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Dehydroxylative Sulfonylation of Alcohols

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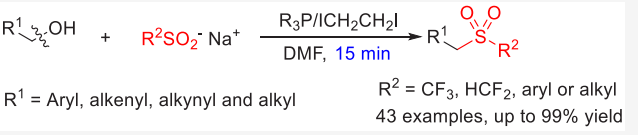
ABSTRACT: Described here is the R_3P/ICH_2CH_2I-promoted dehydroxylative sulfonylation of alcohols with a variety of sulfinates. In contrast to previous dehydroxylative sulfonylation methods, which are usually limited to active alcohols, such as benzyl, allyl, and propargyl alcohols, our protocol can be extended to both active and inactive alcohols (alkyl alcohols). Various sulfonyl groups can be incorporated, such as CF_3SO_2 and HCF_2SO_2, which are fluorinated groups of interest in pharmaceutical chemistry and the installation of which has received increasing attention. Notably, all reagents are cheap and widely available, and moderate to high yields were obtained within 15 min of reaction time.



Sulfones are important structural motifs that are prevalent in diverse biologically active molecules[1] and organic reagents/intermediates.[2] Many sulfone-containing pharmaceuticals have been developed, such as Eletriptan, Rofecoxib, and Chlormezanone. Therefore, the synthesis of sulfones has received considerable attention and the past few years have witnessed some of the most important and revolutionizing advances in the field of sulfonylation.[3] A wide range of sulfonylation reagents have been developed,[4] such as sulfur dioxide,[5] sulfonyl hydrazides,[6] and sulfinic acids and their salts,[7] for the formation of various $C-SO_2$ bonds. Despite these accomplishments, it is still highly desirable to develop mild and efficient protocols for the direct conversions of common functional groups into sulfonyl groups.

The hydroxyl moiety is a functional group which is commonly found in organic molecules. Given the ubiquity of alcohols, the dehydroxylative functionalization of alcohols has become an active research area,[8] and the dehydroxylative sulfonylation of alcohols may be considered as an attractive strategy for the installation of sulfonyl groups. Due to its poor leaving ability, the hydroxyl group usually needs to be activated by a Lewis acid or a Brönsted acid (Scheme 1, eq 1).[6b,9] A Ph_3P/NBS system can also effectively activate the hydroxyl group for arylsulfonylation (eq 2).[10] The Pd-catalyzed allylic substitution with the activation of the hydroxyl group has served as an efficient approach for the dehydroxylative sulfonylation (eq 3).[11] Shen's reagent [N-SCF_3], which has proved to be a good trifluoromethylthiolation reagent,[12] can also act as a CF_3S source for sulfonylation of allylic and propargyl alcohols (eq 4, right side).[13] Recently, it was found that a fluorinated alcohol could also activate allylic alcohols for the installation of SO_2 groups by using sulfinyl amides as reagents (eq 4, left side).[14] Although efficient for dehydroxylative sulfonylation, these reported methods are limited to active alcohols, including benzyl, allyl, and propargyl alcohols. Highly active alcohols, such as benzyl-allyl or benzyl-propargyl alcohols, need to be used in some cases. Furthermore, some methods may suffer from a two-step process or the use of expensive reagents or transition metals.

On the basis of our previous studies which show that R_3P/ICH_2CH_2I can act as an effective reagent system for the activation of hydroxyl groups,[15] we speculated that the R_3P/ICH_2CH_2I system may be able to activate alcohols for sulfonylation. Herein we describe the R_3P/ICH_2CH_2I-promoted dehydroxylative sulfonylation of a wide range of alcohols, including active alcohols and inactive alcohols (alkyl alcohols) (eq 5). All reagents are cheap and widely available. Various sulfonyl groups can be incorporated, such as CF_3SO_2 and HCF_2SO_2, which are fluorinated groups of interest in pharmaceutical chemistry and the installation of which has received increasing attention.[9e,f,13,16] Notably, all reactions occurred rapidly, and full conversions were observed within 15 min of reaction time.

We first examined the sulfonylation of alcohols with CF_3SO_2Na (Table 1). Our previous observations have shown that both DMF[15b] and CH_3CN[15a] can be used as a suitable reaction solvent for the dehydroxylative substitution. DMF and CH_3CN were then screened for the dehydroxylative trifluoromethylsulfonylation (entries 1−2). Almost no desired product was observed in CH_3CN (entry 1). To our delight, the reaction proceeded smoothly in DMF (entry 2). The loadings of R_3P, ICH_2CH_2I, and CF_3SO_2Na were examined (entries 3−7). The use of excessive CF_3SO_2Na was necessary, and Ph_3P/ICH_2CH_2I can be used in slight excess (entry 7). Various

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Scheme 1. Dehydroxylative Sulfonylation of Alcohols

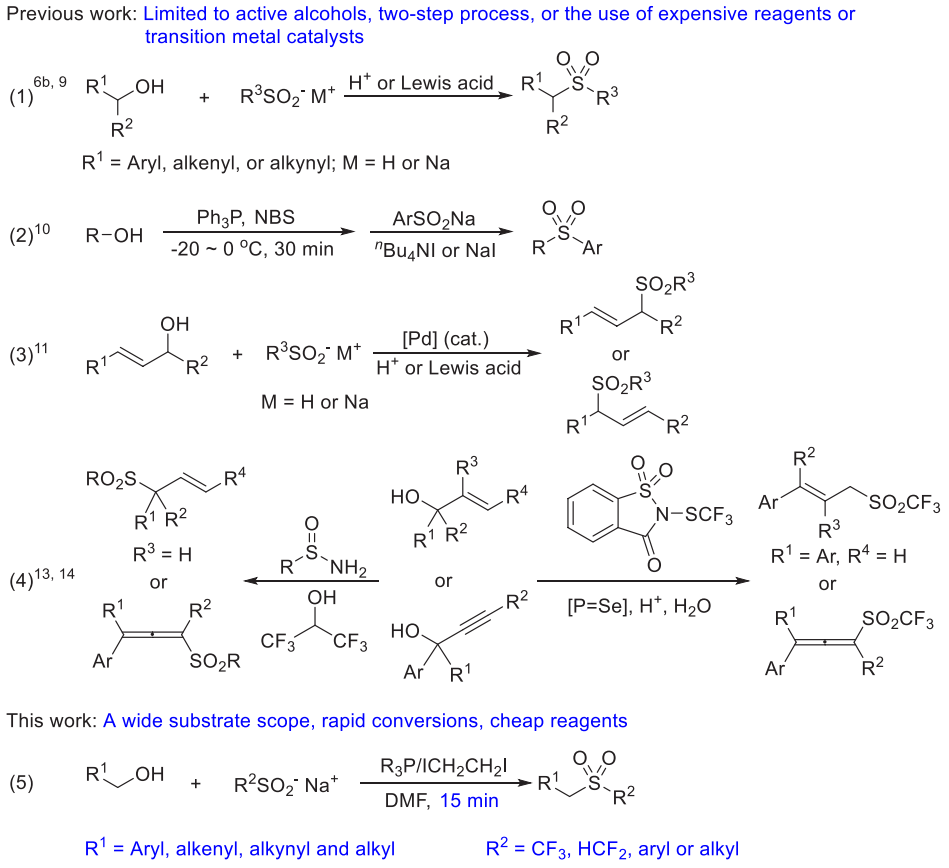
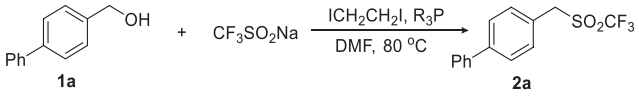


Table 1. Optimization of Dehydroxylative Trifluoromethylsulfonylation of Benzyl Alcohol[a]



entry	R_3P	ratio[b]	yield (%)[c]
1[d]	Ph_3P	1:1.4:1.4:4.0	trace
2	Ph_3P	1:1.4:1.4:4.0	77
3	Ph_3P	1:1.0:1.4:4.0	67
4	Ph_3P	1:2.0:1.4:4.0	63
5	Ph_3P	1:1.0:1.0:4.0	58
6	Ph_3P	1:1.4:2.0:4.0	59
7	Ph_3P	1:1.4:1.4:3.0	79
8	$(p\text{-OMePh})_3P$	1:1.4:1.4:3.0	74
9	$(EtO)_3P$	1:1.4:1.4:3.0	21
10	$(p\text{-MePh})_3P$	1:1.4:1.4:3.0	69
11	$(C_6F_5)_3P$	1:1.4:1.4:3.0	15

[a]Reaction conditions: Substrate **1a** (0.2 mmol), R_3P, ICH_2CH_2I, and CF_3SO_2Na in DMF (1.2 mL) at 80 °C under a N_2 atmosphere for 15 min. [b]Molar ratio of **1a**:R_3P:ICH_2CH_2I:CF_3SO_2Na. [c]The yields were determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as an internal standard. [d]CH_3CN was used as the reaction solvent instead of DMF.

trivalent phosphines (R_3P) were screened, and Ph_3P was found to be a superior choice (entry 7 vs entries 8−11).

