Electronic Supplemental Information

Trifluoromethanesulfonyl Azide as a Bifunctional Reagent for Metal-Free Azidotrifluoromethylation of Unactivated Alkenes

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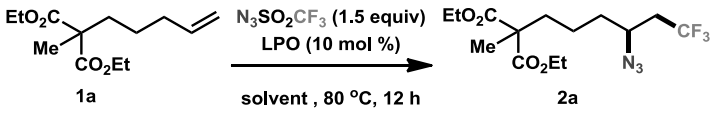
1. General Information

Unless otherwise noted, all experiments were carried out in flame-dried glassware using argon manifolds. Reactions were monitored by thin-layer chromatography (TLC). TLC was performed using Huanghai 8±0.2 μm precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching and Phosphomolybdic acid. Huanghai silica gel (particle size 200 – 300 mess) was used for chromatography. ^{1}H NMR spectra were recorded at room temperature on a Bruker ADVANCE III 400 MHz spectrometer and were reported relative to residual $CDCl_3$ (δ 7.26 ppm). ^{13}C NMR spectra were recorded on a Bruker ADVANCE III 400 MHz spectrometer (100 MHz) and were reported relative to $CDCl_3$ (δ 77.00 ppm). ^{19}F NMR spectra were recorded on a Bruker ADVANCE III 400 MHz spectrometer (376 MHz). Data for ^{1}H NMR were reported as chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration) using standard abbreviations for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Data for ^{13}C NMR and ^{19}F NMR were reported in terms of chemical shifts (δ ppm). High resolution mass spectra (HRMS) were obtained by use of a Bruker Compact TOF mass spectrometer in electrospray ionization mode (ESI^+) and Thermo Scientific Q Exactive HF Orbitrap-FTMS in electrospray ionization mode (ESI^+). All reagents were purchased commercially and used without further purification. Petroleum ether (PE) (60 ~ 90 ^{o}C), Ethyl acetate (EA) were used as eluent for silica gel chromatography. Dry solvents were purchased commercially or were dried by passage through an activated alumina column under argon.[1]

2. Optimization of Reaction Conditions

General Procedure for Condition Optimization: To a sealed tube with a magnetic stirring bar were added **1a** (48.5 mg, 0.2 mmol, 1.0 equiv), initiator (0.02 mmol, 10 mol%), $N_3SO_2CF_3$ (stock solution) and the indicated solvent at room temperature. The contents were stirred at 80 °C behind a safety shield for 12 h. Then the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The yield was determined by ^{19}F NMR analysis of the crude mixture using (trifluoromethoxy)benzene as an internal standard.

Table S1. Screening of Solvents

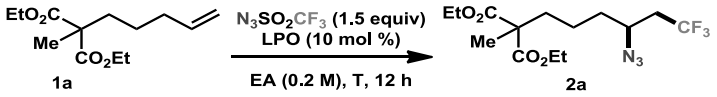


Entry[a]	Solvent	C (mol/L)	Yield of **2a** (%)[b]
1	MeCN	0.1	32
2	DMF	0.1	17
3	DCE	0.1	26
4	$CHCl_3$	0.1	7
5	THF	0.1	N.R.
6	EA	0.1	48
7	MTBE	0.1	trace
8	DMSO	0.1	20
9	*m*-Xylene	0.1	trace
10	Acetone	0.1	37
11	MeOH	0.1	N.R.
12	DME	0.1	35
13	Pentane	0.1	38
14	*n*-Hexane	0.1	30

15	Cyclohexane	0.1	23
16	1,4-Dioxane	0.1	33
17	CPME	0.1	13
18	PhCl	0.1	trace
19	PhCN	0.1	trace
20	**EA**	**0.2**	**48**
21	EA	0.05	47

[a]*Reaction conditions*: **1a** (0.2 mmol), LPO (0.02 mmol), $N_3SO_2CF_3$ (0.3 mmol, 1 M in *n*-hexane) in the indicated solvent at 80 °C for 12 h. [b]Determined by ^{19}F NMR of the crude mixture using trifluoromethyl benzene as an internal standard. CPME: cyclopentyl methyl ether. N.R.: no reaction.

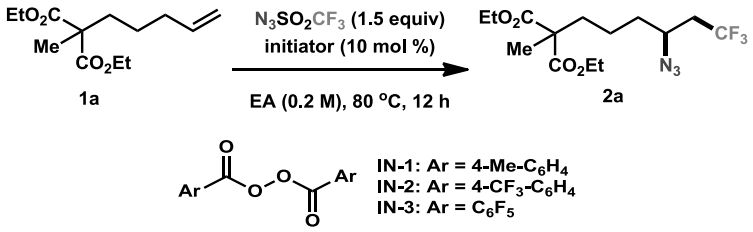
Table S2. Screening of Temperature



Entry[a]	T (°C)	Yield of **2a** (%)[b]
1	60	23
2	**80**	**48**
3	100	50

[a]*Reaction conditions*: **1a** (0.2 mmol), LPO (0.02 mmol), $N_3SO_2CF_3$ (0.3 mmol, 1 M in *n*-hexane) in 1 mL of EA for 12 h. [b]Determined by ^{19}F NMR of the crude mixture using trifluoromethyl benzene as an internal standard.

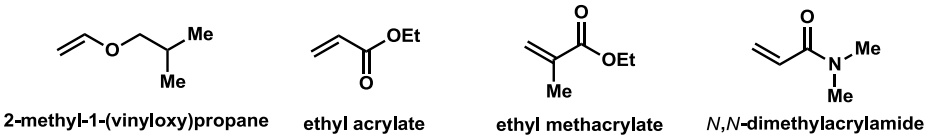
Table S3. Screening of Initiators



Entry[a]	Initiator (10 mol %)	Yield of **2a** (%)[b]
1	BPO	43
2	*tert*-Butyl Benzoperoxoate	22
3	DTBP	trace
4	TBHP	trace
5	TEMPO	trace
6	LPO	48
7	AIBN	20
8	**IN-1**	51
9	**IN-2**	52
10	**IN-3**	65
12[c]	**IN-3**	83
13[d]	**IN-3**	**86 (87)[e]**
14	none	N.R.

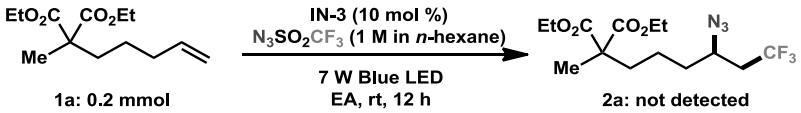
[a]*Reaction conditions*: **1a** (0.2 mmol), initiator (0.02 mmol), $N_3SO_2CF_3$ (0.3 mmol, 1 M in *n*-hexane) in 1 mL of EA at 80 °C for 12 h. [b]Determined by ^{19}F NMR of the crude mixture using trifluoromethyl benzene as an internal standard. [c]With 2.0 equiv of $N_3SO_2CF_3$. [d]With 2.5 equiv of $N_3SO_2CF_3$. [e]Isolated yield. N.R.: no reaction.

Scheme S1. Unsuccessful Substrates



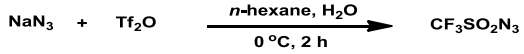
2-methyl-1-(vinyloxy)propane | ethyl acrylate | ethyl methacrylate | *N*,*N*-dimethylacrylamide

Scheme S2. Using Light Irradiation Conditions instead of Heating

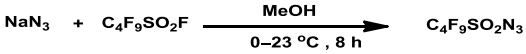


1a: 0.2 mmol | 2a: not detected

3. Preparation of Trifluoromethanesulfonyl Azide and Nonafluorobutanesulfonyl Azide



A reported proceduce was followed[2a]: To a round-bottomed flask equipped with a magnetic stirring bar were added NaN_3 (1.95 g, 30 mmol, 2.0 equiv) and 5 mL of water. After the mixture were cooled to 0 °C, *n*-hexane (10 mL) was added to the vigorously stirred solution. A solution of trifluromethanesulfonic anhydride (4.23 g, 15 mmol) in 5 mL of *n*-hexane was added into above mixture dropwise. The resultant mixture was allowed to stir at 0 °C for another 2 h behind a safety shield. The organic phase was separated and the aqueous layer was extracted with *n*-hexane (3 × 5 mL). The combined organic layers were washed with saturated Na_2CO_3 and water separately, dried over anhydrous sodium sulfate, and filtered. The concentration was determined by ^{19}F NMR using trifluoromethylbenzene as an internal standard. Then additional appropriate amount of *n*-hexane was added to prepare a 1 M stock solution of $CF_3SO_2N_3$.

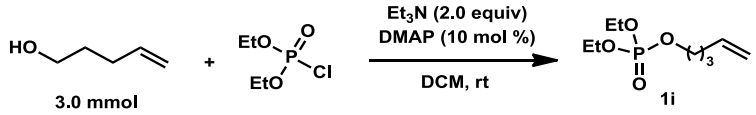


A reported proceduce was followed[2b]: To a round-bottomed flask equipped with a magnetic stirring bar were added NaN_3 (1.32 g, 20 mmol, 2.0 equiv) and 20 mL of MeOH. After the mixture were cooled to 0 °C, 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonyl fluoride (3.6 mL, 20 mmol) was added into above mixture dropwise. The resultant mixture was allowed to stir at 23 °C for another 8 h behind a safety shield. The organic phase was separated was dituled with *n*-hexane (4 × 5 mL). The combined organic layers were washed with water five times, dried over anhydrous sodium sulfate, and filtered. The concentration was determined by ^{19}F NMR using trifluoromethylbenzene as an internal standard. Then additional appropriate amount of *n*-hexane was added to prepare a 1 M stock solution of $C_4F_9SO_2N_3$.

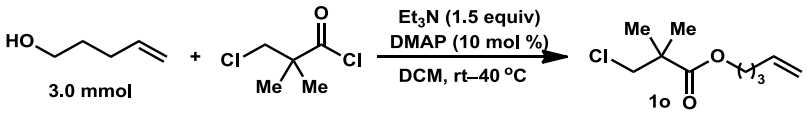
CAUTION: *Trifluoromethanesulfonyl azide and nonafluorobutanesulfonyl azide should be prepared in an organic solvent.*[2c] *Handling pure trifluoromethanesulfonyl azide should be avoided as it may lead to an explosion.*[2d] *Preparation of*

trifluoromethanesulfonyl azide in a biphasic system of CH_2Cl_2/H_2O can potentially lead to the formation of perilous diazidomethane.[2e] *Toluene and hexane are better replacement solvents.*[2a,2f] *It was reported that stock solutions of trifluoromethanesulfonyl azide in n-hexane are stable for several days at 4 day.*[2c] *Although no explosions occurred during all the experiments of our investigations, a safety shield is used for all the azidotrifluoromethylation reactions reported below.*

4. Preparation of New Substrates

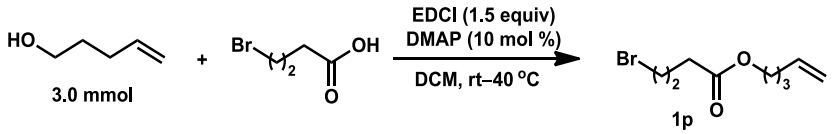


Diethyl pent-4-en-1-yl phosphate 1i: To a solution of pent-4-en-1-ol (0.26 g, 3.0 mmol) in DCM (15 mL) at 0 °C were added Et_3N (0.85 mL, 6.0 mmol, 2.0 equiv) and DMAP (36.8 mg, 0.3 mmol, 10 mol %). Then diethyl phosphorochloridate (0.65 mL, 4.5 mmol, 1.5 equiv) was added dropwise into the mixture. The reaction mixture was warmed to room temperature and stirred until the disappearance of pent-4-en-1-ol as monitored by TLC. The reaction was quenched with water, extracted with DCM (3 x 15 mL), and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (5:1, v:v, R_f = 0.2) as an eluent to give **1i** in 60% yield (400.0 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 4.98 (dq, *J* = 17.2, 1.7 Hz, 1H), 4.93 (dq, *J* = 10.2, 1.5 Hz, 1H), 4.16 – 4.07 (m, 4H), 4.04 (q, *J* = 6.7 Hz, 2H), 2.17 – 2.01 (m, 2H), 1.79 – 1.67 (m, 2H), 1.27 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 115.5, 66.9 (d, *J* = 6.0 Hz), 63.7 (d, *J* = 5.8 Hz), 29.6, 29.4 (d, *J* = 6.6 Hz), 16.2 (d, *J* = 6.7 Hz); HRMS (ESI^+) calc'd for $C_9H_{20}O_4P$ $[M+H]^+$: 223.1094, found 223.1093.

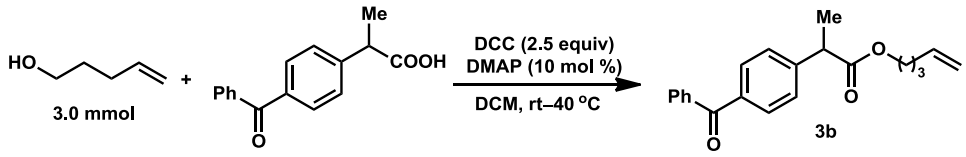


Pent-4-en-1-yl 3-chloro-2,2-dimethylpropanoate 1o: To a solution of pent-4-en-1-ol (0.26 g , 3.0 mmol) in DCM (15 mL) at room temperature were added Et_3N (0.64 mL, 1.5 mmol, 4.5 equiv) and DMAP (36.7 mg, 0.3 mmol, 10 mol %). Then 3-chloro-2,2-dimethylpropanoyl chloride (0.51 mL, 3.9 mmol, 1.3 equiv) was added dropisely into the mixture. The reaction mixture was stirred at 40 °C until the fully conversion of pent-4-en-1-ol as monitored by TLC. The mixture was cooled to room temperature and then diluted with water, extracted with DCM (3 x 15 mL), dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE (R_f = 0.3) as an eluent

to give **1o** in 94% yield (577.1 mg, colorless oil). δ 5.74 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 4.97 (dd, *J* = 17.2, 1.7 Hz, 1H), 4.93 (dd, *J* = 9.8, 1.6 Hz, 1H), 4.06 (t, *J* = 6.5 Hz, 2H), 3.54 (s, 2H), 2.07 (q, *J* = 7.1 Hz, 2H), 1.72 – 1.65 (m, 2H), 1.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 137.4, 115.4, 64.3, 52.1, 44.6, 30.0, 27.8, 23.3; HRMS (ESI^+) calc'd for $C_{10}H_{18}ClO_2$ $[M+H]^+$: 205.0990, found 205.0992.

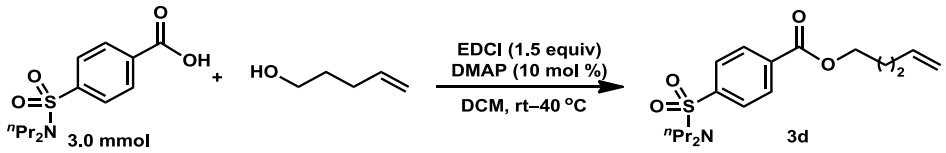


Pent-4-en-1-yl 3-bromopropanoate 1p: To a solution of pent-4-en-1-ol (0.27 g, 3.0 mmol) in DCM (15 mL) at room temperature were added EDCI (0.86 g, 4.5 mmol, 1.5 equiv), DMAP (36.7 mg, 0.3 mmol, 10 mol %), and 3-bromopropanoic acid (0.65 g, 3.9 mmol, 1.3 equiv). The reaction mixture was stirred at 40 °C until the disappearance of pent-4-en-1-ol as monitored by TLC. The mixture was cooled to room temperature and then diluted with water, extracted with DCM (3 x 15 mL), dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE (R_f = 0.3) as an eluent to give **1p** in 25% yield (175.3 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 4.98 (dd, *J* = 17.1, 1.7 Hz, 1H), 4.93 (dd, *J* = 10.2, 1.6 Hz, 1H), 4.03 (t, *J* = 6.6 Hz, 2H), 3.40 (t, *J* = 6.4 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.14 – 2.03 (m, 4H), 1.71 – 1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 137.4, 115.4, 64.1, 32.8, 32.5, 30.0, 27.8; HRMS (ESI^+) calc'd for $C_9H_{15}BrNaO_2$ $[M+Na]^+$: 257.0148, found 257.0141.



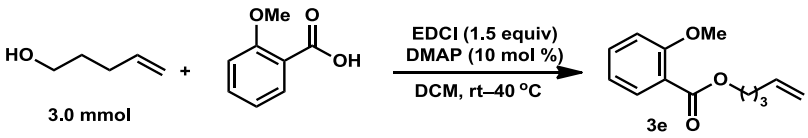
Pent-4-en-1-yl 2-(4-benzoylphenyl)propanoate 3b: To a solution of pent-4-en-1-ol (0.26 g, 3.0 mmol) in DCM (15 mL) at room temperature were added DCC (1.55 g, 7.5 mmol, 2.5 equiv), DMAP (36.7 mg, 0.3 mmol, 10 mol %), and 2-(4-benzoylphenyl)propanoic acid (0.99 g, 3.9 mmol, 1.3 equiv). The reaction mixture was stirred at 40 °C until the disappearance of pent-4-en-1-ol as monitored by TLC. The

mixture was cooled to room temperature, and then diluted with water, extracted with DCM (3 x 15 mL), dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (10:1, v:v, R_f = 0.4) as an eluent to give **3b** in 96% yield (925.5 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.73 (m, 3H), 7.69 – 7.66 (m, 1H), 7.64 – 7.51 (m, 2H), 7.52 – 7.37 (m, 3H), 5.73 (ddt, *J* = 18.1, 9.5, 6.7 Hz, 1H), 4.99 – 4.95 (m, 1H), 4.93 (t, *J* = 1.5 Hz, 1H), 4.08 (t, *J* = 6.6 Hz, 2H), 3.80 (q, *J* = 7.2 Hz, 1H), 2.02 (q, *J* = 7.3 Hz, 2H), 1.76 – 1.58 (m, 2H), 1.54 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 174.1, 141.0, 137.9, 137.5, 137.3, 132.5, 131.5, 130.1, 129.2, 129.0, 128.5, 128.3, 115.4, 64.3, 45.5, 29.9, 27.7, 18.4; HRMS (ESI$^+$) calc'd for $C_{21}H_{23}O_3$ $[M+H]^+$: 323.1642, found 323.1637.

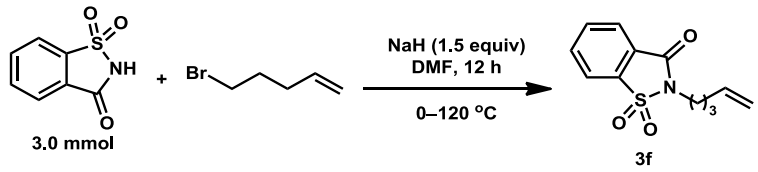


Pent-4-en-1-yl 4-(*N*,*N*-dipropylsulfamoyl)benzoate 3d: To a solution of 4-(*N*,*N*-diisopropylsulfamoyl)benzoic acid (0.86 g, 3.0 mmol) in DCM (15 mL) at room temperature were added EDCI (0.86 g, 1.5 mmol, 4.5 equiv), DMAP (36.7 mg, 0.3 mmol, 10 mol %), and pent-4-en-1-ol (0.31 g, 3.6 mmol, 1.2 equiv). The reaction mixture was stirred at 40 °C until the disappearance of 4-(*N*,*N*-diisopropylsulfamoyl)benzoic acid as monitored by TLC. The mixture was cooled to room temperature, diluted with water, extracted with DCM (3 x 15 mL), dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (10:1, v:v, R_f = 0.4) as an eluent to give **3d** in 66% yield (704.6 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 8.6 Hz, 2H), 5.84 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.07 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.01 (dq, *J* = 10.2, 1.4 Hz, 1H), 4.36 (t, *J* = 6.6 Hz, 2H), 3.15 – 3.05 (m, 4H), 2.27 – 2.18 (m, 2H), 1.86 – 1.79 (m, 2H), 1.60 – 1.46 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 165.3, 144.2, 137.3, 133.7, 130.2, 127.0, 115.6, 65.0, 49.9, 30.1, 27.8, 21.9, 11.2; HRMS (ESI^+) calc'd for $C_{18}H_{28}NO_4S$ $[M+H]^+$: 354.1734, found 354.1727.

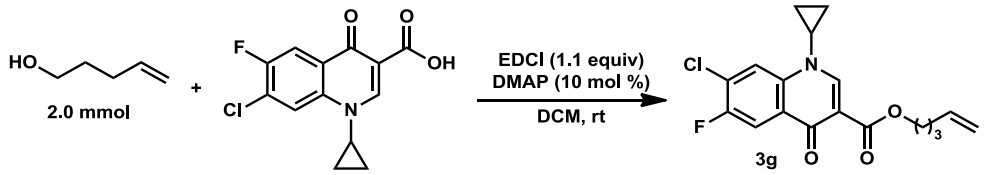


Pent-4-en-1-yl 2-methoxybenzoate 3e: To a solution of pent-4-en-1-ol (0.25 g, 3.0 mmol) in DCM (15 mL) at room temperature were added EDCI (0.86 g, 4.5 mmol, 1.5 equiv), DMAP (36.7 mg, 0.3 mmol, 10 mol %), and 2-methoxybenzoic acid (0.78 g, 3.9 mmol, 1.3 equiv). The reaction mixture was stirred at 40 °C until the disappearance of pent-4-en-1-ol was monitored by TLC. The mixture was cooled to room temperature, diluted with water, extracted with DCM (3 x 15 mL), dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.3) as an eluent to give **3e** in 55% yield (411.6 mg, colorless oil). ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.41 – 7.33 (m, 1H), 6.94 – 6.82 (m, 2H), 5.84 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.06 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.99 (dq, *J* = 10.2, 1.5 Hz, 1H), 4.23 (t, *J* = 6.5 Hz, 2H), 3.81 (s, 3H), 2.17 – 2.11 (m, 2H), 1.80 – 1.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 159.1, 137.6, 133.4, 131.5, 120.4, 120.1, 115.3, 112.0, 64.2, 55.9, 30.2, 27.9; HRMS (ESI^+) calc'd for $C_{14}H_{17}O_3$ $[M+H]^+$:221.1172, found 221.1180.

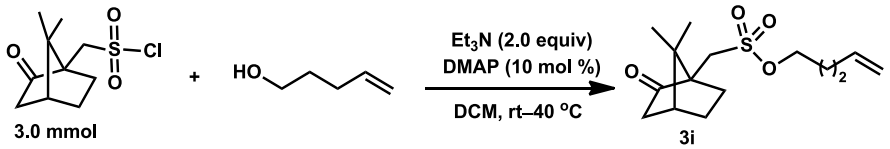


2-(Pent-4-en-1-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide 3f: To a solution of saccharin (0.55 g, 3.0 mmol, 1.0 equiv) in DMF (15 mL) at 0 °C was added NaH (0.18 g, 60% in oil, 4.5 mmol, 1.5 equiv), and the mixture was stirred at 0 °C for 30 minutes. Then 5-bromopent-1-ene (0.90 g, 6.0 mmol, 2.0 equiv) was added into the mixture. The reaction mixture was stirred at 120 °C for 12 h. Then the mixture was cooled to room temperature, diluted with water, extracted with EA (3 x 15 mL) . The combined organic

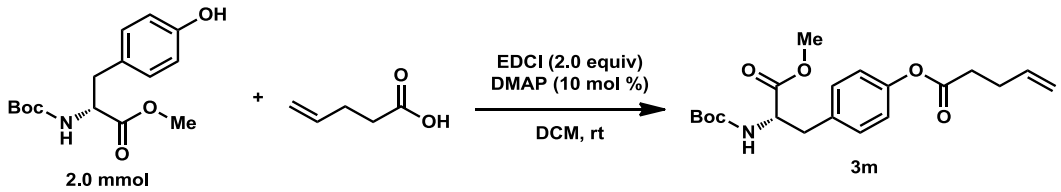
layers were washed with water (3 x 15 mL) and brine, dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.3) as an eluent to give **3f** in 55% yield (411.6 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.92 (m, 1H), 7.91 – 7.66 (m, 3H), 5.75 (ddt, *J* = 16.9, 8.3, 5.1 Hz, 1H), 5.13 – 5.05 (m, 1H), 5.04 – 4.98 (m, 1H), 3.77 (t, *J* = 7.2 Hz, 2H), 2.12 (q, *J* = 7.2 Hz, 2H), 1.92 – 1.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 137.7, 136.9, 134.7, 134.3, 127.4, 125.1, 120.9, 115.8, 38.9, 30.9, 27.4; HRMS (ESI$^+$) calc'd for $C_{12}H_{14}NO_3S$ $[M+H]^+$: 252.0689, found 252.0684.



Hex-5-en-1-yl 7-chloro-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-car--boxylate 3g: To a solution of pent-4-en-1-ol (0.17 g, 2.0 mmol) in DCM (15 mL) at room temperature were added EDCI (0.42 g, 2.2 mmol, 1.1 equiv), DMAP (28.2 mg, 0.2 mmol, 10 mol %), and Q-ACID (0.56 g, 2.0 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature for 24 h. The mixture was diluted with water, extracted with DCM (3 x 15 mL), dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.3) as an eluent to give **3g** in 63% yield (436.5 mg, white solid). m.p. = 151 – 153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.16 (d, *J* = 9.0 Hz, 1H), 7.98 (d, *J* = 5.9 Hz, 1H), 5.85 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.06 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.99 (dq, *J* = 10.2, 1.4 Hz, 1H), 4.32 (t, *J* = 6.7 Hz, 2H), 3.49 – 3.43 (m, 1H), 2.25 – 2.20 (m, 2H), 1.91 – 1.84 (m, 2H), 1.39 – 1.34 (m, 2H), 1.20 – 1.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 165.3, 155.7 (d, *J* = 250.6 Hz), 148.9, 137.6, 137.2 (d, *J* = 2.0 Hz), 128.7 (d, *J* = 5.8 Hz), 127.0 (d, *J* = 20.4 Hz), 119.0, 115.2, 113.9 (d, *J* = 23.0 Hz), 110.8, 64.5, 34.8, 30.1, 27.9, 8.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ – (117.93 – 117.97) (m); HRMS (ESI$^+$) calc'd for $C_{18}H_{18}ClFNO_3$ $[M+H]^+$: 350.0954, found 350.0950.

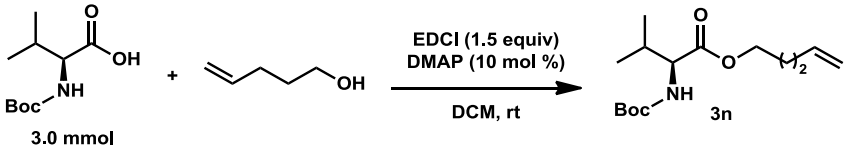


Pent-4-en-1-yl ((*1S,4R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulf--onate 3i: To a solution of D(+)-10-Camphorsulfonyl chloride (0.50 g, 3.0 mmol) in DCM (15 mL) at room temperature were added Et_3N (0.61 g, 6.0 mmol, 2.0 equiv) and DMAP (36.6 mg, 0.3 mmol, 10 mol %). Then pent-4-en-1-ol (0.27 mL, 3.9 mmol, 1.3 equiv) was added dropise into the mixture. The reaction mixture was stirred at 40 °C until the disappearance of pent-4-en-1-ol as monitored by TLC. The mixture was cooled to room temperature, diluted with water, extracted with DCM (3 x 15 mL), dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (50:1, v:v, R_f = 0.4) as an eluent and obtained **3i** in 77% yield (570.6 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.15 – 4.98 (m, 2H), 4.41 – 4.21 (m, 2H), 3.62 (d, *J* = 15.1 Hz, 1H), 3.01 (d, *J* = 15.1 Hz, 1H), 2.60 – 2.38 (m, 2H), 2.25 – 2.03 (m, 4H), 1.98 (d, *J* = 18.5 Hz, 1H), 1.89 – 1.84 (m, 2H), 1.72 – 1.65 (m, 1H), 1.50 – 1.44 (m, 1H), 1.14 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.6, 136.8, 116.0, 69.9, 58.0, 48.0, 46.7, 42.8, 42.5, 29.5, 28.3, 26.9, 24.9, 19.8, 19.7; HRMS (ESI^+) calc'd for $C_{15}H_{24}NaO_4S$ $[M+Na]^+$: 323.1288, found 323.1279.

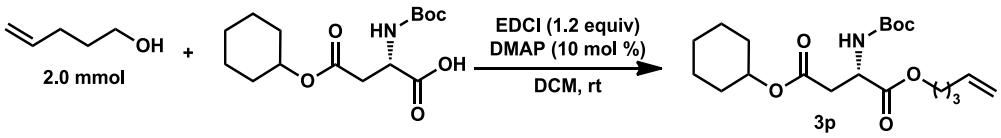


(*R*)-4-(2-((*Tert*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenyl pent-4-enoate 3m: To a solution of Boc-L-tyrosine methyl ester (0.60 g, 2.0 mmol) in DCM (15 mL) at room temperature were added EDCI (0.77 g, 4.0 mmol, 2.0 equiv), DMAP (36.7 mg, 0.2 mmol, 10 mol %), and pent-4-enoic acid (0.31 mL, 2.0 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature for 12 h. The mixture was diluted with water, extracted with DCM (3 x 15 mL), dried over anhydrous sodium sulfate, and

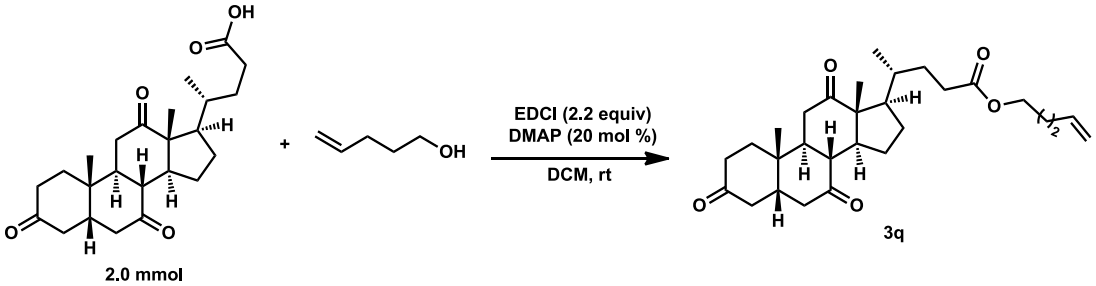
filtered. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (5:1, v:v, R_f = 0.3) as an eluent to give **3m** in 64% yield (726.9 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 5.83 (ddt, *J* = 16.8, 10.2, 6.4 Hz, 1H), 5.07 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.00 (dq, *J* = 10.2, 1.4 Hz, 1H), 4.91 (d, *J* = 8.4 Hz, 1H), 4.57 – 4.45 (m, 1H), 3.64 (s, 3H), 3.09 – 2.91 (m, 2H), 2.61 – 2.59 (m, 2H), 2.47 – 2.38 (m, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 171.5, 155.1, 149.7, 136.3, 133.6, 130.3, 121.6, 116.0, 80.0, 54.4, 52.3, 37.7, 33.6, 28.9, 28.3; HRMS (ESI^+) calc'd for $C_{20}H_{28}NO_6$ $[M+H]^+$: 378.1911, found 378.1906.



(*S*)-Pent-4-en-1-yl 2-((*tert*-butoxycarbonyl)amino)-3-methylbutanoate 3n: To a solution of Boc-L-valine (0.65 g, 3.0 mmol) in DCM (15 mL) at room temperature were added EDCI (0.86 g, 4.5 mmol, 1.5 equiv), DMAP (36.6 mg, 0.3 mmol, 10 mol %), and pent-4-enoic acid (0.26 g, 3.0 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature overnight. The mixture was cooled to room temperature, diluted with water, extracted with DCM (3 x 15 mL), and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (5:1, v:v, R_f = 0.5) as the eluent to give **3n** in 62% yield (526.5 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.06 – 4.88 (m, 3H), 4.19 – 4.10 (m, 1H), 4.13 – 4.00 (m, 2H), 2.09 – 2.04 (m, 3H), 1.72 – 1.65 (m, 2H), 1.38 (s, 9H), 0.90 (d, J = 6.9 Hz, 3H), 0.82 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 155.7, 137.3, 115.5, 79.7, 64.5, 58.6, 31.4, 30.0, 28.3, 27.7, 19.0, 17.6; HRMS (ESI+) calc'd for $C_{15}H_{28}NO_4$ $[M+H]^+$: 286.2013, found 286.2010.



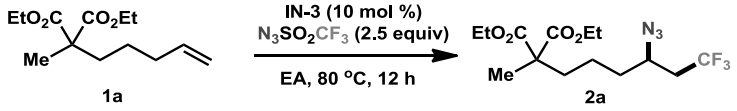
(*S*)-4-Cyclohexyl 1-pent-4-en-1-yl 2-((*tert*-butoxycarbonyl)amino)succinate 3p: To a solution of pent-4-en-1-ol (0.18 g, 2.0 mmol) in DCM (15 mL) at room temperature were added EDCI (0.77 g, 2.4 mmol, 1.2 equiv), DMAP (36.7 mg, 0.2 mmol, 10 mol %), and Boc-Asp(Ochx)-OH (0.86 g, 2.4 mmol, 1.2equiv). The reaction mixture was stirred at room temperature until the disappearance of pent-4-en-1-ol as monitored by TLC. The mixture was diluted with water, extracted with DCM (3 x 15 mL), dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (5:1, v:v, R_f = 0.5) as an eluent to give **3p** in 96% yield (740.1 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.47 (d, *J* = 8.8 Hz, 1H), 5.12 – 4.94 (m, 2H), 4.80 – 4.66 (m, 1H), 4.60 – 4.46 (m, 1H), 4.14 – 4.04 (m, 2H), 2.96 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.78 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.19 – 2.02 (m, 2H), 1.89 – 1.78 (m, 2H), 1.78 – 1.62 (m, 4H), 1.61 – 1.49 (m, 1H), 1.44 (s, 9H), 1.42 – 1.22 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 170.4, 155.5, 137.3, 115.4, 80.0, 73.6, 65.1, 50.1, 37.1, 31.5, 29.9, 28.3, 27.7, 25.3, 23.7; HRMS (ESI^+) calc'd for $C_{20}H_{34}NO_6$ $[M+H]^+$: 384.2381, found 384.2377.



(*R*)-Pent-4-en-1-yl4-((*5S,8R,9S,10S,13R,14S,17S*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate 3q: To a solution of dehydrocholic acid (0.81 g, 2.0 mmol) in DCM (15 mL) at room temperature were added EDCI (0.43 g, 4.4 mmol, 2.2 equiv), DMAP (31.3 mg, 0.4 mmol, 20 mol %), and pent-4-en-1-ol (0.17 g, 2.0 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature until the disappearance of pent-4-en-1-ol as monitored by TLC. The

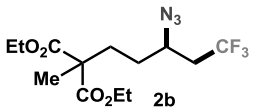
mixture was diluted with water, extracted with DCM (3 x 15 mL), dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (1:1, v:v, R_f = 0.3) as an eluent to give **3q** in 82% yield (774.1 mg, white solid). m.p. = 181 – 184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.02 (dd, *J* = 17.1, 1.6 Hz, 1H), 4.97 (d, *J* = 10.2 Hz, 1H), 4.06 (t, *J* = 6.6 Hz, 2H), 2.95 – 2.76 (m, 3H), 2.45 – 1.89 (m, 17H), 1.88 – 1.78 (m, 2H), 1.76 – 1.67 (m, 2H), 1.64 – 1.56 (m, 1H), 1.38 (s, 3H), 1.37 – 1.17 (m, 3H), 1.05 (s, 3H), 0.83 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.9, 209.1, 208.7, 174.1, 137.5, 115.3, 63.7, 56.9, 51.8, 49.0, 46.8, 45.7, 45.5, 45.0, 42.8, 38.6, 36.5, 36.0, 35.5, 35.3, 31.5, 30.5, 30.1, 27.8, 27.6, 25.1, 21.9, 18.6, 11.9; HRMS (ESI^+) calc'd for $C_{29}H_{42}NaO_5$ $[M+Na]^+$: 493.2924, found 493.2925.

5 General Procedure for Azidotrifluoromethylation of Unactivated Alkenes and Their Characterization Data



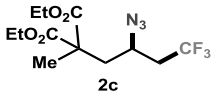
General procedure for the synthesis of **diethyl 2-(4-azido-6,6,6-trifluorohexyl)-2-methylmalonate 2a:** A 10 mL tube equipped with a rubber septum and magnetic stirring bar was charged with **IN-3** (8.4 mg, 0.02 mmol, 10 mol %). After the tube was evacuated and backfilled with argon 3 times, substrate **1a** (48.6 mg, 0.2 mmol, 1.0 equiv), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv), and EA (1 mL) were added under an argon atmosphere. The mixture was sealed and heated at 80 °C behind a safety shield for 12 h. Then the mixture was cooled to room temperature. The solvents were removed under reduced pressure, and the residue was purified directly by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.6) as an eluent to give the desired product **2a** in 87% yield (61.7 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (q, *J* = 7.1 Hz, 4H), 3.63 – 3.52 (m, 1H), 2.36 – 2.09 (m, 2H), 1.88 – 1.73 (m, 2H), 1.61 – 1.47 (m, 2H), 1.45 – 1.25 (m, 5H), 1.18 (t, *J* = 7.1 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.11, 172.09, 125.4 (q, *J* = 277.3 Hz), 61.3, 56.4 (q, *J* = 2.8 Hz), 53.4, 38.6 (q, *J* = 28.2 Hz), 35.0, 34.9, 20.6, 19.9, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.09 (t, *J* = 10.8 Hz); HRMS (ESI^+) calc'd for $C_{14}H_{22}F_3N_3NaO_4$ $[M+Na]^+$: 376.1455, found 376.1440.



2b

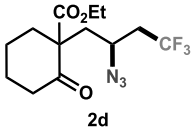
Diethyl 2-(3-azido-5,5,5-trifluoropentyl)-2-methylmalonate 2b: According to the general procedure, the reaction was carried out with diethyl 2-(but-3-en-1-yl)-2-methylmalonate **1b** (45.8 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2b** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.5) as an eluent in 82% yield (55.8 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (q, *J* = 7.1 Hz, 4H), 3.63 – 3.43 (m, 1H), 2.35 – 2.10 (m, 2H), 2.06 – 1.92 (m, 1H), 1.90 – 1.79 (m, 1H), 1.59 – 1.42 (m, 2H), 1.35 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.84, 171.81, 125.6 (q, *J* = 278.1 Hz), 61.5, 56.7 (q, *J* = 3.1 Hz), 53.1, 38.4 (q, *J* = 28.4 Hz), 31.6, 29.6, 20.0, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.15 (t, *J* = 10.3 Hz); HRMS (ESI^+) calc'd for $C_{13}H_{21}F_3N_3O_4$ $[M+H]^+$: 340.1479, found 340.1475.



2c

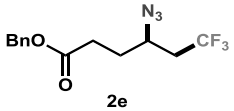
Diethyl 2-(2-azido-4,4,4-trifluorobutyl)-2-methylmalonate 2c: According to the general procedure, the reaction was carried out with diethyl 2-allyl-2-methylmalonate **1c** (42.8 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2c** was obtained by flash column chromatography on silica gel using PE and EA (50:1, v:v, R_f = 0.4) as an eluent in 59% yield (38.3 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 – 3.98 (m, 4H), 3.80 – 3.67 (m, 1H), 2.52 – 2.18 (m, 2H), 2.13 – 1.92 (m, 2H), 1.42 (s, 3H), 1.29 – 1.14 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 171.4, 125.4 (q, *J* = 278.2 Hz), 61.9, 61.7, 53.6 (q, *J* = 2.7 Hz), 52.1, 40.5, 39.5 (q, *J* = 28.3 Hz),

20.3, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.08 (t, *J* = 10.4 Hz); HRMS (ESI^+) calc'd for $C_{12}H_{18}F_3N_3NaO_4$ $[M+Na]^+$: 348.1142, found 348.1139.



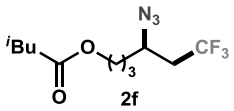
2d

Ethyl 1-2-azido-4,4,4-trifluorobutyl)-2-oxocyclohexanecarboxylate 2d: According to the general procedure, the reaction was carried out with ethyl 1-allyl-2-oxocyclohexanecarboxylate **1d** (46.9 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2d** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.2) as an eluent in 49% yield (38.3 mg, *dr* = 1:1 , colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36 – 4.01 (m, 2H), 4.00 – 3.77 (m, 0.5H)/3.72 – 3.57 (m, 0.5H), 2.63 – 2.53 (m, 1H), 2.53 – 2.13 (m, 4.5H), 2.06 – 1.85 (m, 1.5H), 1.82 – 1.65 (m, 2H), 1.64 – 1.57 (m, 2H), 1.45 – 1.34 (m, 1H), 1.23 – 1.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4/206.9, 171.6/170.9, 125.5 (q, *J* = 275.7 Hz)/125.4 (q, *J* = 278.5 Hz), 62.0/61.9, 59.2/59.1, 54.1 (q, *J* = 2.5 Hz)/53.1 (q, *J* = 3.0 Hz), 41.0/40.7, 40.6/40.1, 39.6/39.6, 38.5/35.4, 27.8/27.4, 22.5/22.1, 14.0/13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 63.82 (t, *J* = 10.4 Hz), – 64.03 (t, *J* = 10.2 Hz); HRMS (ESI^+) calc'd for $C_{13}H_{18}F_3N_3NaO_3$ $[M+Na]^+$: 344.1192, found 344.1190.

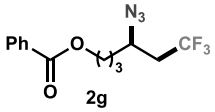


2e

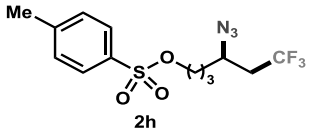
Benzyl 4-azido-6,6,6-trifluorohexanoate 2e: According to the general procedure, the reaction was carried out with benzyl pent-4-enoate **1e** (76.2 mg, 0.4 mmol), **IN-3** (16.9 mg, 0.04 mmol, 10 mol %), $N_3SO_2CF_3$ (1 mL, 1 M in *n*-hexane, 1.0 mmol, 2.5 equiv) in 2 mL of EA. The desired product **2e** was obtained by flash column chromatography on silica gel using PE and EA (30:1, v:v, R_f = 0.2) as an eluent in 59% yield (70.7 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.20 (m, 5H), 5.07 (s, 2H), 3.79 – 3.57 (m, 1H), 2.46 (t, *J* = 7.2 Hz, 2H), 2.35 – 2.14 (m, 2H), 1.99 – 1.84 (m, 1H), 1.80 – 1.65 (m, 1H). The spectroscopic characterization data were consistent with those reported in the literature.[3]



4-Azido-6,6,6-trifluorohexyl 3-methylbutanoate 2f: According to the general procedure, the reaction was carried out with pent-4-en-1-yl 3-methylbutanoate **1f** (35.2 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2f** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.5) as an eluent in 69% yield (38.5 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (t, *J* = 5.6 Hz, 2H), 3.66 – 3.56 (m, 1H), 2.36 – 2.16 (m, 2H), 2.13 (d, *J* = 7.1 Hz, 2H), 2.06 – 1.99 (m, 1H), 1.83 – 1.55 (m, 4H), 0.89 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 125.6 (q, *J* = 277.1 Hz), 63.3, 56.5 (q, *J* = 2.8 Hz), 43.4, 38.7 (q, *J* = 28.3 Hz), 31.4, 25.7, 25.0, 22.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.07 (t, *J* = 10.4 Hz); HRMS (ESI^+) calc'd for $C_{11}H_{19}F_3NO_2$ $[M\text{-}N_2+H]^+$: 254.1362, found 254.1363.

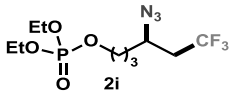


4-Azido-6,6,6-trifluorohexyl benzoate 2g: According to the general procedure, the reaction was carried out with **1g** pent-4-en-1-yl benzoate (38.8 mg, 0.2 mmol), **IN-3** (8.8 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2g** was obtained by flash column chromatography on silica gel using PE and EA (10:1, v:v, R_f = 0.3) as an eluent in 77% yield (49.7 mg, coloerless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.39 – 4.32 (m, 2H), 3.79 – 3.65 (m, 1H), 2.53 – 2.21 (m, 2H), 2.00 – 1.98 (m, 1H), 1.96 – 1.86 (m, 1H), 1.84 – 1.70 (m, 2H). The spectroscopic characterization data were consistent with those reported in the literature.[4]



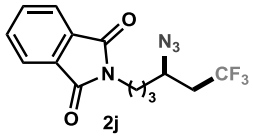
4-Azido-6,6,6-trifluorohexyl 4-methylbenzenesulfonate 2h: According to the general procedure, the reaction was carried out with pent-4-en-1-yl 4-

methylbenzenesulfonate **1h** (48.3 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2h** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.4) as an eluent in 76% yield (53.0 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 4.12 – 3.78 (m, 2H), 3.58 – 3.35 (m, 1H), 2.38 (s, 3H), 2.31 – 2.01 (m, 2H), 1.82 – 1.36 (m, 4H). The spectroscopic characterization data were consistent with those reported in the literature.[4]



2i

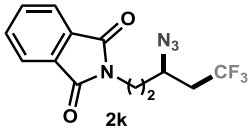
4-Azido-6,6,6-trifluorohexyl diethyl phosphate 2i: According to the general procedure, the reaction was with diethyl pent-4-en-1-yl phosphate **1i** (44.8 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2i** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.2) as an eluent in 66% yield (43.9 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 – 3.84 (m, 6H), 3.76 – 3.47 (m, 1H), 2.44 – 2.10 (m, 2H), 1.85 – 1.52 (m, 4H), 1.28 (t, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.6 (q, *J* = 277.2 Hz), 66.6 (d, *J* = 5.8 Hz), 63.8 (d, *J* = 5.9 Hz), 56.4 (q, *J* = 2.7 Hz), 38.6 (q, *J* = 28.3 Hz), 30.9, 26.5 (d, *J* = 7.1 Hz), 16.1 (d, *J* = 6.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.09 (t, *J* = 6.0 Hz); HRMS (ESI^+) calc'd for $C_{10}H_{19}F_3N_3NaO_4P$ $[M+Na]^+$: 356.0957, found 356.0949.



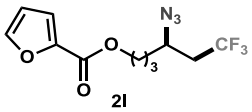
2j

2-(4-Azido-6,6,6-trifluorohexyl)isoindoline-1,3-dione 2j: According to the general procedure, the reaction was carried out with 2-(pent-4-en-1-yl)isoindoline-1,3-dione **1j** (48.6 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2j** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.4) as an eluent in 81% yield (53.1 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 –

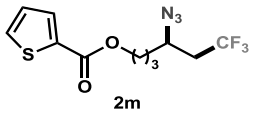
7.74 (m, 2H), 7.71 – 7.61 (m, 2H), 3.75 – 3.54 (m, 3H), 2.33 – 2.10 (m, 2H), 1.91 – 1.79 (m, 1H), 1.78 – 1.68 (m, 1H), 1.66 – 1.50 (m, 2H). The spectroscopic characterization data were found consistent with the reported in the literature.[3]



2-(3-Azido-5,5,5-trifluoropentyl)isoindoline-1,3-dione 2k: According to the general procedure, the reaction was carried out with 2-(but-3-en-1-yl)isoindoline-1,3-dione **1k** (38.6 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2k** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.4) as an eluent in 70% yield (43.4 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.72 (m, 2H), 7.71 – 7.57 (m, 2H), 3.86 – 3.69 (m, 2H), 3.71 – 3.53 (m, 1H), 2.44 – 2.17 (m, 2H), 1.98 – 1.83 (m, 1H), 1.85 – 1.70 (m, 1H). The spectroscopic characterization data were found consistent with those reported in the literature.[3]

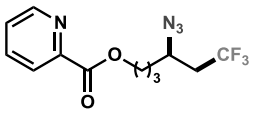


4-Azido-6,6,6-trifluorohexyl furan-2-carboxylate 2l: According to the general procedure, the reaction was carried out with pent-4-en-1-yl furan-2-carboxylate **1l** (33.5 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2l** was obtained by flash column chromatography on silica gel using PE and EA (10:1, v:v, R_f = 0.5) as an eluent in 38% yield (22.3 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.19 (dd, *J* = 3.5, 0.9 Hz, 1H), 6.52 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.52 – 4.15 (m, 2H), 3.95 – 3.31 (m, 1H), 2.48 – 2.20 (m, 2H), 2.03 – 1.82 (m, 2H), 1.82 – 1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 146.5, 144.5, 125.6 (q, *J* = 276.9 Hz), 118.1, 111.9, 64.0, 56.5 (d, *J* = 2.9 Hz), 38.7 (q, *J* = 28.3 Hz), 31.4, 25.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.04 (t, *J* = 10.5 Hz); HRMS (ESI^+) calc'd for $C_{11}H_{12}F_3N_3NaO_3$ $[M+Na]^+$: 314.0723, found 314.0726.



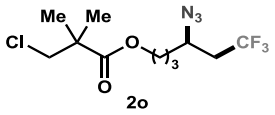
2m

4-Azido-6,6,6-trifluorohexyl thiophene-2-carboxylate 2m: According to the general procedure, the reaction was carried out with pent-4-en-1-yl thiophene-2-carboxylate **1 M** (39.5 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2m** was obtained by flash column chromatography on silica gel using PE and EA (10:1, v:v, R_f = 0.4) as an eluent in 41% yield (25.1 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.57 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.11 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.45 – 4.27 (m, 2H), 3.78 – 3.65 (m, 1H), 2.47 – 2.21 (m, 2H), 2.06 – 1.61 (m, 4H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 133.6, 133.5, 132.6, 127.9, 125.6 (q, *J* = 276.9 Hz), 64.2, 56.4 (q, *J* = 2.6 Hz), 38.7 (q, *J* = 28.3 Hz), 31.4, 25.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.02 (t, *J* = 10.4 Hz); HRMS (ESI^+) calc'd for $C_{11}H_{13}F_3NO_2S$ $[M-N_2+H]^+$: 280.0614, found 280.0615.



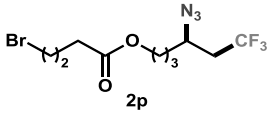
2n

4-Azido-6,6,6-trifluorohexyl picolinate 2n: According to the general procedure, the reaction was carried out with pent-4-en-1-yl picolinate **1n** (38.3 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2n** was obtained by flash column chromatography on silica gel using PE and EA (3:1, v:v, R_f = 0.2) as an eluent in 55% yield (33.2 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.7 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.87 – 7.71 (m, 1H), 7.48 – 7.38 (m, 1H), 4.55 – 4.23 (m, *J* = 6.4 Hz, 2H), 3.88 – 3.57 (m, 1H), 2.46 – 2.26 (m, 2H), 2.11 – 1.86 (m, 2H), 1.86 – 1.63 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 149.9, 147.8, 139.2, 127.0, 125.6 (q, *J* = 278.1 Hz), 125.2, 65.0, 56.5 (q, *J* = 2.8 Hz), 38.7 (q, *J* = 28.3 Hz), 31.4, 25.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.05 (t, *J* = 10.4 Hz); HRMS (ESI^+) calc'd for $C_{12}H_{13}F_3N_4NaO_2$ $[M+Na]^+$: 325.0883, found 325.0882.



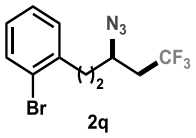
2o

4-Azido-6,6,6-trifluorohexyl 3-chloro-2,2-dimethylpropanoate 2o: According to general procedure, the reaction was carried out with pent-4-en-1-yl 3-chloro-2,2-dimethylpropanoate **1o** (41.1 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2o** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.3) as an eluent in 66% yield (41.9 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24 – 4.00 (m, 2H), 3.70 – 3.56 (m, 1H), 3.54 (s, 2H), 2.39 – 2.11 (m, 2H), 1.91 – 1.47 (m, 4H), 1.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 125.6 (q, *J* = 277.2 Hz), 64.0, 56.3 (q, *J* = 2.8 Hz), 52.0, 44.7, 38.6 (q, *J* = 28.3 Hz), 31.2, 24.9, 23.5, 23.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.05 (t, *J* = 10.7 Hz); HRMS (ESI^+) calc'd for $C_{11}H_{18}ClF_3NO_2$ $[M-N_2+H]^+$: 288.0973, found 288.0975.



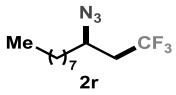
2p

4-Azido-6,6,6-trifluorohexyl 3-bromopropanoate 2p: According to the general procedure, the reaction was carried out with pent-4-en-1-yl 3-bromopropanoate **1p** (46.4 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2p** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.4) as an eluent in 80% yield (53.0 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 – 3.99 (m, 2H), 3.72 – 3.56 (m, 1H), 3.40 (t, *J* = 6.4 Hz, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.34 – 2.16 (m, 2H), 2.16 – 2.04 (m, 2H), 1.85 – 1.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 125.6 (q, *J* = 277.4 Hz), 63.7, 56.4 (q, *J* = 2.9 Hz), 38.6 (q, *J* = 28.2 Hz), 32.7, 32.3, 31.3, 27.6, 24.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.06 (t, *J* = 10.4 Hz); HRMS (ESI^+) calc'd for $C_{10}H_{15}BrF_3N_3NaO_2$ $[M+Na]^+$: 368.0192, found 368.0187.



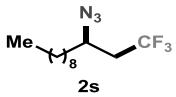
2q

4-Azido-6,6,6-trifluorohexyl diethyl phosphate 2q: According to the general procedure, the reaction was carried out with 1-bromo-2-(but-3-en-1-yl)benzene **1q** (42.5 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2q** was obtianed by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.4) as an eluent in 49% yield (31.6 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 1H), 7.41 – 7.24 (m, 2H), 7.23 – 7.12 (m, 1H), 3.78 – 3.72 (m, 1H), 3.10 – 2.97 (m, 1H), 2.98 – 2.87 (m, 1H), 2.59 – 2.28 (m, 2H), 2.18 – 1.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 132.1, 129.4, 127.2, 126.7, 124.6 (q, *J* = 278.4 Hz), 123.3, 55.2 (q, *J* = 2.4 Hz), 37.6 (q, *J* = 28.3 Hz), 33.7, 31.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 63.97 (t, *J* = 10.4 Hz); HRMS (ESI$^+$) calc'd for $C_{11}H_{11}BrF_3NaN$ $[M-N_2+Na]^+$: 294.0100, found 294.0096.



2r

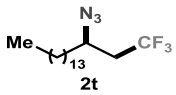
3-Azido-1,1,1-trifluoroundecane 2r: According to the general procedure, the reaction was carried out with dec-1-ene **1r** (28.3 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2r** was obtained by flash column chromatography on silica gel using PE (R_f = 0.8) as an eluent in 58% yield (29.3 mg, colorless). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 – 3.58 (m, 1H), 2.38 – 2.20 (m, 2H), 1.65 – 1.54 (m, 2H), 1.52 – 1.25 (m, 12H), 0.89 (t, *J* = 6.8 Hz, 3H). The spectroscopic characterization data were consistent with the reported in the literature.[4]



2s

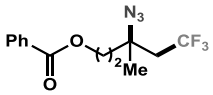
3-Azido-1,1,1-trifluorotridecane 2s: According to the general procedure, the reaction was carried out with undec-1-ene **1s** (30.4 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA.

The desired product **2s** was obtained by flash column chromatography on silica gel using PE (R_f = 0.8) as an eluent in 62% yield (33.0 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 – 3.58 (m, 1H), 2.39 – 2.19 (m, 2H), 1.62 – 1.58 (m, 2H), 1.51 – 1.23 (m, 14H), 0.881 (t, *J* = 6.8 Hz, 3H). The spectroscopic characterization data were consistent with the reported in the literature.[4]



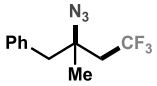
2t

3-Azido-1,1,1-trifluoroheptadecane 2t: According to the general procedure, the reaction was carried out with hexadec-1-ene **1t** (45.0 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2t** was purified by flash column chromatography on silica gel using PE (R_f = 0.8) as an eluent and obtained in 59% yield (39.8 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 – 3.58 (m, 1H), 2.36 – 2.21 (m, 2H), 1.66 – 1.54 (m, 2H), 1.45 – 1.26 (m, 24H), 0.88 (t, *J* = 6.8 Hz, 3H). The spectroscopic characterization data were consistent with the reported in the literature.[4]



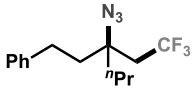
2u

3-Azido-5,5,5-trifluoro-3-methylpentyl benzoate 2u: According to the general procedure, the reaction was carried out with 3-methylbut-3-en-1-yl benzoate **1u** (38.3 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2u** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.4) as an eluent in 81% yield (49.1 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.53 – 7.47 (m, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 4.49 – 4.31 (m, 2H), 2.43 – 2.32 (m, 2H), 2.10 – 1.99 (m, 2H), 1.47 (s, 3H). The spectroscopic characterization data were consistent with the reported in those literature.[3]



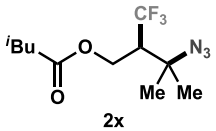
2v

(2-Azido-4,4,4-trifluoro-2-methylbutyl)benzene 2v: According to the general procedure, the reaction was carried out with (2-methylallyl)benzene **1v** (36.3 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2v** was obtained by flash column chromatography on silica gel using PE (R_f = 0.8) as an eluent in 77% yield (37.4 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 3H), 7.25 – 7.16 (m, 2H), 2.89 (ABBA, *J* = 12.5 Hz, 2H), 2.31 (ABBA, *J* = 11.0 Hz, 2H), 1.44 (s, 3H). The spectroscopic characterization data were consistent with the reported in the literature.[5]



2w

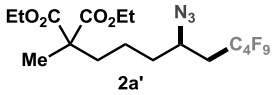
(2-Azido-2-(2,2,2-trifluoroethyl)pentyl)benzene 2w: According to the general procedure, the reaction was carried out with (2-methylenepentyl)benzene **1w** (35.1 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2w** was obtained by flash column chromatography on silica gel using PE (R_f = 0.5) as an eluent in 71% yield (38.0 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.28 (m, 2H), 7.27 – 7.15 (m, 3H), 2.74 – 2.62 (m, 2H), 2.41 (ABBA, *J* = 11.2 Hz, 2H), 2.02 – 1.88 (m, 2H), 1.79 – 1.67 (m, 2H), 1.52 – 1.37 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 128.7, 128.3, 126.3, 125.6 (q, *J* = 278.9 Hz), 63.2, 39.4 (q, *J* = 27.5 Hz), 39.0, 38.8, 30.0, 16.9, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 60.56 (t, *J* = 11.1 Hz); HRMS (ESI^+) calc'd for $C_{14}H_{18}F_3N_3Na$ $[M+Na]^+$: 308.1345, found 308.1346.



2x

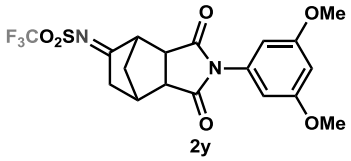
2-Azido-4,4,4-trifluoro-3,3-dimethylbutyl 3-methylbutanoate 2x: According to the general procedure, the reaction was carried out with 3-methylbut-2-en-1-yl 3-methylbutanoate **1x** (34.4 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired

product **2x** was obtained by flash column chromatography on silica gel using PE and EA (50:1, v:v, R_f = 0.3) as an eluent in 49% yield (26.1 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 (dd, *J* = 12.3, 4.0 Hz, 1H), 4.23 (dd, *J* = 12.3, 5.9 Hz, 1H), 2.51 – 2.44 (m, 1H), 2.19 – 2.11 (m, 2H), 2.15 – 2.05 (m, 1H), 1.44 (s, 3H), 1.36 (s, 3H), 0.89 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 172.6, 126.1 (q, *J* = 282.5 Hz), 60.6, 59.5 (q, *J* = 2.9 Hz), 51.0 (q, *J* = 24.4 Hz), 43.2, 26.1, 25.6, 24.0, 22.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 63.52 (d, *J* = 9.5 Hz); HRMS (ESI$^+$) calc'd for $C_{11}H_{19}F_3NO_2$ [M-N_2+H]$^+$: 254.1362, found 254.1365.



2a'

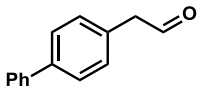
Diethyl 2-(4-azido-6,6,7,7,8,8,9,9,10,10,10-undecafluorodecyl)-2-methylmalonate 2a': According to the general procedure, the reaction was carried out with diethyl 2-methyl-2-(pent-4-en-1-yl)malonate **1a** (49.1 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2C_4F_9$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **2a'** was obtained by flash column chromatography on silica gel using PE and EA (15:1, v:v, R_f = 0.4) as an eluent in 65% yield (65.5 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (q, *J* = 7.1 Hz, 2H), 3.75 – 3.63 (m, 1H), 2.36 – 2.01 (m, 2H), 1.93 – 1.71 (m, 2H), 1.62 – 1.50 (m, 2H), 1.45 – 1.27 (s, 5H), 1.18 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 172.2, 127.4 – 99.7 (m), 61.3, 55.6, 53.5, 35.6, 35.5 (t, *J* = 21.3 Hz), 35.0, 20.6, 19.9, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 81.07 (t, *J* = 9.8 Hz), – (113.34 – 133.62) (m), – (124.42 – 124.50) (m), – 125.93 (t, *J* = 13.0 Hz); HRMS (ESI$^+$) calc'd for $C_{17}H_{23}F_9N_3O_4$ [M+H]$^+$: 504.1539, found 504.1524.



2y

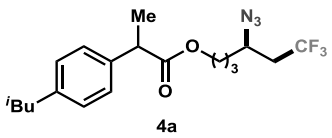
***N*-(2-(3,5-Dimethoxyphenyl)-1,3-dioxohexahydro-1*H*-4,7-methanoisoindol-5(6*H*)-ylidene)-1,1,1-trifluoromethanesulfonamide 2y:** According to the general procedure, the reaction was carried out with diethyl 2-(3,5-dimethoxyphenyl)-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione **1y** (60.3 mg, 0.2 mmol), **IN-3** (8.8

mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. An aldehyde **2y** was obtained by flash column chromatography on silica gel using PE and EA (2:1, v:v, R_f = 0.3) as an eluent in 92% yield (82.6 mg, white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51 (t, *J* = 2.2 Hz, 1H), 6.28 (d, *J* = 2.3 Hz, 2H), 3.78 (s, 6H), 3.43 (s, 2H), 3.41 (dd, *J* = 3.1, 1.7 Hz, 2H), 3.29 (s, 2H), 1.88 (d, *J* = 11.1 Hz, 1H), 1.35 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 161.3, 132.7, 118.7 (q, *J* = 321.2 Hz), 104.9, 101.6, 55.6, 46.9, 39.7, 38.9, 31.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 76.44; HRMS (ESI$^+$) calc'd for $C_{18}H_{18}F_3N_2O_6S$ $[M+H]^+$: 447.0832, found 447.0815,; M.P. = 215 – 217 ^{o}C.



2z

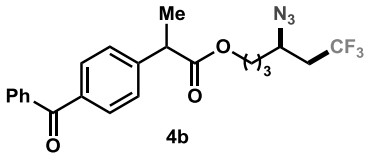
2-([1,1'-Biphenyl]-4-yl)acetaldehyde 2z: According to the general procedure, the reaction was carried out with diethyl 4-vinyl-1,1'-biphenyl (72.1 mg, 0.4 mmol), **IN-3** (16.8 mg, 0.04 mmol, 10 mol %), $N_3SO_2CF_3$ (1.0 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 2 mL of EA. An aldehyde **2z** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.6) as an eluent in 45% yield (35.6 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (t, *J* = 2.3 Hz, 1H), 7.67 – 7.55 (m, 4H), 7.52 – 7.40 (m, 2H), 7.40 – 7.33 (m, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.75 (d, *J* = 2.3 Hz, 2H). The spectroscopic characterization data were consistent with those reported in the literature.[6]



4a

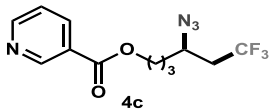
4-Azido-6,6,6-trifluorohexyl 2-(4-isobutylphenyl)propanoate 4a: According to the general procedure with pent-4-en-1-yl 2-(4-isobutylphenyl)propanoate **3a** (59.2 mg, 0.2 mmol), **IN-3** (8.4 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA, **4a** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.4) as an eluent in 76% yield (58.3 mg, *dr* = 1:1, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 4.10 – 3.91 (m, 2H), 3.62 (q, *J* = 7.2 Hz, 1H), 3.55 – 3.41 (m, 1H), 2.37

(d, *J* = 7.2 Hz, 2H), 2.28 – 1.98 (m, 2H), 1.88 – 1.56 (m, 3H), 1.43 – 1.39 (m, 5H), 0.82 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 140.7, 137.702/137.695, 129.4, 127.1, 125.5 (q, *J* = 277.1 Hz), 63.6/63.5 , 56.3 – 56.2 (m), 45.1, 45.13/44.98, 38.5 (q, *J* = 28.3 Hz), 31.2/31.1, 30.2, 24.9/24.8, 22.4, 18.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.08 (t, *J* = 10.7 Hz); HRMS (ESI^+) calc'd for $C_{19}H_{26}F_3N_3NaO_2$ $[M+Na]^+$: 408.1869, found 408.1870.



4b

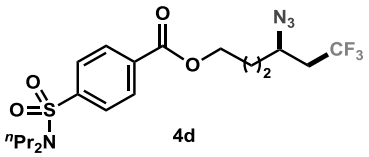
4-Azido-6,6,6-trifluorohexyl 2-(4-benzoylphenyl)propanoate 4b: According to the general procedure, the reaction was carried out with pent-4-en-1-yl 2-(4-benzoylphenyl)propanoate **3b** (63.0 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4b** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.2) as an eluent in 64% yield (53.2 mg, *dr* = 1:1 coloerless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.71 (m, 3H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.55 – 7.42 (m, 4H), 4.16 – 4.07 (m, 2H), 3.81 (q, *J* = 7.2 Hz, 1H), 3.61 – 3.56(m, 1H), 2.36 – 2.10 (m, 2H), 1.87 – 1.75 (m, 1H), 1.74 – 1.68 (m, 1H), 1.61 – 1.44 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 174.0, 140.9/140.8, 138.0, 137.4, 132.6, 131.47/131.46, 130.1, 129.14/129.11, 128.6, 128.4, 125.6 (q, *J* = 277.5 Hz), 64.00/63.95, 56.3 (q, *J* = 3.2 Hz), 45.4, 38.6 (q, *J* = 28.3 Hz), 31.21/31.17, 24.89/24.86, 18.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.02 (t, *J* = 10.5 Hz); HRMS (ESI^+) calc'd for $C_{22}H_{23}F_3N_3O_3$ $[M+H]^+$: 434.1686, found 434.1689.



4c

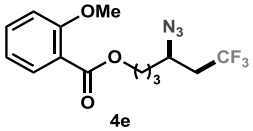
4-Azido-6,6,6-trifluorohexyl nicotinate 4c: According to the general procedure, the reaction was carried out with pent-4-en-1-yl nicotinate **3c** (38.2 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4c** was obtained by flash column chromatography on silica gel using PE and EA (5:1, v:v, R_f = 0.4) as an eluent in 60%

yield (36.0 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.79 (s, 1H), 8.31 (d, *J* = 7.9 Hz, 1H), 7.42 (dd, *J* = 8.0, 4.8 Hz, 1H), δ 4.41 (t, *J* = 6.5 Hz, 2H), 3.79 – 3.64 (m, 1H), 2.48 – 2.26 (m, 2H), 2.10 – 1.68 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 153.4, 150.7, 137.3, 126.1, 125.5 (q, *J* = 278.0 Hz) 123.5, 64.5, 56.4 (q, *J* = 3.6 Hz), 38.7 (q, *J* = 28.5 Hz), 31.3, 25.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.00 (t, *J* = 10.4 Hz); HRMS (ESI^+) calc'd for $C_{12}H_{14}F_3N_4O_2$ $[M+H]^+$: 303.1063, found 303.1063.



4d

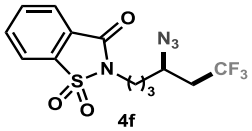
4-Azido-6,6,6-trifluorohexyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate 4d: According to the general procedure, the reaction was carried out with pent-4-en-1-yl 4-(*N*,*N*-dipropylsulfamoyl)benzoate **3d** (64 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4d** was obtained by flash column chromatography on silica gel using PE and EA (5:1, v:v, R_f = 0.5) as an eluent in 66% yield (55.3 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 4.33 (t, *J* = 6.3 Hz, 2H), 3.69 – 3.63 (m, 1H), 3.08 – 2.95 (m, 4H), 2.41 – 2.15 (m, 2H), 2.02 – 1.89 (m, 1H), 1.88 – 1.79 (m, 1H), 1.77 – 1.60 (m, 2H), 1.55 – 1.40 (m, 4H), 0.80 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 144.4, 133.3, 130.2, 127.1, 125.5 (q, *J* = 277.0 Hz), 64.7, 56.4 (q, *J* = 3.1 Hz), 49.9, 38.6 (q, *J* = 28.4 Hz), 31.3, 25.0, 21.9, 11.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.00 (t, *J* = 10.4 Hz); HRMS (ESI^+) calc'd for $C_{19}H_{27}F_3N_4NaO_4S$ $[M+Na]^+$: 487.1597, found 487.1604.



4e

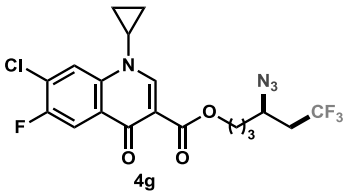
4-Azido-6,6,6-trifluorohexyl 2-methoxybenzoate 4e: According to the general procedure, the reaction was carried out with pent-4-en-1-yl 2-methoxybenzoate **3e** (46.6 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4e** was obtained by flash column chromatography on silica gel using PE and EA (10:1, v:v, R_f = 0.5) as

an eluent in 62% yield (44.8 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.68 – 7.43 (m, 1H), 7.14 – 6.82 (m, 2H), 4.53 – 4.16 (m, 2H), 3.89 (s, 3H), 3.79 – 3.63 (m, 1H), 2.64 – 2.23 (m, 2H), 2.08 – 1.71 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 159.2, 133.7, 131.6, 125.6 (q, *J* = 276.9 Hz), 120.2, 119.9, 112.0, 63.9, 56.5 (q, *J* = 2.8 Hz), 55.9, 38.7 (q, *J* = 28.3 Hz), 31.5, 25.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.03 (t, *J* = 10.4 Hz); HRMS (ESI^+) calc'd for $C_{14}H_{16}F_3N_3NaO_3$ $[M+Na]^+$: 354.1036, found 354.1039.



4f

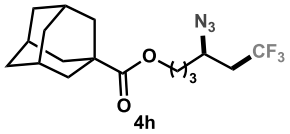
2-(4-Azido-6,6,6-trifluorohexyl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide 4f: According to the general procedure, the reaction was carried out with 2-(pent-4-en-1-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide **3f** (50.6 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4f** was obtained by flash column chromatography on silica gel using PE and EA (10:1, v:v, R_f = 0.4) as an eluent in 65% yield (47.1 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.95 (m, 1H), 7.90 – 7.70 (m, 3H), 3.76 (t, *J* = 7.0 Hz, 2H), 3.71 – 3.57 (m, 1H), 2.36 – 2.14 (m, 2H), 2.06 – 1.94 (m, 1H), 1.95 – 1.82 (m, 1H), 1.76 – 1.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 137.6, 134.9, 134.5, 127.2, 125.6 (q, *J* = 278.0 Hz), 125.3, 121.0, 56.3 (q, *J* = 2.9 Hz), 38.6 (q, *J* = 28.4 Hz), 38.6, 31.9, 24.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.08 (t, *J* = 10.5 Hz); HRMS (ESI^+) calc'd for $C_{13}H_{14}F_3N_2O_3S$ $[M-N_2+H]^+$: 335.0672, found 335.0673.



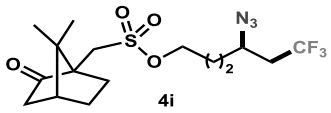
4g

4-Azido-6,6,6-trifluorohexyl 7-chloro-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydro--quinoline-3-carboxylate 4g: According to the general procedure, the reaction was carried out with hex-5-en-1-yl 7-chloro-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylate **3g** (70.5 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10

mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4g** was obtained by flash column chromatography on silica gel using PE and EA (1:1, v:v, R_f = 0.2) as an eluent in 50% yield (49.8 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.18 (d, *J* = 9.0 Hz, 1H), 8.00 (d, *J* = 5.9 Hz, 1H), 4.45 – 4.23 (m, 2H), 3.82 – 3.71 (m, 1H), 3.49 – 4.43 (m, 1H), 2.39 – 2.30 (m, 2H), 2.07 – 1.81 (m, 3H), 1.81 – 1.69 (m, 1H), 1.43 – 1.33 (m, 2H), 1.16 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7 (d, *J* = 2.2 Hz), 165.4, 155.8 (d, *J* = 250.7 Hz), 149.0, 137.2, 129.9 (d, *J* = 2.9 Hz), 128.7 (d, *J* = 6.2 Hz), 127.1 (d, *J* = 20.3 Hz), 125.7 (q, *J* = 278.2 Hz), 119.0, 114.0 (d, *J* = 23.1 Hz), 110.5, 64.2, 56.5 (q, *J* = 2.5 Hz), 38.6 (q, *J* = 28.1 Hz), 34.8, 31.5, 25.0, 8.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 63.98 (t, *J* = 10.5 Hz), – (114.54 – 125.63) (m); HRMS (ESI^+) calc'd for $C_{19}H_{18}ClF_4N_4O_3$ $[M+H]^+$: 461.0998, found 461.0998.

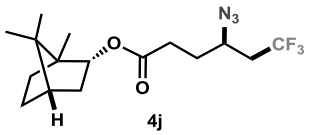


(3*r*,5*r*,7*r*)-4-Azido-6,6,6-trifluorohexyl adamantane-1-carboxylate 4h: According to the general procedure, the reaction was carried out with (3*r*,5*r*,7*r*)-pent-4-en-1-yl adamantane-1-carboxylate **3h** (47.5 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4h** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.5) as an eluent in 82% yield (56.7 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.08 (t, *J* = 5.8 Hz, 2H), 3.70 – 3.65 (m, 1H), 2.45 – 2.20 (m, 2H), 2.01 (s, 3H), 1.91 – 1.81 (m, 7H), 1.78 – 1.59 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 125.6 (q, *J* = 277.2 Hz), 63.1, 56.4 (q, *J* = 2.9 Hz), 40.7, 38.9, 38.6 (q, *J* = 28.5 Hz), 36.5, 31.3, 27.9, 24.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.03 (t, *J* = 10.5 Hz); HRMS (ESI^+) calc'd for $C_{17}H_{25}F_3N_3O_2$ $[M+H]^+$: 360.1893, found 360.1889.



4i

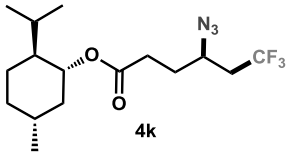
4-Azido-6,6,6-trifluorohexyl ((*1S,4R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate 4i: According to the general procedure, the reaction was carried out with pent-4-en-1-yl ((*1S,4R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate **3i** (60.4 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4i** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.5) as an eluent in 78% yield (64.3 mg, *dr* = 1:1, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 – 4.09 (m, 2H), 3.81 – 3.57 (m, 1H), 3.52 (d, *J* = 15.1 Hz, 1H), 2.93 (d, *J* = 15.1 Hz, 1H), 2.54 – 2.14 (m, 4H), 2.12 – 1.94 (m, 2H), 1.95 – 1.52 (m, 6H), 1.51 – 1.31 (m, 1H), 1.04 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.6, 126.1 (q, *J* = 271.0 Hz), 69.6, 57.9, 56.3 (q, *J* = 2.8 Hz), 48.1, 46.8, 42.7, 42.5, 38.6 (q, *J* = 28.3 Hz), 30.9, 26.9, 25.6, 24.9, 19.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.01 (t, *J* = 10.4 Hz); HRMS (ESI^+) calc'd for $C_{16}H_{24}F_3N_3NaO_4S$ $[M+Na]^+$: 434.1332, found 434.1330.



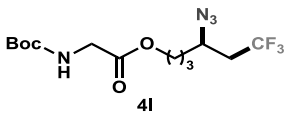
4j

(*1S,2R,4S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 4-azido-6,6,6-trifluorohexan--oate 4j: According to the general procedure, the reaction was carried out with (*1S,2R,4S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl pent-4-enoate **3j** (47.3 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4j** was obtained by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.6) as an eluent in 71% yield (49.1 mg, *dr* = 1:1, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 – 4.70 (m, 1H), 3.92 – 3.65 (m, 1H), 2.50 (t, *J* = 7.2 Hz, 2H), 2.43 – 2.23 (m, 3H), 2.08 – 1.70 (m, 4H), 1.68 (t, *J* = 4.5 Hz, 1H), 1.38 – 1.17 (m, 2H), 0.96 (dt, *J* = 13.8, 3.3 Hz, 1H), 0.90

(s, 3H), 0.87 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 125.5 (q, *J* = 277.2 Hz), 80.5, 56.1 (q, *J* = 2.9 Hz), 48.8, 47.8, 44.9, 38.8 (q, *J* = 28.4 Hz), 36.8, 30.6, 30.0, 28.0, 27.1, 19.7, 18.8, 13.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.07 (t, *J* = 10.8 Hz); HRMS (ESI^+) calc'd for $C_{16}H_{24}F_3N_3NaO_2$ $[M+Na]^+$: 370.1713, found 370.1709.

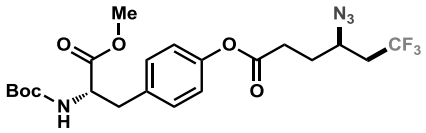


(*1R,2S,5R*)-2-Isopropyl-5-methylcyclohexyl 4-azido-6,6,6-trifluorohexanoate 4k: According to the general procedure, the reaction was carried out with (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl pentanoate **3k** (48.1 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4k** was obtained by flash column chromatography on silica gel using PE and EA (50:1, v:v, R_f = 0.5) as an eluent in 72% yield (48.3 mg, *dr* = 1:1, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 – 4.68 (m, 1H), 3.84 – 3.62 (m, 1H), 2.46 (t, *J* = 7.2 Hz, 2H), 2.38 – 2.24 (m, 2H), 2.06 – 1.89 (m, 2H), 1.89 – 1.77 (m, 2H), 1.72 – 1.64 (m, 2H), 1.54 – 1.43 (m, 1H), 1.43 – 1.32 (m, 1H), 1.18 – 0.94 (m, 2H), 0.95 – 0.82 (m, 7H), 0.75 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 125.5 (q, *J* = 277.0 Hz), 74.7, 56.2 – 56.1 (m), 47.0, 40.89/40.86, 38.8 (q, *J* = 28.4 Hz), 34.2, 31.4, 30.6, 30.0, 26.4/26.3, 23.4, 22.0, 20.7, 16.24/16.23; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.112 (t, *J* = 7.1 Hz), δ – 64.122 (t, *J* = 14.3 Hz); HRMS (ESI^+) calc'd for $C_{16}H_{27}F_3NO_2$ $[M-N_2+H]^+$: 322.1988, found 322.1991.

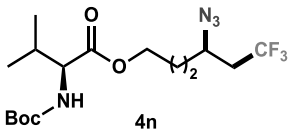


4-Azido-6,6,6-trifluorohexyl 2-((*tert*-butoxycarbonyl)amino)acetate 4l: According to the general procedure, the reaction was carried out with pent-4-en-1-yl 2-((*tert*-butoxycarbonyl)amino)acetate **3l** (49.0 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA.

The desired product **4l** was obtained by flash column chromatography on silica gel using PE and EA (5:1, v:v, R_f = 0.4) as an eluent in 67% yield (47.6 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.98 (brs, 1H), 4.18 – 4.03 (m, 2H), 3.84 (d, *J* = 5.6 Hz, 2H), 3.73 – 3.43 (m, 1H), 2.40 – 2.13 (m, 2H), 1.99 – 1.52 (m, 4H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 155.7, 125.5 (q, *J* = 277.3 Hz), 80.1, 64.4, 56.4 (q, *J* = 3.3 Hz), 42.4, 38.7 (q, *J* = 28.4 Hz), 31.2, 28.3, 24.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.05 (t, *J* = 10.7 Hz); HRMS (ESI^+) calc'd for $C_{13}H_{21}F_3N_4NaO_4$ $[M+Na]^+$: 377.1407, found 377.1405.

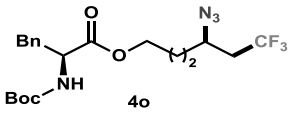


4-((*S*)-2-((*tert*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenyl 4-azido-6,6,6-trifluorohexanoate 4m: According to the general procedure, the reaction was carried out with (*S*)-4-(2-((*tert*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenyl pent-4-enoate **3m** (75.7 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4m** was obtained by flash column chromatography on silica gel using PE and EA (5:1, v:v, R_f = 0.4) as an eluent in 58% yield (52.2 mg, *dr* = 1:1, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H) 5.00 (d, *J* = 7.8 Hz, 1H), 4.60 – 4.55 (m, 1H), 3.85 – 3.79 (m, 1H), 3.71 (s, 3H), 3.14 – 3.01 (m, 2H), 2.74 (t, *J* = 7.2 Hz, 2H), 2.50 – 2.26 (m, 2H), 2.16 – 1.99 (m, 1H), 1.97 – 1.83 (m, 1H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 170.9, 155.1, 149.5, 133.9, 130.4, 125.5 (q, *J* = 277.3 Hz), 121.5, 80.1, 56.2 (q, *J* = 2.7 Hz), 54.4, 52.3, 38.8 (q, *J* = 28.4 Hz), 37.7, 30.4, 29.8, 28.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 63.99 (t, *J* = 10.4 Hz); HRMS (ESI^+) calc'd for $C_{21}H_{27}F_3N_4NaO_6$ $[M+Na]^+$: 511.1775, found 511.1778.



4n

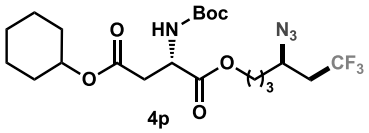
(*2S*)-4-Azido-6,6,6-trifluorohexyl 2-((*tert*-butoxycarbonyl)amino)-3-methylbutan--oate 4n: According to the general procedure, the reaction was carried out with (*S*)-pent-4-en-1-yl 2-((*tert*-butoxycarbonyl)amino)-3-methylbutanoate **3n** (60.9 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4n** was obtained by flash column chromatography on silica gel using PE and EA (5:1, v:v, R_f = 0.4) as an eluent in 64% yield (50.9 mg, *dr* = 1:1, colorless oil). ^{1}HNMR (400 MHz, $CDCl_3$) δ 4.99 (d, *J* = 8.4 Hz, 1H), 4.29 – 3.99 (m, 3H), 3.69 – 3.57 (m, 1H), 2.45 – 2.20 (m, 2H), 2.20 – 1.99 (m, 1H), 1.95 – 1.54 (m, 4H), 1.43 (s, 9H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 155.7, 125.5 (q, *J* = 277.0 Hz), 79.8, 64.13/64.10, 58.6, 56.4 (q, *J* = 2.9 Hz), 38.6 (q, *J* = 29.8 Hz), 38.6 (q, *J* = 28.2 Hz), 31.3/31.2, 28.3, 24.94/24.89, 19.0, 17.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ – (64.03 – 64.10) (m); HRMS (ESI^+) calc'd for $C_{16}H_{27}F_3N_4NaO_4$ $[M+Na]^+$: 419.1877, found 419.1868.



