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Electrolytic partial fluorination of organic compounds. Part 60: Highly regioselective anodic fluorination of aryl propargyl sulfides☆

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Abstract—Aryl propargyl sulfides were subjected to electrochemical fluorination in dimethoxyethane (DME) containing various fluoride supporting electrolytes using an undivided cell to provide the corresponding α-monofluorinated or α,α-difluorinated sulfides selectively as main products in good yields depending on the amount of electricity passed. The α,α-difluorinated sulfides were stable enough to be isolated while the α-monofluorinated ones were very unstable. The α-monofluorinated sulfides were readily converted into the corresponding stable α-monofluoroallenyl sulfides in good yields. Furthermore, synthetic utility of α-monofluoroallenyl sulfides was also investigated.

1. Introduction

Selective incorporation of fluorine atom(s) into organic compounds is of great importance in chemical industry and medicinal chemistry. Organofluorine compounds are currently used as lubricants, coatings, textile chemicals, agrochemicals, and pharmaceuticals.[2]

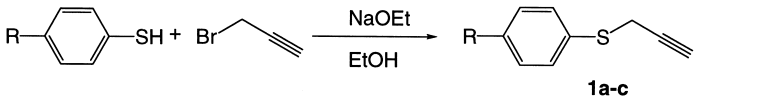
Among organofluorine compounds, difluoromethylene compounds attract much interest since the unique stereoelectronic properties of a *gem*-difluoromethylene group have widespread utilization in pharmacologically active substances. For example, the presence of a difluoromethylene group has aided in the formation of stable hydrate and hemiacetals capable of inhibiting proteases and esterases.[3] A difluoromethylene group has been employed as an isoelectronic–isosteric replacement for the oxygen atom in the phosphate analogues,[4] and in the synthesis of β,β-difluro-α-aminoacids,[5] and fluorinated arachidonic acid.[6] However, the construction of a difluoromethylene group is not easy and very often requires a large amount of oxidizing, toxic or costly reagents.[7] On the other hand, the first synthesis and synthetic application of α-fluoroallenyl phosphonates have very recently been reported.[8] α-Fluoroallenyl sulfides are also expected to be useful as the fluorobuilding blocks. However, there have been no report on the synthesis of α-fluoroallenyl sulfides so far. Previously, we found that sulfides bearing electron-withdrawing groups underwent selective anodic fluorination with good efficiencies.[9] Since an acetylenic group is also an electron-withdrawing group, we have attempted anodic fluorination of sulfides having an acetylenic group, i.e. aryl propargyl sulfides.

In this paper, we report the first successful regioselective anodic mono- and difluorination of aryl propargyl sulfides using various fluoride salts in DME together with the novel synthesis of α-fluoroallenyl sulfides from the anodically fluorinated α-fluoropropargyl sulfides.[10]

2. Results and discussion

2.1. Preparation of aryl propargyl sulfides 1a–c

The starting aryl propargyl sulfides **1a–c** were prepared in



1a-c

1a: R = H; **1b**: R = Cl; **1c**: R = CH_3

Scheme 1.

☆ See Ref. 1.

Keywords: electrochemical fluorination; α-monofluorinated; α-monofluoroallenyl sulfides.

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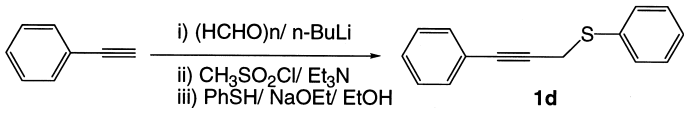


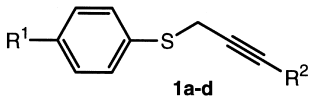
Scheme 2.

good yields by the reaction of the corresponding thiophenols with propargyl bromide in a refluxing ethanol solution containing sodium ethoxide as shown in Scheme 1.[11,12] On the other hand, 3-phenyl-2-propynyl phenyl sulfide (**1d**) was prepared as shown in Scheme 2.[13]

2.2. Oxidation potentials of aryl propargyl sulfides 1–4

In order to investigate the substituent effect on the oxidation potential of sulfides, the anodic peak potentials of **1** were measured by cyclic voltammetry in an anhydrous acetonitrile solution containing Bu_4NBF_4 (0.1 M) using a platinum disc electrode and SSCE as a reference electrode. These sulfides exhibited irreversible anodic waves. The first oxidation peak potentials (E_p^{ox}) of these sulfides **1** are summarized in Table 1.

