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Electrochemical cross-coupling reactions of sodium arenesulfinates with thiophenols and phenols

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ABSTRACT

A green electrochemical oxidative cross-coupling protocol for the generation of thiosulfonates and sulfonate esters using sodium arenesulfinates and thiophenols/phenols is disclosed. The protocol involves using inorganic and non-toxic NaI as both redox catalyst and supporting electrolyte at room temperature without oxidant and base. The reactions provide good yields of products and tolerate broad substrate scope. The mechanistic studies revealed that the reactions proceed via a radical pathway for the formation of SO_2—S and SO_2—O bonds.

1. Introduction

Organosulfur compounds are widely present in nature [1], they generally exist in the form of thiols, thioethers, disulfides. While a lot of other organosulfur compounds are synthesized via chemical process, thus their structures are more diverse and not limited to the natural forms above. Here, two special organosulfur compounds which possess important —SO_2-S- and —SO_2-O- motifs are shown, they are thiosulfonate and sulfates. To the date, thiosulfonates have been reported as antimicrobial, anti-viral, antifungal and anticancer agents [2], they are also used as cysteine scanning reagents [3]. Besides, thiosulfonates have also been employed in polymer production, photographic process and analytic biosensors [4]. In recent years, thiosulfonates have been selected as good sulfenylating reagents for the introduction of RSO_2- [5] and RS- groups [6] into different organic molecule structures via a diverse range of chemical transformations. Another important organosulfur compound is sulfonate ester, it contains —SO_2-O- motif which is often used as coupling functional group (-OTs) for a variety of transitional metal catalyzed reactions in order to generate a variety of aromatic compounds in pharmaceutical, material, chemical industry and so on [7]. Inspired by halogen-mediated electrochemical organic synthesis [8], therefore, any green and eco-friendly methods which can produce both thiosulfonates and sulfonate esters under mild conditions still attract significant attention.

Since wide applications of thiosulfonates and sulfonate esters in organic and medicinal chemistry, several protocols about the synthesis of thiosulfonates and sulfonate esters have been developed by different groups as shown in Scheme 1. Zou et al. reported a copper-catalyzed TBHP-mediated cross-coupling reaction of sulfonylhydrazides with thiols to afford thiosulfonates in good yields [9]. Tang tried the same reaction using an electrochemical method to make thiosulfonates [10]. Chen also reported the same reaction but under different reaction condition [11]. Sarkar's group used phenyl trimethyl ammonium tribromide (PTAB) as a catalyst for oxidative coupling of sodium arenesulfinate with thiophenol in open air [12]. Yadav demonstrated a method for the synthesis of thiosulfonates via iron(III)-catalyzed cross-coupling of thiols with sodium arenesulfinates [13]. Similarly, Taniguchi's group made thiosulfonates by oxidative coupling of thiol with sodium sulfinate via Cu-Ligand [14]. While Liu's group used electrochemical oxidative cross-dehydrogenative coupling of arylsulfinic acids with thiophenols to give thiosulfonates [15]. Similar work was also reported by Waldvogel's group [16]. For the synthesis of sulfonate esters, besides the reaction of sulfonyl chloride with phenol, Yuan reported iodine-induced synthesis of sulfonate esters from sodium

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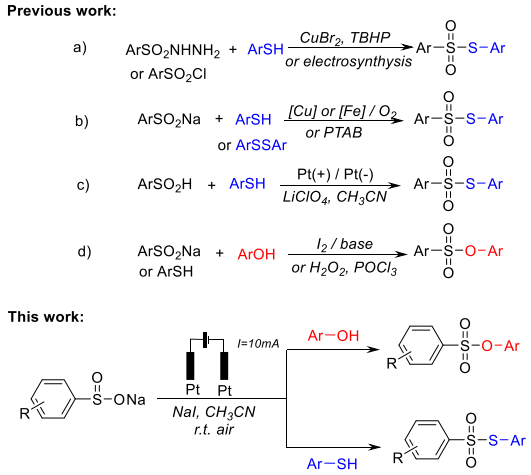


Scheme 1. Different synthetic routes of thiosulfonates and sulfonate esters.

arenesulfinates and phenols [17]. While Abbasi and co-workers used thiolphenol to react with phenols in the presence of H_2O_2/$POCl_3$ to make sulfonate esters [18]. Despite these advances, the methods above still suffer from expensive transition metals and excess of oxidants, resulting in a mass of undesired byproducts and difficult purification. Therefore, a green and practical electrochemical methods are highly desired in order to solve shortcomings mentioned above.

Electrorganic synthesis has been a green alternative to traditional synthesis protocols, it is one of the most attractive tools because it can minimize the waste and give rise to inherently safe processes, meanwhile the electrosynthysis methods can short-cut many steps with milder transformations and precise control. It's also a substitution of chemical redox reagents by electricity [19]. Here we report an electrochemical oxidative cross-coupling reactions of sodium arenesulfinates with thiolphenols or phenols.

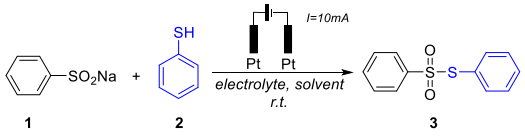
2. Results and discussions

We started our research by choosing sodium benzenesulfinate **1a** and thiophenol **2a** as model reactants. Platinum plates were used as both anode and cathode with a constant current of 10 mA. CH_3CN was selected as the first solvent and sodium iodide was employed as both catalyst and supporting electrolyte. After 4 h, the reaction afforded the desired product thiosulfonates **3a** in a 85% yield (Table 1).

