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Aminochlorination

Aminochlorination of Alkenes with CFBSA

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Abstract: A novel catalyst-free aminochlorination of alkenes was developed by the direct addition of alkenes to *N*-chloro-*N*-fluorobenzenesulfonamide (CFBSA). The reaction produces 2-chloro-3-fluoramino and 3-chloro-2-fluoroamino adducts in 1,2-dichloroethane under reflux and dichloromethane at room temperature, respectively, in a regioselective manner. The electronic and steric effects of the fluorine atom of CFBSA have proven to be crucial for the reactivity and regioselectivity. A variety of transformations have been achieved to form 2-chloroenamines, chloroamines, aziridines and *N*-phenylbenzenesulfonamides under different conditions. Notably, the N–F bond in the adducts formed could be a useful handle for further transformations to useful compounds in organic synthesis.

Introduction

Haloamines are versatile building blocks extensively used in modern chemical syntheses (Figure 1).[1] It was reported that bromoamination was utilized in the synthesis of natural product allosadmin,[2] fluoroamination was applied in the synthesis of GABA-AT inactivator,[3] and enamines can be conveniently synthesized by the elimination of a hydrohalide from haloamines. The difunctionalization of alkenes with aminohalogenating reagents is a typical reaction to achieve aminohalogenation.[4] In the past few years, a variety of reagents have been employed for the aminohalogenation, including NCS,[5] NBS,[6] NIS,[7] NFSI,[8] chloramine-T,[9] bromamine-T,[10] and $TsNCl_2$,[11] However, catalysts are often required for these reactions[12] [Figure 2, (1)].

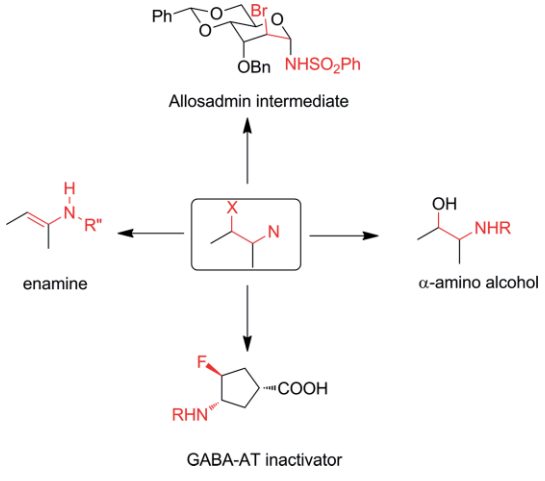

Figure 1. Diverse applications of aminohalogenations.

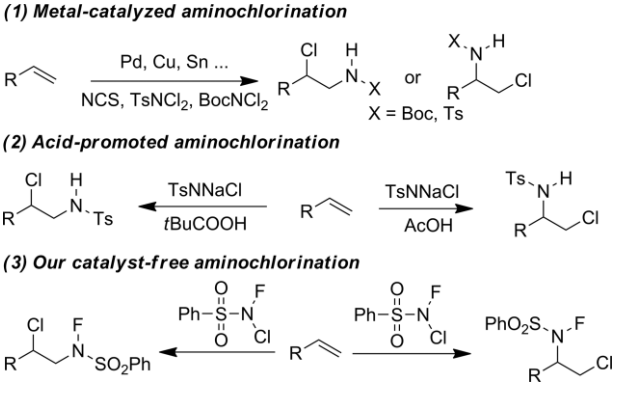

Figure 2. Synthesis of chloramine compounds.

As a good case, in 2014, Muñiz reported an acid-promoted aminochlorination[13] [Figure 2, (2)]. This result encouraged us to explore more efficient aminohalogenation methods.

N-Chloro-*N*-fluorobenzenesulfonamide (CFBSA, **1**) is a reactive chlorinating reagent first explored in our laboratory.[14] As a new chlorinating reagent, it is more reactive than chloramine-B and more stable for storage than $TsNCl_2$. Its high electrophilic chlorination reactivity stems from the strong electron-withdrawing behaviour of the fluorine atom and the phenylsulfonyl group on the nitrogen atom. Herein, we report a catalyst-free aminochlorination of alkenes with CFBSA [Figure 2, (3)]. Unlike conventional Aminochlorination processes, the reaction developed here requires no activating additives and may provide multifunctionalized vicinal *N*-fluoroamino and chloro adducts. Also, the N–F bond in these adducts would probably lead to the development of new chemical reactions.

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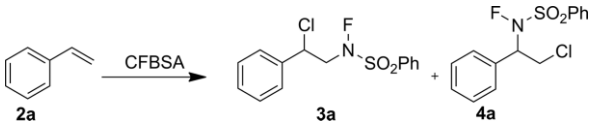
Results and Discussion

We began with the use of styrene (**2a**) as a model substrate. To our delight, without any catalyst a single product **3a** was obtained in 1,2-dichloroethane (DCE) at 85 °C in 96 % yield (Entry 1 in Table 1). Other solvents including toluene, DCM (dichloromethene), hexane, dioxane, CH_3CN and THF were also used. In ethyl acetate a trace amount of product **3a** was detected (Entry 6 in Table 1). The proportion of **2a**/**1** was found to influence both the reaction rate and yield (Entries 1, 9–14 in Table 1). Entry 11 (Table 1) shows the best conditions for the synthesis of 2-chloro-3-fluoramino adducts. Interestingly, when DCE was used as solvent at room temperature, **3a** was separated in 25 % yield with partial starting material retained. However, with DCM as solvent the regioisomeric product **4a** was obtained in 50 % yield as a single product (Entry 16 in Table 1, conditions B in the following experiments). When using CH_3CN, $CHCl_3$, or THF as solvents, a mixture of **3a**/**4a** was obtained (Entries 17–19 in Table 1). Thus, the optimized conditions for the regioselective formation of adduct **3** are conditions A: 1 equiv. of alkene **2**, 1.2 equiv. of CFBSA, DCE as solvent, 85 °C; and for the regioselective generation of adduct **4**, conditions B are chosen: 1 equiv. of alkene **2**, 1.2 equiv. of CFBSA, DCM as solvent, room temperature (less than 30 °C).

Then, the scope of styrenes was tested under optimal reaction conditions. As shown in Table 2, all styrenes regioselectively provided products **3a**–**3h** in good yields under condi-

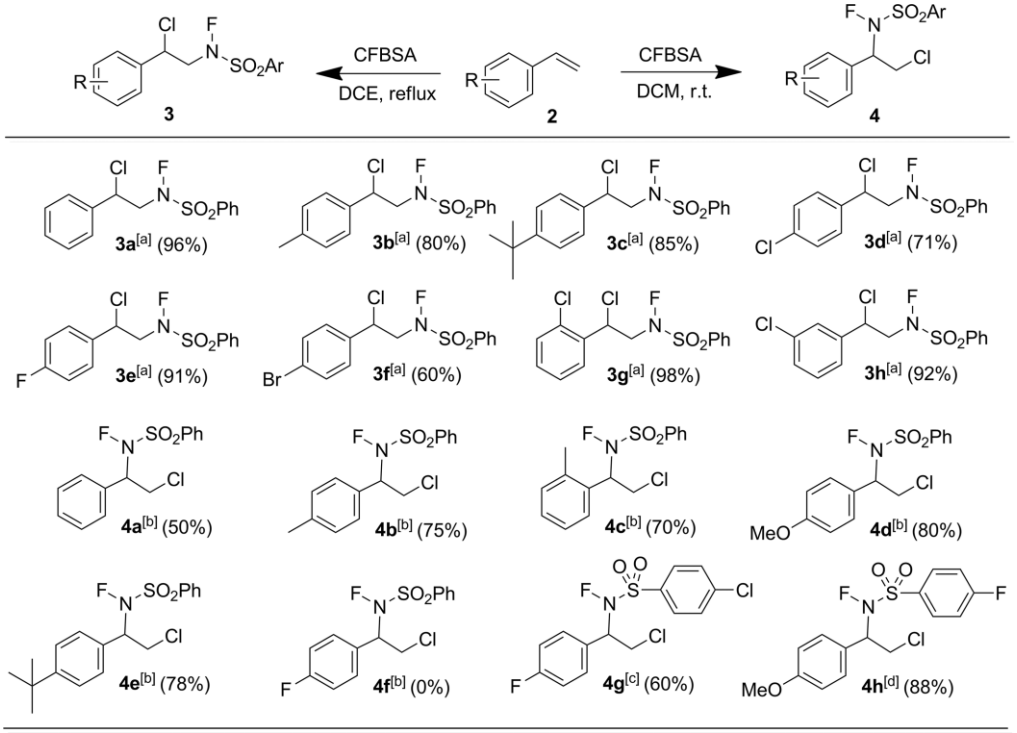
Table 1. Optimization of the reaction conditions.



