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Preparation of α,α-Difluoromethylene Functionalized Sulfones[1]

Zhen-Yu Yang and Donald J. Burton[2]

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, U.S.A.

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ABSTRACT

Sulfination of bromodifluoroacetate or acetamide **1** *with sodium dithionite gives the corresponding sulfinates* **2a** *and* **2b**, *respectively, which upon cuprous bromide catalyzed allylation afford the allylsulfonyldifluoroacetate and acetamides. Phenyl- or alkylsulfonyldifluoroacetates and acetamides can be readily prepared from reaction of* **1** *with thiolates, followed by oxidation with hydrogen peroxide.*

INTRODUCTION

The perfluoroalkylsulfonyl moiety is one of the strongest neutral electron withdrawing groups known [1, 2] and exhibits enormously versatile reactivity, acting both as an electrophile and as a nucleophile [3]. Furthermore, it stabilizes adjacent carbanions [4] and activates unsaturated bonds toward nucleophilic attack [5] and Diels-Alder reactions [6]. Therefore the introduction of this functionality into organic molecules has been attractive to synthetic and mechanistic chemists.

Although several methods for the preparation of fluorinated sulfones have been documented [7–10], most of these reports only described the preparation and reaction of perfluoroalkyl sulfones, specifically triflones. There are few publications describing the preparation of α-functionalized difluoromethylene sulfones. In our continuing effort to develop new methodologies for the preparation of organic compounds containing the difluoromethylene moiety [11–15], herein we wish to report facile methods for the preparation of various α,α-difluoromethylene functionalized sulfones.

RESULTS AND DISCUSSION

Preparation of Alkoxy- and Dialkylaminocarbonyldifluoromethylsulfinates

Huang and coworkers first reported that perfluoroalkyl iodides reacted with sodium dithionite in acetonitrile and water to give the corresponding perfluoroalkyl sulfinates [16]. Recently, we demonstrated the utility of this methodology in the preparation of the first example of a fluorinated mixed phosphonic/sulfonic acid [17]. We have now found that isopropyl bromodifluoroacetate **1a** and N,N-diethylbromodifluoroacetamide **1b** reacted with sodium dithionite under mild conditions to give the corresponding sulfinates in good yields. For example, when **1a** was treated with sodium dithionite in the presence of sodium bicarbonate in a mixture of acetonitrile and water at 50°C for 3 hours, the corresponding sulfinate **2a** was formed in 90% yield by ^{19}F NMR analysis of the reaction mixture. Compound **2a** could be isolated in 68% yield by extraction with isopropyl alcohol followed by recrystallization from isopropyl alcohol. Similarly, **1b** gave sulfinate **2b** in 60% isolated yield.

$$\underset{\mathbf{1}}{BrCF_2COY} + Na_2S_2O_4 \xrightarrow[CH_3CN/H_2O]{50^\circ C} \underset{\mathbf{2}}{NaO_2SCF_2COY}$$

2a Y = $OCH(CH_3)_2$: 68%

2b Y = $N(C_2H_5)_2$: 60%

[1]Dedicated to Professor H.C. Brown on the occasion of his 80th birthday.

[2]To whom correspondence should be addressed.

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The sulfinates **2a** or **2b** are stable solids at room temperature, but were readily oxidized with hydrogen peroxide to afford the corresponding sulfonates in high yields by ^{19}F NMR analysis [17]. When treated with iodine at room temperature, **2a** gave isopropyl iododifluoroacetate. Presumably, a metastable sulfonyl iodide initially formed and decomposed to produce the iododifluoroacetate [18]. However, when bromine was added to a mixture of **2a** and water at room temperature, the isopropoxycarbonyldifluoromethylsulfonyl bromide **3a** precipated and was isolated by distillation under reduced pressure (100°C) without significant decomposition. Upon treatment of **2b** with bromine in water at room temperature followed by addition of CCl_4 to the reaction mixture, the N,N-diethylcarbonyldifluoromethylsulfonyl bromide **3b** was observed by ^{19}F NMR analysis of the CCl_4 solution. However, when the crude 3b was dried over 4Å molecular sieve, **3b** decomposed to give **1b** with the evolution of sulfur dioxide.

Preparation of Allylsulfonyldifluoroacetate and Acetamides

In the presence of a catalytic amount of cuprous bromide, reaction of **2a** or **2b** with allyl bromide in DMF at 40–50°C gave allylsulfonyldifluoroacetates **4a** and **4b** in good yields, respectively. Although in

$$\underset{\mathbf{2}}{NaO_2SCF_2COY} + CH_2{=}CHCH_2Br \xrightarrow[DMF]{CuBr} \underset{\mathbf{4}}{CH_2{=}CHCH_2SO_2CF_2COY}$$

4a: Y = $OCH(CH_3)_2$: 80%

4b: Y = $N(C_2H_5)_2$: 87%

principle the reaction of the sulfinates with allyl halides can involve allylation both at sulfur and oxygen due to the ambident nucleophile [19], spectroscopic analysis of the products indicated that the sulfur atom attacked the allyl halide. Sulfur and/or oxygen allylation of the sulfinates are easily distinguished by virtue of the differences in their IR and ^{19}F NMR spectra. For example, **4a** exhibited strong absorption bands at 1360 cm^{-1} and 1150 cm^{-1} [20], in agreement with the presence of the sulfonyl group. Conversely, if the sulfinate underwent oxygen allylation, a typical sulfinate ester group would be observed in the IR spectrum at around 1120 cm^{-1} [20]. Also, the ^{19}F NMR spectrum of sulfone **4a** exhibited a singlet at $\delta = -109.5$, while the sulfinate ester would have given an AB pattern due to the chirality of the sulfur atom. Similarly, when a substituted allyl halide such as 2-methylallyl chloride was used as a substrate, **2b** afforded the corresponding 2-methylallylsulfone **4c** in 70% yield.

The products **4a**, **4b**, and **4c** are incapable of providing any regiochemical information on the reaction of **2** with allyl halides due to formation of only one regioisomer from allyl bromide or 2-methylallyl chloride. In order to investigate the regioselectivity of the allylation of the sulfinates, we employed various substituted allyl halides as substrates. The products resulting from both α- and γ-attack were observed as illustrated in Table 1. For example, in the case of the reaction of **2a** with 3-chloro-1-butene, 1-(isopropoxycarbonyldifluoromethylsulfonyl)-2-butene **4d** and 3-(isopropoxycarbonyldifluoromethylsulfonyl)-1-butene **4e** were obtained in a 52:48 ratio, determined by ^{19}F NMR analysis. Likewise, treatment of **2a** with 1-chloro-2-butene also gave **4d** and **4e** in the same ratio. When **2a** reacted with 1-chloro-3-methyl-2-butene, 1-(isopropoxycarbonyl-difluoromethylsulfonyl)-3- methyl-2-butene **4f** and 3-methyl-3-(isopropoxycarbonyl-difluoromethylsulfonyl)-1-butene **4g** were obtained in a 78:22 ratio.

