Electrolytic Partial Fluorination of Organic Compounds. 24.[1] Highly Regioselective Anodic Monofluorination of 2-Benzothiazolyl and 5-Chloro-2-benzothiazolyl Sulfides

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Electrochemical fluorination of 2-benzothiazolyl and 5-chloro-2-benzothiazolyl sulfides was successfully carried out using $Et_4NF{\cdot}3HF$ as a supporting electrolyte and fluoride ion source in dimethoxyethane to provide the corresponding α-monofluorinated sulfides in good yields. Fluorination took place selectively at the position α to the sulfur atom of the sulfides, and the heterocyclic moieties were not fluorinated at all.

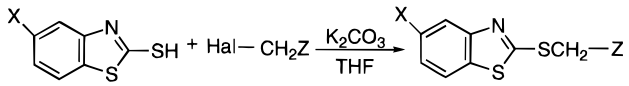
Introduction

Many fluorinated analogues of biologically important compounds have shown dramatic change or enhancement in their biological activities.[2] Therefore, many efforts for developing new fluorination methods for organic molecules have been made in the past decade.[3−5]

On the other hand, anodic oxidative fluorination is very attractive because fluorine atoms can be introduced into organic molecules in one step under safe and mild conditions.[6,7] Anodic partial fluorination of various aromatics and olefines and anodic benzylic fluorination have been reported.[6] However, beside Laurent's[8] and our works,[9] there was no report so far on anodic partial fluorination of chalcogeno compounds. Recently Laurent et al. and our group have independently found that an α-electron-withdrawing group markedly facilitated anodic α-fluorination of sulfides.[8,9a] We demonstrated that the anodic method is widely applicable to mono- and difluorination of various sulfides.[1,9] Furthermore, we have shown that simple sulfides devoid of an electron-withdrawing group could also be fluorinated anodically in good yields when ethereal solvents were used.[9e]

The usefulness of benzothiazole derivatives in various fields such as medicinal and biological chemistry is well documented.[10] Having this in mind, we attempted anodic fluorination of 2-benzothiazolyl sulfides using various fluoride salts as a supporting electrolyte and fluorine source, and it was found that such heterocyclic sulfides could be anodically fluorinated in ethereal solvent such as DME containing $Et_4NF{\cdot}3HF$ to provide the corresponding α-fluoro sulfides in good yields.

Scheme 1



1

1a : X=H, Z=CN
1b : X=H, Z=CH_3CO_2
1c : X=H, Z=CH_3CO
1d : X=Cl, Z=CN
1e : X=Cl, Z=CH_3CO_2
1f : X=Cl, Z=CH_3CO

Results and Discussion

Preparation of Heterocyclic Sulfides. The starting 2-benzothiazolyl sulfides **1a**−**f** were synthesized in good yields by the reacting 2-mercaptobenzothiazole and 5-chloro-2-mercaptobenzothiazole with α-halogeno nitriles, esters, and ketones in boiling THF in the presence of K_2CO_3 as shown in Scheme 1.[11]

Oxidation Potentials of Heterocyclic Sulfides. To investigate the effect of the electron-withdrawing groups on the oxidation potentials of sulfides **1a**−**f**, the anodic peak potentials were measured in anhydrous acetontrile containing $Bu_4N{\cdot}BF_4$ (0.1 M) by cyclic voltammertry (CV). The CV curves were obtained with a three-electrode system using platinum as the working electrode, a platinum wire as the counter electrode, and a 1 M NaCl calomel electrode (SSCE) as the reference electrode. These sulfides showed irreversible anodic waves. The first oxidation peak potentials E_p^{ox} of heterocyclic sulfides **1a**−**f**, 2-(methylthio)benzothiazole (**3**), and benzothiazole (**5**) are given in Table 1.

2-(Methylthio)benzothiazole (**3**) was found to be oxidized at a less positive potential compared with unsubstituted benzothiazole **5**, owing to the easily oxidizable sulfur atom of the methylthio group. 2-Benzothiazolyl

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(1) Part 23: Konno, A.; Fuchigami, T. *J. Org. Chem.* In press.

