Supporting Online Material for

Design, synthesis, and evaluation of a highly effective and safe perfluoro-alternative with "weak site" : potassium 1,1,2,2,3,3,4,4-octafluoro-4-(perfluorobutoxy)butane-1-sulfonate

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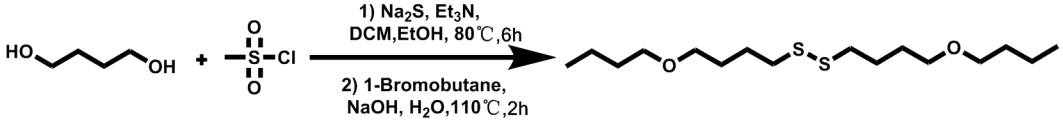
Materials and Methods

Unless otherwise noted, all the materials and solvents were purchased from commercial suppliers and used without further purification. MeOH (performance liquid chromatography) was purchased from Alfa Aesar. $CDCl_3$, Acetone-d_6 and MeOH-d_4 were purchased from Sigma-Aldrich. TLC was performed on silica gel Huanghai $HSGF_{254}$ plates and visualized by quenching of UV fluorescence (λ_{max}= 254 nm). Silica gel (200–300 mesh) was purchased from Qingdao Haiyang Chemical Co., China. ^1H NMR and ^{13}C NMR were recorded on a Bruker AVANCE AV 400 (400MHz and 101MHz). Signal positions were recorded in ppm with the abbreviations s, d, t and m denoting singlet, doublet, triplet, and multiplet respectively. All NMR chemical shifts were reported with the solvent resonance as internal standard. For ^1H NMR: $CDCl_3$ = δ 7.26 ppm, Acetone-d_6 = δ 2.05 ppm, MeOH-d_4 = δ 4.87 ppm. For ^{13}C NMR: $CDCl_3$ = δ 77.1 ppm, Acetone-d_6 = δ 29.9 ppm, δ 206.6 ppm, MeOH-d_4 = δ 48.8 ppm. Mass spectra were acquired on quadrupole/electrostatic field orbitrap high resolution mass spectrometry, Q/OrbitrapHRMS Thermo Q Exactive.

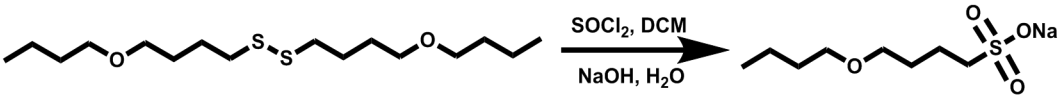
Experimental Data

Synthesis of 1,2-bis(4-butoxybutyl)disulfane



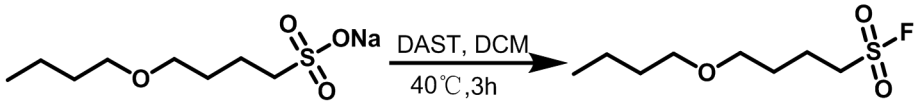
To a solution of 1,4-butanediol (10 g, 110.9 mmol, 1.0 equiv) and triethylamine (12.4 g, 122 mmol, 1.1 equiv) in dichloromethane (80 mL), methanesulfonyl chloride (12.7 g, 110.96 mmol, 1.0 equiv) was slowly added dropwise at 0 °C with stirring for 1 h, and then gradually raising the temperature to 40 °C under reflux for 3 h. After the completion of the reaction, the mixture was then quenched with a saturated sodium thiosulfate solution, and extracted with dichloromethane. The layers were sequentially washed with water and saturated brine, dried, and distilled under reduced pressure to obtain 15.8 g of a colorless oil. This oil was dissolved in ethanol (50 mL), and dried sodium sulfide (8.66 g, 111 mmol, 1.0 equiv) was added. The reaction was refluxed at 80 °C for another 3 h, the temperature was reduced, then concentrated under reduced pressure to obtain the residue without purification for the next reaction (8.2 g of colorless liquid). Then added bromo-n-butane (16.5 g, 122 mmol, 1.1 equiv), ethanol (150 mL), and followed by 3 mol/L sodium hydroxide solution (25 mL) was added dropwise into the mixture at room temperature with stirring at 110 °C for 2 h. After the reaction was completed, the pH of the system was adjusted to neutral, and then the organic phase was obtained by extraction with dichloromethane. The reaction system was distilled under reduced pressure to obtain the yellow oil (12.2 g, 68% yield). R_f = 0.40 (hexanes/ EtOAc 12:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.42 (m, 8H), 2.71 (t, *J = 12 Hz*, 3H), 1.76 (m, 4H), 1.65 (m, 5H), 1.54 (m, 4H), 1.36 (m, 4H), 0.91 (t, *J = 12 Hz*, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 70.8, 70.3, 38.9, 31.9 , 28.6, 26.1, 19.4, 14.0. HRMS-ESI (m/z): Calcd for $C_{16}H_{35}O_2S_2$, $[M+H]^+$ is 323.20785. Found, 323.20767.

Synthesis of sodium 4-butoxybutane-1-sulfonate using by 1,2-bis(4-butoxybutyl)disulfane



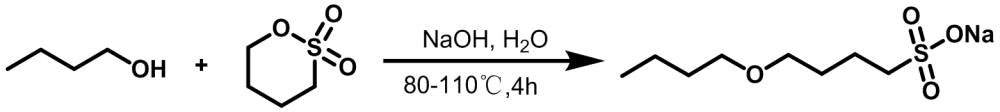
To a solution of 1,2-bis(4-butoxybutyl)disulfane (5 g, 15.5 mmol, 1.0 equiv) in dichloromethane (50 mL), thionyl chloride (11.2 mL, 154 mmol, 5.0 equiv) was slowly added dropwise at room temperature and stirred for 1 h, the system was heated to reflux for 12 h. Then 3 mol/L sodium hydroxide aqueous solution (10 mL) was dropwise added to reaction mixture at room temperature, and continued to stir for 1 h. The reaction system was distilled under reduced pressure to move the solvent, and dried under reduced pressure to obtain the title compound (6.2 g of white solid, 86% yield). R_f = 0.40 (hexanes/ EtOAc 2:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, MeOD) δ 3.40 (t, *J = 12 Hz*, 2H), 3.35 (t, *J = 12, 4.7 Hz*, 2H), 2.79 (d, *J = 8.0 Hz*, 2H), 1.82 (m, 2H), 1.64 (m, 2H), 1.50 (m, 2H), 1.33 (m, 2H), 0.88 (t, *J = 4.8 Hz*, 2H). ^{13}C NMR (400 MHz, MeOD) δ 71.2, 62.3, 52.2, 32.7 , 29.6, 22.8, 20.2, 14.0. The theoretical calculated value of $C_8H_{17}NaO_4S$, $[M-Na]^-$ is 209.08475, found 209.08536 (HRMS).

Snthesis of 4-butoxybutane-1-sulfonyl fluoride using by DAST



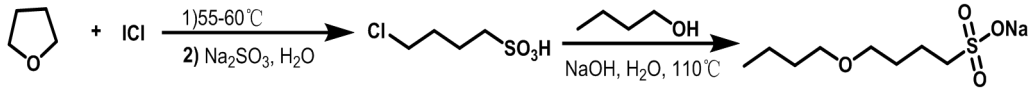
To a solution of sodium 4-butoxybutane-1-sulfonate (100.6 g, 0.433 mol, 1.0 equiv) in dichloromethane (2 L), Diethylaminosulfur trifluoride (DAST, 74.9 g, 0.465 mol, 1.07 equiv) was slowly added at 0 °C with stirring. After the dropwise addition, the temperature was raised to 40 °C and the reaction was stirred for 24-28 hours. After the reaction was completed, the white solid was filtered off (recyclable as starting material). The filtrate was washed twice with purified water, and the obtained organic phase was dried by Na_2SO_4, and then dichloromethane was recovered by distillation under reduced pressure to obtain the title product as a brown-red liquid(the boiling point is 60-65 ^oC at 0.05Mpa)(58 g , 63% yield). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 3.41 (t, *J = 12 Hz*, 2H), 3.39 (t, *J = 12 Hz*, 2H), 3.33 (t, *J = 8.4 Hz*, 2H), 1.97 (m, 2H), 1.67 (m, 2H), 1.47 (m, 2H), 1.28 (m, 2H), 0.85 (t, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 69.4, 53.3, 50.50, 31.6, 27.6, 20.9, 19.2, 13.7. ^{19}F NMR (400 MHz, $CDCl_3$) δ 53.5 (s). $C_8H_{17}FO_3S$, $[M]^-$ is 212.08824, found 212.08765(HRMS).

Snthesis of sodium 4-butoxybutane-1-sulfonate using by 1,4-Butane sultone



To a solution of n-butanol(80 g, 1.08 mol, 1.0 equiv) in sodium hydroxide aqueous solution(250 g, 22% by mass), 1,4-butanesultone(150 g, 1.1 mol, 1.01 equiv) was dropwise added with stirring at 80 °C, then the system was stirred at 110 °C for 6 h. After the reaction was completed, the volatile components were distilled off under reduced pressure. The target product was obtained by drying the residue as a pale yellow solid(242 g, 96.5% yield).

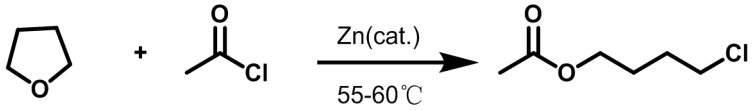
Snthesis of sodium 4-butoxybutane-1-sulfonate using by Tetrahydrofuran and iodine chloride



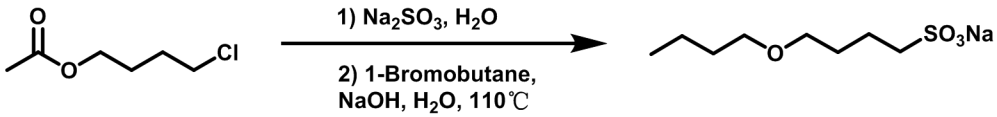
Tetrahydrofuran (2.08 g, 28.9 mmol, 1.0 equiv) and iodine chloride (4.68 g, 28.9 mmol, 1.0 equiv) were slowly mixed with stirring at -10 °C for 4 h. Then aqueous sodium sulfite (4.0 g, 31.7 mmol, 1.1 equiv) was dropwise added to the reaction system at room temperature. After the dropwise addition was completed, the mixture was stirred at 100 °C for another 12 h. The mixture which containing n-butanol(2.15 g, 28.9 mmol, 1.0 equiv) and sodium hydroxide aqueous solution(10.5 g, 22% by mass) was added to the system, then stirred at 110 °C for 10 h. After the reaction was completed, the aqueous phase was distilled under reduced pressure and

the residue was dried in vacuum to obtain the target product (4.7 g , 61% yield).

