**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: Fabrice Anizon, Robert Chow, and Sukhjinder Uppal, Department of Chemistry, Leeds University.

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### Hexafluoro-2-propanol (HFIP)

**Reagent**

The title reagent, when used as the solvent, facilitates the ring opening of oxiranes by aryl amines in the formation of β-aminos.

![Chemical Structure](image)


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

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### N-Hydroxyphthalimide (NHPI) / Cobalt(II) Acetate

**Catalyst**

The title reagent pair catalyse the oxidation of primary and secondary alcohols, and diols with molecular oxygen.

![Chemical Structure](image)


22 examples (yields 47-98%) are reported.

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### 3,5-Di-tert-butylphenyl Ferrocenyl Amine

**Ligand**

The title reagent was developed for use in copper catalysed, enantioselective allylic substitution with organometallic reagents.

![Chemical Structure](image)


8 examples (yields 72-89%, %ee = 44-89%) are reported.

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### Nickel(II) Chloride / Triphenylphosphine Complex

The title reagent catalyses the cross-coupling of aryloboronic acids with arylchlorides for the synthesis of biaryl.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NiCl}_2(\text{PPh}_3)_2 )</td>
<td>( \text{Cl} )</td>
</tr>
<tr>
<td>4-tolyl(BO(_3))(_2) (1.3 eq), ( \text{A} ) (0.03 eq), K(_2)P(_4)O(_7)(\cdot)H(_2)O (2.6 eq)</td>
<td>Ph(_2)CH(OMe)</td>
</tr>
<tr>
<td>( \text{PPh}_3 ) (0.06 eq), PhMe, 80°C, 2 h</td>
<td>99%</td>
</tr>
</tbody>
</table>


22 examples (yields 15, 68-99%) are reported.

### Trifluoromethyltrimethylsilane

The title reagent is used for the trialkylsilylation of terminal alkynes, catalysed by cesium or potassium fluoride.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM(_2)CSF(_3) (1.2 eq)</td>
<td>( \text{TaN}^+\text{SiMe}_3^- )</td>
</tr>
<tr>
<td>THF, rt, 0.5 h</td>
<td>100%</td>
</tr>
</tbody>
</table>


25 examples (yields 40-100%) are reported.

### Indium

The title reagent is used for the reductive coupling of acyl cyanides to give the corresponding 1,2-diketones, in good to moderate yields.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>( \text{PhCN} )</td>
</tr>
<tr>
<td>DMF, rt, 8 h</td>
<td>82%</td>
</tr>
</tbody>
</table>


12 examples (yields 0, 60-78%) are reported.

### Tetraallylstannane

The title reagent is used for the alkylation of N-protected aminoaldehydes to give the corresponding homoallylic alcohols in excellent yields and good diastereoselectivities.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Sn} \text{Ph}_2 \text{NH} )</td>
<td>( \text{Ph} )</td>
</tr>
<tr>
<td>MeOH, 30°C, 1 d</td>
<td>82%</td>
</tr>
</tbody>
</table>


6 examples (yields 68-94%, %de = 50-86%) are reported.

### Palladium Hydroxide / Charcoal

The title catalyst can be used with formaldehyde to methylate \( N \)-mono-alkylated amino acids in good to excellent yields.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%Pd(OH)(_2)/C</td>
<td>( \text{HCHO} ) (5.9 eq)</td>
</tr>
<tr>
<td>( \text{H}_2 ) (50 psi)</td>
<td>( \text{EtOH}, 50^\circ\text{C} )</td>
</tr>
</tbody>
</table>


4 examples (yields 58-92%) are reported.
Bis(methoxyethyl)zirconocene Dihydride

The title reagent can be used for the reductive coupling of alkenes, dienes and enynes.

\[ \text{Reagent} \]


8 examples (yields 28-82%) are reported.

C₂-Symmetric Chiral Quaternary Ammonium Salts

The title phase-transfer catalyst can be used for the asymmetric synthesis of l-Dopa and related amino acid esters.

\[ \text{Catalyst} \]


1 example (yield 80%, %ee = 90%) is reported.

Ferrocenyl Oxazoline

The title reagent catalyses the formation of arylphenylmethanols from benzaldehydes with very high selectivities.

\[ \text{Catalyst} \]


12 examples (yields 64-99%, %ee 83-98%) are reported.

1,1'-Bis(diphenylphosphanyl)ferrocene

The title reagent acts as chiral ligand for palladium-catalysed allylic substitution with high diastereoselectivity and enantioreselectivity.

\[ \text{Ligand} \]


7 examples (%de 20-94%) are reported.

N,N'-Bis(2-pyridinecarboxyl)-1,2-cyclohexanedicarboxamide

The title reagent can be used for microwave-heated molybdenum(0)-catalysed asymmetric allylic alkylations.

\[ \text{Ligand} \]


12 examples (yields 1, 11, 59-94%, %ee = 95-98%) are reported.
### Conjugate Addition Catalyst
The title reagent catalyses the asymmetric conjugate addition of azide to α,β-unsaturated carbonyl compounds.

T. E. Horstmann, D. J. Guerin, S. J. Miller

6 examples (yields 79-97%, %ee = 45-85%) are reported.

### Dodecarbonyltetracobalt / Cyclohexylamine
The title reagent pair catalyse the Pauson-Khand reaction.

M. E. Krafft, L. V. R. Bonaga

10 examples (yields 44-94%) are reported.