Table 1. Oxidation potentials (peak potentials E_p^{ox}) of aryl propargyl sulfides **1a–d**



1a-d

Sulfide			E_p^{ox} (V vs. SSCE)[a]
No.	R^1	R^2	
1a	H	H	1.66
1b	Cl	H	1.85
1c	Me	H	1.62
1d	H	Ph	1.76

[a] Substrate (0.01 M) in 0.1 M $Bu_4N{\cdot}BF_4$/MeCN; sweep rate: 100 mV/s.

Table 2. Oxidation potentials (E_p^{ox}) of organosulfur compounds[a] [PhS–CH_2–EWG]

EWG	E_p^{ox} (V vs. SSCE)
H	1.41
COMe	1.53
COOEt	1.53
C≡CH	1.66[b]
CN	1.75

[a] Substrate (0.01 M) in 0.1 M $NaClO_4$/MeCN; scan rate:100 mV/s.
[b] Substrate (0.01 M) in 0.1 M $Bu_4N{\cdot}BF_4$/MeCN; Pt disc electrode (ϕ=1 mm); scan rate: 100 mV/s.

It was found that substitution on either the acetylenic group or the benzene ring affected the oxidation potentials of sulfides significantly. Substituted acetylenic sulfides **1d** was oxidized at a more positive potential than the corresponding phenyl propargyl sulfide (**1a**) due to the electron-withdrawing effect of the phenyl group. The presence of an electron-withdrawing chlorine atom on the phenyl ring caused a considerable increase in E_p^{ox} while the presence of an electron-donating methyl group caused a little decrease in E_p^{ox} when compared with unsubstituted phenyl propargyl sulfide (**1a**).

As shown in Table 2, the oxidation potential of propargyl sulfide is higher than those of the corresponding acetyl and ester derivatives but lower than that of a cyano derivative.

As shown in Fig. 1, a good linear correlation of oxidation potentials (E_p^{ox}) of the sulfides with Taft's (σ^*) values[14] for these substituent groups was obtained. This indicates that the first electron-transfer from the substrate to the anode may be the oxidation potential determining step.

2.3. Anodic fluorination of aryl propargyl sulfides 1a–d

Anodic fluorination of phenyl propargyl sulfide (**1a**) as a model compound was carried out at a constant current in an undivided cell under various conditions. The results are summarized in Table 3.

Fluorination proceeded regardless of electrolytic conditions

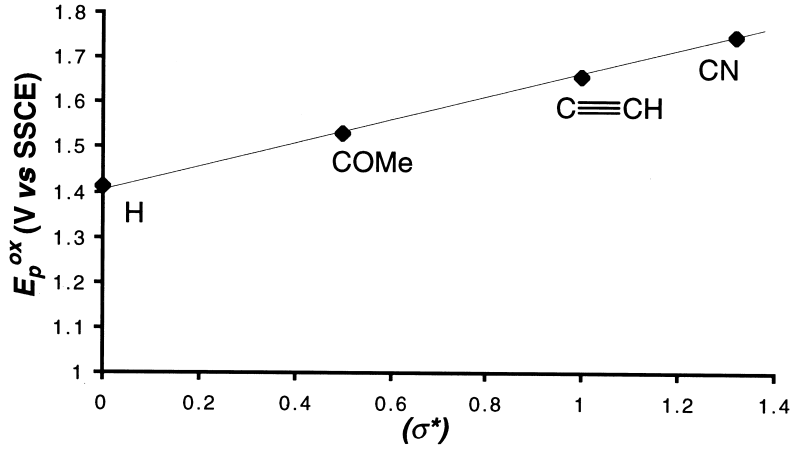
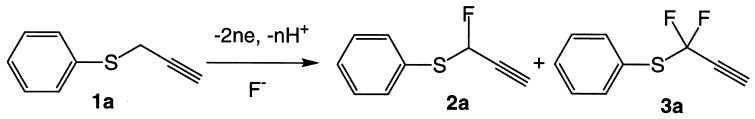


Figure 1. Relationship between oxidation potentials (E_p^{ox}) and substituent constants (σ^*).

