**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:

Robert Chow, John Christopher, Emma Guthrie, Philip Kocienski, Alexander Kuhl, Catherine McCusker, Robert Narquizian, and Sukhjinder Uppal of Glasgow University.

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<table>
<thead>
<tr>
<th>DI-(R)-binaphthyl/Tetraisopropoxytitanium(IV)</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic resolution of racemic enol ester epoxides into chiral α-acyl oxy ketones is achieved by a mixture of 2 equivalents of BINOL and titanium isopropoxide.</td>
<td>([R]-BINOL)$_2$Ti(OPr)$_4$A</td>
</tr>
<tr>
<td><img src="image1" alt="Kinetic resolution reaction" /></td>
<td><img src="image2" alt="Kinetic resolution reaction" /></td>
</tr>
<tr>
<td>Et$_2$O, 0°C, 30 min</td>
<td>52% conversion</td>
</tr>
<tr>
<td>X. Feng, L. Shu, Y. Shi J. Am. Chem. Soc. 1999, 121, 11002.</td>
<td>16 examples (conversions 49-69%, %ee = 22-99%).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polymer-Supported Osmium Catalyst</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>The asymmetric dihydroxylation of olefins by Os$_2$O$_5$ encapsulated in an acrylonitrile-butadiene-polystyrene polymer is reported.</td>
<td><img src="image3" alt="Polymer-Supported Osmium Catalyst" /></td>
</tr>
<tr>
<td><img src="image4" alt="Polymer-Supported Osmium Catalyst" /></td>
<td><img src="image5" alt="Polymer-Supported Osmium Catalyst" /></td>
</tr>
<tr>
<td><img src="image6" alt="Polymer-Supported Osmium Catalyst" /></td>
<td><img src="image7" alt="Polymer-Supported Osmium Catalyst" /></td>
</tr>
<tr>
<td>S. Kobayashi, M. Endo, S. Nagayama J. Am. Chem. Soc. 1999, 121, 11220.</td>
<td>13 examples (yields 36-98%, %ee = 60-98%).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Zinc Trifluoromethanesulfonate</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>A mediates the addition of terminal alkynes to nitrones, aldehydes, ketones and A-tozyl aldimines.</td>
<td>Zn(OtBu)$_2$A</td>
</tr>
<tr>
<td><img src="image8" alt="Zinc Trifluoromethanesulfonate" /></td>
<td><img src="image9" alt="Zinc Trifluoromethanesulfonate" /></td>
</tr>
<tr>
<td><img src="image10" alt="Zinc Trifluoromethanesulfonate" /></td>
<td><img src="image11" alt="Zinc Trifluoromethanesulfonate" /></td>
</tr>
</tbody>
</table>

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
**Diethylene(acetoacetonato)rhomodium(I)**

A. in combination with chiral ligands, catalyses the asymmetric 1,4-addition of phenylboronic acids to 1-alkenylphosphonates.

\[
[Rh(acac)(\eta^2-C_2H_4)]_2
\]

B(OH)\(_3\) (3.5 eq) A (3 mol%) (S)-BINAP (3 mol%) H\(_2\)O (1 eq) 94%, ee = 98:2

18 examples (yields 5-98%, %ee = 84-99%).


**Cyclopentadienyl(1,4-cyclooctadiene)rhenium(I) Chloride / N-Hydroxysuccinimide**

The title reagent pair catalyse the cyclodimerisation-oxidation of homopropargyl alcohols.

\[
\begin{align*}
&\text{1999, 121, 11680.}
\end{align*}
\]

**1,3-Dimesityl-4,5-dihydroimidazol-2-ylidene ruthenium benzylidene**

The title reagent is used in the preparation of trisubstituted alkenes via intermolecular olefin cross-metathesis.

\[
\begin{align*}
&\text{A. K. Chatterjee, R. H. Grubbs Org. Lett.} \\
&\text{1999, 1, 1751.}
\end{align*}
\]

6 examples (yields 53-87%, 2,3:1 = E:Z = 4:1) are reported.

