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Article

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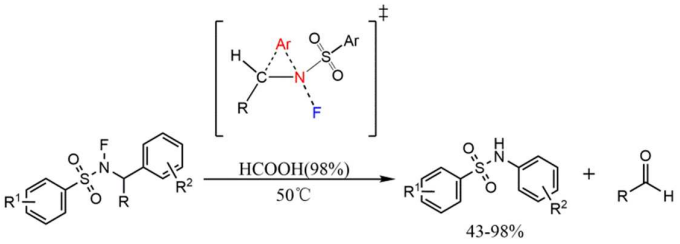
A Rearrangement Reaction Based on the Structure of *N*-fluoro-*N*-alkyl Benzenesulfonamide

Han-Ying Wang,[a†] Xiao-Qiu Pu [b†] and Xian-Jin Yang *[a, b]

[a.]Key Lab for Advanced Material & Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200231, China. E-mail: yxj@ecust.edu.cn

[b.]Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China.

† These authors contributed equally to this work.



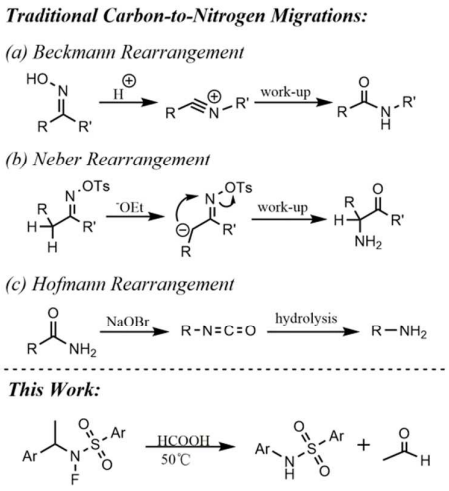
ABSTRACT: A novel rearrangement reaction based on the structure of *N*-fluoro-*N*-alkyl benzenesulfonamide was developed. The reaction proceeded readily at 50°C in formic acid and generated a variety of benzenesulfonamides and aldehydes or ketones simultaneously. The reaction mechanism is believed to be a concerted mechanism that consist of 1,2-aryl migration with the departure of fluorine anion *via* an S_N2 mechanism. This rearrangement reaction features an interesting reaction mechanism, mild reaction conditions, simple operation, and a broad substrate scope.

INTRODUCTION:

The Beckmann rearrangement (BKR) is an important method in organic synthesis for preparing *N*-substituted amides from ketoximes.[1] The conventional BKR is catalyzed by strong Brønsted or Lewis acids, such as concentrated sulfuric acid, PCl_5 in diethyl ether, and hydrogen chloride in acetic anhydride.[2] The concerted or stepwise nature of the BKR mechanism is of theoretical interest.[3] However, until now, few studies[4] about BKR involve fluoronitrogens have been reported.

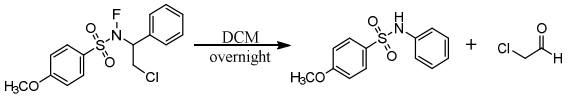
N-F compounds usually serve as electrophilic fluorinating agents, such as Selectfluor[5] and *N*-fluorobenzenesulfonimide.[6] In recent years, a wide variety of N-F compounds have been developed as fluorine sources due to their potential radical fluorination ability.[7] Unlike previous studies, the N-F compounds were utilized as substrates for a rearrangement in this study, which is similar to the BKR, undergoing the departure of one group and the 1,2 migration of another group.

Most rearrangement reactions are migrations from an atom to an adjacent one (called 1,2-shifts), but some occur over longer distances. Migrations from a carbon to a nitrogen atom are used to prepare amines from acid derivatives[8] (Scheme 1c) or ketones (Scheme 1a,b).[9-10] Traditional reactions usually afford one product, whereas two products were generated for this reaction.



Scheme 1 The rearrangement reactions.

Our group recently introduced a new method to synthesize *N*-fluoro-*N*-alkylbenzenesulfonamides.[11] Unexpectedly, this kind of compound decomposed to benzenesulfonamide (yield 45%) and aldehyde simultaneously in dichloromethane (DCM) overnight (Scheme 2). Inspired by this discovery, we investigated the function of the N-F bond in this rearrangement and detected the detailed mechanistic interactions.

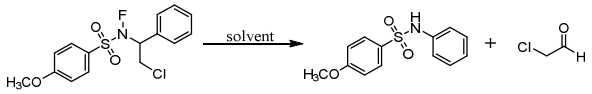


Scheme 2 The discovery of a new rearrangement reaction.

RESULTS AND DISCUSSION:

To determine the optimized conditions, *N*-(2-chloro-1-phenylethyl)-*N*-fluoro-4-methoxybenzenesulfonamide (**1**) was synthesized first as the model substrate to screen the conditions for this reaction. Experiments (Table 1) revealed that the reaction solvent exerted a significant influence on the outcome, and the use of methanol, ethanol, or benzyl alcohol as solvents resulted in no desired product formation [see Supporting Information (SI)]. It was observed that formic acid was the optimal choice (entries 1–8). Notably, the reaction barely progressed without water in the solvent (entries 9–11). However, the yield did not improve when water content in the solvent was optimized (entry 12). Increasing the temperature to 50°C led to an improved yield of 97% as well as a shorter reaction time (1 hour), but an even higher temperature reduced the yield (entries 13–15).

Table 1 Optimization of the reaction conditions.



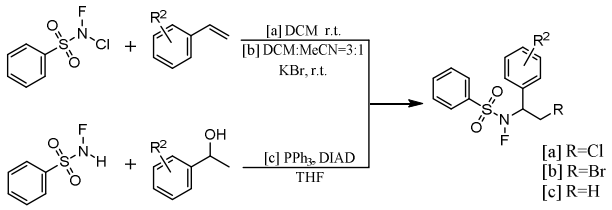
1 **2**

Entry	Solvent	T (°C)	Time (h)	Yield (%)[a]
1	CH_3CN	r.t.	24	23
2	Toluene	r.t.	24	35
3	THF	r.t	24	26
4	Acetone	r.t.	24	40
5	EtOAc	r.t.	24	36
6	CH_2Cl_2	r.t.	24	50

7	1.4-dioxane	r.t.	24	19
8	HCOOH	r.t	24	76
9	CH_2Cl_2[b,c]	r.t	24	nd
10	CH_2Cl_2[b]	r.t.	24	13
11	CH_2Cl_2[c]	r.t.	24	50
12	CH_2Cl_2:H_2O=10:1	r.t.	24	64
13	HCOOH	50	1	97
14	HCOOH	70	0.5	88
15	HCOOH	reflux	0.5	60

[a] Isolated yield after column chromatography. [b] The solvent was dried by refluxing with CaH_2. [c] The reaction was performed under an N_2 atmosphere.

With the optimized conditions in hand, a library of *N*-fluoro-*N*-alkyl benzenesulfonamides was synthesized with structural and electronic modifications to examine the substrate scope and functional group tolerance of the reaction. The substrates were synthesized in two main ways: [a] by directly adding alkenes to *N*-chloro-*N*-fluorobenzenesulfonamide[12] and [b] the Mitsunobu reaction between benzyl alcohol and *N*-fluoro benzenesulfonamide (Scheme 3).

