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无金属条件下亚磺酸钠与酚类化合物形成芳基磺酸酯的电化学合成反应

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摘要 通过电化学氧化方法, 实现了酚与亚磺酸钠类化合物中等到高收率的磺酰化反应, 获得了具有良好官能团耐受性的芳基磺酰酯. 杀螨酯的合成和克级反应的实施, 验证了该绿色方案的实用性. 循环伏安实验表明, 标准条件下亚磺酸盐的氧化先于酚的氧化, 且该过程涉及自由基.

关键词 电化学合成; 芳基磺酸酯; 无金属条件; 绿色方法

Electrochemical Synthesis of Aryl Sulfonates from Sodium Sulfinates and Phenols under Metal-Free Conditions

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Abstract An electrochemical oxidative sulfonylation of phenols with sodium sulfinates has been established to produce arylsulfonyl esters with good functional group tolerance in moderate to high yields. The synthesis of chlorfenson and a gram-scale reaction have been performed to evaluate the practicality of this green protocol. Cyclic voltammetry experiments indicate that the oxidation of sulfinate occurs prior to that of phenol substrate under standard conditions, and free radical is involved in the process.

Keywords electrochemical synthesis; aryl sulfonates; metal-free conditions; green method

1 Introduction

Since sulfonyl esters exhibit remarkable properties in pesticides as well as medicines and serve as versatile intermediates in chemical transformations,[1] they have attracted widespread attention from domestic and foreign researchers.[2] The conventional routes mainly rely on the reactions of sulfonyl chlorides or sulfonamides with alcohols or ketones in the presence of an amine as base.[3] However, many sulfonyl chlorides are highly reactive and difficult to store or handle. Compared with sulfonyl chlorides, aromatic sulfinates are more stable, less corrosive and easier to operate, furthermore, the couplings of aromatic sulfinates under mild conditions have been developed rapidly in recent decade.[4]

Organic electrosynthesis has been recognized as an increasingly viable methodology because redox reagents can be replaced with the electricity in the course of electrolysis.[5] Recently, our group[6] has developed an electrochemical C—H sulfonylation of quinolines by utilizing aromatic sulfinates as sulfonyl source. With these critical features in mind and our interest in the application of electro-chemical methods to organic synthesis,[7] we envision that a green and efficient electrochemical oxidative sulfonylation of phenols with sodium sulfinates is feasible to synthesize aryl benzenesulfonates. During the preparation of this manuscript, the group of Chen[8] has reported the synthesis of sulfonyl esters from phenols and aromatic sulfinates under electrochemical conditions. Compared to

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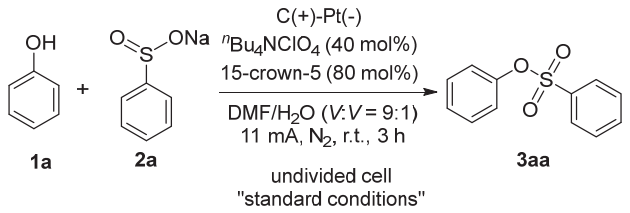
Chen's work, smaller constant current and more coupling partners including alcohols were employed in our work.

2 Results and discussion

Firstly, phenol (**1a**) and sodium benzene sulfinate (**2a**) were selected as model substrates for the optimization of reaction conditions (Table 1). Fortunately, phenyl benzenesulfonate (**3aa**) can be obtained in 90% isolated yield when the electrolysis was carried out using $^{n}Bu_4NClO_4$ as electrolyte and 15-crown-5 as additive as well as *N*,*N*-dimethylformamide (DMF)/H_2O as co-solvent at 11 mA constant current for 3 h (Entry 1). Significantly lower yields were observed in the absence of water or 15-crown-5 in this transformation (Entries 2 and 3). In this regard, 15-crown-5 might be used as sorbent that was able to selectively form stable complexes with sodium metal ion.[9] Employing CH_3CN instead of DMF led to a low yield under otherwise equal conditions (Entry 4). Furthermore, reduced reaction yields were also observed when the operating current was increased or decreased (Entries 5 and 6). Either using a platinum plate to replace the graphite rod anode or using nickel plate to replace the platinum plate cathode led to a decrease in conversion yields (Entries 7, 8). The control experiment showed that no product could be detected without electric current (Entry 9).