4o

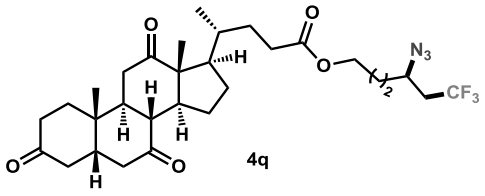
(*2S*)-4-Azido-6,6,6-trifluorohexyl 2-((*tert*-butoxycarbonyl)amino)-3-phenylpro--panoate 4o: According to the general procedure, the reaction was carried out with (*S*)-pent-4-en-1-yl 2-((*tert*-butoxycarbonyl)amino)-3-phenylpropanoate **3o** (60.9 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4o** was obtained by flash column chromatography on silica gel using PE and EA (5:1, v:v, R_f = 0.4) as an eluent in 49% yield (43.8 mg, *dr* = 1:1, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.14 (m, 3H), 7.10 – 7.04 (m, 2H), 4.92 (d, *J* = 8.3 Hz, 1H), 4.51 – 4.45 (m, 1H), 4.15 – 3.94 (m, 2H), 3.66 – 3.44 (m, 1H), 2.99 (d, *J* = 6.4 Hz, 2H), 2.32 – 2.07 (m, 2H), 1.82 – 1.55 (m, 2H), 1.50 – 1.40 (m, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 155.1,

136.04/136.01, 129.3, 128.6, 127.1, 125.6 (q, J = 277.0 Hz), 80.0, 64.32/64.28, 56.4 (q, J = 3.4 Hz), 54.6, 38.6 (q, J = 28.5 Hz), 38.53/38.46, 31.2/31.1, 28.3, 24.80/24.79; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.05 (t, J = 10.4 Hz); HRMS (ESI^+) calc'd for $C_{20}H_{27}F_3N_4NaO_4$ $[M+Na]^+$: 467.1877, found 467.1874.



4p

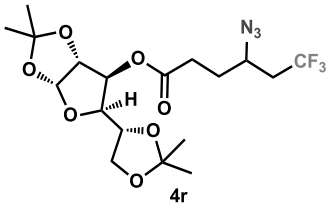
(*2S*)-1-(4-Azido-6,6,6-trifluorohexyl) 4-cyclohexyl 2-((*tert*-butoxycarbonyl)amino) succinate 4p: According to the general procedure, the reaction was carried out with (*S*)-4-cyclohexyl 1-pent-4-en-1-yl 2-((*tert*-butoxycarbonyl)amino)succinate **3p** (76.5 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4p** was obtained by flash column chromatography on silica gel using PE and EA (5:1, v:v, R_f = 0.5) as an eluent in 63% yield (62.7 mg, *dr* = 1:1, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (d, J = 8.8 Hz, 1H), 4.78 – 4.61 (m, 1H), 4.52 – 4.41 (m, 1H), 4.20 – 4.02 (m, 2H), 3.66 – 3.53 (m, 1H), 2.93 – 2.87 (m, 1H), 2.75 – 2.70 (m, 1H), 2.27 – 2.18 (m, 2H), 1.96 – 1.55 (m, 8H), 1.52 – 1.42 (m, 1H), 1.38 (s, 9H), 1.37 – 0.92 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 170.4, 155.4, 125.6 (q, J = 277.5 Hz), 80.1, 73.7, 64.7/64.6, 56.4 (q, J = 2.8 Hz), 50.1, 38.58 (q, J = 28.4 Hz)/38.57 (q, J = 28.5 Hz),, 37.1, 31.5, 31.1, 28.3, 25.2, 24.9/24.8, 23.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.09 (t, J = 10.5 Hz); HRMS (ESI^+) calc'd for $C_{21}H_{33}F_3N_4NaO_6$ $[M+Na]^+$: 517.2244, found 517.2241.



4q

(*4R*)-4-Azido-6,6,6-trifluorohexyl 4-((*5S,8R,9S,10S,13R,14S,17S*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate 4q: According to the general procedure, the reaction was carried out with (*R*)-pent-4-en-1-yl 4-((*5S,8R,9S,10S,13R,14S,17S*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-

cyclopenta[*a*]phenanthren-17-yl)pentanoate **3q** (94.8 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4q** was obtained by flash column chromatography on silica gel using PE and EA (1:1, v:v, R_f = 0.4) as an eluent in 73% yield (86.7 mg, *dr* = 1:1, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 – 3.99 (m, 2H), 3.65 – 3.58 (m, 1H), 2.88 – 2.75 (m, 3H), 2.33 – 1.88 (m, 16H), 1.84 – 1.49 (m, 7H), 1.34 (s, 3H), 1.30 – 1.12 (m, 4H), 1.00 (s, 3H), 0.78 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.0 , 209.1, 208.8, 174.0, 125.6 (q, *J* = 277.1 Hz), 63.4, 56.9, 56.4 (q, *J* = 3.0 Hz), 51.8, 49.0, 46.8, 45.6, 45.5, 45.0, 42.8, 38.64 (q, *J* = 28.4 Hz), 38.63, 36.5, 36.0, 35.5, 35.3, 31.4, 30.4, 27.6, 25.1, 25.0, 21.9, 18.6, 11.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.01 (t, *J* = 10.4 Hz); HRMS (ESI^+) calc'd for $C_{30}H_{42}F_3N_3NaO_5$ $[M+Na]^+$: 604.2969, found 604.2971.

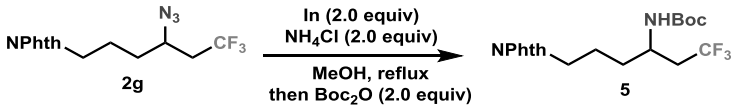


(*3aR,5R,6S,6aR*)-5-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-azido-6,6,6-trifluorohexanoate 4r: According to the general procedure, the reaction was carried out with (*3aR,5R,6S,6aR*)-5-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl pent-4-enoate **3r** (68.3 mg, 0.2 mmol), **IN-3** (8.5 mg, 0.02 mmol, 10 mol %), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv) in 1 mL of EA. The desired product **4r** was obtained by flash column chromatography on silica gel using PE and EA (5:1, v:v, R_f = 0.4) as an eluent in 44% yield (39.5 mg, *dr* = 1:1, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (d, *J* = 3.7 Hz, 1H), 5.24 (d, *J* = 8.3 Hz, 1H), 4.42 (s, 1H), 4.13 (s, 2H), 4.07 – 3.92 (m, 2H), 3.77 – 3.62 (m, 1H), 2.55 – 2.39 (m, 2H), 2.38 – 2.18 (m, 2H), 2.02 – 1.89 (m, 1H), 1.82 – 1.67 (m, 1H), 1.45 (s, 3H), 1.34 (s, 3H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 125.5 (q, *J* = 277.2 Hz), 112.4,

109.50/109.48, 105.09/105.08, 83.4, 79.81/79.78, 76.43/76.36, 72.5/72.4, 67.4, 55.9 – 55.8 (m), 38.7 (q, J = 28.5 Hz), 30.2/30.1, 29.8/29.7, 26.94/26.90, 26.7, 26.2, 25.19/25.17; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 63.98 (t, J = 10.4 Hz); HRMS (ESI^+) calc'd for $C_{18}H_{26}F_3N_3NaO_7$ $[M+Na]^+$: 476.1615, found 476.1611.

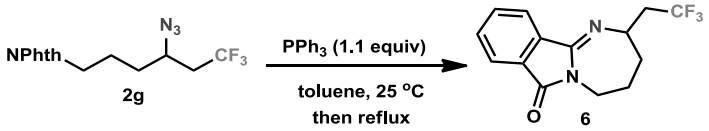
6. Synthetic Application

Synthesis of 2-(4-Amino-6,6,6-trifluorohexyl)isoindoline-1,3-dione 5:



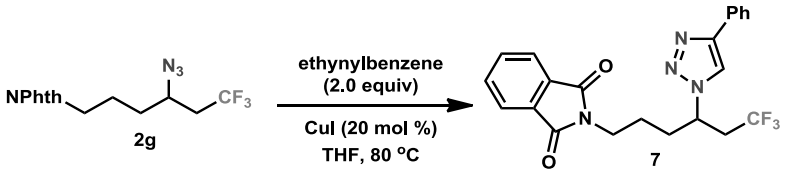
A 10 mL tube equipped with a rubber septum and magnetic stirring bar was charged with **2g** (27.1 mg, 0.1 mmol, 1.0 equiv) and MeOH (1 mL), then indium powder (24.3 mg, 0.2 mmol, 2.0 equiv) and NH_4Cl (11.4 mg, 0.2 mmol, 2.0 equiv) were added. The mixture was refluxed for 2 h. Then the mixture was cooled to room temperature, and added the Boc_2O, the mixture was stirred at room temperature for 6 hours. Then the mixture diluted with EA (5 mL), and filtered through a short pad of celite. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel using PE and EA (8:1, v:v, R_f = 0.2) as an eluent to give **5** in 69% yield (23.7 mg, white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.79 (m, 2H), 7.76 – 7.68 (m, 2H), 4.55 (d, J = 9.1 Hz, 1H), 4.01 – 3.84 (m, 1H), 3.71 (t, J = 7.0 Hz, 2H), 2.38 – 2.20 (m, 2H), 1.86 – 1.69 (m, 2H), 1.65 – 1.51 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 155.1, 134.0, 132.1, 126.1 (q, J = 277.6 Hz), 123.3, 79.8, 45.6, 38.5 (q, J = 27.0 Hz), 37.4, 31.8, 28.3, 25.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 62.85 (t, J = 11.1 Hz); HRMS (ESI^+) calc'd for $C_{19}H_{24}F_3N_2O_4$ $[M+H]^+$: 401.1660, found 401.1683; m.p. = 142 – 143 ^{o}C.

Synthesis of 2-(2,2,2-Trifluoroethyl)-4,5-dihydro-2*H*-[1,3]diazepino[2,1-*a*]isoindol-7(3*H*)-one 6:



A 10 mL tube equipped with a rubber septum and magnetic stirring bar was charged with **2g** (36.5 mg, 0.1 mmol, 1.0 equiv), PPh_3 (30.1 mg, 0.11 mmol, 1.1 equiv) and toluene (1 mL). The mixture was stirred at room temperature for 12 h, then refluxed for another 18 h. The mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (10:1, v:v, R_f = 0.3) as an eluent to give **6** in 44% yield (12.3 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.60 – 7.48 (m, 2H), 4.34 – 4.21 (m, 1H), 3.99 – 3.89 (m, 1H), 3.87 – 3.80 (m, 1H), 2.77 – 2.57 (m, 1H), 2.48 – 2.24 (m, 1H), 2.20 – 2.09 (m, 1H), 2.02 – 1.81 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 149.7, 136.3, 133.1, 131.5, 130.5, 126.4 (q, *J* = 277.3 Hz), 122.8, 121.8, 52.9 (q, *J* = 3.0 Hz), 42.2 (q, *J* = 26.6 Hz), 40.9, 33.5, 24.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 63.26 (t, *J* = 11.1 Hz); HRMS (ESI^+) calc'd for $C_{14}H_{14}F_3N_2O$ $[M+H]^+$: 283.1053, found 283.1057.

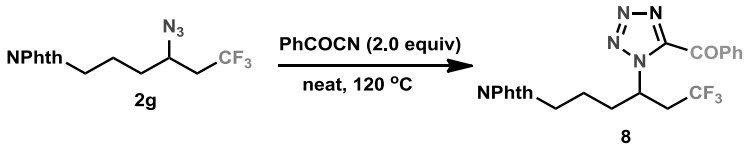
Synthesis of 2-(6,6,6-Trifluoro-4-(4-phenyl-1*H*-1,2,3-triazol-1-yl)hexyl)isoindoline-1,3-dione 7:



A 10 mL tube equipped with a rubber septum and magnetic stirring bar was charged with **2g** (32.6 mg, 0.1 mmol, 1.0 equiv), ethynylbenzene (20.4 mg, 0.2 mmol, 2.0 equiv), CuI (4.8 mg, 0.02 mmol, 20 mol %) and THF (1 mL). The mixture was stirred at 80 °C for 12 h. Then the mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (3:1, v:v, R_f = 0.3) as an eluent to give **7** in 50% yield (21.4 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.79 (m,

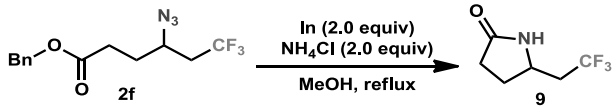
5H), 7.74 – 7.67 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 4.89 – 4.83 (m, 1H), 3.68 (t, *J* = 6.8 Hz, 2H), 3.13 – 2.95 (m, 1H), 2.81 – 2.59 (m, 1H), 2.29 – 2.19 (m, 1H), 2.05 – 1.93 (m, 1H), 1.76 – 1.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 147.6, 134.2, 131.9, 130.3, 128.9, 128.3, 125.8, 125.2 (q, *J* = 278.4 Hz), 123.4, 119.9, 55. 5 (q, *J* = 2.7 Hz), 39.4 (q, *J* = 28.9 Hz), 36.6, 32.6, 24.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.71 (t, *J* = 10.2 Hz); HRMS (ESI^+) calc'd for $C_{22}H_{20}F_3N_4O_2$ $[M+H]^+$: 429.1533, found 429.1529.

Synthesis of 2-(4-(5-Benzoyl-1*H*-tetrazol-1-yl)-6,6,6-trifluorohexyl)isoindoline-1,3-dione 8:



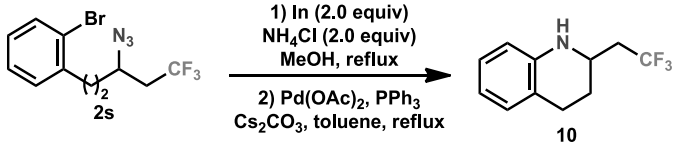
A 10 mL tube was equipped with a rubber septum and magnetic stirring bar was charged with **2g** (33.6 mg, 0.1 mmol, 1.0 equiv) and benzoyl cyanide (65.9 mg, 0.5 mmol, 5.0 equiv). The mixture was stirred at 120 °C for 36 h. Then the mixture was cooled to room temperature and purified by flash column chromatography on silica gel using PE and EA (1:1, v:v, R_f = 0.3) as an eluent to give **8** in 81% yield (34.8 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.20 (m, 2H), 7.77 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.69 – 7.62 (m, 3H), 7.53 – 7.45 (m, 2H), 5.74 – 5.55 (m, 1H), 3.88 – 3.55 (m, 2H), 3.20 – 2.92 (m, 1H), 2.79 – 2.53 (m, 1H), 2.34 – 2.25 (m, 1H), 2.08 – 1.94 (m, 1H), 1.76 – 1.58 (m, 1H), 1.50 – 1.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 168.3, 150.2, 135.4, 134.9, 134.1, 131.9, 131.2, 128.9, 125.0 (q, *J* = 277.1 Hz), 123.4, 54.3 (q, *J* = 3.0 Hz), 39.3 (q, *J* = 29.1 Hz), 36.7, 32.6, 24.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.91 (t, *J* = 10.2 Hz); HRMS (ESI^+) calc'd for $C_{22}H_{19}F_3N_5O_3$ $[M+H]^+$: 458.1435, found 458.1428.

Synthesis of 5-(2,2,2-Trifluoroethyl)pyrrolidin-2-one 9:



A 10 mL tube equipped with a rubber septum and magnetic stirring bar was charged with **2g** (38.5 mg, 0.2 mmol, 1.0 equiv) and MeOH (2 mL), then indium powder (57.4 mg, 0.4 mmol, 2.0 equiv) and NH_4Cl (10.7 mg, 0.4 mmol, 2.0 equiv) were added. The mixture refluxed for 2 h. Then the mixture was cooled to room temperature, diluted with EA (5 mL), and filtered through a short pad of celite. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (3:1, v:v, R_f = 0.3) as an eluent to give **9** in 92% yield (19.8 mg, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 – 3.85 (m, 1H), 2.39 – 2.18 (m, 5H), 1.84 – 1.69 (m, 1H). The spectroscopic characterization data were consistent with those reported in the literature.[3]

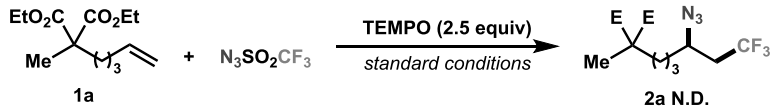
Synthesis of 2-(2,2,2-Trifluoroethyl)-1,2,3,4-tetrahydroquinoline 10:



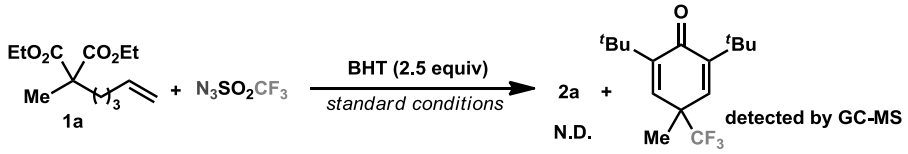
A 10 mL sealed tube was equipped with a rubber septum and magnetic stirring bar and charged with **2s** (32.5 mg, 0.1 mmol, 1.0 equiv) and MeOH (1 mL), then indium powder (23.3 mg, 0.2 mmol, 2.0 equiv) and NH_4Cl (10.7 mg, 0.2 mmol, 2.0 equiv) were added. The mixture was refluxed for 2 h. Then the mixture was cooled to room temperature, diluted with EA (5 mL), and filtered through a short pad of celite. The solvent was removed under reduced pressure to give a crude amine product directly used for the next step without further purification. The crude amine product was transferred into another 10 mL tube, then $Pd(OAc)_2$ (4.5 mg, 2 mol %), PPh_3 (15.7 mg, 6 mol %), Cs_2CO_3 (65.2 mg, 2.0 equiv), and toluene (1 mL) were added. The tube was sealed and refluxed for 2 h. Then the mixture was cooled to room temperature, diluted with EA (5 mL), and filtered through a short pad of celite. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (10:1, v:v, R_f = 0.3) as an eluent to give **10** in 65% yield (11.9 mg, colorless

oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 – 6.82 (m, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 7.9 Hz, 1H), 5.97 (brs, 1H), 3.67 – 3.61 (m, 1H), 2.89 – 2.72 (m, 1H), 2.75 – 2.63 (m, 1H), 2.39 – 2.13 (m, 2H), 2.05 – 1.85 (m, 1H), 1.80 – 1.56 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 129.4, 127.0, 126.7 (q, *J* = 278.2 Hz), 120.7, 118.1, 114.8, 46.0 (q, *J* = 2.8 Hz), 40.3 (q, *J* = 26.3 Hz), 28.2, 25.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.30 (t, *J* = 11.1 Hz).

7. Mechanistic Investigation

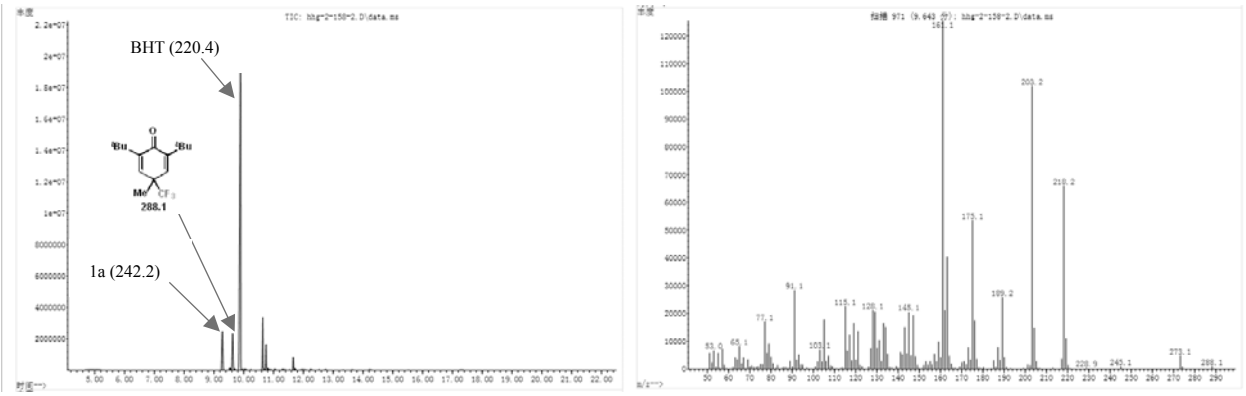


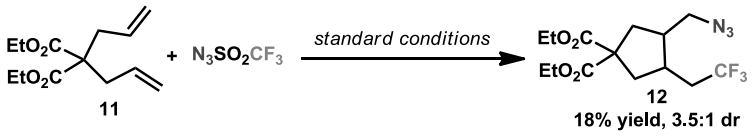
A 10 mL sealed tube equipped with a rubber septum and magnetic stirring bar was charged with **IN-3** (8.4 mg, 0.02 mmol, 10 mol %). After the tube was evacuated and backfilled with argon 3 times, substrate **1a** (48.6 mg, 0.2 mmol, 1.0 equiv), $N_3SO_2CF_3$ (0.5 mL, 1 M in *n*-hexane, 0.5 mmol, 2.5 equiv), TEMPO (2,2,6,6-tetramethyl-1-piperinedinyloxy, 78.1 mg, 0.5 mmol, 2.5 equiv) and EA (1 mL) were added under an argon atmosphere. The mixture was sealed and stirred at 80 °C for 12 h. After the mixture was cooled to room temperature, a portion of the mixture was took out for ^{19}F NMR measurement with trifluoromethyl benzene as an internal standard. Meanwhile, GC-MS analysis of the reaction mixture was carried out. No desired product was observed, which indicates that the addition of TEMPO completely inhibits the azidotrifluoromethylation reaction.



A 10 mL tube equipped with a rubber septum and magnetic stirring bar was charged with **IN-3** (8.4 mg, 0.02 mmol, 10 mol %). After the tube was evacuated and backfilled with argon 3 times, **1a** (48.7 mg, 0.2 mmol, 1.0 equiv), $N_3SO_2CF_3$ (0.5 mL, 1 M in hexane, 0.5 mmol, 2.5 equiv), BHT (2,6-di-*tert*-butyl-4-methylphenol, 110.2 mg, 0.5 mmol, 2.5 equiv) and EA (1 mL) were added under an argon atmosphere. The mixture was sealed and stirred at 80 °C for 12 h. The mixture was cooled to room temperature.

GC-MS analysis of the mixture revealed that no desired product was formed, and the mass of BHT-CF_3 adduct was detected (mw: 288.1).





A 10 mL tube equipped with a rubber septum and magnetic stirring bar was charged with **IN-3** (8.4 mg, 0.02 mmol, 10 mol %). After the tube was evacuated and backfilled with argon 3 times, **11** (48.3 mg, 0.2 mmol, 1.0 equiv), $N_3SO_2CF_3$ (0.5 mL, 1 M in hexane, 0.5 mmol, 2.5 equiv) and EA (1 mL) were added under an argon atmosphere. The mixture was sealed and stirred at 80 ^oC for 12 h. The mixture was cooled to room temperature. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using PE and EA (20:1, v:v, R_f = 0.4) as an eluent to give product **12** in 18% yield (13.1 mg, *dr* = 3.5:1, colorless oil). The characterization data of the major isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 4.13 (q, *J* = 7.1 Hz, 3H), 3.43 – 3.08 (m, 1H), 2.49 – 2.27 (m, 2H), 2.27 – 2.12 (m, 1H), 2.11 – 1.91 (m, 1H), 1.19 (t, *J* = 6.8 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 172.1, 126.8 (q, *J* = 276.9 Hz), 61.9, 61.8, 58.5, 51.4, 41.0, 38.6, 36.9, 35.2 (q, *J* = 2.6 Hz), 33.6 (q, *J* = 28.3 Hz), 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ – 64.56

(t, J = 10.5 Hz); HRMS (ESI$^+$) calc'd for $C_{14}H_{20}F_3N_3NaO_4$ $[M+Na]^+$: 374.1298, found 374.1299.

8. References

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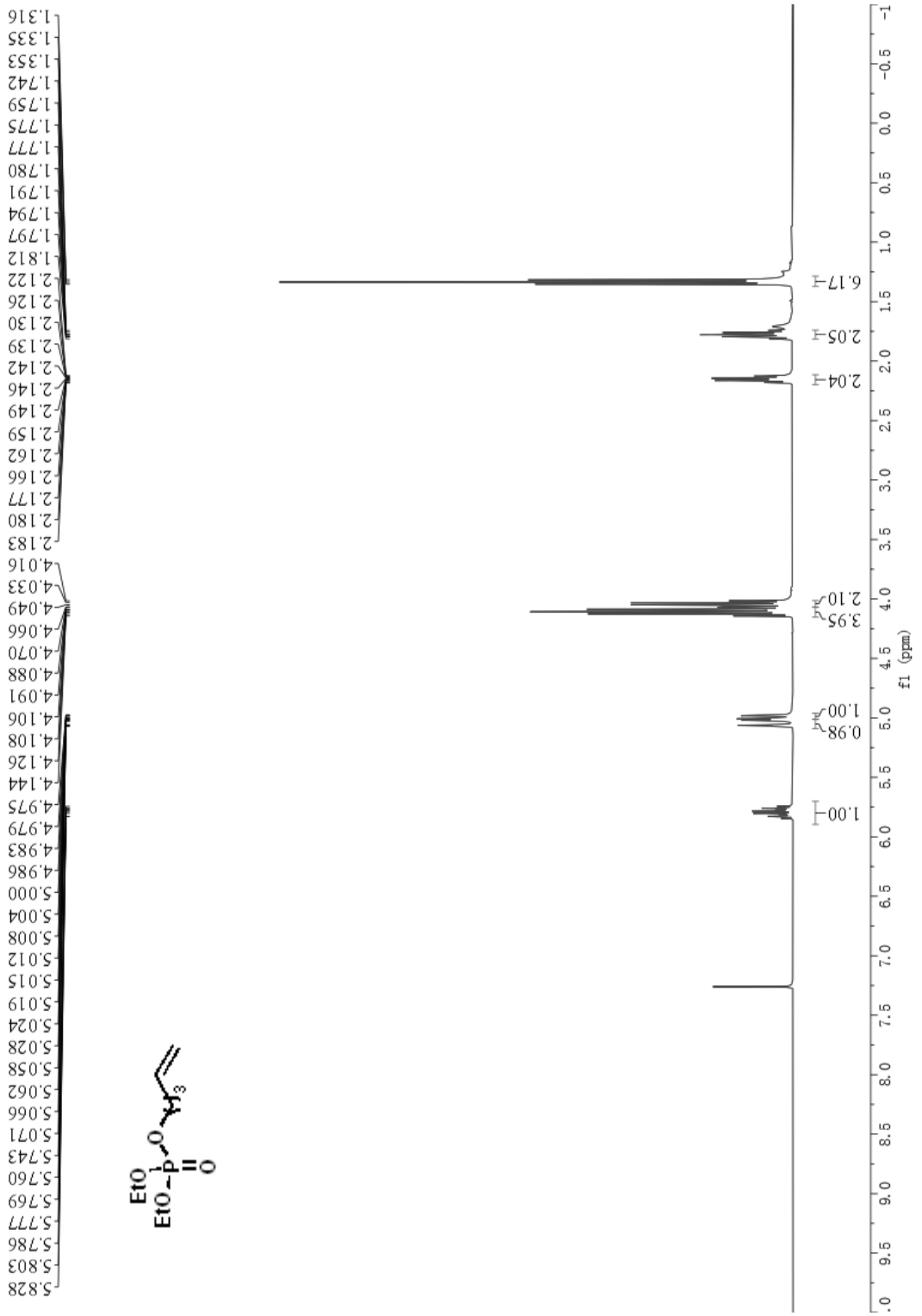
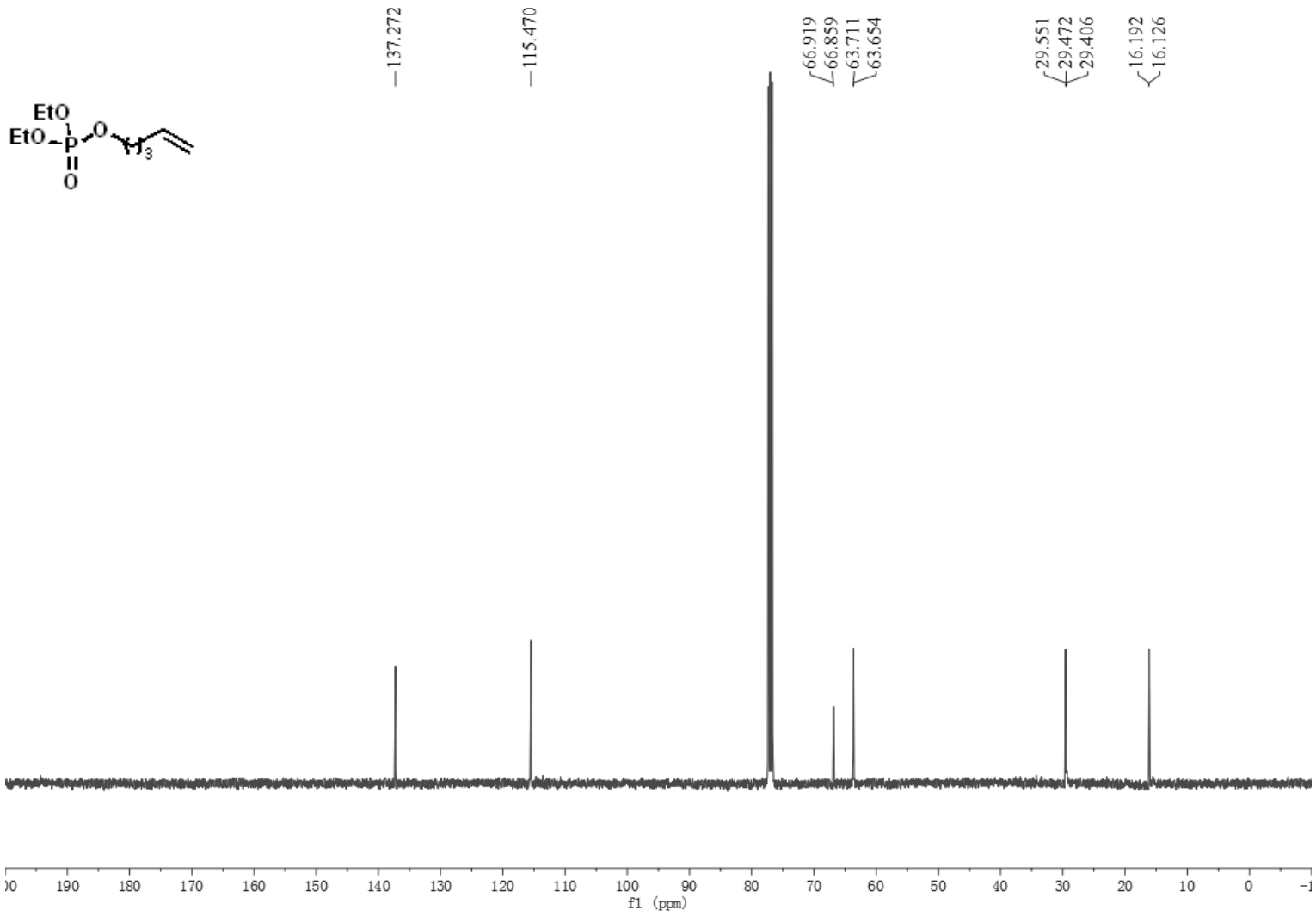
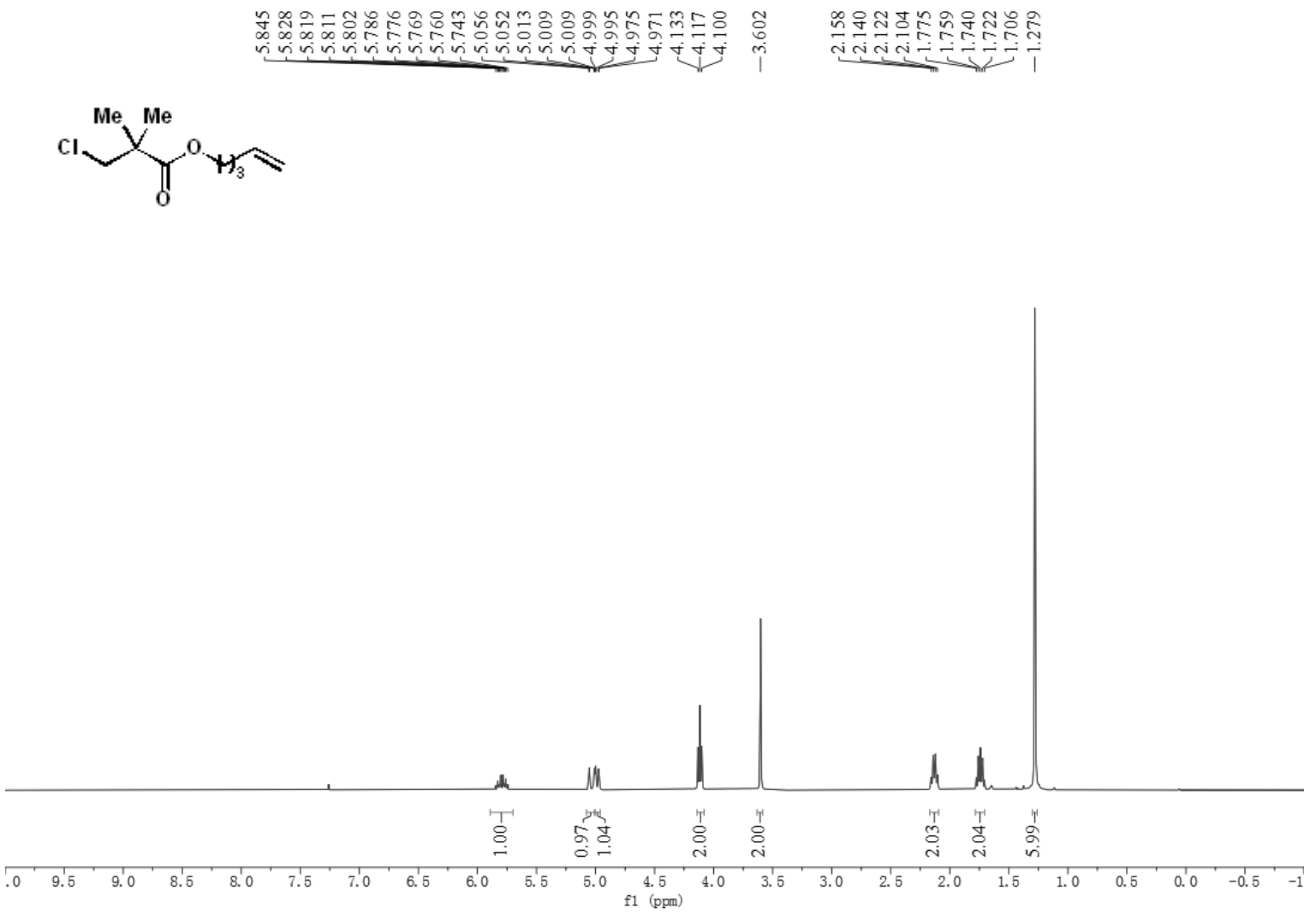
9. NMR Spectra



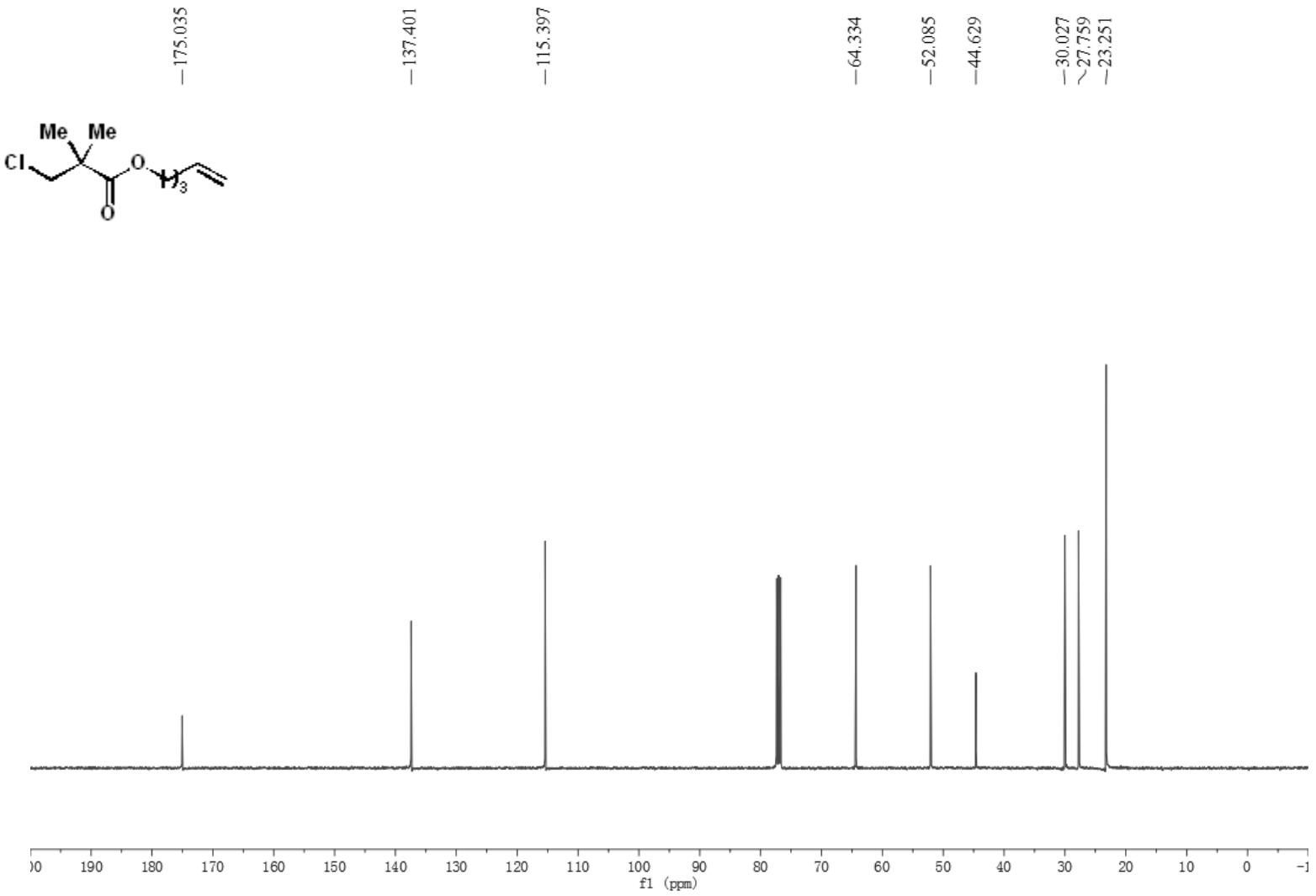
^{1}H NMR (400 MHz, $CDCl_3$) of **1i**



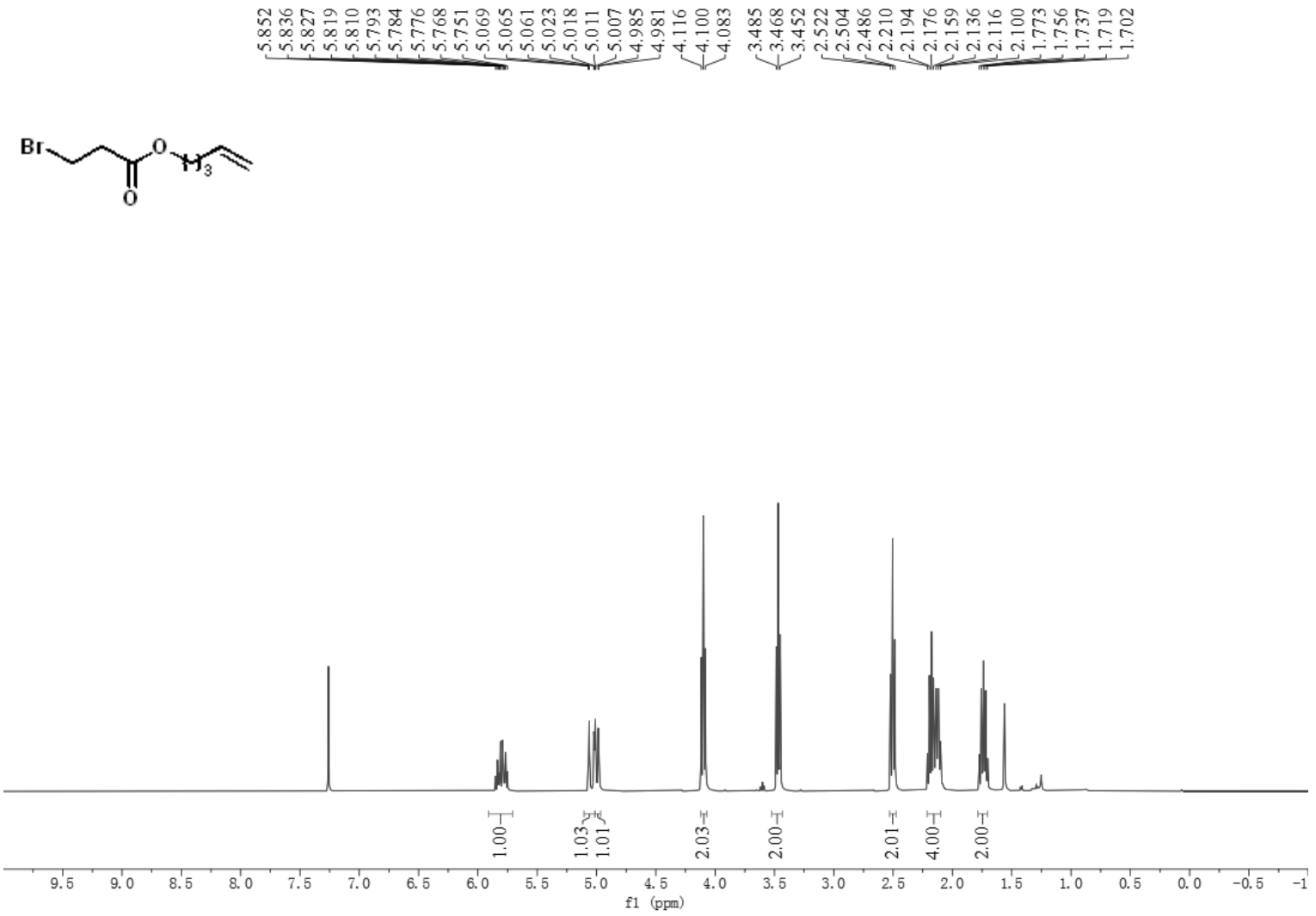
^{13}C NMR (100 MHz, $CDCl_3$) of **1i**



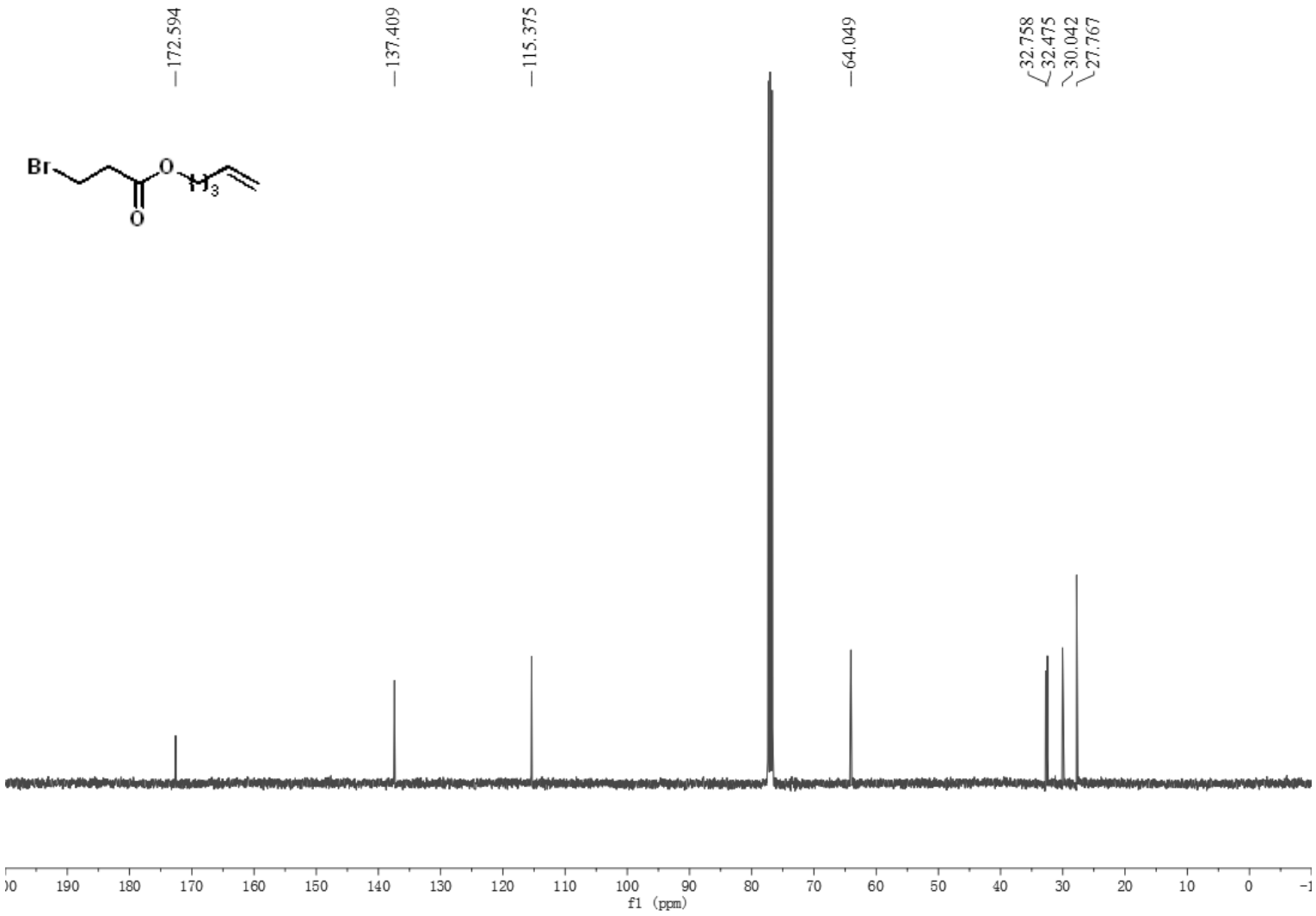
^{1}H NMR (400 MHz, $CDCl_3$) of **1o**



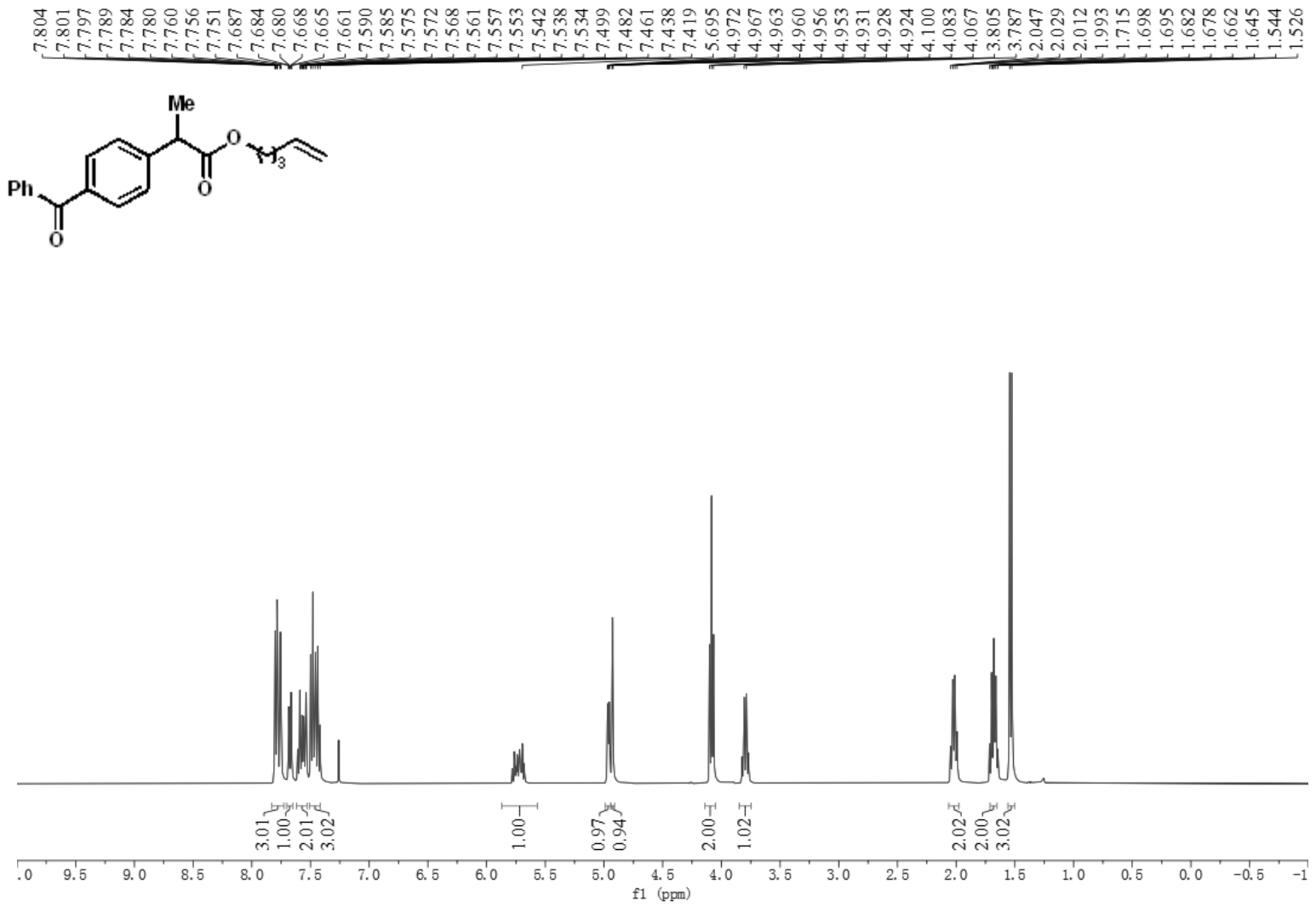
^{13}C NMR (100 MHz, $CDCl_3$) of **1o**



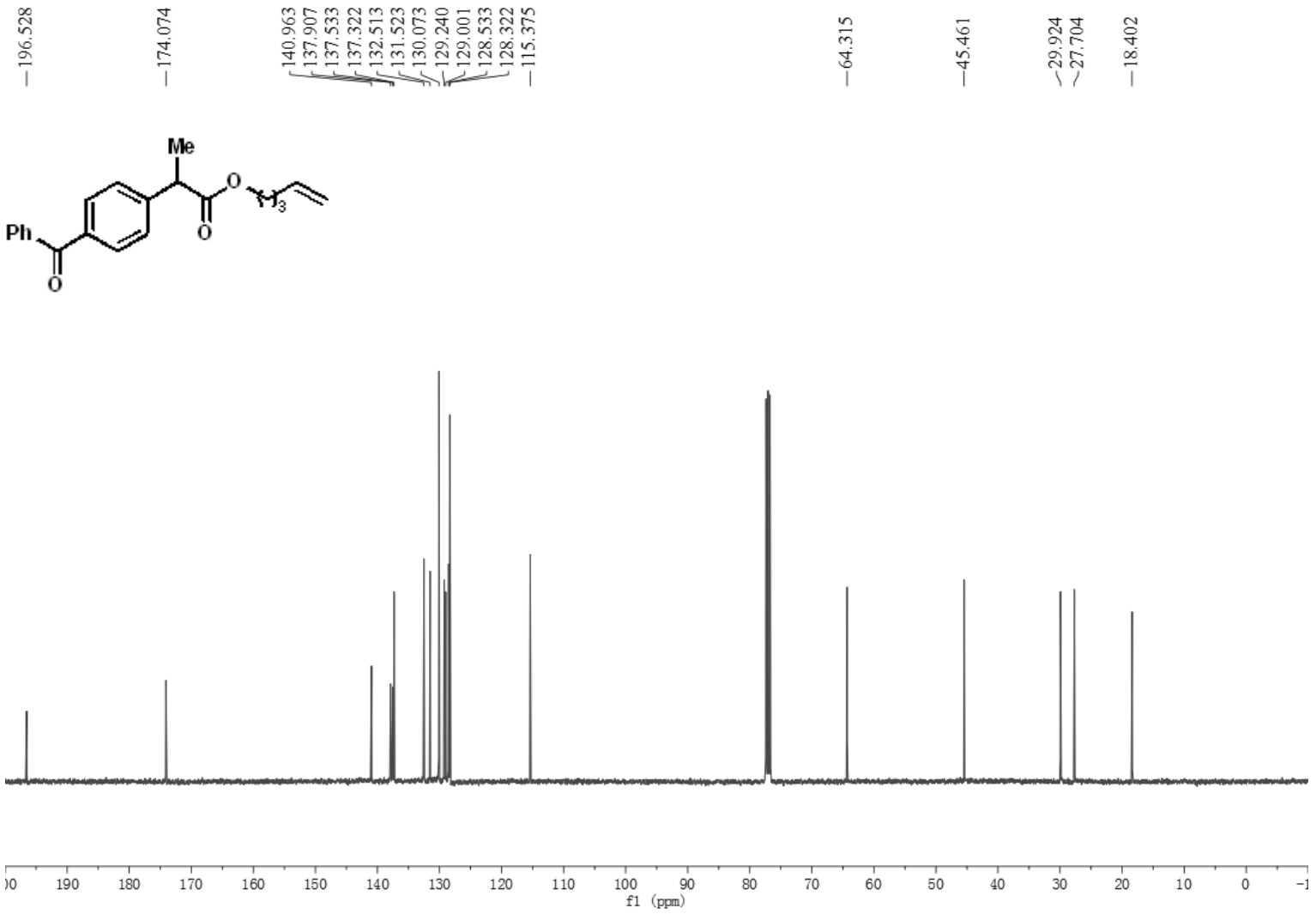
^{1}H NMR (400 MHz, $CDCl_3$) of **1p**



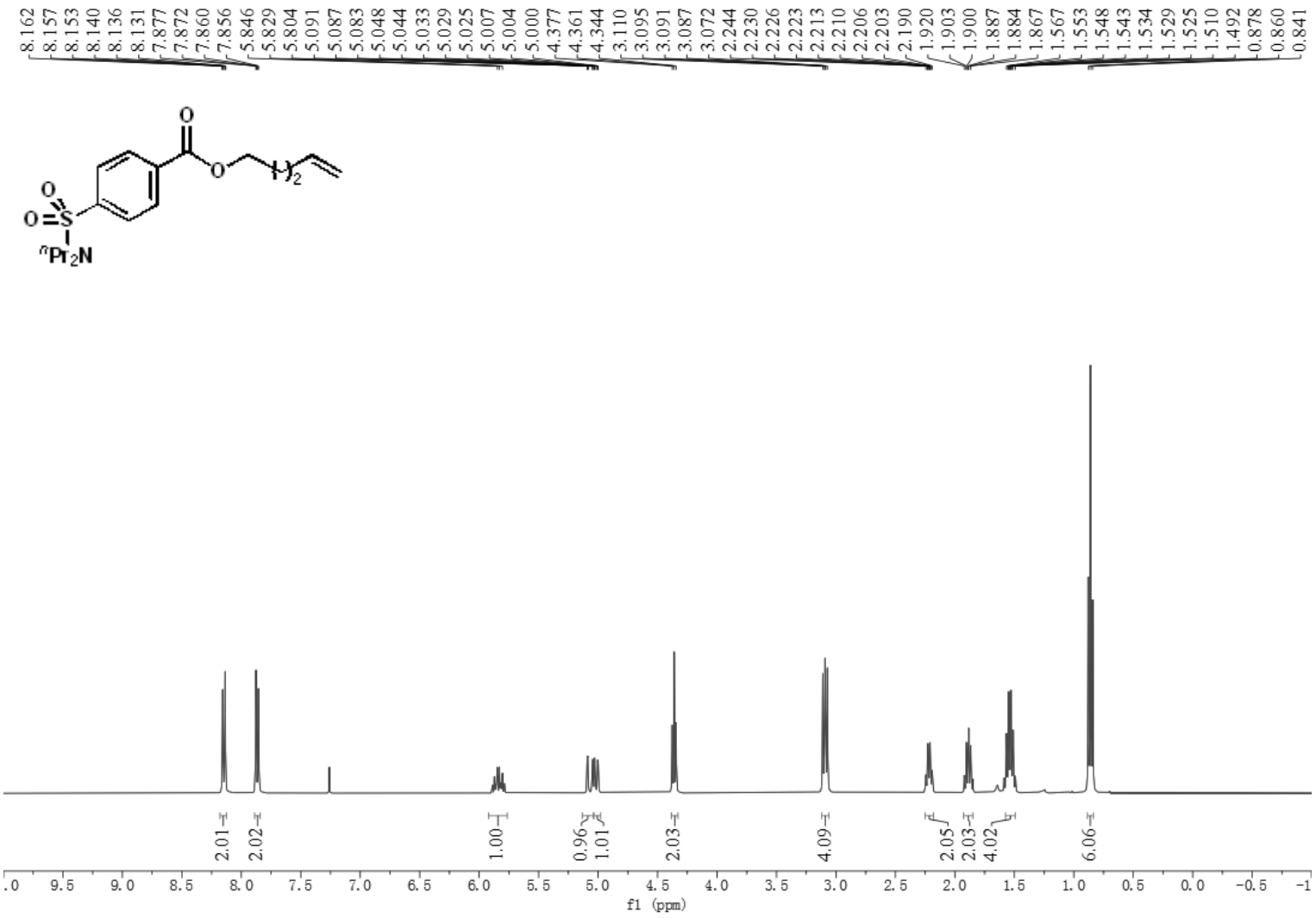
^{13}C NMR (100 MHz, $CDCl_3$) of **1p**



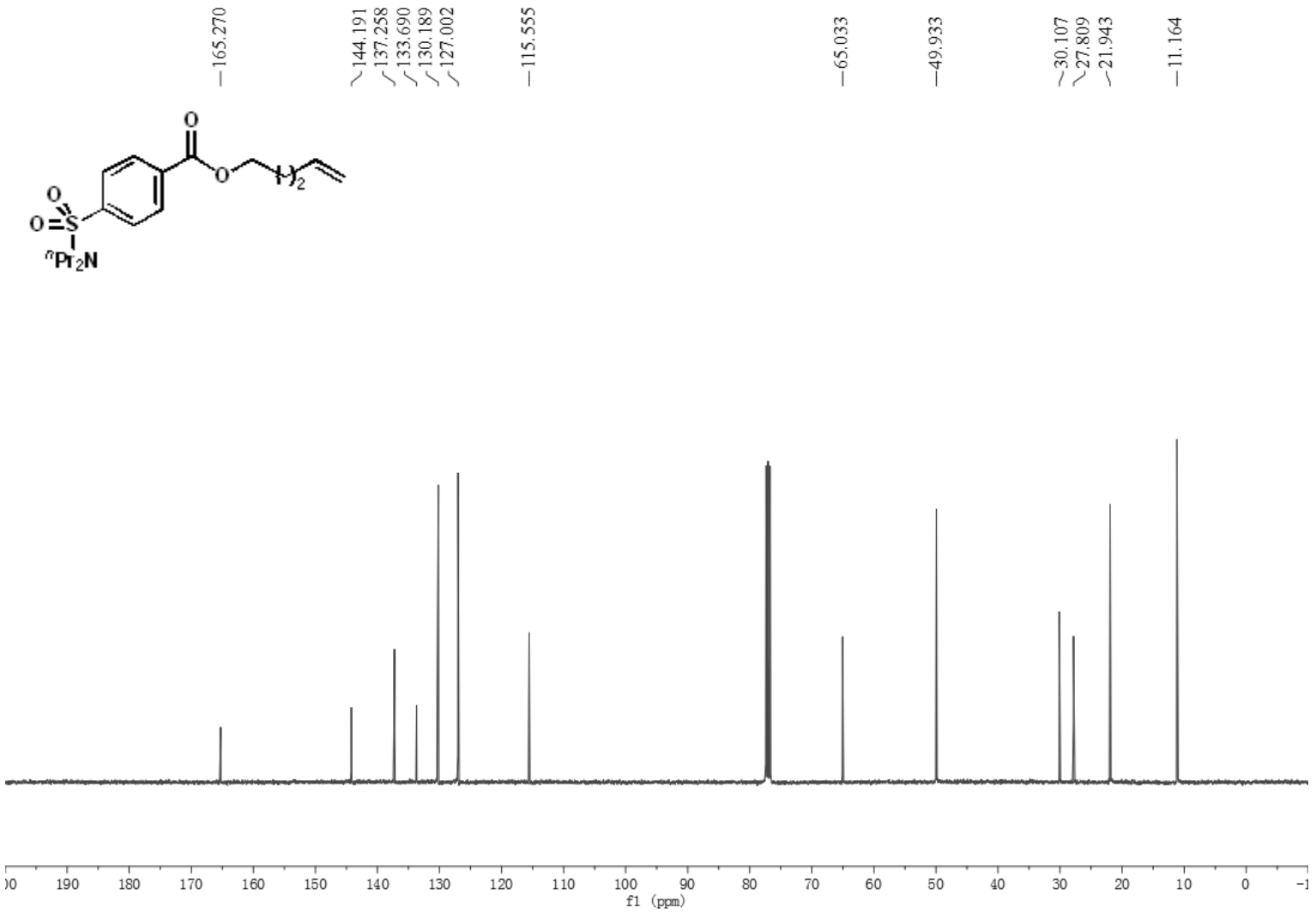
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



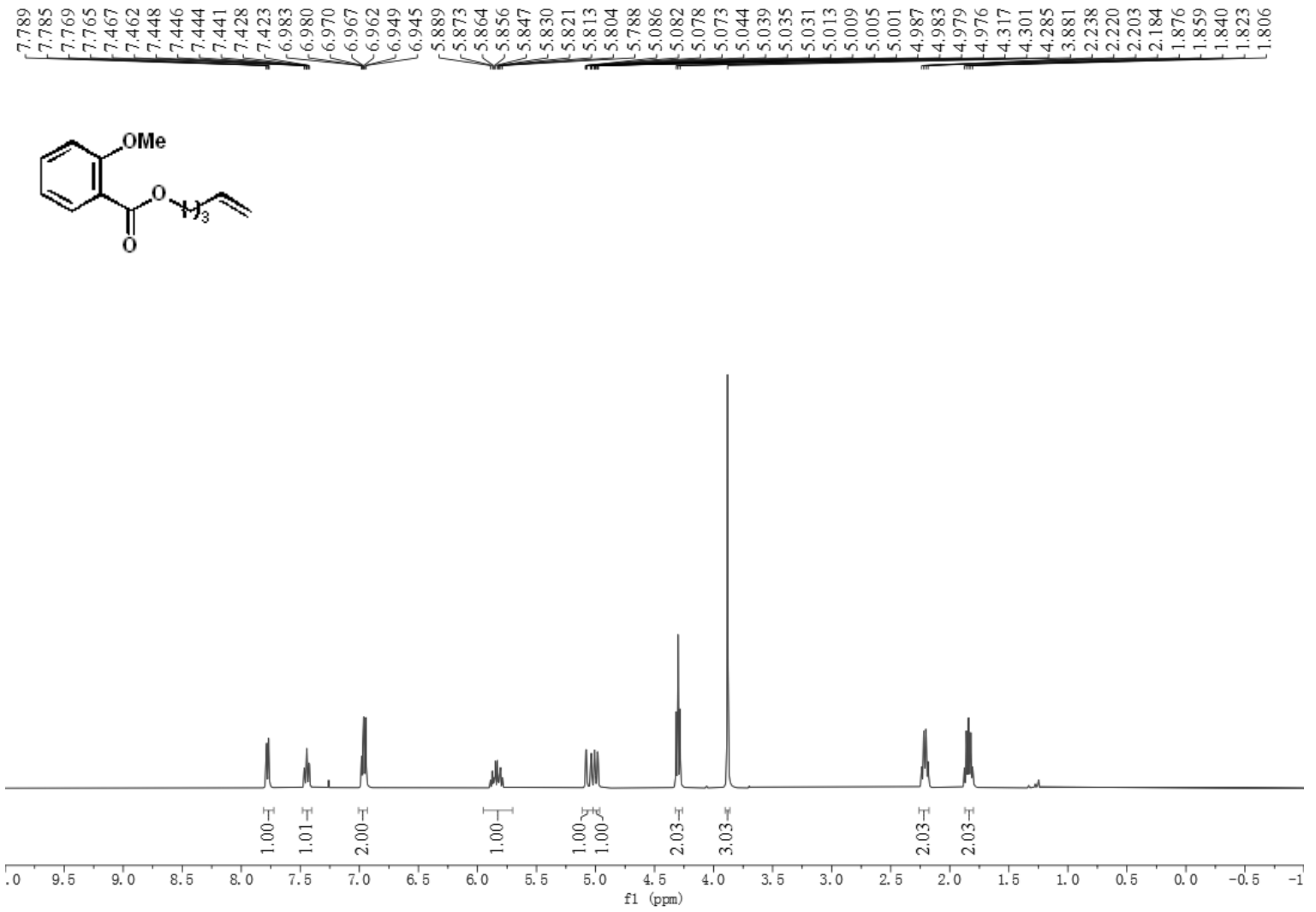
^{13}C NMR (100 MHz, $CDCl_3$) of **3b**



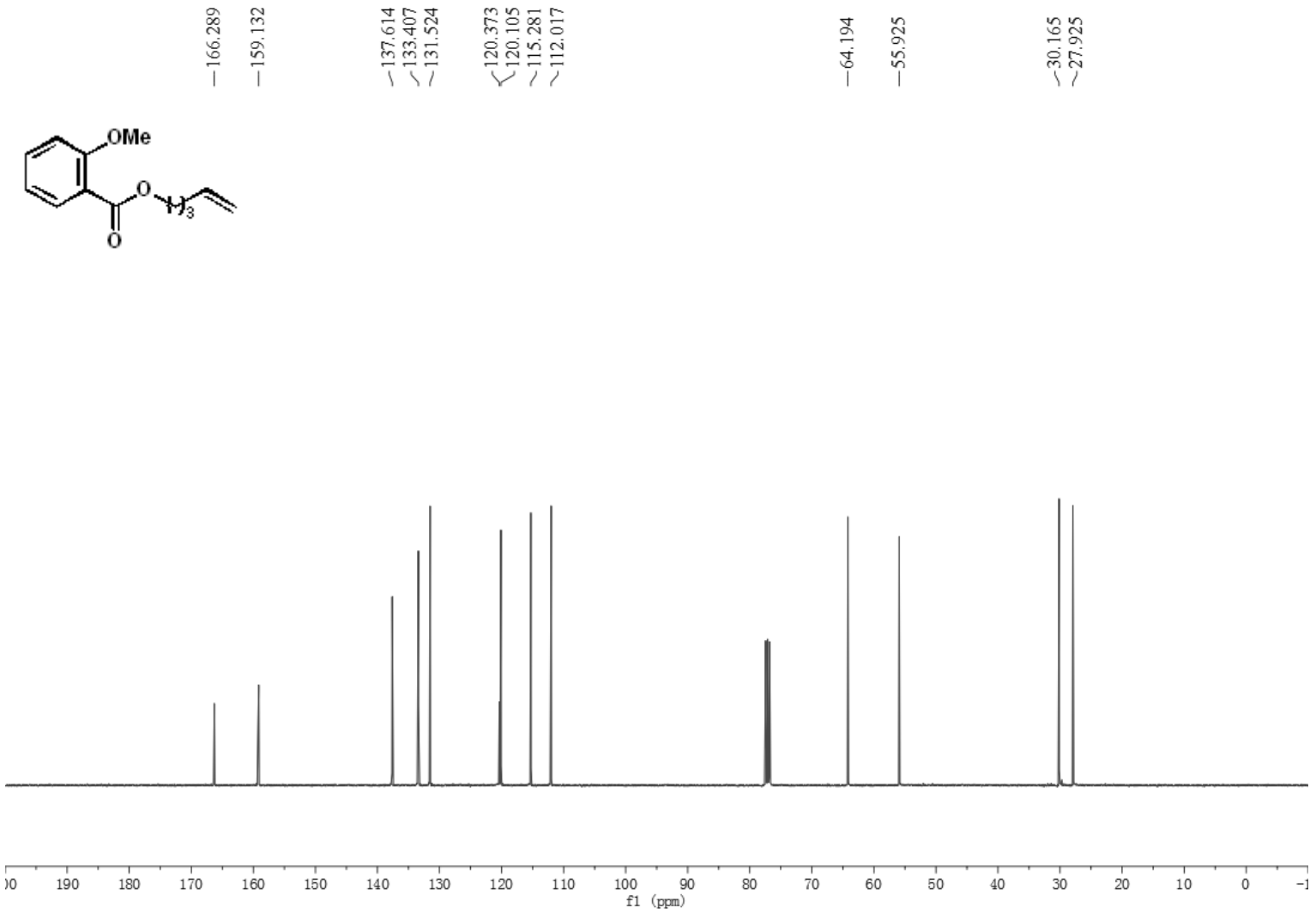
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



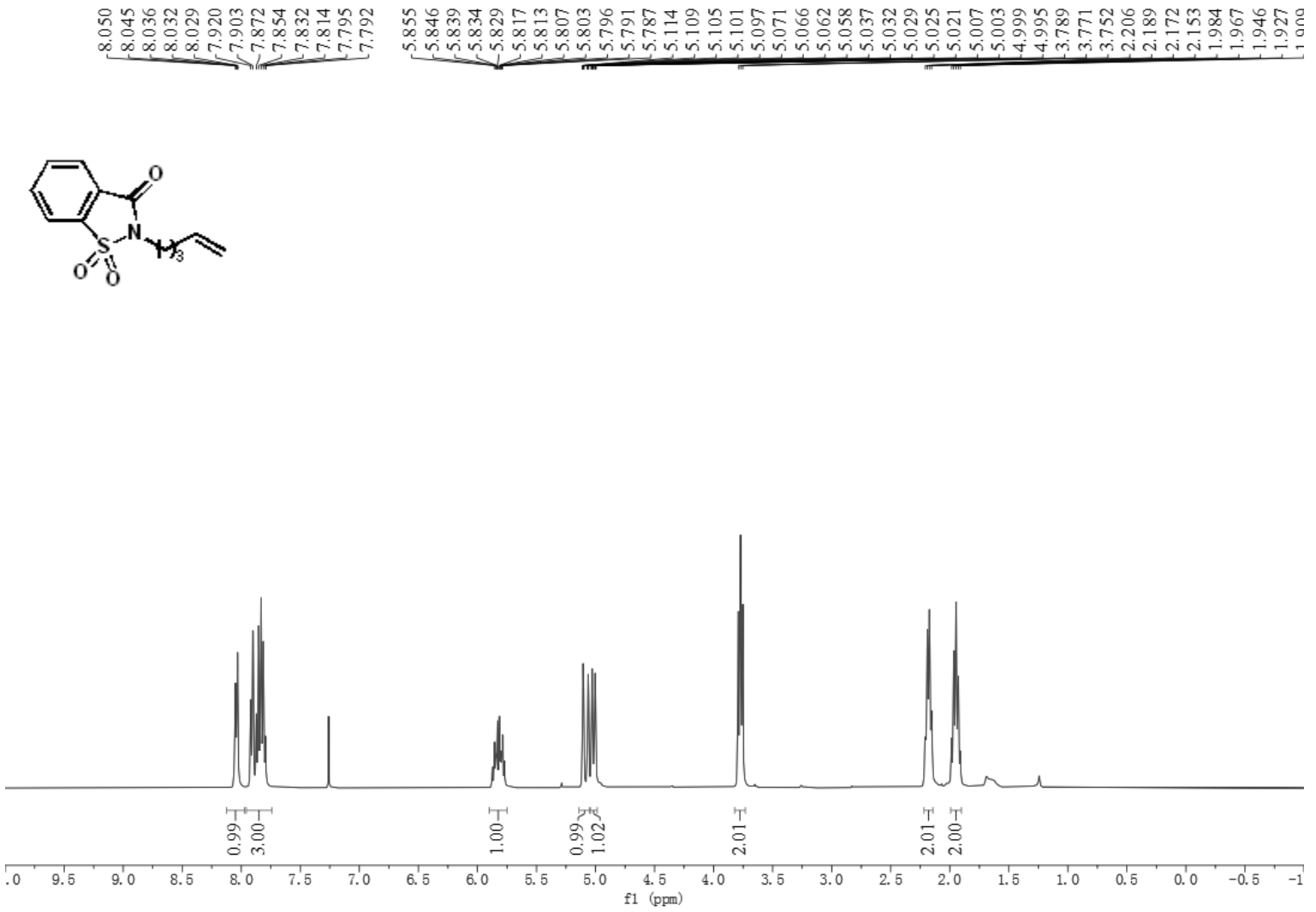
^{13}C NMR (100 MHz, $CDCl_3$) of **3d**



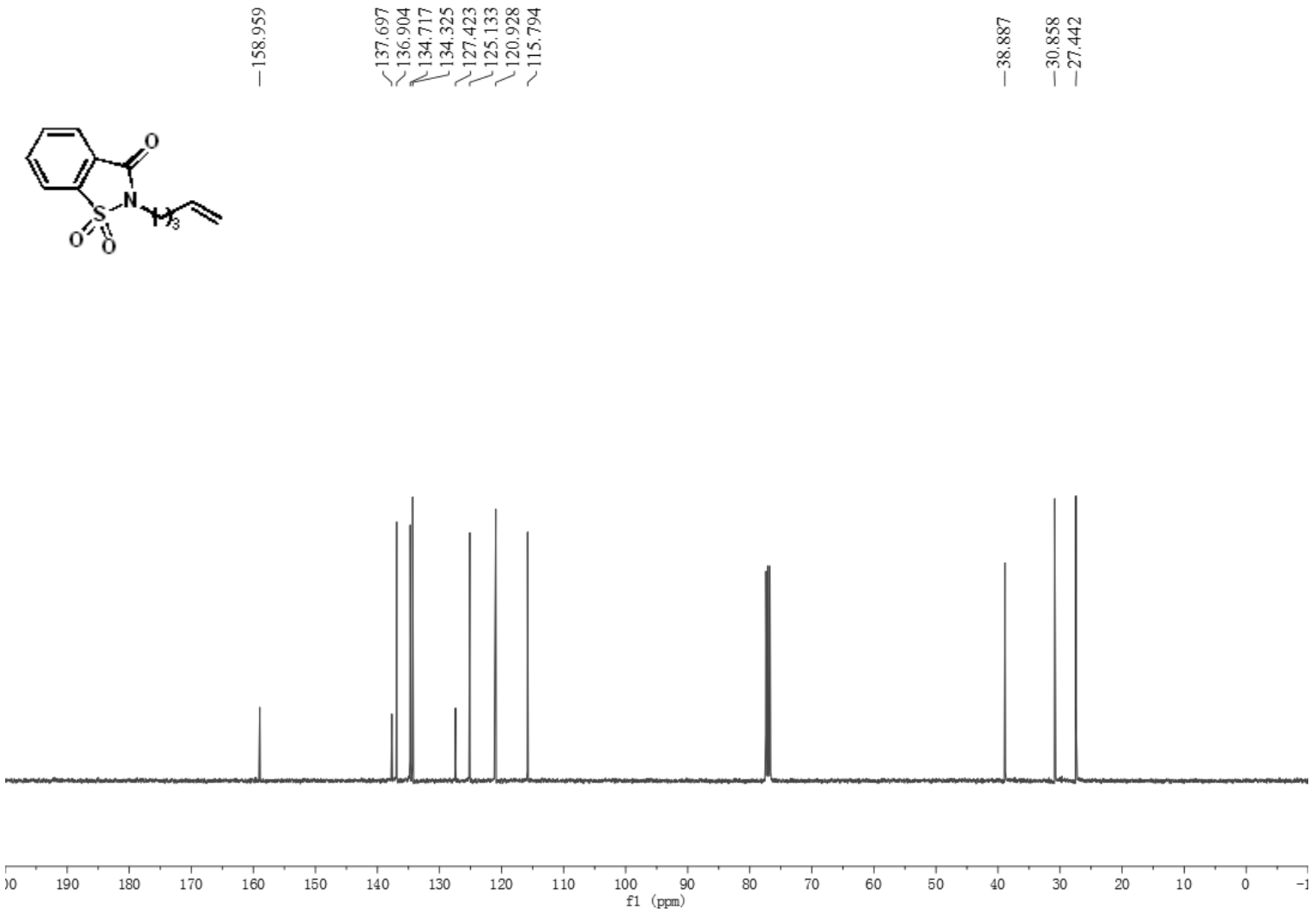
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



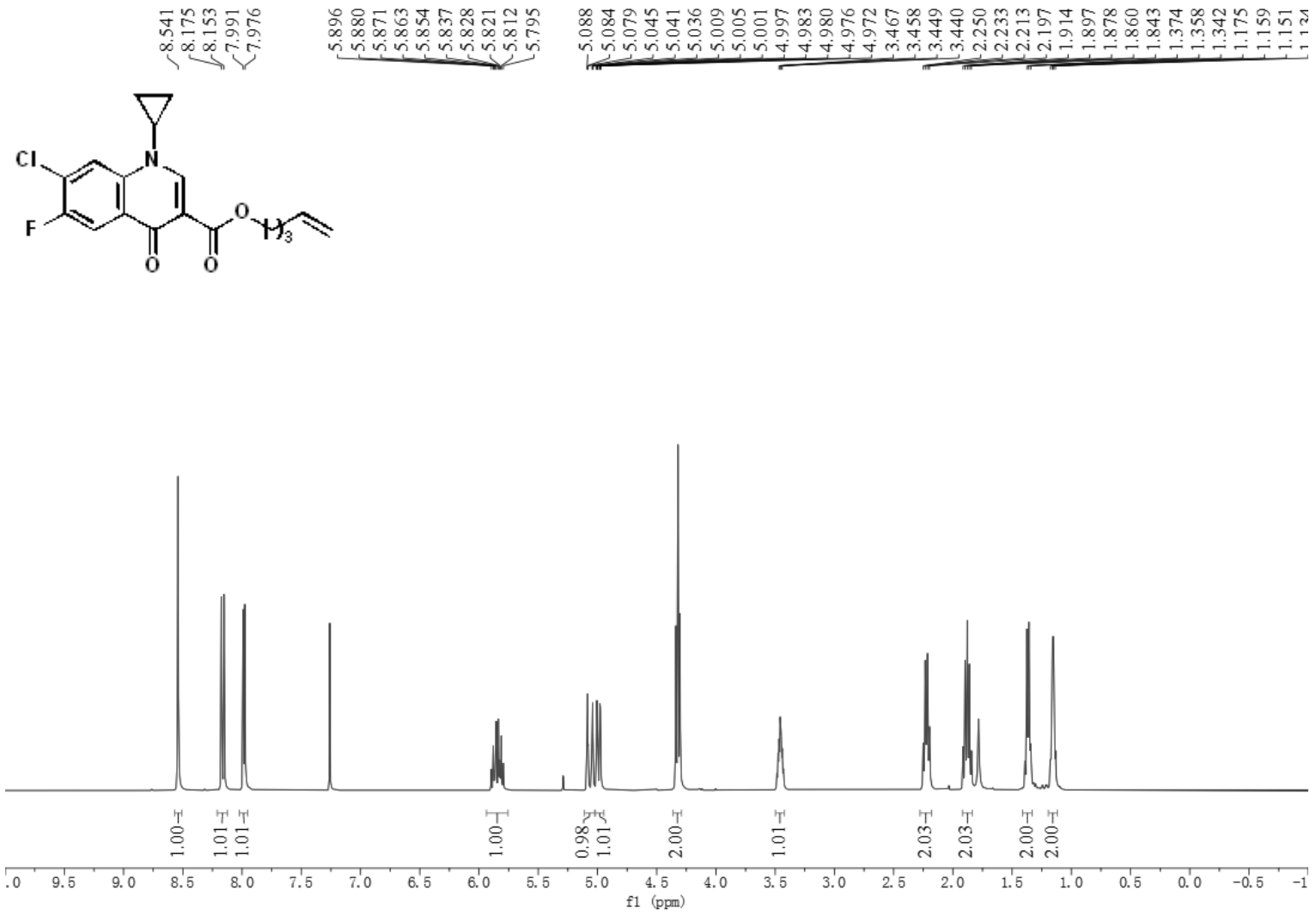
^{13}C NMR (100 MHz, $CDCl_3$) of **3e**



