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Electrolytic partial fluorination of organic compound. Part: 53☆ Highly regioselective anodic mono- and difluorination of 4-arylthio-1,3-dioxolan-2-ones. A marked solvent effect on fluorinated product selectivity

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Abstract—Anodic fluorination of 4-arylthio-1,3-dioxolan-2-ones was investigated using various supporting fluoride salts and solvents. Their fluoro-desulfurization took place predominantly in $Et_4NF{\cdot}5HF/CH_2Cl_2$ while the use of $Et_4NF{\cdot}4HF$/DME resulted in α-fluorination, without the desulfurization, selectively. Electrolytic solvents affected markedly the product selectivity as compared with supporting fluoride salts. This is the first example of a solvent effect on the fluorinated product selectivity in the anodic fluorination.

1. Introduction

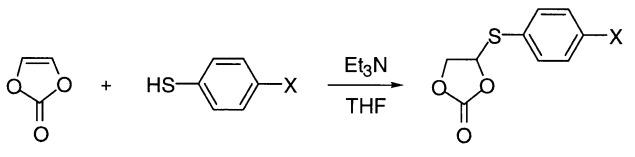
Fluoroorganic compounds have attracted much interest because of their pronounced chemical, physical and potential pharmaceutical properties.[2] The direct fluorination is the simplest way, however it generally requires special equipments and techniques since many fluorinating reagents are usually explosive, toxic, unstable, or hygroscopic.[3] On the other hand, the electrochemical fluorination has recently been shown to be an alternative method for selective direct fluorination; the fluorination can be carried out under mild and safe conditions using relatively simple equipment.[4–6] One of the important factors in the anodic fluorination is supporting fluoride salts.[7] Quite recently, we have found that solvent 1,2-dimethoxyethane (DME) is much more suitable than MeCN which has been conventionally used for the anodic fluorination.[8] This finding enabled us to carry out successfully anodic fluorination of oxygen-containing heterocyclic compounds,[9] of which anodic fluorination has not been reported except for the case of *N*-alkylmorpholines.[10]

Fluorinated ethylene carbonates seem to be promising organic electrolytic solvents or additives for rechargeable Li batteries since introduction of fluorine atom(s) into ethylene carbonate is expected to increase its electrochemical stability and decrease its melting point. With these facts in mind, we have attempted the anodic fluorination of ethylene carbonates having an arylthio group using various supporting fluoride salts and solvents.[11]

2. Results and discussion

2.1. Preparation of 4-arylthio-1,3-dioxolan-2-ones

The starting 4-arylthio-1,3-dioxolan-2-ones were synthesized in good yields by the reaction of vinylenecarbonate with arenethiol in boiling THF in the presence of Et_3N as shown in Scheme 1.



Scheme 1.

2.2. Oxidation potentials of 4-arylthio-1,3-dioxolan-2-ones

The oxidation potentials (anodic peak potentials) of **1a–e** were determined by cyclic voltammetry using a platinum

☆ See Ref. 1 for Part 52.

Keywords: electrolytic partial fluorination; solvent effect; product selectivity.

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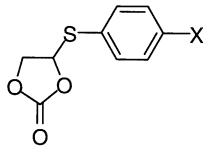
Table 1. Oxidation potentials (peak potentials, E_P^{OX}) of 4-arylthio-1,3,-dioxolan-2-ones



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1	X	E_P^{OX} (V) vs SCE
1a	H	1.92
1b	Me	1.76
1c	Cl	1.94
1d	Br	1.95
1e	OMe	1.57

Pt electrodes; 0.1 M Bu_4NClO_4/MeCN; sweep rate, 100 mV/s.

electrode in 0.1 M $Bu_4N{\cdot}ClO_4$/MeCN and a SCE reference electrode. All the compounds chosen in the present study showed irreversible oxidation waves. The first oxidation peak potentials (E_p^{OX}) were observed in the range of 1.57–1.94 V as shown in Table 1. *p*-Tolylthio- and *p*-anisylthio derivatives **1b**,**e**, respectively were oxidized at a less positive potential as compared with the other three derivatives (**1a**,**c**,**d**), owing to the electron-donating methyl and methoxy substituents on the benzene ring.

