

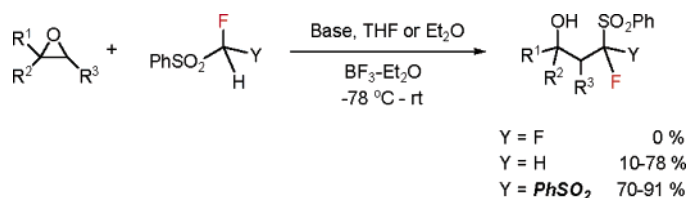
Nucleophilic Fluoroalkylation of Epoxides with Fluorinated Sulfones

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Received May 8, 2006

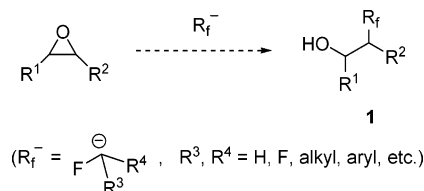


The unprecedented nucleophilic fluoroalkylation of simple epoxides with fluorinated sulfones was achieved to give the β -fluoroalkyl alcohols in one step. The negative “fluorine effect” in the nucleophilic fluoroalkylation of epoxides with fluorinated carbanions was probed by the reactivity comparison between carbanions $\text{PhSO}_2\text{CF}_2^-$ (**3**) and $\text{PhSO}_2\text{CCl}_2^-$ (**4**) and between carbanions $\text{PhSO}_2\text{CHF}^-$ (**7**) and $\text{PhSO}_2\text{CHCl}^-$ (**13**). The mediation of this fluorine effect by introducing another electron-withdrawing benzenesulfonyl group was found to be an effective way to significantly increase the nucleophilicity of the fluorinated carbanions, with the reactivity order $[(\text{PhSO}_2)_2\text{CF}^-]$ (**16**) > $\text{PhSO}_2\text{CFH}^-$ (**7**) $\gg$ $\text{PhSO}_2\text{CF}_2^-$ (**3**).

Introduction

Nucleophilic fluoroalkylation, such as tri-, di-, monofluoromethylation, and perfluoroalkylation, typically involving the transfer of a fluorine-bearing carbanion (R_f^-) to an electrophile, has been widely studied and applied to synthesize fluorine-containing materials and bioactive molecules.^{1–7} However, despite the availability of a variety of good methods (e.g., using the Ruppert–Prakash reagent⁸) and numerous examples of nucleophilic fluoroalkylation of various substrates (such as aldehydes, ketones, imines, nitrones, enones, indanones, esters,

SCHEME 1



lactones, cyclic anhydrides, oxazolidinones, amides, imides, azirines, nitroso compounds, sulfur-based electrophiles, thiocyanates, selenocyanates, alkyl triflates, and alkyl halides, among others),^{1,2} the nucleophilic fluoroalkylation of simple epoxides still remains a challenging task (Scheme 1).^{9–11}

Nucleophilic fluoroalkylation of epoxides, i.e., an oxacycle ring-opening reaction of epoxides with the fluorine-bearing carbanion (R_f^-), is synthetically attractive for synthesizing β -fluoroalkyl alcohols **1** in one step (Scheme 1). Dolbier and

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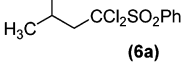
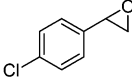
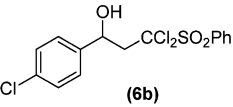
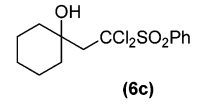
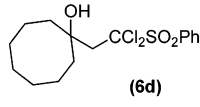
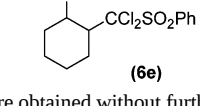
co-workers reported that a trifluoromethyl anion (CF_3^-) derived from a $\text{CF}_3\text{I}/\text{TDAE}$ reagent could not undergo productive reaction with styrene oxide, either alone or in the presence of Lewis acids such as TiCl_4 , BF_3 , or BPh_3 .⁹ Lequeux et al. generated phosphonodifluoromethyl carbanion **2** ($(\text{EtO})_2(\text{O})\text{PCF}_2^-$) both from diethyl difluoromethanephosphonate ($\text{HCF}_2\text{P}(\text{O})(\text{OEt})_2$) with LDA and from diethyl bromodifluoromethanephosphonate with alkyllithium, and they found that in both cases the carbanion **2** could not effectively react with propylene oxide even in the presence of the Lewis acid catalyst $\text{BF}_3\text{--Et}_2\text{O}$.¹⁰ To the best of our knowledge, the only successful example related to nucleophilic fluoroalkylation of epoxides in the literature is the reaction between phosphonodifluoromethyl carbanion **2** (generated from diisopropyl methylsulfanyldifluoromethylphosphonate and *tert*-butyllithium) and epoxides in the presence of $\text{BF}_3\text{--Et}_2\text{O}$, providing moderate product yields.^{10,11}

