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Electron-Driven Nitration of Unsaturated Hydrocarbons

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Abstract: Herein, we introduce an electrochemically assisted paradigm for the generation of nitryl radicals from ferric nitrate under mild reaction conditions using a simple setup with inexpensive graphite and stainless-steel electrodes. Mechanistic evidence of such a unique reaction mode was supported by detailed spectroscopic and experimental studies. Powered by electricity and driven by electrons, the synthetic diversity of this concept has been demonstrated through the development of highly efficient nitration protocols of various unsaturated hydrocarbons. In addition to a broad application area, these protocols are easy of scaling to decagrams, while exhibiting exceptional substrate generality and functional group compatibility.
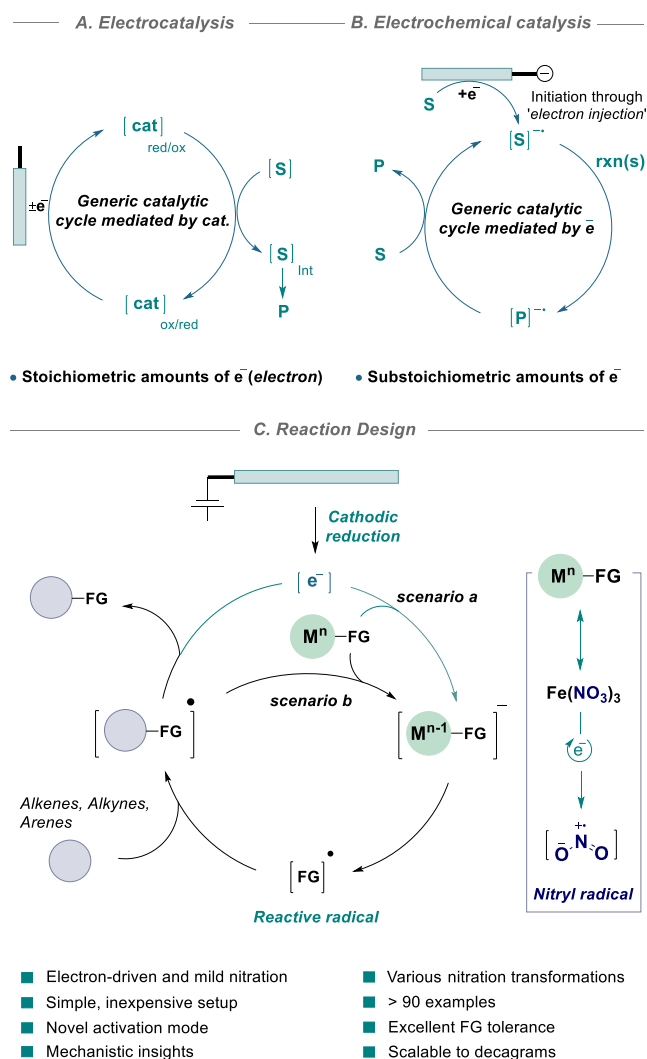
Introduction

Advancements in synthetic organic chemistry, especially in the last 50 years, are undisputedly linked to the progress of catalysis, which has become an indispensable tool with numerous opportunities for discovery, both in academia and across chemical industries.[1] The catalyst not only facilitates and increases the sustainability of countless processes, but it also often provides novel reactivity and allows previously inaccessible transformations to take place in chemo-, regio- or stereoselective manner. The evolution of this field is nicely illustrated by the emergence of biocatalysis,[2] and homogeneous and heterogeneous catalysis,[3] where common key players are enzymes,[4] transition metals,[5] organocatalysts,[6] Lewis acids and bases,[7] and hydrogen-bonding catalysts.[8] At present, catalysis also plays a substantial role in the production of fine chemicals and fuels from renewable feedstock, making a great contribution to the development of 'Green Chemistry'.[9] Therefore, the introduction of a new catalyst paradigm often results in an exponential growth of novel transformations. Among the concepts developed in the last few decades, the use of electrons as a catalyst or initiator has been underexplored. This activation mode, frequently referred to a single electron transfer (SET), allows to forge various redox-neutral transformations that otherwise require harsh reaction conditions and/or additives, and occurs *via* generation of radicals or radical anions as reactive intermediates. Currently, a single electron oxidation/reduction sequence in catalytic cycles is one of the exciting strategies and is widely utilized in photoredox catalysis[5a,10] and electro-organic synthesis.[11] The electron as a catalyst or as initiator is identified as inexpensive, traceless, and green, and its use in substoichiometric amounts often results in achieving excellent selectivity of chemical transformations.[12] In addition to having the highest mass efficiency among other mediators, it does not need to be removed from the mixture after the completion of the reaction.