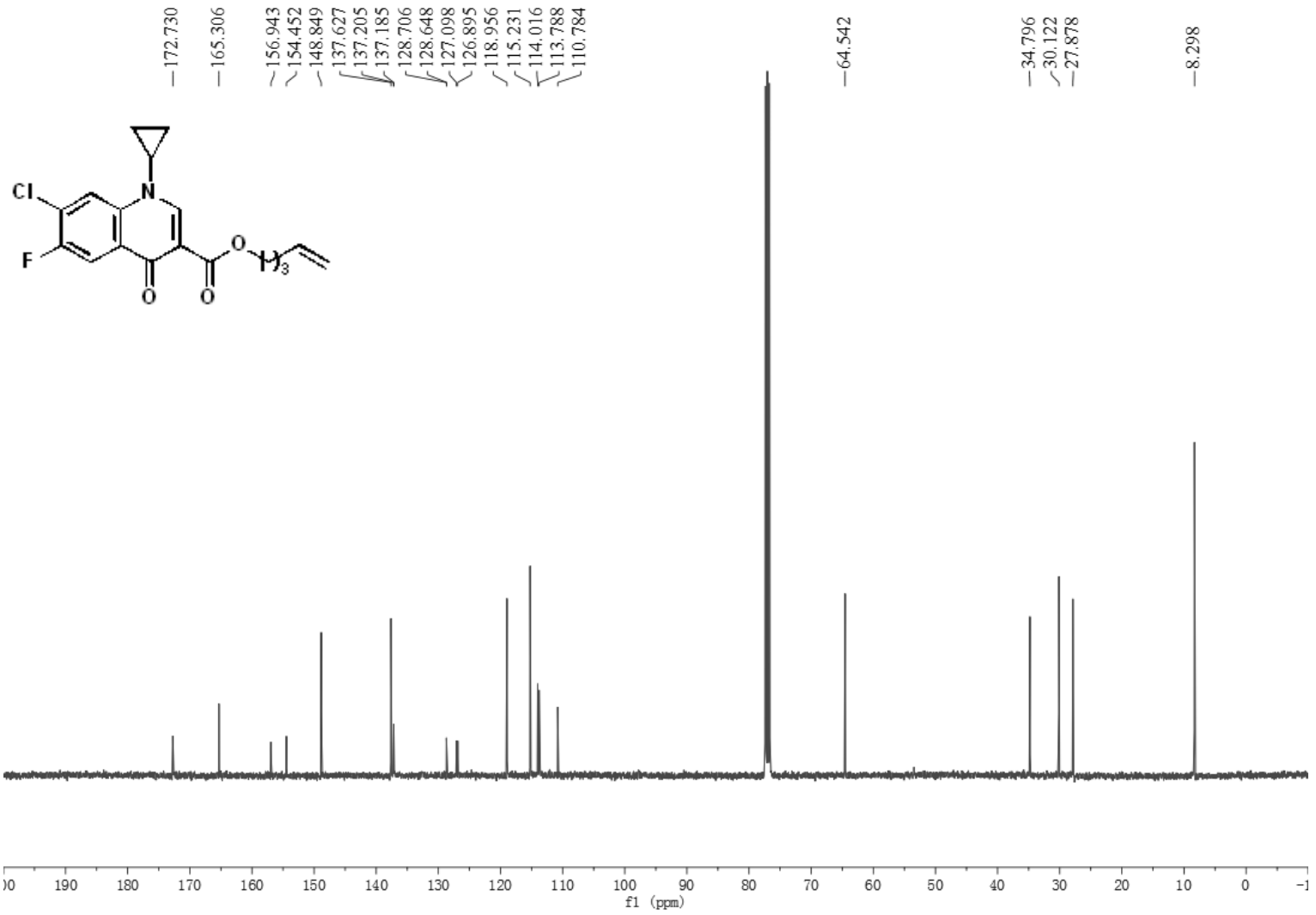
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



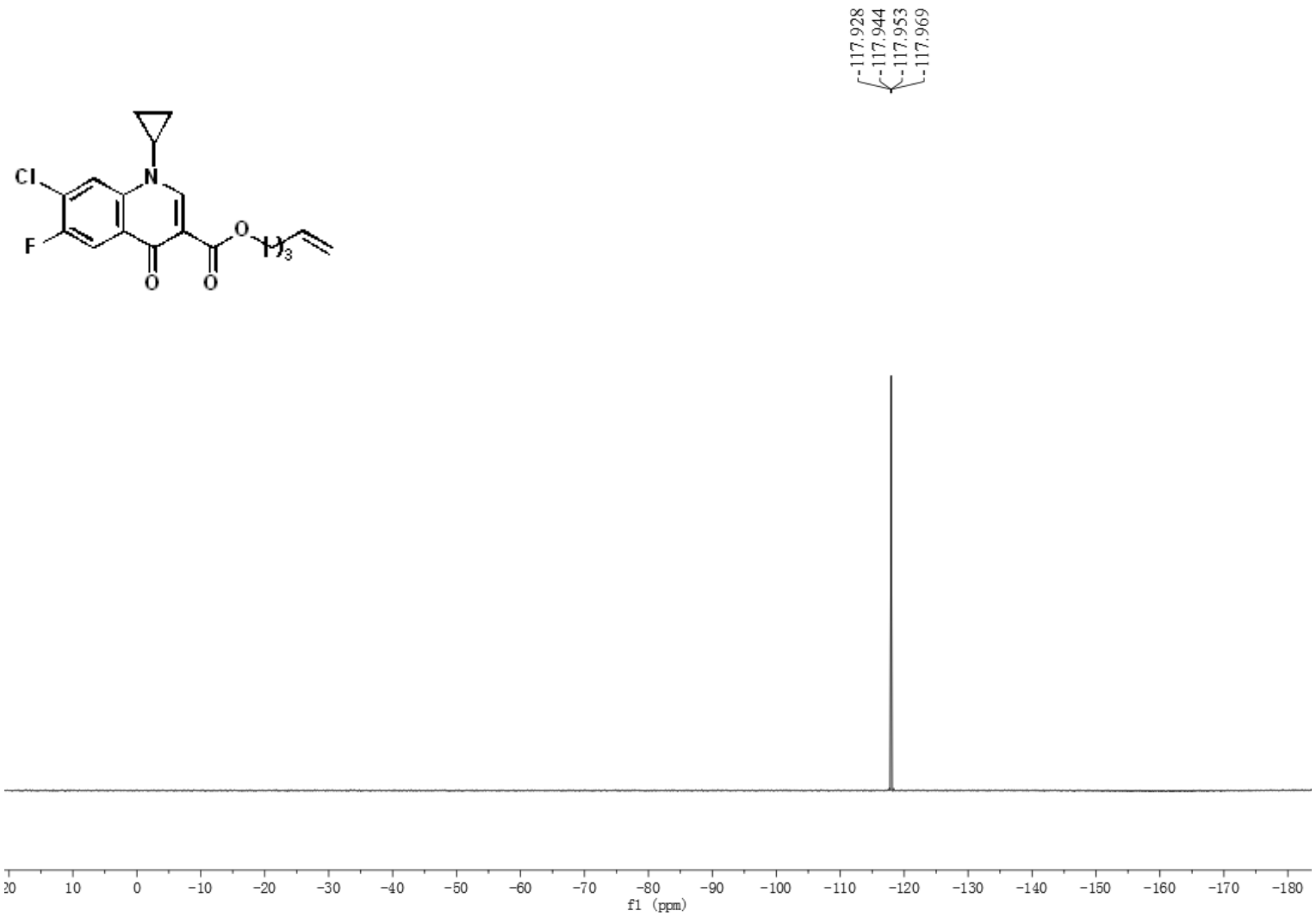
^{13}C NMR (100 MHz, $CDCl_3$) of **3f**



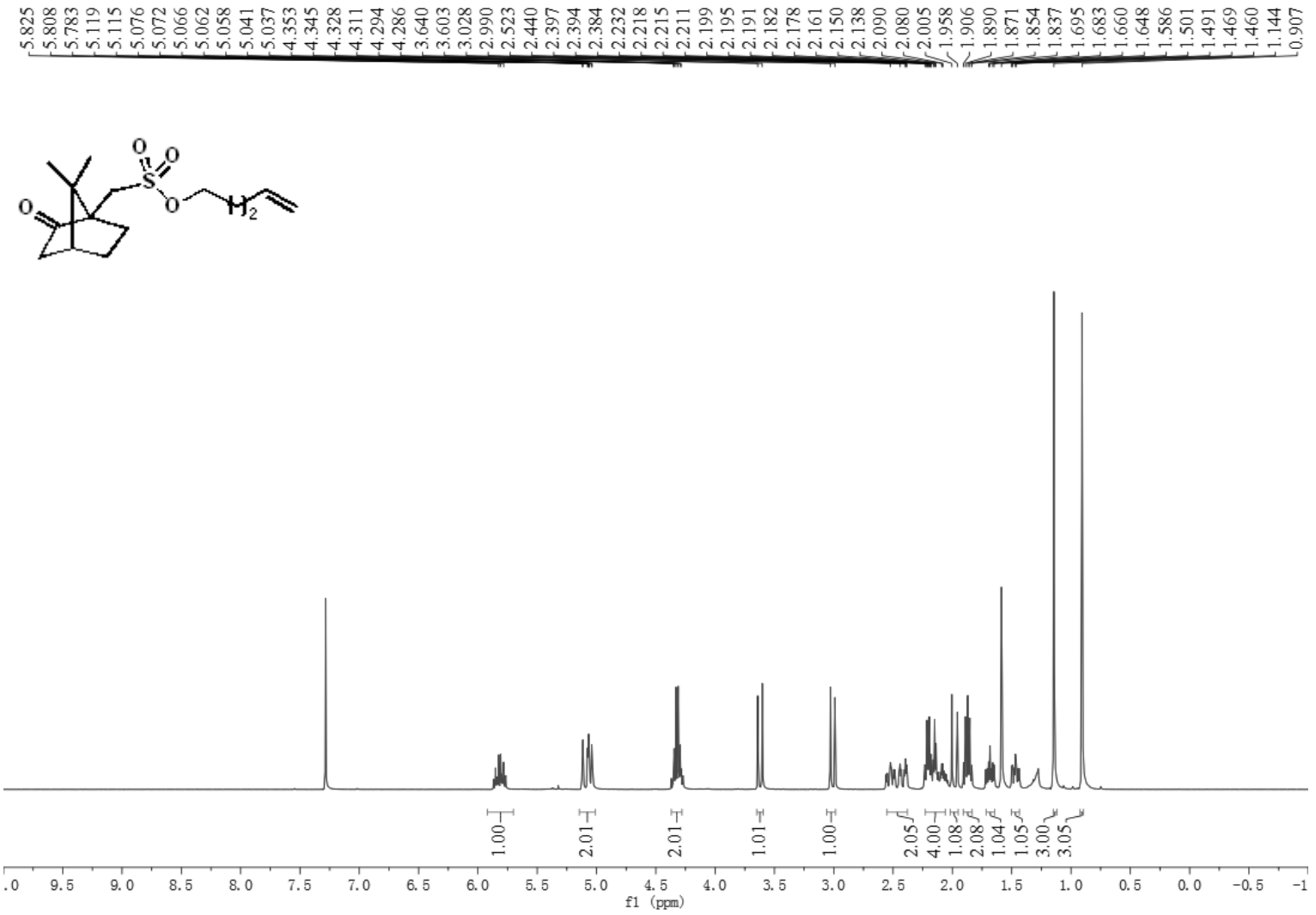
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



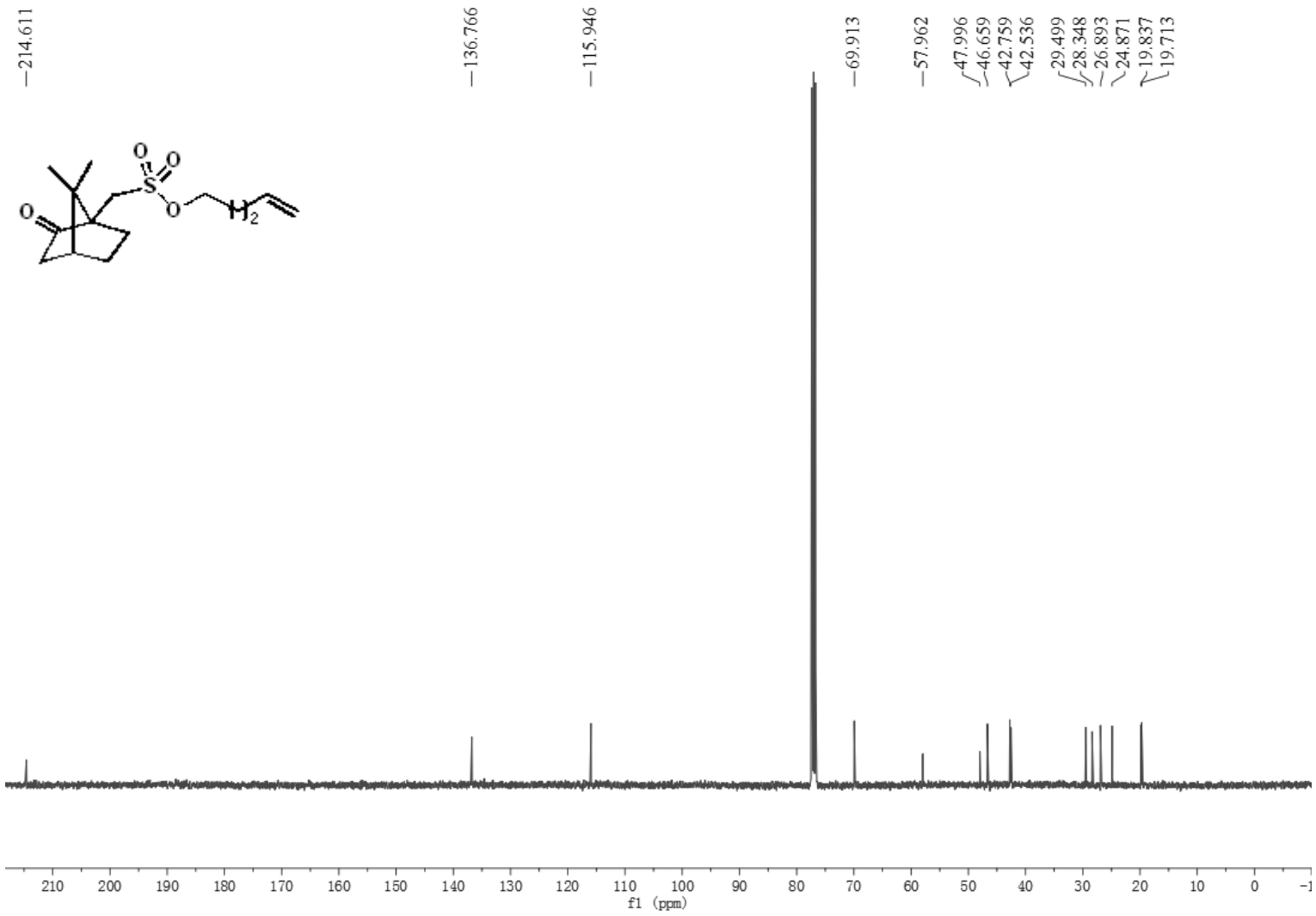
^{13}C NMR (100 MHz, $CDCl_3$) of **3g**



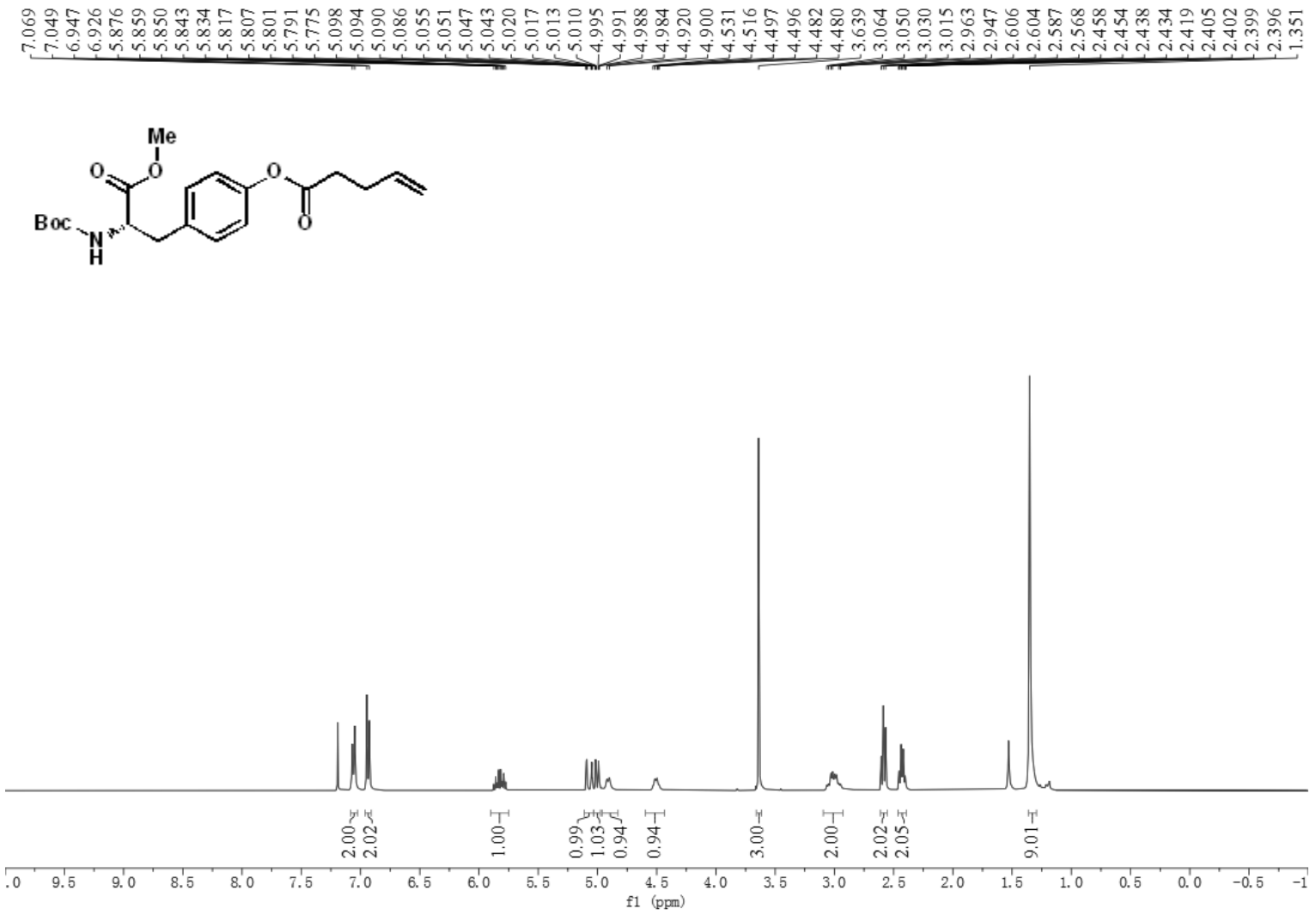
^{19}F NMR (100 MHz, $CDCl_3$) of **3g**



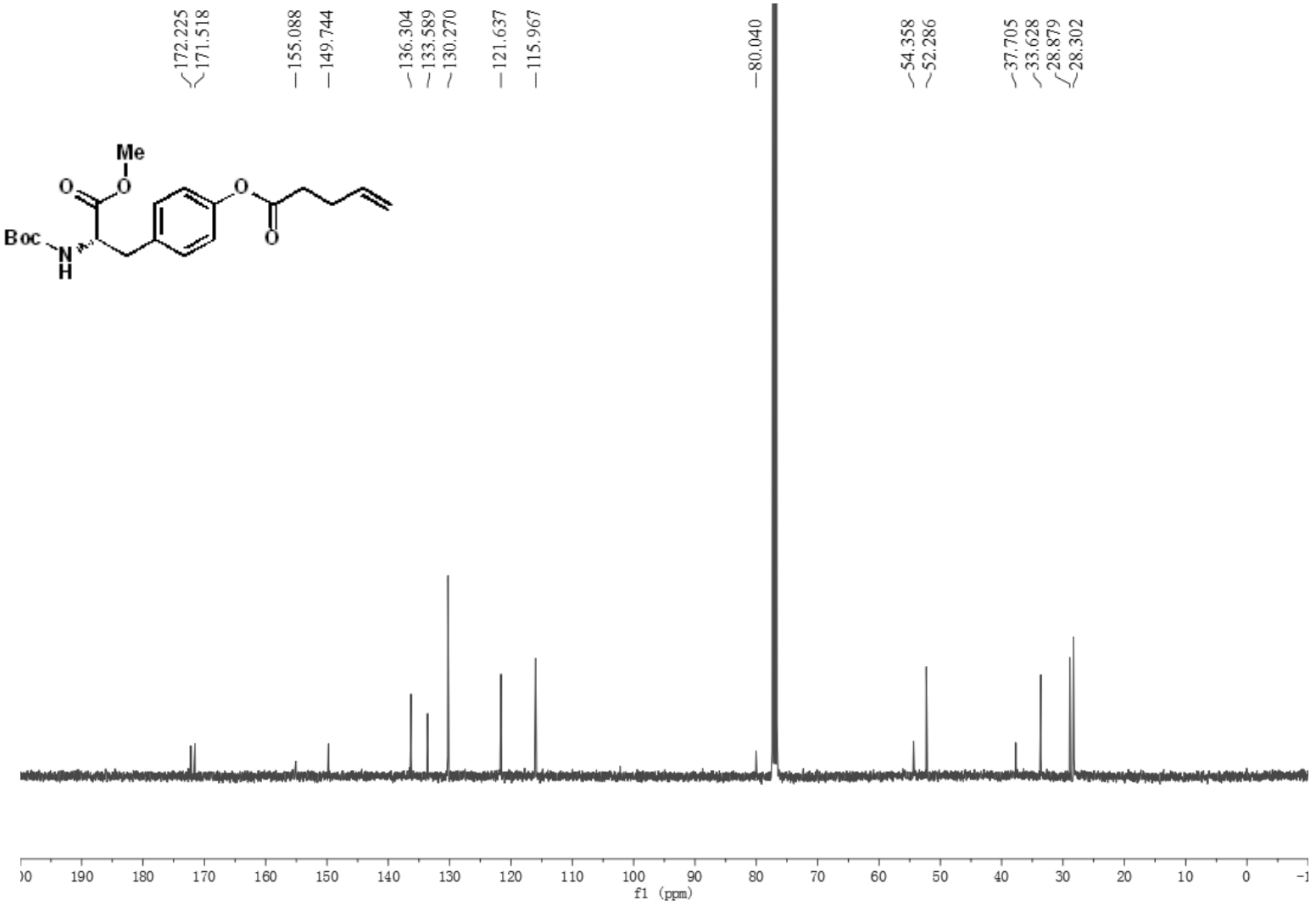
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



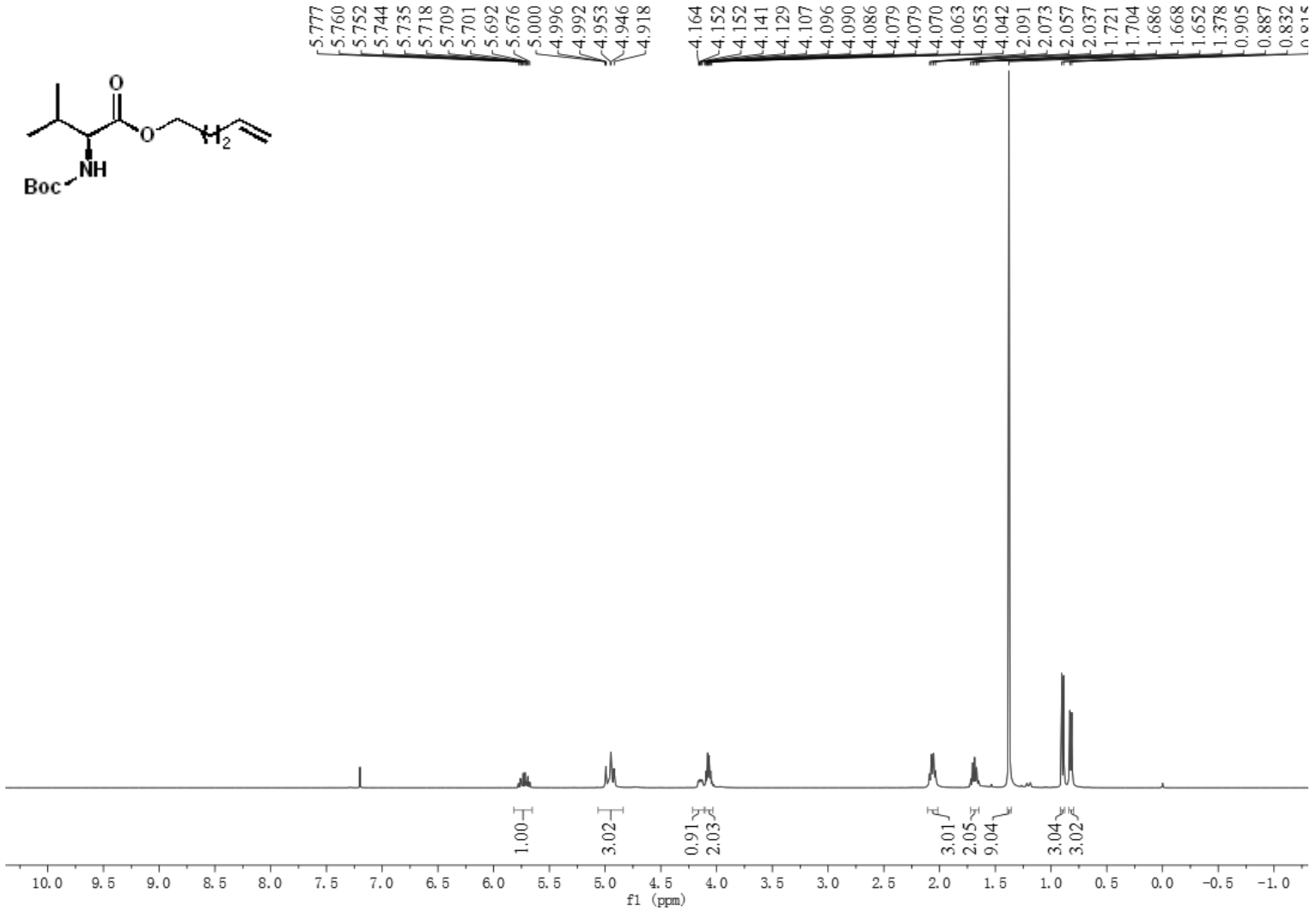
^{13}C NMR (100 MHz, $CDCl_3$) of **3i**



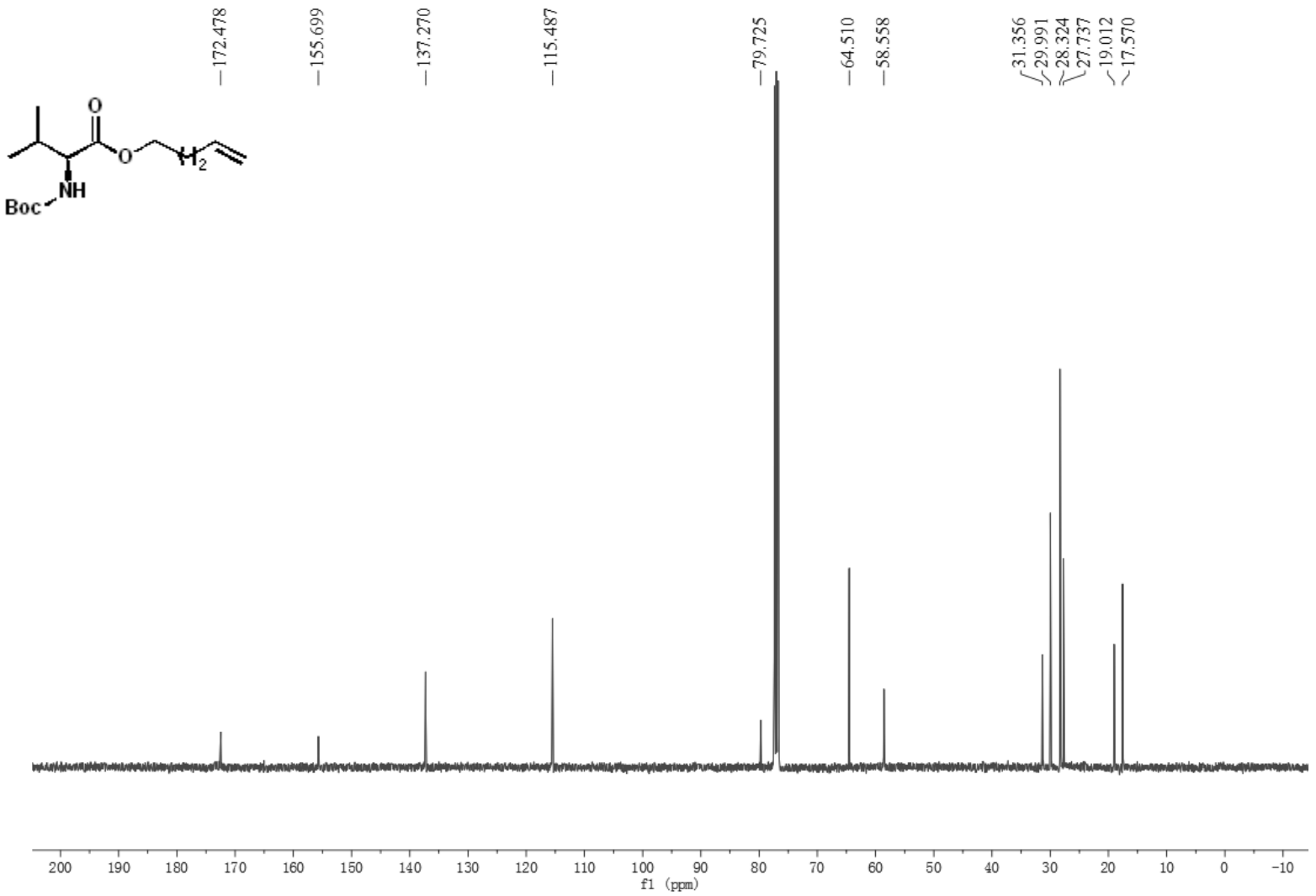
^{1}H NMR (100 MHz, $CDCl_3$) of **3m**



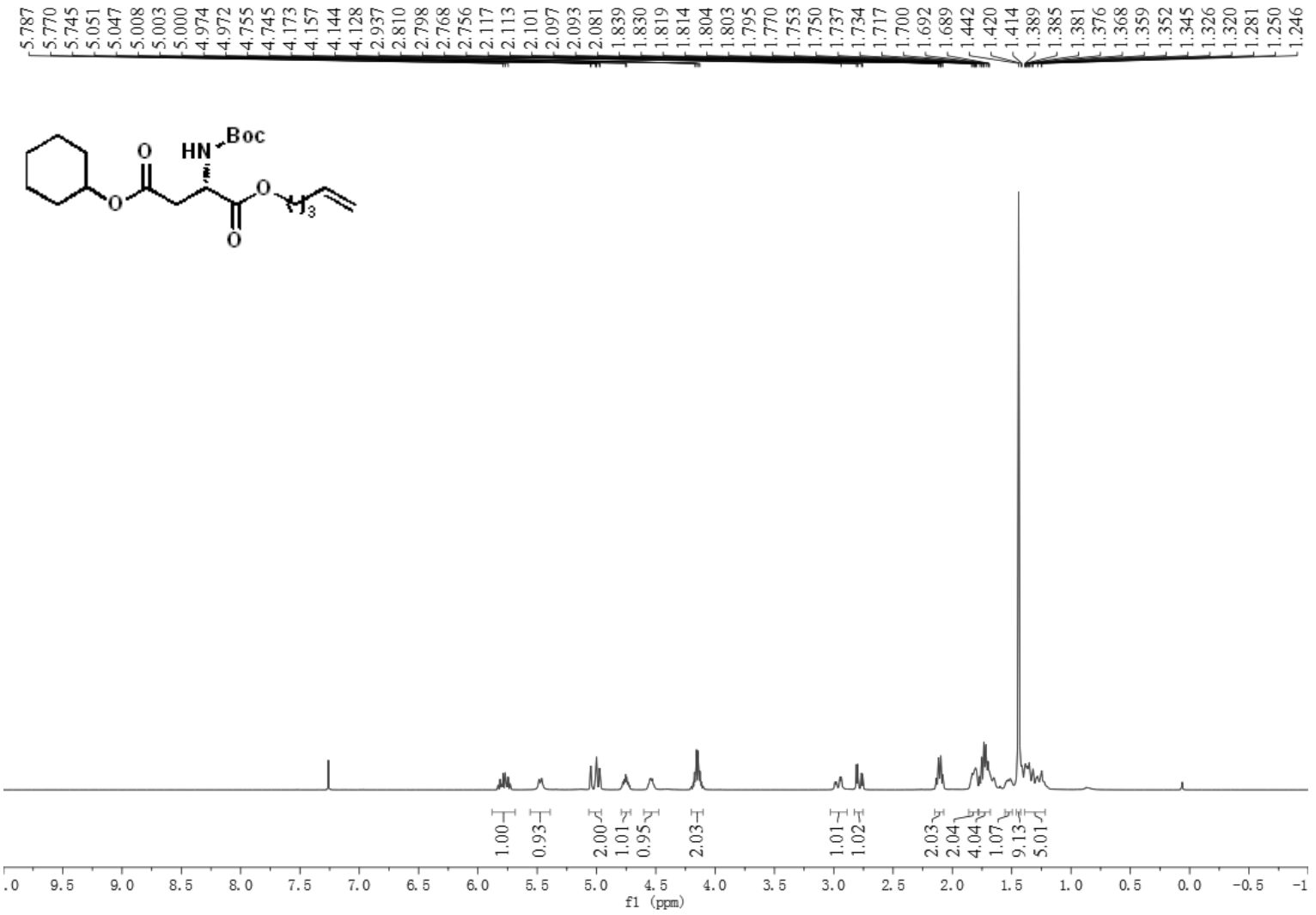
^{13}C NMR (100 MHz, $CDCl_3$) of **3m**



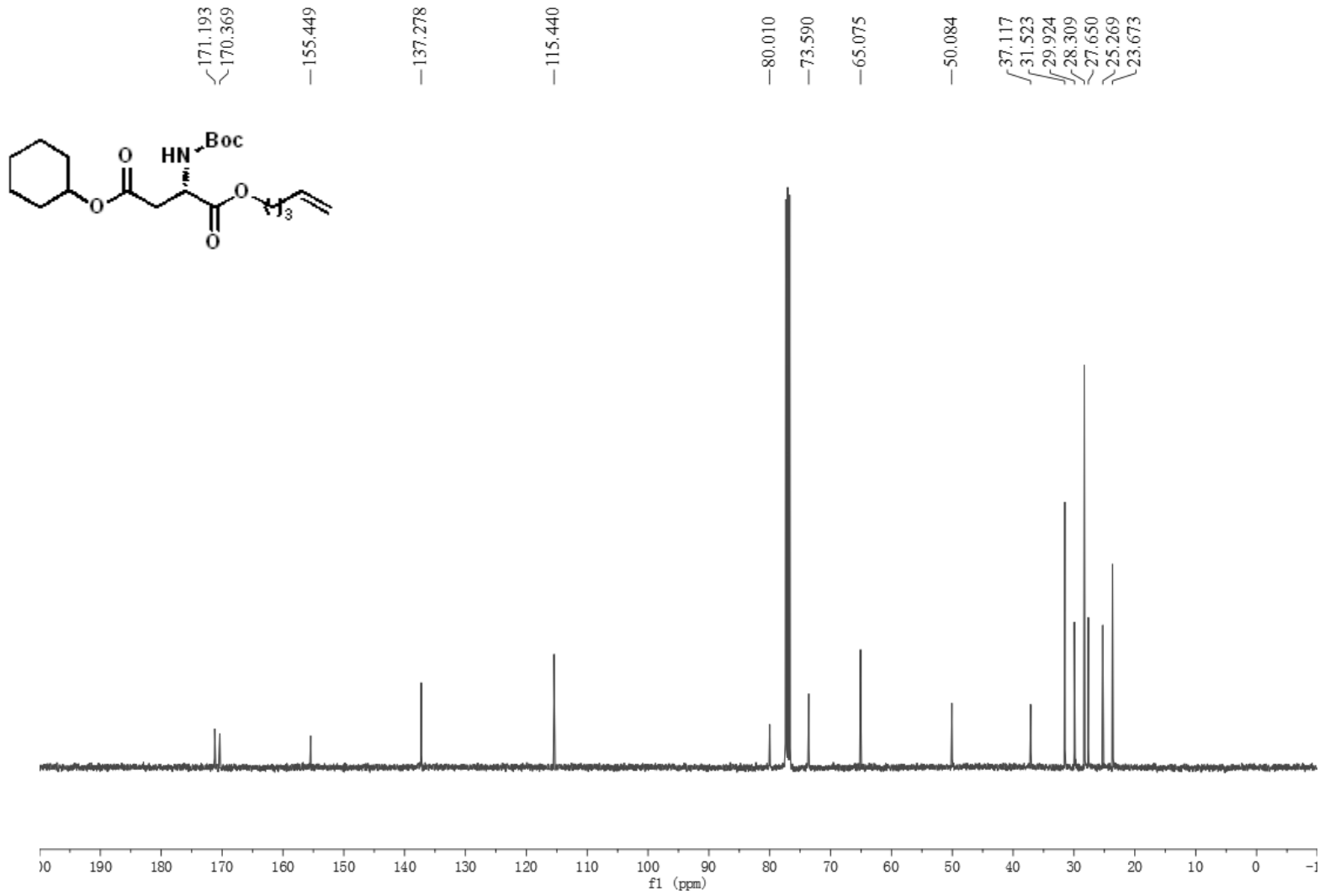
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



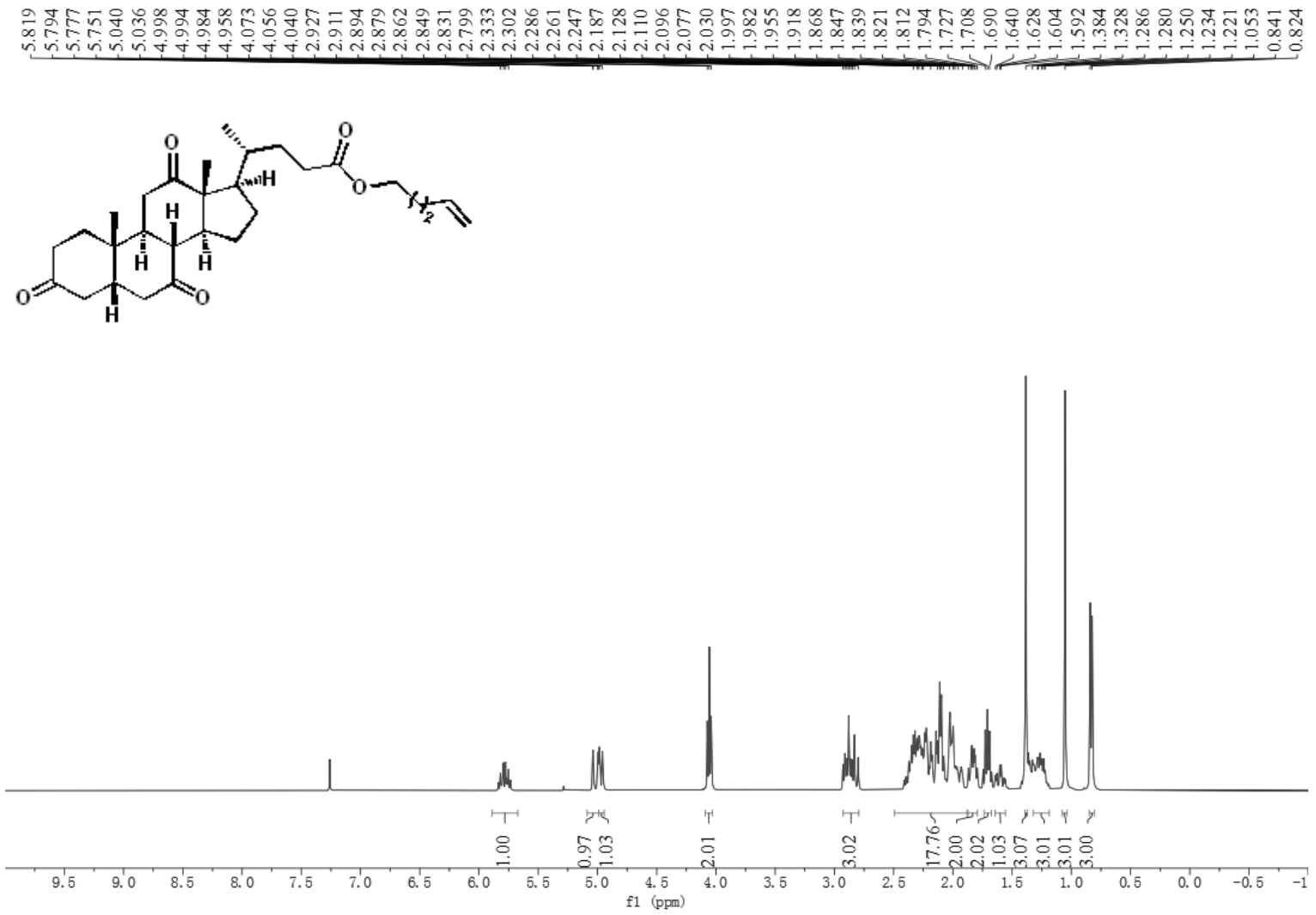
^{13}C NMR (100 MHz, $CDCl_3$) of **3n**



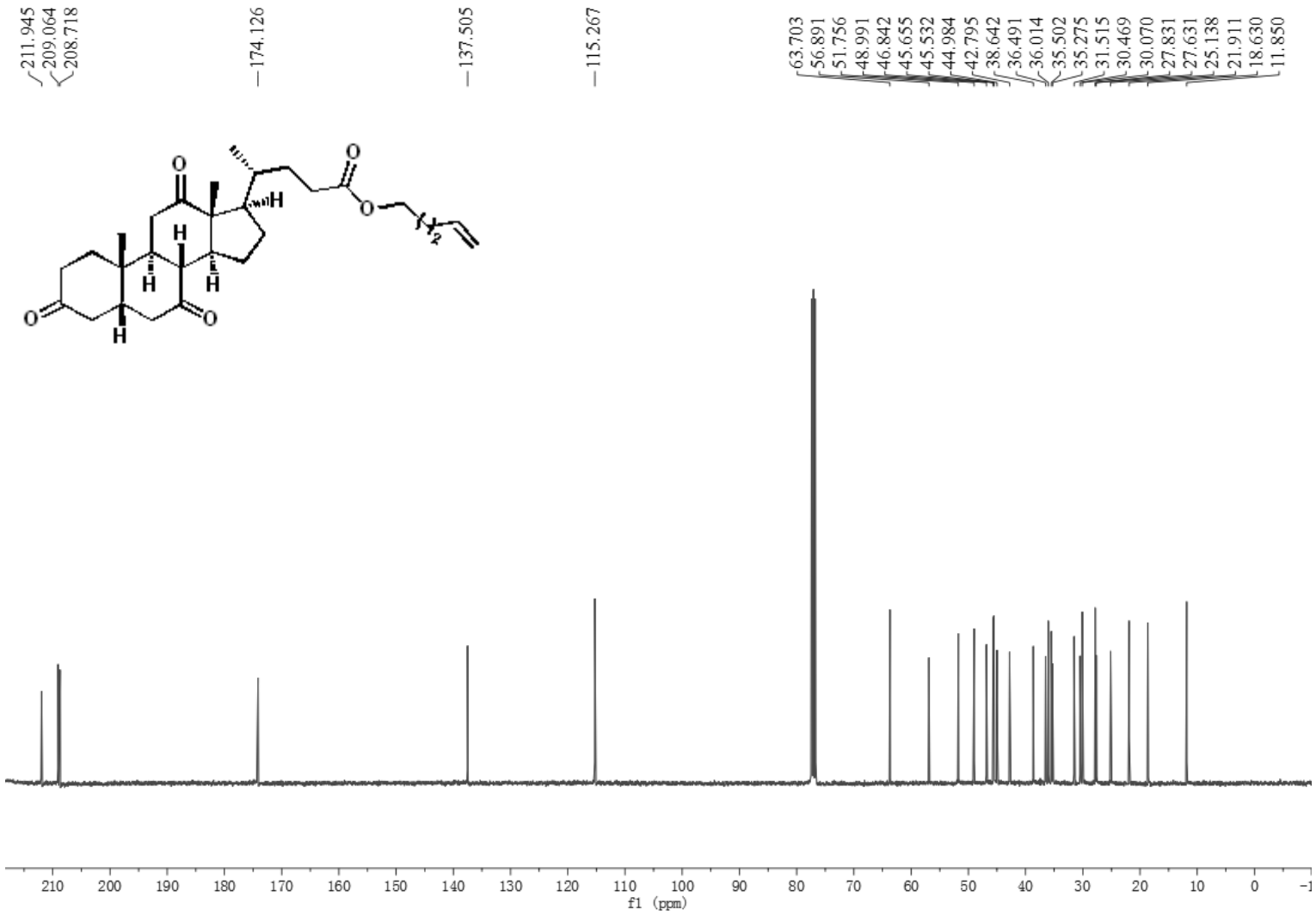
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



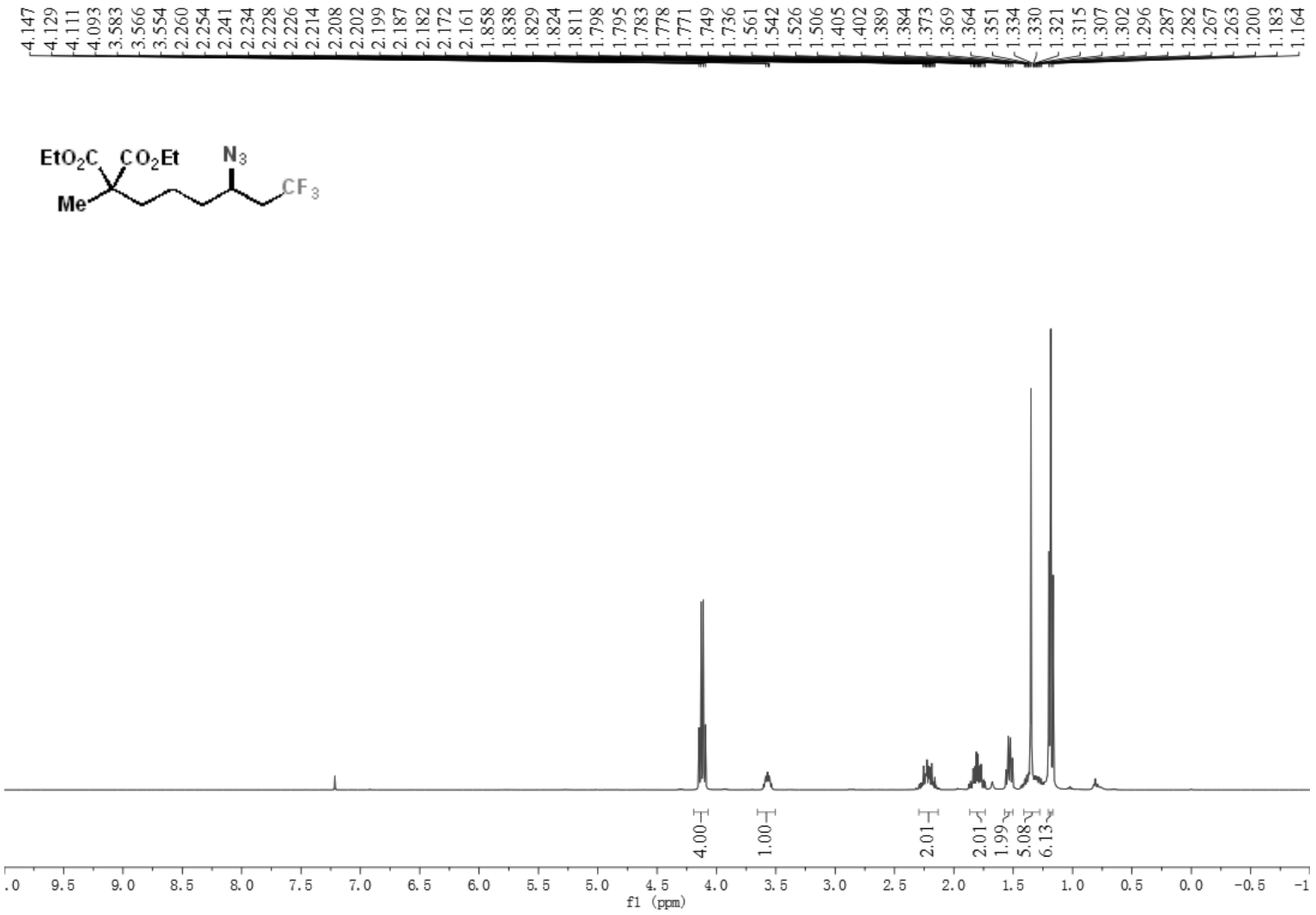
^{13}C NMR (100 MHz, $CDCl_3$) of **3p**



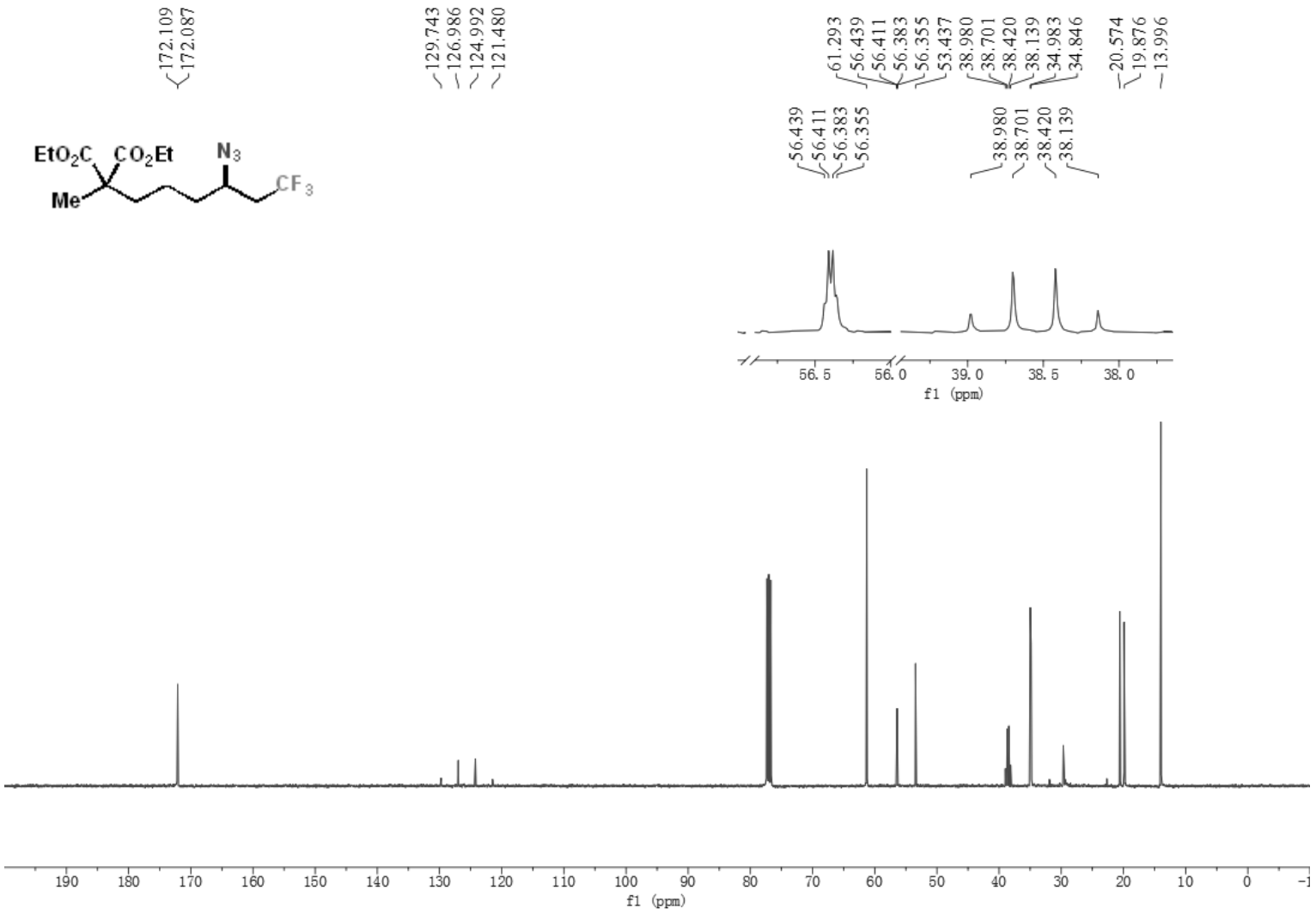
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



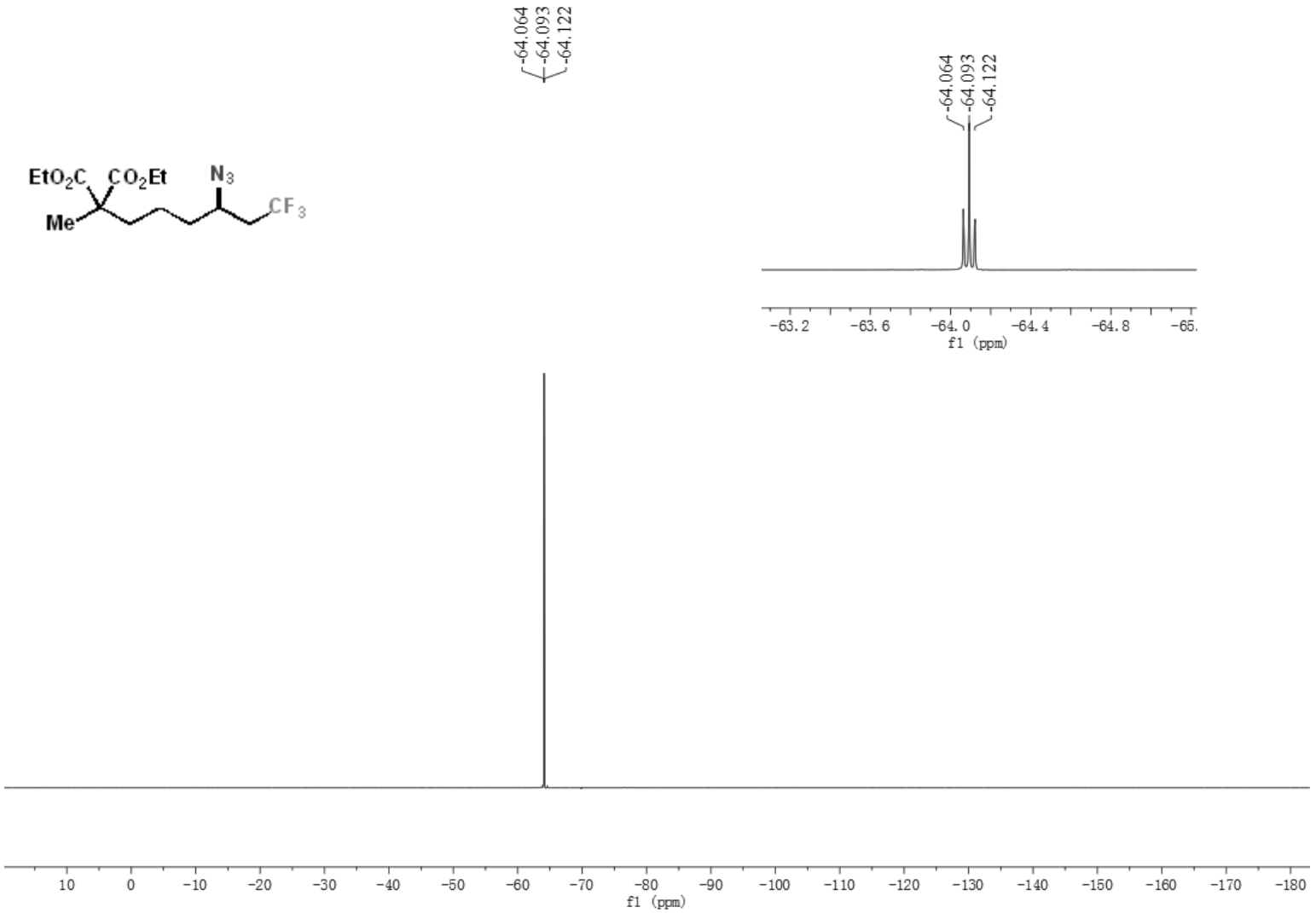
^{13}C NMR (100 MHz, $CDCl_3$) of **3q**



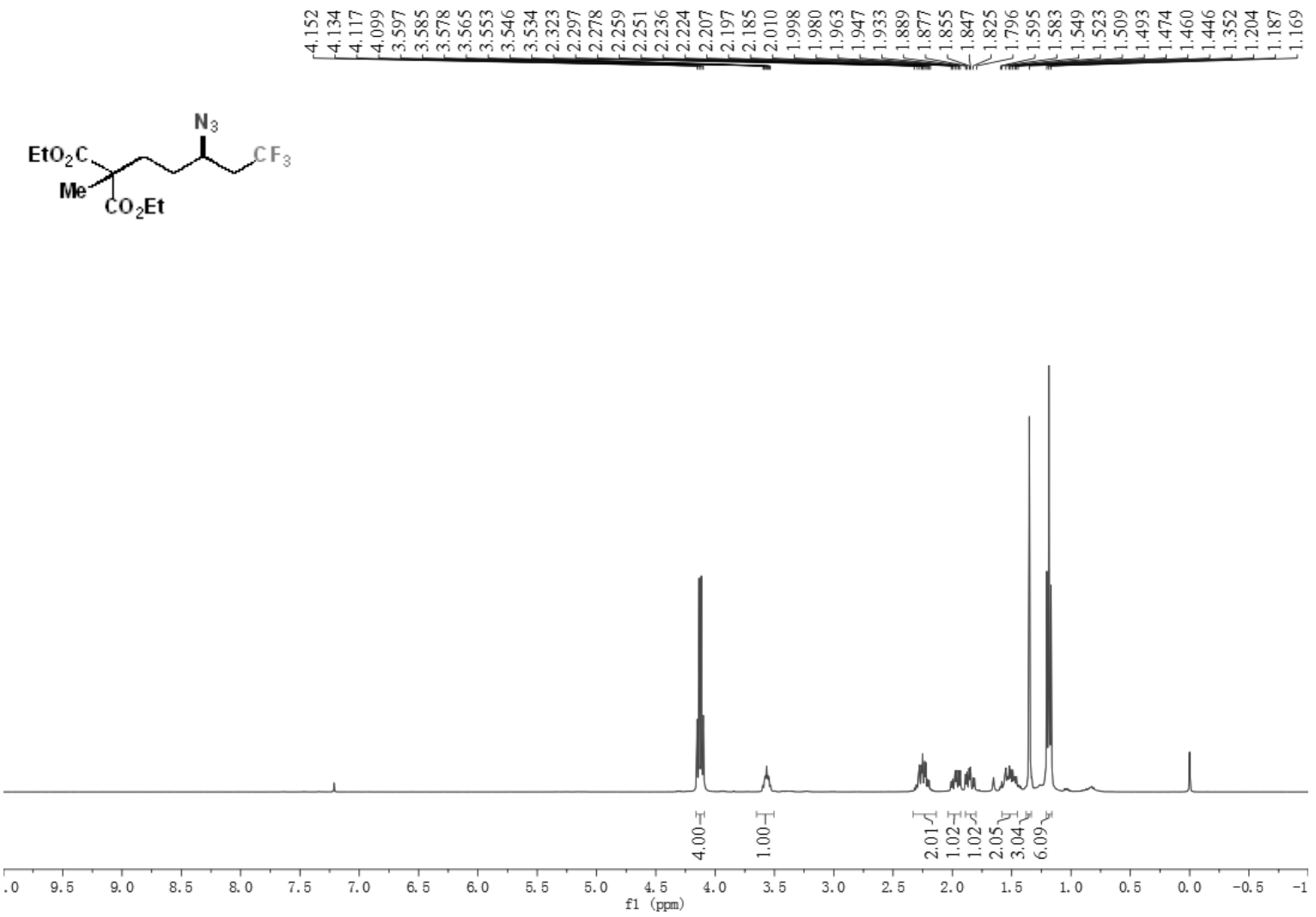
^{1}H NMR (400 MHz, $CDCl_3$) of **2a**



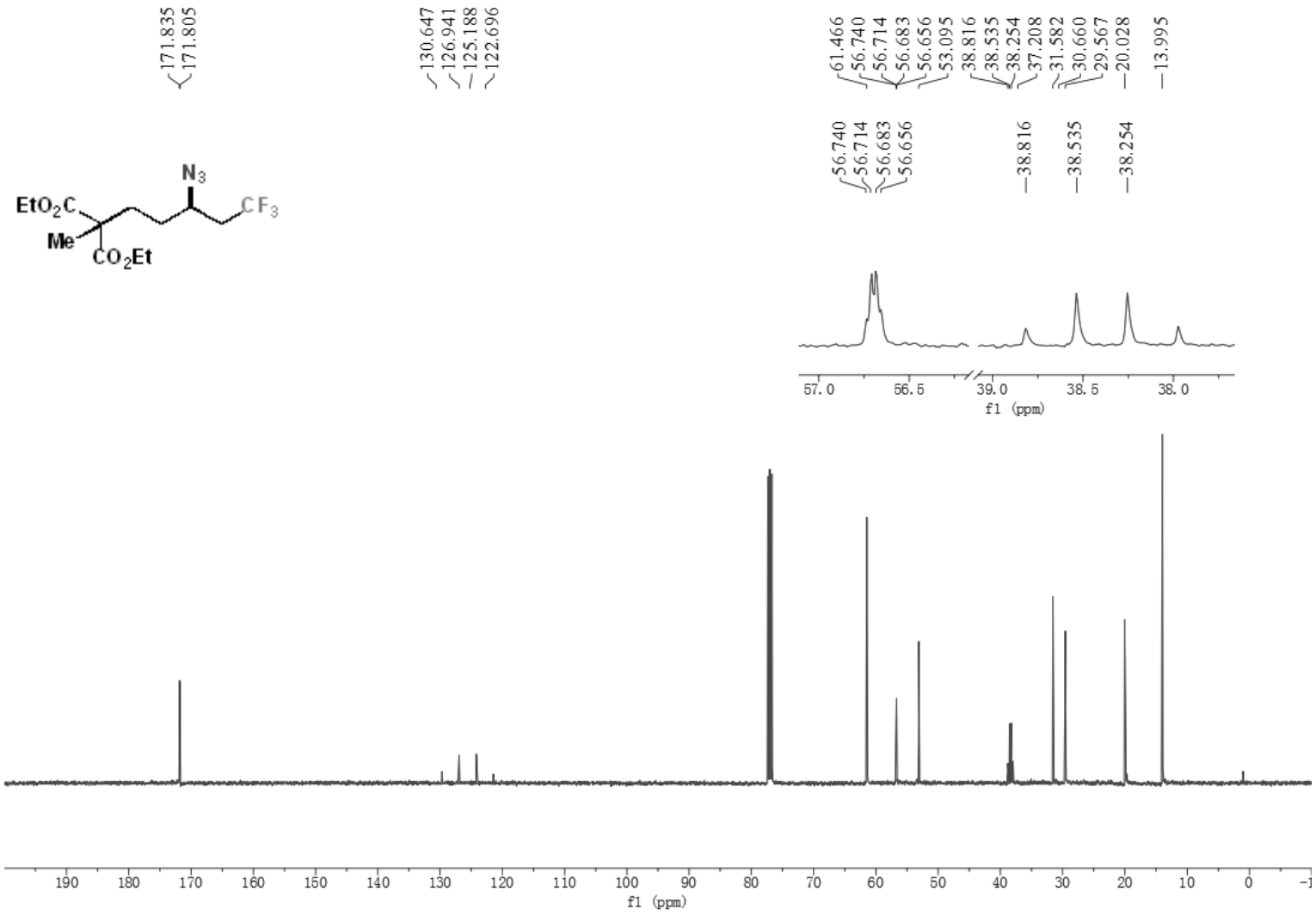
^{13}C NMR (100 MHz, $CDCl_3$) of **2a**



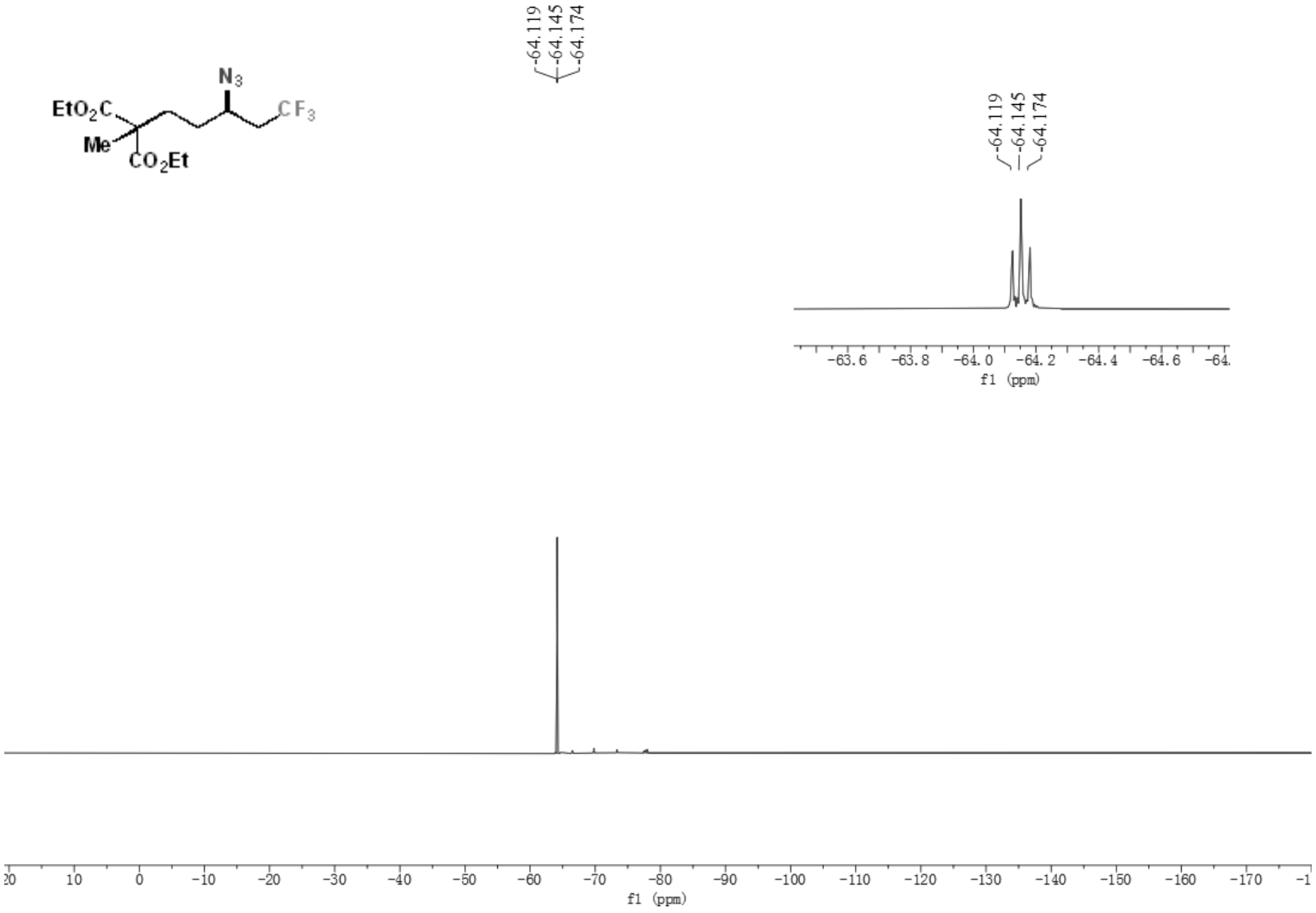
^{19}F NMR (376MHz, $CDCl_3$) of **2a**



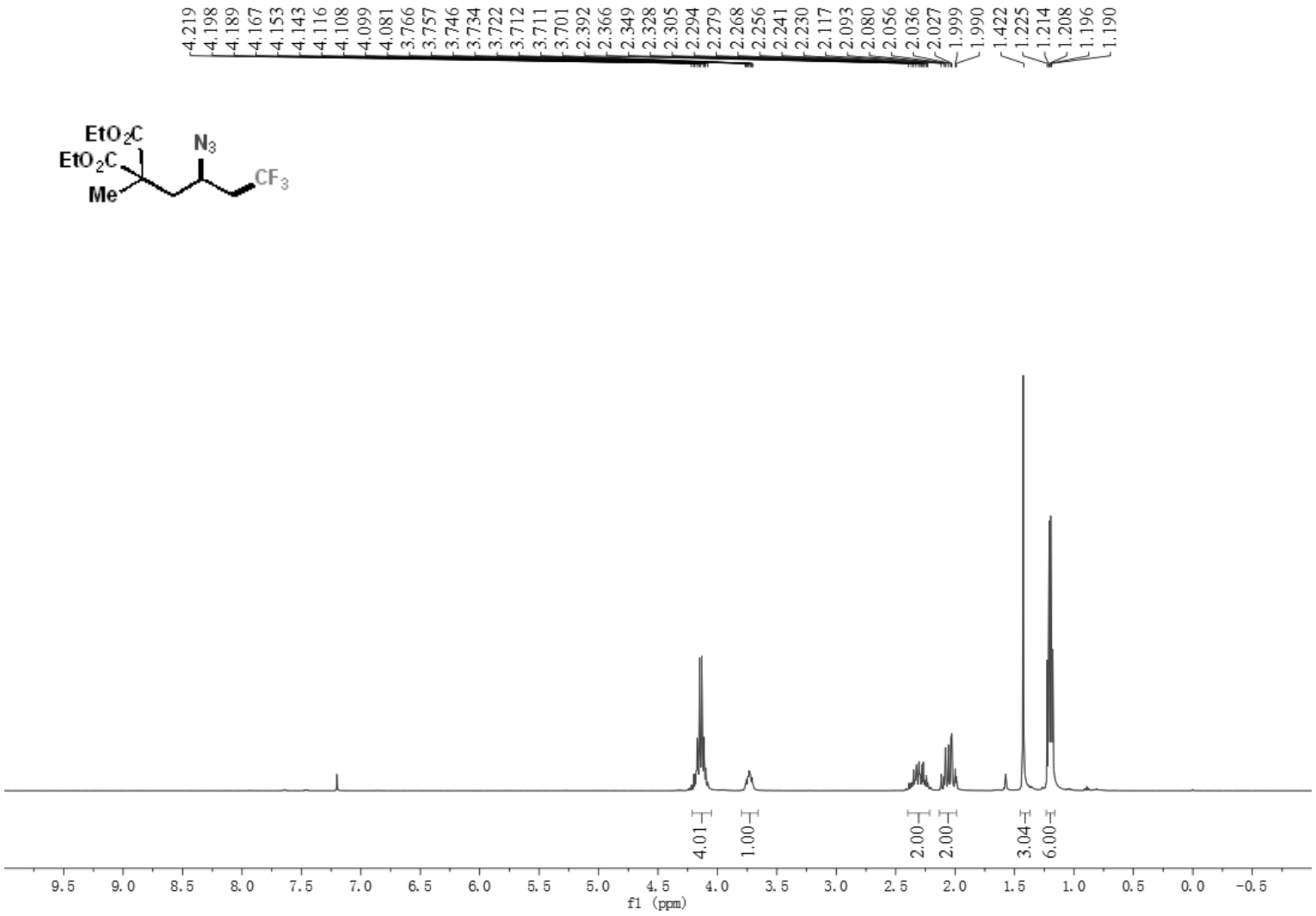
^{1}H NMR (400 MHz, $CDCl_3$) of **2b**



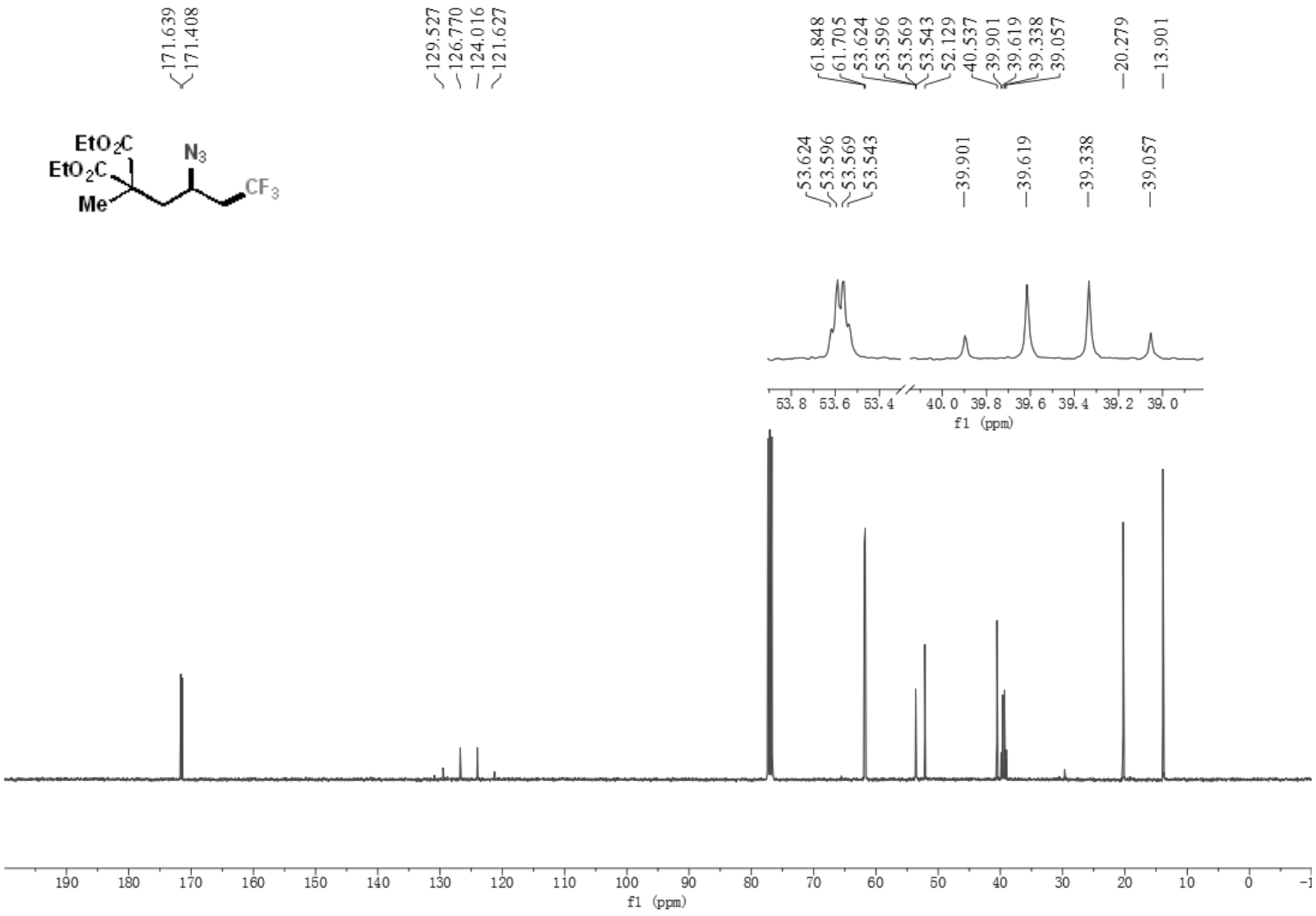
^{13}C NMR (100 MHz, $CDCl_3$) of **2b**



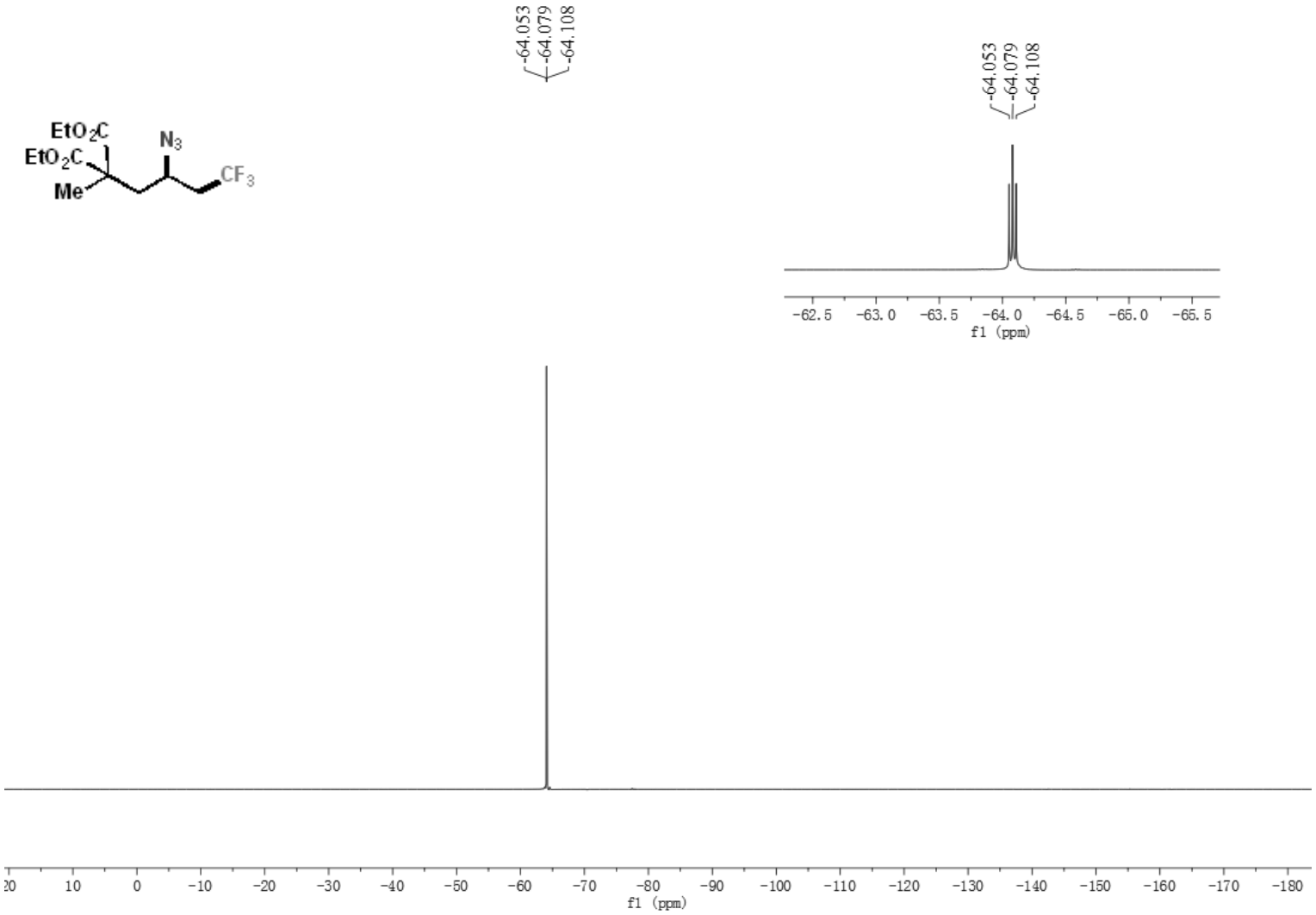
^{19}F NMR (376 MHz, $CDCl_3$) of **2b**



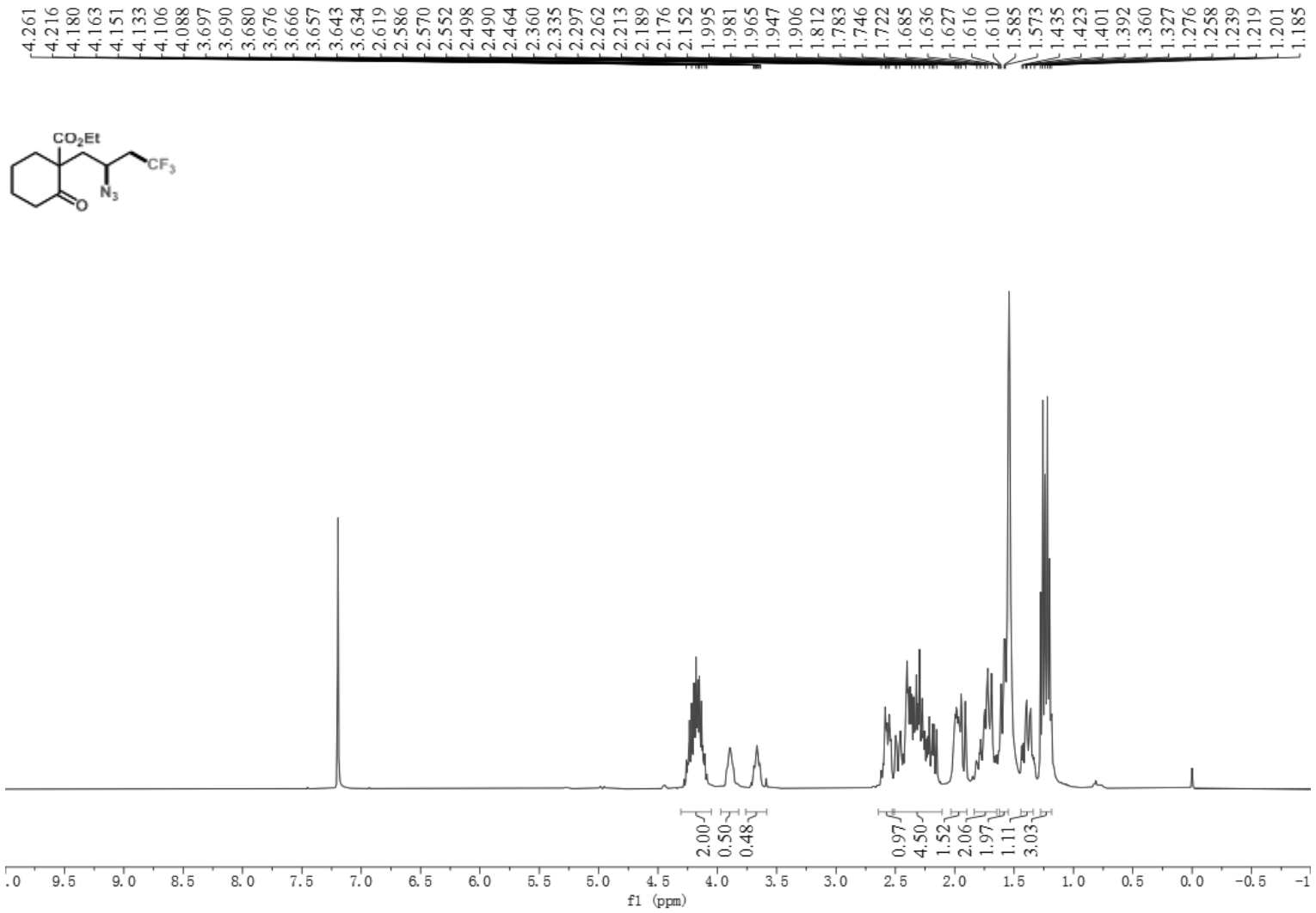
^{1}H NMR (400 MHz, $CDCl_3$) of **2c**



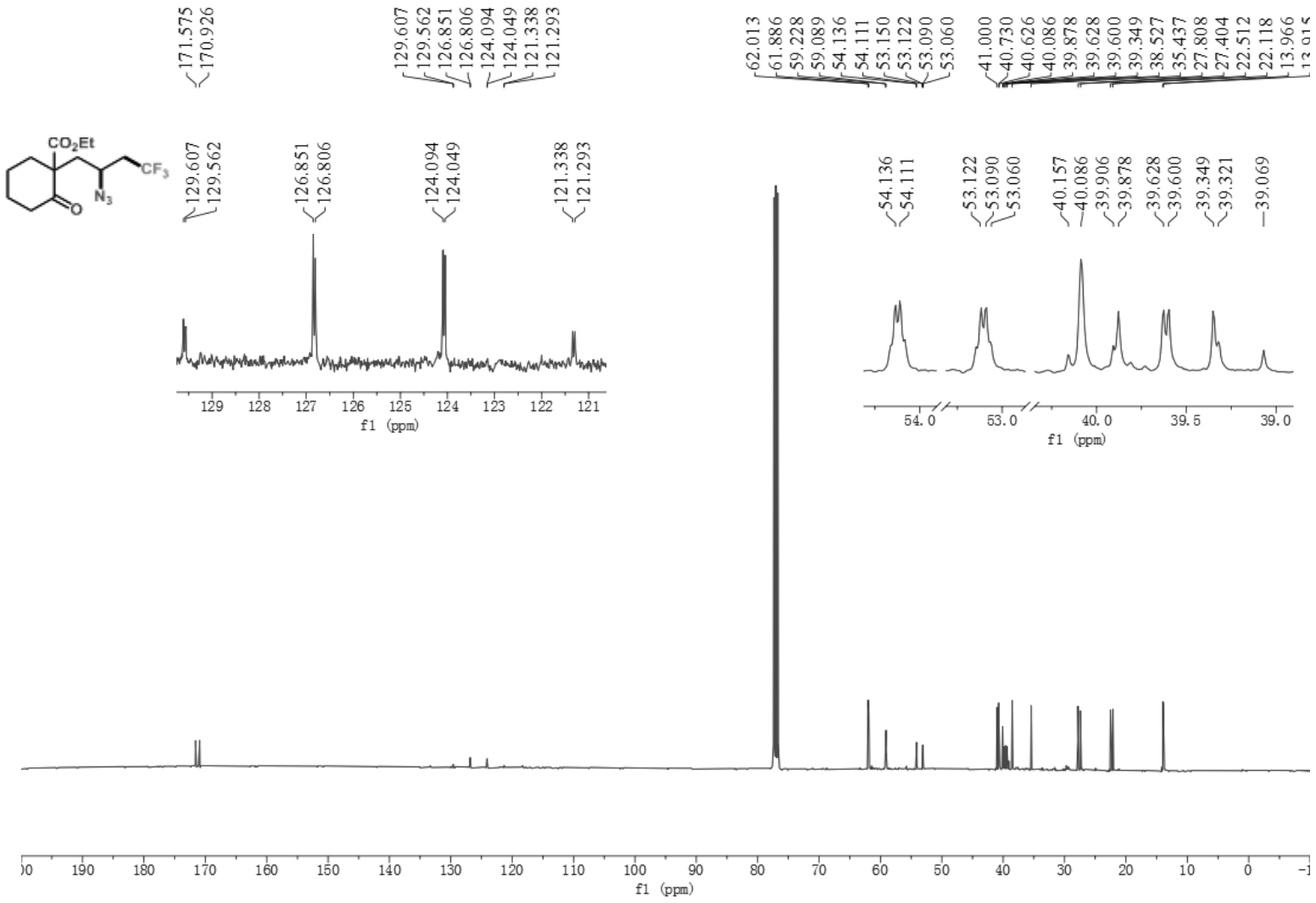
^{13}C NMR (100 MHz, $CDCl_3$) of **2c**



