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Direct electrochemical synthesis of arenesulfonyl fluorides from nitroarenes: a dramatic ionic liquid effect†

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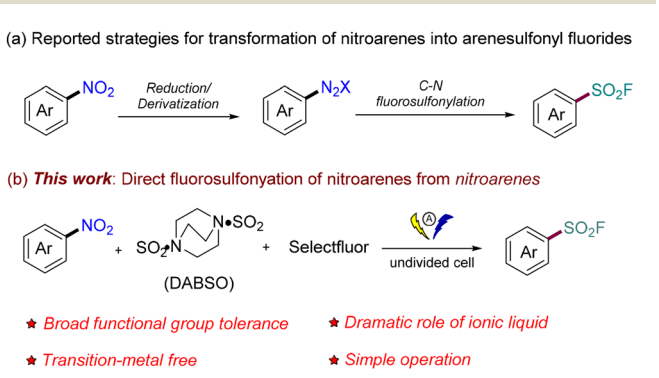
A practical electrochemical strategy for the direct synthesis of arenesulfonyl fluorides from industrial feedstock nitroarenes is described. The key to success lies in using a cheap ionic liquid *N*-methylimidazolium *p*-toluenesulfonate ([Mim]TolSO$_3$) as an effective additive and electrolyte to facilitate the selective reduction of nitroarenes to the corresponding aniline intermediate, promoting the desired fluorosulfonylation with broad functional group tolerance under mild conditions.

Introduction

With the emergence of new applications for fluorinating reagents,[1] ^{18}F radiolabeling agents,[2] and other fluorinated compounds for chemical biology research,[3] interest in the synthesis of sulfonyl fluorides, including arenesulfonyl fluorides, has dramatically increased recently.[4] Aryl sulfonyl fluorides are typically synthesized by chloride–fluoride exchange reactions of the corresponding arenesulfonyl chlorides,[5] oxidative fluorination of sulfur-containing substrates (such as sodium sulfinic,[6] thiols,[7] sulfonyl hydrazides,[8] disulfides,[7b,9] and sulfonates or sulfonic acids[10]) or by converting various prefunctionalized substrates such as aryl (pseudo)halides,[11] aryl boronic acids,[12] aryl diazonium salts,[13] and others.[14] Despite these advances, the development of practical, mild methods for accessing arenesulfonyl fluorides from inexpensive, widely available industrial feedstocks remains highly desirable.

On the other hand, nitroarenes are inexpensive and abundant industrial chemical feedstocks that can be easily accessed by the electrophilic aromatic nitration of arenes.[15] The reported methods for transforming nitroarenes into arenesulfonyl fluorides often require multiple steps, which include the conversion of nitroarenes to the corresponding diazo salts by reduction/derivatization first, and the subsequent transformation with an SO_2 surrogate and fluorinating reagents enables the delivery of arenesulfonyl fluorides (Scheme 1a).[13] Although these reliable multistep methods are widely used in organic synthesis, they have some drawbacks, including the need for tedious separation procedures and the generation of a lot of chemical waste.[13] Therefore, a strategy for the direct denitrative fluorosulfonylation of nitroarenes to afford arenesulfonyl fluorides would be highly desirable in terms of step economy, environmental friendliness, cost, and speed. However, to the best of our knowledge, the use of nitroarenes for the direct synthesis of arenesulfonyl fluorides remains unexplored.

Electrochemistry, which has the advantages of being green and sustainable, has received considerable attention from researchers in academia and industry in the last decade.[16] In this scenario, coupled with our previous success in electrosynthesis[17] and the reductive dialkylation of nitroarenes,[18] we envisioned that the use of electrochemistry tools to reduce nitroarenes *in situ* might provide a meaningful strategy to realize the anticipated denitrative fluorosulfonylation by overcoming the previous methods' tedious reduction and prefunctionalization. Nevertheless, it is nontrivial to achieve this



Scheme 1 Synthesis of arenesulfonyl fluorides from nitroarenes.

