Photoredox Organocatalysis: Asymmetric \(\alpha\)-Perfluoroalkylation of Aldehydes

**Significance:** MacMillan and co-workers report an efficient and highly enantioselective \(\alpha\)-perfluoroalkylation of aldehydes employing photoredox organocatalysis. The proposed mechanism involves an organocatalytic and a photoredox catalytic cycle. The organocatalyst reacts with the aldehyde to form an enamine intermediate which reacts with the trifluoromethyl radical, formed in the photoredox catalytic cycle. The resulting \(\alpha\)-amino radical is oxidized by an excited state species of the photocatalyst, generated by irradiation. The reduced photocatalyst is reoxidized by trifluoromethyl iodide to give a new trifluoromethyl radical.

**Comment:** Since fluorine-containing molecules exhibit interesting biological properties, their stereoselective synthesis has gained much interest during the last years. Herein, the authors present a very sophisticated strategy for the asymmetric \(\alpha\)-trifluoromethylation of aldehydes based on their previously introduced concept of merging organocatalysis with photoredox catalysis (*Science* 2008, 322, 77). The products are obtained in high enantioselectivities and can be converted into other useful enantioenriched fluorine-containing compounds as shown nicely by the authors. Further applications of these coupled catalytic cycles can be expected.