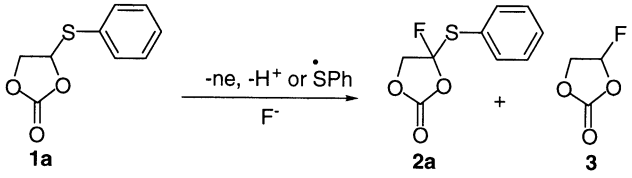
2.3. Anodic fluorination and fluoro-desulfurization of 4-arylthio-1,3-dioxolan-2-ones

Initially, anodic monofluorination was investigated in detail using 4-phenylthio-1,3-dioxolan-2-one (**1a**) as a model compound. The fluorination was carried out at platinum electrodes using an undivided cell in anhydrous acetonitrile, dichloromethane and dimethoxyethane (DME) containing various fluoride salts as the supporting electrolyte and fluoride ion source. A constant current was applied until the starting material was almost consumed. The results are summarized in Table 2.

As shown in Table 2, anodic fluoro-desulfurization of **1a** leading to product **3** proceeded selectively in $Et_4NF{\cdot}4HF/CH_3CN$, $Et_4NF{\cdot}4HF/CH_2Cl_2$ and $Et_3N{\cdot}5HF/CH_2Cl_2$ in moderate to good yields (runs 3, 7 and 8). In sharp contrast, α-fluorination of **1a** to **2a** took place preferentially in $Et_4NF{\cdot}3HF$/DME and $Et_4NF{\cdot}4HF$/DME (runs 10 and 11). In these cases, difluorinated products such as **5** (Scheme 3) were not formed. This can be explained in terms of the oxidation potential of **2a** (E_p^{ox}: 2.2 V vs SCE) being 0.3 V higher than that of **1a** (E_p^{ox}: 1.9 V vs SCE).

Next, we extended this anodic fluorination to other 4-arylthio derivatives **1b–e** as shown in Table 3. Their fluoro-desulfurization proceeded smoothly in $Et_3N{\cdot}5HF/CH_2Cl_2$ regardless of the substituent X groups on the benzene ring to give **3** in moderate to high yields (runs 4, 6, 8 and 10). In sharp contrast, anodic fluorination of **1b–d** in $Et_4NF{\cdot}4HF$/DME was strongly affected by substituents on the benzene ring. In the cases of **1c** and **1d**, the corresponding α-monofluorinated products **2c** and **2d** were obtained selectively in high yields (runs 5 and 7). On the other hand, **1b** and **1e** gave the fluorodesulfurization products **3** as the major products along with the corresponding sulfoxide in 14 and 12% yields, respectively (runs 3 and 9). In the case of **1b**, monofluorination also took place to some extent at the methyl group of the *p*-tolyl group (run 3). Thus, electron-withdrawing chloro and bromo substituents on the benzene ring promote α-fluorination, whereas electron-donating methyl and methoxy groups drastically disfavor it. Therefore, the presence of an electron-withdrawing group is essential for the successful α-fluorination of 4-arylthio-1,3-dioxolane-2-ones (**1**). It is noted that electrolytic conditions, particularly electrolytic solvents greatly affected the fluorinated product selectivity although there are some exceptions (**1b** and **1e**). Such marked product selectivity depending on electrolytic

Table 2. Effect of supporting fluoride salts and solvents on anodic fluorination of 4-phenylthio-1,3-dioxolane-2-one (**1a**)

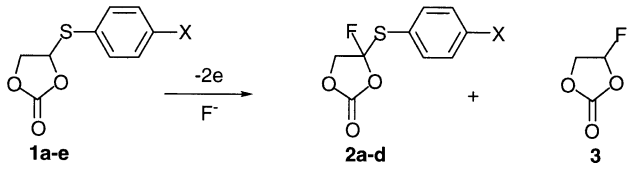


1a **2a** **3**

Run	Solvent	Supporting electrolyte	Charge passed (F/mol)	Yield (%)[a]	
				2a	**3**
1	CH_3CN	$Et_3N{\cdot}3HF$	5.1	28	Trace
2		$Et_4NF{\cdot}3HF$	3.2	11	14
3		$Et_4NF{\cdot}4HF$	4.3	Trace	50
4		$Et_3N{\cdot}5HF$	2.6	Trace	10
5	CH_2Cl_2	$Et_3N{\cdot}3HF$	4.2	28	6
6		$Et_4NF{\cdot}3HF$	3.1	16	29
7		$Et_4NF{\cdot}4HF$	5.2	Trace	53
8		$Et_3N{\cdot}5HF$	5.5	Trace	67
9	DME	$Et_3N{\cdot}3HF$	18.0	5	Trace
10		$Et_4NF{\cdot}3HF$	7.2	40	5
11		$Et_4NF{\cdot}4HF$	3.4	55	28
12		$Et_3N{\cdot}5HF$	4.0	6	40

[a] Determined by ^{19}F NMR spectroscopy.