With the optimal conditions in hand (Table 1, entry 7), we then investigated the substrate scope. As shown in Scheme 2, the sulfonylation process could be extended to a variety of alcohols, many functional groups can be tolerated, and 15 min of reaction time gave moderate to high yields. The aryl substituent electronic effects have almost no impact on the reaction yields (**2a**−**2j**). Heterobenzyl alcohols could also be converted smoothly (**2k**−**2m**). Low yields were obtained for the transformations of secondary alcohols (**2n**−**2o**), probably due to steric effects. This sulfonylation reaction could also be applied to allyl alcohols (**2p**). Alkyl alcohols show lower reactivity, and the further screening of reaction conditions (see Supporting Information) showed that the use of Ph_2PCH_3 instead of Ph_3P and 120 °C of reaction temperature can give the desired product. Although the alkyl alcohols were completely consumed, some unknown byproducts were generated and only moderate yields were obtained (**2q**−**2r**). The successful incorporation of a CF_3SO_2 group encouraged us to investigate the installation of a HCF_2SO_2 group. To our delight, the reactions occurred well to provide the desired products in high yields (**2s**−**2w**).

Due to its unique electronic properties, such as strong electronegativity and a small atomic radius, the fluorine element possesses "magic effects" and thus has found widespread applications in many areas, including pharmaceutical/agrochemical developments and material sciences.[17] Both of the two fluorinated groups, CF_3SO_2 (Hammet constants σ_m = 0.83, σ_p = 0.96) and HCF_2SO_2 (σ_m = 0.75, σ_p = 0.86), show strong electron-withdrawing effects,[18] and the Hansch π constant of CF_3SO_2 has been determined to be 0.55,[18a] which suggests a moderate lipophilic effect. The electronic effects make these two groups attractive, and thus the incorporation of them into organic molecules has become an active research area. For the installation of a CF_3SO_2 group, some reagents have proved to be efficient, including CF_3SO_2Na,[9e,f,16c] a N-SCF_3 type reagent,[13] CF_3SO_2Cl,[16a]

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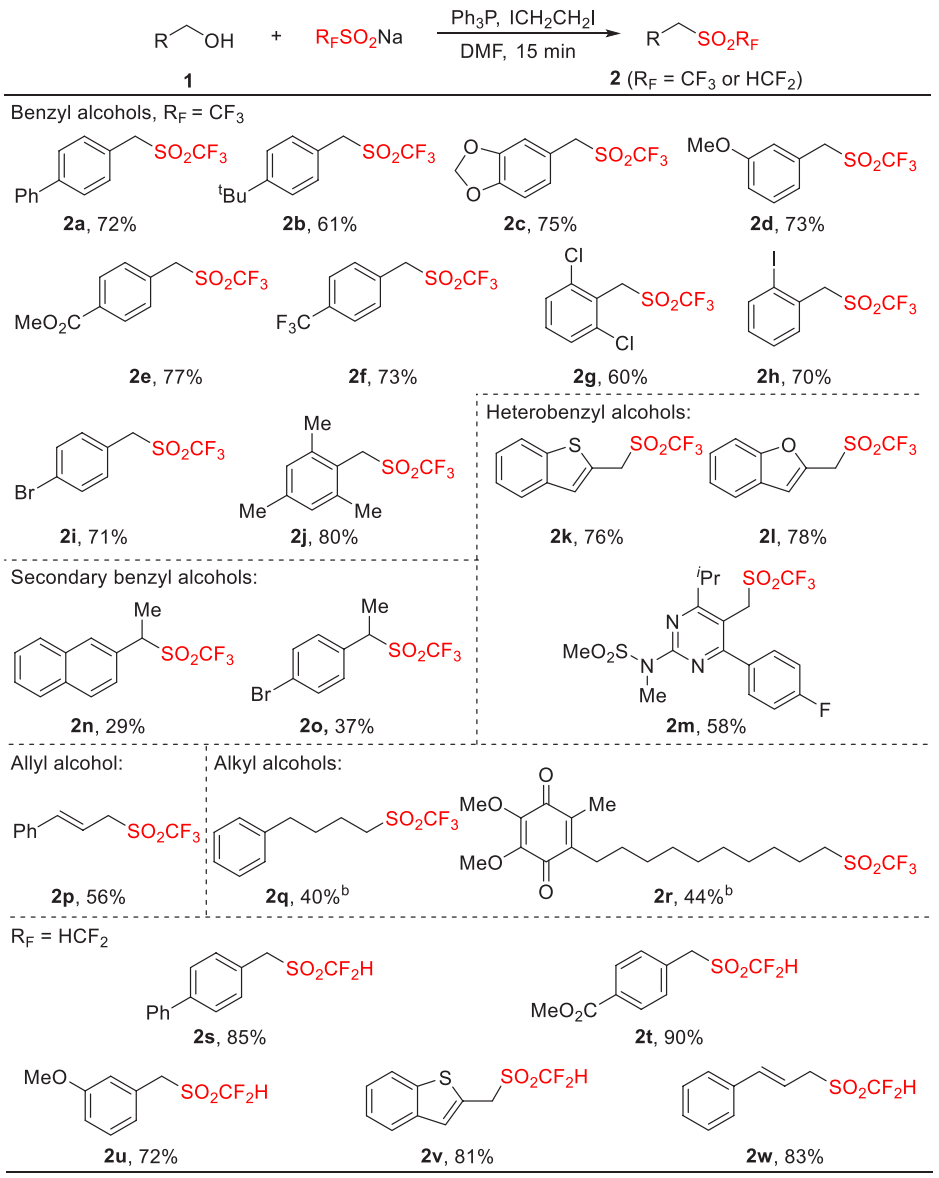
Scheme 2. Sulfonylation of Alcohols with Fluoroalkylsulfinates[a]



[a]Isolated yields are shown. Reaction conditions: substrate **1** (0.5 mmol), Ph_3P (1.4 equiv), ICH_2CH_2I (1.4 equiv), R_FSO_2Na (3 equiv) in DMF (3 mL) at 80 °C for 15 min. [b]Ph_2PCH_3 was used instead of Ph_3P and the reaction temperature was 120 °C in the cases of **2q** and **2r**.

CF_3SOCl,[16e] and a system consisting of Togni reagent and $NH_2C(=NH)SO_2H$.[16d] The installation of a HCF_2SO_2 group has been less explored. Recent effective methods include the Cu-mediated cross coupling of diazo compounds with HCF_2SO_2Na[16b] and the Pd-catalyzed coupling of aryl iodides with $NH_2C(=NH)SO_2H/HCF_2Cl$.[16d] The above methods may suffer from the use of expensive reagents, an expensive transition metal catalyst, highly active substrates, or substrates which are not easily available. In contrast, our protocol may feature a wide substrate scope, wide availability of alcohols, low cost of reagents, and rapid conversions.

Besides fluoroalkylsulfinates, other sulfinates, including aryl- and alkyl-sulfinates, were also investigated. Compared with fluoroalkylsulfinates, in which the strong electronegativity of fluorine atoms decreases the nucleophilicity of the sulfinates, nonfluorosulfinates show higher reactivity so that the use of 2 equiv of sulfinates can afford the desired product in good to high yields (Scheme 3). A wide substrate scope was observed. Various alcohols could be transformed smoothly, including benzyl, allyl, propargyl, and alkyl alcohols. Alkyl alcohols are reactive toward this process, but lower yields were obtained even at 120 °C of reaction temperature (**3q**−**3t**).

In order to further demonstrate the synthetic utility of this sulfonylation process, a gram-scale reaction was carried out (Scheme 4). The reaction still occurred rapidly, and a good yield was obtained.

Our previous studies have shown that the Ph_3P/ICH_2CH_2I-promoted dehydroxylative substitution occurs via an S_N2 process, as evidenced by the inversion of configuration with partial racemization for the substitution of secondary alcohols.[15a,b] In this sulfonylation reaction, the yield was not affected by the presence of a radical scavenger, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), excluding the radical path and supporting the S_N2 path (Scheme 5).

