Copper-Catalyzed Asymmetric Ring Opening of D–A Cyclopropanes

**Significance:** The authors report a copper-catalyzed enantioselective ring-opening reaction of donor–acceptor cyclopropanes with water. A variety of ring-opening products were obtained in high yields (≤96%) and enantioselectivities (≤95% ee).

**Comment:** In this reaction, the copper hydrate serves as both a Lewis acid and a source of water; this affords a system for the controlled release of the appropriate amount of water as a nucleophile in the asymmetric catalysis. The method provides a new and efficient approach for direct access to γ-substituted γ-hydroxybutyric acid derivatives.

**Selected examples:**

<table>
<thead>
<tr>
<th>R</th>
<th>Product Structure</th>
<th>Yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeO</td>
<td><img src="image1" alt="Product Structure" /></td>
<td>95%</td>
<td>93%</td>
</tr>
<tr>
<td>Ph</td>
<td><img src="image2" alt="Product Structure" /></td>
<td>95%</td>
<td>87%</td>
</tr>
<tr>
<td>MeO</td>
<td><img src="image3" alt="Product Structure" /></td>
<td>70%</td>
<td>95%</td>
</tr>
<tr>
<td>BocN</td>
<td><img src="image4" alt="Product Structure" /></td>
<td>95%</td>
<td>87%</td>
</tr>
<tr>
<td>Ph</td>
<td><img src="image5" alt="Product Structure" /></td>
<td>95%</td>
<td>87%</td>
</tr>
<tr>
<td>PMP</td>
<td><img src="image6" alt="Product Structure" /></td>
<td>95%</td>
<td>87%</td>
</tr>
</tbody>
</table>

**Effect of the water loading:**

- **“excessive amount of water”**
  
  H₂O (5.0 equiv)  
  Cu(OTf)₂ (10 mol%)  
  DME, r.t.

- **“appropriate amount of water”**
  
  Cu(ClO₄)₂·6H₂O·L (15 mol%)  
  DME, r.t.

- **“water free”**
  
  Cu(OTf)₂ (10 mol%)  
  DME, r.t.

- **“removal of water”**
  
  4 Å MS  
  Cud(OTf)₂ (10 mol%)  
  DME, r.t.

**Key words**

- ring opening
- cyclopropanes
- copper
- asymmetric catalysis