Table 1 Optimization of the reaction conditions[a]

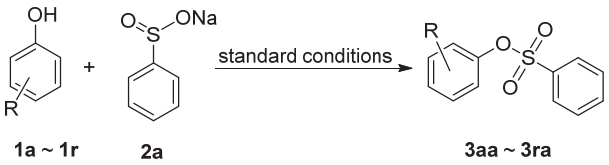


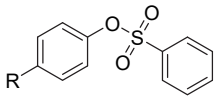
Entry	Variation from the standard conditions	Yield[b]/%
1	None	95 (90)[c]
2	No water	25
3	No 15-crown-5	39
4	CH_3CN instead of DMF	49
5	13 mA instead of 11 mA	76
6	10 mA and 3.3 h instead of 11 mA and 3 h	85
7	Pt(+) instead of C(+)	82
8	Ni(−) instead of Pt(−)	60
9	No electricity	0

[a] Conditions: the reaction was carried out with C anode, Pt cathode, constant current 11 mA, **1a** (0.5 mmol), **2a** (1.5 mmol), $^{n}Bu_4NClO_4$ (0.2 mmol), 15-crown-5 (0.4 mmol), DMF (9 mL), H_2O (1 mL), r.t., 3 h (2.5 F•mol^{-1}). [b] Yield by GC. [c] Isolated yield.

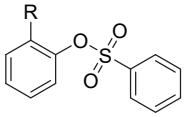
With the optimized protocols in hand, the scope of phenols was examined for this electrochemical sulfonylation transformation. As shown in Table 2, the reactions between various phenols (**1a**～**1r**) and sodium benzene sulfinate (**2**) readily led to the corresponding aryl benzenesulfonates (**3aa**～**3ra**) in good to excellent yields, and the mild electrochemical reaction conditions allowed the tolerance of electronically diverse substituents at different positions of the phenol core. For example, phenols (**1a**～**1k**) bearing electron-donating group or electron-withdrawing group at the *para* position smoothly formed desired sulfonate products in satisfied yields. Owing to the strong electron-withdrawing inductive effect, *p*-trifluoromethyl phenol (**1l**) led to a decreased conversion for electrochemical sulfonylation processes. Notably, the halo-moieties in products (**3fa**～**3ia**) were well tolerated in this electrochemical transformation, which offered the possibility for late-stage functionalization via classical activation of a C—Halo bond. Moreover, steric hindrance did not significantly affect the efficiency of the reaction, *ortho*-substituted phenols (**1m**～**1o**) gave comparable yields with substituents at the *para* position. Not surprisingly, mono- and di-meta substituted phenols (**1p**, **1q**) were viable substrates to afford target compounds with sodium benzene sulfinate in good yields. Finally, sesamol (**1r**) containing ketal functionality was able to undergo electrochemical sulfonylation conversion, albeit in moderate efficiency.

Table 2 Substrate scope of phenols with isolated yields[a]

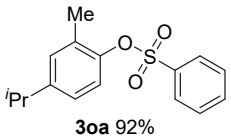




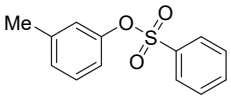
R = H, **3aa** 90%
R = CH_3, **3ba** 78%
R = OCH_3, **3ca** 76%
R = ^{t}Bu, **3da** 95%
R = Ph, **3ea** 71%
R = F, **3fa** 71%
R = Cl, **3ga** 90%
R = Br, **3ha** 73%
R = I, **3ia** 64%
R = EtOCO, **3ja** 69%
R = CN, **3ka** 90%
R = CF_3, **3la** 50%



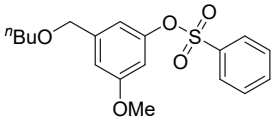
R = allyl, **3ma** 83%
R = F, **3na** 70%



