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Exogenous-oxidant-free electrochemical oxidative C–H sulfonylation of arenes/heteroarenes with hydrogen evolution†

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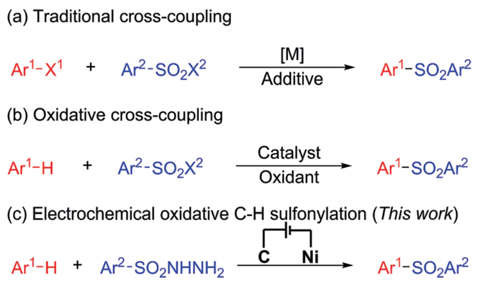
An efficient and environmentally benign electrochemical oxidative radical C–H sulfonylation of arenes/heteroarenes was developed in this work. A series of significant diarylsulfones were prepared under mild catalyst- and exogenous-oxidant-free reaction conditions, which efficiently avoid the issues of desulfonylation or over-reduction of sulfonyl groups.

Arylsulfones are not only versatile intermediates in organic synthesis,[1] but also one of the common structural units in biologically active molecules.[2] Diarylsulfones, in particular, are found in a wide range of pharmaceutically active molecules, which exhibit intriguing biological properties.[3] As a consequence, the development of practical and efficient approaches for the preparation of diarylsulfones has gained significant attention among medicinal and synthetic organic chemists. Traditionally, these valuable compounds are synthesized by oxidation of sulfides,[4] Friedel–Crafts sulfonylation of arenes,[5] or transition metal catalysed cross-coupling reactions (Scheme 1a).[6] However, these methods usually suffer from significant drawbacks, such as the use of strong oxidants or prefunctionalized coupling partners (aryl halides, aryl triflates, aryl boronic or diaryliodonium salts), harsh acidic treatments, high reaction temperatures and low selectivity, which make them environmentally unfavorable and result in poor functional group compatibility. In recent years, oxidative C–H/X–H (X=C, N, O, S, *etc.*) cross-coupling reactions have been developed as an appealing and powerful strategy for the construction of C–X bonds.[7] For example, oxidative cross-coupling reactions between arenes/heteroarenes and sodium sulfinates or sulfonyl hydrazines have been developed to construct diarylsulfones (Scheme 1b).[8] In these reactions, stoichiometric oxidants have to be applied as the sacrificial reagents for taking the surplus electrons, which lead to some wasteful byproducts or oxidation side reactions. Moreover, under these reaction conditions, controlling desulfonylation or over-reduction is also a challenging task because the sulfonyl groups are easily desulfonylated or over-reduced in the presence of certain catalysts.[9,10] Thus, it is highly desirable to develop a more practical and efficient protocol to construct diarylsulfones.



Scheme 1 The pathways to synthesize diarylsulfones.

Electrochemical synthesis has been recognized as an efficient and environmentally benign synthetic strategy and has become a growing research field in chemical syntheses.[11,12] Recently, our group has been interested in the electrochemical oxidative C–C and C–heteroatom bond formation.[13] Herein, we report an efficient and environmentally benign electrochemical oxidative radical C–H sulfonylation between arenes/heteroarenes and sulfonyl hydrazides (Scheme 1c). By employing the constant current instead of an exogenous oxidant, a series of significant diarylsulfones were prepared under mild exogenous oxidant- and catalyst-free reaction conditions, which efficiently avoid the issues of desulfonylation or over-reduction of sulfonyl groups.

