Supporting Information

Nickel-Catalyzed Reductive Cross-Coupling of Difluoromethylated Secondary Alkyl Bromides with Organohalides

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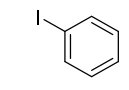
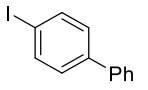
1. General information

Unless otherwise noted, all cross-coupling reactions were run under an N_2 atmosphere and all glassware was oven dried before use. Chemicals were purchased from Leyan, (1134-35-6, 4,4'-Dimethyl-2,2'-bipyridyl), Adamas-beta, Energy Chemical, bidepharm and were used without further purification. NMP was purchased from Adamas-beta and dried with 4Å 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. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded at 297 K 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 = multiplet, br = broad), coupling constants (Hz), integrated intensity.

2. General Procedure for the Preparation of Organohalides



3S



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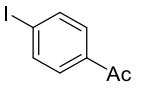

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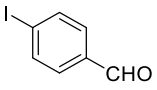
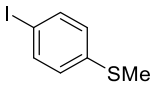
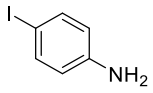


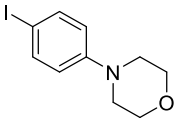
6S



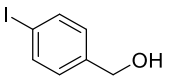
7S



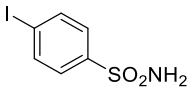
8S



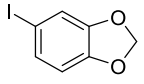
9S



10S



11S



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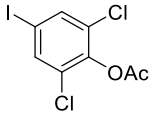

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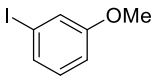
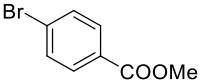
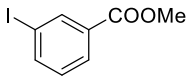


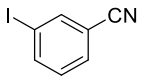
14S



15S'



16S



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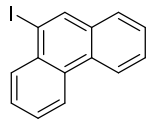
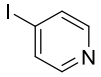
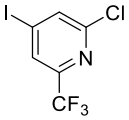


18S

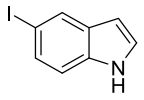


19S

20S



21S



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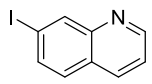

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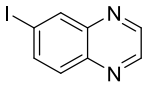
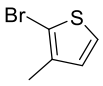
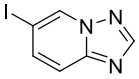


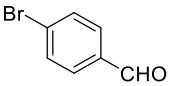
24S



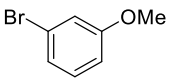
25S



26S



6S'



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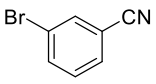
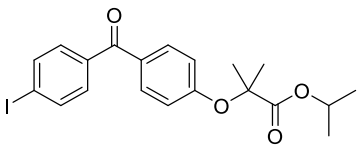
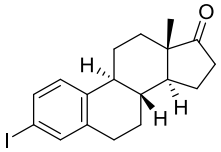


17S'



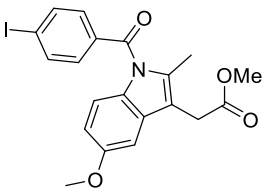
from fenofibrate

27S



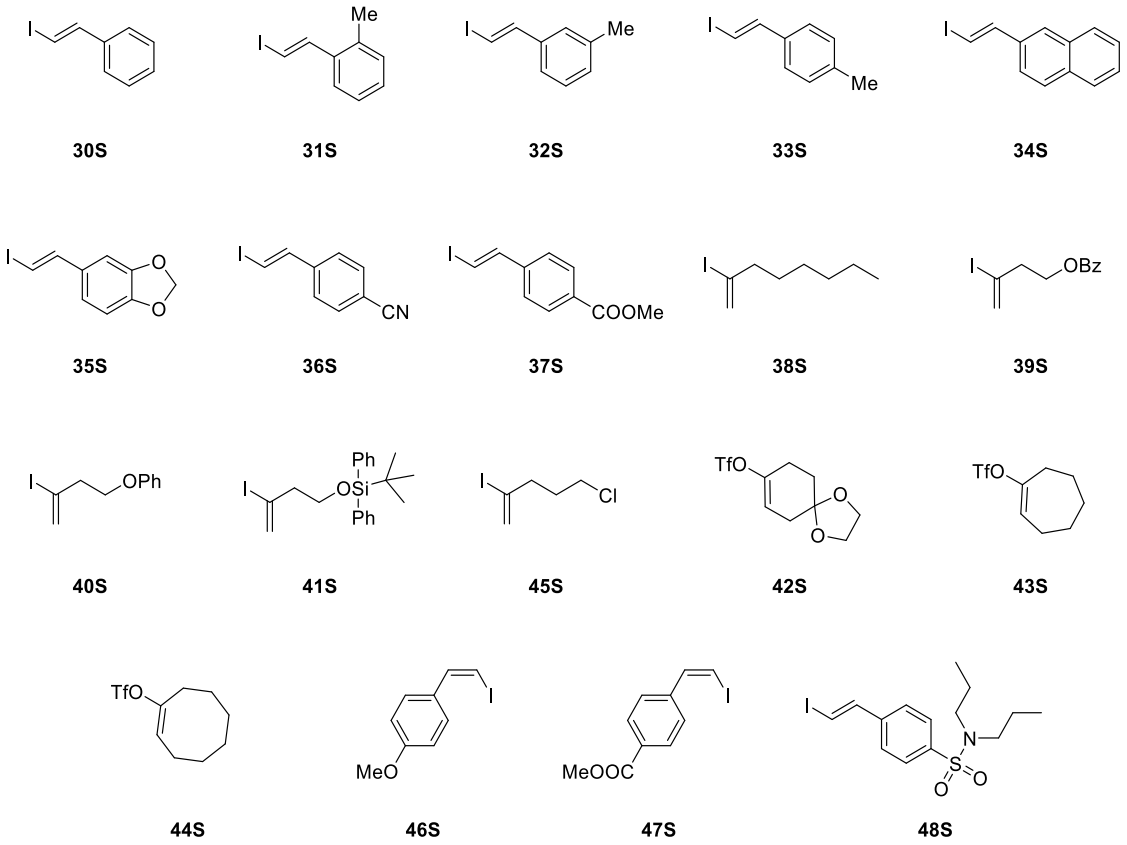
from estrone

28S



from Indomethacin

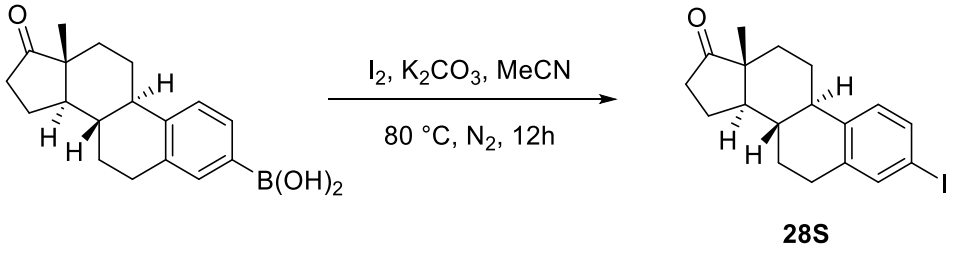
29S



Preparation of aryl iodide

The aryl iodides **3-26S** and aryl bromides **6-17S'**were purchase and used without further purification.

Aryl iodides **27S**, **28S** and **29S** were synthesized via known methods[1] and a typical procedure (synthesis of **28S**) is shown below:

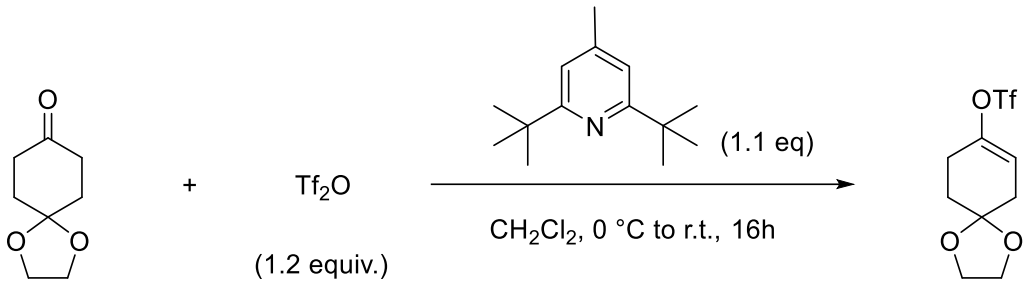


Estrone boronic acid (1 mmol) and K_2CO_3 (2 mmol, 276.0 mg) were added to a 25 mL Schlenk tube equipped with a magnetic stirring bar. The vessel was evacuated and backfilled with N_2 (repeated for 3 times). Acetonitrile (10 mL) and iodine (1.5 mmol, 382 mg) were added to the tube at room temperature under a stream of nitrogen, and

the tube was sealed and put into a pre-heated oil bath at 80 °C for 12 h under nitrogen atmosphere. After the resulting solution was cooled to room temperature, water (20 mL) was added, and the aqueous layer was extracted with EtOAc (3 ×15 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography (PE/EA = 5:1) to give the product (**28S**) as a white solid (83%).

Preparation of enol triflates compounds

General procedure A:enol triflates **42S**,**43S** and **44S** were synthesized via known methods[2] and a typical procedure (synthesis of **42S**) is shown below :



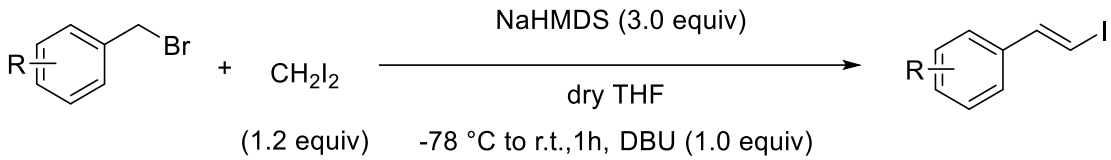
42S

The solution of 1,4-dioxaspiro[4.5]decan-8-one (312 mg, 2 mmol) in dichloromethane (10 mL) was cooled to 0 °C and then 2,6-di-*tert*-butyl-4-methylpyridine (451 mg, 2.2 mmol) and trifluoromethanesulfonic anhydride (0.4 mL, 2.4 mmol) were added to the reaction mixture. The reaction mixture were warmed to room temperature, stirred overnight, and evaporated to dryness. Petroleum ether was added and the solid pyridinium triflate was filtered off (the free base can be recovered) which was washed with petroleum ether. The combined petroleum ether solution was washed subsequently with cool HCl (1 M) and saturated brine, and dried over Na_2SO_4. Evaporation of the solvent followed by distillation gave the product (**42S**) (437 mg, 76%)

Preparation of (*E*)-*β*-Aryl Viny Iodides:

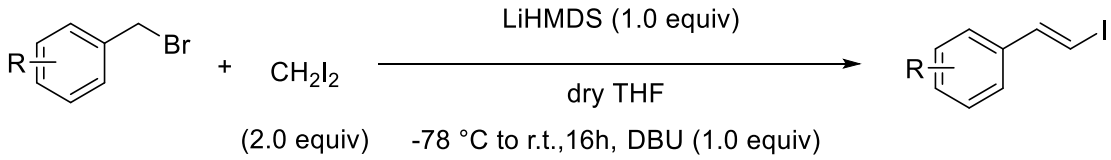
(*E*)-*β*-Aryl Viny Iodides **30-37S**, **48S** were synthesized via known methods[3] and typical procedures is shown below :

General procedure A:

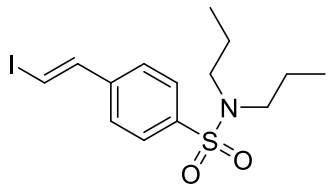


A solution of CH_2I_2 (121 μL, 1.5 mmol) in THF (0.5 mL) was added dropwise to a solution of NaHMDS (3.0 mmol) in THF (2 mL) and ether (2 mL) at –78 °C in the dark. After 20 min, a solution of the benzyl bromide substrate (1.0 mmol) in THF (1 mL) was added dropwise manner. The reaction mixture was stirred further for 90 min and then removed from the cold bath to warm to rt. After 30 min, the solution of DBU (149 μL, 1.0 mmol) was added dropwise and stirred for 1 h before ether (15 mL) was added. The mixture was filtered through a plug of celite/silica and the solvent removed under reduced pressure. The residue was purified by chromatography to provide the pure vinyl iodides **30-33S**.

General procedure B:



A solution of CH_2I_2 (161 μL, 2.0 mmol) in THF (0.5 mL) was added dropwise to a solution of LiHMDS (1.0 mmol) in THF (2 mL) and ether (2mL) at –78 °C in the dark. After 20 min, a solution of the benzyl bromide substrate (1.0 mmol) in THF (1 mL) was added in dropwise fashion. The reaction mixture was stirred at –78 ºC and allowed to warm to rt slowly over 16 h. Then solution of DBU (298 μL, 2.0 mmol) was added dropwise and the stirred further for 1 h before ether (15 mL) was added. The mixture was filtered through a plug of celite and the solvent removed under reduced pressure. The residue was purified by flash chromatography to provide the vinyl iodides **34-37S**. The new compounds **48S** were synthesized and characterized described below.



(*E*)-4-(2-iodovinyl)-N,N-dipropylbenzenesulfonamide (48S)

Light yellow solid, 200 mg, 51% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 20:1, v/v).

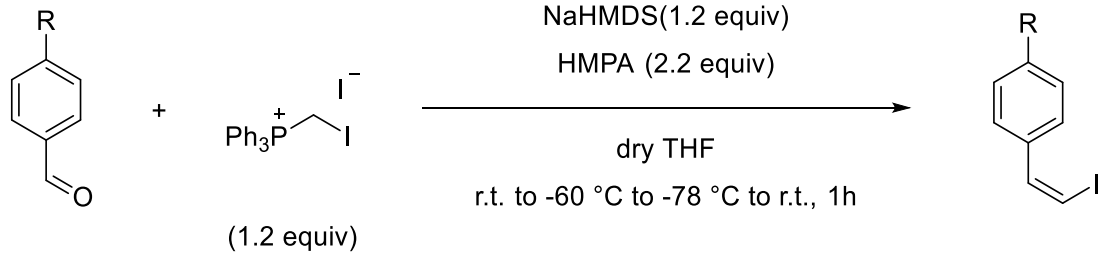
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.46 (d, *J* = 15.0 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.06 (d, *J* = 15.0 Hz, 1H), 3.09 – 3.05 (m, 4H), 1.57 – 1.51 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 141.2, 139.7, 127.7, 126.5, 80.8, 50.1, 22.1, 11.3.

HRMS (ESI) m/z calcd for $C_{14}H_{21}INO_2S[(M+H)^+]$: 394.0332 , found: 394.0326.

Preparation of (*Z*)-*β*-Aryl Viny Iodides

(*Z*)-*β*-Aryl Viny Iodides **46S**, **47S** were synthesized via known methods[3] and the procedure is shown below :

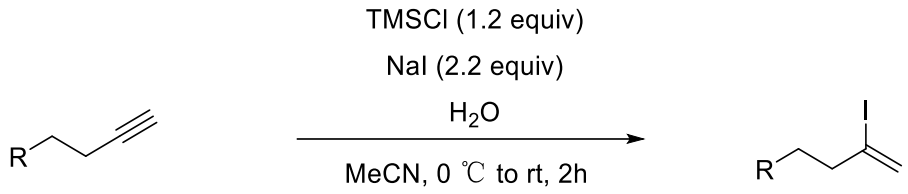


(iodomethyl)triphenylphosphonium iodide (1.2 equiv.), was added in dry THF (giving a 2.3 M solution) followed by dropwise addition of 0.5 M solution of NaHMDS in tetrahydrofuran (1.2 equiv). After addition was complete, the reaction mixture was cooled to -60 °C and HMPA (2.2 equiv.) was added, and the solution was further cooled to -78 °C. The aromatic aldehyde (1 mmol) was then added, the reaction mixture stirred for five minutes and warmed to room temperature. After 60 minutes, diethyl ether was added, and the reaction mixture was filtered through a pad of Celite. The resultant crude

material was purified by normal phase flash chromatography (hexane) to give the desired (Z)-vinyl iodides **46S, 47S.**

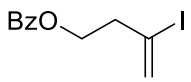
Preparation of Aliphatic Viny Iodides

Aliphatic Viny Iodides **38-45S** were synthesized via known methods[4] and the procedure is shown below :



At room temperature TMSCl (2.35 mL) was added to a solution of NaI (3.2 g) in MeCN (18 mL), followed by water (0.2 mL). The reaction was allowed to stir for 10 minutes, then alkyne (1.21 mL) was added and the reaction was stirred for 1 hour at room temperature. The reaction was then quenched with water. The aqueous layer was washed twice with diethyl ether and the combined organic layers were washed twice with aqueous saturated sodium thiosulfate. The organic layer was concentrated to half volume and washed three times with water to remove any excess MeCN.Then the resultant crude material was purified by normal phase flash chromatography to give the desired vinyl iodides **38-45S**.

The new compounds **39S, 40S** were synthesized according to references and characterized described below.



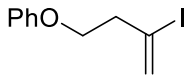
3-iodobut-3-en-1-yl benzoate (39S)

Yellow oil, 205 mg, 68% yield, **R**f =0.2 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.59 – 7.53 (m, 1H), 7.47 – 7.41 (m, 2H), 6.19 (d, *J* = 1.5 Hz, 1H), 5.84 (d, *J* = 1.6 Hz, 1H), 4.45 (t, *J* = 6.3 Hz, 2H), 2.86 (td, *J* = 6.3, 1.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 133.2, 130.1, 129.8, 129.7, 128.6, 128.5, 128.3, 105.8, 63.2, 44.4.

HRMS (CI, CH_4) m/z calcd for $C_{11}H_{12}IO_2[(M+H)^+]$: 302.9877 , found: 302.9880.



((3-iodobut-3-en-1-yl)oxy)benzene (40S)

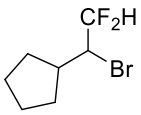
Yellow oil, 134 mg, 49% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.7, 7.2 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 2H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.20 (q, *J* = 1.5 Hz, 1H), 5.85 (d, *J* = 1.6 Hz, 1H) 4.10 (t, *J* = 6.4 Hz, 2H), 2.87 (td, *J* = 6.4, 1.0 Hz, 2H).

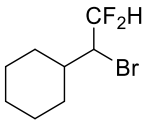
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 129.6, 128.2, 121.1, 114.8, 106.1, 66.4, 44.9.

HRMS (CI, CH_4) m/z calcd for $C_{10}H_{12}IO[(M+H)^+]$: 274.9927 , found:274.9929.

