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Difluoroaminosulfonylation of Styrenes with *N,N*-Difluorobenzenesulfonamide

Wenqing Zhang [a], Xianjin Yang [a,b,*]

[a] Key Lab for Advanced Material & Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, China
[b] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai, 200032, China

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Difluoroaminosulfonylation
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ABSTRACT

A new type of difluoroaminosulfonylation of styrenes with *N,N*-difluorobenzenesulfonamide (DFBSA) was developed, using $NiCl_2$/Mn as catalysts and bipyridine as the ligand, to afford a series of 1-difluoroamino-2-phenylsulfonyl products. Preliminary mechanistic studies proved a free radical process for the reaction.

1. Introduction

Amines and sulfones are key synthons in many synthetic transformations, such as the diazotization of amines [1] and the Junia-Lythgoe olefination of sulfones [2]. More importantly, the amines [3] and the sulfones [4] are widely present in natural products, small-molecule therapeutics and biopharmaceuticals, and agrochemicals, and can engender a variety of biological activities, rendering them important functionalities in the structures of various medicines and agrochemical reagents (Fig.1) [5]. Although there are many mature methods for introducing amines and sulfones into molecules [6, 7], most of them are achieved through multi-step synthesis, and there are few reports on the simultaneous introduction of these two functionalities into molecules [8].

One of the most effective and direct methods to simultaneously introduce two functional groups into a molecule is by the difunctionalization of alkenes. One such type of conversion is the amination of alkenes, including diamination [9], aminohalogenation [10], aminooxygenation [11], and aminoalkylation [12], which can lead to the generation of valuable nitrogen-containing molecules. However, few reports have been successful in achieving the simultaneous aminosulfonylation of alkenes, and, as such this conversion still remains a synthetic challenge.

2. Results and discussion

Fluorine is the most electronegative element in nature, and its atomic radius is the closest to that of hydrogen. Therefore, the introduction of fluorine atoms into molecules often improves the efficacies of drugs and affects the reactivities of chemical reagents. In this communication, we designed and synthesized *N,N*-difluorobenzenesulfonamide (DFBSA, **1**) to evaluate its propensity for enabling the direct aminosulfonylation of styrene. It was hypothesized that the inductive effect of the fluorine atoms in DFBSA will weaken the N–S bond to promote the difluoroaminosulfonylation of alkenes. DFBSA was obtained in yields of up to 73% by the reaction of *N*-fluorobenzenesulfonamide with Selectfluor at 0 °C in acetone in the presence of NaOH (Scheme 1). We found that the N–F bond in DFBSA was very stable and surprisingly difficult to cleave, indicating that DFBSA is stable in water.

Initially, the reaction of DFBSA (**1a**) with styrene was selected as the model reaction to optimize the reaction conditions, and the representative results are shown in Table 1. The solvent screening revealed that EtOAc was the most suitable solvent to afford the target product **3a**. Other evaluated solvents, such as CH_3SOCH_3 and 1,4-dioxane, produced worse results (Table 1, entries 1–11). With ultradry EtOAc, the product yield changed insignificantly, indicating that a small amount of water in the solvent slightly effected the yield (Table 1, entry 12). Then, catalysts or ligands were added to promote the reaction. When $NiCl_2$ catalyst was added, the yield was improved to 43% (Table 1, entry 13). Then, ligands were added to the reaction (Table 1, entries 14–26), and the results

* Corresponding author: Dr Xianjin Yang, East China University of Science and Technology, China. E-mail:
E-mail address: yxj@ecust.edu.cn (X. Yang).

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showed that L_{10} (Bpy) was the optimal ligand with a yield of 52%. The next step was to further screen different catalysts, such as $NiBr_2$, Ni $(COD)_2$, $Pd(OAc)_2$, and copper catalysts (Table 1, entries 27–34), but the yield of the product did not improve.

The temperature screening showed that the reaction did not occur at room temperature, and 120 °C was the optimal reaction temperature (Table 1, entries 35–37). To make Ni(II) catalyst better participate in the reaction, reductants were added to convert Ni(II) into Ni(0). The results showed that Mn was the optimal reductant affording 61% yield (Table 1, entries 38–41). In the absence of Ni(II) catalyst, when only Mn was added, the yield was 39% (Table 1, entry 42). These results showed that the addition of Ni(II) catalyst and Mn was necessary. Then, the reaction time screening revealed that the product yields slightly differed for 10 h, 12 h, and 14 h; Therefore, 12 h was selected as the optimal reaction time (Table 1, entries 43–46). Next, the amount of the catalyst, ligand, and reductant was also screened, and the results indicated that the optimal quantities were as follows: $NiCl_2$ (10 mol%), L_{10} (5 mol%) and Mn (2.0 eq.) (Table 1, entry 47).

With the optimized reaction conditions in hand, the scope of this reaction was evaluated (Table 2). Difluoroaminosulfonylation of styrene with differently substituted DFBSAs provided products **3a–3e** regioselectively in moderate yields (41–61%). For methyl substituted styrenes, the effect of 4-CH_3 styrenes (**3f–3i**) was better than that of 3-CH_3 styrenes (**3j** and **3k**). For halide substituted styrenes, the products **(3l–3x)** from *o-, m-*, and *p*-fluorostyrenes were obtained in 28–51% yields; electronic effect did not affect the reactivity. Differently, the yields of products provided from *o*- and *p*-chlorostyrenes (**3y–3aa, 3ad, 3ae**) were higher than those of *m*-chlorostyrenes (**3ab, 3ac**). However, the effect of bromine substituted styrenes (**3af–3ai**) was not as good as that of chlorine and fluorine substituted olefins. For different substituents (hydrogen, methyl, and halogen) of *p*-substituted styrenes, the yields of the products had a small difference. However, for the same substituents, the effect of *o*- and *p*-substituted styrenes was better than that of *m*-substituted styrenes. When the substrates were *p*-tert-butylstyrene and 2-naphthalene ethylene, the corresponding products (**3aj, 3ak**) were obtained in 25% and 21% yields, respectively. Subsequently, ether, ester, amide, and cyano substituted styrenes (**3al–3ao**) were evaluated; ether and ester substituted styrenes afforded products. Then, the difluoroaminosulfonylation of DFBSA with nonterminal alkenes was studied, but the corresponding product could not be obtained (**3ap, 3aq**).

At the same time, we also studied the reactivity of aromatic heterocyclic olefins and functionalized styrene (α-methylstyrene); however, the corresponding difluoroaminosulfonylated products could not be obtained. We discovered that the expected product of 2-vinylpyridine underwent the elimination of HF to provide imide **4**, and the expected product of α-methylstyrene hydrolyzed to afford the compound **5**, whose structure was further confirmed by X-ray crystallography (Fig. 2). These results indicated that the N–F bond in the products was reactive and could be further converted to other chemical bonds.

Several control experiments were carried out to explore the reaction mechanism, since the reaction proceeded under high temperature conditions, which was speculated that it could be a free radical reaction. At first, in the presence of 2.0 eq. TEMPO (a radical inhibitor), the reaction of **1a** and styrene afforded a trace amount of the target compound **3a**, no matter whether using our standard conditions or pure solvent conditions with heating (Scheme 2a). Moreover, when BHT (2.0 eq.) was used instead of TEMPO, the same result was achieved (Scheme 2b). When we added 1,1-diphenylethylene (2.0 eq.), a free radical inhibitor, to the reaction system, we were able to obtain 20% of compound **6** (Scheme 2c). These results indicated that the reaction might be a free radical process. Therefore, **1a** and allylbenzene were used as model substrates to study the order of the free radical mechanism of the reaction. Then the alkene coupling product **7** was obtained (Scheme 2d), which indicated that the benzenesulfonyl radical first reacted with the alkene.

The proposed mechanism of this reaction is shown in Scheme 3. In path A, the oxidative addition of DFBSA (**1a)** to Ni(0) **A** led to the formation of the Ni(II) complex **B**. Compound **B** tautomerized to form the Ni(I) compound **C** and a benzenesulfonyl radical, which then reacted with styrene (**2a)** to undergo a free radical addition to obtain the free radical intermediate **D**. Intermediate **D** continued to react with the Ni(I) compound **C** to obtain the Ni(II) complex **E**, which finally underwent reductive elimination to obtain the final product **3a** and the recycled Ni (0) catalyst. During our experiments, we found that the reaction could also proceed without the addition of a catalyst and ligand. We speculated that the reaction could also be triggered by heat, so we proposed another possible reaction mechanism. In path B, **1a** was cleaved by thermal initiation to generate a benzenesulfonyl radical and a difluoroamine radical. The benzenesulfonyl radical then reacted with styrene to obtain the free radical intermediate **D**, which reacted with

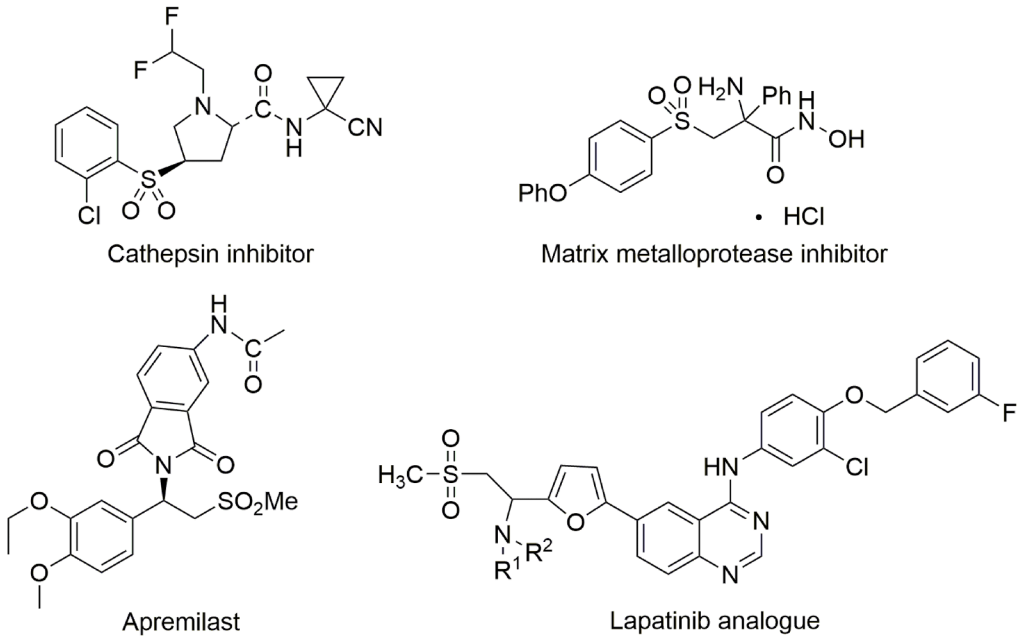
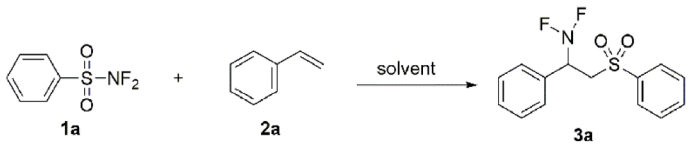


Fig. 1. Examples of active pharmaceutical compounds containing amine and sulfone units.