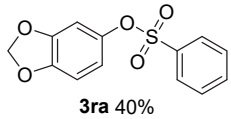
3oa 92%



3pa 80%



3qa 82%



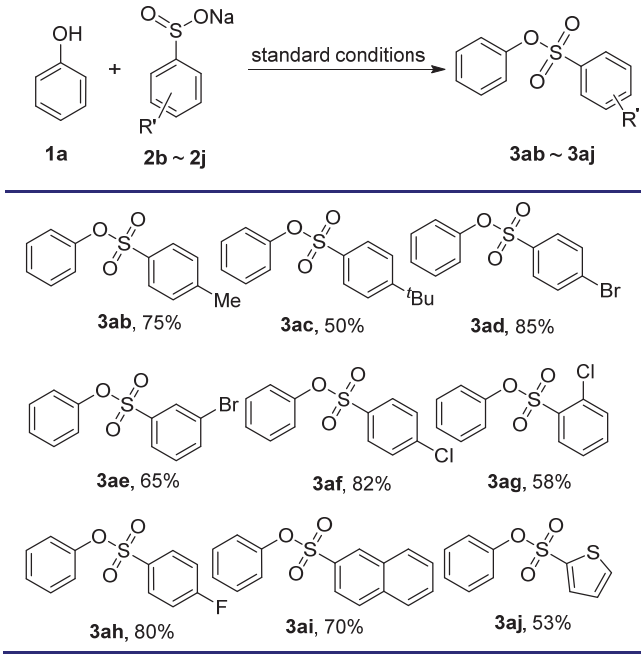
3ra 40%

[a] Conditions: the reaction was carried out with C anode, Pt cathode, constant current = 11 mA, **1** (0.5 mmol), **2a** (1.5 mmol), $^{n}Bu_4NClO_4$ (0.2 mmol), 15-crown-5 (0.4 mmol), DMF (9 mL), H_2O (1 mL), r.t., 3 h (2.5 F•mol^{-1}), isolated yields.

Subsequently, the scope of sulfinates was investigated by varying the substituents at different positions of the aryl core. As shown in Table 3, to our delight, the desired arylsulfonate esters bearing electronically diverse groups were obtained in moderate to good yields. For instance, sulfinate

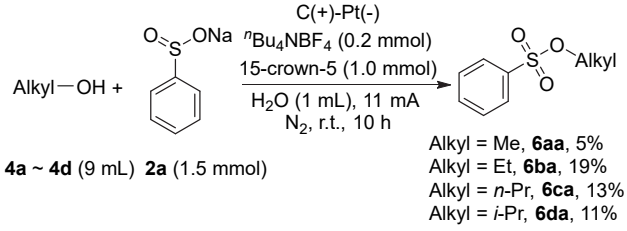
derivatives (**2b**～**2h**) with different functional groups, such as electron-donating groups (R＝Me, *t*Bu) and electron-withdrawing groups (R＝Br, Cl, F), were suitable for this electro-oxidative sulfonylation and furnished the desired products. It is found that benzo-fused sulfinate (**2i**) was compatible with the electrochemical conditions to give the corresponding product in synthetically useful levels. Notably, heterocyclic thienyl sulfinate (**2j**) worked well in the reaction to provide target product in 53% yields. Unfortunately, the attempt to extend the scope of sulfinates to alkyl sulfate failed.

Table 3 Substrate scope of aryl sulfinates with isolated yields[a]



[a] Conditions: the reaction was carried out with C anode, Pt cathode, constant current＝11 mA, **1a** (0.5 mmol), **2** (1.5 mmol), $^{n}Bu_4NClO_4$ (0.2 mmol), 15-crown-5 (0.4 mmol), DMF (9 mL), H_2O (1 mL), r.t., 3 h (2.5 F•mol^{-1}), isolated yields.

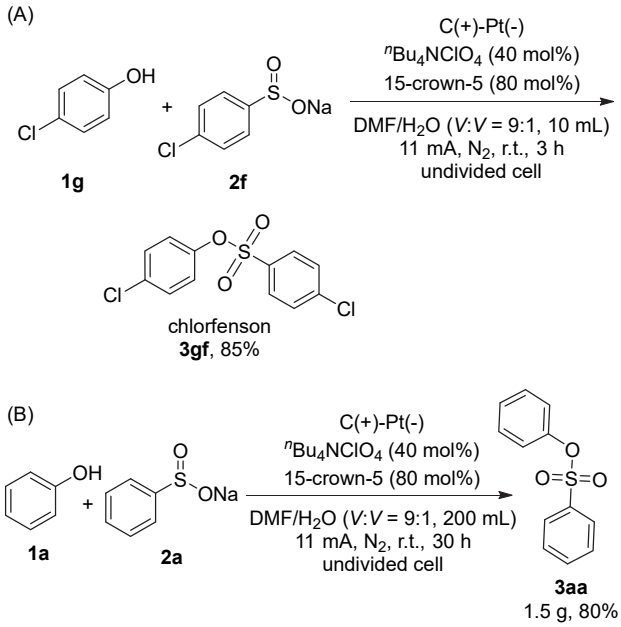
It is noteworthy that the phenol substrate could be extended to alcohols in this method, although slight modification was required for the above reaction conditions due to the different reactivity of alcohols, as shown in Scheme 1. Employing corresponding alcohol as both the coupling partner and the solvent in the reaction system, alcohols such as methanol, ethanol, *n*-propanol and isopropanol were competent substrates to undergo electrochemical sulfonylation with sodium benzene sulfinate (**2a**) to furnish



Scheme 1 Electrochemical oxidative sulfonylation of alcohols

alkyl benzenesulfonates, albeit in low yields.

