Supporting Information

Copper-Mediated Photoinduced perfluoroalkylation of Arylsulfonium Salts

Yongfang Yang [a], Lili Zhao [a], Shengsheng Luo [a], Xujuan Jiang [a], Yanli Yuan [a]*, Xiaojun Zeng[ab]*

[a] School of Chemistry and Chemical Engineering, Nanchang University, Nanchang, Jiangxi, 330031, China.

[b] Chongqing Research Institute of Nanchang University, Chongqing, 402660, China.

Email: xjzeng@ncu.edu.cn; yuanyanli@ncu.edu.cn

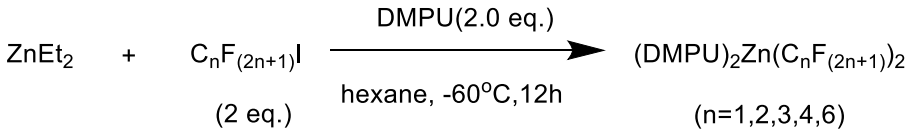
Table of contents

1.General information

Unless otherwise noted, all cross-coupling reactions were run under an N_2 atmosphere and all glassware was oven dried before use. The Photo Reaction Setup and LED lamp were purchased from Xuzhou Ai Jia electronic technology Co LED. Chemicals were purchased from Shanghai Haohong Scientific Co., Ltd, Adamas-beta, Energy Chemical, Leyan, bidepharm and were used without further purification. DCE and DMSO were purchased from Adamas-beta and dried with 4A molecular sieves. GC/MS analysis was performed on a Thermo-Fischer Scientific ISQ QD single quadrupole mass spectrometer. Thin-layer chromatography (TLC) was performed on 0.20 mm silica gel F-254 plates, with resulting chromatograms visualized by fluorescence quenching or $KMnO_4$ stain. ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded at 297K on a Bruker AVANCE AV 400 (400 MHz, 101MHz and 376 MHz) spectrometer. Data is reported in ppm using $CDCl_3$ as the solvent unless otherwise specified. Data is reported as: Chemical shifts (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiple, br = broad), coupling constants (Hz), integrated intensity.

2. General Procedure I: Preparation of $(DMPU)_2Zn(C_nF_{2n+1})_2$

Bis(perfluoroalkyl)zinc reagent $(DMPU)_2Zn(C_nF_{2n+1})_2$ **2a-2e** was synthesized acco rding to Mikami's procedure.[1]



2.1 Preparation of bis(trifluoromethyl)zinc reagent $(DMPU)_2Zn(CF_3)_2$ (2a)

To an oven-dried 100 mL two-neck round-bottom flask equipped with a magnetic stir bar were added hexane (15 mL) and DMPU (2.4 mL, 20 mmol) under an argon atmosphere. Trifluoromethyl iodide (2.8 mL, 25 mmol) was added to the solution. A diethyl zincsolution (1.0 M in hexanes, 10 mL, 10 mmol) was then added dropwise at -60 ℃. After the reaction mixture was stired at -5 ℃ for 24 h, the precipitate was obtained. After removing the solution, the precipitate obtained was washed with hexane

(50 mL) threetimes and dried under a vacuum to give $(DMPU)_2Zn(CF_3)_2$ as a white powder (3.4 g, 72% yield).

2.2 Preparation of bis(pentafluoroethyl)zinc reagent $(DMPU)_2Zn(C_2F_5)_2$ (2b)

To an oven-dried 50-mL two-neck round-bottomed flask equipped with a magnetic stir bar were added hexane (15 mL) and DMPU (2.75 mL, 22.8 mmol) under argon atmosphere. Pentafluoroethyl iodide (ca. 6.9 g, 28 mmol) was bubbled into the solution at 0 °C. Diethyl zinc solution (1.0 M in hexanes, 12 mL, 12 mmol) was then added dropwise at -60 °C. After the reaction mixture was stirred at 0 °C for 48 h, the precipitate was obtained. After removing the solution, the precipitate obtained was washed with Et_2O (20 mL) three times and dried under vacuum to give $(DMPU)_2Zn(C_2F_5)_2$ as a white powder (4.9 g, 77% yield).

2.3 Preparation of bis(heptafluoropropyl)zinc reagent $(DMPU)_2Zn(C_3F_7)_2$ (2c)

To an oven-dried 50-mL two-neck round-bottomed flask equipped with a magnetic stir bar were added hexane (8 mL) and DMPU (1.3 mL, 10 mmol) under argon atmosphere. Heptafluoropropyl iodide (ca. 3.8 g, 12.9 mmol) was added to the solution. Diethyl zinc solution (1.0 M in hexanes, 5 mL, 5 mmol) was then added dropwise at -60 °C. After the reaction mixture was stirred at -20 °C for 48 h, the precipitate was obtained. After removing the solution, the precipitate obtained was washed with hexane (15 mL) three times and dried under vacuum to give $(DMPU)_2Zn(C_3F_7)_2$ as a white powder (2.7 g, 82% yield).

2.4 Preparation of bis(nonafluorobutyl)zinc reagent $(DMPU)_2Zn(C_4F_9)_2$ (2d)

To an oven-dried 50-mL two-neck round-bottomed flask equipped with a magnetic stir bar were added hexane (8 mL) and DMPU (1.3 mL, 10 mmol) under argon atmosphere. Nonafluorobutyl iodide (ca. 4.5 g,12.9 mmol) was added to the solution. Diethyl zinc solution (1.0 M in hexanes, 5 mL, 5 mmol) was then added dropwise at -60 °C. After the reaction mixture was stirred at 0 °C for 48 h, the precipitate was obtained. After removing the solution, the precipitate obtained was washed with hexane

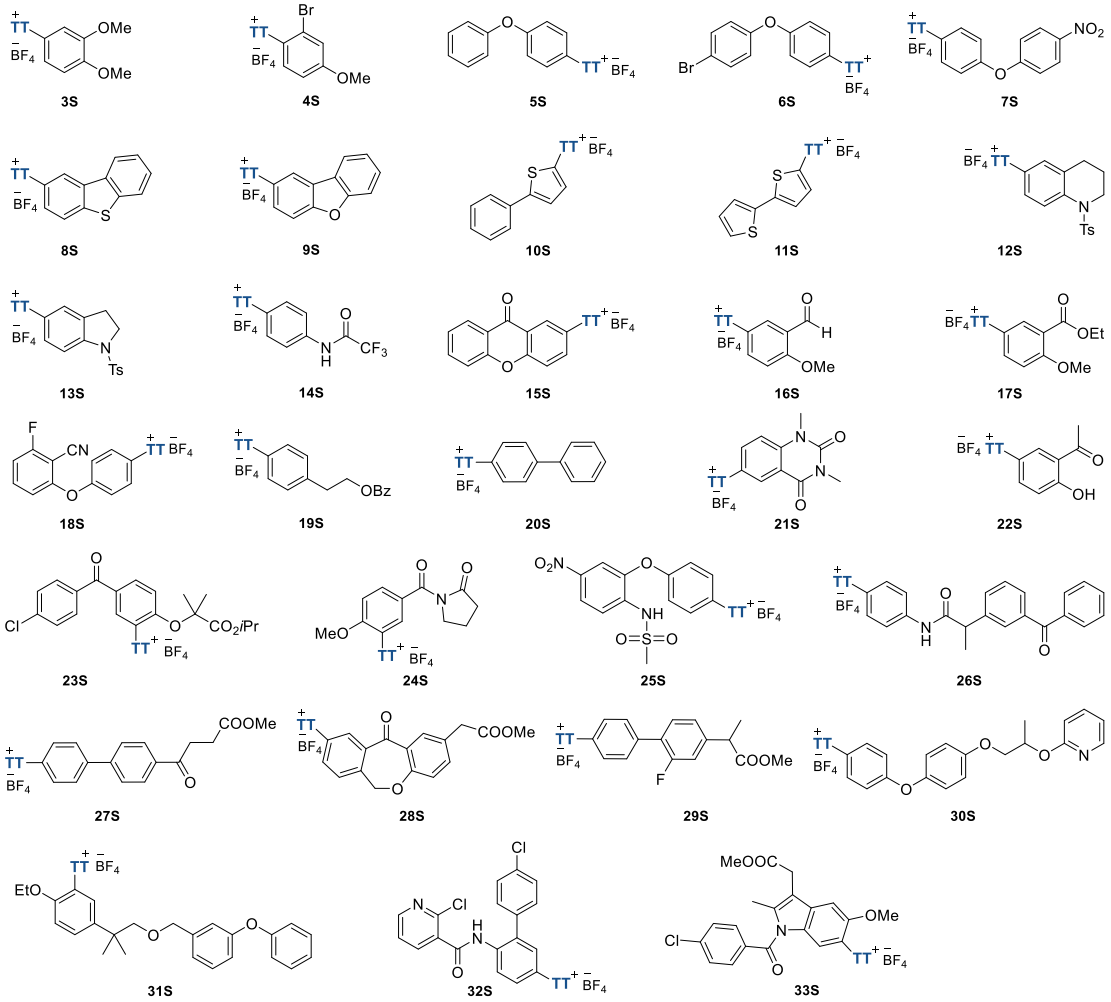
(15 mL) three times and dried under vacuum to give $(DMPU)_2Zn(C_4F_9)_2$ as a white powder (2.8 g, 74% yield).

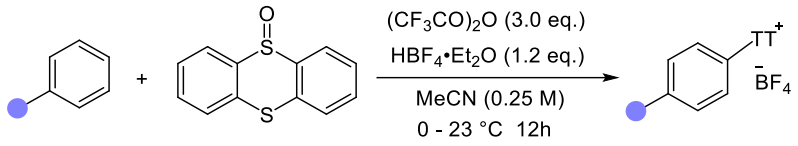
2.5 Preparation of bis(tridecafluorohexyl)zinc reagent $(DMPU)_2Zn(C_6F_{13})_2$ (2e)

To an oven-dried 50-mL two-neck round-bottomed flask equipped with a magnetic stir bar were added hexane (8 mL) and DMPU (1.3 mL, 10 mmol) under argon atmosphere. Tridecafluorohexyl iodide (ca. 5.7 g, 12.9 mmol) was added to the solution. Diethyl zinc solution (1.0 M in hexanes, 5 mL, 5 mmol) was then added dropwise at -60 °C. After the reaction mixture was stirred at 0 °C for 48 h, the precipitate was obtained. After removing the solution, the precipitate obtained was washed with hexane (15 mL) three times and dried under vacuum to give $(DMPU)_2Zn(C_6F_{13})_2$ as a white powder (3.3 g, 70% yield).

3. General Procedure II: Synthesis of Ar-$TT^+BF_4^-$

All the following thianthrenium salts were synthesized as described in the literature.The thianthrenium salts **3S,**[2] **4S,**[3] **5S,**[2] **6S,**[2] **7S,**[4] **8S,**[5] **9S,**[2] **10S,**[3] **11S,**[4] **12S,**[6] **13S,**[7] **14S,**[3] **15S,**[3] **16S,**[3] **17S,**[6] **18S,**[3] **19S,**[3] **20S,**[3] **21S,**[3] **22S,**[4] **23S,**[3] **24S,**[4] **25S,**[8] **26S,**[5] **27S,**[9] **28S,**[4] **29S,**[3] **30S,**[4] **31S,**[4] **32S,**[3] **33S**[3] are known compounds and were prepared in accordance to references. All substrates were prepared according to the reported literatures.





Under an ambient atmosphere, a 20-ml glass vial was charged with arene (5.0 mmol, 1.0 equiv.) and MeCN (5.0 mL, 1.0 M). After cooling to 0 °C, $HBF_4{\cdot}OEt_2$ (0.82 mL, 0.97 g, 6.0 mmol, 1.2 equiv.) and thianthrene 5-oxide (1.16 g, 5.0 mmol, 1.0 equiv.) was added to the vial while stirring the mixture, leading to a suspension. Subsequently, trifluoroacetic anhydride (2.1 mL, 3.1 g, 15 mmol, 3.0 equiv.) was added in one portion at 0 °C, resulting in a color change to deep purple. Subsequently, the reaction mixture was allowed to reach 23 °C and stirred for 12 h. The solution was diluted with DCM (5 mL) and poured onto a mixture of DCM (30 mL) and saturated aqueous $NaHCO_3$ solution (20 mL). After stirring for 5 min at 23 °C, the mixture was poured into a separating funnel, and the layers were separated. The DCM layer was washed with

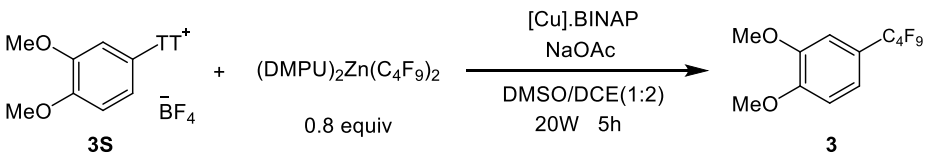
aqueous $NaBF_4$ solution (10% w/w, 4 × ca. 20 mL). The DCM layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel eluting with DCM/MeOH (30:1, v/v), then the solvent was removed in vacuo to afford the thianthrenium salt.

4. Optimization studies

General procedure: In a nitrogen-filled glovebox, to an 8 mL vial equipped with a stir bar were added sequentially stoichiometric amounts of CuCl (0.1 mmol, 1 equiv.), BINAP (0.01 mmol, 0.1 equiv.), NaOAc (0.2 mmol, 2 equiv.), and $(DMPU)_2Zn(C_nF_{2n+1})_2$ (0.08 mmol, 0.8 equiv.). Then, the solvent was added, and the mixture was stirred at room temperature for 10 minutes. Subsequently, thianthrenium salt (0.1 mmol, 1 equiv.) was added, then put it under a 20W LEDs, and stirring was continued for 5 hours. After completion of the reaction, the mixture was diluted with ethyl acetate, and the crude product was purified by flash chromatography.

The light source used for photochemical experiments was a Blue LEDs (20 W), purchased from Taobao; https://item.taobao.com/item.htm?id=623744554239&mi_id=00004FF39FXtmWCDGfIdoxpxSxtVk0SwPjtDyavcsGwJjs0&spm=tbpc.boughtlist.suborder_itemtitle.1.75332e8dNhsf4L&sku_properties=13381687%3A10122;
Manufacturer: Xuzhou Ai Jia electronic technology Co LED; Broadband source: λ = 450-455 nm;
Material of the irradiation vessel: borosilicate reaction bottle.
Distance from the light source to the irradiation vessel: 2.0 cm (Not use any filters)

Table S1 The effect of catalysts on the nonafluorobutylation of thianthrenium salts [a-b].

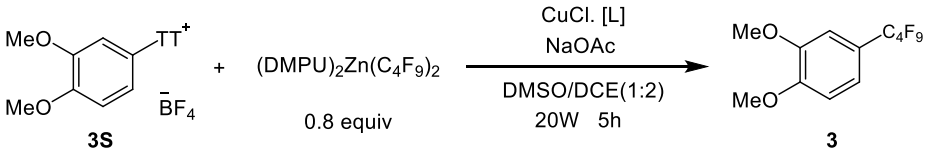


Entry	Catalyst	Yield (%)[b]
1	**CuCl**	**89**
2	CuI	78

3	CuCl (20 mol%)	32
4	$Cu(MeCN)_4BF_4$	38
5	$PdCl_2$	trace
6	$Cu(MeCN)_4PF_6$	13
7	CuOAc	40
8	CuBr	65
9	$Cu(OTf)_2$	50
10	No Cu	nd

[a] Reaction conditions: **3S** (0.1 mmol), [Cu] (0.1 mmol), BINAP (10 mol%), NaOAc (0.2 mmol), $(DMPU)_2Zn(C_4F_9)_2$ (0.08 mmol), DMSO/DCE (1:2) (1.0 mL), 20W LEDs, 5h. [b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

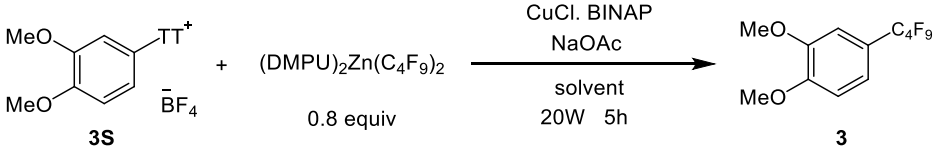
Table S2 The effect of ligands on the nonafluorobutylation of thianthrenium salts [a-b].



Entry	Ligand	Yield (%)[b]
1	**BINAP**	**89**
2	RuPhos	trace
3	No BINAP	nd
4	Dppf	nd
5	XPhos	nd

[a] Reaction conditions: **3S** (0.1 mmol), CuCl (0.1 mmol), Ligand (10 mol%), NaOAc (0.2 mmol), $(DMPU)_2Zn(C_4F_9)_2$ (0.08 mmol), DMSO/DCE (1:2) (1.0 mL), 20W LEDs, 5h. [b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

Table S3 The effect of solvent nonafluorobutylation of thianthrenium salts [a-b].

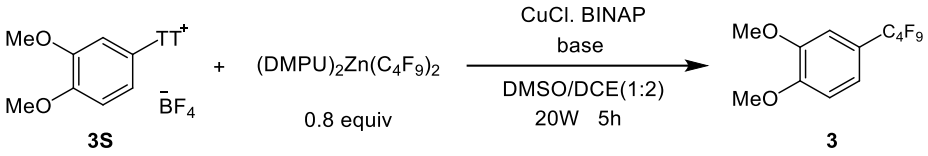


Entry	Solvent	Yield (%)[b]

1	**DMSO/DCE (v/v=1/2)**	**89**
2	DMSO	35
3	1,4-dioxane	13
4	THF	16
5	DCE	42
6	DMSO/DCE (v/v=1/1)	68
7	DMSO/DCE (v/v=2/1)	52
8	MeCN	nd

[a] Reaction conditions: **3S** (0.1 mmol), CuCl (0.1 mmol), BINAP (10 mol%), NaOAc (0.2 mmol), $(DMPU)_2Zn(C_4F_9)_2$ (0.08 mmol), solvent (1.0 mL), 20W LEDs, 5h. [b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

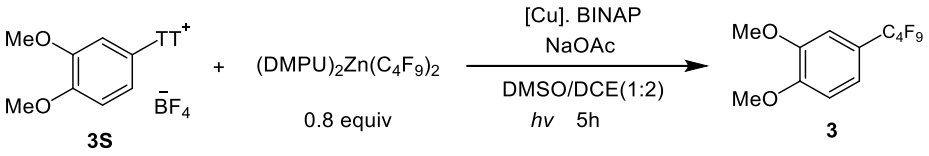
Table S4 The effect of base nonafluorobutylation of thianthrenium salts [a-b].



Entry	Base	Yield (%)[b]
1	**NaOAc**	**89**
2	t-BuOK	trace
3	Cs_2CO_3	6
4	K_3PO_4	9
5	KOAc	14
6	LiOMe	trace
7	Na_2CO_3	trace
8	K_2CO_3	trace

[a] Reaction conditions: **3S** (0.1 mmol), CuCl (0.1 mmol), BINAP (10 mol%), base (0.2 mmol), $(DMPU)_2Zn(C_4F_9)_2$ (0.08 mmol), DMSO/DCE (1.0 mL), 20W LEDs, 5h. [b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

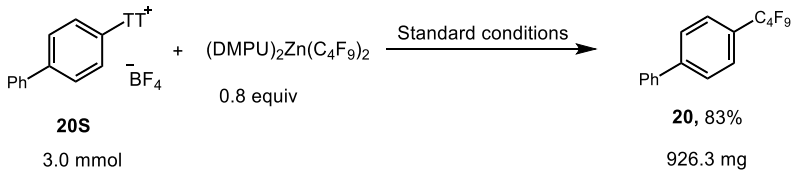
Table S5 The effect of LEDs nonafluorobutylation of thianthrenium salts [a-b].



Entry	LEDs	Yield (%)[b]
1	**20W**	**89**
2	\	nd
3	5W	48
4	40W	56

[a] Reaction conditions: **3S** (0.1 mmol), CuCl (0.1 mmol), BINAP (10 mol%), NaOAc (0.2 mmol), $(DMPU)_2Zn(C_4F_9)_2$ (0.08 mmol), DMSO/DCE (1.0 mL), 20W LEDs, 5h. [b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

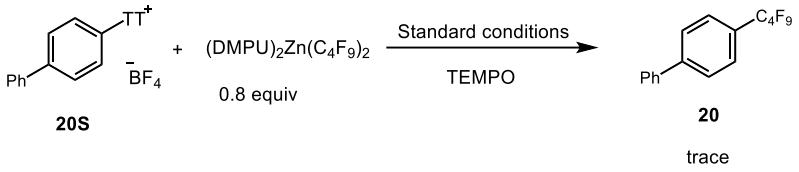
5. Gram-scale reaction



In a nitrogen-filled glovebox, to a 100 mL vial equipped with a stir bar were added sequentially stoichiometric amounts of CuCl (3 mmol, 1 equiv.), BINAP (0.3 mmol, 0.1 equiv.), NaOAc (6 mmol, 2 equiv.), and $(DMPU)_2Zn(C_4F_9)_2$ (2.4 mmol, 0.8 equiv.). Then, DMSO/DCE was added, and the mixture was stirred at room temperature for 10 minutes. Subsequently, **20S** (1.3 g, 3mmol, 1 equiv.) was added, then put it under a 20W LEDs, and stirring was continued for 5 hours. After completion of the reaction, the mixture was diluted with ethyl acetate, and the crude product was purified by flash chromatography. And **20** was detected 926.3 mg (83% yield).

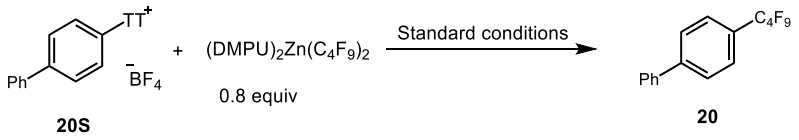
6. Control experiments

6.1 Radical inhibition experiments

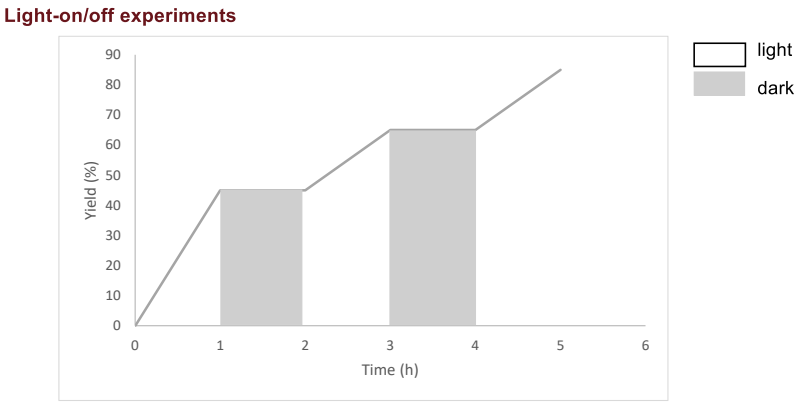


In a nitrogen-filled glovebox, to an 8 mL vial equipped with a stir bar were added sequentially stoichiometric amounts of CuCl (0.1 mmol, 1 equiv.), BINAP (0.01 mmol, 0.1 equiv.), NaOAc (0.2 mmol, 2 equiv.), and $(DMPU)_2Zn(C_4F_9)_2$ (0.08 mmol, 0.8 equiv.). Then, DMSO/DCE was added, and the mixture was stirred at room temperature for 10 minutes. Subsequently, **20S** (45.7 mg, 0.1 mmol, 1 equiv.) was added, then put it under a 20W LEDs, and stirring was continued for 5 hours. And **20** was detected trace when add TEMPO (1 equiv.) as additive (Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard).

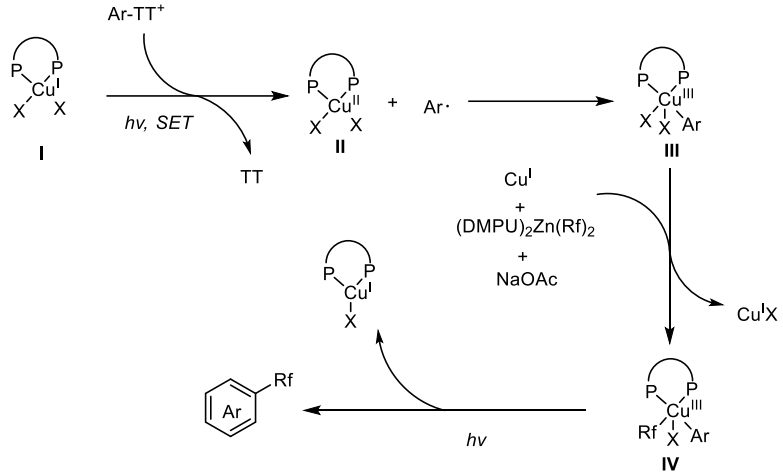
6.2 Light on/off experiment



In a nitrogen-filled glovebox, to an 8 mL vial equipped with a stir bar were added sequentially stoichiometric amounts of CuCl (0.1 mmol, 1 equiv.), BINAP (0.01 mmol, 0.1 equiv.), NaOAc (0.2 mmol, 2 equiv.), and $(DMPU)_2Zn(C_4F_9)_2$ (0.08 mmol, 0.8 equiv.). Then, DMSO/DCE was added, and the mixture was stirred at room temperature for 10 minutes. Subsequently, **20S** (45.7 mg, 0.1 mmol, 1 equiv.) was added, then put it under a 20W LEDs, and stirring was continued for 5 h. The light was switched on for 1 h and then off for 1 h, which was repeated until 5 h. The reaction mixture was monitored after each period by ^{19}F NMR yield with $PhCF_3$ as the internal standard substance.

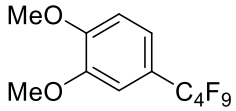


6.3 Rationalization of the mechanism



Photoexcitation of the (BINAP)Cu(I) complex[10] (with NaOAc assistance) enables single-electron transfer to the aryl thianthrenium salt, producing an aryl radical (Ar•) and Cu(II) (II). The aryl radical is quickly trapped at copper to give Cu(III)–Ar (III). Simultaneously, transmetalation from the perfluoroalkyl zinc reagent forms Cu–Rf (IV), which then transfers Rf to intermediate II, yielding Cu(III)(Ar)(Rf) (IV). Photo-promoted reductive elimination from IV furnishes the Ar–Rf product and regenerates Cu(I), completing the cycle.

7. Characterization of Products



3

1,2-dimethoxy-4-(perfluorobutyl)benzene (3), Colorless liquid, 31.7 mg, 89% yield,

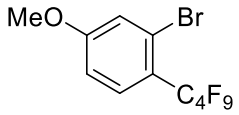
$\mathbf{R_f}$ =0.3 (petroleum ether: ethyl acetate, 10:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.4 Hz, 1H), 7.02 (s, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 3.92 (d, *J* = 5.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 149.1, 121.0 (t, *J* = 24.8 Hz), 120.3 (t, *J* = 7.1 Hz), 110.8, 109.5 (t, *J* = 6.6 Hz), 56.1 (d, *J* = 6.3 Hz), ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.07 (t, *J* = 10.0 Hz, 3F), -109.92 (t, *J* = 13.3 Hz, 2F), -122.79 (q, *J* = 10.0 Hz, 2F), -125.58 – -126.11 (m, 2F).

HRMS (EI) calcd for $C_{12}H_9F_9O_2$ $(M)^+$: 356.0459, found: 356.0450.



4

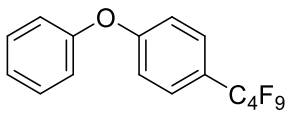
2-bromo-4-methoxy-1-(perfluorobutyl)benzene (4), Colorless liquid, 31.5 mg, 78% yield, $\mathbf{R_f}$ =0.3 (petroleum ether: ethyl acetate, 10:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.9 Hz, 1H), 7.24 (d, *J* = 2.6 Hz, 1H), 6.94 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 131.4 (t, *J* = 8.8 Hz), 121.8 (t, *J* = 3.2 Hz), 121.0, 120.0 (t, *J* = 24.9 Hz), 113.1, 55.8, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.90 (t, *J* = 9.4 Hz, 3F), -105.84 (t, *J* = 14.5 Hz, 2F), -120.72 (q, *J* = 7.6, 5.6 Hz, 2F), -125.78 – -125.89 (m, 2F).

HRMS (EI) calcd for $C_{11}H_6BrF_9O$ $(M)^+$: 403.9458, found: 403.9455.



5

1-(perfluorobutyl)-4-phenoxybenzene (5), Colorless liquid, 33.0 mg, 85% yield, $\mathbf{R_f}$ =0.2 (petroleum ether).

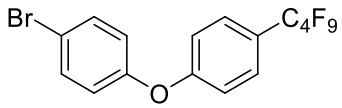
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.6 Hz, 2H), 7.42 (dd, *J* = 8.5, 7.4 Hz, 2H), 7.23 (s, 1H), 7.09 (dd, *J* = 8.4, 6.7 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2 (d, *J* = 2.1 Hz), 155.7, 130.3, 128.9 (t, *J* = 6.5

Hz), 124.8, 120.3, 117.8, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.13 (t, *J* = 10.0 Hz, 3F), -110.22 (t, *J* = 13.6 Hz, 2F), -122.84 (q, *J* = 9.9 Hz, 2F), -125.07 – -126.38 (m, 2F).

HRMS (EI) calcd for $C_{16}H_9F_9O$ $(M)^+$: 388.0510, found: 388.0502.



6

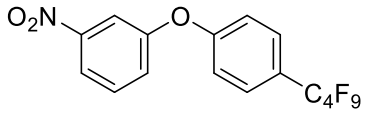
1-bromo-4-(4-(perfluorobutyl)phenoxy)benzene (6), Colorless liquid, 38.2 mg, 82% yield, $\mathbf{R_f}$ =0.3 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.9 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 2.2 Hz, 1H), 6.95 (d, *J* = 2.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 154.9, 133.3, 129.0 (t, *J* = 6.5 Hz), 123.5 (t, *J* = 24.7 Hz), 121.9, 118.0, 117.5, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.04 (t, *J* = 9.4 Hz, 3F), -110.26 (t, *J* = 14.0 Hz, 2F), -122.78 (q, *J* = 10.1 Hz, 2F), -125.45 – -125.75 (m, 2F).

HRMS (EI) calcd for $C_{16}H_8BrF_9O$ $(M)^+$: 465.9615, found: 465.9609.



7

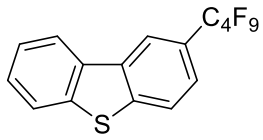
1-nitro-3-(4-(perfluorobutyl)phenoxy)benzene (7), Yellow liquid, 36.4 mg, 84% yield, $\mathbf{R_f}$ =0.2 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.16 (m, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.24 – 7.16 (m, 2H), 7.15 – 7.06 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 158.3, 143.6, 129.3 (t, *J* = 6.5 Hz), 126.1, 125.3 (t, *J* = 24.7 Hz), 119.9, 118.4, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.02 (t, *J* = 9.7 Hz, 3F), -110.43 (t, *J* = 13.7 Hz, 2F), -122.69 (q, *J* = 10.3 Hz, 2F), -125.43 – -125.76 (m, 2F).

HRMS (EI) calcd for $C_{16}H_8F_9NO_3$ $(M)^+$: 433.0360, found: 433.0352.



8

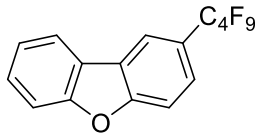
2-(perfluorobutyl)dibenzo[b,d]thiophene (8), Yellow liquid, 36.6 mg, 91% yield, $\mathbf{R}_f$ =0.3 (petroleum ether).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.36 (s, 1H), 8.27 – 8.16 (m, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.94 – 7.84 (m, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.50 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 143.5, 139.9, 135.7, 134.8, 127.8, 125.2, 125.1, 124.5 (t, *J* = 6.5 Hz), 123.2, 123.1, 122.1, 120.4 (t, *J* = 7.0 Hz), ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, CDCl$_3$) δ -80.95 (t, *J* = 9.6 Hz, 3F), -109.77 (t, *J* = 13.4 Hz, 2F), -122.42 (q, *J* = 10.3, 9.8 Hz, 2F), -125.43 – -125.54 (m, 2F).

HRMS (EI) calcd for $C_{16}H_7F_9S$ $(M)^+$: 402.0125, found: 402.0118.



9

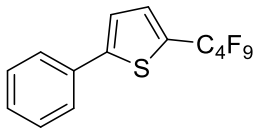
2-(perfluorobutyl)dibenzo[b,d]furan (9), Yellow liquid, 34.7 mg, 90% yield, $\mathbf{R}_f$ =0.3 (petroleum ether).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.19 (s, 1H), 7.99 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.67 (s, 2H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.56 – 7.49 (m, 1H), 7.44 – 7.36 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 158.0, 157.0, 128.4, 125.8 (t, *J* = 6.6 Hz), 124.9, 123.6, 123.5 (t, *J* = 4.0 Hz), 123.4, 121.1, 120.1 (t, *J* = 7.0 Hz), 112.1, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, CDCl$_3$) δ -81.01 (t, *J* = 9.4 Hz, 3F), -109.12 (t, *J* = 13.4 Hz, 2F), -122.44 (q, *J* = 10.2 Hz, 2F), -125.40 – -125.81 (m, 2F).

HRMS (EI) calcd for $C_{16}H_7F_9O$ $(M)^+$: 386.0353, found: 386.0344.



10

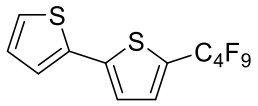
2-(perfluorobutyl)-5-phenylthiophene (10), Colorless liquid, 33.6 mg, 89% yield, $\mathbf{R}_f$ =0.3 (petroleum ether).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.45 – 7.36 (m, 4H), 7.30 (d, *J* = 4.1 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 149.9, 133.0, 131.3 (t, *J* = 6.2 Hz), 129.3, 129.0, 128.0, 126.4, 123.2, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, CDCl$_3$) δ -80.99 (t, *J* = 9.7 Hz, 3F), -101.53 (t, *J* = 13.4 Hz, 2F), -122.46 (q, *J* = 9.4 Hz, 2F), -125.51 – -125.65 (m, 2F).

HRMS (EI) calcd for $C_{14}H_7F_9S$ $(M)^+$: 378.0125, found: 378.0121.



11

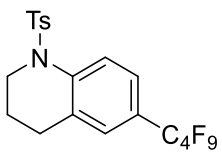
5-(perfluorobutyl)-2,2'-bithiophene (11), Colorless liquid, 28.3 mg, 74% yield, $\mathbf{R}_f$ =0.3 (petroleum ether).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 (dd, *J* = 9.1, 4.4 Hz, 2H), 7.25 (s, 1H), 7.16 (d, *J* = 3.9 Hz, 1H), 7.06 (dd, *J* = 5.1, 3.6 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 142.8, 135.6, 131.2 (d, *J* = 6.1 Hz), 128.3, 127.3 (t, *J* = 29.3 Hz), 126.3, 125.5, 123.6, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, CDCl$_3$) δ -80.97 (t, *J* = 9.7 Hz, 3F), -101.55 (t, *J* = 13.3 Hz, 2F), -122.46 (q, *J* = 9.5, 9.1 Hz, 2F), -125.48 – -125.66 (m, 2F).

HRMS (EI) calcd for $C_{12}H_5F_9S_2$ $(M)^+$: 383.9689, found: 383.9682.



12

6-(perfluorobutyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (12), Colorless liquid, 42.9

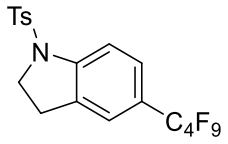
mg, 85% yield, $\mathbf{R_f}$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.9 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 3H), 3.93 – 3.81 (m, 2H), 2.60 (t, *J* = 6.6 Hz, 2H), 2.42 (s, 3H), 1.73 (dt, *J* = 12.5, 6.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 140.4, 136.4, 130.2, 129.8, 127.8 (t, *J* = 6.5 Hz), 127.0, 125.0 (t, *J* = 6.4 Hz), 124.4 (t, *J* = 24.6 Hz), 124.0, 46.6, 27.0, 21.6, 21.3, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.03 (t, *J* = 9.8 Hz, 3F), -110.70 (t, *J* = 13.8 Hz, 2F), -122.80 (q, *J* = 9.9 Hz, 2F), -125.56 – -125.66 (m, 2F).

HRMS (EI) calcd for $C_{20}H_{16}F_9NO_2S$ $(M)^+$: 505.0758, found: 505.0750.



13

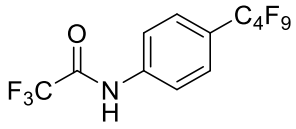
5-(perfluorobutyl)-1-tosylindoline (13), Colorless liquid, 42.2 mg, 86% yield, $\mathbf{R_f}$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 3H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 3H), 3.97 (t, *J* = 8.6 Hz, 2H), 3.01 (t, *J* = 8.6 Hz, 2H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 144.7, 133.8, 132.1, 129.9, 127.3, 127.1 (t, *J* = 6.8 Hz), 123.8 (t, *J* = 7.1 Hz), 123.6 (d, *J* = 14.5 Hz), 113.9, 50.1, 27.4, 21.5, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.07 (t, *J* = 9.8 Hz, 3F), -110.03 (t, *J* = 13.7 Hz, 2F), -122.75 (q, *J* = 10.1 Hz, 2F), -125.52 – -125.91 (m, 2F).

HRMS (EI) calcd for $C_{19}H_{14}F_9NO_2S$ $(M)^+$: 491.0602, found: 491.0595.



14

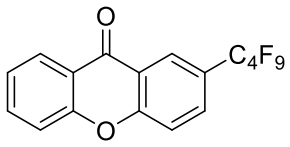
2,2,2-trifluoro-N-(4-(perfluorobutyl)phenyl)acetamide (14), Colorless liquid, 32.5 mg, 71% yield, $\mathbf{R_f}$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1 (q, *J* = 38.4 Hz), 138.6, 128.4 (t, *J* = 6.8 Hz), 126.6 (t, *J* = 25.0 Hz), 120.3, 114.2 (q, *J* = 289.9 Hz), ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (377 MHz, $CDCl_3$) δ -75.68 (m, 3F), -81.01 (t, *J* = 9.9 Hz, 3F), -110.90 (t, *J* = 13.4 Hz, 2F), -122.76 (q, *J* = 9.6 Hz, 2F), -125.43 – -125.71 (m, 2F).

HRMS (EI) calcd for $C_{12}H_5F_{12}NO$ $(M)^+$: 407.0180, found: 407.0187.



15

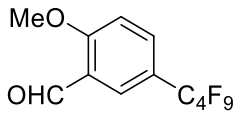
2-(perfluorobutyl)-9H-xanthen-9-one (15), Colorless liquid, 33.1 mg, 80% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 2.3 Hz, 1H), 8.37 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.91 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.79 (td, *J* = 7.9, 7.2, 1.7 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.49 – 7.41 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 158.1, 156.2, 135.7, 132.6 (t, *J* = 6.2 Hz), 127.1, 126.9 (d, *J* = 8.1 Hz), 124.9, 121.9 (d, *J* = 3.6 Hz), 119.2, 118.3, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.95 (t, *J* = 10.0 Hz, 3F), -110.29 (t, *J* = 13.7 Hz, 2F), -122.44 (q, *J* = 10.3, 9.8 Hz, 2F), -125.27 – -125.79 (m. 2F).

HRMS (EI) calcd for $C_{17}H_7F_9O_2$ $(M)^+$: 414.0302, found: 414.0295.



16

2-methoxy-5-(perfluorobutyl)benzaldehyde (16), Colorless liquid, 24.8 mg, 70% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

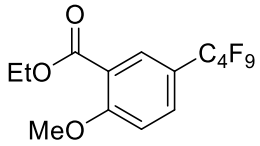
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.06 (d, *J* = 2.4 Hz, 1H), 7.75 (dd, *J* =

8.8, 2.5 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 4.01 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 188.6, 164.1, 134.1 (t, *J* = 6.2 Hz), 127.8 (t, *J* = 6.5 Hz), 124.8, 121.5 (t, *J* = 25.5 Hz), 112.3, 56.2, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, CDCl$_3$) δ -81.09 (t, *J* = 10.0 Hz, 3F), -110.47 (t, *J* = 13.4 Hz, 2F), -122.74 (q, *J* = 10.2, 9.8 Hz, 2F), -125.54 – -125.69 (m, 2F).

HRMS (EI) calcd for $C_{12}H_7F_9O_2$ $(M)^+$: 354.0302, found: 354.0295.



17

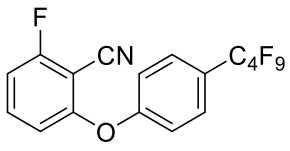
Ethyl 2-methoxy-5-(perfluorobutyl)benzoate (17), Colorless liquid, 29.1 mg, 73% yield, $\mathbf{R_f}$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, *J* = 2.4 Hz, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.96 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 165.1, 161.8, 131.9 (t, *J* = 6.3 Hz), 130.5 (t, *J* = 6.6 Hz), 121.0, 120.5 (t, *J* = 25.3 Hz), 112.2, 61.5, 56.4, 14.3, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, CDCl$_3$) δ -81.08 (t, *J* = 10.0 Hz, 3F), -110.34 (t, *J* = 13.9 Hz, 2F), -122.72 (q, *J* = 10.0 Hz, 2F), -125.39 – -125.97 (m, 2F).

HRMS (EI) calcd for $C_{14}H_{11}F_9O_3$ $(M)^+$: 398.0564, found: 398.0554.



18

2-fluoro-6-(4-(perfluorobutyl)phenoxy)benzonitrile (18), Colorless liquid, 34.9 mg, 81% yield, $\mathbf{R_f}$ =0.3 (petroleum ether: ethyl acetate, 30:1, v/v).

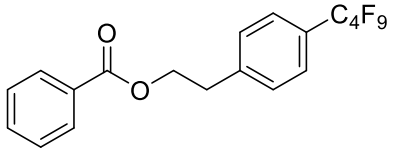
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.56 – 7.48 (m, 1H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.00 (t, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 164.3 (d, *J* = 260.8 Hz), 159.5 (d, *J* = 4.2 Hz), 158.0, 135.3 (d, *J* = 10.2 Hz), 129.4 (t, *J* = 6.5 Hz), 125.8 (t, *J* = 24.8 Hz), 119.9, 113.4 (d, *J* =

3.6 Hz), 111.2 (d, J = 19.6 Hz), 110.8, 95.0 (d, J = 18.1 Hz), ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, CDCl$_3$) δ -80.99 (t, J = 11.3 Hz, 3F), -103.28 – -104.13 (m, 1F), -110.48 (t, J = 13.4 Hz, 2F), -122.70 (q, J = 9.9 Hz, 2F), -125.49 – -125.64 (m, 2F).

HRMS (EI) calcd for $C_{17}H_7F_{10}ON$ $(M)^+$: 431.0368, found: 431.0365.



19

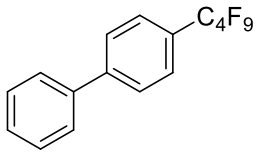
4-(perfluorobutyl)phenethyl benzoate (19), Colorless liquid, 28.0 mg, 63% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (dd, J = 8.4, 1.4 Hz, 2H), 7.56 (d, J = 8.7 Hz, 3H), 7.47 – 7.40 (m, 4H), 4.57 (t, J = 6.8 Hz, 2H), 3.16 (t, J = 6.8 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 166.6, 142.6, 133.2, 130.2, 129.7, 129.4, 128.6, 127.3 (t, J = 7.1 Hz), 127.2 (t), 64.9, 35.1, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, CDCl$_3$) δ -81.06 (t, J = 9.5 Hz, 3F), -110.88 (t, J = 13.4 Hz, 2F), -122.86 (q, J = 9.8 Hz, 2F), -125.50 – -125.90 (m, 2F).

HRMS (EI) calcd for $C_{19}H_{13}F_9O_2$ $(M)^+$: 444.0772, found: 444.0764.



20

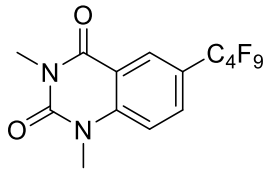
4-(perfluorobutyl)-1,1'-biphenyl (20), Colorless liquid, 35.7 mg, 96% yield, $\mathbf{R}_f$ =0.3 (petroleum ether).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.74 – 7.66 (m, 4H), 7.64 – 7.60 (m, 2H), 7.49 (t, J = 7.4 Hz, 2H), 7.45 – 7.41 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 145.1, 139.8, 129.2, 128.4, 127.8 (t, J = 24.2 Hz) 127.46, 127.45, 127.1 (t, J = 9.1 Hz), ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, CDCl$_3$) δ -81.01 (t, J = 9.7 Hz, 3F), -110.80 (t, J = 13.3 Hz, 2F), -122.68 (q, J = 9.9 Hz, 2F), -125.49 – -125.61 (m, 2F).

HRMS (EI) calcd for $C_{16}H_9F_9$ $(M)^+$: 372.0561, found: 372.0552.



21

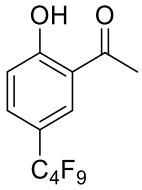
1,3-dimethyl-6-(perfluorobutyl)quinazoline-2,4(1H,3H)-dione (21), Colorless liq uid, 34.7 mg, 85% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.85 (d, *J* = 11.1 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 3.65 (s, 3H), 3.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 150.9, 142.9, 132.9 (t, *J* = 6.2 Hz), 128.4 (t, *J* = 6.7 Hz), 123.5 (t, *J* = 25.7 Hz), 115.6, 114.2, 31.1, 28.7, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.01 (t, *J* = 9.8 Hz, 3F), -110.66 (t, *J* = 13.4 Hz, 2F), -122.63 (q, *J* = 10.2 Hz, 2F), -125.37 – -125.75 (m, 2F).

HRMS (EI) calcd for $C_{14}H_9F_9N_2O_2$ $(M)^+$: 408.0520, found: 408.0518.



22

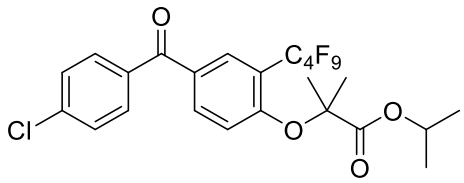
1-(2-hydroxy-5-(perfluorobutyl)phenyl)ethan-1-one (22), Colorless liquid, 24.1 mg, 68% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.57 (s, 1H), 7.94 (s, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.11 (d, *J* = 8.9 Hz, 1H), 2.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 165.1, 134.3 (t, *J* = 6.0 Hz), 129.9 (t, *J* = 6.8 Hz), 119.5, 119.4, 119.4 (t, *J* = 25.4 Hz), 26.8, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.05 (t, *J* = 9.8 Hz, 3F), -110.31 (t, *J* = 12.2 Hz, 2F), -122.69 (q, *J* = 9.9 Hz,2F), -125.49 – -125.62 (m, 2F).

HRMS (EI) calcd for $C_{12}H_7F_9O_2$ $(M)^+$: 354.0302, found: 354.0294.



23

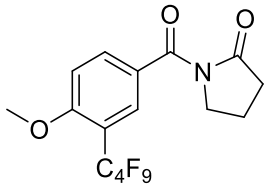
Isopropyl 2-(4-(4-chlorobenzoyl)-2-(perfluorobutyl)phenoxy)-2 methylpropanoate (23), Colorless liquid, 44.5 mg, 77% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 1H), 5.06 (p, *J* = 6.2 Hz, 1H), 1.68 (s, 6H), 1.16 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 172.6, 158.5 (t, *J* = 2.4 Hz), 139.2, 135.3 (d, *J* = 76.9 Hz), 132.2 (t, *J* = 9.0 Hz), 131.3, 129.6, 129.0, 118.6 (t, *J* = 22.9 Hz), 115.8, 80.8, 69.7, 25.1, 21.5, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.89 (t, *J* = 9.8 Hz, 3F), -107.84 (t, *J* = 13.4 Hz, 2F), -121.36 (q, *J* = 9.7 Hz, 2F), -125.58 – -126.85 (m, 2F).

HRMS (EI) calcd for $C_{24}H_{20}ClF_9O_4$ $(M)^+$: 578.0906, found: 578.0897.



24

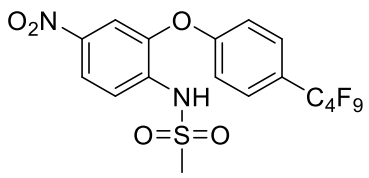
1-(4-methoxy-3-(perfluorobutyl)benzoyl)pyrrolidin-2-one (24), Colorless liquid, 30.2 mg, 69% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 4:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 2H), 7.01 (d, J = 8.5 Hz, 1H), 3.95 (t, J = 7.1 Hz, 2H), 3.92 (s, 3H), 2.62 (t, J = 7.9 Hz, 2H), 2.15 (p, J = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 168.8, 161.3 (t, *J* = 2.2 Hz), 135.4, 131.5 (t, *J* = 9.1 Hz), 126.0, 116.3 (t, *J* = 23.2 Hz), 111.3, 56.2, 46.8, 33.3, 17.6, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.92 (t, *J* = 9.9 Hz, 3F), -108.27 (t, *J* = 14.0 Hz, 2F), -121.94 (q, *J* = 9.7 Hz, 2F), -125.74 – -126.63 (m, 2F).

HRMS (EI) calcd for $C_{16}H_{12}F_9NO_3$ $(M)^+$: 437.0673, found: 437.0667.



25

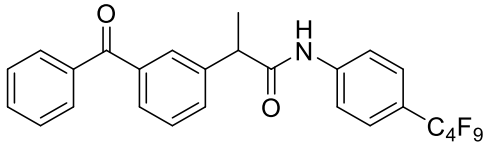
N-(4-nitro-2-(3-(perfluorobutyl)phenoxy)phenyl)methanesulfonamide (25), Yell ow solid, 42.1 mg, 80% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 2:1, v/ v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.6 Hz, 1H), 7.82 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 1H), 7.32 (s, 1H), 3.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 148.9, 144.0, 132.9, 132.1, 128.7, 124.6, 116.9, 113.9, 108.4, 40.3, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.98 (t, *J* = 9.8 Hz, 3F), -110.94 (t, *J* = 13.8 Hz, 2F), -122.62 (q, *J* = 9.7 Hz, 2F), -125.53 – -125.65 (m, 2F).

HRMS (EI) calcd for $C_{17}H_{11}F_9N_2O_5S$ $(M)^+$: 526.0245, found: 526.0236.



26

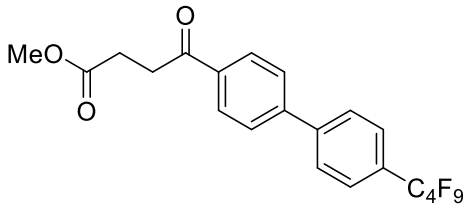
2-(3-(4-(perfluorobutyl)benzoyl)phenyl)-N-phenylpropanamide (26), White soli d,49.8 mg, 91% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.83 (s, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.62 (dq, *J* = 15.1, 7.7 Hz, 5H), 7.48 – 7.41 (m, 5H), 3.82 (q, *J* = 7.0 Hz, 1H), 1.58 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 172.4, 141.5, 141.4, 138.0, 137.2, 132.9, 131.5, 130.1, 129.7, 129.3, 129.0, 128.5, 127.8 (t, *J* = 6.3 Hz), 124.0 (t, *J* = 24.7 Hz), 119.3, 47.9, 18.8, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.11 (t, *J* = 9.9 Hz, 3F), -110.61 (t, *J* = 13.8 Hz, 2F), -122.86 (q, *J* = 9.7 Hz, 2F), -125.37 – -125.88 (m, 2F).

HRMS (EI) calcd for $C_{26}H_{18}F_9NO_2$ $(M)^+$: 547.1194, found: 547.1187.



27

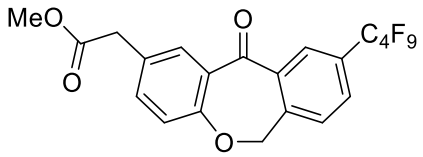
Methyl 4-oxo-4-(4'-(perfluorobutyl)-[1,1'-biphenyl]-4-yl)butanoate (27), Colorless liquid, 35.0 mg, 72% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.03 (m, 2H), 7.72 (dt, *J* = 14.8, 8.3 Hz, 6H), 3.72 (s, 3H), 3.37 (t, *J* = 6.6 Hz, 2H), 2.81 (t, *J* = 6.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 173.5, 144.3, 143.7, 136.2, 128.9, 128.7 (t, *J* = 24.4 Hz), 127.67, 127.66 (t, *J* = 7.1 Hz), 127.65, 52.0, 33.6, 28.1, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.98 (t, *J* = 9.6 Hz, 3F), -110.98 (t, *J* = 13.8 Hz, 2F), -122.68 (q, *J* = 9.8 Hz, 2F), -125.43 – -125.70 (m, 2F).

HRMS (EI) calcd for $C_{21}H_{15}F_9O_3$ $(M)^+$: 486.0877, found: 486.0874.



28

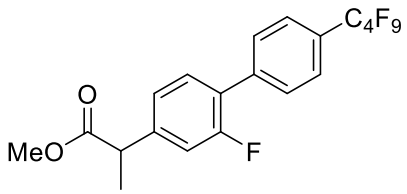
Methyl 2-(11-oxo-9-(perfluorobutyl)-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (28), White solid, 41.0 mg, 82% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 2.4 Hz, 1H), 7.99 (d, *J* = 6.4 Hz, 1H), 7.69 (d, *J* = 2.5 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.38 (dd, *J* = 7.4, 1.2 Hz, 1H), 5.24 (s, 2H), 3.73 (s, 3H), 3.71 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3, 171.3, 159.5, 139.3, 137.7, 136.1, 136.04, 136.02 (t, J = 9.1 Hz), 133.5, 130.4, 129.6, 128.1, 127.9 (d, J = 3.5 Hz), 120.7 (t, J = 22.8 Hz), 74.8, 52.5, 40.0, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.84 (t, *J* = 10.1 Hz, 3F), -106.75 (t, *J* = 14.3 Hz, 2F), -121.54 (q, *J* = 9.9 Hz, 2F), -125.87 – -125.97 (m, 2F).

HRMS (EI) calcd for $C_{21}H_{13}F_9O_4$ $(M)^+$: 500.0670, found: 500.0662.



29

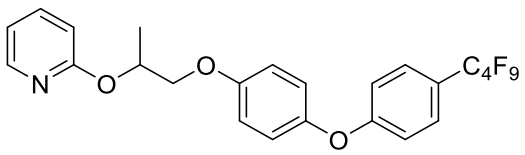
Methyl 2-(2-fluoro-4'-(perfluorobutyl)-[1,1'-biphenyl]-4-yl)propanoate (29), Co lorless liquid, 40.9 mg, 86% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 30: 1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 4H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.22 – 7.12 (m, 2H), 3.78 (q, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 1.55 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 159.7 (d, *J* = 249.8 Hz), 143.0 (d, *J* = 7.6 Hz), 139.3, 130.8 (d, *J* = 3.6 Hz), 129.2 (d, *J* = 3.0 Hz), 128.0 (t, *J* = 24.5 Hz), 127.0 (t, *J* = 6.5 Hz), 126.3 (d, *J* = 13.1 Hz), 123.9 (d, *J* = 3.1 Hz), 115.5 (d, *J* = 23.3 Hz), 52.3, 45.0, 18.4, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.02 (t, *J* = 10.2 Hz, 3F), -110.92 (t, *J* = 13.5 Hz, 2F), -117.16 – -117.32 (m, 1F), -122.63 (q, *J* = 10.2 Hz, 2F), -125.47 – -125.65 (m, 2F).

HRMS (EI) calcd for $C_{20}H_{14}F_{10}O_2$ $(M)^+$: 476.0834, found: 476.0827.



30

2-((1-(4-(4-(perfluorobutyl)phenoxy)phenoxy)propan-2-yl)oxy)pyridine (30), Co lorless liquid, 38.8 mg, 72% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

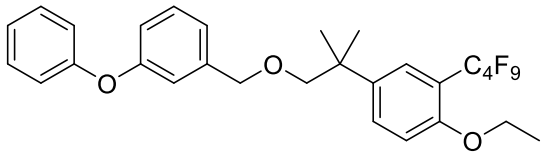
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 5.1 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.49 (d, *J* = 8.9 Hz, 2H), 7.11 – 6.91 (m, 6H), 6.91 – 6.81 (m, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 5.61 (h, *J* = 6.3 Hz, 1H), 4.21 (dd, *J* = 9.8, 5.3 Hz, 1H), 4.10 (dd, *J* = 9.8, 4.8 Hz, 1H), 1.50 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 161.9, 156.1, 148.6, 146.8, 138.8, 128.6 (t, *J* = 6.5 Hz), 122.1 (t, *J* = 24.8 Hz), 121.7, 116.8, 116.7, 116.0, 111.7, 71.0, 69.2, 17.0, ^{13}C

NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.04 (t, *J* = 9.7 Hz, 3F), -110.09 (t, *J* = 13.7 Hz, 2F), -122.80 (q, *J* = 10.2 Hz, 2F), -125.51 – -125.78 (m, 2F).

HRMS (EI) calcd for $C_{24}H_{18}F_9NO_3$ $(M)^+$: 539.1143, found: 539.1139.



31

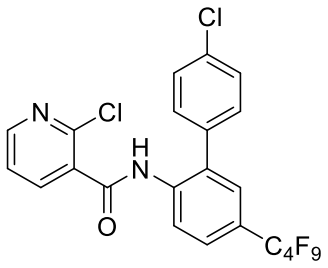
1-methoxy-4-(2-methyl-1-((3-phenoxybenzyl)oxy)propan-2-yl)-2-(perfluorobutyl) benzene (31), Colorless liquid, 36.8 mg, 62% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 50:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.33 (m, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.96 – 6.89 (m, 3H), 4.47 (s, 2H), 4.06 (q, *J* = 6.9 Hz, 2H), 3.44 (s, 2H), 1.41 (t, *J* = 7.0 Hz, 3H), 1.35 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 157.3, 156.1 (t, *J* = 2.7 Hz), 140.9, 139.4, 131.4, 129.9, 129.7, 126.9 (t, *J* = 8.9 Hz), 123.4, 122.1, 119.1, 117.9, 117.7, 113.0, 80.0, 72.9, 64.6, 38.7, 26.2, 14.6, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.90 (t, *J* = 10.2 Hz, 3F), -107.57 (t, *J* = 13.7 Hz, 2F), -121.81 (q, *J* = 9.6 Hz, 2F), -126.01 – -126.09 (m, 2F).

HRMS (EI) calcd for $C_{29}H_{27}F_9O_3$ $(M)^+$: 594.1816, found: 594.1811.



32

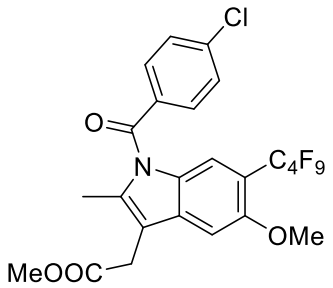
2-chloro-N-(4'-chloro-5-(perfluorobutyl)-[1,1'-biphenyl]-2-yl)nicotinamide (32), Colorless liquid, 41.4 mg, 74% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 2:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.28 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 3H), 7.16 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 150.5, 143.8, 136.9, 136.3, 134.5, 134.0, 133.4, 132.5, 130.6, 130.5, 129.4, 129.2, 126.4, 125.9, 122.7, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.83 (t, *J* = 10.1 Hz, 3F), -108.51 (t, *J* = 13.4 Hz, 2F), -120.59 (q, *J* = 10.0 Hz, 2F), -125.18 – -125.81 (m, 2F).

HRMS (EI) calcd for $C_{22}H_{11}Cl_2F_9N_2O$ $(M)^+$: 560.0105, found: 560.0098.



33

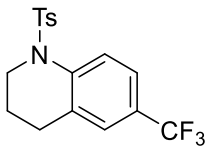
Methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-6-(perfluorobutyl)-1H-indol-3-yl)acetate (33), White solid, 46.5 mg, 79% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 4:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.14 (s, 1H), 7.05 (s, 1H), 3.90 (s, 3H), 3.72 (s, 3H), 3.69 (s, 2H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 168.0, 139.9, 138.7, 133.5, 133.2, 131.2, 129.7, 129.3, 115.2 (t, *J* = 10.3 Hz), 112.1, 101.2, 56.4, 52.3, 30.1, 13.5, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.94 (t, *J* = 10.3 Hz, 3F), -106.73 (t, *J* = 13.8 Hz, 2F), -121.76 (q, *J* = 9.8 Hz, 2F), -125.97 – -126.10 (m, 2F).

HRMS (EI) calcd for $C_{24}H_{17}ClF_9NO_4$ $(M)^+$: 589.0702, found: 589.0699.



34

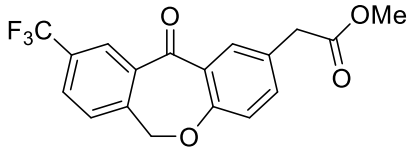
1-tosyl-6-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline (34), Colorless liquid, 25.9 mg, 73% yield, $\mathbf{R_f}$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.7 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.30 (s, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 3.96 – 3.75 (m, 2H), 2.58 (t, *J* = 6.7 Hz, 2H), 2.41 (s, 3H), 1.75 – 1.68 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 140.1, 136.4, 130.4, 129.9, 127.1, 126.4 (q, *J* = 3.9 Hz), 126.3 (q, *J* = 32.7 Hz), 125.5, 124.2, 123.5 (q, *J* = 3.7 Hz), 46.6, 27.0, 21.6, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.23(s, 3F).

HRMS (EI) calcd for $C_{17}H_{16}F_3NO_2S$ $(M)^+$: 355.0854, found: 355.0863.



35

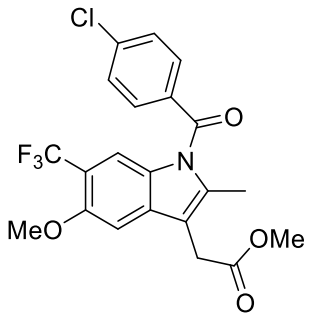
Methyl 2-(11-oxo-9-(trifluoromethyl)-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (35), Colorless liquid, 20.3 mg, 58% yield, $\mathbf{R_f}$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 2.4 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 2.4 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 5.30 (s, 2H), 3.73 (s, 3H), 3.69 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8, 171.4, 158.6, 139.8, 137.0, 135.5, 133.9 (q, *J* = 5.1 Hz), 133.4, 130.1, 129.7, 128.2, 127.6, 127.2, 124.5, 122.3 (q, *J* = 30.1, 29.6 Hz), 74.6, 52.5, 40.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.13(d, 3F).

HRMS (EI) calcd for $C_{18}H_{13}F_3O_4$ $(M)^+$: 350.0766, found: 350.0759.



36

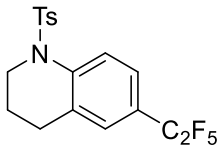
Methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-6-(trifluoromethyl)-1H-indol-3-yl)acetate (36), White solid, 23.7 mg, 54% yield, $\mathbf{R_f}$ =0.3 (petroleum ether: ethyl acetate, 4:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.34 (s, 1H), 7.04 (s, 1H), 3.95 (s, 3H), 3.71 (s, 3H), 3.69 (s, 2H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 168.2, 154.1, 140.0, 138.3, 133.4, 133.2, 131.3, 129.5, 129.4, 124.0 (q, *J* = 271.7 Hz), 114.9 (d, *J* = 30.4 Hz), 113.3 (q, *J* = 6.1 Hz), 112.3, 101.0, 56.5, 52.4, 30.2, 13.71.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.69(s, 3F).

HRMS (EI) calcd for $C_{21}H_{17}ClF_3NO_4$ $(M)^+$: 439.0798, found: 439.0791.



37

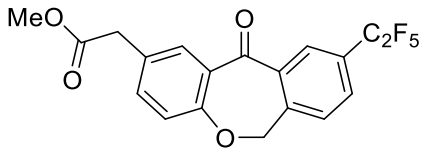
6-(perfluoroethyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (37), Colorless liquid, 32.4 mg, 80% yield, $\mathbf{R_f}$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.7 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.24 (s, 2H), 7.22 (s, 1H), 3.88 – 3.72 (m, 2H), 2.58 (t, *J* = 6.7 Hz, 2H), 2.39 (s, 3H), 1.71 (dt, *J* = 12.5, 6.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 140.5, 136.6, 130.3, 129.9, 127.5 (t, *J* = 6.4 Hz), 127.1, 124.7 (t, *J* = 6.6 Hz), 124.4, 124.1, 46.7, 27.1, 21.6, 21.5, ^{13}C NMR for C_2F_5 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -84.74(s, 3F), -114.44(s, 2F).

HRMS (EI) calcd for $C_{18}H_{16}F_5NO_2S$ $(M)^+$: 405.0822, found: 405.0815.



38

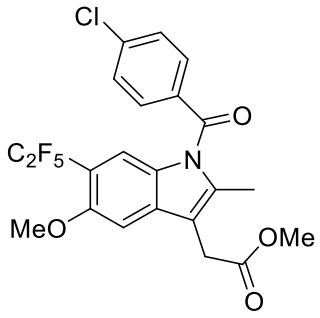
Methyl 2-(11-oxo-9-(perfluoroethyl)-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (38), Colorless liquid, 31.2 mg, 78% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl ace tate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 2.4 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 2.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 5.25 (s, 2H), 3.73 (s, 3H), 3.71 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4, 171.3, 159.3, 139.3, 137.6, 136.0, 135.7 (t, *J* = 8.7 Hz), 133.5, 130.4, 129.6, 128.1, 127.9, 127.9, 120.5 (t, *J* = 22.2 Hz), 74.8, 52.5, 40.0, ^{13}C NMR for C_2F_5 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.35(s, 3F), -110.68(s, 2F).

HRMS (EI) calcd for $C_{19}H_{13}F_5O_4$ $(M)^+$: 400.0734, found: 400.0731.



39

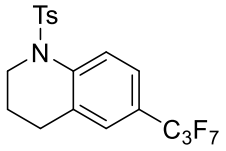
Methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-6-(perfluoroethyl)-1H-indol-3-yl)acetate (39), White solid, 40.1 mg, 82% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 4:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.18 (s, 1H), 7.05 (s, 1H), 3.91 (s, 3H), 3.72 (s, 3H), 3.69 (s, 2H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 168.0, 154.7, 139.9, 138.6, 133.4, 133.2, 131.2, 129.7, 129.3, 114.8 (t, *J* = 10.1 Hz), 112.5 (t, *J* = 22.5 Hz), 112.1, 101.2, 56.4, 52.3, 30.1, 13.5, ^{13}C NMR for C_2F_5 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.67(s, 3F), -110.68(s, 2F).

HRMS (EI) calcd for $C_{22}H_{17}ClF_5NO_4$ $(M)^+$: 489.0766, found: 489.0762.



