

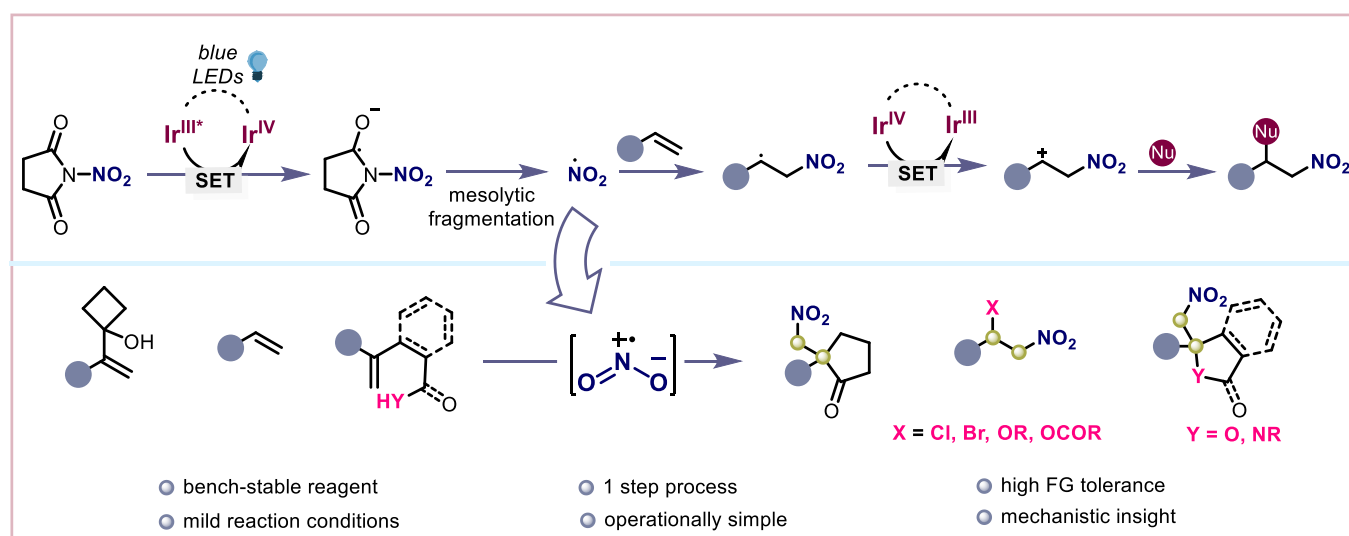
Visible Light-Mediated Regio-Selective De Novo Nitrate Difunctionalization of Alkenes Using Bench-Stable Organic Nitrating Reagent

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Alkenes are readily accessible feedstocks in organic synthesis. Difunctionalization of alkenes is a compelling strategy to construct complex molecules rapidly through chemo- and regioselective installation of two critical functional groups. Despite a significant progress, nitrate difunctionalization is still challenging from both the synthetic and practical perspective.^[1] Methods for direct carbonitration of organic molecules rely on the formation of nitronium (NO_2^+) ion in highly caustic nitric acid mixtures, which limits the scope, especially for the acid-sensitive functional groups.

We herein report a visible light-mediated slow liberation of nitryl radicals ($\bullet\text{NO}_2$) from a bench stable, inexpensive N-nitrosuccinimide reagent allowing highly selective nitrate difunctionalization of unsaturated compounds. This reagent provides access to β -nitro cyclopentanones *via* semipinacol rearrangement, an eco-friendly route to construct all-carbon quaternary stereocenters. Alkenes in the presence of nucleophiles such as alcohols, amines and acids, yield the corresponding 1,2-disubstituted products. In addition, this process makes it possible to synthesize nitro-derived lactams/lactones in good to excellent yields by an intramolecular reaction. Of note, the presence of halogen source in the reaction mixture allows to access structurally important vicinal 1,2-halonitro compounds, which can be further converted into vital small building blocks. Due to the mildness and robustness of this methodology, a large variety of functional groups are well tolerated using standard reaction conditions. Detailed mechanistic studies strongly suggested that a mesolytic N–N bond fragmentation originates liberation of a nitryl radical.^[2] The practicability of this strategy is demonstrated in late-stage functionalization of complex structures and biorelevant molecules.



[1] S. Patra, I. Mosiagin, R. Giri, D. Katayev *Synthesis* **2022**, DOI: 10.1055/s-0040-1719905.

[2] K. Zhang, B. Jelier, A. Passera, G. Jeschke, D. Katayev *Chem. Eur. J.* **2019**, *25*, 12929–12939.