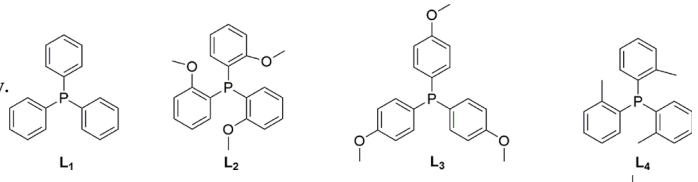
Table 1
Optimization of the Reaction Conditions.[a]



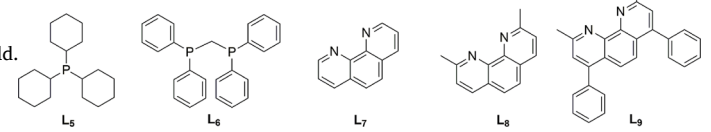
Entry	Solvent	Catalyst	Ligand [b]	T (°C)	Time (h)	Yield (%) [c]
1	DMF	-	-	120	12	18
2	$PhCH_3$	-	-	120	12	14
3	CH_3SOCH_3	-	-	120	12	<5
4	CH_3OH	-	-	120	12	Trace
5	1,4-Dioxane	-	-	120	12	29
6	CH_3CN	-	-	120	12	34
7	THF	-	-	120	12	29
8	EtOAc	-	-	120	12	35
9	DCE	-	-	120	12	31
10	Butyronitrile	-	-	120	12	35
11	HFIP	-	-	120	12	5
12	EtOAc [d]	-	-	120	12	37
13	EtOAc	$NiCl_2$	-	120	12	43
14	EtOAc	$NiCl_2$	L_1	120	12	37
15	EtOAc	$NiCl_2$	L_2	120	12	43
16	EtOAc	$NiCl_2$	L_3	120	12	47
17	EtOAc	$NiCl_2$	L_4	120	12	37
18	EtOAc	$NiCl_2$	L_5	120	12	18
19	EtOAc	$NiCl_2$	L_6	120	12	38
20	EtOAc	$NiCl_2$	L_7	120	12	48
21	EtOAc	$NiCl_2$	L_8	120	12	42
22	EtOAc	$NiCl_2$	L_9	120	12	38
23	EtOAc	$NiCl_2$	L_{10}	120	12	52
24	EtOAc	$NiCl_2$	L_{11}	120	12	41
25	EtOAc	$NiCl_2$	L_{12}	120	12	43
26	EtOAc	$NiCl_2$	L_{13}	120	12	39
27	EtOAc	$NiBr_2$	L_{10}	120	12	35
28	EtOAc	NiI_2	L_{10}	120	12	20
29	EtOAc	$Ni(COD)_2$	L_{10}	120	12	47
30	EtOAc	$Ni(Cp)_2$	L_{10}	120	12	44
31	EtOAc	Ni(allyl)(Cp)	L_{10}	120	12	46
32	EtOAc	Cu [e]	L_{10}	120	12	Trace
33	EtOAc	$PdCl_2$	L_{10}	120	12	16
34	EtOAc	$Pd(OAc)_2$	L_{10}	120	12	20
35	EtOAc	$NiCl_2$	L_{10}	100	12	34
36	EtOAc	$NiCl_2$	L_{10}	60	12	Trace
37	EtOAc	$NiCl_2$	L_{10}	r.t.	12	N. R.
38	EtOAc	$NiCl_2$-Zn	L_{10}	120	12	43
39	EtOAc	$NiCl_2$-Fe	L_{10}	120	12	28
40	EtOAc	$NiCl_2$-Mg	L_{10}	120	12	40
41	EtOAc	$NiCl_2$-Mn	L_{10}	120	12	61
42	EtOAc	Mn	L_{10}	120	12	39
43	EtOAc	$NiCl_2$-Mn	L_{10}	120	14	58
44	EtOAc	$NiCl_2$-Mn	L_{10}	120	10	56
45	EtOAc	$NiCl_2$-Mn	L_{10}	120	8	52
46	EtOAc	$NiCl_2$-Mn	L_{10}	120	6	26
47 [f]	EtOAc	$NiCl_2$-Mn	L_{10}	120	12	61

[a] The reaction was carried out with styrene (**2a**, 0.8 mmol), catalyst (10 mol%), ligand (5 mol%), DFBSA (**1a**, 1.2 eq.), reductant (2 eq.) in solvent at 120 °C under air.

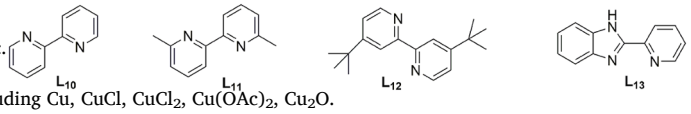
[b] Ligands only.



[c] Isolated yield.



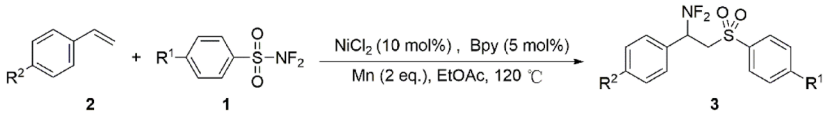
[d] Ultradry EtOAc.



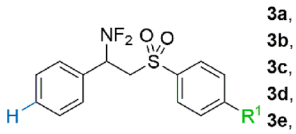
[e] Cu catalysts including Cu, CuCl, $CuCl_2$, $Cu(OAc)_2$, Cu_2O.

[f] Equivalent screening for $NiCl_2$ (10 mol%, 15 mol%, 20 mol%), L_{10} (5 mol%, 7.5 mol%) and Mn (10 mol%, 0.8 eq., 1.2 eq., 1.5 eq., 2.0 eq., 3.0 eq.) and the optimal equivalents were $NiCl_2$ (10 mol%), L_{10} (5 mol%) and Mn (2.0 eq.).

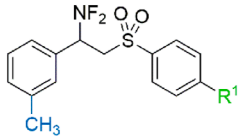
Table 2
Substrate Scope of Alkenes [a,b]

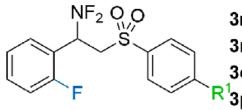


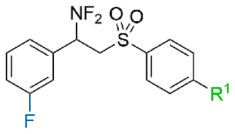
2 1 3

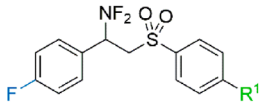

3a, R^1 = H, 61%
3b, R^1 = CH_3, 51%
3c, R^1 = F, 48%
3d, R^1 = Cl, 42%
3e, R^1 = NO_2, 41%

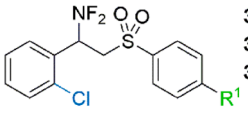

3f, R^1 = H, 45%
3g, R^1 = CH_3, 37%
3h, R^1 = F, 25%
3i, R^1 = Cl, 37%

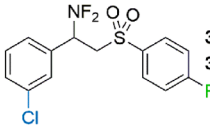

3j, R^1 = H, 37%
3k, R^1 = CH_3, 28%

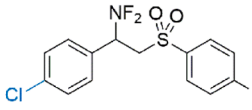

3l, R^1 = H, 51%
3m, R^1 = CH_3, 48%
3n, R^1 = F, 40%
3o, R^1 = Cl, 51%
3p, R^1 = NO_2, 45%

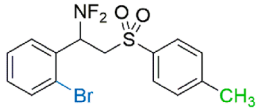

3q, R^1 = H, 48%
3r, R^1 = CH_3, 41%
3s, R^1 = Cl, 28%
3t, R^1 = NO_2, 33%

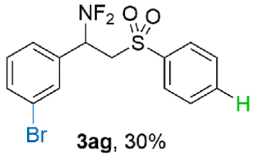

3u, R^1 = H, 48%
3v, R^1 = CH_3, 43%
3w, R^1 = Cl, 45%
3x, R^1 = NO_2, 43%

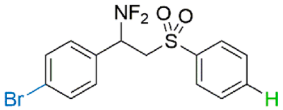

3y, R^1 = H, 40%
3z, R^1 = CH_3, 52%
3aa, R^1 = NO_2, 37%

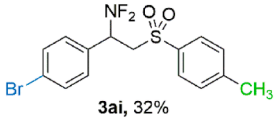

3ab, R^1 = H, 32%
3ac, R^1 = Cl, 22%

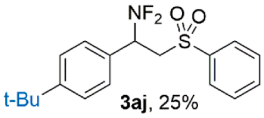

3ad, R^1 = CH_3, 43%
3ae, R^1 = Cl, 53%

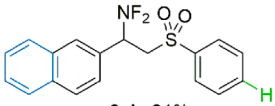

3af, 43%

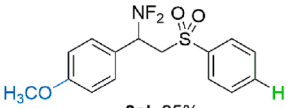

3ag, 30%

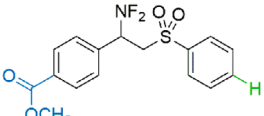

3ah, 25%

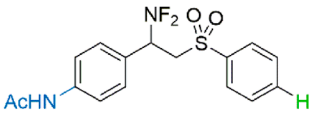

3ai, 32%

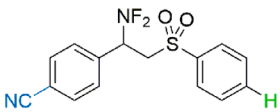

3aj, 25%

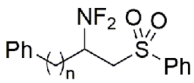

3ak, 21%

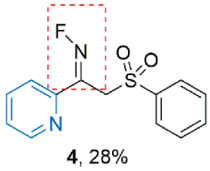

3al, 35%

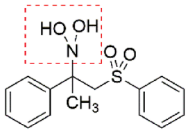

3am, 39%


3an, trace


3ao, 0%


n=1, **3ap**, 0%
n=2, **3aq**, 0%


4, 28%


5, 75%

[a] Reaction conditions: alkene (0.8 mmol), DFBSA (1.2 eq.), $NiCl_2$ (10 mol%), Bpy (5 mol %), Mn (2 eq.) in 4.0 mL of EtOAc at 120 °C oil bath for 12 h under air.
[b] Isolated yield.