40

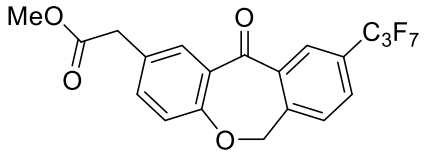
6-(perfluoropropyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (40), Colorless liquid, 32.4 mg, 75% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.7 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 11.1 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 3H), 3.87 – 3.79 (m, 2H), 2.57 (t, *J* = 6.6 Hz, 2H), 2.39 (s, 3H), 1.71 (dt, *J* = 12.5, 6.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 140.5, 136.5, 130.4, 129.9, 127.8 (t, *J* = 6.6 Hz), 127.1, 125.0 (t, *J* = 6.5 Hz), 124.4 (t, *J* = 24.4 Hz), 124.1, 46.7, 27.1, 21.6, 21.4, ^{13}C NMR for C_3F_7 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.05 (t, *J* = 9.7 Hz, 3F), -111.46 (q, *J* = 10.0 Hz, 2F), -126.49(s, 2F).

HRMS (EI) calcd for $C_{19}H_{16}F_7NO_2S$ $(M)^+$: 455.0790, found: 455.0790.



41

Methyl 2-(11-oxo-9-(perfluoropropyl)-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (41), Colorless liquid, 31.5 mg, 67% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

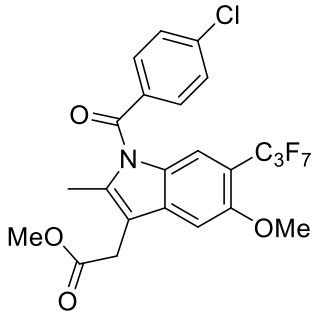
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 2.4 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 2.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 5.22 (s, 2H), 3.72 (s, 3H), 3.70 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4, 171.3, 159.4, 139.3, 137.7, 136.0, 135.8 (d, *J* = 9.1 Hz), 133.5, 130.4, 129.6, 128.1, 127.9, 127.8, 120.6 (t, *J* = 22.6 Hz), 74.8, 52.5, 40.0, ^{13}C NMR for C_3F_7 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -74.61 – -88.53 (m, 3F), -107.44 (q, *J* = 9.0, 8.3 Hz,

2F), -125.16 (d, J = 7.1 Hz, 2F).

HRMS (EI) calcd for $C_{20}H_{13}F_7O_4$ $(M)^+$: 450.0702, found: 450.0696.



42

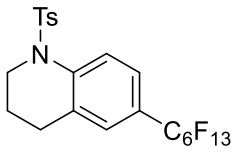
Methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-6-(perfluoropropyl)-1H-indol-3-yl)acetate (42), White solid, 37.7 mg, 70% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 4:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 7.14 (s, 1H), 7.05 (s, 1H), 3.90 (s, 3H), 3.72 (s, 3H), 3.69 (s, 2H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 168.0, 154.9, 139.9, 138.8, 133.5, 133.2, 131.2, 129.7, 129.3, 115.2 (t, J = 10.1 Hz), 112.7 (t, J = 22.2 Hz), 112.1, 101.2, 56.5, 52.3, 30.1, 13.5, ^{13}C NMR for C_3F_7 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.43 (t, J = 9.7 Hz, 3F), -107.44 (q, J = 9.7 Hz, 2F), -121.52 – -133.41 (m, 2F).

HRMS (EI) calcd for $C_{23}H_{17}ClF_7NO_4$ $(M)^+$: 539.0734, found: 539.0736.



43

6-(perfluorohexyl)-1-tosyl-1,2,3,4-tetrahydroquinoline (43), Colorless liquid, 34.5 mg, 57% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

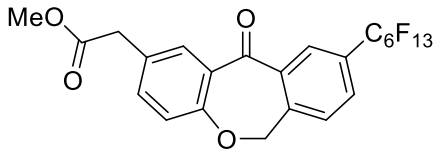
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.7 Hz, 1H), 7.52 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.8 Hz, 1H), 7.22 (d, J = 7.9 Hz, 3H), 3.92 – 3.72 (m, 2H), 2.58 (t, J = 6.6 Hz, 2H), 2.39 (s, 3H), 1.71 (p, J = 6.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 140.5, 136.5, 130.3, 129.9, 127.9 (t, J = 6.2 Hz), 127.2, 125.2 (t, J = 6.3 Hz), 124.7 (t, J = 24.4 Hz), 124.1, 46.8, 27.1, 21.6, 21.4, ^{13}C

NMR for C_6F_{13} could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.82 (t, *J* = 9.7 Hz, 3F), -110.46 (t, *J* = 14.5 Hz, 2F), -121.47 (t, *J* = 14.4 Hz, 2F), -121.93 (t, *J* = 11.8 Hz, 2F), -122.66 – -123.25 (m, 2F), -126.06 – -126.26 (m, 2F).

HRMS (EI) calcd for $C_{22}H_{16}F_{13}NO_2S$ $(M)^+$: 605.0694, found: 605.0687.



44

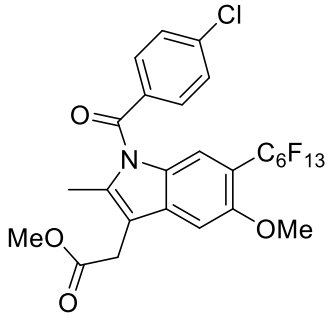
Methyl 2-(11-oxo-9-(perfluorohexyl)-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (44), Colorless liquid, 37.2 mg, 62% yield, $\mathbf{R_f}$ =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 2.4 Hz, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 2.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 5.24 (s, 2H), 3.72 (s, 3H), 3.71 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3, 171.3, 159.5, 139.3, 137.7, 136.06 (t, *J* = 4.4 Hz), 136.05, 135.9, 133.5, 130.4, 129.6, 128.1, 127.9, 120.8 (d, *J* = 23.2 Hz), 74.8, 52.4, 40.0, ^{13}C NMR for C_6F_{13} could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.76 (d, *J* = 9.4 Hz, 3F), -106.61 (t, *J* = 15.2 Hz, 2F), -120.64 – -120.91 (m, 2F), -121.82 (t, *J* = 14.9 Hz, 2F), -122.59 – -122.87 (m, 2F), -126.05 – -126.26 (m, 2F).

HRMS (EI) calcd for $C_{23}H_{13}F_{13}O_4$ $(M)^+$: 600.0606, found: 600.0598.



45

Methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-6-(perfluorohexyl)-1H-indol-

3-yl) acetate (45), White solid, 37.2 mg, 54% yield, $\mathbf{R}_f$ =0.3 (petroleum ether: ethyl acetate, 4:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.12 (s, 1H), 7.05 (s, 1H), 3.90 (s, 3H), 3.72 (s, 3H), 3.69 (s, 2H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 168.0, 154.9, 139.9, 138.8, 133.5, 133.2, 131.2, 129.7, 129.3, 115.2 (t, *J* = 10.1 Hz), 112.7 (d, *J* = 22.2 Hz), 112.1, 101.2, 56.5, 52.3, 30.1, 13.5, ^{13}C NMR for C_6F_{13} could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.75 (t, *J* = 9.9 Hz, 3F), -106.55 (t, *J* = 15.0 Hz, 2F), -120.88 (d, *J* = 22.0 Hz, 2F), -121.64 – -122.26 (m, 2F), -122.54 – -123.30 (m, 2F), -125.36 – -127.21 (m, 2F).

HRMS (EI) calcd for $C_{26}H_{17}ClF_{13}NO_4$ $(M)^+$: 689.0639, found: 689.0634.

8. References

(1) Aikawa, K.; Nakamura, Y.; Yokota, Y.; Toya, W.; Mikami, K. Stable but Reactive Perfluoroalkylzinc Reagents: Application in Ligand-Free Copper-Catalyzed Perfluoroalkylation of Aryl Iodides. *Chem. Eur. J.* **2015**, *21* (1), 96–100.

(2) Xu, H.; Li, X.; Dong, Y.; Ji, S.; Zuo, J.; Lv, J.; Yang, D. Thianthrenium-Enabled Phosphorylation of Aryl C–H Bonds via Electron Donor–Acceptor Complex Photoactivation. *Org. Lett.* **2023**, *25* (20), 3784–3789.

(3) Ye, F.; Berger, F.; Jia, H.; Ford, J.; Wortman, A.; Börgel, J.; Genicot, C.; Ritter, T. Aryl Sulfonium Salts for Site-Selective Late-Stage Trifluoromethylation. *Angew. Chem. Int. Ed.* **2019**, *58* (41), 14615–14619.

(4) Jiang, X.; Gong, W.; Li, X.; Wang, S.; Gu, Z.; Yang, Y.; Zeng, X. Pd-Catalyzed Divergent Site-Selective Difluoromethylation and Difluoromethylcarbonylation of Aryl Sulfonium Salts. *ACS Catal.* **2024**, *14* (18), 13557–13566.

(5) Zhao, Y.; Empel, C.; Liang, W.; Koenigs, R. M.; Patureau, F. W. Gem-Difluoroallylation of Aryl Sulfonium Salts. *Org. Lett.* **2022**, *24* (48), 8753–8758.

(6) Wu, Y.; Huang, Y.-H.; Chen, X.-Y.; Wang, P. Site-Selective Silylation of Arenes Mediated by Thianthrene S-Oxide. *Org. Lett.* **2020**, *22* (16), 6657–6661.

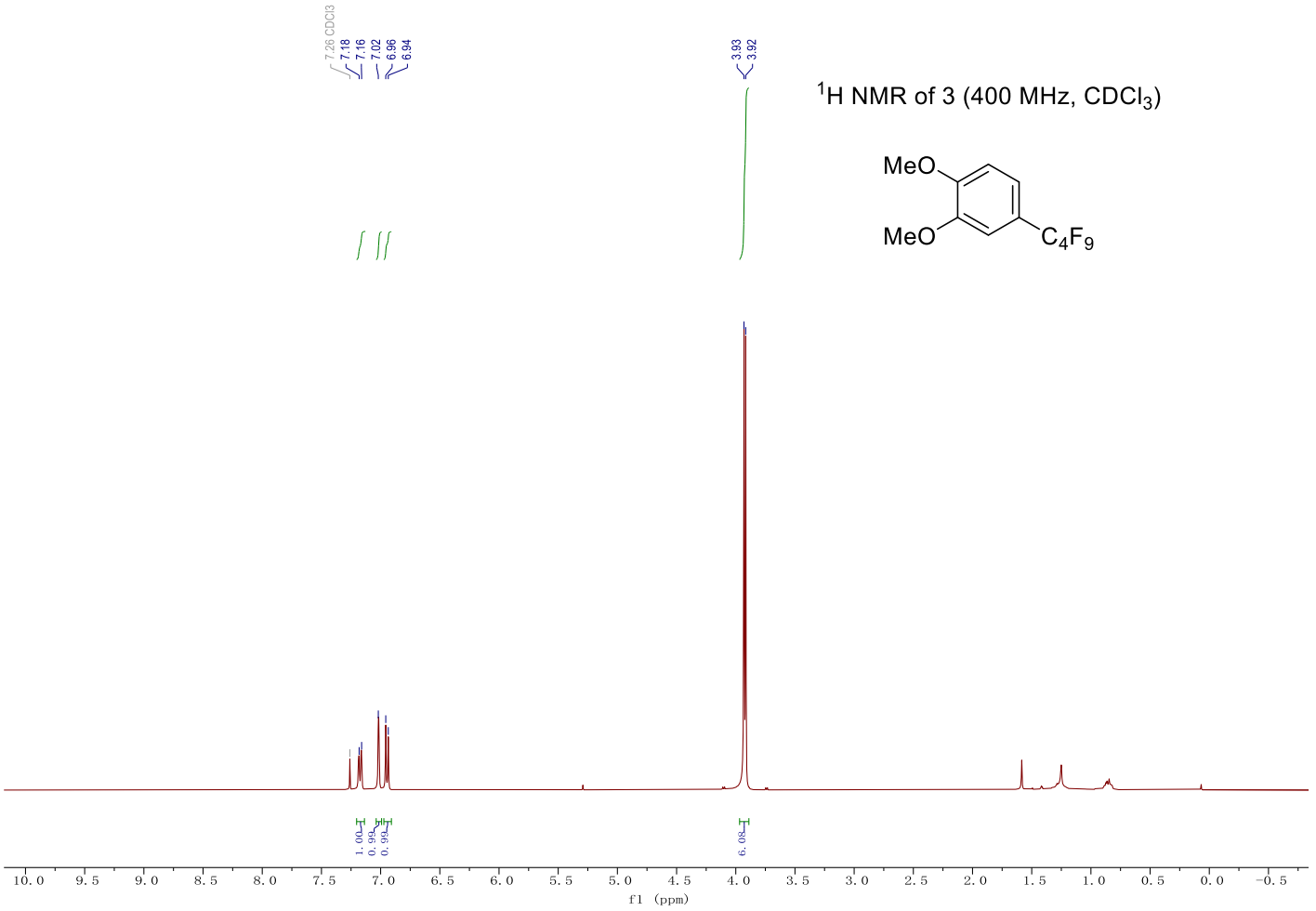
(7) Peng, B.; Dai, L.; Liu, R. Thianthrenation-Enabled Pyrrolidin-2-yl and Tetrahydrofuran-2-yl Methylation of (Hetero)Arenes. *Org. Lett.* **2023**, *25* (15), 2606–2610.

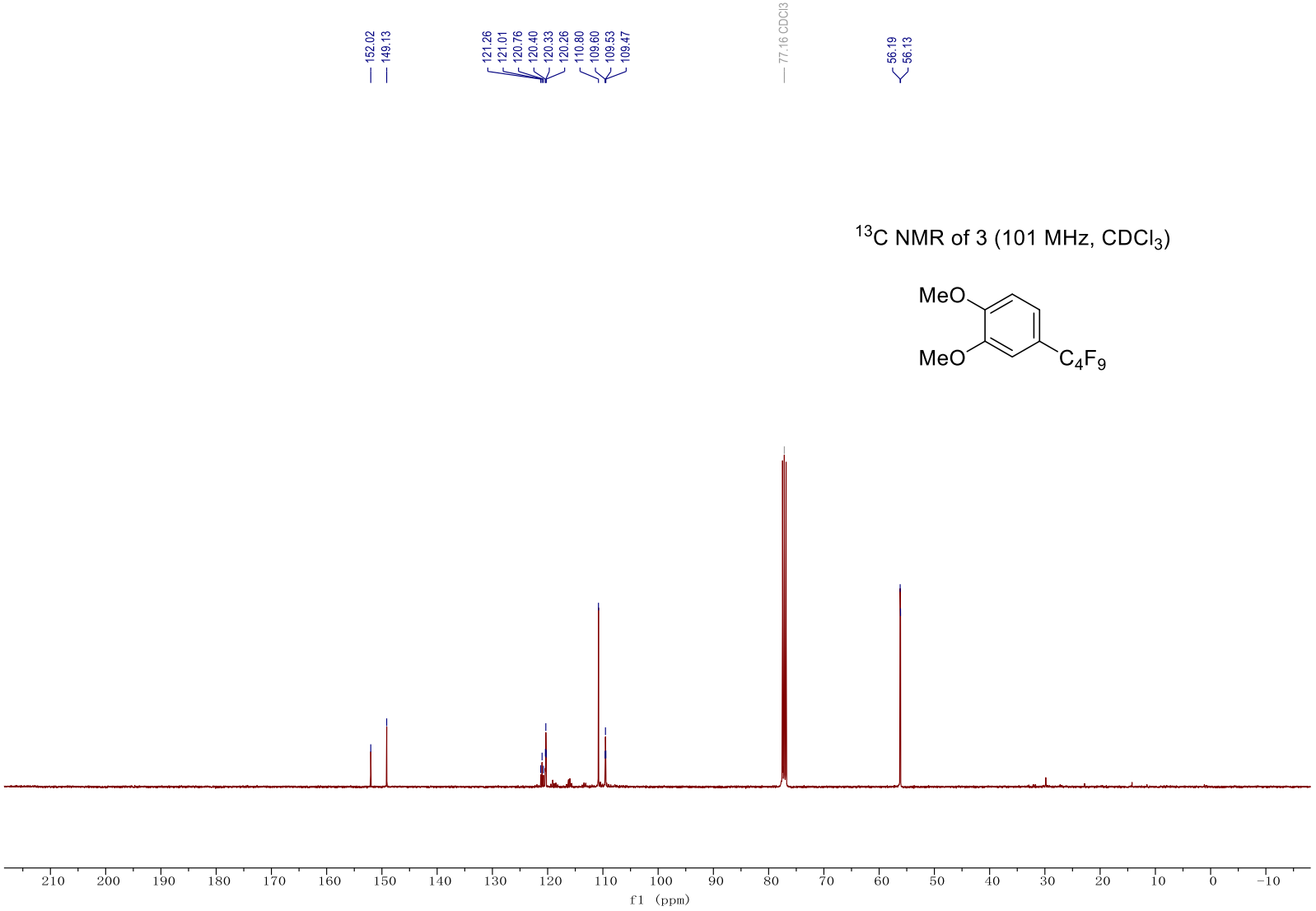
(8) Cai, Y.; Chatterjee, S.; Ritter, T. Photoinduced Copper-Catalyzed Late-Stage Azidoarylation of Alkenes via Arylthianthrenium Salts. *J. Am. Chem. Soc.* **2023**, *145* (25), 13542–13548.

(9) Engl, P. S.; Häring, A. P.; Berger, F.; Berger, G.; Pérez-Bitrián, A.; Ritter, T. C–N Cross-Couplings for Site-Selective Late-Stage Diversification via Aryl Sulfonium Salts. *J. Am. Chem. Soc.* **2019**, *141* (34), 13346–13351.

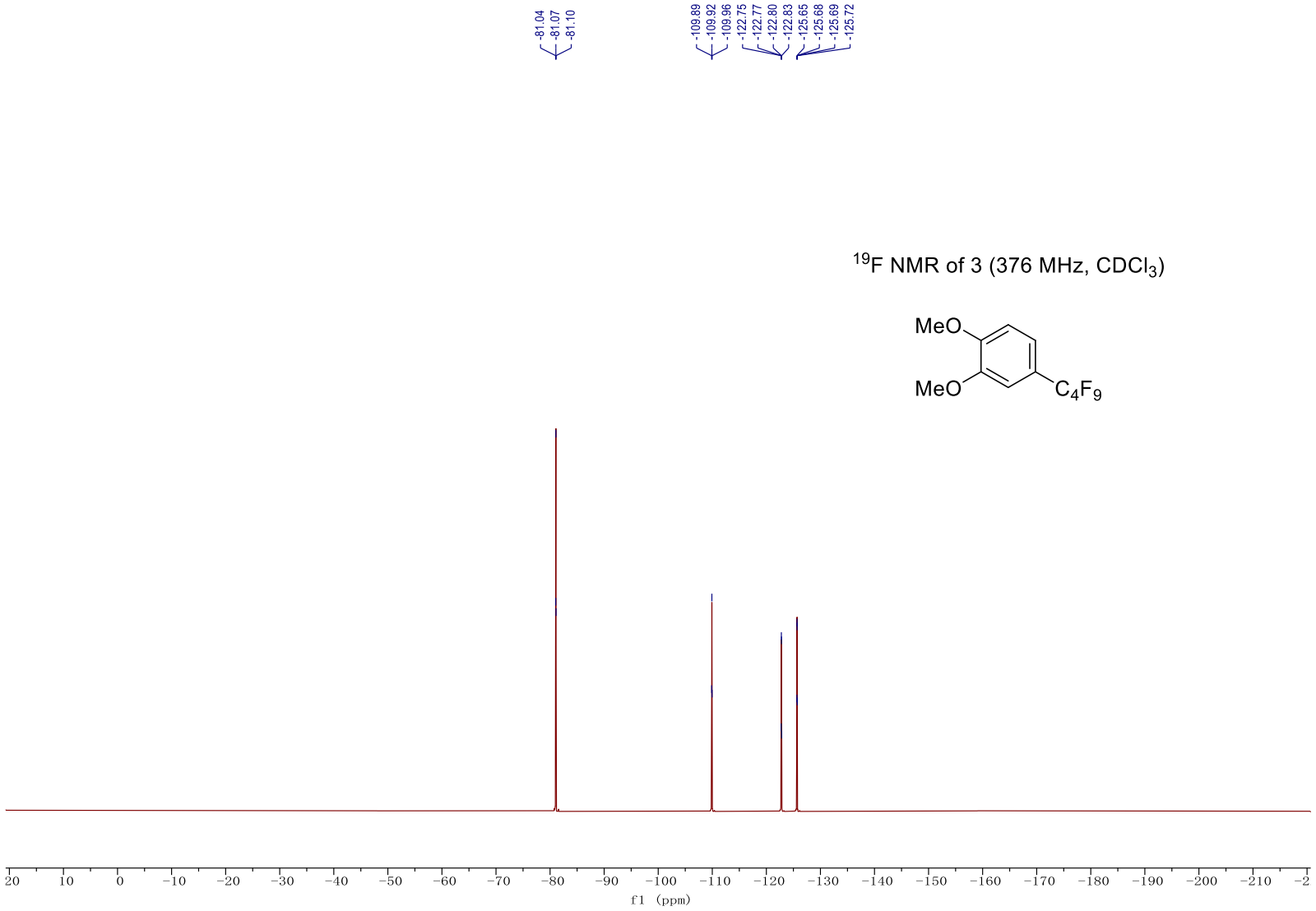
(10) Matier, C. D.; Schwaben, J.; Peters, J. C.; Fu, G. C. Copper-Catalyzed Alkylation of Aliphatic Amines Induced by Visible Light. *J. Am. Chem. Soc.* **2017**, *139* (49), 17707–17710.

9. NMR Spectra

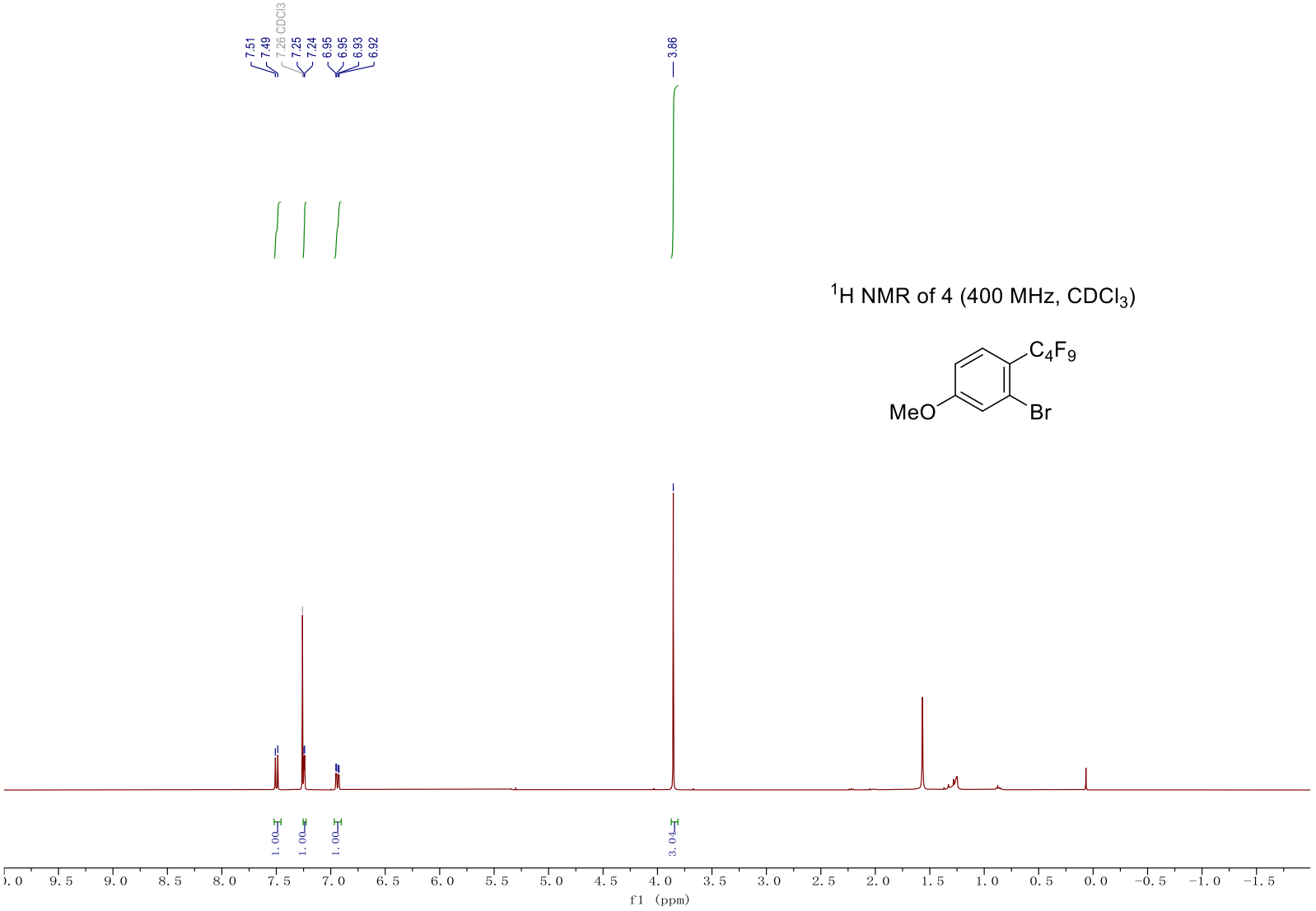




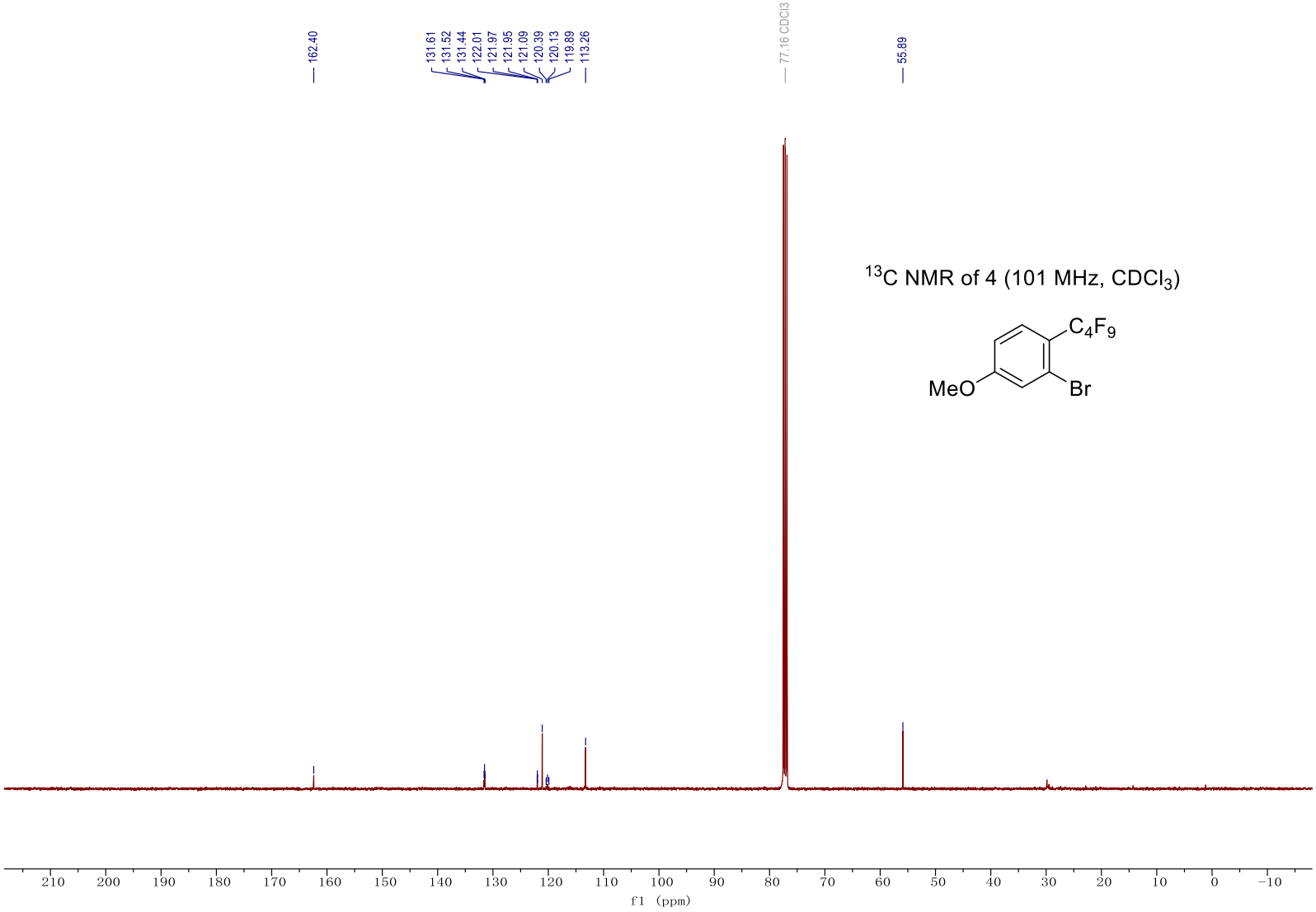
^{13}C NMR of 3 (101 MHz, $CDCl_3$)



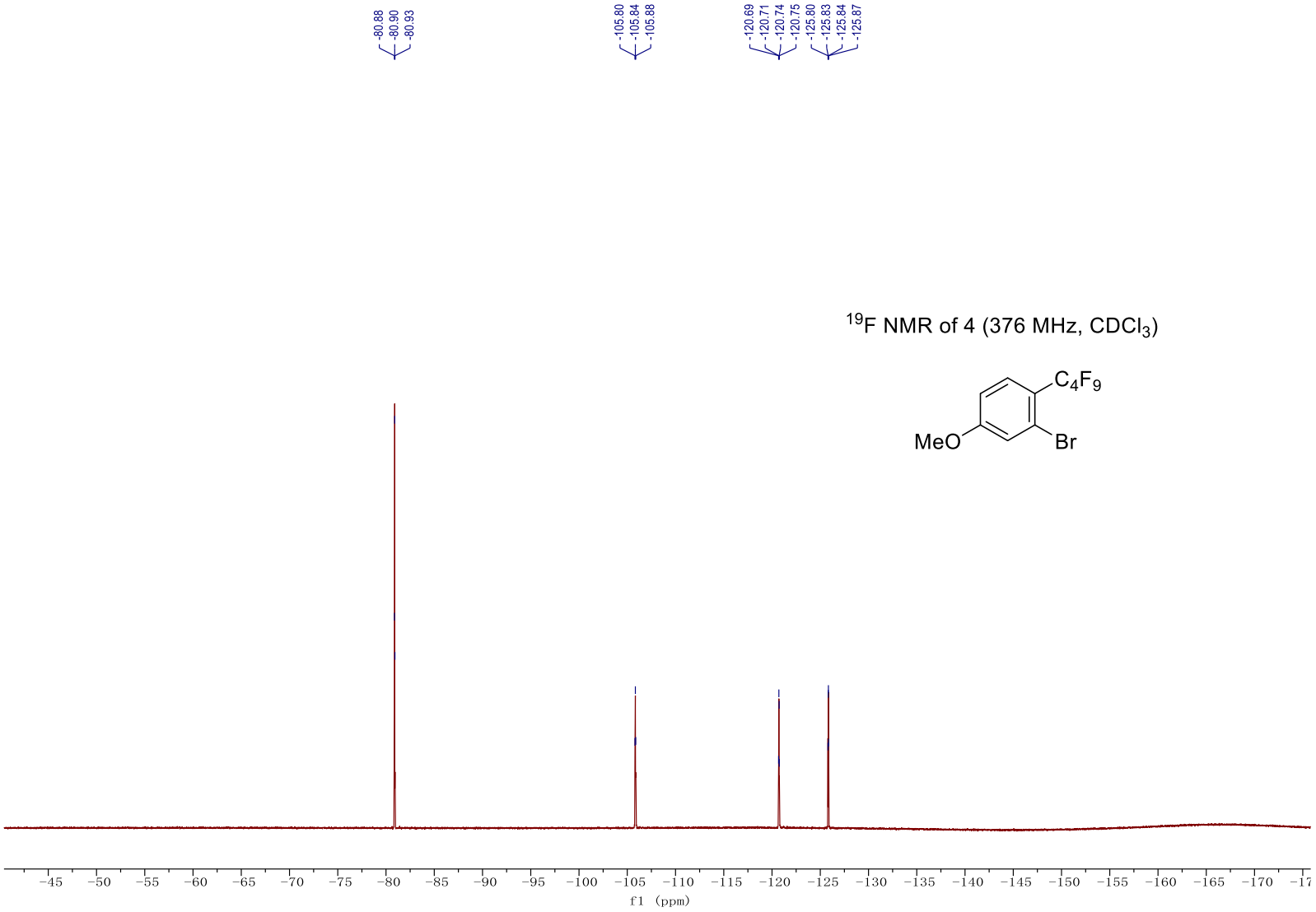
^{19}F NMR of 3 (376 MHz, $CDCl_3$)

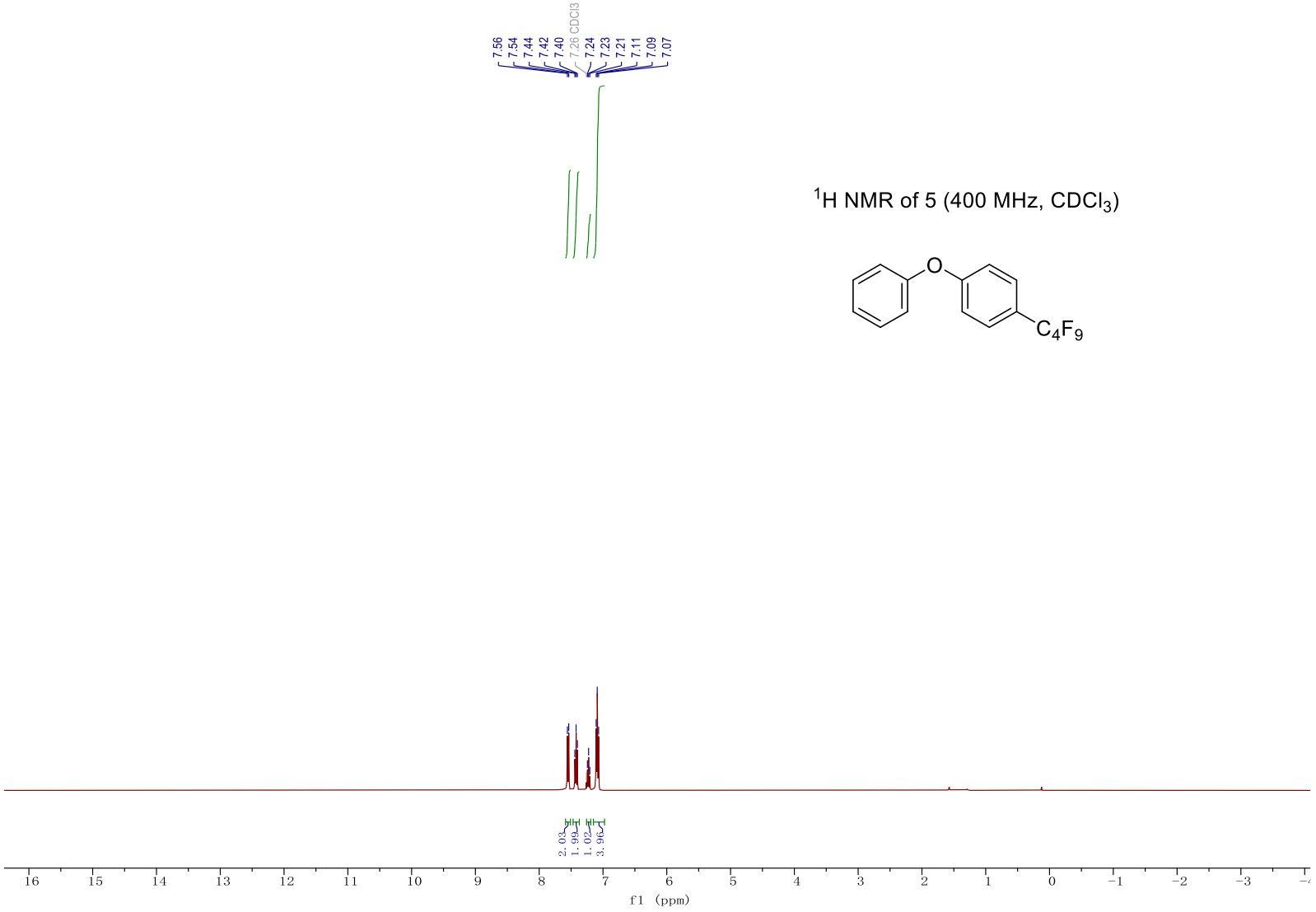


^{1}H NMR of 4 (400 MHz, $CDCl_3$)



^{13}C NMR of 4 (101 MHz, $CDCl_3$)

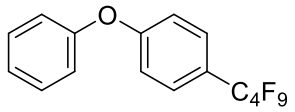

-80.88
-80.90
-80.93
-105.80
-105.84
-105.88
-120.69
-120.71
-120.74
-120.75
-125.80
-125.83
-125.84
-125.87
^{19}F NMR of 4 (376 MHz, $CDCl_3$)
C_4F_9
MeO
Br
−45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155 −160 −165 −170 −17
f1 (ppm)

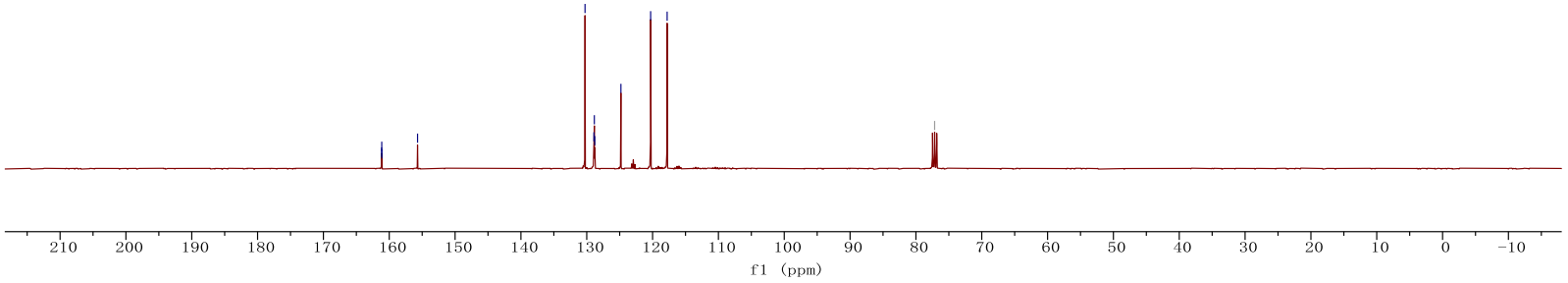


^{1}H NMR of 5 (400 MHz, $CDCl_3$)

161.16
161.14
161.12
155.70
130.26
128.91
128.85
128.78
124.81
120.30
117.79
77.16 CDCl3

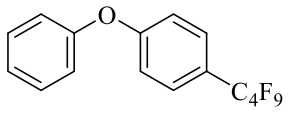
^{13}C NMR of 5 (101 MHz, $CDCl_3$)

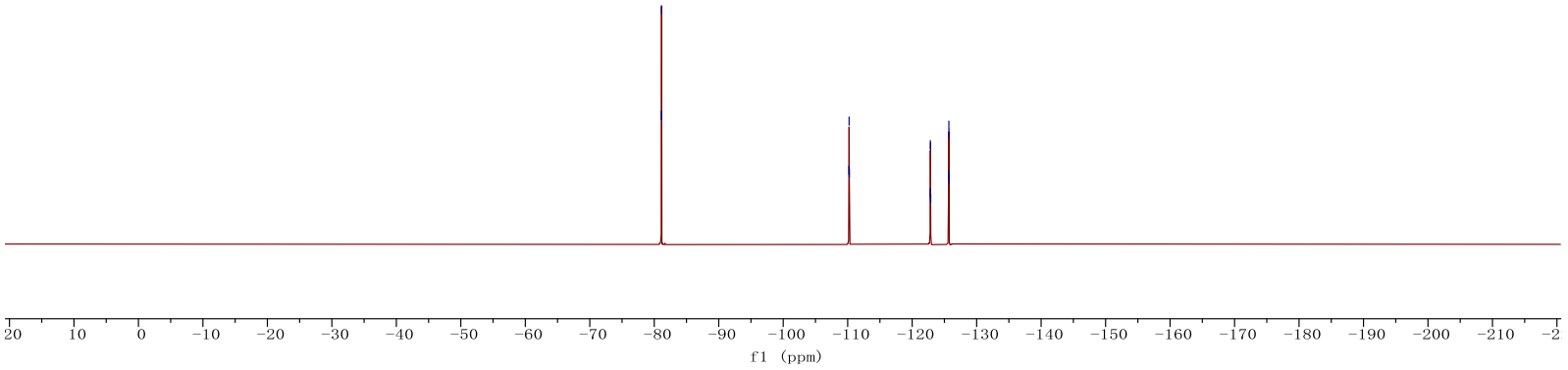


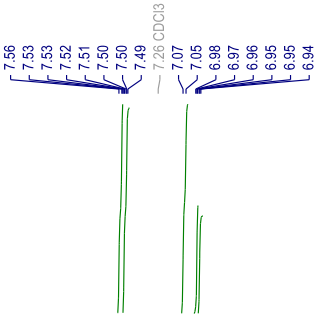


-81.11
-81.13
-81.16
-110.18
-110.22
-110.26
-122.80
-122.82
-122.85
-122.88
-125.66
-125.69
-125.71
-125.73

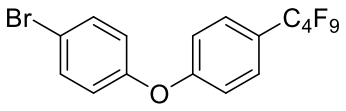
^{19}F NMR of 5 (376 MHz, $CDCl_3$)

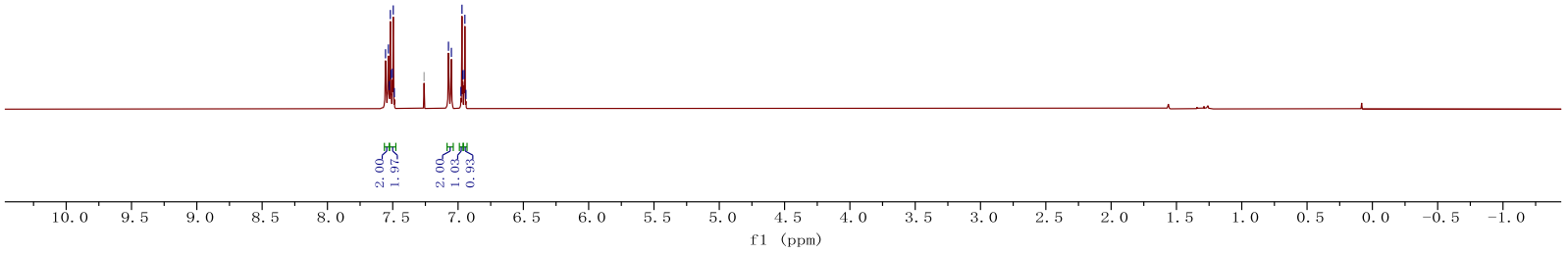


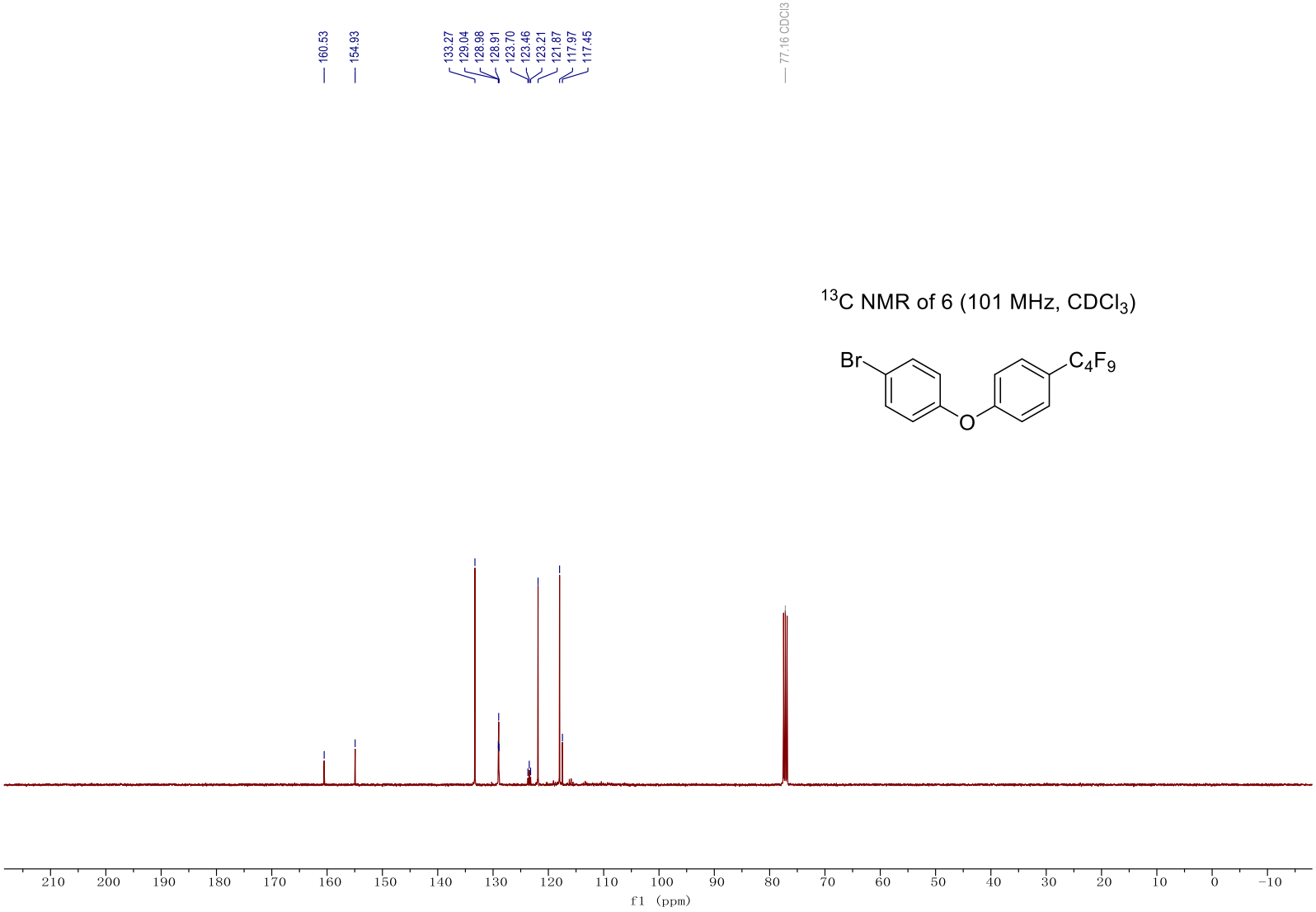




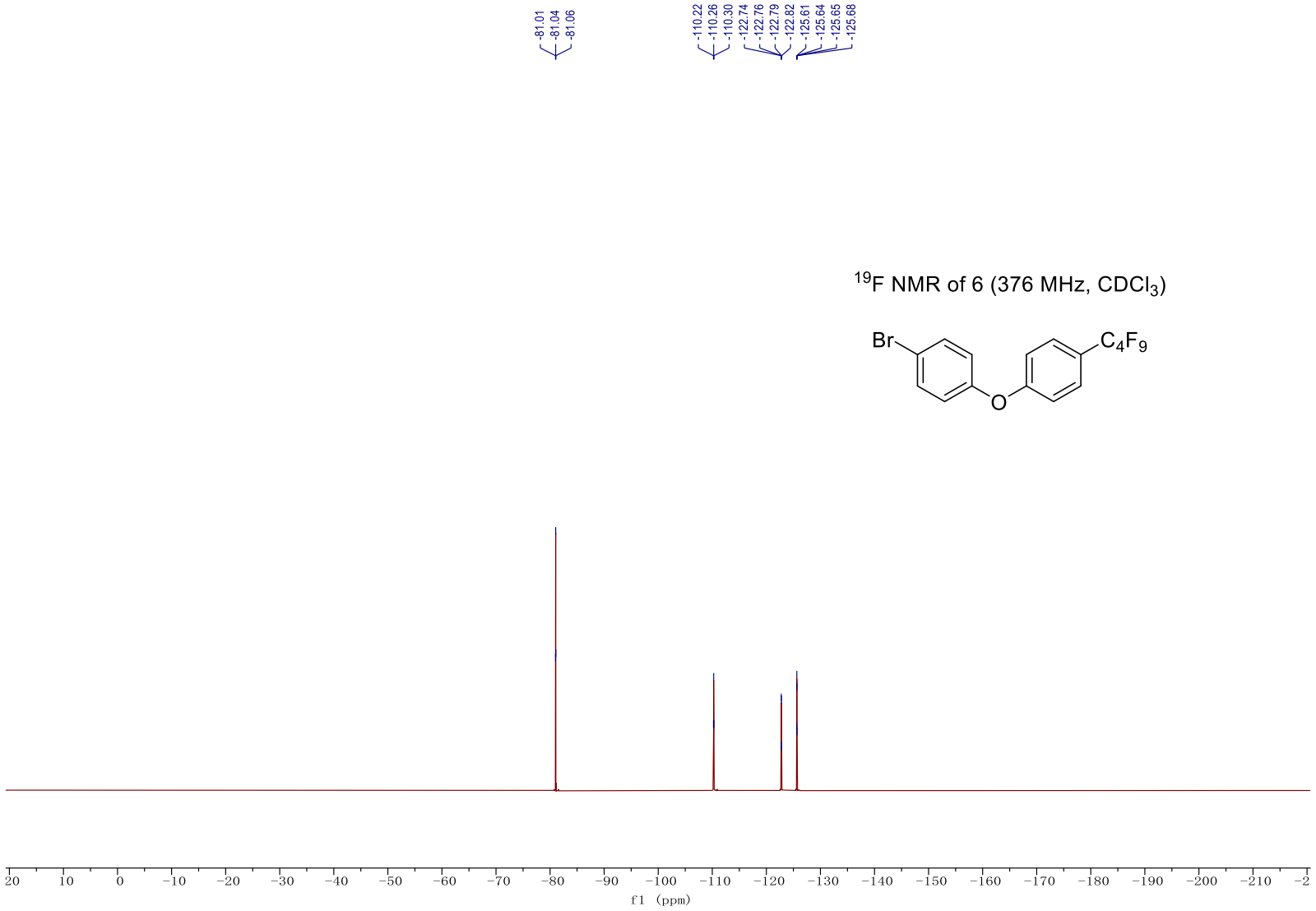
^{1}H NMR of 6 (400 MHz, $CDCl_3$)



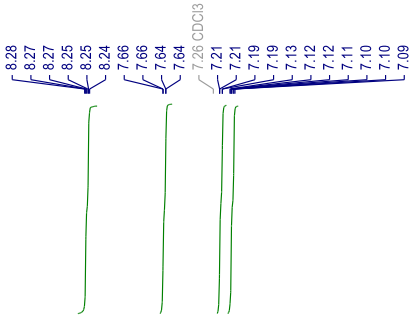




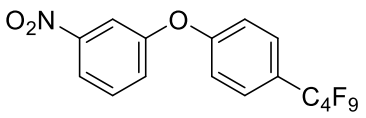
^{13}C NMR of 6 (101 MHz, $CDCl_3$)

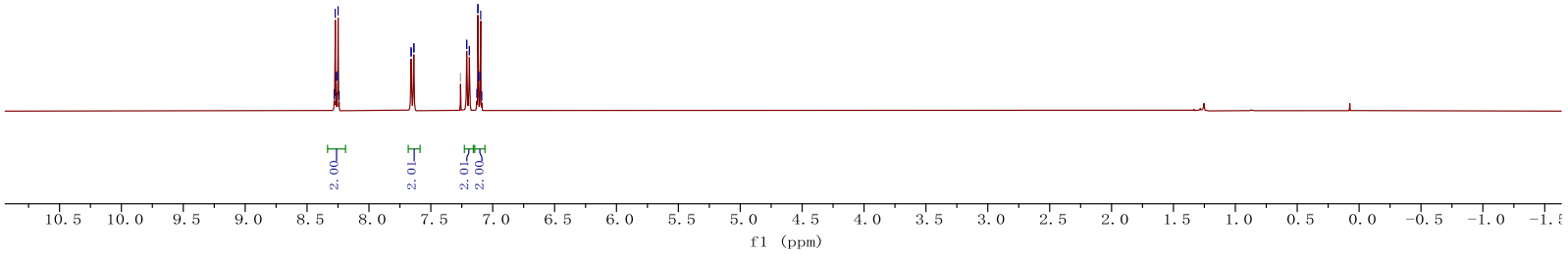


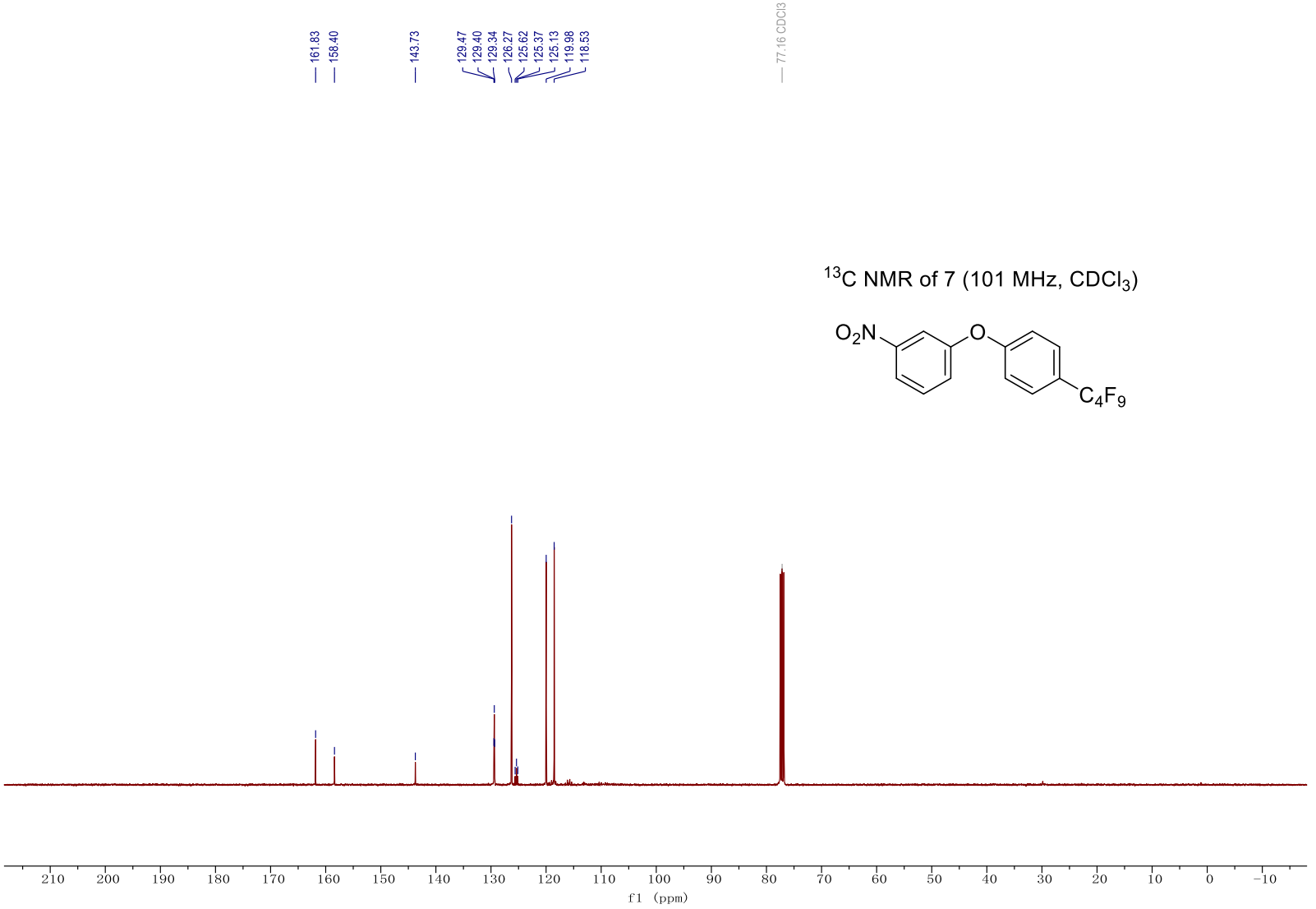
^{19}F NMR of 6 (376 MHz, $CDCl_3$)



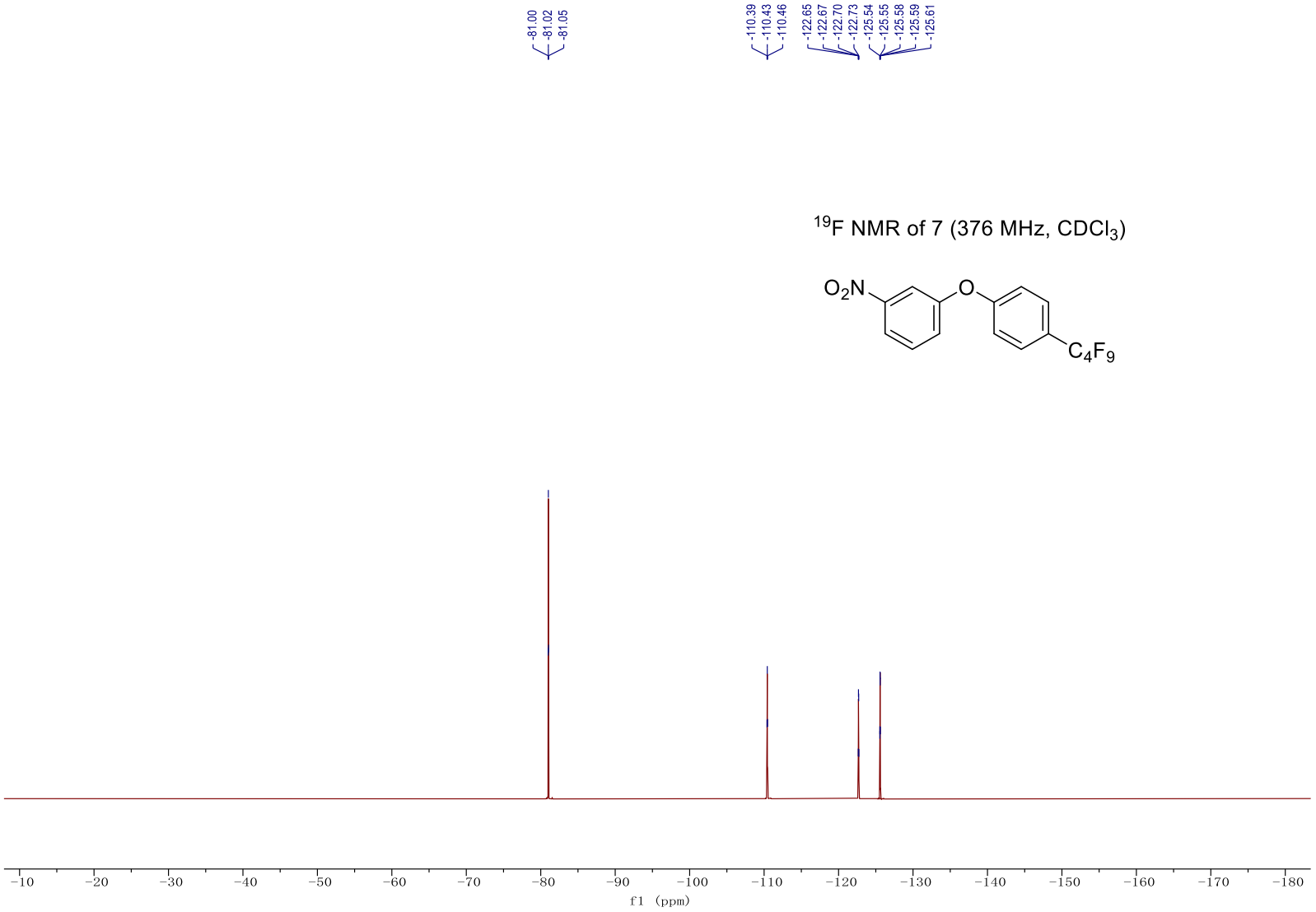
^{1}H NMR of 7 (400 MHz, $CDCl_3$)



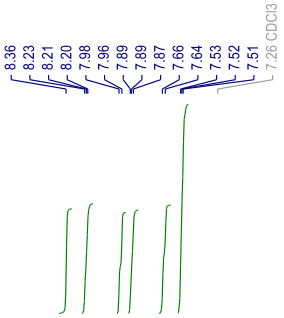




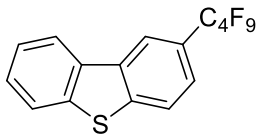
^{13}C NMR of 7 (101 MHz, $CDCl_3$)

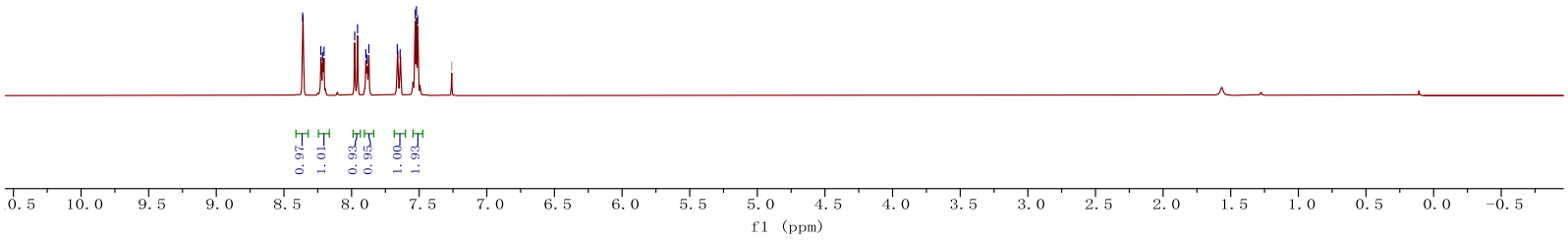


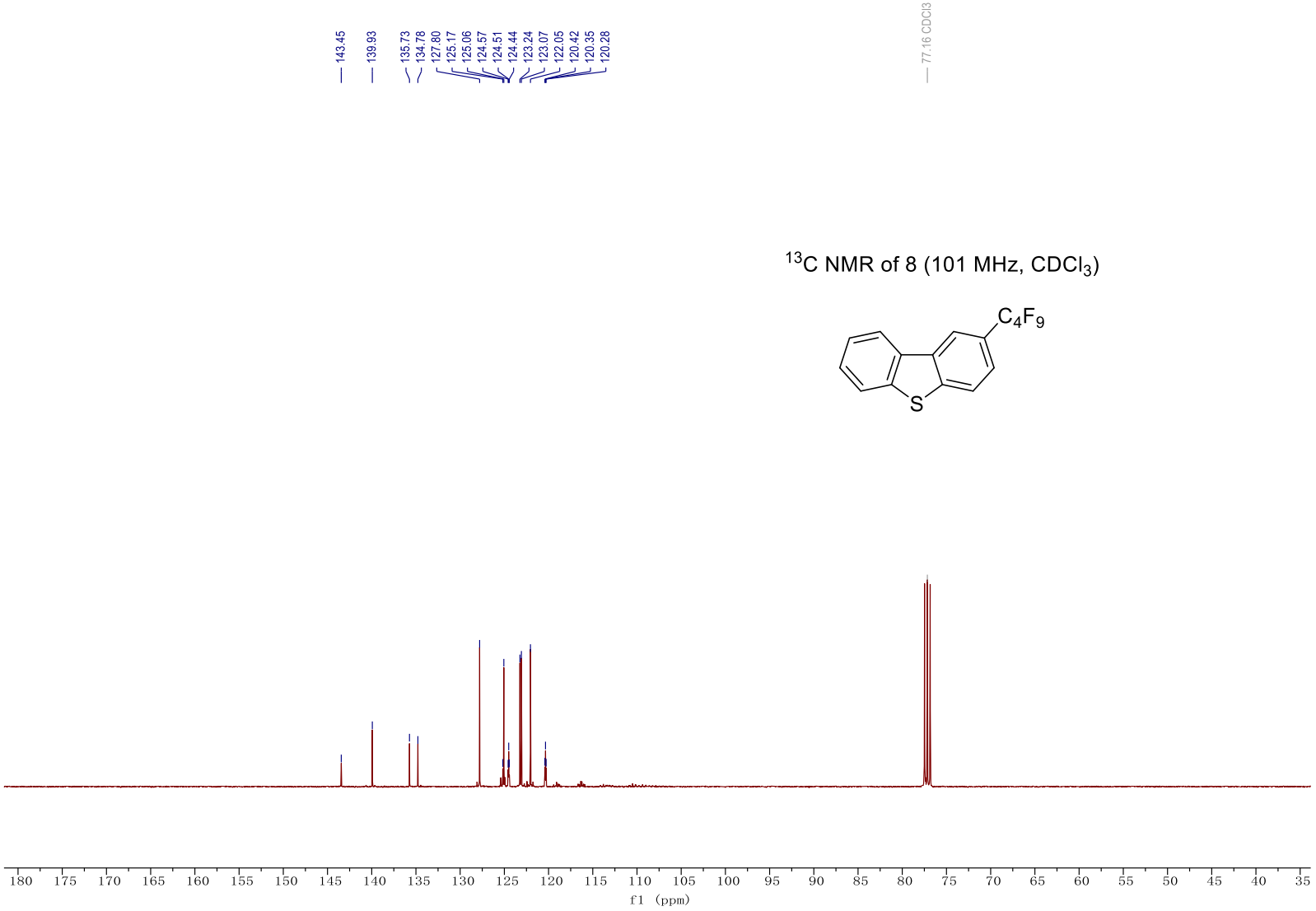
^{19}F NMR of 7 (376 MHz, $CDCl_3$)

