# Electrochemical Alkoxysulfonylation Difunctionalization of Styrene Derivatives Using Sodium Sulfinates as Sulfonyl Sources

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S Supporting Information

ABSTRACT: An eco-friendly method for the synthesis of β-alkoxy sulfones via electrochemical alkoxysulfonylation reaction of styrenes with sodium sulfinates as sulfonyl sources has been established. The reaction is conducted in an undivided cell at room temperature and tolerates a wide scope of styrenes, sodium sulfinates, and alcohols. The reaction does not need any chemical oxidants and transition-metal catalysts, which provides a new and green access to β-alkoxy sulfones.

*sodium sulfinates as sulfonyl sources*
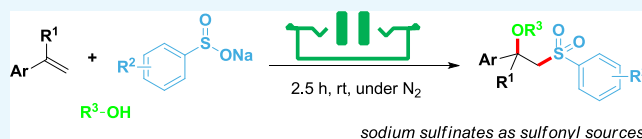
INTRODUCTION

Sulfones and their derivatives belong to an important type of organic compounds,[1] as well as key functional units found in variety of pharmaceuticals, materials, and natural products. Furthermore, they are also very useful building blocks in organic transformations.[2] At the same time, the introduction of additional groups, such as amino, keto, hydroxyl, and alkoxyl, along with sulfonyl group into a molecule usually leads to compounds bearing good bioactivities.[3] Therefore, development of the related efficient synthetic methodologies has gained many interests in this research area.[4] Among them, difunctionalization of alkenes turned out to be an efficient synthetic strategy, as an additional functional group along with sulfonyl group could be introduced at the same time in one reaction.[5] However, the traditional difunctionalizaton reactions usually needed chemical oxidants, transition-metal catalysts and even additives. Thus, the development of green difunctionalizaton reactions becomes very urgent.

Currently, electrochemical difunctionalization[6] of alkenes has become one of the hottest research areas in organic synthetic chemistry. It has been proved to be a powerful and green tool for the construction of complex organic compounds, as no chemical oxidant is needed, thus avoiding generation of reagent wastes and use of harsh reaction conditions.[7] All these promising features result in many unprecedented developments on the difunctionalization of the C−C unsaturated bond to be possible for the synthesis of polyfunctionalized molecules in a very simple manner. In the past years, Moeller,[8] Ackermann,[9] Lei,[10] Lin,[11] Xu,[12] and other groups[13] have independently reported their elegant works in this area, such as electrochemical difunctionalization of alkenes, intermolecular annulation, and intramolecular cyclization. Recently, Lei's group reported an electrochemical oxidative difunctionalization of alkenes for the synthesis of β-alkoxy sulfones with sulfonyl hydrazides as the sulfonyl sources.[14] Very recently, the Sun group developed sulfinic acids as sulfonyl precursors for the electrochemical alkoxysulfonylation reaction of alkenes.[15]

However, only two examples were presented in this reaction with moderate chemical yields. Considering sodium sulfinate[16] as an available, easy-to-handle and stable sulfonyl source compared with sulfonyl azide, sulfonyl hydrazide, sulfonyl cyanide, sulfonyl halide, and sulfinic acid,[16,17] we envision that sodium sulfinate can be used as the substrate for the synthesis of β-alkoxy sulfones via electrochemical difunctionalization reaction. Thus, we herein reported an electrochemical procedure to synthesize the β-alkoxy sulfones with sodium sulfinates as sulfonyl precursors via alkoxysulfonylation reaction with aryl alkenes and alcohols (Scheme 1).

Scheme 1. Electrochemical Alkoxysulfonylation of Styrenes, Sodium Sulfinates, and Alcohols

♦ electrochemical difunctionalization of alkenes
♦ sodium sulfites as sulfonyl sources
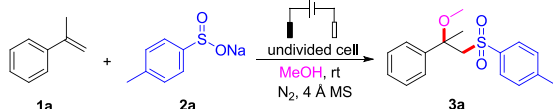♦ oxidant-, metal-free ♦ green method
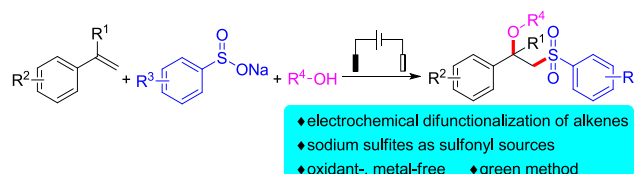
RESULTS AND DISCUSSION

We carried out our initial studies on this electrochemical difunctionalization reaction using α-methyl styrene **1a**, sodium 4-methylbenzenesulfinate **2a**, and methanol as model substrates (Table 1). When the reaction was conducted in an undivided cell at a constant current of 10 mA with a carbon anode and a carbon plate cathode using LiClO$_4$ as an electrolyte, the desired alkoxysulfonylation product **3a** was obtained in 60% yield after 3 h at room temperature under a nitrogen atmosphere (entry 1). The addition of 4 Å MS was