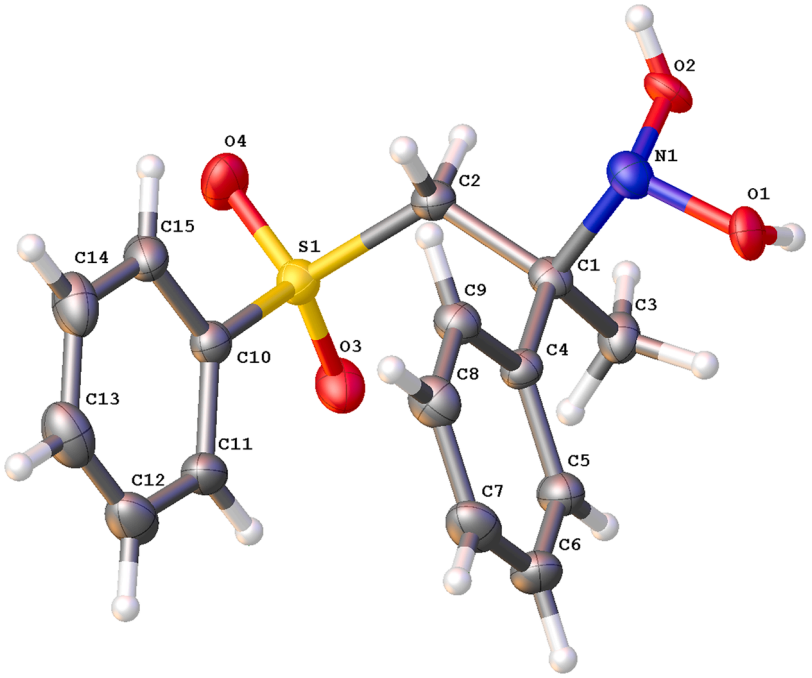
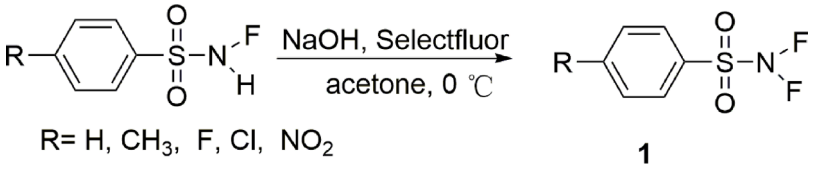
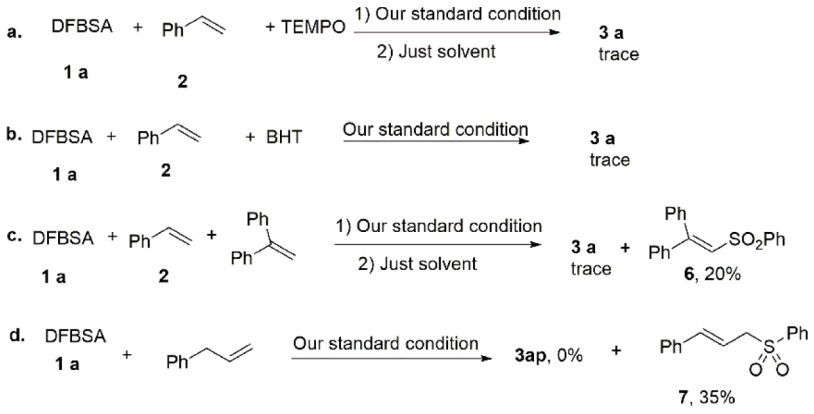


Fig. 2. X-ray crystal structure of **5**.



Scheme 1. The synthesis of DFBSAs



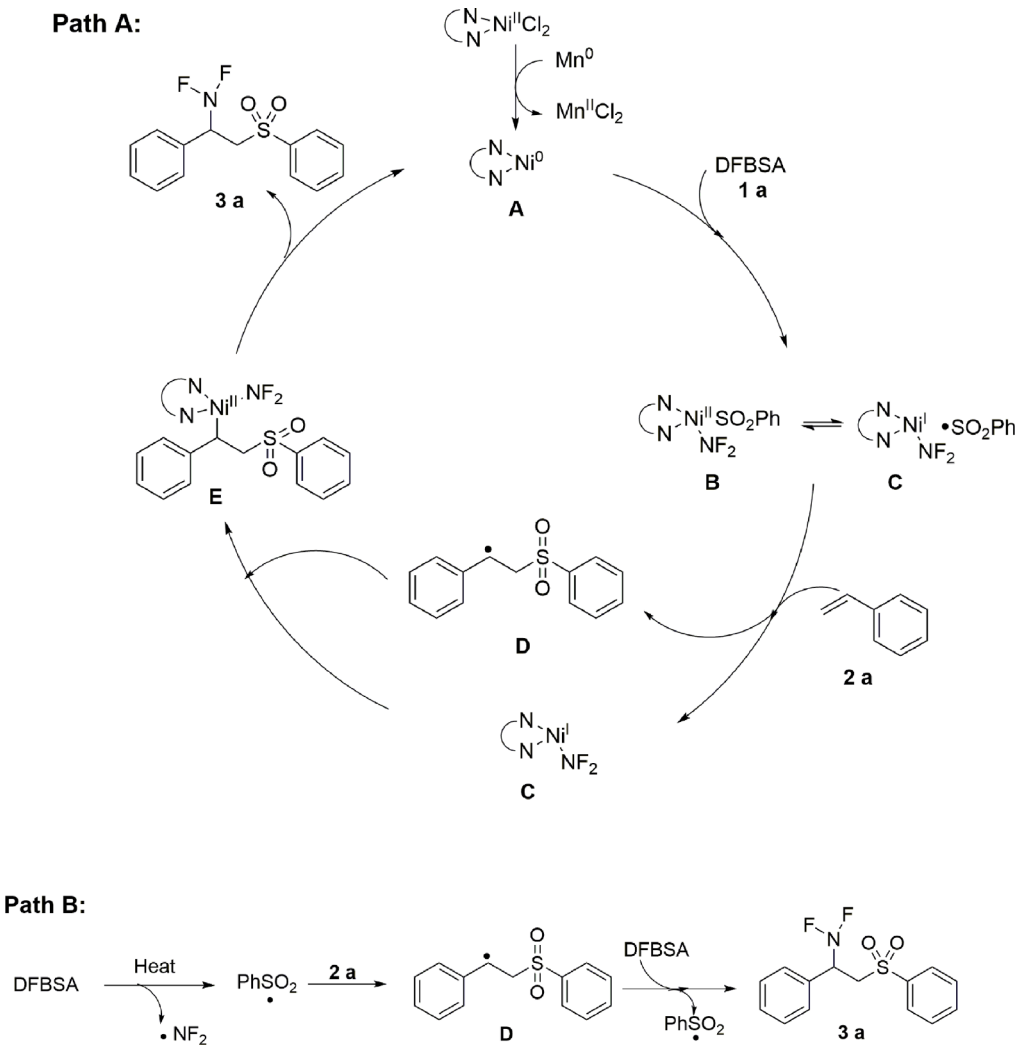
Scheme 2. Control experiments

DFBSA to obtain the final product **3a**.

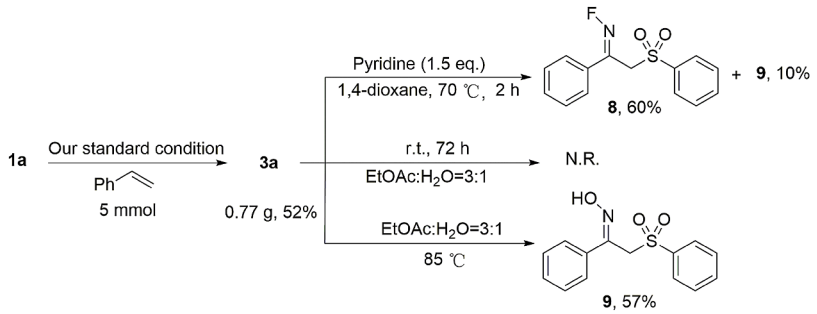
The moderate yields might have been attributed to the instability of the product itself. Therefore, we studied the reactivity of the N–F bond of the product using **3a** as a model substrate (Scheme 4). In the presence of pyridine, HF was easily eliminated from **3a** to form compound **8** and the hydrolyzed product **9**. Interestingly, **3a** was found to be stable in wet solvents at room temperature, but **3a** underwent hydrolysis in the presence of water in EtOAc at higher temperature (85 °C) to obtain compound **9**.

3. Conclusion

In summary, we developed a new method to synthesize DFBSAs, which were then used as reagents for the nickel-catalyzed aminosulfonylation of alkenes to provide the corresponding *N,N*-difluoroaminosulfonylated products. For most alkenes used in this study, the reaction produced moderate yields and demonstrated excellent regioselectivity. Preliminary mechanistic studies indicated that the reaction was free radical-promoted, with DFBSA being a benzenesulfonyl radical precursor. Overall, the incorporation of *N,N*-difluoroaminosulfonyl functional groups into small molecules, such as drug pharmacophores,



Scheme 3. Proposed mechanism.



Scheme 4. Gram reaction scale and the reactivity of *N*–F bond of aminosulfonylated products.

may manifest promising biological (i.e. physicochemical) properties. Moreover, these *N,N*-difluoroaminosulfones can serve as intermediates to undergo further conversion to other functional groups using established or novel methodologies.

