JOC Article

Electrolytic Partial Fluorination of Organic Compounds.71.[1] Highly Diastereoselective Anodic Fluorination of Sulfides Having Oxygen-Containing Heterocyclic Groups

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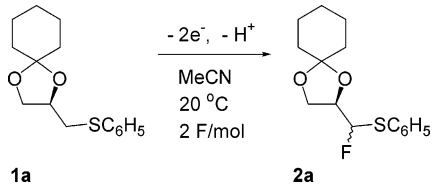
Diastereoselective anodic fluorination of sulfides having various oxygen-containing heterocyclic substituents such as 2-furanyl, 1,3-dioxolanyl, 2,2-dimethyl-1,3-dioxolanyl, 2-spirocyclohexyl-1,3-dioxolanyl, 2-spiroadamantyl-1,3-dixolanyl, and 1,3-dioxolanonyl groups at the β-position was comparatively studied. Among the oxygen-containing heterocyclic substituents, the 2-spirocyclohexyl-1,3-dioxolanyl group gave the best diastereoselectivity (80% de). The diastereoselectivity was also affected by supporting fluoride salts and solvents. Chemical fluorination using selectfluor resulted in much lower diastereoselectivity and extremely poor yield. The fluorinated products were readily converted into the corresponding fluorinated diol in good yields by acidic hydrolysis.

Introduction

Although a diastereoselective fluorination with an electrophilic reagent proceeds with high diastereoselectivity, a diastereoselective nucleophilic fluorination is generally difficult, probably because of the smallness of the fluoride ion and the necessity of the use of polar solvents for electric conductivity.[2] Therefore, only a few studies have been reported on diastereoselective anodic fluorination.[2] Kabore et al. obtained up to 60% de in the anodic fluorination of α-phenylacetates having various chiral auxiliaries,[3] while we obtained a much lower de of 20% in the anodic fluorination of α-phenylthioacetates having similar chiral auxiliaries.[4] Quite recently, we reported a highly diastereoselective anodic fluorination of *N*-acylthiazolidines derived from L-cysteine[5] and chiral 1,3-oxothiolan-5-ones derived from champhorsulfonamide.[6] On the other hand, chiral fluorine-containing 1,2-diols are useful building blocks for the preparation of valuable organofluorine compounds such as fluorinated sugars.[7] However, their preparation methods are limited. Therefore, the development of new synthetic methods for fluorinated diols is of much importance.[8]

SCHEME 1



In this study, we carried out successfully highly diastereoselective anodic fluorination of sulfides having oxygen-containing heterocycles and converted the fluorinated sulfides to the corresponding chiral fluorine-containing diol.

Results and Discussion

At first, anodic fluorination of (*R*)-4-[(phenylthio)-methyl]-2-spirocyclohexyl-1,3-dioxolane (**1a**) as a model compound was carried out in acetonitrile (MeCN) containing various supporting fluoride salts. The electrolysis was conducted at a constant current, and 2 F/mol of electricity was passed. The results are shown in Scheme 1 and Table 1. Among the supporting electrolytes used, $Et_3N{\cdot}3HF$ was the most suitable for the anodic fluorination since its use provided the highest diastereoselectivity and yield. In a strongly acidic solution, the deprotection of the diol moiety of **1a** took place; therefore, the desired anodic fluorinations did not proceed at all (runs 4−6). Thus, both the yield and diastereoselectivity of the anodic fluorination were found to be greatly affected by supporting fluoride salts.

Next, the solvent effect on the anodic fluorination of **1a** was investigated using various solvents containing

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TABLE 1. Effect of Supporting Electrolytes on the Anodic Fluorination of 1a[a]

run	supporting electrolyte	yield[b] (%)	*de*[b,c] (%)
1	Et_3N·2HF	8	62
2	Et_3N·3HF	54	80
3	Et_3N·4HF	6	58
4	Et_3N·5HF	0	
5	Et_4NF·3HF	trace	
6	Et_4NF·4HF	0	

[a] Charge passed 2 F/mol. [b] Determined by ^{19}F NMR. [c] The absolute configuration of the major diastereomer is (1*R*,2*S*).

TABLE 2. Solvent Effect on the Anodic Fluorination of 1a[a]

run	solvent (DN)[b]	yield[c] (%)	de[c] (%)
1	CH_2Cl_2 (0)[d]	60	69
2	NM (2.7)	0	
3	MeCN (14.1)	54	80
4	dioxane (14.8)	14	64
5	PC (15.1)	43	58
6	DME (20.0)	62	51
7	DMSO (29.8)	0	

[a] Charge passed 2 F/mol. [b] Gutmann's donor number. [c] Determined by ^{19}F NMR. [d] Donor number estimated from CH_2ClCH_2Cl (DN = 0).

Et_3N·3HF. The results at 2 F/mol of electricity passed are shown in Table 2. The solvents also affected considerably the anodic fluorination. Higher yields were obtained in DME and dichloromethane compared with acetonitrile. DMSO and nitromethane were not suitable for the fluorination.

Among the solvents used, acetonitrile gave the highest diastereoselectivity. Notably, the diastereoselectivity increased with a decrease in the donor number[9] (DN) of solvents except for dichloromethane. This can be explained in terms of the decrease of the nucleophilicity (reactivity) of fluoride ions in solvents having smaller donor numbers.[10] In support of this, we measured ^{19}F NMR spectra of Et_3N·3HF in DME, dioxane, MeCN, and CH_2Cl_2. Previously, we observed the fluorine signal of fluoride ions of Et_4NF·*n*HF (*n* = 3, 4) in solvents having larger donor numbers at higher magnetic field since such solvents solvate more strongly the cations of Et_3N·3HF to make the fluoride ions naked like KF in crown ethers.[10] In fact, it was found that the fluorine signal due to Et_3N·3HF in DME appeared at higher magnetic field (δ −98.8 ppm) than that in PC (δ −98.5 ppm), dioxane (δ −97.4 ppm), AN (δ −97.1 ppm), and CH_2Cl_2 (δ −96.2 ppm). On the other hand, no clear correlation of yield and DN was observed because the electrochemical fluorination was also influenced by the electrochemical stability (runs 4 and 6) and the viscosity (runs 4 and 5) of the electrolytic solvents.

Thus, it was found that electrolytic solvents affected significantly the diastereoselectivity as well as the yield.

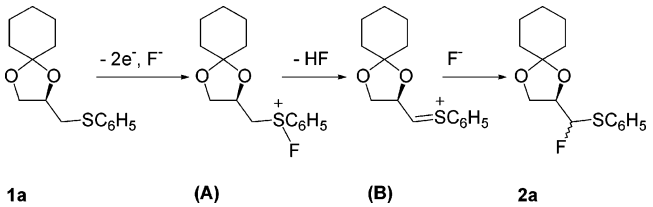
Next, the temperature effect on electrochemical fluorination was investigated. The reactions were carried out until starting materials were consumed completely (monitored by gas chromatography). At first, anodic fluorination in MeCN was investigated at various temperature as shown in Table 3. At a low temperature such as 0 °C, the anodic fluorination did not proceed effectively and a large excess amount of electricity was required to complete the electrolysis (run 1).