Electrochemical set up is one of the privileged methods to study electron-driven transformations, since it allows a direct count of electrons provided to the reaction mixture. However, there are several ways to merge electrochemistry with catalysis, which should not be confused with each other. One of them is electrocatalysis, where catalytic manifold occurs either heterogeneously on the surface of electrodes or homogeneously and is mediated by an external catalyst (Scheme 1A).[13] In both cases, a stoichiometric amount of charge is necessary to complete the reaction. This mode should not be attributed to electron catalysis. The use of electric current in substoichiometric amounts to promote redox-neutral reactions is associated with electrochemical catalysis and is a particular case of electron catalysis.[14] From a generic mechanistic point of view, an electron shuttle between an electrode and a neutral starting material takes place, leading to a radical anion intermediate formation, which upon a single or plural transformation, converts into a product. The final backward electron transfer can either occur at the electrode or with the starting material, closing the catalytic cycle (Scheme 1B). This type of catalysis often amplifies thermodynamically favored but kinetically hindered processes. Despite the enormous potential of electron catalysis, real synthetic examples are still scarce in the literature. It is important to highlight several preconditions for electron catalysis, though most of them have been mentioned in several review articles.[13-15] The number of electrons required for a complete conversion should be substoichiometric. The electron which enters as a catalyst should be transferred within the catalytic cycle, while the oxidation state of the intermediates should be changing over the course of the reaction. Finally, the initiation step should not

RESEARCH ARTICLE

A. Electrocatalysis — B. Electrochemical catalysis

Generic catalytic cycle mediated by cat.

Generic catalytic cycle mediated by $\bar{e}$

Initiation through 'electron injection'

- Stoichiometric amounts of $\bar{e}$ (electron)
- Substoichiometric amounts of $\bar{e}$

C. Reaction Design

Cathodic reduction

scenario a

scenario b

Alkenes, Alkynes, Arenes

Reactive radical

Nitryl radical

- Electron-driven and mild nitration
- Simple, inexpensive setup
- Novel activation mode
- Mechanistic insights
- Various nitration transformations
- > 90 examples
- Excellent FG tolerance
- Scalable to decagrams

Scheme 1. A-B) Concepts of electrocatalysis and electrochemical catalysis. C) This work: reaction design towards electrochemically driven nitration using ferric nitrate. Scenario a – mechanistic picture viewing the electron as a catalyst, scenario b – classical representation.

include atom transfer since this is a major evidence for radical-chain reactions.[16] To differentiate real electron catalysis *vs* electron-initiation process in radical transformations is highly challenging as formal mechanism can be overlooked by several scenarios. It can be well seen on examples of classical $S_{RN}1$-type[14,17] and base-promoted homolytic aromatic substitution (BHAS)[18] reactions where these mechanisms can be considered as electron-catalyzed processes.[12] At present, only few known transformations can be ascribed to electron catalysis including but not limited to olefin isomerization,[19] radical Heck-type reactions,[20] cross-dehydrogenative couplings,[21] radical arene trifluoromethylations,[22] alkoxycarbonylations[23] and molecular recognition.[24] Notably, these reactions are specific to selective substrates and often lack practicality, versatility, and scalability. Thus, we aimed to strengthen the concept and develop a comprehensive example of an electron-driven transformation. In order to design such process, several elementary steps that are of decisive importance should be selected thoroughly (Scheme 1C). Electron-mediated reactions can in principle be initiated by various setups, while the electrochemical approach allows for precise, external control of chemoselectivity and the flux of

electrons into the reaction mixture by regulating the applied potential.

Recent studies have demonstrated that earth-abundant metal-based complexes can undergo light-induced homolysis, providing access to various reactive radical species.[25] On the other hand, our research group has a long-term interest in nitration chemistry.[26] The aforementioned considerations led us to choose ferric nitrate as a suitable reagent that can potentially be activated under electrochemically assisted conditions, liberating nitryl radicals through electron transfer mechanism.[27] In addition, iron possesses several stable oxidation states that can interconvert with each other, ensuring the continuous presence of reactive intermediates. As further outlined in Scheme 1C, unsaturated hydrocarbons have been opted as model substrates due to their ensuing reactivity towards electron-deficient radicals. The subsequent downstream SET-induced transformation would lead to the formation of the product and restore an electron, completing the catalytic cycle (scenario a). On the other hand, it can be seen that organic radical intermediate will undergo SET with ferric nitrate, delivering the desired product and re-activating ferric nitrate (scenario b). We suspected, therefore, that this electron-driven manifold would be a highly efficient process to generate nitryl radicals under mild and controllable conditions and could be a valuable entry in organic synthesis for the preparation of a broad range of nitro-derived molecules.

Herein, we disclose a unified and modular protocol to access various nitro group-containing building blocks from unsaturated hydrocarbons that proceed under electrochemically induced reaction conditions and utilizes ferric nitrate as an inexpensive nitrating reagent. Detailed mechanistic studies based on a wide range of spectroscopic and control experiments suggest the vital role of the electron as determinative in the activation of ferric nitrate, delivering nitryl radicals to the reaction mixture at ambient temperature. Consequently, this protocol demonstrated exceptional chemo- and regioselectivity as well as great functional group tolerance and can be applied for a series of nitrative functionalization reactions..

Results and Discussion

To establish the proof of concept, we carried out electrolysis experiments to design direct bromonitration methodology of olefins using 4-(*tert*-butyl)styrene (**1**) as model substrate, oxidatively robust graphite as the anode (working electrode) and stainless-steel as the cathode (counter electrode) in an undivided cell (Tables S1–S8). Our mechanistic hypothesis is outlined in Scheme 2A. As for the nitro source, various metal nitrate and nitrite salts were investigated (Table S2) as their activation to liberate nitryl radicals has been previously reported, although under thermal conditions or in combination with additives.[28] Our efforts in this regard revealed an unprecedented formation of nitryl radicals *via* a single electron activation of ferric nitrate nonahydrate that occurs under mild conditions at room temperature (step **a**). Upon addition of nitryl radical to olefin (step **b**) the corresponding nitroalkyl radical species is formed. The latter intermediate is highly reactive and often leads to the formation of by-products through pathways that are inherent to radical species, such as dimerization, polymerization, and possible interactions with electrode surface.

