

Visible Light-Mediated and Electrochemically Catalyzed Nitration of Unsaturated Hydrocarbons

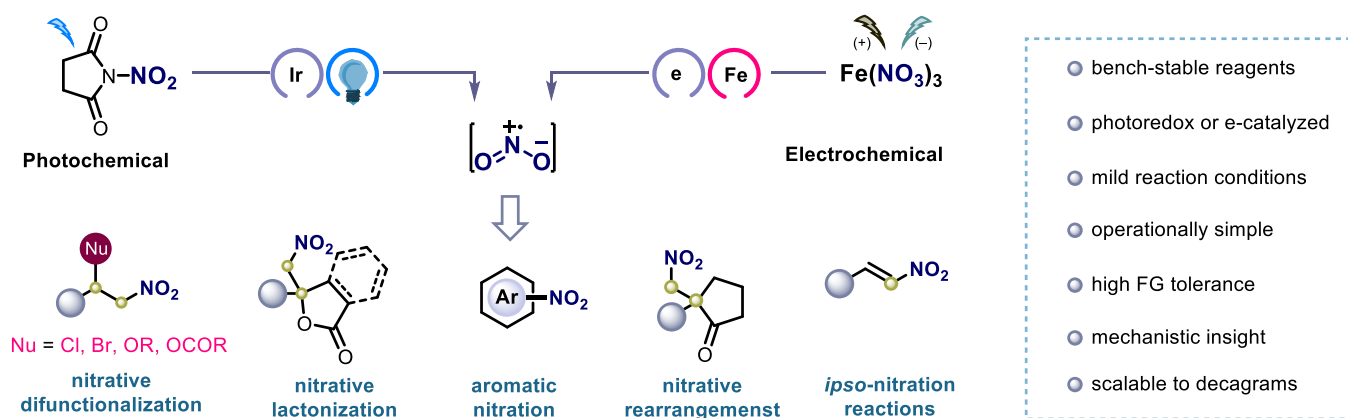
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Nitro group (NO₂) is one of the pivotal functional groups employed in both industry and academia. Despite significant progress, nitrative functionalization reactions are still challenging from both synthetic and practical perspectives.^[1] Methods for direct carbonitration of organic molecules rely on the formation of nitronium (NO₂⁺) ion in highly caustic acid mixture, mostly consisting of nitric and sulfuric acids, which limits the application scope, especially for the molecules bearing acid-sensitive functional groups. Therefore, protocols to make nitration reactions safe, controllable, chemo- and regioselective, and under mild conditions are on high demand.

Herein we introduce photochemically and electrochemically assisted paradigms for the facile interconversion of unsaturated hydrocarbons to the corresponding nitro-derived molecules. First, a visible light-mediated slow liberation of nitryl radicals (•NO₂) was developed from a bench stable, inexpensive, *N*-nitrosuccinimide reagent, allowing to carry out diverse nitrative difunctionalization of alkenes. Detailed mechanistic studies strongly suggested that a mesolytic N–N bond fragmentation resulted in the formation of a nitryl radicals.^[2] Second, we introduced an electrochemically catalyzed process for the generation of •NO₂ from ferric nitrate under mild reaction conditions using a simple setup with inexpensive graphite and stainless steel electrodes.^[3] Powered by electricity and catalyzed by electrons, the synthetic diversity of this concept has been demonstrated through the development of highly efficient nitration of a wide range of organic compounds. Both concepts tolerate multiple nitration protocols, exhibit remarkable substrate generality, scalable to decagrams, and delivers the corresponding adducts with high levels of chemo-, stereo- and regioselectivities, while generating by-products that are less toxic and can be easily separated upon completion of the reaction. We envision that these robust and operationally simple protocols will enhance the accessibility of a diverse range of nitro compounds that are difficult to reach using classical chemical methods.



[1] S. Patra, I. Mosiagin, R. Giri, D. Katayev, *Synthesis*, **2022**, 54, 3432-3472.

[2] (a) K. Zhang, B. Jelier, A. Passera, G. Jeschke, D. Katayev *Chem. Eur. J.* **2019**, 25, 12929–12939. (b) R. Giri, S. Patra, D. Katayev, **2022**, submitted.

[3] S. Patra, I. Mosiagin, R. Giri, T. Nauser, D. Katayev, **2022**, submitted.