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:
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Hexafluoro-2-propanol (HFIP)

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


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

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

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


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

3,5-Di-tert-butylphenyl Ferrocenyl Amine

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


8 examples (yields 72-89%, ee = 44-89%) are reported.
### Nickel(II) Chloride / Triphenylphosphine Complex

The title reagent catalyses the cross-coupling of aryboronic acids with aryliodo compounds for the synthesis of biaryl derivatives.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCl₂(PPh₃)₂</td>
<td>4-tolyl(B(OH))₂ (1.3 eq), A (0.03 eq), K₂PO₄·H₂O (2.6 eq)</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>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMSCF₃</td>
<td>TaN</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>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>CN</td>
</tr>
</tbody>
</table>


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

### Tetraallylstannane

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

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Sn)₄</td>
<td>NH₂OH</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>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%Pd(OH)₂/C</td>
<td></td>
</tr>
</tbody>
</table>


4 examples (yields 58-92%) are reported.
**SYNTHESIS ALERTS**

**Bis(methoxyethyl)zirconocene Dihydride**

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

![Chemical structure](image)

(a) A (0.5 eq) THF, rt, 4 h
(b) Br₂ (1.6 eq) 0°C, 1 h
82%


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.

![Chemical structure](image)

A (1 mol%) toluene-50% KOH aq, 0°C, 1 h
1M citric acid THF, rt, 10 h
1 example (yield 80%, %ee = 90%) is reported.


**Ferrocenyloxazoline**

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

![Chemical structure](image)

A (10 mol%) ZnPh₂ (0.65 eq) ZnEt₂ (1.3 eq) PhMe, 10°C, 12 h

86%

er = 98:2

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 enantioselectivity.

![Chemical structure](image)

A (10 mol%) THF, 16°C, 16 h

67%

dr = 97:3

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


**N,N'-Bis(2-pyridinecarboxyl)-1,2-cyclohexanediamine**

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

![Chemical structure](image)

N₂O-bis(trimethylsilyl)acetamide (1.2 eq) A (5 mol%) CH(COOH)² (1.1 eq)
Mo(CO)₅ (4 mol%) THF, 120 W, 5 min
86%

er = 99:1

12 examples (yields 1, 11, 59-94%, %ee = 95-99%) are reported.

### Conjugate Addition Catalyst

The title reagent catalyses the asymmetric conjugate addition of azide to $\alpha,\beta$-unsaturated carbonyl compounds.

![Conjugate Addition Catalyst](image)

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

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

### Dodecacarbonyltetracobalt / Cyclohexylamine

The title reagent pair catalyse the Pauson-Khand reaction.

![Dodecacarbonyltetracobalt / Cyclohexylamine](image)

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.

![3,3'-dimethyl-1,1'-binaphth-2,2'-diamine](image)

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

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

### Dicarboxy(acetylacetone)rhodium

The title reagent catalyses the carboxylation of organomercurial chlorides to generate aldehydes.

![Dicarboxy(acetylacetone)rhodium](image)

S. T. Serraf, J. L. Leighton

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

### $\eta^2$-Allylpalladium Chloride

The title reagent catalyses the cross-coupling of aryl halides with ($\alpha$-alkoxyvinyl)silanol and ($\alpha$-alkoxyvinyl)silyl hydrides in the presence of tetraethylammonium fluoride or hydroxide.

![$\eta^2$-Allylpalladium Chloride](image)

S. E. Denmark, L. Neuville

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

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-butadien-2-ylmethane.

$$\text{In} \quad \text{A} \xrightarrow{1,4\text{-dibromo-2-butyne (1.5 eq)}} \text{B} \quad \text{H}_2\text{O, rt, 6 h} \quad 53\%$$


7 examples (yields 53-66%) are reported.

### (R,R)-Pseudoephedrine Chiral Auxiliary

The title reagent can be utilised as a chiral auxiliary for synthesizing α-substituted β-amino acids.

$$\text{Me} \quad \text{N} \quad \text{H} \quad \text{OH} \quad \text{A} \quad \text{BocNHCH(OH)} \quad \text{COH} \quad \text{N}\text{H}_{2} \quad \text{A} \quad \text{H}_{2}\text{N}\text{CH(OH)COH}$$

(a) A, CHCl₃, TEA
(b) HCl, H₂O/MeOH (1:1)
(c) MeLi, LHMDS, LiCl
(d) H₂O, ∆


4 examples (yields 52-74%, %ee = 75-99%) are reported.

### Methyl Bis(2,2,2-trifluoroethoxy)bromophosphonooacetate Reagent

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

$$\text{OCH}_3\text{CH}_3$$

$$\text{CF}_2\text{H}_2\text{O} \quad \text{P} \quad \text{O}$$

$$\text{MeO}$$

$$\text{A} \quad \text{A} \quad \text{1.1 eq)} \quad \text{BuOK (1.06 eq)} \quad \text{18-crown-6 (1.3 eq)}$$

$$\text{THF, -78°C, 20 min} \quad \text{MeO}_{2}\text{C}$$

$$\text{Br} \quad \text{Br} \quad 94\%$$

$$E:Z = 30:1$$


24 examples (yields 43, 64-99%, 7:1 ≤ E:Z ≤ 1:0) are reported.

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

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

$$\text{Rh(COD)}\text{BF}_4$$

$$\text{SnMe}_3$$

$$\text{A} \quad \text{A} \quad \text{6 mol%) PhCHO (1 eq)}$$

$$\text{H}_2\text{O, 100°C} \quad \text{82%}$$


11 examples (yields 52-92%) are reported.

### Aluminium Tris(2,6-diphenylphenoxy) Reagent

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

$$\text{Ph} \quad \text{Ph} \quad \text{O} \quad \text{A} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph}$$

(a) A (1.1 eq) BuMgCl (3 eq) 
(b) HCl, –78°C, rt, 24 h

$$\text{Ph} \quad \text{OH} \quad \text{Ph} \quad \text{COH} \quad \text{Bu} \quad 90\%$$

$$1,6:1,4:15:1$$


10 examples (yields 41-99%, 3:4:1 ≤ 1:6:1,4:1 ≤ 99:1) are reported.
### Tris(2,6-diphenylbenzyl)silyl Bromide (TDS-Br)

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

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 Hydroxylic Acid 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 = 76-96%) are reported.

### PINDY

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 (yields 96%, %ee = 48-75%) are reported.

### Ytterbium Trflate

The title reagent catalyses the oxymercuration of hemiketals and hemiacetals derived from homoalcoholic alcohols and acetone or benzaldehyde, with HgOAc.

![Chemical Structure](image)


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