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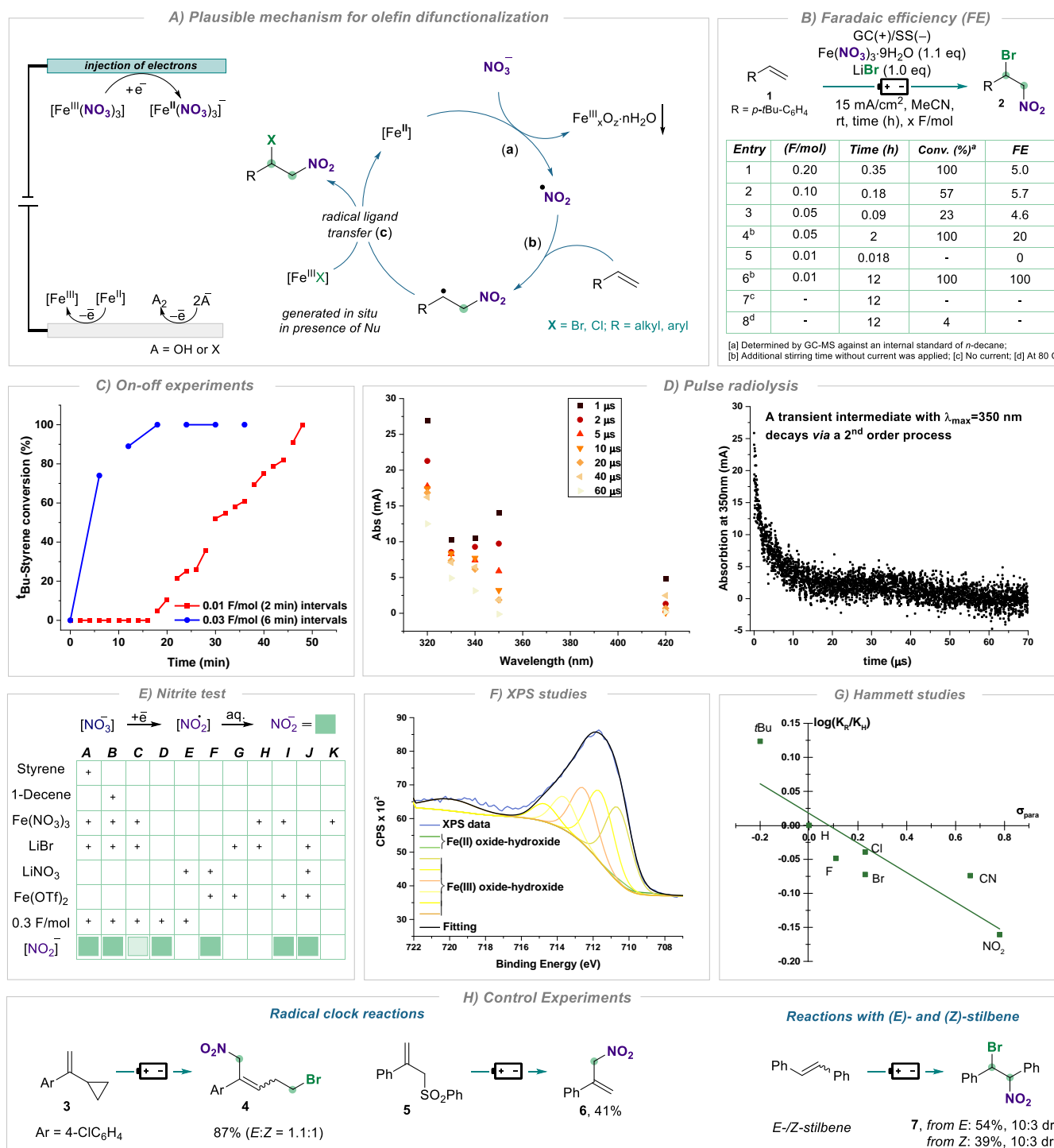
Scheme 2. Mechanistic investigations.

Herein, we assumed that a high level of selectivity in the formation of carbon–halogen bond can be achieved *via* bromo-transfer step with an iron bromide [Fe-Br] intermediate generated *in situ* with the nucleophile.[29] After thorough optimization of bromide sources, LiBr was identified as both an optimal reagent and as a suitable electrolyte (Table S3). Notably, this radical group transfer manifold (step **c**) produces Fe^{II} species that are needed to further maintain the presence of nitryl radicals in the reaction media. The choice of the solvent can be ascribed as a crucial parameter considering the solubility factor of inorganic salts and conductivity.

Optimal results were obtained in acetonitrile, performing the reaction with 1.1 equivalents of Fe(NO$_3$)$_3$×9H$_2$O and 1.0 equivalent of LiBr at room temperature, providing the targeted 1-bromo-2-nitroalkane **2** in 77% yield when 1.1 F of electricity with respect to 4-(*tert*-butyl)styrene (**1**) was applied (Tables S1-S8). Next, we turned our attention to the Faradaic efficiency of this transformation, and preliminary optimizations displayed that applied electricity can significantly be lowered with respect to olefin, while maintaining the bromonitration reaction at high conversion (Scheme 2B, Table S7).

