**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:
Fabrice Anizon, Robert Chow, and Sukhjinder Uppal, Department of Chemistry, Leeds University.

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**Copper(II) (Salen) Complex**

The title complex is used as a phase transfer catalyst for the asymmetric synthesis of α-methyl α-amino acids.

![Copper(II) (Salen) Complex](image)

Y. N. Belckon, R. G. Davies, M. North

12 examples (yields 0, 42-95%, %ee = 43-86%) are reported.

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**Polymeric Titanium(IV) Glycolate**

Reagent A catalyses the epoxidation of allylic alcohols by tert-butyl hydroperoxide (TBHP) under heterogeneous conditions. One other Ti(IV) catalyst is shown.

![Polymeric Titanium(IV) Glycolate](image)

A. Massa, A. Scorti
*Synlett* **2000**, **1348**.

4 examples (yields 50-95%) are reported.

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**Titanocene Dichloride**

The title reagent catalyses 5-exo cyclisations of epoxides to afford substituted cyclopentanes and tetrahydrofurans.

![Titanocene Dichloride](image)

A. Gansauer, M. Pierbon
*Synlett* **2000**, **1357**.

11 examples (yields 54-90%) are reported.

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The journals regularly covered by the abstractors are:
- 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
2,6-Lutidine Hydrochloride

The title reagent catalyses the chlorination of aldehydes with chlorine for the preparation of 2,2-dichloroaldehydes.

$$\text{H}_2\text{C}-\text{N}^-\text{CH}_3$$

+HCl

A

$$\begin{align*}
\text{CH}_2\text{Cl}_2, 75^\circ\text{C}, 3 \text{ h} \\
\text{90\%}
\end{align*}$$


6 examples (yields 90-98%) are reported.

Sulfur-Containing Palladacycle

Palladacycle A is a catalyst precursor for the Suzuki cross-coupling reaction of aryl halides with phenylboronic acid under mild conditions.

$$\begin{align*}
\text{Me} \\
\text{S} \\
Pd \\
\text{Cl}_2 \\
\text{Br} \\
\text{MeO} \\
\text{Me}
\end{align*}$$

A

$$\begin{align*}
\text{A (0.5 mol\%)} \\
\text{Pb(OH)}_2 (1.5 \text{ eq}) \\
\text{K}_{3}\text{PO}_4 (2 \text{ eq}) \\
\text{Bu}_4\text{NBBr (20 mol\%)} \\
\text{DMF, rt, 1.5 d} \\
\text{99\%}
\end{align*}$$


19 examples (yields 13-99%) are reported.

N-Methylanthracenyquininium Chloride

The title reagent promotes the Michael addition of dimethyl malonate to enones by asymmetric solid-liquid phase-transfer catalysis in solvent-free conditions.

$$\begin{align*}
\text{OMe} \\
\text{A}
\end{align*}$$

$$\begin{align*}
\text{A (11 mol\%)} \\
\text{K}_{2}\text{CO}_3 (16 \text{ eq}) \\
\text{CH}_2\text{(COO)}_2\text{Me}_2 (30 \text{ eq}) \\
\text{-20\°C, 2 d}
\end{align*}$$


1 example (yield 91%, %ee = 90%) is reported.

L-Proline / trans-2,5-Dimethylpipperazine

The title reagent pair catalyse the asymmetric conjugate addition of nitroalkanes to cycloalkenones.

$$\begin{align*}
\text{A} \\
\text{B}
\end{align*}$$

$$\begin{align*}
\text{A (4 mol\%)} \\
\text{B (1 eq)} \\
\text{(CH}_3\text{)}_2\text{CHNO}_2 (2 \text{ eq}) \\
\text{CHCl}_3, \text{rt, 2.5 d} \\
\text{88\%} \\
\text{ee = 96:4}
\end{align*}$$


15 examples (yields 30-88%, %ee = 62-93%) are reported.

C₂-Symmetric Zinc(II)-L-Phe-L-Phe Complex

Reagent A catalyses the enantioselective addition of dialkylzincs to aliphatic and aromatic aldehydes.

$$\begin{align*}
\text{Ph} \\
\text{N=CPH}_2 \\
\text{N=CPH}_2 \\
\text{Ph}
\end{align*}$$

$$\begin{align*}
\text{A (3 mol\%)} \\
\text{(CH}_3\text{)}_2\text{Zn (1.3 eq)} \\
\text{THF, -78\°C \rightarrow rt, 18 h} \\
\text{80\%} \\
\text{ee = 96:4}
\end{align*}$$


4 examples (yields 27-80%, %ee = 86-96%) are reported.
### Zinc / Ruthenium Carbene Catalyst

The carbocyclisation of carbohydrates is accomplished by a novel A-mediated domino reaction to give functionalised dienes followed by B-catalysed ring-closing olefin metathesis.


