**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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### (3S,8R,9S)-10,11-Dihydro-3,9-epoxy-6'-hydroxychinconane

A and similar Cinchona alkaloids mediate the enantioselective Bömmel-Hillman reaction.

![Chemical Structure](image)


Catalyst

\[
\text{H}_2\text{C} = \text{C} = \text{CHCOCH}_2\text{CF}_3 \quad \text{(1,3 eq)}
\]

\[
\begin{align*}
\text{A} & \quad (10 \text{ mol\%}) \\
\text{DMF, } -55^\circ\text{C, 2 d} & \quad 57\%, \text{ ee } = 98.2
\end{align*}
\]

8 examples (yields 31-58%, %ee = 91-99%).

### 1,3-Dimethyl-5-ethyl-5,10-dihydrooxazine / N-Methylmorpholine

The title reagents are used as co-catalysts in the cesium-catalysed dihydroxylation of olefins by hydrogen peroxide.

![Chemical Structure](image)


Catalyst

\[
\begin{align*}
\text{A} & \quad (5 \text{ mol\%}) \\
\text{B} & \quad (27 \text{ mol\%}) \\
\text{OsO}_4 & \quad (2 \text{ mol\%}) \\
\text{Et}_3\text{NNOAc} & \quad (2 \text{ eq}) \\
\text{H}_2\text{O}_2 & \quad (1.5 \text{ eq}) \\
\text{Acetone-H}_2\text{O} (3:1) & \quad \text{rt, 1 d} \\
\end{align*}
\]

8 examples (yields 72-95%).

### (6R,5S)-2-Cyclopentadienyl]tris(acetonitrile) ruthenium(II) Pentafluorophosphate

A catalyses the Michael addition of allenes to \(\alpha,\beta\)-unsaturated ketones, resulting in the subsequent formation of cyclic ethers.

![Chemical Structure](image)


Catalyst

\[
\begin{align*}
\text{H}_2\text{C} = \text{CHCOMe} & \quad (1.5 \text{ eq}) \\
\text{H} & \quad \text{A} (10 \text{ mol\%}) \\
\text{DMF, } 60^\circ\text{C, 2 h} & \quad 74\%
\end{align*}
\]

9 examples (yields 62-82%).
### Chiral Tridentate Schiff Base Chromium(III) Complex

A catalyses the enantioselective ring opening of meso aziridines.


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5 examples (yields 73-95%, %ee = 60-94%) are reported.

### Chromium(II) Chloride

The title reagent is used as a catalyst in the one-pot transformation of aldehydes to (E)-1-alkenytrichloromethylsilanes.


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4 examples (yields 73-80%) are reported.

### Dirhodium Tetrakis(1,1′-binaphthyl)-2,2′-dilyl phosphate) Catalyst

A (and similar catalysts) are utilised in the enantioselective intramolecular 1,3-dipolar cycloaddition of the illustrated α-diazo-β-keto ester.


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Optimisation of the yield and enantioselectivity of the above reaction is described.

### Magnesium Iodide

A catalyses ring expansion reactions of cyclopropanes by amidines to give the corresponding spiro[pyrrolidin-3,3′-oxindoles].


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18 examples (yields 55-99%, %de = 4,28-96%) including 1 example of cyclopropane ring opening using an isocyanate and 1 example of carboxamide ring opening with an amidine.

### Lanthanum(III) Trifluoromethanesulfonate

The title reagent catalyses the formation of aziridines from imines. The reaction is highly selective for cis aziridines in protic media.


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10 examples (yields 49-60%, 5:1 ≤ cis/trans ≤ 100:0).
### N,N-Dimethylalloxan

A catalyses the epoxidation of a range of di- and tri-substituted alkenes in good to excellent yield.

```
O
| O
|  
| NMe
|   
| NMe
```

**Catalyst**

\( \text{A} \) (30 mol%) Oxone (4 eq)

\[ \text{NaHCO}_3 \ (12 \text{ eq}) \]

\[ \text{MeCN-H}_2\text{O} (3:2), 0^\circ \text{C}, 8 \text{ h} \]

70%

8 examples (yields 64-92%) are reported.


