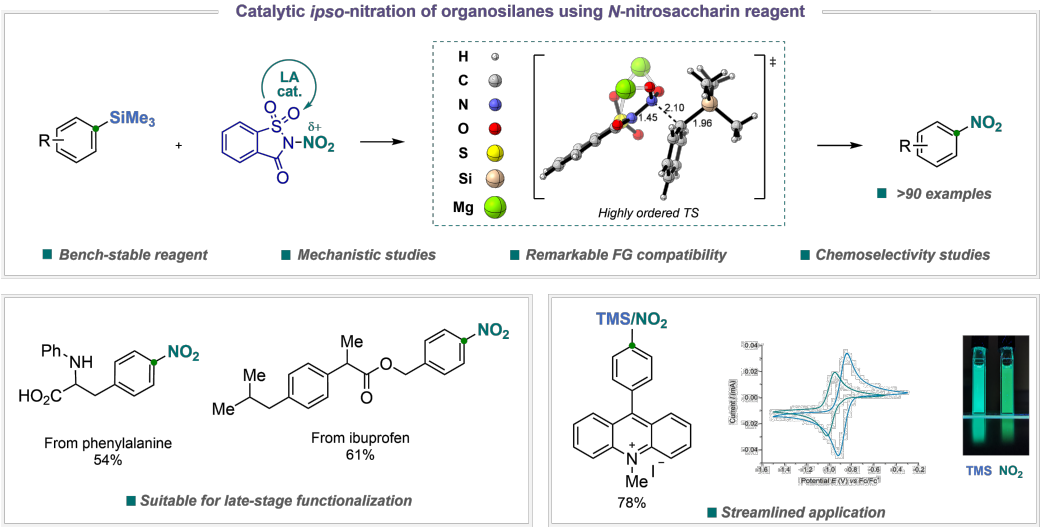
Catalytic *ipso*-Nitration of Organosilanes Enabled by Electrophilic *N*-Nitrosaccharin Reagent

A. J. Fernandes[1], I. Mosiagin[2], A. Budinská[3], L. Hayriyan[3], K. E. Ylijoki[4]*, D. Katayev[2,1]*

[1]Departement für Chemie, Biochemie und Pharmazie, Universität Bern, Freiestrasse 3, 3012 Bern (Switzerland), [2]Department of Chemistry, University of Fribourg, Chemin du Musée 9, 1700 Fribourg (Switzerland), [3]Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 2, CH-8093 Zürich (Switzerland), [4]Department of Chemistry, Saint Mary's University, 923 Robie Street, Halifax, NS B3H 3C3 (Canada)

Nitroaromatic compounds represent one of the essential classes of molecules that are widely used not only as feedstock for the synthesis of intermediates on both laboratory and industrial scales, but also for the preparation of nitro-derived pharmaceuticals, agrochemicals, and materials.[1,2] Therefore, the development of sustainable, chemo- and regiospecific nitration processes that utilize bench-stable, easily accessible and non-acidic reagents and operate under catalytic manifold and eco-friendly conditions remain in high demand. We herein disclose the efficient, mild, and catalytic *ipso*-nitration of organotrimethylsilanes, which is enabled by electrophilic *N*-nitrosaccharin reagent[3,4] and allows for the chemoselective nitration under mild reaction conditions, while exhibiting remarkable substrate generality and functional group compatibility. Conversely, the reaction conditions proved to be orthogonal to other common functionalities, allowing to program molecular complexity *via* successive transformations or late-stage nitration. Detailed mechanistic investigation by experimental and computational approaches strongly supported a classical electrophilic aromatic substitution (S_EAr) mechanism, which was found to proceed through a highly ordered transition state.



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