The unusual difficulty of the ring-opening reaction between an epoxide and a fluorine-bearing carbanion, although not fully understood, arguably can be attributed to the intrinsic property of the fluorine-bearing carbanion (R_f^-), i.e., its low thermal stability (caused by its high tendency to undergo α -elimination of a fluoride ion due to the electron repulsion between the electron pairs on the small fluorine atom(s) and the electron lone pair occupying the p-orbital of the carbanion center) as well as its weak nucleophilicity toward epoxides. We surmised that the possible solution to this problem is to apply a proper auxiliary group connecting to the fluorinated carbanion to increase its thermal stability and nucleophilicity toward epoxides. The benzenesulfonyl group (PhSO_2) is one of the choices, for its good ability to stabilize and soften fluorinated carbanions and its varying chemical reactivities (e.g., easy to remove via reductive desulfonylation).^{7,12} Herein, as part of our ongoing effort to prepare β -fluoroalkyl alcohols for further elaborations, we wish to disclose the studies toward the nucleophilic fluoroalkylation of epoxides with fluorinated carbanions bearing the benzenesulfonyl functionality.

Results and Discussion

Attempted Reaction with (Benzenesulfonyl)difluoromethyl and (Benzenesulfonyl)dichloromethyl Anions. First, we examined the nucleophilic fluoroalkylation of epoxides with (benzenesulfonyl)difluoromethyl anion **3** ($\text{PhSO}_2\text{CF}_2^-$). Unfortunately, carbanion **3**^{7,12} generated in situ from $\text{PhSO}_2\text{CF}_2\text{H}$ and a base (LHMDS or *t*-BuOK) in THF at -78°C would not react with propylene oxide, and after the regular workup, the starting materials were recovered. Addition of a Lewis acid such as $\text{BF}_3\text{--Et}_2\text{O}$ did not lead to any improvement of the reaction. The carbanion **3** was also generated from both $\text{PhSO}_2\text{CF}_2\text{Br}/^n\text{BuLi}$ and $\text{PhSO}_2\text{CF}_2\text{SCH}_3/^n\text{BuLi}$ systems, but in both cases, the generated anion **3** would not react with propylene oxide even in the presence of the $\text{BF}_3\text{--Et}_2\text{O}$ catalyst. These results were particularly interesting given the facts that the nonfluorinated (benzenesulfonyl)methyl anion **5** ($\text{PhSO}_2\text{CH}_2^-$) can readily react with epoxides¹³ and that anion **3** itself is known to have

TABLE 1. (Benzenesulfonyl)dichloromethylation of Epoxides

$\text{PhSO}_2\text{CHCl}_2 \xrightarrow[\text{ii) } \text{BF}_3\text{--Et}_2\text{O (1.2 eq), 5 min}]{\text{i) } ^n\text{BuLi (1.2 eq), THF, } -78^\circ\text{C, 30 min}}$ $\xrightarrow[\text{2-3 h, } -78^\circ\text{C - rt}]{\text{iii) epoxide (1.0 eq)}} \text{R}^1\text{CH(OH)CH(R}^2\text{)CCl}_2\text{SO}_2\text{Ph}$ 6			
entry	epoxide	product 6	yield (%) ^{a,b}
1		 (6a)	72
2		 (6b)	73
3		 (6c)	75
4		 (6d)	80
5		 (6e)	84

^a Isolated yield. ^b The yields were obtained without further optimization.

good nucleophilicity even toward alkyl halides and imines.^{7b,12a} To understand the unusual inertness of carbanion **3** toward epoxides, we studied the reactivity of the chlorinated analogue (benzenesulfonyl)dichloromethyl anion **4** ($\text{PhSO}_2\text{CCl}_2^-$) that was generated from dichloromethyl phenyl sulfone and *n*-butyllithium. The data are summarized in Table 1.