3

RESEARCH ARTICLE

Performing the reaction under established conditions and interrupting electrolysis upon passage of 0.2 F/mol resulted in complete consumption of **1** (Scheme 2B, entry 1), while reducing it further led to a significant drop in the product yield (entries 2-3). Full conversion was found when the reaction was stirred for an additional 2 h after electron injection, suggesting that a longer time is required with fewer electrons. It was also shown that the electrolysis under a constant current of 15 mA for 0.01 F/mol electricity followed by an addition stirring of 12 h results in the complete conversion of **1** (entries 4-6). No product formation or traces were detected when the reaction is carried out without electricity or at elevated temperature (entries 7-8). To support the fact that the electron can be regarded as an efficient driving force, we conducted a series of on-off experiments on bromonitration reaction of **1** and their graphical representation is summarized in Scheme 2C (page S10). We were pleased to find that conversion of the starting material at room temperature gradually increased not only during electrolysis but also when electricity is off. Notably, the turnover number (TON) of the reaction was much greater when on-off time intervals were increased from 2 minutes to 6 minutes, as it can be seen in the comparison of steps with 0.01 F/mol vs 0.03 F/mol (Scheme 2C).

Encouraged by these results, we next examined the reaction mechanism. Our attention was first dragged to the role of electrons in reactivity of ferric nitrate, as the formation of nitryl radicals from it at ambient temperature *via* single electron activation strategy has not been previously investigated. To acquire an initial understanding, we started with pulse radiolysis, which is a powerful method to examine the nature of short living and highly reducing / oxidizing intermediates and radicals.[30] Our first attempts to observe fragmentation products following single electron reduction of iron nitrate were not successful, since Fe^{III} blocks the window of observation needed for UV/Vis absorption spectroscopy of products of one-electron reduced nitrate. To mimic our reaction conditions, various nitrate salts and non-protic solvents were explored. Acetonitrile as a solvent was not ideal for these measurements due to its unsaturated nature, while irradiation of an argon-saturated solution of cesium nitrate in THF (1 mM) with a 29 Gy dose showcased a build-up of a transient species with an absorbance maximum at 350 nm (Scheme 2D, left), which in the sequel decayed by a second-order process (Scheme 2D right; pages S11-S13). These data indicate the likelihood of a single electron reduction of NO_3^- to $NO_3^{\bullet 2-}$, which upon reaction with H^+ affords $\bullet NO_2$.[31] The cyclic voltammetry (CV) studies of the reaction mixture indicated an irreversible reduction of Fe^{III} to Fe^{II} (E_{pc} at 0.74 V vs. SCE) along with the appearance of a new anodic event at 1.59 V vs SCE, which was absent during the measurement of the individual components (pages S13-S15). The latter peak was attributed to the oxidation of an *in situ* generated bromide-bound Fe^{II} species to the corresponding Br–Fe^{III} intermediate, which then enters in ligand transfer step **c** (Scheme S8).[29d-f] To further demonstrate the formation of $\bullet NO_2$ from $Fe(NO_3)_3$ under electrolysis, we performed a series of nitrite test experiments (Scheme 2E; pages S17-S18). As presented on the chart, upon passage of the electricity through the saturated solution of ferric nitrate (test D), detection of nitrite ions NO_2^- indicates the formation of nitryl radicals during the course of reaction. The role of Fe^{II} in the regeneration of $\bullet NO_2$ has

been further elucidated by mixing $Fe(NO_3)_3 \times 9H_2O$ or $LiNO_3$ with Fe^{II} source (tests F and I). Although the results of pulse radiolysis suggest an $NO_3^- / NO_3^{\bullet 2-}$ conversion *via* SET, the possibility of reduction of NO_3^- through direct oxygen atom transfer to Fe^{II} cannot be neglected. The precipitate formed upon completion of the bromonitration reaction, conceivably during step **a** of the mechanism, has been additionally analyzed by X-ray photoelectron spectroscopy (XPS), which revealed the presence of Fe^{II} and Fe^{III} oxide/hydroxide by-products (Scheme 2F; pages S19-S22). The radical nature of the step **b**, addition of $\bullet NO_2$ to olefin, was indicated by Hammett studies showing a slightly negative reaction parameter ($\rho = -0.2$) (Scheme 2G, page S23). In addition, adducts generated in radical clock experiments with olefins **3** and **5** further supported the feasibility of step **b**, while electrochemically initiated bromonitration of (*Z*)- and (*E*)-stilbene yielded the corresponding products **7** with similar d.r. values (Scheme 2H; pages S24-S27). Notably, formation of product **4** further revealed, that bromination reaction of nitro-alkyl radical intermediate *via* ligand transfer (step **c**) is faster compared to either hydrogen radical elimination or radical cyclization.[32] It is worth mentioning, that since electrolysis experiment at 0.77 V constant voltage did not affect the formation of **2**, direct cathodic reduction of styrene **1** (ca. –1.2 V) in the reaction is unlikely under standard conditions. This is also in agreement with our hypothesis that nitryl radical formation is initiated by a single electron reduction of $Fe(NO_3)_3 \times 9H_2O$ ($E_0(Fe^{III}/Fe^{II})$ = 0.74 V vs. SCE). Finally, the radical ligand transfer step **c** closes the catalytic cycle and regenerates the electrochemically injected electron in the form of Fe^{II} intermediate. Nevertheless, stabilization of alkyl radical *via* coordination to iron followed by inner sphere ligand transfer cannot be excluded. Preservation of an active electron in the reaction mixture can presumably be explained by several anodic events occurring outside the main cycle (Scheme 2A). To rule out the potential oxidation of nitroalkyl radical to the corresponding carbocation, we attempted nitrative difunctionalization of **1** with various nucleophiles (AcO^-, F^-, N_3^-), which are less prone to radical ligand transfer event from iron.[33] Indeed, only traces or no product formation were detected (page S27). On the other hand, halonitration reactions of **1** in the presence of radical trapping agents such as CBr_4 and CCl_4 resulted in the products **2** and **17** formation in 11% and 5% yield, respectively (page S26). With these experimental observations, our bromonitration protocol can also be considered as electron-catalyzed since a substoichiometric number of electrons originate the transformation consisting of a series of SET events, and electrons do not exit the cycle in form of product or by-product, meeting the requirements of electron catalysis.[12]

