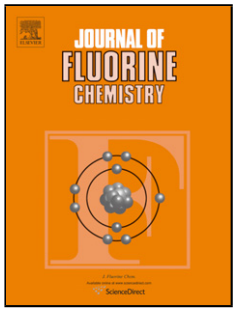

Title: Solvent-Free Synthesis of Alkyl and Fluoroalkyl Sulfonium Salts from Sulfides and Fluoroalkyl Trifluoromethanesulfonates

Author: Hai-Xia Song Shi-Meng Wang Xiao-Yan Wang Jia-Bin Han Ying Gao Su-Jiao Jia Cheng-Pan Zhang

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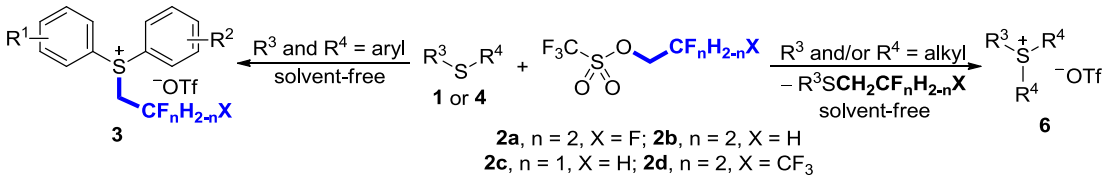
<AT>Solvent-Free Synthesis of Alkyl and Fluoroalkyl Sulfonium Salts from Sulfides and Fluoroalkyl Trifluoromethanesulfonates

<AU>Hai-Xia Song, Shi-Meng Wang, Xiao-Yan Wang, Jia-Bin Han, Ying Gao, Su-Jiao Jia, Cheng-Pan Zhang* ##Email##cpzhang@whut.edu.cn##/Email##, ##Email##zhangchengpan1982@hotmail.com##/Email##
<AU>

<AFF>School of Chemistry, Chemical Engineering and Life Science, Wuhan University of Technology, 205 Luoshi Road, Wuhan, 430070, China

<PA>*Corresponding author Graphic.

<ABS-HEAD>Abstract►



<ABS-HEAD>Highlights► Solvent-free facile synthesis of alkyl and fluoroalkyl sulfonium salts. ► Fluoroalkyl trifluoromethanesulfonates were used as fluoroalkyl sources. ► The reaction could selectively afford alkyl- or fluoroalkylsulfonium salts. ► The reactants and reaction temperature dramatically affected the reaction.

<ABS-HEAD>Abstract

<ABS-P>A series of diaryl(fluoroalkyl)sulfonium salts were synthesized from electron-rich diaryl sulfides and fluoroalkyl trifluoromethanesulfonates under solvent-free conditions. Unlike diaryl sulfides, dialkyl and alkyl(aryl) sulfides reacted with fluoroalkyl trifluoromethanesulfonates (e.g. $CF_3SO_3CH_2CF_3$, $CF_3SO_3CH_2CF_2H$) to provide trialkyl- and aryl(dialkyl)sulfonium trifluoromethanesulfonates in good yields, wherein dialkyl- and alkyl(aryl)(fluoroalkyl)sulfonium salts were formed, respectively, and nucleophilically attacked by a second sulfide to yield the non-fluorinated sulfoniums. The S_N2-type reaction could stop at the first step and exclusively afford dialkyl- and alkyl(aryl)(fluoroalkyl)sulfonium salts, which was dramatically dependent upon the structure of sulfides, the nature of fluoroalkyl trifluoromethanesulfonates, the reactant ratio, and/or the reaction temperature. This protocol allows for an efficient and convenient access to a variety of alkyl and fluoroalkyl sulfonium salts.

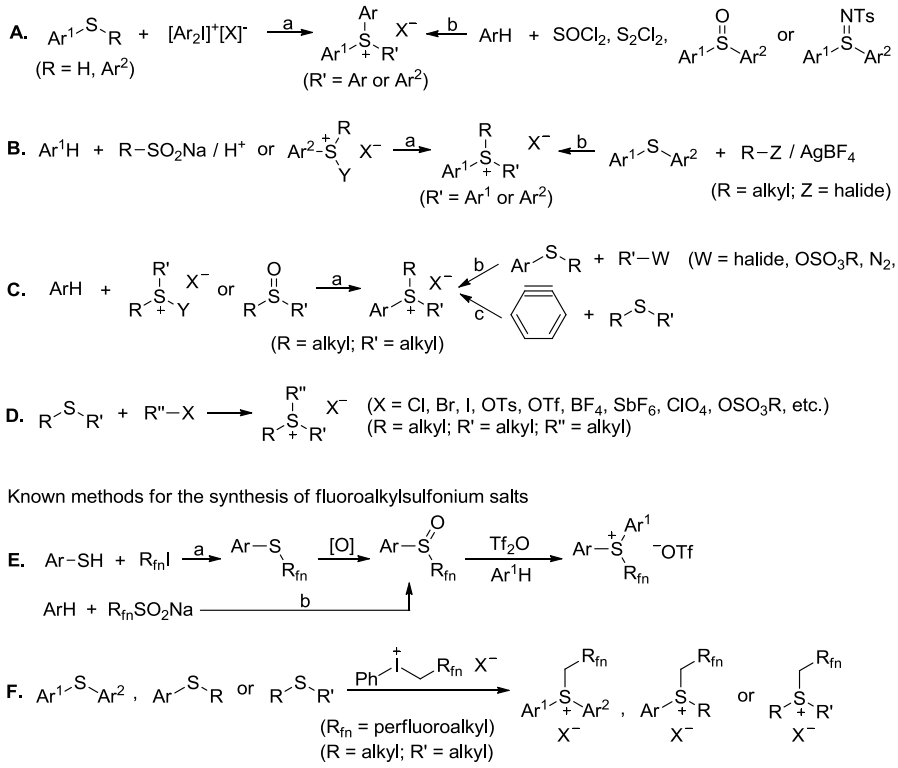
<KWD>Keywords: sulfides; fluoroalkyl trifluoromethanesulfonates; sulfonium salts.

<H1>1. Introduction

Sulfonium salts are versatile reagents in the fields of chemistry and materials science [1,2]. Triarylsulfonium salts have been widely used as photoinitiators in cationic polymerizations and as photoacid generators in the areas of coatings, adhesives, photoresists, microfabrication, and patterning [2,3]. Vinylsulfoniums can *in situ* form

sulfur ylides via nucleophilic conjugate addition, leading to a variety of useful cyclization reactions [4,5]. Alkylsulfoniums have become the most common ylide precursors, generating sulfur ylides in the presence of appropriate bases to furnish a great quantity of cyclopropane derivatives [6]. They can also undergo elimination and displacement for numerous synthetic purposes [7]. Diaryl(perfluoroalkyl)sulfonium salts are powerful electrophilic perfluoroalkylation reagents which have perfluoroalkylated a wide range of nucleophiles and electrophiles under mild conditions [8]. Moreover, diaryl(fluoroalkyl)sulfonium trifluoromethanesulfonates have been used as effective fluoroalkylation and arylation reagents in transition-metal-catalyzed cross-couplings during the past few years [9,10]. Owing to their wide applications, the development of efficient methods to the synthesis of these sulfonium salts is of particular importance [1,6].

Previous synthetic methods for triaryl-, alkyl(diaryl)-, aryl(dialkyl)- and trialkylsulfonium salts



Known methods for the synthesis of fluoroalkylsulfonium salts

In general, triarylsulfonium salts were prepared by the reactions of arylthiols or diaryl sulfides with diaryliodonium salts, and the reactions of arenes with sulfur monochloride, diaryl sulfoxides or sulfimides [1a,1d,1e]. Alkyl(diaryl)sulfonium salts were synthesized from the reactions of arenes with alkyl(aryl)(halo)sulfoniums or sodium methanesulfinate, and the reactions of diaryl sulfides or sulfoxides with alkylation reagents [1d]. Aryl(dialkyl)sulfonium salts were derived from the reactions of arenes with dialkyl(halo)sulfonium salts, dialkyl sulfoxides, dialkyl(aza)sulfoniums or dialkyl(nitrosyl)sulfoniums, the reactions of aryl(alkyl)sulfoxides or sulfides with alkylation reagents, and the reaction of dialkyl sulfides with benzyne [1d]. Trialkylsulfonium salts were simply constructed by the reactions of dialkyl sulfides with alkylation reagents such as alkyl halides and sulfates [6]. Different from the

non-fluorinated sulfonium salts, diaryl(perfluoroalkyl)sulfonium salts were tediously synthesized from arenethiols via several steps (e.g. perfluoroalkylation of thiols, oxidation, and electrophilic aromatic substitution) [8]. The direct nucleophlic perfluoroalkylation of diarylsulfides by $R_{fn}X$ failed to give the desired products because of the strong electronegativity and huge steric hindrances of perfluoroalkyl groups (R_{fn}) compared to the non-fluorinated analogues.
In contrast to diaryl(perfluoroalkyl)sulfonium salts, diaryl(α,α-dihydroperfluoroalkyl)sulfonium trifluoromethanesulfonates including $[Ph_2SCH_2CF_3][OTf]$ were successfully synthesized by the reactions of diarylsulfides with (α,α-dihydroperfluoroalkyl)phenyliodonium salts (or 2,2,2-trifluoroethyl trifluoromethanesulfonate) [8-10]. Their analogues such as dialkyl- and alkyl(aryl)(polyfluoroalkyl)sulfonium salts, however, were rarely reported. To our knowledge, there have been only few examples derived from dialkyl or alkyl(aryl) sulfides and (α,α-dihydroperfluoroalkyl)phenyliodonium [11]. Therefore, we are motivated in the development of an effective and practical method to the synthesis of these sulfoniums with easily accessed reagents.
<H1>2. Results and Discussions

