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Anti-Markovnikov Hydrochlorination and Hydronitrooxylation of α-Olefins via Visible-Light Photocatalysis
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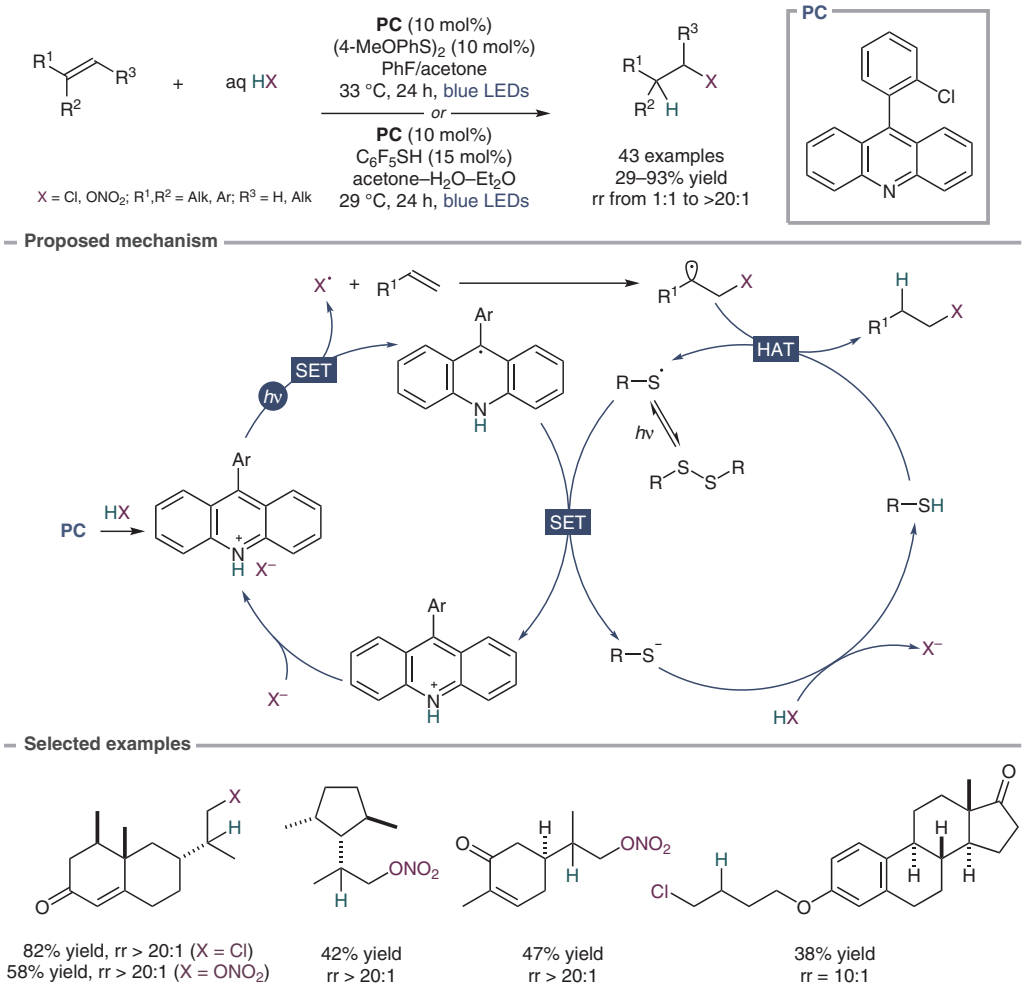
Visible-Light Photocatalysis Enables Anti-Markovnikov Hydrofunctionalization of α-Olefins



Significance: Ritter and co-workers disclose an anti-Markovnikov hydrofunctionalization of terminal olefins with aqueous mineral acids. The transformation is enabled by ion pair formation via proton transfer from the acid to the basic acridine photocatalyst as well as the introduction of a thiol/disulfide HAT catalyst, which circumvents chain propagation. Various substrates, including 1,1-disubstituted alkenes, are tolerated, furnishing the corresponding chlorides and nitrates in moderate to excellent yields.

Comment: Due to the high-energy nature of primary carbocations, addition of acids to α-olefins typically affords branched Markovnikov products, while the opposite regioselectivity has thus far only been achieved via stoichiometric redox processes. The reported photocatalytic method is therefore a breakthrough as it selectively furnishes linear products that can easily undergo further transformations, for example, into primary alcohols.

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