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

Tetrakis[N-(4-dodecylphenyl)-sulfonyl]-prolinate] Dirhodium Catalyst

The title reagent promotes the catalytic asymmetric synthesis of highly functionalised cyclopentenes by a [3+2] cycloaddition.


Oxygen/Palladium(II) Acetate Catalyst

The title reagent pair promotes enantioselective oxidations of alcohols.


Iodosylbenzene/p-Toluenesulfonylamine/Tetrakis(acetonitrile)copper(I) Hexafluorophosphate Catalyst

The title reagents promote the formation of aziridines via a copper-catalysed nitrogen transfer.

### Oxygen/Palladium(II) Norbornadiene dichloride

**Catalyst**

The title reagents promote enantioselective oxidations of alcohols.


\[
\begin{align*}
\text{Pd(nbd)Cl}_2 & \quad \text{A} \\
\text{O}_2 & \quad \text{O} \\
\text{B} & \\
\text{OH} & \quad \text{+} \\
\text{OH} & \\
\%\text{conv} = 60\% & \quad \text{er} = 99:1 \\
\text{11 examples (%conv 48–70%, %ee 69–100%).}
\end{align*}
\]

### Copper(I) Iodide/(-)-Trans-1,2-cyclohexanediamine

**Catalyst**

The title reagent pair promotes the amidation of aryl halides and the N-arylation of nitrogen heterocycles.


\[
\begin{align*}
\text{CuI} & \quad \text{A} \\
\text{MeNHCHO (1.2 equiv)} & \quad \text{B} \\
\text{K}_3\text{PO}_4 (2 equiv) & \\
\text{dioxane, 110 °C, 23 h} & \\
\text{96\%} & \\
\text{48 examples (yields 62–100%).}
\end{align*}
\]

### Ansa-Titanocene Dicarbonyl Complex

**Catalyst**

The title reagent promotes the formation of \(\gamma\)-butyrolactones via a catalytic asymmetric cyclocarbonylation.


\[
\begin{align*}
\text{Ti CO} & \quad \text{A} \\
\text{CO (50 psi)} & \\
\text{PhMe, 100 °C, 36–40 h} & \\
\text{88\%} & \quad \text{er} = 95:5 \\
\text{8 examples (yields 80–96%, %ee 0–90%).}
\end{align*}
\]

### 9-Dihydroquinidyloxyphenanthrene

**Catalyst**

The title reagent promotes the cyanation of ketones to afford optically pure cyanohydrin carbonates.


\[
\begin{align*}
\text{MeO} & \quad \text{A} \\
\text{EtO} & \\
\text{EtO} & \\
\text{EtO} & \\
\text{EtO} & \\
\text{99\%} & \quad \text{er} = 97:3 \\
\text{4 examples (yields 65–99%, %ee 90–96%).}
\end{align*}
\]

### Binaphthyl Bis-phosphoramidine\(^a\)

**Catalyst**

The title reagent promotes catalytic enantioselective allylation and propargylation of aldehydes.


\[
\begin{align*}
\text{SiCl}_4 (1.1.\text{equiv}) & \quad \text{A} \\
\text{CH}_2\text{Cl}_2, –78 °C, 6 h & \\
\text{8 examples (yields 65–94%, %ee 11–94%).}
\end{align*}
\]

\(^a\)((R,R)-N,N'- Bis[4,5-dihydro-3,5-dimethyl-2-(3H-dinaphth[2,1-d:1',2'-f]-
[1,3,2]-2-oxo-diazaphosphepino)]-N,N'-dimethyl-1,5-pentanediamine

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### Triruthenium Dodecacarbonyl Catalyst


- **Ru$_3$(CO)$_{12}$**
- **A**
- $\text{A} \text{(3 mol%), CO (5 atm)}$
- $\text{Et$_3$N, 100 °C, 4 h, 71\%}$
- 7 examples (yields 66–85%).

### Nickel(II) Acetylacetonate/1,3-Bis-(2,6-diisopropylphenyl)-3H-imidazol-1-ium Catalyst


- **Ni(acac)$_2$**
- **A**
- **B**
- **A** (2 mol%), **B** (4 mol%), BuOH (0.12 equiv), NaH (1.22 equiv), THF, 65 °C, 10 h, 75%
- 13 examples (yields 47–99%).