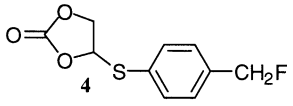
Table 3. Anodic fluorination of 4-arylthio-1,3-dioxolan-2-ones



1a-e **2a-d** **3**

Run	Substrate		Supporting electrolyte	Solvent	Electricity (F mol^{-1})	Yield (%)[a]	
	No.	X				**2**	**3**
1	**1a**	H	$Et_4NF{\cdot}4HF$	DME	3.4	55 (44)[b]	28
2	**1a**	H	$Et_3N{\cdot}5HF$	CH_2Cl_2	5.5	Trace	67
3[c]	**1b**	Me	$Et_4NF{\cdot}4HF$	DME	3.1	4	23
4	**1b**	Me	$Et_3N{\cdot}5HF$	CH_2Cl_2	7.2	0	40
5	**1c**	Cl	$Et_4NF{\cdot}4HF$	DME	5.2	80 (70)[b]	20
6	**1c**	Cl	$Et_3N{\cdot}5HF$	CH_2Cl_2	3.4	0	96 (75)[b]
7	**1d**	Br	$Et_4NF{\cdot}4HF$	DME	7.2	84 (66)[b]	4
8	**1d**	Br	$Et_3N{\cdot}5HF$	CH_2Cl_2	4.0	0	54
9[d]	**1e**	OMe	$Et_4NF{\cdot}4HF$	DME	4.2	Trace	41
10	**1e**	OMe	$Et_3N{\cdot}5HF$	CH_2Cl_2	4.3	0	62

[a] Determined by ^{19}F NMR spectroscopy.
[b] Isolated yield.
[c] The corresponding sulfoxide (14%) and 4-(4′-fluoromethylphynylthio)-1,3-dioxo-2-one (**4**) (5%) were formed.
[d] The corresponding sulfoxide (12%) was formed



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solvents has never been reported in the anodic fluorination so far.

In order to clarify the solvent effects, we investigated anodic fluorination of **1b** in a mixed solvent of DME and dichloromethane containing $Et_4NF{\cdot}4HF$. As shown in Fig. 1, the product ratio of **3** to **2c** increased with an increase in the ratio of CH_2Cl_2 to DME. Notably, addition of only 25% CH_2Cl_2 into DME caused a dramatic change in the product ratio and **3** was mainly formed in ca. 60% yield.

This interesting phenomenon can be explained as follows. The fluorination can be rationalized by postulating a radical cation intermediate **A** as shown in Scheme 2.

Dichloromethane has a poor ability to solvate carbocations.

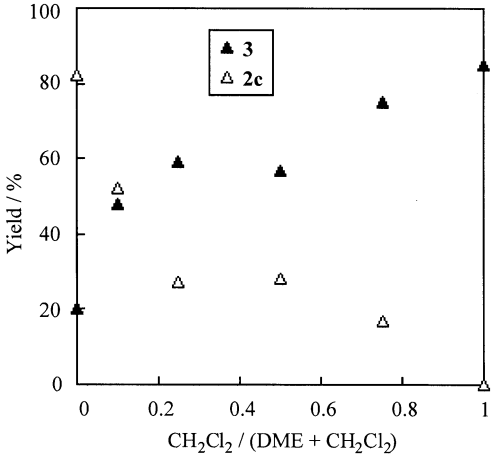
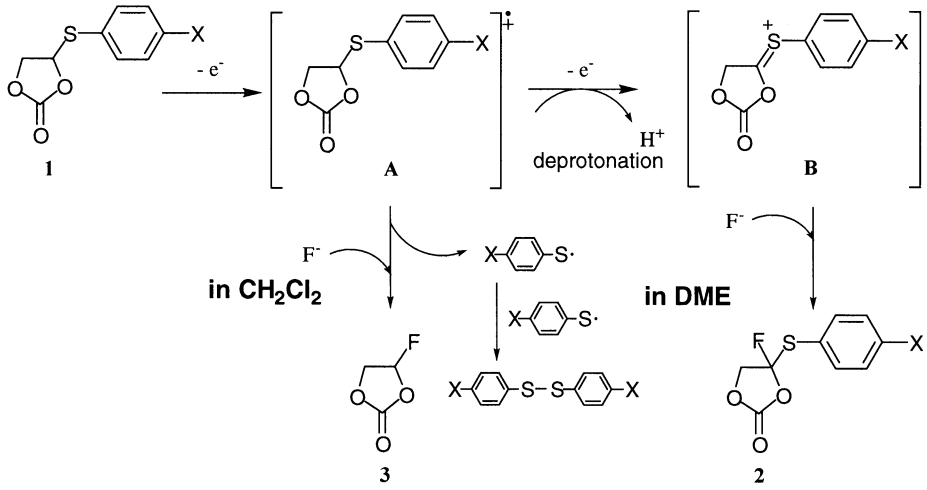