Our investigation was commenced with 4-chlorobenzenesulfonyl hydrazide (**1a**) and 3-phenylbenzofuran (**2a**) as starting materials, K_2CO_3 as base, $^nBu_4NBF_4$ as electrolyte and CH_3CN/H_2O as co-solvent. As shown in Table 1, by employing a two-electrode system with a graphite rod as an anode and a nickel plate as a

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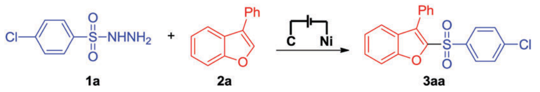
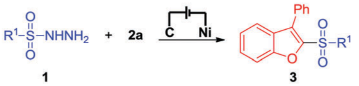
Table 1 Optimization of the exogenous-oxidant-free electrochemical oxidative C–H sulfonylation[a]

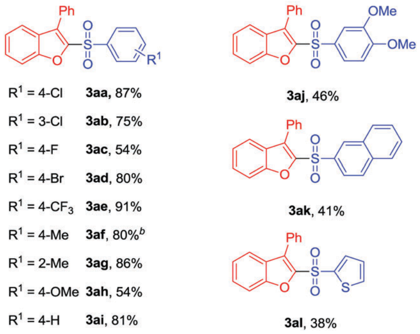


Entry	Variation(s) from the standard conditions	Yield[b] (%)
1	None	87
2	6 mA, 6 h	74
3	18 mA, 2 h	45
4	C(+)|Pt(−)	88
5	C(+)|Fe(−)	58
6	C(+)|C(−)	Trace
7	^{n}Bu$_4$NPF$_6$	57
8	^{n}Bu$_4$NClO$_4$	75
9	Na_2CO_3	77
10	$NaHCO_3$	85
11	1.2 equiv. of K_2CO_3	77
12	2.0 equiv. of K_2CO_3	82
13	CH_3CN/H_2O = 9/1	46
14	CH_3OH/H_2O	40
15	No electrical current	n.d.

[a] Reaction conditions: C anode, Ni cathode, undivided cell, constant current = 12 mA, **1a** (1.5 equiv.), **2a** (0.25 mmol), K_2CO_3 (1.5 equiv.), ^{n}Bu$_4$NBF$_4$ (0.1 mmol), MeCN (9.5 mL), H_2O (0.5 mL), RT, N_2, 3 h. [b] Isolated yields.

Table 2 Substrate scope of the exogenous-oxidant-free electrochemical oxidative C–H sulfonylation with various sulfonyl hydrazides[a]





R^1 = 4-Cl	**3aa**, 87%
R^1 = 3-Cl	**3ab**, 75%
R^1 = 4-F	**3ac**, 54%
R^1 = 4-Br	**3ad**, 80%
R^1 = 4-CF_3	**3ae**, 91%
R^1 = 4-Me	**3af**, 80%[b]
R^1 = 2-Me	**3ag**, 86%
R^1 = 4-OMe	**3ah**, 54%
R^1 = 4-H	**3ai**, 81%

[a] Standard conditions: C anode, Ni cathode, undivided cell, constant current = 12 mA, **1** (1.5 equiv.), **2a** (0.25 mmol), K_2CO_3 (1.5 equiv.), ^{n}Bu$_4$NBF$_4$ (0.1 mmol), MeCN (9.5 mL), H_2O (0.5 mL), RT, N_2, 3 h, isolated yields. [b] $NaHCO_3$ as base.

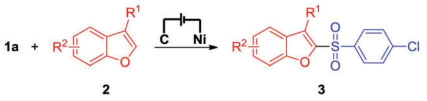
cathode, the desired C–H sulfonylated **3aa** was produced in 87% yield with a 12 mA constant current in an undivided cell (entry 1). Either decreasing or increasing the operating current led to decreased reaction yields (entries 2 and 3). When the platinum plate and iron plate were used as the cathode materials, the desired products **3aa** were isolated in 88% and 58% yields (entries 4 and 5), respectively. A much worse result was obtained while the reaction was performed with a graphite rod cathode (entry 6). As for the choice of electrolyte, ^{n}Bu$_4$NPF$_6$ and ^{n}Bu$_4$NClO$_4$ showed decreased reaction efficiencies (entries 7 and 8). A slight loss of yield was observed when Na_2CO_3 or $NaHCO_3$ was employed instead of K_2CO_3 (entries 9 and 10). By increasing or decreasing the amount of K_2CO_3, a lower yield was obtained (entries 11 and 12). The effect of solvent was explored as well. When 1.0 mL of water was used, the reaction showed decreased efficiency (entry 13). Using methanol instead of acetonitrile also showed decreased reaction efficiency (entry 14). As was expected, no reaction could be observed in the absence of the electrical current (entry 15). Note that this reaction required 1.5 equiv. of sulfonyl hydrazide, probably due to the self-reactions of sulfonyl hydrazide under the current reaction conditions. The by-products thiosulfonate and disulfide could be detected by GC-MS in the reaction mixture.