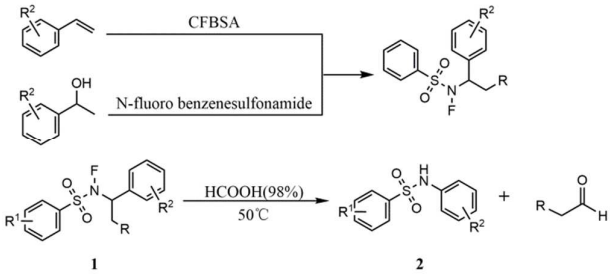


Scheme 3 Synthesis of *N*-fluoro-*N*-alkyl benzenesulfonamides.

First, the aryl substituent in styrene or benzyl alcohol was varied, and the data were summarized. As shown in Table 2, the *para*-substituted aryls bearing electron-donating, such as alkyl and alkoxyl groups, effectively yielded the corresponding products **2a–2d**, while the aryl bearing strong electron-withdrawing group CF_3 failed to afford the arrangement product **2e**. Interestingly, changing the R group to a halogen (bromine) had no significant effect on yield. In addition, *meta*-methyl and *ortho*-substituent aryls also exhibited good reactivities to give the desired products **2f–2h** in moderate to good yields. Substrate with di-substitutents on the aryl ring was also compatible to give product **2i** with a considerable yield. Furthermore, substrates with thienyl and naphthyl rings also afforded the corresponding products **2j** and **2k** at 60% and 96% yields, respectively.

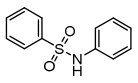
Next, the scope of the *N*-fluoro benzenesulfonamide was explored (Table 2). Again, the para-substituted aryls effectively produced the target products **2l–2p** with excellent yields.

Table 2 Scope of *N*-fluoro-*N*-alkyl benzenesulfonamides.



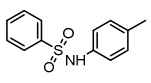
1 2

styrenes and benzyl alcohols

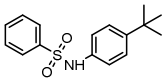


R in substrate 1:
R=H 96 %[c]
R=Br 93 %[b]

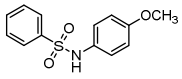
2a



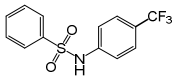
2b 93%[c]



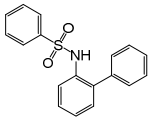
2c 93%[a]



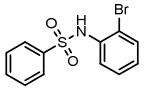
2d 97%[a]



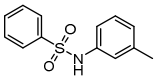
2e 0%[c]



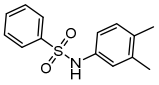
2f 72%[c]



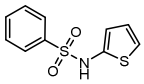
2g 43%[c]



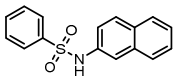
2h 98%[c]



2i 96%[c]

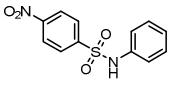


2j 60%[cd]

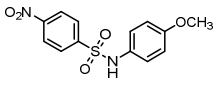


2k 96%[c]

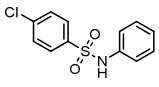
N-fluoro benzenesulfonamides



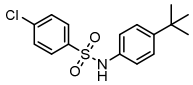
2l 95%[c]



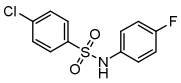
2m 98%[a]



2n 97%[c]



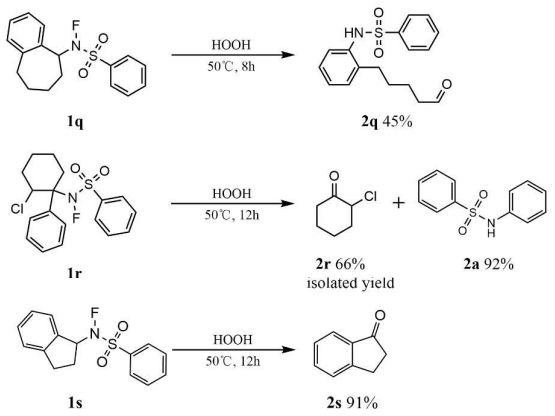
2o 93%[a]



2p 89%[a]

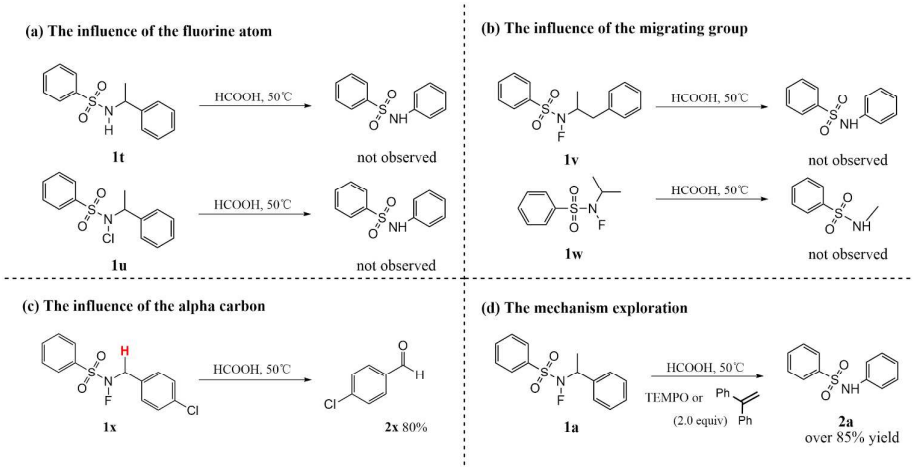
[a] Reactions were performed using 0.25 mmol of substrates in 2 mL of formic acid at 50°C for 1–6 h. Isolated yields are given. [a] R = Cl. [b] R = Br. [c] R = H. [d] At room temperature.

Because of the volatility of the aliphatic aldehydes in our reactions, the other product was difficult to isolate and purify. Therefore, some substrates with special skeletons were tested to afford the alpha-chlorocyclohexanone **2r** and the corresponding ring-opening product **2q**, whose structure contained aromatic amine and carbonyl groups (Scheme 4). The compound **1s** was anticipated to provide the ring-opening product. Nevertheless, it was converted to 1-indanone **2s**, which may have been due to high ring strain.



Scheme 4 Substrates with special skeletons.