Table 3. Anodic fluorination of phenyl propargyl sulfide **1a** under various electrolytic conditions



Run	Solvent	Supporting electrolyte	Charge passed (F/mol)	Yield (%)[a]	
				2a	**3a**
1	DME	$Et_4NF{\cdot}4HF$	1	30	0
2	DME	$Et_4NF{\cdot}4HF$	2	43	5
3	DME	$Et_4NF{\cdot}4HF$	3	52	11
4	DME	$Et_4NF{\cdot}4HF$	4	64	13
5	DME	$Et_3N{\cdot}3HF$	4	53	40
6	DME	$Et_3N{\cdot}5HF$	4	77	17
7	MeCN	$Et_4NF{\cdot}4HF$	4	25	12

[a] Calculated by ^{19}F NMR.

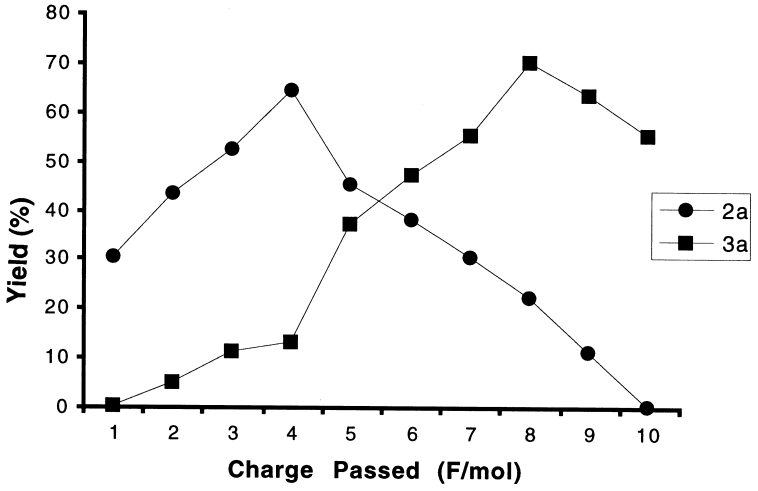
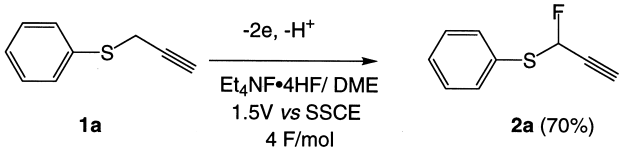


Figure 2. Effect of charge passed on the anodic fluorination of phenyl propargyl sulfide (**1a**) in $Et_4NF{\cdot}4HF$/DME.

to provide α-mono- and α,α-difluorinated products **2a** and **3a**. A fluorine atom was regioselectively introduced into the position α to the sulfur atom. Fluorination at the acetylenic group or phenyl ring did not take place at all. Regardless of supporting fluoride salts, acetonitrile was not suitable for the fluorination due to the passivation of the anode (run 7). On the other hand, the use of DME provided mainly α-mono-fluorinated sulfide **2a**. Among the fluoride salts used, $Et_3N{\cdot}5HF$ gave the best result (run 6) and $Et_4NF{\cdot}4HF$ was also suitable for the selective formation of **2a** (run 4). When $Et_3N{\cdot}3HF$ was used, the fluorinated product **2a** was formed considerably (run 5).

Next, the relationship between the yields of the products, **2a** and **3a** and the electricity passed was investigated at a constant current using $Et_4NF{\cdot}4HF$. As shown in Fig. 2, the yield of α-monofluorinated sulfide **2a** increased with an increase of the electricity and at 4 F/mol of electricity the maximum yield (64%) was obtained, and then the yield decreased. On the other hand, the yield of α,α-difluorinated sulfide **3a** increased largely after 4 F/mol was passed. At 8 F/mol of electricity, the maximum yield (70%) was obtained. Even at 2 F/mol, α,α-difluorinated sulfide **3a** was already formed appreciably as a by-product. When 10 F/mol was passed, α,α-difluorinated product **3a** was obtained exclusively. These results clearly suggest that **3a** was formed *via* **2a**.