On the basis of the above results and our previous studies,[15] we propose the plausible reaction mechanism as shown in

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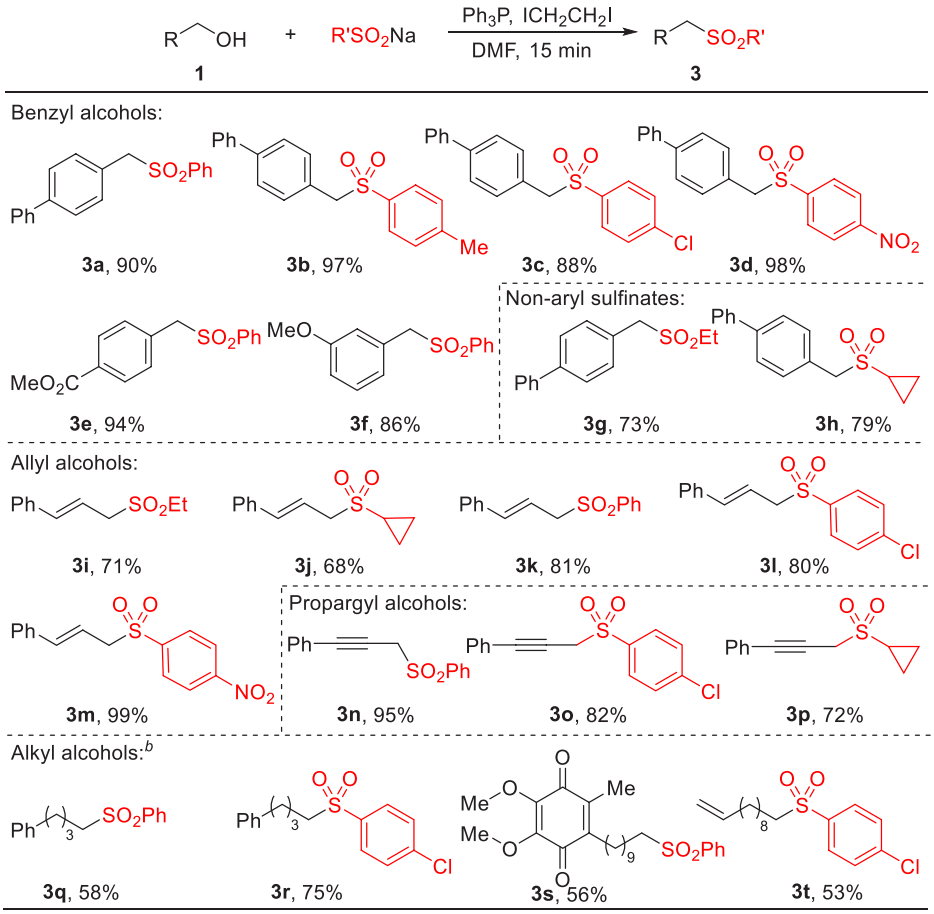
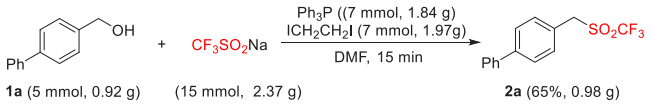
Scheme 3. Sulfonylation of Alcohols with Nonfluorosulfinates[a]

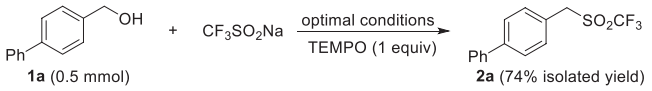


[a]Isolated yields are shown. Reaction conditions: substrate **1** (0.5 mmol), Ph_3P (1.4 equiv), ICH_2CH_2I (1.4 equiv), $R'SO_2Na$ (2 equiv) in DMF (3 mL) at 80 °C for 15 min. [b]Ph_2PCH_3 was used instead of Ph_3P and the reaction temperature was 120 °C in the cases of alkyl alcohols (**3q**–**3t**).

Scheme 4. Gram-Scale Reaction

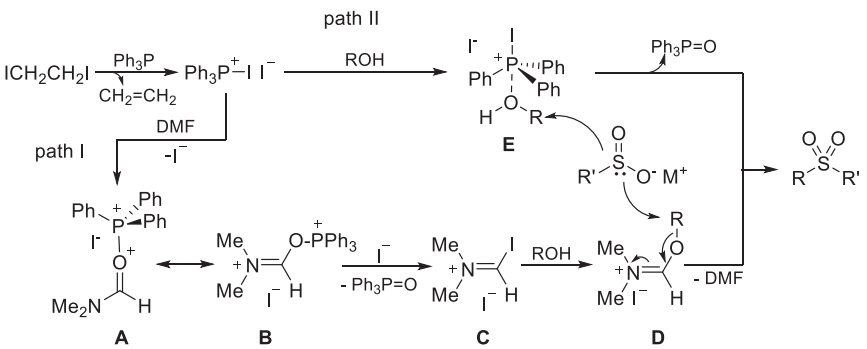


Scheme 5. Experimental Evidence



Scheme 6. A halogen bonding between Ph_3P and ICH_2CH_2I drives the formation of iodophosphonium salt Ph_3P^+-I I^-, which is a highly electrophilic intermediate and can rapidly react with DMF to form intermediate **A** (path I, predominant path). The DMF cation part in intermediate **A** can be stabilized by the resonance effect (intermediates **A** and **B**), but is also quite reactive toward nucleophiles. The attack of an iodide anion produces a Vilsmeier–Haack-type intermediate (**C**), which can easily activate alcohols by forming intermediate **D**. The nucleophilic attack of sulfinates at intermediate **D** provides final products. On the other hand, Ph_3P^+-I I^- may

Scheme 6. Plausible Reaction Mechanism



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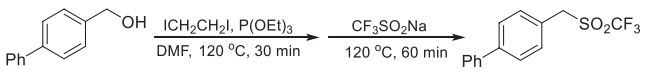
also directly activate alcohols, allowing for the subsequent nucleophilic substitution (path II).

The sulfonylation process generates $Ph_3P{=}O$, which may cause some inconvenience for the product isolation by flash column chromatography. Ph_3P was therefore replaced with $(EtO)_3P$. We were hopeful that the $(EtO)_3P{=}O$ byproduct could be removed by washing with water, which would be helpful for the column chromatography isolation. The optimal $(EtO)_3P/ICH_2CH_2I$-promoted sulfonylation conditions were identified after screening various effects (see Supporting Information). Indeed, phosphorus-containing species were almost completely removed by washing, and the desired product was isolated in a 60% yield (Scheme 7). Due to a lower reactivity of $(EtO)_3P$, a two-step process is required.

Scheme 7. Use of $(EtO)_3P$ Instead of Ph_3P



1a (0.5 mmol) **2a** (60% isolated yield)

In summary, we have described the dehydroxylative sulfonylation of alcohols promoted by a R_3P/ICH_2CH_2I system. Various sulfonyl groups can be installed, such as CF_3SO_2 and HCF_2SO_2, which are of interest in pharmaceutical chemistry. The sulfonylation process could be applied to a wide range of alcohols, including benzyl, allyl, propargyl, and alkyl alcohols. This work may represent an efficient sulfonylation protocol with a very wide substrate scope. The protocol also features a low cost of reagents, wide availability of alcohols, and rapid reaction rates. These features may make this protocol attractive for the synthesis of SO_2-containing biologically active molecules.

EXPERIMENTAL SECTION

General Information. The ^1H and ^{19}F NMR spectra were recorded on 400 MHz NMR spectrometers. ^{13}C was obtained at 100 MHz. The chemical shifts (δ) for ^1H, ^{13}C, and ^{19}F NMR were reported as ppm. The spectral data were recorded as follows: multiplicity (s = singlet, d = doublet, t= triplet, q = quartet, m = multiplet, quin = quintet, coupling constant (s) in Hz). Low-resolution mass spectrum (MS) was obtained on GC-MS (EI) or LC-MS (ESI), and high-resolution mass spectrometry (HRMS) data were measured on a Waters Premier GC-TOF MS instrument with an electron impact (EI) ionization mode, or on a Thermo Scientific Q Exactive HF Orbitrap-FTMS instrument with electrospray ionization (ESI) mode. All reactions were monitored by TLC or ^{19}F NMR. Flash column chromatography was carried out using 300−400 mesh silica gel at medium pressure. Melting points were measured on a melting point apparatus. Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. All reactions were performed in 25 mL sealed tube. The heat source is an oil bath. All starting materials are commercially available, and were purchased and directly used without further purification.