Snthesis of sodium 4-butoxybutane-1-sulfonate using by Tetrahydrofuran and zinc powder

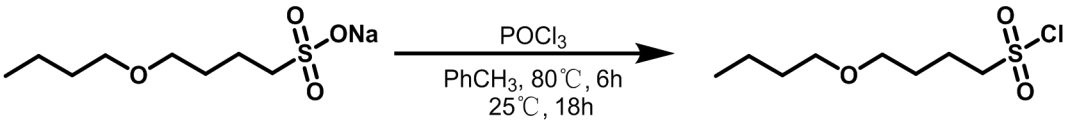


To a mixture of tetrahydrofuran(2.08 g, 28.9 mmol, 1.0 equiv) and zinc powder(18.5 mg, 0.289 mmol, 0.01 equiv), acetyl chloride(5.63 g, 72.3 mmol, 2.5 equiv) was dropwise added into it at 25 °C. After the dropwise addition, the reaction is held for half an hour, then slowly heated to 60 °C for 4 h. After the reaction was completed, the mixture was filtrated to gave crude chlorobutyl acetate. Then the residue was distilled under reduced pressure to obtain the target product(the boiling point is 55-60 ^{o}C at 0.05Mpa) (3.8 g , 87% yield). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (t, *J = 8 Hz*, 2H), 3.54 (t, *J = 8 Hz*, 2H), 2.02 (s, 3H), 1.80 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 170.3, 63.0, 44.0, 28.7, 25.6, 20.3.



4-chlorobutyl acetate (19.5 g, 167 mmol, 1.0 equiv) was mixed with 85 ml of sodium sulfite (23.3 g, 185 mmol, 1.1 equiv) aqueous solution, the temperature was raised to 105 °C, and the reaction was stirred for 8 h. Then sodium hydroxide (14.8 g, 370 mmol, 2.2 equiv) was added to the system, and followed by bromo-n-butane (27.9 g, 204 mmol, 1.2 equiv) was dropwise added into it, the mixture was stirred at 110 °C for 12 hours. After the reaction was completed, the volatile components and water are distilled off under reduced pressure, and then dried to obtain the target compound sodium 4-butoxy-1-butylsulfonate (330 g, 85% yield).

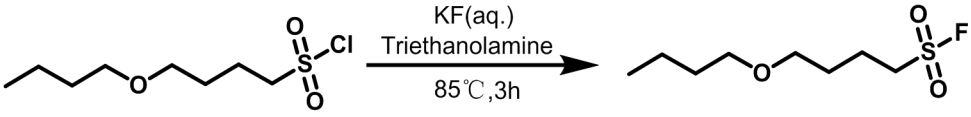
Snthesis of 4-butoxybutane-1-sulfonyl chloride using by sodium 4-butoxybutane-1-sulfonate



To a solution of sodium 4-butoxy-1-butylsulfonate(100 g, 0.43 mol, 1.0 equiv) in toluene(1 L) phosphorus oxychloride(250 g, 1.63 mol, 3.8 equiv) was slowly dropwise added into it, and the reaction was stirred at 80 °C for 8 h. Then the reaction was stirred at 25 °C for another 10 h. After the reaction was completed, the obtained organic phase was successively washed with water, sodium bicarbonate solution and saturated brine, dried over Na_2SO_4, and distilled off under reduced pressure to obtain the target product as a yellow liquid(the boiling point is 70-75 ^{o}C at 0.05Mpa) (59 g, 60% yield). R_f = 0.50 (hexanes/ EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (t, *J = 12 Hz*, 2H), 3.45 (t, *J = 12 Hz*, 2H), 3.15 (t , *J = 8.4 Hz*,

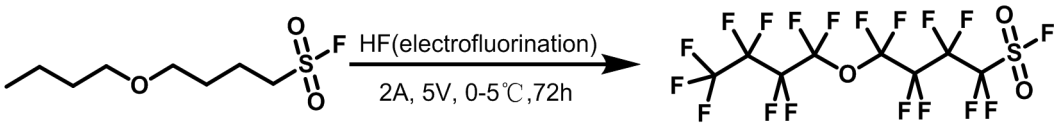
2H), 1.96 (m, 2H), 1.73 (m, 2H), 1.52 (m, 2H), 1.44 (m, 2H), 0.94 (t, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 51.3, 50.5, 42.4, 31.5, 24.6, 21.9, 18.7, 13.5. $C_8H_{17}ClO_3S$, $[M+Na]^+$ is 251.004846, found 251.004784(HRMS).

Snthesis of 4-butoxybutane-1-sulfonyl fluoride using by 4-butoxybutane-1-sulfonyl chloride



To a solution of sodium fluoride aqueous solution (105 g, 1.81 mol, 1.0 equiv), triethanolamine (486 g, 3.26 mol, 1.8 equiv) and 4-butoxy-1-butylsulfonyl chloride (412 g, 1.81 mol, 1.0 equiv) were added at room temperature. The reaction mixture was stirred at 85 °C for 3 h. After completion of the reaction, the reaction mixture was extracted with dichloromethane (200mL *3). The organic layer was washed with water, then was dried over $MgSO_4$. After removal of the solvent, the residue was distilled under reduced pressure to afford the title product(the boiling point is 60-65 °C at 0.05Mpa) (326 g, 85% yield). R_f = 0.40 (hexanes/ EtOAc 5:1 (v/v)).^{1}H NMR (400 MHz, $CDCl_3$) δ 3.41 (t, *J = 12 Hz*, 2H), 3.39 (t, *J = 12 Hz*, 2H), 3.33 (t, *J = 8.4 Hz*, 2H), 1.97 (m, 2H), 1.67 (m, 2H), 1.47 (m, 2H), 1.28 (m, 2H), 0.85 (t, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 69.4, 53.3, 50.50, 31.6, 27.6, 20.9, 19.2, 13.7. ^{19}F NMR (400 MHz, $CDCl_3$) δ 53.5 (s). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_8H_{17}FO_3S$ $[M]^-$, 212.08824. Found, 212.08765.

Snthesis of 1,1,2,2,3,3,4,4-octafluoro-4-(perfluorobutoxy)butane-1-sulfonyl fluoride



To a solution of hydrogen fluoride in a carbon steel alloy reactor(50 L), electrolysis fluorination anode and cathode used nickel alloy plate material, a current of 2 A, a voltage of 5 V, and 1 kg of 4-butoxy-1-butylsulfonyl fluoride were added in batches. A very small amount of water was removed from the liquid hydrogen fluoride solution for 3-5 hs at -40 °C. The reaction mixture was stirred for 72 hs at 0-5 °C. After electrolysis fluorination, it was allowed to stand, excess calcium chloride was added in batches to the aqueous solution containing hydrogen fluoride in the upper layer under stirring. After precipitation was obtained, the mother liquid is filtered with sodium hydroxide aqueous solution to adjust the pH value to 6-7, and the calcium fluoride is obtained by solid drying. The lower layer was obtained to obtain a target product as a pale yellow liquid, the liquid was washed in batches with a large amount of pure water(500 mL*3), and then it was extracted and separated to collect the lower fluorine phase liquid. The resulting aqueous phase is combined with the upper liquid after the reaction. Finally, fluorine phase liquid was purified by distilling under reduced pressure to afford the title product (1,1,2,2,3,3,4,4-octafluoro-4-(perfluorobutoxy)butane-1-sulfonyl fluoride)(the boiling point is 75-80 °C at 0.01Mpa)(8% yield). NMR Spectroscopy: ^{19}F NMR (400 MHz, DMSO-D_6) δ 44.1, -83.5,

-84.6, -84.9, -110.1, -112.0, -126.9, -128.2, -128.4. ^{13}C NMR (400 MHz, DMSO-D_6) δ 120.1, 119.2, 116.3, 114.9~113.8, 113.0~112.2, 111.7, 110.5~109.2, 106.4~106.3.

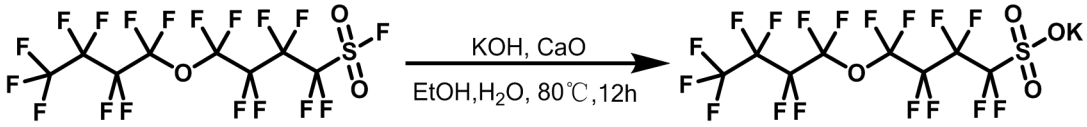
In order to improve the electrolytic fluorination efficiency, butane-1-sulfonyl fluoride or methylcyclohexane was added to the electrolytic fluorination system. The optimization batches and results are shown in the table below:

Table S1. The optimization effect table of electrolytic fluoridation yield using different additives

Added compounds	The mole ratio of the added compound to BBSF	Electrolytic fluorination yield
None	-	6.2%
Butane-1-sulfonyl fluoride	1:1	8%
Toluene	1:1	7.5%
Methylcyclohexane	1:1	7.2%
Methylcyclohexane[a]	1:1	7.5%
Toluene and methylcyclohexane (1:1)	1:1	7.1%

a. add to the system in batches

Snthesis of potassium 1,1,2,2,3,3,4,4-octafluoro-4-(perfluorobutoxy)butane-1-sulfonate



To a solution of potassium hydroxide (2 g, 35.7 mmol, 1.0 equiv) in ethanol and H_2O(v/v=3:1), calcium oxide (2 g, 64.3 mmol, 1.8 equiv) and 1,1,2,2,3,3,4,4-octafluoro-4-(perfluorobutoxy)butane-1-sulfonyl fluoride (5g, 35.7 mmol, 1.0 equiv) were added at room temperature. The reaction mixture was stirred at 80 ºC for 12 h. The mixture was filtered while hot, and the obtained residue was evaporated to dryness, and then recrystallized at -20 ºC to give 4.8 g of the desired compound (potassium 1,1,2,2,3,3,4,4-octafluoro-4-(perfluorobutoxy)butane-1-sulfonate)(F404K)as a white solid(85% yield). NMR Spectroscopy: ^{19}F NMR (400 MHz, CD_3OD) δ -82.6, -84.3, -84.5, -115.9, -112.1, -126.5, -127.7. ^{13}C NMR (400 MHz, CD_3OD) δ 121.3, 119.0, 116.1~115.6, 113.3~111.8, 109.1, 108.0~107.7, 106.5~106.4, 105.3~105.0. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_8F_{17}KO_4S$, $[M-K]^-$ is 514.92458. Found, 514.92474. And the second-order mass spectrometry data is: The theoretical calculated value of $[C_4F_9O]^-$ is 234.99805, and the high-resolution mass spectrometer (HRMS-MS2) was determined to be 234.99802. The theoretical calculated value of $[C_3F_7]^-$ was 168.99888, and high-resolution mass spectrometry (HRMS-MS2) was determined to be 168.99884.

Surface tension test of perfluoro alternatives

The surface tension of the aqueous solution of F404K was tested under the platinum plate method in a JK99C automatic tensiometer according to the basic operation of the instrument. The surface tensions of similar structures and different types of perfluoro compounds were compared, that is, the surface tensions of three PFOS-K, F404K and FC-248 perfluoro compounds at the same temperature and different concentrations were compared. The results are shown in Figure

S1 below.

