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Unexpected formation of *N*-fluoroalkaneacyl anilides from the reactions of fluoroalkanesulfonyl azides with nitrobenzene and its derivatives

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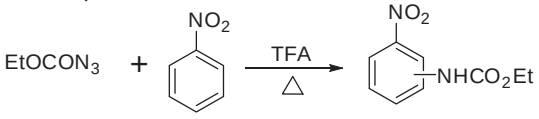
ABSTRACT

The thermal reactions of fluoroalkanesulfonyl azides $R_fCF_2SO_2N_3$ **1** with nitrobenzene and its derivatives $XC_6H_4NO_2$ (X=H, F, Cl, CF_3) gave the unexpected *N*-fluoroalkaneacyl anilides $R_fCONHC_6H_4X$ (X=H, Cl, F, CF_3) in addition to fluoroalkanesulfonyl amides $R_fCF_2SO_2NH_2$. Under the same reaction conditions, however, nitrobenzene containing an electron-donating group $RC_6H_4NO_2$ (R=CH_3, OCH_3) reacted with **1** affording the corresponding *N*-fluoroalkanesulfonyl anilides $R_fCF_2SO_2NHC_6H_3(NO_2)R$. Other electron-poor benzene derivatives, such as benzaldehyde, benzoate, and acetophenone C_6H_5Y(Y=CHO, $COCH_3$, CO_2CH_3) all gave the *meta*-substituted *N*-fluoroalkanesulfonyl anilides $R_fCF_2SO_2NHC_6H_4Y$.

1. Introduction

Reactions of nitrenes with benzene and its derivatives are among the most studied reactions of nitrenes. The reaction involves an electron-deficient nitrogen carbene species that abstract electron from aromatic nuclei.[1–3] The thermal decomposition of sulfonyl azides in aromatic solvents was first reported by Curtius and Schemit,[4,5] who proposed that a radical intermediate was involved.[6,7] Detar and Sagmanli also proposed a radical mechanism for the formation of *N*-arylphenylsulfonyl amide from the thermal reaction of phenylsulfonylazide in aromatic solvent. Later, Abramovitch et al.[8] reported the reactions of methanesulfonyl azide with benzene and its derivatives and rationalized these results in terms of the addition of the singlet nitrene to the aromatic molecules. They proposed formation of a benzaziridine intermediate, which gave *N*-mesylazepine under kinetic condition or *N*-mesylaniline under thermodynamic condition. However, they also found that when the methanesulfonyl azide reacted with nitrobenzene, the products were nitro-*N*-methanesulfonyl anilide (5.3%), phenyl methanesulfonate, phenyl methanesulfonate, and methanesulfonamide (Scheme 1).[9]

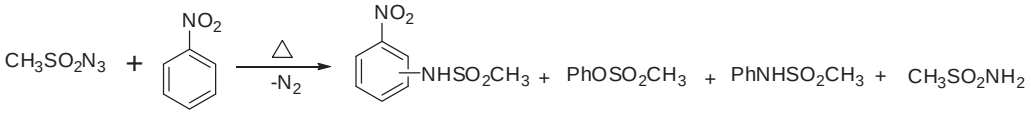
In 1984, Takeuchi and Mastubara also reported the thermal reaction of nitrobenzene with ethoxycarbonyl azide in the present of TFA (Scheme 2).[10]



Scheme 2.

Comparing with the hydrocarbon analogues, the reaction of fluorinated sulfonyl azides has been studied rarely. Our research group has been studying the fluoroalkanesulfonyl azides $R_fSO_2N_3$ **1** (R_f: $X(CF_2)_2O(CF_2)_2$, C_4F_9) since 1994.[11–13] We have reported their reactions with alkenes, triphenyl phosphene, pyridine, and DMSO etc. Recently, we reported their reactions with the electron-rich benzene derivatives $R_nC_6H_{6-n}$ (R=CH_3, n=1,2,4,6; R=OCH_3, n=1,2; R=$C_6H_5CH_2$ n=1.) and gave *N*-aryl fluoroalkanesulfonyl amides (Scheme 3).[14]

As an extension of the exploration of fluorosulfonyl nitrenes, we systematically studied the thermolysis reaction of **1** with nitrobenzene and other electron-poor benzene derivatives, It was found



Scheme 1.

that, the thermal reactions of $R_fCF_2SO_2N_3$ **1** with nitrobenzene or it derivatives bearing an electron-withdrawing group $NO_2C_6H_4X$ **2**

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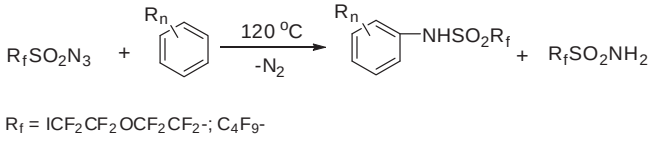


Scheme 3.

(X=H, Cl, CF_3) all gave unexpected *N*-fluoroalkaneacyl anilides $R_fCONHC_6H_4X$ in addition to $R_fCF_2SO_2NH_2$.

By contrast, under some thermal reaction conditions, other aromatic reactants bearing an electron-withdrawing substitute, such as benzaldehyde, benzoate, and acetophenone C_6H_5Y (Y=CHO, CO_2CH_3, $COCH_3$) all gave the *meta*-substituted *N*-fluoroalkanesulfonyl anilides $R_fCF_2SO_2NHC_6H_4Y$.

Herein, we would like to report these results.

2. Results and discussions

The thermal reaction of azide $ICF_2CF_2OCF_2CF_2SO_2N_3$ **1a** (2.4 mmol) and nitrobenzene $C_6H_5NO_2$ (2.0 mmol) was investigated firstly. After heating at 120 °C in an oil bath for 48 h (monitored by TLC), the reaction was finished. Purification by flash column chromatography using petroleum ether/ether (1:1) as eluent afforded two products. The major product (44%) was readily identified as $ICF_2CF_2OCF_2CF_2SO_2NH_2$ **4a**. To our surprise, the second product was *N*-fluoroalkaneacyl anilide $ICF_2CF_2OCF_2CONHC_6H_5$ **3aa**. Its structure was characterized by spectra methods, elemental analysis, and further confirmed by single crystal X-ray diffraction analysis. The IR spectrum of **3aa** shows a strong fluorinated carbonyl absorption at 1708 cm^{-1}. Its ^{19}F NMR spectrum contains only three peaks, i.e., −64.5 (ICF_2), −78.1(CF_2O), and −85.6 (OCF_2) ppm. Comparing to the starting material azide **1a**, which has four peaks, the signal of CF_2S (at −113.2 ppm) disappeared. The ^1H NMR shows six proton peaks including one amino proton 7.85(−NH) and five aromatic protons 7.57(2H), 7.41(2H), and 7.25(1H) ppm. The MS spectrum of **3aa** shows its molecular ion peak at *m*/*z* 413(M^+, 100) and major fragment peak 120 ($C_6H_5NHCO^+$, 85). Finally, the new product **3aa** was further elucidated by a single crystal X-ray diffraction analysis. Its molecular structure was shown in Fig. 1. An intermolecular hydrogen bonding existed between the carbonyl oxygen atom and the amino proton (NH). There is neither nitro nor sulfonyl group in the structure of **3aa**. The carbonyl group may be transformed from the CF_2S group in the azide **1a**. In order to find, which group offered the nitrogen atom, the ^{15}N-nitrobenzene (**2a′**) reacted with azide **1a** to give an *N*-fluoroalkaneacyl anilide compound **3aa′** (Scheme 5). The MS spectrum of this product **3aa′** showed its molecular ion peak at *m*/*z* 414(M^+, 100). This result explained the nitrogen atom of the **3aa′** was from the starting nitrobenzene.