Entry	Solvent	Temp.	2a/1	Time [h]	Product (yield [%])[c]
1	DCE	85 °C	1:2	0.5	**3a** (96)
2[a]	DCM	85 °C	1:2	0.5	**3a** (89)
3[a]	hexane	85 °C	1:2	0.5	**3a** (94)
4	dioxane	85 °C	1:2	0.5	**3a** (78)
5	toluene	85 °C	1:2	0.5	**3a** (95)
6[a]	ethyl acetate	85 °C	1:2	0.5	**3a** (trace)
7[a]	THF	85 °C	1:2	0.5	**3a** (75)
8	CH_3CN	85 °C	1:2	0.5	**3a** (91)
9	DCE	85 °C	1:1	8	**3a** (79)
10	DCE	85 °C	1:1.1	3	**3a** (86)
11	DCE	85 °C	1:1.2	3	**3a** (96)
12	DCE	85 °C	1:1.3	1	**3a** (96)
13	DCE	85 °C	1:1.4	0.5	**3a** (96)
14	DCE	room temp.	1:2	12	**3a** (25)
15[b]	DCE	room temp.	1:2	0.5	**3a** (83)
16	DCM	room temp.	1:2	12	**4a** (50)
17	CH_3CN	room temp.	1:2	12	**4a** (5), **3a** (38)
18	$CHCl_3$	room temp.	1:2	12	**4a** (27), **3a** (7)
19	THF	room temp.	1:2	12	**4a** (13), **3a** (28)

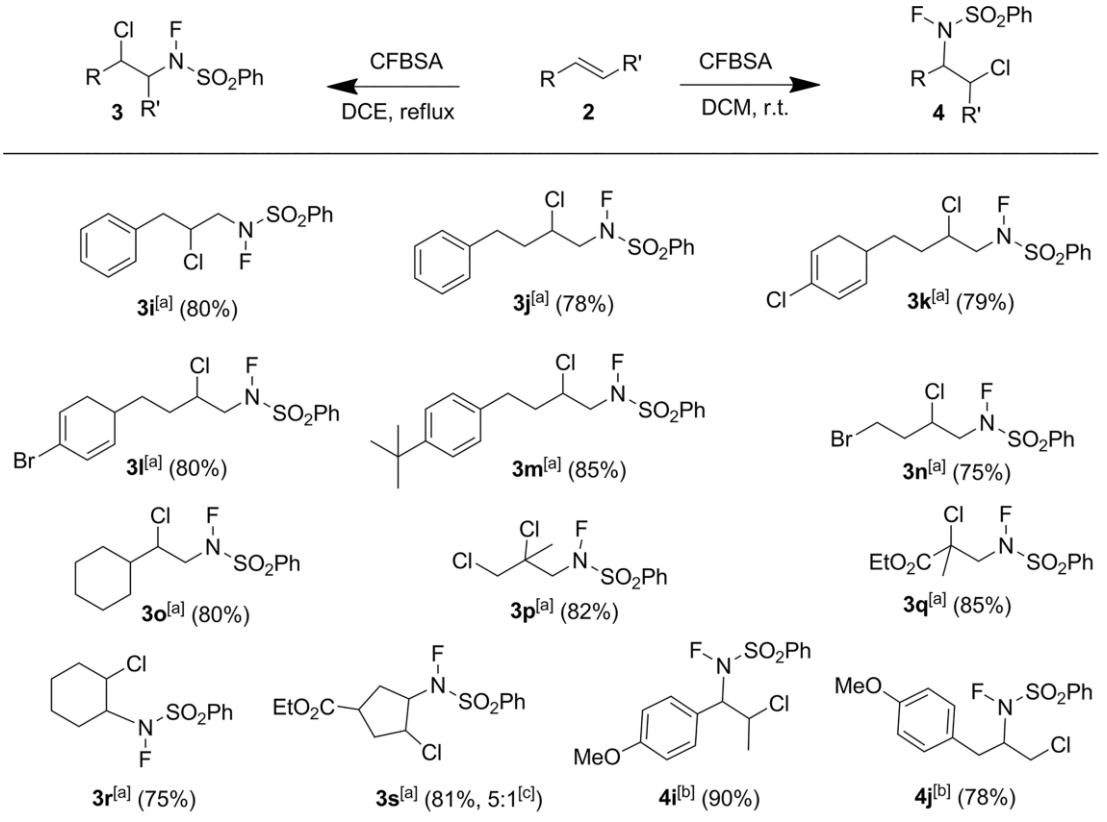
[a] The reaction proceeded in a pressure glass tube. [b] 10 mol-% AgOAc was added as catalyst in the reaction. [c] Isolated yields.

Table 2. Scope of substrates: aminochlorination for styrenes.



[a] Reaction conditions: **2** (1.0 mmol), CFBSA (250 mg, 1.2 mmol) and DCE (5.0 mL) at 85 °C. [b] Reaction conditions: **2** (1.0 mmol), CFBSA (250 mg, 1.2 mmol) and DCM (5.0 mL) at room temp. (room temp. means < 30 °C). [c] Reaction conditions: **2** (1.0 mmol), CFBSA (250 mg, 1.2 mmol), *N*-fluoro-4-chlorobenzenesulfonamide (1.0 mmol) and DCM (5.0 mL) at room temp. [d] Reaction conditions: **2** (1.0 mmol), CFBSA (250 mg, 1.2 mmol), *N*-fluoro-4-fluoro-benzenesulfonamide (1.0 mmol) and DCE (5.0 mL) at room temp.

Table 3. Scope of substrates: aminochlorination of other alkenes.



[a] Reaction condition A: 2 (1.0 mmol), CFBSA (250 mg, 1.2 mmol) and DCE (5.0 mL) at 85 °C. [b] Reaction conditions B: 2 (1.0 mmol), CFBSA (250 mg, 1.2 mmol) and DCM (5.0 mL) at room temp. [c] Two stereoisomers of **3s** with a ratio of 5:1 (determined by the peak area ratio in the ^{1}H NMR spectrum).

tions A. Of *para*-substituted styrenes, 4-bromostyrene produced a low yield of **3f**. With chlorine as substituent, *ortho*- and *meta*-substituted substrates produced higher yields of **3g** and **3h**, respectively, than that of **3d** with a *para*-chloro substituent. Under conditions B, electron-rich styrenes afforded products **4a**–**4e** in moderate yields. However, minimal products were produced for styrenes with electron-withdrawing substituents (NO_2, F and Cl). Nevertheless, the addition of *N*-fluoro-4-chlorobenzenesulfonamide or *N*-fluoro-4-fluoro-benzenesulfonamide to the above reactions enhanced the yield of adducts **4g** and **4h**.

