Unlocking Molecular Design via Dihalogenation of Unsaturated Hydrocarbons

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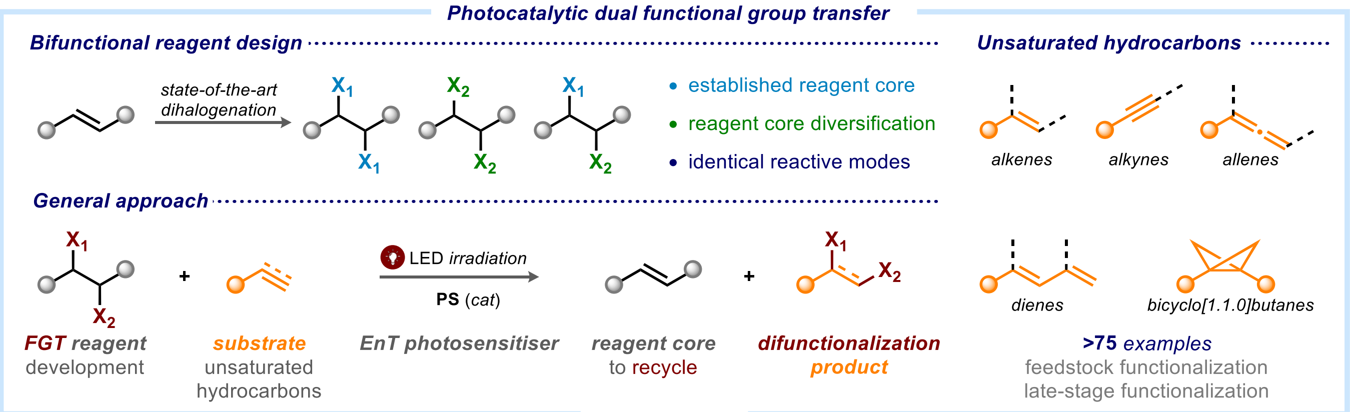
Functional group transfer (FGT) in organic chemistry is a fascinating research field of scientific discovery that provides opportunities for innovation in the area of advanced organic synthesis. These processes enable the creation of a wide range of complex molecules with diverse structures and functionalities in a straightforward and atom-economic fashion, which greatly facilitates the development of new chemical entities and materials. To date, the concept of monofunctional group transfer for installing singular transferrable functionality has been actively investigated by chemists and has already found widespread application in molecular design[1]. In contrast, dual functional group transfer is poorly examined and, as a relatively new concept in scientific exploration, has very promising applicability and significant fundamental advances. Given the strengths of photocatalytic methodologies that possess inexpensive, effective and wasteless protocols for efficient organization of chemical synthesis[2], we wish to report the unique fusion of energy transfer photocatalysis and dual functional group transfer that exhibits unprecedented atomic efficiency and overall low-cost of manipulation for dihalogenation of unsaturated compounds.

Initially, extensive research on reagent design was carried out to find key chemical frameworks suitable for sequential transfer of two halogens to unactivated olefins in a mild and selective manner and further reinstallation of desired functionalities to the reagent core for recycling purposes. Following investigations were conducted on optimization of the conditions for photocatalytic energy transfer, specifically targeting powerful photosensitizer possessing tolerance towards highly derivatized starting materials. Additionally, performed comprehensive mechanistic studies revealed the fundamentals of precisely controlled stepwise dihalogenations. Finally, the broad scope of unsaturated hydrocarbons (alkenes, alkynes, allenes, dienes and bicyclobutanes) was successively employed in the developed protocol of EnT-mediated dihalogen transfer, empowering methodology application and chemical diversification to advance late-stage functionalization in the fields of drug design and fine organic synthesis.



Key outputs

- Bench-stable reagent development
- Up to 50 gram scale synthesis
- EnT photocatalysis
- Mechanistic investigations
- Dual functional group transfer
- Transfer of mixed FGs
- Chemical diversification
- Broad FG tolerance

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[2] L. Candish, K. D. Collins, G. C. Cook, J. J. Douglas, A. Gómez-Suárez, A. Jolit, S. Kees *Chem. Rev.* **2022**, *122*, 2907-2980