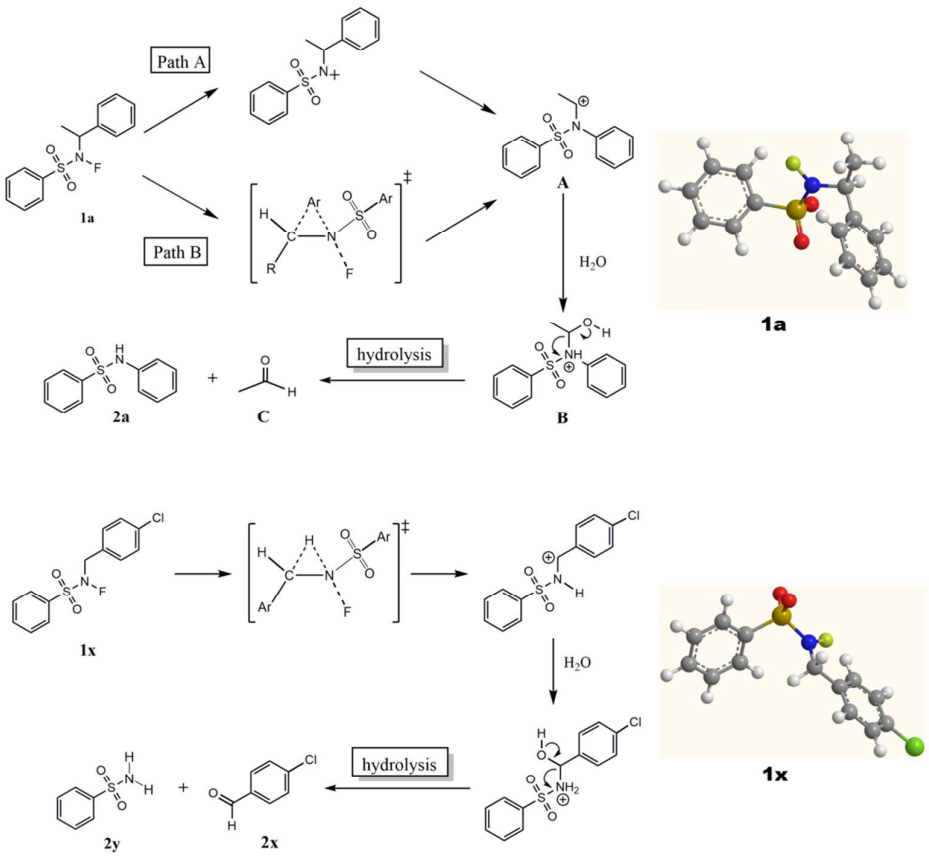
A variety of control experiments were carried out to gain mechanistic insight. At first, compounds **1t** and **1u** failed to react under our standard conditions (Scheme 5a) and the importance of the fluorine atom in this reaction was confirmed. Then the inapplicability of compounds **1v** and **1w** (Scheme 5b) indicated that only aryl migration was feasible. The experiment (Scheme 5c) showed that when there was no substituent on the alpha carbon, an aromatic aldehyde was generated instead of the rearrangement product. This observation probably suggested an S_N2 mechanism, which would be discussed in a later section. In the presence of radical inhibitors 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), the compound **1a** gave **2a** in 87% yield (Scheme 5d). Moreover, when the radical trap 1,1-diphenylethylene was subjected to the standard reaction conditions, the targeted product **2a** were identified with 89% yield (Scheme 5d), which indicated that the rearrangement may not go through a radical process.



Scheme 5 Control experiments.

The proposed mechanism of this reaction is shown in Scheme 6. Since the arylsulfonyl group destabilizes alpha nitrenium cation (Path A), the concerted mechanism (Path B) is much more reasonable in this work. The formic acid promoted the departure of fluorine anion and the beta-aryl group carrying a pair of electrons migrated to the electron-deficient nitrogen atom synchronously to generate the intermediate **A**. Then the water was proposed to be served as an nucleophile attacking the carbonium ions to generate the intermediate **B**. The intermediate **B** would further decompose into the product **2a** and **C** by hydrolysis. This concerted mechanism is also consistent with the result of the substrate **1x**. By comparison, the benzene ring and the fluorine atom of compound **1x** are in the same

plane, so the backside route of attack was hindered and the 1,2-hydrogen shift occurred. This difference of two substrates might provide some evidence for the proposed S_N2 mechanism.



Scheme 6 The proposed mechanism.

CONCLUSION:

In summary, we developed a novel rearrangement reaction based on the structure of *N*-fluoro-*N*-alkyl benzenesulfonamide, which generated benzene sulfonamide in situ and aldehyde or ketone. The concerted reaction mechanism is believed to consist of an aryl or hydrogen migration with expulsion of the fluorine anion *via* an S_N2 mechanism. This finding will allow us to further develop the organic reactions in which the N-F bond participates. Further studies are underway in our laboratory.

EXPERIMENTAL SECTION:

General Considerations. Unless otherwise noted, all commercially available compounds were purchased without further purification. Dry THF was obtained by refluxing with Na. Flash column chromatography was carried out on silica gel (300-400 mesh). Thin layer chromatography (TLC) was performed using silica gel HSGF 254 plates and visualized by UV light (254nm). NMR spectra were recorded on a Brucker AM-400 (400 MHz for ^{1}H; 376 MHz for ^{19}F; 100MHz for ^{13}C) spectrometer. IR spectra were recorded on a Bruker TENSOR 27 FTIR Spectrometer equipped with a Platinum ATR detector. LRMS and HRMS Mass Spectra were recorded on a Waters GCT Premier mass spectrometer with electron impact (70eV). Chemical shifts are given in parts per million (ppm) using residual solvent signals as internal standard ($CHCl_3$, δ = 7.26 ppm or DMSO-d_6, δ = 2.50 ppm for ^{1}H NMR, δ = 77.16 ppm or DMSO-d_6, δ = 39.52 ppm for ^{13}C

NMR). HRMS (EI) Mass Spectra were recorded on a Waters GCT Premier ms spectrometer with electron impact.

General Procedures. To a round bottom flask equipped with a magnetic stir bar, *N*-fluoro-*N*-alkyl benzenesulfonamide **1** (1.0 equiv.) was dissolved as well as possible in methanoic acid (0.2 M). The reaction was allowed to stir at 50 °C and was monitored by TLC (Thin Layer Chromatography). Then the mixture was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate, 20:1) to afford the products 2a-2x. The isolated yields of the products 2a-2x do not take into account residual solvents.

Preparation of Substrate N-Fluoro-N-alkyl benzenesulfonamide. Method A: To a solution of the styrene (1.0 equiv.) in DCM (0.5 M), CFBSA (1.2 equiv.) was added dropwise. Then the mixture stirred at room temperature for 12 hours. The solvent was then removed under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 60:1). **Method B**: To a solution of the CFBSA (1.0 equiv.) in DCM:MeCM = 3:1 (0.5 M), potassium bromide (1.5 equiv.) was added . Then the mixture stirred at room temperature for 6 hours or until completion observed by TLC. The styrene (1.0 equiv.) was added. When the reaction completed, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 60:1). **Method C:** To a solution of the alcohol (1.0 equiv.), *N*-fluorobenzenesulfonamide (1.2 equiv.) and PPh_3 (1.2 equiv.) in dry THF (0.2 M), diisopropyl azodicarboxylate (1.2 equiv.) was added dropwise at 0 °C. The reaction then stirred for 1-12 hour at room temperature, or until completion observed by TLC. The solvent was then removed under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 40:1). All yields are not optimized.

