**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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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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**The title reagent catalyses the enantioselective aldol reaction of trimethoxysilyl enol ethers with aldehydes.**


**Catalyst**

The title reagent catalyses the enantioselective aldol reaction of trimethoxysilyl enol ethers with aldehydes.

(R)-p-Tol-BINAP· AgFComplex

<chem>
\begin{align*}
\text{R} & \text{R} \\
\text{AgF} & \text{PhCHO (1 eq)} \quad \text{MeOH, –78°C, 4 h}
\end{align*}
\end{chem>

11 examples (yields 56-87%, 74:26 > syn:anti > 99:1, %ee 85-97%).

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**Reagent A acts as a chiral initiator in the enantioselective addition of diisopropylzinc to 2-alkynylpyrimidine-5-carbaldehyde to afford the corresponding 2-alkynylpyrimidyl alkanol.**


**Catalyst**

**Dimethylphenylsilylcopper(I)**

The title reagent catalyses the reductive bromination of the Hajos dione.


- **Catalyst**

  (R)-4-Carboxy[2.2]paracyclophane

  <chem>
  \begin{align*}
  \text{HO}_2\text{C} & \text{A} \\
  \text{t-Bu} & \text{t-Bu} \quad \text{PhMe, 0°C, 4 h}
  \end{align*}
  \end{chem>

  1 example (yield 96%, %ee 97%) and 2 other initiators are reported.

  - **Catalyst**

    Dimethylphenylsilylcopper(I)

    <chem>
    \begin{align*}
    \text{PhMe}_2\text{SiCu} & \text{A} \\
    \text{O} & \text{O} \\
    \end{align*}
    \end{chem>

    1 example (70% yield) is reported.
### [Rh(dppe)]ClO₄ Catalyst

The title reagent catalyses an intramolecular hydroacylation reaction for the synthesis of eight-membered rings. Examples with [Rh(dppe)]OTf are also reported.


![Reaction Scheme](attachment:image.png)

5 examples (yields 54-65%) are reported.

### Ruthenium Carbonyl Catalyst

The title reagent catalyses the intramolecular cyclo-coupling of ketones, alkenes or alkynes, and carbon monoxide for the synthesis of functionalised γ-butyrolactones.


![Reaction Scheme](attachment:image.png)

56 examples (yields 13-99%) are reported.

### [RhCl(CO)₂]₂ Catalyst

The title reagent catalyses the carbonylation of sp³ C-H bonds adjacent to the nitrogen of cyclic alkylamines.


![Reaction Scheme](attachment:image.png)

8 examples (yields 12-84%) are reported.

### Tetrabutylammonium Chloride Catalyst

The title reagent catalyses the azidolysis of epoxides to give the corresponding azido alcohol in solvent free conditions.

Schneider, C. Synlett 2000, 1840.

![Reaction Scheme](attachment:image.png)

7 examples (yields 5-89%) are reported.

### Molybdenum Metathesis Catalyst

Reagent A, when activated in situ by dichloromethane, catalyses the cross metathesis reaction of functionalised alkynes.


![Reaction Scheme](attachment:image.png)

15 examples (yields 47-82%) are reported.
### Chloro(1,5-cyclooctadiene)rhodium(I) Dimer

The title reagent catalyses the Beckmann rearrangement of oximes to give the corresponding amides.

![Chemical structure](image)


16 examples (yields 30-99%) are reported.

### Bis(dibenzylideneacetone)palladium

The title reagent catalyses the cross-coupling of alkylidenesilacyclopentanes with aryl or alkenyl halides to give trisubstituted homoallylic alcohols.

![Chemical structure](image)


13 examples (yields 45-88%) are reported.

### Phthalocyanatoiron [PcFe(II)] / Sodium Borohydride

The title reagent pair, in the presence of 2-bromoethanol, catalyses the reduction of nitroarenes.

![Chemical structure](image)


7 examples (yields 67-95%) are reported.

### [(S)-t-Bu-BOX]Cu(OTf)₂ Complex

The title reagent catalyses the asymmetric Friedel-Crafts alkylation of β,γ-unsaturated α-ketoesters.

![Chemical structure](image)


13 examples (yields 69-99%, %ee 79-99.5%).

