Intramolecular Asymmetric Desymmetrization via Copper Catalysis

**Significance:** Hydroxy- and amino-functionalized C3-fragments play a pivotal role as synthetic intermediates. Whereas enantioselective desymmetrization of diols and glycerol were developed to provide hydroxyl-containing C3-fragments, the corresponding preparation of amino-containing C3-fragments has been rarely documented. Herein, Gu and co-workers present the asymmetric desymmetrization of 1,3-diazido-2-propanols catalyzed by copper–PhBox.

**Comment:** The title transformation is enabled in an enantioselective fashion by CuPF$_6$(MeCN)$_4$ in the presence of (S,S)-PhBox and NaBARF with the larger and non-coordinating BARF$^-$ anion. The new method provides reliable access to enanti-enriched azido-substituted 5,6-dihydro-1,4-oxazin-2-ones, which can be further converted into useful N-containing scaffolds.

**Selected examples:**

- 96% yield, 89% ee (41 h)
- 98% yield, 90% ee (18 h)
- 97% yield, 93% ee (72 h)
- 99% yield, 91% ee (53 h)
- 89% yield, 90% ee (31 h)
- 99% yield, 58% ee (43 h)
- 99% yield, 89% ee (43 h)
- 99% yield, 87% ee (43 h)
- 98% yield, 91% ee (25 h)

**CuPF$_6$(MeCN)$_4$ (5 mol%), ligand (6 mol%), NaBARF (6 mol%)**

**CHCl$_3$, –5 °C**

NaBARF = sodium tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate