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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Department of Chemistry, Leeds University.

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Article Identifier:
1437-210X,E:2001,0,03,0499,0504,ftx,en;X00301SS.pdf

<table>
<thead>
<tr>
<th>Hexafluoro-2-propanol (HFIP)</th>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>The title reagent, when used as the solvent, facilitates the ring opening of oxiranes by aryl amines in the formation of β-amaionics.</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>OH</td>
<td>F₃C-CF₃</td>
</tr>
<tr>
<td>A</td>
<td>A (10 eq), Δ, 2.5 h 92% 11 examples (yields 68-92%) are reported.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>N-Hydroxyphthalimide (NHPI) / Cobalt(II) Acetate</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>The title reagent pair catalyse the oxidation of primary and secondary alcohols, and diols with molecular oxygen.</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td><img src="image" alt="Chemical Structure" /></td>
<td>A (10 mol%), B (0.5 mol%), m-chlorobenzoic acid (5 mol%), O₂ (1 atm) 22 examples (yields 47-98%) are reported.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3,5-Di-tert-butylphenyl Ferrocenyl Amine</th>
<th>Ligand</th>
</tr>
</thead>
<tbody>
<tr>
<td>The title reagent was developed for use in copper catalysed, enantioselective allylic substitution with organometallic reagents.</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td><img src="image" alt="Chemical Structure" /></td>
<td>A (10 mol%), CuBr₂·SMe₂ (1 mol%), THF, -30°C, 3 h 8 examples (yields 72-89%, ee = 44-89%) are reported.</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
Helvética 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
### Nickel(II) Chloride / Triphenylphosphine Complex

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

<table>
<thead>
<tr>
<th>NiCl₂(PPh₃)₂</th>
<th>4-tolyl(B(OH))₂ (1.3 eq), A (0.03 eq), K₂PO₄·H₂O (2.6 eq) PhMe, 80°C, 2 h 99%</th>
</tr>
</thead>
</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>TMSCF₃</th>
<th>TsnN₃I</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></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>In</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PhCN</td>
</tr>
</tbody>
</table>


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

### Tetraallyltannane

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>(Sn)₄A</th>
<th>A (0.25 eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MeOH, 30°C, 1 d</td>
</tr>
<tr>
<td></td>
<td>PhN amide</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>20%Pd(OH)₂/C</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PhHCHO (5.9 eq) H₂ (50 psi) EtOH, 50°C 73%</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.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>(a) A [0.5 eq] THF, rt, 4 h</th>
<th>(b) Br₂ [1.6 eq] 0°C, 1 h 82%</th>
</tr>
</thead>
</table>

P. Wipf, X. Wang Tetrahedron Lett. 2000, 41, 8237. 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.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>A</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>Ph</td>
<td>OMe</td>
</tr>
<tr>
<td>Ph</td>
<td>OMe</td>
<td>Br</td>
</tr>
</tbody>
</table>

T. Ooi, M. Kameda, H. Tannai, K. Maruoka Tetrahedron Lett. 2000, 41, 8339. 1 example (yield 80%, %ee = 90%) is reported.

### Ferrocenyl Oxazoline

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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>PhMe, 10°C, 12 h 96% er = 98:2</td>
</tr>
</tbody>
</table>

C. Bolm, N. Hermans, J. P. Hildebrand, K. Muniz Angew. Chem., Int. Ed. Engl. 2000, 39, 3465. 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.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₂P</td>
<td>Fe</td>
</tr>
<tr>
<td>Ph₂P</td>
<td>Fe</td>
</tr>
</tbody>
</table>

M. Braun, F. Laicher, T. Meier Angew. Chem., Int. Ed. Engl. 2000, 39, 3494. 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 alkylations.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂N</td>
<td>CH₂COCH₂</td>
</tr>
<tr>
<td>N₂N</td>
<td>CH₂COCH₂</td>
</tr>
</tbody>
</table>

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.

Dodecacarbonyltetracobalt / 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. Kornanaga, T. Ohkuma, R. Noyori

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

Dicarbonylacetylacetone)rhomodium

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)silanol and (α-alkoxyvinyl)silyl hydrides in the presence of tetraethylammonium 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-butene with carbonyl compounds in aqueous media to give good yields of the 1,3-butadien-2-ylmethanol.

\[
\text{In} \quad A \quad (3 \text{ eq}) \quad 1,4\text{-dibromo-2-butene (1.5 eq)} \quad \text{H}_2\text{O, rt, 6 h} \quad 53\%
\]

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


(R,R)-Pseudoephedrine

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

\[
\text{Me}^+ \quad \text{OH}^- \quad A
\]


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

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

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

\[
\text{OCH}_2\text{CH}_3
\]

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


Bis(1,4-cyclooctadiene)rhodium Tetrafluoroborate

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

\[
\text{Rh(COD)}_2\text{BF}_4
\]

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


Aluminium Tris(2,6-diphenylphenoxide)

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

\[
\text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph}
\]

10 examples (yields 41-99\%, 3.4:1 ≤ 1.6-1.4 ≤ 99:1) are reported.

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

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

![Chemical structure of TDS-Br](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 of Ligand](image)

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

### Chiral Hydroxamic Acid Ligand

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

![Chemical structure of Ligand](image)

9 examples (yields 58-99%, %ee = 76-99%) 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 of Ligand](image)

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

### Ytterbium Triflate

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

![Chemical structure of Catalyst](image)

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