Supporting information

Selective Fluorosulfonylation of Thianthrenium Salts enabled by Electrochemistry

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Table of Contents

Supporting information……..S1

1. General information…….. S3

2. General procedures for the synthesis of starting material……..S4

3. Condition Optimization……..S5

4. General procedure……...…….....S7

5. Mechanistic studies. …… ……...S19

6. References……..S22

7. Copies of NMR spectra…….. ….… S23

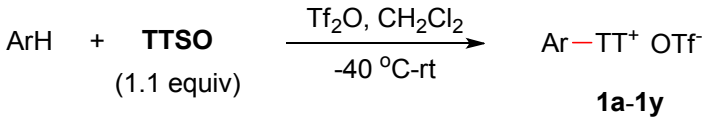
1. General information

Commercial reagents and solvents were obtained from the commercial providers and used without further purification. The products were purified using a commercial flash chromatography system or a regular glass column. TLC was developed on silica gel 60 F254 glassplates.^{1}H NMR (500 MHz or 400 MHz) , ^{13}C NMR (126 MHz or 101 MHz) and ^{19}F NMR (471 MHz) spectra were recorded on a Bruker NMR apparatus. The chemical shifts are reported in δ (ppm) values (^{1}H and ^{13}C NMR relative to $CHCl_3$, δ 7.26 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR). Or alternatively, ^{1}H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm). Multiplicities are recorded by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), td (triplet of doublets), tq (triplet of quartets), ddd (doublet of doublet of doublets), and br (broad). Coupling constants (*J*), are reported in Hertz (Hz). Commercial reagents were used without any further purification.

2. General procedures for the synthesis of starting material

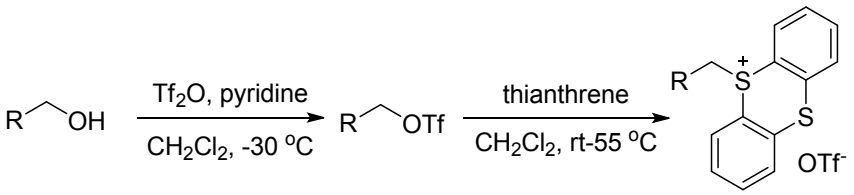
2.1 General procedure for preparation of Thianthrenium Salts 1

2.1.1 Aryl sulfonium salts **1a-1y** were prepared according to reported synthetic procedures[1].



The known aryl sulfonium salts **1a-1y** was synthesized according to the literature1. A 100 mL schlenk tube was charged with thianthrene S-oxide (**TTSO**) (5.5 mmol, 1.1 equiv.), CH_2Cl_2 (25 mL) and anisole (5 mmol, 1.0 equiv.) under a nitrogen atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature. Tf_2O (6 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was stirred at -40 °C for 30 min, and then allowed to stir at room temperature for 12 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM / diethyl ether system to afford aryl sulfonium salts **1a-1y**.

2.1.2 Alkyl Thianthrenium Salts **1z-1af** were prepared according to reported synthetic procedures[2].



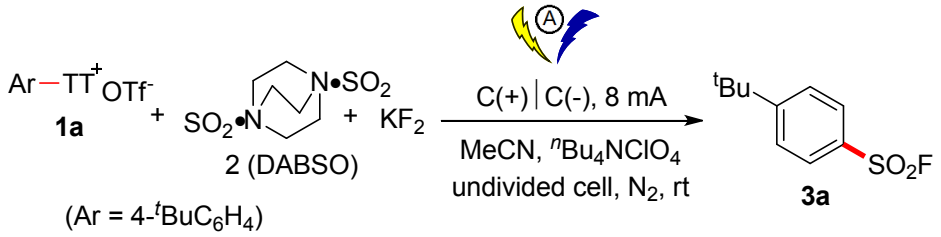
A flame-dried 100 mL flask was placed under an atmosphere of nitrogen and charged with a stir bar and alcohol (5.0 mmol, 1.0 equiv). The alcohol was dissolved in CH_2Cl_2 (20.0 mL) and cooled to -30 °C before adding pyridine (483 μL, 6.0 mmol, 1.2 equiv). While stirring, triflic anhydride (1.0 mL, 29.3 mmol, 1.20 equiv) was added dropwise, and then the reaction mixture stirred for 3 h while remaining at -5 °C. While the flask was still in a -5 °C bath, 0.5 M H_2SO_4 (30 mL) was added. The flask was removed from the cold bath, and the mixture was transferred to a separatory funnel and extracted with 3 × 20 mL of CH_2Cl_2. The organic layers were combined and washed 1 × 50mL of distilled water. The collected organic layers were then dried over $MgSO_4$, then filtered

and concentrated to a 10 mL liquid under vacuum (without heating), which was used directly in the next step. Flame-dried 25 mL Schlenk tube was added thianthrene (1.08 g, 5.0 mmol), then the above liquid was added. The mixture was stirred at 55 °C for 24 h. The mixture was carefully condensed under reduced pressure at 25 ºC and purified by precipitation with Et_2O/CH_2Cl_2.

3. Condition Optimization

To identify the suitable conditions for the anticipated fluorosulfonylation reaction, easy-to-handle *p-tert*-butyl phenyl thianthrenium salt **1a**, DABSO **2** and KHF_2 have been chosen as the model substrates. After extensive screen of various parameters, we were pleased to find out that the desired fluorosulfonylation product **3a** could be isolated with 82% yield under the optimal conditions (I = 8 mA, with voltage from 1.5 V to 2.0 V, and the Faraday efficiency is 84%) (Table S1). No external redox reagent or metal- or photo-catalyst[21] was necessary. During this process, at least seven points should be highlighted. (1) The use of MeCN as solvent is essential for the transformation, as the use of others such as DMF, DMSO, MeOH, CH_2Cl_2 or mixed system (MeCN and H_2O) only led to lower yields (entries 2–4). (2) Electrolyte *n*-Bu_4NClO_4 also plays an important role. Control experiments have identified that the use of others such as *n*-Bu_4NPF_6, Et_4NOTs and $LiClO_4$ gave poor yields (entries 5–6). (3) The employment of cheap carbon felt electrodes is best to promote the transformation. We also tested other commonly used electrodes and it turns out they all have inferior effect on the result (entries 7–8). The cheap nature of electrodes makes our method attractive. (4) While changing the anion of thianthrenium salt to BF_4^- has marginal effect on the result (entry 9), both the fluoro source and the electric current is important (entries 10–11). (5) The electrochemical nature has been proven by the fact that no reaction took place without electric current (entry 12). (6) Both thianthrenium salt **1a** and inexpensive DABSO **2** has been used as the limiting reagent in our hands. (7) Moreover, no reaction took place when the reaction was conducted in a divided cell (entry 13).

Table S1 Reaction optimization[a]



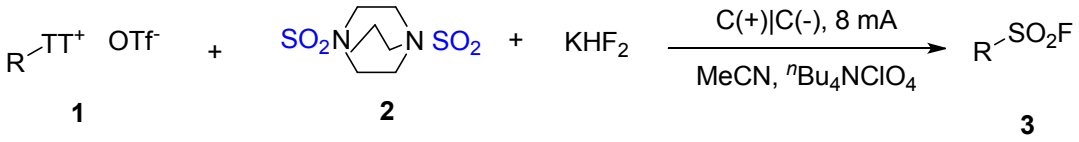
Entry	Variation from standard conditions	Yield of **3a** (%)[b]
1	None	82
2	DMF or DMSO instead of CH_3CN	62/16
3	MeOH or CH_2Cl_2 instead of CH_3CN	trace/trace
4	CH_3CN: H_2O (9:1) instead of CH_3CN	42
5	No *n*-Bu_4NClO_4	59
6	$^nBu_4NPF_6$, Et_4NOTs, $LiClO_4$ instead of $^nBu_4NClO_4$	73/NR/23
7	Pt(+) | C(−), Pt(+) | Pt(−), C(+) | Pt(−) instead of C(+) | C(−)	79/80/73
8	RVC(+) | RVC(−), RVC(+) | Pt(−)instead of C(+) | C(−)	70/62
9	*p*-$^tBuC_6H_4TT^+BF_4^-$ instead of **1a**	79
10	$Et_3N{\cdot}3HF$ instead of KHF_2	49
11	10 mA or 5 mA instead of 8 mA	73/60
12	No electric current	No reaction
13	Divided Cell	0

[a] Standard conditions: Carbon felt (1.0 × 1.0 cm^2) anode and cathode was used, I = 8 mA, **1a** (0.20 mmol), **2** (0.10 mmol), KHF_2 (0.60 mmol), n-Bu_4NClO_4 (0.05 M), MeCN (4 mL), at r.t. under N_2 atmosphere for 4 h; [b]Isolated yields.

4. General Procedure

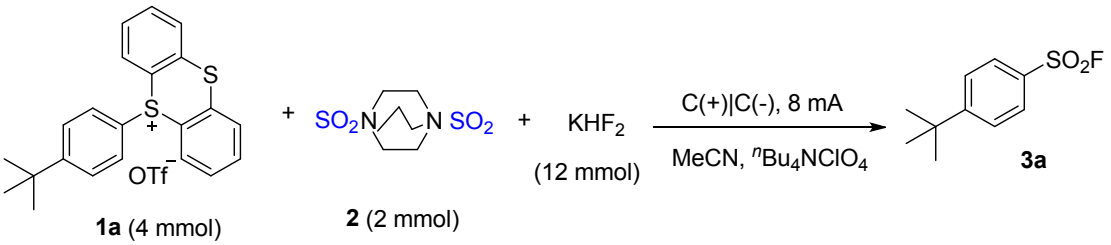
4.1 General Procedure

Figure S1 Electrolysis setup: Left) The Carbon felt (size: 10 mm × 10 mm × 0.3 mm). (Bought from Shandong Guanzhi New Material Technology Co., Ltd, China.); Right) Constant potential rectifier was used as the power sources for our reaction (Bought from Shenzhen Maxtec Electronics Co., Ltd China.).

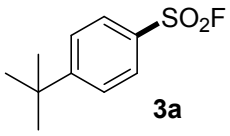


To the cell was added thianthrenium salts **1** (0.2 mmol), DABSO (24 mg, 0.1 mmol), KHF_2 (46.8 mg, 0.6 mmol), n-Bu_4NClO_4 (0.3 mmol, 68.2 mg), CH_3CN (4 mL). The tube was installed with a Carbon felt (1.0 × 1.0 cm^2) as the cathode and Carbon felt (1.0 × 1.0 cm^2) as the anode. The mixture was electrolyzed using 8 mA at room temperature under magnetic stirring. The reaction mixture was poured into ethyl acetate (30 mL), washed with water two times (20 mL × 2), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent to afford the desired pure product.

4.2 General Procedure for Gram-Scale Experiments

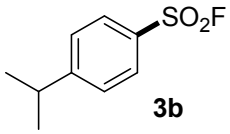


To the cell was added thianthrenium salts **1** (1.99 g, 4 mmol), DABSO (0.48 g, 2 mmol), KHF_2 (0.936 mg, 12 mmol), *n*-Bu_4NClO_4 (6 mmol, 2.1 g), CH_3CN (80 mL). The tube was installed with a Carbon felt (2.0 × 2.0 cm^2) as the cathode and Carbon felt (2.0 × 2.0 cm^2) as the anode. The mixture was electrolyzed using 8 mA at room temperature under magnetic stirring until complete consumption of the substrate (monitored by TLC). The reaction mixture was poured into ethyl acetate (30 mL), washed with water two times (20 mL × 2), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc (50:1) as eluent to afford the desired pure product (0.7 g, 81%).



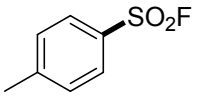
3a

4-(*tert*-Butyl)benzenesulfonyl fluoride (**3a**), 35.4 mg, 82% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 160.02, 130.0, 129.93 (d, *J* = 25 Hz), 129.8, 128.3, 126.7, 35.5, 30.9. ^{19}F NMR (376 MHz, Chloroform-d) δ 66.20. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{14}FO_2S$ 217.0699; Found 217.0693. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



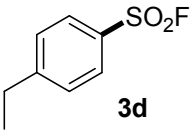
3b

4-Isopropylbenzenesulfonyl fluoride (**3b**), 31.9 mg, 79% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.88 – 7.80 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 2.96 (d, *J* = 6.9 Hz, 1H), 1.21 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 157.70, 130.25 (d, *J* = 24 Hz), 128.6, 127.8, 34.5, 23.5. ^{19}F NMR (376 MHz, Chloroform-d) δ 66.19. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{12}FO_2S$ 203.0542; Found 203.0537. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



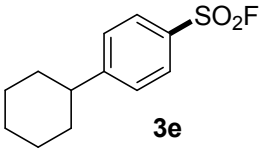
3c

(4-Fluorophenyl)(phenyl)methanone (**3c**), 26.5 mg, 76% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.37 (m, 2H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 147.1, 130.3, 130.2 (d, *J* = 24 Hz), 128.4, 21.8. ^{19}F NMR (376 MHz, Chloroform-d) δ 66.25. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_7H_7FO_2SNa$ 197.0048; Found 197.0043. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



3d

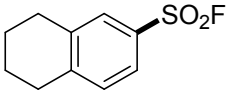
4-Ethylbenzenesulfonyl fluoride (**3d**), 25.6 mg, 68% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.98 – 7.87 (m, 2H), 7.51 – 7.39 (m, 2H), 2.78 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 153.2, 130.2 (d, *J* = 24 Hz), 129.2, 128.6, 29.0, 14.9. ^{19}F NMR (376 MHz, Chloroform-d) δ 66.23. HRMS (EI) m/z: $[M+Na]^+$ Calcd for $C_8H_9FO_2SNa$ 211.0205; Found 211.0199. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



3e

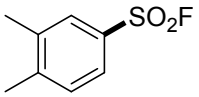
4-Cyclohexylbenzenesulfonyl fluoride (**3e**), 37.3 mg, 77% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 2.63 (t, *J* = 10.6 Hz, 1H), 1.86 (d, *J* = 11.7 Hz, 4H), 1.76 (d, *J* = 13.1 Hz,

1H), 1.42 (h, J = 12.7 Hz, 4H), 1.28 (t, J = 12.1 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 156.9, 130.1 (d, J = 19 Hz), 128.5, 128.2, 44.8, 33.9, 26.5, 25.8. ^{19}F NMR (471 MHz, Chloroform-d) δ 66.30. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{15}FO_2SNa$ 265.0674; Found 265.0674. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



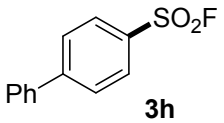
3f

4-Cyclohexylbenzenesulfonyl fluoride (**3f**), 26.5 mg, 62% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.76 – 7.63 (m, 2H), 7.29 (d, J = 8.0 Hz, 1H), 2.86 (q, J = 5.5 Hz, 4H), 1.84 (p, J = 3.1 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.32, 139.25, 130.36, 129.8, 129.6, 129.43 (d, J = 23 Hz), 129.0, 125.1, 29.7, 29.3, 22.4, 22.3. ^{19}F NMR (471 MHz, Chloroform-d) δ 66.20. HRMS (EI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{12}FO_2S$ 215.0542; Found 215.0537. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



3g

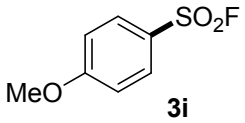
3,4-Dimethylbenzenesulfonyl fluoride (**3g**), 22.2 mg, 59% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.76 (d, J = 2.0 Hz, 1H), 7.74 (dd, J = 7.9, 2.1 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 145.8, 138.7, 130.7, 130.1 (d, J = 24 Hz), 129.0, 126.0, 20.2, 19.8. ^{19}F NMR (376 MHz, Chloroform-d) δ 66.28. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_8H_9FO_2SNa$ 211.0205; Found 211.0199. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



3h

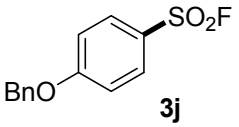
[1,1'-Biphenyl]-4-sulfonyl fluoride (**3h**), 38.7 mg, 82% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.04 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 7.3 Hz, 2H), 7.48 (dt, J = 11.6, 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 148.7, 138.5, 131.4 (d, J = 24 Hz), 129.3, 129.2, 129.0, 128.2, 127.5. ^{19}F NMR (376 MHz, Chloroform-d) δ 66.56. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_9FO_2SNa$ 259.0205; Found 259.0199. The

isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



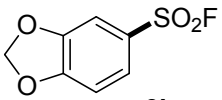
3i

4-Methoxybenzenesulfonyl fluoride (**3i**), 31.5 mg, 83% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.93 (d, *J* = 9.0 Hz, 2H), 7.12 – 6.98 (m, 2H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 165.3, 130.8, 123.7 (d, *J* = 24 Hz), 114.9, 55.9. ^{19}F NMR (376 MHz, Chloroform-d) δ 67.26. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_7H_7FO_3SNa$ 212.9998; Found 212.9992. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



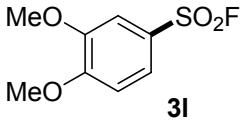
3j

4-(Benzyloxy)benzenesulfonyl fluoride (**3j**), 43.1 mg, 81% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.98 – 7.90 (m, 2H), 7.49 – 7.41 (m, 4H), 7.41 – 7.34 (m, 1H), 7.16 – 7.09 (m, 2H), 5.17 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 164.3, 135.3, 130.9, 128.9, 128.6, 127.5, 124.3 (d, *J* = 20 Hz),115.7, 70.7. ^{19}F NMR (376 MHz, Chloroform-d) δ 67.28. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}FO_3S$ 267.0491; Found 267.0486. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



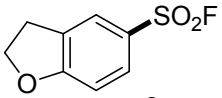
3k

Naphthalen-2-yl(phenyl)methanone (**3k**), 28.6 mg, 70% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.61 (ddd, *J* = 8.3, 1.9, 0.7 Hz, 1H), 7.38 (d, *J* = 2.0 Hz, 1H), 6.97 (dd, *J* = 8.3, 0.9 Hz, 1H), 6.16 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 154.0, 148.7, 125.5 (d, *J* = 20 Hz), 125.2, 108.8, 108.2, 103.0. ^{19}F NMR (471 MHz, Chloroform-d) δ 66.82. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_7H_5FO_4SNa$ 226.9790; Found 226.985. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 10%, v/v).



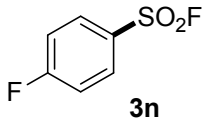
3l

3,4-Dimethoxybenzenesulfonyl fluoride (**3l**), 29.9 mg, 67% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.68-7.65 (m, 1H), 7.40 (d, *J* = 2.2 Hz, 1H), 7.02 (dd, *J* = 8.7, 0.9 Hz, 1H), 3.98 (d, *J* = 14.2 Hz, 6H).^{13}C NMR (126 MHz, Chloroform-d) δ 155.0, 149.5, 123.8 (d, *J* = 19 Hz), 123.2, 123.15, 110.9, 110.2, 110.15, 56.4, 56.4, 56.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ 67.12. HRMS (ESI) m/z: $[M+K]^+$ Calcd for $C_8H_9FO_4SK$ 258.9843; Found 258.9834. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 10%, v/v).



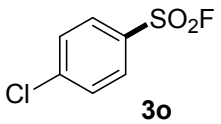
3m

2,3-Dihydrobenzofuran-6-sulfonyl fluoride (**3m**), 32.3 mg, 80% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.89 – 7.77 (m, 2H), 6.93 (d, *J* = 9.1 Hz, 1H), 4.75 (t, *J* = 8.9 Hz, 2H), 3.32 (t, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 130.7, 129.2, 125.8, 124.4 (d, *J* = 24 Hz), 110.2, 72.8, 28.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ 67.47. HRMS (EI) m/z: $[M+H]^+$ Calcd for $C_8H_8FO_3S$ 203.0178; Found 203.0173. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



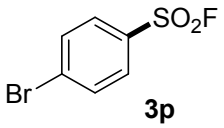
3n

4-Fluorobenzenesulfonyl fluoride (**3n**), 26.9 mg, 76% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.77 (dt, *J* = 8.0, 1.3 Hz, 1H), 7.66 (dt, *J* = 7.6, 2.1 Hz, 1H), 7.58 (tdd, *J* = 8.0, 5.1, 1.2 Hz, 1H), 7.43 (td, *J* = 8.2, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 253 Hz), 134.7 (d, *J* = 18 Hz)，131.7 (d, *J* = 8 Hz), 124.4 (d, *J* = 3 Hz)，123.0 (d, *J* = 21 Hz), 115.9 (d, *J* = 25 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ 65.88, -107.58 – -107.66 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_6H_5F_2O_2S$ 178.9978; Found 178.9980. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



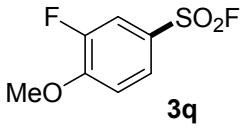
3o

4-Chlorobenzenesulfonyl fluoride (**3o**), 30.0 mg, 77% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.63 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 142.7, 131.4 (d, *J* = 26 Hz), 130.1, 129.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ 66.42. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_6H_5{}^{35}ClFO_2S$ 194.9683; Found 194.9680. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



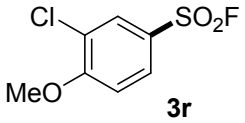
3p

4-Bromobenzenesulfonyl fluoride (**3p**), 36.1 mg, 76% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.88 (d, *J* = 8.7 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.1, 132.2, 131.9, 131.3, 129.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ 66.38. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_6H_5{}^{79}BrFO_2S$ 238.9178; Found 238.9176. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



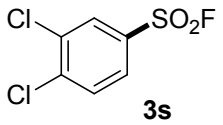
3q

3-Fluoro-4-methoxybenzenesulfonyl fluoride (**3q**), 35.2 mg, 69% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.81 (dt, *J* = 8.7, 1.9 Hz, 1H), 7.72 (dd, *J* = 9.9, 2.3 Hz, 1H), 7.18 – 7.09 (m, 1H), 4.01 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 154.0 (d, *J* = 8 Hz), 151.7 (d, *J* = 202 Hz), 126.4 (d, *J* = 3 Hz), 124.1 (d, *J* = 21 Hz), 116.5 (d, *J* = 18 Hz), 113.3 (d, *J* = 1 Hz), 56.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ 67.30, -130.01. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_7H_7F_2O_3S$ 209.0084; Found 209.0085. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



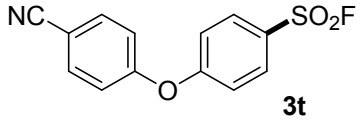
3r

3-Chloro-4-methoxybenzenesulfonyl fluoride (**3r**), 28.7 mg, 71% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.02 (d, *J* = 2.3 Hz, 1H), 7.91 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 1H), 4.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 130.5, 129.2, 125.0, 124.7, 124.2, 112.0, 56.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ 67.52. HRMS (ESI) m/z: $[M]^+$ Calcd for $C_7H_7{}^{35}ClFO_3S$ 224.9788; Found 224.9783. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



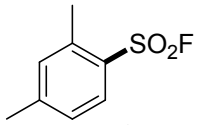
3s

3,4-Dichlorobenzenesulfonyl fluoride (**3s**), 33.6 mg, 74% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.11 (d, *J* = 2.2 Hz, 1H), 7.85 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.73 (dd, *J* = 8.4, 1.0 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 141.2, 134.7, 132.4 (d, *J* = 21 Hz), 131.8, 130.3, 127.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ 66.65. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_6H_3{}^{35}Cl_2FO_2SNa$ 250.9113; Found 250.9113. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



3t

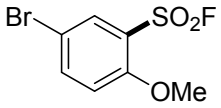
4-(4-Cyanophenoxy)benzenesulfonyl fluoride (**3t**), 47.6 mg, 86% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.06 – 8.00 (m, 2H), 7.77 – 7.70 (m, 2H), 7.24 – 7.19 (m, 2H), 7.19 – 7.14 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 161.9, 158.5, 134.7, 131.3, 127.9 (d, *J* = 20 Hz), 120.4, 119.3, 118.1, 108.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ 66.87. HRMS (EI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_8FNO_3SNa$ 300.0107; Found 300.0101. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 10%, v/v).



3u

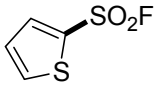
2,4-Dimethylbenzenesulfonyl fluoride (**3u**), 25.9 mg, 69% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.15 (m, 2H), 2.64 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 138.8, 133.5,

130.2, 129.3 (d, J = 22 Hz), 127.2, 21.5, 20.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ 60.83. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_8H_9FO_2SNa$ 211.0205; Found 211.0199. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



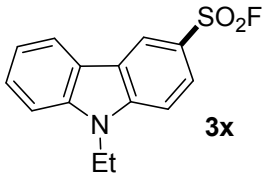
3v

p-Tolyl(4-(trifluoromethyl)phenyl)methanone (**3v**), 24.7 mg, 46% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.05 (d, J = 2.5 Hz, 1H), 7.79 (dd, J = 8.9, 2.5 Hz, 1H), 7.01 (d, J = 8.9 Hz, 1H), 4.01 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 157.1, 139.9, 127.9 (d, J = 25 Hz), 114.5, 112.2, 56.90. ^{19}F NMR (376 MHz, $CDCl_3$) δ 58.93. HRMS (EI) m/z: $[M+H]^+$ Calcd for $C_7H_7{}^{79}BrFO_3S$ 268.9283; Found 268.9287. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



3w

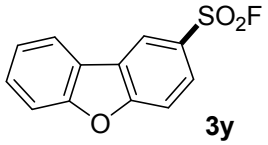
(4-Methoxyphenyl)(*p*-tolyl)methanone (**3w**), 18.4 mg, 56% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.93 (dt, J = 3.9, 1.4 Hz, 1H), 7.88 (dd, J = 5.0, 1.4 Hz, 1H), 7.24 (ddd, J = 4.9, 3.9, 0.9 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 136.9, 136.6, 131.4 (d, J = 23 Hz), 128.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ 71.76. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_4H_4FO_2S_2$ 166.9637; Found 166.9641. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



3x

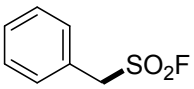
9-Ethyl-9*H*-carbazole-3-sulfonyl fluoride (**3x**), 42.1 mg, 76% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.66 (d, J = 1.9 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.97 (dd, J = 8.8, 1.9 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.44 (dd, J = 13.8, 8.5 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 4.33 (t, J = 7.3 Hz, 2H), 1.39 (d, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 140.9, 131.6 (d, J = 22 Hz), 127.7, 125.4, 123.0, 122.3, 122.2, 121.1, 121.0, 109.4, 109.0, 38.1,

13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ 69.30. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{12}FNO_2SNa$ 300.0470; Found 300.0465. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 10%, v/v).



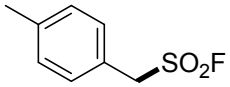
3y

Dibenzo[*b*,*d*]furan-2-sulfonyl fluoride (**3y**), 36.5 mg, 73% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.64 (d, *J* = 2.2 Hz, 1H), 8.12 (dt, *J* = 8.7, 2.2 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.77 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.66 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.60 (tq, *J* = 8.4, 1.4 Hz, 1H), 7.47 (td, *J* = 7.5, 1.7 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 159.6, 157.2, 129.3, 127.3, 127.2 (d, *J* = 20 Hz), 125.6, 124.2, 122.5, 122.4, 121.4, 113.0, 112.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ 68.07. HRMS (EI) m/z: $[M+H]^+$ Calcd for $C_{12}H_8FO_3S$ 251.0178; Found 251.0175. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



3z

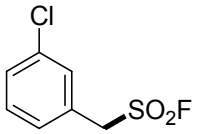
Phenylmethanesulfonyl fluoride (**3z**), 17.7 mg, 51% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.44 (p, *J* = 1.9 Hz, 5H), 4.59 (d, *J* = 3.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.7, 129.9, 129.3, 125.5, 56.9 (d, *J* = 18 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ 51.42. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_7H_7FO_2SNa$ 197.0048; Found 197.0043. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



3aa

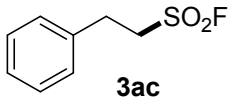
p-Tolylmethanesulfonyl fluoride (**3aa**), 14.6 mg, 38% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.34 – 7.29 (m, 1H), 7.25 (t, *J* = 3.8 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 4.55 (d, *J* = 3.1 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.2, 131.3, 130.7, 129.2, 127.7, 125.3, 56.8 (d, *J* = 14 Hz), 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ 51.46.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_8H_9FO_2SNa$ 211.0205; Found 211.0199. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



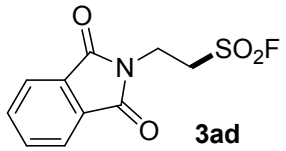
3ab

(3-Chlorophenyl)methanesulfonyl fluoride (**3ab**), 17.8 mg, 43% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.43 (dd, *J* = 6.7, 1.5 Hz, 2H), 7.37 (dd, *J* = 8.9, 7.4 Hz, 1H), 7.31 (dt, *J* = 7.9, 1.5 Hz, 1H), 4.56 (d, *J* = 3.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.2, 130.7, 130.6, 130.2, 128.9, 127.4, 56.1 (d, *J* = 15 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ 52.13. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_7H_7{}^{35}ClFO_2S$ 208.9839; Found 208.9837. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



3ac

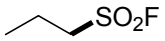
2-Phenylethane-1-sulfonyl fluoride (**3ac**), 17.3 mg, 46% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.32 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.22 – 7.17 (m, 2H), 3.66 – 3.47 (m, 2H), 3.23 – 3.11 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.1, 129.2, 128.4, 127.6, 52.1 (d, *J* = 12 Hz), 29.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ 53.33. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_8H_9FO_2SNa$ 211.0205; Found 211.0199. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 5%, v/v).



3ad

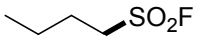
2-(1,3-Dioxoisoindolin-2-yl)ethane-1-sulfonyl fluoride (**3ad**), 21.6 mg, 42% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.28 (t, *J* = 6.7 Hz, 2H), 3.84 (td, *J* = 6.6, 4.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 134.6, 131.6, 123.8, 48.1 (d, *J* = 14 Hz), 32.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.03. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{10}H_8FNO_4SNa$ 280.0056; Found 280.0061.

The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 15%, v/v).



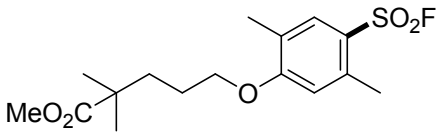
3ae

Propane-1-sulfonyl fluoride (**3ae**), 6.7 mg, 27% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 3.40 – 3.32 (m, 1H), 1.99 (h, *J* = 7.5 Hz, 1H), 1.13 (td, *J* = 7.4, 1.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 52.3 (d, *J* = 13 Hz), 17.2, 12.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ 53.35. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_3H_8FO_2S$ 127.0229; Found 127.0232. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 1%, v/v).



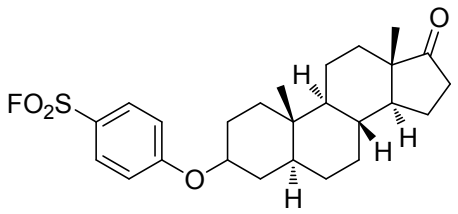
3af

Butane-1-sulfonyl fluoride (**3af**), 10.0 mg, 36% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 3.40 – 3.32 (m, 2H), 1.96 – 1.88 (m, 2H), 1.52 (q, *J* = 7.5 Hz, 2H), 0.98 (td, *J* = 7.3, 1.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 50.5 (d, *J* = 13 Hz), 25.2, 21.0, 13.08, 13.07. ^{19}F NMR (471 MHz, $CDCl_3$) δ 52.79. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_4H_{10}FO_2S$ 141.0386; Found 141.0380. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 1%, v/v).



4

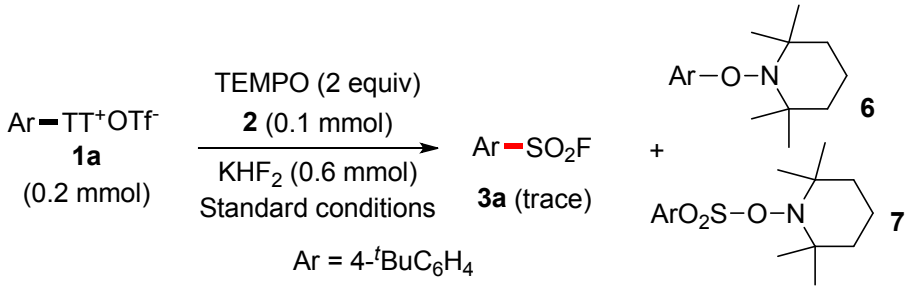
Methyl 5-(4-(fluorosulfonyl)-2,5-dimethylphenoxy)-2,2-dimethylpentanoate (**4**), 29.1 mg, 42% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.77 (s, 1H), 6.73 (s, 1H), 4.02 (t, *J* = 6.1 Hz, 2H), 3.67 (s, 3H), 2.62 (s, 3H), 2.22 (s, 3H), 1.83 – 1.75 (m, 2H), 1.75 – 1.68 (m, 2H), 1.23 (s, 6H).^{13}C NMR (126 MHz, Chloroform-d) δ 178.1, 162.2, 139.2, 132.3, 125.3, 122.5 (d, *J* = 18 Hz), 122.4, 114.2, 68.6, 51.8, 42.1, 36.8, 25.2, 24.9, 20.5, 15.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ 62.52. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{23}FO_5SNa$ 369.1148; Found 369.1142. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 10%, v/v).



5

4-(((5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)benzenesulfonyl fluoride (**5**), 71.7 mg, 80% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.00 – 7.82 (m, 2H), 7.10 – 6.89 (m, 2H), 4.68 (t, *J* = 2.6 Hz, 1H), 2.50 – 2.36 (m, 1H), 2.08 (dt, *J* = 19.0, 9.0 Hz, 1H), 1.98 – 1.88 (m, 2H), 1.85 – 1.76 (m, 2H), 1.75 – 1.44 (m, 10H), 1.40 – 1.20 (m, 7H), 1.03 (qd, *J* = 12.1, 6.0 Hz, 1H), 0.87 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6, 130.9, 123.3 (d, *J* = 20 Hz), 116.1, 73.2, 54.2, 51.5, 47.8, 39.6, 36.0, 35.8, 35.0, 32.5, 32.3, 31.5, 30.7, 28.0, 25.5, 21.8, 20.1, 13.8, 11.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ 67.32. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{34}FO_4S$ 449.2162; Found 449.2156. The isolated yield was obtained by flash chromatography column on silica gel (gradient eluent of EtOAc in Petroleum ether: 0 ~ 10%, v/v).

5. Mechanistic studies



To the cell was added thianthrenium salt **1a** (0.2 mmol), DABSO (24 mg, 0.1 mmol), KHF_2 (46.8 mg, 0.6 mmol), TEMPO (0.4 mmol, 62.4 mg), *n*-Bu_4NClO_4 (0.3 mmol, 68.2 mg), CH_3CN (4 mL). The tube was installed with a Carbon felt (1.0 × 1.0 cm^2) as the cathode and Carbon felt (1.0 × 1.0 cm^2) as the anode. The mixture was electrolyzed using 8 mA at room temperature under magnetic stirring. As showed in the ESI-HRMS spectrum, product **6** and **7** were obtained, which imply the existence of acyl radical intermediate.

Table S2 ESI-HRMS spectra data.

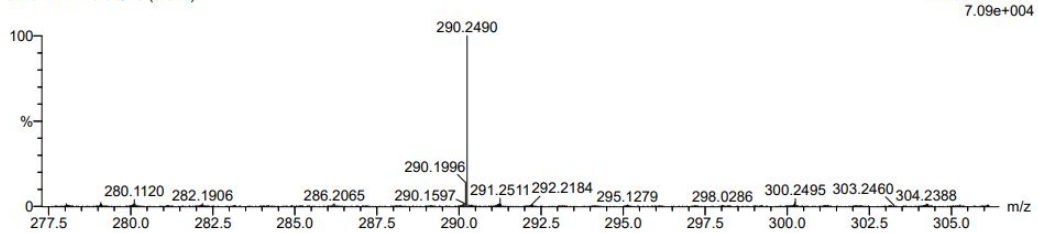
Formula (M)	Ion Formula	Measured	Calc.	Figure
$C_{19}H_{32}NO$ (**6**)	$[M+H]^+$	290.2490	290.2484	S2
$C_{19}H_{32}NO_3S$ (**7**)	$[M+H]^+$	354.2094	354.2103	S3

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
124 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 19-19 H: 1-70 N: 0-10 O: 1-12
3
0723-7-ZDN-3-3Q 48 (0.317)

1: TOF MS ES+
7.09e+004



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
290.2490	290.2484	0.6	2.1	4.5	647.6	n/a	n/a	C19 H32 N O

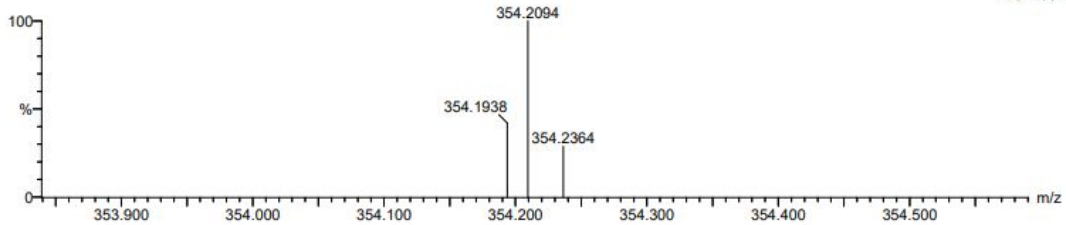
Figure S2 ESI-HRMS spectrum for **6**.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
252 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 19-19 H: 1-70 N: 0-10 O: 1-12 S: 1-2
3
0723-7-ZDN-3-3Q 49 (0.330)

1: TOF MS ES+
1.73e+002



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
354.2094	354.2103	-0.9	-2.5	4.5	27.3	n/a	n/a	C19 H32 N O3 S

Figure S3 ESI-HRMS spectrum for **7**.

Cyclic voltammetric (CV) analyses (vs. Ag/AgCl) of TEMPO and the mixture by adding TMEPO

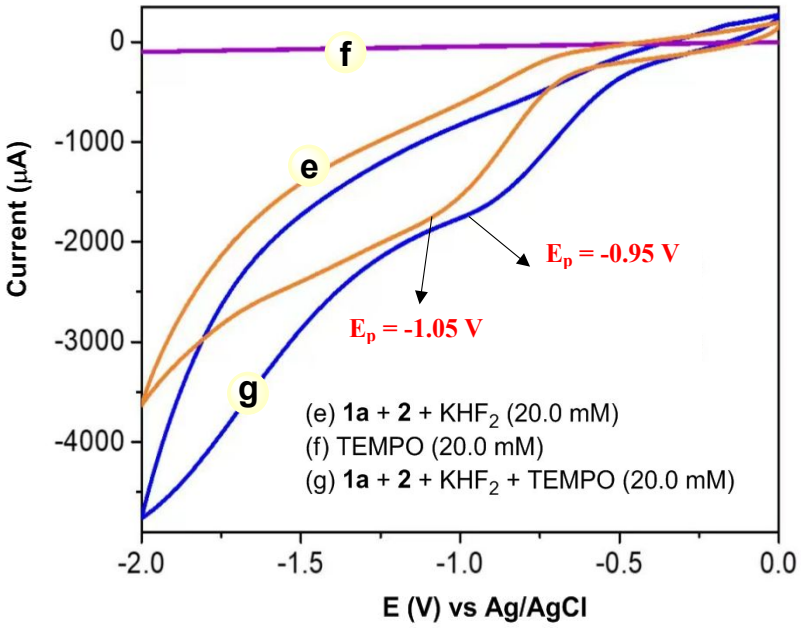


Figure S4 Cyclic voltammograms (scan rate: 100 mV/s) in a three-electrode cell with a glass carbon as working electrode (size: 10 mm × 10 mm × 0.3 mm), Ag/AgCl in 0.1 M KCl as reference electrode and Carbon wire (size: 10 mm × 10 mm × 0.3 mm) as counter electrode in anhydrous MeCN under N_2 atmosphere at rt: (e) **1a** + **2** + KHF_2 (20.0 mM for each); (f) TEMPO (20 mM); (g) **1a** + **2** + KHF_2 + TEMPO (20.0 mM for each). CV plotting convention along with the voltammogram is IUPAC.

Figure S5 The electrochemical workstation for CV measurement. (Bought from Shanghai Chenhua Instrument Co., Ltd.)

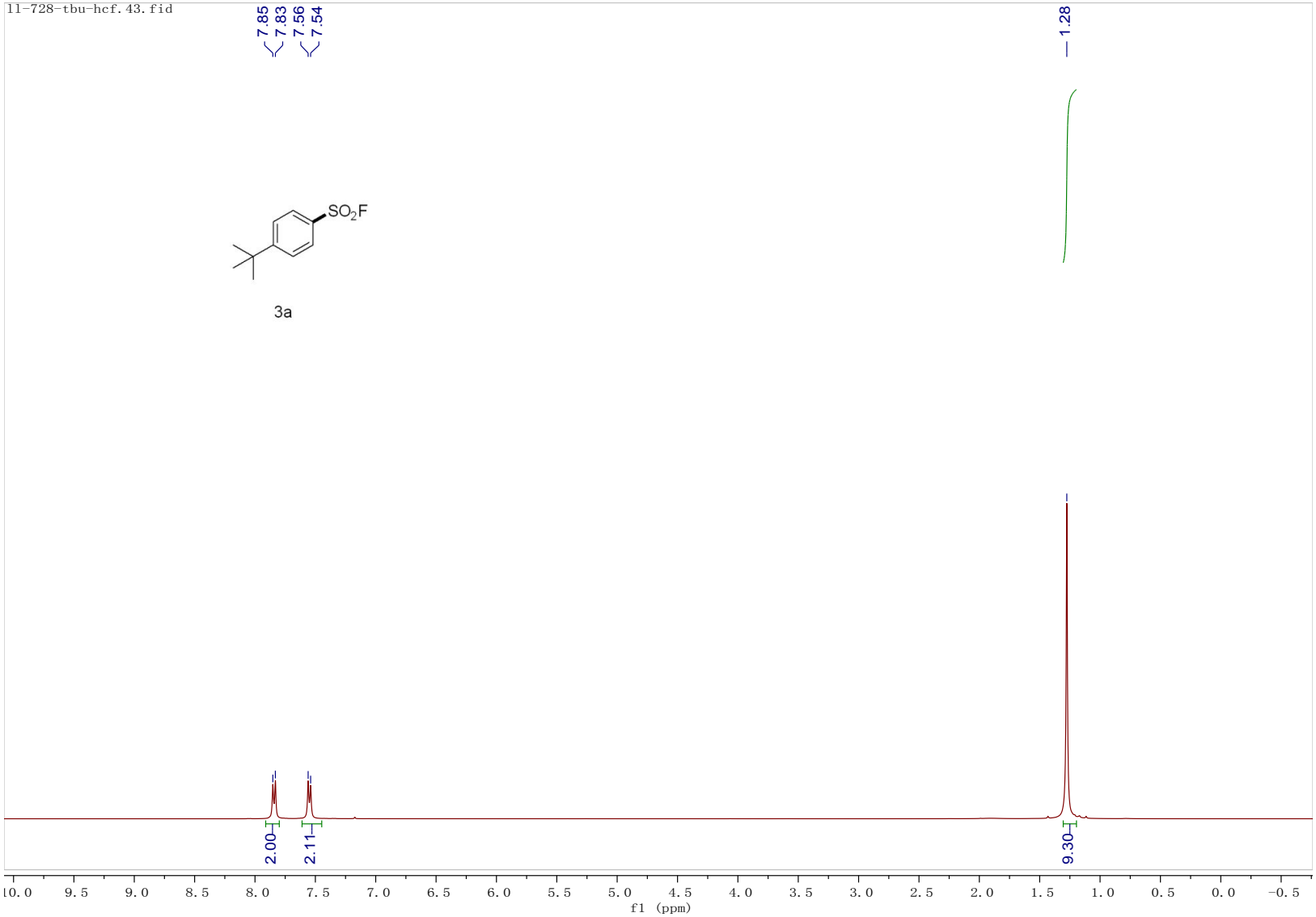
6. References

1. (a) Sang, R.-C.; Korkis, S.-E.; Su, W.-Q.; Ye, F.; Engl, P.-S.; Berger, F.; Ritter, T. Site-Selective C−H Oxygenation via Aryl Sulfonium Salts. *Angew. Chem. Int. Ed.* **2019**, *58*, 16161-16166. (b) Ye, F.; Berger, F.; Jia, H.; Ford, J.; Wortman, A.; s Bçrgel, J; Genicot, C.; Ritter, T. Aryl Sulfonium Salts for Site-Selective Late-Stage Trifluoromethylation. *Angew. Chem. Int. Ed*. **2019**, *58*, 14615–14619. (c) Wu, J.;Wang, W.-Z.; Chen, X.-Y.; Wu, Y.-C.; Wang, D.-M.; Peng, Q.; Wang, P. Para-Selective Borylation of Monosubstituted Benzenes Using a Transient Mediator. *Sci. Chin. Chem*. **2020**, *63*, 336-340..

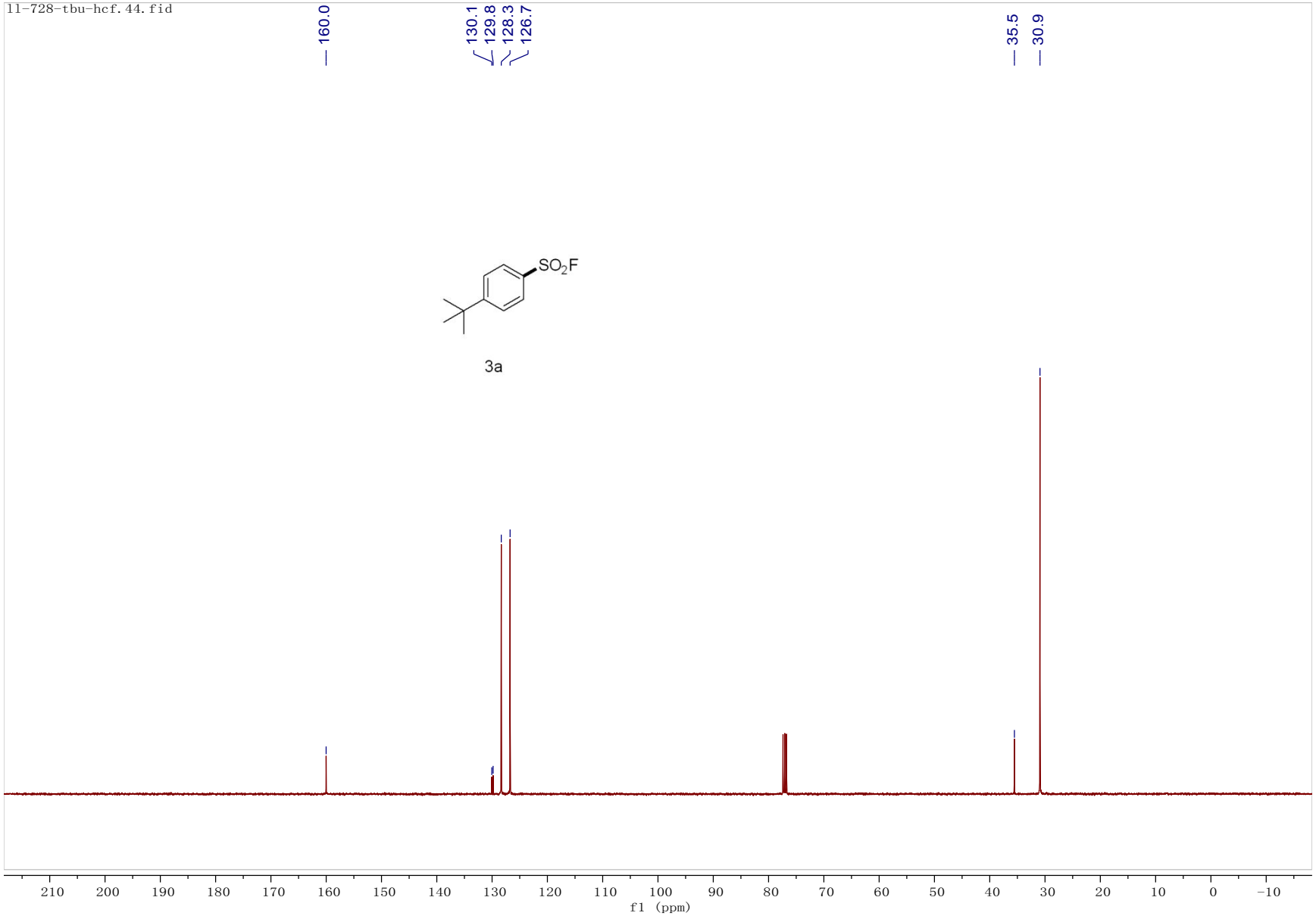
2. (a) Chen, C; Wang, M.-Y.; Lu, H.-J.; Zhao, B.-L.; Shi, Z.-Z. Enabling the Use of Alkyl Thianthrenium Salts in Cross-Coupling Reactions by Copper Catalysis. *Angew. Chem. Int. Ed*. **2021**, *60*, 21756-21760. (b) Chen, C.; Wang, Z.-J.; Lu, H.-J.; Zhao, Y.; Shi, Z.-Z. Generation of Non-Stabilized Alkyl Radicals from Thianthrenium Salts for C–B and C–C Bond Formation. *Nat.Commun*. **2021**, *12*, 4526-4534.

6. Copies of NMR spectra

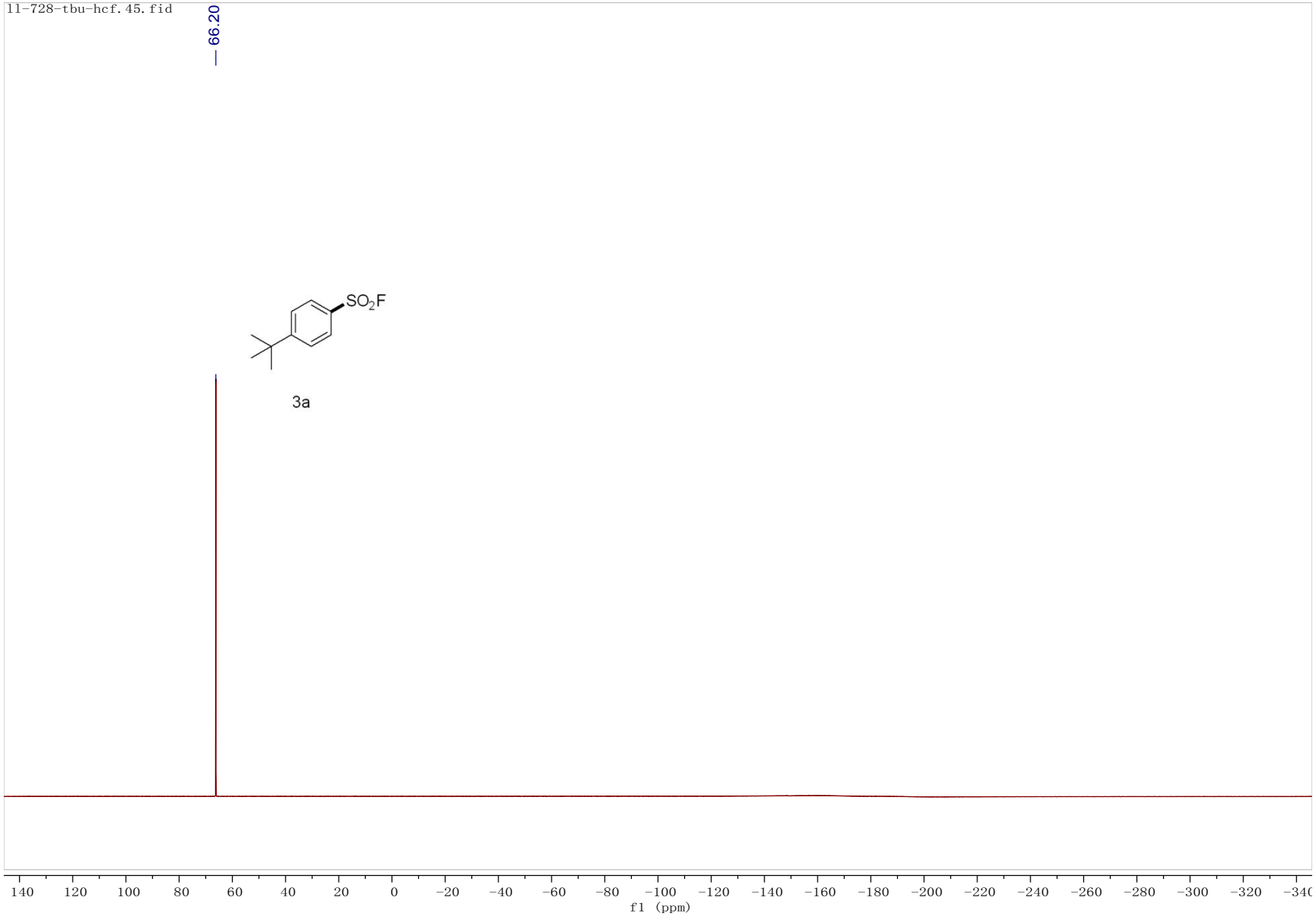
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**.



