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
Chemistry-A European Journal
Collection of Czechoslovak Chemical Communications
European Journal of Organic Chemistry
Helvatica 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.

Catalytic enantio- and position-selective dihydroxylation of polyisoprenoids.

Enantioselective ruthenium-catalysed ring closing metathesis.
Simple direct \(\alpha\)-allylation of aldehydes with allyl alcohols.


\[
\begin{align*}
\text{Pd(OAc)}_2 & (10 \text{ mol\%}) \\
\text{Ph}_3 \text{P} & (20 \text{ mol\%}) \\
\text{Et}_3 \text{B} & (2.4 \text{ equiv.}) \\
\text{Et}_3 \text{N} & (1.2 \text{ equiv.}) \\
\text{LiCl} & (1 \text{ equiv.}) \
\end{align*}
\]

THF, rt, 36 h

89%

\[
\begin{align*}
\text{Ph} & \equiv \text{OH} \\
\text{OH} & \equiv \text{Ph} \\
\text{CHO} & \\
\end{align*}
\]

12 examples (yields 63-90%). The allylation works for a variety of 1° and 2° allylic alcohols. 5 Aldehydes and 6 different alcohols used.

Three-component catalytic asymmetric synthesis of aliphatic amines.


\[
\begin{align*}
\text{Et}_2 \text{Zn} & (6 \text{ equiv.}) \\
\text{PhMe}, 0^\circ \text{C} \rightarrow \text{rt}, 1 \text{ d} \\
\end{align*}
\]

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

Olefin metathesis involving ruthenium enoic carbene complexes.


\[
\begin{align*}
\text{t-BuLi} & (4 \text{ equiv.}) \\
\text{Et}_2 \text{O-THF}, -78^\circ \text{C}, 1 \text{ h} \\
\text{CO}, -78^\circ \text{C}, 1 \text{ h} \\
\text{Me}_2 \text{SO_4} & (2 \text{ equiv.}) \\
\text{−78}^\circ \text{C} \rightarrow \text{rt}, 1 \text{ h, 70}\% \\
\end{align*}
\]

13 examples (yield 58-91%). Benzyl bromide, allyl bromide and methyl iodide were also used as electrophiles.
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.

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

\[ \text{MeCN} \rightarrow \text{esterification} \rightarrow \text{amide (93%)} \]

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

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

\[ \text{RCHO (1 equiv.) BuSnCl}_3 \text{ (1.3 equiv.) CH}_2 \text{Cl}_2, -50 \rightarrow 0 °C, 1 \text{ h} \text{KF / Celite, rt, 2 h} \]

\[ \text{RCHO} \rightarrow \text{yield (96%)} \text{anti:syn (97:3)} \]

11 examples (yields 47-99%).

NiCl\(_2\)(PCy\(_3\))\(_2\)-catalyzed cross-coupling of aryl tosylates and arylboronic acids.

\[ \text{PCy}_3 \text{ (6-12 mol%) PhB(OH)}_2 \text{ (1.5 equiv.) NiCl}_2\text{(PCy}_3\text{)}\_2 \text{ (1.5-3 mol%) K}_3\text{PO}_4 \text{ (2 equiv.) dioxane, 130 °C, 14-60 h} \]

\[ \text{R} \text{COMe} \text{CN} \text{OMe} \text{t-Bu} \text{Me} \text{yield (94%)} \text{96%} \text{89%} \text{83%} \text{79%} \]

16 examples (yields 47-99%).

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

\[ \text{Li(TMS)}_2\text{, PhSeBr THF, -78 °C} \]

\[ \text{R} = \text{Boc} \text{H}_2, \text{Pd/C THF-EtOH,} \text{ ∆, 2 h} \]

\[ \text{H}_2, \text{Pd/C THF-EiOH,} \text{ ∆, 2 h} \]

Chemoselective dibutyltin oxide-mediated transesterification.

\[ \text{Bu}_2\text{SnO (0.1 equiv.) MeOH,} \text{ ∆, 12 h 95%} \]

\[ \text{MeO} \text{OEt} \text{Bu}_2\text{SnO (0.1 equiv.) MeOH,} \text{ ∆, 12 h 86%} \]

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

![Chemical structure](image1)

Reduction

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

Palladium-catalyzed arylation of cyclic allylic benzoates.

![Chemical structure](image2)

sp³–sp² Coupling

12 examples (yields 9-88%).

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

![Chemical structure](image3)

N-Radical Cyclisations

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.

![Chemical structure](image4)

Oxidation

Functionalised 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.

![Chemical structure](image5)

Conjugate Addition

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

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

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

sp\(^3\)-sp\(^2\) Coupling

2 examples of (+)-discodermolide models and 2 examples of callystatin A models.

Enantioselective ring cleavage of dioxane acetals: Application to desymmetrization of \(\text{meso}\)-1,3-diols.

Enantioselective Ring Cleavage

4 examples (yields 26-36%, %ee 86-94%).

Nickel-promoted alkylative or arylative carboxylation of alkynes.

sp\(^3\)-sp\(^2\) Coupling: Carboxylation

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. \(\beta\)-Hydride elimination only occurred when Et\(_2\)Zn was employed.

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

Amination

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 aminophenylsilane (5 examples; yields 85-98%) are also reported.