Diphenyl(2,2,2-trifluoroethyl)sulfonium trifluoromethanesulfonate (**3aa**) was readily prepared by the reaction of diphenyl sulfides (**1a**) and 2,2,2-trifluoroethyl trifluoromethanesulfonate (**2a**) or phenyl(2,2,2-trifluoroethyl)iodonium salt [8,9], which was already applied as a cross-coupling partner in transition-metal-catalyzed fluoroalkylation and phenylation [9,10]. This strategy ought to be suitable for the synthesis of other diaryl-, dialkyl-, and alkyl(aryl)sulfonium trifluoromethanesulfonates [10]. Since (2,2-difluoroethyl)- and (2-fluoroethyl)phenyliodonium salts are not available at present, the use of 2,2-difluoroethyl and 2-fluoroethyl trifluoromethanesulfonates as the alkylation reagents [12] to prepare the corresponding 2,2-difluoroethyl and 2-fluoroethyl sulfonium salts is reasonably adopted. Here we report a solvent-free reaction of diaryl, dialkyl, and aryl(alkyl) sulfides with 2,2,2-trifluoroethyl trifluoromethanesulfonate (**2a**), 2,2-difluoroethyl trifluoromethanesulfonate (**2b**), 2-fluoroethyl trifluoromethanesulfonate (**2c**), and 2,2,3,3,3-pentafluoropropyl trifluoromethanesulfonate (**2d**), which conveniently constructed a variety of fluoroalkyl or alkyl sulfonium salts in up to quantitative yields.
As shown in Table 1, reaction of **2a** with diphenyl sulfide (**1a**, 5 equiv) at 150 ^oC for 48 h under a solvent-free condition gave **3aa** in 61% yield (entry 1) [9,10], and lowering the reaction temperature from 150 ^oC to 120 ^oC caused none of the desired product. A mixture of **2b** and **1a** (3 equiv) or **2b** (3 equiv) and **1a** heated at 120 ^oC for 48 h produced (2,2-difluoroethyl)diphenylsulfonium trifluoromethanesulfonate (**3ab**) in 94% or 84% yield (entries 2 and 3, Table 1). Treatment of **2c** with **1a** (1.5 equiv) at 60 ^oC for 15 h formed diphenyl(2-fluoroethyl)sulfonium trifluoromethanesulfonate (**3ac**) in 84% yield (entry 4, Table 1). 2,2,3,3,3-Pentafluoropropyl trifluoromethanesulfonate (**2d**) reacted with **1a** at 150 ^oC for 72 h to provide diphenyl(2,2,3,3,3-pentafluoropropyl)sulfonium trifluoromethanesulfonate (**3ad**) in 7% yield, which was tentatively attributed to the steric hindrance of perfluoroalkyl

group (entry 5, Table 1). These results implied that the order of fluoroalkylation ability of **2a-d** toward sulfide is **2c** > **2b** > **2a** > **2d** (from strong to weak). Although the electronegativity of the fluoroalkyl groups of **2a** and **2d** is stronger than that of **2b** and **2c**, the steric hindrances of the former counteract the electrophilicity of the carbon centers (adjacent to $CF_2H_{2-n}X$ group (see Table 1)), thus leading to poor reactivity of **2a** and **2d**.

Moreover, the substituents on the phenyl rings of diaryl sulfides had a considerable impact on the reaction. 4-Methoxyphenyl phenyl sulfide (**1b**) reacted with **2a-c** under solvent-free conditions to give the corresponding fluoroalkyl diarylsulfonium salts (**3ba**, **3bb**, and **3bc**) in good to high yields (entries 6-8, Table 1). Reaction of 4-chlorophenyl phenyl sulfide (**1c**) with **2a** didn't provide the desired product (entry 9, Table 1). When **1c** was analogously treated with 2,2-difluoroethyl trifluoromethanesulfonate (**2b**) and 2-fluoroethyl trifluoromethanesulfonate (**2c**), the respective fluoroalkyl(diaryl)sulfonium salts (**3cb** and **3cc**) were formed in 66% and 93% yields (entries 10 and 11, Table 1). Replacing **1c** by the more electron-deficient 4-nitrophenyl phenyl sulfide (**1d**), only the reaction of **1d** with **2c** furnished the desired product (**3dc**) (entry 12, Table 1). Furthermore, reaction of dibenzothiophene (**1e**) with **2b** at 120 ^oC for 48 h provided **3eb** in 15% yield (entry 13, Table 1) and treatment of **1e** with **2c** at 100 ^oC for 15 h afforded **3ec** in 61% yield (entry 14, Table 1). All these results again suggested the stronger fluoroalkylation ability of **2c**.

To shed light on the structure of fluoroalkyl(diaryl)sulfonium salts, the representative crystalline **3aa** and **3ab** were analyzed by single crystal X-ray diffraction (**Figure 1**) [13]. The study revealed that the length of S-CH_2CF_3 bond (1.789(5) Å) in **3aa** is very close to that of S-Ph bonds (1.779(4)–1.789(5) Å), while the length of S-CH_2CF_2H bond (1.805(3) Å) in **3ab** is longer than that of S-Ph bonds (1.772(3)–1.781(3) Å) (Table 2). This feature (especially for **3ab**) is in accordance with the previous observation for non-fluorinated analogue that the S-Ph bond in $[Ph_2SCH_3][OTf]$ is somewhat shorter than the S-Me bond [6f]. In addition, the C-F bonds in the cations of **3aa** (1.310(6)–1.320(7) Å) are much shorter than those in **3ab** (1.338(4)–1.341(3) Å) (Table 2). The C3-S-C9 angle in **3aa** is 105.6(2)°, and that for **3ab** is smaller at 103.71(7)°. The bond distance of C1-H(1A) and C1-H(1B) [0.9700 Å] is identical in both **3aa** and **3ab** and is shorter than that of C2-H2 [0.9800 Å] in **3ab**. All these data hint a considerable ``fluorine effect'', which might illustrate the different stability and phenylation power of **3aa** and **3ab** in Pd-catalyzed Mizoroki-Heck and Suzuki-Miyaura cross-couplings [10].

Next, reactions of dialkyl sulfides with fluoroalkyl trifluoromethanesulfonates under solvent-free conditions provided trialkyl- or dialkyl(fluoroalkyl)sulfonium trifluoromethanesulfonates in up to quantitative yields (entries 1-12, Table 3). The outcomes of the reaction were dramatically dependent upon the structure of sulfides, the nature of fluoroalkyl trifluoromethanesulfonates, the reactant ratio, and/or the reaction temperature. For instance, dibutyl sulfide (**4a**, 3 equiv.) reacted with **2a** or **2b** at 100 ^oC for 24 h to afford tributylsulfonium trifluoromethanesulfonate (**6a**) in 55% or 97% yield, respectively (entries 1 and 2, Table 3). The reaction might involve dibutyl(2,2,2-trifluoroethyl)- or dibutyl(2,2-difluoroethyl)sulfonium intermediate,