Allylation of acetamide **2b** exhibited better regioselectivity with substituted allyl halides than did **2a**. On treatment of **2b** with 1-chloro-2-butene, 93% of 1-(N,N-diethylaminocarbonyldifluoromethylsulfonyl)-2-butene **4h** was formed, and only 7% of its regioisomer **4i** was observed. The same ratio of **4h/4i** was observed in the reaction of **2b** with 3-chloro-1-butene. When **2b** reacted with 1-chloro-3-methyl-2-butene, regiospecific formation of the (N, N-diethylaminocarbonyldifluoromethylsulfonyl) substituted alkene **4j** was observed via attack at the least hindered carbon.

Although the mechanism of the reaction has not been investigated in detail, we propose that the intermediate copper sulfinate is formed from the reaction of sodium sulfinate with cuprous bromide. The copper sulfinate attacks the least sterically hindered carbon of the allyl halide to form the sulfone. Recent work in our laboratories has demonstrated that copper perfluoroalkylsulfinates could be readily prepared by insertion of sulfur dioxide into perfluoroalkylcopper reagents and the resultant copper sulfinates were active toward a variety of allyl halides compared to other metal sulfinates such as cadmium sulfinates [21]. Consequently, cuprous halide could be used to catalyze allylation of perfluoroalkylsulfinates.

Preparation of Phenyl- or Alkylsulfonyldifluoroacetate and Acetamides

It is known that cuprous perfluoroalkylsulfinates do not react with aromatic iodides to give the corresponding sulfones although they do readily react with allyl halides [19]. In order to prepare the phenyl- or alkylsulfonyldifluoroacetates and acetamides, we

TABLE 1 Preparation of Allylsulfonyldifluoroacetate and Acetamides

Y	*Allyl Halides*	*Products*	*Isomeric Ratio*[a]	*Yield*[b]
$OCHMe_2$	$CH_2{=}CHCH_2Br$	$CH_2{=}CHCH_2SO_2CF_2CO_2CHMe_2$ (**4a**)	100	80
NEt_2	$CH_2{=}CHCH_2Br$	$CH_2{=}CHCH_2SO_2CF_2CONEt_2$ (**4b**)	100	87
NEt_2	$CH_2{=}CMeCH_2Cl$	$CH_2{=}CMeCH_2SO_2CF_2CONEt_2$ (**4c**)	100	78
$OCHMe_2$	$MeCHClCH{=}CH_2$	$MeCH{=}CHCH_2SO_2CF_2CO_2CH_4Me_2$ (**4d**)	52	94
		$CH_2{=}CHCHMeSO_2CF_2CO_2CHMe_2$(**4e**)	48	
$OCHMe_2$	$MeCH{=}CHCH_2Cl$	$MeCH{=}CHCH_2SO_2CF_2CO_2CHMe_2$ (**4d**)	52	87
		$CH_2{=}CHCHMeSO_2CF_2CO_2CHMe_2$ (**4e**)	48	
$OCHMe_2$	$Me_2C{=}CHCH_2Cl$	$Me_2C{=}CHCH_2SO_2CF_2CO_2CHMe_2$ (**4f**)	78	97
		$CH_2{=}CHCMe_2SO_2CF_2CO_2CHMe_2$ (**4g**)	22	
NEt_2	$MeCH{=}CHCH_2Cl$	$MeCH{=}CHCH_2SO_2CF_2CONEt_2$(**4h**)	93	77
		$CH_2{=}CHCHMeSO_2CF_2CONEt_2$ (**4i**)	7	
NEt_2	$MeCHClCH{=}CH_2$	$MeCH{=}CHCH_2SO_2CF_2CONEt_2$ (**4h**)	93	91
		$CH_2{=}CHCHMeSO_2CF_2CONEt_2$ (**4i**)	7	
NEt_2	$Me_2C{=}CHCH_2Cl$	$Me_2C{=}CHCH_2SO_2CF_2CONEt_2$ (**4j**)	100	83

a) Isomeric ratio was determined by ^{19}F NMR.
b) Isolated yields.

needed to develop an alternative approach to these compounds. Our strategy was to prepare and oxidize the corresponding alkyl or phenyl sulfides.

Although perfluoroalkyl iodides are resistant to S_N2 or S_N1 reactions [22], they are powerful electron acceptors and readily undergo single electron transfer reactions [23]. Perfluoroalkylation of thiols could be accomplished with perfluoroalkyl iodides in either a polar organic solvent [24], under phase transfer conditions [25] or UV irradiation [26, 27]. A radical chain mechanism for these reactions has been proposed. Although perfluoroalkyl bromides have also been reported to react with thiophenoxide, only lower yields (12–46%) of products were obtained even when a large excess of thiophenoxide was employed [28]. We anticipated that **1** would be a good substrate for reaction with mercaptides since it is activated by an adjacent carbonyl group. When **1** was treated with mercaptides in DMF at –30°C or room temperature, the corresponding sulfides were obtained. The results are summarized in Table 2. With N,N-diethylbromodifluoroacetamide **1b**, phenyl and alkyl mercaptides generally give good yields of the corresponding sulfides. Reaction of isopropyl or ethyl bromodifluoroacetates with mercaptides also

$$BrCF_2COY \;(\mathbf{1}) + RSNa \xrightarrow[-30^\circ C \text{ to RT}]{DMF} RSCF_2COY \;(\mathbf{5})$$

5a: R = C_6H_5, Y=N(C_2H_5)2
5b: R = C_5H_{11}, Y=N(C_2H_5)$_2$
5c: R = C_6H_{13}, Y=N(C_2H_5)$_2$
5d: R = C_6H_5, Y=OCH_3
5e: R = C_6H_5, Y=OC_2H_5
5f: R = C_6H_5, Y=$OCH(CH_3)_2$

afforded the sulfides in good yields. However, when methyl bromodifluoroacetate was used as a substrate, only a moderate yield (37%) of the sulfide was obtained. Presumably thiophenoxide attacked the methyl group of the ester and resulted in dealky-

TABLE 2 Reaction of Organothiolates with Bromodifluoroacetamide or Acetates

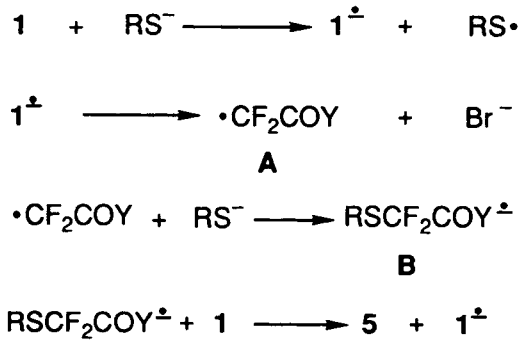
$$RSNa + BrCF_2COY \xrightarrow{DMF} RSCF_2COY$$