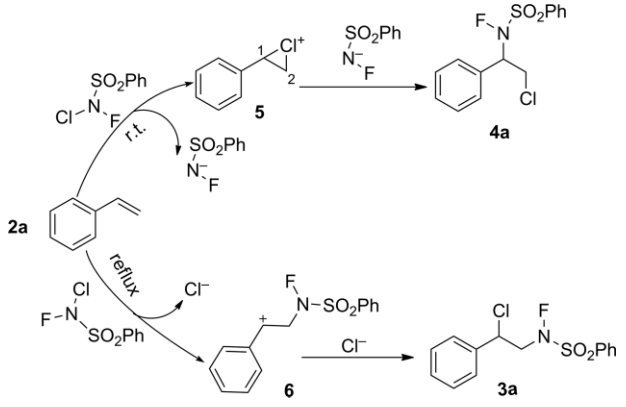
The scope of alkenes was also tested (Table 3). Under conditions A, 3-phenyl-1-propylene and 4-phenyl-1-butylene were tolerated in this reaction with the formation of **3i**, **3j**, **3k**, **3l**, **3m** in 78–85 % yields. For chain alkenes 4-bromo-1-butylene, 1-cyclohenylethylene and 3-chloro-2-methyl-1-propylene, **3n**, **3o** and **3p** were smoothly afforded as single isomers in 75–82 % yields. An α,β-unsaturated aliphatic ester specifically yielded **3q** in 85 % yield; we note that this is the first report for an aminochlorination of α,β-unsaturated aliphatic esters. Cyclohexene and ethyl 3-cyclopentene-1-carboxylate provided **3r** and **3s** in 75 % and 81 % yield, respectively. In the ^{1}H NMR spectrum of product **3s**, two different configurations with a ratio of 5:1 were observed. Under conditons B, while no reaction was observed for the majority of the above substrates, adducts **4i** and **4j** were regioselectively produced in 90 % and 78 % yield for electron-rich 1-(4-methoxyphenyl)-1-propylene and 3-(4-methoxyphenyl)-1-propylene, respectively.

Figure 3. Single-crystal X-ray diffraction of **3c** and **4e**.

In order to clarify the structures of **3** and **4**, we determined the single-crystal structures of **3c** and **4e** (Figure 3).

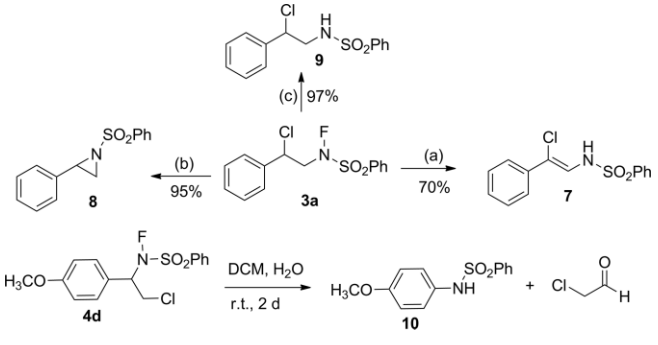
Although the exact mechanism still requires further investigation, we suggest the following reaction process (Scheme 1). In our reaction, product **4** was regioselectively formed in dichloromethane (DCM) at room temperature. In DCM, styrene attacks C-I of CFBSA at room temperature to generate chlorinium ion **5**. Subsequently, the $PhSO_2NF^-$ anion could selectively attack C-1 to give **4**. The regioselectivity could be determined by the following two factors: (1) the stability of the $PhSO_2NF^-$

anion could largely increase in comparison that of $PhSO_2NNa^-$ or $PhSO_2NH^-$ in Chloroamine B, or $PhSO_2NCl^-$ in $PhSO_2NCl_2$; (2) C-1^+ is a much more stable cation than C-2^+ in **5** for its conjugation with the benzene ring. The high eletrophilic chlorination reactivity[14] and the good aminochlorination reactivity to *p*-methoxystyrene (Table 2, **4b**) could corroborate this proposed route. However, compound **3** was rapidly formed instead of compound **4** at high temperature. Thus, a different mechanism including the initial nucleophilic attack of styrene onto the nitrogen atom and a subsequent or concerted nucleophilic attack of the chlorine anion onto the carbenium or aziridium species is proposed. In this process, the increase of the N–Cl bond length resulting from the increased temperature facilitates the departure of the chloride anion. An additional proof for this process was supplied by a similar reaction with AgOAc as catalyst (Entry 15 in Table 1).



Scheme 1. Possible mechanism for the addition of styrenes to CFBSA.

We also envisioned that the conversion of the N–F bond in adducts **3** or **4** would endow this reaction with additional values. As shown in Scheme 2, several conversions proceeded smoothly. 2-Chloroenamines are valuable synthetic intermediates.[15] Usual elimination of chloroamine compounds can only supply enamines, and 2-chloroenamines must be prepared by aminochlorination of alkynes under catalysis.[16] Herein, 2-chloroenamine **7** was generated in 70 % yield by elimination of HF from **3a** in the presence of Et_3N. When **3a** was treated with 2 equiv. of NaOH, aziridine **8** was produced in high yield. Compound **9** was afforded by a conversion of the N–F into an N–H bond when **3a** was treated with K_2CO_3 in refluxing methanol. Surprisingly, compound **10** was produced when **4d** was stirred with a small amount of water at room temperature for 2 d. The presence of aldehyde in the reaction mixture (detected by ^1H and ^{13}C NMR spectroscopy) probably suggests that 2-chloroacetaldehyde was generated along with the formation of compound **10**; the reaction mechanism is not clear at present, however (Scheme 2). Although the above conversions occurred easily under basic conditions, it is interesting to note that these adducts are much more stable under neutral or acidic circumstances. Thus, these adducts could be precursors of enamines and aziridines for medicinal chemistry, or as agents for controlled release of fluorine under basic conditions.



Scheme 2. Conversion of compounds **3a** and **4d**. Reaction conditions: (a) acetonitrile (10 mL), **3a** (1.0 mmol), Et_3N (1.0 mmol), room temp.; (b) DCE (10 mL), **3a** (1.0 mmol), NaOH (2.0 mmol), reflux; (c) methanol (10 mL), **3a** (1.0 mmol), K_2CO_3 (1.0 mmol) room temp.

Conclusions

We have described a catalyst-free aminochlorination of alkenes with CFBSA. Different from previous methods, no activated additives were required in the chloroamination process, and special fluoroamino adducts were obtained. Pure 2-chloro-3-fluoroamino adducts **3** were afforded in high yields under reflux in DCE. The regioisomeric adducts **4** were selectively formed when the reaction was carried out at room temperature with DCM as solvent. The reaction gave good reactivities and regioselectivities for most terminal alkenes used with both aromatic and aliphatic substituents. The electronic and steric effects of the fluorine atom in CFBSA are crucial for the good reactivity and regioselectivity. In addition, the *N*-fluoroamino chlorinated adducts **3** can be further converted into 2-chloroenamines, chloroamines and aziridines. Interestingly, **4d** could also be transformed into *N*-phenylphenylsulfonamide **10**. These conversions endow the adducts with potential applications as precursors in chemical synthesis.

