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Electrolytic partial fluorination of organic compounds 89: Regioselective anodic fluorination of tetrazolyl sulfides

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Abstract

Anodic fluorination of five-membered nitrogen-containing heterocyclic sulfides like tetrazolyl sulfides was comparatively studied. The anodic fluorination of tetrazolyl sulfides having α-electron-withdrawing groups was successfully carried out to provide α-monofluorinated tetrazolyl derivatives in moderate yields. This is in sharp contrast to the low efficient anodic fluorination of triazolyl sulfides. Thus, it was found that the efficiency of anodic fluorination is greatly affected by the basicity of the heterocyclic groups of the starting heterocyclic sulfides.
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1. Introduction

Tetrazole derivatives have attracted much attention due to wide range of pharmacological activity. Replacement of a carboxyl group in biologically active compounds by a tetrazole group is undertaken because of the close similarity in pK_a values, and the steric and electronic similarities. The introduction of tetrazolyl group in place of the carboxyl group has also substantial importance in studies of structure activity relationship in the peptide field. Atherton and Lambert investigated a new class of antibacterial agents, synthetic phosphonopeptide mimetics related to D-Ala-D-Ala, in which the carboxyl group was replaced by a tetrazole function [1,2]. The tetrazole analogues of L-glutamic acid and its derivatives were investigated by Grzonka and co-workers. They supposed that tetrazole analogues of hormones in which the carboxyl group is bonded through the covalent bond should have different biological activities in comparison to the parent hormones [3].

Anderson et al. have reported the diastereoselective synthesis of tetrazole, designed to mimic 3-aminonocardicinic acid, the nucleus of the nocardicin family of antibiotics [4].

Losartan potassium, the first of a new class of drugs called angiotensin II receptor antagonists, has recently been developed for treatment of high blood pressure and heart failure [5]. This compound has also a tetrazole ring as a key component.

On the other hand, it is well known that introduction of fluorine atom(s) into organic substrates markedly enhances or dramatically changes their biological properties [6]. We have systematically studied anodic monofluorination at the side chain of various heterocyclic compounds [7–10]. For example, selective anodic fluorination at the side chain of various heterocyclic compounds such as six-membered (2-pyridyl- and 4-pyrimidyl-), and five-membered (2-thiadiazolyl, 2-oxadiazolyl and 2-triazolyl) heterocycles was comparatively studied (Schemes 1 and 2) [11–16]. Thus, the active methylenethio group attached to various heterocyclic rings is selectively fluorinated to give the corresponding α-fluorinated products in moderate to good yields. As shown in Scheme 2, the anodic fluorination of thiadiazolyl sulfides at the side chain proceeded much more efficiently than that of the corresponding oxygen analogues 2-oxadiazolyl sulfides [15]. In sharp contrast, anodic fluorination of 2-triazolyl sulfides resulted in extremely low yields (2–18%) due to the salt formation with HF and anode passivation during the electrolysis. It was found that anodic fluorination efficiency is greatly affected by the ring system of the starting heterocyclic sulfides.

From these viewpoints, regioselective anodic monofluorination at the side chain of the tetrazolyl sulfide derivatives was studied under various electrolytic conditions. The basicity as well as ring system of the starting heterocyclic sulfides would

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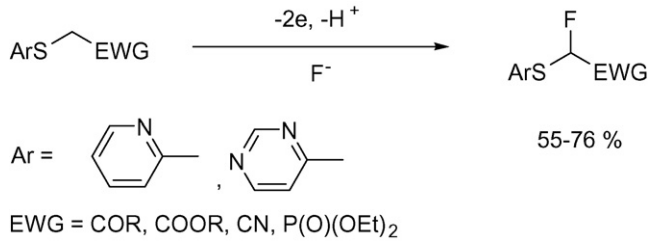
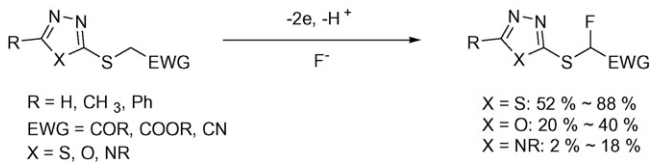


Scheme 1.



