Q.-K. KANG, L. WANG, Q.-J. LIU, J.-F. LI, Y. TANG* (SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY AND COLLABORATIVE INNOVATION CENTER OF CHEMICAL SCIENCE AND ENGINEERING, TIANJIN, P. R. OF CHINA)

Asymmetric H$_2$O-Nucleophilic Ring Opening of D–A Cyclopropanes: Catalyst Serves as a Source of Water


**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 $\gamma$-substituted $\gamma$-hydroxybutyric acid derivatives.

**Selected examples:**

![Chemical structures and yields](image)

Effect of the water loading:

- Excessive amount of water
  - H$_2$O (5.0 equiv), Cu(OTf)$_2$ (10 mol%) in DME, r.t.
  - 23% yield, 92% ee

- Appropriate amount of water
  - Cu(ClO$_4$)$_2$·6H$_2$O (15 mol%), Cu(OTf)$_2$ (10 mol%) in DME, r.t.
  - 91% yield, 66 $^{18}$O%

- Water free
  - Cu(OTf)$_2$ (10 mol%), Cu(OTf)$_2$ (10 mol%) in DME, r.t.
  - 34% yield, 90% ee

- Removal of water
  - 4 Å MS, Cu(OTf)$_2$ (10 mol%), Cu(OTf)$_2$ (10 mol%) in DME, r.t.
  - Product not observed

**Key words**

- ring opening
- cyclopropanes
- copper
- asymmetric catalysis