Entry	*Y*	*R*	*Products*	*Yield(%)*[a]
1	NEt_2	C_6H_5	$C_6H_5SCF_2CONEt_2$(**5a**)	77
2	NEt_2	n-C_5H_{11}	n-$C_5H_{11}SCF_2CONEt_2$ (**5b**)	86
3	NEt_2	n-C_6H_{13}	n-$C_6H_{13}SCF_2CONEt_2$(**5c**)	73
4	OMe	C_6H_5	$C_6H_5SCF_2COOMe$ (**5d**)	45
5	OEt	C_6H_5	$C_6H_5SCF_2COOEt$ (**5e**)	78
6	$OCHMe_2$	C_6H_6	$C_6H_5SCF_2COCHMe_2$ (**5f**)	75

a) Isolated yields.

lation of the ester. Even when the thiophenoxide solution was slowly added to **1d** at 0°C, the yield of the desired product was only slightly improved from 37% to 45%.

The reaction of **1** with mercaptide may proceed through an $S_{RN}1$ process as described in Scheme 1. The initiation step is likely to be electron transfer from mercaptide to **1** to form the radical anion, which decomposes to produce radical **A**. Capture of **A** by mercaptide generates a second anion radical **B**, which transfers its electron to **1**, propagating the chain process.

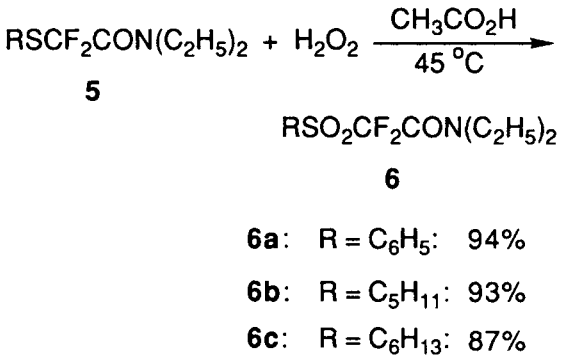


SCHEME 1

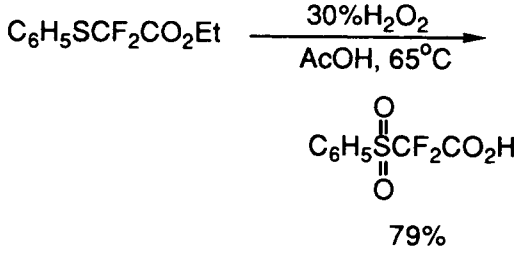
The inhibition of the reaction by an electron scavenger is consistent with the proposed mechanism. For example, when **1c** was treated with 1.5 equivalents of thiophenoxide in the presence of 0.5 equivalents of para-dinitrobenzene (p-DNB) for 2 hours, conversion of **1** decreased to 65% as compared with the control experiment without p-DNB. It is well known that the $S_{RN}1$ reaction can be suppressed by oxygen and radical inhibitors [29]. However, neither oxygen nor galvinoxyl affected the reaction, since the reaction with **1** proceeded too fast to be inhibited.

Thiolation of perfluoroalkyl iodides could be inhibited by styrene, and the radical intermediate generated by an electron transfer process could be trapped by alkenes to give the addition products [22]. However, when reaction of **1c** with thiophenoxide in DMF was carried out in the presence of diallyl ether, only phenylthiodifluoroacetamide was obtained, and no allyl ether addition product was observed. Styrene also did not inhibit the reaction. The difference in the reactivity between perfluoroalkyl iodide and **1** can be ascribed to the stronger carbon-bromine bond of **1** than the carbon-iodine bond of the perfluoroalkyl iodide. Thus, in the mercaptide initiated addition of 1 to alkene, the efficiency of the chain propagation step could be diminished, resulting in the absence of the addition product.

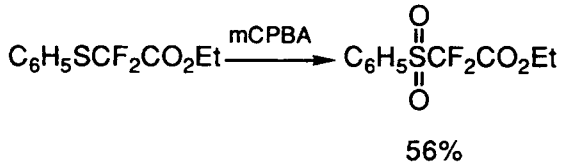
The organothiodifluoroacetamides were readily oxidized by treatment with hydrogen peroxide in acetic acid. This oxidation reaction was quite clean and gave high yields of the sulfones. For example, when phenylthiodifluoroacetamide reacted with 50% hydrogen peroxide in acetic acid at 45°C, usual work-up gave phenylsulfonyldifluoroacetamide as



the sole product. However, when phenylthiodifluoroacetates were oxidized with hydrogen peroxide under similar conditions, the corresponding sulfones were observed in addition to the sulfonyldifluoroacetic acid contaminant. For example, when ethyl phenylthiodifluoroacetate was treated with hydrogen peroxide in acetic acid at 45°C overnight, ^{19}F NMR analysis of the reaction mixture indicated that sulfonylacetate and sulfonylacetic acid were formed in a 1:1 ratio. After work-up, the ethyl phenylsulfonyldifluoroacetate, **6e**, was isolated in 46% yield, and phenylsulfonyldifluoroacetic acid was obtained in 50% yield. When the reaction mixture was heated with stirring at 65°C for 20 hours, only phenylsulfonyldifluoroacetic acid was formed.



The lower yields of sulfonyldifluoroacetate on oxidation of organothiodifluoroacetates with hydrogen peroxide in acetic acid are due to hydrolysis of the esters under these conditions. In order to avoid the hydrolysis, we used meta-chloroperoxybenzoic acid (mCPBA) as the oxidation reagent in dichloromethane. Upon treatment of ethyl phenylthiodifluoroacetate with mCPBA in CH_2Cl_2 at room temperature, the corresponding sulfone was formed in good yield. No hydrolysis product was observed.



In conclusion, the reaction of bromodifluoroacetates or acetamides with sodium dithionite in a mixture of water and acetonitrile gave the corresponding functionalized α,α-difluoromethylsulfinates in good yields. The cuprous bromide catalyzed allylation reaction of the α,α-difluorosulfinates with allyl halides afforded a variety of allyl functionalized difluoro sulfones. Phenyl or alkylsulfonyldifluoroacetates and acetamides were readily prepared from the reaction of mercaptides with bromodifluoroacetates or acetamides, followed by oxidation. These two methods provide facile routes to various organosulfonyldifluoroacetates and acetamides.