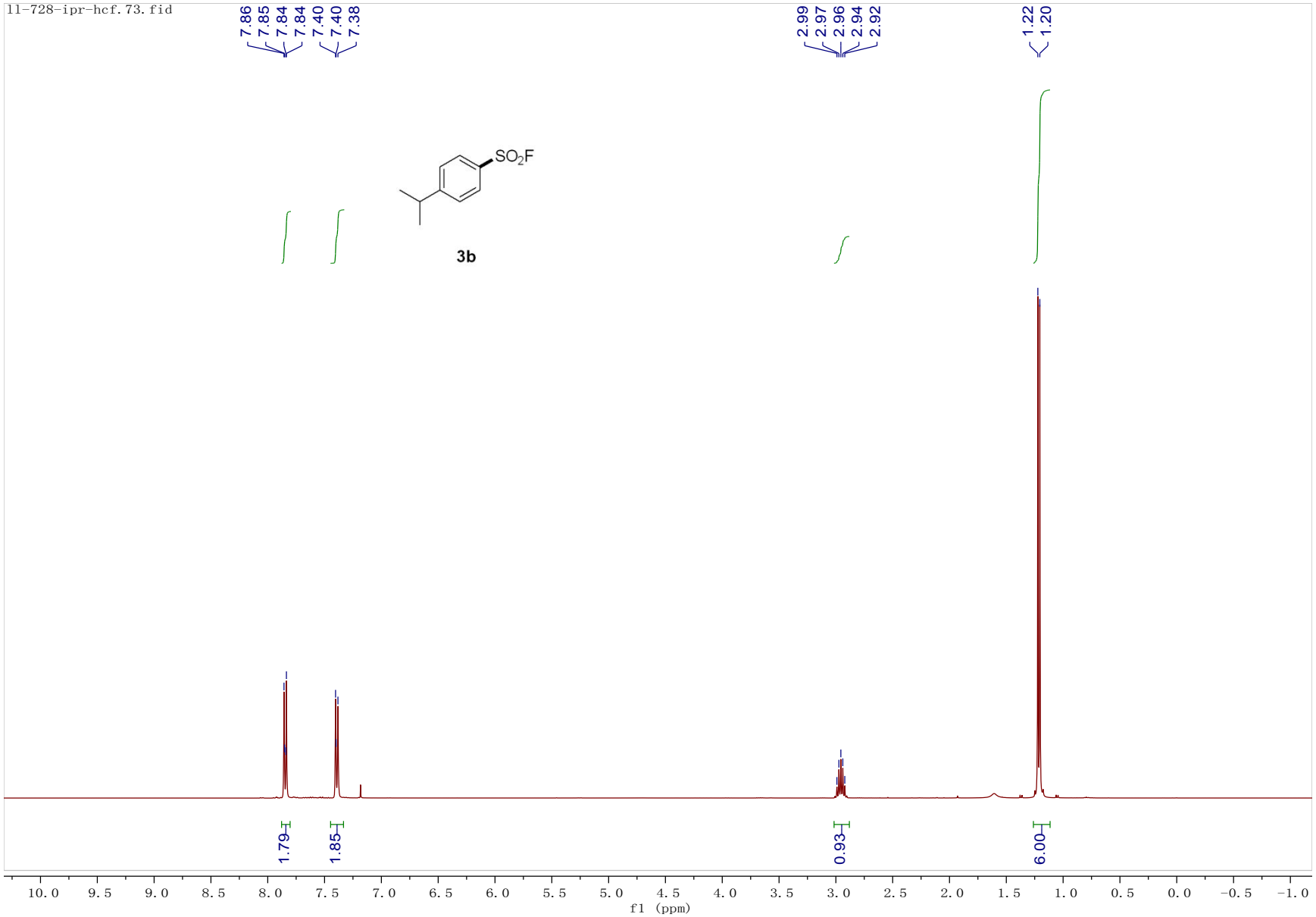
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3a**.



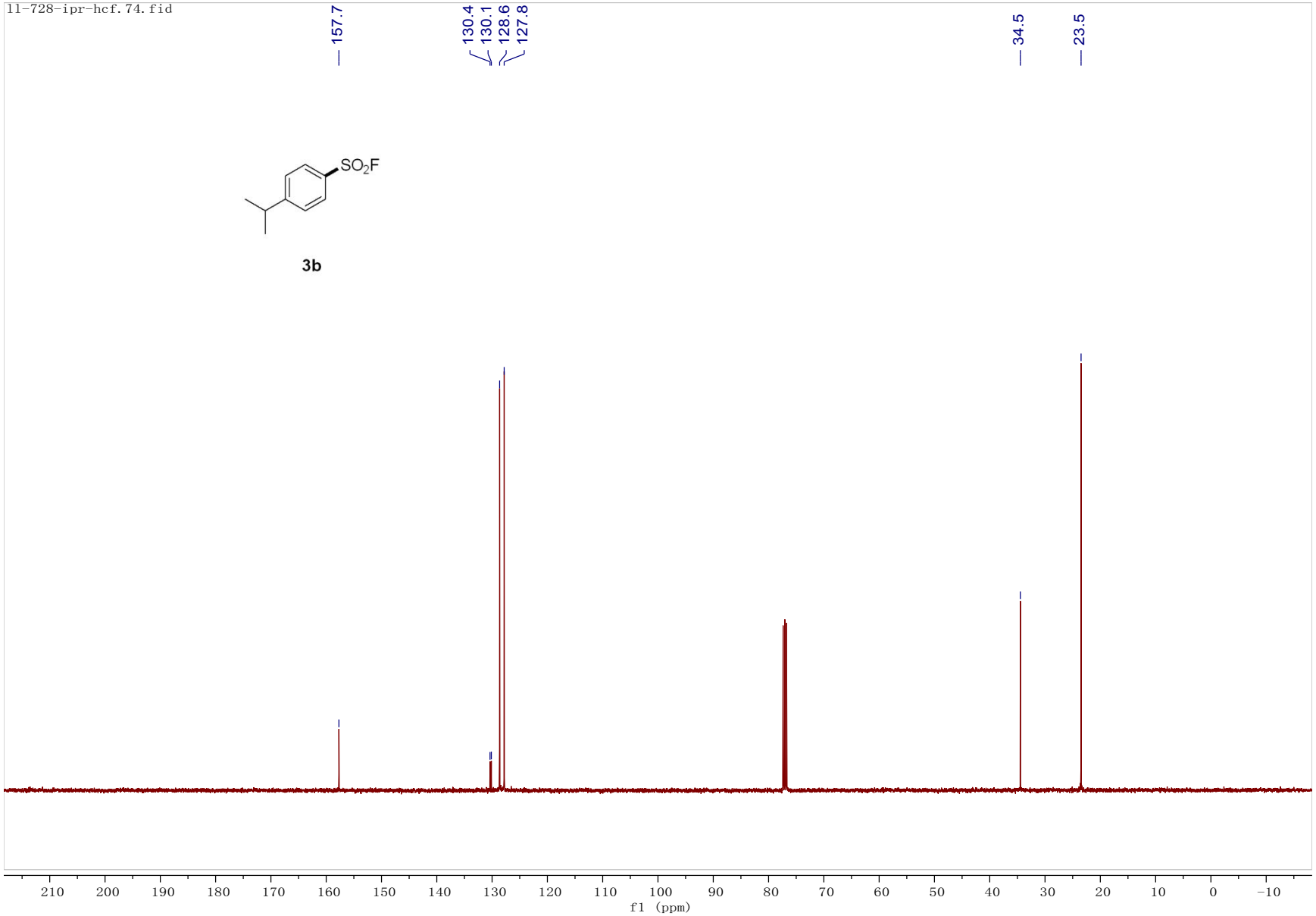
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3a**.



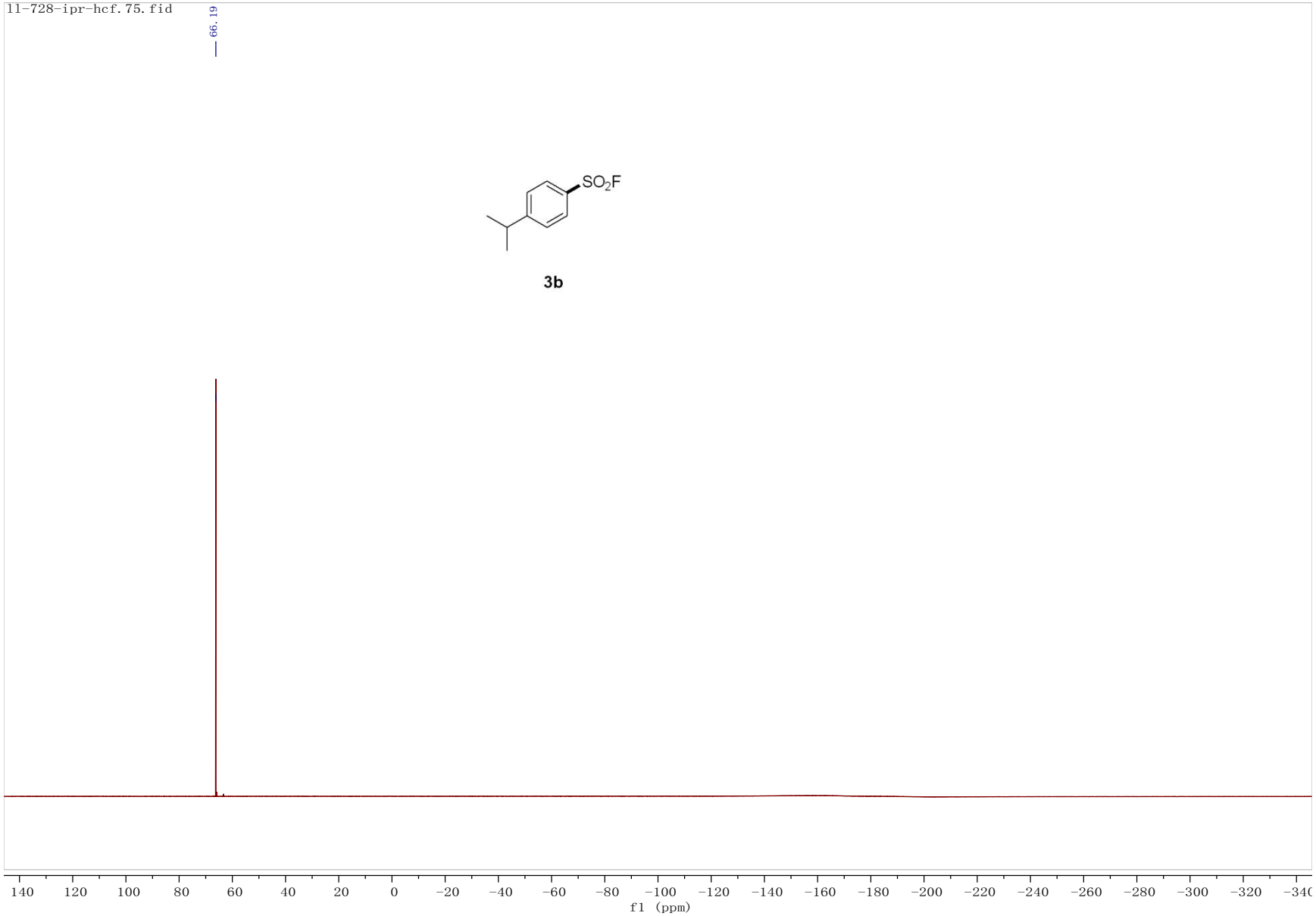
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**.



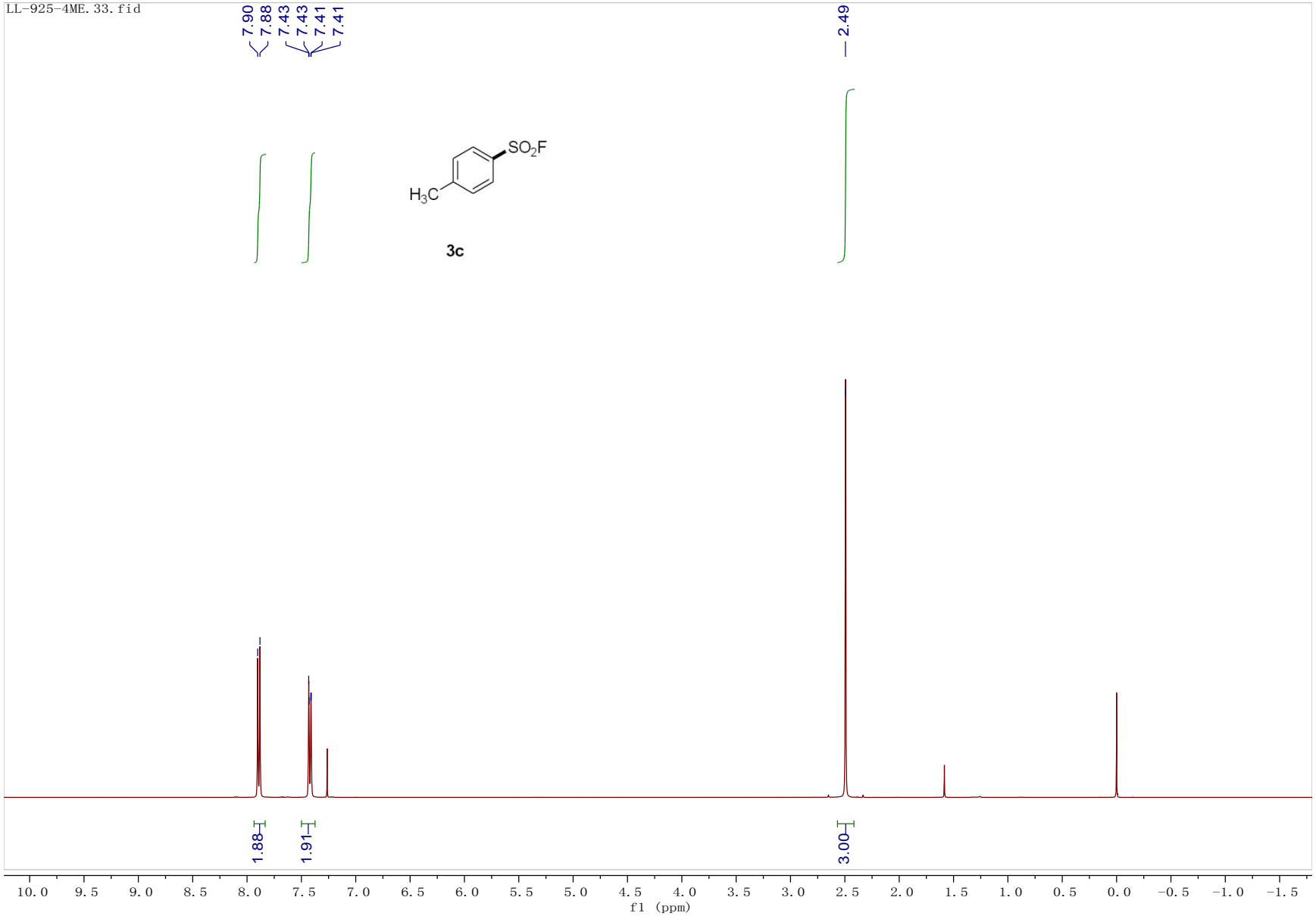
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3b**.



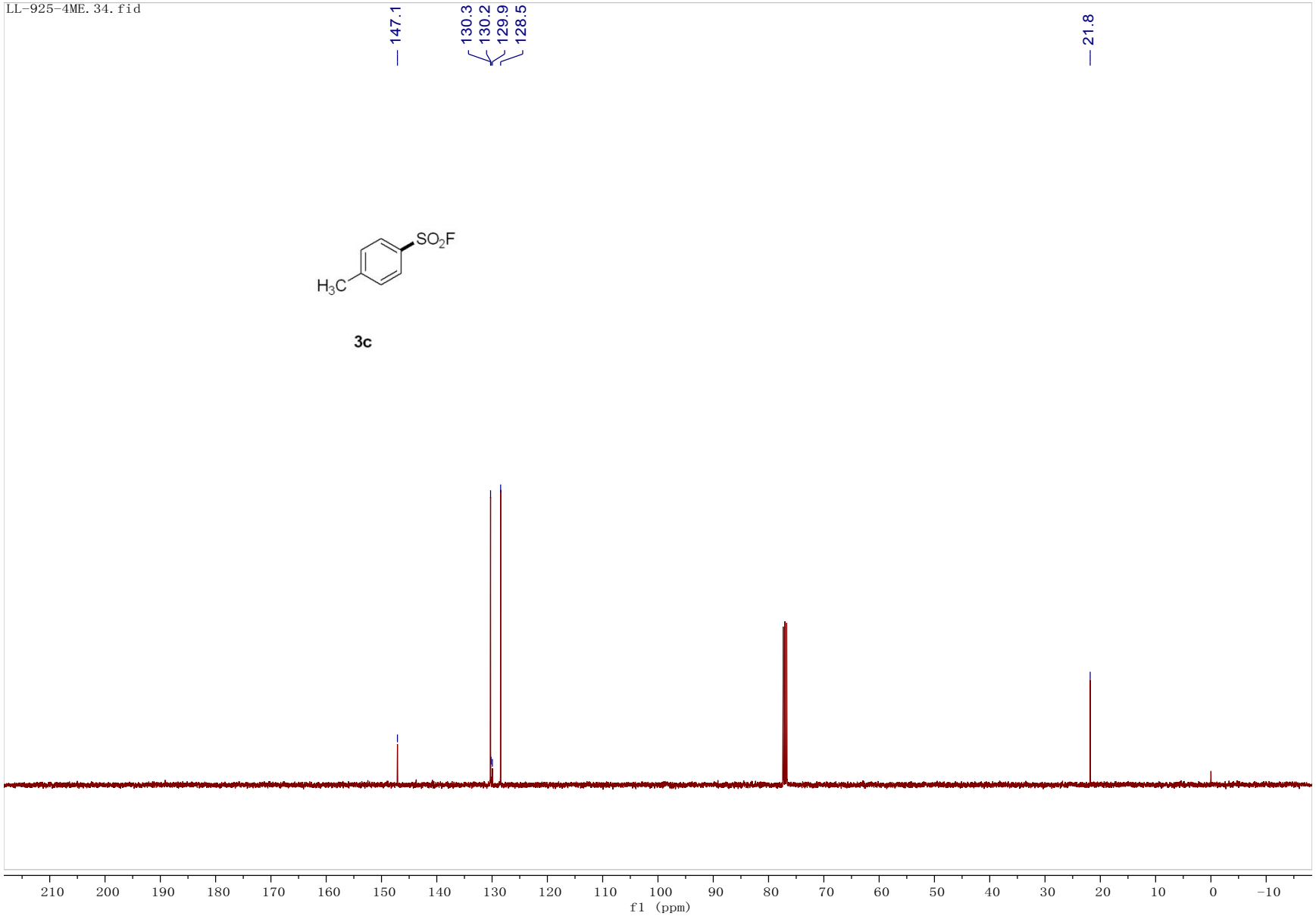
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3b**.



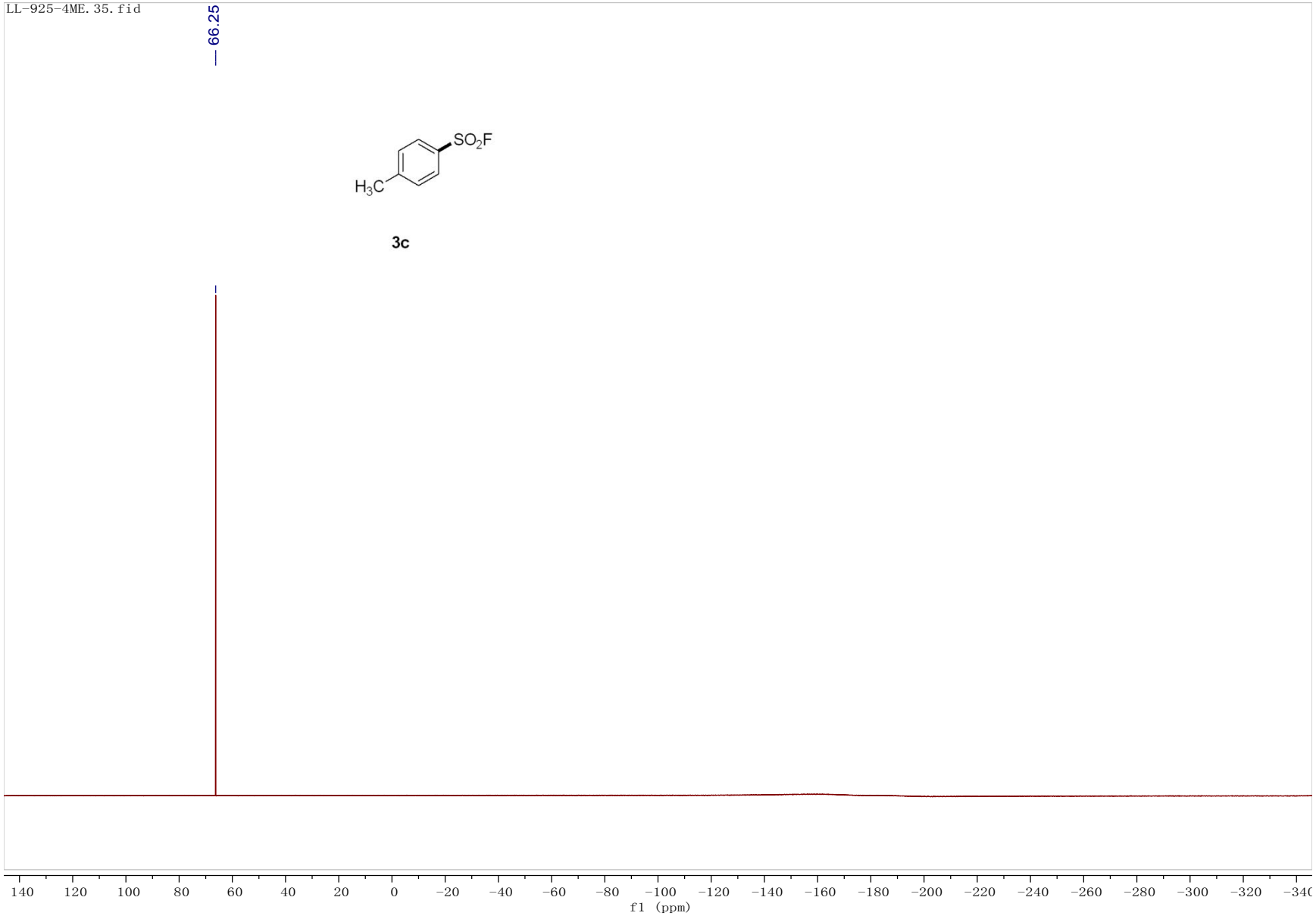
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3c.



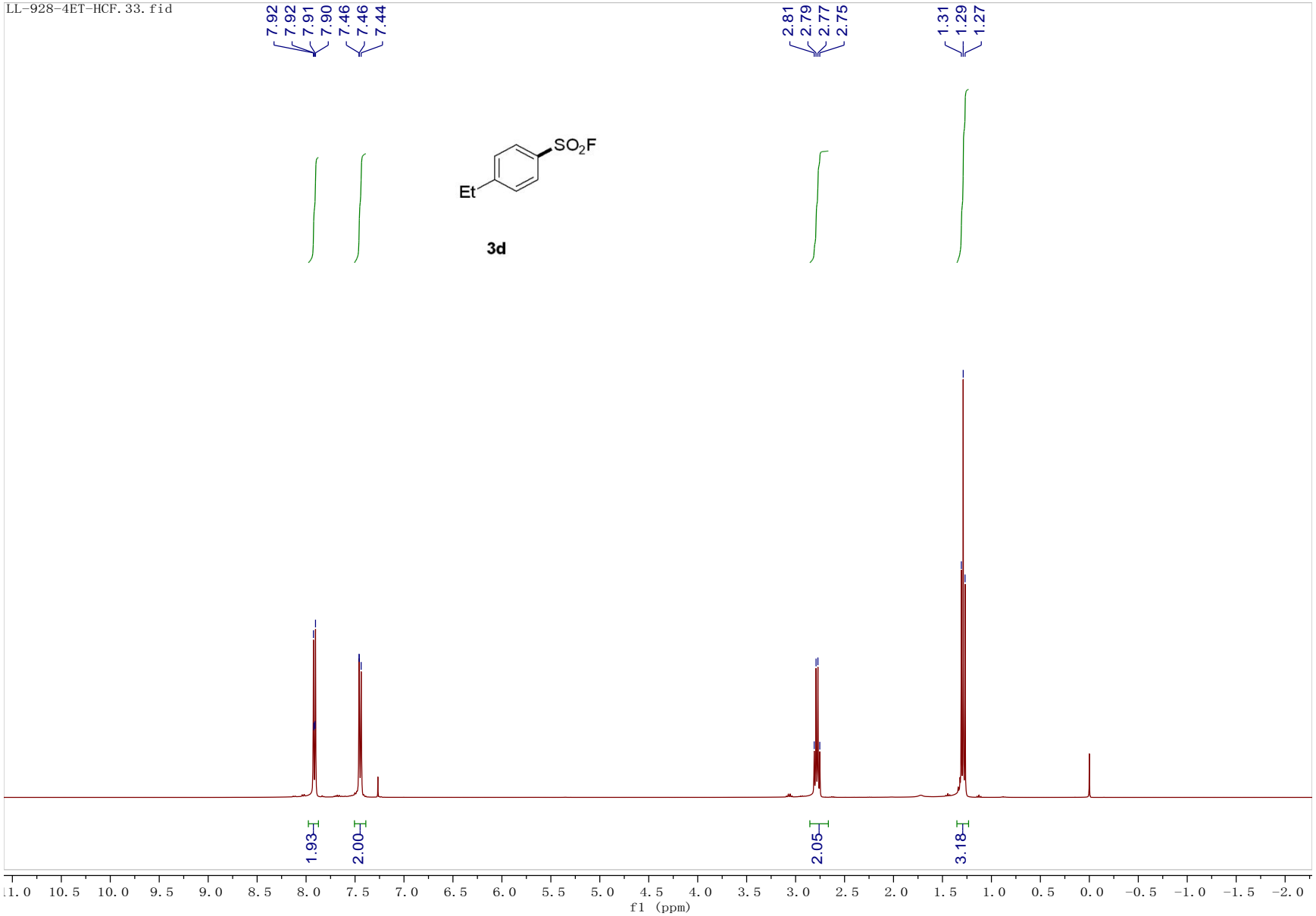
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3c**.



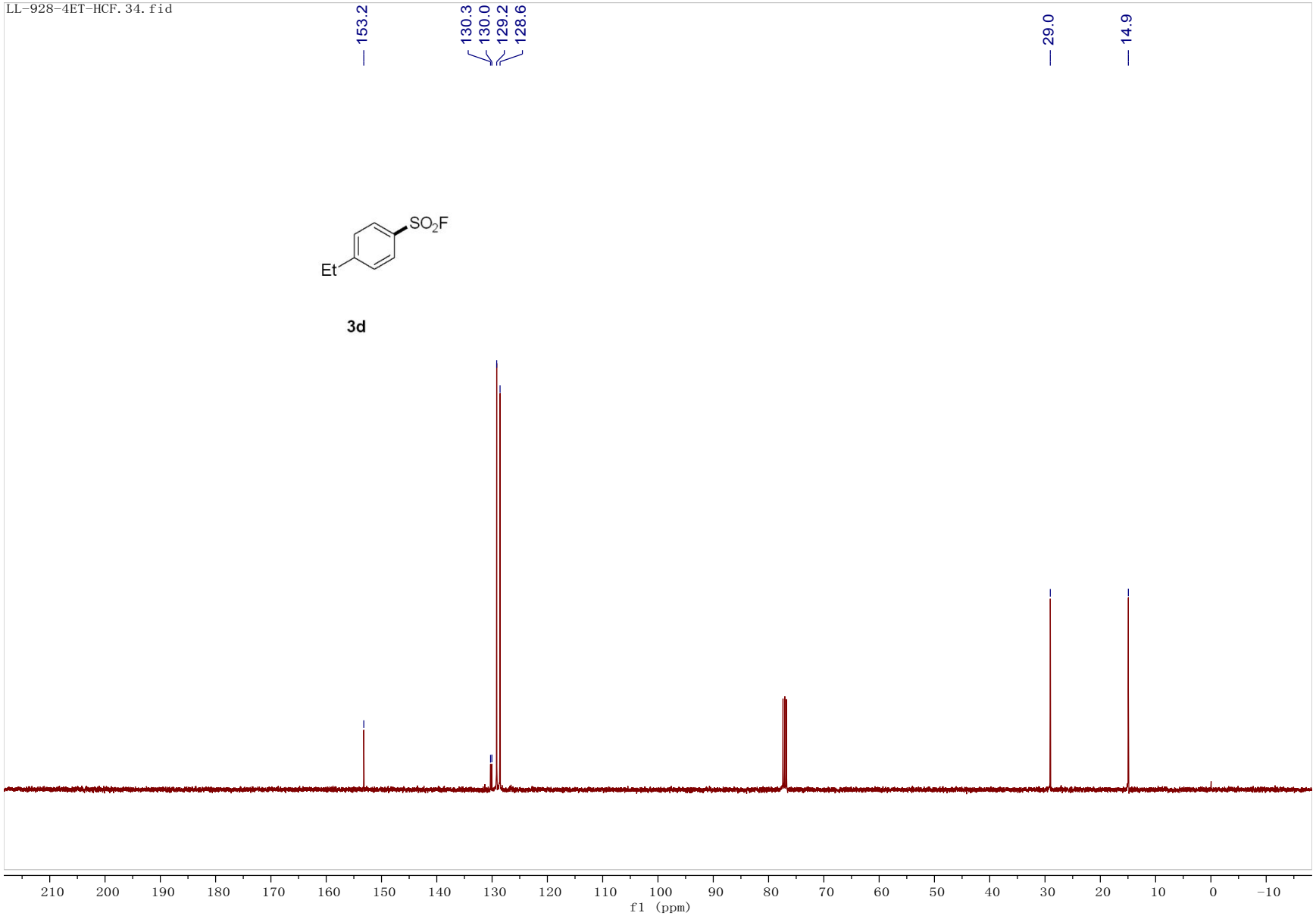
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3c.



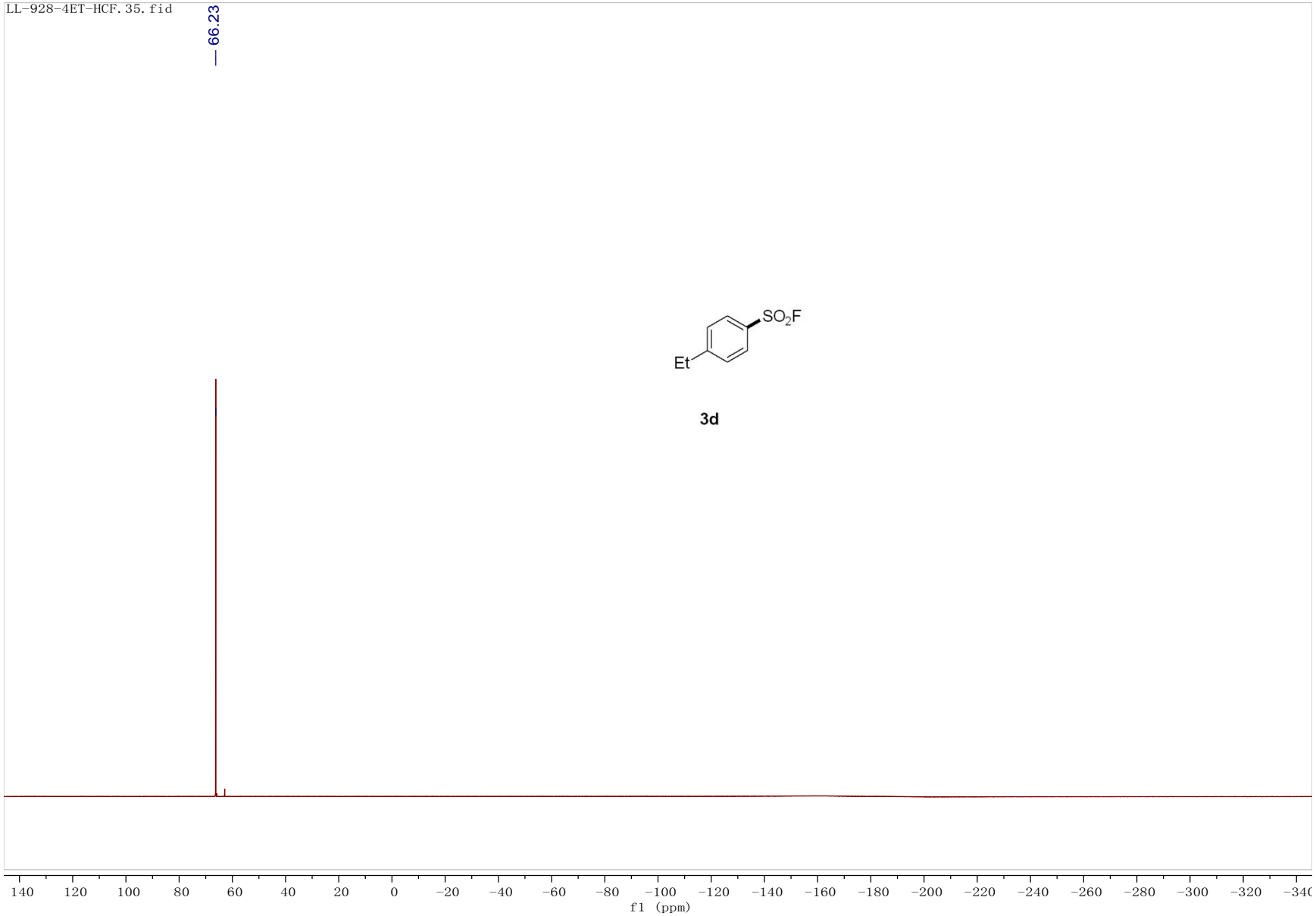
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3d**.



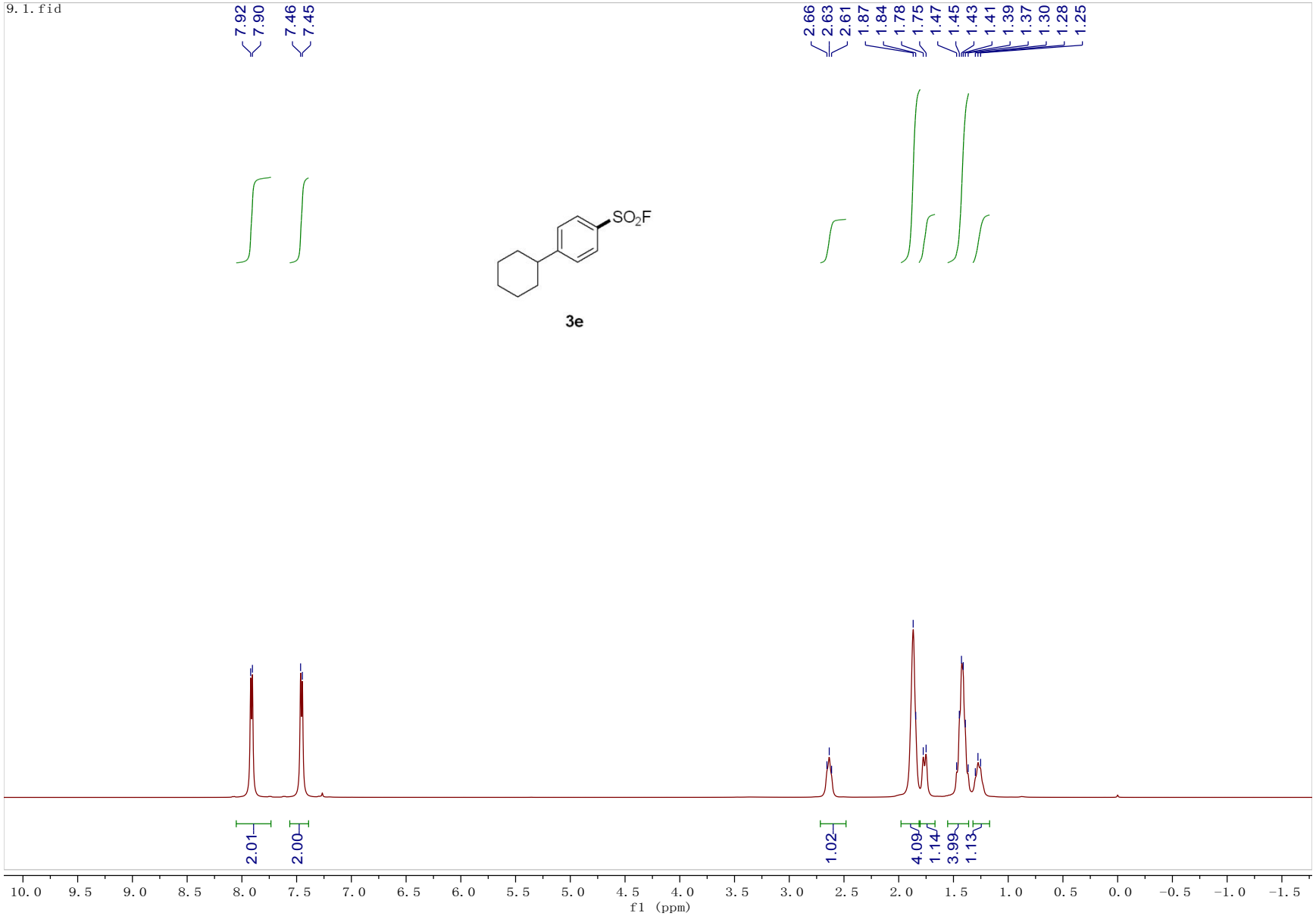
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3d**.



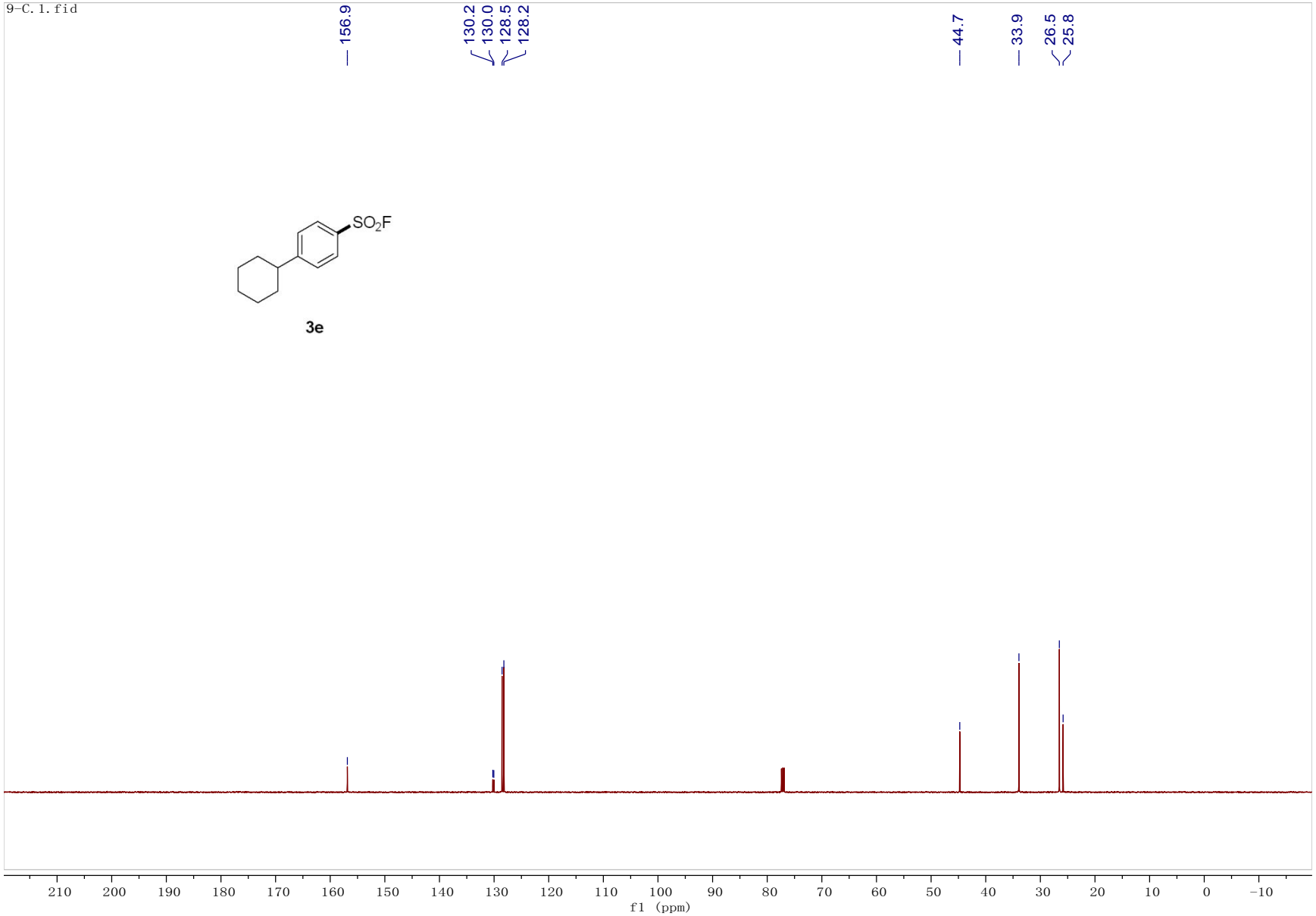
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3d**.



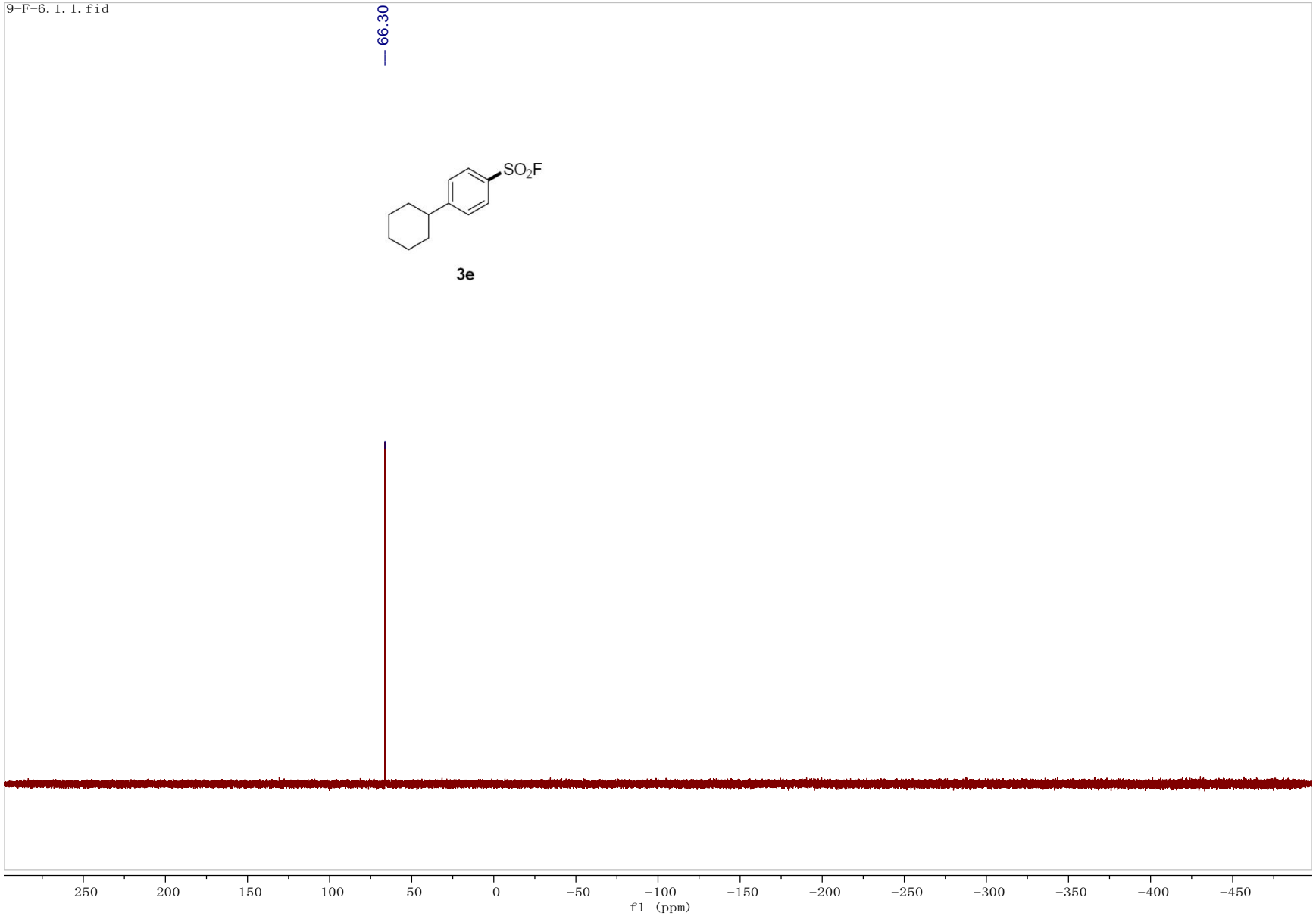
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3e**.



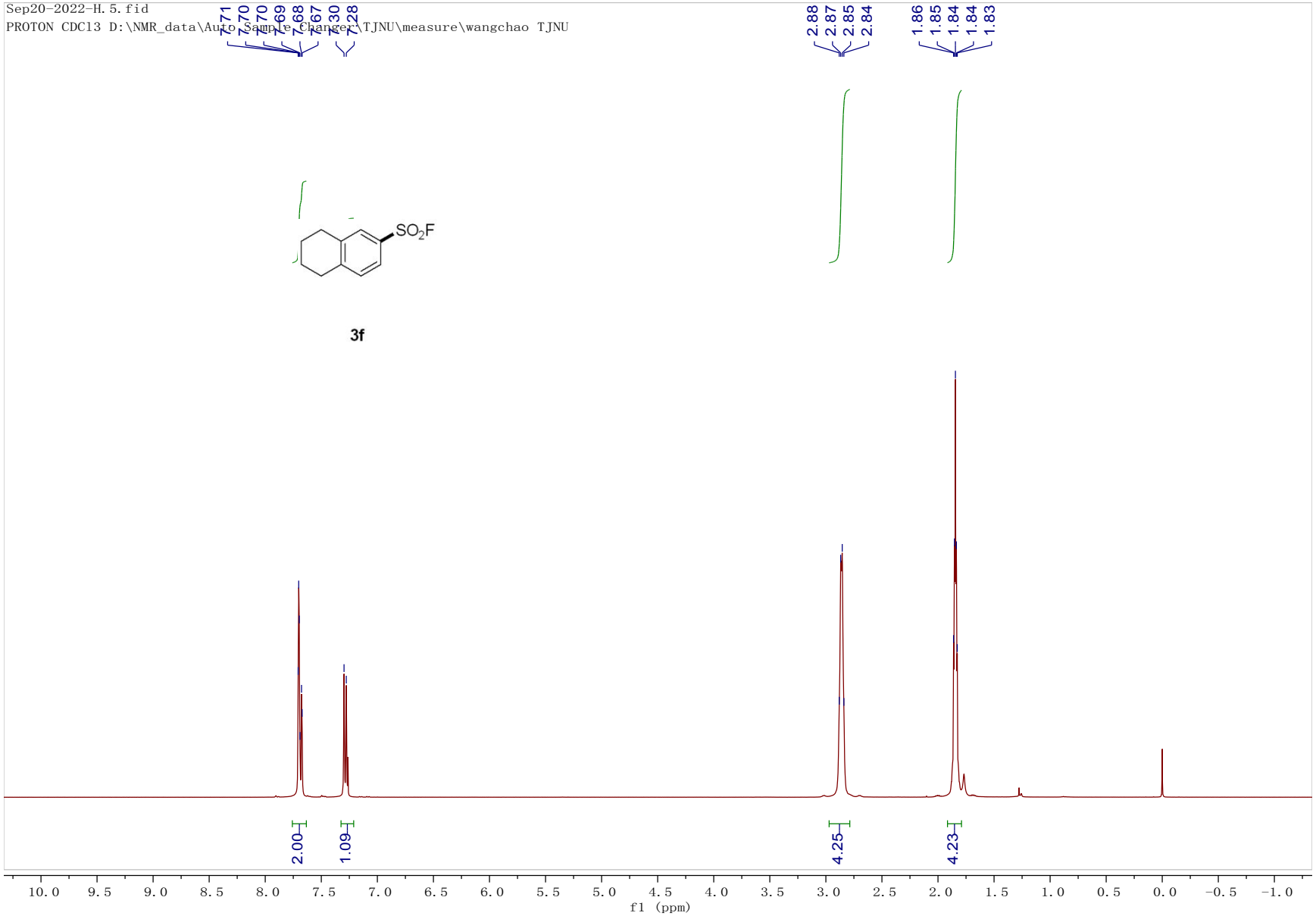
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3e**.



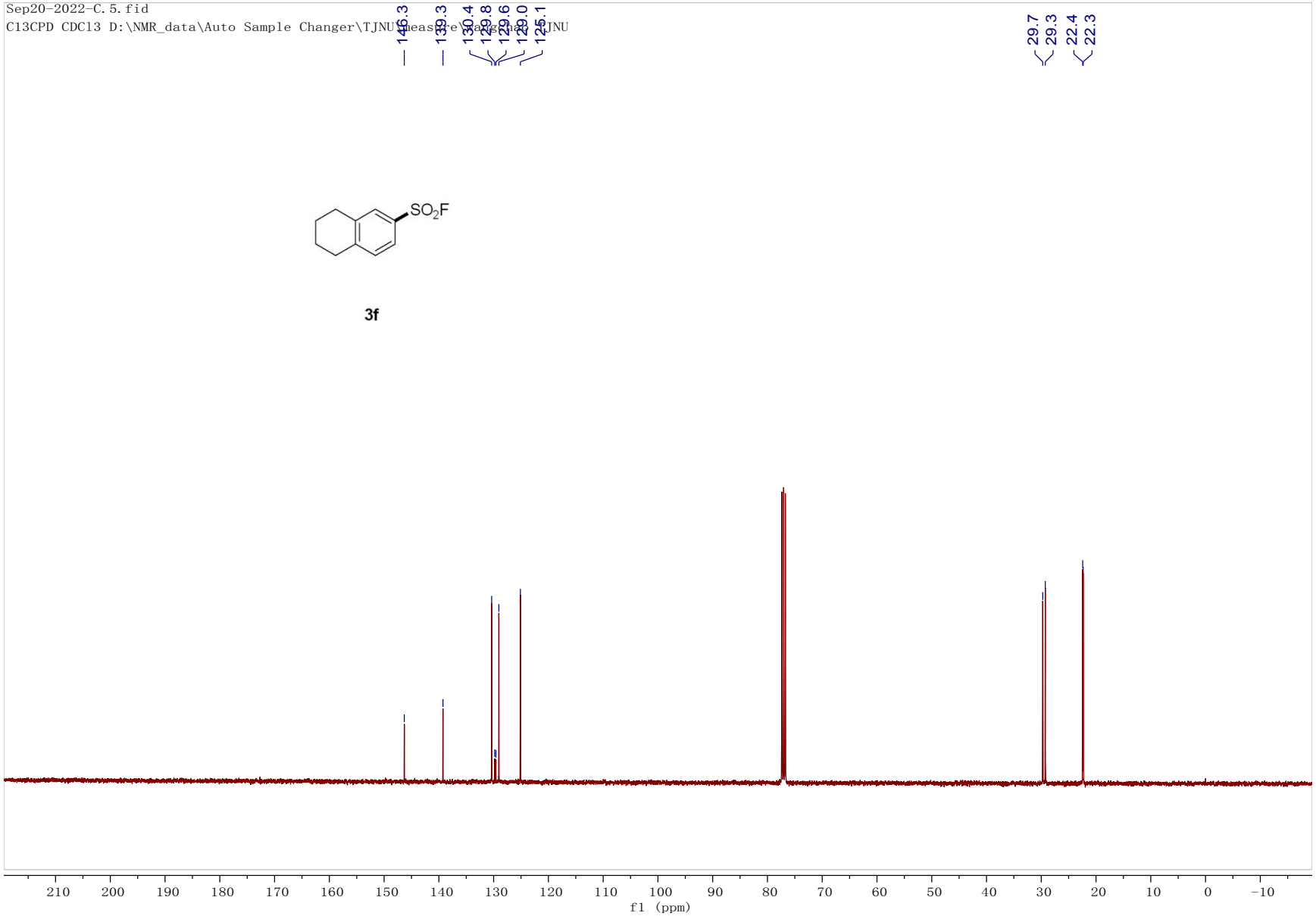
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **3e**.