### Palladium Black Catalyst


- **Pd**
- **A**
- **A** (0.5 equiv), PhI (0.9 equiv)
- MeOH, $\Delta$, 4 h, 92%
- 18 examples (yields 74–98%).

### Modified Guanidine Catalyst


- **NMeMeN**
- **PhPh**
- **N**
- **CH$_2$Ph**
- **OH**
- **O**
- **O**
- **O**
- **Ph**
- **CO$_2$Bu**
- **t**
- **NPh**
- **Ph**
- **CO$_2$Bu**
- **CH$_2$CH$_2$CO$_2$Et**
- **A** (0.2 equiv), CH$_2$C=CHOEt (3.6 equiv), r.t., 3 d, 85%
- er = 99:1
- 4 examples (yields 79–98%, %ee 55–97%).

### $\beta$-Ketoiminato Cationic Cobalt(III) Complex Catalyst


- **CoSbF$_6$**
- **A**
- Ph$_2$C=CH$_2$(CH$_2$)$_2$N$_2$Ph$_2$ (5 mol%), CH$_2$C=CHOEt (0.5 equiv), CHCl$_3$, $-20$ °C, 48 h, 92%
- er = 94:6
- 8 examples (yields 56–92%, %ee 76–94%).
Benzoylquinine **Catalyst**
The title reagent catalyses the enantioselective α-bromination of acid chlorides.

\[
\begin{align*}
\text{Ph} & \quad \text{Cl} \\
\text{Ph} & \quad \text{O} \\
\text{Cl} & \quad \text{Ph} \\
\text{Br} & \quad \text{A} \\
\text{A} & \quad \text{(10 mol%)} \\
\text{PhMe}, -78 & \rightarrow 25 ^\circ \text{C}, 24 \text{ h} \\
76% & \\
er & = 96:4 \\
\end{align*}
\]

6 examples (yields 58–76%, %ee 86–98%).

Copper(II) Acetate **Catalyst**
The title reagent catalyses the coupling of arylboronic acids and amines.

\[
\begin{align*}
\text{Cu(OAc)}_2 \\
\text{A} \\
\text{A} & \quad \text{(5 mol%)} \\
\text{PhB(OH)}_2 & \quad (1.5 \text{ equiv}) \\
\text{Myristic acid} & \quad (10 \text{ mol%}) \\
2,6-lutidine & \quad (1 \text{ equiv}) \\
\text{PhMe}, \text{ r.t.}, 24 \text{ h} \\
79% \\
\end{align*}
\]

23 examples (yields 50–91%).

β-Ketoiminato Cobalt Complex **Catalyst**
The title reagent catalyses the reductive desymmetrization of 2-alkyl-1,3-diketones.

\[
\begin{align*}
\text{N} \\
\text{O} \\
\text{O} \\
\text{Co} \\
\text{A} \\
\text{A} & \quad \text{(5 mol%)} \\
\text{NaBH}_4 & \quad (1 \text{ equiv}) \\
\text{EtOH} & \quad (1 \text{ equiv}) \\
\text{THFA} & \quad (14 \text{ equiv}) \\
\text{CHCl}_3 , 0 ^\circ \text{C}, 10 \text{ h} \\
93% \\
er & = 99:1 \\
\end{align*}
\]

9 examples (yields 45–97%, %ee 91–99%).

Cationic Rhodium Complex **Catalyst**
The title reagent catalyses the 1,4-addition of arylboronic acids to acetylated enones derived from glycals.

\[
\begin{align*}
\text{Rh(I)(cod)}_2 \text{BF}_4 \\
\text{A} \\
\text{A} & \quad \text{(5 mol%)} \\
\text{PhB(OH)}_2 & \quad (2 \text{ equiv}) \\
\text{Dioxane/H}_2 \text{O}, 100 ^\circ \text{C}, 4 \text{ h} \\
76% \\
\end{align*}
\]

7 examples (yields 50–81%).