EXPERIMENTAL

General

All the reactions were performed in an oven dried apparatus that consisted of a two- or three-necked flask equipped with an addition funnel, a Teflon® coated magnetic stirring bar and a reflux condenser connected to a nitrogen source and mineral oil bubbler. All boiling points were determined during fractional distillation using a partial immersion thermometer and are uncorrected. ^{19}F NMR, ^{1}H NMR and ^{13}C NMR spectra were recorded on 90MHz multinuclear and Bruker AC-300MHz spectrometers. All chemical shifts are reported in parts per million downfield (positive) of the standard. ^{19}F NMR spectra are referenced against internal $CFCl_3$; ^{1}H NMR and ^{13}C NMR spectra against internal tetramethylsilane. IR and FT-IR spectra were recorded as CCl_4 solutions using a solution cell with 0.1 cm path length. GC-MS spectra were performed at 70 eV in the electron impact mode. GLPC analyses were performed on a 5%OV-101 column with a thermal conductivity detector.

Materials

Sodium dithionite (85% purity), mCPBA (50–60% purity), organothiols, and cuprous bromide were obtained from Aldrich Chemical Co., and allyl halides were purchased from Wiley Organics or Aldrich Chemical Co. and were used without further purification.

Preparation of Sodium Isopropoxycarbonyldifluoromethyl Sulfinate (**2a**)

A mixture of 4.3 g (20 mmol) of isopropyl bromodifluoroacetate, 3.5 g (20 mmol) of $Na_2S_2O_4$ and 1.7 g (20 mmol) of $NaHCO_3$ in 15 mL of water and 15 mL of acetonitrile was stirred under N_2 at 50 to 60°C for 3 hours. After removal of the solvents, the residue was dried at 110°C under full vacuum for one hour and then 50 mL of Me_2CHOH (IPA) was added. After refluxing for 10 minutes, the solids were removed by suction filtration and washed with boiling IPA three times. The combined filtrates were evaporated to give 4.6 g of white solids, which were recrystallized from IPA to give 2.9 g (64%) of **2a**. ^{19}F NMR (CD_3COCD_3): –121.8 (s); ^{1}H NMR(CD_3COCD_3): 5.12 (hept, J = 6.4 Hz, 1H), 1.33 (d, J = 3.4 Hz, 6H).

Preparation of Sodium N,N-Diethylaminocarbonyldifluoromethylsulfinate (**2b**)

A mixture of 13.8 g (60 mmol) of **1b**, 13.2 g (80 mmol) of $Na_2S_2O_4$ and 7.0 g (80 mmol) of $NaHCO_3$ in 50 mL of water and 50 mL of acetonitrile was stirred at 50°C overnight. Usual work-up gave a residue (9.9 g), which was recrystallized from IPA to give 8.5 g (60%) of **2b**. ^{19}F NMR(CD_3COCD_3): –112.8 (s); ^{1}H NMR(D_2O/ CD_3COCD_3): 3.59 (q, J = 7.0 Hz, 2H), 3.45 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.0 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (D_2O/CD_3COCD_3): 154.13 (t, J = 24.4 Hz), 111.63 (t, J = 297.2 Hz), 34.64 (t, J = 4.5 Hz), 33.86, 5.98, 3.82.

Oxidation of **2a** with Hydrogen Peroxide

A NMR tube was charged with 50 mg of **2a** and 0.5 mL of acetone-d_6, followed by addition of 0.5 mL of 50% H_2O_2 and the resultant mixture was kept at room temperature for 4 hours. After evaporation of solvents, 48 mg (95%) of sodium isopropoxycarbonyldifluorosulfonate was obtained. ^{19}F NMR(CD_3COCD_3): –110.1(s); ^{1}H NMR (CD_3COD_3): 5.16 (m, 1H), 1.35 (d, J = 6.4 Hz, 6H).

Reaction of **2a** with Bromine

Bromine was added at room temperature to a flask containing 1.1 g (5 mmol) of **2a** and 15 mL of water with stirring until the appearance of a red solution persisted. The organic layer was separated by a pipet and washed with saturated Na_2SO_3 solution, water and dried over 4Å molecular sieves. Distillation of the crude product gave 1.15 g (82%) of **3a**, bp: 73–74°C/2 mmHg.^{19}F NMR ($CDCl_3$); –100.2 (s); ^{1}H NMR($CDCl_3$): 5.25 (hept, J = 6.3 Hz, 1H), 1.43 (d, J = 6.3 Hz, 6H); IR (CCl_4): 2980 (m), 1770 (s), 1390 (s), 1295 (s), 1150–1200 (s), 1100 (s), 975 (s) cm^{-1}.

Reaction of **2a** with Allyl Bromide

In a typical experimental procedure, a two-necked flask fitted with a rubber septum, a stir bar and a condenser topped with a nitrogen inlet was charged with 1.8 g (8 mmol) of **2a**, 0.3 g (2.1 mmol) of cuprous bromide and 8 mL of DMF. Allyl bromide, 1.2 g (10 mmol), was added via syringe and the reaction mixture was stirred at 40°C for six hours. The mixture was poured into a beaker with water and dichloromethane, the solids removed by filtration, the organic layer separated, washed with water, and

dried over $MgSO_4$. After evaporation of dichloromethane, the residue was distilled at reduced pressure to give **4a**, 1.5 g (80%). bp: 112–113 °C/2 mmHg; ^{19}F NMR ($CDCl_3$): –109.5(s). ^1H NMR ($CDCl_3$): 5.88–5.82 (m, 1H), 5.60–5.54(m, 2H), 5.26(hept, J = 6.2 Hz, 1H), 4.02 (dt, J = 6.1 Hz, J = 1.0 Hz, 2H), 1.38 (d, J = 6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$): 157.98(t, J = 27 Hz), 126.91, 121.18, 113.90(t, J = 299.4 Hz), 74.23, 54.89, 21.32; IR (CCl_4): 2980(m), 1760(s), 1640(m), 1360(s), 1305(s), 1150–1200(vs), 1100(s) cm^{-1}; GC-MS: 241(M^+ –1, 0.1), 136(24.8), 116(18.3), 91(27.5), 43(81.5), 41(100). HRMS Calcd for $C_8H_{12}F_2SO_4$: 242.0423, Found: 227.0214 $(M - CH_3)^+$.