When perfluorobutanesulfonyl azide $C_4F_9SO_2N_3$ (**1d**) or *i*-$C_3H_7O_2CCF_2SO_2N_3$ (**1f**) was treated with nitrobenzene, the corresponding product was $C_3F_7CONHC_6H_5$ (**3da**) and *i*-$C_3H_7O_2C$-$CONHC_6H_5$ (**3fa**), respectively. Based on above results we supposed that the carbonyl group in the product **3** may come from the difluoromethylene group, which is bonded to the sulfonyl group in the starting azide **1**. However, the detailed mechanism of this thermal reaction is not clear.

Other nitrobenzenes bearing an electron-withdrawing group, such as 3-trifluoromethylnitrobenzene (**2b**), 4-fluoronitrobenzene (**2c**) or 2-chloro-5-trifluoromethyl nitrobenzene (**2f**) all gave corresponding anilides $R_fCONHAr$ (Ar: FC_6H_4−, $CF_3C_6H_4$−, and 2-Cl-5-$CF_3C_6H_3$−) when they reacted with the fluoroalkanesulfonyl azides $R_fCF_2SO_2N_3$ **1**(**a**–**f**) (Table 1) (Scheme 4).

As we reported before, thermal reactions of the azides **1** with the electron-rich benzene derivatives, such as toluene, anisole, and diphenyl methane etc. all gave corresponding *N*-aryl fluoroalkanesulfonyl amides $R_fCF_2SO_2NHAr$. Similar treatment of the *p*-methyl nitrobenzene or *p*-methoxy nitrobenzene azide **1** afforded the nitro-*N*-fluoroalkanesulfonyl anilides **5** in 35%–38% yields in addition to the $R_fCF_2SO_2NH_2$ **4**. In this reaction, the nitro group remained. It was also noticed that in product **5** the *N*-fluoroalkanesulfonyl amino group was at the *othro* position of the electron-donating group CH_3 or CH_3O, and at the *meta*-position for the nitro group. (Scheme 7) This confirmed the electron-deficient property of fluoroalkanesulfonyl nitrene ($R_fCF_2SO_2N$) (Scheme 6) (Table 2).

Other thermal reactions of **1** with electron-poor benzene derivatives, such as benzaldehyde, benzoate and acetophenone were also studied, for instance, after C_6H_5CHO **6a** (2 mmol) and $C_4F_9SO_2N_3$ **1d** (2.4 mmol) were heated at 120 °C without any solvent for 48 h, similar work-up and purification gave *meto-N*-perfluorobutanesulfonyl benzaldehyde in 48% yield. The same reaction results were obtained when 4-methoxyl benzaldehyde **6d**, methyl benzoate **6c** or acetophenone **6b** was heated together with **1** (Table 3).

3. Conclusion

In summary, the thermal reactions of fluoroalkanesulfonyl azides with nitrobenzene and bringing an electron-withdrawing group, such as $CF_3C_6H_4NO_2$ (**2b**) and $FC_6H_4NO_2$ (**2c**) etc. gave the unexpected *N*-fluoroalkaneacyl anilides. Other electron-poor benzene derivatives, such as **5a**, **6b**, and **6c** all formed the

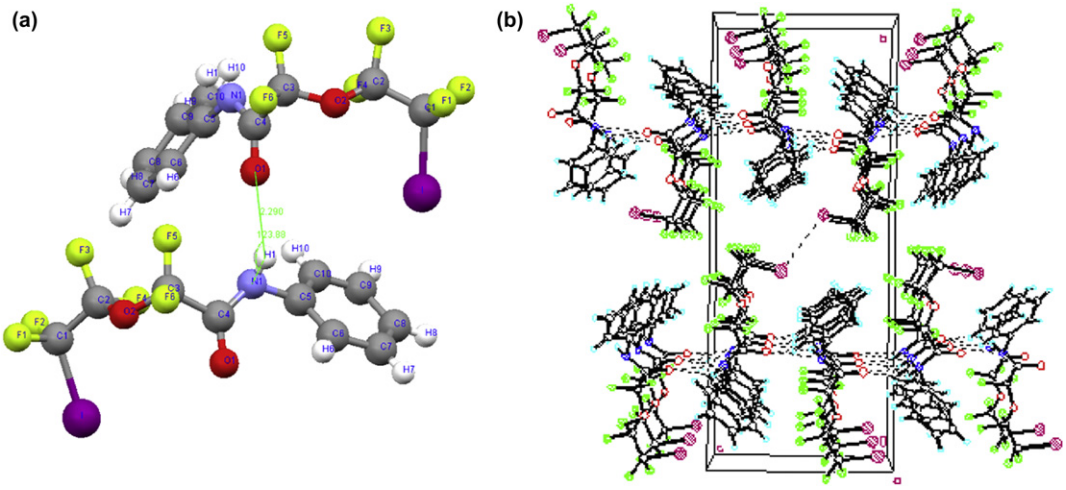
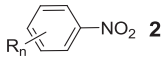
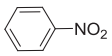
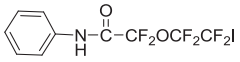
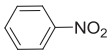
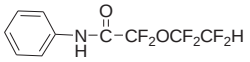
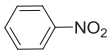
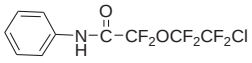
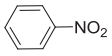
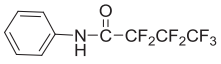
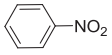
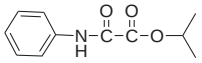
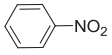
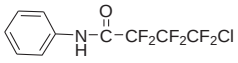
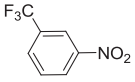
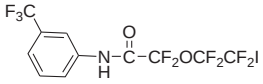
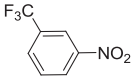
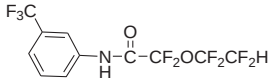
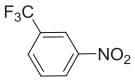
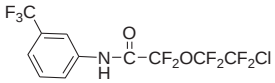
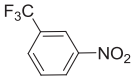
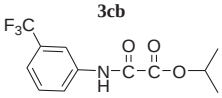
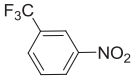
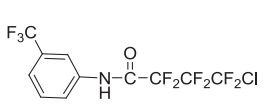
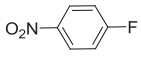
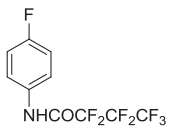


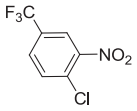
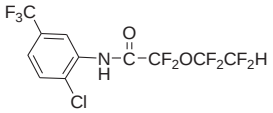
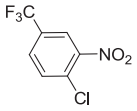
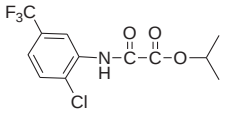
Fig. 1. a) The molecular structure of the product **3aa**; (b) The packing map of **3aa**.

