**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, John Christopher, Emma Guthrie, Philip Kocienski, Alexander Kuhl, Catherine McCusker, and Robert Narquizian, and Sukhjinder Uppal of Glasgow University.

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

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<table>
<thead>
<tr>
<th>Chlorotrism(3,5-dimethylphenyl)ltert-butylamidomolybdenum(IV)</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong> mediates the efficient ring-closing metathesis of functionalized dienes.</td>
<td>![Chemical Structure]</td>
</tr>
<tr>
<td>[MoCl(N-Bu/m-Xyl)₃]</td>
<td>A (10 mol%)</td>
</tr>
<tr>
<td>CH₂Cl₂ (25 eq)</td>
<td>PhMe, 80°C, 20 h</td>
</tr>
<tr>
<td>88%</td>
<td>9 examples (yields 60-91%)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tris(dibenzylideneacetone)dipalladium(0)</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong> catalyses cross-coupling of bromoarenes with zirconocene stabilized aryl complexes, obtained by halogen metal exchange and transmetalation. Iodination of the in-situ formed zirconocene aryne complexes gives rise to the final products.</td>
<td>![Chemical Structure]</td>
</tr>
<tr>
<td>Pd₂dba</td>
<td>(a) n-BuLi (1.5 eq)</td>
</tr>
<tr>
<td>THF, -50°C, 15 min</td>
<td>(c) A (2 mol%), DPEphos</td>
</tr>
<tr>
<td>(6 mol%), o-BrPhMe (1.0 eq)</td>
<td>(d) I₂ (3 eq), 36°C, rt, 10h</td>
</tr>
<tr>
<td>THF, 60°C, 1h</td>
<td>17 examples (yields 40-90%, 27:1 • meta : ortho•100:0).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tetrachlorobis(tetrahydrofuranyltitanium(IV))</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong> mediates the acyl Claisen rearrangement of N-acyl morpholine derivatives and ketenes formed in-situ from acid chlorides.</td>
<td>![Chemical Structure]</td>
</tr>
<tr>
<td>[TiCl₄(THF)₂]</td>
<td>A (5 mol%)</td>
</tr>
<tr>
<td>Et₂COCl (1.2 eq)</td>
<td>i-Pr₂NEt (1.5 eq)</td>
</tr>
<tr>
<td>CH₂Cl₂, rt, 10 h</td>
<td>10 examples (yields 70-95%, %de = 80-98%)</td>
</tr>
</tbody>
</table>

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
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene Hydrochloride

A and a Pd(0)-source mediate the cross-coupling of aryl chlorides with aryl Grignard reagents.

\[
\begin{align*}
\text{PhMeBr (1.2 eq)} & \quad \text{Pd}_{2}(dppf)\text{Cl}_2 \quad \text{A (4 mol\%)} \\
& \quad \text{Dioxane-THF, 80ºC, 3 h} \\
& \quad 99\%
\end{align*}
\]


16 examples (yields 0, 69-99%).

Molybdenum Isocyanide Complex

A catalyses the regioselective hydrostannation of several types of alkenes, giving preferentially \(\alpha\)-stannylated products.

\[
\begin{align*}
\text{Mo}(&\text{CO})_3\text{(R)\text{Cl}}_2\text{(MoB} & \text{)}_3) \\
\text{R} & = \text{CNH-Bu}
\]


11 examples (yields 38-98%, 63.37 \(\leq \alpha/\beta \leq 95.5\)) are reported.

1,1′-Binaphthalene-2,2′-dicol / Dichloro-di-isopropoxytitanium(IV)

The title reagent pair catalysyze the asymmetric allylation of ketones.

\[
\begin{align*}
\text{O} & \quad \text{A (20 mol\%) } \\
& \quad \text{B (20 mol\%)} \\
& \quad \text{(CH}_3\text{CH}_2\text{)}_2\text{SnBu}_3 (40 \text{ mol\%}) \\
& \quad \text{CH}_2\text{Cl}_2, rt, 2 h
\end{align*}
\]


8 examples (yields 75-91%, \(\%\text{ee} = 29-65\%\)) are reported.