TABLE 3. Temperature Effect on the Anodic Fluorination of 1a

run	solvent	charge passed (F/mol)	temp (°C)	yield[a] (%)	de[a] (%)
1	MeCN	8	0	31	76
2	MeCN	3	20	66	80
3[b]	MeCN	3	40	45	78
4	DME	6	20	89	51
5	DME	5	40	90	52
6	DME/MeCN (1:1)	5	20	92	61
7	DME/MeCN (1:1)	3	40	>99	59

[a] Determined by ^{19}F NMR. [b] Difluoroination of monofluorinated product **2a** also took place.

SCHEME 2



At a higher temperature such as 20 °C, the yield was increased significantly and the required amount of electricity was decreased to 3 F/mol (run 2). As we have already reported previously,[11] the deprotonation of the fluorosulfonium ion intermediate (**A**) in the rate-determining step from **A** to **B** in Scheme 2 should be facilitated at a higher temperature.

However, at 40 °C, the yield decreased since difluorination took place simultaneously (run 3). On the other hand, the anodic fluorination proceeded efficiently in DME to provide a good yield (runs 4 and 5) since DME enhances the nucleophilicity of fluoride ions, as reported previously.[10,11−13] Even at 40 °C, no difluorination took place because DME was sacrificially (simultaneously) oxidized instead of monofluorinated product **2a** once formed.

In DME solely as an electrolytic solvent, a large excess amount of electricity was required because of its simultaneous oxidation. Since MeCN is rather stable against anodic oxidation, a mixed solvent of DME/MeCN (1:1) was used for the anodic fluorination (runs 6 and 7). An excellent yield and much better current efficiency were achieved at 40 °C (run 7).[14] However, the diastereoselectivity was much lower than that in MeCN. Interestingly, the diastereoselectivity (de) was not affected appreciably by temperature although de was changed significantly depending on the solvents. Thus, high diastereoselectivity (80% de) was obtained in MeCN although the yield was moderate (run 2).

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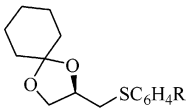
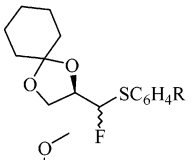
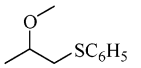
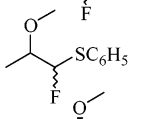
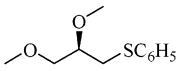
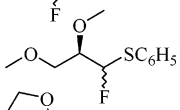
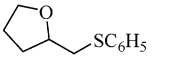
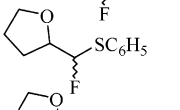
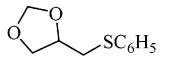
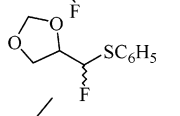
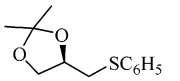
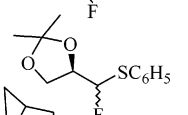
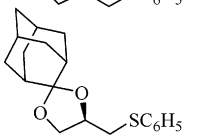
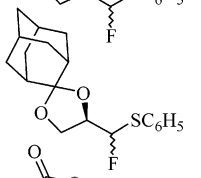
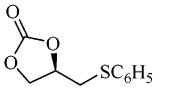
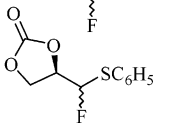
TABLE 4. Anodic Fluorination of Sulfides Having Oxygen-Containing Heterocyclic and Oxygen Substituents

run	sbustrates		products	yield. (%) [a]	*d.e.* (%) [a] [c]
1		R = H (**1a**)		54 (40)[b] (**2a**)	80
2		*p*-Cl (**1b**)		77 (71)[b] (**2b**)	70
3		*p*-NO_2 (**1c**)		67 (54)[b] (**2c**)	58
4		*p*-OMe (**1d**)		trace (**2d**)	-
5		(**3**)		10 (**4**)	30
6		(**5**)		30 (**6**)	60
7		(**7**)		28 (**8**)	60
8		(**9**)		51 (**10**)	68
9		(**11**)		45 (**12**)	70
10		(**13**)		22 (**14**)	55
11		(**15**)		22 (19)[b] (**16**)	13

[a] Determined by ^{19}F NMR. [b] Isolated yield. [c] The absolute configuration of the major diastereomer is (1*R*,2*S*).

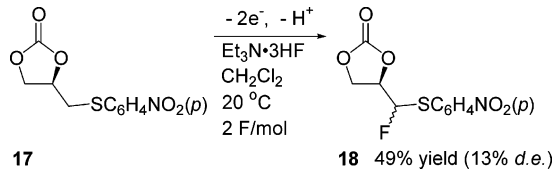
Since anodic fluorination of **1a** in $Et_3N{\cdot}3HF$/MeCN at 20 °C gave the highest diastereoselectivity, anodic fluorination of sulfides having various oxygen-containing heterocyclic and open-chain alkoxy groups was examined. To compare the diastereoselectivity, 2 F/mol of electricity was passed (the starting sulfides were not always consumed completely). The results are shown in Table 4.

The low yields in some cases are due to the recovered starting materials. The de values of the fluorinated sulfides would be changed during the electrolysis if their carbon−fluorine bond cleavage/formation were reversible in the electrolytic solution. To confirm this point, the fluorinated product **2a** was left overnight in the electrolytic solution at room temperature. However, the de value did not change at all. The diastereoselectivity of the anodic fluorination of sulfide **5** having two methoxy groups is much higher than that of sulfide **3** with one methoxy group. However, sulfide **7** having a 2-furanyl group also showed the same de as sulfide **5**. These results may suggest that a γ-substituent as well as a γ-methoxy one play an important role in the diastereoselectivity. Next, the protecting group effect of 1,2-diol moieties on the regioselective anodic fluorination was investigated. Although the dimethyl group in the dioxolanyl group made de slightly increase (run 9), the spirocyclohexyl group was very effective for the diastereoselectivity and 80% de was obtained in the case of **1a** (run 1). This result seems to suggest that bulkier protecting groups would give higher de. However, the extremely bulky spiroadamantyl group decreased the diastereoselectivity, and the de was lower compared with that of the smallest protecting group (sulfide **9**, run 8). In sharp contrast to these protecting groups, a carbonyl protecting group of sulfide **15** decreased the de drastically to 13% (run 11). Furthermore, anodic fluorination of *para*-substituted phenyl sulfides **1b**−**d** was carried out to investigate the substituent effect on the diastereoselectivity (runs 2−4). The fluorination of **1d** having an electron-donating methoxy group did not proceed. In contrast, the sulfides containing electron-withdrawing groups such as chloro and nitro groups underwent anodic fluorination more efficiently than **1a**, but the diastereoselectivity was lower (**1b**) or much lower (**1c**) compared with that of **1a**. These results suggest that the cationic character of the anodically generated sulfenium ion intermediate **B** (Scheme 2) also appreciably affects the diastereoselectivity. Thus, it was found that the diastereoselectivity of the anodic fluorination of sulfides is not always controlled by their molecular bulkiness.

