**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 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, Derek Johnston, Philip Kocienski, and Sukhjinder Uppal of Glasgow University.
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
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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
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Synthesis
Tetrahedron
Tetrahedron Asymmetry and Tetrahedron Letters

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**Chiral (salen)VO Catalyst**

The title reagent catalyzes the asymmetric conversion of aromatic and aliphatic aldehydes into the corresponding trimethylsilyl ethers of cyanohydrins.

[Diagram of the catalyst and reaction](image)


8 examples (%ee = 68-95%) are reported.

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**Ytterbium Tridecafluoride**

The title reagent is used in a fluorous biphasic catalytic Friedel–Crafts acylation of arenes with acid anhydrides. The catalyst is recovered by extraction of the spent acylation reaction mixture with perfluoromethyldecalin.

[Diagram of the catalyst and reaction](image)


1 example (yield 74%) and 2 other ytterbium tris(perfluoroalkanesulfonyl)methide catalysts are reported.

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**Chiral Zirconocene Catalyst**

Reagent A catalyzes the enantioselective methylamination of terminal alkenes. The reaction is accelerated by the addition of either water or methylaluminoxane.

[Diagram of the catalyst and reaction](image)


10 examples (yields 35-94%, %ee = 55-90%) are reported.
### Pd(PhCN)₂Cl₂ / Tri-tert-butyolphosphine

The title reagent pair serves as an efficient and versatile catalyst for Sonogashira reactions of aryl bromides at room temperature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(PhCN)₂Cl₂</td>
<td>A (3 mol%), B (6 mol%)</td>
</tr>
<tr>
<td>P(t-Bu)₃</td>
<td>CuI (2 mol%), HN(i-Pr)₃ (1.2 eq)</td>
</tr>
<tr>
<td></td>
<td>dioxane, rt, 30 min</td>
</tr>
<tr>
<td></td>
<td>94%</td>
</tr>
</tbody>
</table>


12 examples (yields 63-95%) are reported.

### trans-RuCl₂((R)-xylibnap)((R)-daipen)

The title reagent acts as an efficient catalyst for asymmetric hydrogenation of hetero-aromatic ketones.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-MeOC₆H₄</td>
<td>A (0.02 mol%), t-BuOK (0.15 mol%), H₂ (8 atm)</td>
</tr>
<tr>
<td>Cl-R′-Cl</td>
<td>2-propanol, rt, 12 h</td>
</tr>
<tr>
<td>(R)-xylibnap</td>
<td>98%</td>
</tr>
<tr>
<td>(R)-daipen</td>
<td>er &gt; 100:1</td>
</tr>
</tbody>
</table>


14 examples (yields 51, 91-96%, %ee = 91-100%) are reported.

### Palladium-Thiourea-1,3-bis(diphenyolphosphino)propane complex

The title complex catalyses the carboxylative annulation of iodophenol acetates with arylacetylenes to construct the corresponding flavones.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(Ph₃P)₂Cl₂</td>
<td>A (5 mol%), B (5 mol%), C (0.005 mol%)</td>
</tr>
<tr>
<td>H₂NCSCNH₂</td>
<td>DBU (5 eq)</td>
</tr>
<tr>
<td>dppp</td>
<td>HNEt₂, 40°C, 2 d</td>
</tr>
<tr>
<td></td>
<td>92%</td>
</tr>
</tbody>
</table>


8 examples (yields 68-92%) are reported.

### Palladium/Carbon-Ethylene diamine

The title reagent pair catalyse the chemoselective hydrogenation of olefin, nitro and azide functions in the presence of epoxides.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>A/B (5 mol%)</td>
</tr>
<tr>
<td>H₂NCCH₂CH₂NH₂</td>
<td>THF, rt, 3 h</td>
</tr>
<tr>
<td></td>
<td>95%</td>
</tr>
</tbody>
</table>


14 examples (yields 85-100%) are reported.

### Chiral Zirconium Catalyst

The title reagent catalyses the anti-selective aldol reaction of silyl enol ethers with aldehydes.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A (10 mol%)</td>
</tr>
<tr>
<td></td>
<td>PhMe, 0°C, 18 h</td>
</tr>
<tr>
<td></td>
<td>98%</td>
</tr>
<tr>
<td></td>
<td>anti/syn = 95:5</td>
</tr>
<tr>
<td></td>
<td>er = 100:1</td>
</tr>
</tbody>
</table>


12 examples (yields 38-98%, %ee = 81-99%) are reported.
### Palladium Acetate

The title reagent in combination with tr-n-butylyphosphine catalyses the intramolecular cyclisation of alkynes and imines to synthesise indoles.

| Catalyst | \[
\begin{array}{c}
Pd(OAc)_{2} \\
\cellcolor{Gray} A
\end{array}
\]  \[
\begin{array}{c}
\text{A (5 mol\%)} \\
\text{\textit{n-Bu}P (20 mol\%)}
\end{array}
\]
|  \[
\begin{array}{c}
\text{1,4-dioxiane, 100\°C, 1 d} \\
\text{58%}
\end{array}
\]  |


9 examples (yields 55-71\%) are reported.