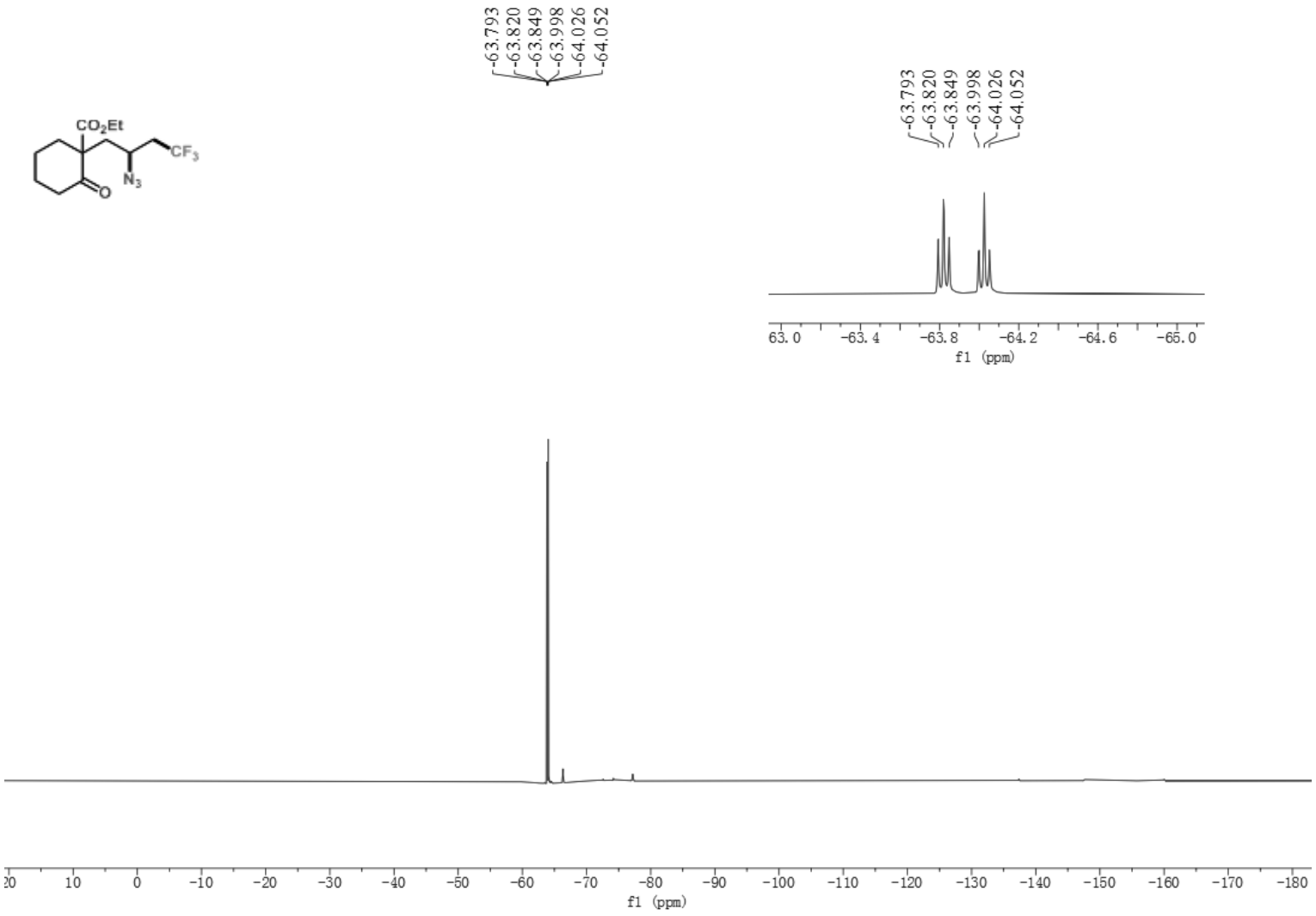
^{19}F NMR (376 MHz, $CDCl_3$) of **2c**



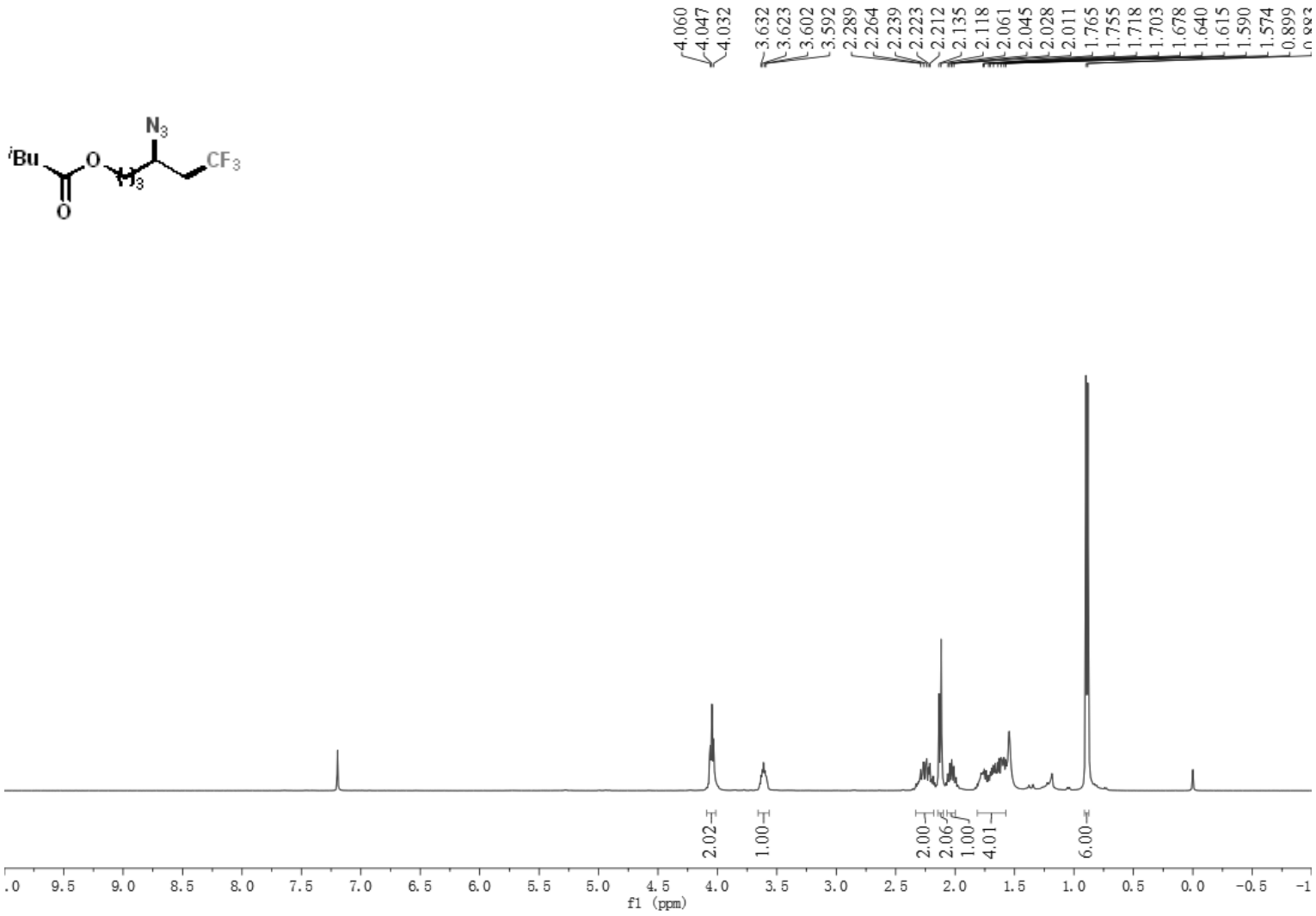
^{1}H NMR (400 MHz, $CDCl_3$) of **2d**



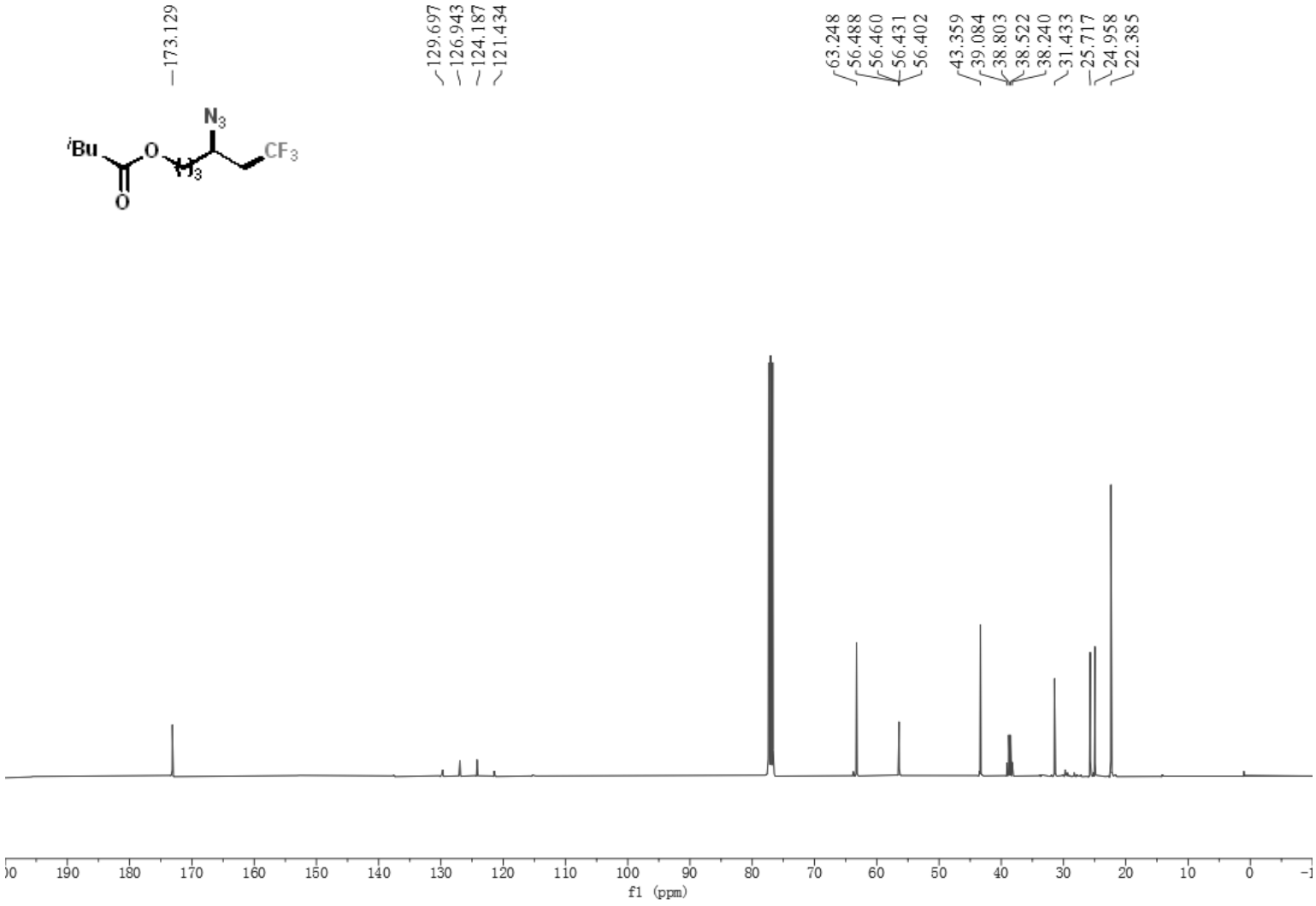
^{13}C NMR (100 MHz, $CDCl_3$) of **2d**



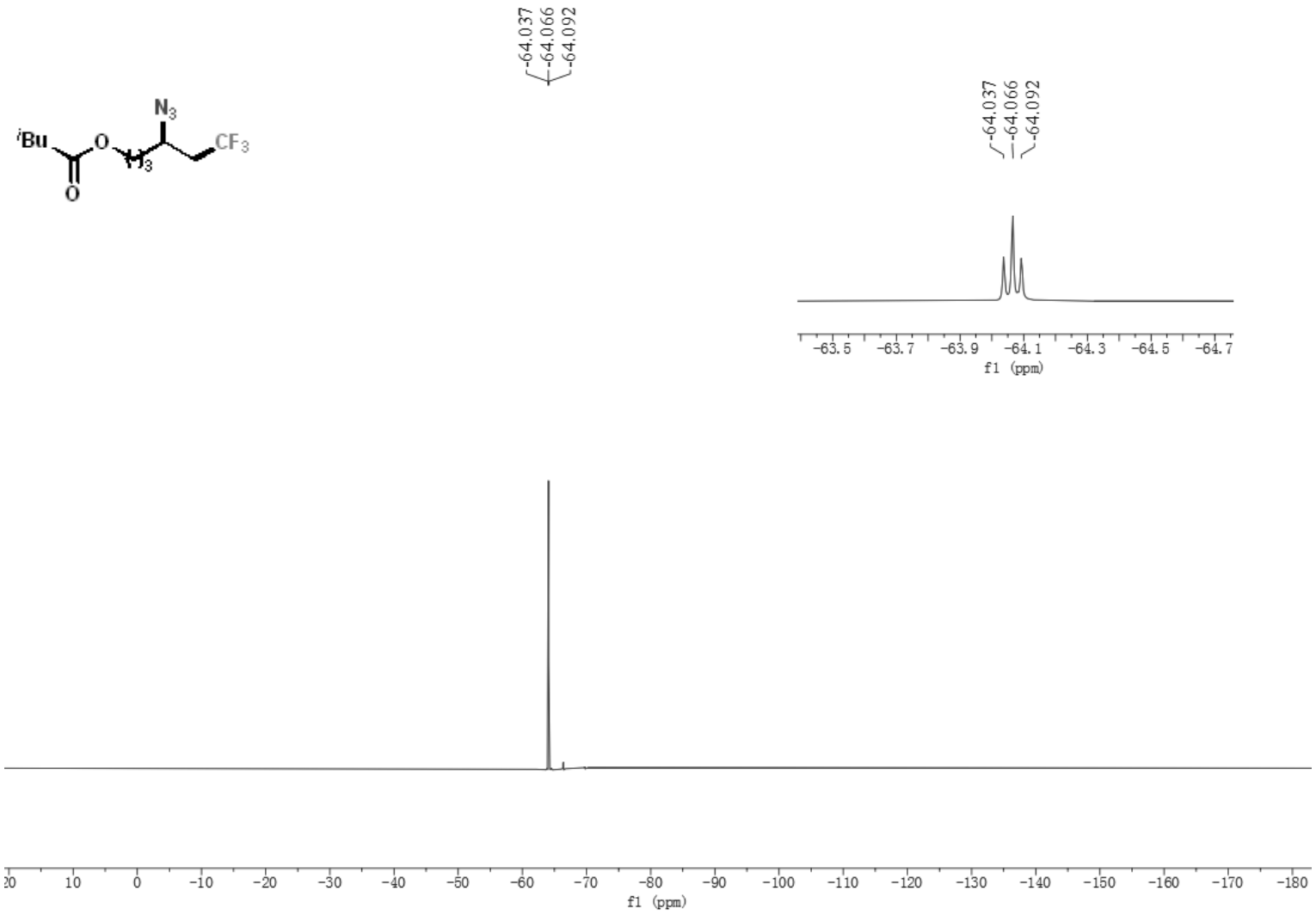
^{19}F NMR (376 MHz, $CDCl_3$) of **2d**



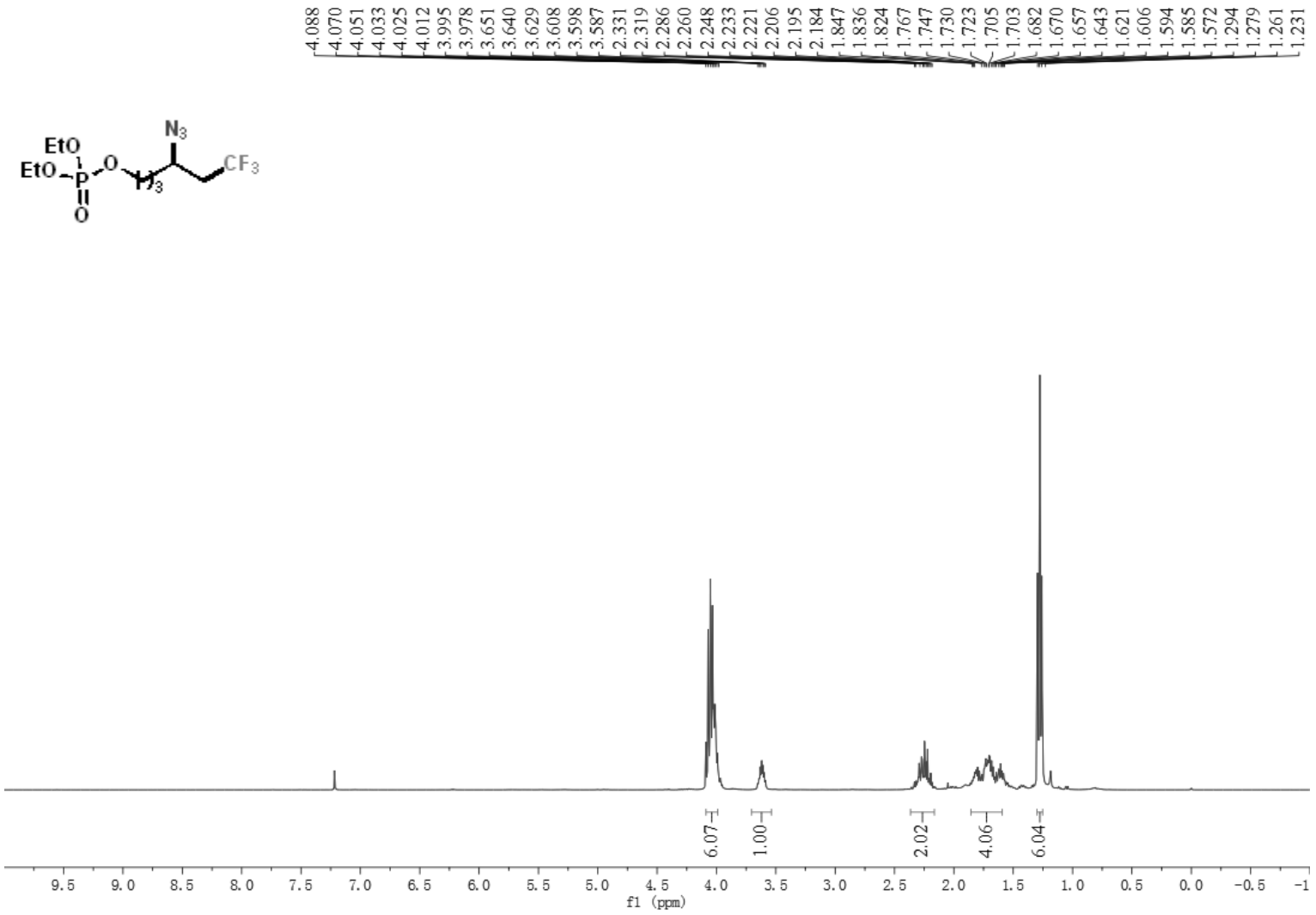
^{1}H NMR (400 MHz, $CDCl_3$) of **2f**



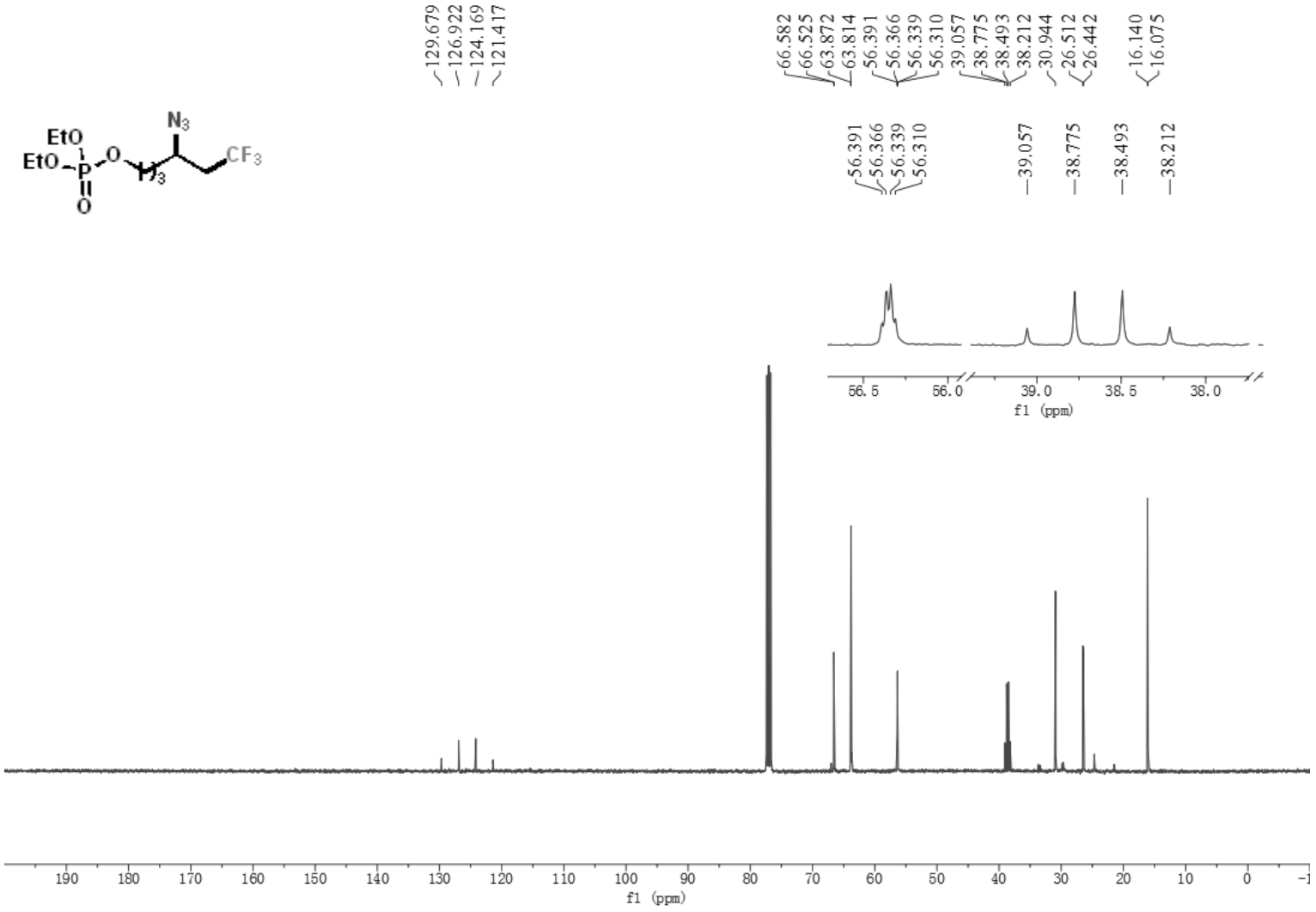
^{13}C NMR (100 MHz, $CDCl_3$) of **2f**



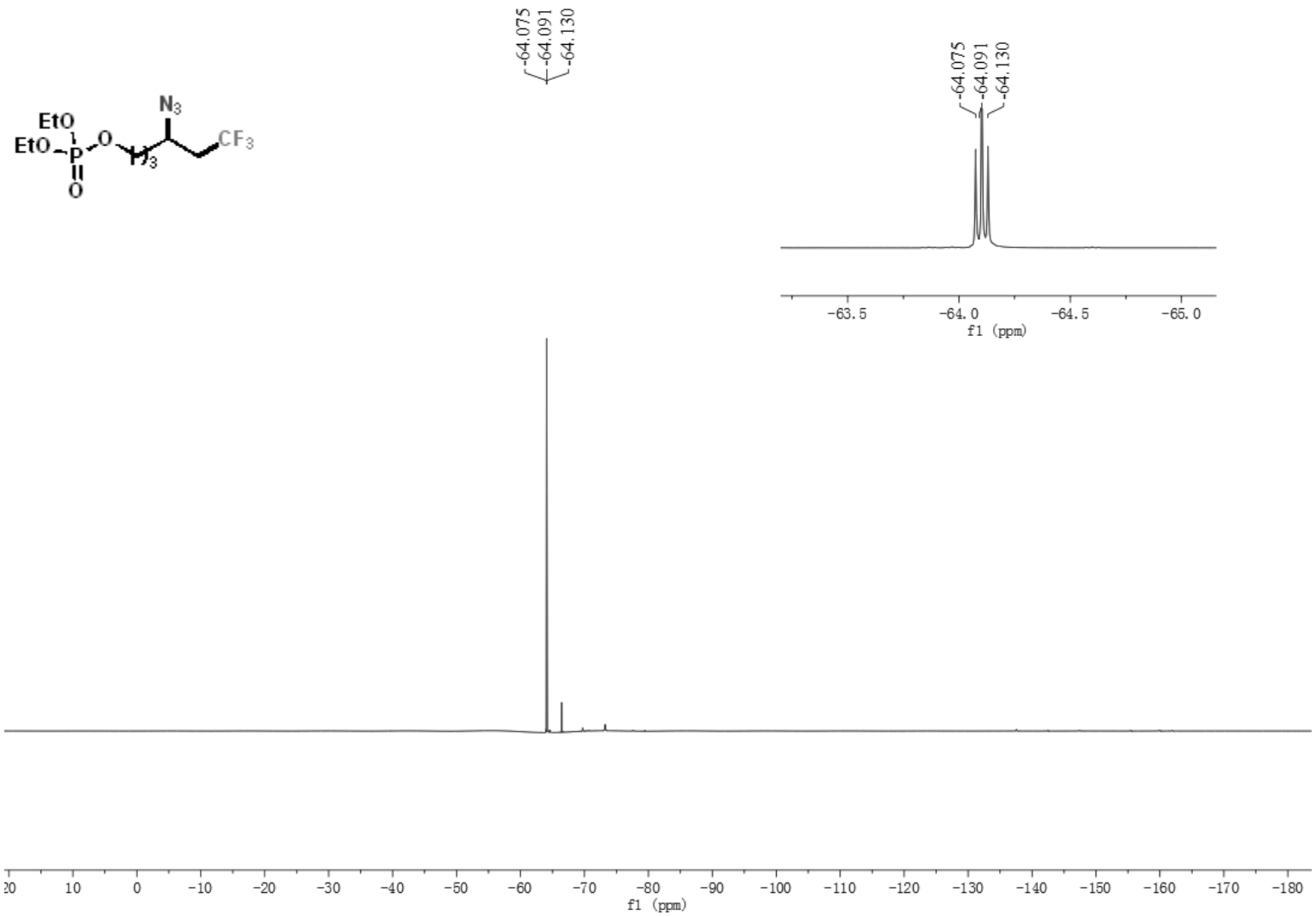
^{19}F NMR (376 MHz, $CDCl_3$) of **2f**



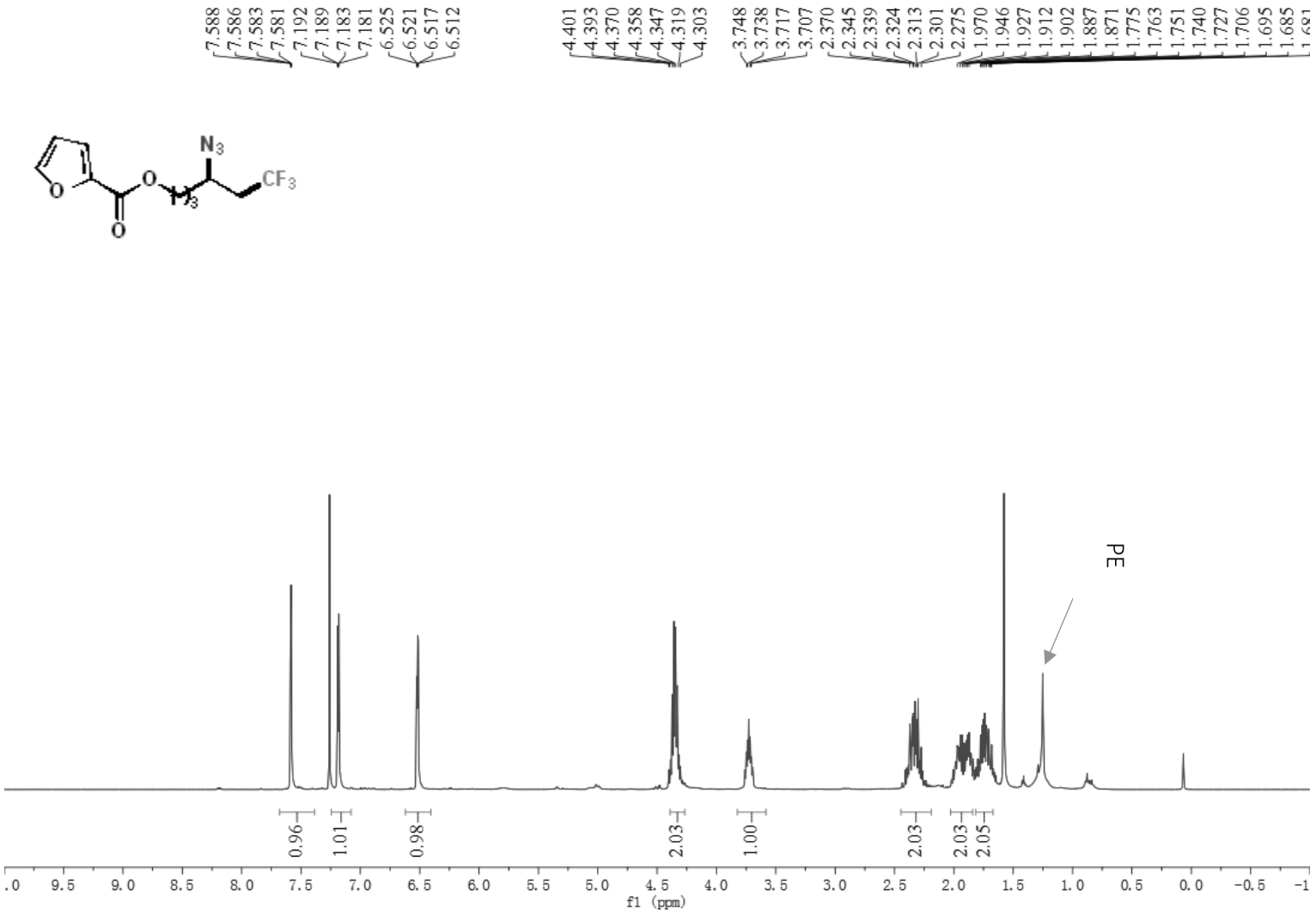
^{1}H NMR (400 MHz, $CDCl_3$) of **2i**



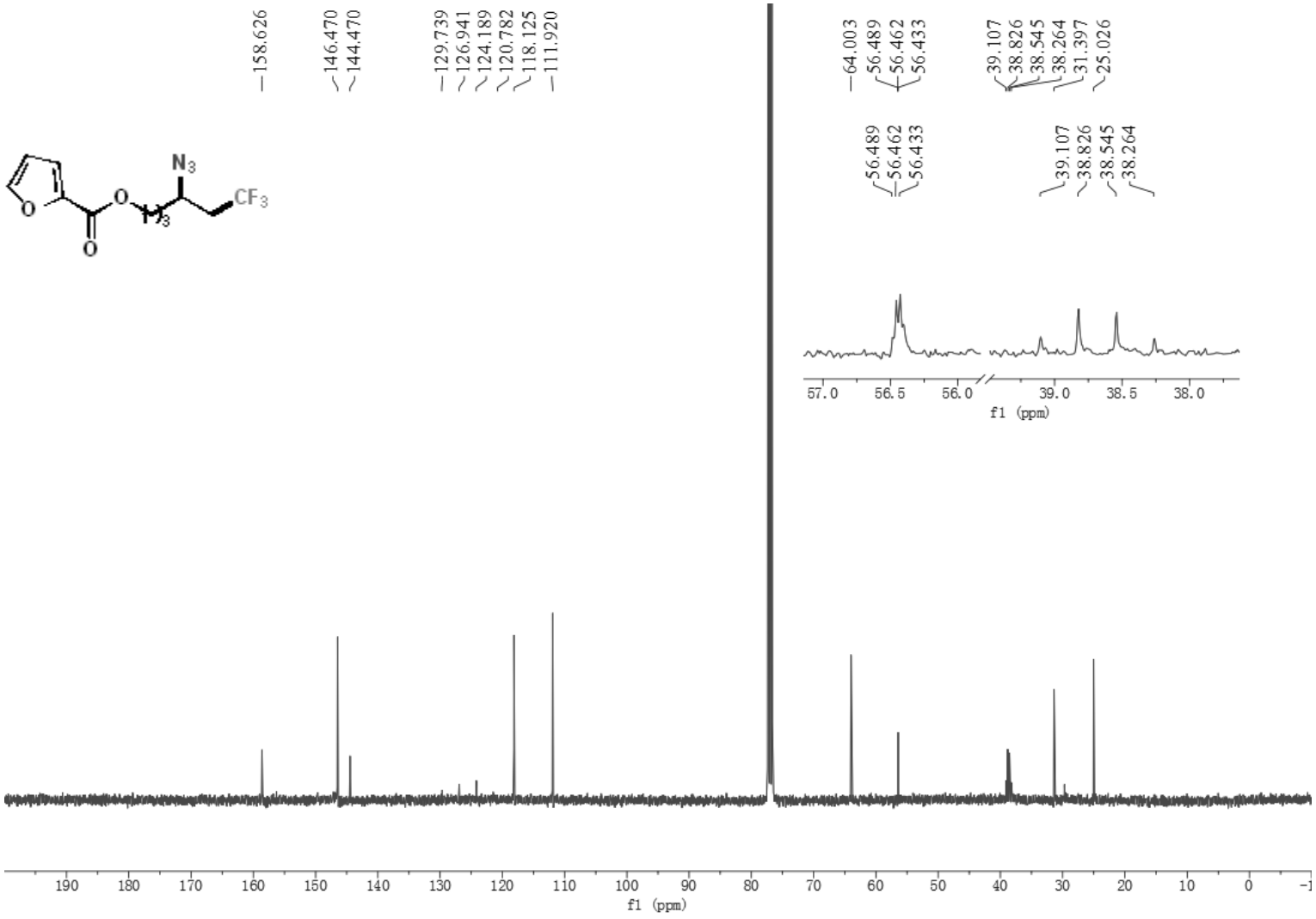
^{13}C NMR (100 MHz, $CDCl_3$) of **2i**



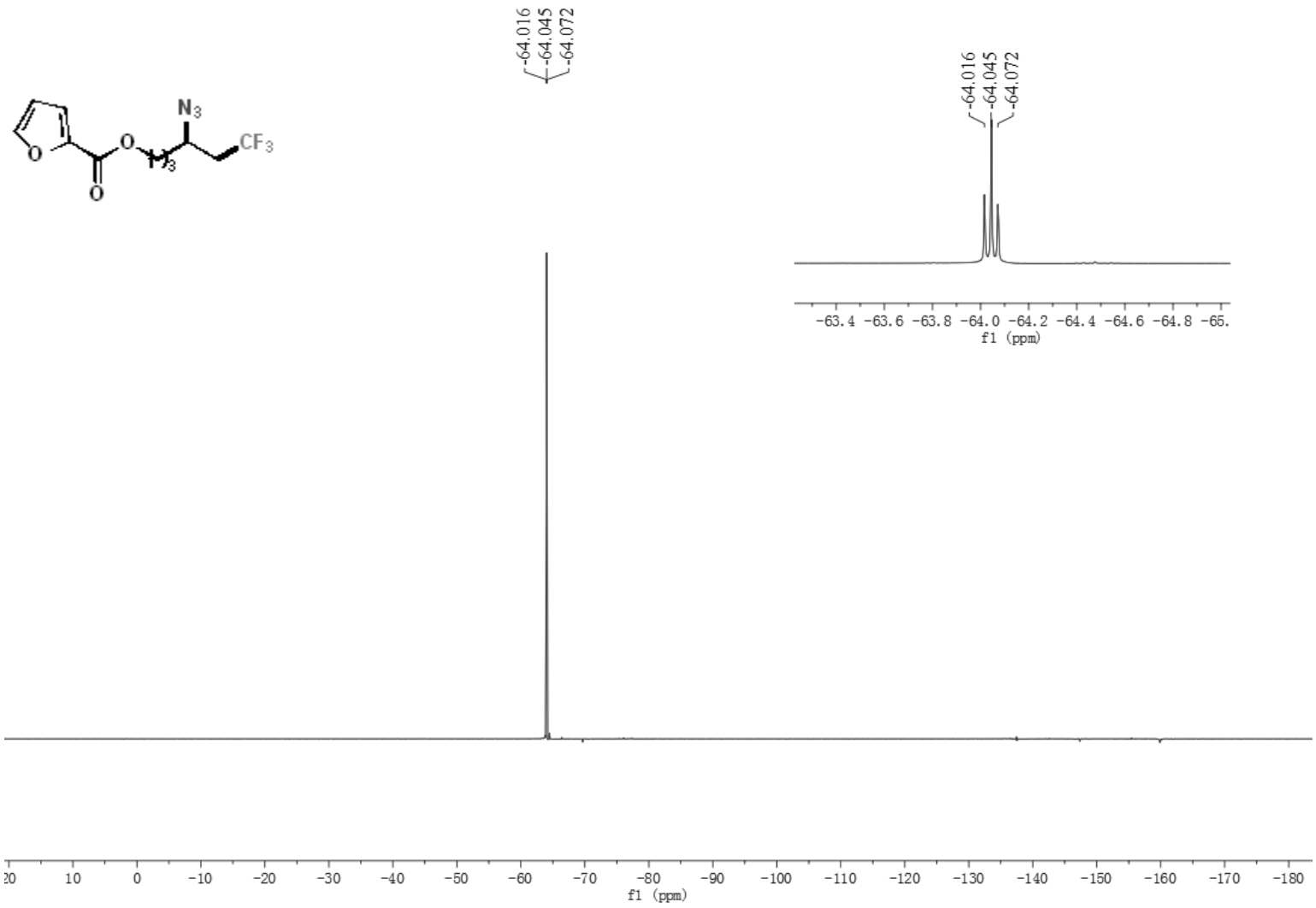
^{19}F NMR (376 MHz, $CDCl_3$) of **2i**



^{1}H NMR (400 MHz, $CDCl_3$) of **2l**



^{13}C NMR (100 MHz, $CDCl_3$) of **2l**



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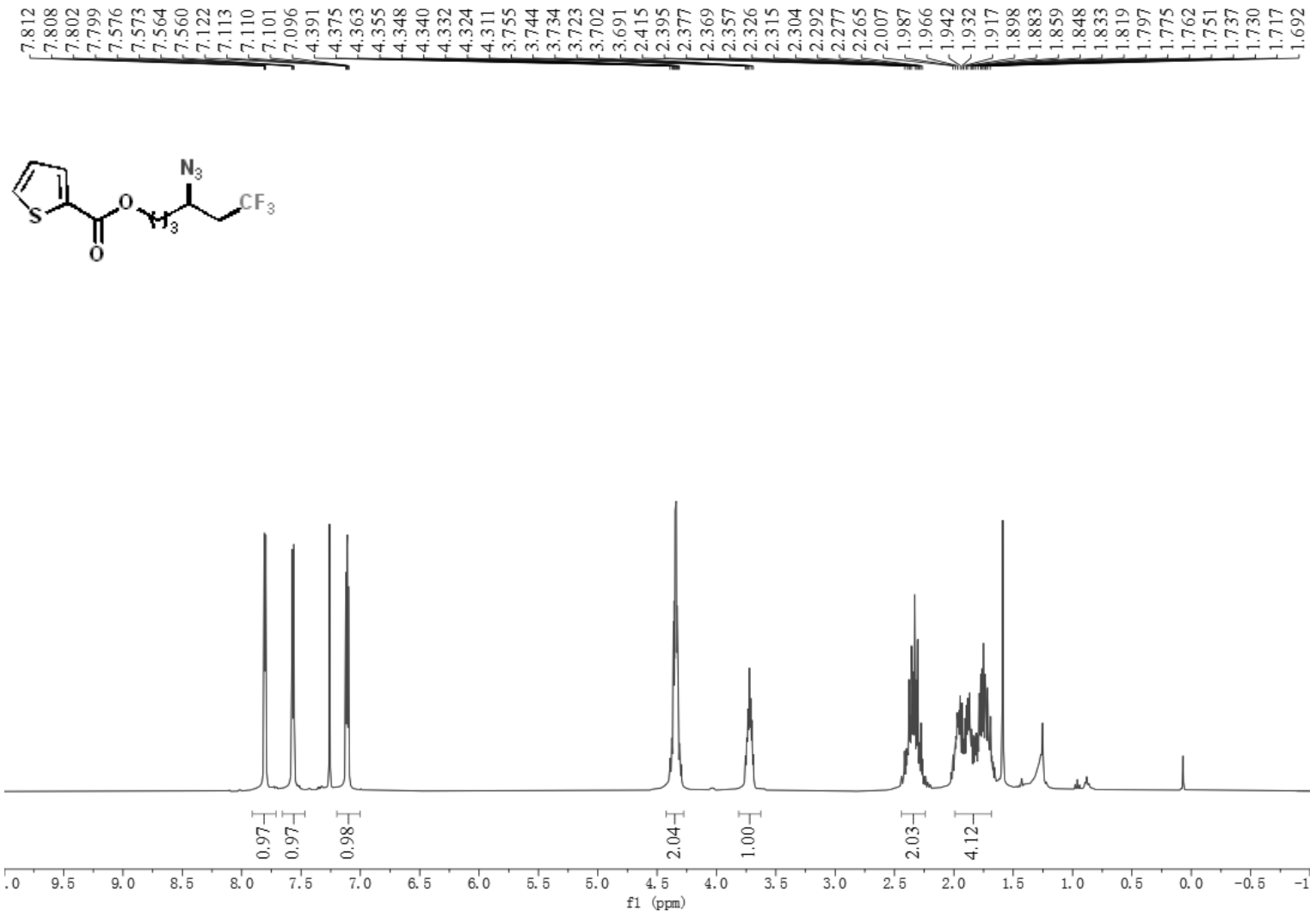
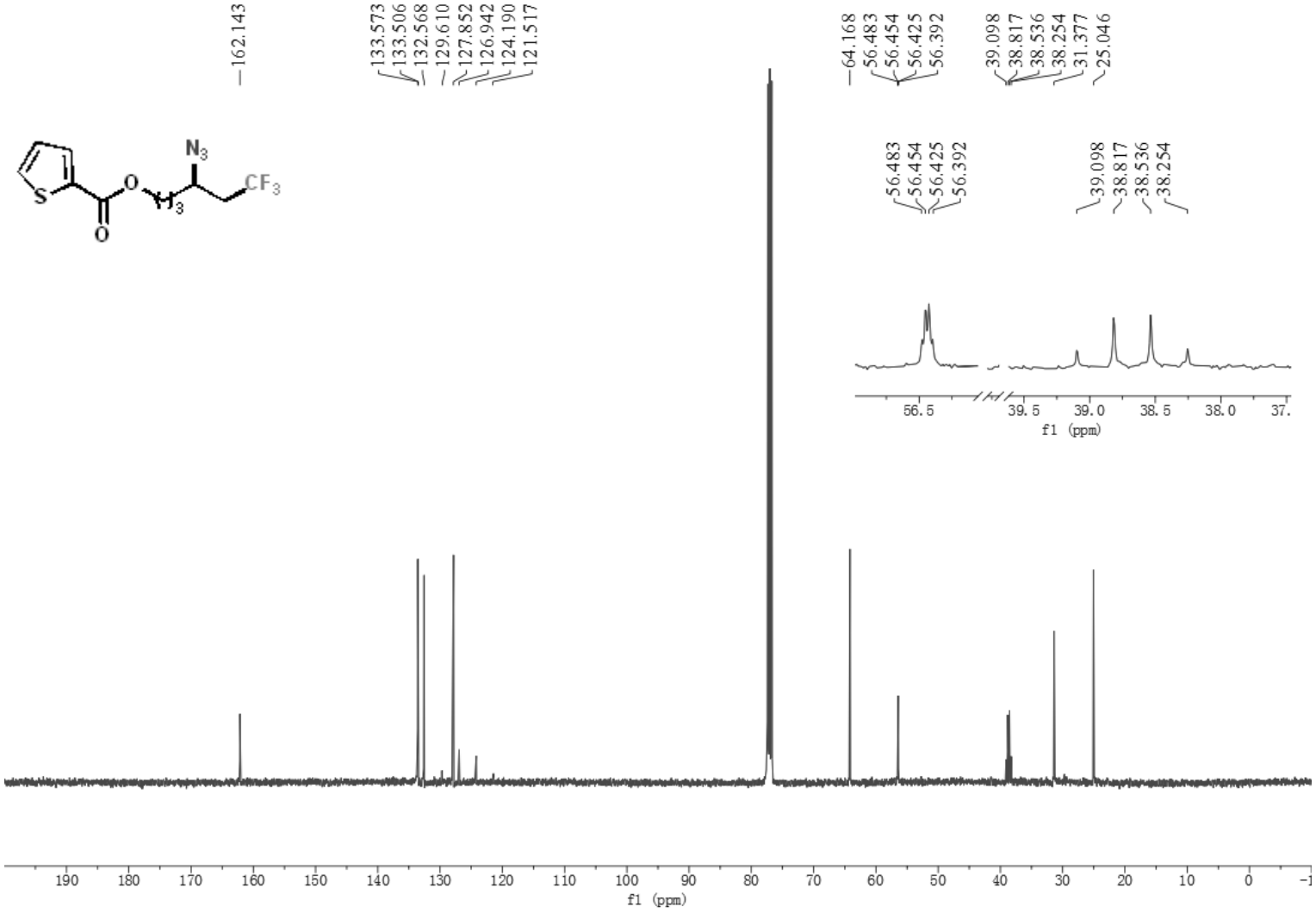
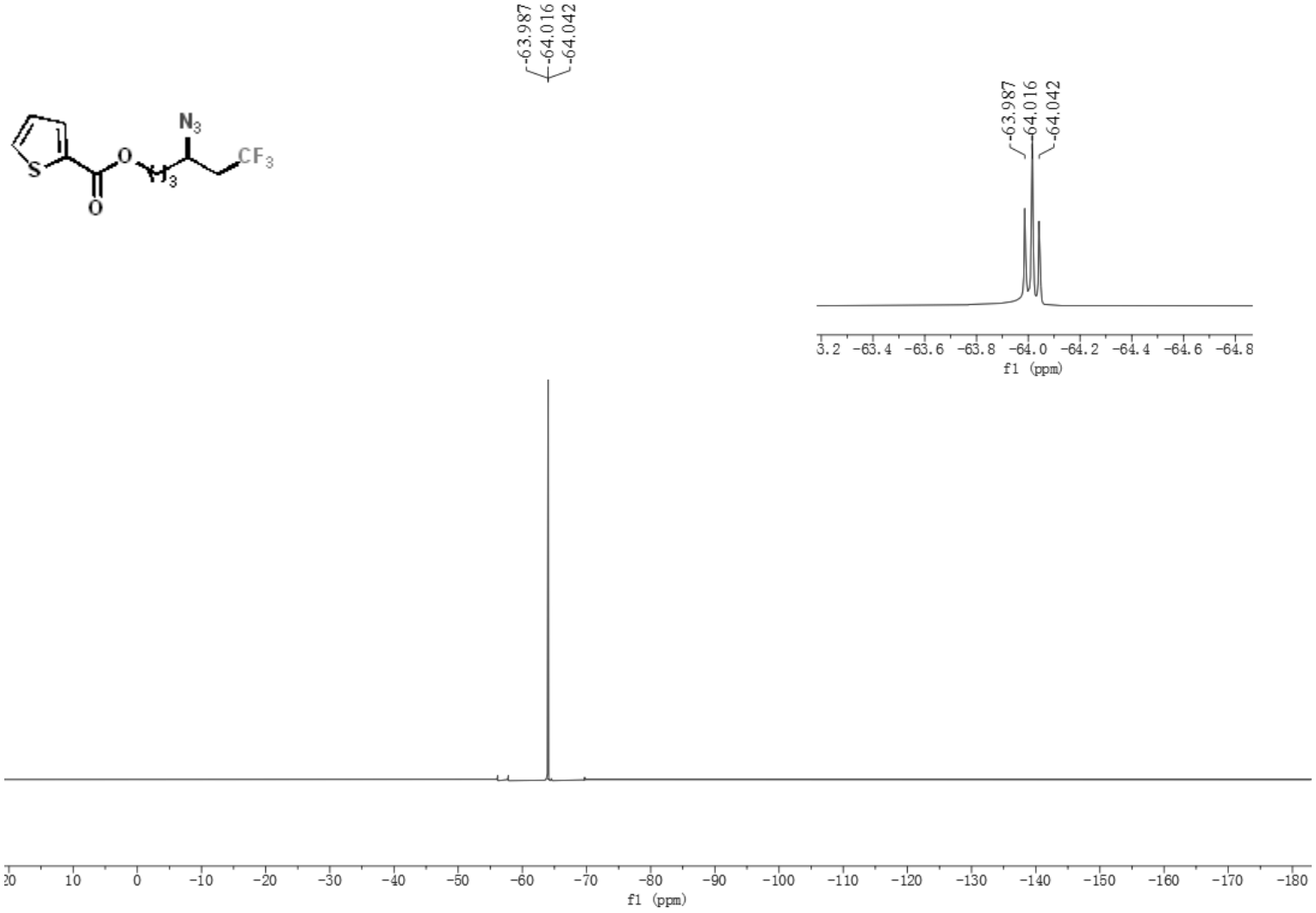


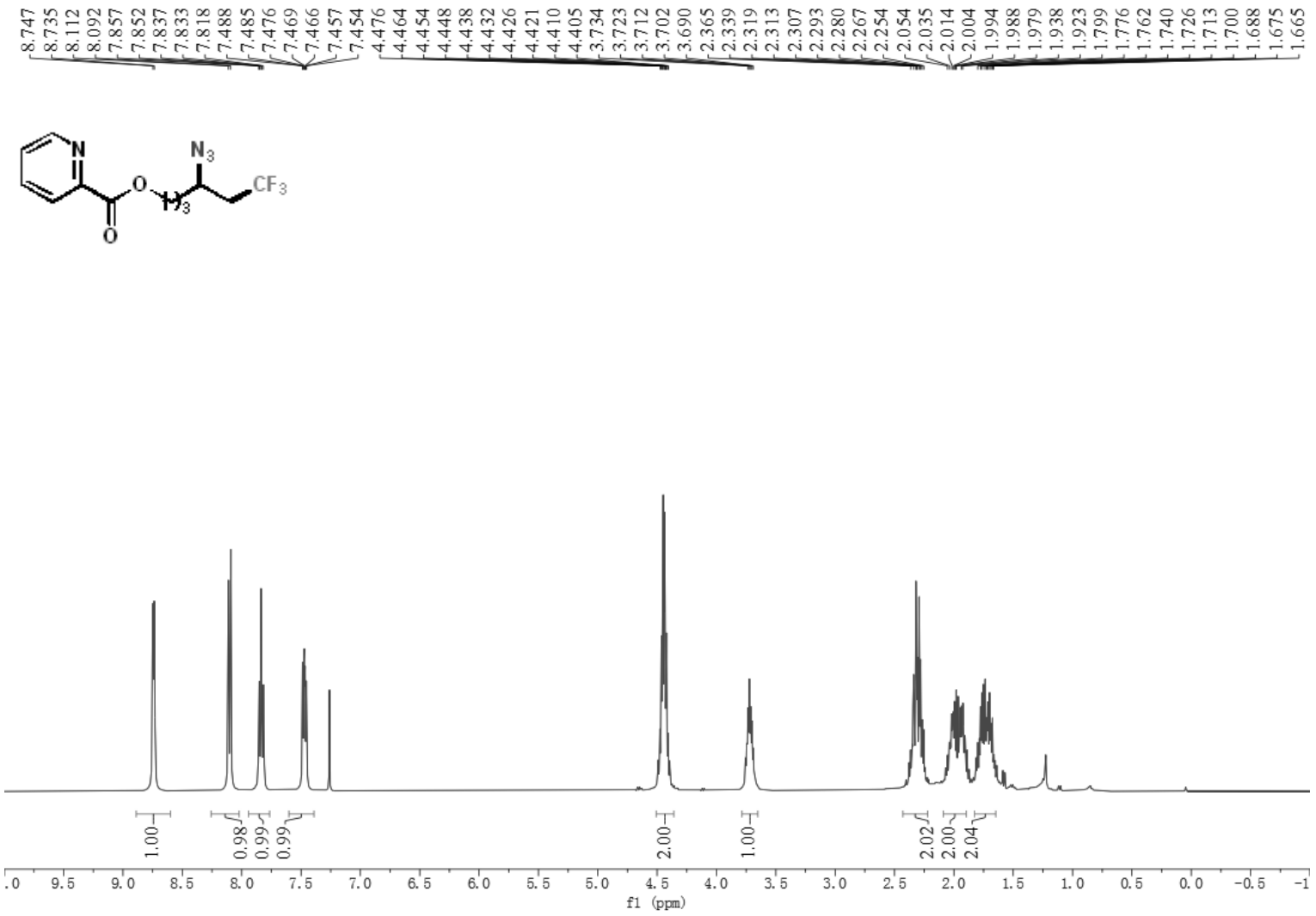
^{1}H NMR (400 MHz, $CDCl_3$) of **2m**



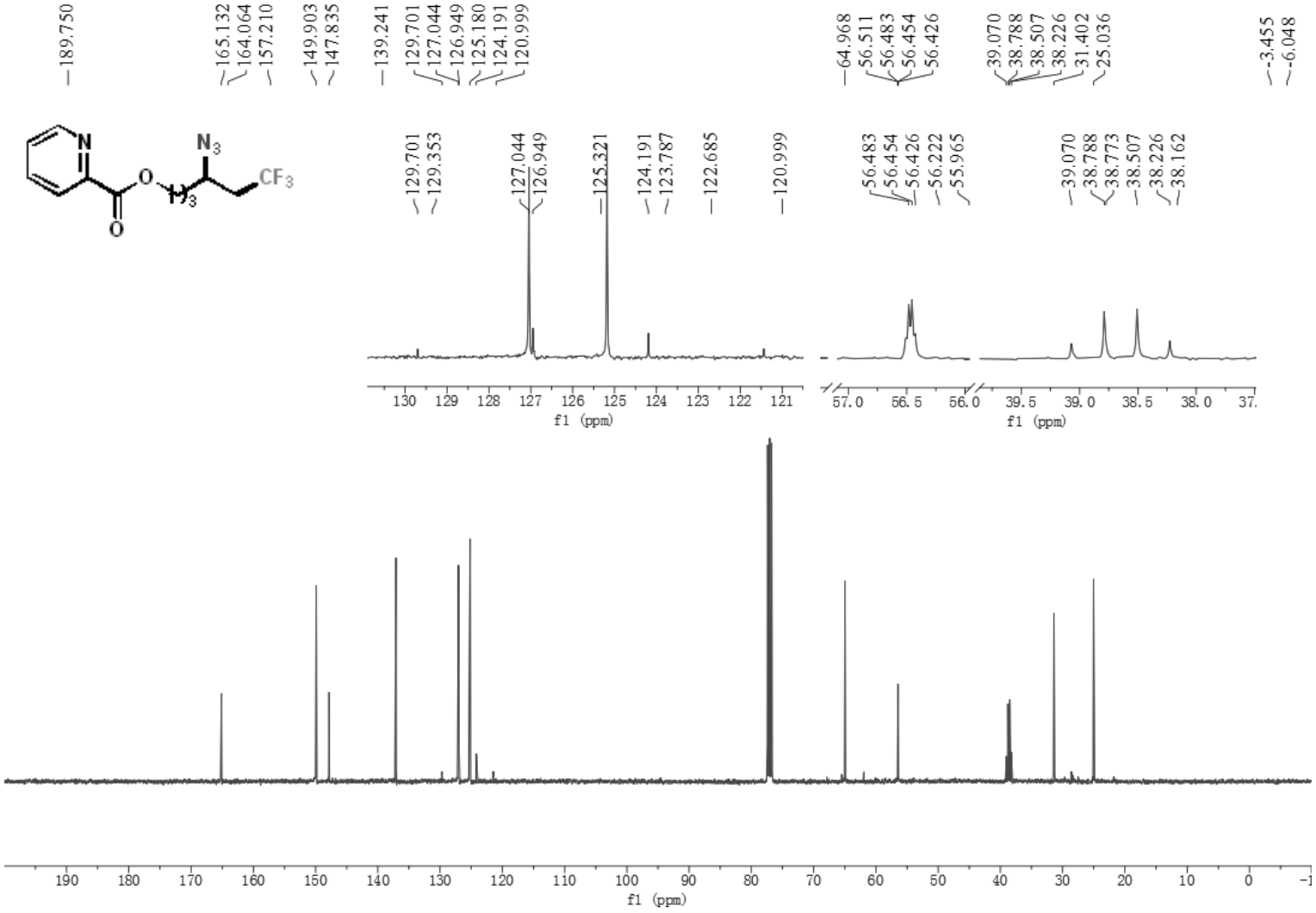
^{13}C NMR (100 MHz, $CDCl_3$) of **2m**



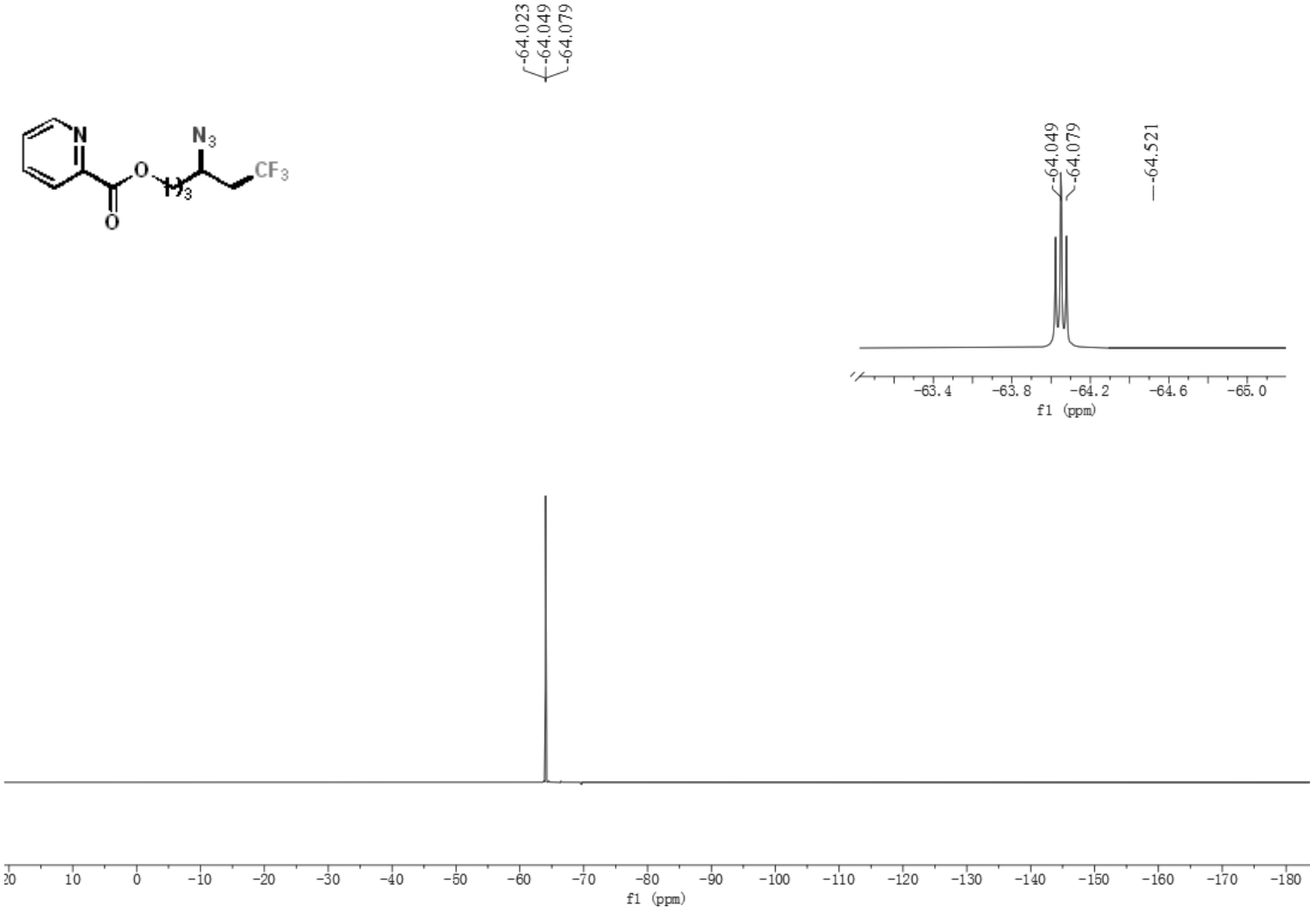
^{19}F NMR (376 MHz, $CDCl_3$) of **2m**



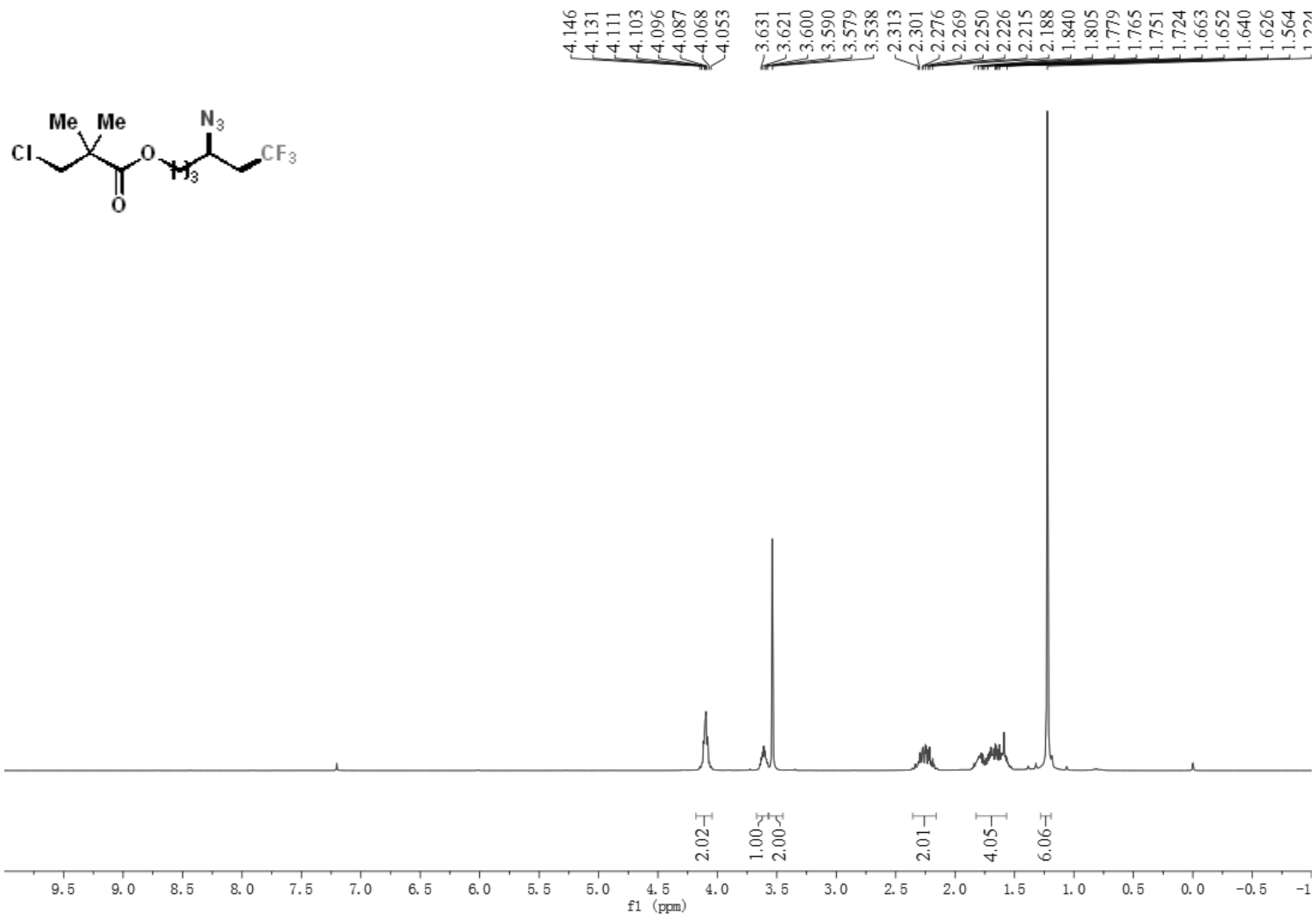
^{1}H NMR (400 MHz, $CDCl_3$) of **2n**



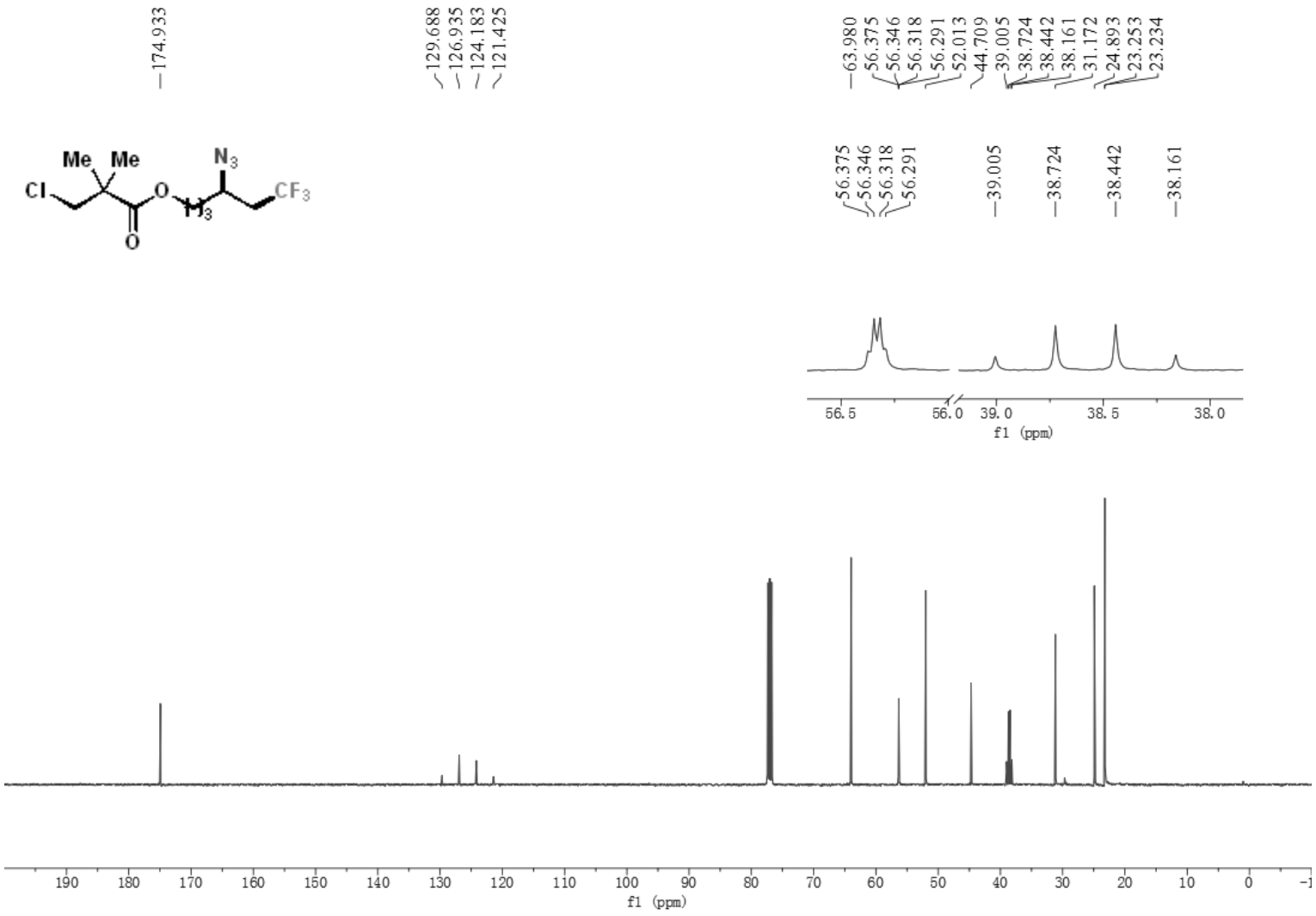
^{13}C NMR (100 MHz, $CDCl_3$) of **2n**



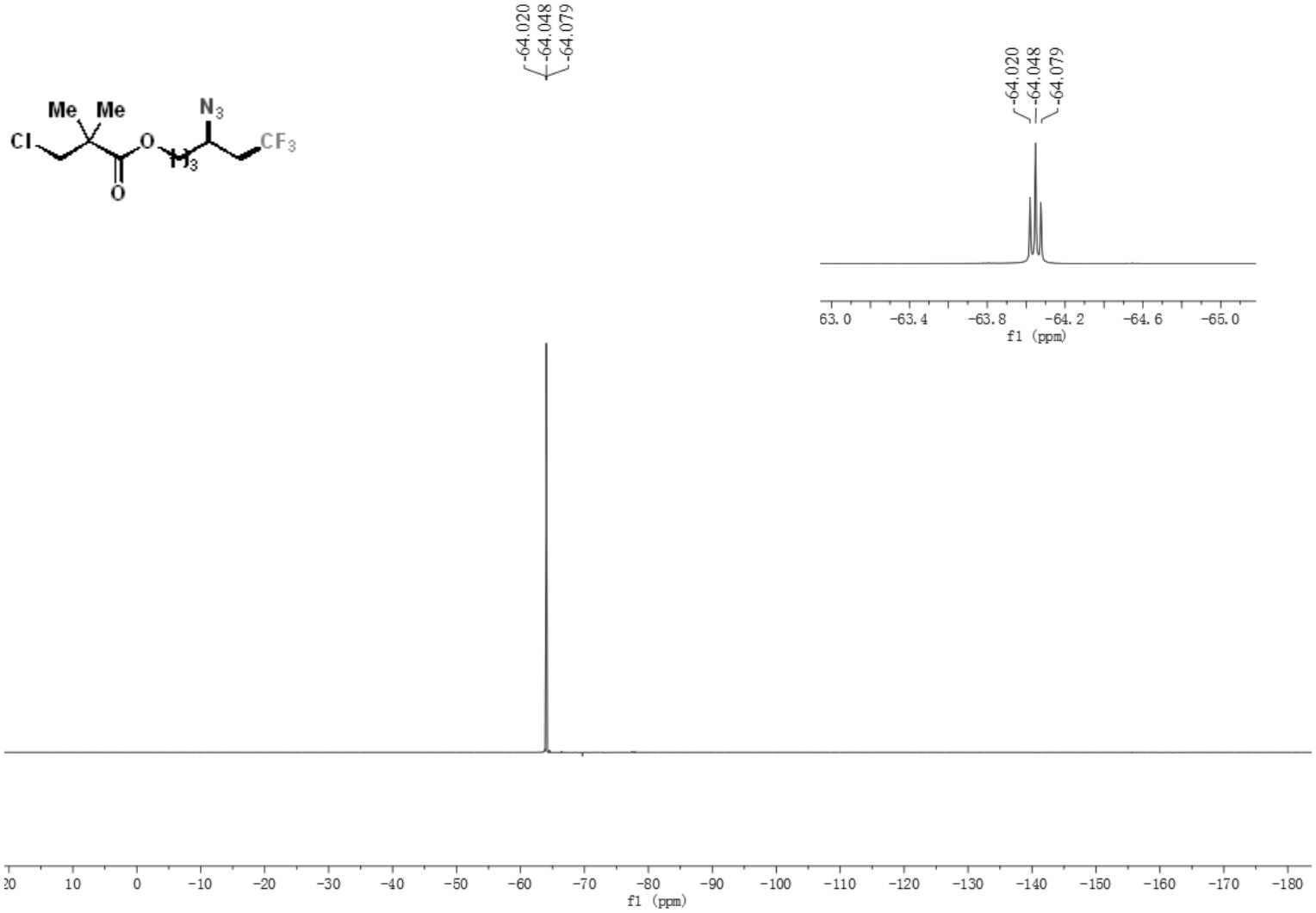
^{19}F C NMR (376 MHz, $CDCl_3$) of **2n**



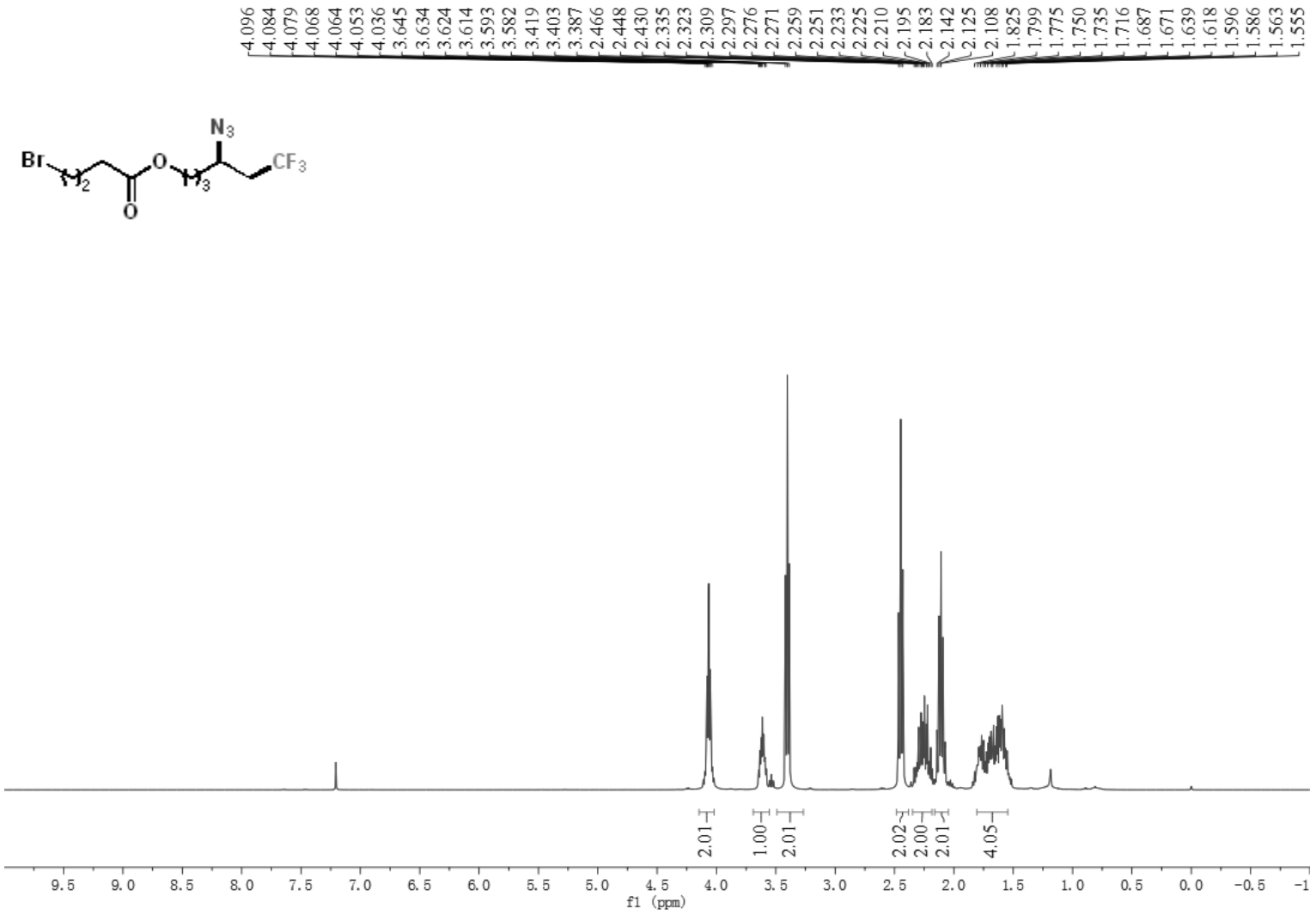
^{1}H NMR (400 MHz, $CDCl_3$) of **2o**



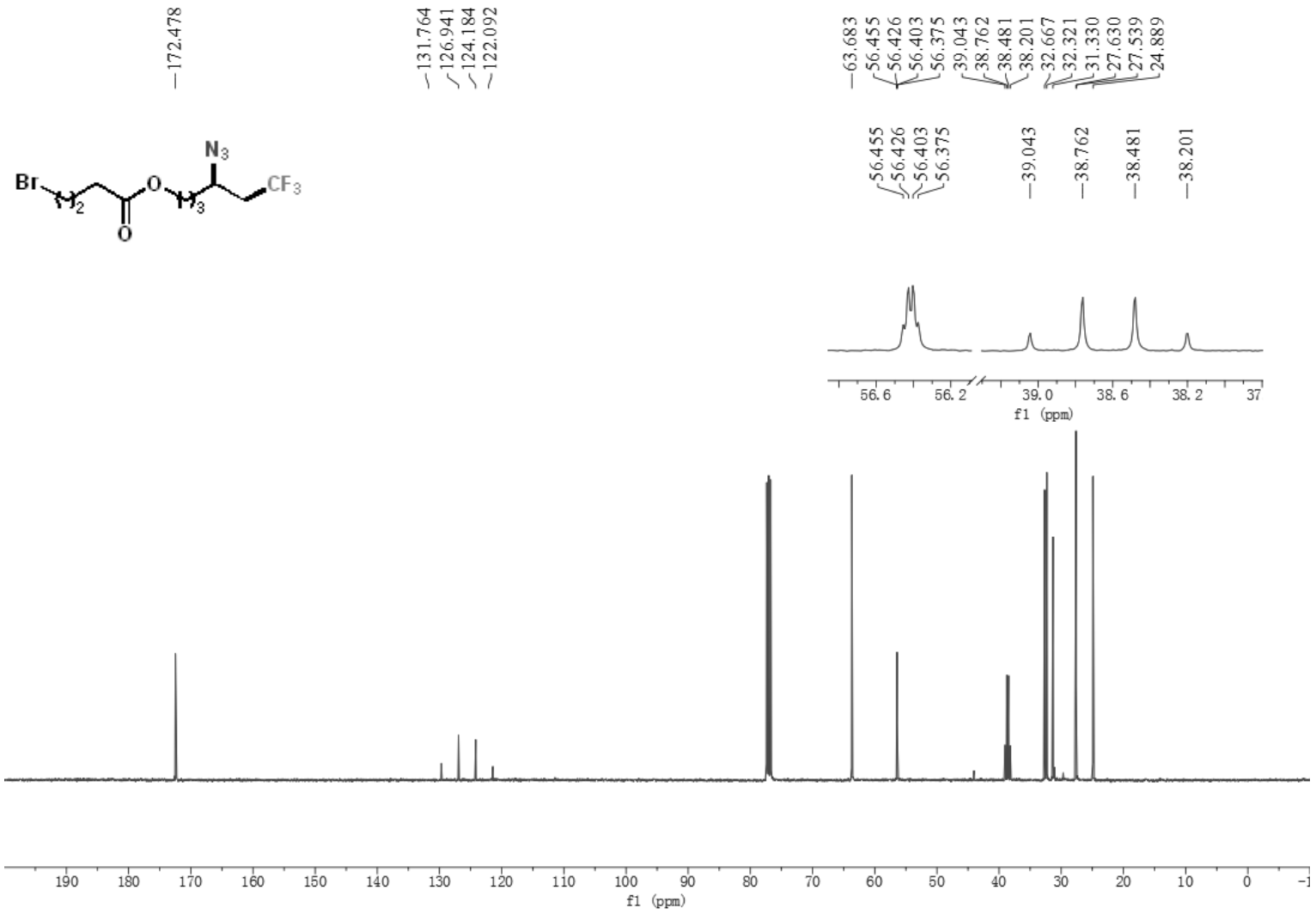
^{13}C NMR (100 MHz, $CDCl_3$) of **2o**