Experimental Section

1. General Information: All starting chemicals were commercially available and used without further purification. Fluorinating reagent Selectfluor and chlorinating reagent CFBSA were purchased from Shanghai Science Bio-pharmaceutical Co. Ltd. Substrates were purchased from Energy Chemical Co. Ltd. and Damas-beta Co. Ltd. Flash column chromatography was performed using silica gel (300–400 mesh). ^1H NMR spectra were recorded with a Bruker spectrometer at 400 MHz. ^{19}F NMR spectra were recorded with a Bruker spectrometer at 376 MHz. ^{13}C NMR spectra were recorded with a Bruker spectrometer at 100 MHz. Chemical shifts (δ values) are reported in ppm downfield from the signal of internal tetramethylsilane (TMS). *J* values are reported in Hz. IR spectra (film) were recorded with a Nicolet 6700 spectrophotometer in the range of 400–4000 cm^{-1}. HRMS (EI) spectra were recorded with a Waters GCT Premier mass spectrometer with electron impact mode. CCDC 1465265 (for **3c**), and 1465267 (for **4e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

2. Experimental Details

Preparation of *N*-Chloro-*N*-fluorobenzenesulfonamide (CFBSA): In a 250 mL round-bottomed flask equipped with a large magnetic stir bar, Chloramine-B (5.35 g, 0.025 mol, 1.0 equiv.) and Selectfluor

(13.50 g, 0.038 mol, 1.5 equiv.) were dissolved in water (100 mL) at room temperature. The reaction mixture was stirred at room temperature overnight (12 h). The mixture was extracted with dichloromethane (3 × 30 mL), and the organic layer was dried with sodium sulfate. The solvent was removed under reduced pressure, and the crude product (yellow liquid) was further purified by flash column chromatography.

General Procedure for the Preparation of *N*-Fluorobenzenesulfonamides 3 (3a as an Example): Styrene **2a** (104 mg, 1.0 mmol), CFBSA (250 mg, 1.2 mmol) and 1,2-dichloroethane (5.0 mL) were added into a tube. The mixture was stirred at 85 °C for 3 h. The reaction mixture was concentrated under reduced pressure. The product was isolated by flash chromatography (silica gel; petroleum ether/EtOAc = 20:1) to give **3a** (300 mg, 96 %) as a white solid.

General Procedure for the Preparation of 4 (4a as an Example): Styrene **2a** (104 mg, 1.0 mmol), CFBSA (250 mg) and DCM (5 mL) were added into a tube. Then the mixture was stirred at room temp. for 12 h. The reaction mixture was concentrated under reduced pressure. The product was isolated by flash chromatography (silica gel; petroleum ether/EtOAc = 20:1) to give **4a** (157 mg, 50 %) as a colorless liquid.

Procedure for the Preparation of 7: Compound **3a** (1.0 mmol), Et_3N (1.0 mmol) and acetonitrile (10 mL) were added into round-bottomed flask (25 mL). Then the mixture was stirred at room temp. for 3 h. The reaction mixture was concentrated under reduced pressure. The product was isolated by flash chromatography (silica gel; petroleum ether/EtOAc = 20:1) to give **7** (70 %) as a white solid.

Procedure for the Preparation of 8: Compound **3a** (1.0 mmol), NaOH (2.0 mmol) and DCE (10 mL) were added into round-bottomed flask (25 mL). Then the mixture was stirred under reflux for 2 h. The reaction mixture was concentrated under reduced pressure. The product was isolated by flash chromatography (silica gel; petroleum ether/EtOAc = 20:1) to give **8** (95 %) as a white solid.

Procedure for the Preparation of 9: Compound **3a** (1.0 mmol), K_2CO_3 (1.0 mmol) and methanol (10 mL) were added into round-bottomed flask (25 mL). Then the mixture was stirred at room temp. for 3 h. The reaction mixture was concentrated under reduced pressure. The product was isolated by flash chromatography (silica gel; petroleum ether/EtOAc = 20:1) to give **9** (97 %) as a white solid.

3. Analytical Data for the Products

***N*-Chloro-*N*-fluorobenzenesulfonamide (CFBSA):** Yellow liquid; R_f = 0.55 (10 % ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 7.8 Hz, 2 H), 7.86 (t, J = 7.5 Hz, 1 H), 7.69 (t, J = 7.9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.78, 131.66, 129.70, 128.74 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = 17.72 (s, 1 F) ppm. IR (neat): $\tilde{\nu}$ = 3071, 1582, 1450, 1390, 1190, 1085, 753, 682, 683, 615, 559 cm^{-1}. HRMS-EI: calcd. for $C_6H_5ClFNO_2S$ 208.9714, found 208.9716.

***N*-(2-Chloro-2-phenylethyl)-*N*-fluorobenzenesulfonamide (3a):** White solid; m.p. 84.1–84.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.70–3.89 (m, 2 H), 5.09 (t, J = 7.6 Hz, 1 H), 7.35–7.40 (m, 5 H), 7.62 (t, J = 8.0 Hz, 2 H), 7.76 (t, J = 7.6 Hz, 1 H), 7.94 (d, J = 7.27 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 57.58, 60.21 (d, J = 16.1 Hz), 123.70, 127.48, 129.06, 129.31, 129.62, 130.02, 135.40, 137.77 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –46.16 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3091, 3066, 2933, 1652, 1582, 1496, 1449, 1384, 1186 cm^{-1}. HRMS-EI: calcd. for $C_{14}H_{13}ClFNO_2S$: 313.0340, found for $C_{14}H_{12}O_2ClNS$ [M$^+$ – HF] 293.0276.

***N*-[2-Chloro-2-(*p*-tolyl)ethyl]-*N*-fluorobenzenesulfonamide (3b):** White solid; m.p. 108.3–108.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 3.63–3.91 (m, 2 H), 5.07 (t, J = 7.2 Hz, 1 H), 7.19 (d, J = 8.0 Hz, 2 H), 7.25–7.28 (m, 2 H), 7.61 (t, J = 7.6 Hz, 2 H), 7.75 (t, J = 7.6 Hz, 1 H), 7.94 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.33, 57.58, 60.23 (dd, J = 11.6 Hz), 127.39, 129.61, 129.74, 130.03, 132.04, 134.89, 135.37, 139.32 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –46.24 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3004, 2925, 2860, 1589, 1463, 1428, 1373, 1176, 1109 cm^{-1}. HRMS-EI: calcd. for $C_{15}H_{15}ClFNO_2S$ 327.0496, found for $C_{15}H_{14}ClNO_2S$ [M$^+$ – HF] 307.0434.

***N*-{2-[4-(*tert*-Butyl)phenyl]-2-chloroethyl}-*N*-fluorobenzenesulfonamide (3c):** White solid; m.p. 84.7–85.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 9 H), 3.65–3.93 (m, 2 H), 5.07–5.11 (m, 1 H), 7.32 (d, J = 8.4 Hz, 2 H), 7.40 (d, J = 8.4 Hz, 2 H), 7.61–7.65 (m, 2 H), 7.74–7.78 (m, 1 H), 7.94–7.96 (dm, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.32, 34.76, 57.50, 60.23 (d, J = 11.6 Hz), 126.00, 127.15, 129.59, 129.99, 131.93, 134.73, 135.36, 152.40 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = 46.49 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3073, 3033, 3039, 2957, 2903, 2867, 1584, 1450, 1416, 1371, 1186, 1176, 1091, 1027 cm^{-1}. HRMS-EI: calcd. for $C_{18}H_{21}ClFNO_2S$ 369.0966, found for $C_{18}H_{20}ClNO_2S$ [M$^+$ – HF] 349.0904.

***N*-[2-Chloro-2-(4-chlorophenyl)ethyl]-*N*-fluorobenzenesulfonamide (3d):** White solid; m.p. 100.9–101.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.66–3.88 (m, 2 H), 5.06 (t, J = 7.2 Hz, 1 H), 7.32–7.38 (m, 4 H), 7.63 (t, J = 8.0 Hz, 2 H), 7.77 (t, J = 7.6 Hz, 1 H), 7.93 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.72, 59.97 (d, J = 11.7 Hz), 128.96, 129.29, 129.66, 130.04, 131.97, 135.32, 135.48, 136.34 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –46.82 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3098, 3073, 2922, 2854, 1598, 1494, 1449, 1365, 1174, 1091 cm^{-1}. HRMS-EI: calcd. for $C_{14}H_{12}Cl_2FNO_2S$ 346.9950, found for $C_{14}H_{11}Cl_2NO_2S$ [M$^+$ – HF] 326.9890.

