**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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A highly active and air stable ruthenium complex for olefin metathesis.


![Image of ruthenium complex](image)

**Olefin Metathesis**

7 examples (yields 95-99%).

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Synthesis of α-amino phosphonates from alkynes.


![Image of reaction](image)

**Hydroamination/1,2-Addition**

10 examples (yields 52-97%).

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Synthesis of 3-chlorocyclohexanols.


![Image of reaction](image)

**1,2-Addition**

9 examples (yields 50-93%).
Conjugate Addition

Use of deuterium as a blocking group in the synthesis of aziridinomitosenes by anionic cyclization.

\[
\begin{align*}
\text{CO}_2\text{Et} & \quad \text{SnBu}_3 \\
\text{N} & \quad \text{NCPh}_3 \\
\text{D} & \quad \text{D}
\end{align*}
\]

\[
\begin{align*}
\text{MeLi (4 equiv.)} & \quad \text{THF, } -78 \degree \text{C} \rightarrow -65 \degree \text{C, 25 min} \\
\text{Li}^+ \cdot \text{CO}_2\text{Et} & \quad \text{PhSeCl (4.6 equiv.)} \\
\text{PhMe, } -65 \degree \text{C} \rightarrow \text{rt, 20 min} & \quad \text{80%}
\end{align*}
\]

This deuterium serves as a blocking group in the tin-lithium exchange step.

Cross Metathesis/Allylboration

One-pot cross metathesis/allylboration reaction.

\[
\begin{align*}
\text{A} & \quad \text{B} \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

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

12 examples (yields 25-79%).

[2+2] Cycloadditions of N,N-dialkylhydrazones to benzyloxyketene.

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

9 examples [yields 56-91% (2 steps), %de 52-98%, syn:anti 85:15 → 99:1].

[2+2] Cycloaddition

6-Bromomethyl-4H-1,3-dioxin as a vinyl ketone equivalent for heterocycle and carbocycle construction.

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

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

11 examples (yield 59-94%).

Cu-catalyzed asymmetric conjugate additions of alkylzinc reagents to acyclic aliphatic enones.

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

5 examples involving sequential catalytic cross metathesis/asymmetric conjugate addition (yield 67-91%, %ee 74-95%). 12 examples involving an asymmetric conjugate addition (yield 42-93%, %ee 58-95%).

Conjugate Addition

Use of deuterium as a blocking group in the synthesis of aziridinomitosenes by anionic cyclization.

**sp²-sp² Coupling**

\[
\begin{align*}
\text{CHO} & \quad \text{Ni(acac)}_2 (10 \text{ mol\%}) \\
\text{PhMe} & \quad \text{DIBAL} (10 \text{ mol\%}) \\
\text{THF} & \quad 0^\circ \text{C, 2.5 h} \rightarrow \text{rt, 2.5 h} \\
49\% & \\
\end{align*}
\]

8 examples (yield 41-74% for the first step, 71-86% for the cyclization).

Intramolecular silicon-assisted cross-coupling reactions.

**sp²-sp² Coupling**

8 examples (yield 55-77%).

A route to either enantiomer of α- and β-amino acid derivatives.

**Enantioselective 1,2-Addition**

7 examples (yield 57-89%, %ee 93-99%, %de 5-90%).

Asymmetric azidation-cycloaddition with open-chain peptide-based catalysts.

**Asymmetric Azidation-Cycloaddition**

7 examples for azidation/cycloaddition sequence (yield 73-85%, %ee 82-92%). 5 examples for β-azidation (yield 44-90%, %ee 78-92%).

Asymmetric synthesis of huperzine A via enantioselective palladium-catalyzed bicycloannulation reaction.

**Bicycloannulation**

The reaction is a key step in the synthesis of huperzine A. 11 different ligands and 3 different allylic agents were used during optimization (yields 13-98%, %ee 6-90%).
Enantioselective reducing agent from (-)-α,α-diphenylpyrrolidinemethanol and 9-borabicyclo[3.3.1]nonane.

Enantioselective Reduction

$$\text{PhPh} \quad \text{O} \quad \text{A} \quad \text{A} \quad \text{BH}_3 \cdot \text{THF} \quad (0.6 \text{ equiv.}) \quad \text{THF, } 0 \degree \text{C}$$

er = 99.5:0.5

Desymmetrization of anhydrides by addition of Grignard reagents.

