SYNTHESIS ALERTS

*Synthesis Alerts* is a new 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.


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### MeO-Polyethylene glycol-Bound DHQ and DHQD Ligands

<table>
<thead>
<tr>
<th>Catalyst</th>
<th><a href="#">MeO-Polyethylene glycol-Bound DHQ and DHQD Ligands</a></th>
<th><a href="#">Catalyst</a></th>
</tr>
</thead>
<tbody>
<tr>
<td>Asymmetric dihydroxylation with the title polymer-modified ligand yields diols with comparable enantioselectivity to the original Sharpless system (up to 98:2 er).</td>
<td><a href="#">DHQDO</a></td>
<td><a href="#">Catalyst</a></td>
</tr>
<tr>
<td>A, OsO₄ (0.4 mol%)</td>
<td><a href="#">K[Fe(CN)₆]</a></td>
<td>acetone / H₂O</td>
</tr>
<tr>
<td>Me</td>
<td><a href="#">C₆H₅</a></td>
<td>89%, er = 98:2</td>
</tr>
</tbody>
</table>

Four further examples are reported with results comparable to homogeneous phase catalysis conditions. The polymer supported catalyst is easily recovered by filtration.

### Ruthenium Hydride and Dihydride Phosphine Complexes

<table>
<thead>
<tr>
<th>Catalyst</th>
<th><a href="#">Ruthenium Hydride and Dihydride Phosphine Complexes</a></th>
<th><a href="#">Catalyst</a></th>
</tr>
</thead>
<tbody>
<tr>
<td>The title complexes act as very active catalysts for transfer hydrogenation of ketones and imines by propan-2-ol.</td>
<td><a href="#">RuHCl(PPh₃)₃</a></td>
<td>A</td>
</tr>
<tr>
<td>RuH₂(PPh₃)₄</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>2-naphthol</td>
<td>Me</td>
<td>A (0.1 mol%)</td>
</tr>
<tr>
<td>KOH (20 mol%)</td>
<td>propan-2-ol, 1 h, 85°C</td>
<td>83%</td>
</tr>
<tr>
<td>2-naphthol</td>
<td>Me</td>
<td></td>
</tr>
<tr>
<td>8 examples of ketones, 7 examples of imines (yields 50-96%). Using more catalyst, the reaction may be performed without any KOH.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### (1S,5R,8S)-8-Hydroxy-8-(6-naphthyl)methyl)-2-(4-pyridyl)-2-azabicyclo[3.3.0]octane

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<tr>
<th>Catalyst</th>
<th><a href="#">(1S,5R,8S)-8-Hydroxy-8-(6-naphthyl)methyl)-2-(4-pyridyl)-2-azabicyclo[3.3.0]octane</a></th>
<th><a href="#">Catalyst</a></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nenzy-matic kinetic resolution of racemic alcohols through an induced fit process.</td>
<td><a href="#">OCOPr</a></td>
<td><a href="#">Catalyst</a></td>
</tr>
<tr>
<td>[(I-Bu)₂CO]₂O (1.4 eq)</td>
<td>A (5 mol%)</td>
<td></td>
</tr>
<tr>
<td>2,6-collidine (1 eq)</td>
<td>PhMe, rt, 5h</td>
<td></td>
</tr>
<tr>
<td>racemic</td>
<td>69%</td>
<td></td>
</tr>
<tr>
<td>The influence of ring size (4 examples) and the nature of the ester functional group (7 examples) has been studied.</td>
<td><a href="#">OCOPr</a></td>
<td><a href="#">Catalyst</a></td>
</tr>
<tr>
<td><a href="#">OCOPr</a></td>
<td>27%, er = 86:12</td>
<td></td>
</tr>
</tbody>
</table>
### Tris[(E,E)-1,5-diphenylpenta-1,4-dien-3-one]bis[palladium(0)]

**Catalyst**

<table>
<thead>
<tr>
<th>Palladium catalyzed intermolecular carbon oxygen bond formation: a new synthesis ofaryl ethers.</th>
<th>Pd$_2$(dba)$_3$</th>
<th>A</th>
</tr>
</thead>
</table>


A comparison between catalysed and uncatalysed etherification reactions was carried out (12 examples).