To our surprise, under similar reaction conditions, (benzenesulfonyl)dichloromethyl anion **5** readily reacted with a variety of epoxides to provide the products **6** with good regioselectivity (reacting at the less hindered site of the epoxide) and high yields (see Table 1). The striking reactivity difference between the (benzenesulfonyl)difluoromethyl anion **3** and (benzenesulfonyl)dichloromethyl anion **5** indicates a remarkable *negative* fluorine effect accounting for the low reactivity of **3** toward epoxides.

Reaction with the (Benzenesulfonyl)monofluoromethyl Anion. On the basis of the above studies, we turned our interest to the nucleophilic fluoroalkylation of epoxides with (benzenesulfonyl)monofluoromethyl anion **7** ($\text{PhSO}_2\text{CHF}^-$), assuming that the less fluorine-substituted carbanion **7** would have better nucleophilicity than **3**. The carbanion **7** can be generated from monofluoromethyl phenyl sulfone and a base, and its reactions with carbonyl compounds, alkyl halides, and imines have been reported previously.^{7c,14} Thus, we carefully optimized the experimental conditions of the reaction between $\text{PhSO}_2\text{CFH}_2$ /base and propylene oxide (see Table 2) and found that Et_2O is the best solvent (although THF is also suitable, the yield is

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TABLE 2. Survey of the Reaction Conditions

$\text{PhSO}_2\text{CH}_2\text{F} \xrightarrow[\text{iii) propylene oxide (9)}]{\text{i) base, solvent, -78}^\circ\text{C, 30 min; ii) BF}_3 \cdot \text{Et}_2\text{O, 5 min}} \text{H}_3\text{C}-\text{CH}(\text{OH})-\text{CH}(\text{F})-\text{SO}_2\text{Ph}$					
8				10a	
entry ^a	base (11)	solvent	Lewis acid (12)	molar ratio (8/9/11/12)	yield (%) ^b
1	<i>n</i> -BuLi	Et ₂ O	BF ₃ –Et ₂ O	1:2:1.2:2	67
2	<i>n</i> -BuLi	Et ₂ O	BF ₃ –Et ₂ O	1:2:2:2	78
3	LiHMDS	Et ₂ O–HMPA	—	1:2:2:—	68
4	<i>n</i> -BuLi	THF–HMPA	—	1:2:2:—	59
5 ^c	LiHMDS	Et ₂ O	BF ₃ –Et ₂ O	1:2:2:2	0
6	<i>n</i> -BuLi	Et ₂ O	TiCl ₄	1:2:2:2	68

^a Typical reaction conditions: into the mixture of sulfone 7 and solvent was added base at -78°C , and the reaction mixture was stirred for 30 min, followed by addition of Lewis acid and propylene oxide subsequently.

^b Isolated yield. ^c Sulfone 8, epoxide, and Lewis acid were first mixed, into which base was added.

somehow low) and that in the presence of BF₃–Et₂O the addition of 2 equiv of *n*-BuLi is necessary to ensure the good product yield (see Table 2, entry 2). *n*-Butyllithium worked as a better base than lithium hexamethyldisilazide (LiHMDS) (entries 3 and 5), and the addition of HMPA or TiCl₄ did not significantly improve the product yield (entries 3, 4, and 6). With the optimized reaction conditions (Table 2, entry 2), we examined the scope of this new nucleophilic ring-opening reaction of epoxides with carbanion 7. The results are summarized in Table 3. In all cases, the reactions were found to be highly regioselective with the fluorinated carbanion 7 attacking the less-hindered sites of epoxides. For alkyl monosubstituted epoxides, the reaction provided satisfactory to good product yields (Table 3, entries 1 and 2). However, the reaction yields dropped in the cases of aryl monosubstituted and other disubstituted epoxides (entries 3–7). These results indicate that the monofluoro-substituted carbanion 7 has better nucleophilicity than (benzenesulfonyl)difluoromethyl anion 3 for the ring-opening reaction with epoxides. For comparison, the nucleophilic addition reactions of epoxides with monochlorine-substituted carbanion 13 (PhSO₂CHCl[−]) were also studied (see Table 4). As expected, the reactions between epoxides and (benzenesulfonyl)monochloromethyl anion 13 (generated from monochloromethyl phenyl sulfone 14 and a base) gave better product yields than those with (benzenesulfonyl)monofluoromethyl anion 7, confirming that the fluorine substitution of a carbanion will decrease the latter's nucleophilicity (negative fluorine effect).