***N*-(2-Bromo-1-phenylethyl)-*N*-fluorobenzenesulfonamide (*1a*^{b})**: White solid, 235.6 mg, yield 66%; m.p.: 96.2-98.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97-7.91 (m, 2H), 7.79-7.73 (m, 1H), 7.89-7.66 (m, 2H), 7.41-7.30 (m, 5H), 5.12 (t, *J* = 7.4 Hz, 1H), 3.99-3.95 (m, 1H), 3.88 (dd, *J* = 7.4, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.2, 135.4, 132.1, 130.0, 129.6, 129.3, 129.1, 127.9, 59.9 (d, $^2J_{C\text{-}F}$ = 11.8 Hz, 1C), 47.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -71.59 (s, 1F). IR (KBr, cm^{-1}): 3067.4, 3021, 2981, 2852, 1603, 1522, 1511, 1423; HRMS (EI-TOF) m/z: $[M - HF]^+$ Calcd for $C_{14}H_{12}BrNO_2S$ 336.9772; Found 336.9776.

***N*-Fluoro-*N*-(1-phenylethyl)benzenesulfonamide (*1a*^{c})**: White solid, 145.1 mg, yield 52%; m.p.: 40.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91-7.89 (m, 2H), 7.68-7.64 (m, 1H), 7.54-7.49 (m, 2H), 7.35-7.27 (m, 5H), 4.97 (dq, *J* = 33.4, 6.8 Hz, 1H), 1.68 (dd, *J* = 6.9, 1.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.9 (d, $J_{C\text{-}F}$ = 2.3 Hz, 1C), 134.8, 134.6, 129.6, 129.2, 128.6, 128.4, 127.7, 63.0 (d, $^2J_{C\text{-}F}$ = 13.0 Hz, 1C), 18.8 (d, $^3J_{C\text{-}F}$ = 9.1 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -67.08 (s, 1F). IR (KBr, cm^{-1}): 3006.2, 2913.4, 2855.6; HRMS (EI-TOF) m/z: $[M - HF]^+$ Calcd for $C_{14}H_{13}NO_2S$ 259.0667; Found 259.0665.

***N*-Fluoro-*N*-(1-(p-tolyl)ethyl)benzenesulfonamide (*1b*)**: White solid, 181.7 mg, yield 62%; m.p.: 42.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92-7.87 (m, 2H), 7.69-7.63 (m, 1H), 7.55-7.48 (m, 2H), 7.25-7.20 (m, 2H), 7.14-7.09 (m, 2H), 2.33 (s, 1H), 4.95 (dq, *J* = 33.5, 6.8 Hz, 1H), 1.66 (dd, *J* = 6.9, 1.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.2, 135.8 (d, $J_{C\text{-}F}$ = 2.6 Hz, 1C), 134.9, 134.5, 129.5, 129.3, 129.1, 127.7, 62.8 (d, $^2J_{C\text{-}F}$ = 13.0 Hz, 1C), 21.2, 18.8 (d, $^3J_{C\text{-}F}$ = 8.8 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -67.29 (s, 1F). IR (KBr, cm^{-1}): 3098.1, 3073.4, 2945.1, 2854.8; HRMS (EI-TOF) m/z: $[M - HF]^+$ Calcd for $C_{15}H_{15}NO_2S$ 273.0823; Found 273.0822.

***N*-(1-(4-(tert-Butyl)phenyl)-2-chloroethyl)-*N*-fluorobenzenesulfonamide (*1c*)**: White solid, 324.8 mg, yield 88%; m.p.: 84.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80-7.78 (m, 2H), 7.61-7.56 (m, 1H), 7.44-7.39 (m, 2H), 7.30-7.25 (m, 2H), 7.20-7.17 (m, 2H), 5.14 (dt, *J* = 39.3, 7.2 Hz, 1H), 4.17 (dd, *J* = 11.5, 7.2 Hz, 1H), 3.88 (dd, *J* = 11.5, 7.3 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.4, 134.6, 134.5, 130.0, 129.5, 129.0, 128.8, 125.6, 68.0 (d, $^2J_{C\text{-}F}$ = 11.5 Hz, 1C), 43.6, 34.7, 31.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -74.14 (s, 1F). IR (KBr, cm-1): 3066.6, 1583.5, 1130.6, 898.3, 687.3; HRMS (EI-TOF) m/z: $[M - HF]^+$ Calcd for $C_{18}H_{20}ClNO_2S$ 349.0903; Found 349.0906.

***N*-(2-Chloro-1-(4-methoxyphenyl)ethyl)-*N*-fluorobenzenesulfonamide (1*d*)**: White solid, 295.0 mg, yield 86%; m.p.: 71.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80(d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.48-7.44 (m, 2H), 7.21(d, *J* = 8.4 Hz, 2H), 6.82-6.79 (m, 2H), 5.08 (dt, *J* = 7.2 Hz, 39.2Hz, 1H), 4.15-4.10 (m, 1H), 3.88-3.83 (m,1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: ^{13}C NMR (100MHz, CDCl3) :160.4, 134.8, 134.6, 130.4, 129.5, 129.2, 125.2 (d, J_{C-F} = 4.7 Hz, 2C), 114.1, 67.7 (d, $^{2}J_{C-F}$ = 11.6 Hz, 1C), 55.6, 43.7 (d, $^{3}J_{C-F}$ = 5.4 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -72.10 (s, 1F). IR (KBr, cm^{-1}): 3056.4, 2961.3, 2923.2, 2838.6; HRMS (EI-TOF) m/z: $[M - HF]^+$ Calcd for $C_{15}H_{14}ClNO_3S$ 323.0383; Found 323.0385.

***N*-Fluoro-*N*-(1-(4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide (*1e*)**: Colorless oil, 156.2 mg, yield 45%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90-7.87 (m, 2H), 7.70-7.65 (m, 2H), 7.57-7.50 (m, 4H), 7.46-7.43 (m, 2H), 5.04 (dq, *J* = 33.1, 6.9 Hz, 1H), 1.68 (dd, *J* = 6.9, 1.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.71, 134.85, 134.49, 130.56 (d, J_{C-F} = 32.6 Hz), 129.54, 129.30, 128.08, 125.65 (q, J_{C-F} = 3.8 Hz, 1C), 62.43 (d, $^{2}J_{C-F}$ = 13.0 Hz), 18.82 (d, $^{3}J_{C-F}$ = 9.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.68 (s, 3F), -67.25 (s, 1F). IR (KBr, cm^{-1}): 3252.2, 3248.3, 2918.2, 1511.8, 1362.7, 1132.5, 978.2, 753.2; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{15}H_{13}F_4NO_2S$ 347.0603; Found 347.0609.

***N*-(1-([1,1'-Biphenyl]-2-yl)ethyl)-*N*-fluorobenzenesulfonamide (*1f*)**: White solid, 259.2 mg, yield 73%; m.p.: 79.5-80.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79-7.74 (m, 2H), 7.66-7.00 (m, 2H), 7.49-7.30 (m, 7H), 7.28-7.20 (m, 3H), 5.03 (dq, *J* = 26.7, 6.7 Hz, 1H), 1.56 (dd, *J* = 6.8, 1.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.1, 140.4, 137.2 (d, J_{C-F} = 2.0 Hz, 1C), 134.6, 133.9, 130.3, 129.5, 129.4, 129.1, 128.4, 127.9, 127.9, 127.5, 127.4, 59.5 (d, $^{2}J_{C-F}$ = 12.9 Hz, 1C), 19.5 (d, $^{3}J_{C-F}$ = 10.3 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -61.88 (s, 1F). IR (KBr, cm^{-1}): 3150.5, 1369.2, 1180.3, 745.3, 572.1; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{20}H_{18}FNO_2S$ 355.1042; Found 355.1040.

