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Sulfinate Synthesis

Sodium Arenesulfinates-Involved Sulfinate Synthesis Revisited: Improved Synthesis and Revised Reaction Mechanism

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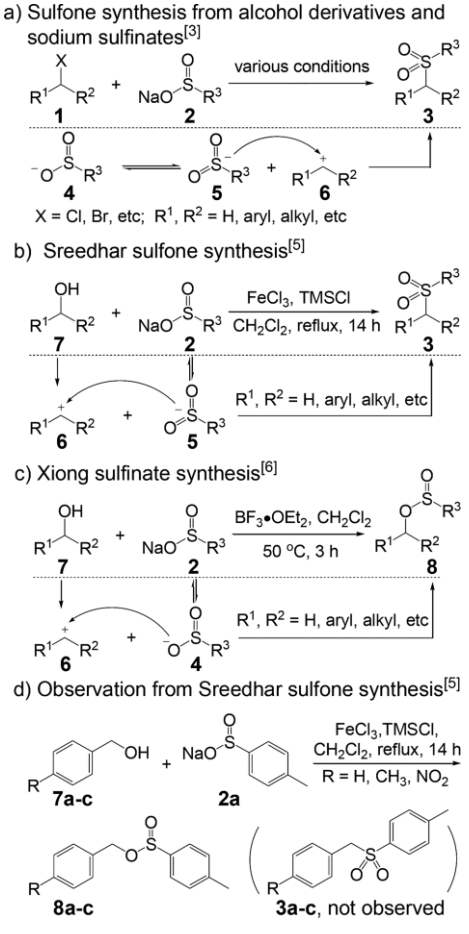
Abstract: Reaction of alcohols with sodium arenesulfinates could afford either sulfones or sulfinates, and O-attack of sulfinate anions onto the in situ generated carbocation intermediates from alcohols was the previous proposed reaction mechanism in many syntheses of sulfinates. This concept, which is often used consciously or unconsciously, was revised herein by using isotopic labeling experiments and development of an improved sulfinate synthesis. The improved sulfinate synthetic protocol possesses many advantages such as a high sulfinate/sulfone selectivity, a broad substrate scope, metal-free, and mild reaction conditions. The revised reaction mechanism necessitates revision of many previous proposed reaction mechanisms in literatures.

Introduction

Alcohols are highly attractive starting materials in organic synthesis as they are abundant, inexpensive, and often readily available.[1] Since hydroxyl group is a poor leaving group, substitution of an alcohol usually consists of transformation of the hydroxyl group to a better leaving group such as a halide and a sulfonate, and subsequently substitution of the resulting alcohol derivative with an appropriate nucleophile.[2] For instance, substitution of alcohol derivatives, mainly alkyl halides **1**, with sodium arenesulfinates **2** has been extensively investigated for the preparation of sulfones **3** (Scheme 1a).[3] Although an arenesulfinate anion (**4** or **5**) is a gemini nucleophile, the sulfur acts as the attack atom in the most cases because of its higher nucleophilicity compared to the one of oxygen.[4] Inspiringly, Sreedhar reported a direct sulfonylation of alcohols **7** with sodium arenesulfinates **2** using iron chloride ($FeCl_3$) and trimethylsilyl chloride (TMSCl) as promoters, in which S-attack of arenesulfinate anions **5** onto the in situ generated carbocations **6** was the proposed reaction mechanism (Scheme 1b).[5] Xiong reported a direct sulfination of alcohols **7** with sodium sulfinates **2** promoted by boron trifluoride etherate (BF_3•Et_2O), in which O-attack of sulfinate anions **4** onto the carbocations **6** was the proposed reaction pathway (Scheme 1c).[6] Actually, reaction of primary benzyl alcohols **7a**–**c** with sodium arenesulfinate **2a** under Sreedhar's procedure[5] also afforded sulfinates **8a**–**c**, not sulfones **3a**–**c**, based on the NMR spectroscopic data and spectra reported by Sreedhar (Scheme 1d).[5] Considering the importance of sulfinates in the field of chemistry, biology



Scheme 1. Selected synthetic protocols for the synthesis of sulfones or sulfinates.

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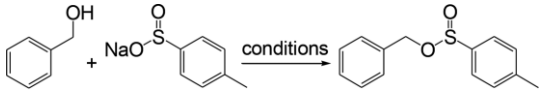
and pharmaceutical sciences,[7,8] this inspiring result triggered us to optimize the reaction conditions for the synthesis of sulfinates.

Results and Discussion

Reaction of benzyl alcohol (**7a**) with sodium *p*-toluenesulfinate (**2a**) was used as a probe for evaluating the reaction conditions, and the representative results are summarized in Table 1.

Following Sreedhar's procedure [$FeCl_3$ (15 mol-%), TMSCl (1.2 equiv.), CH_2Cl_2, 45 °C],[5] the treatment of benzyl alcohol (**7a**, 1.0 equiv.) and sodium *p*-toluenesulfinate (**2a**, 1.2 equiv.) afforded sulfinate **8a** in 43 % yield within 3 h (Table 1, entry 1). The yield of sulfinate **8a** was increased from 43 % to 55 % by treating benzyl alcohol (**7a**) with a slight excess of sodium *p*-toluenesulfinate (**2a**) under otherwise identical conditions (entries 1 and 2). The reaction went equally well at room temperature (25 °C, entries 2 and 3). A higher yield of sulfinate **8a** was observed when the reaction was performed in the absence of $FeCl_3$ (entries 3 and 4). A series of other silicon reagents such as TIPSCl, TBDMSCl and DMSCl were further investigated for this reaction, but no better results were obtained in comparison to that with the use of TMSCl as the promoter (entries 4–7). The solvent played an important role in this reaction. The reaction did not work with the use of DMF, THF or 1,4-dioxane as the solvent (entries 8–10). With the use of DCE, toluene, CH_3CN, CH_3NO_2 and DMSO in comparison to CH_2Cl_2, lower yields were observed (entries 7 and 11–15). The molar ratio of **7a** to **2a** was also important for this reaction, and increasing yields of sulfinate **8a** were observed with the use of appropriate amounts of excess benzyl alcohol (**7a**, entries 4 and 16–17). The yield of sulfinate **8a** was further increased to 83 % when the molar ratio of **7a** to **2a** was increased from 1 to 2 (entries 16–18). No further increase was observed when the molar ratio of **7a** to **2a** exceeded 2 (entries 16–19). Parameter optimization identified the most effective loading of TMSCl as the 2.0 equivalents of sodium *p*-toluenesulfinate (**2a**, entries 18 and 20–23). A slight lower yield of sulfinate **8a** was observed when the reaction was performed under reflux (45 °C) in comparison to that at room temperature (25 °C, entries 22 and 24). The choice of reaction time was also found to be of importance to improve this reaction efficiency, and the complete consumption of sodium *p*-

Table 1. Optimization of the reaction conditions.[a]



7a **2a** **8a**

Entry	Promoter	Solvent	Temp.	Yield [b]
1[c]	$FeCl_3$, TMSCl	CH_2Cl_2	45 °C	43 %
2	$FeCl_3$, TMSCl	CH_2Cl_2	45 °C	55 %
3	$FeCl_3$, TMSCl	CH_2Cl_2	25 °C	55 %
4	TMSCl	CH_2Cl_2	25 °C	67 %
5	TIPSCl	CH_2Cl_2	25 °C	0
6	TBDMSCl	CH_2Cl_2	25 °C	44 %
7	DMSCl	CH_2Cl_2	25 °C	65 %
8	TMSCl	DMF	25 °C	0
9	TMSCl	THF	25 °C	0
10	TMSCl	1,4-dioxane	25 °C	0
11	TMSCl	DCE	25 °C	51 %
12	TMSCl	toluene	25 °C	55 %
13	TMSCl	CH_3CN	25 °C	12 %
14	TMSCl	CH_3NO_2	25 °C	26 %
15	TMSCl	DMSO	25 °C	trace
16[d]	TMSCl	CH_2Cl_2	25 °C	61 %
17[e]	TMSCl	CH_2Cl_2	25 °C	75 %
18[f]	TMSCl	CH_2Cl_2	25 °C	83 %
19[g]	TMSCl	CH_2Cl_2	25 °C	83 %
20[f]	–	CH_2Cl_2	25 °C	0
21[f,h]	TMSCl	CH_2Cl_2	25 °C	87 %
22[f,i]	TMSCl	CH_2Cl_2	25 °C	93 %
23[f,j]	TMSCl	CH_2Cl_2	25 °C	93 %
24[f,i]	TMSCl	CH_2Cl_2	45 °C	91 %
25[f,i,k]	TMSCl	CH_2Cl_2	25 °C	85 %
26[f,i,l]	TMSCl	CH_2Cl_2	25 °C	94 %
27[f,i,m]	TMSCl	CH_2Cl_2	25 °C	93 %
28[f,i,l,n]	TMSCl	CH_2Cl_2	25 °C	93 %