General Procedure for the Dehydroxylative Sulfonylation of Alcohols. *Sulfonylation of Alcohols with Fluoroalkylsulfinates.* Into a solution of alcohol **1** (0.5 mmol, 1.0 equiv) and Ph_3P (0.7 mmol, 183.6 mg, 1.4 equiv) (if alkyl alcohols (**2q−2r**) were used as substrates, Ph_2PCH_3 (0.7 mmol, 140.2 mg, 1.4 equiv) was used instead of Ph_3P and the reaction temperature was 120 °C) in DMF (3 mL) in a 25 mL sealed tube was added ICH_2CH_2I (0.7 mmol, 197.3 mg, 1.4 equiv) under a N_2 atmosphere. After the reagents were completely dissolved, R_FSO_2Na (R_F = CF_3 or HCF_2) (1.5 mmol, 3.0 equiv) was added. The tube was sealed and the resulting mixture was stirred at 80 °C for 15 min (oil bath). The reaction mixture was cooled to room temperature. Dichloromethane was added and the resulting solution was washed with water. The organic layer was removed by concentration under reduced pressure and the residue was subjected to flash column chromatography to give products.

4-[[(Trifluoromethyl)sulfonyl]methyl]-1,1′-biphenyl[16f] ***(2a).*** The crude product was purified by column chromatography on silica gel (PE:EA = 50:1) to afford 4-[[(Trifluoromethyl)sulfonyl]methyl]-1,1′-biphenyl **2a** (108 mg, 72% yield) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 7.4 Hz, 2H), 7.54−7.43 (m, 4H), 7.39 (t, J = 7.3 Hz, 1H), 4.53 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −76.39 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.0, 139.9, 131.7, 128.9, 128.0, 127.2, 121.8, 119.8 (q, J = 328.3 Hz), 55.9.

4-t-Butylbenzyl triflone[19] ***(2b).*** The crude product was purified by column chromatography on silica gel (PE:EA = 60:1) to afford 4-*t*-butylbenzyl triflone (**2b**) (85 mg, 61% yield) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51−7.44 (m, 2H), 7.39−7.33 (m, 2H), 4.46 (s, 2H), 1.34 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −76.63 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.3, 131.0, 126.3, 119.8, 119.8 (q, J = 328.3 Hz), 55.7, 34.8, 31.2.

5-(((Trifluoromethyl)sulfonyl)methyl)benzo[d][1,3]dioxole ***(2c).*** The crude product was purified by column chromatography on silica gel (PE:EA = 40:1) to afford 5-(((trifluoromethyl)sulfonyl)methyl)-benzo[*d*][1,3]dioxole (**2c**) (101 mg, 75% yield) as a white solid. mp 76.4−76.9 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 6.94−6.82 (m, 3H), 6.24−5.74 (m, 3H), 4.39 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −76.38 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.3, 148.4, 125.5, 119.8 (q, J = 328.6 Hz), 116.0, 111.1, 108.9, 101.7, 56.0. HRMS (FI) m/z $[M]^+$ calcd for $C_9H_7F_3O_4S$ 268.0012, found 268.0016. IR (KBr) (cm^{-1}) 3007, 2957, 2900, 2781, 1855, 1742, 1503, 1450, 1410, 1444, 1360, 1340, 1246, 1220, 1199, 1149, 1122, 1069, 1037, 926, 873, 817, 781, 736, 665, 655.

1-Methoxy-3-(((trifluoromethyl)sulfonyl)methyl)benzene ***(2d).*** The crude product was purified by column chromatography on silica gel (PE:EA = 20:1) to afford 1-methoxy-3-(((trifluoromethyl)-sulfonyl)methyl)benzene (**2d**) (93 mg, 73% yield) as a yellow solid. mp 44.3−44.6 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, J = 7.9 Hz, 1H), 7.06−6.91 (m, 3H), 4.45 (s, 2H), 3.82 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −76.58 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.1, 130.3, 124.3, 123.5, 119.8 (q, J = 328.2 Hz), 116.7, 115.7, 56.1, 55.3. HRMS (FI) m/z $[M]^+$ calcd for $C_9H_9F_3O_3S$ 254.0219, found 254.0223. IR (KBr) (cm^{-1}) 2943, 2841, 1602, 1587, 1492, 1457, 1438, 1409, 1365, 1321, 1301, 1271, 1219, 1167, 1152, 1119, 1048, 996, 938, 920, 874, 791, 692, 649.

4-(Methoxycarbonyl)benzyl triflone[19] ***(2e).*** The crude product was purified by column chromatography on silica gel (PE:EA = 10:1) to afford methyl 4-(methoxycarbonyl)benzyl triflone (**2e**) (108 mg, 77% yield) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 4.53 (s, 2H), 3.93 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −76.39 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.2, 131.8, 131.3, 130.4, 128.0, 119.7 (q, J = 328.0 Hz), 55.8, 52.4.

4-Trifluoromethylphenylmethyl trifluoromethyl sulfone[20] ***(2f).*** The crude product was purified by column chromatography on silica gel (PE:EA = 15:1) to afford 4-trifluoromethylphenylmethyl trifluoromethyl sulfone (**2f**) (107 mg, 73% yield) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 8.1 Hz, 2H), 4.53 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.08 (s, 3F), −76.40 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 132.3 (q, J = 33.0 Hz), 131.7, 127.3, 126.2 (q, J = 3.7 Hz), 123.6 (d, J = 272.5 Hz), 119.7 (d, J = 328.0 Hz), 55.5.

1,3-Dichloro-2-(((trifluoromethyl)sulfonyl)methyl)benzene ***(2g).*** The crude product was purified by column chromatography on silica gel (PE:EA = 10:1) to afford 1,3-dichloro-2-(((trifluoromethyl)-sulfonyl)methyl)benzene (**2g**) (88 mg, 60% yield) as a colorless transparent oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.3 Hz, 2H), 7.34 (dd, J = 8.8, 7.3 Hz, 1H), 5.03 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −78.16 (s, 3F). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 137.6, 131.7, 129.0, 122.2, 119.6 (q, J = 328.1 Hz), 51.9. HRMS (FI) m/z $[M]^+$ calcd for $C_8H_5{}^{35}Cl_2F_3O_2S$ 291.9334, found 291.9331. IR

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(KBr) (cm^{-1}) 3087, 3002, 2951, 1581, 1565, 1440, 1402, 1373, 1209, 1120, 1093, 977, 888, 873, 832, 782, 766, 698, 642.

1-Iodo-2-(((trifluoromethyl)sulfonyl)methyl)benzene (**2h**). The crude product was purified by column chromatography on silica gel (PE:EA = 20:1) to afford 1-iodo-2-(((trifluoromethyl)sulfonyl)-methyl)benzene (**2h**) (122 mg, 70% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 8.0, 1.3 Hz, 1H), 7.53 (dd, J = 7.7, 1.7 Hz, 1H), 7.43 (td, J = 7.6, 1.3 Hz, 1H), 7.13 (td, J = 7.7, 1.7 Hz, 1H), 4.79 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −77.28 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.7, 132.3, 131.5, 129.0, 127.4, 119.7 (q, J = 328.0 Hz), 102.3, 59.9. HRMS (FI) m/z [M]$^+$ calcd for $C_8H_6F_3IO_2S$ 349.9080, found 349.9085. IR (KBr) (cm^{-1}) 2935, 1587, 1566, 1471, 1438, 1405, 1367, 1277, 1220, 1148, 1120, 1047, 1016, 858, 767, 731, 702, 649, 628, 606, 561, 527.

1-Bromo-4-(((4-trifluoromethyl)sulfonyl)methyl)benzene[21] (**2i**). The crude product was purified by column chromatography on silica gel (PE:EA = 10:1) to afford 1-bromo-4-(((4-trifluoromethyl)-sulfonyl)methyl)benzene (**2i**) (107 mg, 71% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 4.43 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −76.30 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 132.8, 132.6, 124.8, 122.1, 119.7 (q, J = 328.2 Hz), 55.5.

1,3,5-Trimethyl-2-[[(trifluoromethyl)sulfonyl]methyl]benzene[20] (**2j**). The crude product was purified by column chromatography on silica gel (PE:EA = 80:1) to afford 1,3,5-trimethyl-2-[[(trifluoromethyl)sulfonyl]methyl]benzene (**2j**) (107 mg, 80% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 2H), 4.63 (s, 2H), 2.44 (s, 6H), 2.30 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −78.54 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.9, 139.7, 129.9, 120.0 (q, J = 328.3 Hz), 117.0, 49.8, 21.0, 20.3.