16 examples of diene formation (yields 54-100%) and 8 examples of RCM (yields 55-95%) are reported.

### (Acetylacetonato)dicarbonylrhodium(I)

The title reagent catalyses tandem intramolecular silylformylation-allylsilylation of dialkylsilanes in an approach to polyol synthesis.


5 examples (yields 45-65%) are reported.

### Bis(1,5-cyclooctadiene)nickel(0)

The title reagent catalyses the stereoselective acylstannylation of 1,3-dienes. Transformation of the resulting α-oxoalystsannanes to unconjugated enones are also reported.


11 examples (yields 36-86%) are reported.

### C₂-Symmetric Bis(oxazoline)-Copper(II) Complex

The title reagent catalyses the enantioselective Mukaiyama Michael reaction of allylalcohol malonates and enolates.


19 examples (yields 10-99%, εee = 0-99%) are reported.

### L-Proline

The title reagent catalyses the enantioselective three-component Mannich reaction.


7 examples (yields 35-90%, εee = 70-96%) are reported.
## Mono Lithium Salt of [(R,R)-N,N'-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine] [(R,R)-(-)-SALEN]

The title reagent catalyses the asymmetric addition of trimethylsilylcyanide to aldehydes to afford TMS ethers of cyanhydrins.

**Catalyst**

![Catalyst Diagram]


13 examples (yields 64-99%, %ee = 0-97%) are reported.

## Grubbs' Catalyst

The title reagent catalyses enyne metathesis of acetylenic boronates for the construction of cyclic-1,3-diakynylboronic esters.

**Catalyst**

![Catalyst Diagram]


9 examples (yields 65-95%) are reported.

## Bidentate N,P Ligand

Ligand A is applied in the palladium-catalysed asymmetric allylation and Heck reaction. A is from a new class of phosphine-oxazoline ligands, bearing a chiral phosphinooctomethylidienyl (P-donor) and an oxazoline (N-donor).

**Ligand**

![Ligand Diagram]


The synthesis of A and 2 examples of application (yields 91-100%, %ee = 93-94%) are reported.

## Lithium N-Trityl-N-(R)-1-Phenethylamide

The title reagent is a readily available and useful base for the enantioselective formation of chiral enolates from achiral ketones.

**Reagent**

![Reagent Diagram]


4 examples (yields 50-92%, %ee = 89-92%) are reported.

## (R)-2′,2′′-Bis[2-(trimethylsilyl)ethoxymethoxy]-1,1′-binaphthyl-Tin Tetrachloride Complex [(R)-BINOL-(SEM)2]SnCl4

The title reagent is used for the enantioselective Prins reaction (acetal-ene reaction) of trisubstituted alkenes to afford optically active homoallylic ethers.

**Reagent**

![Reagent Diagram]


4 examples (yields 75-92%, %ee = 73-84%) are reported.
### Sodium Bromate / Sodium Hydrosulfite

The title reagent pair is used for the chemoselective cleavage of benzyl ether protecting groups in the presence of benzyloxy carbonyl functions.

<table>
<thead>
<tr>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBrO₃</td>
</tr>
<tr>
<td>Na₂S₂O₄</td>
</tr>
</tbody>
</table>


### Tetrabutylammonium Fluoride / Acetic Acid

The title reagent pair selectively deprotects t-butyldiphenylsilyl ethers in the presence of t-butyldimethylsilyl ethers.

<table>
<thead>
<tr>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu₄NF</td>
</tr>
<tr>
<td>AcOH</td>
</tr>
</tbody>
</table>


### (3aR,7aR)-2-Allylocta-1H-1,3,3-dimethyl-1,3,2-benzadiazaphosphole 2-Oxide

The anion derived from A is used in asymmetric 1,4-addition reactions to α,β-unsaturated carbonyl compounds.

<table>
<thead>
<tr>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&lt;br&gt;(a) n-BuLi (1.2 eq)&lt;br&gt;THF, -78°C&lt;br&gt;80%&lt;br&gt;dr = 93:7&lt;br&gt;12 examples (yields 48–93%) are reported.</td>
</tr>
<tr>
<td>(b) CH₂=CH₂=O (1.2 eq)&lt;br&gt;THF, -78°C, 30 min&lt;br&gt;(c) MeOH</td>
</tr>
</tbody>
</table>


### (R,R)-5,6-Diphenyl-1,4-dioxan-2-one

The boron enolate of A undergoes asymmetric aldol reactions with aldehydes to give protected anti-1,2-diols.