**Sodium Tetracarbonylcobaltate**

The title reagent catalyses the acylation of alcohols with acetic anhydride. The first example of a catalysed Staudinger reaction using a similar reagent is also reported.

\[
\begin{align*}
&\text{H. Wack, W. J. Drury III, A. E. Taggi,} \\
&\text{D. Ferraris, T. Lectka Org. Lett. 1999, 1, 1985.}
\end{align*}
\]

4 examples (yields 95-100%) are reported.

**Scandium Tris(perfluorobutanesulfonyl)methide Complex**

The title reagent is shown to be an efficient Lewis acid catalyst for Friedel-Crafts acylation and Diels-Alder reactions.

\[
\begin{align*}
&\text{J. Nishikido, F. Yamamoto, H. Nakajima,} \\
&\text{Y. Mikami, Y. Matsumoto, K. Mikami Synlett} \\
&\text{1999, 1990.}
\end{align*}
\]

1 example of a Friedel–Crafts acylation (yield 93%) and 1 example of a Diels–Alder reaction (yield 95%) are reported.
(R)-Binaphthol / Yb(Oi-Pr)3 / KO-t-Bu

A. generated from the title reagents catalyses an asymmetric nitro-Mannich-type reaction to give aminooxime products.

\[
\begin{align*}
&\text{H}^+ \quad \text{O} \quad \text{Yb}^3+ \\
&\quad \text{K}^+ \\
&\text{N}^+ \quad \text{H}^+ \\
&\text{Skeleon} \quad \text{1,1-binaphthyl} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} \quad \text{N} \quad \text{Ph} \\
\text{Ph} \quad \text{N} \quad \text{Ph} \\
\text{P} \quad \text{P} \\
\text{Br} \quad \text{H} \\
\end{align*}
\]

A (20 mol%), \(\text{CH}_2\text{NO}_2\) (5 eq), \(\text{PhMe-THF}(7:1)\), \(-40^\circ\text{C} \rightarrow \text{rt}, 3\) d

79%, \(\text{ee} = 96:4\)


5 examples (yields 41-93%, \(\text{ee} = 69-91\%\)).

\(\rho\)-2,2'-Bis(di-p-tolylphosphinyl)-1,1'-binaphthyl - Silver(I) Fluoride Complex

The title compound catalyses the asymmetric addition of allylic trimethoxysilanes to aldehydes generating the corresponding homoallylic alcohols.

\[
\begin{align*}
\text{PhCH}_2\text{CHO} (1\ \text{eq}) \\
\text{A} (6\ \text{mol}%), \text{B} (10\ \text{mol}%) \\
\end{align*}
\]

\[
\begin{align*}
\text{Si(OMe)}_3 \\
\text{MeOH, \(-20^\circ\text{C}, 4\) h} \\
\end{align*}
\]

80%, \(\text{ee} = 97:3\)


6 examples (yields 67-93%, \(\text{ee} = 79-94\%\) and 3 similar examples using \(\gamma\)-substituted allylic-trimethoxysilanes (yields 77-99, \(\text{ee} = 60-62\%\), 92:8 \(<\text{anti: syn} < 94:6\)).

Benzylimino(tris(dimethylamino))phosphorane

The title reagent catalyses the acylation of primary alcohols with enol esters in excellent yield and high selectivity.

\[
\begin{align*}
\text{NMe}_2 \\
\text{Ph} \\
\text{NMe}_2 \\
\end{align*}
\]

A (10 mol%), \(\text{CH}_2=\text{CHOCOMe}(5\ \text{eq})\)

THF, \(\text{rt}, 8.5\) h

99%


13 examples, including the selective protection of primary hydroxyls in the presence of secondary hydroxyls (yields 74-99%).

