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Electrolytic partial fluorination of organic compounds. 36 [1]. Regioselective anodic fluorination of phenylthiolated benzofuranone and benzothiazole derivatives

Seiichiro Higashiya, Kamal M. Dawood[1], Toshio Fuchigami*

Department of Electronic Chemistry, Tokyo Institute of Technology, 4259, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

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Dedicated to the 75th birthday of Dr. Yoshiro Kobayashi, Emeritus Professor of Tokyo University of Pharmacy and Life Science

Abstract

The anodic fluorination of 3-phenylthio-2-benzofuranones and α-phenylthio-2-benzothiazolylacetonitrile was investigated. Both derivatives were selectively fluorinated in good yields at the carbon α to the sulfur atoms in $Et_4NF{\cdot}3HF$/DME using a platinum anode and an undivided cell. The fluorination yields of the benzofuranone derivatives were improved by the addition of Ph_2S, which was not effective in the case of the benzothiazole derivative. The fluorination yield of the benzothiazole derivative was strongly affected by the stirring state of the electrolytic solution or the applied anode potential.

Keywords: Selective anodic fluorination; Benzofuranone; Benzothiazole; Phenylthio group; Electroauxiliary; Mediator

1. Introduction

The incorporation of fluorine atom(s) into organic or bioorganic compounds sometimes drastically changes their physical, chemical, and biological properties [2,3]. We have been investigating the oxidative incorporation of fluorine atom(s), especially, using an electrochemical method, i.e., anodic fluorination to synthesize potent biologically active compounds [4–10]. In these studies, organic molecules were regioselectively fluorinated in excellent to good yields under very mild conditions.

In this paper, we report the selective anodic fluorination of biologically active benzofuranone [11] and benzothiazole derivatives [12,13] to provide more potent active analogs.

2. Results and discussion

2.1. Synthesis, electrochemical and chemical properties of phenylthiolated benzofuranone 2 and benzothiazolylacetonitrile derivatives 4

5-Chloro-2-benzofuranone **1b** was synthesized via the chlorination of commercially available 2-benzofuranone (2-coumaranone) **1a** by *N*-chlorosuccinimide (NCS) without any radical initiators in a polar solvent as CH_3CN. The synthesis of the 3-phenylthiolated 2-benzofuranones (**2**) and α-phenylthiolated 2-benzothiazolylacetonitrile (**4**) were achieved via phenylthiolation of **1** and **3**, respectively, by diphenyl disulfide in the presence of a base (Scheme 1).

In the case of **2**, the yields were not so high, because the parent benzofuranones **1** easily underwent the Claisen condensation to give dimerized product **5** under basic conditions [11,14]. The methine protons of these phenylthiolated compounds **2** and **4** seems to be acidic, because their extraction from alkaline aqueous solutions was not efficient. The ^1H NMR of the methine proton of **4** in DMSO appeared in a very low field around 12.5 ppm as two broad singlets,

*Corresponding author. Fax: +81-45-924-5406
E-mail address: fuchi@echem.titech.ac.jp (T. Fuchigami)

[1]UNESCO Research Fellow (1997–1998). Present address: Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt.

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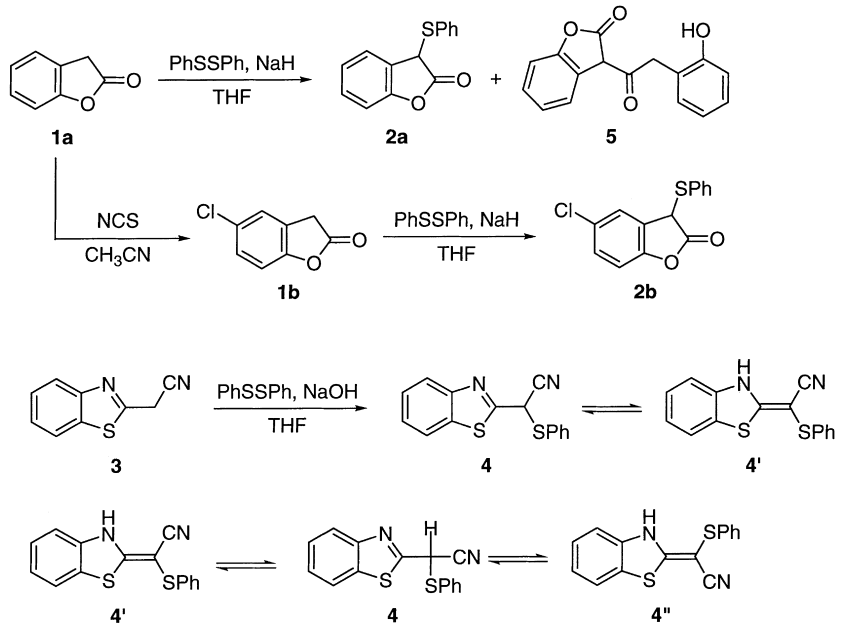