***N*-(1-(2-Bromophenyl)ethyl)-*N*-fluorobenzenesulfonamide (*1g*)**: Yellow oil, 146.3 mg, yield 41%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98-7.96 (m, 2H), 7.70-7.66 (m, 1H), 7.57-7.49 (m, 4H), 7.29-7.24 (m, 1H), 7.15-7.11 (m, 1H), 5.48 (dq, *J* = 30.8, 6.8 Hz, 1H), 1.62 (dd, *J* = 6.8, 1.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.6 (d, $^{3}J_{C-F}$ = 1.5 Hz, 1C), 134.8, 134.4, 133.1, 129.7, 129.7, 129.3, 128.9 (d, J_{C-F} = 2.5 Hz, 1C), 127.9, 123.2, 61.8 (d, $^{2}J_{C-F}$ = 13.1 Hz, 1C), 17.9 (d, $^{3}J_{C-F}$ = 10.7 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -66.42 (s, 1F). IR (KBr, cm^{-1}): 3435.7, 3066.9, 1448.4, 1365.9, 1179.5, 1084.7, 757.9, 561.9; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{14}H_{13}BrFNO_2S$ 356.9834; Found 356.9832.

***N*-Fluoro-*N*-(1-(m-tolyl)ethyl)benzenesulfonamide (*1h*)**: Colorless oil, 190.5 mg, yield 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92-7.88 (m, 2H), 7.69-7.63 (m, 1H), 7.55-7.49 (m, 2H), 7.23-7.07 (m, 4H), 4.94 (dq, *J* = 33.5, 6.9 Hz, 1H), 2.32 (s, 3H), 1.67 (dd, *J* = 6.9, 1.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.7 (d, J_{C-F} = 2.2 Hz), 138.3, 134.8, 134.5, 129.5, 129.1, 129.1, 128.5, 128.4, 124.7, 63.1 (d, $^{2}J_{C-F}$ = 13.0 Hz, 1C), 21.5, 18.8 (d, $^{3}J_{C-F}$ = 9.2 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -66.96 (s, 1F). IR (KBr, cm^{-1}): 3097.8, 2954.5, 2925.1, 2856.5; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{15}H_{16}FNO_2S$ 293.0886; Found 293.0887.

***N*-(1-(3,4-Dimethylphenyl)ethyl)-*N*-fluorobenzenesulfonamide (*1i*)**: Yellow oil, 224.2 mg, yield 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91-7.86 (m, 2H), 7.68-7.62 (m, 1H), 7.54-7.48 (m, 2H), 7.10-7.04 (m, 3H), 4.91 (dq, *J* = 33.8, 6.9 Hz, 1H), 2.22 (d, *J* = 2.8 Hz, 6H), 1.66 (dd, *J* = 6.9, 1.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.9, 136.8, 136.2 (d, J_{C-F} = 2.4 Hz, 1C), 134.9, 134.4, 129.8, 129.5, 129.0, 129.0, 125.2, 63.0 (d, $^{2}J_{C-F}$ = 13.0 Hz, 1C), 19.9, 19.6, 18.9 (d, $^{3}J_{C-F}$ = 8.9 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -67.32 (s, 1F). IR (KBr, cm^{-1}): 3427.2, 2940.122, 1448.9, 1364.2, 1177.3, 735.5, 606.0; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{16}H_{18}FNO_2S$ 307.1042; Found 307.1040.

***N*-Fluoro-*N*-(1-(thiophen-2-yl)ethyl)benzenesulfonamide (*1j*)**: Yellow oil, 116.8 mg, yield 41%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92-7.87 (m, 2H), 7.67-7.61 (m, 1H), 7.53-7.47 (m, 2H), 7.22 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.03-7.00 (m, 1H), 6.93-6.88 (m, 1H), 5.46 (dq, *J* = 37.4, 6.9 Hz, 1H), 1.75 (dd, *J* = 6.9, 1.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.6 (d, J_{C-F} = 2.5 Hz, 1C), 134.9, 134.6, 129.4, 129.1, 126.7, 126.5, 126.1, 58.4 (d, $^{2}J_{C-F}$ = 13.3 Hz, 1C),

19.6 (d, $^3J_{C\text{-}F}$ = 8.3 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -72.65 (s, 1F). IR (KBr, cm^{-1}): 3069.9, 2992.3, 1663.5, 1448.7, 1363.4, 1176.9, 1088.7, 905.3, 707.8, 551.6; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{12}H_{12}FNO_2S_2$ 285.0293; Found 285.0290.

***N*-Fluoro-*N*-(1-(naphthalen-2-yl)ethyl)benzenesulfonamide (*1k*)**: White solid, 213.9 mg, yield 65%; m.p.: 89.3-91.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20-8.14 (m, 1H), 7.95-7.85 (m, 3H), 7.83-7.78 (m, 1H), 7.66-7.54 (m, 3H), 7.55-7.40 (m, 4H), 5.99 (dq, *J* = 33.6, 6.8 Hz, 1H), 1.87 (dd, *J* = 6.8, 1.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.0, 134.7, 134.3, 134.0, 130.91, 129.5, 129.2, 129.2, 129.2, 126.8, 125.9, 125.6, 125.5, 125.3, 122.9, 57.9 (d, $^2J_{C\text{-}F}$ = 13.8 Hz, 1C), 17.1 (d, $^3J_{C\text{-}F}$ = 11.4 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -70.68 (s, 1F). IR (KBr, cm^{-1}): 2967.7, 2913.2, 2822.5; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{18}H_{16}FNO_2S$ 329.0886; Found 329.0884.

***N*-Fluoro-4-nitro-*N*-(1-phenylethyl)benzenesulfonamide (*1l*)**: White solid, 187.9 mg, yield 58%; m.p.: 96.7-97.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28-8.25 (m, 2H), 7.99 (m, 2H), 7.30-7.22 (m, 5H), 5.09 (dd, *J* = 37.5, 6.93 Hz, 1H), 1.73 (dd, *J* = 6.93, 1.30 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.0, 140.6, 137.7, 130.8, 128.8, 128.7, 128.0, 124.1, 63.4 (d, $^2J_{C\text{-}F}$ = 13.17 Hz, 1C), 19.0 (d, $^3J_{C\text{-}F}$ = 7.82 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -70.58 (s, 1F). IR (KBr, cm^{-1}): 3336.5, 3250.5, 2922.8, 1524.8, 1347.7, 1306.9, 1156.8, 982.9, 738.8; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{14}H_{13}FN_2O_4S$ 324.0580; Found 324.0582.