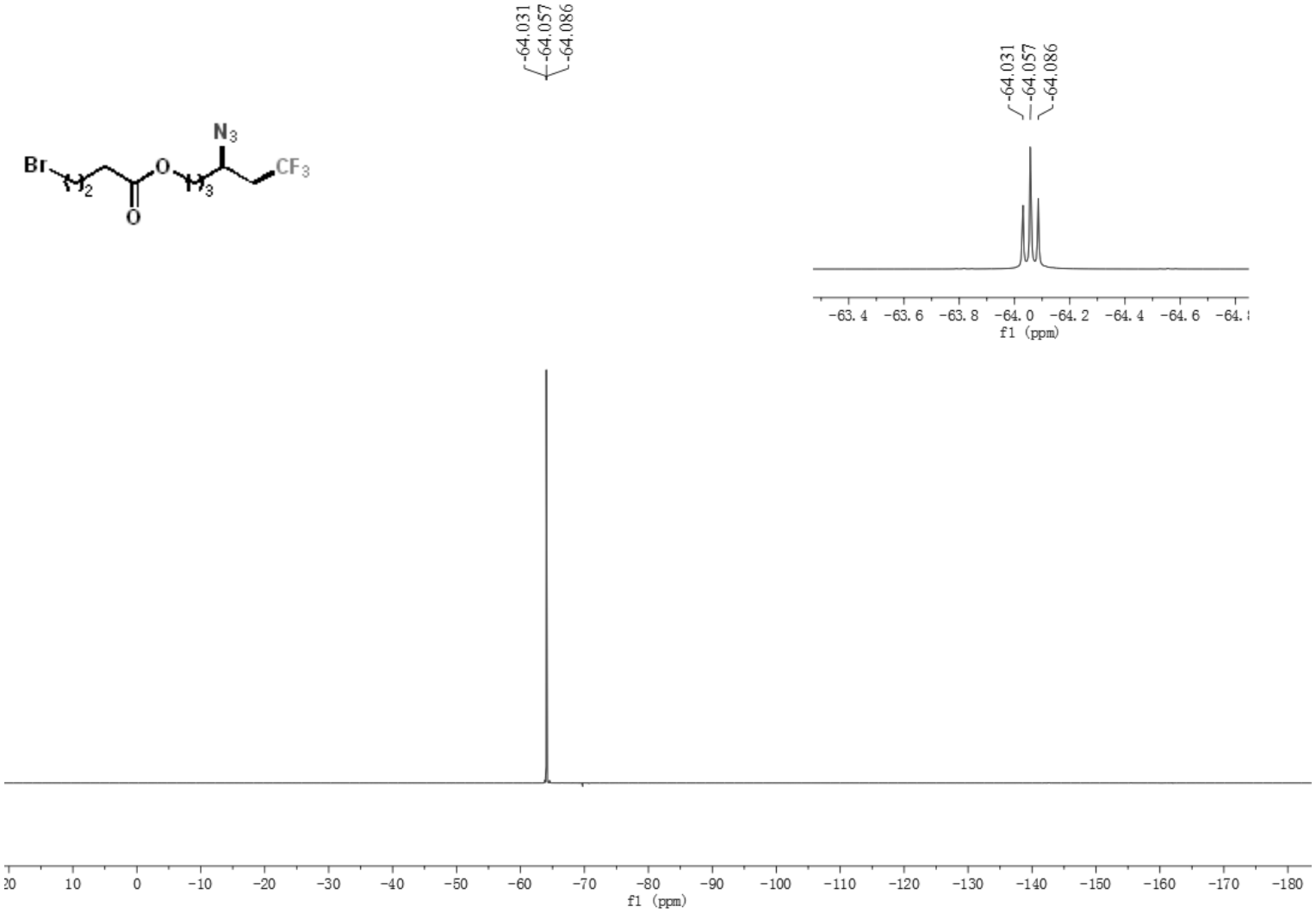
^{19}F NMR (376 MHz, $CDCl_3$) of **2o**



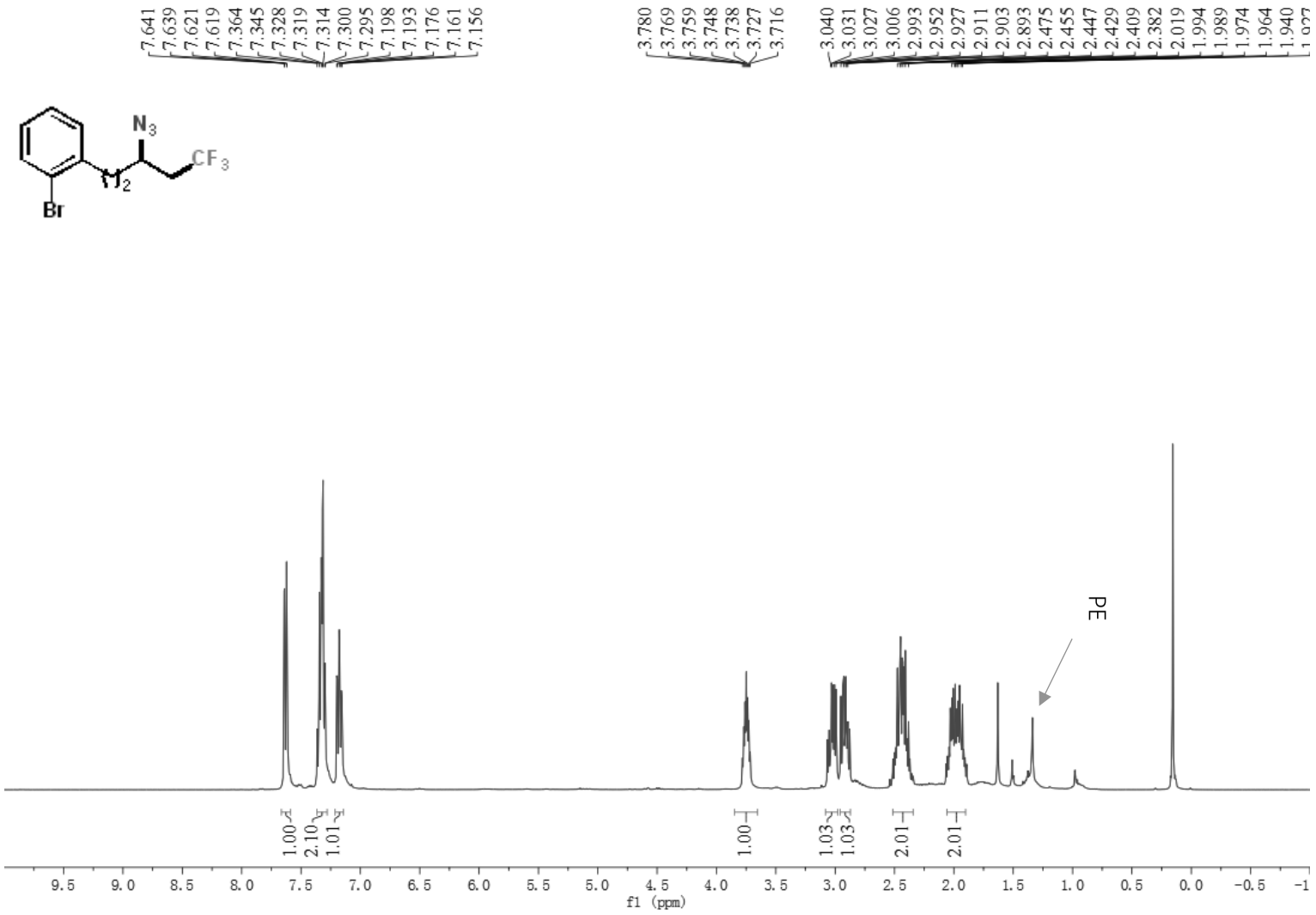
^{1}H NMR (400 MHz, $CDCl_3$) of **2p**



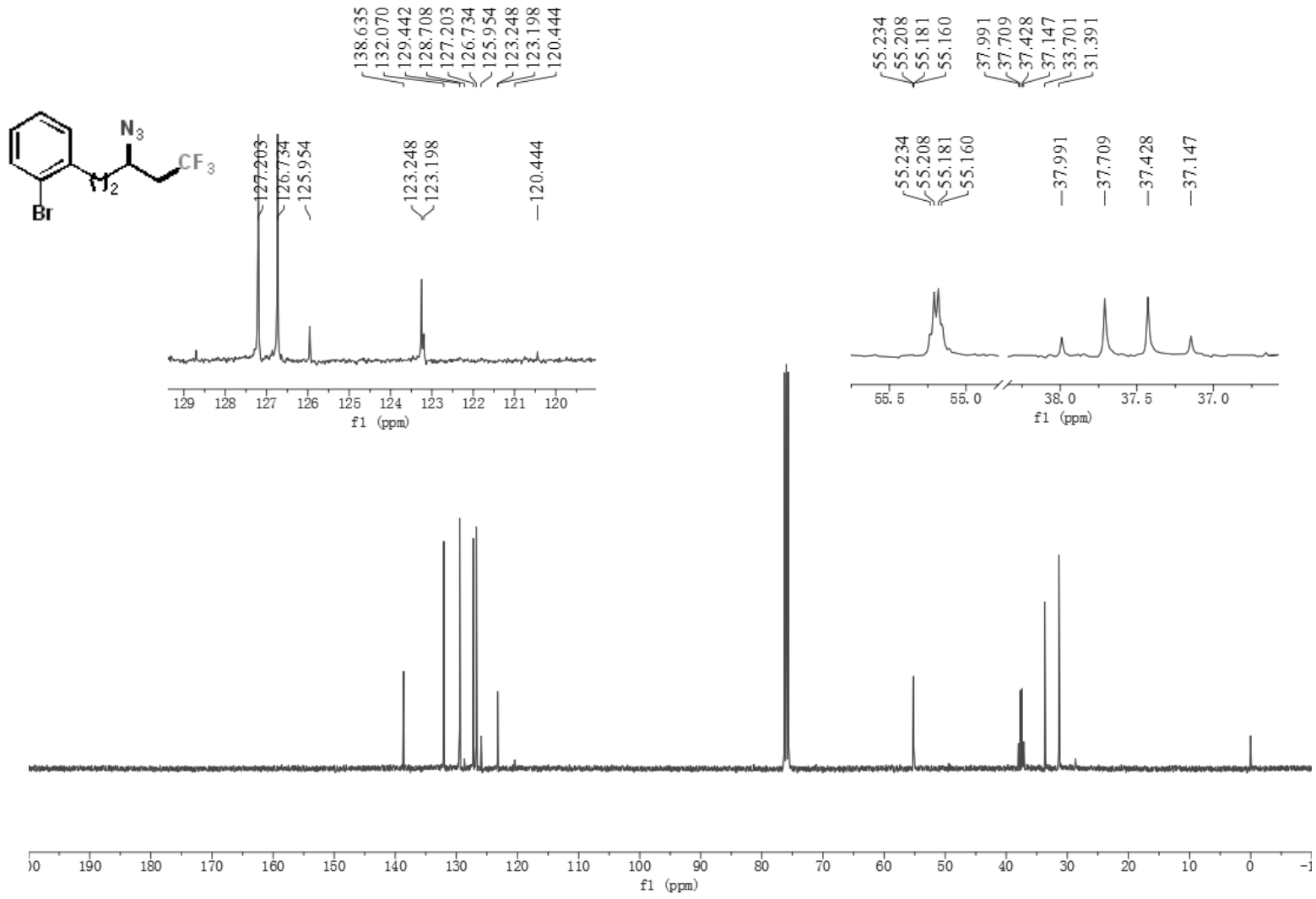
^{13}C NMR (100 MHz, $CDCl_3$) of **2p**



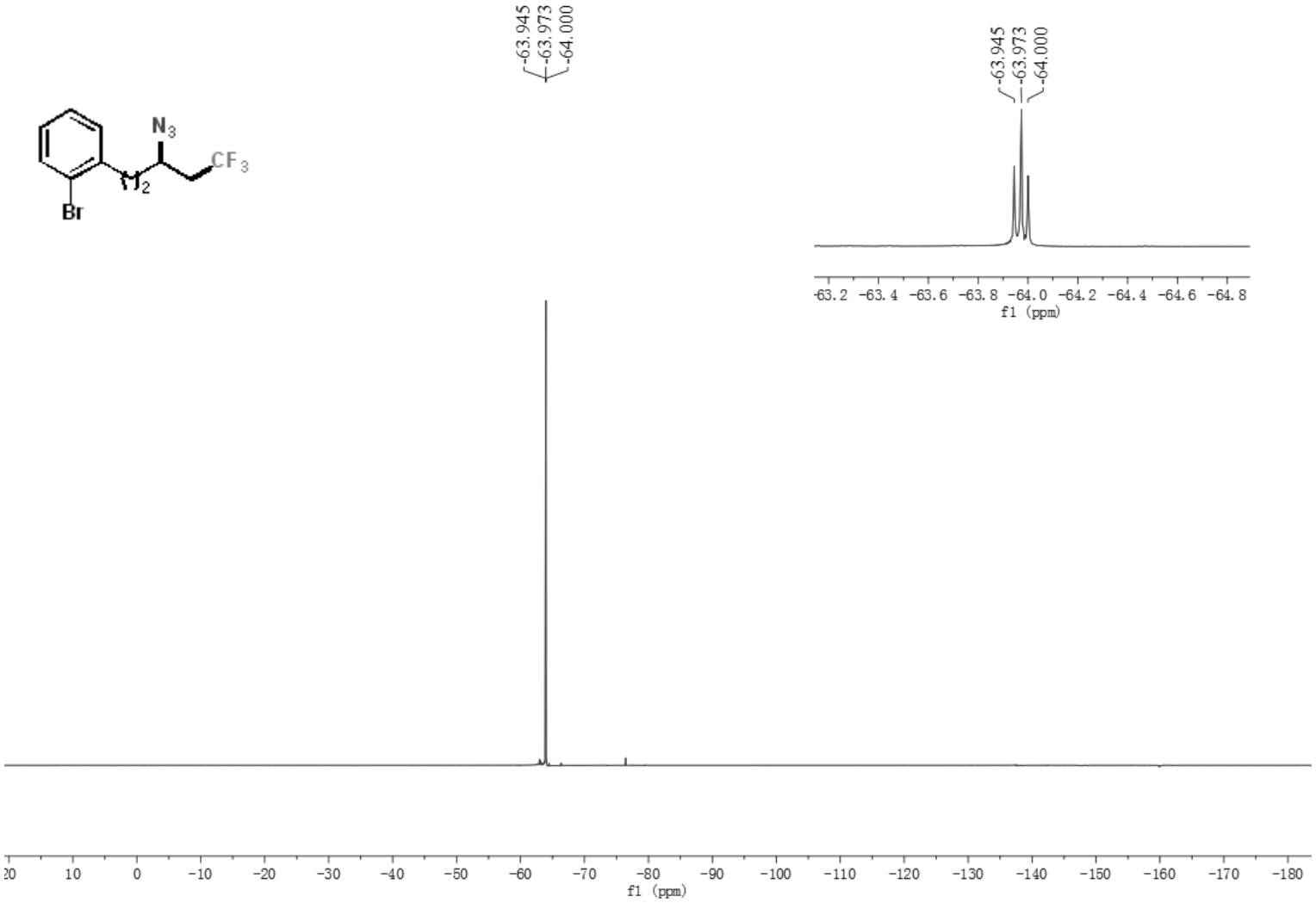
^{19}F NMR (376 MHz, $CDCl_3$) of **2p**



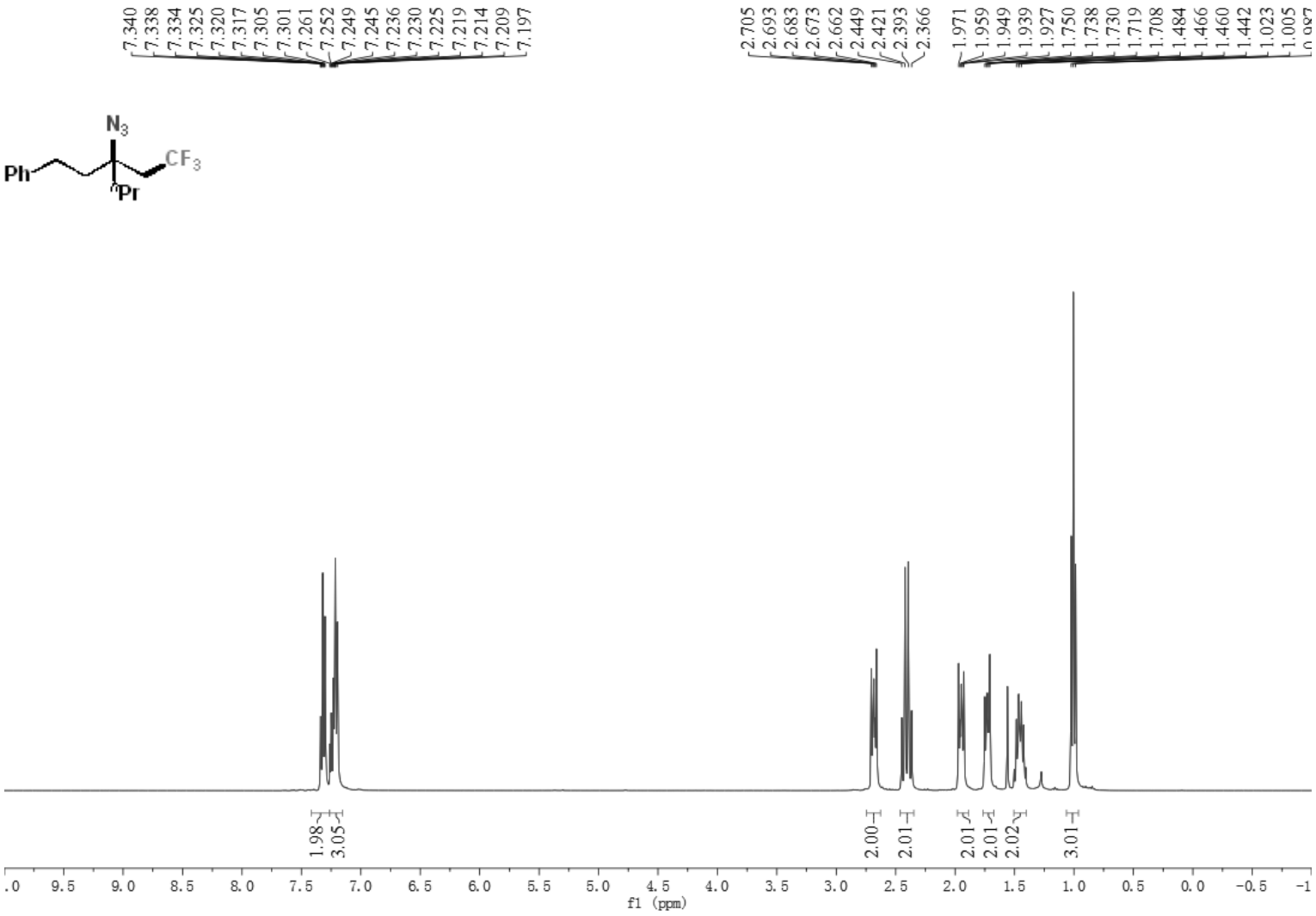
^{1}H NMR (400 MHz, $CDCl_3$) of **2q**



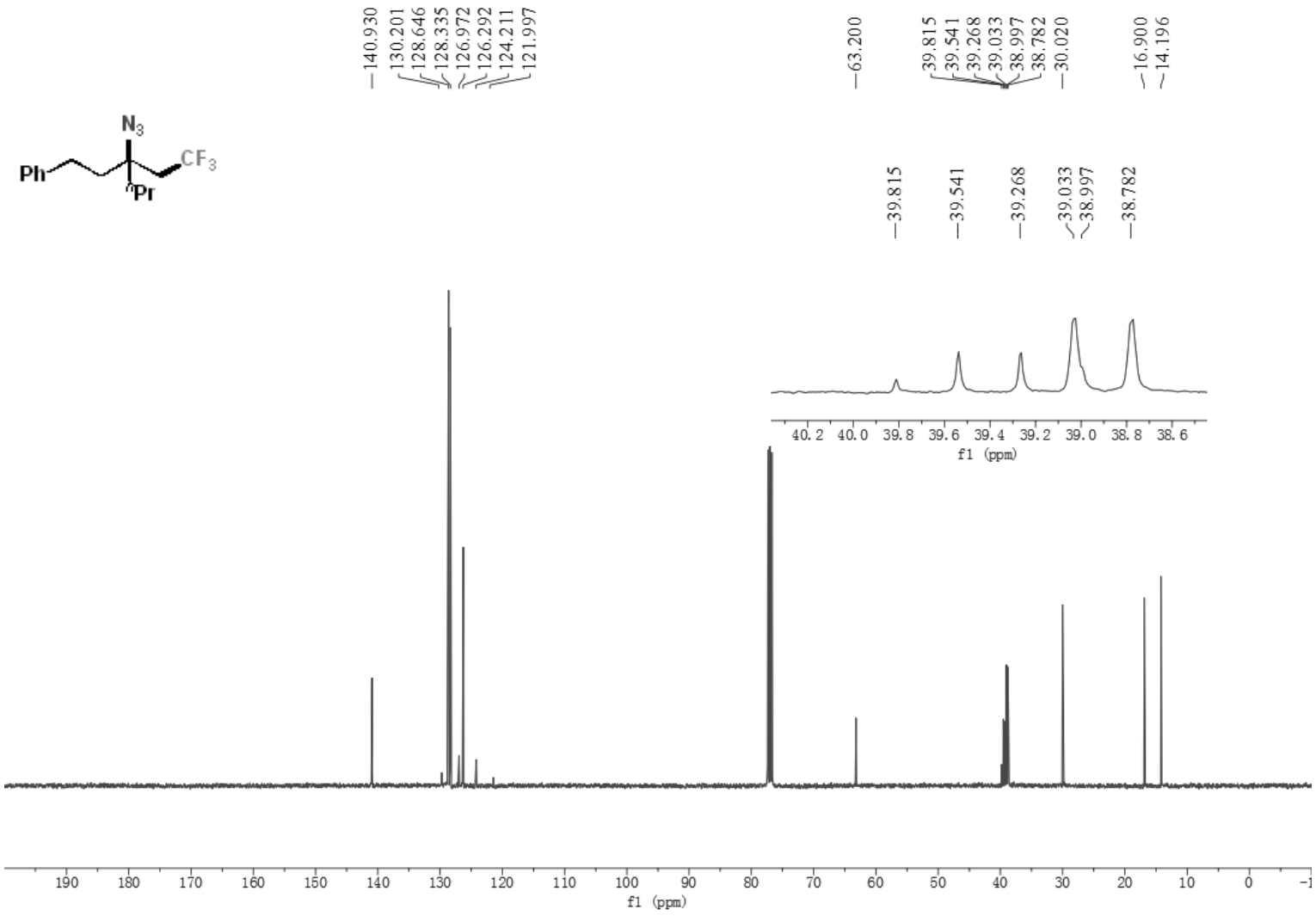
^{13}C NMR (100 MHz, $CDCl_3$) of **2q**



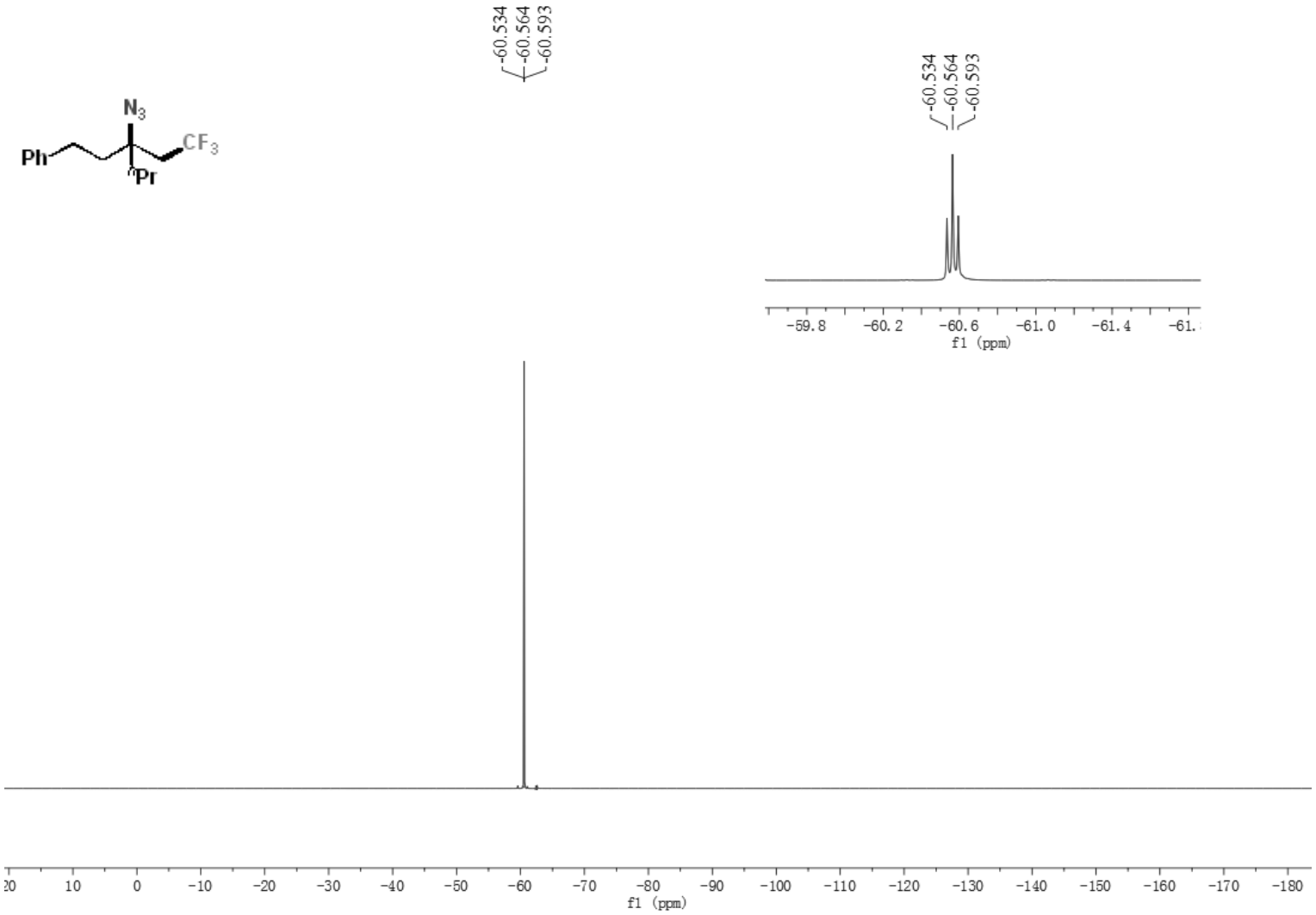
^{19}F NMR (376 MHz, $CDCl_3$) of **2q**



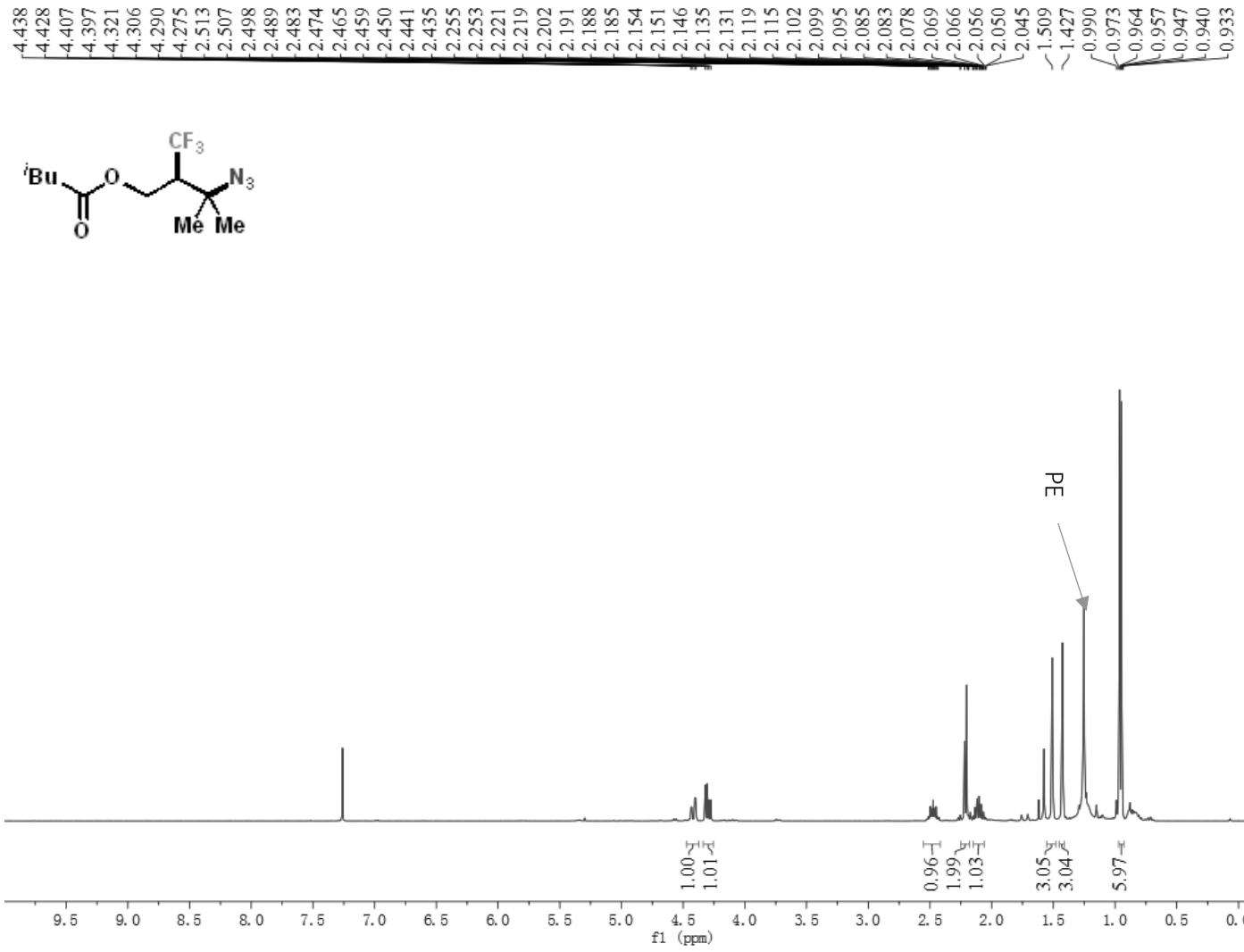
^{1}H NMR (400 MHz, $CDCl_3$) of **2w**



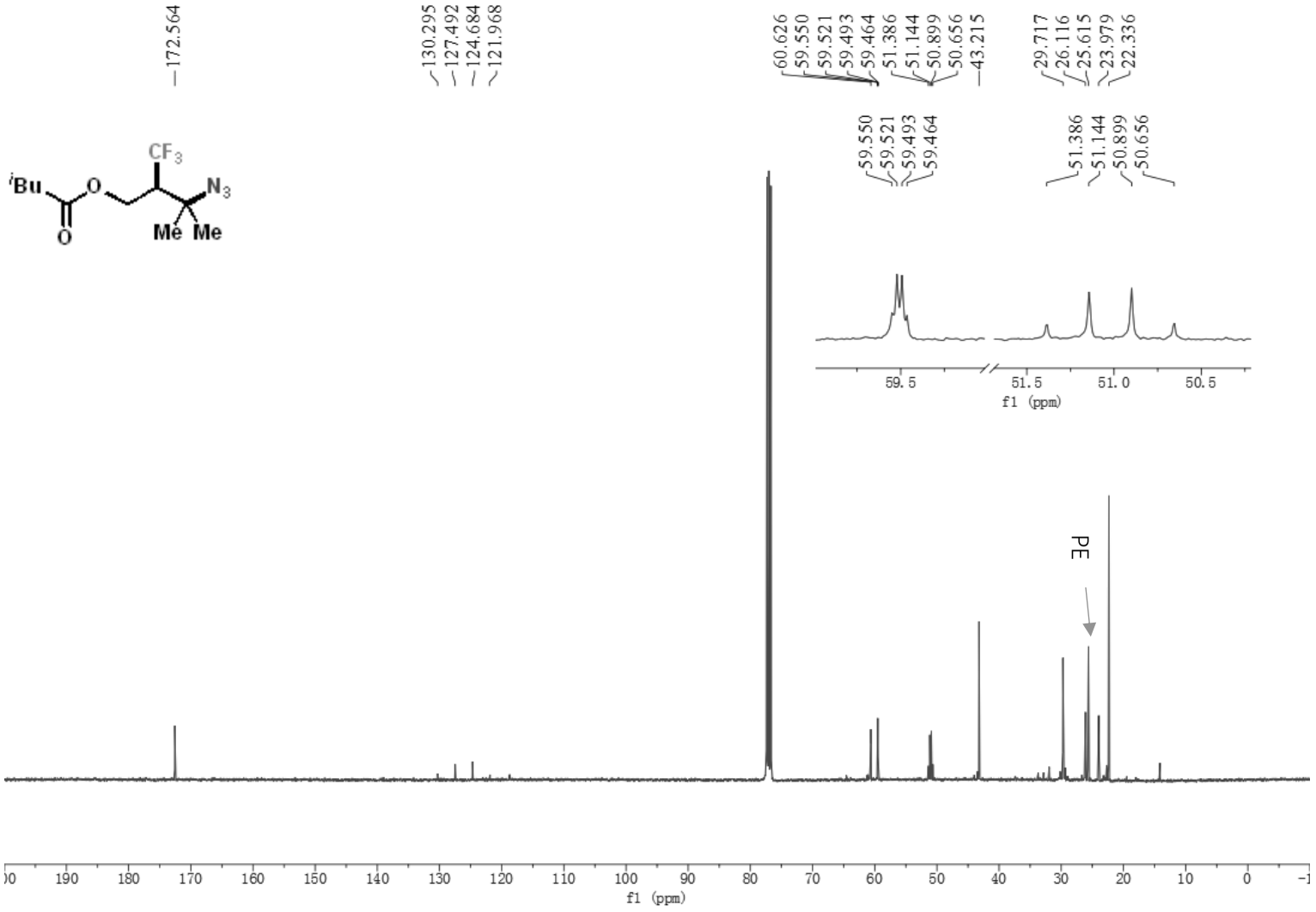
^{13}C NMR (100 MHz, $CDCl_3$) of **2w**



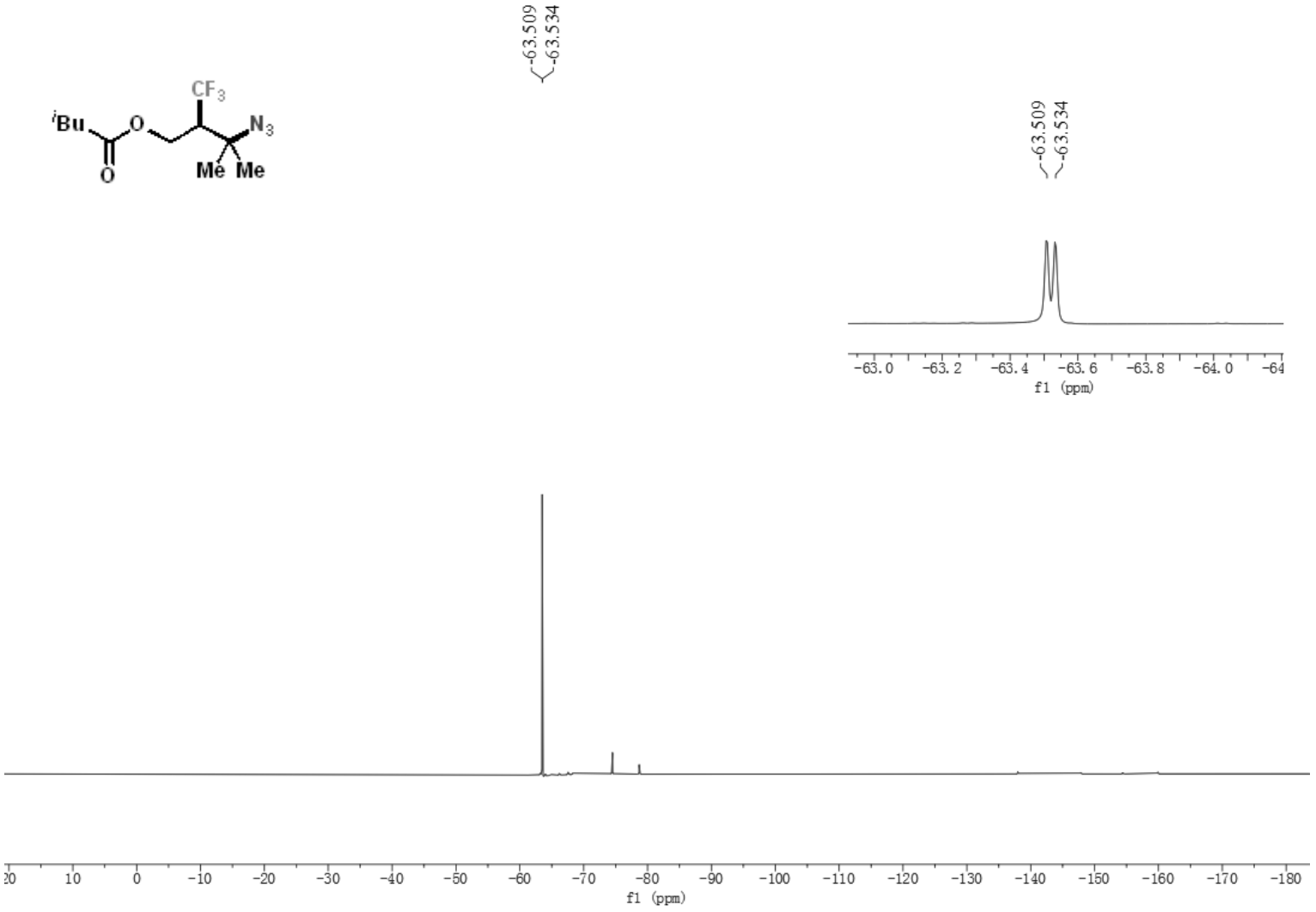
^{19}F NMR (376) MHz, $CDCl_3$) of **2w**



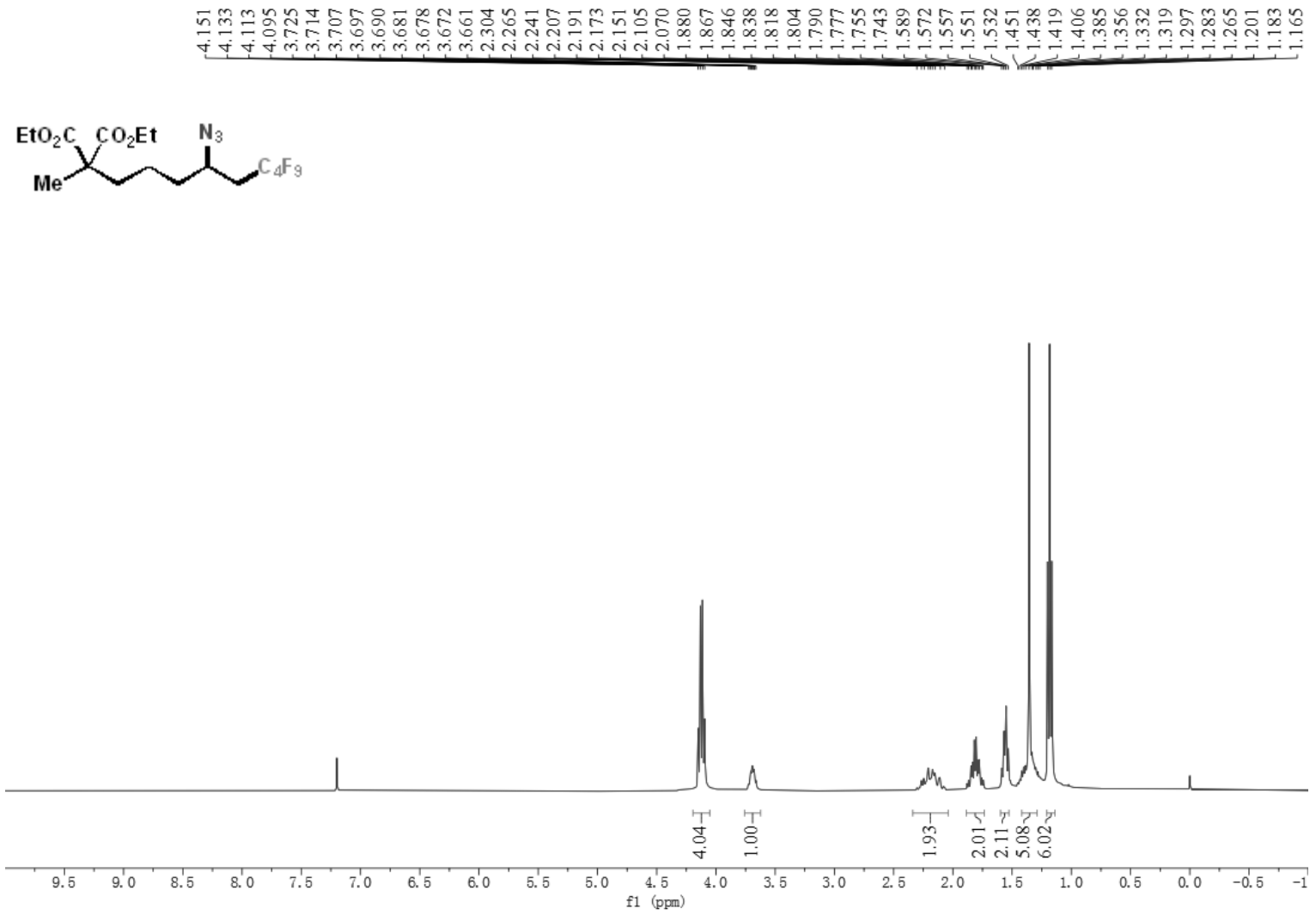
^{1}H NMR (400 MHz, $CDCl_3$) of **2x**



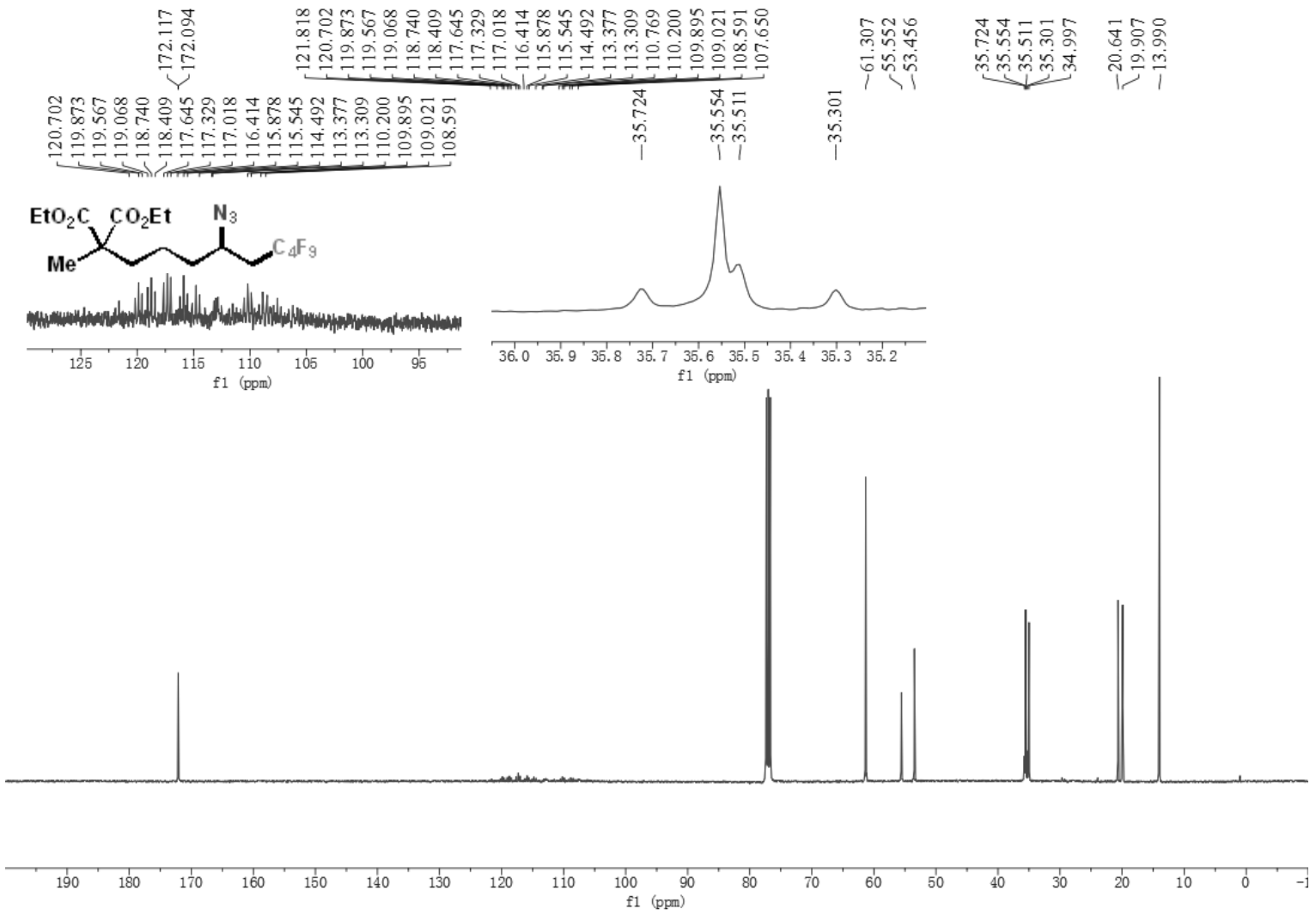
^{13}C NMR (100 MHz, $CDCl_3$) of **2x**



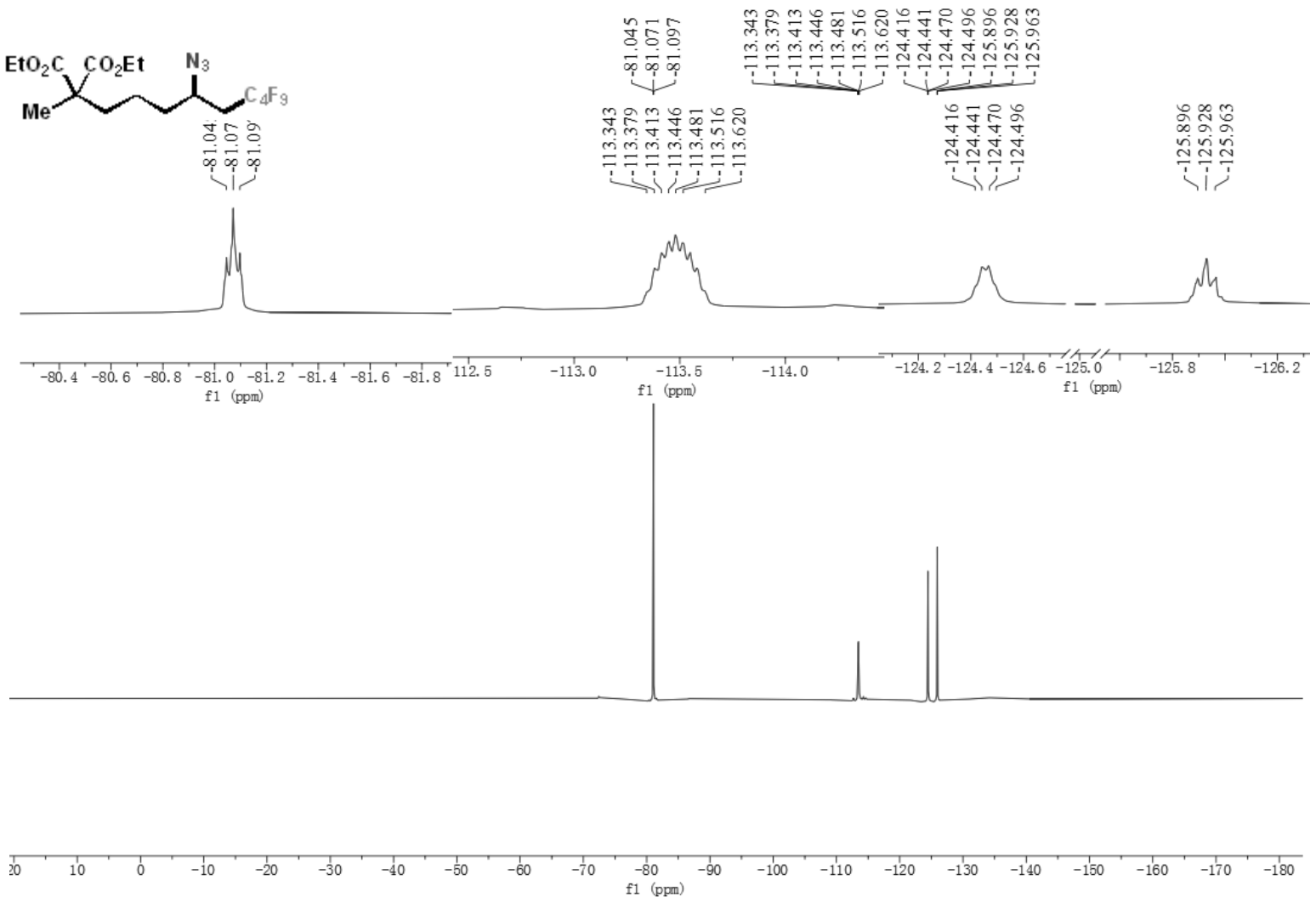
^{19}F NMR (376 MHz, $CDCl_3$) of **2x**



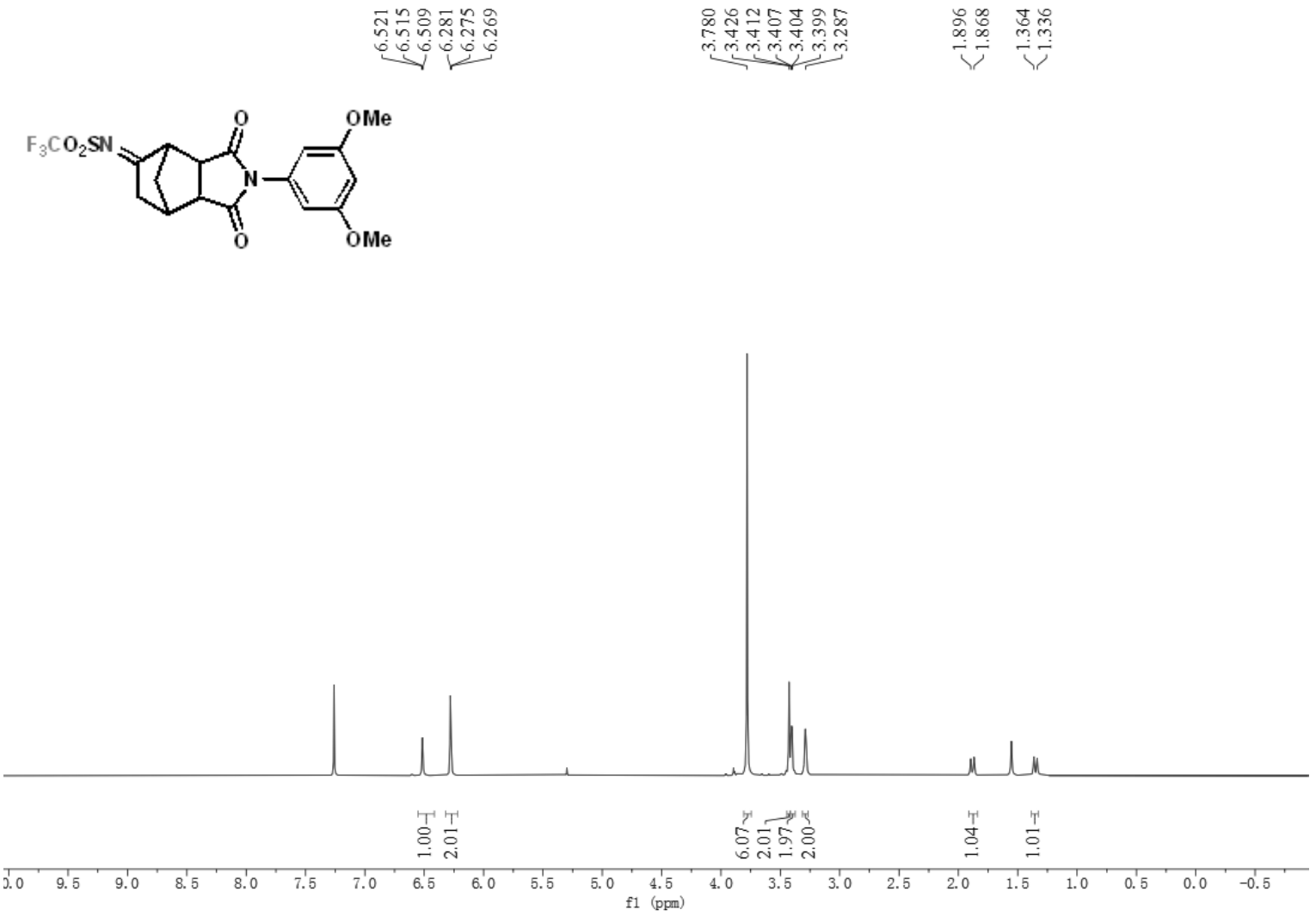
^{1}H NMR (400 MHz, $CDCl_3$) of **2a'**



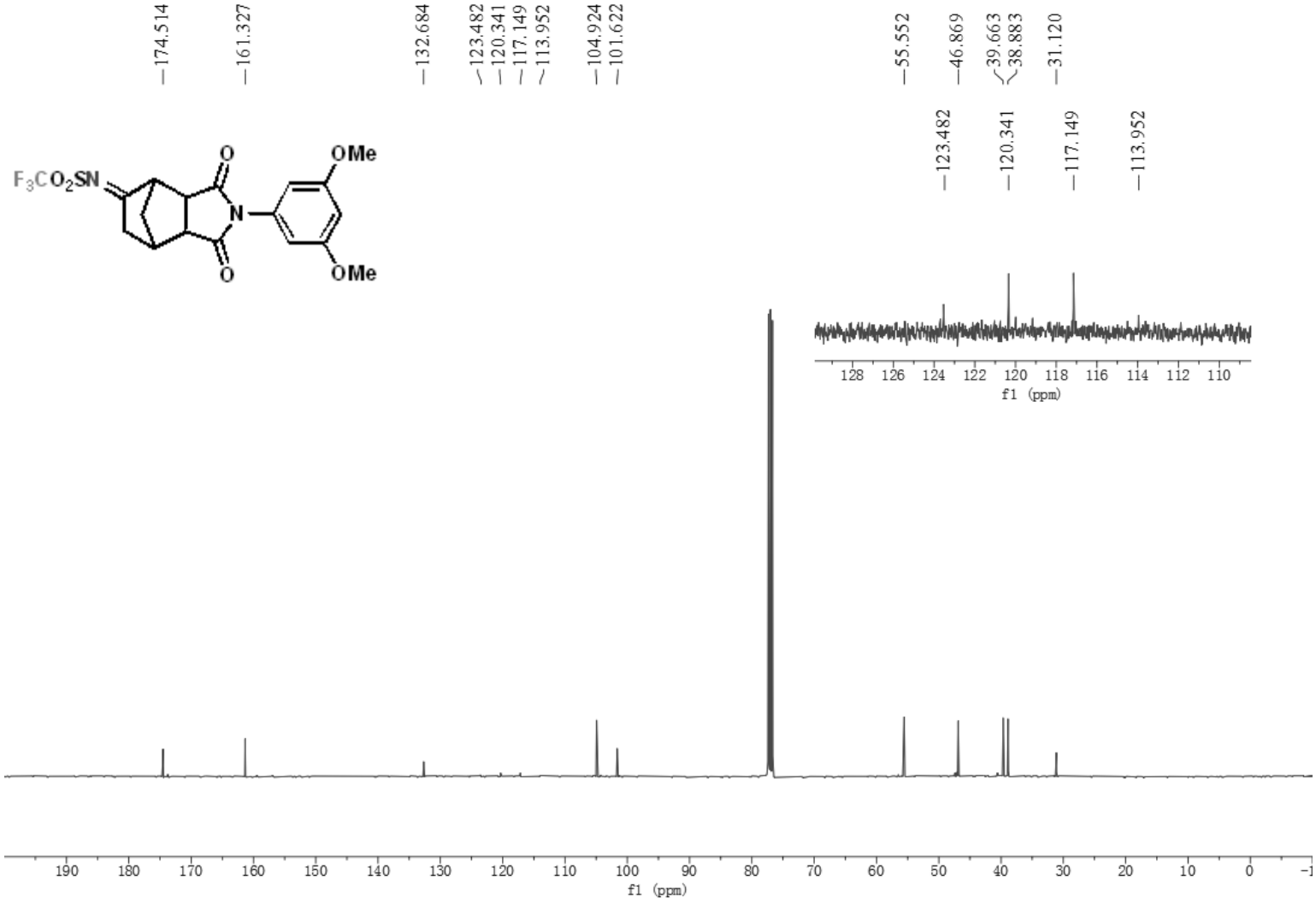
^{13}C NMR (100 MHz, $CDCl_3$) of **2a'**



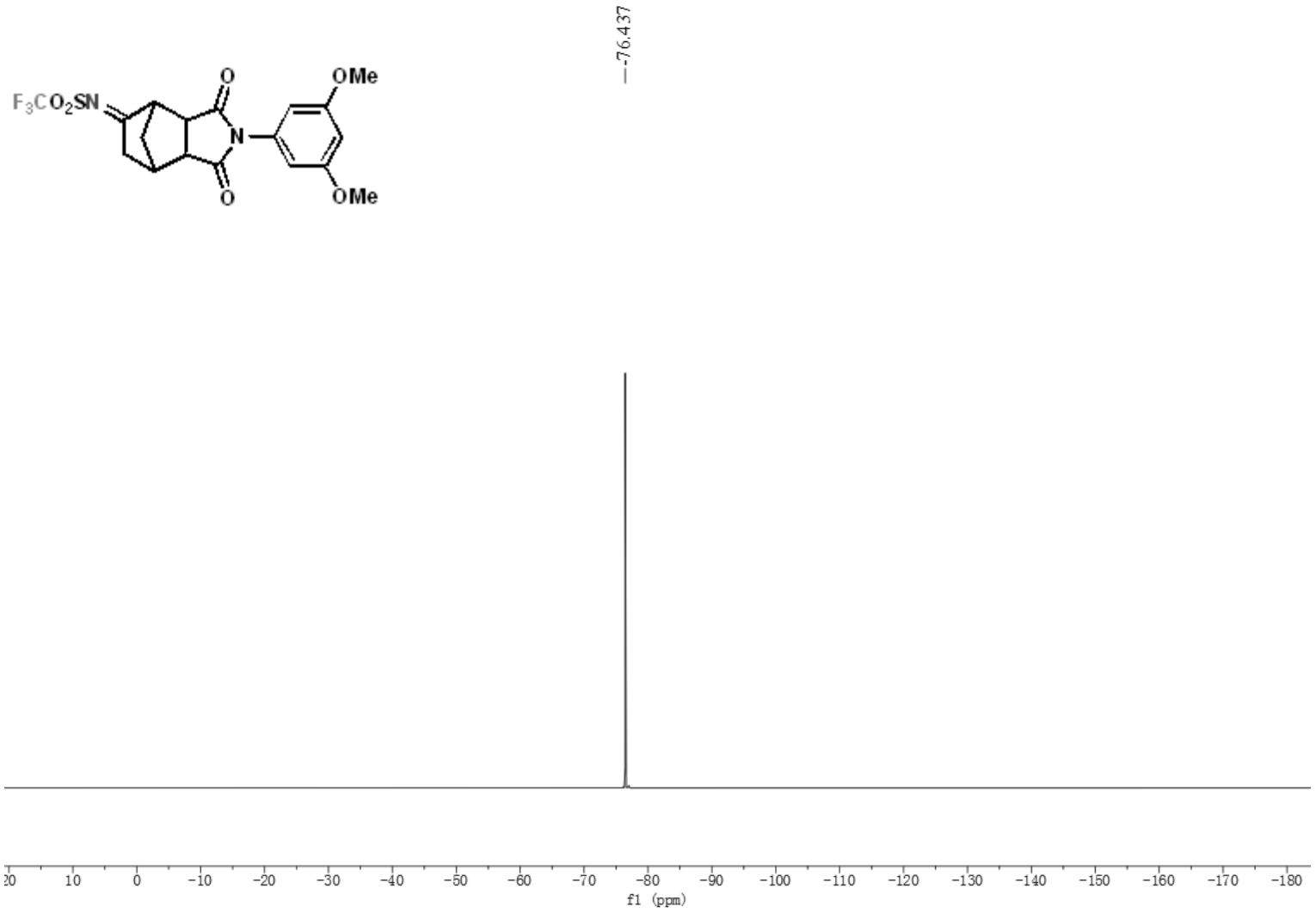
^{19}F NMR (376 MHz, $CDCl_3$) of **2a'**



^{1}H NMR (400 MHz, $CDCl_3$) of **2y**



^{13}C NMR (100 MHz, $CDCl_3$) of **2y**



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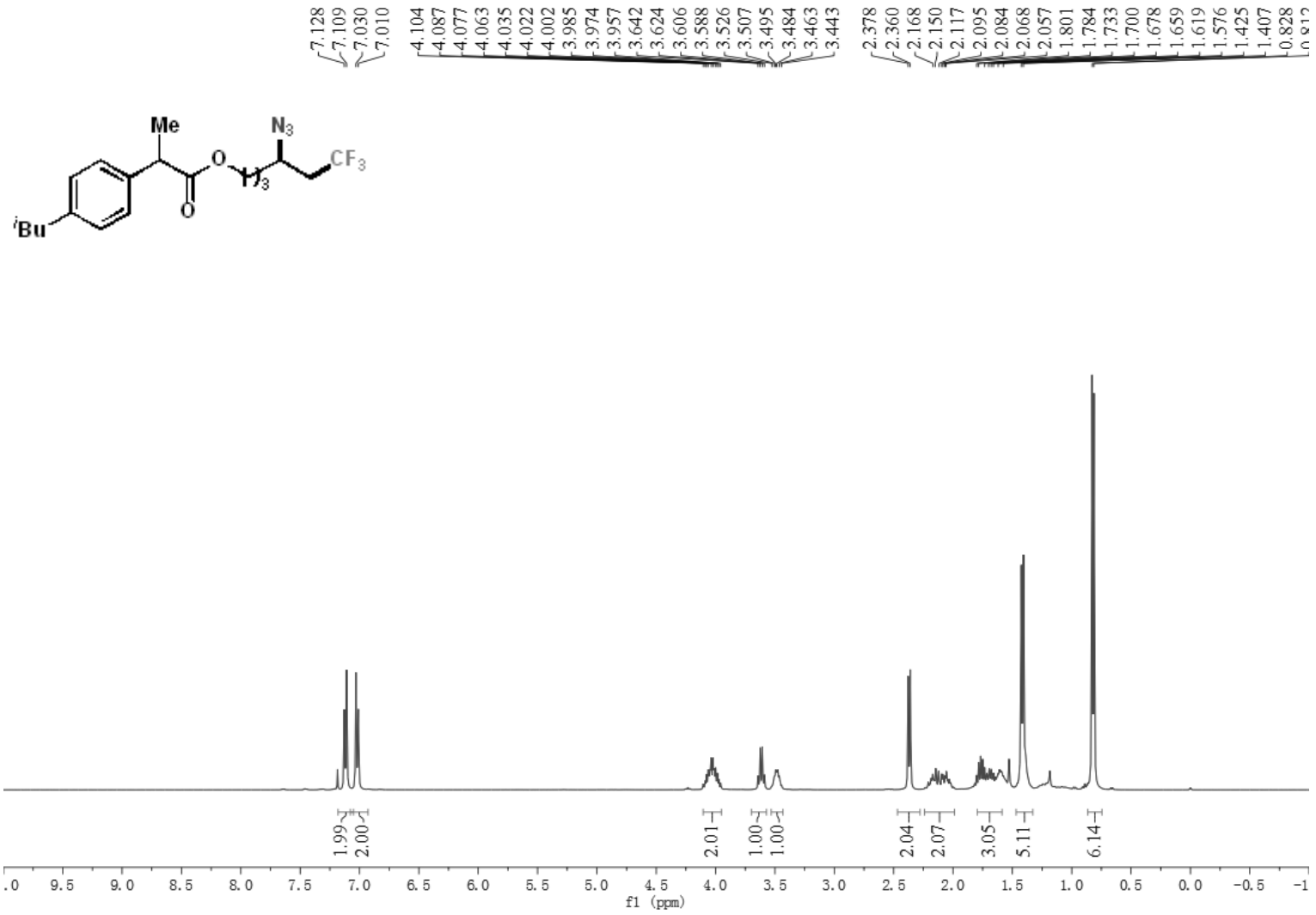
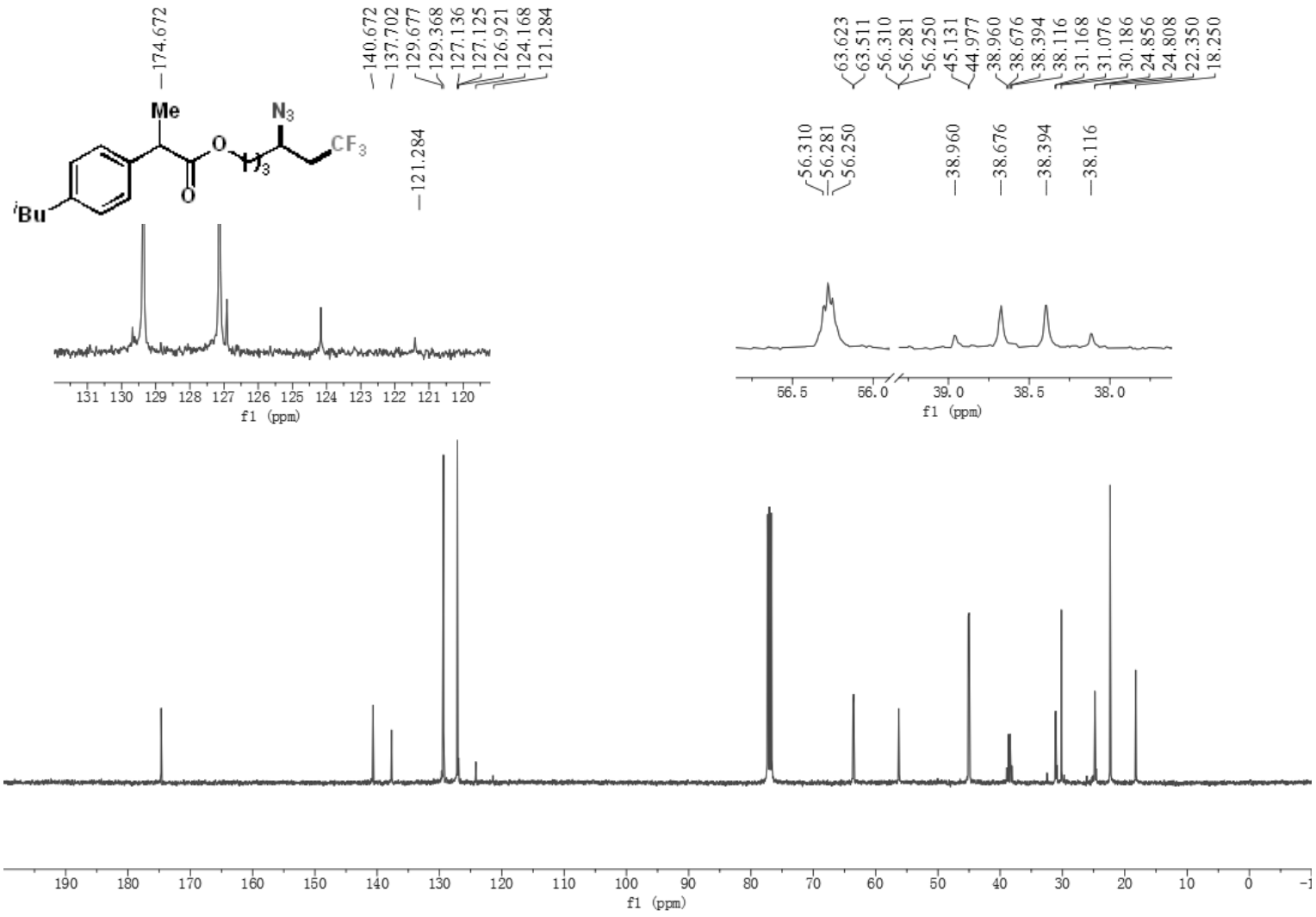
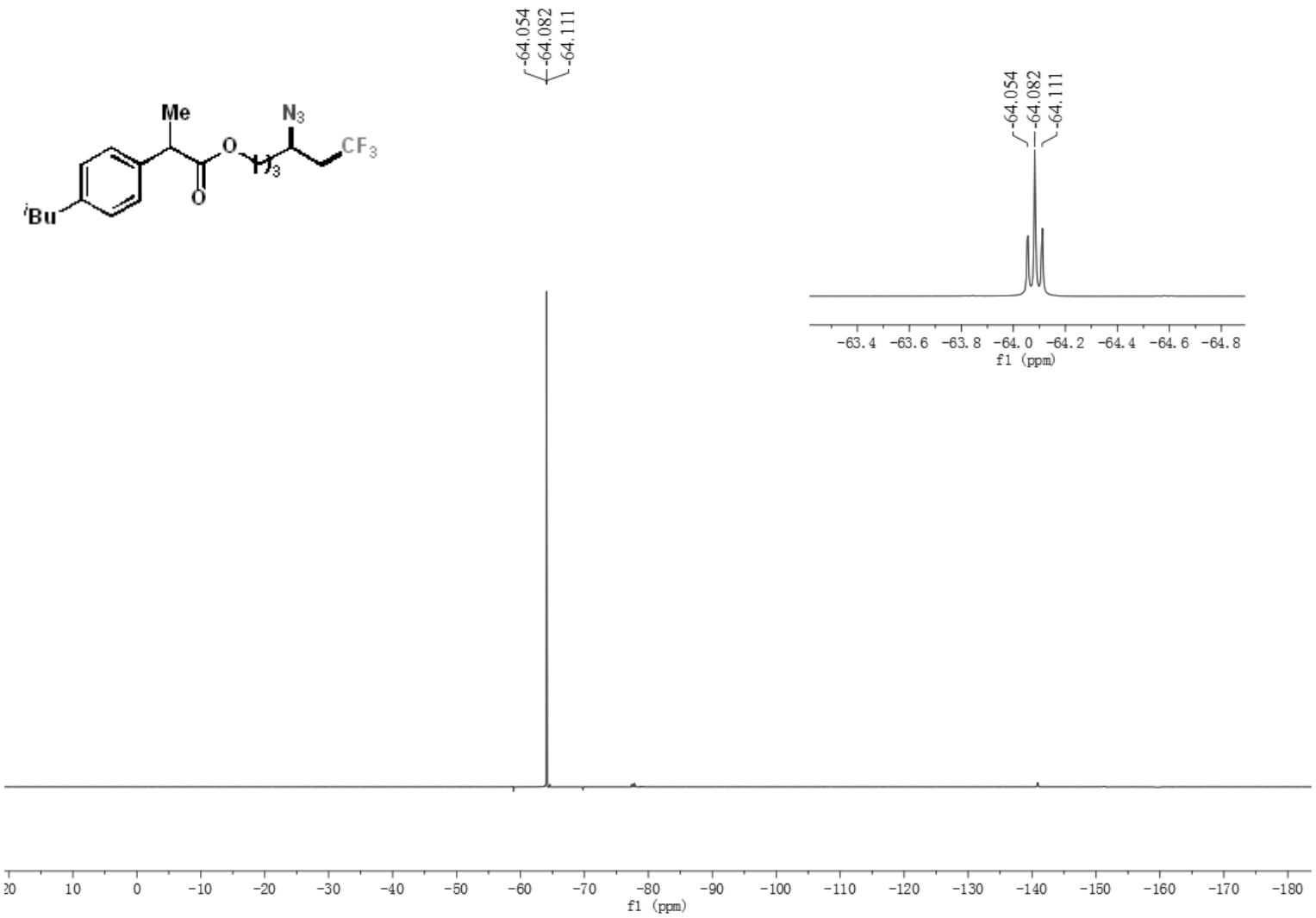


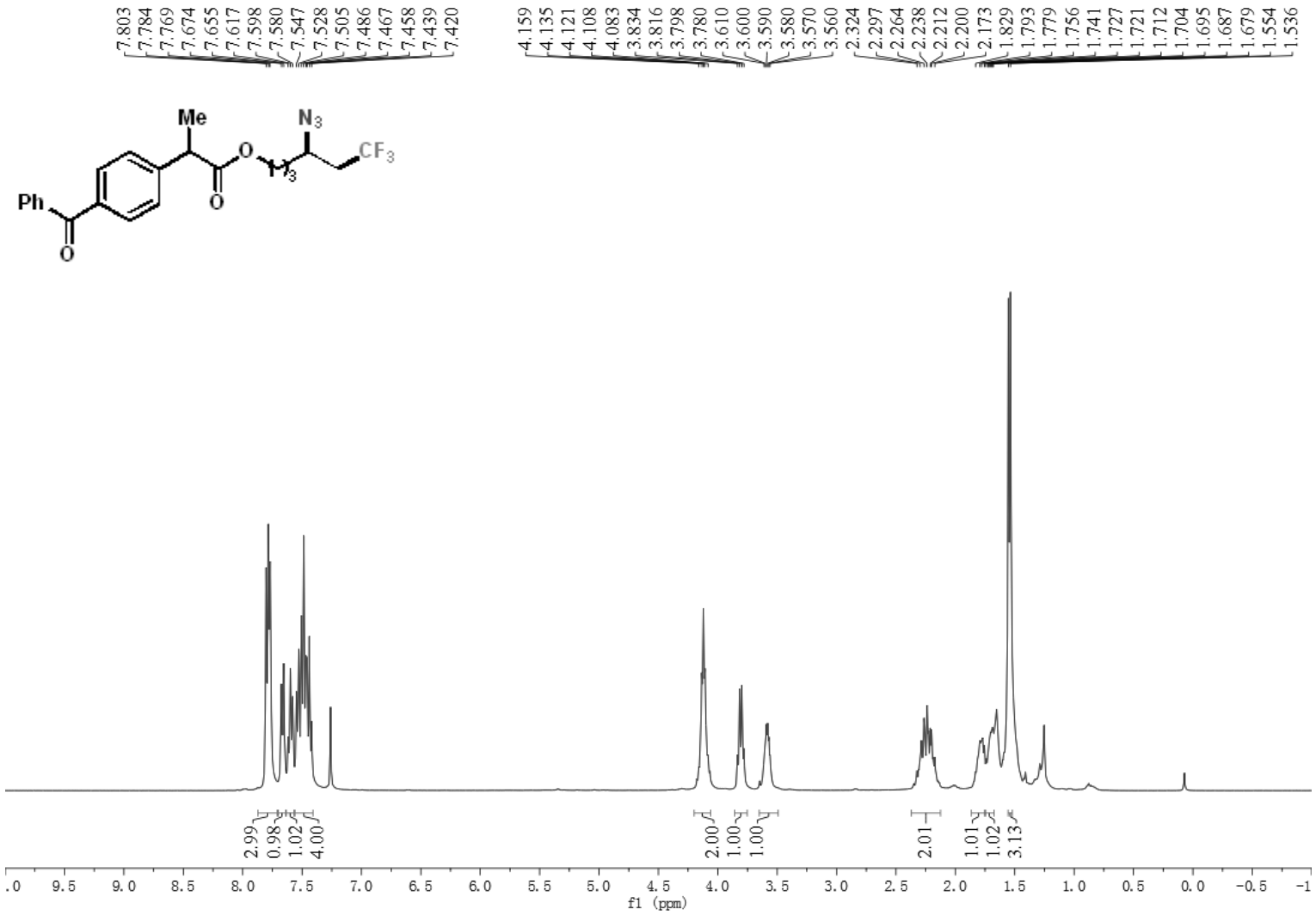
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



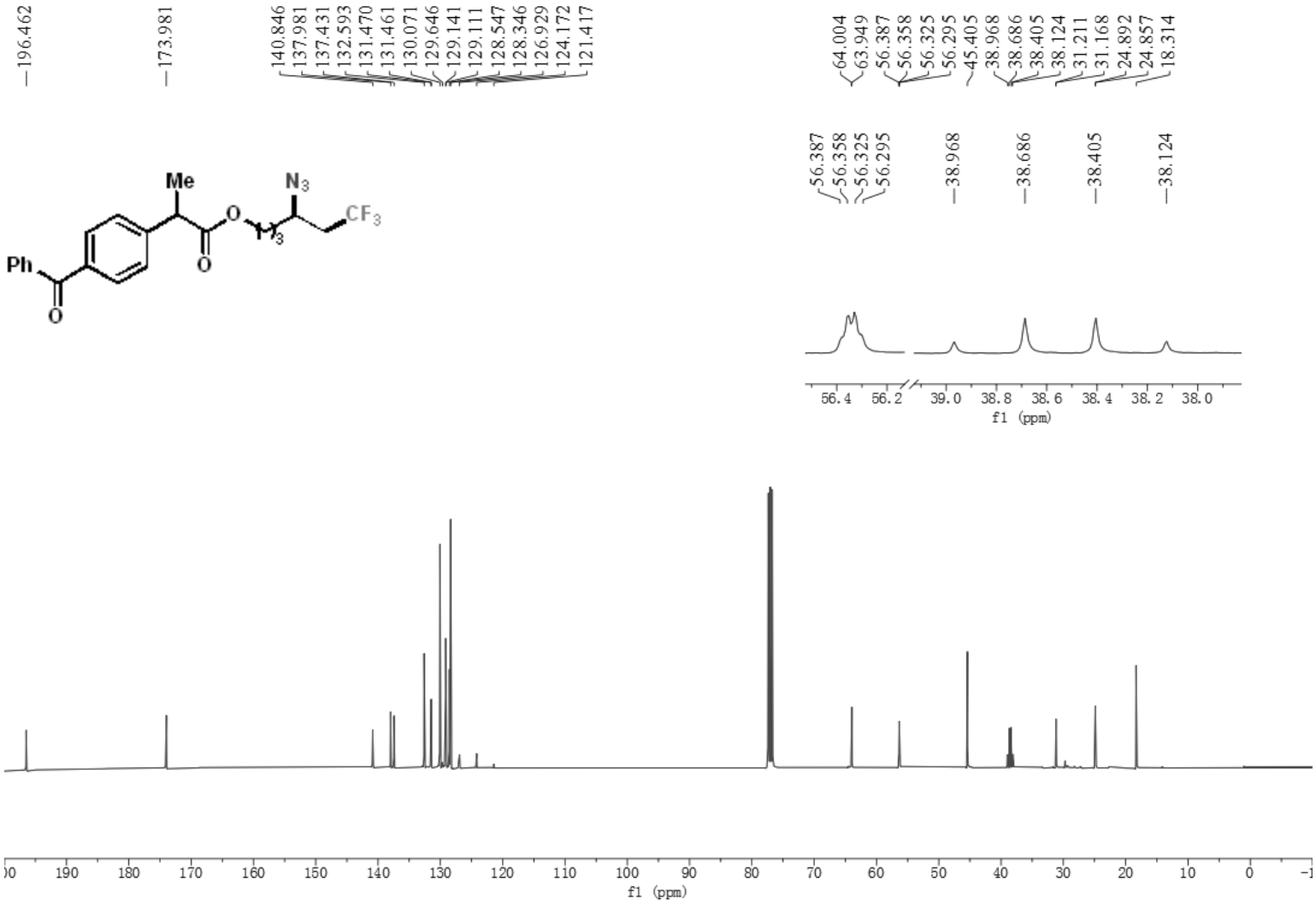
^{13}C NMR (100 MHz, $CDCl_3$) of **4a**



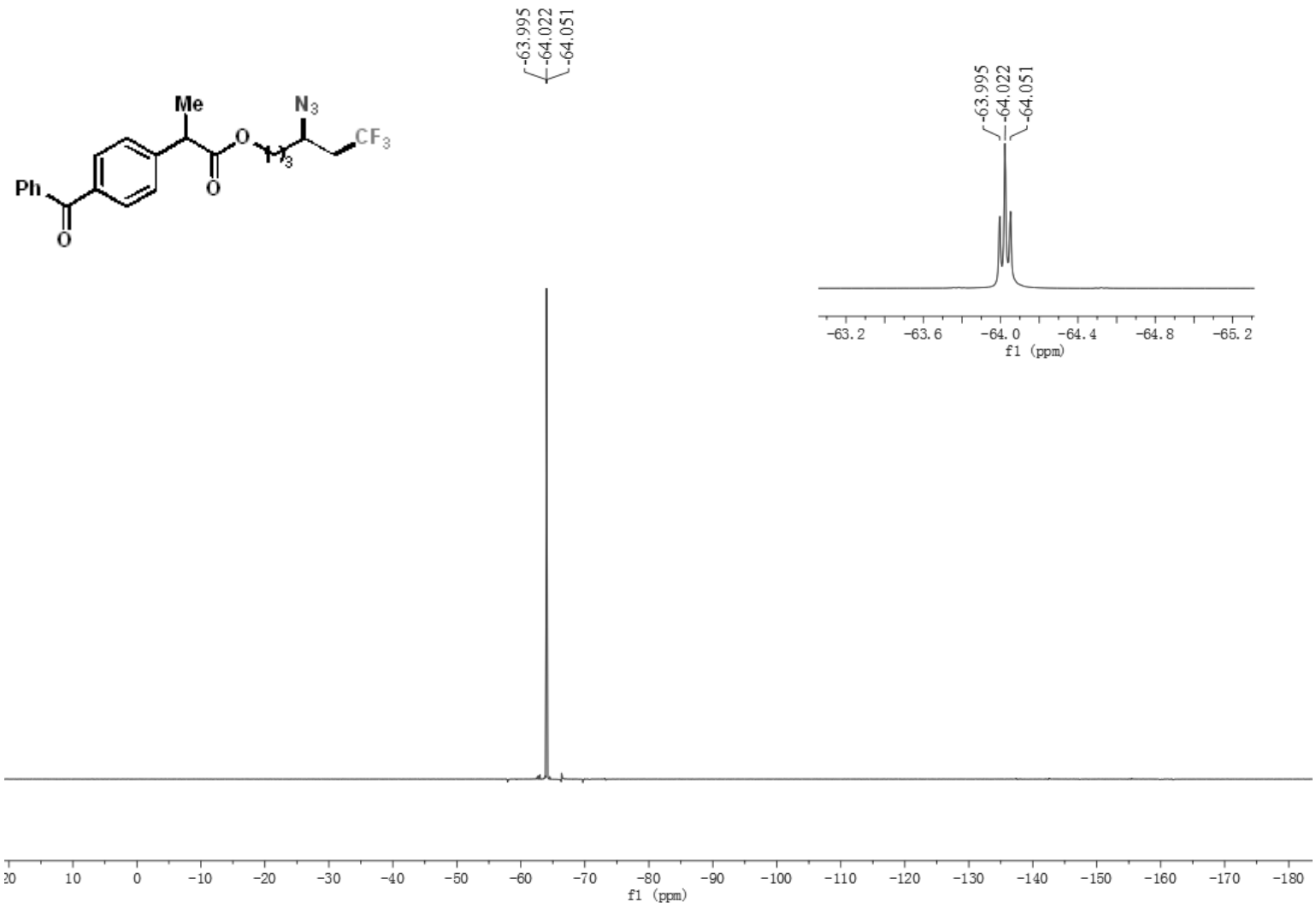
^{19}F NMR (376 MHz, $CDCl_3$) of **4a**



