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:
Stephen Brand, John Christopher, Emma Guthrie, Philip Kocienski, Louise Lea, Russell McDonald, Graeme McAllister and Robert Narquizian of Glasgow University.

Georg Thieme Verlag does not accept responsibility for the accuracy, content, or selection of the data.

### Ytterbium Trifluoromethanesulfonate / Benzoic acid

The title reagent pair catalyse the allylation of aldehydes with allyltributyltin in acetonitrile.

\[
\begin{align*}
\text{Yb(OTf)}_3 & \quad A \\
\text{PhCO}_2\text{H} & \quad B \\
\end{align*}
\]

H. C. Aspinall, N. Greesves, E. G. Mclver

9 examples (yields 68-96%) are reported.

### Copper(I) Triflate

In the presence of a chiral Schiff base, the title reagent catalyses the asymmetric carbeneoid insertion of methyl aryl acetonates into the silicon-hydrogen bonds of silanes.

\[
\begin{align*}
\text{CuOTf} & \quad A \\
\end{align*}
\]

L. A. Dakin, S. E. Schaus, E. N. Jacobsen, J. S. Panek

5 examples (yields 45-82%, %ee = 40-84%).

### Chiral Cobalt(II) Complex

Enantioselective 1,4-reduction of \(\alpha,\beta\)-unsaturated carboxamides catalysed by the title compound is achieved in high yield and excellent selectivity.

\[
\begin{align*}
\text{A} & \quad (0.5 \text{ mol}) \\
\text{NaB} & \quad \text{H}_4 \quad (4 \text{ eq}) \\
\text{THPM} & \quad (8 \text{ eq}) \\
\text{CH}_2\text{Cl}_2, \quad \text{rt, 2 h} \\
\end{align*}
\]

T. Yamada, Y. Ohitsuuka, T. Ikeno

12 examples (yields 69-99%, %ee = 49-91%).

THPM = Tetrahydropyran-2-methanol

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*
*European Journal of Organic Chemistry*
*Helvetica Chimica Acta*
*Heterocycles*
*Journal of the American Chemical Society*
*Journal of Organic Chemistry*
*Organometallics*
*Perkin Transactions 1*
*Synlett*
*Synthesis*
*Tetrahedron*
*Tetrahedron Asymmetry and Tetrahedron Letters*
(R)-8-Methyl-4,5,5-triphenyl-1,3,2-oxazaborolidine

The title compound catalyses the borane-mediated reduction of symmetric diketones in high yield with excellent selectivity.

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{HN} & \quad \text{B} \\
\text{O} & \quad \text{Me}
\end{align*}
\]

A

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

\[
\begin{align*}
\text{A} & \quad \text{BH}_3\text{SMe}_2 (2.2 \text{ eq}) \\
& \quad \text{A (2.0 eq)} \\
\text{THF} & \quad 0^\circ \text{C}, 15 \text{ min}
\end{align*}
\]

98%, df/meso = 86:14
er = 99:1

10 examples with both unsaturated and saturated diketones (yields 75-98%, 93:7 ≤ df/meso ≤ 58:42, %ee = 40-99%) are described.


2,2-Bis[2-[(4R)-(2'-naphthyl)-1,3-oxazolinyl]]propane

The title compound catalyses the asymmetric Diels-Alder reaction between N-alkenoyl oxazolidin-2-one derivatives and cyclopentadiene with high enantioselectivity.

\[
\begin{align*}
\text{N} & \quad \text{O} \\
\text{N} & \quad \text{Ar} \\
\text{Ar} & \quad \text{Ar}
\end{align*}
\]

A

\[
\text{Ar} = 2\text{-Napth}
\]

\[
\begin{align*}
\text{A} & \quad \text{A (10 mol%)}, \text{Mg(OtBu)}_2 (10 \text{ mol%), C}_2\text{H}_2 (3.2 \text{ eq}) \\
& \quad \text{CH}_2\text{Cl}_2, -50^\circ \text{C}, 16 \text{ h}
\end{align*}
\]

100%
endo/exo = 90:10
er = 97:3

2 examples (yields 100%, endo/exo = 90:10 and 88:12, %ee = 94, 92%).


(Acetylacetonato)dicarbonylrhodium(I)

The rhodium catalysed addition of organoboronic acids to aldehydes is reported.

\[
\begin{align*}
\text{[Rh(acac)(CO)]} & \quad \text{PhB(OH)}_2 (2 \text{ eq}) \\
& \quad \text{A (3 mol%), dppf (3 mol%)} \\
& \quad \text{DME}-\text{H}_2\text{O} (2:3), 80^\circ \text{C}, 16 \text{ h}
\end{align*}
\]

18 examples (yields 0, 43-99%).