### Methylirhenium Trioxide (MTO)

**Catalyst**

Aqueous catalysis: methyl rhenum trioxide as a homogeneous catalyst for the Diels-Alder reaction.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
</tr>
</thead>
</table>


The β-substituted dienophiles are less reactive under these conditions (32 examples).

### (SS,SR,9R)-8,9-(Isopropyldenedioxy)-2,2-dimethyl-1,3,6-trioxaspiro[4,5]decan-10-one

**Catalyst**

Treatment of ketone A with oxone generates a dioxirane intermediate capable of asymmetric epoxidation of olefins. Strict pH control was necessary for good results.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
</tr>
</thead>
</table>


8 examples (yields 66-93%, see 90-97%).

### Bis(triphenylphosphine)palladium Dichloride

**Catalyst**

Catalyses the cross-coupling reaction of unsaturated vinyl chlorides with Grignard reagents.

<table>
<thead>
<tr>
<th></th>
<th>Cs</th>
<th>BrMg</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdCl$_2$(PPh$_3$)$_2$</td>
<td>A</td>
<td>(2 eq)</td>
</tr>
</tbody>
</table>


16 examples (yields 42-95%). All products were isomerically pure.

### Magnesium Triflimide

A useful alternative to magnesium perchlorate for the catalysis of nucleophilic substitution reactions of allylic and benzylic acetates.

<table>
<thead>
<tr>
<th></th>
<th>Mg(N Tf)$_2$</th>
</tr>
</thead>
</table>


10 examples (yields 48, 76-99%). In the majority of cases catalyst A is superior to Mg(ClO$_4$)$_2$. 

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### Tetra-n-propylammonium Perruthenate (TPAP)

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Treatment of alkyl boranes with a catalytic quantity of TPAP (A) in the presence of N-methylmorpholine N-oxide (NMO) results in their oxidation to carbonyl compounds. A hydroboration / oxidation sequence allows for a one-pot synthesis of carbonyl compounds from olefins.</td>
</tr>
</tbody>
</table>


### Chiral Diiron Acyl Complex

<table>
<thead>
<tr>
<th>Chiral Auxiliary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis of and asymmetric cycloaddition with chiral diiron acyl complexes.</td>
</tr>
</tbody>
</table>


### (2S)-(N-Benzoylpyrroloidin-2-yl)diphenylcarbinol

<table>
<thead>
<tr>
<th>Ligand</th>
</tr>
</thead>
<tbody>
<tr>
<td>The title compound is a ligand for the asymmetric Nozaki-Hiyama coupling of organochromium reagents with aldehydes.</td>
</tr>
</tbody>
</table>


### 2,2'-Bis[(4S)-4-isopropyl-1,3-oxazolin-2-yl]biphenyl

<table>
<thead>
<tr>
<th>Ligand</th>
</tr>
</thead>
<tbody>
<tr>
<td>The title ligand forms one diastereoisomer when complexed with Cu(I). The resultant complex catalyses the asymmetric cyclopropanation of styrene.</td>
</tr>
</tbody>
</table>


### (1,1')-Bis(dibenzofuranyl)-2,2'-dichlor (BIFOL)

<table>
<thead>
<tr>
<th>Ligand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution of the C2-symmetric title compound via recrystallisation of a 1:1 mixture of diastereometric cyclic phosphoramidites gave both enantiomers in good yield and with &gt;98% enantio-purity.</td>
</tr>
</tbody>
</table>

N-Substituted-2,5-bis[(tri isopropyl]oxy]pyrrole (BISOP)

Primary amines are diprotected as their BISOP derivatives A.

Protecting Group

(a) t-BuLi, EtO

(b) n-HexCHO

7 examples of protection (yields 68-97%).

Eth-1-ynyl-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane

The title reagent is a novel and easy to handle propiolate anion equivalent; a concise preparation is presented.

Triallylmanganese/magnesium Chloride

The title reagent was used for the alylation and diallylation of acetylenic compounds in moderate to good yields.

Poly-(l)-Leucine

Urea-hydrogen peroxide complex in an organic solvent in the presence of DBU and the title polymer causes rapid asymmetric epoxidation of enones.

Poly(ethylen glycol)-triarylphosphine Conjugate

The title reagent may be employed in the Staudinger and Mitsunobu reactions as a liquid phase reagent support. The PEG reagent is in solution but, when spent, may be easily precipitated making product isolation a simple procedure.

