JOC The Journal of Organic Chemistry

pubs.acs.org/joc Article

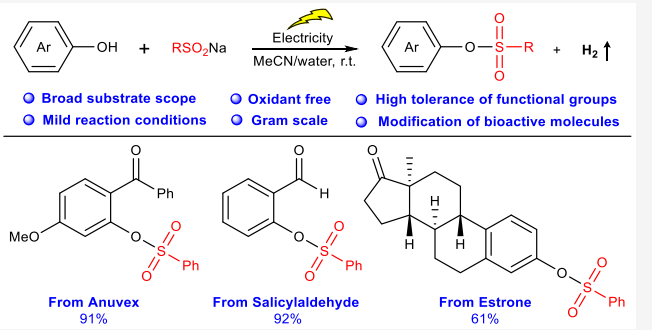
# Practical Electro-Oxidative Sulfonylation of Phenols with Sodium Arenesulfinates Generating Arylsulfonate Esters

Zhibin Tian, Qihang Gong, Tianzeng Huang, Long Liu, and Tieqiao Chen*

Cite This: https://doi.org/10.1021/acs.joc.1c00260 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

**ABSTRACT:** A practical and sustainable synthesis of arylsulfonate esters has been developed through electro-oxidation. This reaction employed the stable and readily available phenols and sodium arenesulfinates as the starting materials and took place under mild reaction conditions without additional oxidants. A wide range of arylsulfonate esters including those bearing functional groups were produced in good to excellent yields. This reaction could also be conducted at a gram scale without a decrease of reaction efficiency. Those results well demonstrated the potential synthetic value of this reaction in organic synthesis.





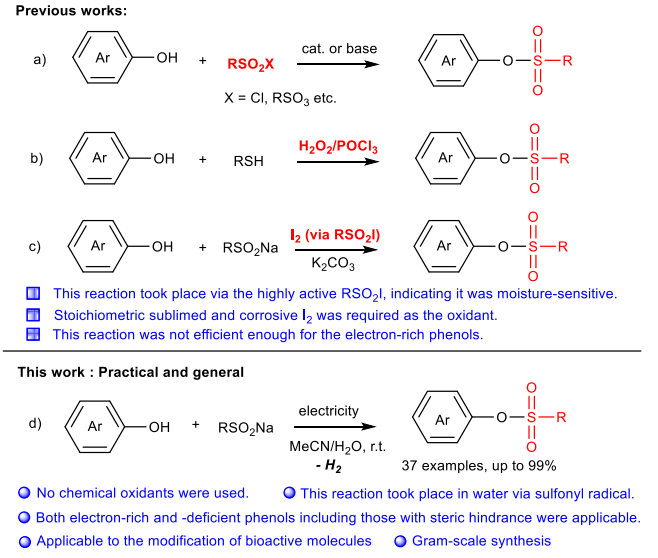

## INTRODUCTION

Electro-oxidation uses electrons as clean redox reagents and is recognized as an environmentally friendly alternative[1] to chemical oxidation, which requires additional overstoichiometric oxidants.[2] During the past decades, great progress has been made, and many groups such as Lei's group,[1c,3] Xu's group,[4] and Baran's group[5] have contributed greatly to this field.

Arylsulfonate esters are a type of important compound commonly occurring in many drugs and materials.[6] Those compounds are also valuable building blocks and widely used in coupling chemistry.[7] However, methods for their synthesis are limited and usually suffer from harsh reaction conditions and (or) compatibility issues with functional groups. Thus, the nucleophilic substitution of active sulfonyl reagents like sulfonyl halides and sulfonic anhydrides with phenols was extensively used for their synthesis (Scheme 1a).[8] The reaction of phenols with thiols using a $H_2O_2/POCl_3$ system could also produce arylsulfonate esters (Scheme 1b).[9] In 2015, Yuan and coauthors reported an oxidative sulfonylation of phenols with sodium sulfinates[10] using a stoichiometric amount of sublimed and corrosive $I_2$ as the oxidant (Scheme 1c).[11] This reaction took place via the highly active $RSO_2I$, indicating it was moisture sensitive. In addition, the reaction does not seem efficient enough for the electron-rich phenols, since high yields were obtained with electron-deficient phenols, while for the electron-rich phenols, only derivatives bearing alkyl group at the benzene ring were demonstrated with moderate yields. There also were no substrates with high steric hindrance reported.

Herein, we reported a practical, clean, and general synthesis of arylsulfonate esters starting from phenols and sodium arenesulfinates through electro-oxidation in MeCN/water (Scheme 1d). This reaction was conducted in an undivided cell and avoided the use of chemical oxidants. Both electron-rich and electron-deficient phenols including those with high

**Scheme 1. Methods for the Synthesis of Arylsulfonate Esters**




**Special Issue:** Electrochemistry in Synthetic Organic Chemistry

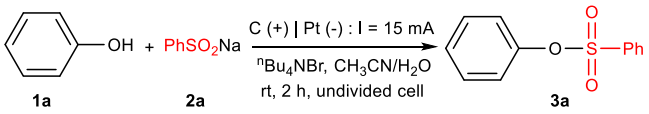
**Received:** February 2, 2021

steric hindrance coupled with sodium arenesulfinates readily to produce the corresponding arylsulfonate esters in high yields. Wide functional group tolerance was also observed; i.e., alkyl, MeO, MeS, $CF_3O$, F, Cl, Br, ester, carbonyl, aldehyde and vinyl groups all survived well under the reaction conditions. These advantages are also the embodiment of sustainable chemical principles.[12]

## RESULTS AND DISCUSSION

It is reported that phenolic radical can be generated under the electrochemical conditions. The strategy has been extensively applied in the synthesis of various phenols.[3m,13] Therefore, the challenge of this reaction is the competing generation of phenolic radicals which might homocouple to produce biphenols[14] or cross couple with arenesulfinates to produce *o*-hydroxyl arylsulfones.[15] We chose the oxidative coupling of phenol **1a** with sodium benzenesulfinate **2a** as the model reaction and successfully overcame the challenge after extensive reaction optimization. Thus, when the reaction was carried out in an undivided cell with the use of graphite rod as an anode, platinum plate as a cathode, and tetrabutylammonium bromide ($^nBu_4NBr$) as an electrolyte, the corresponding product **3a** was generated almost quantitatively in the MeCN/$H_2O$ mixing solvent under a 15 mA constant current (Table 1, entry 1). The current yield is ca. 35.7%. When the reaction time was reduced to 1 h, only 66% yield of **3a** was produced (Table 1, entry 2). KBr worked comparably to $^nBu_4NBr$ as an electrolyte; KCl also gave a good yield; while low yields of **3a** were given with $^nBu_4NBF_4$, $^nBu_4NI$, or KI or in the absence of electrolyte (Table 1, entries 3−8). Under the premise of constant electric quantity, the electric current was subsequently screened with 15 mA being the best choice (Table 1, entries 1, 9, and 10). Without $H_2O$ or $CH_3CN$, the yield of **3a** dramatically decreased (Table 1, entries 11 and 12). The results would be ascribed to the poor solubility of sodium benzenesulfinate in MeCN and phenol in water. The reaction could also proceed smoothly in THF/$H_2O$ (Table 1, entry 13) but poorly in MeOH/$H_2O$ (Table 1, entry 14). By addition of 2 equiv of NaOH, the yield slightly decreased (Table 1, entry 15). Probably due to the suppressed generation of phenolate anion, the reaction progressed sluggishly in the presence of 2 equiv of HOAc (Table 1, entry 16). When the electrodes were switched to Pt(+)|Pt(−) or Pt(+)|C(−), the reaction efficiency decreased to some extent (Table 1, entries 17 and 18). The results might be ascribed to the better hydrogen-producing properties of Pt cathode which would be beneficial to anodic oxidation. A high yield of **3a** was also obtained under $N_2$ atmosphere (Table 1, entry 19). The result ruled out the possibility that air acted as an oxidant in the reaction. Finally, electricity is essential to this reaction, since no reaction took place without electric current (Table 1, entry 20).

**Table 1. Optimization of Reaction Parameters**[a]




| entry | variation from the standard conditions | yield[b] (%) |
|---|---|---|
| 1 | none | >99 |
| 2 | 15 mA, 1 h | 66 |
| 3 | KBr instead of $^nBu_4NBr$ | 97 |
| 4 | KCl instead of $^nBu_4NBr$ | 76 |
| 5[c] | $^nBu_4NBF_4$ instead of $^nBu_4NBr$ | 45 |
| 6[c] | $^nBu_4NI$ instead of $^nBu_4NBr$ | 18 |
| 7[c] | KI instead of $^nBu_4NBr$ | 12 |
| 8 | without $^nBu_4NBr$ | 35 |
| 9 | 30 mA, 1 h | 96 |
| 10 | 7.5 mA, 4 h | 86 |
| 11 | without $H_2O$ | 43 |
| 12 | without $CH_3CN$ | 9 |
| 13 | THF instead of $CH_3CN$ | 82 |
| 14 | MeOH instead of $CH_3CN$ | 40 |
| 15 | add to 2 equiv of NaOH | 74 |
| 16 | add to 2 equiv of HOAc | 3 |
| 17 | Pt(+)\|Pt(−) | 82 |
| 18 | Pt(+)\|C(−) | 59 |
| 19 | under $N_2$ | 89 |
| 20 | no electric current | n.d. |

[a]Reaction conditions: graphite rod anode (Φ 6 mm), platinum plate cathode (15 mm × 15 mm × 0.1 mm), constant current = 15 mA, **1a** (0.20 mmol), **2a** (0.30 mmol), $^nBu_4NBr$ (2.0 equiv), $CH_3CN$ (7.0 mL), $H_2O$ (0.50 mL), room temperature, 2 h, undivided cell. [b]The yield of **3a** was determined by GC using tridecane as the internal standard, nd = not detected. [c]The surface of graphite rod was damaged.

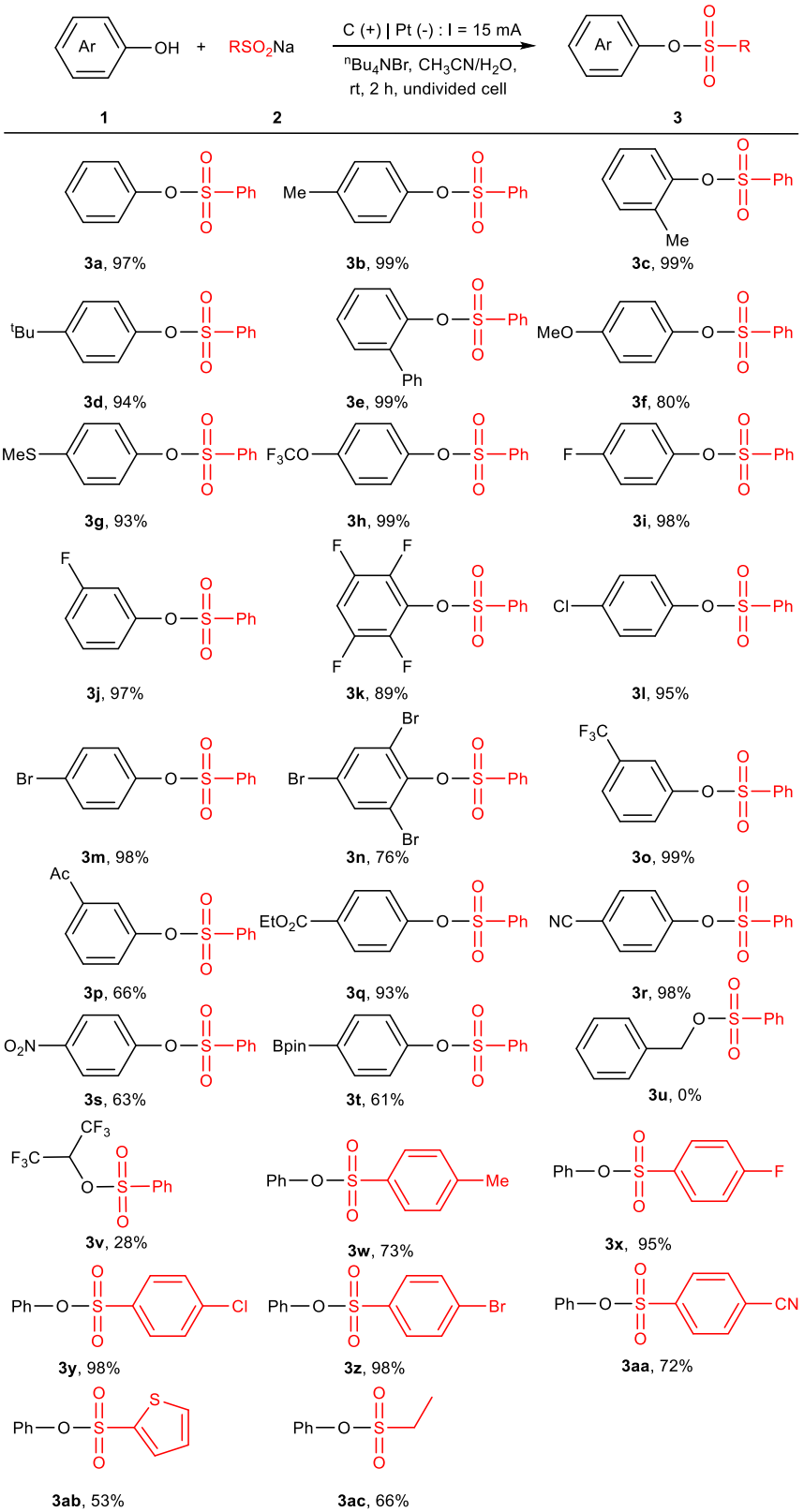
With the optimized reaction conditions in hand, we subsequently investigated the substrate scope. As shown in Table 2, a variety of phenols coupled readily with sodium arenesulfinates produced the corresponding sulfonate esters in high yields. Thus, phenols bearing methyl, *tert*-butyl, phenyl, methoxy, thiomethoxy, and the easily hydrolyzed trifluoromethoxy all were transformed smoothly into the expected products (**3b**−**3h**). Worth noting is that the substrates with high steric hindrance exemplified as **3c** and **3e** served well under the reaction conditions. Halo groups like fluoro, chloro and bromo groups were compatible, facilitating further functionalization of the products via cross coupling (**3i**−**3o**). The electron-deficient phenols also proved to be the right substrates, furnishing the desired products in excellent yields (**3p**−**3t**). Under the reaction conditions, 1,1,1,3,3,3-hexafluoropropan-2-ol could also give the coupling product **3u** in 28% yield. However, 2-phenylethan-1-ol was not applicable to this reaction (**3v**). As for the scope of sodium arenesulfinates, derivatives bearing Me, F, Cl, Br, and CN all served well as the substrates. It is worth mentioning that heteroaromatic cyclic sodium 2-thiophene sulfinate and aliphatic sodium ethyl sulfinate could also give the corresponding arylsulfonate esters **3ab** and **3ac** in good yields under the current reaction conditions.