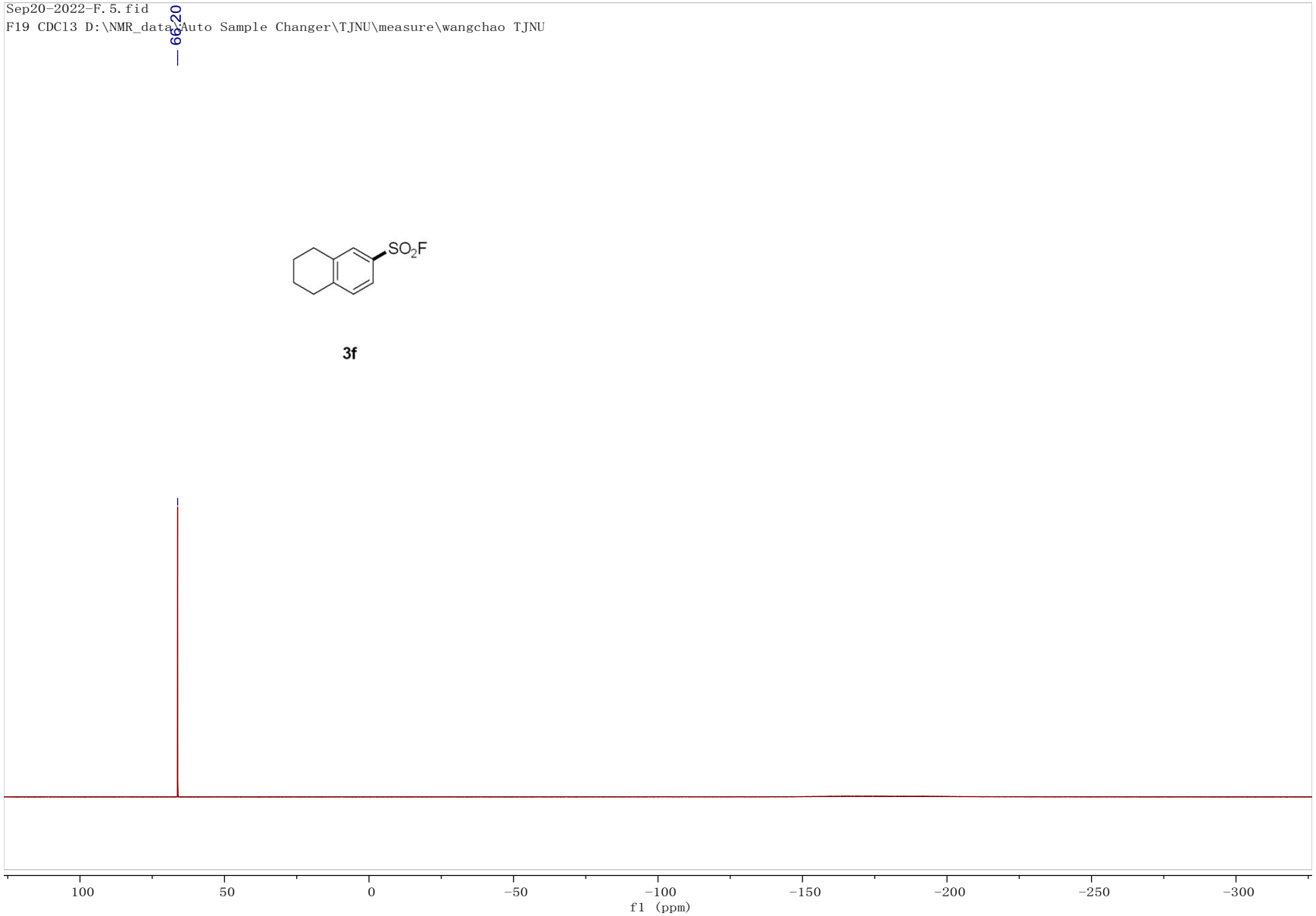
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3f**.



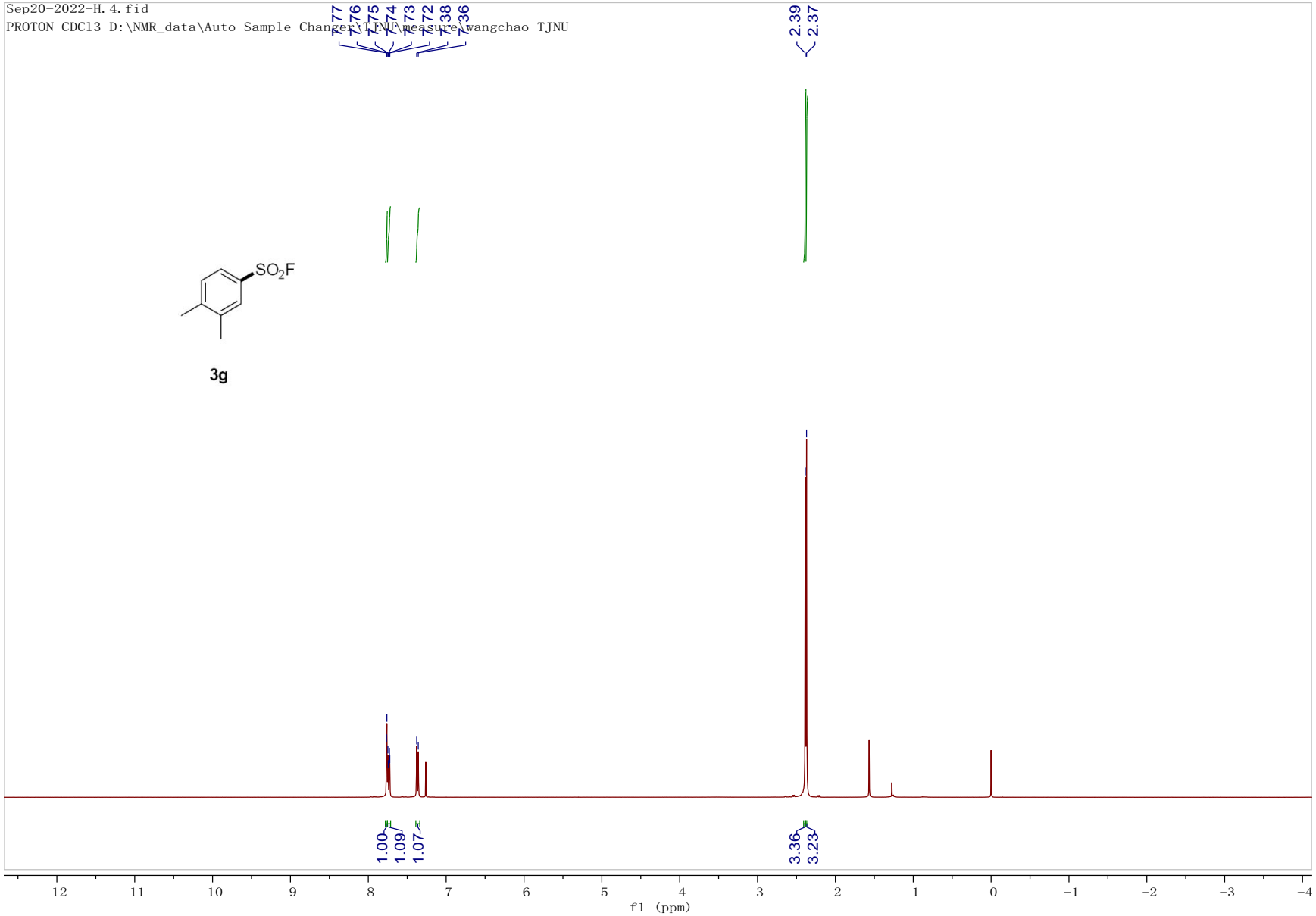
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3f**.



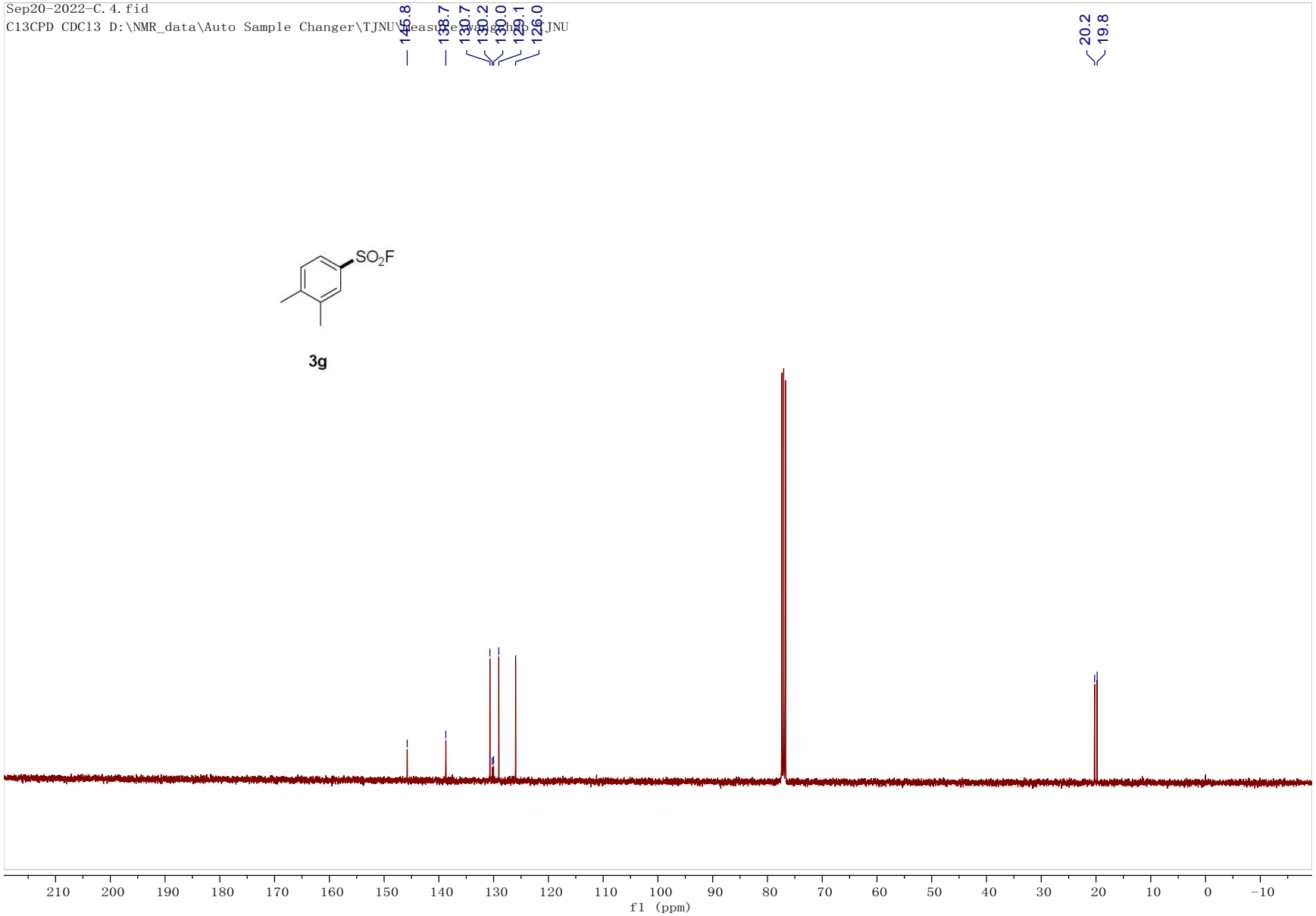
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **3f**.



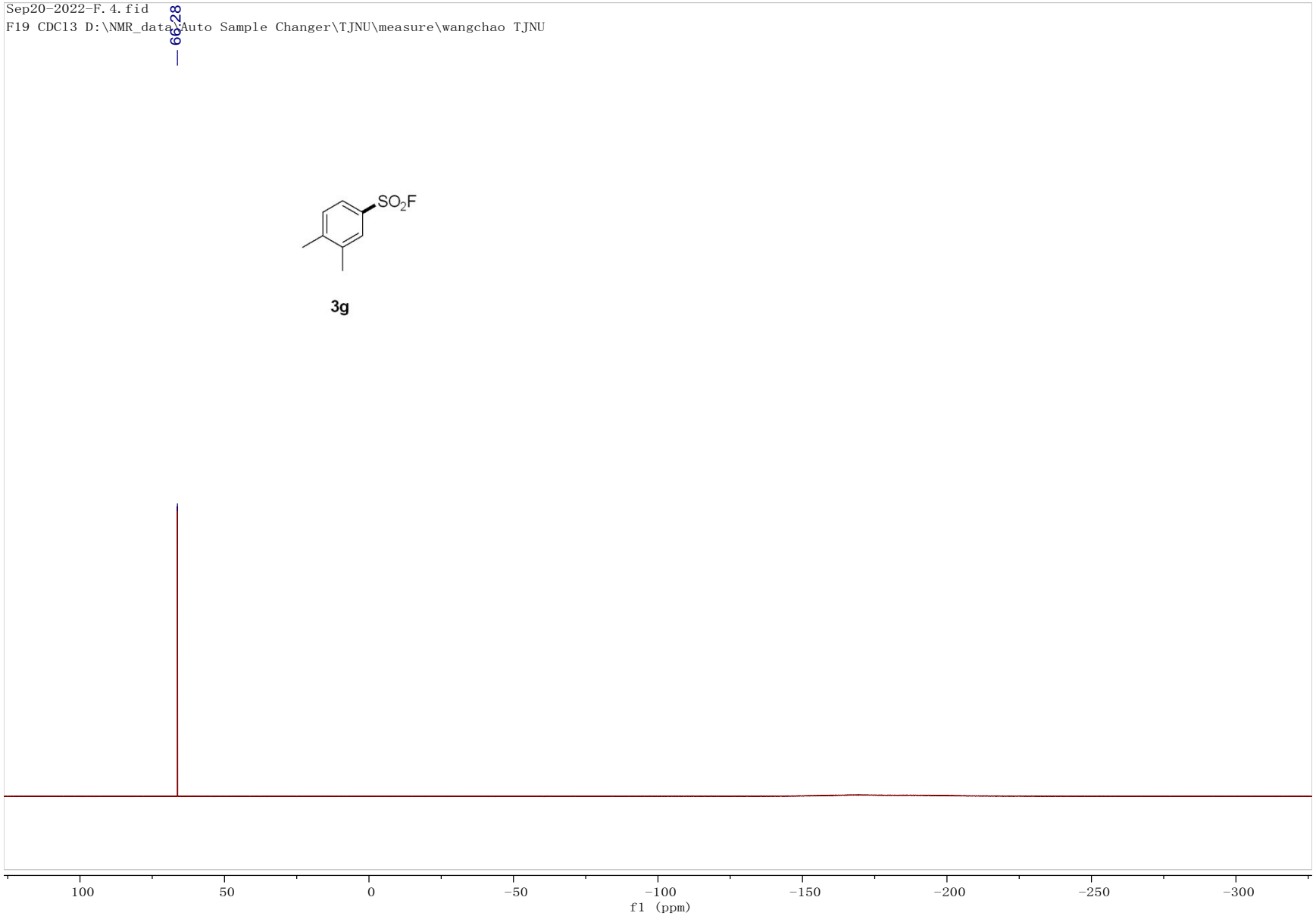
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3g**.



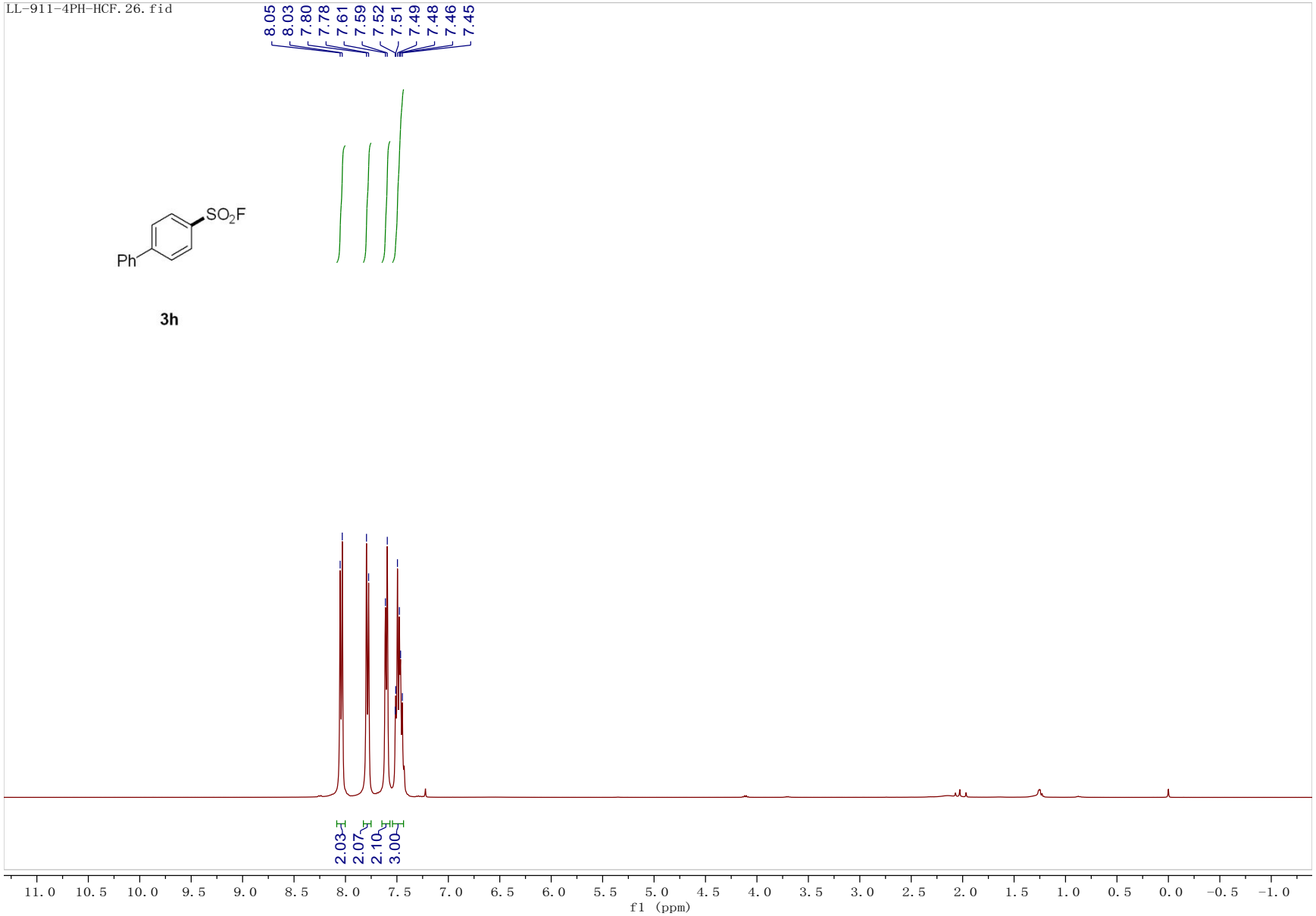
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3g**.



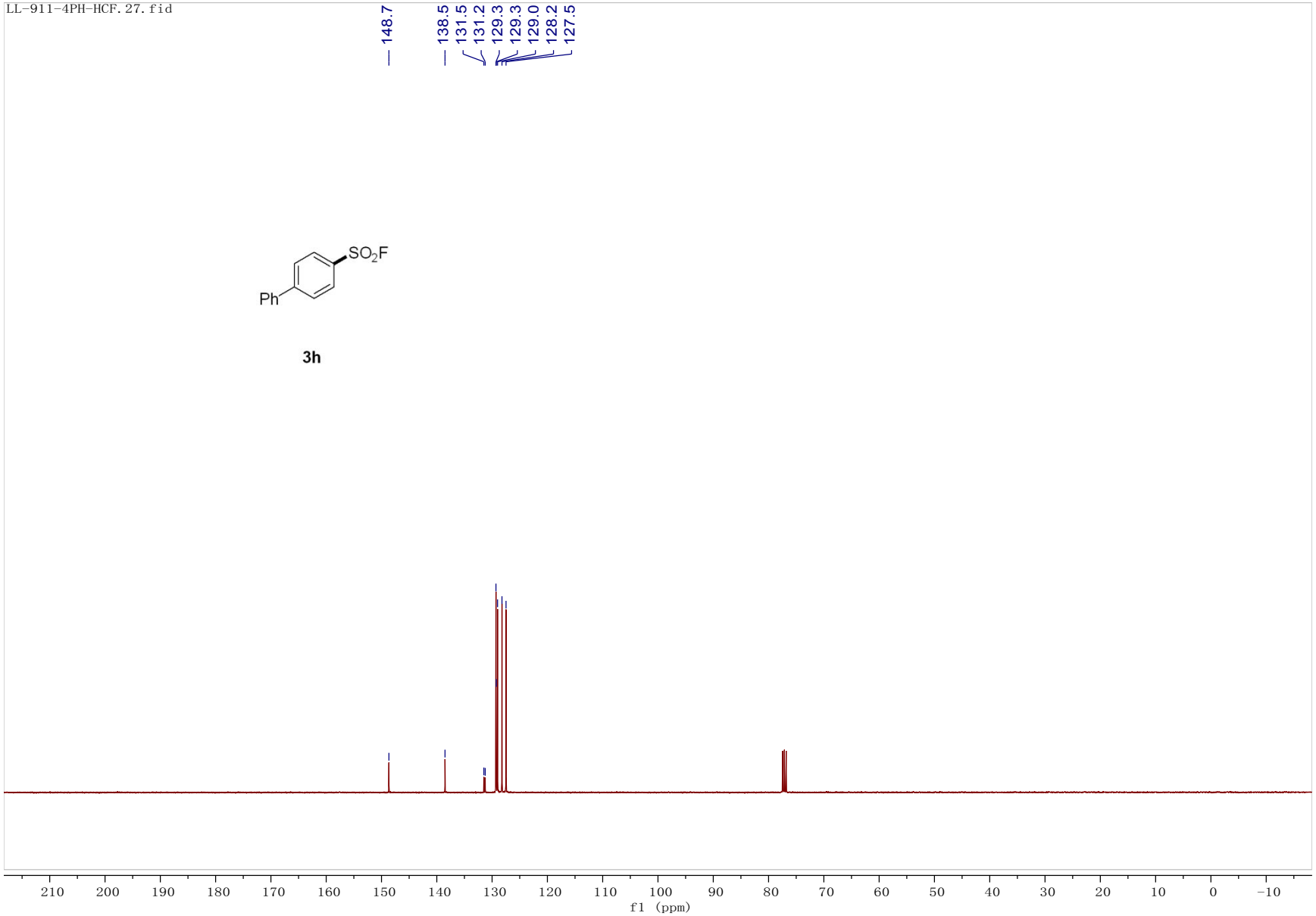
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3g**.



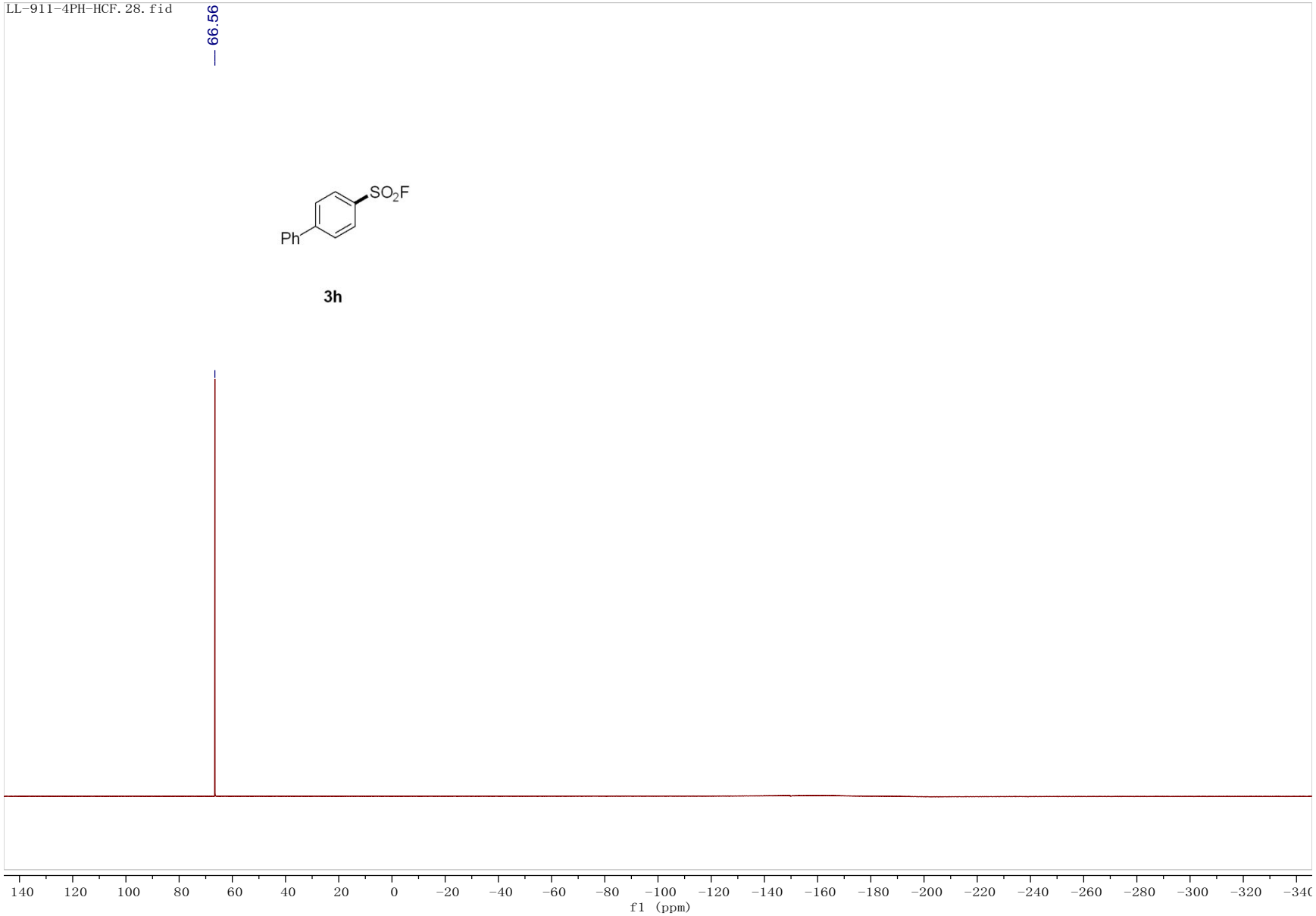
1H NMR (400 MHz, $CDCl_3$) spectrum of **3a**.



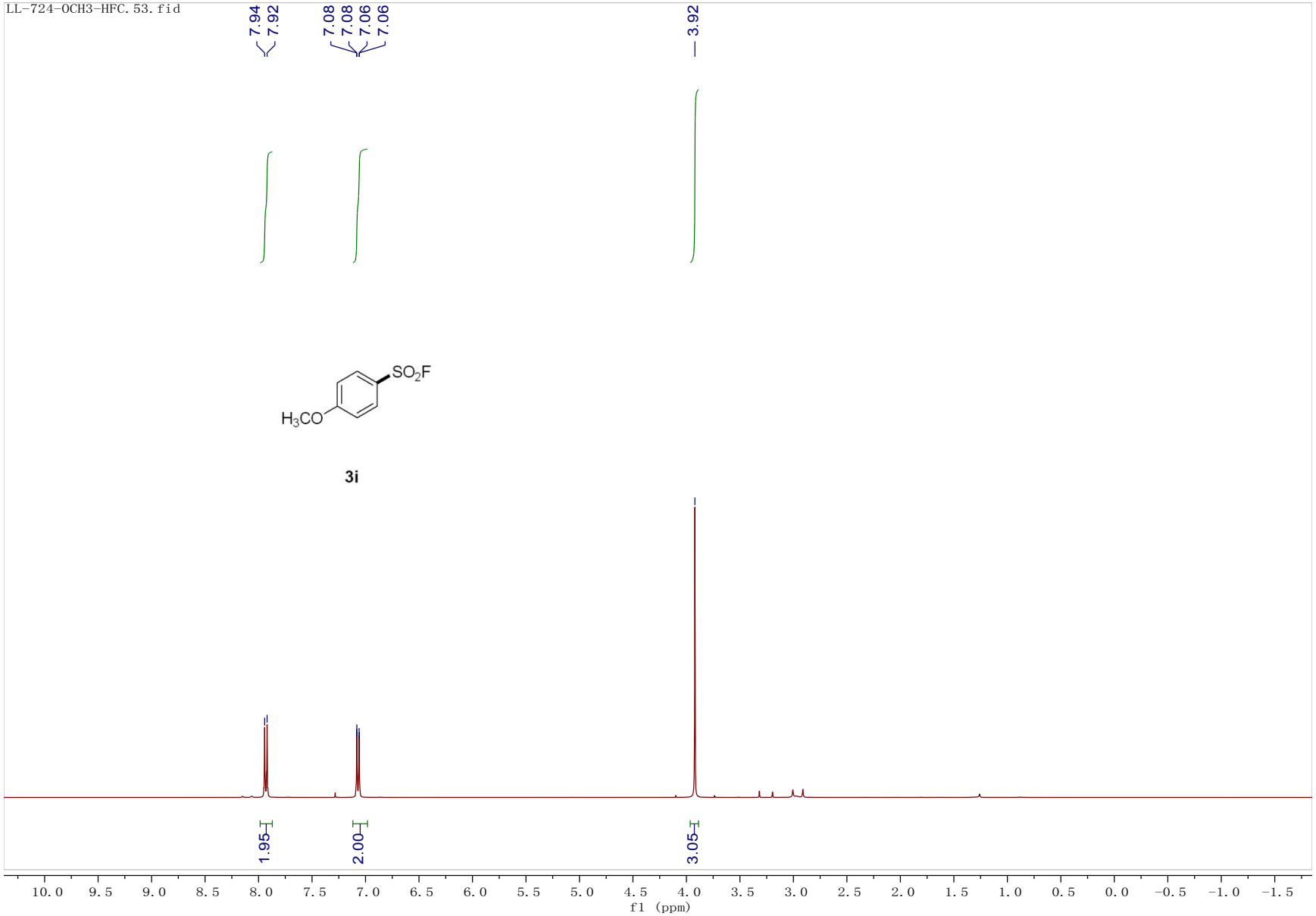
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3h**.



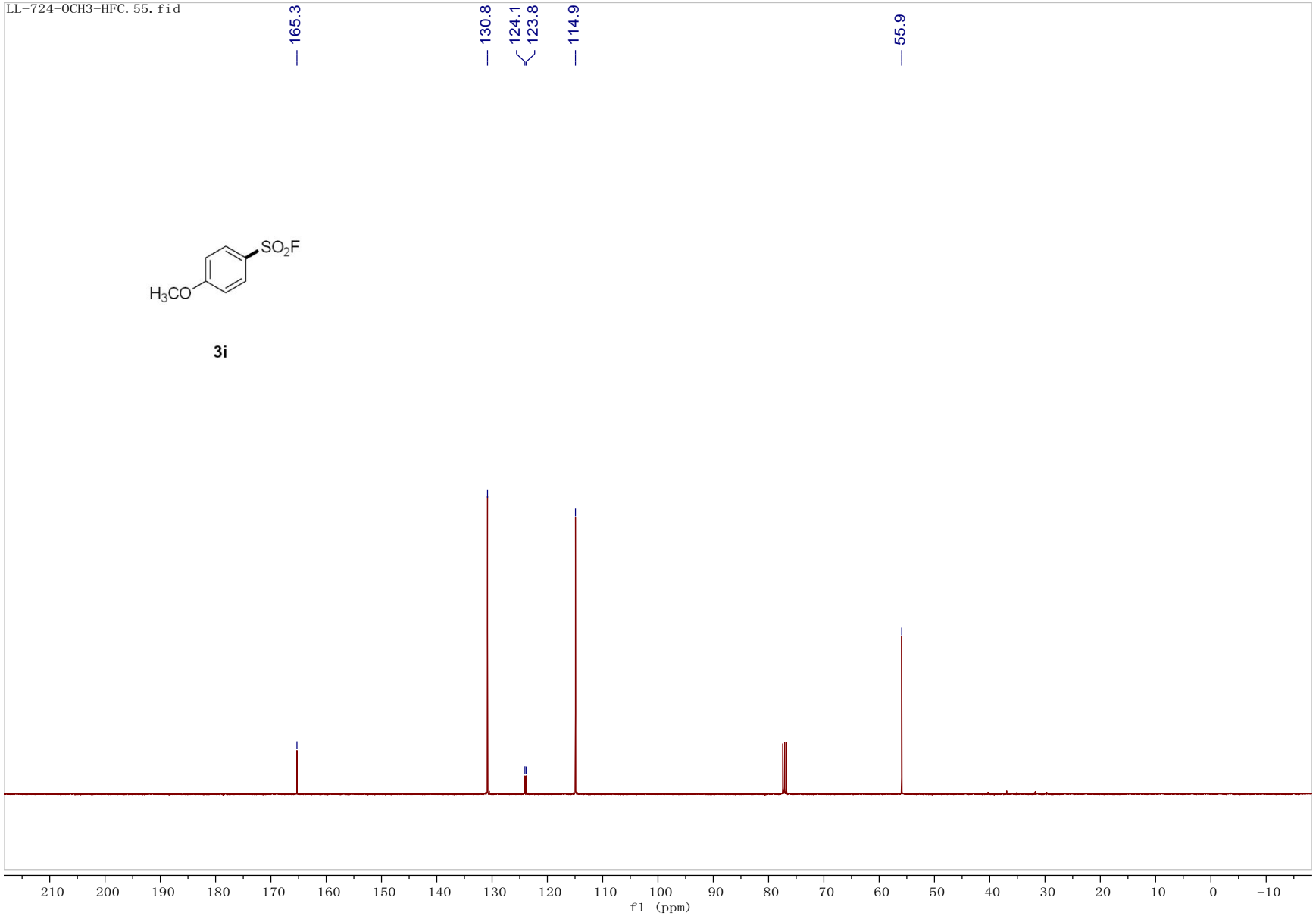
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3h**.



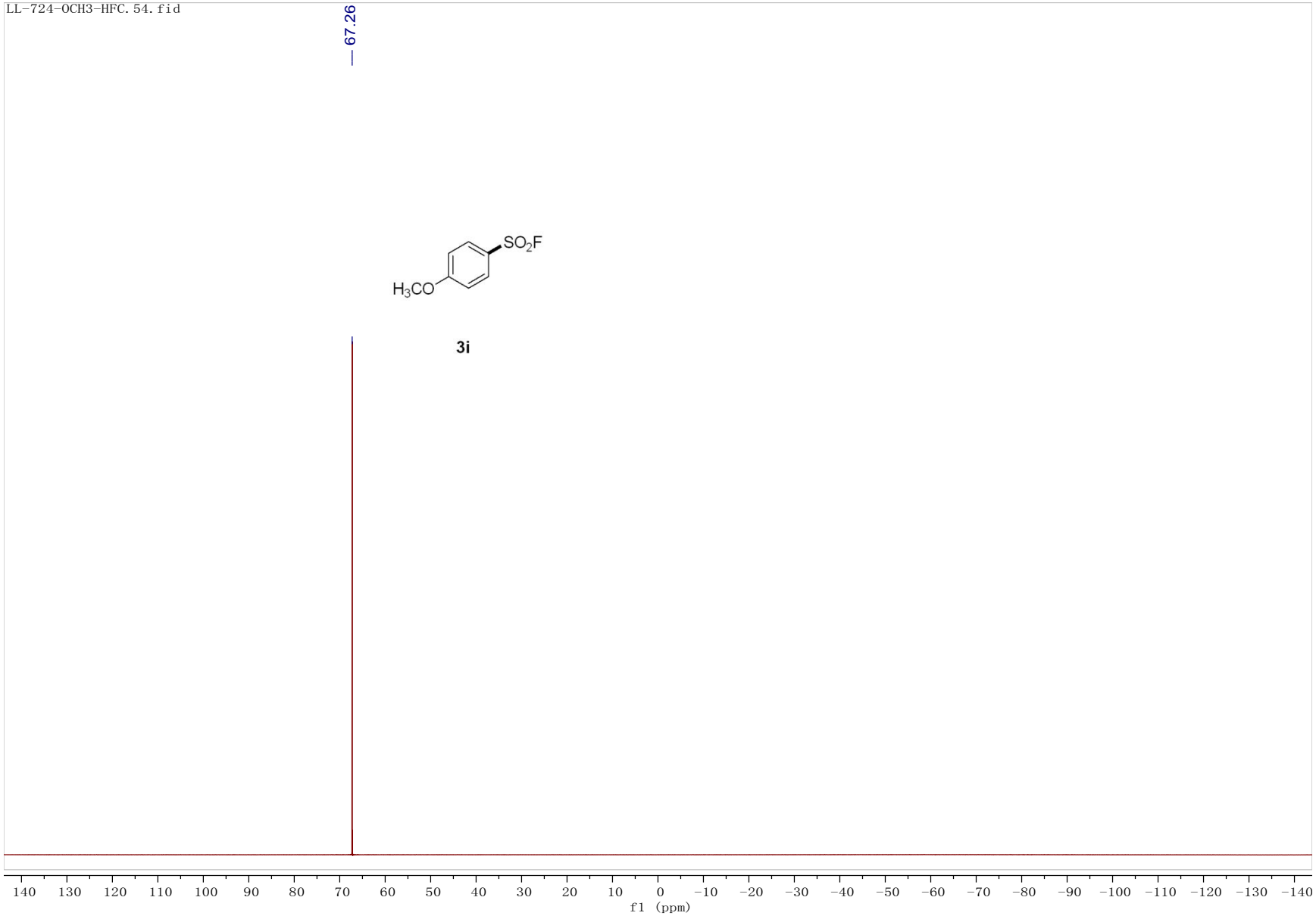
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3i**.



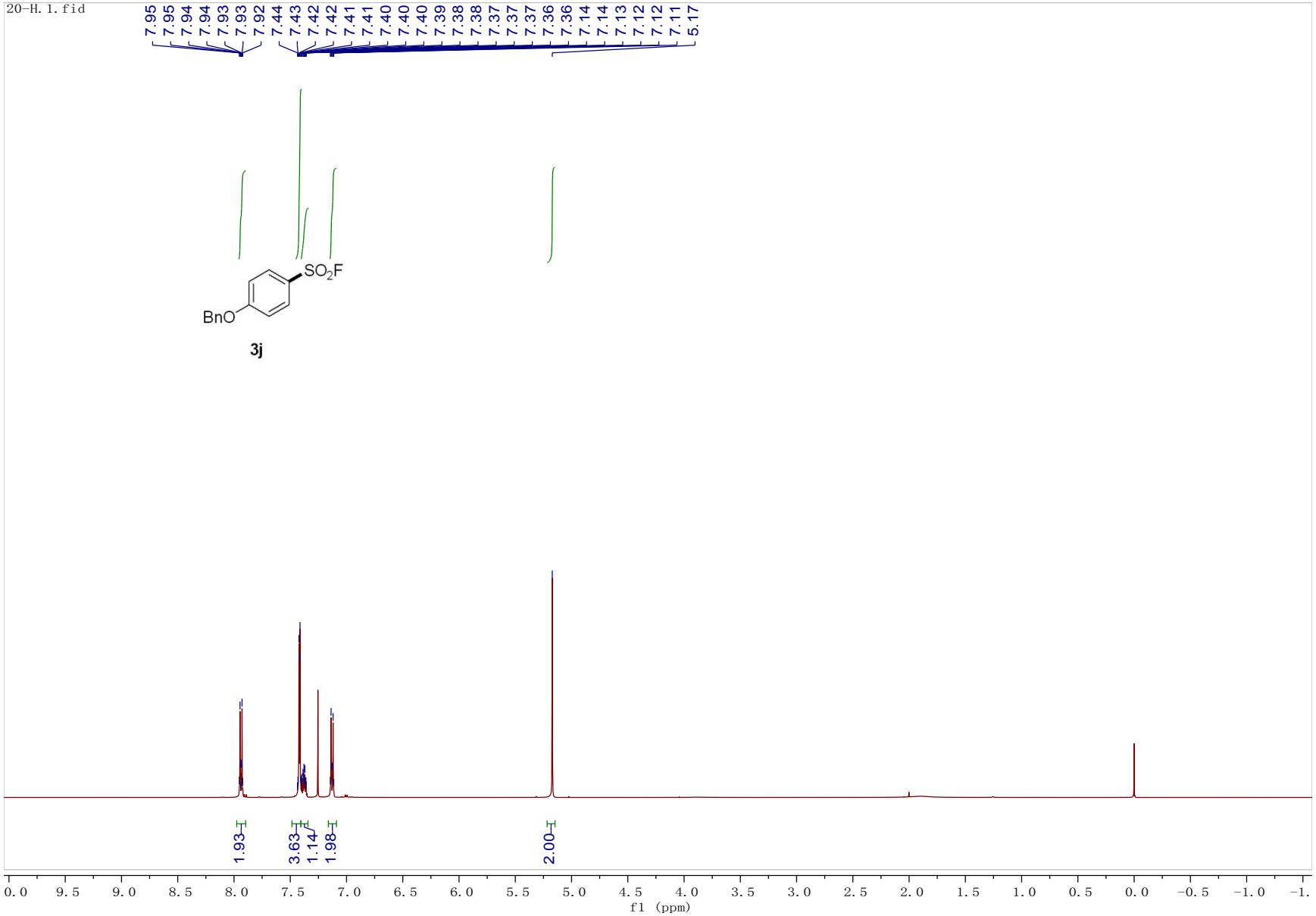
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3i**.



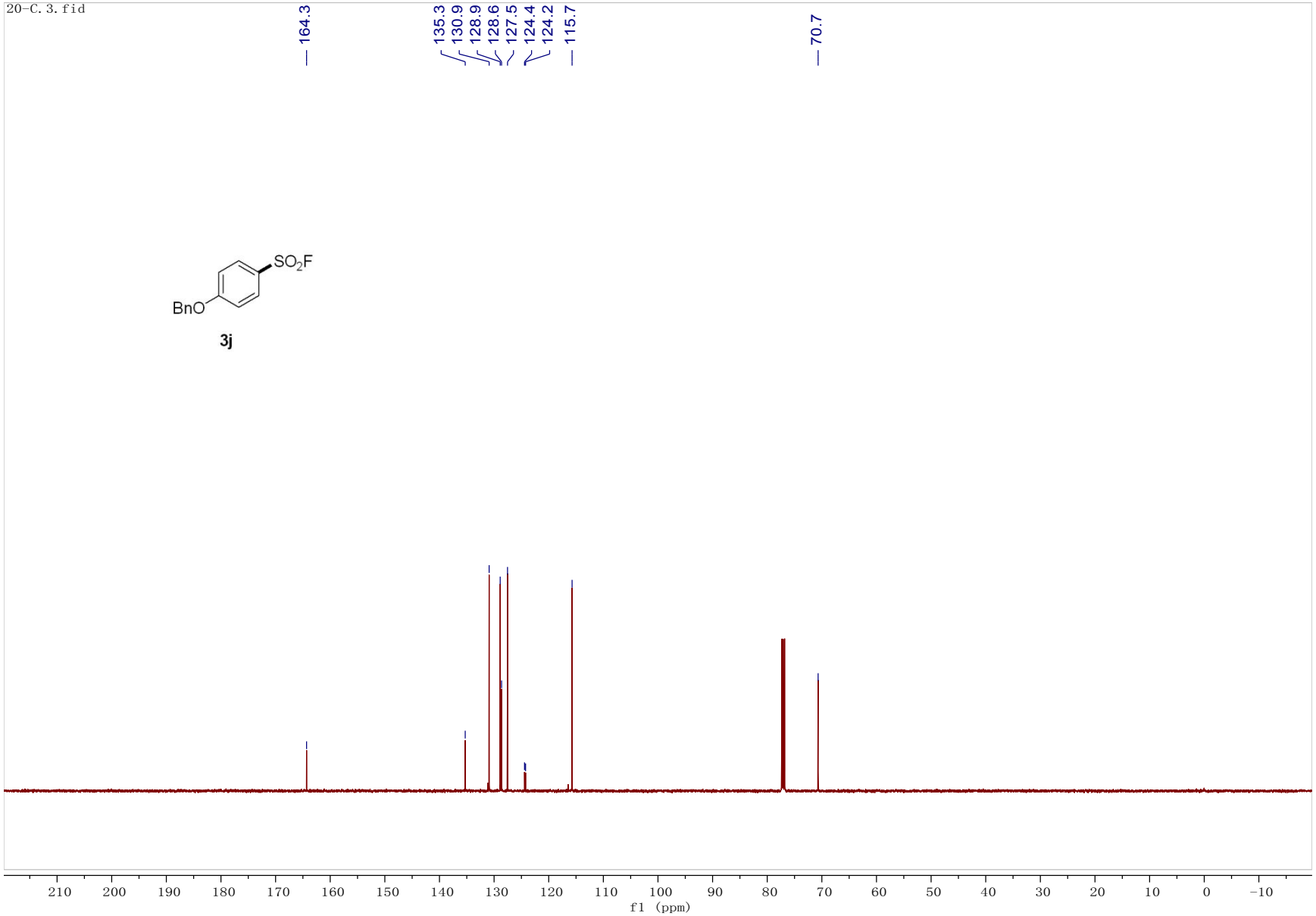
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3i**.



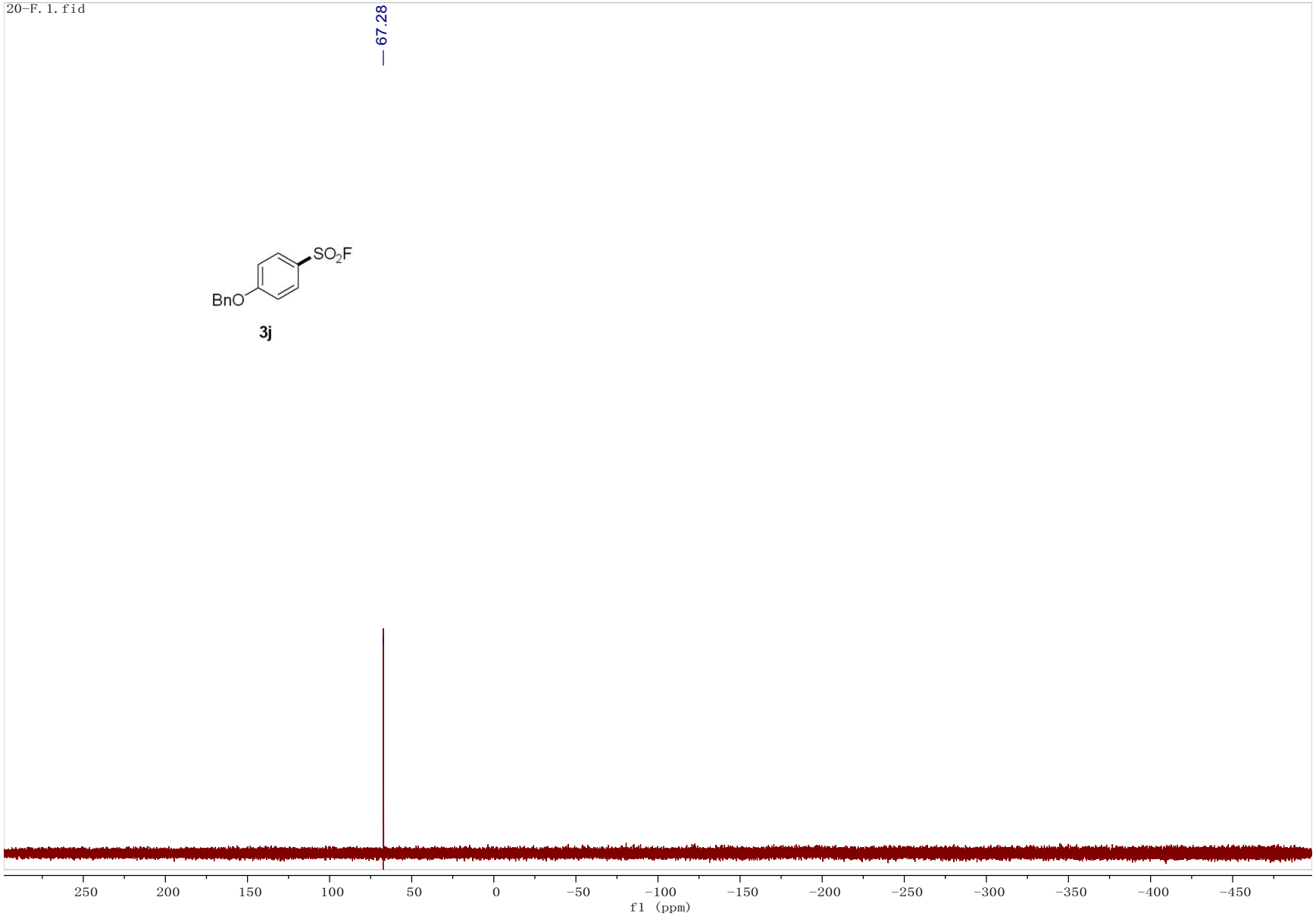
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3j**.



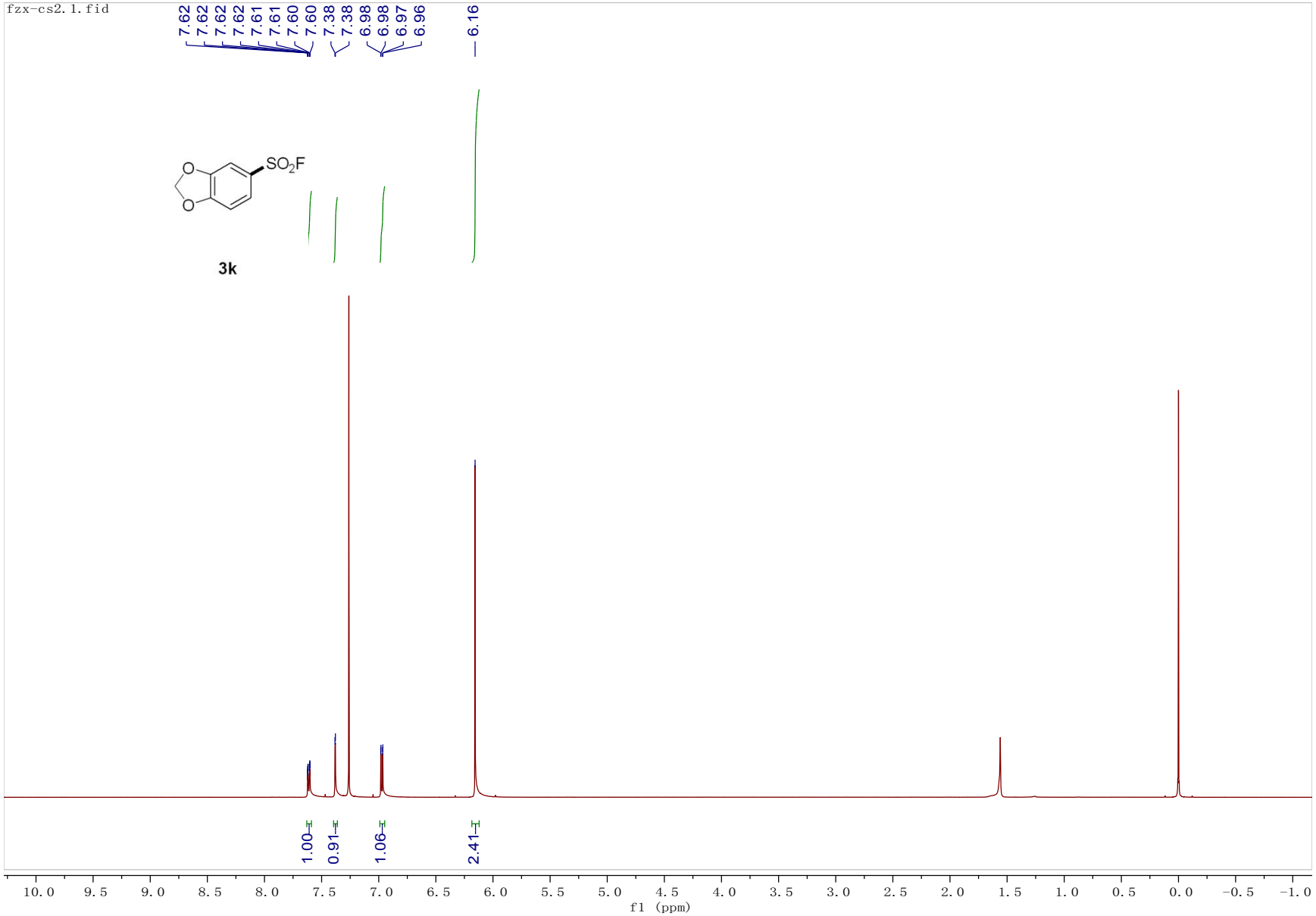
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3j**.



