N-Nitrosuccinimide: Versatile Organic Reagent for Radical Nitration

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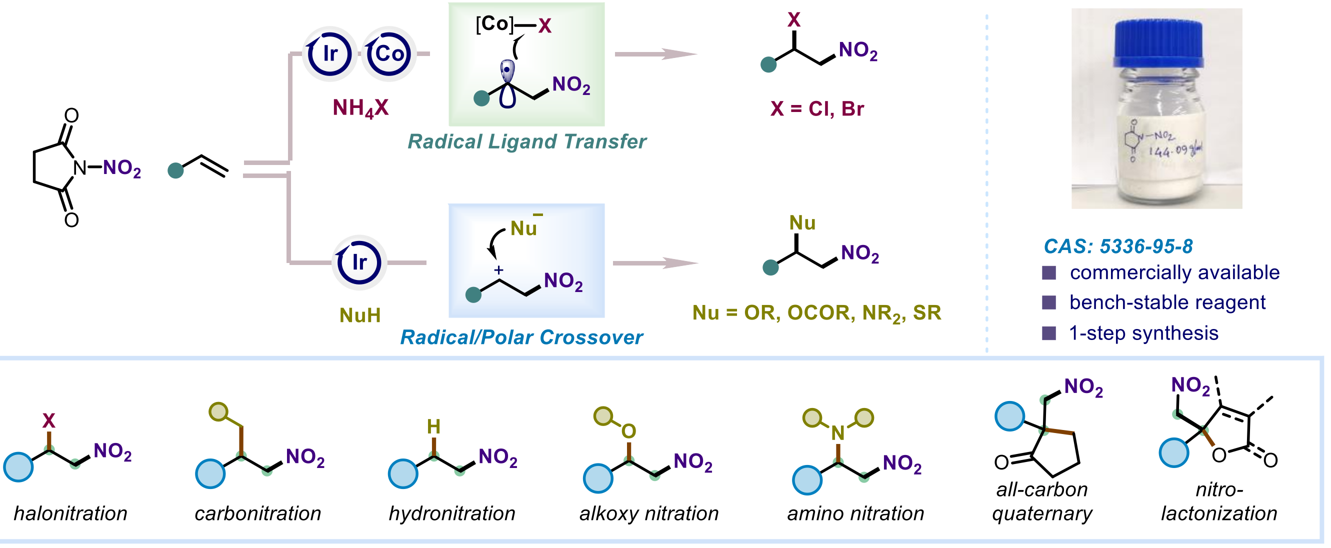
Nitrating reactions hold significant importance in organic synthesis and are foundational topics taught in schools. While the classical electrophilic nitration method using strong mineral acids prevailed for many years since its discovery in the 19th century, recent decades have seen a shift towards exploring new reactivity and reagents. Researchers now seek practical and mild reaction conditions for accessing nitro compounds. Organic nitrating reagents have emerged as key players in this endeavor, offering enhanced reactivity and enabling eco-friendly and sustainable nitration processes.[1]

Herein, we present a novel dual photoredox-mediated paradigm for difunctionalization of alkenes, yielding challenging 1,2-halonitroalkane molecules. We employ N-Nitrosuccinimide as a redox-active nitrating reagent to introduce a controlled amount of nitryl radicals into reaction mixture, while cobalt-mediated radical ligand transfer (RLT) facilitates the transfer of a secondary functionality into the organic scaffold. This synergistic process between photocatalyst and cobalt operates under mild conditions, enabling a one-pot synthesis of 1,2-chloronitro- and 1,2-bromonitroalkanes with excellent chemo- and regioselectivity, demonstrating exceptional functional group tolerance. Detailed mechanistic studies supported the role of cobalt as a radical halogen transfer catalyst. Furthermore, employing a net-neutral radical/polar crossover (RPC) approach under cobalt-free reaction conditions allowed to accommodate a variety of external protic nucleophiles, including thiols, alcohols, acids, and, notably, substituted amines.[2,3] Highly functionalized olefin scaffolds also successfully underwent nitrative difunctionalization, demonstrating the viability of these protocols for the late-stage functionalization of bioactive molecules.



[1] S. Patra, I. Mosiagin, R. Giri, D. Katayev, *Synthesis*, **2022**, *54*, 3432.
[2] R. Giri, S. Patra, D. Katayev, *ChemCatChem*, **2023**, *15*, e202201427.
[3] S. Patra, R. Giri, D. Katayev, *ACS Catal*. **2023**, *13*, 16136.