Nonnatural Reactivity of Cofactor-Dependent Enzymes upon Light Irradiation

Selected examples:

Proposed mechanism:

Significance: An asymmetric light-mediated reductive debromination of racemic α -bromolactones is reported by the Hyster group. The combination of a ketoreductase derived from either *Lactobacillus kefir* (LKADH) or *Ralstonia* (RasADH), NADP⁺, and blue LED light furnished the desired lactones in high yields ($\leq 91\%$) and good to excellent enantioselectivities (er $\leq 98:2$).

SYNFACTS Contributors: Benjamin List, Grigory A. Shevchenko
Synfacts 2017, 13(03), 0309 Published online: 15.02.2017

DOI: 10.1055/s-0036-1590002; **Reg-No.:** B00117SF

Comment: A great challenge in biocatalysis is the discovery and development of novel reaction pathways and catalytic functions. The authors demonstrate that a nicotinamide-dependent ketoreductase can change its natural function from carbonyl reduction to that of a radical initiator and chiral source of hydrogen, simply by irradiation of the cofactor with light. This strategy leads to novel and selective radical-mediated reactions.