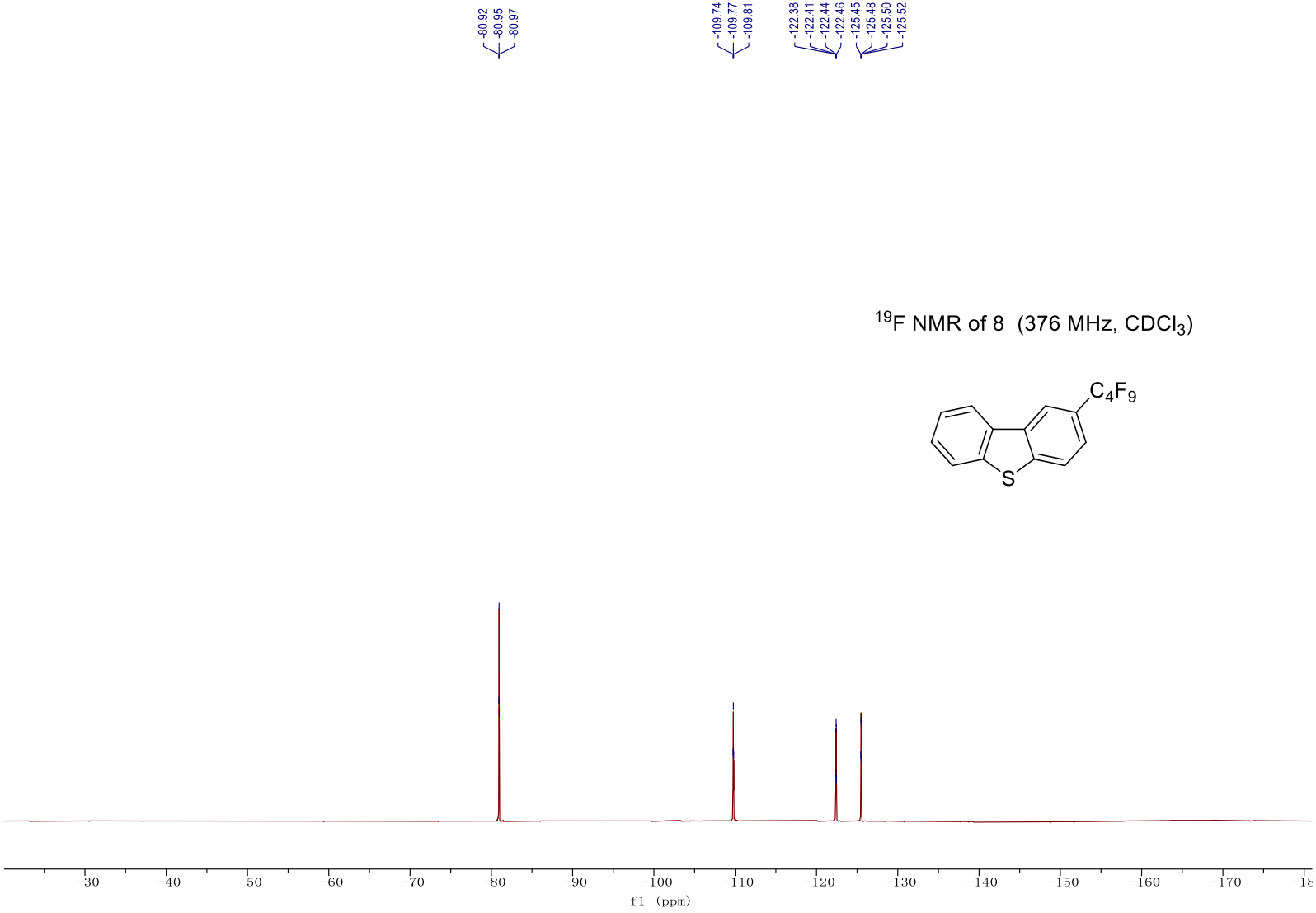


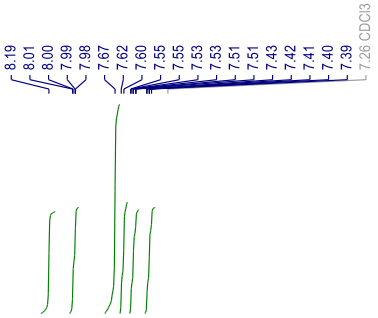
^{1}H NMR of 8 (400 MHz, $CDCl_3$)



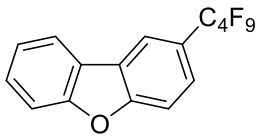


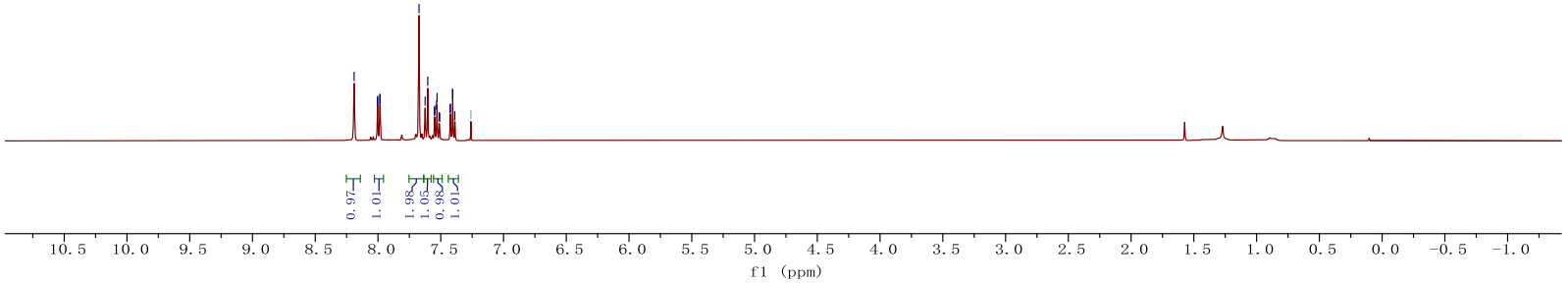

143.45
139.93
135.73
134.78
127.80
125.17
125.06
124.57
124.51
124.44
123.24
123.07
122.05
120.42
120.35
120.28
77.16 CDCl3
^{13}C NMR of 8 (101 MHz, $CDCl_3$)
C_4F_9
S
180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)

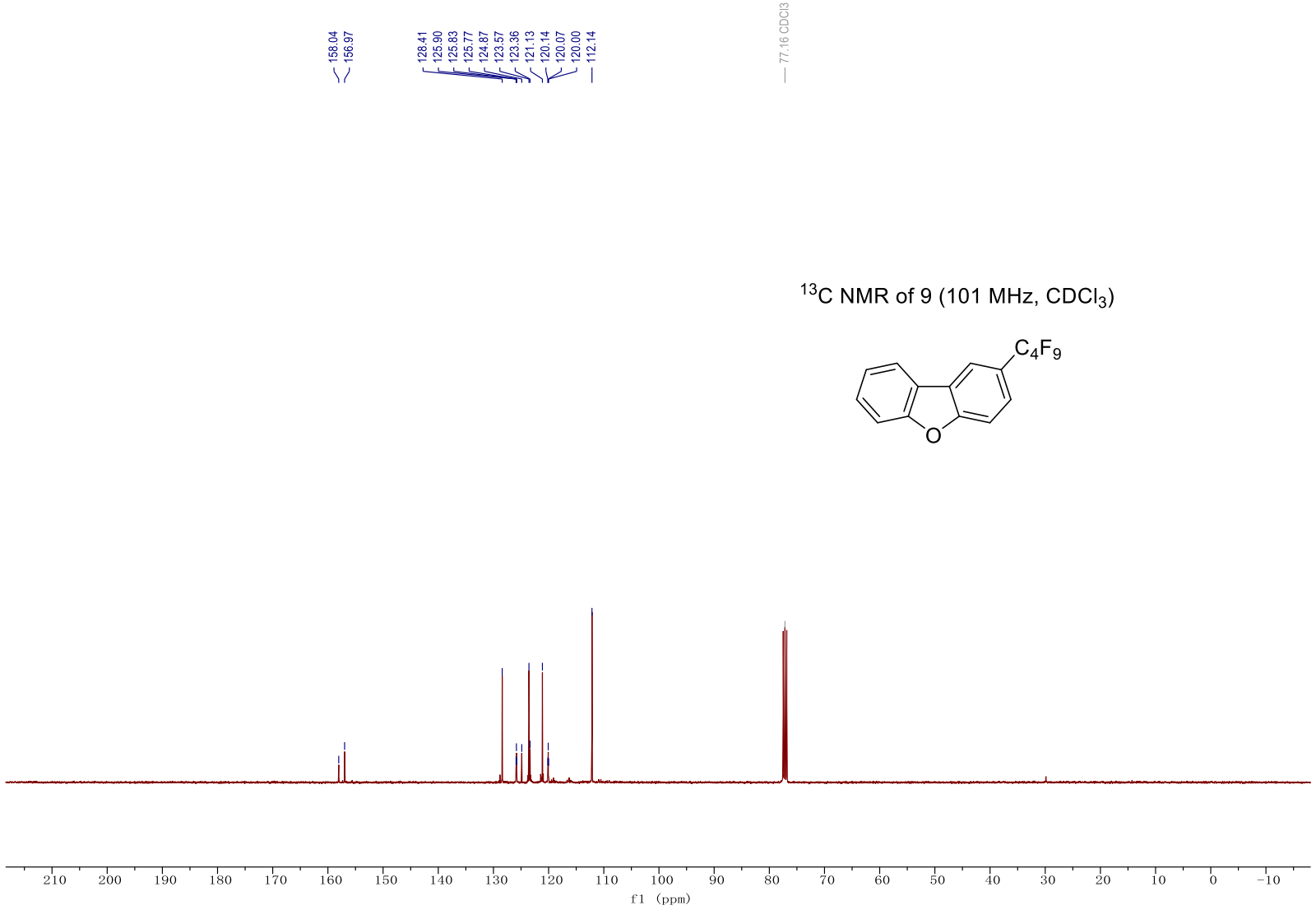

-80.92
-80.95
-80.97
-109.74
-109.77
-109.81
-122.38
-122.41
-122.44
-122.46
-125.45
-125.48
-125.50
-125.52
^{19}F NMR of 8 (376 MHz, $CDCl_3$)
C_4F_9
S
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
f1 (ppm)



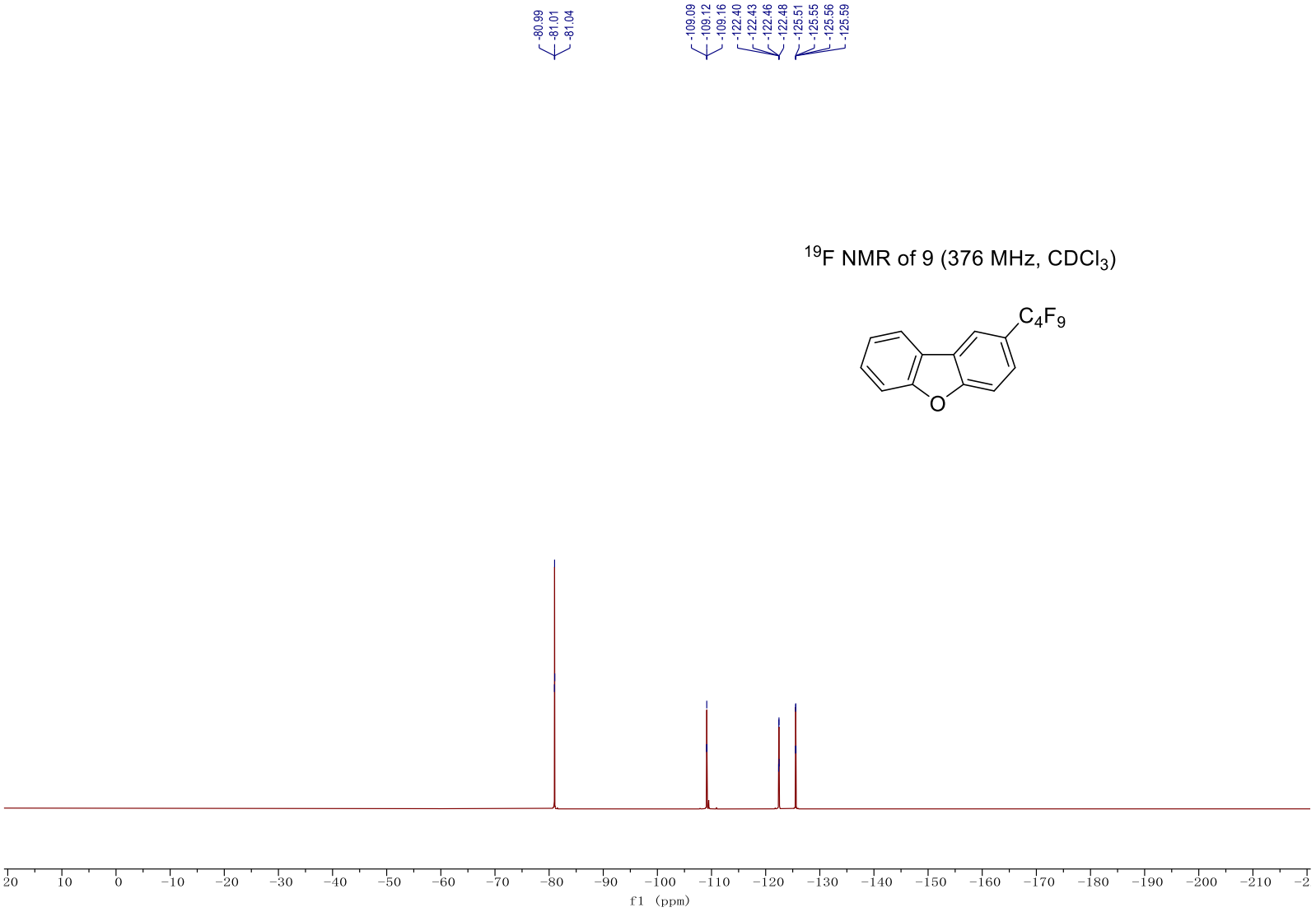
^{1}H NMR of 9 (400 MHz, $CDCl_3$)

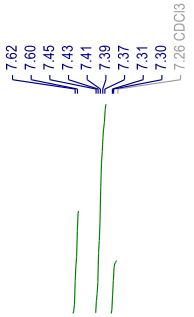




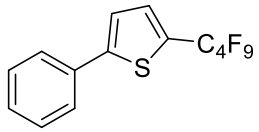


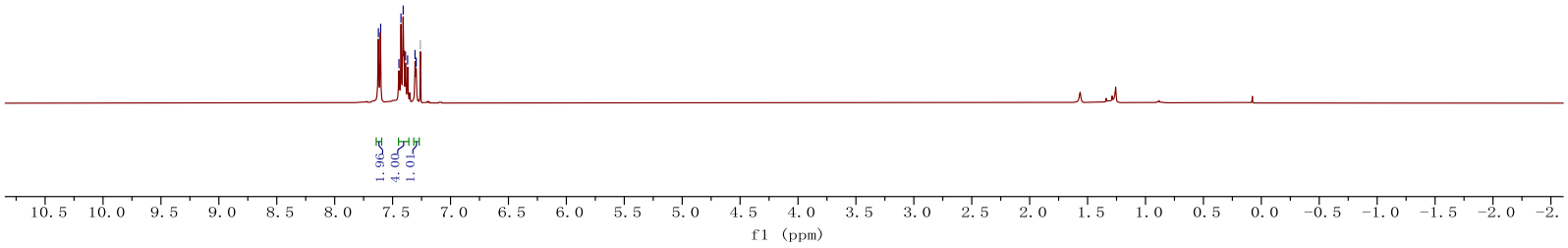
^{13}C NMR of 9 (101 MHz, $CDCl_3$)

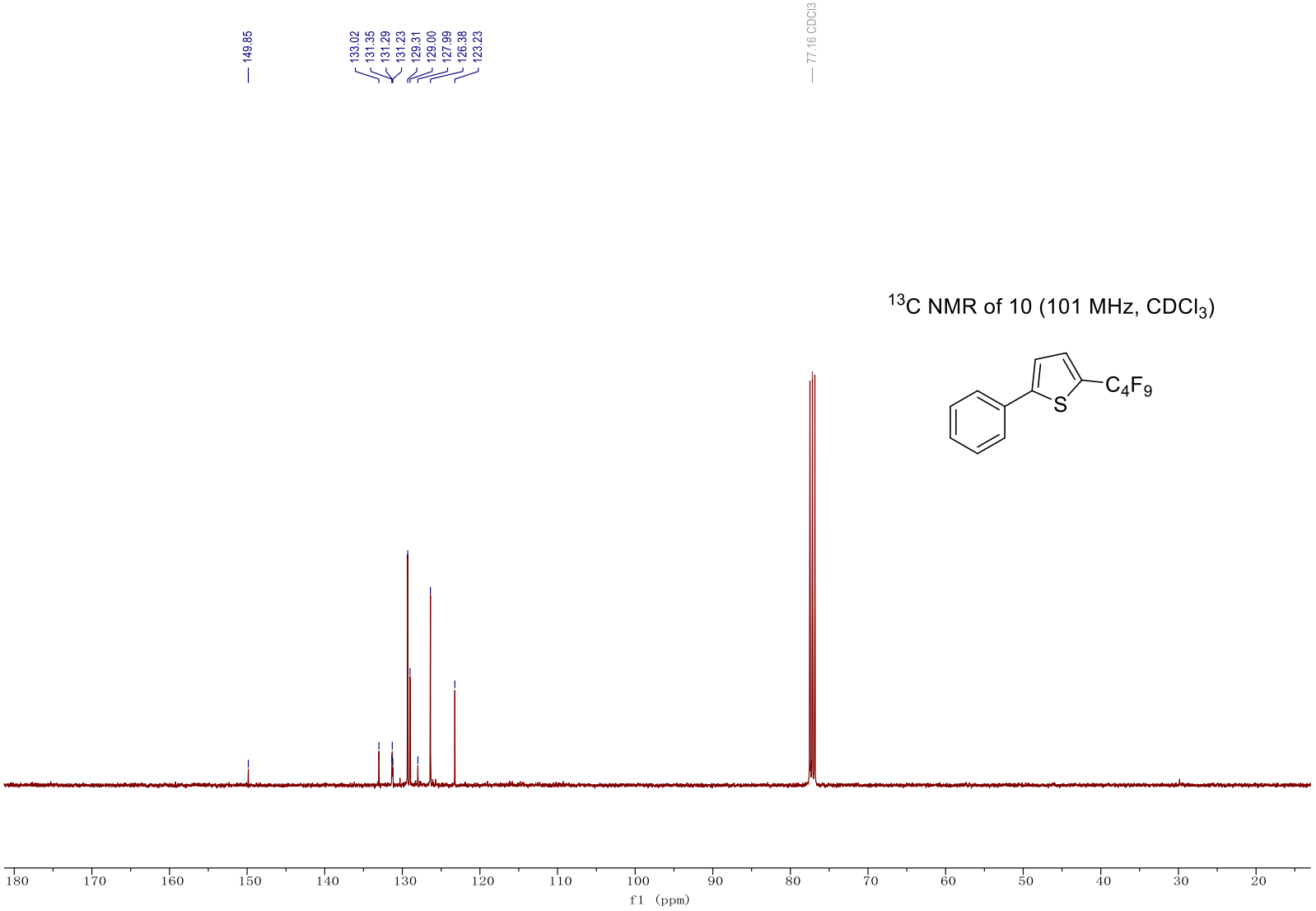

-80.99
-81.01
-81.04
-109.09
-109.12
-109.16
-122.40
-122.43
-122.46
-122.48
-125.51
-125.55
-125.56
-125.59
^{19}F NMR of 9 (376 MHz, $CDCl_3$)
C_4F_9
O
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

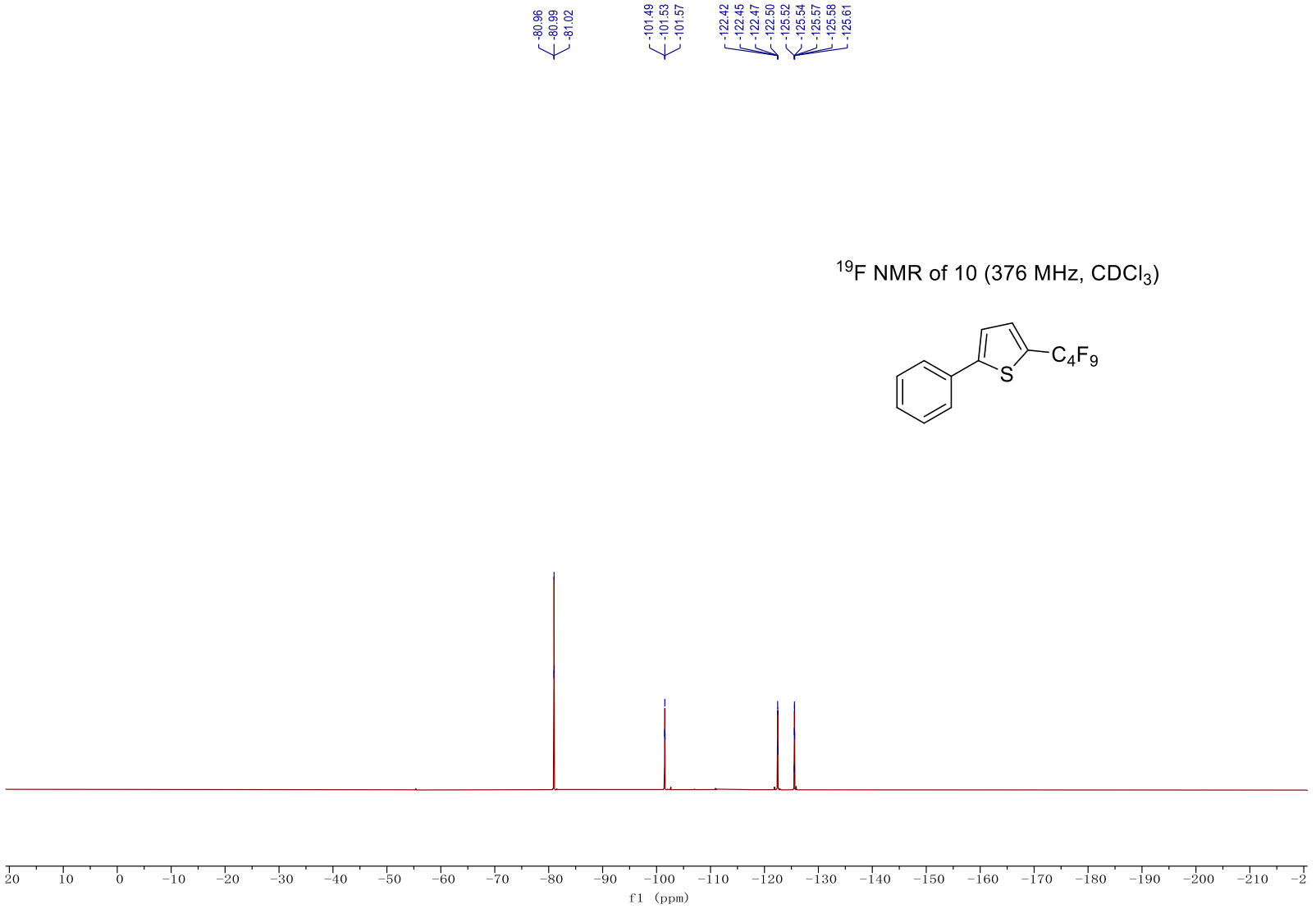


^{1}H NMR of 10 (400 MHz, $CDCl_3$)

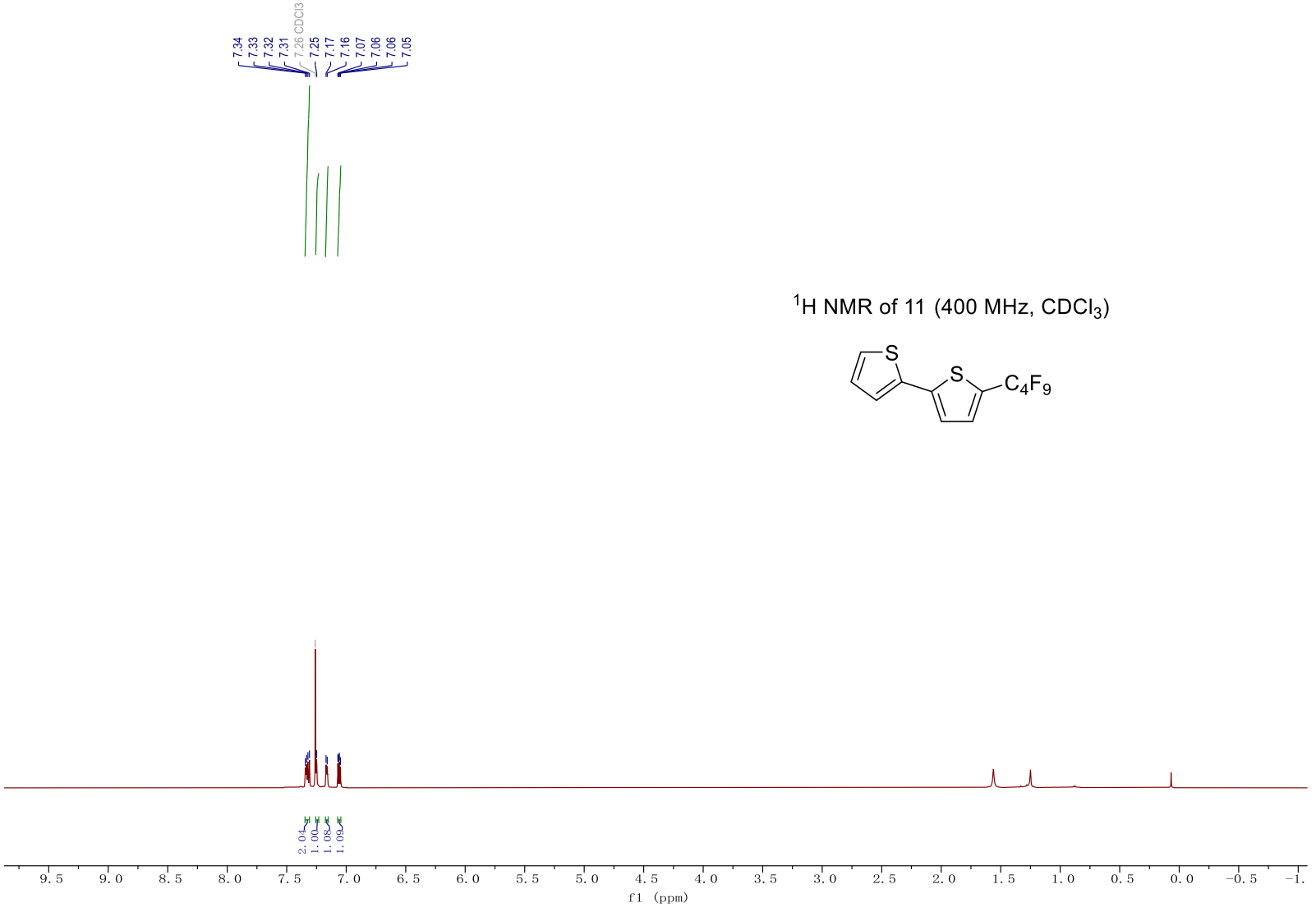




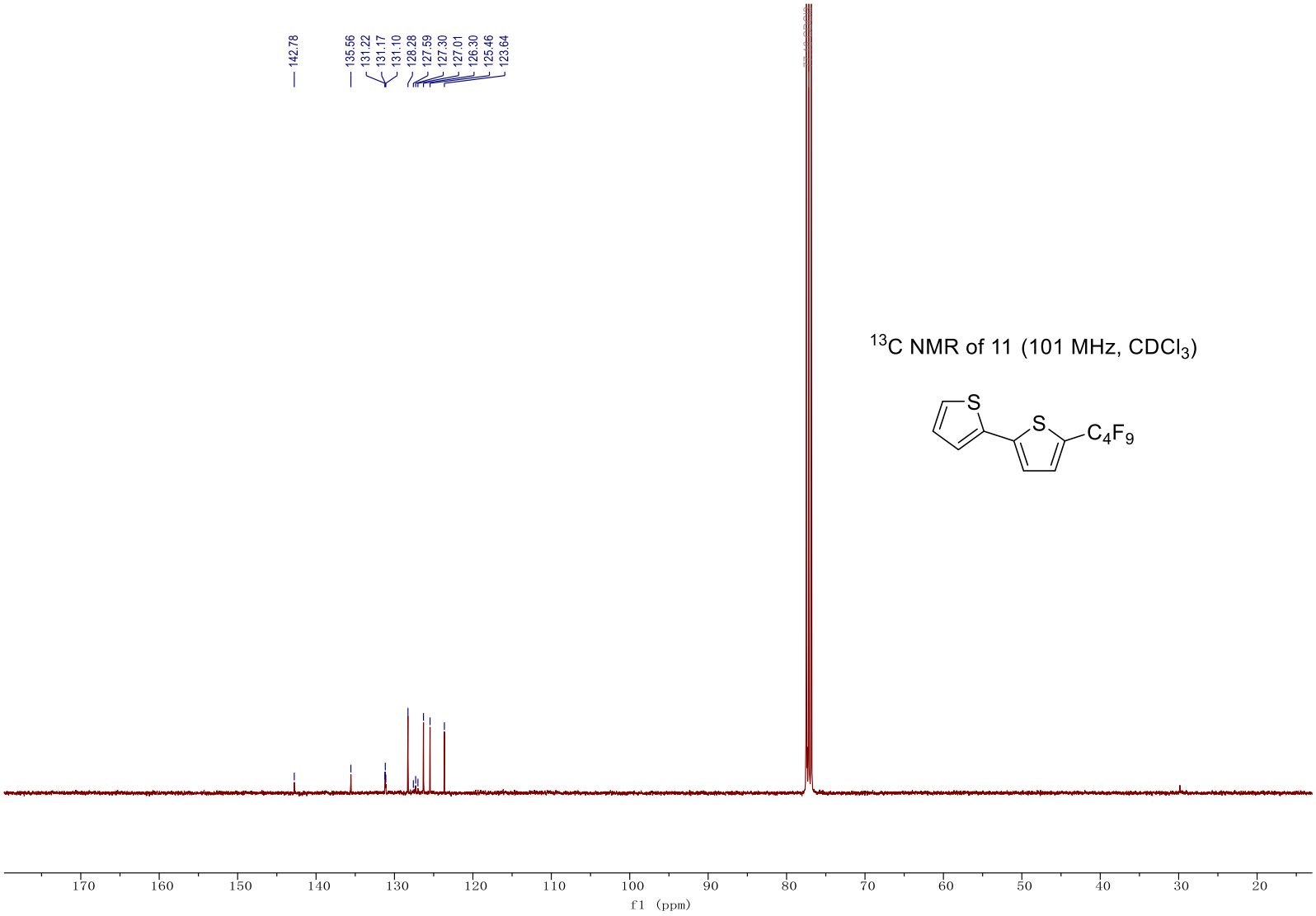

149.85
133.02
131.35
131.29
131.23
129.31
129.00
127.99
126.38
123.23
77.16 CDCl3
^{13}C NMR of 10 (101 MHz, $CDCl_3$)
C_4F_9
S
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)



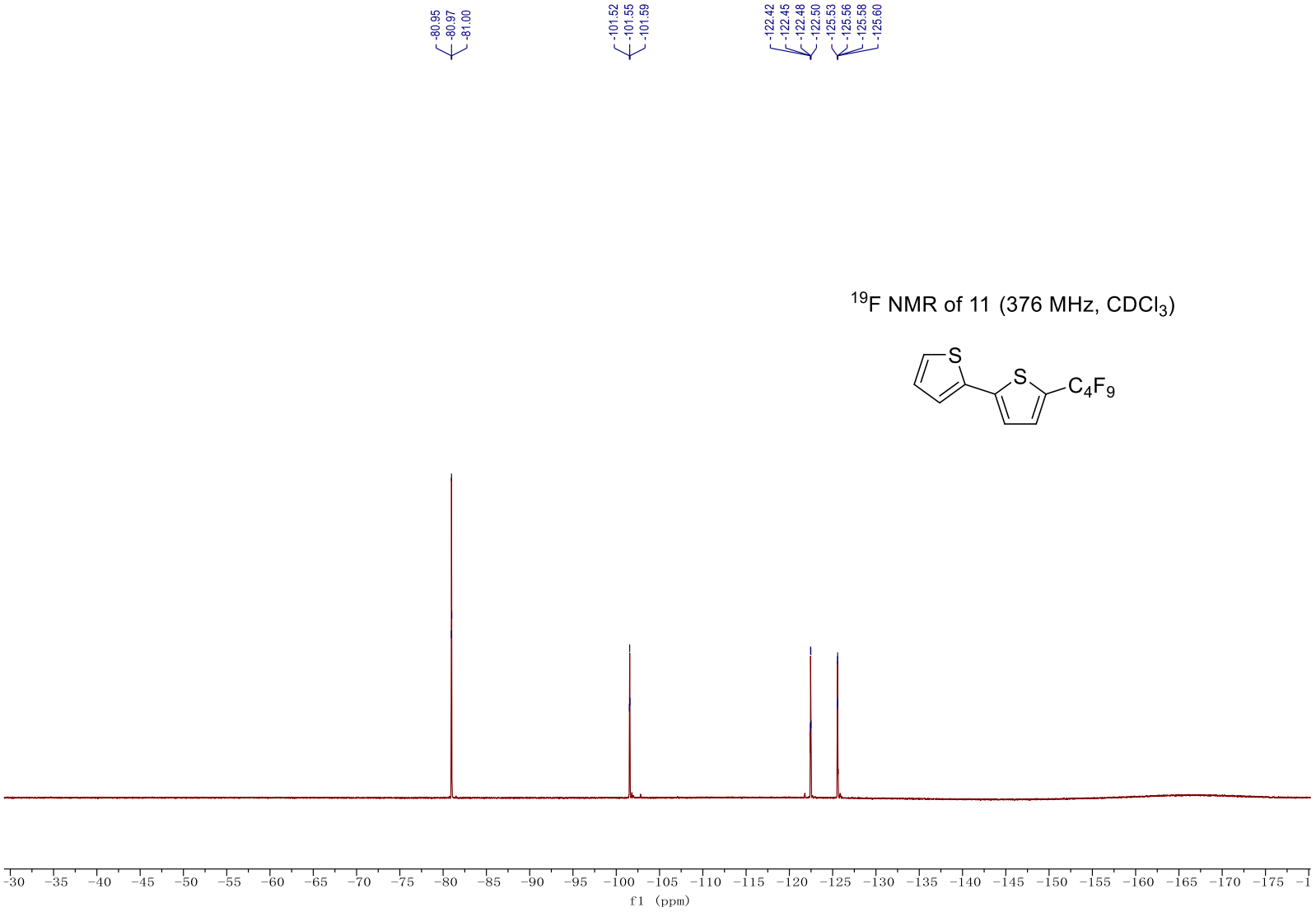
^{19}F NMR of 10 (376 MHz, $CDCl_3$)



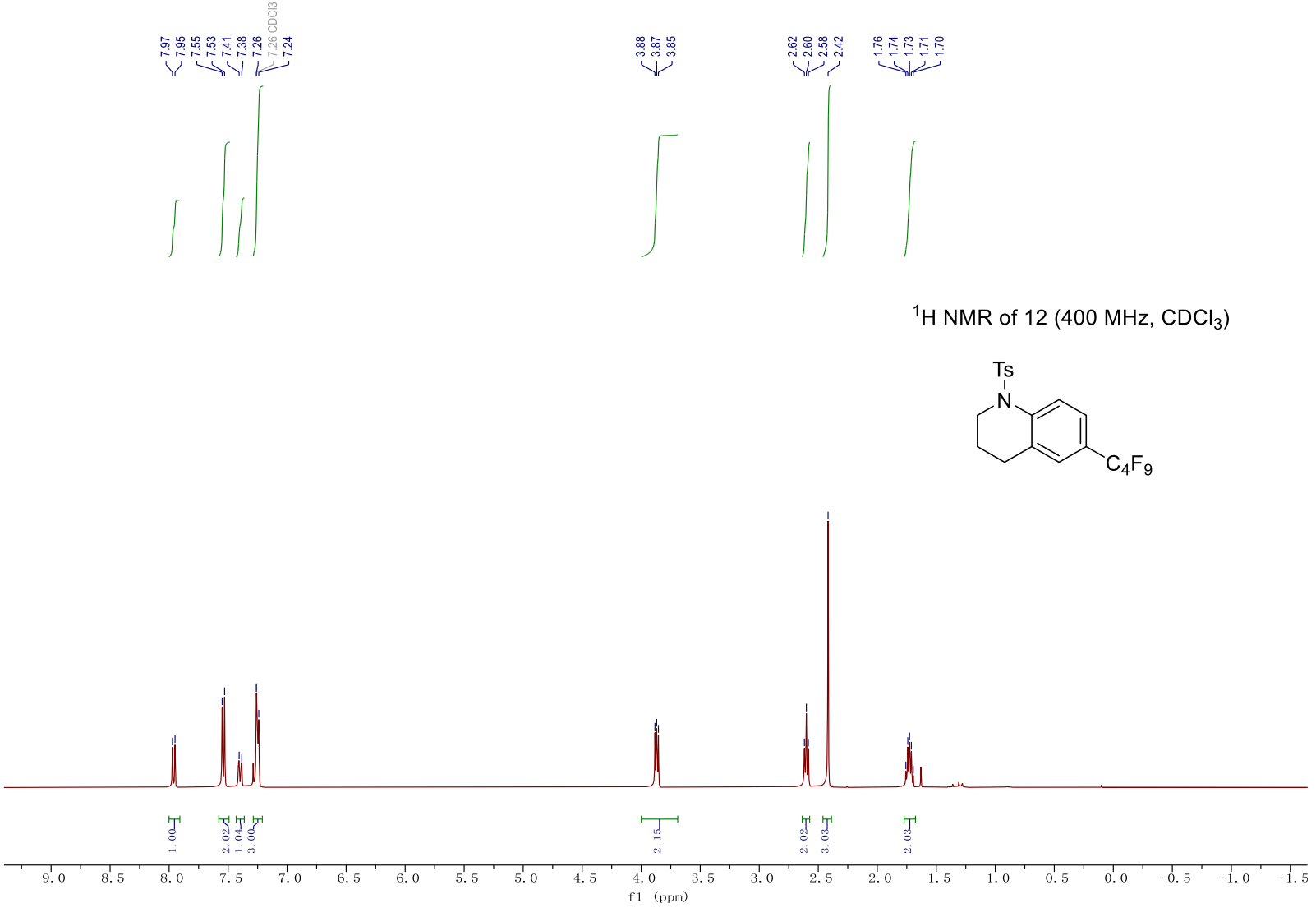
^{1}H NMR of 11 (400 MHz, $CDCl_3$)



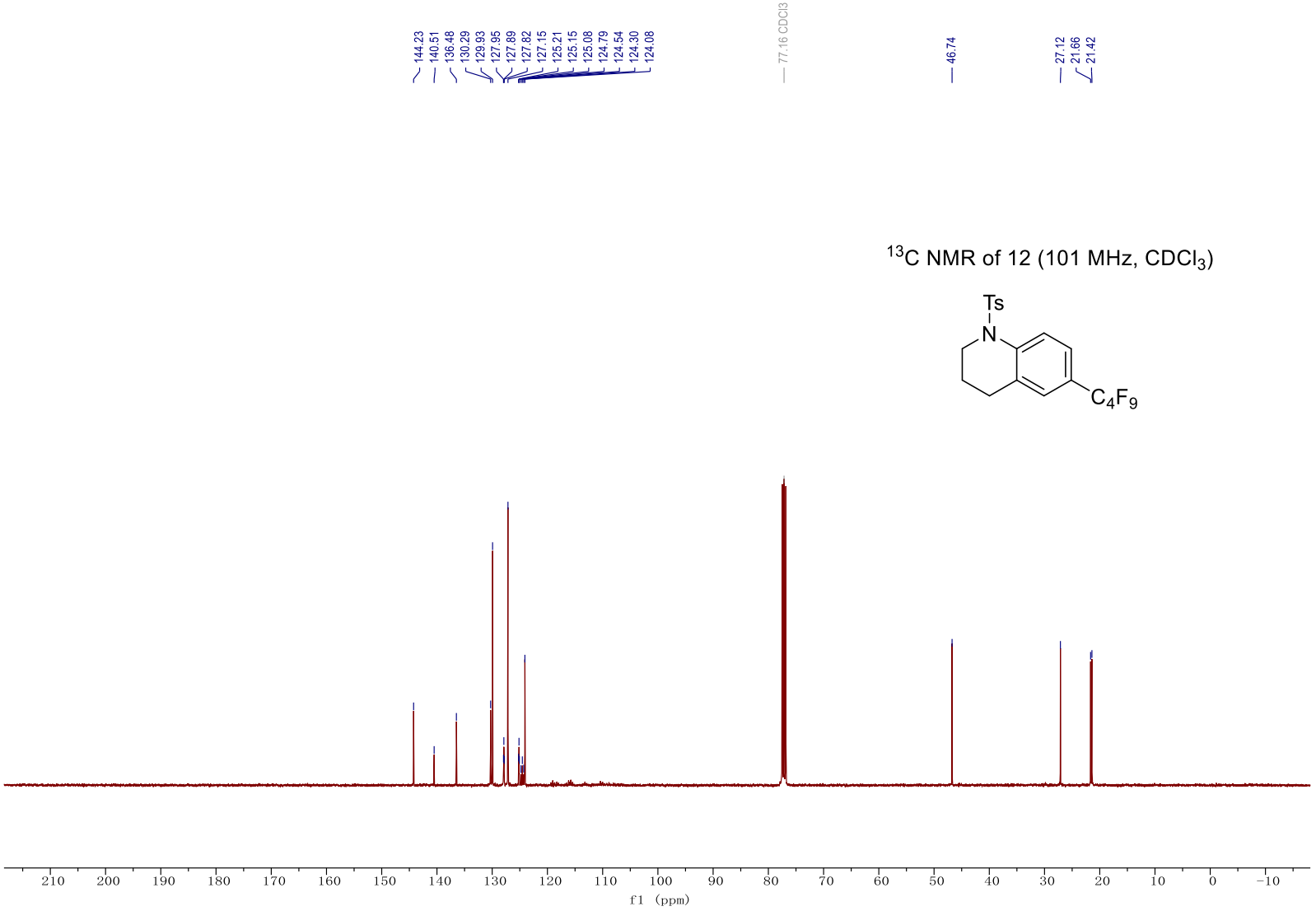
^{13}C NMR of 11 (101 MHz, $CDCl_3$)



^{19}F NMR of 11 (376 MHz, $CDCl_3$)

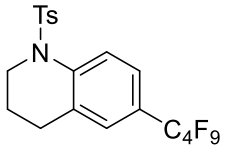


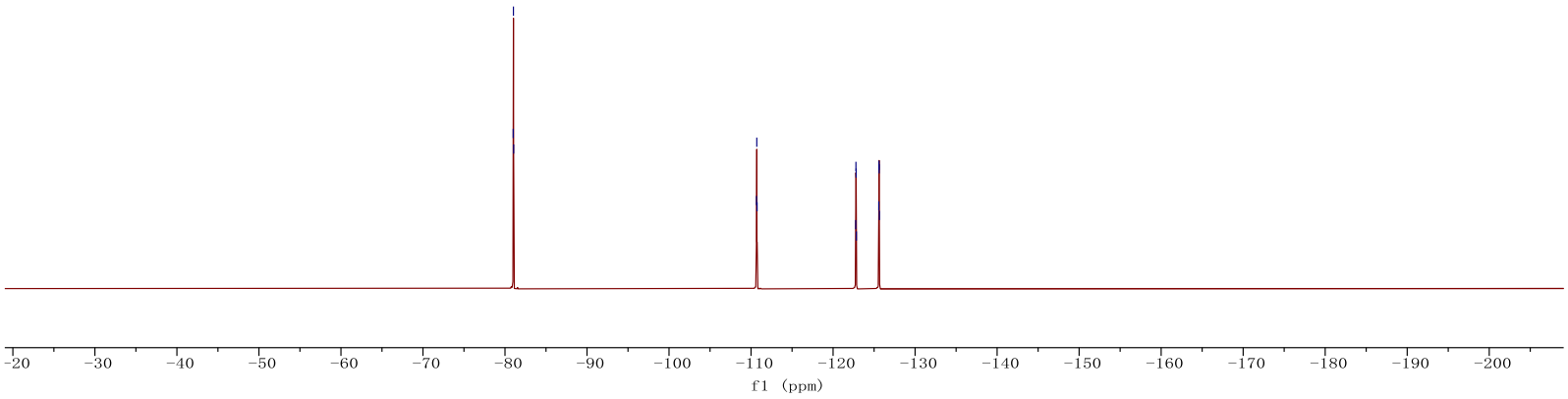
^{1}H NMR of 12 (400 MHz, $CDCl_3$)

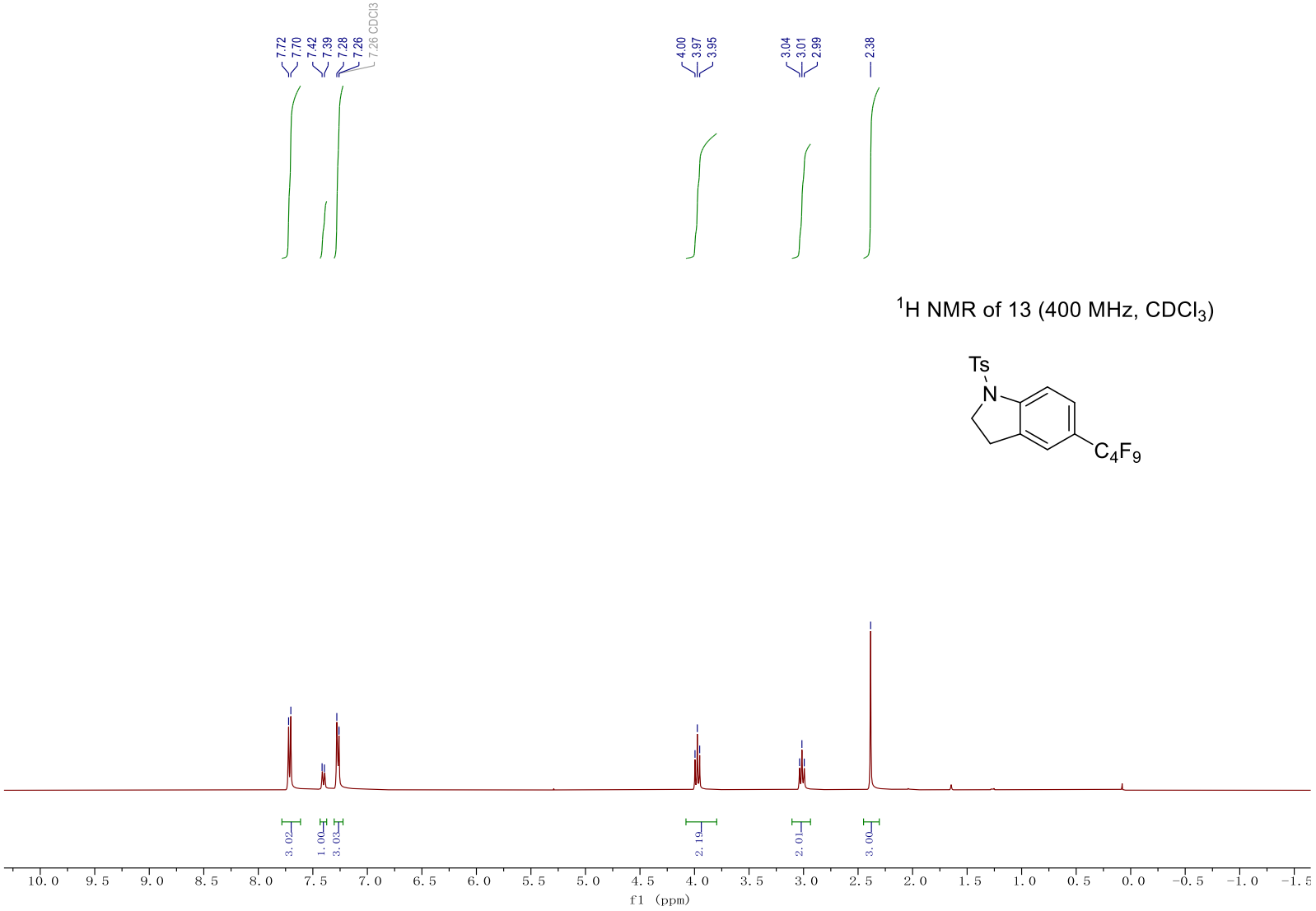


^{13}C NMR of 12 (101 MHz, $CDCl_3$)

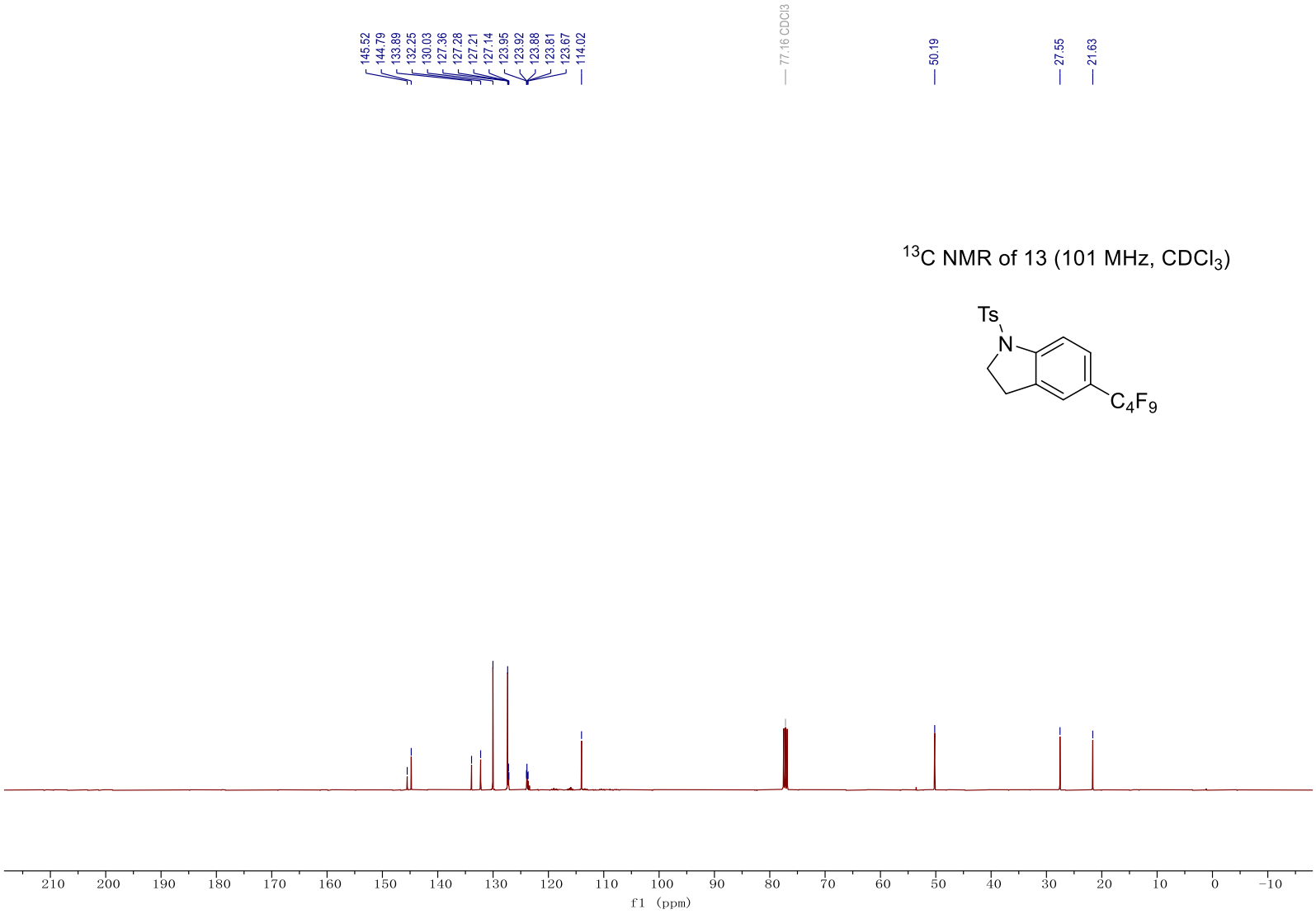
^{19}F NMR of 12 (376 MHz, $CDCl_3$)



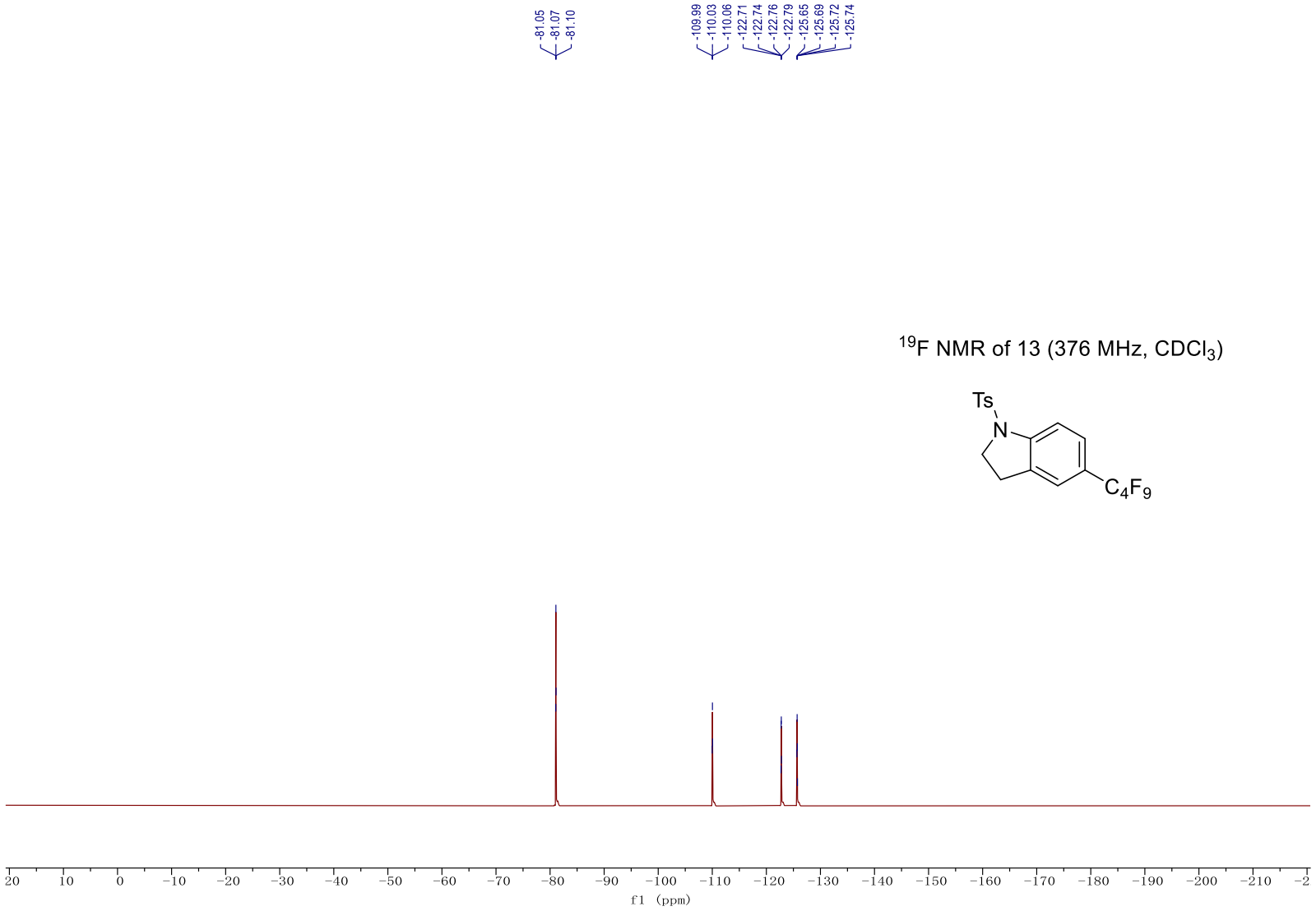




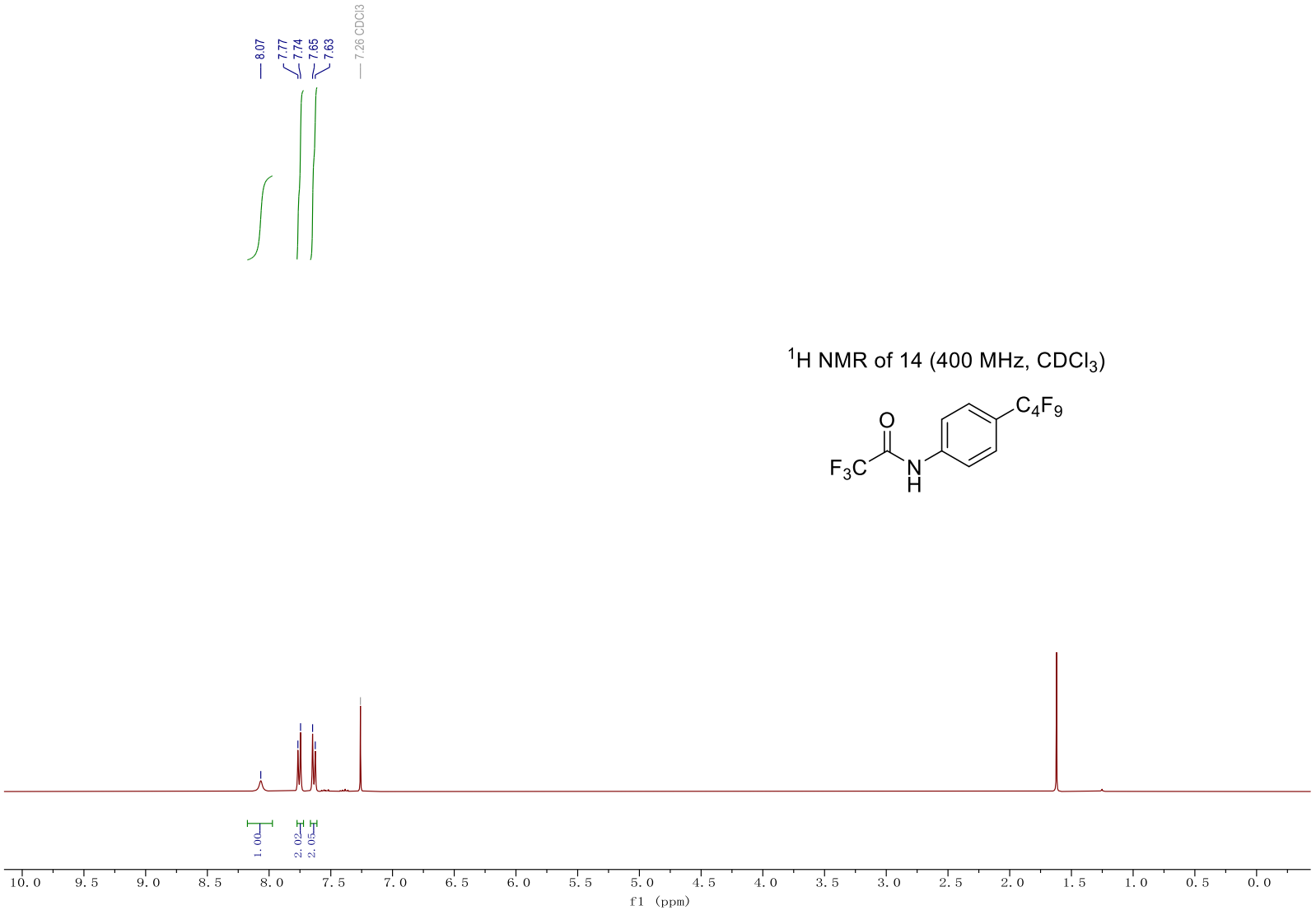
^{1}H NMR of 13 (400 MHz, $CDCl_3$)



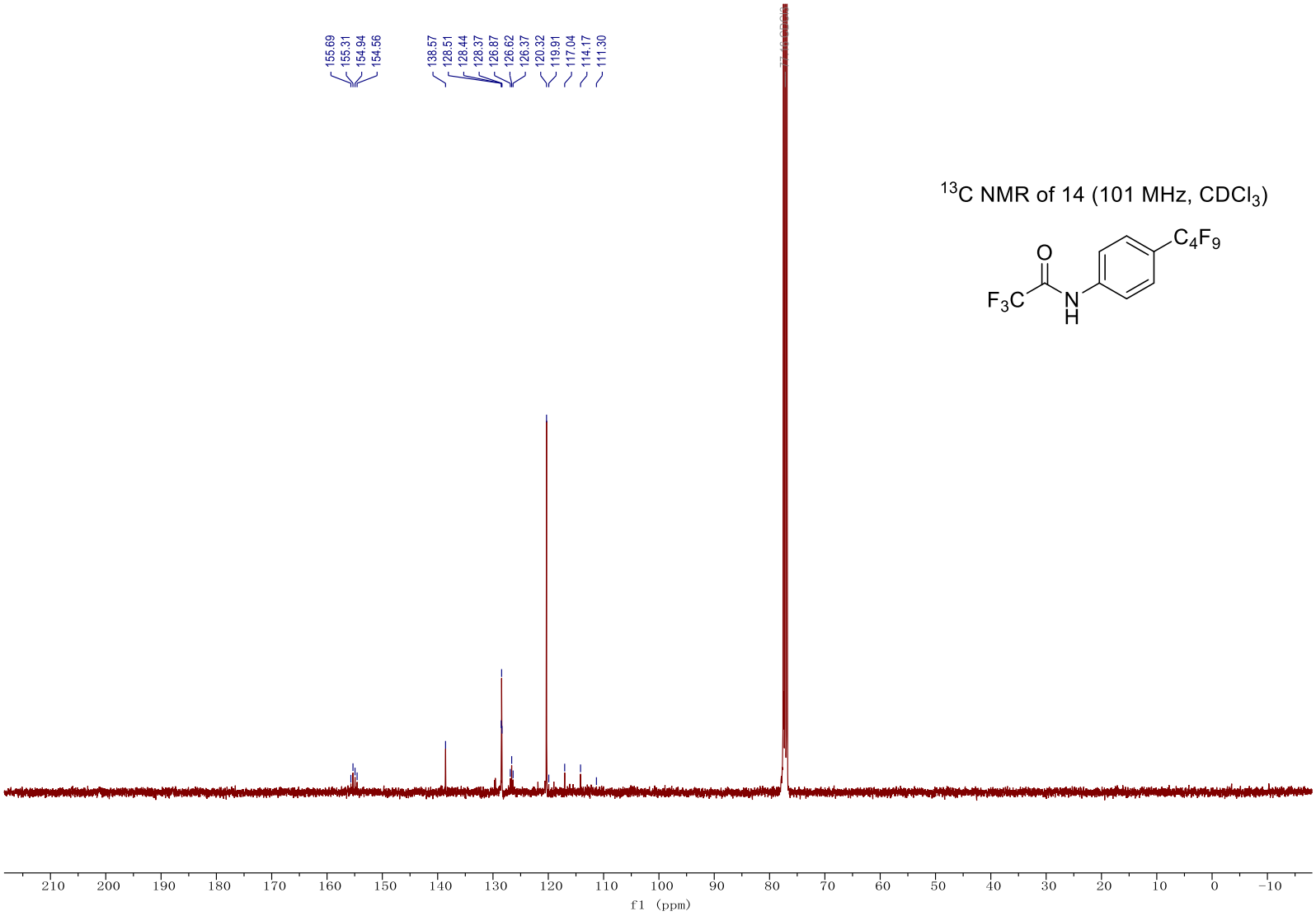
^{13}C NMR of 13 (101 MHz, $CDCl_3$)

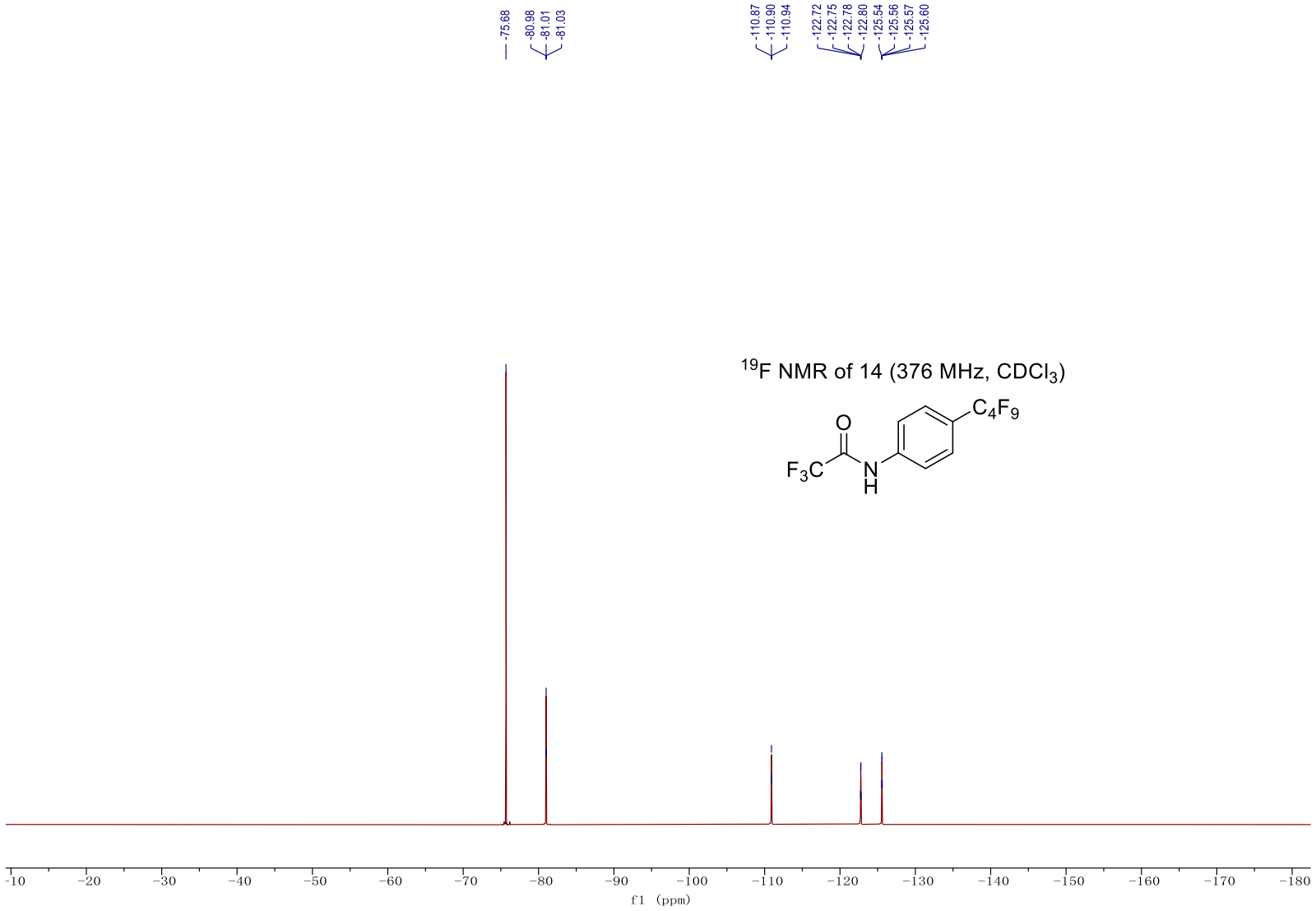


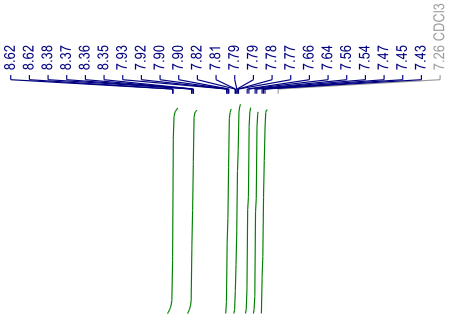
^{19}F NMR of 13 (376 MHz, $CDCl_3$)