Scheme 1.

instead of the usual field around 5–6 ppm, possibly due to tautomers **4′** and **4″** in a very polar solvent like DMSO as described in Scheme 1.

Prior to the anodic fluorination of **2** and **4**, we measured the oxidation peak potentials by cyclic voltammetry (Table 1). Compound **4** showed a prepeak at 0.95 V vs. a sodium saturated calomel electrode (SSCE). This prepeak was found to be related to the yield of the anodic fluorination of **4**, as described later (Section 2.3).

2.2. *Anodic fluorination of 3-phenylthiolated benzofuranone derivatives* **2**

First of all, we attempted anodic fluorination of 3-phenylthio-2-benzofuranone (**2a**) using 1 M $Et_4NF{\cdot}3HF$ solutions (Table 2).

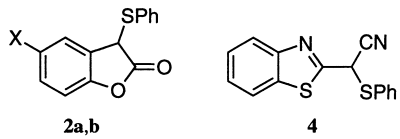
1,2-Dimethoxyethane (DME, run 2) gave the corresponding α-fluorinated product **6a** in a higher yield than CH_3CN (run 1), and the addition of Ph_2S [15] also improved the yield from 76% to 84% (run 3). Potentiostatic electrolysis did not significantly improve the yield (run 4). The product **6a** was unstable, especially in the crude and concentrated state. It rapidly decomposed at temperature higher than 50°C and gradually decomposed even at room temperature. Compound **6a** also decomposed by eliminating hydrogen fluoride and the PhS group to produce an unidentified products and a dithioacetal derivative **7** as denoted in Scheme 2, during the removal of the electrolyte by extraction or passing through a silica gel column if the silica gel was not well-dried. Such migration of a PhS group was previously reported by our group [16].

A dimerized compound **8** was also found. It seems to be formed via the dimerization of the anodically generated radical intermediate **A**, which should be stabilized by captodative and resonance effects.

Finally, the product **6a** was partly purified using the silica gel which was well-dried by heating in vacuo and then deactivated by ethyl acetate in order to reduce the heat generated when the substrate was adsorbed on the silica gel.

This unstability of **6a** could be attributed to the stabilization of the benzylic cation by the phenolic oxygen atom. Considering this point, we next tried the anodic fluorination of **2b** which has a chlorine atom on the benzene ring to destabilize the corresponding benzyl cation generated from the fluorinated product **6b**. As expected, **6b** was more stable than **6a**, but the yield was much lower under the same conditions used for the anodic fluorination of **2a** (Table 2, run 5). However, when the stirring of the solution was stopped during the electrolysis (still condition), the yield of **6b** was significantly increased (run 6). Use of $Et_4NF{\cdot}4HF$/DME and Ph_2S also improved markedly the

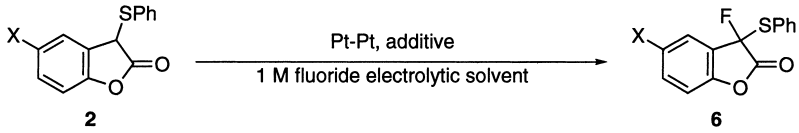
Table 1
Oxidation peak potentials (E_p^{ox}) of phenylthiolated benzofuranone and benzothiazolylacetonitrile derivatives **2**, **4**[a]



Substrate	X	E_p^{ox} (V vs. SSCE[b])
2a	H	1.85, 1.98
2b	Cl	1.88, 2.72
4	–	0.95, 2.8 (sh)

[a] In 0.1 M Et_4NClO_4/CH_3CN. Sweep rate: 100 mV s^{-1}.
[b] Sodium saturated calomel electrode.