\(N\-p\-(Toluene sulfonyl)-1,2-diphenylethenediamine(\(\eta^5\)-arene) Ruthenium(II) Chloride

The title reagent catalyses the asymmetric transfer hydrogenation of benzils to prepare chiral hydrobenzoins.

\[
\begin{align*}
\text{O} & \quad \text{A (20 mol\%)} \\
& \quad \text{B (20 mol\%)} \\
& \quad \text{HCO_2H (4.4 eq)} \\
& \quad \text{Et}_2\text{N (2.2 eq)} \\
& \quad \text{DMF, 40ºC, 30 h}
\end{align*}
\]


5 examples (yields 67-100%, \(\%\text{ee} > 99\%\)) are reported.

Palladium(II) Acetate

A catalyses the Ullmann-type reductive coupling of aryl halides under an air atmosphere in aqueous acetone.

\[
\begin{align*}
\text{Pd(OAc)}_2 & \quad \text{A (8 mol\%)} \\
& \quad \text{Zn (3 eq)} \\
& \quad \text{Me_2CO-H_2O (1:1), rt, 30 min}
\end{align*}
\]


13 examples (yields 0, 64-96%) are reported.
Indium(III) Chloride
The title reagent catalyses the one-pot preparation of α-amino phosphonates from aldehydes or ketones and amines.

\[ \text{InCl}_3 \quad \overrightarrow{\text{A}} \quad \text{Ph} \quad \text{Me} \quad \text{O} \quad \text{Me} \]


24 examples (yields 76-95%) are reported.

1,3-Bis(2,6-disoproplypheny)imidazo[2,1-α]imidazole Hydrochloride
The title reagent catalyses the amination of aryl halides.

\[ \text{A} \quad \text{Ph} \quad \text{Cl} \quad \text{A} \quad \text{Me} \quad \text{O} \quad \text{Me} \quad \text{NHPh} \quad \text{PhMe}, 100^\circ \text{C}, 3 \text{ h} \]


16 examples (yields 59-99%) are reported.

Guanidinium Phosphine Ligand / Palladium(II) Acetate
The title reagent pair, supported on glass beads, is utilised in Heck reactions and Sonogashira couplings. The catalyst is recyclable and features low leaching of palladium into the system.

\[ \text{A} \quad \text{Me}_2\text{N} \quad \text{NHCl} \quad \text{Pd(OAc)}_2 \quad \text{B} \quad \text{PhMe}, 100^\circ \text{C}, 16 \text{ h} \]


7 examples of Heck reactions (yields 55-87%) and 4 examples of Sonogashira couplings (yields 58-87%) are reported.

Chiral Titanocene Dichloride Complex
A catalyses the enantioselective opening of meso-epoxides via a β-titanoxy radical intermediate.

\[ \text{A} \quad \text{Ph} \quad \text{O} \quad \text{OEt} \quad \text{Zn} \quad \text{A} \quad \text{OEt} \quad \text{OH} \quad \text{OEt} \]


6 examples (yields 60-68%, \%ee = 74-93%) are reported.

1,6-Bis(dimethylamino)hexane
A is used in the tosylation of various alcohols. The reported method has advantages over the more traditional use of pyridine / TsCl in that the reaction rate is higher, and undesired chlorination reactions are avoided. A can also be used in mesylation reactions.

\[ \text{A} \quad \text{Me}_2\text{N(CH}_2_2)_2\text{Me} \quad \text{OEt}_2\text{C(CH}_2_2)_2\text{CH}_2\text{OH} \quad \text{Et}_2\text{N} \quad \text{MeCN}, 0^\circ \text{C}, 1 \text{ h} \]