[a] General conditions: **7a** (0.6 mmol), **2a** (0.5 mmol), silicon reagent (0.6 mmol) with/without $FeCl_3$ (15 mol-%) in solvent (2.0 mL) at 25 °C for 3 h. [b] Isolated yields. [c] 0.5 mmol of **7a** and 0.6 mmol of **2a**. [d] 0.5 mmol of **7a**. [e] 0.8 mmol of **7a**. [f] 1.0 mmol of **7a**. [g] 1.2 mmol of **7a**. [h] 0.8 mmol of TMSCl. [i] 1.0 mmol of TMSCl. [j] 1.2 mmol of TMSCl. [k] 0.5 h. [l] 1.0 h. [m] 1.5 h. [n] Reaction was carried out at 1.07 g scale of **2a** (6.0 mmol). TMS = trimethylsilyl. TIPS = triisopropylsilyl. TBDMS = *tert*-butyldimethylsilyl. DMS = dimethylsilyl. DCE = 1,2-dichloroethane. DMSO = dimethyl sulfoxide. DMF = N,N-dimethylformamide. THF = tetrahydrofuran. Temp. = temperature.

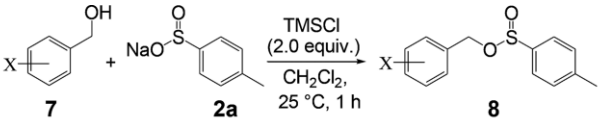
toluenesulfinate (**2a**) cannot guarantee to yield the highest yield of sulfinate **8a**. Parameter optimization based on this consideration identified 1 h as the most appropriate reaction time (entries 22 and 25–27). Indeed, treatment of benzyl alcohol (**7a**) and sodium *p*-toluenesulfinate (**2a**) under the optimized reaction conditions for 1 h afforded sulfinate **8a** in 94 % yield (entries 26). Furthermore, scaling up sodium *p*-toluenesulfinate (**2a**) to 1.07 g (6.0 mmol) the reaction provided the yield at an excellent level (Table 1, entry 28).

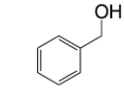
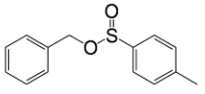
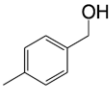
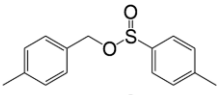
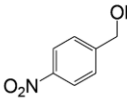
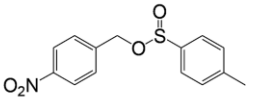
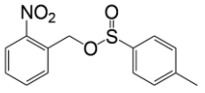
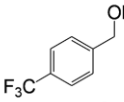
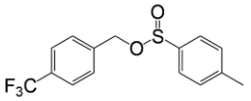
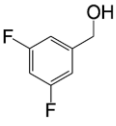
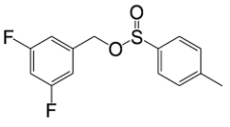
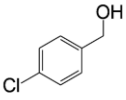
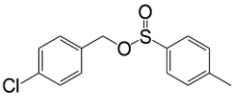
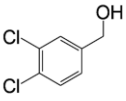
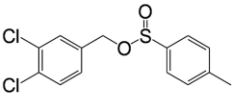
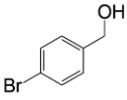
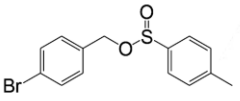
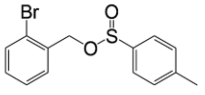
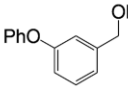
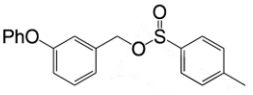
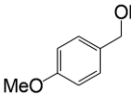
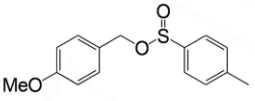
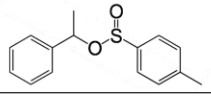
The optimized reaction conditions proved to be effective for a wide range of benzyl alcohols, and the representative results are listed in Table 2. With the aromatic ring bearing hydrogen atoms, electron-donating and electron-withdrawing groups, benzyl alcohols **7a**–**k** reacted smoothly with sodium *p*-toluenesulfinate (**2a**) in the presence of TMSCl (2 equiv.) in CH_2Cl_2 at 25 °C to afford sulfinates **8a**–**k** in 63–94 % yields within 1 h (Table 2, entries 1–11). A decreasing yield was observed with the use of a 2-substituted benzyl alcohol (**7d** or **7j**) in comparison to a 4-substituted benzyl alcohol (**7c** or **7i**) as the substrate, indicating that the steric factor of benzyl alcohols **7** affects the reaction (Table 2, entries 3 and 4, 9 and 10). The treatment of 4-methoxybenzyl alcohol (**7l**) with sodium p-toluenesulfinate (**2a**) gave a sulfone product in $FeCl_3$/TMSCl system, whereas it provided exclusively sulfinate **8l** under our conditions, albeit at a lower reaction temperature (Table 2, entry 12). Reaction of 1-phenylethanol (**7m**) with **2a** under the same conditions gave sulfinate **8m** as a sole product (90 % yield, Table 2, entries 12 and 13). However, this reaction in either the $FeCl_3$/TMSCl or $BF_3{\cdot}Et_2O$ system yielded exclusively a sulfone product based on its NMR spectroscopic data reported by Sreedhar[5] and Xiong.[6] The result indicated that our sulfinate method expanded the substrate scope of alcohols.

Sulfination of alkyl and allyl alcohols with sodium *p*-toluenesulfinate (**2a**) were subsequently investigated (Table 3). Simple primary/secondary alkyl alcohols, such as methanol (**7n**), ethanol (**7o**) and isopropanol (**7p**), reacted smoothly with **2a**. under the standard conditions to give sulfinates **8n**–**p** in 90–91 % yields (Table 3, entries 1–3). *tert*-Butanol, a sterically hindered alkyl alcohol, reacted uneventfully with **2a** under the standard conditions to afford sulfinate **8q** in 50 % yield (entry 4). Phenethyl alcohol (**7r**) has also been investigated, which reacted with **2a** under the standard conditions to give sulfinate **8r** in 92 % yield (entry 5). Cyclic alcohols, including cyclopentanol (**7s**), 2,3-dihydro-1*H*-inden-2-ol (**7t**) and cyclohexanol (**7u**), reacted with **2a** under the standard conditions to afford exclusively sulfinates **8s**–**u** in 75–82 % yields (Table 3, entries 6–8). Instead, the reaction of **7u** with **2a** under Sreedhar's procedure gave a sulfone as the sole product.[5] Our sulfinate synthesis and Sreedhar sulfone synthesis could complement each other to enrich the reaction diversity. Cinnamyl alcohol (**7v**) and methallyl alcohol (**7w**), two allyl alcohols, reacted with **2a** successfully to afford sulfinates **8v**–**w** in 75 % and 82 % yields, respectively (Table 3, entries 9–10). These reactions are extremely easy to perform without the need for using anhydrous solvent and inert atmosphere and under mild reaction conditions.