Having examined the nature of the electron-mediated activation of ferric nitrate, we next set out to explore this concept in the context of halonitration of olefines. Although chloronitration reactions of alkenes have already been attempted,[34] however with poor chemo- and regioselectivity along with the formation of various by-products, bromonitration presents a formidable challenge using available methods. The optimized reaction conditions were further evaluated with respect to a wide array of readily available olefin building blocks as well as to the tolerance with common functionalities (Scheme 3).

4

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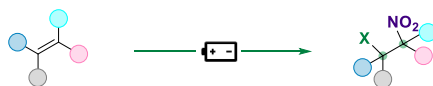
standard conditions (⊕⊖): Fe(NO₃)₃·9H₂O (1.1 eq), LiX (1.0 eq), GC(+)/SS(−), 0.3 F/mol, MeCN, 15 mA/cm², rt, ~30 min, 1.0 mmol.
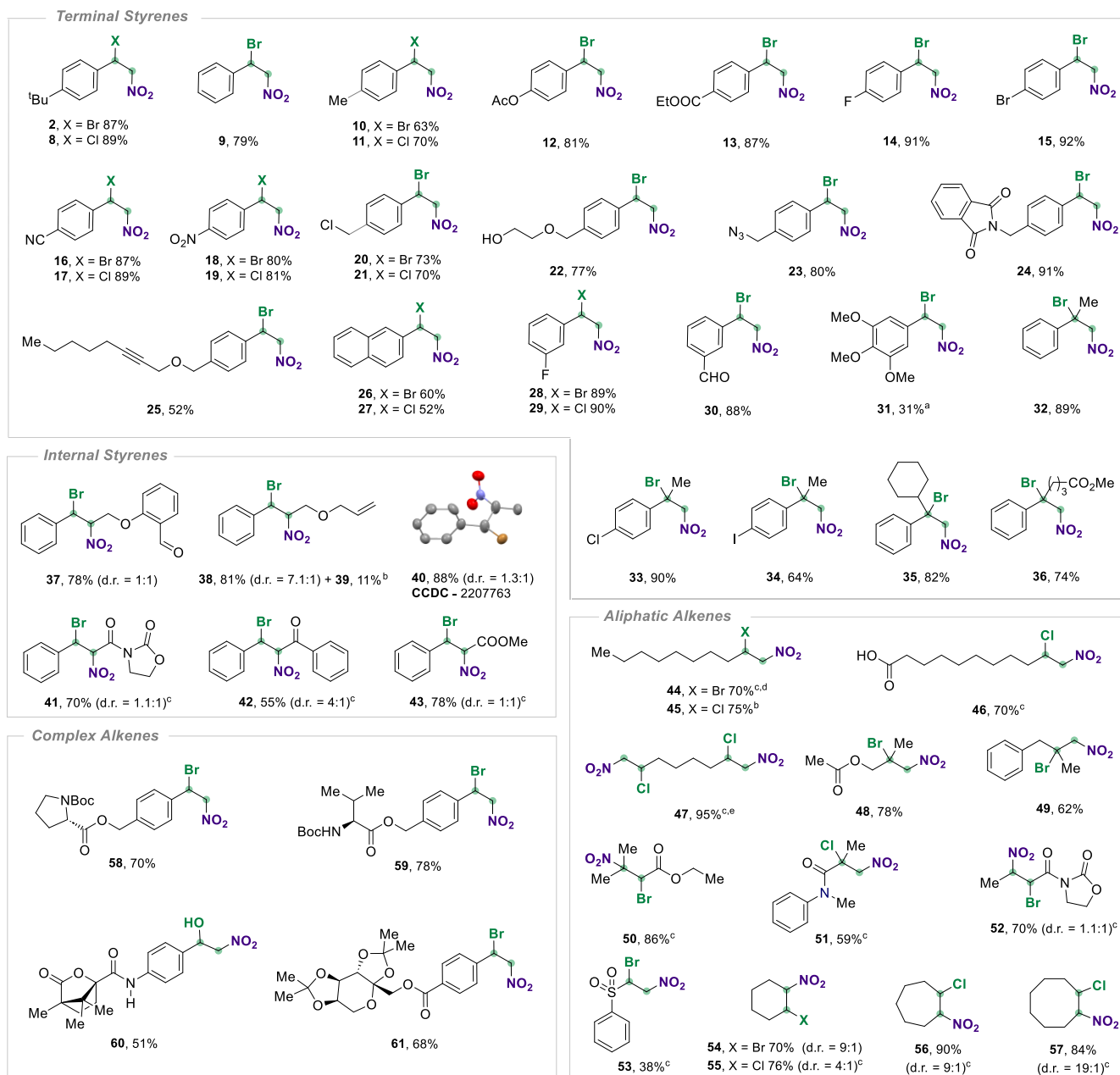
Scheme 3. Scope of halonitration of alkenes. Isolated yields are reported. [a] Unstable compound. [b] Intramolecular radical cyclization adduct **39** (page S26). [c] Additional 12 h stirring without electricity was applied. [d] CBr₄ (1.0 mmol) was used instead of LiBr. [e] 2 equiv of reagents were added.