4. Experimental section

4.1. General information

All the starting chemicals were commercially available and used as received without further purification, except *N*-(4-vinylphenyl) acetamide [13]. *N*-Fluorobenzenesulfonamide and its derivatives were purchased from Aldrich or Shanghai Science Bio-pharmaceutical Co. Ltd. Flash column chromatography was used on silica gel (300–400 mesh). NMR spectra were recorded on a Bruker AM-400 (400 MHz for ^{1}H; 101 MHz or 151 MHz for ^{13}C; 376 MHz for ^{19}F which is decoupled with 1H) spectrometer. Chemical shifts (δ value) were reported in ppm down field from internal tetramethylsilane (TMS). IR spectra (Film) were recorded on a Nicolet 6700 spectrophotometer in the range of 400–4000 cm^{-1}. HRMS (EI) Mass spectra were recorded on a Waters GCT Premier mass spectrometer with electron impact.

4.2. Preparation of the substrates DFBSA

Take **1a** as an example: N-fluorobenzene sulfonamide (1.75 g, 0.01 mol, 1.0 eq.) in acetone (20 mL), and NaOH (0.48 g, 0.012 mol, 1.2 eq.) were added several times in small amounts, and the reaction mixture was stirred for 0.5 h. Then, Selectfluor (4.2 g, 0.012 mol, 1.2 eq.) was added in two portions, and the reaction mixture was stirred at 0 °C for 4 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (eluent: PE/EA=50:1 v/v). A conventional method to prepare the DFBSA derivatives **1b, 1c, 1d**, and **1e**.

4.2.1. N,N-difluorobenzenesulfonamide (1a)

A yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.5 Hz, 2H), 7.90 (t, J = 7.5 Hz, 1H), 7.71 (t, J = 7.9 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 40.40 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.38, 132.08, 129.97, 127.90; IR (ATR, cm^{-1}): ν 3074, 1581, 1450, 1392, 1189, 1083; HRMS-EI (m/z) *calcd*. for ($C_6H_5SO_2NF_2$-NF_2) 141.0010, *found* 141.0012.

4.2.2. N,N-difluoro-4-methylbenzenesulfonamide (1b)

A brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 2.53 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 40.36 (s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.42, 132.12, 130.67, 124.65, 22.20; IR (ATR, cm^{-1}): ν 3068, 1593, 1392, 1305, 1176, 1084; HRMS-EI (m/z) *calcd*. for ($C_7H_7SO_2NF_2$-NF_2) 155.0167, *found* 155.0169.

4.2.3. N,N,4-trifluorobenzenesulfonamide (1c)

A brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, J = 8.8, 4.9 Hz, 2H), 7.39 (t, J = 8.4 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 40.99 (s, 2F), -96.03 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.33 (d, J = 262.9 Hz), 135.31 (d, J = 10.6 Hz), 123.62, 117.74 (d, J = 23.1 Hz); IR (ATR, cm^{-1}): ν 3110, 1587, 1492, 1396, 1299, 1247, 1188, 1156, 1084; HRMS-EI (m/z) *calcd*. for ($C_6H_4SO_2NF_3$-NF_2) 158.9916, *found* 158.9920.

4.2.4. 4-chloro-N,N-difluorobenzenesulfonamide (1d)

A white solid; m.p.: 59.2–59.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.7 Hz, 2H), 7.69 (d, J = 8.7 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 41.03 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.95, 133.39, 130.50, 126.18; IR (ATR, cm^{-1}): ν 3068, 1593, 1392, 1305, 1176, 1084; HRMS-EI (m/z) *calcd*. for ($C_6H_4ClSO_2NF_2$-NF_2) 174.9612, *found* 174.9617.

4.2.5. N,N-difluoro-4-nitrobenzenesulfonamide (1e)

A yellow solid; m.p.: 63.1–63.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 9.0 Hz, 2H), 8.30 (d, J = 8.9 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 41.71 (s);^{13}C NMR (101 MHz, $CDCl_3$) δ 152.88, 133.65, 133.42, 124.96; IR (KBr, cm^{-1}): ν 3116, 1610,1537, 1408, 1351, 1314, 1215, 1195, 1083; HRMS-EI (m/z) *calcd*. for ($C_6H_4SO_4N_2F_2$-NF_2) 185.9861, *found* 185.9860.

4.3. General Procedures

Styrene (0.8 mmol), DFBSA (1.2 eq.), $NiCl_2$ (10 mol%), Bpy (5 mol %), and Mn (2 eq.) in 4.0 mL ethyl acetate were added to a sealed tube equipped with a magnetic stir bar. The reaction mixture was stirred at 120 °C on oil bath for 12 h. Then, the reaction mixture was purified by silica gel chromatography (eluent: PE/EA=20:1 v/v) to afford the products.

4.3.1. N,N-difluoro-1-phenyl-2-(phenylsulfonyl)ethan-1-amine (3a)

A white solid; m.p.: 89.8–91.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.66 (m, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.8 Hz, 2H), 7.33 (t, J = 7.1 Hz, 1H), 7.30–7.25 (m, 2H), 7.22 (d, J = 7.3 Hz, 2H), 5.04 (dddd, J = 26.1, 23.0, 9.3, 3.5 Hz, 1H), 4.03 (dd, J = 14.7, 3.5 Hz, 1H), 3.86 (dd, J = 14.6, 9.3 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 42.51 (d, J = 579.0 Hz, 1F), 41.87 (d, J = 575.3 Hz, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.11, 134.04, 130.63 (t, J = 5.6 Hz), 130.06, 129.68, 129.34, 129.00, 128.02, 73.86, 55.53; IR (KBr, cm^{-1}): ν 3063, 2989, 2922, 1584, 1495, 1452, 1409, 1332, 1306, 1148, 1084; HRMS-EI (m/z) *calcd*. for ($C_{14}H_{13}NO_2F_2S$-F_2) 259.0667, *found* 259.0664.

4.3.2. N,N-difluoro-1-phenyl-2-tosylethan-1-amine (3b)

A yellow solid; m.p.: 70.7–71.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.3 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 7.20 (t, J = 7.3 Hz, 2H), 7.12 (dd, J = 12.2, 7.7 Hz, 4H), 4.93 (tdd, J = 26.1, 9.2, 4.6 Hz, 1H), 3.92 (dd, J = 14.6, 3.5 Hz, 1H), 3.75 (dd, J = 14.6, 9.2 Hz, 1H), 2.30 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.38 (d, J = 579.0 Hz, 1F), 41.92 (d, J = 575.3 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.16, 136.04, 130.73 (t, J = 6.0 Hz), 129.92, 129.87, 129.68, 128.92, 128.04, 73.84, 55.57, 21.73; IR (KBr, cm^{-1}): ν 3035, 2991, 2935, 1595, 1494, 1458, 1415, 1328, 1300, 1142, 1084; HRMS-EI (m/z) *calcd*. for ($C_{15}H_{15}NO_2F_2S$-F_2) 273.0824, *found* 273.0819.

4.3.3. N,N-difluoro-2-((4-fluorophenyl)sulfonyl)-1-phenylethan-1-amine (3c)

A yellow solid; m.p.: 95.6–96.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 8.7, 5.0 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.28 (t, J = 7.7 Hz, 2H), 7.21 (d, J = 7.4 Hz, 2H), 7.04 (t, J = 8.5 Hz, 2H), 5.12–4.95 (m, 1H), 4.04 (dd, J = 14.7, 3.5 Hz, 1H), 3.86 (dd, J = 14.7, 9.4 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.26 (d, J = 575.3 Hz, 1F), 41.91 (d, J = 579.0 Hz, 1F), -102.66 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.89 (d, J = 257.3 Hz), 135.11 (d, J = 3.3 Hz), 131.02, 130.97 (d, J = 9.7 Hz), 130.38 (t, J = 6.1 Hz), 129.72, 129.05, 116.60 (d, J = 22.8 Hz), 73.90, 55.62; IR (KBr, cm^{-1}): ν 3070, 2960, 1590, 1492, 1406, 1312, 1292, 1225, 1146, 1084; HRMS-EI (m/z) *calcd*. for ($C_{14}H_{12}NO_2F_3S$-F_2) 277.0573, *found* 277.0576.

4.3.4. 2-((4-chlorophenyl)sulfonyl)-N,N-difluoro-1-phenylethan-1-amine (3d)

A yellow solid; m.p.: 83.7–86.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.5 Hz, 2H), 7.41 (t, J = 7.0 Hz, 3H), 7.35 (t, J = 7.5 Hz, 2H), 7.27 (d, J = 7.5 Hz, 2H), 5.09 (tdd, J = 25.9, 9.4, 4.7 Hz, 1H), 4.11 (dd, J = 14.7, 3.5 Hz, 1H), 3.93 (dd, J = 14.7, 9.4 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.35 (d, J = 575.3 Hz, 1F), 41.92 (d, J = 575.3 Hz, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.90, 137.54, 130.38 (t, J = 5.4 Hz), 130.16, 129.76, 129.61, 129.52, 129.10, 73.81, 55.64; IR (KBr, cm^{-1}): ν 3064, 2993, 2943, 1639, 1580, 1475, 1402, 1334, 1306, 1143, 1087; HRMS-EI (m/z) *calcd*. for ($C_{14}H_{12}NO_2F_2SCl$-F_2) 293.0277, *found* 293.0273.

4.3.5. N,N-difluoro-2-((4-nitrophenyl)sulfonyl)-1-phenylethan-1-amine (3e)

A yellow solid; m.p.: 121.1–122.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.8 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.28–7.23 (m, 2H), 7.19 (d, J = 7.5 Hz, 2H), 5.06 (tdd, J = 25.6, 9.4, 4.7 Hz, 1H), 4.11 (dd, J = 14.9, 3.8 Hz, 1H), 3.92 (dd, J = 14.9, 9.5 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.28 (d, J = 579.0 Hz, 1F), 42.00 (d, J = 579.0 Hz, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.76, 144.58, 130.42, 129.99 (t, J = 5.4 Hz), 129.81, 129.54, 129.17, 124.30, 73.74, 55.68; HRMS-EI (m/z) calcd. for ($C_{14}H_{12}N_2O_4F_2S$-F_2) 304.0518, found 304.0512.

4.3.6. N,N-difluoro-2-(phenylsulfonyl)-1-(P-tolyl)ethan-1-amine (3f)

A white solid; m.p.: 96.7–97.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.3 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.09 (q, J = 8.2 Hz, 4H), 5.00 (tdd, J = 26.1, 9.3, 3.5 Hz, 1H), 4.01 (dd, J = 14.6, 3.6 Hz, 1H), 3.84 (dd, J = 14.6, 9.4 Hz, 1H), 2.31 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.36 (d, J = 575.3 Hz, 1F), 41.68 (d, J = 575.3 Hz, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.18, 139.19, 133.89, 129.68, 129.59, 129.28, 128.06, 127.57 (t, J = 5.6 Hz), 73.59, 55.57, 21.33; IR (KBr, cm^{-1}): ν 3035, 2986, 2941, 1633, 1516, 1447, 1422, 1329, 1302, 1142, 1084; HRMS-EI (m/z) *calcd*. for ($C_{15}H_{15}NO_2F_2S$-F_2) 273.0824, *found* 273.0827.

*4.3.7. N,N-difluoro-1-(p-tolyl)-2-tosylethan-1-amine (**3g**)*

A white solid; m.p.: 106.7–107.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.13–7.05 (m, 4H), 4.96 (tdd, *J* = 26.1, 9.3, 4.7 Hz, 1H), 3.98 (dd, *J* = 14.6, 3.5 Hz, 1H), 3.81 (dd, *J* = 14.5, 9.3 Hz, 1H), 2.40 (s, 3H), 2.32 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.21 (d, *J* = 575.3 Hz, 1F), 41.72 (d, *J* = 575.3 Hz, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.09, 140.09, 136.19, 129.88, 129.61, 128.66, 128.09, 127.71 (t, *J* = 5.4 Hz), 73.64, 55.60, 21.71, 21.32; IR (KBr, cm^{-1}): ν 3083, 2988, 2938, 1622, 1598, 1515, 1422, 1328, 1301, 1141, 1086; HRMS-EI (m/z) *calcd.* for ($C_{16}H_{17}NO_2F_2S$-F_2) 291.0980, *found* 291.0985.

*4.3.8. N,N-difluoro-2-((4-fluorophenyl)sulfonyl)-1-(p-tolyl)ethan-1-amine (**3h**)*

A white solid; m.p.: 93.2–93.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.9, 5.0 Hz, 2H), 7.06 (d, *J* = 13.6 Hz, 6H), 4.98 (dddd, *J* = 26.0, 23.0, 9.6, 3.8 Hz, 1H), 4.01 (dd, *J* = 14.7, 3.6 Hz, 1H), 3.84 (dd, *J* = 14.7, 9.5 Hz, 1H), 2.33 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.12 (d, *J* = 579.0 Hz, 1F), 41.65 (d, *J* = 575.3 Hz, 1F), -102.87 (s, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.93 (d, *J* = 256.8 Hz), 140.39, 135.22 (d, *J* = 2.7 Hz), 131.01 (d, *J* = 9.7 Hz), 129.68 (d, *J* = 11.0 Hz), 127.34 (t, *J* = 5.8 Hz), 116.60, 116.45, 73.65, 55.63, 21.30; IR (KBr, cm^{-1}): ν 3102, 2984, 2937, 1590, 1492, 1330, 1306, 1141, 1083; HRMS-EI (m/z) *calcd.* for ($C_{15}H_{14}NO_2F_3S$-F_2) 291.0729, *found* 291.0733.

*4.3.9. 2-((4-chlorophenyl)sulfonyl)-N,N-difluoro-1-(p-tolyl)ethan-1-amine (**3i**)*

A white solid; m.p.: 106.5–108.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.06 (s, 4H), 4.97 (td, *J* = 24.7, 9.4 Hz, 1H), 4.01 (d, *J* = 14.6 Hz, 1H), 3.89–3.80 (m, 1H), 2.33 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.25 (d, *J* = 575.3 Hz, 1F), 41.66 (d, *J* = 575.3 Hz, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.73, 140.47, 137.52, 129.69, 129.64, 129.52, 129.46, 127.15 (t, *J* = 5.4 Hz), 73.63, 55.52, 21.29; IR (KBr, cm^{-1}): ν 3092, 3033, 2992, 2944, 1580, 1516, 1419, 1395, 1335, 1310, 1280, 1144, 1089; HRMS-EI (m/z) *calcd.* for ($C_{15}H_{14}NO_2F_2SCl$-F_2) 307.0434, *found* 307.0439.

*4.3.10. N,N-difluoro-2-(phenylsulfonyl)-1-(m-tolyl)ethan-1-amine (**3j**)*

A yellow solid; m.p.: 54.1–56.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.54 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.4 Hz, 1H), 6.85 (s, 1H), 4.89 (tdd, *J* = 22.8, 9.3, 4.6 Hz, 1H), 3.92 (dd, *J* = 14.7, 3.5 Hz, 1H), 3.77 (dd, *J* = 14.7, 9.3 Hz, 1H), 2.14 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.91 (d, *J* = 575.3 Hz, 1F), 42.03 (d, *J* = 575.3 Hz, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.01, 138.68, 133.90, 130.75, 130.35 (t, *J* = 5.2 Hz), 130.15, 129.13, 128.83, 127.92, 126.79, 73.86, 55.34, 21.26; IR (ATR, cm^{-1}): ν 3037, 2927, 2956, 1448, 1307, 1146, 1088; HRMS-EI (m/z) *calcd.* for ($C_{15}H_{15}NO_2F_2S$-F_2) 273.0824, *found* 273.0825.

*4.3.11. N,N-difluoro-1-(m-tolyl)-2-tosylethan-1-amine (**3k**)*

A yellow solid; m.p.: 71.4–73.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.15 (dd, *J* = 14.8, 7.7 Hz, 4H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.93 (s, 1H), 4.96 (tdd, *J* = 26.2, 9.3, 3.4 Hz, 1H), 3.99 (dd, *J* = 14.6, 3.5 Hz, 1H), 3.83 (dd, *J* = 14.6, 9.3 Hz, 1H), 2.38 (s, 3H), 2.24 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.76 (d, *J* = 575.3 Hz, 1F), 41.97 (d, *J* = 575.3 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.02, 138.64, 136.07, 130.59, 130.47 (d, *J* = 5.7 Hz), 130.18 (d, *J* = 3.1 Hz), 129.78, 128.83, 128.02, 126.88, 73.95, 55.49, 21.68, 21.31; HRMS-EI (m/z) *calcd.* for ($C_{16}H_{17}NO_2F_2S$-F_2) 291.0980, *found* 291.0976.

*4.3.12. N,N-difluoro-1-(2-fluorophenyl)-2-(phenylsulfonyl)ethan-1-amine (**3l**)*

A white solid; m.p.: 63.8–66.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.33 (ddd, *J* = 15.4, 5.3, 1.7 Hz, 1H), 7.22 (t, *J* = 6.8 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 9.3 Hz, 1H), 5.33 (tdd, *J* = 24.1, 9.2, 3.8 Hz, 1H), 4.01 (dd, *J* = 14.7, 3.9 Hz, 1H), 3.94 (dd, *J* = 14.7, 9.2 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 44.97 (d, *J* = 582.8 Hz, 1F), 43.91 (d, *J* = 579.0 Hz, 1F), -114.58 (s, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.34 (d, *J* = 251.1 Hz), 138.68, 134.21, 132.13 (d, *J* = 8.5 Hz), 130.89, 129.41, 128.05, 124.62, 117.87 (dt, *J* = 12.3, 6.0 Hz), 116.23 (d, *J* = 22.2 Hz), 67.72, 54.50; IR (KBr, cm^{-1}): ν 3067, 2922, 1618, 1587, 1495, 1454, 1311, 1238, 1149, 1086; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{12}NO_2F_3S$-F_2) 277.0573, *found* 277.0569.

*4.3.13. N,N-difluoro-1-(2-fluorophenyl)-2-tosylethan-1-amine (**3m**)*

A colorless solid; m.p.: 47.3–48.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.33 (q, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 3H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 9.3 Hz, 1H), 5.31 (tdd, *J* = 24.2, 9.2, 3.7 Hz, 1H), 3.98 (dd, *J* = 14.7, 3.9 Hz, 1H), 3.90 (dd, *J* = 14.6, 9.2 Hz, 1H), 2.38 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 44.79 (d, *J* = 582.8 Hz, 1F), 43.95 (d, *J* = 582.8 Hz, 1F), -114.64 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.32 (d, *J* = 250.8 Hz), 145.36, 135.64, 131.91 (d, *J* = 8.7 Hz), 130.88, 129.98, 128.07, 124.57 (d, *J* = 3.4 Hz), 117.99 (dt, *J* = 12.7, 6.4 Hz), 116.14 (d, *J* = 22.3 Hz), 67.71, 54.59, 21.71; IR (KBr, cm^{-1}): ν 3060, 2988, 2931, 1594, 1495, 1457, 1331, 1237, 1145, 1089; HRMS-EI (m/z) *calcd.* for ($C_{15}H_{14}NO_2F_3S$-F_2) 291.0729, *found* 291.0728.

*4.3.14. N,N-difluoro-1-(4-fluorophenyl)-2-((4-fluorophenyl)sulfonyl) ethan-1-amine (**3n**)*

A yellow solid; m.p.: 60.2–62.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.7, 5.0 Hz, 2H), 7.34 (q, *J* = 6.2, 5.7 Hz, 1H), 7.21 (t, *J* = 7.1 Hz, 1H), 7.08 (t, *J* = 8.4 Hz, 3H), 7.00 (t, *J* = 9.3 Hz, 1H), 5.32 (tdd, *J* = 24.0, 9.1, 3.7 Hz, 1H), 4.01 (dd, *J* = 14.8, 3.9 Hz, 1H), 3.94 (dd, *J* = 14.8, 9.3 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 44.71 (d, *J* = 586.6 Hz, 1F), 43.99 (d, *J* = 582.8 Hz, 1F), -102.37 (s, 1F), -114.52 (s, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.02 (d, *J* = 257.2 Hz), 161.29 (d, *J* = 251.0 Hz), 134.69, 132.22 (d, *J* = 9.2 Hz), 131.03 (d, *J* = 9.9 Hz), 130.91, 124.70 (d, *J* = 3.8 Hz), 117.98–117.56 (m), 116.69 (d, *J* = 23.2 Hz), 116.25 (d, *J* = 22.0 Hz), 67.74, 54.64; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{11}NO_2F_4S$-F_2) 295.0479, *found* 295.0478.