2-(((Trifluoromethyl)sulfonyl)methyl)benzo[b]thiophene (**2k**). The crude product was purified by column chromatography on silica gel (PE:EA = 15:1) to afford 2-(((trifluoromethyl)sulfonyl)methyl)-benzo[*b*]thiophene (**2k**) (106 mg, 76% yield) as a white solid. mp 162.5−163.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.78 (m, 2H), 7.48 (s, 1H), 7.45−7.36 (m, 2H), 4.79 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −75.71 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.1, 139.1, 129.0, 125.7, 125.0, 124.2, 123.8, 122.3, 119.8 (q, J = 328.7 Hz), 51.9. HRMS (FI) m/z [M]$^+$ calcd for $C_{10}H_7F_3O_2S_2$ 279.9834, found 279.9832. IR (KBr) (cm^{-1}) 2998, 1758, 1361, 1346, 1241, 1221, 1197, 1124, 1050, 773, 734, 522.

2-(((Trifluoromethyl)sulfonyl)methyl)benzofuran (**2l**). The crude product was purified by column chromatography on silica gel (PE:EA = 15:1) to afford 2-(((trifluoromethyl)sulfonyl)methyl)benzofuran (**2l**) (136 mg, 78% yield) as a light yellow solid. mp 109.8−110.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.7 Hz, 1H), 7.52 (d, J = 8.3 Hz, 1H), 7.36 (tt, J = 8.3, 1.2 Hz, 1H), 7.31−7.25 (m, 1H), 4.74 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −76.14 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.8, 140.4, 127.6, 125.9, 123.6, 121.6, 119.6 (q, J = 328.4 Hz), 111.6, 110.9, 50.5. HRMS (FI) m/z [M]$^+$ calcd for $C_{10}H_7F_3O_3S$ 264.0063, found 264.0057. IR (KBr) (cm^{-1}) 3116, 2989, 2926, 2360, 2341, 1453, 1395, 1368, 1353, 1321, 1261, 1220, 1194, 1155, 1118, 953, 942, 758, 757, 668, 635.

N-(4-(4-Fluorophenyl)-6-isopropyl-5-(((trifluoromethyl)sulfonyl)-methyl)pyrimidin-2-yl)-N-methylmethanesulfonamide (**2m**). The crude product was purified by column chromatography on silica gel (PE:EA = 5:1) to afford *N*-(4-(4-fluorophenyl)-6-isopropyl-5-(((trifluoromethyl)sulfonyl)methyl)pyrimidin-2-yl)-*N*-methylmethanesulfonamide (**2m**) (136 mg, 58% yield) as a yellow solid. mp 153.7−154.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.48 (m, 2H), 7.22−7.13 (m, 2H), 4.68 (s, 2H), 3.56 (s, 3H), 3.50 (s, 3H), 3.39 (hept, J = 6.5 Hz, 1H), 1.35 (d, J = 6.5 Hz, 7H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −78.12 (s, 3F), −110.48 − −110.53 (m, 1F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 178.6, 169.4, 163.6 (d, J = 250.7 Hz), 158.8, 133.2 (d, J = 3.3 Hz), 130.8 (d, J = 8.6 Hz), 119.5 (q, J = 328.2 Hz), 115.9 (d, J = 21.8 Hz), 106.3, 48.5, 42.5, 33.2, 32.7, 22.0. HRMS (FI) m/z [M]$^+$ calcd for $C_{17}H_{19}F_4N_3O_4S_2$ 469.0748, found 469.0751. IR (KBr) (cm^{-1}) 2975, 2875, 1607, 1550, 1511, 1443, 1379, 1342, 1223, 1157, 1120, 1068, 963, 910, 836, 774, 734, 635, 619.

2-(1-((Trifluoromethyl)sulfonyl)ethyl)naphthalene (**2n**). The crude product was purified by column chromatography on silica gel (PE:EA = 20:1) to afford 2-(1-((trifluoromethyl)sulfonyl)ethyl)-naphthalene (**2n**) (41 mg, 29% yield) as a white solid. mp 49.2−50.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.84 (m, 4H), 7.64−7.48 (m, 3H), 4.73 (q, J = 7.2 Hz, 1H), 1.99 (d, J = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.44 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 133.8, 133.1, 129.7, 129.1, 128.2, 127.8, 127.7, 127.4, 126.9, 126.0, 120.1 (q, J = 329.8 Hz), 62.6, 14.7. HRMS (FI) m/z [M]$^+$ calcd for $C_{13}H_{11}F_3O_2S$ 288.0426, found 288.0423. IR (KBr) (cm^{-1}) 3060, 2918, 2849, 1507, 1456, 1355, 1210, 1115, 1046, 913, 860, 818, 771, 748, 697, 650, 621, 609.

1-Bromo-4-(1-((trifluoromethyl)sulfonyl)ethyl)benzene (**2o**). The crude product was purified by column chromatography on silica gel (PE:EA = 40:1) to afford 1-bromo-4-(1-((trifluoromethyl)sulfonyl)-ethyl)benzene (**2o**) (59 mg, 37% yield) as a yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 4.52 (q, J = 7.2 Hz, 1H), 1.86 (d, J = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.38 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 132.4, 131.1, 129.3, 124.6, 120.0 (q, J = 329.8 Hz), 61.7, 14.4. HRMS (FI) m/z [M]$^+$ calcd for $C_9H_8{}^{79}BrF_3O_2S$ 315.9375, found 315.9377. IR (KBr) (cm^{-1}) 2998, 2947, 1906, 1685, 1592, 1490, 1459, 1408, 1359, 1321, 1209, 1114, 1076, 1050, 1012, 829, 789, 762,748, 722, 690.

(E)-(3-(Trifluoromethyl)sulfonyl)prop-1-en-1-yl)benzene[9f] (**2p**). The crude product was purified by column chromatography on silica gel (PE:EA = 25:1) to afford (*E*)-(3-(trifluoromethyl)sulfonyl)prop-1-en-1-yl)benzene (**2p**) (67 mg, 56% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.41 (m, 3H), 7.40−7.31 (m, 2H), 6.82 (d, J = 15.8 Hz, 1H), 6.15 (dt, J = 15.5, 7.6 Hz, 1H), 4.15 (d, J = 7.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −76.25 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.7, 135.0, 129.3, 128.9, 127.0, 119.7 (q, J = 328.5 Hz), 110.2, 54.5.

(4-((Trifluoromethyl)sulfonyl)butyl)benzene (**2q**). The crude product was purified by column chromatography on silica gel (PE:EA = 20:1) to afford (4-((trifluoromethyl)sulfonyl)butyl)-benzene (**2q**) (53 mg, 40% yield) as a colorless transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.26 (m, 2H), 7.25−7.13 (m, 3H), 3.20 (t, J = 7.9 Hz, 2H), 2.68 (t, J = 7.5 Hz, 2H), 2.01−1.91 (m, 2H), 1.81 (quin, J = 7.5 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −78.25 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.7, 128.6, 128.4, 126.3, 119.5 (q, J = 327.1 Hz), 49.5, 35.1, 30.0, 20.3. HRMS (FI) m/z [M]$^+$ calcd for $C_{11}H_{13}F_3O_2S$ 266.0583, found 266.0587. IR (KBr) (cm^{-1}) 2930, 1497, 1455, 1363, 1219, 1121, 913, 772, 670, 612, 537.

2,3-Dimethoxy-5-methyl-6-(10-((trifluoromethyl)sulfonyl)decyl)-cyclohexa-2,5-diene-1,4-dione (**2r**). The crude product was purified by column chromatography on silica gel (PE:EA = 10:1) to afford 2,3-dimethoxy-5-methyl-6-(10-((trifluoromethyl)sulfonyl)decyl)-cyclohexa-2,5-diene-1,4-dione (**2r**) (101 mg, 44% yield) as an orange yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (s, 3H), 3.96 (s, 3H), 3.20 (t, J = 8.0 Hz, 2H), 2.43 (t, J = 7.4 Hz, 2H), 1.99 (s, 3H), 1.52−1.42 (m, 2H), 1.41−1.21 (m, 14H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −78.25 (s, 3F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 184.7, 184.2, 144.3, 144.3, 143.0, 138.7, 119.5 (q, J = 327.2 Hz), 61.1, 49.6, 29.7, 29.2, 29.2, 29.1, 28.8, 28.7, 28.3, 26.4, 20.7, 11.9. HRMS (FI) m/z [M]$^+$ calcd for $C_{20}H_{29}F_3O_6S$ 454.1631, found 454.1635. IR (KBr) (cm^{-1}) 2929, 2856, 1650, 1611, 1457, 1364, 1267, 1219, 1123, 1072, 772, 617.