1, entry 1). Using potassium iodide instead of NaI under the same reaction condition gave a 79% yield of the expected product **3a** (entry 2). When *tetra*-butylammonium iodide was selected as the supporting electrolyte instead of NaI, a decreased yield of **3a** was obtained (entry 3). Utilizing ammonium iodide as the supporting electrolyte and catalyst, CH_3CN as the solvent, the thiosulfonates **3a** was obtained in a 72% yield (entry 4). Replacement of sodium iodide by *tetra*-butylammonium hexafluorophosphate gave a low yield of **3a** (entry 5). While using *tetra*-butylammonium tetrafluoroborate as the supporting electrolyte provided **3a** less than 5% yield (entry 6). Interestingly, increasing electronic current to 15 mA or reducing electronic current to 5 mA resulted in slightly decreased yield of **3a** (entry 7, 8). Since using NaI as both catalyst and supporting electrolyte gave a highest yield, so from entry 9, NaI was selected as a catalyst and supporting electrolyte for all left reactions with constant current of 10 mA. Changing solvent CH_3CN into CH_3OH, after 4 h, the reaction afforded a lower yield (55%) of thiosulfonates **3a** (entry 9). Using DMSO as the solvent afforded **3a** in a 58% yield (entry 10). Similarly, replacing CH_3CN solvent with DMF led to a 53% yield (entry 11). Using 1,4-dioxane or THF as solvent gave a trace amount or very low yield of thiosulfonates **3a** (entry 12, 13), this result demonstrated that different solvents have really different impacts on reaction yields. Compared with CH_3CN, all other solvents showed less efficiency. Finally, the variation of supporting electrolyte amount decreased the yield from 85% to 72% or 80%, respectively (entry 14, 15).

With the optimized condition in hand, the scope and generality of this electrochemical oxidative cross-coupling were examined in detail. A variety of substituted sodium benzenesulfinate and thiophenols with both electron-withdrawing and electron-donating substitutes on their benzene ring were screened and results are shown in Table 1. Unsubstituted thiophenol was reacted with unsubstituted sodium benzenesulfinate gave the desired product **3a** in an 85% yield under the optimized condition. Thiophenol with electron-donating groups (-NH_2, −CH_3) on benzene ring provided a little better yield than thiophenol with electron-withdrawing groups (-F, -Cl) (**3b**, **3d**, **3c** and **3e**). When both sodium benzenesulfinates and thiophenols with electron-withdrawing substitutes (-F and -Cl) on the *para*-positions of their benzene rings, the cross-coupling reaction afforded a decreased yield of 59% (**3f**). When sodium *p*-toluenesulfinate and electron-rich thiophenols were employed as the cross-coupling partners, all reactions gave the desired products in good yields regardless these substitutes were −H, −CH_3, −NH_2 or -OMe (**3g**, **3h**, **3i** and **3j**). But if one partner had electron-withdrawing group on its benzene ring, then the reactions furnished slightly decreased product yields, depending on how strong electron-withdrawing capacity of these substitutes are (**3k**, **3l**, **3m**, **3n**). In **3n** case, there are two electron-withdrawing substitutes on both benzene rings, so its yield is a little lower than with the electron-withdrawing substitute. 2-thiophenethiol was selected as a starting material to react with sodium *p*-toluenesulfinate, the reaction exhibited good reactivity and gave thiosulfonate (**3o**) in a 78% yield. Finally, methyl sulfinate was also applied in our protocol, which offord **3p** only 35% yield.

Table 1
Optimization of reaction conditions[a,b].