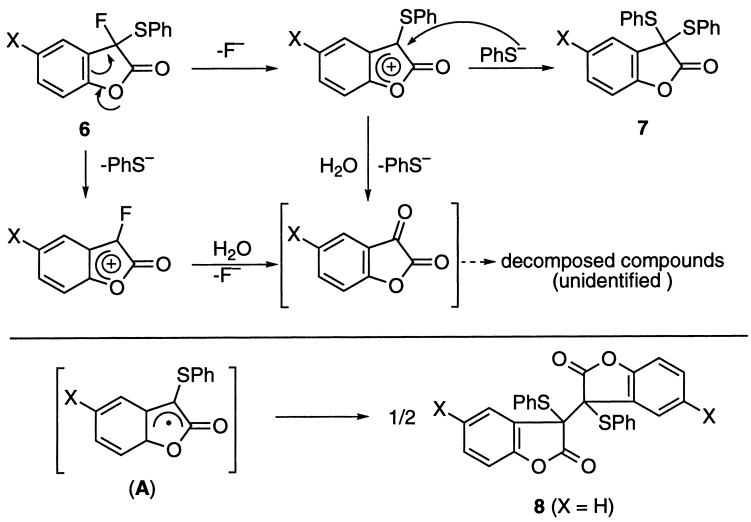
Table 2
Anodic fluorination of 3-phenylthiolated benzofuranone derivatives **2**



2 **6**

Run	Substrate	Fluoride Salt/electrolytic solvent	Additive (equiv.)	Other conditions	Electricity (F mol^{-1})	Yield of **6** (%)[a]
1	**2a** (X = H)	$Et_4NF{\cdot}3HF/CH_3CN$	–	5 mA cm^{-2}[b], stirr	3.0	40
2		$Et_4NF{\cdot}3HF$/DME	–	5 mA cm^{-2}[b], stirr	2.2	76 (23)
3		$Et_4NF{\cdot}3HF$/DME	Ph_2S (0.5)	5 mA cm^{-2}[b], stirr	2.5	84
4		$Et_4NF{\cdot}3HF$/DME	Ph_2S (0.5)	1.6 V vs. Ag/0.01 M Ag^{+}[c]	2.2	76
5	**2b** (X = Cl)	$Et_4NF{\cdot}3HF$/DME	–	5 mA cm^{-2}[b], stirr	3.0	14
6		$Et_4NF{\cdot}3HF$/DME	–	5 mA cm^{-2}[b], stirr	3.5	49
7		$Et_4NF{\cdot}4HF/CH_3CN$	–	5 mA cm^{-2}[b], stirr	3.5	49
8		$Et_4NF{\cdot}4HF$/DME	–	5 mA cm^{-2}[b], stirr	3.0	61 (42)
9		$Et_4NF{\cdot}4HF$/DME	Ph_2S (0.5)	5 mA cm^{-2}[b], stirr	3.5	74

[a] Determined by ^{19}FNMR; isolated yields are denoted in parentheses.
[b] Potentiostatic electrolysis.
[c] Galvanostatic electrolysis.



Scheme 2.

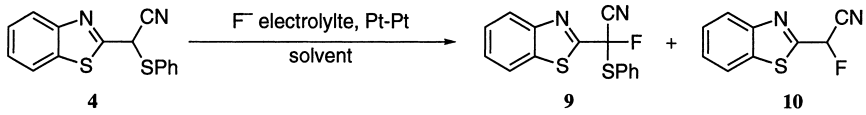
yields of **6b** (runs 8 and 9), but when the solvent was changed to CH_3CN, the yield was decreased (run 7).

2.3. *Anodic fluorination of* α*-phenylthiolated benzothiazolylacetonitrile* **4**

Next, α-phenylthiolated benzothiazolylacetonitrile **4** was subjected to anodic fluorination under various electrolytic conditions (Table 3).

In almost all the cases, the α-fluorinated product **9** was formed with a trace amount of the desulfurizatively fluorinated product **10** (the maximum yield was 5% (run 12)). Compound **9** was much more stable than the α-fluorinated benzofuranone derivatives **6**. DME gave better yields than CH_3CN (run 1) similar to the case of compounds **2**. $Et_4NF{\cdot}4HF$ (run 2) and $Et_4NF{\cdot}3HF$ (run 3) gave almost the same results, but the current efficiency of the latter was better, and $Et_4NF{\cdot}3HF$ is less corrosive to the glassware compared to the former. The addition of Ph_2S (run 4) or the use of a divided cell (run 5) had almost no effect on the yields, but when the electrolytic solution was not stirred during the electrolysis (run 6), the yield of **9** significantly increased. These results implied that a higher anodic potential gave the better yield in this case. Therefore, we carried out the anodic fluorination of **4** at various anodic potentials and the resulting yield-anodic potential relationship (runs 7–13) was compared with the linear sweep voltammogram of the substrate **4** (Fig. 1).

