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:
Advanced Synthesis and Catalysis
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
Journal of the American Chemical Society
Organic Letters
Organometallics
Perkin Transactions 1
Synlett
Synthesis
Tetrahedron
Tetrahedron Asymmetry
Tetrahedron Letters

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

Olefin Metathesis

Synthesis of 3-chlorocyclohexanols.

1,2-Addition

Hydroamination/1,2-Addition

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

One-pot cross metathesis/allylboration reaction.

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

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

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

Asymmetric 1,2-Addition

Enantioselective Desymmetrization

Desymmetrization of anhydrides by addition of Grignard reagents.

Enantioselective Desymmetrization

Asymmetric synthesis of lignans.

Asymmetric 1,2-Addition

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

Enantioselective reducing agent from (-)-α,α-diphenylpyrrolidinemethanol and 9-borabicyclo[3.3.1]nonane.
Stereoselective ring expansion via bicyclooxonium ion.

Reductive annulation of nitrosoarenes with alkynes.

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

Photochemical radical decarboxylation with quinone trapping.

Decarboxylation/Addition
The total synthesis of (–)-limaquinone is reported.

Tungsten-catalyzed cycloisomerization.

Cycloisomerization

Dearomatizing annulation of five-membered rings to naphthalenes by organolithium cyclization.


\[
\text{MeLi (1.2 equiv.), TMEDA (2 equiv.)}
\quad \text{THF, \(-78 \degree C, 1 \text{ h}\)}
\quad \text{sat. aq. NH}_4\text{Cl}
\quad \text{\(-78 \degree C \rightarrow \text{rt}\)}
\quad 74\%
\]

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

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


\[
\text{BuLi (1.4 equiv.)}
\quad \text{PhMe, \(-78 \degree C, 5 \text{ h}\)}
\quad \text{MeOH}
\quad \text{HCl, \(-78 \degree C \rightarrow \text{rt}\)}
\quad 63\%
\quad \text{er = 79:21}
\]

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

P,N ligands for enantioselective iridium-catalyzed hydrogenation.


\[
\text{A (1 mol%)}
\quad \text{H}_2 (50 \text{ bar})
\quad \text{CH}_2\text{Cl}_2, \text{rt, 2 h}}
\quad \text{Ar}
\quad \text{R}
\quad \%\text{ee}
\quad \text{Ph}
\quad \text{Ph}
\quad 99\%
\quad \text{CO}_2\text{Et}
\quad 94\%
\quad \text{p-MeOC}_6\text{H}_4
\quad 99\%
\]

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

2-deoxyxylonolactams via enantioselective carbon-hydrogen insertion


\[
\text{Ph}
\quad \text{NH}
\quad \text{MeNMe}
\quad \text{A}
\quad \text{Me}
\quad \text{COOMe}
\quad \text{Ph}
\quad \text{N}
\quad \text{Ph}
\quad \text{A}
\quad \text{N}
\quad \text{Ph}
\quad \text{Ph}
\quad \text{O2CPh}
\quad \text{CO2Me}
\quad \text{Ph}
\quad \text{Ph}
\quad \text{N}
\quad \text{Ph}
\quad \text{Ph}
\quad \text{CH}_2\text{Cl}_2, \Delta, 2 \text{ h}}
\quad \text{H}_2 (50 \text{ bar})
\quad \text{Ph}
\quad \text{PPh}_3
\quad \text{NMe}
\quad \text{Ph}
\quad \text{Ph}
\quad \text{O2CPh}
\quad \text{CO2Me}
\quad \text{Ph}
\quad \text{Ph}
\quad \text{N}
\quad \text{Ph}
\quad \text{Ph}
\quad \text{CH}_2\text{Cl}_2, \Delta, 2 \text{ h}}
\quad \text{75%}
\quad \text{er = 93:7}
\]

Stereospecific preparation of [4,5]-spiroketal.


\[
\text{TMSCLiN}_2 (1.9 \text{ equiv.})
\quad \text{THF, \(-78 \degree C, 30 \text{ min}\)}
\quad \text{85%}
\quad \text{TMSCLiN}_2 (1.9 \text{ equiv.})
\quad \text{THF, \(-78 \degree C, 30 \text{ min}\)}
\quad \text{61%}
\]

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

Stereoselective syntheses of anti-1,2-amino alcohols.

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


Selective Cyclopropanation

\[
\begin{align*}
\text{Pd(OAc)}_2 (5 \text{ mol\%}) & \quad \text{CH}_2\text{N}_2 (1 \text{ equiv.}) \\
\text{Et}_2\text{O}, 0 \degree \text{C} & \quad 47\%
\end{align*}
\]

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

Enantioselective O,S-Rearrangement

\[
\begin{align*}
\text{A (1.5 mol\%)} & \quad \text{Pd(dba)}_2\text{CHCl}_3 (1.25 \text{ mol\%}) \\
\text{CH}_2\text{Cl}_2, \text{rt, 15 h} & \quad n, \text{yield}, \%\text{ee}
\end{align*}
\]

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.

Ketone Reduction

\[
\begin{align*}
\text{Pd(PPh}_3\text{)}_4 (1 \text{ mol\%}) & \quad \text{Bu}_2\text{SnH}_2 (2 \text{ equiv.}) \\
\text{PhMe, rt, 3 h} & \quad 94\%
\end{align*}
\]

13 examples (yields 31-100%).

Asymmetric Allylation

\[
\begin{align*}
\text{SnBu}_3 (1.1 \text{ equiv.}) & \quad (S)-\text{BINOL} (10 \text{ mol\%}) \\
\text{Zr(OBu}_4\text{)}_4 (13 \text{ mol\%}) & \quad 4 \text{ Å MS}
\end{align*}
\]

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

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


Esterification

\[
\begin{align*}
\text{A (1 eq.)} & \quad \text{Et}_3\text{N (1 eq.)} \\
\text{DMF, rt, 30 min} & \quad 51\%
\end{align*}
\]

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