Notably, this reaction was applicable to the modification of bioactive phenols (Scheme 2). Hordenine, raspberry ketone, eugenol, salicylaldehyde, anuvex, methyl vanillate, and estrone all coupled with sodium benzenesulfinate to produce the corresponding arylsulfonate esters (**3ad**−**3ak**). Regarding the high reactivity of arylsulfonate esters in coupling chemistry, this reaction provided a reliable indirect method for the modification of those bioactive and medicinal phenols.

Practically, this reaction could be scaled up. As shown in Scheme 3, phenol (**1a**, 12 mmol) coupled readily with sodium benzenesulfinate (**2a**, 18 mmol) under the optimal reaction conditions (the electricity amount was also increased in 60 times by increasing the time and (or) electric current). After evaporation and passing of the reaction residue through a short $SiO_2$ chromatographic column, the analytically pure **3a** was obtained in high yields.


https://doi.org/10.1021/acs.joc.1c00260
J. Org. Chem. XXXX, XXX, XXX−XXX

**Table 2. Electro-Oxidative Sulfonylation of Phenols with Sodium Sulfinates**[a]



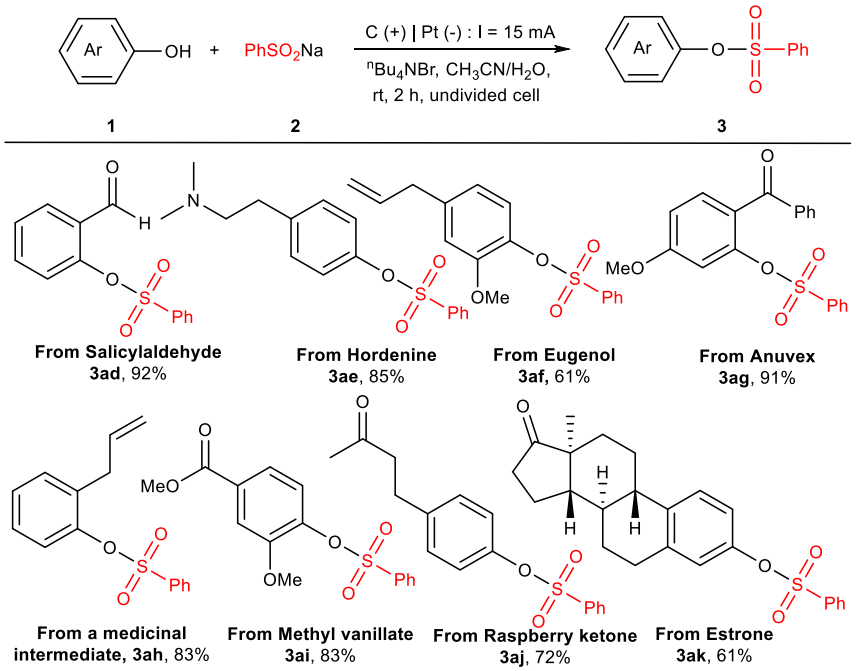

[a]Reaction conditions: graphite rod anode, platinum plate cathode, constant current = 15 mA, **1** (0.20 mmol), **2** (0.30 mmol), $^{n}Bu_4NBr$ (2.0 equiv), $CH_3CN$ (7.0 mL), $H_2O$ (0.50 mL), room temperature, air, 2 h. Isolated yields.

In order to gain insight into the reaction mechanism, several control experiments were conducted. When electron-rich **1d** and electron-deficient **1r** were allowed to couple with **2a** competitively, the product from electron-rich phenol was more favored (Scheme 4, eq 1). By addition of 2 equiv of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, a radical scavenger), the



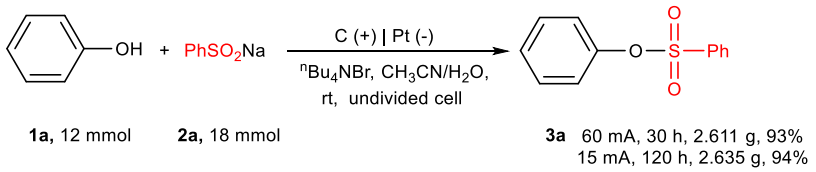
https://doi.org/10.1021/acs.joc.1c00260
J. Org. Chem. XXXX, XXX, XXX−XXX

**Scheme 2. Modification of Bioactive Phenols**[a]

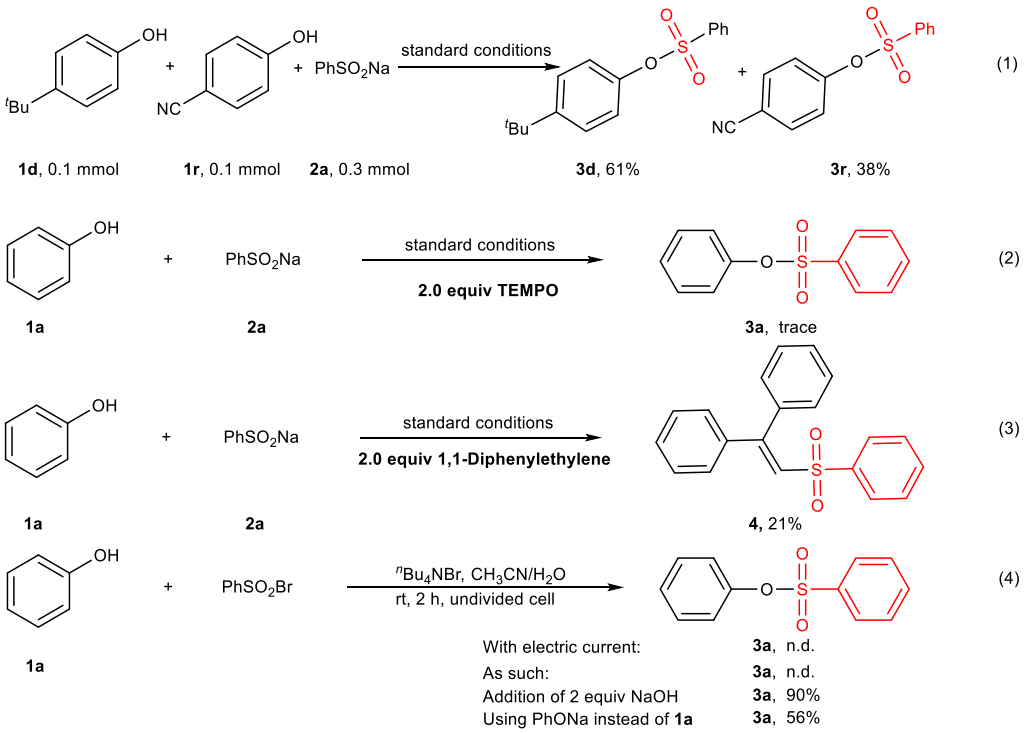



[a]Reaction conditions: graphite rod anode, platinum plate cathode, constant current = 15 mA, **1** (0.20 mmol), **2** (0.30 mmol), $^{n}Bu_4NBr$ (2.0 equiv), $CH_3CN$ (7.0 mL), $H_2O$ (0.50 mL), room temperature, air, 2 h. Isolated yields.

**Scheme 3. Gram-Scale Synthesis**




**Scheme 4. Control Experiments**






https://doi.org/10.1021/acs.joc.1c00260
J. Org. Chem. XXXX, XXX, XXX−XXX

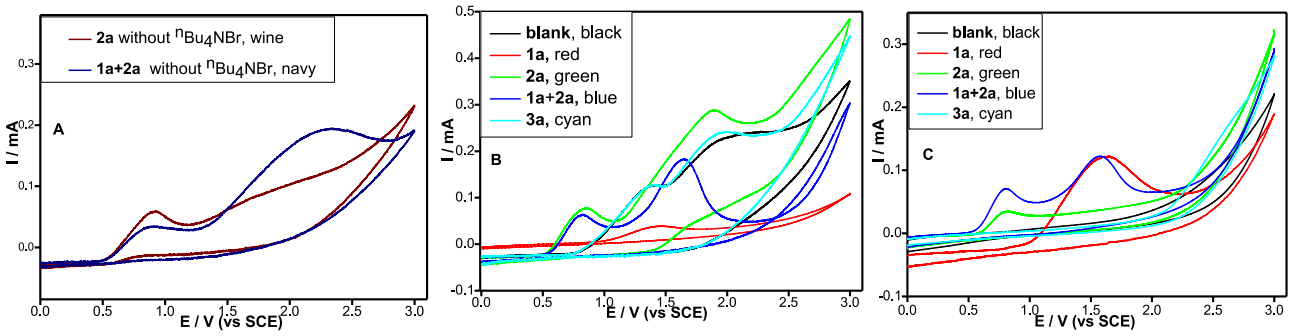
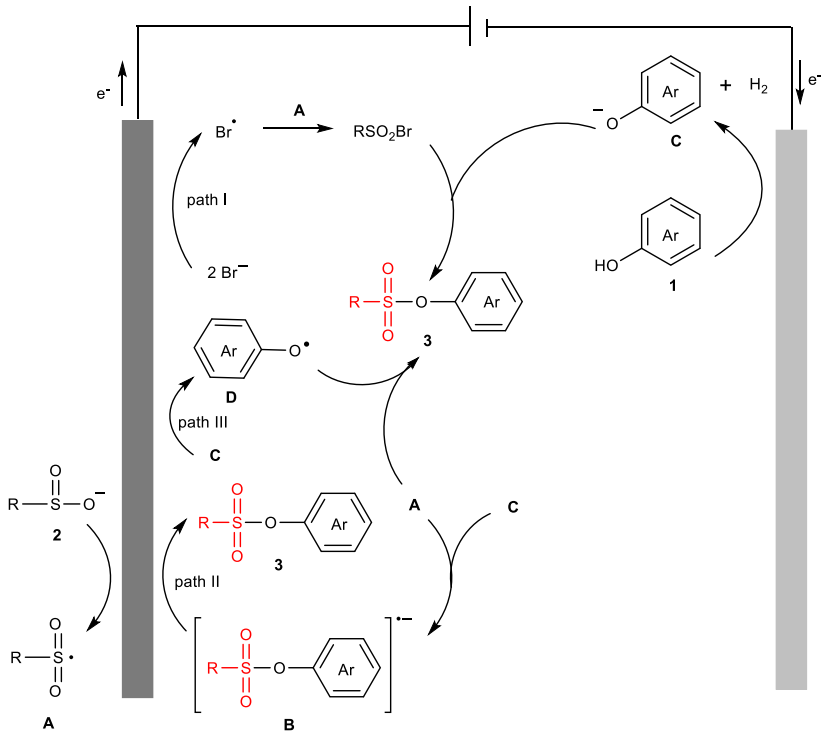



**Figure 1.** Cyclic voltammograms of reactants using a glassy carbon working electrode, a platinum plate counter electrode and a SCE electrode submerged in saturated KCl solution as the reference. (A) Cyclic voltammograms in $CH_3CN$ and $H_2O$, **1a** (0.01 M), **2a** (0.01 M), **3a** (0.01 M). (B) Cyclic voltammograms in $CH_3CN$ and $H_2O$ with 0.01 M $^nBu_4NBr$, **1a** (0.01 M), **2a** (0.01 M), **3a** (0.01 M). (C) Cyclic voltammograms in $CH_3CN$ and $H_2O$ with 0.01 M $^nBu_4NBF_4$, **1a** (0.01 M), **2a** (0.01 M), **3a** (0.01 M).