(2) (a) *Biomedicinal Aspects of Fluorine Chemistry*; Filler, R., Kobayashi, Y., Eds.; Kodansha & Elsevier Biomedical: Tokyo, 1982. (b) *Fluorine in Bioorganic Chemistry*; Welch, J. T., Eswarakrishnan, S., Eds.; Wiley: New York, 1991. (c) *Selective Fluorination in Organic and Bioorganic Chemistry*; Welch, J. T., Ed.; American Chemical Society: Washington, DC, 1991. (e) *Organofluorine Compounds in Medicinal Chemistry and Biomedical Applications*; Filler, R., Kobayashi, Y., Yagupolskii, L. M., Eds.; Elsevier: Amsterdam, 1992.

(3) Wilkinson J. A. *Chem. Rev.* **1992**, *92*, 505.

(4) Purrington, S. T.; Kagen, B. S.; Partrick, T. B. *Chem. Rev.* **1986**, *86*, 997.

(5) (a) Welch, J. T. *Tetrahedron* **1987**, *43*, 3123. (b) Silverster, M. J. *Aldrichimica Acta* **1991**, *24*, 32.

(6) Childs, W. V.; Christensen, L.; Klink, F. W.; Koipin, C. F. In *Organic Electrochemistry*, 3rd ed.; Lunt, H., Baizer, M. M., Eds.; Marcel Dekker: New York, 1991; Chapter 24.

(7) (a) Fuchigami, T. *Rev. Heteroatom. Chem.* **1994**, *10*, 155. (b) Fuchigami, T.; Konno, A. *J. Org. Synth. Chem. Jpn.* **1997**, *55*, 301. (c) Fuchigami, T.; Nishiyama, S. *J. Electrochem. Soc. (DENKI KAGAKU)* **1977**, *65*, 626.

(8) Brigand, J.; Laurent, E. *Tetrahedron Lett.* **1990**, *31*, 2287.

(9) (a) Fuchigami, T.; Shimojo, M.; Konno, A.; Nakagawa, K. *J. Org. Chem.* **1990**, *55*, 6074. (b) Fuchigami, T.; Narizuka, S.; Konno, A. *J. Org. Chem.* **1992,** *57*, 3755. (c) Konno, A.; Naito, W.; Fuchigami, T. *Tetrahedron Lett.* **1992**, *33*, 7017. (d) Narizuka, S.; Fuchigami, T. *J. Org. Chem.* **1993**, *58*, 4200. (e) Fuchigami, T.; Konno, A.; Nakagawa, K.; Shimojo, M. *J. Org. Chem.* **1994**, *59*, 5937. (f) Erian, A. W.; Konno, A.; Fuchigami, T. *J. Org. Chem.* **1995**, *60*, 7654.

(10) For example: Kahen, R.; Huang, F.; Khanduala, A.; Leibowitz, M. *J. Med. Chem.* **1984**, *27*, 121. (b) White, E. H.; McCapra, F.; Field, G. F. *J. Am. Chem. Soc.* **1963** *85*, 337. (c) Suzuki, N.; Goto, T. *Tetrahedron* **1972**, *28*, 4075.

(11) (a) Litvinov, V. P.; Rodinovskaya, L. A.: Sharanin, Yu. A.; Shestopalov, A. M. *Sulfur Rep.* **1992**, *13*, 1. (b) Elnagdi, M. H.; Abdelragek, F. M.; Ibrahim, N. S.; Erian, A. W. *Tetrahedron* **1989**, *45*, 3597.

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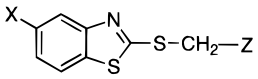
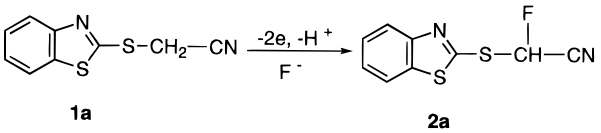
Table 1. Oxidation Potentials (Peak Potentials, E_p^{ox}) of 2-Benzothiazolyl Sulfides and Benzothiazole[a]



sulfide no.	X	Z	E_p^{ox} (V vs SSCE)
1a	H	CN	2.02
1b	H	CO_2Me	1.82
1c	H	COMe	1.82
1d	Cl	CN	2.04
1e	Cl	CO_2Me	1.95
1f	Cl	COMe	1.90
3	H	H	1.72
5	benzothiazole		2.17

[a] In 0.1 M $Bu_4N{\cdot}BF_4$/MeCN. Sweep rate: 100 m V/s.