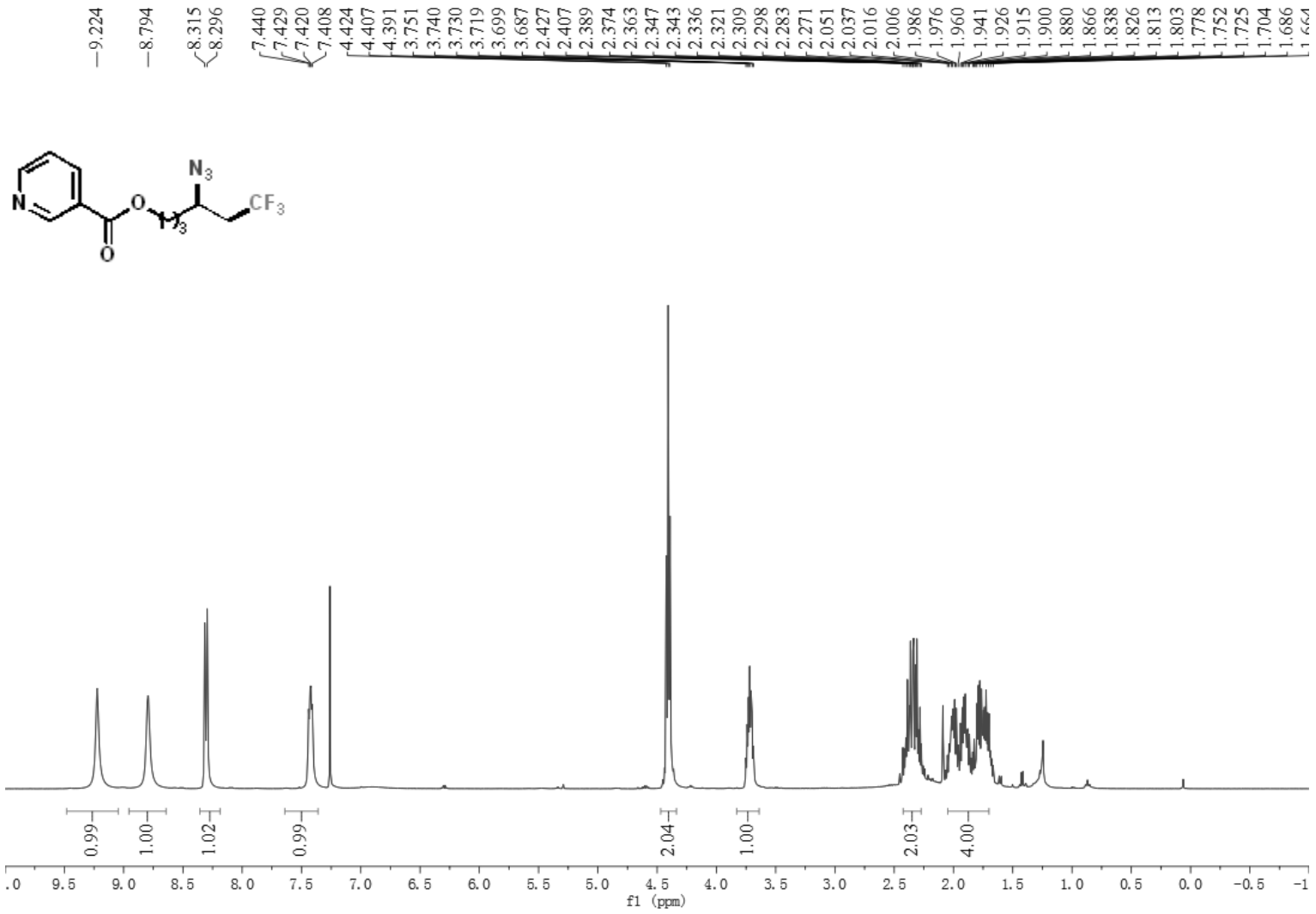
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



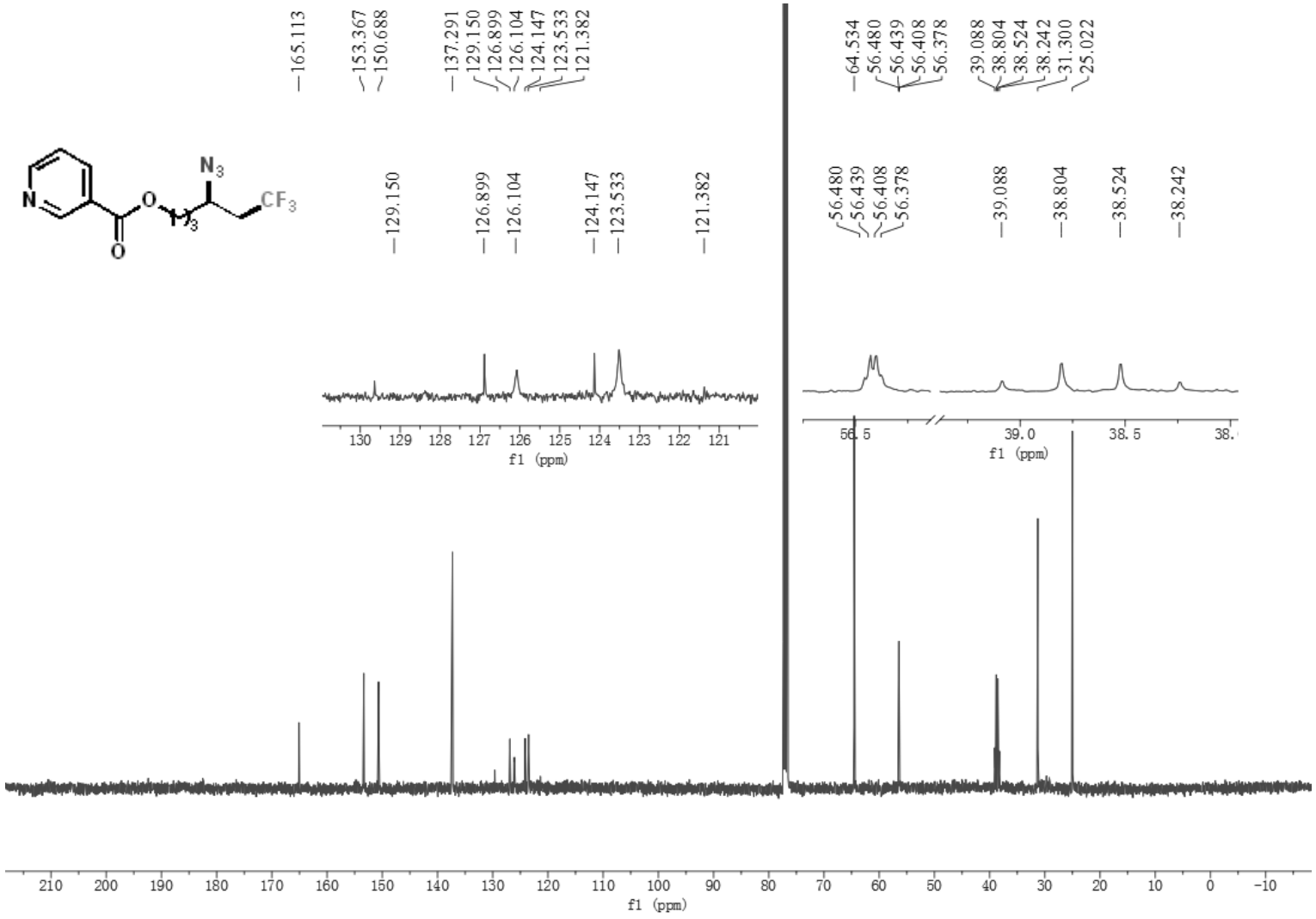
^{13}C NMR (100 MHz, $CDCl_3$) of **4b**



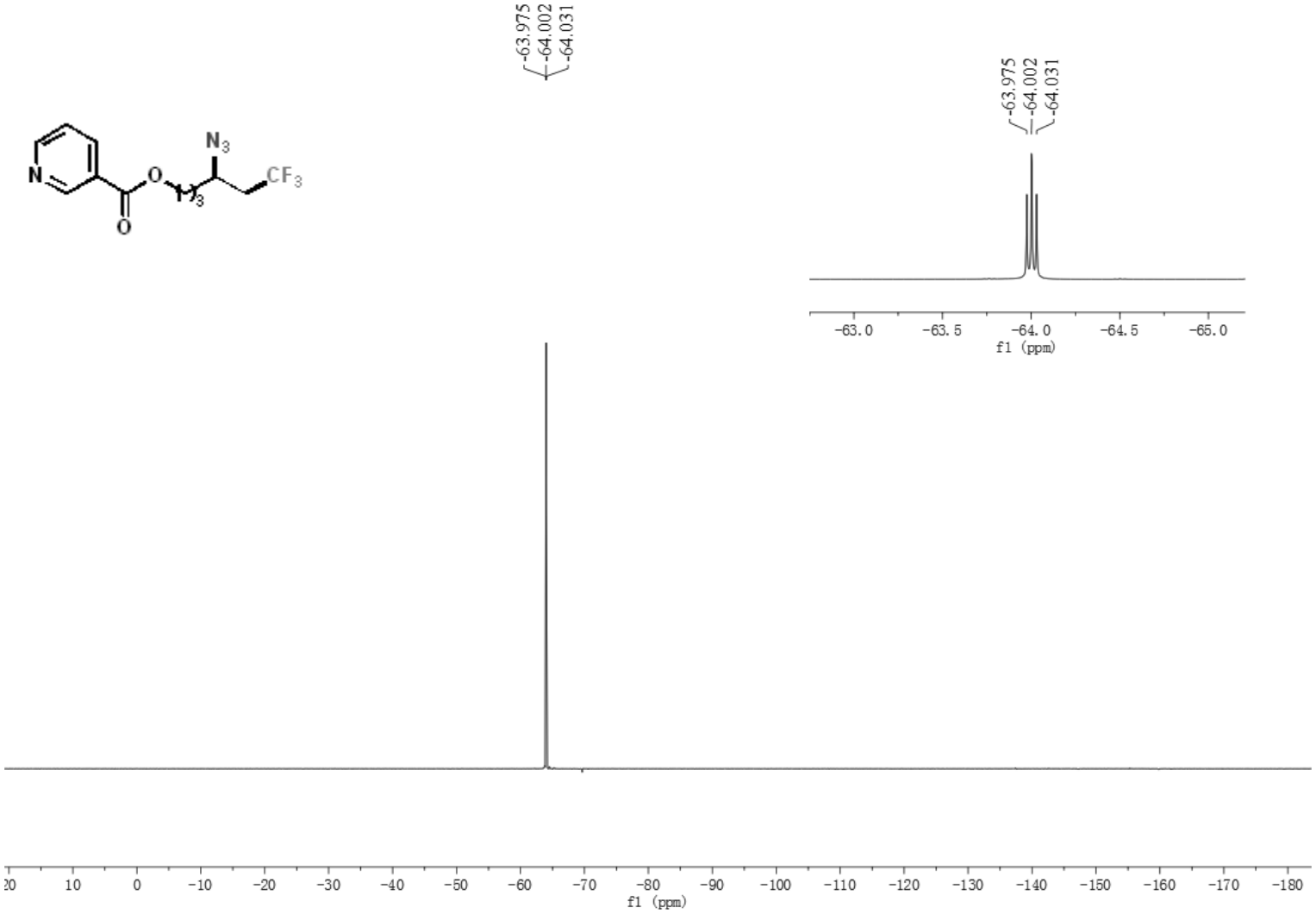
^{19}F NMR (376 MHz, $CDCl_3$) of **4b**



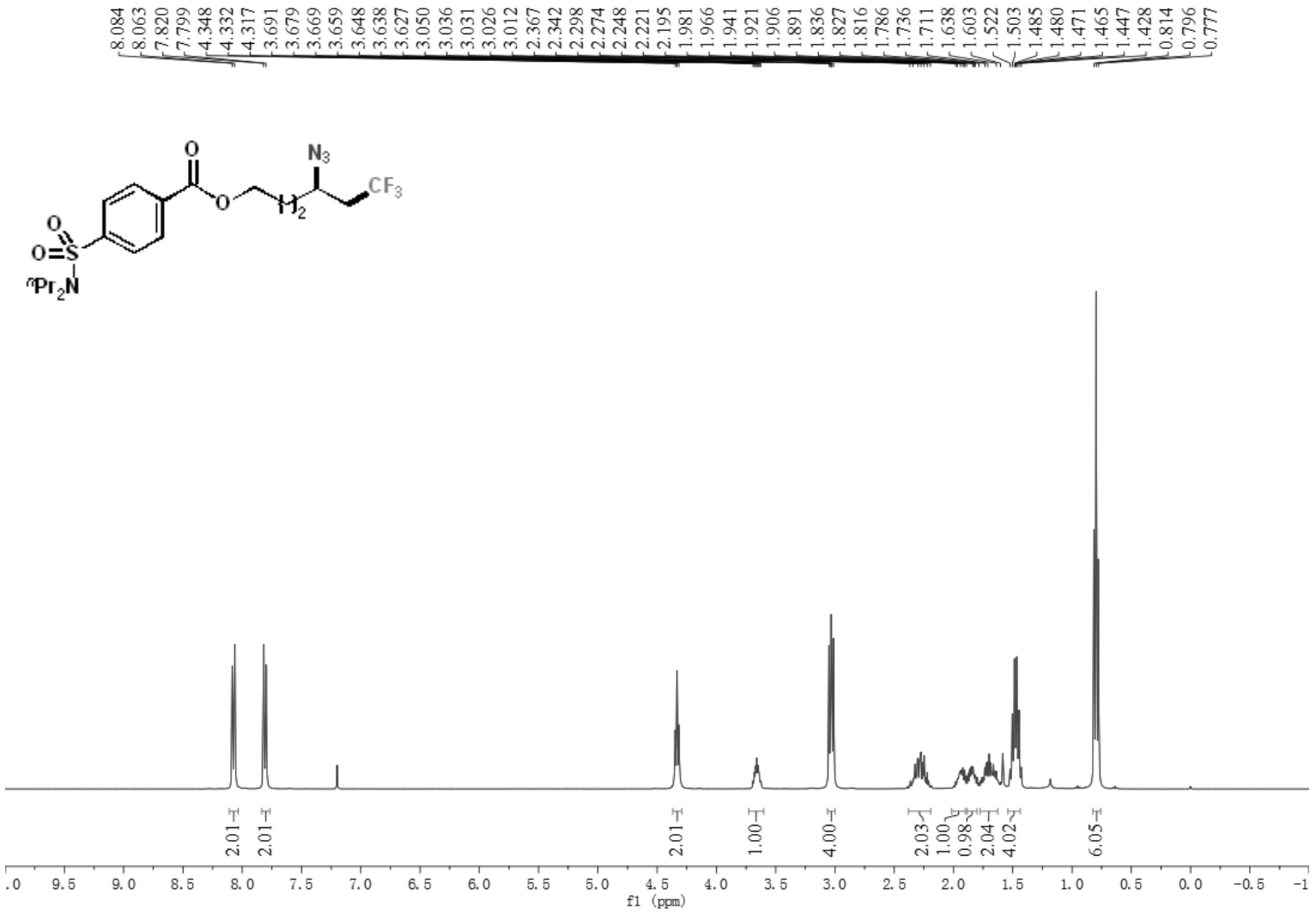
^{1}H NMR (400 MHz, $CDCl_3$) of **4c**



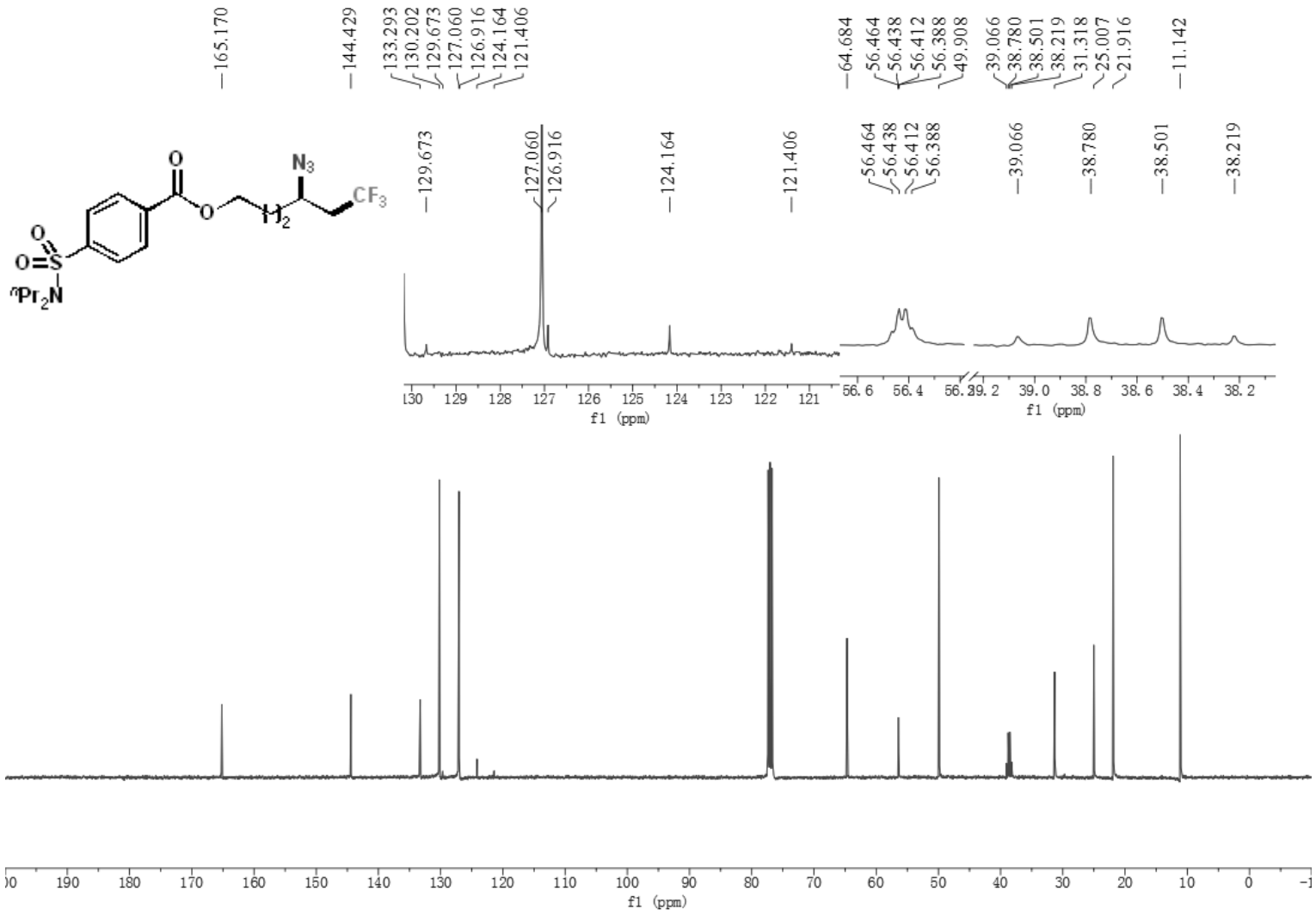
^{13}C NMR (100 MHz, $CDCl_3$) of **4c**



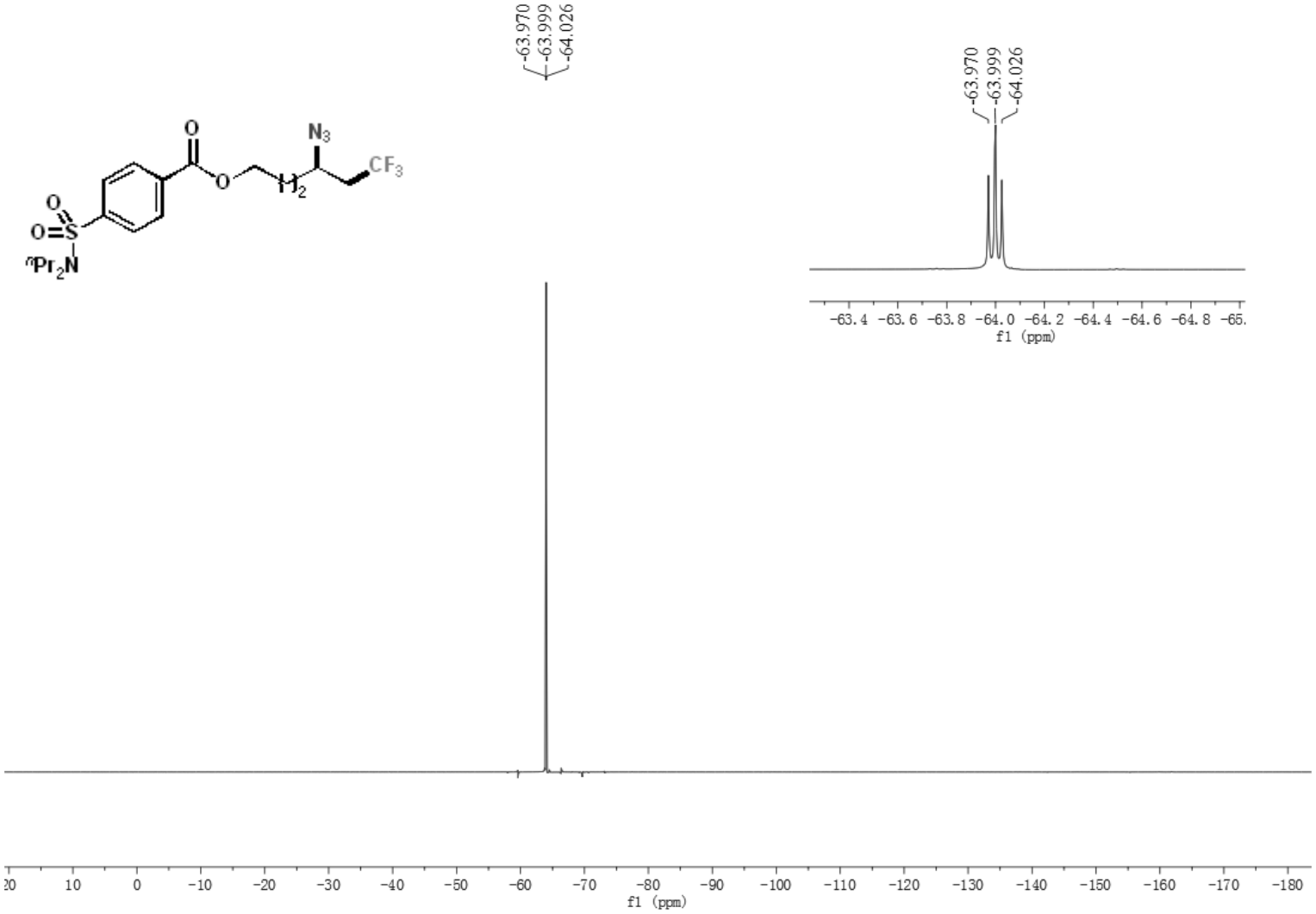
^{19}F NMR (376 MHz, $CDCl_3$) of **4c**



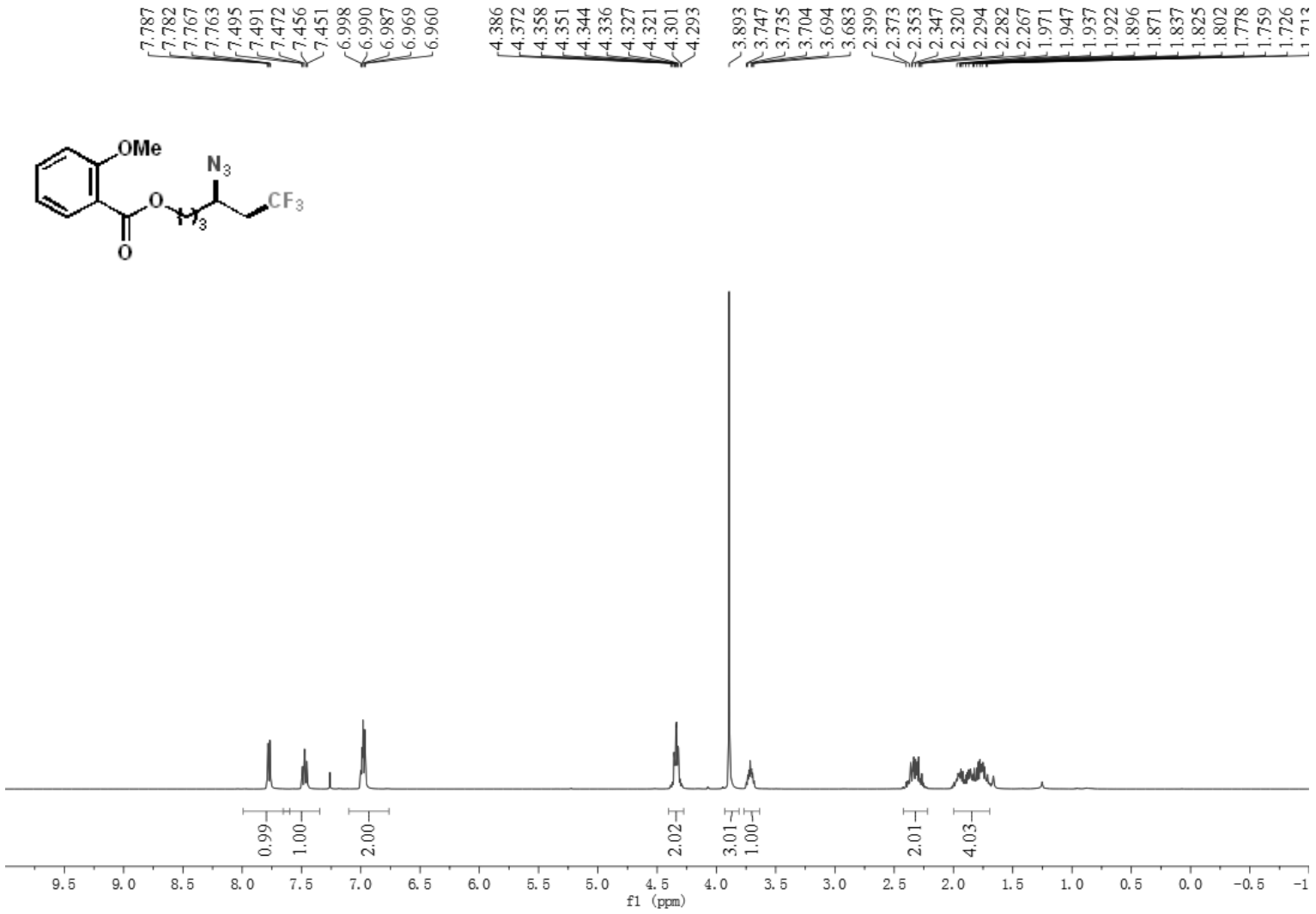
^{1}H NMR (400 MHz, $CDCl_3$) of **4d**



^{13}C NMR (100 MHz, $CDCl_3$) of **4d**



^{19}F NMR (376 MHz, $CDCl_3$) of **4d**



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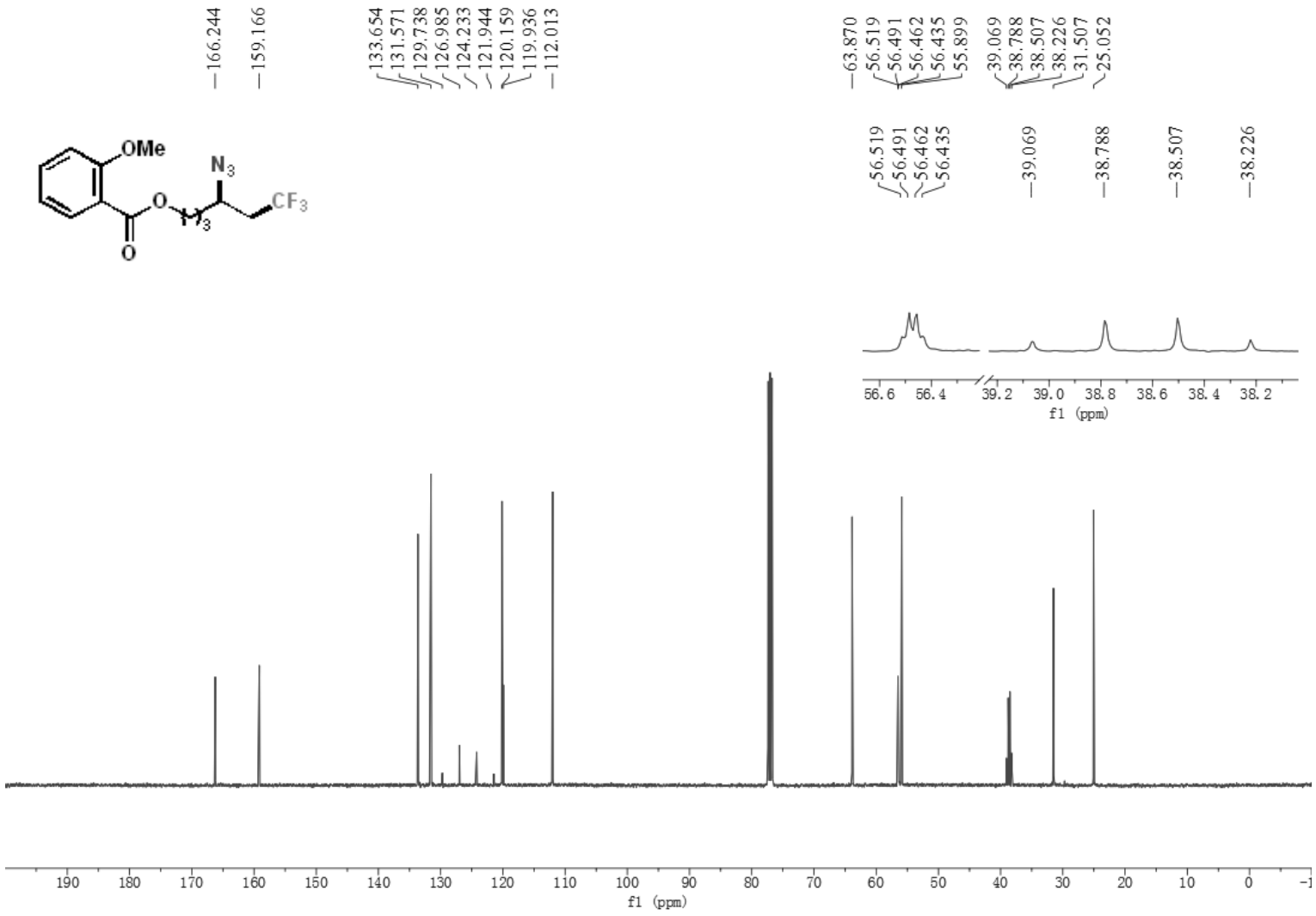
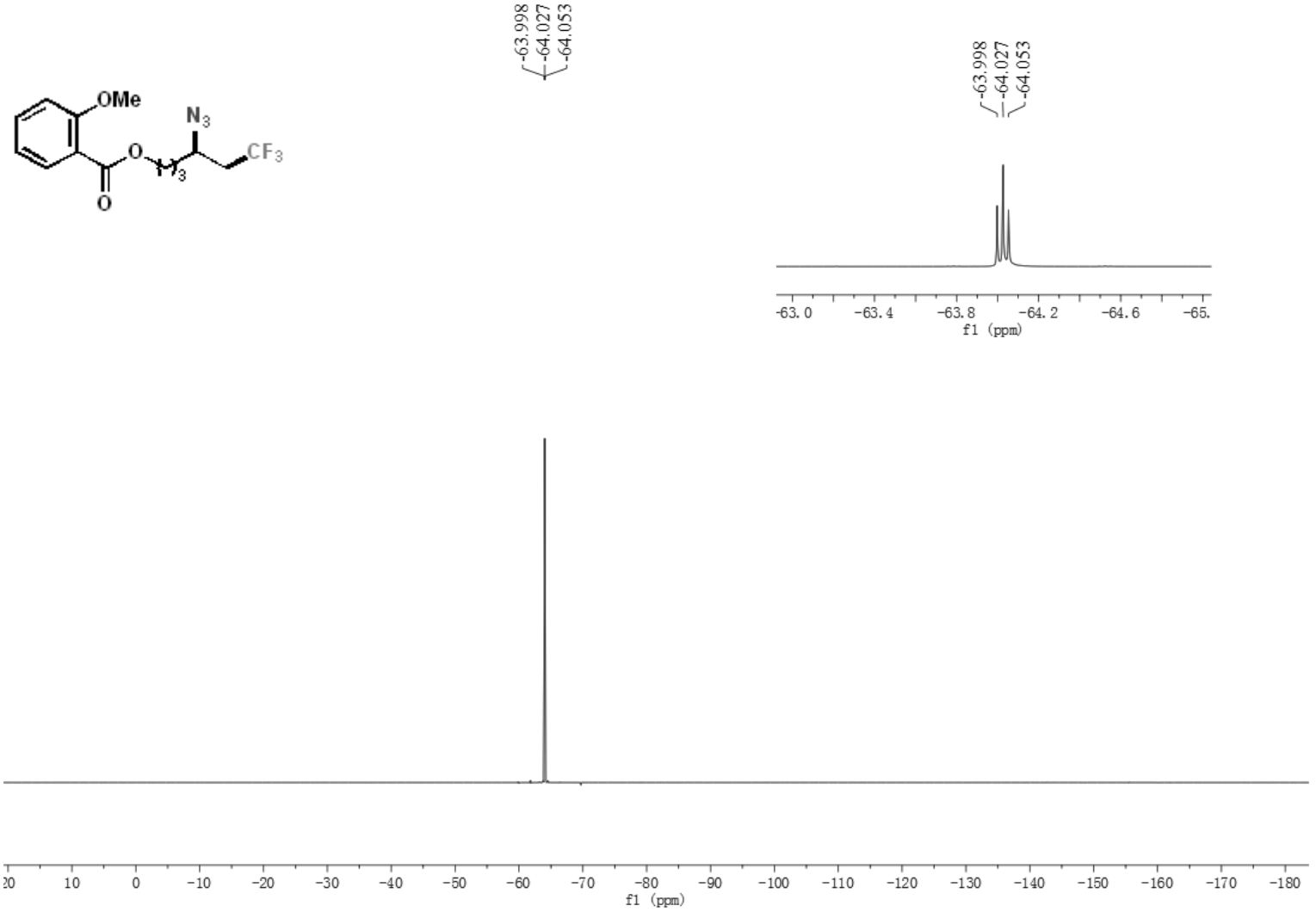
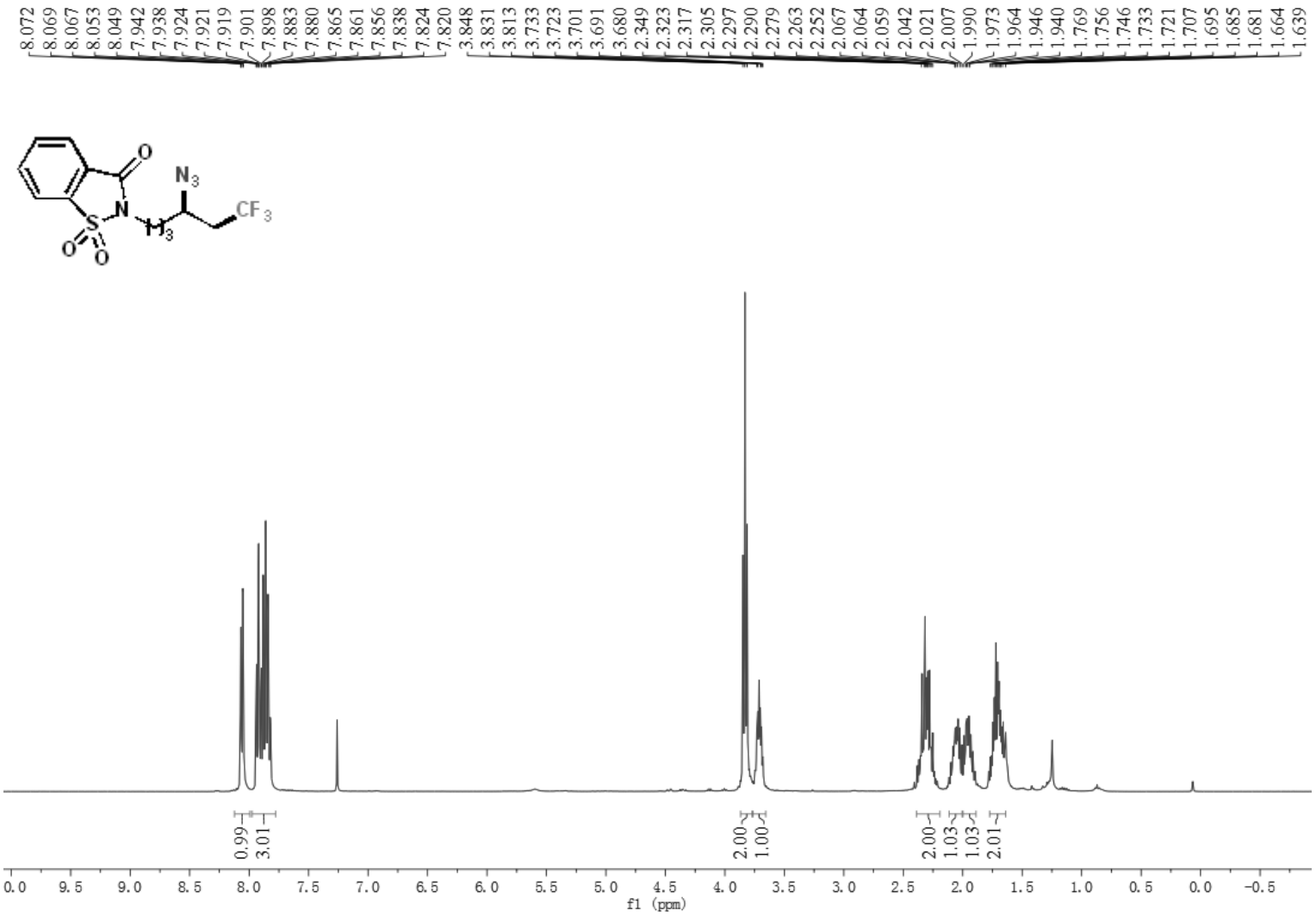


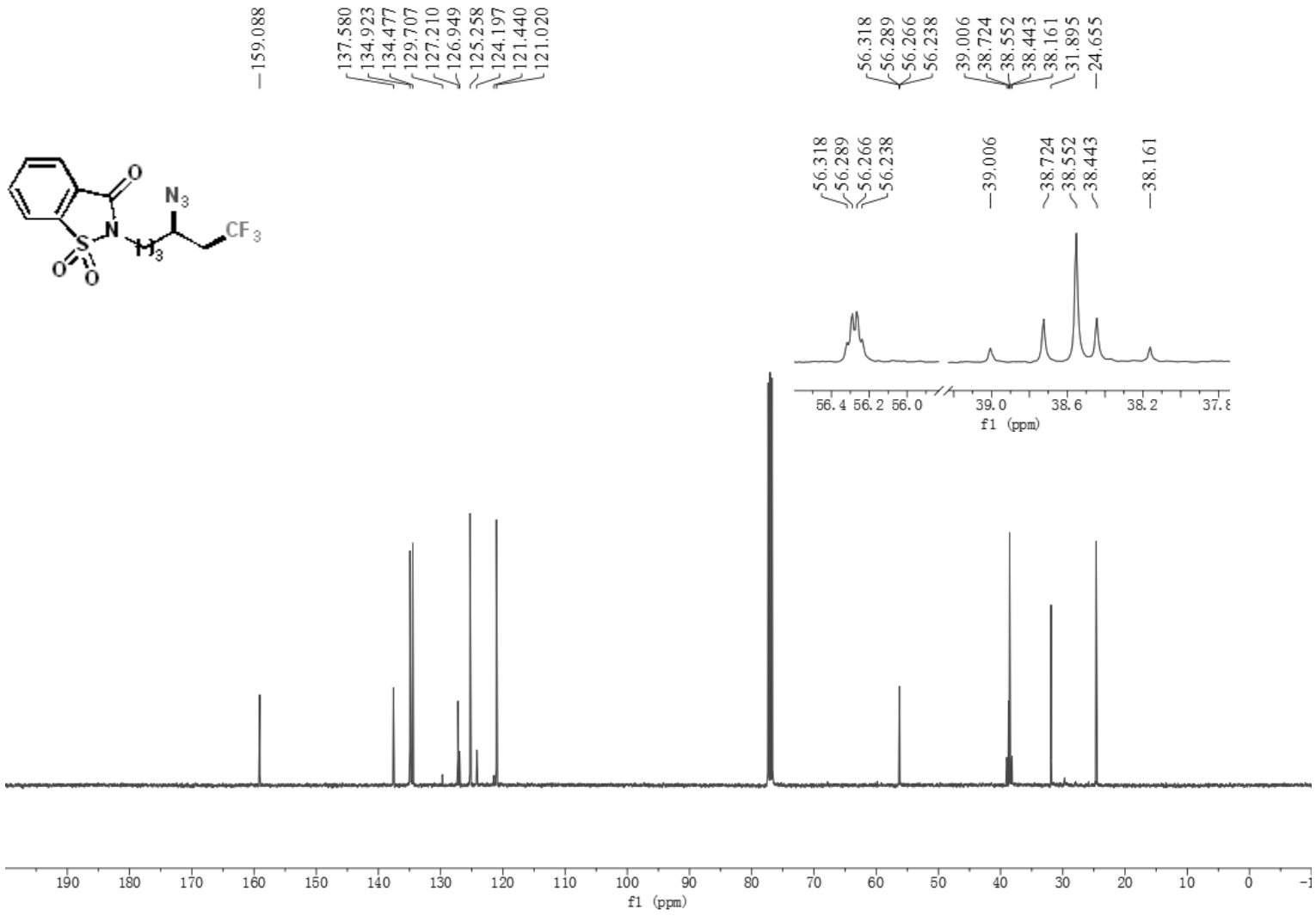
^{13}C NMR (100 MHz, $CDCl_3$) of **4e**



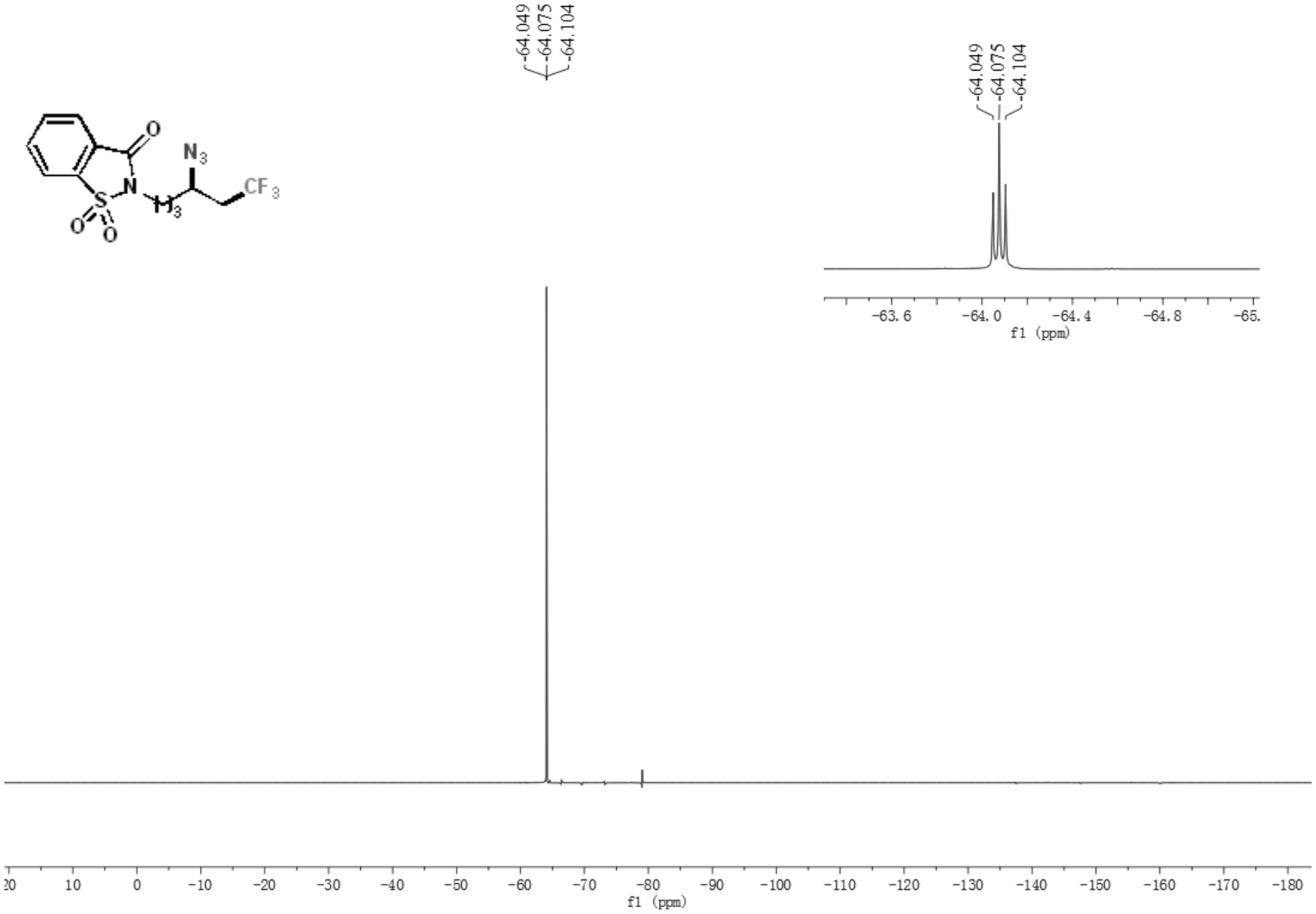
^{19}F NMR (376 MHz, $CDCl_3$) of **4e**



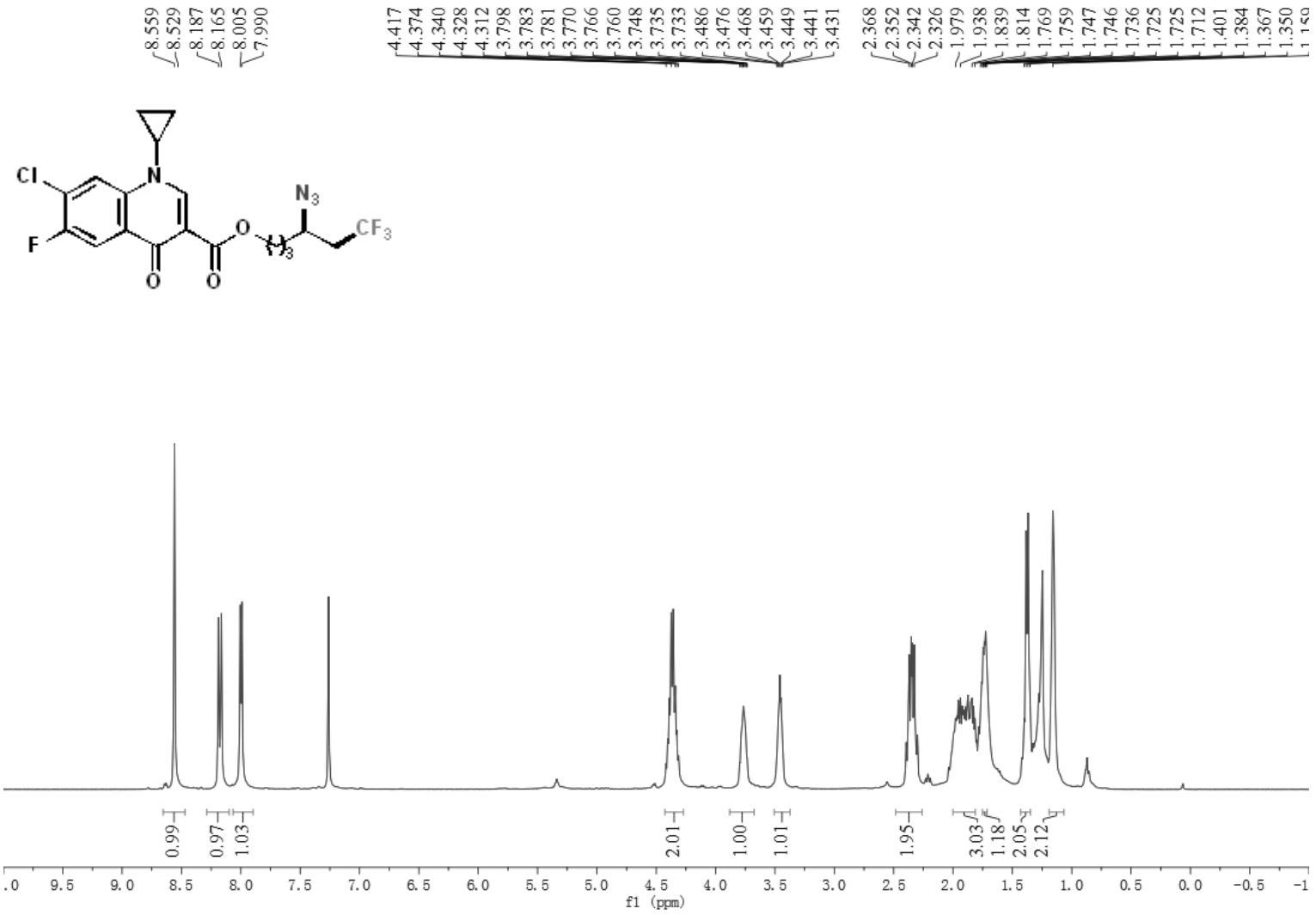
^{1}H NMR (400 MHz, $CDCl_3$) of **4f**



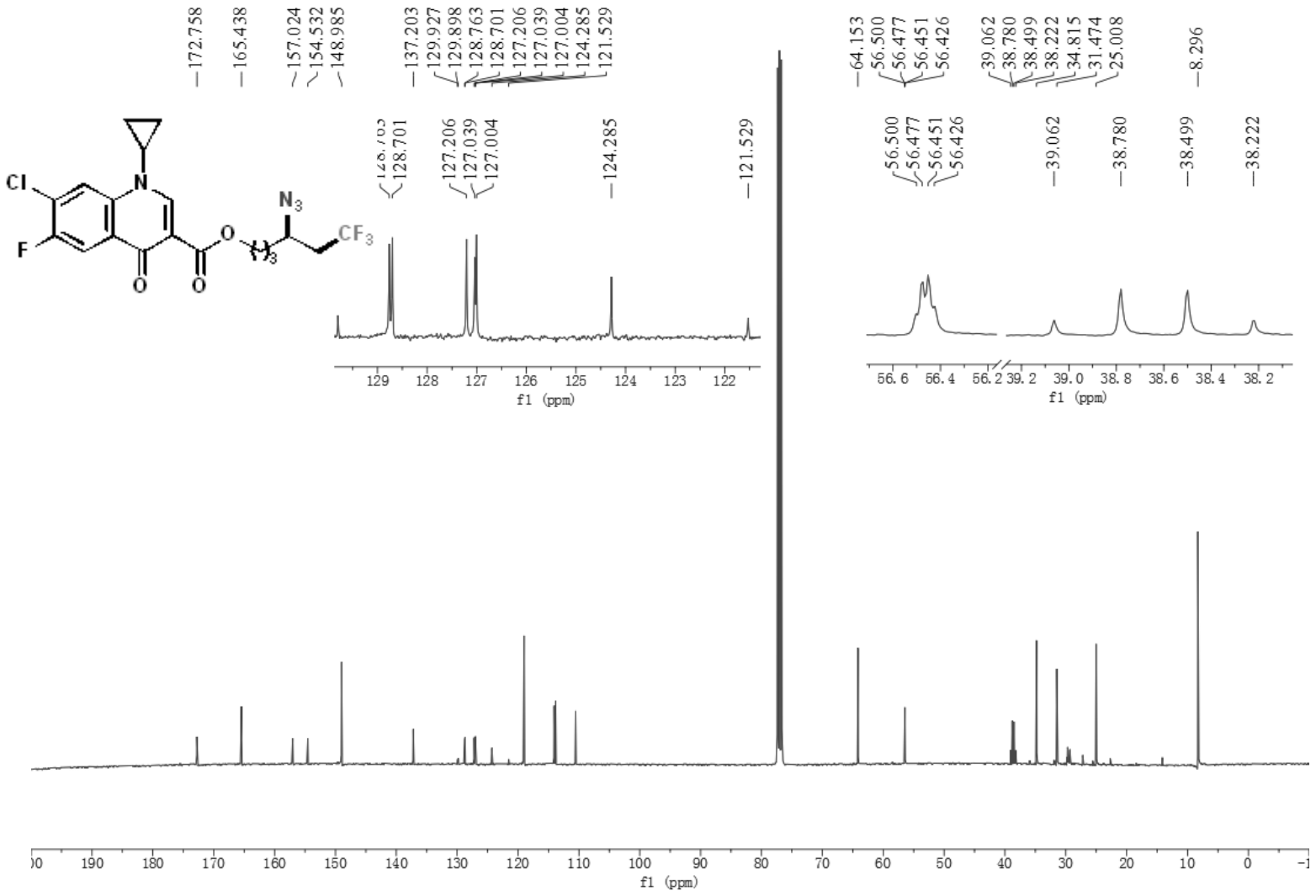
^{13}C NMR (100 MHz, $CDCl_3$) of **4f**



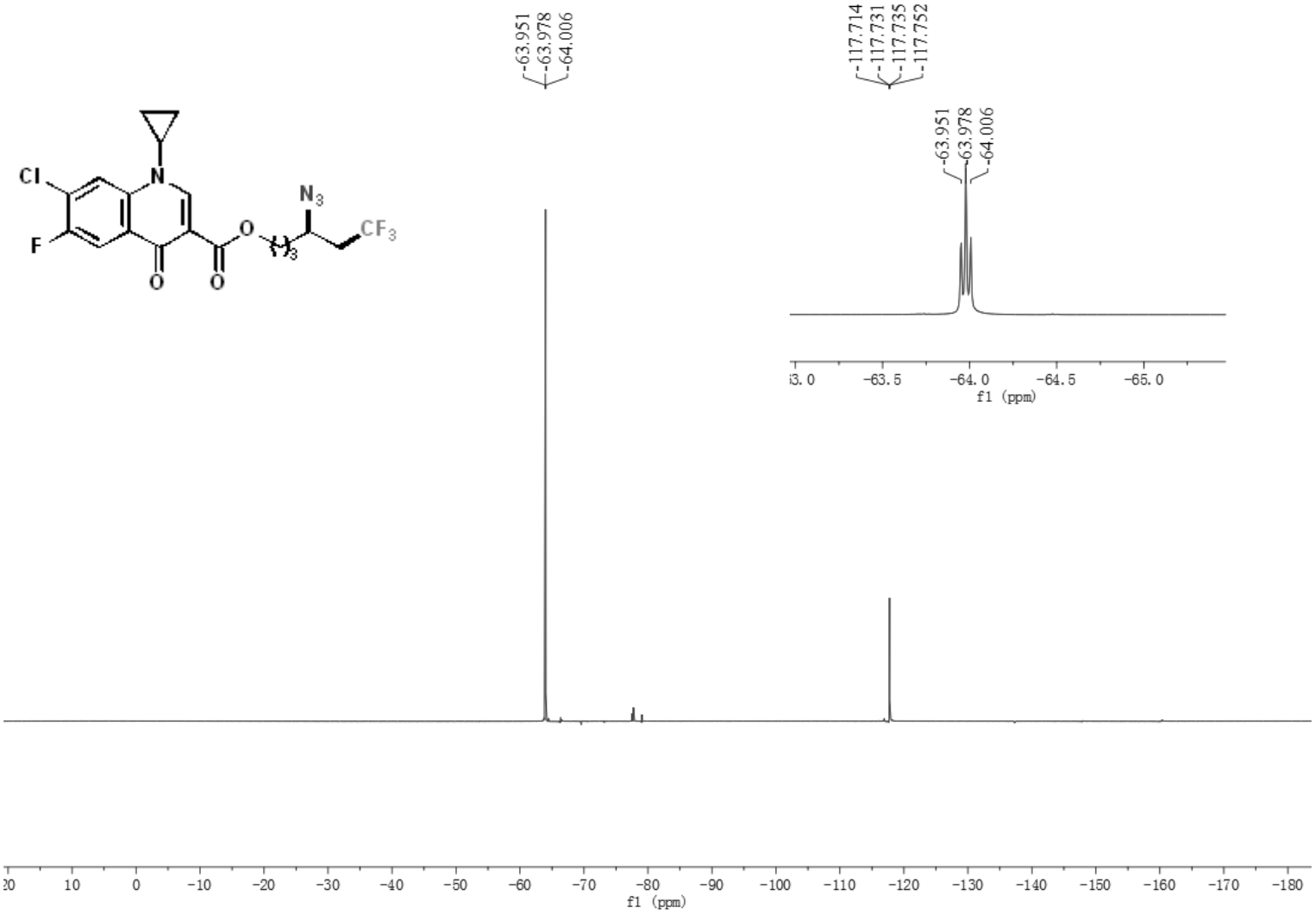
^{19}F NMR (376 MHz, $CDCl_3$) of **4f**



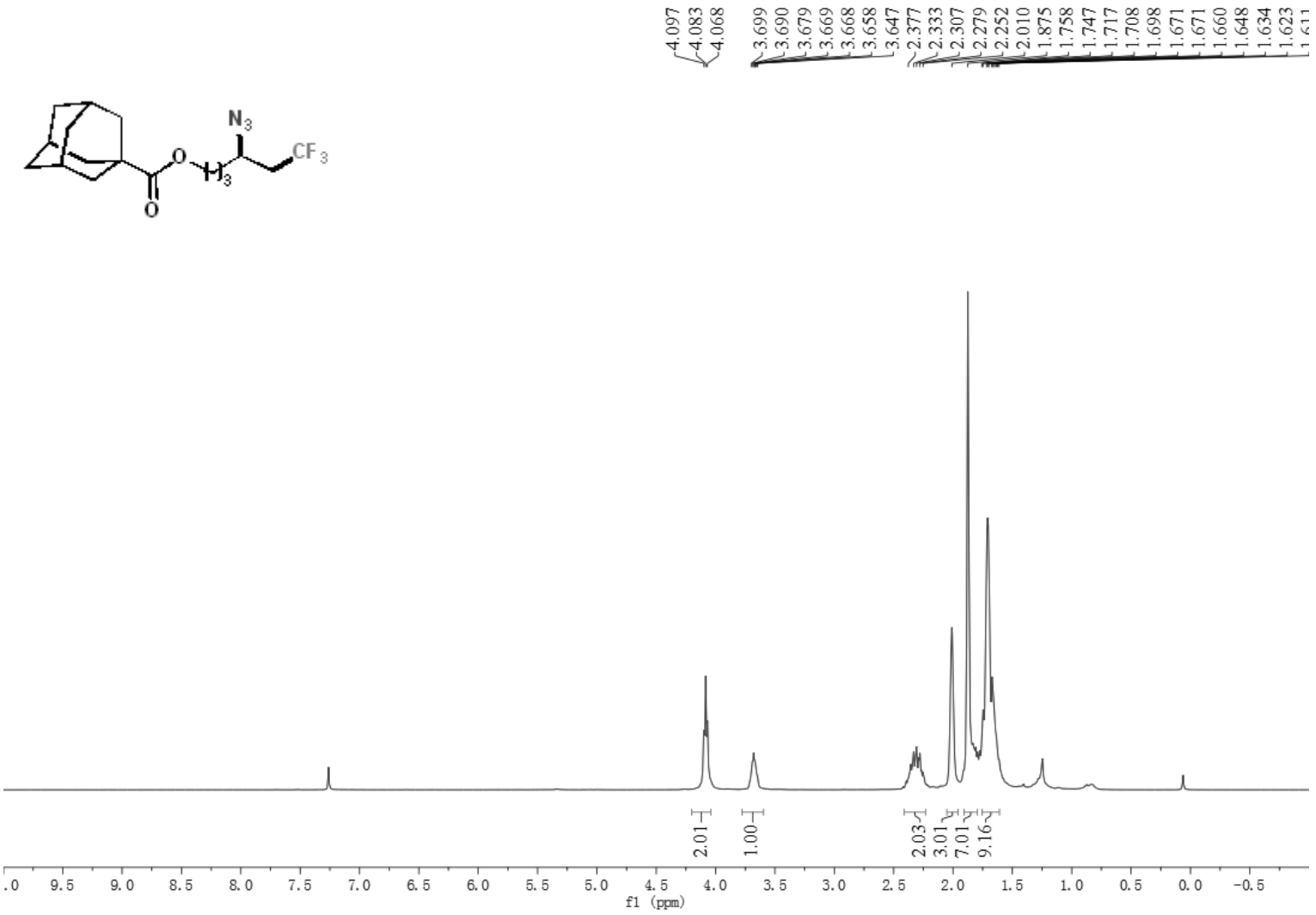
^{1}H NMR (400 MHz, $CDCl_3$) of **4g**



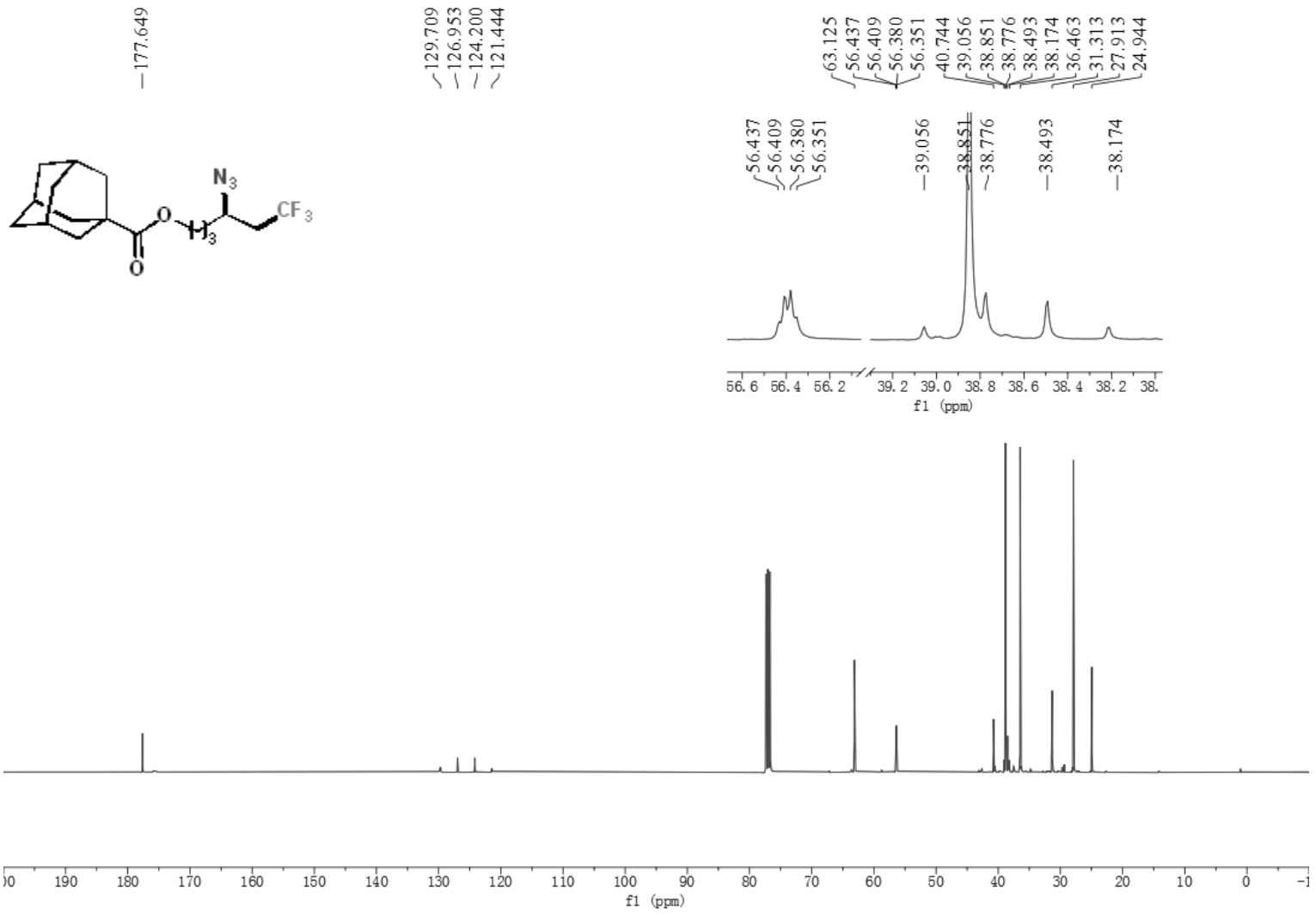
^{13}C NMR (100 MHz, $CDCl_3$) of **4g**



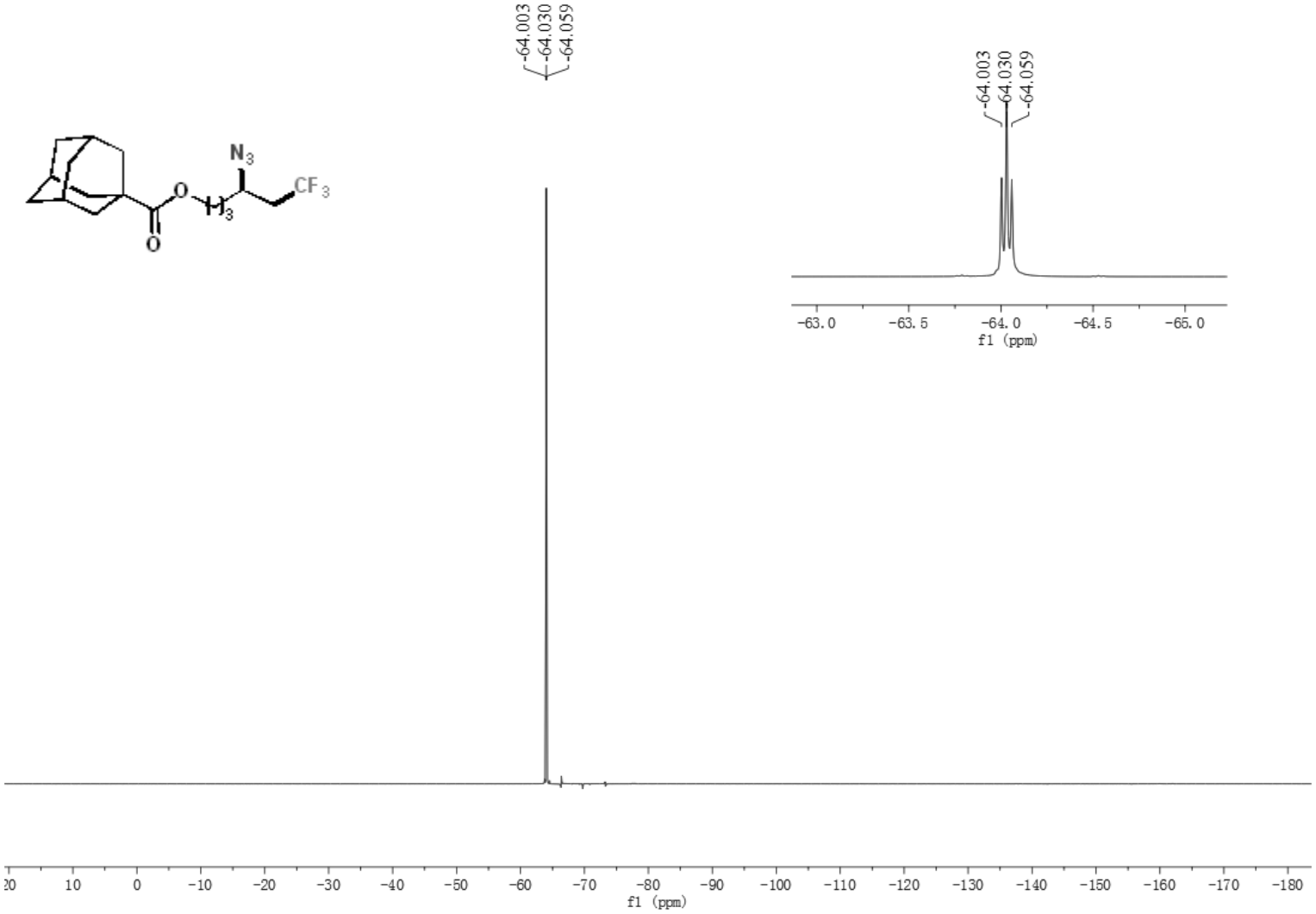
^{19}F NMR (376 MHz, $CDCl_3$) of **4g**



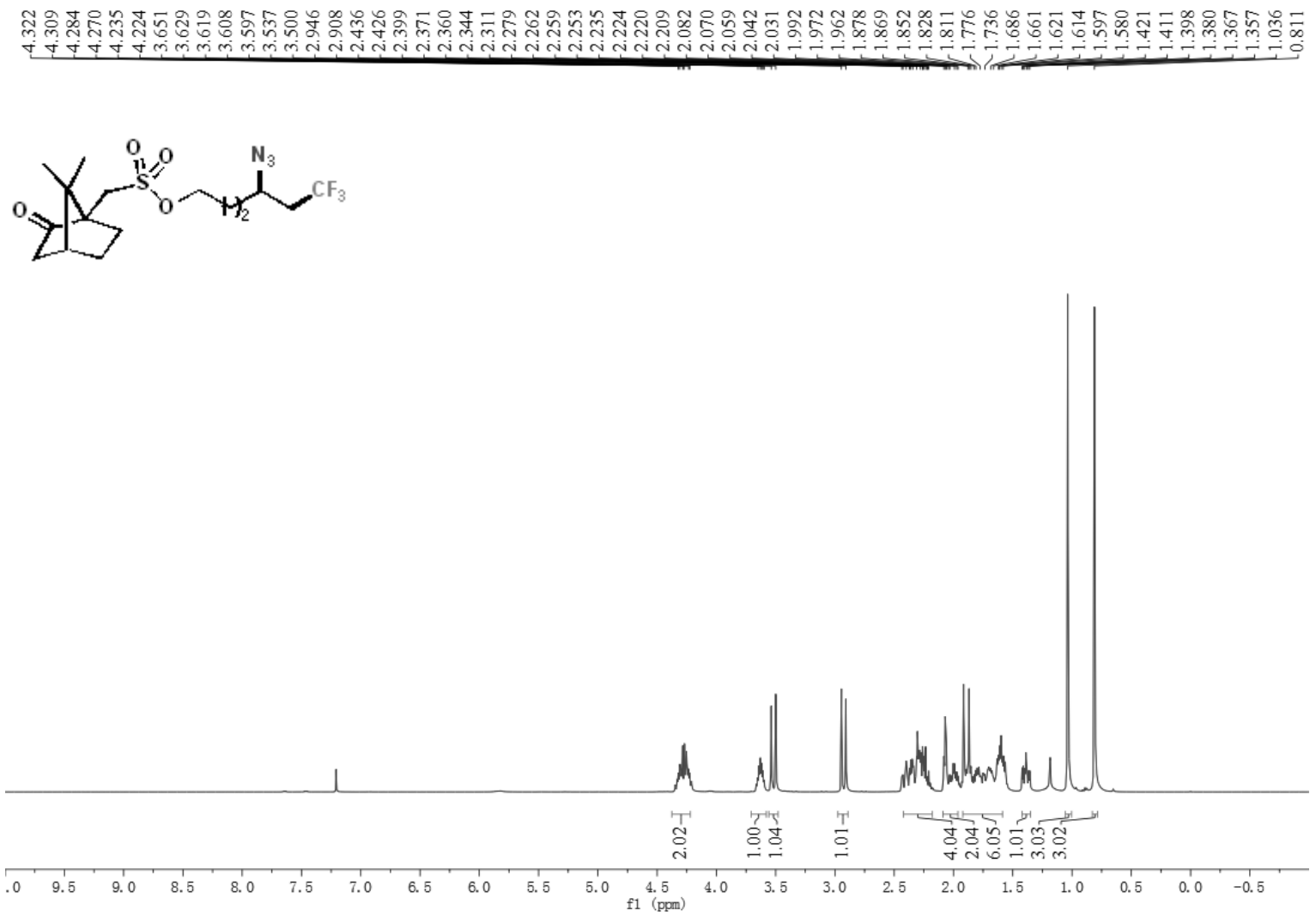
^{1}H NMR (400 MHz, $CDCl_3$) of **4h**



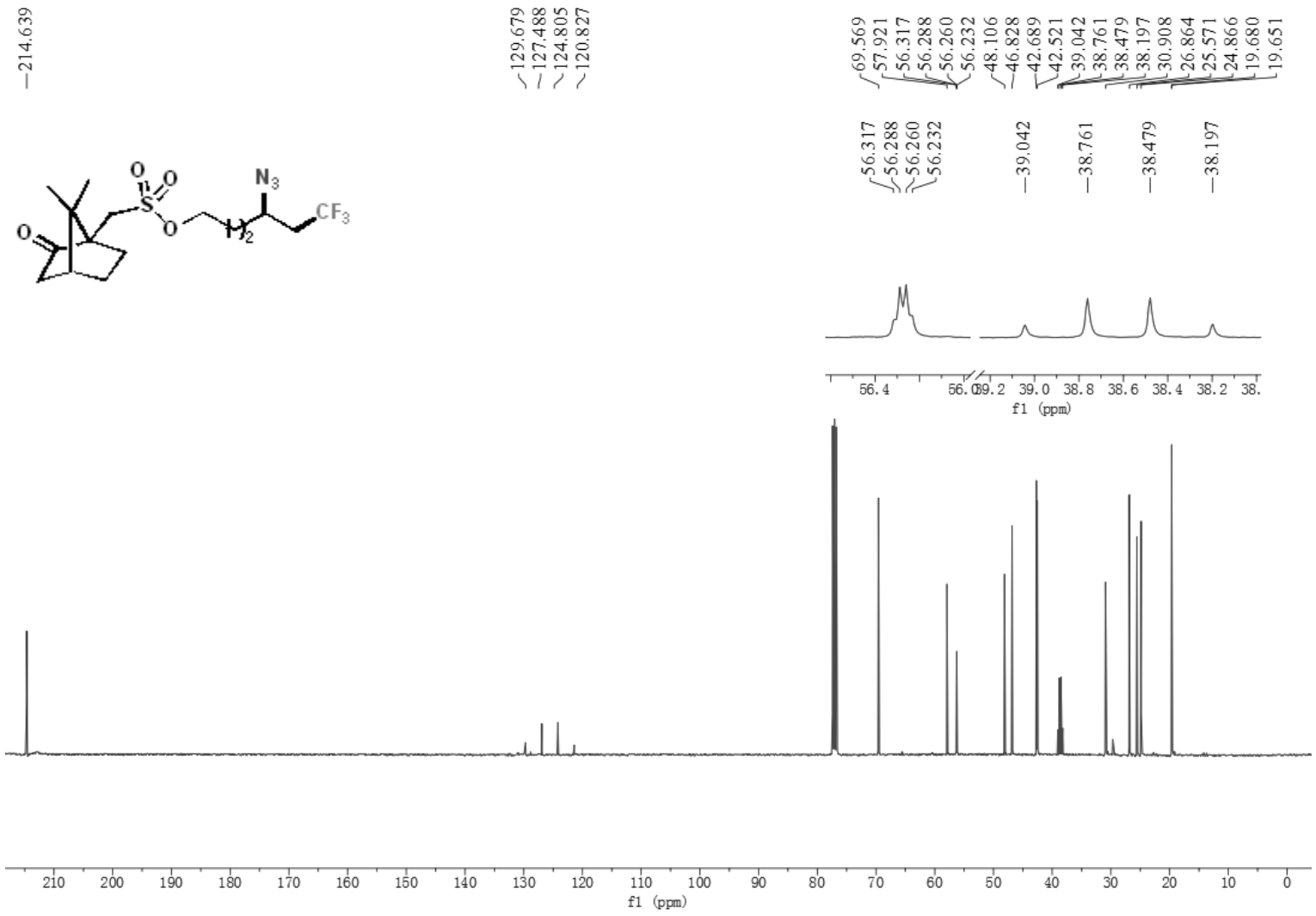
^{13}C NMR (100 MHz, $CDCl_3$) of **4h**



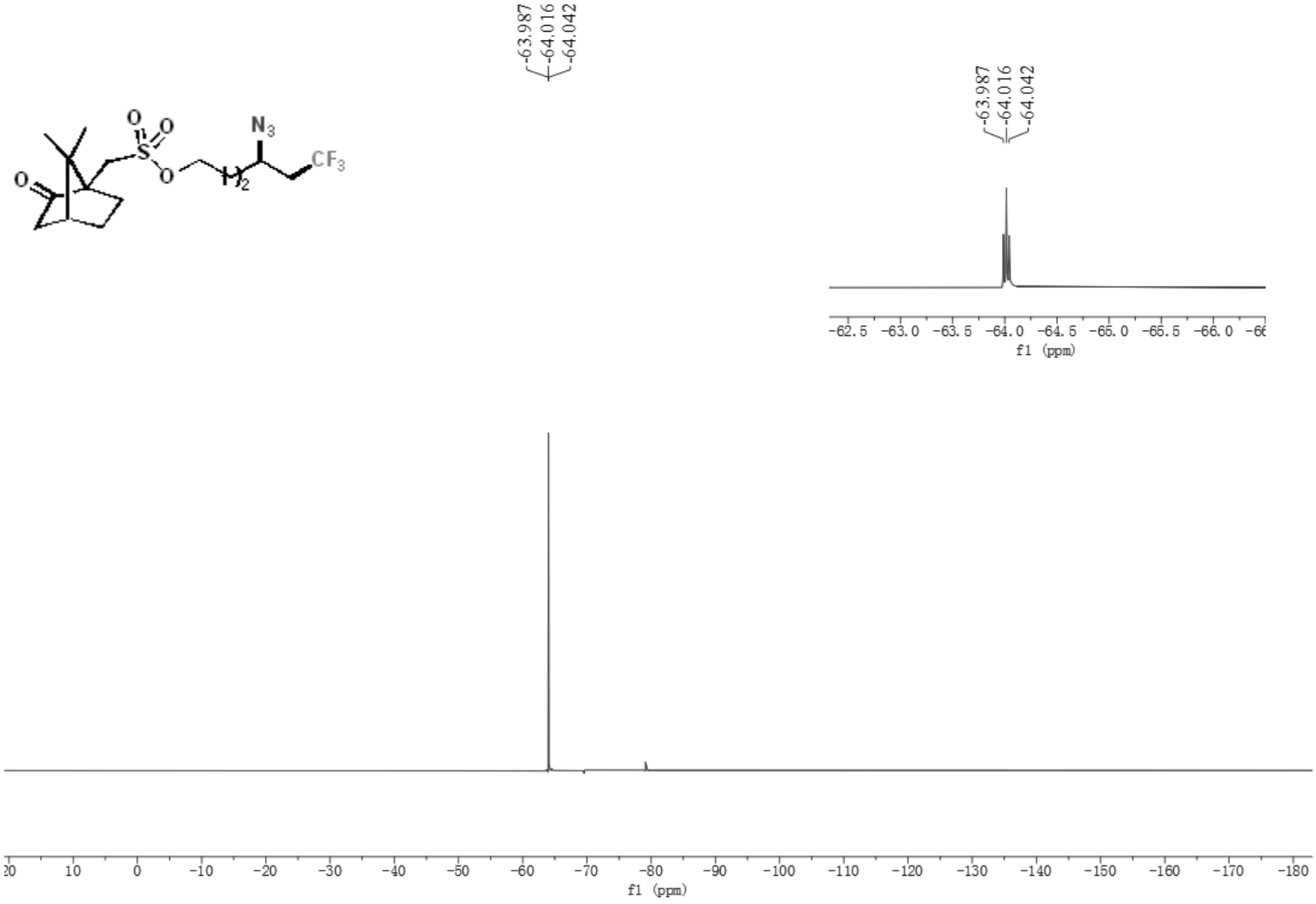
^{19}F NMR (376 MHz, $CDCl_3$) of **4h**