A broad range of terminal styrene derivatives carrying electron-donating and electron-withdrawing aryl substituents at the *ortho*-, *meta*-, and *para*-positions (**2**, **8-19**, **26-27**, **31**) underwent bromonitration and chloronitration, delivering the corresponding products in good to excellent yields. Of note, halogen atoms, located at different parts of aryl olefins (**12-13**, **20-21**, **28-29**) as well as potentially sensitive functionalities, such as ether (**22**, **25**), azide (**23**), free alcohol (**22**), amide (**24**), aldehyde (**30**), ester (**36**) remained untouched, confirming the exceptional robustness and mildness of this methodology and enabling follow-up derivatization. Linear chain adorned with alkyne group of styrene
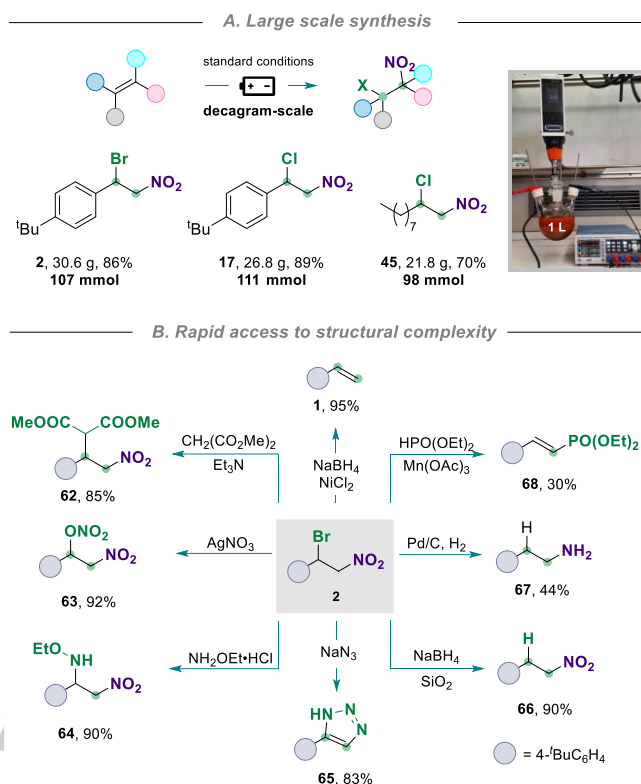
derivative led to exclusive reaction on the olefin fragment, allowing to isolate the corresponding product **25** in good yield. Adducts with α-substituents (**32-36**), reacted decently, regardless of their steric and electronic nature. Various 1,2-disubstitued styrenes bearing a wide variety of acid-sensitive functionalities performed well under electrochemical conditions (**37-39**), while the presence of a carbonyl group at olefin β-center makes the reaction sluggish (**41-43**). Structure of compound **40** was unambiguously demonstrated by single-crystal X-ray crystallography.[35] We next investigated unactivated alkenes, and, despite their chemical inertness, we were pleased to find their

5

RESEARCH ARTICLE

valuable reactivity. Terminal alkenes with long alkyl linear chains or 6-, 7-, and 8-membered cyclic systems all provided the corresponding 1,2-disubstituted products (**45**, **46**, **54-57**). Bromonitration of 1-decene was challenging and led to the formation of **43** with only 15% isolated yield. The product formation could be enhanced to 70% in the presence of 1 equivalent of CBr$_4$. The efficiency of the reaction does not diminish even in the presence of carboxylic acid (**46**). Using 2 equivalents of reagents also allowed to successfully perform the simultaneous substitution of two olefin fragments of 1,7-octadien, delivering the corresponding product (**47**) with high chemical efficiency. Great synthetic flexibility was showcased with aliphatic mono- and disubstituted alkenes holding ester, carbonyl, amide, and sulfonyl functionalities, and formed the corresponding adducts in decent isolated yields (**48-54**). Encouraged by the unusually broad functional group tolerance, we also illustrated the application of this protocol in the late-stage functionalization. Our methodology was equally successful in the formation of 1-bromo-2-nitro substituted adducts for the derivatives of natural amino-acids (**58**, **59**) and D-fructopyranose (**61**), while alkene with L-camphanic acid moiety resulted in the formation of nitrohydrine product **60**. This latter example clearly demonstrates that the electronic nature of the benzyl radical plays an important role in the ligand transfer step and may significantly alter the chemoselectivity of the transformation.[36]

