**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, Robert Chow, Jennifer Delaney, Marcel de Puit and Sukhjinder Uppal, Department of Chemistry, Leeds University, Leeds, LS2 9JT, UK.

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Hartwig’s Pre-catalyst

The title reagent promotes regioselective aromatic borylations in cyclohexane to afford aryl boronate esters.

Tse, M. K.; Cho, J.-Y.; Smith, M. R. III

Chloro(1,5-cyclooctadiene)rhodium(I) Dimer/Me-DuPhos

The title reagent pair promotes the two-step reductive aldol reaction.

Zhao, C.-X.; Bass, J.; Morken, J. P.

Tridentate Chromium(III) Catalyst

Reagent A promotes the asymmetric reaction between an aldehyde and a substituted diene in an entry into the A-D ring system of Gambierol.

Cox, J. M.; Rainier, J. D.

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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 I
- Synlett
- Synthesis
- Tetrahedron
- Tetrahedron Asymmetry and Tetrahedron Letters

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### 1-Adamantyl Oxazoline Iridium Complex

The title reagent promotes asymmetric hydrogenation of aryl alkenes.


\[
\text{Ad}^+ \text{BARF}^-
\]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Formula</th>
<th>Reaction Conditions</th>
<th>Yield</th>
<th>%ee</th>
<th>Example Yield %ee %de</th>
</tr>
</thead>
</table>
| A (0.2–0.6 mol%) | 50 bar H₂ | CH₂Cl₂, r.t., 2 h | 99% | 99:1 | 8 examples (yields 90–99%, %ee 31–98%).

### Osmium Tetroxide

The title reagent, when immobilized on layered double hydroxides (LDH), promotes asymmetric dihydroxylation of olefins.


\[
\text{LDH-OsO}_4^-
\]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Formula</th>
<th>Reaction Conditions</th>
<th>Yield</th>
<th>%ee</th>
<th>Example Yield %ee %de</th>
</tr>
</thead>
</table>
| A (1 mol%) | (DHOD)_2PHAL (1 mol%) | NMO (1.3 equiv) | 96% | 99:5:1.5 | 9 examples (yields 89–97%, %ee 77–99%).

### Lanthanum-(S)-1,1′-bi-2-naphthol-triphenylarsine Oxide

The title reagent catalyse the asymmetric synthesis of α,β-epoxy esters.


\[
\text{La(OAs}_3\text{Ph}_3
\]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Formula</th>
<th>Reaction Conditions</th>
<th>Yield</th>
<th>%ee</th>
<th>Example Yield %ee %de</th>
</tr>
</thead>
</table>
| A (10 mol%) | t-BuO₂H (2.4 equiv) | MgO (2.3 equiv) | 90% | 97.3 | 9 examples (yields 57–92%, %ee 72–97%, %de 90–98%).

### Aminio Phosphoryl Derivative

The title reagent promotes catalytic, enantioselective addition of allylic trichlorosilanes to aldehydes.


\[
(\text{CH}_2)_5\text{N}\text{Me}_2\text{OP}(\text{CH}_2)_5\text{N}\text{Me}_2
\]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Formula</th>
<th>Reaction Conditions</th>
<th>Yield</th>
<th>%ee</th>
<th>Example Yield %ee %de</th>
</tr>
</thead>
</table>
| A (5 mol%) | SiCl₃ (2 equiv) | CH₂Cl₂+Pr₂NEt (1:1), –78 °C, 10 h | 89% | 97:3 | 21 examples (yields 57–92%, %ee 72–97%, %de 90–98%).

### Rhodium(II) Acetate Dimer

The title reagent promotes the formation of 1,3-difunctionalized amine derivatives through selective C-H bond oxidation.


\[
\text{Rh}_2(\text{OAc})_4
\]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Formula</th>
<th>Reaction Conditions</th>
<th>Yield</th>
<th>%ee</th>
<th>Example Yield %ee %de</th>
</tr>
</thead>
</table>
| A (2 mol%) | Ph(OAc)₂ (1.1 equiv) | MgO (2.3 equiv) | 90% | | 9 examples (yields 60–91%).

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### Iron(III) Acetylacetonate/Dinitrogen Pentoxide

The title reagent pair provides mild conditions for the nitration of aromatics in high yields.


![Chemical structure](Image)

7 examples (yields 91–99%).

### Tris(dipivaloylmethanato)manganese (III)

The title reagent catalyses the reduction of saturated aldehydes and ketones by phenylsilane in the presence of dioxygen.


![Chemical structure](Image)

23 examples (yields 1–99%).

### (±)-BINOL/Zr(Oi-Pr)4/i-PrOH

The title reagent pair catalyses the selective reduction of aldehydes in the presence of ketones.


![Chemical structure](Image)

13 examples (yields 50–100%).