4-(((Difluoromethyl)sulfonyl)methyl)-1,1′-biphenyl (**2s**). The crude product was purified by column chromatography on silica gel (PE:EA = 5:1) to afford 4-(((difluoromethyl)sulfonyl)methyl)-1,1′-biphenyl (**2s**) (120 mg, 85% yield) as a white solid. mp 164.1−164.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.63 (m, 2H), 7.62−7.57 (m, 2H), 7.53−7.42 (m, 4H), 7.43−7.34 (m, 1H), 6.16 (t, J = 52.8 Hz, 1H), 4.45 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −123.00 (d, J = 52.6 Hz, 2F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.7, 140.0, 131.7, 128.9, 128.0, 127.9, 127.2, 122.7, 114.7 (t, J = 286.4 Hz), 54.4. HRMS (FI) m/z [M]$^+$ calcd for $C_{14}H_{12}F_2O_2S$ 282.0521, found 282.0527. IR (KBr) (cm^{-1}) 3033, 2408, 1545, 1444, 1339, 1316, 1220, 1171, 1150, 1113, 913, 781, 686, 674, 505.

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*Methyl 4-(((difluoromethyl)sulfonyl)methyl)benzoate (**2t**).* The crude product was purified by column chromatography on silica gel (PE:EA = 5:1) to afford methyl 4-(((difluoromethyl)sulfonyl)-methyl)benzoate (**2t**) (110 mg, 90% yield) as a yellow solid. mp 79.3−80.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 6.15 (t, J = 52.6 Hz, 1H), 4.42 (s, 2H), 3.89 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −122.52 (d, J = 52.4 Hz, 2F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.3, 131.3, 130.2, 129.0, 114.9 (t, J = 286.5 Hz), 54.2, 52.4. HRMS (FI) m/z [M]$^+$ calcd for $C_{10}H_{10}F_2O_4S$ 264.0262, found 264.0264. IR (KBr) (cm^{-1}) 3001, 2949, 1720, 1438, 1418, 1343, 1313, 1284, 1219, 1171, 1152, 1116, 913, 772.

*1-(((Difluoromethyl)sulfonyl)methyl)-3-methoxybenzene (**2u**).* The crude product was purified by column chromatography on silica gel (PE:EA = 5:1) to afford 1-(((difluoromethyl)sulfonyl)methyl)-3-methoxybenzene (**2u**) (85 mg, 72% yield) as a yellow oil. mp 51.7−52.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, J = 7.8 Hz, 1H), 7.02−6.91 (m, 3H), 6.12 (t, J = 52.8 Hz, 1H), 4.36 (s, 2H), 3.82 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −123.41 (d, J = 52.7 Hz, 2F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.1, 130.2, 125.3, 123.4, 116.7, 115.4, 114.4 (t, J = 286.1 Hz), 55.4, 54.7. HRMS (FI) m/z [M]$^+$ calcd for $C_9H_{10}F_2O_3S$ 236.0313, found 236.0316. IR (KBr) (cm^{-1}) 3033, 2408, 1545, 1442, 1344, 1220, 1101, 1036, 914, 781, 685, 674.

*2-(((Difluoromethyl)sulfonyl)methyl)benzo[b]thiophene (**2v**).* The crude product was purified by column chromatography on silica gel (PE:EA = 5:1) to afford 2-(((difluoromethyl)sulfonyl)methyl)-benzo[*b*]thiophene (**2v**) (106 mg, 81% yield) as a yellow solid. mp 118.3−119.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.74 (m, 2H), 7.46 (s, 1H), 7.43−7.35 (m, 2H), 6.23 (t, J = 52.7 Hz, 1H), 4.70 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −122.73 (d, J = 52.8 Hz, 2F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.0, 139.2, 128.6, 125.5, 125.0, 124.1, 122.3, 114.5 (t, J = 286.8 Hz), 50.4. HRMS (FI) m/z [M]$^+$ calcd for $C_{10}H_8F_2O_2S_2$ 261.9928, found 261.9930. IR (KBr) (cm^{-1}) 2993, 1434, 1347, 1219, 1170, 1155, 1115, 912, 777, 686, 674, 570.

*(E)-(3-((Difluoromethyl)sulfonyl)prop-1-en-1-yl)benzene (**2w**).* The crude product was purified by column chromatography on silica gel (PE:EA = 5:1) to afford (*E*)-(3-((difluoromethyl)sulfonyl)prop-1-en-1-yl)benzene (**2w**) (96 mg, 83% yield) as a yellow solid. mp 67.3−68.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.28 (m, 5H), 6.80 (d, J = 15.8 Hz, 1H), 6.21 (t, J = 52.3 Hz, 1H), 6.20−6.12 (m, 1H), 4.06 (dd, J = 7.7, 1.3 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −122.88 (d, J = 52.4 Hz, 2F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.0, 135.2, 129.1, 128.8, 126.9, 114.9 (t, J = 286.5 Hz), 111.1, 53.0. HRMS (FI) m/z [M]$^+$ calcd for $C_{10}H_{10}F_2O_2S$ 232.0364, found 232.0370. IR (KBr) (cm^{-1}) 3032, 1496, 1450, 1347, 1219, 1103, 968, 772, 691, 623.

Sulfonylation of Alcohols with Nonfluorosulfinates. Into a solution of alcohol **1** (0.5 mmol, 1.0 equiv) and Ph_3P (0.7 mmol, 183.6 mg, 1.4 equiv) (if alkyl alcohols (**3q**−**3t**) were used as substrates, Ph_2PCH_3 (0.7 mmol, 140.2 mg, 1.4 equiv) was used instead of Ph_3P and the reaction temperature was 120 °C) in DMF (3 mL) in a 25 mL sealed tube was added ICH_2CH_2I (0.7 mmol, 197.3 mg, 1.4 equiv) under a N_2 atmosphere. After the reagents were completely dissolved, R′SO_2Na (1.0 mmol, 2.0 equiv) was added. The tube was sealed and the resulting mixture was stirred at 80 °C for 15 min (oil bath). The reaction mixture was cooled to room temperature. Dichloromethane was added and the resulting solution was washed with water. The organic layer was removed by concentration under reduced pressure and the residue was subjected to flash column chromatography to give products.

*4-[(Phenylsulfonyl)methyl]-1,1′-biphenyl[22] (**3a**).* The crude product was purified by column chromatography on silica gel (PE:EA = 5:1) to afford 4-[(phenylsulfonyl)methyl]-1,1′-biphenyl (**3a**) (139 mg, 90% yield) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 2H), 7.64−7.54 (m, 3H), 7.53−7.41 (m, 6H), 7.36 (t, J = 7.7 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 4.36 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.7, 140.2, 138.0, 133.8, 131.3, 129.0, 128.9, 128.7, 127.7, 127.3, 127.1, 127.0, 62.6.

*4-(Tosylmethyl)-1,1′-biphenyl[23] (**3b**).* The crude product was purified by column chromatography on silica gel (PE:EA = 5:1) to afford 4-(tosylmethyl)-1,1′-biphenyl (**3b**) (150 mg, 97% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.53 (m, 4H), 7.49 (d, J = 8.1 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.24 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 4.32 (s, 2H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.8, 141.6, 140.3, 135.1, 131.3, 129.6, 128.9, 128.7, 127.7, 127.2, 127.2, 127.1, 62.7, 21.7.

*4-(((4-Chlorophenyl)sulfonyl)methyl)-1,1′-biphenyl (**3c**).* The crude product was purified by column chromatography on silica gel (PE:EA = 5:1) to afford 4-(((4-chlorophenyl)sulfonyl)methyl)-1,1′-biphenyl (**3c**) (151 mg, 88% yield) as a white solid. mp 229.6−230.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.55 (m, 4H), 7.54−7.50 (m, 2H), 7.48−7.41 (m, 4H), 7.40−7.34 (m, 1H), 7.17 (d, J = 8.6 Hz, 2H), 4.35 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.8, 140.6, 140.1, 136.4, 131.2, 130.2, 129.3, 128.9, 127.8, 127.4, 127.1, 126.7, 62.7. HRMS (FI) m/z [M]$^+$ calcd for $C_{19}H_{15}{}^{35}ClO_2S$ 342.0476, found 342.0480. IR (KBr) (cm^{-1}) 1313, 1219, 1153, 831, 772, 527.