### 1,2-Bis(phospholanyl)benzene-Modified Diiodonickel Complex

The title reagent, when activated with LiBH₂Et₃, catalyses the highly enantioselective isomerization of 4,7-dihydro-1,3-dioxepins.

![Chemical structure](image)


3 examples (yields 74-75%, %ee 90-98%) are reported.
### (R,R,Sp,Sp)-N-[2-(diphenylphosphino)ferrocenylcarbonyl]-diaminocyclohexane Derivative

The title ligand is used in palladium-catalysed asymmetric alkylation of ketone enolates.


![Ligand](image1)

3 examples (yields 77-95%, %ee 66-87%) are reported.

### (1R,3R,5R,8S)-11,11-Dimethyl-4-oxa-5-(2-diphenylphosphino)phenyl-6-thiatricyclo[6.2.1.0]undecane

The title ligand is used in palladium-catalysed asymmetric allylic substitution reactions.


![Ligand](image2)

4 examples (yields 74-98%, %ee 76-94%) are reported.

### (S)-(−)-2-Cyclohexylphosphino-2'-dimethylamino-1,1'-binaphthyl

The title ligand is used in the Pd-catalysed asymmetric Suzuki coupling for the preparation of biaryl compounds.


![Ligand](image3)

17 examples (yields 74-98%, %ee 57-92%) are reported.

### Chiral Amidophosphine

Ligand A is used in the Cu-catalysed asymmetric addition of diethylzinc to N-sulfonylimines.


![Ligand](image4)

16 examples (yields 22-99%, %ee 5-94%) are reported.

### Chloramine-T

The title reagent is used for the preparation of N-sulfonylsulfilimines from sulfides.


![Reagent](image5)

15 examples (yields 70-99%) are reported.
### Chiral Oxazaborolidinone

The title reagent mediates the enantioselective ring-cleavage of diastereomeric 1,3-dioxolane acetals.


![Chemical Structure](image)

6 examples (yields 46-92%, %ee 83-98%) are reported.

### Cp₂Zr(H)Cl (Schwartz reagent)

The title reagent reduces tertiary amides to aldehydes.


![Chemical Structure](image)

16 examples (yields 74-99%) are reported.

### tert-Butyldimethylsilyloxymalononitrile

The title reagent is used in a one-pot synthesis of α-silyloxyamides from aldehydes and ketones.


![Chemical Structure](image)

26 examples (yields 35-97%) are reported.

### Mesityllithium

The title reagent is used as a selective lithiating agent for the preparation of arylithium compounds having alkoxycarbonyl groups.


![Chemical Structure](image)

8 examples (yields 57-97%) are reported.

### Diisopinocampheylborane

The title reagent is used for the reduction of α-, β-, and γ-keto acids to give corresponding hydroxy acids with high enantioselectivity.


![Chemical Structure](image)

6 examples (yields 75-90%, %ee 77-90%) are reported.
### Copper(I) Thiophene-2-carboxylate (CuTC)

The title reagent mediates the Pd-catalysed cross-coupling of thioalkyne derivatives with boronic acids to give functionalized alkynes.

![CuTC](image)


11 examples (yields 39-91%) are reported.

### Tetrabromomethane/Methanol

The title reagent pair is used for the highly chemoselective esterification of sp3-C tethered carboxylic acids in the presence of sp2-C and sp-C tethered carboxylic acids.

![CBr4MeOH](image)


11 examples (yields 39-91%) are reported.

### Cyanomethylenetrimethylphosphorane (CMMP)

The title reagent mediates Mitsunobu-type alkylation of prenyl and geranyl phenyl sulfone with primary and secondary alcohols.

![NC PMe3OH](image)


12 examples (yields 54-100%) are reported.

### Iodomethylin 2,4,6-Trichlorophenoxide

The title reagent is used for the cyclopropanation of alkyl-substituted alkenes.

![OZnCH2I](image)


6 examples (yields 90-98%) are reported.

### Phenylaziridine

The title reagent undergoes [3+2] dipolar cycloaddition with geminal alkenes, in the presence of a Lewis acid, to give single products.

![Ph](image)


4 examples (yields 72-78%) are reported.