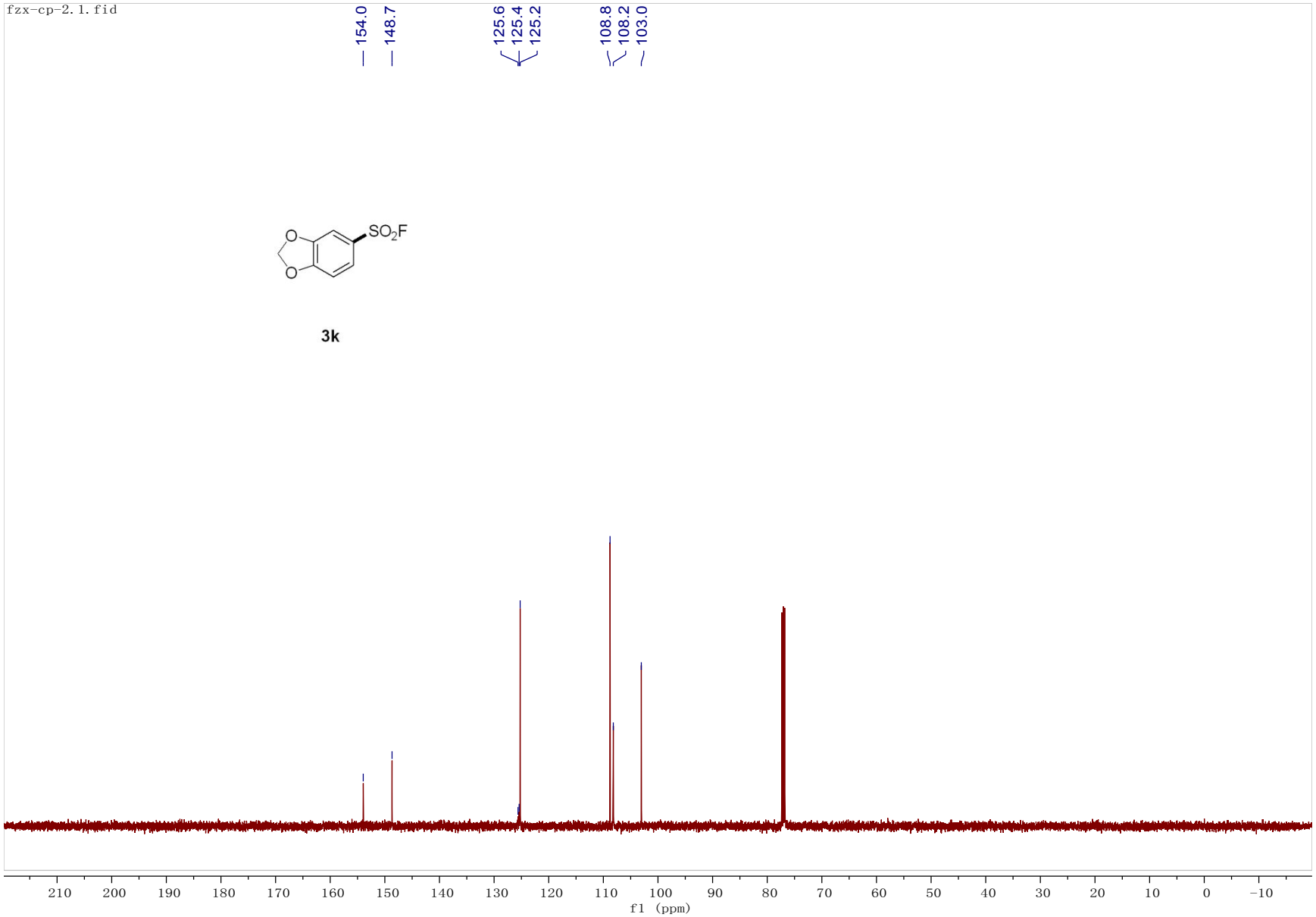
^{19}F NMR (376 MHz, CDCl3) spectrum of **3j**.



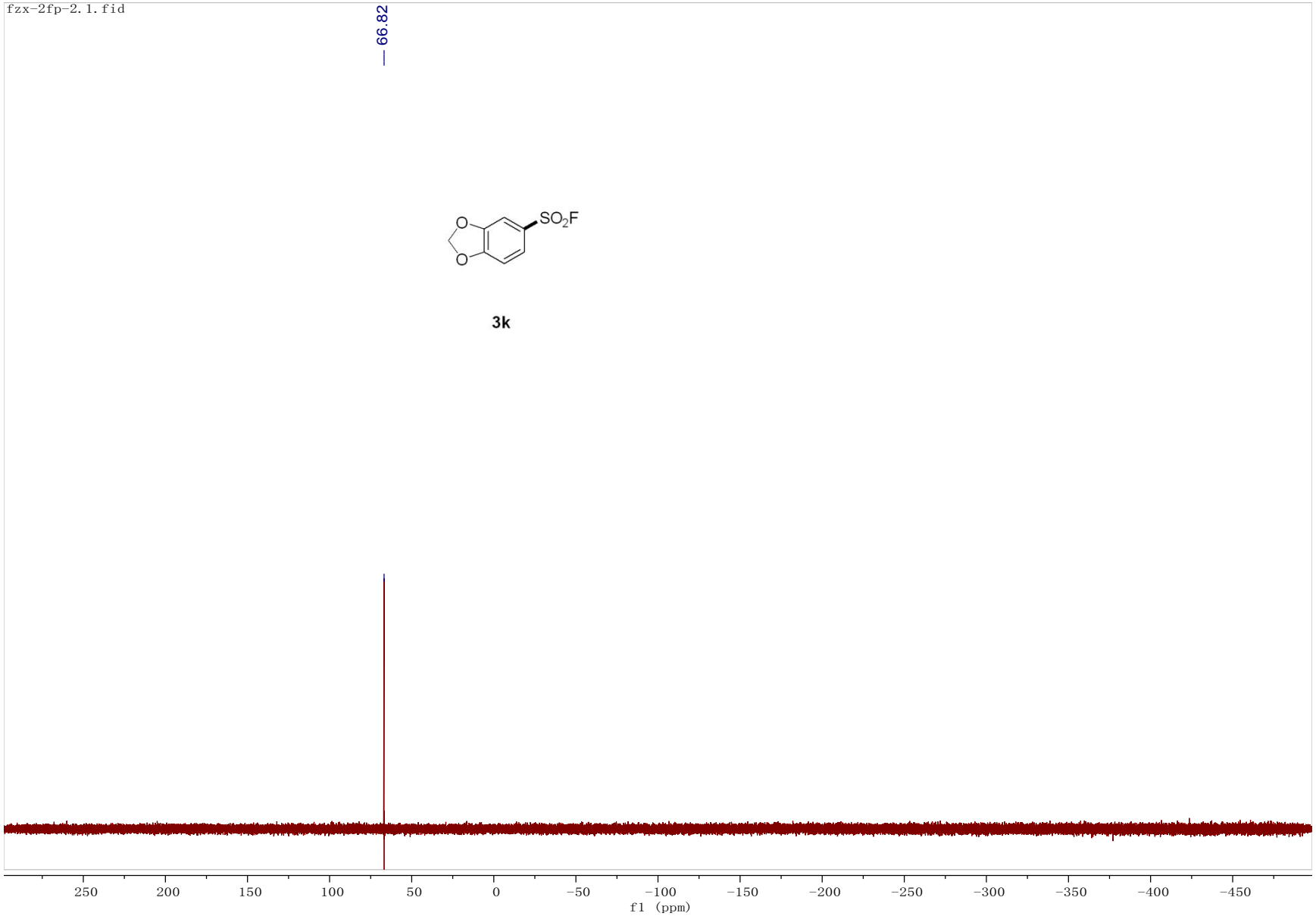
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3k**.



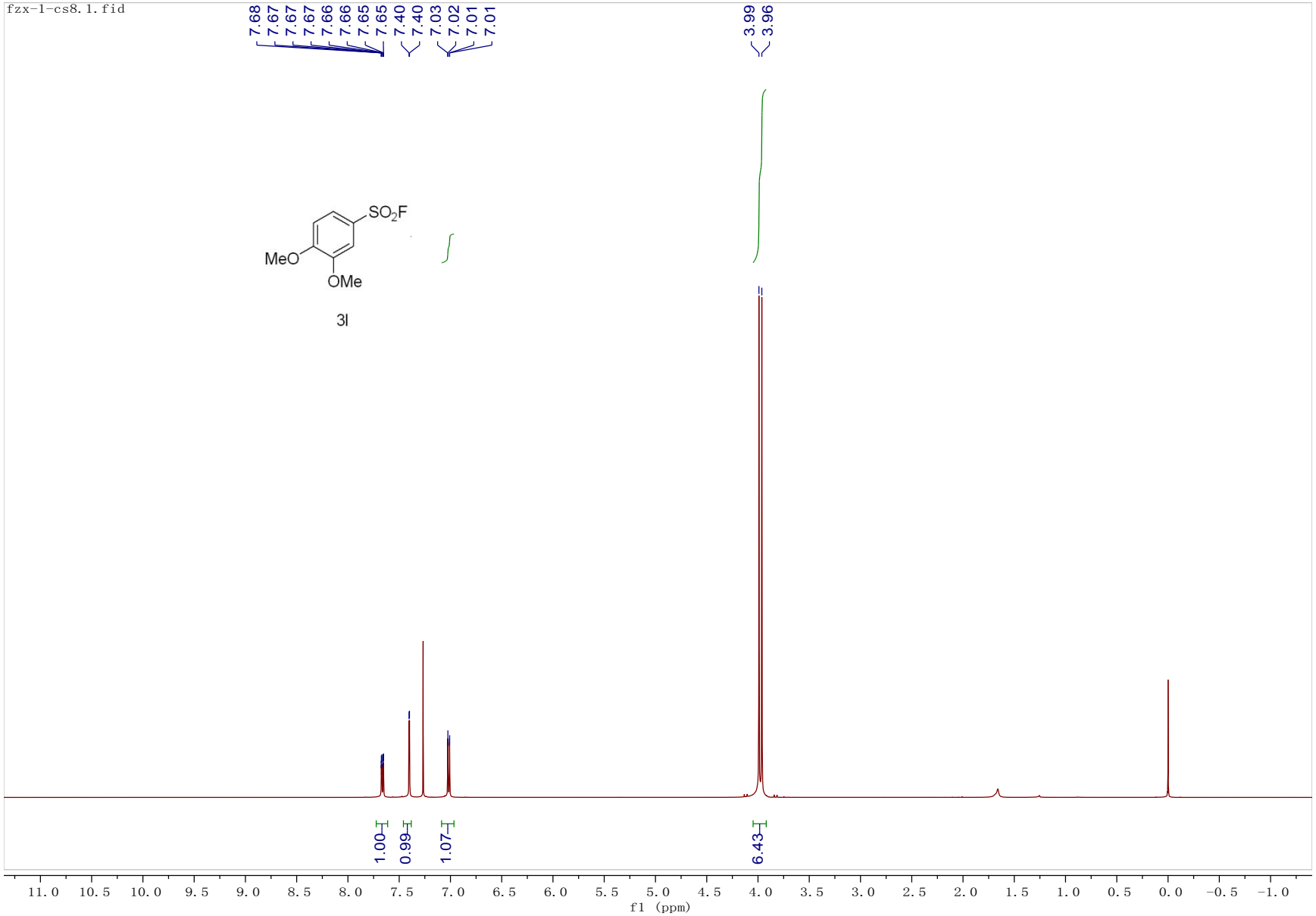
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3k**.



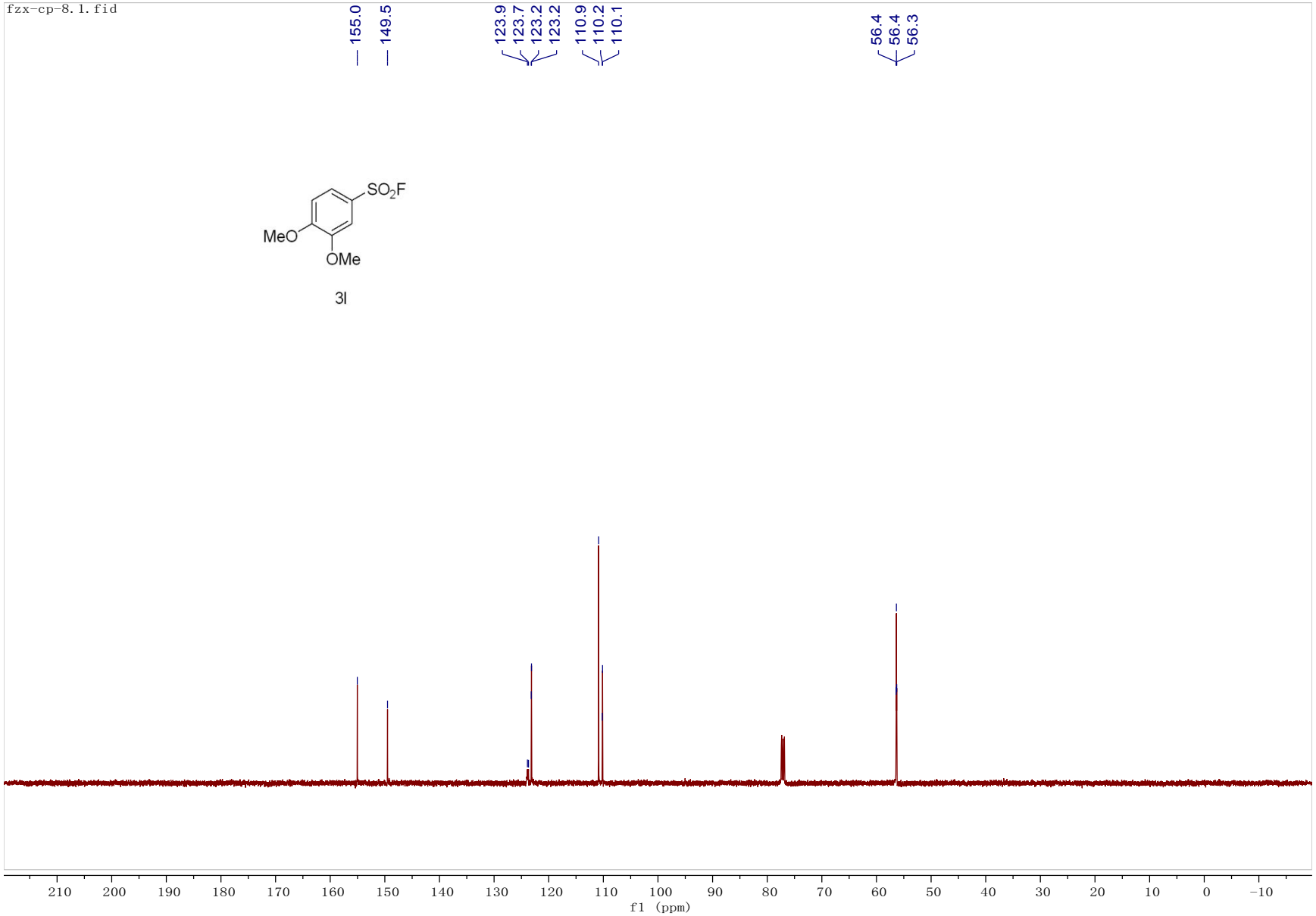
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3k**.



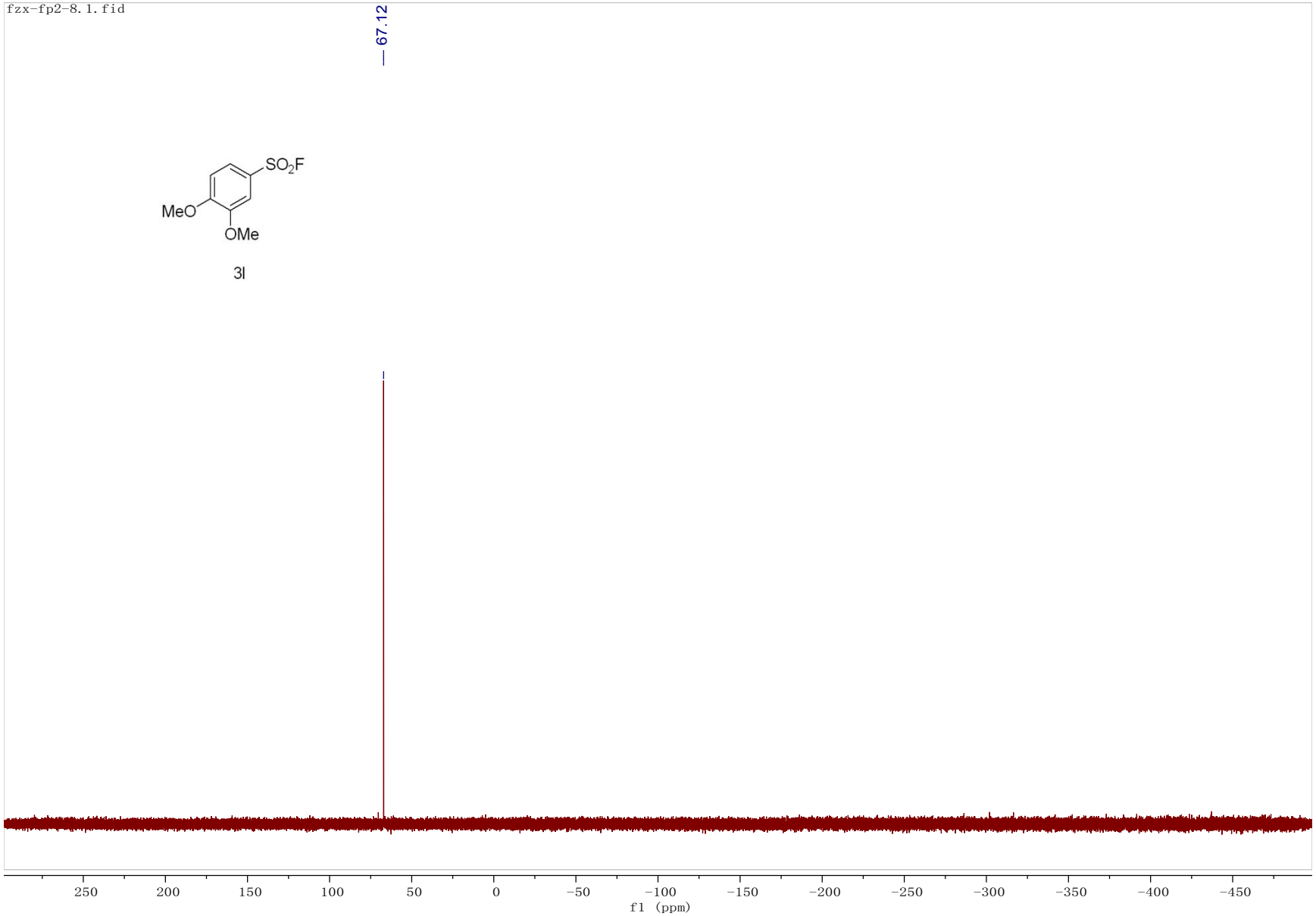
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3l**.



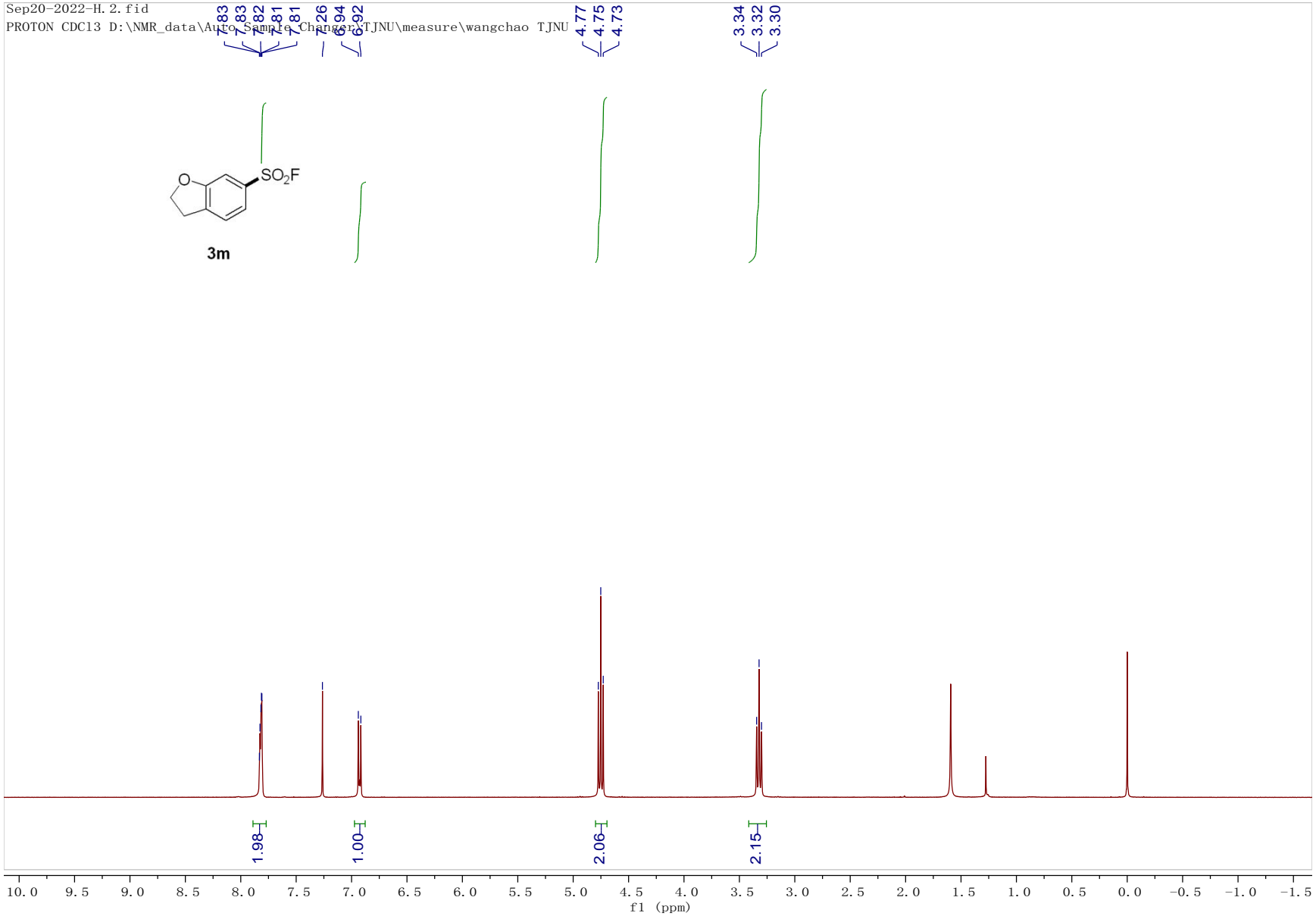
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3l**.



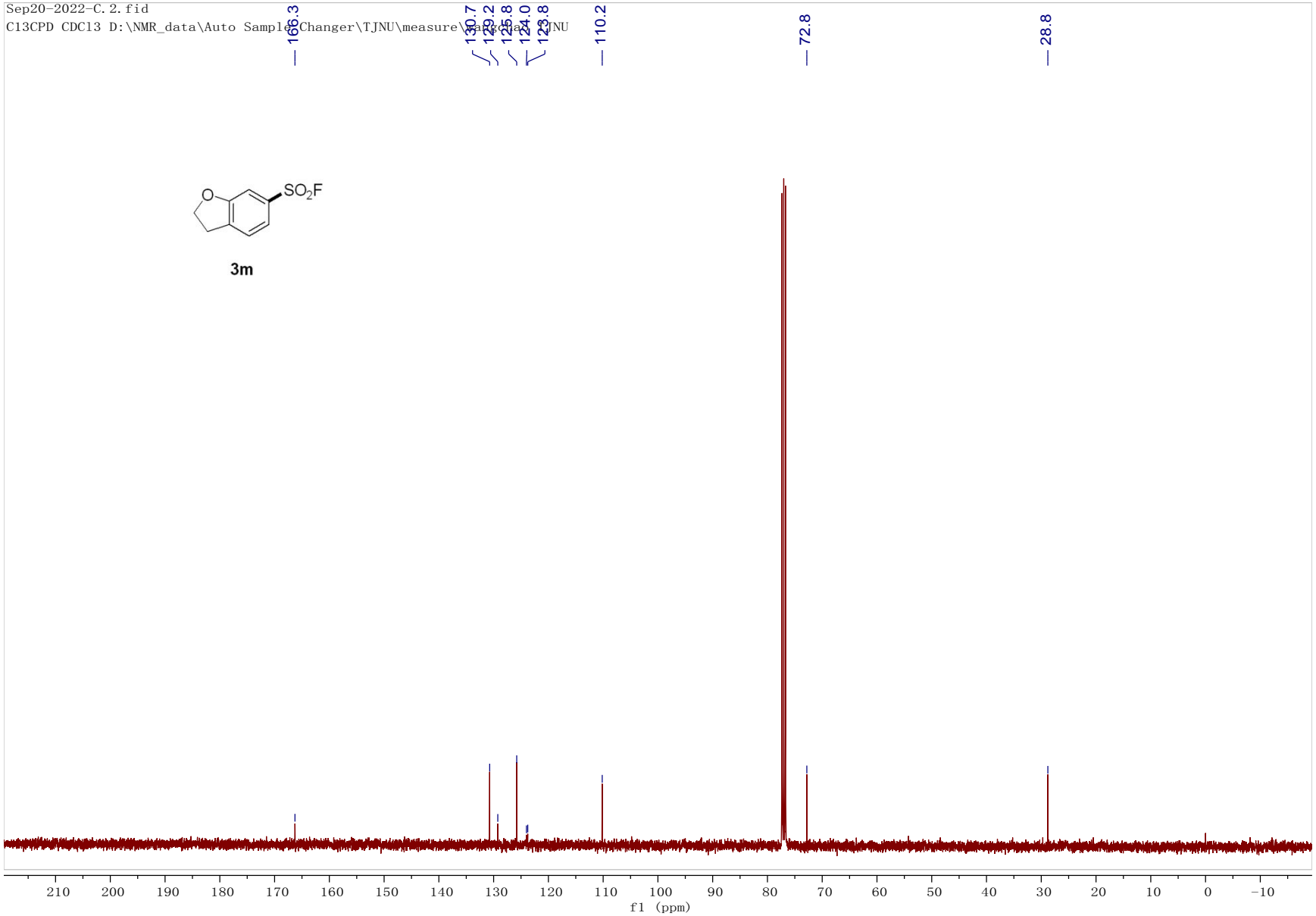
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **3l**.



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3m**.

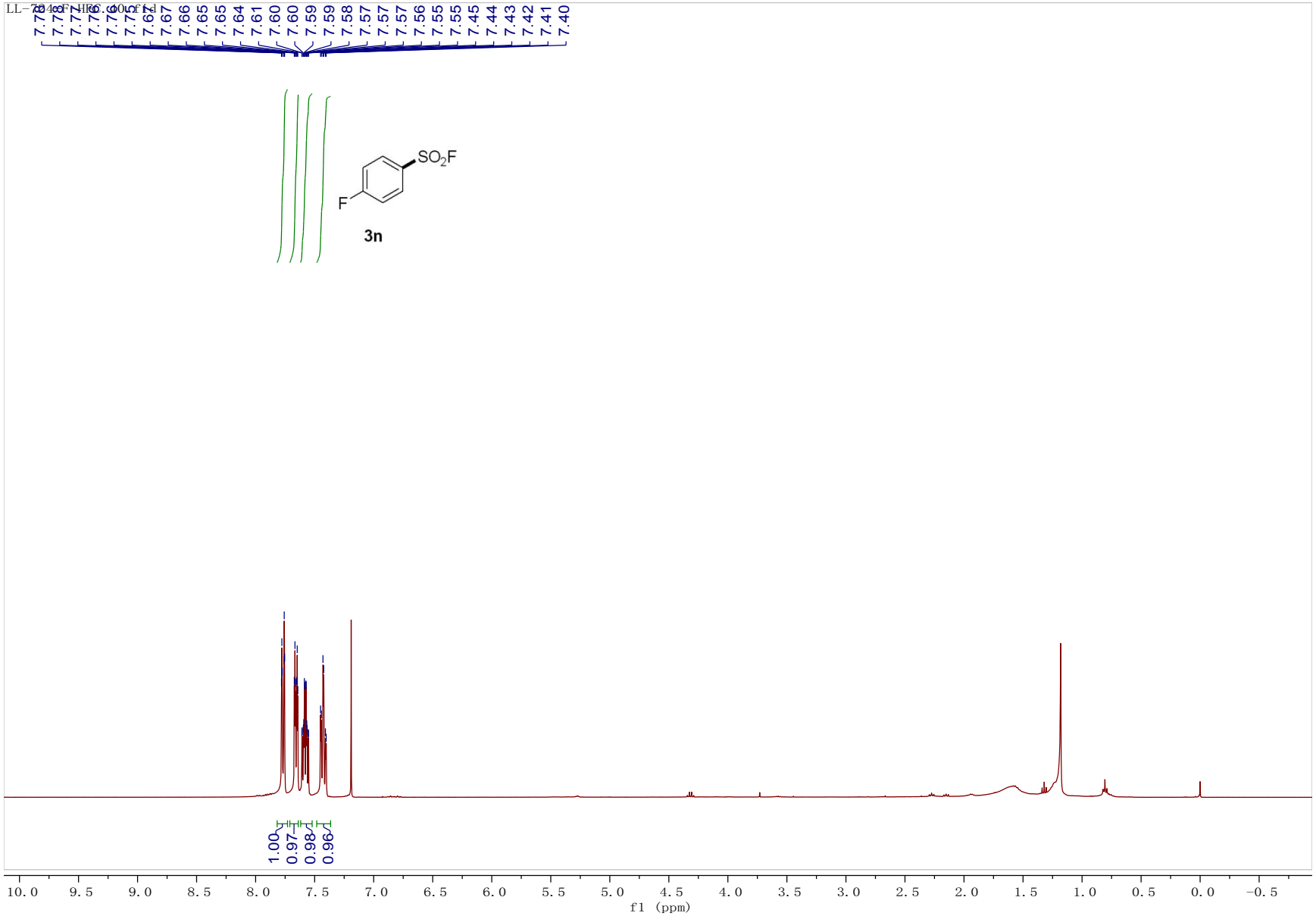


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3m**.

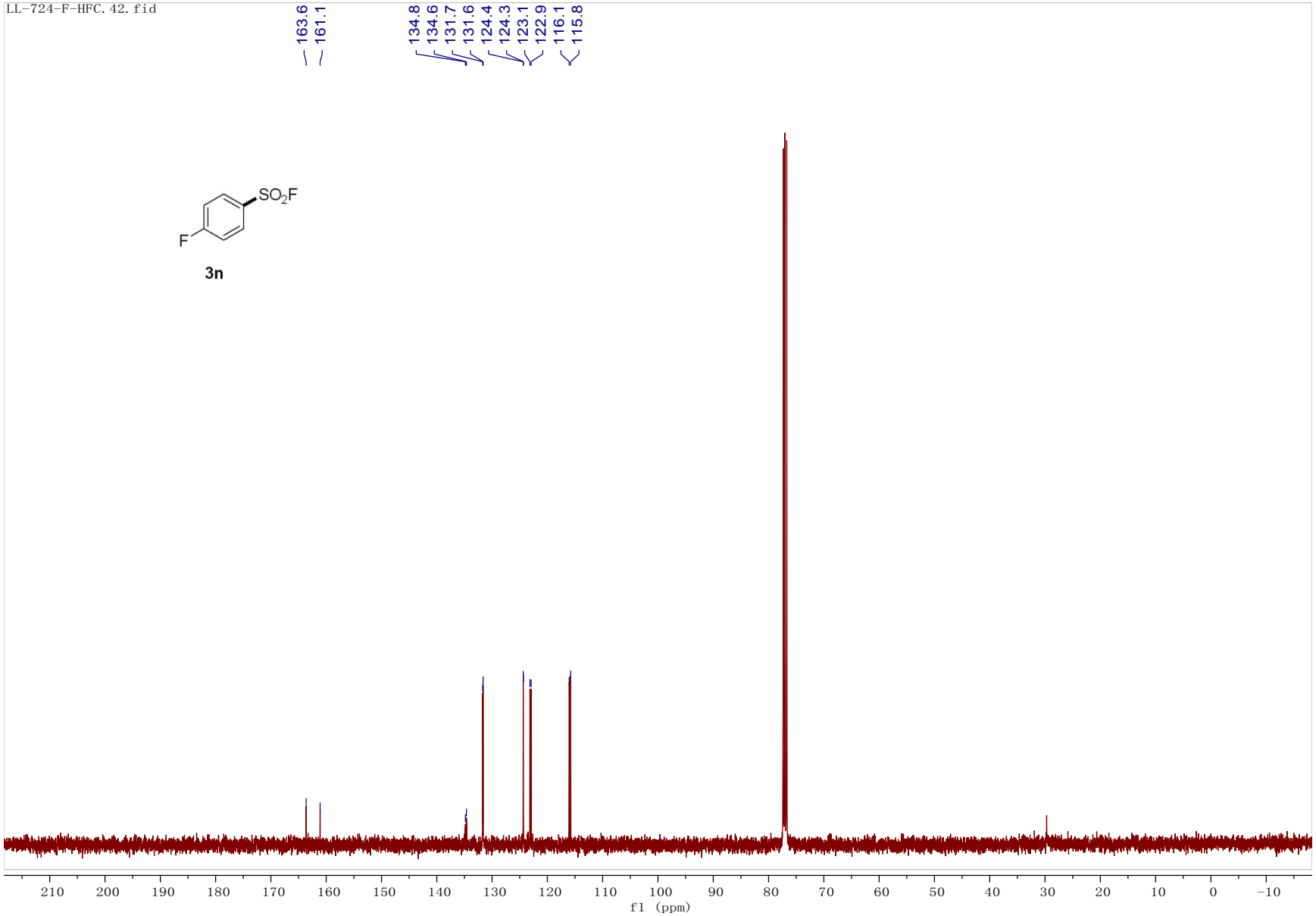


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3m**.

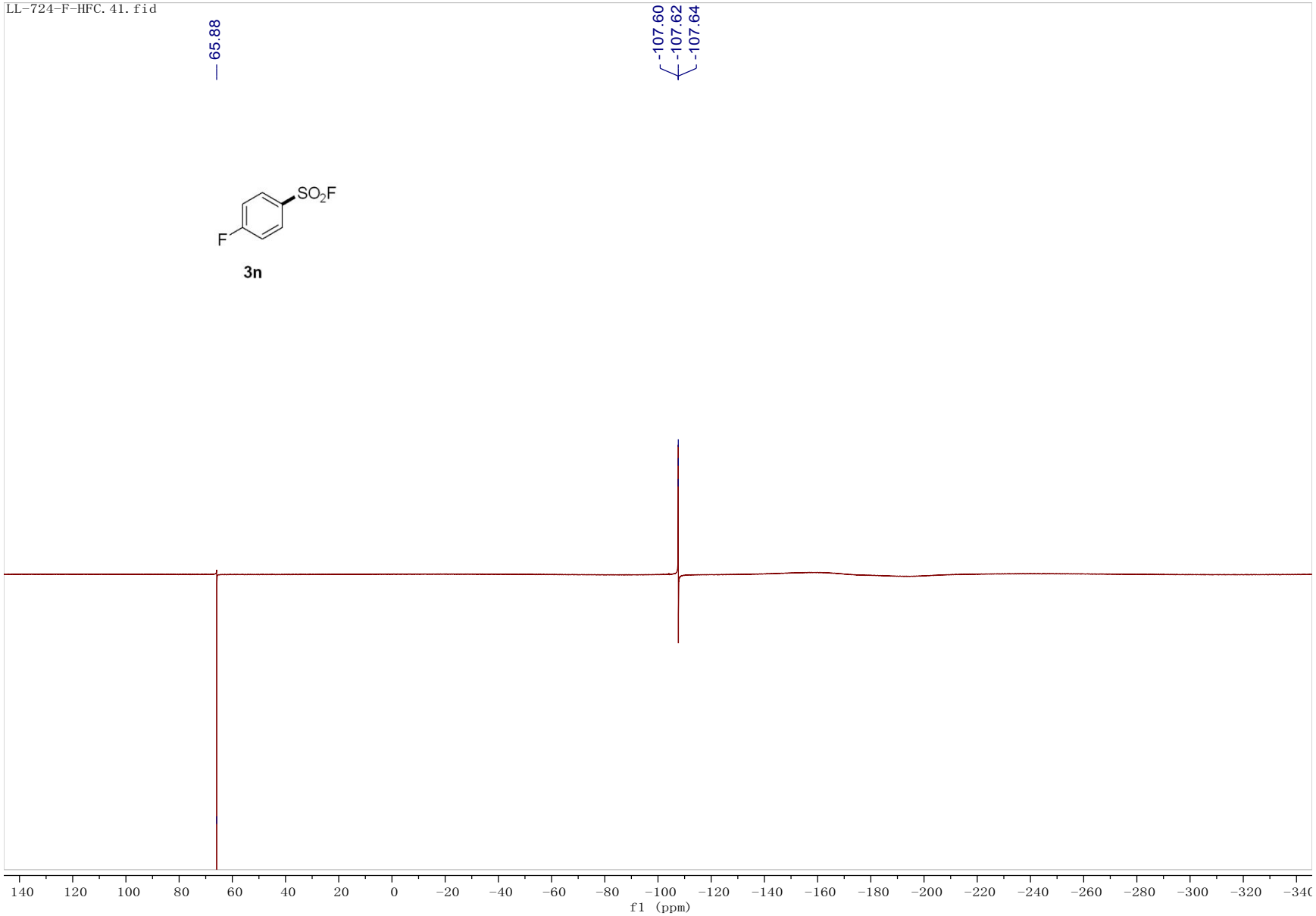
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3n**.



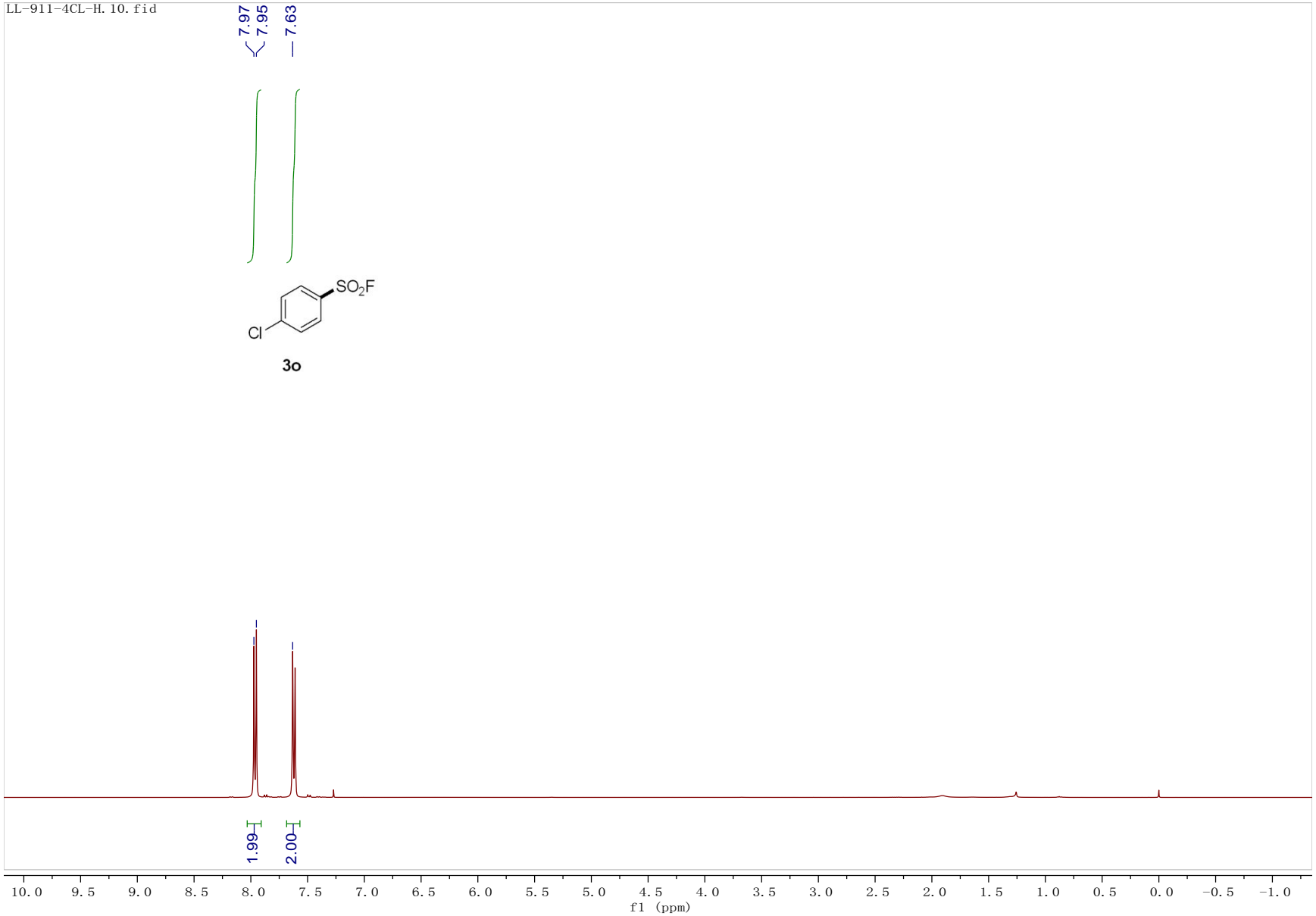
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3n**.



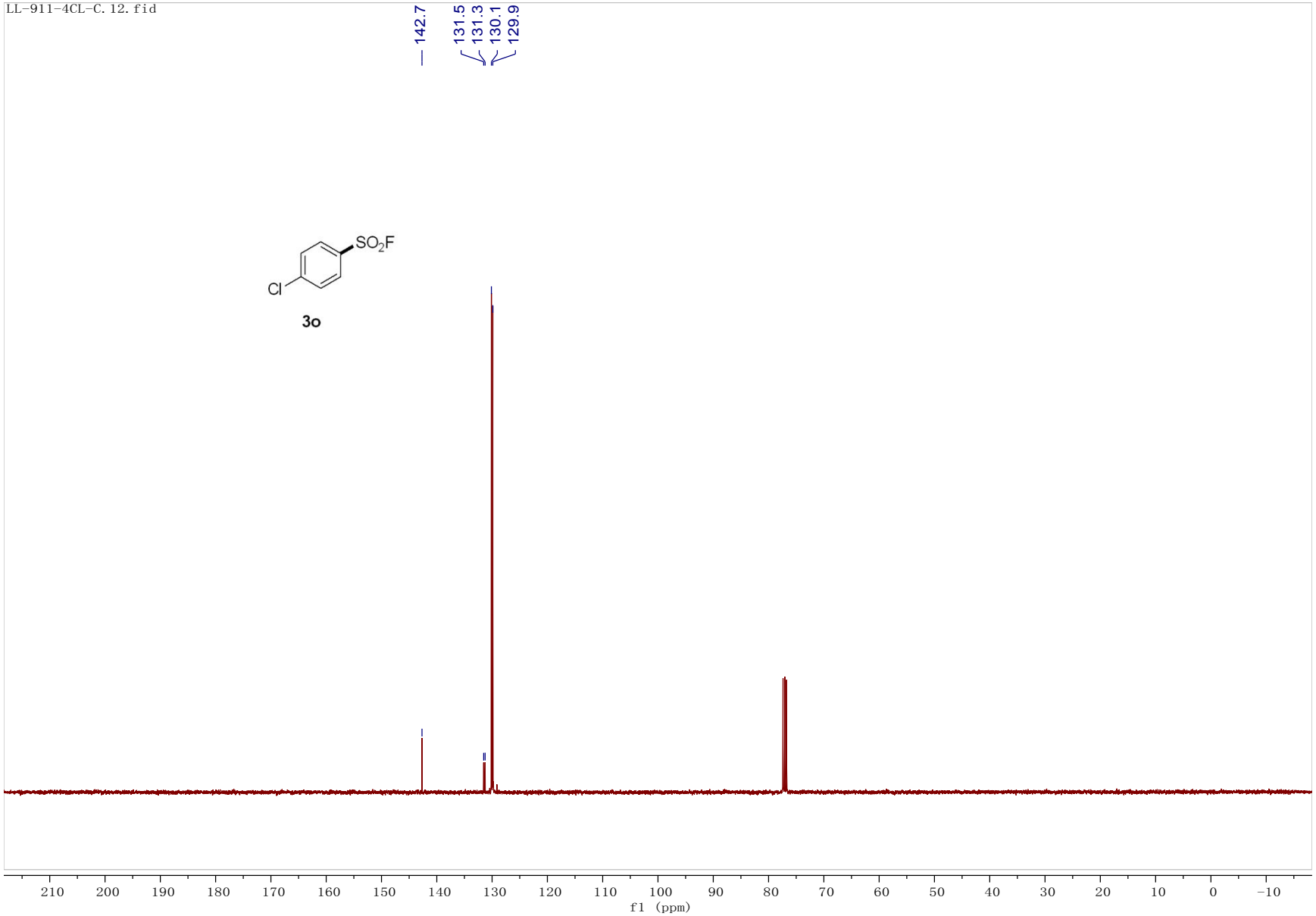
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3n**.



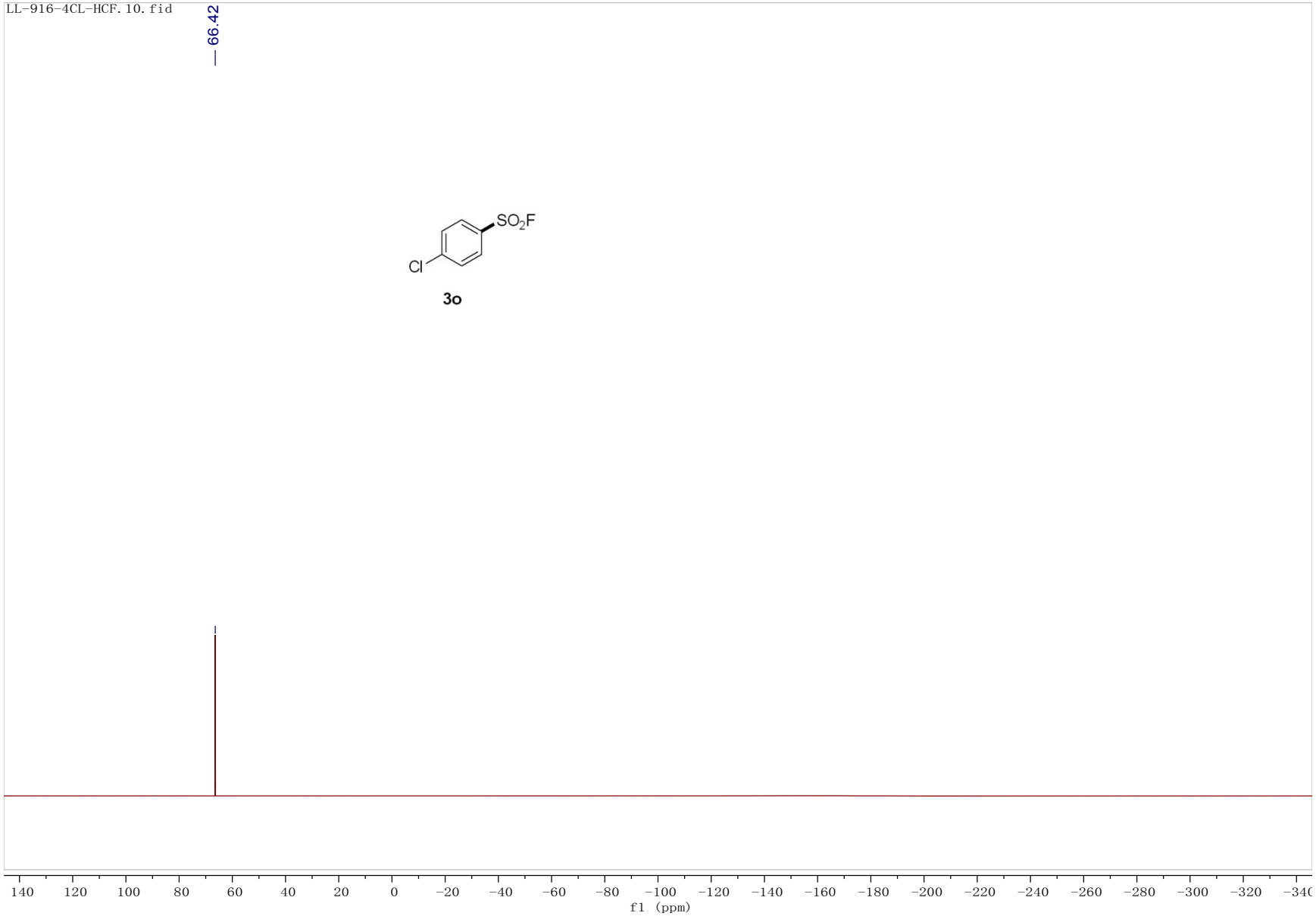
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3o**.



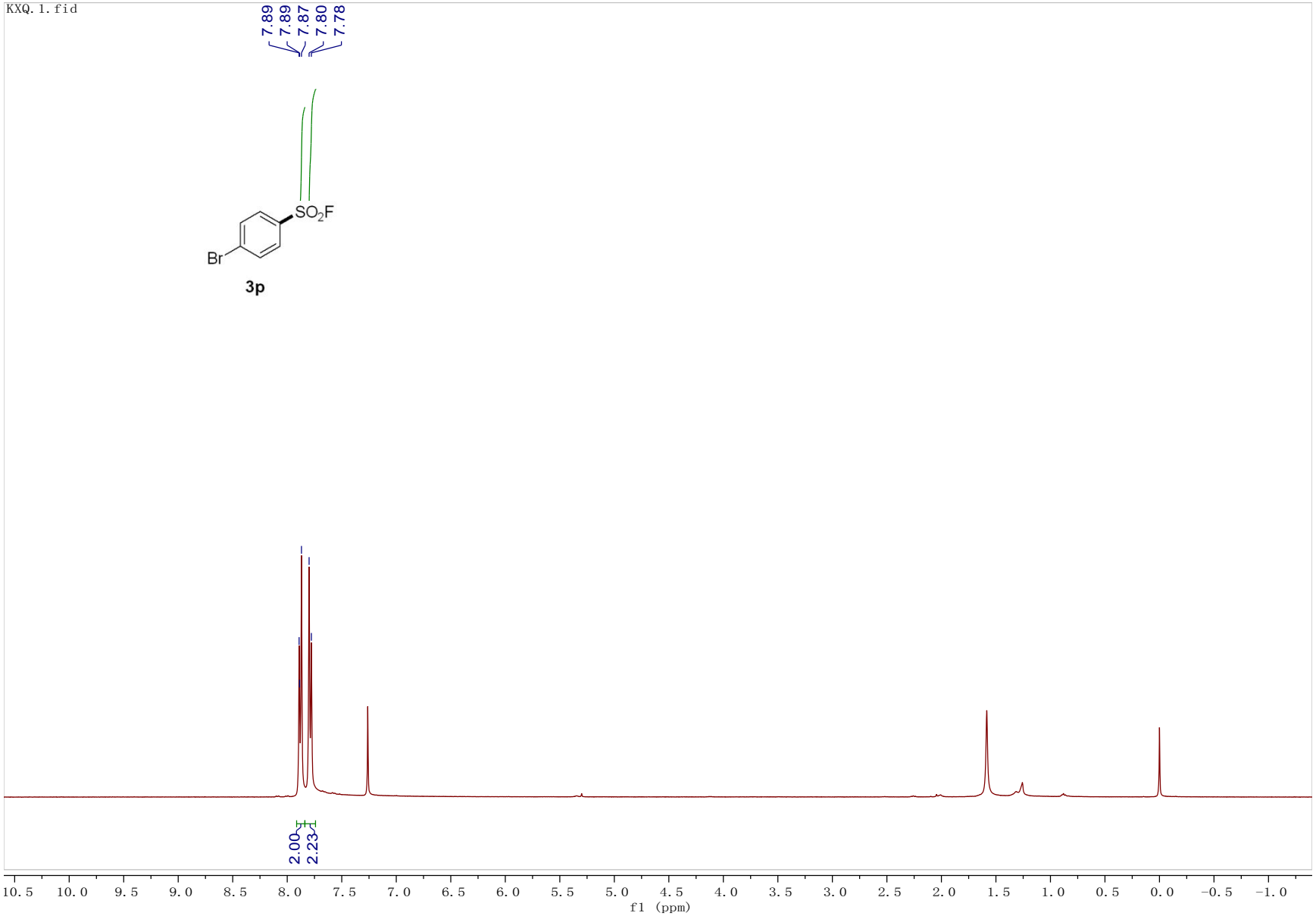
^{13}C NMR (01 MHz, $CDCl_3$) spectrum of **3o**.