**Scheme 5. Proposed Mechanism**




electro-oxidative coupling reaction of **1a** with **2a** was suppressed almost completely (Scheme 4, eq 2). The result indicated that this reaction might take place through a radical process. The hypothesis was further supported by a control experiment. When 2 equiv of 1,1-diphenylethylene was added under the standard reactions, the coupling product **4** was obtained in 21% GC yield, implying the generation of a sulfonyl radical in the reaction (Scheme 4, eq 3). Meanwhile, it is possible that $Br^-$ might be oxidized under the reaction conditions, and the resulting oxidative product would further react with $PhSO_2Na$ or its radical to produce benzenesulfonyl bromide ($PhSO_2Br$),[16] which might act as an active intermediate in this reaction. Thus, we synthesized $PhSO_2Br$ and allowed it to react with phenol (Scheme 4, eq 4);[17,18] however, no **3a** was detected with or without electric current. This result might be ascribed to the absence of phenolate anion under the reaction conditions. Indeed, by addition of 2 equiv NaOH, the yield of **3a** was 90%. Using PhONa instead of PhOH, **3a** was produced in 56% yield under similar reaction conditions.

The cyclic voltammetric (CV) measure was also performed (Figure 1). In the absence of electrolyte, **2a** has a peak at 0.85 V (Figure 1A, wine) (the CV measure of **1a** was also conducted, but no useful signs were obtained probably due to the low conductivity), the mixture of **1a**+**2a** has two peaks at 0.84 and 2.20 V (Figure 1A, navy). In the presence of electrolyte $^nBu_4NBF_4$, **1a** has a peak at 1.59 V (Figure 1C, red), **2a** has a peak at 0.81 V (Figure 1C, green), the mixture of **1a** +**2a** has two peaks at 0.81 and 1.59 V (Figure 1C, blue). When $^nBu_4NBr$ was used as the electrolyte, it has two oxidation peaks of its own at 1.34 and 1.88 V (Figure 1B, black).[19] Compound **1a** has a weak peak at 1.39 V (0.02 M) (Figure 1B, red), **2a** has two peaks at 0.84 and 1.86 V (Figure 1B, green), the mixture of **1a**+**2a** has two peaks at 0.82 and 1.62 V (Figure 1B, blue), and **3a** has almost the same curve as $^nBu_4NBr$ (Figure 1B, cyan). Those data indicate that **2a** was first oxidized to produce radical under these reaction conditions. The oxidative


https://doi.org/10.1021/acs.joc.1c00260
J. Org. Chem. XXXX, XXX, XXX−XXX

potential of **1a** might also be 1.39 V when using $^{n}Bu_4NBr$ as the electrolyte; however, at present, it is difficult to distinguish the peak at 1.62 V in the curve of the mixture of **1a**+**2a** in the presence of $^{n}Bu_4NBr$ to be the oxidative peak of **2a** or $Br^-$.

On the basis of these control experiments, previous literatures[10] and cyclic voltammetric (CV) results, we proposed that this reaction might take place through different processes under different reaction conditions (Scheme 5). Under all these reaction conditions, cathodic reduction of phenol with the generation of phenolate anion **C** and dihydrogen would take place. In the absence of external electrolyte, sodium phenylsulfinates **2** were oxidized to give a sulfonyl radical **A** at the anode, which then reacted with **C** to produce the intermediate **B**. The intermediate **B** was oxidized to produce the product **3** at the anode. Due to the inefficient migration through the solution of unstable radical anion **B**, the yield was low under the reaction conditions. When $^{n}Bu_4NBF_4$ was used as the electrolyte, it would be a radical/radical coupling process that sulfonyl radical **A** coupled with phenoxy radical generated at the anode to produce the corresponding product. When $^{n}Bu_4NBr$ was used as the electrolyte, we proposed that sulfonyl radical **A** might couple with Br radical to produce arenesulfonyl bromide, which then reacted with phenolate anion **C** to produce the product. It should be noted the radical/radical coupling cannot be excluded out completely in the absence of external electrolyte or with $^{n}Bu_4NBr$ at present.

## CONCLUSIONS

In conclusion, we have disclosed an electro-oxidative sulfonylation of phenols with sodium arenesulfinates under mild reaction conditions. This reaction avoided the use of external stoichiometric oxidant, and showed wide substrate scope and high functional group tolerance. The scale-up (gram-scale) experiment also demonstrated its potential practicality in organic synthesis. This reaction provided a clean and general method for the synthesis of arylsulfonate esters.

## EXPERIMENTAL SECTION

**General Information.** The reactions were carried out in an oven-dried undivided three-necked bottle (25 mL) stirred at room temperature. For reactions that require heating, a heating mantle was used as the heat source. Phenols were used as received. Sodium sulfinates except sodium 4-cyanobenzenesulfinate (**2aa**) and sodium 2-thiophenesulfinate (**2ab**) were purchased for direct use. Other reagents such as electrolytes, acids, and base were also used as received. Solvents were purified according to standard operation procedures. The instrument for electrolysis is a dual-display potentiostat (DJS-292B) (made in China). The anodic electrode was a graphite rod (Ø 6 mm), and the cathodic electrode was platinum plate (15 mm × 15 mm × 0.1 mm). Column chromatography was performed using silica gel 60 (200−300 mesh). The reactions were monitored by GC and GC−MS. GC−MS results were recorded on a GC−MS QP2010, and GC analysis was performed on GC 2014. The $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker ADVANCE III spectrometer at 400 and 100 MHz, respectively, and chemical shifts were reported in parts per million (ppm). The electron ionization (EI) method was used as the ionization method for the HRMS measurement, and the mass analyzer type is TOF for EI. All solvents and reagents purchased were from Energy Chemical, Alfa Aesar, and Aladdin.

**General Experimental Procedure for the Electro-oxidative Esterification of Phenols with Sodium Benzensulfinates to Access Arylsulfonate Esters.** An oven-dried undivided three-necked bottle (25 mL) was charged with phenols **1** (0.2 mmol), sodium benzenesulfinates **2** (0.3 mmol, 1.5 equiv), and $^{n}Bu_4NBr$ (0.4 mmol, 2.0 equiv). The bottle was then equipped with graphite rod (Ø 6 mm, about 15 mm immersion depth in solution) as the anode and platinum plate (15 mm × 15 mm × 0.1 mm) as the cathode. Subsequently, acetonitrile (7 mL) and deionized water (0.5 mL) were added under air. Then the electrolysis system was stirred at a constant current of 15 mA under room temperature for 2 h. After completion of the reaction, the reaction mixture was extracted with EtOAc (3 × 10 mL) and $H_2O$ (3 × 10 mL), dried over $Na_2SO_4$, and concentrated under vacuum. The desired product was isolated by column chromatography over silica gel (200−300 mesh) using ethyl acetate−petroleum ether as the eluent (1:5).

*Procedure for the Synthesis of Sodium Sulfinates (**2aa** and **2ab**).*[11] Sodium 4-cyanobenzenesulfinate (**2aa**) was prepared by heating 2.01 g of 4-cyanobenzenesulfonyl chloride with a heating mantle, 1.68 g of sodium bicarbonate, and 2.5 g of sodium sulfite in 9 mL of water at 80 °C for 6 h. Water was removed under vacuum after cooling to room temperature. The residue was extracted by ethanol. The pure product (white solid) was obtained in 55% yield (1.04 g) via recrystallization. Similarly, sodium 2-thiophenesulfinate (**2ab**) was prepared from the corresponding sulfonyl chloride. **Sodium 4-cyanobenzenesulfinate (2aa).** $^{1}H$ NMR (400 MHz, $CD_3OD$): $\delta$ 7.80 (d, $J$ = 1.2 Hz, 4 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):$\delta$ 162.3, 133.5, 128.9, 126.3, 125.4, 119.5, 113.9. HRMS (ESI-TOF) $m/z$: $[M + Na]^+$ Calcd for $C_7H4NNa_2O_2S$ 211.9753; Found 211.9748. **Sodium 2-thiophenesulfinate (2ab).** $^{1}H$ NMR (400 MHz, $CD_3OD$): $\delta$ 7.47 (dd, $J_1$ = 4.8 Hz, $J_2$ = 1.2 Hz, 2H), 7.24 (dd, $J_1$ = 3.6 Hz, $J_2$ = 1.2 Hz, 2H), 7.01 (dd, $J_1$ = 4.8 Hz, $J_2$ = 3.6 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CD_3OD$):$\delta$ 162.7, 128.2, 127.9, 126.3. HRMS (ESI-TOF) $m/z$: $[M + Na]^+$ Calcd for $C_4H_3Na_2O_2S_2$ 192.9364; Found 192.9368.

*Procedure for the Synthesis of Benzenesulfonyl Bromide from Sodium Benzensulfinate.*[16] A 25 mL Schlenk tube was charged with sodium benzenesulfinate (164 mg, 1.0 mmol), NBS (267 mg, 1.5 mmol), and DCM (6 mL). The mixture was stirred at room temperature for 12 h. After completion of the reaction, the reaction mixture was extracted with ethyl acetate (3 × 5 mL), and the combined organic layer was dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure. The crude product obtained was purified by column chromatography over silica gel (200−300 mesh).

**Procedure for Gram-Scale Synthesis of 3a.** An oven-dried undivided three-necked bottle (250 mL) was charged with phenol **1a** (1129.3 mg, 12 mmol), sodium benzenesulfinates **2a** (3939.8 mg, 18 mmol, 1.5 equiv), and $^{n}Bu_4NBr$ (7736.9 mg, 24 mmol, 2.0 equiv). The bottle was equipped with graphite rod (Ø 6 mm, about 15 mm immersion depth in solution) as the anode and platinum plate (15 mm × 15 mm × 0.1 mm) as the cathode. Subsequently, acetonitrile (150 mL) and deionized water (15 mL) were added under air. Then the electrolysis system was stirred at a constant current of 60 mA (15 mA) at room temperature for 30 h (120 h). After completion of the reaction, the reaction mixture was extracted with EtOAc (3 × 40 mL) and $H_2O$ (3 × 40 mL), dried over $Na_2SO_4$, and concentrated under vacuum. The desired product was isolated by column chromatography over silica gel (200−300 mesh) using ethyl acetate/petroleum ether as eluent. Compound **3a** was obtained in 93% (94%) yield.

**Procedure for the Control Experiment (Scheme 4, eq 1).** An oven-dried undivided three-necked bottle (25 mL) was charged with 4-*tert*-butylphenol **1d** (15.0 mg, 0.1 mmol), 4-hydroxybenzonitrile **1r** (11.9 mg, 0.1 mmol), sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol), and $^{n}Bu_4NBr$ (129 mg, 0.4 mmol). The bottle was equipped with graphite rod as the anode and platinum plate as the cathode. Acetonitrile (7 mL) and deionized water (0.5 mL) were added under air. Then the electrolysis system was stirred at a constant current of 15 mA under room temperature for 2 h. 61% yield of **3d** and 38% yield of **3r** were detected by GC.

**Procedure for the Control Experiment (Scheme 4, eq 2).** An oven-dried undivided three-necked bottle (25 mL) was charged with phenol **1a** (18.8 mg, 0.2 mmol), sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), TEMPO (0.4 mmol, 2.0 equiv), and


https://doi.org/10.1021/acs.joc.1c00260
J. Org. Chem. XXXX, XXX, XXX−XXX

$^{n}Bu_4NBr$ (129 mg, 0.4 mmol, 2.0 equiv). The bottle was equipped with a graphite rod as the anode and platinum plate as the cathode. Acetonitrile (7 mL) and deionized water (0.5 mL) were added under air. Then the electrolysis system was stirred at a constant current of 15 mA under room temperature for 2 h. Only a trace amount of **3a** was detected by GC.

**Procedure for the Control Experiment (Scheme 4, eq 3).** An oven-dried undivided three-necked bottle (25 mL) was charged with phenol **1a** (18.8 mg, 0.2 mmol), sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), 1,1-diphenylethylene (0.4 mmol, 2.0 equiv), and $^{n}Bu_4NBr$ (129 mg, 0.4 mmol, 2.0 equiv). The bottle was equipped with a graphite rod as the anode and platinum plate as the cathode. Acetonitrile (7 mL) and deionized water (0.5 mL) were added under air. Then the electrolysis system was stirred at a constant current of 15 mA under room temperature for 2 h. Vinyl sulfone **4** was produced in 21% isolated yield.

**Procedures for the Control Experiment (Scheme 4, eq 4).** (1) An oven-dried undivided three-necked bottle (25 mL) was charged with phenol **1a** (18.8 mg, 0.2 mmol), benzenesulfonyl bromide (0.3 mmol, 1.5 equiv), and $^{n}Bu_4NBr$ (129 mg, 0.4 mmol, 2.0 equiv). The bottle was equipped with a graphite rod as the anode and platinum plate as the cathode. Acetonitrile (7 mL) and deionized water (0.5 mL) were added under air. Then the electrolysis system was stirred at a constant current of 15 mA under room temperature for 2 h. No **3a** was detected. (2) An oven-dried undivided three-necked bottle (25 mL) was charged with phenol **1a** (18.8 mg, 0.2 mmol), benzenesulfonyl bromide (0.3 mmol, 1.5 equiv), and $^{n}Bu_4NBr$ (129 mg, 0.4 mmol, 2.0 equiv). The bottle was equipped with graphite rod as the anode and platinum plate as the cathode. Acetonitrile (7 mL) and deionized water (0.5 mL) was added under air. Then the electrolysis system was stirred at room temperature for 2 h (electric current was zero). No **3a** was detected. (3) An oven-dried undivided three-necked bottle (25 mL) was charged with phenol **1a** (18.8 mg, 0.2 mmol), benzenesulfonyl bromide (0.3 mmol, 1.5 equiv), $^{n}Bu_4NBr$ (129 mg, 0.4 mmol, 2.0 equiv), NaOH (0.4 mmol, 2.0 equiv), and PhONa (0.2 mmol). The bottle was equipped with a graphite rod as the anode and platinum plate as the cathode. Acetonitrile (7 mL) and deionized water (0.5 mL) were added under air. Then the electrolysis system was stirred at room temperature for 2 h (electric current was zero), 90% yield of **3a** was detected. (4) An oven-dried undivided three-necked bottle (25 mL) was charged with PhONa (0.2 mmol), benzenesulfonyl bromide (0.3 mmol, 1.5 equiv), and $^{n}Bu_4NBr$ (0.4 mmol, 2.0 equiv). The bottle was equipped with a graphite rod as the anode and platinum plate as the cathode. Acetonitrile (7 mL) and deionized water (0.5 mL) were added under air. Then the electrolysis system was stirred room temperature for 2 h (electric current was zero), 56% yield of **3a** was detected by GC.

