**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:
- Angewandte Chemie
- Chemical Communications
- Chemisty-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

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


![Allylindium addition to α,β-unsaturated enones.](image)

**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 alkylindium 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.

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


![Catalytic enantio- and position-selective dihydroxylation of polyisoprenoids.](image)

**Enantioselective Dihydroxylation**

![Enantioselective Dihydroxylation](image)

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

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


![Enantioselective ruthenium-catalysed ring closing metathesis.](image)

**Ring Closing Metathesis**

![Ring Closing Metathesis](image)

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.

\[ \text{Ph} \equiv \text{CHO} + \text{H}_2\text{N-CH(Ph)} \rightarrow \text{Ph} - \text{CH(CHO)} \]

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.

\[ \text{R} - \text{O} + \text{H}_2\text{N-CH(Ph)} \rightarrow \text{R} - \text{N}(\text{Ph})\text{CH}_2\text{NH}_2 \]

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

Olefin metathesis involving ruthenium enoic carbene complexes.

\[ \text{A} \] 3 equiv.

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.

\[ \text{A} \] 5 mol%.

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.
Palladium-catalyzed acylation of allylic esters with acylsilanes. 

An efficient intermolecular palladium-catalyzed synthesis of aryl ethers.

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

Enantioselective direct addition of propargyl acetate to aldehydes.

Mild and chemoselective oxidation of alcohols to carbonyl compounds.
Esterification and amidation using dimethylsulfamoyl chloride and N,N-dimethylamines.

\[
\text{CO}_2 \text{H} + \begin{array}{c}
\text{N}
\end{array} \quad \begin{array}{c}
\text{H}
\end{array}
\xrightarrow{\text{Me}_2\text{NSO}_2\text{Cl} \text{ (2 equiv.)}}
\text{BuNMe}_2 \text{ (3 equiv.)}
\xrightarrow{\text{DMAP (10 mol%)}}
\text{MeCN, 40-45 °C, 1 h}
\]

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

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

\[
\text{TMS-SnBu}_3 \quad \text{R} \quad \text{OH}
\xrightarrow{\text{RCHO (1 equiv.) BuSnCl}_3 \text{ (1.3 equiv.) CH}_2\text{Cl}_2, -50 \to 0 \degree C, 1 h}}
\xrightarrow{\text{KF / Celite, rt, 2 h}}
\text{RCHO}
\]

(a) isobutyraldehyde (96% yield, 97:3 anti: syn)
(b) benzaldehyde (96% yield, 97:3 anti: syn)
(c) crotonaldehyde (96% yield, 97:3 anti: syn)
(d) hydrocinnamaldehyde (98% yield, 97:3 anti: syn)
(e) pivaldehyde (96% yield, 98:2 anti: syn)

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

\[
\text{NiCl}_2(\text{PCy}_3)_2 \text{-catalyzed cross-coupling of aryl tosylates and arylboronic acids.}
\]


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.

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

\[
\text{Li(TMS)₂, PhSeBr}
\xrightarrow{\text{THF, −78 ºC}}
\]

(a) Li(TMS)₂, PhSeBr
(b) AchH₂, n-Bu₃SnH, AIBN

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

Chemoselective dibutyltin oxide-mediated transesterification.

\[
\text{Bu}_2\text{SnO (0.1 equiv.) MeOH, Δ, 12 h 99%}
\]

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


Reduction

\[
\text{A} (10 \text{ mol\%}) \quad \text{H}^+ \text{PrOH (10 equiv.)}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{OH} \\
\text{Cl} & \quad \text{OH} \\
\text{OCl} & \quad \text{OHCl}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{Cl}_2, \text{rt}, 5 \text{ h} & \quad 98\% \\
\text{CH}_2\text{Cl}_2, \text{rt}, 3.5 \text{ h} & \quad 99\%
\end{align*}
\]

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

Palladium-catalyzed arylation of cyclic allylic benzoates.


\[\begin{align*}
\text{PhO} & \quad + \quad \text{R} \quad \text{Si(\text{OE}i)_3} \\
\text{2.0 equiv.}
\end{align*}\]

\[
\begin{align*}
\text{Pd(db}a)_2 (10 \text{ mol\%}) \\
\text{TBAF (2 equiv.)}
\end{align*}
\]

\[
\text{THF, 50-60 °C, 12-48 h}
\]

\[
\begin{array}{c|c}
\text{R} & \text{Yield} \\
\hline
\text{p-Me} & 87\% \\
\text{m-Me} & 86\% \\
\text{o-Me} & 77\% \\
\text{p-OMe} & 84\% \\
\text{m-OMe} & 88\%
\end{array}
\]

12 examples (yields 9-88%).

Imidyl and amidyl radical cyclisations: application to \((\pm)\)-peduncularine.


\[\begin{align*}
\text{PhSe} \quad \text{2 equiv.} \\
\text{2.6 equiv.} \\
\text{(EtO)}_2 \text{PCl (1.6 equiv.)} \\
\text{–50 °C} \rightarrow \text{rt, 2 h}
\end{align*}\]

\[70\%\]

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.


\[\begin{align*}
\text{A} (2 \text{ mol\%}) \\
\text{hv, air, d}_6 \text{-benzene} \\
\text{rt, 12 h}
\end{align*}\]

Functionalisled 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

\[\begin{align*}
\text{(a) t-BuLi (2.2 equiv.)} \\
\text{HMPA (2.5 equiv.)} \\
\text{TMSCl (4 equiv.)} \\
\text{THF, –78 °C} \rightarrow \text{rt, 20 min}
\end{align*}\]

\[\begin{align*}
\text{(b) H}_2\text{O}
\end{align*}\]

\[\begin{align*}
\text{R}_1 \quad \text{R}_2 \quad \text{R}_3 \quad \text{R}_1 \\
\text{A} & \quad \text{OH} \\
\text{quantitative}
\end{align*}\]

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**

![Chemical structure](image)

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

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


**sp^3–sp^2 Coupling**

![Chemical structure](image)

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**

![Chemical structure](image)

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

Nickel-promoted alkylative or arylative carboxylation of alkynes.


**sp^3–sp^2 Coupling: Carboxylation**

![Chemical structure](image)

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 Et₂Zn was employed.

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


**Amination**

![Chemical structure](image)

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 aminetriphenylsilane (5 examples; yields 85-88%) are also reported.