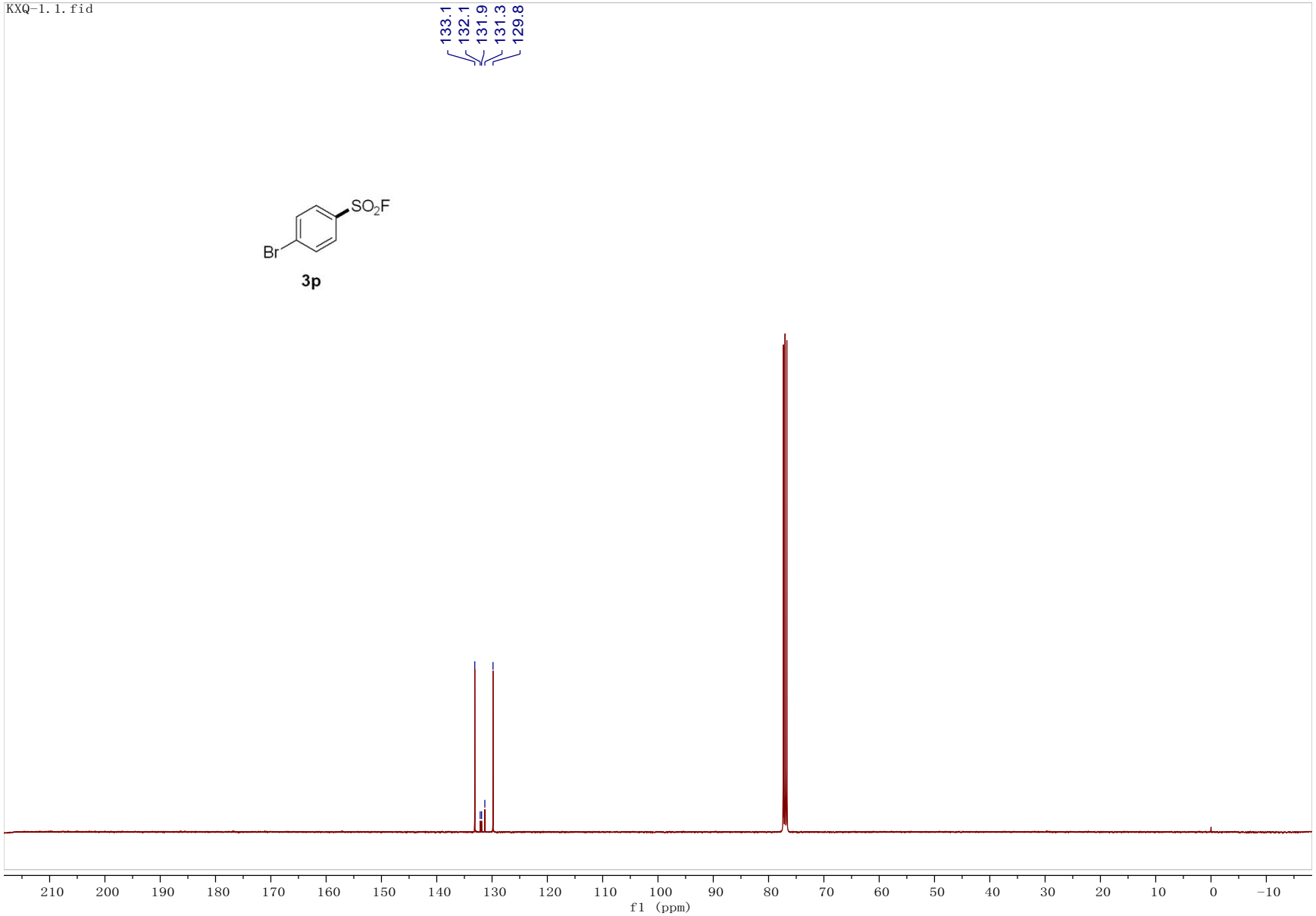
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3o**.



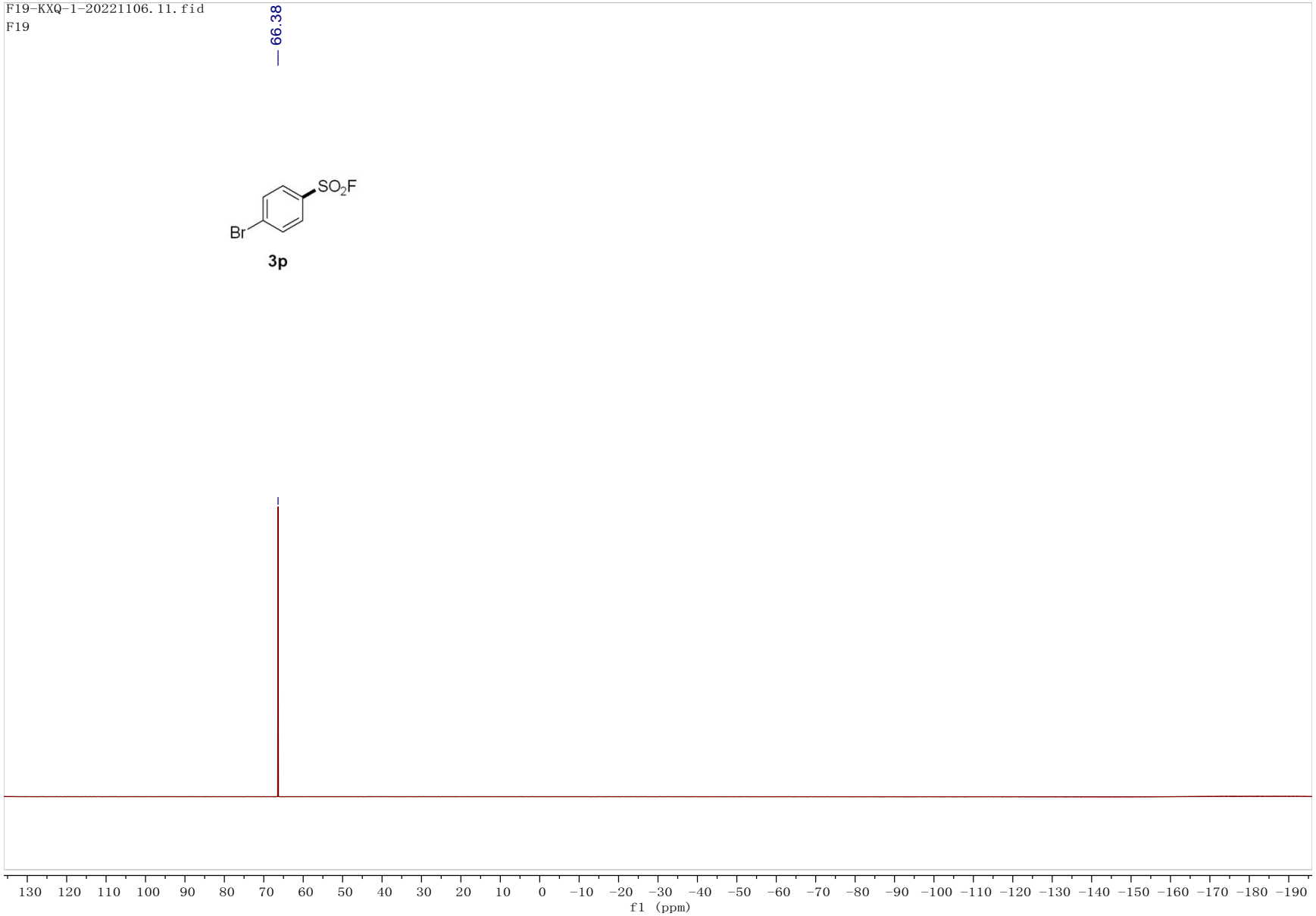
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3p**.



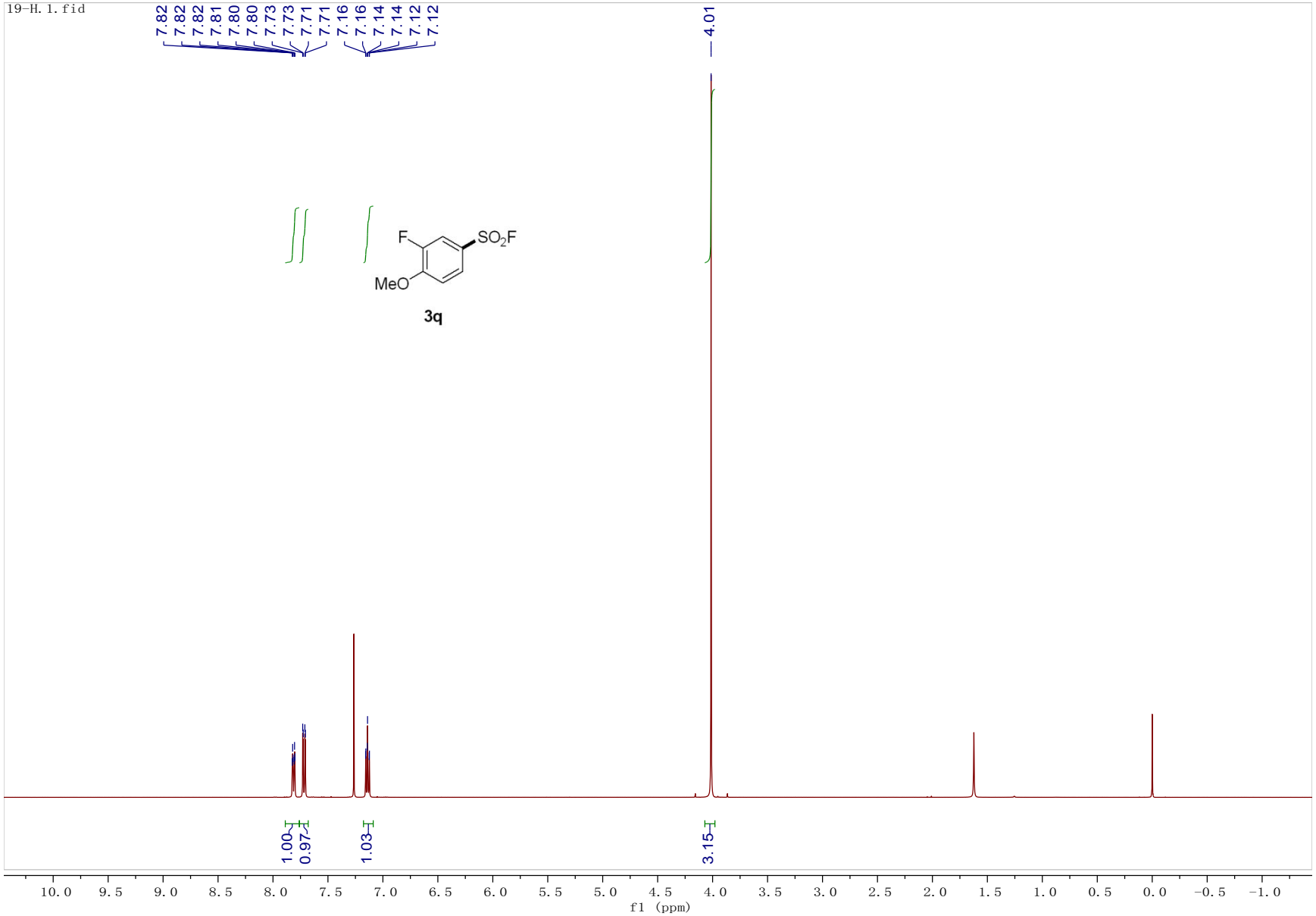
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3p**.



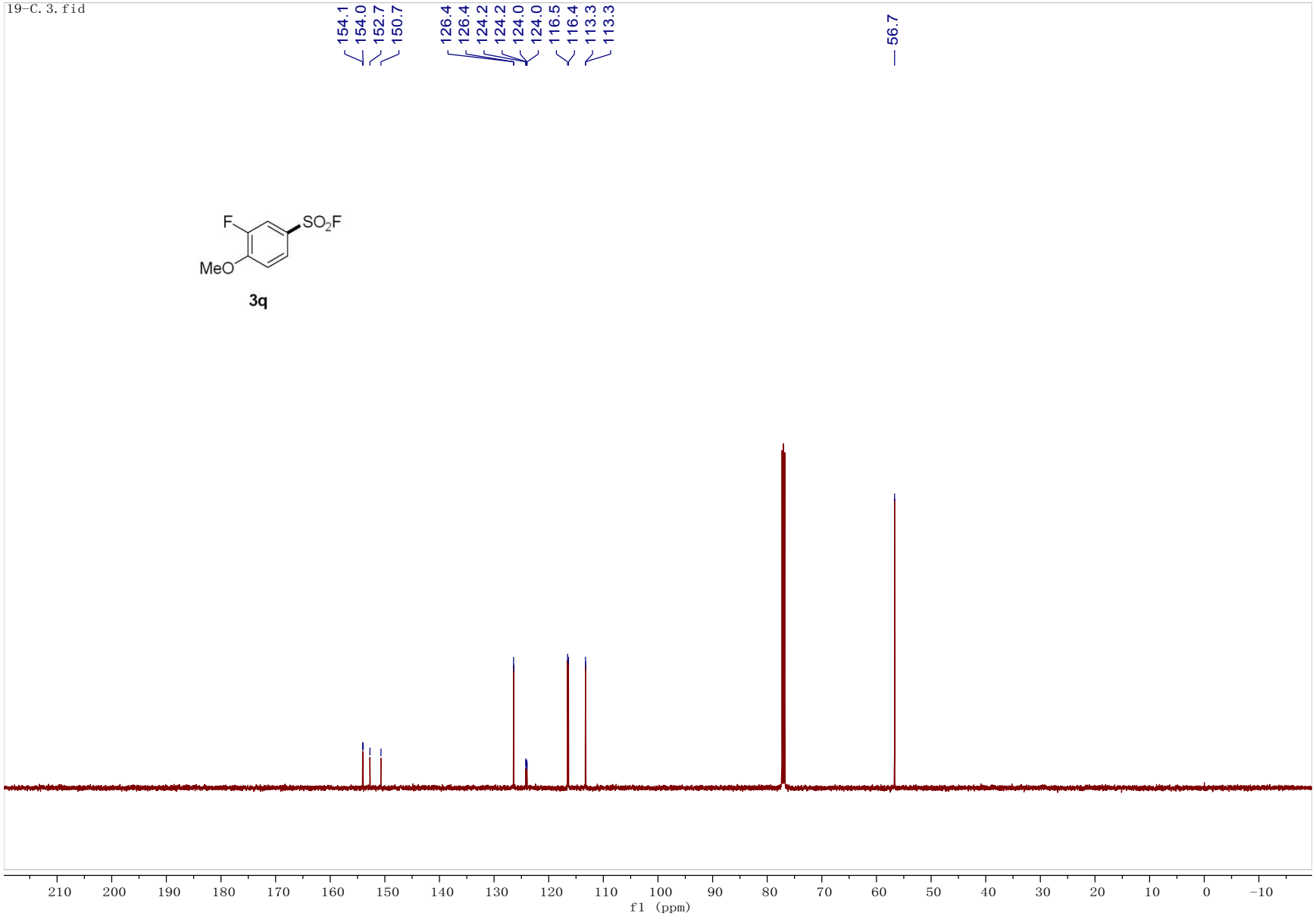
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3p**.



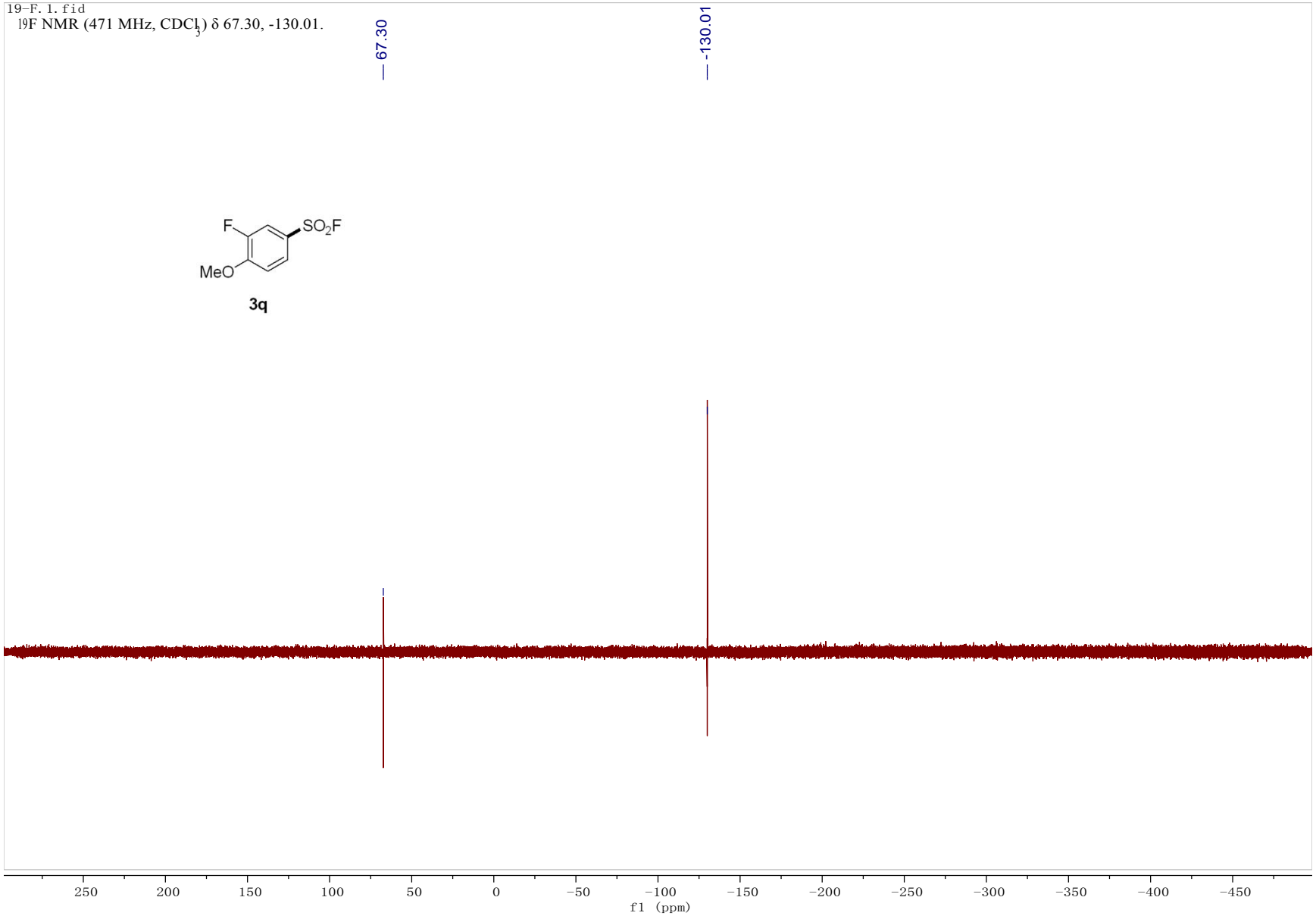
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3q**.



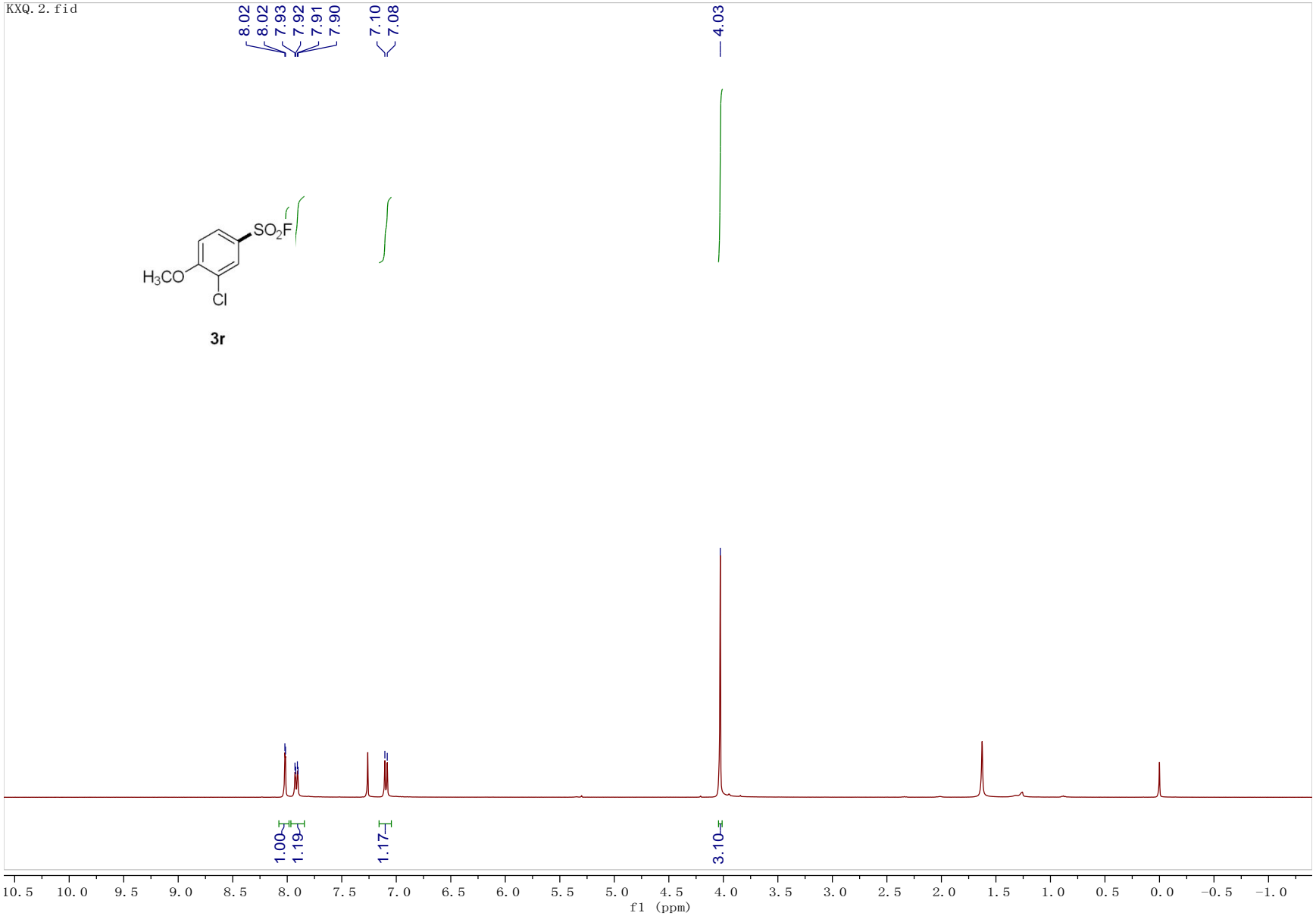
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3q**.



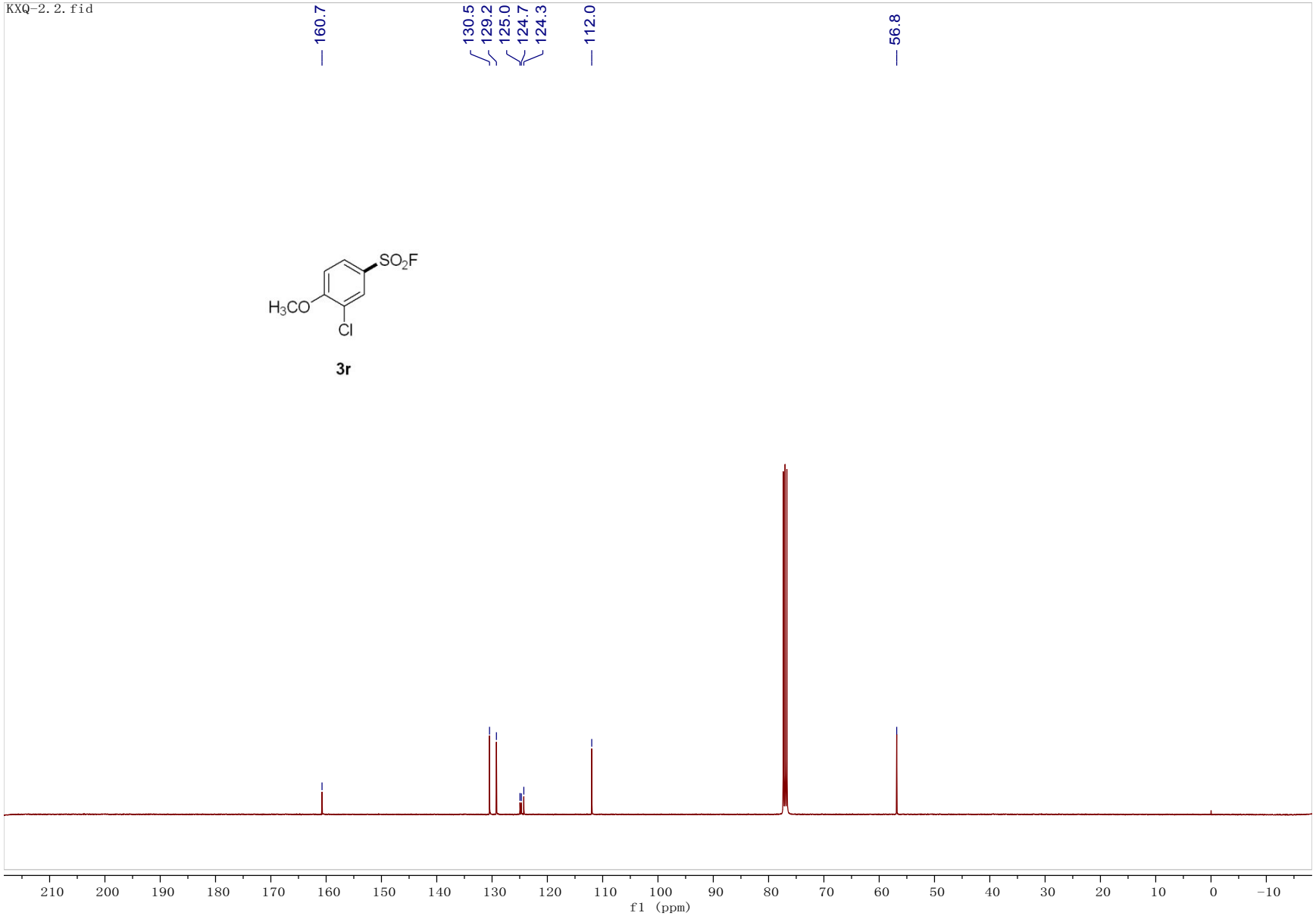
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **3q**.



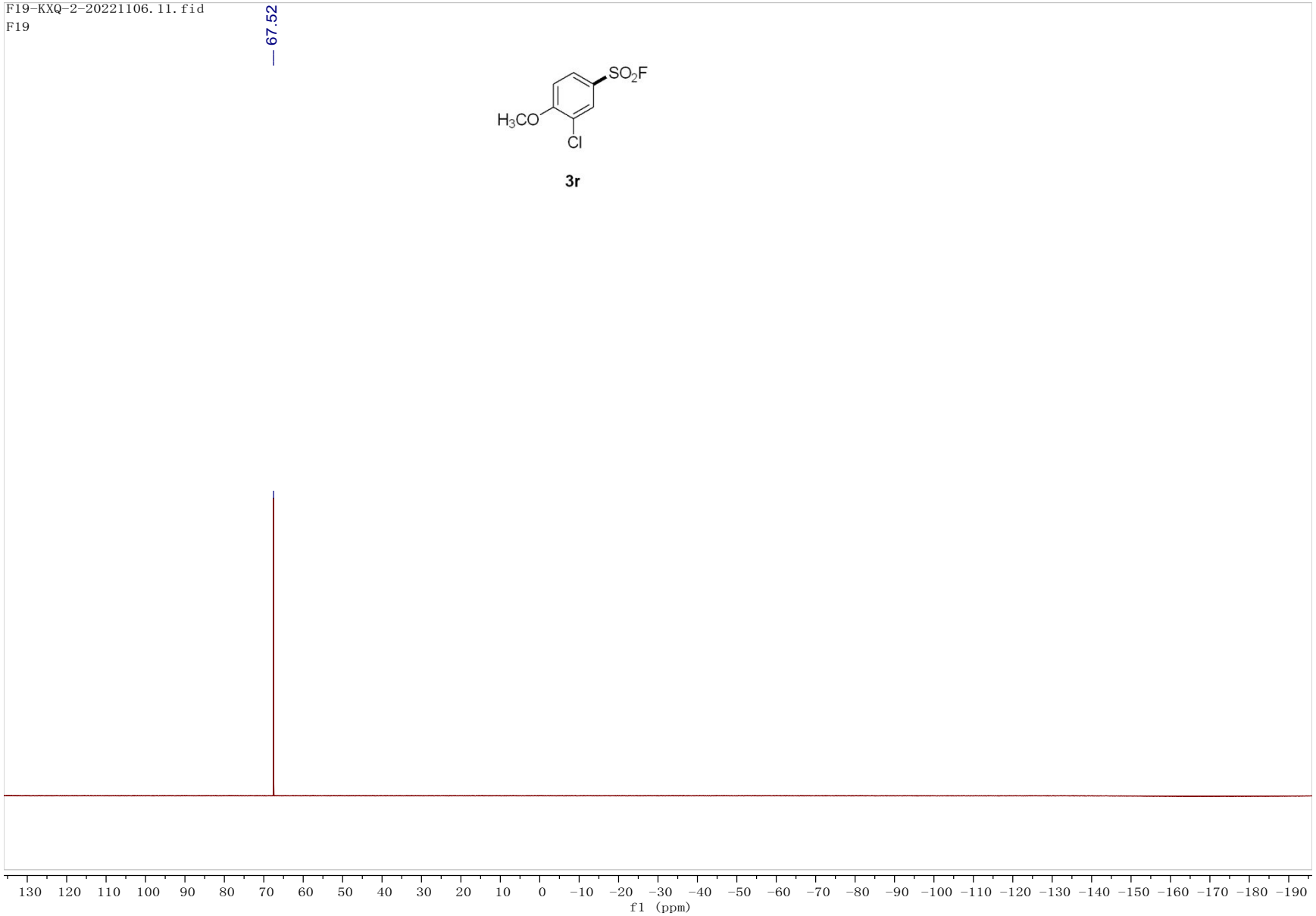
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3r**.



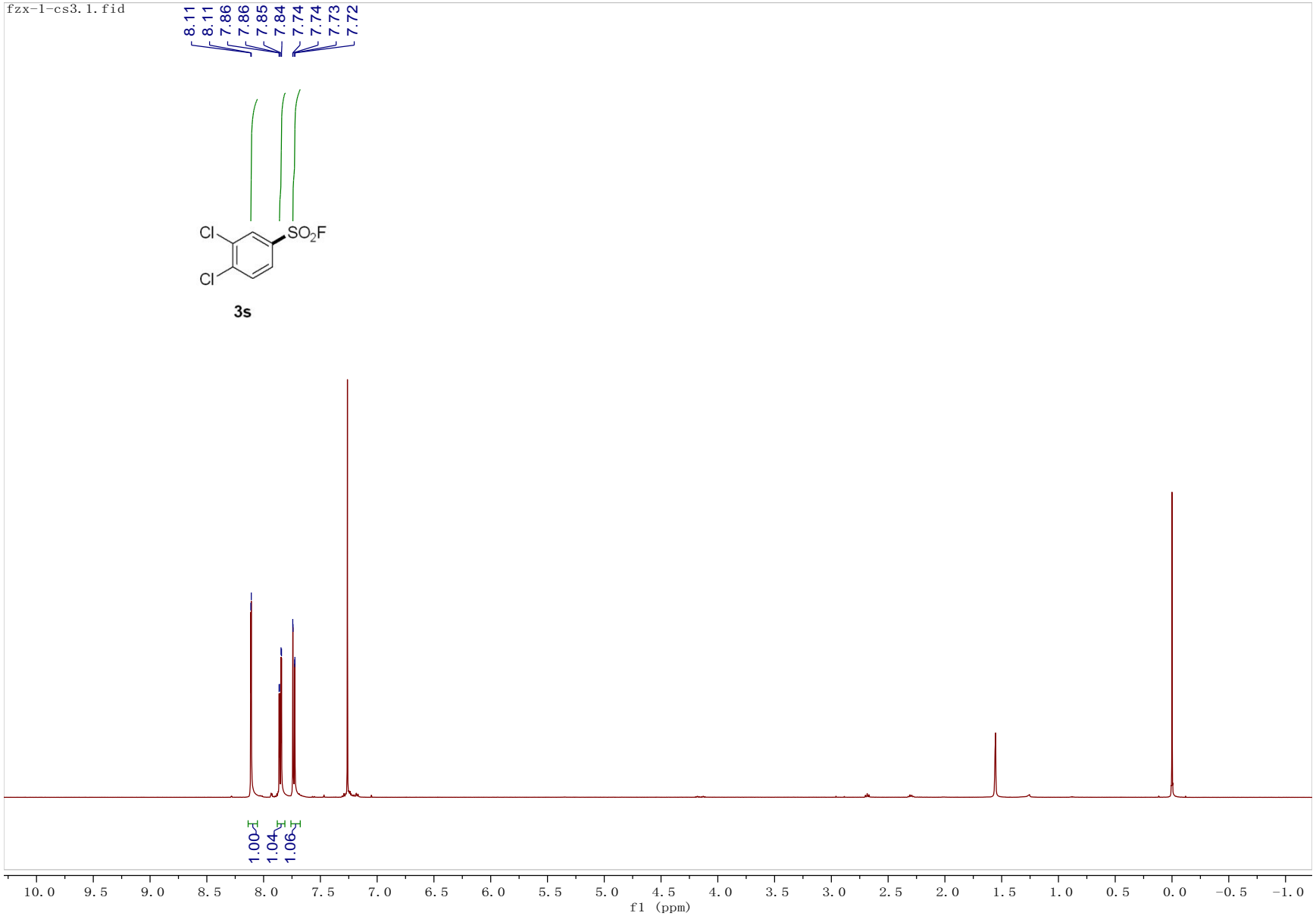
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3r**.



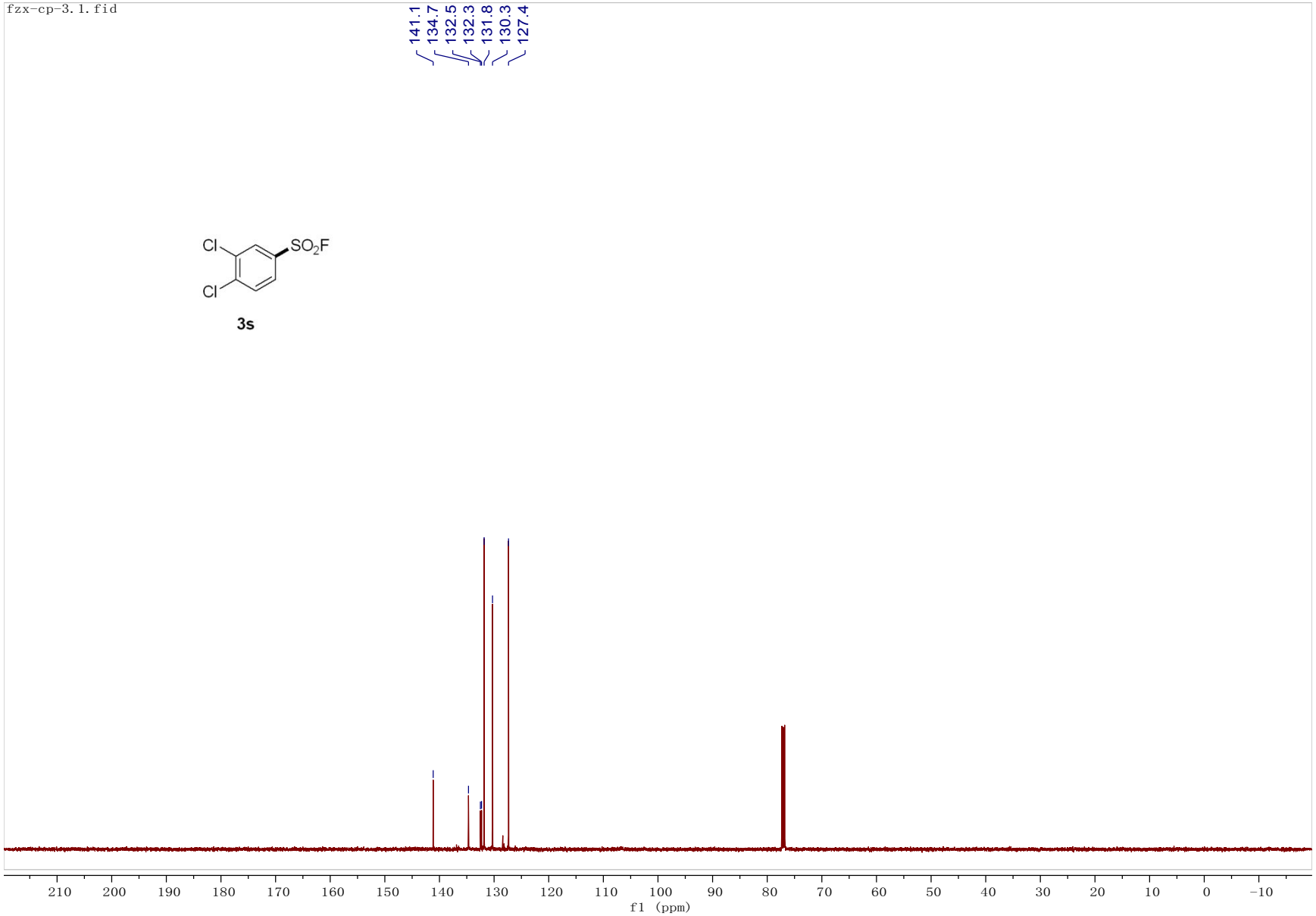
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3r**.



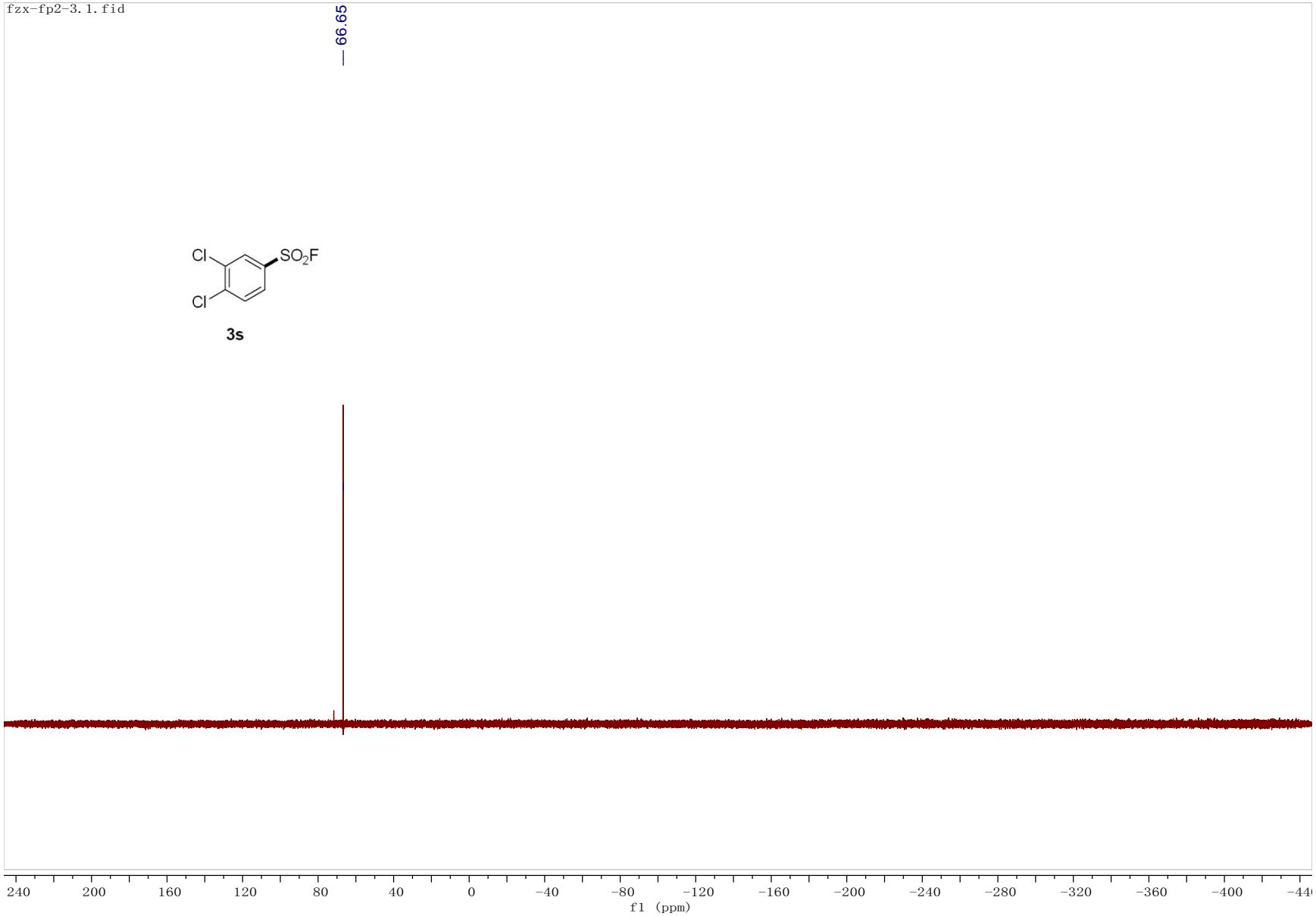
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3s**.



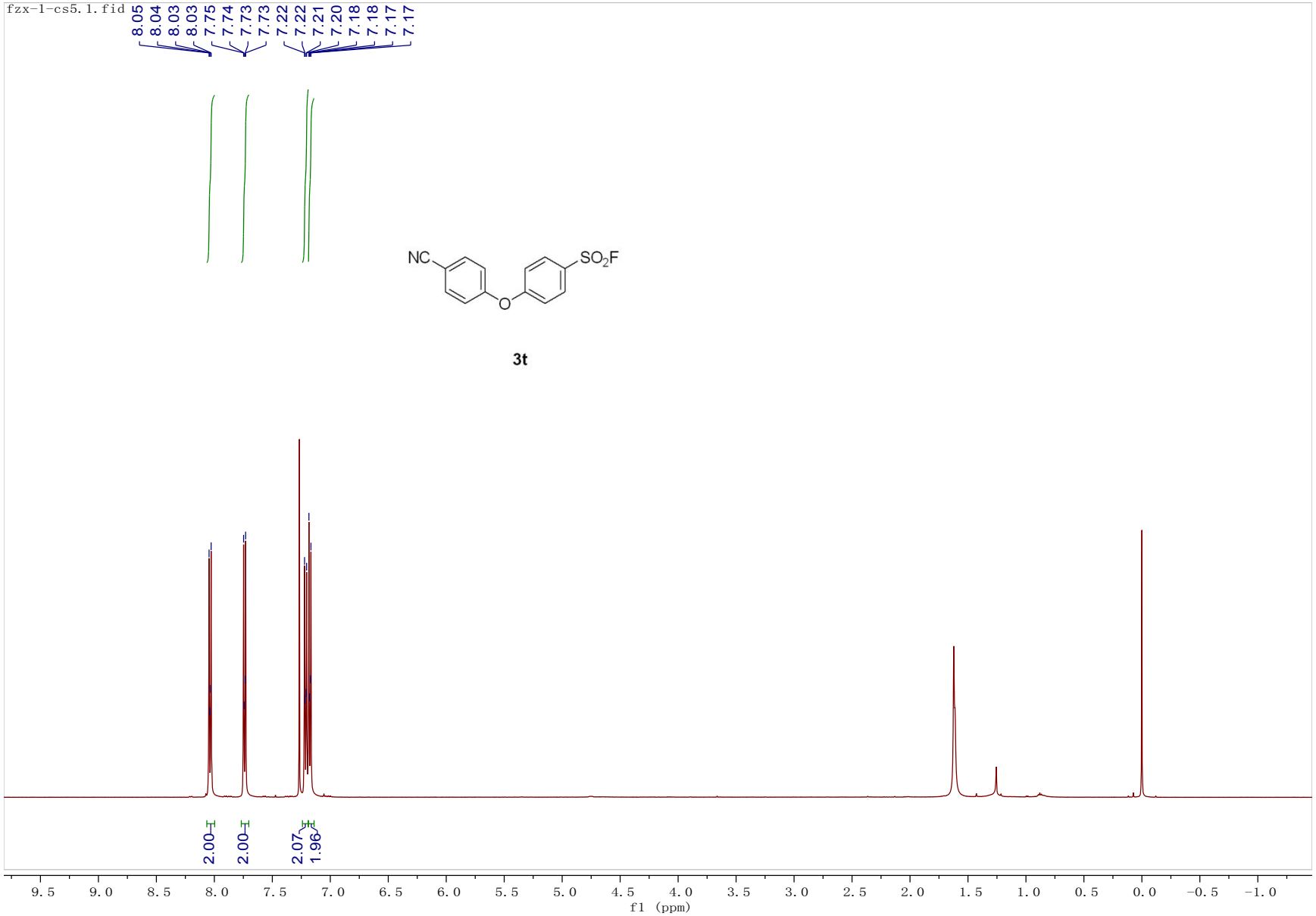
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3s**.



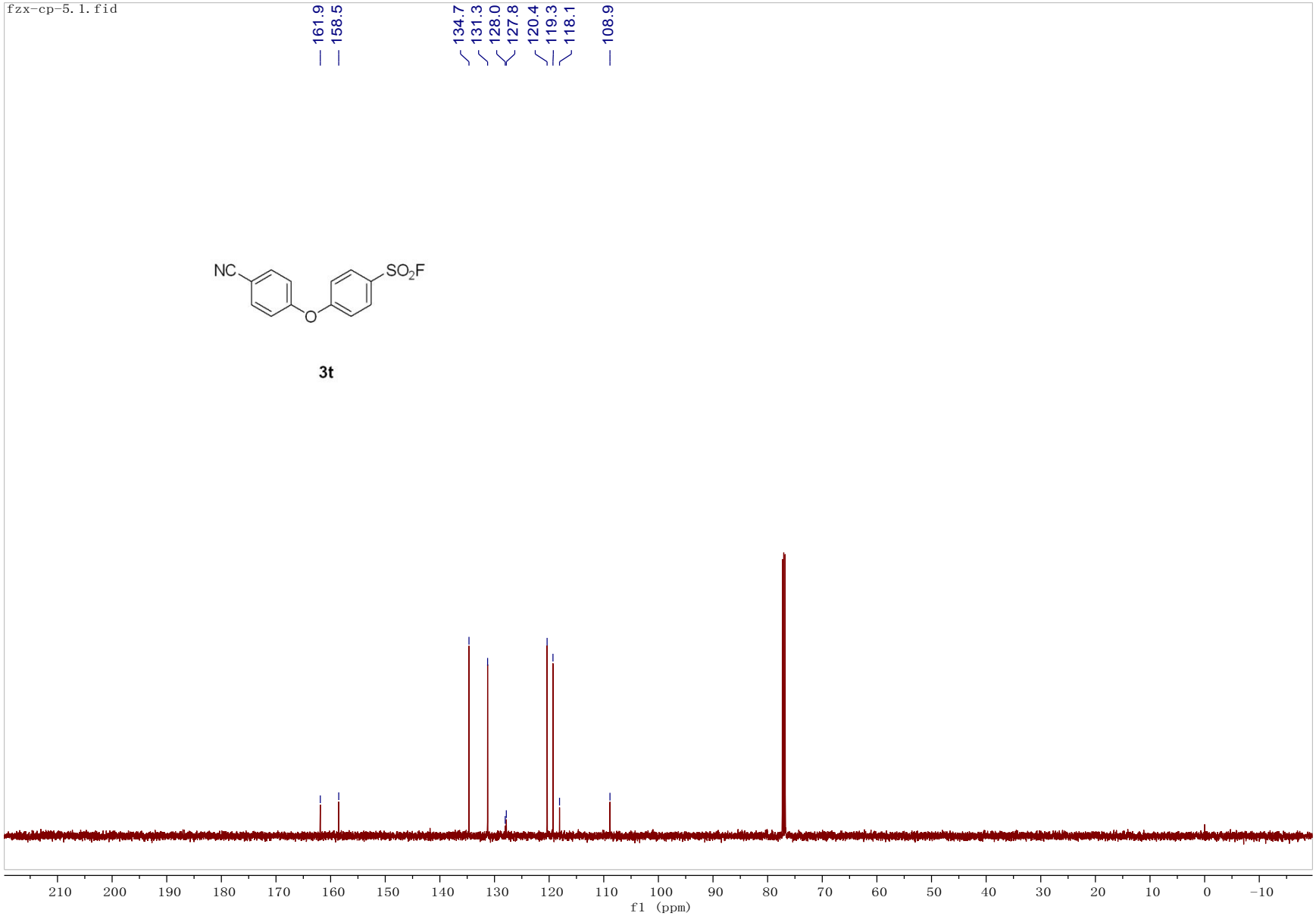
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **3s**.



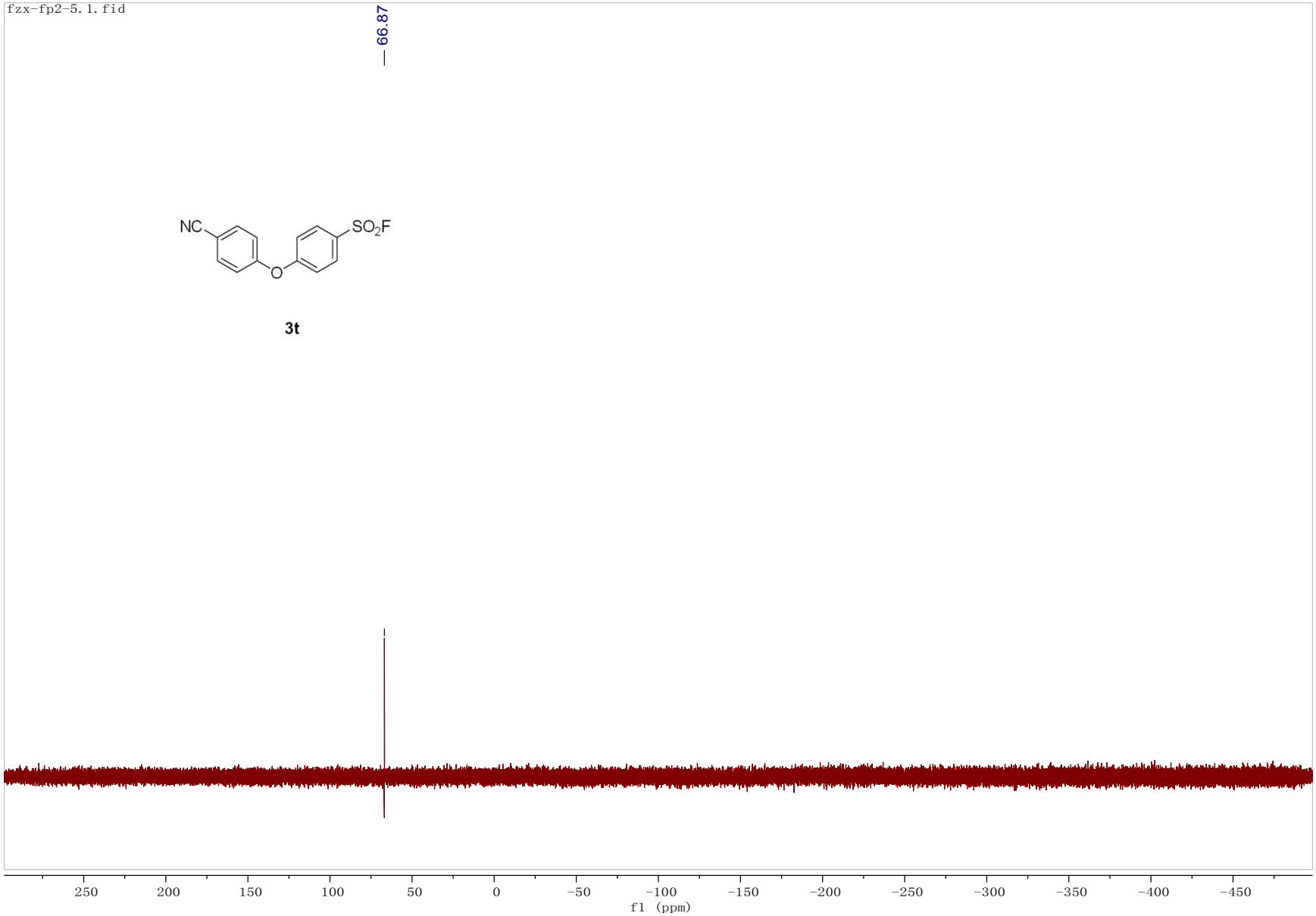
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3t**.