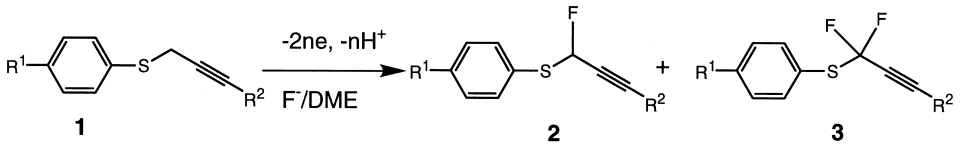


Scheme 3.

As shown in Table 3 and Fig. 2, α,α-difluorinated sulfide **3a** was always formed as a by-product under constant current electrolytic conditions even at the early stage of the electrolysis. Therefore, constant potential anodic oxidation of **1a** at 1.5 V (vs SSCE) was attempted. In this case, the desired monofluorinated product **2a** was formed exclusively in good yield as shown in Scheme 3.

Next, the effect of supporting fluoride salts on the anodic difluorination of **1a** was investigated. In this case, a large excess amount of electricity was passed in order to obtain **3a** selectively. As shown in Table 4, the use of $Et_3N{\cdot}3HF$ gave

Table 4. Anodic difluorination of aryl propargyl sulfides **1a–d**



Run	Sulfide			Supporting electrolyte	Charge passed (F/mol)	Yield (%)[a]	
	No.	R^1	R^2			**2**	**3**
1	**1a**	H	H	$Et_4NF{\cdot}4HF$	8	22	70
2	**1a**	H	H	$Et_4NF{\cdot}4HF$	10	0	55
3	**1a**	H	H	$Et_3N{\cdot}3HF$	8	21	75(70)
4	**1a**	H	H	$Et_3N{\cdot}5HF$	8	20	65
5	**1b**	Cl	H	$Et_3N{\cdot}3HF$	8	5	72 (66)
6	**1c**	Me	H	$Et_3N{\cdot}3HF$	6	20	67 (62)
7	**1d**	H	Ph	$Et_3N{\cdot}3HF$	10	0	65 (63)

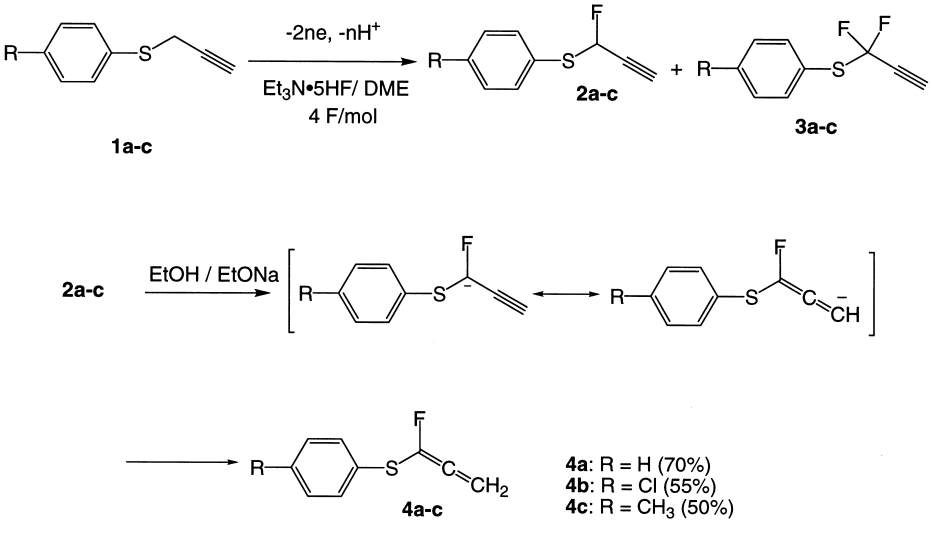
[a] Determined by ^{19}F NMR; isolated yields are shown in parantheses.