Benzylidene-bis(tricyclohexylphospine)dichlororuthenium

Ring-closing enyne metathesis is used to prepare alkenyl substituted six- and seven membeered cyclic enol ethers in moderate to good yield.

\[
\begin{align*}
\text{Cl}_2\text{Ru(PCy}_3)_2\text{CHPh} & \quad \text{A (10 mol%)}, \text{CH}_2\text{Cl}_2, \Delta, 4 \text{ h} \\
\text{A} & \quad 85\%
\end{align*}
\]

5 examples (yields 20-77%).


Mercury(II) Acetate

The title compound catalyses transilolation from trimethylsilyl to trichlorosilyl enol ethers.

\[
\begin{align*}
\text{Hg(OAc)}_2 & \quad \text{A} \\
\text{PivO} & \quad \text{OTMS} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

\[
\begin{align*}
\text{A (1 mol%), SiCl}_4 (2 \text{ eq}) & \quad \text{CH}_2\text{Cl}_2, \text{rt} \\
& \quad 78\%
\end{align*}
\]

14 examples (yields 60-83%).

**Homochiral Phosphoramidate Lewis Base**

A catalysts the highly 1,4-syn selective aldol addition of trichlorosilyl enolates to aldehydes.

```
\text{Me} \quad \text{Me} \\
\text{Ph} \quad \text{N} \quad \text{P} \quad \text{N} \quad \text{Me}
\text{A}
```


4 examples (yields 77-86%, 6:1 ≤ syn:anti ≤ 73:1).

**Palladium(II) Acetate**

The title compound catalyses the synthesis of aryl sulfides from aryl triflates.

```
\text{Pd(OAc)2} \\
\text{A}
```


9 examples (yields 54-93%).

**Benzyldiene-bis[N,N-dimethyl-4-piperidinium-dicyclohexylphosphine]dichlororuthenium**

The title compound catalyses ring-closing metathesis in methanol or water.

```
\text{R = } \text{O-C6H3}
```


8 examples (yields 5, 55-95%).

**Bis(1,5-cyclooctadiene)nickel(0)**

The title compound catalyses the conjugate addition of triorganonium compounds to \( \alpha,\beta \)-unsaturated systems.

```
\text{Ni(COD)2} \\
\text{A}
```


10 examples (yields 50-88%).

**(S)-2-(4-Methylpiperazin-1-ylmethyl)indoline**

The title compound catalyses the enantioselective addition of dialkylzincs to aldehydes.

```
\text{A}
```


8 examples (yields 67-91%, \%ee 59-97%)
Cp*RuCl(cod) 

<table>
<thead>
<tr>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>The first addition of organic disulfides to alkenes catalysed by the title compound enables the rapid synthesis of vicinal-dithioethers.</td>
</tr>
<tr>
<td>Cp*RuCl(cod)</td>
</tr>
<tr>
<td>CO$_2$Me</td>
</tr>
<tr>
<td>10 equiv.</td>
</tr>
<tr>
<td>PhMe, 100 °C, 8 h</td>
</tr>
<tr>
<td>PhS$\rightleftharpoons$Ph</td>
</tr>
<tr>
<td>CO$_2$Me</td>
</tr>
</tbody>
</table>


Ni(COD)$_2$

<table>
<thead>
<tr>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>The title compound catalyses the [2+2+2] cycloaddition between an alkyne enone and an electron-deficient alkene.</td>
</tr>
<tr>
<td>Ni(COD)$_2$</td>
</tr>
<tr>
<td>Ph</td>
</tr>
<tr>
<td>65%</td>
</tr>
</tbody>
</table>


Palladium(II) Chloride

<table>
<thead>
<tr>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>The title compound catalyses the conversion of silanes to halosilanes in halocarbon solvents. Two examples reported.</td>
</tr>
<tr>
<td>PdCl$_2$</td>
</tr>
<tr>
<td>Pr$^t$-Si-O-Si-$^t$-Pr$^t$</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>Pr$^t$-Si-O-Si-$^t$-Cl</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Me</td>
</tr>
<tr>
<td>Bu$^t$-Si-H</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Me</td>
</tr>
<tr>
<td>Bu$^t$-Si-Br</td>
</tr>
</tbody>
</table>