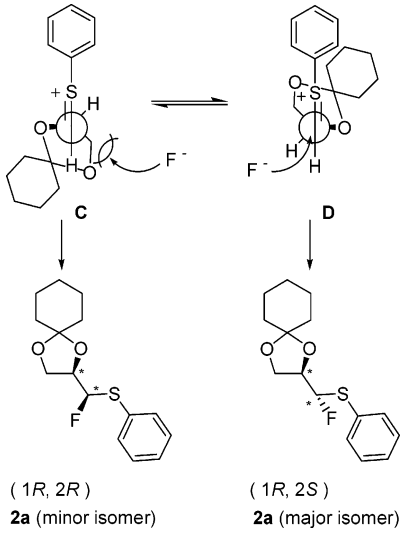
Determination of the stereochemistry of major isomers was attempted by their X-ray analyses. However, suitable crystals of fluorinated products for the X-ray crystal structure analysis were not obtained. After many attempts, a suitable crystalline form of the major diastereomer of **18** was obtained by the anodic fluorination of *p*-nitrophenyl sulfide **17** having a 1,3-dioxolanonyl group (Scheme 3).

Since X-ray analysis of the major diastereomer of **18** shows that the configuration is (1*R*,2*S*), the configuration of other major isomers is assumed to be (1*R*,2*S*). On the

SCHEME 3



SCHEME 4



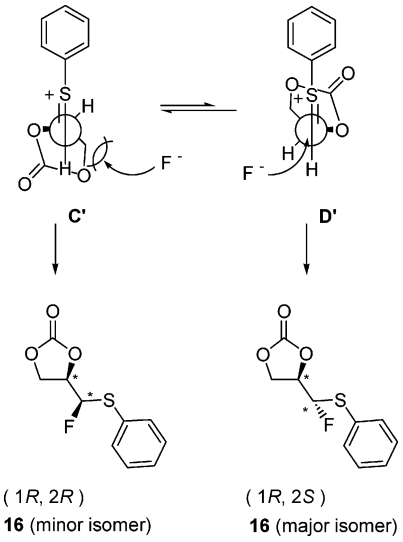
basis of this result, we considered the detailed mechanism of the stereochemical control in nucleophilic reactions as shown in Scheme 4 using the Felkin−Anh model generally employed for this type of reaction via a cationic intermediate.

For the two possible conformations **C** and **D**, fluoride ion attack at the activated carbon atom is usually explained to occur from the other side of the perpendicular C−O bond, and conformation **D** should experience less steric repulsion with the incoming fluoride with the possible electrostatic attraction of the β-oxygen atom and the sulfenium ion. Thus, the reaction of a fluoride ion was realized from the *si* face of conformation **D**, leading to the formation of the (1*R*,2*S*) isomer, which is totally consistent with the above X-ray analysis data. Conformation **D** is preferable as long as a suitably bulky protecting group is employed and good to excellent diastereoselectivity is obtained, but the use of the extremely hindered spiroadamantyl group decreased the diastereoselectivity. This can be explained as the result of the increased instability of **D** and allowing the reaction path through **C** to some extent.

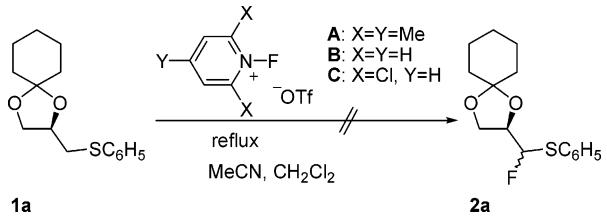
In the case of sulfide **15**, the electron density of the ring oxygen atoms should decrease due to the electron-withdrawing carbonyl group, which decreases the electrostatic attraction of **15** (**D′** conformation), as shown in Scheme 5. Therefore, conformation **C′** becomes more favorable than **D′**. Thus, a fluoride ion also attacks the activated carbon of **C′**. Consequently, the diastereoselectivity of the fluorination of **15** decreases.

N-Fluoropyridinium salts have been widely used for the selective fluorination of various organic compounds in recent years.[15] They are safe, easy to handle, and commercially available. It was expected that the fluorination would proceed similarly to the anodic fluorination

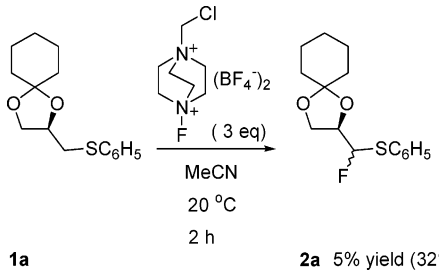
SCHEME 5



SCHEME 6



SCHEME 7



since it is known that the fluorination of sulfides proceeds via a fluorosulfonium ion intermediate.[14b] We attempted the chemical fluorination of **1a** using various *N*-fluoropyridinium salts **A**−**C** as shown in Scheme 6. However, the fluorinations did not proceed at all. In the case of weakly fluorinating reagent **A**, the starting material was mostly recovered, while the use of strongly fluorinating reagents **B** and **C** caused decomposition.

Additionally, we used selectfluor[16] for the fluorination of **1a**, and the desired fluorinated product was obtained; however, both the yield and de were much lower than those of electrochemical fluorination as shown in Scheme 7. In this case, the starting material **1a** was mostly recovered. Hence, the electrochemical fluorination proved to be a useful way for diastreoselective fluorination of sulfides having diol moieties.

In the final part of this paper, we examine the deprotection of fluorinated products. Acid hydrolysis of

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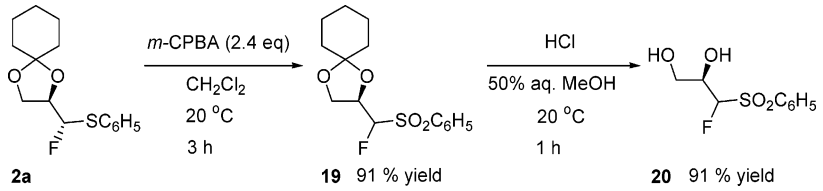
(16) Lal, G. S. *J. Org. Chem.* **1993**, *58*, 2791.

SCHEME 8



2a resulted in decomposition. Therefore, **2a** was converted into the corresponding sulfone **19** by oxidation with *m*-CPBA, and then the acid hydrolysis reaction of **19** was carried out at room temperature to provide the corresponding diol derivative **20** quantitatively as shown in Scheme 8. The major diastereomer of **2a** was easily separated, and it was similarly converted to optically pure **20**. The monofluorinated diol **20** thus obtained has multifunctional groups; therefore, **20** seems to be a useful fluorinated building block.