The feasibility of this sulfinate synthesis was also checked by using a serial of sodium arenesulfinates **2** as the substrates

Table 2. TMSCl-promoted sulfinate synthesis from benzyl alcohols **7** and sodium *p*-toluenesulfinate (**2a**).[a]

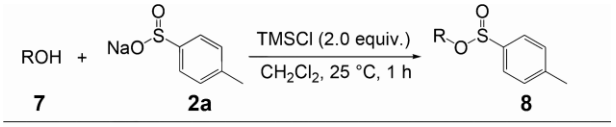


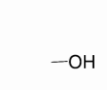
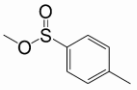
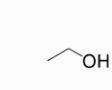
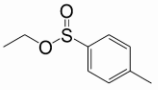
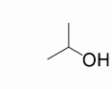
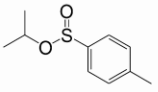
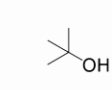
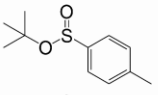
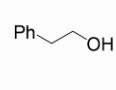
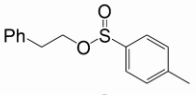
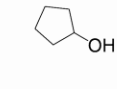
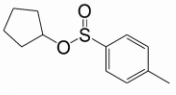
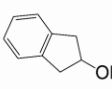
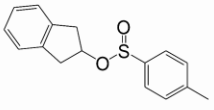
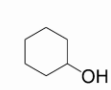
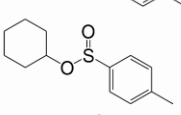
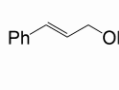
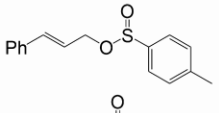
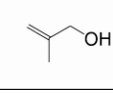
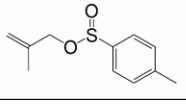
Entry	7	Product 8 and Yield [b]
1	 **7a**	 **8a:** 94%
2	 **7b**	 **8b:** 93%
3	 **7c**	 **8c:** 73%
4	 **7d**	 **8d:** 63%
5	 **7e**	 **8e:** 86%
6	 **7f**	 **8f:** 80%
7	 **7g**	 **8g:** 86%
8	 **7h**	 **8h:** 85%
9	 **7i**	 **8i:** 83%
10	 **7j**	 **8j:** 78%
11	 **7k**	 **8k:** 85%
12 [c]	 **7l**	 **8l:** 65%
13 [c]	 **7m**	 **8m:** 90%

[a] General conditions: **7** (1.0 mmol), **2a** (0.5 mmol) and TMSCl (1.0 mmol) in CH_2Cl_2 (2.0 mL) at 25 °C for 1 h. [b] Isolated yields. [c] The reaction was performed at 0 °C.

(Table 4). The treatment of sodium benzenesulfinate (**2b**) with benzyl alcohol (**7a**), ethanol (**7o**), phenethyl alcohol (**7r**) and 2,3-dihydro-1*H*-inden-2-ol (**7t**) under the standard conditions afforded sulfinates **8x**–**aa** in 64–77 % yields (Table 4, entries 1–4). Sodium 4-fluorobenzenesulfinate (**2c**) reacted smoothly with

Table 3. TMSCl-promoted sulfinate synthesis from alkyl/allyl alcohols **7** and sodium *p*-toluenesulfinate (**2a**).[a]

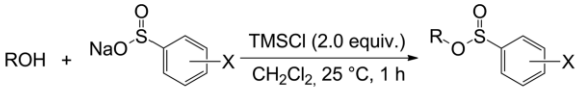


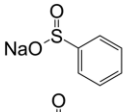
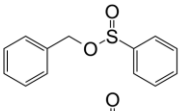
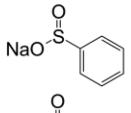
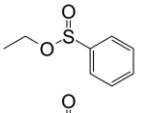
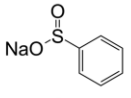
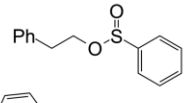
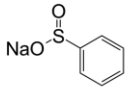
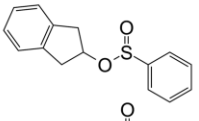
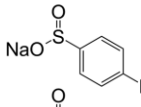
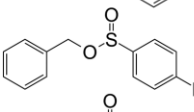
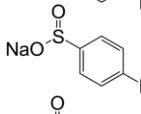
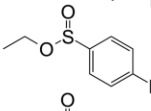
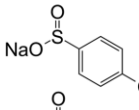
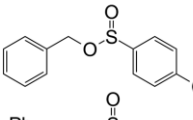
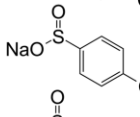
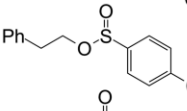
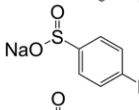
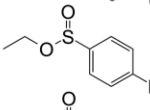
Entry	7	Product 8 and Yield [b]
1	 **7n**	 **8n:** 91%
2	 **7o**	 **8o:** 90%
3	 **7p**	 **8p:** 90%
4	 **7q**	 **8q:** 50%
5	 **7r**	 **8r:** 92%
6	 **7s**	 **8s:** 80%
7	 **7t**	 **8t:** 75%
8	 **7u**	 **8u:** 82%
9 [c]	 **7v**	 **8v:** 75%
10	 **7w**	 **8w:** 82%

[a] General conditions: **7** (1.0 mmol), **2a** (0.5 mmol) and TMSCl (1.0 mmol) in CH_2Cl_2 (2.0 mL) at 25 °C for 1 h. [b] Isolated yields. [c] The reaction was performed at 0 °C.

benzyl alcohol (**7a**) and ethanol (**7o**) under the standard conditions to generate sulfinates **8ab**–**ac** in 80 % and 81 % yields, respectively (entries 5 and 6). Sodium 4-chlorobenzenesulfinate (**2d**) reacted equally well with benzyl alcohol (**7a**) and phenethyl alcohol (**7r**) under the standard conditions to give sulfinates **8ad**–**ae** in 84 % and 86 % yields, respectively (entries 7 and 8). By treatment of Sodium 4-bromobenzenesulfinate (**2e**) with ethanol (**7o**) in the presence of TMSCl (2 equiv.) in CH_2Cl_2 at room temperature (25 °C) for 1 h, sulfinate **8af** was isolated in 83 % yield (entry 9). The treatment of benzyl alcohol (**7a**) with sodium 4-methoxybenzenesulfinate (**2f**), sodium 4-nitrobenzenesulfinate (**2g**), sodium 3-bromobenzenesulfinate (**2h**) sodium 2-chlorobenzenesulfinate (**2i**) and sodium thiophene-2-sulfinate (**2j**) under the standard conditions afforded sulfinates **8ag**–**ak** in 70–95 % yields (entries 10–14). Sodium naphthalene-1-sulfinate (**2k**) was also investigated and it reacted smoothly with ethanol (**7o**) under the standard conditions to afford

Table 4. TMSCl-promoted sulfinate synthesis from sodium arenesulfinates **2** and alcohols **7**.[a]

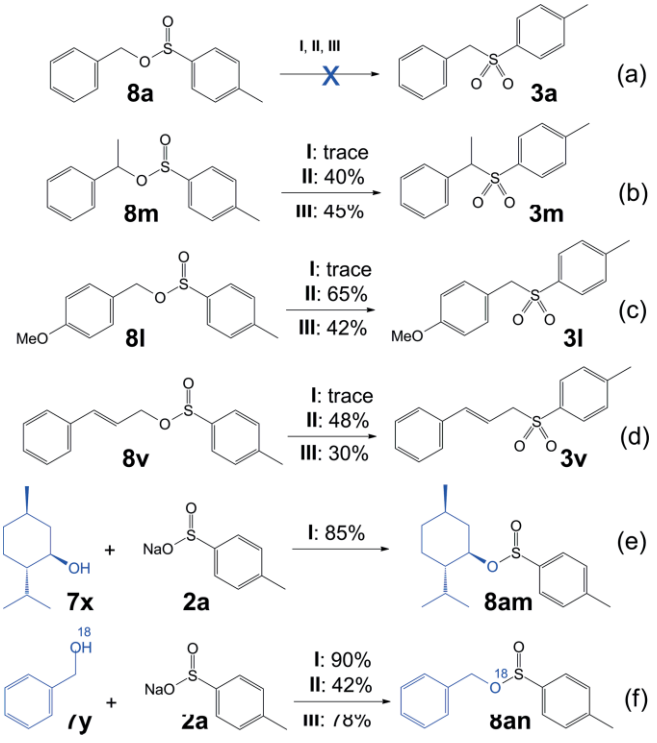


Entry	2	7	Product 8 and Yield [b]
1	 **2b**	**7a**	 **8x:** 77%
2	 **2b**	**7o**	 **8y:** 75%
3	 **2b**	**7r**	 **8z:** 73%
4	 **2b**	**7t**	 **8aa**: 64%
5	 **2c**	**7a**	 **8ab:** 80%
6	 **2c**	**7o**	 **8ac:** 81%
7	 **2d**	**7a**	 **8ad:** 84%
8	 **2d**	**7r**	 **8ae:** 86%
9	 **2e**	**7o**	 **8af:** 83%
10	**2f**	**7a**	**8ag:** 95%
11	**2g**	**7a**	**8ah:** 74%
12	**2h**	**7a**	**8ai:** 89%
13	**2i**	**7a**	**8aj:** 85%
14	**2j**	**7o**	**8ak:** 70%
15	**2k**	**7o**	**8al:** 82%

[a] General conditions: **7** (1.0 mmol), **2a** (0.5 mmol) and TMSCl (1.0 mmol) in CH_2Cl_2 (2.0 mL) at 25 °C for 1 h. [b] Isolated yields.

sulfinate **8aj** in 82 % yield (Table 4, entry 15). This sulfinate synthetic protocol offers attractive industrial prospects in the view point of metal-free, high selectivity, and facile reaction conditions.