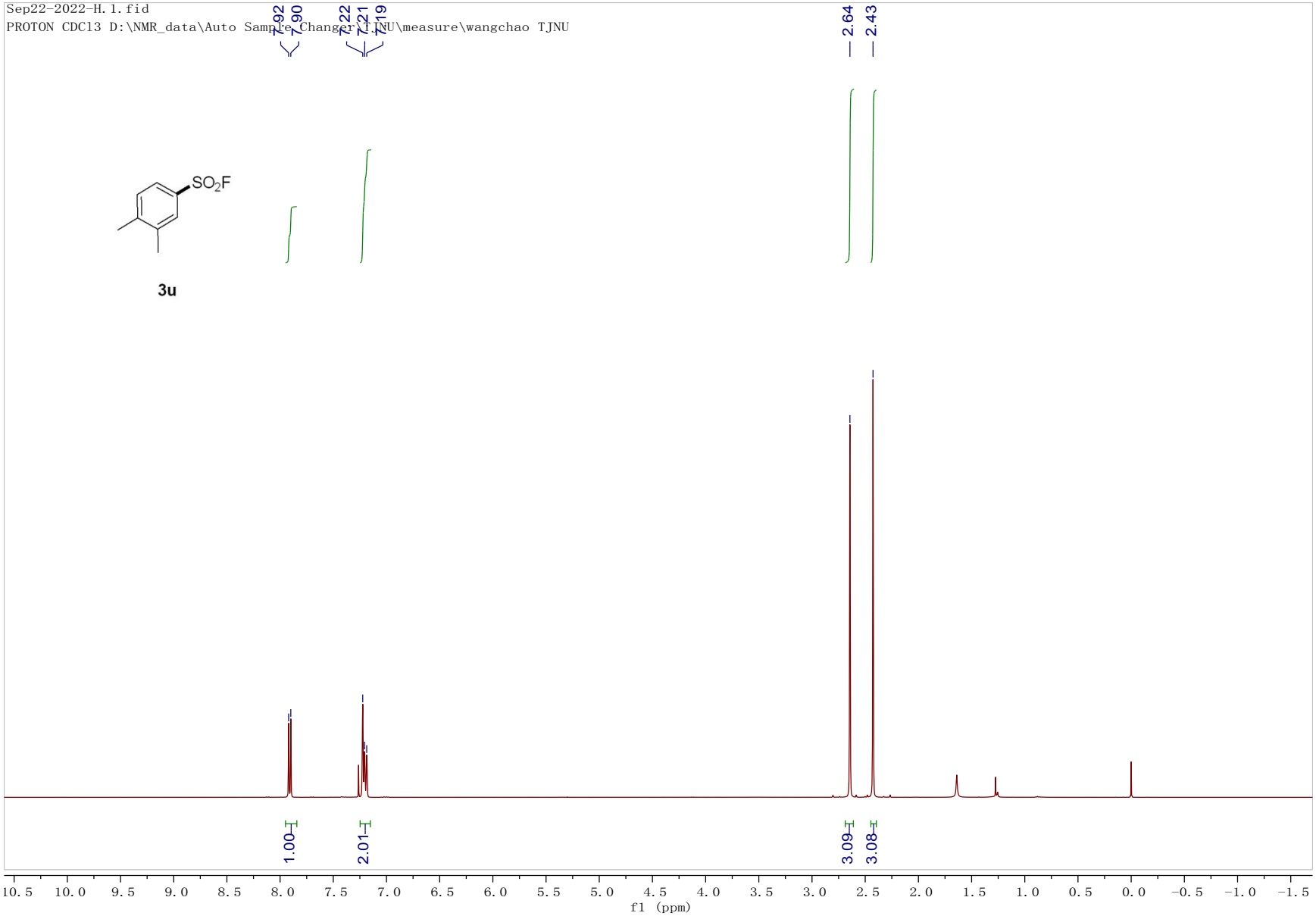
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3t**.



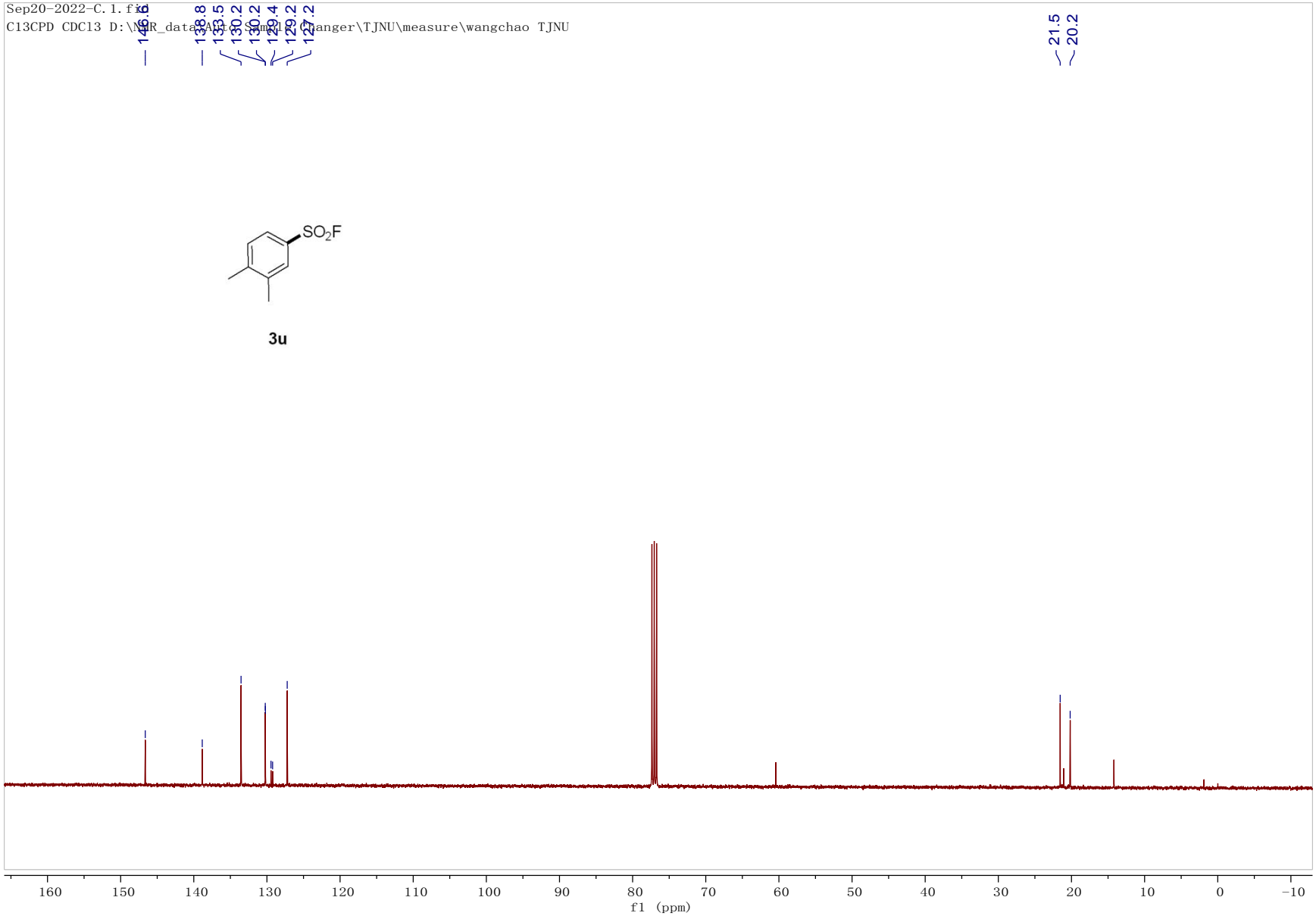
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **3t**.



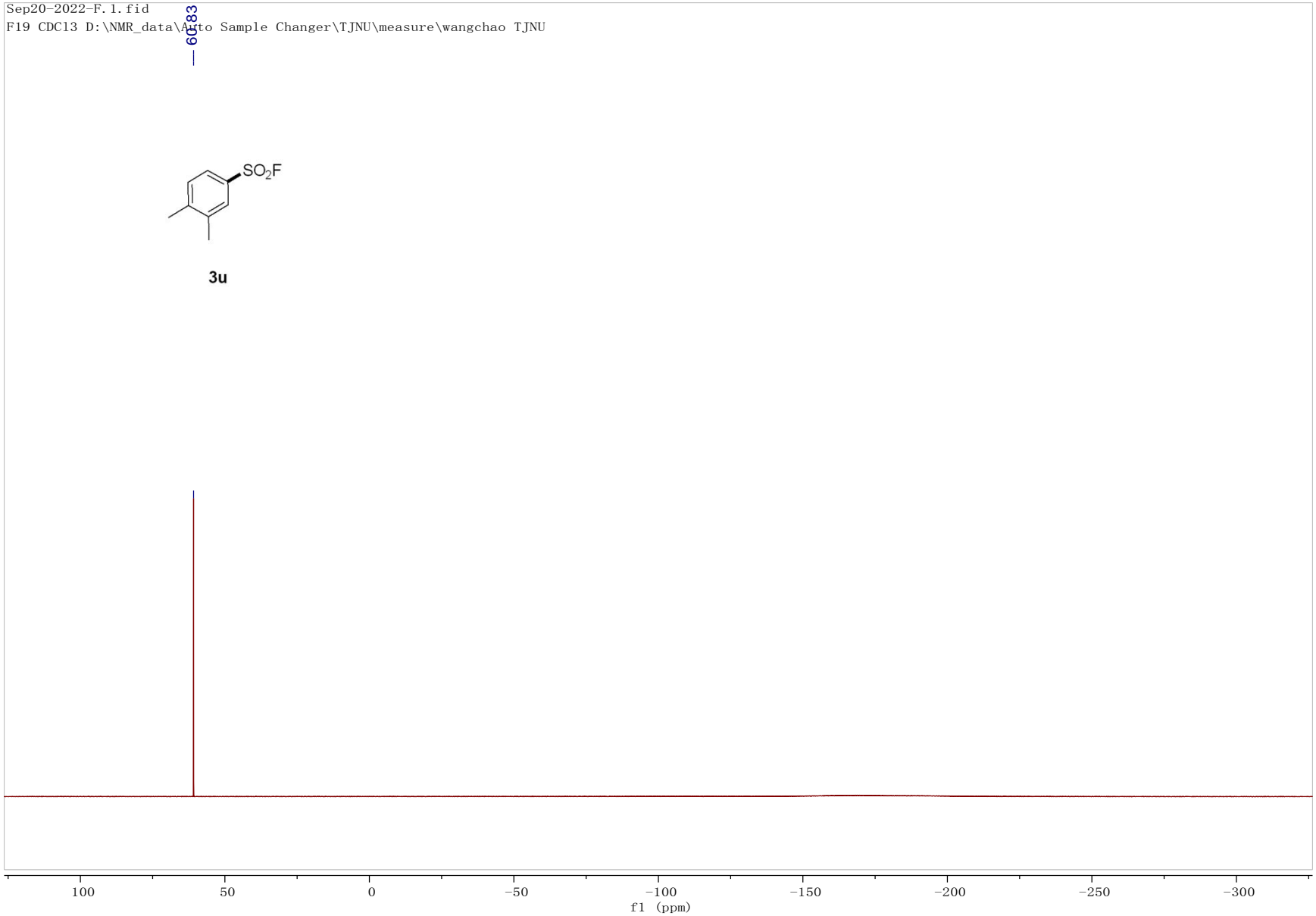
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3u**.



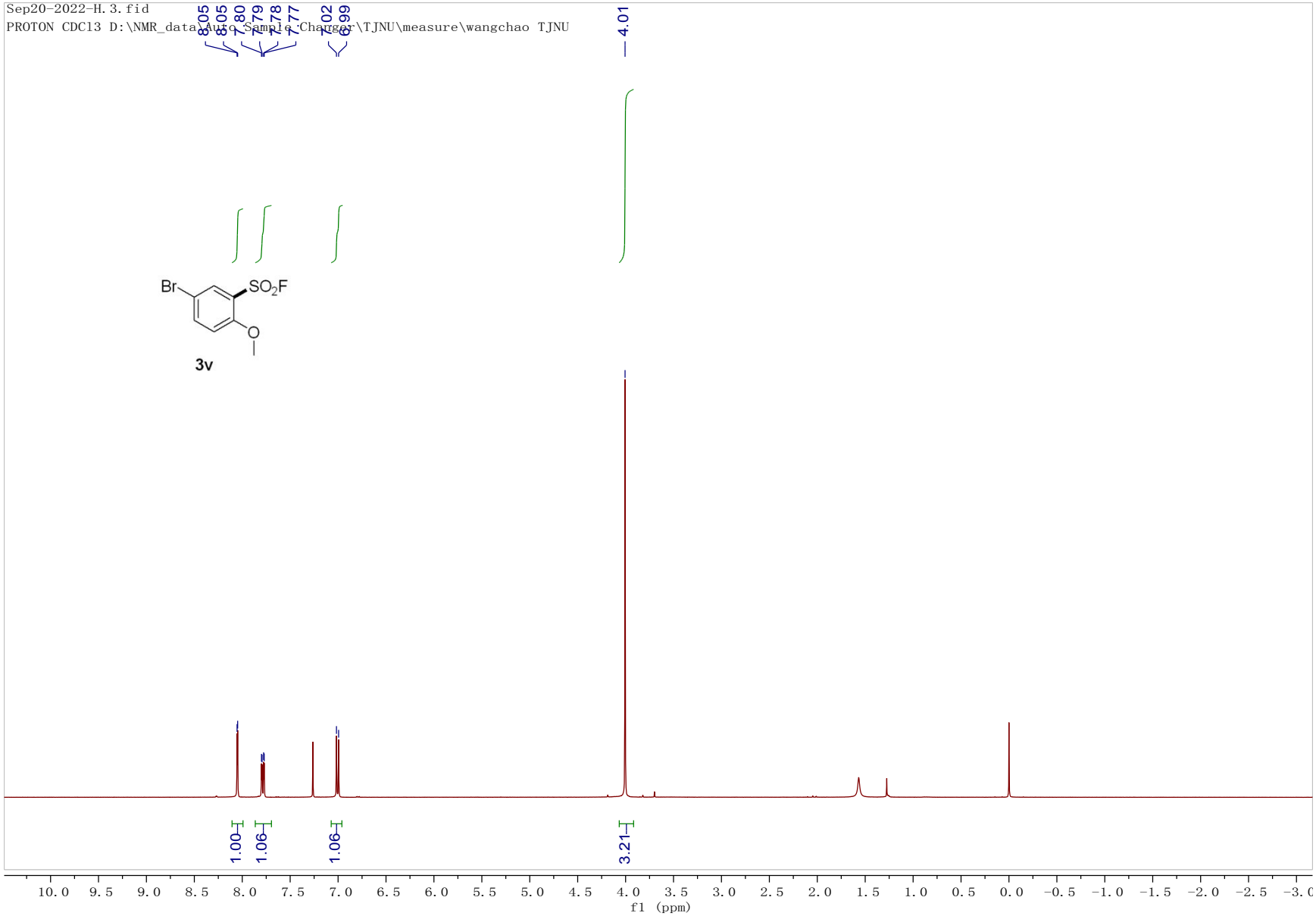
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3u**.



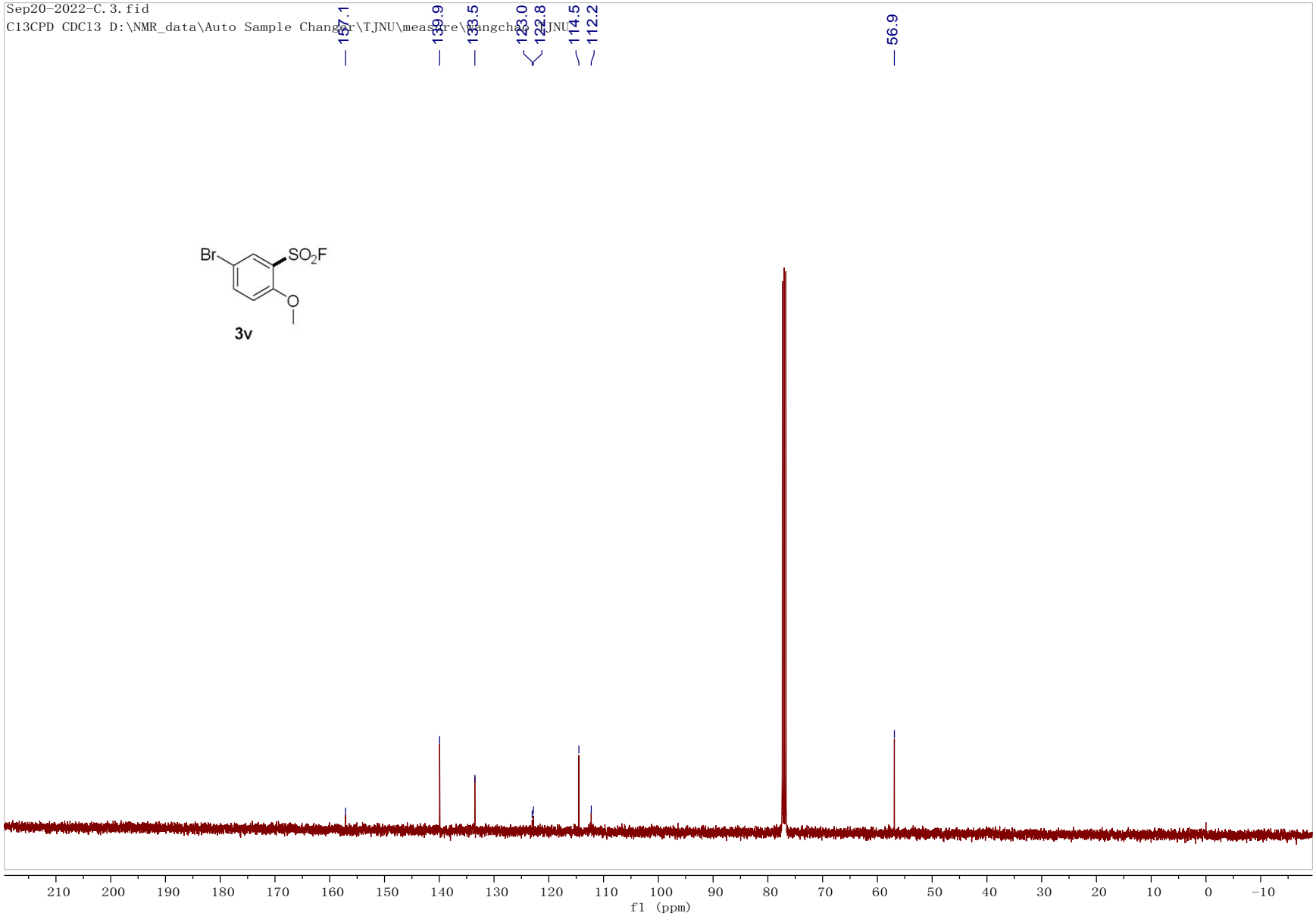
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3u**.



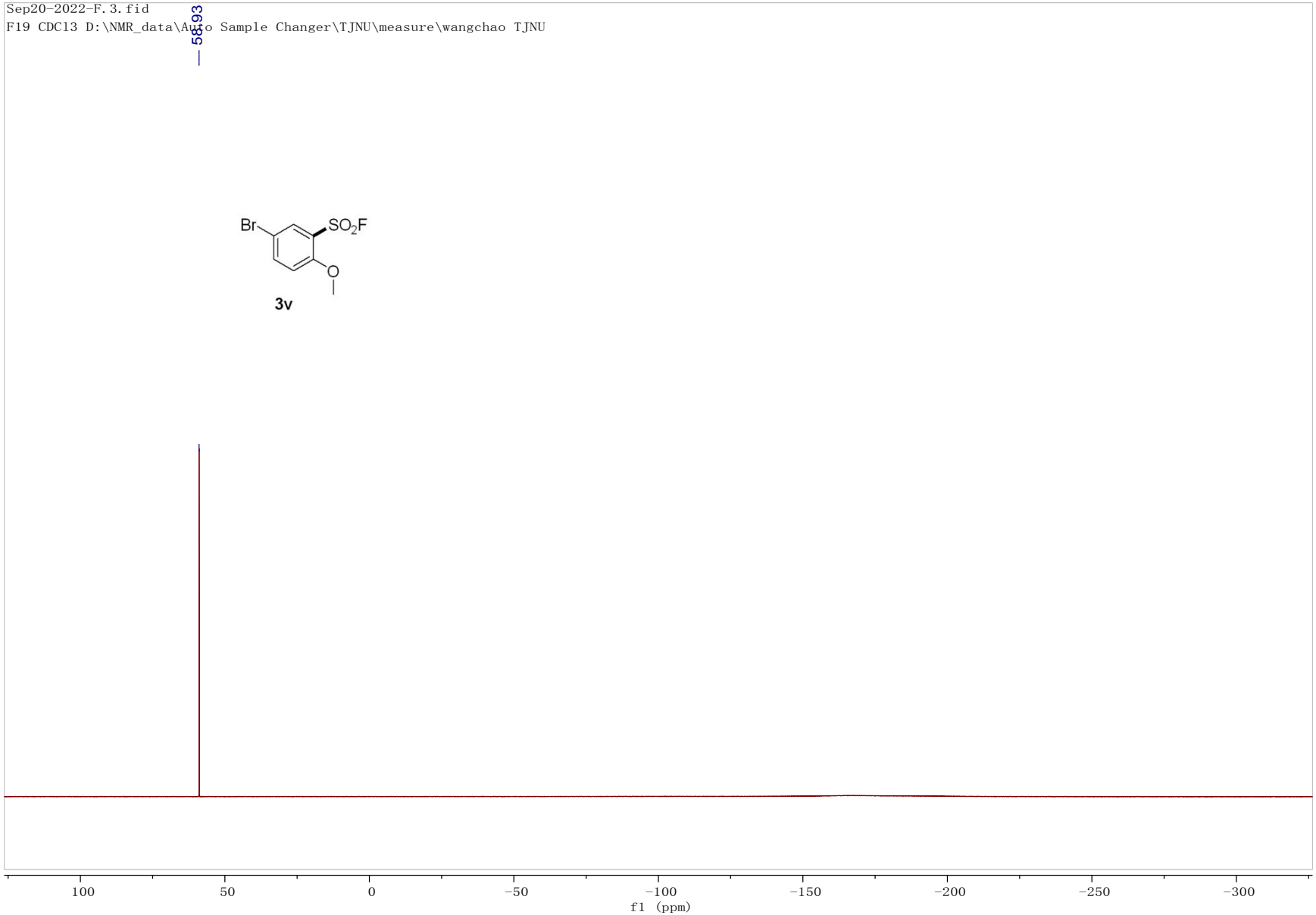
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3v**.



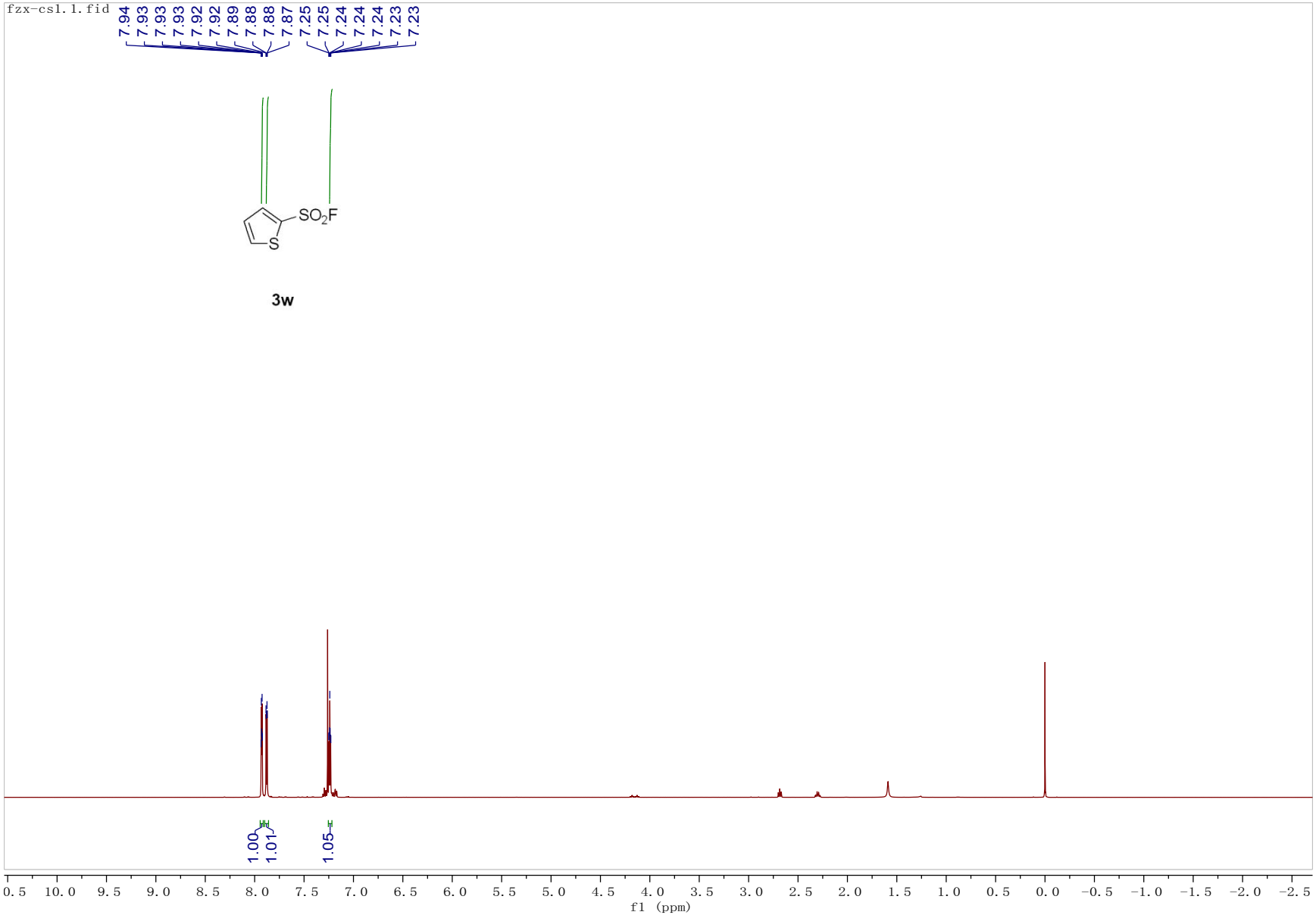
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3v**.



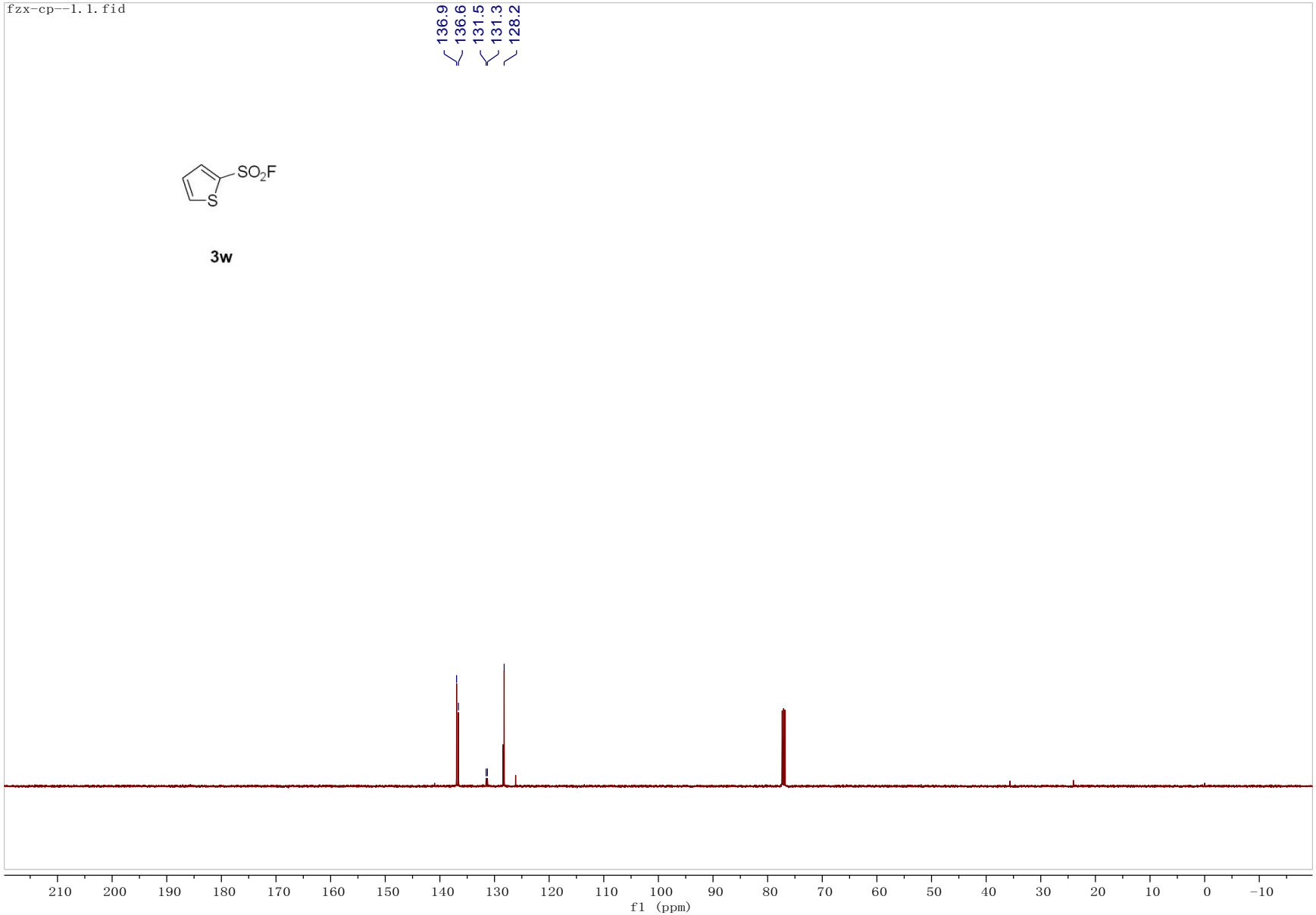
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3v.**



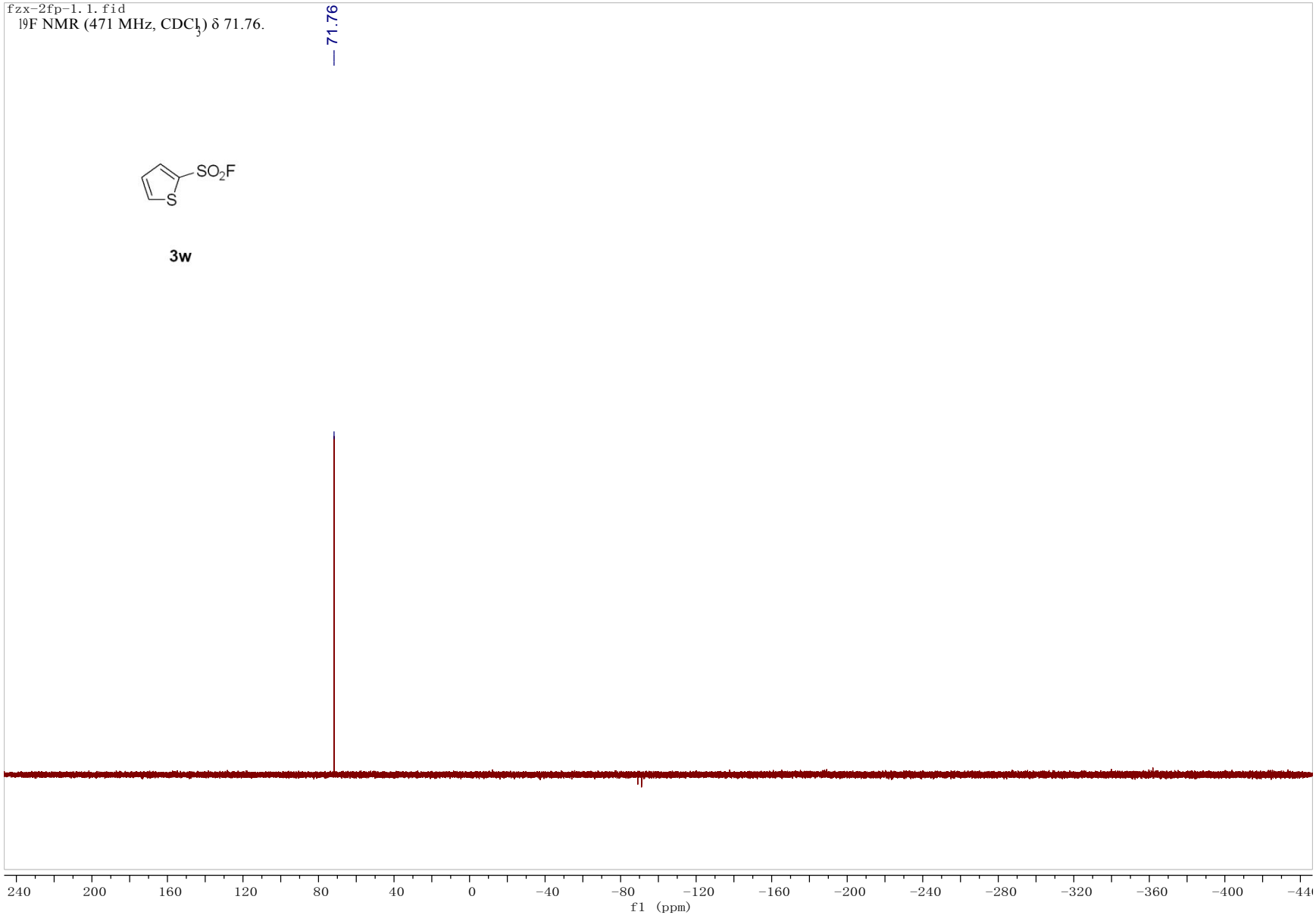
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3w**.



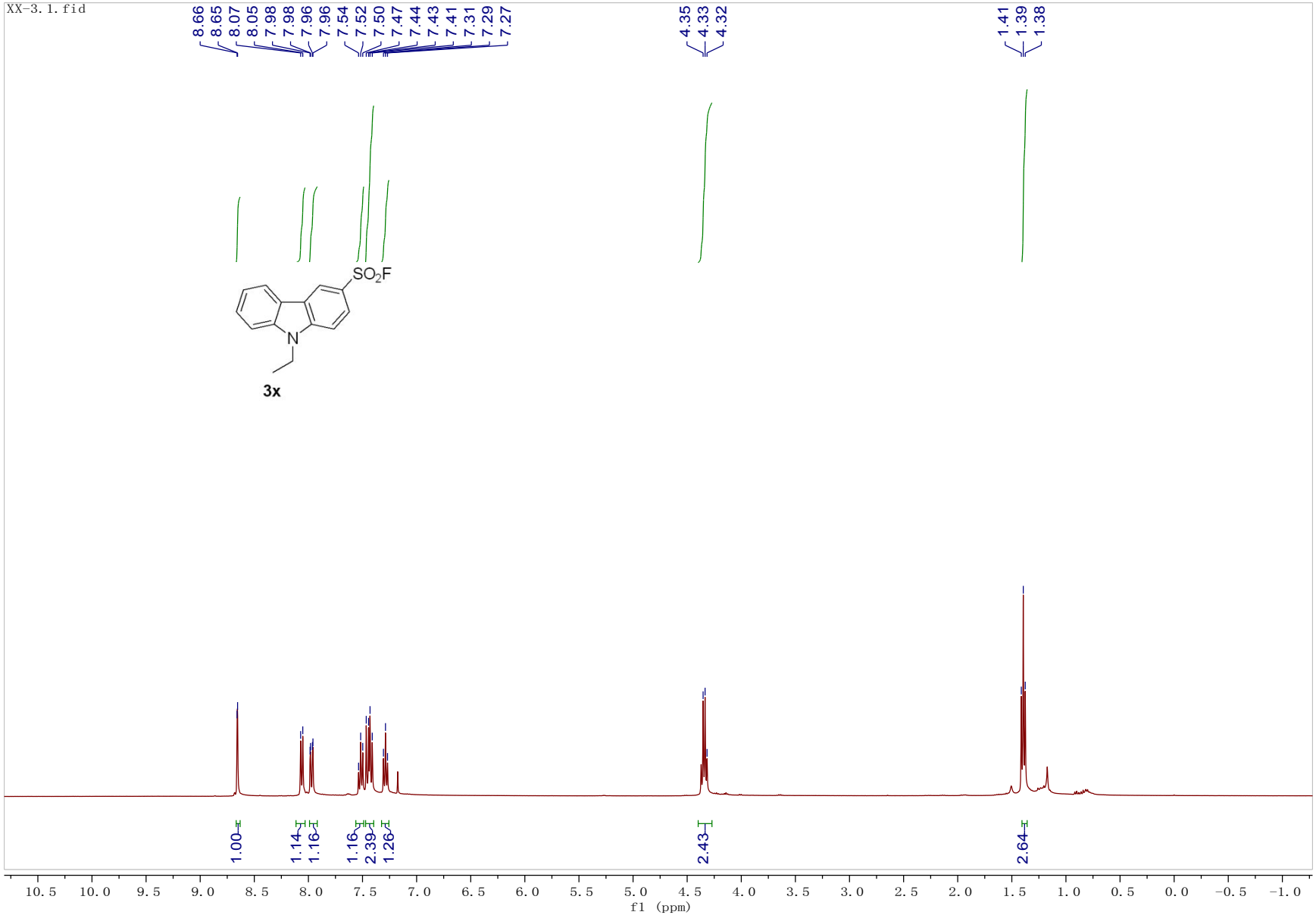
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3w**.



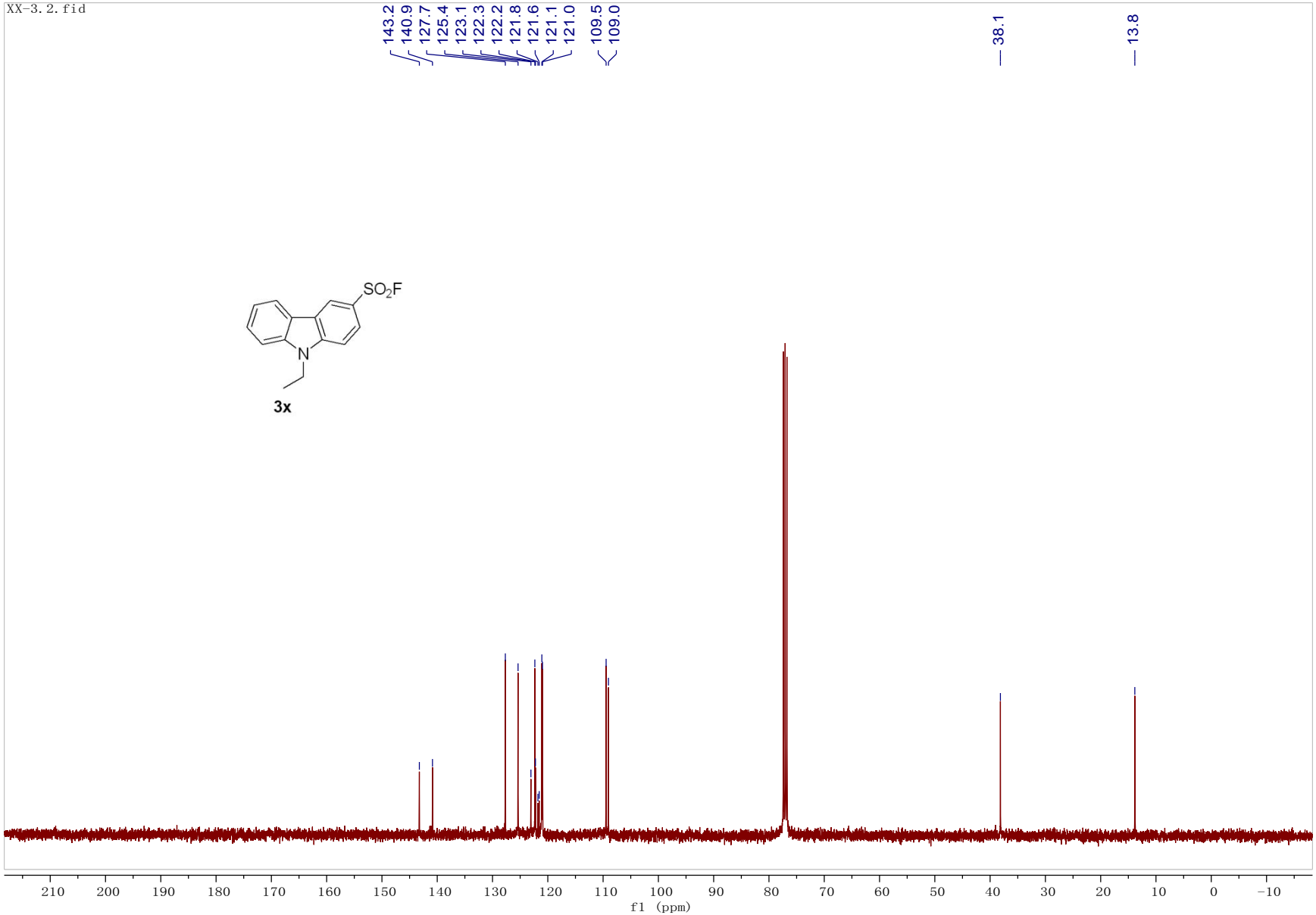
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **3w**.



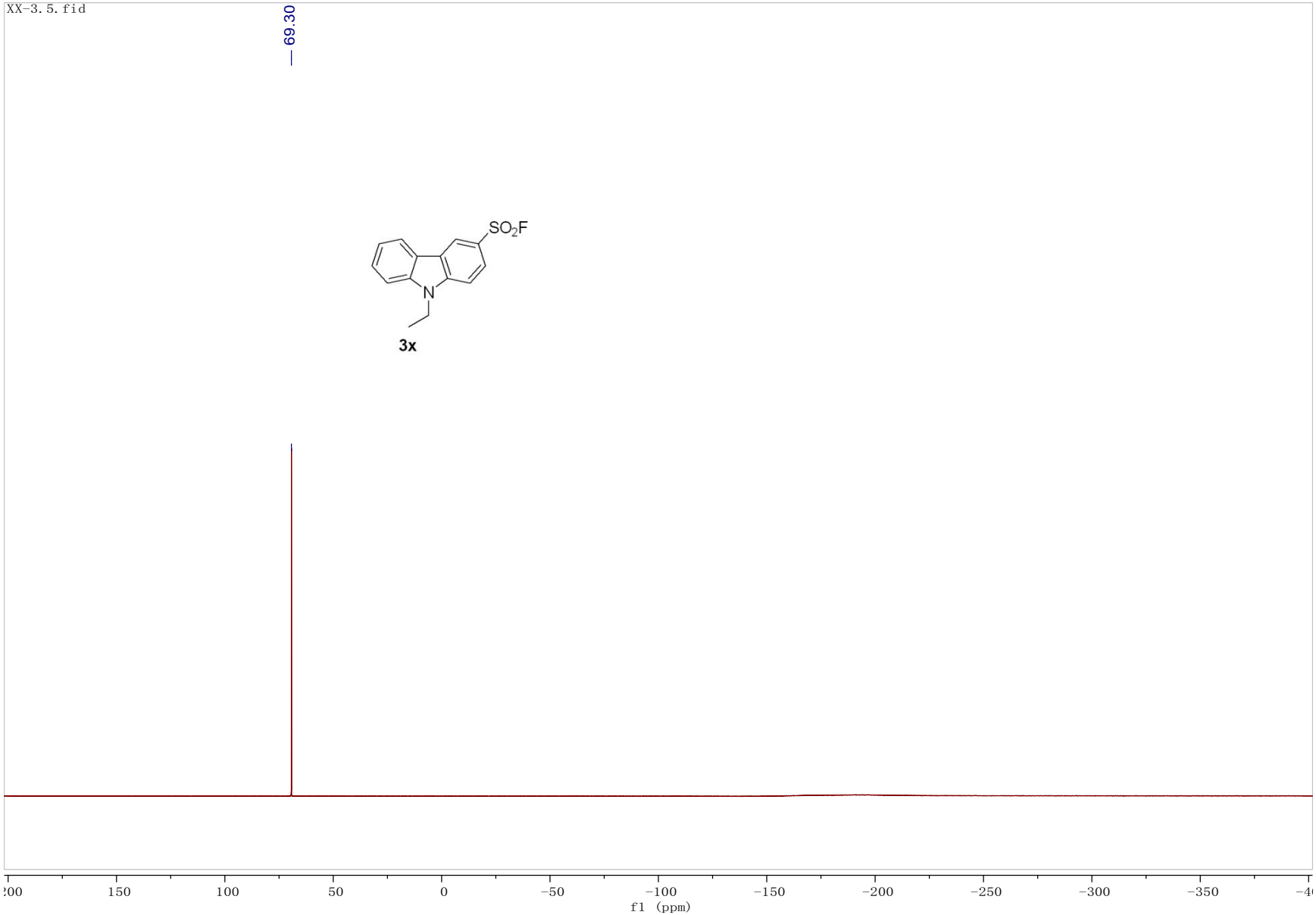
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3x**.



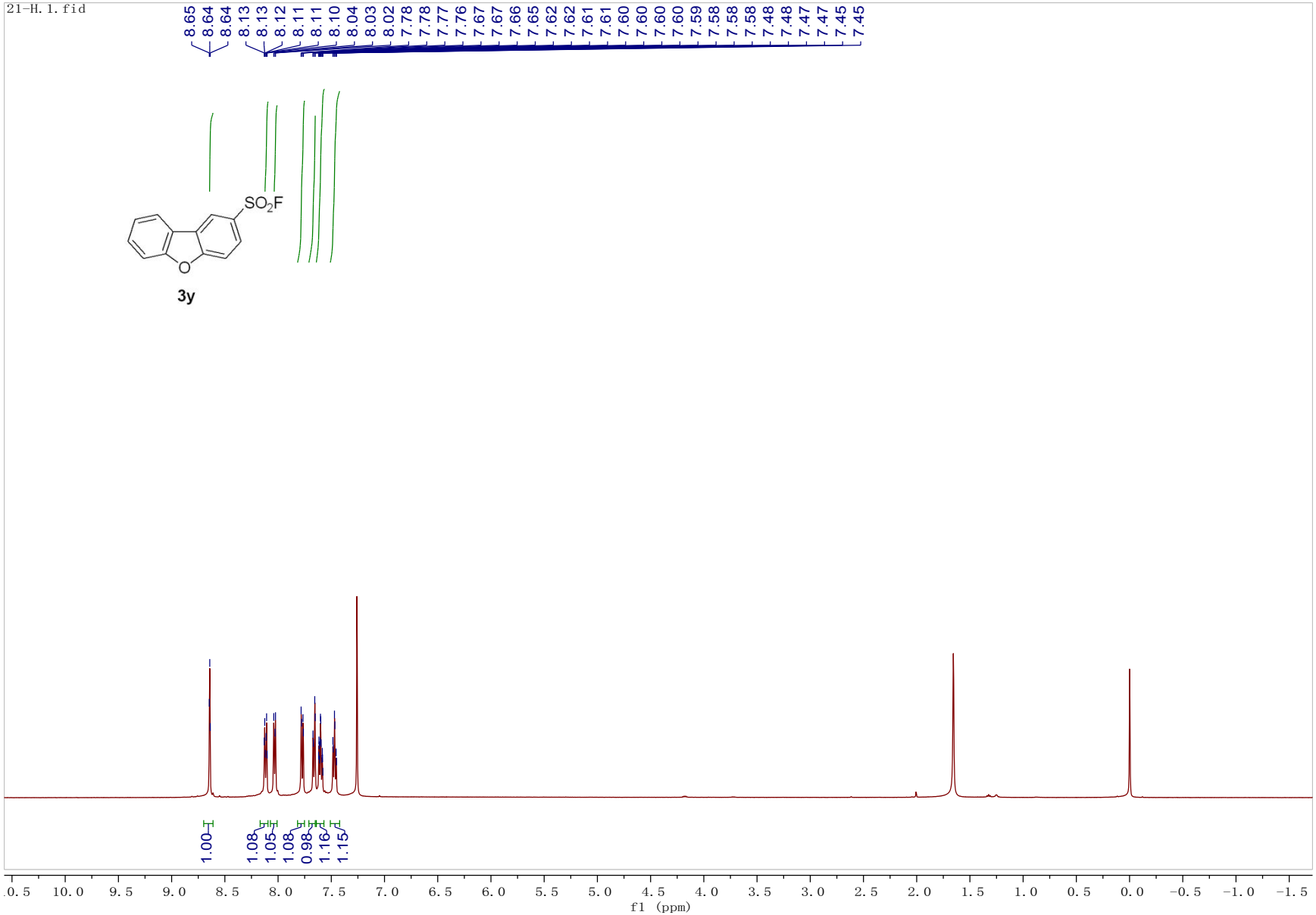
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3x**.



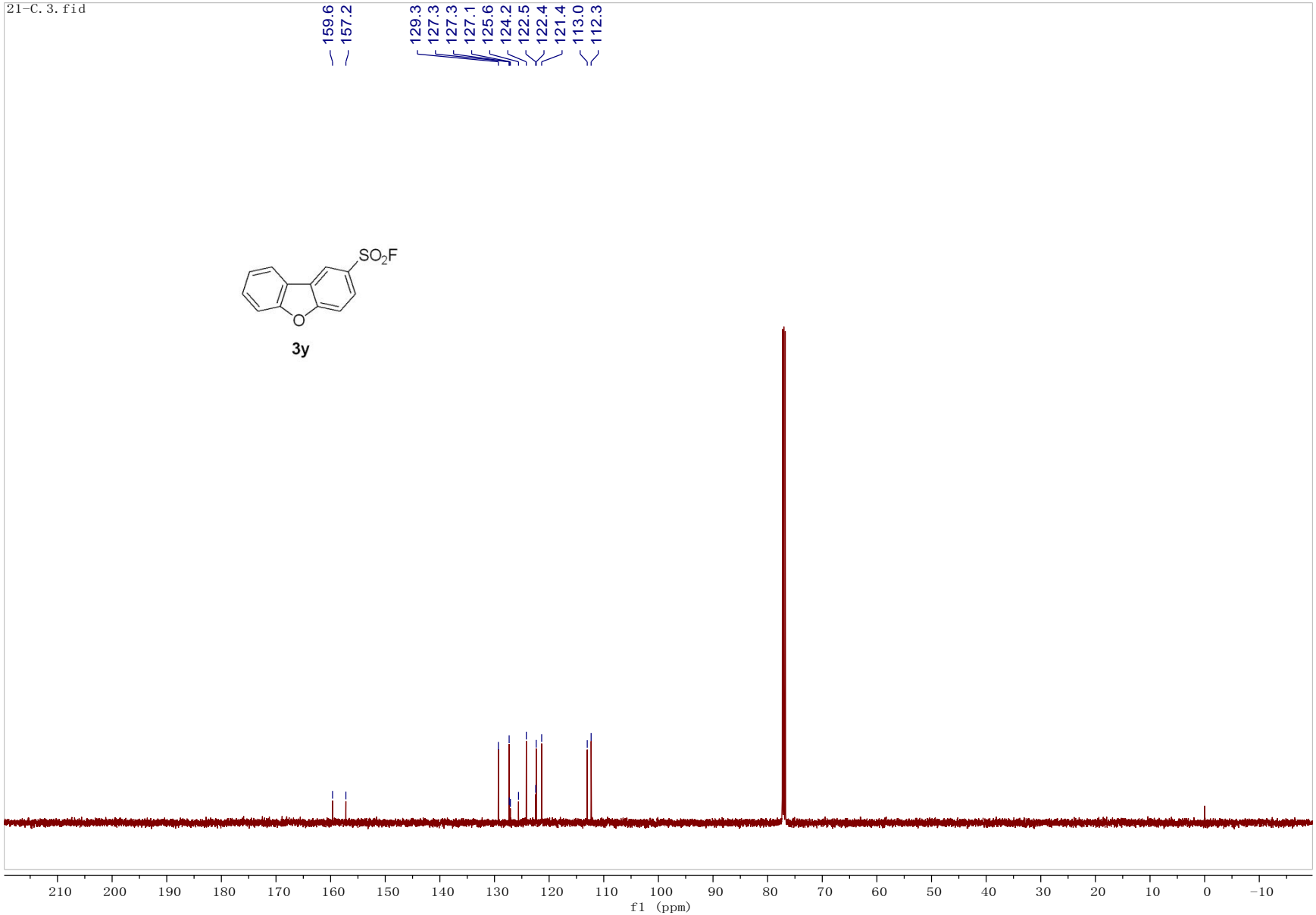
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3x**.