Figure 1. Dependence of yield of **2c** and **3** on the ratio of CH_2Cl_2 to DME.

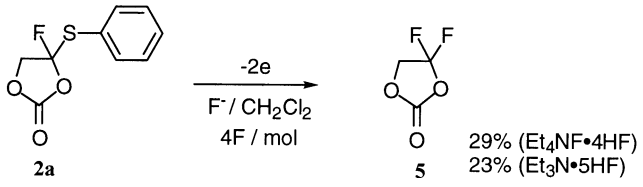
Therefore, **A** seems to be unstable in CH_2Cl_2. Reasonably, the desulfurization of **A** followed by fluorination mainly takes place prior to α-fluorination of **A**. On the other hand, DME is known to coordinate cations strongly.[12] Therefore, DME should stabilize the intermediate **A** and also enhance the fluoride ion nucleophilicity.[8] Then, the deprotonation of **A** with fluoride ions takes place prior to desulfurization followed by further oxidation to generate cation **B**, and this cation reacts with a fluoride ion to provide α-fluorinated product. In addition to these solvent effects, the deprotonation process should be also greatly affected by the substituent groups on the benzene ring.[13] In fact, electron-withdrawing groups promoted this deprotonation process significantly, while the electron-donating groups suppressed drastically.

Furthermore, we examined anodic fluoro-desulfurization of **2a**. As shown in Scheme 3, electrolysis of **2a** in $Et_4NF{\cdot}4HF/CH_2Cl_2$ and $Et_3N{\cdot}5HF/CH_2Cl_2$ gave desired difluorinated product **5** in reasonable yield. However, anodic fluorodesulfurization of **2a** did not take place at all in $Et_4NF{\cdot}4HF$/DME and most of **2a** was recovered. In this case, the oxidation of solvent DME preferentially occurred to give fluorinated DMEs.[9a]

It is well-known that methods for direct introduction of fluorine atom(s) into organic compounds often require expensive or hazardous reagents. In recent years, *N*-fluoropyridinium triflates have been shown to be effective fluorinating reagents with various fluorinating power.[14] Therefore, fluorination of **1a** as a model compound with various *N*-fluoropyridinium triflates was attempted. As shown in Table 4, less powerful *N*-fluoropyridinium and *N*-fluoro-2,4,6-trimethylpyridinium triflates gave only a trace amount of **3**, and **1a** was recovered mostly (runs 1



Scheme 2.



Scheme 3.

and 2). On the other hand, a more powerful *N*-fluoro-2,6-dichloropyridinium triflate provided **3** in low yield although **1a** was completely consumed. Therefore, the electrochemical fluorination is more advantageous than the conventional chemical methods for such heterocyclic sulfides.

In summary, the anodic fluorination of 4-arylthio-1,3-dioxolane-2-ones **1** provided α-fluorinated and/or fluorodesulfurization products **2** and **3**. The product selectivity was greatly affected by electrolytic solvents, supporting fluoride salts, and substituents on the benzene ring. Thus, we found the first example of a unique marked solvent effect on the fluorinated product selectivity. The fluorodesulfurization of **2** leading to difluorinated ethylene carbonate **5** was also successfully carried out. Application of fluorinated products **3** and **5** to electrolytic solvents or additives for rechargeable Li batteries will be reported somewhere.