Table 3
Anodic fluorination of α-phenylthiolated benzothiazolylacetonitrile **4**



4 **9** **10**

Run	Electrolyte	Solvent	Other conditions	Electricity (F mol^{-1})	Yield of **9** (%)[a]
Galvanostatic, 5 mA cm^{-2}					
1	1 M $Et_4NF{\cdot}3HF$	CH_3CN		3.0	4
2	1 M $Et_4NF{\cdot}4HF$	DME		6.0	11
3	1 M $Et_4NF{\cdot}3HF$			3.0	11
4			Ph_2S (0.5 equiv.)	3.5	12
5			Divided cell[b]	3.0	14
6			Still	3.5	52
Potentiostatic, vs. Ag/0.01 M Ag					
7			0.6 V	1.5	0
8			1.0 V	1.4	9
8			1.4 V	1.2	16
10			1.8 V	2.8	39
11			2.1 V	4.0	39
12			2.1 V, still	4.0	53[c]
13			2.4 V	8.0	33

[a] Determined by ^{19}F NMR.
[b] The cell was divided using an anion exchange membrane.
[c] **10** was formed in 5% yield.

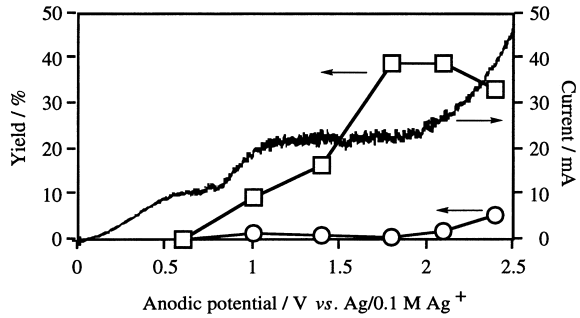


Fig. 1. Yield-potential plot and linear sweep voltammogram of α-phenylthiolated benzothiazolylacetonitrile **4** (electrolytic solution: 1 M $Et_4NF{\cdot}3HF$/DME; Pt electrodes; yield-potential plot, □ : yield of **9**; ○: yield of **10**; notched line: linear sweep voltammogram of **4** at a sweep rate of 50 mV s^{-1} with stirring).

As expected, the yield increased as the anodic potential increased, but the yields in the stirring cases (runs 7–11, 13) were lower than those in the still cases (runs 6,12). Even when the anodic fluorination was carried out at 0.6 V vs. Ag/0.01 M Ag^+ which corresponded to the prepeak potential (ca. 0.9 V vs. SSCE), the substrate was almost consumed, but the desired product **9** was not formed. In the linear sweep voltammogram, two waves were observed at 0.5 and 1.0 V, and the fluorinated product could be obtained in moderate yield above the potential of the second wave.

During the electrolysis, a needle-like, highly crystalline reddish-orange precipitate began to deposit from the solution after the charge of ca. 0.2F mol^{-1} was passed. This compound was not yet well-defined because of its quite low solubility even in DMSO, but the result of the elemental analysis predicted the structure as the oxidatively desulfurizative dimer **11** denoted in Scheme 3.

After the first oxidation step, if the anodic potential is not high enough or the intermediate cation radical **B** migrates to the bulk from the anodic surface, the second oxidation does not take place and the cation radical intermediate **B** releases a proton and the phenylthio radical. The latter radical dimerizes to diphenyl disulfide and in some cases, diphenyl disulfide is further oxidized to *S*-phenyl thiobenzenesulfonate. The resulting benzothiazolylacetonitrile carbene **C** seems to dimerize to yield **11**.