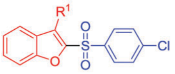
With the best reaction conditions established, the scope of this electrochemical oxidative C–H sulfonylation was explored. Firstly, different sulfonyl hydrazides (**1**) were applied as the C–H sulfonylation partners (Table 2). Benzenesulfonyl hydrazides bearing halide substituents including F, Cl, and Br showed good reaction efficiency, affording the C–H sulfonylation products in 54–87% yields (Table 2, **3aa–3ad**). Similarly, benzenesulfonyl hydrazides bearing strong electron-withdrawing trifluoromethyl groups or weak electron-donating methyl substituents were also suitable, and the desired products were obtained in 86–91% yields (Table 2, **3ae–3ag**). By contrast, strong electron-rich benzenesulfonyl hydrazides exhibited decreased reaction efficiency (Table 2, **3ah** and **3aj**). In addition, benzenesulfonyl hydrazide afforded the desired product in 81% yield (Table 2, **3ai**). Besides aryl-substituted sulfonyl hydrazide, 2-thienyl sulfonyl hydrazide could also furnish the desired product (Table 2, **3al**). However, aliphatic sulfonyl hydrazides were not suitable for this transformation.

Next, the scope with respect to the benzofurans was explored. As shown in Table 3, benzofurans bearing electron-neutral substituents such as methyl or *tert*-butyl at the 3-phenyl moiety showed good reaction efficiency (Table 3, **3ba and 3ca**). However, halide substituents, or electron-withdrawing or electron-donating groups at the 3-phenyl moiety of benzofurans decreased the reaction efficiency (Table 3, **3da–3ga**). Note that the C-3 substituent has a significant effect on the reaction efficiency. When 3-naphthylbenzofurans were used as the reaction partners, desired C–H sulfonylation products were isolated in moderate yields (Table 3, **3ha and 3ia**). Besides 3-arylbenzofurans, 3-alkylbenzofurans such as 3-methylbenzofuran also delivered the corresponding products in good yield (Table 3, **3ja**). However, when there was no substituent in the C-3 position, benzofuran delivered the corresponding product in low yield (Table 3, **3ka**). Notably, 3-phenylbenzofurans bearing electron-neutral or electron-donating groups at the benzofuran ring were also suitable substrates for the reaction, affording the desired products in 39–95% yields (Table 3, **3la**, **3ma**, **3oa**).

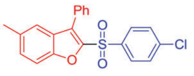
Besides benzofurans, other electron-rich heteroarenes/arenes were also applied as substrates in this electrochemical reaction (Table 4). Electron-rich thiophenes, such as 3-phenylbenzothiophene and 3,4-ethylenedioxythiophene, delivered the C–H sulfonylation products in 54% and 58% yields (Table 4, **5a** and **5b**), respectively. The electron-rich pyrrole and imidazopyridine derivatives were also suitable for this transformation

Table 3 Substrate scope of the exogenous-oxidant-free electrochemical oxidative C–H sulfonylation with various benzofurans[a]

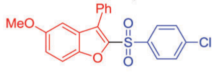




R^1 = 4-MeC$_6$H$_5$	**3ba**, 80%[b]
R^1 = 4-^{t}BuC$_6$H$_5$	**3ca**, 95%
R^1 = 4-ClC$_6$H$_5$	**3da**,39%[c]
R^1 = 3-ClC$_6$H$_5$	**3ea**, 77%
R^1 = 4-CF$_3$C$_6$H$_5$	**3fa**, 52%
R^1 = 4-OMeC$_6$H$_5$	**3ga**, 52%
R^1 = 1-naphthyl	**3ha**, 42%
R^1 = 2-naphthyl	**3ia**, 34%
R^1 = Me	**3ja**, 60%
R^1 = H	**3ka**, 24%