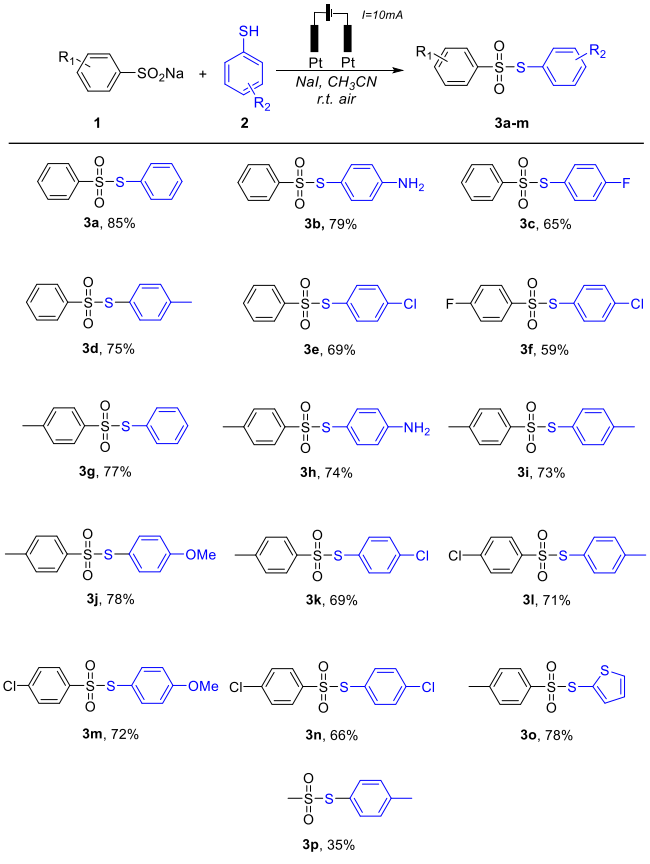


Entry	Solvent	Supporting electrolyte	J (mA/cm^2)	Yield (%)
1	CH_3CN	NaI	10	85
2	CH_3CN	KI	10	79
3	CH_3CN	TBAI	10	51
4	CH_3CN	NH_4I	10	72
5	CH_3CN	*n*-Bu_4NPF_6	10	<5
6	CH_3CN	*n*-Bu_4NBF_4	10	<5
7	CH_3CN	NaI	15	78
8	CH_3CN	NaI	5	68
9	CH_3OH	NaI	10	55
10	DMSO	NaI	10	58
11	DMF	NaI	10	53
12	Dioxane	NaI	10	trace
13	THF	NaI	10	<5
14	CH_3CN	NaI	10	72[c]
15	CH_3CN	NaI	10	80[d]

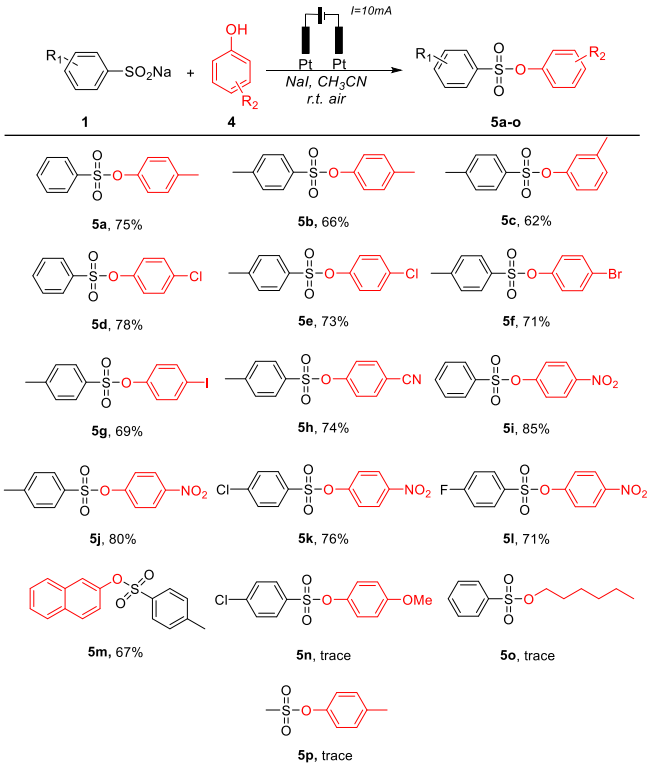
[a] Reaction conditions: Platinum plate is used as anode (1 cm × 1 cm), platinum plate as cathode (1 cm × 1 cm), undivided cell, constant current = 10 mA, **1a** (0.6 mmol), **2a** (0.3 mmol), supporting electrolyte (20 mol%), solvent (5 mL), under air at room temperature for 4 h. [b] Isolated yields. [c] Supporting electrolyte (10 mol%). [d] Supporting electrolyte (40 mol%).

The success of electrochemical oxidative cross-coupling of thiolphenols with benzenesulfinate salt led us further to explore the cross-coupling reactions of phenols with sodium benzenesulfinate under the same reaction condition. Because O and S element belong to the same group in periodic table, so thiophenols and phenols should show some kind of similar reactivity, therefore we continued our exploration by replacing thiolphenols with phenols.

We started our investigation of electrochemical reaction of sodium benzenesulfinate with *p*-methylphenol using the same reaction condition shown in Scheme 2. To our delight, the reaction also proceeded well and afforded sulfonate ester **5a** in a 75% yield. To extend the scopes of exploration, different phenols with both electron-withdrawing and electron-donating substitutes on the benzene ring of phenols were screened and results are shown in Scheme 3. It can be seen that when sodium benzenesulfinate was employed as a reactant, different phenol partners afforded slightly different yields of sulfonate esters. Phenol with electron-donating substitute (-CH_3) on its benzene ring (**5a**) gave slightly lower yield than phenols with electron-withdrawing substitute (-Cl, $-NO_2$) on their benzene ring (**5d**, **5i**). The same situation happened when sodium *p*-tolylsulfinate was employed instead of sodium benzenesulfinate, all phenols with electron-withdrawing substitutes (-Cl, -Br, —I, —CN , -NO_2) (**5e**, **5f**, **5g**, **5h** and **5j**) furnished slightly higher yield than phenols with electron-donating group (**5b**). When the same phenol (*p*-nitrophenol) was used, electron-withdrawing substitutes on sodium benzenesulfinate led to lower yields (**5j**, **5k** and **5l**). Using naphthol provided sulfonate ester in a 67% yield (**5m**). But when electron-rich *p*-methoxyphenol was used as one reactant, the reaction didn't give the expected product **5n**.



Scheme 2. Reaction conditions: Pt plate as anode (1 cm × 1 cm), Pt plate as cathode (1 cm × 1 cm), undivided cell, constant current = 10 mA, **1a** (0.6 mmol), **2a** (0.3 mmol), catalyst (10 mol%), solvent (5 mL), at room temperature for 4 h (3 F/mol).