Scheme 2.

affect significantly on the anodic fluorination. The basicity of the tetrazole is lower than that of the triazole. Therefore, we expected that anodic fluorination of tetrazolyl sulfides would proceed more efficiently in comparison with triazolyl sulfides.

2. Results and discussion

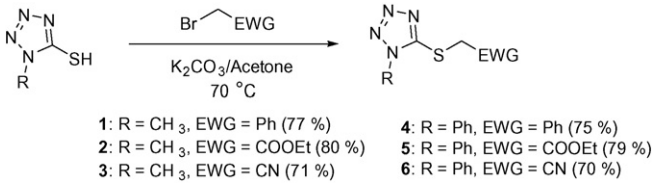
2.1. Preparation of starting materials

Starting tetrazolyl sulfides **1–6** were prepared in good yields by the reaction of 1-methyl-5-mercaptotetrazole or 1-phenyl-5-mercaptotetrazole with α-bromo derivatives of ethyl acetate, acetonitrile, and toluene in boiling acetone containing potassium carbonate (Scheme 3).

2.2. Oxidation potentials of tetrazolyl sulfides

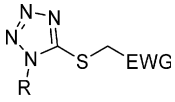
In order to investigate the effects of electron-withdrawing groups and substituents R on the oxidation potentials of sulfides **1–6**, the anodic peak potentials of **1–6** were measured in anhydrous acetonitrile containing $Bu_4N{\cdot}BF_4$ (0.1 M) by cyclic voltammetry. The CV curves were obtained with three electrode system using a platinum disk as a working electrode, a platinum wire as a counter electrode and 1 M NaCl calomel electrode (SSCE) as a reference electrode. Most sulfides showed irreversible anodic peaks. However, sulfides having an ester group **2** and **5** did not show any clear oxidation peaks. The first oxidation peak potentials (E_p^{ox}) of the tetrazolyl sulfides **1**, **3**, **4**, and **6** are summarized in Table 1.

As shown in Table 1, these sulfides have rather positive oxidation potentials. It was found that sulfides **3** and **6** having a



Scheme 3.

Table 1
Oxidation potentials (peak potentials, E_p^{ox}) of tetrazolyl sulfides **1–6**



[a] **1 ~ 6**

Substrate			E_p^{ox} (*V* vs. SCE)
No.	R	EWG	
1	CH_3	C_6H_5	2.26
2	CH_3	$COOC_2H_5$	–
3	CH_3	CN	2.55
4	C_6H_5	C_6H_5	2.3
5	C_6H_5	$COOC_2H_5$	–
6	C_6H_5	CN	2.68

[a] In 0.1 M Bu_4NBF_4/CH_3CN, sweep rate: 100 mV/s.

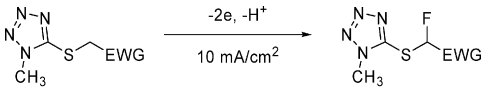
cyano group were oxidized at more positive potentials than the corresponding sulfides having a phenyl group owing to the strongly electron-withdrawing effect of the cyano group. This clearly indicates that the polar effect of the substituent (EWG) plays a significant role in the electron transfer step from the sulfur atom of these sulfides. In addition, *N*-methyl derivatives **1** and **3** have less positive oxidation potentials compared with *N*-phenyl derivatives **4** and **6**.

2.3. Anodic monofluorination of tetrazolyl sulfides *1–6*

Anodic fluorination of 1-methyl-5-tetrazolyl benzyl sulfide (**1**), ethyl α-[5-(1-methyltetrazolyl)thio]acetate (**2**), α-[5-(1-methyltetrazolyl)thio]acetatonitrile (**3**) was investigated in detail. The fluorination was carried out at platinum plate electrodes in anhydrous dimethoxyethane (DME), acetonitrile or **1**:**1** mixture of DME/acetonitrile containing various fluoride salts as the supporting electrolytes and fluoride ion sources using an undivided cell, and a constant current (10 mA/cm^2) was passed at room temperature. The results are summarized in Table 2.