3. Experimental

3.1. General

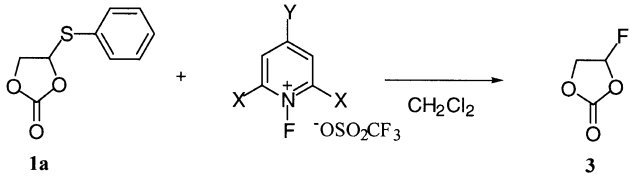
$Et_4NF{\cdot}4HF$ and $Et_3N{\cdot}5HF$ were obtained from Morita Chemical Industries Co. Ltd (Japan). They are toxic and cause serious burns if they are exposed to unprotected skin. $Et_4NF{\cdot}3HF$ and $Et_3N{\cdot}3HF$ are much less aggressive. However, proper safety precautions should be taken at all times.[15] It is therefore recommended to use hand protection.

^1H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded at 270, 254 and 68 MHz, respectively, with $CDCl_3$ as a solvent. The chemical shifts for ^1H and ^{19}F NMR are given in δ (ppm) from internal TMS and monofluorobenzene (−36.5 ppm), respectively. High-resolution mass spectra were obtained with a JEOL JMS-700 mass spectrometer. Cyclic voltammetry was performed with a Hokutodenko potentiostat/galvanostat HAB-151, and preparative electrolysis experiments were carried out with a Metronnix Corp. Tokyo constant current power supply.

3.2. Preparation of starting materials

A typical procedure for the synthesis of 4-arylthio-1,3-dioxolan-2-ones **1** is as follows. To a solution of 1,3-dioxolen-2-one (15 mmol) and arenethiol (20 mmol) in 30 mL of THF, was added Et_3N (20 mmol). The reaction mixture was

Table 4. Chemical fluorination of **1a** using *N*-fluoropyridinium salts



Run	*N*-Fluoropyridinium salt (X, Y)	Condition	Reaction time (h)	Yield (%)
1	X=Y=Me	Reflux	12	Trace
2	X=Y=H	Reflux	12	Trace
3	X=Cl, Y=H	0°C	5	9

heated under reflux for 4 h. The reaction mixture was concentrated under reduced pressure and then purified by column chromatography on silica gel (hexane/EtOAc=5:1) to provide the pure product **1**.

3.2.1. 4-Phenylthio-1,3-dioxolan-2-one (1a). 73% Yield; colorless oil, ^{1}H NMR δ 7.55–7.53 (m, 2H), 7.50–7.38 (m, 3H), 5.91 (dd, *J*=8.9, 6.4 Hz, 1H), 4.72 (dd, *J*=9.2, 8.9 Hz, 1H), 4.22 (dd, *J*=9.2, 6.4 Hz, 1H); ^{13}C NMR δ 153.48, 133.61, 129.34, 128.99, 83.16, 68.27; MS *m/z* 196 (M^+), 152, 123, 109, 87; Anal. Calcd for $C_8H_8O_3S$: C, 55.09; H, 4.11. Found: C, 55.40; H, 4.15.

3.2.2. 4-(*p*-Tolylthio)-1,3-dioxolan-2-one (1b). 84% Yield; colorless solid; mp 60.0–61.0°C; ^{1}H NMR δ 7.43 (d, *J*=7.7 Hz, 2H), 7.19 (d, *J*=7.7 Hz, 2H), 5.85 (dd, *J*=8.2, 6.4 Hz, 1H), 4.70 (dd, *J*=9.2, 8.2 Hz, 1H), 4.22 (dd, *J*=9.2, 6.4 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR δ 153.55, 140.00, 134.30, 130.20, 124.94, 83.27, 68.25, 21.27; MS *m/z* 210 (M^+), 137, 124, 83. HRMS *m/z* Calcd for $C_{10}H_{10}O_3S$: 210.0351. Found: 210.0547.

3.2.3. 4-(*p*-Chlorophenylthio)-1,3-dioxolan-2-one (1c). 100%; Colorless solid; mp 74.0–75.0°C; ^{1}H NMR δ 7.53–7.48 (m, 2H), 7.39–7.34 (m, 2H), 5.89 (dd, *J*=8.4, 6.3 Hz, 1H), 4.75 (dd, *J*=9.4, 8.4 Hz, 1H), 4.24 (dd, *J*=9.4, 6.3 Hz, 1H); ^{13}C NMR δ 153.30, 136.12. 135.09, 129.70, 127.50, 83.06, 68.30; MS *m/z* 232 (M^++2), 230 (M^+), 188, 186, 157, 146, 144, 108, 87. HRMS: *m/z* Calcd for $C_9H_7ClO_3S$: 229.9804. Found: 229.9812.