*Reaction of **2b** with Allyl Bromide*

A mixture of 0.51 g (2.0 mmol) of **2b**, 0.08 g (0.55 mmol) of CuBr, and 0.36 g (3 mmol) of allyl bromide in 5 mL of DMF was stirred at 35°C for 2 hours. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water and dried over 4Å molecular sieves. After evaporation of the dichloromethane, 0.44 g (87%) of **4b** was obtained, ^{19}F NMR($CDCl_3$): –102.8 (s); ^1H NMR($CDCl_3$): 5.95–5.85 (m, 1H), 5.58–5.53 (m, 2H), 4.11 (d, J = 7.3 Hz, 2H), 3.54 (qt, J = 7.1 Hz, J = 1.9 Hz, 2H), 3.46 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR($CDCl_3$): 157.40 (t, J = 23.1 Hz), 126.59, 121.58, 115.93 (t, J = 301 Hz), 55.61, 42.76, 42.68 (t, J = 15.1 Hz), 14.51, 12.09; GC-MS: 256 (M^+ + 1, 0.3), 255 (M^+ , 0.1), 214 (2.8), 150 (14.6), 100 (100), 72 (45.0), 41 (14.7). HRMS Calcd for $C_9H_{15}F_2NSO_3$: 255.0740, Found: 240.0506 $(M\text{-}CH_3)^+$.

*Reaction of **2b** with 3-Chloro-2-methylpropene (**4c**)*

A mixture of 0.47 g (2 mmol) of **2b**, 0.14 g (0.1 (mmol) of CuBr, and 0.3 g (3 mmol) of 3-chloro-2-methylpropene in 2 mL of DMF was stirred at 35°C overnight. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water and dried over 4Å molecular sieves. After evaporation of the dichloromethane, 0.42 g (78%) of **4c** was obtained. ^{19}F NMR($CDCl_3$): –103.4 (s); ^1H NMR($CDCl_3$): 5.34 (s, 1H), 5.24 (s, 1H), 4.08 (s, 2H), 3.54 (m, 4H), 2.01 (s, 3H), 1.23 (m, 6H); IR (CCl_4): 2950 (s), 1660 (s), 1445 (s), 1340 (s), 1285–1260 (s), 1180 (s), 1110 (s), 1020 (s) cm^{-1}; GC-MS: 270 (M^+ + 1, 0.4), 269 (M^+, 1.1), 190 (21.1), 150 (10.0), 100 (100), 72 (50.8), 55 (33.1).

*Reaction **2a** with 3-Chloro-1-butene (**4d** and **4e**)*

A mixture of 0.45 g (2 mmol) of **2a**, 0.086 g (0.6 mmol) of CuBr, and 0.3 g (3 mmol) of 3-chloro-1-butene in 2 mL of DMF was stirred at 35°C overnight. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water and dried over 4Å molecular sieves. After evaporation of the dichloromethane, 0.48 g (94%) of a mixture of **4d** and **4e** in a 52:48 ratio was obtained, 96.3% GLPC purity. ^{19}F NMR($CDCl_3$): a mixture of geometric isomers of **4d** and **4e**: **4d**: –109.8; **4e**: –106.0 (s). ^1H NMR($CDCl_3$): a mixture of geometric isomers of **4d** and **4e**: 5.97–5.15 (m), 4.26–3.94 (m), 1.82 (d, J = 5.4 Hz), 1.61 (d, J = 7.1 Hz), 1.40 (d, J = 6.3 Hz); IR(CCl_4): mixture of **4d** and **4e**: 2985 (s), 1765 (s), 1685 (w), 1550 (s), 1360 (s), 1305 (s), 1170 (s), 1145 (s), 1100 (s) cm^{-1}; GC-MS: **4d**: 215 (0.1), 150 (2.2), 138 (7.7), 96 (6.8), 78 (4.5), 74 (5.9), 55 (100), 43 (20.2): **4e**: 215 (0.2), 214 (0.5), 150 (6.6), 138 (9.9), 130 (9.8), 96 (6.8), 78 (4.6), 74 (5.4), 55 (100).

*Reaction of **2a** with 1-Chloro-2-butene (**4d** and **4e**)*

A mixture of 0.45 g (2 mmol) of **2a**, 0.086 g (0.6 mmol) of CuBr, and 0.3 g (3 mmol) of 1-chloro-2-butene in 2 mL of DMF was stirred at 35°C overnight. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water and dried over 4Å molecular sieves. After evaporation of the dichloromethane, 0.45 g (88%) of a mixture of **4d** and **4e** in a 52:48 ratio was obtained, 98% GLPC purity.

*Reaction of **2a** with 1-Chloro-3-methyl-2-butene (**4f** and **4g**)*

A mixture of 0.45 g (2 mmol) of **2a**, 0.086 g (0.6 mmol) of CuBr, and 0.3 g (3 mmol) of 1-chloro-3-methyl-2-butene in 2 mL of DMF was stirred at 35°C overnight. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water and dried over 4Å molecular sieves. After evaporation of the dichloromethane, 0.5 g (97%) of a mixture of **4f** and **4g** in a 78:22 ratio was obtained. ^{19}F NMR($CDCl_3$): mixture of **4f** and **4g**: **4f**: –110.4 (s); **4g**: –101.8 (s); ^1H NMR($CDCl_3$): mixture of **4f** and **4g**: 5.37–5.10 (m), 4.05 (d, J = 8.0 Hz), 1.88 (s), 1.80 (s), 1.66 (s), 1.41 (d, J = 5.8 Hz); IR (CCl_4): mixture of **4f** and **4g**: 2950 (m), 1760 (s), 1360 (s), 1305 (s), 1200 (s), 1145 (s), 1100 (s), 1000 (s), 910 (s) cm^{-1}, GC-MS: **4f**: 228 (0.1), 186 (2.2), 144 (3.8), 94 (2.2), 78 (3.3), 69 (100), 43 (11.4), 41 (29.2); **4g**: 186 (0.1), 144 (1.1), 94 (2.0), 69 (100), 43 (9.5), 41 (27.4).

*Reaction of **2b** with 1-Chloro-2-butene (**4h** and **4i**)*

A mixture of 0.47 g (2 mmol) of **2b**, 0.1 g (0.69 mmol) of CuBr, and 0.3 g (3 mmol) of 1-chloro-2-

butene in 8 mL of DMF was stirred at 40°C overnight. The reaction mixture was poured into water and extracted with ether (3 × 15 mL). The combined ether layers were washed with water and dried over $MgSO_4$. After evaporation of the ether, the remaining solvent was removed under vacuum for two hours to give 0.41 g (77%) of **4h** as a mixture of geometric isomers in a 1:2 ratio and **4i** in a 93:7 ratio, 98.2% GLPC purity. ^{19}F NMR ($CDCl_3$): mixture of **4h** and **4i**: -103.7 (s, 1.4 F), -103.4 (s, 0.7F) for geometric isomers of **4h**: -99.4 (s) -98.9 (s) for **4i.** ^1H NMR($CDCl_3$): mixture of **4h** and **4i**: **4h**: 6.13–5.93 (m, 1H), 5.54– 5.47 (m, 1H), 4.16 (d, J = 7.7 Hz, 0.7H), 4.03 (d, J = 7.5 1.4H), 3.54 (q, J = 7.1 Hz, 2H), 3.46 (q, J = 7.1 Hz, 2H), 1.80 (d, J = 6.7 Hz, 1H), 1.77 (d, J = 8.9 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H); FT-IR (CCl_4): mixture of **4h** and **4i**: 2977 (m), 1688 (m), 1684 (m), 1670 (s), 1351 (s), 1191 (s), 1163 (s), 1117 (s) cm^{-1}; GC-MS for **4h**: 269 (M^+, 3.1), 151 (20.2), 136 (18.7), 122 (43.7), 100 (100), 72 (50.4), 56 (17.5), 55 (86.6), 44 (20.5).