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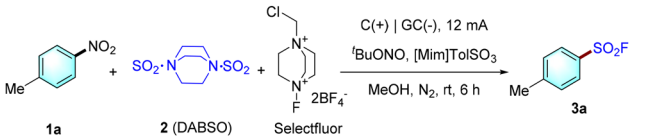
goal, as precedent examples have identified that depending on the specific reduction conditions, the intermediates for the reduction of nitroarenes might be completely different and complicated.[19] For example, the reduction of nitrobenzene could result in nitrosobenzene, *N*-phenyl hydroxylamine, azoxybenzene, azobenzene, 1,2-diphenylhydrazine, or $PhNH_2$.[18,19] To this end, a prerequisite for the desired fluorosulfonylation lies in choosing suitable conditions that enable the selective reduction of nitroarenes to be realized in a controllable way. In addition, such reduction conditions should be compatible with the subsequent fluorosulfonylation process. Herein, by successfully overcoming the aforementioned challenges, we wish to report our preliminary results on the electrochemical denitrative fluorosulfonylation of nitroarenes (Scheme 1b). As detailed below, our strategy enables the preparation of arenesulfonyl fluorides with high efficiency and shows broad functional group tolerance.

Results and discussion

To find the optimal conditions for the desired denitrative fluorosulfonylation of nitroarenes, 4-nitrotoluene (**1a**) was chosen as the model substrate. After extensive screening of various reaction parameters, we were pleased to notice that the desired product **3a** could be facilely isolated with 72% yield using commercially available 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) (DABSO, **2**) as an SO_2 surrogate, Selectfluor as a fluorinating reagent in an undivided cell with a graphite anode and a glassy carbon (GC) cathode (Table 1). As shown in entry 1, the reaction for 6 h at room temperature in an 8 : 1 (v/v) mixture of *N*-methylimidazolium *p*-toluenesulfonate ([Mim]$TolSO_3$) and MeOH containing *tert*-butyl nitrite (^{t}BuONO) as an additive at a constant current of 12 mA gave the best result. During the whole process, the voltage of the cell was 2.6–3.0 V. The essential dual role (as an electrolyte and a key additive for the selective reduction of nitroarenes) of [Mim]$TolSO_3$ will be detailed later. In comparison, replacing MeOH with MeCN, DMF, EtOH, CF_3CH_2OH or $(CF_3)_2CHOH$ led to a lower or trace yield (entries 2–4). The replacement of [Mim]$TolSO_3$ with various alternative ionic liquids or common Brønsted acids (such as TsOH, H_2SO_4, or HCl) also decreased the yield (entries 5 and 6). This indicates that both the cation and anion parts of (Mim)$TolSO_3$ play very important roles for achieving good results. Other electrode combinations—RVC(+)/RVC(−) (RVC = reticulated vitreous carbon), Pt(+)/GC(−), and GC(+)/GC(−)—also gave similar yields (entry 7), as did alternative SO_2 surrogates (entry 8) and fluoride sources (entry 9). In addition, reducing or increasing the current lowered the yield (entry 10). Under an air atmosphere, the yield was only 43% (entry 11). The control experiment showed that ^{t}BuONO played a vital role in this transformation (entry 12), as did the electric current and [Mim]$TolSO_3$ (entry 13); none of the desired product was obtained in their absence.

With the optimal conditions in hand, we carefully evaluated various nitroarene substrates **1** (Table 2). Nitroarenes with

Table 1 Reaction optimization[a]