Table 1
Reactions of fluoroalkanesulfonyl azides **1** with nitrobenzene **2**[a]

Entry	$R_fCF_2SO_2N_3$ **1**	 **2**	Products **3**	Yield (%)[b]
1	**1a**	 **2a**	 **3aa**	16
2	**1b**	 **2a**	 **3ba**	15
3	**1c**	 **2a**	 **3ca**	12
4	**1d**	 **2a**	 **3da**	18
5	**1e**	 **2a**	 **3ea**	15
6	**1f**	 **2a**	 **3fa**	10
7	**1a**	 **2b**	 **3ab**	9
8	**1b**	 **2b**	 **3bb**	13
9	**1c**	 **2b**	 **3cb**	13
10	**1d**	 **2b**	 **3db**	15
11	**1e**	 **2b**	 **3cb**	9
12	**1c**	 **2c**	 **3cc**	15

(*continued on next page*)

Table 1 (*continued*)

Entry	$R_fCF_2SO_2N_3$ **1**	R_n–C$_6$H$_4$–NO_2 **2**	Products **3**	Yield (%)[b]
13	**1b**	 **2d**	 **3bd**	12
14	**1e**	 **2d**	 **3ed**	12

[a] mol ratio 1: 2-1.2 :1.
[b] Isolated yields based on azide **1**, and all the reactions gave the corresponding amides **4** in 40–44% yields.

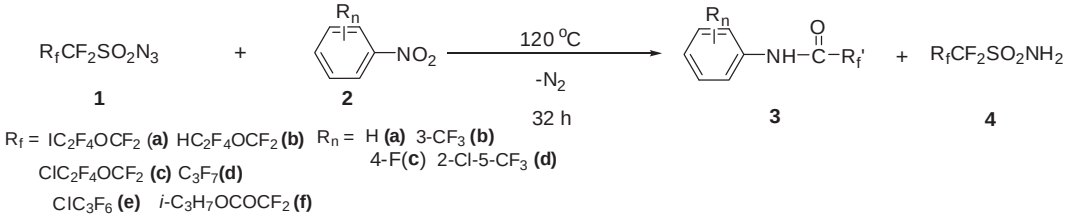
meta-substituted *N*-fluoroalkanesulfonyl amides. While, *p*-nitrotoluene and *p*-nitroanisole under same reaction conditions also formed the *N*-fluoroalkanesulfonyl amides.

4. Experimental

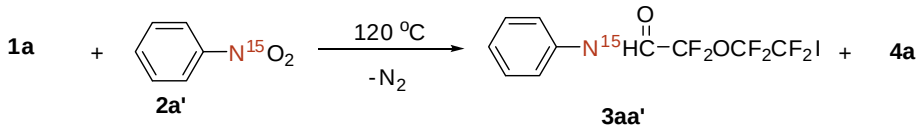
4.1. General

Melting points were measured on a Temp-Melt. Apparatus was uncorrected. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker AM-300 instruments with Me_4Si and $CFCl_3$ as the internal and external standards, respectively. FTIR spectra were obtained with a Nicolet AV-360 spectrophotometer. Low resolution mass spectra (LRMS) or high resolution mass spectra (HRMS) were obtained on a Finnigan GC–MS 4021 or a Finnigan MAT-8430 instrument using the electron impact ionization technique (70 eV), respectively. Elemental analyses were performed by VARIO EL III in the institute. Single crystal X-ray structure analysis was performed on a Bruker P4 instrument.

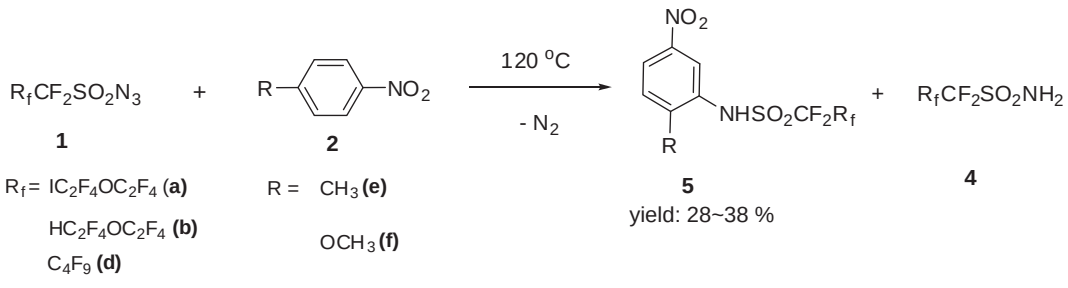
Typical experimental method: Under argon atmosphere, polyfluoroalkanesulfonyl azides **1** (2.4 mmol) and nitrobenzene (2.0 mmol) were put into a schlenk tube, and heated the mixture to 120 °C. After stirring for 48 h, the mixture was purified by column chromatogram (pet. ether/ether=5:1/v:v). The product **3** was



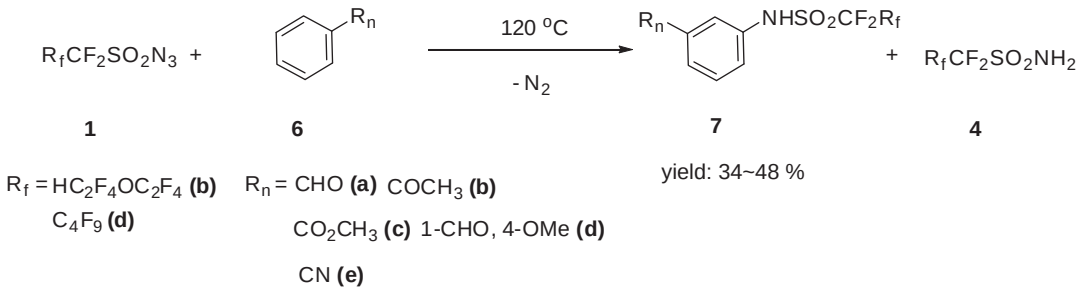
Scheme 4.



Scheme 5.



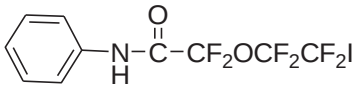
Scheme 6.



Scheme 7.

obtained in 9–18% yield, and the major product **4** was obtained in 40–44%yield.

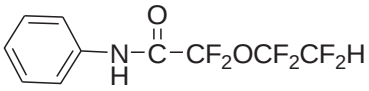
*4.1.1. 2,2-Difluoro-2-(2-iodo-1,1,2,2-tetrafluoroethoxy)acetanilide **3aa**.*



White solid, mp 109–110 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.85 (1H, br s, NH), 7.57 (2H, d, J=8.1 Hz), 7.41 (2H, t, J=8.4 Hz), 7.25 (1H, t, J=7.2 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −64.5 (2F, t, J=5.6 Hz, ICF_2), −78.1 (2F, t, J=12.4 Hz, CF_2O), −85.6 (2F, m, OCF_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 154.9 (C=O, t, J=34 Hz), 135.1, 129.3, 126.3, 120.5, 117.9 (CF_2O, t-t, $^1J_{C-F}$=235 Hz, $^2J_{C-F}$=34 Hz), 110.0 (CF_2CO, t, ^1J=284 Hz), 84.5 (ICF_2, t-t, $^1J_{C-F}$=235 Hz, $^2J_{C-F}$=34 Hz). IR (KBr) cm^{-1}: 3302, 1708, 1559, 1543, 1313, 1153, 1119, 1080. MS (EI) m/z: 413 (M^+, 100), 286 (M^+−I, 6), 120 ($PhNHCO^+$, 85), 92 ($PhNH^+$, 43), 77 (C_6H_{5+}, 50). HRMS (ESI) m/z 413.9424 ($[M+H]^+$, $C_{10}H_7F_6INO_2$ required 413.9420).

