**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:

Robert Chow, Derek Johnston, Philip Kocienski, Alexander Kuhl, Catherine McCusker, Robert Narquizian, 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
- Chemistry Letters
- Collection Czechoslovak Chemical Communications
- 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 Synlett
- Synthesis
- Tetrahedron
- Tetrahedron Asymmetry and Tetrahedron Letters

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Article Identifier: 1437-210X.E;2000,0,08,1180,1185,ftx,en;X00800SS.pdf

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### Nickel(II) Acetylacetonate

The title reagent is reduced with DiBAL-H in the presence of PPh₃ to generate a nickel(0)-catalyst to promote the intramolecular cyclisation of a 1,3-diene with a tethered carbonyl group. The addition of 1,3-cyclohexadiene to the reaction mixture affords the regiochemistry of the olefin in the cyclised product.

**Catalyst**

\[ \text{Ni(acac)}_2 \]


9 examples (yields 43-86%) are reported.

### Zinc Trifluoromethanesulfonate

In combination with (+)-N-methylpseudephedrine, the title reagent mediates the enantioselective synthesis of propargylic alcohols by direct coupling of aldehydes with terminal alkynes.

**Catalyst**

\[ \text{Zn(CF}_3\text{SO}_2\text{)}_2 \]


17 examples (yields 39-99%, %ee = 80-99%) are reported.

### Tetrakis(triphenylphosphine)palladium(0)

The title reagent catalyses the hydrofurylation of alkylidenecyclopropanes.

**Catalyst**

\[ \text{Pd(PPh}_3\text{)}_4 \]


9 examples (yields 35-77%) are reported.

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Synthesis 2000, No. 8, 1180–1185  ISSN 0039-7881  © Thieme Stuttgart · New York
### Bis(triphenyolphosphine)palladium(II) Acetate

The title reagent catalyses the decarboxylative carbonylation of 5-vinylloxazolidin-2-ones in an enantioselective synthesis of 3,6-dihydro-1H-pyridin-2-ones.

\[
\begin{align*}
(PPh_3)_2Pd(OAc)_2 & \quad \text{A} \\
\text{CO (65 atm)} & \quad \text{EtOH, 70°C, 5 d} \\
& \quad 74% \\
8 \text{ examples (yields 0, 57-87%) are reported.}
\end{align*}
\]


### Palladium(II) Bis[1,2-bis(diphenyolphosphino)ethane] [Pd(DIPHOS)]

The title reagent catalyses the cross-coupling reactions of boronic acids with free or polymer-bound aryl halides.

\[
\begin{align*}
Pd(DIPHOS)_2 & \quad \text{A} \\
\text{A (1 mol%)} & \quad \text{PhB(OH)}_2 (1 \text{ eq}) \\
& \quad K_2CO_3 (2.4 \text{ eq}) \\
& \quad \text{THF-MeOH (4:1), 5, 4 h} \\
& \quad 95% \\
13 \text{ examples (yields 55-96%) are reported.}
\end{align*}
\]


### Yttrium(III) Acetylacetonate

The title reagent catalyses the acyl transfer reactions of enol esters. In selected cases, the yttrium catalyst promotes the selective O-acylation of amino alcohols without the formation of the amide.

\[
\begin{align*}
Y_3(O-Pr)_{12}O & \quad \text{A} \\
& \quad \text{AcO} \\
& \quad \text{CH}_3 \\
& \quad (4.5 \text{ eq}) \\
& \quad \text{rt, 5 min} \\
& \quad 95% \\
13 \text{ examples (yields 49, 82-99%) are reported.}
\end{align*}
\]


### (S,S)-2,6-Bis(4′-phenyloxazolin-2′-yl)pyridine/Ytterbium Trichloride

The title ligand is used together with ytterbium (III) chloride to catalyse the asymmetric ring opening of meso epoxides with TMSOCN to yield the 1-ethyl-1-oxido nitro ring-opened products with good enantioselectivities.