As shown in Table 2, anodic fluorination of **1** in DME proceeded to give the corresponding α-monofluorinated product **7**. Among the supporting electrolytes used, $Et_4NF{\cdot}4HF$ 4HF gave the best result. On the other hand, $Et_4NF{\cdot}3HF$ gave much lower product yield and $Et_3N{\cdot}3HF$ was not effective (Runs 2 and 1). This is probably due to the following two reasons: the first one is the rather high oxidation potential of sulfide **1**, and the second one is that $Et_3N{\cdot}3HF$ is easily oxidized whereas $Et_4NF{\cdot}4HF$ is stable against oxidation. Therefore, $Et_4NF{\cdot}4HF$ is effective for the fluorination but $Et_3N{\cdot}3HF$ is not suitable. Furthermore, since tetrazoles are rather basic, **1** should be protonated in a strongly acidic electrolytic solution. This seems to be one of the reasons for the requirement of a large excess amount of electricity. In fact, after extremely excess amount of electricity (11 F/mol) was passed, the molecular conversion increased to ca. 60%, and the fluorinated product **7** was obtained in 53% yield based on the consumed **1** (Run 7). A mixed solvent of DME and acetonitrile (**1**:**1**) was not so effective (Run 4). The yield was extremely low in MeCN (Run 5) and fluorinated product was not obtained in nitromethane

Table 2
Anodic monofluorination of the 1-methyl-5-tetrazolyl sulfides **1–3**



Run	Substrate		Solvent	Supporting electrolyte (1 M)	Electricity (F/mol)	Conversion (%)	Product	
	No.	EWG					No.	Yield (%)[a]
1	**1**	C_6H_5	DME	$Et_3N{\cdot}3HF$	8	–	**7**	Trace
2	**1**	C_6H_5	DME	$Et_4NF{\cdot}3HF$	8	–	**7**	11
3	**1**	C_6H_5	DME	$Et_4NF{\cdot}4HF$	8	48	**7**	32[b](25)[c]
4	**1**	C_6H_5	DME/CH_3CN	$Et_4NF{\cdot}4HF$	8	–	**7**	18
5	**1**	C_6H_5	CH_3CN	$Et_4NF{\cdot}4HF$	8	–	**7**	2
6	**1**	C_6H_5	CH_3NO_2	$Et_4NF{\cdot}4HF$	8	–	**7**	0
7	**1**	C_6H_5	DME	$Et_4NF{\cdot}4HF$	11	59	**7**	53[b](40)[c]
8	**1**	C_6H_5	DME	$Et_4NF{\cdot}4HF$	15	–	**7**	25
9	**2**	$COOC_2H_5$	DME	$Et_3N{\cdot}3HF$	8	–	**8**	0
10	**2**	$COOC_2H_5$	DME/CH_3CN	$Et_4NF{\cdot}4HF$	10	–	**8**	24
11	**2**	$COOC_2H_5$	DME	$Et_4NF{\cdot}4HF$	10	–	**8**	5
12	**2**	$COOC_2H_5$	CH_3CN	$Et_4NF{\cdot}4HF$	10	61	**8**	62[b](50)[c]
13	**2**	$COOC_2H_5$	CH_3CN	$Et_4NF{\cdot}4HF$	13	–	**8**	43
14	**3**	CN	DME/CH_3CN	$Et_4NF{\cdot}4HF$	8	–	**9**	0
15	**3**	CN	DME	$Et_4NF{\cdot}4HF$	8	–	**9**	0
16	**3**	CN	CH_3CN	$Et_4NF{\cdot}4HF$	8	–	**9**	42
17	**3**	CN	CH_3CN	$Et_4NF{\cdot}4HF$	12	–	**9**	53(45)[d]
18	**3**	CN	CH_3CN	$Et_4NF{\cdot}4HF$	15	–	**9**	19

[a] Determined by ^{19}F NMR.
[b] Based on consumed starting material.
[c] Isolated yield based on consumed starting material.
[d] Absolute isolated yield.