Scheme 2



1a **2a**

Table 2. Effect of Supporting Electrolyte and Solvent on Anodic Fluorination of 2-Benzothiazolyl Cyanomethyl Sulfide (1a)

solvent	supporting electrolyte	charge passed, F/mol	yield (%)
CH_3CN	$Et_3N{\cdot}3HF$	7.5	9[a]
CH_3CN	$Et_3N{\cdot}5HF$	4	18
CH_3CN	$Et_4NF{\cdot}3HF$	9	4[a]
DME	$Et_3N{\cdot}3HF$	6	40
DME	$Et_3N{\cdot}5HF$	8	20[a]
DME	$Et_4NF{\cdot}3HF$	5.8	48
CH_2Cl_2	$Et_4NF{\cdot}3HF$	6	17

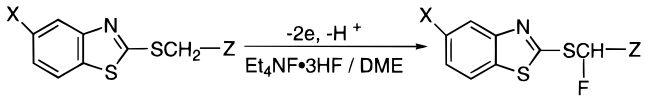
[a] Starting material **1a** was recovered.

sulfides **1a**−**f**, were oxidized at more positive potentials than unsubstituted sulfide **3**, owing to the electron-withdrawing effect exerted by substituents Z. It is worth noting that 2-benzothiazolyl sulfides **1a**−**f** showed also less positive oxidation potential as compared to **5**. It was also found that the oxidation potential increases almost linearly with the increase of the electron-withdrawing ability of substituents Z in the following order: H < CH_3CO < CH_3COO < CN. This clearly indicates that the polar effect of substituents Z plays a significant role in the electron-transfer step from the sulfur atom of the methylthio group to the anode. Moreover, the chloro atom at the benzothiazolyl ring also shifts, slightly (**1d**) or significantly (**1e**, **1f**), the oxidation potential of the sulfides toward more positive values.

Anodic Fluorination of 2-Benzothiazolyl Sulfides. Initially, anodic monofluorination was investigated in detail using 2-benzothiazolyl cyanomethyl sulfide (**1a**) as a model compound (Scheme 2). The fluorination was carried out in an undivided cell at constant current using platinum plate electrodes and anhydrous acetonitrile or dimethoxyethane (DME) containing various fluoride salts as the supporting electrolyte and fluoride ion source. The results are summarized in Table 2.

As shown in Table 2, anodic fluorination of **1a** in DME proceeded to give the corresponding monofluorinated product **2a**. Among supporting electroclytes used, $Et_4NF{\cdot}3HF$ gave the best result. A series of $Et_3N{\cdot}n$HF and $R_4NF{\cdot}n$HF salts developed recently as effective fluoride ion source and supporting electrolyte have been successfully applied to the anodic fluorination of organic

Scheme 3

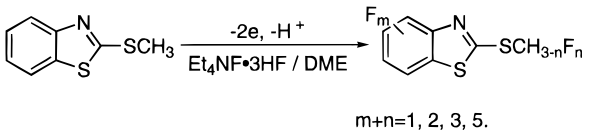


1a~1f **2a~2f**

Table 3. Anodic Fluorination of 2-Benzothiazolyl and 2-(5-Chlorobenzothiazolyl) Sulfides Having Electron-Withdrawing Groups

sulfide no.	X	Z	charge passed (F/mol)	yield (%)
1a	H	CN	5.8	**2a** 48
1b	H	CO_2Me	3.5	**2b** 62
1c	H	COMe	3.8	**2c** 46
1d	Cl	CN	4.5	**2d** 51
1e	Cl	CO_2Me	2.5	**2e** 82
1f	Cl	COMe	3	**2f** 58

Scheme 4



3 **4**

compounds.[12−14] $Et_3N{\cdot}3HF$ was shown to be excellent for selective anodic fluorination of organo sulfur compounds while $Et_3N{\cdot}5HF$[14] was demonstrated to be effective for the anodic fluorination of organic compounds having high oxidation potentials. However, these reagents exhibited low reactivity and gave low product yields due to a nonconductive polymer deposition on the surface of the anode to cause in both cases strong passivation during the electrolysis. On the contrary, the use of $Et_4NF{\cdot}3HF$/DME did not cause any passivation and gave a reasonable yield of **2a**. Thus, $Et_4NF{\cdot}3HF$/DME was found to be a suitable electrolytic solution for the anodic fluorination of heterocyclic sulfides.