Table 1. Optimization of the Reaction Conditions[a]

entry	electrode	electrolyte	current (mA)	additive	time (h)	yield (%)[b]
1	C/C	LiClO₄	10		3	60
2[c]	C/C	LiClO₄	10		3	52
3	C/C	LiClO₄	10	AcOH	3	43
4	C/C	LiClO₄	10	TsOH	3	77
5	C/C	LiClO₄	10	TsOH	4.5	72
6	C/C	LiClO₄	10	TsOH	2.5	79
7	C/C	LiClO₄	10	TsOH	2	74
8	C/C	LiClO₄	5	TsOH	4.5	78
9	C/C	LiClO₄	15	TsOH	2	74
10	C/Pt	LiClO₄	10	TsOH	2.5	66
11	C/Ni	LiClO₄	10	TsOH	2.5	51
12	C/Cu	LiClO₄	10	TsOH	2.5	32
13	C/Fe	LiClO₄	10	TsOH	2.5	31
14	C/C	Bu₄NBF₄	10	TsOH	2.5	63
15	C/C		10	TsOH	2.5	82
16	C/C		10		2.5	53
17[d]	C/C		10	TsOH	2.5	67
18[e]	C/C		10	TsOH	2.5	68
19[f]	C/C		10	TsOH	2.5	0

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (2.0 equiv), MeOH (8 mL), electrolyte (0.5 mmol), additive (0.5 mmol), 4 Å MS (200 mg), undivided cell, room temperature, and nitrogen atmosphere. [b]Yields based on **1a**. [c]Under air without 4 Å MS. [d]**2a** (1.5 equiv). [e]**2a** (3.0 equiv). [f]Without electric current.

essential for this system, as a lower yield was observed when the reaction was conducted under air without using 4 Å MS (52%, entry 2), and some α-methyl styrene remained. To improve the reaction outcome, we tried to add some additives into the system; the results of entries 3 and 4 indicated that *p*-toluenesulfonic acid was a good choice leading to an increased yield (77%). Variations of reaction time and electric current showed no obvious effects on the reaction (entries 5–7); however, prolonging the reaction time to 4.5 h at 10 mA resulted in a slightly lower yield (entry 5). Further screening of the electrode was carried out, which was found to show a significant influence on the reaction (entries 10–13). Changing the carbon plate cathode into Pt, Ni, Cu, or Fe resulted in noticeably decreased yields (31–66%). Surprisingly, further exploration of electrolyte indicated that this reaction could proceed smoothly and result in the highest yield without the addition of additional electrolyte (82%, entry 15). It worth mentioning that TsOH played a crucial role in this transformation. In the absence of TsOH, a significant decline of yield was observed (53%, entry 16). It is mainly because of the in situ generation of sulfinic acid,[15] which makes the reduction of proton easier at the cathode to release hydrogen gas. Changing the loading amount of sodium 4-methylbenzenesulfinate **2a** from 2.0 to 1.5 or 3.0 equiv did not provide any improvement in yield (entries 17 and 18). Finally, the control experiment was performed without electricity, and no conversion occurred with all the starting materials remaining (entry 19).

Under optimized reaction conditions, we turned our attention to investigate the substrate structural generalities of

this electrochemical alkoxysulfonylation system. First, we carried out the reactions of α-methyl styrene **1a** in methanol using varieties of sodium sulfinates, and the results are shown in Scheme 2. All the examined arylsulfinates worked very well

Scheme 2. Substrate Scope Study of Substituted Sodium Sulfinates[a,b]
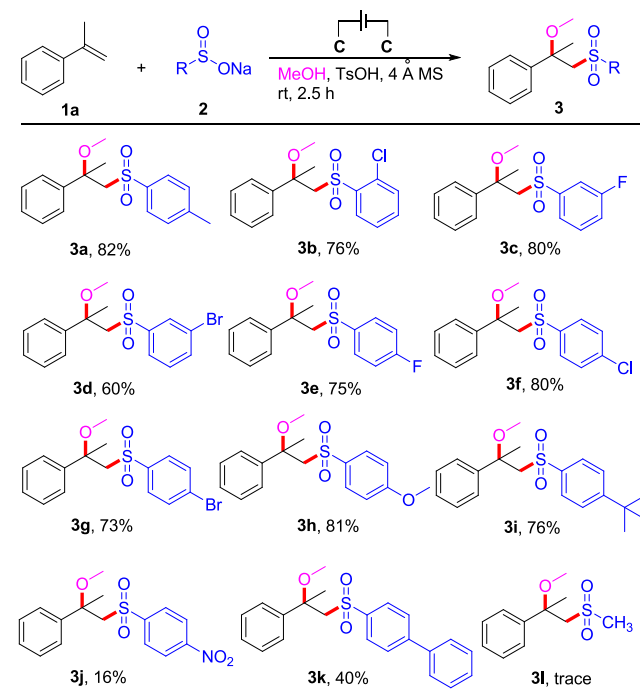
[a]Reaction conditions: **1a** (0.5 mmol), **2** (1.0 mmol), MeOH (8 mL), TsOH (0.5 mmol), 4 Å MS (200 mg), and constant current = 10 mA, in undivided cell at room temperature under nitrogen atmosphere for 2.5 h. [b]Yields.

in this reaction, providing the target products **3a–i** in good yields (60–82%). In particular, sodium arylsulfinates bearing strong electron-donating (methoxyl, **3h**) and strong electron-withdrawing (fluoro, **3c, e**) substituents on the aromatic ring were all tolerated. The position of the substituents on phenyl had almost no influence on this transformation, as the ortho- and para-substituted sulfinates provided a similar outcome (76 and 80% for **3b** and **3f**, respectively). The reaction of the sodium arylsulfinates with nitro on the para-position was complex, and the corresponding product was isolated with poor yield (16%, **3j**), with almost all the olefin starting material consumed. This is mainly because the nitro group might change the basicity of the sulfinate and influence its equilibrium with the TsOH present. One aliphatic sodium sulfinate **2l** was also tried in this reaction; unfortunately, only a trace of the desired **3l** was observed.