### Triphenylcarbenium Tetrakis(pentafluorophenyl)borate

A catalyses the alkylmetallation of alkenes via alkylzirconium species, generated by the hydrozirconation of alkenes.

\[ \text{[Ph}_3\text{C}^+]\text{[B(C}_6\text{F}_5)_4^-} \]

**Catalyst**

\( \text{A} \)

(a) \( \text{Cp}_2\text{(Cl)}\text{Zr}(\text{η}_5\text{C}_5\text{H}_5) \)

(b) \( \text{MeOH, 40}^\circ \text{C, 30 min} \)

\[ \text{MeO} \]

95%, regioselectivity = 91:9

6 examples (yields 80-95%, 91:9 ≤ regioselectivity ≤ 94:6).


### Chiral 1,1-Bisoxazolinylicyclopropane Ligand

A catalytic facial selective Michael addition of 1,3-dicarbonyl nucleophiles to nitroalkanes is reported. Due to a rapid anolisation at the α-carbon, a 1:1 mixture of diastereoisomers is isolated but β-selectivity is moderate to good.

\[ \text{A} \]

**Ligand**

\[ \text{MeCOCH}_2\text{CCO}_2\text{Et (1.2 eq)} \]

\( \text{A} \) (5.5 mol%)

\[ \text{Mg(OTf)}_2 \ (5 \text{ mol%}) \]

\[ \text{N-Methylmorpholine (6 mol%)} \]

\[ 4\text{ Å MS} \]

\[ \text{CH}_2\text{Cl}_2, \text{rt}, 2 \text{ h} \]

95%

β-Selectivity = 90:10

14 examples (yields 29-97%, β-selectivity = 33-94%).


### 9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene

A serves as ligand in the Pd(0) catalysed preparation of N-aryl benzophenone hydrazones which are further employed for Fischer indole synthesis.

\[ \text{A} \]

**Ligand**

\[ \text{3.5-Me}_2\text{C}_6\text{H}_4\text{Br (1.0 eq)} \]

\( \text{A} \) (0.1 mol%)

\[ \text{Pd(OAc)}_2 \ (0.1 \text{ mol%}) \]

\[ \text{NaOH-Bu (1.4 eq)} \]

\[ \text{PhMe, 80}^\circ \text{C, 4 h} \]

93%

5 examples (yields 71-98%).


### (R,R)-1,2-Bis(aminoacarbonylphenyl-2'-diphenylphosphino)cyclohexane

A catalytic asymmetric synthesis of quaternary amino acids is reported employing A and palladium catalysis.

\[ \text{A} \]

**Ligand**

\[ \text{A} \] (7.5 mol%)

\[ [\eta^5-C_3\text{H}_5\text{PdCl}]_2 \] (2.5 mol%)

\[ \text{H}_2\text{CsOCH}_2\text{MeOAc (1 eq)} \]

\[ \text{PhMe, rt, 3 h} \]

72%, er = 99:1

22 examples (yields 32-96%, %ee 72-99%).

### Chiral Ferrocenyl Ligand

A and similar ligands give good enantioselectivities in the catalytic reduction of β-dicarbonyl compounds and functionalised double bonds. Enantiomeric products can be obtained by modifying the benzyl substituent of A.


12 examples including the double reduction of β-diketones and the reduction of substituted alkenes (%ee = 19, 52-99%, %ide = 90-99%).

### (R,R)-N,N-Bis(3,5-di-tert-butyl-salicylidene)-1,2-cyclohexanediadimine (Salen)

A chromium(II) complex formed from A catalyses the enantioselective Nozaki-Hiyama coupling of allyl halides and aliphatic or aromatic aldehydes.


7 examples (yields 40-67%, %ee = 65-89%).

### (2R,5S)-3-Phenyl-2-(8-quinolinooxy)-1,3-diaza-2-phosphabicyclo-[3.3.0]-octane (QUIPHOS)

A practical method for the large-scale synthesis of the title ligand is described.