To further demonstrate synthetic potential of the method, electro-oxidative sulfonylation between *p*-chlorophenol (**1g**) and sodium 4-chlorobenzene sulfonate (**2f**) was carried out under standard conditions to prepare chlorfenson (**3gf**) in 85% isolated yield in a concise route (Scheme 2, A). It is reported that chlorfenson is a drug to treat onychomycosis (nail fungus).[10] Moreover, a 20-fold scale-up of electrochemical oxidative sulfonylation of phenol (**1a**) with sodium sulfinate (**2a**) was performed in DMF/H_2O (V∶V=9∶1, 200 mL) mixed solvents under room temperature, and remarkably, the desired product phenyl benzenesulfonate (**3aa**) was obtained in 80% isolated yield (1.50 g) after 30 h of constant current electrolysis (Scheme 2, B), indicating that this electrochemical process has potential of the practical utility.



Scheme 2 Synthesis of chlorfenson (**3gf**) and gram scale synthesis of phenyl benzenesulfonate (**3aa**)

Subsequent, cyclic voltammetric (CV) studies were carried out to clarify oxidation process of the substrates, and all oxidation potentials were recorded using Ag/AgCl electrode as reference. As shown in Figure 1, the substrate **2a** had two oxidation potentials at 0.8 and 1.6 V, respectively, while the substrate **1a** had an oxidation potential over 1.8 V. Thus, the results indicated that **2a** was oxidized preferentially under the optimized conditions. Furthermore, no desired product (**3aa**) was observed when 3 equiv. of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) was added as a radical scavenger into the model reaction (Scheme 2, A), and the detection of TEMPO-sulfonyl adduct suggested the presence of a free radical intermediate during electrolysis (Scheme 3).

Based on CV results, radical trapping experiment and previous reports,[6,11] a possible mechanism for this electrochemical oxidative sulfonylation of phenols is proposed

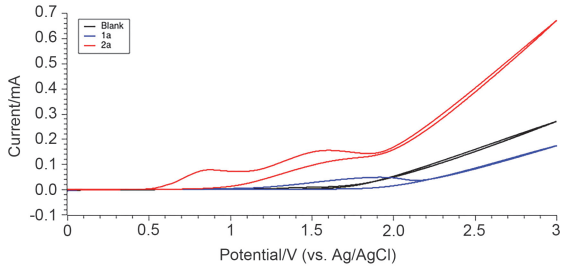
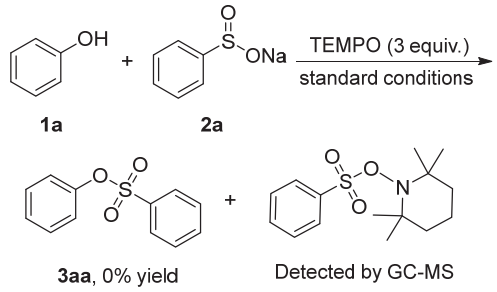
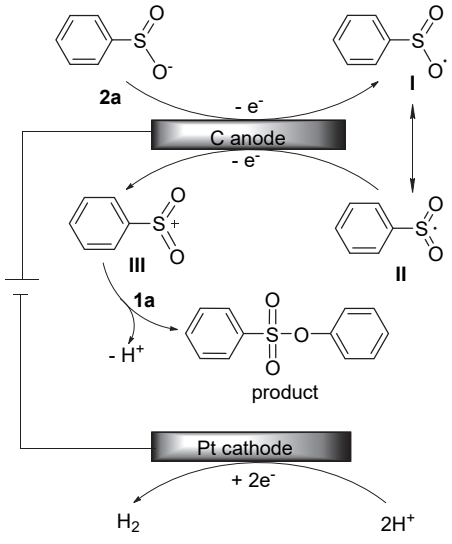


Figure 1 Cyclic voltammograms of substrate **1a**, **2a**



Scheme 3 Radical-trapping experiment

in Scheme 4. Firstly, sodium benzene sulfinate (**2a**) is oxidized at the anode to give the oxygen-centered radical **I**, followed by the resonation to more stable sulfonyl radical **II**. Subsequently, intermediate **II** undergoes further single electron transfer (SET) oxidation to generate sulfonyl cation **III**, which reacts with phenol **1a** to give desired product **3a** through a deprotonation process. At the cathode, electroreduction of proton releases hydrogen gas during the reaction.



