**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 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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**Catalytic enantioselective addition of terminal alkynes to aldehydes.**


Reaction works best when the aldehyde has an α-branch. Lower yields but useful ee's obtained even with unbranched aldehydes. The reaction can be performed without solvent in which case no aqueous workup is necessary. 10 Aldehydes and 15 different alkynes used: yields typically >80%, ee's >90%.

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**Enantioselective 1,2-Addition**

<table>
<thead>
<tr>
<th>R</th>
<th>Yield</th>
<th>ee</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br₂NCH₂</td>
<td>91%</td>
<td>97%</td>
</tr>
<tr>
<td>Ph(CH₂)₂</td>
<td>89%</td>
<td>94%</td>
</tr>
<tr>
<td>Ph</td>
<td>94%</td>
<td>94%</td>
</tr>
<tr>
<td>(EtO)₂CH</td>
<td>88%</td>
<td>94%</td>
</tr>
<tr>
<td>n-Bu</td>
<td>81%</td>
<td>93%</td>
</tr>
<tr>
<td>TMSC(Me)₂</td>
<td>80%</td>
<td>99%</td>
</tr>
<tr>
<td>Et₃Si</td>
<td>85%</td>
<td>96%</td>
</tr>
</tbody>
</table>

er = 89%

---

**Enantioselective hydrometallation–alkylation: equivalent to umpolung of a Michael addition.**


alkylation with propargyl bromide and 1-bromoalkynes also reported

---

**Asymmetric 1,4-Addition**

<table>
<thead>
<tr>
<th>R</th>
<th>time</th>
<th>Yield</th>
<th>ee(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂Et</td>
<td>3 d</td>
<td>85%</td>
<td>97</td>
</tr>
<tr>
<td>CO₂Me</td>
<td>15 h</td>
<td>90%</td>
<td>80</td>
</tr>
<tr>
<td>CN</td>
<td>5 d</td>
<td>79%</td>
<td>55</td>
</tr>
<tr>
<td>CO₃Me</td>
<td>3 d</td>
<td>98%</td>
<td>93</td>
</tr>
</tbody>
</table>
A remarkably stable rhodium Lewis acid catalyst for hydrosilation, Mukaiyama aldol and cyclopropanation reactions.

**Novel Lewis Acid**

\[
\text{Rh} \left( \begin{array}{c}
\text{Pr} \\
\text{Pr} \\
\text{Pr}
\end{array} \right) + [\text{BAR}_{4}]^{-} \rightarrow \text{A}
\]

\(A\) is a remarkably stable, cationic, three-coordinate 14e complex that can be generated in situ. It forms \(\eta^1\)-complexes with carbonyls in dichloromethane solution.

\[
\text{A} + \text{OSiEt}_3 \rightarrow \text{OSiEt}_3
\]

\(\text{A}\) is a remarkably stable, cationic, three-coordinate 14e complex that can be generated in situ. It forms \(\eta^1\)-complexes with carbonyls in dichloromethane solution.

\[
\text{Os} + \text{Et}_3\text{SiH} \rightarrow \text{ClC}_6\text{H}_5, 70^\circ\text{C}, 17\text{~h}
\]

**Catalytic asymmetric allyl transfer reactions promoted by a BINOL-Ti complex.**


\[
\text{Asymmetric Addition}
\]

**Asymmetric Addition**

\[
\text{R} = \text{PhCH}_2\text{CH}_2, \text{n-C}_6\text{H}_{13}, \text{c-C}_6\text{H}_{11}, \text{Ph}, \text{PhCH}=\text{CH}, \text{PhC}=\text{C}.
\]

**Salen-derived catalysts containing secondary basic groups in the addition of diethylzinc to aldehydes.**


**Asymmetric Addition**

**Appendage of a quaternary centre to an indole via aryllead(IV) reagents.**


**sp\(^3\)–sp\(^2\) Coupling**

**Heteroannulation**

**Appendage of a quaternary centre to an indole via aryllead(IV) reagents.**


**Asymmetric Addition**

**Heteroannulation**

Intramolecular [2+2] photocycloaddition/thermal fragmentation approach toward 5–8–5 ring systems.

\[
\begin{align*}
\text{(a) LAH (53\%)} & \\
\text{(b) PhH, 140 °C (94\%)} & \\
\end{align*}
\]

Electrophilic cyclisations of vinylcyclopropanols to tethered aldehydes.

\[
\begin{align*}
\text{(a) TBAF} & \\
\text{(b) Swern ox.} & \\
\text{PPTS or SiO\textsubscript{2}} & 91\% \\
\end{align*}
\]

Highly diastereoselective aldel additions of a chiral ethyl ketone enolate under Lewis base catalysis.