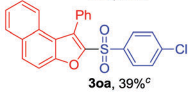


3la, 62%[c]



3ma, 95%

3na, 42%[d]



3oa, 39%[c]

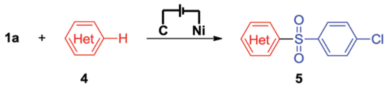
[a] Standard conditions: C anode, Ni cathode, undivided cell, constant current = 12 mA, **1a** (1.5 equiv.), **2** (0.25 mmol), K_2CO_3 (1.5 equiv.), $^nBu_4NBF_4$ (0.1 mmol), MeCN (9.5 mL), H_2O (0.5 mL), RT, N_2, 3 h, isolated yields. [b] $NaHCO_3$ as base. [c] C anode, Pt cathode. [d] **1a** (3.0 equiv.).

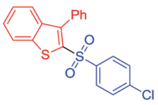
and afforded the corresponding products in 36% and 62% isolated yields (Table 4, **5c** and **5d**), respectively. To further establish the scope of this transformation, electron-rich arenes were also tested under the electrolysis conditions. For example, when the highly electron rich 1,3,5-trimethoxybenzene and 3,5-dimethoxytoluene were used, the corresponding C–H sulfonylation products were produced in 51% and 56% yields (Table 4, **5e** and **5f**), respectively. By contrast, less electron rich pentamethylbenzene showed slightly low reactivity in this transformation (Table 4, **5g**). In addition to electron rich benzenes, naphthalene and its derivatives were also compatible with the reaction conditions, providing the products in moderate yields (Table 4, **5h** and **5i**). Unfortunately, indole derivatives, such as 1-methylindole, are not amendable to this procedure. The main reason for this may because most indole derivatives are well-known electroactive compounds that are readily oxidized than **1a.**

To gain some insights into the mechanism for this electrochemical oxidative C–H sulfonylation reaction, cyclic voltammetry experiments on the reactants were carried out (see the ESI,† Fig. S2). In the absence of K_2CO_3, the first oxidation peaks of **1a** and **2a** were observed at 2.21 and 1.99 V, respectively, whereas under the conditions of adding K_2CO_3, the oxidation peaks of **1a** and **2a** were observed at 1.80 and 1.88 V, respectively. These results indicated that **1a** was likely to be first oxidized under the electrolytic conditions and K_2CO_3 as a base played a crucial role in promoting the oxidation of sulfonyl hydrazine. A radical-trapping experiment was also conducted by employing *N*-methyl-*N*-phenylmethylacrylamide (Scheme 2). When 1.0 equiv. of *N*-methyl-*N*-phenylmethylacrylamide was added in the standard reaction, a trace amount of sulfonyl radical trapping compound was detected; on the other hand, the reaction of **1a** with *N*-methyl-*N*-phenylmethylacrylamide in the absence of **2a** under the standard reaction conditions gave the trapping compound in 29% yield. This result indicates that the reaction presumably proceeds through a sulfonyl radical intermediate and electron rich **2a** is a better sulfonyl radical receptor than *N*-methyl-*N*-phenylmethylacrylamide under the current reaction conditions.