*4.3.15. 2-((4-chlorophenyl)sulfonyl)-N,N-difluoro-1-(2-fluorophenyl) ethan-1-amine (**3o**)*

A white solid; m.p.: 72.4–72.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.51 (m, 2H), 7.37 (d, *J* = 7.2 Hz, 3H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 9.2 Hz, 1H), 5.31 (td, *J* = 23.8, 8.5 Hz, 1H), 4.00 (d, *J* = 13.4 Hz, 1H), 3.97–3.90 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 44.91 (d, *J* = 582.8 Hz, 1F), 44.01 (d, *J* = 579.0 Hz, 1F), -114.34 (s, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.32 (d, *J* = 251.1 Hz), 141.10, 137.10, 132.68, 132.23 (d, *J* = 9.0 Hz), 130.97 (d, *J* = 2.3 Hz), 129.63 (d, *J* = 17.8 Hz), 124.74 (d, *J* = 3.7 Hz), 117.73 (dt, *J* = 12.2, 6.0 Hz), 116.32 (d, *J* = 22.2 Hz), 67.80, 54.65; IR (KBr, cm^{-1}): ν 3096, 2992, 2935, 1617, 1579, 1493, 1458, 1416, 1314, 1282, 1178, 1150, 1086; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{11}NO_2F_3SCl$-F_2) 311.0183, *found* 311.0185.

*4.3.16. N,N-difluoro-1-(2-fluorophenyl)-2-((4-nitrophenyl)sulfonyl) ethan-1-amine (**3p**)*

A yellow solid; m.p.: 127.2–127.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.40–7.31 (m, 1H), 7.21 (t, *J* = 6.7 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.01 –6.95 (m, 1H), 5.43–5.25 (m, 1H), 4.09 (dd, *J* = 15.0, 4.1 Hz, 1H), 4.00 (dd, *J* = 14.9, 9.2 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 44.89 (d, *J* = 579.0 Hz, 1F), 44.09 (d, *J* = 582.8 Hz, 1F), -114.09 (s, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.30 (d, *J* = 252.0 Hz), 150.98, 144.22, 132.56 (d, *J* = 8.9 Hz), 131.07 (d, *J* = 2.3 Hz), 129.65, 124.85 (d, *J* = 3.9 Hz), 124.43, 117.78–117.33 (m), 116.38 (d, *J* = 22.0 Hz), 67.80, 54.68; IR (KBr, cm^{-1}): ν 3100, 2946, 1610, 1529, 1493, 1350, 1305, 1149, 1086; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{11}N_2O_4F_3S$-F_2) 322.0424, *found*

322.0420.

4.3.17. N,N-difluoro-1-(3-fluorophenyl)-2-(phenylsulfonyl)ethan-1-amine (3q)

A white solid; m.p.: 71.2–72.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.3 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.31–7.24 (m, 1H), 7.08–7.01 (m, 2H), 6.91 (d, J = 9.3 Hz, 1H), 5.12–4.95 (m, 1H), 4.00 (dd, J = 14.7, 3.4 Hz, 1H), 3.81 (dd, J = 14.6, 9.4 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.27 (d, J = 579.0 Hz, 1F), 42.18 (d, J = 579.0 Hz, 1F), -111.52 (s, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.69 (d, J = 248.3 Hz), 138.98, 134.26, 132.87 (q, J = 6.3 Hz), 130.65 (d, J = 8.3 Hz), 129.43, 128.01, 125.58, 117.20 (d, J = 20.8 Hz), 116.64 (d, J = 23.2 Hz), 73.2, 55.44; IR (KBr, cm^{-1}): ν 3068, 2989, 2940, 1621, 1592, 1492, 1449, 1406, 1333, 1306, 1241, 1144, 1084; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{12}NO_2F_3S$-F_2) 277.0573, *found* 277.0576.

4.3.18. N,N-difluoro-1-(3-fluorophenyl)-2-tosylethan-1-amine (3r)

A white solid; m.p.: 96.0–97.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.3 Hz, 2H), 7.31–7.21 (m, 3H), 7.08–7.01 (m, 2H), 6.89 (d, J = 9.3 Hz, 1H), 5.09–4.93 (m, 1H), 3.97 (dd, J = 14.6, 3.4 Hz, 1H), 3.77 (dd, J = 14.6, 9.4 Hz, 1H), 2.40 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.18 (d, J = 579.0 Hz, 1F), 42.26 (d, J = 579.0 Hz, 1F), -111.71 (s, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.71 (d, J = 247.9 Hz), 145.48, 135.98, 133.01 (q, J = 6.3 Hz), 130.61 (d, J = 7.9 Hz), 130.04, 128.08, 125.64 (d, J = 2.7 Hz), 117.03 (d, J = 21.5 Hz), 116.65 (d, J = 22.4 Hz), 73.28, 55.57, 21.74; IR (KBr, cm^{-1}): ν 3068, 2992, 2944, 1593, 1492, 1453, 1421, 1330, 1301,1248, 1142, 1085; HRMS-EI (m/z) *calcd.* for ($C_{15}H_{14}NO_2F_3S$-F_2) 291.0729, *found* 291.0724.

4.3.19. 2-((4-chlorophenyl)sulfonyl)-N,N-difluoro-1-(3-fluorophenyl) ethan-1-amine (3s)

A white solid; 96.3–96.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.38 (m, 4H), 7.29 (dd, J = 14.2, 8.3 Hz, 1H), 7.12–7.00 (m, 2H), 6.92 (d, J = 9.2 Hz, 1H), 5.11–4.95 (m, 1H), 4.00 (dd, J = 14.7, 3.5 Hz, 1H), 3.79 (dd, J = 14.7, 9.4 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.05 (d, J = 579.0 Hz, 1F), 42.31 (d, J = 582.8 Hz, 1F), -111.19 (s, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.71 (d, J = 248.3 Hz), 137.38, 132.70, 130.75 (d, J = 8.3 Hz), 129.70, 129.50, 125.60 (d, J = 2.6 Hz), 117.31, 117.24 (d, J = 20.9 Hz), 116.71 (d, J = 23.1 Hz), 73.14, 55.52; IR (KBr, cm^{-1}): ν 3095, 2994, 2944, 1592, 1493, 1454, 1396, 1333, 1306,1251, 1143, 1089, 1008; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{11}NO_2F_3SCl$-F_2) 311.0183, *found* 311.0184.

4.3.20. N,N-difluoro-1-(3-fluorophenyl)-2-((4-nitrophenyl)sulfonyl) ethan-1-amine (3t)

A yellow solid; m.p.: 69.5–71.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.8 Hz, 2H), 7.32 (s, 1H), 7.07 (t, J = 8.3 Hz, 2H), 6.92 (d, J = 9.1 Hz, 1H), 5.08 (tdd, J = 23.9, 9.1, 4.0 Hz, 1H), 4.08 (dd, J = 14.9, 4.0 Hz, 1H), 3.86 (dd, J = 14.9, 9.2 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 44.78 (d, J = 582.8 Hz, 1F), 42.41 (d, J = 582.8 Hz, 1F), -110.77 (s, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.74 (d, J = 248.8 Hz), 150.98, 144.52, 132.35 (q, J = 5.9 Hz), 130.91 (d, J = 8.1 Hz), 129.58, 125.65 (d, J = 2.7 Hz), 124.48, 117.55 (d, J = 20.9 Hz), 116.74 (d, J = 22.4 Hz), 72.97, 55.61; IR (KBr, cm^{-1}): ν 3109, 2996, 2941, 1610, 1534, 1490, 1404, 1350, 1309, 1244, 1149, 1085; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{11}N_2O_4F_3S$-F_2) 322.0424, *found* 322.0427.

4.3.21. N,N-difluoro-1-(4-fluorophenyl)-2-(phenylsulfonyl)ethan-1-amine (3u)

A white solid; m.p.: 80.3–81.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.3 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.21 (dd, J = 8.6, 5.2 Hz, 2H), 6.96 (t, J = 8.6 Hz, 2H), 5.12–4.95 (m, 1H), 4.01 (dd, J = 14.6, 3.4 Hz, 1H), 3.82 (dd, J = 14.6, 9.6 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 44.82 (d, J = 579.0 Hz, 1F), 41.68 (d, J = 575.3 Hz, 1F), -110.54 (s, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.63 (d, J = 249.8 Hz), 139.09, 134.18, 131.67 (d, J = 8.4 Hz), 129.43, 128.02, 126.45, 116.13 (d, J = 21.6 Hz), 73.07, 55.51; IR (KBr, cm^{-1}): ν 3080, 2920, 1606, 1514, 1447, 1409, 1329, 1305, 1236, 1146, 1084; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{12}NO_2F_3S$-F_2) 277.0573, *found* 277.0575.

4.3.22. N,N-difluoro-1-(4-fluorophenyl)-2-tosylethan-1-amine (3v)

A white solid; m.p.: 98.1–100.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.3 Hz, 2H), 7.22 (t, J = 7.7 Hz, 4H), 6.97 (t, J = 8.6 Hz, 2H), 5.09–4.93 (m, 1H), 3.98 (dd, J = 14.6, 3.4 Hz, 1H), 3.78 (dd, J = 14.5, 9.6 Hz, 1H), 2.41 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 44.71 (d, J = 579.0 Hz, 1F), 41.75 (d, J = 579.0 Hz, 1F), -110.71 (s, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.63 (d, J = 250.3 Hz), 145.41, 136.11, 131.68 (d, J = 8.7 Hz), 130.01, 128.06, 126.63–126.40 (m), 116.05 (d, J = 21.8 Hz), 73.11, 55.57, 21.71; HRMS-EI (m/z) *calcd.* for ($C_{15}H_{14}NO_2F_3S$-F_2) 291.0729, *found* 291.0723.