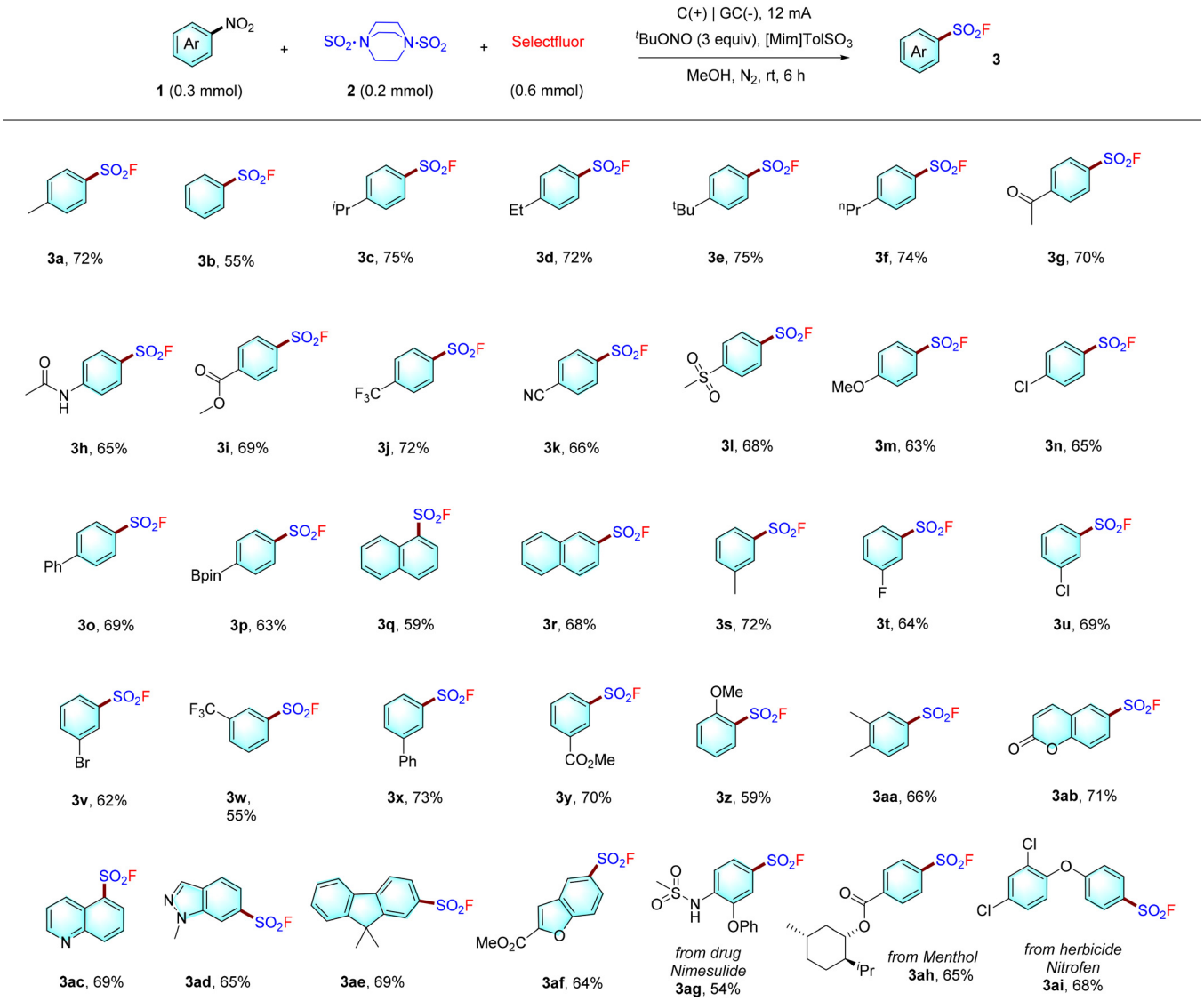
Entry	Variation from standard conditions	Yield of **3a**[b] (%)
1	None	72
2	CH_3CN instead of MeOH	32
3	DMF instead of MeOH	42
4	EtOH, CF_3CH_2OH, $(CF_3)_2CHOH$ instead of MeOH	65/trace/trace
5	[Bmim]Br, [Bmim]PF_6, [Bmim]OAc, [Mim]Cl, [Mim]OAc, or [Mim]HSO_4 instead of [Mim]$TolSO_3$	Trace/8/13/0/0/13
6	H_2SO_4, HCl, TsOH instead of [Mim]$TolSO_3$	0/0/0
7	RVC(+)/RVC(−), Pt(+)/GC(−), or GC(+)/GC(−) instead of C(+)/GC(−)	64/66/70
8	$K_2S_2O_5$, CF_3SO_2Na, or $Na_2S_2O_5$ instead of DABSO	8/0/43
9	$Et_3N{\cdot}3HF$, NFSI, KHF_2 or KBF_4 instead of Selectfluor	54/56/40/15
10	10 or 15 mA instead of 12 mA	69/53
11	Air instead of N_2	43
12	No ^{t}BuONO	0
13	No electric current or [Mim]$TolSO_3$	0

