Category

Organo- and Biocatalysis

Key words

photoredox catalysis

hydroetherification

anti-Markovnikov selectivity

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Direct Catalytic Anti-Markovnikov Hydroetherification of Alkenols
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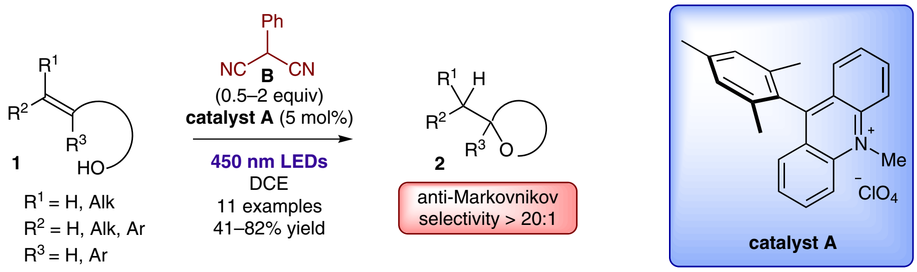
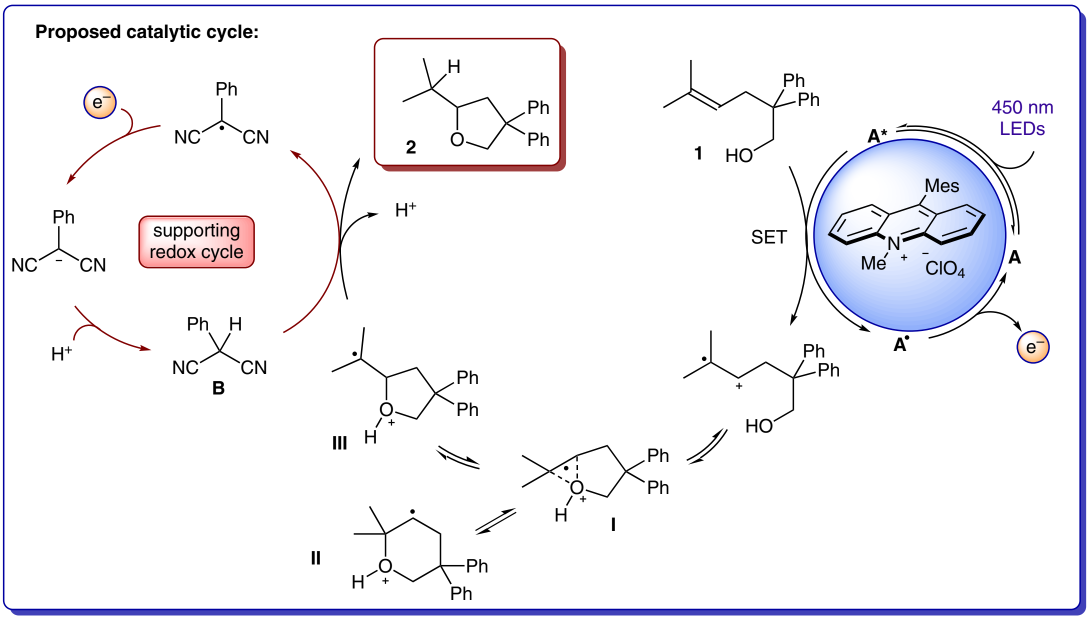
Photocatalytic Anti-Markovnikov Hydroetherification





Significance: A direct photocatalytic anti-Markovnikov hydroetherification has been described by the Nicewicz group. The reported procedure is promoted by the commercially available sensitizer 9-mesityl-10-methylacridinium perchlorate (**A**) and the H-atom donor 2-phenylmalonitrile (**B**). The authors suggest that the methodology is based on two different redox cycles. A primary one, which initiates the reaction by a single-electron transfer (SET) and a supporting one, which simultaneously facilitates the hydrogen exchange and serves as an electron-redox mediator.

Comment: The study of catalytic anti-Markovnikov additions of nucleophiles to olefins has gained great interest in the last decades since it had been described as one of the 'top ten challenges for catalysis' [J. Haggin *Chem. Eng. News* **1993**, *71* (*22*), 23]. In this work, the authors describe the addition of alcohols to alkenes via a newly developed two-component organic photoredox catalytic system. The reaction affords a wide range of cyclic ethers with complete selectivity, which reflects the thermodynamic equilibrium between the three radical intermediates **I**, **II** and **III**.

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