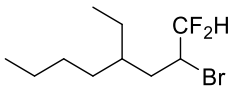
3. General Procedure for the Preparation of Secondary Alkyl Bromides



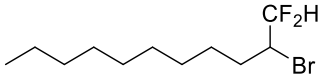
49S



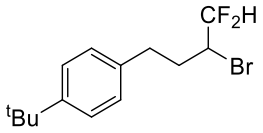
50S



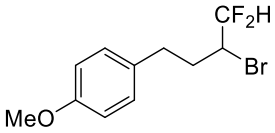
51S



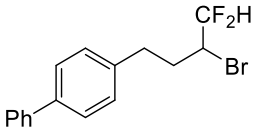
52S



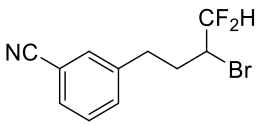
53S



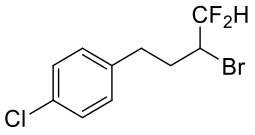
54S



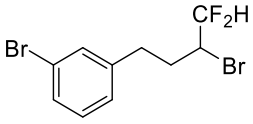
55S



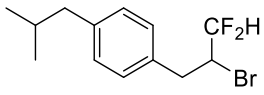
56S



57S



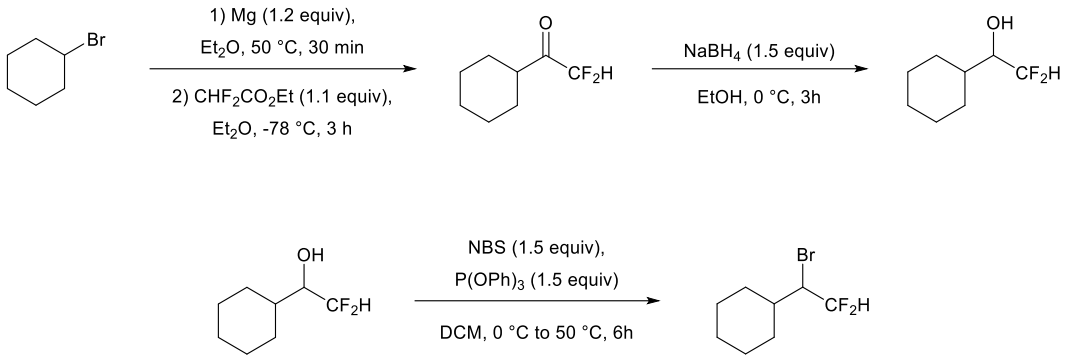
58S



59S

General procedure A: Synthesis of Secondary Alkyl Bromides **49-52S**

A typical procedure (synthesis of **50S**) is shown below[5]:



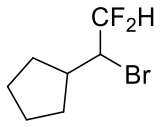
Step 1 :A solution of bromocyclohexane (2.0 mL, 16.3 mmol, 1.0 equiv.)in dry Et_2O (6.0 mL)was dropwise added to a flame dried 100 mL three-necks round-bottom flask equipped with a magnetic stirring bar and a reflux condenser charged with magnesium (425 mg, 19.6 mmol, 1.2 equiv.), a piece of iodine and dry Et_2O (2 mL). The resulting mixture was stirred at reflux for 30 min. After this time, the Grignard solution was dropwise added to a solution of ethyl difluoroacetate (1.8 mL, 17.9 mmol, 1.1 equiv.)in dry Et_2O (10 mL)at -78 °C. The reaction mixture was stirred at this temperature for 3 h and then was quenched with NH_4Cl (20 mL) and HCl (15 mL, 1 M). The mixture was diluted with H_2O (15 mL) and extracted with pentane (3 x 25 mL). The combined organic layers were washed with brine, dried over $MgSO_4$and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel using pentane to afford the desired product.

Step 2 : $NaBH_4$ (15 mmol, 1.5 equiv.) was added in portions to a solution of the ketone (10 mmol) in EtOH (10 mL) at 0 °C. After the addition was complete, the reaction mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was cooled to 0 °C, and quenched with saturated aqueous NH_4Cl solution. The EtOH was removed, 20 mL H_2O was added. The resulting mixture was extracted with Et_2O (3 x 50 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography on silica gel to give alcohol.

Step 3 : Triphenylphosphite (2.34 g, 4.8 mmol, 1.5 equiv.) was added over 5 min to a solution of N-bromosuccinimide (1.34 g, 7.5 mmol, 1.5 equiv.) in CH_2Cl_2 (15 mL) at 0 °C. Next, a solution of the alcohol (5 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) was added to the mixture at 0 °C. The reaction mixture was heated to 50 °C and then stirred for 6 h. Next, the solvent was evaporated, and the product was purified by flash

chromatography on silica gel.

The new compounds **49-52S** were synthesized and characterized described below.



(1-bromo-2,2-difluoroethyl)cyclopentane (49S)

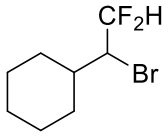
Colorless oil, 340 mg, 32% yield, **R**f =0.8 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (td, *J* = 55.8, 3.9 Hz, 1H), 4.05 (dtd, *J* = 14.6, 6.7, 3.3 Hz, 1H), 2.33 – 2.22 (m, 1H), 1.95 – 1.81 (m, 2H), 1.78 – 1.62 (m, 2H), 1.66 – 1.54 (m, 2H), 1.51 – 1.35 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 114.7 (t *J* = 245.4 Hz), 56.7 (t, *J* = 22.2 Hz), 40.8 (t, *J* = 2.5 Hz), 31.0, 30.4, 25.7, 24.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ -118.19 – -119.64 (m).

HRMS (CI, CH_4) m/z calcd for $C_7H_{10}BrF_2[(M-H)^+]$: 210.9928 , found: 210.9928.



(1-bromo-2,2-difluoroethyl)cyclohexane (50S)

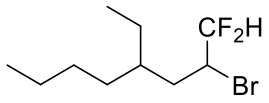
Colorless oil, 460 mg, 41% yield, **R**f =0.8 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 – 5.74 (m, 1H), 3.97 – 3.87 (m, 1H), 1.81 – 1.75 (m, 4H), 1.70 – 1.65 (m, 2H), 1.36 – 1.25 (m, 4H), 1.23 – 1.14 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 114.5 (t, *J* = 244.9 Hz), 58.0 (t, *J* = 22.2 Hz), 39.0 (t, *J* = 2.6 Hz), 31.1, 28.9, 26.0, 26.0, 25.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.53 – -120.61 (m).

HRMS (CI, CH_4) m/z calcd for $C_8H_{12}BrF_2[(M-H)^+]$: 225.0085 , found: 225.0084.



2-bromo-4-ethyl-1,1-difluorooctane (51S)

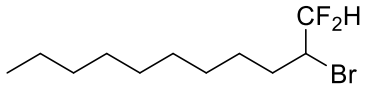
Light yellow oil, 330 mg, 26% yield, **R**f =0.8 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (t, *J* = 56.0 Hz, 1H), 4.09 – 3.95 (m, 1H), 1.85 – 1.72 (m, 2H), 1.45 – 1.40 (m, 1H), 1.33 – 1.17 (m, 8H), 0.92 – 0.83 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 115.2 (t, *J* = 245.7 Hz), 49.5 (t, *J* = 23.6 Hz), 36.2, 35.7, 34.8, 34.5, 32.8, 31.4, 29.8 (t, *J* = 4.0 Hz), 28.8, 28.1, 26.2, 24.3, 23.2, 23.1, 14.2, 10.9, 9.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -104.08 – -128.92 (m).

HRMS (CI, CH_4) m/z calcd for $C_{10}H_{18}BrF_2[(M-H)^+]$: 255.0553 , found: 255.0555.



2-bromo-1,1-difluoroundecane (52S)

Colorless oil, 280 mg, 21% yield, **R**f =0.8 (petroleum ether).

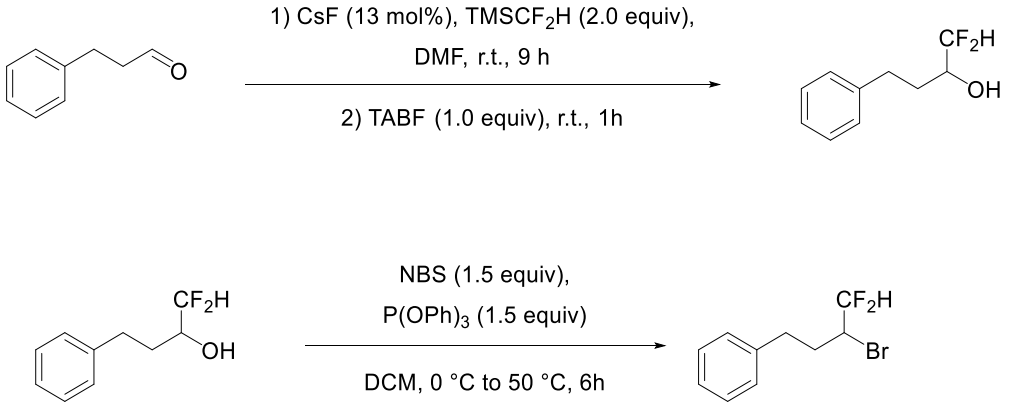
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (td, *J* = 56.0, 3.8 Hz, 1H), 4.03 – 3.88 (m, 1H), 2.02 – 1.91 (m, 1H), 1.86 – 1.76 (m, 1H), 1.36 – 1.23 (m, 16H), 0.93 – 0.77 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 114.9 (t, *J* = 243.5 Hz), 50.9 (t, *J* = 23.8 Hz), 31.9, 30.9 (t, *J* = 2.3 Hz), 29.5, 29.3, 29.3, 28.8, 26.8, 22.7, 14.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -106.00 – -137.95 (m).

HRMS (CI, CH_4) m/z calcd for $C_{11}H_{20}BrF_2[(M-H)^+]$: 269.0710 , found: 269.0708.

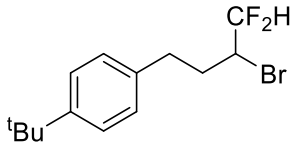
General procedure B: Secondary Alkyl Bromides **53-59S** were synthesized via known methods[6] and the procedure is shown below :



Step 1 : Under N_2 atmosphere, CsF (40 mg, 0.28 mmol) was added to a solution of phenylpropyl aldehyde (2.0 mmol) and (difluoromethyl)trimethylsilane Me_3SiCF_2H (496 mg, 4.0 mmol) in 2 mL of DMF, then the mixture was stirred at room temperature overnight. A solution of TBAF (2.0 ml, 1 M in THF) was then added, and the whole mixture was stirred for another 1h. After extraction with Et_2O and H_2O, the organic phase was washed with brine, and then dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography to give the step 1 product as colorless oil.

Step 2 : The bromination step is the same with **General procedure A**.

The new compounds **53-59S** were synthesized and characterized described below.



1-(3-bromo-4,4-difluorobutyl)-4-(tert-butyl)benzene (53S)

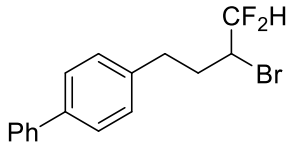
Colorless oil, 280 mg, 46% yield, **R**f =0.5 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 8.0, 2.4 Hz, 2H), 7.24 – 7.16 (dd, *J* = 8.0, 2.4 Hz, 2H), 6.03 – 5.70 (m, 1H), 3.94 (td, *J* = 13.6, 7.1 Hz, 1H), 3.00 (dt, *J* = 13.5, 5.9 Hz, 1H), 2.79 (dt, *J* = 14.8, 8.3 Hz, 1H), 2.33 (ddd, *J* = 19.5, 10.6, 5.2 Hz, 1H), 2.23 – 2.09 (m, 1H), 1.37 (d, *J* = 2.9 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 136.8, 128.3, 125.7, 114.9 (t, *J* = 245.6 Hz), 50.1 (t, *J* = 23.9 Hz), 34.5, 32.4 (t, *J* = 2.5 Hz), 32.2, 31.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -110.18 – -134.17 (m).

HRMS (CI, CH_4) m/z calcd for $C_{14}H_{19}BrF_2[M^+]$: 304.0633 , found: 304.0627.



4-(3-bromo-4,4-difluorobutyl)-1,1'-biphenyl (55S)

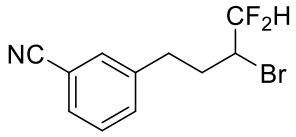
Colorless oil, 340 mg, 52% yield, **R**f =0.5 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 4H), 7.50 – 7.44 (m, 2H), 7.40 – 7.34 (m, 1H), 7.34 – 7.29 (m, 2H), 5.87 (td, *J* = 55.9, 3.6 Hz, 1H), 4.08 – 3.85 (m, 1H), 3.19 – 2.96 (m, 1H), 2.83 (dt, *J* = 13.9, 8.2 Hz, 1H), 2.40 – 2.29 (m, 1H), 2.27 – 2.10 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 139.6, 138.9, 129.1, 128.9, 127.5, 127.4, 127.1, 114.9 (t, *J* = 245.8 Hz), 49.9 (t, *J* = 24.0 Hz), 32.3 (t, *J* = 2.5 Hz), 32.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ -115.96 – -124.06 (m).

HRMS (ESI) m/z calcd for $C_{16}H_{16}BrF_2[(M+H)^+]$: 325.0398 , found: 325.0391.



3-(3-bromo-4,4-difluorobutyl)benzonitrile (56S)

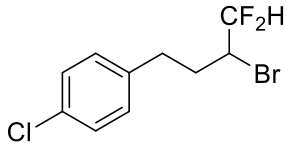
Light yellow oil, 205 mg, 38% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 10.2 Hz, 2H), 7.49 – 7.36 (m, 2H), 5.86 (t, *J* = 55.8 Hz, 1H), 3.85 (q, *J* = 11.3, 10.7 Hz, 1H), 3.10 – 2.96 (m, 1H), 2.80 (dt, *J* = 14.8, 8.5 Hz, 1H), 2.28 (dt, *J* = 17.4, 8.2 Hz, 1H), 2.19 – 2.05 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 133.2, 132.1, 130.5, 129.6, 118.8, 114.7 (t, *J* = 246.0 Hz), 112.8, 49.3 (t, *J* = 24.3 Hz), 32.4, 31.9 (t, *J* = 2.8 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -112.88 – -129.13 (m).

HRMS (ESI) m/z calcd for $C_{11}H_{11}BrF_2N[(M+H)^+]$: 274.0038 , found: 274.0033.



1-(3-bromo-4,4-difluorobutyl)-4-chlorobenzene (57S)

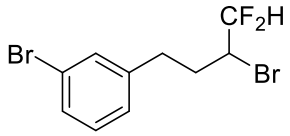
Light yellow oil, 230 mg, 41% yield, **R**f =0.4 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.19 – 7.11 (m, 2H), 5.84 (td, *J* = 55.9, 3.6 Hz, 1H), 3.93 – 3.77 (m, 1H), 3.01 – 2.88 (m, 1H), 2.74 (dt, *J* = 13.9, 8.2 Hz, 1H), 2.31 – 2.18 (m, 1H), 2.19 – 2.03 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 132.5, 130.0, 128.9, 114.8 (t, *J* = 245.9 Hz), 49.6 (t, *J* = 24.1 Hz), 32.2 (t, *J* = 2.5 Hz), 32.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -108.90 – -142.76 (m).

HRMS (CI, CH_4) m/z calcd for $C_{10}H_9BrClF_2[(M-H)^+]$: 280.9544 , found: 280.9541.



1-bromo-3-(3-bromo-4,4-difluorobutyl)benzene (58S)

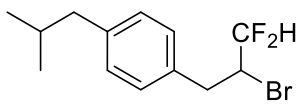
Light yellow oil, 228 mg, 35% yield, **R**f =0.5 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.21 – 7.14 (m, 2H), 5.85 (td, *J* = 55.8, 3.6 Hz, 1H), 3.96 – 3.79 (m, 1H), 3.01 – 2.92 (m, 1H), 2.74 (dt, *J* = 13.9, 8.3 Hz, 1H), 2.31 – 2.22 (m, 1H), 2.17 – 2.06 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 131.7, 130.4, 129.8, 127.3, 122.8, 114.8 (t, *J* = 245.9 Hz), 49.6 (t, *J* = 24.2 Hz), 32.5, 32.2(t, *J* = 2.4 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -110.60 – -146.88 (m).

HRMS (ESI) m/z calcd for $C_{10}H_{10}Br_2F_2[(M+H)^+]$: 326.9190 , found: 326.9198.



1-(2-bromo-3,3-difluoropropyl)-4-isobutylbenzene (59S)

Colorless oil, 158 mg, 27% yield, **R**f =0.5 (petroleum ether).

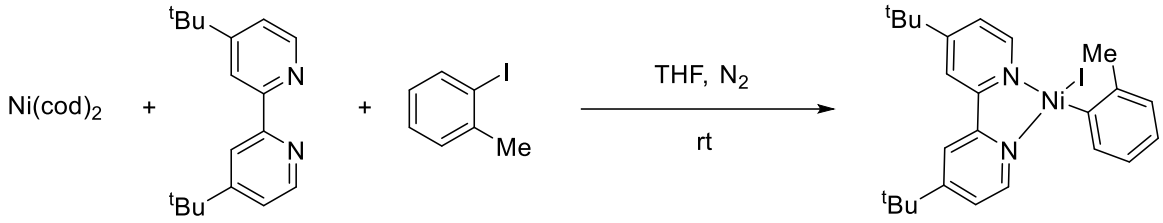
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.10 (m, 4H), 5.81 (td, *J* = 55.7, 3.2 Hz, 1H), 4.25 – 4.12 (m, 1H), 3.38 – 3.06 (m, 2H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.87 (dp, *J* = 13.6, 6.8 Hz, 1H), 0.91 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 133.5, 129.6, 129.1, 114.1 (t, *J* = 246.4 Hz), 51.1 (t, *J* = 23.2 Hz), 45.2, 37.6 (t, *J* = 3.2 Hz), 30.3, 22.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -119.56 – -122.84 (m).

HRMS (ESI) m/z calcd for $C_{13}H_{18}BrF_2[(M+H)^+]$: 291.0555 , found: 291.0555.

4. Synthesis of (dtbpy)Ni^{II}(2-tolyl)I:



60

The nickel complex (dtbpy)Ni^{II}(2-tolyl)I **(60)** was synthesized via known methods[7].