**Procedure for Cyclic Voltammetry (CV).** Cyclic voltammetry was performed in a three-electrode cell at room temperature. The working electrode was a glassy carbon and the counter electrode a platinum plate. The reference was an SCE electrode submerged in saturated KCl solution. Ten milliliters of $CH_3CN$ (9.5 mL) and $H_2O$ (0.5 mL) containing 0.01 M $^{n}Bu_4NBr$ ($^{n}Bu_4NBF_4$) was poured into the electrochemical cell in all experiments. The CV of all substrates was measured at the concentration of 0.01 M. The scan rate is 0.1 V/s, ranging from 0 to 3.0 V. In the absence of electrolyte, **2a** has a peak at 0.85 V (the CV measure of **1a** was also conducted, but no useful signs were obtained probably due to the low conductivity) and the mixture of **1a**+**2a** has two peaks at 0.84 and 2.20 V. In the presence of electrolyte $^{n}Bu_4NBF_4$, **1a** has a peak at 1.59 V, **2a** has a peak at 0.81 V, and the mixture of **1a**+**2a** has two peaks at 0.81 and 1.59 V. When $^{n}Bu_4NBr$ was used as the electrolyte, it has two oxidation peaks of its own at 1.34 and 1.88 V (black line). Compound **1a** has a weak peak at 1.39 V (0.02 M), **2a** has two peaks at 0.84 and 1.86 V, the mixture of **1a**+**2a** has two peaks at 0.82 and 1.62 V, and **3a** has almost the same curve as $^{n}Bu_4NBr$. Those data indicate that **2a** was first oxidized to produce radical under these reaction conditions. The oxidative potential of **1a** might also be 1.39 V when using $^{n}Bu_4NBr$ as the electrolyte; however, at present, it is difficult to distinguish the peak at 1.62 V in the curve of the mixture of **1a**+**2a** in the presence of $^{n}Bu_4NBr$ to be the oxidative peak of **2a** or $Br^-$.

*Phenyl Benzenesulfonate (**3a**).*[20] The title compound was prepared according to the general procedure using phenol **1a** (18.8 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3a** (45.4 mg, 97% yield) as a colorless oil. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.87(d, $J$ = 7.2 Hz, 2H), 7.7 (t, $J$ = 7.6 Hz, 1H), 7.56 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 7.34−7.26(m, 3H), 7.01(d, $J$ = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$):$\delta$ 149.6, 135.4, 134.1, 129.6, 129.1, 128.4, 127.1, 122.3. This compound is known.

*p-Tolyl Benzenesulfonate (**3b**).*[20] The title compound was prepared according to the general procedure using *p*-cresol **1b** (21.6 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3b** (49.1 mg, 99% yield) as a pale-yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.83 (d, $J$ = 7.2 Hz, 2H), 7.66 (t, $J$ = 7.6 Hz, 1H), 7.52 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 7.06 (d, $J$ = 8.4 Hz, 2H), 6.84 (d, $J$ = 8.4 Hz, 2H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 147.3, 137.0, 135.3, 134.0, 130.0, 129.0, 128.3, 121.8, 20.7. This compound is known.

*O-Tolyl Benzenesulfonate (**3c**).*[20] The title compound was prepared according to the general procedure using *o*-cresol **1c** (21.6 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3c** (49.1 mg, 99% yield) as a pale-yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.87 (d, $J$ = 7.6 Hz, 2H), 7.68 (t, $J$ = 7.6 Hz, 1H), 7.54 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 7.17−7.09 (m, 3H), 6.99 (d, $J$ = 7.2 Hz, 1H), 2.06 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 148.3, 136.1, 134.1, 131.6, 131.5, 129.1, 128.3, 127.0, 126.9, 122.2, 16.2. This compound is known.

*4-tert-Butyl Phenyl Benzenesulfonate (**3d**).*[21] The title compound was prepared according to the general procedure using 4-*tert*-butyl phenol **1d** (30.0 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3d** (54.5 mg, 94% yield) as a colorless oil. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.90 (d, $J$ = 7.2 Hz, 2H), 7.71 (t, $J$ = 7.6 Hz, 1H), 7.58 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 7.33 (d, $J$ = 8.8 Hz, 2H), 6.93 (d, $J$ = 8.8 Hz, 2H), 1.32 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 150.2, 147.2, 135.7, 134.1, 129.1, 128.5, 126.6, 121.6, 34.6, 33.3. This compound is known.

*[1,1′-Biphenyl]-2-yl Benzenesulfonate (**3e**).*[22] The title compound was prepared according to the general procedure using [1,1′-biphenyl]-2-ol **1e** (34.0 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3e** (61.4 mg, 99% yield) as a pale-yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.55 (d, $J$ = 8.0 Hz, 1H), 7.50 (t, $J$ = 7.4 Hz, 1H), 7.45−7.35 (m, 4H), 7.31−7.26 (m, 4H), 7.22 (dd, $J_1 = J_2$ = 8.0 Hz, 2H), 7.17−7.15 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 146.3, 136.4, 135.4, 135.0, 133.5, 131.0, 129.2, 128.6, 128.5, 128.0, 127.9, 127.4, 127.2, 123.8. This compound is known.

*4-Methoxyphenyl Benzenesulfonate (**3f**).*[20] The title compound was prepared according to the general procedure using 4-methoxyphenol **1f** (24.8 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3f** (42.2 mg, 80% yield) as a pale-yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.81 (d, $J$ = 7.2 Hz, 2H), 7.66 (t, $J$ = 7.6 Hz, 1H), 7.51 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 6.87 (d, $J$ = 8.8 Hz, 2H), 6.76 (t, $J$ = 8.8 Hz, 2H), 3.75 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 158.2, 142.9, 135.3, 134.1, 129.0, 128.5, 123.3, 114.4, 55.5. This compound is known.

*4-(Methylthio)phenyl Benzenesulfonate (**3g**).* The title compound was prepared according to the general procedure using 4-(methylthio)phenol **1g** (28.0 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3g** (52.1 mg, 93% yield) as a pale-yellow oil. $^1H$ NMR (400


https://doi.org/10.1021/acs.joc.1c00260
J. Org. Chem. XXXX, XXX, XXX−XXX

MHz, $CDCl_3$): δ 7.83 (d, J = 7.2 Hz, 2H), 7.67 (t, J = 7.6 Hz, 1H), 7.57 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.9, 137.8, 135.2, 134.2, 129.1, 128.5, 127.2, 122.8, 15.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}O_3S_2$ 281.0301; Found 281.0308.

*4-(Trifluoromethoxy)phenyl Benzenesulfonate (**3h**).* The title compound was prepared according to the general procedure using 4-(trifluoromethoxy)phenol **1h** (35.6 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3h** (63.0 mg, 99% yield) as a pale-yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.86−7.83 (m, 2H), 7.72−7.67 (m, 1H), 7.57−7.52 (m, 2H), 7.15−7.12 (m, 2H), 7.03−6.99 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.6 (q, J = 2.0 Hz), 147.5, 135.0, 134.5, 129.3, 128.5, 123.8, 122.1, 120.2 (q, J = 256.4 Hz).

*4-Fluorophenyl Benzenesulfonate (**3i**).*[23] The title compound was prepared according to the general procedure using 4-fluorophenol **1i** (22.4 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3i** (49.4 mg, 98% yield) as a pale-yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 7.2 Hz, 2H), 7.68 (t, J = 7.6 Hz, 1H), 7.54 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 6.99−6.92 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.0 (C−F, $^1J_{C-F}$ = 245.3 Hz), 145.3, 135.0, 134.4, 129.2, 128.5, 124.0 (C−F, $^3J_{C-F}$ = 8.7 Hz), 116.4 (C−F, $^2J_{C-F}$ = 23.6 Hz). This compound is known.

*3-Fluorophenyl Benzenesulfonate (**3j**).* The title compound was prepared according to the general procedure using 3-fluorophenol **1j** (22.4 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3j** (48.9 mg, 97% yield) as a pale-yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 7.2, 2H), 7.74 (t, J = 7.6 Hz, 1H), 7.59 (dd, $J_1 = J_2$ = 8.0 Hz, 2H), 7.33−7.27 (m, 1H), 7.02 (ddd, $J_1 = J_2$ = 8.4 Hz, $J_3$ = 2.4 Hz, 1H), 6.86−6.78 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.6 (C−F, $^1J_{C-F}$ = 247.8 Hz), 150.1 (C−F, $^4J_{C-F}$ = 10.6 Hz), 135.0, 134.5, 130.4 (C−F, $^5J_{C-F}$ = 9.2 Hz), 129.2, 128.4, 118.1 (C−F, $^6J_{C-F}$ = 3.4 Hz), 114.4 (C−F, $^3J_{C-F}$ = 20.9 Hz), 110.4 (C−F, $^2J_{C-F}$ = 24.5 Hz). HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{12}H_8FO_3S$ 251.0184; Found 251.0185.

*2,3,5,6-Tetrafluorophenyl Benzenesulfonate (**3k**).* The title compound was prepared according to the general procedure using 2,3,5,6-tetrafluorophenol **1k** (33.2 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3k** (54.5 mg, 89% yield) as a pale-yellow solid. mp: 64−66 °C. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.99 (m, 2H), 7.77 (m, 1H), 7.64−7.59 (m, 2H), 7.04 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.0 (m), 141.6 (m), 135.2, 135.0, 129.5, 128.5, 104.6 (m). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_6F_4O_3SNa$ 328.9866; Found 328.9863.

*4-Chlorophenyl Benzenesulfonate (**3l**).*[20] The title compound was prepared according to the general procedure using 4-chlorophenol **1l** (25.7 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3l** (50.9 mg, 95% yield) as a colorless oil. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.88−7.85 (m, 2H), 7.73 (t, J = 7.6 Hz, 1H), 7.58 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.9, 135.0, 134.4, 132.8, 129.7, 129.2, 128.4, 123.7. This compound is known.

*4-Bromophenyl Benzenesulfonate (**3m**).*[20] The title compound was prepared according to the general procedure using 4-bromophenol **1m** (34.6 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3m** (61.3 mg, 98% yield) as a colorless oil. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.83−7.81 (m, 2H), 7.68 (t, J = 7.6 Hz, 1H), 7.54 (dd, $J_1 = J_2$ = 8.0 Hz, 2H), 7.40 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.5, 135.0, 134.4, 132.7, 129.2, 128.4, 124.1, 120.7. This compound is known.

*2,4,6-Tribromophenyl Benzenesulfonate (**3n**).* The title compound was prepared according to the general procedure using 2,4,6-tribromophenol **1n** (66.1 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3n** (71.4 mg, 76% yield) as a pale-yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.0 Hz, 2H), 7.73−7.68 (m, 3H), 7.58 (t, J = 8.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.3, 137.4, 135.6, 134.6, 129.2, 128.6, 120.8, 119.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_7Br_3O_3SNa$ 494.7517; Found 494.7522.

*3-(Trifluoromethyl)phenyl Benzenesulfonate (**3o**).*[24] The title compound was prepared according to the general procedure using 3-(trifluoromethyl) phenol **1o** (32.4 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3o** (59.8 mg, 99% yield) as yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.84−7.82 (m, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.57−7.52 (m, 3H), 7.45 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.17 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.5, 134.8, 134.6, 132.2 (q, J = 33.2 Hz), 130.4, 129.3, 128.5, 126.0, 124.0 (J = 3.6 Hz), 123.1 (q, J = 270.9 Hz), 119.7(q, J = 3.7 Hz). This compound is known.

*3-Acetylphenyl Benzenesulfonate (**3p**).*[20] The title compound was prepared according to the general procedure 3-acetylphenol **1p** (27.2 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3p** (36.4 mg, 66% yield) as a colorless oil. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.85−7.83 (m, 3H), 7.69 (t, J = 7.6 Hz, 3H), 7.54 (dd, $J_1 = J_2$ = 8.0 Hz, 2H), 7.49 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 7.41 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 7.23 (ddd, $J_1$ = 8.0 Hz, $J_2$ = 2.4 Hz, $J_3$ = 0.8 Hz, 1H), 2.51(s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.3, 149.7, 138.6, 135.1, 134.5, 130.0, 129.3, 128.5, 127.0, 126.9, 122.1, 26.6. This compound is known.