(Run 6). Thus, $Et_4NF{\cdot}4HF$/DME was found to be a suitable electrolytic solution for the anodic fluorination of **1** and gave the best result as shown in Run **7**.

The anodic fluorination of sulfide having an ester group **2** in $Et_3N{\cdot}3HF$/DME did not provide a fluorinated product **8** at all (Run 9). Then, anodic fluorination of **2** in DME, MeCN and DME/MeCN (**1**:**1**) was comparatively studied using $Et_4NF{\cdot}4HF$ (Runs 10–12), and it was found that the use of acetonitrile gave the best yield of the desired fluorinated product **8** (Run 12). When 13 F/mol of electricity was passed, the absolute yield was increased to 43% (Run 13).

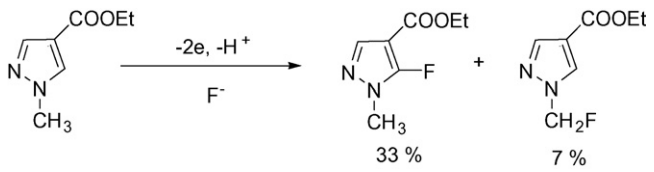
The anodic fluorination of sulfide having a cyano group **3** in $Et_4NF{\cdot}4HF$/DME or DME/MeCN (**1**:**1**) did not proceed at all (Runs 15 and 14). However, MeCN was found to be the best solvent for the fluorination of **3** to provide **9** in 53% absolute yield (Run 17).

It is notable that the *N*-methyl group was not fluorinated at all regardless of substrates. This is in sharp contrast to the anodic fluorination of ethyl **1**-methylpyrazole-**4**-carboxylate as shown in Scheme 4 [17]. In this case, *N*-methyl group was also fluorinated in addition to ring fluorination.

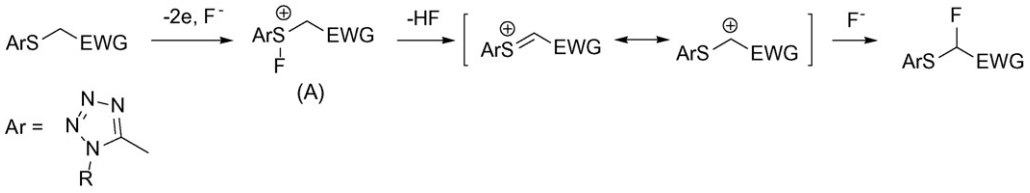
Furthermore, anodic fluorination of **1**-phenyltetrazolyl sulfides **4–6** was attempted. Based on the results of anodic fluorination of **1**-methyl sulfides **1–3**, DME was used in the case of **4** and MeCN was used in the cases of **5** and **6**. A large excess amount of electricity was required to carry out anodic fluorination of **4–6**, however, the starting materials were recovered considerably. Eventually, as shown in Table 3, it was found that anodic fluorination of tetrazolyl sulfides **4–6** using $Et_4NF{\cdot}4HF$ as a supporting electrolyte and DME (in case of **4**) or MeCN (in cases of **5** and **6**) as a solvent gave the corresponding α-monofluorinated products **10–12** in moderate yields based on the consumed **4–6**.

Thus, DME was suitable for the anodic fluorination of **1** and **4**, while MeCN was suitable for other sulfides. The solvent effects can be explained as follows. The cationic intermediates anodically generated from **1** and **4** are stable benzylic cations, whose electrophilicity is low. Therefore, in order to achieve efficient fluorination, the nucleophilicity of fluoride ions must be enhanced. Since DME is known to greatly enhance the nucleophilicity of fluoride ions [18,19], DME is suitable for these cases. On the other hand, other sulfides **2**, **3**, **5**, and **6** have relatively high oxidation potentials due to strong electron-withdrawing groups. Therefore, anodically stable MeCN is suitable for their fluorination.