which was nucleophilically attacked by a second dibutyl sulfide to yield **6a** due to the strong electron-withdrawing ability of polyfluoroethyl group. If the reaction of **4a** and **2b** was performed at room temperature for 24 h, dibutyl(2,2-difluoroethyl)sulfonium trifluoromethanesulfonate (**5ab**) was formed in 91% yield (entry 3, Table 3). Furthermore, a mixture of **4a** and **2c** (2 equiv) or **4a** (3 equiv) and **2c** heated at 60 °C for 15 h furnished dibutyl(2-fluoroethyl)sulfonium trifluoromethanesulfonate (**5ac**) in almost quantitative yields (entries 4 and 5, Table 3). Treatment of diallyl sulfide (**4b**, 3 or 5 equiv.) with **2a** at 100 °C for 24 h, with **2b** at 60 °C for 24 h, or with **2c** at 60 °C for 15 h provided triallylsulfonium trifluoromethanesulfonate (**6b**) in 43%, 99%, or 92% yield, respectively (entries 6-8, Table 3). If **4b** reacted with **2c** (2 equiv.) at room temperature for 15 h, diallyl(2-fluoroethyl)sulfonium trifluoromethanesulfonate (**5bc**) was obtained in > 99% yield (entry 9, Table 3). Besides, reaction of diethyl sulfide (**4c**, 5 equiv) with **2a** at 100 °C for 24 h constructed triethylsulfonium trifluoromethanesulfonate (**6c**) in 27% yield (entry 10, Table 3). Treatment of **4c** (3 equiv) with **2b** at room temperature, 60 °C, or 100 °C supplied a mixture of **5cb** and **6c**, which was determined by NMR spectroscopy (entry 11, Table 3). Nonetheless, if **4c** (3 equiv) was reacted with **2c** at 60 °C for 15 h, diethyl(2-fluoroethyl)sulfonium trifluoromethanesulfonate (**5cc**) was formed in 99% yield (entry 12, Table 3). Likewise, the solvent-free reaction of aryl(alkyl) sulfides with fluoroalkyl trifluoromethanesulfonates constructed a series of dialkyl(aryl)- or alkyl(aryl)fluoroalkylsulfonium trifluoromethanesulfonates in up to > 99% yields (entries 13-21, Table 3). The use of excess methyl phenyl sulfide (**4d**) to work with **2a** at 100 °C for 24 h or **2b** at 60 °C for 24 h provided (dimethyl)(phenyl)sulfonium trifluoromethanesulfonate (**6d**) in 21% or 98% yield (entries 13 and 14, Table 3), whereas the reaction of **4d** with **2c** (2 equiv.) at 60 °C for 5 h supplied (2-fluoroethyl)(methyl)(phenyl)sulfonium trifluoromethanesulfonate (**5dc**) in 97% yield (entry 15, Table 3). The exact structure of **6d** was determined by single crystal X-ray diffraction (**Figure 1**) [13]. It should be mentioned that the previous methods to the preparation of **6d** required highly toxic and expensive CH_3OTf or AgOTf / CH_3I mixture [1f,6f], which limited their use on large scales. Alternatively, the present reaction provided a safe and convenient access to **6d**. Similar product distributions were also observed for ethyl phenyl sulfide (**4e**) and butyl phenyl sulfide (**4f**) when they were treated with **2a-c** under solvent-free conditions (entries 16-21, Table 3). In addition, the reaction of tetrahydrothiophene (**4g**) with 2 equiv. of **2a** at 100 °C for 4 h afforded 1-(4-((2,2,2-trifluoroethyl)thio)butyl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate (**6ga**) in 98% yield (**Scheme 1**). If the reaction was run at 60 °C with either excess or insufficient **2c**, 1-(2-fluoroethyl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate (**5gc**) was furnished in > 99% or 77% yield, respectively (**Scheme 1**). Furthermore, when the steric hindered diisopropyl sulfide (**4h**) reacted with **2a** or **2b** at 100 °C for 24 h, triisopropylsulfonium trifluoromethanesulfonate (**6h**) was formed in 31% or 87% yield (**Scheme 2**). Nevertheless, if **4h** was treated with **2b** at 60 °C for 8 h or at room temperature for 24 h, (2,2-difluoroethyl)diisopropylsulfonium trifluoromethanesulfonate (**5hb**) was synthesized in 83% or 30% yield, respectively

(**Scheme 2**). These results suggested that the secondary alkyl substituent on **4h** did not obviously impact the reaction.

Since the fluoroalkyl groups activated dialkyl- and alkyl(aryl)(fluoroalkyl)sulfonium salts (**5**), the reaction didn't stop at the first step in some cases and finally afforded trialkyl- and dialkyl(aryl)sulfonium trifluoromethanesulfonates (**6**) in good to quantitative yields. The results indicated that fluoroalkylsulfoniums (**5**) with heavier fluorine content on the alkyl groups (e.g. CF_nH_{3-n} = CF_3, CF_2H) might more easily undergo a second attack by sulfide to form the overreacted products (**6**). In other words, because **2a** is less electrophilic than **2b** and **2c**, the reaction of **2a** with dialkyl and alkylaryl sulfides (**4**) required higher temperatures and provided non-fluorinated alkylsulfonium salts as the final products. For **2b**, the reaction with **4** gave either difluoroalkyl sulfoniums or the overreacted products, which was dependent upon the temperatures. Notably, if **2c** was reacted with **4**, monofluoroethyl sulfonium salts were prepared in most cases.

<H1>3. Conclusion

In conclusion, we have synthesized a number of fluoroalkyl(diaryl)sulfonium salts by S_N2-type reactions of electron-rich diaryl sulfides with fluoroalkyl trifluoromethanesulfonates under solvent-free conditions. Different from diaryl sulfides, dialkyl and alkyl(aryl) sulfides reacted with fluoroalkyl trifluoromethanesulfonates providing trialkyl- or dialkyl(fluoroalkyl)sulfoniums and dialkyl(aryl)- or alkyl(aryl)(fluoroalkyl)sulfoniums in good to quantitative yields. The formation of trialkyl- and dialkyl(aryl)sulfonium trifluoromethanesulfonates might involve dialkyl- and alkyl(aryl)(fluoroalkyl)sulfonium intermediates, respectively, which were attacked by a second sulfide, owing to the strong electron-withdrawing ability of fluoroalkyl groups and leading to the overreacted products. The reaction could stop at the first step in some cases and afforded fluoroalkylated sulfonium salts, which was dramatically dependent upon the structure of sulfides, the nature of fluoroalkyl trifluoromethanesulfonates, the reactant ratio, and/or the reaction temperature. Moreover, fluoroalkyl trifluoromethanesulfonates were easily prepared by the reaction of Tf_2O with fluoroalkyl alcohols, so the accessibility of fluoroalkylation reagents is no longer problematic. Overall, this protocol supplies an efficient and convenient access to a variety of alkyl and fluoroalkyl sulfonium salts.

<H1>4. Experimental Section

All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$, CD_3COCD_3, or CD_3SOCD_3 on a 500 or 400 MHz (for ^1H), 471 or 376 MHz (for ^{19}F), and 126 or 100 MHz (for ^{13}C) spectrometer. All chemical shifts were reported in ppm relative to TMS (^1H NMR, 0 ppm) or $PhCF_3$ (^{19}F NMR, -63.5 ppm) as an internal or external standard. Melting points of the products were measured and uncorrected. Diaryl and aryl(alkyl) sulfides (**1b**, **1c**, **1d**, **1e**, **4e**, and **4f**) were synthesized according to the literature [14]. Fluoroalkyl trifluoromethanesulfonate (**2a**, **2b**, **2c**, and **2d**) were synthesized according to the literatures [12,15]. Other reagents were all purchased from commercial sources and used without further purification.

<H2>4.1. Procedures for the synthesis of 2a, 2b, 2c, and 2d [12,15]

4.1.1. Trifluoromethanesulfonic anhydride (42.3 g, 150.0 mmol) was added dropwise to 2,2,2-trifluoroethanol (15.0 g, 150.0 mmol) in a 250 mL Schlenk flask (equipped with a condenser) at 0 °C. Then the mixture was heated at reflux for 1.5 h, cooled to room temperature, washed with aqueous $NaHCO_3$ solution (30 mL) and brine (3 × 50 mL), dried over anhydrous $MgSO_4$, and distilled to give *2,2,2-trifluoroethyl trifluoromethanesulfonate (**2a**)* as a colorless liquid (18.1 g, 78.0 mmol, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (q, *J* = 7.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.4 (s, 3F), -74.7 (t, *J* = 7.5 Hz, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.0 (q, *J* = 278.0 Hz), 118.4 (q, *J* = 321.4 Hz), 68.6 (q, *J* = 39.8 Hz).

4.1.2. Trifluoromethanesulfonic anhydride (42.3 g, 150.0 mmol) was added dropwise to 2,2-difluoroethanol (12.3 g, 150.0 mmol) in a 250 mL Schlenk flask (equipped with a condenser) at -20 °C. The mixture was then heated at reflux for 1.5 h, cooled to room temperature, washed with aqueous $NaHCO_3$ solution (30 mL) and brine (3 × 50 ml), dried over anhydrous $MgSO_4$, and distilled to give *2,2-difluoroethyl trifluoromethanesulfonate (**2b**)* as a colorless liquid (19.6 g, 91.6 mmol, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (tt, *J* = 53.8 Hz, *J* = 3.4 Hz, 1H), 4.58 (td, *J* = 12.4 Hz, *J* = 2.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.1 (s, 3F), -126.5 (td, *J* = 54.8 Hz, *J* = 12.8 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.5 (q, *J* = 315.8 Hz), 110.7 (t, *J* = 246.8 Hz), 71.0 (t, *J* = 31.3 Hz).

4.1.3. Trifluoromethanesulfonic anhydride (10.3 g, 55.0 mmol) was added dropwise to a solution of 2-fluoroethanol (2.1 g, 33.3 mmol) and NEt_3 (3.7 g, 36.7 mmol) in anhydrous CH_2Cl_2 (40 mL) at -50 °C over a period of 20 min with vigorous stirring. The mixture was warmed to room temperature for 2 h, quenched with H_2O, neutralized by aqueous $NaHCO_3$ solution, washed with brine (3 × 50 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give *2-fluoroethyl trifluoromethanesulfonate (**2c**)* as pale brown liquid (4.6 g, 23.5 mmol, 71%). The product was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.76 (q, *J* = 7.6 Hz, 2H), 4.66 (dm, *J* = 6.8 Hz, 2H). ^{19}F NMR (476 MHz, $CDCl_3$) δ -75.8 (s, 3F), -226.6 (m, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.6 (q, *J* = 321.2 Hz), 80.8 (d, *J* = 176.0 Hz), 74.4 (d, *J* = 20.6 Hz).

4.1.4. Trifluoromethanesulfonic anhydride (42.3 g, 150.0 mmol) was added dropwise to 2,2,3,3,3-pentafluoropropanol (22.5 g, 150.0 mmol) in a 250 mL Schlenk flask (equipped with a condenser) at 0 °C. The mixture was heated at reflux for 1.5 h, cooled to room temperature, washed with aqueous $NaHCO_3$ solution (30 mL) and brine (3 × 50 mL), dried over anhydrous $MgSO_4$, and distilled to give *2,2,3,3,3-pentafluoropropyl trifluoromethanesulfonate (**2d**)* as a colorless liquid (13.8 g, 48.9 mmol, 33%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.77 (t, *J* = 12.2 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.2 (s, 3F), -83.7 (s, 3F), -123.9 (t, *J* = 11.6 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.4 (q, *J* = 320.5 Hz), 67.7 (t, *J* = 29.6 Hz).

