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>A</strong></td>
<td>(5 mol%)</td>
<td>Nal (1 equiv.)</td>
<td></td>
<td></td>
<td></td>
<td>THF, 38 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3 examples (yields 78-96%, %ee 35-90%). Syntheses of the chiral catalysts are also reported.
Simple direct \(\alpha\)-allylation of aldehydes with allyl alcohols.

\[
\text{Ph} \overset{\text{OH}}{\rightleftharpoons} \text{CHO} \overset{\text{Ph}}{\rightleftharpoons} \text{Et} \\
\]

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

Three-component catalytic asymmetric synthesis of aliphatic amines.

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{N} & \quad \text{Bu} \\
\text{N} & \quad \text{Bu} \\
\text{N} & \quad \text{Bu} \\
\end{align*}
\]

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

Olefin metathesis involving ruthenium enoic carbene complexes.

\[
\begin{align*}
\text{H} & \quad \text{R} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

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.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{Bu} & \quad \text{Bu} \\
\text{Bu} & \quad \text{Bu} \\
\text{Bu} & \quad \text{Bu} \\
\end{align*}
\]

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

Photohydration and photoamidation of heterocycles leading to bicyclic oxazolines and functionalized cyclopentenes.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

Synthesis 2002, No. 1, 146–151  ISSN 0039-7881  © Thieme Stuttgart · New York
Palladium-catalyzed acylation of allylic esters with acylsilanes.

Acylation

\[
\begin{array}{c}
\text{Ph} \quad \text{O} \\
\text{SiMe}_3 \\
\end{array}
\]

0.5 equiv.

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{SiMe}_3 \\
\end{array}
\]

0.5 equiv.

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{OCOCF}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{OCOCF}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{OCOCF}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{OCOCF}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{OCOCF}_3 \\
\end{array}
\]

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

An efficient intermolecular palladium-catalyzed synthesis of aryl ethers.

C–O sp²-sp³ Coupling

\[
\begin{array}{c}
\text{Ph} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Br} \\
\text{Me}_{2}N \\
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{Bu} \\
\end{array}
\]

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

Enantioselective construction of a quaternary stereocentre via a Reissert-type reaction catalyzed by an electronically tuned bifunctional catalyst.

Enantioselective Addition

\[
\begin{array}{c}
\text{Ph} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Br} \\
\text{Me}_{2}N \\
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{Bu} \\
\end{array}
\]

11 examples (yields 59-96%, %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

\[
\begin{array}{c}
\text{Ph} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Me}_{2}N \\
\end{array}
\]

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

\[
\begin{array}{c}
\text{Ph} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Me} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Me} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Me} \\
\end{array}
\]

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 hydroxylaldehydes (yields 55-98%).
Esterification and amidation using dimethylsulfamoylchloride and N,N-dimethylamines.

```
+  (1 equiv.)
```

```
MeNO2Cl (2 equiv.)
BuNMe2 (3 equiv.)
DMAP (10 mol%) 
MeCN, 40-45 °C, 1 h
```

```
93% (E only)
```

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

Diastereoselective synthesis of propargylic 1,2-anti-diol derivatives.

```
RCHO (1 equiv.)
BuSnCl3 (1.3 equiv.) 
CH2Cl2, –50 → 0 °C, 1 h
```

```
KF / Celite, rt, 2 h
```

```
RCHO
isobutyraldehyde
benzaldehyde
crotonaldehyde
hydrocinnamaldehyde
pivaldehyde
```

```
96%
96%
96%
98%
96%
```

```
anti : syn
97:3
97:3
96:4
97:3
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.

NiCl2(PCy3)2-catalyzed cross-coupling of aryl tosylates and arylboronic acids.

```
R RCOMe
CN
OMe
t-Bu
Me
```

```
Yield
94%
96%
89%
83%
79%
```

```
NiCl2(PCy3)2 (1.5-3 mol%)
PhB(OH)2 (1.5 equiv.)
K3PO4 (2 equiv.)
dioxane, 130 °C, 14-60 h
```

```
11 examples (yields 47-99%).
```

Radical addition of Williams’ glycinate auxiliaries to α-amidoacrylates.

```
(a) Li(TMS)2, PhSeBr
THF, –78 °C
(b) AicHN
```

```
H2, Pd/C
THF-EtOH, ∆, 2 h
```

```
H2O2
CO2Me
```

```
H2O2
```

Chemoselective dibutyltin oxide-mediated transesterification.

```
BuSnO (0.1 equiv.)
MeOH, ∆, 12 h
96%
```

```
BuSnO (0.1 equiv.)
MeOH, ∆, 12 h
88%
```

```
MeO
```

```
MeO
```

16 examples (yields 77-96%). tert-Butyl alcohol cannot be used for transesterification.
Meerwein–Ponndorf–Verley reduction with new aluminium catalysts.


Reduction

\[
\begin{align*}
\text{O} & \quad \text{Me-O-Pr} \\
\text{SO}_2 \text{C}_8 \text{F}_{17} & \quad \text{OH} & \text{Cl} & \text{OH} & \text{Cl}
\end{align*}
\]

A (10 mol%) i-PrOH (10 equiv.)

CH\(_2\)Cl\(_2\), rt, 5 h

98%

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

\[
\begin{align*}
\text{O} & \quad \text{Me-O-Pr} \\
\text{Si(OEt)}_3 & \quad \text{2.0 equiv.}
\end{align*}
\]

Pd(db\(_{2}\)) (10 mol%) TBAF (2 equiv.)

THF, 50-60 °C, 12-48 h

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

\[
\begin{align*}
\text{MeO} & \quad \text{N-O} \\
\text{OH} & \quad \text{SePh}
\end{align*}
\]

DIEA (2.6 equiv.) (PhSe)\(_2\) (2 equiv.)

\((\text{EtO})_2\) PCl (1.6 equiv.)

–50 °C \(\rightarrow\) rt, 2 h

70%

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

\[
\begin{align*}
\text{O} & \quad \text{Me-O-Pr} \\
\text{OH} & \quad \text{O}
\end{align*}
\]

A (2 mol%) hv, air, d\(_6\)-benzene

rt, 12 h

quantitative

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

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_3 & \quad \text{I}
\end{align*}
\]

(a) t-BuLi (2.2 equiv.) HMPA (2.5 equiv.) TMSCl (4 equiv.)

THF, –78 °C \(\rightarrow\) rt, 20 min

(b) H\(_2\)O

8 examples using alkenyl functions (yields 72-91%) and 3 examples using aryl functions (yields 75-90%).
Zirconium-catalyzed asymmetric carboalumination of alkenes towards the synthesis of chiral oligoisoprenoids.


Carboalumination

ZrCl2

Me3Al (1 equiv.)

O2

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

Stereoselective synthesis of functionalized trisubstituted alkenes via palladium(0)-catalyzed cross-coupling.


sp3–sp2 Coupling

Enantioselective ring cleavage of dioxane acetals: Application to desymmetrization of meso-1,3-diols.


Enantioselective Ring Cleavage

Nickel-promoted alkylative or arylative carboxylation of alkenes.


sp3–sp2 Coupling: Carboxylation

New ammonia equivalents for the Pd-catalysed amination of aryl halides.


Amination

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 aminophenylsilane (5 examples; yields 85-98%) are also reported.