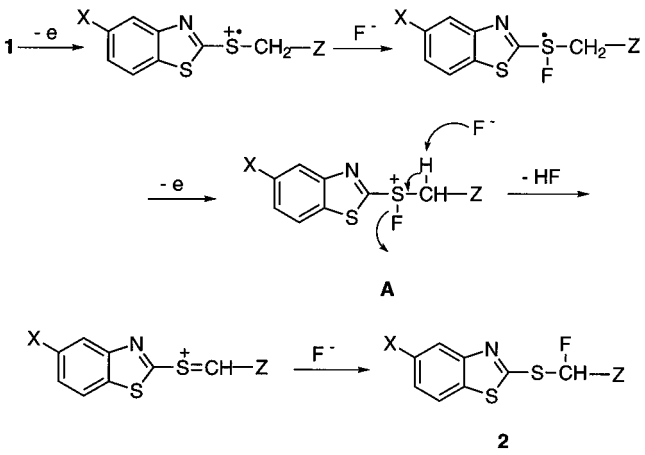
Next, the reaction was extended to various 2-benzothiazolyl sulfides bearing electron-withdrawing groups (**1b**−**f**) (Scheme 3). The monofluorination proceeded well regardless of nature of the electron-withdrawing substitutent. A fluorine atom was introduced exclusively into the position α to both the sulfur atom and the electron-withdrawing group to afford compounds **2** in good yields as shown in Table 3.

Moreover, we attempted anodic fluorination of 2-(methylthio)benzothiazole (**3**) devoid of an electron-withdrawing group. In contrast to alkyl phenyl sulfides which underwent anodic fluorination to provide α-monofluoro sulfides successfully,[9e] selective anodic fluorination did not occurr and complex polyfluorinated products **4** were formed as shown in Scheme 4. Therefore, the presence of an electron-withdrawing group is essential for a successful selective fluorination of 2-benzothiazolyl sulfides **1a**−**f**.

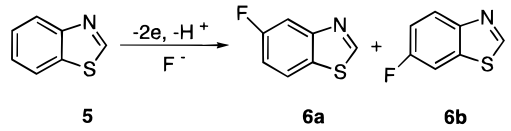
An $EC_{Nu}EC_{Nu}$ (electrochemical, chemical, electrochemical, chemical) mechanism is widely accepted for anodic nuclephilic substitution.[15] However, anodic fluorination of sulfides does not follow such simple mechanism. We have already proposed a Pummerer type mechanism *via*

(12) $R_4NF{\cdot}n$HF ($n \geq 4$): Momota, K.; Morita, M.; Matsuda, Y. *Electrochim. Acta* **1993**, *38*, 619.
(13) Meurs, J. H. H.; Eilenberg, W. *Tetrahedron* **1991**, *47*, 705.
(14) (a) Yoneda, N.; Chen, S.-Q.; Hatakeyama, T.; Hara, S.; Fukura, T. *Chem. Lett.* **1994**, *849*. (b) Hara, S.; Chen, S.-Q.; Yoneda, N. *Tetrahedron Lett.* **1995**, *36*, 6511.

Scheme 5



Scheme 6



the fluorosulfonium ion for this reaction as shown in Scheme 5.[9e,f] Considering failure of anodic fluorination of 2-(methylthio)benzothiazole (**3**), the regioselectivity can be explained in terms of facilitated deprotonation of **A**. Due to the effect of the electron-withdrawing group, deprotonation of **A** derived from **1** should occur more easily as compared to **A** derived from **3**; therefore, high regioselectivity observed in these anodic fluorinations is reasonable.

Anodic fluorination of simple benzothiazole **5** was also attempted (Scheme 6). The formation of 5- and 6-fluorobenzothiazoles **6a** and **6b** was detected by MS [*m*/*z* 153 (M^+), 134 ($M^+ - F$), 126 ($M^+ - HCN$)] and ^{19}F NMR spectra [δ −34.53 (dd, J = 5.6, 9.3 Hz) and −45.37 (dd, J = 4.5, 10.1 Hz)]. However, compound **6** could not be isolated because of extremely low yields. In this case, the thiazolyl ring was not fluorinated at all as shown by the ^{19}F NMR spectra mentioned above. This result is quite similar to the cases of the anodic fluorination of oxindole in $Me_4NF{\cdot}4HF$[16] and isoquinoline in $Et_4NF{\cdot}4HF$/MeCN.[17] In those cases, polyfluorination took place at the benzene ring predominately and the heterocyclic moiety was not fluorinated at all. The reason is not clear at the present stage.