Notably, the phenyl group was not fluorinated at all and the fluorination always took place at α to the sulfur atom. Since the sulfur atom of tetrazolyl sulfides is most easily oxidized, the

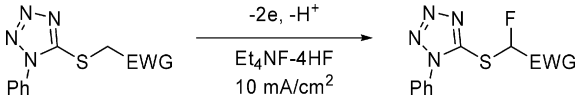


Scheme 4.



Scheme 5.

Table 3
Anodic monofluorination of the 1-phenyl-5-tetrazolyl sulfides **4–6**



4 ~ 6 **10 ~ 12**

Run	Substrate		Solvent	Electricity (F/mol)	Conversion (%)	Product	
	No.	EWG				No.	Yield (%)[a,b]
1	**4**	C_6H_5	DME	O	54	**10**	45(38)[c]
2	**5**	$COOC_2H_5$	CH_3CN	O	62	**11**	54(46)[c]
3	**6**	CN	CH_3CN	CM	48	**12**	26(20)[c]

[a] Determined by ^{19}F NMR.
[b] Based on consumed starting material.
[c] Isolated yield based on consumed starting material.

initial electron transfer should take place at the sulfur atom and the reaction seems to proceed *via* a Pummerer type mechanism as proposed previously (Scheme 5) [20].

Selectfluor and *N*-fluoropyridinium salts derived from fluorine gas are known to be fluorinating reagents of sulfides, however they are not suitable for large-scale fluorination. In contrast, electrochemical fluorination does not require any hazardous reagents and the large-scale fluorination is easily achieved [21]. Thus, electrochemical method is more advantageous.

3. Conclusions

Highly regioselective anodic fluorination of five-membered nitrogen-containing heterocyclic sulfides like tetrazolyl sulfides has been successfully carried out to provide the corresponding α-monofluorinated tetrazolyl sulfides in moderate yields. This is in sharp contrast to extremely low efficient anodic fluorination of triazolyl sulfides in our previous study. This is probably due to less basicity of tetrazolyl sulfides compared with triazolyl sulfides. Although the oxidation potentials of tetrazolyl sulfides are higher than those of triazolyl sulfides, the anodic fluorination of tetrazolyl sulfides proceeded more efficiently compared with triazolyl sulfides. Thus, it was disclosed that the efficiency of anodic α-fluorination of heterocyclic sulfides is greatly affected by their ring systems, particularly the basicity of a heterocyclic moiety.

4. Experimental

4.1. General

^1H NMR (270 MHz), ^{13}C NMR (68 MHz) and ^{19}F NMR (254 MHz) spectra were determined using $CDCl_3$ as a solvent. The chemical shift for ^{19}F NMR is given in δ (ppm) upfield from the peak for external trifluoroacetic acid. The product yields were determined by ^{19}F NMR using monofluorobenzene as an internal standard material. Mass spectra were obtained with Shimadzu GC–MS QP5050A spectrometer. Cyclic voltammetry was performed using a BAS ALS/HCH Instruments Model 600A, and preparative electrolysis experiments were carried out using a METRONIX constant current power supply 5944 and Coulomb/Amperehour meter HF-201.

4.2. Materials

The starting tetrazolyl sulfides **1–6** were prepared as follows. To a stirred mixture containing 1 mmol of corresponding 5-mercaptotetrazole derivatives and 1 mmol potassium carbonate (K_2CO_3) in 20 ml of acetone, was added dropwise 1.3 mmol of α-bromotoluene, ethyl α-bromoacetate or α-bromoacetonitrile. Then, the mixture was stirred at 70 °C for 2 h and then cooled down to room temperature. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using ethyl acetate as an eluent to give the corresponding tetrazolyl sulfides in 70–80% yields.