A solution of (dtbbpy)Ni(cod) was generated by stirring 176 mg of $Ni(cod)_2$ (0.6 mmol) and 160 mg of 4,4'-di-tert-butyl-2,2'-bipyridine (0.6 mmol) in 6 mL of THF overnight at room temperature in an argon-filled glovebox. Upon dissolution of the solids, the reaction mixture became dark purple. To this purple mixture was added 0.091 mL of 2-iodotoluene (157 mg, 0.72 mmol) and the color rapidly changed to red, indicating formation of **60**. The solution was stirred for an additional 2 h before the solvent was removed under vacuum. The solid was triturated with dry, degassed pentane three times to remove residual cyclooctadiene and 2-iodotoluene and then dried under vacuum overnight to provide 260 mg of **60** (78% yield).

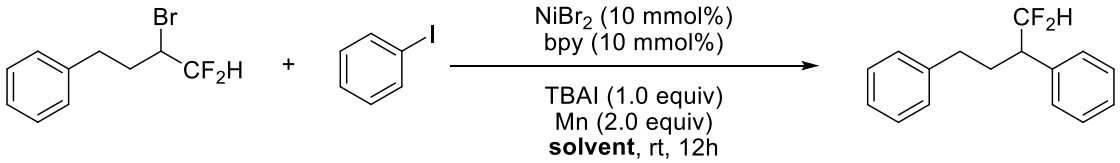
5. Optimization studies.

5.1 Screening of reaction conditions for the Cross-coupling product.

General procedure: In a nitrogen-filled glovebox, to a 8 mL vial equipped with a

stir bar was added catalyst (0.02 mmol, 10 mmol%), ligand (0.02mmol, 10 mmol%.), and solvent was added and stirred at rt for 10 min, then difluoroalkyl bromides **1** (0.2 mmol, 1.0 equiv.) and Aryl iodine (0.2 mmol, 1.0 equiv.) was added to the mixture and stirred for 12 h . After the reaction was completed, the mixture was diluted with EtOAc, the crude products were purified by flash chromatography.

Table S1 The effects of solvent on the reaction [a-b].

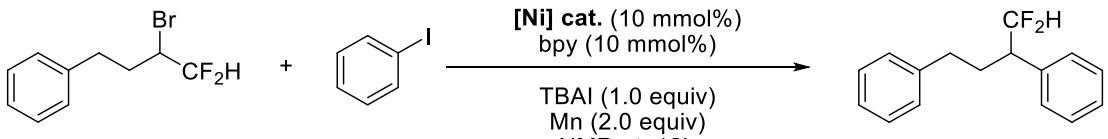


entry	solvent	Yield(%)[b]
1	THF	nd
2	DMF	32
3	1,4-dioxane	nd
4	MeCN	nd
5	**NMP**	**72**
6	DMA	62
7	DMSO	nd
8	Toluene	nd

[a] Reaction conditions: secondary alkyl bromides **1** (0.1 mmol), aryl iodide **2** (0.1 mmol), Catalyst (10 mmol%), Ligand (10 mmol%), TBAI (0.1 mmol), reductant (0.2 mol), solvent (1.0 mL), 12 h.

[b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

Table S2 The effects of catalysts on the reaction [a-b].



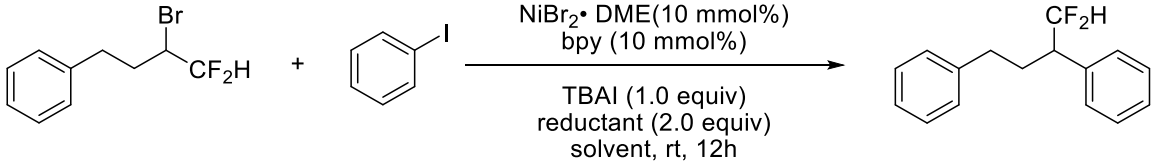
entry	catalyst	Yield(%)[b]

1	$NiCl_2$	51
2	$NiBr_2$	72
3	$NiCl_2{\cdot}6H_2O$	43
4	$NiBr_2{\cdot}6H_2O$	49
5	$NiCl_2{\cdot}DME$	53
6	**$NiBr_2{\cdot}DME$**	**79**
7	$Ni(OAc)_2$	nd
8	$Ni(OTf)_2$	nd

[a] Reaction conditions: secondary alkyl bromides **1** (0.1 mmol), aryl iodide **2** (0.1 mmol), Catalyst (10 mmol%), Ligand (10 mmol%), TBAI (0.1 mmol), reductant (0.2 mol), solvent (1.0 mL), 12 h.

[b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

Table S3 The effects of Reductants on the reaction[a-b].



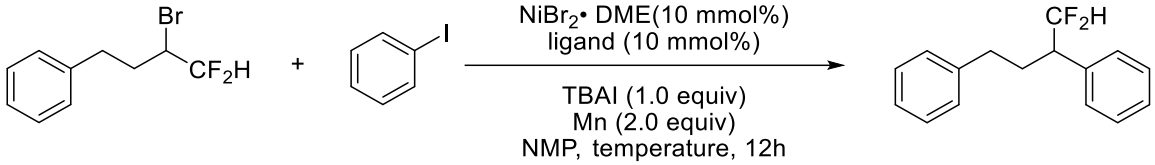
entry	catalyst	Yield(%)[b]
1	**Mn**	**82**
2	Zn	24
3	$FeCl_2$	ND
4	$FeBr_2$	14
5	B_2Pin_2, Cs_2CO_3	21

[a] Reaction conditions: secondary alkyl bromides **1** (0.1 mmol), aryl iodide **2** (0.1 mmol), Catalyst (10 mmol%), Ligand (10 mmol%), TBAI (0.1 mmol), reductant (0.2

mol), solvent (1.0 mL), 12 h.

[b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

Table S4 The effects of ligand and temperature on the reaction[a-b].

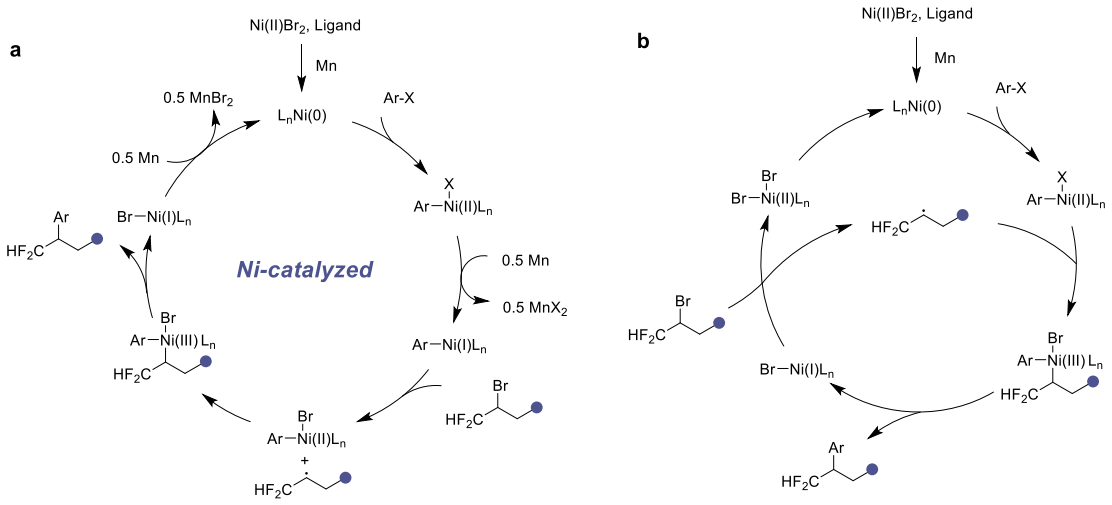


entry	Temperature (℃)	ligand	Yield(%)[b]
1	rt	tpy	33%
2	rt	dtbpy	67%
3	rt	bpy	77%
4	rt	dmbpy	83%
5	rt	1,10-phenanthroline	32%
6	40 ℃	dmbpy	81%
7	**50 ℃**	**dmbpy**	**88%**
8	60 ℃	dmbpy	88%
9	80 ℃	dmbpy	79%

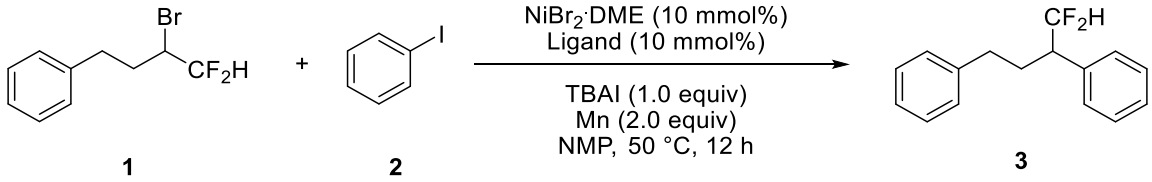
[a] Reaction conditions: secondary alkyl bromides **1** (0.1 mmol), aryl iodide **2** (0.1 mmol), Catalyst (10 mmol%), Ligand (10 mmol%), TBAI (0.1 mmol), reductant (0.2 mol), solvent (1.0 mL), 12 h.

[b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

6. Proposed Mechanism: a) Radical-cage-rebound process; b) A radical chain process



6. General Procedure for the Synthesis of the product

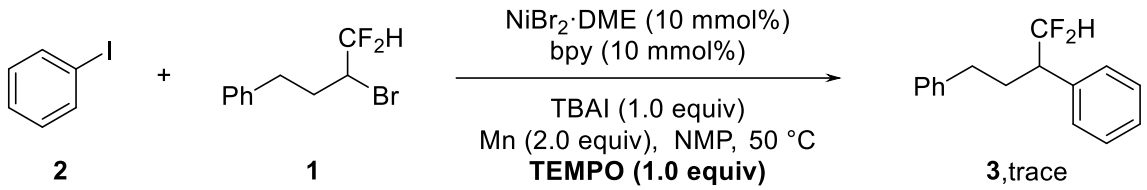


Product **3** as an example :

To an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was charged with aryl iodide **2** (0.2 mmol, 1.0 equiv.), $NiBr_2$·DME (3.8 mg, 0.012 mmol, 10 mmol%), and 4,4'-Dimethyl-2,2'-bipyridyl (5.2 mg, 0.016 mmol, 10 mmol%), Mn (22.0 mg, 0.4 mmol, 2 equiv.), TBAI (73.8 mg, 0.2 mmol, 1.0 equiv.). The tube was sealed with a Teflon-lined screw cap.After evacuated and backfilled with nitrogen three times, NMP (2.0 mL) were added via a syringe followed by addition of **1** (68.1 mg, 0.2 mmol, 1.0 equiv.). The reaction mixture was allowed to stir for 12 h under N_2 atmosphere at 50 ˚C After the reaction was completed, the mixture was diluted with EtOAc (3 x 10 mL), washed with H_2O and brine. The organic layer was combined, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography.

7.Mechanistic Studies:

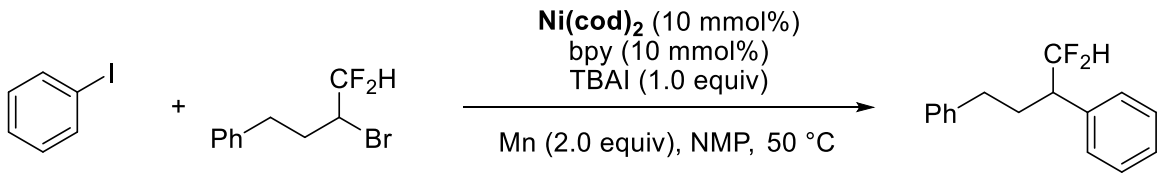
7.1. Radical Capture Experiment:



2 **1** **3**,trace

To a 10 mL of Schlenk tube were added $NiBr_2$ DME(10 mmol %, 0.01 mmol), bpy (10 mmol %, 0.01 mmol) and Mn (2.0 equiv., 0.2 mmol) under air. The vessel was evacuate and backfilled wit N_2 (3 times), and **1** (1.0 equiv, 0.1 mmol), **2** (1.0 equiv., 0.1 mmol), Tempo (1.0 equiv., 0.1 mmol) and NMP (1.0 mL) were then added via syringe. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 50 ˚C for 12 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (~10 mL) and filtered through a pad of celite.

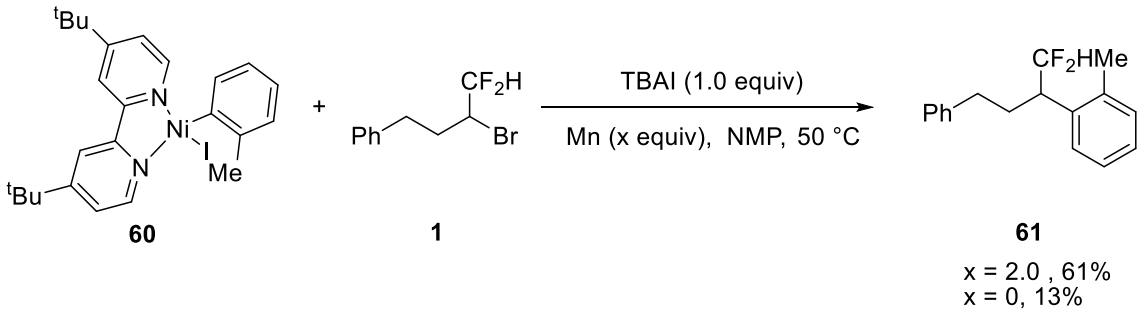
7.2. Procedure of Monofluoroalkylation with Ni^0 Used as the Catalyst



2 **1** **3**, 76%

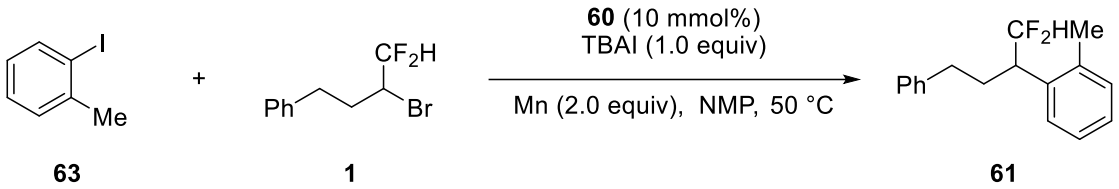
To a 10 mL of Schlenk tube were added $Ni(cod)_2$ (10 mmol %, 0.01 mmol), bpy (10 mmol %, 0.01 mmol) and Mn (2.0 equiv., 0.2 mmol) in glove box. Then **1** (1.0 equiv., 0.1 mmol), **2** (1.0 equiv., 0.1 mmol) and NMP (1.0 mL) were added via syringe. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 50 ˚C for 12 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (~10 mL) and filtered through a pad of celite. The filtrate was added into brine (10 mL) and extracted with EtOAc (2 × 10 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was concentrated under vacuum and purified by flash column chromatography (PE) to give product **3** in 76% yield

7.3. Procedure of Stoichiometric Reactions of Organonickel Complex 60



To a 25 mL of Schlenk tube was added complex **60** (1.0 equiv, 0.1 mmol) and Mn (x equiv) in glove box. Then **1** (1.0 equiv., 0.1 mmol) and NMP (1.0 mL) were added via syringe. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 50 ˚C for 12 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (~10 mL) and filtered through a pad of celite. The filtrate was added into brine (20 mL) and extracted with EtOAc (2 × 15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was concentrated under vacuum and purified by flash column chromatography (PE) to give product **61**.

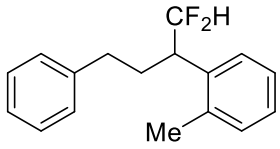
7.4. Procedure of Difluoromethylation with Organonickel Complex 60 Used as the Catalyst



To a 10 mL of Schlenk tube were added complex 73 (10 mmol %, 0.02 mmol) and Mn (2.0 equiv.) in glove box. Then 2-iodotoluene (1.0 equiv, 0.2 mmol), **1** (1.0 equiv., 0.22 mmol) and NMP (1.0 mL) were added via syringe. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 50 ˚C for 12 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (~10 mL) and filtered through a pad of celite. The filtrate was added into brine (20 mL) and extracted with EtOAc (2 × 15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated

under vacuum. The residue was concentrated under vacuum and purified by flash column chromatography (PE) to give product **61**.

The new compounds **61** were synthesized and characterized described below.



1-(1,1-difluoro-4-phenylbutan-2-yl)-2-methylbenzene (61)

Colorless oil, 46.1 mg, 89% yield, **R**f =0.5 (petroleum ether).

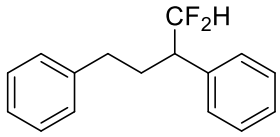
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 3H), 7.26 – 7.23 (m, 1H), 7.23 – 7.15 (m, 3H), 7.12 – 7.03 (m, 2H), 5.81 (td, *J* = 56.7, 4.4 Hz, 1H), 3.50 – 3.21 (m, 1H), 2.69 – 2.54 (m, 1H), 2.54 – 2.41 (m, 1H), 2.37 – 2.24 (m, 1H), 2.21 (s, 3H), 2.17 – 1.99 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 137.8, 135.1 (t, J = 4.2 Hz), 130.8, 128.6, 128.5, 127.4, 127.2, 126.6, 126.2, 118.5 (t, J = 244.9 Hz), 43.6 (t, J = 19.7 Hz), 32.7, 30.1, 20.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -110.82 – -135.80 (m).

HRMS (CI) m/z calcd for $C_{17}H_{18}F_2[M^+]$: 260.1372 , found: 260.1370.

8. Characterization of products



4-(4,4-difluorobutane-1,3-diyl)dibenzene (3)

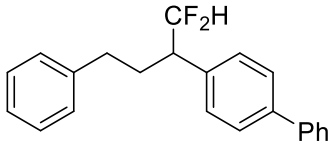
Colorless oil, 43.2 mg, 88% yield, **R**f =0.5 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.33 (m, 3H), 7.31 – 7.27 (m, 4H), 7.20 (t, *J* = 7.1 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 2H), 5.84 (t, *J* = 56.7 Hz, 1H), 3.01 (q, *J* = 13.3 Hz, 1H), 2.66 – 2.38 (m, 2H), 2.31 – 2.03 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 136.7 (t, *J* = 4.0 Hz), 129.1, 128.9, 128.6, 128.6, 127.8, 126.2, 118.0 (t, *J* = 244.5 Hz), 49.3 (t, *J* = 19.7 Hz), 32.9, 29.9 (t, *J* = 3.8 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -117.12 – -123.68 (m).

HRMS (ESI) m/z calcd for $C_{16}H_{17}F_2[(M+H)^+]$: 247.1293 , found: 247.1294.