Subsequently, a variety of styrene derivatives were investigated under optimized reaction conditions. The reactions of the alkenes bearing different substituents on the aromatic ring proceeded smoothly, giving rise to the corresponding product in 58–78% yields (Scheme 3). For example, α-methyl styrene bearing 4-methyl, 4-methoxyl, 4-fluoro, and 3,5-dimethyl groups on a phenyl ring worked very well to afford **4a–d** in good yields. It is worth mentioning that styrene **1e** was also a suitable substrate for this reaction and was converted into the corresponding product **4e** in 78%

Scheme 3. Substrate Scope Study of Substituted Styrenes[a,b]

4a, 58%   4b, 70%   4c, 60%

4d, 57%   4e, 78%   4f, 70%

4g, 63%   4h, 74%
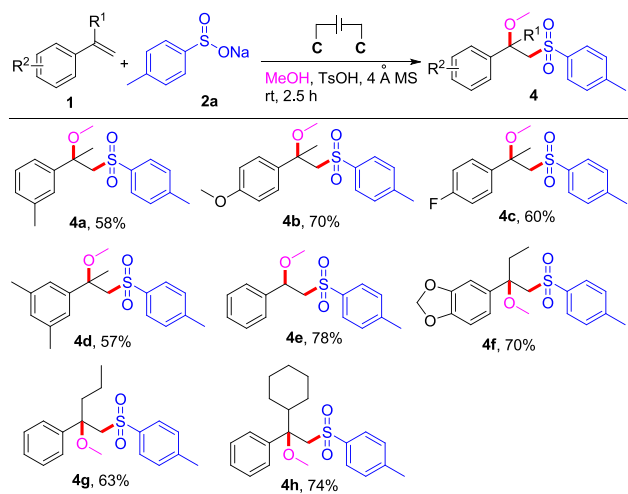
[a]Reaction conditions: **1** (0.5 mmol), **2a** (1.0 mmol), MeOH (8 mL), TsOH (0.5 mmol), 4 Å MS (200 mg), constant current = 10 mA, 2.5 h, undivided cell, and at room temperature under a nitrogen atmosphere. [b]Yields.

chemical yield. Then, a series of different α-substituted styrene derivatives were employed in this reaction for the investigation of steric hindrance effect. Replacing the α-substituted group from methyl by ethyl (**1f**) or propyl (**1g**), no obvious effect was found and the desired products were obtained in the yields of 70 and 63%, respectively. Even the cyclohexyl-substituted styrene (**1h**) could well participate in this reaction, affording the expected product **4h** in 74% yield.

As the final objective of the substrate scope study, we tried to extend methanol to other aliphatic alcohols for this reaction (Scheme 4). Owing to the very low solubility of sodium 4-

Scheme 4. Substrate Scope Study of Different Alcohols[a,b]

5a, 60%   5b, 45%   5c, 29%
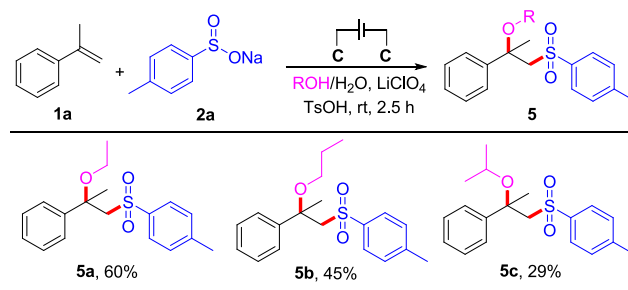
[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), alcohol (8 mL), H$_2$O (1 mL), TsOH (0.5 mmol), LiClO$_4$ (1.5 mmol), constant current = 10 mA, in undivided cell at room temperature under a nitrogen atmosphere for 2.5 h. [b]Yields.

methylbenzenesulfinate **2a** in these aliphatic alcohols, water was used as a co-solvent in these reactions. We were pleased to find that the reactions of ethanol and propanol could proceed smoothly to afford the corresponding alkoxysulfonylation products (**5a−b**) in 60 and 45% yields, respectively. Unfortunately, the reaction with isopropanol only provided 29% yield of the desired product (**5c**), and the competing reaction, hydroxysulfonylation, with water as a coupling partner was observed.

To demonstrate the practical application of this electrochemical difunctionalization system, we then examined the gram-scale preparation about this electrochemical reaction (Scheme 5). The reaction was carried out using 5 mmol of α-

Scheme 5. Large-Scale Synthesis
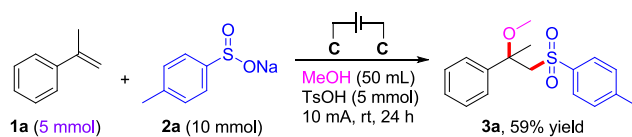
methyl styrene **1a** under the standard reaction conditions. The transformation proceeded smoothly to afford the target compound **3a** with 59% yield after 24 h. The result underscores that the current electrochemical system is a practical and eco-friendly way for the synthesis of functionalized β-alkoxysulfones.