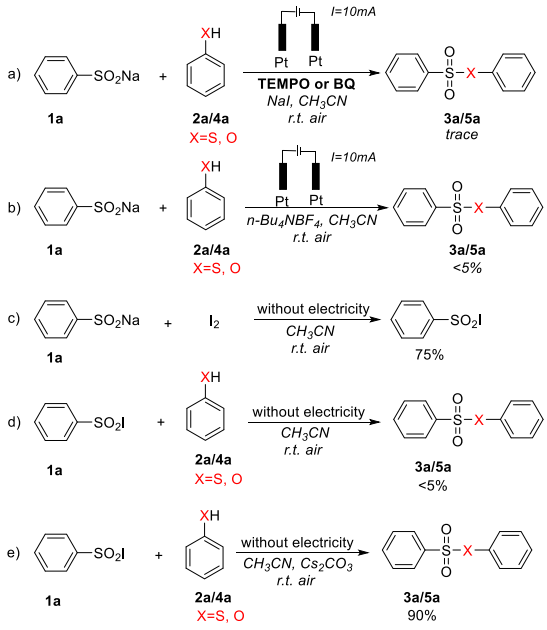
Scheme 3. Reaction conditions: Pt plate as anode (1 cm × 1 cm), Pt plate as cathode (1 cm × 1 cm), undivided cell, constant current = 10 mA, **1a** (0.6 mmol), **4a** (0.3 mmol), catalyst (10 mol%), solvent (5 mL), at room temperature for 4 h (3 F/mol).

Interestingly, linear fatty alcohol didn't react with sodium benzenesulfinate under this electrochemical condition and no expected product was formed. Finally, methyl sulfinate was also used to react with *p*-cresol, but only gave trace yield.

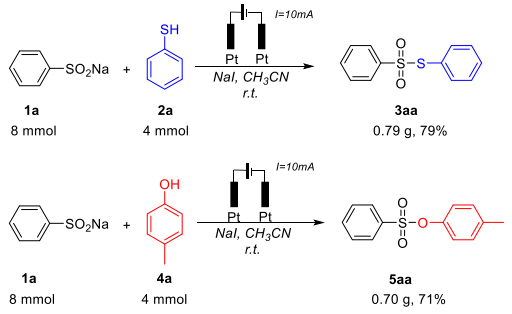
To display the practicality and scalability of our method, the electrochemical oxidative cross-coupling reaction was scaled more than 10-fold and performed on a gram scale (Scheme 5). Using 8 mmol **1a** and 4 mmol **2a** by prolonging the reaction time, the product **3aa** could be obtained in 79% yield, while 8 mmol **1a** and 4 mmol **4a** offord 71% yield of **5aa**, only slightly decreased compared with small scale (85%).

To gain insights into the mechanism of the two reactions, a series of control experiments were conducted under the optimal condition (Scheme 4). When radical scavenger TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) or BQ (1,4-benzoquinone) was introduced into the reaction, the electrochemical oxidative cross-coupling reaction was obviously inhibited and only trace amount of expected product **3a** and **5a** were observed. (Scheme 2, a), indicating that both reactions may undergo a radical pathway in the electrochemical oxidative cross-coupling processes. When NaI was fully replaced by *n*-Bu_4NBF_4, the reactions didn't provide product **3a** or **5a** at all (Scheme 2, b). This means that the electrochemical oxidation of benzenesulfinate anions to give benzenesulfonyl radical was not favored route in our case, while the electrooxidation of I ions to I_2 plays a key role in this transformation. When sodium benzenesulfinate and I_2 were put together, after 4 h, the reaction afforded 65% yield of benzenesulfonyl iodide at room temperature. When thiolphenol or phenol was added into the solution of benzenesulfonyl iodide at room temperature in acetonitrile, only less than 5% the expected products **3a** or **5a** were observed.

Cyclic voltammetry (CV) experiments were also carried out to find out the oxidation potential voltages of reactants involving the



Scheme 4. Control experiments.



Scheme 5. Gram-scale reaction.

oxidative cross-coupling process. From Fig. 1. It can be seen that the oxidation voltage of NaI occurs at 0.55 V and 0.90 V, which obviously corresponds to the halide system of (I^-–I_3^-–I_2). $PhSO_2Na$ gave an oxidation peak at about 1.35 V. The oxidation peak of thiophenol was observed at 1.25 V in our case, while phenol gave the oxidation peak at 1.72 V, so the reaction began with the oxidation of iodide ion.

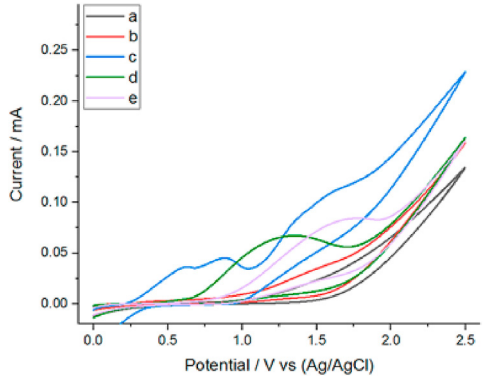


Fig. 1. Cyclic voltammograms of reactants and their mixtures in 0.1 M n-Bu_4NBF_4/CH_3CN using a glassy carbon disk working electrode (diameter, 3 mm), Pt plate and Ag/AgCl (0.1 M in KCl) as counter and reference electrode at 100 mV/s scan rate: (a) Background, (b) $PhSO_2Na$ (10 mmol/L), (c) NaI (10 mmol/L), (d) Thiophenol (10 mmol/L), (e) Phenol (10 mmol/L).