*Reaction of **2b** with 3-Chloro-1-butene (**4h** and **4i**)*

A mixture of 0.47 g (2 mmol) of **2b**, 0.1 g (0.69 mmol) of CuBr, and 0.3 g (3 mmol) of 3-chloro-1-butene in 5 mL of DMF was stirred at 40°C for 20 hours. The reaction mixture was poured into water and CH_2Cl_2 and solids were removed by filtration. The CH_2Cl_2 layer was washed with water and dried over 4Å molecular sieves. After evaporation of the solvents, the remaining solvent was removed under full vacuum for two hours to give 0.49 g (91%) of **4h** and **4i** in a 93:7 ratio as determined by ^{19}F NMR and GLPC analysis.

*Reaction of **2b** with 1-Chloro-3-methyl-2-butene (**4j**)*

A mixture of 0.47 g (2 mmol) of **2b**, 0.05 g (0.35 mmol) of CuBr, and 0.31 g (3 mmol) of 1-chloro-3-methyl-2-butene in 8 mL of DMF was stirred at 40°C for 3 hours. The reaction mixture was poured into water and extracted with ether (4 × 15 mL). The combined ether layers were washed with water and dried over $MgSO_4$. After evaporation of the ether, the residue was evacuated under full vacuum for two hours to give 0.47 g (83%) of **4j**. ^{19}F NMR ($CDCl_3$); ^1H NMR($CDCl_3$): 5.26 (tt, J = 7.8 Hz, J = 1.2 Hz, 1H), 4.09 (d, J = 7.9 Hz, 2H), 3.54 (qt, J = 7.1 Hz, J = 2.0 Hz, 2H), 3.46 (q, J = 7.1 Hz, 2H), 1.86 (s, 3H), 1.77 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR($CDCl_3$): 157.74 (t, J = 23.1 Hz), 145.85, 116.10 (t, J = 300.6 Hz), 106.61, 51.03, 42.77, 42.74 (t, J = 6.5 Hz), 26.09, 18.54, 14.52, 12.08; FT-IR(CCl_4): 2978 (m), 1669 (s), 1351 (s), 1344 (s), 1191 (s), 1165 (s), 1117 (s) cm^{-1}; GC-MS: 283 (M^+, 1.5), 151 (51.9), 136 (11.7), 122 (36.0), 100 (64.5), 72 (37.4), 69 (100), 41 (62.6).

*Preparation of N,N-Diethylphenylthiodifluoroacetamide (**5a**)*

A three-necked flask fitted with a stir bar and a nitrogen inlet was charged with 20 mL of DMF and 0.28 g (12 mmol) of sodium. 1.3 g (12 mmol) of thiophenol was added to the flask and the resultant mixture was stirred at room temperature until the sodium had disappeared. Then 2.3 g (10 mmol) of **1b** was added and the reaction mixture was stirred for 1.5 hours and then poured into a beaker with water and dichloromethane. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over $MgSO_4$. After evaporation of the dichloromethane, the residue (3.1 g) was distilled under reduced pressure to give 2.0 g (77%) of **5a**, bp: 161–162°C/2 mmHg. ^{19}F NMR($CDCl_3$): -74.1 (s); ^1H NMR($CDCl_3$): 7.61 (d, J = 6.6 Hz, 2H), 7.48–7.25 (m, 3H), 3.50 (q, J = 7.0 Hz, 2H), 3.36 (q, J = 7.1 Hz, 2H), 1.16 (t, J = 7.0 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H); ^{13}C NMR($CDCl_3$): 160.39 (t, J = 27.0 Hz), 136.74, 130.05, 129.12, 125.75, 124.62 (t, J = 290.4 Hz), 42.16 (t, J = 4.7 Hz), 41.83, 14.16, 12.19; GC-MS: 259 (M^+, 8.8), 159 (12.9), 109 (10.9), 100 (100), 72 (61.4).

*Preparation of N,N-Diethylpentylthiodifluoroacetamide (**5b**)*

4.6 g (20 mmol) of **1b** was added to the sodium salt of n-pentanethiol solution prepared from the reaction of 2.3 g (22 mmol) of n-pentanethiol and 0.5 g (22 mmol) of sodium in 20 mL of DMF and resultant mixture was stirred at room temperature for 1.5 hours. The DMF was evaporated under reduced pressure and the residue was dissolved in water and ether. The ether layer was separated and washed with water and dried over $MgSO_4$. After evaporation of the ether, the residue was distilled under reduced pressure to give 3.7 g (73%) of **5b**, bp: 134–136°C/2 mmHg. ^{19}F NMR($CDCl_3$): -76.6 (s); ^1H NMR($CDCl_3$): 3.54 (q, J = 7.1 Hz, 2H), 3.41 (q, J = 7.1 Hz, 2H), 2.85(t, J = 7.4 Hz, 2H), 1.68 (pent, J = 7.1 Hz, 2H), 1.41–1.32 (m, 4H), 1.22 (t, J = 7.1 Hz, 3H), 1.17 (t, J = 7.0 Hz, 3H), 0.90 (t, J = 7.1 Hz, 3H); FT-IR(CCl_4): 2962 (m), 1671 (s), 1450 (m), 1094 (m), 1038 (m) cm^{-1}; GC-MS: 253 (M^+, 0.1), 151 (43.0), 122 (8.1), 100 (100), 72 (87.1), 43 (32.6).

*Preparation of N,N-Diethylhexylthiodifluoroacetamide (**5c**)*

9.2 g (40 mmol) of **1b** was added to the sodium salt of n-hexanethiol solution prepared from the reaction of 5.1 g (43 mmol) of n-hexanethiol and 0.98 g (43 mmol) of sodium in 40 mL of DMF and resultant mixture was stirred at room temperature overnight. The DMF was evaporated under reduced pressure and the residue was dissolved in water and ether.

