

Stereoconvergent Reduction of Activated Alkenes by a Nicotinamide-Free Synergistic Photobiocatalytic System

Background/objective

Interest is growing in the development of cooperative chemoenzymatic reactions to take advantage of the reactivity of chemical catalysts and the selectivity of enzymes to cleanly and efficiently produce non-racemic chiral compounds. Here, the researchers designed and tested a new cooperative chemoenzymatic reaction, i.e., a one-pot, light-driven cooperative photobiocatalytic system.

Approach

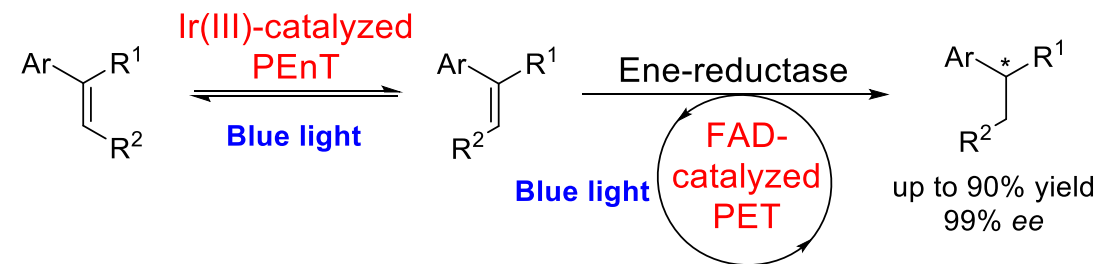
Different photocatalysts, electron donors, and ene-reductases (ERs) were investigated to ensure that: 1) photoinduced electron transfer (PET) can quickly regenerate the co-factor, FMN, of ER; 2) photosensitized energy transfer (PEnT) can quickly isomerize less reactive alkenes to more reactive ones; and 3) appropriate reaction kinetics can be achieved such that the cooperative enzymatic reduction step could be much faster than the background reactions — including FAD-catalyzed alkene reduction.

Results

- ❖ A synergistic photobiocatalytic system consisting of PEnT, PET, and enzymatic reduction was built to convert less reactive alkenes to enantioenriched products without using expensive cofactors (i.e., nicotinamide).
- ❖ The researchers demonstrated the feasibility of efficiently producing value-added chiral molecules using cooperative chemoenzymatic synthesis.

Significance

A nicotinamide-free, synergistic photobiocatalytic system was developed. It holds great potential for synthesis of enantioenriched precursors of pharmaceuticals and bioactive compounds using biomass-derived alkenes.



Combination of a photosensitized energy transfer reaction (PEnT), a photoinduced electron transfer reaction (PET), and an enzymatic reduction of alkenes without using NAD(P)H. The asterisk indicates the chiral center; Ar, aryl.