It is well-known that fluorinated sulfides could be prepared from the corresponding sulfides using XeF_2 or DAST; however, the former reagent is costly and the latter one requires the corresponding sulfoxides as the starting material. Recently, *N*-fluoropyridinium triflates and tetrafluoroborates have been shown to be alternative fluorination reagents.[18] However, fluorination of **1e** as a model compound with various types of *N*-fluoropyridinium triflates resulted in no formation of the desired product. Therefore, the electrochemical fluorination is more advantageous than the conventional chemical methods for such heterocyclic sulfides: successful fluorination can be achieved in one step under mild conditions.

In summary, we successfully carried out anodic monofluorination of 2-benzothiazolyl and 5-chloro-2-benzothiazolyl sulfides and have found that this fluorination is greatly affected by the supporting fluoride salts as well as the electrolytic solvents. These findings could be of importance for future selective anodic fluorination of organic molecules.

Experimental Section

Caution. $Me_4NF{\cdot}3HF$, $Et_3N{\cdot}3HF$, and $Et_3N{\cdot}5HF$ are toxic and if in contact with skin causes serious burn, so proper safety precautions should be taken all the time. It is therefore recommended to protect hands with rubber gloves.

^1H NMR and ^{19}F NMR spectra were recorded at 270 MHz using $CDCl_3$ as a solvent. The chemical shifts for ^1H and ^{19}F NMR are given in δ ppm downfield from TMS and TFA, respectively. Analytical instruments are described in our previous paper.[16b]

Preparation of 2-Benzothiazolyl Sulfides 1a−c and 5-Chloro-2-benzothiazolyl Sulfides 1d−f. To a solution of 2-mercaptobenzothiazole or 5-chloro-2-mercaptobenzothiazole (0.02 mol) in 40 mL of THF containing 3 g (0.024 mol) of K_2CO_3 was added α-halogeno compound (0.02 mol). The reaction mixture was heated under reflux for 1 h. The product was purified by column chromatography on silica gel (hexane: AcOEt = 5:1) to provide the desired product **1**.

2-Benzothiazolyl cyanomethyl sulfide (1a):[19a] ^1H NMR δ 4.19 (s, 2H), 7.36 (td, J = 7.4, 1.3 Hz, 1H), 7.47 (td, J = 7.3, 1.3 Hz, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 7.6 Hz, 1H); MS *m*/*z* 206 (M^+), 166 ($M^+ - CH_2CN$). Anal. Calcd for $C_9H_6N_2S_2$: C, 52.40; H, 2.93; N, 13.58. Found: C, 52.30; H, 2.74; N, 13.57.

2-Benzothiazolyl (methoxycarbonyl)methyl sulfide (1b):[19a] ^1H NMR δ 3.79 (s, 3H), 4.20 (s, 2H), 7.30 (td, J = 7.3, 1.3 Hz, 1H), 7.42 (td, J = 7.3, 1.3 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 8.9 Hz, 1H); MS *m*/*z* 239 (M^+), 180 ($M^+ - CH_3CO_2$). Anal. Calcd for $C_{10}H_9NO_2S_2$: C, 50.19; H, 3.79; N, 5.85. Found: C, 50.09; H, 3.43; N, 5.78.

2-Acetonyl benzothiazolyl sulfide (1c):[19b] ^1H NMR δ 2.40 (s, 3H), 4.24 (s, 2H), 7.30 (td, J = 7.9, 1.3 Hz, 1H), 7.42 (td, J = 7.3, 1.3 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.83 (d, J = 7.3 Hz, 1H); MS *m*/*z* 223 (M^+), 208 ($M^+ - CH_3$), 180 ($M^+ - CH_3CO$). Anal. Calcd for $C_{10}H_9NOS_2$: C, 53.79; H, 4.06; N, 6.27. Found: C, 53.70; H, 3.85; N, 6.22.

2-(5-Chlorobenzothiazolyl) cyanomethyl sulfide (1d):[19c] ^1H NMR δ 4.19 (s, 2H), 7.34 (dd, J = 8.6, 2.0 Hz, 1H), 7.71 (d, J = 8.6 Hz, 1H), 7.94 (d, J = 2.0 Hz, 1H); MS *m*/*z* 240 (M^+), 200 ($M^+ - CH_2CN$). Anal. Calcd for $C_9H_5ClN_2S_2$: C, 44.91; H, 2.09; N, 11.64. Found: C, 44.94; H, 1.83; N, 11.69.