The ether layer was separated and washed with water and dried over $MgSO_4$. After evaporation of the ether, the residue was distilled under reduced pressure to give 8.2 g (86%) of **5c**, bp: 141–142°C/2 mmHg. ^{19}F NMR($CDCl_3$): –76.6 (s); ^1H NMR($CDCl_3$): 3.54 (q, J = 7.1 Hz, 2H), 3.40 (q, J = 7.1 Hz, 2H), 2.85 (t, J = 7.4 Hz, 2H), 1.68 (pent, J = 7.2 Hz, 2H), 1.45–1.30 (m, 6H), 1.21 (t, J = 7.0 Hz, 3H), 1.17 (t, J = 7.0 Hz, 3H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR($CDCl_3$): 160.68 (t, J = 28.0 Hz), 125.00 (t, J = 285.7 Hz), 42.52 (t, J = 4.6 Hz), 41.81, 31.04, 29.56, 28.40, 28.36, 22.27, 14.28, 13.94, 12.31; FT-IR(CCl_4): 2933 (s), 1672 (s), 1463 (s), 1286 (m), 1094 (s), 1038 (s), 1012 (s) cm^{-1}; GC-MS: 268 (M^+ + 1, 0.8), 151 (41.5), 100(100), 72 (75.5), 56 (17.6), 55 (14.0), 43 (44.5), 41 (47.4).

*Preparation of Methyl Phenylthiodifluoroacetate (**5d**)*

A flask fitted with a stir bar and a nitrogen inlet was charged with 0.9 g (5 mmol) of **1d** and 2 mL of DMF. Sodium thiophenoxide (5.5 mmol) in 5.5 mL of DMF solution was added slowly at 0°C and the resultant mixture was stirred for 3 hours. The reaction mixture was poured into water and extracted with ether (3 × 30 mL). The combined ether layers were washed with water and dried over $MgSO_4$. After evaporation of the ether, the residue was distilled to give 0.5 g (45%) of **5d**, bp: 72–73°C/0.25 mmHg. ^{19}F NMR($CDCl_3$): –82.5 (s); ^1H NMR ($CDCl_3$): 7.62–7.43 (m, 5H), 3.25 (s, 3H): ^{13}C NMR($CDCl_3$): 162.12 (t, J = 32.7 Hz), 136.83, 130.82, 129.45, 127.64, 120.41 (t, J = 276.9 Hz), 53.71; FT-IR(CCl_4): 3067 (w), 2957 (w), 1774 (s), 1292 (m), 1113 (m), 1088 (s), 994 (m) cm^{-1}; GC-MS: 219 (M^+ + 1, 10.9), 218 (M^+, 80.5), 159 (100), 109 (67.8), 77 (92.7), 65 (55.1), 59 (42.4), 51 (33.7).

*Preparation of Ethyl Phenylthiodifluoroacetate (**5e**)*

8.1 g (40 mmol) of **1c** was added to a sodium thiophenoxide solution prepared from 0.92 g (40 mmol) of sodium and 4.4 g (40 mmol) of thiophenol in 40 mL of DMF at –30°C. After stirring at –30°C for 10 min, the resultant mixture was warmed to room temperature with stirring for 3 hours. The reaction mixture was poured into water and extracted with ether (2 × 60 mL). The combined ether layers were washed with water and dried over $MgSO_4$. After evaporation of the ether, the residue was distilled to give 7.3 g (79%) of ethyl phenylthiodifluoroacetate, bp: 80–82°C/0.25 mmHg. ^{19}F NMR ($CDCl_3$): –82.4 (s); ^1H NMR ($CDCl_3$): 7.59– 7.56 (m, 2H), 7.43–7.28 (m, 3H), 4.15 (q, J = 7.2 Hz, 2H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): 161.54 (t, J = 32.8 Hz), 136.79, 131. 71, 130.77, 129.45, 120.38 (t, J = 287.0 Hz), 63.61, 13.70; FT-IR(CCl_4): 3066 (w), 2986 (m), 2769 (s), 1288 (s), 1122 (s), 1108 (s), 1068 (s), 979 (s) cm^{-1}; GC-MS: 233 (M^+ + 1, 12.3), 232 (M^+, 81.7), 159 (100), 110 (43.1), 109 (61.4), 77 (98.0), 65 (52.3), 51 (41.0).

*Preparation of Isopropyl Phenylthiodifluoroacetate (**5f**)*

1.1 g (5 mmol) of **1a** was added to a sodium thiophenoxide solution prepared from 0.12 g (5.2 mmol) of sodium and 0.57 g (5.2 mmol) of thiophenol in 5 mL of DMF at room temperature and resultant mixture was stirred for 3 hours. The reaction mixture was poured into water, extracted with ether (3 × 30 mL), and the combined ether layers were washed with water and dried over $MgSO_4$. After evaporation of the ether, the residue was distilled to give 0.9 g (75%) of **5f**, bp: 75–77°C/0.1 mmHg-. ^{19}F NMR($CDCl_3$): –82.5 (s), ^1H NMR($CDCl_3$): 7.63–7.31 (m, 5H), 5.01 (hept, J = 6.3 Hz, 1H), 1.19 (d, J = 6.3 Hz); ^{13}C NMR($CDCl_3$): 161.06 (t, J = 32.6 Hz), 136.64, 130.61, 129.35, 120.16 (t, J = 287.4 Hz), 72.16, 21.25; FT-IR(CCl_4): 2986 (m), 1765 (s), 1377 (s), 1292 (s), 1099 (s), 1088 (s), 985 (s); GC-MS: 264 (M^+, 6.8), 159 (24.5), 109 (16.3), 77 (30.9), 65 (20.3), 43 (100), 41 (32.1).

*Preparation of N,N-Diethylphenylsulfonyldifluoroacetamide (**6a**)*

A mixture of 0.52 g (2 mmol) of N, N-diethylphenylthiodifluoroacetamide, **5a**, 0.4 g (6 mmol) of 50% H_2O_2 in 5 mL of acetic acid was stirred at 50°C overnight. The reaction mixture was poured into a beaker with ether and saturated $NaHCO_3$ solution. The organic layer was separated, washed with water and dried over $MgSO_4$. After evaporation of the ether, 0.55 g (94%) of **6a** was obtained. ^{19}F NMR($CDCl_3$): –100.8 (s), ^1H NMR($CDCl_3$): 8.00 (d, J = 7.7 Hz, 2H), 7.78 (t, J = 7.6 Hz, 1H), 7.63 (m, 2H), 3.61 (q, J = 7.1 Hz, 2H), 3.44 (q, $^3J_{H,H}$ = 7.1 Hz, 2H), 1.24 (q, J = 7.1 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): 156.72 (t, J = 23.3 Hz), 135.87, 130.81, 129.44, 115.91 (t, $^1J_{C,F}$ = 299.2 Hz), 42.70 (t, $^4J_{C,F}$ = 5.5 Hz), 42.57, 14.50, 12.13; FT-IR(CCl_4): 2981 (m), 1679 (s), 1450 (s), 1354 (s), 1193 (m), 1167 (s), 1118 (s) cm^{-1}; GC-MS: 291 (M^+, 0.1), 276 (3.9), 150 (26.9), 125 (28.2), 100 (100), 77 (95.2), 72 (96.5), 51 (49.6).