^{1}H NMR (400 MHz, $CDCl_3$) of **4i**

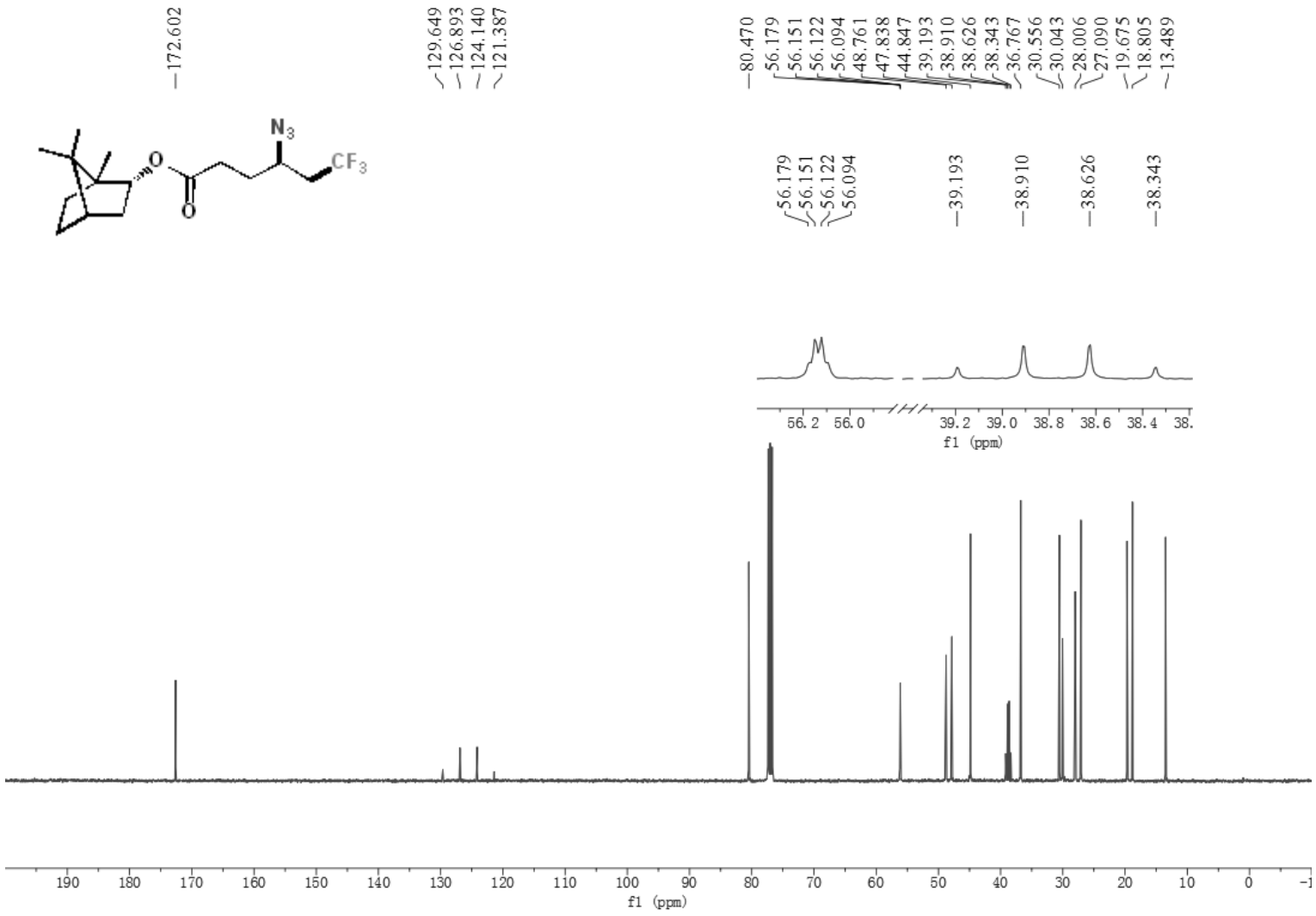


^{13}C NMR (100 MHz, $CDCl_3$) of **4i**



^{19}F NMR (376 MHz, $CDCl_3$) of **4i**

^{1}H NMR (400 MHz, $CDCl_3$) of **4j**



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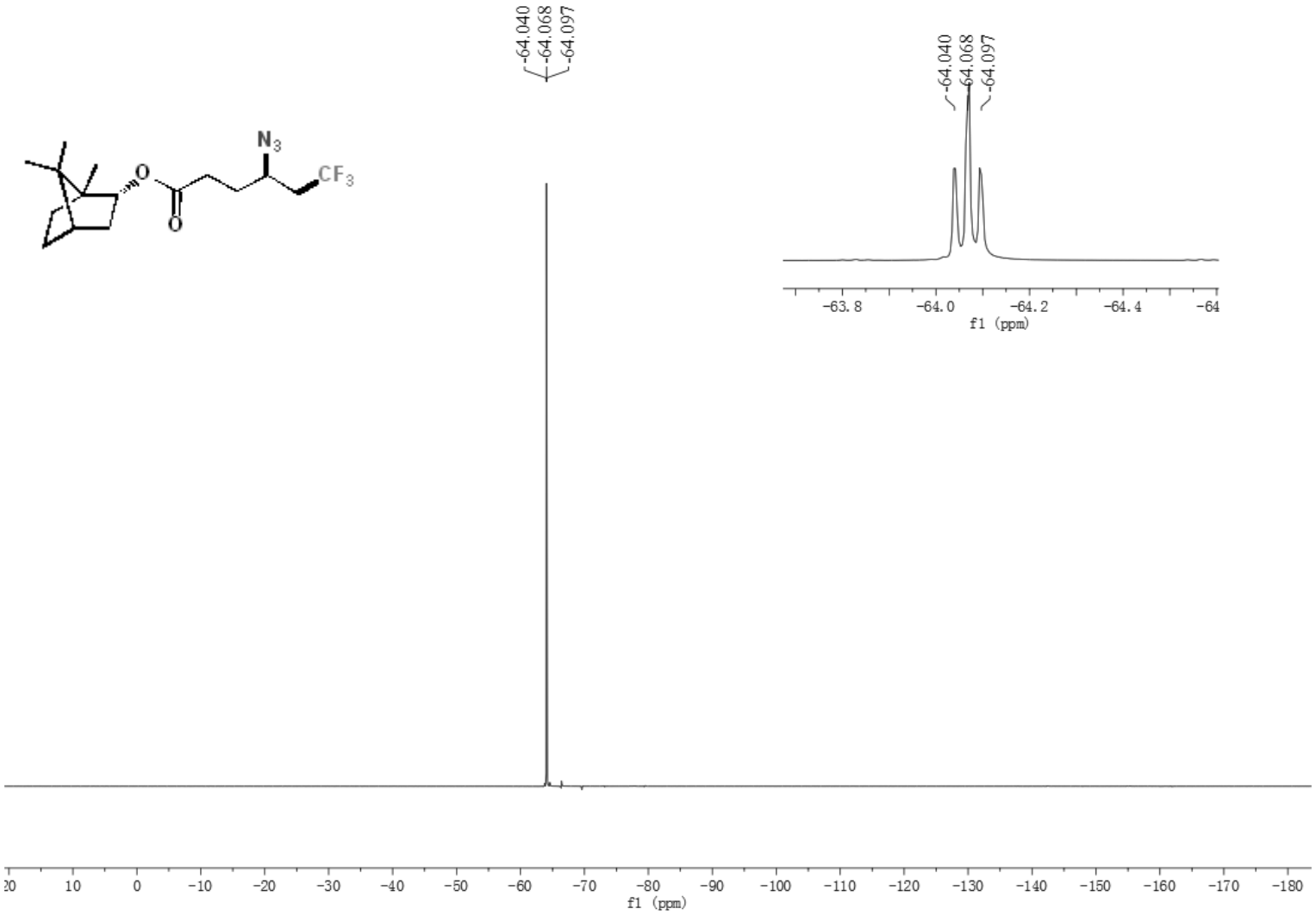

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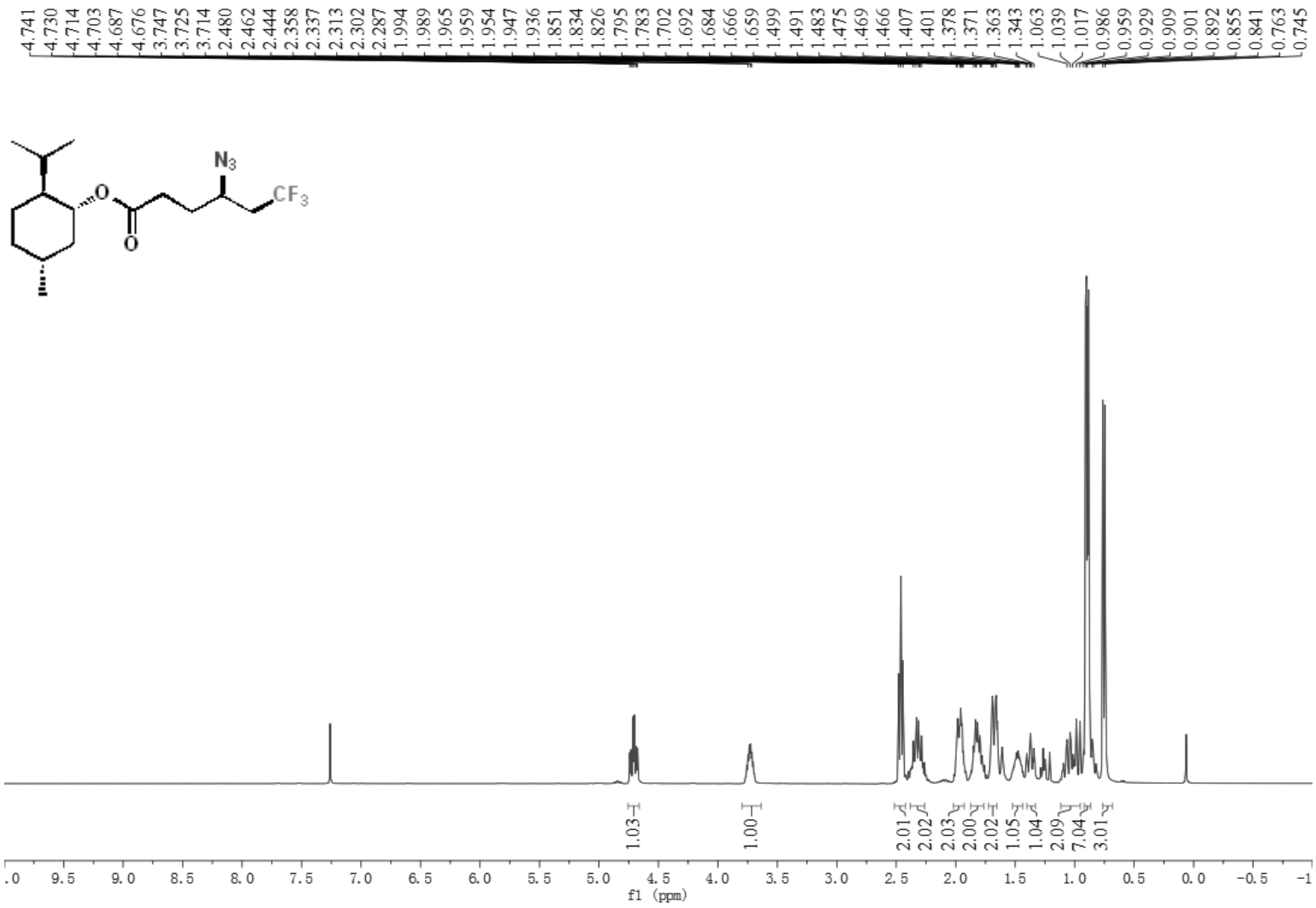
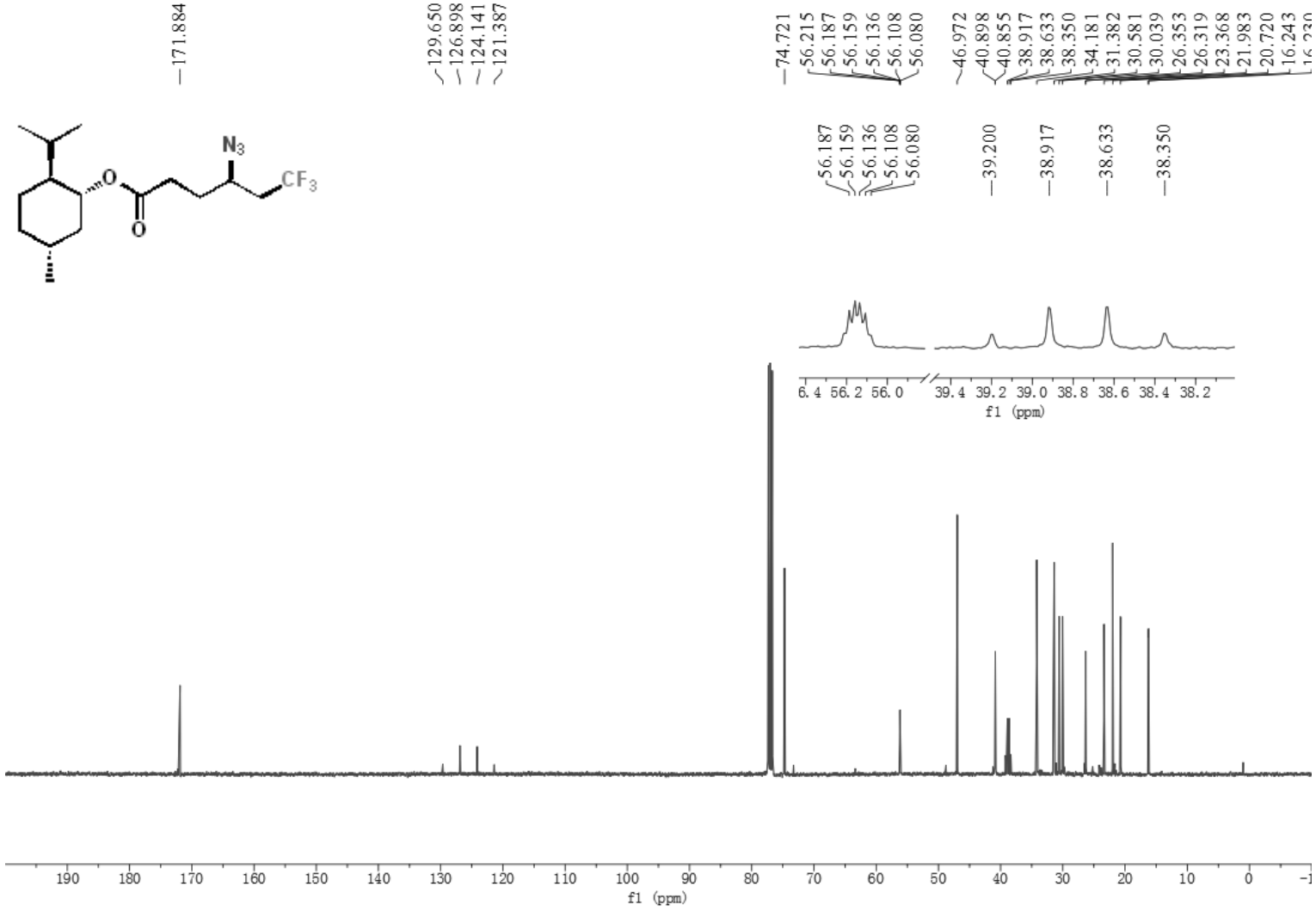
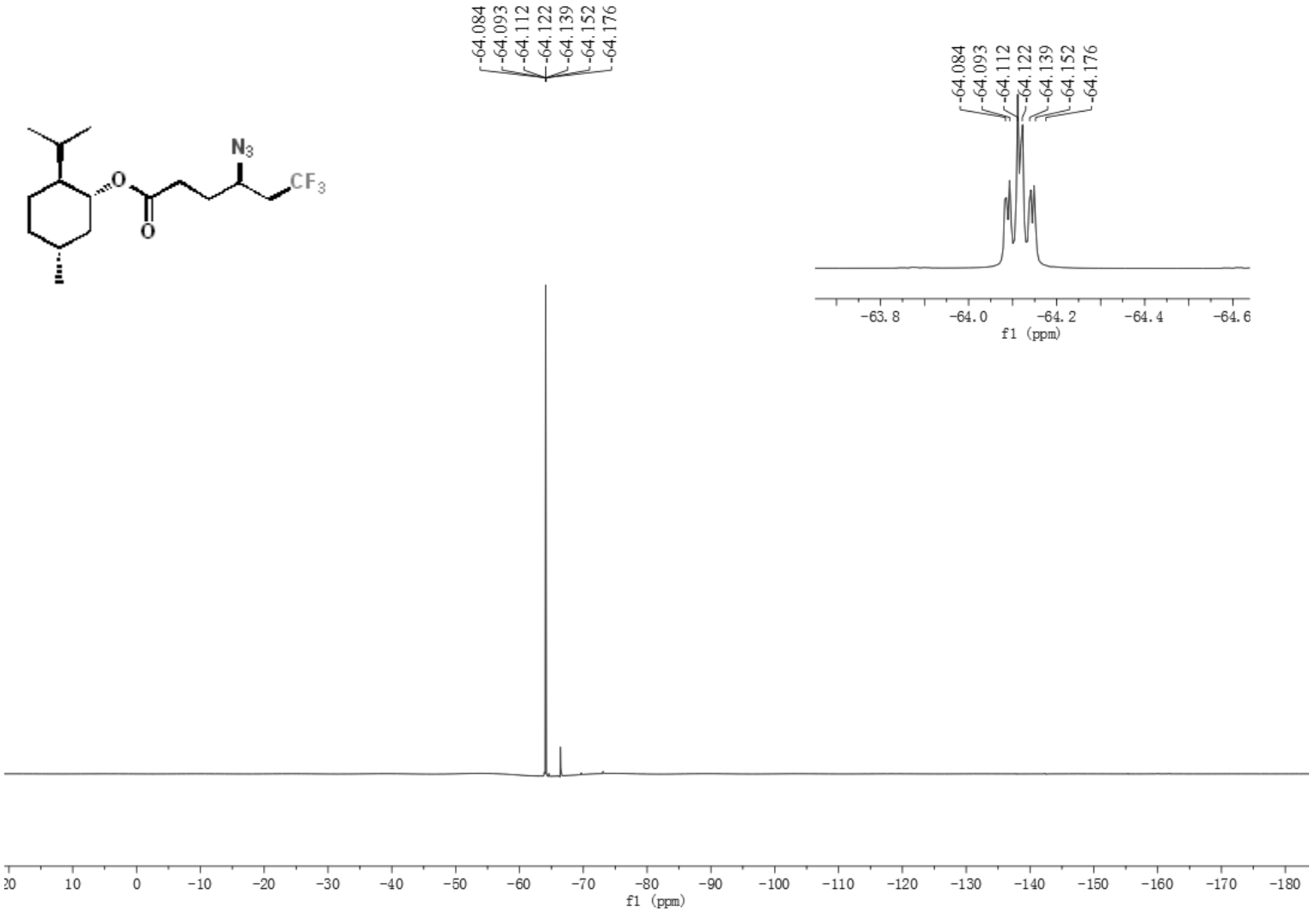


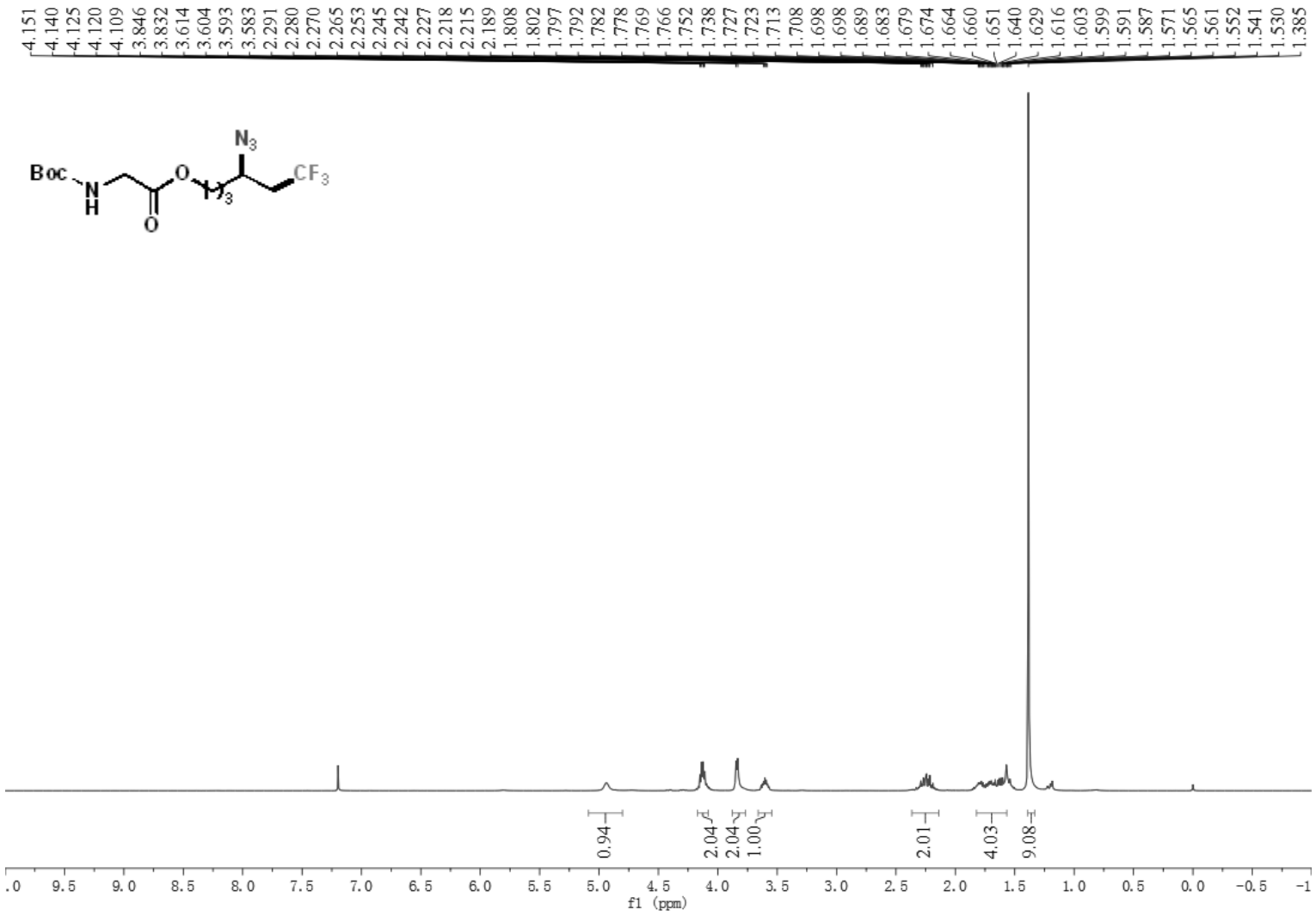
^{13}C NMR (100 MHz, $CDCl_3$) of **4k**



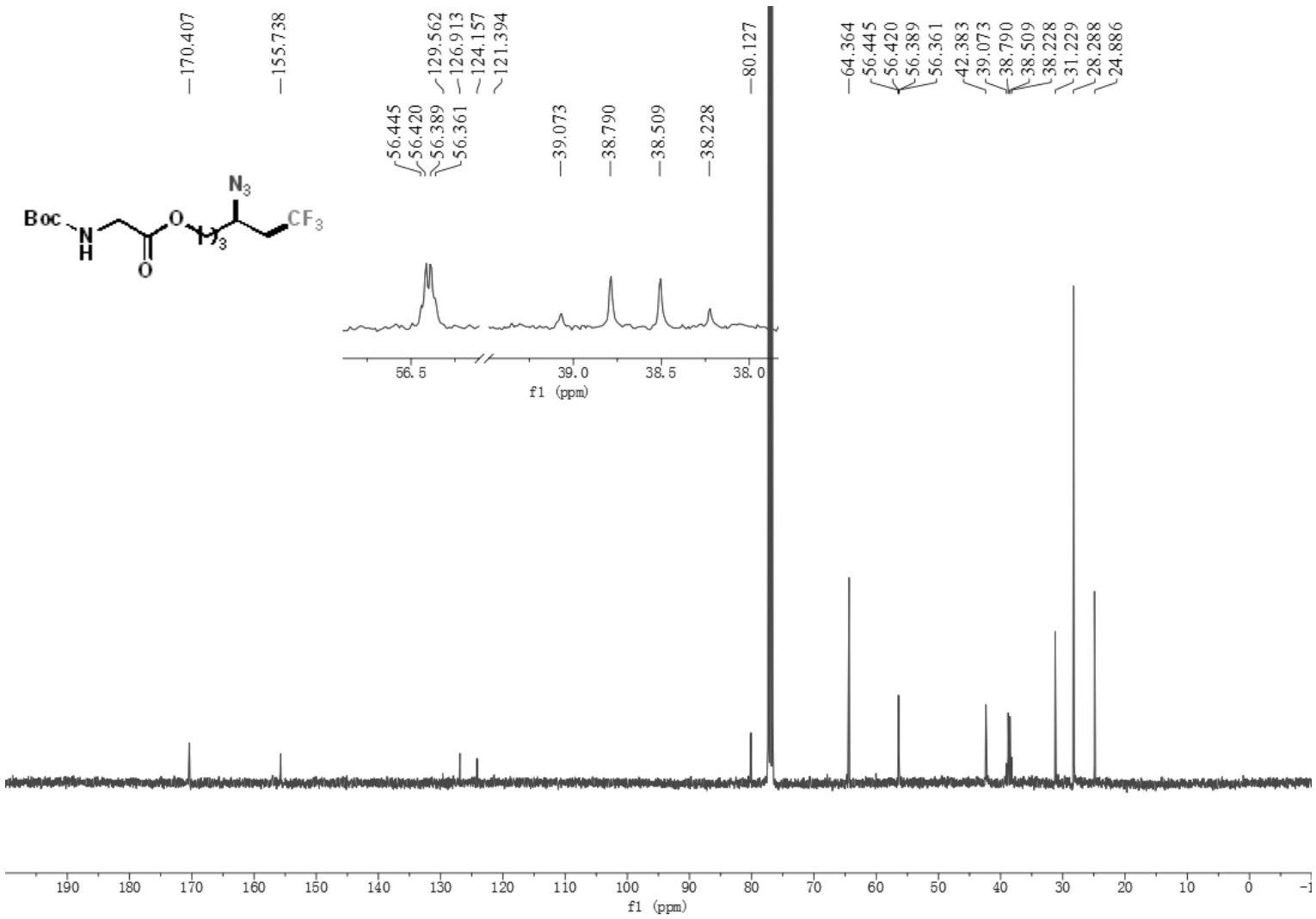
^{13}C NMR (100 MHz, $CDCl_3$) of **4k**



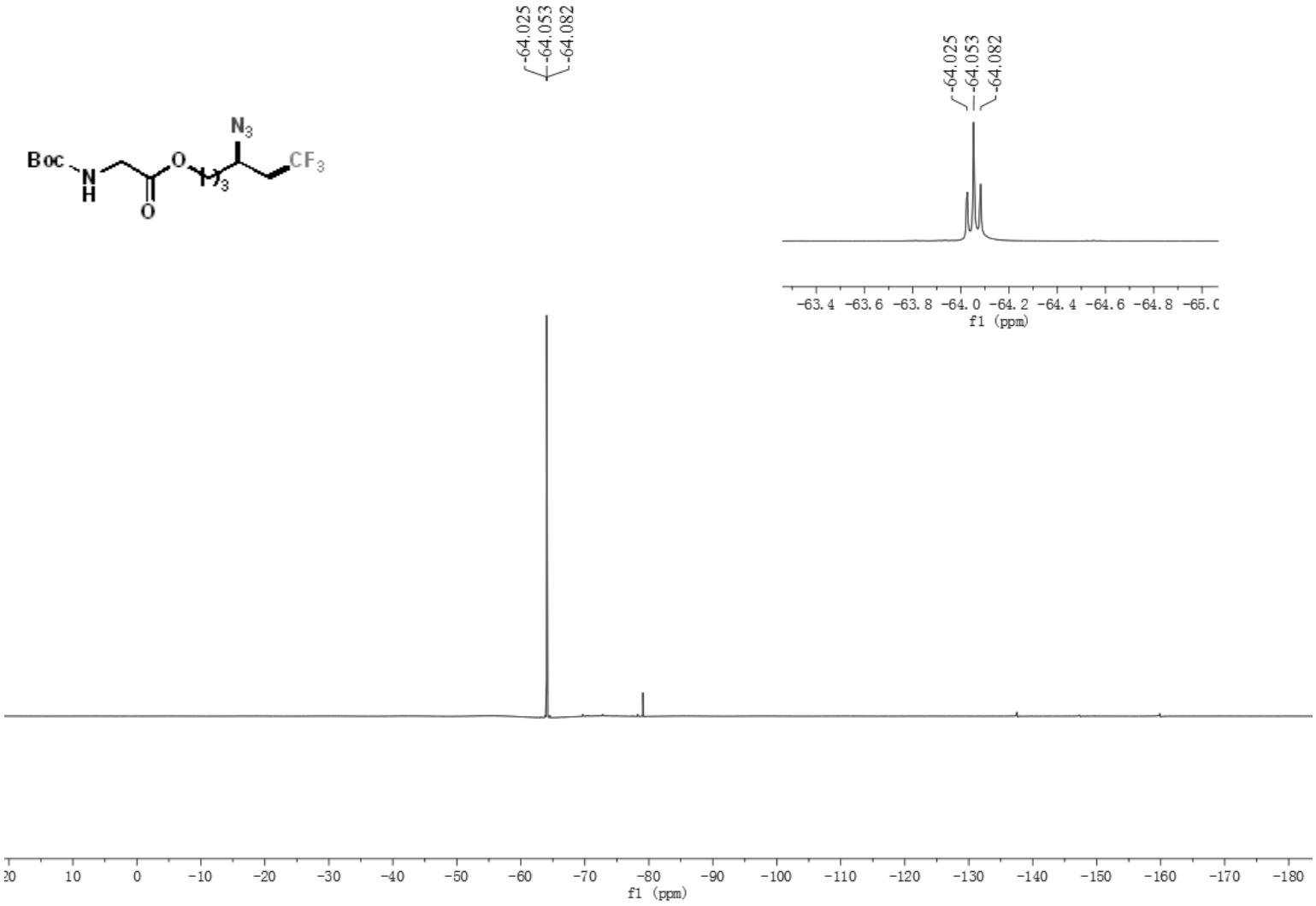
^{19}F NMR (376 MHz, $CDCl_3$) of **4k**



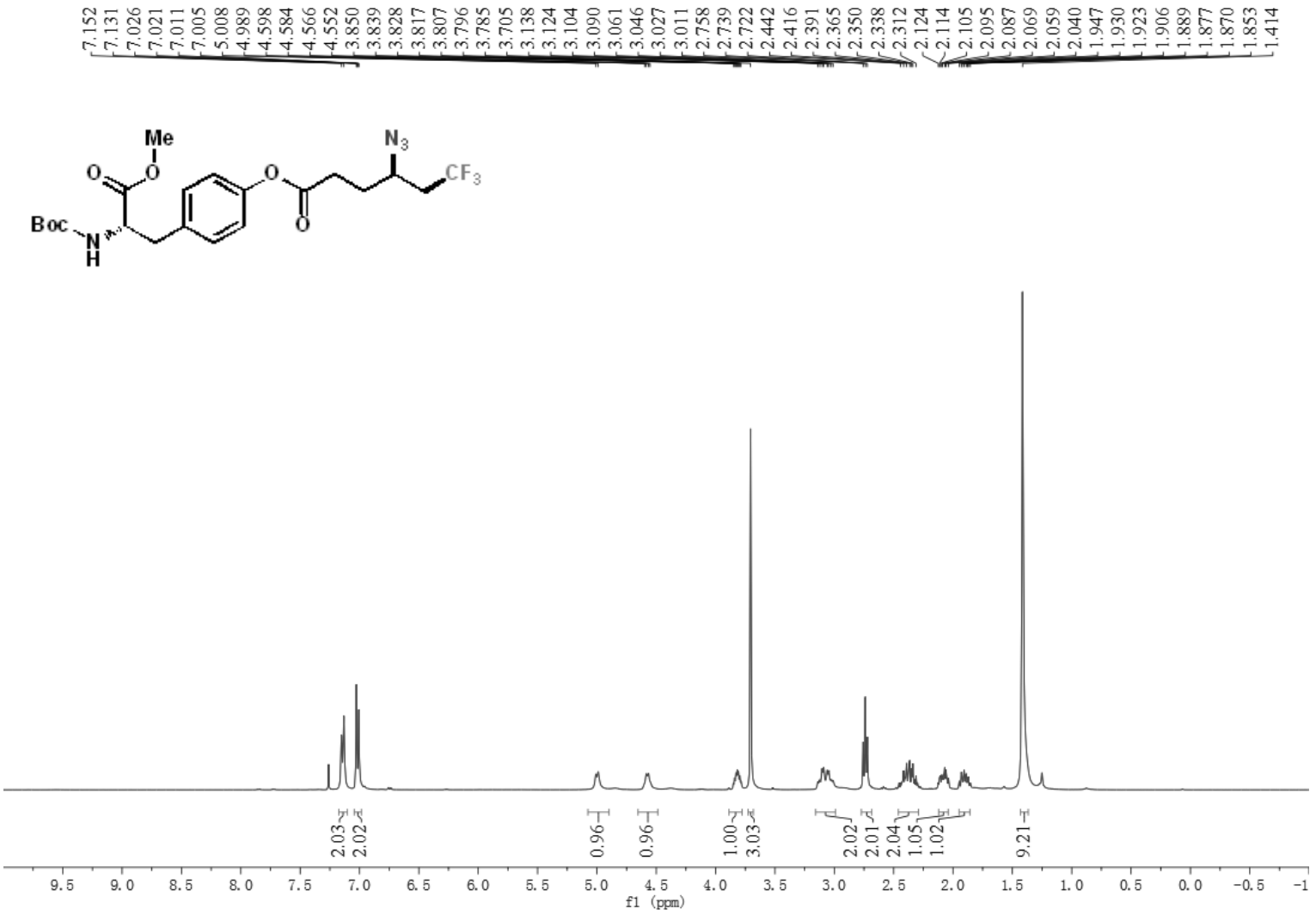
^{1}H NMR (400 MHz, $CDCl_3$) of **4l**



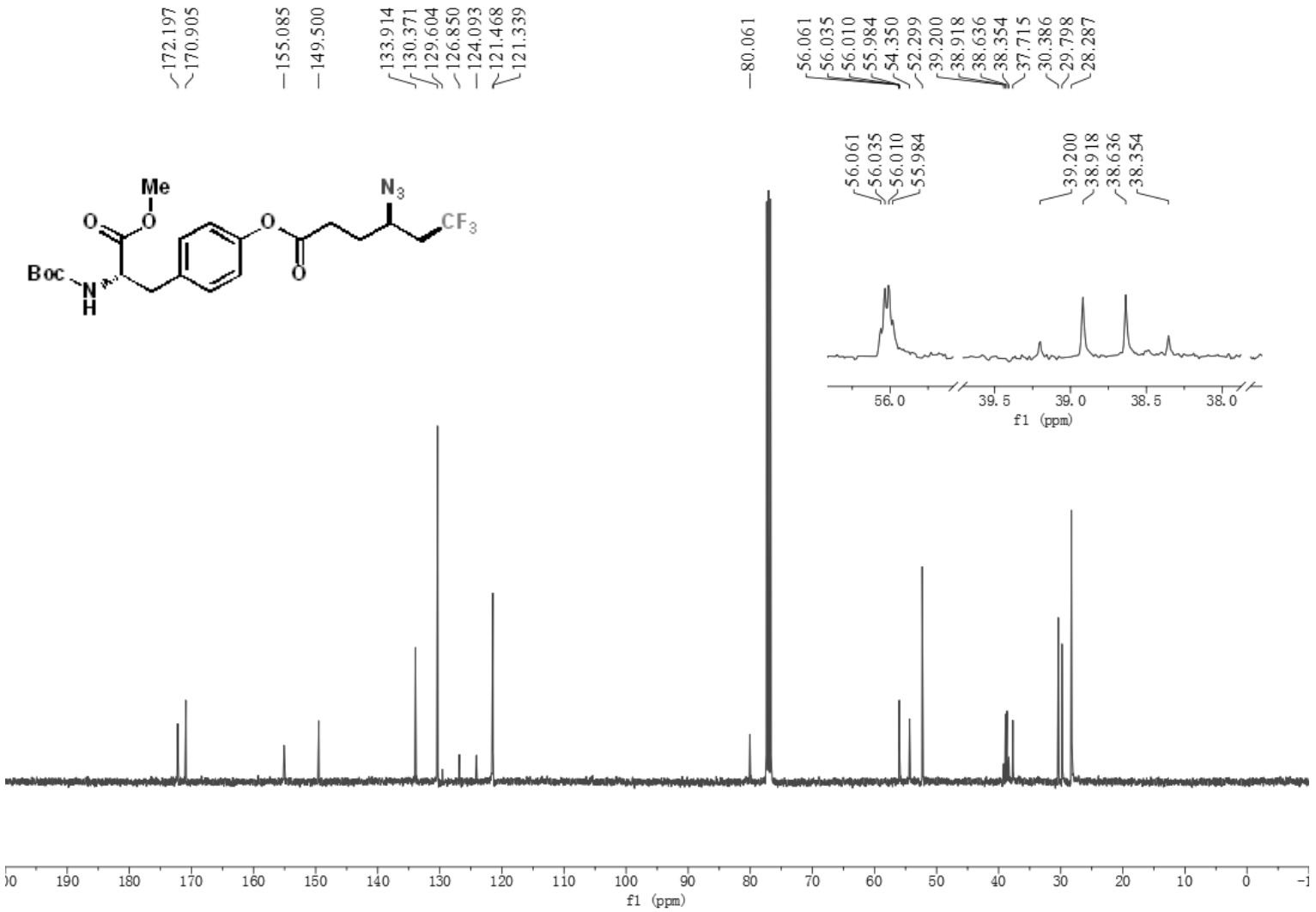
^{13}C NMR (100 MHz, $CDCl_3$) of **4l**



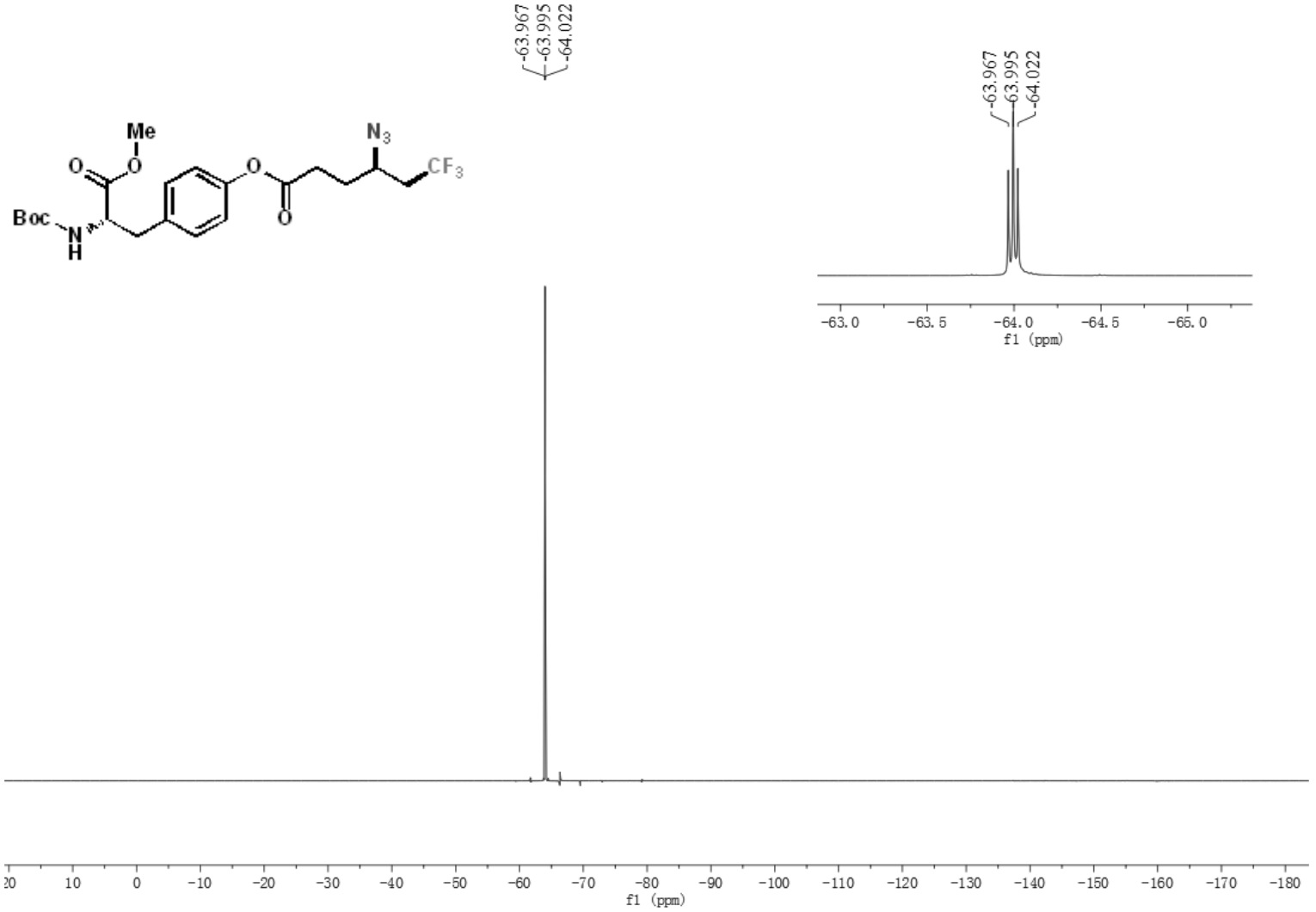
^{19}F NMR (376MHz, $CDCl_3$) of **4l**



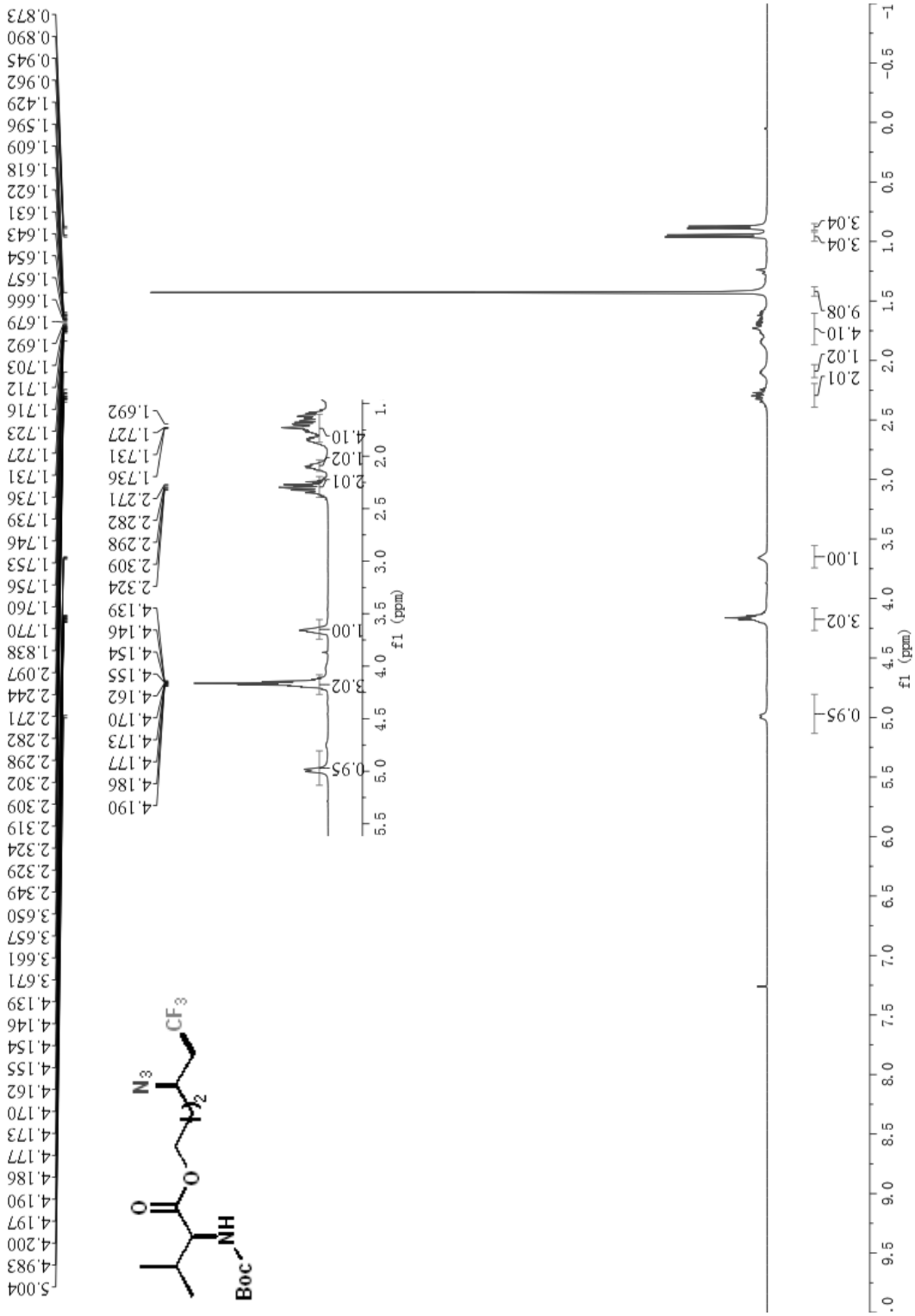
^{1}H NMR (400 MHz, $CDCl_3$) of **4m**



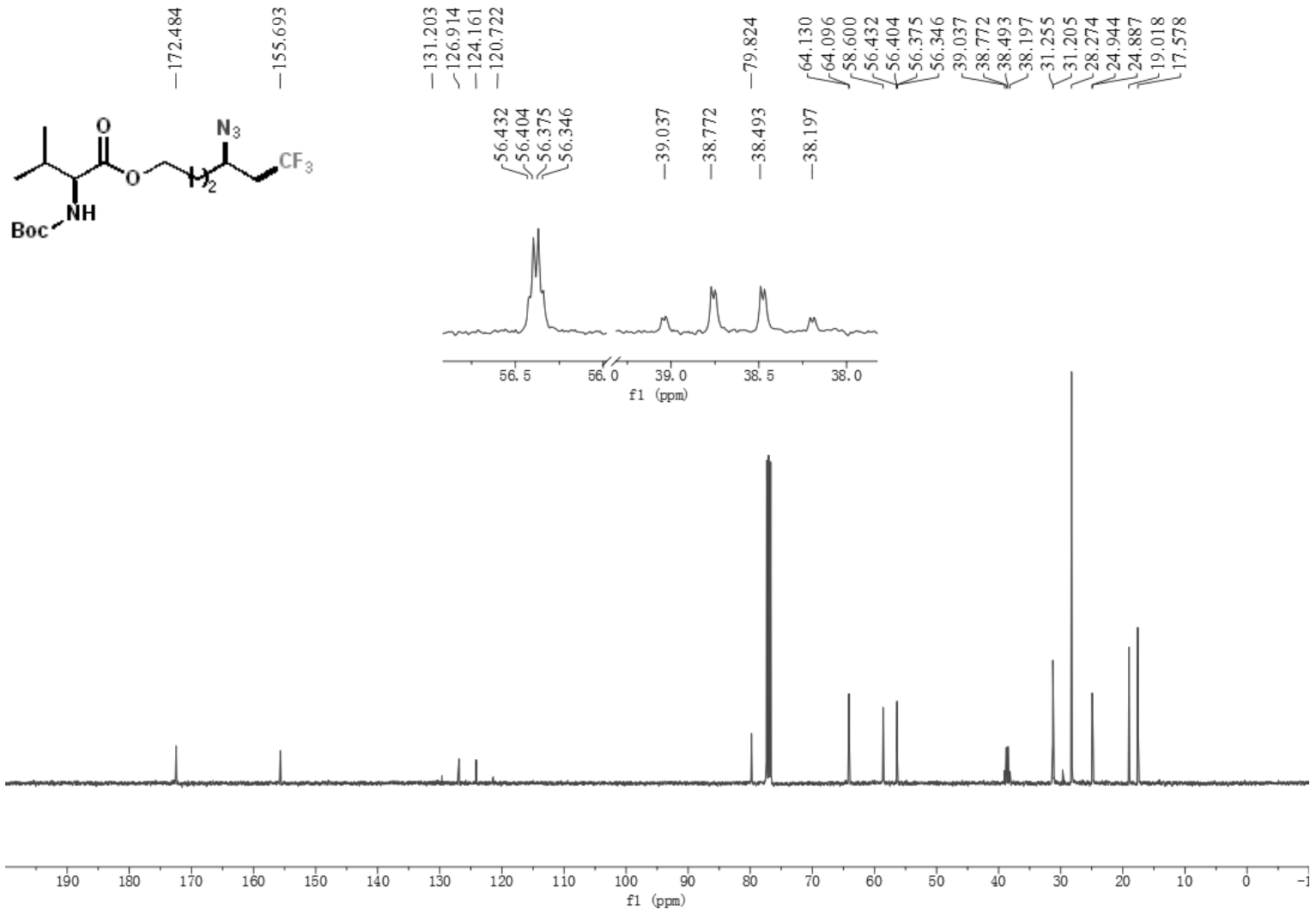
^{13}C NMR (100 MHz, $CDCl_3$) of **4m**



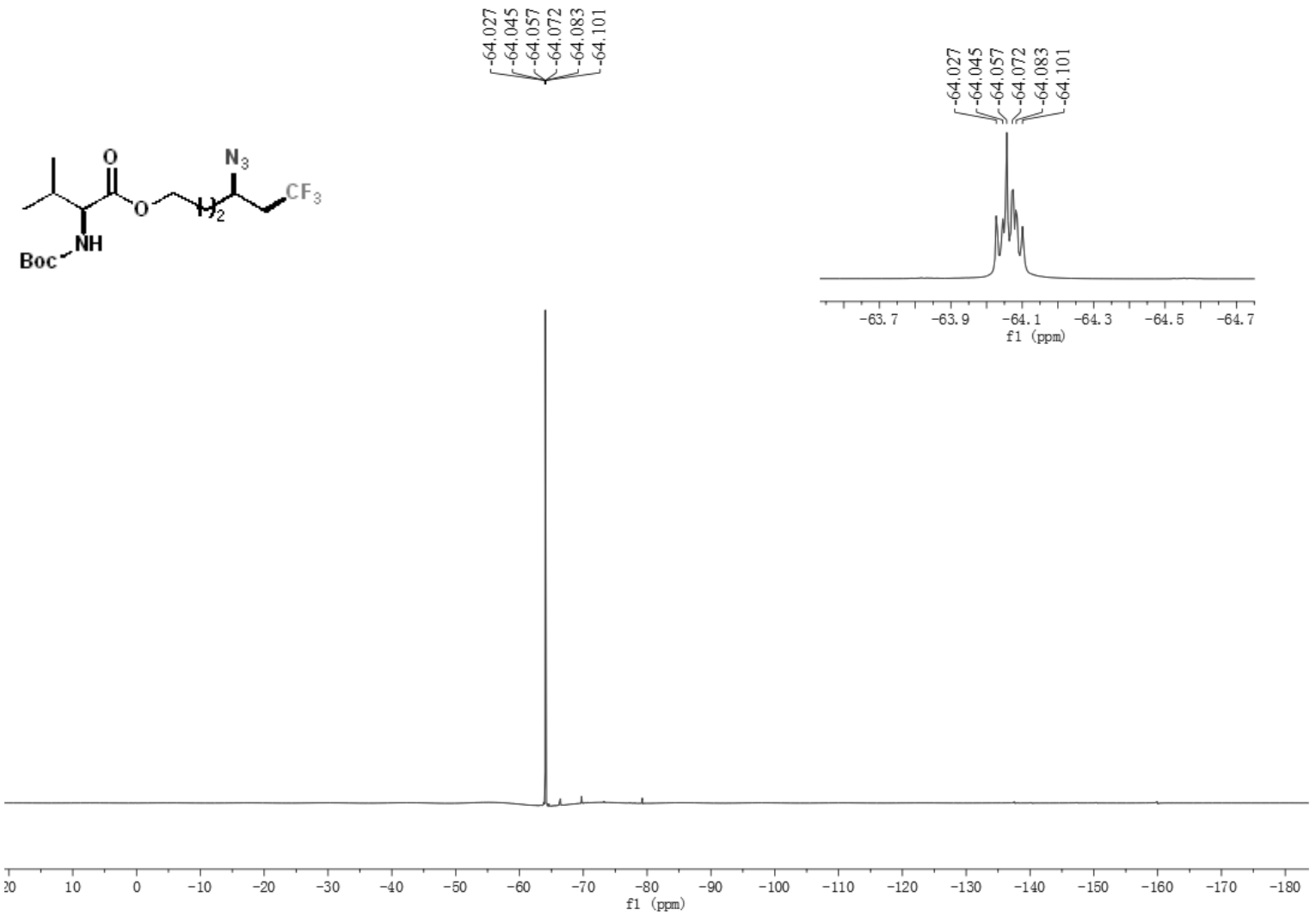
^{19}F NMR (376 MHz, $CDCl_3$) of **4m**



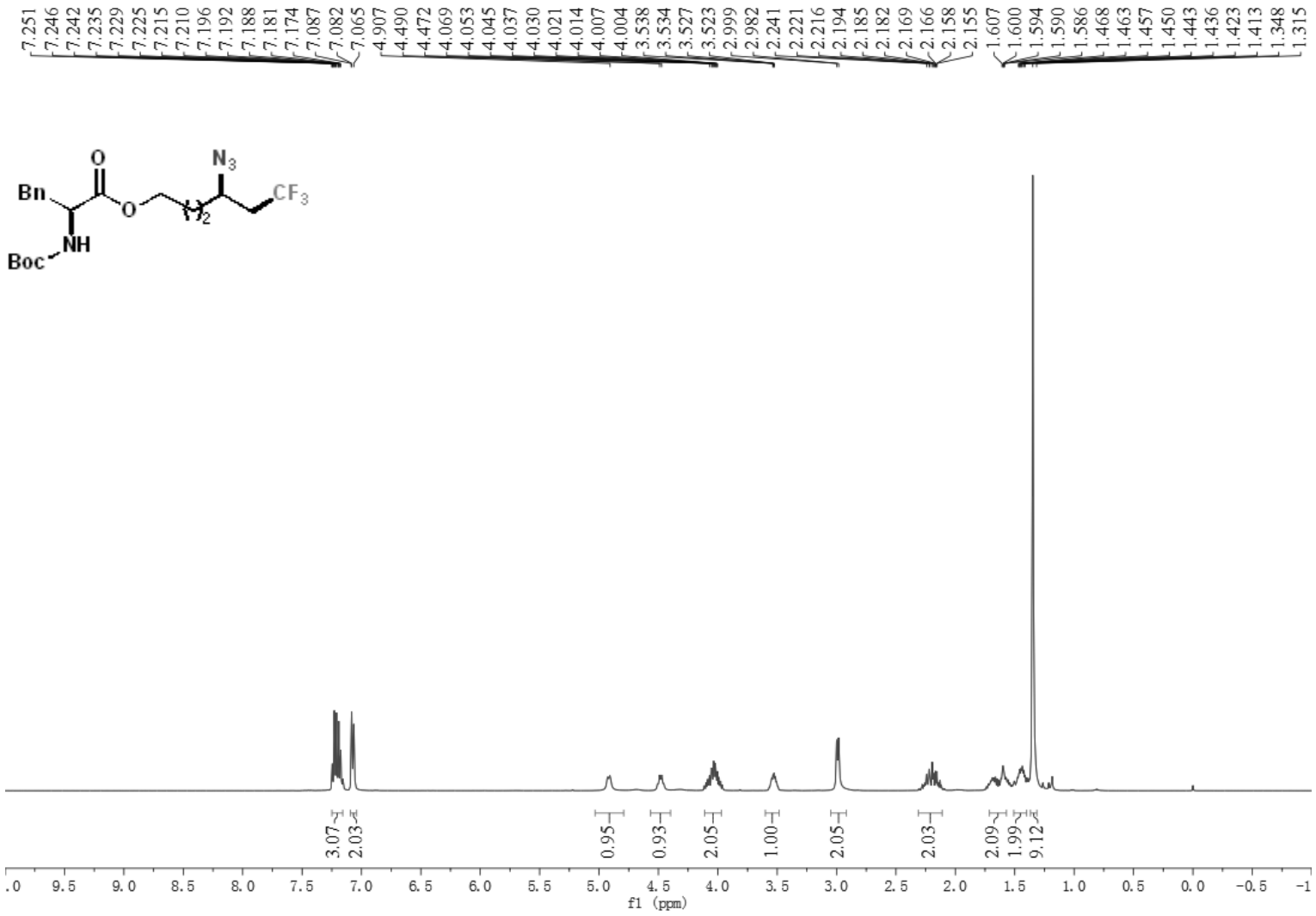
^{1}H NMR (400 MHz, $CDCl_3$) of **4n**



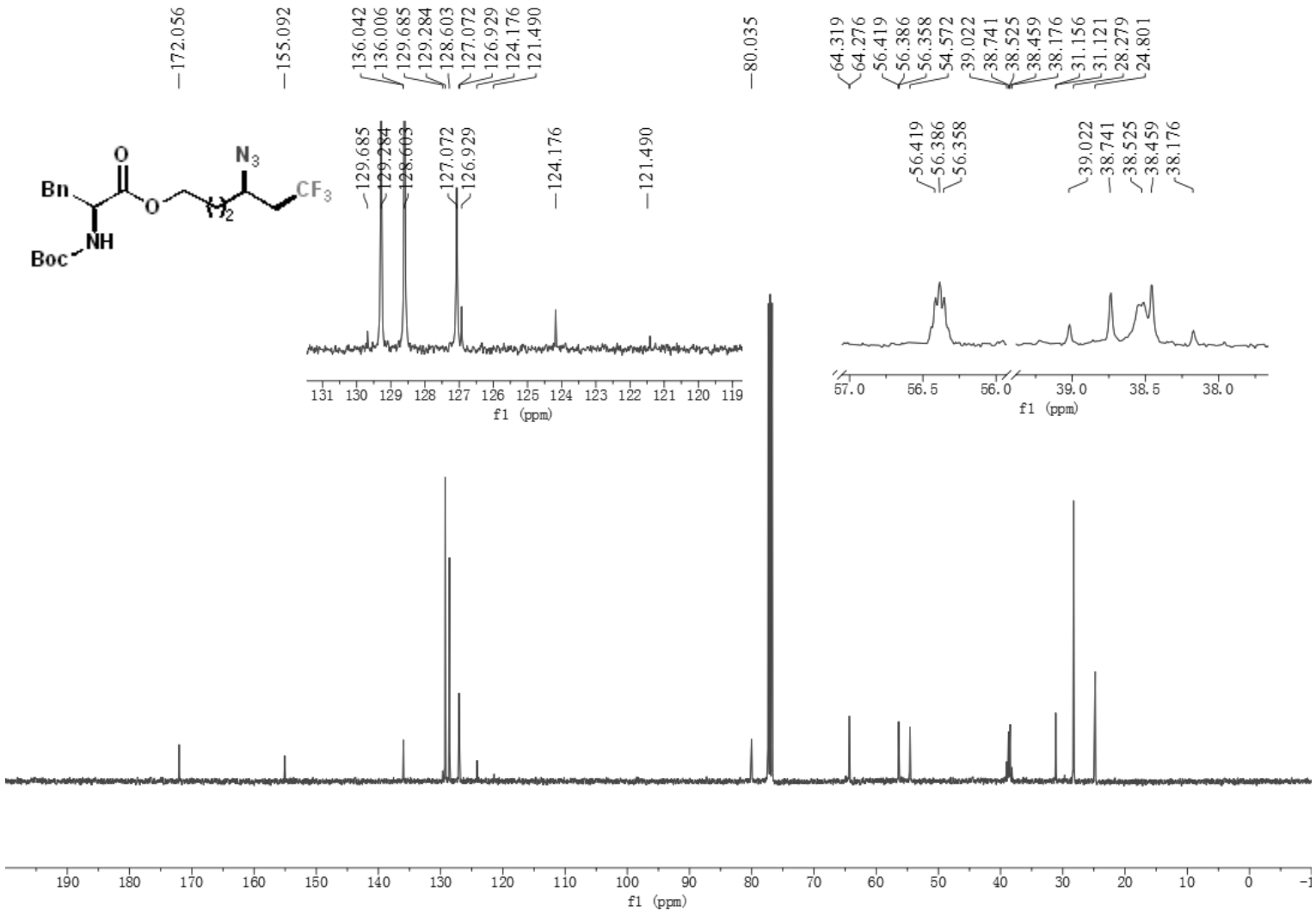
^{13}C NMR (100 MHz, $CDCl_3$) of **4n**



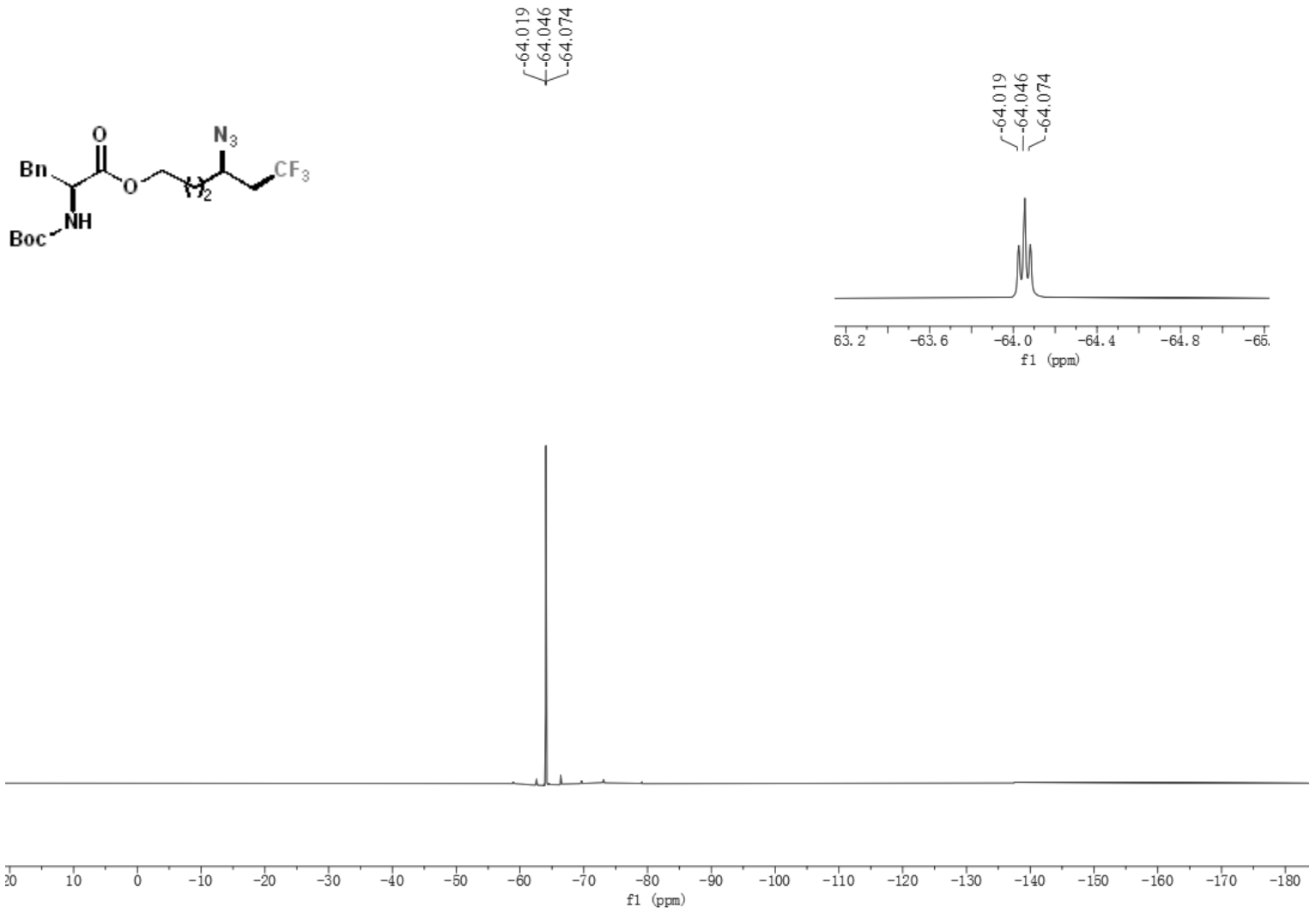
^{19}F NMR (376 MHz, $CDCl_3$) of **4n**



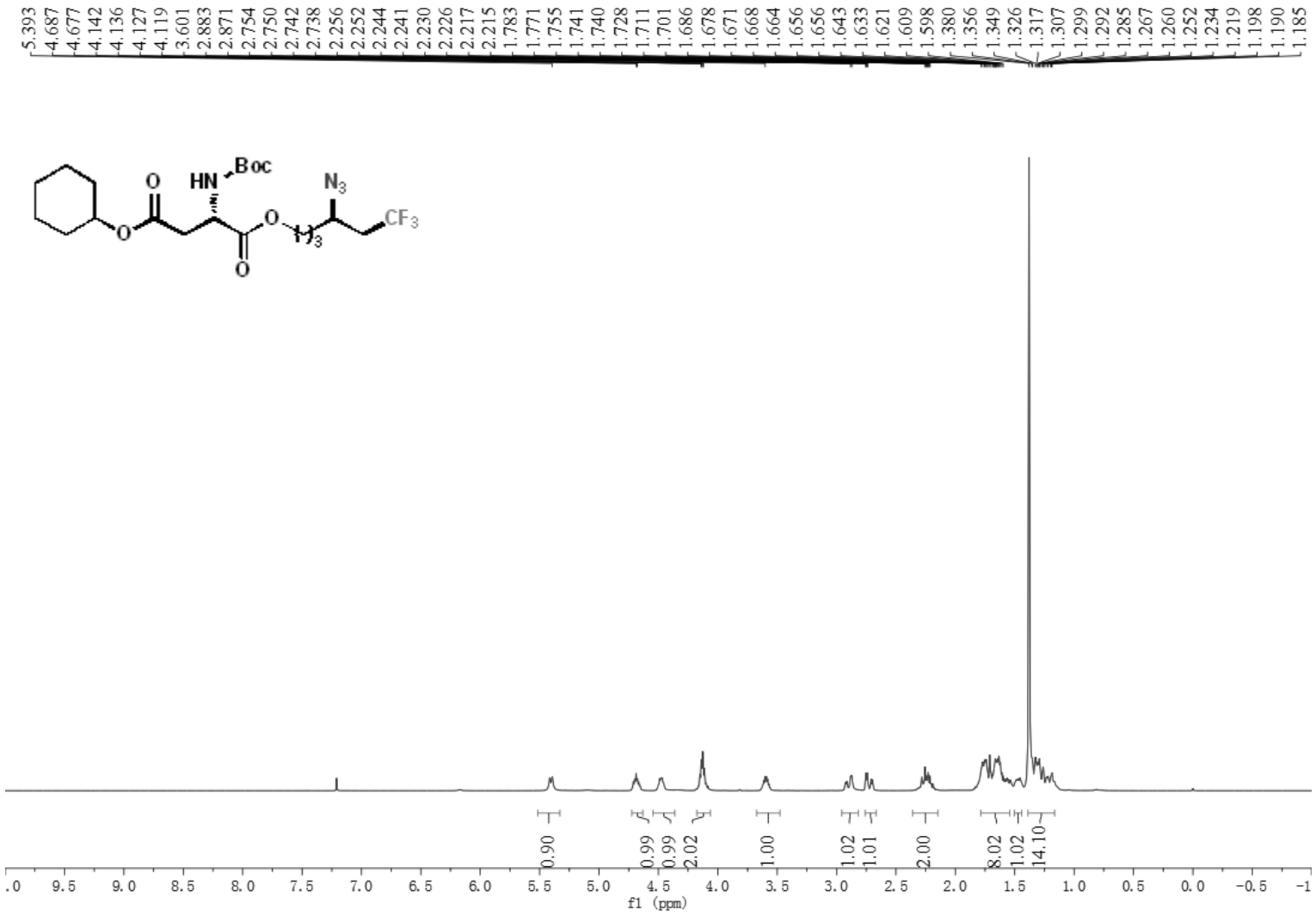
^{1}H NMR (400 MHz, $CDCl_3$) of **4o**



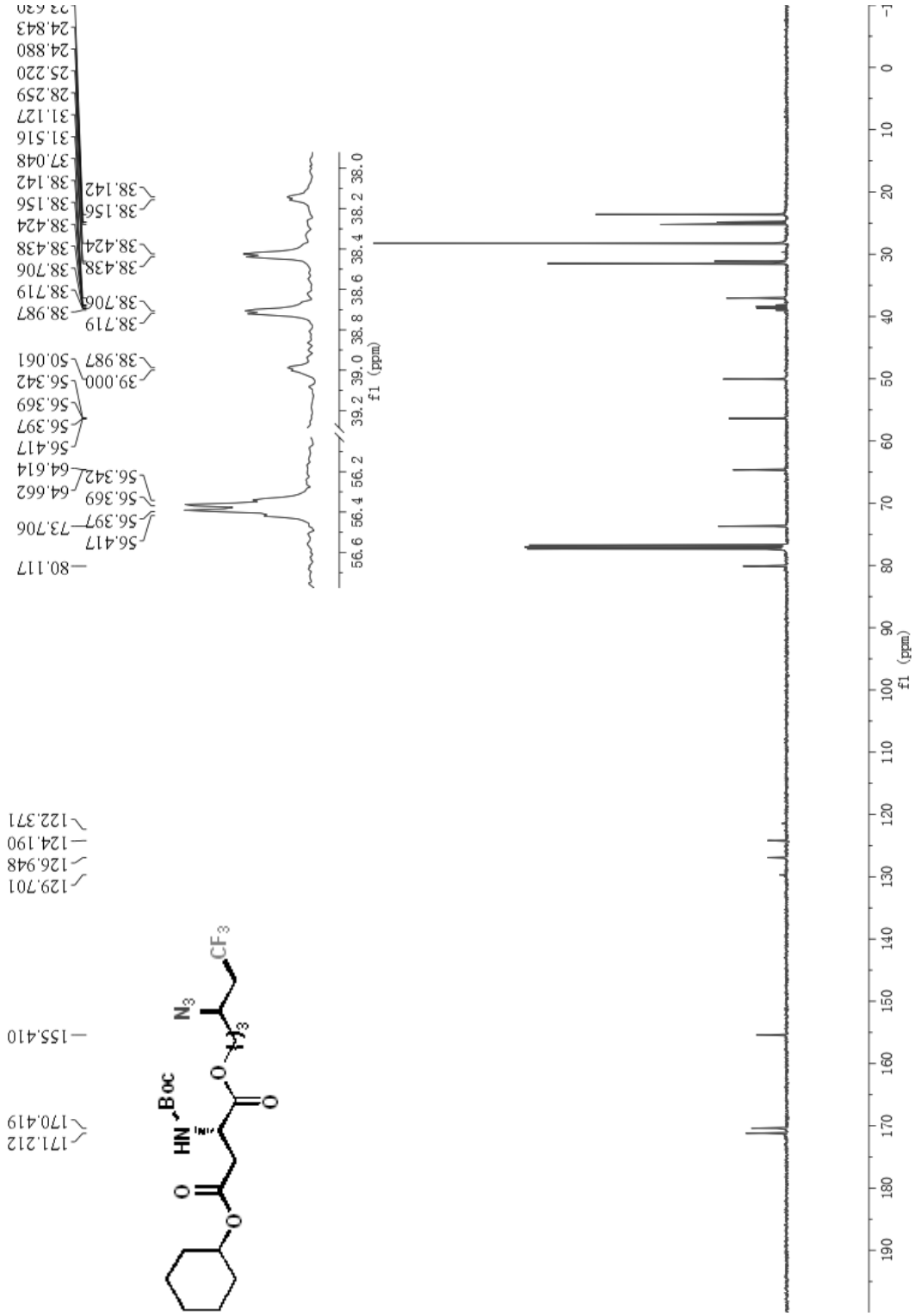
^{13}C NMR (100 MHz, $CDCl_3$) of **4o**



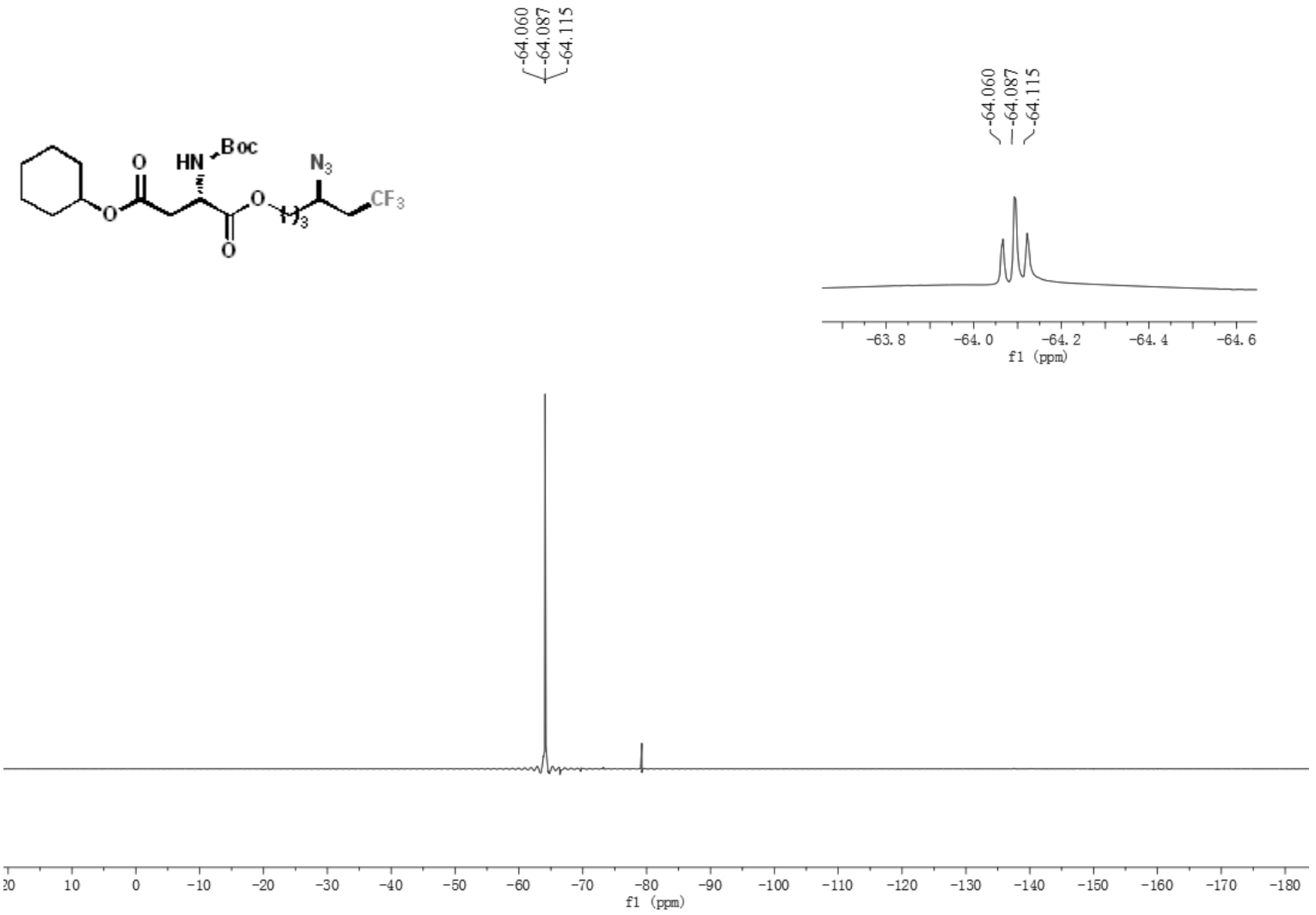
^{19}F NMR (376 MHz, $CDCl_3$) of **4o**



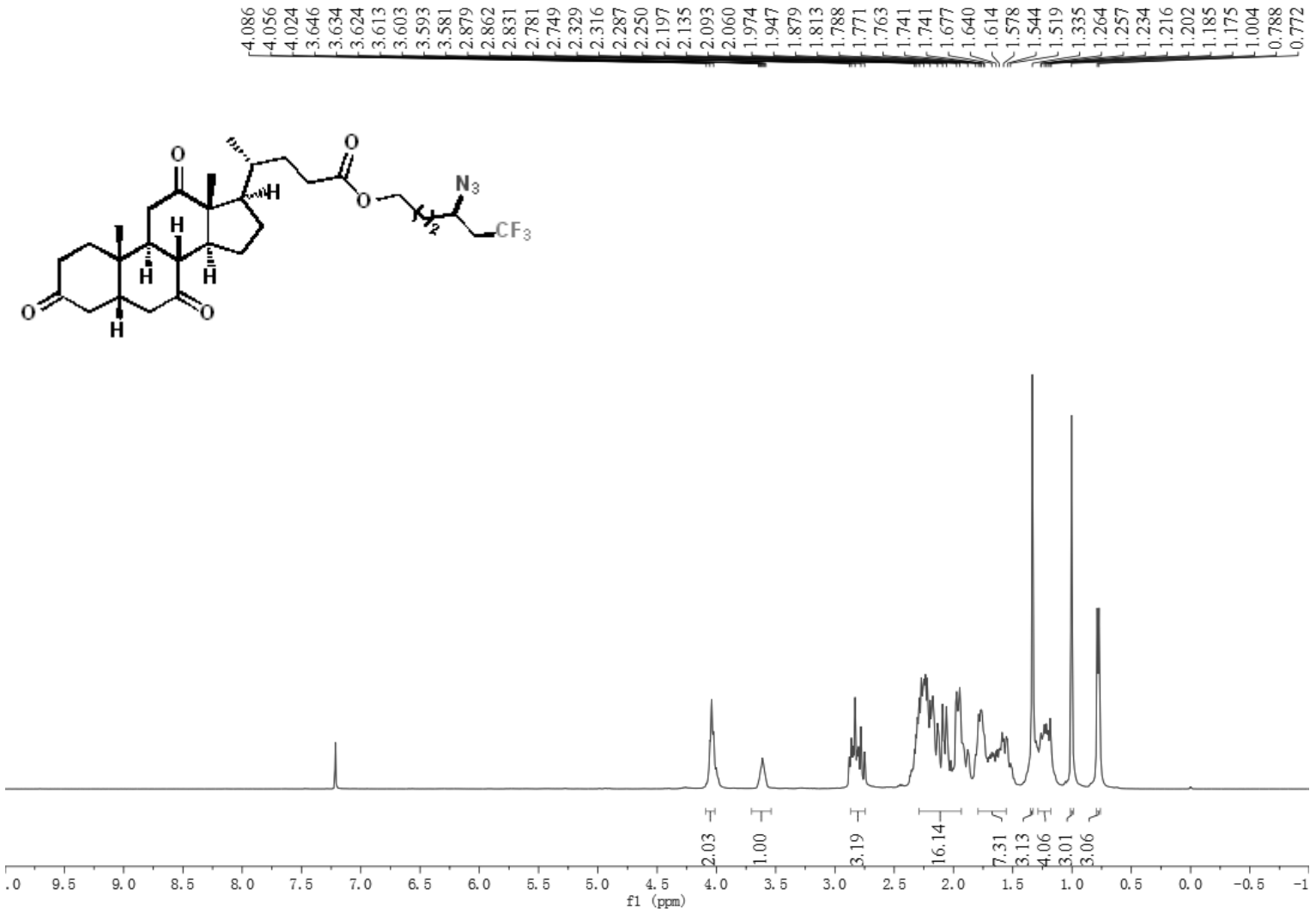
^{1}H NMR (400 MHz, $CDCl_3$) of **4p**



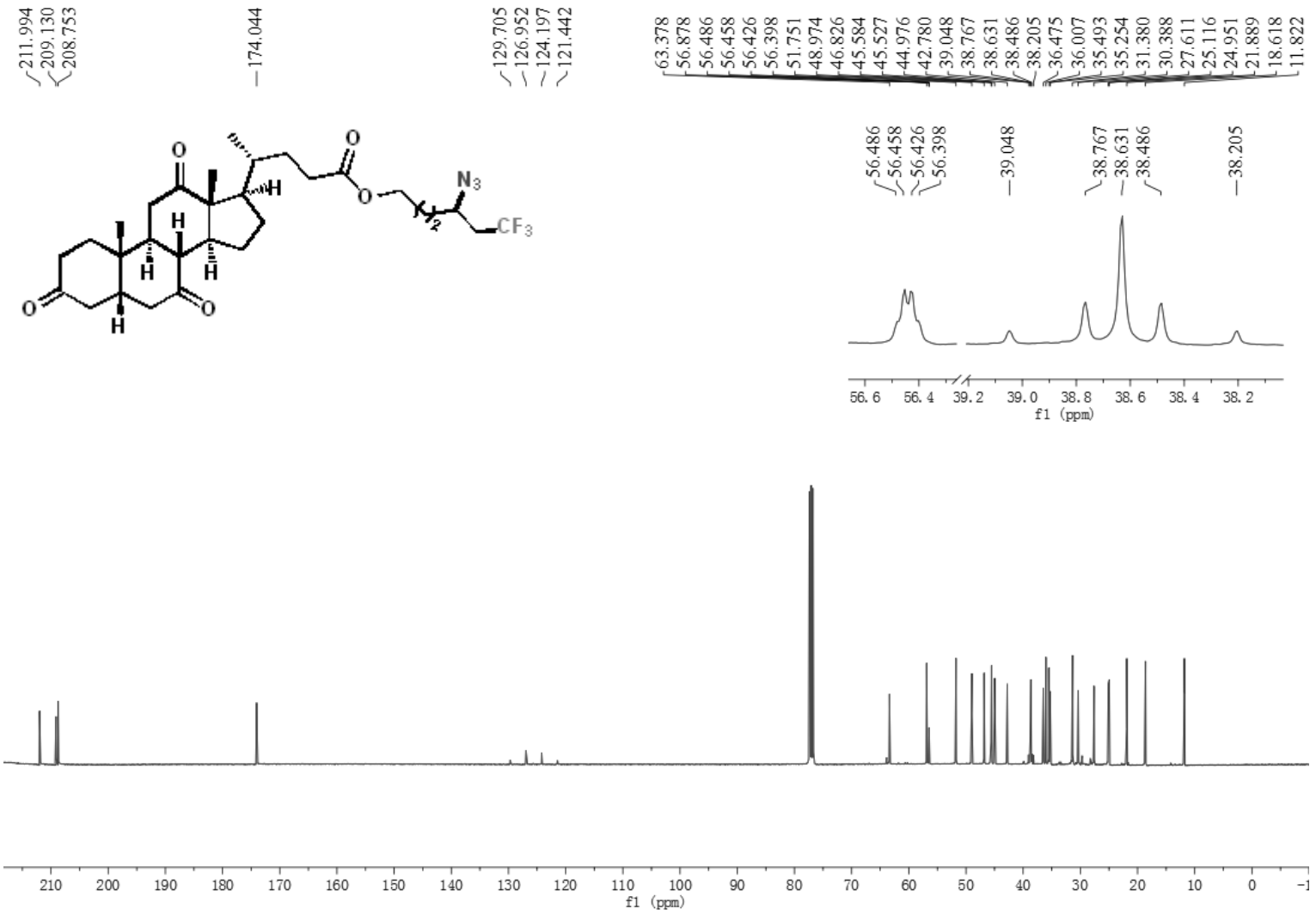
^{13}C NMR (100 MHz, $CDCl_3$) of **4p**