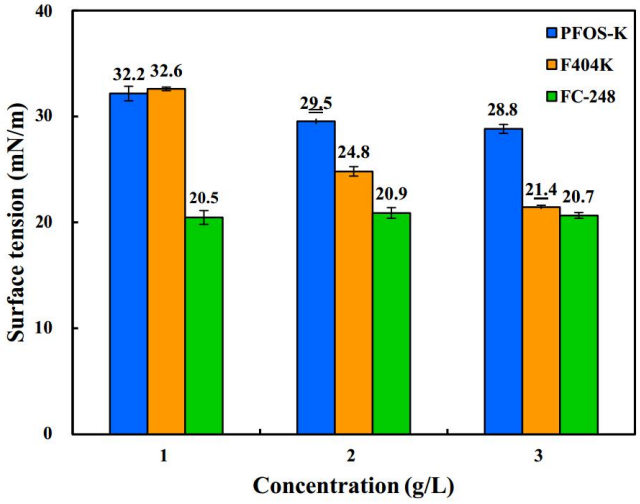


Figure S1 Comparison of surface tension of three different perfluoride compounds at different concentrations (22°C)

From the figure above, when using lower concentrations of perfluoro compounds, the surface tension values of PFOS-K and F404K were higher at 32.2 and 32.6, respectively. As the concentration increases, the surface tension of PFOS-K and F404 gradually decreases, but the surface tension value of FC-248 did not change much. The surface tension values of perfluoro compounds F404 and FC-248 were getting closer and closer. In contrast, the surface tension value of FC-248 was the lowest. Therefore, the F404K was better than the existing PFOS-K and had a surface-active effect close to that of FC-248.

According to the above method, the surface tension values of PFOS-K and F404K at the same temperature and different concentrations were compared as follows:

Table S2. surface tension values of two perfluorinated compounds at different concentrations

Sample	concentration (g/L)	F404K (mN/m)	PFOS-K (mN/m)	T (°C)
$1_{\text{Pure water}}$	0.0	72.9	71.9	28.0
$2_{\text{Pure water}}$	0.0	72.2	71.9	28.0
$3_{\text{Pure water}}$	0.0	72.5	71.2	28.0
4	0.1	45.0	54.8	28.0
5	0.1	46.4	54.9	28.0
6	0.1	45.0	54.7	28.0
7	0.2	35.8	47.1	28.0
8	0.2	36.3	48.0	28.0
9	0.2	35.0	47.8	28.0
10	0.3	29.3	44.9	28.0
11	0.3	29.8	43.2	28.0
12	0.3	29.7	43.7	28.0
13	0.4	26.6	41.2	28.0
14	0.4	25.6	40.5	28.0
15	0.4	25.6	40.5	28.0

16	0.6	23.8	37.0	28.0
17	0.6	22.4	36.7	28.0
18	0.6	22.1	37.1	28.0
19	0.8	22.9	35.6	28.0
20	0.8	22.5	35.8	28.0
21	0.8	22.2	35.6	28.0
22	1.0	20.0	35.7	28.0
23	1.0	19.8	36.1	28.0
24	1.0	19.8	36.2	28.0
25	2.0	18.2	30.2	28.0
26	2.0	17.9	29.6	28.0
27	2.0	18.0	28.9	28.0
28	3.0	18.2	27.0	28.0
29	3.0	18.2	27.0	28.0
30	3.0	18.1	26.8	28.0
31	4.0	18.1	24.6	28.0
32	4.0	18.1	24.9	28.0
33	4.0	18.1	25.3	28.0
34	5.0	18.2	24.8	28.0
35	5.0	18.2	24.6	28.0
36	5.0	17.6	25.7	28.0
37	6.0	18.3	24.6	28.0
38	6.0	17.8	24.8	28.0
39	6.0	17.9	25.0	28.0

Chrome mist inhibitor additive test

After testing the surface tension, in order to better verify the effectiveness of the newly synthesized perfluorinated substitute as a chromium mist inhibitor during electroplating, electroplating experiments were performed in the laboratory(Figure S2). The specific operations were: (1). Chromic acid solution preparation: Weight 200 g chromium trioxide in a 500 mL beaker, added distilled water, poured it into a 1L brown reagent bottle, add distilled water to dissolve, then added 1.08 mL concentrated sulfuric acid and made up to 1 L of aqueous solution, shaked well. (2). The amount of PFOS-K or F404K was added according to requirements. For 0.08 g/L PFOS-K chromic acid solution, adding 13.33 mL of 6 ‰ PFOS-K, PFOS-K to 1L chromic acid solution, F404K solution should be heated to complete the dissolution before adding. (3). Plating: The chromic acid solution was heated to 60 °C, and the voltage was kept constant to 15A, and the plating was performed. An absorption bottle containing 10 mL of a 2% nitric acid solution was placed at the mouth of the plating tank, and a continuous flow of 1.5 L/min was sampled. 0-1 min (sampling point 1), 2-3 min (sampling point 2), 4-5 min (sampling point 3), 6-7 min (sampling point 4), and 8-9 min (sampling) Point 5). The air sample at the

plating slot was diluted with 2% nitric acid and tested by ICP-MS for total chromium content (Sampling point 0 in the chromium plating haze curve was the sample from the beginning of chromic acid plating without added surfactant for 0-1 minutes). During electrolysis, if there was no addition of perfluorinated compounds, no bubbles would be generated. When adding 6 ‰ F404K aqueous solution, a large number of clear and transparent bubbles would appear within 1-2 seconds. The thickness of the bubbles was 2-4 cm. The solution was completely covered and was not easily broken, indicating that the perfluoro compound had a good effect of inhibiting the volatilization of chromium mist.

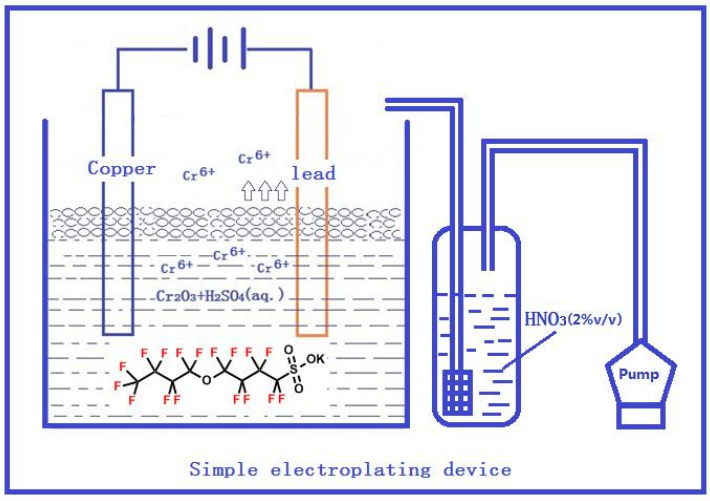


Figure S2 A simple device for the experiment of chromium inhibition

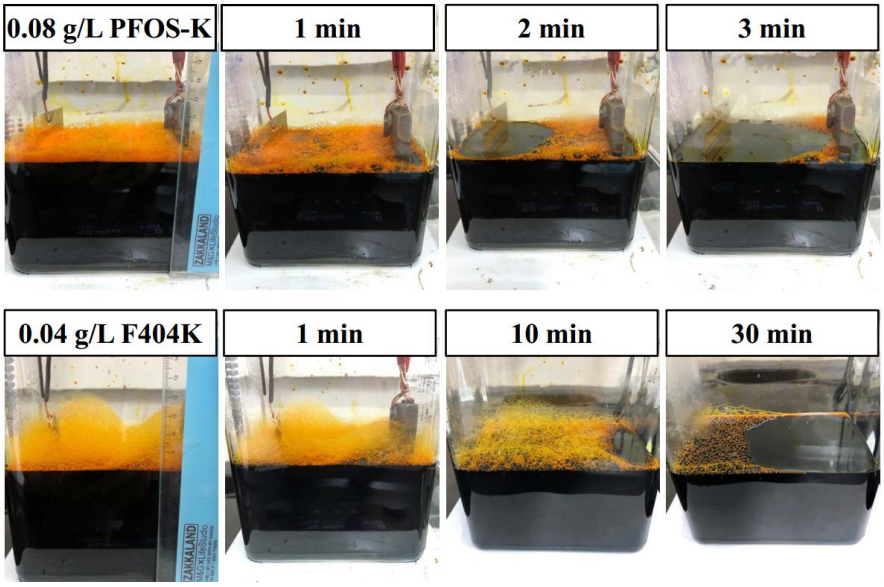


Figure S3 Comparison of defoaming time of two perfluorinated compounds at different concentrations

We also described that different concentrations of PFOS-K and F404K solutions were added to the plating system as chromium mist inhibitors. The concentration of chromium mist in the air

was detected to correspond to different time points. A comparative study on foam coverage, foaming time, foam thickness, and defoaming time were also conducted to evaluate the Chrome mist suppression effect. After plating, the defoaming time and corresponding thickness of each plating system were compared. The specific experimental phenomenon were shown in Figure S2. From the figure S3: when using 0.08 g/L PFOS-K as an additive, the defoaming time was 3 minutes after the end of electrolysis; 0.04 g/L F404K defoaming time was 30 minutes, low-concentration F404K had a higher concentration than PFOS-K better foam durability, which can better inhibit the volatilization of chromium mist at the end of electrolysis under high temperature conditions. From the above experimental data and phenomena, it was concluded that during and after the electrolysis, low concentration of F404K could replace the corresponding concentration of PFOS-K. There were certain advantages in bubble time, which can fundamentally provide health assurance to practitioners. At the same time, we had also explored the durability of F404K as a chromium mist inhibitor during electroplating. Using the same solution system, electroplating sampling was performed every 30 days to detect the content of chromium mist in the air. It was found that the perfluoro alternative F404K could be used continuously for a long time. Based on the above, from the perspective of small-scale experiments in the laboratory, the new perfluoro alternative F404K could be used in various aspects as a substitute for PFOS-K when used in chromium plating, which providing strong scientific research data support and guidance for industrial applications.