*Preparation of N,N-Diethylpentylsulfonyldifluoroacetamide (**6b**)*

A mixture of 1.3 g (5 mmol) of **5b**, and 0.8 g (12 mmol) of 50% H_2O_2 in 5 mL of AcOH was stirred at 50°C overnight. The reaction mixture was poured into a beaker with ether and saturated $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with water and dried over $MgSO_4$. After evaporation of the ether, 1.3 g

(93%) of **6b** was obtained. ^{19}F NMR($CDCl_3$): –104.1 (s); ^1H NMR($CDCl_3$): 3.54 (qt, J = 7.1 Hz, J = 2.0 Hz, 2H), 3.46 (q, J = 7.1 Hz, 2H), 3.32 (t, J = 6.8 Hz, 2H), 1.93 (pent, J = 7.7 Hz, 2H), 1.51–1.32 (m, 4H), 1.26 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H), 0.92 (t, J = 7.1 Hz, 3H); ^{13}C NMR($CDCl_3$): 157.62 (t, J = 23.2 Hz), 115.82 (t, J = 299.1 Hz), 50.62, 42.83 (t, J = 4.0 Hz), 30.63, 22.19, 20.76, 14.57, 13.71, 12.11; FT-IR(CCl_4): 2962 (s), 1669 (s), 1451 (s), 1348 (s), 1191 (s), 1164 (s), 1117 (s); GC-MS: 286 (M^+ + 1, 0.1), 149 (34.5), 136 (14.5), 122 (15.4), 100(100), 78 (18.6), 72 (100), 70 (41.7), 56 (37.0), 43 (73.0), 41 (65.4).

Preparation of N,N-Diethylhexylsulfonyldifluoroacetamide (6c)

A mixture of 2.7 g (10 mmol) of **5c**, and 2 mL of 50% H_2O_2 in 8 mL of AcOH was stirred at 55°C overnight. The reaction mixture was poured into a beaker with ether and saturated $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with water and dried over $MgSO_4$. After evaporation of the ether, 2.6 g (87%) of **6c** was obtained. ^{19}F NMR ($CDCl_3$): –104.0 (s), ^1H NMR($CDCl_3$): 3.54 (q, J = 7.0 Hz, 2H), 3.45 (q, J = 7.1 Hz, 2H), 3.33 (t, J = 8.0 Hz, 2H), 1.90 (pent, J = 8.0 Hz, 2H), 1.43 (m, 2H), 1.34 (m, 4H), 1.24 (t, J = 7.1 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H), 0.90 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$): 157.67 (t, J = 23.2 Hz), 115.88 (t, J = 299.2 Hz), 50.69, 42.87, 31.30, 28.71, 22.45, 21.09, 14.59, 13.97, 12.13; GC-MS: 299 (M^+, 0.1), 150 (52.9), 149 (52.8), 100 (100), 72 (95.0), 70 (28.3), 56 (26.8), 43 (38.9), 41 (44.3).

Reaction of Ethyl Phenylsulfonyldifluoroacetate with Hydrogen Peroxide

A mixture of 0.5 g (2.1 mmol) of ethyl phenylthiodifluoroacetate, **5e**, and 1 mL of 50% H_2O_2 in 2 mL of AcOH was stirred at 45°C overnight. After the volatile materials were removed under vacuum at 50°C, the residue was diluted with 30 mL of ether and poured into 40 mL of saturated $NaHCO_3$ solution. The ether layer was separated and aqueous layer was extracted with ether. The combined ether layers were washed with water and dried over $MgSO_4$. After evaporation of the ether, 0.26 g (46%) of ethyl phenylsulfonyldifluoroaceate **6e** was obtained. ^{19}F NMR($CDCl_3$): –108.3 (s); ^1H NMR ($CDCl_3$): 8.00 (d, J = 7.4 Hz, 2H), 7.82 (t, J = 7.6 Hz, 1H), 7.66 (t, J = 7.4 Hz, 2H), 4.41 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H); ^{13}C NMR($CDCl_3$): 158.42 (t, J = 28 Hz), 136.24, 132.23, 130.92, 129.66, 113.62 (t, J = 298.0 Hz), 64.89, 13.78; FT-IR(CCl_4): 2986 (m), 1780 (s), 1449 (s), 1364 (s), 1305 (s), 1139 (s), 1025 (m) cm^{-1}; GC-MS: 264 (M^+, 0.1), 141 (80.7), 127 (14.5), 125 (35.7), 78 (34.8), 77 (100), 51 (52.4). The aqueous layer was acidified with 2N H_2SO_4 and extracted with ether (2 × 35 mL), dried over $MgSO_4$. After evaporation of the ether, 0.25 g (50%) of phenylsulfonyldifluoroacetic acid was obtained, which could be further purified by recrystalization from benzene, mp: 124–126°C. ^{19}F NMR(CD_3COCD_3): –109.6 (s); 1H NMR(CD_3COCD_3): 11.59 (s, 1H), 8.10–7.79 (m, 5H); ^{13}C NMR (CD_3COCD_3): 159.58 (t, J = 27.6 Hz), 137.25, 133.40, 131.64, 130.72, 114.70 (t, J = 296.4 Hz); DIP-MS: 236 (M^+, 0.5), 192 (6.7), 141 (50.6), 125 (18.2), 78 (42.9), 77 (100), 51 (68.5), 44 (61.9).

Preparation of Phenylsulfonyldifluoroacetic Acid

A mixture of 1.0 g (4.3 mmol) of **5e** and 3 mL of 30% H_2O_2 in 6 mL of CH_3CO_2H was stirred at 65°C for 20 hours. The reaction mixture was poured into 40 mL of 2N H_2SO_4 and extracted with ether (2 × 50 mL). The combined ether layers were washed with 2N H_2SO_4 and dried over $MgSO_4$. After evaporation of the ether, 0.95 g of a white solid was obtained which was recrystallized from benzene to give 0.80 g (79%) of phenylsulfonyldifluoroacetic acid.

Preparation of Ethyl Phenylsulfonyldifluoroacetate

To a solution of 0.5 g (2.2 mmol) of **5e** in 4mL of CH_2Cl_2 was added a solution of 1.9 g (5.5 mmol, 50–60%) of mCPBA in 15 mL of CH_2Cl_2 and the mixture was stirred at room temperature overnight. The resulting solution was diluted with 20 mL of CH_2Cl_2 and washed with saturated $NaHCO_3$ solution (4 × 30 mL), water and dried over $MgSO_4$. After evaporation of the CH_2Cl_2, the residue was purified by column chromatography with hexane-ethyl acetate (8:2) as eluant to give 0.33 g (56%) of **6e**.

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