5-(1,1-difluoro-4-phenylbutan-2-yl)-1,1'-biphenyl (4)

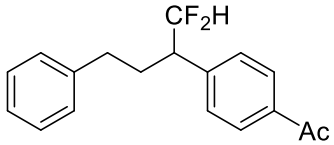
White solid, 40.0 mg, 62% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.5 Hz, 4H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.45 – 7.25 (m, 6H), 7.19 (d, *J* = 7.3 Hz, 2H), 5.92 (t, *J* = 56.7 Hz, 1H), 3.11 (q, *J* = 14.5 Hz, 1H), 2.76 – 2.64 (m, 1H), 2.61 – 2.51 (m, 1H), 2.40 – 2.28 (m, 1H), 2.26 – 2.15 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 140.8, 140.7, 136.0 (t, *J* = 4.0 Hz), 129.9, 129.3, 128.9, 127.9, 127.8, 127.5, 126.5, 118.3 (t, *J* = 244.6 Hz), 49.3 (t, *J* = 19.7 Hz), 33.2, 30.2 (t, *J* = 3.7 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.71 – -124.04 (m).

HRMS (ESI) m/z calcd for $C_{22}H_{21}F_2[(M+H)^+]$: 323.1606, found: 323.1609.



1-(4-(1,1-difluoro-4-phenylbutan-2-yl)phenyl)ethan-1-one (5)

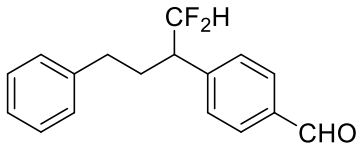
Colorless oil, 49.8 mg, 86% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 2H), 5.81 (t, *J* = 56.4, 3.4 Hz, 1H), 3.12 – 2.97 (m, 1H), 2.58 (s, 3H), 2.58 – 2.49 (m, 1H), 2.47 – 2.34 (m, 1H), 2.29 – 2.17 (m, 1H), 2.16 – 2.01 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 142.0 (t, *J* = 3.7 Hz), 140.8, 136.7, 129.5, 128.9, 128.6, 128.5, 126.3, 117.5 (t, *J* = 244.8 Hz), 49.2 (t, *J* = 19.9 Hz), 32.7, 29.9 (t, *J* = 3.7 Hz), 26.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.25 (dd, *J* = 761.1, 278.2 Hz).

HRMS (ESI) m/z calcd for $C_{18}H_{19}F_2O[(M+H)^+]$: 289.1399 , found: 289.1397.



4-(1,1-difluoro-4-phenylbutan-2-yl)benzaldehyde (6)

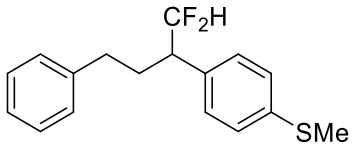
White solid, 45.3 mg, 83% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 9.1 Hz, 2H), 7.16 (t, *J* = 7.1 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 2H), 5.82 (t, *J* = 56.4 Hz, 1H), 3.05 (dd, *J* = 15.9, 10.3 Hz, 1H), δ 2.64 – 2.50 (m, 1H), 2.48 – 2.35 (m, 1H), 2.31 – 2.18 (m, 1H), 2.17 – 2.04 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 143.6 (t, *J* = 3.7 Hz), 140.7, 136.0, 130.2, 129.9, 128.7, 128.5, 126.4, 117.3 (t, *J* = 244.9 Hz), 49.4 (t, *J* = 19.9 Hz), 32.8, 29.9 (t, *J* = 3.8 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -117.83 – -122.64 (m).

HRMS (ESI) m/z calcd for $C_{17}H_{16}F_2ONa[(M+Na)^+]$: 297.1061 , found: 297.1052.



(4-(1,1-difluoro-4-phenylbutan-2-yl)phenyl)(methyl)sulfane (7)

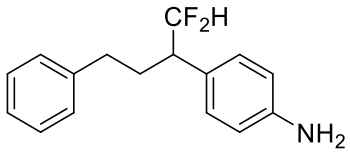
White solid 45.9 mg, 79% yield, **R**f =0.2 (petroleum ether: ethyl acetate, 50:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.1 Hz, 4H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 7.4 Hz, 2H), 5.84 (t, *J* = 56.7 Hz, 1H), 3.11 – 2.88 (m, 1H), 2.70 – 2.58 (m, 1H), 2.54 (s, 3H), 2.53 – 2.40 (m, 1H), 2.36 – 2.21 (m, 1H), 2.20 – 2.03 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 138.0, 133.3 (t, *J* = 4.1 Hz), 129.6, 128.6, 128.5, 126.9, 126.2, 117.9 (t, *J* = 244.6 Hz), 48.7 (t, *J* = 19.7 Hz), 32.8, 29.7 (t, *J* = 3.8 Hz), 15.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -108.04 – -129.12 (m).

HRMS (ESI) m/z calcd for $C_{17}H_{19}F_2S[(M+H)^+]$: 293.1170 , found: 293.1174.



4-(1,1-difluoro-4-phenylbutan-2-yl)aniline (8)

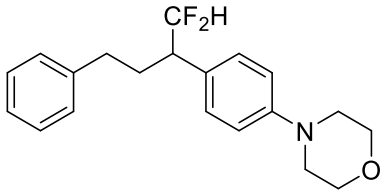
Yellow oil, 37.8 mg, 72% yield, **R**f =0.2 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.71 (d, *J* = 7.9 Hz, 2H), 5.78 (td, *J* = 56.9, 3.6 Hz, 1H), 3.67 (s, 2H), 2.94 – 2.78 (m, 1H), 2.67 – 2.58 (m, 1H), 2.52 – 2.42 (m, 1H), 2.27 – 2.17 (m, 1H), 2.12 – 2.01 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 141.6, 130.0, 128.6, 128.5, 126.1, 118.3 (t, *J* = 244.4 Hz), 115.5, 48.5 (t, *J* = 19.7 Hz), 32.9, 29.8 (t, *J* = 4.0 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -106.64 – -133.54 (m).

HRMS (ESI) m/z calcd for $C_{16}H_{18}F_2N[(M+H)^+]$: 2612.1402 , found: 262.1397.



4-(4-(1,1-difluoro-4-phenylbutan-2-yl)phenyl)morpholine (9)

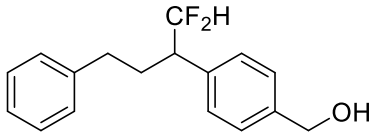
Colorless oil, 51.8 mg, 78% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 15:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.3 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.4 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.80 (t, *J* = 56.8, 2.8 Hz, 1H), 3.89 (t, *J* = 4.4 Hz, 4H), 3.20 (t, *J* = 4.8 Hz, 4H), 2.94 (q, *J* = 15.1 Hz, 1H), 2.67 – 2.55 (m, 1H), 2.52 – 2.40 (m, 1H), 2.29 – 2.17 (m, 1H), 2.14 – 1.99 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 141.6, 130.0, 128.5, 128.5, 127.8 (t, *J* = 4.0 Hz), 126.2, 120.7, 118.3, 115.9, 67.1, 49.3, 48.5 (t, *J* = 19.6 Hz), 32.9, 29.9 (t, *J* = 3.6 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -114.80 – -126.12 (m).

HRMS (ESI) m/z calcd for $C_{20}H_{24}F_2NO[(M+H)^+]$: 332.1821 , found: 332.1824.



(4-(1,1-difluoro-4-phenylbutan-2-yl)phenyl)methanol (10)

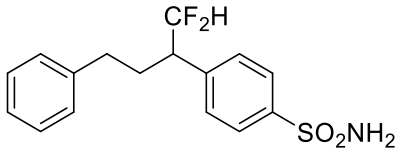
Colorless oil, 40.1 mg, 73% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 3:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.28 (s, 1H), 7.24 (s, 3H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 2H), 5.81 (t, *J* = 56.6 Hz, 1H), 4.71 (s, 2H), 3.05 – 2.93 (m, 1H), δ 2.66 – 2.52 (m, 1H), 2.51 – 2.36 (m, 1H), 2.31 – 2.17 (m, 1H), 2.15 – 2.01 (m, 1H), 1.77 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 140.5, 136.1 (t, *J* = 4.1 Hz), 129.4, 128.6, 128.5, 127.6, 126.2, 118.0 (t, *J* = 244.5 Hz), 65.2, 49.0 (t, *J* = 19.7 Hz), 32.8, 29.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ -112.03 – -129.77 (m).

HRMS (ESI) m/z calcd for $C_{17}H_{19}F_2O[(M+H)^+]$: 277.1399 , found: 277.1393.



4-(1,1-difluoro-4-phenylbutan-2-yl)benzenesulfonamide (11)

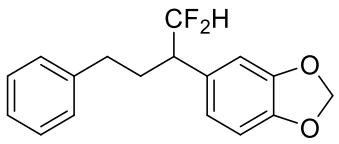
White solid, 55.4 mg, 85% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 2:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 2H), 5.80 (t, *J* = 56.3 Hz, 1H), 5.25 (s, 2H), 3.15 – 2.91 (m, 1H), 2.63 – 2.49 (m, 1H), 2.47 – 2.34 (m, 2H), 2.30 – 2.17 (m, 1H), 2.14 – 1.99 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8 (t, *J* = 3.7 Hz), 141.5, 140.6, 130.0, 128.7, 128.5, 126.9, 126.4, 117.2 (t, *J* = 244.8 Hz), 49.0 (t, *J* = 19.9 Hz), 32.7, 29.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ -119.27 – -121.30 (m).

HRMS (ESI) m/z calcd for $C_{16}H_{18}F_2NO_2S[(M+H)^+]$: 326.1021 , found: 326.1012.



5-(1,1-difluoro-4-phenylbutan-2-yl)benzo[1,3]dioxole (12)

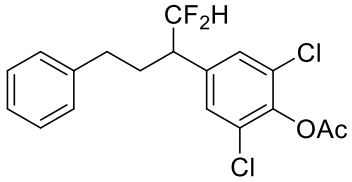
Colorless oil, 50.5 mg, 87% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 2H), 7.22 – 7.13 (m, 1H), 7.10 (d, *J* = 7.3 Hz, 2H), 6.83 – 6.63 (m, 3H), 5.96 (s, 2H), 5.76 (t, *J* = 56.7 Hz, 1H), 2.89 (q, *J* = 14.6 Hz, 1H), 2.68 – 2.52 (m, 1H), 2.49 – 2.37 (m, 1H), 2.31 – 2.11 (m, 1H), 2.08 – 1.93 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 147.2, 141.3, 130.3 (t, *J* = 4.3 Hz), 128.6, 128.6, 126.2, 122.7, 118.0 (t, *J* = 244.6 Hz), 109.0, 108.6, 101.3, 48.9 (t, *J* = 19.8 Hz), 32.8, 29.9 (t, *J* = 3.8 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.39 – -124.93 (m).

HRMS (ESI) m/z calcd for $C_{17}H_{17}F_2O_2[(M+H)^+]$: 291.1191 , found: 291.1192.



2,6-dichloro-4-(1,1-difluoro-4-phenylbutan-2-yl)phenyl acetate (13)

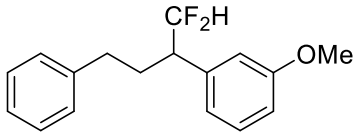
Colorless oil, 60.0 mg, 81% yield, **R**f =0.5 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 2H), 5.81 (t, *J* = 2.5 Hz, 1H), 3.06 – 2.85 (m, 1H), 2.73 – 2.58 (m, 1H), 2.57 – 2.43 (m, 1H), 2.41 (s, 3H), 2.34 – 2.19 (m, 1H), 2.14 – 1.96 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 143.6, 140.5, 136.4 (t, *J* = 3.9 Hz), 129.3, 129.2, 128.7, 128.5, 126.5, 116.9 (t, *J* = 245.2 Hz), 48.4 (t, *J* = 20.1 Hz), 32.8, 29.7, 20.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ -117.65 – -123.69 (m).

HRMS (ESI) m/z calcd for $C_{18}H_{17}Cl_2F_2O_2[(M+H)^+]$: 373.0568 , found: 373.0569.



1-(1,1-difluoro-4-phenylbutan-2-yl)-3-methoxybenzene (14)

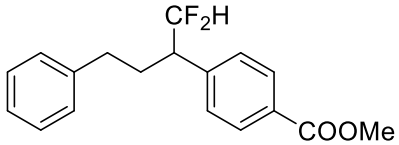
Colorless oil, 42.0 mg, 76% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 50:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (q, *J* = 7.8 Hz, 3H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.3 Hz, 2H), 6.90 – 6.83 (m, 2H), 6.81 (s, 1H), 5.83 (t, *J* = 56.6, 3.9 Hz, 1H), 3.83 (s, 3H), 3.05 – 2.90 (m, 1H), 2.64 – 2.55 (m, 1H), 2.47 (dt, *J* = 13.9, 8.4 Hz, 1H), 2.28 – 2.18 (m, 1H), 2.14 – 2.02 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 141.4, 138.4 (t, *J* = 4.3 Hz), 129.9, 128.6, 128.6, 126.2, 121.4, 118.0 (t, *J* = 244.6 Hz), 115.1, 112.9, 55.4, 49.4 (t, *J* = 19.8 Hz), 32.9, 29.9 (t, *J* = 3.8 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -113.52 – -128.35 (m).

HRMS (ESI) m/z calcd for $C_{17}H_{19}F_2O[(M+H)^+]$: 277.1399 , found: 277.1400.



Methyl 4-(1,1-difluoro-4-phenylbutan-2-yl)benzoate (15)

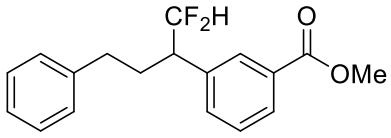
Colorless oil, 52.1 mg, 86% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.23 (m, 2H), 7.24 – 7.16 (m, 1H), 7.12 – 7.05 (m, 2H), 5.84 (td, *J* = 56.4, 3.9 Hz, 1H), 3.93 (s, 3H), 3.14 – 2.97 (m, 1H), 2.69 – 2.52 (m, 1H), 2.50 – 2.37 (m, 1H), 2.34 – 2.20 (m, 1H), 2.20 – 1.96 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 141.9 (t, *J* = 3.8 Hz), 140.9, 130.1, 129.8, 129.3, 128.6, 128.5, 126.3, 117.5 (t, *J* = 244.9 Hz), 52.3, 49.2 (t, *J* = 19.9 Hz), 32.7, 29.8 (t, *J* = 3.9 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -112.87 – -125.16 (m).

HRMS (ESI) m/z calcd for $C_{18}H_{19}F_2O_2$[(M+H)$^+$]: 305.1348 , found: 305.1345.



Methyl 3-(1,1-difluoro-4-phenylbutan-2-yl)benzoate (16)

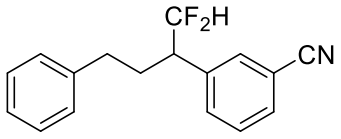
Yellow solid, 53.7 mg, 88% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 24.6 Hz, 2H), 7.42 (d, *J* = 4.5 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 2H), 5.81 (t, *J* = 56.5 Hz, 1H), 3.90 (s, 3H), 3.15 – 2.92 (m, 1H), 2.63 – 2.50 (m, 1H), 2.48 – 2.36 (m, 1H), 2.30 – 2.20 (m, 1H), 2.16 – 2.02 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 141.0, 137.1 (t, *J* = 4.1 Hz), 133.8, 130.8, 130.2, 129.1, 129.0, 128.6, 128.5, 126.3, 117.7 (t, *J* = 244.6 Hz), 52.4, 49.1 (t, *J* = 19.9 Hz), 32.8, 29.9 (t, *J* = 4.0 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -117.23 – -124.12 (m).

HRMS (ESI) m/z calcd for $C_{18}H_{19}F_2O_2$[(M+H)$^+$]: 305.1348 , found: 305.1348.



3-(1,1-difluoro-4-phenylbutan-2-yl)benzonitrile (17)

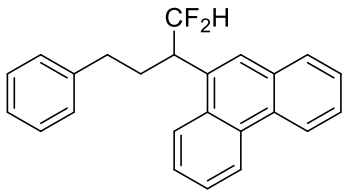
Colorless oil, 39.0 mg, 72% yield, **R**f =0.2 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.50 (s, 1H), 7.45 (s, 2H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.17 (t, *J* = 6.8 Hz, 2H), 7.03 (d, *J* = 7.0 Hz, 1H), 5.79 (t, *J* = 56.2 Hz, 2H), 2.99 (q, *J* = 12.4 Hz, 1H), 2.63 – 2.49 (m, 1H), 2.48 – 2.33 (m, 1H), 2.30 – 2.15 (m, 1H), 2.15 – 1.99 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 138.1 (t, *J* = 3.7 Hz), 133.8, 132.9, 131.6, 129.7, 128.7, 128.4, 126.5, 118.7, 117.1 (t, *J* = 244.9 Hz), 113.1, 48.7 (t, *J* = 19.9 Hz), 32.7, 29.8 (t, *J* = 3.8 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -119.90 – -121.47 (m).

HRMS (ESI) m/z calcd for $C_{17}H_{16}F_2N[(M+H)^+]$: 272.1246 , found: 272.1236.



9-(1,1-difluoro-4-phenylbutan-2-yl)phenanthrene (18)

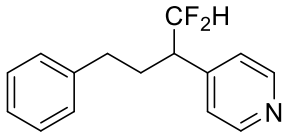
Colorless oil, 50.5 mg, 73% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 50:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 8.1 Hz, 1H), 8.72 (d, *J* = 8.0 Hz, 1H), 7.96 (dd, *J* = 30.9, 7.8 Hz, 2H), 7.83 (s, 1H), 7.73 – 7.62 (m, 4H), 7.28 (s, 1H), 7.21 (dd, *J* = 15.8, 9.1 Hz, 2H), 7.09 (d, *J* = 7.1 Hz, 2H), 6.04 (t, *J* = 56.5 Hz, 1H), 4.14 – 3.94 (m, 1H), 2.74 – 2.40 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 131.4, 131.0, 130.1, 128.8, 128.7, 128.6, 127.1, 127.0, 126.7, 126.2, 123.6, 123.5, 122.6, 118.2 (t, *J* = 245.0 Hz), 42.1, 33.0, 30.2 (t, *J* = 3.7 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -119.25 (dd, *J* = 2034.5, 275.1 Hz).

HRMS (ESI) m/z calcd for $C_{24}H_{21}F_2[(M+H)^+]$: 347.1606 , found: 347.1604.



