

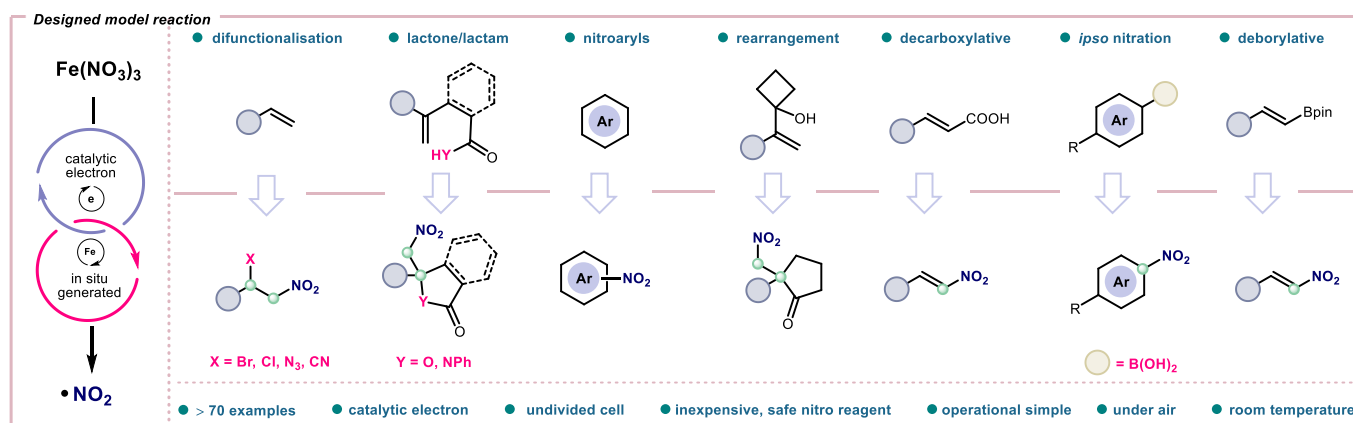
## A PRACTICAL, VERSATILE NITRATION PROTOCOL: ELECTROCATALYTIC ACTIVATION OF FERRIC NITRATE

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Catalysis, a key technology in organic chemistry, is among the most important and fascinating areas of discovery in both academic and industry research. Chemical and enzymatic catalysis has been recognized at least 16 times by the Nobel Foundation. Among manifold catalysts, which are often based on transition metals and complex ligand systems, the proton is the smallest one, while the electron is just a charged particle. The principle of electron catalysis was introduced almost 60 years ago, however this field is still poorly explored, and today only a handful of reactions that have used electrons in a catalytic or sub-stoichiometric amounts are known.<sup>[1]</sup> Electrocatalysis is among such rare transformations, where a large excess of toxic reductants/oxidants is replaced by electrons using a controlled potential, making the overall process mild, robust, and sustainable. Hence, the design of concepts of 'the electron as a catalyst' is challenging, but a very promising field for solving problems with inefficient reactions in modern organic synthesis.

Chemo- and regioselective nitration of carbon-hydrogen bonds is our long-term interest.<sup>[2]</sup> Iron is the most abundant metal on earth and is also known to form intermediates with diverse valences, which makes this metal an ideal catalyst for designing new directions in catalysis. Ferric nitrate, a potential inorganic nitrating reagent, is inexpensive, safe, bench-stable solids, soluble in various organic solvents, and additionally, can serve as both an electrolyte and a catalyst. Herein, we introduce an electrochemically assisted paradigm for the facile interconversion of organic frameworks to the corresponding nitro-derived molecules. The reaction is demonstrated using iron nitrate to functionalize with a nitro group a wide range of unsaturated and aromatic compounds in a simple setup with inexpensive electrodes. These mild reaction conditions tolerate multiple nitration protocols, as well as vast functionalities, is scalable on decagrams, and delivers the corresponding adducts with high level of chemo- and regioselectivity. The waste, mainly consisting of iron oxide and hydroxides, is generated as only by-product and can be easily separated upon completion of the reaction. Detailed mechanistic studies, including spectroscopic investigations and controlled experiments, highlight the evidence of a fleeting nitryl radical under the concept of electron catalysis.<sup>[3]</sup>



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