***N*-(2-Chloro-1-(4-methoxyphenyl)ethyl)-*N*-fluoro-4-nitrobenzenesulfonamide (*1m*)**: White solid, 380.3 mg, yield 98%; m.p.: 99.3°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25-8.21 (m, 2H), 7.93-7.90 (m, 2H), 7.17-7.14 (m, 2H), 6.78-6.73 (m, 2H), 5.15 (dt, *J* = 41.0, 7.4 Hz, 1H), 4.13 (dd, *J* = 11.6, 7.9 Hz, 1H), 3.80-3.86 (m, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.9, 140.3, 140.1, 130.7, 129.5, 129.4, 129.0, 129.0, 123.9, 68.4 (d, $^2J_{C\text{-}F}$ = 11.6 Hz, 1C), 43.3 (d, $^3J_{C\text{-}F}$ = 4.6 Hz, 1C), 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -74.67 (s, 1F). IR (KBr, cm^{-1}): 3433.9, 3066.8,2942.3,1473.3, 1046.6, 686.9; HRMS (EI-TOF) m/z: $[M - HF]^+$ Calcd for $C_{15}H_{13}ClN_2O_5S$ 368.0234; Found 368.0236.

4-Chloro-*N*-fluoro-*N*-(1-phenylethyl)benzenesulfonamide (*1n*): White oil, 187.8 mg, yield 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80-7.77 (m, 2H), 7.48-7.44 (m, 2H), 7.32-7.28 (m, 5H), 4.99 (dq, *J* = 34.9, 6.9 Hz, 1H), 1.69 (dd, *J* = 6.9, 1.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.48, 138.45 (d, $J_{C\text{-}F}$ = 2.3 Hz, 1C), 138.4, 133.3, 130.9, 129.5, 128.7, 128.5, 127.8, 63.1 (d, $^2J_{C\text{-}F}$ = 12.9 Hz. 1C), 19.0 (d, $^3J_{C\text{-}F}$ = 8.7 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -68.03 (s, 1F). IR (KBr, cm^{-1}): 3342.2, 3150.3, 2914.8, 1641.3, 1212.7, 1241.9, 1108.7, 875.3, 730.3; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{14}H_{13}ClFNO_2S$ 313.0340; Found 313.0338.

***N*-(1-(4-(tert-Butyl)phenyl)-2-chloroethyl)-4-chloro-*N*-fluorobenzenesulfonamide (*1o*)**: White solid, 382.9 mg, yield 95%; m.p.: 69.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16-8.11 (m, 2H), 7.88-7.83 (m, 2H), 7.22-7.16 (m, 2H), 7.12-7.06 (m, 2H), 5.06-5.25 (m, 1H), 4.13 (dd, *J* = 11.7, 8.1 Hz, 1H), 3.81 (dd, *J* = 11.7, 6.6 Hz, 1H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.2, 150.8, 140.3, 130.8, 129.3 (d, $J_{C\text{-}F}$ = 3.8 Hz, 2C), 128.8 (d, $J_{C\text{-}F}$ = 2.1 Hz, 2C), 125.7, 123.8, 68.6 (d, $^2J_{C\text{-}F}$ = 11.4 Hz, 1C), 43.4 (d, $^3J_{C\text{-}F}$ = 4.3 Hz, 1C), 34.7, 31.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -76.49 (s, 1F). IR (KBr, cm^{-1}): 3101.6, 3045.1, 2875.4, 2875.1, 2745.2; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{18}H_{20}C_{l2}FNO_2S$ 403.0576; Found 403.0574.

4-Chloro-*N*-(2-chloro-1-(4-fluorophenyl)ethyl)-*N*-fluorobenzenesulfonamide (*1p*): White solid, 226.3 mg, yield 62%; m.p.: 59.5-60.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75-7.70 (m, 2H), 7.46-7.44 (m, 2H), 7.32-7.28 (m, 2H), 7.04-6.99 (m, 2H), 5.13 (dt, *J* = 37.8, 7.2 Hz, 1H), 4.13 (dd, *J* = 11.5, 6.9 Hz, 1H), 3.86 (dd, *J* = 11.4, 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.6, 162.1, 141.9, 133.1, 131.0 (dd, $J_{C\text{-}F}$ = 8.4, 1.8 Hz, 2C), 130.9, 129.6, 115.9 (d, $J_{C\text{-}F}$ = 21.7 Hz, 2C), 67.3 (d, $^2J_{C\text{-}F}$ = 11.6 Hz, 1C), 43.4 (d, $^3J_{C\text{-}F}$ = 5.6 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -71.80, -111.19. IR (KBr, cm^{-1}): 3263.3, 3100.2, 2966.7, 2905.5; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{14}H_{11}Cl_2F_2NO_2S$ 364.9856; Found 364.9853.

***N*-Fluoro-*N*-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-yl)benzenesulfonamide (*1q*)**: White solid, 146.8 mg, yield 46%; m.p.: 86.8-88.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00-7.96 (m, 2H), 7.76-7.70 (m, 1H), 7.64-7.58 (m,

2H), 7.22-7.08 (m, 4H), 4.87 (d, J = 25.0 Hz, 1H), 3.20-3.05 (m, 1H), 2.76-2.65 (m, 1H), 2.20-2.00 (m, 2H), 1.95-1.85 (m, 1H), 1.80-1.73 (m, 1H), 1.73-1.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.3, 134.8, 134.5, 132.4 (d, $J_{C\text{-}F}$ = 10.7 Hz, 1C), 130.1, 129.7, 129.3, 128.6 (d, $J_{C\text{-}F}$ = 12.5 Hz, 1C), 128.2, 126.2, 67.6, 35.7, 31.2 (d, $^2J_{C\text{-}F}$ = 8.6 Hz, 1C), 27.5, 27.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -52.70 (s, 1F). IR (KBr, cm^{-1}): 2941.2, 2916.0, 2849.9, 1447.9, 1373.5, 1356.8, 1170.2, 1090.3, 895.0, 753.6, 681.1, 619.8, 565.5; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{17}H_{18}FNO_2S$ 319.1042; Found 319.1044.

***N*-(2-Chloro-1-phenylcyclohexyl)-*N*-fluorobenzenesulfonamide (*1r*)**: Colorless oil, 242.2 mg, yield 66%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60-7.46 (m, 3H), 7.40-7.25 (m, 4H), 7.24-7.11 (m, 3H), 5.19-5.13 (m, 1H), 3.08 (d, J = 13.9 Hz, 1H), 2.40-2.56 (m, 2H), 1.90-2.14 (m, 3H), 1.77 (dd, J = 47.2, 13.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.6, 136.0, 133.9, 129.0 (d, $J_{C\text{-}F}$ = 1.1 Hz, 2C), 128.8, 128.7, 128.1, 127.2 (d, $J_{C\text{-}F}$ = 1.9 Hz, 2C), 72.4, 72.3, 61.8, 61.7, 29.5, 28.9 (d, $^2J_{C\text{-}F}$ = 6.9 Hz, 1C), 21.1, 19.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -76.92 (s, 1F). IR (KBr, cm^{-1}): 3152.8, 2875.7, 2631.5; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{18}H_{19}ClFNO_2S$ 367.0809; Found 367.0805.