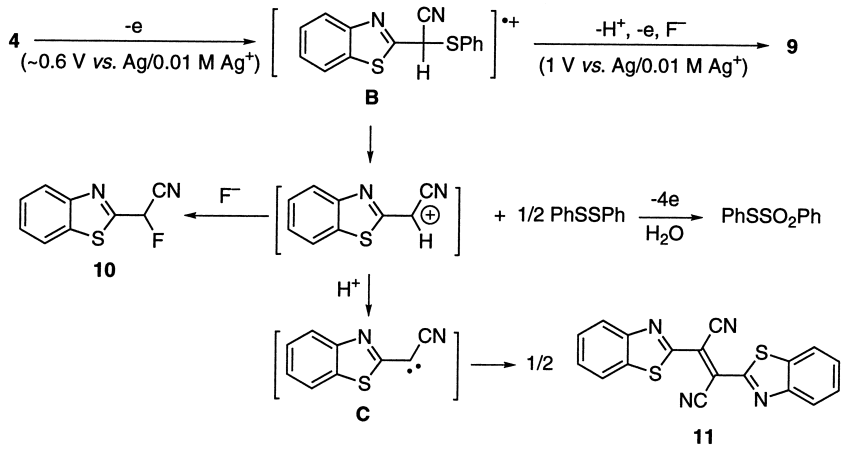
Under still conditions, **10** was formed in a maximum yield as 5%. Therefore, the proposed mechanism as shown in Scheme 3 would be reasonable.

3. Experimental

3.1. General

Caution: $Et_4NF{\cdot}4HF$ is toxic and may cause serious burns if it comes in contact with unprotected skin, while $Et_4NF{\cdot}3HF$ is much less aggressive, so proper safety precautions should be taken at all times. Therefore, the use of rubber gloves is recommended to protect the hands.[17]

^1H NMR, ^{19}F NMR, and ^{13}C NMR spectra were recorded at 270, 254, and 68 MHz, respectively, in $CDCl_3$ as the solvent using a JEOL EX-270 spectrometer. The chemical shifts for the ^1H and ^{13}C NMRs are given in δ ppm downfield



Scheme 3.

from internal TMS and the ^{19}F NMR chemical shifts are given in δ ppm downfield from external CF_3COOH. To determine the crude yield of the fluorinated products, a certain amount of monofluorobenzene was added to the crude solution, and the yield was calculated by comparison between the integration values of the fluorine NMR signals of the fluorinated products and monofluorobenzene. Mass spectra were obtained with Shimadzu GCMS-QP2000A and JEOL JMS-700 mass spectrometers. Cyclic voltammetry was performed using a Hokuto Denko Potentiostat/Galvanostat HA 6-151 at a scan speed of 100 mV s^{-1} in 0.1 M Et_4NClO_4/CH_3CN. Preparative electrolysis experiments were carried out using a Potentiostat/Galvanostat HA-501 and a Coulomb/Amperehour meter HF-201 (Hokuto Denko,) with a reference electrode (Ag wire/0.01 M $AgNO_3$, 0.1 M Et_4NBF_4 in CH_3CN) for the potentiostatic electrolysis, and a Metronix Corp. (Tokyo) constant current power supply for the galvanostatic electrolysis.

3.2. Preparation of 5-chloro-2-benzofuranone **1b**

To a 100-ml round flask, 2-benzofuranone **1a** (2-coumaranone, 1.92 g, 14.3 mmol), *N*-chlorosuccinimide (5.72 g, 42.6 mmol) and anhydrous CH_3CN (50 ml) were added and the solution was vigorously stirred for 1 week. CH_3CN was then evaporated and the residue was diluted with toluene. The organic solution was washed with one portion of aq. $Na_2S_2O_3$ and two portions of H_2O, then dried over $MgSO_4$. After removal of the $MgSO_4$, the solvent was evaporated and the residue was purified by silica gel column chromatography using a linear gradient of 0–50% toluene in hexane. After removal of the solvent, the residue was recrystallized from Et_2O/hexane to give the product **1b** in 74% yield (1.78 g). m.p. 126–127°C (lit. 127–129°C [11]); Anal. Calcd. for $C_8H_5ClO_2$: C, 57.00%; H, 2.99%; Cl, 21.03%. Found C, 56.99%; H, 3.05%; Cl, 21.00%; ^1H NMR δ 7.3 ~ 7.2(m, 2H), 7.0 (m, 1H), 3.74 (s, 2H); ^{13}C NMR δ 173.10, 152.97, 129.20, 128.81, 124.82, 124.67, 111.73, 32.87; MS *m/e* 168 (M^+), 140, 112, 77.