6 examples (yields 92-95%) are reported.
<table>
<thead>
<tr>
<th><strong>Bis(triethylamino)nickel(II) Dichloride</strong></th>
<th><strong>Catalyst</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>The title reagent can be used as an alternative to Pd(PPh₃)₄ in the catalysis of Suzuki reactions. A is effective in the presence of water and the lack of phosphine ligands prevents unwanted side reactions occurring.</td>
<td></td>
</tr>
<tr>
<td><img src="image1" alt="Reaction scheme" /></td>
<td>NiCl₂(NEt₂)₂  [\text{PhBr} \rightarrow \text{PhCO₂H}]  (A)  (\text{PhB(OH)}_2) (1.2 eq)  (\text{A} (3 \text{ mol%), NaPO₄ (20 eq)})  Dioxane, 95°C, 16 h  (66%)  8 examples (yields 0, 48-80%).</td>
</tr>
<tr>
<td>N. E. Leadbeater, S. M. Resouly  <em>Tetrahedron</em> 1999, 55, 11889</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Chiral Chromium Salen Catalyst</strong></th>
<th><strong>Catalyst</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>A is reported as an efficient catalyst for the kinetic resolution of 2,2-disubstituted epoxides.</td>
<td></td>
</tr>
<tr>
<td><img src="image2" alt="Reaction scheme" /></td>
<td>A  (\text{Ph}(\text{O})\text{CH} \rightarrow \text{Ph}(\text{O})\text{CH} \delta\text{Bu}) (\text{A} (2 \text{ mol%) TMSN₃ (0.60 eq) } \beta\text{-PrOH (0.60 eq) TBME, 0°C} \rightarrow \text{rt, 6 h} )  44%  er = 99:1  7 examples (yields 42-68%, %ee = 90-99%).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Palladium Catalyst</strong></th>
<th><strong>Catalyst</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>A is reported to be a highly active catalyst for the Heck reaction.</td>
<td></td>
</tr>
<tr>
<td><img src="image3" alt="Reaction scheme" /></td>
<td>((\text{ArO})_2\text{P-Pd-P(OAr)}_2)  (\text{Ar} = \text{p-OMe} )  (\text{MeO} )  (\text{MeO} )  (\text{NMe} )  (\text{NMe} )  (\text{H}_2\text{C} = \text{C} \text{CHCO₂H} \rightarrow \text{Bu} (1.2 \text{ eq) NMP, 180°C, 22 h} )  89%  3 examples (yields 95-100%) are described.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Ruthenium Catalyst</strong></th>
<th><strong>Catalyst</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>A is reported as an effective catalyst for alkene-alkyne coupling.</td>
<td></td>
</tr>
<tr>
<td><img src="image4" alt="Reaction scheme" /></td>
<td>([\text{CpRu(MeCN)}<em>3])⁺PF₆⁻  (\text{CH₂CN} \rightarrow \text{H}</em>{17} )  (\text{A} (10 \text{ mol%) DMF, rt} )  15 examples (yields 62-91%, 1.2:1 ≤ regioselectivity ≤ 100:0) are described.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>(2,7-Dimethyl-1,8-biphenylenedioxy)bis(diisopropoxaluminium)</strong></th>
<th><strong>Catalyst</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>The high-speed Tishchenko reaction of aldehydes using A is reported. Highly stereoselective intramolecular Tishchenko reduction of ß-hydroxy ketones is also described.</td>
<td></td>
</tr>
<tr>
<td><img src="image5" alt="Reaction scheme" /></td>
<td>(\text{CHO} \rightarrow \text{PhMe, rt, 5 h} )  (88%)  6 examples of the Tishchenko reaction (yields 67-99%) and 2 examples of reduction (yields 92, 99%, 96:4 ≤ ant: syn ≤ 99:1) are described.</td>
</tr>
</tbody>
</table>

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**2.2′-Bis(di-p-tolylphosphino)-1,1′-binaphthyl**  
*Synthesis 1999, No. 2, 321–328 ISSN 0039-7881 © Thieme Stuttgart · New York*

A Cu(I) catalyst formed from the title ligand is used in the asymmetric conjugate reduction of α,β-unsaturated esters.

![Chemical structure of 2.2′-Bis(di-p-tolylphosphino)-1,1′-binaphthyl]


9 examples (yields 84-96%, %ee 80-91%).