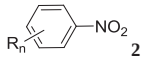
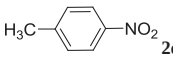
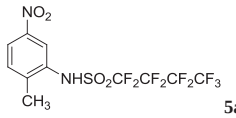
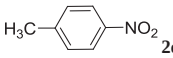
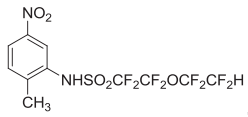
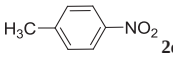
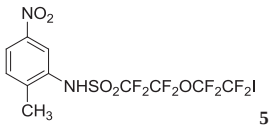
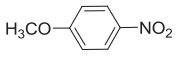
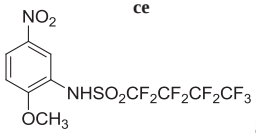
Crystal data for $C_{10}H_6F_6INO_2$: MW=413.06, monoclinic, space group $P2(1)/c$, a=5.5993 (6), b=24.153(3), c=9.8805(10) Å, β=90.607(2), V=1336.2(2) Å^3, Z=4, Dc=2.053 mg/m^3, F(000)=784, crystal dimension 0.34×0.30×0.05 mm, radiation, Mo Kα (λ=0.711 Å), 3.38≤2θ≤56.54, intensity data were collected at 293 K with a Bruker axs D8 diffractometer, and employing ω/2θ scanning technique, in the range of −7≤h≤7, −32≤k≤23, −13≤l≤11; The structure was solved by a direct method, all non-hydrogen atoms were positioned and anisotropic thermal parameters refined from 3123 observed reflections with R (int)=0.0946 by a full-matrix least-squares technique converged to R=0.1799 and Rw=0.2558.

*4.1.2. 2,2-Difluoro-2-(1,1,2,2-tetrafluoroethoxy)acetanilide **3ba**.*



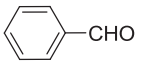
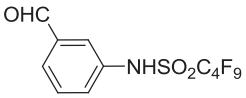
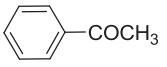
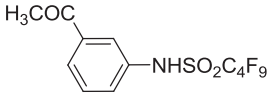
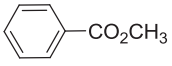
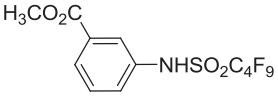
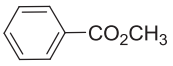
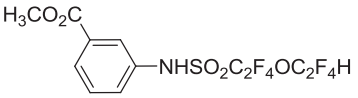
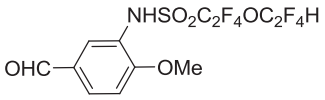
Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.01 (1H, br s, NH), 7.56 (2H, d, J=7.5 Hz), 7.39 (2H, t, J=7.5 Hz), 7.27–7.22 (1H, m), 5.89 (1H,

Table 2
Reactions of fluoroalkanesulfonyl azides **1** with nitrobenzene derivatives **2**[a]

Entry	$R_fCF_2SO_2N_3$ **1**	 **2**	Products **3**	Yield (%)[b]
1	**1a**	 **2e**	 **5ae**	38
2	**1b**	 **2e**	 **5** **be**	35
3	**1c**	 **2e**	 **5** **ce**	28
4	**1a**	 **2f**	 **5af**	35

[a] mol ratio 1: 9-1.2 :1.
[b] Isolated yield based on azide **1**, and all the reactions gave the corresponding amides **4** in 40–44% yields.

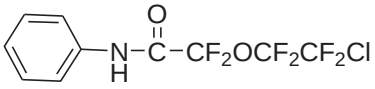
Table 3
Reactions of fluoroalkanesulfonyl azides **1** with electron-poor benzene derivatives **6**[a]

Entry	Azide	**6**	Product	Yield (%)[b]
1	**1d**	 **(6a)**	 **(7da)**	48
2	**1d**	 **(6b)**	 **(7db)**	45
3	**1d**	 **(6c)**	 **(7dc)**	38
4	**1b**	 **(6c)**	 **(7bc)**	34
5	**1b**	 **(6d)**	 **(7bd)**	37

[a] mol ratio **1**:**6**=1.2:1.
[b] Isolated yields based on azide **1**, and all the reactions gave the corresponding amides **4** in 40–44% yields.

t-t, J=53, 3.0 Hz, HCF_2). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −78.3 (2F, t, J=12.4 Hz, CF_2O), −88.8 (2F, m, OCF_2), −137.6 (2F, td, J=54, 4.2 Hz, CF_2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 155.5 (C=O, t, $^2J_{C-F}$=34 Hz), 135.1, 129.3, 126.3, 120.6, 114.1 (CF_2CO, t, ^1J=284 Hz), 116.2 (CF_2O, t-t, $^1J_{C-F}$=250 Hz, $^2J_{C-F}$=34 Hz),106.3 (HCF_2, t-t, J=252,34 Hz). IR (KBr) cm^{-1}: 3314, 1713, 1604, 1552, 1452, 1275, 1240, 1155, 1092. MS (EI) m/z: 287 (M^+, 98), 170 ($PhNHCOCF_2^+$, 12), 120 ($PhNHCO^+$, 100), 92 ($PhNH^+$, 70), 77 ($C_6H_5^+$, 72). HRMS (EI) m/z calcd for $C_{10}H_7F_6NO_2$: 287.0381; found: 287.0371.

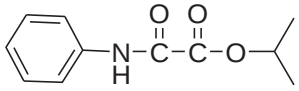
*4.1.3. 2,2-Difluoro-2-(2-chloro-1,1,2,2-tetrafluoroethoxy)acetanilide **3ca**.*



Yellow solid, mp 90–92 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.93 (1H, br s, NH), 7.57 (2H, d, J=7.5 Hz), 7.41 (2H, t, J=7.5 Hz), 7.28–7.23 (1H, m). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −74.0 (2F, s, $ClCF_2$), −78.7 (2F, t, J=10 Hz, CF_2O), −87.2 (2F, t, J=11.8 Hz, OCF_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 155.7 (t, $^2J_{C-F}$=34 Hz), 135.3, 129.4, 126.5, 120.8, 116.2 (OCF_2, t-t, $^1J_{C-F}$=239 Hz, $^2J_{C-F}$=34 Hz), 114.3 (CF_2CO, t, ^1J=282 Hz), 107.0 ($ClCF_2$, t-t, $^1J_{C-F}$=235 Hz, $^2J_{C-F}$=34 Hz). IR (KBr) cm^{-1}: 3307, 1713, 1605, 1551, 1500, 1452, 1181, 1124, 1095. MS (EI) m/z: 323/321 (M^+, 20/62), 286 (M^+−Cl, 13), 170 ($PhNHCOCF_2^+$, 9), 120 ($PhNHCO^+$, 100), 92 ($PhNH^+$, 53), 77 ($C_6H_5^+$, 58). HRMS (EI) m/z 286.0305 ($[M-Cl]^+$, $C_{10}H_6F_6NO_2$ required 286.0303).