To further demonstrate the operational simplicity and scalability of the protocol, the process was applied to decagram-scale (20 grams of alkene) in batch to three representative examples, and under standard electrolysis the corresponding products **2**, **17**, and **45** were obtained (Scheme 4A). To be noted, when the reaction was carried out under air using commercially available inexpensive electrodes and automated overhead stirrer, no significant drop in product yields was observed, indicating the robustness of the method and the possibility of accessing a wide variety of useful chemicals on a large scale both in the laboratory and in the industry. The resulting crude adduct **2** can be further manipulated in an expedient mode. In a single operation utilizing judicious choices of nucleophiles, it provides added-value building blocks by installing two functional handles (Scheme 4B). The newly formed C-Br bond can sequentially be substituted, resulting in the formation of dimethylmalonate **62** or nitrate **63** derivatives, while in the presence of a reducing reagent it can be transformed to nitroalkane **66**. Compound **2** was also converted to 2-nitro-1-hydroxylamine derivative **64**, which is a masked precursor for accessing of vital 1,2-diamines. The synthetic value of the nitro group was further exposed through a set of derivatization reactions including the preparation of amine (**67**), dialkylphosphite (**68**) and triazole (**65**) derivatives. Applying common reducing agents to compound **2**, the original olefin **1** can be obtained in 95%, demonstrating the synthetic modularity of halo-nitro alkanes.

Nitration processes have tremendous importance on academic and industrial levels and traditionally rely on the use of a so-called ´mixed acid approach´.[26a,37] These conditions are prone to unselective over-nitration, providing minimum chemoselectivity and functional group tolerance. To address this, a number of elegant methodologies and reagents have been developed in the past few decades.[26a,38] However, it is still rare to find nitration concept that is mild and demonstrates consistent performance across different classes of organic molecules. Thus, we were interested in the application of our electron-mediated protocol for

A. Large scale synthesis

standard conditions
decagram-scale

2, 30.6 g, 86%
107 mmol

17, 26.8 g, 89%
111 mmol

45, 21.8 g, 70%
98 mmol

B. Rapid access to structural complexity

1, 95%

62, 85%
CH$_2$(CO$_2$Me)$_2$ / Et$_3$N

NaBH$_4$ / NiCl$_2$

HPO(OEt)$_2$ / Mn(OAc)$_3$
68, 30%

63, 92%
AgNO$_3$

Br NO$_2$
2

Pd/C, H$_2$
67, 44%

64, 90%
NH$_2$OEt•HCl

NaN$_3$

NaBH$_4$ / SiO$_2$
66, 90%

65, 83%

= 4-^{t}BuC$_6$H$_4$

Scheme 4. Scale-up and product derivatization.

a broader range of organic reactions that would result in the formation of nitro-derived molecules. Subjecting several activated and non-activated alkenes to standard electrolysis and performing it in slightly basic media, in less than 6 hours the corresponding nitro-alkenes were formed in both a chemoselective and regioselective fashion and in typically 51-83% isolated yields (**69-80**) (Scheme 5A).[39] Besides various substitution patterns, the reaction outcome was not altered by the presence of heterocycles such as pyridine (**74**) or thiazole (**75**). γ-Butyrolactones are presented in many bioactive molecules,[40] and are important building blocks in organic synthesis.[41] When 4-phenylpent-4-enoic acid or 2-(1-phenylvinyl)benzoic acid were exposed to electrochemical conditions, nitrative lactonization takes place, affording γ-lactones **81** and **82**, respectively (Scheme 5B).[42] Next, we investigated the possibility of introducing nitro group *via ipso*-nitration reactions. Aromatic α,β-unsaturated carboxylic acids were smoothly converted to nitro-alkenes (**69**, **83-85**) in up to 64% yield (Scheme 5C; page S43).[43] Similarly, vinylboronates were likewise compatible (**69**, **72**) (Scheme 5D; page S44).[44] Pleasantly, aromatic nitro compounds **86** and **87** can also be formed in excellent yields *via ipso*-nitration of the respective aryl boronic acids (Scheme 5E, page S44).[26c,44] Owing to the fundamental importance of aromatic nitro compounds, we approached our electron-driven strategy to the direct nitration of arenes. Nitration of anisole resulted in a slight excess of the *para*-regioisomeric product (**86**) with an overall 98% yield, which is in good agreement with results from nitration under mixed acid conditions or using nitronium salts.[28c,45] Without further optimizations, the protocol proved amenable for the nitration of diverse sets of electron-rich arenes, affording the corresponding products (**86-95**) in up to 98% yield and good regioselectivity (Scheme 5F; page S44).[46]

