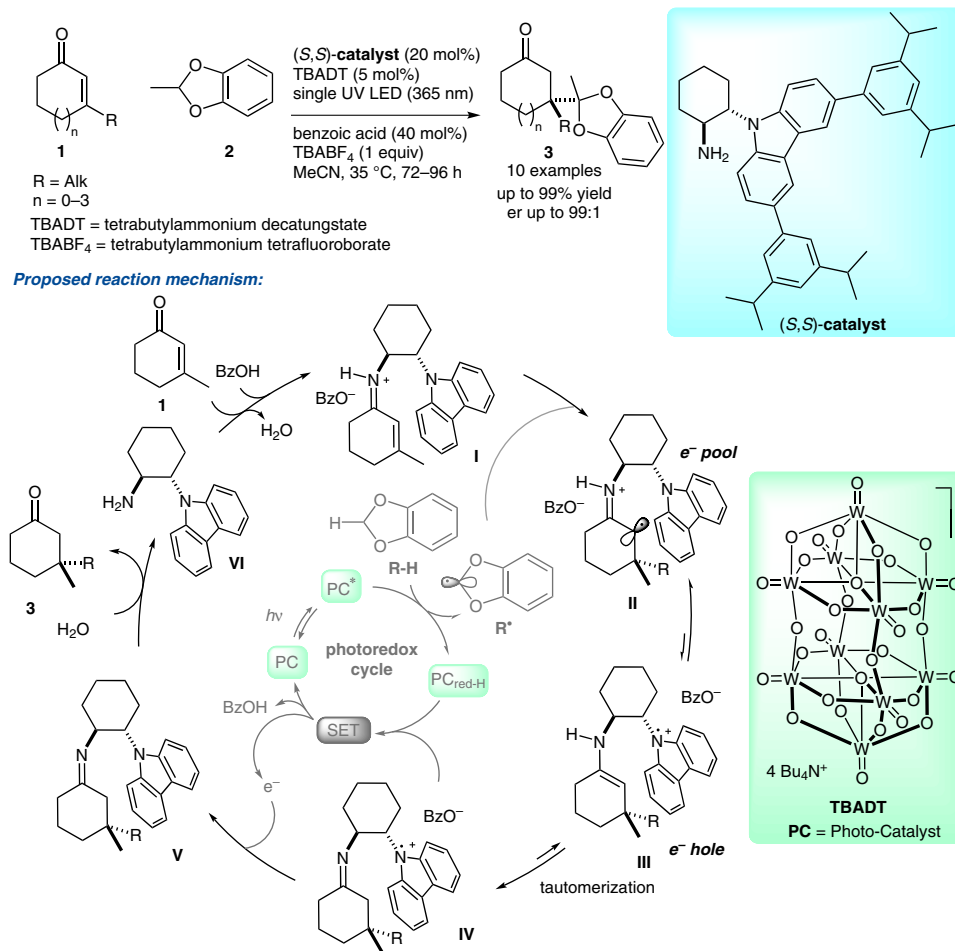


J. J. MURPHY, D. BASTIDA, S. PARIÀ, M. FAGNONI, P. MELCHIORRE* (BARCELONA INSTITUTE OF SCIENCE AND TECHNOLOGY, TARRAGONA AND CATALAN INSTITUTION FOR RESEARCH AND ADVANCED STUDIES, BARCELONA, SPAIN; UNIVERSITY OF PAVIA, ITALY)

Asymmetric Catalytic Formation of Quaternary Carbons by Iminium Ion Trapping of Radicals

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Enantioselective Formation of Quaternary Carbons by Radical Conjugated Addition



Significance: Melchiorre and co-workers report the first example of a radical conjugated addition to β,β -disubstituted cyclic enones by a combination of photoredox and asymmetric organocatalysis to give quaternary stereocenters with high enantioselectivity. This method exploits iminium ion catalysis, previously applied only in polar chemistry, within the field of radical reactivity.

Comment: The chiral organocatalyst has been elegantly designed with a redox-active carbazole moiety that drives the formation of the iminium ion I. This reaction is followed by stereoselective trapping of the photochemically generated, carbon-centered radical R•. The new radical species II leads, through an electron-relay mechanism, to III and, after tautomerization and reduction, the product is formed with high enantioselectivity.

SYNFACTS Contributors: Benjamin List, Francesca Mandrelli
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