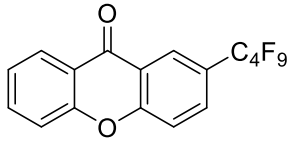
^{1}H NMR of 14 (400 MHz, $CDCl_3$)

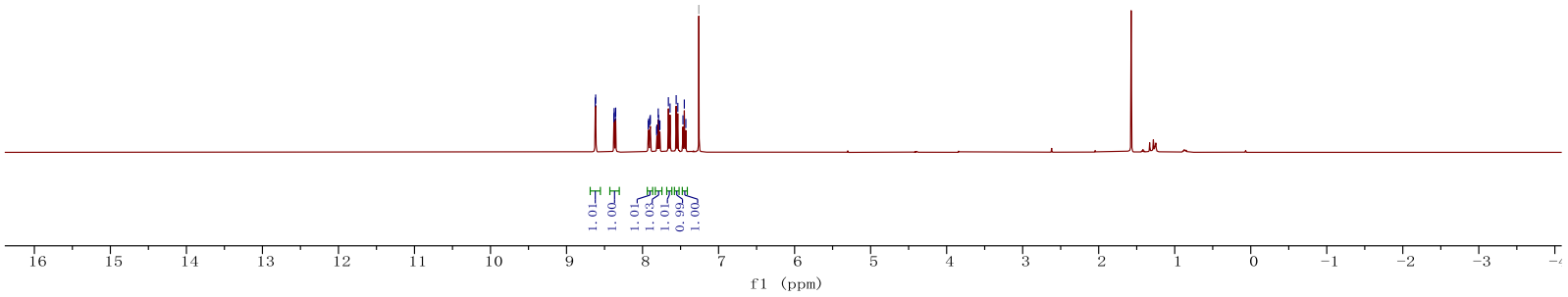

155.69
155.31
154.94
154.56
138.57
128.51
128.44
128.37
126.87
126.62
126.37
120.32
119.91
117.04
114.17
111.30
77.46
77.04
76.62
^{13}C NMR of 14 (101 MHz, $CDCl_3$)
C_4F_9
O
F_3C
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

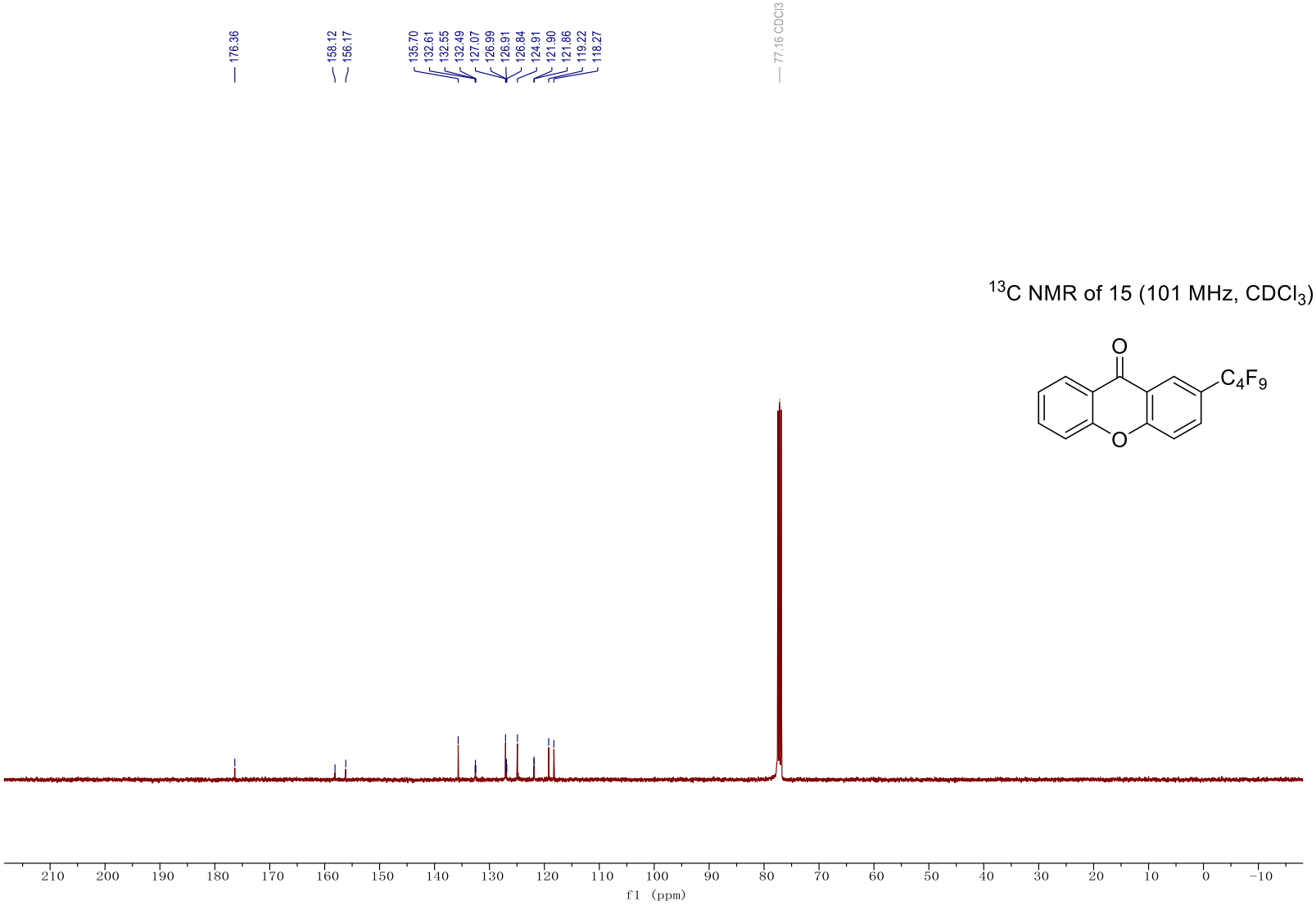

-75.68
-80.98
-81.01
-81.03
-110.87
-110.90
-110.94
-122.72
-122.75
-122.78
-122.80
-125.54
-125.56
-125.57
-125.60
^{19}F NMR of 14 (376 MHz, $CDCl_3$)
C_4F_9
O
F_3C
N
H
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)



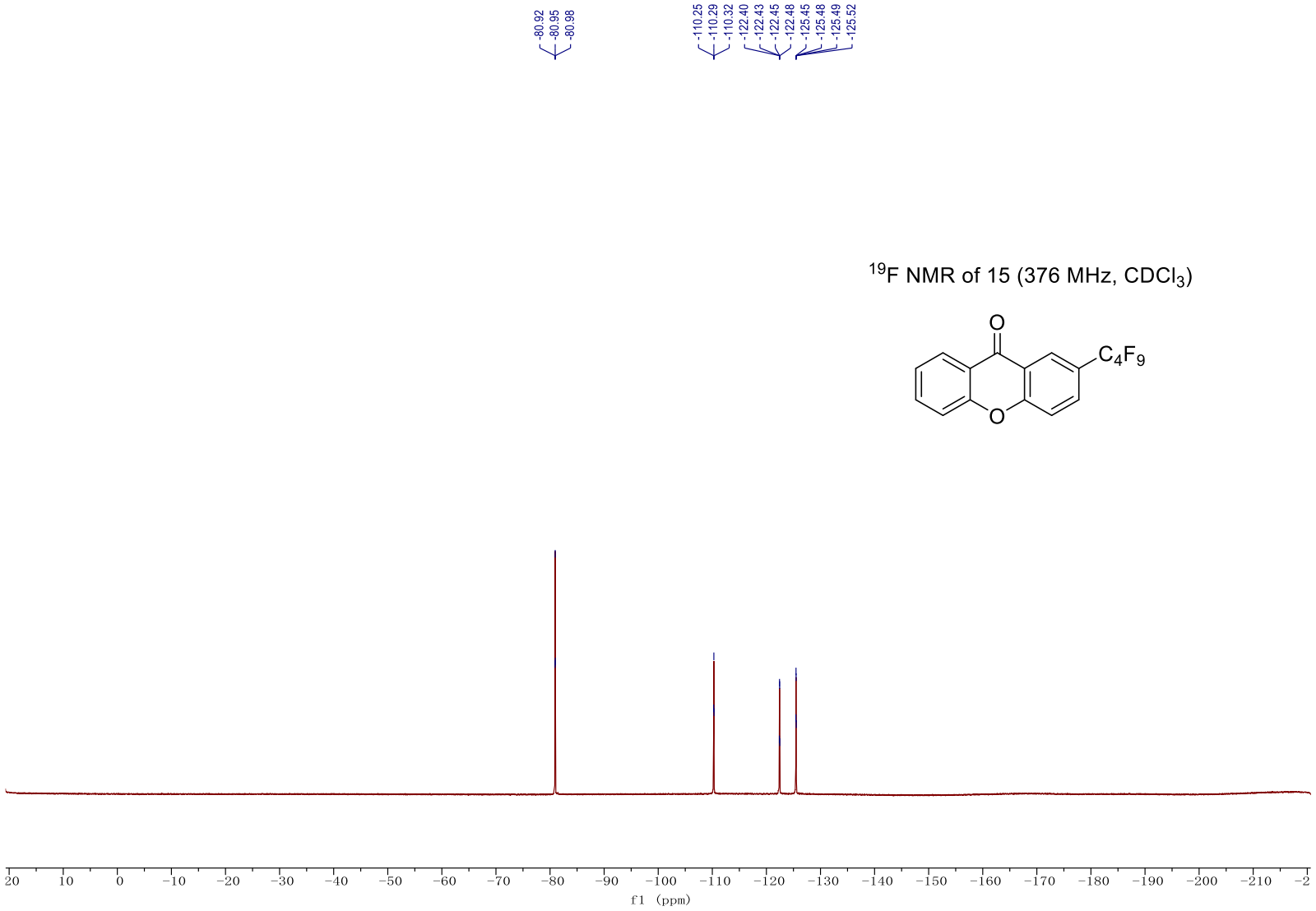
^{1}H NMR of 15 (400 MHz, $CDCl_3$)



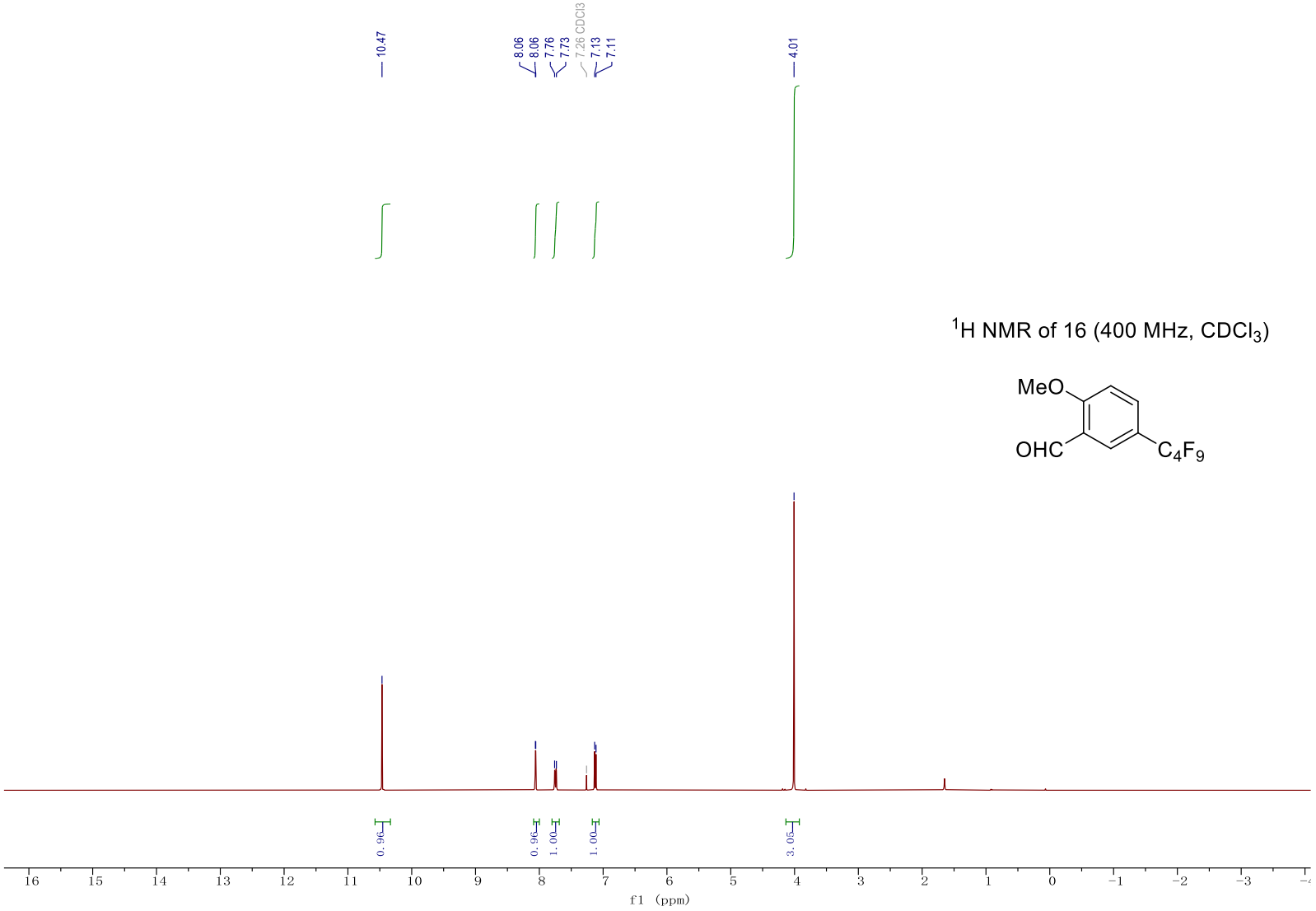




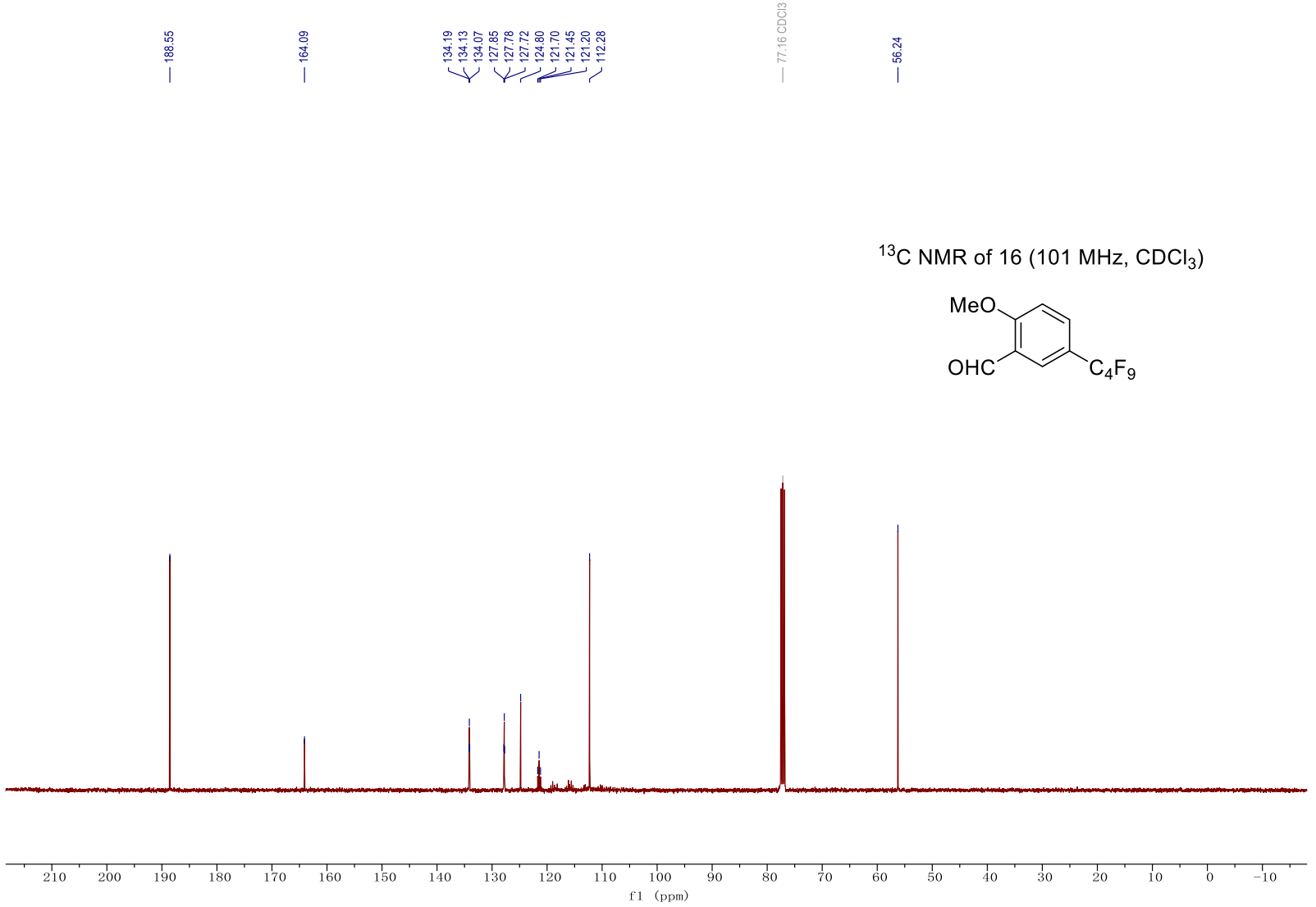
^{13}C NMR of 15 (101 MHz, $CDCl_3$)



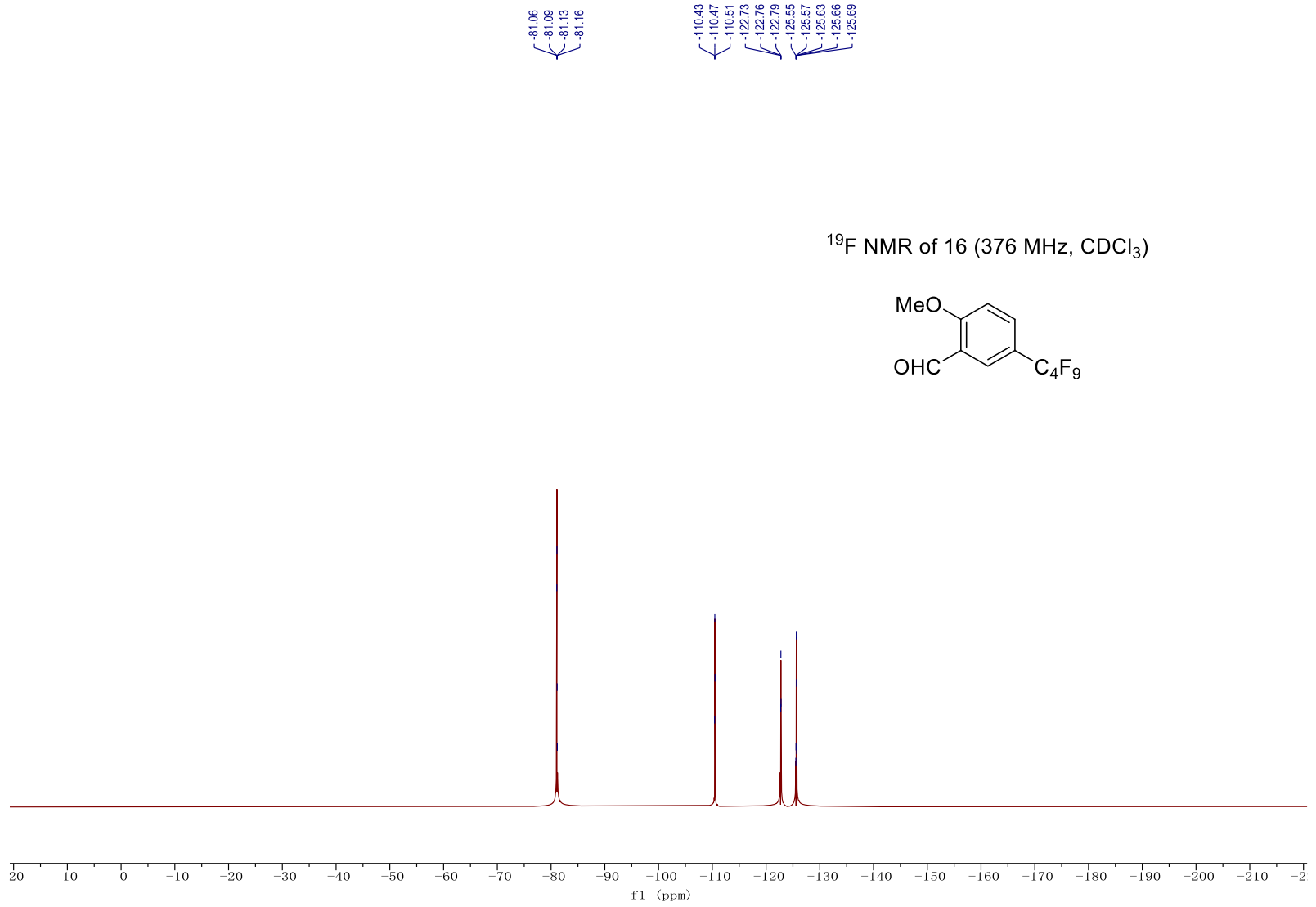
^{19}F NMR of 15 (376 MHz, $CDCl_3$)



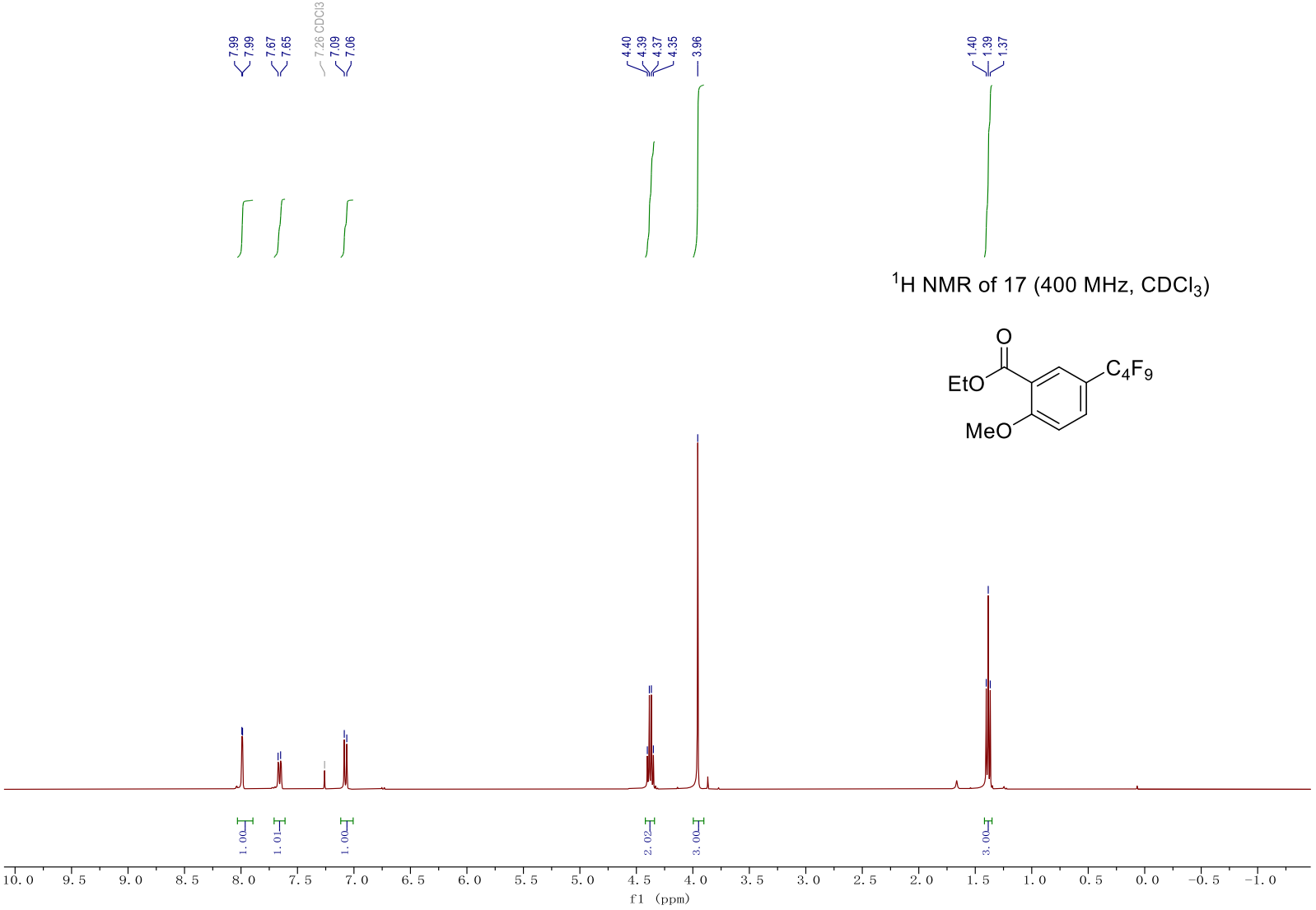
^{1}H NMR of 16 (400 MHz, $CDCl_3$)

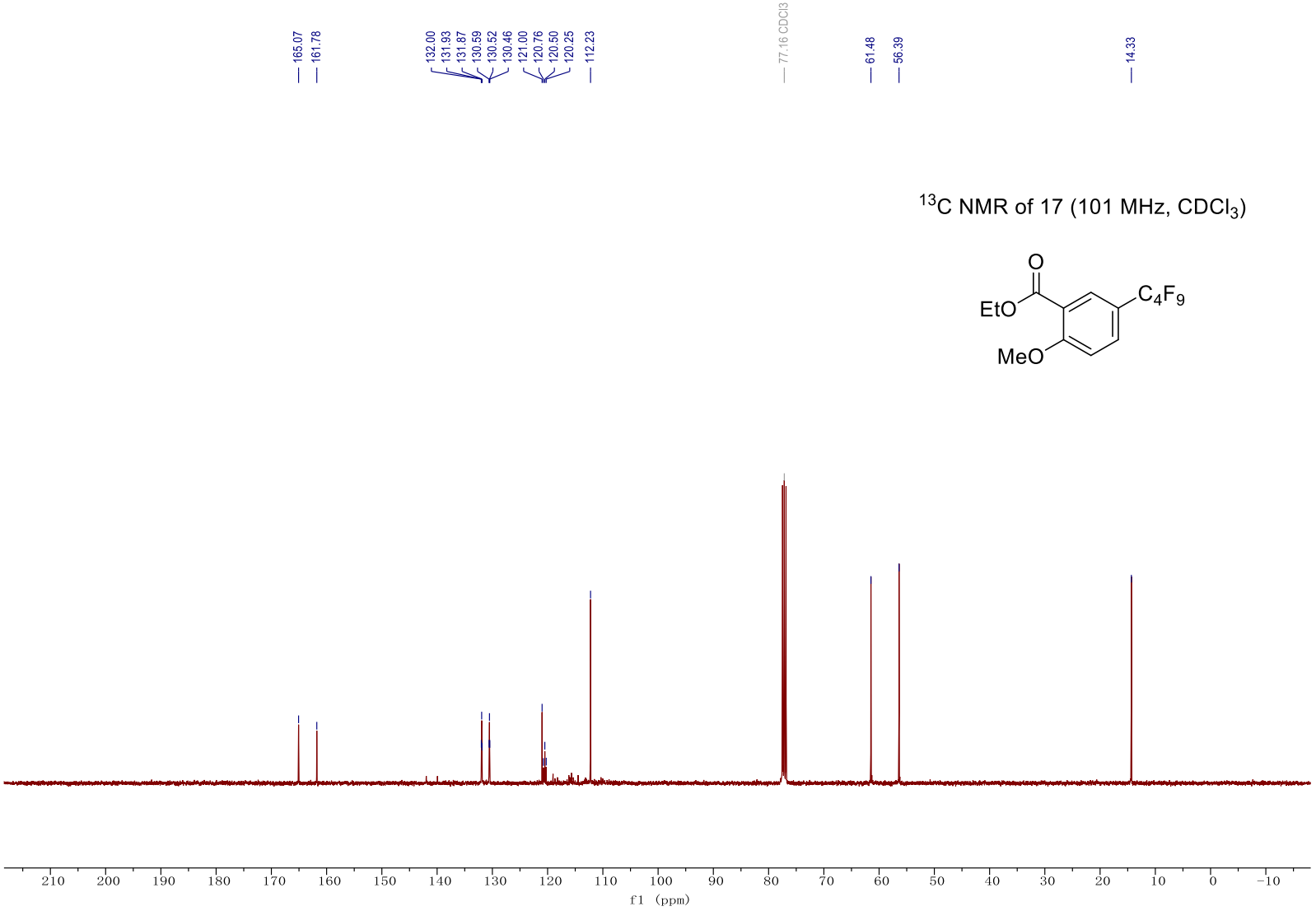


^{13}C NMR of 16 (101 MHz, $CDCl_3$)



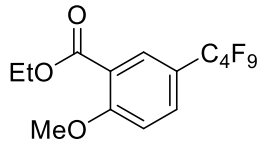
^{19}F NMR of 16 (376 MHz, $CDCl_3$)

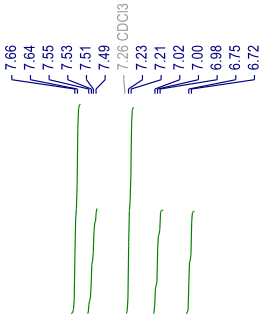

7.99
7.99
7.67
7.65
7.26 CDCl3
7.09
7.06
4.40
4.39
4.37
4.35
3.96
1.40
1.39
1.37
1H NMR of 17 (400 MHz, CDCl3)
O
EtO
MeO
C4F9
1.00
1.01
1.00
2.02
3.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



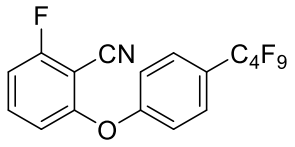
^{13}C NMR of 17 (101 MHz, $CDCl_3$)

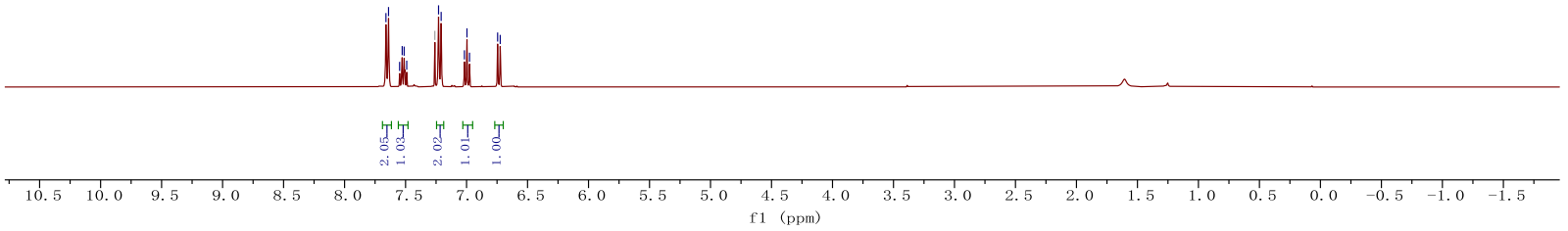
^{19}F NMR of 17 (376 MHz, $CDCl_3$)

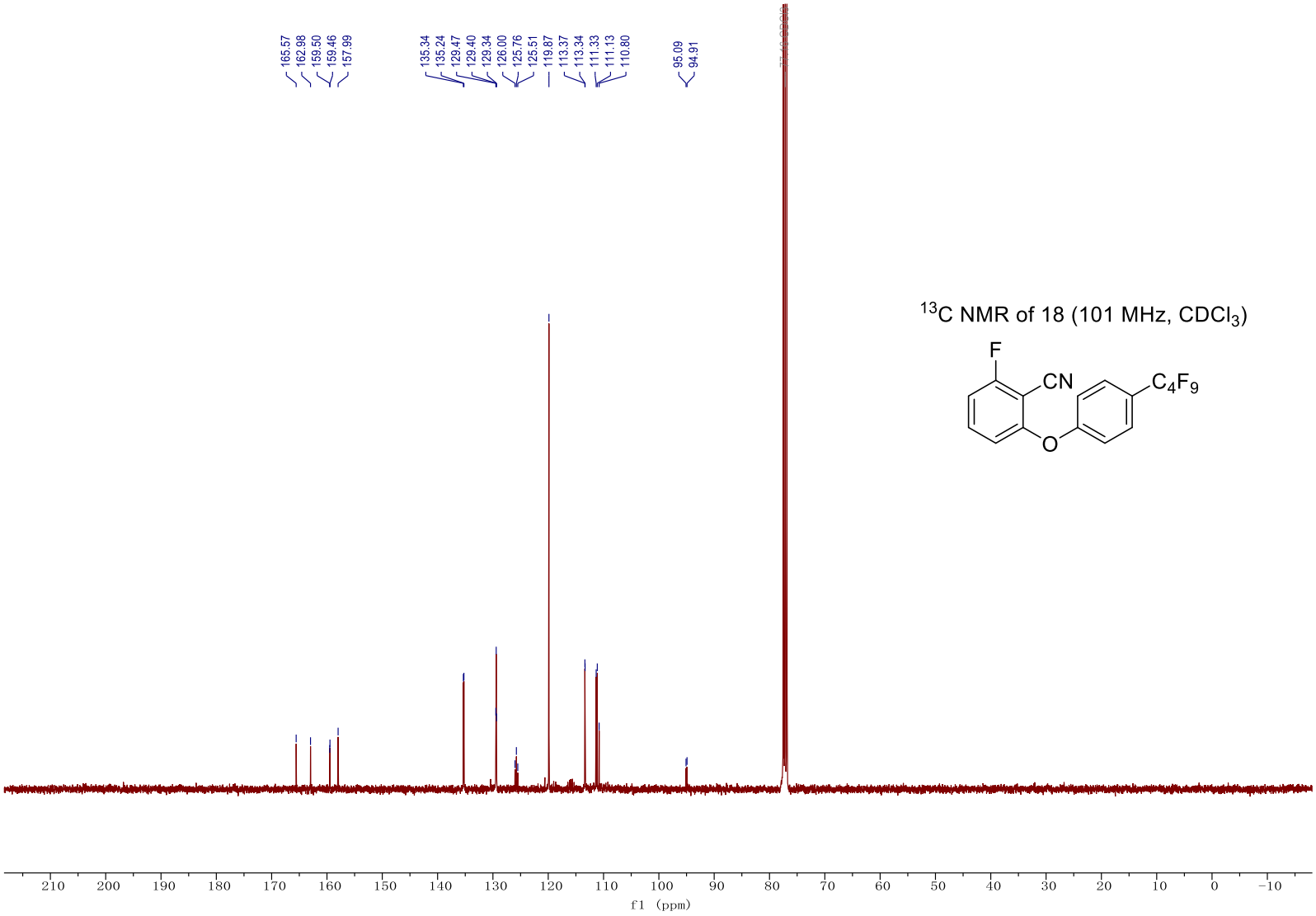




^{1}H NMR of 18 (400 MHz, $CDCl_3$)

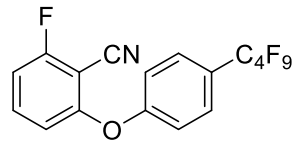


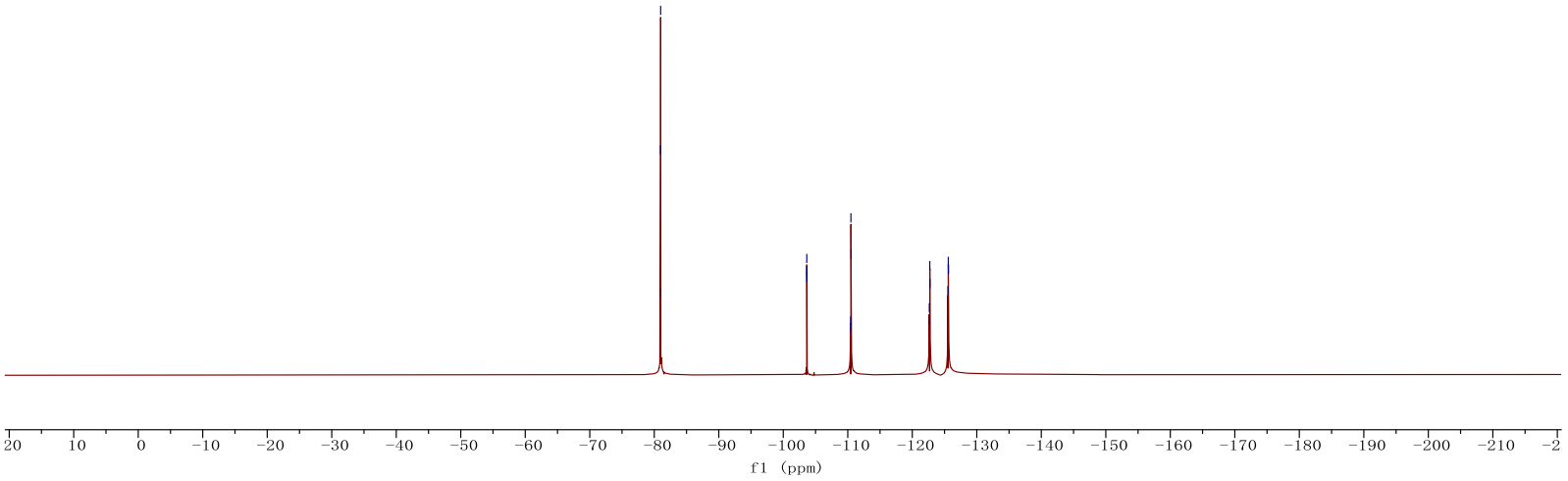


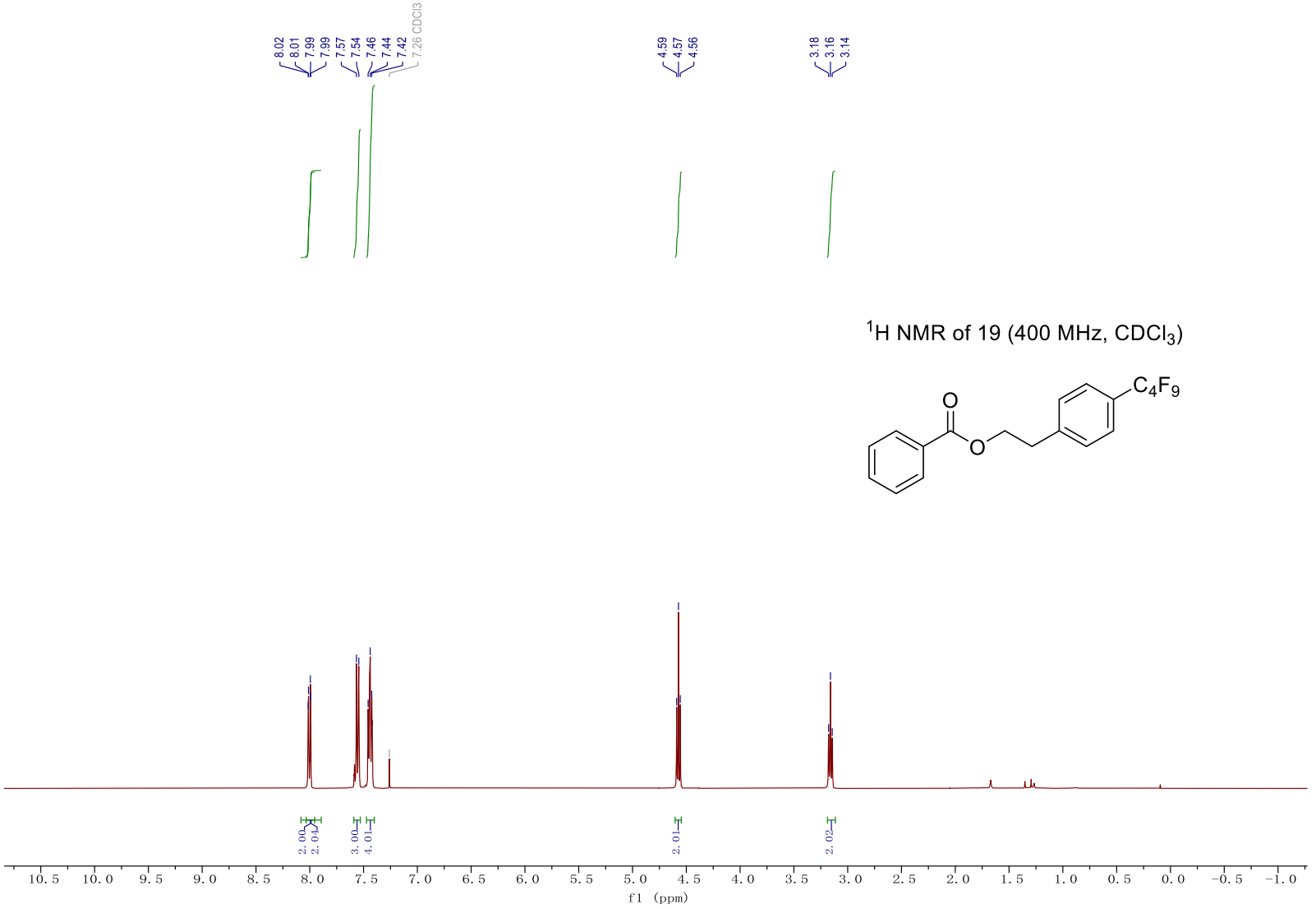

165.57
162.98
159.50
159.46
157.99
135.34
135.24
129.47
129.40
129.34
126.00
125.76
125.51
119.87
113.37
113.34
111.33
111.13
110.80
95.09
94.91
77.40
77.08
76.76
^{13}C NMR of 18 (101 MHz, $CDCl_3$)
F
CN
C_4F_9
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

-80.96
-80.99
-81.01
-103.64
-103.66
-103.66
-110.43
-110.45
-110.49
-110.52
-122.65
-122.67
-122.72
-122.74
-125.53
-125.58
-125.62

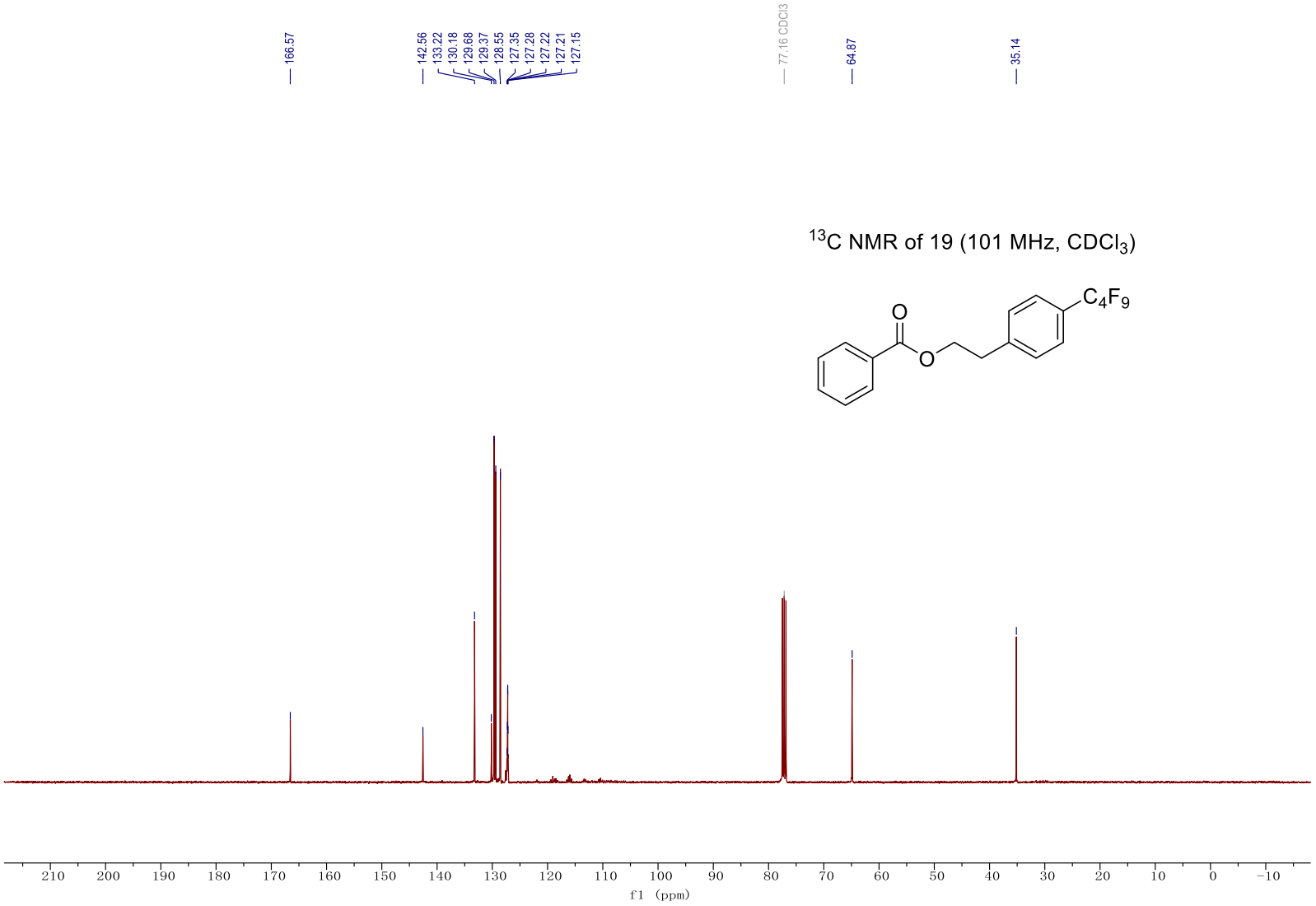
^{19}F NMR of 18 (376 MHz, $CDCl_3$)



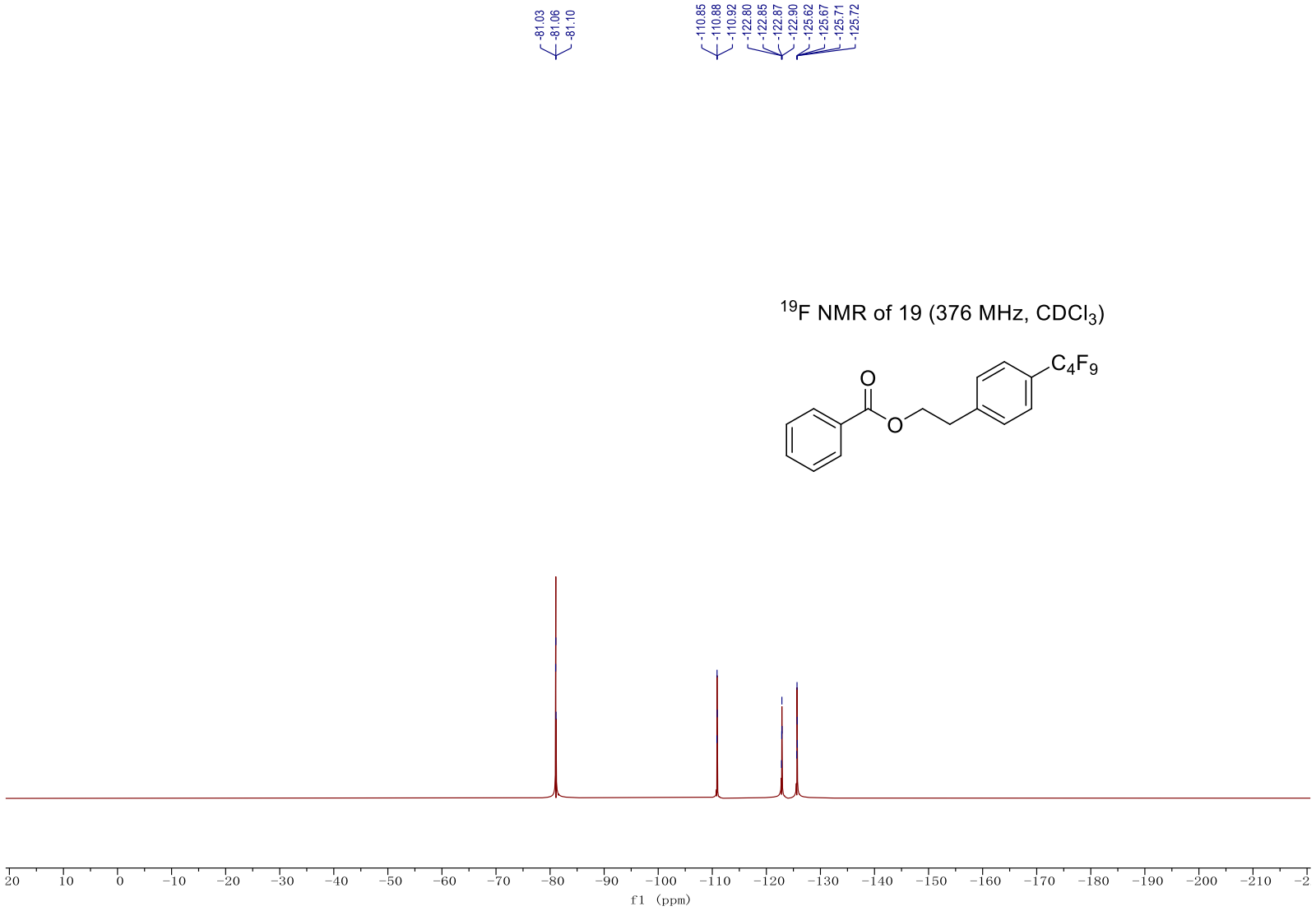




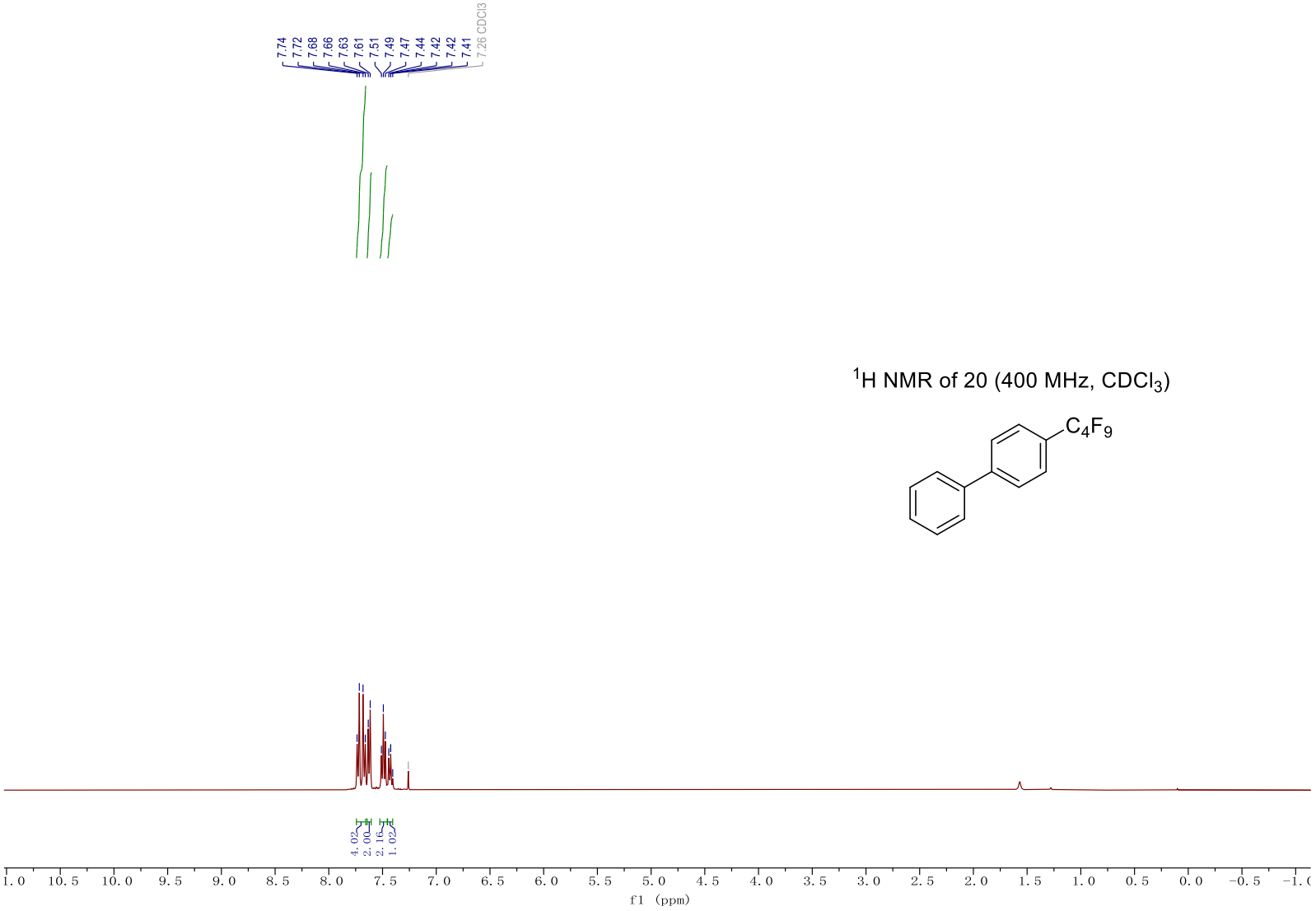
^{1}H NMR of 19 (400 MHz, $CDCl_3$)



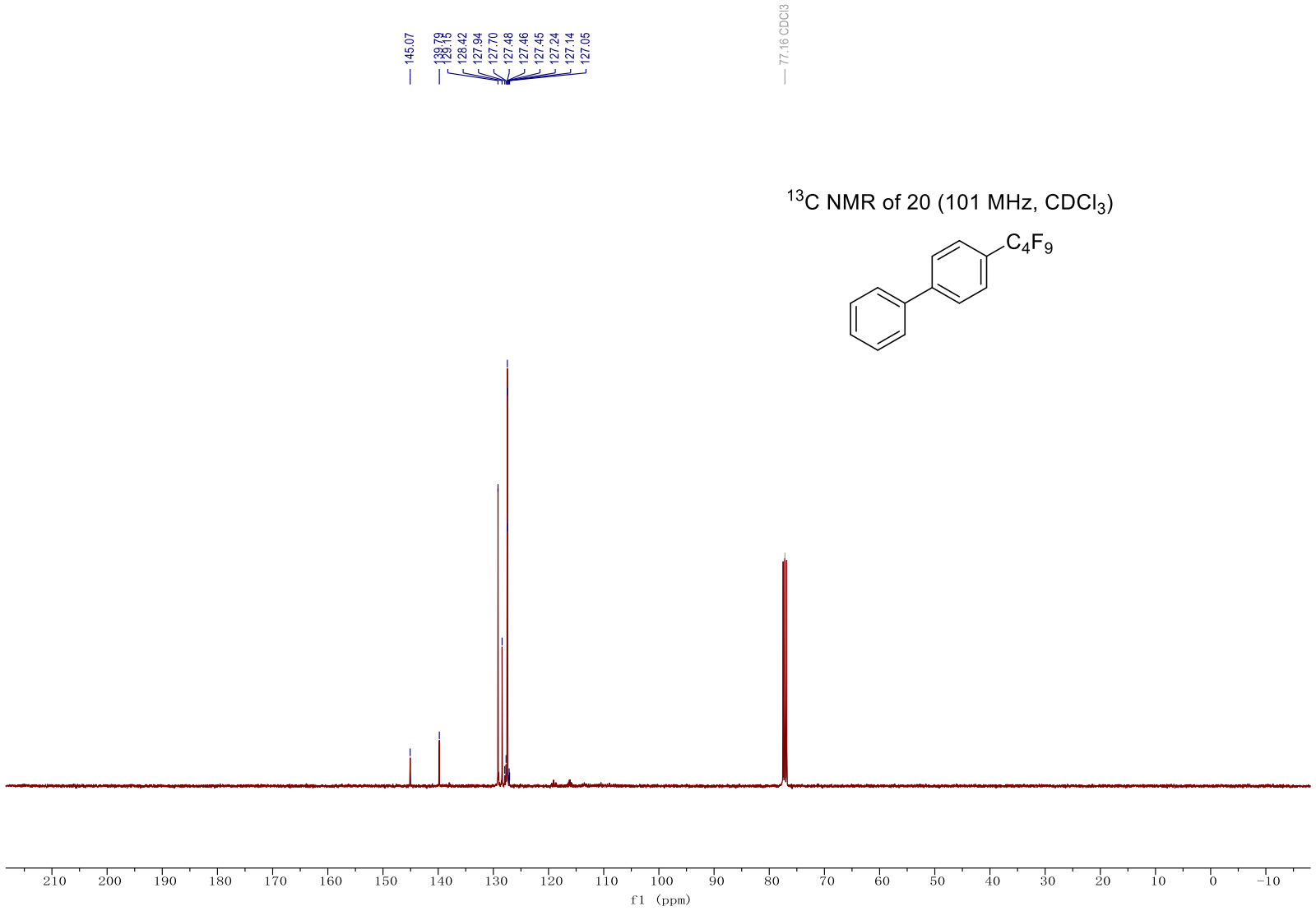
^{13}C NMR of 19 (101 MHz, $CDCl_3$)

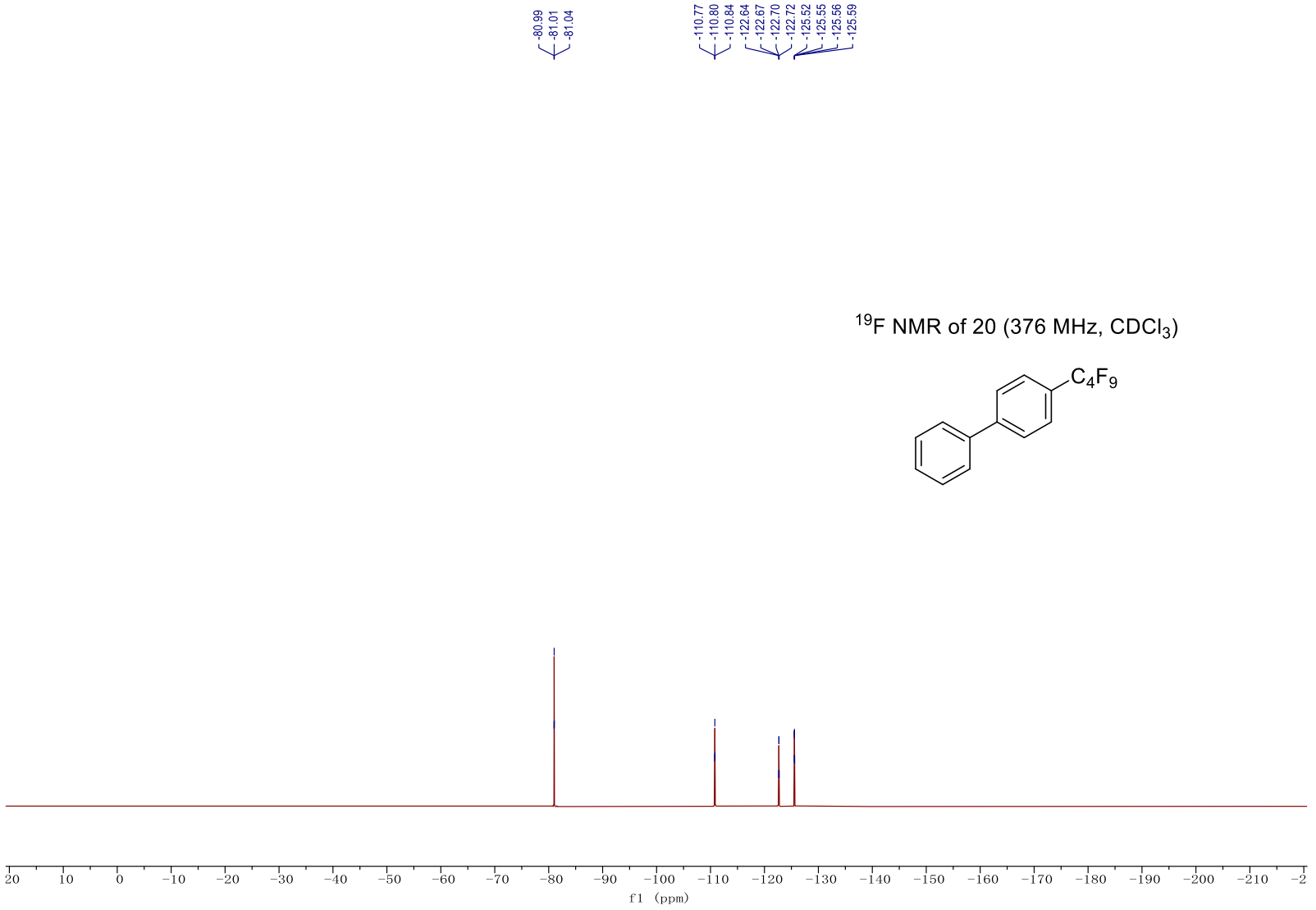


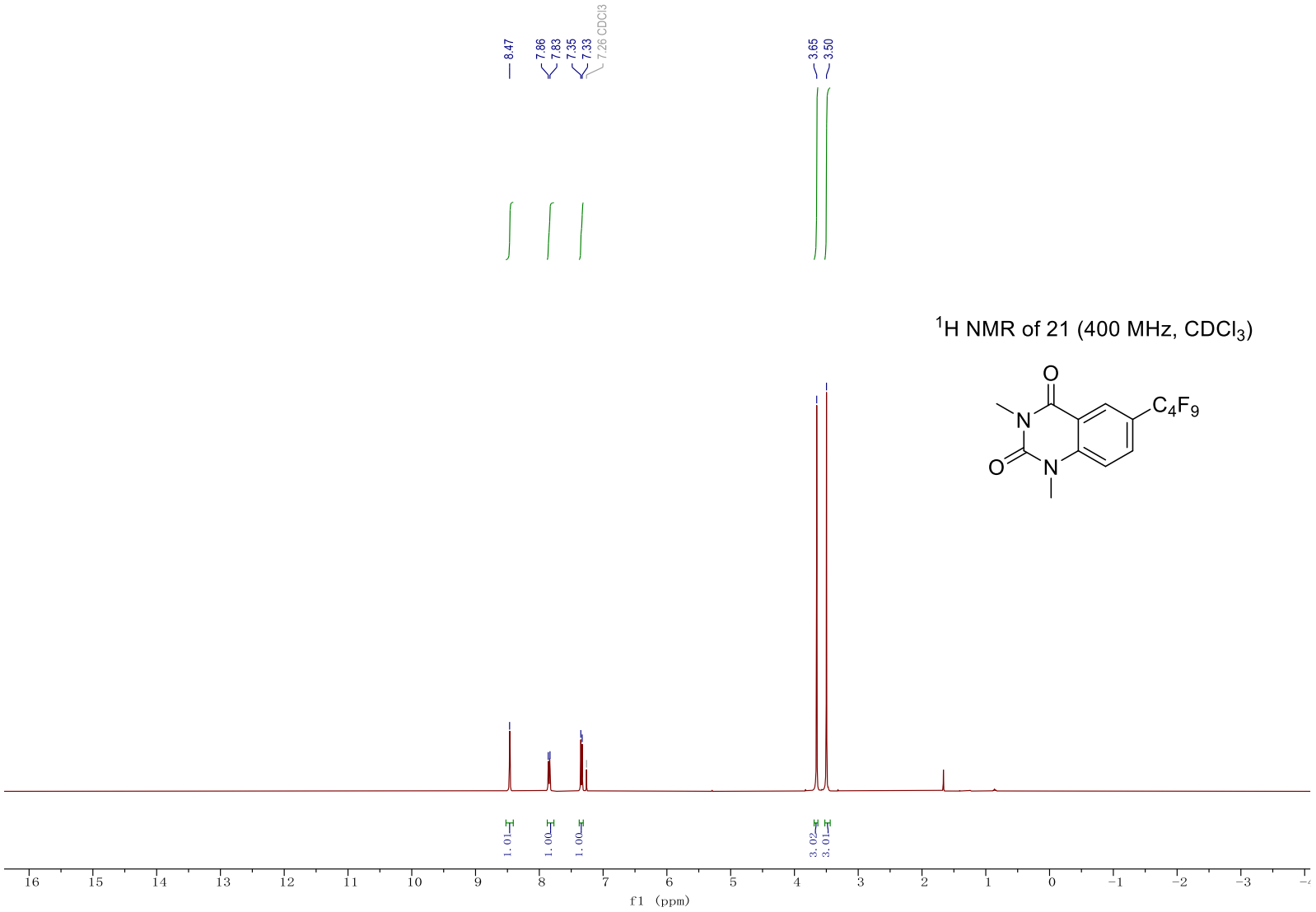
^{19}F NMR of 19 (376 MHz, $CDCl_3$)