### Tetrabutylammonium Iodide

The title reagent mediates palladium(0)-catalysed cross-coupling between benzylic bromides and aryl or alkenyl triflates. The reagent also allows a new nickel(0)-catalysed cross-coupling between functionalised benzylic zine reagents and primary alkyl halides.


9 examples of Pd(0)-catalysed cross-coupling (yields 76-94%) and 6 examples of Ni(0)-catalysed cross-coupling (yields 63-81%) are reported.

### Potassium Fluoride / Aluminium Oxide

The title reagent pair are utilised with palladium black for solventless Suzuki coupling reactions.


11 examples (yields 0, 5-98%) are reported.
Chloromethyl Trimethylsilylmethyl Sulfide

The title reagent is used for the preparation of enantiomerically pure trans-3,4-disubstituted tetrahydrothiophenes by diastereoselective thioacarbonyl ylide addition to chiral α,β-unsaturated amides.

\[ \text{Me}3\text{SiSLi} + \text{Cl} \rightarrow \text{Me3SiSMe} \]


3 examples (yields 89-95%, %de = 78-80%) are reported.

Iodomethyl Pivalate

Iodine-magnesium exchange yields a functionalised magnesium carbonyl from A which can be reacted with various electrophiles.

\[ \text{PhCO} + \text{PhMgCl} \rightarrow \text{PhCO} + \text{PhMgCl} \]


13 examples using A and 2 similar iodides (yields 74-88%). NBP = N-butylypyrrolidinone

4,4,4′,5,5′,6-Octamethyl-2,2′-bi-1,3,2-dioxaborolan (B₂pin₂)

A is used to generate terminal organoborane products from alkanes and aliphatic ethers in a rhodium-catalysed photochemical process.

\[ \text{B} + \text{CO} \rightarrow \text{Bpin} \]


7 examples (yields 75-100%).

Samarium(II) Iodide

The title reagent is used to promote hydroxy-directed intermolecular ketone-olefin couplings.

\[ \text{SmI}_2 + \text{CH}_2\text{CH(OH)}_2 \rightarrow \text{CH}_2\text{CH(OH)}_2 \]


6 examples (yields 62-91%, %de = 87-100%).

Tetraethylammonium Chloride / Methyl(dicyclohexyl)amine

The title reagents are used as part of a phosphine-free catalytic system for the Heck reaction. Aryl iodides or bromides are coupled with disubstituted alkenes to give highly E-selective trisubstituted alkenes under mild conditions.

\[ \text{Et}_4\text{NCl} + \text{Pd(OAc)}_2 \rightarrow \text{Pd(OAc)}_2 \]


13 examples (yields 51-87%, 7.1 ≤ E,Z ≤ 100:1), DMAD = dimethylacetamide
Trifluorophenylsilane

$N$-Silylated azomethine ylides are generated from A and $n$-silylimidates. The ylides, which can be regarded as synthetic equivalents of nitrite ylides, are utilised in cycloaddition reactions.


3 examples (yields 88-97%).

Benzyl Vinylcarbamate

A convenient procedure for the introduction of $\beta$-aminoethyl groups into arenes and alkenes is described.


11 examples (77-97%).

Dibutyltin Oxide / Benzoyl Isothiocyanate / Tetrabutylammonium Bromide

The title reagents mediate the one-pot conversion of syn-diols into protected syn-amino alcohols.


6 examples (yields 58-83%).

1,1,4,7,10-Hexamethyltetrahydronaphthalene

A enhances the rate of reaction of the lithium enolate of 1-tetralone with alkyl halides. The ratio of the monosilylated product to dialkylated product is also increased.


4 examples (yields 39, 60-80%) are reported.

Phenyl Vinyl Thioether

A can be used to generate a 1,1-dithioethylene synthon, taking advantage of two well established reactions: (a) $\alpha$-deprotonation of a thioether and (b) sulfur-lithium exchange.


5 examples (yields 31-62%) are reported.