\[
\begin{align*}
& \quad \text{A} \\
& \quad YbCl_3 \\
& \quad \text{A (12 mol%)} \\
& \quad \text{YbCl}_3 (10 \text{ mol%}) \\
& \quad \text{TMSOCl (1.2 eq)} \\
& \quad \text{CHCl}_3 -45°C, 4 \text{ d} \\
& \quad 90 \% \\
& \quad er = 96:4 \\
2 \text{ examples (yields 80-90%, %ee = 90-91%) are reported.}
\end{align*}
\]


### Gallium Nonfluorobutanesulfonate

The title gallium compound catalyses the Friedel-Crafts acylation of aromatics including inactivated benzenes.

\[
\begin{align*}
& \quad \text{Ga(ONF)}_3 \\
& \quad \text{A} \\
& \quad \text{A (5 mol%)} \\
& \quad \text{PhCOCl (1 eq)} \\
& \quad \text{d, 1 d} \\
& \quad 90% \\
8 \text{ examples (yields 65-100%) are reported.}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Chiral Schiff Base Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>The title reagent catalyses the enantioselective addition of HCN to ketomimics. The α-aminoiminotitile adducts are converted to the corresponding α-quaternary α-amino acids by a formylation/hydrolysis sequence. Two polystyrene supported catalysts are also described.</strong></td>
<td></td>
</tr>
<tr>
<td><img src="image1" alt="Chemical structure" /></td>
<td><img src="image2" alt="Chemical structure" /></td>
</tr>
<tr>
<td>P. Vechal, E. N. Jacobsen</td>
<td>Org. Lett. 2000, 2, 867.</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Copper(I) Chloride</th>
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</thead>
<tbody>
<tr>
<td><strong>The title reagent mediates coupling reactions of alkynes/silanes to afford conjugate diynes and disubstituted ethynes.</strong></td>
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<tr>
<td><img src="image3" alt="Chemical structure" /></td>
<td><img src="image4" alt="Chemical structure" /></td>
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<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Bis(tricyclohexylphosphine)benzylidene Ruthenium(IV) Dichloride</th>
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</thead>
<tbody>
<tr>
<td><strong>The title catalyst mediates terminal alkyne-ethylene cross-metathesis to afford 2-substituted butadienes.</strong></td>
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<tr>
<td><img src="image5" alt="Chemical structure" /></td>
<td><img src="image6" alt="Chemical structure" /></td>
</tr>
<tr>
<td>J. A. Smulik, S. T. Diver</td>
<td>J. Org. Chem. 2000, 65, 1788.</td>
</tr>
</tbody>
</table>

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<thead>
<tr>
<th>Catalyst</th>
<th>(Trimethylsilyloxy)trioxorhenium</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>The title reagent mediates the isomerisation of allylic alcohols and allylic ethers at room temperature.</strong></td>
<td></td>
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<tr>
<td><img src="image7" alt="Chemical structure" /></td>
<td><img src="image8" alt="Chemical structure" /></td>
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</tbody>
</table>

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<tr>
<th>Catalyst</th>
<th>Gadolinium Tri(iso-propoxide)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>The title reagent catalyses the Meerwein-Ponndorf-Verley-type reductive acetylation of carbonyl compounds to acetates in the presence of iso-propenyl acetate.</strong></td>
<td></td>
</tr>
<tr>
<td><img src="image9" alt="Chemical structure" /></td>
<td><img src="image10" alt="Chemical structure" /></td>
</tr>
<tr>
<td>Y. Nakano, S. Sakaguchi, Y. Ishii</td>
<td>Tetrahedron Lett. 2000, 41, 1565.</td>
</tr>
</tbody>
</table>
### Camphor-Based Acyl Hydrazide Chiral Auxiliary

The illustrated chiral auxiliary is employed in asymmetric Baylis-Hillman reactions. Both diastereometric products can be obtained in high optical purity by alteration of the reaction conditions.


14 examples (yields 0, 68-92%, \%de = 16-98%) are reported.

### Thiazolidinethione Chiral Auxiliary

The use of chiral auxiliary A in asymmetric aldol reactions is described. A switch in diastereoselectivity resulting from an alteration of the amount of base employed is described.