Conclusions

In this study, we investigated various effects of supporting electrolytes, solvents, temperature, and molecular structures on the diastereoselectivity in the electrochemical fluorination of sulfides having protected 1,2-diol moieties. The results of our experiment definitely show that the diastereoselectivity and yield were affected by the electrolytic conditions, particularly, solvents and protecting groups. We successfully carried out highly diastereoselective anodic monofluorination of a sulfide having a 2-spirocyclohexyl-1,3-dioxolanyl group, and the fluorinated products were easily converted into monofluorodiol derivative in good yield.

Experimental Section

General Procedures. $Et_3N{\cdot}nHF$ (n = 2−5) and $Et_4NF{\cdot}nHF$ (n = 3, 4) were obtained from a commercial supplier. They are toxic and may cause serious burns if they come in contact with unprotected skin. $Et_3N{\cdot}nHF$ (n = 2, 3) and $Et_4NF{\cdot}3HF$ are much less aggressive. However, proper safety precautions should be taken at all times. It is therefore recommended that rubber gloves be used. ^{1}H 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.

Materials. The typical procedure for the preparation of starting sulfide **1a** is as follows. To a solution of (*R*)-(−)-3-chloro-1,2-propanediol (0.92 mL, 11 mmol) and benzenethiol (1.1 g, 10 mmol) in DMF (30 mL) was added potassium carbonate (0.28 g, 20 mmol) at room temperature for 6 h. After the reaction, water was added to the resulting solution. The resulting solution was extracted repeatedly with ethyl acetate, and the extracts were dried over $MgSO_4$. The solution was concentrated in vacuo, and the residue, 1,1-dimethoxycyclohexane (2.02 g, 14 mmol) and *p*-toluenesulfonic acid monohydrate (0.09 g, 0.5 mmol), was stirred at room temperature for 1 h. After the reaction, water was added. The resulting solution was extracted repeatedly with ethyl acetate, and the extracts were dried over $MgSO_4$. The extraction solvent was removed by evaporation, and the remaining material was subjected to column chromatography on silica gel (hexane:EtOAc = 9:1) to give 2.49 g (94.1% yield) of pure (*R*)-4-[(phenylthio)methyl]-2-spirocyclohexyl-1,3-dioxolane (**1a**).

Electrolysis. Constant-current electrolysis (10 mA/cm^2) of sulfide (1 mmol) was carried out at platinum electrodes (2 × 2 cm^2) in 10 mL of solvents containing 1.0 M fluoride salt using an undivided PP (polypropylene) cell under a nitrogen atmosphere. After the electrolysis, the resulting electrolytic solution was subjected to short column chromatography on silica gel using ethyl acetate to remove the fluoride salt. The eluent was evaporated under vacuum, and the residue was purified by silica gel column chromatography (hexane:EtOAc = 4−9:1).

Data for (*R*)-4-[(phenylthio)methyl]-2-spirocyclohexyl-1,3-dioxolane (1a): $[\alpha]_D^{22}$ +6.7 (*c* 0.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.38−7.18 (5H, m), 4.26−4.21 (1H, m), 4.05 (1H, dd, J = 8.6, 5.9 Hz), 3.74 (1H, dd, J = 8.4, 5.7 Hz), 3.26−2.88 (2H, m), 1.65−1.38 (10H, m) ppm; ^{13}C NMR ($CDCl_3$) δ 135.3, 129.5, 128.8, 126.2, 110.1, 74.3, 68.3, 37.3, 35.0, 25.1, 24.0, 23.8 ppm; MS (*m*/*z*) 264 (M^+), 141 ($M^+ - CH_2SC_6H_5$); HRMS (*m*/*z*) calcd for $C_{15}H_{20}O_2S$ 264.1184, found 264.1184. Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.14; H, 7.62; S, 12.13. Found: C, 68.24; H, 7.48; S, 11.85.

Data for (*R*)-4-[[(*p*-chlorophenyl)thio]methyl]-2-spirocyclohexyl-1,3-dioxolane (1b): yield 84.2%; ^{1}H NMR ($CDCl_3$) δ 7.33−7.24 (4H, m), 4.23−4.14 (1H, m), 4.10−3.71 (2H, m), 3.20−2.89 (2H, m), 1.60−1.26 (10H, m) ppm; ^{13}C NMR ($CDCl_3$) δ 134.7, 131.2, 130.9, 129.0, 110.3, 74.3, 68.3, 37.6, 36.7, 35.0, 25.2, 24.1, 23.9 ppm; MS (*m*/*z*) 298 (M^+), 141 ($M^+ - CH_2SC_6H_4Cl$); HRMS (*m*/*z*) calcd for $C_{15}H_{19}ClO_2S$ 298.0794, found 298.0794.

Data for (*R*)-4-[[(*p*-nitrophenyl)thio]methyl]-2-spirocyclohexyl-1,3-dioxolane (1c): yield 77.9%; ^{1}H NMR ($CDCl_3$) δ 8.26−8.10 (2H, m), 7.52−7.36 (2H, m), 4.69−4.56 (1H, m), 4.48−4.23 (2H, m), 3.48−3.21 (2H, m), 1.66−1.37 (10H, m) ppm; ^{13}C NMR ($CDCl_3$) δ 143.1, 141.8, 129.0, 126.4, 107.4, 73.8, 68.1, 37.2, 36.1, 25.3, 24.2 ppm; MS (*m*/*z*) 309 (M^+), 141 ($M^+ - CH_2SC_6H_4NO_2$); HRMS (*m*/*z*) calcd for $C_{15}H_{19}NO_4S$ 309.1035, found 309.1035.

Data for (*R*)-4-[[(*p*-methoxyphenyl)thio)methyl]-2-spirocyclohexyl-1,3-dioxolane (1d): yield 96.1%; ^{1}H NMR ($CDCl_3$) δ 7.39−7.36 (2H, m), 6.85−6.82 (2H, m), 4.20−4.13 (1H, m), 4.05 (1H, dd, J = 8.1, 5.9 Hz), 3.79 (3H, s), 3.69 (1H, dd, J = 8.1, 5.9 Hz), 3.17−2.78 (2H, m), 1.61−1.38 (10H, m) ppm; ^{13}C NMR ($CDCl_3$) δ 159.0, 133.5, 125.3, 114.5, 109.9, 74.6, 68.4, 55.3, 39.3, 36.7, 35.1, 25.1, 24.0, 23.8 ppm; MS (*m*/*z*) 294 (M^+), 155 ($M^+ - CH_2SC_6H_4OCH_3$); HRMS (*m*/*z*) calcd for $C_{16}H_{22}O_3S$ 294.1290, found 294.1290.

