Enantio- and Diastereoselective $\alpha$-Allylation

**Significance:** A dual metal-catalyzed asymmetric allylation of $\alpha$-hydroxyketones is described. Chiral iridium and zinc complexes are employed for this transformation to furnish stereodefined $\alpha$-hydroxyketones.

**Comment:** Multi-metal asymmetric catalysis is a newly emerging field in catalysis. Exploitation of the preferential binding affinity of chiral ligands to specific metal centers allows chemoselective formation of the desired products.

**Selected examples:**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>Yield</th>
<th>Ee</th>
<th>dr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{HO} + \text{R} \rightarrow \text{HO}$</td>
<td>90%</td>
<td>97% ee</td>
<td>14:1</td>
<td></td>
</tr>
<tr>
<td>$\text{O}_2N + \text{R} \rightarrow \text{O}_2N$</td>
<td>95%</td>
<td>99% ee</td>
<td>14:1</td>
<td></td>
</tr>
<tr>
<td>$\text{Br} + \text{R} \rightarrow \text{Br}$</td>
<td>67%</td>
<td>96% ee</td>
<td>14:1</td>
<td></td>
</tr>
<tr>
<td>$\text{BnO} + \text{R} \rightarrow \text{BnO}$</td>
<td>91%</td>
<td>98% ee</td>
<td>17:1</td>
<td></td>
</tr>
</tbody>
</table>

**Derivatization:**

- **1.** allyl iodide, DMF
  - $\text{Cs}_2\text{CO}_3$, r.t., 6 h
  - 76% yield
- **2.** Grubbs–Hoveyda catalyst
  - $\text{CH}_2\text{Cl}_2$, 40 °C, 12 h
  - 52–95% yield

**Comment:**

- Multi-metal asymmetric catalysis is a newly emerging field in catalysis. Exploitation of the preferential binding affinity of chiral ligands to specific metal centers allows chemoselective formation of the desired products.

Key words: $\alpha$-hydroxyketones
dual metal catalysis
asymmetric allylation

Category:
Metal-Catalyzed
Asymmetric
Synthesis and
Stereoselective
Reactions

SYNFACTS Contributors: Mark Lautens, Alvin Jang

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