PMHS = polymethylhydroxiloxane

**α-(Di-tert-buty1phosphino)biphenyl**

A in combination with Pd(OAc)$_2$ catalyses the efficient Suzuki-coupling of aryl bromides and chlorides.

![Chemical structure of α-(Di-tert-buty1phosphino)biphenyl]


21 examples (yields 81-98%).

**Chiral Bis(trifluoromethanesulfonamide) Ligand**

Asymmetric acry halide aldehyde cyclocondensations are mediated by ligand A and Me$_2$Al or Et$_2$AlCl.

![Chemical structure of Chiral Bis(trifluoromethanesulfonamide) Ligand]


10 examples (yields 56-91%, %ee = 54-93%).

**(R,R)-2′-Benzoyloxymethyl(phenyl)-2,5-dimethylphospholane**

A is reported as an efficient ligand in the Ni-mediated hydrosylation of styrene.

![Chemical structure of (R,R)-2′-Benzoyloxymethyl(phenyl)-2,5-dimethylphospholane]


5 examples (yields 2-94%, %ee = 29-50%)

**Chiral 2-(phosphinoaryl)pyridine Ligand**

Asymmetric allylic alkylations using a palladium catalyst derived from ligand A are reported.

![Chemical structure of Chiral 2-(phosphinoaryl)pyridine Ligand]


4 examples (yields 77-85%, %ee = 71-93%) are reported.
1,1'-Binaphthyl-2-yl(phenyl)iodonium Tetrafluoroborate

Chiral diaryl iodonium salt A and analogues are utilised in the asymmetric \(\alpha\)-phenylation of cyclic \(\beta\)-keto esters.

\[
\begin{align*}
\text{A} & \quad \text{Reagent} \\
\text{R} & \quad \text{t-BuOK (1 eq)} \quad \text{A (0.9 eq)} \\
& \quad \text{t-BuOH, 20 h, rt} \\
& \quad 65\%, \ \text{ee} = 69:31 
\end{align*}
\]

9 examples (yields 15-71\%, \text{ee} = 37-53\%).

\(\rho\)-Tolythioglycolic Acid

A and similar thioglycolic acids, undergo Ni-mediated cross-couplings with organozinc reagents.

\[
\begin{align*}
\text{A} & \quad \text{Reagent} \\
\text{Me}_2\text{Zn} (2 \text{ eq}) & \quad (\text{MePh}_2\text{P})_3\text{NiCl}_2 (5 \text{ mol\%}) \\
& \quad \text{THF, 50°C, 12 h} \\
& \quad 80\% 
\end{align*}
\]

18 examples (yields 40-100\%).

2,6-Bis(trimethylstannyl)pyridine

The title reagent is used in Stille-type coupling procedures to prepare new pyridine-based ligands for supramolecular chemistry.

\[
\begin{align*}
\text{A} & \quad \text{Reagent} \\
\text{PhMe}_3\text{Sn} \quad \text{Pd}(\text{Ph}_{3}\text{P})_2\text{Br} (2.5 \text{ eq}) \\
& \quad \text{PhMe}_3, 4 \text{ d} \\
& \quad 68\% 
\end{align*}
\]

Preparation of A (69\%) and 3 examples of ligand synthesis (yields 42-66\%) are reported.

Hydroquinone

The title reagent is used as a homogeneous reductant in the palladium-catalysed Ullmann-type homocoupling of aryl halides.

\[
\begin{align*}
\text{A} & \quad \text{Reagent} \\
\text{A (50 \text{ mol\%})} & \quad \text{Pd}((\text{acac})_2 (4 \text{ mol\%}) \\
& \quad \text{As(\OE)I}_3 (4 \text{ mol\%}) \\
& \quad \text{Cs}_2\text{CO}_3 (1 \text{ eq}) \\
& \quad \text{DMA, rt, 1 d} \\
& \quad 72\% 
\end{align*}
\]

17 examples (yields 54-95\%) are reported.