Based on the above experimental results and previous related literatures [20], we proposed a plausible mechanism shown in Scheme 6. Initially, the oxidation of iodide anion on the anode would produce iodine radical, which could form iodine I_2 quickly. Then iodine further reacts with sodium benzenesulfinate to give benzenesulfonyl iodide which might undergo nucleophelic reactions with phenols or thiophenols (or disulfides) to generate products 3 or 5 respectively. Another possible route is that benzenesulfinate ion could be oxidized on the anode to give benzenesulfinate radical which could also react with iodine to generate benzenesulfonyl iodide. Thiophenol could be oxidized on the anode to produce disulfide which might further react with benzenesulfonyl iodide to give product 3. Finally, the direct cathodic reduction of protons released from thiophenol and phenol during the reaction process could provide hydrogen gas.

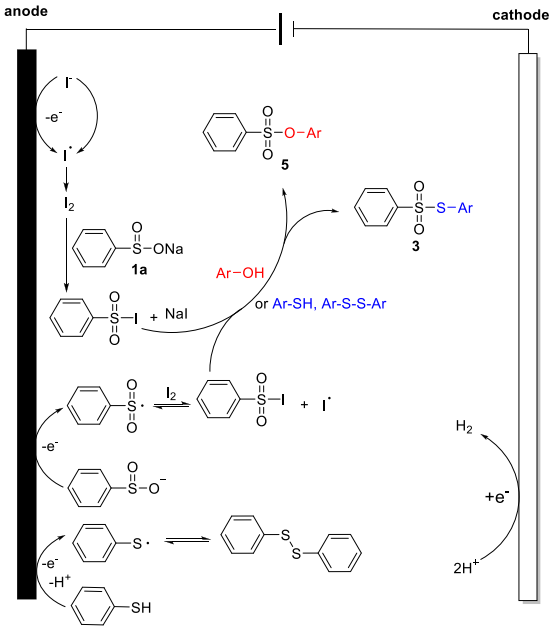
3. Conclusion

In conclusion, we have developed a green electrochemical oxidative cross-coupling protocol for the generation of thiosulfonates and sulfonate esters via using sodium arenesulfonates and thiophenols/phenols without usage of oxidants and bases. In this protocol, inorganic and nontoxic NaI was employed both as the redox catalyst and supporting electrolyte in acetonitrile at room temperature, generating good yields of unsymmetric thiosulfonates and sulfonate esters. The cross-coupling reactions tolerate broad substrate scopes. The mechanism study reveals that both reactions undergo radical pathways and sodium iodide plays an important role in initiating reactions. Further efforts on electrochemical transformations are currently under way in our lab.

4. Experimental section

4.1. General information and materials

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The



Scheme 6. Proposed mechanism.

instrument for electrolysis was dual display potentiostat (QJ3005T) (made in China). The anodic electrode was platinum plate (10 mm × 10 mm × 1 mm) and cathodic electrode was platinum plate (10 mm × 10 mm × 1 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 was between 60 and 90 °C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they were listed as vol/vol ratios. 1H and 13C NMR spectra were recorded on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz respectively. HRMS spectrometry (LC-HRMS) was recorded on a LXQ Spectrometer (Thermo Scientific) operating on ESI-TOF (MeOH as a solvent).

4.2. General procedure for syntheses of compounds 3a-p

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, benzenesulfinate salt **1a** (0.6 mmol), thiols **2a** (0.3 mmol), sodium iodide (0.2 equiv), MeCN (5 mL) was added. The bottle was equipped with platinum plate (10 mm × 10 mm) as the anode and platinum plate (10 mm × 10 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA at room temperature for 4 h. After completion of the reaction, as indicated by TLC and GC-MS, the pure product was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 40–30 : 1). The same procedure was applied to the production of other compounds **3a-p**.

4.2.1. S-phenyl benzenesulfonothioate (*3a*)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.58 (dt, *J* = 8.8, 2.1 Hz, 3H), 7.52–7.47 (m, 1H), 7.44 (dd, *J* = 8.5, 7.2 Hz, 2H), 7.40–7.32 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 142.93, 136.58, 133.67, 131.43, 129.45, 128.82, 127.82, 127.55, 77.27. **HRMS** (ESI-TOF) *m/z* calculated for $C_{12}H_{10}NaO_2S_2^+$ $(M + Na)^+$ 273.0014, found 273.0006.

4.2.2. S-(4-aminophenyl) benzenesulfonothioate (*3b*)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.64–7.55 (m, 3H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.13–7.05 (d, *J* = 8.0 Hz, 2H), 6.61–6.54 (d, *J* = 8.0 Hz, 2H), 4.08 (s, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 149.82, 143.07, 138.31, 133.38, 128.75, 127.61, 115.23, 114.54. **HRMS** (ESI-TOF) *m/z* calculated for $C_{12}H_{11}NNaO_2S_2^+$ $(M + Na)^+$ 288.0123, found 288.0130.