Scheme 4 Proposed mechanism

3 Conclusions

In summary, we have developed an electrochemical oxidative sulfonylation of cheap phenols towards the synthesis of valuable sulfonyl esters. A series of arylsulfonyl esters products were produced in moderate to high yields. Key features of this simple strategy included (a) using constant current instead of an exogenous oxidant, (b) generation of hydrogen as the only side-products and (c) synthesis of valuable sulfonyl esters from easily available starting materials.

4 Experimental section

4.1 General information

All glasswares were oven dried at 110 ℃ for hours and cooled down under vacuum. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). The anode electrode is graphite rod (d=6 mm) and cathode electrode is platinum electrodes (1.5 cm×1.5 cm×0.3 mm). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200～300 mesh silica gel in petroleum (boiling point is 60～90 ℃). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they were listed as volume/volume ratio. NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), while tetramethylsilane was used as an internal standard. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument.

4.2 General procedure for electrochemical sulfonylation of phenols with sodium sulfinates

In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, phenol (0.50 mmol), sodium benzene sulfinate (1.5 mmol, 3 equiv.), ^{n}Bu$_4$NClO$_4$ (0.2 mmol, 0.4 equiv.), 15-crown-5 (0.4 mmol, 0.8 equiv.), DMF (9 mL) and H_2O (1 mL) were combined and added. The flask was equipped with platinum electrodes (1.5 cm×1.5 cm×0.3 mm) as cathode, graphite rod (d=6 mm) as anode and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 11 mA under room temperature for 3 h. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

Phenyl benzenesulfonate (**3aa**): Colorless oil, 90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82～7.80 (m, 2H), 7.66～7.62 (m, 1H), 7.52～7.48 (m, 2H), 7.28～7.22 (m, 3H), 6.97～6.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.6, 135.4, 134.3, 129.7, 129.2, 128.5, 127.3, 122.4. HRMS (ESI) calcd for $C_{12}H_{10}O_3S$ ($M+H^+$) 234.0351, found 234.0349.

p-Tolyl benzenesulfonate (**3ba**):[12] Colorless oil, 78% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83～7.81 (m, 2H), 7.67～7.64 (m, 1H), 7.53～7.49 (m, 2H), 7.05 (d, J=8.0 Hz, 2H), 6.85～6.83 (m, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.4, 137.1, 135.4, 134.2, 130.2, 129.2, 128.5, 122.1, 20.9.

4-Methoxyphenyl benzenesulfonate (**3ca**):[13] Colorless

oil, 76% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81～7.79 (m, 2H), 7.67～7.63 (m, 1H), 7.52～7.48 (m, 2H), 6.87～6.84 (m, 2H), 6.76～6.74 (m, 2H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 142.9, 135.2, 134.3, 129.2, 128.6, 123.3, 114.5, 55.6.

4-(*tert*-Butyl)phenyl benzenesulfonate (**3da**):[14] Colorless oil, 95% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, J=8.0 Hz, 2H), 7.65 (q, J=7.2 Hz, 1H), 7.50 (t, J=8.0 Hz, 2H), 7.26 (t, J=7.6 Hz, 2H), 6.87 (t, J=7.6 Hz, 2H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.2, 147.2, 135.5, 134.2, 129.2, 128.5, 126.6, 121.7, 34.6, 31.3.

(1,1'-Biphenyl)-4-yl benzenesulfonate (**3ea**): White solid, 71% isolated yield. m.p. 99～100 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, J=7.6 Hz, 2H), 7.68 (t, J=8.0 Hz, 1H), 7.55～7.37 (m, 9H), 7.07 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.8, 140.2, 139.6, 135.2, 134.3, 129.2, 128.9, 128.5, 128.3, 127.7, 127.0, 122.6. HRMS (ESI) calcd for $C_{18}H_{14}O_3S$ ($M+H^+$) 311.0736, found 311.0730.