Diphenyl-(S)-(5-8-quinolinesulfonyl)-2-pyrrolidin-2-yl)methanol

The title compound catalyses the enantioselective borane reduction of aromatic ketones.

\[
\begin{align*}
\text{N} \quad \text{SO}_2 \\
\text{OH} \\
\text{Ph} \\
\end{align*}
\]

A (10 mol%), \(\text{BH}_3\cdot\text{SMMe}_3(1.1\ \text{eq})\)

PhMe, \(\text{rt}, 2\) h

96%


6 examples (yields 89-99%, \(\text{ee} = 65-91\%\)).

Palladium Diacetate / Tri-tert-butyolphosphine

The title reagent pair catalyses the reaction of aryl halides with sodium t-butoxide to give aryl t-butoxy ethers.

\[
\begin{align*}
\text{Pd(OAc)}_2 \\
\text{B} \\
\text{Ph(t-Bu)}_3 \\
\end{align*}
\]

A (0.5 mol%), \(\text{t-BuONa}(1.2\ \text{eq})\)

Xylene, \(120^\circ\text{C}, 1\) h

88%


12 examples (yields 20-94%).
Triethylsilane / Tri(pentafluorophenyl)borane

A novel reduction of alcohols and alkyl ethers using the title reagent pair is reported.

\[ \text{HSiEt}_3 \]

| Catalyst | \[ \text{CH}_2\text{OH} \] \[ \text{B}(10 \text{ mol\%}) \] \[ \text{CH}_2\text{O}_2, \text{rt, 20 h} \] \[ \text{CH}_3 \] 91% |
|---|---|---|---|---|


10 examples of the reduction of alcohols (yields 86-99%) and 11 examples of alkyl ethers (yields 0, 87-99%).

(1S)-(−)-N,N-Diisopropyl-10-camphorsulfonamide

The title reagent is employed in the enantioselective synthesis of \( \alpha \)-hydroxy acids.

\[ \text{Pr}_2\text{NO}_2\text{S} \]

<table>
<thead>
<tr>
<th>Chiral Auxiliary</th>
<th>[ \text{MeOH} ] [ \text{CH}_2\text{Cl}_2 ] [ \text{PTSA}, 94% ]</th>
<th>[ \text{LDA}, \text{HMPA} ] [ \text{CH}_2\text{Cl}_2 ] [ \text{THF, -100°C} \rightarrow \text{-78°C} ]</th>
<th>[ \text{NaOH}, \text{MeOH}, \text{HCl} ] [ \text{HO}^{-} ] [ \text{CO}_2\text{H} ] 77% [ \text{dr &gt; 99:1} ]</th>
</tr>
</thead>
</table>


5 examples of alkylation (yields 67-82%, %de > 98%) and 3 examples of the subsequent hydrolysis to acids (yields 94-98%) are reported.

Tricyclic Chiral Sultam Auxiliary

The use of the illustrated chiral auxiliary in asymmetric alkylation is described.

\[ \text{CO}_2\text{Me} \]

<table>
<thead>
<tr>
<th>Chiral Auxiliary</th>
<th>[ \text{HC} = \text{CC} = \text{CH}_2\text{Br} (2 \text{ eq}) ] [ \text{LHMDS} (1.1 \text{ eq}) ] [ \text{HMPA} (2 \text{ eq}) ]</th>
<th>[ \text{THF, -78°C} ], 10 h</th>
<th>[ \text{X}_2 ] [ \text{X}_2 ] 67% [ \text{dr} = 90:10 ]</th>
</tr>
</thead>
</table>


13 examples (yields 35-86%, %de = 0, 20-94%).

(−)-Cinchonidine

The title reagent is used in the enantioselective indium-mediated alkylation of aldehydes.

\[ \text{HO}^{-} \text{N} = \text{CH} \]

<table>
<thead>
<tr>
<th>Ligand</th>
<th>[ \text{H}_2\text{C} = \text{CHCH}_2\text{Br} (6 \text{ eq}) ] [ \text{A} (2 \text{ eq}), \text{in 2 eq} ]</th>
<th>[ \text{THF-hexane (3:1)}, \text{-78°C, 2 h} ]</th>
<th>[ \text{Ph} ] [ \text{Ph} ] 73% [ \text{er} = 88:12 ]</th>
</tr>
</thead>
</table>


14 examples (yields 73-99%, %ee = 41-90%) are reported.