***N*-[2-Chloro-2-(4-fluorophenyl)ethyl]-*N*-fluorobenzenesulfonamide (3e):** White solid; m.p. 88.9–89.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67–3.88 (m, 2 H), 5.08 (t, J = 7.2 Hz, 1 H), 7.04–7.10 (m, 2 H), 7.36–7.40 (m, 2 H), 7.63 (t, J = 8.0 Hz, 2 H), 7.62–7.65 (m, 2 H), 7.77 (t, J = 7.6 Hz, 1 H), 7.94 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.78, 60.17 (d, J = 11.4 Hz), 116.05 (d, J = 21.3 Hz), 129.41, (d, J = 9.5 Hz), 129.64, 129.99, 131.88, 133.69, 133.70, 135.46, 163.02 (d, J = 247.2 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –46.97, –111.93 ppm. IR (KBr): $\tilde{\nu}$ = 3079, 2926, 2862, 1604, 1509, 1512, 1393, 1211, 1098 cm^{-1}. HRMS-EI: calcd. for $C_{14}H_{12}ClF_2NO_2S$ 331.0245, found for $C_{14}H_{11}ClFNO_2S$ [M$^+$ – HF] 311.0182.

***N*-[2-(4-Bromophenyl)-2-chloroethyl]-*N*-fluorobenzenesulfonamide (3f):** White solid; m.p. 113.2–113.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.66–3.87 (m, 2 H), 5.04 (t, J = 7.2 Hz, 1 H), 7.26–7.29 (m, 2 H), 7.50–7.54 (m, 2 H), 7.63 (t, J = 8.0 Hz, 2 H), 7.77 (t, J = 7.6 Hz, 1 H), 7.93 (d, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 57.77, 59.95 (d, J = 11.1 Hz), 123.38, 129.33, 129.68, 130.02, 131.87, 132.24, 135.50, 136.85 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –45.78 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3099, 3071, 2921, 2852, 1638, 1492, 1448, 1365, 1175 cm^{-1}. HRMS-EI: calcd. for $C_{14}H_{12}BrClFNO_2S$ 390.9445, found for $C_{14}H_{11}BrClNO_2S$ [M$^+$ – HF] 370.9395.

***N*-[2-Chloro-2-(2-chlorophenyl)ethyl]-*N*-fluorobenzenesulfonamide (3g):** White solid; m.p. 72.9–73.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.77 (d, J = 7.2 Hz, 1 H), 3.86 (d, J = 7.2 Hz, 1 H), 5.66 (t, J = 6.8 Hz, 1 H), 7.26–7.38 (m, 3 H), 7.58–7.64 (m, 3 H), 7.54 (t, J = 7.6 Hz, 1 H), 7.95 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.65, 59.00 (d, J = 11.7 Hz), 127.73, 128.98, 129.62, 130.00, 130.02, 132.01, 133.26, 135.15, 135.43 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –45.16 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3097, 2954,

2925, 2856, 1582, 1477, 1448, 1378, 1186, 1088 cm^{-1}. HRMS-EI: calcd. for $C_{14}H_{12}Cl_2FNO_2S$ 346.9950, found $C_{14}H_{11}Cl_2NO_2S$ [M^+ – HF] 326.9890.

***N*-[2-Chloro-2-(3-chlorophenyl)ethyl]-*N*-fluorobenzenesulfonamide (3h):** White solid; m.p. 73.4–74.2 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.57–3.81 (m, 1 H), 4.96 (t, J = 7.2 Hz, 1 H), 7.18–7.27 (m, 3 H), 7.32 (s, 1 H), 7.55 (t, J = 7.6 Hz, 2 H), 7.69 (t, J = 7.6 Hz, 1 H), 7.86 (t, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.69, 60.08 (d, J = 11.5 Hz), 125.73, 127.80, 129.50, 129.66, 130.03, 130.35, 135.49, 139.74 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –45.75 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3065, 2961, 2926, 2870, 1600, 1519, 1479, 1377, 1186, 1086 cm^{-1}. HRMS-EI: calcd. for $C_{14}H_{12}Cl_2FNO_2S$ 346.9950, found $C_{14}H_{11}Cl_2NO_2S$ [M^+ – HF] 326.9889.

***N*-(2-Chloro-3-phenylpropyl)-*N*-fluorobenzenesulfonamide (3i):** Colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.03 (dd, J = 8.0, J = 14.4 Hz, 1 H), 3.32 (dd, J = 4.4, 14.4 Hz, 2 H), 3.51–3.67 (m, 2 H), 4.28–4.35 (m, 1 H), 7.23–7.34 (m, 5 H), 7.63 (t, J = 8.0 Hz, 2 H), 7.70 (t, J = 7.6 Hz, 1 H), 7.95 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.51, 57.22, 58.64 (d, J = 11.7 Hz), 127.30, 128.63, 129.62, 129.81, 130.07, 131.84, 135.43, 136.20 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –44.12 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3061, 3021, 2966, 2875, 1603, 1584, 1497, 1450, 1380, 1185, 1098 cm^{-1}. HRMS-EI: calcd. for $C_{15}H_{15}Cl_2FNO_2S$ 327.496, found for $C_{15}H_{14}Cl_2NO_2S$ [M^+ – HF] 307.0434.

***N*-(3-Chloro-5-phenylpentyl)-*N*-fluorobenzenesulfonamide (3j):** Grayish solid; m.p. 60.5–61.0 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.99–2.08 (m, 1 H), 2.25–2.35 (m, 1 H), 2.74–2.81 (m, 1 H), 2.92–2.99 (m, 1 H), 3.48 (d, J = 6.8 Hz, 1 H), 3.57 (d, J = 6.8 Hz, 1 H), 4.05–4.11 (m, 1 H), 7.22 (t, J = 7.6 Hz, 3 H), 7.31 (t, J = 8.0 Hz, 2 H), 7.64 (t, J = 8.0 Hz, 2 H), 7.78 (t, J = 7.6 Hz, 1 H), 7.96 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.01, 37.12, 56.38, 59.33 (d, J = 11.5 Hz), 126.39, 128.61, 128.67, 129.60, 130.01, 131.80, 135.40, 140.36 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –43.86 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3071, 3024, 2960, 2872, 1603, 1584, 1450, 1380, 1185, 1089 cm^{-1}. HRMS-EI: calcd. for $C_{16}H_{17}Cl_2FNO_2S$ 341.0653, found 341.0652.

***N*-[2-Chloro-4-(4-chlorophenyl)butyl]-*N*-fluorobenzenesulfonamide (3k):** Colorless liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.95–2.04 (m, 1 H), 2.20–2.30 (m, 1 H), 2.67–2.77 (m, 1 H), 2.85–2.94 (m, 1 H), 3.42 (d, J = 6.6 Hz, 1 H), 3.55 (d, J = 6.3 Hz, 1 H), 4.01–4.03 (m, 1 H), 7.11 (d, J = 8.1 Hz, 2 H), 7.24 (d, J = 7.8 Hz, 2 H), 7.62 (t, J = 7.8 Hz, 2 H), 7.76 (t, J = 7.5 Hz, 1 H), 7.93 (d, J = 7.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.29, 36.83, 56.11, 59.29 (d, J = 11.7 Hz), 128.70, 129.60, 129.95, 131.50, 132.02, 135.44, 138.75 ppm. ^{19}F NMR (136 MHz, $CDCl_3$): δ = –44.36 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3166, 3067, 2955, 2927, 2866, 1584, 1492, 1381, 1185, 1091, 1061 cm^{-1}. HRMS-EI: calcd. for $C_{16}H_{16}Cl_2FNO_2S$ 375.0263, found for $C_{16}H_{15}Cl_2NO_2S$ [M^+ – HF] 355.0212.