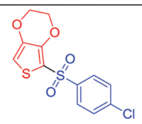
According to the above experimental results, a plausible reaction mechanism is proposed in Scheme 3. Firstly, 4-chlorobenzenesulfonyl hydrazide (**1a**) was converted to the corresponding sulfonyl radical **B** in the presence of base *via* three times single electron transfer (SET) oxidation and deprotonation as well as further release of molecular nitrogen. Addition of the sulfonyl radical **B** to 3-phenylbenzofuran (**2a**) formed the key carbon-centered radical **C**. Subsequently, intermediate **C** underwent further single electron transfer (SET) oxidation and finally resulted in the desired product **3aa** after a deprotonation process. Concomitant cathodic reduction of protons led to hydrogen liberation. Note that for 2-phenylbenzofuran (Table 3, **3na**) and some less electron-rich arenes (Table 4, **5g** and **5h**) the radical addition processes are difficult, so a large excess of sulfonyl

Table 4 Substrate scope of the exogenous-oxidant-free electrochemical oxidative C–H sulfonylation with various (hetero)arenes[a]

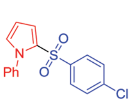




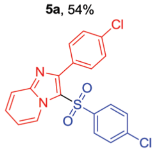
5a, 54%



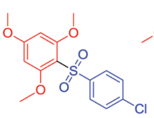
5b, 58%



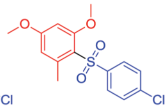
5c, 36%



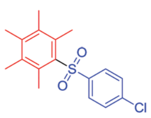
5d, 62%[b]



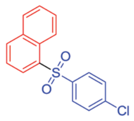
5e, 51%



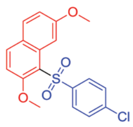
5f, 56%



5g, 40%[c]

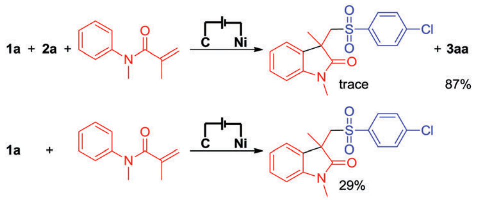


5h, 59%[c]

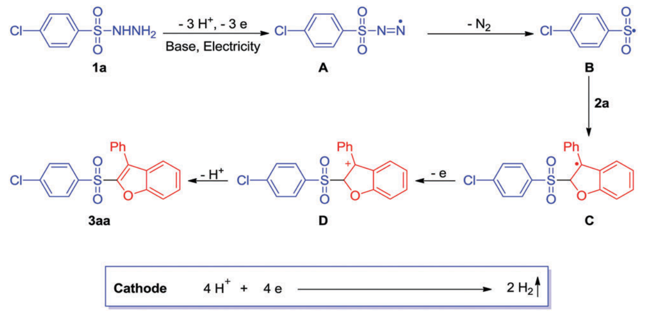


5i, 39%

[a] Standard conditions: C anode, Ni cathode, undivided cell, constant current = 12 mA, **1a** (1.5 equiv.), **4** (0.25 mmol), K_2CO_3 (1.5 equiv.), $^nBu_4NBF_4$ (0.1 mmol), MeCN (9.5 mL), H_2O (0.5 mL), RT, N_2, 3 h, isolated yields. [b] The yield was determined by ^1H NMR spectroscopy with CH_2Br_2 as the internal standard. [c] Reaction conditions: C anode, Ni cathode, constant current = 12 mA, **1a** (0.25 mmol), **4** (5.0 equiv.), K_2CO_3 (1.0 equiv.), $^nBu_4NBF_4$ (0.1 mmol), MeCN (9.5 mL), H_2O (0.5 mL), RT, N_2, 2 h.



Scheme 2 The radical-trapping experiment.



Scheme 3 Proposed mechanism of **1a** and **2a**.

hydrazides or arenes is often required to increase the probability of radical addition.

In summary, we have disclosed an electrochemical oxidative radical C–H sulfonylation of arenes/heteroarenes towards the synthesis of diarylsulfones. A series of C–H sulfonylated products were produced in moderate to high yields. During the reaction, the constant current is utilized instead of an exogenous oxidant, and hydrogen and nitrogen are produced as the only side-products. Moreover, mild catalyst-free electrochemical conditions are employed, which efficiently avoid the issues of desulfonylation or over-reduction of sulfonyl groups.

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Conflicts of interest

There are no conflicts to declare.

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