Cytotoxicity test

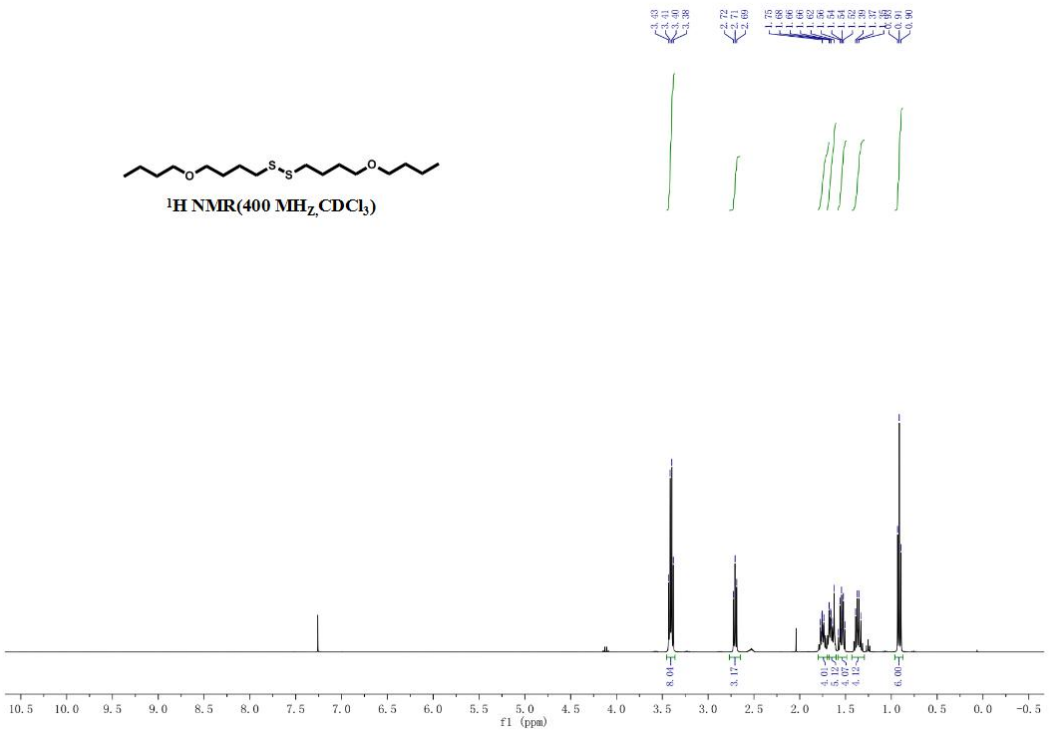
Subsequently, we performed a cytotoxicity test on the perfluoro alternative F404K. Common human liver cancer cells HepG2 were selected. Under the same experimental conditions, two other perfluorinated compounds F53B and PFOS-K were compared. The specific experimental steps were: human liver cancer cells HepG2 were digested and transferred to 96-well plates. 10,000 pieces/well. After the cells were allowed to adhere overnight, they were exposed to 100 μL of potassium 4-perfluorobutoxy-1-perfluorobutyl sulfonate (diluted to 10, 50, 100, 200, 500 and 1000 μM), and a blank control group was set at the same time, each group was 6 in parallel. After 24 hours of exposure, aspirate the exposure solution, add 100 μL of diluted CCK-8 reagent (10%, Biosharp) in the dark, and incubate in the carbon dioxide incubator for 2 hours. The microplate reader will detect the absorbance at 450 nm. Calculate the average and standard deviation of each group of data, and further convert it into a percentage relative to the control group. Using cell survival rate (%) as the Y value and F404K exposure concentration (mol/L) as the X value, a four-parameter logistic model was used to fit the curve, and the IC50 (half inhibitory concentration) value was determined to be 402 ± 21.9 μM . In the experiment, PFOS-K and F53B were used as positive control with the IC50 values were 245 ± 7.8 μM, 189 ± 15.3 μM respectively.

Study on degradability under acidic conditions

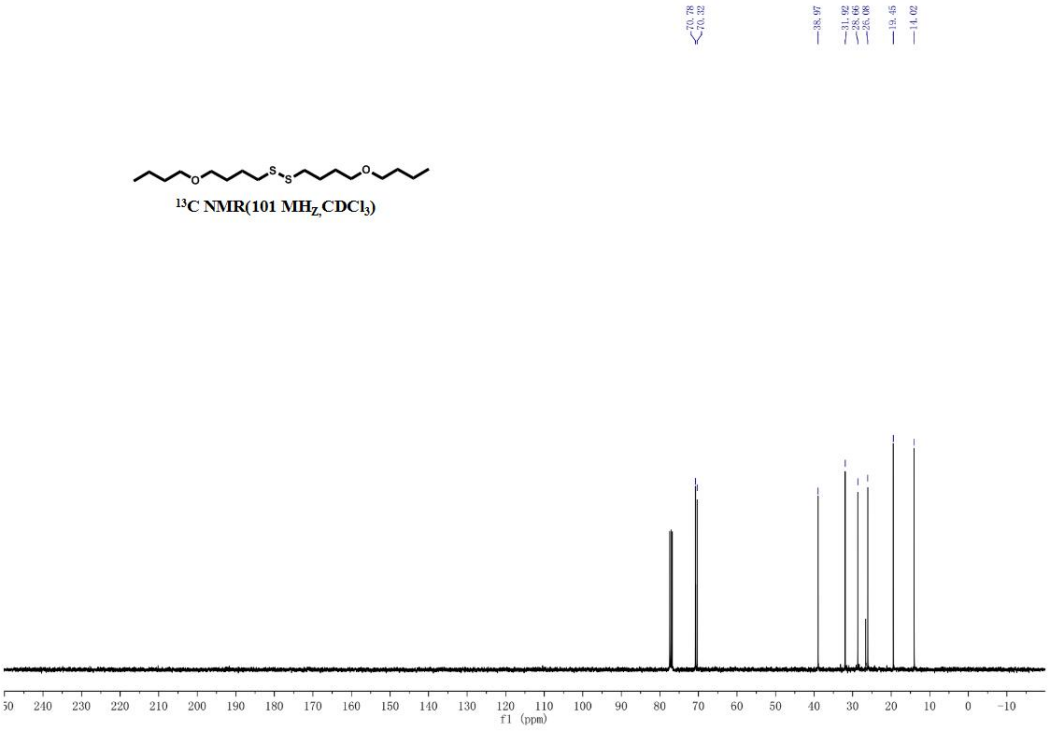
In order to study the stability of the substance and its impact on the environment, the acidic, hydrogen peroxide and titanium dioxide were used as photosensitizers under different conditions to investigate the degradation ability of F404K. (1). The specific experimental steps under acidic conditions were: dissolving F404K in deionized water to prepare two concentrations of 1 mg/L and 3 mg/L, then 9 mL samples were took of two concentrations to form A and B systems, 1 mL of hydrobromic acid aqueous solution (40%) was added, the system were heated to 110 °C and stirred for 4 h. Then the mixture were cooled to room temperature, the pH value of the system was adjusted to neutral by the aqueous solution. The contents of systems A and B were determined to be 185 ng/mL and 368 ng/mL by UPLC-MS/MS after the volume was adjusted. The detection system had established and completed the standard curve of correspondence between mass and concentration. Before the degradation reaction, the system concentration were 265 ng/mL and 696 ng/mL respectively, the degradation rates obtained were as follows: System A was (265-185) /265*100%=30.2%, System B was (696-368) /696*100%=47.1%.

It is preliminary indicated that the perfluoro alternative F404K could be degraded to a certain extent, and the degradation rate increases with increasing concentration under heated acidic conditions. (2). The specific steps of the 30% hydrogen peroxide solution degradation experiment were: F404K was dissolved in deionized water to make a concentration of 3 mg/L. 9.99 mL of water, 10 μL F404K aqueous solution (3 ‰), and 1 mL of hydrogen peroxide solution (30%) were mixxed, the system was stirred at 110 °C for 4 h. Then the mixture were cooled to room temperature, the pH value of the system was adjusted to neutral by the aqueous solution. The content of the test system was determined to be 320 ng/mL by UPLC-MS/MS after the volume was adjusted. Compared with the system concentration of 396 ng/mL before the degradation reaction, the obtained degradation rate was as follows: (396-320) /396*100%=19.2%, which indicating that the perfluoro alternative F404K could be degraded with a small amount under the conditions of hydrogen peroxide and heating.

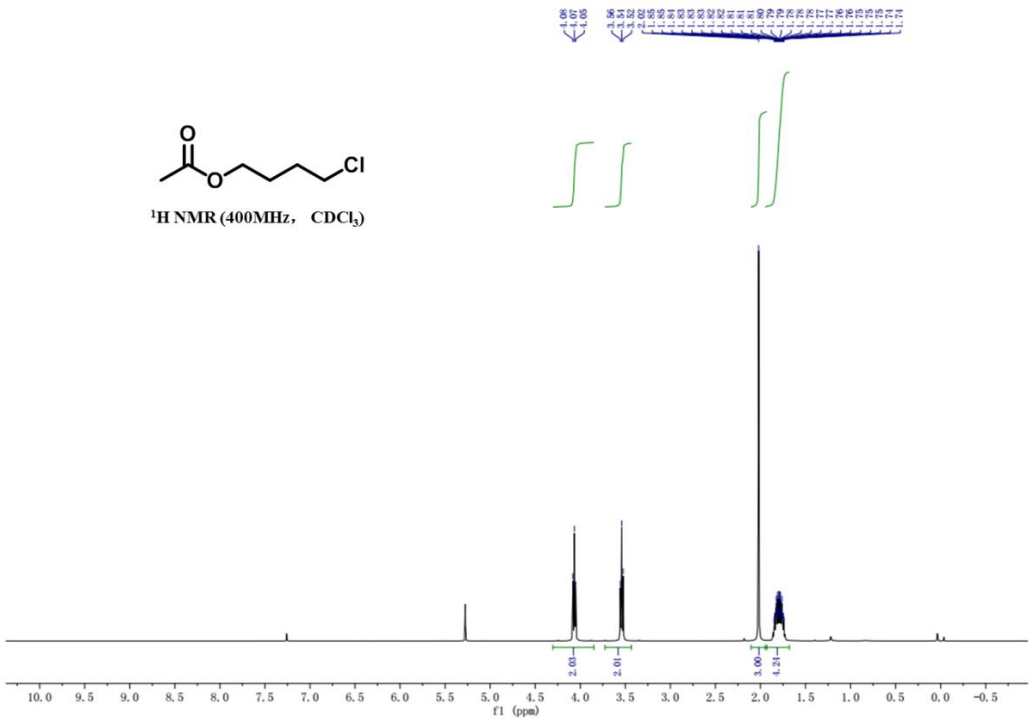
Nuclear Magnetic Resonance Spectrometry Data