[a] Standard conditions: graphite (C, 0.8 × 0.2 cm^2) anode, glassy carbon (GC, 0.8 × 0.2 cm^2) cathode, 12 mA, **1a** (0.30 mmol), **2** (0.20 mmol), Selectfluor (0.60 mmol), ^{t}BuONO (0.90 mmol), [Mim]$TolSO_3$ (0.5 mL), MeOH (4 mL), room temperature (rt), N_2 atmosphere, and 6 h. [b] Isolated yields. NFSI: *N*-fluorobenzenesulfonamide. [Bmim]: 1-butyl-3-methylimidazolium hexafluorophosphate.

alkyl groups (**1a–1f**), electron-withdrawing substituents (**1g–1l**, **1n**), methoxy (**1m**), phenyl (**1o**), or a readily transformable bis(pinacolato)diboron substituent (**1p**) at the *para* position of the phenyl ring were successfully converted to the desired products **3a–3p** in moderate to good yields (63–75%). Two naphthalene-based nitro compounds underwent fluorosulfonylation to give the desired products **3q** and **3r** in moderate yields. In addition, nitro compounds with a *meta* methyl (**3s**), halogen (**3t–3v**), trifluoromethyl (**3w**), phenyl (**3x**), or ester (**3y**) substituent were tolerated. We also evaluated *ortho*-methoxy substrates, which gave **3z** under the standard conditions, albeit with moderate yield (59%). 3,5-Dimethyl substituted substrate was also tolerated (**3aa**). Furthermore, heteroarenesulfonyl fluorides with a coumarin, quinoline, indazole, fluorene or benzofuran core (**3ab–3ad**, **3af**) were also accessed in reasonable yields. Finally, to our delight, sulfonyl fluorides derived from the pharmaceutical nimesulide, the natural product menthol, and the pesticide nitrofen could also be obtained (**3ag–3ai**), highlighting the good functional group tolerance of our strategy. It is noteworthy that denitrative arenes can often by detected in these cases as the major byproduct.

To further demonstrate the green metrics of our method, Table 3 summarizes the green metrics of our method with the known protocols reported by Liu *et al.*[13a,b] and Weng,[13c] and product **3a** has been chosen as a model example. For the four

Table 2 Substrate scope[a]

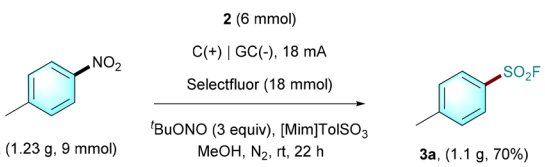


[a] For details, see the ESI.†

Table 3 Calculation of green chemistry metrics

Entry	Work of different groups	*E*-Factor	AE	RME	PMI
1	This work	21.3	20.8%	4.5%	22.4
2	Chen and Liu[13a]	43.3	32.7%	2.3%	44.3
3	Zheng, Hu and Liu[13b]	48.2	15.9%	2.0%	49.2
4	Weng[13c]	45.1	16.3%	2.2%	46.1