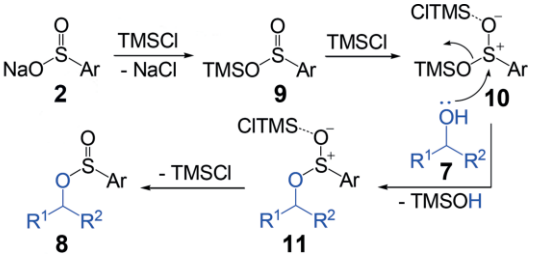
The reaction mechanism of sodium arenesulfinates-involved sulfinate synthesis was next studied. Usually, nucleophilic substitution of alcohol derivatives **1** with sodium arenesulfinates **2** affords sulfones **3** instead of sulfinates **8** (Scheme 1a).[3] Although this concept may be not always valid due to the different reaction conditions, the chemoselectivity of this nucleophilic substitution reaction is quite clear.[3] The sulfur of an arenesulfinate anion (**4** or **5**) has a higher nucleophilicity than the one of oxygen, and thus acts as the attacking atom (Scheme 1a).[4,9] Direct reaction of alcohols **7** with sodium arenesulfinates **2** could afford either sulfones **3** or sulfinates **8** (Scheme 1b and Scheme 1c).[5,6] Interestingly, the sulfinate/sulfone selectivity was found to be related to the reactivity of alcohols **7**. Treatment of primary benzyl alcohol **7a** with sodium arenesulfinate **2a** under Sreedhar'[5] or Xiong's[6] reaction conditions gave exclusively sulfinate **8a**. In contrast, sulfone **3m** (Scheme 2) instead of sulfinate **8m** was obtained as the sole product when secondary benzyl alcohol **7m**, a relatively more activated alcohol compared to primary benzyl alcohol **7a**, was used as the substrate under otherwise identical conditions.[5,6] To understand this unexpected result, a serial of control experiments were performed and the representative results were illustrated in Scheme 2. When sulfinate **8a** was subjected to Sreedhar'[5] or Xiong's[6] reaction conditions, no reaction took place and the starting material was recovered (Scheme 2a). Instead, sulfinate **8m** under Sreedhar' or Xiong's reaction conditions was converted to sulfone **3m** in 40 % and 45 % yields, respectively (Scheme 2b). As in the case of sulfinate **8m**, sulfinates **8l** and **8v** under Sreedhar' or Xiong's reaction conditions were converted to sulfones **3m** and **3v**, respectively (Scheme 2c and Scheme 2d). The results supported that reaction of benzyl alcohol **7a** with sodium arenesulfinate **2a** under Sreedhar' or Xiong's reaction conditions could afford sulfinate **8a**, whereas sulfones **3l**, **3m** and **3v** were obtained with the use of relatively more activated alcohols **7l**, **7m** and **7v** as the substrates under otherwise identical conditions. In contrast to Sreedhar' and Xiong's synthetic procedures,[5,6] our sulfinate synthesis were carried out under milder conditions (TMSCl, 25 °C or 0 °C), which tolerated more sulfinates and thus expanded the substrate scope of substrates (Scheme 2a–d). Treatment of L-menthol (**7x**) with sodium arenesulfinate **2a** under the reaction conditions of our sulfinate synthesis afforded sulfinate **8am** in 85 % yield in a 1:1 diastereomeric ratio (Scheme 2e),[10] similar to the result reported by Oliveira,[7f] indicating that the in situ generation of a carbocation intermediate (Scheme 1c) from alcohol **7l** maybe not a major pathway for this reaction. In order to get more information, reaction of ^{18}O-labelled benzyl alcohol (**7y**) and sodium *p*-toluenesulfinate (**2a**) was performed in the presence of TMSCl in CH_2Cl_2 at room temperature (25 °C), which afforded sulfinate **8an** in 90 % yield within 1 h (Scheme 2f). When this reaction was carried out following Sreedhar'[5] and Xiong's[6] procedures, sulfinate **8an** was obtained in 42 % and 78 % yields, respectively (Scheme 2f). These results indicated that the previous proposed reaction mechanism involving O-attack of a sulfinate anion onto an in situ generated carbocation intermediate (Scheme 1c) might be not right in most cases.



Scheme 2. Verification experiments. I) our procedure (25 °C for equation a, e–f, 0 °C for Equation b–d). II) Sreedhar's procedure.[5] III) Xiong's procedure.[6]

However, the concept that one oxygen atom of an arenesulfinate anion **4** acting as the nucleophilic attacking atom is often used consciously or unconsciously to explain the formation of sulfinates **8** (Scheme 1c), in which the arenesulfinate anion **4** was generated in situ from various reagents.[6,7c,7e,7i,11] Our work necessitates revision of these previous proposed reaction mechanisms in literatures.

Based on the above results and related reports in the literature, a possible reaction mechanism is illustrated in Scheme 3. Silyllation of sodium arenesulfinates **2** with TMSCl formed compounds **9**, which were converted to intermediates **10** by chelating with TMSCl. Nucleophilic substitution reaction of **10** with alcohols **7** generated intermediates **11**. Finally, detachment of TMSCl from **11** afforded sulfinates **8** (Scheme 3).



Scheme 3. Proposed mechanism.

Conclusions

We have developed an improved sulfinate synthesis via the tandem reaction of alcohols and sodium arenesulfinates in the presence of trimethylsilyl chloride. The synthetic protocol offers attractive industrial prospects as the reaction took place at room/zero temperature without the need for using transition metal catalysts and inert atmosphere, and displayed a high sulfinate/sulfone selectivity and a broad substrate scope. Importantly, the reaction mechanism of many sulfinate syntheses from alcohols and sodium arenesulfinates was revised by using isotopic labeling experiments and development of an improved sulfinate synthesis. The result will put the related mechanistic consideration for arenesulfinate anions-involved sulfinate formation back on the right track.

Experimental Section

General Experimental Methods: Common reagents and materials were purchased from commercial sources and were used without further purification. Organic extracts were, in general, dried with anhydrous sodium sulfate (Na_2SO_4). TLC plates were visualized by exposure to ultra violet light (UV). IR spectra were recorded by using an Electrothemal Nicolet 380 spectrometer. High-resolution mass spectra (HRMS) were recorded by using an Electrothemal LTQ-Orbitrap mass spectrometer. Melting points were measured by using a Gongyi X-5 microscopy digital melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained by using a Bruker Avance III 400 MHz NMR spectrometer. Chemical shifts for protons are reported in parts per million (δ scale) and are referenced to residual protium in the NMR solvents [$CDCl_3$: δ 7.26]. Chemical shifts for carbon resonances are reported in parts per million (δ scale) and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, *t* = triplet, q = quartet, m = multiplet, br = broad), integration, and coupling constant in Hertz (Hz).

General Experimental Procedure for the synthesis of Sulfinates: The mixture of an alcohol (1.0 mmol), a sodium arylsulfinate (0.5 mmol) and TMSCl (1 mmol) in CH_2Cl_2 (3.0 mL) was stirred at 25 °C for 1 h, then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried with anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh) to afford the desired sulfinate **8a**–**8an**.