*Ethyl 4-((Phenylsulfonyl)oxy)benzoate (**3q**).*[25] The title compound was prepared according to the general procedure using ethyl 4-hydroxybenzoate **1q** (33.2 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3q** (56.9 mg, 93% yield) as a pale-yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.8 Hz, 2H), 7.83−7.81 (m, 2H), 7.67 (t, J = 7.6 Hz, 1H), 7.52 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.4, 152.7, 135.0, 134.4, 131.2, 129.3, 129.2, 128.4, 122.2, 61.3, 14.2. This compound is known.

*4-Cyanophenyl Benzenesulfonate (**3r**).*[26] The title compound was prepared according to the general procedure using 4-hydroxybenzonitrile **1r** (23.8 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3r** (50.8 mg, 98% yield) as a colorless oil. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 7.2 Hz, 2H), 7.71 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 8.8 Hz, 2H), 7.56 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 7.13 (ddd, $J_1$ = 8.8 Hz, $J_2 = J_3$ = 2.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.4, 134.8, 133.9, 129.4, 128.4, 123.4, 117.6, 111.3. This compound is known.

*4-Nitrophenyl Benzenesulfonate (**3s**).*[20] The title compound was prepared according to the general procedure using 4-nitrophenol **1s** (27.8 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3s** (35.2 mg, 63% yield) as a yellow oil. $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.20−8.16 (m, 2H), 7.85 (d, J = 7.2 Hz, 2H), 7.72 (t, J = 7.6 Hz, 1H), 7.57 (dd, $J_1 = J_2$ = 8.0 Hz, 2H), 7.26−7.17 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.8, 146.2, 134.9, 134.8, 129.5, 128.4, 125.4, 123.2. This compound is known.

*4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl Benzenesulfonate (**3t**).* The title compound was prepared according to the general procedure using 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol **1t** (44.0 mg, 0.2 mmol) and sodium benzenesulfinate **2a**


https://doi.org/10.1021/acs.joc.1c00260
J. Org. Chem. XXXX, XXX, XXX−XXX

(49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3t** (43.9 mg, 61% yield) as a white solid. mp: 106−108 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.82 (d, $J$ = 8.4 Hz, 2H), 7.72 (d, $J$ = 8.0 Hz, 2H), 7.65 (t, $J$ = 7.2 Hz, 1H), 7.51 (dd, $J_1 = J_2$ = 8.0 Hz, 2H), 6.97 (d, $J$ = 7.6 Hz, 2H), 1.32 (s, 12H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 151.9, 136.3, 135.3, 134.3, 129.1, 128.5, 121.6, 84.1, 29.7, 24.8. HRMS (ESI-TOF) $m/z$: $[M + Na]^+$ Calcd for $C_{18}H_{21}BO_5SNa$ 383.1095; Found 383.1084.

*1,1,1,3,3,3-Hexafluoropropan-2-yl Benzenesulfonate (**3v**).*[27] The title compound was prepared according to the general procedure using 1,1,1,3,3,3-hexafluoropropan-2-ol **1v** (33.6 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3v** (17.2 mg, 28% yield) as a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.95 (d, $J$ = 7.2 Hz, 2H), 7.75 (t, $J$ = 7.6 Hz, 1H), 7.61 (dd, $J$ = 8.0 Hz, 2H), 5.34−5.26 (m, 1H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 135.2, 135.0, 129.6, 128.1, 119.8 (C−F, $^1J_{C-F}$ = 281.5 Hz), 72.0 (C−F, $^2J_{C-F}$ = 35.3 Hz). This compound is known.

*Phenyl 4-Methylbenzenesulfonate (**3w**).*[11] The title compound was prepared according to the general procedure using phenol **1a** (18.8 mg, 0.2 mmol) and sodium 4-methylbenzenesulfinate **2w** (53.4 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3w** (36.2 mg, 73% yield) as a white solid. Mp: 94.6−94.9 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.74 (d, $J$ = 8.4 Hz, 2H), 7.36−7.26 (m, 5H), 7.03−7.01 (m, 2H), 2.49(s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 149.6, 145.3, 132.4, 129.7, 129.6, 128.5, 127.0, 122.3, 21.7. This compound is known.

*Phenyl 4-Fluorobenzenesulfonate (**3x**).*[9] The title compound was prepared according to the general procedure phenol **1a** (18.8 mg, 0.2 mmol) and sodium 4-fluorobenzenesulfinate **2x** (54.6 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3x** (47.9 mg, 95% yield) as a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.88−7.84 (m, 2H), 7.34−7.28 (m, 3H), 7.22 (dd, $J$ = 8.4 Hz, 2H), 7.01−6.99 (m, 2H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 166.0 (C−F, $^1J_{C-F}$ = 255.8 Hz), 149.4, 131.4, 131.3 (C−F, $^3J_{C-F}$ = 9.6 Hz), 129.7, 127.3, 122.3, 116.5 (C−F, $^2J_{C-F}$ = 22.7 Hz). This compound is known.

*Phenyl 4-Chlorobenzenesulfonate (**3y**).*[28] The title compound was prepared according to the general procedure using phenol **1a** (18.8 mg, 0.2 mmol) and sodium 4-chlorobenzenesulfinate **2y** (59.6 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3y** (52.5 mg, 98% yield) as a white solid. Mp: 92.4−92.9 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.68 (d, $J$ = 8.8 Hz, 2H), 7.50 (d, $J$ = 8.4 Hz, 2H), 7.33−7.26 (m, 3H), 7.00−6.97 (m, 2H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 149.4, 141.0, 133.7, 129.9, 129.8, 129.5, 127.4, 122.3. This compound is known.

*Phenyl 4-Bromobenzenesulfonate (**3z**).*[28] The title compound was prepared according to the general procedure using phenol **1a** (18.8 mg, 0.2 mmol) and sodium 4-bromobenzenesulfinate **2x** (72.9 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3z** (61.3 mg, 98% yield) as a white solid. Mp: 115.5−116.8 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.62−7.59 (m, 4H), 7.24−7.20 (m, 3H), 6.93−6.90 (m, 2H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 149.4, 134.3, 132.5, 129.9, 129.8, 129.6, 127.4, 122.2. This compound is known.

*Phenyl 4-Cyanobenzenesulfonate (**3aa**).*[29] The title compound was prepared according to the general procedure phenol **1a** (18.8 mg, 0.2 mmol) and sodium 4-cynaobenzenesulfinate **2aa** (56.7 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3aa** (37.3 mg, 72% yield) as a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.95 (d, $J$ = 8.8 Hz, 2H), 7.83 (d, $J$ = 8.4 Hz, 2H), 7.35−7.28 (m, 3H), 7.00−6.97 (m, 2H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 149.2, 139.4, 132.8, 129.9, 129.1, 127.6, 122.2, 117.9, 116.8. This compound is known.

*Phenyl Thiophene-2-sulfonate (**3ab**).*[30] The title compound was prepared according to the general procedure using phenol **1a** (18.8 mg, 0.2 mmol) and sodium thiophene-2-sulfinate **2ab** (51.1 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3ab** (25.5 mg, 53% yield) as a pale-yellow oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.71 (dd, $J$ = 5.2 Hz, 1H), 7.57 (dd, $J$ = 3.6 Hz, 1H), 7.32−7.27 (m, 3H), 7.09 (dd, $J$ = 4.2 Hz, 1H), 7.05−7.03 (m, 2H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 149.6, 135.4, 134.5, 129.7, 127.5, 127.4, 122.2. This compound is known.

*Phenyl Ethanesulfonate (**3ac**).*[31] The title compound was prepared according to the general procedure using phenol **1a** (18.8 mg, 0.2 mmol) and sodium 4-bromobenzenesulfinate **2ac** (34.8 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3ac** (24.6 mg, 66% yield) as a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.41 (d, $J$ = 7.6 Hz, 2H), 7.33−7.27(m, 3H), 3.27 (q, $J$ = 7.6 Hz, 2H), 1.54 (t, $J$ = 7.6 Hz, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 149.1, 129.9, 127.1, 121.9, 44.9, 8.2. This compound is known.

*2-Formylphenyl Benzenesulfonate (**3ad**).* The title compound was prepared according to the general procedure using 2-hydroxybenzaldehyde **1ad** (24.4 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3ad** (48.2 mg, 92% yield) as a pale-yellow oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 10.00 (s, 1H), 7.89−7.84 (m, 3H), 7.72 (d, $J$ = 7.2 Hz, 1H), 7.59−7.54 (m, 3H), 7.41 (t, $J$ = 7.2 Hz, 1H), 7.20 (d, $J$ = 8.0 Hz, 1H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 187.2, 151.1, 135.4, 134.9, 134.4, 129.6, 129.3, 128.8, 128.5, 127.7, 123.7. HRMS (ESI-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{13}H_{11}O_4S$ 263.0373; Found 263.0374.

*4-(2-(Dimethylamino)ethyl)phenyl Benzenesulfonate (**3ae**).* The title compound was prepared according to the general procedure 4-(2-(dimethylamino)ethyl)phenol **1ae** (33.0 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3ae** (51.9 mg, 85% yield) as a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.83 (d, $J$ = 7.6 Hz, 2H), 7.65 (t, $J$ = 7.6 Hz, 1H), 7.51 (dd, $J_1 = J_2$ = 8.0 Hz, 2H), 7.10 (d, $J$ = 8.4 Hz, 2H), 7.87 (d, $J$ = 8.8 Hz, 2H), 2.72 (t, $J$ = 7.6 Hz, 2H), 2.47 (t, $J$ = 7.6 Hz, 2H), 2.26 (s, 6H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 147.8, 139.5, 135.5, 134.1, 129.7, 129.1, 128.4, 122.1, 61.1, 45.3, 33.6. HRMS (ESI-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{16}H_{20}NO_3S$ 306.1158; Found 306.1153.

*4-Allyl-2-methoxyphenyl Benzenesulfonate (**3af**).* The title compound was prepared according to the general procedure using 4-allyl-2-methoxyphenol **1af** (32.8 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3af** (37.1 mg, 61% yield) as a pale-yellow oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.88−7.86 (m, 2H), 7.64 (t, $J$ = 7.6 Hz, 1H), 7.50 (dd, $J_1 = J_2$ = 8.0 Hz, 2H), 7.06 (d, $J$ = 8.4 Hz, 1H), 6.71(dd, $J_1$ = 8.0 Hz, $J_2$ = 2.0 Hz, 1H), 6.64 (d, $J$ = 2.0 Hz, 1H), 5.91 (ddt, $J_1$ = 16.8 Hz, $J_2$ = 10.4 Hz, $J_3$ = 6.4 Hz, 1H), 5.09−5.04(m, 2H), 3.50 (s, 3H), 3.33 (d, $J$ = 6.4 Hz, 2H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 151.5, 140.4, 136.61, 136.57, 136.3, 133.8, 128.6, 128.5, 123.8, 120.6, 116.4, 112.8, 55.4, 40.0. HRMS (ESI-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{16}H_{17}O_4S$ 305.0842; Found 305.0847.

*2-Benzoyl-5-methoxyphenyl Benzenesulfonate (**3ag**).* The title compound was prepared according to the general procedure using (2-hydroxy-4-methoxyphenyl)(phenyl)methanone **1ag** (45.6 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3ag** (67.0 mg, 91% yield) as a pale-yellow solid. Mp: 75−77 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.62−7.58 (m, 4H), 7.55−7.51(m, 2H), 7.44−7.36 (m, 5H), 3.85 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 192.8, 162.6, 147.8, 137.4, 134.9, 134.2, 132.8, 132.3, 129.9, 129.0, 128.4, 128.1, 117.2, 112.9, 109.2, 55.8. HRMS (ESI-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{20}H_{17}O_5S$ 369.0797; Found 369.0794.

*2-Allylphenyl Benzenesulfonate (**3ah**).* The title compound was prepared according to the general procedure using 2-allylphenyl **1ah** (26.8 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3


https://doi.org/10.1021/acs.joc.1c00260
J. Org. Chem. XXXX, XXX, XXX−XXX

mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3ah** (45.5 mg, 83% yield) as a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.89 (d, $J$ = 7.6 Hz, 2H), 7.69 (t, $J$ = 7.6 Hz, 1H), 7.55 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 7.20−7.13 (m, 3H), 7.04 (d, $J$ = 8.0 Hz, 1H), 5.75 (ddt, $J_1$ = 16.8 Hz, $J_2$ = 10.0 Hz, $J_3$ = 6.8 Hz, 1H), 5.05−4.97 (m, 2H), 3.22 (d, $J$ = 6.8 Hz, 2H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 147.8, 136.1, 135.4, 134.2, 133.4, 130.7, 129.2, 128.4, 127.4, 127.2, 122.2, 116.7, 33.8. HRMS (ESI-TOF) $m/z$: $[M - H]^-$ Calcd for $C_{15}H_{13}O_5S$ 273.0591; Found 273.0592.

*Methyl 3-Methoxy-4-((phenylsulfonyl)oxy)benzoate (**3ai**).*[32] The title compound was prepared according to the general procedure using methyl 4-hydroxy 3-methoxybenzoate **1ai** (36.4 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3ai** (53.5 mg, 83% yield) as a pale-yellow oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.85 (d, $J$ = 7.2 Hz, 2H), 7.65 (t, $J$ = 7.2 Hz, 1H), 7.59 (dd, $J_1$ = 8.4 Hz, $J_2$ = 2.0 Hz, 1H), 7.54−7.48 (m, 3H), 7.23 (d, $J$ = 8.4 Hz, 1H), 3.89 (s, 3H), 3.56 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 165.9, 151.5, 141.7, 135.9, 134.1, 129.8, 128.8, 128.5, 123.9, 122.2, 113.5, 55.6, 52.3. This compound is known.