2-[[[(R)-2-Methylthiobutyl]-1-ferrocenyl]diphenylphosphane

A, which has planar and central chirality, is utilised in Pd-catalysed allylic substitutions.

\[ \text{Fe} \]

| Ligand | \[ \text{Ph} \] \[ \text{Ph} \] \[ \text{CH}_2\text{CO}_2\text{Me} \] \[ \text{MeO}_2\text{C} \] \[ \text{CO}_2\text{Me} \] 99% \[ \text{er} = 100:1 \] |
|---|---|---|---|---|---|


2 examples (yields 50, 99%, %ee = 94, 98%) are reported.
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**A** promotes the Cu-catalysed enantioselective 1,4-addition of diethylzinc to acyclic enones.

![Chemical Structure](Image)

**Ligand**

7 examples (yields 53-97%, %ee = 86-98%).

---

**d-Quartz**

**Reagent**

A or its l-enantiomorph promotes the enantioselective addition of disopropyl zinc to a pyrimidinyl carbaldheyde.

![Chemical Structure](Image)


17 examples (yields 90-97%, %ee = 80-97%).

---

**Disopropyloxy-n^2-propenititanium(II)**

**Reagent**

A, in combination with chiral acetals, serves as a chiral propionaldehyde homocoumate equivalent which reacts with imines.

![Chemical Structure](Image)


6 examples (yields 71-85%, %ee = 83-88%, E/Z = 92:8).

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**Allyltributyltin**

**Reagent**

A mediates the carbonylative radical coupling of alkyl iodides with phenylsulfonyl oxime ethers.

![Chemical Structure](Image)


13 examples (yields 19-85%).

---

**Cesium Hydroxide Monohydrate**

**Reagent**

The title reagent promotes the selective \(N\)-alkylation of primary amines.

![Chemical Structure](Image)


23 examples (yields 45-93%) are reported.
### tert-Butyl Hydroperoxide

The title reagent is used in the oxidative palladium-catalysed coupling of arenes with olefins.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>A</th>
<th>H</th>
<th>CO$_2$Et</th>
<th>Ph</th>
<th>H</th>
<th>CO$_2$Et</th>
</tr>
</thead>
<tbody>
<tr>
<td>^3BuOOH</td>
<td></td>
<td>H</td>
<td></td>
<td>Ph</td>
<td>H</td>
<td></td>
</tr>
</tbody>
</table>


23 examples (yields 10-74%) are reported.

### Dimethylidioxirane

The title reagent is used to generate stable neutral solutions of hypochlorous acid, which is trapped in situ by addition to olefins to afford the corresponding ylides.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>A</th>
<th>Ph</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeO</td>
<td>Me</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


14 examples (yields 0, 44-65%) are reported.

### Phenytrimethoxysilane

The title reagent is used in palladium-catalysed cross coupling reactions with aryl halides.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>A</th>
<th>Ph</th>
<th>MeO</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhSi(OCH$_3$)$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


8 examples (yields 29, 62-86%) are reported.

### Tetrakis(dimethylamino)ethylene (TDAE)

The title reagent is a potent electron source in the chromium-mediated alkylation of aldehydes and ketones.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>A</th>
<th>Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_2$N$_2$NMe$_2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


10 examples (yields 0, 36-94%) are reported.

### Nickel(II) Chloride Dihydrate

A in conjunction with lithium and catalytic di-tertbutyliphenyl (DTBB) reduces alkyl and aryl mesylates, dimesylates and triflates to the corresponding hydrocarbons. The reaction conditions also provide a reasonable alternative to the Birch reduction.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>NiCl$_2$·2H$_2$O</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li (8 eq)</td>
<td></td>
</tr>
</tbody>
</table>


19 examples (yields 21-85%).