Benzyl 4-methylbenzenesulfinate (8a): Pale yellow oil, 115.6 mg, 94 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* = 7.9 Hz, 2H), 7.38–7.29 (m, 7H), 5.06 (d, *J* = 11.4 Hz, 1H), 4.58 (d, *J* = 11.4 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.8, 141.5, 135.4, 129.7, 128.5, 128.4, 125.2, 65.5, 21.4; FTIR (film): 3408, 3031, 2922, 2850, 2537, 1596, 1454, 1131, 1104, 1080, 1036, 904, 812, 764, 695 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{14}H_{14}NaO_2S$ [M + Na]$^+$: 269.0607, found 269.0604.

4-Methylbenzyl 4-methylbenzenesulfinate (8b): Yellow oil, 120.9 mg, 93 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.00 (d, *J* = 11.1 Hz, 1H), 4.53 (d, *J* = 11.1 Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.7, 141.6, 138.3, 132.4, 129.6, 129.2, 128.6, 125.3, 65.6, 21.4, 21.1; FTIR (film): 2923, 1596, 1518, 1453, 1134, 1081, 908, 852, 811, 767, 732 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{15}H_{16}NaO_2S$ [M + Na]$^+$: 283.0763, found 283.0768.

4-Nitrobenzyl 4-methylbenzenesulfinate (8c): White solid; m.p. = 38–39 °C; 106.2 mg, 73 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 7.1 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 7.3 Hz, 2H), 5.07 (d, *J* = 12.6 Hz, 1H), 4.59 (d, *J* = 12.6 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6, 143.3, 143.0, 140.9, 129.8, 128.6, 125.2, 123.6, 63.3, 21.5; FTIR (film): 2925, 2855, 1522, 1346, 1135, 1081, 852, 814, 736 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{14}H_{14}NO_4S$ [M + H]$^+$: 292.0638, found 292.0640.

2-Nitrobenzyl 4-methylbenzenesulfinate (8d): Yellow oil; 91.7 mg, 63 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 8.1 Hz, 1H), 7.70–7.60 (m, 4H), 7.45 (t, *J* = 7.3 Hz, 1H), 5.43 (d, *J* = 14.5 Hz, 1H), 5.02 (d, *J* = 14.5 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.2, 143.3, 141.1, 133.7, 132.4, 129.8, 129.5, 128.7, 125.1, 124.8, 62.5, 21.5; FTIR (film): 2925, 2856, 1525, 1342, 1134, 1081, 813, 729 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{14}H_{13}NNaO_4S$ [M + Na]$^+$: 314.0457, found 314.0452.

4-(Trifluoromethyl)benzyl 4-methylbenzenesulfinate (8e): Yellow foam, 135.1 mg, 86 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 5.05 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 12.1 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.2, 141.2, 139.7, 130.4 (q, J_{C-F} = 32.5 Hz, 1C), 129.8, 128.4, 125.4 (q, J_{C-F} = 3.7 Hz, 1C), 125.3, 64.1, 21.4; FTIR (film): 1613, 1579, 1429, 1308, 1134, 1082, 1036, 881, 859, 814, 790, 674 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{15}H_{13}F_3NaO_2S$ [M + Na]$^+$: 337.0481, found 337.0479.

3,5-Difluorobenzyl 4-methylbenzenesulfinate (8f): Colorless oil; 112.8 mg, 80 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 6.78–6.69 (m, 3H), 4.94 (d, *J* = 12.2 Hz, 1H), 4.48 (d, *J* = 12.3 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:162.9 (dd, J_{C-F} = 249.2, 12.7 Hz, 1C), 143.3, 141.1, 139.6 (t, J_{C-F} = 9.29 Hz, 1C), 129.8, 125.2, 110.8 (dd, J_{C-F} = 18.7, 7.1 Hz, 1C), 103.6 (t, J_{C-F} = 25.2 Hz, 1C), 63.5, 21.4; FTIR (film): 1629, 1599, 1464, 1368, 1323, 1137, 1119, 946, 854, 813, 759, 673 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{14}H_{12}F_2NaO_2S$ [M + Na]$^+$: 305.0418, found 305.0421.

4-Chlorobenzyl 4-methylbenzenesulfinate (8g): Colorless oil; 120.4 mg, 86 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 7.7 Hz, 2H), 4.99 (d, *J* = 11.6 Hz, 1H), 4.52 (d, *J* = 11.6 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.0, 141.4, 134.2, 134.1, 129.8, 129.7, 128.6, 125.2, 64.5, 21.4; FTIR (film): 2923, 2852, 1596, 1476, 1446, 1365, 1140, 1081, 1057, 919, 870, 812, 767, 747, 696 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{14}H_{13}ClNaO_2S$ [M + Na]$^+$: 303.0217, found 303.0221.

3,4-Dichlorobenzyl 4-methylbenzenesulfinate (8h): Yellow oil; 133.4 mg, 85 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 7.6 Hz, 2H), 7.37–7.32 (m, 3H), 7.28 (s, 1 H), 4.91 (d, *J* = 11.9 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.2, 141.1, 135.8, 132.5, 132.3, 130.4, 130.2, 129.8, 127.5, 125.2, 63.3, 21.5; FTIR (film): 2925, 2852, 1596, 1473, 1400, 1360, 1133, 1081, 1033, 873, 813, 757, 710, 662 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{14}H_{12}Cl_2NaO_2S$ [M + Na]$^+$: 336.9827, found 336.9831.

4-Bromobenzyl 4-methylbenzenesulfinate (8i): Colorless oil; 134.4 mg, 83 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 4.95 (d, *J* = 11.7 Hz, 1H), 4.48 (d, *J* = 11.7 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.0, 141.3, 134.6, 131.6, 130.0, 129.7, 125.2, 122.4, 64.5, 21.4; FTIR (film): 2923, 1595, 1490, 1234,

1134, 1070, 1014, 920, 847, 802, 733 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{14}H_{13}BrNaO_2S$ $[M + Na]^+$: 346.9712, found 346.9709.

2-Bromobenzyl 4-methylbenzenesulfinate (8j): Yellow oil; 126.7 mg, 78 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 5.15 (d, *J* = 12.1 Hz, 1H), 4.74 (d, *J* = 12.1 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.0, 141.4, 135.1, 132.7, 130.4, 129.9, 129.7, 127.5, 125.3, 123.4, 65.4, 21.5; FTIR (film): 2922, 1596, 1472, 1443, 1364, 1143, 1081, 1031, 919, 869, 812, 767, 744, 694, 658, 626 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{14}H_{13}BrNaO_2S$ $[M + Na]^+$: 346.9712, found 346.9714.

3-Phenoxybenzyl 4-methylbenzenesulfinate (8k): Colorless oil; 143.6 mg, 85 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 7.9 Hz, 2H), 7.37–7.27 (m, 5H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.03–6.92 (m, 5H), 4.99 (d, *J* = 11.6 Hz, 1H), 4.53 (d, *J* = 11.6 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.4, 156.8, 142.8, 141.4, 137.5, 129.8, 129.69, 129.68, 125.2, 123.4, 123.0, 119.0, 118.54, 118.45, 64.9, 21.4; FTIR (film): 2924, 2852, 1584, 1446, 1365, 1214, 1132, 1081, 926, 880, 815, 754, 691 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{20}H_{18}NaO_3S$ $[M + Na]^+$: 361.0869, found 361.0873.

4-Methoxybenzyl 4-methylbenzenesulfinate (8l): The reaction was performed at 0 °C. Colorless oil; 89.7 mg, 65 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.97 (d, *J* = 11.1 Hz, 1H), 4.51 (d, *J* = 11.1 Hz, 1H), 3.79 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.7, 142.7, 141.6, 130.3, 129.6, 127.4, 125.3, 113.9, 65.5, 55.2, 21.4; FTIR (film): 2932, 2836, 1612, 1514, 1250, 1130, 1033, 907, 812, 792 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{15}H_{16}NaO_3S$ $[M + Na]^+$: 299.0712, found 299.0717.

