

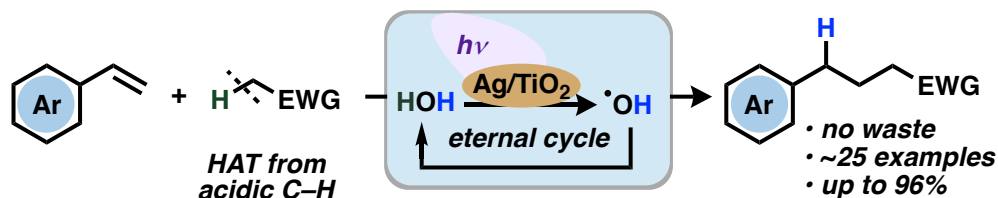
Addition of C(sp³)–H Bonds to Styrenes via Hydrogen Atom Transfer to Aqueous Hydroxyl Radical under Photocatalysis

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Keywords: Semiconductor photocatalyst, photoreaction, water oxidation, hydroxyl radical, hydrogen atom transfer

To date, the development of photocatalytic hydrogen atom transfer (HAT) methodologies has enabled the functionalization of hydridic to neutral C(sp³)–H bonds under mild conditions. In contrast, photocatalytic HAT strategies for relatively acidic C(sp³)–H bonds remain elusive. Recently, the HAT was demonstrated to occur from acidic C(sp³)–H bonds to aryl radicals (Ar•)¹ or *O*-centered carboxyl radicals (RCOO•)² generated under photocatalytic conditions, where these radicals were used as sacrificial agents.

Herein, we report addition reactions of the α-C–H bonds of acetonitrile and acetone to styrenes (olefin insertion to C–H bonds) at ambient temperature.³ The HAT from relatively acidic C(sp³)–H bonds was enabled by aqueous hydroxyl radicals generated eternally via the oxidation of water by silver-nanoparticle-loaded titania (Ag/TiO₂) under photocatalytic conditions without using any stoichiometric oxidation agents. This mild, environmentally friendly, and redox-neutral protocol accommodates the transformation of a wide variety of styrenes into the corresponding longer-chain nitriles and ketones in good to excellent yield with very high atom efficiency.



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