4.3.23. N,N-difluoro-1-(4-fluorophenyl)-2-tosylethan-1-amine (3w)

A yellow solid; m.p.: 76.3–77.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 24.7, 9.0 Hz, 2H), 7.41 (d, J = 7.6 Hz, 2H), 7.22 (s, 2H), 7.00 (t, J = 8.0 Hz, 2H), 5.03 (td, J = 23.7, 8.9 Hz, 1H), 4.01 (d, J = 14.6 Hz, 1H), 3.80 (dd, J = 14.5, 9.6 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 44.55 (d, J = 579.0 Hz, 1F), 41.76 (d, J = 579.0 Hz, 1F), -110.04 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.72 (d, J = 250.9 Hz), 141.13, 137.50, 132.71, 131.68 (d, J = 8.4 Hz), 129.61 (d, J = 21.4 Hz), 126.72–125.56 (m), 116.21 (d, J = 22.1 Hz), 72.91, 55.63; IR (KBr, cm^{-1}): ν 3086, 2937, 1603, 1578, 1512, 1474, 1398, 1319, 1226, 1148, 1089, 1011; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{11}NO_2F_3SCl$-F_2) 311.0183, *found* 311.0187.

4.3.24. N,N-difluoro-1-(4-fluorophenyl)-2-((4-nitrophenyl)sulfonyl) ethan-1-amine (3x)

A yellow solid; m.p.: 89.9–91.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.7 Hz, 2H), 7.91 (d, J = 8.7 Hz, 2H), 7.27–7.23 (m, 2H), 7.01 (t, J = 8.4 Hz, 2H), 5.09 (tdd, J = 24.1, 9.3, 4.0 Hz, 1H), 4.09 (dd, J = 14.8, 4.0 Hz, 1H), 3.86 (dd, J = 14.8, 9.1 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 44.18 (d, J = 579.0 Hz, 1F), 41.87 (d, J = 579.0 Hz, 1F), -109.36 (s, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.84 (d, J = 252.3 Hz), 151.00, 144.67, 131.75, 129.61, 126.09 (q, J = 5.6 Hz), 124.51, 116.37 (d, J = 22.0 Hz), 72.75, 55.84; IR (KBr, cm^{-1}): ν 3104, 2943, 2853, 1606, 1532, 1513, 1404, 1350, 1307, 1234, 1148, 1084; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{11}N_2O_4F_3S$-F_2) 322.0424, *found* 322.0425.

4.3.25. 1-(2-chlorophenyl)-N,N-difluoro-2-(phenylsulfonyl)ethan-1-amine (3y)

A yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.3 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.8 Hz, 2H), 7.36 (d, J = 8.1 Hz, 1H), 7.26–7.21 (m, 1H), 7.19 (d, J = 7.1 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 5.69 (tdd, J = 25.7, 9.4, 4.7 Hz, 1H), 4.04 (dd, J = 14.8, 3.4 Hz, 1H), 3.91 (dd, J = 14.8, 9.5 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.86 (d, J = 579.0 Hz, 1F), 41.64 (d, J = 579.0 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.58, 135.86, 134.19, 131.18, 130.31, 130.26, 129.37, 128.37 (t, J = 5.8 Hz), 127.99, 127.24, 69.55, 54.81; IR (ATR, cm^{-1}): ν 3066, 2927, 1479, 1446, 1309, 1149, 1086; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{12}NO_2F_2SCl$-F_2) 293.0277, *found* 293.0275.

4.3.26. 1-(2-chlorophenyl)-N,N-difluoro-2-tosylethan-1-amine (3z)

A yellow solid; m.p.: 53.5–54.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.30–7.25 (m, 1H), 7.21 (d, J = 7.9 Hz, 3H), 7.19–7.13 (m, 1H), 5.75–5.58 (m, 1H), 4.02 (dd, J = 14.7, 3.3 Hz, 1H), 3.88 (dd, J = 14.7, 9.5 Hz, 1H), 2.38 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.73 (d, J = 579.0 Hz, 1F), 41.62 (d, J = 579.0 Hz, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.35, 135.93, 135.61, 130.98, 130.29, 129.99, 129.87, 128.55 (t, J = 5.2 Hz), 128.07, 127.20, 69.50, 54.83, 21.68; IR (ATR, cm^{-1}): ν 3068, 2932, 1596, 1478, 1442, 1303, 1142, 1087, 1037; HRMS-EI (m/z) *calcd.* for ($C_{15}H_{14}NO_2F_2SCl$-F_2) 307.0434, *found* 307.0433.

*4.3.27. 1-(2-chlorophenyl)-N,N-difluoro-2-((4-nitrophenyl)sulfonyl) ethan-1-amine (**3aa**)*

A white solid; m.p.: 138.1–138.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.8 Hz, 2H), 7.93 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 8.1 Hz, 1H), 7.30–7.26 (m, 1H), 7.15 (dt, J = 14.9, 6.7 Hz, 2H), 5.80–5.62 (m, 1H), 4.13 (dd, J = 15.0, 3.5 Hz, 1H), 3.97 (dd, J = 15.0, 9.4 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 46.02 (d, J = 582.8 Hz, 1F), 41.96 (d, J = 579.0 Hz, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.97, 144.16, 135.97, 131.53, 130.56, 130.31, 129.64, 128.12 (t, J = 5.2 Hz), 127.42, 124.43, 69.37, 54.99; IR (KBr, cm^{-1}): ν 3108, 2931, 1609, 1532, 1476, 1443, 1412, 1350, 1308, 1149, 1086, 1040; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{11}N_2O_4F_2ClS$-F_2) 338.0128, *found* 338.0126.

*4.3.28. 1-(3-chlorophenyl)-N,N-difluoro-2-(phenylsulfonyl)ethan-1-amine (**3ab**)*

A colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.3 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.29 (d, J = 8.3 Hz, 1H), 7.21 (t, J = 8.1 Hz, 1H), 7.14 (d, J = 6.2 Hz, 2H), 5.01 (tdd, J = 24.6, 9.5, 3.4 Hz, 1H), 4.00 (dd, J = 14.7, 3.4 Hz, 1H), 3.82 (dd, J = 14.7, 9.5 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.23 (d, J = 579.0 Hz, 1F), 42.56 (d, J = 579.0 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.74, 134.82, 134.26, 132.30 (t, J = 6.2 Hz), 130.23, 129.69, 129.61, 129.33, 127.90, 127.80, 73.16, 55.13; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{12}NO_2F_2ClS$-F_2) 293.0277, *found* 293.0267.

*4.3.29. 1-(3-chlorophenyl)-2-((4-chlorophenyl)sulfonyl)-N,N-difluoroethan-1-amine (**3ac**)*

A yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.2 Hz, 1H), 7.26–7.22 (m, 1H), 7.14 (d, J = 8.2 Hz, 2H), 5.00 (tdd, J = 24.2, 9.6, 3.4 Hz, 1H), 4.01 (dd, J = 14.7, 3.5 Hz, 1H), 3.81 (dd, J = 14.7, 9.6 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.05 (d, J = 582.8.0 Hz, 1F), 42.54 (d, J = 579.0 Hz, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.20, 137.28, 135.06, 132.13 (t, J = 5.6 Hz), 130.35, 130.33, 129.74, 129.68, 129.43, 128.12, 73.22, 55.36; IR (ATR, cm^{-1}): ν 3093, 2926, 1580, 1476, 1332, 1147, 1089; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{11}NO_2F_2SCl_2$-F_2) 326.9888, *found* 326.9891.

*4.3.30. 1-(4-chlorophenyl)-N,N-difluoro-2-tosylethan-1-amine (**3ad**)*

A white solid; m.p.: 94.1–97.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.3 Hz, 2H), 7.26–7.20 (m, 4H), 7.15 (d, J = 8.5 Hz, 2H), 4.99 (tdd, J = 24.7, 9.7, 3.2 Hz, 1H), 3.97 (dd, J = 14.6, 3.4 Hz, 1H), 3.78 (dd, J = 14.5, 9.7 Hz, 1H), 2.42 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 44.96 (d, J = 575.3 Hz, 1F), 42.22 (d, J = 579.0 Hz, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.48, 136.27, 135.99, 131.07, 130.01, 129.17, 129.08 (t, J = 5.8 Hz), 128.04, 73.21, 55.45, 21.74; IR (KBr, cm^{-1}): ν 3058, 2927, 1639, 1596, 1493, 1416, 1326, 1303, 1146, 1088; HRMS-EI (m/z) *calcd.* for ($C_{15}H_{14}NO_2F_2SCl$-F_2) 307.0434, *found* 307.0433.

*4.3.31. 1-(4-chlorophenyl)-2-((4-chlorophenyl)sulfonyl)-N,N-difluoroethan-1-amine (**3ae**)*

A white solid; m.p.: 102.4–103.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 5.01 (tdd, J = 24.4, 9.5, 3.6 Hz, 1H), 4.00 (dd, J = 14.7, 3.6 Hz, 1H), 3.79 (dd, J = 14.6, 9.5 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 44.79 (d, J = 579.0 Hz, 1F), 42.25 (d, J = 582.8 Hz, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.20, 137.44, 136.59, 131.05, 129.74, 129.48, 129.33, 128.84 (t, J = 5.8 Hz), 73.03, 55.57; IR (KBr, cm^{-1}): ν 3092, 3002, 2939, 1582, 1494, 1476, 1415, 1329, 1307, 1146, 1089; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{11}NO_2F_2SCl_2$-F_2) 326.9888, *found* 326.9883.

*4.3.32. 1-(2-bromophenyl)-N,N-difluoro-2-(phenylsulfonyl)ethan-1-amine (**3af**)*

A yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2H), 7.60–7.55 (m, 1H), 7.22 (s, 1H), 7.21–7.17 (m, 4H), 5.78–5.61 (m, 1H), 4.03 (dd, J = 14.8, 3.3 Hz, 1H), 3.88 (dd, J = 14.7, 9.4 Hz, 1H), 2.38 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.72 (d, J = 582.8 Hz, 1F), 40.79 (d, J = 582.8 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.30, 135.51, 133.61, 131.16, 130.37, 129.95, 128.31, 128.05, 127.77, 126.60, 71.85, 54.81, 21.69; HRMS-EI (m/z) *calcd.* for ($C_{15}H_{14}NO_2F_2SBr$-F_2) 350.9929, *found* 350.9930.

*4.3.33. 1-(3-bromophenyl)-N,N-difluoro-2-(phenylsulfonyl)ethan-1-amine (**3ag**)*

A yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.4 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.8 Hz, 3H), 7.29 (s, 1H), 7.22–7.13 (m, 2H), 5.00 (tdd, J = 24.6, 9.5, 3.3 Hz, 1H), 4.00 (dd, J = 14.7, 3.4 Hz, 1H), 3.81 (dd, J = 14.7, 9.5 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.28 (d, J = 579.0 Hz, 1F), 42.63 (d, J = 579.0 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.75, 134.28, 133.17, 132.54, 130.46, 129.52, 129.34, 128.45, 127.90, 122.90, 73.19, 55.22; IR (ATR, cm^{-1}): ν 3066, 2928, 2850, 1572, 1477, 1448, 1307, 1146, 1085; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{12}NO_2F_2SBr$-F_2) 336.9772, *found* 336.9768.