### RuCp(MeCN)$_3$PF$_6$

The title reagent catalyses the hydrative cyclisation and [4+2] cycloaddition of yne-enones to afford pyrans and cyclic diketones.

| Catalyst | \[
\begin{array}{c}
\text{RuCp(MeCN)$_3$PF$_6$} \\
\cellcolor{Gray} A
\end{array}
\]  |
|  \[
\begin{array}{c}
\text{A (5 \%)} \\
\text{CSA (10 mol\%)} \\
\text{H$_2$O (1.3 eq)}
\end{array}
\]
|  \[
\begin{array}{c}
\text{acetone, rt, 4 h} \\
\text{70%}
\end{array}
\]  |


14 examples (yields 45-89\%) are reported.

### Perfluoroalkyl-Substituted 2,2'-Bipyridine

The title reagent is used as a catalyst ligand for the oxidation of various alcohols to aldehydes and ketones under fluoruous biphasic conditions.

| Catalyst | \[
\begin{array}{c}
\text{C$_8$F$_{17}$} \\
\text{C$_4$F$_{17}$} \\
\cellcolor{Gray} A
\end{array}
\]  |
|  \[
\begin{array}{c}
\text{A (2 \%)} \\
\text{CuBr:Me$_3$S (2 \%)} \\
\text{TEMPO (3.5 \%)}
\end{array}
\]
|  \[
\begin{array}{c}
\text{C$_8$F$_{10}$/PhCl, 90\°C, O$_2$, 4 h} \\
\text{96%}
\end{array}
\]  |


13 examples (yields 31, 69-96\%) are reported.

### (R,R)-2,6-Bis(2-isopropylphenyl)-3,5-dimethylphenol

The title reagent is an effective chiral auxiliary in asymmetric Mannich-type reactions of certain aldimines.

| Chiral Auxiliary | \[
\begin{array}{c}
\text{HO} \\
\text{A}
\end{array}
\]  \[
\begin{array}{c}
\text{(a) BuLi (1 eq)} \\
\text{THF, \textit{--78\°C}, 30 min}
\end{array}
\]
|  \[
\begin{array}{c}
\text{(b) Et$_2$Zn (1 eq)} \\
\text{THF, \textit{--78\°C}, 27 h}
\end{array}
\]  |
|  \[
\begin{array}{c}
\text{OMe} \\
\text{A}
\end{array}
\]  \[
\begin{array}{c}
\text{OMe} \\
\text{A}
\end{array}
\]  \[
\begin{array}{c}
\text{X_C} \\
\text{X_C}
\end{array}
\]  \[
\begin{array}{c}
\text{82\%} \\
\text{dr = 96:4}
\end{array}
\]  |


13 examples (yields 29-82\%, \textit{ее} = 84-96\%) are reported.

### 2(S)-(Diphenylphosphino)-1-[4(S)-isopropyl-2-oxazolin-2-yl]ferrocene [(S)-i-Pr-DIPOF]

The title ligand is used in the enantioselective ring opening of oxabicyclic alkenes.

| Ligand | \[
\begin{array}{c}
\text{O} \\
\text{Fe}
\end{array}
\]  \[
\begin{array}{c}
\text{A}
\end{array}
\]  \[
\begin{array}{c}
\text{PPh$_2$}
\end{array}
\]  \[
\begin{array}{c}
\text{Fe}
\end{array}
\]  \[
\begin{array}{c}
\text{Pr}
\end{array}
\]  \[
\begin{array}{c}
\text{P}
\end{array}
\]
|  \[
\begin{array}{c}
\text{A (5 \%)} \\
\text{Pd(CH$_2$CH$_2$)$_2$Cl$_2$ (5 \%)} \\
\text{Me$_2$Zn (2 eq)} \\
\text{(CH$_2$Cl)$_2$}
\end{array}
\]
|  \[
\begin{array}{c}
\text{87\%} \\
\text{er = 96:4}
\end{array}
\]  |


8 examples (yields 19-92\%, \textit{ее} = 87-95\%) are reported.
### Diphosphate Ferrocene Ligand

The title ligand mediates the rhodium-catalysed asymmetric ring-opening reaction of oxazaborinorbornadienes using alcohol and amine nucleophiles.


16 examples (yields 53-96%, %ee = 45-99%) are reported.

### Diphosphanylferrocene (FerroTANE)

The title ligand is used in the enantioselective rhodium-catalysed hydrogenation of ilaconate derivatives.


13 examples (%ee = 88-99%) are reported.

### 1-(2-Methoxyethoxy)-1-vinylcyclopropane

The title reagent is used as a five-carbon component in metal-catalysed [3+2] cycloadditions to prepare substituted cycloheptenones.


11 examples (yields 75-97%) are reported.

### Bis(2,4-dichlorophenyl)chlorophosphite

The title reagent is used in a one-pot preparation of alkyl azides from alkanols.


8 examples (yields 76-92%) are reported.

### Bis(2,2,2-trifluoroethyl)bromophosphonoacetate

The title reagent is used in the presence of t-BuOK and 18-C-6 to prepare (E)-ω-bromo-acylates by Horner-Emmons-Wadsworth-Emmons (HWE) reaction with various aldehydes.


12 examples (yields 47-100%, 9:1 = E:Z = 30:1) are reported.