Reaction with the Bis(benzenesulfonyl)monofluoromethyl Anion. To further increase the nucleophilicity of a fluorinated carbanion toward epoxides, we tried to attach two benzenesulfonyl groups to the fluorine-bearing carbanion, i.e., to study the reactivity of bis(benzenesulfonyl)monofluoromethyl anion 16 ([PhSO₂)₂CF[−]], generated from bis(benzenesulfonyl)monofluoromethane 17 and a base). Because the benzenesulfonyl functionality is able to delocalize the electron density from the carbanion center, bis(benzenesulfonyl) substitution on a fluorinated carbanion can thus increase its stability and nucleophilicity by diminishing the electron repulsion between the electron pairs on the small fluorine atom and the electron lone pair occupying the p-orbital of the carbanion center.

The initial attempt to prepare bis(benzenesulfonyl)monofluoromethane 17 ((PhSO₂)₂CHF) through the reaction of PhSO₂CH₂F/*n*-BuLi with PhSSPh (or PhSO₂SPh) was not

TABLE 3. (Benzenesulfonyl)monofluoromethylation of Epoxides

$\text{PhSO}_2\text{CH}_2\text{F} \xrightarrow[\text{iii) epoxide, 3-12 h, -78}^\circ\text{C-RT}]{\text{i) } n\text{-BuLi, Et}_2\text{O, -78}^\circ\text{C, 30 min; ii) BF}_3 \cdot \text{Et}_2\text{O, 5 min}} \text{R}^2-\text{CH}(\text{OH})-\text{CH}(\text{F})-\text{SO}_2\text{Ph}$			
8		10	
entry	epoxide	product 10	yield (%) ^a
1			78
2			65
3 ^b			46
4			10 ^c
5			30
6			19
7			48

^a Isolated yields. ^b When the ratio of epoxide/7/^{*n*}BuLi^{−1} was 1:1.5:1.6, the isolated yield was 48%. ^c The yield was determined by ¹⁹F NMR using PhCF₃ as the internal standard.

TABLE 4. (Benzenesulfonyl)monochloromethylation of Epoxides

$\text{PhSO}_2\text{CH}_2\text{Cl} \xrightarrow[\text{iii) epoxide (2.0 eq), 2-3 h, -78}^\circ\text{C-RT}]{\text{i) } n\text{-BuLi (1.1 eq), THF, -78}^\circ\text{C, 30 min; ii) BF}_3 \cdot \text{Et}_2\text{O (1.1 eq), 5 min}} \text{R}^2-\text{CH}(\text{OH})-\text{CH}(\text{Cl})-\text{SO}_2\text{Ph}$			
14		15	
entry	epoxide	product 15	yield (%) ^a
1			71
2			67
3			60

^a Isolated yield.

successful (Scheme 2). After a quick screening of different preparation methods, finally we were able to obtain compound 17 in 48% yield via an electrophilic fluorination reaction of bis(benzenesulfonyl)methane with Selectfluor (see Table 5).