4-(1,1-difluoro-4-phenylbutan-2-yl)pyridine (19)

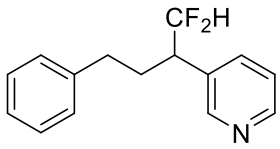
Colorless oil, 27.5 mg, 56% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 5.0 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 6.8 Hz, 3H), 7.09 (d, *J* = 7.5 Hz, 2H), 5.85 (td, *J* = 56.2, 3.6 Hz, 1H), 3.11 – 2.84 (m, 1H), 2.67 – 2.54 (m, 1H), 2.53 – 2.39 (m, 1H), 2.38 – 2.20 (m, 1H), 2.19 – 1.98 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 145.7 (t, *J* = 3.7 Hz), 140.5, 128.7, 128.5, 126.5, 124.5, 117.0 (t, *J* = 245.1 Hz), 48.7 (t, *J* = 20.1 Hz), 32.7, 29.5 (t, *J* = 3.9 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -118.45 – -122.22 (m).

HRMS (ESI) m/z calcd for $C_{15}H_{16}F_2N[(M+H)^+]$: 248.1246 , found: 248.1247.



3-(1,1-difluoro-4-phenylbutan-2-yl)pyridine (20)

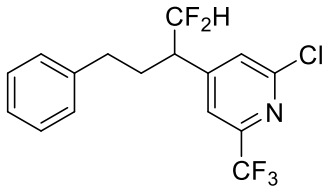
Colorless oil, 30.0 mg, 61% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 38.4 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.31 (dd, *J* = 15.6, 7.3 Hz, 3H), 7.15 (dd, *J* = 49.5, 7.1 Hz, 3H), 5.85 (t, *J* = 56.3 Hz, 1H), 3.02 (q, *J* = 14.2 Hz, 1H), 2.61 (dt, *J* = 13.6, 6.8 Hz, 1H), 2.46 (dt, *J* = 14.5, 8.3 Hz, 1H), 2.34 – 2.24 (m, 1H), 2.12 (q, *J* = 13.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 149.4, 140.6, 136.4, 132.1 (t, *J* = 3.5 Hz), 128.7, 128.5, 126.4, 123.8, 117.3 (t, *J* = 244.8 Hz), 46.7 (t, *J* = 20.1 Hz), 32.7, 29.6 (t, *J* = 3.6 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -117.91 – -124.18 (m).

HRMS (ESI) m/z calcd for $C_{15}H_{16}F_2N[(M+H)^+]$: 248.1246 , found: 248.1248.



2-chloro-4-(1,1-difluoro-4-phenylbutan-2-yl)-6-(trifluoromethyl)pyridine (21)

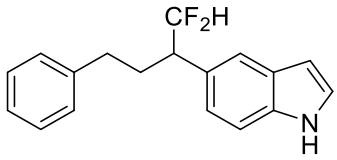
Colorless oil, 37.0 mg, 53% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.41 (s, 1H), 7.22 (d, *J* = 7.7 Hz, 2H), 7.12 (dd, *J* = 31.6, 7.4 Hz, 3H), 6.10 (td, *J* = 56.4, 5.9 Hz, 1H), 3.48 – 3.32 (m, 1H), 2.72 – 2.54 (m, 2H), 2.48 – 2.27 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9 (d, *J* = 7.3 Hz), 149.6 (q, *J* = 35.0 Hz), 146.8, 140.6, 128.6, 128.5, 126.5, 125.4, 121.2 (q, *J* = 163.5 Hz), 117.8 (t, J = 227.1 Hz), 117.3, 51.4 (t, *J* = 20.4 Hz), 33.0, 29.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -67.99, -115.46 – -125.58 (m).

HRMS (EI) m/z calcd for $C_{16}H_{13}ClF_5N(M)^+$: 349.0651, found: 349.0648.



5-(1,1-difluoro-4-phenylbutan-2-yl)-1H-indole (22)

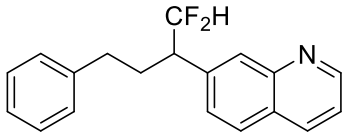
Green solid, 38.4 mg, 67% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.55 (s, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.18 – 7.08 (m, 3H), 6.57 (s, 1H), 5.88 (td, *J* = 56.8, 3.3 Hz, 1H), 3.21 – 3.01 (m, 1H), 2.67 – 2.56 (m, 1H), 2.54 – 2.41 (m, 1H), 2.43 – 2.22 (m, 1H), 2.23 – 2.05 (m, 1H), 1.66 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 135.4, 128.6, 128.5, 128.3, 128.0 (t, *J* = 4.0 Hz), 126.1, 124.9, 123.0, 121.2, 118.6 (t, *J* = 244.5 Hz), 111.4, 102.7, 49.4 (t, *J* = 19.5 Hz), 33.0, 30.1 (t, *J* = 3.7 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.38 – -123.83 (m).

HRMS (ESI) m/z calcd for $C_{18}H_{18}F_2N[(M+H)^+]$: 286.1402 , found: 286.1393.



7-(1,1-difluoro-4-phenylbutan-2-yl)quinoline (23)

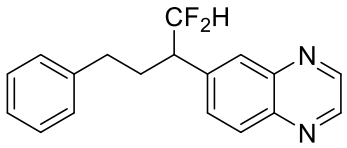
White solid, 44.5 mg, 75% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 4:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.67 (s, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.39 (dd, *J* = 8.2, 4.1 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 2H), 5.89 (td, *J* = 56.5, 3.6 Hz, 1H), 3.25 – 3.10 (m, 1H), 2.58 (td, *J* = 9.0, 4.6 Hz, 1H), 2.52 – 2.42 (m, 1H), 2.37 – 2.27 (m, 1H), 2.24 – 2.16 (m, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 147.9, 141.0, 136.1, 135.0 (t, *J* = 44.4 Hz), 130.3, 130.1, 128.6, 128.5, 128.4, 128.3, 126.3, 121.6, 117.8 (t, *J* = 244.8 Hz), 49.2 (t, *J* = 19.9 Hz), 32.9, 32.0, 29.2 (t, *J* = 4.0 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.38 – -123.83 (m).

HRMS (ESI) m/z calcd for $C_{19}H_{18}F_2N[(M+H)^+]$: 298.1402 , found: 298.1399.



6-(1,1-difluoro-4-phenylbutan-2-yl)quinoxaline (24)

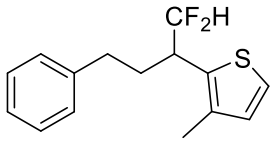
White solid, 40.0 mg, 67% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 2H), 8.15 (d, *J* = 8.6 Hz, 1H), 8.03 (s, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.29 (d, *J* = 7.1 Hz, 2H), 7.20 (t, *J* = 7.1 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 2H), 5.95 (t, *J* = 56.3 Hz, 1H), 3.28 (q, *J* = 12.7 Hz, 1H), 2.67 – 2.58 (m, 1H), 2.55 – 2.46 (m, 1H), 2.40 – 2.23 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 145.3, 143.1, 142.6, 140.8, 139.0 (t, *J* = 3.7 Hz), 131.2, 130.0, 130.0, 128.7, 128.5, 126.4, 117.5 (t, *J* = 245.0 Hz), 49.2 (t, *J* = 19.9 Hz), 32.8, 30.0 (t, *J* = 3.9 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -117.29 – -123.24 (m).

HRMS (ESI) m/z calcd for $C_{18}H_{17}F_2N_2[(M+H)^+]$: 299.1355 , found: 299.1350.



2-(1,1-difluoro-4-phenylbutan-2-yl)-3-methylthiophene (25)

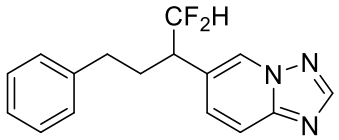
Colorless oil, 30.7 mg, 58% yield, **R**f =0.3 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 6.7 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.94 – 6.82 (m, 1H), 5.76 (t, *J* = 56.7 Hz, 1H), 3.37 (q, *J* = 13.2, 11.8 Hz, 1H), 2.75 – 2.65 (m, 1H), 2.57 – 2.47 (m, 1H), 2.31 – 2.22 (m, 1H), 2.12 (s, 3H), 2.07 – 1.97 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 136.6, 132.7 (t, *J* = 4.4 Hz), 130.1, 128.6, 126.3, 123.8, 117.5 (t, *J* = 245.4 Hz), 42.4 (t, *J* = 20.9 Hz), 32.8, 31.6 (t, *J* = 3.5 Hz), 14.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.90 – -122.43 (m).

HRMS (ESI) m/z calcd for $C_{15}H_{17}F_2S[(M+H)^+]$: 267.1014 , found: 267.1007.



6-(1,1-difluoro-4-phenylbutan-2-yl)-[1,2,4]triazolo[1,5-a]pyridine (26)

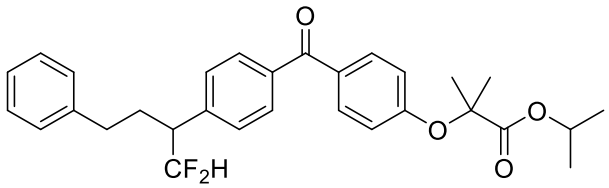
Yellow oil, 35.5 mg, 62% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 3:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.37 (s, 1H), 7.79 (d, *J* = 9.2 Hz, 1H), 7.46 (d, *J* = 9.2 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 2H), 5.90 (t, *J* = 56.1 Hz, 1H), 3.08 (q, *J* = 14.1 Hz, 1H), 2.79 – 2.62 (m, 1H), 2.61 – 2.45 (m, 1H), 2.42 – 2.27 (m, 1H), 2.25 – 1.97 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 150.2, 140.2, 130.8, 128.8, 128.6, 128.4, 126.6, 123.1 (t, *J* = 3.7 Hz), 117.0, 116.8 (t, *J* = 245.1 Hz), 46.2 (t, *J* = 20.3 Hz), 32.7, 29.6 (t, *J* = 3.6 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -118.92 – -122.73 (m).

HRMS (ESI) m/z calcd for $C_{16}H_{16}F_2N_3[(M+H)^+]$: 288.1307 , found: 288.1305.



Isopropyl 2-(4-(4-(1,1-difluoro-4-phenylbutan-2-yl)benzoyl)phenoxy)-2-methylpropanoate (27)

Colorless oil, 85.0 mg, 86% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 5:1, v/v).

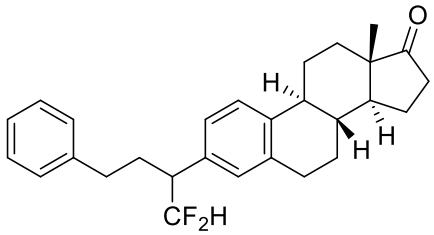
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, *J* = 7.1 Hz, 4H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.28 (s, 1H), 7.24 (s, 1H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 5.85 (t, *J* = 56.4 Hz, 1H), 5.14 – 5.02 (m, 1H), 3.08 (d, *J* = 13.8 Hz, 1H),

2.58 (d, *J* = 6.5 Hz, 1H), 2.45 (dt, *J* = 14.3, 8.4 Hz, 1H), 2.36 – 2.06 (m, 2H), 1.66 (s, 6H), 1.19 (d, *J* = 6.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1, 173.2, 159.7, 140.9, 137.6, 132.1, 130.5, 130.3, 129.1, 128.6, 128.5, 126.3, 117.5 (t, *J* = 244.7 Hz), 117.2, 79.4, 69.4, 49.2 (t, *J* = 19.8 Hz), 32.8, 29.8, 25.4, 21.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -117.34 – -123.56 (m).

HRMS (ESI) m/z calcd for $C_{30}H_{33}F_2O_4[(M+H)^+]$: 495.2342 , found: 495.2341.



(8R,9S,13S,14S)-3-(1,1-difluoro-4-phenylbutan-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta^{2}phenanthren-17-one (28)

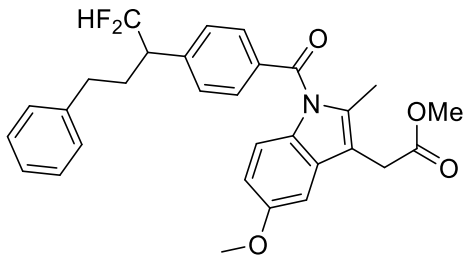
Colorless oil, 61.6 mg, 73% yield, **R**f =0.5 (petroleum ether: ethyl acetate, 10:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.6 Hz, 3H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.08 – 7.03 (m, 1H), 7.00 (s, 1H), 5.83 (td, *J* = 56.7, 3.9 Hz, 1H), 2.95 (dd, *J* = 9.3, 4.4 Hz, 3H), 2.67 – 2.44 (m, 4H), 2.35 (dd, *J* = 10.9, 4.0 Hz, 1H), 2.29 – 2.16 (m, 2H), 2.16 – 2.03 (m, 4H), 2.03 – 1.96 (m, 1H), 1.74 – 1.59 (m, 3H), 1.59 – 1.42 (m, 4H), 0.94 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 139.2, 136.9, 134.1, 129.7, 129.6, 128.5, 126.4, 126.3, 126.1, 125.8, 125.8, 118.1 (t, *J* = 244.4 Hz), 50.6, 48.8 (t, *J* = 19.6 Hz), 48.1, 44.4, 38.1, 35.9, 32.9, 31.7, 29.8 (q, *J* = 3.5 Hz), 29.5 (d, *J* = 3.6 Hz), 26.6, 25.7, 21.7, 13.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ -108.70 – -136.24 (m).

HRMS (ESI) m/z calcd for $C_{28}H_{33}F_2O[(M+H)^+]$: 423.2494 , found: 423.2489.



Methyl 2-(1-(4-(1,1-difluoro-4-phenylbutan-2-yl)benzoyl)-5-methoxy-2-methyl -1H-indol-3-yl)acetate (29)

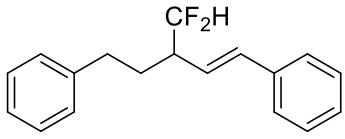
Yellow oil, 77.4 mg, 77% yield, **R**f =0.2 (petroleum ether: ethyl acetate, 10:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 2H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.62 (dd, *J* = 9.0, 2.4 Hz, 1H), 5.84 (td, *J* = 56.3, 3.7 Hz, 1H), 3.79 (s, 3H), 3.66 (s, 3H), 3.63 (s, 2H), 3.06 (m, 1H), 2.56 (m, 1H), 2.47 – 2.40 (m, 1H), 2.33 (s, 3H), 2.29 – 2.20 (m, 1H), 2.16 – 2.04 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 169.2, 156.1, 141.9 (t, *J* = 3.9 Hz), 140.8, 136.1, 135.2, 131.1, 130.7, 130.2, 129.6, 128.6, 128.6, 126.4, 117.4 (t, *J* = 245.0 Hz), 115.1, 112.5, 111.6, 101.4, 55.8, 52.3, 49.2 (t, *J* = 19.9 Hz), 30.3, 29.9 (t, *J* = 3.6 Hz), 13.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -113.93 – -126.81 (m).

HRMS (ESI) m/z calcd for $C_{30}H_{30}F_2NO_4[(M+H)^+]$: 506.2138, found: 506.2137.



(*E*)-(3-(difluoromethyl)pent-1-ene-1,5-diyl)dibenzene (30)

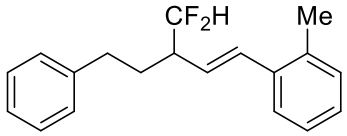
Colorless oil, 48.0 mg, 88% yield, **R**f =0.4 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 8.2 Hz, 3H), 7.29 (d, *J* = 5.7 Hz, 2H), 7.20 (t, *J* = 8.7 Hz, 3H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.04 (dd, *J* = 15.9, 9.3 Hz, 1H), 5.75 (t, *J* = 56.7 Hz, 1H), 2.85 – 2.74 (m, 1H), 2.69 – 2.53 (m, 2H), 2.17 – 1.96 (m, 1H), 1.94 – 1.68 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 136.7, 135.2, 128.8, 128.6, 128.6, 128.0, 126.5, 126.2, 124.8 (t, *J* = 4.8 Hz), 117.8 (t, *J* = 244.1 Hz), 47.0 (t, *J* = 19.8 Hz), 32.9, 29.2 (t, *J* = 3.9 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -119.17 – -124.20 (m).

HRMS (ESI) m/z calcd for $C_{18}H_{19}F_2[(M+H)^+]$: 273.1450 , found: 273.1443.



(*E*)-1-(3-(difluoromethyl)-5-phenylpent-1-en-1-yl)-2-methylbenzene (31)

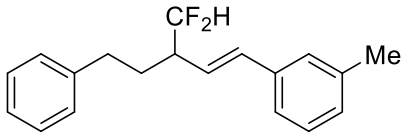
Colorless oil, 42.2 mg, 74% yield, **R**f =0.3 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 5.2, 3.6 Hz, 1H), 7.31 (dd, *J* = 8.5, 6.2 Hz, 2H), 7.26 – 7.15 (m, 6H), 6.76 (d, *J* = 15.7 Hz, 1H), 5.92 (dd, *J* = 15.9, 9.2 Hz, 1H), 5.76 (t, *J* = 56.7 Hz, 1H), 2.90 – 2.77 (m, 1H), 2.73 – 2.56 (m, 2H), 2.38 (s, 3H), 2.14 – 1.98 (m, 1H), 1.94 – 1.73 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 136.0, 135.5, 133.3, 130.5, 128.6, 128.6, 127.9, 126.3, 126.2, 125.9, 117.8 (t, *J* = 244.0 Hz), 47.2 (t, *J* = 19.7 Hz), 32.8, 29.2, 20.0.

^{19}F NMR (377 MHz, $CDCl_3$) δ -119.22 – -124.71 (m).

HRMS (CI, CH_4) m/z calcd for $C_{19}H_{19}F_2[(M-H)^+]$: 285.1455 , found: 285.1451.



(*E*)-1-(3-(difluoromethyl)-5-phenylpent-1-en-1-yl)-3-methylbenzene (32)

Colorless oil, 43.5 mg, 76% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 100:1, v/v).