the highest yield of **3a** (run 3) and $Et_4NF{\cdot}4HF$ was also effective for the difluorination (run 1). The use of $Et_3N{\cdot}5HF$ gave lower yield (run 4). Longer electrolysis of **1a** resulted in exclusive formation of **3a** although the yield decreased appreciably (run 2). Previously, we found that $Et_4NF{\cdot}4HF$/MeCN was effective for α,α-difluorination of sulfides having various electron-withdrawing groups but $Et_3N{\cdot}3HF$/MeCN was not suitable.[15] In contrast, only poor yield (14%) of **2a** was obtained in $Et_4NF{\cdot}4HF$/MeCN but the use of $Et_3N{\cdot}3HF$/DME gave **3a** in good yield (75%) (run 3). Consequently, MeCN electrolytic solutions were not suitable for the formation of **3**. On the other hand, DME was suitable because it did not cause anode passivation although excess amount of electricity is necessary due to oxidation of DME itself. Furthermore, DME strongly solvates the cationic part of the fluoride salt to make the fluoride ion more reactive. Consequently, the fluoride ion easily attacks on the anodically generated cationic intermediate (Scheme 6).[16] In support of this, DME has much higher donor number (23.9) than MeCN (14.1).[17] Therefore, a solvent effect of DME on the anodic fluorination is notable.[16]

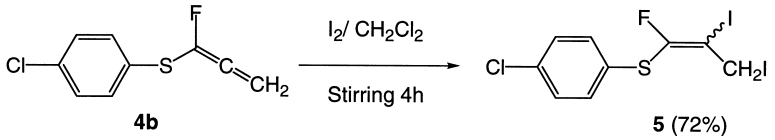
Anodic difluorination of other aryl propargyl sulfides **1b–d** was also carried out in $Et_3N{\cdot}3HF$/DME. As shown in Table 4, α,α-difluorinated sulfides **3b–d** were predominantly (runs 5 and 6) or exclusively (run 7) formed. In this case, fluorination of DME also occurred simultaneously.[18] The difluorinated products **3b–d** were readily isolated by column chromatography. In the case of *p*-tolyl sulfide **1c**, benzylic fluorination did not take place at all although anodic benzylic substitution easily takes place (run 6). In the case of **1d**, neither phenyl nor acetylenic fluorination did not occur and α,α-difluorinated product **3d** was obtained exclusively. Therefore, this fluorination is highly regioselective.

2.4. Synthesis of α-fluoroallenyl sulfides 4a–c

Although α-fluoropropargyl sulfide **2a** was formed in good yield, the isolation of pure **2a** was unsuccessful due to its unstability.[19] Therefore, we attempted to convert **2a** into a more stable derivative. Thus, the electrolytic solution containing a crude product **2a** was basified by addition of an ethanol solution of sodium ethoxide and the resulting



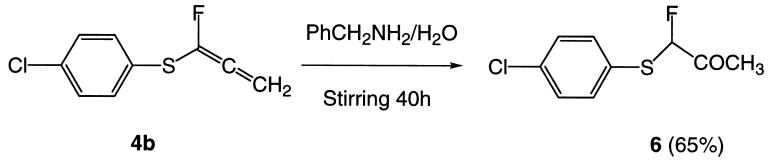
Scheme 4.



Scheme 5.

stable α-fluoroallenyl sulfide **4a** was easily isolated in good yield as shown in Scheme 4 (isolated yields of **4** were shown). Other α-fluoropropargyl sulfides **2b** and **2c** were similarly converted into the corresponding α-fluoroallenyl sulfides **4b** and **4c** in moderate yields. Thus, we successfully prepared α-fluoroallenyl sulfides for the first time.

On the other hand, treatment of **4b** with benzylamine provided α-fluoroacetonyl sulfide **6** due to the contaminated water in benzylamine as shown in Scheme 6. However, even when anhydrous benzylamine was used, no hydroamination product was formed and the starting **4b** was mostly recovered. This is in sharp contrast to that α-fluoroallenyl phosphonates undergo hydroamination efficiently.

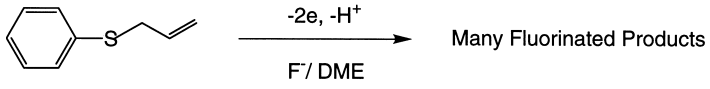


Scheme 6.

2.5. Synthetic utility of α-fluoroallenyl sulfides

The allene unit itself is a synthetically useful functional group,[20] and its chiral nature has recently been used advantageously in asymmetric synthesis.[21] α-Fluoroallenyl sulfides **4a–c** are hitherto unknown fluorinated molecules, which seem to be useful fluorinated building blocks. Zepta and Hammond reported the reaction of α-fluoroallenyl phosphonates with various reagents such as iodine and amines.[8] To investigate the synthetic utility of α-fluoroallenyl sulfides, the addition of iodine was initially examined. Generally, 1,1-disubstituted allenes regioselectively add I_2 across the C_2–C_3 bond to afford the more highly substituted olefines.[22] In this case, treatment of α-fluoroallenyl sulfide **4b** with I_2 in CH_2Cl_2 at room temperature afforded exclusively (*E*)-diiodo **5** equipped with two valuable synthetic handles such as allyl- and vinyl-iodine in moderate yield as shown in Scheme 5.