SCHEME 2

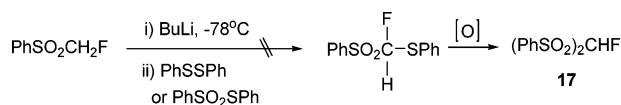
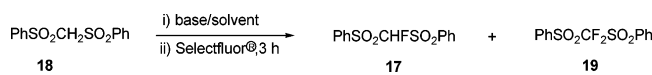


TABLE 5. Preparation of Bis(benzenesulfonyl)fluoromethane



entry	base	solvent	temp	yield (%) ^a	
				17	19
1	LiHDMS (1equiv)	THF	-78 °C to rt	32	20
2	<i>t</i> -BuOK (1equiv)	<i>t</i> -BuOH	rt	39	0
3	<i>t</i> -BuOK (1equiv)	DMF	rt	48	not determined

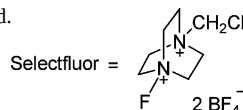
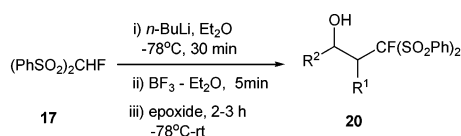
^a Isolated yield.

TABLE 6. Bis(benzenesulfonyl)monofluoromethylation of Epoxides

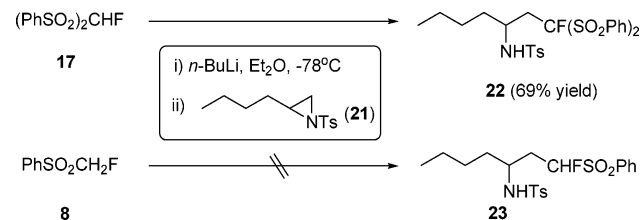


entry	epoxide	product 20	yield (%) ^a
1			91
2			89
3			37
			33
4			87
5			72
6			84

^a Isolated yield.

With compound **17** in hand, we carried out the fluoroalkylation reaction of epoxides with bis(benzenesulfonyl)monofluoromethyl anion **16**. The results are as shown in Table 6. The product yields of the reaction range from good to excellent, indicating that the bis(benzenesulfonyl)-substituted carbanion [(PhSO₂)₂CF⁻] (**16**) possesses much better nucleophilicity than

SCHEME 3



both PhSO₂CF₂⁻ (**3**) and PhSO₂CFH⁻ (**7**), and the benzenesulfonyl group(s) played a very important role in mediating the negative fluorine effect and tuning the reactivity order **16** > **7** >> **3**. It should be mentioned that the reactions between **16** and epoxides were highly regioselective (see Table 6, entries 1, 2, and 4–6), except the reaction with styrene oxide that gave two regioisomers **20c** and **20d**, which is probably caused by the electron-withdrawing nature of the benzene ring (entry 3).

Considering that aziridines usually have a reactivity similar to epoxides, we extended our nucleophilic fluoroalkylation chemistry with aziridine **21** (Scheme 3). The reaction between carbanion PhSO₂CHF⁻ (**7**, generated from PhSO₂CHF and *n*-BuLi) and aziridine **21** was not successful, and an unidentified complex mixture was obtained. However, the similar reaction between **21** and [(PhSO₂)₂CF⁻] (**16**) was found to be rewarding, and the fluoroalkylated amine **22** was obtained in 69% isolated yield (Scheme 3).

Conclusions

The unprecedented nucleophilic fluoroalkylation of simple epoxides with fluorinated sulfones was achieved to give the β-fluoroalkyl alcohols in one step. The negative “fluorine effect” in the nucleophilic fluoroalkylation of epoxides with fluorinated carbanions was probed by a reactivity comparison between carbanions PhSO₂CF₂⁻ (**3**) and PhSO₂CCl₂⁻ (**4**) and between carbanions PhSO₂CHF⁻ (**7**) and PhSO₂CHCl⁻ (**13**). The mediation of this fluorine effect with the introduction of another electron-withdrawing benzenesulfonyl group was found to be an effective way to significantly increase the nucleophilicity of the fluorinated carbanions, with the reactivity order [(PhSO₂)₂CF⁻] (**16**) > PhSO₂CFH⁻ (**7**) >> PhSO₂CF₂⁻ (**3**). These interesting results provide an insight into the nucleophilic fluoroalkylation chemistry, and this new methodology promises to be a useful tool for synthetic chemists.