3.3. Preparation of 3-phenylthio-2-benzofuranone derivatives **2a**,**b**

To a two-necked 200-ml round flask fitted with a dropping funnel equipped with a three-way cock on the top (one of which was a rubber balloon filled with nitrogen), and a septum rubber cap, diphenyl disulfide (2.84 g, 13 mmol, 1.3 equiv.) and 60% NaH (0.60 g, 15 mmol, 1.5 equiv.) was added and purged by nitrogen. To the flask, anhydrous THF or DME (50 ml) was added through the septum cap, and to the dropping funnel, 2-benzofuranone **1a** (1.34 g, 10 mmol) dissolved in the same solvent (50 ml) was added. The solution of **1a** was slowly added for 1 h and stirred for additional 1 h. The solution was diluted with toluene (150 ml) and then 1 M aq. H_2SO_4 was slowly added to this solution. This mixture was separated, and the organic phase was washed twice with H_2O, then dried over anhydrous Na_2SO_4. The volatile solvent was evaporated and the residue was purified on the silica gel column chromatography (100 g). At first, the by-products were washed out by hexane then the product was eluted out using 5% ethyl acetate in hexane, to give the crude product in 49% yield (1.177 g). After recrystallization from ethyl acetate/hexane, the analytically pure product 3-phenylthio-2-benzofuranone **2a** was obtained in 47% yield (1.135 g). m.p. 82–83°C; Anal. Calcd. for $C_{14}H_{10}O_2S$: C, 69.40%; H, 4.16%; S, 13.23%. Found C, 69.47%; H, 4.07%; S, 13.42%; ^1H NMR δ 7.4 (m, 3H), 7.3–7.1 (m, 6H), 6.91 (d, J = 7.9 Hz, 1H), 4.77 (s, 1H); ^{13}C NMR δ 173.69, 153.41, 134.65, 129.94, 129.74, 129.36, 129.02, 125.45, 124.46, 110.71, 47.32; MS *m/e* 242 (M^+), 133 (M^+–PhS), 109, 105, 77.

Based on almost the same procedure, 3-phenylthio-5-chloro-2-benzofuranone **2b** was obtained in 52% yield (5.76 g) from 5-chloro-2-benzofuranone **1b** (6.78 g, 40.2 mmol), diphenyl disulfide (17.57 g, 80.5 mmol, 2 equiv.), and 60% NaH (2.41 g, 60.3 mmol, 1.5 equiv.). m.p. 67–68°C; Anal. Calcd. for $C_{14}H_9ClO_2S$: C, 60.76%; H, 3.28%; Cl, 12.81%; S, 11.59%. Found C, 61.04%; H, 3.35%; Cl, 12.60%; S, 11.33%; ^1H NMR δ 7.5~7.1 (m, 7H), 6.84 (d, 1H, J = 5.8 Hz), 4.74 (s, 1H); ^{13}C NMR δ 172.90, 151.68,

134.72, 129.92, 129.63, 129.58, 129.18, 129.09, 126.24, 125.54, 125.50, 111.82, 47.26; MS *m/e* 276 (M^+), 167 (M^+–S), 109 (PhS^+).

3.4. Preparation of α-phenylthio-2-benzothiazolylacetonitrile **4**

To a 200-ml round flask, 2-benzothiazolylacetonitrile **3** [18] (2.96 g, 16.6 mmol), diphenyl disulfide (4.45 g, 20.6 mmol, 1.2 equiv.), KOH (3.73 g, 66.4 mmol, 4 equiv.), and THF (80 ml) were added and stirred overnight. The solvent was partly evaporated and the residue was dissolved in a 1 : 1 mixture of toluene and ethyl acetate, then sequentially washed with 2 M aq. HCl and H_2O. The organic phase was dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was recrystallized from MeOH and dried in vacuo at 100°C to remove the diphenyl disulfide. The dried product was recrystallized again to give the product 4 in 72% yield (3.41 g). m.p. 181–182°C; Anal. Calcd. for $C_{15}H_{10}N_2S_2$: C, 63.80%; H, 3.57%; N, 9.92%; S, 22.71%. Found C, 63.89%; H, 3.52%; N, 9.96%; S, 21.78%; ^{1}H NMR (in DMSO-d_6) δ 12.69, 12.36 (2s, 1H), 7.72, 7.61 (2d, 1H, J = 7.9 Hz), 7.34 (m, 8H), 7.19, 7.12 (t and m, 1H, J = 6.8 Hz); ^{13}H NMR (in DMSO-d_6) δ 172.20, 168.18, 142.25, 140.94, 136.89, 136.03, 129.40, 127.03, 126.60, 125.82, 124.96, 124.87, 124.75, 123.04, 122.72, 122.46, 122.10, 121.48, 119.86, 112.76, 112.56, 53.23, 52.74; MS *m/e* 282 (M^+), 173 (M^+–PhS), 146, 109 (PhS^+).