***N*-[4-(4-Bromophenyl)-2-chlorobutyl]-*N*-fluorobenzenesulfonamide (3l):** White solid; m.p. 73.2–73.8 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.05–1.93 (m, 1 H), 2.32–2.21 (m, 1 H), 2.72–2.74 (m, 1 H), 2.85–2.89 (m, 1 H), 3.43 (d, J = 6.3 Hz, 1 H), 3.58–3.56 (m, 1 H), 4.04–4.02 (m, 1 H), 7.07 (d, J = 8.0 Hz, 2 H), 7.39 (d, J = 8.1 Hz, 2 H), 7.64 (t, J = 7.8 Hz, 2 H), 7.77 (t, J = 7.5 Hz, 1 H), 7.94 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.38, 36.79, 56.11, 59.25 (d, J = 11.6 Hz), 120.13, 129.61, 129.97, 130.37, 131.61, 131.68, 135.44, 139.28 ppm. ^{19}F NMR (176 MHz, $CDCl_3$): δ = 43.82 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3069, 3024, 2955, 2925, 2863, 1585, 1448, 1381, 1185, 1091, 1016 cm^{-1}. HRMS-EI: calcd. for $C_{16}H_{16}BrClFNO_2S$ 418.9757, found for $C_{16}H_{15}BrClNO_2S$ [M^+ – HF] 398.9688.

***N*-{4-[4-(*tert*-Butyl)phenyl]-2-chlorobutyl}-*N*-fluorobenzenesulfonamide (3m):** White solid; m.p. 67.5–67.9 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 9 H), 2.08–1.95 (m, 1 H), 2.35–2.24 (m, 1 H), 2.79–2.69 (m, 1 H), 2.96–2.87 (m, 1 H), 3.46 (d, J = 6.6 Hz, 1 H), 3.59 (d, J = 6.3 Hz, 1 H), 4.11–4.07 (m, 1 H), 7.14 (d, J = 8.1 Hz, 2 H), 7.33 (d, J = 9.6 Hz, 2 H), 7.64 (t, J = 7.8 Hz, 2 H), 7.78 (t, J = 7.5 Hz, 1 H), 7.96 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.50, 34.51, 37.15, 56.48, 59.25, 59.41, 125.57, 128.28, 129.61, 130.04, 131.84, 135.40, 137.27, 149.21 ppm. ^{19}F NMR (136 MHz, $CDCl_3$): δ = –44.30 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3070, 3023, 2991, 2869, 1585, 1510, 1448, 1372, 1310, 1182, 1090 cm^{-1}. HRMS-EI: calcd. for $C_{20}H_{25}ClFNO_2S$ 397.1278, found for $C_{20}H_{24}ClNO_2S$ [M^+ – HF] 377.1208.

***N*-(5-Bromo-2-chloropentyl)-*N*-fluorobenzenesulfonamide (3n):** Gray solid; m.p. 50.1–50.4 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.16–2.25 (m, 1 H), 2.45–2.54 (m, 1 H), 3.50–3.62 (m, 4 H), 4.30–4.37 (m, 1 H), 7.66 (t, J = 8.0 Hz, 2 H), 7.79 (t, J = 7.6 Hz, 1 H), 7.97 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.04, 38.18, 54.97, 58.90 (d, J = 12.7 Hz), 129.68, 130.05, 131.81, 135.53 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –43.14 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3093, 3060, 2977, 2964, 2919, 2853, 2818, 1448, 1367, 1254, 1185 cm^{-1}. HRMS-EI: calcd. for $C_{10}H_{12}BrClFNO_2S$ 342.9443, found for $C_{10}H_{12}BrClFNO_2S$ 342.9442.

***N*-(2-Chloro-2-cyclohexylethyl)-*N*-fluorobenzenesulfonamide (3o):** White solid; m.p. 88.9–89.4 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.20–1.40 (m, 5 H), 1.63–1.86 (m, 6 H), 3.41–3.70 (m, 2 H), 4.03–4.08 (m, 1 H), 7.64 (t, J = 8.0 Hz, 2 H), 7.75–7.80 (m, 1 H), 7.99 (d, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.71, 26.05, 26.07, 26.24, 30.28, 40.69, 56.97 (d, J = 11.8 Hz), 62.31, 129.50, 129.94, 131.90, 135.25 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –45.76 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3071, 2988, 2930, 2855, 1637, 1583, 1448, 1379, 1185 cm^{-1}. HRMS-EI: calcd. for $C_{14}H_{19}ClFNO_2S$ 319.0809 found for $C_{14}H_{19}ClFNO_2S$ [M^+ – HF] 299.0749.

***N*-(2,4-Dichloro-2-methylbutyl)-*N*-fluorobenzenesulfonamide (3p):** Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.73 (s, 3 H), 3.52–3.86 (m, 4 H), 7.67 (t, J = 4.4 Hz, 2 H), 7.78 (t, J = 7.6 Hz, 1 H), 7.80 (d, J = 7.3 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.70, 51.17, 60.39 (d, J = 11.2 Hz), 67.21, 129.10, 130.00, 132.21, 135.49 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –36.78 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3061, 2980, 2935, 2860, 1569, 1450, 1355, 1268, 1180 cm^{-1}. HRMS-EI: calcd. for $C_{10}H_{12}Cl_2FNO_2S$ 298.9950, found for $C_{10}H_{11}Cl_2NO_2S$ [M^+ – HF] 278.9869.

Ethyl 2-Chloro-3-(*N*-fluorophenylsulfonamido)-2-methylpropanoate (3q): Colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, J = 7.2 Hz, 3 H), 1.80 (s, 3 H), 3.59 (dd, J = 10.2, J = 7.2 Hz) 3.47 (dd, J = 9.2, J = 12.8 Hz, 1 H), 4.17–4.24 (m, 2 H), 7.61 (t, J = 8.0 Hz, 2 H), 7.75 (t, J = 7.6 Hz, 1 H), 7.92 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.80, 25.37, 61.36 (d, J = 11 Hz), 62.75, 126.39, 63.93, 129.60, 129.82, 131.85, 135.45, 168.77 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –38.84 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3041, 2980, 2935, 2864, 1745, 1585, 1449, 1381, 1312, 1242, 1186 cm^{-1}. HRMS-EI: calcd. for $C_{12}H_{15}ClFNO_4S$ 323.0394, found 323.0392.

***N*-(2-Chlorocyclohexyl)-*N*-fluorobenzenesulfonamide (3r):** Colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.25–1.33 (m, 1 H), 1.48–1.51 (m, 1 H), 1.70–1.84 (m, 4 H), 2.01–2.10 (m, 2 H), 3.83–3.90 (m, 1 H), 4.59 (s, 1 H), 7.60 (t, J = 7.6 Hz, 2 H), 7.73 (t, J = 7.6 Hz, 1 H), 7.98 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.87, 22.83 (d, J = 10.08 Hz), 24.49 (d, J = 2.7 Hz), 33.36, 60.07 (d, J = 2.9 Hz), 64.75 (d, J = 11.5 Hz), 129.44, 129.64, 134.29, 129.64, 134.29, 135.03 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = 62.14 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3074, 2976, 2940, 2862, 1582, 1449, 1368, 1310, 1162 cm^{-1}. HRMS-EI: calcd. for $C_{12}H_{15}ClFNO_2S$ 291.0496, found 291.0495.