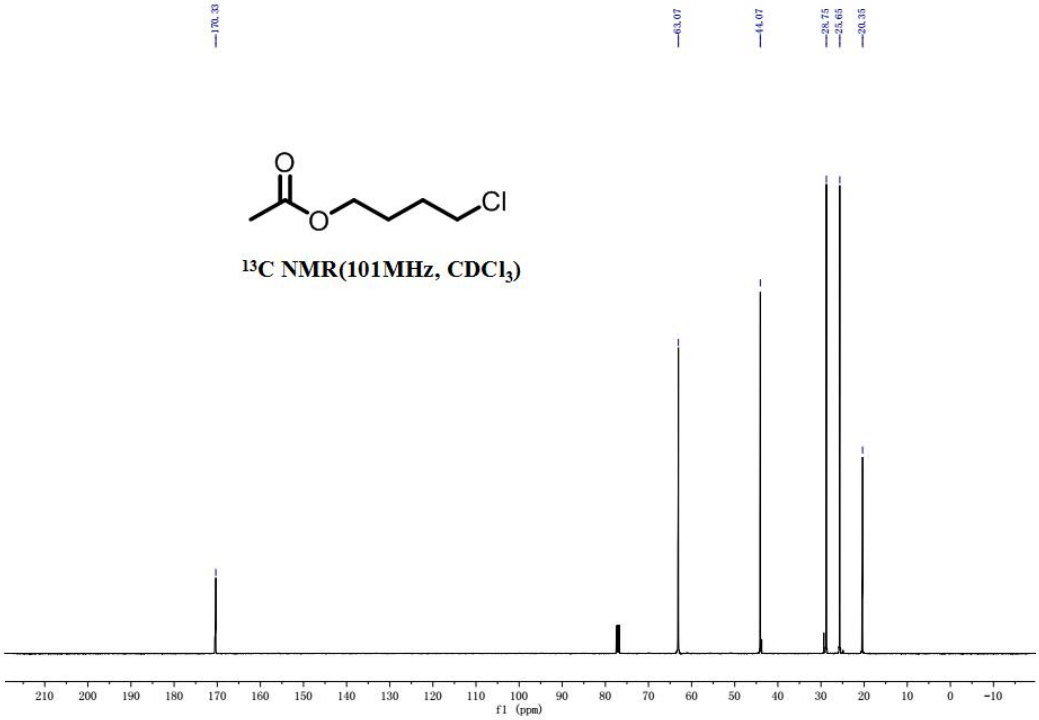
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 1,2-bis(4-butoxybutyl)disulfane



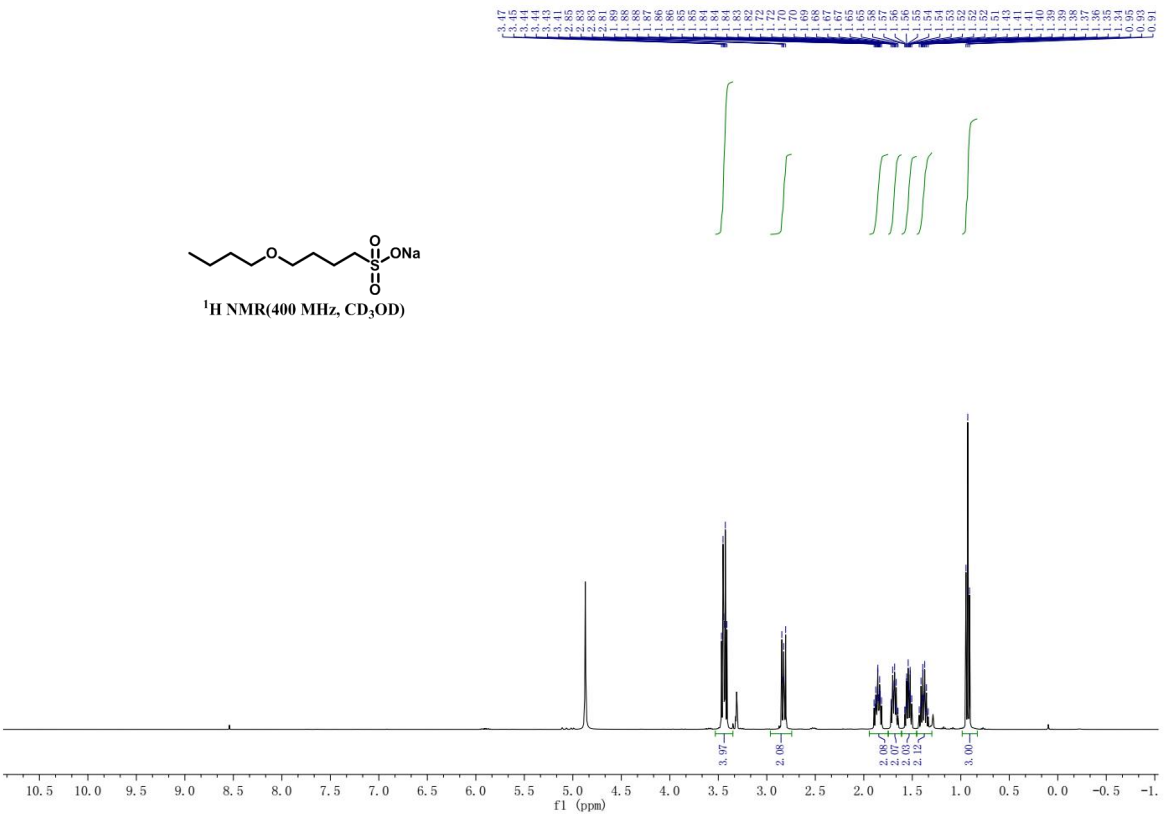
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of 1,2-bis(4-butoxybutyl)disulfane



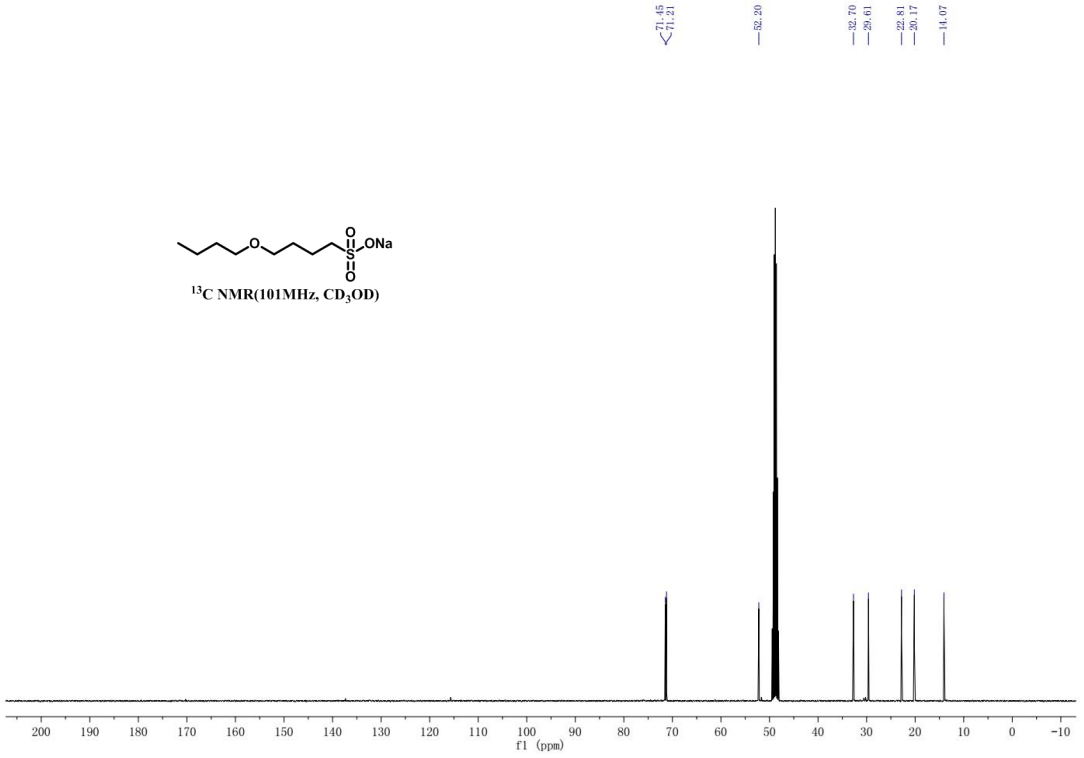
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 4-chlorobutyl acetate



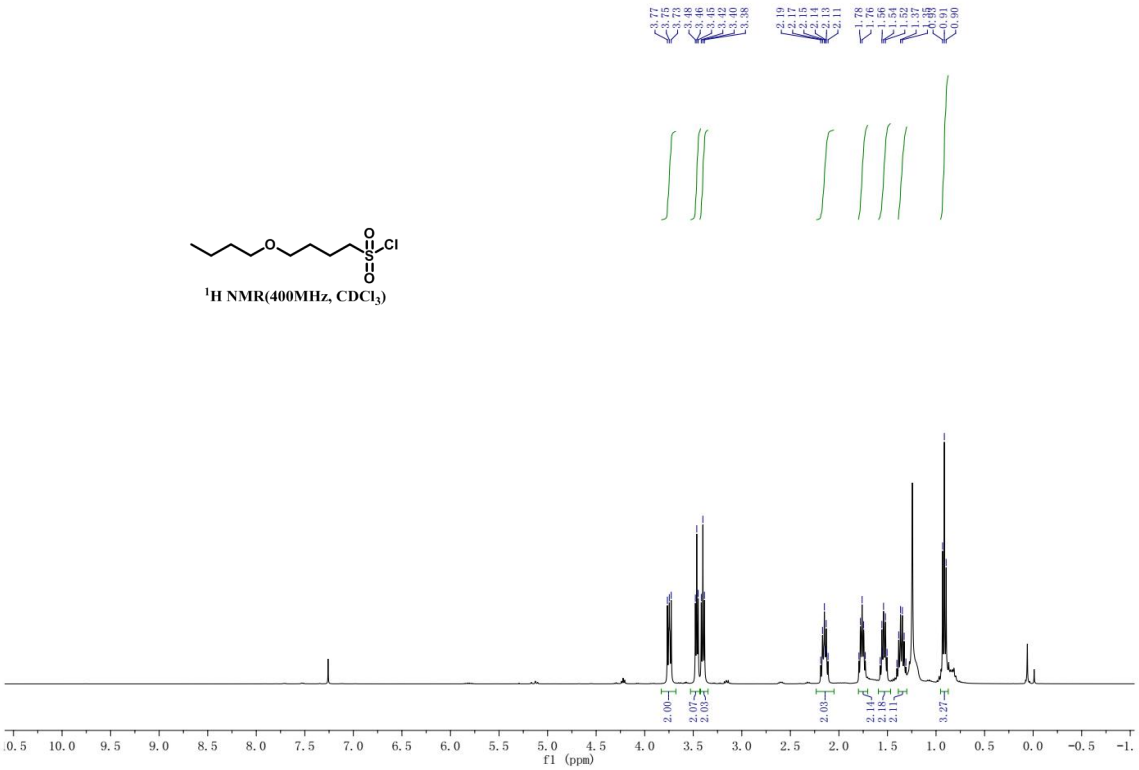
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of 4-chlorobutyl acetate