Experimental Section

(Benzenesulfonyl)dichloromethylation of Epoxides. *n*-Butyllithium in hexane (2.4 mmol) was added into the THF (10 mL) solution of dichloromethyl phenyl sulfone (450 mg, 2.0 mmol) at -78 °C, and after 30 min at that temperature, BF₃·Et₂O (0.30 mL, 2.4 mmol) was added followed by the addition of propylene oxide (0.28 mL, 4.0 mmol). The reaction mixture was stirred at temperatures ranging from -78 °C to room temperature for another 2 h then quenched by the addition of 5 mL of saturated sodium bicarbonate solution. The reaction mixture was extracted with diethyl ether, and the ether phase was washed with brine. After drying over anhydrous magnesium sulfate and solvent removal, the crude product was further purified by flash chromatography using silica gel.

1-Benzenesulfonyl-1,1-dichloro-3-butanol (6a). 73% yield, colorless oil. ¹H NMR (CDCl₃): δ 1.36 (d, *J* = 6.5 Hz, 3H), 2.63–2.85 (m, 2H), 4.46 (md, *J* = 6.6, 2.6 Hz, 1H), 7.63 (m, 2H), 7.80 (m, 1H), 8.10 (m, 2H). ¹³C NMR (CDCl₃): δ 24.2, 48.1, 64.8,

98.5, 128.8, 131.4, 132.4, 135.3. MS (EI, m/z): 283, 265, 143, 125. HRMS (MALDI): m/z calcd for $C_{10}H_{12}^{35}Cl_2SO_3Na$ ($M + Na^+$) 304.9782, found 304.9776. IR (film): 3539, 3414, 3068, 2975, 2933, 1449, 1334, 1315, 1156, 1122, 1082 cm^{-1} .

(Benzenesulfonyl)monofluoromethylation of Epoxides. To the Et_2O solution (5 mL) of fluoromethylphenyl sulfone (174 mg, 1.0 mmol) was added a hexane solution of *n*-butyllithium (2.0 mmol) at $-78^\circ C$. After 30 min, $BF_3 \cdot Et_2O$ (2.0 mmol) was added and the solution was stirred for 5 min at the same temperature. Then, propylene oxide (2.0 mmol in 2 mL of Et_2O) was slowly added. The reaction mixture was stirred at $-78^\circ C$ for an additional 2 h and finally quenched with sodium bicarbonate solution. After usual workup and purification as above, the desired product **10a** was obtained.

1-Benzenesulfonyl-1-fluoro-3-butanol (10a). 78% yield, colorless oil. Two stereoisomers were obtained in a 1:1 ratio. 1H NMR ($CDCl_3$): δ 1.27–1.35 (m, 6H), 1.93–2.45 (m, 6H), 4.06 (m, 0.5H), 4.25 (m, 0.5H), 5.28–5.51 (dddd, $J = 48.5, 7.8, 4.5, 1.2$ Hz, 0.5H), 5.35–5.58 (dddd, $J = 49, 10.5, 2.3, 1.2$ Hz, 0.5H), 7.56–8.02 (m, 10H). ^{19}F NMR ($CDCl_3$): δ -176.0 (ddd, $J = 48, 30, 17$ Hz, 0.5F); δ -181.5 (ddd, $J = 49, 37, 13$ Hz, 0.5F). ^{13}C NMR ($CDCl_3$): δ 22.9/23.5 (C-4), 36.2 (d, $J = 18$ Hz)/36.4 (d, $J = 23$ Hz) (C-2), 63.9/64.0 (C-3), 100.3 (d, $J = 270$ Hz)/100.7 (d, $J = 265$ Hz) (C-1), 129.0, 129.19, 129.26, 129.30, 134.49, 134.55, 134.94, 135.11 (Ar-C for all isomers). MS (EI, m/z): 233 ($M^+ + 1$), 215, 143, 125. HRMS (MALDI): m/z calcd for $C_{10}H_{13}FSO_3Na$ ($M + Na^+$) 255.04671, found 255.04617. IR (film): 3545, 3410, 2980, 2920, 1455, 1320, 1160, 1085 cm^{-1} .