(Dimethylphenylsilyl)pinacolborane

The title reagent is used in the palladium catalysed regioselective elaboration of 3-substituted 1,2-dienes. The utility of the 2-boryl allylsilane derivatives is demonstrated by Pd-catalysed coupling reactions with aryl halides.

\[
\begin{align*}
\text{A} & \quad \text{Reagent} \\
\text{PhMe}_3\text{Si} & \quad \text{Pd}((\text{acac})_2 (1.5 \text{ eq}) \\
& \quad 2,6\text{-xylol isocyanide (8 mol\%)} \\
& \quad \text{Octane, 120°C, 2 h} \\
& \quad 96\% 
\end{align*}
\]

7 examples (yields 79-99\%, regioselectivity > 86:14) are reported.
<table>
<thead>
<tr>
<th>Reagent</th>
<th>Iodoethane / Ethylmagnesium Bromide</th>
</tr>
</thead>
<tbody>
<tr>
<td>The title reagent pair are used in the coupling reaction of arylmagnesium compounds and THF to prepare 2-aryltetrahydrofurans.</td>
<td></td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{(R)-1-tert-Butylsulfanyl-1-cyclopentene} & \quad \text{Reagent} \\
\text{The title reagent is used in an asymmetric Heck reaction with a variety of para- and meta-substituted arenes diazonium tetrafluoroborates.} \\
\end{align*}
\]

\[
\begin{align*}
\text{Molecular Oxygen} & \quad \text{Reagent} \\
\text{Oxygen is used in atom-efficient osmium-catalyzed dihydroxylation in which both oxygen atoms are incorporated into the product.} \\
\end{align*}
\]

\[
\begin{align*}
\text{N,N,N',N'-Tetramethylandicarboxamide (TMAD) / Tributylphosphine} & \quad \text{Reagent} \\
\text{The title reagent pair are utilised in the direct transformation of primary and secondary alcohols to the corresponding nitrites in the presence of acetone cyanhydrin.} \\
\end{align*}
\]

\[
\begin{align*}
\text{Trimethylsilylsulfonyl Chloride / Iodosobenzene} & \quad \text{Reagent} \\
\text{A method for the preparation of sulfur trioxide in situ from the title reagent pair in the absence of Lewis bases is described. The procedure is utilised in the preparation of sultones from alkenes.} \\
\end{align*}
\]
### iso-Propylmagnesium Bromide

A (or i-Pr₂Mg) is utilised in the preparation of polyfunctional aryl or heteroaryl magnesium reagents from brominated precursors. Excellent chemoselectivity is observed in the Br-Mg exchange of di- or tribromoheterocycles.

![Chemical Structure](image)

M. Abarbri, F. Dehmler, P. Knochel

18 examples using A or i-Pr₂Mg (yields 55-88%) are described.

### Diethylaminotrimethylsilane / Methyl Iodide

The title reagents mediate the ring-opening iodosilation of cyclic ethers.

![Chemical Structure](image)

J. Ohshita, A. Iwata, F. Kanetani, A. Kural, Y. Yamamoto, C. Matsui

24 examples, including the use of different halide sources (yields 33-90%) are described.

### 1-Trisopropylsilyloxy-1,2-propanediene

The title reagent reacts with aldehydes or ketones to give α,β-unsaturated acyl silanes.

![Chemical Structure](image)

I. A. Stergiades, M. A. Tius

21 examples (yields 27-92%) are described.

### 4-Nitrophenyltrifluoromethanesulfonate

The title reagent is reported as a new trifluoromethanesulfonyl transfer agent.

![Chemical Structure](image)

L. Neuville, A. Bigot, M. E. T. H. Dau, J. Zhu

9 examples (yields 60-92%) are reported.

### Cyanomethylene[trimethylphosphorane (CMMP)]

The title compound mediates the alkylation of arylmethyl phenyl sulfones with primary and secondary alcohols. Arylmethyl phenyl sulfones of pKa up to 23.5 can be utilized in the CMMP mediated Mitsunobu reaction.

![Chemical Structure](image)

T. Tsunoda, K. Uemoto, T. Ohtani, H. Kaku, S. Ito

12 examples (yields 83-100%).

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