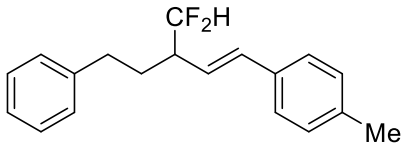
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.16 (m, 6H), 7.12 – 7.06 (m, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.03 (dd, *J* = 15.9, 9.3 Hz, 1H), 5.75 (td, *J* =

56.7, 3.4 Hz, 1H), 2.87 – 2.73 (m, 1H), 2.67 – 2.52 (m, 2H), 2.37 (s, 3H), 2.15 – 1.98 (m, 1H), 1.96 – 1.73 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 138.4, 136.7, 135.3, 128.8, 128.7, 128.6, 128.6, 127.2, 126.2, 124.6 (t, *J* = 4.9 Hz), 123.7, 117.8 (t, *J* = 244.0 Hz), 47.0 (t, *J* = 19.7 Hz), 32.9, 29.2, 21.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -119.24 – -125.89 (m).

HRMS (ESI) m/z calcd for $C_{19}H_{21}F_2[(M+H)^+]$: 287.1606 , found: 287.1612.



(*E*)-1-(3-(difluoromethyl)-5-phenylpent-1-en-1-yl)-4-methylbenzene (33)

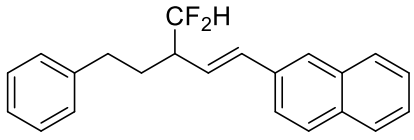
Colorless oil, 47.7 mg, 83% yield, **R**f =0.3 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 4H), 7.19 – 7.07 (m, 5H), 6.46 (d, *J* = 15.9 Hz, 1H), 5.93 (dd, *J* = 15.8, 9.3 Hz, 1H), 5.69 (t, *J* = 56.7 Hz, 1H), 2.82 – 2.67 (m, 1H), 2.54 (dt, *J* = 14.7, 8.4 Hz, 2H), 2.30 (s, 3H), 2.07 – 1.92 (m, 1H), 1.87 – 1.68 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 137.9, 135.1, 134.0, 129.4, 128.6, 126.4, 126.2, 123.8 (t, *J* = 5.0 Hz), 117.8 (t, *J* = 244.1 Hz), 47.0 (t, *J* = 19.7 Hz), 32.9, 29.2 (t, *J* = 3.7 Hz), 21.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.16 – -123.47 (m).

HRMS (CI, CH_4) m/z calcd for $C_{19}H_{19}F_2[(M-H)^+]$: 285.1455 , found: 285.1450.



(*E*)-2-(3-(difluoromethyl)-5-phenylpent-1-en-1-yl)naphthalene (34)

Colorless oil, 50.7 mg,79% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 50:1, v/v).

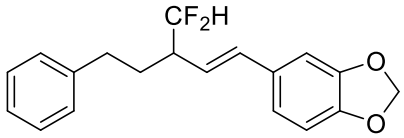
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.71 (m, 4H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.54 – 7.42 (m, 2H), 7.31 (d, *J* = 7.0 Hz, 2H), 7.21 (d, *J* = 7.1 Hz, 3H), 6.71 (d, *J* = 15.9 Hz,

1H), 6.18 (dd, *J* = 15.7, 9.2 Hz, 1H), 5.80 (t, *J* = 56.7 Hz, 1H), 2.92 – 2.78 (m, 1H), 2.77 – 2.56 (m, 2H), 2.21 – 2.04 (m, 1H), 1.99 – 1.78 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 135.3, 134.2, 133.7, 133.2, 128.6, 128.6, 128.4, 128.1, 127.8, 126.52, 126.50, 126.2, 126.1, 125.2 (t, *J* = 4.7 Hz), 123.6, 117.8 (t, *J* = 244.1 Hz), 47.1 (t, *J* = 19.8 Hz), 32.9, 29.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -117.71 – -125.02 (m).

HRMS (ESI) m/z calcd for $C_{22}H_{21}F_2[(M+H)^+]$: 323.1606 , found: 323.1615.



(*E*)-5-(3-(difluoromethyl)-5-phenylpent-1-en-1-yl)benzo[1,3]dioxole (35)

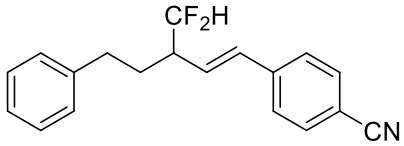
Colorless oil, 57.8 mg, 91% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 50:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 3H), 6.96 (d, *J* = 2.5 Hz, 1H), 6.87 – 6.72 (m, 2H), 6.44 (d, *J* = 15.8 Hz, 1H), 5.97 (s, 2H), 5.94 – 5.83 (m, 1H), 5.74 (td, *J* = 56.7, 3.4 Hz, 1H), 2.84 – 2.72 (m, 1H), 2.67 – 2.51 (m, 2H), 2.13 – 1.98 (m, 1H), 1.88 – 1.73 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 147.5, 141.4, 134.7, 131.2, 128.6, 128.6, 126.2, 122.9 (t, *J* = 4.8 Hz), 121.2, 117.8 (t, *J* = 244.0 Hz), 108.4, 105.8, 101.3, 46.9 (t, *J* = 19.8 Hz), 32.9, 29.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.18 – -123.18 (m).

HRMS (ESI) m/z calcd for $C_{19}H_{19}F_2O_2[(M+H)^+]$: 317.1348 , found: 317.1353.



(*E*)-4-(3-(difluoromethyl)-5-phenylpent-1-en-1-yl)benzonitrile (36)

Colorless oil, 41.0 mg, 69% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 30:1, v/v).

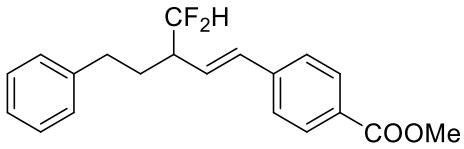
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 2H), 6.54 (d, *J* =

16.0 Hz, 1H), 6.18 (dd, *J* = 16.0, 9.2 Hz, 1H), 5.77 (td, *J* = 56.5, 3.3 Hz, 1H), 2.81 – 2.72 (m, 1H), 2.71 – 2.55 (m, 2H), 2.13 – 2.02 (m, 1H), 1.89 – 1.80 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 141.0, 133.7, 132.6, 128.9 (t, *J* = 4.3 Hz), 128.7, 128.5, 127.0, 126.4, 119.0, 117.3 (t, *J* = 243.8 Hz), 111.2, 47.0 (t, *J* = 19.8 Hz), 32.9, 29.3 (t, *J* = 3.7 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -118.07 – -125.59 (m).

HRMS (ESI) m/z calcd for $C_{19}H_{18}F_2N[(M+H)^+]$: 298.1402 , found: 298.1402.



Methyl (*E*)-4-(3-(difluoromethyl)-5-phenylpent-1-en-1-yl)benzoate (37)

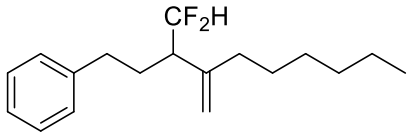
Colorless oil, 53.9 mg, 82% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 7.1 Hz, 3H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.17 (dd, *J* = 15.9, 9.2 Hz, 1H), 5.77 (t, J = 56.5, 3.3 Hz, 1H), 3.92 (s, 3H), 2.82 – 2.72 (m, 1H), 2.72 – 2.54 (m, 2H), 2.13 – 2.01 (m, 1H), 1.92 – 1.78 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 141.2, 141.1, 134.4, 130.1, 129.4, 128.7, 128.5, 127.6 (t, *J* = 4.9 Hz), 126.4, 126.3, 117.5 (t, *J* = 244.0 Hz), 52.3, 47.0 (t, *J* = 19.8 Hz), 32.9, 29.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -119.77 – -123.92 (m).

HRMS (ESI) m/z calcd for $C_{20}H_{21}F_2O_2[(M+H)^+]$: 331.1504 , found: 331.1503.



(3-(difluoromethyl)-4-methylenedecyl)benzene (38)

Colorless oil,44.1 mg, 79% yield, **R**f =0.5 (petroleum ether).

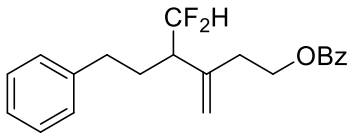
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.14 (m, 3H), 5.69 (td, *J* = 56.8, 4.7 Hz, 1H), 5.07 (s, 1H), 4.98 (s, 1H), 2.68 (dt, *J* = 10.3, 4.6 Hz, 1H), 2.60

– 2.49 (m, 1H), 2.52 – 2.40 (m, 1H), 2.08 – 1.94 (m, 3H), 1.88 – 1.78 (m, 1H), 1.51 – 1.39 (m, 2H), 1.36 – 1.27 (m, 6H), 0.94 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4 (t, *J* = 3.8 Hz), 141.7, 128.6, 128.5, 126.1, 118.3 (t, *J* = 244.0 Hz), 113.4, 49.5 (t, *J* = 19.1 Hz), 35.6, 33.1, 31.9, 29.2, 29.0 (t, *J* = 4.2 Hz), 27.5, 22.8, 14.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -110.60 – -128.55 (m).

HRMS (CI, CH_4) m/z calcd for $C_{18}H_{25}F_2[(M-H)^+]$: 279.1930 , found: 279.1921.



4-(difluoromethyl)-3-methylene-6-phenylhexyl benzoate (39)

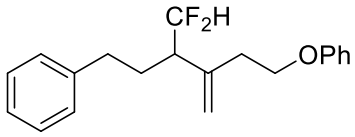
Colorless oil, 55.9 mg, 81% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.21 (m, 2H), 7.14 (dd, *J* = 19.4, 7.2 Hz, 3H), δ 5.70 (td, *J* = 56.6, 4.4 Hz, 1H), 5.20 (s, 1H), 5.10 (s, 1H), 4.44 (td, *J* = 6.8, 1.6 Hz, 2H), 2.75 – 2.63 (m, 1H), 2.60 – 2.43 (m, 4H), 2.08 – 1.93 (m, 1H), 1.92 – 1.76 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 141.3, 141.0 (t, *J* = 3.7 Hz), 133.1, 130.3, 129.7, 128.6, 128.5, 128.4, 126.2, 118.0 (t, *J* = 244.7 Hz), 116.2, 62.8, 49.4 (t, *J* = 19.5 Hz), 34.2, 32.9, 28.8 (t, *J* = 4.0 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.22 – -123.60 (m).

HRMS (ESI) m/z calcd for $C_{21}H_{23}F_2O_2[(M+H)^+]$: 345.1661 , found: 345.1669.



((4-(difluoromethyl)-3-methylene-6-phenylhexyl)oxy)benzene (40)

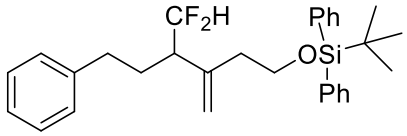
Colorless oil, 42.2 mg, 67% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 4H), 7.22 – 7.14 (m, 3H), 7.01 – 6.93 (m, 1H), 6.93 – 6.87 (m, 2H), 5.74 (td, *J* = 56.6, 4.4 Hz, 1H), 5.23 (s, 1H), 5.13 (s, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 2.81 – 2.66 (m, 1H), 2.67 – 2.48 (m, 4H), 2.12 – 1.96 (m, 1H), 1.95 – 1.80 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 141.6 (t, *J* = 3.8 Hz), 141.5, 129.6, 128.6, 128.5, 126.2, 121.0, 118.1 (t, *J* = 244.5 Hz), 116.0, 114.6, 66.2, 49.5 (t, *J* = 19.3 Hz), 34.8, 32.9, 28.8 (t, *J* = 4.1 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.22 – -123.60 (m).

HRMS (ESI) m/z calcd for $C_{20}H_{23}F_2O[(M+H)^+]$: 317.1712 , found: 317.1713.



Tert-butyl((4-(difluoromethyl)-3-methylene-6-phenylhexyl)oxy)diphenylsilane (41)

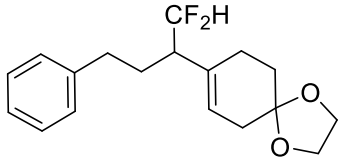
Colorless oil, 80.0 mg, 84% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 50:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 6.5 Hz, 4H), 7.44 – 7.35 (m, 6H), 7.30 – 7.24 (m, 2H), 7.22 – 7.16 (m, 1H), 7.15 – 7.11 (m, 2H), 5.62 (td, *J* = 56.7, 4.5 Hz, 1H), 5.08 (s, 1H), 5.02 (s, 1H), 3.79 (t, *J* = 6.9 Hz, 2H), 2.72 – 2.59 (m, 1H), 2.54 – 2.40 (m, 2H), 2.36 – 2.22 (m, 2H), 2.00 – 1.89 (m, 1H), 1.84 – 1.73 (m, 1H), 1.06 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9 (t, *J* = 4.0 Hz), 141.6, 135.7, 133.9, 129.8, 129.7, 128.5, 128.5, 127.8, 127.7, 126.1, 118.0 (t, *J* = 244.3 Hz), 115.7, 62.6, 49.4 (t, *J* = 19.2 Hz), 38.2, 33.0, 28.7, 27.0, 19.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -109.76 – -131.26 (m).

HRMS (ESI) m/z calcd for $C_{30}H_{37}F_2OSi[(M+H)^+]$: 479.2576 , found: 479.2583.



8-(1,1-difluoro-4-phenylbutan-2-yl)-1,4-dioxaspiro[4.5]dec-7-ene (42)

Colorless oil, 43.7 mg, 71% yield, **R**f =0.3 (petroleum ether).

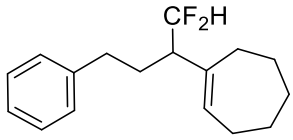
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.23 – 7.14 (m, 3H), 5.70 (td, *J* = 56.8, 4.3 Hz, 1H), 5.53 – 5.50 (m, 1H), 3.99 (d, *J* = 1.5 Hz, 4H), 2.71 – 2.63 (m, 1H), 2.57 – 2.40 (m, 2H), 2.36 – 2.31 (m, 2H), 2.28 – 2.15 (m, 2H), 1.99 – 1.91 (m, 1H),

1.87 – 1.74 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 132.7 (t, *J* = 4.2 Hz), 128.6, 128.5, 126.1, 124.6, 118.1 (t, *J* = 244.6 Hz), 107.8, 64.6, 64.6, 50.1 (t, *J* = 19.4 Hz), 36.0, 33.0, 31.2, 27.5 (t, *J* = 3.9 Hz), 25.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -111.38 – -130.41 (m).

HRMS (ESI) m/z calcd for $C_{18}H_{23}F_2O_2[(M+H)^+]$: 309.1661 , found: 309.1661.



1-(1,1-difluoro-4-phenylbutan-2-yl)cyclohept-1-ene (43)

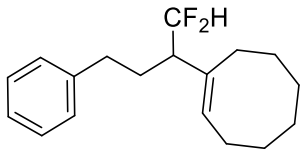
Colorless oil, 47.8 mg, 90% yield, **R**f =0.5 (petroleum ether: ethyl acetate, 100:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.8 Hz, 2H), 7.31 – 7.23 (m, 3H), 5.90 – 5.83 (m, 1H), 5.74 (tt, *J* = 56.9, 4.0 Hz, 1H), 2.81 – 2.72 (m, 1H), 2.64 – 2.55 (m, 1H), 2.54 – 2.41 (m, 1H), 2.31 – 2.21 (m, 4H), 2.05 – 1.95 (m, 1H), 1.88 – 1.84 (m, 2H), 1.64 – 1.54 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 139.2 (t, *J* = 4.0 Hz), 133.1, 128.4, 128.4, 126.0, 118.3 (t, *J* = 244.1 Hz), 52.7 (t, *J* = 19.1 Hz), 33.2, 32.7, 29.8, 28.5, 27.4 (t, *J* = 3.8 Hz), 26.9, 26.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -113.51 – -127.91 (m).

HRMS (CI, CH_4) m/z calcd for $C_{17}H_{21}F_2[(M-H)^+]$: 263.1606 , found: 263.1603.



(*E*)-1-(1,1-difluoro-4-phenylbutan-2-yl)cyclooct-1-ene (44)

Colorless oil, 45.5 mg, 82% yield, **R**f =0.4 (petroleum ether).

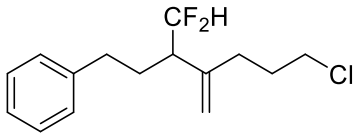
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 5.68 (td, *J* = 56.9, 4.7 Hz, 1H), 5.57 – 5.53 (m, 1H), 2.73 – 2.65 (m, 1H), 2.57 – 2.48 (m, 1H), 2.48

– 2.37 (m, 1H), 2.26 – 2.13 (m, 4H), 2.00 – 1.92 (m, 1H), 1.85 – 1.76 (m, 1H), 1.57 – 1.42 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 136.0 (t, *J* = 4.0 Hz), 130.2, 128.5, 126.1, 118.4 (t, *J* = 244.1 Hz), 51.5 (t, *J* = 19.1 Hz), 33.4, 29.4, 29.0, 28.4 (t, *J* = 4.0 Hz), 28.0, 26.4, 26.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -112.87 – -128.14 (m).

HRMS (ESI) m/z calcd for $C_{18}H_{25}F_2[(M+H)^+]$: 279.1919 , found: 279.1916.



(7-chloro-3-(difluoromethyl)-4-methyleneheptyl)benzene (45)

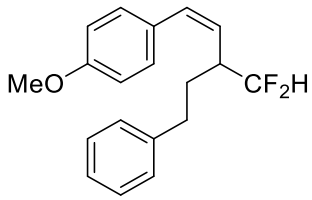
Yellow oil, 39.4 mg, 72% yield, **R**f =0.3 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.14 (m, 3H), 5.70 (td, *J* = 56.7, 4.7 Hz, 1H), 5.07 (d, *J* = 23.4 Hz, 1H), 3.57 (t, *J* = 6.4 Hz, 1H), 2.68 (td, *J* = 10.2, 9.7, 5.0 Hz, 1H), 2.62 – 2.38 (m, 2H), 2.25 – 2.18 (m, 1H), 2.08 – 1.71 (m, 4H), 1.72 – 1.51 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6 (t, *J* = 3.6 Hz), 141.3, 128.5, 128.4, 126.1, 118.0 (t, *J* = 244.3 Hz), 114.3, 49.3 (t, *J* = 19.5 Hz), 44.4, 32.9, 32.3, 30.2, 29.0 (t, *J* = 4.1 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -103.87 – -128.72 (m).

HRMS (EI) m/z calcd for $C_{15}H_{19}ClF_2(M)^+$: 272.1138, found: 272.1136.



(*Z*)-1-(3-(difluoromethyl)-5-phenylpent-1-en-1-yl)-4-methoxybenzene (46)

Colorless oil, 50.5 mg, 84% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 50:1, v/v).