4-Fluorophenyl benzenesulfonate (**3fa**):[13] Colorless oil, 71% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, J=8.0 Hz, 2H), 7.69～7.65 (m, 1H), 7.55～7.51 (m, 2H), 6.98～6.94 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.1 (d, J=245.4 Hz), 145.3, 134.9, 134.47, 129.3, 128.5, 124.0 (d, J=8.8 Hz), 116.4 (d, J=23.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: －114.3.

4-Chlorophenyl benzenesulfonate (**3ga**):[12] Yellow oil, 90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82～7.80 (m, 2H), 7.69～7.65 (m, 1H), 7.55～7.50 (m, 2H), 7.23 (t, J=3.0 Hz, 2H), 6.91 (d, J=4.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.0, 135.0, 134.5, 132.9, 129.8, 129.3, 128.5, 123.8.

4-Bromophenyl benzenesulfonate (**3ha**):[14] Colorless oil, 73% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83～7.81 (m, 2H), 7.70～7.66 (m, 1H), 7.53 (t, J=7.2 Hz, 2H), 7.40 (q, J=9.2 Hz, 2H), 6.85 (q, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.5, 134.9, 134.6, 132.8, 129.4, 128.6, 124.2, 120.8.

4-Iodophenyl benzenesulfonate (**3ia**):[15] Yellow oil, 64% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83～7.81 (m, 2H), 7.68～7.66 (m, 1H), 7.61～7.52 (m, 4H), 6.73 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 138.8, 134.9, 134.5, 129.3, 128.5, 124.5, 91.9.

Ethyl 4-(phenoxysulfonyl)benzoate (**3ja**): Colorless oil, 69% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96～7.94 (m, 2H), 7.81～7.81 (m, 2H), 7.67～7.63 (m, 1H), 7.53～7.48 (m, 2H), 7.04～7.01 (m, 2H), 4.35～4.29 (m, 2H), 1.36～1.31 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.4, 152.8, 135.0, 134.6, 131.3, 129.4, 129.3, 128.4, 122.3, 61.3, 14.3; HRMS (ESI) calcd for $C_{15}H_{14}O_5S$ ($M+H^+$) 307.0635, found 307.0632.

4-Cyanophenyl benzenesulfonate (**3ka**):[13] Colorless oil, 90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, J=10.8 Hz, 2H), 7.70～7.67 (m, 1H), 7.60～7.52 (m, 4H), 7.10 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.3, 134.8, 134.6, 133.9, 129.4, 128.3, 123.4, 117.7, 111.2.

4-(Trifluoromethyl)phenyl benzenesulfonate (**3la**): Colorless oil, 50% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86～7.83 (m, 2H), 7.72～7.68 (m, 1H), 7.58～7.53 (m, 4H), 7.12 (t, J=2.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.9, 135.0, 134.8, 129.5 (q, J=32.8 Hz), 129.5, 128.5, 127.2 (q, J=3.7 Hz), 123.6 (q, J=270.7 Hz), 123.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: －62.4; HRMS (ESI) calcd for $C_{13}H_9F_3O_3S$ ($M+H^+$) 303.0297, found 303.0285.

2-Allylphenyl benzenesulfonate (**3ma**): Colorless oil, 83% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88～7.86 (m, 2H), 7.68～7.64 (m, 1H), 7.53～7.50 (m, 2H), 7.19～7.12 (m, 3H), 7.06～7.04 (m, 1H), 5.81～5.70 (m, 1H), 5.04～4.97 (m, 2H), 3.23 (d, J=6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.7, 135.8, 135.3, 134.3, 133.2, 130.7, 129.2, 128.2, 127.4, 127.2, 122.1, 116.7, 33.8; HRMS (ESI) calcd for $C_{15}H_{14}SO_3$ ($M+H^+$) 275.0736, found 275.0735.

2-Fluorophenyl benzenesulfonate (**3na**): White solid, 70% isolated yield. m.p. 65～67 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, J=9.2 Hz, 2H), 7.69 (t, J=4.0 Hz, 1H), 7.54 (t, J=7.6 Hz, 2H), 7.21 (t, J=4.0 Hz, 2H), 7.11～7.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.6 (d, J=251.2 Hz), 136.8 (d, J=12.6 Hz), 135.3, 134.6, 129.3, 128.6, 128.5 (d, J=7.0 Hz), 124.9, 124.7 (d, J=4.0 Hz), 117.2 (d, J=18.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: －128.0; HRMS (ESI) calcd for $C_{12}H_9SO_3F$ ($M+H^+$) 253.0329, found 253.0342.

