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

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**Olefin Metathesis**

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

![Olefin Metathesis](image)

7 examples (yields 95-99%).

**Hydroamination/1,2-Addition**

Synthesis of α-amino phosphonates from alkynes.

![Hydroamination/1,2-Addition](image)

10 examples (yields 52-97%).

**1,2-Addition**

Synthesis of 3-chlorocyclohexanols.

![1,2-Addition](image)

9 examples (yields 50-93%).
Use of deuterium as a blocking group in the synthesis of aziridinomitosenes by anionic cyclization.

Conjugate Addition

One-pot cross metathesis/allylboration reaction.

Cross Metathesis/Allylboration

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

[2+2] Cycloaddition

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

Annulation

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

Conjugate Addition

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

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%).

![Chemical structure](image.png)
Enantioselective reducing agent from (-)-α,α-diphenylpyrroolidinemethanol and 9-borabicyclo[3.3.1]nonane.

Enantioselective Reduction

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\begin{align*}
\text{Ph} & \quad 92\% \\ 
\text{Bn} & \quad 92\% \\ 
\text{i-Bu} & \quad 91\% \\ 
\text{n-Bu} & \quad 91\% \\ 
\text{TBSO} & \quad 87\% \\
\end{align*}
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Desymmetrization of anhydrides by addition of Grignard reagents.

Enantioselective Desymmetrization

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Asymmetric synthesis of lignans.

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

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Enantiomerically pure α-amino acids via hybroboration-Suzuki cross-coupling.
Stereoselective ring expansion via bicycliconium ion.

Ring Expansion

7 examples (combined yields 48-96%).

Photochemical radical decarboxylation with quinone trapping.

Decarboxylation/Addition

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

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

Metallation/Retro-Mannich

8 examples (yields 21-51%).

Reductive annulation of nitrosoaranes with alkynes.

Reductive Annulation

4 examples (yields 21-53%) and 10 examples using an alternative 2 step route (yields 29-64%).

Synthesis 2002, No. 8, 1124–1131  ISSN 0039-7881 © Thieme Stuttgart · New York
Dearomatizing annulation of five-membered rings to naphthalenes by organolithium cyclization. 


**Annulation**

![Chemical structure](image)

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

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


**Carbolithiation**

![Chemical structure](image)

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

P,N ligands for enantioselective iridium-catalyzed hydrogenation.


**Hydrogenation**

![Chemical structure](image)

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

2-deoxxylonolactams via enantioselective carbon-hydrogen insertion


**C-H Insertion**

![Chemical structure](image)

Stereospecific preparation of [4,5]-spiroketals.


**Insertion**

![Chemical structure](image)

6 examples (yields 59-89%).
Stereoselective syntheses of syn- and anti-1,2-amino alcohols.

Stereoselective Reduction

8 examples of anti-selective reduction of carbamate-protected amino ketones (yields 80-89%, %de 90%) and 3 examples of syn-selective reduction of trityl-protected amino ketones (yields 88-91%, dr 4:1 → 18:1) are reported.
Regio- and stereoselective cyclopropanation of functionalized dienes.


Selective Cyclopropanation

![Cyclopropanation Reaction](image)

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

Palladium(0)-catalyzed enantioselective O,S-rearrangement of racemic O-allylic thiocarbamates.


Enantioselective O,S-Rearrangement

![O,S-Rearrangement Reaction](image)

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

O-Succinimidyl-1,3-dimethyl-1,3-trimethyleneuronium salts as efficient reagents in active ester synthesis.


Esterification

![Esterification Reaction](image)

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

Palladium-catalyzed reduction of ketones with Bu₂SnH₂.


Ketone Reduction

![Ketone Reduction Reaction](image)

13 examples (yields 31-100%).

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


Asymmetric Allylation

![Asymmetric Allylation Reaction](image)

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