Finally, a control experiment was performed to get an insight into the mechanism of this transformation (Scheme 6). After

Scheme 6. Control Experiment
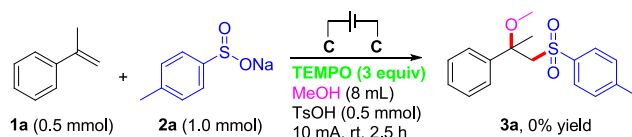
adding a radical inhibitor TEMPO (3 equiv) to the reaction under optimized reaction conditions, the reaction was totally inhibited and no desired product **3a** was obtained at all, with almost all the starting material α-methyl styrene **1a** remaining. This result clearly indicates that a radical pathway may be involved in the electrochemical transformation.

According to the above experimental results and the previous literature reports,[13b,14,15] a plausible mechanism was proposed in Scheme 7 for the electrochemical transformation.

Scheme 7. Proposed Mechanism
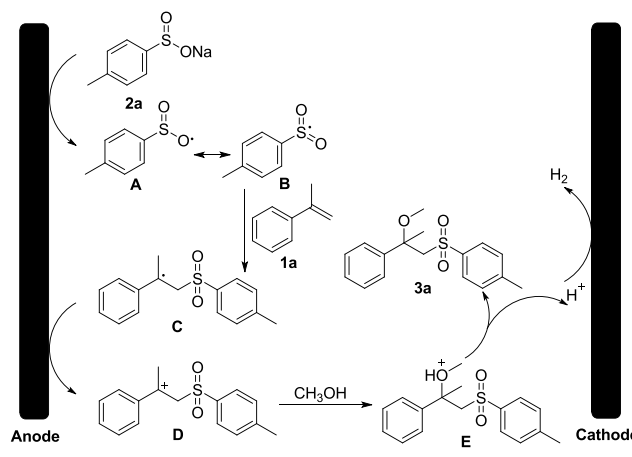
Initially, sodium 4-methylbenzenesulfinate **2a** is oxidized at the graphite anode to generate radical **A**, which easily tautomerizes to sulfonyl radical **B**.[13b] Then, sulfonyl radical **B** adds to the C−C double bond of α-methyl styrene **1a** to afford the alkyl radical **C**. Subsequently, anodic oxidation of radical intermediate **C** generates alkyl cation **D**, which undergoes a nucleophilic attack reaction by methanol to produce

intermediate **E**.[13a] Finally, deprotonation of **E** provides the target product **3a**, as well as the release of H_2 at the cathode.

■ CONCLUSIONS

In summary, we developed an efficient electrochemical oxidative alkoxysulfonylation of aryl alkenes with alcohols and sodium sulfinates. This environmentally benign alkoxysulfonylation of alkenes used sodium sulfinate as a new sulfonyl precursor and could easily afford a series of β-alkoxy sulfones in good yields without the use of any metal catalysts or chemical oxidants. This reaction enriches the contents of electrochemical difunctionalization of olefins and provides a new way for the synthesis of β-alkoxy sulfones.

■ EXPERIMENTAL SECTION

Reaction of α-Methyl Styrene with Methanol and Various Sodium Sulfinates. An undivided cell was equipped with a graphite anode and a graphite cathode and connected to a DC power supply. Into the cell flushed with nitrogen were taken α-methyl styrene **1a** (0.5 mmol, 59 mg), sodium sulfinate **2** (1.0 mmol), TsOH (0.5 mmol, 86 mg), 4 Å MS (200 mg), and MeOH (8 mL). The mixture was electrolyzed under constant current (10 mA) at room temperature for 2.5 h. Then, the reaction was diluted with H_2O (20 mL) and extracted with EtOAc (20 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography using hexane/EtOAc (5:1, v/v) as an eluent to afford the desired product **3**.

1-((2-Methoxy-2-phenylpropyl)sulfonyl)-4-methylbenzene (3a).[14] White solid, 82% yield, mp 94−95 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.65 (d, J = 8.2 Hz, 2H), 7.31−7.27 (m, 4H), 7.26−7.23 (m, 3H), 3.63 (d, J = 14.7 Hz, 1H), 3.49 (d, J = 14.6 Hz, 1H), 2.98 (s, 3H), 2.42 (s, 3H), 1.98 (s, 3H).

1-Chloro-2-((2-methoxy-2-phenylpropyl)sulfonyl)benzene (3b). White solid, 76% yield, mp 113−115 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84−7.82 (m, 1H), 7.47−7.43 (m, 2H), 7.32−7.29 (m, 3H), 7.24−7.22 (m, 2H), 7.20−7.17 (m, 1H), 3.97 (d, J = 14.9 Hz, 1H), 3.86 (d, J = 14.9 Hz, 1H), 2.91 (s, 3H), 1.95 (s, 3H). ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ = 141.5, 138.4, 134.0, 132.3, 131.4, 131.2, 128.4, 128.0, 127.1, 126.3, 77.2, 65.2, 49.9, 21.5. HRMS (ESI): calculated for $C_{16}H_{18}ClO_3S^+$ [M + H]$^+$ 325.0660, found 325.0656.