Enantioselective Desymmetrization

<table>
<thead>
<tr>
<th>R</th>
<th>%ee</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>92%</td>
<td>91%</td>
</tr>
<tr>
<td>Bn</td>
<td>92%</td>
<td>87%</td>
</tr>
<tr>
<td>i-Bu</td>
<td>91%</td>
<td>76%</td>
</tr>
<tr>
<td>n-Bu</td>
<td>91%</td>
<td>64%</td>
</tr>
<tr>
<td>TBSO</td>
<td>87%</td>
<td>51%</td>
</tr>
</tbody>
</table>

9 examples (yields 51-91%, %ee 97-92%)

Asymmetric synthesis of lignans.

Asymmetric 1,2-Addition

$$\text{ArCHO} \quad (1.2 \text{ equiv.}) \quad \text{THF, } -100 \degree \text{C, } 20 \text{ min} \quad \text{NH}_4 \text{Cl, } \text{H}_2 \text{O} \quad \text{AgNO}_3 \quad (4 \text{ equiv.}) \quad \text{THF-H}_2 \text{O, } \text{rt, } 15 \text{ min}$$

%ee 99%

16 examples (yields 51-91%, %ee 97-92%)

Enantioselectively pure α-amino acids via hybroboration-Suzuki cross-coupling.

Asymmetric 1,2-Addition

$$\text{sp}^2\text{-sp}^3 \text{ coupling}$$

16 examples (yields 47-84%). The products were then converted into N-protected α-amino acids via a one-pot cleavage-oxidation.

Aluminium-catalyzed addition of TMSCN to ketones.

Asymmetric 1,2-Addition

$$\text{A} \quad (20 \text{ mol%}) \quad \text{Al(Oi-Pr)}_3 \quad (20 \text{ mol%}) \quad \text{MeOH} \quad (20 \text{ mol%}) \quad \text{TMSCN} \quad (2 \text{ equiv.)} \quad \text{PhMe, } -78 \degree \text{C, } 2 \text{ d}$$

87%

er = 94.6

15 examples (yields 66-98%, %ee 80-95%).
Stereoselective ring expansion via bicyclooxonium ion.

Ring Expansion

7 examples (combined yields 48-96%).

Photochemical radical decarboxylation with quinone trapping.

Decarboxylation/Addition

The total synthesis of (−)-llimaquinone is reported.

Tungsten-catalyzed cycloisomerization.

Cycloisomerization

2 examples (yield 98%). Used towards the synthesis of vancoamine and saccharosamine.

Directed ortho metatllation and retro-Mannich approach to 3,4-substituted indoles.

Metallation/Retro-Mannich

8 examples (yields 21-51%).

Reducive annulation of nitrosoarenes with alkynes.

Reductive Annulation

4 examples (yields 21-53%) and 10 examples using an alternative 2 step route (yields 29-64%).
Dearomatizing annulation of five-membered rings to naphthalenes by organolithium cyclization.

[Diagram of annulation]

3 further examples (Yields 41-79%). Lower yields were obtained in absence of TMEDA.

Stereoselective intermolecular carbolithiation of 1-aryl, 1-alkenyl carbamates.

[Diagram of carbolithiation]

Configurationally stable lithiated intermediates have been trapped with a range of electrophiles.

P,N ligands for enantioselective iridium-catalyzed hydrogenation.

[Diagram of hydrogenation]

6 different ligands (%ee > 80%) were used.

2-deoxyxylonolactams via enantioselective carbon-hydrogen insertion

[Diagram of C-H Insertion]

Six examples (%ee > 80%) were used.

Stereospecific preparation of [4,5]-spiroketal.

[Diagram of insertion]
Stereoselective synths of syn- and anti-1,2-amino alcohols.

Stereoselective synths of syn- and anti-1,2-amino alcohols.

Stereoselective synths of syn- and anti-1,2-amino alcohols.

Stereoselective synths of syn- and anti-1,2-amino alcohols.
Regio- and stereoselective cyclopropanation of functionalized dienes.


Selective Cyclopropanation

![Chemical structure](image1)

7 examples (yields 61-70%) of cyclopropanation of dienylboronates.

Selective Cyclopropanation

![Chemical structure](image2)

17 examples (yields 76%, %ee 64-99%) with variation of the N-substituent. Preparation of the O-allylic thiocarbamates; further derivatization of the products and application to the solid-phase are also reported.

Esterification

![Chemical structure](image3)

15 examples (yields 51-89%) and preparation of A are reported.

Ketone Reduction

![Chemical structure](image4)

13 examples (yields 31-100%).

Catalytic asymmetric allylations of achiral and chiral aldehydes via BINOL-Zr complex.


Asymmetric Allylation

![Chemical structure](image5)

24 examples (yields 45-90%, %ee 85-98%). Diastereoselectivity of protected chiral β-hydroxy aldehydes was influenced by choice of protecting group.

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