4.2.3. S-(4-fluorophenyl) benzenesulfonothioate (*3c*)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.64–7.56 (m, 3H), 7.49–7.43 (dd, *J* = 1.0, 12 Hz, 2H), 7.39–7.32 (m, 2H), 7.09–7.00 (dd, *J* = 8.0, 8.0 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 142.72, 138.88, 138.79, 133.81, 128.92, 127.57, 116.92, 116.70, 77.24. **HRMS** (ESI-TOF) *m/z* calculated for $C_{12}H_9FNaO_2S_2^+$ $(M + Na)^+$ 290.9920, found 290.9913.

4.2.4. S-(p-tolyl) benzenesulfonothioate (*3d*)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.65–7.56 (m, 3H), 7.49–7.43 (m, 2H), 7.26–7.23 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 143.15, 142.15, 136.49, 133.50, 130.23, 128.77, 127.57, 124.42, 77.21, 21.47. **HRMS** (ESI-TOF) *m/z* calculated for $C_{13}H_{12}NaO_2S_2^+$ $(M + Na)^+$ 287.0171, found 287.0166.

4.2.5. S-(4-chlorophenyl) benzenesulfonothioate (*3e*)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.67–7.56 (m, 3H), 7.47 (dd, *J* = 8.6, 7.1 Hz, 2H), 7.37–7.26 (m, 5H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 142.87, 138.31, 137.71, 133.85, 129.75, 128.96, 127.56, 126.34. **HRMS** (ESI-TOF) *m/z* calculated for $C_{12}H_9ClNaO_2S_2^+$ $(M + Na)^+$ 306.9625, found 306.9617.

4.2.6. S-(4-chlorophenyl) 4-fluorobenzenesulfonothioate (*3f*)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.67–7.58 (d, *J* = 8.0 Hz, 2H), 7.40–7.28 (m, 4H), 7.19–7.10 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 166.91, 164.35, 137.70, 130.50, 130.40, 129.88, 116.38, 116.15. **HRMS** (ESI-TOF) *m/z* calculated for $C_{12}H_8ClFNaO_2S_2^+$ $(M + Na)^+$ 324.9531, found 324.9707.

4.2.7. S-phenyl 4-methylbenzenesulfonothioate (*3g*)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.64–7.55 (d, *J* = 8.0 Hz, 2H), 7.54–7.41 (m, 4H), 7.41–7.32 (m, 5H), 7.22 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 136.58, 131.32, 129.45, 129.40, 129.38, 128.81, 127.59, 127.55, 77.26, 21.68. **HRMS** (ESI-TOF) *m/z* calculated for $C_{13}H_{12}NaO_2S_2^+$ $(M + Na)^+$ 287.0171, found 287.0166.

4.2.8. S-(4-aminophenyl) 4-methylbenzenesulfonothioate (*3h*)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.53–7.46 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.16–7.07 (m, 2H), 6.63–6.54 (m, 2H), 4.05 (s, 2H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 149.69, 144.35, 140.43, 138.31, 129.32, 127.64, 115.22, 114.90, 77.25, 21.67. **HRMS** (ESI-TOF) *m/z* calculated for $C_{13}H_{13}NNaO_2S_2^+$ $(M + Na)^+$ 302.0280, found 302.0281.

4.2.9. S-(p-tolyl) 4-methylbenzenesulfonothioate (*3i*)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.48–7.43 (d, *J* = 8.0 Hz, 2H), 7.26–7.20 (m, 4H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 144.72, 142.12, 140.34, 136.45, 130.25, 129.43, 127.55, 124.52, 21.69, 21.51. **HRMS** (ESI-TOF) *m/z* calculated for $C_{14}H_{14}NaO_2S_2^+$ $(M + Na)^+$ 301.0327, found 301.0321.

4.2.10. S-(4-methoxyphenyl) 4-methylbenzenesulfonothioate (*3j*)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.51–7.44 (m, 2H), 7.32–7.25 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.27–7.20 (m, 2H), 6.90–6.82 (m, 2H), 3.85 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 162.25, 144.56, 138.33, 129.38, 127.61, 118.75, 114.94, 55.48, 21.67. **HRMS** (ESI-TOF) *m/z* calculated for $C_{14}H_{14}NaO_3S_2^+$ $(M + Na)^+$ 317.0277, found 317.0271.

4.2.11. S-(4-chlorophenyl) 4-methylbenzenesulfonothioate (*3k*)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.52–7.44 (d, *J* = 8.0 Hz, 2H), 7.38–7.27 (m, 4H), 7.25 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 145.05, 140.13, 138.17, 137.72, 129.71, 129.55, 127.59, 126.52, 21.71. **HRMS** (ESI-TOF) *m/z* calculated for $C_{12}H_{11}ClNaO_2S_2^+$ $(M + Na)^+$ 320.9782, found 320.9776.

4.2.12. S-(p-tolyl) 4-chlorobenzenesulfonothioate (*3l*)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.55–7.49 (d, *J* = 8.0 Hz, 2H), 7.46–7.37 (d, *J* = 8.0 Hz, 2H), 7.31–7.23 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 142.43, 141.56, 140.16, 136.47, 130.39, 129.07, 128.96, 124.12, 21.50. **HRMS** (ESI-TOF) *m/z* calculated for $C_{13}H_{11}ClNaO_2S_2^+$ $(M + Na)^+$ 320.9781, found 320.9776.