***N*-(2,3-Dihydro-1*H*-inden-1-yl)-*N*-fluorobenzenesulfonamide (*1s*)**: Colorless oil, 203.7 mg, yield 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11-7.98 (m, 2H), 7.74 (m, 1H), 7.64-7.58 (m, 2H), 7.48-7.44 (m, 2H), 7.33-7.20 (m, 2H), 5.54 (ddd, J = 39.9, 8.1, 5.5 Hz, 1H), 3.10-3.00 (m, 1H), 2.95-2.80 (m, 1H), 2.45-2.34 (m, 1H), 2.65-2.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.1, 138.4, 135.2, 134.9, 129.6, 129.4, 129.0, 126.9, 125.5, 124.9, 67.7 (d, $^2J_{C\text{-}F}$ = 13.2 Hz, 1C), 31.1, 26.7 (d, $^3J_{C\text{-}F}$ = 10.3 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -71.14 (s, 1F). IR (KBr, cm^{-1}): 3142.5, 2621.0, 2545.8; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{15}H_{14}FNO_2S$ 291.0729; Found 291.0726.

***N*-(1-Phenylethyl)benzenesulfonamide (*1t*):** White solid, 248.0 mg, yield 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76-7.69 (m, 2H), 7.51-7.46 (m, 1H), 7.40-7.35 (m, 2H), 7.19-7.15 (m, 3H), 7.08-7.05 (m, 2H), 4.97 (d, J = 6.9 Hz, 1H), 4.50 (p, J = 6.9 Hz, 1H), 1.43 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.9, 140.7, 132.5, 128.9, 128.7, 127.7, 127.1, 126.2, 53.9, 23.7.

***N*-Chloro-*N*-(1-phenylethyl)benzenesulfonamidee (*1u*)**: White solid, 265.5 mg, yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98-7.90 (m, 2H), 7.67-7.60 (m, 1H), 7.56-7.50 (m, 2H), 7.43-7.39 (m, 2H), 7.36-7.30 (m, 3H), 5.56 (q, J = 6.7 Hz, 1H), 1.52 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.7, 136.5, 134.0, 129.1, 128.5, 128.4, 127.91, 60.8, 16.6. HRMS (EI-TOF) m/z: M^+ Calcd for $C_{14}H_{14}ClNO_2S$ 295.0434; Found 295.0432.

***N*-Fluoro-*N*-(1-phenylpropan-2-yl)benzenesulfonamide (*1v*)**: Colorless oil, 190.5 mg, yield 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86-7.80 (m, 2H), 7.65-7.58 (m, 1H), 7.52-7.44 (m, 2H), 7.30-7.05 (m, 5H), 4.38 (d, J = 41.1 Hz, 1H), 4.37-4.12 (m, 1H), 3.16-3.07 (m, 1H), 1.19 (dd, J = 6.6, 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.7, 135.8, 134.6, 129.5, 129.3, 128.6, 126.8, 60.5 (d, $^2J_{C\text{-}F}$ = 12.9 Hz, 1C), 40.4 (d, $^3J_{C\text{-}F}$ = 2.9 Hz, 1C), 15.6 (d, $^3J_{C\text{-}F}$ = 9.7 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -79.17 (s, 1F). IR (KBr, cm^{-1}): 3021.8, 2917.5, 2856.5; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{15}H_{16}FNO_2S$ 293.0886.; Found 293.0884.

***N*-Fluoro-*N*-isopropylbenzenesulfonamide (*1w*)**: Colorless oil, 141.1 mg, yield 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99-7.94 (m, 2H), 7.73-7.67 (m, 1H), 7.67-7.54 (m, 2H), 4.12 (dp, J = 34.6, 6.5 Hz, 1H), 1.31 (dd, J = 6.6, 1.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.4, 134.6, 129.4, 129.3, 55.5 (d, $^2J_{C\text{-}F}$ = 13.4 Hz, 1C), 19.4 (d, $^3J_{C\text{-}F}$ = 6.8 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -75.91 (s, 1F). IR (KBr, cm^{-1}): 3002.8, 2856.3, 2813.5; HRMS (EI-TOF) m/z: M^+ Calcd for $C_9H_{12}FNO_2S$ 217.0573; Found 217.0569.

***N*-(4-Chlorobenzyl)-*N*-fluorobenzenesulfonamide (*1x*)**: Colorless oil,194.4 mg, yield 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05-7.99 (m, 2H), 7.85-7.75 (m, 1H), 7.70-7.60 (m, 2H), 7.35-7.25 (m, 4H), 4.38 (d, J = 41.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.3, 134.8, 132.2, 131.1, 130.5, 130.1, 129.6, 129.1, 56.7 (d, $^2J_{C\text{-}F}$ = 13.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -46.09 (s, 1F). IR (KBr, cm^{-1}): 3102.6, 2934.5, 2876.3; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{13}H_{11}ClFNO_2S$ 299.0183; Found 299.0179.

***N*-Phenylbenzenesulfonamide (*2a*)**: White solid, 55.3 mg, yield 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81-7.78 (m, 2H), 7.55-7.51 (m, 1H), 7.45-7.41 (m, 2H), 7.25-7.21 (m, 2H), 7.14(s, 1H), 7.12-7.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.5, 133.2, 129.5, 129.2, 127.4, 125.6, 121.8.

***N*-(p-Tolyl)benzenesulfonamide (*2b*)**: White solid, 57.4 mg, yield 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79-7.77 (m, 2H), 7.54-7.51 (m, 1H), 7.42-7.39 (m, 2H), 7.21 (s, 1H), 7.03-6.96 (m, 4H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.1, 135.5, 133.8, 133.0, 130.0, 129.1, 127.4, 20.9.

***N*-(4-(tert-Butyl)phenyl)benzenesulfonamide (*2c*)**: White solid, 67.2 mg, yield 93%; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.20 (s, 1H), 7.77-7.75 (m, 2H), 7.62-7.52 (m, 3H), 7.24-7.22 (m, 2H), 7.02-6.98 (m, 2H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 146.4, 139.8, 134.96, 132.8, 129.3, 126.6, 125.9, 119.9, 34.0, 31.1.

***N*-(4-Methoxyphenyl)benzenesulfonamide (*2d*)**: White solid, 63.8 mg, yield 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, J = 8.0 Hz, 2H), 7.54 (t, J = 7.6Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 8.0 Hz, 2H), 6.38 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.5, 114.6, 125.7, 127.4, 128.8, 129.1, 133.0, 139.0, 158.2.

***N*-([1,1'-Biphenyl]-2-yl)benzenesulfonamide (*2f*)**: White solid, 55.6 mg, yield 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75-7.71 (m, 1H), 7.59-7.52 (m, 3H), 7.43-7.29 (m, 6H), 7.19-7.07 (m, 2H), 6.84-6.78 (m, 2H), 6.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.1, 137.2, 134.3, 133.6, 133.1, 130.4, 129.2, 129.1, 128.9, 128.8, 128.2, 127.2, 125.2, 121.8.