Group-selective hydroalumination of bis-alkynyl carbinols: application to malyngolide.


Oxidative Annulation


[4+2] Cycloaddition


Enantioselective crotylation of aldehydes via an allyl transfer reaction from a chiral crotyl donor.


Asymmetric 1,2-Addition

\[
\begin{align*}
\text{R–CHO} & \quad \text{(0.5 equiv.)} \\
& \quad \text{TsOHH}_2 \text{O (10 mol%)} \\
\rightarrow & \quad \text{CH}_2\text{Cl}_2, 20^\circ\text{C}, 20\text{ h} \\
\rightarrow & \quad \text{H}_2\text{O} \\
\rightarrow & \quad >99\% \text{ ee}
\end{align*}
\]

9 examples; 2 failed: citronellal and 2-octenal. The corresponding asymmetric allylation reaction gave lower ee.

Thiazolium-catalysed cross-coupling of aldehydes with acylimines.


1,2-Addition

\[
\begin{align*}
\text{R–CHO} & \quad \text{(0.5 equiv.)} \\
& \quad \text{DtsOHH}_2 \text{O (5 mol%)} \\
\rightarrow & \quad \text{CH}_2\text{Cl}_2, 35^\circ\text{C}, 30\text{ min} \\
\rightarrow & \quad \text{PhI} \\
\rightarrow & \quad \text{nBuSn} \quad 71\% \\
\rightarrow & \quad \text{PhBr} \\
\rightarrow & \quad \text{nBuSn} \quad 76\% \\
\rightarrow & \quad \text{PhBr} \\
\rightarrow & \quad \text{nBuSn} \quad 68\% \\
\rightarrow & \quad \text{PhBr} \\
\rightarrow & \quad \text{nBuSn} \quad 54\%
\end{align*}
\]

21 examples; yields typically >70%

Hydrometallation

Annulation of aromatic imines via directed C–H activation with Wilkinson's catalyst.


Annulation

\[
\begin{align*}
\text{N–C sp}^3 \text{ Coupling}
\end{align*}
\]

Iridium-catalysed allylic amination of allylic esters.


\[
\text{[2+2+2] Cycloaddition}
\]

N\O\NHAc\n\text{CoCp}
(a) KOH
(b) Fe(NO)\text{3}
\rightarrow
\text{Pd(0)-, Ni(0)- or radical-mediated cyclisation reactions}

(s)-Strychnine synthesised in 1.9% overall yield in 14 steps (longest linear sequence).

Catalytic enantioselective cyanosilylation of ketones.
Yabu, K.; Masumoto, S.; Yamasaki, S.; Hamashima, Y.; Kanai, M.; Du, W.; Curran, D. P.; Shibasaki, M.

\[
\text{Enantioselective 1,2-Addition}
\]

7 additional examples using Gd(OPr\text{i})\text{3} as Lewis acid; yields typically ≥90%. Aromatic methyl ketones give the best ee’s (89–97%) followed by enones (80–89%). Phenethyl methyl ketone gave 90% yield but only 62% ee.

Diastereoselective [2,3]-sigmatropic rearrangement of metallated O-allylic-(N-benzyl)hydroxylamines.

\[
\text{[2,3]-Sigmatropic Rearrangement}
\]

\[
\text{Alkyl–alkyl Suzuki cross-coupling of bromoalkanes.}
\]
Netherton, M. R.; Dai, C.; Neuschütz, K.; Fu, G. C.

\[
\text{sp}^3\text{-sp}^3 \text{ Coupling}
\]

10 examples; yields 66-93%. Tricyclohexylphosphane is uniquely effective. With other phosphanes, \beta\text{-elimination} competes or predominates.

Polymer-bound tert-butanesulfinamide.
Dragoli, D. R.; Burdett, M. T.; Ellman, J. A.

\[
\text{Asymmetric 1,2-Addition}
\]

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