1-Fluoro-3-((2-methoxy-2-phenylpropyl)sulfonyl)benzene (3c). White solid, 80% yield, mp 81−82 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.56−7.55 (m, 1H), 7.46−7.42 (m, 1H), 7.41−7.39 (m, 1H), 7.29−7.24 (m, 6H), 3.66 (d, J = 14.8 Hz, 1H), 3.54 (d, J = 14.8 Hz, 1H), 2.97 (s, 3H), 1.98 (s, 3H). ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ = 162.9 (d, J = 249.8 Hz), 143.2 (d, J = 6.5 Hz), 141.7, 130.6 (d, J = 7.5 Hz), 128.5, 128.0, 126.3, 123.6 (d, J = 3.3 Hz), 120.3 (d, J = 21.1 Hz), 115.4 (d, J = 24.3 Hz), 77.3, 67.7, 50.0, 21.3. ^{19}F NMR (565 MHz, $CDCl_3$): δ = −110.2. HRMS (ESI): calculated for $C_{16}H_{18}FO_3S^+$ [M + H]$^+$ 309.0955, found 309.0957.

1-Bromo-3-((2-methoxy-2-phenylpropyl)sulfonyl)benzene (3d). White solid, 60% yield, mp 95−97 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.80 (s, 1H), 7.69−7.66 (m, 2H), 7.33−7.31 (m, 1H), 7.28−7.25 (m, 5H), 3.65 (d, J = 14.9 Hz, 1H), 3.55 (d, J = 14.9 Hz, 1H), 2.98 (s, 3H), 1.98 (s, 3H). ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ = 142.9, 141.4, 136.0, 131.0, 130.2, 128.4, 128.2, 126.4, 126.3, 122.7, 77.3, 67.8, 50.0,

21.3. HRMS (ESI): calculated for $C_{16}H_{18}BrO_3S^+$ [M + H]$^+$ 369.0155, found 369.00151.

1-Fluoro-4-((2-methoxy-2-phenylpropyl)sulfonyl)benzene (3e). White solid, 75% yield, mp 58−60 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.76−7.73 (m, 2H), 7.28−7.25 (m, 5H), 7.12−7.09 (m, 2H), 3.65 (d, J = 14.9 Hz, 1H), 3.52 (d, J = 14.8 Hz, 1H), 2.96 (s, 3H), 1.97 (s, 3H). ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ = 166.2 (d, J = 253.8 Hz), 141.9, 137.3 (d, J = 3.2 Hz), 130.8 (d, J = 9.5 Hz), 128.5, 127.9, 126.3, 116.0 (d, J = 7.5 Hz), 77.4, 67.8, 50.0, 21.4. ^{19}F NMR (565 MHz, $CDCl_3$): δ = −104.7. HRMS (ESI): calculated for $C_{16}H_{18}FO_3S^+$ [M + H]$^+$ 309.0955, found 309.0952.

1-Chloro-4-((2-methoxy-2-phenylpropyl)sulfonyl)benzene (3f). White solid, 80% yield, mp 94−95 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67−7.65 (m, 2H), 7.41−7.39 (m, 2H), 7.28−7.25 (m, 5H), 3.65 (d, J = 14.9 Hz, 1H), 3.52 (d, J = 14.8 Hz, 1H), 2.95 (s, 3H), 1.96 (s, 3H). ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ = 141.8, 139.7, 139.6, 129.4, 129.0, 128.5, 127.9, 126.3, 77.3, 67.7, 50.0, 21.3. HRMS (ESI): calculated for $C_{16}H_{18}ClO_3S^+$ [M + H]$^+$ 325.0660, found 325.0657.

1-Bromo-4-((2-methoxy-2-phenylpropyl)sulfonyl)benzene (3g). White solid, 73% yield, mp 111−113 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.60−7.56 (m, 4H), 7.30−7.26 (m, 5H), 3.65 (d, J = 14.8 Hz, 1H), 3.52 (d, J = 14.9 Hz, 1H), 2.96 (s, 3H), 1.97 (s, 3H). ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ = 141.8, 140.2, 132.0, 129.5, 128.5, 128.3, 127.9, 126.3, 77.3, 67.8, 50.0, 21.3. HRMS (ESI): calculated for $C_{16}H_{18}BrO_3S^+$ [M + H]$^+$ 369.0155, found 369.0155.

1-Methoxy-4-((2-methoxy-2-phenylpropyl)sulfonyl)-benzene (3h). White solid, 81% yield, mp 83−85 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.69 (d, J = 8.9 Hz, 2H), 7.31−7.24 (m, 5H), 6.91 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 3.63 (d, J = 14.7 Hz, 1H), 3.50 (d, J = 14.6 Hz, 1H), 2.98 (s, 3H), 1.97 (s, 3H). ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ = 163.2, 142.3, 133.0, 130.1, 128.4, 127.8, 126.3, 114.0, 77.5, 67.7, 55.6, 50.1, 21.5. HRMS (ESI): calculated for $C_{17}H_{20}NaO_4S^+$ [M + Na]$^+$ 343.0975, found 343.0971.