*4.3.34. 1-(4-bromophenyl)-N,N-difluoro-2-(phenylsulfonyl)ethan-1-amine (**3ah**)*

A yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.3 Hz, 2H), 7.62–7.56 (m, 1H), 7.45–7.37 (m, 4H), 7.09 (d, J = 8.4 Hz, 2H), 5.01 (tdd, J = 24.8, 9.6, 3.3 Hz, 1H), 3.99 (dd, J = 14.6, 3.4 Hz, 1H), 3.81 (dd, J = 14.6, 9.6 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.13 (d, J = 579.0 Hz, 1F), 42.37 (d, J = 579.0 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.93, 134.09, 132.15, 131.26, 129.46, 129.41, 127.93, 124.53, 73.18, 55.33; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{12}NO_2F_2SBr$-F_2) 336.9772, *found* 336.9748.

*4.3.35. 1-(3-bromophenyl)-N,N-difluoro-2-(phenylsulfonyl)ethan-1-amine (**3ai**)*

A white solid; m.p.: 102.1–103.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 5.06–4.89 (m, 1H), 3.96 (dd, J = 14.6, 3.3 Hz, 1H), 3.77 (dd, J = 14.5, 9.8 Hz, 1H), 2.42 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.01 (d, J = 579.0 Hz, 1F), 42.32 (d, J = 579.0 Hz, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.51, 135.97, 132.14, 131.33, 130.03, 129.56 (t, J = 5.3 Hz), 128.03, 124.52, 73.31, 55.39, 21.78; IR (KBr, cm^{-1}): ν 3097, 3056, 2926, 1639, 1594, 1491, 1415, 1327, 1301, 1146, 1082, 1009; HRMS-EI (m/z) *calcd.* for ($C_{15}H_{14}NO_2F_2SBr$-F_2) 352.9912, *found* 352.9908.

*4.3.36. 1-(4-(tert-butyl)phenyl)-N,N-difluoro-2-(phenylsulfonyl)ethan-1-amine (**3aj**)*

A yellow solid; m.p.: 97.3–98.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.5 Hz, 2H), 7.38 (t, J = 7.5 Hz, 1H), 7.23 (t, J = 7.8 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 7.00 (d, J = 8.3 Hz, 2H), 4.93 (tdd, J = 26.1, 9.3, 3.2 Hz, 1H), 3.95 (dd, J = 14.7, 3.4 Hz, 1H), 3.80 (dd, J = 14.7, 9.5 Hz, 1H), 1.17 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.58 (d, J = 575.3 Hz, 1F), 41.52 (d, J = 575.3 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.97, 138.93, 133.75, 129.32, 129.09, 127.90, 127.19–126.95 (m), 125.79, 73.61, 55.15, 34.65, 31.16; HRMS-EI (m/z) *calcd.* for ($C_{18}H_{21}NO_2F_2S$-F_2) 315.1293, *found* 315.1286.

*4.3.37. N,N-difluoro-1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethan-1-amine (**3ak**)*

A reddish brown solid; m.p.: 96.7–97.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.5 Hz, 1H), 7.68–7.60 (m, 3H), 7.53 (d, J = 7.7 Hz, 2H), 7.47–7.39 (m, 2H), 7.26 (t, J = 7.7 Hz, 1H), 7.18 (d, J = 8.6 Hz, 1H), 7.16–7.08 (m, 2H), 5.12 (td, J = 24.7, 8.9 Hz, 1H), 4.02 (d, J = 14.6 Hz, 1H), 3.95–3.84 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 46.07 (d, J = 575.3 Hz, 1F), 42.33 (d, J = 579.0 Hz, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.02, 133.83, 133.80, 132.92, 130.28, 129.11, 128.98, 128.32, 127.96, 127.76, 127.43, 126.87, 125.69, 74.09, 55.64; IR (KBr, cm^{-1}): ν 3064, 2932, 1601, 1580, 1508, 1474, 1446, 1412, 1302, 1236, 1146, 1084; HRMS-EI (m/z) *calcd.* for ($C_{18}H_{15}NO_2F_2S$-F_2) 309.0824, *found*

309.0830.

4.3.38. N,N-difluoro-1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethan-1-amine (3al)

Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.3 Hz, 2H), 7.55 (t, J = 7.0 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 4.98 (tdd, J = 26.0, 9.5, 3.5 Hz, 1H), 4.01 (dd, J = 14.6, 3.5 Hz, 1H), 3.87–3.80 (m, 1H), 3.77 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 44.99 (d, J = 575.3 Hz, 1F), 41.13 (d, J = 571.5 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.80, 139.18, 133.93, 131.03 (d, J = 7.0 Hz), 129.28, 128.02, 122.30 (t, J = 6.1 Hz), 114.36 (d, J = 8.5 Hz), 73.27, 55.51, 55.37; HRMS-EI (m/z) *calcd.* for ($C_{15}H_{15}NO_3F_2S$-F_2) 289.0773, *found* 289.0776.

4.3.39. methyl 4-(1-(difluoroamino)-2-(phenylsulfonyl)ethyl)benzoate (3am)

Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 7.3 Hz, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.8 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 5.03 (tdd, J = 24.7, 9.3, 3.3 Hz, 1H), 3.95 (dd, J = 14.6, 3.5 Hz, 1H), 3.83 (s, 3H), 3.78 (dd, J = 14.6, 9.3 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 45.46 (d, J = 582.8 Hz, 1F), 42.82 (d, J = 579.0 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.14, 138.76, 135.21 (t, J = 5.9 Hz), 134.15, 131.53, 129.96, 129.67, 129.33, 127.88, 73.22, 55.26, 52.47; HRMS-EI (m/z) *calcd.* for ($C_{16}H_{15}NO_4F_2S$-F_2) 317.0722, *found* 317.0732.

4.3.40. N-fluoro-2-(phenylsulfonyl)-1-(pyridin-2-yl)ethan-1-imine (4)

A brown solid; m.p.: 100.6–101.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53–8.47 (m, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.83 (d, J = 7.6 Hz, 2H), 7.75 (t, J = 7.8 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.4 Hz, 2H), 7.35 (s, 1H), 5.11 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 37.50 (s, 1F); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.90 (d, J = 17.6 Hz), 149.53, 147.82 (d, J = 20.7 Hz), 139.42, 137.17, 134.21, 129.19, 128.47, 125.97, 122.60, 52.16 (d, J = 22.3 Hz); IR (KBr, cm^{-1}): ν 3072, 3003, 2929, 1573, 1472, 1443, 1394, 1316, 1167, 1143, 1082, 1043; HRMS-EI (m/z) *calcd.* for ($C_{13}H_{12}N_2O_2FS$-F) 260.0619, *found* 260.0617.

4.3.41. N-hydroxy-N-(2-phenyl-1-(phenylsulfonyl)propan-2-yl) hydroxylamine (5)

A white solid; m.p.: 93.6–95.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.64–7.57 (m, 3H), 7.44 (dd, J = 12.8, 7.3 Hz, 4H), 7.25 (t, J = 7.2 Hz, 1H), 7.19 (t, J = 7.4 Hz, 2H), 4.62 (d, J = 14.8 Hz, 1H), 4.01 (d, J = 14.8 Hz, 1H), 1.98 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 140.05, 133.67, 133.51, 129.02, 128.90, 128.02, 127.90, 127.42, 75.59, 59.13, 15.73; IR (KBr, cm^{-1}): ν 3448, 3064, 2929, 1632, 1498, 1446, 1316, 1278, 1167, 1137, 1083; HRMS-EI (m/z) *calcd.* for ($C_{15}H_{17}NO_4S$-2OH, -SO_2) 208.1126, *found* 208.1122.

4.3.42. (2-(phenylsulfonyl)ethene-1,1-diyl)dibenzene (6)

A yellow solid; m.p.: 109.9–110.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.56 (m, 2H), 7.49 (m, 1H), 7.40–7.26 (m, 9H), 7.24–7.19 (m, 2H), 7.10–7.06 (m, 2H), 7.03 (s, 1H).

4.3.43. (cinnamylsulfonyl)benzene (7)

A yellow solid; m.p.: 108.5–109.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.4 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.7 Hz, 2H), 7.33–7.27 (m, 5H), 6.37 (d, J = 15.9 Hz, 1H), 6.10 (dt, J = 15.6, 7.6 Hz, 1H), 3.96 (d, J = 7.6 Hz, 2H).

4.3.44. N-fluoro-1-phenyl-2-(phenylsulfonyl)ethan-1-imine (8)

A yellow solid; m.p.: 63.5–65.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.8 Hz, 2H), 7.69 (d, J = 7.7 Hz, 3H), 7.53 (t, J = 7.8 Hz, 3H), 7.44 (t, J = 7.5 Hz, 2H), 4.72 (d, J = 4.1 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ 35.99 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.33 (d, J = 17.5 Hz), 134.62, 132.07, 131.33, 129.40, 129.20, 128.57, 127.83, 127.80, 54.12 (d, J = 26.8 Hz); HRMS-EI (m/z) *calcd.* for ($C_{14}H_{12}NO_2S$-HF) 257.0511, *found* 257.0517.

4.3.45. 1-phenyl-2-(phenylsulfonyl)ethan-1-one oxime (9)

A white solid; m.p.: 126.1–127.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.93 (d, J = 7.7 Hz, 2H), 7.69 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.7 Hz, 2H), 7.49 (d, J = 7.9 Hz, 2H), 7.33 (t, J = 7.8 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 4.20 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.64, 134.80, 129.72, 129.24, 128.29, 125.35, 120.35, 63.10; HRMS-EI (m/z) *calcd.* for ($C_{14}H_{15}NO_3S$) 275.0616, *found* 275.0613.

Declaration of Competing Interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled "Difluoroaminosulfonylation of Styrenes with *N,N*-Difluorobenzenesulfonamide".

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2021.109823.

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