*4-(3-Oxobutyl)phenyl Benzenesulfonate (**3aj**).* The title compound was prepared according to the general procedure using 4-(4-hydroxyphenyl)butan-2-one **1aj** (32.8 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3aj** (43.8 mg, 72% yield) as a pale-yellow oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.82 (d, $J$ = 7.6 Hz, 2H), 7.66 (t, $J$ = 7.6 Hz, 1H), 7.52 (dd, $J_1 = J_2$ = 7.6 Hz, 2H), 7.08 (d, $J$ = 8.4 Hz, 2H), 6.87 (d, $J$ = 8.4 Hz, 2H), 2.84 (t, $J$ = 7.6 Hz, 2H), 2.71 (t, $J$ = 7.6 Hz, 2H), 2.11 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 207.4, 147.8, 140.1, 135.4, 134.1, 129.4, 129.0, 128.4, 122.2, 44.7, 30.0, 28.8. HRMS (ESI-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{16}H_{17}O_4S$ 305.0842; Found 305.0836.

*(8R,9S,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl benzenesulfonate (**3ak**).* The title compound was prepared according to the general procedure using (8*R*,9*S*,13*S*,14*S*)-3-hydroxy-13-methyl-6,7,8,9,-11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one **1ak** (32.8 mg, 0.2 mmol) and sodium benzenesulfinate **2a** (54.1 mg, 0.3 mmol, 1.5 equiv), purified by column chromatography on silica gel, and eluted with petroleum ether to afford **3ak** (50.3 mg, 61% yield) as a white solid. mp: 148−150 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.86 (d, $J$ = 8.0 Hz, 2H), 7.67 (t, $J$ = 7.6 Hz, 1H), 7.54 (d, $J$ = 8.0 Hz, 2H), 7.16 (d, $J$ = 8.8 Hz, 1H), 6.76 (s, 1H), 6.66 (d, $J$ = 8.4 Hz, 1H), 2.82 (t, $J$ = 4.8 Hz, 2H), 2.53−2.47 (m, 1H), 2.35−2.33 (m, 2H), 2.11−1.93 (m, 4H), 1.61−1.38 (m, 6H), 0.90 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 220.7, 147.3, 138.8, 138.4, 135.6, 134.0, 129.0, 128.4, 126.4, 122.3, 119.1, 50.3, 47.8, 44.0, 37.7, 35.7, 31.4, 29.2, 26.1, 25.6, 21.5, 13.7. HRMS (ESI-TOF) $m/z$: $[M + H]^+$ Calcd for $C_{24}H_{27}O_4S$ 411.1625; Found 411.1625.

*(2-(Phenylsulfonyl)ethene-1,1-diyl)dibenzene (**4**).*[33] The title compound was prepared according to the general procedure, purified by column chromatography on silica gel, and eluted with petroleum ether to afford **4** (13.5 mg, 21% yield) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.62 (dd, $J_1$ = 7.6 Hz, 2H), 7.52 (dt, $J_1$ = 7.6 Hz, 2H), 7.41−7.31 (m, 8H), 7.31 (d, $J_1$ = 7.2 Hz, 1H), 7.12 (d, $J_1$ = 7.2 Hz, 2H), 7.06 (s, 1H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 155.2, 141.4, 139.1, 135.4, 132.8, 130.3, 129.7, 128.9, 128.7, 128.65, 128.64, 128.64, 128.57, 128.2, 127.8, 127.6. This compound is known.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00260.

General information, experimental procedures, characterization data, and copies of $^1$H and $^{13}$C NMR spectroscopies (PDF)

## ■ AUTHOR INFORMATION


### Corresponding Author

**Tieqiao Chen** − *Key Laboratory of Ministry of Education for Advanced Materials in Tropical Island Resources, Hainan Provincial Key Lab of Fine Chemicals, Hainan Provincial Fine Chemical Engineering Research Center, Hainan University, Haikou 570228, China;* orcid.org/0000-0002-9787-9538; Email: chentieqiao@hnu.edu.cn

### Authors

**Zhibin Tian** − *Key Laboratory of Ministry of Education for Advanced Materials in Tropical Island Resources, Hainan Provincial Key Lab of Fine Chemicals, Hainan Provincial Fine Chemical Engineering Research Center, Hainan University, Haikou 570228, China*

**Qihang Gong** − *Key Laboratory of Ministry of Education for Advanced Materials in Tropical Island Resources, Hainan Provincial Key Lab of Fine Chemicals, Hainan Provincial Fine Chemical Engineering Research Center, Hainan University, Haikou 570228, China*

**Tianzeng Huang** − *Key Laboratory of Ministry of Education for Advanced Materials in Tropical Island Resources, Hainan Provincial Key Lab of Fine Chemicals, Hainan Provincial Fine Chemical Engineering Research Center, Hainan University, Haikou 570228, China*

**Long Liu** − *Key Laboratory of Ministry of Education for Advanced Materials in Tropical Island Resources, Hainan Provincial Key Lab of Fine Chemicals, Hainan Provincial Fine Chemical Engineering Research Center, Hainan University, Haikou 570228, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.1c00260


### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Partial financial support from the HNNSFC (No. 219MS005) and the NSFC (No. 21871070) is gratefully acknowledged. We also thank Bin Song for reproducing **3v** and **3ac** with this method.

## ■ REFERENCES

(1) (a) Sperry, J. B.; Wright, D. L. The application of cathodic reductions and anodic oxidations in the synthesis of complex molecules. *Chem. Soc. Rev.* **2006**, *35*, 605−621. (b) Yoshida, J.-I.; Kataoka, K.; Horcajada, R.; Nagaki, A. Modern Strategies in Electroorganic Synthesis. *Chem. Rev.* **2008**, *108*, 2265−2299. (c) Wang, H.; Gao, X.; Lv, Z.; Abdelilah, T.; Lei, A. Recent Advances in Oxidative $R^1$-H/$R^2$-H Cross-Coupling with Hydrogen Evolution *via* Photo-/Electrochemistry. *Chem. Rev.* **2019**, *119*, 6769−6787. (d) Jiang, Y.; Xu, K.; Zeng, C. Use of Electrochemistry in the Synthesis of Heterocyclic Structures. *Chem. Rev.* **2018**, *118*, 4485−4540. (e) Waldvogel, S. R.; Lips, S.; Selt, M.; Riehl, B.; Kampf, C. J. Electrochemical Arylation Reaction. *Chem. Rev.* **2018**, *118*, 6706−6765. (f) Badalyan, A.; Stahl, S. S. Cooperative electrocatalytic alcohol oxidation with electron-proton-transfer mediators. *Nature* **2016**, *535*, 406−410. (g) Lips, S.; Wiebe, A.; Elsler, B.; Schollmeyer, D.; Dyballa, K. M.; Franke, R.; Waldvogel, S. R. Synthesis of *meta*-Terphenyl-2,2″-diols by Anodic C-C Cross-Coupling Reactions. *Angew. Chem., Int. Ed.* **2016**, *55*, 10872−10876. (h) Amatore, C.; Cammoun, C.; Jutand, A. Electrochemical Recycling of Benzoquinone in the Pd/Benzoquinone Catalyzed Heck-Type Reactions from Arenes. *Adv. Synth. Catal.* **2007**, *349*, 292−296.

(2) (a) Yi, H.; Zhang, G.; Wang, H.; Huang, Z.; Wang, J.; Singh, A. K.; Lei, A. Recent Advances in Radical C-H Activation/Radical Cross-Coupling. *Chem. Rev.* **2017**, *117*, 9016−9085. (b) Zhang, J. S.; Liu, L.; Chen, T.; Han, L.-B. Cross-Dehydrogenative Alkynylation: A Powerful Tool for the Synthesis of Internal Alkynes. *ChemSusChem* **2020**, *13*, 4776. (c) Chen, T.; Han, L.-B. Optically Active H-Phosphinates and Their Stereospecific Transformations into Optically Active *P*-Stereogenic Organophosphoryl Compounds. *Synlett* **2015**, *26*, 1153−1163. (d) Zhu, Y.; Chen, T.; Li, S.; Shimada, S.; Han, L.-B. Efficient Pd-Catalyzed Dehydrogenative Coupling of P(O)H with RSH: A Precise Construction of P(O)-S Bonds. *J. Am. Chem. Soc.* **2016**, *138*, 5825−5828. (e) Chen, T.; Han, L.-B. Nickel-Catalyzed C-O/C-H Cross-Coupling Reactions for C-C Bond Formation. *Angew. Chem., Int. Ed.* **2015**, *54*, 8600−8602. (f) Xu, Y.; Jiao, C.; Li, J.; Tian, R.; Duan, Z.; Mathey, F. An Approach to Peri-Fused Heterocycles: A Metal-Mediated Cascade Carbonylative Cyclization/Dearomatic Diels-Alder Reaction. *Org. Lett.* **2019**, *21*, 9512−9515. (g) Kang, Q.; Wu, W.; Li, Q.; Wei, W.-T. Photochemical strategies for C-N bond formation via metal catalyst-free (hetero) aryl C($sp^2$)-H functionalization. *Green Chem.* **2020**, *22*, 3060−3068. (h) Huang, X.; Qin, F.; Liu, Y.; Wu, S.; Li, Q.; Wei, W.-T. Acylation/cyclization of 1,6-dienes with ethers under catalyst-and base-free conditions. *Green Chem.* **2020**, *22*, 3952−3955. (i) Song, S.; Meng, Y.; Li, Q.; Wei, W.-T. Recent Progress in the Construction of C-N Bonds via Metal-Free Radical C($sp^3$)-H Functionalization. *Adv. Synth. Catal.* **2020**, *362*, 2120−2134. (j) Qin, F.; Huang, X.; Liu, Y.; Liang, H.; Li, Q.; Cao, Z.; W, W.-T.; He, W.-M. Alcohols controlled selective radical cyclization of 1,6-dienes under mild conditions. *Chin. Chem. Lett.* **2020**, *31*, 3267−3270.

(3) (a) Yuan, Y.; Lei, A. Electrochemical Oxidative Cross-Coupling with Hydrogen Evolution Reactions. *Acc. Chem. Res.* **2019**, *52*, 3309−3324. (b) Zeng, L.; Li, H.; Hu, J.; Zhang, D.; Hu, J.; Peng, P.; Wang, S.; Shi, R.; Peng, J.; Pao, C.-W.; Chen, J.-L.; Lee, J.-F.; Zhang, H.; Chen, Y.-H.; Lei, A. Electrochemical oxidative aminocarbonylation of terminal alkynes. *Nature Catal.* **2020**, *3*, 438−445. (c) Wang, H.; Liang, K.; Xiong, W.; Samanta, S.; Li, W.; Lei, A. Electrochemical oxidation-induced etherification via C($sp^3$)-H/O-H cross-coupling. *Sci. Adv.* **2020**, *6*, No. eaaz0590. (d) Duan, Z.; Zhang, L.; Zhang, W.; Lu, L.; Zeng, L.; Shi, R.; Lei, A. Palladium-Catalyzed Electro-oxidative C-H Amination toward the Synthesis of Pyrido [1,2-a] benzimidazoles with Hydrogen Evolution. *ACS Catal.* **2020**, *10*, 3828−3831. (e) Yuan, Y.; Zheng, Y.; Zheng, Y.; Xu, B.; Liao, J.; Bu, F.; Wang, S.; Hu, J.-G.; Lei, A. Mn-Catalyzed Electrochemical Radical Cascade Cyclization toward the Synthesis of Benzo[4,5]imidazo[2,1-a]-isoquinolin-6(5*H*)-one Derivatives. *ACS Catal.* **2020**, *10*, 6676−6681. (f) Yuan, Y.; Lei, A. Is electrosynthesis always green and advantageous compared to traditional methods? *Nat. Commun.* **2020**, *11*, 802. (g) Wan, Z.; Wang, D.; Yang, Z.; Zhang, H.; Wang, S.; Lei, A. Electrochemical oxidative C($sp^3$)-H azolation of lactams under mild conditions. *Green Chem.* **2020**, *22*, 3742−3747. (h) Hu, X.; Nie, L.; Zhang, G.; Lei, A. Electrochemical Oxidative [4 + 2] Annulation for the $\pi$-Extension of Unfunctionalized Heterobiaryl Compounds. *Angew. Chem., Int. Ed.* **2020**, *59*, 15238−15243. (i) Song, C.; Liu, K.; Jiang, X.; Dong, X.; Weng, Y.; Chiang, C.-W.; Lei, A. Electrooxidation Enables Selective Dehydrogenative [4 + 2] Annulation between Indole Derivatives. *Angew. Chem., Int. Ed.* **2020**, *59*, 7193−7197. (j) Wang, P.; Tang, S.; Huang, P.; Lei, A. Electrocatalytic Oxidant-Free Dehydrogenative C-H/S-H Cross-Coupling. *Angew. Chem., Int. Ed.* **2017**, *56*, 3009−3013. (k) Tang, S.; Liu, Y.; Lei, A. Electrochemical Oxidative Cross-coupling with Hydrogen Evolution: A Green and Sustainable Way for Bond Formation. *Chem.* **2018**, *4*, 27−45. (l) Yuan, Y.; Yu, Y.; Qiao, J.; Liu, P.; Yu, B.; Zhang, W.; Liu, H.; He, M.; Huang, Z.; Lei, A. Exogenous-oxidant-free electrochemical oxidative C-H sulfonylation of arenes/heteroarenes with hydrogen evolution. *Chem. Commun.* **2018**, *54*, 11471−11474. (m) Tang, S.; Wang, S.; Liu, Y.; Cong, H.; Lei, A. Electrochemical Oxidative C-H Amination of Phenols: Access to Triarylamine Derivatives. *Angew. Chem., Int. Ed.* **2018**, *57*, 4737−4741. (n) Li, D.; Li, S.; Peng, C.; Lu, L.; Wang, S.; Wang, P.; Chen, Y.-H.; Cong, H.; Lei, A. Electrochemical oxidative C-H/S-H cross-coupling between enamines and thiophenols with $H_2$ evolution. *Chem. Sci.* **2019**, *10*, 2791−2795. (o) Liu, K.; Song, C.; Wu, J.; Deng, Y.; Tang, S.; Lei, A. Electrochemical oxidation synergizing with Brønsted-acid catalysis leads to [4 + 2] annulation for the synthesis of pyrazines. *Green Chem.* **2019**, *21*, 765−769.