(2'-Dicyclohexylphosphanylbiphenyl-2-yI)-dimethylamine **Ligand**
The title reagent promotes ω-arylation of esters in the presence of palladium(II) acetate.

\[
\begin{align*}
\text{A} \\
\text{A} & \quad \text{(6.3 mol%)} \\
\text{CH}_3 \text{CO}_2 \text{tBu} & \quad (2.3 \text{ equiv}) \\
Pd(OAc)_2 & \quad (3.0 \text{ mol%}) \\
\text{LiHMDS} & \quad (2.5 \text{ equiv}) \\
\text{PhCH}_3 , 80 ^\circ \text{C}, 1 \text{ h} \\
84% \\
\end{align*}
\]

27 examples (yields 48–92%).
### (+)-1,2-Bis-N-[2-(diphenylphosphino)benzoyl]-1(R),2(R)-diamino-1,2-diphenylethane

**Ligand**


![Chemical Structure](image)

8 examples (yields 58–100%, %ee 85–92%).

### (DHQD)$_2$PHAL-PEG-OMe

**Ligand**

The title reagent is a soluble polymer-bound ligand, which when complexed to osmium, catalyses the asymmetric dihydroxylation of alkenes. Kuang, Y. Q.; Zhang, S. Y. Y.; Wei, L. L. *Tetrahedron Lett.* 2001, 42, 5925.

![Chemical Structure](image)

6 examples (yields 81–92%, %ee 82–98%).

### Phenol Ligand

**Ligand**


![Chemical Structure](image)

9 examples (yields 12–89%, %ee 76–94%).

### Ethylzincmethyl Perfluoropentanoate

**Reagent**


![Chemical Structure](image)

6 examples (%conv 41–99%).

### 1-(1-Naphthylmethyl)-2-[(E)-2-butenoyl]-5,5-dimethylpyrazolidin-3-one

**Reagent**


![Chemical Structure](image)

6 examples (%ee 66–99%).
<table>
<thead>
<tr>
<th>Reagent</th>
<th>Potassium Trimethylsilylaluminate</th>
</tr>
</thead>
<tbody>
<tr>
<td>The title reagent promotes the palladium-catalysed cross-coupling reaction of organosilicon compounds with organic iodides.</td>
<td>KOSiMe$_3$ A</td>
</tr>
<tr>
<td>![Reaction Scheme]</td>
<td>n-C$_3$H$_7$, Me $\text{OH}$ (1.1 equiv) A (2 equiv) Pd(dba)$_2$ (5 mol%) DMF, r.t., 7.5 h 86% 14 examples (yields 76–95%).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Dicyclohexylmethylamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>The title reagent promotes the Heck reaction of aryl chlorides and bromides with olefins, in the presence of Pd/P(t-Bu)$_3$ catalyst.</td>
<td>Cy$_2$NMe A</td>
</tr>
<tr>
<td>![Reaction Scheme]</td>
<td>CO$_2$Me (1.1 equiv) A (1.1 equiv) P(t-Bu)$_3$ (3 mol%) Pd$_2$(dba)$_3$ (1.5 mol%) dioxane, r.t., 36 h 79% 30 examples (yields 52–97%).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Dimethyldioxirane</th>
</tr>
</thead>
<tbody>
<tr>
<td>The title reagent promotes epoxidations of 1-amidoallenes as a general entry to chiral nitrogen-substituted oxallyl cation equivalents for stereoselective [4+3] cycloaddition.</td>
<td>O-O A</td>
</tr>
<tr>
<td>![Reaction Scheme]</td>
<td>A (2–3 equiv) ZnCl$_2$ (2.0 equiv) furan (10 equiv) THF, –40 °C, 8 h O N Ph ¥ O N Ph O 40% dr = 95:5 8 examples (yields 40–83%, %de 5–90%).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Tin(II) Triflate</th>
</tr>
</thead>
<tbody>
<tr>
<td>The title reagent promotes the formation of optically pure 2,5-disubstituted-3-pyrrolidinones via an asymmetric [3+2] cycloaddition reaction involving chiral alkenyl Fischer carbene complexes and imines.</td>
<td>Sn(OTf)$_2$ A</td>
</tr>
<tr>
<td>![Reaction Scheme]</td>
<td>(a) NPh Ph A (1.2 equiv) CICH$_2$CH$_2$Cl, A, 3 h 51% (b) 6M HCl THF, r.t., 3 h 96% er = 99:1 9 examples (yields 85–98%, %ee 96–99%).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Chiral Sulfide</th>
</tr>
</thead>
<tbody>
<tr>
<td>The title reagent mediates the aziridination of imines with alkyl bromides via the imino Corey–Chaykovsky reaction.</td>
<td>S$_2$Ph$_2$ A</td>
</tr>
<tr>
<td>![Reaction Scheme]</td>
<td>A (1 equiv), Br$_2$Br (3 equiv), K$_2$CO$_3$ (3 equiv) MeCN, r.t. Ts Ph N Ph 99% dr = 75:25 er = 97:3 10 examples (yields 79–99%, %de 8–58%, %ee 42–95%).</td>
</tr>
</tbody>
</table>
Titanium Tetraisopropoxide/Isopropylmagnesium Bromide