<H2>4.2. General procedure for the synthesis of alkyl and fluoroalkyl sulfonium salts

Diaryl, dialkyl, or aryl(alkyl) sulfides and fluoroalkyl trifluoromethanesulfonate were placed in a sealed tube under a N_2 atmosphere with vigorous stirring. The mixture was reacted at a temperature for 5-72 h (see Table 1 and Table 3), cooled to room

temperature, washed with diethyl ether or hexane (till the excess sulfide or sulfonate was completely removed), and dried in vacuum to give the title compounds. In some cases (see below), the product was decolored by activated charcoal in CH_2Cl_2 (refluxing for 0.5 h) to afford a light color oil.

4.2.1. Diphenyl(2,2,2-trifluoroethyl)sulfonium trifluoromethanesulfonate (**3aa**). White solid, 102.0 mg from 2.00 mmol of **1a** and 0.400 mmol of **2a**, 0.244 mmol, 61% yield. ^{1}H NMR (500 MHz, CD_3SOCD_3) δ 8.34 (d, *J* = 7.78 Hz, 4H), 8.17 (t, *J* = 7.5 Hz, 2H), 8.07 (t, *J* = 7.8 Hz, 4H), 5.44 (q, *J* = 8.6 Hz, 2H). ^{19}F NMR (376 MHz, CD_3SOCD_3) δ -61.4 (t, *J* = 8.8 Hz, 3F), -79.3 (s, 3F). ^{13}C NMR (126 MHz, CD_3SOCD_3) δ 135.0 (s), 131.3 (s), 130.7 (s), 124.4 (s), 122.5 (q, *J* = 280.8 Hz), 120.7 (q, *J* = 322.2 Hz), 43.7 (q, *J* = 31.8 Hz).

4.2.2. (2,2-Difluoroethyl)diphenylsulfonium trifluoromethanesulfonate (**3ab**). White solid, 225.6 mg from 1.80 mmol of **1a** and 0.600 mmol of **2b**, 0.564 mmol, 94% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 4H), 7.75 (t, *J* = 7.4 Hz, 2H), 7.69 (t, *J* = 7.6 Hz, 4H), 6.51 (t, *J* = 53.7 Hz, 1H), 4.95 (t, *J* = 15.3 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.5 (s, 3F), -114.2 (dt, *J* = 53.8 Hz, *J* = 15.0 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.0 (s), 131.7 (s), 130.6 (s), 124.4 (s), 120.7 (q, *J* = 320.0 Hz), 111.6 (t, *J* = 244.8 Hz), 47.4 (t, *J* = 23.6 Hz).

4.2.3. Diphenyl(2-fluoroethyl)sulfonium trifluoromethanesulfonate (**3ac**). Light grey solid, 192.5 mg from 0.900 mmol of **1a** and 0.600 mmol of **2c**, 0.504 mmol, 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.1 Hz, 4H), 7.74 (t, *J* = 7.3 Hz, 2H), 7.69 (t, *J* = 7.0 Hz, 4H), 4.86 (d, *J* = 46.7 Hz, 2H), 4.72 (d, *J* = 23.7 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.4 (s, 3F), -218.5 (m, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0 (s), 131.7 (s), 130.9 (s), 123.6 (s), 120.7 (q, *J* = 320.0 Hz), 77.5 (d, *J* = 173.4 Hz), 46.3 (d, *J* = 18.1 Hz).

4.2.4. Diphenyl(2,2,3,3,3-pentafluoropropyl)sulfonium trifluoromethanesulfonate (**3ad**). White solid, 13.1 mg from 2.00 mmol of **1a** and 0.400 mmol of **2d**, 0.028 mmol, 7% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.1 Hz, 4H), 7.77 (t, *J* = 7.4 Hz, 2H), 7.71 (t, *J* = 7.6 Hz, 4H), 5.31 (t, *J* = 15.1 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.6 (s, 3F), -84.0 (s, 3F), -111.4 (t, *J* = 15.1 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5 (s), 131.8 (s), 131.0 (s), 123.7 (s), 120.6 (q, *J* = 319.9 Hz), 44.9 (t, *J* = 21.8 Hz).

4.2.5. (4-Methoxyphenyl)(phenyl)(2,2,2-trifluoroethyl)sulfonium trifluoromethanesulfonate (**3ba**). Brown oil, 113.4 mg from 4.00 mmol of **1b** and 0.800 mmol of **2a**, 0.253 mmol, 32% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.11 (m, 4H), 7.77-7.67 (m, 3H), 7.17 (d, *J* = 9.3 Hz, 2H), 5.25 (q, *J* = 8.3 Hz, 2H), 3.88 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.8 (t, *J* = 8.6 Hz, 3F), -78.5 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4 (s), 135.1 (s), 133.5 (s), 131.7 (s), 130.5 (s), 124.5 (s), 121.8 (q, *J* = 278.4 Hz), 120.7 (q, *J* = 318.5 Hz), 117.4 (s), 111.9 (s), 56.1 (s), 46.6 (q, *J* = 34.2 Hz). IR (KBr): 3099, 2992, 2936, 2848, 1591, 1575, 1499, 1448, 1419, 1332, 1312, 1268, 1160, 1095, 1081, 1029, 999, 834, 750, 684, 639, 518 cm^{-1}. ESI-MS (m/z): 298.9 ([M]$^+$). Anal. Calcd for $C_{16}H_{14}F_6O_4S_2$: C, 42.86; H, 3.15; Found: C, 43.18; H, 3.44.

4.2.6. (2,2-Difluoroethyl)(4-methoxyphenyl)(phenyl)sulfonium trifluoromethanesulfonate (**3bb**). Brown oil, 306.3 mg from 2.10 mmol of **1b** and 0.700 mmol of **2b**, > 99% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 4H), 7.64

(t, *J* = 7.3 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.42 (t, *J* = 53.6 Hz, 1H), 4.76 (t, *J* = 14.9 Hz, 2H), 3.79 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ, -78.4 (s, 3F), -114.6 (dt, *J* = 53.5 Hz, *J* = 16.3 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.9 (s), 134.7 (s), 133.0 (s), 131.5 (s), 130.0 (s), 125.4 (s), 120.7 (q, *J* = 318.5 Hz), 117.2 (s), 113.0 (s), 111.7 (t, *J* = 245.9 Hz), 56.0 (s), 47.7 (t, *J* = 23.8 Hz). IR (KBr): 3516, 3099, 3065, 2997, 2945, 2847, 1591, 1499, 1463, 1448, 1418, 1371, 1259, 1163, 1111, 1081, 1030, 999, 944, 835, 800, 750, 684, 639, 574, 518 cm^{-1}. ESI-MS (m/z): 281.0 ([M]$^+$). Anal. Calcd for $C_{16}H_{15}F_5O_4S_2$•0.5H_2O: C, 43.73; H, 3.67; Found: C, 43.77; H, 3.99.

4.2.7. (2-Fluoroethyl)(4-methoxyphenyl)(phenyl)sulfonium trifluoromethanesulfonate (**3bc**). Brown oil, 1211.6 mg from 3.00 mmol of **1b** and 6.00 mmol of **2c**, 2.94 mmol, 98% yield. ^{1}H NMR (500 MHz, CD_3COCD_3) δ 8.04 (d, *J* = 7.8 Hz, 4H), 7.75-7.70 (m, 3H), 7.20 (d, *J* = 8.4 Hz, 2H), 4.90 (dd, *J* = 32.4 Hz, *J* = 14.2 Hz, 2H), 4.63 (d, *J* = 23.5 Hz, 2H), 3.89 (s, 3H). ^{19}F NMR (471 MHz, CD_3COCD_3) δ -78.5 (s, 3F), -218.9 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.8 (s), 134.5 (s), 133.1 (s), 131.4 (s), 130.1 (s), 124.9 (s), 120.5 (q, *J* = 321.1 Hz), 117.1 (s), 112.4 (s), 77.4 (d, *J* = 173.2 Hz), 55.9 (s), 46.1 (d, *J* = 18.8 Hz). IR (KBr): 3492, 3098, 2995, 2947, 2847, 1591, 1575, 1499, 1465, 1447, 1418, 1267, 1225, 1163, 1063, 1030, 835, 754, 685, 639, 574, 518 cm^{-1}. ESI-MS (m/z): 263.0 ([M]$^+$). Anal. Calcd for $C_{16}H_{16}F_4O_4S_2$•2H_2O: C, 42.85, H, 4.50; Found: C, 42.97; H, 4.38.