3.2.4. 4-(*p*-Bromophenylthio)-1,3-dioxolan-2-one (1d). 75%; Colorless solid; mp 84.5–85.0°C; ^{1}H NMR δ 7.54–7.41 (m, 4H), 5.93 (dd, *J*=8.4, 6.3 Hz, 1H), 4.75 (dd, *J*=9.6, 8.4 Hz, 1H), 4.24 (dd, *J*=9.6, 6.3 Hz, 1H); ^{13}C NMR δ 153.29, 1135.11, 132.59, 128.23, 124.19, 82.96, 68.29; MS *m/z* 276 (M^++2), 274 (M^+), 203, 201, 190, 188, 122, 108, 69. HRMS: *m/z* Calcd for $C_9H_7O_3BrS$: 273.9300. Found: 273.9299.

3.2.5. 4-(*p*-Methoxyphenylthio)-1,3-dioxolan-2-one (1e). 29% Yield; colorless solid; mp 61.0–61.5°C; ^{1}H NMR δ 7.51–7.47 (m, 2H), 6.93–6.88 (m, 2H), 5.80 (dd, *J*=8.2, 6.3 Hz, 1H), 4.69 (dd, *J*=9.4, 8.2 Hz, 1H), 4.23 (dd, *J*=9.4, 6.3 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR δ 161.01, 153.57, 136.69, 118.49, 115.05, 83.34, 68.19, 55.42; MS *m/z* 226 (M^+), 182, 153, 140, 139. HRMS: *m/z* Calcd for $C_{10}H_{10}O_4S$: 226.0300. Found: 226.0269.

3.3. Anodic fluorination of 4-arylthio-1,3-dioxolan-2-ones

A general procedure for the anodic fluorination of 4-arylthio-1,3-dioxolan-2-ones is as follows. Anodic oxidation of **1** (1 mmol) was carried out with platinum-plate electrodes (2×2 cm^2) in 1.0 M $Et_4NF{\cdot}4HF$ (40 equiv. of F^- to **1**)/ DME, CH_2Cl_2 and/or MeCN (10 mL) in a cylindrical undivided cell under nitrogen atmosphere at room temperature. Constant current (5 mA/cm^2) was passed until the starting material **1** was completely consumed (checked by silica gel TLC). After electrolysis, the electrolytic solution was passed through a short column filled with silica gel using ethyl acetate to remove fluoride salts. The resulting solution was evaporated under reduced pressure, and the residue was further purified by column chromatography on silica gel using hexane/ethyl acetate (5:1) as an eluent.

3.3.1. 4-Fluoro-4-phenylthio-1,3-dioxolan-2-one (2a). Colorless oil; ^{1}H NMR δ 7.66–7.62 (m, 2H), 7.50–7.39 (m, 3H), 4.63 (dd, *J*=17, 11 Hz, 1H), 4.47 (dd, *J*=26, 11 Hz, 1H); ^{13}C NMR δ 150.64, 136.21, 130.89, 129.70, 125.03, 119.54 (d, *J*=270 Hz), 73.88 (d, *J*=31 Hz); ^{19}F NMR δ 0.54 (dd, *J*=27, 17 Hz); MS (*m/z*) 214 (M^+), 123, 109; HRMS *m/z* Calcd for $C_9H_7FO_3S$: 214.0100. Found: 214.0133.

3.3.2. 4-Fluoro-4-(*p*-tolylthio)-1,3-dioxolan-2-one (2b). Colorless oil; ^{1}H NMR δ 7.51 (d, *J*=8.1 Hz, 2H), 7.23 (d, *J*=8.1 Hz, 2H), 4.61 (dd, *J*=17, 11 Hz, 1H), 4.45 (dd, *J*=27, 11 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR δ 150.61, 141.45, 136.19 (d, *J*=1.1 Hz) 130.44, 121.46 (d, *J*=3.4 Hz), 119.57 (d, *J*=270 Hz), 73.80 (d, *J*=31 Hz), 21.44; ^{19}F NMR δ −0.24 (dd, *J*=27, 17 Hz); MS (*m/z*) 228 (M^+), 208 (M^+−HF), 135, 123; HRMS *m/z* Calcd for $C_{10}H_9FO_3S$: 228.0256. Found: 228.0254.