Phenyl 4-isopropyl-2-methylbenzenesulfonate (**3oa**): Colorless oil, 92% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88～7.86 (m, 2H), 7.70～7.66 (m, 1H), 7.56～7.52 (m, 2H), 7.09～7.07 (m, 1H), 7.02～7.00 (m, 1H), 6.70 (s, 1H), 2.81～2.74 (m, 1H), 2.09 (s, 3H), 1.12 (d, J=2.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.2, 148.1, 136.1, 134.2, 131.4, 129.2, 128.7, 128.5, 125.3, 120.1, 33.4, 23.8, 16.0; HRMS (ESI) calcd for $C_{16}H_{18}SO_3$ ($M+H^+$) 291.1049, found 291.1038.

m-Tolyl benzenesulfonate (**3pa**): Colorless oil, 80% isolated yield. ^{1}H NMR (400 MHz $CDCl_3$) δ: 7.83 (d, J=8.4 Hz, 2H), 7.68～7.64 (m, 1H), 7.52(t, J=8.0 Hz, 2H), 7.14 (t, J=8.0 Hz, 1H), 7.04 (d, J=7.6 Hz, 1H), 6.83 (s, 1H), 6.72 (q, J=2.4 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 140.0, 135.5, 134.2, 129.3, 129.2, 128.5, 128.0, 123.0, 119.2, 21.3; HRMS (ESI) calcd for $C_{13}H_{12}O_3S$ ($M+H^+$) 248.0507, found 248.0511.

Phenyl 3-methoxy-5-(pentyloxy)benzenesulfonate (**3qa**): Colorless oil, 82% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84～7.82 (m, 2H), 7.63～7.60 (m, 1H), 7.49～7.45 (m, 2H), 7.10～7.08 (m, 1H), 6.82～6.81 (m, 2H), 4.41 (s, 2H), 3.48～3.42 (m, 5H), 2.67 (t, J=1.4 Hz, 1H), 1.60～1.53 (m, 2H), 1.41～1.32 (m, 2H), 0.89 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.6, 139.2, 137.4, 136.1, 134.0, 128.7, 128.5, 123.8, 119.3, 111.5, 72.1, 70.4, 55.4, 31.8, 19.4, 14.0; HRMS (ESI) calcd for $C_{18}H_{22}O_5S$ ($M+H^+$) 351.1261, found 351.1255.

Benzo[*d*][1,3]dioxol-5-ylbenzenesulfonate (**3ra**): Col-

orless oil, 40% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85～7.82 (m, 2H), 7.69～7.65 (m, 1H), 7.55～7.51 (m, 2H), 6.63 (d, J=8.8 Hz, 1H), 6.52 (d, J=2.4 Hz, 1H), 6.36 (q, J=2.4 Hz, 1H), 5.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.1, 146.6, 143.8, 135.2, 134.4, 129.3, 128.7, 115.3, 108.0, 104.5, 102.1; HRMS (ESI) calcd for $C_{13}H_{10}O_5S$ ($M+H^+$) 279.0322, found 279.0310.

Phenyl 4-methylbenzenesulfonate (**3ab**):[16] Colorless oil, 75% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (t, J=7.6 Hz, 2H), 7.31～7.24 (m, 5H), 6.97 (d, J=7.6 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.7, 145.5, 132.3, 129.8, 129.5, 128.7, 127.2, 122.5, 21.8.

Phenyl 4-(*tert*-butyl)benzenesulfonate (**3ac**): Colorless oil, 50% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73～7.71 (m, 2H), 7.49 (t, J=1.6 Hz, 2H), 7.27～7.19 (m, 3H), 6.98～6.96 (m, 2H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.4, 149.7, 132.5, 129.7, 128.4, 127.2, 126.2, 122.5, 35.4, 31.1; HRMS (ESI) calcd for $C_{16}H_{18}O_3S$ ($M+H^+$) 291.1049, found 291.1044.

Phenyl 4-bromobenzenesulfonate (**3ad**): Colorless oil, 85% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (t, J=10.0 Hz, 4H), 7.32～7.24 (m, 3H), 6.98 (d, J=7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 134.4, 132.6, 123.0, 129.9, 129.7, 127.5, 122.4; HRMS (ESI) calcd for $C_{12}H_9BrO_3S$ ($M+H^+$) 312.9529, found 312.9520.