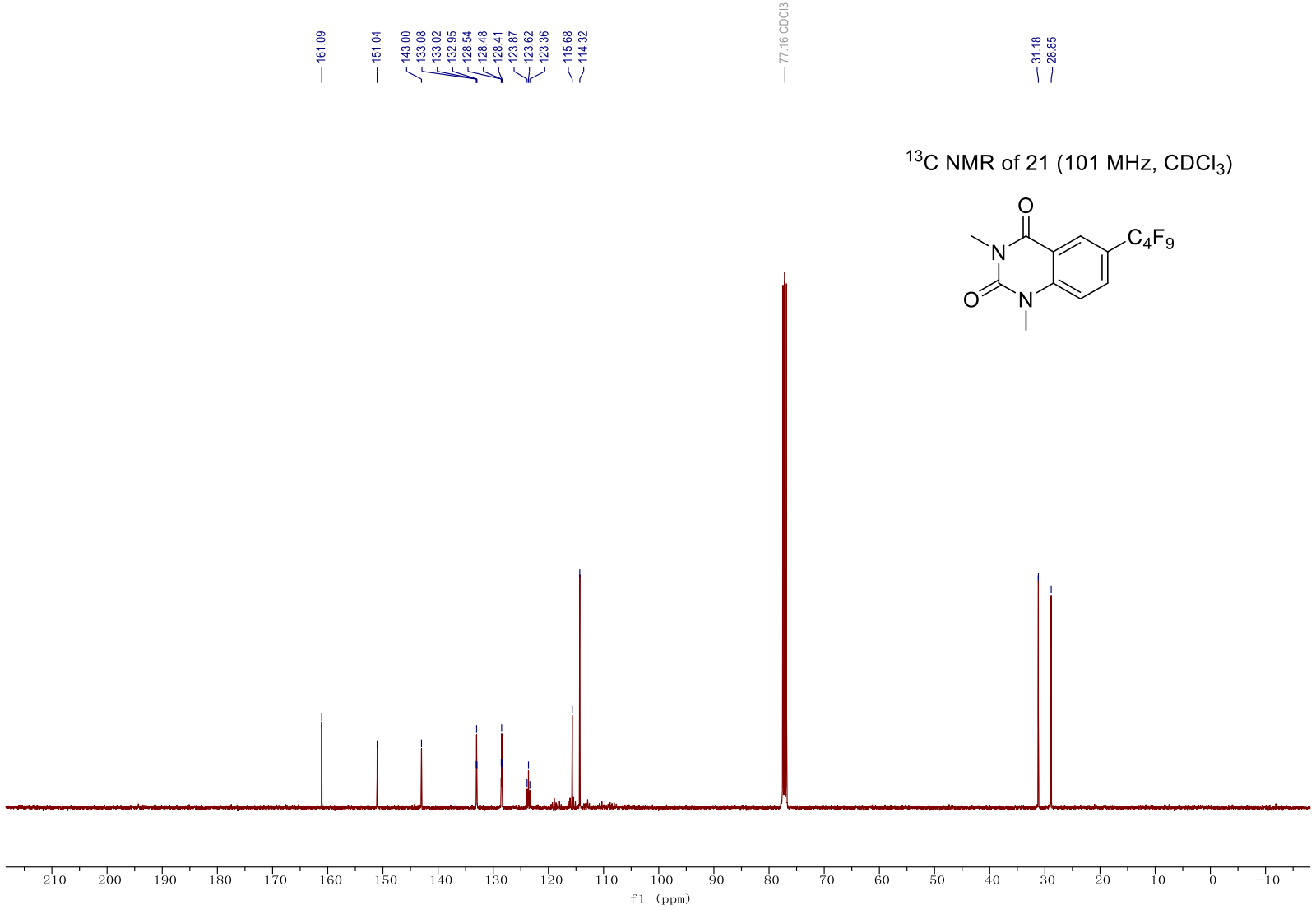
^{1}H NMR of 20 (400 MHz, $CDCl_3$)


145.07
138.79
138.15
128.42
127.94
127.70
127.48
127.46
127.45
127.24
127.14
127.05
77.16 CDCl3
^{13}C NMR of 20 (101 MHz, $CDCl_3$)
C_4F_9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

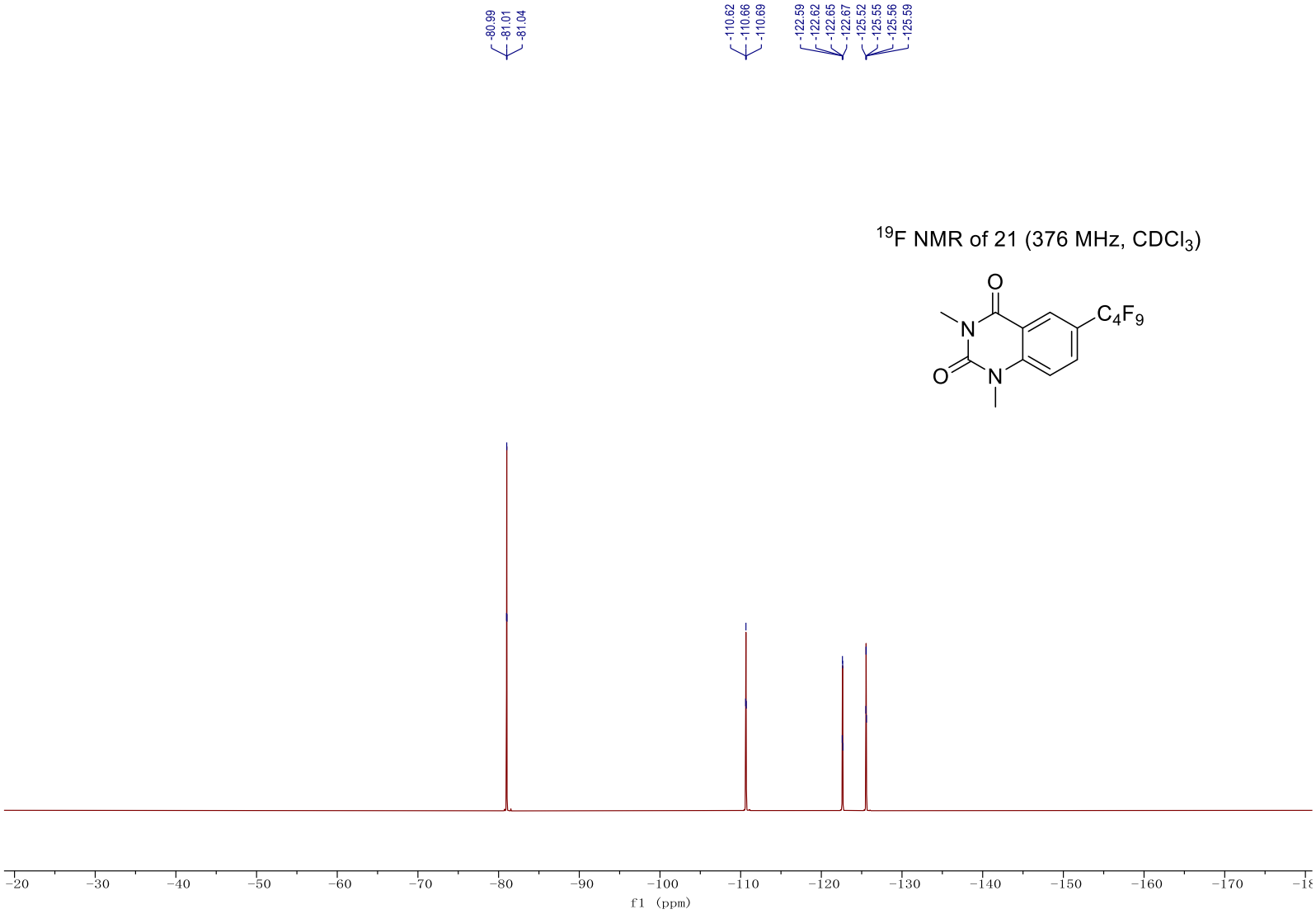

-80.99
-81.01
-81.04
-110.77
-110.80
-110.84
-122.64
-122.67
-122.70
-122.72
-125.52
-125.55
-125.56
-125.59
^{19}F NMR of 20 (376 MHz, $CDCl_3$)
C_4F_9
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)



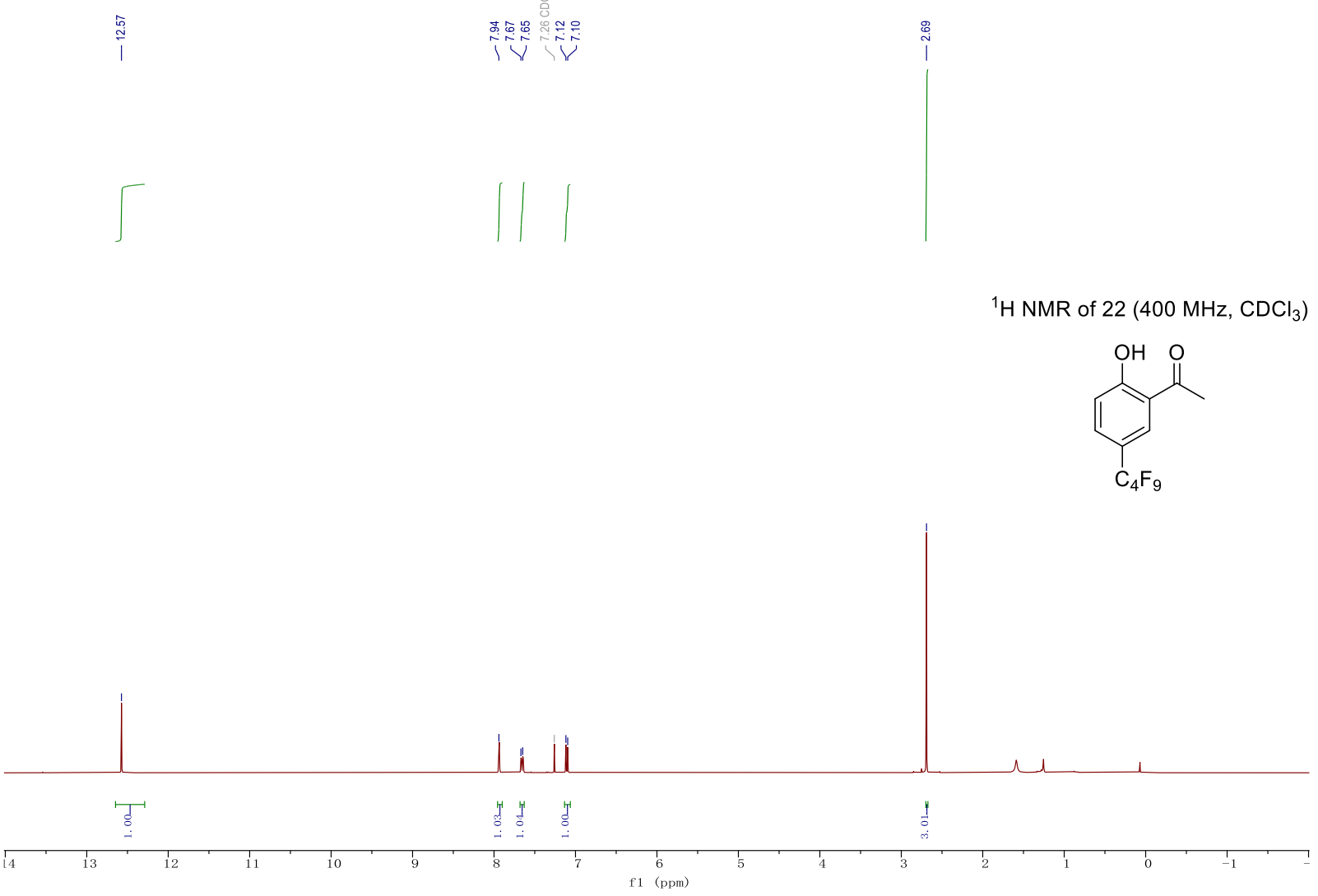
^{1}H NMR of 21 (400 MHz, $CDCl_3$)



^{13}C NMR of 21 (101 MHz, $CDCl_3$)

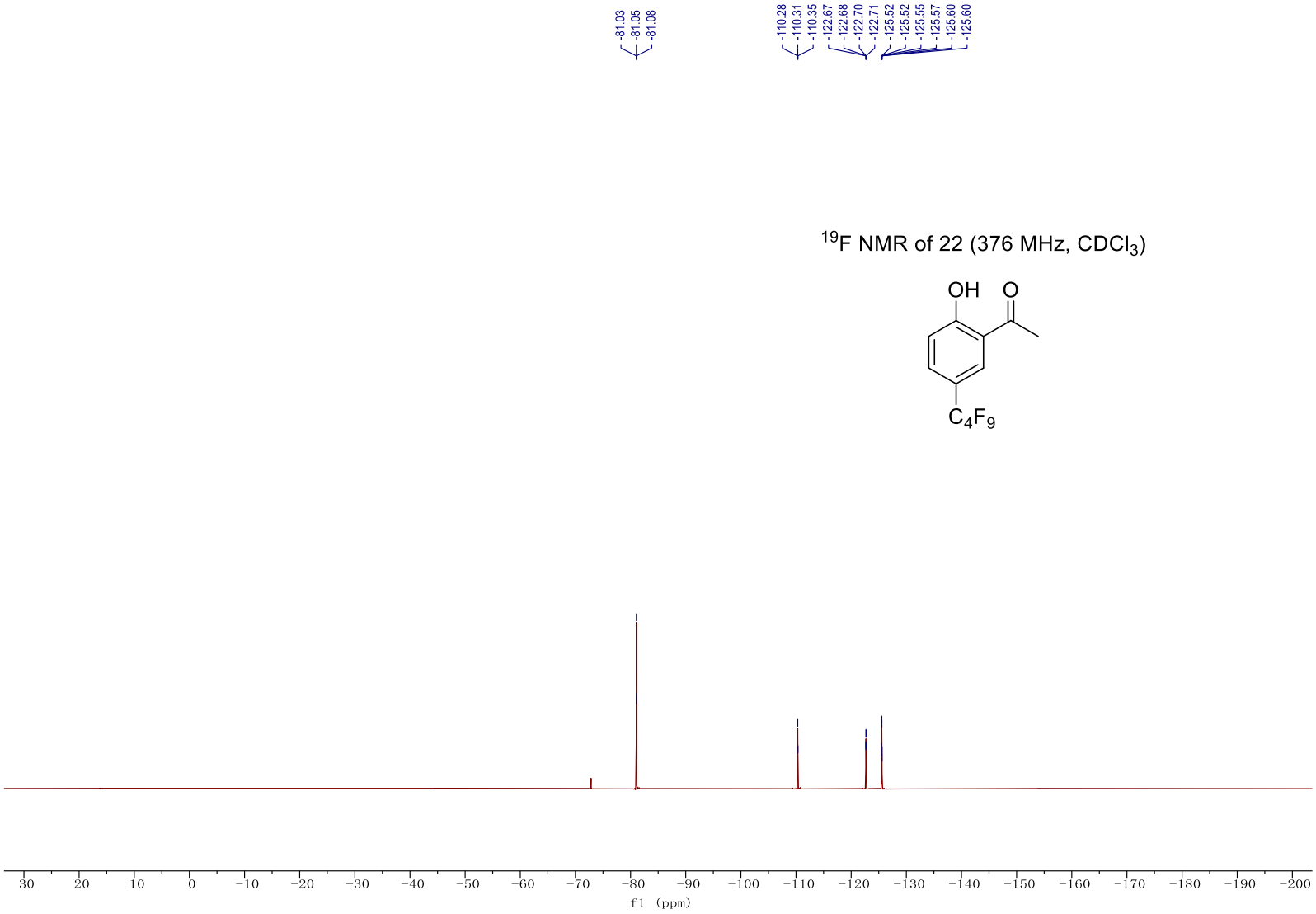


^{19}F NMR of 21 (376 MHz, $CDCl_3$)

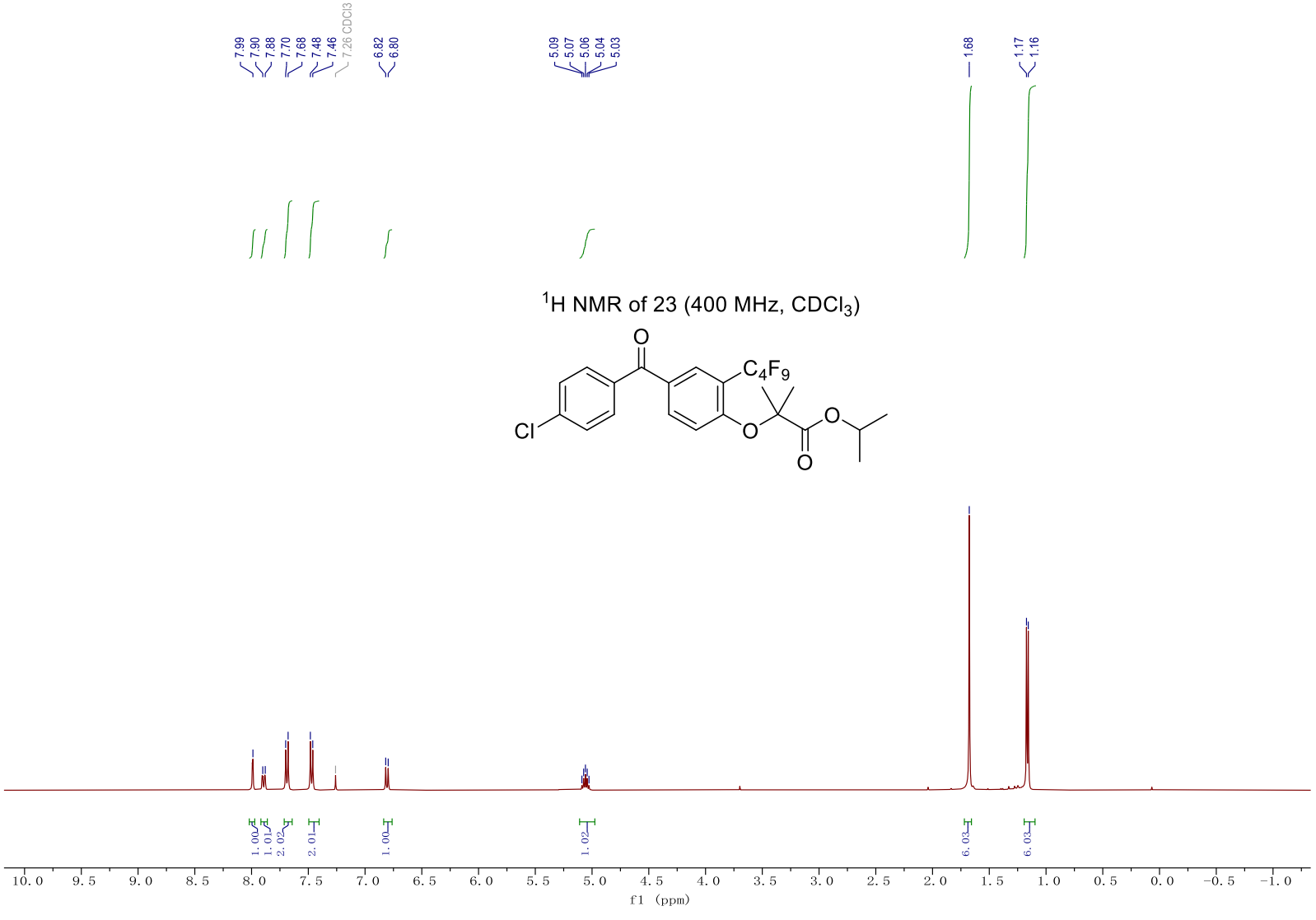


^{1}H NMR of 22 (400 MHz, $CDCl_3$)

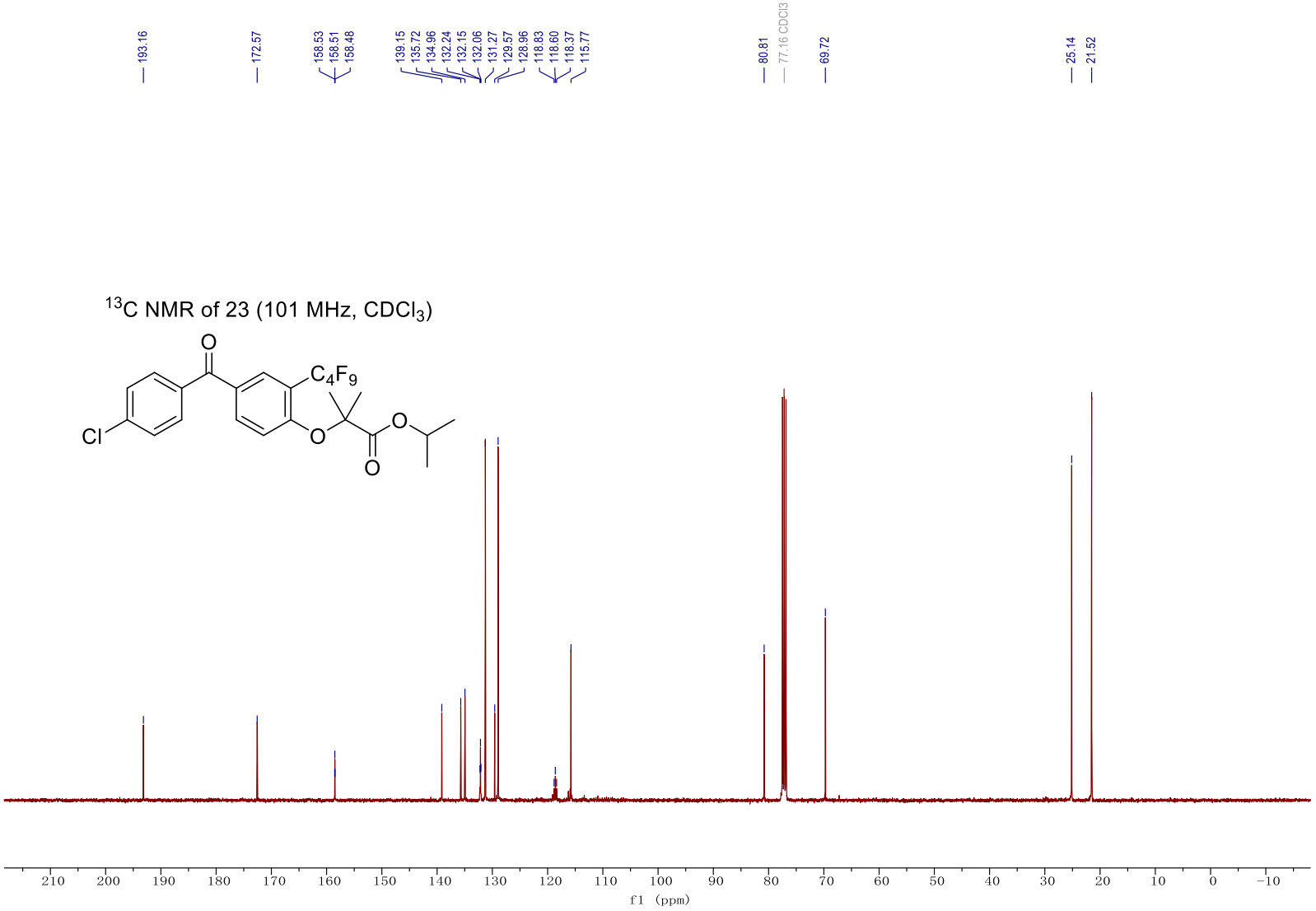
^{13}C NMR of 22 (101 MHz, $CDCl_3$)

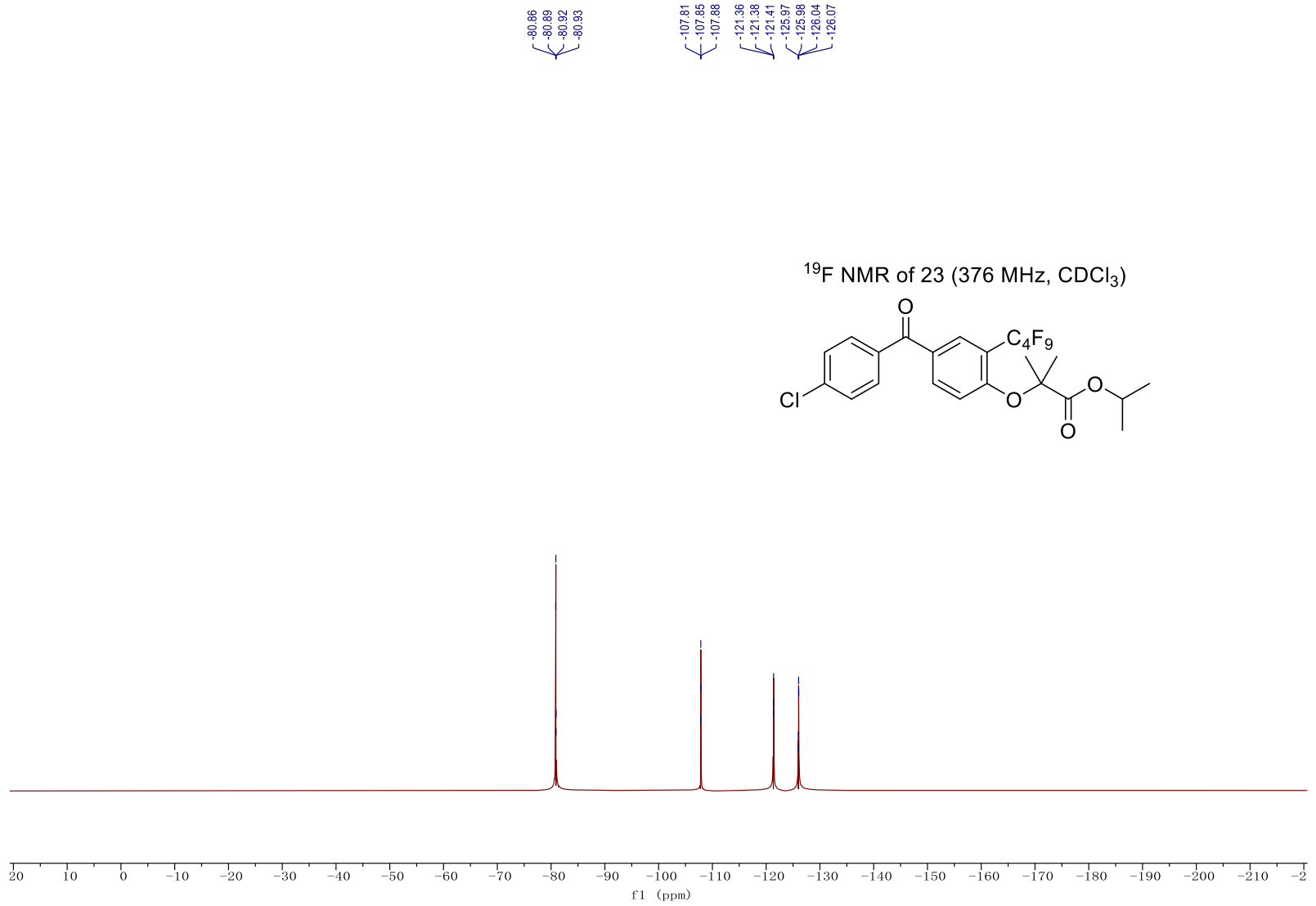


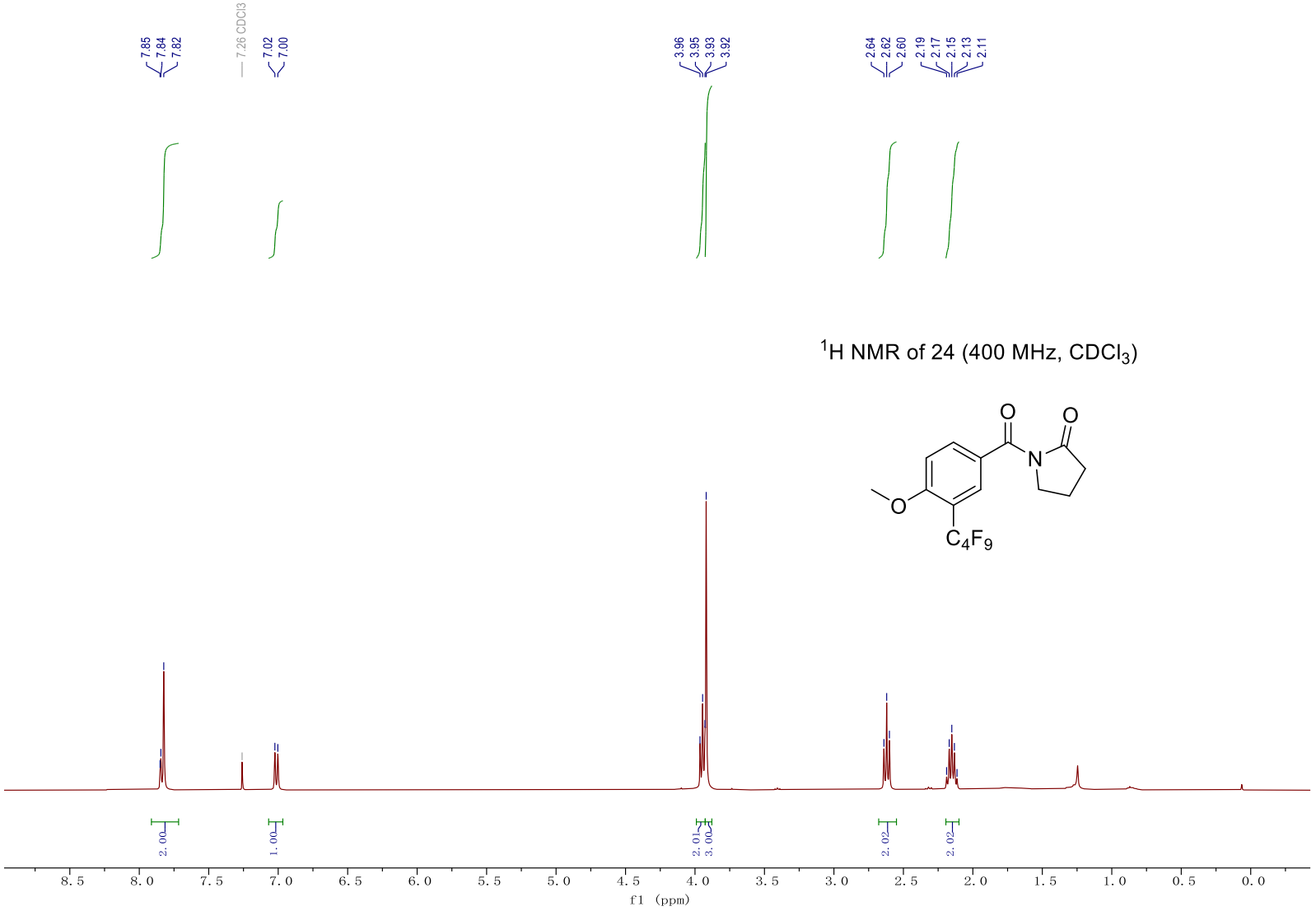
^{19}F NMR of 22 (376 MHz, $CDCl_3$)



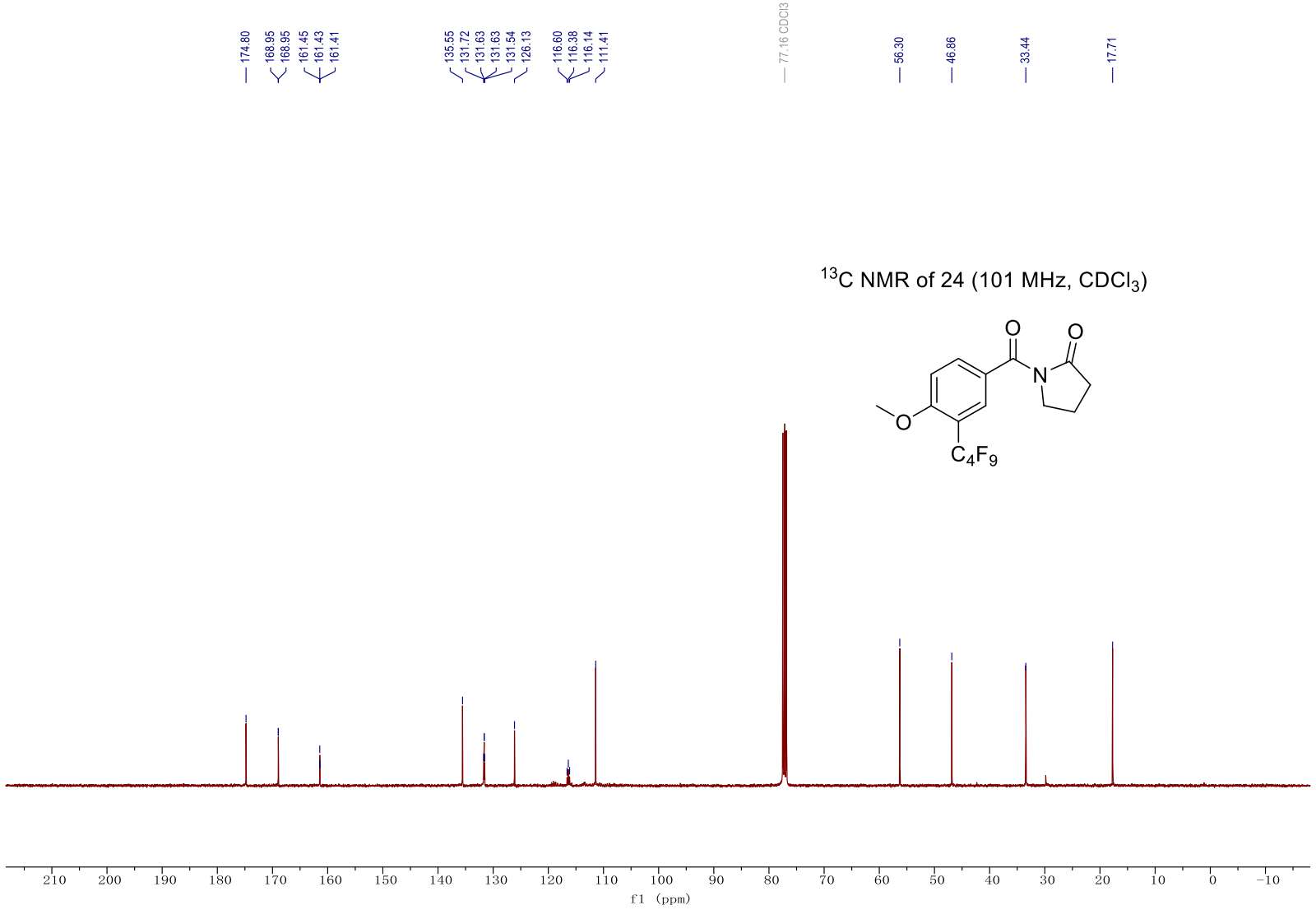
^{1}H NMR of 23 (400 MHz, $CDCl_3$)


193.16
172.57
158.53
158.51
158.48
139.15
135.72
134.96
132.24
132.15
132.06
131.27
129.57
128.96
118.83
118.60
118.37
115.77
80.81
77.16 CDCl3
69.72
25.14
21.52
13C NMR of 23 (101 MHz, CDCl3)
O
C4F9
Cl
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

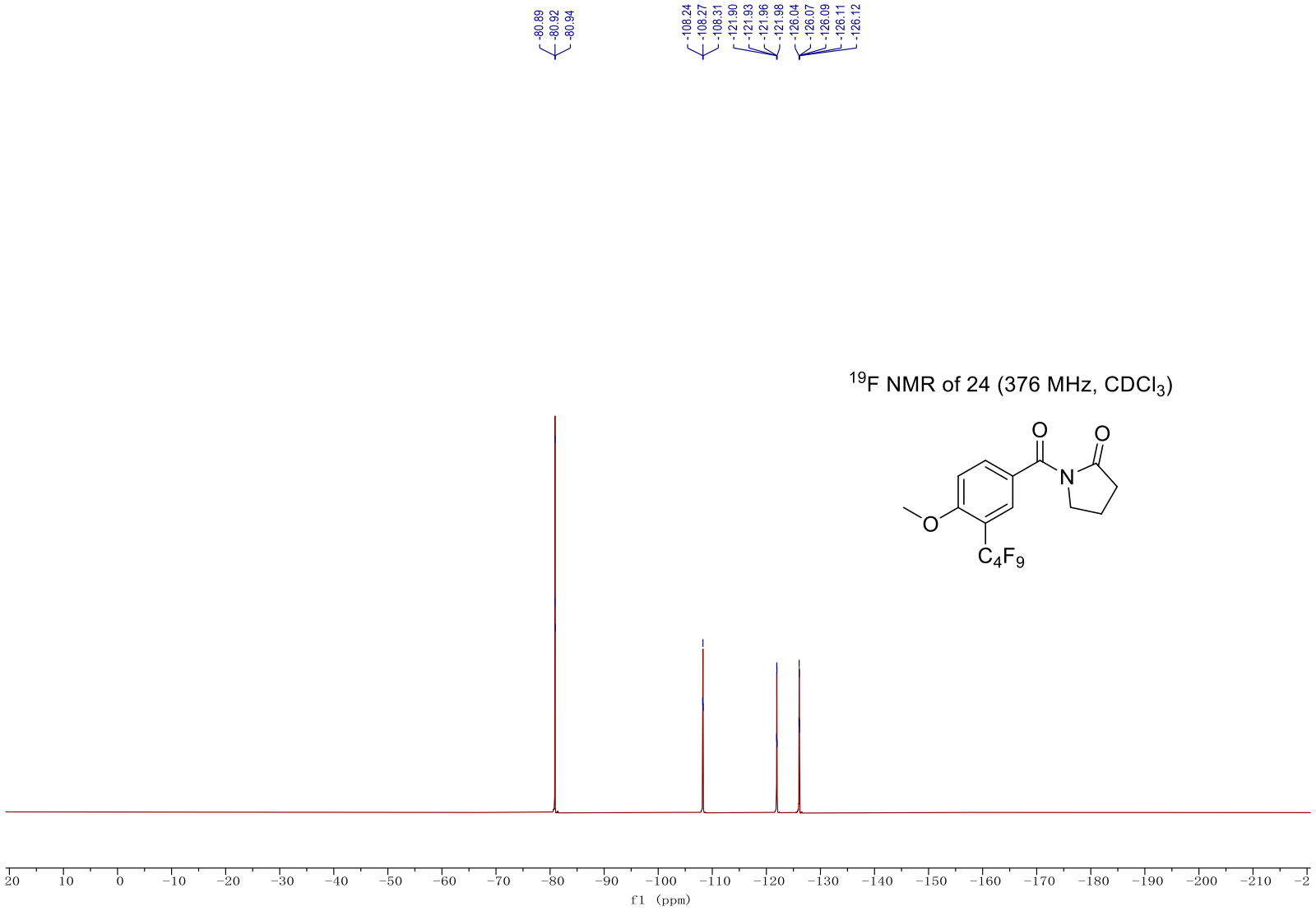

-80.86
-80.89
-80.92
-80.93
-107.81
-107.85
-107.88
-121.36
-121.38
-121.41
-125.97
-125.98
-126.04
-126.07
19F NMR of 23 (376 MHz, CDCl3)
O
C4F9
Cl
O
O
O
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)



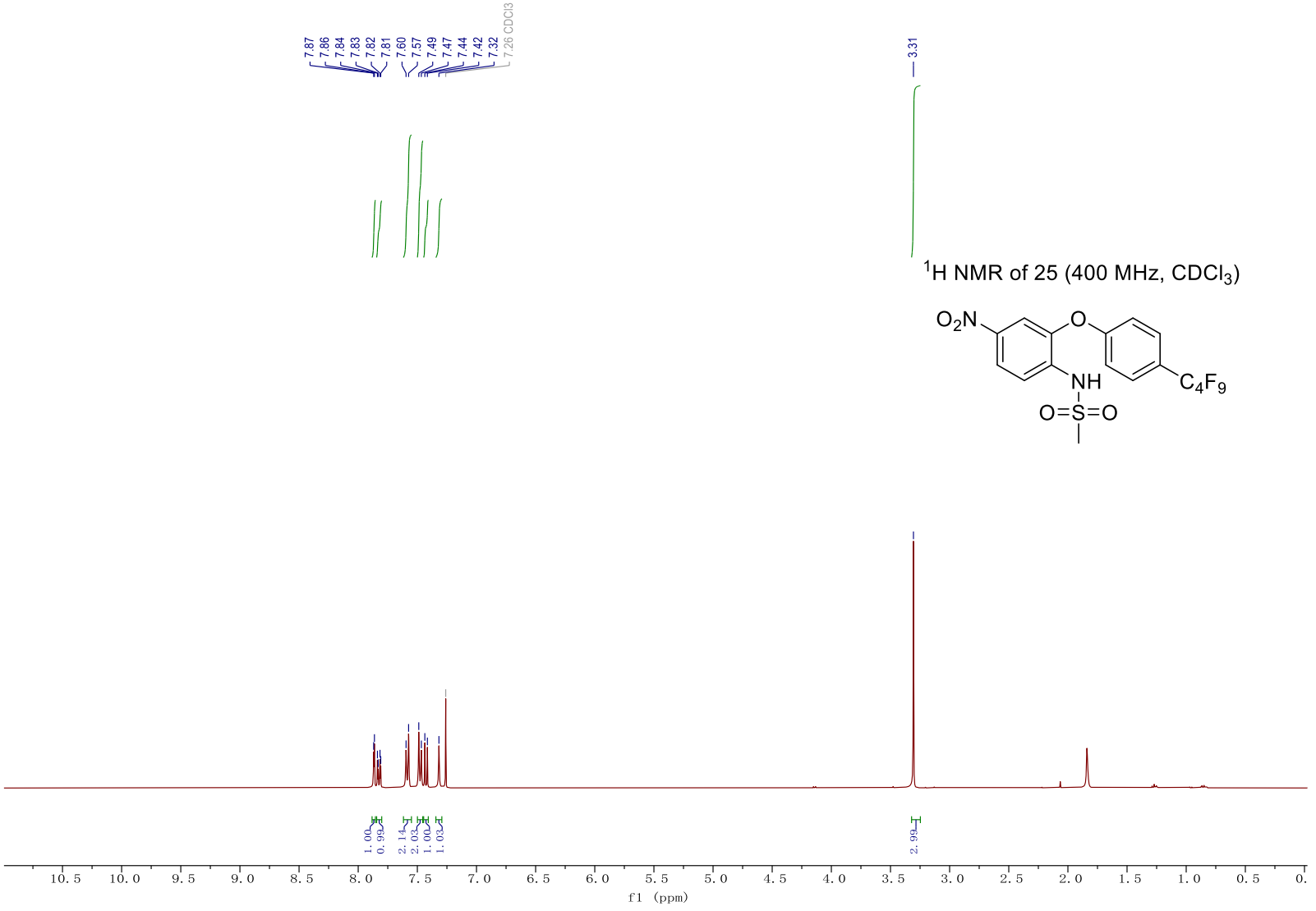
^{1}H NMR of 24 (400 MHz, $CDCl_3$)

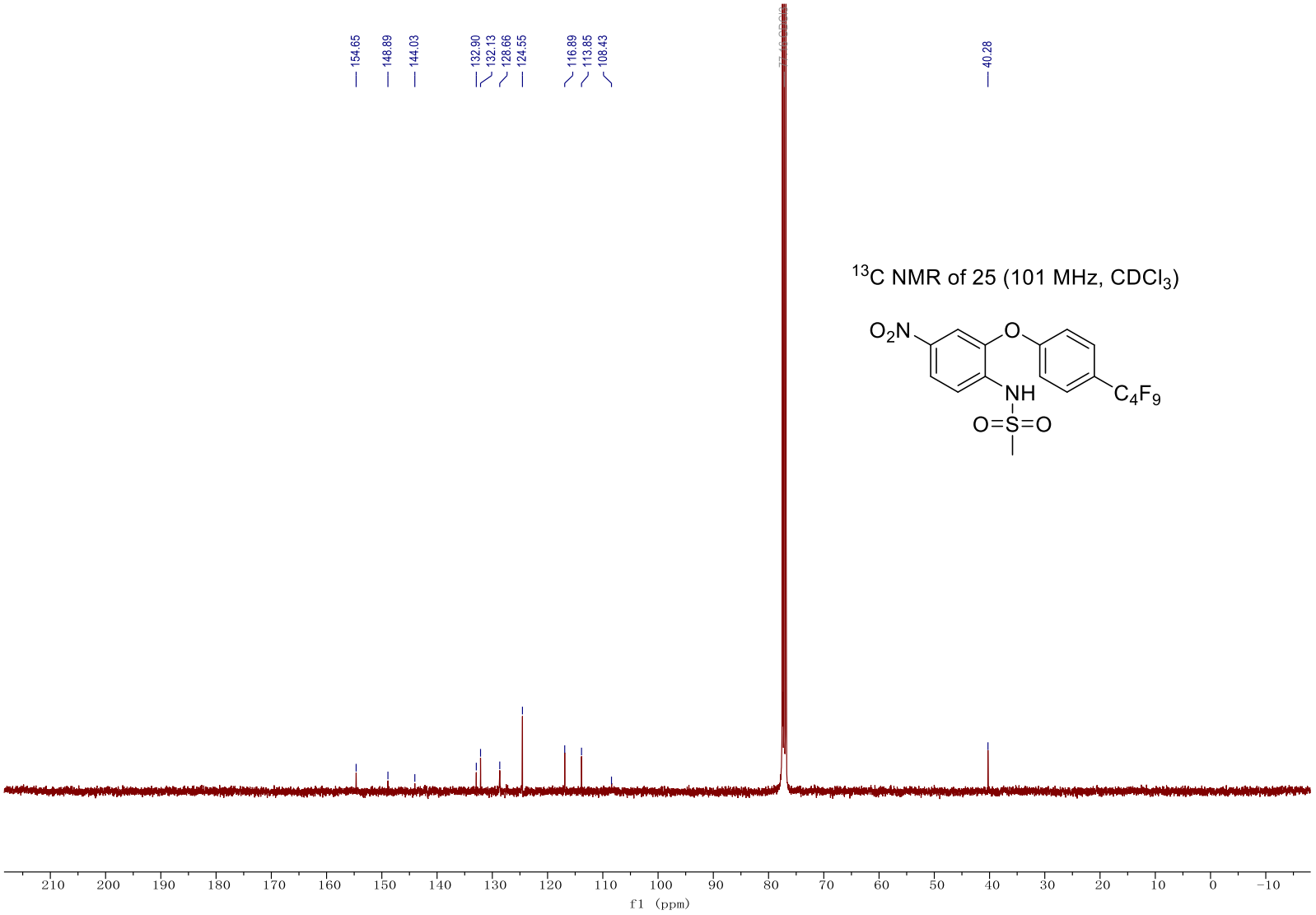


^{13}C NMR of 24 (101 MHz, $CDCl_3$)



^{19}F NMR of 24 (376 MHz, $CDCl_3$)


7.87
7.86
7.84
7.83
7.82
7.81
7.60
7.57
7.49
7.47
7.44
7.42
7.32
7.26 CDCl3
3.31
1H NMR of 25 (400 MHz, CDCl3)
O2N
O
NH
C4F9
O=S=O
1.00
0.99
2.14
2.03
1.00
1.03
2.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

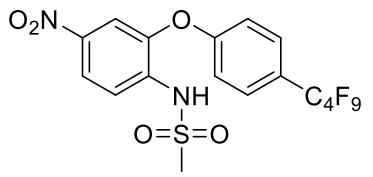


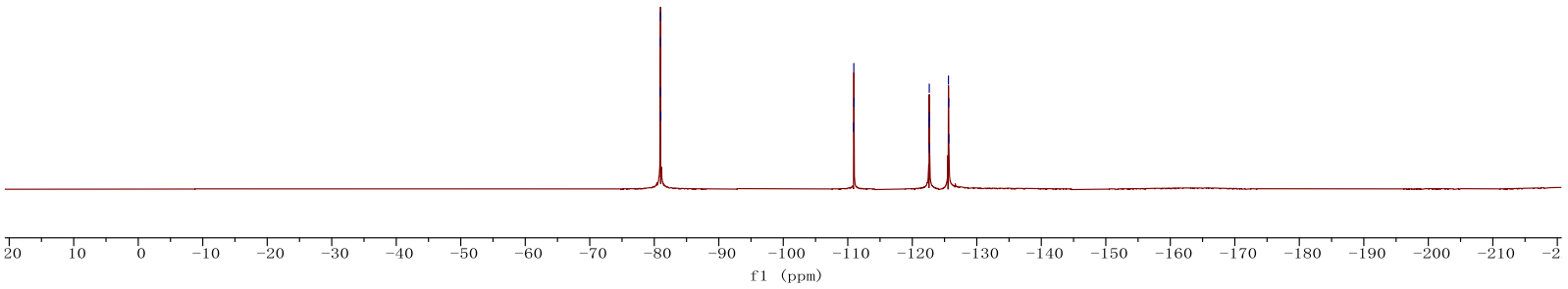
^{13}C NMR of 25 (101 MHz, $CDCl_3$)

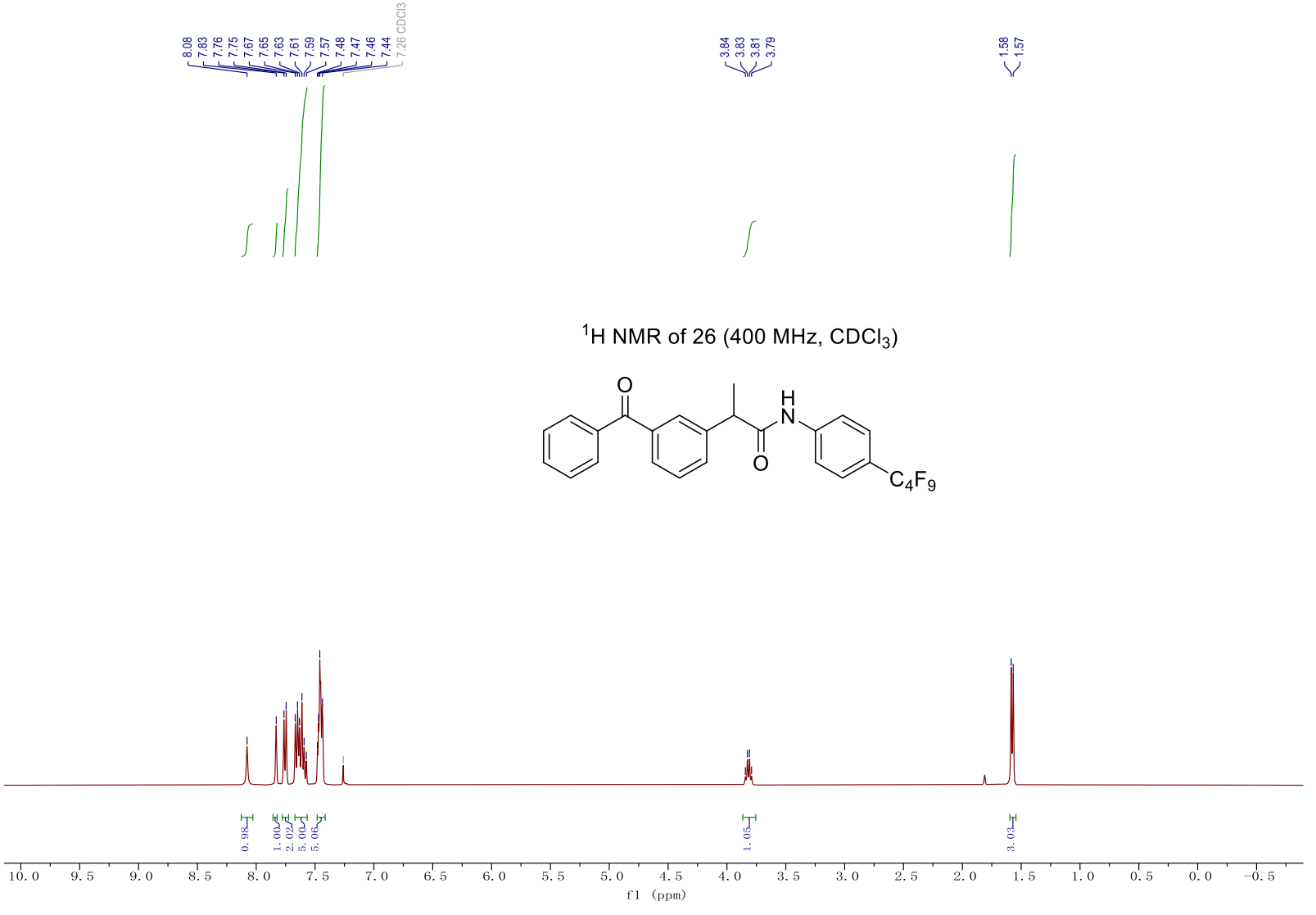
-80.94
-80.95
-80.97
-81.02

-110.90
-110.94
-110.97
-122.61
-122.63
-122.66
-122.68
-125.61
-125.64
-125.66

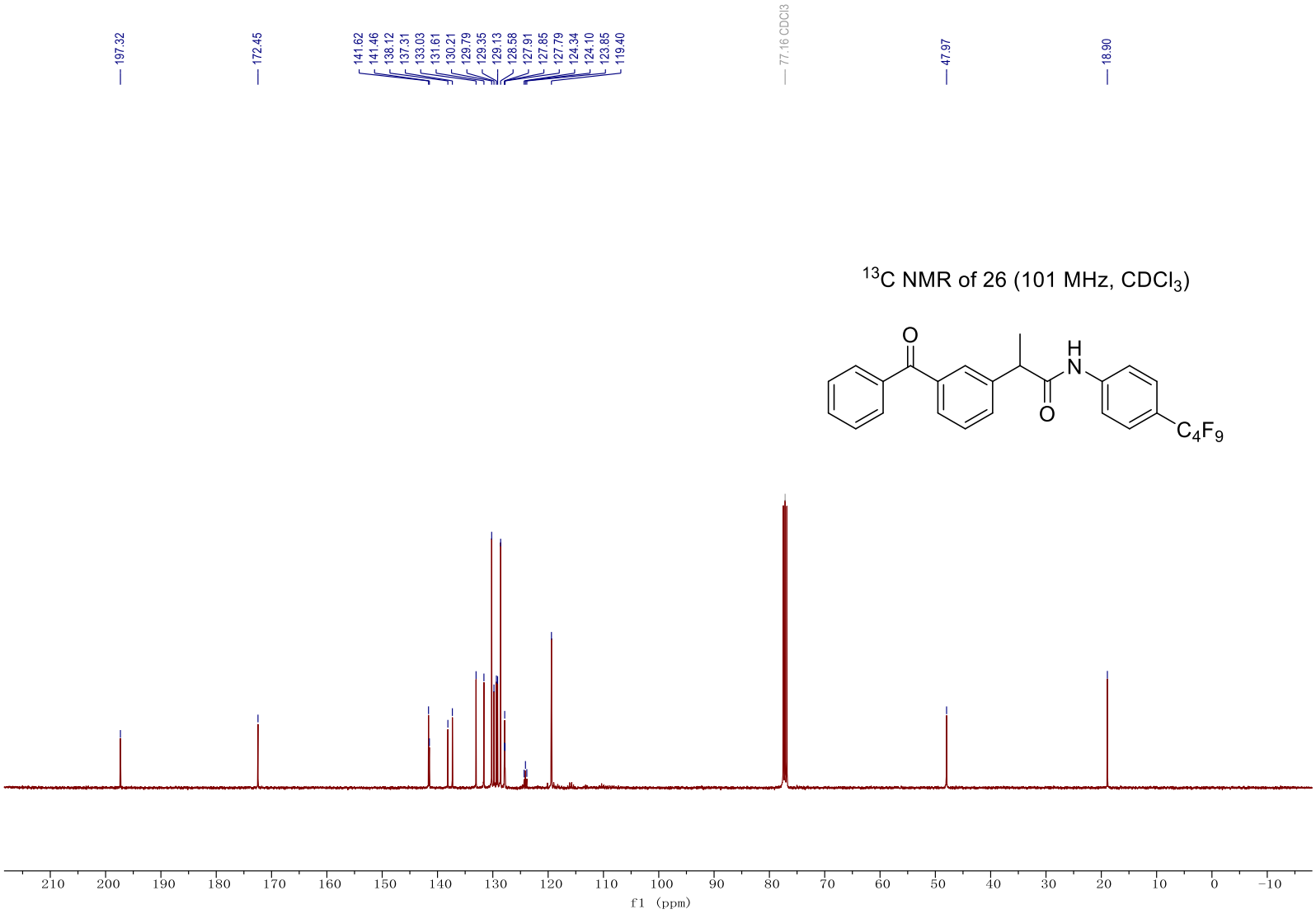
^{19}F NMR of 25 (376 MHz, $CDCl_3$)



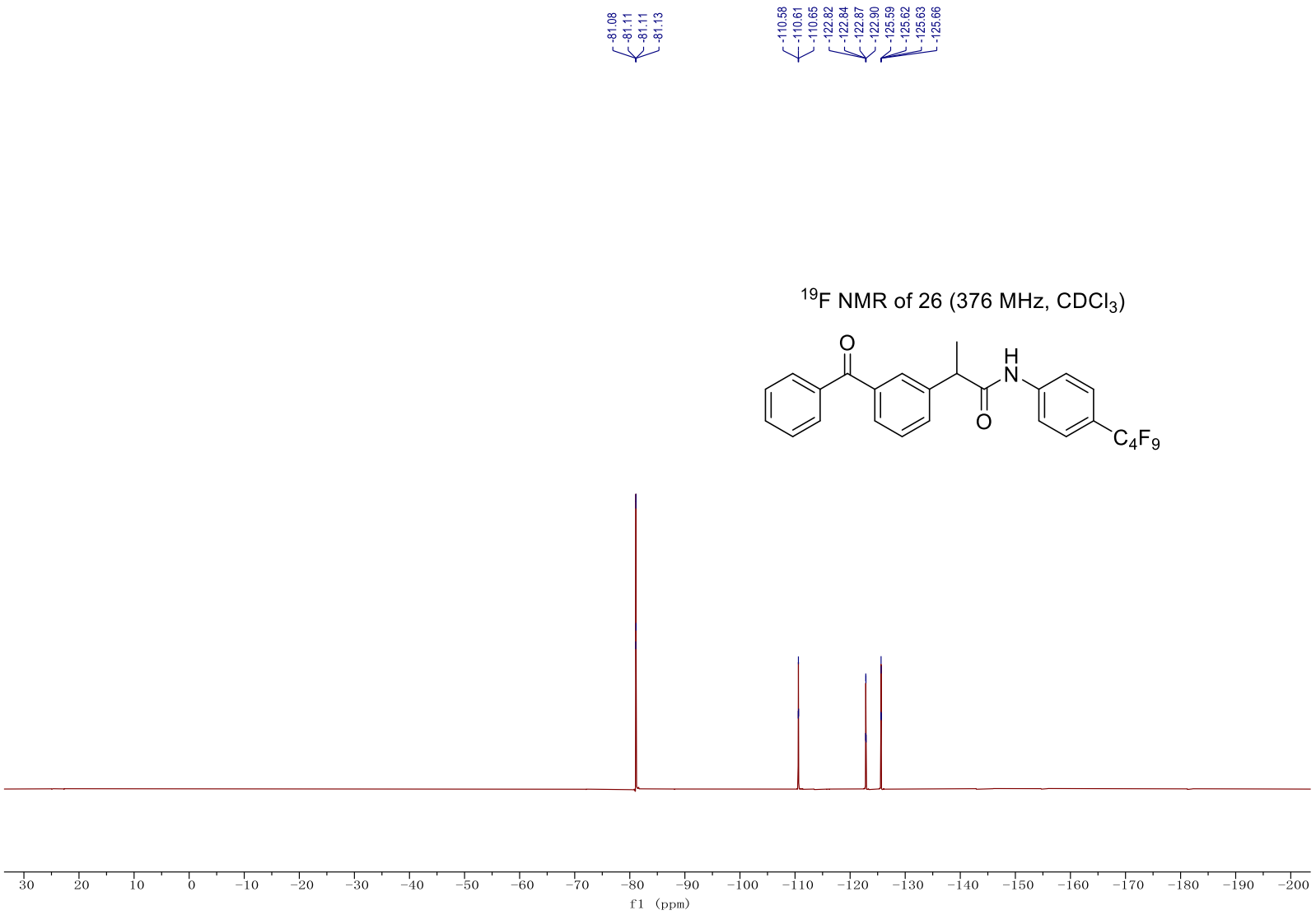




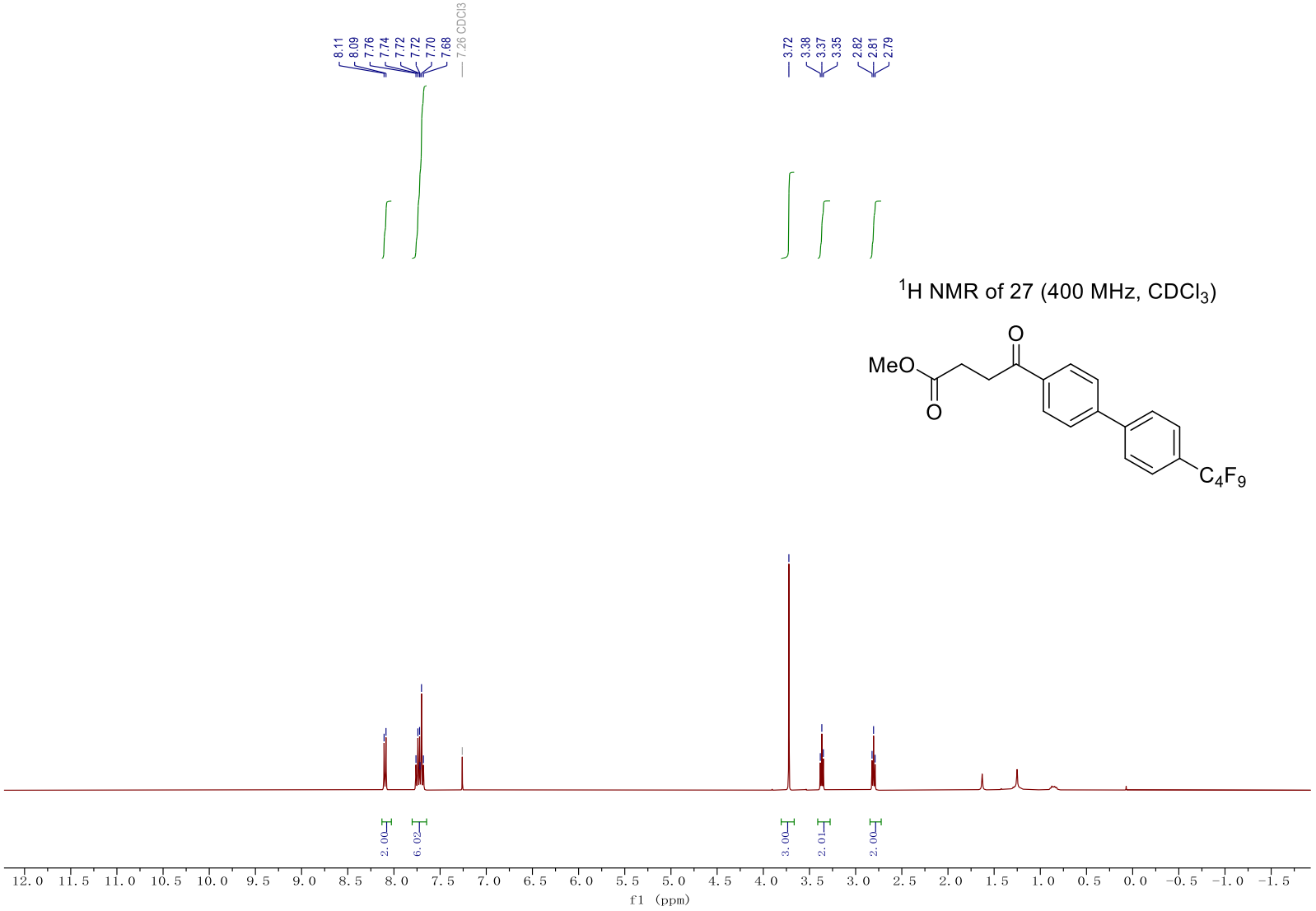
^{1}H NMR of 26 (400 MHz, $CDCl_3$)



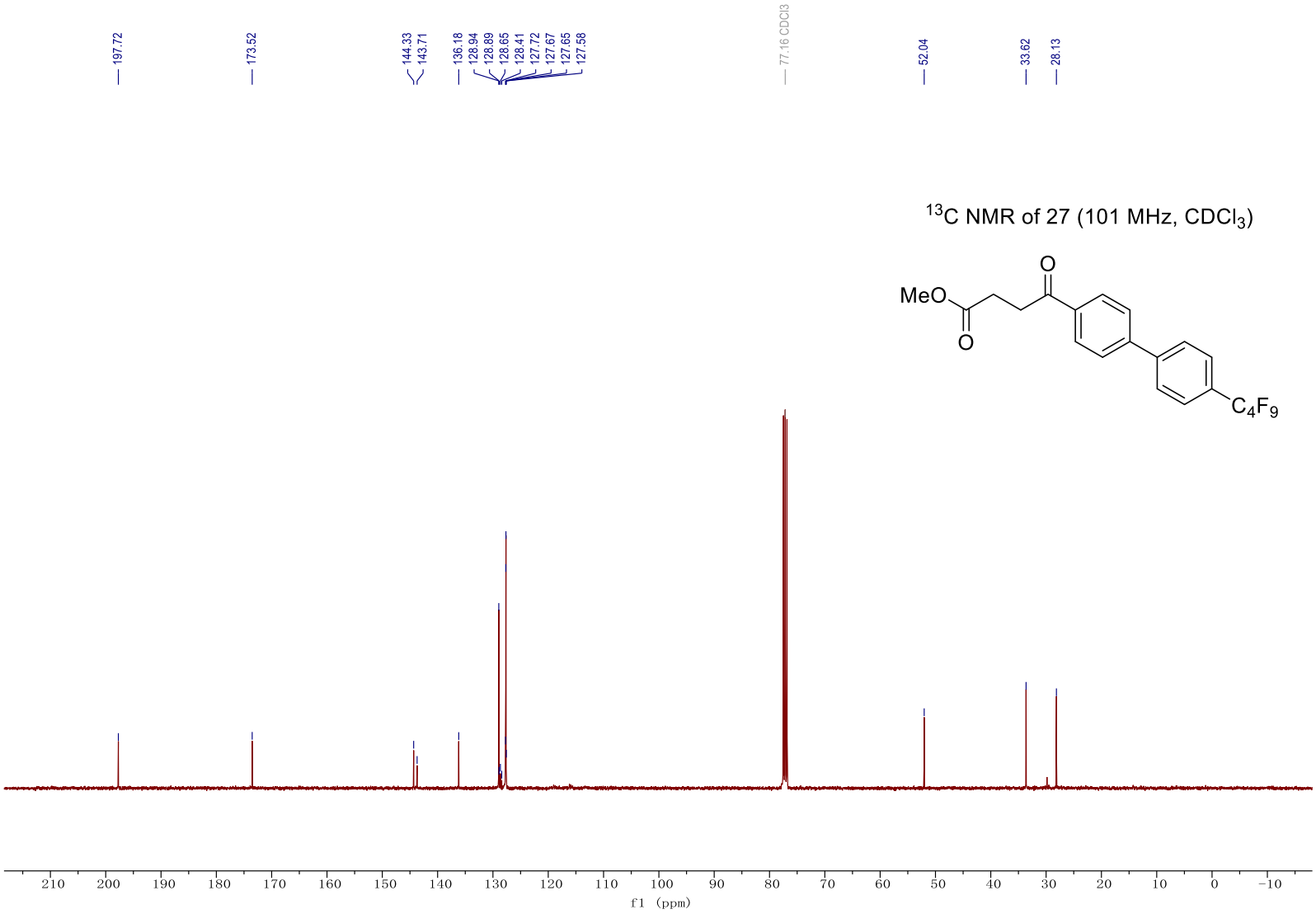
^{13}C NMR of 26 (101 MHz, $CDCl_3$)