(4) (a) Xiong, P.; Xu, H.-C. Chemistry with Electrochemically Generated N-Centered Radicals. *Acc. Chem. Res.* **2019**, *52*, 3339−3350. (b) Xu, P.; Chen, P.-Y.; Xu, H.-C. Scalable Photo-electrochemical Dehydrogenative Cross-Coupling of Heteroarenes with Aliphatic C-H Bonds. *Angew. Chem., Int. Ed.* **2020**, *59*, 14275−14280. (c) Xiong, P.; Zhao, H.-B.; Fan, X.-T.; Jie, L.-H.; Long, H.; Xu, P.; Liu, Z.-J.; Wu, Z.-J.; Cheng, J.; Xu, H.-C. Site-selective electrooxidation of methylarenes to aromatic acetals. *Nat. Commun.* **2020**, *11*, 2706. (d) Lai, X.-L.; Shu, X.-M.; Song, J.; Xu, H.-C. Electrophotocatalytic Decarboxylative C-H Functionalization of Heteroarenes. *Angew. Chem., Int. Ed.* **2020**, *59*, 10626−10632. (e) Xu, F.; Long, H.; Song, J.; Xu, H.-C. De Novo Synthesis of Highly Functionalized Benzimidazolones and Benzoxazolones through an Electrochemical Dehydrogenative Cyclization Cascade. *Angew. Chem., Int. Ed.* **2019**, *58*, 9017−9021. (f) Zhu, L.; Xiong, P.; Mao, Z.; Wang, Y.; Yan, X.; Lu, X.; Xu, H.-C. Electrocatalytic Generation of Amidyl Radicals for Olefin Hydroamidation: Use of Solvent Effects to Enable Anilide Oxidation. *Angew. Chem., Int. Ed.* **2016**, *55*, 2226−2229. (g) Hou, Z.-W.; Mao, Z.-Y.; Song, J.; Xu, H.-C. Electrochemical Synthesis of Polycyclic N-Heteroaromatics through Cascade Radical Cyclization of Diynes. *ACS Catal.* **2017**, *7*, 5810−5813. (h) Hou, Z.-W.; Mao, Z.-Y.; Melcamu, Y. Y.; Lu, X.; Xu, H.-C. Electrochemical Synthesis of Imidazo-Fused N-Heteroaromatic Compounds through a C-N Bond-Forming Radical Cascade. *Angew. Chem., Int. Ed.* **2018**, *57*, 1636−1639. (i) Xiong, P.; Xu, H.-H.; Song, J.; Xu, H.-C. Electrochemical Difluoromethylarylation of Alkynes. *J. Am. Chem. Soc.* **2018**, *140*, 2460−2464. (j) Xu, H.-C.; Moeller, K. D. Intramolecular Anodic Olefin Coupling Reactions: The Use of a Nitrogen Trapping Group. *J. Am. Chem. Soc.* **2008**, *130*, 13542−13543. (k) Xu, H.-C.; Moeller, K. D. Intramolecular Anodic Olefin Coupling Reactions and the Synthesis of Cyclic Amines. *J. Am. Chem. Soc.* **2010**, *132*, 2839−2844.

(5) (a) Yan, M.; Kawamata, Y.; Baran, P. S. Synthetic Organic Electrochemical Methods Since 2000: On the Verge of a Renaissance. *Chem. Rev.* **2017**, *117*, 13230−13319. (b) Peters, B. K.; Rodriguez, K. X.; Reisberg, S. H.; Beil, S. B.; Hickey, D. P.; Kawamata, Y.; Collins, M.; Starr, J.; Chen, L.; Udyavara, S.; Klunder, K.; Gorey, T. J.; Anderson, S. L.; Neurock, M.; Minteer, S. D.; Baran, P. S. Scalable and safe synthetic organic electroreduction inspired by Li-ion battery chemistry. *Science* **2019**, *363*, 838−845. (c) Xiang, J.; Shang, M.; Kawamata, Y.; Lundberg, H.; Reisberg, S. H.; Chen, M.; Mykhailiuk, P.; Beutner, G.; Collins, M. R.; Davies, A.; Bel, M.; Gallego, G. M.; Spangler, J. E.; Starr, J.; Yang, S.; Blackmond, D. G.; Baran, P. S. Hindered dialkyl ether synthesis with electrogenerated carbocations. *Nature* **2019**, *573*, 398−402. (d) Horn, E. J.; Rosen, B. R.; Chen, Y.; Tang, J.; Chen, K.; Eastgate, M. D.; Baran, P. S. Scalable and sustainable electrochemical allylic C-H oxidation. *Nature* **2016**, *533*, 77−81. (e) Kawamata, Y.; Vantourout, J. C.; Hickey, D. P.; Bai, P.; Chen, L.; Hou, Q.; Qiao, W.; Barman, K.; Edwards, M. A.; Garrido-Castro, A. F.; Gruyter, J. N.; Nakamura, H.; Knouse, K.; Qin, C.; Clay, K. J.; Bao, D.; Li, C.; Starr, J. T.; Garcia-Irizarry, C.; Sach, N.; White, H. S.; Neurock, M.; Minteer, S. D.; Baran, P. S. Electrochemically Driven, Ni-Catalyzed Aryl Amination: Scope, Mechanism, and Applications. *J. Am. Chem. Soc.* **2019**, *141*, 6392−6402. (f) Horn, E. J.; Rosen, B. R.; Baran, P. S. Synthetic Organic Electrochemistry: An Enabling and Innately Sustainable Method. *ACS Cent. Sci.* **2016**, *2*, 302−308.

(6) (a) Zhou, H.; Comninos, J. S.; Stossi, F.; Katzenellenbogen, B. S.; Katzenellenbogen, J. A. Synthesis and Evaluation of Estrogen Receptor Ligands with Bridged Oxabicyclic Cores Containing a Diarylethylene Motif: Estrogen Antagonists of Unusual Structure. *J. Med. Chem.* **2005**, *48*, 7261−7264. (b) Elder, D. P.; Delaney, E.; Teasdale, A.; Eyley, S.; Reif, V. D.; Jacq, K.; Facchine, K. L.; Oestrich,



https://doi.org/10.1021/acs.joc.1c00260
*J. Org. Chem.* XXXX, XXX, XXX−XXX

R. S.; Sandra, P.; David, F. The Utility of Sulfonate Salts in Drug Development. *J. Pharm. Sci.* **2010**, *99*, 2948−2961. (c) Wang, P.; Min, J.; Nwachukwu, J. C.; Cavett, V.; Carlson, K. E.; Guo, P.; Zhu, M.; Zheng, Y.; Dong, C.; Katzenellenbogen, J. A.; Nettles, K. W.; Zhou, H. Identification and Structure-Activity Relationships of a Novel Series of Estrogen Receptor Ligands Based on 7-Thiabicyclo[2.2.1]-hept-2-ene-7-oxide. *J. Med. Chem.* **2012**, *55*, 2324−2341. (d) Pisani, L.; Bareletta, M.; Soto-Otero, R.; Nicolotti, O.; Mendez-Alvarez, E.; Catto, M.; Introcaso, A.; Stefanachi, A.; Cellamare, S.; Altomare, C.; Carotti, A. Discovery, Biological Evaluation, and Structure-Activity and -Selectivity Relationships of 6′-Substituted (*E*)-2-(Benzofuran-3(2*H*)-ylidene)-*N*-methylacetamides, a Novel Class of Potent and Selective Monoamine Oxidase Inhibitors. *J. Med. Chem.* **2013**, *56*, 2651−2664.

(7) (a) Stang, P. J. Alkynyl carboxylate, phosphate, and sulfonate esters. *Acc. Chem. Res.* **1991**, *24*, 304−310. (b) Nguyen, H. N.; Huang, X.; Buchwald, S. L. The First General Palladium Catalyst for the Suzuki-Miyaura and Carbonyl Enolate Coupling of Aryl Arenesulfonates. *J. Am. Chem. Soc.* **2003**, *125*, 11818−11819. (c) Singh, A. K.; Yi, H.; Zhang, G.; Bian, C.; Pei, P.; Lei, A. Photoinduced Oxidative Cross-Coupling for O-S Bond Formation: A Facile Synthesis of Alkyl Benzenesulfonates. *Synlett* **2017**, *28*, 1558−1563. (d) Cho, C. H.; Yun, H. S.; Park, K. Nickel(0)-Catalyzed Cross-Coupling of Alkyl Arenesulfonates with Aryl Grignard Reagents. *J. Org. Chem.* **2003**, *68*, 3017−3025. (e) Tang, Z.; Hu, Q. Room-Temperature Ni(0)-Catalyzed Cross-Coupling Reactions of Aryl Arenesulfonates with Arylboronic Acids. *J. Am. Chem. Soc.* **2004**, *126*, 3058−3059. (f) Cai, C.; Rivera, N. R.; Balsells, J.; Sidler, R. R.; McWilliams, J. C.; Shultz, C. S.; Sun, Y. An Efficient Catalyst for Pd-Catalyzed Carbonylation of Aryl Arenesulfonates. *Org. Lett.* **2006**, *8*, 5161−5164. (g) Miller, S. C. Profiling Sulfonate Ester Stability: Identification of Complementary Protecting Groups for Sulfonates. *J. Org. Chem.* **2010**, *75*, 4632−4635. (h) Pauff, S. M.; Miller, S. C. Synthesis of Near-IR Fluorescent Oxazine Dyes with Esterase-Labile Sulfonate Esters. *Org. Lett.* **2011**, *13*, 6196−6199. (i) Terent'ev, A. O.; Mulina, O. M.; Parshin, V. D.; Kokorekin, V. A.; Nikishin, G. I. Electrochemically induced oxidative S-O coupling: synthesis of sulfonates from sulfonyl hydrazides and N-hydroxyimides or N-hydroxybenzotriazoles. *Org. Biomol. Chem.* **2019**, *17*, 3482−3488.

(8) (a) Caddick, S.; Wilden, J. D.; Judd, D. B. Direct Synthesis of Sulfonamides and Activated Sulfonate Esters from Sulfonic Acids. *J. Am. Chem. Soc.* **2004**, *126*, 1024. (b) Meshram, G. A.; Patil, V. D. A simple and efficient method for sulfonylation of amines, alcohols and phenols with cupric oxide under mild conditions. *Tetrahedron Lett.* **2009**, *50*, 1117−1121.

(9) Bahrami, K.; Khodaei, M. M.; Abbasi, J. Synthesis of sulfonamides and sulfonic esters via reaction of amines and phenols with thiols using $H_2O_2$-$POCl_3$ system. *Tetrahedron* **2012**, *68*, 5095−5101.