4.2.8. (4-Chlorophenyl)(2,2-difluoroethyl)(phenyl)sulfonium trifluoromethanesulfonate (**3cb**). Brown oil, 288.3 mg from 3.00 mmol of **1c** and 1.00 mmol of **2b**, 0.664 mmol, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 4H), 7.75-7.60 (m, 5H), 6.48 (tt, *J* = 53.6 Hz, *J* = 2.8 Hz, 1H), 4.93 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.5 (s, 3F), -114.2 (dt, *J* = 54.0 Hz, *J* = 15.0 Hz, 2F). ^{13}C NMR (126 MHz, CD_3COCD_3) δ 141.0 (s), 135.1 (s), 132.7 (s), 131.6 (s), 131.6 (s), 130.9 (s), 124.8 (s), 123.9 (s), 121.2 (q, *J* = 320.2 Hz), 112.5 (t, *J* = 242.6 Hz), 46.5 (t, *J* = 23.9 Hz). IR (KBr): 3505, 3094, 3002, 2944, 1634, 1572, 1480, 1449, 1399, 1371, 1259, 1168, 1096, 1030, 1010, 944, 827, 745, 683, 640, 575, 517 cm^{-1}. ESI-MS (m/z): 285.0 ([M]$^+$). Anal. Calcd for $C_{15}H_{12}ClF_5O_3S_2$•3H_2O: C, 36.85; H, 3.71; Found: C, 36.74; H, 3.60.

4.2.9. (4-Chlorophenyl)(2-fluoroethyl)(phenyl)sulfonium trifluoromethanesulfonate (**3cc**). The product derived from 2.00 mmol of **1c** and 4.00 mmol of **2c** was decolored by activated charcoal in CH_2Cl_2 refluxing for 0.5 h to give 770.4 mg of **3cc** as a light yellow oil, 1.85 mmol, 93% yield. ^{1}H NMR (500 MHz, CD_3COCD_3) δ 8.24 (t, *J* = 9.5 Hz, 4H), 7.86 (d, *J* = 7.4 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 3H), 5.07 (d, *J* = 46.9 Hz, 2H), 4.93 (d, *J* = 23.5 Hz, 2H). ^{19}F NMR (471 MHz, CD_3COCD_3) δ -78.9 (s, 3F), -219.4 (m, 1F). ^{13}C NMR (126 MHz, CD_3COCD_3) δ 140.8 (s), 134.9 (s), 132.7 (s), 131.5 (s), 131.5 (s), 130.9 (s), 124.7 (s), 123.8 (s), 121.1 (q, *J* = 321.4 Hz), 78.1 (d, *J* = 170.5 Hz), 45.8 (d, *J* = 18.8 Hz). IR (KBr): 3491, 3093, 2989, 2934, 1573, 1480, 1448, 1398, 1256, 1226, 1165, 1096, 1063, 1029, 1010, 826, 745, 684, 639, 516 cm^{-1}. HRMS-ESI Calcd for [$C_{14}H_{13}ClFS^+$] (M^+): 267.0405; Found: 267.0406.

4.2.10. (2-Fluoroethyl)(4-nitrophenyl)(phenyl)sulfonium trifluoromethanesulfonate (**3dc**). Brown oil, 730.0 mg from 3.00 mmol of **1d** and 6.00 mmol of **2c**, 1.71 mmol, 57% yield. ^{1}H NMR (500 MHz, CD_3COCD_3) δ 8.54 (q, 4H), 8.28 (d, *J* = 7.6 Hz, 2H), 7.92 (t, *J* = 6.8 Hz, 1H), 7.83 (t, *J* = 6.8 Hz, 2H), 5.21-5.09 (m, 2H), 5.04 (m, 2H). ^{19}F

NMR (471 MHz, CD_3COCD_3) δ -79.0 (s, 3F), -219.1 (m, 1F). ^{13}C NMR (126 MHz, CD_3COCD_3) δ 153.7 (s), 151.2 (s), 135.3 (s), 132.4 (s), 131.7 (s), 131.6 (s), 125.8 (s), 123.7 (s), 121.2 (q, *J* = 320.5 Hz), 78.2 (d, *J* = 172.2 Hz), 46.1 (d, *J* = 18.6 Hz). IR (KBr): 3491, 3106, 2925, 1533, 1479, 1448, 1348, 1256, 1225, 1162, 1062, 1029, 854, 755, 741, 727, 638 cm^{-1}. HRMS-ESI Calcd for [$C_{14}H_{13}FNO_2S^+$] ([M]$^+$): 278.0646; Found: 278.0646.

4.2.11. 5-(2,2-Difluoroethyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (**3eb**). Gray solid, 300.7 mg from 10.0 mmol of **1e** and 5.00 mmol of **2b**, 0.756 mmol, 15% yield. M.p. 120-122 °C. ^1H NMR (500 MHz, CD_3COCD_3) δ 8.55 (d, *J* = 7.3 Hz, 2H), 8.49 (d, *J* = 6.3 Hz, 2H), 8.03 (s, 2H), 7.87 (s, 2H), 6.56 (t, *J* = 53.2 Hz, 1H), 4.77 (t, *J* = 14.9 Hz, 2H). ^{19}F NMR (471 MHz, CD_3COCD_3) δ -78.9 (s, 3F), -114.6 (dt, *J* = 54.0 Hz, *J* = 16.4 Hz, 2F). ^{13}C NMR (126 MHz, CD_3COCD_3) δ 140.1 (s), 134.5 (s), 131.3 (s), 128.9 (s), 128.3 (s), 124.5 (s), 120.7 (q, *J* = 321.1 Hz), 112.5 (t, *J* = 243.8 Hz), 50.2 (t, *J* = 25.4 Hz). IR (KBr): 3049, 2924, 2853, 1723, 1445, 1427, 1251, 1229, 1169, 1068, 1031, 742, 734, 709, 638, 576, 517 cm^{-1}. HRMS-ESI Calcd for [$C_{14}H_{11}F_2S^+$] (M^+): 249.0544; Found: 249.0544.

4.2.12. 5-(2-Fluoroethyl)-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate (**3ec**). White solid, 578.1 mg from 2.50 mmol of **1e** and 5.00 mmol of **2c**, 1.52 mmol, 61% yield. ^1H NMR (500 MHz, CD_3COCD_3) δ 8.53 (d, *J* = 8.0 Hz, 2H), 8.45 (d, *J* = 7.5 Hz, 2H), 8.00 (t, *J* = 7.4 Hz, 2H), 7.85 (t, *J* = 7.6 Hz, 2H), 4.86 (d, *J* = 45.8 Hz, 2H), 4.62 (d, *J* = 25.2 Hz, 2H). ^{19}F NMR (471 MHz, CD_3COCD_3) δ -78.9 (s, 3F), -217.9 (m, 1F). ^{13}C NMR (126 MHz, CD_3COCD_3) δ 140.2 (s), 134.1 (s), 131.1 (s), 128.8 (s), 128.6 (s), 124.3 (s), 122.3 (q, *J* = 321.0 Hz), 78.1 (d, *J* = 168.9 Hz), 50.7 (d, *J* = 19.4 Hz). IR (KBr): 3491, 3051, 2925, 2839, 1719, 1450, 1427, 1249, 1228, 1172, 1030, 743, 704, 639, 576, 517 cm^{-1}. HRMS-ESI Calcd for [$C_{14}H_{12}FS^+$] (M^+): 231.0638; Found: 231.0639.

4.2.13. Tributylsulfonium trifluoromethanesulfonate (**6a**). White solid, 77.5 mg from 2.00 mmol of **4a** and 0.400 mmol of **2a**, 0.220 mmol, 55% yield; 204.4 mg from 1.80 mmol of **4a** and 0.600 mmol of **2b**, 0.581 mmol, 97% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 3.38 (t, *J* = 7.8 Hz, 6H), 1.76 (m, 6H), 1.51 (m, 6H), 0.98 (t, *J* = 7.3 Hz, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 120.7 (q, *J* = 321.1Hz), 39.9 (s), 26.6 (s), 21.7 (s), 13.3 (s).

4.2.14. Dibutyl(2,2-difluoroethyl)sulfonium trifluoromethanesulfonate (**5ab**). Colorless oil, 197.0 mg from 1.80 mmol of **4a** and 0.600 mmol of **2b**, 0.547 mmol, 91% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 6.41 (tt, *J* = 54.1 Hz, *J* = 2.8 Hz, 1H), 4.02 (td, *J* = 16.7 Hz, *J* = 2.8 Hz, 2H), 3.51 (t, *J* = 8.0 Hz, 4H), 1.80 (m, 4H), 1.50 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.7 (s, 3F), -114.5 (dt, *J* = 54.6 Hz, *J* = 16.8 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 120.7 (q, *J* = 320.9 Hz), 111.9 (t, *J* = 242.8 Hz), 42.6 (t, *J* = 23.5 Hz), 45.1 (s), 26.3 (s), 21.4 (s), 13.1 (s). IR (KBr): 3501, 2968, 2940, 2880, 1645, 1468, 1418, 1375, 1259, 1227, 1166, 1070, 1031, 757, 639, 574, 518 cm^{-1}. ESI-MS (m/z): 211.1 ([M]$^+$). Anal. Calcd for $C_{11}H_{21}F_5O_3S_2$•0.5H_2O: C, 35.77; H, 6.00; Found: C, 35.87; H, 5.80.

