**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.

The journals regularly covered by the abstractors are:
- Advanced Synthesis & Catalysis
- 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

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**Total synthesis of Batzelladine D.**

**1,3-Dipolar Cycloaddition**

\[
\begin{align*}
\text{(a) PhMe, 100 °C} & \quad \rightarrow \quad \text{Batzelladine D} \\
\text{(b) mCPBA, CH}_2\text{Cl}_2, 0 °C & \quad 59\% \text{ over 3 steps}
\end{align*}
\]

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**Microwave-accelerated O-alkylation of carboxylic acids with O-alkylisoureas.**

**Esterification**

\[
\begin{align*}
\text{(4.5 equiv.) microwave irradiation} & \quad \rightarrow \quad 87\%
\end{align*}
\]

8 examples (yields 81-94%). Solid phase application (8 examples, yields 75-92%, purity >98%) is also reported.

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**Intramolecular olefination of an ester using Cp}_2\text{Ti[PO(Et)]}_2.**

**Olefination**

\[
\begin{align*}
\text{Cp}_2\text{Ti[P(OEt)]}_2 (4 \text{ equiv.}) & \quad \rightarrow \quad 52-67\%
\end{align*}
\]

Application to the HIJKLM fragment of ciguatoxin CTX3C is also reported.
**Diastereoselective Rh-catalyzed reductive Ireland-Claisen rearrangement.**

![Chemical structure](image)

[3,3]-Sigmatropic Rearrangement

9 examples (yields 16-91%, %de 50-92%).

**(R)-Bipyridine dioxide catalyzed allylation of aldehydes.**

![Chemical structure](image)

1.2-Addition

5 examples (yields 83-99%, %ee 56-98%).

**Atroposelective lactone cleavage.**

![Chemical structure](image)

1.2-Addition

**Diastereoselective Pd-catalyzed hydrogenation of alkenylboronic esters.**

![Chemical structure](image)

Hydrogenation

6 examples (yields 77-99%, %de 89-98%).

**Hetero Diels–Alder multicomponent coupling.**

![Chemical structure](image)

**Hetero Diels–Alder**
In-catalyzed C-alkynylation of glycals with alkynylsilanes.

1,4-Addition

Enantioselective catalytic Michael reaction of α-substituted malonates.

1,2-Addition

Enantioselective Zn-catalyzed Henry reaction.

1,4-Addition

Kinetic resolution of racemic lactones by conjugate additions of allylic organolithium species.

Oxidation

Al-catalyzed Oppenauer oxidation of alcohols.

15 examples (yields 80-98%). The use of t-BuCHO as a hydride acceptor is also reported.
Enantioselective Rh-catalyzed intermolecular allylic C−H insertion.

\[
\text{R} = \text{C}_1\text{H}_{25}
\]

5 examples (yields 40–64%).


Alkyldiene carbene insertion at anomic C−H bonds.

2 examples (yields 65–76%).

Oxidation of acetals to esters and THP/TBDMS ether deprotection using \( \text{V}_2\text{O}_5\cdot\text{H}_2\text{O}_2 \).

Selective DBU-promoted Nef reaction of secondary nitroalkanes under basic conditions.

11 examples (yields 54–80%). Primary nitroalkanes (3 examples) do not react under these conditions.
Pt-catalyzed synthesis of carbocycles from dienynes.

Enantioselective Zr-catalyzed synthesis of methyl-substituted alkanols.

Position-selective deprotonation of cyclopropane carboxamides.

Enantioselective Rh-catalyzed synthesis of [l]-amino acids.

Construction of the cyclopentenedione core of the (+)-madindolines via an azidoquinone ring contraction.

Synthesis 2002, No. 18, 2786–2793 ISSN 0039-7881 © Thieme Stuttgart · New York

**[5+2] Cycloaddition**

\[
\begin{align*}
\text{TIPSO} + \text{EtAlCl}_2 \text{ (2.2 equiv.)} \rightarrow \text{TIPSO} + \text{Co(CO)}_3 \text{ (1.1 equiv.)} \\
\text{CH}_2\text{Cl}_2, 0 \degree\text{C} \\
\text{EtAlCl}_2 \text{ (2.2 equiv.)} \rightarrow \text{59%}
\end{align*}
\]

9 examples (yields 57-98%, %de 84-100%).

**Ethynylation of silyl enol ether with chlorosilyl ethyne.**

Ethynylation

\[
\begin{align*}
\text{(a) Cl}\cdots\text{SiMe}_3 \text{ (2 equiv.)} \rightarrow \text{Ph}\cdots\text{OSiMe}_3 \\
\text{GaCl}_3 \text{ (4 equiv.)} \rightarrow \text{Ph}\cdots\text{OSiMe}_3 \\
\text{methylcyclohexane, } -40 \degree\text{C, 5 min} \\
\text{MeOH, then H}^+ \rightarrow \text{73%}
\end{align*}
\]

14 examples (yields 40-95%).