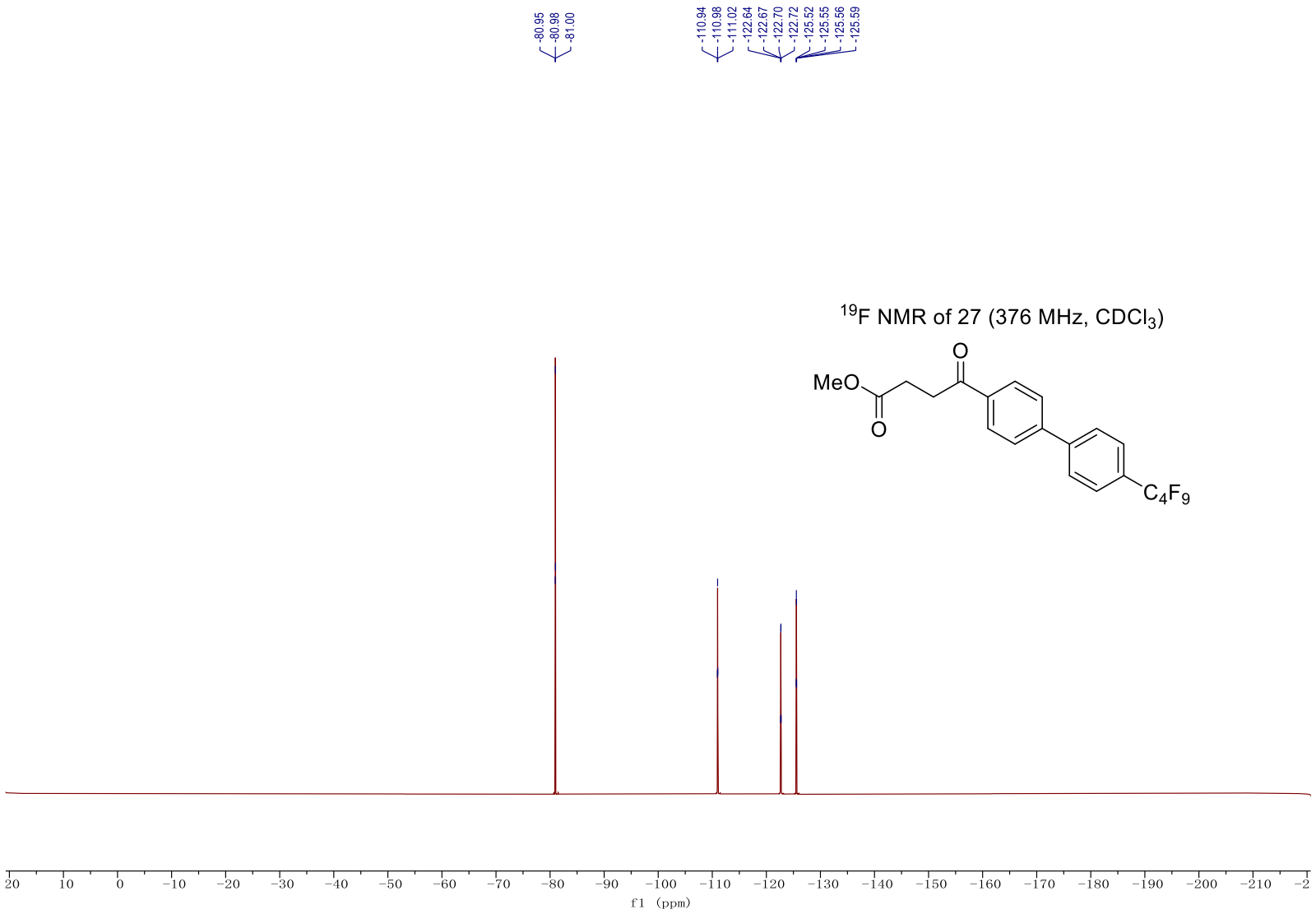
^{19}F NMR of 26 (376 MHz, $CDCl_3$)

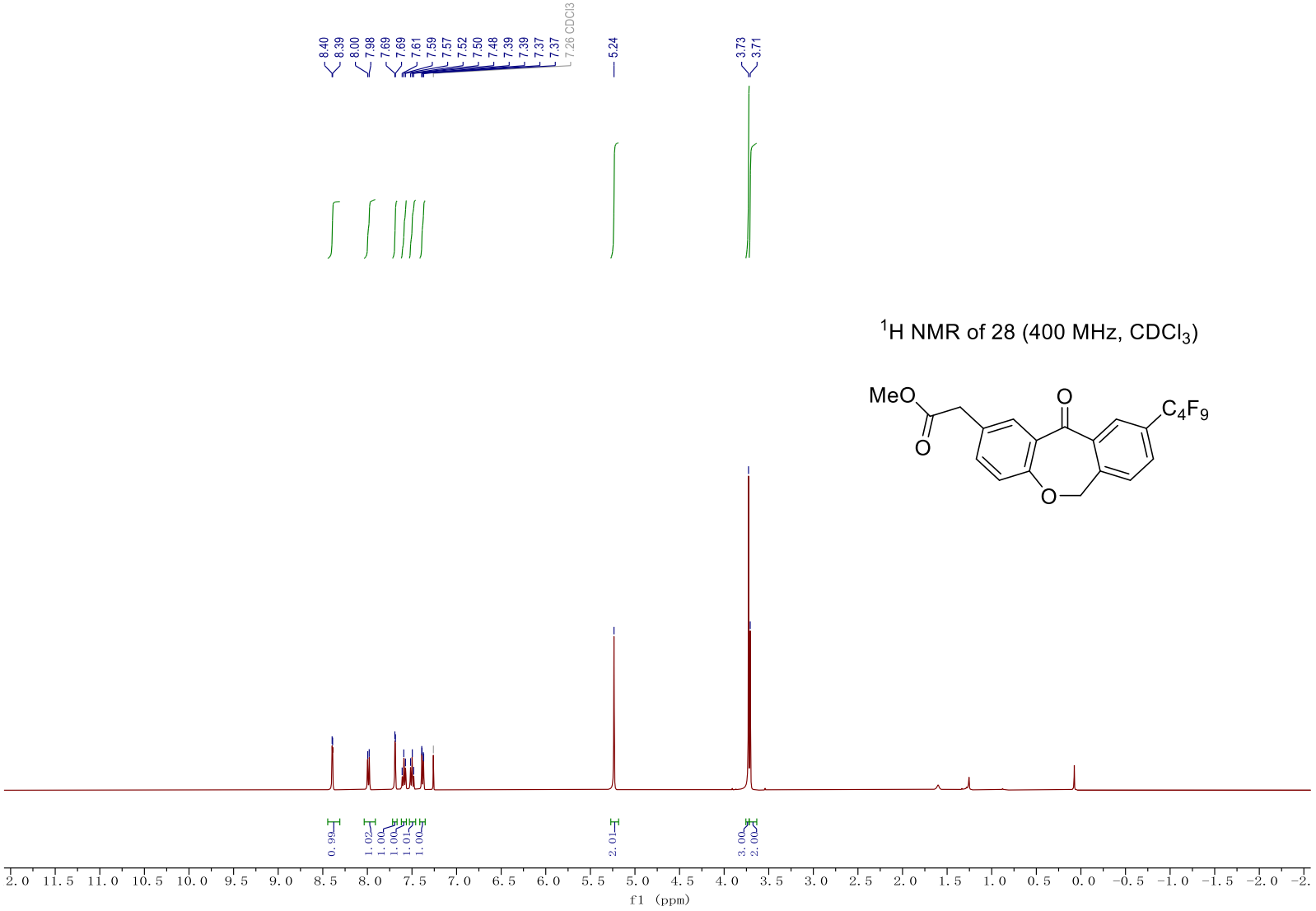


^{1}H NMR of 27 (400 MHz, $CDCl_3$)

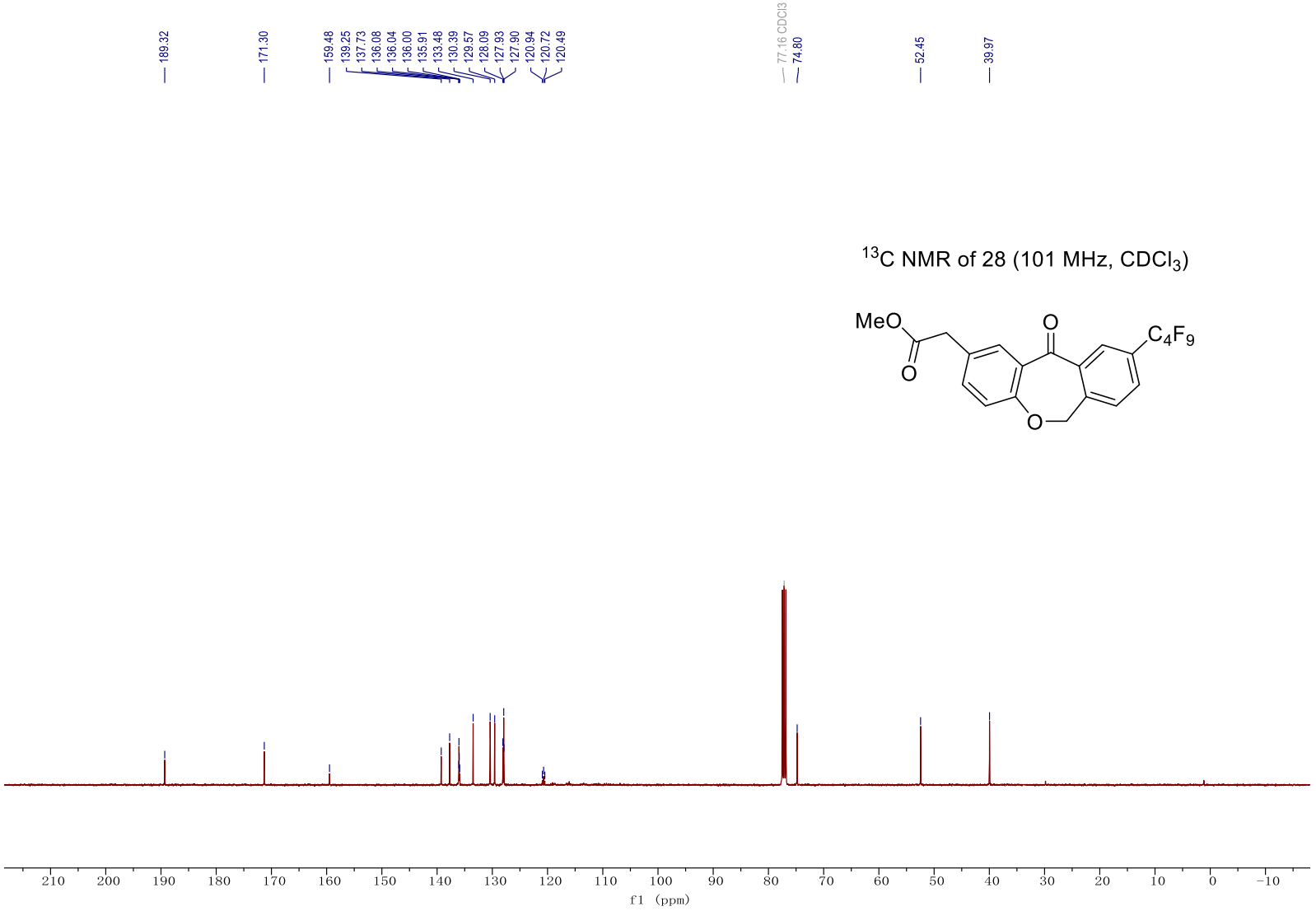


^{13}C NMR of 27 (101 MHz, $CDCl_3$)


-80.95
-80.98
-81.00
-110.94
-110.98
-111.02
-122.64
-122.67
-122.70
-122.72
-125.52
-125.55
-125.56
-125.59
19F NMR of 27 (376 MHz, CDCl3)
MeO
O
O
O
C4F9
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)



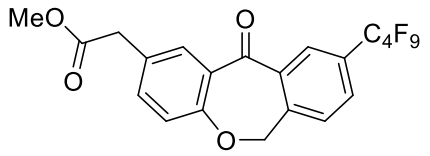
^{1}H NMR of 28 (400 MHz, $CDCl_3$)

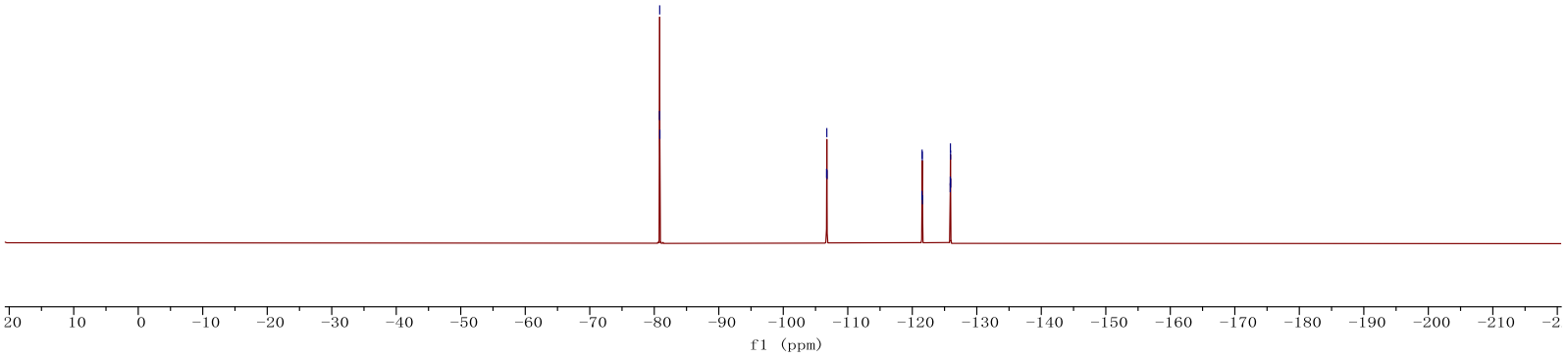


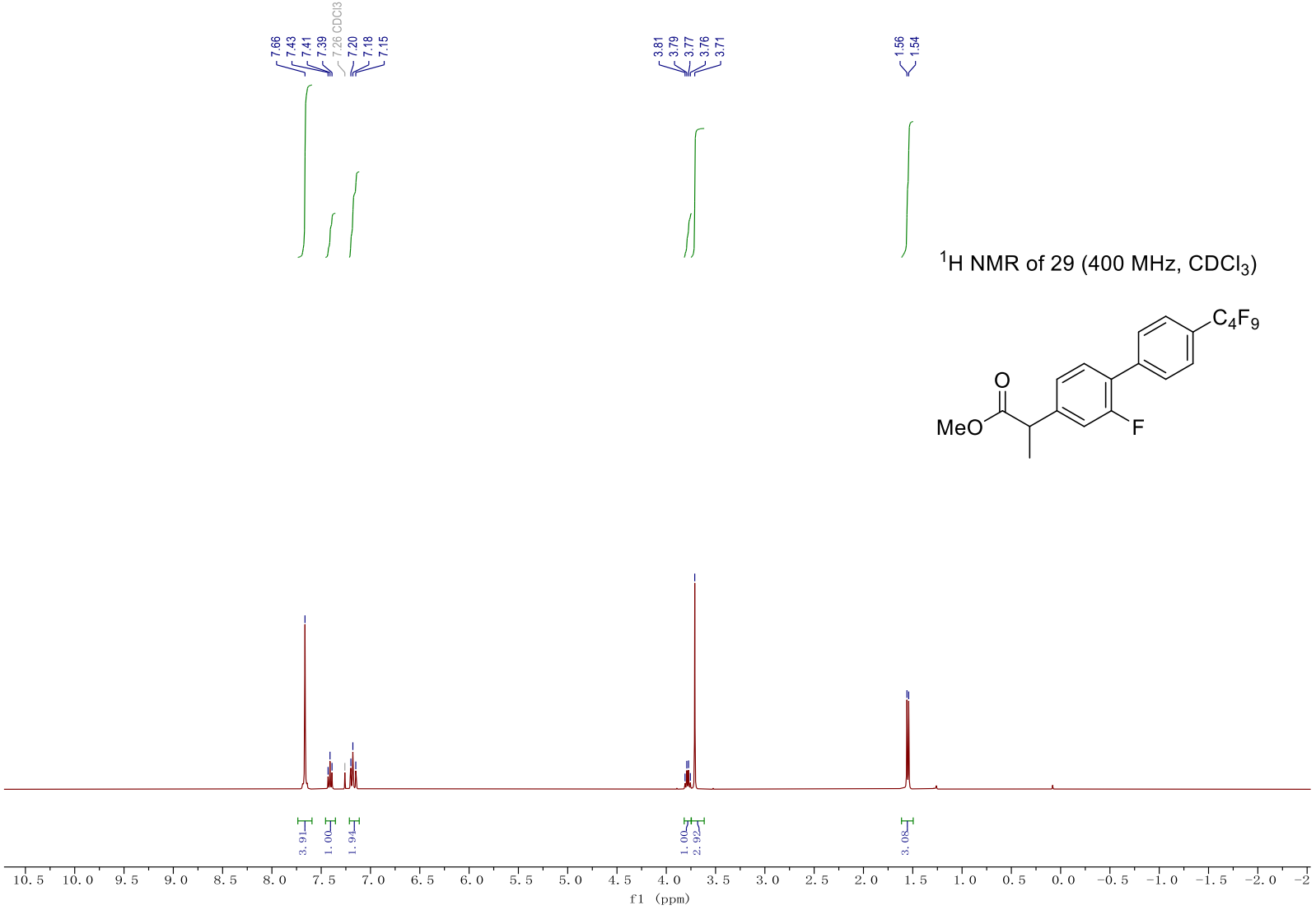
^{13}C NMR of 28 (101 MHz, $CDCl_3$)

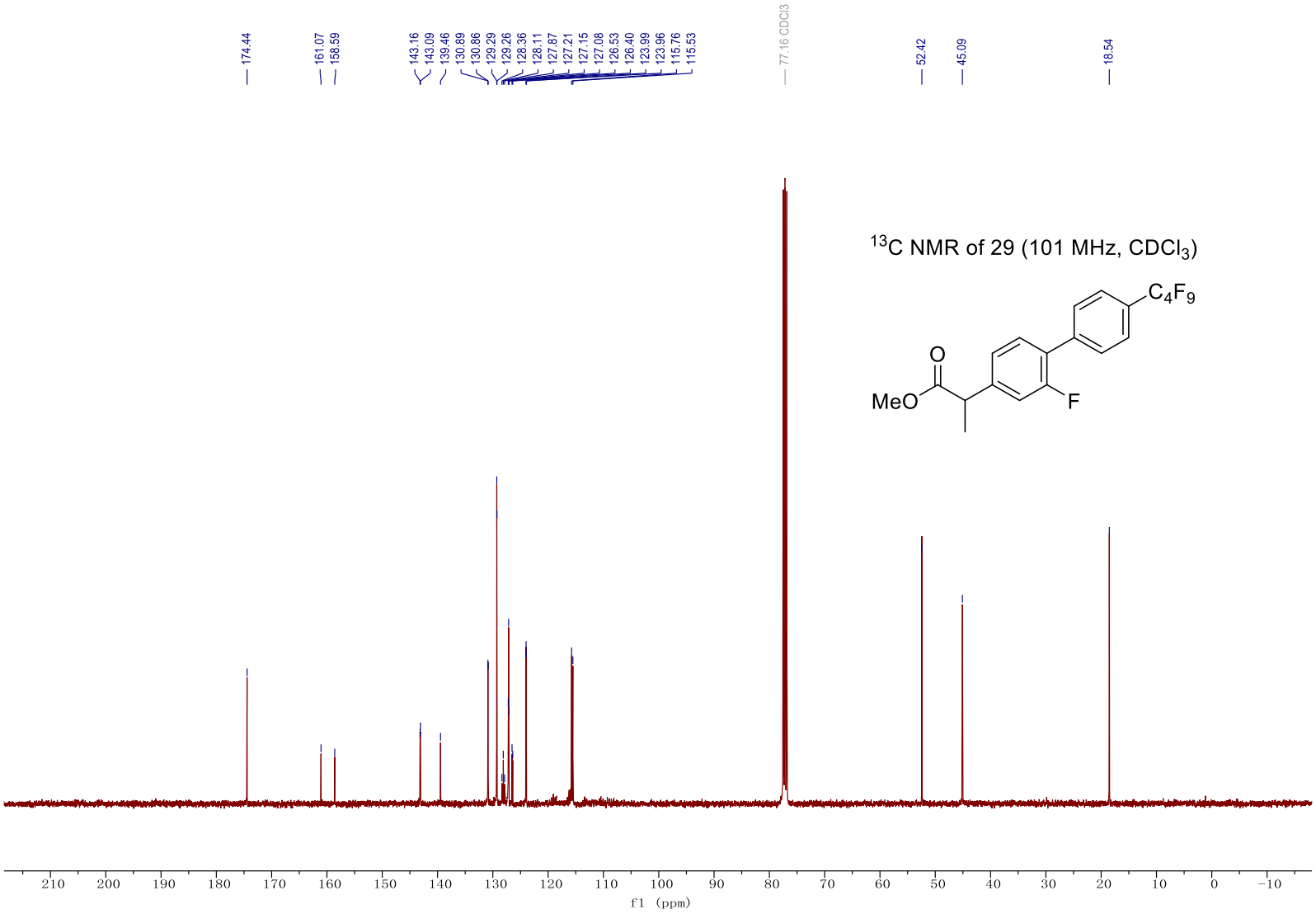
-80.82
-80.84
-80.87
-106.72
-106.75
-106.79
-121.50
-121.52
-121.55
-121.58
-125.88
-125.89
-125.91
-125.93
-125.95

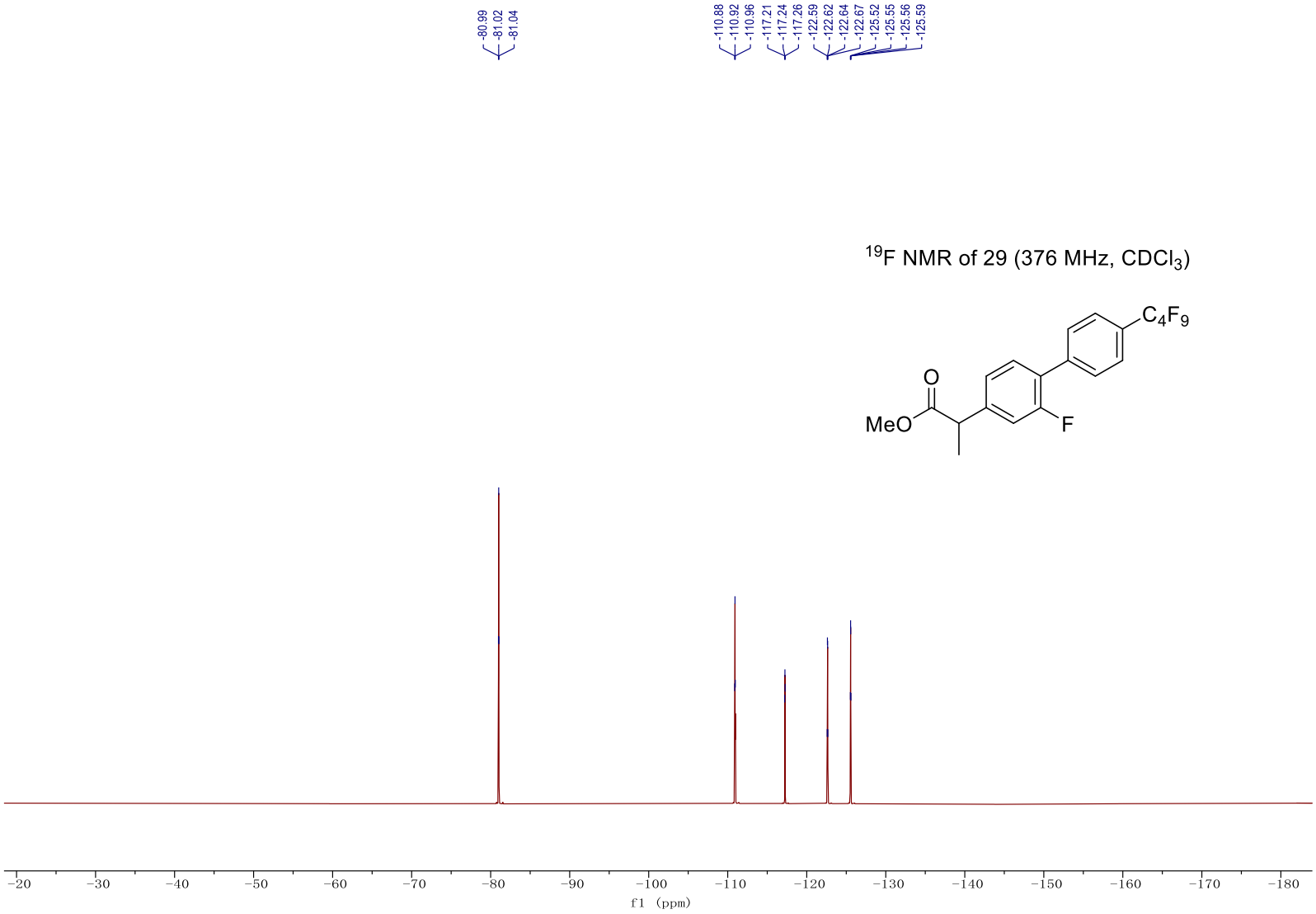
^{19}F NMR of 28 (376 MHz, $CDCl_3$)

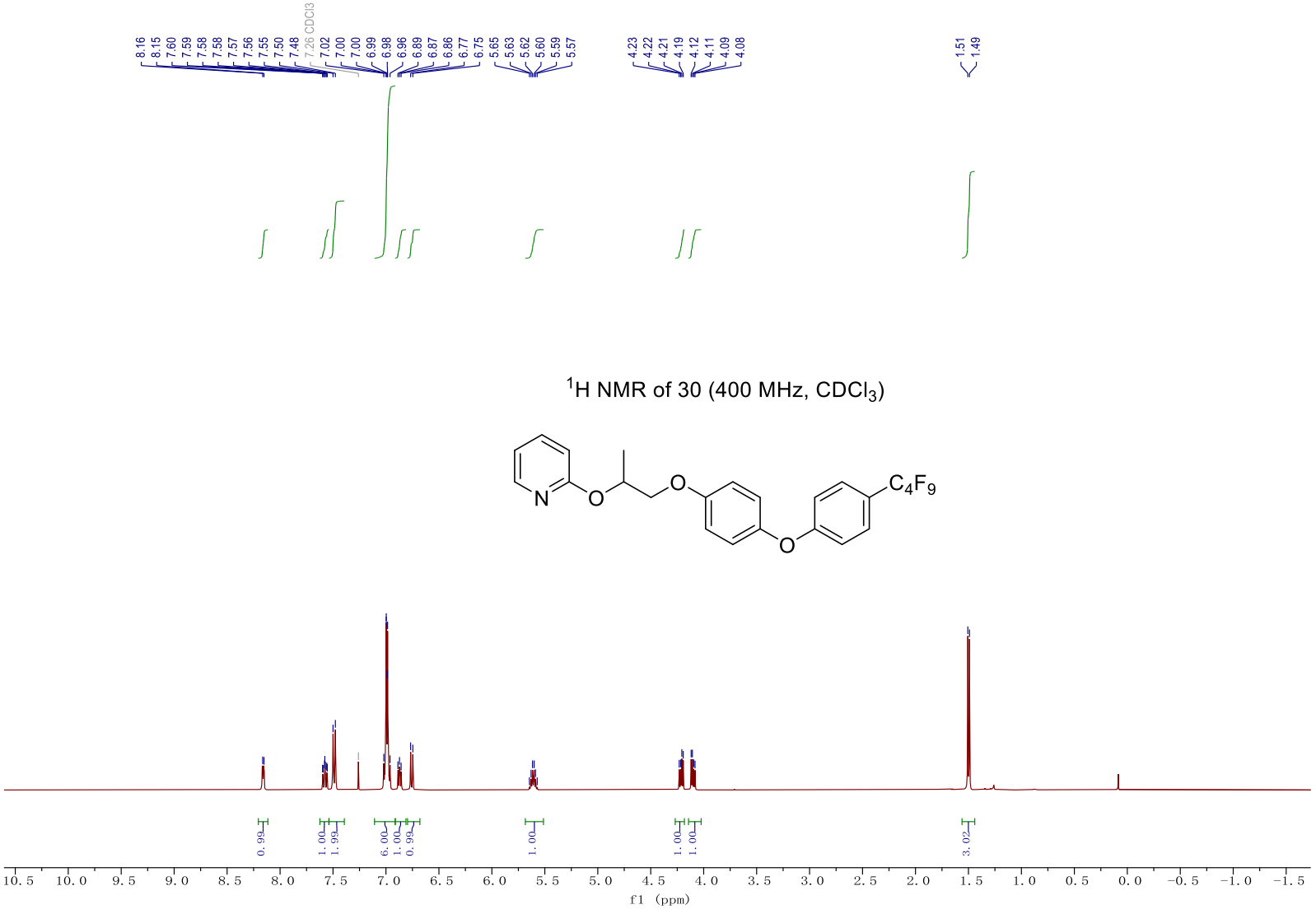




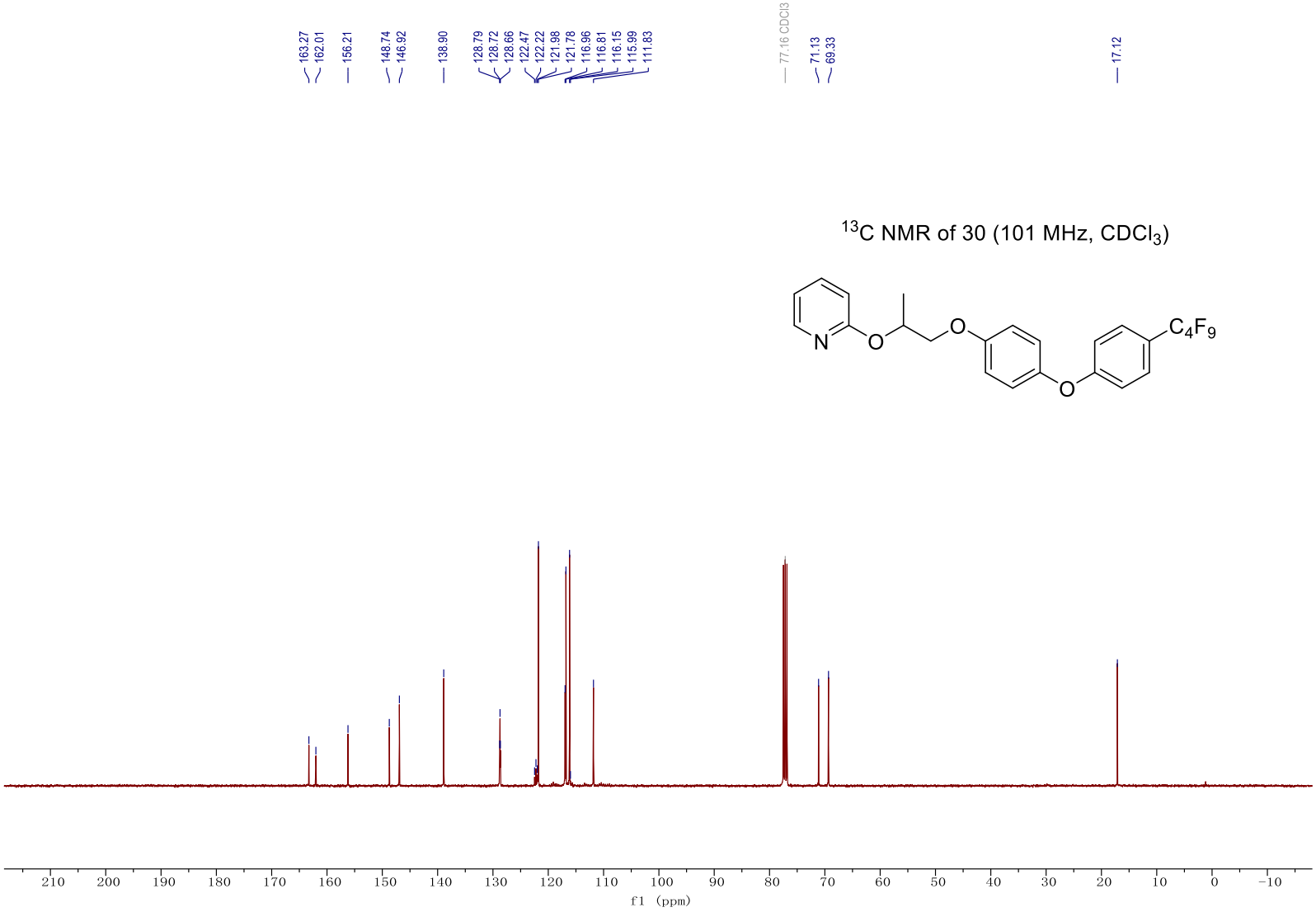

7.66
7.43
7.41
7.39
7.26 CDCl3
7.20
7.18
7.15
3.81
3.79
3.77
3.76
3.71
1.56
1.54
1H NMR of 29 (400 MHz, CDCl3)
C4F9
O
MeO
F
3.91
1.00
1.94
1.00
2.92
3.08
f1 (ppm)


174.44
161.07
158.59
143.16
143.09
139.46
130.89
130.86
129.29
129.26
128.36
128.11
127.87
127.21
127.15
127.08
126.53
126.40
123.99
123.96
115.76
115.53
77.16 CDCl3
52.42
45.09
18.54
13C NMR of 29 (101 MHz, CDCl3)
C4F9
O
MeO
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

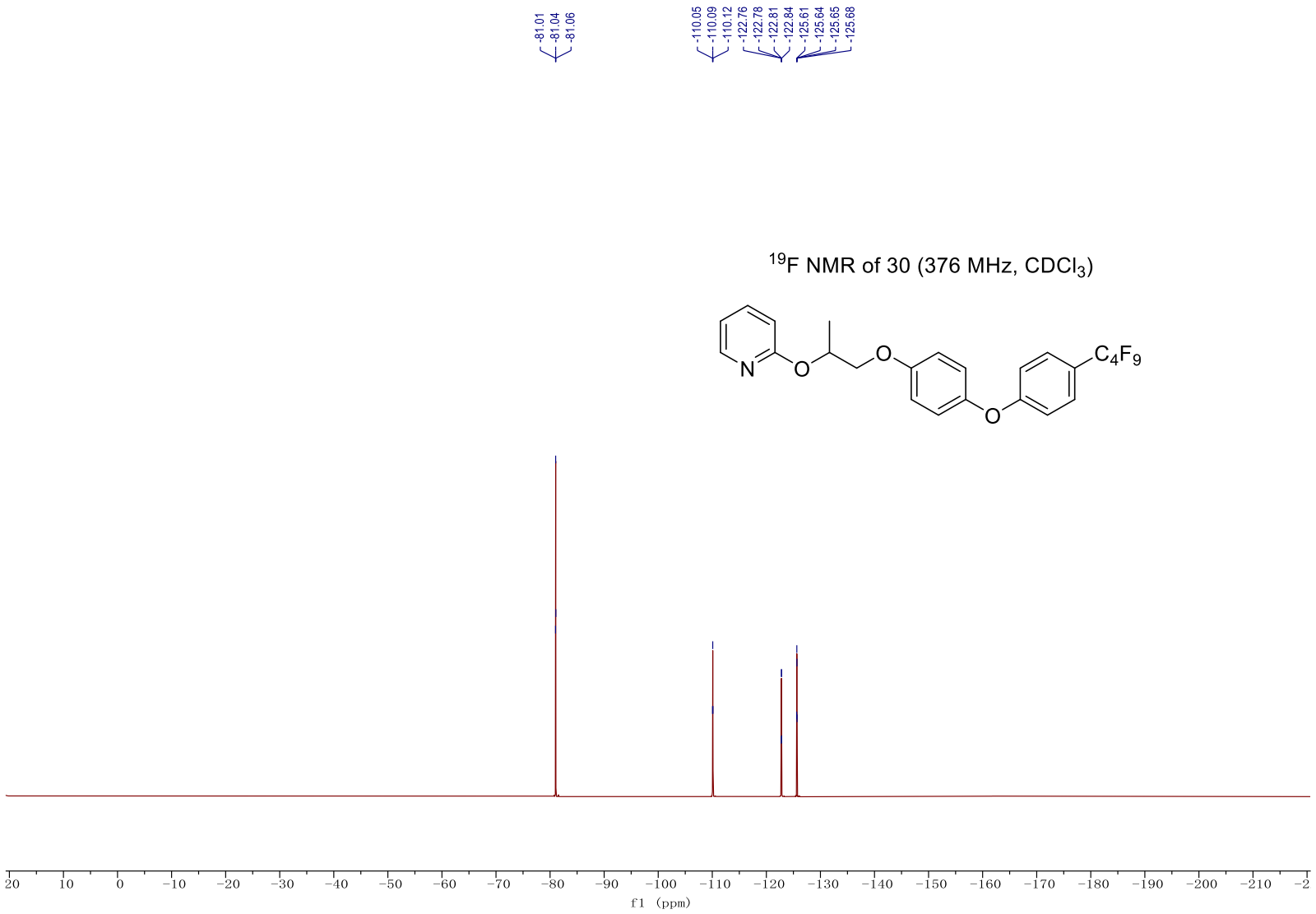

-80.99
-81.02
-81.04
-110.88
-110.92
-110.96
-117.21
-117.24
-117.26
-122.59
-122.62
-122.64
-122.67
-125.52
-125.55
-125.56
-125.59
^{19}F NMR of 29 (376 MHz, $CDCl_3$)
C_4F_9
O
MeO
F
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
f1 (ppm)

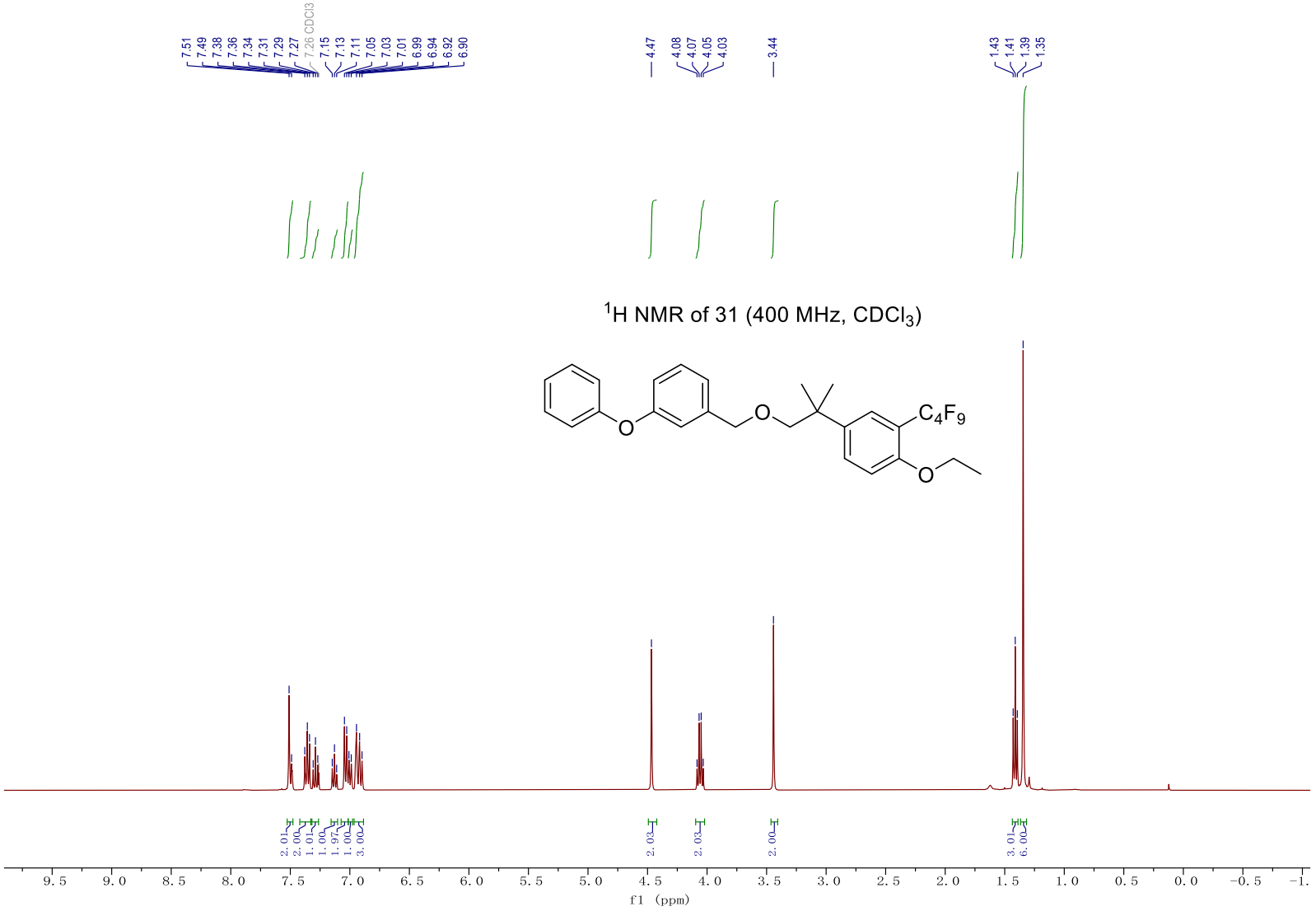


^{1}H NMR of 30 (400 MHz, $CDCl_3$)

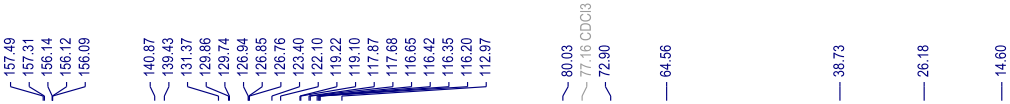


^{13}C NMR of 30 (101 MHz, $CDCl_3$)

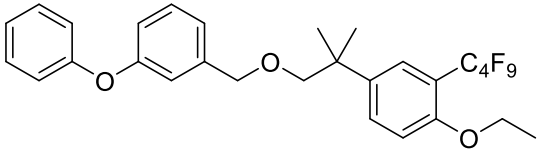

-81.01
-81.04
-81.06
-110.05
-110.09
-110.12
-122.76
-122.78
-122.81
-122.84
-125.61
-125.64
-125.65
-125.68
19F NMR of 30 (376 MHz, CDCl3)
N
O
O
O
C4F9
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−2
f1 (ppm)

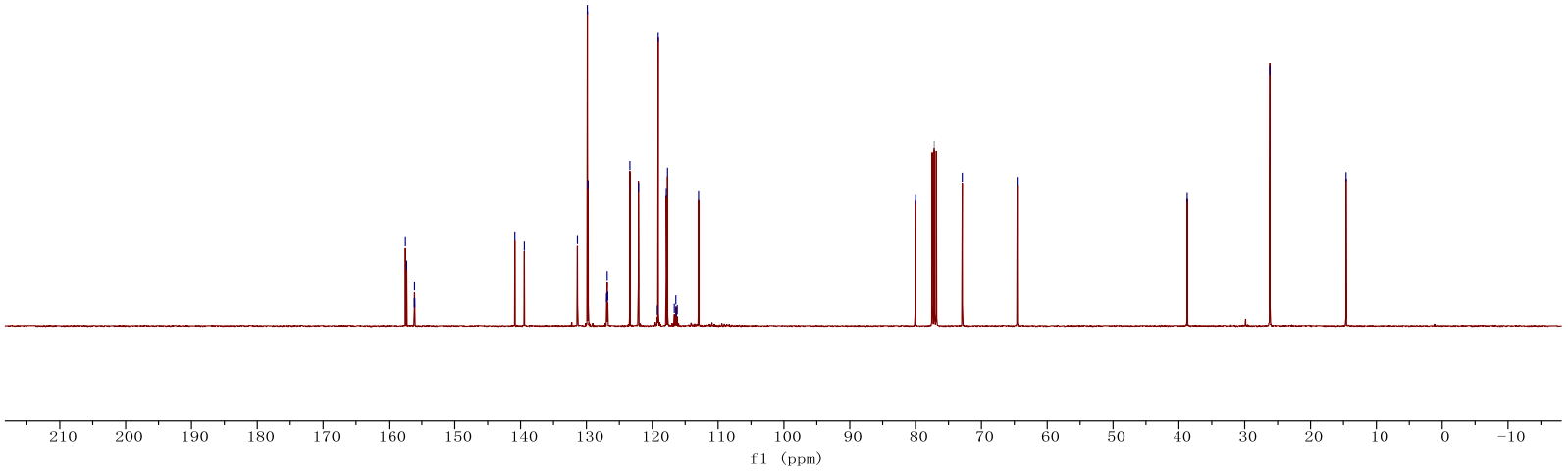


^{1}H NMR of 31 (400 MHz, $CDCl_3$)



^{13}C NMR of 31 (101 MHz, $CDCl_3$)

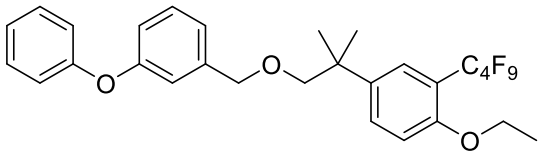


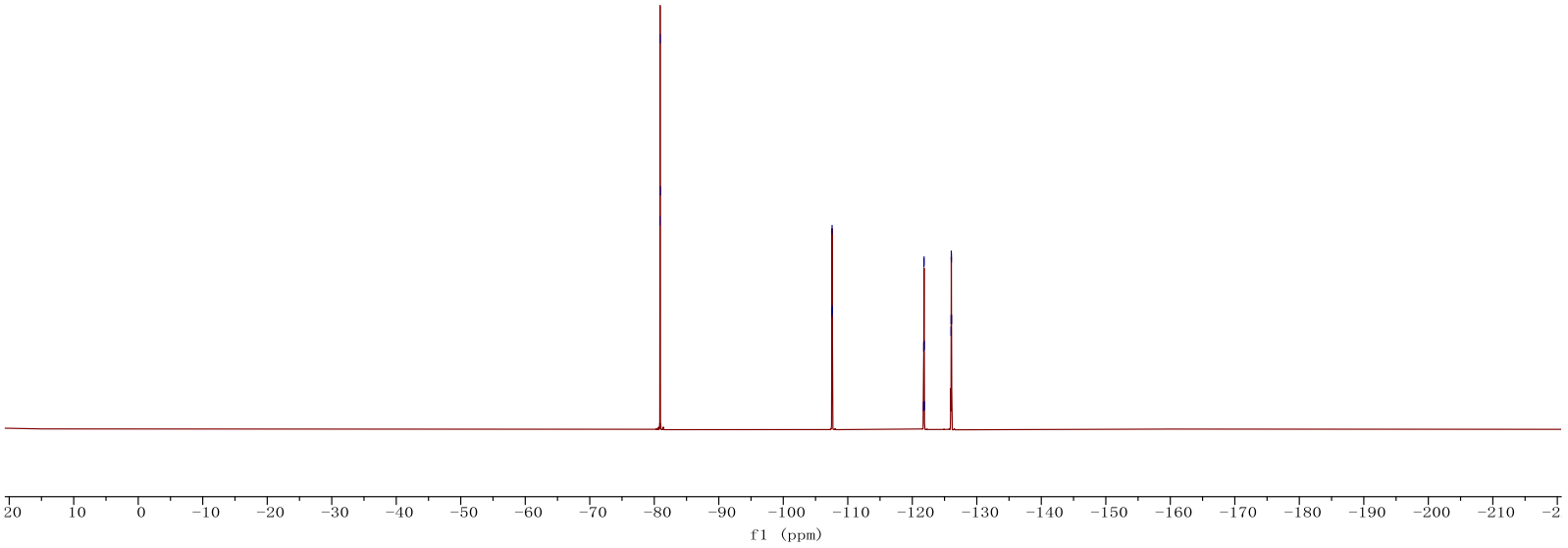


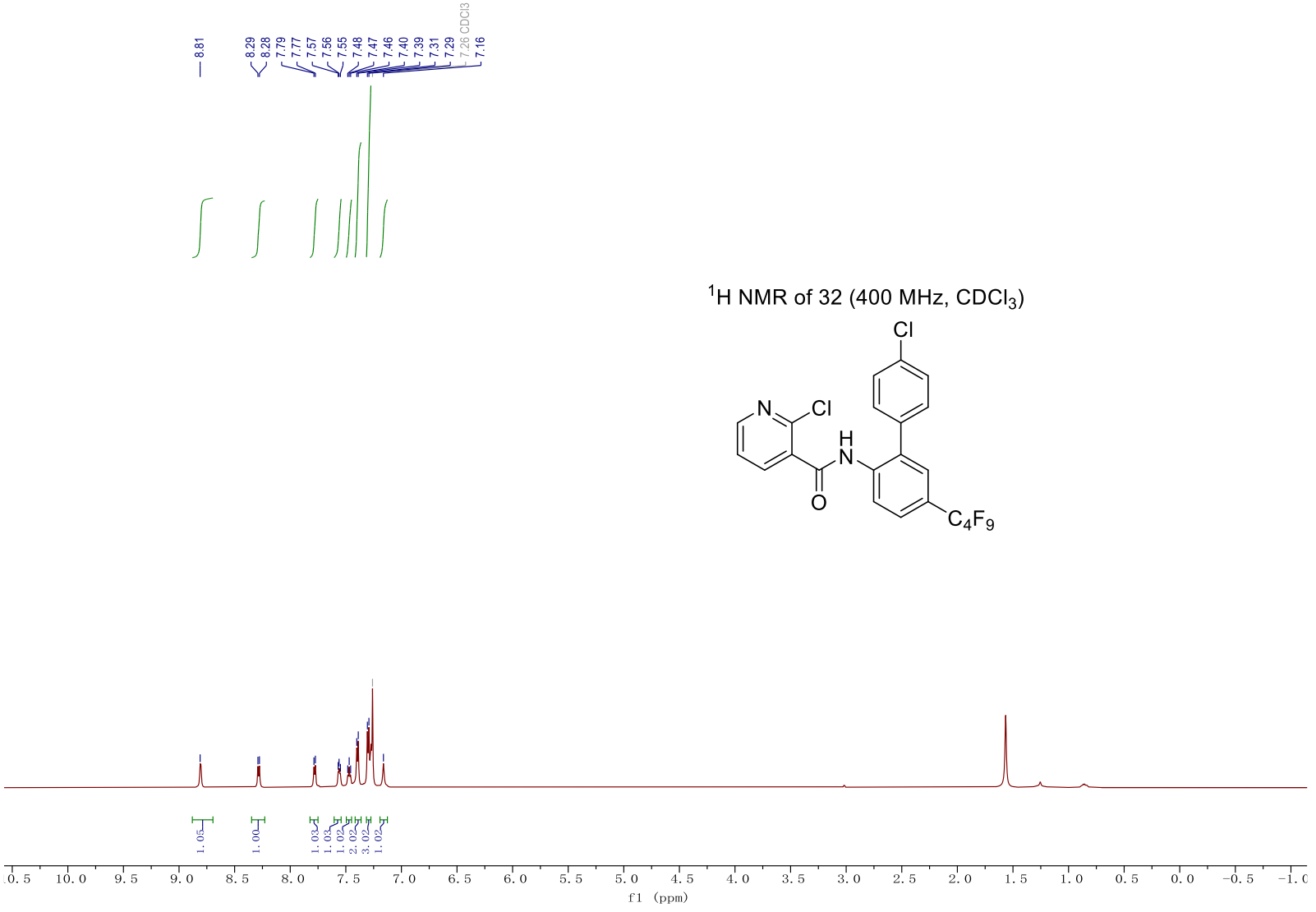
-80.88
-80.90
-80.93

-107.53
-107.57
-107.60
-121.75
-121.78
-121.80
-121.83
-121.85
-121.88
-126.01
-126.02
-126.05
-126.06
-126.09

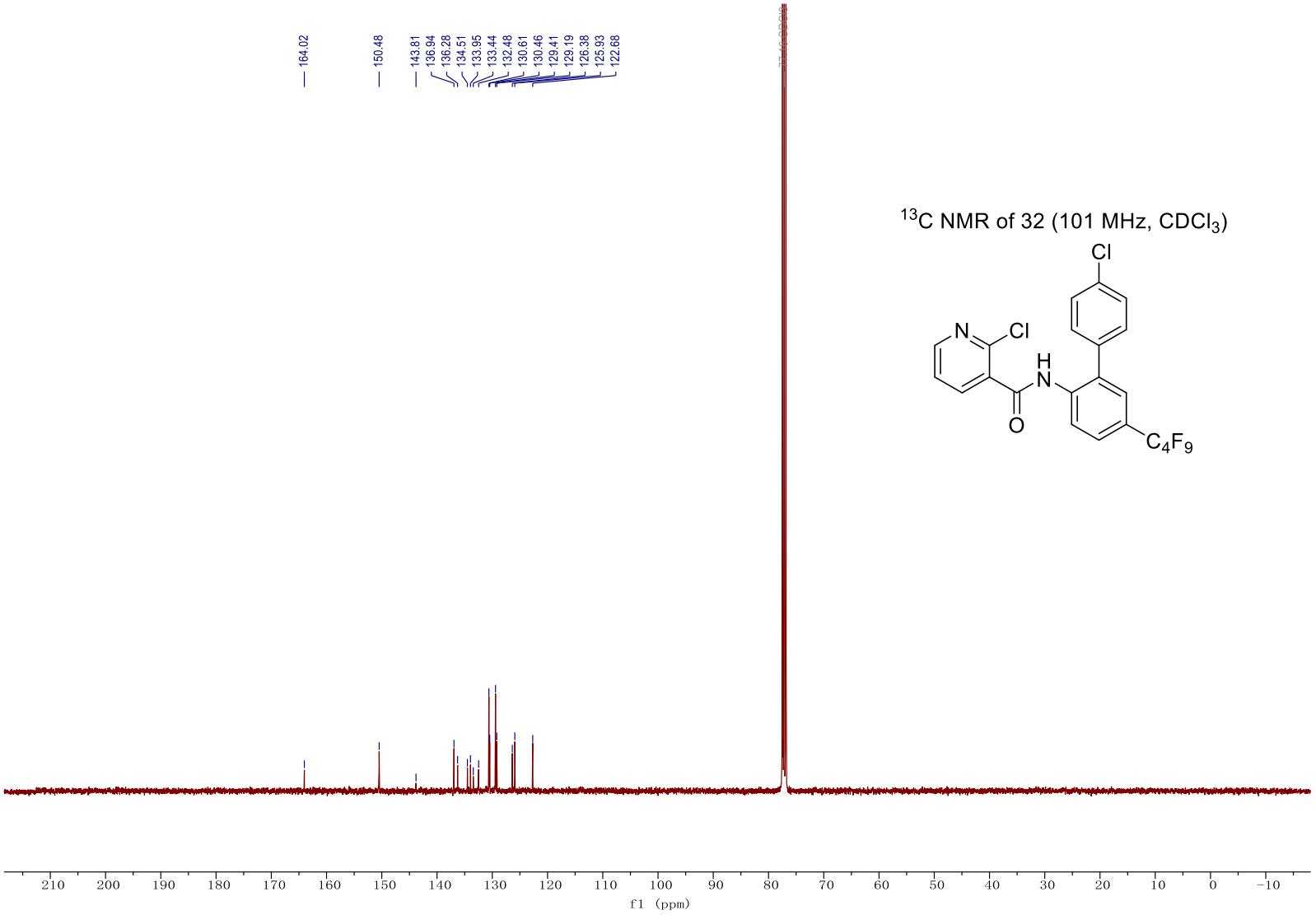
^{19}F NMR of 31 (376 MHz, $CDCl_3$)





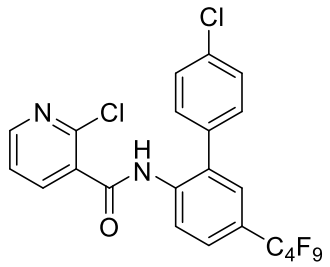


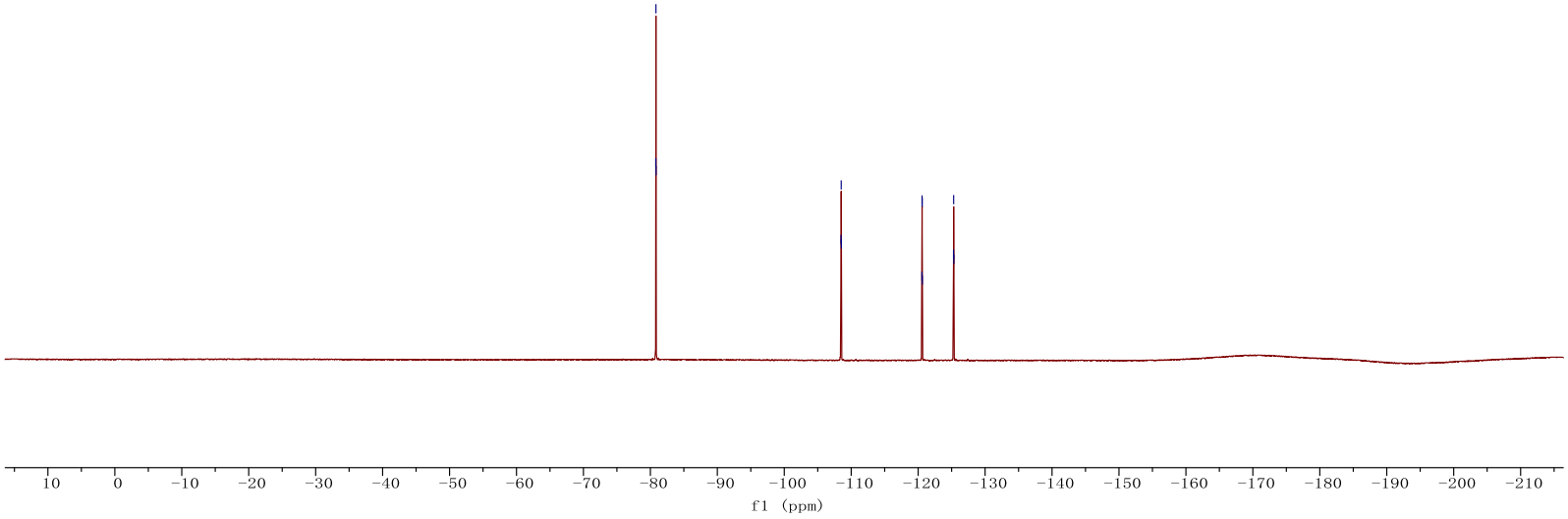
^{1}H NMR of 32 (400 MHz, $CDCl_3$)

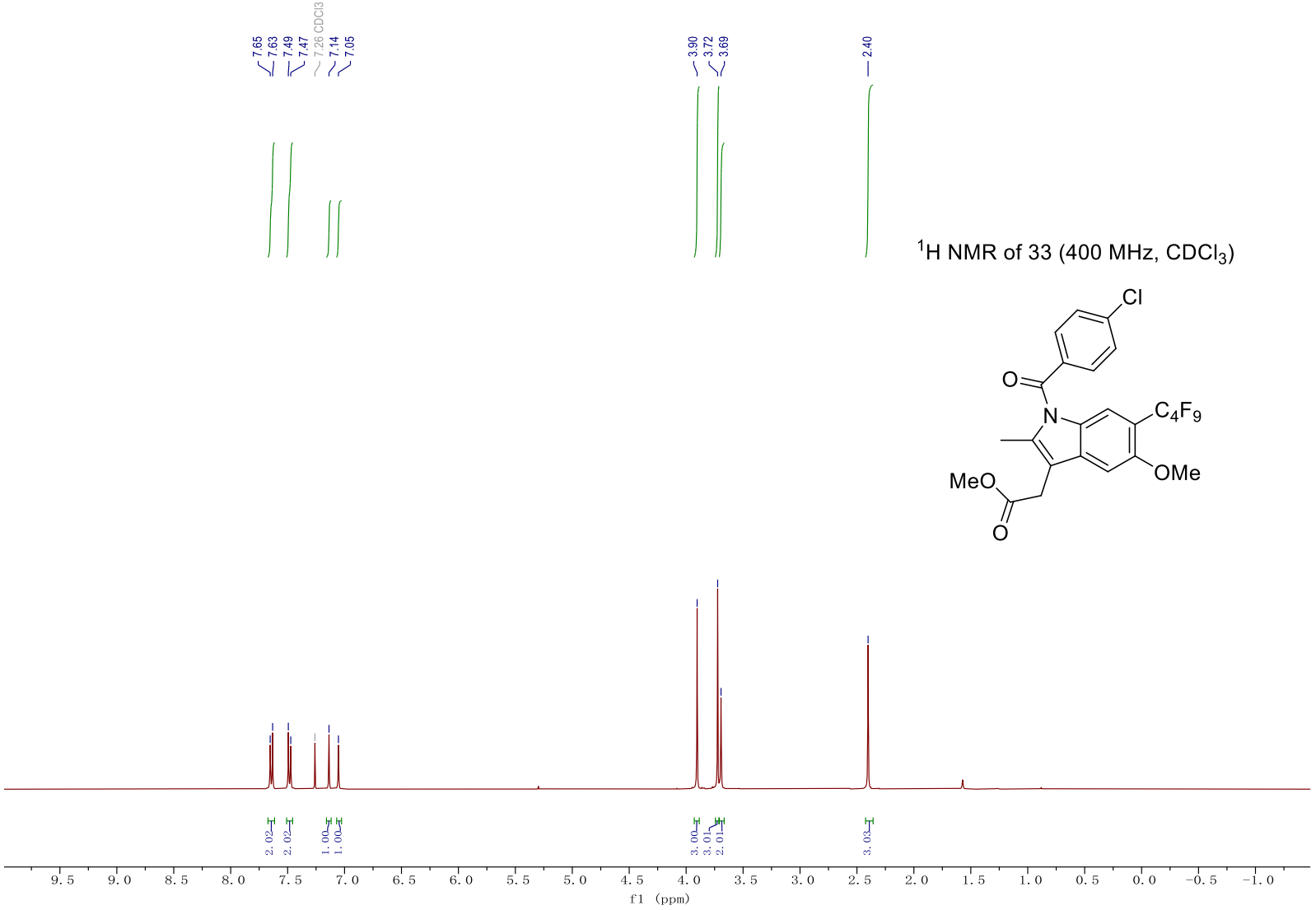

164.02
150.48
143.81
136.94
136.28
134.51
133.95
133.44
132.48
130.61
130.46
129.41
129.19
126.38
125.93
122.68
77.46
77.00
76.55
^{13}C NMR of 32 (101 MHz, CDCl$_3$)
Cl
N
Cl
H
N
O
C$_4$F$_9$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

-80.81
-80.83
-80.85
-108.49
-108.51
-108.53
-120.57
-120.59
-120.60
-120.62
-125.28
-125.31
-125.33

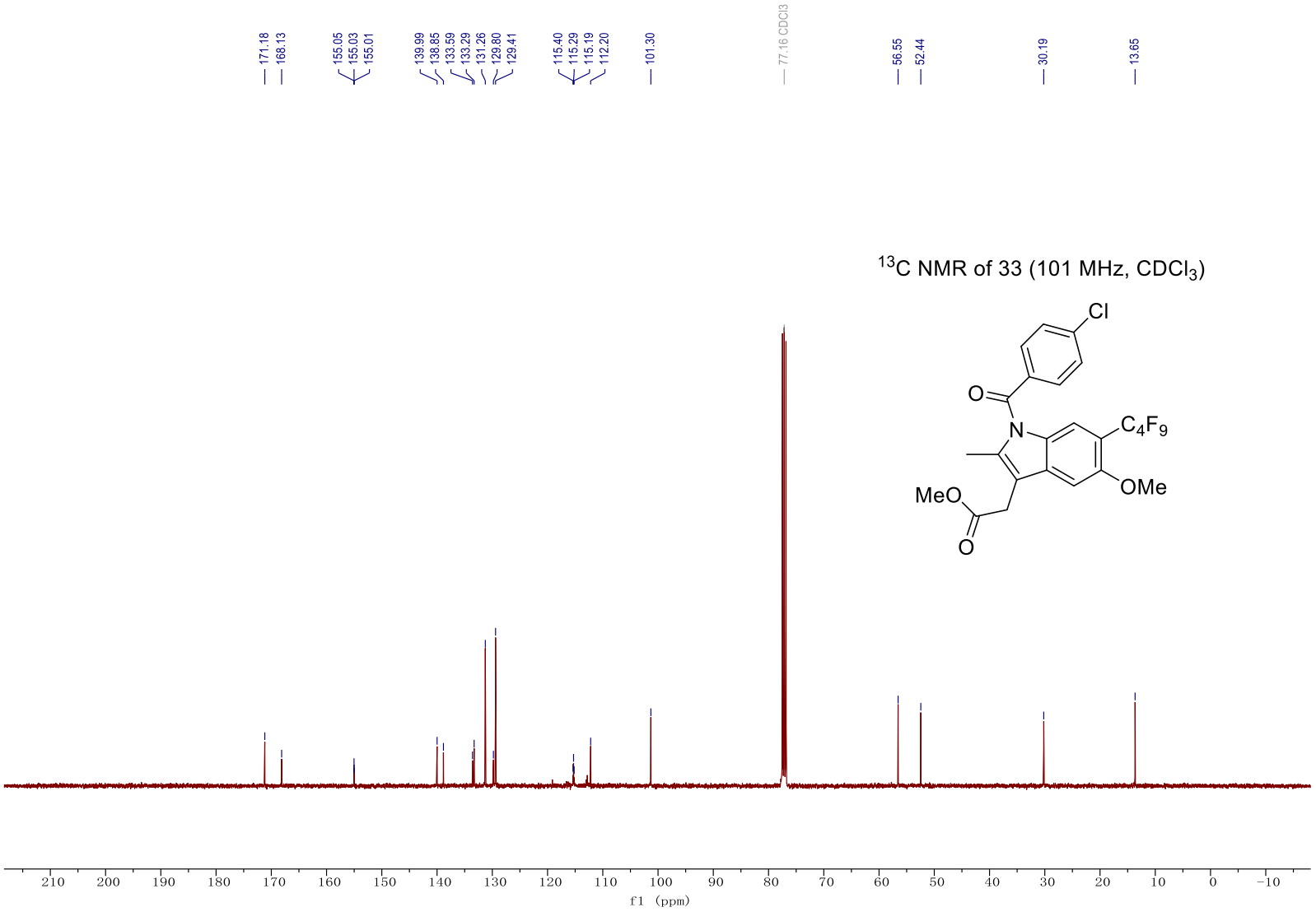
^{19}F NMR of 32 (376 MHz, $CDCl_3$)