3.3.3. 4-Fluoro-4-(*p*-chlorophenylthio)-1,3-dioxolan-2-one (2c). Colorless needles; mp 60.0–61.0°C; ^{1}H NMR δ 7.60–7.57 (m, 2H), 7.43–7.40 (m, 2H), 4.66 (dd, *J*=17, 11 Hz, 1H), 4.47 (dd, *J*=26, 11 Hz, 1H); ^{13}C NMR δ 150.40, 137.72, 137.43, 129.96, 123.34, 119.21 (d, *J*=270 Hz), 73.83 (d, *J*=31 Hz); ^{19}F NMR δ 0.93 (dd, *J*=27, 17 Hz); MS (*m/z*) 250 (M^++2), 248 (M^+), 159, 157, 145, 143, 108; HRMS *m/z* Calcd for $C_9H_6ClFO_3S$: 247.9710. Found: 247.9720.

3.3.4. 4-Fluoro-4-(*p*-bromophenylthio)-1,3-dioxolan-2-one (2d). Colorless oil; ^{1}H NMR δ 7.58–7.48 (m, 4H), 4.66 (dd, *J*=11, 17 Hz, 1H), 4.48 (dd, *J*=17, 26 Hz, 1H); ^{13}C NMR δ 150.35, 137.52, 132.85, 125.91, 123.88, 119.08 (d, *J*=270 Hz), 73.81 (d, *J*=31 Hz); ^{19}F NMR δ 1.02 (dd, *J*=27, 17 Hz); MS (*m/z*) 294 (M^++2), 292 (M^+), 203, 201, 189, 187, 108; HRMS *m/z* Calcd for $C_9H_6BrFO_3S$: 291.9205. Found: 291.9213.

3.3.5. 4-Fluoro-1,3-dioxolan-2-one (3). Colorless cubes; mp 19.0–20.0°C; ^{1}H NMR δ 6.35 (ddd, *J*=64, 3.6, 0.7 Hz, 1H), 4.66 (ddd, *J*=34, 11, 3.6 Hz, 1H), 4.55 (ddd, *J*=21, 11, 0.7 Hz, 1H); ^{13}C NMR δ 152.69 (d, *J*=1.7 Hz), 105.10 (d, *J*=236 Hz), 70.71 (d, *J*=28 Hz); ^{19}F NMR δ −44.75 (ddd, *J*=64, 34, 21 Hz); MS (*m/z*) 106 (M^+), 62; Anal. Calcd for $C_3H_3FO_3$: C, 33.98%; H, 2.85%; F, 17.91%. Found: C, 33.73%; H, 2.91%; F, 17.72%.

3.3.6. 4-(*p*-Fluoromethylphenylthio)-1,3-dioxolan-2-one (4). Colorless oil; ^{1}H NMR δ 7.59 (d, *J*=7.9 Hz, 2H), 7.39 (d, *J*=7.9 Hz, 2H), 5.92 (dd, *J*=8.4, 6.4 Hz, 1H), 5.40 (d, *J*=47 Hz, 2H), 4.75 (dd, *J*=9.6, 8.4 Hz, 1H), 4.25 (dd, *J*=9.6, 6.4 Hz, 1H); ^{13}C NMR δ 153.40, 137.73 (d, *J*=17 Hz), 133.80, 129.59 (d, *J*=2.8 Hz), 128.01 (d, *J*=6.1 Hz), 83.57 (d, *J*=170 Hz), 83.09, 68.32; ^{19}F NMR δ −134.13 (t, *J*=47 Hz); MS (*m/z*) 228 (M^+), 155, 142, 109; HRMS *m/z* Calcd for $C_{10}H_9FO_3S$: 228.0256. Found: 228.0253.

3.3.7. 4,4-Difluoro-1,3-dioxolan-2-one (5). ^{1}H NMR δ 4.72 (t, *J*=12 Hz, 2H); ^{19}F NMR δ 3.90 (t, *J*=12 Hz); MS (*m/z*)

124 (M^+), 109; HRMS *m/z* Calcd for $C_3H_2F_2O_3$: 123.9972. Found: 123.9939.

3.4. Chemical fluorination of 4-phenylthio-1,3-dioxolan-2-one (1a)

To a solution of **1a** (1.0 mmol) in CH_2Cl_2 (8 mL), was added *N*-fluoro-2,6-dichloropyridinium triflate at 0°C under N_2. The reaction mixture was stirred at 0°C for 5 h. After the starting material was completely consumed, the reaction mixture was passed through a short column of silica gel ($CHCl_3$). The yield of **3** was determined by ^{19}F NMR spectrometry.

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