2-(5-Chlorobenzothiazolyl) (methoxycarbonyl)methyl sulfide (1e):[19a] ^1H NMR δ 3.79 (s, 3H), 4.18 (s, 2H), 7.28 (dd, J = 8.6, 2.0 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 2.2 Hz, 1H); MS *m*/*z* 273 (M^+), 214 ($M^+ - CH_3CO_2$) Anal. Calcd for $C_{10}H_8ClNO_2S_2$: C, 43.88; H, 2.95; N, 5.12. Found: C, 44.22; H, 2.73; N, 5.13.

Acetonyl 2-(5-chlorobenzothiazolyl) sulfide (1f): solid; ^1H NMR δ 2.40 (s, 3H), 4.24 (s, 2H), 7.28 (dd, J = 8.6, 2.0 Hz, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 2.0 Hz, 1H); MS *m*/*z* 257 (M^+), 242 ($M^+ - CH_3$), 214 ($M^+ - CH_3CO$). Anal. Calcd for $C_{10}H_8ClNOS_2$: C, 46.60; H, 3.13; N, 5.43. Found: C, 46.67; H, 3.16; N, 5.36.

(15) (a) Weinberg, N. L.; Reddy. T. B. *J. Am. Chem. Soc.* **1968**, *90*, 91. (b) Shono, T.; Hamaguchi, H.; Matsumura, Y. *J. Am. Chem. Soc.* **1975**, *97*, 4264. (c) Fuchigami, T.; Yamamoto, K.; Nakagawa, Y. *J. Org. Chem.* **1991**, *56*, 137. (d) Fuchigami, T.; Yamamoto, K.; Konno, A. *Tetrahedron* **1991**, *47*, 625. (e) Fuchigami, T.; Ichikawa, S. *J. Org. Chem.* **1994**, *59*, 607.

(16) (a) Hou, Y.; Higashiya, S.; Fuchigami, T. *Synlett* **1997**, 655. (b) Hou, Y.; Higashiya, S; Fuchigami, T. *J. Org. Chem.* In press.

(17) Kato, K.; Momota, K. The 18th Symposium on Electroorganic Chemistry, Nagoya, Jpn, 1995, Abstr. 101.

(18) (a) Umemoto, T.; Tomizawqa, G. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3625 (b) Umemoto, T.; Tomizawa, G. *J. Org. Chem.* **1995**, *60*, 6563.

(19) (a) D'Amoco; John, J. U.S. Patent 4448399, 1984; *Chem. Abstr.* **1984**, *101*, 151837h. (b) Antonova, A.; Kalcheva, V. *Izv. Khim.* **1989**, *22*, 158. (c) Wei, P. H. L.; Bell, S. C. U.S. Patent 4443606, 1982; *Chem. Abstr.* **1984**, *101*, 23468b.

Anodic Fluorination of Benzothiazolyl Sulfides 1a−f. Typical Procedure. The electrolyses were carried out with platinum plate electrodes (2 × 2 cm^2) in a 1 M $Et_4NF·3HF$/DME system (10 mL) to which compound **1** (1 mmol) was added. An undivided cell was used under a nitrogen atmosphere at room temperature. Constant current (5 mA/cm^2) was passed until the starting material **1** was consumed (checked by TLC and GC-MS). After the electrolysis, the electrolyte was neutralized with 10% aqueous ammonia solution and the resulting aqueous solution was extracted repeatedly with ether. The combined extracts were dried over anhydrous $MgSO_4$, and fluorinated compound **2** was isolated by column chromatography on silica gel (hexane:AcOEt = 10:1).

2-Benzothiazolyl fluorocyanomethyl sulfide (2a): ^{1}H NMR δ 7.32 (d, J = 49.2 Hz, 1H), 7.43 (td, J = 7.3, 1.3 Hz, 1H), 7.53 (td, J = 7.3 Hz, 1.3 Hz, 1H), 7.86 (d, J = 7.7 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H); ^{19}F NMR δ −79.92 (d, J = 49.2 Hz); MS m/z 224 (M^+), 179 ($M^+ - CN - F$); HRMS m/z calcd for $C_9H_5FN_2S_2$ 223.9878, found 223.9879.