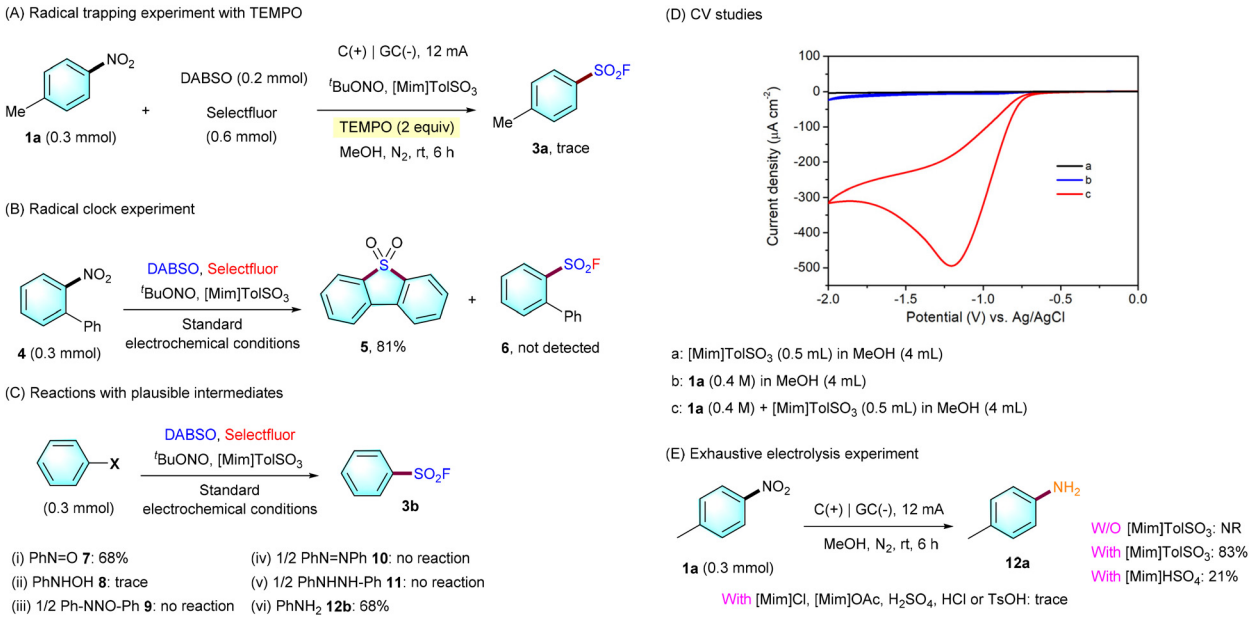
major green chemistry metrics we analysed, that is the *E*-factor, atom economy (AE), reaction mass efficiency (RME), and process mass intensity (PMI), lower values of the *E*-factor and the PMI, as well as higher values of RME, were observed for our protocol (for details, please see Part 5, ESI†). These indicate less waste is formed and a smaller total mass of reagents is required for our protocol along with better atom efficiency.[20]



Scheme 2 Gram-scale reaction.

This novel electrochemical method could be performed on a gram scale. For example, the reaction of 9 mmol of **1a** with DABSO **2** and Selectfluor gave the desired product **3a** in 70% isolated yield under slightly modified conditions (Scheme 2).

To gain insight into the mechanism of this denitrative fluorosulfonylation of nitroarenes, a series of control experiments were conducted (Scheme 3). (1) First of all, the addition



Scheme 3 Mechanistic studies (for details, please see the ESI†).

of 2 equiv. of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to the model reaction only led to a trace amount of **3a** (Scheme 3a). (2) Second, a radical clock experiment involving 2-nitro-1,1-biphenyl **4** only afforded dibenzo[*b*,*d*]thiophene 5,5-dioxide **5** in 81% yield, and sulfonyl fluoride product **6** could not be detected (Scheme 3b). These results suggest that an aryl radical might be generated during this transformation. (3) To identify the key intermediate for the transformation, a variety of plausible intermediates, such as nitrosobenzene **7**, *N*-phenyl hydroxylamine **8**, azoxybenzene **9**, azobenzene **10**, 1,2-diphenylhydrazine **11**, or $PhNH_2$ **12**, were tested under the optimal conditions (Scheme 3c). It turns out that only the use of nitrosobenzene **7** or $PhNH_2$ **12b** enables the delivery of a comparable yield of **3b**. In addition, no **3b** could be detected in the absence of electricity using either **7** or **12b** as the substrate. This indicates that either **7** or **12b** might serve as the reactive species for our fluorosulfonylation. (4) To give a deep understanding of the role of $[Mim]TolSO_3$, cyclic voltammetry (CV) studies were conducted.[19c–l] As shown in Scheme 3d, while no signal was observed from 0 to −2.0 V for **1a**, only one irreversible reduction peak at −1.2 V was observed in the presence of $[Mim]TolSO_3$.[19k] This is different from the previous work of Zhang,[19i] who reported that two obvious reduction peaks were observed for the reduction of $PhNO_2$ in the presence of $^nBuNHSO_4$. (5) To further identify the key role of $[Mim]TolSO_3$, an exhaustive electrolysis experiment was performed. As shown in Scheme 3e, it was noticed that the presence of $[Mim]TolSO_3$ was crucial for the selective reduction of the nitro group. While the presence of $[Mim]TolSO_3$ enabled us to isolate intermediate **12a** with 83% yield, no **12a** was detected when the reaction was carried out without $[Mim]TolSO_3$. Furthermore, while the use of $[Mim]HSO_4$ could deliver **12a** with 21% yield, the presence of other acids such as [Mim]Cl, [Mim]OAc, H_2SO_4, HCl or TsOH instead of $[Mim]TolSO_3$ only led to trace **12a**. These results not only demonstrate that such an ionic liquid is essential for promoting the selective reduction of nitroarenes to the corresponding aniline intermediate, but also indicate that aniline might serve as the key intermediate for the transformation.