1-Phenylethyl 4-methylbenzenesulfinate (8m): The reaction was performed at 0 °C. Yellow oil; 117.0 mg, 90 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.40–7.30 (m, 4H), 7.22–7.20 (m, 2H), 7.15–7.13 (m, 1H), 5.46 (dd, *J* = 13.0, 6.4 Hz, 0.5H), 5.37 (dd, *J* = 12.8, 6.4 Hz, 0.5 H), 2.41 (s, 1.6H), 2.38 (s, 1.4H), 1.71 (s, 3H), 1.67 (d, *J* = 6.5 Hz, 1.4H), 1.58 (d, *J* = 6.5 Hz, 1.6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.6, 142.5, 142.4, 141.9, 141.6, 141.3, 129.5, 129.3, 128.5, 128.2, 128.1, 127.7, 126.3, 126.1, 125.2, 124.8, 75.3, 24.1, 23.9, 21.4, 21.3; FTIR (film): 3032, 2979, 2927, 1596, 1493, 1134, 872, 764, 697 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{15}H_{16}NaO_2S$ $[M + Na]^+$: 283.0763, found 283.0768.

Methyl 4-methylbenzenesulfinate (8n): Colorless oil; 77.3 mg, 91 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 3.45 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.7, 140.9, 129.6, 125.3, 49.3, 21.4; FTIR (film): 2939, 1596, 1452, 1138, 1081, 963, 813, 682, 637 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_8H_{10}NaO_2S$ $[M + Na]^+$: 193.0294, found 193.0296.

Ethyl 4-methylbenzenesulfinate (8o): Pale yellow oil, 82.8 mg, 90 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 4.12–4.04 (m, 1H), 3.75–3.67 (m, 1H), 2.41 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.6, 141.8, 129.6, 125.1, 60.7, 21.4, 15.5; FTIR (film): 2980, 2925, 2854, 1597, 1443, 1385, 1126, 1080, 1006, 883, 813, 710 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_9H_{12}NaO_2S$ $[M + Na]^+$: 207.0450, found 207.0464.

Isopropyl 4-methylbenzenesulfinate (8p): Colorless oil; 89.1 mg, 90 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.7 Hz, 2H), 4.62–4.53 (m, 1H), 2.40 (s, 3H), 1.36 (d, *J* = 6.2 Hz, 1H), 1.22 (d, *J* = 6.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.6, 142.3, 129.5, 124.9, 72.5, 23.8, 23.6, 21.3; FTIR (film): 2977, 2924, 1597, 1452, 1384, 1373, 1142, 1103, 1083, 917, 841, 812, 743, 637 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{10}H_{14}NaO_2S$ $[M + Na]^+$: 221.0607, found 221.0610.

***tert*-Butyl 4-methylbenzenesulfinate (8q):** Colorless oil; 53.0 mg, 50 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 7.7 Hz, 2H), 2.40 (s, 3H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.6, 141.9, 129.5, 124.7, 82.5, 29.8, 21.3; FTIR (film): 3411, 2923, 2852, 1712, 1596, 1456, 1288, 1144, 1080, 812, 683, 655 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{11}H_{16}NaO_2S$ $[M + Na]^+$: 235.0763, found 235.0769.

Phenethyl 4-methylbenzenesulfinate (8r): Colorless oil; 119.6 mg, 92 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 7.8 Hz, 2H), 7.33–7.23 (m, 5H), 7.18 (t, *J* = 7.1 Hz, 2H), 4.26 (dd, *J* = 16.5, 7.6 Hz, 1H), 3.84 (dd, *J* = 16.6, 7.5 Hz, 1H), 2.96 (t, *J* = 7.0 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.5, 141.4, 137.2, 129.5, 128.8, 128.3, 126.5, 125.1, 64.6, 36.1, 21.4; FTIR (film): 2960, 2888, 1597, 1497, 1454, 1362, 1175, 1130, 1082, 1043, 1006, 990, 911, 867, 814, 734, 701 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{15}H_{16}NaO_2S$ $[M + Na]^+$: 283.0763, found 283.0769.

Cyclopentyl 4-methylbenzenesulfinate (8s): Pale yellow oil, 89.6 mg, 80 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 4.83–4.80 (m, 1H), 2.41 (s, 3H), 1.90–1.87 (m, 2H), 1.72–1.49 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.8, 142.4, 129.6, 125.1, 80.7, 34.1, 33.7, 23.30, 23.28, 21.4; FTIR (film): 2960, 2872, 1597, 1493, 1451, 1355, 1167, 1133, 1080, 955, 933, 849, 812, 637, 627 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{12}H_{16}NaO_2S$ $[M + Na]^+$: 247.0763, found 247.0776.

2,3-Dihydro-1*H*-inden-2-yl 4-methylbenzenesulfinate (8t): Pale yellow oil, 102.0 mg, 75 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, *J* = 8.0 Hz, 2H), 7.36–7.16 (m, 6H), 5.19–5.14 (m, 1H), 3.37–2.98 (m, 4H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.6, 142.2, 139.8, 139.7, 129.6, 126.8, 125.3, 125.1, 124.49, 124.46, 77.8, 40.9, 40.4, 21.4; FTIR (film): 3024, 2923, 1596, 1483, 1460, 1420, 1358, 1211, 1178, 1131, 1081, 1035, 1003, 943, 855, 813, 742 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{16}H_{16}NaO_2S$ $[M + Na]^+$: 295.0763, found 295.0775.

Cyclohexyl 4-methylbenzenesulfinate (8u): Yellow oil; 97.6 mg, 82 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 4.34–4.30 (m, 1H), 2.40 (s, 3H), 2.01–1.98 (m, 1H), 1.76–1.69 (m, 3H), 1.61–1.43 (m, 3H), 1.39–1.17 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.8, 142.3, 129.5, 124.9, 77.6, 33.6, 33.5, 25.0, 23.79, 23.77, 21.4; FTIR (film): 2934, 2857, 1596, 1493, 1449, 1400, 1135, 1083, 941, 800, 7560, 638 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{13}H_{18}NaO_2S$ $[M + Na]^+$: 261.0920 Found: 261.0924.

Cinnamyl 4-methylbenzenesulfinate (8v): The reaction was performed at 0 °C. Yellow oil; 102.2 mg, 75 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* = 7.7 Hz, 2H), 7.38–7.28 (m, 7H), 6.59 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.8, 6.5 Hz, 1H), 4.68 (dd, *J* = 12.0, 6.5 Hz, 1H), 4.33 (dd, *J* = 11.9, 6.6 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.8, 141.6, 135.9, 134.8, 129.7, 128.5, 128.1, 126.6, 125.2, 123.2, 64.8, 21.4; FTIR (film): 2923, 2867, 1597, 1493, 1449, 1366, 1133, 1080, 967, 912, 837, 813, 754, 734, 693 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{16}H_{16}NaO_2S$ $[M + Na]^+$: 295.0763, found 295.0766.

2-Methylallyl 4-methylbenzenesulfinate (8w): Colorless oil; 86.1 mg, 82 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 6.7 Hz, 2H), 7.32 (d, *J* = 7.1 Hz, 2H), 4.96 (s, 1H), 4.91 (s, 1H), 4.41 (d, *J* = 11.9 Hz, 1H), 3.97 (d, *J* = 11.9 Hz, 1H), 2.41 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.7, 141.6, 139.8, 129.6, 125.1, 114.4, 67.7, 21.4, 19.3; FTIR (film): 2984, 2927, 2870, 1597, 1457, 1402, 1380, 1316, 1289, 1177, 1148, 1130, 1087, 914, 815, 734, 709, 683 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{11}H_{14}NaO_2S$ $[M + Na]^+$: 233.0607, found 233.0611.

Benzyl benzenesulfinate (8x): Colorless oil, 94.7 mg, 77 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79–7.77 (m, 2H), 7.59–7.57 (m, 3H), 7.36–7.29 (m, 5H), 5.07 (d, *J* = 11.4 Hz, 1H), 4.60 (d, *J* = 11.4 Hz, 1H)); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.5, 135.4, 132.2, 129.1, 128.6, 128.5, 125.3, 65.9; FTIR (film): 3408, 3031, 2922, 2850, 2537, 1596, 1454, 1131, 1104, 1080, 1036, 904, 812, 764, 695 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{13}H_{12}NaO_2S$ [M + Na]$^+$: 255.0450, found 255.0454.