<table>
<thead>
<tr>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&lt;br&gt;E₂N (2.4 eq)&lt;br&gt;o-Hex-BOTf (3 eq)&lt;br&gt;PhCHO (1.1 eq)&lt;br&gt;CH₂Cl₂, -78°C, 2 h&lt;br&gt;81%&lt;br&gt;dr = 66:14&lt;br&gt;8 examples (yields 70–92%, %de = 60–90%) are reported.</td>
</tr>
</tbody>
</table>


### 1,3-Dichloro-5,5-dimethylhydantoin

The title reagent is used in a one-pot preparation of chiral 4,5-disubstituted oxazolidin-2-ones utilising a modified Sharpless asymmetric aminohydroxylation of β-substituted styrene derivatives followed by base-mediated ring closure.

<table>
<thead>
<tr>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&lt;br&gt;(a) A (1.5 eq)&lt;br&gt;K₂[OsO₂(OH)₆] (2 mol%)&lt;br&gt;(DHQ)₂PHAL (2.5 mol%)&lt;br&gt;NaOH (3 eq), urethane (3 eq)&lt;br&gt;n-PrOH-H₂O (1:1), rt, 3 h&lt;br&gt;72%&lt;br&gt;er = 90:10&lt;br&gt;8 examples (yields 28–81%, %ee = 81–98%) are reported.</td>
</tr>
</tbody>
</table>

(Trimethylsilyl)tributylstannane

The title reagent mediates the cyclisation of 1,6-dynes to afford chiral (Z,2)-1,3-dienes. The helical chirality in 1,4-disubstituted (Z,2)-1,3-dienes is demonstrated.

\[
\text{Me}_3\text{SiSnBu}_3 \quad \text{A}
\]

\[
\begin{array}{c}
\text{MeO}_2\text{C} \quad \text{CO}_2\text{Me} \\
\text{MeO}_2\text{C} \quad \text{CO}_2\text{Me}
\end{array}
\]

\[
\begin{array}{c}
\text{A} (1 \text{ eq}) \\
Pd_2(dba)_3 (1.25 \text{ mol%}) \\
(2-Me-C_6\text{F}_5)_3\text{P} (5 \text{ mol%})
\end{array}
\]

\[
\begin{array}{c}
\text{PHH, } \Delta \text{ 2 h} \\
79\%
\end{array}
\]

\[
\begin{array}{c}
\text{Me}_3\text{Si} \\
\text{SnBu}_3
\end{array}
\]

5 examples (yields 66-79%) are reported.

(Diacetoxyiodo)benzene (DIB)

Aroyl azides are readily prepared from the corresponding aryl aldehydes with the aid of the title reagent and sodium azide.

\[
\begin{array}{c}
\text{OAc} \\
\text{OAc}
\end{array}
\]

\[
\begin{array}{c}
\text{A}
\end{array}
\]

\[
\begin{array}{c}
\text{A} (1.5 \text{ eq}) \\
\text{NaN}_3 (2.5 \text{ eq})
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3\text{Cl}_2, \text{ rt, 2 h} \\
67\%
\end{array}
\]


8 examples (yields 43-92%) are reported.

t-Butyl-(2,6-dimethoxy-1-methylcyclohexa-2,5-dienyl)-dimethylsilane

The title reagent is used as an alternative to toxic tin hydrides in free radical chemistry.

\[
\text{TBDMS} \\
\text{MeO} \\
\text{MeO}
\]

\[
\begin{array}{c}
\text{A}
\end{array}
\]

\[
\begin{array}{c}
\text{A} (1.5 \text{ eq}) \\
\text{AIBN} (0.5 \text{ eq})
\end{array}
\]

\[
\begin{array}{c}
\text{hexane, } \Delta \text{ 7 h} \\
82\%
\end{array}
\]


12 examples (yields 42-99%) are reported.

Ammonium Nitrate / Trifluoroacetic Anhydride

The title reagent pair is used for the regioselective ipso-nitration of aryboronic acids to afford nitroaromatics. Dinitro products are obtained under different conditions.

\[
\text{NH}_2\text{NO}_3
\]

\[
\begin{array}{c}
\text{A}
\end{array}
\]

\[
\begin{array}{c}
\text{A} (1.1 \text{ eq}) \\
\text{B} (1.1 \text{ eq})
\end{array}
\]

\[
\begin{array}{c}
\text{MeCN, } -35^\circ\text{C, 4 h} \\
78\%
\end{array}
\]


8 examples (yields 52-79%) are reported.

Titanium Tetraiodide

The title reagent is used for the chemoselective deoxygenation of sulfones.

\[
\text{Ti}_4
\]

\[
\begin{array}{c}
\text{A}
\end{array}
\]

\[
\begin{array}{c}
\text{Me}\quad \text{S} \\
\text{Me}
\end{array}
\]

\[
\begin{array}{c}
\text{A} (1.5 \text{ eq}) \\
\text{MeCN, 0}^\circ\text{C, 10 min}
\end{array}
\]

\[
\begin{array}{c}
93\%
\end{array}
\]


19 examples (yields 80-97%) are reported.