Diethyl isopropylthioborane

With this borane, efficient catalytic asymmetric prop-2-ynylation of achiral aldehydes with allenyltributylstannane promoted by a BINOL-Ti(IV) complex is achieved with high ee.

C.-M. Yu, S.-K. Yoon, H.-S. Choi, K. Baek

Nitrido[\(N,N'-(1,1,2,2\text{-tetramethyl}ethylenediaminato)\]manganese(V)

Novel stereoselective synthesis of 2-amino saccharides


Phthalimidesulfonyl Chloride

Sulfonamide derivatives generated by reaction of the title compound with phenols react with pyridine to generate \(o\)-thioguanines which undergo cycloaddition with electron-rich alkenes and alkylides to give 1,4-benzooxathins.


Quinolinium fluorochromate (QFC)

The title compound selectively desilylates 1′ TBS ethers with concomitant oxidation of the liberated alcohol to aldehydes in the presence of secondary TBS ethers.


Aluminum Tris(2,6-diphenylphenoxy) (ATPH)

Enone complexation with ATPH allows Michael addition of alkylolithiums and lithium enolates.

**B-Chlorodi isopinocampheyborane (DIP-Chloride™)**

An in situ preparation of DIP-Chloride™ (A) is described.

\[
\begin{align*}
\text{BCl}_2 & \\
\text{A} & \\
\end{align*}
\]


Reduction of an oxo ester with this material gave the corresponding hydroxy ester quantitatively with %ee 94-97%.

DME = 1,2-Dimethoxyethane

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**Dimethylaluminium Chloride / N-Methoxy- N-methylene Hydrochloride**

N-Methoxy-N-methyl amides (Weinreb amides) can be efficiently prepared from lactones and esters by treatment with the title reagent pair.

\[
\begin{array}{ccc}
\text{MgCl}_2 & \text{A} & \text{MeONHMeHCl} \\
\text{B} & & \\
\end{array}
\]


11 examples (yields 21, 84-99%). In each case the analogous reaction employing Me₃Al in the place of A, requires extended reaction time and is lower yielding.

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**Lithium 1-Butyl- N-tosyloxycarbamate (LiBTOC)**

The title reagent provides a competent (+)-NHBOc synthon. Chiral cis-aminoindanol derived amide cyanocuprates are electrosexively aminated by A in a highly diastereoselective manner.

\[
\begin{array}{ccc}
\text{LiO} & \text{NTs} & \text{A} \\
\text{Bn} & \text{N} & \text{Bn} \\
\text{C} & \text{C} & \text{C} \\
\end{array}
\]


7 examples of amination (yields 51-77%, %ee 96, 99%).

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**(2R)-N-[(R)-p-Tolysulfinyl]bornane-10,2-sultam**

The use of camphor sultam A as a chiral sulfinyl transfer reagent is described.

\[
\begin{array}{ccc}
\text{A} & & \text{B} \\
\text{Br} & \text{N} & \text{N} \\
\text{SO} & \text{SO} & \text{SO} \\
\end{array}
\]


13 examples of preparation of sulfoxides (yields 79-97%, %ee 96-99%) and 6 examples of the preparation of sulfinamines (yields 65-84%, %ee 98, 99.9%). In all cases Oppolzer's bornane-10,2-sultam was recoverable in high yield (>85%) and with excellent optical purity.

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**η³-Propenitetaniumum iodopropoxide**

Treatment of cyclic allylic bromides and carbonates with A yields the corresponding allylic titanium complexes. These undergo diastereoselective addition to aldehydes and imines.

\[
\begin{array}{ccc}
\text{Br} & \text{A} & \text{OH} \\
\text{ThF, -78°C, 1 h} & \text{ThF, -78°C} & \text{O} \\
\text{MgCl} & \text{LiHMDS} & \text{H}_2\text{O} \rightarrow \text{CHO} (1.1 \text{eq}) \\
\text{95%, er = 98:2} & \text{65%, er = 19:1} & \\
\end{array}
\]


10 examples, including one example of addition to an imine (yields 3, 26-98%, syncri = >80:20). Low yields and stereoselectivities are observed for 6 and 7 membered rings.