Ethyl benzenesulfinate (8y): Pale yellow oil, 63.8 mg, 75 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73–7.71 (m, 2H), 7.55–7.51 (m, 3H), 4.16–4.08 (m, 1H), 3.77–3.69 (m, 1H), 1.28 (t, *J* = 7.1Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.7, 131.9, 128.9, 125.1, 60.9, 15.4; FTIR (film): 2982, 2928, 1475, 1444, 1385, 1328, 1133, 1097, 1081, 1067, 1004, 882, 755, 697 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_8H_{10}NaO_2S$ [M + Na]$^+$: 193.0294, found 193.0299.

Phenethyl benzenesulfinate (8z): Pale yellow oil, 89.8 mg, 73 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 7.1 Hz, 2H), 7.47–7.39 (m, 3H), 7.22–7.13 (m, 3H), 7.06 (d, *J* = 7.2 Hz, 2H), 4.17 (dt, *J* = 9.9, 7.2 Hz, 1H), 3.74 (dt, *J* = 9.9, 7.2 Hz, 1H), 2.86 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.5, 137.2, 132.0, 129.0, 128.9, 128.5, 126.6, 125.2, 65.0, 36.2; FTIR (film): 3028, 2924, 1497, 1454, 1444, 1373, 1132, 1081, 1066, 964, 908, 864, 750, 697 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{14}H_{14}NaO_2S$ [M + Na]$^+$: 269.0607, found 269.0619.

2,3-Dihydro-1*H*-inden-2-yl benzenesulfinate (8aa): Pale yellow oil, 83.8 mg, 64 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73–7.71 (m, 2H), 7.55–7.52 (m, 3H), 7.23–7.16 (m, 4H), 5.21–5.16 (m, 1H), 3.37–3.20 (m, 2H), 3.10–2.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.2, 139.8, 139.7, 132.1, 129.0, 126.9, 125.2, 124.5, 78.2, 40.9, 40.5; FTIR (film): 2919, 2849, 1481, 1461, 1444, 1419, 1356, 1313, 1210, 1189, 1129, 1081, 1066, 1001, 939, 899, 852, 801, 736, 699 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{15}H_{14}NaO_2S$ [M + Na]$^+$: 281.0607, found 281.0618.

Benzyl 4-fluorobenzenesulfinate (8ab): Colorless oil, 101.2 mg, 81 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76–7.73 (m, 2H), 7.37–7.33 (m, 3H), 7.28–7.26 (m, 2H), 7.22 (t, *J* = 8.5 Hz, 2H), 5.04 (d, *J* = 11.4 Hz, 1H), 4.60 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.0 (d, $J_{C\text{-}F}$ = 253.2 Hz, 1C), 163.7, 140.4 (d, $J_{C\text{-}F}$ = 2.8 Hz, 1C), 135.1, 128.5, 128.5, 128.5, 127.8 (d, $J_{C\text{-}F}$ = 9.1 Hz, 1C), 116.3 (d, $J_{C\text{-}F}$ = 22.6 Hz, 1C), 66.0; FTIR (film): 3066, 2926, 1587, 1489, 1228, 1130, 1078, 934, 903, 836, 723, 693 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{13}H_{11}FNaO_2S$ [M + Na]$^+$: 273.0356, found 273.0360.

Ethyl 4-fluorobenzenesulfinate (8ac): Pale yellow oil; 76.1 mg, 81 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.17 (m, 4H), 4.13–4.05 (m, 1H), 3.76–3.67 (m, 1H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9 (d, $J_{C\text{-}F}$ = 251.1 Hz, 1C), 140.6 (d, $J_{C\text{-}F}$ = 3.1 Hz, 1C), 127.6 (d, $J_{C\text{-}F}$ = 9.1 Hz, 1C), 116.2 (d, $J_{C\text{-}F}$ = 22.3 Hz, 1C), 61.0, 15.5. FTIR (film): 2988, 2901, 1587, 1490, 1404, 1394, 11228, 1132, 1077, 1066, 1057, 1012, 880, 837, 813, 713, 668 cm^{-1}. HRMS (ESI) *m/z*: Calcd for $C_8H_9FNaO_2S$ [M + Na]$^+$: 211.0199, found 211.0209.

Benzyl 4-chlorobenzenesulfinate (8ad): Colorless oil, 111.7 mg, 84 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.37–7.36 (m, 3H), 7.30 (d, *J* = 7.7 Hz, 2H), 5.07 (d, *J* = 11.4 Hz, 1H), 4.62 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.1, 138.6, 135.1, 129.4, 128.6, 128.5, 126.82, 66.2; FTIR (film): 3372, 1644, 1584, 1478, 1394, 1087, 1003, 824, 757, 647 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{13}H_{11}ClNaO_2S$ [M + Na]$^+$: 289.0060, found 269.0058.

Phenethyl 4-chlorobenzenesulfinate (8ae): Pale yellow oil, 120.4 mg, 86 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.50–7.41 (m, 4H), 7.30–7.20 (m, 3H), 7.14–7.12 (m, 2H), 4.24 (dt, *J* = 10.0, 6.9 Hz, 1H), 3.81 (dt, *J* = 9.9, 7.0 Hz, 1H), 2.93 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.9, 138.3, 137.0, 129.1, 128.8, 128.4, 126.6, 65.2, 36.0; FTIR (film): 2924, 2851, 1574, 1497, 1474, 1454, 1391, 1136, 1087, 1013, 963, 865, 827, 744, 699 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{14}H_{13}ClNaO_2S$ [M + Na]$^+$: 303.0217, found 303.0225.

Ethyl 4-bromobenzenesulfinate (8af): Pale yellow oil; 103.3 mg, 83 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.67 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.15–4.07 (m, 1H), 3.76–3.68 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ: 143.8, 132.2, 126.8, 126.8, 61.2, 15.5; FTIR (film): 2987, 2900, 1573, 1472, 1386, 1136, 1095, 1065, 1009, 882, 820, 728, 712 cm^{-1}. HRMS (ESI) *m/z*: Calcd for $C_8H_9BrNaO_2S$ [M + Na]$^+$: 270.9399, found 270.9412.

Benzyl 4-methoxybenzenesulfinate (8ag): Pale yellow oil; 124.5 mg, 95 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.67 (d, *J* = 8.8 Hz, 2H), 7.36–7.26 (m, 5H), 7.02 (d, *J* = 8.8 Hz, 2H), 5.01 (d, *J* = 11.4 Hz, 1H), 4.56 (d, *J* = 11.4 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ: 162.6, 135.9, 135.5, 128.4, 128.4, 128.3, 127.1, 114.3, 65.3, 55.4. FTIR (film): 2938, 1599, 1479, 1136, 1086, 1012, 923, 728 cm^{-1}. HRMS (ESI) *m/z*: Calcd for $C_{14}H_{14}NaO_3S$ [M + Na]$^+$: 285.0556, found 285.0549.

Benzyl 4-nitrobenzenesulfinate (8ah): Pale yellow oil; 102.5 mg, 74 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ: 8.37 (d, *J* = 8.6 Hz, 2H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.37–7.34 (m, 3H), 7.29–7.26 (m, 2H), 5.10 (d, *J* = 11.4 Hz, 1H), 4.68 (d, *J* = 11.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ: 150.9, 150.0, 134.6, 128.8, 128.7, 128.6, 126.7, 124.2, 67.2. FTIR (film): 2928, 2860, 1523, 1386, 1136, 1095, 1074, 1009, 823, 721 cm^{-1}. HRMS (ESI) *m/z*: Calcd for $C_{13}H_{11}NNaO_4S$ [M + Na]$^+$: 300.0301, found 300.0304.

Benzyl 3-bromobenzenesulfinate (8ai): Pale yellow oil; 138.0 mg, 89 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.91 (s, 1H), 7.71–7.67 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.38–7.30 (m, 5H), 5.08 (d, *J* = 11.4 Hz, 1H), 4.64 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ: 146.6, 135.2, 134.9, 130.5, 128.6, 128.6, 128.5, 128.3, 123.9, 123.3, 66.2. FTIR (film): 2922, 1593, 1489, 1446, 1131, 1089, 1063, 883, 724 cm^{-1}. HRMS (ESI) *m/z*: Calcd for $C_{13}H_{11}BrNaO_2S$ [M + Na]$^+$: 332.9555, found 332.9559.