4.2.15. Dibutyl(2-fluoroethyl)sulfonium trifluoromethanesulfonate (**5ac**). Brown oil, 201.6 mg from 1.80 mmol of **4a** and 0.600 mmol of **2c**, 0.589 mmol, 98% yield. ^1H

NMR (400 MHz, CD_3SOCD_3) δ 4.94 (dt, *J* = 46.8 Hz, *J* = 4.7 Hz, 2H), 3.82 (dt, *J* = 27.0 Hz, *J* = 5.0 Hz, 2H), 3.41 (t, *J* = 7.8 Hz, 4H), 1.72 (m, 4H), 1.42 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 6H). ^{19}F NMR (471 MHz, CD_3SOCD_3) δ -77.8 (s, 3F), -216.6 (m, 1F). ^{13}C NMR (126 MHz, CD_3COCD_3) δ 120.7 (q, *J* = 320.9 Hz), 78.7 (d, *J* = 169.6 Hz), 40.3 (d, *J* = 16.9 Hz), 39.9 (s), 26.0 (s), 21.4 (s), 12.7 (s). IR (KBr): 3529, 2965, 2934, 2877, 1723, 1468, 1260, 1225, 1160, 1061, 1030, 756, 638 cm^{-1}. ESI-MS (m/z): 193.1 ($[M]^+$). Anal. Calcd for $C_{11}H_{22}F_4O_3S_2 \bullet H_2O$: C, 36.66; H, 6.71; Found: C, 36.21; H, 6.41.

4.2.16. Triallylsulfonium trifluoromethanesulfonate (**6b**). Light yellow oil, 52.3 mg from 2.00 mmol of **4b** and 0.400 mmol of **2a**, 0.172 mmol, 43% yield; 902.8 mg from 9.00 mmol of **4b** and 3.00 mmol of **2b**, 2.97 mmol, 99% yield; 278.9 mg from 3.00 mmol of **4b** and 1.00 mmol of **2c**, 0.917 mmol, 92% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 5.92 – 5.81 (m, 3H), 5.68 (dd, *J* = 28.9 Hz, *J* = 10.0 Hz, 6H), 4.08 (d, *J* = 7.2 Hz, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 128.1 (s), 123.7 (s), 120.6 (q, *J* = 320.0 Hz), 41.5 (s). IR (KBr): 3504, 2984, 2934, 1638, 1428, 1406, 1260, 1227, 1167, 1031, 992, 951, 759, 740, 640, 575, 518 cm^{-1}. ESI-MS (m/z): 155.1 ($[M]^+$). Anal. Calcd for $C_{10}H_{15}F_3O_3S_2 \bullet 0.5H_2O$: C, 38.33; H, 5.15; Found: C, 38.47; H, 5.07.

4.2.17. Diallyl(2-fluoroethyl)sulfonium trifluoromethanesulfonate (**5bc**). Brown oil, 638.2 mg from 2.00 mmol of **4b** and 4.00 mmol of **2c**, > 99% yield. ^1H NMR (500 MHz, CD_3COCD_3) δ 6.11-6.05 (m, 2H), 5.78 (d, *J* = 16.9 Hz, 2H), 5.67 (d, *J* = 10.0 Hz, 2H), 5.05 (d, *J* = 47.1 Hz, 2H), 4.34 (d, *J* = 6.8 Hz, 4H), 3.88 (d, *J* = 25.8 Hz, 2H). ^{19}F NMR (471 MHz, CD_3COCD_3) δ -79.0 (s, 3F), -218.2 (m, 1F). ^{13}C NMR (126 MHz, CD_3COCD_3) δ 127.4 (s), 124.4 (s), 120.0 (q, *J* = 287.2 Hz), 78.6 (d, *J* = 169.3 Hz), 42.2 (s), 39.1 (d, *J* = 20.0 Hz). IR (KBr): 3508, 2988, 2939, 1639, 1470, 1429, 1406, 1260, 1226, 1166, 1061, 1031, 994, 956, 759, 740, 640, 575, 518 cm^{-1}. ESI-MS (m/z): 161.1 ($[M]^+$). Anal. Calcd for $C_9H_{14}F_4O_3S_2 \bullet 1.5H_2O$: C, 32.04; H, 5.08; Found: C, 32.07; H, 4.75.

4.2.18. Triethylsulfonium trifluoromethanesulfonate (**6c**). Light yellow oil, 28.9 mg from 2.00 mmol of **4c** and 0.400 mmol of **2a**, 0.108 mmol, 27% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 3.42 (q, *J* = 7.5 Hz, 6H), 1.51 (t, *J* = 7.5 Hz, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.5 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 120.6 (q, *J* = 320.3 Hz), 33.3 (s), 9.2 (s). IR (KBr): 3501, 2986, 2921, 2850, 1633, 1457, 1425, 1392, 1259, 1227, 1167, 1084, 1031, 978, 760, 640, 576, 518 cm^{-1}. ESI-MS (m/z): 387.1 ($\{[Et_3S]_2[OTf]\}^+$). Anal. Calcd for $C_7H_{15}F_3O_3S_2 \bullet 0.5H_2O$: C, 30.32; H, 5.82; Found: C, 30.31; H, 5.88.

4.2.19. Diethyl(2-fluoroethyl)sulfonium trifluoromethanesulfonate (**5cc**). Dark brown oil, 169.6 mg from 1.80 mmol of **4c** and 0.600 mmol of **2c**, 0.593 mmol, 99% yield. ^1H NMR (400 MHz, CD_3SOCD_3) δ 4.93 (dt, *J* = 46.5 Hz, *J* = 5.0 Hz, 2H), 3.77 (dt, *J* = 27.1 Hz, *J* = 5.0 Hz, 2H), 3.41 (q, *J* = 7.4 Hz, 4H), 1.36 (t, *J* = 7.4 Hz, 6H). ^{19}F NMR (471 MHz, CD_3SOCD_3) δ -77.8 (s, 3F), -216.6 (m, 1F). ^{13}C NMR (126 MHz, CD_3SOCD_3) δ 121.2 (q, *J* = 322.5 Hz), 79.0 (d, *J* = 167.2 Hz), 38.9 (d, *J* = 19.7 Hz), 33.8 (s), 9.0 (s). IR (KBr): 3502, 2985, 2922, 2850, 1645, 1457, 1425, 1393, 1257, 1226, 1161, 1084, 1031, 976, 758, 639, 574, 518 cm^{-1}. ESI-MS (m/z): 137.1 ($[M]^+$). Anal. Calcd for $C_7H_{14}F_4O_3S_2 \bullet H_2O$: C, 27.63; H, 5.30; Found: C, 27.78; H, 5.30.

4.2.20. Dimethyl(phenyl)sulfonium trifluoromethanesulfonate (**6d**)**.** White solid, 31.1 mg from 2.00 mmol of **4d** and 0.400 mmol of **2a**, 0.108 mmol, 27% yield; 169.3 mg from 1.80 mmol of **4d** and 0.600 mmol of **2b**, 0.588 mmol, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.77 (t, *J* = 7.4 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 2H), 3.40 (s, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.4 (s, 3F). ^{13}C NMR (126 MHz, CD_3SOCD_3) δ 133.6 (s), 130.3(s), 129.7 (s), 126.6 (s), 120.6 (q, *J* = 320.8 Hz), 28.1 (s).
4.2.21. (2-Fluoroethyl)(methyl)(phenyl)sulfonium trifluoromethanesulfonate (**5dc**). Brown oil, 310.0 mg from 1.00 mmol of **4d** and 2.00 mmol of **2c**, 1.00 mmol, 97% yield. ^{1}H NMR (500 MHz, CD_3COCD_3) δ 7.69 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 6.2 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 2H), 4.53 (dm, *J* = 46.1 Hz, 1H), 4.33 (dm, *J* = 46.7 Hz, 1H), 3.92-3.73 (m, 2H), 3.09 (s, 3H). ^{19}F NMR (471 MHz, CD_3COCD_3) δ -78.9 (s, 3F), -219.8 (m, 1F). ^{13}C NMR (126 MHz, CD_3COCD_3) δ 134.8 (s), 131.1 (s), 130.9 (s), 123.7 (s), 121.2 (q, *J* = 320.5 Hz), 77.7 (d, *J* = 169.4 Hz), 46.8 (d, *J* = 19.0 Hz), 26.5 (s). IR (KBr): 3051, 2925, 2852, 1715, 1449, 1256, 1225, 1159, 1068, 1029, 751, 685, 637, 516 cm^{-1}. ESI-MS (m/z): 171.0 ([M]$^+$). Anal. Calcd for $C_{10}H_{12}F_4O_3S_2$•$2H_2O$: C 33.71, H 4.53; Found: C, 33.69; H, 4.61.
4.2.22. Diethyl(phenyl)sulfonium trifluoromethanesulfonate (**6e**). Light yellow oil, 8.9 mg from 2.00 mmol of **4e** and 0.400 mmol of **2a**, 0.028 mmol, 7% yield; 203.7 mg from 1.80 mmol of **4e** and 0.600 mmol of **2b**, > 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 8.5 Hz, 2H), 3.88-3.70 (dm, *J* = 34.5 Hz, 4H), 1.29 (t, *J* = 7.4 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.4 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1 (s), 131.6 (s), 131.5 (s), 120.7 (q, *J* = 320.7 Hz), 120.1 (s), 38.9 (s), 9.4 (s). IR (KBr): 3511, 3064, 2965, 2937, 2877, 1629, 1582, 1467, 1448, 1425, 1386, 1252, 1226, 1163, 1031, 1000, 927, 756, 688, 639, 574, 518 cm^{-1}. ESI-MS (m/z): 167.1 ([M]$^+$). Anal. Calcd for $C_{11}H_{15}F_3O_3S_2$•$1.5H_2O$: C, 38.48; H, 5.28; Found: C, 38.48; H, 5.17.
4.2.23. Ethyl(2-fluoroethyl)(phenyl)sulfonium trifluoromethanesulfonate (**5ec**). The product derived from 1.00 mmol of **4e** and 2.00 mmol of **2c** was decolored by activated charcoal in CH_2Cl_2 refluxing for 0.5 h to give 325.0 mg of **5ec** as a light yellow oil, 0.973 mmol, 97% yield. ^{1}H NMR (500 MHz, CD_3COCD_3) δ 8.21 (d, *J* = 6.2 Hz, 2H), 7.92 (t, *J* = 8.2 Hz, 1H), 7.82 (t, *J* = 7.2 Hz, 2H), 5.08 (dm, *J* = 46.6 Hz, 1H), 4.85 (dm, *J* = 46.6 Hz, 1H), 4.40 (m, 2H), 4.06 (m, 2H),1.41 (t, *J* = 6.3 Hz, 3H). ^{19}F NMR (471 MHz, CD_3COCD_3) δ -78.9 (s, 3F), -219.3 (m, 1F). ^{13}C NMR (126 MHz, CD_3COCD_3) δ 135.1 (s), 131.8 (s), 131.3 (s), 121.3 (q, *J* = 321.4 Hz), 121.2 (s), 78.3 (d, *J* = 169.8 Hz), 44.7 (d, *J* = 19.2 Hz), 39.5 (s), 8.8 (s). IR (KBr): 2921, 2849, 1712, 1449, 1254, 1225, 1163, 1029, 751, 685, 638 cm^{-1}. HRMS-ESI Calcd for [$C_{10}H_{14}FS^+$] (M^+): 185.0795; Found: 185.0795.
4.2.24. Dibutyl(phenyl)sulfonium trifluoromethanesulfonate **(6f)**. Light yellow oil, 17.5 mg from 2.00 mmol of **4f** and 0.400 mmol of **2a**, 0.047 mmol, 12% yield; 226.1 mg from 1.80 mmol of **4f** and 0.600 mmol of **2b**, > 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.5 Hz, 2H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 2H), 3.78 (m, 4H), 1.66-1.36 (m, 8H), 0.85 (t, *J* = 7.2 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.4 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9 (s), 131.4 (s), 131.4 (s), 120.7(s), 120.6 (q, *J* = 320.5 Hz), 43.7 (s), 26.3 (s), 21.0 (s), 13.1 (s). IR (KBr): 3502, 2983, 2921, 2849,