4.2.1. 1-Methyl-5-benzylthiotetrazole (*1*)

^1H NMR δ 3.84 (s, 3H), 4.52 (s, 2H), 7.25–7.69 (m, 5H); ^{13}C NMR δ 33.37, 37.92, 128.15, 128.67, 128.82, 135.46, 153.35; MS (EI), *m/z* 266 (M^+); HRMS, *m/z* calcd. for $C_9H_{10}N_4S$ 206.0627 and found: 206.0626.

4.2.2. Ethyl α-[5-(1-methyltetrazolyl)thio]acetate (*2*)

^1H NMR δ 1.29 (t, *J* = 7.29 Hz, 3H), 3.98 (s, 3H), 4.15 (s, 2H), 4.22 (q, *J* = 7.29 Hz, 2H); ^{13}C NMR δ 14.06, 33.65, 35.40, 62.51, 152.79, 167.25; MS (EI), *m/z* 202 (M^+); HRMS, *m/z* calcd. for $C_6H_{10}N_4O_2S$ 202.0525 and found: 202.0525.

4.2.3. α-[5-(1-Methyltetrazolyl)thio]acetonitrile (*3*)

^1H NMR δ 4.01 (s, 3H), 4.16 (s, 2H); ^{13}C NMR δ 18.69, 33.87, 114.72, 150.83; MS (EI), *m/z* 155 (M^+); HRMS, *m/z* calcd. for $C_4H_5N_5S$ 155.0266 and found: 155.0270.

4.2.4. 1-Phenyl-5-benzylthiotetrazole (*4*)

^1H NMR δ 4.62 (s, 2H), 7.25–7.41 (m, 8H), 7.52 (d, *J* = 2.97Hz, 2H); MS(EI), *m/z*, 268 (M^+); HRMS, *m/z* calcd for $C_{14}H_{12}N_4S$ 268.0783 and found: 268.0765.

4.2.5. Ethyl α-[5-(1-phenyltetrazolyl)thio]acetate (*5*)

^1H NMR δ 1.28 (t, *J* = 4.32 Hz, 3H), 4.21 (s, 2H), 4.28 (q, *J* = 7.29 Hz, 2H), 7.55–7.59 (m, 5H); ^{13}C NMR δ 14.15, 35.24,

62.48, 123.68, 129.79, 130.2, 132.5, 153.67, 167.21; MS (EI), *m/z* 264 (M^+); HRMS, *m*/z calcd. for $C_{11}H_{12}N_4O_2S$ 264.0681 and found: 264.0668.

*4.2.6. α-[5-(1-Phenyltetrazolyl)thio]acetonitrile (**6**)*

^{1}H NMR δ 4.24(s, 2H), 7.52–7.69 (m, 5H); MS (EI), *m/z* 217 (M^+); HRMS, *m/z* calcd. for $C_9H_7N_5S$ 217.0422 and for 217.0413.

4.3. Electrolytic procedure for fluorination

A typical procedure is as follows. Anodic oxidation of **1** (0.5 mmol) was carried out in an undivided cell equipped with platinum plate electrodes (2 cm × 1.5 cm) in 10 ml of 1 M $Et_4NF{\cdot}4HF$/dimethoxyethane or acetonitrile at room temperature. Constant current (10 mA/cm^2) was passed and the reaction was monitored by TLC. After electrolysis, the electrolytic solution was passed through a short column filled with silica gel using ethyl acetate as an eluent to remove fluoride salts. The eluent was evaporated under reduced pressure, and the residue was further purified by column chromatography on silica gel using ethyl acetate to give pure fluorinated products. The products were identified by spectroscopic data.