### Manganese(II) Nitrate/Cobalt(II) Nitrate/2,2',6,6'-Tetramethylpiperidine-N-oxyl

The title reagents catalyse the selective oxidation of aldehydes and ketones to primary and secondary alcohols.


![Chemical structure](Image)

11 examples (yields 96–100%).

### Neutral Organotin Catalyst

The title reagent catalyses the deprotection of acetyl esters.


![Chemical structure](Image)

18 examples (yields 21–100%).
<table>
<thead>
<tr>
<th>catalyst</th>
<th>example</th>
<th>conditions</th>
<th>yield</th>
<th>ee (or de)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrosyl(salen)ruthenium(II) Complex</td>
<td>RuCl(C₆H₄N₂O₂)(NO)</td>
<td>A</td>
<td>2,6-Cl₂C₆H₄NO (1 equiv) Et₂O, r.t., 32 h</td>
<td>64%</td>
</tr>
<tr>
<td>Wilkinson’s Catalyst</td>
<td>RhCl(PPh₃)₃</td>
<td>A</td>
<td>TMSCHN₂ (1.4 equiv) i-PrOH (1.1 equiv) PPh₃ (1.1 equiv) THF, r.t., 0.5 h</td>
<td>88%</td>
</tr>
<tr>
<td>Rhodium Complex</td>
<td>Rh(acac)(CO)₂</td>
<td>A</td>
<td>CO (1000 psi) PhH, 60 °C, 3 h n-Bu₄NF (3 equiv) THF, ∆, 2 h</td>
<td>88%</td>
</tr>
<tr>
<td>Indium(III) Trflate</td>
<td>In(OTf)₃</td>
<td>A</td>
<td>CH₂Cl₂, r.t.</td>
<td>81%</td>
</tr>
<tr>
<td>Bisoxazoline-Copper Complex</td>
<td>Cu(NO₃)(OTf)₂</td>
<td>A</td>
<td>C₆H₉NO₂ (1.5 equiv) Et₃N (20 mol%) CH₂Cl₂, r.t., 5 d</td>
<td>81%</td>
</tr>
</tbody>
</table>
### Bisoxazoline-Copper(II) Complex

**Catalyst**

The title reagent catalyses the asymmetric direct Mannich reactions of carbonyl with \(\alpha\)-imino esters.

**Synthesis** 2001, No. 16, 2521–2526


![Catalyst](image)

4 examples (yields 70–98%, %ee 78–98%, %de 50–82%).

### 3aS-[2(3'aR,8'aS,3aa,8aa)]-2-2'-(cyclopropylidene)-bis[3a,8a-dihydro-8H-indeno[1,2-d]-oxazole]

**Ligand**

The title reagent, when complexed to a Cu or Mg Lewis acid, promotes enantioselective tandem addition-trapping reactions to enolate derivatives.


![Ligand](image)

16 examples (yields 66–95%, %ee 53–97%, %de 41–98%).

### cis,cis,cis-1,2,3,4-Tetakis(diphenylphosphinomethyl)cyclopentane

**Ligand**

The title reagent, when complexed with \([\text{PdCl(C}_3\text{H}_5])_2\), catalyses the Suzuki cross-coupling of sterically hindered substrates.


![Ligand](image)

25 examples (yields 0–100%).

### Diethylphosphonoacetic Acid

**Reagent**

The title reagent is applied in a one-pot multicomponent reaction of isocyanides, glyoxals and acetophosphonic acid diethylesters, followed by an intramolecular Wittig-type reaction for the synthesis of butenolides.


![Reagent](image)

5 examples (yields 52–87%).

### 2,6-Pyridinecarboxylic Acid N-Oxide

**Reagent**

The title reagent is used for the cleavage of a \(p\)-anislooxymethyl-protected alcohol.


![Reagent](image)

1 example (yield 77%).
### 5-Magnesiated-1,3-dioxin-4-one Reagent

The title reagent can be reacted with a wide variety of electrophiles.

![Structure](image)


10 examples (yields 57–83%).

### Titanium Isopropoxide/Isopropylmagnesium Chloride Reagent

The title reagent pair is used for the preparation of optically active propargyl stannanes from the corresponding propargyl phosphates.

![Structure](image)


4 examples (yields 77–80%)

### 2-(1S)-1-(Methylthio)ethylphenyl Selenyl Triflate Reagent

The title reagent promotes asymmetric selenocyclization reactions.

![Structure](image)


17 examples (yields 40–95%, %de 50–88%).

### Diphenylborinic Acid Reagent

The title reagent can be used as a boron source for Mukaiyama aldol reactions in water.

![Structure](image)


13 examples (yields 51–93%, %de 6–94%).

### Diisopropylzinc/Copper Cyanide-Lithium Chloride Reagent

The title reagent pair is used for sequential boron-zinc exchange and copper-mediated allylation of the hydroboration products of unsaturated acetals.

![Structure](image)


16 examples (yields 46–69%, %de 6–98%).

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