Benzyl 2-chlorobenzenesulfinate (8aj): Pale yellow oil; 113.1 mg, 85 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ: 8.03–8.00 (m, 1H), 7.51–7.46 (m, 2H), 7.43–7.40 (m, 1H), 7.36–7.28 (m, 5H), 5.10 (d, *J* = 11.3 Hz, 1H), 4.72 (d, *J* = 11.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ: 141.6, 135.0, 133.3, 132.6, 130.2, 128.5, 128.5, 128.4, 127.1, 126.4, 67.4. FTIR (film): 3374, 2976, 1577, 1475, 1392, 1084, 1044, 1002, 834, 749 cm^{-1}. HRMS (ESI) *m/z*: Calcd for $C_{13}H_{11}ClNaO_2S$ [M + Na]$^+$: 289.0060, found 289.0053.

Benzyl thiophene-2-sulfinate (8ak): Pale yellow oil; 83.3 mg, 70 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.67 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.53 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.38–7.30 (m, 5H), 7.17 (dd, *J* = 4.8, 3.8 Hz, 1H), 5.15 (d, *J* = 11.4 Hz, 1H), 4.75 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ: 147.6, 135.1, 131.6, 129.9, 128.6, 128.5, 127.7, 65.5. FTIR (film): 3177, 2955, 1513, 1444, 1332, 1035, 1009, 898, 735 cm^{-1}. HRMS (ESI) *m/z*: Calcd for $C_{11}H_{10}NaO_2S_2$ [M + Na]$^+$: 261.0014, found 261.0018.

Ethyl naphthalene-1-sulfinate (8al): Pale yellow oil; 90.2 mg, 82 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ: 8.28 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 6.6 Hz, 2H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.92 (d, *J* = 7.3 Hz, 2H), 7.60–7.54 (m, 3H), 4.17–4.11 (m, 1H), 3.62–3.55 (m, 1H), 1.19 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ: 139.1, 133.6, 132.7, 129.2, 128.7, 127.3, 126.6, 124.7, 124.2, 122.2, 60.5, 15.3. FTIR (film): 2980, 1505, 1441, 1383, 1345, 1262, 1191, 1144, 1125, 1096, 1004, 879, 801, 770, 738, 706, 667 cm^{-1}. HRMS (ESI) *m/z*: Calcd for $C_{12}H_{12}NaO_2S$ [M + Na]$^+$: 243.0450, found 243.0469.

(1*R*, 2*S*, 5*R*)-2-Isopropyl-5-methylcyclohexyl 4-methylbenzenesulfinate (8am): Yellow solid; m.p. = 105–106 °C; 125.2 mg, 85 % yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 2H), 4.18 (td, *J* = 10.5, 3.6 Hz, 0.5H), 4.11 (td, *J* = 10.4, 3.5 Hz, 0.5H), 2.40 (s, 3H), 2.28–2.11 (m, 2H), 1.82–1.66 (m, 2H), 1.46–1.17 (m, 4H), 1.07–0.70 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.2, 143.0, 142.4, 142.3, 129.5, 124.8, 124.4, 81.9, 80.0, 48.1, 47.7, 43.5, 42.8, 33.9, 33.8, 31.7, 31.6, 29.6, 25.3, 25.1, 23.0, 22.9, 21.9, 21.8, 21.4, 20.7, 15.5, 15.3; FTIR (film): 2954, 2923, 2869, 1597, 1456, 1371, 1135, 956, 914, 851, 776, 757, 639 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{17}H_{26}NaO_2S$ [M + Na]$^+$: 317.1546, found 317.1549. The data match with the literature.[7f]

(1R, 2S, 5R)-2-Isopropyl-5-methylcyclohexan-1-ol (7x) (CAS: 2216–51–5): The sulfinate **8ah** (0.2 mmol) was hydrolyzed with excess 10 % aq. KOH in methanol (1 mL) at room temperature for 0.5 h, then water (5 mL) and EtOAc (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed by brine, dried with anhydrous Na_2SO_4, filtered, and concentrated to give 93 % of menthol **7x**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.39 (dt, *J* = 10.4, 4.3 Hz, 1H), 2.21–2.10 (m, 1H), 1.96–1.93 (m, 1H), 1.69–1.57 (m, 2H), 1.52 (s, 1H), 1.47–1.34 (m, 1H), 1.13–1.06 (m, 1H), 1.01–0.94 (m, 1H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.90 (d, *J* = 6.2 Hz, 3H), 0.88–0.84 (m, 1H), 0.79 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 71.4, 50.0, 44.9, 34.4, 31.5, 25.7, 23.0, 22.1, 20.9, 16.0; FTIR (film): 3234, 2953, 2926, 2869, 1462, 1446, 1044, 1025, 918, 669 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{10}H_{20}NaO$ [M + Na]$^+$: 179.1406, found 179.1409. The data match with the literature.[10]

General Experimental Procedure for the synthesis of Sulfones:

Reaction conditions: **I**) The mixture of a sulfinate **8** (0.5 mmol) and TMSCl (1 mmol) in CH_2Cl_2 (2.0 mL) was stirred at 0 °C for 1 h, then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried with anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh) to afford the desired sulfones **3**.

Reaction conditions: **II**) The mixture of a sulfinate **8** (0.5 mmol), $FeCl_3$ (0.075 mmol) and TMSCl (0.6 mmol) in CH_2Cl_2 (2.0 mL) was stirred at 45 °C for 14 h, then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried with anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh) to afford the desired sulfones **3**.

Reaction conditions: **III**) The mixture of a sulfinate **8** (0.5 mmol) and $BF_3{\cdot}Et_2O$ (0.9 mmol) in CH_2Cl_2 (1.5 mL) was stirred at 50 °C for 3 h, then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried with anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh) to afford the desired sulfones **3**.

1-Methoxy-4-(tosylmethyl)benzene (3l): White solid; m.p. = 122–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 4.22 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.9, 144.5, 131.9, 129.4, 128.6, 120.1, 113.9, 62.2, 55.2, 21.5; FTIR (film): 2924, 2851, 1597, 1474, 1291, 1136, 1089, 865 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{15}H_{16}NaO_3S$ [M + Na]$^+$: 299.0712, found 299.0715.

1-Methyl-4-((1-phenylethyl)sulfonyl)benzene (3m): White solid; m.p. = 130–131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 8.2 Hz, 2H), 7.33–7.25 (m, 3H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 1H), 2.41 (s, 3H), 1.77 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.3, 133.8, 129.3, 129.2, 129.1, 128.6, 128.2, 65.9, 21.5, 14.0; FTIR (film): 2920, 2854, 1659, 1645, 1457, 1373 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{15}H_{16}NaO_2S$ [M + Na]$^+$: 283.0763, found 283.0769.

1-(Cinnamylsulfonyl)-4-methylbenzene (3v): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 8.2 Hz, 2H), 7.33–7.28 (m, 7H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.10 (dt, *J* = 15.4, 7.6 Hz, 1H), 3.93 (d, *J* = 7.6 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.7, 138.9, 135.8, 135.5, 129.7, 128.6, 128.5, 128.4, 126.6, 115.3, 60.5, 21.6; FTIR (film): 2923, 2865, 1493, 1444, 1351, 1132, 1080, 813 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{16}H_{16}NaO_2S$ [M + Na]$^+$: 295.0763, found 295.0766.

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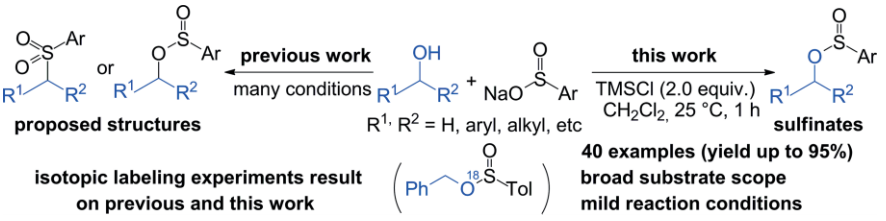

Reaction of alcohols with sodium arenesulfinates could afford either sulfones or sulfinates, and O-attack of sulfinate anions onto in situ generated carbocation intermediates from alcohols was the previous proposed mechanism in many syntheses of sulfinates. This concept, which is often used consciously or unconsciously, was revised herein by using isotopic labeling experiments and development of an improved sulfinate synthesis.

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