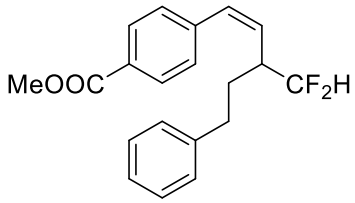
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.11 (m, 5H), 7.02 (d, *J* = 6.4 Hz, 2H), 6.92 – 6.83 (m, 2H), 6.77 (d, *J* = 11.6 Hz, 1H), 5.76 (td, *J* = 56.8, 3.6 Hz, 1H), 5.45 (t, *J* =

11.2 Hz, 1H), 3.83 (s, 3H), 3.25 – 3.05 (m, 1H), 2.82 – 2.63 (m, 1H), 2.52 – 2.38 (m, 1H), 2.04 – 1.89 (m, 1H), 1.78 – 1.66 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 141.4, 134.0, 129.9, 129.3, 128.5, 128.4, 126.0, 125.9 (t, *J* = 4.7 Hz), 118.0 (t, *J* = 243.9 Hz), 113.9, 55.4, 41.4 (t, *J* = 19.6 Hz), 32.7, 30.6 (t, *J* = 3.8 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.64 – -121.37 (m).

HRMS (ESI) m/z calcd for $C_{19}H_{21}F_2O[(M+H)^+]$: 303.1555 , found: 303.1557.



Methyl (*Z*)-4-(3-(difluoromethyl)-5-phenylpent-1-en-1-yl)benzoate (47)

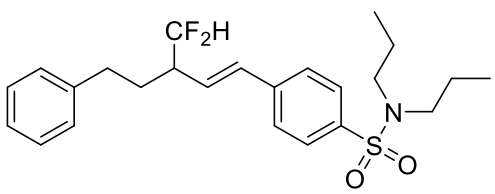
Colorless oil, 52.1 mg, 79% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 4H), 7.19 – 7.12 (m, 3H), 6.98 (dd, *J* = 7.6, 1.9 Hz, 2H), 6.84 (d, *J* = 11.7 Hz, 1H), 5.74 (td, *J* = 56.7, 3.4 Hz, 1H), 5.62 (d, *J* = 11.5 Hz, 1H), 3.93 (s, 3H), 3.14 – 3.00 (m, 1H), 2.72 – 2.62 (m, 1H), 2.46 – 2.36 (m, 1H), 2.00 – 1.89 (m, 1H), 1.77 – 1.66 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 141.4, 141.0, 133.7, 129.8, 129.0, 128.9 (t, *J* = 4.7 Hz), 128.6, 128.5, 128.5, 126.2, 117.7 (t, *J* = 243.9 Hz), 52.3, 41.6 (t, *J* = 19.6 Hz), 32.7, 30.5 (t, *J* = 3.9 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -114.50 – -128.91 (m).

HRMS (ESI) m/z calcd for $C_{20}H_{21}F_2O_2[(M+H)^+]$: 331.1504 , found: 331.1508.



(*E*)-4-(3-(difluoromethyl)-5-phenylpent-1-en-1-yl)-N,N-dipropylbenzenesulfonamide (48)

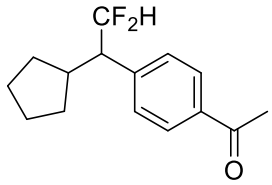
Yellow oil, 59.0 mg, 68% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.20 (dd, *J* = 16.6, 7.2 Hz, 3H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.17 (dd, *J* = 16.0, 9.2 Hz, 1H), 5.77 (td, *J* = 56.5, 3.3 Hz, 1H), 3.12 – 3.03 (m, 4H), 2.81 – 2.73 (m, 1H), 2.70 – 2.56 (m, 2H), 2.12 – 2.04 (m, 1H), 1.89 – 1.81 (m, 1H), 1.57 (dt, *J* = 15.2, 7.4 Hz, 6H), 1.25 (s, 2H), 0.88 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 140.4, 139.0, 133.6, 128.6, 128.4, 128.0, 127.5, 126.8, 126.2, 117.3 (t, *J* = 244.0 Hz), 50.0, 46.9 (t, *J* = 19.8 Hz), 32.8, 29.7, 29.2, 22.0, 11.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.05 – -122.87 (m).

HRMS (ESI) m/z calcd for $C_{24}H_{32}F_2NO_2S[(M+H)^+]$: 436.2117 , found: 436.2116.



1-(4-(1-cyclopentyl-2,2-difluoroethyl)phenyl)ethan-1-one (49)

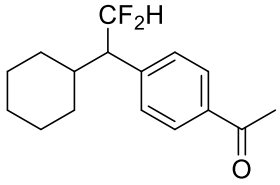
Colorless oil, 44.9 mg, 89% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 5.99 (td, *J* = 56.2, 3.0 Hz, 1H), 2.89 – 2.77 (m, 1H), 2.61 – 2.58 (m, 3H), 2.37 – 2.27 (m, 1H), 2.11 – 2.02 (m, 1H), 1.75 – 1.69 (m, 1H), 1.61 – 1.40 (m, 4H), 1.38 – 1.29 (m, 1H), 1.01 – 0.90 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 142.9, 136.4, 129.7, 128.5, 117.3 (t, *J* = 244.1 Hz), 55.5 (t, *J* = 18.6 Hz), 40.5, 40.5, 31.9, 31.4, 26.7, 25.3, 24.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -115.58 – -126.44 (m).

HRMS (ESI) m/z calcd for $C_{15}H_{19}F_2O[(M+H)^+]$: 253.1399 , found: 253.1403.



1-(4-(1-cyclohexyl-2,2-difluoroethyl)phenyl)ethan-1-one (50)

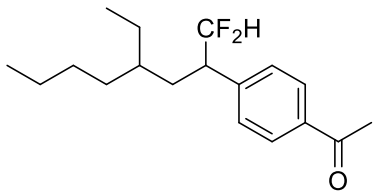
Colorless oil, 47.0 mg, 88% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 6.13 (td, *J* = 56.1, 3.4 Hz, 1H), 2.88 – 2.78 (m, 1H), 2.60 (s, 3H), 2.01 – 1.89 (m, 2H), 1.80 – 1.74 (m, 1H), 1.64 – 1.57 (m, 2H), 1.40 – 1.25 (m, 2H), 1.16 – 1.06 (m, 3H), 0.86 – 0.77 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 142.2, 136.3, 130.0, 128.5, 116.7 (t, *J* = 241.8 Hz), 55.7 (t, *J* = 18.7 Hz), 38.3 (t, *J* = 3.7 Hz), 31.3, 31.1, 26.7, 26.3, 26.2, 26.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -118.98 – -122.65 (m).

HRMS (ESI) m/z calcd for $C_{16}H_{21}F_2O[(M+H)^+]$: 267.1555 , found: 267.1558.



1-(4-(4-ethyl-1,1-difluorooctan-2-yl)phenyl)ethan-1-one (51)

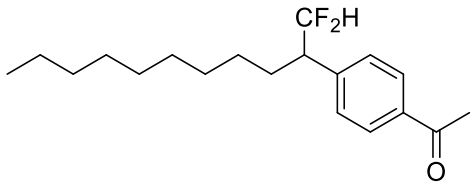
Colorless oil, 53.9 mg, 91% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 5.98 – 5.68 (m, 1H), 3.24 – 3.10 (m, 1H), 2.61 (s, 3H), 1.85 – 1.71 (m, 2H), 1.30 – 1.05 (m, 9H), 0.88 – 0.75 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 142.8, 136.5, 129.4, 128.8, 117.9 (t, *J* = 244.8 Hz), 47.8 (t, *J* = 19.6 Hz), 35.6, 35.2, 33.1, 32.1 (t, *J* = 3.3 Hz), 31.8 (t, *J* = 3.7 Hz), 31.8, 28.8, 28.1, 26.8, 26.5, 24.6, 23.2, 23.0, 14.2, 14.2, 10.9, 9.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ -117.87 – -123.01 (m).

HRMS (ESI) m/z calcd for $C_{18}H_{27}F_2O[(M+H)^+]$: 297.2025 , found: 297.2029.



1-(4-(1,1-difluoroundecan-2-yl)phenyl)ethan-1-one (52)

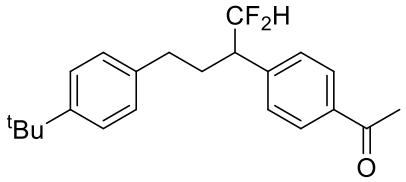
Colorless oil, 51.5 mg, 83% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 5.84 (t, *J* = 56.5 Hz, 1H), 3.05 (q, *J* = 14.2 Hz, 1H), 2.59 (s, 3H), 1.93 – 1.72 (m, 2H), 1.20 (s, 14H), 0.85 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 142.7 (t, *J* = 3.8 Hz), 138.0, 136.5, 129.9, 129.8, 129.3, 128.7, 117.6 (t, *J* = 244.4 Hz), 50.1 (t, *J* = 19.7 Hz), 31.9, 29.6, 29.5, 29.4, 29.3, 28.5 (t, *J* = 4.0 Hz), 26.9, 26.7, 22.8, 14.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -111.39 – -131.26 (m).

HRMS (ESI) m/z calcd for $C_{19}H_{29}F_2O[(M+H)^+]$: 311.2181 , found: 311.2183.



1-(4-(4-(4-(tert-butyl)phenyl)-1,1-difluorobutan-2-yl)phenyl)ethan-1-one (53)

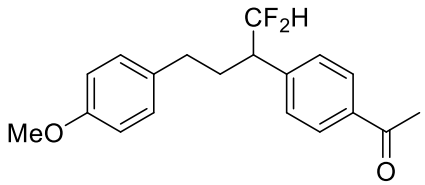
Colorless oil, 56.9 mg, 83% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.1, 2.9 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (dd, *J* = 8.3, 2.8 Hz, 2H), 7.03 (dd, *J* = 8.2, 2.9 Hz, 2H), 5.86 (td, *J* = 56.4, 3.8 Hz, 1H), 3.09 (t, *J* = 15.0 Hz, 1H), 2.63 (s, 3H), 2.58 – 2.51 (m, 1H), 2.47 – 2.39 (m, 1H), 2.27 (qd, *J* = 9.7, 5.4 Hz, 1H), 2.17 – 2.08 (m, 1H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 149.2, 142.2 (t, *J* = 3.8 Hz), 137.8, 136.7, 129.5, 128.9, 128.1, 125.5, 117.5 (t, *J* = 244.8 Hz), 49.2 (t, *J* = 19.8 Hz), 34.5, 32.2, 31.5, 29.9 (t, *J* = 3.9 Hz), 26.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -111.17 – -133.52 (m).

HRMS (ESI) m/z calcd for $C_{22}H_{27}F_2O[(M+H)^+]$: 345.2025 , found: 345.2030.



1-(4-(1,1-difluoro-4-(4-methoxyphenyl)butan-2-yl)phenyl)ethan-1-one (54)

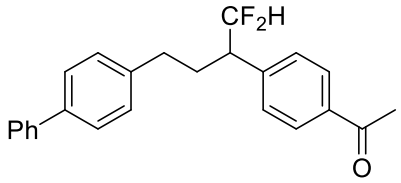
Colorless oil, 54.8 mg, 86% yield, **R**f =0.2 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.84 (td, *J* = 56.4, 3.8 Hz, 1H), 3.79 (s, 3H), 3.12 – 3.01 (m, 1H), 2.62 (s, 3H), 2.56 – 2.49 (m, 1H), 2.41 – 2.34 (m, 1H), 2.27 – 2.19 (m, 1H), 2.15 – 2.06 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 158.1, 142.1 (t, *J* = 3.9 Hz), 136.7, 132.8, 129.5, 129.4, 128.8, 117.5 (t, *J* = 244.8 Hz), 114.0, 55.4, 49.1 (t, *J* = 19.8 Hz), 31.8, 30.0 (t, *J* = 3.8 Hz), 26.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -112.87 – -132.67 (m).

HRMS (ESI) m/z calcd for $C_{19}H_{21}F_2O_2[(M+H)^+]$: 319.1504 , found: 319.1504.



1-(4-(4-([1,1'-biphenyl]-4-yl)-1,1-difluorobutan-2-yl)phenyl)ethan-1-one (55)

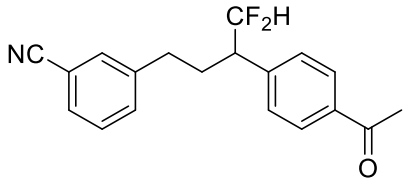
Colorless oil, 52.2 mg, 72% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.98 (m, 2H), 7.61 – 7.57 (m, 2H), 7.54 – 7.51 (m, 2H), 7.47 – 7.42 (m, 2H), 7.41 – 7.38 (m, 2H), 7.37 – 7.33 (m, 1H), 7.19 – 7.16 (m, 2H), 5.88 (td, J = 56.4, 3.8 Hz, 1H), 3.18 – 3.06 (m, 1H), 2.67 – 2.58 (m, 1H), 2.63 (s, 3H), 2.54 – 2.46 (m, 1H), 2.37 – 2.28 (m, 1H), 2.23 – 2.13 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 142.0 (t, *J* = 3.9 Hz), 141.0, 139.9, 139.3, 136.7, 129.5, 128.9, 128.9, 128.9, 127.3, 127.3, 127.1, 117.5 (t, *J* = 244.7 Hz), 49.2 (t, *J* = 19.8 Hz), 32.4, 29.8 (t, *J* = 3.7 Hz), 26.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -113.94 – -130.83 (m).

HRMS (ESI) m/z calcd for $C_{24}H_{23}F_2O[(M+H)^+]$: 365.1712 , found: 365.1719.



3-(3-(4-acetylphenyl)-4,4-difluorobutyl)benzonitrile (56)

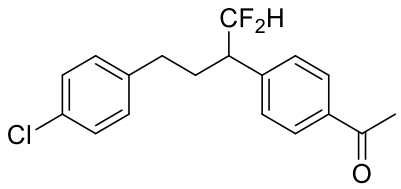
Yellow oil, 50.6 mg, 81% yield, **R**f =0.2 (petroleum ether: ethyl acetate, 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.50 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.40 – 7.31 (m, 5H), 5.86 (td, *J* = 56.3, 3.8 Hz, 1H), 3.13 – 3.00 (m, 1H), 2.63 (s, 3H), 2.60 – 2.46 (m, 2H), 2.32 – 2.24 (m, 1H), 2.17 – 2.06 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 142.3, 141.5 (t, *J* = 3.6 Hz), 136.9, 133.1, 132.0, 130.2, 129.5, 129.3, 129.1, 118.9, 117.2 (t, *J* = 244.1 Hz), 112.7, 49.3 (t, *J* = 20.2 Hz), 32.5, 29.5 (t, *J* = 4.0 Hz), 26.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.23 – -125.73 (m).

HRMS (ESI) m/z calcd for $C_{19}H_{18}F_2NO[(M+H)^+]$: 314.1351 , found: 314.1354.



1-(4-(4-(4-chlorophenyl)-1,1-difluorobutan-2-yl)phenyl)ethan-1-one (57)

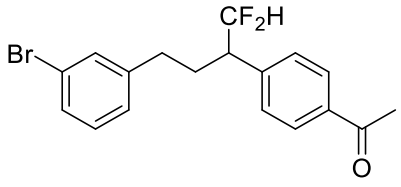
Yellow oil, 47.4 mg, 74% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 10:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 5.84 (td, *J* = 56.3, 3.8 Hz, 1H), 3.11 – 2.98 (m, 1H), 2.62 (s, 3H), 2.57 – 2.49 (m, 1H), 2.46 – 2.37 (m, 1H), 2.28 – 2.20 (m, 1H), 2.15 – 2.05 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 141.8 (t, *J* = 4.0 Hz), 139.3, 136.8, 132.1, 129.8, 129.4, 128.9, 128.8, 117.4 (t, *J* = 244.9 Hz), 49.2 (t, *J* = 20.0 Hz), 32.1, 29.7 (t, *J* = 3.9 Hz), 26.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -114.84 – -127.17 (m).

HRMS (ESI) m/z calcd for $C_{18}H_{18}ClF_2O[(M+H)^+]$: 323.1009 , found: 323.1016.



1-(4-(4-(3-bromophenyl)-1,1-difluorobutan-2-yl)phenyl)ethan-1-one (58)

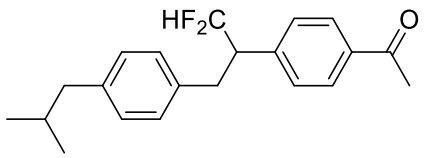
Yellow oil, 56.2 mg, 77% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H), 7.37 – 7.32 (m, 3H), 7.22 (t, *J* = 1.8 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.01 (dt, *J* = 7.7, 1.4 Hz, 1H), 5.85 (td, *J* = 56.4, 3.8 Hz, 1H), 3.11 – 3.01 (m, 1H), 2.63 (s, 3H), 2.56 – 2.49 (m, 1H), 2.46 – 2.39 (m, 1H), 2.29 – 2.22 (m, 1H), 2.15 – 2.07 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 141.8 (t, *J* = 3.7 Hz), 136.8, 131.6, 130.2, 129.5, 129.4, 129.0, 127.2, 122.7, 117.3 (t, *J* = 245.0 Hz), 49.3 (t, *J* = 20.1 Hz), 32.5, 29.6 (t, *J* = 4.0 Hz), 26.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -111.17 – -130.41 (m).

HRMS (ESI) m/z calcd for $C_{18}H_{18}BrF_2O[(M+H)^+]$: 367.0504 , found: 367.0508.



1-(4-(1,1-difluoro-3-(4-isobutylphenyl)propan-2-yl)phenyl)ethan-1-one (59)

Colorless oil, 60.0 mg, 91% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.02 – 6.91 (m, 4H), 5.92 (td, *J* = 56.2, 3.3 Hz, 1H), 3.44 – 3.31 (m, 1H), 3.25 (dd, *J* = 13.8, 6.1 Hz, 1H), 3.05 – 2.95 (m, 1H), 2.59 (s, 3H), 2.40 (d, *J* = 7.2 Hz, 2H), 1.86 – 1.74 (m, 1H), 0.86 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 142.0 (t, *J* = 3.2 Hz), 140.1, 136.5, 134.9, 129.5, 129.4, 128.8, 128.6, 116.9 (t, *J* = 244.2 Hz), 51.7 (t, *J* = 19.7 Hz), 45.0, 35.0 (t, *J* = 4.4 Hz), 30.3, 26.7, 22.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ -121.48 – -121.95 (m).