Data for (*R*)-4-[fluoro(phenylthio)methyl]-2-spirocyclohexyl-1,3-dioxolane (2a) (more polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.53−7.27 (5H, m), 5.72 (1H, dd, J = 54.1, 5.4 Hz), 4.34−4.20 (1H, m), 4.07−3.70 (2H, m), 1.87−1.39 (10H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −80.12 (dd, J = 54.6, 11.2 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 132.8, 129.2, 128.6, 126.3, 110.8, 101.1 (d, J = 222.0 Hz), 75.3 (d, J = 27.3 Hz), 63.6 (d, J = 2.8 Hz), 35.8, 34.6, 30.8, 25.3, 23.9 ppm; MS (*m*/*z*) 282 (M^+), 141 ($M^+ - CHFSC_6H_5$); HRMS (*m*/*z*) calcd for $C_{15}H_{19}FO_2S$ 282.1090, found 282.1090.

Data for 2a (less polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.54−7.27 (5H, m), 5.62 (1H, dd, J = 54.1, 7.0 Hz), 4.35−4.21 (1H, m), 4.09−3.72 (2H, m), 1.67−1.40 (10H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −79.52 (dd, J = 54.5, 9.4 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 132.7, 129.5, 128.8, 126.3, 110.0, 101.5 (d, J = 222.0 Hz), 75.5 (d, J = 27.3 Hz), 63.4 (d, J = 2.8 Hz), 36.0, 34.7, 30.9, 25.1, 23.8 ppm; MS (*m*/*z*) 282 (M^+), 141 ($M^+ - CHFSC_6H_5$); HRMS (*m*/*z*) calcd for $C_{15}H_{19}FO_2S$ 282.1090, found 282.1090.

Data for (*R*)-4-[fluoro[(*p*-chlorophenyl)thio]methyl]-2-spirocyclohexyl-1,3-dioxolane (2b) (more polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.35−7.25 (4H, m), 5.93 (1H,

dd, J = 53.8, 3.0 Hz), 4.71−4.63 (1H, m), 4.50−4.31 (2H, m), 1.70−1.41 (10H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −79.91 (dd, J = 53.6, 11.2 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 139.3, 131.2, 130.0, 128.1, 108.9, 101.1 (d, J = 224.1 Hz), 74.5, 69.1, 38.5, 36.5, 25.1, 23.1 ppm; MS (m/z) 316 (M^+), 141 ($M^+ - CHFSC_6H_4NO_2$); HRMS (m/z) calcd for $C_{15}H_{18}ClFO_2S$ 316.0700, found 316.0700.

Data for 2b (less polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.37−7.26 (4H, m), 5.88 (1H, dd, J = 53.0, 4.7 Hz), 4.73−4.63 (1H, m), 4.51−4.33 (2H, m), 1.70−1.42 (10H, m) ppm;^{19}F NMR ($CDCl_3$) δ −79.36 (dd, J = 53.6, 9.1 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 139.2, 131.3, 130.1, 128.0, 108.9, 101.3 (d, J = 224.0 Hz), 74.6, 69.6, 38.4, 36.5, 25.2, 23.1 ppm; MS (m/z) 316 (M^+), 141 ($M^+ - CHFSC_6H_4NO_2$); HRMS (m/z) calcd for $C_{15}H_{18}ClFO_2S$ 316.0700, found 316.0700.

Data for (*R*)-4-[fluoro[(*p*-nitrophenyl)thio]methyl]-2-spirocyclohexyl-1,3-dioxolane (2c) (more polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 8.20−8.17 (2H, m), 7.64−7.60 (2H, m), 5.87 (1H, dd, J = 54.6, 5.4 Hz), 4.41−4.38 (1H, m), 4.15−4.02 (2H, m), 1.69−1.40 (10H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −79.08 (dd, J = 46.3, 9.2 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 143.6, 141.1, 129.8, 126.4, 109.3, 101.1 (d, J = 223.1 Hz), 74.7, 68.1, 38.2, 36.2, 25.7, 23.1 ppm; MS (m/z) 327 (M^+), 141 ($M^+ - CHFSC_6H_4NO_2$); HRMS (m/z) calcd for $C_{15}H_{18}FNO_4S$ 327.0941, found 327.0941.

Data for 2c (less polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 8.19−8.16 (2H, m), 7.61−7.55 (2H, m), 5.82 (1H, dd, J = 54.7, 6.2 Hz), 4.41−4.39 (1H, m), 4.15−4.02 (2H, m), 1.69−1.40 (10H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −82.59 (dd, J = 55.4, 13.0 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 143.8, 141.2, 129.9, 126.4, 109.3, 101.0 (d, J = 223.1 Hz), 74.5, 68.1, 38.3, 36.1, 25.6, 23.3 ppm; MS (m/z) 327 (M^+), 141 ($M^+ - CHFSC_6H_4NO_2$); HRMS (m/z) calcd for $C_{15}H_{18}FNO_4S$ 327.0941, found 327.0941.

Data for 2-methoxypropyl phenyl sulfide (3): ^{1}H NMR ($CDCl_3$) δ 7.37−7.13 (5H, m), 3.53−3.44 (1H, m), 3.34 (3H, s), 3.18−2.83 (1H, m), 1.26 (3H, d, J = 6.3 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 133.6, 129.1, 128.8, 125.9, 75.9, 55.5, 37.7, 19.0 ppm; MS (m/z) 182 (M^+), 123 ($M^+ - CH(OCH_3)CH_3$); HRMS (m/z) calcd for $C_{10}H_{14}OS$ 182.0765, found 182.0770.

Data for 2-methoxy-1-fluoropropyl phenyl sulfide (4) (more polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.51−7.26 (5H, m), 5.82 (1H, dd, J = 51.3, 3.0 Hz), 3.63−3.55 (1H, m), 3.41 (3H, s), 1.26 (3H, d, J = 6.3 Hz) ppm; ^{19}F NMR ($CDCl_3$) δ −75.76 (dd, J = 54.2, 12.9 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 134.3, 130.3, 128.6, 126.3, 108.1, 74.6, 51.4, 14.0 ppm; MS (m/z) 200 (M^+), 109 ($M^+ - CHFCH(OCH_3)CH_3$); HRMS (m/z) calcd for $C_{10}H_{13}FOS$ 200.0671, found 200.0671.

Data for 4 (less polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.51−7.26 (5H, m), 5.68 (1H, dd, J = 50.1, 5.5 Hz), 3.63−3.55 (1H, m), 3.38 (3H, s), 1.25 (3H, d, J = 6.3 Hz) ppm; ^{19}F NMR ($CDCl_3$) δ −80.68 (dd, J = 55.6, 14.3 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 134.1, 130.1, 128.3, 126.0, 107.9, 74.2, 51.2, 13.8 ppm; MS (m/z) 200 (M^+), 109 ($M^+ - CHFCH(OCH_3)CH_3$); HRMS (m/z) calcd for $C_{10}H_{13}FOS$ 200.0671, found 200.0671.

