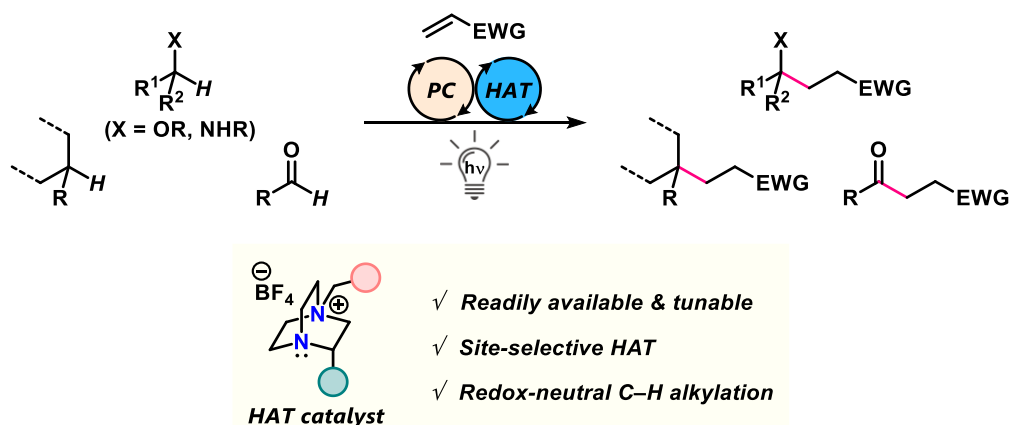


Cationic DABCO-based Catalyst for Site-Selective C–H Alkylation via Photoinduced Hydrogen-Atom Transfer

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Hydrogen-atom transfer (HAT) provides powerful synthetic methods to directly functionalize C–H bonds in atom- and step-economical manners. The recent progress by merging HAT catalysis with photochemistry has enabled diverse functionalizations of various C–H bonds that are difficult by classical methods.¹ Since the reactivity and selectivity of the HAT process are highly dependent on the structure of HAT mediator, the development of HAT catalysts with different structural characteristics is important to expand the potential of HAT chemistry. Here, we have designed a novel class of cationic HAT catalysts based on the readily available and tunable 1,4-diazabicyclo[2.2.2]octane (DABCO) structure. A cooperative use of the HAT catalyst with an organophotoredox catalyst under visible-light irradiation enables efficient C–H alkylation of substrates ranging from unactivated hydrocarbons to complex molecules. Notably, a HAT catalyst with an additional substituent adjacent to nitrogen atom as the catalytic center has improved the site-selectivity. Mechanistic studies suggested that the *N*-substituent of the catalyst plays a crucial role, assisting in the generation of a dicationic aminium radical as an active species for the HAT process.



1) For recent reviews, see: a) Cao, H.; Tang, X.; Tang, H.; Yuan, Y.; Wu, J. *Chem Catalysis* **2021**, *1*, 523–598. b) Capaldo, L.; Ravelli, D.; Fagnoni, M. *Chem. Rev.* doi: 10.1021/acs.chemrev.1c00263.