The title reagent pair, when reacted with 2-alkynal tetramethylethylene acetals and then aldehydes, provides a one-pot route to 2-substituted and 2,3-disubstituted furans. Teng, X.; Takeshi, W.; Okamoto, S.; Sato, F. *Tetrahedron Lett.* 2001, 42, 5501.

Cesium Carbonate


Copper(I) Thiophene-2-carboxylate (CuTC)


Nickel(II) Acetylacetonate/Diethylzinc


N-(tert-Butoxycarbonyl)-N-[4-(dimethylazaniumylidene)-1,4-dihydropyridin-1-ylsulfonyl]azanide

**tert-Butyl[pyrazol-1-yl(toluene-4-sulfonylimino)methyl] Carbamoate**

The title reagent can be used for the preparation of guanidine-containing peptides.


\[
\text{BocHN} \quad \text{NTs} \quad \text{A (1.1 equiv)}
\]

\[
\text{THF, r.t., 5 min}
\]

100%

8 examples (yields 0–100%).

---

**1-tert-Butylperoxy-1,2-benziodoxol-3(1H)-one**

The title reagent can be used for the oxidative cleavage of five-membered cyclic acetals to the corresponding hydroxy esters under mild conditions.


\[
\text{A (1 equiv)}
\]

\[
\text{t-BuOOH (5 equiv)}
\]

\[
\text{K}_2\text{CO}_3 \quad (2 \text{ equiv})
\]

\[
\text{PhH, r.t., 24 h}
\]

94%

9 examples (yields 54–94%).

---

**Azidomethyl Phenyl Sulfide**

The title reagent can be used for the amination of Grignard reagents.


\[
\text{PhSCH}_2\text{N}_3
\]

\[
\text{ClCl}
\]

\[
\text{EtMgCl (5 equiv)}
\]

\[
\text{THF, –78 \rightarrow –30 ^\circ \text{C}, 1.5 h}
\]

\[
\text{A (20 equiv), –78 ^\circ \text{C}, 1 h}
\]

\[
\text{Ac}_2\text{O, –30 ^\circ \text{C}, 1 h}
\]

\[
\text{KOH, DMSO, r.t., 3 h}
\]

82%

er = 96:4

1 example (yield 82%, %ee 92%).

---

**Tricyclohexylphosphine**

The title reagent promotes the Mitsunobu cyclodehydration of chiral phenethane-1,2-diols when used with diisopropylazodicarboxylate (DIAD).


\[
\text{OH}
\]

\[
\text{OH}
\]

\[
\text{A (1.5 equiv)}
\]

\[
\text{DIAD (1.45 equiv)}
\]

\[
\text{THF, r.t., 2 h}
\]

80%

%ee 91:9

8 examples (yields 65–92%, %ee 76–96%).

---

**Lithium Bis(trimethylsilyl)amide**

The title reagent can be used for the palladium-catalysed synthesis of arylamines from aryl halides.


\[
\text{Me}_3\text{Si} \quad \text{Li}
\]

\[
\text{SiMe}_3
\]

\[
\text{A (1 equiv)}
\]

\[
\text{Pd(dba)}_2 \quad (0.5 \text{ mol%})
\]

\[
\text{P(t-Bu)}_3 \quad (0.5 \text{ mol%})
\]

\[
\text{PhMe, 70 ^\circ \text{C}, 18 h}
\]

\[
\text{HCl}
\]

76%

23 examples (yields 62–99%).