*4.3.1. 1-Methyl-5-[(α-fluorobenzyl)thio]tetrazole (**7**)*

Yellow oil. ^{1}H NMR δ 3.73 (s, 3H), 7.11 (d, J = 53.55 Hz, CHF), 7.27–7.69 (m, 5H); ^{19}F NMR δ −68.88 (d, J_{HF} = 53.6 Hz); MS (EI), *m/z* 224 (M^+), 147, 109, 83; HRMS, *m/z* calcd. for $C_9H_9N_4FS$ 224.0532 and found: 224.0522.

*4.3.2. Ethyl α-fluoro-α-[5-(1-methyltetrazolyl)thio]acetate (**8**)*

Colorless oil. ^{1}H NMR δ 1.33 (t, J = 7.02 Hz, 3H), 4.18 (s, 3H), 4.31 (q, J = 7.02 Hz, 2H), 6.49 (d, J = 50.1 Hz, CHF); ^{13}C NMR δ 14.03, 29.69, 62.44, 92.08 (d, J = 239.27 Hz, CHF) 152.79, 167.23; ^{19}F NMR δ −82.45 (d, J_{HF} = 50.05 Hz); MS (EI), *m/z* 220 (M^+), 202, 147, 84; HRMS, *m/z* calcd. for $C_6H_9N_4O_2FS$ 220.0430 and found: 220.0431.

*4.3.3. α-Fluoro-α-[5-(1-methyltetrazolyl)thio]acetonitrile (**9**)*

Yellow oil. ^{1}H NMR δ 4.12 (s, 2H), 6.92 (d, J = 48.02Hz, CHF); ^{13}C NMR δ 33.88, 81.35 (d, J = 235.94 Hz, CHF), 110.68, 143.8; ^{19}F NMR δ −78.65 (d, J_{HF} = 48.02 Hz); MS (EI), *m/z* 173 (M^+), 145, 115, 58. HRMS, *m/z* calcd. for $C_4H_4N_5FS$ 173.0182 and found: 173.0182.

*4.3.4. 1-Phenyl-[5-(α-fluorobenzyl)thio]tetrazole (**10**)*

Yellow oil. ^{1}H NMR δ 7.24–7.58 (m, 10H), 6.91 (d, J = 51.8 Hz, CHF); ^{19}F NMR δ −70.37 (d, J_{HF} = 51.82 Hz); MS (EI), *m/z* 286 (M^+), 177, 166, 109; HRMS, *m/z* calcd. for $C_{14}H_{11}N_4FS$ 286.0689 and found: 286.0695.

*4.3.5. Ethyl α-fluoro-α-[5-(1-phenyltetrazolyl)thio]acetate (**11**)*

Colorless oil. ^{1}H NMR δ 1.34 (t, J = 6.85Hz, 3H), 4.37 (q, J = 7.29Hz, 2H), 6.91 (d, J = 51.48 Hz, CHF), 7.54–7.95 (m, 5H); ^{13}C NMR δ 14.1, 60.6, 103.5 (d, J = 236.11Hz, CHF), 123.68, 129.79, 130.2, 132.5, 153.67, 167.21; ^{19}F NMR δ −84.71 (d, J_{HF} = 51.5 Hz); MS(EI), *m/z* 282 (M^+), 264, 117, 106; HRMS, *m/z* calcd. for $C_{11}H_{11}N_4O_2FS$ 282.0587 and found: 282.0576.

*4.3.6. α-Fluoro-α-[5-(1-phenyltetrazolyl)thio]acetonitril e (**12**)*

Yellow oil. ^{1}H NMR δ 7.05 (d, J = 48.01 Hz, CHF), 7.45–7.61 (m, 5H); ^{13}C NMR δ 91.3 (d, J = 231.65 Hz, CHF), 116.75, 123.6, 129.73, 129.9, 130.38, 151.67; ^{19}F NMR δ −81.45 (d, J_{HF} = 48.01 Hz); MS (EI), *m/z* 235 (M^+), 207, 217, 149, 130; HRMS, *m/z* calcd. for $C_9H_6N_5FS$ 235.0328 and found: 235.0309.

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