### (R)-3,3'-dimethyl-1,1'-binaphth-2,2'diamine (DM-DABN)
The title reagent catalyses the hydrogenation of ketones through asymmetric activation / deactivation.

K. Mikami, T. Koranaga, T. Ohkuma, R. Noyori

7 examples (yields 99%, %ee = 91-96%) are reported.

### Dicarbonyl(acetylacetonate)rhenium
The title reagent catalyses the carbonylation of organomercurial chlorides to generate aldehydes.

S. T. Sarraf, J. L. Leighton

5 examples (yields 60-79%) are reported.

### η²- Allylpalladium Chloride
The title reagent catalyses the cross-coupling of aryl halides with (α-alkoxyvinyl)silanols and (α-alkoxvinyl)stil hydrides in the presence of tetrabutylammonium fluoride or hydroxide.

S. E. Denmark, L. Neuville

14 examples (yields 71-94%) are reported.
### Indium

The title reagent mediates the coupling of 1,4-dibromo-2-butyne with carbonyl compounds in aqueous media to give good yields of the 1,3-butenadien-2-ylmethanol.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>$\text{In}$</th>
<th><img src="image" alt="Reaction" /></th>
<th>H$_2$O, rt, 6 h</th>
<th>53%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td><img src="image" alt="Product" /></td>
<td>7 examples (yields 53-66%) are reported.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


### (R,R)-Pseudoephedrine

The title reagent can be utilised as a chiral auxiliary for synthesizing $\alpha$-substituted $\beta$-amino acids.

<table>
<thead>
<tr>
<th>Chiral Auxiliary</th>
<th><img src="image" alt="Molecule" /></th>
<th>(a) A, PVCl, TEA THF, 0°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(b) HCl, H$_2$O:MeOH (1:1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(c) MeI, LHMDS, LiCl THF, $-5\rightarrow 0^\circ$C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(d) H$_2$O, $\Delta$</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Product" /></td>
<td>4 examples (yields 52-74%, $%ee = 75-99%$) are reported.</td>
</tr>
</tbody>
</table>


### Methyl Bis(2,2,2-trifluoroethoxy)bromophosphonoacetate

The title reagent can be used for the preparation of (E)-$\alpha$-bromoacylates, using the Horner–Wadsworth–Emmons reaction, with high stereoselectivity and excellent yield.

<table>
<thead>
<tr>
<th>Reagent</th>
<th><img src="image" alt="Molecule" /></th>
<th>OCH$_2$CH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image" alt="Product" /></td>
<td>24 examples (yields 43, 64-99%, 7:1 $\leq$ E:Z $\leq$ 1:0) are reported.</td>
</tr>
</tbody>
</table>


### Bis(1,4-cyclooctadiene)rhodium Tetrafluoroborate

The title reagent catalyses the Grignard-type carbonyl phenylation of aldehydes by trimethylphosphystannane, in water and under air atmosphere.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th><img src="image" alt="Molecule" /></th>
<th>Rh(COD)$_2$BF$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image" alt="Product" /></td>
<td>11 examples (yields 52-92%) are reported.</td>
</tr>
</tbody>
</table>


### Aluminium Tris(2,6-diphenylphenoxide)

The title reagent complexes with aromatic acyl chlorides allowing conjugate addition of nucleophiles to aromatic systems.

<table>
<thead>
<tr>
<th>Reagent</th>
<th><img src="image" alt="Molecule" /></th>
<th>(a) A (1.1 eq) BuMgCl (3 eq) PhH/THF, $-78^\circ$C, 30 min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image" alt="Product" /></td>
<td>(b) HCl, $-78^\circ$C, rt, 24 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="image" alt="Conversion" /> 90% 1,6 : 1,4 = 15:1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 examples (yields 41-99%, 3.4:1 $\leq$ 1.6:1,4 $\leq$ 99:1) are reported.</td>
</tr>
</tbody>
</table>

### Tris(2,6-diphenylbenzyl)silyl Bromide (TDS-Br)

**Protection Group**

The title reagent can be used to protect carboxylic acids against various nucleophilic attacks and α-deprotonation.

![Chemical Structure](image)


4 examples (yields 84-93%) are reported.

### Chiral Phosphine Ligand

**Ligand**

The title reagent acts as a chiral bidentate ligand for the asymmetric intermolecular Pauson-Khand reaction.

![Chemical Structure](image)


5 examples (yields 92-99%, %ee = 57-99%) are reported.

### Chiral Hydroxy Acid Ligand

**Ligand**

The title reagent is used as a ligand for the vanadium-catalysed asymmetric epoxidation of allylic alcohols.

![Chemical Structure](image)


9 examples (yields 58-99%, %ee = 76-98%) are reported.

### PINDY

**Ligand**

The title ligand, when complexed with copper, can be used to catalyse asymmetric allylic oxidation, with high efficiency and good enantioselectivity.

![Chemical Structure](image)


3 examples (yield 96%, %ee = 48-75%) are reported.

### Ytterbium Triflate

**Catalyst**

The title reagent catalyses the oxymercuration of hemiketals and hemiacetals derived from homoallylic alcohols and acetone or benzaldehyde, with Hg(OTf)2.

![Chemical Structure](image)


9 examples (yields 54-85%) are reported.