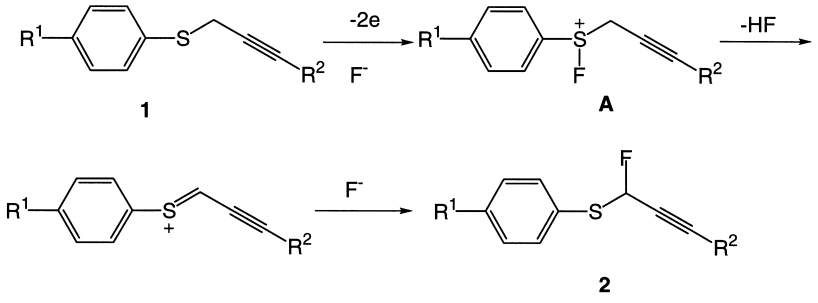
In order to disclose the role of acetylenic group, anodic fluorination of allyl phenyl sulfide was attempted. However, many complicated products were formed. Therefore, a strongly electron-withdrawing acetylenic group is essential for this regioselective anodic fluorination (Scheme 7).



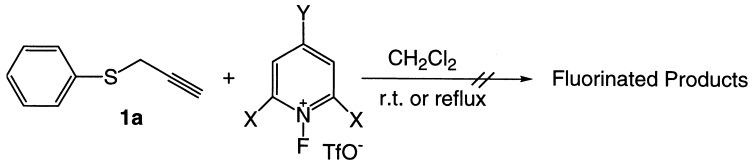
Scheme 7.

The high regioselectivity can be explained in terms of facilitation of deprotonation of the fluorosulfonium ion intermediate **A** by the strong electron-withdrawing acetylenic group as shown in Scheme 8.[23]

N-Fluoropyridinium salts are known to be good fluorinating reagents.[24] The chemical fluorination of phenyl propargyl sulfide **1a** as a model compound was also attempted. However, treatment of **1a** with various *N*-fluoropyridinium triflates in dichloromethane at either room temperature or under reflux resulted in no formation of fluorinated products as shown in Scheme 9. The fluorination did not proceed even in the presence of Et_3N.[25]



Scheme 8.



Scheme 9.

In summary, we have successfully carried out anodic mono- and difluorination of aryl propargyl sulfides for the first time and the monofluorinated products were readily transformed into stable α-fluoroallenyl sulfides. Synthetic utility of α-fluoroallenyl sulfides was also demonstrated.

3. Experimental

Caution. $Et_4NF{\cdot}4HF$ and $Et_3N{\cdot}5HF$ are toxic and if in contact with skin causes serious burns, and therefore proper safety precautions should be taken all the time; it is therefore recommended to protect hands with rubber gloves.[26]

^1H NMR and ^{19}F NMR spectra were recorded at 270 and 254 MHz respectively, in $CDCl_3$. The chemical shifts for ^1H NMR are given in δ ppm downfield from internal TMS, and the chemical shifts for ^{19}F NMR are given in δ ppm downfield from external CF_3COOH.

Materials. Phenyl propargyl sulfide (**1a**),[11] *p*-tolyl propargyl sulfide (**1c**),[11] *p*-chlorophenyl propargyl sulfide (**1b**),[12] and 3-phenyl-2-propynylphenyl sulfide (**1d**)[13] were prepared according to the literature. $Et_4NF{\cdot}4HF$ and $Et_3N{\cdot}5HF$ were obtained from Morita Chemical Industries Co. Ltd. (Japan).