6 examples (yields 30-85%, \%de = 68-98%) are reported.

### (R,R)-3,3'-Diphenyl-1,1'-binaphthol

The title reagent mediates the asymmetric conjugate addition of alkynylboronates to enones.


13 examples (yields 50-999, \%ee = 16-98%) are reported.

### N,N'-Dimethyl-1,5-diaza-cis-decalin

The title ligand is from a new class of chiral diamine ligands which are moderately effective in the asymmetric deprotonation-substitution of benzylic substrates.


4 examples (no yields reported, \%ee = 6, 39-45%).

### Chiral Schiff Base Ligand

A library of 100 chiral ligands was designed for copper-catalysed enantioselective Michael addition of diethylzinc to cyclic enones, of which the illustrated reagent is one of the most efficient.


20 optimised examples (\%ee = 67-82%) are described.
### (2-Phenyl-2-trimethylsilyl)ethyl Esters (PTMSE)

Reagent A has been developed for the protection of the carboxylic group, e.g. in peptide chemistry. The protecting group is stable under coupling conditions usually applied in peptide synthesis and can be rapidly cleaved by treatment with TBAF.

![Chemical structure of A](image)

M. Wagner, H. Kunz *Synlett* 2000, 400.

Preparation of A (2 steps, 64% yield) and 6 examples of the protection of amino acid derivatives (yields 57, 83-91%) are reported.

### 10-Mercaptoisoborneol

The title reagent is used in the asymmetric reduction of acyclic α,β-unsaturated ketones via tandem Michael addition/Meerwein-Ponndorf-Verley reduction.

![Chemical structure of A](image)


12 examples (yields 80-93%, %ee = 93-98%) are reported.

### Thulium Diodide

The title reagent is used for the coupling of ketones with alkyl halides. Results show the reagent to be a more powerful version of $\text{SnI}_2(\text{THF})_2\text{HMPA}$.

![Chemical structure of A](image)


11 examples (yields 36, 83-99%) are reported.

### 4-Perfluorohexyl-benzeneselenyl Chloride

The title reagent is used in an efficient one-pot conversion of carbonyl compounds to their α,β-unsaturated derivatives. The organoselenium reagent is recovered in high yields by continuous fluoruous extraction.

![Chemical structure of A](image)


5 examples (yields 84-99%) are reported.

### Triphenylphosphonium Bromide

The title reagent is used as a mild source of hydrogen bromide for the chemoselective ring opening of epoxides to bromohydrins.

![Chemical structure of A](image)


8 examples (yields 56-97%) are reported.
**Glycine Schiff Base Ni(II) Complex**

Reagent A is used in asymmetric Michael additions with enantiopure (S)- or (R)-(3E)-enoyl-4-phenyl-1,3-oxazolidin-2-ones. Complete control of simple and face diastereoselectivity is observed in these reactions.


9 examples (yields 15, 96-99%, %de = 94-99%).

---

**Samarium Diiodide**

The title reagent mediates the asymmetric samarium-Reformatsky reaction of chiral α-bromoacryl-2-oxazolidinones with aldehydes.


17 examples (yields 32-92%, %de = 49-99%) are reported.

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**p-Tolyl α-Lithio-β-(trimethylsilyl)ethyl Sulfoxide**

Reaction of the title compound with α,β-un saturated esters affords conjugate addition products as a single diastereomer. The intermediate enolates are subsequently trapped with various electrophiles with high stereocontrol. The stereo- and regioselective elimination of the vinyl group gives chiral homocycloxy carbonylates.


9 examples (yields 21-98%, %de > 90%) are reported.

---

**Trichloroacetic Acid / Sodium Trichloroacetate**

The title reagent pair are used in a practical preparation of terminal alkynes from aldehydes.


8 examples (yields 49-87%).

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**B-Methyl-9-borabicyclo[3.3.1]nonane**

A variety of trisalkylboranes, including the title reagent, promotes the methanolyisis of N-trimethylstilbenediimines to afford N-unsubstituted imine-borane adducts which are isolable and stable at room temperature.


11 examples; yields 69-89%