Phenyl 3-bromobenzenesulfonate (**3ae**): Colorless oil, 65% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (s, 1H), 7.79～7.73 (m, 2H), 7.39 (t, J=8.0 Hz, 1H), 7.33～7.24 (m, 3H), 6.99 (t, J=1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 137.4, 137.1, 131.3, 130.7, 129.9, 127.5, 127.1, 123.1, 122.3; HRMS (ESI) calcd for $C_{12}H_9SO_3Br$ ($M+H^+$) 312.9529, found 312.9529.

Phenyl 4-chlorobenzenesulfonate (**3af**):[17] Colorless oil, 82% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (q, J=2.0 Hz, 2H), 7.50～7.48 (m, 2H), 7.33～7.24 (m, 3H), 7.00～6.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 141.1, 133.8, 130.0, 129.9, 129.6, 127.5, 122.4.

Phenyl 2-chlorobenzenesulfonate (**3ag**): Colorless oil, 58% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91(d, J=7.6 Hz, 1H), 7.64～7.56 (m, 2H), 7.37～7.24 (m, 4H), 7.13～7.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4, 135.3 133.4, 133.3, 132.5 132.2, 129.9, 127.5, 127.2, 122.1; HRMS (ESI) calcd for $C_{12}H_9SO_3Cl$ ($M+H^+$) 269.0034, found 269.0036.

Phenyl 4-fluorobenzenesulfonate (**3ah**):[2b] Colorless oil, 80% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86～7.83 (m, 2H), 7.33～7.27 (m, 3H), 7.22～7.18 (m, 2H), 7.00～6.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.1 (d, J=256.0 Hz), 149.5, 131.5, 131.4 (d, J=9.7 Hz), 129.8, 127.4, 122.4, 116.6 (d, J=22.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: －102.1.

Phenyl naphthalene-2-sulfonate (**3ai**):[2c] Colorless oil, 70% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (s, 1H), 8.00～7.84 (m, 4H), 7.72～7.61 (m, 2H), 7.26～7.24 (m, 3H), 7.01～6.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.7, 135.5, 132.3, 131.9, 130.6, 129.8, 129.7, 129.6, 129.6, 128.1, 128.0, 127.3, 123.0, 122.5.

Phenyl thiophene-2-sulfonate (**3aj**):[2c] Colorless oil, 53% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, J=4.8 Hz, 1H), 7.56 (t, J=2.4 Hz, 1H), 7.32～7.26 (m, 3H), 7.08～7.02 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.7, 135.6, 134.7, 134.6, 129.8, 127.6, 127.5, 122.3.

4-Chlorophenyl 4-chlorobenzenesulfonate (**3gf**):[4c] White solid, 85% isolated yield. m.p. 81～83 ℃ (lit.[4c] 84 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (dd, J=6.6 Hz, 2H), 7.52 (dd, J=6.6 Hz, 2H), 7.28 (dd, J=6.6 Hz, 2H), 6.94 (q, J=2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.9, 141.4, 133.6, 133.2, 130.3, 130.0, 129.8, 123.8.

Methyl benzenesulfonate (**6aa**):[18] Colorless oil, 5% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (q, J=1.2 Hz, 2H), 7.69～7.65 (m, 1H), 7.59～7.55 (m, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.4, 134.0, 129.5, 128.2, 56.5.

Ethyl benzenesulfonate (**6ba**):[3i] Colorless oil, 19% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92～7.89 (m, 2H), 7.67～7.63 (m, 1H), 7.57～7.53 (m, 2H), 4.11 (q, J=7.2 Hz, 2H), 1.29 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.4, 133.8, 129.3, 127.9, 67.2, 14.8.

Propyl benzenesulfonate (**6ca**):[19] Colorless oil, 13% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89～7.87 (m, 2H), 7.65～7.61 (m, 1H), 7.55～7.51 (m, 2H), 3.98 (t, J=6.4 Hz, 2H), 1.69～1.60 (m, 2H), 0.87 (q, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.2, 133.7, 129.3, 127.8, 72.5, 22.3, 10.0.

Isopropyl benzenesulfonate (**6da**):[20] Colorless oil, 11% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91～7.89 (m, 2H), 7.65～7.61 (m, 1H), 7.55～7.51 (m, 2H), 4.78～4.72 (m, 1H), 1.26 (d, J=6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.6, 132.6, 128.3, 126.7, 76.6, 21.9.

Supporting Information The detailed procedure for the synthesis of **3aa** and cyclic voltammetry (CV) experiment, copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR of the products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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