3.1. Anodic mono- and difluorination of aryl propargyl sulfides

In a typical anodic fluorination, constant current electrolysis (5 mA/cm^2) of **1** (1 mmol) was carried out at platinum electrodes (3×3 cm^2) at room temperature in DME (30 mL) containing 0.37 M fluoride salt using an undivided cell under nitrogen atmosphere. After electrolysis, the supporting electrolyte was removed by silica gel short column chromatography using ethyl acetate and the eluent was evaporated under reduced pressure to give **2a**–**c** and **3a**–**d**. The yields of the fluorinated products were estimated by means of ^{19}F NMR using a known amount of monofluorobenzene as an internal standard: the yields were calculated on the basis of the integral ratios between the monofluorobenzene and the fluorinated products. The products **2a**–**c** could not be purified completely due to their instability. On the other hand, the products **3a**–**d** were further purified by column chromatography on silica gel using pentane as eluent to obtain pure **3a**–**d**.

3.1.1. α-Fluoropropargyl phenyl sulfide (2a). ^1H NMR δ 3.03 (dd, 1H, J=4.6, 2.3 Hz), 6.41 (dd, 1H, J=53.8, 2.3 Hz), 7.3–7.6 (m, 5H); ^{19}F NMR δ −62.82 (dd, J=53.8, 4.6 Hz); MS (*m*/*z*) 166 (M^+), HRMS calcd for C_9H_7FS: 166.0253. Found: 166.0239.

3.1.2. *p*-Chlorophenyl α-fluoropropargyl sulfide (2b). ^1H NMR δ 2.97 (dd, 1H, J=4.6, 2 Hz), 6.31 (dd, 1H, J=54, 2 Hz), 7.34 (d, 2H, J=8.6 Hz), 7.51 (d, 2H, J=8.6 Hz); ^{19}F NMR δ −62.52 (dd, J=54, 4.6 Hz); MS (*m*/*z*) 200 (M^+), HRMS calcd for C_9H_6ClFS: 199.9863. Found: 199.9860.

3.1.3. α-Fluoropropargyl *p*-tolyl sulfide (2c). ^1H NMR δ 3.03 (dd, 1H, J=4.6, 2.3 Hz), 6.41 (dd, 1H, J=54, 2.3 Hz), 7.1–7.3 (m, 4H); ^{19}F NMR δ −63.48 (dd, J=54, 4.6 Hz); MS (*m*/*z*) 180 (M^+), HRMS calcd for $C_{10}H_9FS$: 180.0409. Found: 180.0412.

3.1.4. α,α-Difluoropropargyl phenyl sulfide (3a). ^1H NMR δ 2.98 (t, 1H, J=4.3 Hz), 7.2–7.6 (m, 5H); ^{19}F NMR δ 16.7 (d, J=4.3 Hz); MS (*m*/*z*) 184 (M^+), HRMS calcd for $C_9H_6F_2S$: 184.0158. Found: 184.0157.

3.1.5. *p*-Chlorophenyl α,α-difluoropropargyl sulfide (3b). ^1H NMR δ 3.03 (t, 1H, J=4.2 Hz), 7.4 (d, 2H, J=8.2 Hz), 7.5 (d, 2H, J=8.2 Hz); ^{19}F NMR δ 15.6 (d, J=4.2 Hz); MS (*m*/*z*) 218 (M^+), 183 (M^+-Cl). Anal. calcd for $C_9H_5ClF_2S$: C, 49.44; H, 2.30. Found: C, 49.11; H, 2.78.

3.1.6. α,α-Difluoropropargyl *p*-tolyl sulfide (3c). ^1H NMR δ 2.9 (t, 1H, J=4.6 Hz), 2.38 (s, 3H), 7.1–7.6 (m, 4H); ^{19}F NMR δ 15.7 (d, J=4.6 Hz); MS (*m*/*z*) 198 (M^+), 183 (M^+-CH_3), HRMS calcd for $C_{10}H_8F_2S$: 198.0315. Found: 198.0324.

3.1.7. 1,1-Difluoro-1-phenylthio-3-phenylpropyne (3d). ^1H NMR δ 7.3–7.7 (m, 10H); ^{19}F NMR δ 18.5 (s); MS (*m*/*z*) 260 (M^+), 183 (M^+-Ph). Anal. calcd for $C_{15}H_{10}F_2S$: C, 69.21; H, 3.87. Found: C, 69.19; H, 4.10.