Methyl α-fluoro-α-(2-benzothiazolylthio)acetate (2b): ^{1}H NMR δ 3.89 (s, 3H), 6.97 (d, J = 50.8 Hz, 1H), 7.38 (td, J = 7.9, 1.3 Hz, 1H), 7.48 (td, J = 7.3, 1.3 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.98 (d, J = 7.9 Hz, 1H); ^{19}F NMR δ −84.8 (d, J = 50.2 Hz); MS m/z 257 (M^+), 226 ($M^+ - CH_3O$), 198 ($M^+ - CH_3CO_2$); HRMS m/z calcd for $C_{10}H_8FNO_2S_2$ 256.9981, found 256.9982. Anal. Calcd for $C_{10}H_8FNO_2S_2$: C, 46.69; H, 3.13; N, 5.44. Found: C, 47.20; H, 3.23; N,5.25.

2-Benzothiazolyl α-fluoroacetonyl sulfide (2c): ^{1}H NMR δ 2.46 (d, J = 3.3 Hz, 1H), 6.80 (d, J = 50.5, 1H), 7.36 (td, J = 8.6, 1.3 Hz, 1H), 7.46 (td, J = 7.3, 1.3 Hz, 1H), 7.79 (d, J = 7.3 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H); ^{19}F NMR δ −85.75 (dq, J = 50.5, 3.1 Hz); MS m/z 241 (M^+), 166 ($M^+ - CH_3COCHF$). Anal. Calcd for $C_{10}H_8FNOS_2$: C, 49.78; H, 3.34; N, 5.80. Found: C, 49.70; H, 3.29; N, 5.78.

2-(5-Chlorobenzothiazolyl) fluorocyanomethyl sulfide (2d): ^{1}H NMR δ 7.31 (d, J = 48.8 Hz, 1H), 7.40 (dd, J = 8.6, 2.0 Hz, 1H), 7.76 (d, J = 8.3 Hz, 1H), 7.99 (d, J = 2.0 Hz, 1H); ^{19}F NMR δ −80.40 (d, J = 48.4 Hz); MS m/z 258 (M^+), 213 ($M^+ - F - CN$); HRMS m/z calcd for $C_9H_4ClFN_2S_2$ 257.9488, found 257.9499. Anal. Calcd for $C_9H_4ClFN_2S_2$: C, 41.78; H, 1.56; N, 10.83. Found: C, 41.75; H, 1.48; N, 10.67.

Methyl α-fluoro-α-[[2-(5-chlorobenzothiazolyl)]thio]-acetate (2e): ^{1}H NMR δ 3.93 (s, 3H), 6.98 (d, J = 50.5 Hz, 1H), 7.35 (dd, J = 8.6, 2.0 Hz, 1H), 7.71 (d, J = 8.6 Hz, 1H), 7.94 (d, J = 2.0 Hz, 1H); ^{19}F NMR δ −85.14 (d, J = 50.2 Hz); MS m/z 291 (M^+), 232 ($M^+ - CH_3CO_2$); HRMS m/z calcd for $C_{10}H_7ClFNO_2S_2$ 290.9591, found 290.9592. Anal. Calcd for $C_{10}H_7ClFNO_2S_2$: C, 41.17; H, 2.42; N, 4.80. Found: C, 41.21; H, 2.44; N, 4.84.

2-(5-Chlorobenzothiazolyl) α-fluoroacetonyl sulfide (2f): ^{1}H NMR δ 2.49 (d, J = 3.3 Hz, 3H), 6.80 (d, J = 50.2 Hz, 1H), 7.34 (dq, J = 8.6, 2.0 Hz, 1H), 7.69 (d, J = 8.6 Hz, 1H), 7.91 (d, J = 1.7 Hz, 1H); ^{19}F NMR δ −85.51 (dd, J = 50.2, 3.3 Hz); MS m/z 275 (M^+), 213 ($M^+ - CH_3CO - F$), 200($M^+ - CH_3COCHF$); HRMS m/z calcd for $C_{10}H_7ClFNOS_2$ 274.9642, found 274.9647. Anal. Calcd for $C_{10}H_7ClFNOS_2$: C, 43.56; H, 2.56; N, 5.08. Found: C, 43.51; H, 2.30; N, 5.20.

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