Ethyl 3-chloro-4-(*N*-fluorophenylsulfonamido)cyclopentanecarboxylate (3s): Colorless liquid. ^{1}H NMR (400 MH, $CDCl_3$): δ = 1.24 (t, J = 7.2 Hz, 3 H), 2.16–2.41 (m, 4 H), 2.93 (t, J = 7.6 Hz, 1 H), 4.10–4.17 (m, 2 H), 4.27–4.43 (m, 2 H), 7.59–7.63 (m, 2 H) 7.75 (t, J = 8.0 Hz, 1 H), 7.98 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.24, 28.44 (dd, J = 10.0 Hz), 38.11, 40.96, 70.90 (d, J = 11.4 Hz), 129.55, 129.78, 133.70, 133.75, 135.29, 173.62 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –63.71 (s, 1 F), –65.76 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 30291, 2984, 2945, 2862, 1740, 1495, 1403, 1372, 1230 cm^{-1}. HRMS-EI: calcd. for $C_{14}H_{17}ClFNO_4S$ 349.0551, found 349.0549.

***N*-(2-Chloro-1-phenylethyl)-*N*-fluorobenzenesulfonamide (4a):** Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.88 (dd, J = 7.6, J = 11.6 Hz, 1 H), 4.13 (dd, J = 7.6, J = 11.6 Hz, 1 H), 5.11 (dt, J = 7.2, J = 37.2 Hz, 2 H), 7.13–7.22 (m, 5 H), 7.32 (t, J = 8.0 Hz, 2 H), 7.48 (t, J = 7.2 Hz, 1 H), 7.69 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.45 (d, J = 6.0 Hz), 67.06 (d, J = 11.4 Hz), 127.64, 128.03, 128.04, 128.09, 128.39, 132.15 (d, J = 4.3 Hz), 133.34, 133.68 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –71.64 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3004, 3072, 2965, 1584, 1499, 1445, 1389, 1189 cm^{-1}. HRMS-EI: calcd. for $C_{14}H_{13}ClFNO_2S$ 313.0340, found 313.0342.

***N*-[2-Chloro-1-(*p*-tolyl)ethyl]-*N*-fluorobenzenesulfonamide (4b):** Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 3.88 (dd, J = 7.6, J = 11.2 Hz, 1 H), 4.15 (dd, J = 11.6, J = 7.2 Hz, 1 H), 5.10 (dt, J = 37.2, J = 7.6 Hz, 1 H), 7.10 (d, J = 7.6 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H), 7.46 (t, J = 7.6 Hz, 2 H), 7.63 (t, J = 7.6 Hz, 1 H), 7.81 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.25, 43.49 (d, J = 5.9 Hz), 67.82 (d, J = 12.5 Hz), 128.99, 129.00, 129.08, 129.32, 129.49, 130.23 (d, J = 4.5 Hz), 134.50, 134.59 (d, J = 6.3 Hz), 139.40 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –71.61 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3098, 3073, 2945, 2854, 1586, 1462, 1372, 1172, 1107 cm^{-1}. HRMS-EI: calcd. for $C_{15}H_{15}ClFNO_2S$ 327.0496, found 327.0495.

***N*-[2-Chloro-1-(*o*-tolyl)ethyl]-*N*-fluorobenzenesulfonamide (4c):** Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.07 (s, 3 H), 4.0–4.15 (m, 2 H), 7.34–7.38 (m, 3 H), 7.48–7.52 (m, 4 H), 7.83 (d, J = 8.0 Hz, 2 H), 7.65 (t, J = 7.6 Hz, 1 H), 7.81 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.12 (d, J = 5.4 Hz), 50.43 (d, J = 7.4 Hz), 72.33 (d, J = 12.5 Hz), 127.04, 128.27, 128.65, 129.02, 134.40, 134.50, 136.59, 137.68 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –63.32 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3066, 3031, 3003, 2922, 2851, 1584, 1497, 1448, 1363, 1174, 1088 cm^{-1}. HRMS-EI: calcd. for $C_{15}H_{15}ClFNO_2S$ 327.0496, found 327.0495.

***N*-[2-Chloro-1-(4-methoxyphenyl)ethyl]-*N*-fluorobenzenesulfonamide (4d):** White solid; m.p. 71.1–72.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3 H), 3.83–3.88 (m, 1 H), 4.10–4.15 (m, 1 H), 5.08 (dt, J = 7.2, 39.2 Hz, 1 H), 6.79–6.82 (m, 2 H), 7.21 (d, J = 8.4 Hz, 2 H), 7.44–7.48 (m, 2 H), 7.62 (t, J = 7.6 Hz, 1 H), 7.80 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.70 (d, J = 5.4 Hz), 55.56, 67.67 (d, J = 11.6 Hz), 114.07, 125.19 (d, J = 4.7 Hz), 129.12, 129.51, 130.41, 134.62, 134.76, 160.36 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –72.10 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3056, 2952, 2860, 1653, 1638, 1616, 1448, 1377, 1357 cm^{-1}. HRMS-EI: calcd. for $C_{15}H_{15}ClFNO_3S$ 343.0445, found 343.0446.

***N*-{1-[4-(*tert*-Butyl)phenyl]-2-chloroethyl}-*N*-fluorobenzenesulfonamide (4e):** White solid; m.p. 85.1–85.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 9 H), 3.85 (dd, J = 7.2, J = 11.2 Hz,1 H), 4.14 (dd, J = 7.2, J = 11.2 Hz, 1 H), 5.12 (dt, J = 7.2, J = 39.2 Hz, 1 H), 7.17 (d, J = 8.0 Hz, 2 H), 7.25 (d, J = 7.6 Hz, 2 H), 7.40 (t, J = 8.0 Hz, 2 H),7.56 (t, J = 7.6 Hz, 1 H), 7.76 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.36, 34.72, 43.64, 68.09, 125.63, 128.51, 129.51, 130.00, 134.50, 152.36 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –74.14 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3108, 3070, 3039, 2964, 2869, 1582, 1449, 1366, 1176, 1109, 1086, 1025 cm^{-1}. HRMS-EI: calcd. for $C_{18}H_{21}ClFNO_2S$ 369.0966, found for $C_{18}H_{20}ClNO_2S$ 369.0973.

***N*-[2-Chloro-1-(4-fluorophenyl)ethyl]-*N*-fluoro-4-nitrobenzenesulfonamide (4f):** White solid; m.p. 130.4–130.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.87 (dd, J = 7.2, J = 11.6 Hz,1 H), 4.15 (dd, J = 7.2, J = 11.6 Hz, 1 H), 5.22 (dt, J = 7.2, J = 38.0 Hz, 1 H), 7.00–7.04 (m, 2 H), 7.30–7.34 (m, 2 H), 8.00–8.03 (m, 2 H), 8.31–8.34 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.09, 67.26 (d, J = 11.7 Hz), 116.03 (d, J = 21.6 Hz), 124.31, 128.70, 130.84, 131.06 (d, J = 10.1 Hz), 140.44, 156.78 (d, J = 97.6 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –110.48 (s, 1 F), –72.85 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3100, 3037, 3011, 2964, 2926, 2867, 1605, 1528, 1510, 1383, 1349, 1227, 1182 cm^{-1}. HRMS-EI: calcd. for $C_{14}H_{11}ClF_2N_2O_4S$ 376.0096, found 376.0100.