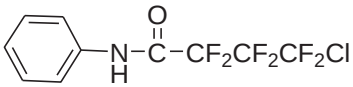
*4.1.4. 2,2,3,3,4,4,4-Heptafluorobutyranilide **3da**.* White solid, mp 84–86 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.82 (1H, br s, NH), 7.50 (2H, d, J=8.1 Hz), 7.34 (2H, t, J=7.8 Hz), 7.21–7.17 (1H, m). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −80.5 (3F, t, J=8.7 Hz, CF_3), −120.3 (2F, m, CF_2), −126.7 (2F, s, CF_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 155.6 (C=O, t, ^2J=34 Hz), 136.7, 129.6, 126.3, 121.9, 117.7 (CF_3, q-t, J=286, 34 Hz), 108.9 (CF_2, t-t, J=266, 31 Hz), 108.8 (CF_2, t-t-q, J=266, 34, 31 Hz). IR (KBr) cm^{-1}: 3321, 1699, 1545, 1450, 1237, 1147, 1126. MS (ESI) m/z: 312.0 ($[M+Na]^+$). HRMS (ESI) m/z 290.0424 ($[M+H]^+$, $C_{10}H_7F_7NO$ required 290.0410). Anal. Calcd for $C_{10}H_6F_7NO$: C, 41.54; H, 2.09; N, 4.84%. Found: C, 41.20; H, 2.39; N, 4.80%.

*4.1.5. Isopropoxyoxalanilide **3ea**.*



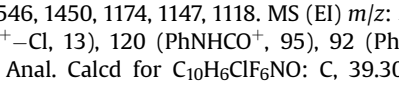
Yellow oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.91 (1H, br s, NH), 7.58 (2H, d, J=7.8 Hz), 7.29 (2H, t, J=7.8 Hz), 7.11 (1H, t, J=7.8 Hz), 5.12 (1H, q, J=6.0 Hz, OCH), 1.32 (6H, d, J=6.0 Hz, 2× CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.4, 154.1, 136.3, 129.1, 125.4, 119.7, 72.1, 29.6, 21.4. IR (KBr) cm^{-1}: 2985, 1693, 1601, 1541, 1445, 1288, 1181, 1102. MS (EI) m/z: 207 (M^+, 13), 165 ($M^+-C_3H_6$, 4), 120 ($PhNHCO^+$, 47), 92 ($PhNH^+$, 24), 77 ($C_6H_5^+$, 28), 43 ($C_3H_7^+$, 100). HRMS (EI) m/z calcd for $C_{11}H_{13}NO_3$: 207.0895; found: 207.0901.

*4.1.6. 4-Chloro-2,2,3,3,4,4-hexafluorobutyranilide **3fa**.*



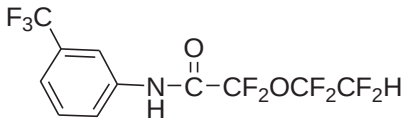
White solid, mp 82–84 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.98 (1H, br s, NH), 7.57–7.55 (2H, m), 7.39 (2H, t, J=7.8 Hz), 7.27–7.22 (1H, m). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −67.7 (2F, t, J=12 Hz, $ClCF_2$), −118.8 (2F, t, J=12.1 Hz, CF_2), −120.9 (2F, s, CF_2). IR (KBr) cm^{-1}: 3323, 1698, 1602, 1546, 1450, 1174, 1147, 1118. MS (EI) m/z: 307/305 (M^+, 1/3), 270 (M^+−Cl, 13), 120 ($PhNHCO^+$, 95), 92 ($PhNH^+$, 72), 77 ($C_6H_5^+$, 100). Anal. Calcd for $C_{10}H_6ClF_6NO$: C, 39.30; H, 1.98; N, 4.58%. Found: C, 39.48; H, 2.04; N, 4.58%.

*4.1.7. 3′-Trifluoromethyl-2,2-difluoro-2-(2-iodo-1,1,2,2-tetrafluoroethoxy)acetanilide **3ab**.*



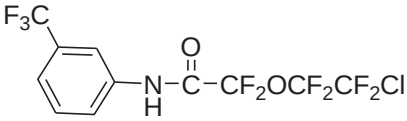
Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.12 (1H, br s, NH), 7.87 (1H, s), 7.80 (1H, d, J=6.6 Hz), 7.57–7.52 (2H, m). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −63.1 (3F, s, $ArCF_3$), −64.9 (2F, s, ICF_2), −78.4 (2F, t, J=12 Hz, CF_2O), −85.6 (2F, t, J=12.4 Hz, OCF_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.2 (t, $^2J_{C-F}$=34 Hz), 135.7, 132.0 (q, $^2J_{C-F}$=33 Hz), 130.1, 123.6, 123.5 (q, J=271 Hz), 123.0 (q, J=4.0 Hz), 117.4 (q, $^3J_{C-F}$=4.0 Hz), 114.8 (t-t, J=285 , 31 Hz), 113.9 (t, J=285 Hz), 89.5 (t-t, J=318, 42 Hz). IR (KBr) cm^{-1}: 3314, 2929, 1720, 1560, 1456, 1332, 1148. MS (EI) m/z: 481 (M^+, 21), 226 (ICF_2CF_{2+}−1, 25), 187 ($ArNHCO^+$−1, 100), 160 ($ArNH^+$, 84), 145 ($CF_3C_6H_{4+}$, 67), 100 (HCF_2CF_{2+}−1, 59). HRMS (EI) m/z calcd for $C_{11}H_5F_9INO_2$: 480.9221; found: 480.9222.

4.1.8. 3′-Trifluoromethyl-2,2-difluoro-2-(1,1,2,2-tetrafluoroethoxy) acetanilide ***3bb****.*



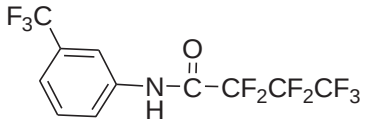
Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.15 (1H, br s, NH), 7.86 (1H, s), 7. 79 (1H, d, J=6.9 Hz), 7.56–7.49 (2H, m), 5.90 (1H, t-t, J=3.0, 53 Hz, HCF_2). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −63.3 (3F, s, $ArCF_3$), −78.2 (2F, t, J=12 Hz, CF_2O), −88.5 (2F, s, OCF_2), −137.5 (2F, d, J=53.3 Hz, CF_2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.2 (C=O, t, J=35 Hz), 135.7, 131.8 (q, J=33 Hz), 129.9, 124.0, 123.5 (CF_3, q, J=271 Hz), 123.0 (q, ^2J=4.0 Hz), 117.7 (q, J=4.0 Hz), 116.3 (t-t, J=252, 40 Hz), 114.0 (OCF_2, t, J=284 Hz), 106.9 (HCF_2, t-t, J=252, 39 Hz). IR (KBr) cm^{-1}: 3435, 3311, 1722, 1610, 1563, 1497, 1456, 1333, 1131. MS (EI) m/z: 355 (M^+, 28), 188 ($ArNHCO^+$, 100), 160 ($ArNH^+$, 79), 145 ($CF_3C_6H_{4+}$, 66), 101 (HCF_2CF_{2+}, 63), 51 (HCF_{2+}, 55). HRMS (EI) m/z calcd for $C_{11}H_6F_9NO_2$: 355.0255; found: 355.0257.