Data for 2,3-dimethoxypropyl phenyl sulfide (5): ^{1}H NMR ($CDCl_3$) δ 7.39−7.18 (5H, m), 3.55−3.49 (2H, m), 3.52−3.45 (1H, m), 3.41 (3H, s), 3.34 (3H, s), 3.12−3.10 (2H, m) ppm; ^{13}C NMR ($CDCl_3$) δ 136.8, 129.2, 128.8, 126.0, 79.1, 72.7, 59.3, 57.7, 34.5 ppm; MS (m/z) 212 (M^+), 123 ($M^+ - CH(OCH_3)CH_2(OCH_3)$); HRMS ($m/z$) calcd for $C_{11}H_{16}O_2S$ 212.0871, found 212.0871.

Data for 2,3-dimethoxy-1-fluoropropyl phenyl sulfide (6) (more polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.41−7.30 (5H, m), 5.94 (1H, dd, J = 54.0, 3.0 Hz), 3.81−3.73 (1H, m), 3.51−3.47 (2H, m), 3.41 (3H, s), 3.31 (3H, s) ppm; ^{19}F NMR ($CDCl_3$) δ −74.82 (dd, J = 53.6, 13.0 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 135.7, 129.8, 127.6, 126.0, 101.3, 79.3, 64.1, 55.7, 52.4 ppm; MS (m/z) 230 (M^+), 109 ($M^+ - CHFCH(OCH_3)CH_2OCH_3$); HRMS ($m/z$) calcd for $C_{11}H_{15}FO_2S$ 230.0777, found 230.0777.

Data for 6 (less polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.42−7.26 (5H, m), 5.90 (1H, dd, J = 54.3, 4.3 Hz), 3.72−3.64 (1H, m), 3.53−3.51 (2H, m), 3.37 (3H, s), 3.27 (3H, s) ppm; ^{19}F NMR ($CDCl_3$) δ −85.19 (dd, J = 54.6, 16.8 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 135.9, 130.0, 127.9, 126.3, 102.1, 79.7, 64.3, 56.0, 52.7 ppm; MS (m/z) 230 (M^+), 109 ($M^+ - CHFCH(OCH_3)CH_2OCH_3$); HRMS ($m/z$) calcd for $C_{11}H_{15}FO_2S$ 230.0777, found 230.0777.

Data for 1-[(phenylthio)methyl]tetrahydrofuran (7): yield 67.4%; ^{1}H NMR ($CDCl_3$) δ 7.38−7.13 (5H, m), 4.08−4.03 (1H, m), 3.94−3.72 (2H, m), 3.19−2.93 (2H, m), 1.96−1.86 (2H, m), 1.72−1.65 (2H, m) ppm; ^{13}C NMR ($CDCl_3$) δ 136.2, 129.0, 128.7, 125.8, 77.5, 68.3, 38.9, 31.0, 25.8 ppm; MS (m/z) 194 (M^+), 123 ($M^+ - CH_2SC_6H_5$); HRMS (m/z) calcd for $C_{11}H_{14}OS$ 194.0765, found 194.0765.

Data for 1-[(phenylthio)fluoromethyl]tetrahydrofuran (8) (more polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.38−7.23 (5H, m), 5.78 (1H, dd, J = 55.5, 4.1 Hz,), 4.29−4.18 (1H, m), 3.96−3.78 (2H, m), 1.99−1.88 (2H, m), 1.71−1.66 (2H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −78.19 (dd, J = 55.6, 14.7 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 136.1, 129.1, 128.7, 125.9, 103.3 (d, J = 223.1 Hz), 79.3, 68.9, 31.2, 23.7 ppm; MS (m/z) 212 (M^+), 141 ($M^+ - CHFSC_6H_5$); HRMS (m/z) calcd for $C_{11}H_{13}FOS$ 212.0671, found 212.0671.

Data for 8 (less polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.38−7.24 (5H, m), 5.66 (1H, dd, J = 54.6, 5.4 Hz), 4.29−4.18 (1H, m), 4.01−3.81 (2H, m), 1.98−1.86 (2H, m), 1.74−1.70 (2H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −80.07 (dd, J = 54.5, 16.5 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 136.2, 129.1, 128.8, 125.9, 103.4 (d, J = 223.1 Hz), 79.4, 69.1, 31.1, 24.0 ppm; MS (m/z) 212 (M^+), 141 ($M^+ - CHFSC_6H_5$); HRMS (m/z) calcd for $C_{11}H_{13}FOS$ 212.0671, found 212.0671.

Data for 4-[(Phenylthio)methyl]-1,3-dioxolane (9): ^{1}H NMR ($CDCl_3$) δ 7.40−7.21 (5H, m), 5.06 (2H, s), 4.22−4.17 (1H, m), 4.00−3.68 (2H, m), 3.27−2.92 (2H, m) ppm; ^{13}C NMR ($CDCl_3$) δ 134.1, 129.7, 128.2, 126.3, 97.6, 75.6, 68.3, 39.3 ppm; MS (m/z) 196 (M^+), 123 ($M^+ - CH_2SC_6H_5$); HRMS (m/z) calcd for $C_{10}H_{12}O_2S$ 196.0558, found 196.0558.

Data for 4-[fluoro(phenylthio)methyl]-1,3-dioxolane (10) (more polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.40−7.18 (5H, m), 5.59 (1H, dd, J = 54.6, 5.7 Hz), 5.09 (2H, s), 4.72−4.59 (1H, m), 4.41−4.28 (2H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −81.31 (dd, J = 54.5, 13.0 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 135.6, 128.7, 126.6, 124.9, 100.4, 97.9, 90.0, 72.1 ppm; MS (m/z) 214 (M^+), 141 ($M^+ - CHFSC_6H_5$); HRMS (m/z) calcd for $C_{10}H_{11}FO_2S$ 214.0464, found 214.0464.

Data for 10 (less polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.43−7.22 (5H, m), 5.51 (1H, dd, J = 54.2, 7.0 Hz), 5.11 (2H, s), 4.75−4.60 (1H, m), 4.40−4.25 (2H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −79.16 (dd, J = 53.6, 13.0 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 135.1, 127.9, 126.8, 124.7, 100.7, 98.1, 90.1, 71.7 ppm; MS (m/z) 214 (M^+), 141 ($M^+ - CHFSC_6H_5$); HRMS (m/z) calcd for $C_{10}H_{11}FO_2S$ 214.0464, found 214.0464.

Data for (*R*)-4-[(phenylthio)methyl]-2,2-dimethyl-1,3-dioxolane (11): yield 86.3%; ^{1}H NMR ($CDCl_3$) δ 7.39−7.19 (5H, m), 4.26−4.14 (1H, m), 4.05−3.72 (2H, m), 3.24−2.90 (2H, m), 1.43 (3H, s), 1.33 (3H, s) ppm; ^{13}C NMR ($CDCl_3$) δ 136.6, 130.0, 129.4, 126.8, 110.0, 75.1, 69.2, 27.5, 25.8 ppm; MS (m/z) 224 (M^+), 123 ($M^+ - CH_2SC_6H_5$); HRMS (m/z) calcd for $C_{12}H_{16}O_2S$ 224.0871, found 224.0871.

