**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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### 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.

### 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. Scocci *Synlett* **2000**, *1348*.

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

### 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.

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

Catalyst

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

\[
\begin{align*}
\text{Catalyst} & \quad \text{HCl} \\
& \quad \text{CH}_2\text{Cl}_2, 75^\circ\text{C}, 3 \text{ h} \\
& \quad 90\%
\end{align*}
\]


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

Sulfur-Containing Palladacycle

Catalyst

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

\[
\begin{align*}
\text{Catalyst} \\
& \quad \text{BuMeS}-\text{PdCl}_2 \quad \text{MeO}_2 \quad \text{Ph}
\end{align*}
\]


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

N-Methylanthracyclquininium Chloride

Catalyst

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

\[
\begin{align*}
\text{Catalyst} & \quad \text{OMe} \\
& \quad -20^\circ\text{C}, 2 \text{ d} \\
& \quad 91\% \\
& \quad \text{er} = 95:5
\end{align*}
\]


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

L-Proline / trans-2,5-Dimethylpyrrolidine

Catalyst

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

\[
\begin{align*}
\text{Catalyst} & \quad \text{NO}_2 \\
& \quad \text{CHCl}_3, \text{rt}, 2.5 \text{ d} \\
& \quad 88\% \\
& \quad \text{er} = 96:4
\end{align*}
\]


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

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

Catalyst

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

\[
\begin{align*}
\text{Catalyst} \\
& \quad \text{Ph} \\
& \quad \text{THF, } -78^\circ\text{C} \rightarrow \text{rt}, 18 \text{ h} \\
& \quad 80\% \\
& \quad \text{er} = 96:4
\end{align*}
\]


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 55-90%) are reported.

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**Acetyldicarboxylrhodium(I)**

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


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

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

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


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

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**Cp-Symmetric Bis(oxazoline)-Copper(II) Complex**

The title reagent catalyses the enantioselective Mukaiyama Michael reaction of alkylidene malonates and enolisilanes.


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

---

**L-Proline**

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


7 examples (yields 35-90%, %ee = 70-96%) are reported.
Mono Lithium Salt of \((R,R)(-)-N,N'-\text{Bis}(3,5\text{-di-tert-butyisalicylidene})-1,2\text{-cyclohexanediame}\) ([\(R,R(\text{--})-\text{SALEN}\)])

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

\[
\begin{align*}
\text{Catalyst} & \\
\begin{array}{c}
\end{array}
\end{align*}
\]

Grubbs' Catalyst

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

\[
\begin{align*}
\text{Catalyst} & \\
\begin{array}{c}
\end{array}
\end{align*}
\]

Bidentate N,P Ligand

Ligand A is applied in the palladium-catalysed asymmetric alkylation and Hock reaction. A is from a new class of phosphorus-oxazoline ligands, bearing a chiral phosphonitroimidazolyl (P-donor) and an oxazoline (N-donor).

\[
\begin{align*}
\text{Ligand} & \\
\begin{array}{c}
\end{array}
\end{align*}
\]

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.

\[
\begin{align*}
\text{Reagent} & \\
\begin{array}{c}
\text{J. Busch-Petersen, E. J. Corey Tetrahedron Lett. 2000, 41, 6941.}
\end{array}
\end{align*}
\]

\((R)-2,2'-\text{Bis}[2-(\text{trimethylallyl})\text{ethoxymethoxy}]\)-1,1'-binaphthyl-Tin Tetrachloride Complex ([\(R\)]-BINOL-(SEM)$_2$SnCl$_4$)

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

\[
\begin{align*}
\text{Reagent} & \\
\begin{array}{c}
\text{K. Ishihara, H. Nakamura, H. Yamamoto Synlett 2000, 1245.}
\end{array}
\end{align*}
\]
**Sodium Bromate / Sodium Hydrosulfit**

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

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Reaction</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBrO₃</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>B</td>
<td></td>
</tr>
</tbody>
</table>

7 examples (yields 68–95%) are reported.


**Tetrahydrofuran / Acetic Acid**

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

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Reaction</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu₄NF</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>AcOH</td>
<td>B</td>
<td></td>
</tr>
</tbody>
</table>

4 examples (yields 68–100%) are reported.


**3aR,7aR)-2-Allylocta-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>
<th>Reaction</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) n-BuLi (1.2 eq) THF, -78°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) CH₂CH₂H₂(O) (1.2 eq) THF, -78°C, 30 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) MeOH</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

12 examples (yields 48–93%) are reported.


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

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

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Reaction</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et₃N (2.4 eq) n-Hex₂BOTf (3 eq) PhCHO (1.1 eq) CH₂Cl₂, -78°C, 2 h</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

8 examples (yields 70–92%, %de = 60–90%) are reported.


**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>
<th>Reaction</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) A (1.5 eq) K₂[OsO₂(OH)]₂ (2 mol%) (DHQ₂)²PHAL (2.5 mol%) Na₂O₃ (3 eq), urethane (3 eq) n-PrOH + H₂O (1:1), rt, 3 h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) NaOH, rt, 1 h</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

8 examples (yields 28–81%, %ee = 81–98%) are reported.

### (Trimethylsilyl)tributyllastannane

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

![Chemical Structure](image)


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.

![Chemical Structure](image)


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

### tert-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.

![Chemical Structure](image)


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.

![Chemical Structure](image)


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

### Titanium Tetraisodide

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

![Chemical Structure](image)


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