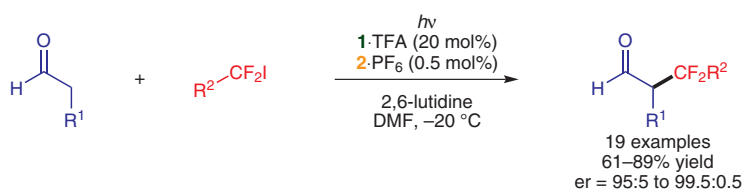
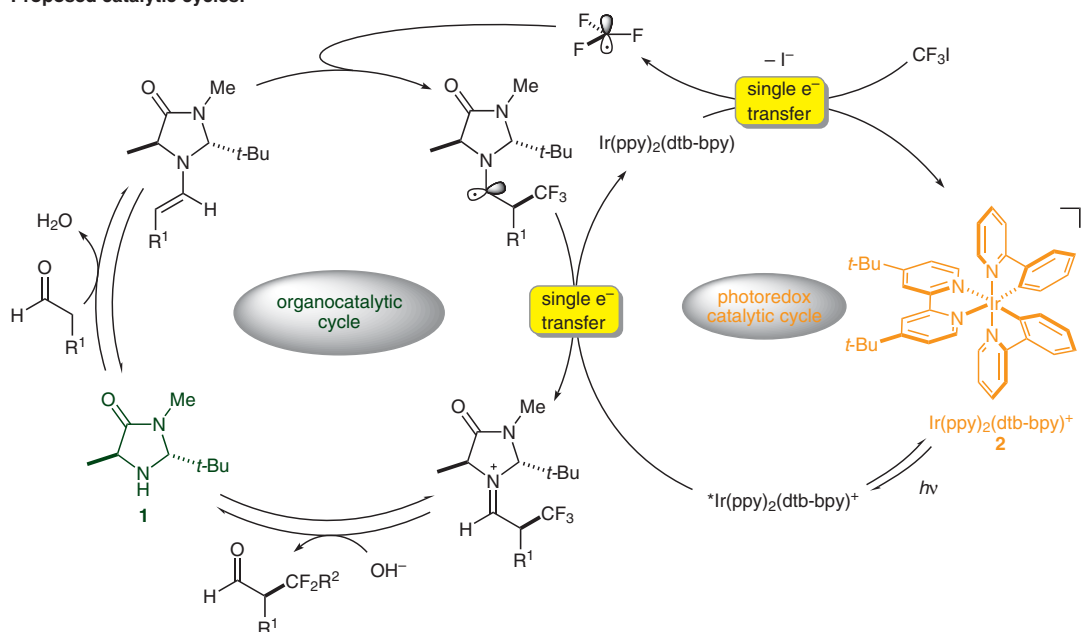


Photoredox Organocatalysis: Asymmetric α -Perfluoroalkylation of Aldehydes



Proposed catalytic cycles:



Significance: MacMillan and co-workers report an efficient and highly enantioselective α -perfluoroalkylation of aldehydes employing photoredox organocatalysis. The proposed mechanism involves an organocatalytic and a photoredox catalytic cycle. The organocatalyst **1** reacts with the aldehyde to form an enamine intermediate which reacts with the trifluoromethyl radical, formed in the photoredox catalytic cycle. The resulting α -amino radical is oxidized by an excited state species of the photocatalyst **2**, generated by irradiation. The reduced photocatalyst is reoxidized by trifluoromethyl iodide to give **2** and 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 α -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.

SYNFACTS Contributors: Benjamin List, Steffen Müller
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