Data for (*R*)-4-[fluoro(phenylthio)methyl]-2,2-dimethyl-1,3-dioxolane (12) (more polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.57−7.30 (5H, m), 5.71 (1H, dd, J = 54.1, 5.7 Hz), 4.38−4.28 (1H, m), 4.11−3.99 (2H, m), 1.48 (3H, s), 1.37 (3H, s) ppm; ^{19}F NMR ($CDCl_3$) δ −79.55 (dd, J = 54.5, 11.2 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 132.6, 131.7, 129.0, 128.3, 110.4, 101.4 (d, J = 222.0 Hz), 75.8 (d, J = 27.3 Hz), 65.7 (d, J = 2.8 Hz), 26.4, 25.2 ppm; MS (m/z) 242 (M^+), 133 ($M^+ - SC_6H_5$); HRMS (m/z) calcd for $C_{12}H_{15}FO_2S$ 242.0777, found 242.0777.

Data for 12 (less polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.54−7.32 (5H, m), 5.63 (1H, dd, J = 54.0, 7.0 Hz), 4.39−4.28 (1H, m), 4.14−3.93 (2H, m), 1.48 (3H, s), 1.37 (3H, s) ppm; ^{19}F NMR ($CDCl_3$) δ −79.00 (dd, J = 53.6, 11.2 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 132.6, 131.3, 129.1, 128.3, 110.8, 101.3 (d, J

= 224.8 Hz), 76.4 (d, J = 22.3 Hz), 66.0 (d, J = 2.2 Hz), 26.5, 25.4 ppm; MS (m/z) 242 (M^+), 133 ($M^+ - SC_6H_5$); HRMS (m/z) calcd for $C_{12}H_{15}FO_2S$: 242.0777, found 242.0777.

Data for (*R*)-4-[(phenylthio)methyl]-2-(2-spiroadamantyl)-1,3-dioxolane (13): yield 54.6%; ^{1}H NMR ($CDCl_3$) δ 7.39−7.16 (5H, m), 4.27−4.20 (1H, m), 4.09−3.73 (2H, m), 3.27−2.88 (2H, m), 1.98−1.57 (14H, m) ppm; ^{13}C NMR ($CDCl_3$) δ 135.5, 129.7, 128.9, 126.3, 112.6, 74.5, 68.3, 38.3, 37.6, 34.8, 27.1, 26.9 ppm; MS (m/z) 316 (M^+), 123 ($M^+ - CH_2SC_6H_5$); HRMS (m/z) calcd for $C_{19}H_{24}O_2S$ 316.1497, found 316.1497.

Data for (*R*)-4-[fluoro(phenylthio)methyl]-2-(2-spiroadamantyl)-1,3-dioxolane (14) (more polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.50−7.27 (5H, m), 5.61 (1H, dd, J = 54.0, 7.0 Hz), 4.39−4.28 (1H, m), 4.14−3.94 (2H, m), 2.00−1.61 (14H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −79.68 (dd, J = 53.6, 11.2 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 134.4, 130.3, 127.7, 126.3, 112.5, 101.1, 77.3, 60.6, 38.1, 34.7, 26.2, 25.9 ppm; MS (m/z) 334 (M^+), 123 ($M^+ - CH_2SC_6H_5$); HRMS (m/z) calcd for $C_{19}H_{23}FO_2S$ 334.1403, found 334.1403.

Data for 14 (less polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.49−7.26 (5H, m), 5.68 (1H, dd, J = 54.1, 7.2 Hz), 4.39−4.28 (1H, m), 4.14−3.94 (2H, m), 2.00−1.61 (14H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −79.01 (dd, J = 53.6, 11.2 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 134.6, 130.0, 127.8, 126.3, 112.5, 102.1, 77.8, 60.4, 38.2, 34.7, 26.3, 26.1 ppm; MS (m/z) 334 (M^+), 123 ($M^+ - CH_2SC_6H_5$); HRMS (m/z) calcd for $C_{19}H_{23}FO_2S$ 334.1403, found 334.1403.

Data for 4-[(Phenylthio)methyl]-1,3-dioxolan-2-one (15): yield 81.0%; ^{1}H NMR ($CDCl_3$) δ 7.44−7.26 (5H, m), 4.76−4.74 (1H, m), 4.56−4.49 (1H, m), 4.29−4.23 (1H, m), 3.43−3.03 (2H, m) ppm; ^{13}C NMR ($CDCl_3$) δ 155.3, 133.8, 131.1, 129.5, 127.8, 74.7, 68.6, 37.1 ppm; MS (m/z) 210 (M^+), 123 ($M^+ - CH(OC(=O)O)CH_{2-}$); HRMS (m/z) calcd for $C_{10}H_{10}O_3S$ 210.0351, found 210.0358.

Data for 4-[fluoro(phenylthio)methyl]-1,3-dioxolan-2-one (16) (more molar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.54−7.35 (5H, m), 5.90 (dd, J = 53.5, 2.7 Hz), 5.00−4.91 (1H, m), 4.56−4.36 (2H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −88.96 (dd, J = 53.6, 16.8 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 153.6, 136.3, 130.6, 129.2, 129.0, 99.3 (d, J = 225.4 Hz), 75.4 (d, J = 26.2 Hz), 64.8 (d, J = 3.3 Hz) ppm; MS (m/z) 228 (M^+), 141 ($M^+ - CH(OC(=O)O)CH_{2-}$); HRMS (m/z) calcd for $C_{10}H_9FO_3S$ 228.0256, found 228.0252.

Data for 16 (less polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 7.55−7.35 (5H, m), 5.76 (dd, J = 51.7, 5.9 Hz), 4.92−4.80 (1H, m), 4.57−4.38 (2H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −83.73 (dd, J = 51.8, 13.0 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 153.8, 133.3, 133.1, 129.4, 129.2, 99.6 (d, J = 226.5 Hz), 75.7 (d, J = 25.1 Hz), 65.6 (d, J = 1.7 Hz) ppm; MS (m/z) 228 (M^+), 141 ($M^+ - CH(OC(=O)O)CH_{2-}$); HRMS (m/z) calcd for $C_{10}H_9FO_3S$ 228.0256, found 228.0252.