Preparation of bis(benzenesulfonyl)monofluoromethane (17). Under a nitrogen atmosphere, *t*-BuOK (224 mg, 2.0 mmol) was added to the DMF (30 mL) solution of $(PhSO_2)_2CH_2$ (592 mg, 2.0 mmol) at $0^\circ C$ and the solution was stirred at the same temperature for 1 h. Then, Selectfluor (2 mmol, 706 mg) dissolved in 20 mL of DMF was added slowly at the same temperature. After removing the ice-water bath, the reaction mixture was stirred for an additional 3 h at room temperature and then quenched with 20 mL of 10% sulfuric acid. The mixture was then extracted with Et_2O (3×50 mL), and the organic phase was subsequently washed with 10% $NaHCO_3$ (20 mL) and brine (25 mL). After drying over $MgSO_4$ and removal of the solvents, the residue was purified by flash

chromatography to afford the desired product **16** as a white solid (304 mg, 48.5% yield). Mp $105\text{--}106^\circ C$. 1H NMR ($CDCl_3$): δ 5.70 (d, $J = 46$ Hz, 1H), 7.60–7.66 (t, $J = 7.6$ Hz, 2H), 7.74–7.82 (t, $J = 7.6$ Hz, 1H), 7.95–8.03 (d, $J = 8.2$ Hz, 2H). ^{19}F NMR ($CDCl_3$): δ -168.2 (d, $J = 45.8$ Hz, 1F). ^{13}C NMR ($CDCl_3$): δ 105.7 (d, $J = 264$ Hz), 129.5, 130.2, 135.3, 135.8. MS (EI, m/z): 315 ($M + H^+$), 173, 141, 125, 109, 77. HRMS (MALDI): m/z calcd for $C_{13}H_{11}FO_4S_2Na$ ($M + Na^+$) 336.9981, found 336.9987. IR (KBr): 3067, 3072, 2956, 1429, 1359, 1171, 1077 cm^{-1} .

Bis(benzenesulfonyl)monofluoromethylation of Aziridines. *n*-Butyllithium in hexane (0.6 mmol) was added into the Et_2O (3 mL) solution of **17** (157 mg, 0.5 mmol) at $-78^\circ C$, and after 30 min at that temperature, aziridine **21** (0.6 mmol) was added. The reaction mixture was stirred at temperatures ranging from $-78^\circ C$ to room temperature for another 2 h and then quenched with saturated sodium bicarbonate solution. The desired product **22** was obtained after the usual workup and purification.

***N*-[3-(1,1-Bis(benzenesulfonyl)-1-fluoro)heptyl] *p*-toluenesulfonamide (22).** 69% yield, white solid. 1H NMR ($CDCl_3$): δ 0.72 (t, $J = 6.8$ Hz, 3H), 0.91–1.13 (m, 4H), 1.21–1.53 (m, 2H), 2.40–2.83 (m, 2H), 2.43 (s, 3H), 3.64 (m, 1H), 4.68 (d, $J = 6.9$ Hz, 1H), 7.27–7.91 (m, 14H). ^{19}F NMR ($CDCl_3$): δ -147.4 (t, $J = 17.2$ Hz, 1F). ^{13}C NMR ($CDCl_3$): δ 13.8, 21.6, 22.2, 26.9, 34.4 (d, $J = 7.1$ Hz), 35.2 (d, $J = 2.1$ Hz), 50.0 (d, $J = 3.4$ Hz), 114.6 (d, $J = 275$ Hz), 127.3, 129.1, 129.2, 129.6, 130.8 (d, $J = 1.4$ Hz), 131.0, 134.2, 134.4, 135.5, 137.9, 135.5, 143.3. MS (ESI, m/z): 606.1 ($M + K^+$), 590.2 ($M + Na^+$), 568.2 ($M + H^+$). HRMS (MALDI): m/z calcd for $C_{26}H_{30}NFO_6S_3Na$ ($M + Na^+$) 590.1117, found 590.1111. IR (film): 3301, 2957, 2929, 2862, 1449, 1336, 1155, 1079 cm^{-1} .

Acknowledgment. We thank the Chinese Academy of Sciences (Hundreds-Talent Program), the National Natural Science Foundation of China (20502029), and the Shanghai Rising-Star Program (06QA14063) for funding.

Supporting Information Available: Experimental details and characterization data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO060955L