*4-(((4-Nitrophenyl)sulfonyl)methyl)-1,1′-biphenyl (**3d**).* The crude product was purified by column chromatography on silica gel (PE:EA = 8:1) to afford 4-(((4-nitrophenyl)sulfonyl)methyl)-1,1′-biphenyl (**3d**) (173 mg, 98% yield) as a yellow solid. mp 242.5−242.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 7.61−7.50 (m, 4H), 7.45 (t, J = 7.57 Hz, 2H), 7.38 (t, J = 7.7 Hz, 1H), 7.17 (d, J = 7.8 Hz, 2H), 4.42 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.9, 143.5, 142.2, 139.8, 131.2, 130.2, 129.0, 127.9, 127.5, 127.1, 126.0, 124.1, 62.6. HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{19}H_{15}NNaO_4S$ 376.0614, found 376.0614. IR (KBr) (cm^{-1}) 1523, 1306, 1219, 1150, 845, 772, 690, 522.

*4-(Methoxycarbonyl)benzyl phenyl sulfone[24] (**3e**).* The crude product was purified by column chromatography on silica gel (PE:EA = 3:1) to afford 4-(methoxycarbonyl)benzyl phenyl sulfone (**3e**) (153 mg, 94% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.2 Hz, 2H), 7.66−7.56 (m, 3H), 7.44 (t, J = 7.8 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 4.35 (s, 2H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.5, 137.6, 134.0, 133.1, 130.9, 130.5, 129.8, 129.1, 128.6, 62.7, 52.3.

*1-Methoxy-3-((phenylsulfonyl)methyl)benzene[25] (**3f**).* The crude product was purified by column chromatography on silica gel (PE:EA = 3:1) to afford 1-methoxy-3-((phenylsulfonyl)methyl)benzene (**3f**) (112 mg, 86% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.63 (m, 2H), 7.62−7.57 (m, 1H), 7.45 (t, J = 7.9 Hz, 2H), 7.15 (t, J = 7.9 Hz, 1H), 6.89−6.79 (m, 1H), 6.68−6.55 (m, 2H), 4.28 (s, 2H), 3.69 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.6, 137.9, 133.7, 129.6, 129.4, 128.9, 128.7, 123.2, 115.9, 114.8, 62.9, 55.2.

*4-((Ethylsulfonyl)methyl)-1,1′-biphenyl (**3g**).* The crude product was purified by column chromatography on silica gel (PE:EA = 4:1) to afford 4-((ethylsulfonyl)methyl)-1,1′-biphenyl (**3g**) (96 mg, 73% yield) as a yellow solid. mp 170.2−170.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66−7.56 (m, 4H), 7.52−7.42 (m, 4H), 7.42−7.33 (m, 1H), 4.27 (s, 2H), 2.91 (q, J = 7.5 Hz, 2H), 1.39 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.0, 140.2, 131.0, 128.9, 127.8, 127.8, 127.1, 126.9, 58.4, 45.6, 6.5. HRMS (FI) m/z [M]$^+$ calcd for $C_{15}H_{16}O_2S$ 260.0866, found 260.0864. IR (KBr) (cm^{-1}) 2360, 1312, 1219, 1123, 772, 687, 674.

*4-((Cyclopropylsulfonyl)methyl)-1,1′-biphenyl (**3h**).* The crude product was purified by column chromatography on silica gel (PE:EA = 4:1) to afford 4-((cyclopropylsulfonyl)methyl)-1,1′-biphenyl (**3h**) (107 mg, 79% yield) as a yellow solid. mp 142.2−143.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.57 (m, 4H), 7.55−7.42 (m, 4H), 7.41−7.34 (m, 1H), 4.31 (s, 2H), 2.33−2.21 (m, 1H), 1.22−1.12 (m, 2H), 1.04−0.92 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.8, 140.2, 131.3, 128.9, 127.7, 127.6, 127.2, 127.1, 60.0, 28.4, 4.9. HRMS (FI) m/z [M]$^+$ calcd for $C_{16}H_{16}O_2S$ 272.0866, found 272.0863. IR (KBr) (cm^{-1}) 3053, 1409, 1317, 1281, 1219, 1160, 1139, 1127, 913, 849, 834, 777, 735, 687, 674.

*(E)-(3-(Ethylsulfonyl)prop-1-en-1-yl)benzene[11d] (**3i**).* The crude product was purified by column chromatography on silica gel (PE:EA

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= 3:1) to afford (*E*)-(3-(ethylsulfonyl)prop-1-en-1-yl)benzene (**3i**) (75 mg, 71% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.4 Hz, 2H), 7.38−7.25 (m, 3H), 6.70 (d, J = 15.9 Hz, 1H), 6.26 (dt, J = 15.4, 7.6 Hz, 1H), 3.86 (d, J = 7.6 Hz, 2H), 3.02 (q, J = 7.5 Hz, 2H), 1.40 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.8, 135.6, 128.8, 128.8, 126.7, 115.5, 56.6, 45.8, 6.5.

(E)-(3-(Cyclopropylsulfonyl)prop-1-en-1-yl)benzene[11d] ***(3j)***. The crude product was purified by column chromatography on silica gel (PE:EA = 3:1) to afford (*E*)-(3-(cyclopropylsulfonyl)prop-1-en-1-yl)benzene (**3j**) (76 mg, 68% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.39 (m, 2H), 7.37−7.25 (m, 3H), 6.72 (d, J = 15.7 Hz, 1H), 6.28 (dt, J = 15.7, 7.6 Hz, 1H), 3.91 (d, J = 7.6 Hz, 2H), 2.47−2.39 (m, 1H), 1.28−1.21 (m, 2H), 1.06−0.98 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.8, 135.8, 128.8, 128.6, 126.7, 115.5, 58.2, 28.5, 4.7.

Cinnamylsulfonylbenzene[26] ***(3k)***. The crude product was purified by column chromatography on silica gel (PE:EA = 5:1) to afford cinnamylsulfonylbenzene (**3k**) (105 mg, 81% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.3 Hz, 2H), 7.67−7.58 (m, 1H), 7.56−7.48 (m, 2H), 7.34−7.20 (m, 5H), 6.36 (d, J = 15.7 Hz, 1H), 6.09 (dt, J = 15.7, 7.6 Hz, 1H), 3.95 (d, J = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.2, 138.4, 135.8, 133.8, 129.1, 128.7, 128.6, 128.5, 126.6, 115.2, 60.5.

1-Chloro-4-(cinnamylsulfonyl)benzene[11d] ***(3l)***. The crude product was purified by column chromatography on silica gel (PE:EA = 6:1) to afford 1-chloro-4-(cinnamylsulfonyl)benzene (**3l**) (117 mg, 80% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.7 Hz, 2H), 7.48 (d, J = 7.7 Hz, 2H), 7.36−7.22 (m, 5H), 6.38 (d, J = 15.9 Hz, 1H), 6.08 (dt, J = 15.9, 7.6 Hz, 1H), 3.94 (d, J = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.6, 139.5, 136.9, 135.6, 130.1, 129.5, 128.8, 128.7, 126.7, 114.8, 60.5.

1-(Cinnamylsulfonyl)-4-nitrobenzene[11d] ***(3m)***. The crude product was purified by column chromatography on silica gel (PE:EA = 5:1) to afford 1-(cinnamylsulfonyl)-4-nitrobenzene (**3m**) (150 mg, 99% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.7 Hz, 2H), 8.08 (d, J = 8.7 Hz, 2H), 7.43−7.17 (m, 5H), 6.40 (d, J = 15.8 Hz, 1H), 6.10 (dt, J = 15.8, 7.6 Hz, 1H), 4.02 (d, J = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.9, 144.0, 140.1, 135.2, 130.1, 129.0, 128.8, 126.7, 124.3, 114.0, 60.5.

(3-Phenylprop-2-ynylsulfonyl)benzene[27] ***(3n)***. The crude product was purified by column chromatography on silica gel (PE:EA = 8:1) to afford (3-phenylprop-2-ynylsulfonyl)benzene (**3n**) (121 mg, 95% yield) as a yellow solid. mp 110.1−110.8 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11−7.95 (m, 2H), 7.75−7.66 (m, 1H), 7.64−7.53 (m, 2H), 7.37−7.27 (m, 5H), 4.19 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.8, 134.3, 131.8, 129.1, 129.1, 129.0, 128.4, 121.7, 87.7, 76.8, 49.5.

1-Chloro-4-((3-phenylprop-2-yn-1-yl)sulfonyl)benzene ***(3o)***. The crude product was purified by column chromatography on silica gel (PE:EA = 8:1) to afford 1-chloro-4-((3-phenylprop-2-yn-1-yl)-sulfonyl)benzene (**3o**) (120 mg, 82% yield) as a white solid. mp 100.3−101.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−7.91 (m, 2H), 7.60−7.48 (m, 2H), 7.39−7.27 (m, 5H), 4.20 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.1, 136.2, 131.8, 130.5, 129.5, 129.2, 128.5, 121.5, 87.9, 76.6, 49.5. HRMS (FI) m/z $[M]^+$ calcd for $C_{15}H_{11}{}^{35}ClO_2S$ 290.0163, found 290.0166. IR (KBr) (cm^{-1}) 3087, 2953, 2908, 1583, 1490, 1475, 1443, 1395, 1327, 1281, 1220, 1165, 1141, 1088, 1014, 913, 873, 830, 771, 729, 691.

