**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 I
- Synlett
- Synthesis
- Tetrahedron
- Tetrahedron Asymmetry and Tetrahedron Letters

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**Nickel(II) Acetylacetonate**

The title reagent is reduced with DiBAL-H in the presence of PPh$_3$ 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 affects the regiochemistry of the olefin in the cyclised product.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni(acac)$_2_3$</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y. Sato, M. Takimoto, M. Mori J. Am. Chem. Soc. <strong>2000</strong>, 122, 1624.</td>
<td>9 examples (yields 43-86%) are reported.</td>
<td></td>
</tr>
</tbody>
</table>

**Zinc Trifluoromethanesulfonate**

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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Zn(CF$_3$SO$_2$)$_2$</th>
<th>A</th>
</tr>
</thead>
</table>

**Tetrakis(triphenylphosphine)palladium(0)**

The title reagent catalyses the hydrofulurination of alkylidencyclopropanes.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd(PPh$_3$)$_4$</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Nakamura, S. Saito, Y. Yamamoto J. Am. Chem. Soc. <strong>2000</strong>, 122, 2661.</td>
<td>9 examples (yields 35-77%) are reported.</td>
<td></td>
</tr>
</tbody>
</table>
**Bis(triphenylphosphine)palladium(II) Acetate**

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

![Chemical structure](image)


8 examples (yields 0, 57–87%) are reported.

**Palladium(II) Bis[1,2-bis(diphenylphosphino)ethane] [Pd(DIPhos)₂]**

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

![Chemical structure](image)


13 examples (yields 55–96%) are reported.

**Y₃(O-Pr)₁₄O**

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.

![Chemical structure](image)


13 examples (yields 49, 82–99%) are reported.

**(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 TMSCN to yield the &beta;-methylsilyloxy nitro ring-opened products with good enantioselectivities.

![Chemical structure](image)


2 examples (yields 80–90%, %ee = 90–91%) are reported.

**Gallium Nonfluorobutanesulfonate**

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

![Chemical structure](image)


8 examples (yields 65–100%) are reported.
### Chiral Schiff Base Catalyst

The title reagent catalyses the enantioselective addition of HCN to ketomines. The $\alpha$-aminonitrile adducts are converted to the corresponding $\alpha$-quaternary $\alpha$-amino acids by a formylation/hydrolysis sequence. Two polystyrene supported catalysts are also described.


17 examples (yields 45, 95-100%, %ee = 41-95%) are reported.

### Copper(I) Chloride

The title reagent mediates coupling reactions of alkynylsilanes to afford conjugate diarynes and disubstituted ethynes.


34 examples (yields 0-99%) are reported.

### Bis(tricyclohexylphosphine)benzylidene Ruthenium(IV) Dichloride

The title catalyst mediates terminal alkyne-ethylene cross-metathesis to afford 2-substituted butadienes.


8 examples (yields 57-92%) are reported.

### (Trimethylsilyloxy)trioxorhenium

The title reagent mediates the isomerisation of allylic alcohols and allylic ethers at room temperature.


12 examples (26:74 $\leq$ 1:2 $\leq$ 62:38) are reported.

### Gadolinium Tri/iso-propoxide

The title reagent catalyses the Meerwein-Ponndorf-Verley-type reductive acetylation of carbonyl compounds to acetates in the presence of iso-propenyl acetate.


12 examples (yields 25-96%) are reported.
### Camphor-Based Acyl Hydrazide Chiral Auxiliary

The illustrated chiral auxiliary is employed in asymmetric Baylis-Hillman reactions. Both diastereomeric 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 50-99%, %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 benzyllic 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 Reagent A](image)

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

**Protecting Group**

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

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**10-Mercaptoisoborneol**

The title reagent is used in the asymmetric reduction of acyclic \(\alpha,\beta\)-unsaturated ketones via tandem Michael addition/ Meerwein-Ponndorf-Verley reduction.

![Chemical Structure of Reagent A](image)


**Reagent**

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

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**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 \(\text{Sm}_{2} (\text{THF})_{2} \cdot \text{HMPA}\).

![Chemical Structure of Reagent A](image)


**Reagent**

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

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**4-Perfluorohexyl-benzeneselenyl Chloride**

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

![Chemical Structure of Reagent A](image)


**Reagent**

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

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**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 Reagent A](image)


**Reagent**

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

Reagent

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


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

Samarium Diiodide

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


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

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

Reaction of the title compound with α,β-unsaturated esters affords conjugate addition products as a single diastereomer. The intermediate enolates are subsequently trapped with various electrophiles with high stereoselectivity. The stereo- and regioselective elimination of the sulfanyl group gives chiral homoallylic carboxylates.


9 examples (yields 21–98%, %de > 96%) 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%).

B-Methyl-9-borabicyclo[3.3.1]nonane

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


11 examples; yields 69–89%.