(±)-4-Phenyl-2-oxazolidinone

<table>
<thead>
<tr>
<th>Chiral Auxiliary</th>
</tr>
</thead>
<tbody>
<tr>
<td>A novel method for the N-acylation of 2-oxazolidinone chiral auxiliaries with acids in the presence of pivaloyl chloride and triethylamine is described.</td>
</tr>
<tr>
<td>Ph</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>H</td>
</tr>
</tbody>
</table>


(1R,2R)-Cyclohexane-1,2-diphenylmethanol

<table>
<thead>
<tr>
<th>Ligand</th>
</tr>
</thead>
<tbody>
<tr>
<td>The title ligand is utilised in the Ti(IV)-catalysed asymmetric addition of trimethylaluminium to aldehydes.</td>
</tr>
<tr>
<td>Ph</td>
</tr>
<tr>
<td>OH</td>
</tr>
<tr>
<td>OH</td>
</tr>
</tbody>
</table>


27 examples (yields 14, 44-93%) utilising A and 2 other auxiliaries are described.

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2-Amino-2'-diphenylphosphino-1,1'-binaphtyl (MAP)

The title compound exhibits a dramatic accelerating effect on the Pd(0)-catalysed Haraig-Buchwald N-phenylation of an amino alcohol and a diamine.

\[
\text{NMe}_2 \quad \text{PhP}_3
\]

Synthesis of A and 2 examples of N-phenylation (yields 100%) are described.

\[
\text{MeN} \quad \text{NMe}_2 \quad \text{Ph}
\]

\[
\text{MeN} \quad \text{NMe}_2 \quad \text{Ph}
\]

N-(2S)-6,9-Dimethyl-2-phenyl-3,6,9-triazadecyl)piperidine

A in the presence of lithium bromide is utilised in the enantioselective alkylation of lactams and lactones with active alkylating agents in non-chelating solvents.

\[
\text{PhN} \quad \text{MeN}
\]

11 examples (yields 7-76%, \%ee = 68-98%).

\[
\text{MeN} \quad \text{PhCH}_2\text{Br}
\]

TMTHF = 2,2,5,5-tetramethyltetrahydrofuran

(R,R)-1,2-Diphenyl-1,2-\{di-(pentfluorophenyl)-phosphanoxy\}ethane

Ligand A (BIPHOP-F) derived from (R,R) or (S,S)-hydrobenezoin is reported. The ligand is effective in the Fe(II) catalysed Diels Alder reaction of \(\alpha,\beta\)-enals with dienes.

\[
\text{PhOP}(\text{CF}_3)_2 \quad \text{PhOP}(\text{CF}_3)_2
\]

5 examples (yields 44-86%, \%ee = 85-99%).

(1R,2R)-1,2-Dimethoxy-1,2-diphenylethane

Ligand A mediates the enantioselective conjugate addition of organolithiums to naphthaldehyd imine and cyclic and acyclic \(\alpha,\beta\)-unsaturated aldimines.

\[
\text{PhMeO} \quad \text{OMe}
\]

9 examples using A (yields 19-62%, \%ee = 59-99%) and 6 examples using (2S,3S)-2,3-dimethoxybutane (yields 42-80%, \%ee = 80-94%) are reported.

Dicobalt Octacarbonyl

Propargyl/xoicarbonyl (Proco) groups and propargyl esters are inert to TFA and Lewis acids but are cleaved by treatment with 5% TFA in dichloromethane in the presence of 1 eq. of the title compound.

\[
\text{CO}_2\text{(CO)}_8
\]

99%
sec-Butyllithium / (-)-sparteine

The title reagent pair induces the enantioselective carbocation cyclization of (E)-6-phenyl-5-hexenyl carbamates to afford trans-1,2-disubstituted cyclopentane derivatives.


2 examples (yields 40, 47%, %ee > 95%) are described.

Sodium Cyclopentadienyltricarbonylmolybdate

A is used to form mixed Co/Mo alkyne complexes which are used to facilitate cyclopentene formation, in an asymmetric variant of the Pauson-Khand reaction.


8 examples of Pauson-Khand reactions with both Norbornene and Norbornadiene (yields 32-97%) are reported.

1,1-Diethoxy-2-chloroethene

Di-tert-butylbiphenyl (DBB) catalysed lithiation of A and condensation with a variety of carbonyl compounds is reported. Formation and reaction of 2-methyl-4-ethoxy butadienyl lithium is also described.


20 examples (yields 0, 50-100%).

(S,S)-1,2-Diaminocyclohexane

Stereoactive allylation of a C2 symmetric imidazoline derived from A is reported, allowing efficient formation of a quaternary benzylic centre.


2 examples (yields 58, 70%, %de = 75, >95%).