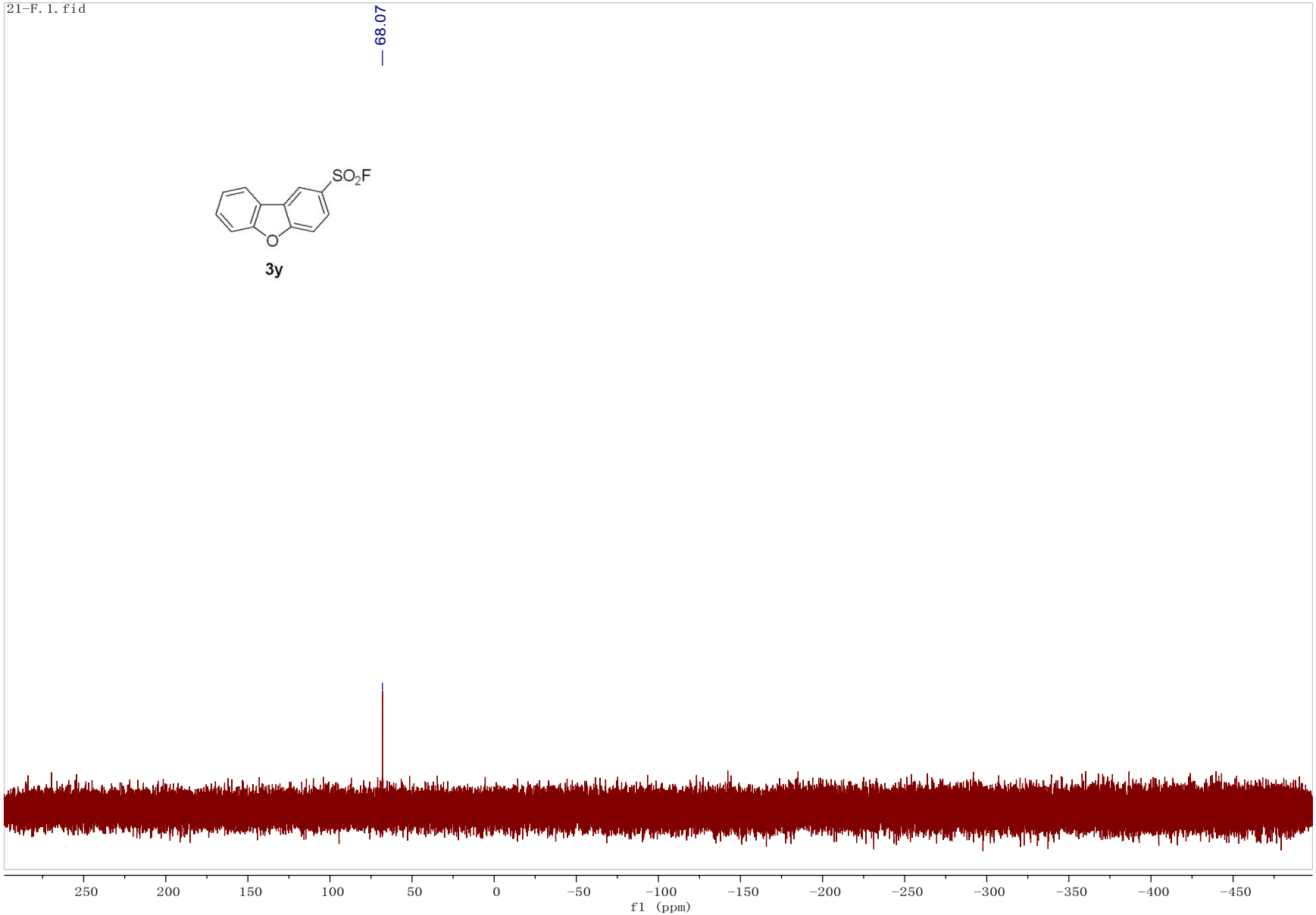
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3y**.



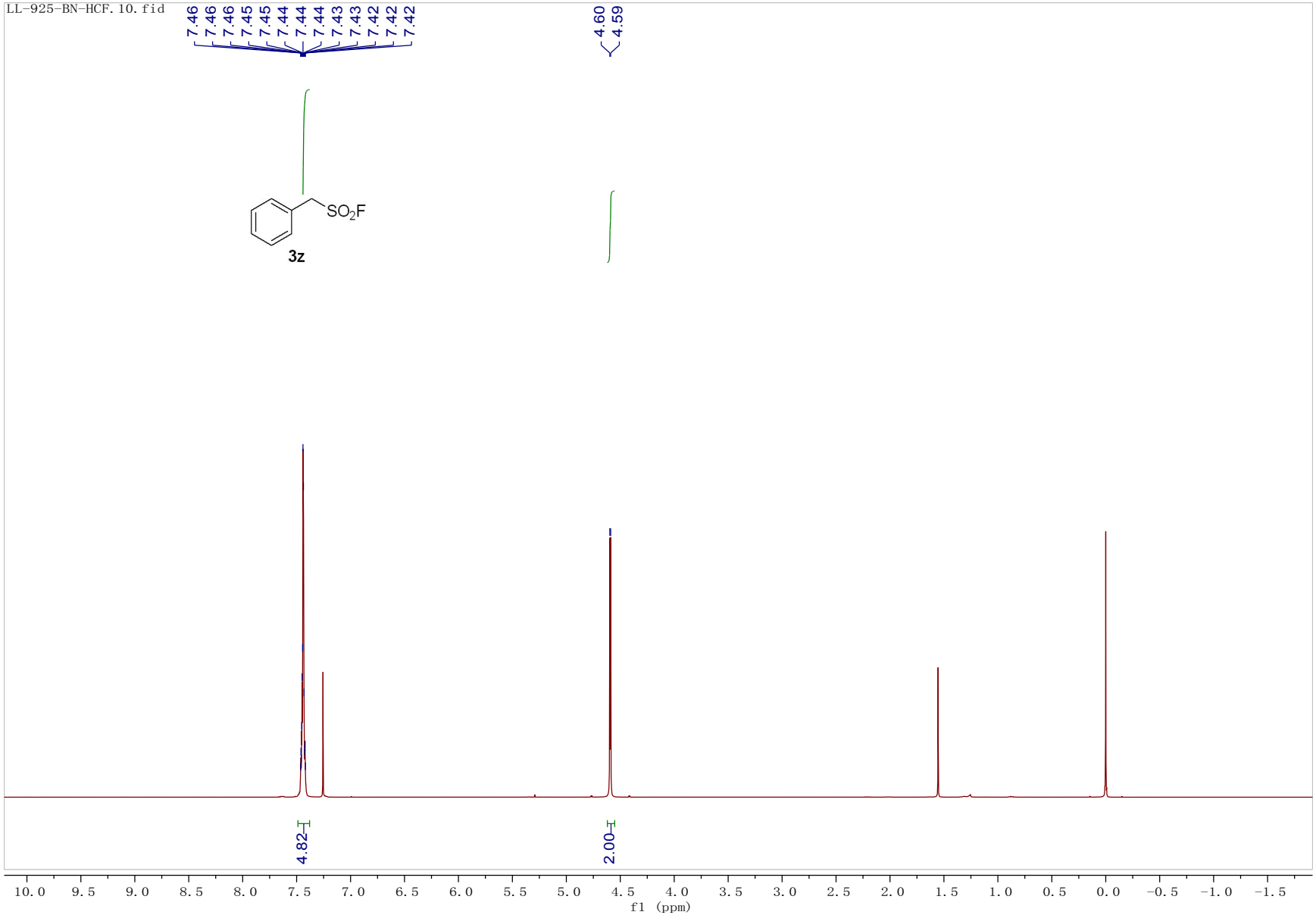
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3y**.



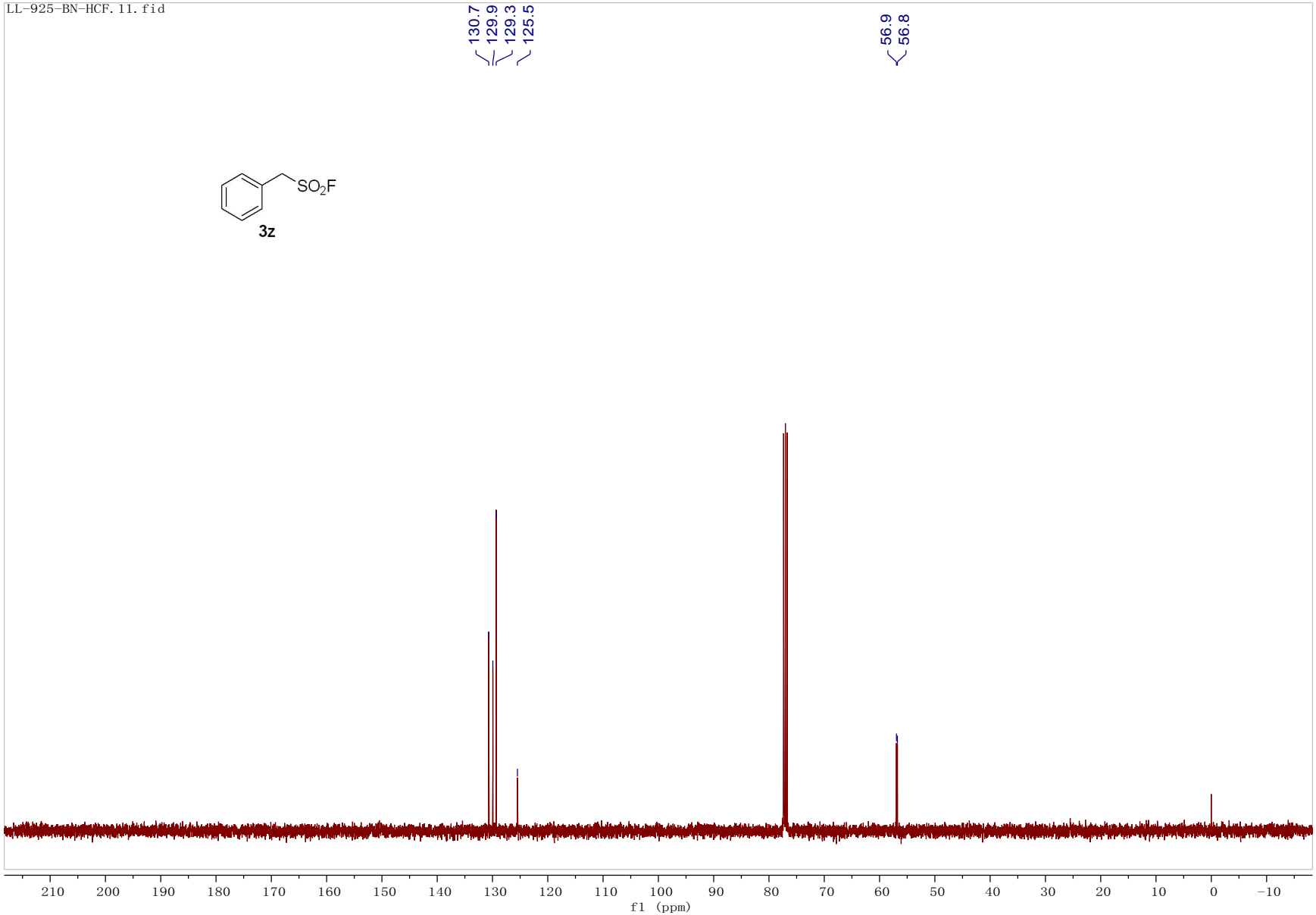
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **3y**.



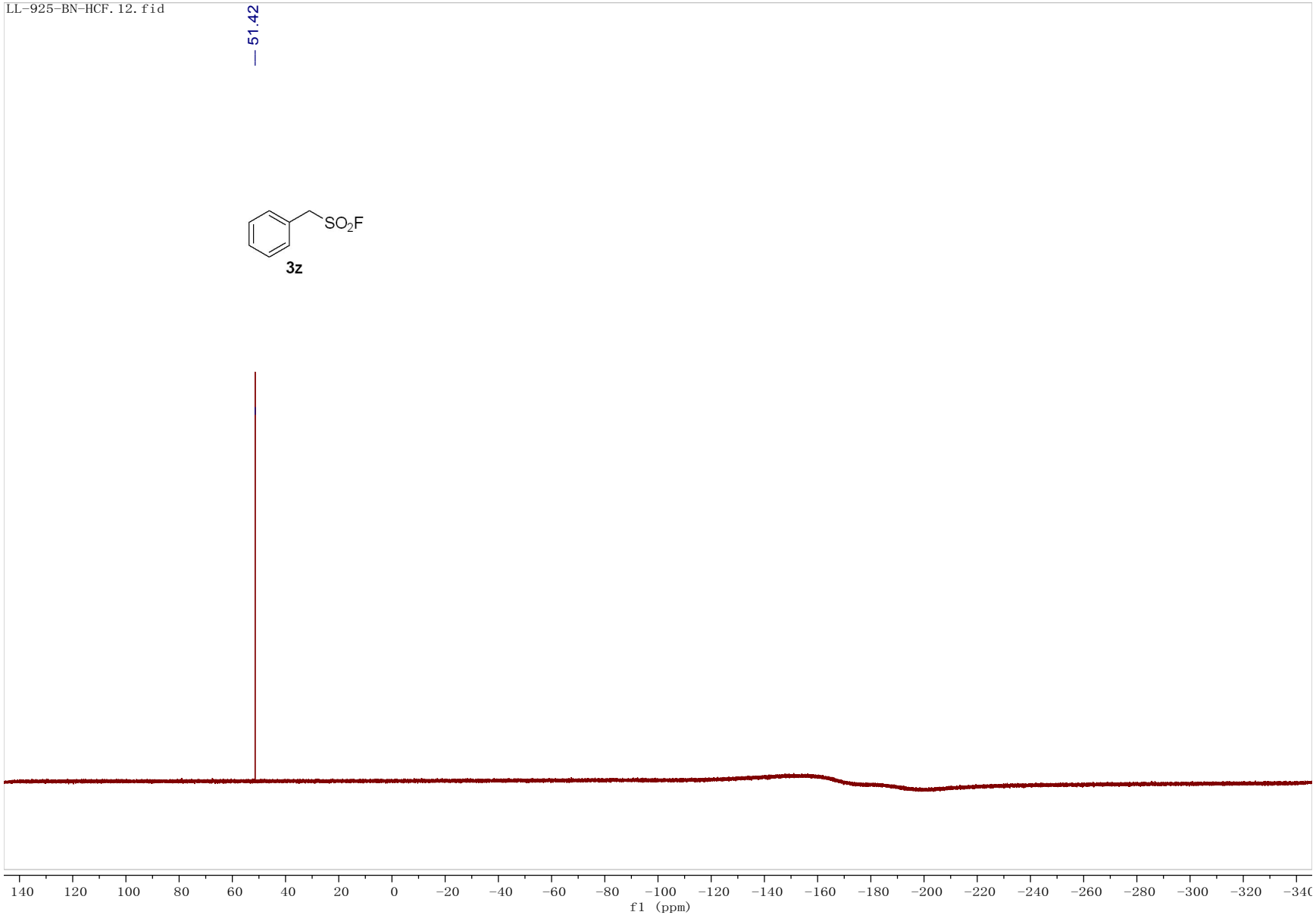
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3z**.



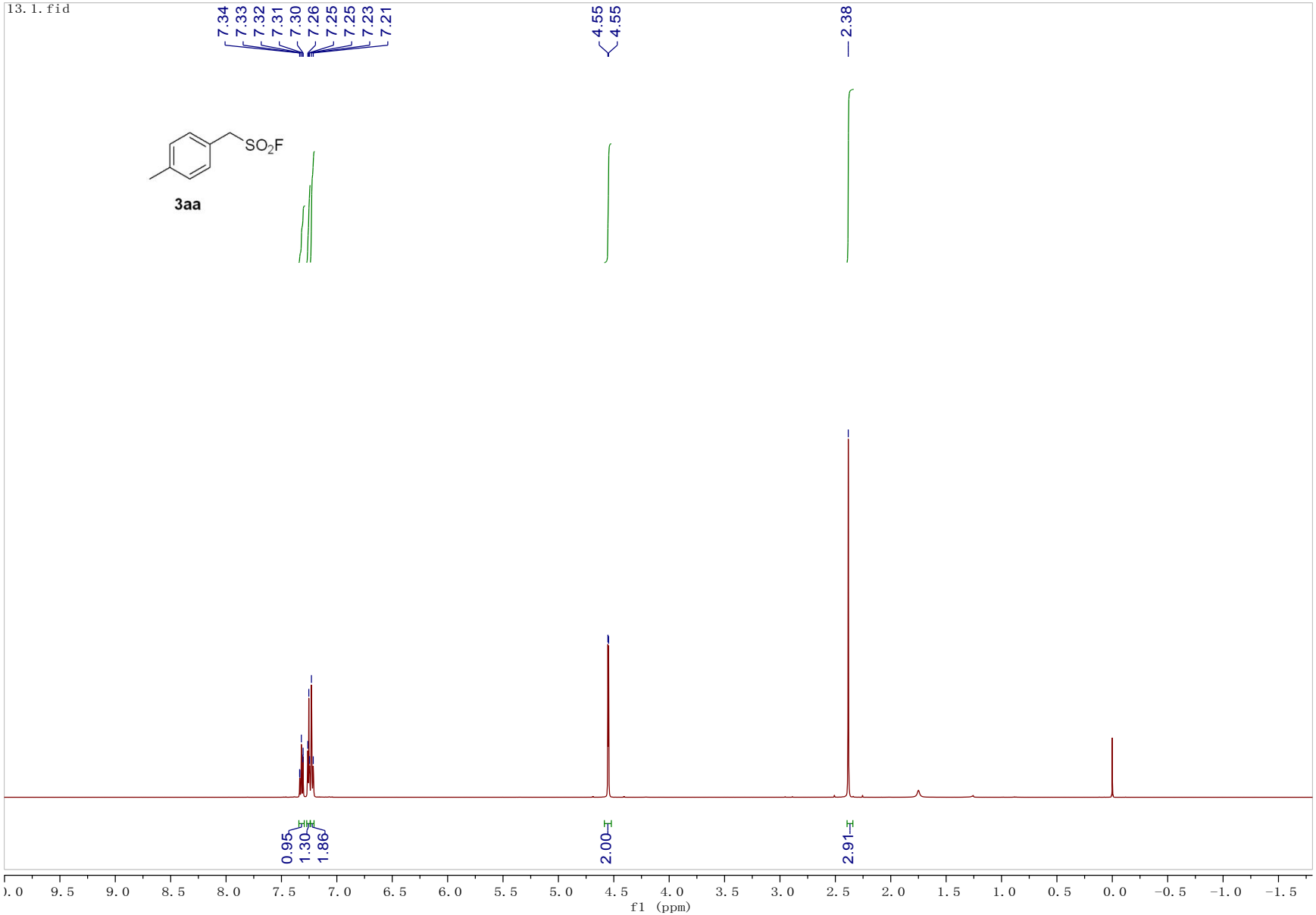
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3z**.



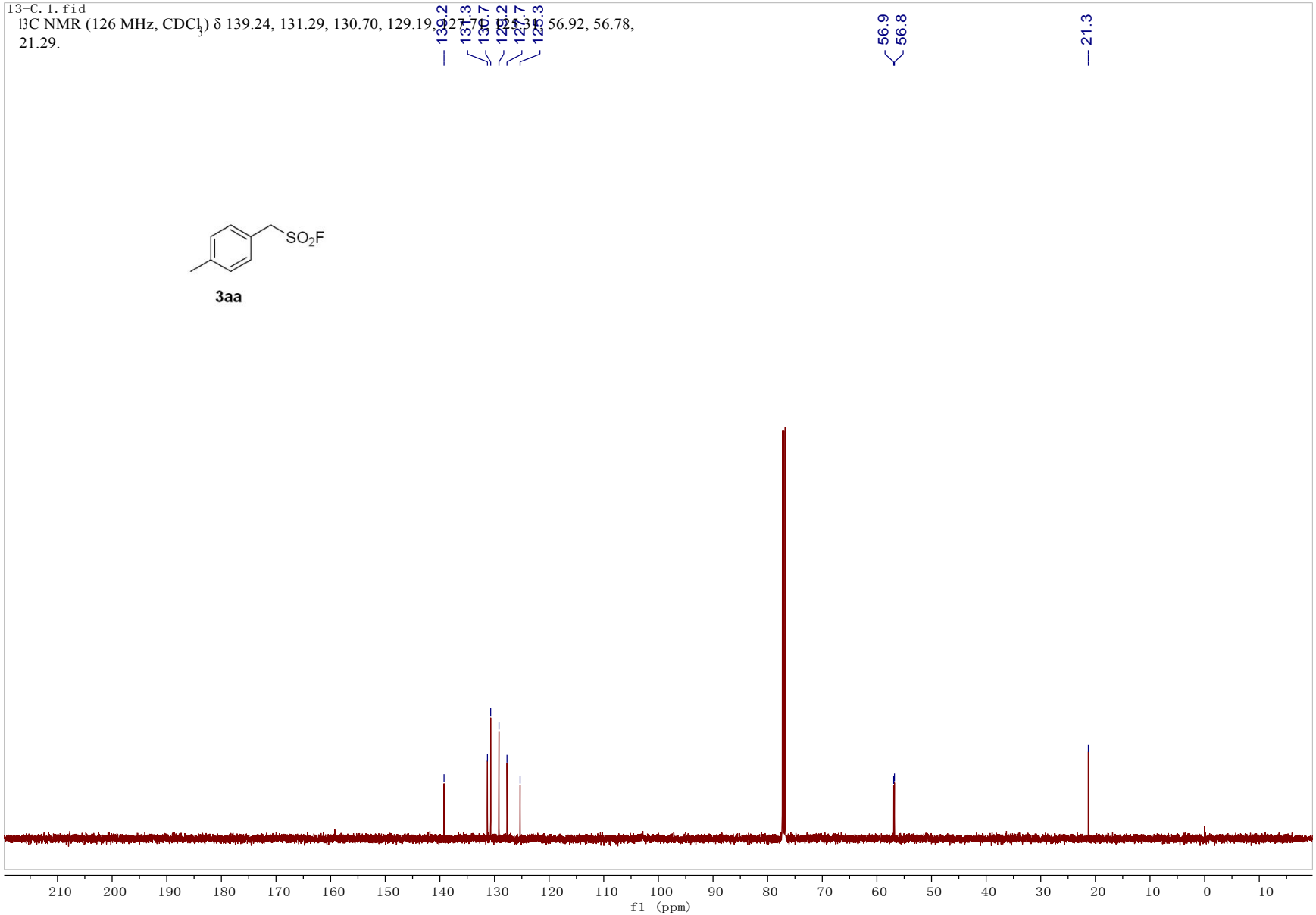
^{19}F NMR (376 MHz, CDCl3) spectrum of **3z**.



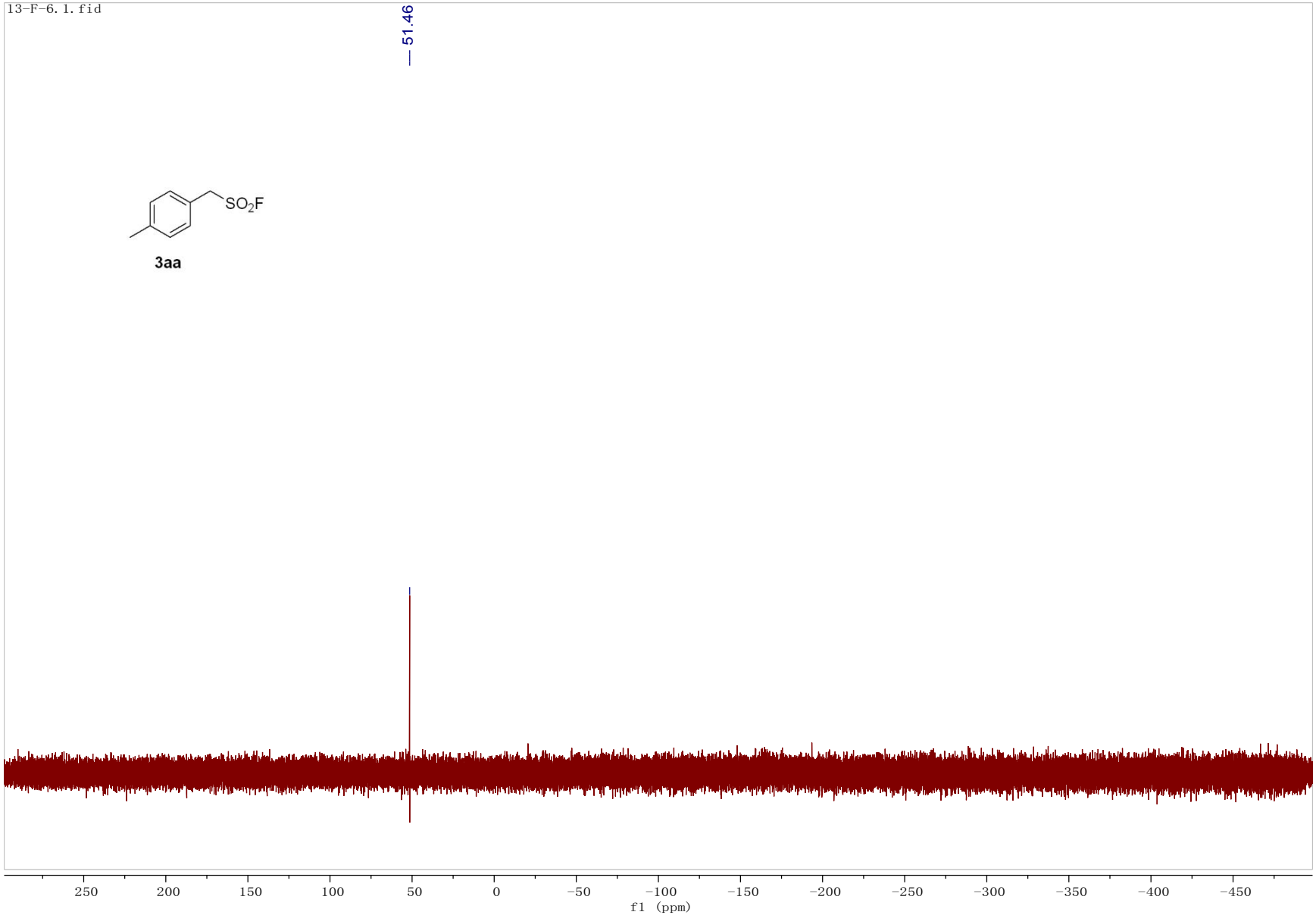
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3aa**.



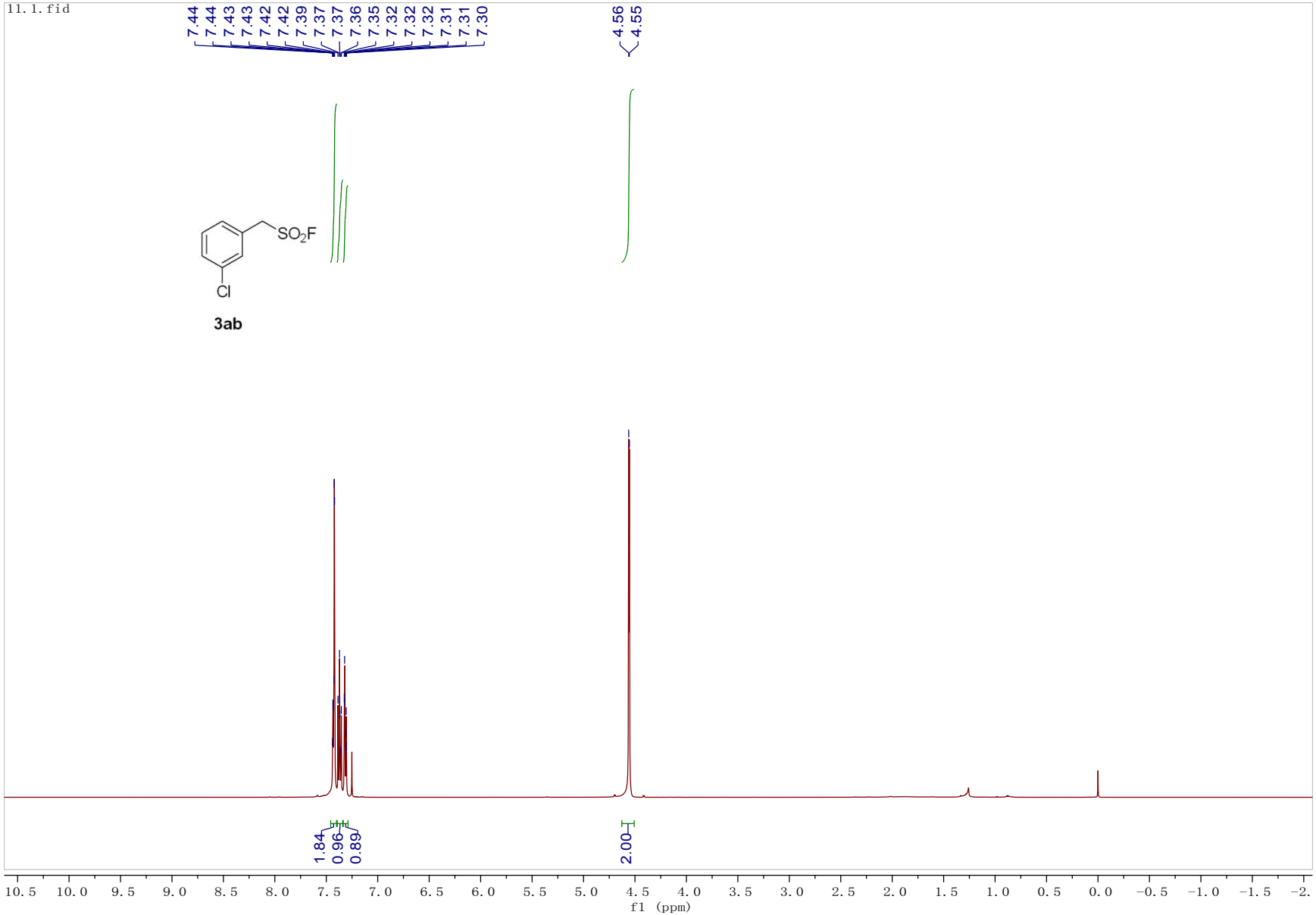
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3aa**.



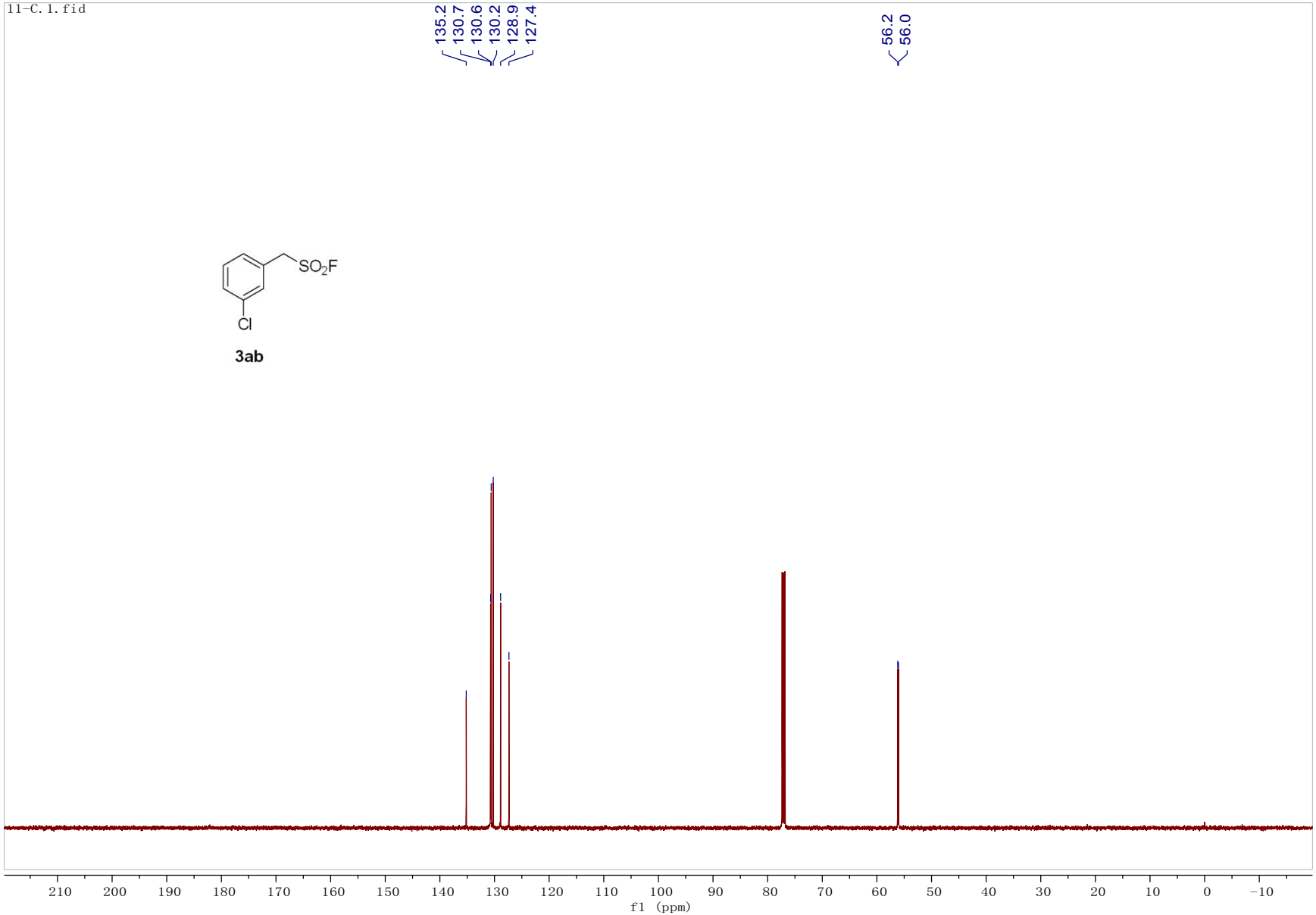
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3aa**.



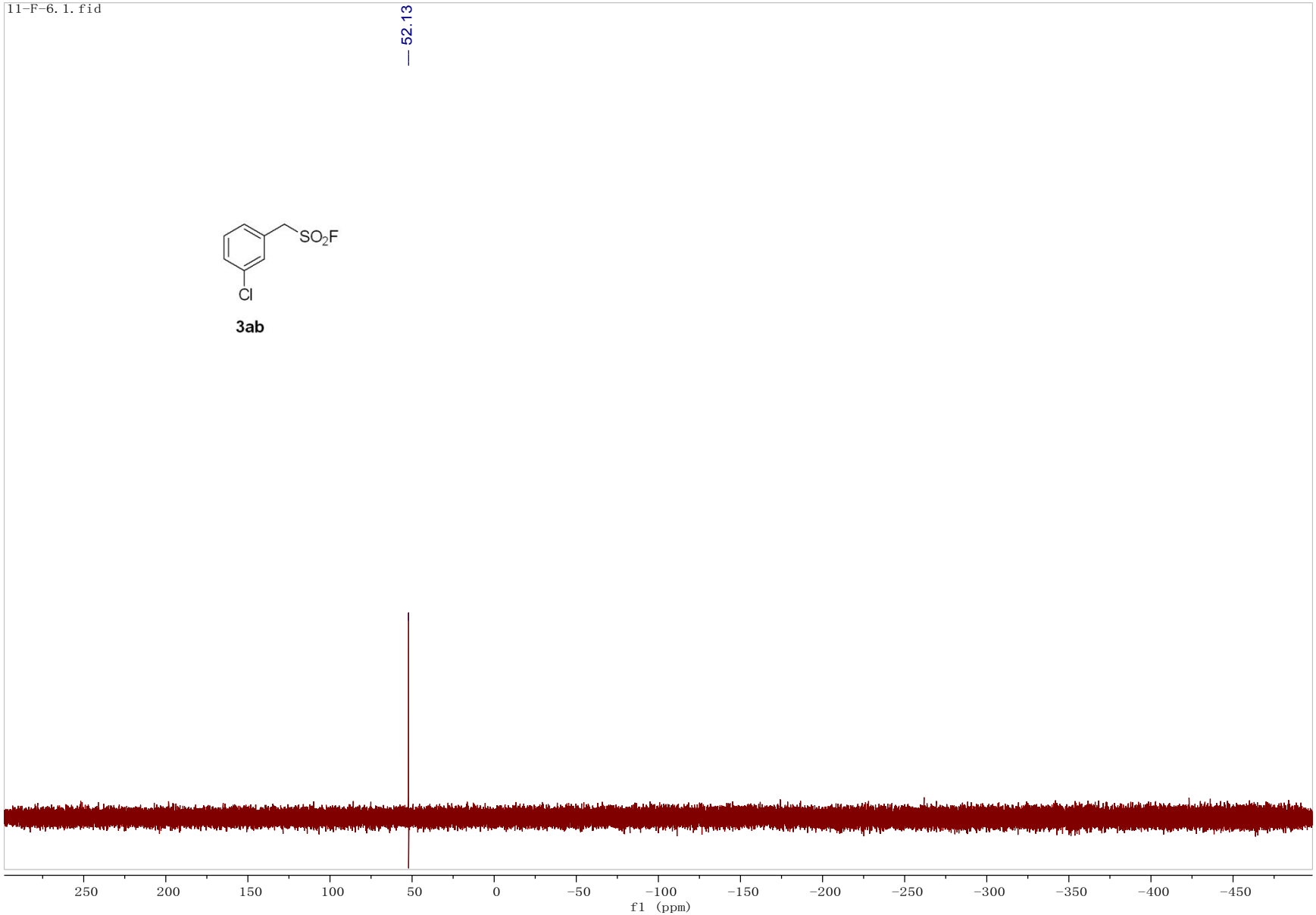
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3ab**.



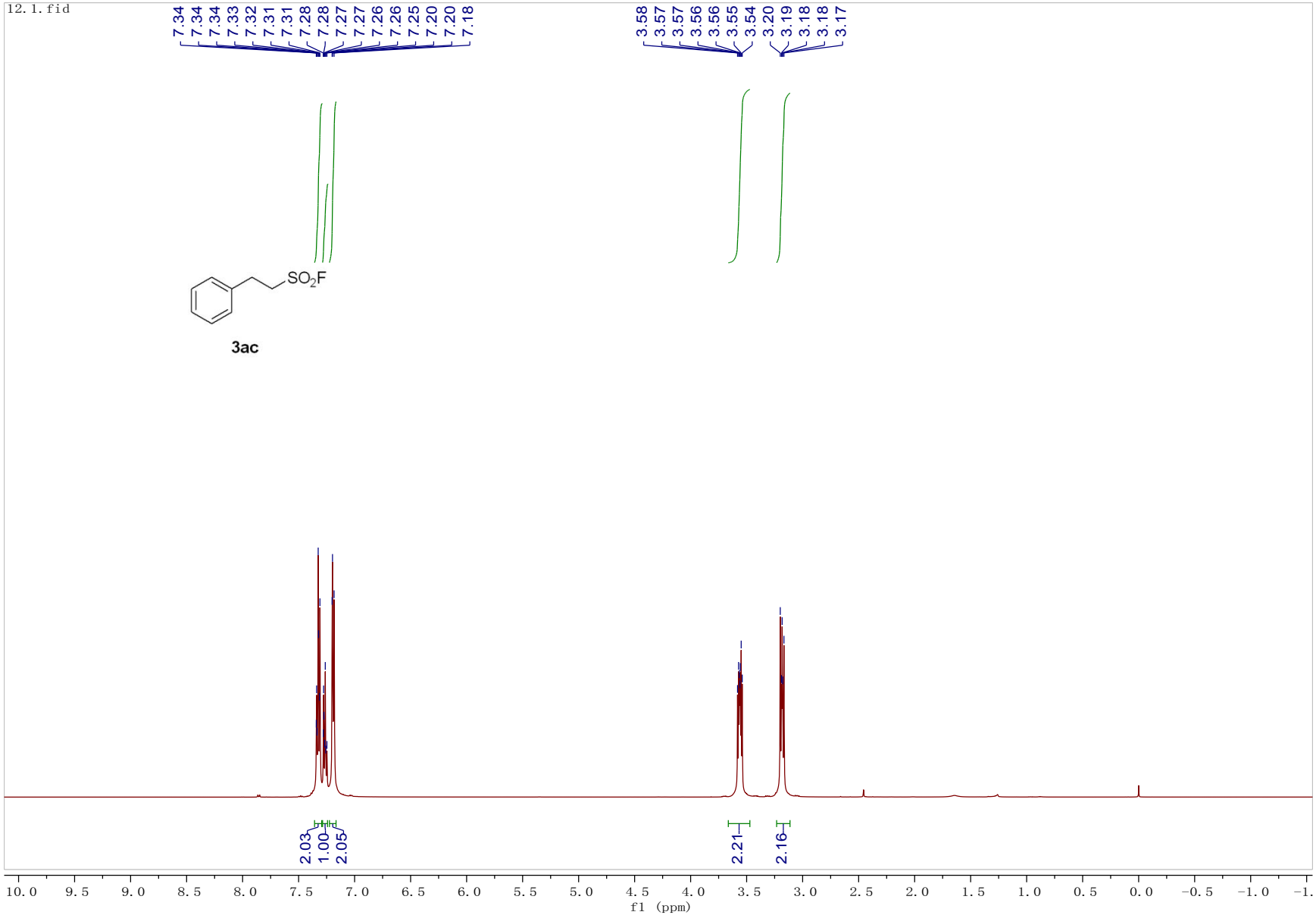
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3ab**.



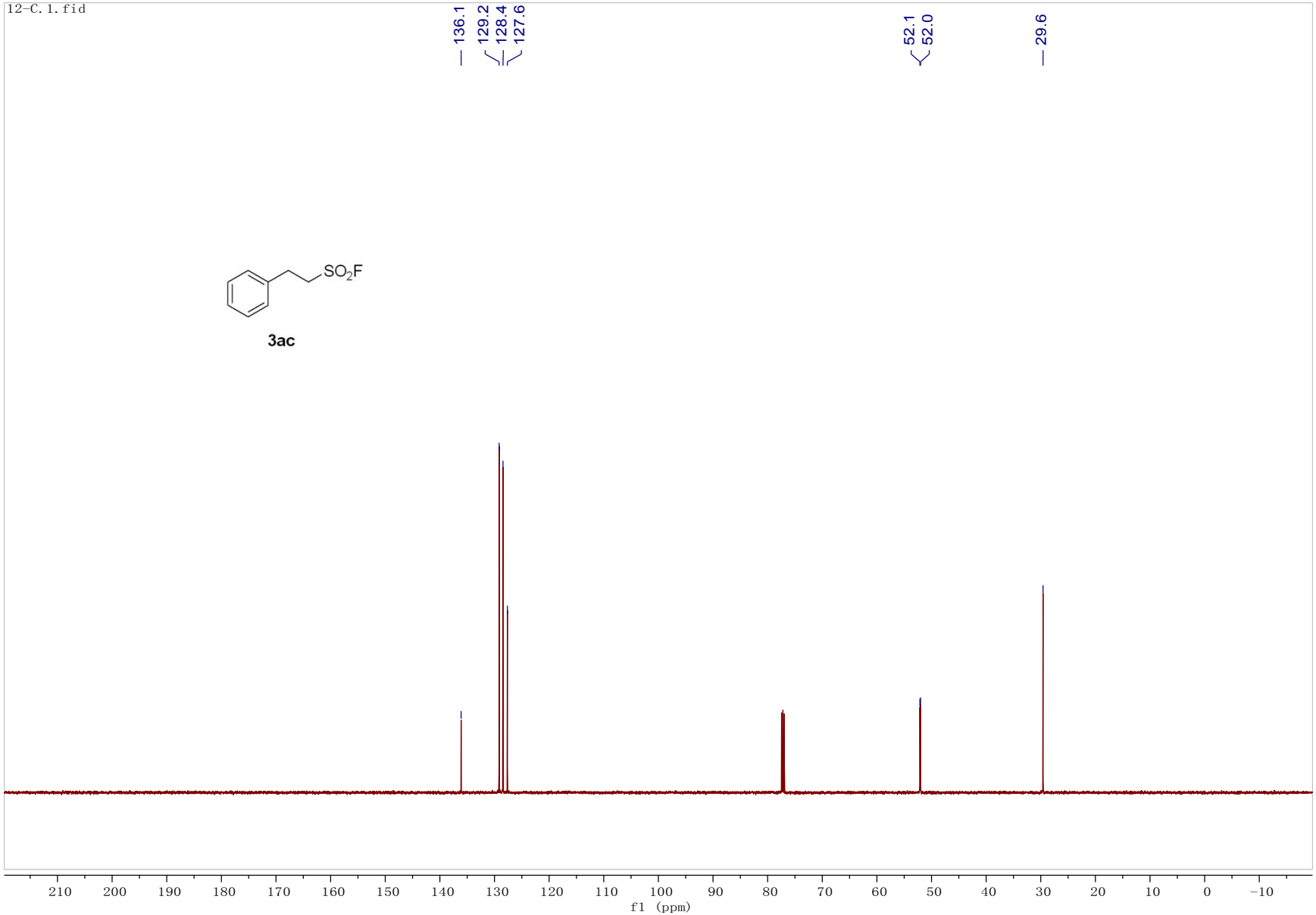
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ab**.



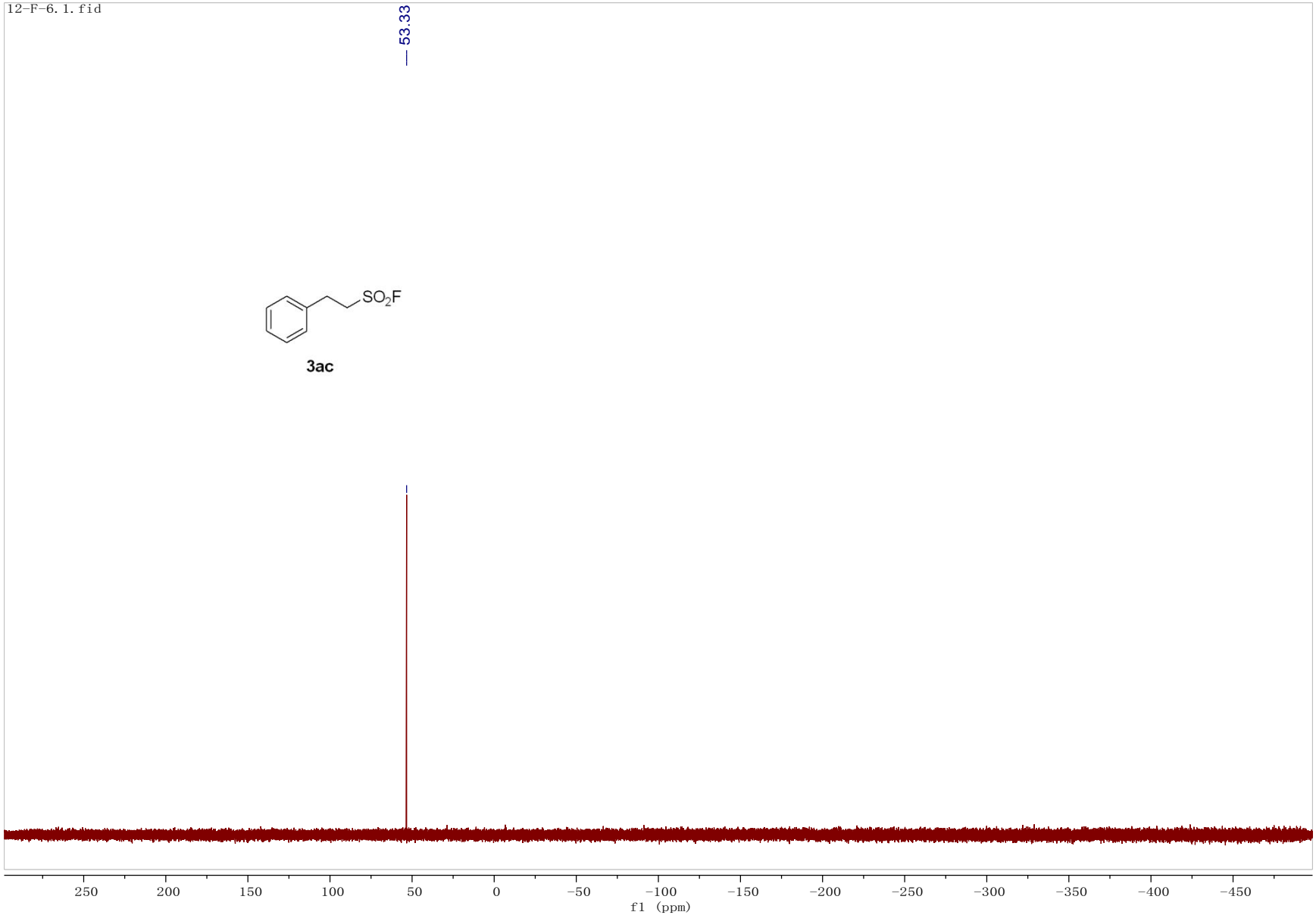
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3ac**.



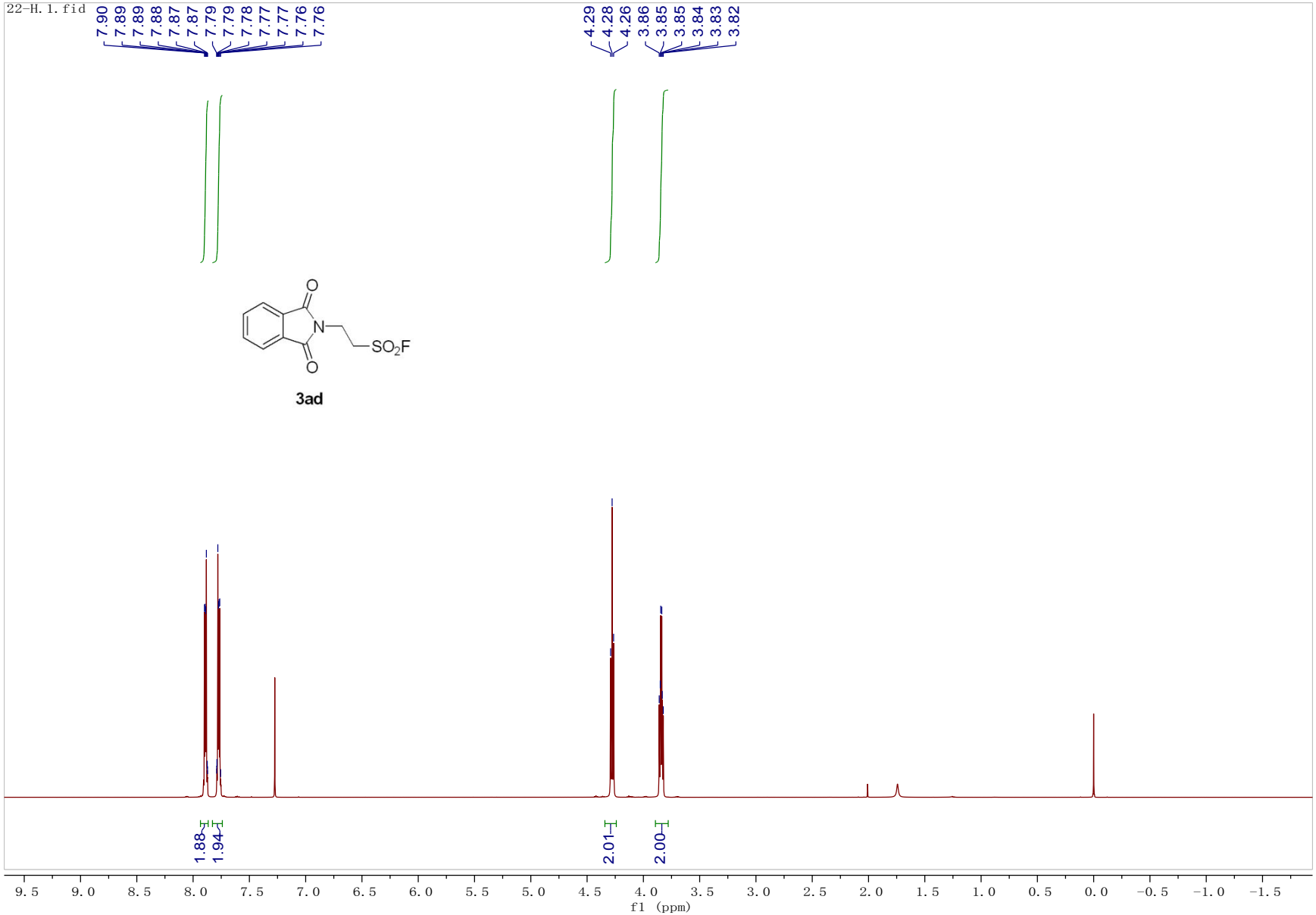
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3ac**.