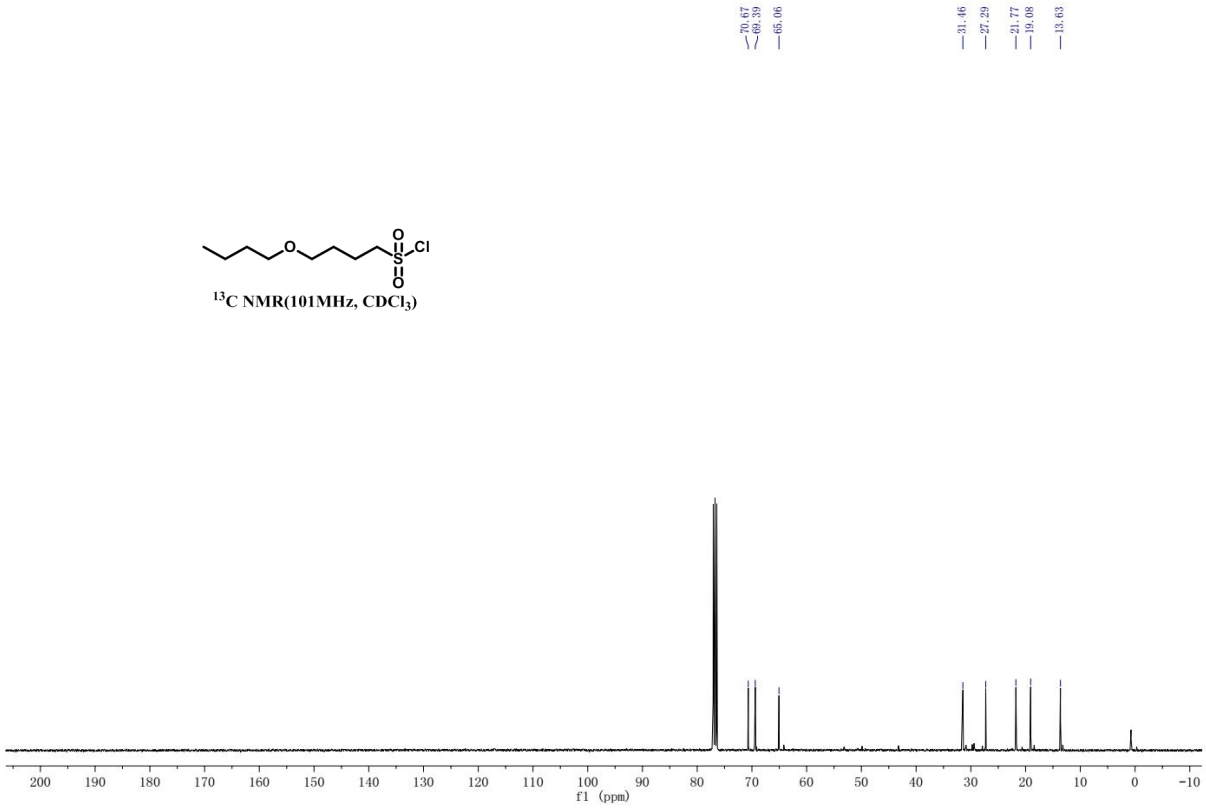
^{1}H NMR spectrum (400 MHz, CD_3OD, 23 ºC) of sodium 4-butoxybutane-1-sulfonate



^{13}C NMR spectrum (101 MHz, CD_3OD, 23 ºC) of sodium 4-butoxybutane-1-sulfonate



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 4-butoxybutane-1-sulfonyl chloride



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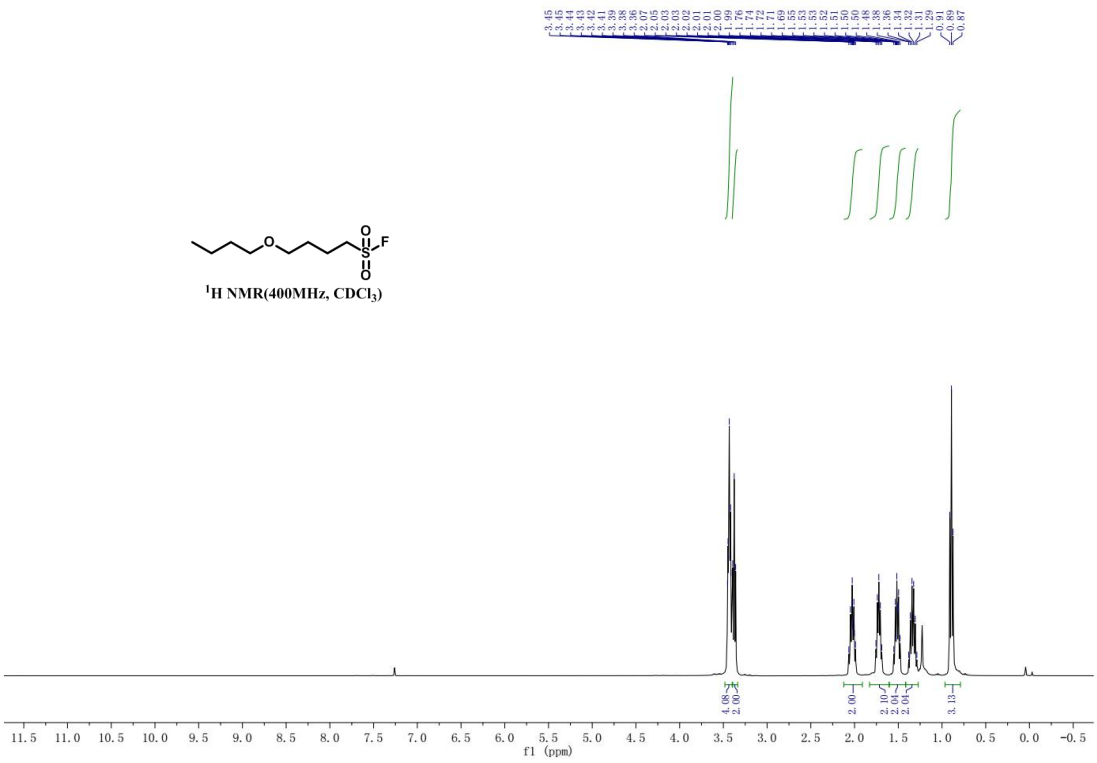
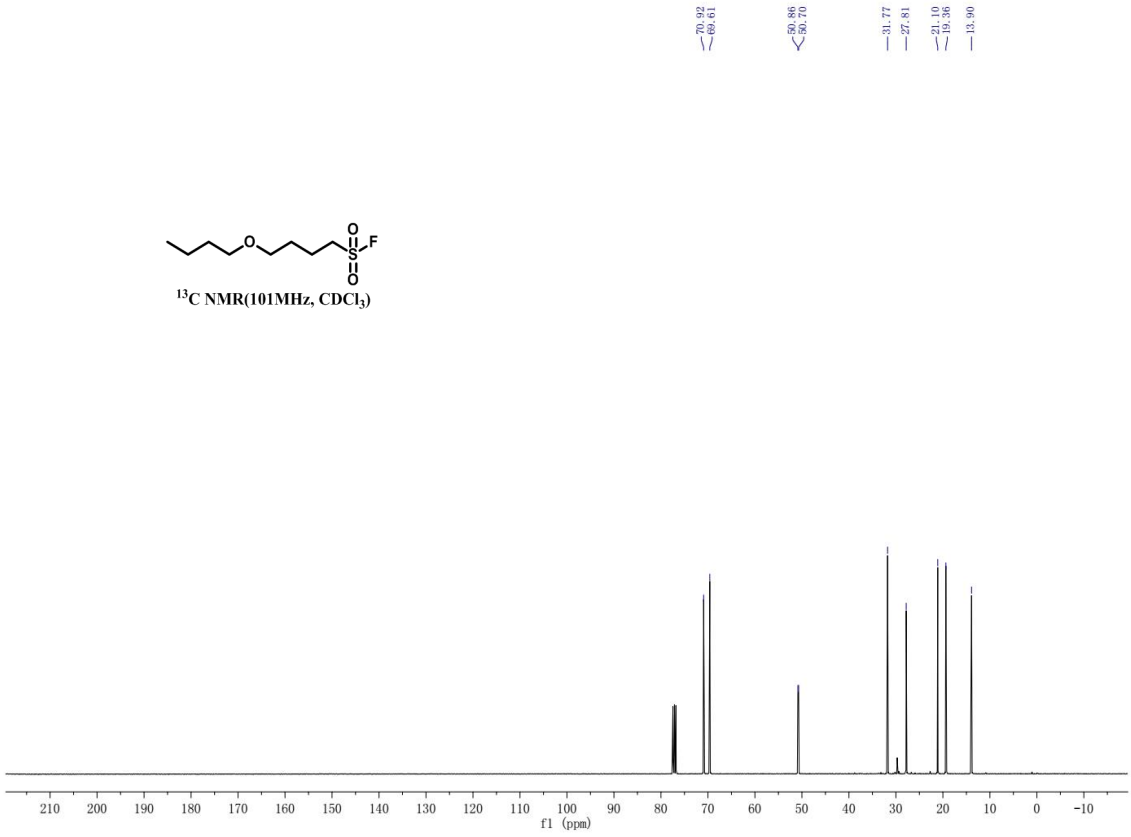
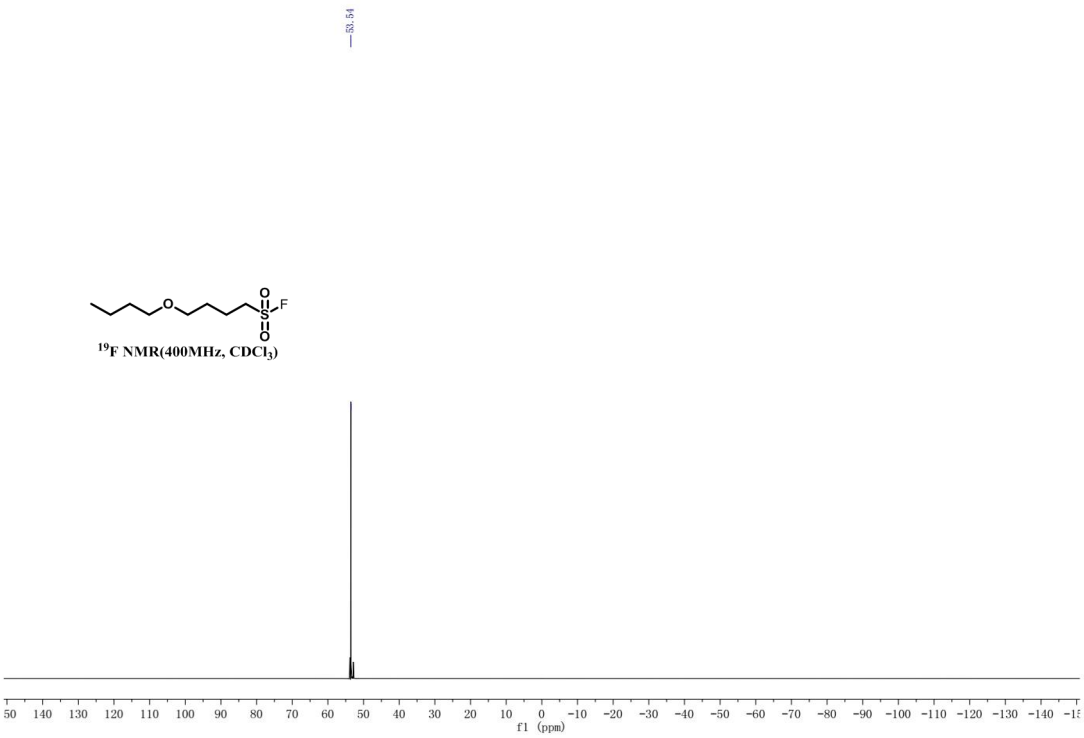