1-(tert-Butyl)-4-((2-methoxy-2-phenylpropyl)sulfonyl)-benzene (3i). White solid, 76% yield, mp 103−104 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.30−7.21 (m, 5H), 3.64 (d, J = 14.6 Hz, 1H), 3.53 (d, J = 14.6 Hz, 1H), 2.98 (s, 3H), 1.99 (s, 3H), 1.34 (s, 9H). ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ = 156.8, 142.0, 138.1, 128.4, 127.8, 127.6, 126.3, 125.8, 77.5, 67.4, 50.0, 35.1, 31.1, 21.5. HRMS (ESI): calculated for $C_{20}H_{27}O_3S^+$ [M + H]$^+$ 347.1675, found 347.1672.

1-((2-Methoxy-2-phenylpropyl)sulfonyl)-4-nitrobenzene (3j). White solid, 16% yield, mp 123−125 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.28 (d, J = 8.8 Hz, 2H), 7.92 (d, J = 8.8 Hz, 2H), 7.27−7.24 (m, 5H), 3.71 (d, J = 15.1 Hz, 1H), 3.58 (d, J = 15.1 Hz, 1H), 2.93 (s, 3H), 1.98 (s, 3H). ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ = 150.2, 146.8, 141.5, 129.4, 128.6, 128.2, 126.2, 123.7, 77.2, 68.0, 49.9, 21.1. HRMS (ESI): calculated for $C_{16}H_{17}NNaO_5S^+$ [M + Na]$^+$ 358.0720, found 358.0725.

4-((2-Methoxy-2-phenylpropyl)sulfonyl)-1,1′-biphenyl (3k). White solid, 40% yield, mp 101−103 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.80−7.78 (m, 2H), 7.64−7.60 (m, 4H), 7.52−7.50 (m, 2H), 7.46−7.44 (m, 1H), 7.32−7.30 (m, 2H), 7.28−7.24 (m, 3H), 3.70 (d, J = 14.8 Hz, 1H), 3.58 (d, J = 14.8 Hz, 1H), 2.99 (s, 3H), 2.01 (s, 3H). ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ = 145.9, 142.0, 139.7, 139.4, 129.0, 128.5, 128.4, 128.3, 127.8, 127.4, 127.3, 126.3, 77.5, 67.7, 50.0, 21.5.

HRMS (ESI): calculated for $C_{22}H_{23}O_3S^+$ [M + H]$^+$ 367.1362, found 367.1355.

Reaction of Styrene Derivatives with Sodium 4-Methylbenzenesulfinate and Methanol. An undivided cell was equipped with a graphite anode and a graphite cathode and connected to a DC power supply. Into the cell flushed with nitrogen were taken styrene derivatives **1** (0.5 mmol), sodium 4-methylbenzenesulfinate **2a** (1.0 mmol, 178 mg), TsOH (0.5 mmol, 86 mg), 4 Å MS (200 mg), and MeOH (8 mL). The mixture was electrolyzed under constant current (10 mA) at room temperature for 2.5 h. Then, the reaction was diluted with H$_2$O (20 mL) and extracted with EtOAc (20 mL × 3). The combined organic layers were dried with anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography using hexane/EtOAc (5:1, v/v) as an eluent to afford the desired product **4**.

1-(2-Methoxy-1-tosylpropan-2-yl)-3-methylbenzene (4a). Colorless oil, 58% yield. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.62 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.18–7.15 (m, 1H), 7.11 (d, J = 7.9 Hz, 1H), 7.05–7.03 (m, 2H), 3.63 (d, J = 14.7 Hz, 1H), 3.50 (d, J = 14.7 Hz, 1H), 2.97 (s, 3H), 2.42 (s, 3H), 2.28 (s, 3H), 1.96 (s, 3H). ^{13}C{^{1}H}NMR (150 MHz, CDCl$_3$): δ = 143.8, 142.0, 138.3, 138.0, 129.3, 128.5, 128.3, 127.9, 126.9, 123.4, 77.4, 67.5, 50.0, 21.6, 21.5, 21.4. HRMS (ESI): calculated for $C_{18}H_{23}O_3S^+$ [M + H]$^+$ 319.1362, found 319.1362.

1-Methoxy-4-(2-methoxy-1-tosylpropan-2-yl)benzene (4b). White solid, 70% yield, mp 85–87 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.61 (d, J = 8.3 Hz, 2H), 7.23–7.21 (m, 2H), 7.20–7.18 (m, 2H), 6.78–6.76 (m, 2H), 3.80 (s, 3H), 3.62 (d, J = 14.7 Hz, 1H), 3.50 (d, J = 14.7 Hz, 1H), 2.94 (s, 3H), 2.42 (s, 3H), 1.95 (s, 3H). ^{13}C{^{1}H}NMR (150 MHz, CDCl$_3$): δ = 159.2, 143.7, 138.4, 133.8, 129.3, 127.9, 127.7, 113.6, 77.1, 67.7, 55.2, 49.7, 21.5, 21.4. HRMS (ESI): calculated for $C_{18}H_{22}NaO_4S^+$ [M + Na]$^+$ 357.1131, found 357.1128.