(3-(Cyclopropylsulfonyl)prop-1-yn-1-yl)benzene ***(3p)***. The crude product was purified by column chromatography on silica gel (PE:EA = 8:1) to afford (3-(cyclopropylsulfonyl)prop-1-yn-1-yl)benzene (**3p**) (97 mg, 72% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.43 (m, 2H), 7.40−7.29 (m, 3H), 4.13 (s, 2H), 2.78−2.64 (m, 1H), 1.40−1.32 (m, 2H), 1.17−1.09 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 131.9, 129.1, 128.4, 121.8, 87.3, 76.7, 46.9, 28.9, 5.2. HRMS (FI) m/z $[M]^+$ calcd for $C_{12}H_{12}O_2S$ 220.0553, found 220.0548. IR (KBr) (cm^{-1}) 3021, 2955, 2911, 1491, 1443, 1326, 1221, 1167, 1126, 1071, 1042, 913, 889, 785, 691, 674, 564, 501.

((4-Phenylbutyl)sulfonyl)benzene[28] ***(3q)***. The crude product was purified by column chromatography on silica gel (PE:EA = 8:1) to afford ((4-phenylbutyl)sulfonyl)benzene (**3q**) (80 mg, 58% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.7 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.28−7.20 (m, 2H), 7.16 (t, J = 7.1 Hz, 1H), 7.08 (d, J = 7.5 Hz, 2H), 3.14−2.97 (m, 2H), 2.57 (t, J = 7.2 Hz, 2H), 1.82−1.62 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.2, 139.2, 133.7, 129.33, 128.4, 128.3, 128.1, 126.0, 56.1, 35.3, 30.0, 22.3.

1-Chloro-4-((4-phenylbutyl)sulfonyl)benzene ***(3r)***. The crude product was purified by column chromatography on silica gel (PE:EA = 6:1) to afford 1-chloro-4-((4-phenylbutyl)sulfonyl)benzene (**3r**) (115 mg, 75% yield) as a white solid. mp 62.3−63.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.31−7.21 (m, 2H), 7.21−7.15 (m, 1H), 7.09 (d, J = 7.1 Hz, 2H), 3.12−3.04 (m, 2H), 2.59 (t, J = 7.0 Hz, 2H), 1.81−1.64 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.1, 140.4, 137.7, 129.6, 129.6, 128.5, 128.3, 126.1, 56.1, 35.2, 29.9, 22.3. HRMS (FI) m/z $[M]^+$ calcd for $C_{16}H_{17}{}^{35}ClO_2S$ 308.0632, found 308.0629. IR (KBr) (cm^{-1}) 3033, 2408, 1220, 1546, 1444, 1318, 1220, 1150, 1088, 1013, 914, 781, 685, 674, 626, 557.

2,3-Dimethoxy-5-methyl-6-(10-(phenylsulfonyl)decyl)cyclohexa-2,5-diene-1,4-dione ***(3s)***. The crude product was purified by column chromatography on silica gel (PE:EA = 3:1) to afford 2,3-dimethoxy-5-methyl-6-(10-(phenylsulfonyl)decyl)cyclohexa-2,5-diene-1,4-dione (**3s**) (129 mg, 56% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.83 (m, 2H), 7.70−7.60 (m, 1H), 7.56 (t, J = 7.7 Hz, 2H), 4.11−3.86 (m, 6H), 3.18−2.97 (m, 2H), 2.41 (t, J = 7.4 Hz, 2H), 1.98 (s, 3H), 1.75−1.61 (m, 2H), 1.44−1.08 (m, 14H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 184.7, 184.1, 144.3, 144.3, 143.0, 139.3, 138.7, 133.6, 129.3, 128.0, 61.1, 56.3, 29.7, 29.3, 29.2, 29.2, 28.9, 28.7, 28.2, 26.4, 22.6, 11.9. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{25}H_{35}O_6S$ 463.2149, found 463.2151. IR (KBr) (cm^{-1}) 2928, 2854, 1651, 1610, 1447, 1266, 1220, 1148, 784, 688, 673.

Chloro-4-(undec-10-en-1-ylsulfonyl)benzene ***(3t)***. The crude product was purified by column chromatography on silica gel (PE:EA = 15:1) to afford 1-chloro-4-(undec-10-en-1-ylsulfonyl)-benzene (**3t**) (88 mg, 53% yield) as a yellow solid. mp 36.5−37.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 5.89−5.67 (m, 1H), 5.08−4.80 (m, 2H), 3.16−2.97 (m, 2H), 2.08−1.94 (m, 2H), 1.76−1.60 (m, 2H), 1.43−1.28 (m, 5H), 1.22 (s, 7H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.4, 139.1, 137.7, 129.6, 114.2, 56.4, 33.8, 29.3, 29.1, 29.0, 29.0 28.9, 28.2, 22.7. HRMS (FI) m/z $[M]^+$ calcd for $C_{17}H_{25}{}^{35}ClO_2S$ 328.1258, found 328.1263. IR (KBr) (cm^{-1}) 3074, 2926, 2854, 1640, 1583, 1476, 1466, 1394, 1320, 1277, 1151, 1089, 1014, 994, 910, 830, 789, 759, 760, 628, 573.

Gram-Scale Reaction. Into a solution of alcohol **1a** (5 mmol, 0.921 g, 1.0 equiv) and Ph_3P (7 mmol, 1.836 g, 1.4 equiv) in DMF (30 mL) in a 100 mL sealed tube was added ICH_2CH_2I (7 mmol, 1.973 g, 1.4 equiv) under a N_2 atmosphere. After the reagents were completely dissolved, CF_3SO_2Na (15 mmol, 2.371 g, 3.0 equiv) was added. The tube was sealed and the resulting mixture was stirred at 80 °C for 15 min. The reaction mixture was cooled to room temperature. Dichloromethane was added and the resulting solution was washed with water. The organic layer was removed by concentration under reduced pressure and the residue was subjected to flash column chromatography to give the desired product (65%, 0.98 g).

Trifluoromethylsulfonylation in the Presence of TEMPO. Into a solution of alcohol **1a** (0.5 mmol, 92.1 mg, 1.0 equiv), Ph_3P (0.7 mmol, 183.6 mg, 1.4 equiv), and TEMPO (0.5 mmol, 78.1 mg, 1.0 equiv) in DMF (3 mL) in a 25 mL sealed tube was added ICH_2CH_2I (0.7 mmol, 197.3 mg, 1.4 equiv) under a N_2 atmosphere. After the reagents were completely dissolved, CF_3SO_2Na (1.5 mmol, 237.1 mg, 3.0 equiv) was added. The tube was sealed and the resulting mixture was stirred at 80 °C for 15 min. The reaction mixture was cooled to room temperature. Dichloromethane was added and the resulting solution was washed with water. The organic layer was removed by concentration under reduced pressure and the residue was subjected to flash column chromatography to give the desired product (74%, 111.2 mg).

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Procedure for Sulfonylation of Alcohols with the Use of $(EtO)_3P$. Into a solution of alcohol **1a** (0.5 mmol, 91.2 mg, 1.0 equiv) and $(EtO)_3P$ (0.7 mmol, 116.3 mg, 1.4 equiv) in DMF (3 mL) in a 25 mL sealed tube was added ICH_2CH_2I (0.7 mmol, 197.3 mg, 1.4 equiv) under a N_2 atmosphere. After the reagents were stirred at 120 °C for 30 min, CF_3SO_2Na (1.5 mmol, 237.1 mg, 3.0 equiv) was added under a N_2 atmosphere. The tube was sealed and the resulting mixture was stirred at 120 °C for 60 min. The reaction mixture was cooled to room temperature. Dichloromethane was added and the resulting solution was washed with water. The organic layer was removed by concentration under reduced pressure and the residue was subjected to flash column chromatography to give the desired product (60%, 89.8 mg).

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.2c03085.

Optimization of dehydroxylation sulfonation reactions; Optimization of dehydroxylation trifluoromethylsulfonylation of benzyl alcohol with the use of $(EtO)_3P$; Copies of ^1H NMR, ^{19}F NMR, and $^{13}C\{^1H\}$ NMR spectra of products (PDF)

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Notes

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