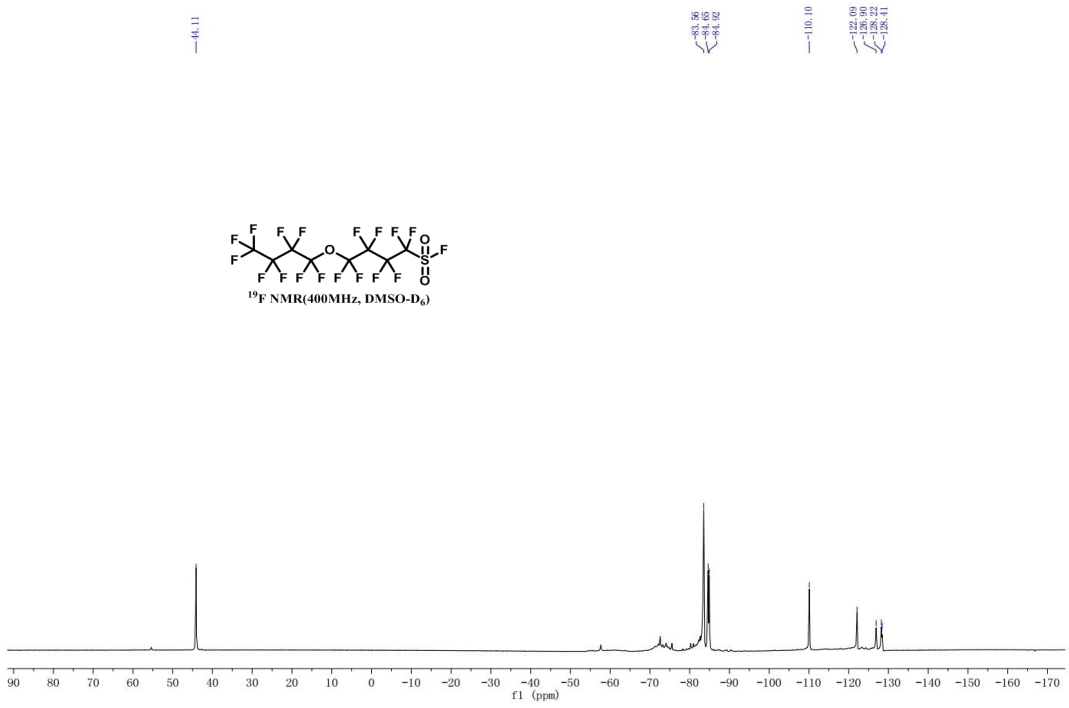
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 4-butoxybutane-1-sulfonyl fluoride



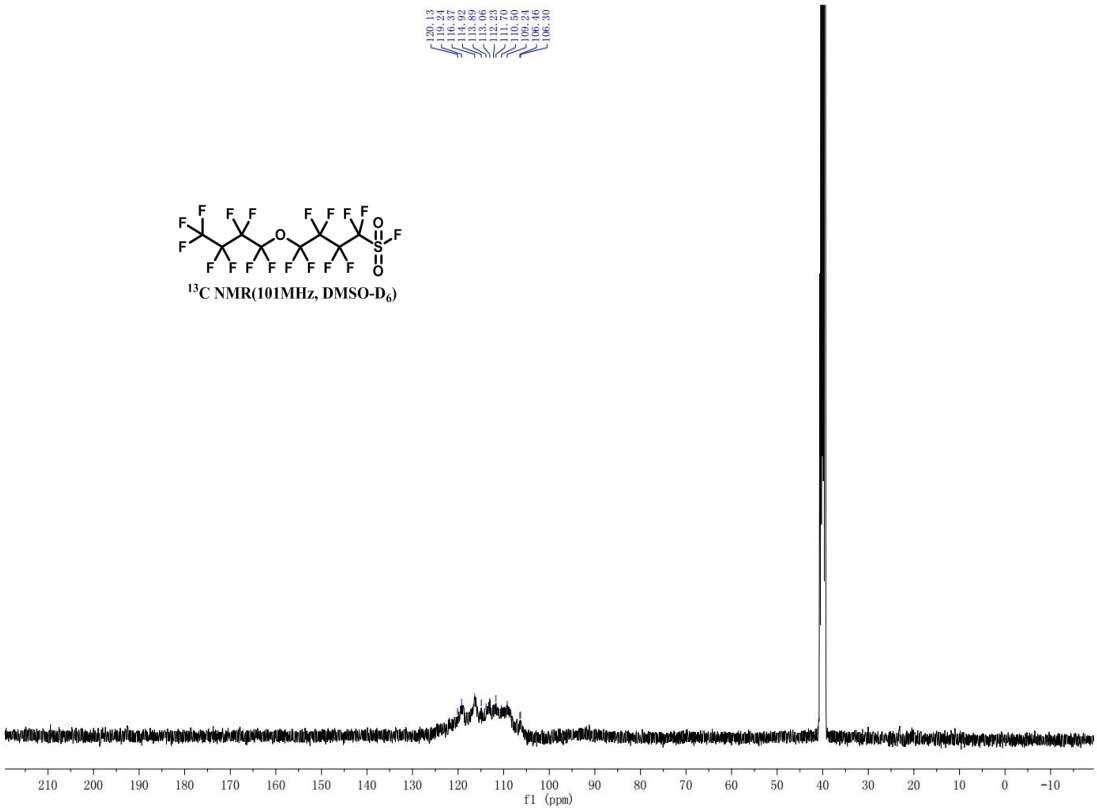
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ºC) of 4-butoxybutane-1-sulfonyl fluoride



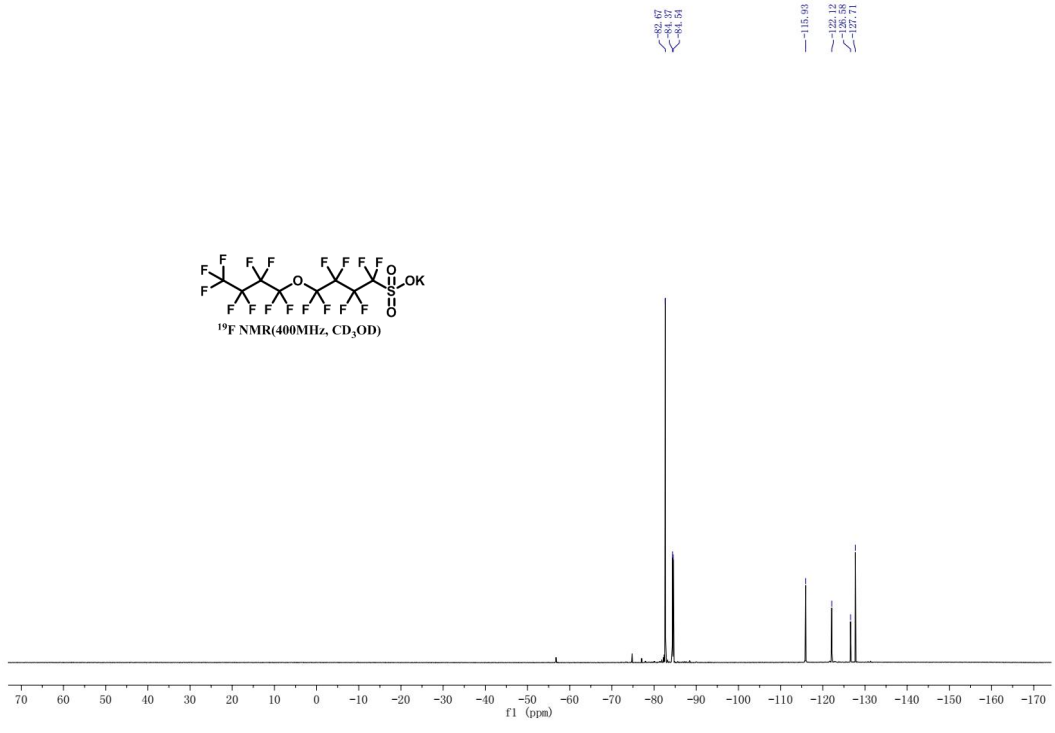
^{19}F NMR spectrum (400 MHz, $CDCl_3$, 23 ºC) of 4-butoxybutane-1-sulfonyl fluoride



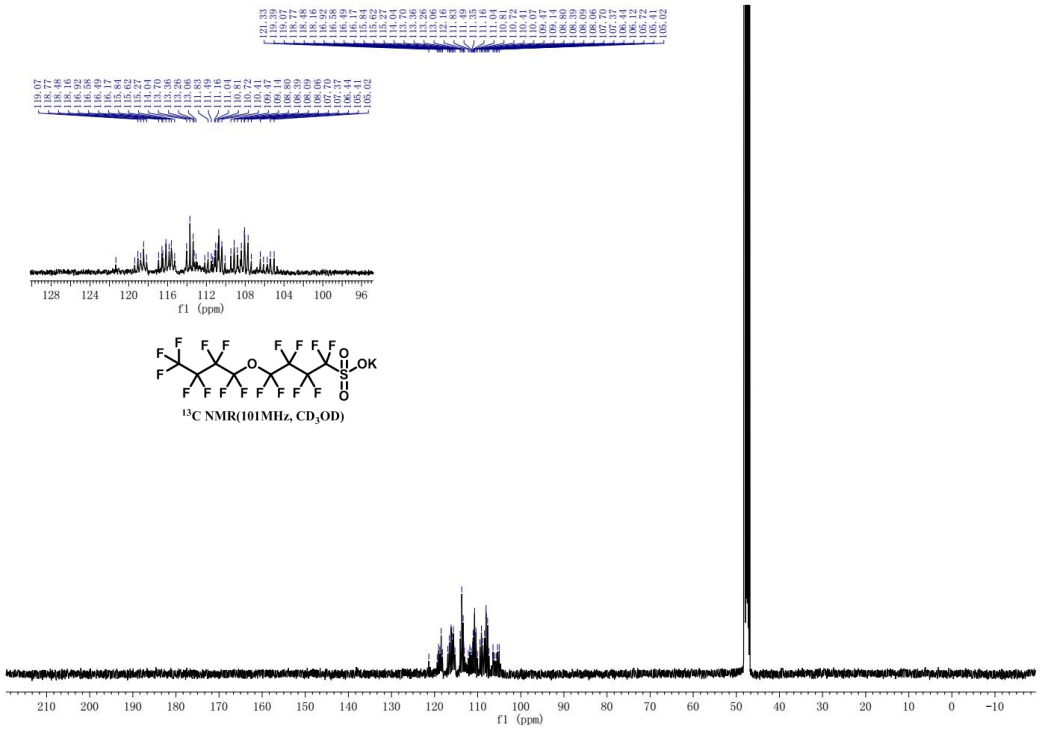
^{19}F NMR spectrum (400 MHz, DMSO-D_6, 23 ºC) of 1,1,2,2,3,3,4,4-octafluoro-4-(perfluorobutoxy)butane-1-sulfonyl fluoride