1-Fluoro-4-(2-methoxy-1-tosylpropan-2-yl)benzene (4c). White solid, 60% yield, mp 101–103 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.60 (d, J = 8.2 Hz, 2H), 7.27–7.23 (m, 4H), 6.95–6.92 (m, 2H), 3.61 (d, J = 14.7 Hz, 1H), 3.52 (d, J = 14.7 Hz, 1H), 2.97 (s, 3H), 2.43 (s, 3H), 1.95 (s, 3H). ^{13}C{^{1}H}NMR (150 MHz, CDCl$_3$): δ = 163.1 (d, J = 245.6 Hz), 144.0, 138.2, 137.7 (d, J = 3.3 Hz), 129.4, 128.3 (d, J = 8.0 Hz), 127.8, 115.2 (d, J = 21.2 Hz), 77.0, 67.6, 49.8, 21.6, 21.5. ^{19}F NMR (565 MHz, CDCl$_3$): δ = −114.6. HRMS (ESI): calculated for $C_{17}H_{20}FO_3S^+$ [M + H]$^+$ 323.1112, found 323.1108.

1-(2-Methoxy-1-tosylpropan-2-yl)-3,5-dimethylbenzene (4d). White solid, 57% yield, mp 119–121 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.60 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 6.85 (s, 2H), 6.83 (s, 1H), 3.62 (d, J = 14.7 Hz, 1H), 3.50 (d, J = 14.8 Hz, 1H), 2.97 (s, 3H), 2.41 (s, 3H), 2.24 (s, 6H), 1.94 (s, 3H). ^{13}C{^{1}H}NMR (150 MHz, CDCl$_3$): δ = 143.7, 141.8, 138.2, 137.8, 129.3, 129.2, 127.9, 124.1, 77.4, 67.5, 50.0, 21.5, 21.4, 21.3. HRMS (ESI): calculated for $C_{19}H_{25}O_3S^+$ [M + H]$^+$ 333.1519, found 333.1515.

1-((2-Methoxy-2-phenylethyl)sulfonyl)-4-methylbenzene (4e).[14] White solid, 78% yield, mp 104–106 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.83 (d, J = 8.3 Hz, 2H), 7.36–7.33 (m, 4H), 7.32–7.29 (m, 1H), 7.28–7.26 (m, 2H), 4.77 (dd, J = 2.8, 9.4 Hz, 1H), 3.66 (dd, J = 9.5, 14.8 Hz, 1H), 3.30 (dd, J = 2.8, 14.7 Hz, 1H), 3.13 (s, 3H), 2.45 (s, 3H).

5-(2-Methoxy-1-tosylbutan-2-yl)benzo[d][1,3]dioxole (4f). White solid, 70% yield, mp 114–116 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.52 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.73–6.71 (m, 1H), 6.66–6.64 (m, 2H), 5.93–5.90 (m, 2H), 3.75 (d, J = 15.0 Hz, 1H), 3.65 (d, J = 15.0 Hz, 1H), 2.93 (s, 3H), 2.41 (s, 3H), 2.39–2.34 (m, 1H), 2.12–2.06 (m, 1H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H}NMR (150 MHz, CDCl$_3$): δ = 147.6, 146.8, 143.8, 137.7, 134.8, 129.2, 127.9, 120.4, 107.6, 107.3, 101.0, 79.0, 61.6, 49.2, 27.0, 21.5, 7.3. HRMS (ESI): calculated for $C_{19}H_{22}NaO_5S^+$ [M + Na]$^+$ 385.1080, found 385.1076.

1-((2-Methoxy-2-phenylpentyl)sulfonyl)-4-methylbenzene (4g). White solid, 63% yield, mp 56–58 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.56 (d, J = 8.2 Hz, 2H), 7.25–7.20 (m, 5H), 7.18 (d, J = 7.9 Hz, 2H), 3.79 (d, J = 14.9 Hz, 1H), 3.74 (d, J = 14.9 Hz, 1H), 2.94 (s, 3H), 2.40 (s, 3H), 2.30–2.25 (m, 1H), 2.11–2.06 (m, 1H), 1.29–1.24 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H}NMR NMR (150 MHz, CDCl$_3$): δ = 143.9, 141.2, 138.0, 129.4, 128.1, 127.9, 127.3, 126.5, 79.3, 61.7, 49.6, 37.6, 21.5, 16.4, 14.2. HRMS (ESI): calculated for $C_{19}H_{25}O_3S^+$ [M + H]$^+$ 333.1519, found 333.1520.

1-((2-Cyclohexyl-2-methoxy-2-phenylethyl)sulfonyl)-4-methylbenzene (4h). White solid, 74% yield, mp 120–121 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.78 (d, J = 8.2 Hz, 2H), 7.28–7.23 (m, 5H), 7.14–7.12 (m, 2H), 4.03 (d, J = 15.1 Hz, 1H), 3.81 (d, J = 15.1 Hz, 1H), 3.20 (s, 3H), 2.44 (s, 3H), 2.33–2.29 (m, 1H), 2.01 (d, J = 12.3 Hz, 1H), 1.73 (d, J = 12.1 Hz, 1H), 1.68–1.66 (m, 2H), 1.57 (d, J = 12.9 Hz, 1H), 1.29–1.19 (m, 2H), 0.89–0.82 (m, 1H), 0.71–0.64 (m, 1H), 0.45–0.38 (m, 1H). ^{13}C{^{1}H}NMR (150 MHz, CDCl$_3$): δ = 144.3, 138.5, 129.5, 128.2, 127.4, 127.2, 127.0, 126.0, 83.2, 57.8, 50.9, 44.8, 28.7, 26.5, 26.4, 26.2, 26.1, 21.6. HRMS (ESI): calculated for $C_{22}H_{28}NaO_3S^+$ [M + Na]$^+$ 395.1651, found 395.1653.