4.2.13. S-(4-methoxyphenyl) 4-chlorobenzenesulfonothioate (*3m*)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.56–7.48 (m, 2H), 7.46–7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 6.8 Hz, 2H), 6.93–6.84 (m, 2H), 3.86 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 162.47, 141.46, 140.14, 138.33, 129.10, 128.99, 118.18, 115.14, 77.25, 55.53. **HRMS** (ESI-TOF) *m/z* calculated for $C_{13}H_{11}ClNaO_3S_2^+$ $(M + Na)^+$ 336.9730, found 337.9720.

S-(4-chlorophenyl) 4-chlorobenzenesulfonothioate (**3n**).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.35 (d, 2 H, *J* = 8.4 Hz),

7.39 (d, 2 H, J = 8.8 Hz), 7.46 (d, 2 H, J = 9.2 Hz), 7.52 (d, 2 H, J = 8.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-d) δ 141.31, 140.56, 138.56, 137.68, 129.92, 129.28, 128.93, 126.02. **HRMS** (ESI-TOF) *m/z* calculated for $C_{12}H_8Cl_2NaO_2S_2^+$ $(M + Na)^+$ 340.9235, found 340.9241.

*4.2.14. S-(thien-2-yl) 4-chlorobenzenesulfonothioate (**3o**)*

^{1}H NMR (400 MHz, Chloroform-d) δ 7.63 (dd, J = 5.3, 1.3 Hz, 1H), 7.58−7.51 (m, 2H), 7.27 (d, J = 9.2 Hz, 2H), 7.16 (dd, J = 3.7, 1.3 Hz, 1H), 7.08 (dd, J = 5.4, 3.7 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 145.16, 139.41, 139.36, 135.16, 129.56, 128.37, 127.85, 125.27, 21.75. **HRMS** (ESI-TOF) *m/z* calculated for $C_{10}H_7ClNaO_2S_3^+$ $(M + Na)^+$ 312.9189, found 312.3608.

*4.2.15. S-p-tolyl methanesulfonothioate (**3p**)*

^{1}H NMR (400 MHz, Chloroform-d) δ 7.63, 7.62, 7.61, 7.60, 7.60, 7.59, 7.32, 7.32, 7.32, 7.31, 7.30, 7.30, 7.30, 7.30, 7.30, 7.29, 7.28, 3.19, 2.44.**^{13}C NMR** (101 MHz, Chloroform-d) δ 142.47, 136.17, 130.69, 124.54, 47.20, 21.46. **HRMS** (ESI-TOF) *m/z* calculated for $C_8H_{10}NaO_2S_2^+$ $(M + Na)^+$ 225.0014, found 225.0009.

4.3. General procedure for the synthesis of compounds 5a-p

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, benzenesulfinate salt **1a** (0.6 mmol), phenols **4a** (0.3 mmol), sodium iodide (0.2 equiv), MeCN (5 mL) was added. The bottle was equipped with platinum plate (10 mm × 10 mm) as the anode and platinum plate (10 mm × 10 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA at room temperature for 4 h. After completion of the reaction, as indicated by TLC and GC-MS, the pure product was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 40−30 : 1). The same procedure was applied to the production of other compounds **5a-p**.

*4.3.1. p-tolyl benzenesulfonate (**5a**)*

^{1}H NMR (400 MHz, Chloroform-d) δ 7.83 (d, J = 7.5 Hz, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 2.29 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 147.45, 137.11, 135.41, 134.26, 130.17, 129.18, 128.46, 122.01, 20.84. **HRMS** (ESI-TOF) *m/z* calculated for $C_{13}H_{12}NaO_3S^+$ $(M + Na)^+$ 271.0399, found 271.0395.

*4.3.2. p-tolyl 4-methylbenzenesulfonate (**5b**)*

^{1}H NMR (400 MHz, Chloroform-d) δ 7.76−7.69 (m, 2H), 7.32 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.3 Hz, 2H), 6.90−6.84 (m, 2H), 2.47 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 147.51, 145.17, 136.92, 130.07, 129.68, 128.89, 128.54, 122.07, 21.70, 20.87. **HRMS** (ESI-TOF) *m/z* calculated for $C_{14}H_{14}NaO_3S^+$ $(M + Na)^+$ 280.0556, found 280.0991.

*4.3.3. m-tolyl 4-methylbenzenesulfonate (**5c**)*

^{1}H NMR (400 MHz, Chloroform-d) δ 7.73 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.15 (t, J = 7.9 Hz, 1H), 7.08−7.04 (m, 1H), 6.88 (s, 1H), 6.77−6.72 (m, 1H), 2.46 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 149.61, 145.29, 139.97, 132.59, 129.71, 129.22, 128.49, 127.86, 122.99, 119.13, 21.69, 21.23. **HRMS** (ESI-TOF) *m/z* calculated for $C_{14}H_{14}NaO_3S^+$ $(M + Na)^+$ 285.0556, found 280.0991.

*4.3.4. 4-Chlorophenyl benzenesulfonate (**5d**)*

^{1}H NMR (400 MHz, Chloroform-d) δ 7.84 (d, J = 7.3 Hz, 2H), 7.70 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.9 Hz, 2H), 7.26 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 147.98, 135.03, 134.48, 132.89, 129.77, 129.29, 128.50, 123.75. **HRMS** (ESI-TOF) *m/z* calculated for $C_{12}H_9ClNaO_3S^+$ $(M + Na)^+$ 290.9853, found 290.9842.