3.5. Synthesis of the fluorinated products by anodic fluorination

3.5.1. Anodic fluorination of 3-phenylthio-2-benzofuranone derivatives **2a**,**b** and α-phenylthio-2-benzothiazolylacetonitrile **4**. General procedure

Under a nitrogen atmosphere, electrolysis was carried out with platinum electrodes (2 cm × 2 cm) in a 1 M $Et_4NF{\cdot}nHF$ (n = 3,4) electrolytic solution (15 ml) containing the substrate (1.5 mmol) and in the presence or absence of diphenyl sulfide (0.75 mmol) using a cylindrical undivided cell or H-type divided cell with an anion-exchange membrane (IE-DF 34-5 TOSOH) at ambient temperature. In the cases of constant potential electrolysis and the linear sweep voltammetry of **4**, a reference electrode (Ag wire/0.01 M $AgNO_3$, 0.1 M Et_4NBF_4 in CH_3CN) was used. After the starting material was almost consumed (determined by silica gel TLC), the solvent was evaporated and the ^{19}F NMR was measured to estimated the product yield.

3.5.2. Isolation and identification of the products of the anodic fluorination of 3-phenylthio-2-benzofuranone derivatives **2a**,**b**

After the electrolysis, the solution was diluted with cold ethyl acetate. In order to remove the supporting electrolyte, the other polymeric and highly polar compounds, the cold solution was allowed to pass through a short column of the silica gel which had been dried in vacuo and immersed in ethyl acetate before use. The eluent was evaporated (ca. 10% of **2** was lost during this procedure) and the residue was further purified by column chromatography using the above-mentioned dried silica gel which was deactivated by ethyl acetate, then the eluent was displaced by hexane. The product was eluted out using a linear gradient of 0–50% toluene in hexane as rapidly as possible. Compounds **2** were immediately decomposed on the silica gel TLC, therefore, they appeared as spots at the starting point after the development.

3-Fluoro-3-phenylthio-2-benzofuranones (**6a**): ^{1}H NMR δ 7.62 (d, 2H, J = 7.3 Hz), 7.56–7.40 (m, 4H), 7.24–7.12 (m, 3H); ^{19}F NMR δ-56.90 (s); ^{13}C NMR δ 166.67 (d, J = 61.3 Hz), 151.87 (d, J = 6.1 Hz), 136.57, 136.53, 132.65 (d, J = 2.4 Hz), 130.69, 129.18, 126.60, 124.83 (d, J = 8.5 Hz), 123.20 (d, J = 22.0 Hz), 111.56, 95.18 (d, J = 247.8 Hz),; MS *m/e* 260 (M^+), 151 (M^+–PhS), 109 (PhS^+); HRMS Calcd. for $C_{14}H_9FO_2S$: *m/e* 260.0607. Observed 260.0608.

3,3-Di(phenylthio)-2-benzofuranone (**7**): ^{1}H NMR δ 7.40–7.34 (m, 4H),7.32–7.28 (m, 2H), 7.24–7.14 (m, 6H), 7.10–7.04 (m, 1H), 6.78–6.74 (m, 1H); ^{13}C NMR δ 172.61, 151.86, 136.75, 130.28, 128.86, 128.64, 126.60, 125.52, 124.26, 110.51, 61.04; MS *m/e* 350 (M^+), 241 (M^+–PhS), 213, 184, 152, 133, 109, 77. HRMS Calcd. for $C_{20}H_{14}O_2S_2$: *m/e* 350.0435. Observed 350.0436.

3,3′-Di(phenylthio-2-benzofuranonyl) (**8**): ^{1}H NMR δ 7.55 (m, 2H), 7.2 (m, 6H), 7.3–7.0 (m, 8H), 6.5 (m, 2H); ^{13}C NMR δ 171.51, 151.86, 137.14, 137.07, 130.46, 130.19, 128.41, 127.89125.25, 124.74, 110.24, 62.50; MS *m/e* 482 (M^+), 373 (M^+–PhS), 264 (M^+–PhSSPh), 241 ($M/2^+$), 218 (PhSSPh). HRMS Calcd. for $C_{28}H_{18}O_4S_2$: *m/e* 482.0647. Observed 482.0645.