4.1.9. 3′-Trifluoromethyl-2,2-difluoro-2-(2-chloro-1,1,2,2-tetrafluoroethoxy)acetanilide ***3cb****.*



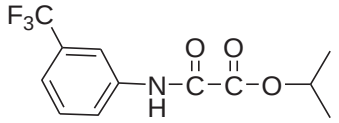
Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.11 (1H, br s, NH), 7.87 (1H, s), 7. 80 (1H, d, J=6.0 Hz), 7.57–7.52 (2H, m). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −62.9 (3F, s, $ArCF_3$), −73.6 (2F, s, $ClCF_2$), −78.2 (2F, t, J=12.1 Hz, CF_2O), −86.7 (2F, t, J=12.1 Hz, OCF_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 155.3 (t, J=34 Hz), 135.7, 131.9 (q, J=33 Hz), 130.0, 123.7, 123.5 (q, J=271 Hz), 123.1 (q, J=4 Hz), 117.5 (q, J=4 Hz). IR (KBr) cm^{-1}: 3313, 1718, 1561, 1456, 1333, 1180, 1137. MS (EI) m/z: 388 (M^+−1, 12), 188 ($ArNHCO^+$, 100), 160 ($ArNH^+$, 63), 145 ($CF_3C_6H_{4+}$, 43), 135 ($ClCF_2CF_{2+}$, 30), 85 ($ClCF_{2+}$, 29). HRMS (EI) m/z calcd for $C_{11}H_5F_9ClNO_2$: 388.9865; found: 388.9865.

4.1.10. 3′-Trifluoromethyl-2,2,3,3,4,4,4-heptafluorobutyranilide ***3db****.*



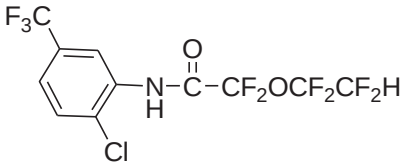
Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.10 (1H, br s, NH), 7.86 (1H, s), 7. 79 (1H, d, J=6.9 Hz), 7.55–7.52 (2H, m). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −62.9 (3F, s, $ArCF_3$), −80.5 (3F, t, J=8.7 Hz, CF_3), −120.3 (2F, quart, J=8.5 Hz, CF_2), −126.7 (2F, s, CF_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 155.2 (C=O, t, J=34 Hz), 135.6, 131.9 (q, J=32 Hz), 130.0, 123.9, 123.4 (CF_3, q, J=271 Hz), 123.2 (q, ^3J=4.0 Hz), 117.7 (q, ^3J=4.0 Hz). IR (KBr) cm^{-1}: 3316, 1712, 1558, 1455, 1334, 1227, 1171, 1137, 1073. MS (EI) m/z: 357 (M^+, 27), 188 ($ArNHCO^+$, 78), 160 ($ArNH^+$, 100), 145 ($CF_3C_6H_{4+}$, 94), 69 (CF_{3+}, 99). HRMS (EI) m/z calcd for $C_{11}H_5F_{10}NO$: 357.0211; found: 357.0207.

4.1.11. 3′-Trifluoromethyl-isopropoxyoxalanilide ***3eb****.*



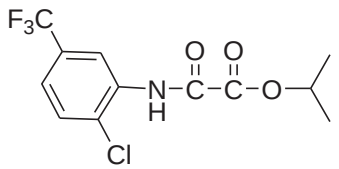
Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.10 (1H, br s, NH), 7.94 (1H, s), 7.89 (1H, d, J=7.8 Hz), 7.48 (2H, quint, J=7.8 Hz), 5.21 (1H, sept, J=6.3 Hz, OCH), 1.40 (6H, d, J=6.0 Hz, $2CH_3$). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −62.8 (3F, s, $ArCF_3$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.2, 154.6, 137.0, 131.6 (q, J=33 Hz), 129.8, 123.7 (q, J=270 Hz), 123.0, 122.0 (q, J=4.0 Hz), 116.7 (d, J=3.0 Hz), 72.5, 21.5. IR (KBr) cm^{-1}: 3292, 2987, 1698, 1552, 1452, 1333, 1168, 1128, 1073. MS (EI) m/z: 275 (M^+, 10), 188 ($ArNHCO^+$, 17), 160 ($ArNH^+$, 14), 145 ($CF_3C_6H_{4+}$, 10), 43 (C_3H_{7+}, 100). HRMS (EI) m/z calcd for $C_{12}H_{12}F_3NO_3$: 275.0769; found: 275.0765.

4.1.12. 2′-Chloro-5′-trifluoromethyl-2,2-difluoro-2-(1,1,2,2-tetrafluoroethoxy)acetanilide ***3bd****.*



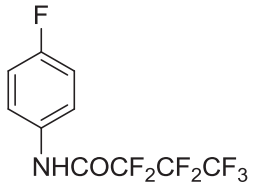
Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.68 (1H, s), 8.58 (1H, br s, NH), 7.59 (1H, d, J=8.7 Hz), 7.45 (1H, dd, J=2.1, 8.7 Hz), 5.92 (1H, tt, J=2.7, 52.8 Hz, HCF_2). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −62.9 (3F, s, $ArCF_3$), −77.8 (2F, t, J=11.8 Hz, CF_2O), −88.0 (2F, m, OCF_2), −137.1 (2F, td, J=4.5, 55.5 Hz, CF_2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 155.5 (t, J=35.0 Hz), 132.8, 130.6 (q, J=33 Hz), 129.9, 127.3, 123.3 (q, J=3.0 Hz), 123.2 (q, J=271 Hz), 118.6 (q, J=5.0 Hz), 116.3 (t-t, J=280, 30 Hz), 113.7 (t, J=284 Hz), 106.9 (t-t, J=252, 40 Hz). IR (KBr) cm^{-1}: 3402, 1745, 1596, 1547, 1435, 1333, 1133, 1083. MS (EI) m/z: 391/389 (M^+, 3/10), 354 (M^+−Cl, 40), 222 ($ArNHCO^+$, 33), 194 ($ArNH^+$, 54), 101 (HCF_2CF_{2+}, 100), 51 (HCF_{2+}, 51). HRMS (EI) m/z calcd for $C_{11}H_5ClF_9NO_2$: 388.9865; found: 388.9849.

4.1.13. 2-Chloro-5′-trifluoromethyl-isopropoxyoxalanilide ***3fd****.*



Orange solid, mp 58–60 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.58 (1H, br s, NH), 8.81 (1H, s), 7.55 (1H, d, J=8.1 Hz), 7.39 (1H, d, J=8.1 Hz), 5.24 (1H, sept, J=6.3 Hz, OCH), 1.43 (6H, d, J=6.6 Hz, $2CH_3$). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −62.8 (3F, s $ArCF_3$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.5, 154.3, 133.9, 130.3 (q, J=33 Hz), 129.7, 126.6 (m), 123.2 (q, J=271 Hz), 122.2 (q, J=4.0 Hz), 117.8 (q, J=4.0 Hz), 72.6, 21.4. IR (KBr) cm^{-1}: 3365, 2987, 1722, 1534, 1330, 1129, 1102, 1082. MS (EI) m/z: 311/309 (M^+, 1/3), 43 (C_3H_{7+}, 100). HRMS (EI) m/z calcd for $C_{12}H_{11}ClF_3NO_3$: 309.0380; found: 309.0384.