(10) Sodium sulfinates are stable and readily available. They have been used as an efficient sulfonylating reagent for preparing organosulfur compounds. For selected examples on electrochemical oxidation, see: (a) Mei, H.; Pajkert, R.; Wang, L.; Li, Z.; Röschenthaler, G.-V.; Han, J. Chemistry of electrochemical oxidative reactions of sulfinate salts. *Green Chem.* **2020**, *22*, 3028−3059. (b) Luo, M.-J.; Liu, B.; Li, Y.; Hu, M.; Li, J.-H. Electrochemical Three-Component 1,2-Aminosulfonylation of Alkenes: Entry to 2-sulfonylethan-1-amines. *Adv. Synth. Catal.* **2019**, *361*, 1538−1542. (c) Jiang, Y.-Y.; Liang, S.; Zeng, C.-C.; Hu, L.-M.; Sun, B.-G. Electrochemically initiated formation of sulfonyl radicals: synthesis of oxindoles *via* difunctionalization of acrylamides mediated by bromide ion. *Green Chem.* **2016**, *18*, 6311−6319. (d) Jiang, Y.-Y.; Wang, Q.-Q.; Liang, S.; Hu, L.-M.; Little, R. D.; Zeng, C.-C. Electrochemical Oxidative Amination of Sodium Sulfinates: Synthesis of Sulfonamides Mediated by $NH_4I$ as a Redox Catalyst. *J. Org. Chem.* **2016**, *81*, 4713−4719. (e) Yavari, I.; Shaabanzadeh, S. Electrochemical Synthesis of β-Ketosulfones from Switchable Starting Materials. *Org. Lett.* **2020**, *22*, 464−467. (f) Meng, X.; Xu, H.; Cao, X.; Cai, X.-M.; Luo, J.; Wang, F.; Huang, S. Electrochemically Enabled Sulfonylation of Alkynes with Sodium Sulfinates. *Org. Lett.* **2020**, *22*, 6827−6831. For selected examples on chemical oxidation, see: (g) Mulina, O. M.; Ilovaisky, A. I.; Parshin, V. D.; Terent'ev, A. O. Oxidative Sulfonylation of Multiple Carbon-Carbon bonds with Sulfonyl Hydrazides, Sulfinic Acids and their Salts. *Adv. Synth. Catal.* **2020**, *362*, 4579−4654. (h) Xu, Y.; Tang, X.; Hu, W.; Wu, W.; Jiang, H. Transition-metal-free synthesis of vinyl sulfones *via* tandem cross-decarboxylative/coupling reactions of sodium sulfinates and cinnamic acids. *Green Chem.* **2014**, *16*, 3720−3723. (i) Rao, W.; Jiang, L.; Liu, X.; Chen, M.; Chen, F.; Jiang, X.; Zhao, J.; Zou, G.; Zhou, Y.; Tang, L. Copper(II)-Catalyzed Alkene Aminosulfonylation with Sodium Sulfinates For the Synthesis of Sulfonylated Pyrrolidones. *Org. Lett.* **2019**, *21*, 2890−2893. (j) Ansari, M. Y.; Kumar, N.; Kumar, A. Regioselective Intermolecular Sulfur-Oxygen Difunctionalization (Phenoxysulfonylation) of Alkynes: One-Pot Construction of (Z)-β-Phenoxy Vinylsulfones. *Org. Lett.* **2019**, *21*, 3931−3936. (k) He, X.; Yue, X.; Zhang, L.; Wu, S.; Hu, M.; Li, J. Multiple-functionalizations of terminal alkynes with sodium sulfinates and *tert*-butyl nitrite: facile synthesis of 2*H*-azirines. *Chem. Commun.* **2019**, *55*, 3517−3520. (l) Wang, J.-J.; Yu, W. Hydrosulfonylation of Unactivated Alkenes by Visible Light Photoredox Catalysis. *Org. Lett.* **2019**, *21*, 9236−9240. (m) Yu, Y.; Wu, Q.; Liu, D.; Yu, L.; Tan, Z.; Zhu, G. Silver-Promoted Decarboxylative Sulfonylation of Aromatic Carboxylic Acids with Sodium Sulfinates. *J. Org. Chem.* **2019**, *84*, 11195−11202. (n) Wu, Y. C.; Jiang, S. S.; Luo, S. Z.; Song, R. J.; Li, J. H. Transition-metal- and oxidant-free directed anodic C-H sulfonylation of *N,N*-disubstituted anilines with sulfinates. *Chem. Commun.* **2019**, *55*, 8995−8998.

(11) Gao, J.; Pan, X.; Liu, J.; Lai, J.; Chang, L.; Yuan, G. Iodine-induced synthesis of sulfonate esters from sodium sulfinates and phenols under mild conditions. *RSC Adv.* **2015**, *5*, 27439−27442.

(12) (a) Anastas, P.; Eghbali, N. Green Chemistry: Principles and Practice. *Chem. Soc. Rev.* **2010**, *39*, 301−312. (b) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: New York, 1998.

(13) (a) Röckl, J. L.; Pollok, D.; Franke, R.; Waldvogel, S. R. A Decade of Electrochemical Dehydrogenative C,C-Coupling of Aryls. *Acc. Chem. Res.* **2020**, *53*, 45−61. (b) Liu, K.; Tang, S.; Huang, P.; Lei, A. External oxidant-free electrooxidative [3 + 2] annulation between phenol and indole derivatives. *Nat. Commun.* **2017**, *8*, 775. (c) Wiebe, A.; Lips, S.; Schollmeyer, D.; Franke, R.; Waldvogel, S. R. Single and Twofold Metal- and Reagent-Free Anodic C-C Cross-Coupling of Phenols with Thiophenes. *Angew. Chem., Int. Ed.* **2017**, *56*, 14727−14731. (d) Kirste, A.; Elsler, B.; Schnakenburg, G.; Waldvogel, S. R. Efficient anodic and direct phenol-arene C,C cross-coupling: the benign role of water or methanol. *J. Am. Chem. Soc.* **2012**, *134*, 3571−3576. (e) Kirste, A.; Schnakenburg, G.; Stecker, F.; Fischer, A.; Waldvogel, S. R. Anodic phenol-arene cross-coupling reaction on boron-doped diamond electrodes. *Angew. Chem., Int. Ed.* **2010**, *49*, 971−975.

(14) (a) Riehl, B.; Dyballa, K. M.; Franke, R.; Waldvogel, S. R. Electro-organic Synthesis as a Sustainable Alternative for Dehydrogenative Cross-Coupling of Phenols and Naphthols. *Synthesis* **2016**, *49*, 252−259. (b) Röckl, J. L.; Schollmeyer, D.; Franke, R.; Waldvogel, S. R. Dehydrogenative Anodic C-C Coupling of Phenols Bearing Electron-Withdrawing Groups. *Angew. Chem., Int. Ed.* **2020**, *59*, 315−319. (c) Elsler, B.; Schollmeyer, D.; Dyballa, K. M.; Franke, R.; Waldvogel, S. R. Metal- and reagent-free highly selective anodic cross-coupling reaction of phenols. *Angew. Chem., Int. Ed.* **2014**, *53*, 5210−5213. (d) de Kruijff, G. H. M.; Goschler, T.; Beiser, N.; Stenglein, A.; Türk, O. M.; Waldvogel, S. R. Sustainable access to biobased biphenol epoxy resins by electrochemical dehydrogenative dimerization of eugenol. *Green Chem.* **2019**, *21*, 4815.

(15) The reaction used the special solvent HFIP, which could stabilize radical and cationic intermediates by solvation. It was deduced that the phenoxyl radical was generated and then was captured by sulfinate anion to produce a radical anion, leading to the formation of a C−S bond. Nikl, J.; Lips, S.; Schollmeyer, D.; Franke, R.; Waldvogel, S. R. Direct Metal- and Reagent-Free Sulfonylation of


https://doi.org/10.1021/acs.joc.1c00260
J. Org. Chem. XXXX, XXX, XXX−XXX

Phenols with Sodium Sulfinates by Electrosynthesis. *Chem. - Eur. J.* **2019**, *25*, 6891−6895.
(16) Doomes, E.; Clarke, U.; Neitzel, J. J. Synthesis and properties of 1-substituted-2-(phenylsulfonyl)-3-phenyl-2-propene. *J. Org. Chem.* **1987**, *52*, 1540−1543.
(17) (a) Madabhushi, S.; Jillella, R.; Sriramojua, V.; Singhb, R. Oxyhalogenation of thiols and disulfides into sulfonyl chlorides/bromides using oxone-KX (X = Cl or Br) in water. *Green Chem.* **2014**, *16*, 3125−3131. (b) Jereb, M.; Hribernik, L. Conversion of thiols into sulfonyl halogenides under aerobic and metal-free conditions. *Green Chem.* **2017**, *19*, 2286−2295. (c) Han, F.; Su, B.; Song, P.; Wang, Y.; Jia, L.; Xun, S.; Hu, M.; Zou, L. *N*-bromosuccinimide mediated decarboxylative sulfonylation of *β*-keto acids with sodium sulfinates toward *β*-keto sulfones: Evaluation of human carboxylesterase 1 activity. *Tetrahedron* **2018**, *74*, 5908−5913.
(18) We did the reaction of $PhSO_2Br$ with 1,1-diphenylethylene under the present electro-oxidative conditions, and no vinyl sulfone products were detected. Vinyl bromine was obtained in 19% GC yield instead. The result indicated that $PhSO_2Br$ could not react with 1,1-diphenylethylene to produce vinyl sulfone through a radical process under the reaction conditions.
(19) (a) Guo, S.; Li, S.; Yan, W.; Liang, Z.; Fu, Z.; Cai, H. Environmentally Sustainable Production and Application of Acyl Phosphates. *Green Chem.* **2020**, *22*, 7343. (b) Liu, Q.; Sun, B.; Liu, Z.; Kao, Y.; Dong, B.-W.; Jiang, S.-D.; Li, F.; Liu, G.; Yang, Y.; Mo, F. A general electrochemical strategy for the Sandmeyer reaction. *Chem. Sci.* **2018**, *9*, 8731. (c) Inokuchi, T.; Matsumoto, S.; Torii, S. Indirect electrooxidation of alcohols by a double mediatory system with two redox couples of $[R_2N^+{=}O]/R_2NO$. cntdot. and [Br.cntdot. or $Br^+$]/$Br^-$ in an organic-aqueous two-phase solution. *J. Org. Chem.* **1991**, *56*, 2416.
(20) Alam, M. S.; Koo, S. Deprotection of durable benzenesulfonyl protection for phenols-efficient synthesis of polyphenols. *Synth. Commun.* **2018**, *48*, 247−254.
(21) Munday, R. H.; Martinelli, J. R.; Buchwald, S. L. Palladium-Catalyzed Carbonylation of Aryl Tosylates and Mesylates. *J. Am. Chem. Soc.* **2008**, *130*, 2754−2755.
(22) Colbert, J. C.; Denny, D. P. Chromatographic Separation of Nitration Products of Ester-Blocked 2-Hydroxybiphenyl. *J. Org. Chem.* **1959**, *24*, 348−352.
(23) Dond, B. D.; Thore, S. N. NFSI/KF mediated mild and chemoselective interconversion of aryl TBDMS ethers to their benzene sulfonate. *Tetrahedron Lett.* **2020**, *61*, 151660.
(24) Ratushnyy, M.; Kamenovaa, M.; Gevorgyan, V. A mild light-induced cleavage of the S-O bond of aryl sulfonate esters enables efficient sulfonylation of vinylarenes. *Chem. Sci.* **2018**, *9*, 7193−7197.
(25) Cahiez, G.; Lefevre, G.; Moyeux, A.; Guerret, O.; Gayon, E.; Guillonneau, L.; Lefevre, N.; Gu, Q.; Zhou, E. Gram-Scale, Cheap, and Eco-Friendly Iron-Catalyzed Cross-Coupling between Alkyl Grignard Reagents and Alkenyl or Aryl Halides. *Org. Lett.* **2019**, *21*, 2679−2683.
(26) Babtie, A. C.; Lima, M. F.; Kirby, A. J.; Hollfelder, F. Kinetic and computational evidence for an intermediate in the hydrolysis of sulfonate esters. *Org. Biomol. Chem.* **2012**, *10*, 8095−8101.
(27) Jing, Li.; Yu, X.; Guan, M.; Wu, X.; Wang, Q.; Wu, Y. An Efficient Method for Sulfonylation of Amines, Alcohols and Phenols with *N*-Fluorobenzenesulfonimide Under Mild Conditions. *Chem. Res. Chin. Univ.* **2018**, *34*, 191−196.
(28) Rasheed, O. K.; Hardcastle, I. R.; Raftery, J.; Quayle, P. Aryne generation *vs.* Truce-Smiles and fries rearrangements during the Kobayashi fragmentation reaction: a new bi-aryl synthesis. *Org. Biomol. Chem.* **2015**, *13*, 8048−8052.
(29) Perez, K. A.; Rogers, C. R.; Weiss, E. A. Quantum Dot-Catalyzed Photoreductive Removal of Sulfonyl-BasedProtecting Groups. *Angew. Chem., Int. Ed.* **2020**, *59*, 14091−14095.
(30) Kang, K.; Huang, L.; Weix, D. J. Sulfonate Versus Sulfonate: Nickel and Palladium Multimetallic Cross-Electrophile Coupling of Aryl Triflates with Aryl Tosylates. *J. Am. Chem. Soc.* **2020**, *142*, 10634−10640.
(31) Laudadio, G.; Bartolomeu, A. A.; Verwijlen, L. M. H. M.; Cao, Y.; Oliveira, K. T.; Noël, T. Sulfonyl Fluoride Synthesis through Electrochemical Oxidative Coupling of Thiols and Potassium Fluoride. *J. Am. Chem. Soc.* **2019**, *141*, 11832−11836.
(32) Yanagita, H.; Yamamoto, N.; Fuji, H.; Liu, X.; Ogata, M.; Yokota, M.; Takaku, H.; Hasegawa, H.; Odagiri, T.; Tashiro, M.; Hoshino, T. Mechanism of Drug Resistance of Hemagglutinin of Influenza Virus and Potent Scaffolds Inhibiting Its Function. *ACS Chem. Biol.* **2012**, *7*, 552−562.
(33) Zheng, D.; Yu, J.; Wu, J. Generation of Sulfonyl Radicals from Aryldiazonium Tetrafluoroborates and Sulfur Dioxide: The Synthesis of 3-Sulfonated Coumarins. *Angew. Chem., Int. Ed.* **2016**, *55*, 11925−11929.


https://doi.org/10.1021/acs.joc.1c00260
*J. Org. Chem.* XXXX, XXX, XXX−XXX