Chiral Schiff Base

Aldimine A catalyses the enantioselective ring opening of cyclohexane oxides with phenyl lithium.


3 examples (yields 53-92%, %ee = 76-86%).
1,3-Dimethyl-2-trimethylstannyl-2-bora-1,3-diazacyclopentane

Regio- and stereoselective 1,4-addition of A to 1,3-dienes under palladium catalysis is reported. Reaction of the products with aldehydes provides a facile method for the preparation of homoallyl alcohols.

S. Onozawa, Y. Hatanaka, M. Tanaka

Lauroyl Peroxide

The title reagent is utilized in a modified Barton-McCombie reaction.

B. Quiciet-Sire, S. Z. Zard

Hexacarbonyl (propiolaldehyde diethyl acetal) dicobalt

A one-pot synthesis of tricyclic ring systems via an intermolecular Nicholas reaction followed by a tandem intramolecular Nicholas reaction is reported.

E. Tyrrell, C. Tillett

(R,R)-Disopropyltartrate (DIPT)

Asymmetric 1,3-dipolar cycloaddition of nitrile oxides to y-substituted allicy alcohols in the presence of A is reported, yielding 3,4,5-trisubstituted-2-oxazolines with high regio- and enantioselectivity.

Y. Yoshida, Y. Ukaji, S. Fujinami, K. Inomata

O,O'-Di(2-pyridyl) thiocarbonate (DPTC)

A variety of carboxylic esters have been prepared from the corresponding acids and hindered alcohols using the title compound and a catalytic amount of DMAP.

K. Sakai, I. Shima, T. Mukaiyama
Pivalic Anhydride

Hydrogenation of carboxylic acids to the corresponding aldehydes catalysed by palladium in the presence of A is reported.

\[
\text{A} (3 \text{ eq}) \quad \text{Pd(PPh\textsubscript{3})\textsubscript{4} (2 \text{ mol\%})} \\
\text{H\textsubscript{2}} (3 \text{.0 MPA}) \\
\text{THF, 80\textdegree C, 1 d} \\
99\% \\
\text{19 examples (yields 13, 63-99\%) are described.}
\]


Trimethyl Orthoformate

The non-dehydrative Pinacol coupling of a variety of diols in the presence of A and a Lewis acid is reported.

\[
\text{SnCl\textsubscript{4} (20 \text{ mol\%})} \\
\text{A (1 eq)} \\
\text{CH\textsubscript{2}Cl\textsubscript{2}, 0\textdegree C, 7 h} \\
97\% \\
15 examples using a variety of Lewis acids (yields 0, 15-97\%) are reported.
\]


Cyclopropenone Propane-1,3-Diyl Ketal

Ring opening cross metathesis of A and terminal olefins is described. The reaction is carried out in the presence of Grubbs ruthenium catalyst to afford 1,4-divinyl ketone ketalts.

\[
\text{A (0.9 eq)} \\
\text{Cl\textsubscript{2}(Cy\textsubscript{3}P)\textsubscript{2}Ru=CHPh (5 \text{ mol\%})} \\
\text{PhH, \Delta, 2 h} \\
76\% \\
E:Z = 85:15 \\
\]


tert-Butyl-N-Hydroxycarbamate

The nitrogen nucleophile A reacts with non-racemic chiral tricarbonylcobalt(0) complexes of benzylic ethers with retention of configuration to provide a novel approach to non-racemic N-hydroxycarbamates and amines.

\[
\text{A (4 eq)} \\
\text{HBF\textsubscript{4} \cdot OMé\textsubscript{2} (2 eq)} \\
\text{CH\textsubscript{2}Cl\textsubscript{2}, -40\textdegree C, 25 min} \\
53\% \\
er = 98:2 \\
5 examples (yields 43-85\%, %ee = 80-99\%).
\]


(4-Trimehylsilylbut-2-ynyl)stannane

Catalytic enantioselective addition of A to aldehydes provides trimethylsilyl/methylallyl alcohol with high enantioselectivity. The adducts can be converted to diynyl alcohols with retention of configuration, by reaction with an electrophile.

\[
\text{A} \quad \text{PhCH\textsubscript{2}CH\textsubscript{2}CHO (S-BINOL (10 mol\%))} \\
\text{Ti(O\textsubscript{3}Pr\textsubscript{3}) (5 mol\%)} \\
\text{Et\textsubscript{2}BS+Pr} \\
\text{CH\textsubscript{2}Cl\textsubscript{2}, -20\textdegree C, 18 h} \\
62\% \\
er = 96:4 \\
8 examples (yields 39-83\%, %ee = 83-97\%).
\]