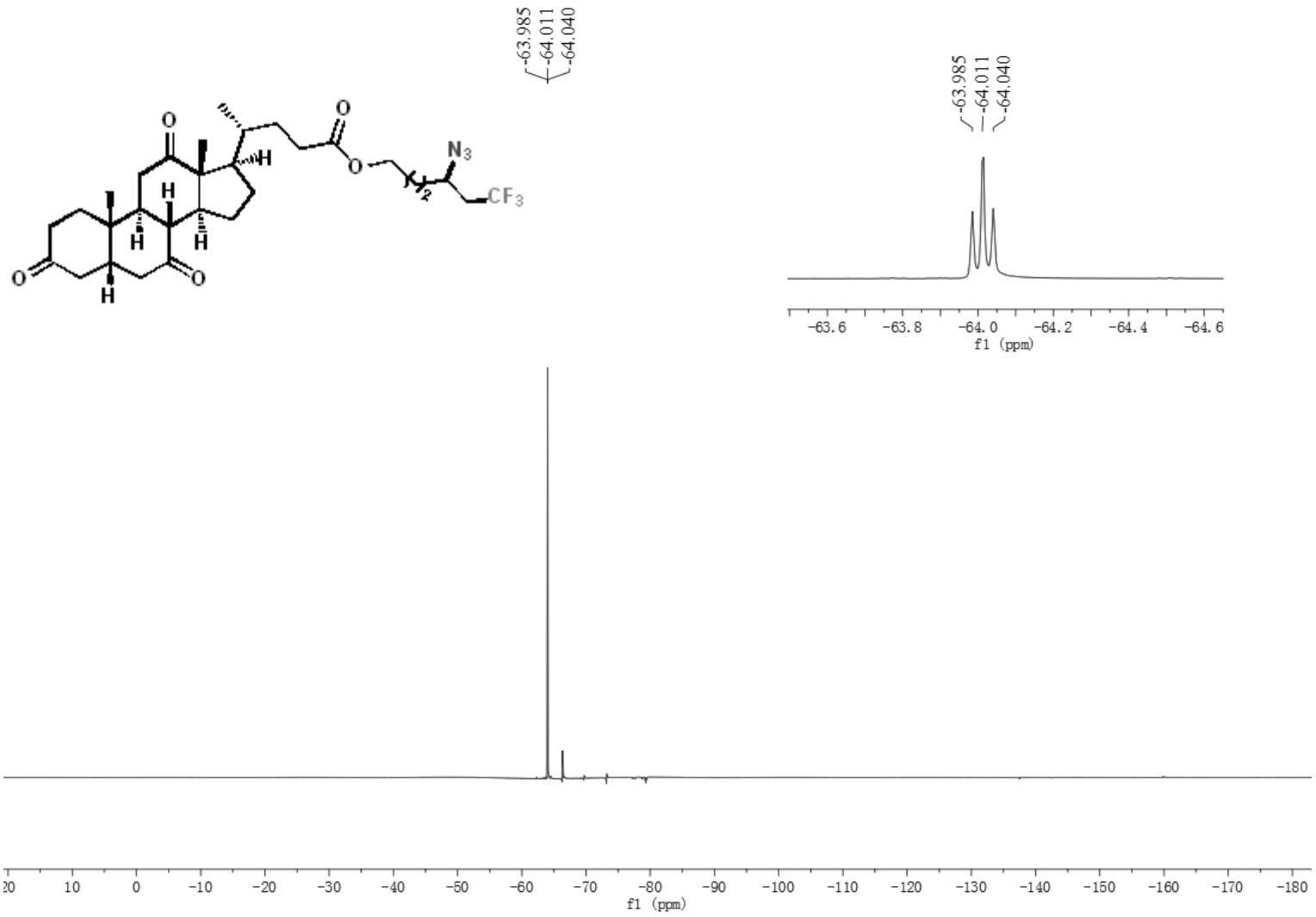
^{19}F NMR (376 MHz, $CDCl_3$) of **4p**



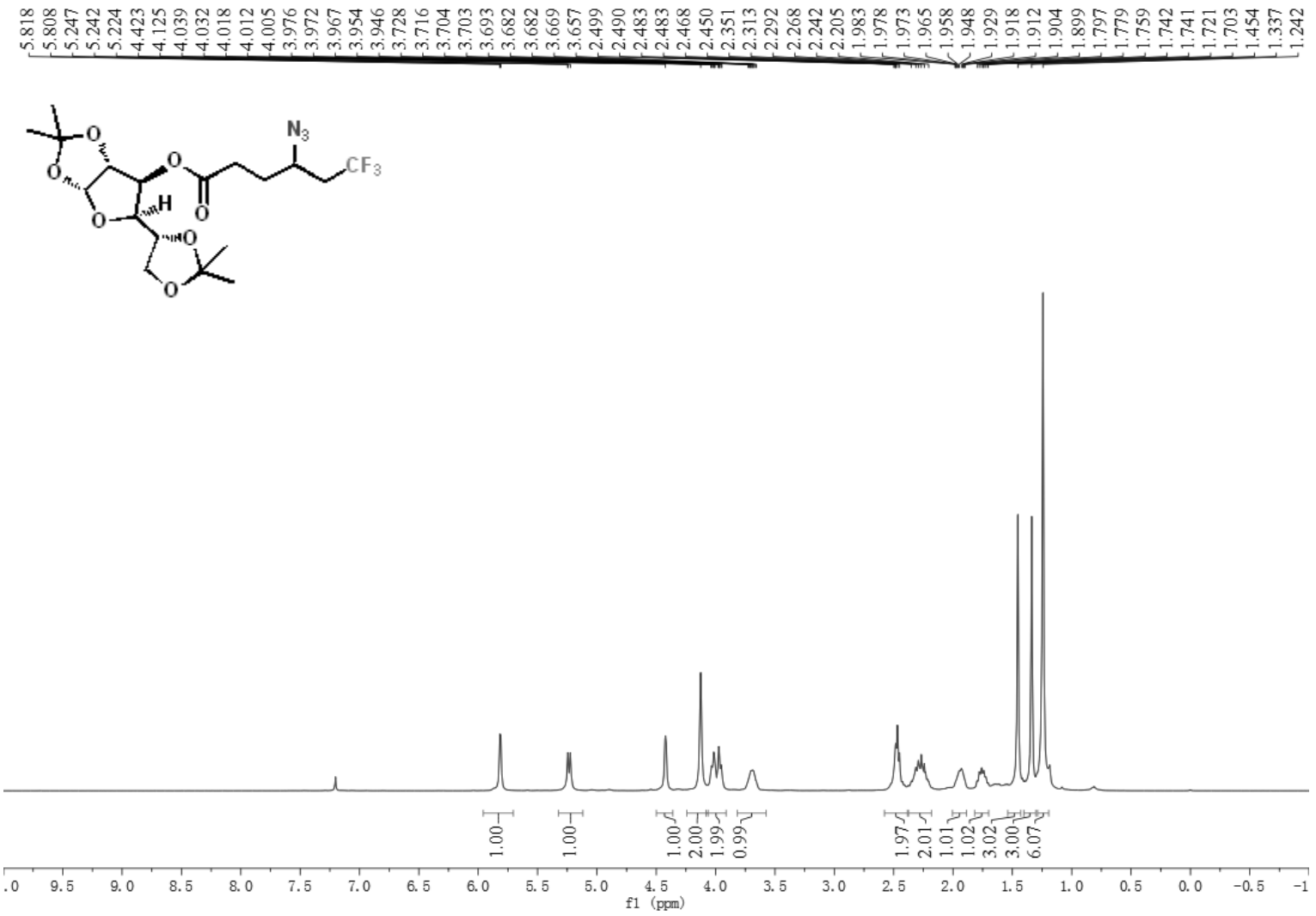
^{1}H NMR (400 MHz, $CDCl_3$) of **4q**



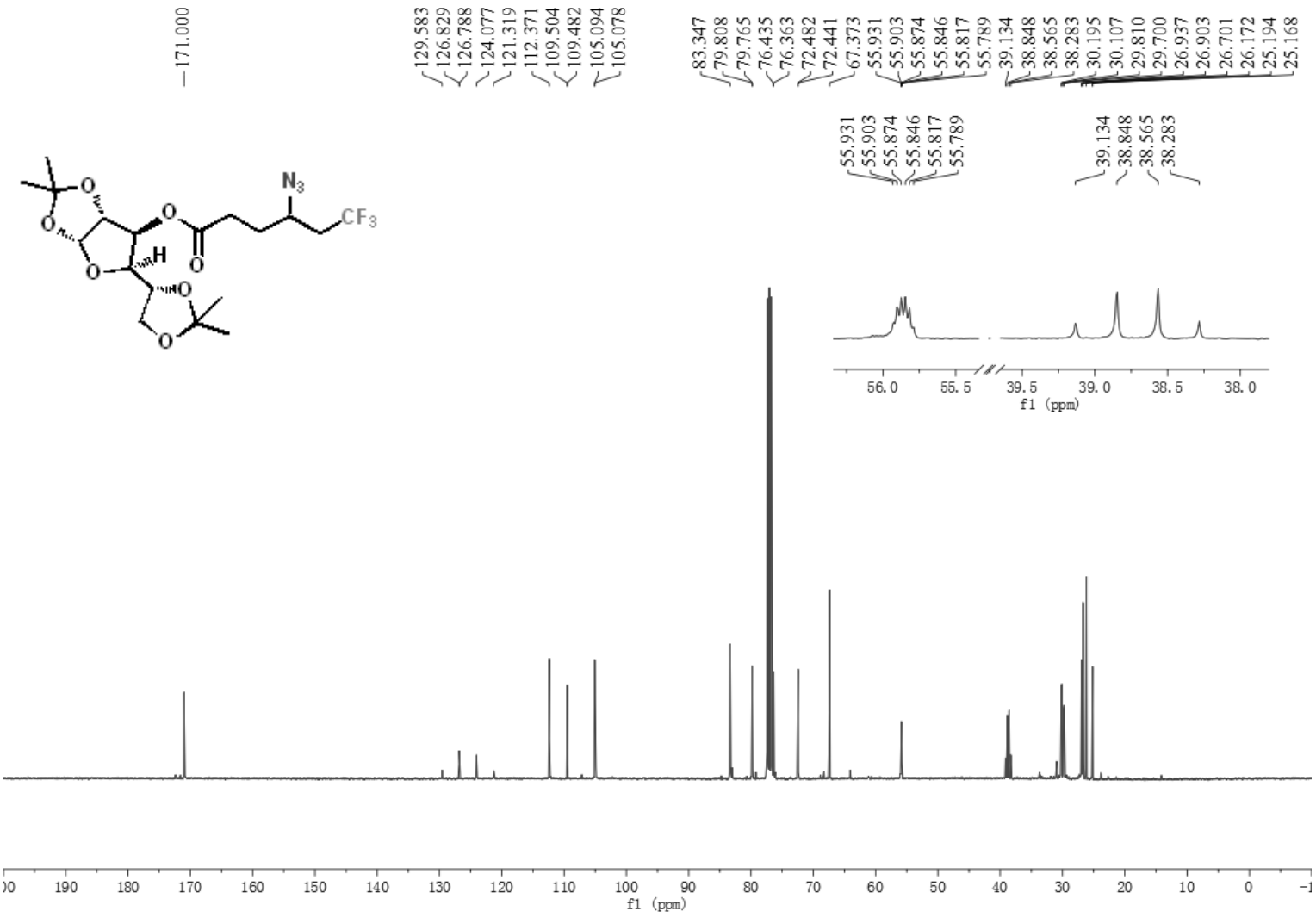
^{13}C NMR (100 MHz, $CDCl_3$) of **4q**



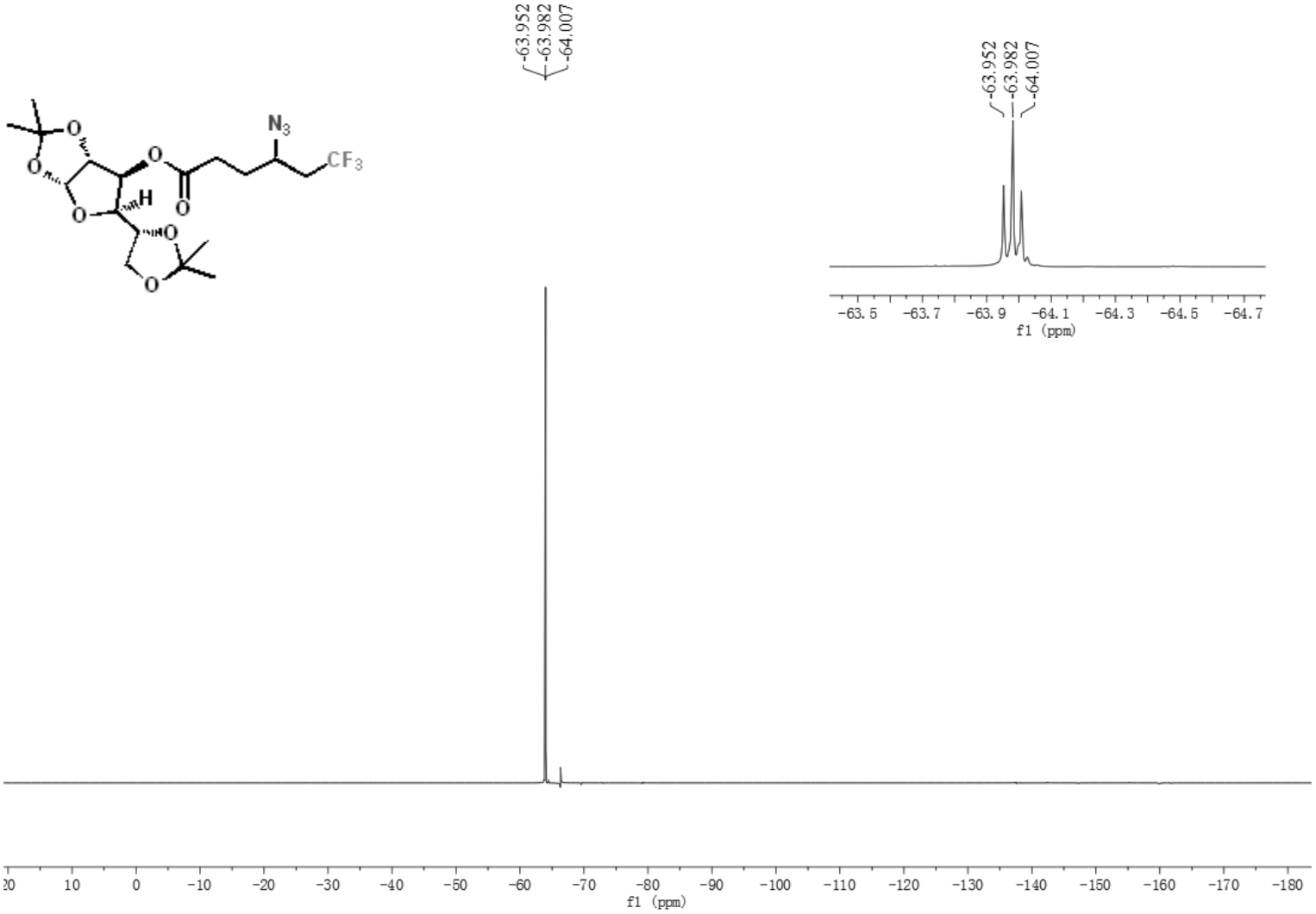
^{19}F NMR (376 MHz, $CDCl_3$) of **4q**



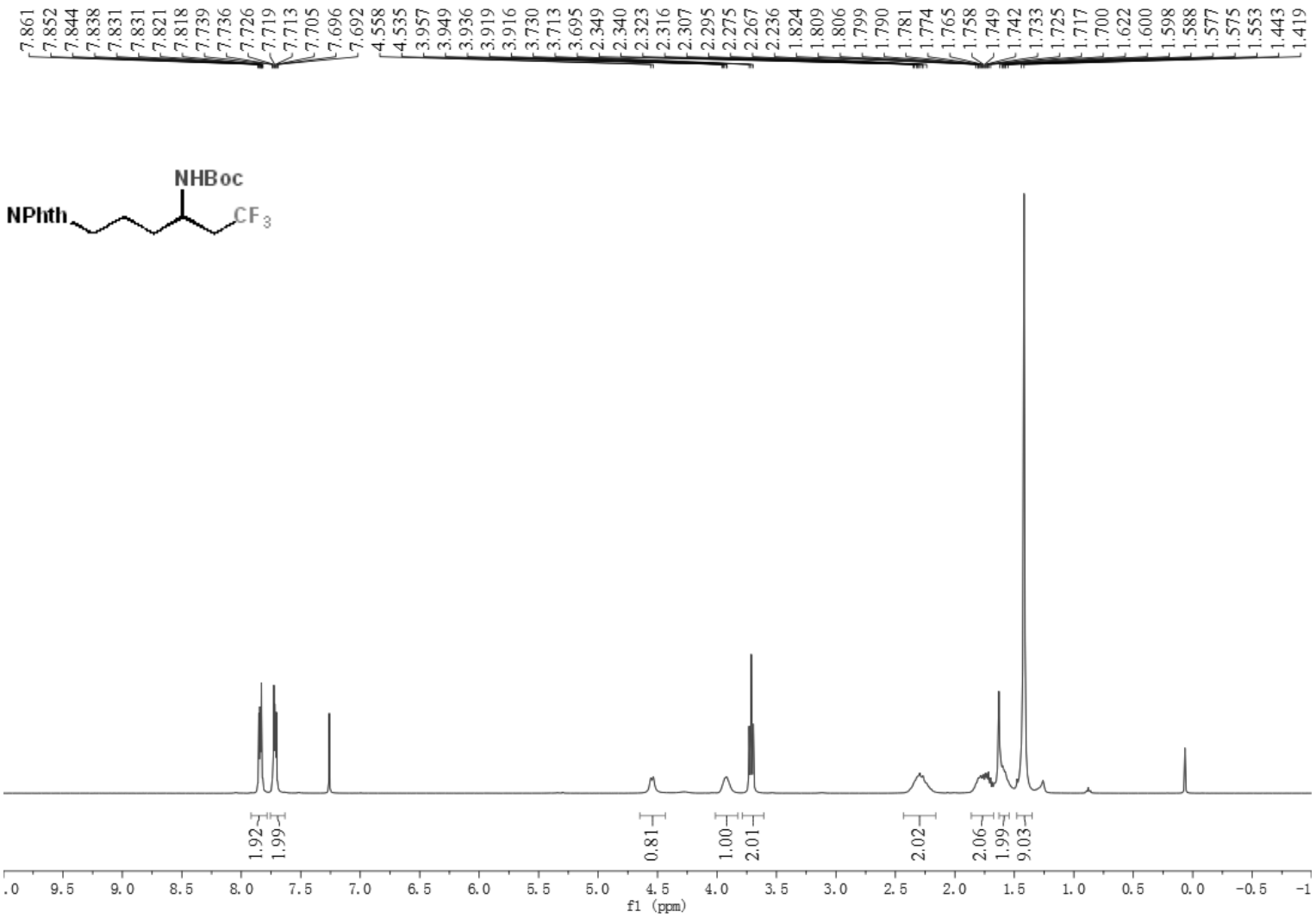
^{1}H NMR (400 MHz, $CDCl_3$) of **4r**



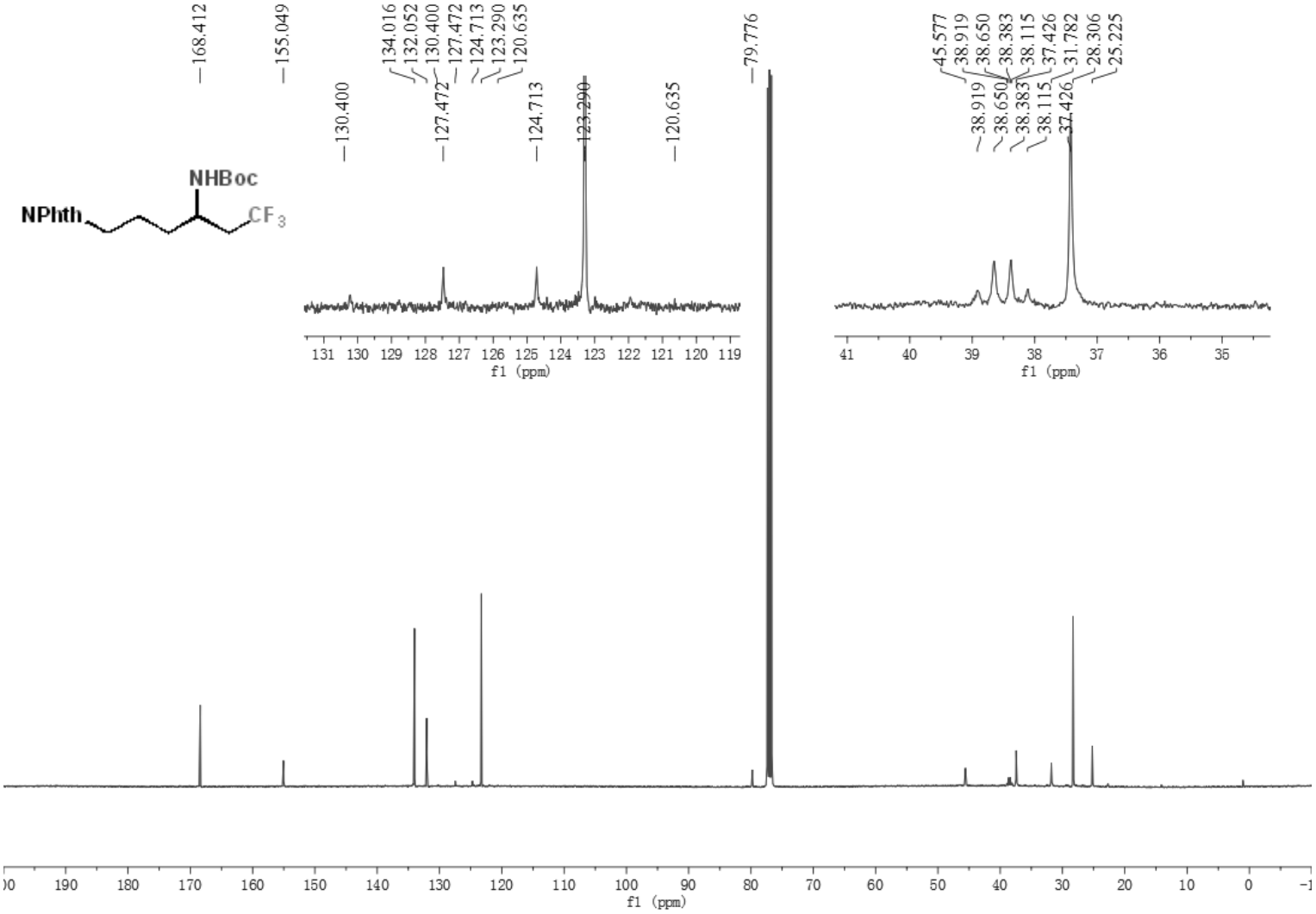
^{13}C NMR (100 MHz, $CDCl_3$) of **4r**



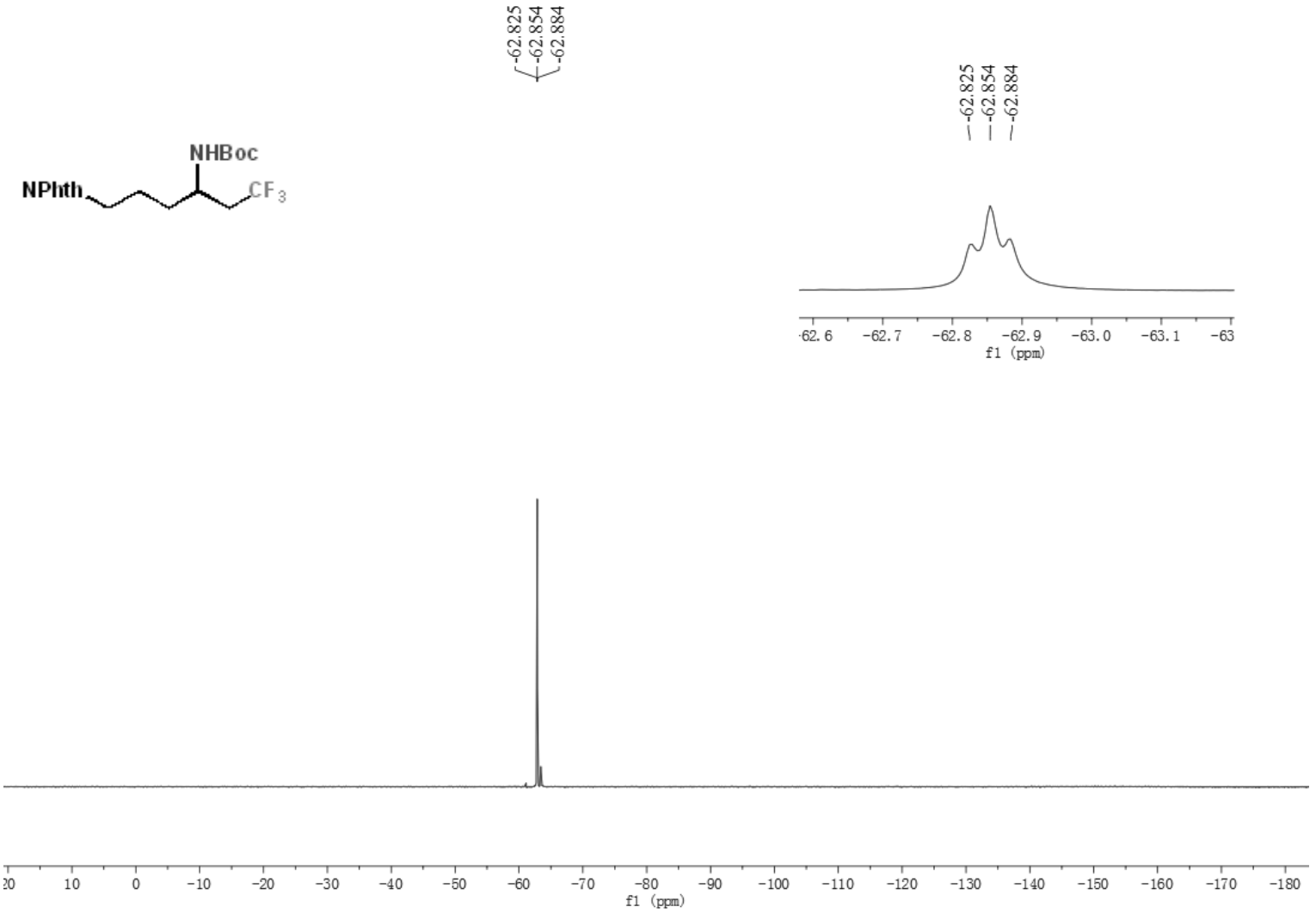
^{19}F NMR (376 MHz, $CDCl_3$) of **4r**



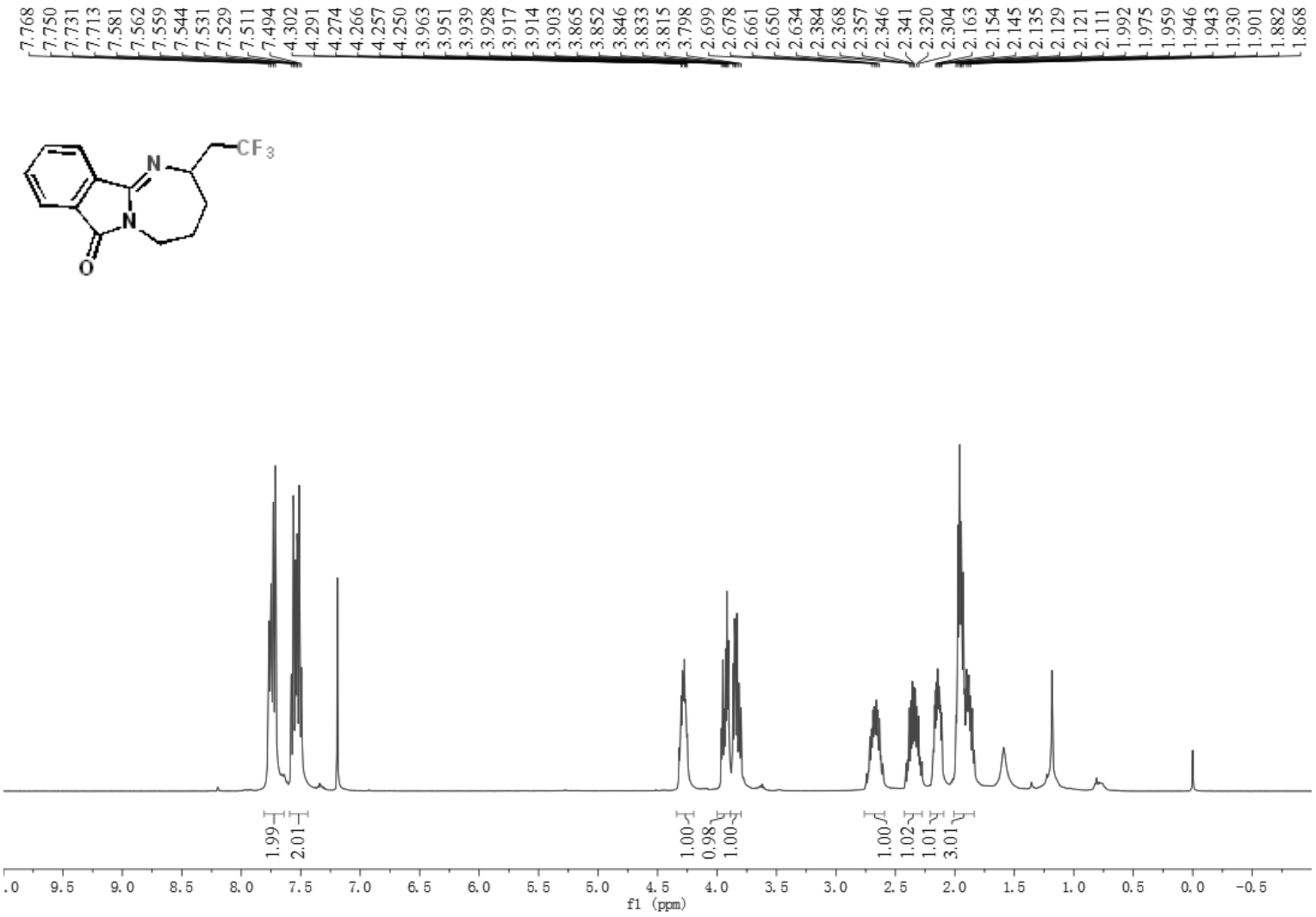
^{1}H NMR (400 MHz, $CDCl_3$) of **5**



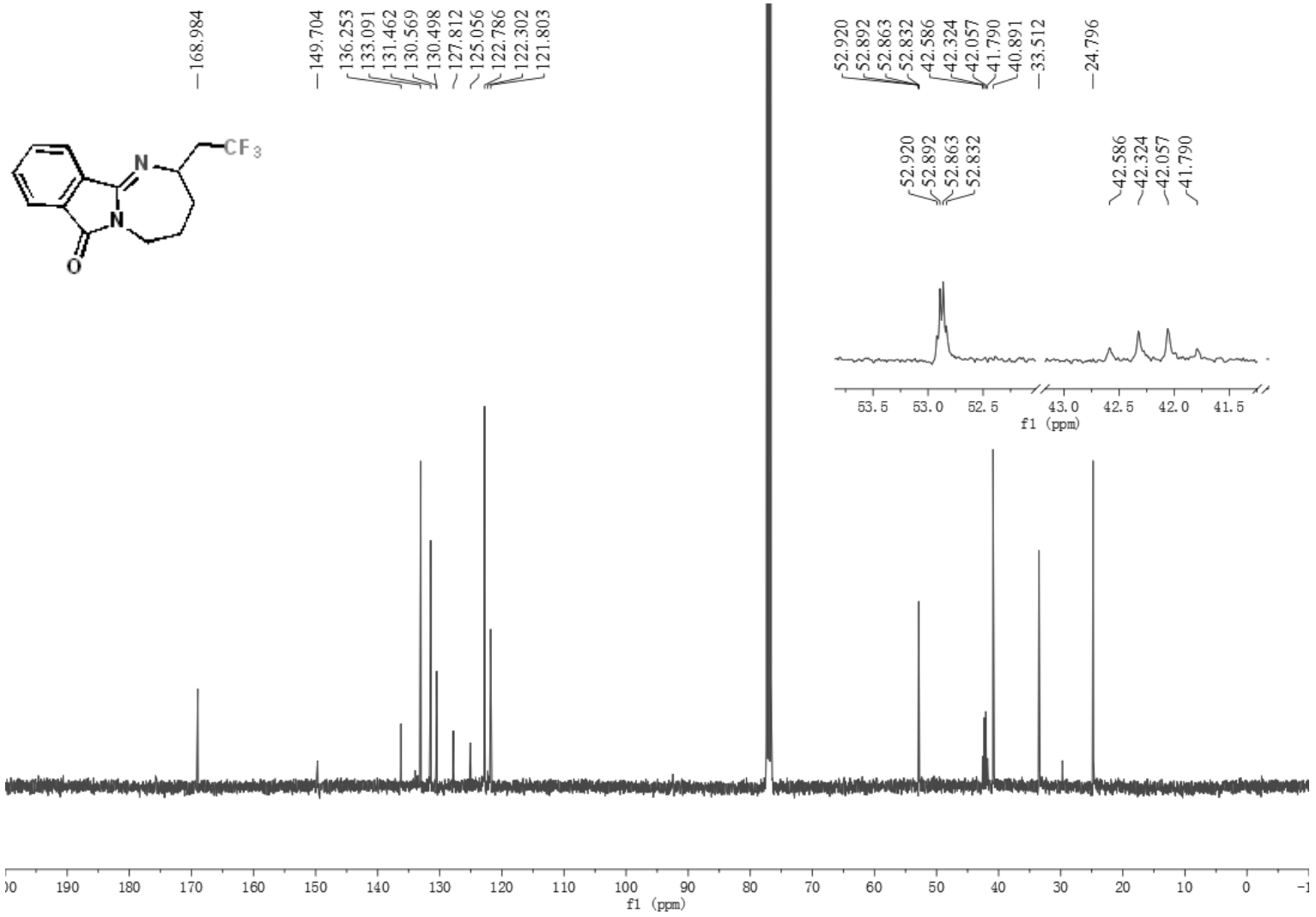
^{13}C NMR (100 MHz, $CDCl_3$) of **5**



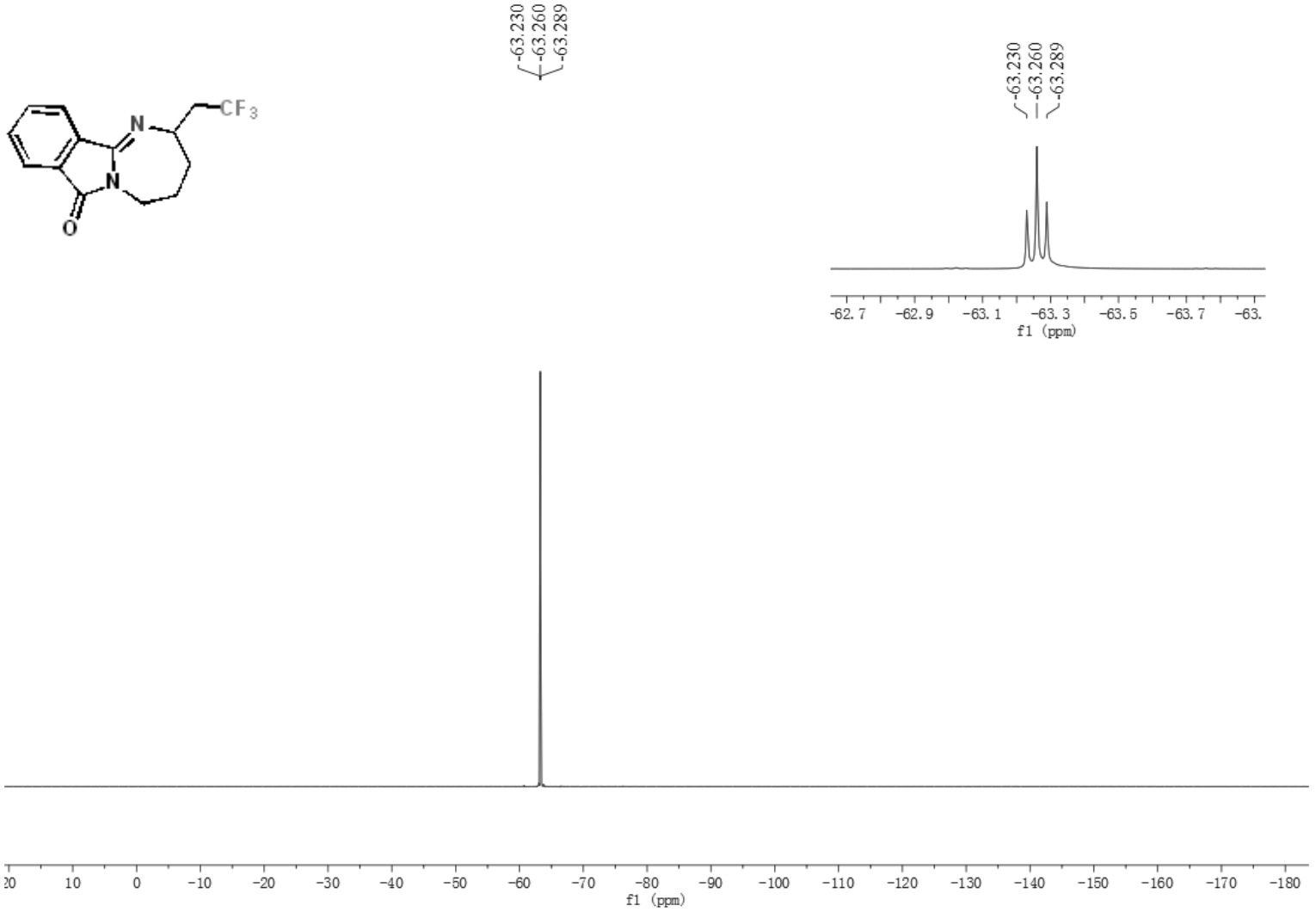
^{19}F NMR (376 MHz, $CDCl_3$) of **5**



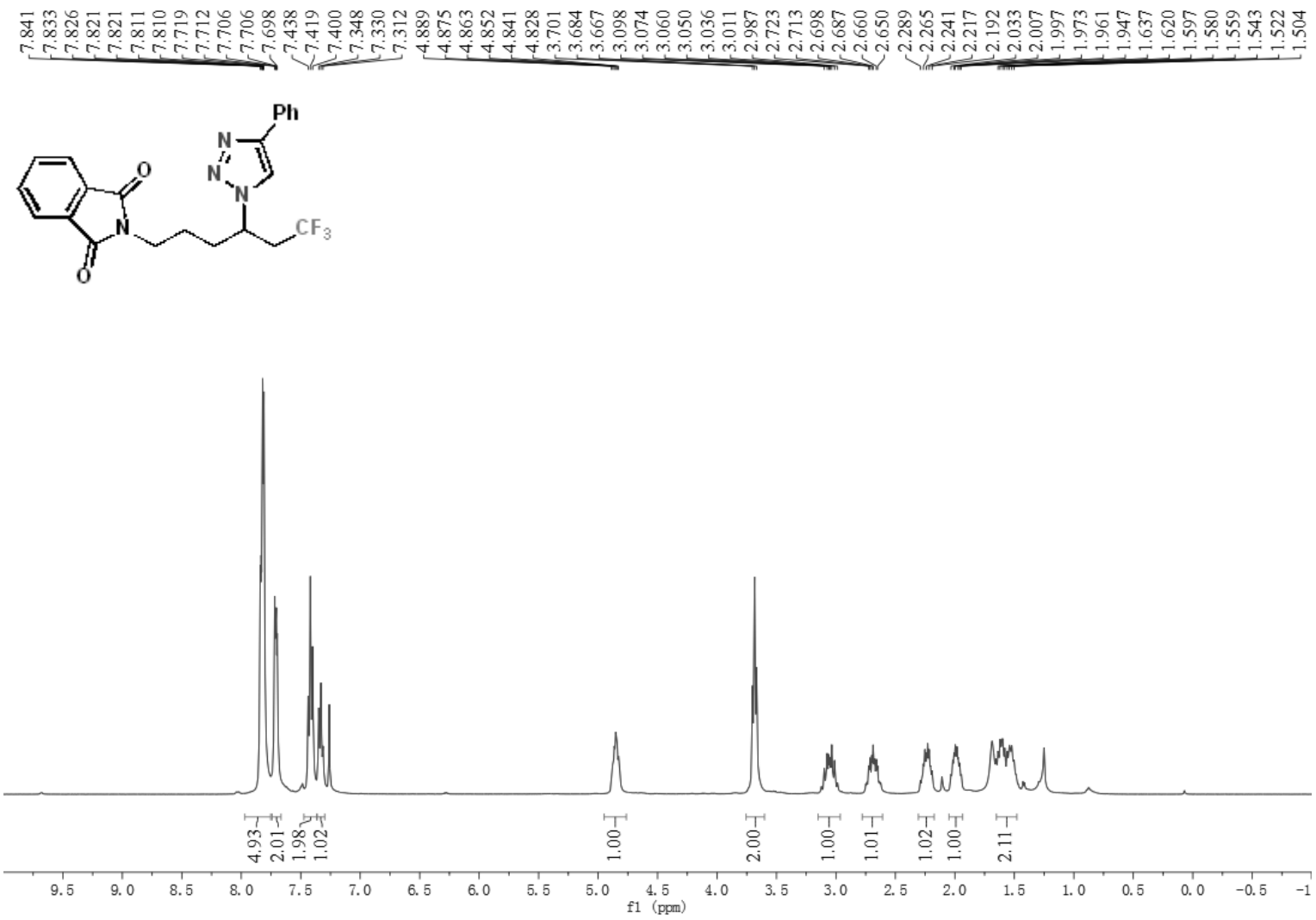
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



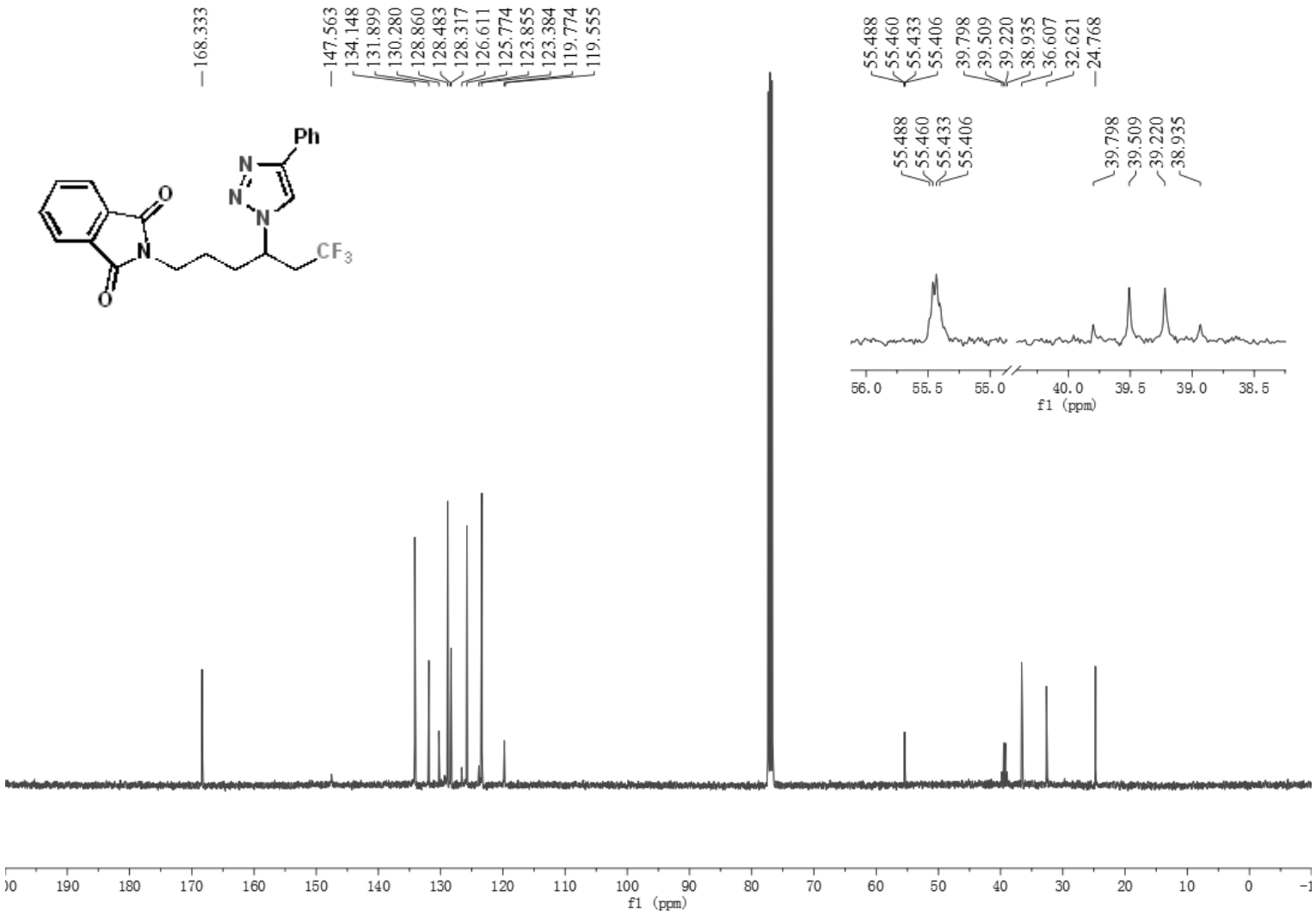
^{13}C NMR (100 MHz, $CDCl_3$) of **6**



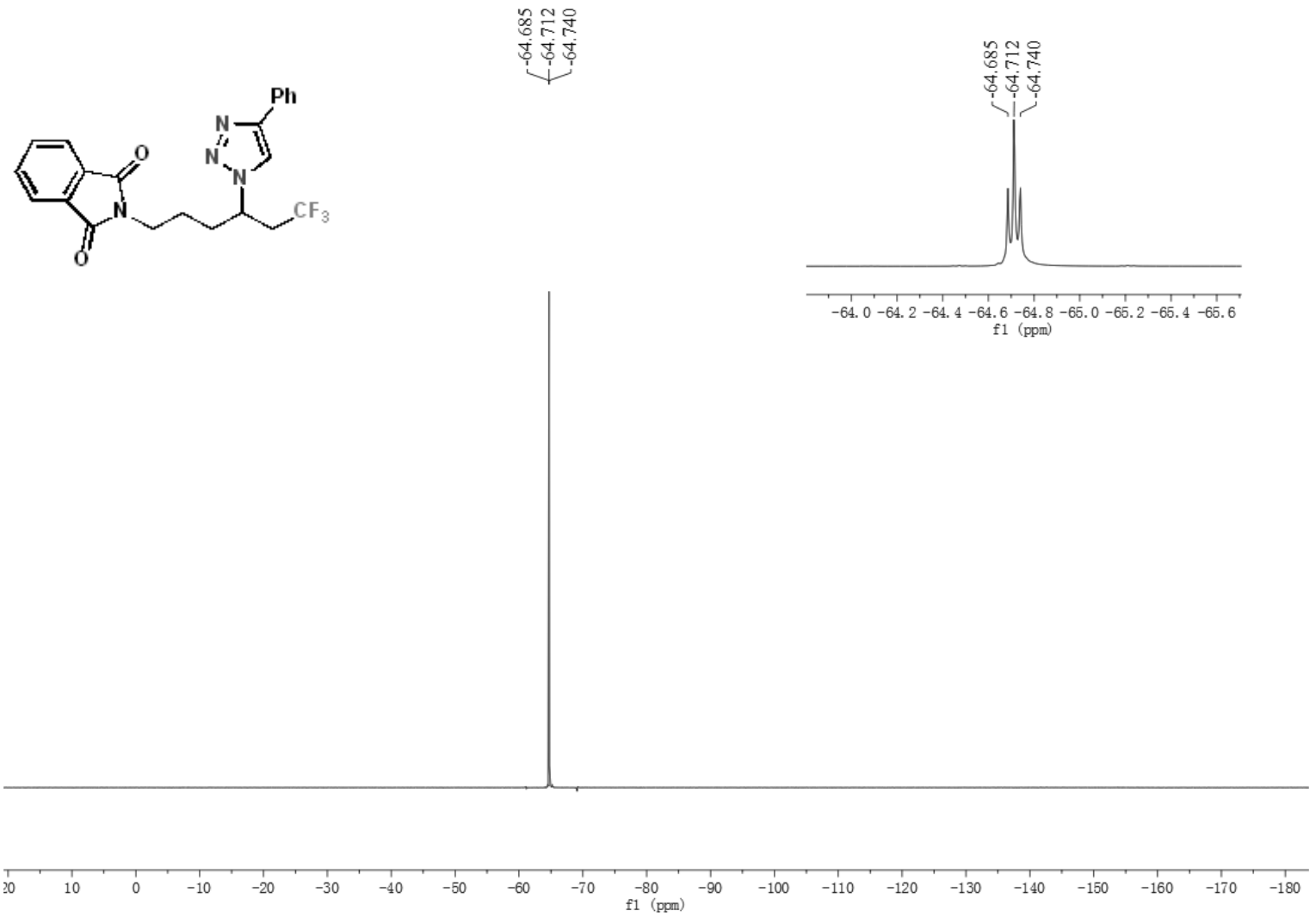
^{19}F NMR (376 MHz, $CDCl_3$) of **6**



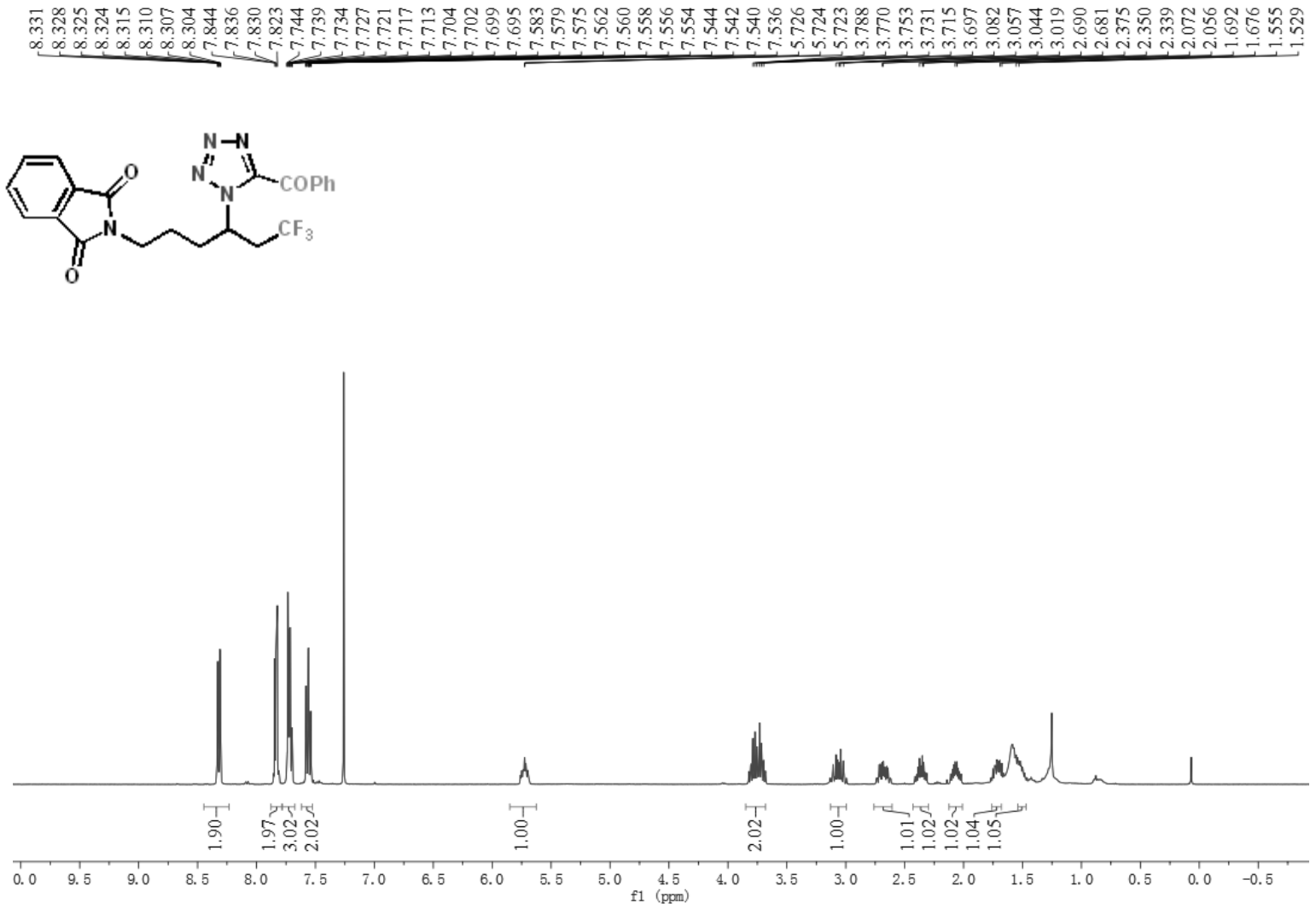
^{1}H NMR (400 MHz, $CDCl_3$) of **7**



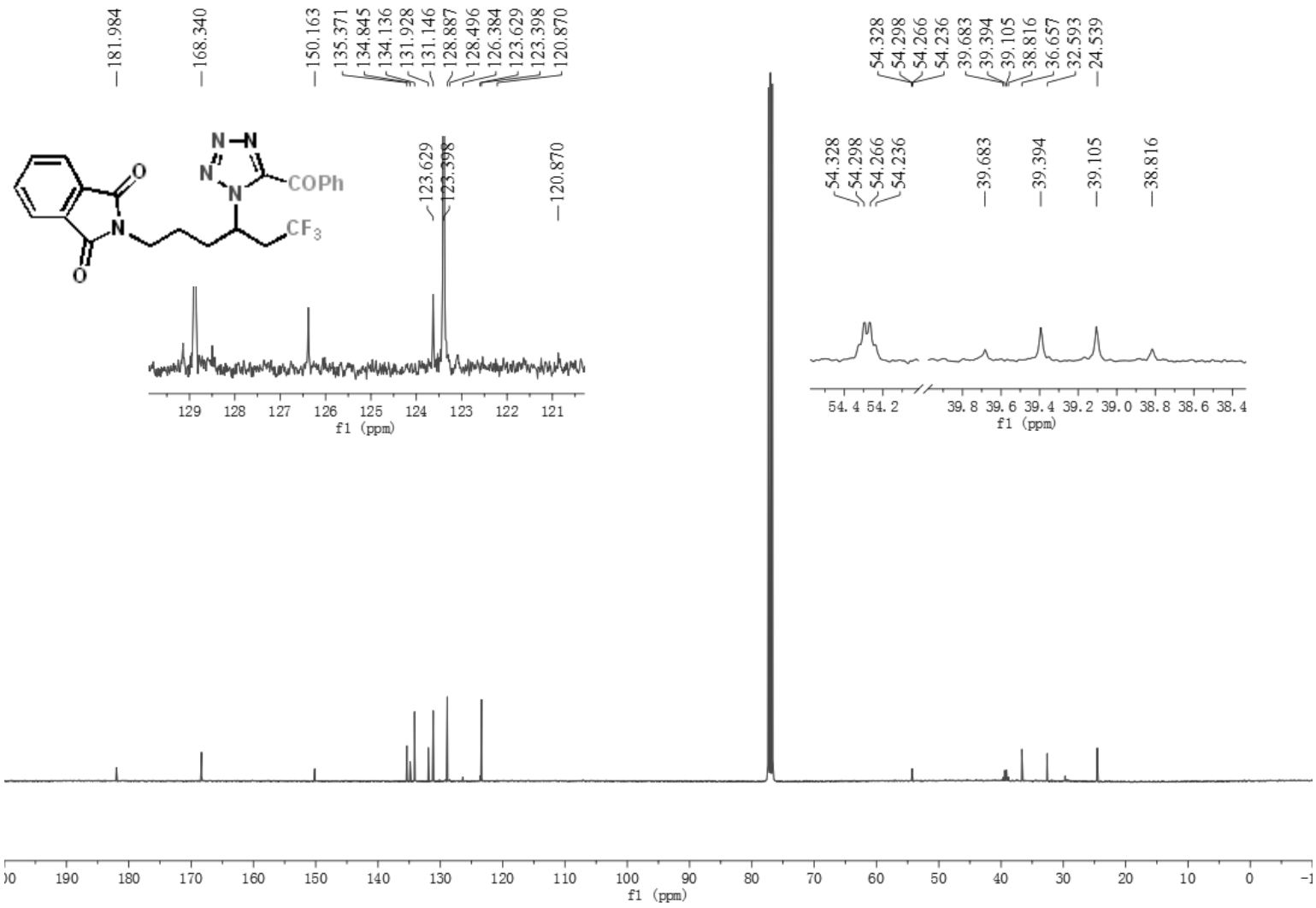
^{13}C NMR (100 MHz, $CDCl_3$) of **7**



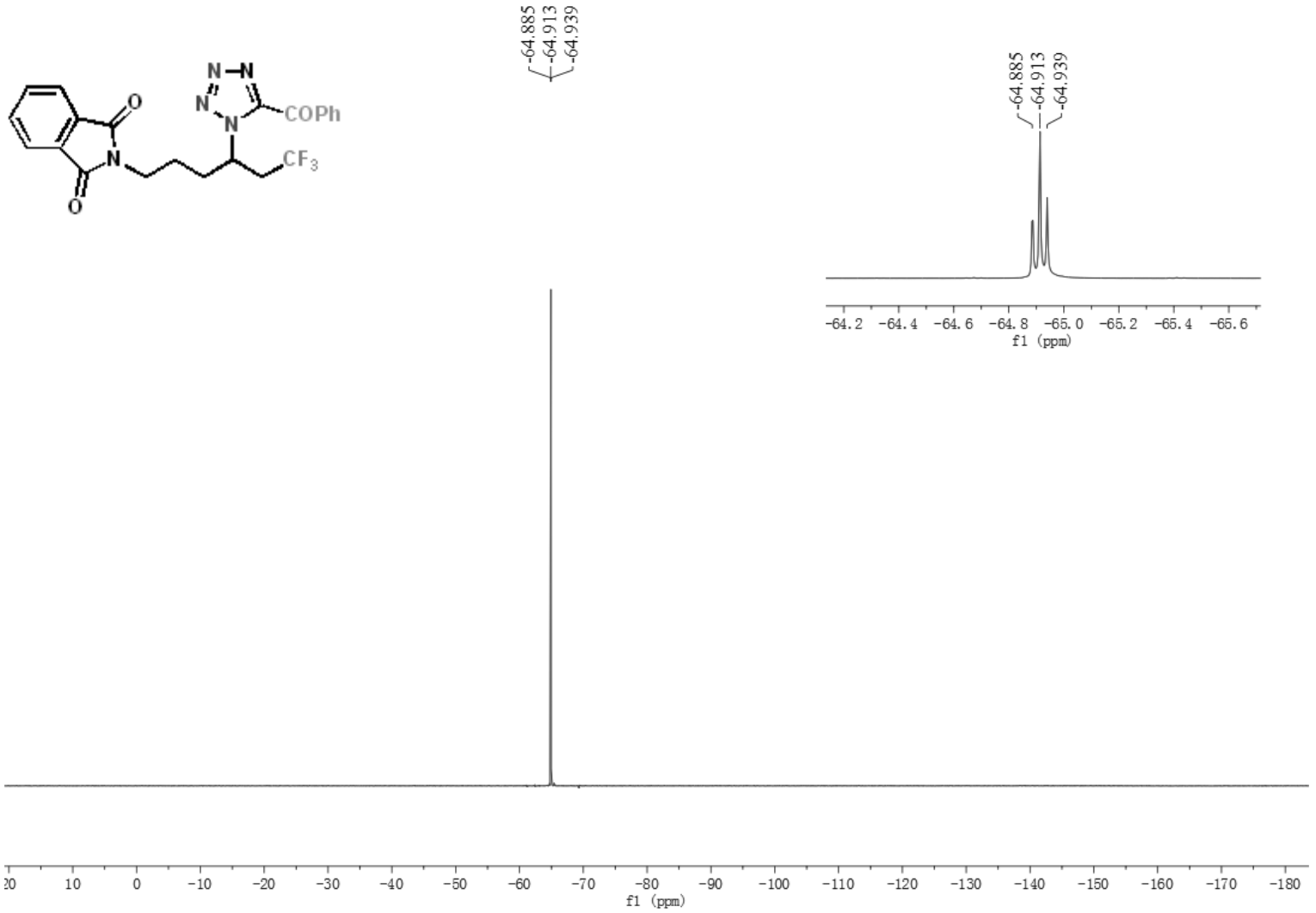
^{19}F NMR (376 MHz, $CDCl_3$) of **7**



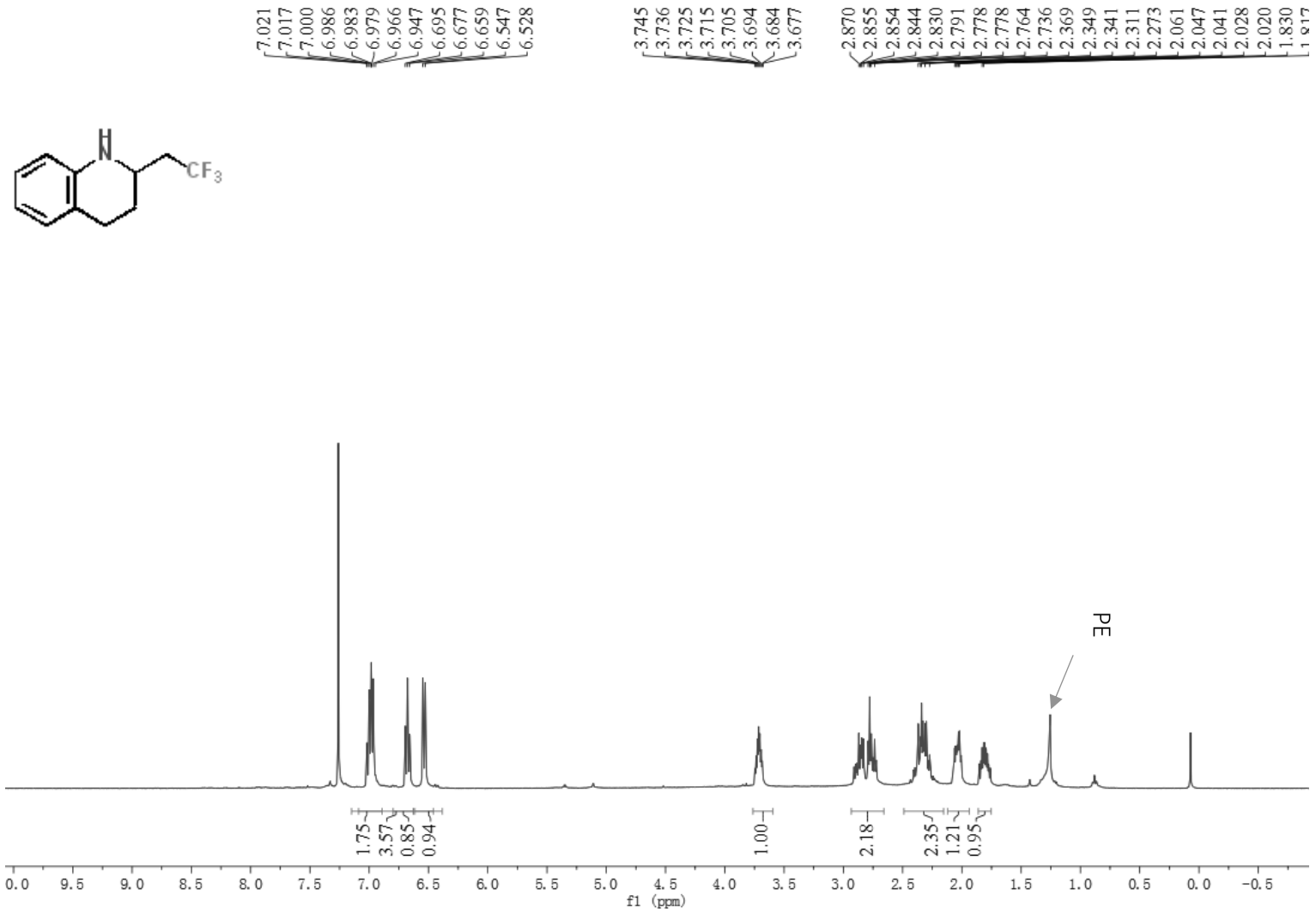
^{1}H NMR (400 MHz, $CDCl_3$) of **8**



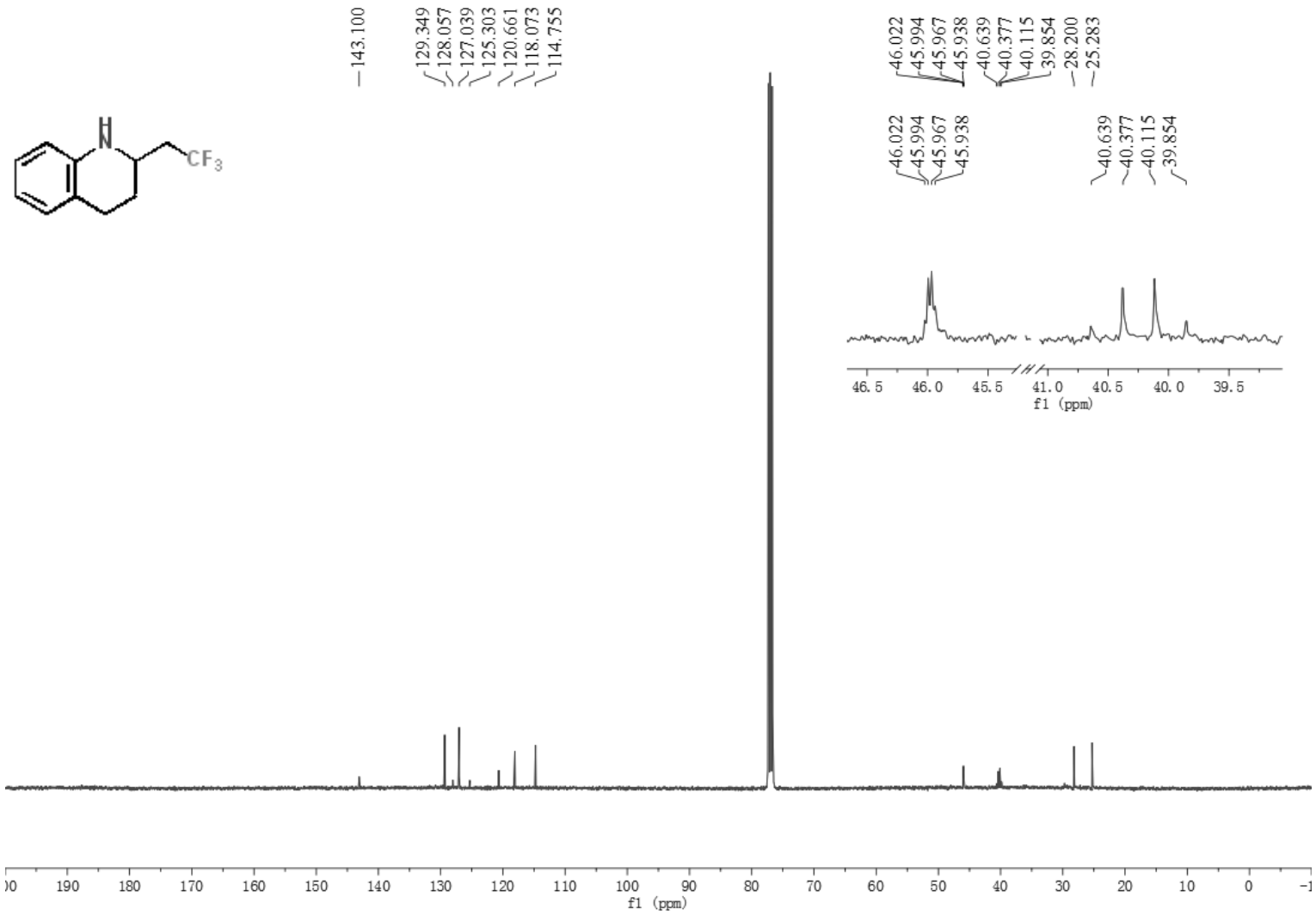
^{13}C NMR (100 MHz, $CDCl_3$) of **8**



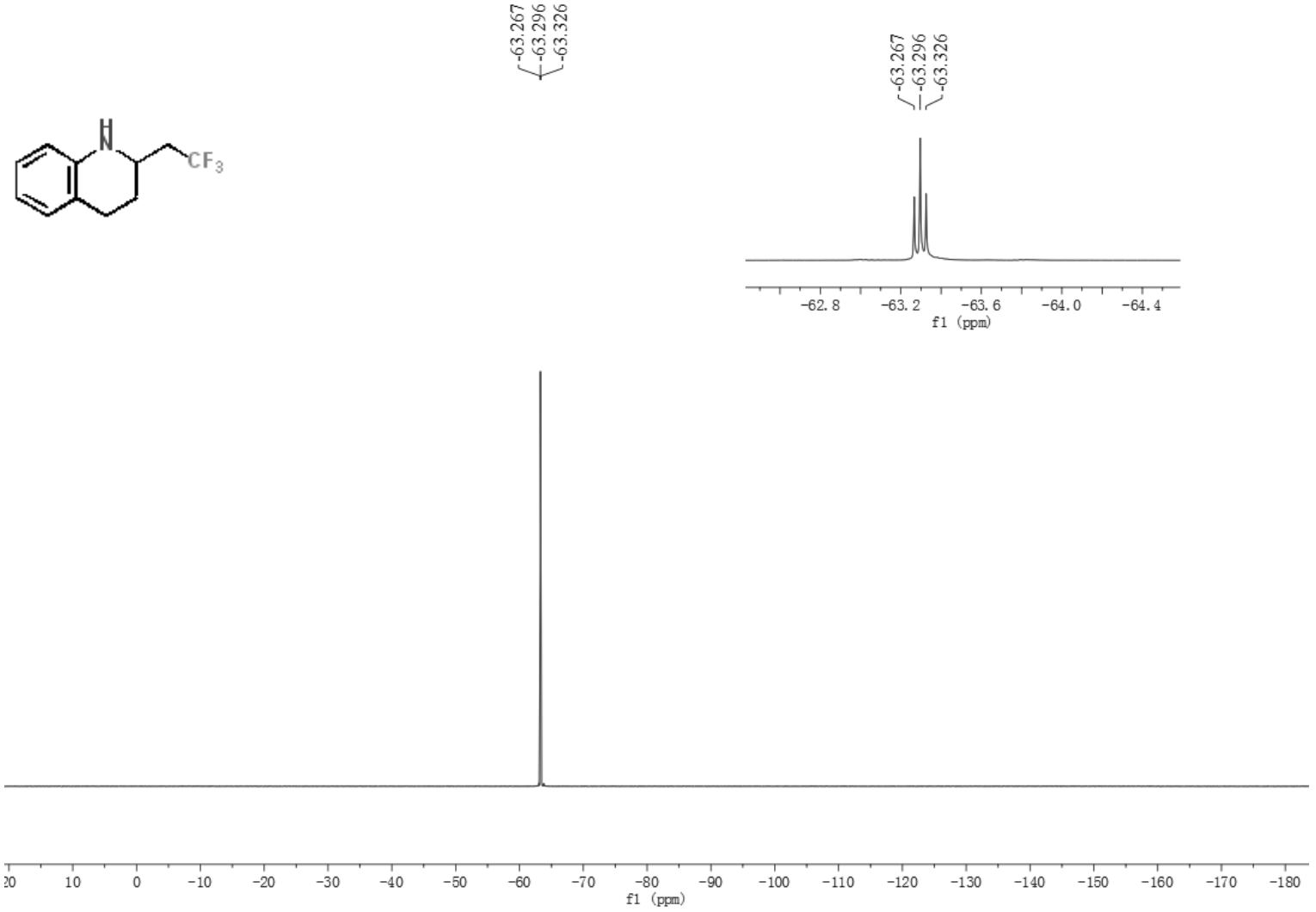
^{19}F NMR (376 MHz, $CDCl_3$) of **8**



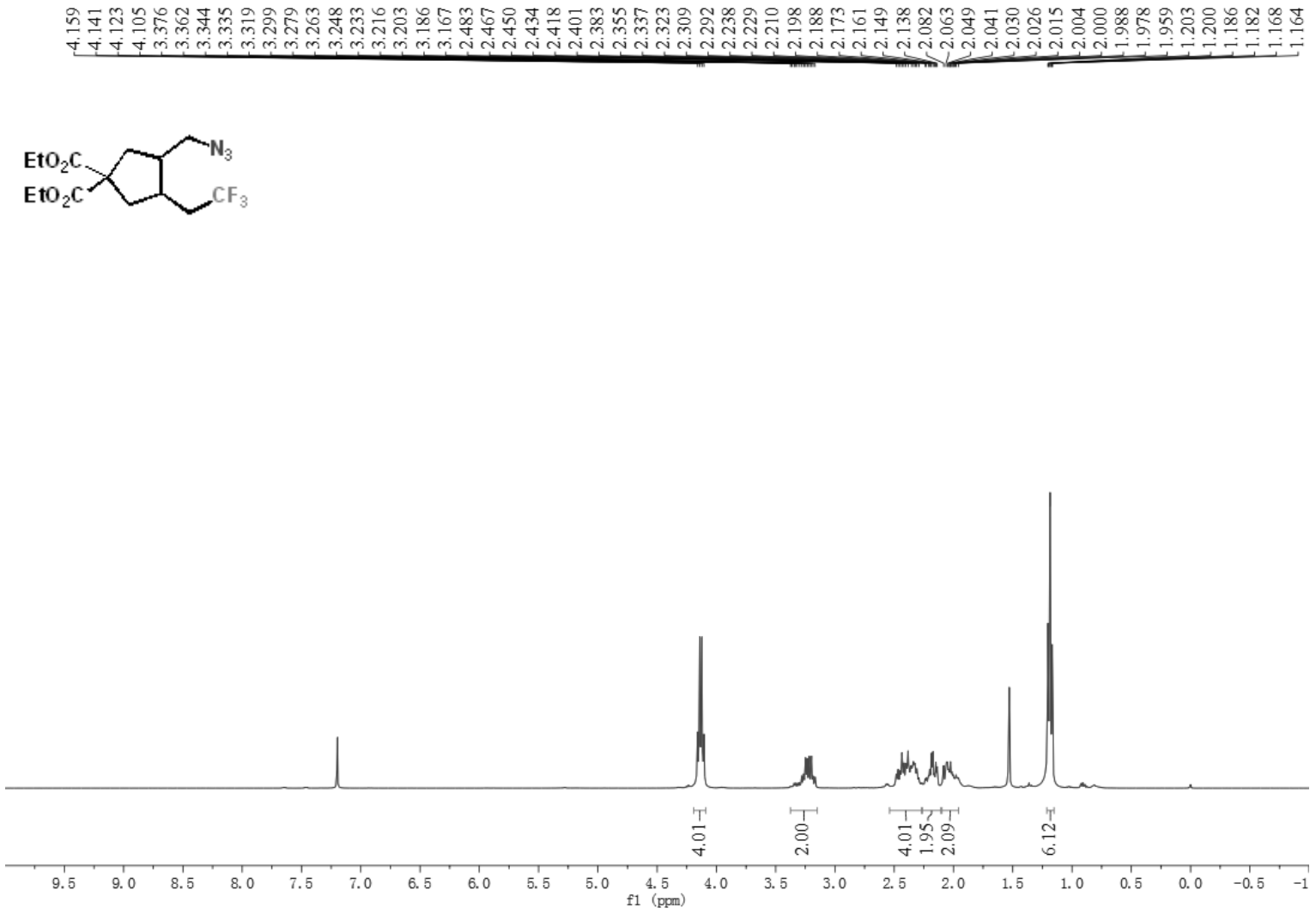
^{1}H NMR (400 MHz, $CDCl_3$) of **10**



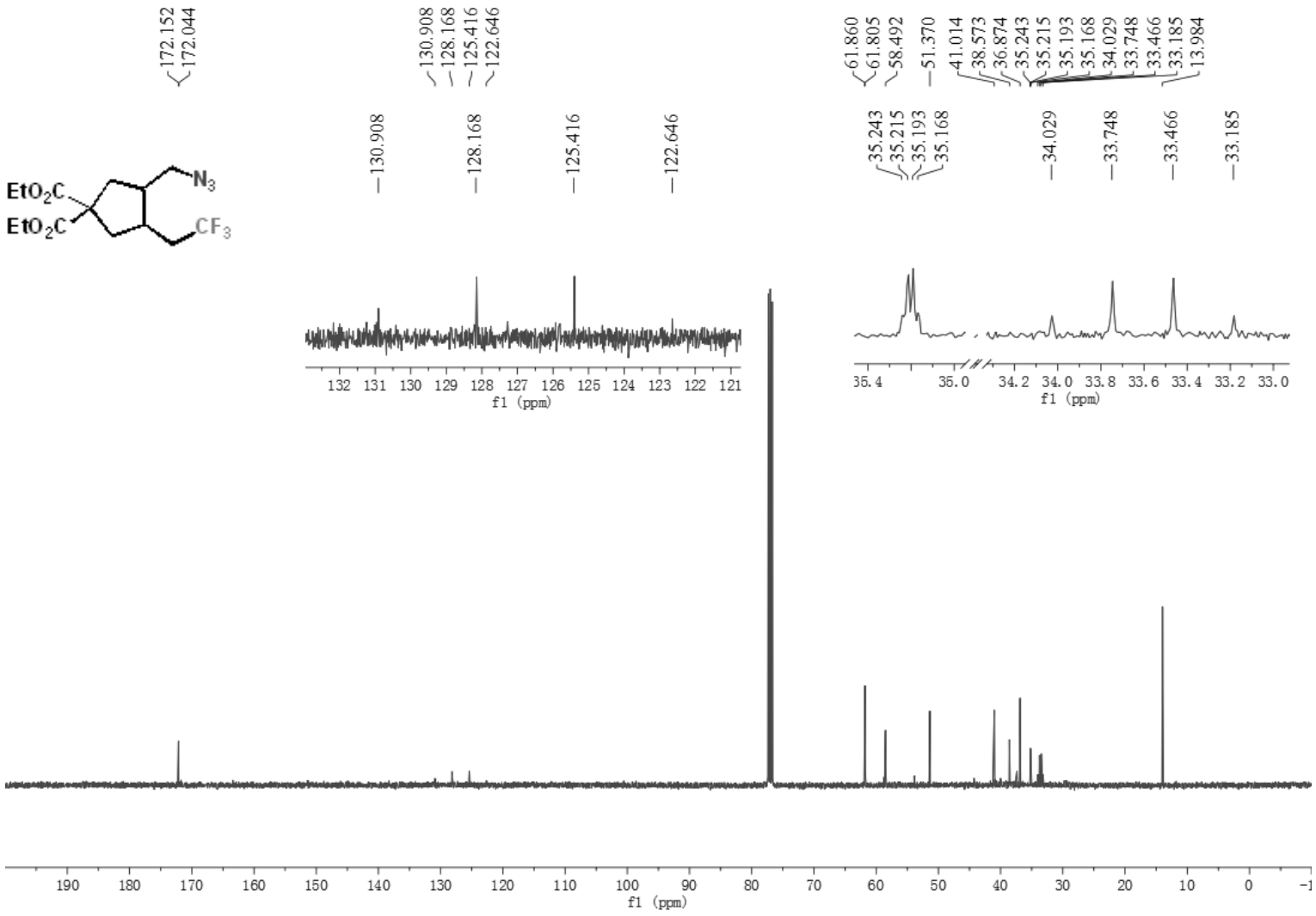
^{13}C NMR (100 MHz, $CDCl_3$) of **10**



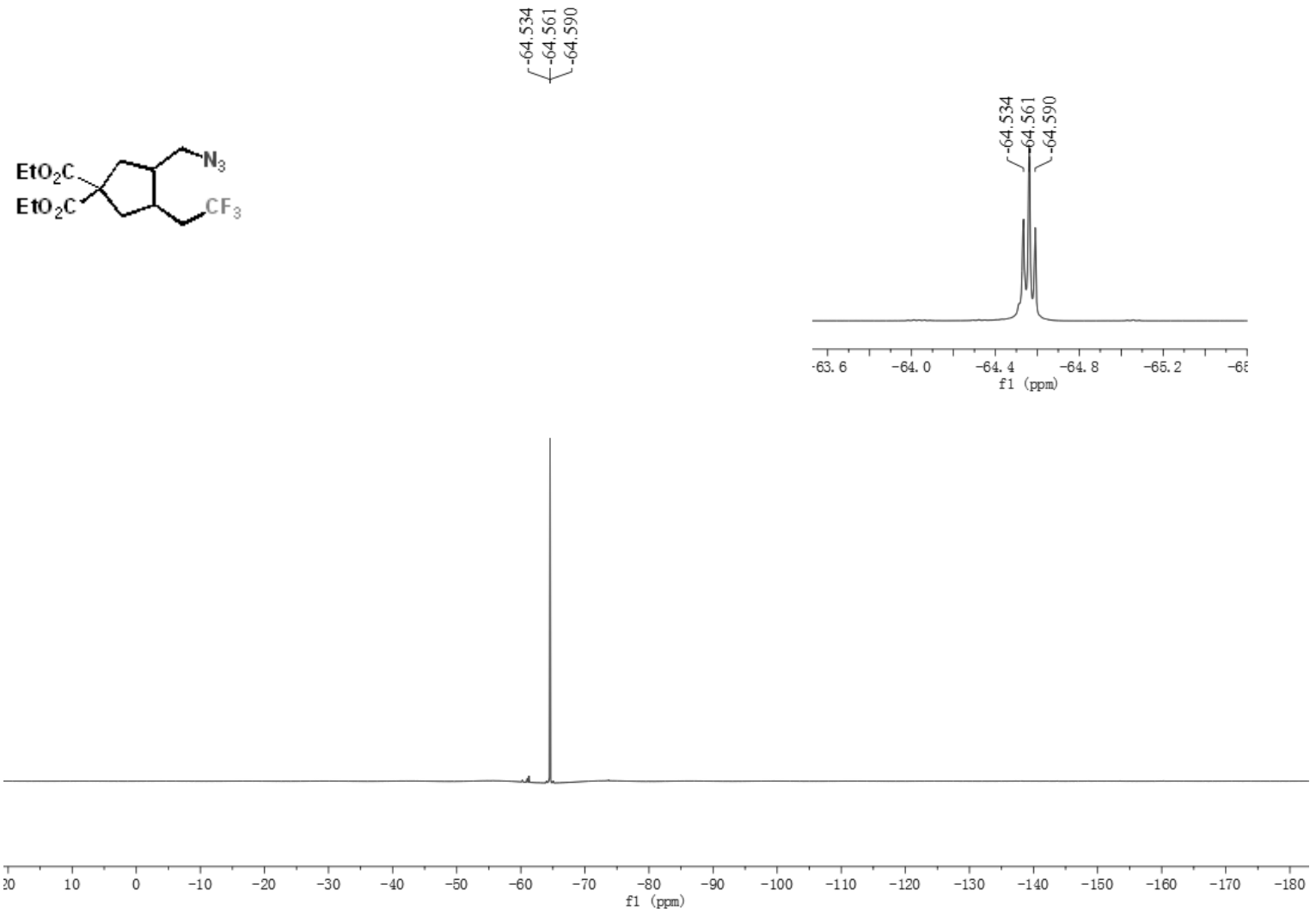
^{19}F NMR (376 MHz, $CDCl_3$) of **10**



^{1}H NMR (100 MHz, $CDCl_3$) of **12**



^{13}C NMR (100 MHz, $CDCl_3$) of **12**



^{19}F NMR (376 MHz, $CDCl_3$) of **12**