3.2. Preparation of α-fluoroallenyl sulfides 4a–c

After electrolytic fluorination was carried out as above, the electrolytic solution containing α-fluoropropargyl sulfides **2a**–**c** were dissolved in ethanolic sodium ethoxide solution prepared from sodium metal (0.023 g, 1 mg atom) in ethanol (20 mL) and the mixture was stirred at room temperature for 3 h and then the reaction mixture was neutralized with aq. HCl. The product was extracted with chloroform and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified with preparative thin layer chromatography using pentane as eluent.

3.2.1. α-Fluoroallenyl phenyl sulfide (4a). ^1H NMR δ 5.09 (d, 2H, J=3.2 Hz), 7.2–7.5 (m, 5H); ^{19}F NMR δ −40.05 (t, J=3.2 Hz); MS (*m*/*z*) 166 (M^+), 165 (M^+-H), HRMS calcd for C_9H_7FS: 166.0253. Found: 166.0239.

3.2.2. *p*-Chlorophenyl α-fluoroallenyl sulfide (4b). ^1H NMR

δ 5.5 (d, 2H, J=2.6 Hz), 7.4 (d, 2H, J=8.2 Hz), 7.5 (d, 2H, J=8.2 Hz); ^{19}F NMR δ −45.13 (t, J=2.6 Hz); MS (m/z) 200 (M^+), 165 (M^+-Cl). Anal. calcd for C_9H_6ClFS: C, 53.87; H, 3.01. Found: C, 53.53; H, 3.06, HRMS calcd for C_9H_6ClFS: 199.9863. Found: 199.9874.

3.2.3. α-Fluoroallenyl *p*-tolyl sulfide (4c). ^{1}H NMR δ 2.31 (s, 3H), 5.5 (d, 2H, J=3.1 Hz), 7.1–7.4 (m, 4H); ^{19}F NMR δ −45.84 (t, J=3.1 Hz); MS (m/z) 180 (M^+), 165 (M^+-CH_3), HRMS calcd for $C_{10}H_9FS$: 180.0409. Found: 180.0414.

3.3. Iodination of α-fluoroallenyl sulfide 4b

To a stirred solution of **4b** (0.2 g, 1 mmol) was added a solution of iodine (0.304 g, 1.2 mmol) in CH_2Cl_2 (15 mL), and the mixture was stirred at room temperature for 4 h. The reaction mixture was quenched with 5% $Na_2S_2O_3$ (25 mL), and extracted with $CHCl_3$. The combined organic layers were dried and concentrated. The crude product was purified by column chromatography on silica gel using pentane as an eluent.

3.3.1. (*E*)-*p*-Chlorophenyl 1-fluoro-2,3-diiodo-1-propenyl sulfide (5). ^{1}H NMR δ 4.6 (s, 2H), 7.4 (d, 2H, J=8.2 Hz), 7.5 (d, 2H, J=8.2 Hz); ^{19}F NMR δ 18.84 (s); MS (m/z) 327 (M^+-I). Anal. calcd for $C_9H_6ClFI_2S$: C, 23.79; H, 1.33; I, 55.85; S, 7.06. Found: C, 23.88; H, 1.38; I, 55.64, S, 7.11.

3.4. Reaction of α-fluoroallenyl sulfide 4b with benzylamine

The mixture of α-fluoroallenyl sulfide **4b** (0.2 g, 1 mmol) and benzylamine (0.107 g, 1 mmol) in THF (20 mL) was stirred at room temperature for 40 h. The reaction was diluted with water, and extracted with chloroform repeatedly. The combined organic layers were collected, dried over anhydrous $MgSO_4$ and filtered. The filtrate was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel using a hexane/ethylacetate eleuent (5:1) to give pure **6**.

3.4.1. *p*-Chlorophenyl α-fluoroacetonyl sulfide (6). ^{1}H NMR δ 2.14 (s, 3H), 5.87 (d, 1H, J=51 Hz), 7.34 (d, 2H, J=8.2 Hz), 7.45 (d, 2H, J=8.2 Hz); ^{19}F NMR δ −82.92 (d, J=51 Hz)); ^{13}C NMR δ 27.43 (CH_3), 98.55, 128.64, 130.66, 136.41, 137.13 (CH), 199.77 (CO); MS (m/z) 218 (M^+). Anal. calcd for C_9H_8ClFOS: C, 49.43; H, 3.69; S, 14.66. Found: C, 49.29; H, 3.51; S, 14.42.

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