***N*-(2-Bromophenyl)benzenesulfonamide (*2g*)**: White solid, 33.6 mg, yield 43%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77-7.74 (m, 2H), 7.68 (dd, J = 8.2, 1.5 Hz, 1H), 7.57-7.52 (m, 1H), 7.46-7.39 (m, 3H), 7.31-7.26 (m, 1H), 7.02-6.93 (m, 1H), 6.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.9, 134.7, 133.5, 132.7, 129.2, 128.8, 127.4, 126.6, 123.0, 116.1.

N*-(m-Tolyl)benzenesulfonamide *(2h): White solid, 60.5 mg, yield 98%; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.23 (s, 1H), 7.78-7.73 (m, 2H), 7.63-7.21 (m, 3H), 7.12-7.06 (m, 1H), 6.90 (s, 1H), 6.90-6.80 (m, 2H), 2.18(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.5, 139.2, 136.4, 133.1, 129.2, 129.1, 127.4, 126.4, 122.4, 118.7, 21.5.

***N*-(3,4-Dimethylphenyl)benzenesulfonamide (*2i*)**: White solid, 62.6 mg, yield 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81-7.76 (m, 2H), 7.55-7.49 (m, 1H), 7.46-7.29 (m, 2H), 6.98-6.95 (m, 1H), 6.94-6.90 (s, 1H), 6.88-6.84 (m, 1H), 6.81-6.77 (m, 1H), 2.16 (d, J = 2.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.2, 137.8, 134.3, 133.9, 133.0, 130.4, 129.1, 127.4, 123.7, 119.7, 19.9, 19.3.

***N*-(Thiophen-2-yl)benzenesulfonamide (*2j*)**: White solid, 35.8 mg, yield 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81-7.73 (m, 2H), 7.62-7.55 (m, 1H), 7.51-7.43 (m, 2H), 7.02 (dd, J = 5.6, 1.4 Hz, 1H), 6.83-6.78 (m, 1H), 6.72-6.68 (m, 1H), 6.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.4, 136.9, 133.4, 129.2, 127.7, 125.9, 124.2, 123.7.

N*-(Naphthalen-2-yl)benzenesulfonamide *(2k): White solid, 67.9 mg, yield 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83-7.70 (m, 5H), 7.52-7.31 (m, 7H), 6.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.6, 134.7, 133.4, 131.6, 129.4, 129.4, 128.9, 127.9, 127.7, 127.1, 126.8, 125.9, 123.7, 121.8.

4-Nitro-*N*-phenylbenzenesulfonamide (*2l*): White solid, 66.0 mg, yield 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30-8.26 (m, 2H), 7.93-7.90 (m, 2H), 7.31-7.26 (m, 2H), 7.26-7.18 (m, 2H), 7.09-7.05 (m, 2H), 6.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.4, 144.8, 135.4, 129.8, 128.7, 126.6, 124.4, 122.6.

***N*-(4-Methoxyphenyl)-4-nitrobenzenesulfonamide (*2m*)**: White solid, 75.47 mg, yield 98%; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.24 (s, 1H), 8.78-8.34 (m, 2H), 7.92-7.87 (m, 2H), 6.99-6.95 (m, 2H), 6.83-6.80 (m, 2H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 156.2, 149.3, 144.1, 128.5, 127.6, 124.2, 123.4, 114.1, 55.3.

4-Chloro-*N*-phenylbenzenesulfonamide (*2n*): White solid, 64.8 mg, yield 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70-7.68 (m, 2H), 7.41-7.39 (m, 2H), 7.28-7.24 (m, 2H), 7.16-7.13 (m, 1H), 7.08-7.06 (m, 2H), 6.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.8, 137.5, 136.1, 129.6, 129.5, 128.8, 126.0, 122.1.

***N*-(4-(tert-Butyl)phenyl)-4-chlorobenzenesulfonamide (*2o*)**: White solid, 75.1 mg, yield 93%; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.52 (s, 1H), 8.39-8.35 (m, 2H), 8.01-7.98 (m, 2H), 7.28-7.24 (m, 2H), 7.04-7.00 (m, 2H), 1.19 (s, 9H); ^{13}C NMR (100 Hz, DMSO-d_6) δ: 149.8, 147.1, 145.2, 134.2, 128.2, 126.1, 124.7, 120.5, 34.0, 31.0.

4-Chloro-*N*-(4-fluorophenyl)benzenesulfonamide (*2p*): White solid, 63.4 mg, yield 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67-7.64 (m, 2H), 7.43-7.39 (m, 2H), 7.07-7.03 (m, 3H), 6.98-6.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.3, 159.8, 139.9, 137.2, 131.9, 131.8, 129.6, 128.8, 125.2, 125.1, 116.6, 116.3.

***N*-(2-(5-Oxopentyl)phenyl)benzenesulfonamide (*2q*)**: Yellow oil, 35.7 mg, yield 45%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.71 (t, J = 1.7 Hz, 1H), 7.77-7.71 (m, 2H), 7.57-7.52 (m, 1H), 7.46-7.41 (m, 2H), 7.25-7.22 (m, 1H), 7.14-7.09 (m, 3H), 6.77 (s, 1H), 2.43-2.34 (m, 3H), 1.88-1.70 (m, 1H), 1.56-1.50 (m, 2H), 1.45-1.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.6, 139.7, 136.1, 133.9, 133.1, 129.9, 129.1, 127.3, 127.1, 126.8, 125.3, 43.6, 30.6, 29.5, 21.8. IR (KBr, cm-1): 3336.5, 3250.5, 2922.8, 1524.8, 1347.7, 1306.9, 1156.8, 982.9, 738.8; HRMS (EI-TOF) m/z: M^+ Calcd for $C_{17}H_{19}NO_3S$ 317.1086; Found 317.1091.

Chlorocyclohexan-1-one (*2r*): Colorless oil, 21.8 mg, yield 66%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.36-4.24 (m, 1H), 2.85-2.80 (m, 1H), 2.55-2.51 (m, 2H), 1.70-1.69 (m, 3H), 1.59-1.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 203.6, 63.0, 42.1, 39.6, 37.6, 23.1.

2,3-Dihydro-1H-inden-1-one (*2s*): White solid, 52.8 mg, yield 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78-7.72 (m, 1H), 7.62-7.54 (m, 1H), 7.52-7.44 (m, 1H), 7.40-7.32 (m, 1H), 3.20-3.10 (m, 2H), 2.75-2.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.3, 155.3, 137.2, 134.7, 127.4, 126.8, 123.9, 36.4, 25.9.

4-Chlorobenzaldehyde (*2x*): White solid, 28.0 mg, yield 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.98 (s, 1H); 7.85-7.80 (m, 2H), 7.54-7.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.0, 141.1, 134.8, 131.1, 129.6.

Benzenesulfonamide (*2y*): White solid, 30.6 mg, yield 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96-7.92 (m, 2H), 7.63-7.59 (m, 1H); 7.58-7.59 (m, 2H), 4.87 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.09, 132.95, 129.31, 126.57.

ASSOCIATED CONTENT:

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Screening of the reaction conditions and NMR spectra of compounds (PDF)

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