^{13}C NMR spectrum (400 MHz, DMSO-D$_6$, 23 ºC) of 1,1,2,2,3,3,4,4-octafluoro-4-

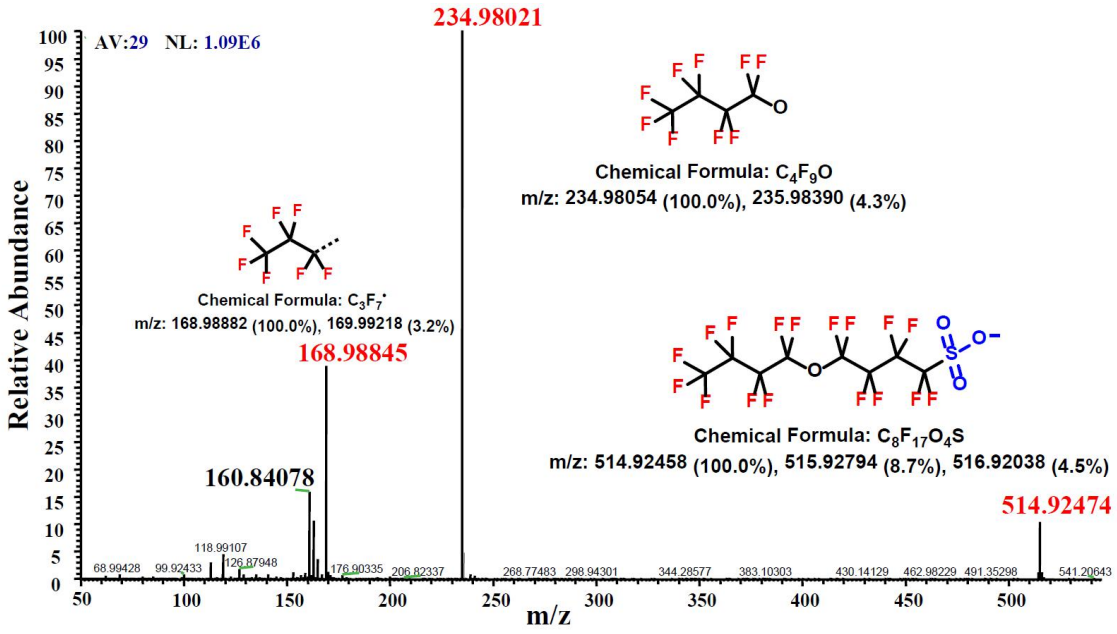


^{19}F NMR spectrum (400 MHz, CD$_3$OD, 23 ºC) of potassium 1,1,2,2,3,3,4,4-octafluoro-4-(perfluorobutoxy)butane-1-sulfonate

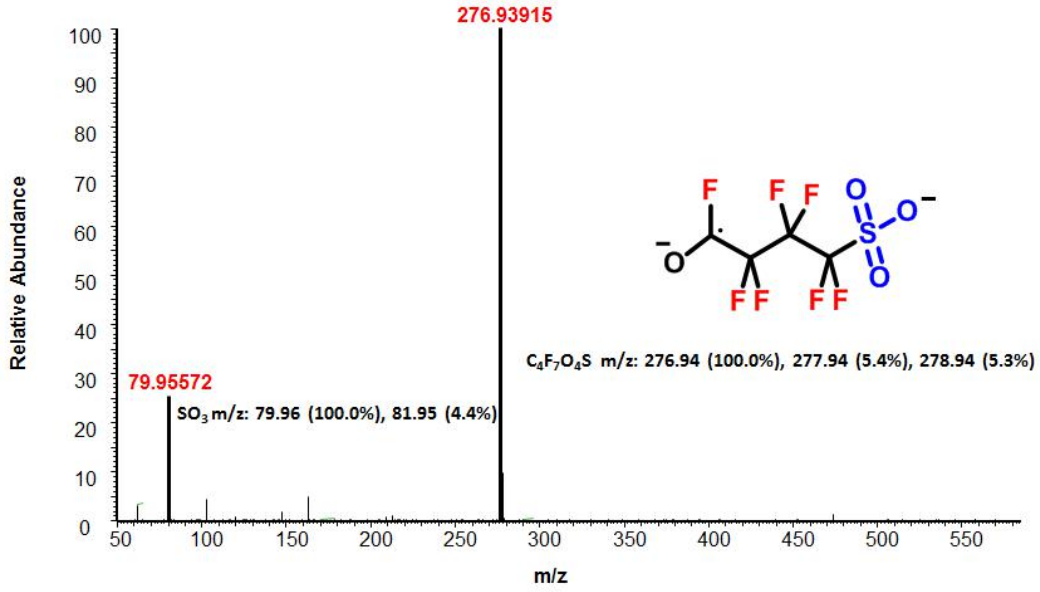


^{13}C NMR spectrum (101 MH, CD_3OD, 23 ºC) of potassium 1,1,2,2,3,3,4,4-octafluoro-4-(perfluorobutoxy)butane-1-sulfonate

High Resolution Mass Spectrometry Data

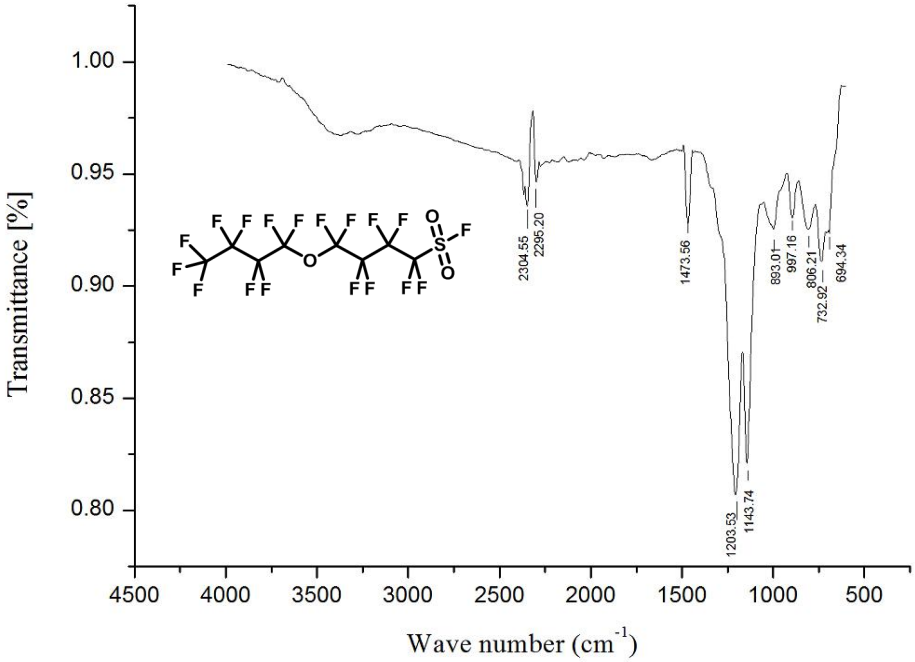


The theoretical calculated value of $C_8F_{17}KO_4S$, $[M-K]^-$ is 514.92458, the high resolution mass spectrometry (HRMS) is 514.92474, the second-order mass spectrometry data is: the theoretical calculated value of $[C_4F_9O]^-$ is 234.98054, and the HRMS-MS2 is determined with 234.98021, $[C_3F_7]^-$ was 168.98882, and the HRMS-MS2 was determined to be 168.98845.

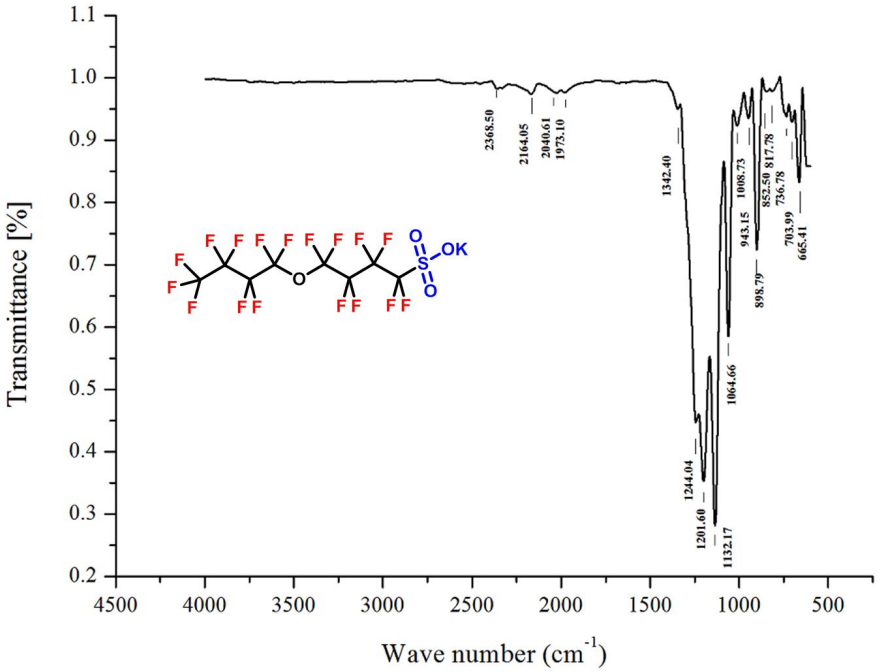


The theoretical calculated value of $C_4F_7O_4S^{\cdot 2-}$, $[M]^-$ is 276.94165, the high resolution mass spectrometry (HRMS) is 276.93915.

Fourier infrared spectroscopy data



The peak at 732 cm^{-1} in the infrared spectrum is the CF_3-CF_2 bond, the peak at 1143 cm^{-1} is the C-F bond, and the peak at 1203 cm^{-1} is the extension peak of the C-O-C bond.



The peak at 736 cm^{-1} in the infrared spectrum is the CF_3-CF_2 bond, the peak at 1132 cm^{-1} is the C-F bond, and the peak at 1201 cm^{-1} is the extension peak of the C-O-C bond. Main characteristic peaks of sulfonic acid groups: absorption peaks of 1342cm^{-1}, 1244cm^{-1}, 1064cm^{-1}, 665cm^{-1} are more obvious.