Data for 4-[[(*p*-nitrophenyl)thio]methyl]-1,3-dioxolan-2-one (17): yield 66.7%; ^{1}H NMR ($CDCl_3$) δ 8.21−8.14 (2H, m), 7.49−7.23 (2H, m),4.96−4.86 (1H, m), 4.63−4.57 (1H, m), 4.35−4.29 (1H, m), 3.52−3.27 (2H, m) ppm; ^{13}C NMR ($CDCl_3$) δ 128.0, 124.3, 131.1, 74.0, 68.2, 35.4 ppm; MS (m/z) 255 (M^+), 168 ($M^+ - CH(OC(=O)O)CH_{2-}$); HRMS (m/z) calcd for $C_{10}H_9NO_5S$ 255.0211, found 255.0197.

Data for 4-[fluoro[(*p*-nitrophenyl)thio]methyl]-1,3-dioxolan-2-one (18) (more molar diastereomer): ^{1}H NMR ($CDCl_3$) δ 8.28−8.24 (2H, m), 7.75−7.68 (2H, m), 6.08 (dd, J = 54.0, 2.9 Hz), 5.01−4.96 (1H, m), 4.66−4.57 (2H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −88.78 (dd, J = 54.2, 15.6 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 153.8, 133.3, 133.1, 129.4, 129.2, 99.6 (d, J = 226.5 Hz), 75.7 (d, J = 25.1 Hz), 65.6 (d, J = 1.7 Hz) ppm; MS (m/z) 273 (M^+), 186 ($M^+ - CH(OC(=O)O)CH_{2-}$); HRMS (m/z) calcd for $C_{10}H_8FNO_5S$ 273.0107, found 273.0107. Anal. Calcd for $C_{10}H_8FNO_5S$: C, 43.96; H, 2.95; F, 6.95; N, 5.13; S, 11.74. Found: C, 43.89; H, 3.16; F, 6.77; N, 5.00; S, 11.74.

Data for 18 (less polar diastereomer): ^{1}H NMR ($CDCl_3$) δ 8.25−8.22 (2H, m), 7.69−7.66 (2H, m), 5.96 (dd, J = 52.5, 4.3 Hz), 5.04−5.02 (1H, m), 4.65−4.47 (2H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −85.32 (dd, J = 52.4, 12.9 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 153.6, 136.3, 130.6, 129.2, 129.0, 99.3 (d, J = 225.4 Hz), 75.4 (d, J = 26.2 Hz), 64.8 (d, J = 3.3 Hz) ppm; MS (m/z) 273 (M^+), 186 ($M^+ - CH(OC(=O)O)CH_{2-}$); HRMS (m/z) calcd for $C_{10}H_8FNO_5S$ 273.0107, found 273.0107.

Data for (1*R*, 2*S*)-4-[fluoro(phenylsulfonyl)methyl]-2-spirocyclohexyl-1,3-dioxolane (19): $[\alpha]^{23}_D$ −8.0 (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.91−7.55 (5H, m), 5.21 (1H, dd, J = 48.3, 9.2 Hz), 4.41−4.23 (1H, m), 4.13−4.10 (2H, m), 1.62−1.38 (10H, m) ppm; ^{19}F NMR ($CDCl_3$) δ −117.66 (dd, J = 46.0, 20.3 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 136.5, 132.1, 130.8, 129.6, 110.9, 100.1(d, J = 224.9 Hz), 71.5 (d, J = 22.7 Hz), 63.9 (d, J = 5.2 Hz), 35.7, 34.5, 25.0, 23.9, 23.8 ppm; MS (m/z) 314 (M^+), 141 ($M^+ - CHFSO_2C_6H_5$); HRMS (m/z) calcd for $C_{15}H_{19}FO_4S$ 314.0988, found 314.0988. Anal. Calcd for $C_{15}H_{19}FO_4S$: C, 57.31; H, 6.09; F, 6.04; S; 10.20. Found: C, 57.35; H, 5.97; F, 6.12; S; 10.02.

Hydrolysis of Fluorinated Sulfide 2a to the Corresponding Diol 20. A mixture of fluoroalkylated dioxolane **2a** (282 mg, 1.0 mmol), methanol (2 mL), and concd hydrochloric acid (1 mL) was stirred under reflux for 1 h (the complete conversion of **2a** was checked by ^{19}F NMR). Methanol was removed on a rotary evaporator, and water was then added. The resulting solution was extracted repeatedly with ethyl acetate, and the extraction solvent was removed by evaporation. The remaining residue was subjected to column chromatography on silica gel (hexane:EtOAc = 4:1) to give 0.21 g (91.1% yield) of pure **20**.

Data for (1*R*,2*S*)-3-fluoro-3-(phenylsulfonyl)-1,2-propanediol (20): $[\alpha]^{22}_D$ +36.6 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.99−7.60 (5H, m), 5.24 (1H, dd, J = 46.4, 8.1 Hz), 4.26−4.20 (1H, m), 3.93−3.78 (2H, m), 3.48 (1H, br), 2.64 (1H, br) ppm; ^{19}F NMR ($CDCl_3$) δ −117.66 (dd, J = 46.0, 20.3 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 136.5, 132.1, 130.8, 129.6, 110.9, 100.1 (d, J = 224.9 Hz), 71.5 (d, J = 22.7 Hz), 63.9 (d, J = 5.2 Hz), 35.7, 34.5, 25.0, 23.9, 23.8 ppm; MS (m/z) 234 (M^+); HRMS (m/z) calcd for $C_9H_{11}FO_4S$ 234.0362, found 234.0362, found 234.0364. Anal. Calcd for $C_9H_{11}FO_4S$: C, 46.15; H, 4.73; F, 8.11; S; 13.69. Found: C, 46.28; H, 4.79; F, 7.95; S; 13.95.

Chemical Fluorination Using *N*-Fluoropyridinium Salts. To a solution of **1a** (282.0 mg, 1.0 mmol) in dry solvent (MeCN, CH_2Cl_2) (2 mL) were added *N*-fluoropyridinium salts **A**−**C** (2 equiv), and the resulting solution was stirred under reflux in a nitrogen atmosphere for 12 h.

Chemical Fluorination Using Selectfluor. To a solution of **1a** (282.0 mg, 1.0 mmol) in dry MeCN (4 mL) was added selectfluor (3 equiv), and the resulting solution was stirred at 20 °C in a nitrogen atmosphere for 2 h.

X-ray Crystallography. X-ray diffraction with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at −60 ± 1 °C to a maximum 2θ value of 55.0°. Crystal data for **18**: $C_{10}H_8O_5NSF$, fw = 273.24, monoclinic, space group $P2_1/n$ (No. 14), a = 10.085(4) Å, b = 20.080(7) Å, c = 5.430(2) Å, β = 90.23(2)°, V = 1099.6(6) Å^3, Z = 4, D_{calcd} = 1.650 g/cm^3, μ = 3.22 cm^{-1}.

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Supporting Information Available: ^{1}H NMR spectra of **1b**−**d**, **2a**−**c**, and **3**−**17** and ^{19}F NMR spectra of **2a**−**c**, **4**, **6**, **8**, **12**, **14**, and **16** (PDF). X-ray crystal structure of compound **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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