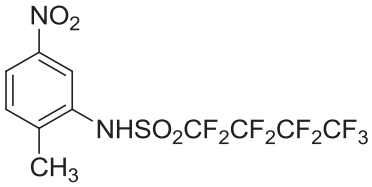
*4.1.14. 4′-Fluoro-2,2,3,3,4,4,4-heptafluorobutyranilide **3cc**.*



Orange solid, mp 71–73 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.93 (1H, br s, NH), 7.54 (2H, quart, J=4.5 Hz), 7.10 (2H, t, J=8.7 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −80.7 (3F, t, J=8.0 Hz, CF_3), −114.7 (1F, s, ArF), −120.6 (2F, q, J=8.0 Hz, CF_2), −127.0 (2F, s, CF_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.7 (d, J=246 Hz), 155.5 (t, J=26 Hz), 131.0 (d, J=3.0 Hz), 122.8 (d, J=8.0 Hz), 117.7 (CF_3, q-t, $^1J_{C-F}$=268 Hz, $^2J_{C-F}$=34 Hz),116.2 (d, J=23 Hz), 108.9 (CF_2, t-t, $^1J_{C-F}$=268 Hz, $^2J_{C-F}$=31 Hz), 108.7 (CF_2CO, t-q-t, $^1J_{C-F}$=268 Hz, $^2J_{C-F}$=34 Hz, $^3J_{C-F}$=31 Hz). IR (KBr) cm^{-1}: 3323, 1712, 1615, 1513, 1415, 1353, 1220, 1121, 1080. MS (ESI) m/z: 305.9 ([M−H]$^-$). HRMS (ESI) m/z 306.0182 ([M−H]$^-$, $C_{10}H_4F_8NO$: required 306.0171).

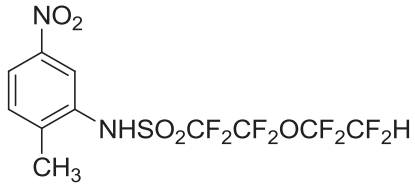
Typical experimental method: Under argon atmosphere, perfluoroalkanesulfonyl azides **1a** (780 mg, 2.4 mmol) and 4-methylnitrobenzene **2d** (274 mg, 2.0 mmol) were put into a schlenk tube, and heat the mixture to 120 °C. After stirred for 32 h, the mixture was purified by column chromatogram (pet. ether/ether=1:1/v:v). The products **5ad** 380 mg were obtained in38% yield, and the major products **4** were obtained in 44%yield.

*4.1.15. 1,1,2,2,3,3,4,4,4-Nonafluoro-N-(2-methyl-5-nitrophenyl)butane-1-sulfonamide **5ad**[15].*



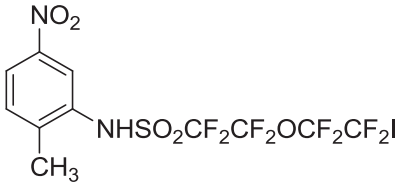
Yellow solid. Mp 83–85 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.35 (1H, d, J=1.8 Hz), 8.13 (1H, dd, J=2.4, 8.1 Hz), 7.47 (1H, d, J=9.0 Hz), 6.98 (1H, br s, NH), 2.50 (3H, s, $ArCH_3$). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −82.2 (3F, t, J=10.3 Hz, CF_3), −112.6 (2F, t, J=13.0 Hz, CF_2S), −122.3 (2F, s, CF_2), −127.4 (2F, t, J=14.7 Hz, CF_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.9, 140.6, 133.3, 131.9, 122.9, 120.8, 18.2. IR (KBr) cm^{-1}: 3295, 1542, 1430, 1353, 1200, 1144, 1035. MS (ESI) m/z: 432.7 ([M−H]$^-$). HRMS (ESI) m/z 432.9906 ([M−H]$^-$, $C_{11}H_6F_9N_2O_4S$: required 432.9910). Anal. Calcd for $C_{11}H_7F_9N_2O_4S$: C, 30.43; H, 1.62; N, 6.45%. Found: C, 30.89; H, 1.57; N, 6.20%.

*4.1.16. 1,1,2,2-Tetrafluoro-N-(2-methyl-5-nitrophenyl)-2-(1,1,2,2-tetrafluoroethoxy)ethanesulfonamide **5bd**[15].*



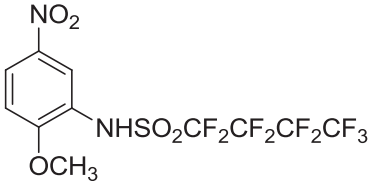
Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.34 (1H, s), 8.12 (1H, d, J=8.7 Hz), 7.45 (1H, d, J=8.7 Hz), 6.99 (1H, br s, NH), 5.86 (1H, t, J=52.5 Hz, HCF_2), 2.49 (3H, s, $ArCH_3$). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.2 (2F, t, J=12.4 Hz, CF_2O), −88.4 (2F, s, OCF_2), −115.0 (2F, s, CF_2S), −137.5 (2F, d, J=53.6 Hz, CF_2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.2, 141.3, 133.8, 132.2, 123.1, 121.3, 18.5. IR (KBr) cm^{-1}: 3297, 2927, 1722, 1531, 1429, 1351, 1284, 1143. MS (ESI) m/z: 430.8 ([M−H]$^-$). HRMS (ESI) m/z 430.9949 ([M−H]$^-$, $C_{11}H_7F_8N_2O_5S$: required 430.9953).

*4.1.17. 1,1,2,2-Tetrafluoro-N-(2-methyl-5-nitrophenyl)-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonamide **5cd**[15].*



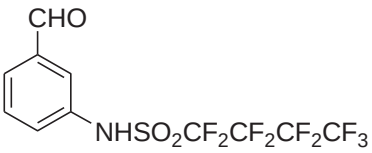
Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.34 (1H, s), 8.12 (1H, d, J=8.4 Hz), 7.45 (1H, d, J=8.7 Hz), 7.08 (1H, br s, NH), 2.50 (3H, s, $ArCH_3$). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −65.0 (2F, d, J=8.2 Hz, ICF_2), −81.3 (2F, t, J=12.4 Hz, CF_2O), −85.3 (2F, s, OCF_2), −114.6 (2F, s, CF_2S). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.1, 141.5, 133.9, 132.3, 123.1, 121.3, 116.0 (tt, J=30.6, 288.0 Hz), 115.2 (tt, J=31.4, 286.5 Hz), 113.5 (tt, J=37.2, 295.6 Hz), 89.0 (tt, J=41.5, 317.9 Hz), 18.5. IR (KBr) cm^{-1}: 3291, 2928, 1707, 1529, 1434, 1349, 1137, 1092. MS (ESI) m/z: 556.7 ([M−H]$^-$). HRMS (ESI) m/z 556.8908 ([M−H]$^-$, $C_{11}H_6F_8IN_2O_5S$: required 556.8920).

*4.1.18. 1,1,2,2,3,3,4,4,4-Nonafluoro-N-(2-methoxy-5-nitrophenyl)butane-1-sulfonamide **5ae**[15].*



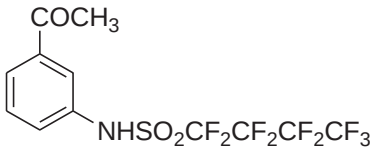
Black oil. ^{1}H NMR (acetone-d_6, 300 MHz): δ 8.38 (1H, d, J=1.8 Hz), 8.07 (1H, dd, J=1.8, 6.6 Hz), 7.24 (1H, d, J=6.6 Hz), 4.05 (3H, s, OCH_3). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −80.9 (3F, t, J=10.3 Hz, CF_3), −111.4 (2F, t, J=14.4 Hz, CF_2S), −121.2 (2F, s, CF_2), −126.2 (2F, t, J=12.4 Hz, CF_2). ^{13}C NMR (acetone−d_6, 100 MHz): δ 159.1, 142.1, 130.3, 122.2, 120.2, 112.0, 57.2. IR (KBr) cm^{-1}: 3267, 2925, 1714, 1599, 1524, 1346, 1191, 1093. MS (ESI) m/z: 448.8 ([M−H]$^-$). HRMS (ESI) m/z 448.9874 ([M−H]$^-$, $C_{11}H_6F_9N_2O_5S$: required 448.9859).