4-Chloro-*N*-[2-chloro-1-(4-fluorophenyl)ethyl]-*N*-fluorobenzenesulfonamide (4g): White solid; m.p. 59.5–60.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (dd, J = 7.6, J = 11.2 Hz, 1 H), 4.13 (dd, J = 7.4, J = 11.6 Hz, 1 H), 5.13 (dt, J = 4.6, J = 38.0 Hz, 1 H), 7.01 (td, J = 8.4 Hz, 2 H), 7.30 (t, J = 8.4 Hz), 7.46 (d, J = 8.4 Hz, 2 H), 7.74 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.39 (d, J = 5.6 Hz), 67.26 (d, J = 11.5 Hz), 115.87 (d, J = 21.5 Hz), 129.60, 130.88, 130.99 (d, J = 1.8 Hz), 141.91, 163.89 (d, J = 248.1 Hz) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –111.18, –71.80 ppm. IR (KBr): $\tilde{\nu}$ = 3263, 3100, 2966, 2905, 1605, 1513, 1403, 1241, 1151 cm^{-1}. HRMS-EI: calcd. for $C_{14}H_{11}Cl_2F_2NO_2S$ 364.9856, found 364.9853.

***N*-[2-Chloro-1-(4-methoxyphenyl)ethyl]-*N*,4-difluorobenzenesulfonamide (4h):** White solid; m.p. 72.5–73.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3 H), 3.86 (dd, J = 7.2, J = 11.2 Hz, 1 H), 4.13 (dd, J = 7.2, J = 11.2 Hz, 1 H), 5.09 (dt, J = 7.2, J = 39.20 Hz, 1 H), 6.78–6.82 (m, 2 H), 7.08–7.14 (m, 2 H), 7.19 (d, J = 8.4 Hz, 2 H), 7.76–6.82 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.66 (d, J = 5.1 Hz), 55.39, 67.80 (d, J = 11.5 Hz), 114.07, 116.48 (d, J = 22.7 Hz), 124.96 (d, J = 4.8 Hz), 130.43 (d, J = 1.7 Hz), 130.72 (d, J = 3.1 Hz), 132.46 (d, J = 9.8 Hz), 160.48, 166.35 (d, J = 256.6 Hz) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –101.51, –72.75 ppm. IR (KBr): $\tilde{\nu}$ = 3106, 3069, 2965, 2933, 2862, 1611, 1512, 1364, 1262, 1176, 1158, 1028 cm^{-1}. HRMS-EI: calcd. for $C_{15}H_{14}ClFNO_3S$ 361.0351, found 361.0355.

***N*-[2-Chloro-1-(4-methoxyphenyl)propyl]-*N*-fluorobenzenesulfonamide (4i):** White solid; m.p. 70.5–71.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.74 (d, J = 6.3 Hz, 3 H), 3.77 (s, 3 H), 4.52–4.43 (m, 1 H), 4.84 (dd, J = 8.7, 8.7 Hz, 1 H), 6.72 (d, J = 8.7 Hz, 2 H), 7.16 (d, J = 8.4 Hz, 2 H), 7.38 (t, J = 7.8 Hz, 2 H), 7.57 (t, J = 7.5 Hz, 1 H), 7.68 (t, J = 7.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.95, 55.28, 57.06, 72.01 (d, J = 11.2 Hz), 113.57, 124.66 (d, J = 5.6 Hz), 128.93, 129.39, 131.06 (d, J = 2.0 Hz), 134.32, 134.64, 160.06 ppm. ^{19}F NMR (136 MHz, $CDCl_3$): δ = –74.36 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3073, 2989, 2973, 2936, 2837, 1608, 1584, 1513, 1400, 1250, 1172, 1029 cm^{-1}. HRMS-EI: calcd. for $C_{16}H_{17}ClFNO_3S$ 357.0602, found 357.0605.

***N*-[1-Chloro-3-(4-methoxyphenyl)propan-2-yl]-*N*-fluorobenzenesulfonamide (4j):** Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.06–3.20 (m, 2 H), 3.65–3.74 (m, 2 H), 3.81 (s, 3 H), 4.31–4.45 (m,1 H), 6.86 (d, J = 8.0 Hz, 2 H), 7.15 (d, J = 8.0 Hz, 2 H), 7.6 (t, J = 7.6 Hz, 2 H), 7.73 (t, J = 7.6 Hz, 1 H), 7.96 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.53, 54.32, 56.44, 56.48 (d, J = 11.6 Hz), 112.97, 127.07, 128.59, 129.03, 129.86, 130.76, 134.42, 157.81 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –72.10 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3056, 2965, 2926, 2839, 1601, 1581, 1493, 1448, 1072 cm^{-1}. HRMS-EI: calcd. for $C_{16}H_{17}ClFNO_3S$ 357.0602, found 357.0608.

(*Z*)-*N*-(2-Chloro-2-phenylvinyl)benzenesulfonamide (7): White solid; m.p. 78.0–79.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95–7.01 (m, 2 H), 7.29–7.36 (m, 3 H), 7.45 (d, *J* = 7.6 Hz, 2 H), 7.55 (t, *J* = 8.0 Hz, 2 H), 7.62 (t, *J* = 7.6 Hz, 1 H), 7.90 (t, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.09, 119.76, 125.67, 126.80, 128.48, 128.72, 129.61, 133.53, 135.10, 139.92 ppm. IR (KBr): $\tilde{\nu}$ = 3274, 3075, 3032, 2922, 2850, 1652, 1593, 1448, 14401, 1347, 1165, 1092 cm^{-1}. HRMS-EI: calcd. for $C_{14}H_{12}ClNO_2S$ 293.2771, found 293.0279.

2-Phenyl-1-(phenylsulfonyl) aziridine (8):[17] White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (d, *J* = 4.4 Hz, 1 H), 3.03 (d, *J* = 7.2 Hz, 1 H), 3.82 (t, *J* = 7.2 Hz, 1 H), 7.21–7.22 (m, 2 H), 7.29–7.55 (m, 3 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.64 (t, *J* = 7.6 Hz, 1 H), 8.0 (d, *J* = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.15, 41.28, 126.69, 128.02, 128.50, 128.72, 129.27, 133.80, 135.80, 138.16 ppm.

***N*-(2-Chloro-2-phenylethyl)benzenesulfonamide (9):** White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.33–3.47 (m, 2 H), 4.79 (dd, *J* = 6.0, 7.6 Hz, 1 H), 4.93 (t, *J* = 6.0 Hz, 1 H), 7.18–7.22 (m, 2 H), 7.24–7.27 (m, 3 H), 7.43–7.48 (m, 2 H), 7.51–7.55 (m, 1 H), 7.76–7.79 (d, *J* = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.44, 61.74, 127.05, 127.30, 129.01, 129.20, 129.38 ppm.

***N*-(4-Methoxyphenyl)benzenesulfonamide (10):** White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76 (s, 3 H), 6.38 (s, 1 H), 6.77 (d, *J* = 8.0 Hz, 2 H), 6.96 (d, *J* = 8.4 Hz), 7.43 (t, *J* = 7.6 Hz, 2 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.69 (d, *J* = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.54, 114.56, 125.72, 127.41, 128.82, 129.06, 132.99, 139.03, 158.16 ppm.

Supporting Information (see footnote on the first page of this article): Experimental procedures, new compounds' characterization and crystal structure data.

Note: The authors declare no competing financial interests.

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Aminochlorination

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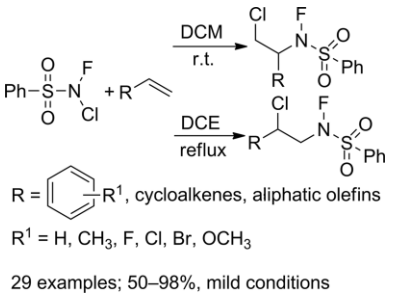
Aminochlorination of Alkenes with CFBSA



Alkenes were aminochlorinated in high yields and good regioselectivity by the direct, catalyst-free addition of alkenes to CFBSA (*N*-chloro-*N*-fluorobenzenesulfonamide).

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