On the basis of the above-described results and previous reports,[11–15,19] two plausible mechanisms have been proposed (Fig. 1). Initially, under the assistance of $[Mim]TolSO_3$, nitroarenes **1** could accept six electrons at the cathode, along with protons, to form aniline **B** *via* ArNO intermediate **A**. The aniline **B** could react with ^{t}BuONO to afford aryl diazo salt **C**,

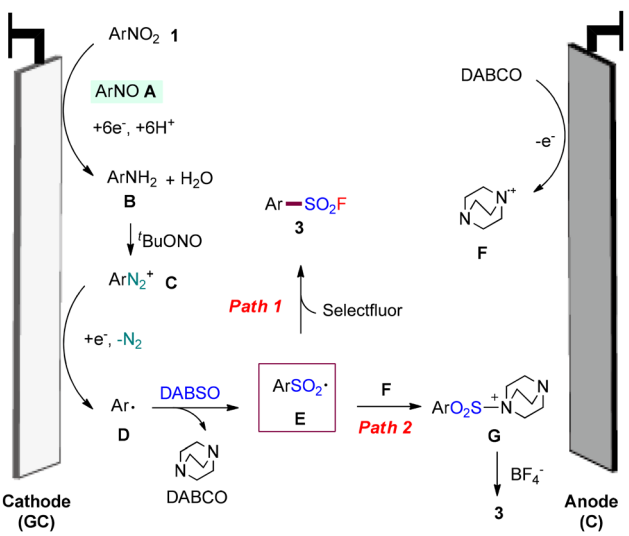


Fig. 1 Two plausible mechanisms.

which undergoes single-electron reduction on the cathode, to form aromatic radical **D** with the elimination of N_2.[19i] The aryl radical **D** could be rapidly captured by SO_2 to form the corresponding aryl sulfonyl intermediate **E**. After this, intermediate **E** could be converted to desired arenesulfonyl fluoride **3** *via* rapid radical fluorination by Selectfluor.[13a,21] Alternatively, intermediate **E** could combine with radical cation **F** (formed *via* the oxidation of DABCO at the cathode), giving rise to the species **G**.[22] The subsequent nucleophilic substitution with BF_4^- (the anion of Selectfluor) gives rise to the observed **3**. This is consistent with the fact that the use of KBF_4 as a fluoro source also enables the production of product **3a**, albeit with low yield (Table 1, entry 8).

Conclusions

In summary, we have developed the first electrochemical fluorosulfonylation of nitroarenes. This practical, efficient method affords arenesulfonyl fluorides in moderate to good yields and shows good functional group tolerance. The method, which utilizes inexpensive electrodes and simple ionic liquid as a mediator to help the selective reduction of nitroarenes and does not require additional oxidants or reducing agents, can be expected to be a valuable addition to the toolkit for the preparation of aromatic hydrocarbon sulfonyl fluorides.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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