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Catalytic Enantioselective Desymmetrization of 1,3-Diazido-2-propanol via Intramolecular Interception of Alkyl Azides with Diazo(aryl)acetates

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Intramolecular Asymmetric Desymmetrization via Copper Catalysis

Selected examples:

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 $\text{CuPF}_6(\text{MeCN})_4$ in the presence of (S,S)-PhBox and NaBARF with the larger and non-coordinating BARF^- anion. The new method provides reliable access to enantioenriched azido-substituted 5,6-dihydro-1,4-oxazin-2-ones, which can be further converted into useful N-containing scaffolds.

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