Electrophilic aromatic nitration remains one of the most extensively studied transformations in organic synthesis, and nitroaromatics and nitroheteroaromatics have become an essential class of compounds which serve as key building blocks and intermediates in the preparation of a variety of industrial products. Nevertheless, there remains a lack of mild and practical methodologies to access these compounds. Electrophilic nitration using a mixture of HNO₃ and H₂SO₄ remains the fundamental process for the production of nitro(hetero)aromatics on both a laboratory and industrial scale, however, the reaction presents a number of critical drawbacks including poor functional group tolerance, the formation of side products and the generation of nitrogen oxides and superstoichiometric amounts of acidic waste [1].

Using N-nitrosaccharin 1 as an organic, bench stable nitrating reagent, we demonstrate a general protocol for the direct nitration of an extensive range of arenes and heteroarenes under mild and neutral conditions, and demonstrating an exceptionally broad functional group tolerance. Our methodology was also applicable to the late stage functionalization of biorelevant molecules, pharmaceuticals, agrochemicals and materials which would be unsuitable substrates for existing nitration methods. The reagent can be synthesized in one step and in excellent yield from saccharin, and the saccharin by-product following nitration can be recovered and recycled [2].

Comprehensive experimental work in combination with computational studies support a polar electrophilic aromatic nitration. The unique and highly ordered transition state found by DFT elucidates how our reagent behaves as a controllable source of the nitronium ion, enabling such a general and functional group tolerant reaction [2]. We anticipate that our practical and mild electrophilic aromatic nitration will find application across a broad range of disciplines at both an academic and industrial level.