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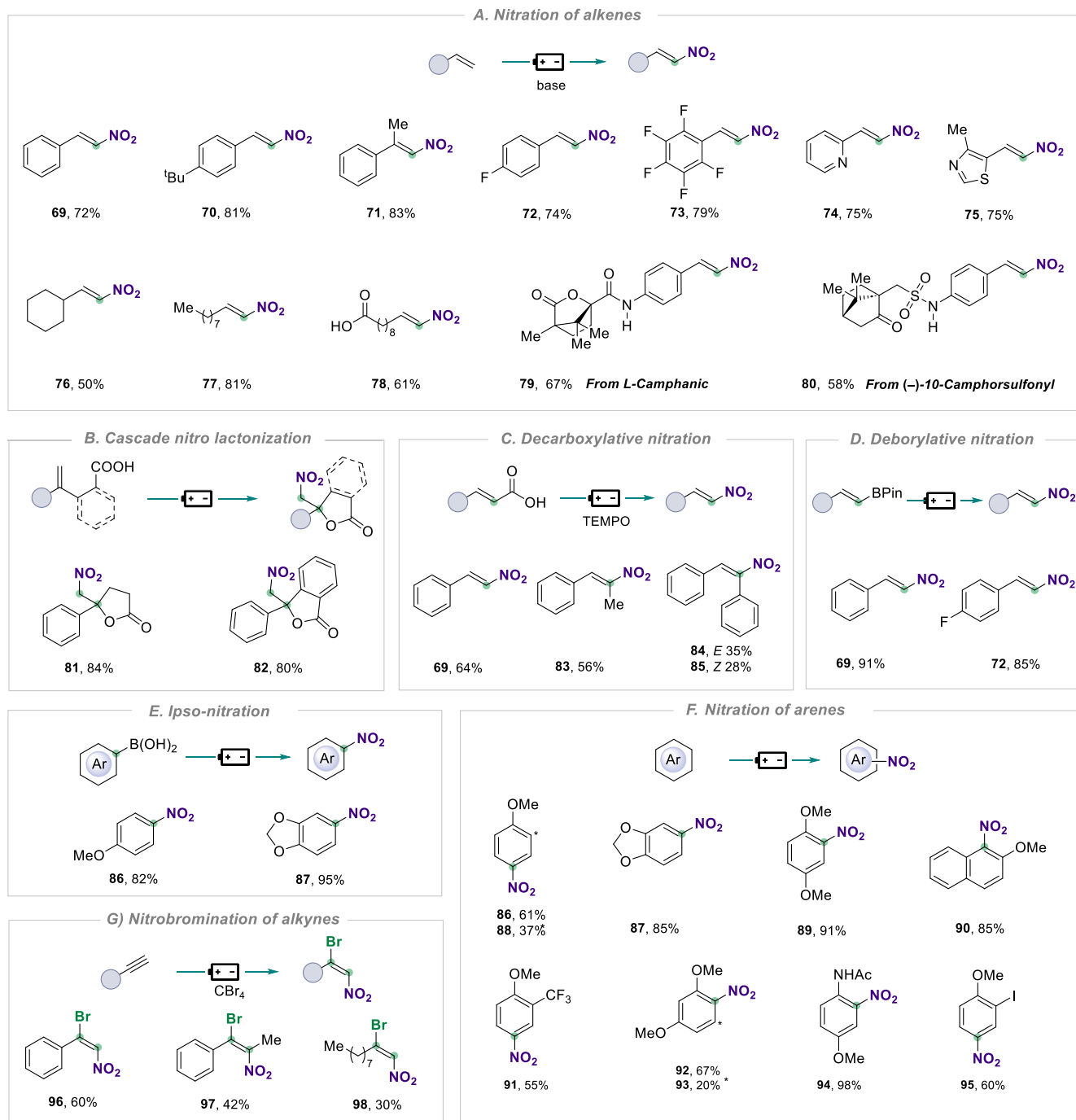
Scheme 5. Miscellaneous applications.

Lastly, aromatic and aliphatic alkynes, mainly phenylacetylene, 2-methylphenylacetylene, and 1-decyne, were engaged in electrochemically catalyzed conditions (**96-98**).[47] Conveniently, 1-bromo-2-nitrovinyl products were obtained with satisfactory results and in exclusive (*E*)-configuration, however, CBr₄ was used as brominating reagent.

Conclusion

In conclusion, we introduced an electrochemically assisted concept to access a broad array of nitro compounds by activating ferric nitrate under mild and room temperature conditions.

Designed process can be applied on an unprecedentedly broad number of functionalization reactions, covering most of the known nitro-group installation reactions involving nitryl radical intermediate. Generality and scalability of this paradigm have been demonstrated *via* the nitration of unsaturated hydrocarbons including alkenes, alkynes, and arenes, with high levels of chemo- and regioselectivity and with exceptional functional group tolerance. The performed experimental and spectroscopic mechanistic studies strongly suggest that an electrochemically injected substoichiometric amount of electrons is the driving force capable to liberate the nitryl radicals from ferric nitrate and to promote nitration. We envision that these robust and operationally

7

RESEARCH ARTICLE

simple protocols will enhance the accessibility of diverse ranges of nitro compounds that are difficult to reach using classical chemical methods.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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9

RESEARCH ARTICLE
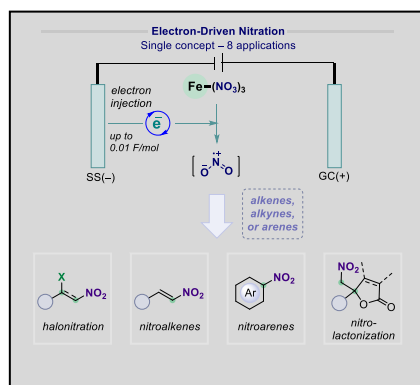
Herein, we present a concept for the generation of nitryl radicals from ferric nitrate that is driven by substoichiometric amounts of electrons, introduced electrochemically. This protocol enables access to a variety of nitro-derived molecules from unsaturated hydrocarbons including alkenes, alkynes, and arenes, in addition to promoting *ipso*-nitration reactions and nitrative cyclizations with high levels of chemo- and regioselectivity.

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