**Asymmetric synthesis of 2-alkenyl-1-cyclopentanols via intramolecular cycloalkylation.**

Asymmetric synthesis of 2-alkenyl-1-cyclopentanols via intramolecular cycloalkylation.

\[
\begin{align*}
\text{BuLi (1.5 equiv.)} \rightarrow \text{BuLi (1.5 equiv.)} \\
\text{THF, } -78 \degree\text{C, 4 h} \\
\text{OCb} \rightarrow \text{OCb} \\
96\% \\
\text{dr > 98:2} \\
\text{er > 97.5:2.5}
\end{align*}
\]

10 examples (yields 6-96%, %de 90-96%).

**Asymmetric synthesis of 2-alkenyl-1-cyclopentanols via intramolecular cycloalkylation.**

Asymmetric synthesis of 2-alkenyl-1-cyclopentanols via intramolecular cycloalkylation.

\[
\begin{align*}
\text{(E)-Selective cyclocarbolithiation of } \alpha\text{-lithiated alkenyl carbamates.} \\
\end{align*}
\]

(E)-Selective cyclocarbolithiation of \( \alpha \)-lithiated alkenyl carbamates.

Cyclocarbolithiation

\[
\begin{align*}
\text{dr} = 50:50 \\
\text{er} = 97:3
\end{align*}
\]

7 examples (yields 35-92%), \( \text{Cb} = \text{C(O)N}^-\text{Pr}_2 \).

**Formation of a quaternary centre via a Ni(cod)\(_2\)-mediated Heck-type reaction.**

Formation of a quaternary centre via a Ni(cod)\(_2\)-mediated Heck-type reaction.

1,4-Addition

\[
\begin{align*}
\text{EtCO}_2\text{CHO} \rightarrow \text{OSEM} \\
\text{Br} \rightarrow \text{Br} \\
\text{DMF, 80 °C, 2 h} \\
\text{60%} \\
\text{dr = 3:2}
\end{align*}
\]

Model studies towards azadirachtin.
1,4-Hydrosilylation of α,β-unsaturated carbonyl compounds.

\[
\text{HSiMe}_2\text{OSiMe}_3 \quad (1.1 \text{ equiv.}) \quad [\text{Rh(OH)cod}]_2 \quad (0.15 \text{ mol%)}
\]

THF, rt, 10 min
99%

13 examples (yields 80-99%).

Preparation and reactions of α-functionalized alkenylmagnesium reagents.

1,4-Addition

\[
\text{HSiMe}_2\text{OSiMe}_3 \quad (1.1 \text{ equiv.)} \quad \text{[Rh(OH)(cod)]}_2 \quad (0.15 \text{ mol%})
\]

THF, rt, 10 min
99%

Nucleophilic Addition

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>Y</th>
<th>E⁺</th>
<th>Yield</th>
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</thead>
<tbody>
<tr>
<td>Pr</td>
<td>Pr</td>
<td>CN</td>
<td>Me₃SiCl</td>
<td>93%</td>
</tr>
<tr>
<td>Me</td>
<td>Me</td>
<td>CO₂Bu</td>
<td>Bu₃SnCl</td>
<td>53%</td>
</tr>
<tr>
<td>Me</td>
<td>Me</td>
<td>CONEt₂</td>
<td>PhCHO</td>
<td>76%</td>
</tr>
<tr>
<td>H</td>
<td>Ph</td>
<td>SO₂Ph</td>
<td>allyl bromide</td>
<td>76%</td>
</tr>
</tbody>
</table>

44 examples (yields 45-93%).

Selective deprotonation of meso-epoxides.

Desymmetrization

| (–)-sparteine (1.3 equiv.) | s-BuLi (1.25 equiv.) | Et₂O, –90 °C, 3 h |
|（a） | （b） |
| EtCONMe₂ (1.5 equiv.) | Et₂O, –90 °C, 3 h |

79% er = 88.5:11.5

57% er = 87:13

12 examples (yields 48-84%, %ee 73-81%).

Ru-catalyzed olefin metathesis.

Metathesis

A (1 mol%) CH₂Cl₂, rt, 10 min 99%

E:Z = 97:3

13 examples (yields 82-99%).

Stereoselective alkylation of α,α-disubstituted amide enolates.

Alkylation

LiDBB (1 equiv.) THF, –78 °C 71%

dr = 97.5:2.5

9 examples (yields 74-84%, %de 88->95%).
Solid-phase synthesis of β-mannosides.

Polyphenylene as an electron transfer catalyst in lithiation processes.

Asymmetric nucleophilic addition to α- and β-silyloxy carbonyl compounds.

Synthesis of enantiomerically pure (R)- and (S)-bicalutamide.

Pd-catalyzed coupling reaction of alkenylgalliums with arylhalides.