5-Chloro-3-fluoro-3-phenylthio-2-benzofuranone (**6b**): Anal. Calcd. for $C_{14}H_8ClFO_2S$: C, 57.05%; H, 2.74%; Cl, 12.03%; F, 6.45%; S, 10.88%. Found C, 57.31%; H, 2.78%; Cl, 12.05%; F, 6.44%; S, 10.97%; ^{1}H NMR δ 7.60 (d, 2H, J = 7.6 Hz), 7.51 (d, 1H, J = 7.3 Hz), 7.43 (m, 3H), 7.07 (d, 2H, J = 8.6 Hz); ^{13}H NMR δ 166.49 (d, J = 31.7 Hz), 150.57 (d, J = 4.9 Hz), 137.09, 133.03, 131.43, 130.67, 129.76, 126.51, 125.43, 124.94 (d, J = 22.0 Hz), 113.30, 95.47 (d, J = 249.1 Hz); ^{19}F NMR δ-58.17 (s); MS *m/e* 294 (M^+), 185 (M^+–PhS), 129, 109 (PhS^+). HRMS Calcd. for $C_{14}H_8ClFO_2S$: *m/e* 293.9918. Observed 293.9932.

3.5.3. Isolation and identification of the products of the anodic fluorination of α-phenylthio-2-benzothiazolylacetonitrile **4**

After the electrolysis, the solution was filtered to separate the reddish-orange precipitate, i.e., **11**, and the filtrate was diluted with cold ethyl acetate. To remove the electrolyte, the other polymeric and highly polar compounds, the cold solution was allowed to pass through a short column of the silica gel. The eluent was evaporated and the residue was further purified by silica gel column chromatography using a linear gradient of 0–20% ethyl acetate in hexane.

α-fluoro-α-phenylthio-2-benzothiazolylacetonitrile (**9**): m.p. 103–104°C; Anal. Calcd. for $C_{15}H_9FN_2S_2$: C, 59.98%; H, 3.02%; N, 9.33%; F, 6.33%; S, 21.35%. Found C, 60.25%; H, 2.89%; N, 9.31%; F, 6.42%; S, 21.30%; ^{1}H NMR δ 8.20 (d, 1H, J = 8.3 Hz), 7.95 (d, 1H, J = 7.9 Hz), 7.78 (d, 2H, J = 7.3 Hz), 7.64–7.42 (m, 5H); ^{13}C NMR δ 160.74 (d, J = 31.7 Hz), 152.17, 136.78, 135.54, 131.54, 129.69, 127.20, 127.01, 126.58, 124.71, 121.87, 112.44 (d, J = 44.0 Hz), 94.86 (d, J = 227.1 Hz); ^{19}F NMR δ -33.63 (s); MS *m/e* 300 (M^+), 191 (M^+–SPh), 134 (M^+–CFSPhCN), 109 (PhS^+), 102; HRMS Calcd. for $C_{15}H_9FN_2S_2$: *m/e* 300.0191. Observed 300.0200.

α-fluoro-2-benzothiazolylacetonitrile (**10**): ^{1}H NMR δ 8.16 (d, 1H, J = 7.6 Hz), 7.99 (dd, 1H, J = 7.1, 1.3 Hz), 7.61 (td, 1H, J = 7.4, 1.3 Hz), 7.54 (td, 1H, J = 7.4, 1.3 Hz), 6.49 (d, 1H, J = 46.2 Hz); ^{13}C NMR δ 158.89 (d, J = 26.8 Hz), 152.34, 135.58, 127.22, 127.10, 124.55, 122.09, 112.99 (d, J = 31.7 Hz), 77.29 (d, J = 185.6 Hz); ^{19}F NMR δ -97.63 (d, J = 45.9 Hz); MS *m/e* 192 (M^+); HRMS Calcd. for $C_9H_5FN_2S$: 192.0157. Observed 192.0155.

1,2-Dicyano-1,2-bis(2′-benzothiazolyl)ethene (**11**): Anal. Calcd. for $C_{18}H_8N_4S_2$: C, 62.77%; H, 2.34%; N, 16.27%. Found C, 62.97%; H, 2.45%; N, 16.44%. MS *m/e* 344 (M^+), 318 (M^+–CN).

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