1645, 1449, 1386, 1259, 1226, 1160, 1084, 1030, 753, 688, 638, 574, 518 cm^{-1}. ESI-MS (m/z): 223.1 ($[M]^+$). Anal. Calcd for $C_{15}H_{23}F_3O_3S_2 \bullet 0.5H_2O$: C, 47.23; H, 6.34; Found: C, 46.75; H, 6.16.

4.2.25. Butyl(2-fluoroethyl)(phenyl)sulfonium trifluoromethanesulfonate (**5fc**). Dark brown oil, 356.7 mg from 1.00 mmol of **4f** and 2.00 mmol of **2c**, 0.985 mmol, 99% yield. ^{1}H NMR (500 MHz, CD_3COCD_3) δ 8.23 (d, *J* = 7.5 Hz, 2H), 7.91 (t, *J* = 6.9 Hz, 1H), 7.81 (t, *J* = 7.4 Hz,2H), 5.06 (dm, *J* = 45.5 Hz, 1H), 4.82 (dm, *J* = 47.4 Hz, 1H), 4.39 (m, 2H), 4.04 (t, *J* = 7.4 Hz, 2H), 1.70 (tm, *J* = 27.3 Hz, 2H), 1.50 (m, 2H), 0.89 (t, *J* = 6.7 Hz, 3H). ^{19}F NMR (471 MHz, CD_3COCD_3) δ -78.9 (s, 3F), -219.4 (m, 1F). ^{13}C NMR (126 MHz, CD_3COCD_3) δ 135.1 (s), 131.8 (s), 131.3 (s), 121.4 (s), 121.2 (q, *J* = 321.9 Hz), 78.3 (d, *J* = 169.7 Hz), 45.2 (d, *J* = 19.0 Hz), 44.0 (s), 26.2 (s), 21.0 (s), 12.7 (s). IR (KBr): 3492, 2967, 2926, 2875, 1645, 1468, 1449, 1389, 1257, 1225, 1162, 1062, 1030, 754, 686, 638, 518 cm^{-1}. ESI-MS (m/z): 213.0 ($[M]^+$). Anal. Calcd for $C_{13}H_{18}F_4O_3S_2 \bullet 2.5H_2O$: C, 38.32; H, 5.69; Found: C, 37.94; H, 5.18.

4.2.26. 1-(4-((2,2,2-Trifluoroethyl)thio)butyl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate (**6ga**). Colorless oil, 160.0 mg from 2.00 mmol of **4g** and 0.400 mmol of **2b**, 0.392 mmol, 98% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.70-3.63 (m, 2H), 3.50-3.44 (m, 2H), 3.33 (t, *J* = 7.8 Hz, 2H), 3.11 (q, *J* = 9.9 Hz, 2H), 2.75 (t, *J* = 7.0 Hz, 2H), 2.48-2.32 (dm, *J* = 48.7 Hz, 4H), 1.95-1.76 (dm, *J* = 52.8 Hz, 4H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -66.4 (t, *J* = 9.8 Hz, 3F), -78.4 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 124.4 (q, *J* = 275.6 Hz), 122.0 (q, *J* = 320.4 Hz), 43.5 (s), 41.8 (s), 34.2 (q, *J* = 33.2 Hz), 32.1 (s), 28.6 (s), 27.2 (s), 24.0 (s). IR (KBr): 3052, 2942, 2860, 1645, 1417, 1259, 1225, 1159, 1116, 1030, 757, 638, 574, 518 cm^{-1}. ESI-MS (m/z): 259.0 ($[M]^+$). Anal. Calcd for $C_{11}H_{18}F_6O_3S_3 \bullet H_2O$: C, 30.98; H, 4.73; Found: C, 30.97; H, 4.57.

4.2.27. 1-(2-Fluoroethyl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate (**5gc**). Dark brown oil, 169.5 mg from 0.500 mmol of **4g** and 1.00 mmol of **2c**, > 99% yield. ^{1}H NMR (400 MHz, CD_3COCD_3) δ 4.95 (t, *J* = 5.2 Hz, 1H), 4.84 (t, *J* = 4.8 Hz, 1H), 3.68 (t, *J* = 5.2 Hz, 1H), 3.61 (t, *J* = 5.0 Hz,1H), 3.58-3.43 (dm, *J* = 21.8 Hz, 4H), 2.28-2.11 (m, 4H). ^{19}F NMR (471 MHz, CD_3COCD_3) δ -77.8 (s, 3F), -218.2 (m, 1F). ^{13}C NMR (126 MHz, CD_3COCD_3) δ 121.4 (q, *J* = 325.6Hz), 79.2 (d, *J* = 167.2 Hz), 44.2 (s), 42.9 (d, *J* = 19.0 Hz), 28.5 (s). IR (KBr): 3048, 2950, 1755, 1429, 1402, 1256, 1226, 1163, 1029, 952, 638, 516 cm^{-1}. ESI-MS (m/z): 135.0 ($[M]^+$). Anal. Calcd for $C_7H_{12}F_4O_3S_2 \bullet 3H_2O$: C, 24.85; H, 5.36; Found: C, 25.16; H, 4.95.

4.2.28. Triisopropylsulfonium trifluoromethanesulfonate (**6h**). Light brown oil, 95.7 mg from 5.00 mmol of **4h** and 1.00 mmol of **2a**, 0.31 mmol, 31% yield; 269.0 mg from 3.00 mmol of **4h** and 1.00 mmol of **2b**, 0.87 mmol, 87% yield. ^{1}H NMR (500 MHz, CD_3COCD_3) δ 4.16 (m, 3H), 1.68 (d, *J* = 5.7 Hz, 18H). ^{19}F NMR (471 MHz, CD_3COCD_3) δ -79.0 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 120.7 (q, *J* = 319.4 Hz), 43.3 (s), 20.0 (s). IR (KBr): 2987, 2947, 2876, 1647, 1466, 1397, 1383, 1283, 1249, 1168, 1030, 941, 876, 761, 640, 575 cm^{-1}. HRMS-ESI Calcd for $[C_9H_{21}S^+]$ (M^+): 161.1358; Found: 161.1351.

4.2.29. (2,2-Difluoroethyl)diisopropylsulfonium trifluoromethanesulfonate (**5hb**). White solid, 275.0 mg from 3.00 mmol of **4h** and 1.00 mmol of **2b** (at 60 °C for 8 h), 0.83 mmol, 83% yield; 98.9 mg from 3.00 mmol of **4h** and 1.00 mmol of **2b** (at r.t. for

24 h), 0.30 mmol, 30% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.44 (t, *J* = 54.2 Hz, 1H), 4.05 (m, 2H), 3.99 (t, *J* = 17.9 Hz, 2H), 1.59 (s, 12H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.6 (s, 3F), -114.3 (dt, *J* = 54.2, 17.7 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 120.6 (q, *J* = 319.9 Hz), 111.1 (t, *J* = 242.9 Hz), 45.9 (s), 37.2 (t, *J* = 21.8 Hz), 18.8 (s), 17.6 (s). IR (KBr): 2997, 2950, 1635, 1466, 1400, 1382, 1259, 1160, 1030, 943, 874, 757, 639, 575 cm^{-1}. HRMS-ESI Calcd for [$C_8H_{17}F_2S^+$] (M^+): 183.1014; Found: 183.1005.

