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SYNFACTS Highlights in Chemical Synthesis

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P. XIONG, I. IVLEV, S. E. MEGGERS^{*} (PHILIPPS-UNIVERSITÄT MARBURG, GERMANY) Photoelectrochemical Asymmetric Dehydrogenative [2+2] Cycloaddition between C–C Single and Double Bonds via the Activation of Two C(sp³)–H Bonds *Nat. Catal.* **2023**, DOI: 10.1038/s41929-023-01050-y.

Photoelectrocatalyzed Synthesis of Chiral Cyclobutanes



Category

Metals in Synthesis

Key words

rhodium catalysis

photoelectrocatalysis

C–H bond activation



Significance: Meggers and co-workers describe an enantioselective [2+2] photocycloaddition between alkyl ketones and alkenes to synthesize cyclobutanes. The method utilizes electrocatalysis to activate two C(sp³)–H bonds, and, under blue light irradiation, promotes coupling with two C(sp²) carbons. The procedure highlights a sustainable approach to asymmetric small ring synthesis. **Comment:** Alkyl tethered (hetero)aryl ketones and various aryl- and alkyl-substituted alkenes can react in a highly enantioselective fashion. The transformation can be performed on gram-scale. It is proposed that the role of ferrocene serves as a redox mediator to turn over the electrocatalytic system, while a chiral rhodium Lewis acid mediates the dehydrogenation of the ketone (I to VI) and the subsequent cycloaddition (VII to IX).

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