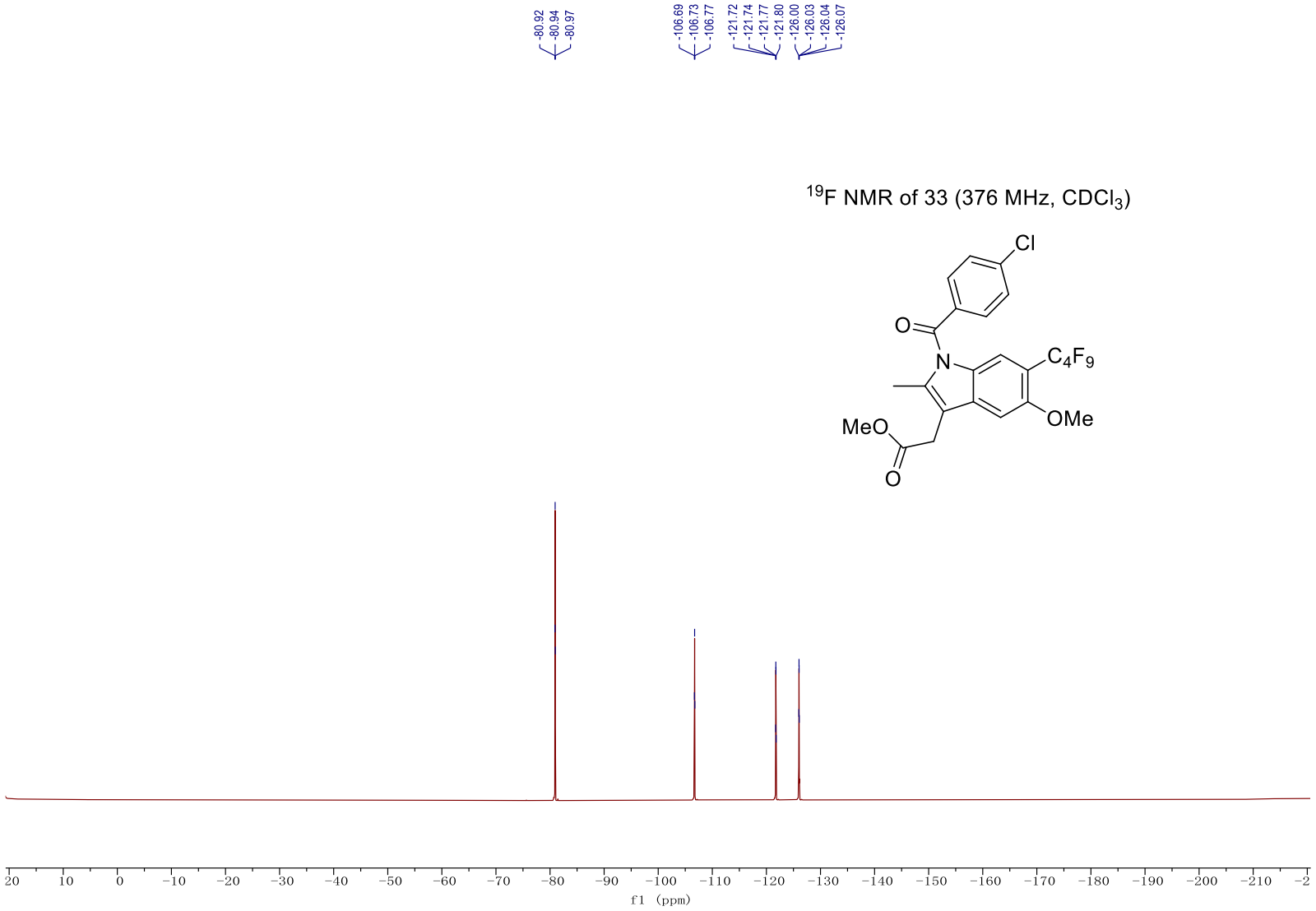


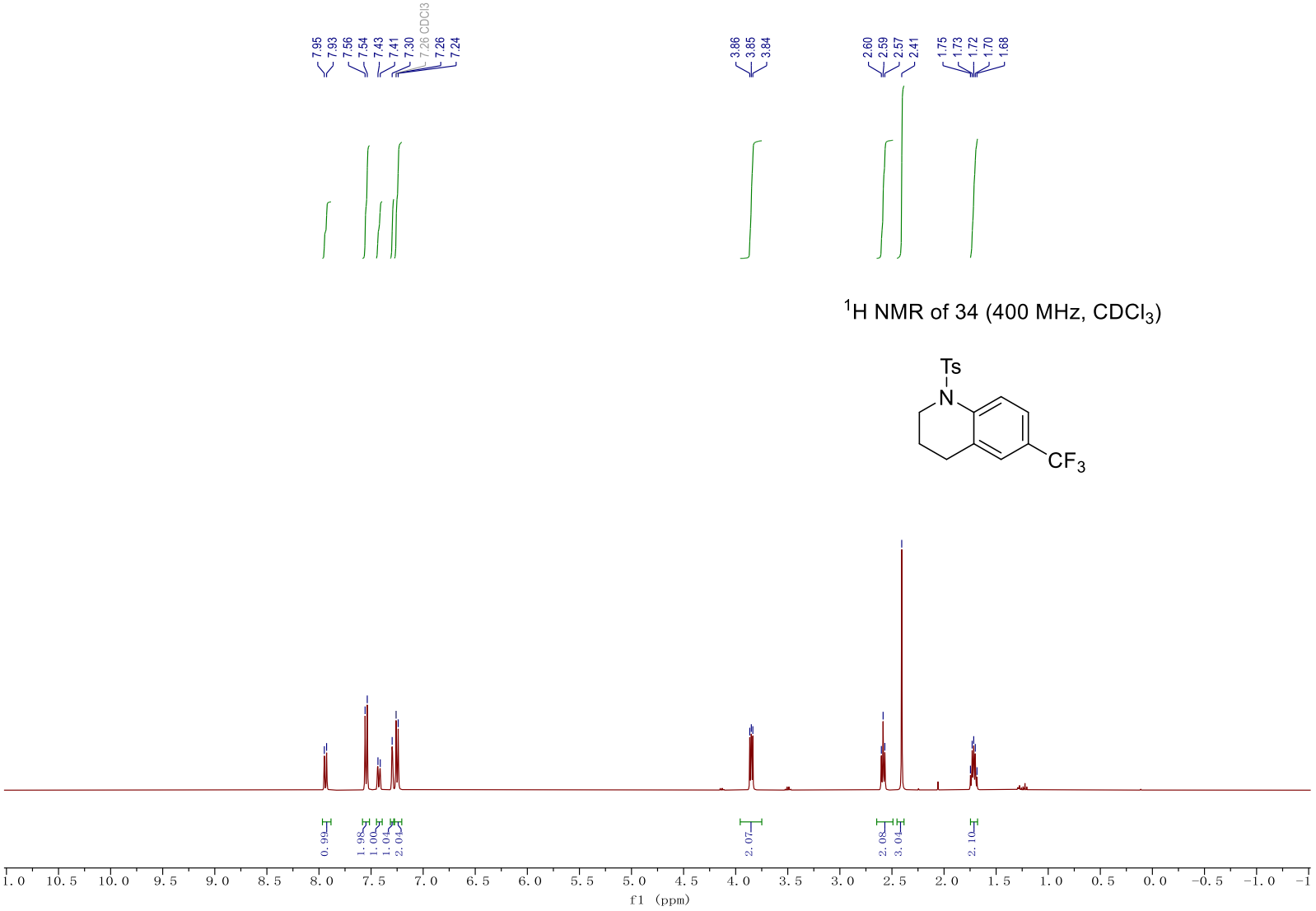




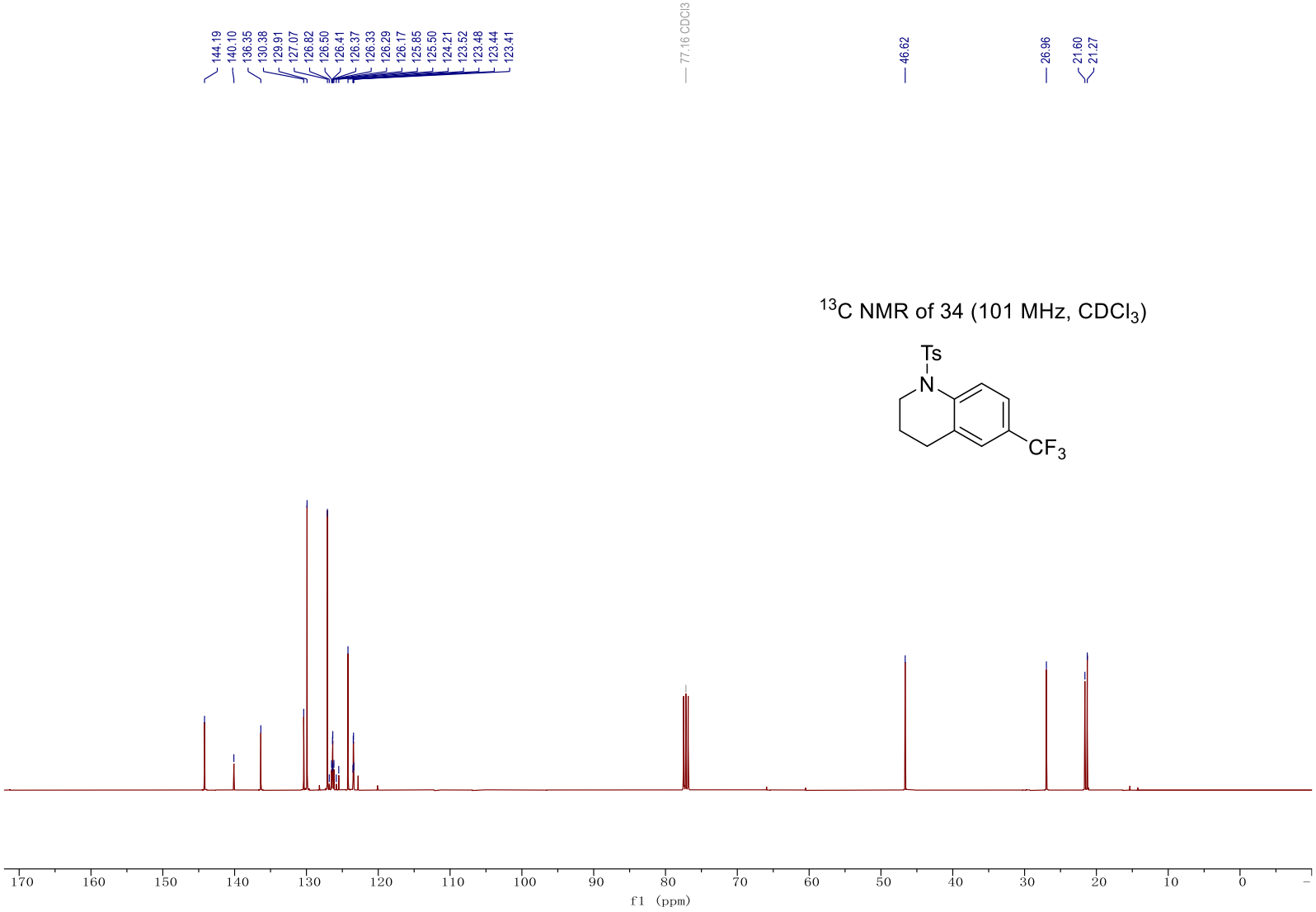
^{1}H NMR of 33 (400 MHz, $CDCl_3$)


171.18
168.13
155.05
155.03
155.01
139.99
138.85
133.59
133.29
131.26
129.80
129.41
115.40
115.29
115.19
112.20
101.30
77.16 CDCl3
56.55
52.44
30.19
13.65
13C NMR of 33 (101 MHz, CDCl3)
Cl
O
N
C4F9
OMe
MeO
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

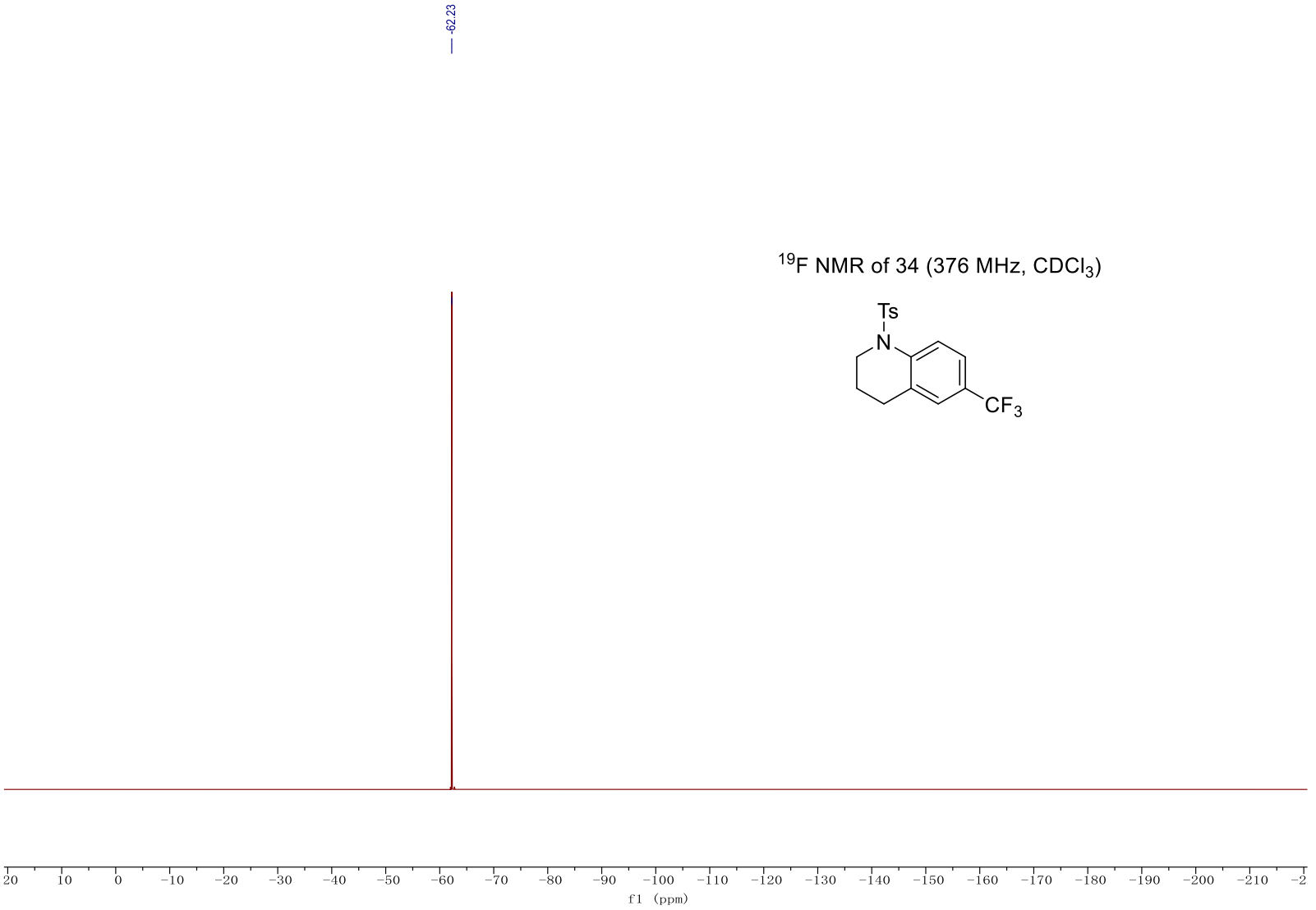

-80.92
-80.94
-80.97
-106.69
-106.73
-106.77
-121.72
-121.74
-121.77
-121.80
-126.00
-126.03
-126.04
-126.07
19F NMR of 33 (376 MHz, CDCl3)
Cl
O
N
C4F9
OMe
MeO
O
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

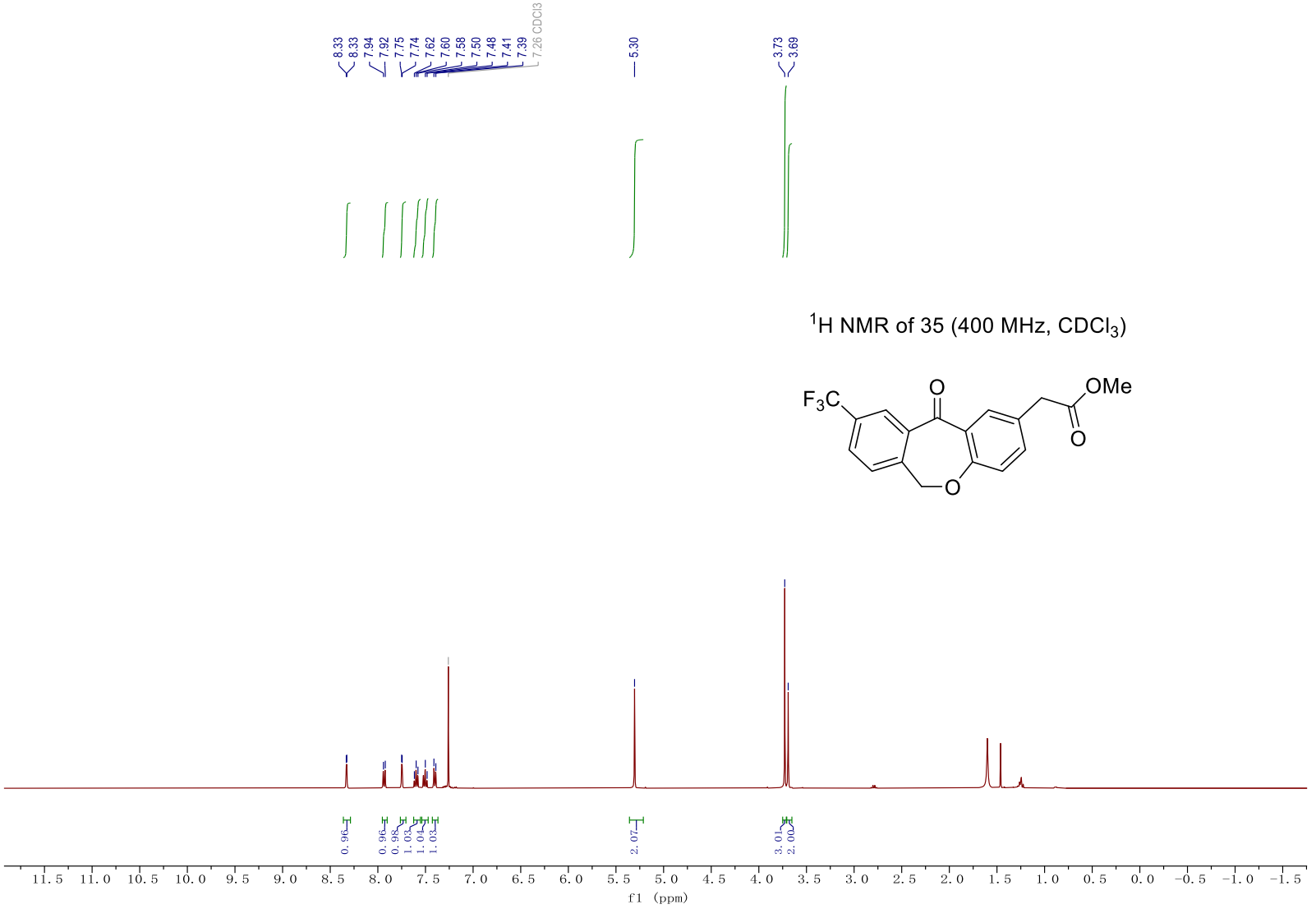


^{1}H NMR of 34 (400 MHz, $CDCl_3$)

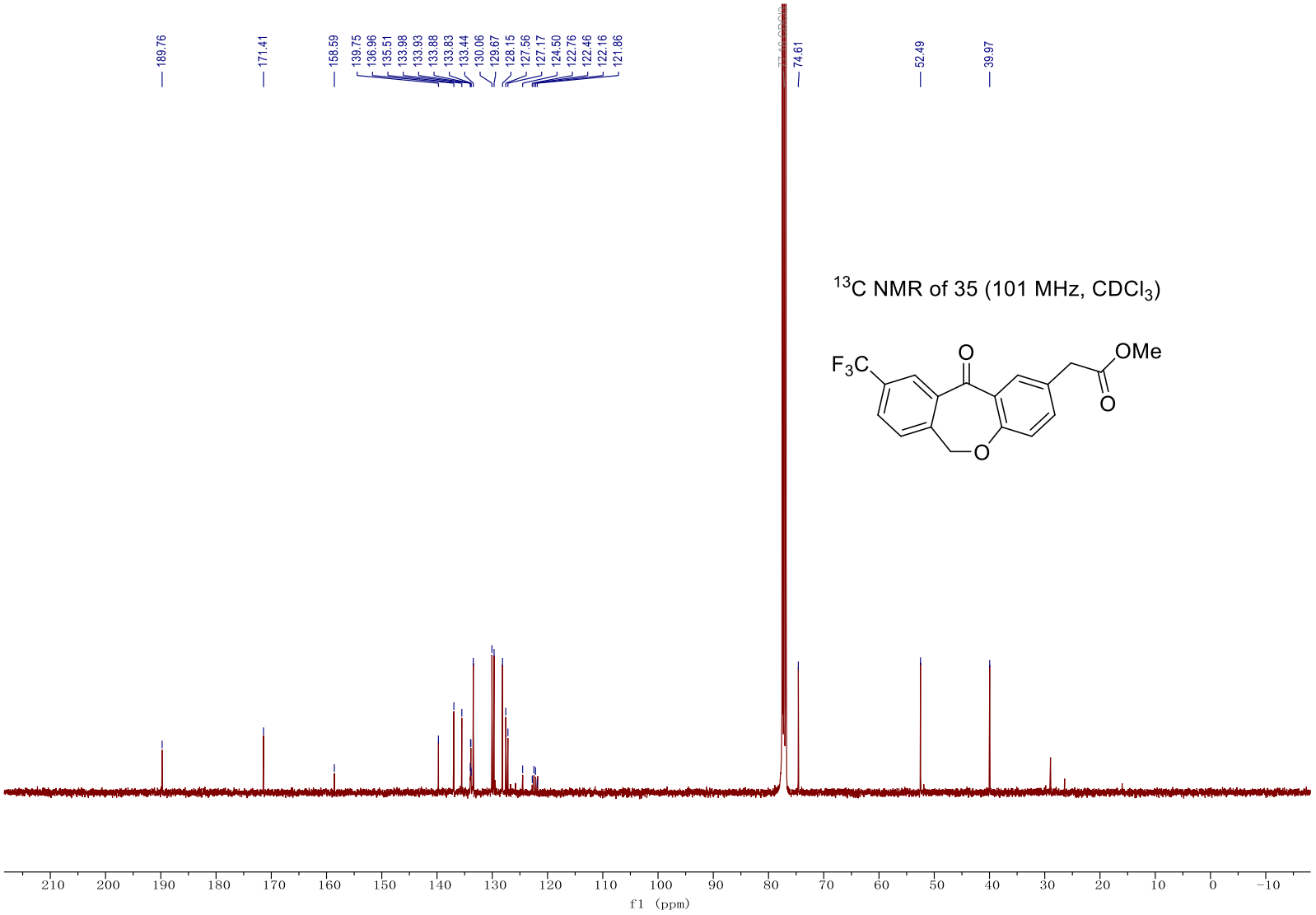

144.19
140.10
136.35
130.38
129.91
127.07
126.82
126.50
126.41
126.37
126.33
126.29
126.17
125.85
125.50
124.21
123.52
123.48
123.44
123.41
77.16 CDCl3
46.62
26.96
21.60
21.27
13C NMR of 34 (101 MHz, CDCl3)
Ts
N
CF3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

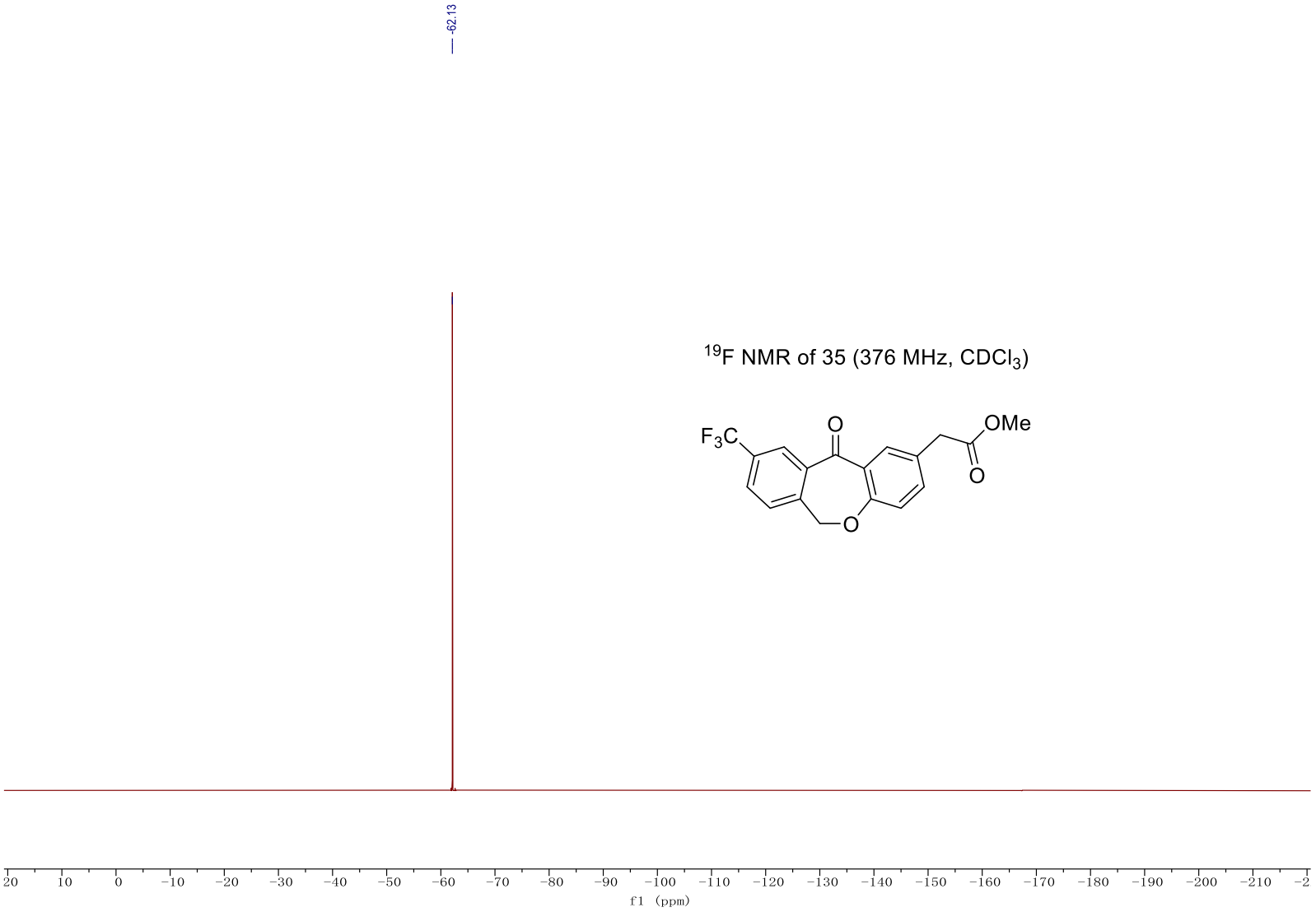
^{19}F NMR of 34 (376 MHz, $CDCl_3$)

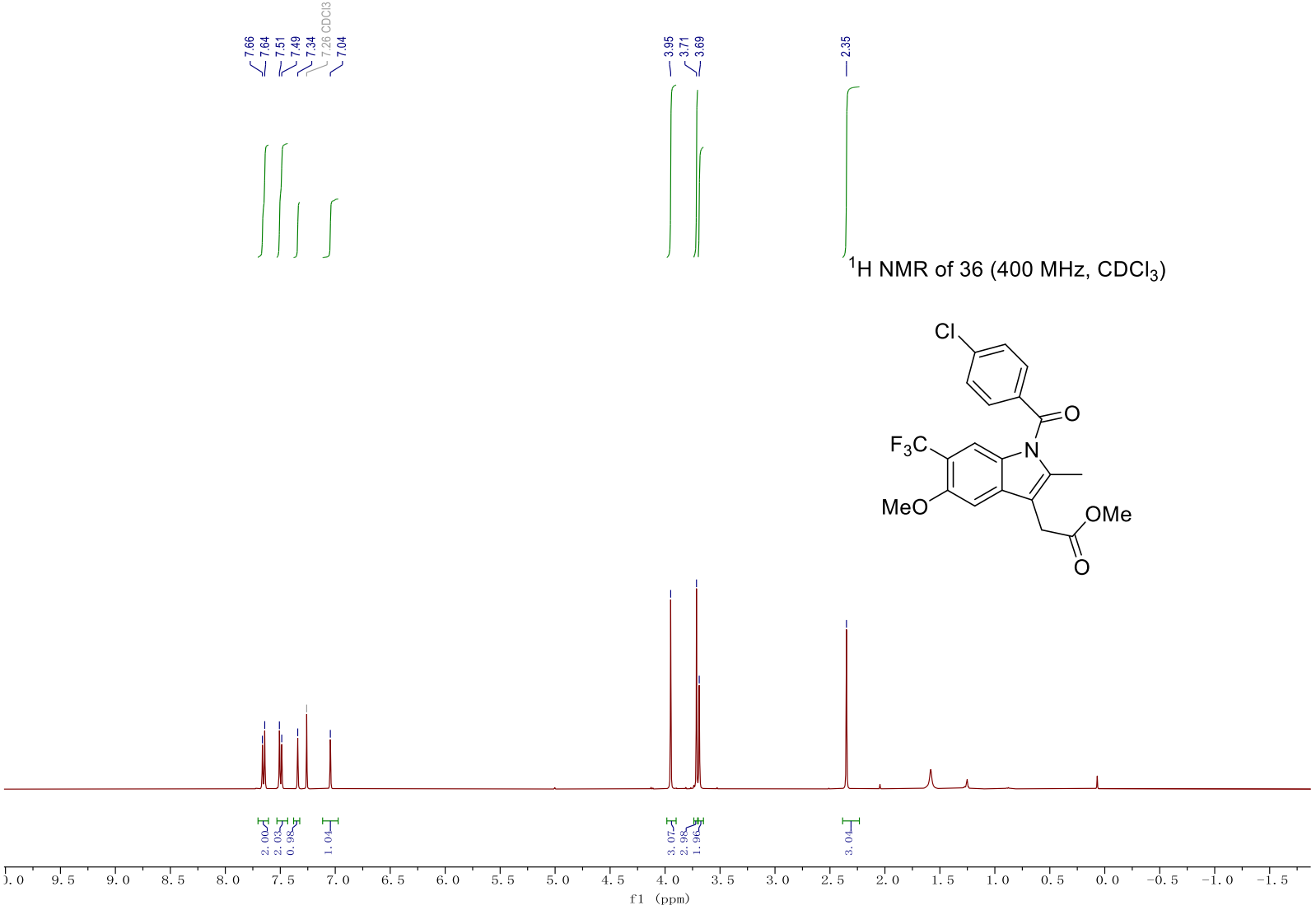




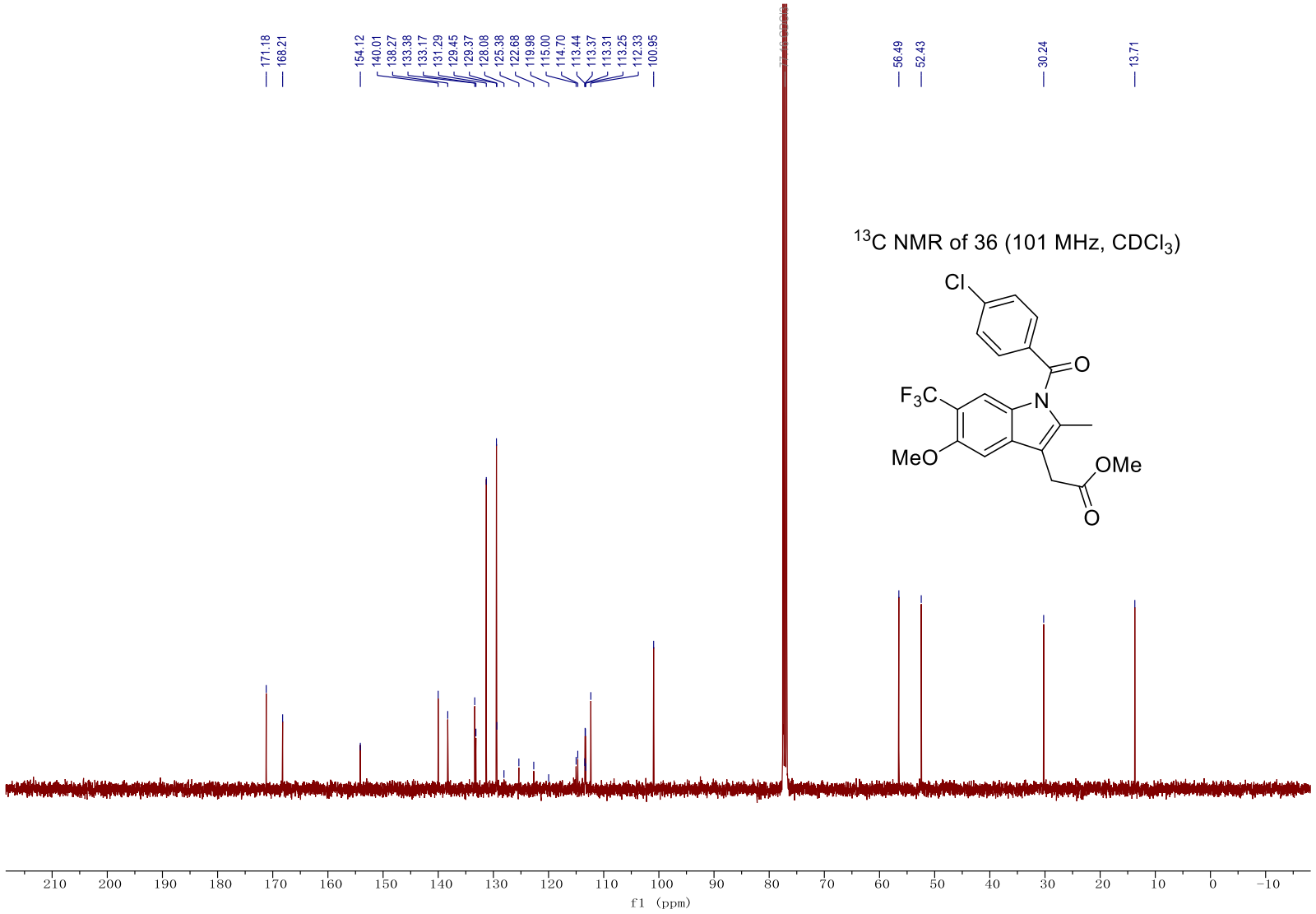
^{1}H NMR of 35 (400 MHz, $CDCl_3$)


189.76
171.41
158.59
139.75
136.96
135.51
133.98
133.93
133.88
133.83
133.44
130.06
129.67
128.15
127.56
127.17
124.50
122.76
122.46
122.16
121.86
77.46 CDCl3
74.61
52.49
39.97
13C NMR of 35 (101 MHz, CDCl3)
F3C
O
OMe
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

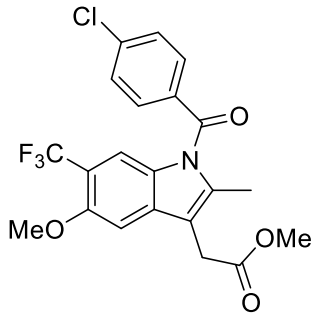

-62.13
^{19}F NMR of 35 (376 MHz, $CDCl_3$)
F_3C
O
OMe
O
O
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

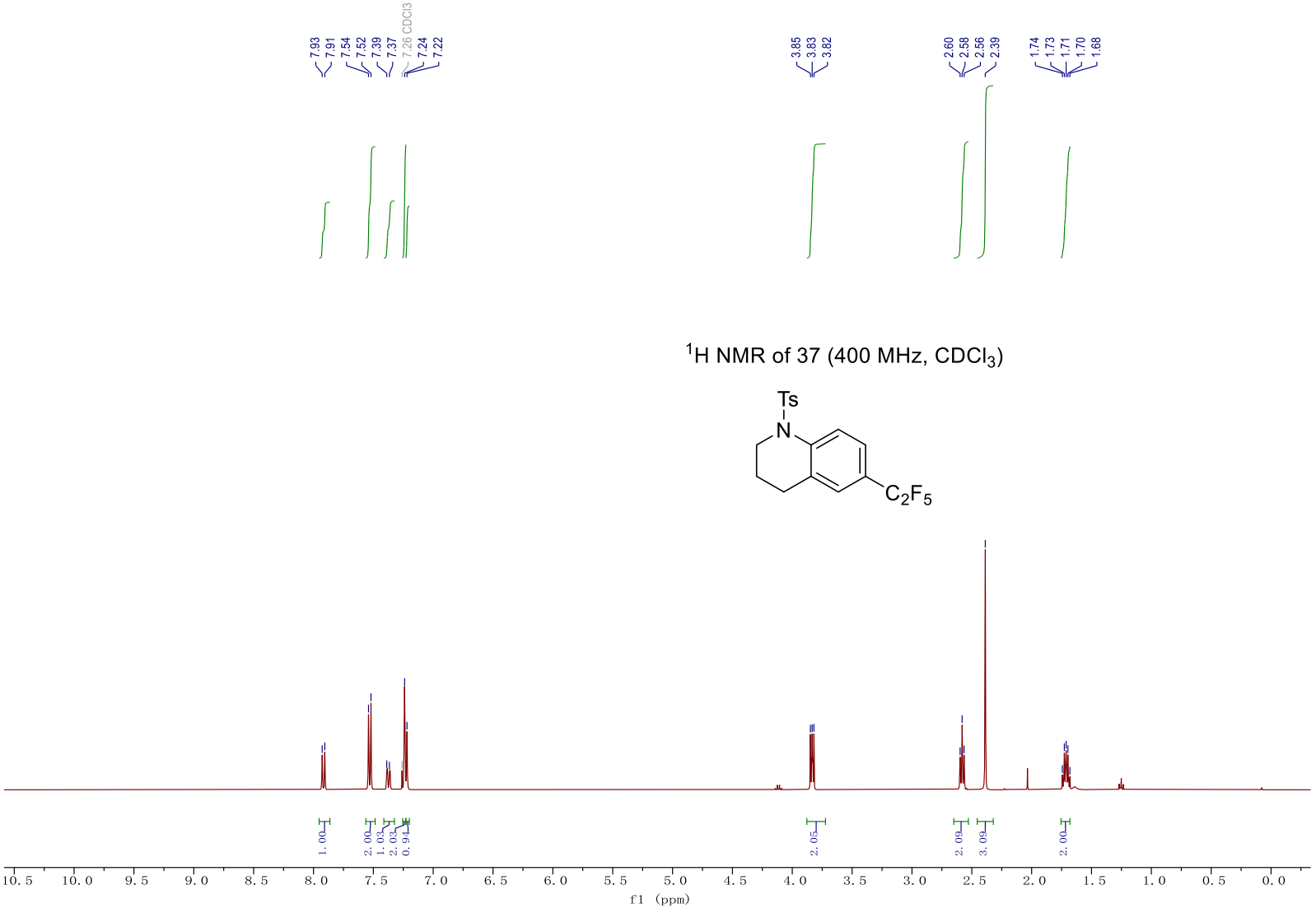


^{1}H NMR of 36 (400 MHz, $CDCl_3$)

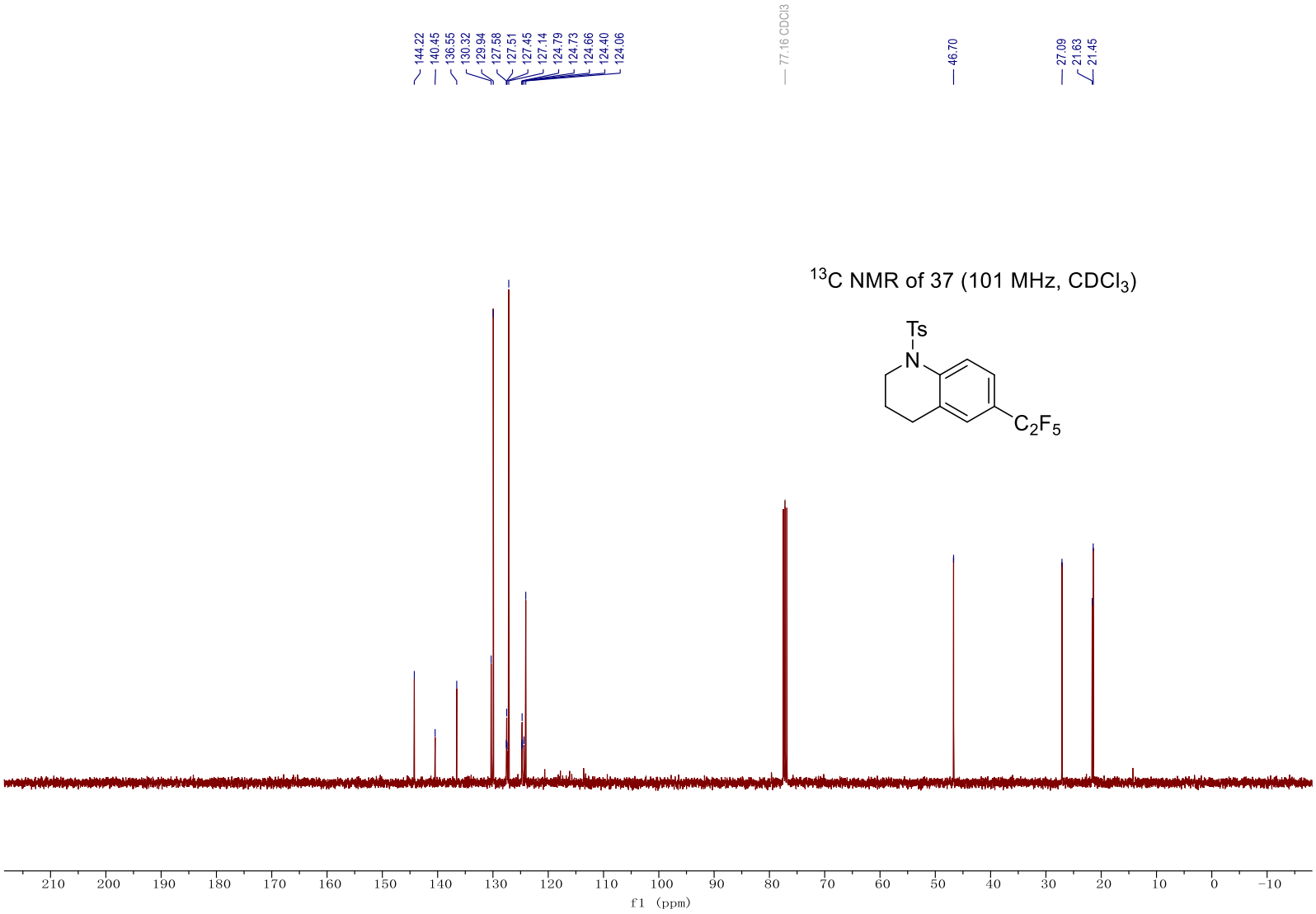

171.18
168.21
154.12
140.01
138.27
133.38
133.17
131.29
129.45
129.37
128.08
125.38
122.68
119.98
115.00
114.70
113.44
113.37
113.31
113.25
112.33
100.95
56.49
52.43
30.24
13.71
^{13}C NMR of 36 (101 MHz, $CDCl_3$)
Cl
O
F_3C
N
MeO
OMe
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

^{19}F NMR of 36 (376 MHz, $CDCl_3$)





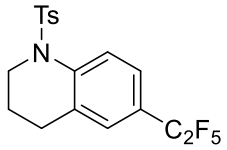
^{1}H NMR of 37 (400 MHz, $CDCl_3$)

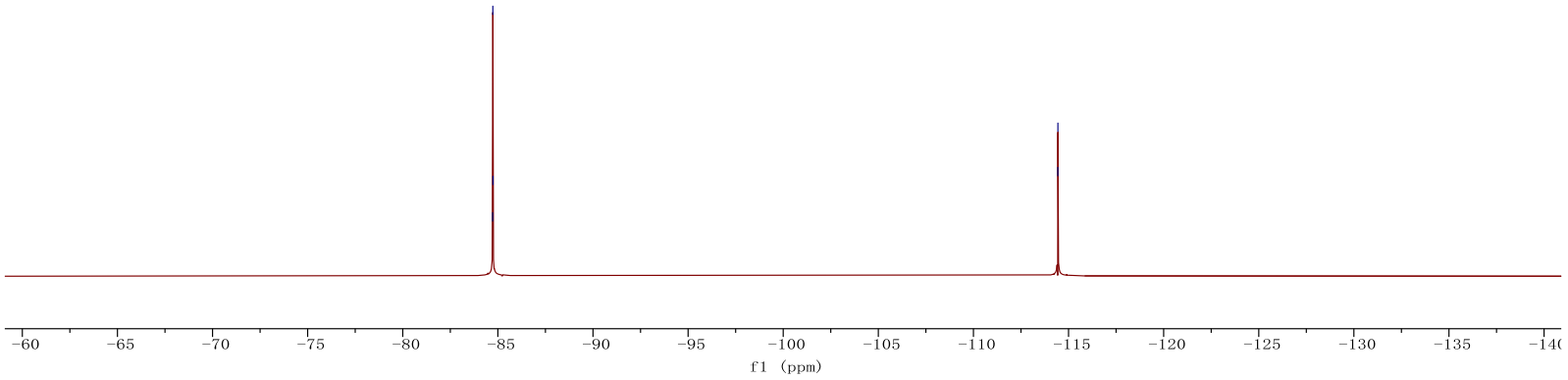

144.22
140.45
136.55
130.32
129.94
127.58
127.51
127.45
127.14
124.79
124.73
124.66
124.40
124.06
77.16 CDCl3
46.70
27.09
21.63
21.45
13C NMR of 37 (101 MHz, CDCl3)
Ts
N
C2F5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

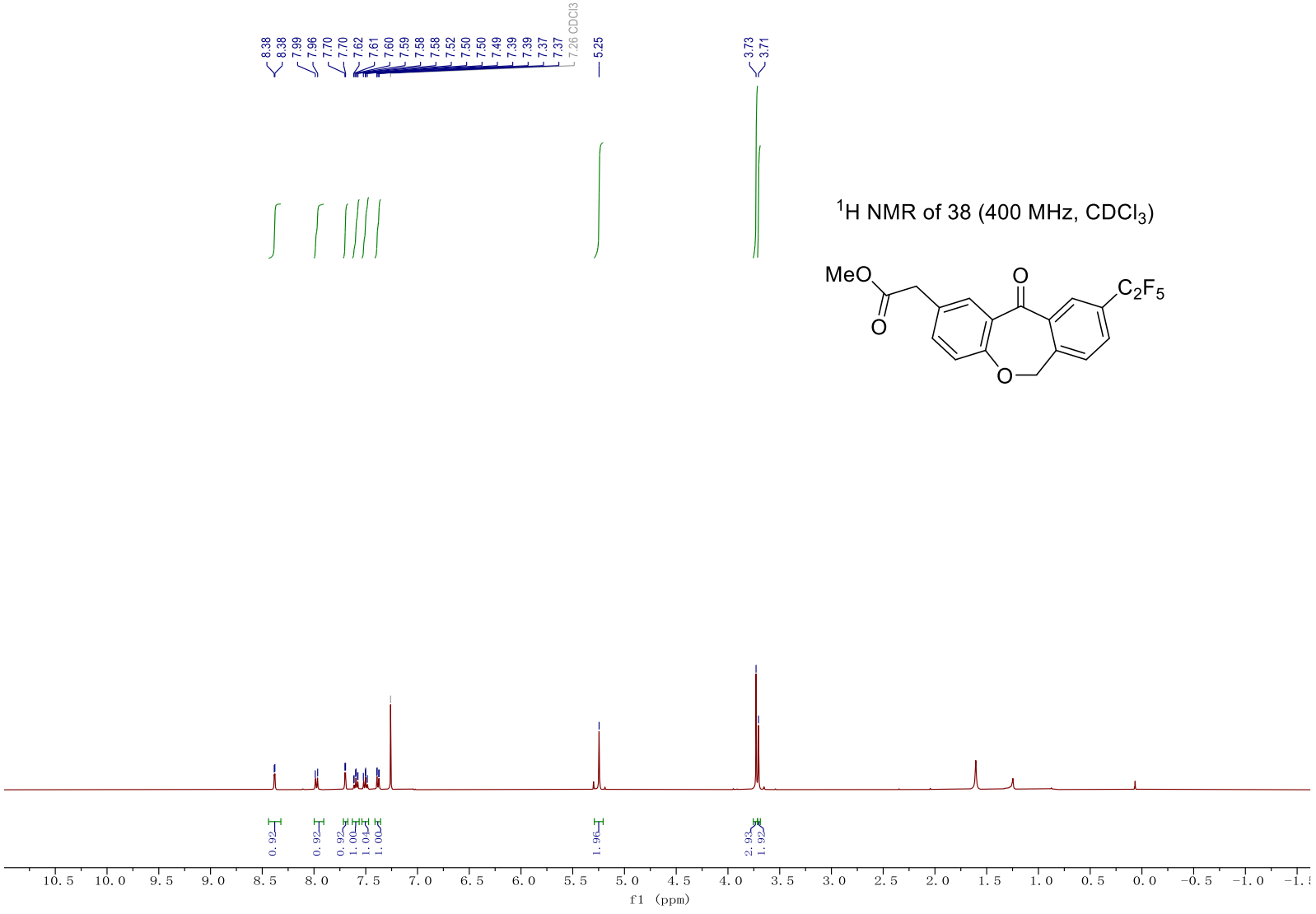
-84.72
-84.74
-84.74

-114.44
-114.44

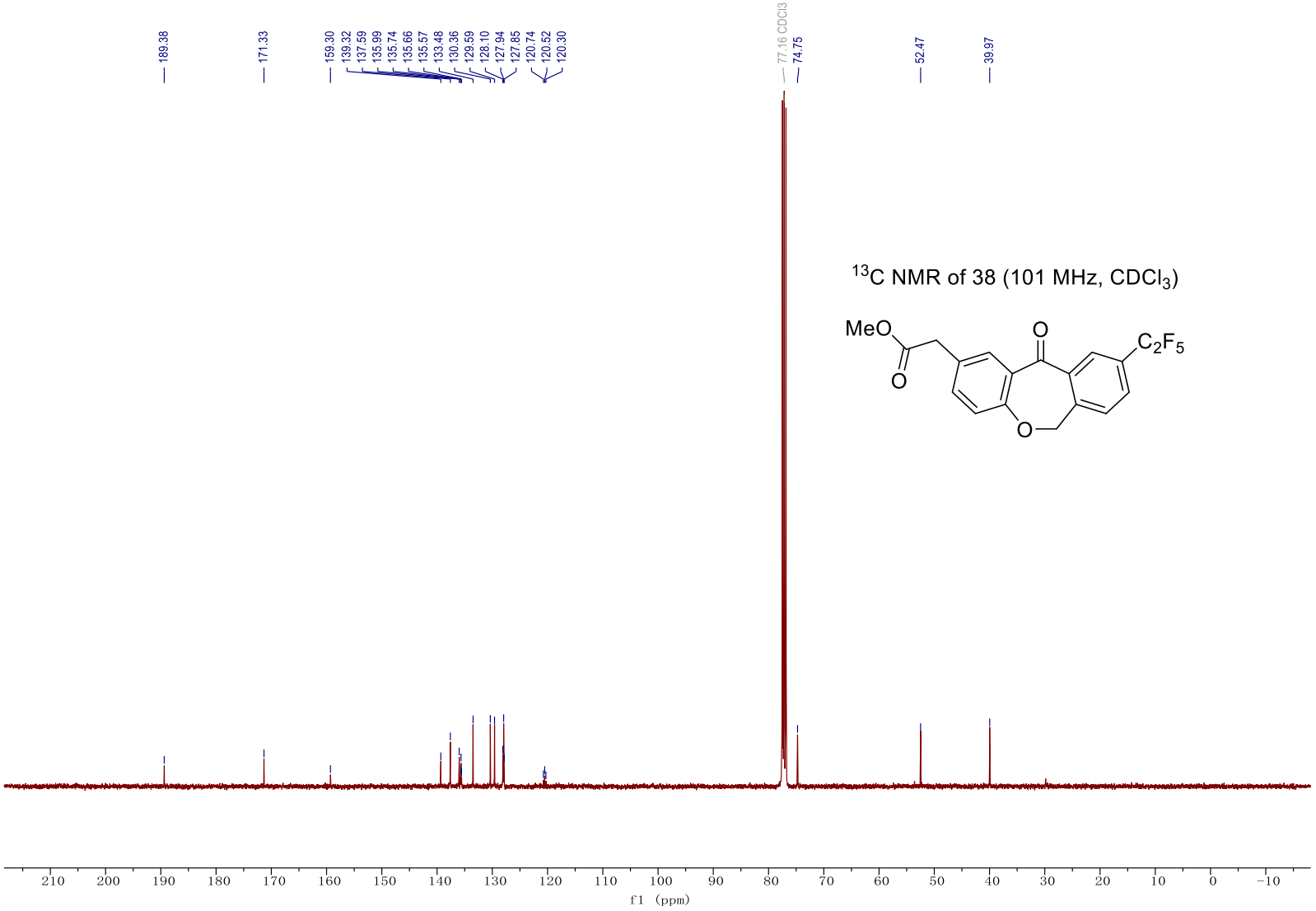
^{19}F NMR of 37 (376 MHz, $CDCl_3$)

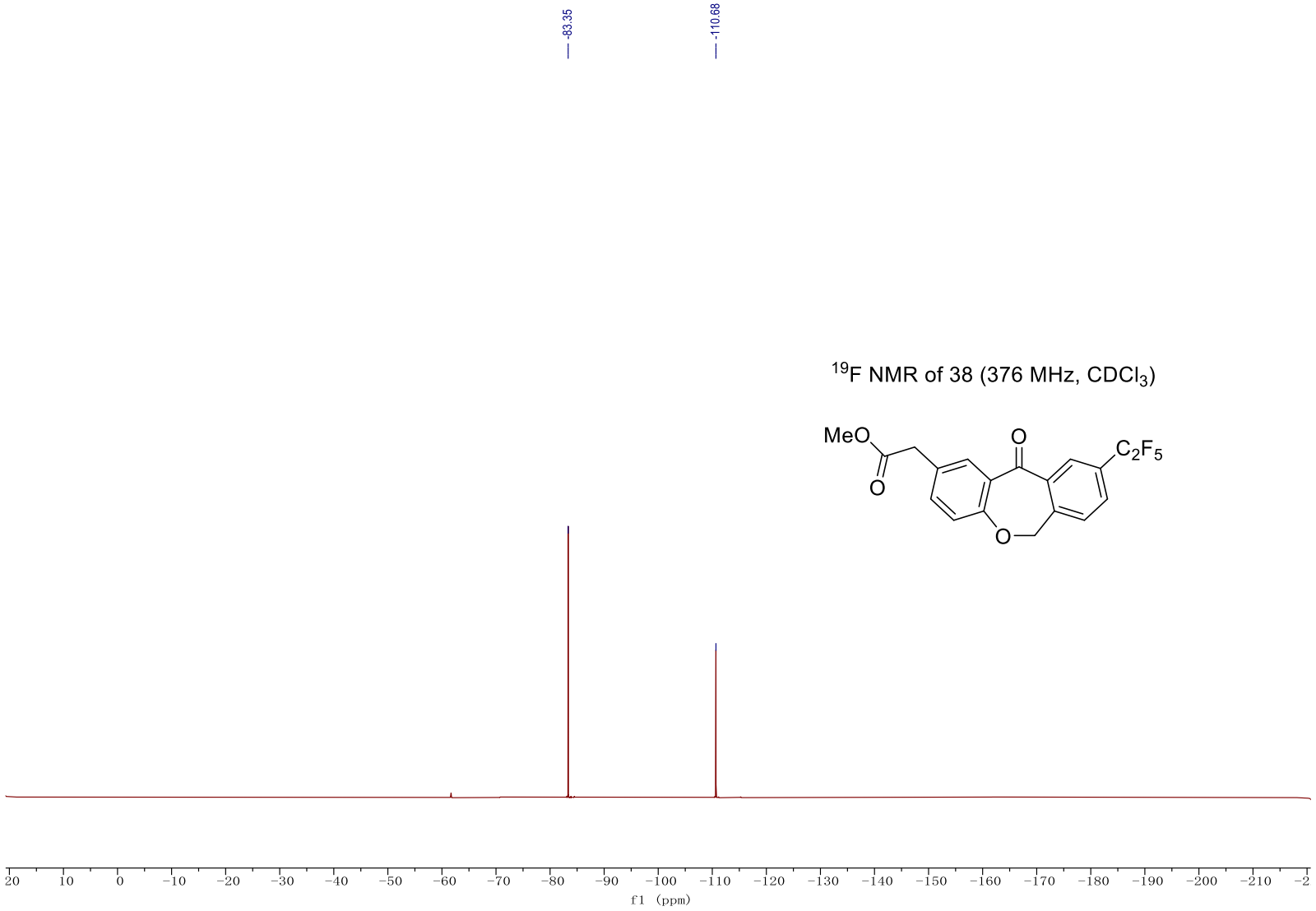




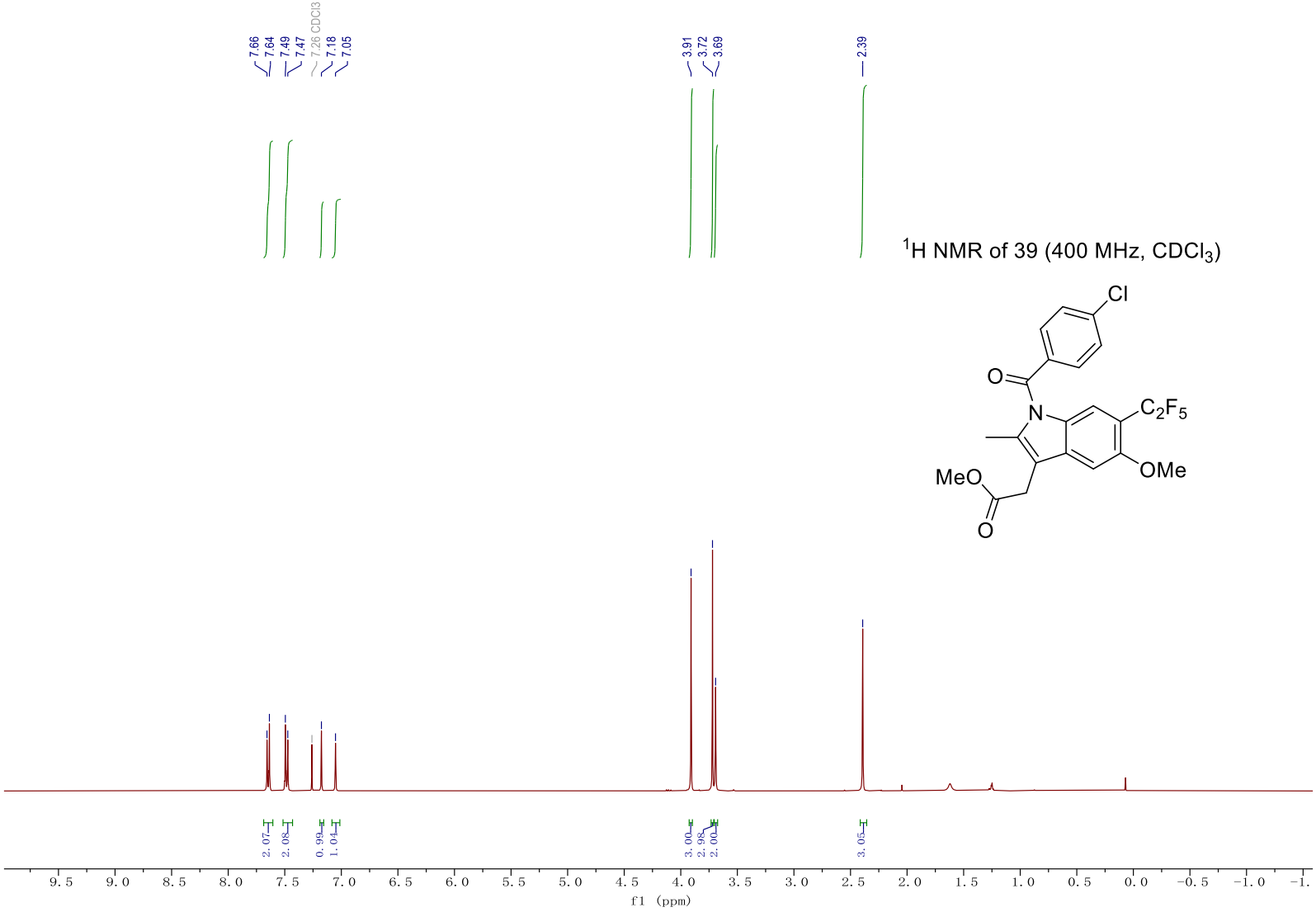


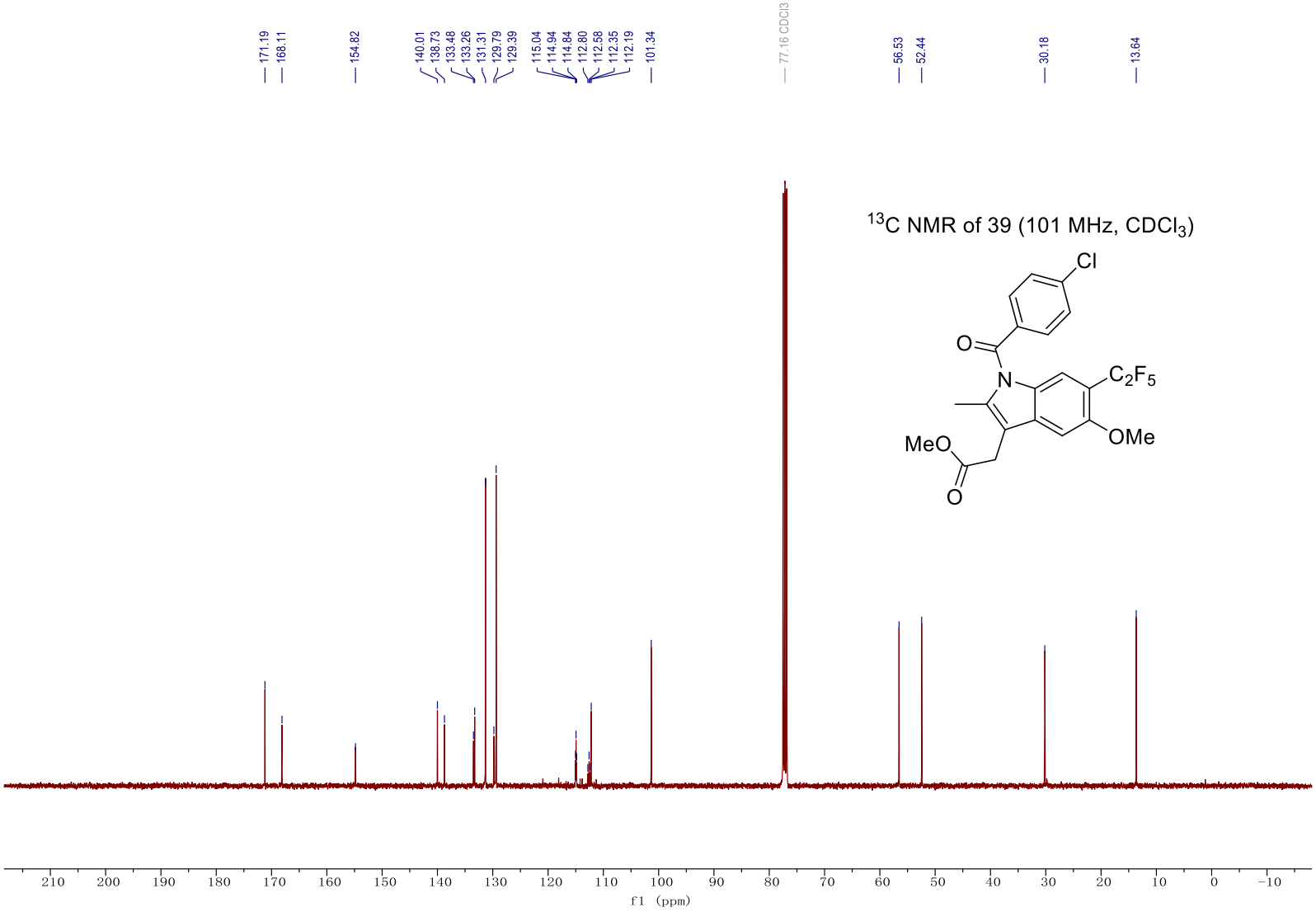
^{1}H NMR of 38 (400 MHz, $CDCl_3$)