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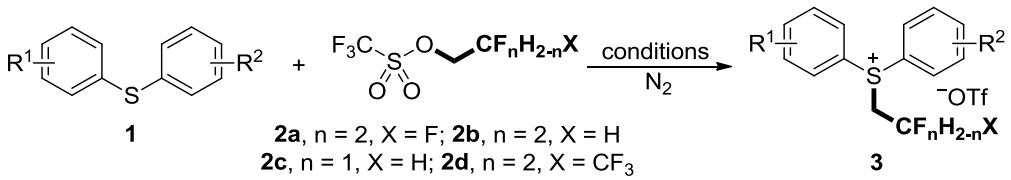
<Figure>**Figure 1** ORTEP diagrams of **3aa** (left), **3ab** (middle), and **6d** (right). Ellipsoids are shown at the 50% probability level.

<Figure>**Scheme 1** The S_N2-type reactions between **4g** and **2a** or **2c**

<Figure>**Scheme 2** The solvent-free reactions of steric hindered **4h** with **2a** or **2b**

<Table>Table 1 The solvent-free reactions between diaryl sulfides and **2a-d**



Entry	R^1	R^2	$CF_nH_{2-n}X$	Molar ratio	Conditions	Yield (**3**, %)[a]
1	H	H	CF_3	**1a** / **2a** (5 : 1)	150 °C, 48 h	**3aa**, 61
2	H	H	CF_2H	**1a** / **2b** (3 : 1)	120 °C, 48 h	**3ab**, 94
3	H	H	CF_2H	**1a** / **2b** (1 : 3)	120 °C, 48 h	**3ab**, 84
4	H	H	CH_2F	**1a** / **2c** (1.5 : 1)	60 °C, 15 h	**3ac**, 84
5	H	H	CF_2CF_3	**1a** / **2d** (5 : 1)	150 °C, 72 h	**3ad**, 7
6	H	OCH_3	CF_3	**1b** / **2a** (5 : 1)	150 °C, 48 h	**3ba**, 32
7	H	OCH_3	CF_2H	**1b** / **2b** (3 : 1)	120 °C, 48 h	**3bb**, > 99
8	H	OCH_3	CH_2F	**1b** / **2c** (1 : 2)	60 °C, 15 h	**3bc**, 98
9	H	Cl	CF_3	**1c** / **2a** (5 : 1)	150 °C, 48 h	complicated
10	H	Cl	CF_2H	**1c** / **2b** (3 : 1)	120 °C, 48 h	**3cb**, 66
11	H	Cl	CH_2F	**1c** / **2c** (1 : 2)	80 °C, 15 h	**3cc**, 93[b]
12	H	NO_2	CH_2F	**1d** / **2c** (1 : 2)	80 °C, 15 h	**3dc**, 57
13[c]	H	H	CF_2H	**1e** / **2b** (1 : 2)	120 °C, 48 h	**3eb**, 15
14[c]	H	H	CH_2F	**1e** / **2c** (1 : 2)	100 °C, 15 h	**3ec**, 61

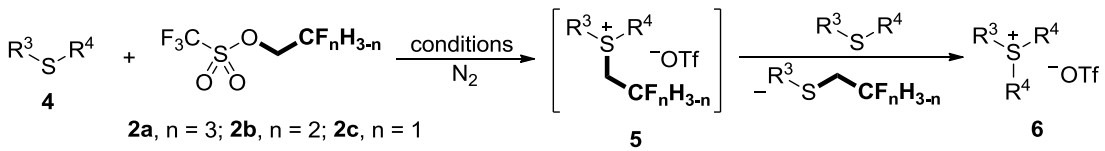
[a] Isolated yield. [b] The product was decolored by activated charcoal in CH_2Cl_2 refluxing for 0.5 h. [c] Dibenzothiophene (**1e**) was used instead of diaryl sulfide.

<Table>Table 2. Selected bond lengths [Å] and angles [deg] for $[Ph_2SCH_2CF_3][OTf]$ (**3aa**), $[Ph_2SCH_2CF_2H][OTf]$ (**3ab**), and $[PhS(CH_3)_2][OTf]$ (**6d**).[a]

Atoms	Bond length (Å)	Atoms	Angles (deg)
$[Ph_2SCH_2CF_3][OTf]$ (**3aa**)			
S1-C1	1.789(5)	C3-S1-C1	103.1(2)
S1-C3	1.779(4)	C9-S1-C1	104.8(2)
S1-C9	1.789(5)	C3-S1-C9	105.6(2)
C1-H(1A), C1-H(1B)	0.9700	H(1A)-C1-H(1B)	107.9
F1-C2	1.310(6)	F1-C2-F2	106.4(6)
F2-C2	1.314(7)	F1-C2-F3	107.8(5)
F3-C2	1.320(7)	F2-C2-F3	106.3(5)
$[Ph_2SCH_2CF_2H][OTf]$ (**3ab**)			
S1-C1	1.805(3)	C9-S1-C1	104.01(13)
S1-C3	1.781(3)	C3-S1-C1	104.34(13)
S1-C9	1.772(3)	C9-S1-C3	103.71(13)
C1-H(1A), C1-H(1B)	0.9700	H(1A)-C1-H(1B)	108.1
C2-H2	0.9800	F2-C2-H2	109.9
F1-C2	1.341(3)	F1-C2-H2	109.9
F2-C2	1.338(4)	F2-C2-F1	105.8(3)
$[PhS(CH_3)_2][OTf]$ (**6d**)			
S1-C7	1.785(5)	C1-S1-C7	103.1(3)
S1-C8	1.775(5)	C1-S1-C8	104.4(3)
S1-C1	1.768(6)	C8-S1-C7	101.6(3)
C7-H(7B), C8-H(8B)	0.9600		

a: Bond lengths are in angstroms. Angles are in degrees. Estimated standard deviations are given in parentheses.

<Table>Table 3 The solvent-free reactions of dialkyl and alkylaryl sulfides with **2a-c**



Entry	R^3	R^4	CF_nH_{3-n}	Molar ratio	Conditions	Yield (**5**/**6**, %)[a]

1	C_4H_9	C_4H_9	CF_3	**4a** / **2a** (3 : 1)	100 °C, 24 h	**6a**, 55
2	C_4H_9	C_4H_9	CF_2H	**4a** / **2b** (3 : 1)	100 °C, 24 h	**6a**, 97
3	C_4H_9	C_4H_9	CF_2H	**4a** / **2b** (3 : 1)	r.t., 24 h	**5ab**, 91
4	C_4H_9	C_4H_9	CH_2F	**4a** / **2c** (1 : 2)	60 °C, 15 h	**5ac**, > 99
5	C_4H_9	C_4H_9	CH_2F	**4a** / **2c** (3 : 1)	60 °C, 15 h	**5ac**, 98
6	allyl	allyl	CF_3	**4b** / **2a** (5 : 1)	100 °C, 24 h	**6b**, 43
7	allyl	allyl	CF_2H	**4b** / **2b** (3 : 1)	60 °C, 24 h	**6b**, 99
8	allyl	allyl	CH_2F	**4b** / **2c** (3 : 1)	60 °C, 15 h	**6b**, 92
9	allyl	allyl	CH_2F	**4b** / **2c** (1 : 2)	r.t, 15 h	**5bc**, > 99
10	C_2H_5	C_2H_5	CF_3	**4c** / **2a** (5 : 1)	100 °C, 24 h	**6c**, 27
11[b]	C_2H_5	C_2H_5	CF_2H	**4c** / **2b** (3 : 1)	100 °C, 24 h	**5cb**, 34 / **6c**, 65
12	C_2H_5	C_2H_5	CH_2F	**4c** / **2c** (3 : 1)	60 °C, 15 h	**5cc**, 99
13	C_6H_5	CH_3	CF_3	**4d** / **2a** (5 : 1)	100 °C, 24 h	**6d**, 21
14	C_6H_5	CH_3	CF_2H	**4d** / **2b** (3 : 1)	60 °C, 24 h	**6d**, 98
15	C_6H_5	CH_3	CH_2F	**4d** / **2c** (1 : 2)	60 °C, 5 h	**5dc,** 97
16	C_6H_5	C_2H_5	CF_3	**4e** / **2a** (5 : 1)	120 °C, 24 h	**6e**, 7
17	C_6H_5	C_2H_5	CF_2H	**4e** / **2b** (3 : 1)	100 °C, 24 h	**6e**, > 99
18	C_6H_5	C_2H_5	CH_2F	**4e** / **2c** (1 : 2)	60 °C, 5 h	**5ec**, 97[c]
19	C_6H_5	*n*-C_4H_9	CF_3	**4f** / **2a** (5 : 1)	120 °C, 24 h	**6f**, 12
20	C_6H_5	*n*-C_4H_9	CF_2H	**4f**/ **2b** (3 : 1)	100 °C, 8 h	**6f**, > 99
21	C_6H_5	*n*-C_4H_9	CH_2F	**4f** / **2c** (1 : 2)	60 °C, 5 h	**5fc**, 99

[a] Isolated yield. [b] The molar ratio of **5cb** and **6c** was determined by NMR spectroscopy.

[c] The product was decolored by activated charcoal in CH_2Cl_2 refluxing for 0.5 h.

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