Reaction of α-Methyl Styrene with Sodium 4-Methylbenzenesulfinate and Different Alcohols. An undivided cell was equipped with a graphite anode and a graphite cathode and connected to a DC power supply. Into the cell flushed with nitrogen were taken α-methyl styrene **1a** (0.5 mmol), sodium 4-methylbenzenesulfinate **2a** (1.0 mmol, 178 mg), TsOH (0.5 mmol, 86 mg), LiClO$_4$ (1.5 mmol), alcohol (8 mL), and H$_2$O (1 mL). The mixture was electrolyzed under constant current (10 mA) at room temperature for 2.5 h. Then, the reaction was diluted with H$_2$O (20 mL) and extracted with EtOAc (20 mL × 3). The combined organic layers were dried with anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography using hexane/EtOAc (5:1, v/v) as an eluent to afford the desired product **5**.

1-((2-Ethoxy-2-phenylpropyl)sulfonyl)-4-methylbenzene (5a). White solid, 60% yield, mp 40–41 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.67 (d, J = 8.2 Hz, 2H), 7.31–7.27 (m, 4H), 7.26–7.23 (m, 3H), 3.65 (d, J = 14.8 Hz, 1H), 3.49 (d, J = 14.8 Hz, 1H), 3.27–3.22 (m, 1H), 2.98–2.93 (m, 1H), 2.43 (s, 3H), 1.96 (s, 3H), 0.93 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H}NMR (150 MHz, CDCl$_3$): δ = 143.8, 143.0, 138.5, 129.3, 128.4, 128.0, 127.7, 126.1, 77.0, 68.0, 57.6, 21.9, 21.5, 15.1. HRMS (ESI): calculated for $C_{18}H_{23}O_3S^+$ [M + H]$^+$ 319.1362, found 319.1359.

1-Methyl-4-((2-phenyl-2-propoxypropyl)sulfonyl)benzene (5b). Colorless oil, 45% yield. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.66 (d, J = 8.3 Hz, 2H), 7.31–7.23 (m, 7H), 3.67 (d, J = 14.8 Hz, 1H), 3.49 (d, J = 14.8 Hz, 1H), 3.15–3.12 (m, 1H),

2.86−2.82 (m, 1H), 2.43 (s, 3H), 1.97 (s, 3H), 1.34−1.31 (m, 2H), 0.75 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H}NMR (150 MHz, CDCl$_3$): δ = 143.8, 142.8, 138.5, 129.3, 128.3, 128.0, 127.7, 126.2, 76.8, 68.0, 63.7, 23.0, 21.8, 21.5, 10.5. HRMS (ESI): calculated for C$_{19}$H$_{25}$O$_3$S$^+$ [M + H]$^+$ 333.1519, found 333.1520.

1-((2-Isopropoxy-2-phenylpropyl)sulfonyl)-4-methylbenzene (5c). White solid, 29% yield, mp 87−88 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.61 (d, J = 8.3 Hz, 2H), 7.35−7.33 (m, 2H), 7.26−7.22 (m, 5H), 3.69 (d, J = 14.8 Hz, 1H), 3.48 (d, J = 14.8 Hz, 1H), 3.43 (hept, J = 6.1 Hz, 1H), 2.43 (s, 3H), 2.02 (s, 3H), 1.04 (d, J = 6.0 Hz, 3H), 0.77 (d, J = 6.1 Hz, 3H). ^{13}C{^{1}H}NMR (150 MHz, CDCl$_3$): δ = 143.6, 143.0, 138.5, 129.2, 128.0, 127.9, 127.8, 126.9, 77.2, 68.6, 65.5, 24.7, 24.1, 22.3, 21.5. HRMS (ESI): calculated for C$_{19}$H$_{25}$O$_3$S$^+$ [M + H]$^+$ 333.1519, found 333.1518.

Large-Scale Synthesis. An undivided cell was equipped with a graphite anode and a graphite cathode and connected to a DC power supply. Into the cell flushed with nitrogen were taken α-methyl styrene **1a** (5 mmol), sodium 4-methylbenzenesulfinate **2a** (10 mmol), TsOH (5 mmol), 4 Å MS (1 g), and MeOH (50 mL). The mixture was electrolyzed under constant current (10 mA) at room temperature for 24 h. Then, the reaction was diluted with H$_2$O (100 mL) and extracted with EtOAc (50 mL × 3). The combined organic layers were dried with anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography using hexane/EtOAc (5:1, v/v) as an eluent to afford the desired product **3a**.

Control Experiment. An undivided cell was equipped with a graphite anode and a graphite cathode and connected to a DC power supply. Into the cell flushed with nitrogen were taken α-methyl styrene **1a** (0.5 mmol), sodium 4-methylbenzenesulfinate **2a** (1.0 mmol), TsOH (0.5 mmol), TEMPO (1.5 mmol), 4 Å MS (200 mg), and MeOH (8 mL). The mixture was electrolyzed under constant current (10 mA) at room temperature for 2.5 h. No desired product **3a** was detected.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02442.

Copies of ^{1}H NMR and ^{13}C NMR spectra (PDF)

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Notes
The authors declare no competing financial interest.

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