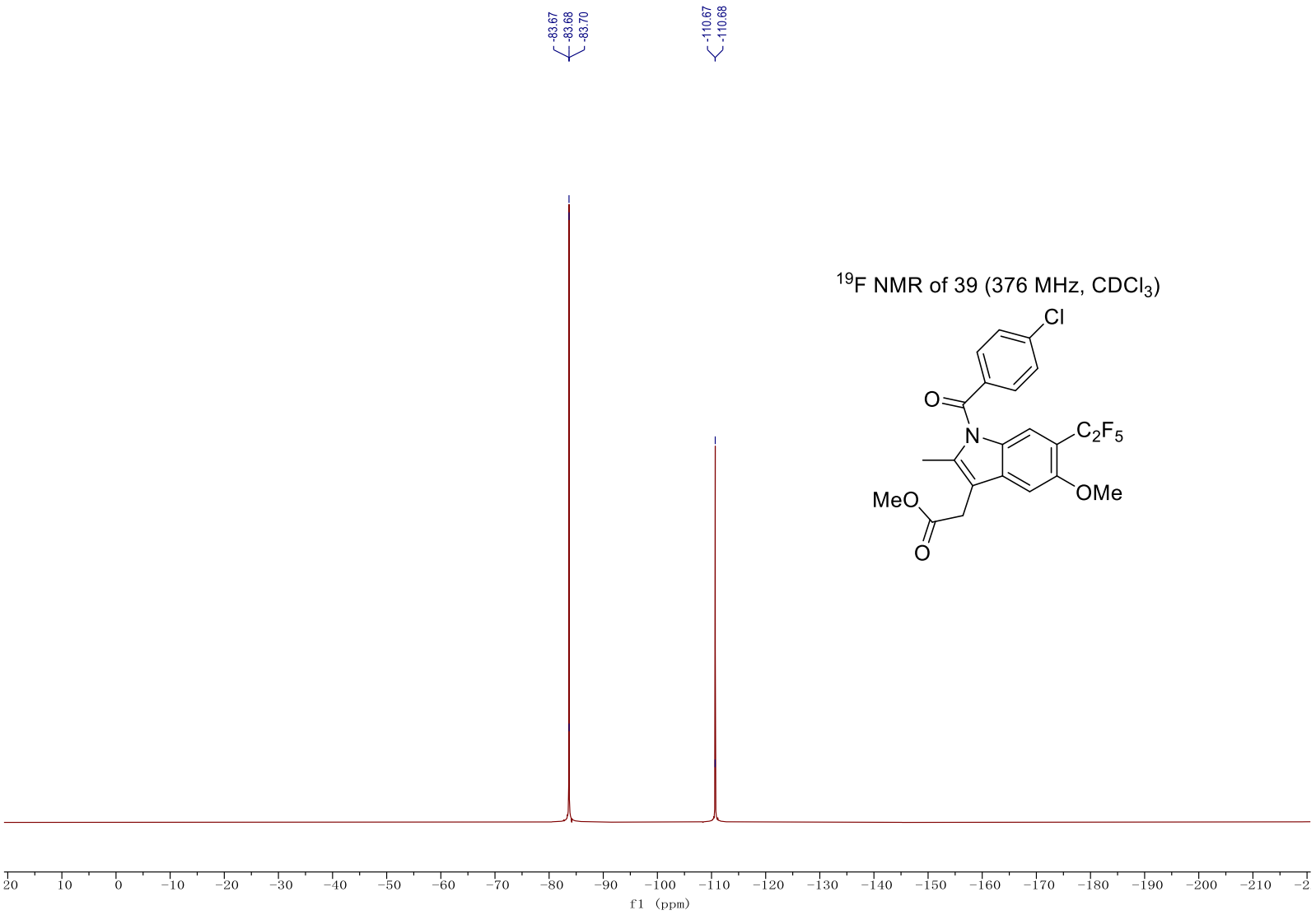

189.38
171.33
159.30
139.32
137.59
135.99
135.74
135.66
135.57
133.48
130.36
129.59
128.10
127.94
127.85
120.74
120.52
120.30
77.16 CDCl3
74.75
52.47
39.97
13C NMR of 38 (101 MHz, CDCl3)
MeO
O
O
O
C2F5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

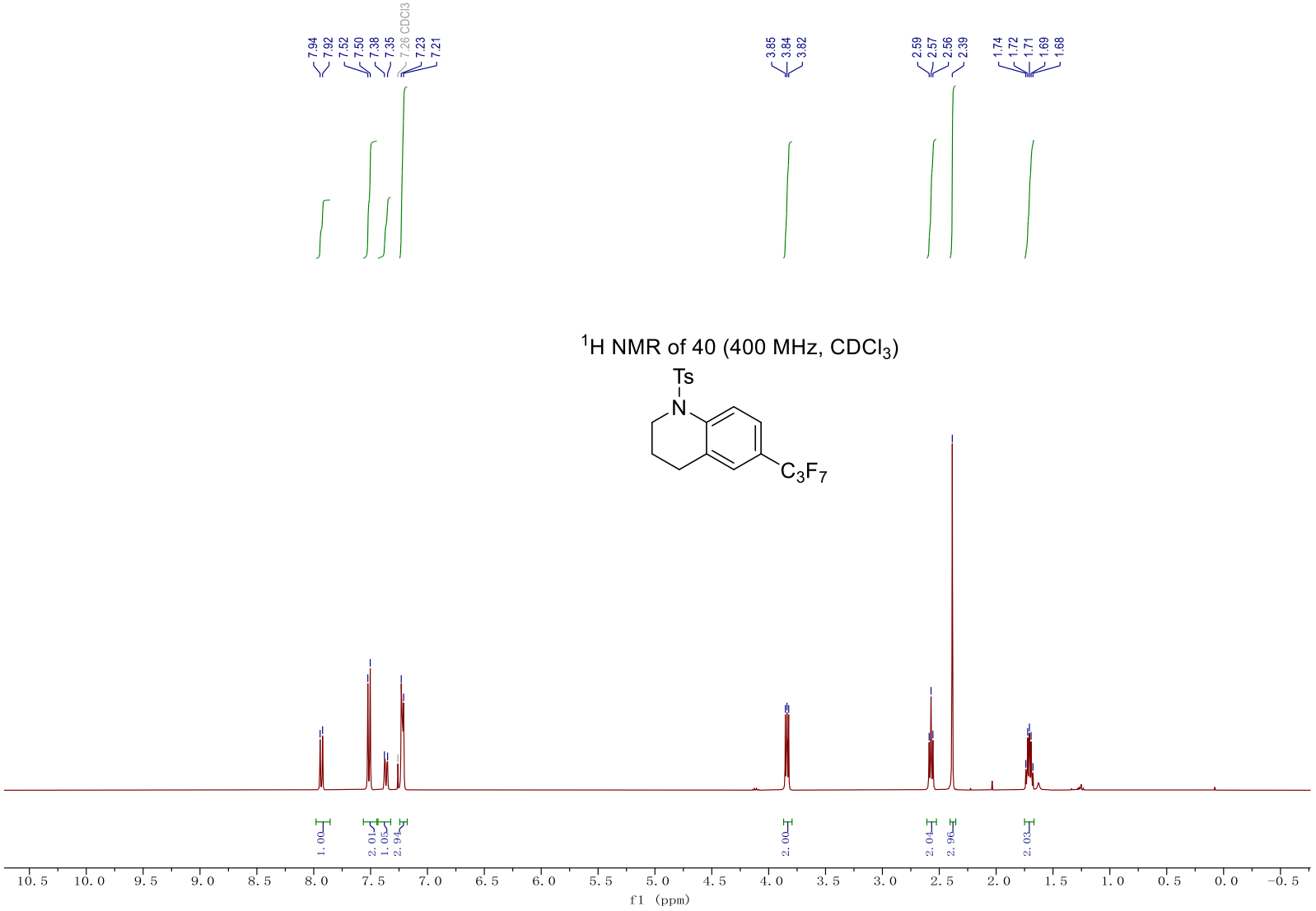


^{19}F NMR of 38 (376 MHz, $CDCl_3$)

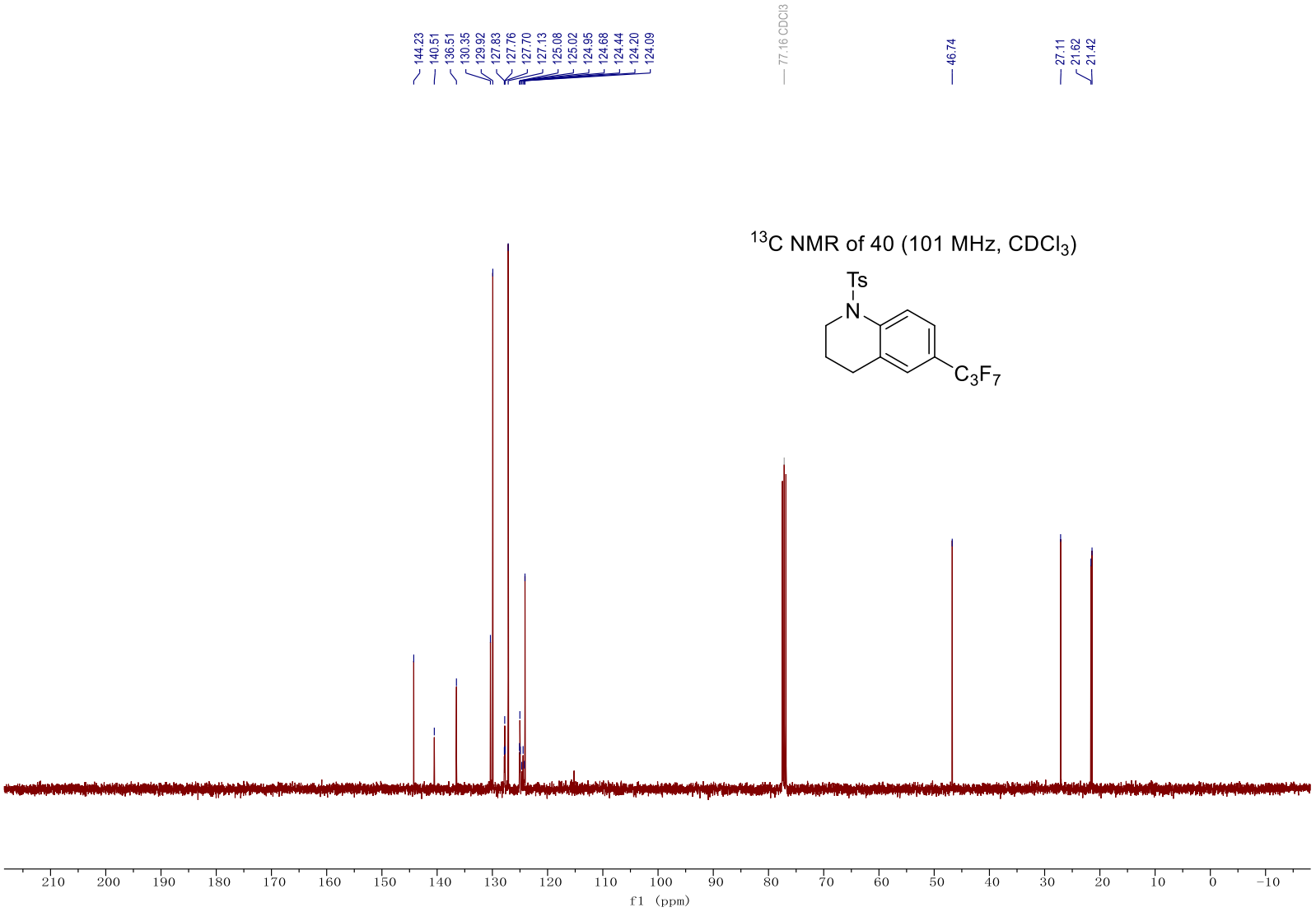

7.66
7.64
7.49
7.47
7.26 CDCl3
7.18
7.05
3.91
3.72
3.69
2.39
1H NMR of 39 (400 MHz, CDCl3)
Cl
O
N
C2F5
OMe
MeO
O
2.07
2.08
0.99
1.04
3.00
2.98
2.00
3.05
f1 (ppm)


171.19
168.11
154.82
140.01
138.73
133.48
133.26
131.31
129.79
129.39
115.04
114.94
114.84
112.80
112.58
112.35
112.19
101.34
77.16 CDCl3
56.53
52.44
30.18
13.64
13C NMR of 39 (101 MHz, CDCl3)
Cl
O
N
C2F5
OMe
MeO
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

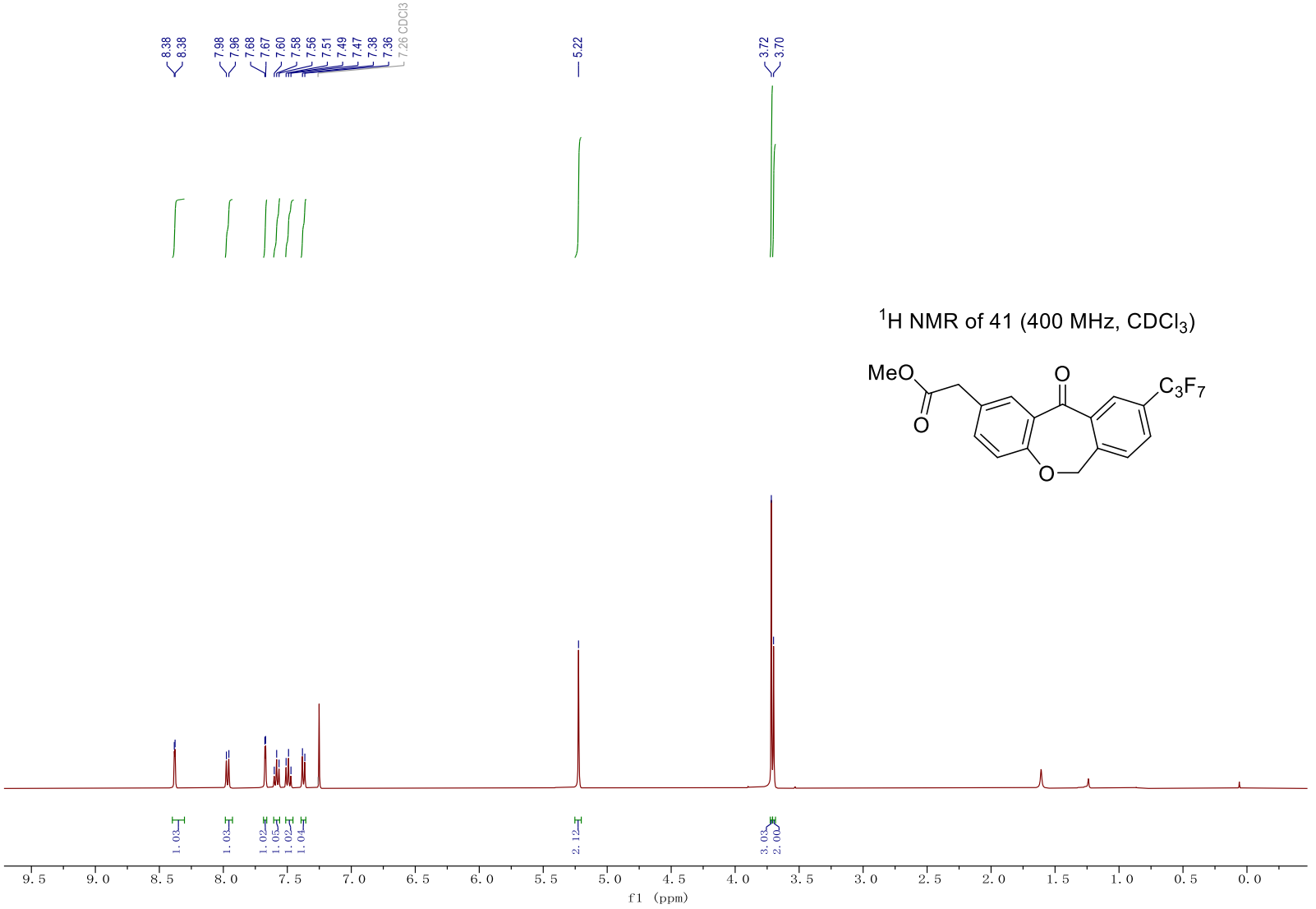

-83.67
-83.68
-83.70
-110.67
-110.68
^{19}F NMR of 39 (376 MHz, $CDCl_3$)
Cl
O
N
C_2F_5
MeO
OMe
O
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)



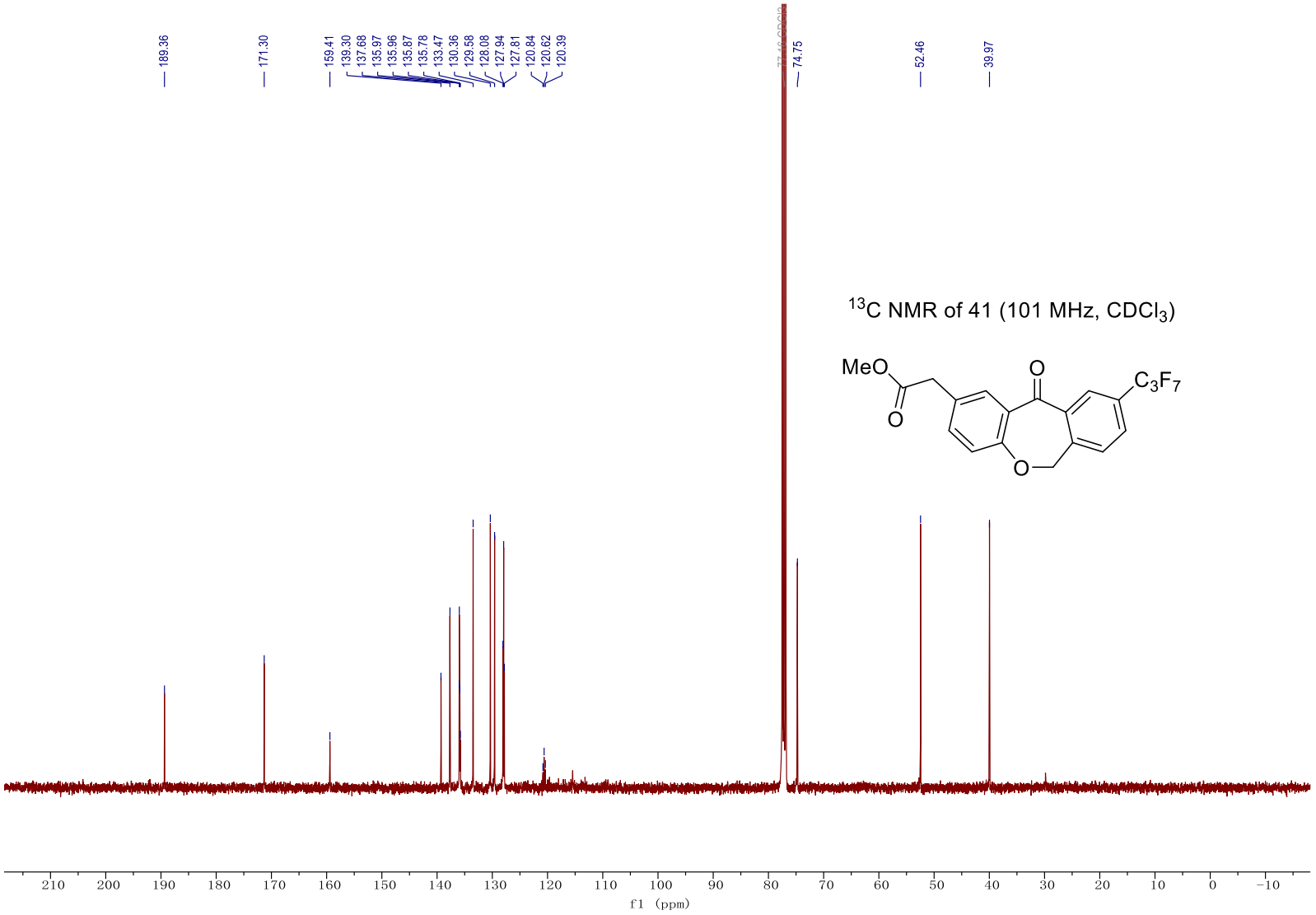
^{1}H NMR of 40 (400 MHz, $CDCl_3$)

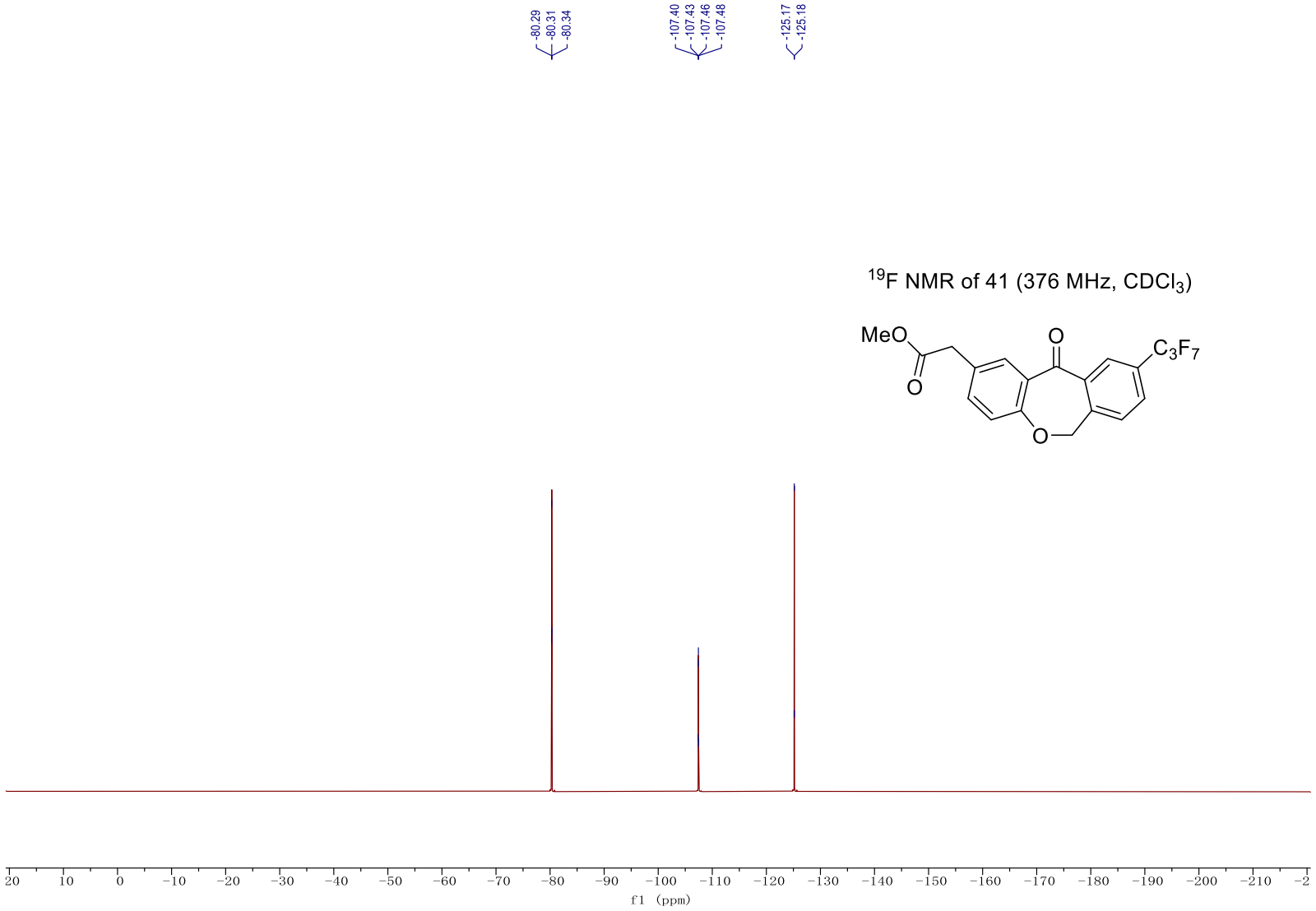

144.23
140.51
136.51
130.35
129.92
127.83
127.76
127.70
127.13
125.08
125.02
124.95
124.68
124.44
124.20
124.09
77.16 CDCl3
46.74
27.11
21.62
21.42
13C NMR of 40 (101 MHz, CDCl3)
Ts
N
C3F7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-80.02
-80.05
-80.08
-111.42
-111.45
-111.47
-111.50
-126.49
19F NMR of 40 (376 MHz, CDCl3)
Ts
N
C3F7
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

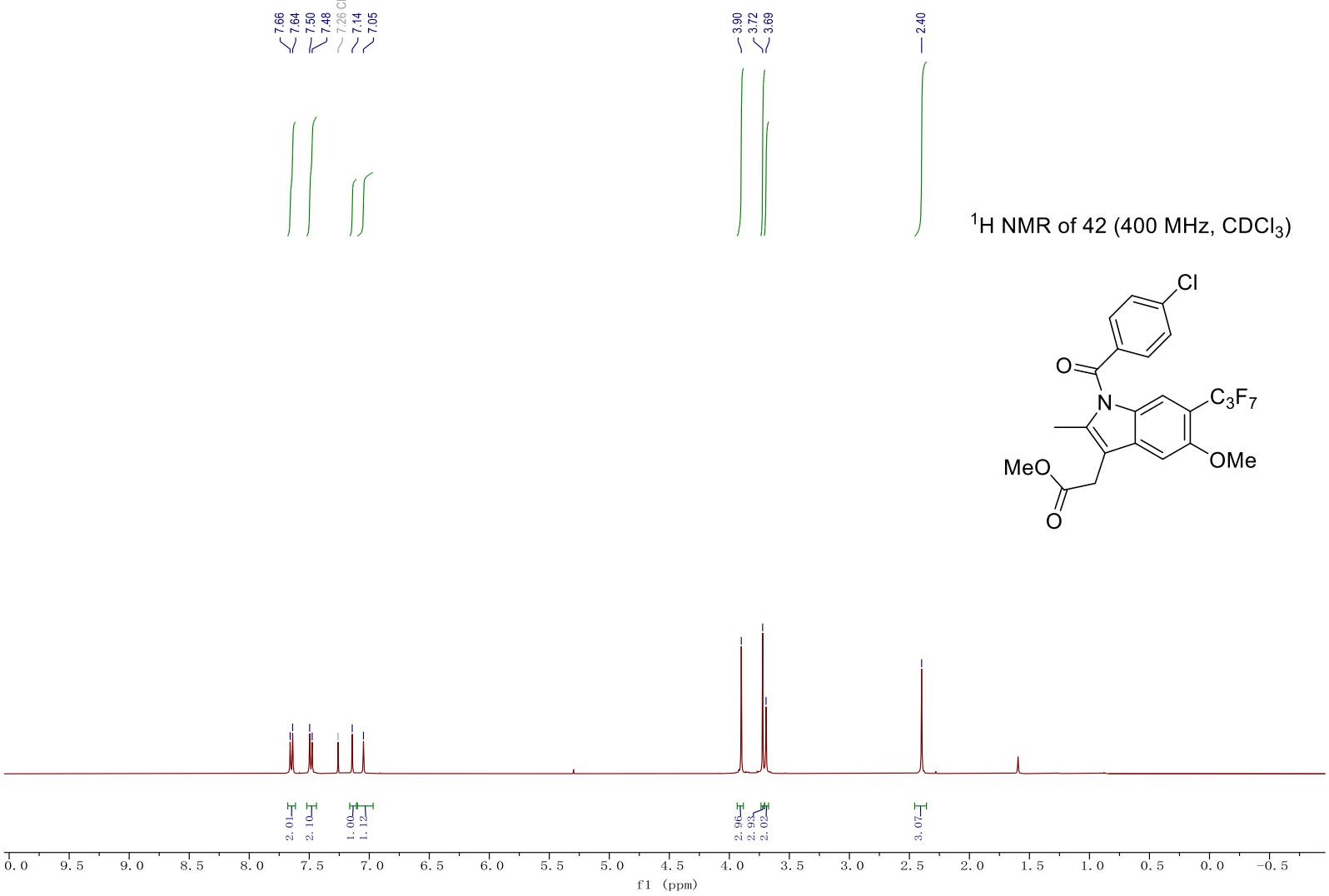


^{1}H NMR of 41 (400 MHz, $CDCl_3$)

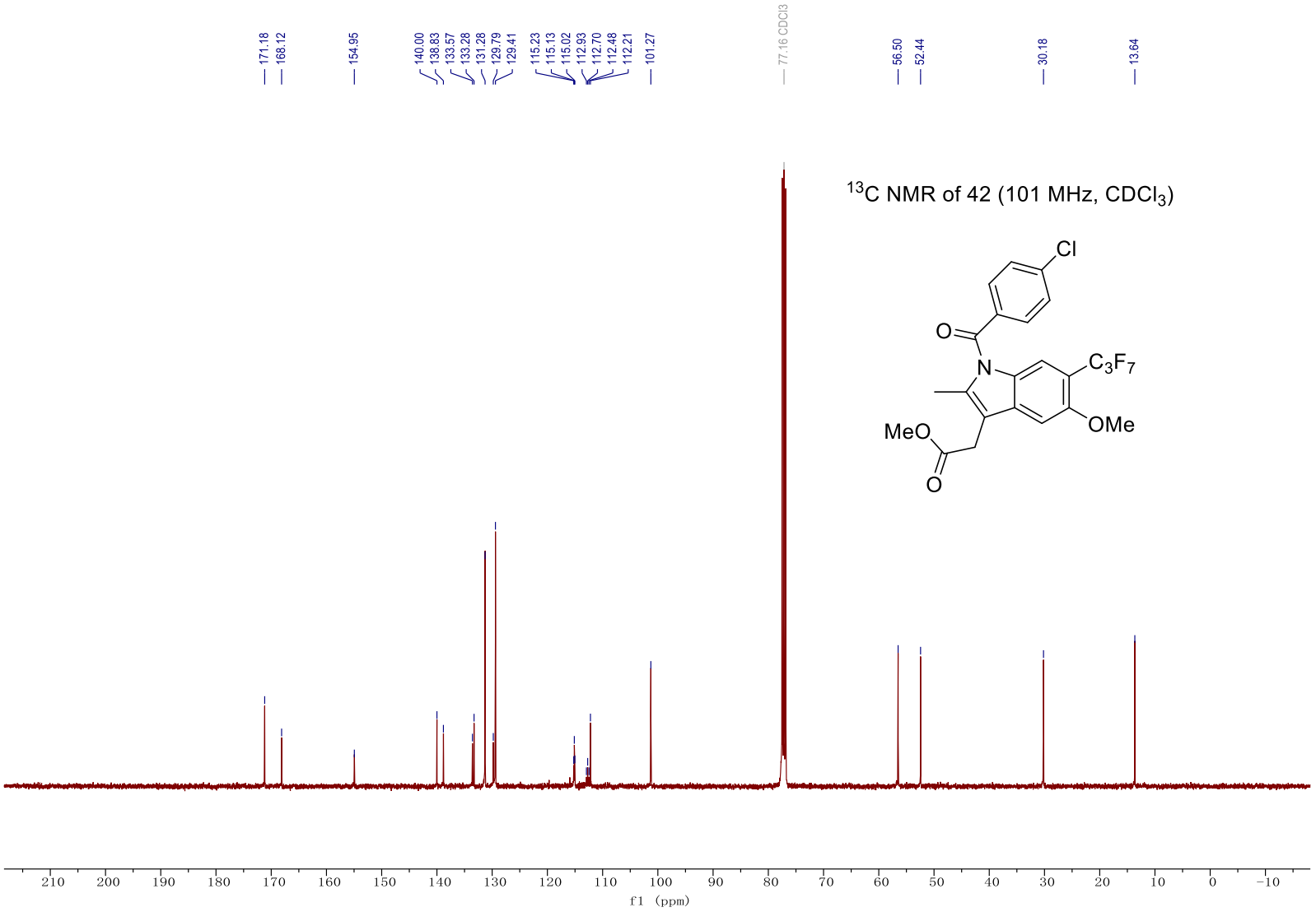

189.36
171.30
159.41
139.30
137.68
135.97
135.96
135.87
135.78
133.47
130.36
129.58
128.08
127.94
127.81
120.84
120.62
120.39
77.46 CDCl3
74.75
52.46
39.97
13C NMR of 41 (101 MHz, CDCl3)
MeO
O
O
O
C3F7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

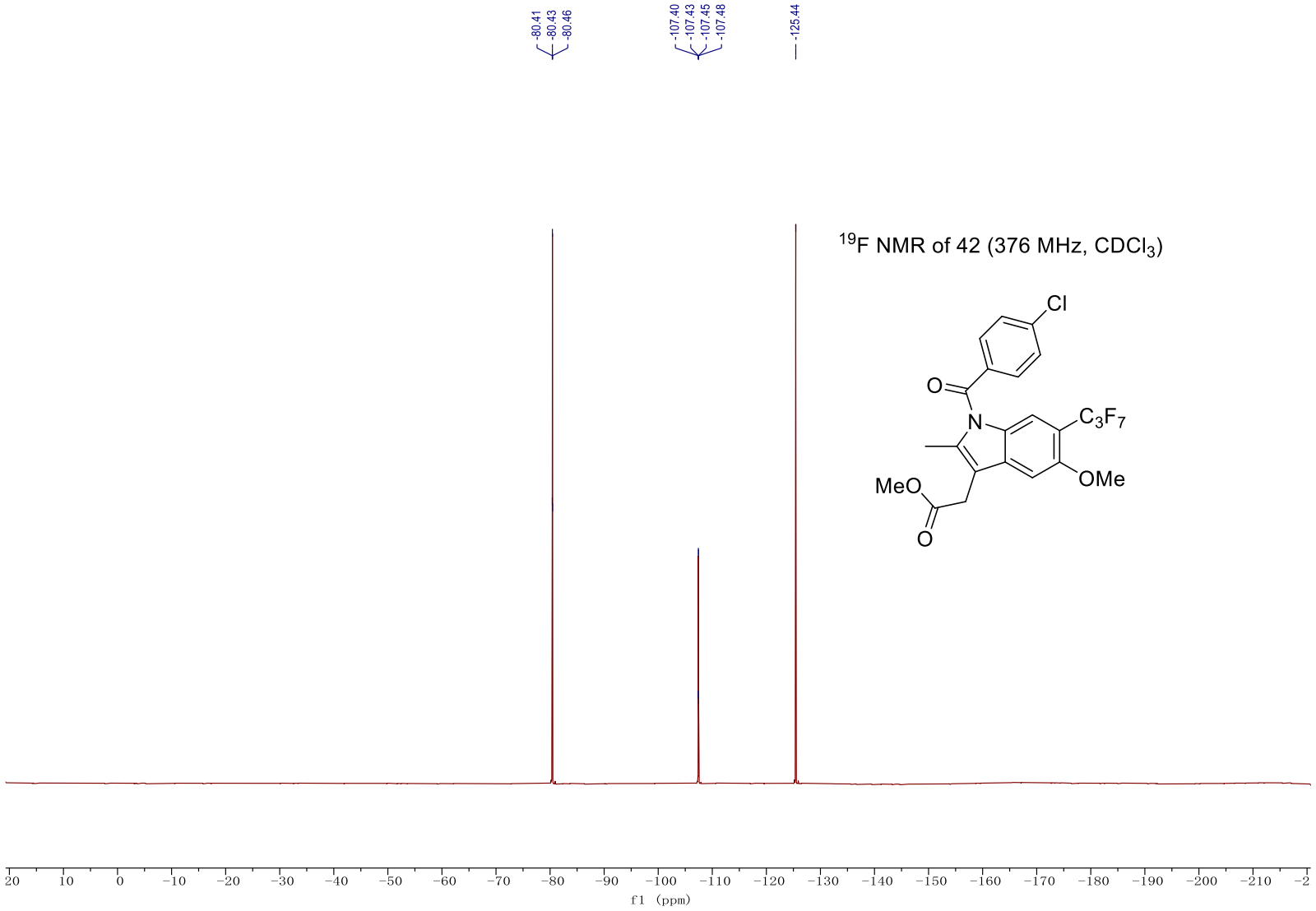


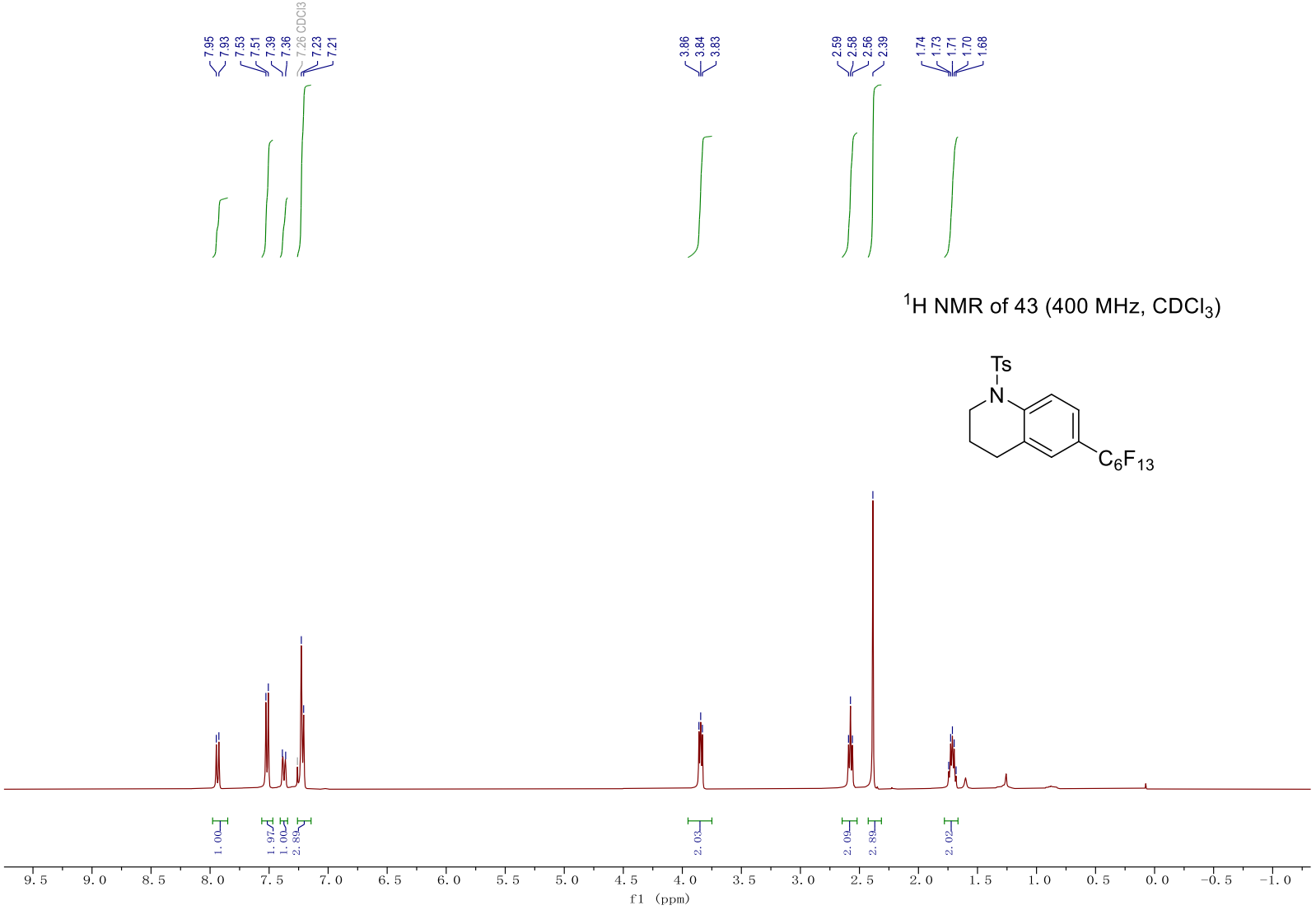
^{19}F NMR of 41 (376 MHz, $CDCl_3$)



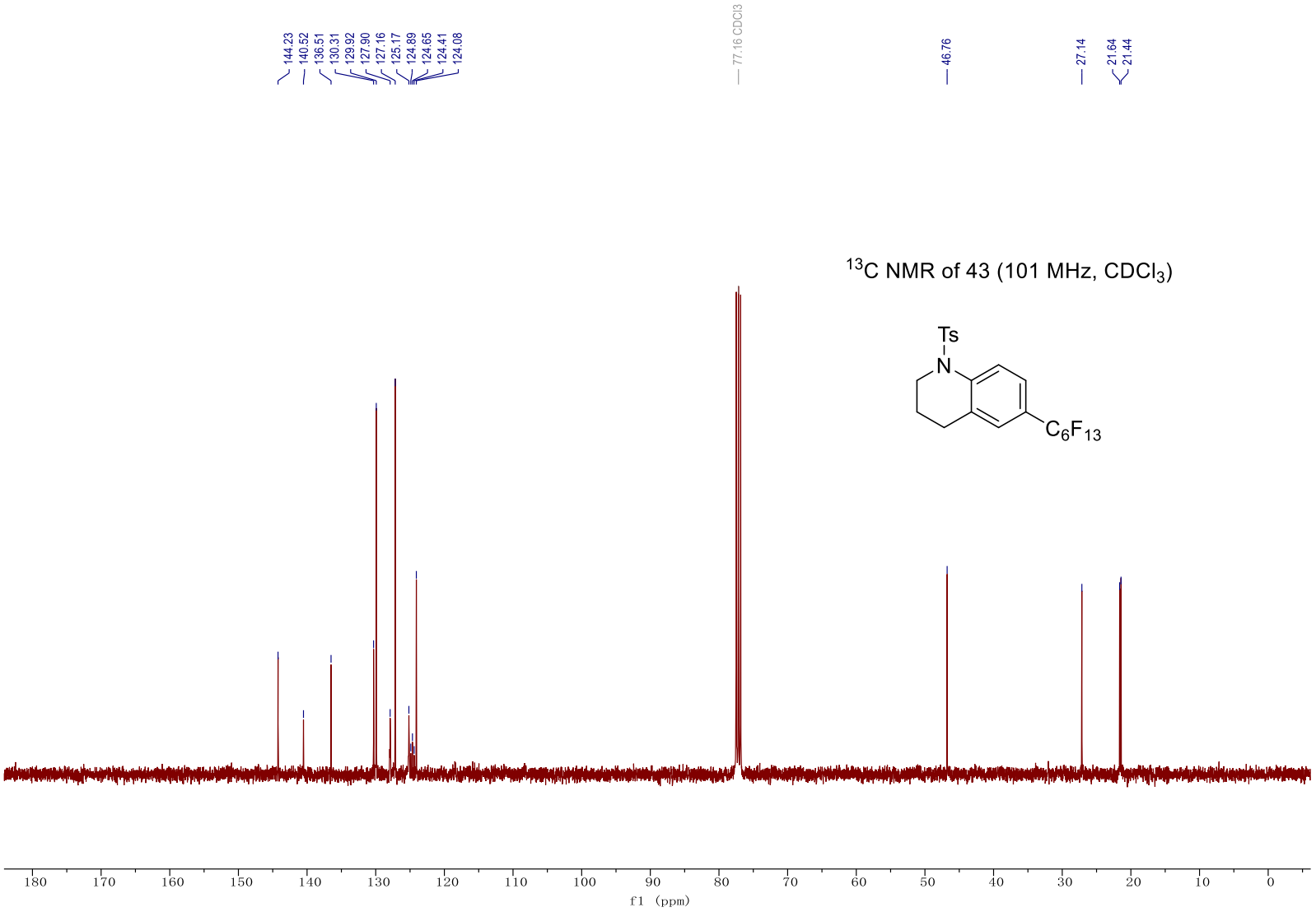
^{1}H NMR of 42 (400 MHz, $CDCl_3$)

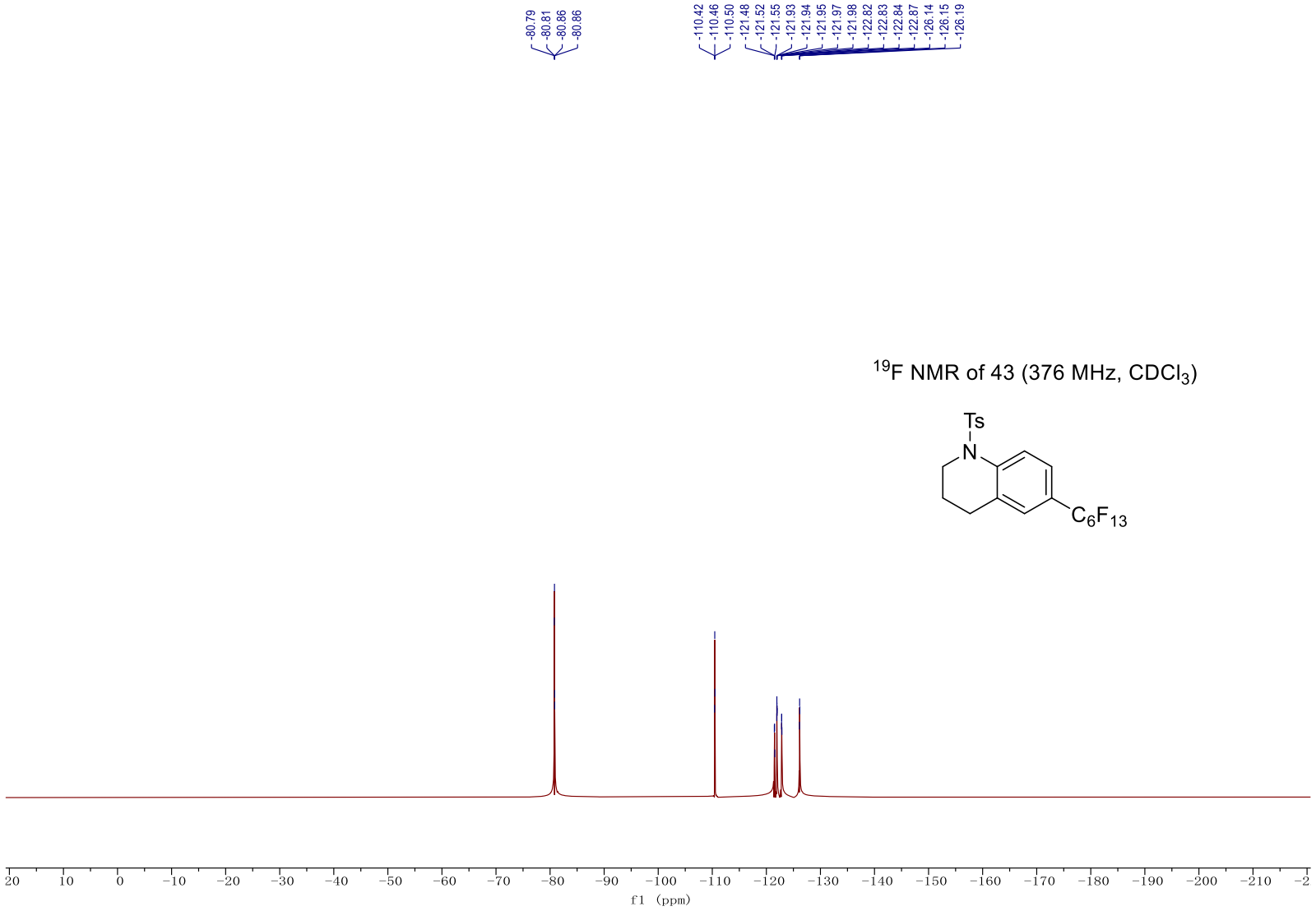

171.18
168.12
154.95
140.00
138.83
133.57
133.28
131.28
129.79
129.41
115.23
115.13
115.02
112.93
112.70
112.48
112.21
101.27
77.16 CDCl3
56.50
52.44
30.18
13.64
13C NMR of 42 (101 MHz, CDCl3)
Cl
O
N
C3F7
OMe
MeO
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-80.41
-80.43
-80.46
-107.40
-107.43
-107.45
-107.48
-125.44
19F NMR of 42 (376 MHz, CDCl3)
Cl
O
N
C3F7
MeO
OMe
O
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

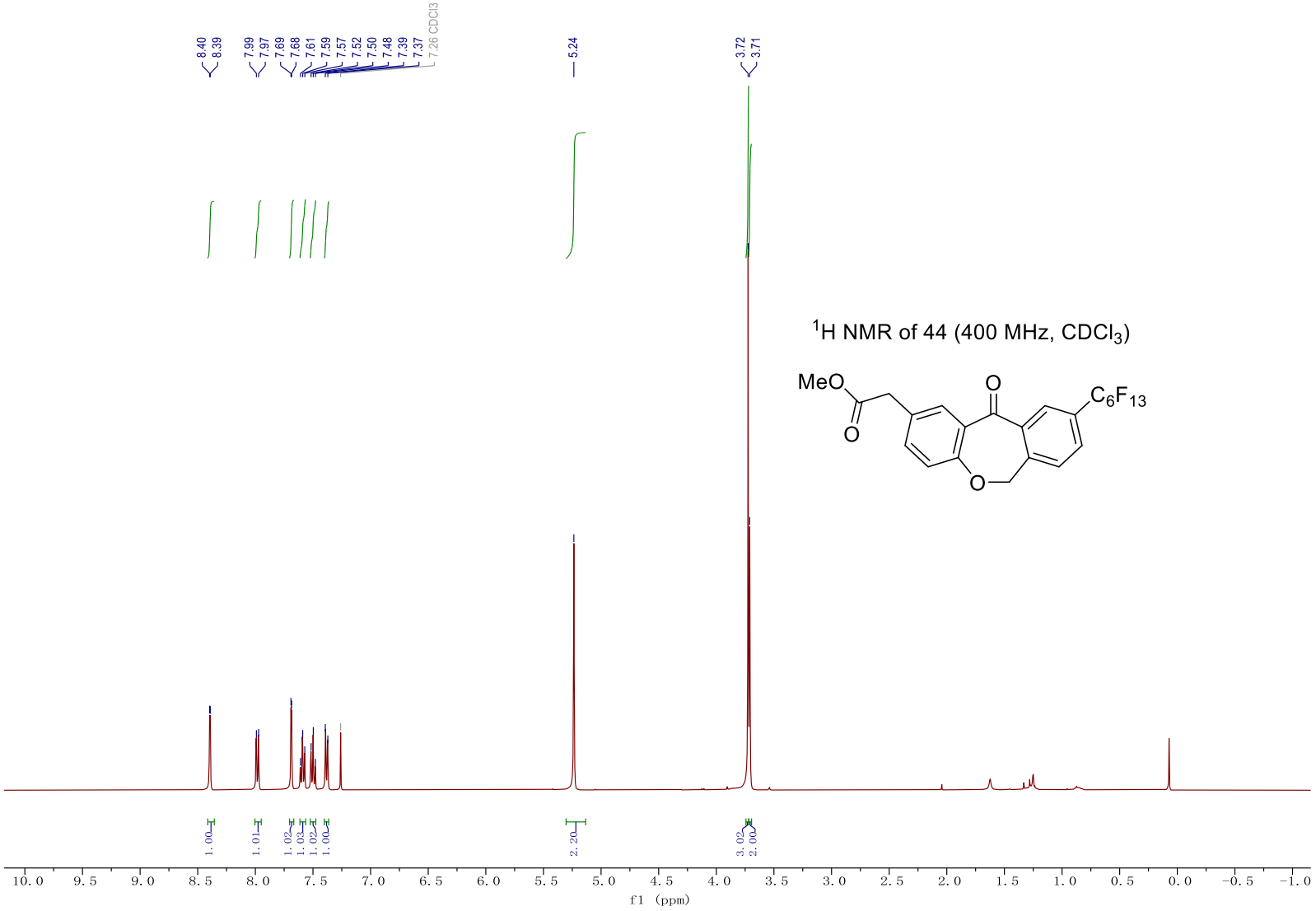


^{1}H NMR of 43 (400 MHz, $CDCl_3$)

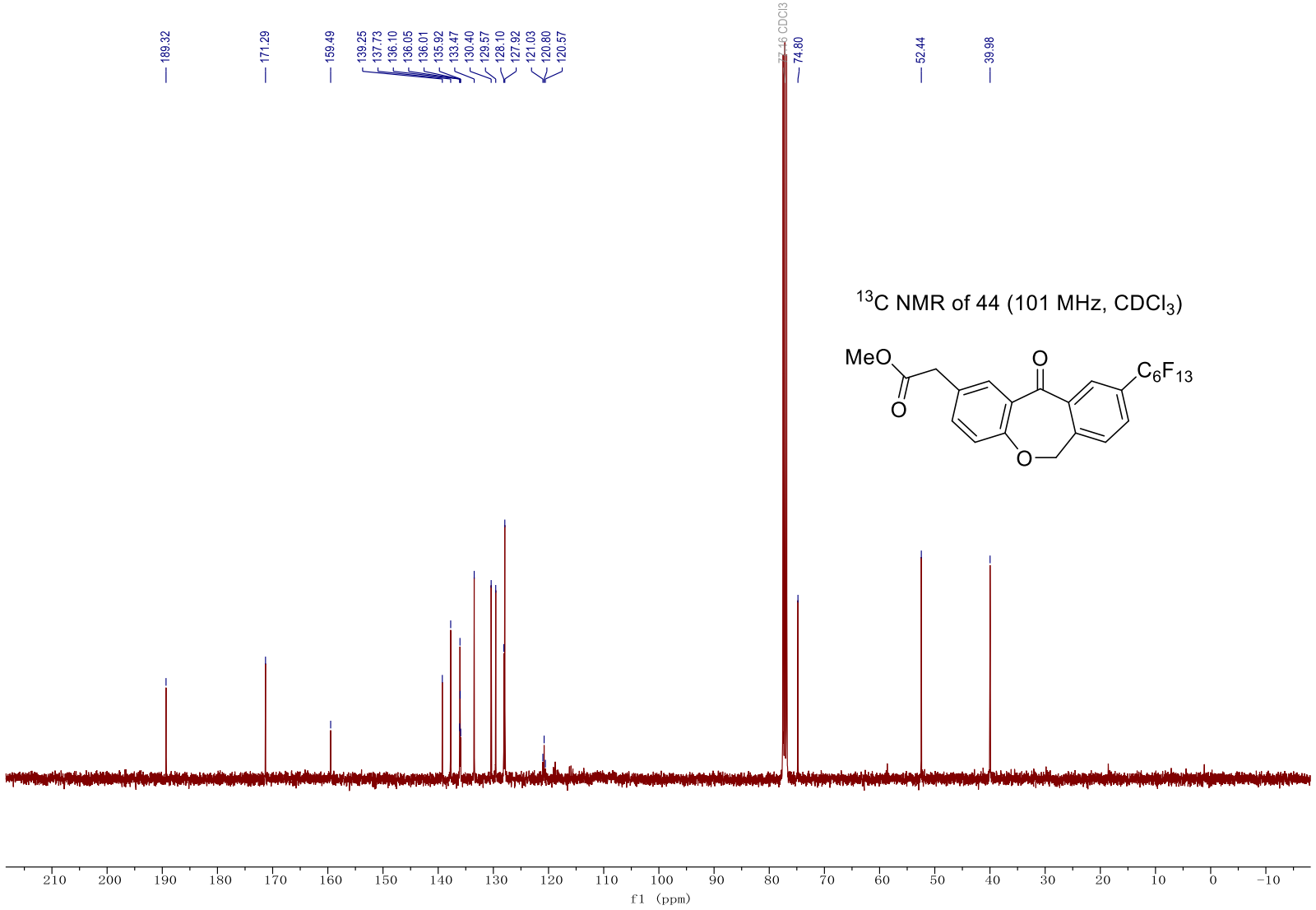

144.23
140.52
136.51
130.31
129.92
127.90
127.16
125.17
124.89
124.65
124.41
124.08
77.16 CDCl3
46.76
27.14
21.64
21.44
13C NMR of 43 (101 MHz, CDCl3)
Ts
N
C6F13
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

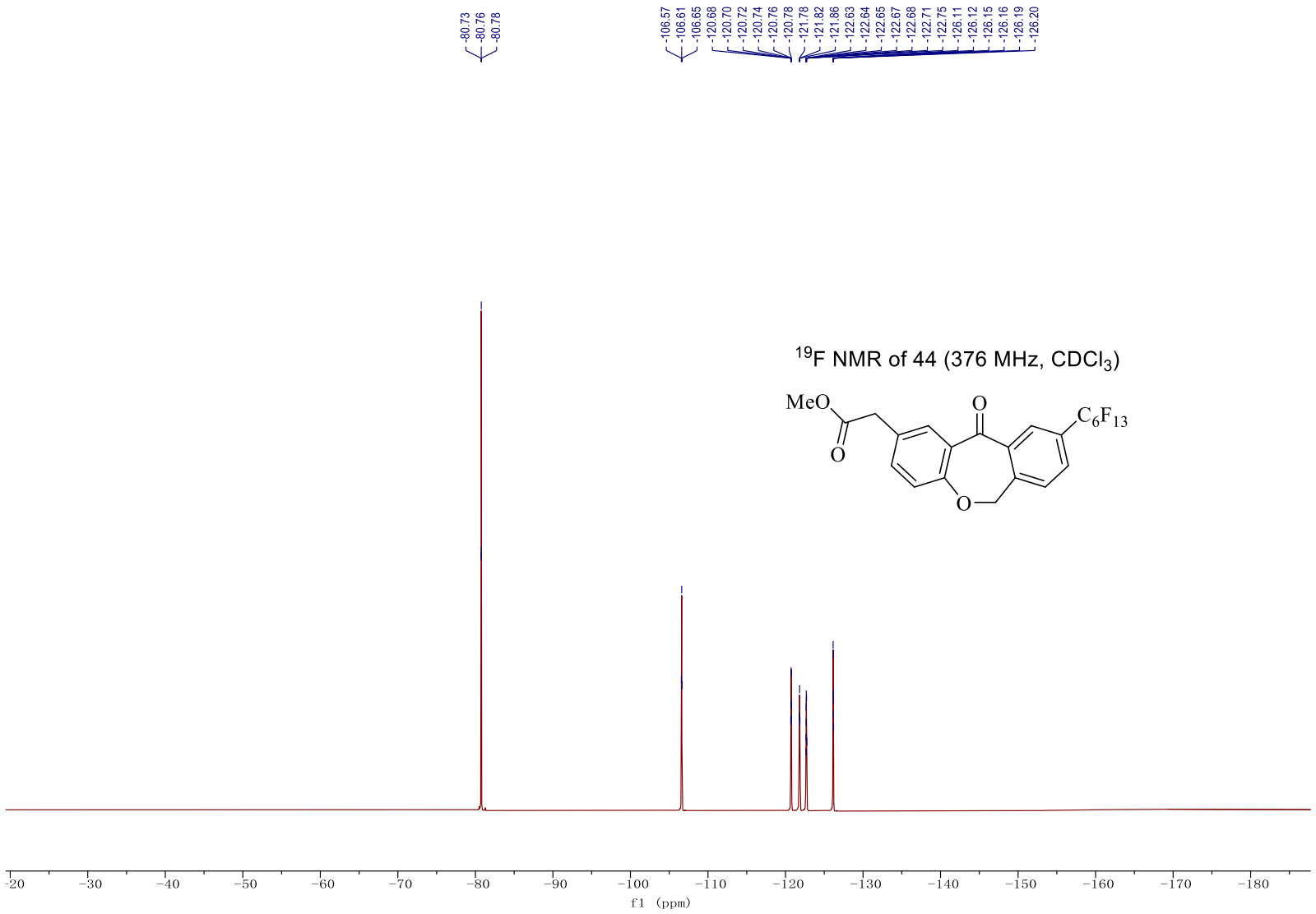


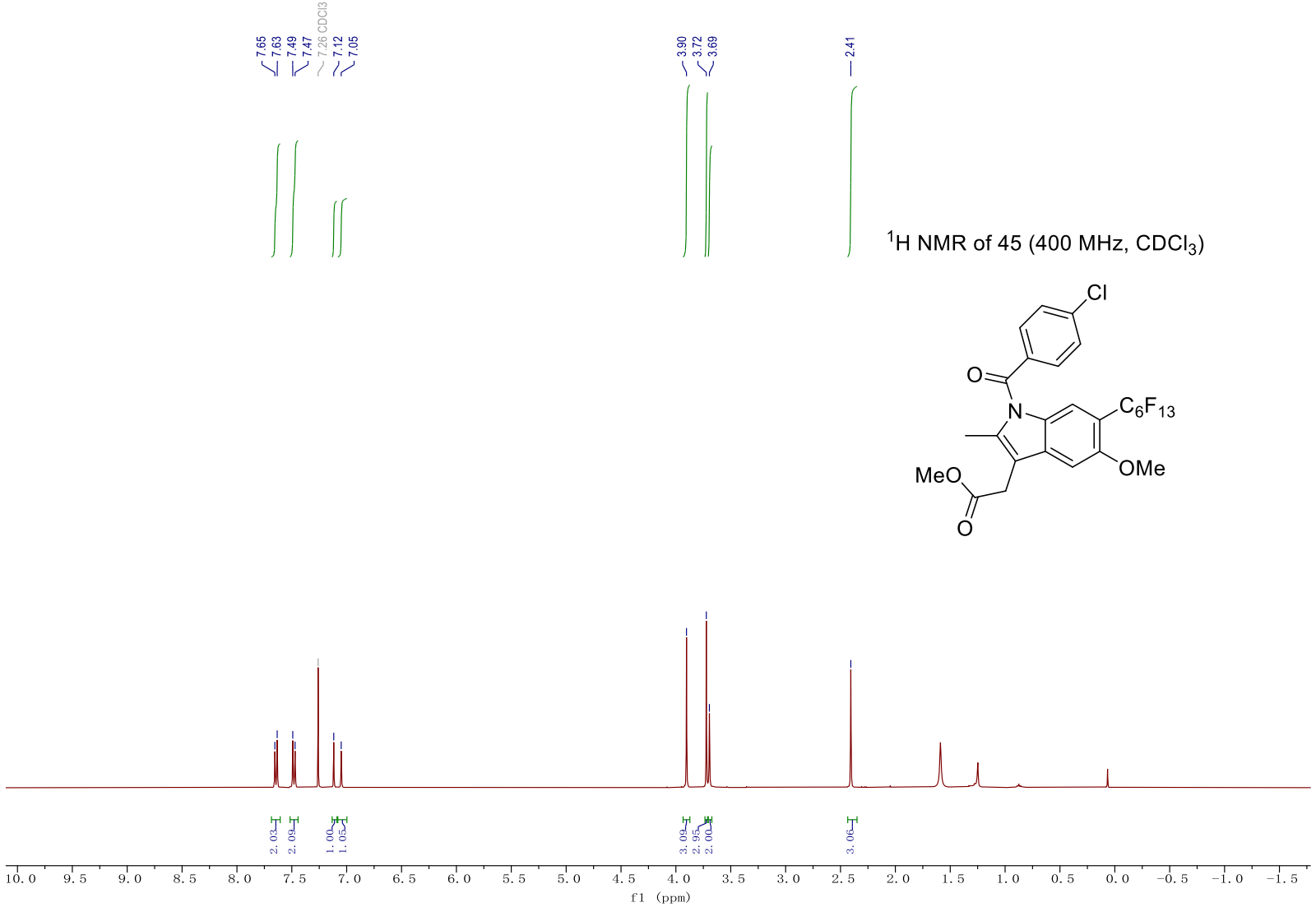
^{19}F NMR of 43 (376 MHz, $CDCl_3$)



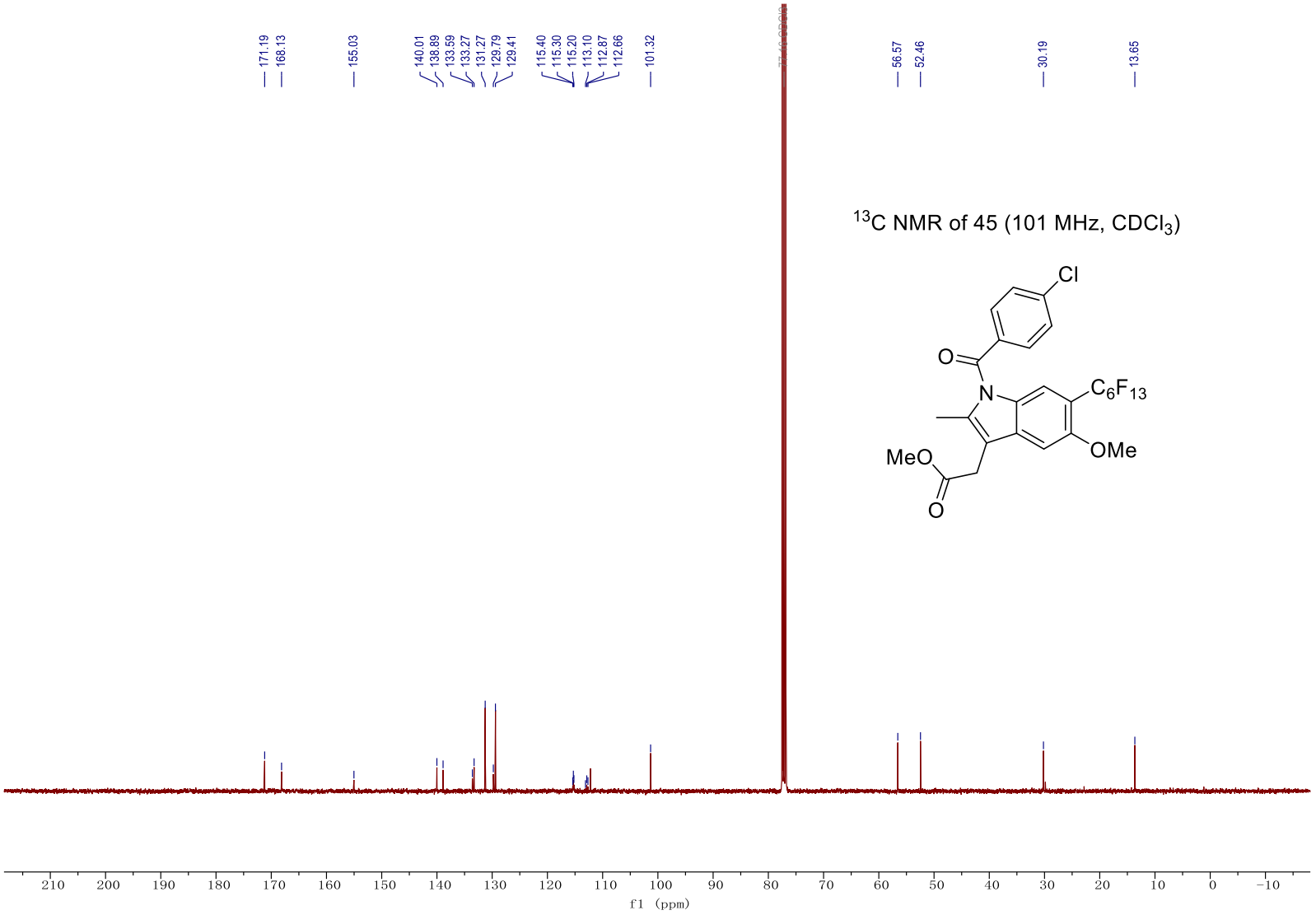
^{1}H NMR of 44 (400 MHz, $CDCl_3$)


189.32
171.29
159.49
139.25
137.73
136.10
136.05
136.01
135.92
133.47
130.40
129.57
128.10
127.92
121.03
120.80
120.57
77.46 CDCl3
74.80
52.44
39.98
^{13}C NMR of 44 (101 MHz, $CDCl_3$)
MeO
O
O
O
C_6F_{13}
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-80.73
-80.76
-80.78
-106.57
-106.61
-106.65
-120.68
-120.70
-120.72
-120.74
-120.76
-120.78
-121.78
-121.82
-121.86
-122.63
-122.64
-122.65
-122.67
-122.68
-122.71
-122.75
-126.11
-126.12
-126.15
-126.16
-126.19
-126.20
19F NMR of 44 (376 MHz, CDCl3)
MeO
O
O
O
O
C6F13
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)



^{1}H NMR of 45 (400 MHz, $CDCl_3$)


171.19
168.13
155.03
140.01
138.89
133.59
133.27
131.27
129.79
129.41
115.40
115.30
115.20
113.10
112.87
112.66
101.32
56.57
52.46
30.19
13.65
^{13}C NMR of 45 (101 MHz, $CDCl_3$)
Cl
O
N
C_6F_{13}
OMe
MeO
O
f1 (ppm)

-80.72
-80.75
-80.77
-106.51
-106.55
-106.59
-120.85
-120.89
-120.94
-121.87
-121.91
-121.95
-122.75
-126.14
-126.16
-126.18
-126.20

^{19}F NMR of 45 (376 MHz, $CDCl_3$)