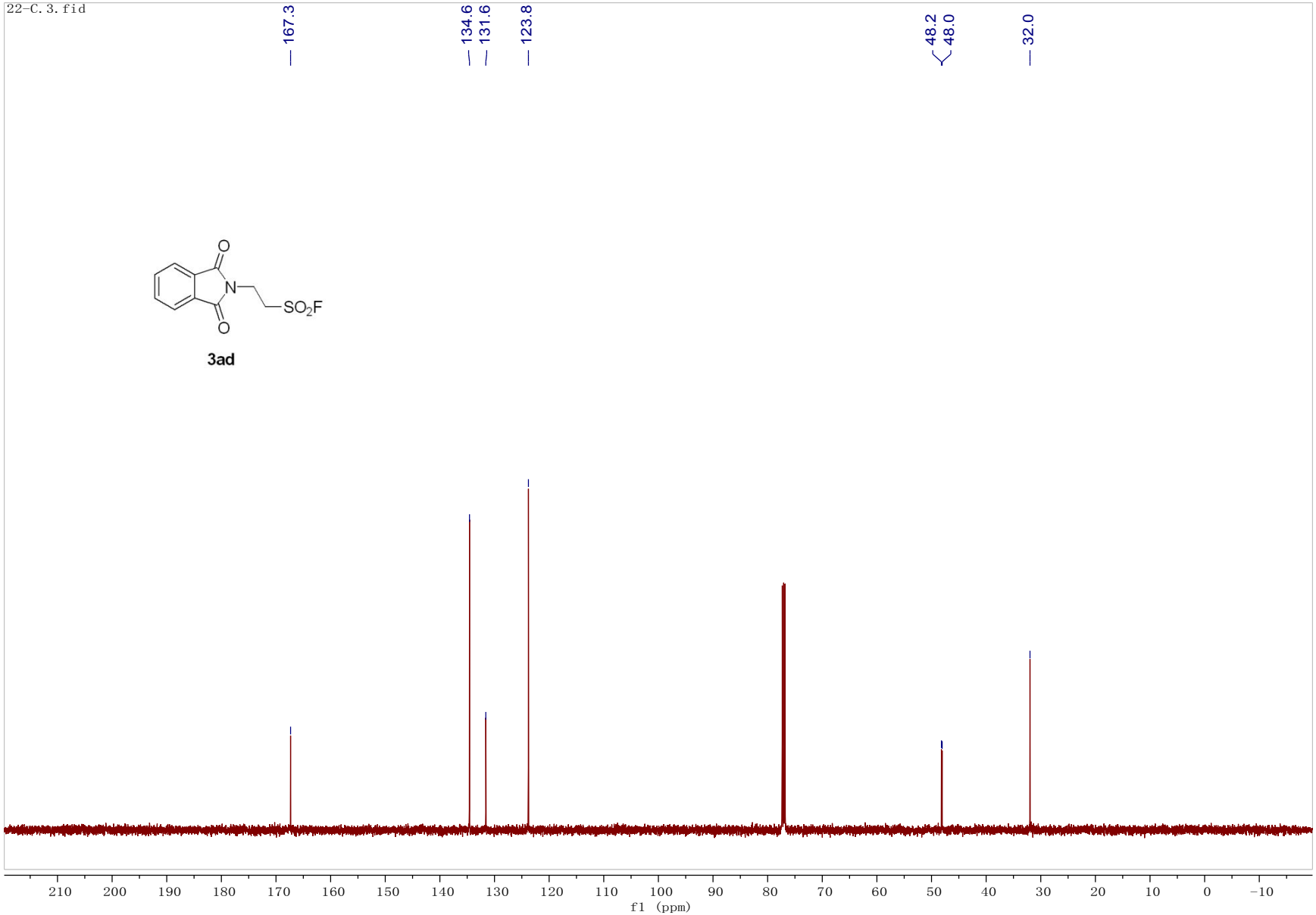
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ac**.



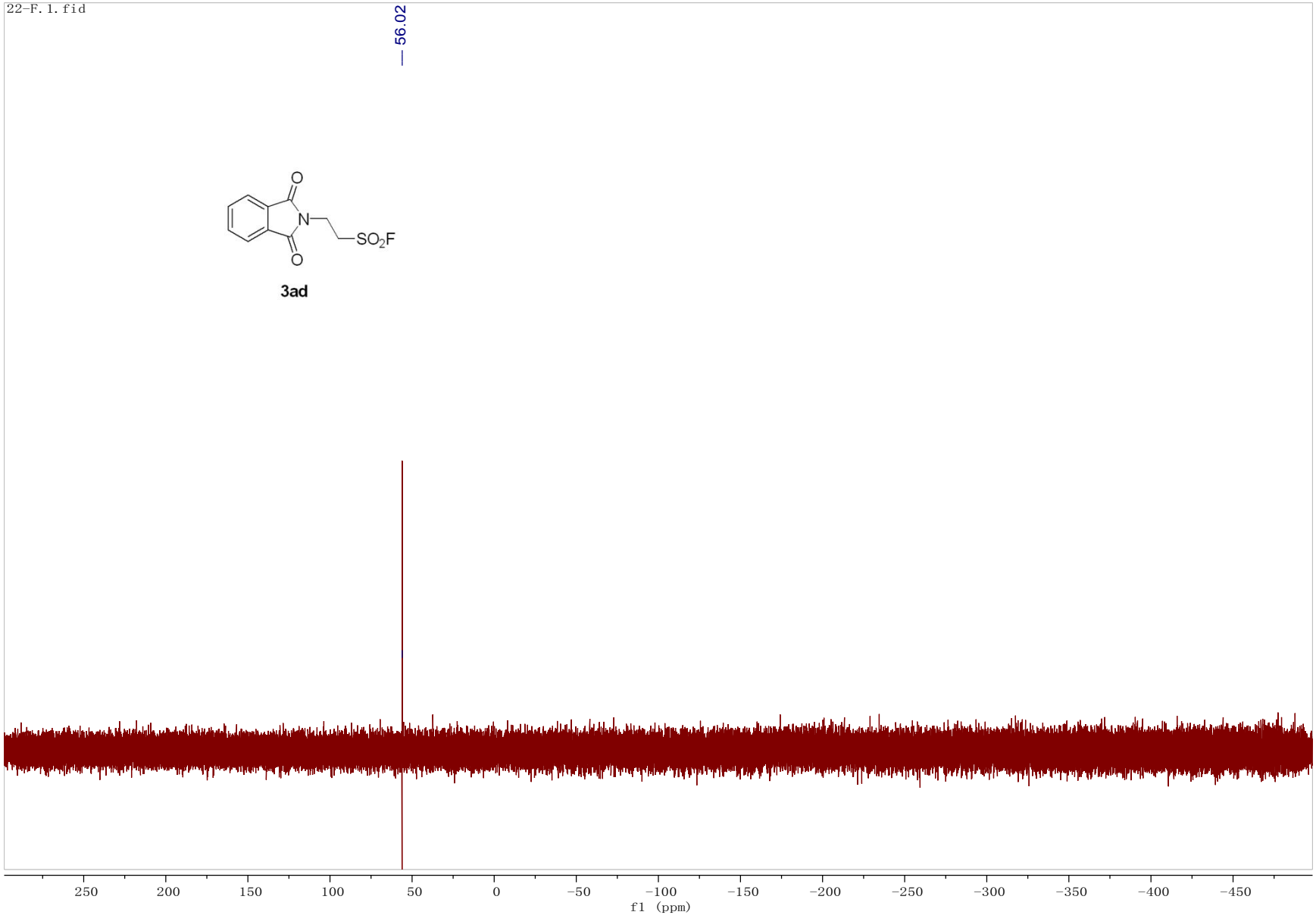
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3ad**.



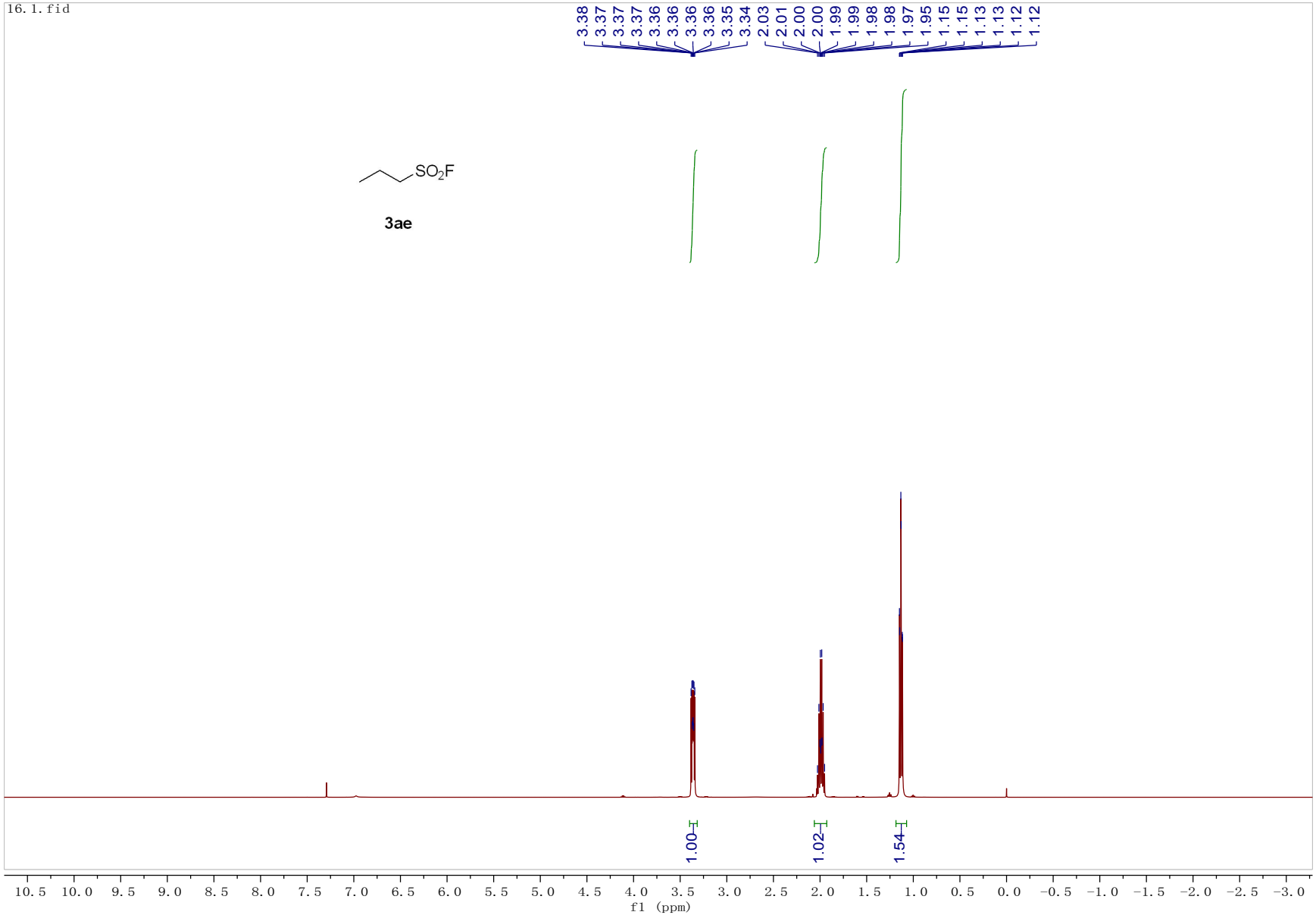
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3ad**.



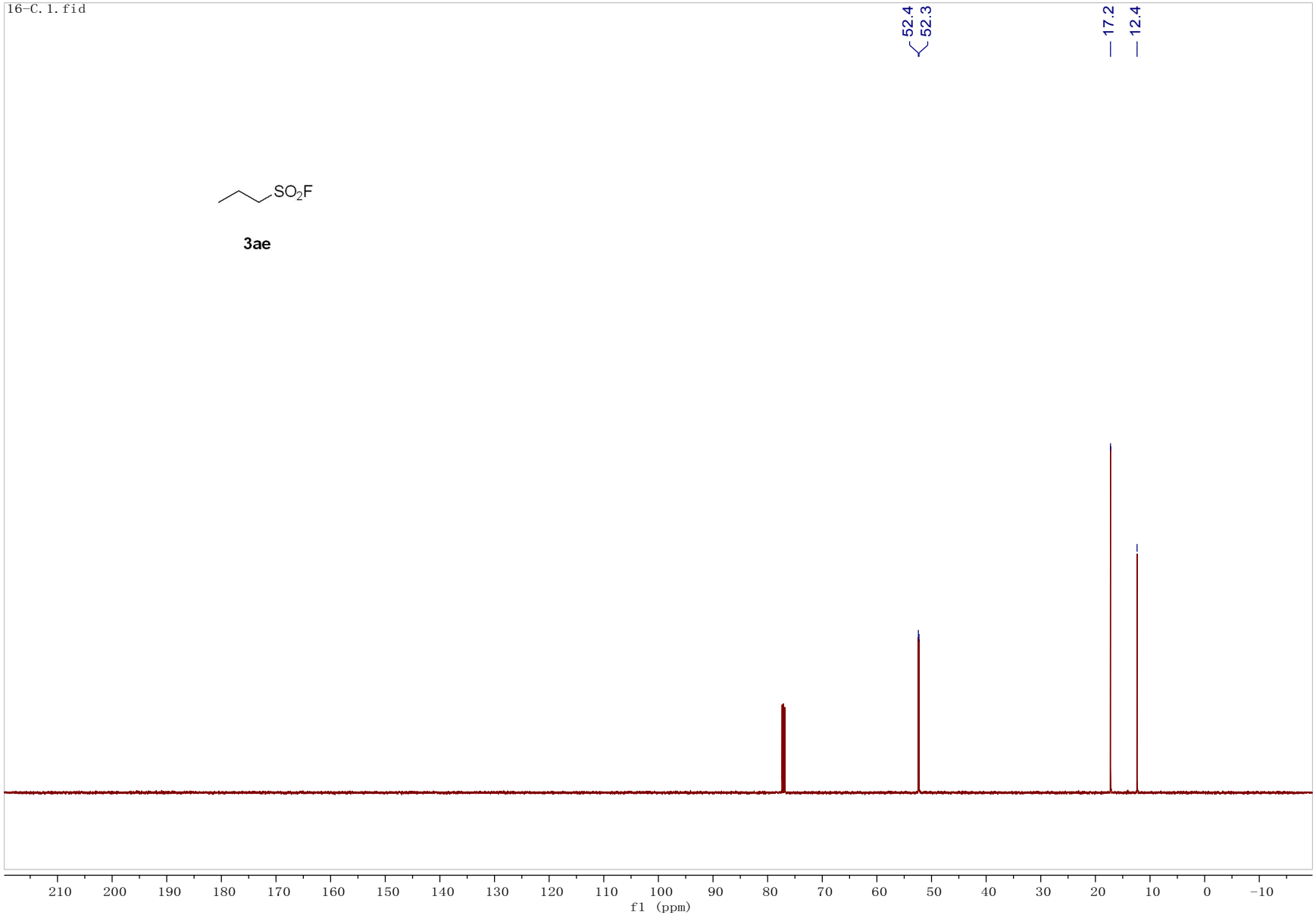
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **3ad**.



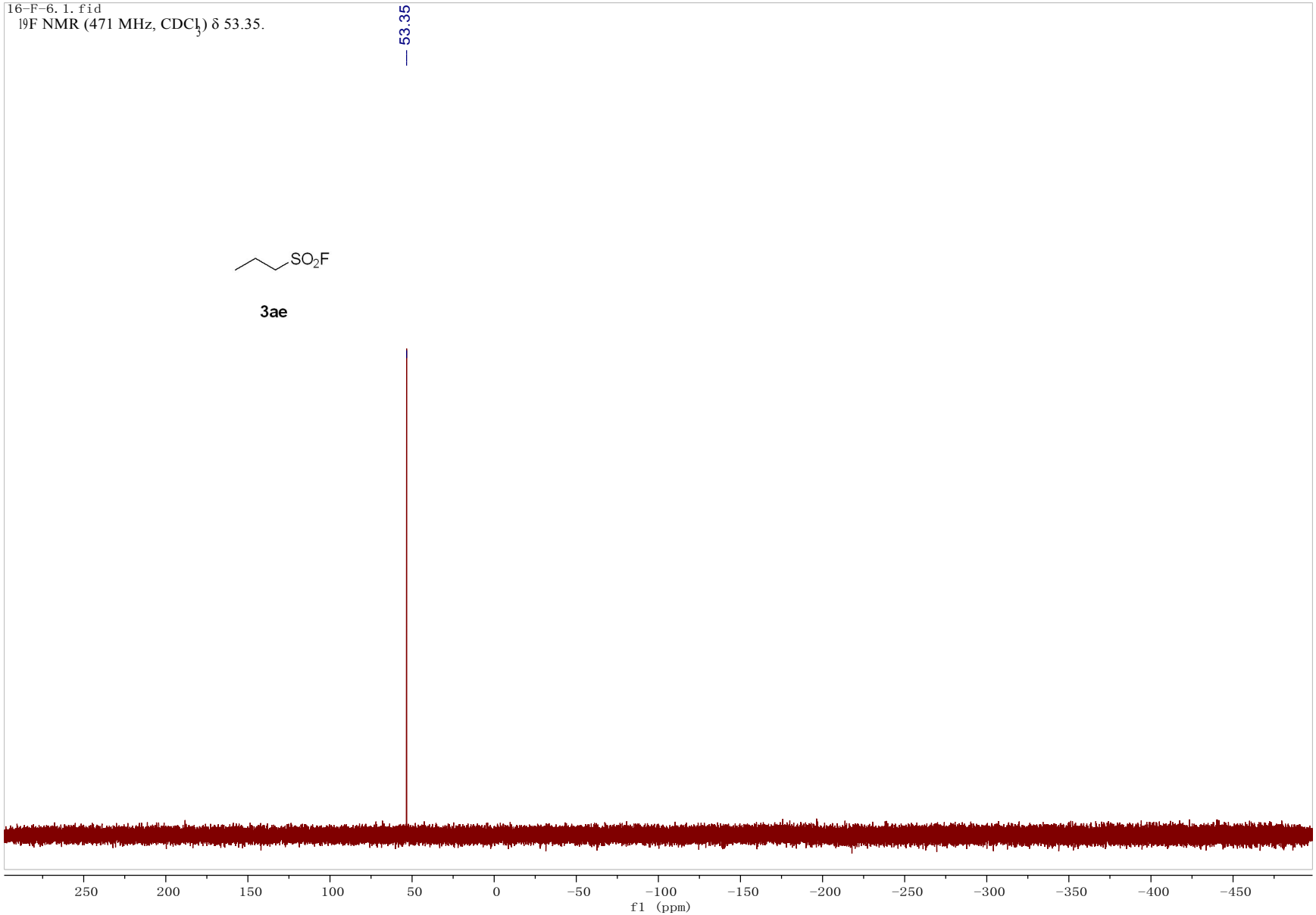
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3ae**.



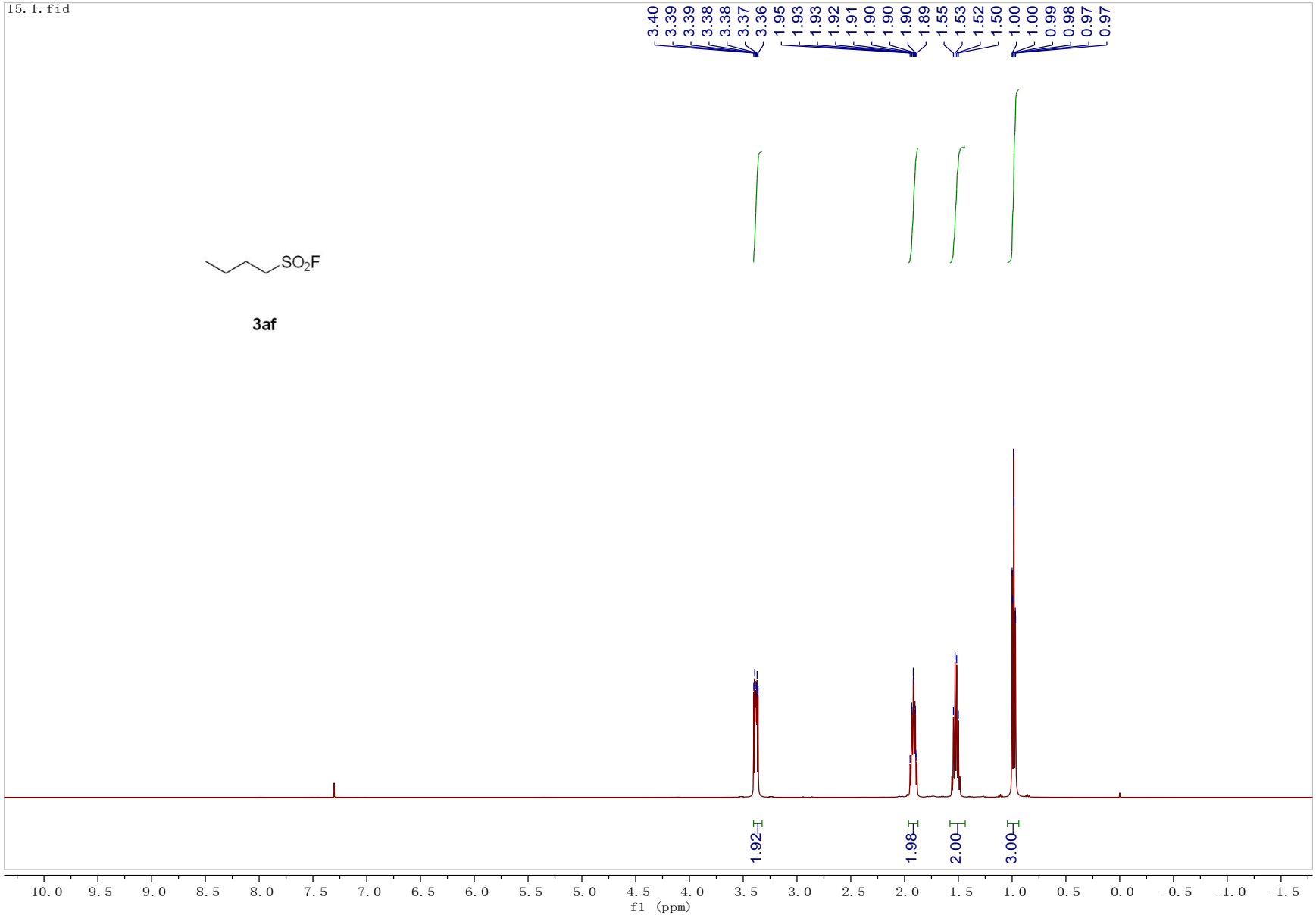
^{13}C NMR (126 MHz, CDCl3) spectrum of **3ae**.



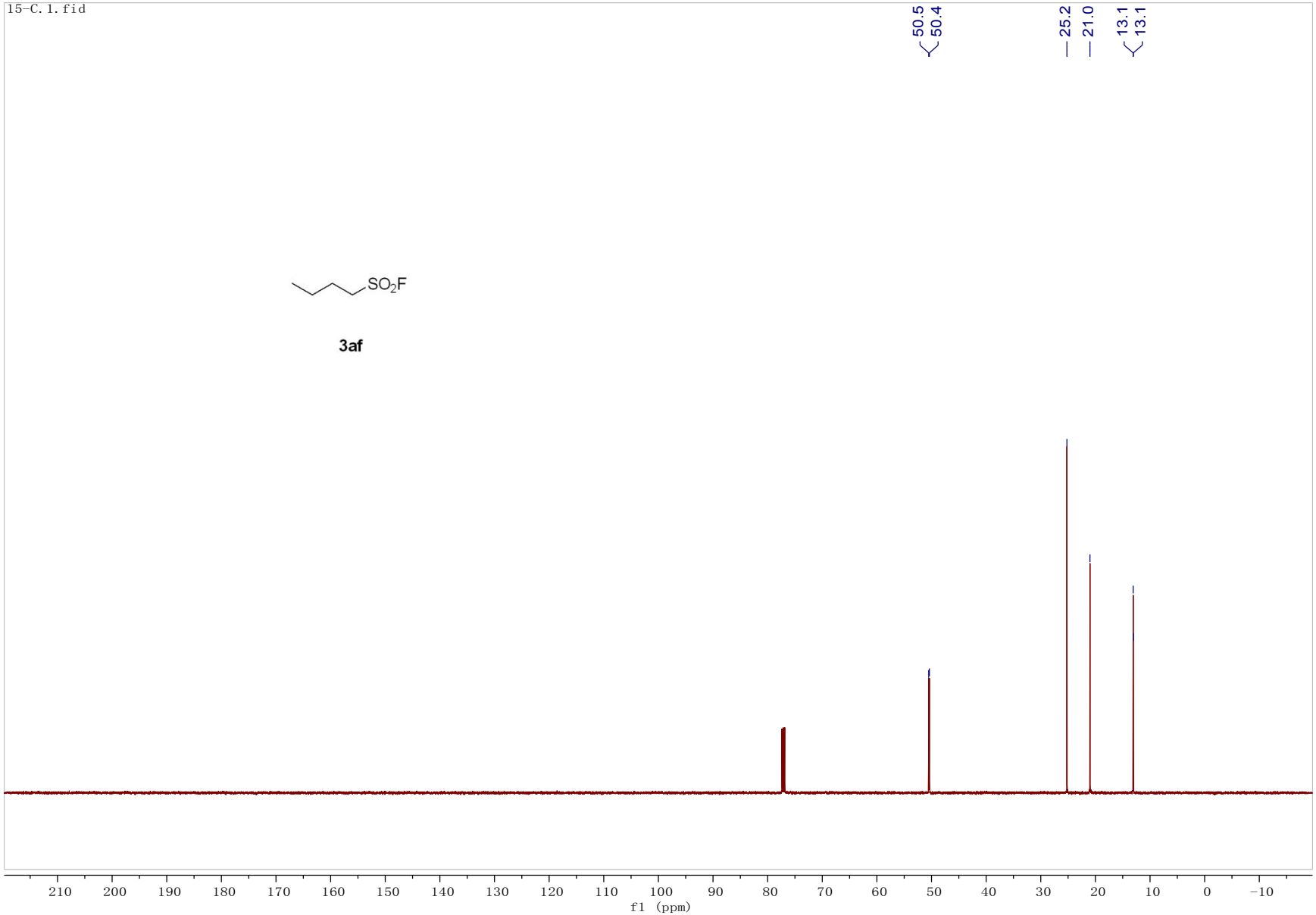
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **3ae**.



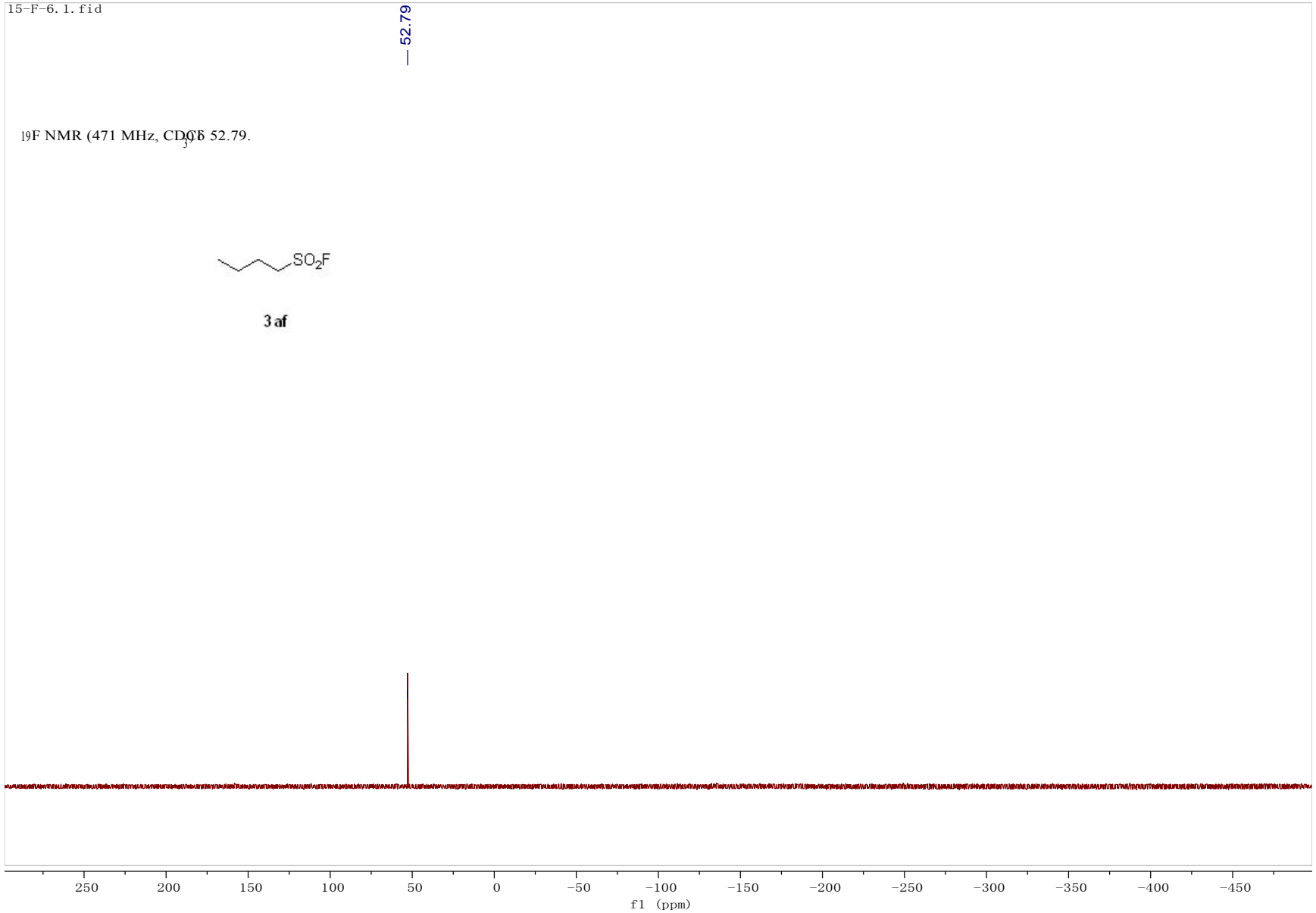
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3af**.



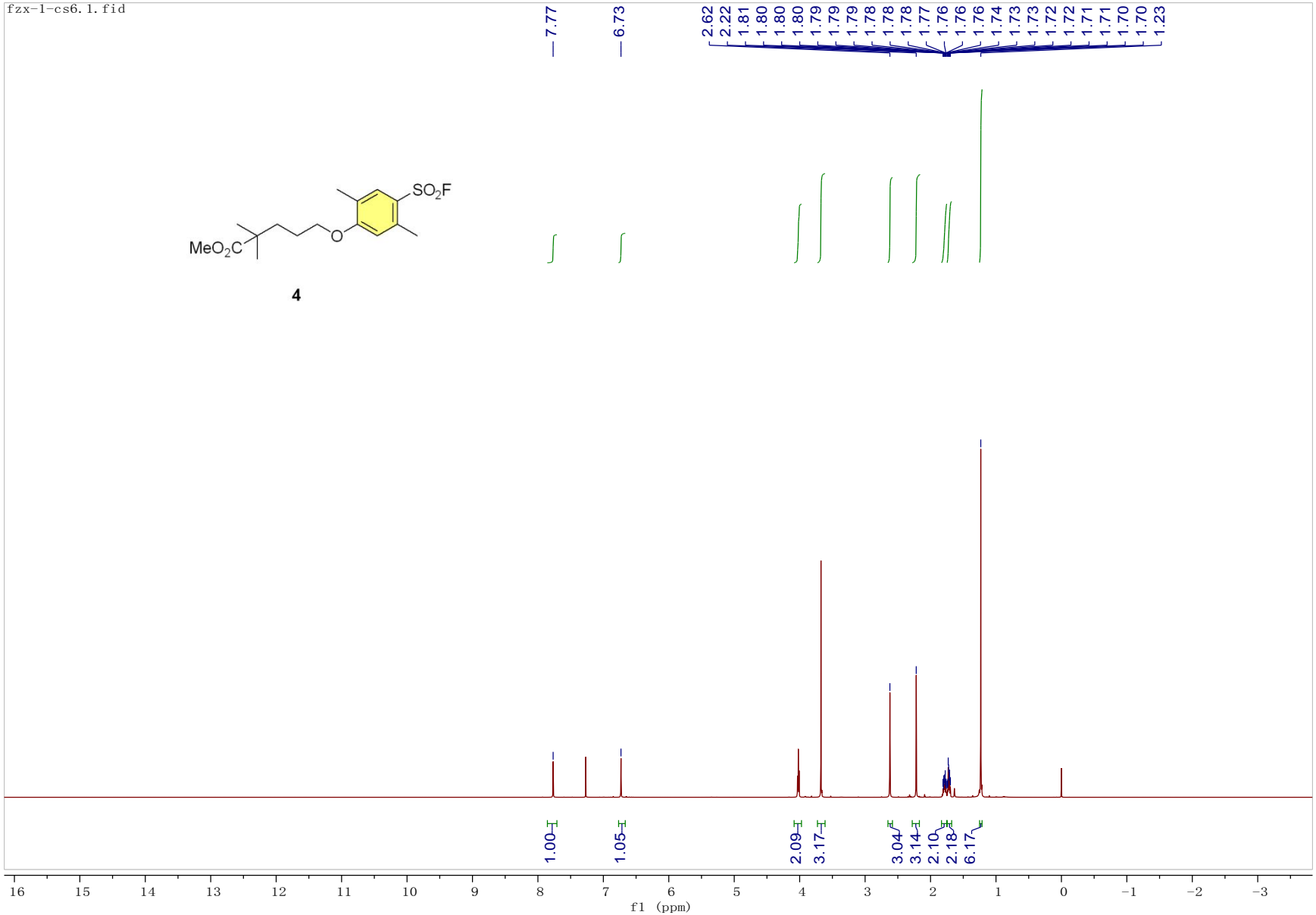
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3af**.



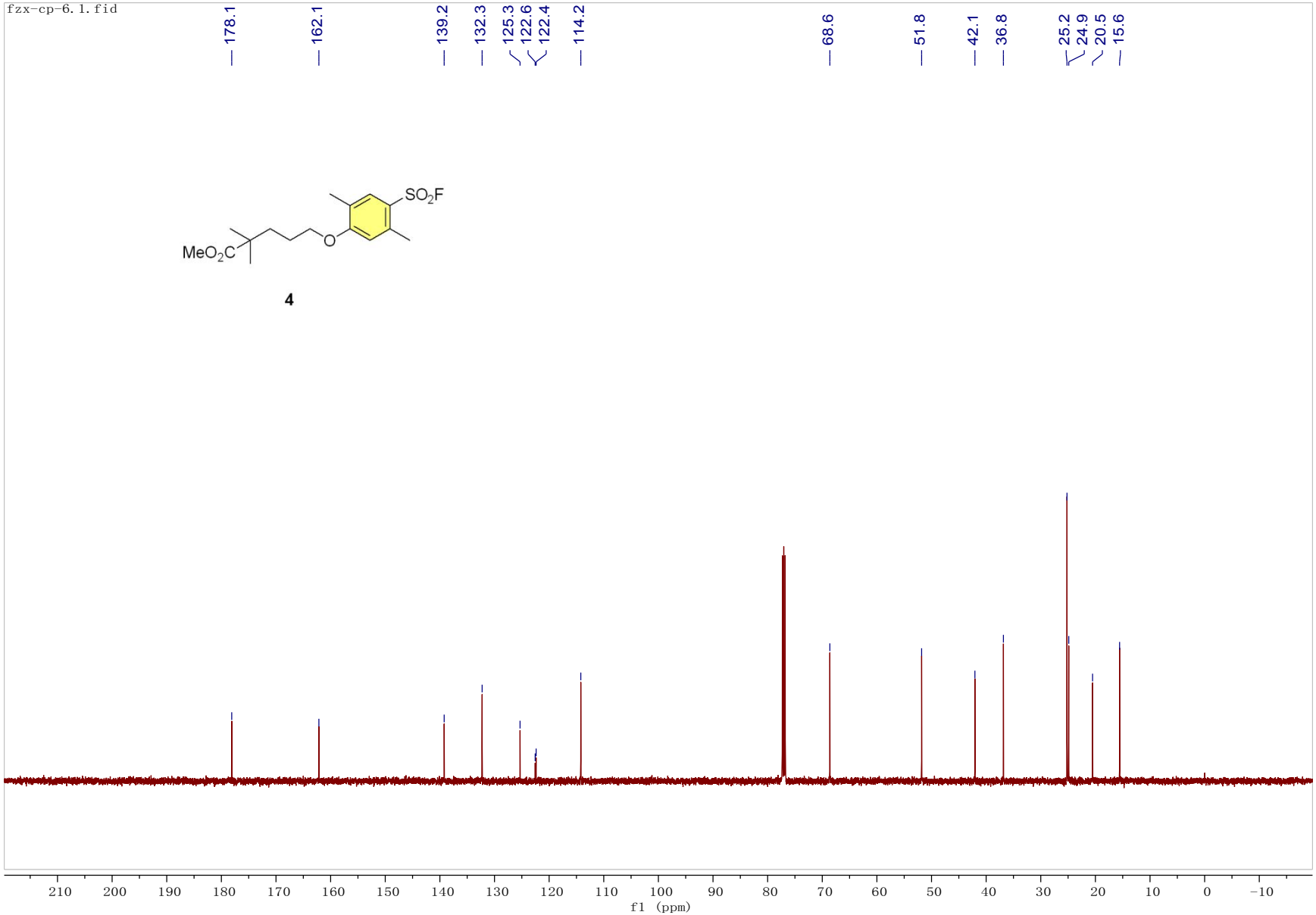
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **3af**.



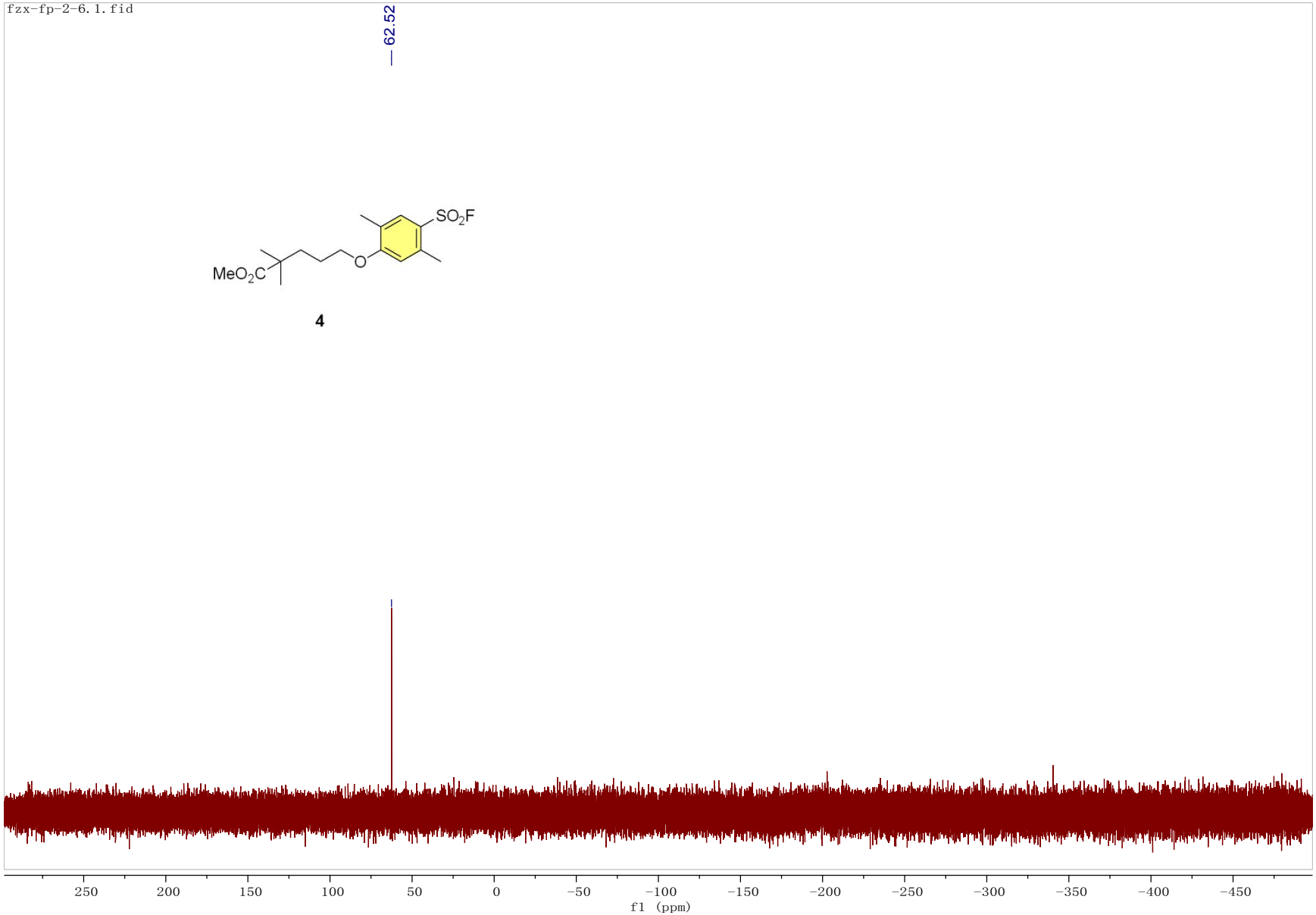
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4**.



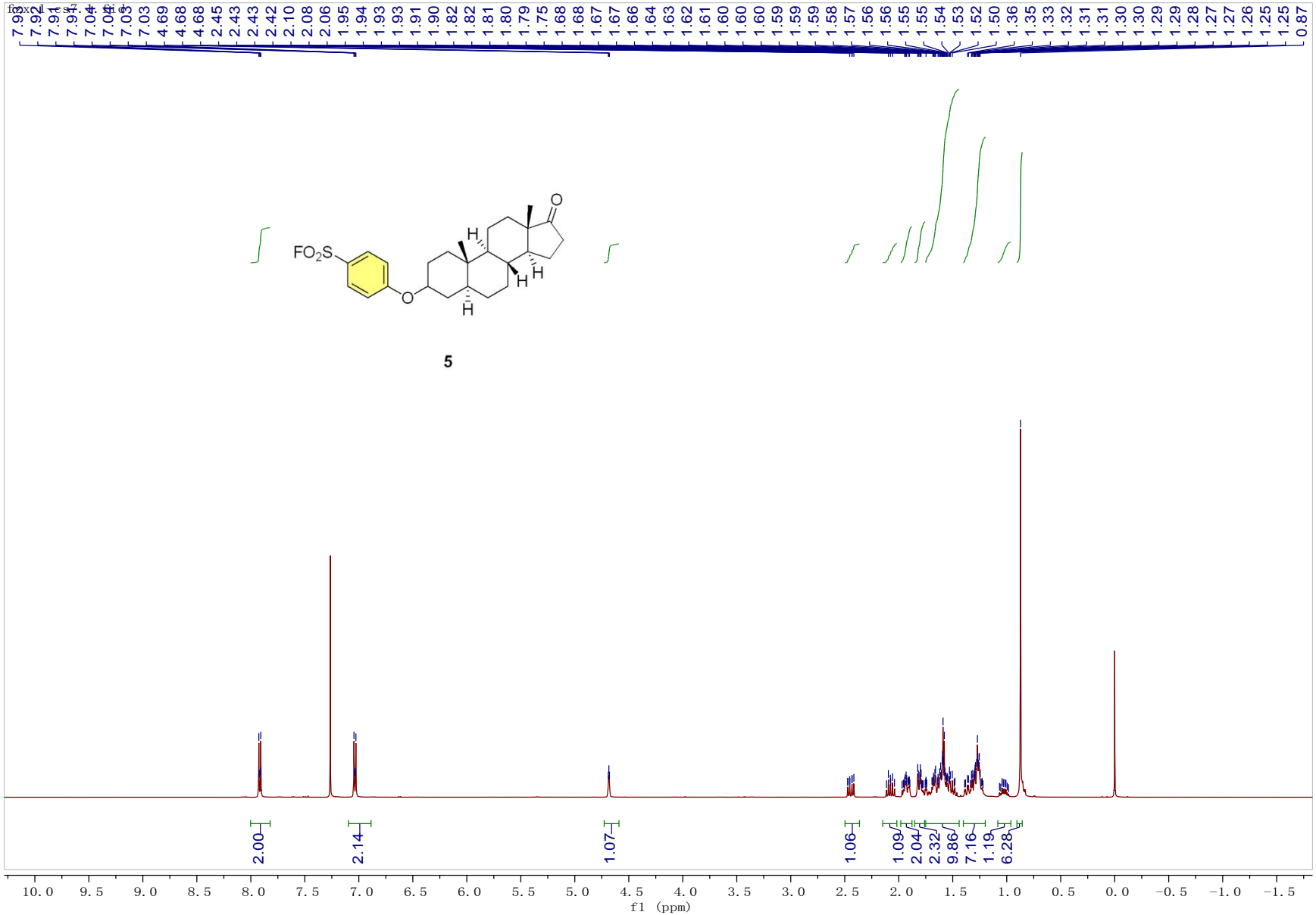
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4**.



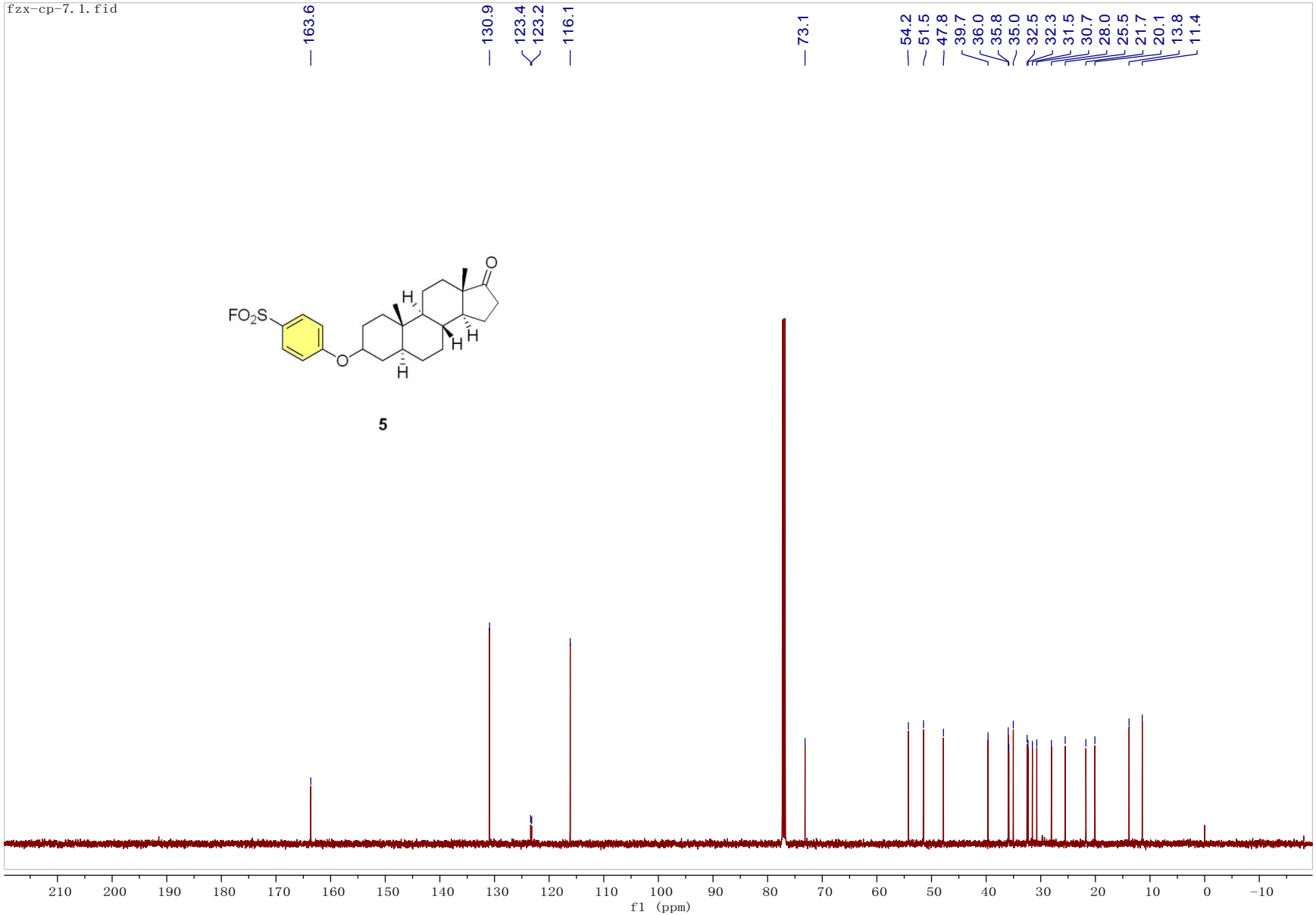
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **4**.



1H NMR (500 MHz, $CDCl_3$) spectrum of **5**.



^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **5**.



^{19}F NMR (471 MHz, $CDCl_3$) spectrum of **5**

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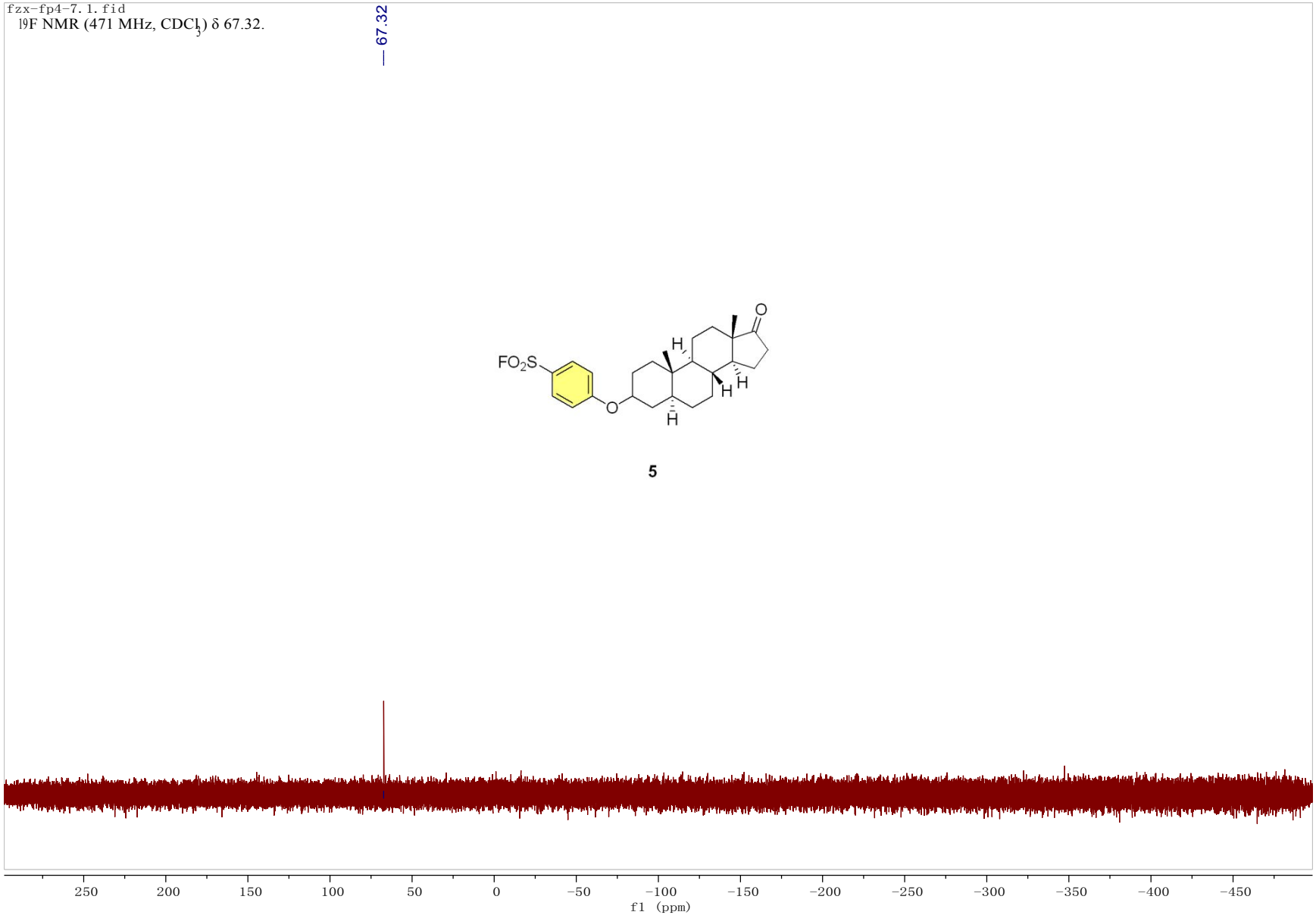
^{19}F NMR (471 MHz, $CDCl_3$) δ 67.32.



5