Copper-Catalyzed Asymmetric Ring Opening of D–A Cyclopropanes

Selected examples:

\[
\begin{align*}
\text{MeO} & \quad \text{MeO} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} \\
\text{Ph} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

95% yield 93% ee
95% yield 91% yield 87% ee
95% yield 70% yield 95% ee
95% yield 87% ee
95% yield 93% ee
70% yield 95% ee
91% yield 82% ee
96% yield 87% ee

Effect of the water loading:

"excessive amount of water"

\[
\begin{align*}
\text{H}_2\text{O} & \quad \text{Cu(OTf)}_2 (10 \text{ mol%}) & \quad \text{DME, r.t.} & \quad \text{PMP} & \quad \text{OH} & \quad \text{CO}_2(2-\text{Ad}) & \quad \text{CO}_2(2-\text{Ad}) \\
\end{align*}
\]

23% yield, 92% ee
91% yield, 66% 18O%

"appropriate amount of water"

\[
\begin{align*}
\text{CuClO}_4 \cdot 6\text{H}_2\text{O} (15 \text{ mol%}) & \quad \text{DME, r.t.} & \quad \text{PMP} & \quad \text{OH} & \quad \text{CO}_2(2-\text{Ad}) & \quad \text{CO}_2(2-\text{Ad}) \\
\end{align*}
\]

50% yield
34% yield, 90% ee
90% yield, 87% ee

"water free"

\[
\begin{align*}
\text{Cu(OTf)}_2 (10 \text{ mol%}) & \quad \text{DME, r.t.} & \quad \text{PMP} & \quad \text{OH} & \quad \text{CO}_2(2-\text{Ad}) & \quad \text{CO}_2(2-\text{Ad}) \\
\end{align*}
\]

34% yield, 90% ee
91% yield, 66% 18O%

"removal of water"

\[
\begin{align*}
\text{Cu(OTf)}_2 (10 \text{ mol%}) & \quad \text{DME, r.t.} & \quad \text{PMP} & \quad \text{OH} & \quad \text{CO}_2(2-\text{Ad}) & \quad \text{CO}_2(2-\text{Ad}) \\
\end{align*}
\]

product not observed

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.