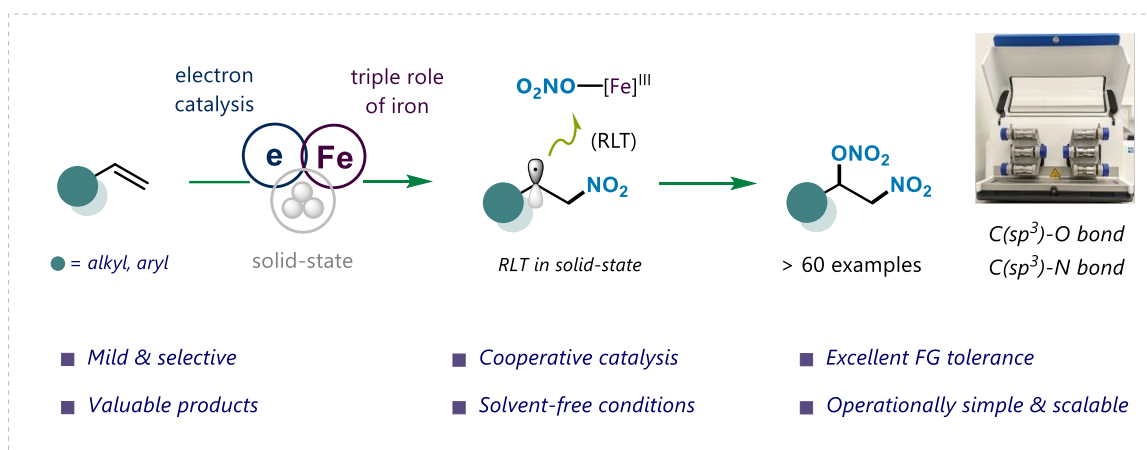


Ball-milling-enabled Alkene Difunctionalization Through Radical Ligand Transfer and Electron Catalysis

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The nitro group (NO_2) plays a pivotal role in organic synthesis and finds extensive application across industry and academia. Despite significant advancements made in the field of nitration chemistry over past decades, nitration reactions of organic frameworks remain challenging from both experimental and practical standpoints.^[1] Conventional methods for the direct functionalization of organic molecules involve the formation of the nitronium (NO_2^+) ion species in a highly corrosive acid mixture. However, this approach imposes various limitations, particularly for compounds containing acid-sensitive functional groups. Hence, there is a growing demand for protocols that ensure safety, as well as high level of chemo- and regioselectivity in nitration reactions, while operating under mild conditions.



Herein, we report a general and modular protocol for olefin difunctionalization through mechanochemistry, facilitated by cooperative radical ligand transfer (RLT) and electron catalysis.^[2] Utilizing mechanochemical force and catalytic amounts of TEMPO, ferric nitrate can leverage nitryl radicals, transfer nitrooxy-functional group via RLT, and mediate an electron catalysis cycle under room temperature. A diverse range of activated and unactivated alkenes exhibited chemo- and regioselective 1,2-nitronitroxylation under solvent-free or solvent-less conditions, showcasing excellent functional group tolerance. It also demonstrated remarkable substrate compatibility, selectivity, and scalability. Mechanistic studies indicated a significant impact of mechanochemistry and highlighted the radical nature of this nitrative difunctionalization process. Additionally, the versatility of this catalytic concept is further highlighted by its ability to selectively introduce various other functional groups.

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

[2] S. Patra, B. N. Nandasana, V. Valsamidou, D. Katayev, *Adv. Sci.* **2024**, accepted.