*4.3.5. 4-Chlorophenyl 4-methylbenzenesulfonate (**5e**)*

^{1}H NMR (400 MHz, Chloroform-d) δ 7.71 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 2.46 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 148.05, 145.72, 132.77, 131.96, 129.91, 129.73, 128.53, 123.81, 21.74. **HRMS** (ESI-TOF) *m/z* calculated for $C_{13}H_{11}ClNaO_3S^+$ $(M + Na)^+$ 305.0010, found 305.0000.

*4.3.6. 4-Bromophenyl 4-methylbenzenesulfonate (**5f**)*

^{1}H NMR (400 MHz, Chloroform-d) δ 7.71 (d, J = 8.4 Hz, 2H), 7.46−7.37 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 2.47 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 148.62, 145.68, 132.73, 132.02, 129.89, 128.53, 124.17, 120.58, 21.74. **HRMS** (ESI-TOF) *m/z* calculated for $C_{13}H_{11}BrNaO_3S^+$ $(M + Na)^+$ 348.9504, found 348.9496.

*4.3.7. 4-Iodophenyl 4-methylbenzenesulfonate (**5g**)*

^{1}H NMR (400 MHz, Chloroform-d) δ 7.71 (dd, J = 8.3, 1.5 Hz, 2H), 7.61 (dd, J = 8.7, 1.9 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 8.8 Hz, 2H), 2.46 (d, J = 2.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 149.47, 145.71, 138.75, 132.01, 129.92, 128.53, 124.51, 91.78, 21.78. **HRMS** (ESI-TOF) *m/z* calculated for $C_{13}H_{11}INaO_3S^+$ $(M + Na)^+$ 396.9366, found 396.9359.

*4.3.8. 4-Cyanophenyl 4-methylbenzenesulfonate (**5h**)*

^{1}H NMR (400 MHz, Chloroform-d) δ 7.72 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.7 Hz, 2H), 2.47 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 152.57, 146.15, 133.91, 131.83, 130.07, 128.46, 123.45, 117.74, 111.20. **HRMS** (ESI-TOF) *m/z* calculated for $C_{14}H_{11}NNaO_3S^+$ $(M + Na)^+$ 296.0352, found 296.0339.

*4.3.9. 4-Nitrophenyl benzenesulfonate (**5i**)*

^{1}H NMR (400 MHz, Chloroform-d) δ 8.21 (d, J = 9.1 Hz, 2H), 7.88 (d, J = 7.1 Hz, 2H), 7.75 (t, J = 7.5 Hz, 1H), 7.60 (t, J = 7.9 Hz, 2H), 7.21 (d, J = 9.1 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 153.81, 146.28, 134.89, 134.83, 129.51, 128.45, 125.44, 123.20. **HRMS** (ESI-TOF) *m/z* calculated for $C_{12}H_9NNaO_5S^+$ $(M + Na)^+$ 302.0094, found 302.0319.

*4.3.10. 4-Nitrophenyl 4-methylbenzenesulfonate (**5j**)*

^{1}H NMR (400 MHz, Chloroform-d) δ 8.20 (d, J = 9.1 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 9.2 Hz, 2H), 2.48 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 153.93, 146.26, 146.21, 131.75, 130.12, 128.48, 125.40, 123.22, 21.76. **HRMS** (ESI-TOF) *m/z* calculated for $C_{13}H_{11}NNaO_5S^+$ $(M + Na)^+$ 316.0250, found 316.0235.

*4.3.11. 4-Nitrophenyl 4-chlorobenzenesulfonate (**5k**)*

^{1}H NMR (400 MHz, Chloroform-d) δ 8.24 (d, J = 9.1 Hz, 2H), 7.82 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 8.7 Hz, 2H), 7.23 (d, J = 9.2 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 153.58, 146.41, 141.83, 133.24, 129.92, 129.84, 125.56, 123.15. **HRMS** (ESI-TOF) *m/z* calculated for $C_{12}H_8ClNNaO_5S^+$ $(M + Na)^+$ 335.9704, found 336.0381.

*4.3.12. 4-Nitrophenyl 4-fluorobenzenesulfonate (**5l**)*

^{1}H NMR (400 MHz, Chloroform-d) δ 8.23 (d, J = 9.1 Hz, 2H), 7.91 (dd, J = 8.9, 4.9 Hz, 2H), 7.31−7.20 (m, 5H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 165.08, 153.63, 131.47, 131.37, 125.54, 123.18, 117.13, 116.90. **HRMS** (ESI-TOF) *m/z* calculated for $C_{12}H_8FNNaO_5S^+$ $(M + Na)^+$ 319.9999, found 320.0185.

*4.3.13. Naphtha-2-yl 4-methylbenzenesulfonate (**5 m**)*

^{1}H NMR (400 MHz, Chloroform-d) δ 7.87–7.82 (m, 1H), 7.76 (t, J = 8.8 Hz, 4H), 7.55–7.47 (m, 3H), 7.32 (d, J = 8.1 Hz, 2H), 7.12 (dd, J = 8.9, 2.4 Hz, 1H), 2.47 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 147.25, 145.51, 133.47, 132.45, 131.92, 129.85, 129.82, 128.56, 127.89, 127.80, 126.93, 126.45, 121.19, 119.98, 21.71. **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{14}NaO_3S^+$ $(M + Na)^+$ 321.0556, found 321.0545.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence our work reported in this paper.

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Appendix A. Supplementary data

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