*4.1.19. 1,1,2,2,3,3,4,4,4-Nonafluoro-N-(3-aldehydylphenyl)butane-1-sulfonamide **7da**[15].*



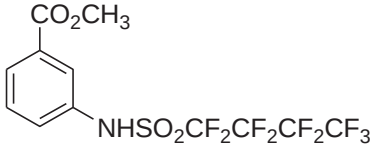
Red-brown solid, mp 89–91 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.02 (1H, s, CHO), 7.86–7.82 (1H, m), 7.80 (1H, br s, NH), 7.62–7.60 (2H, m), 7.30 (1H, br s). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −80.7 (3F, m, CF_3), −111.2 (2F, m, CF_2S), −120.9 (2F, m, CF_2), −125.8 (2F, m, CF_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 192.2, 137.3, 135.7, 130.5, 128.9, 128.6, 122.9. IR (KBr) cm^{-1}: 3088, 2847, 1682, 1588, 1514, 1441, 1162, 1139. MS (ESI) m/z: 426.0 ([M+Na]$^+$). HRMS (EI) m/z calcd for $C_{11}H_6F_9NO_3S$: 402.9925; found: 402.9926.

4.1.20. 1,1,2,2,3,3,4,4,4-Nonafluoro-N-(3-acetylphenyl)butane-1-sulfonamide ***7db***[15].



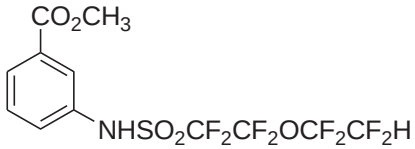
White solid, mp 98–100 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.95 (1H, br s), 7.93 (1H, br s, NH), 7.88 (1H, t, J=7.8 Hz), 7.63 (1H, dd, J=1.5, 8.4 Hz), 7.53 (1H, t, J=8.1 Hz), 2.65 (3H, s, $COCH_3$). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.1 (3F, t, J=9.9 Hz, CF_3), −111.0 (2F, t, J=14.1 Hz, CF_2S), −121.4 (2F, m, CF_2), −126.3 (2F, dt, J=7.6, 13.5 Hz, CF_2). IR (KBr) cm^{-1}: 3160, 1685, 1432, 1382, 1189, 1132, 1037. MS (ESI) m/z: 439.9 ([M+Na]$^+$). HRMS (ESI) m/z 439.9987 ([M+Na]$^+$, $C_{12}H_8F_9NO_3SNa$ required 439.9973). Anal. Calcd for $C_{12}H_8F_9NO_3S$: C, 34.54; H, 1.93; N, 3.36%. Found: C, 34.42; H, 1.95; N, 3.33%.

4.1.21. Methyl,N-(perfluorobutane-1-sulfonamide)aminobenzoate ***7dc***[15].



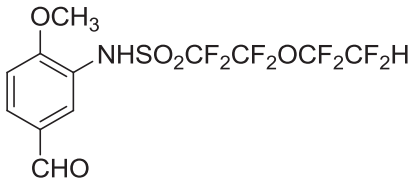
White solid, mp 124–126 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.04 (1H, br s), 7.97 (1H, d, J=8.1 Hz), 7.92 (1H, br s, NH), 7.67 (1H, dd, J=1.8, 8.4 Hz), 7.50 (1H, t, J=8.1 Hz), 3.97 (3H, s, OCH_3). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.1 (3F, t, J=9.3 Hz, CF_3), −111.0 (2F, t, J=12.4 Hz, CF_2S), −121.5 (2F, m, CF_2), −126.4 (2F, d-t, J=3.0, 14 Hz, CF_2). IR (KBr) cm^{-1}: 3180, 1708, 1484, 1381, 1187, 1134, 1039. MS (ESI) m/z: 455.9 ([M+Na]$^+$). HRMS (ESI) m/z 455.9939 ([M+Na]$^+$, $C_{12}H_8F_9NO_4SNa$ required 455.9923). Anal. Calcd for $C_{12}H_8F_9NO_4S$: C, 33.27; H, 1.86; N, 3.23%. Found: C, 33.28; H, 1.95; N, 3.19%.

4.1.22. Methyl,N-(2-(1,1,2,2-tetrafluoroethoxyl)-1,1,2,2-tetrafluoroehthane-1-sulfonamide) aminobenzoate ***7bc***[15].



Yellow solid, mp 59–61 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.99–7.97 (1H, m), 7.95 (1H, br s, NH), 7.63–7.60 (2H, m), 7.48 (1H, t, J=8.1 Hz), 5.84 (1H, tt, J=3.0, 52.5 Hz, HCF_2), 3.96 (3H, s, OCH_3). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.2 (2F, m, CF_2O), −88.2 (2F, m, OCF_2), −114.1 (2F, s, CF_2S), −137.2 (2F, m, CF_2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.2, 135.3, 131.1, 129.9, 127.8, 126.7, 123.6, 52.9. IR (KBr) cm^{-1}: 3286, 1716, 1592, 1443, 1396, 1331, 1230, 1012. MS (ESI) m/z: 453.9 ([M+Na]$^+$). HRMS (ESI) m/z 453.9956 ([M+Na]$^+$, $C_{12}H_9F_8NO_5SNa$ required 453.9966).

4.1.23. 3-N-(2-(1,1,2,2-Tetrafluoroethoxyl)-1,1,2,2-tetrafluoroehthane-1-sulfonamide)amino-4-methoxyl benzaldehyde ***7bd***[15].



Yellow solid, mp 108–110 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.89 (1H, d, J=1.2 Hz, CHO), 8.06 (1H, t, J=1.8 Hz), 7.79 (1H, dt, J=1.5, 8.7 Hz), 7.08 (1H, dd, J=1.2, 8.4 Hz), 5.86 (1H, tt, J=1.8, 52.5 Hz, HCF_2), 4.01 (3H, d, J=0.9 Hz, OCH_3). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −81.2 (2F, t, J=13.1 Hz, CF_2O), −88.3 (2F, m, OCF_2), −115.0 (2F, s, CF_2S), −137.3 (2F, dt, J=4.5, 52.2 Hz, CF_2H). ^{13}C NMR (acetone-d_6, 75 MHz): δ 190.6, 158.4, 131.2, 130.6, 126.1, 125.9, 112.3, 56.5. IR (KBr) cm^{-1}: 3034, 2876, 1665, 1605, 1512, 1125, 1020. MS (EI) m/z: 431 (M$^+$, 25), 150 (M$^+$−R_fSO_2, 100). HRMS (EI) m/z calcd for $C_{12}H_9F_8NO_5S$: 431.0074; found: 431.0081.

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References and notes

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15. In the ^{13}C-NMR spectrum of all these products, chemical shift and the comploug constants for the fluorinated carbon are complicated and not be assigned.