HRMS (ESI) m/z calcd for $C_{21}H_{25}F_2O[(M+H)^+]$: 331.1868 , found: 331.1862.

9. References

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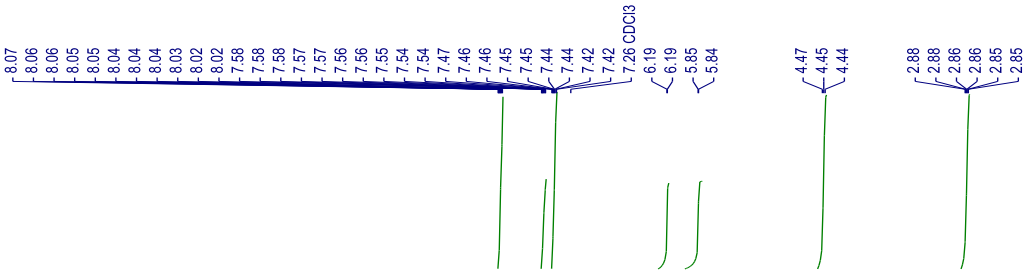
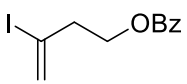
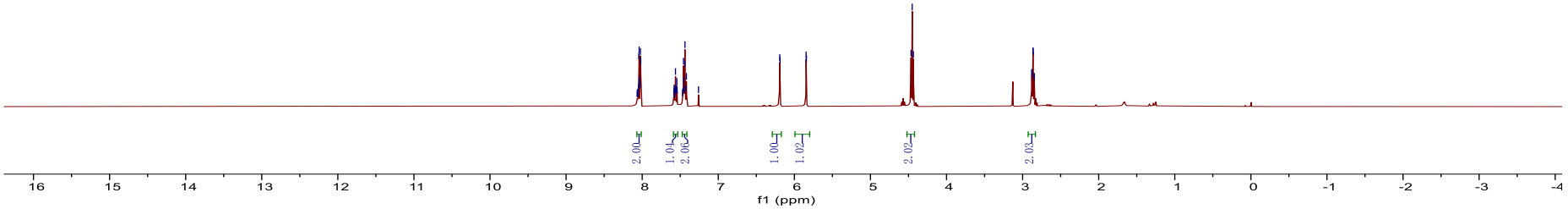
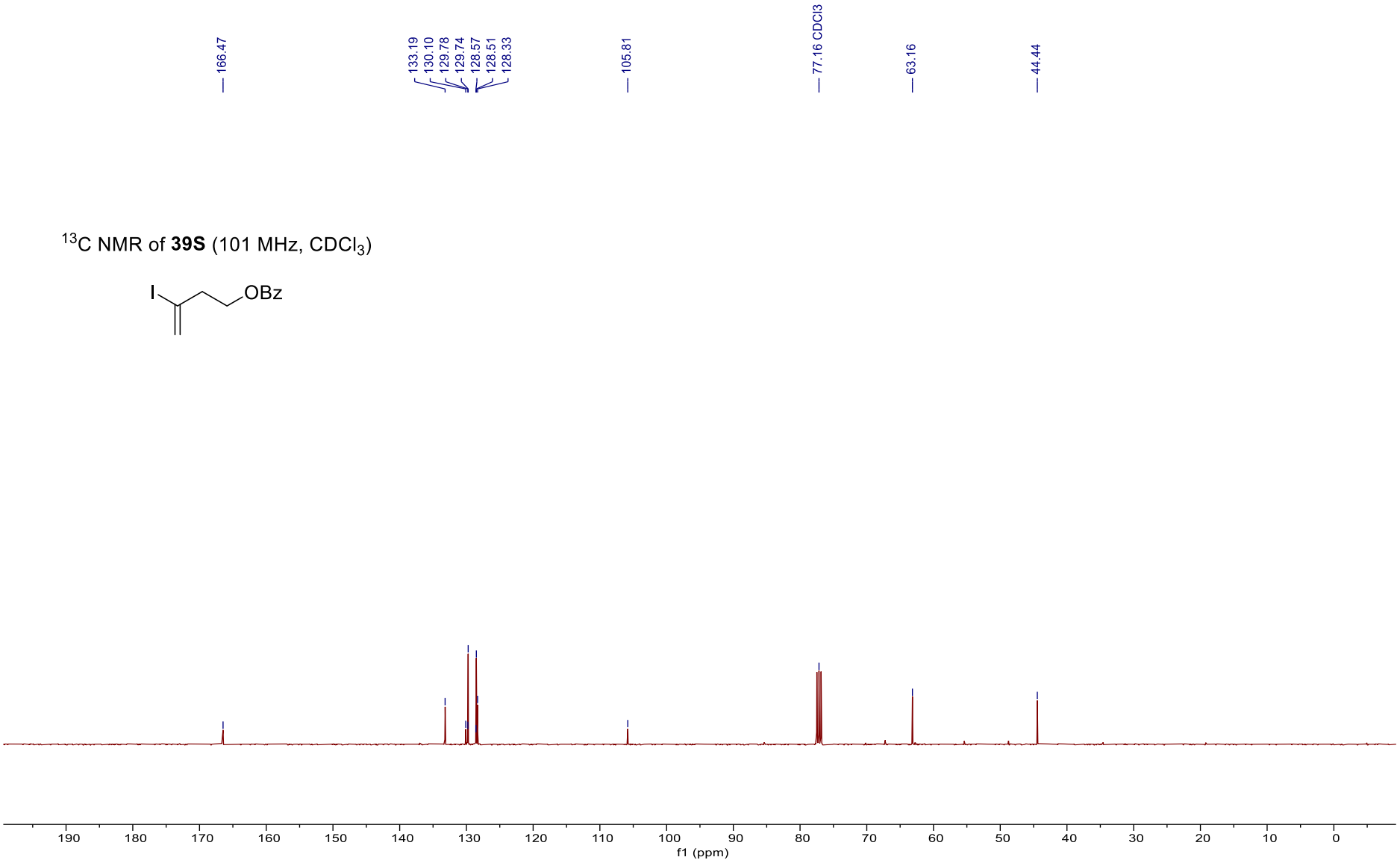
10. NMR Spectra



^{1}H NMR of **39S**(400 MHz, $CDCl_3$)

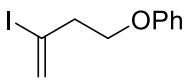


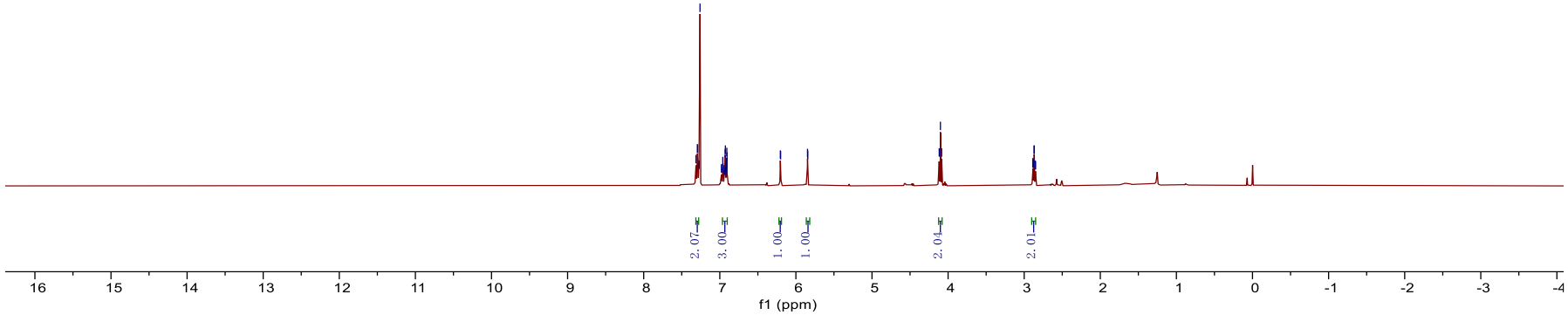


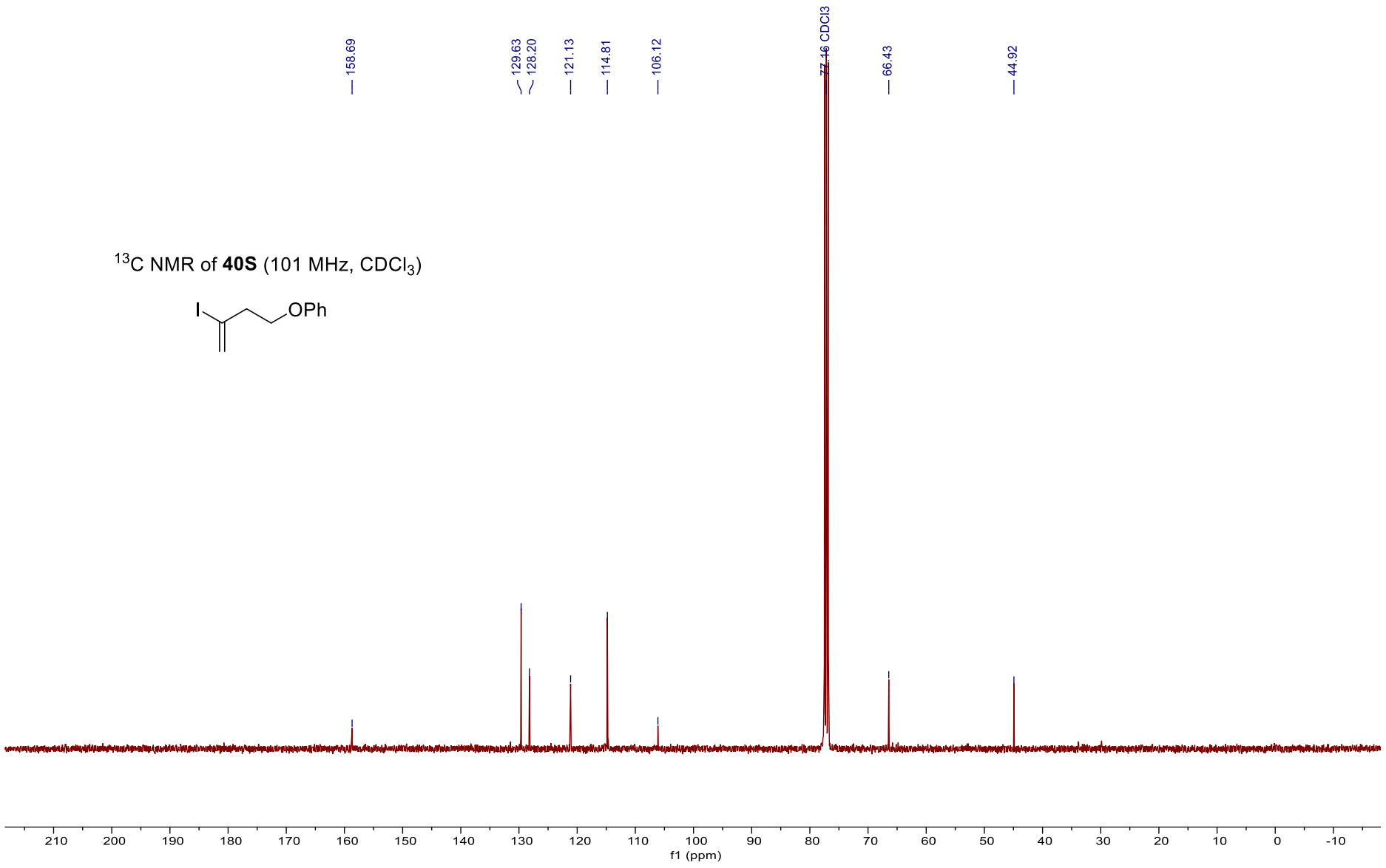


^{13}C NMR of **39S** (101 MHz, $CDCl_3$)

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

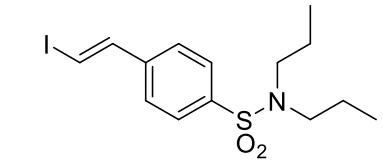


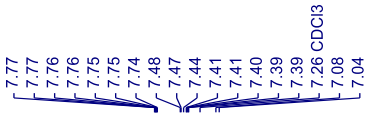


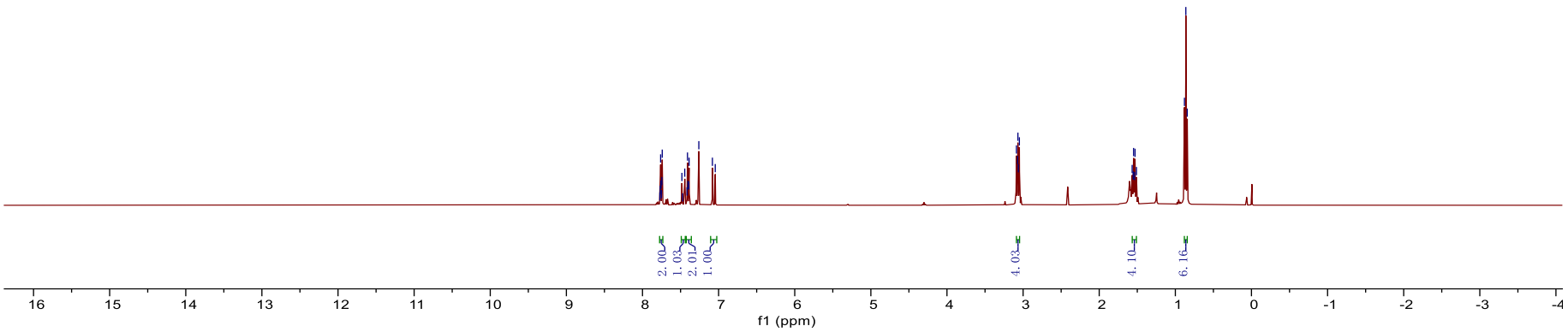


^{13}C NMR of **40S** (101 MHz, $CDCl_3$)

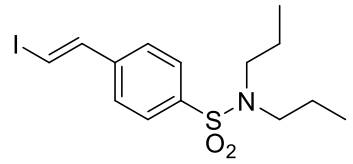
^{1}H NMR of **48S** (400 MHz, $CDCl_3$)

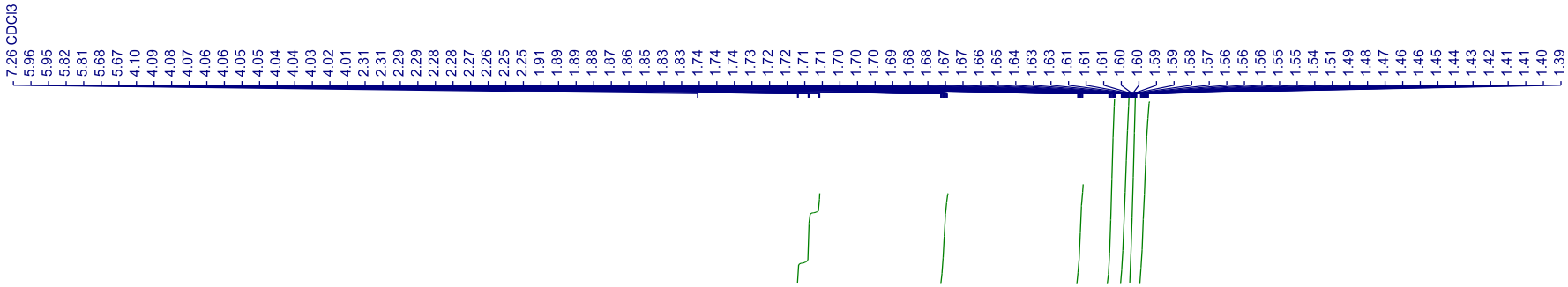




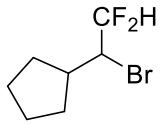


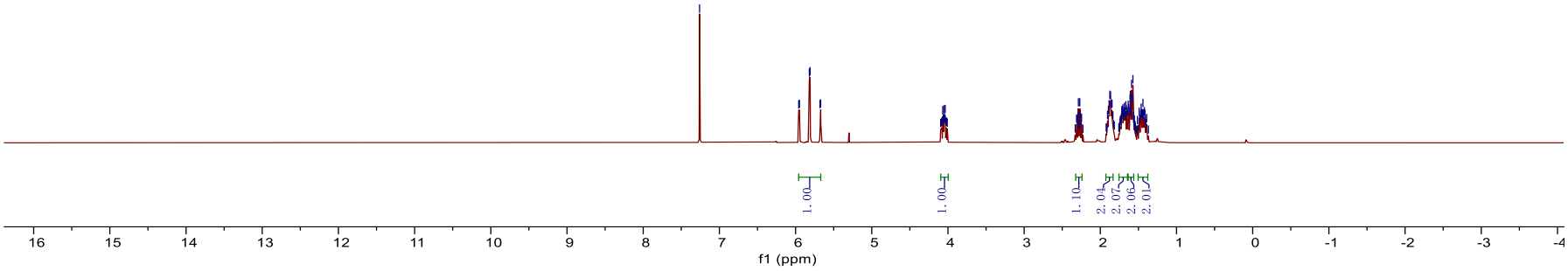
^{13}C NMR of **48S** (101 MHz, $CDCl_3$)



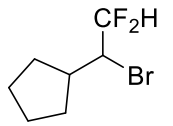


^{1}H NMR of **49S** (400 MHz, $CDCl_3$)

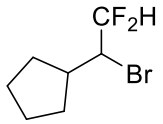




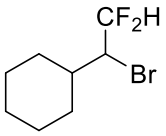
^{19}F NMR of **49S** (376 MHz, $CDCl_3$)



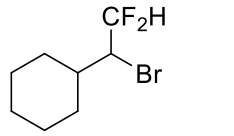
^{13}C NMR of **49S** (101 MHz, $CDCl_3$)

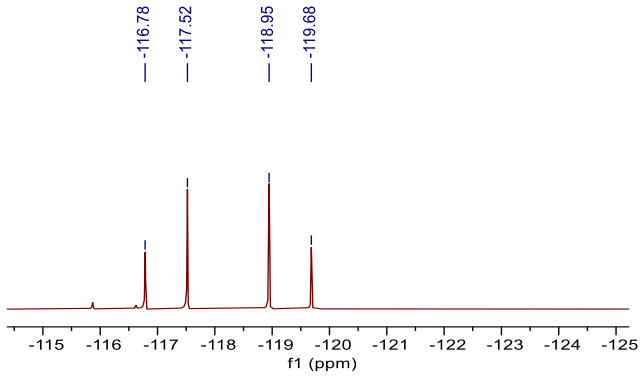


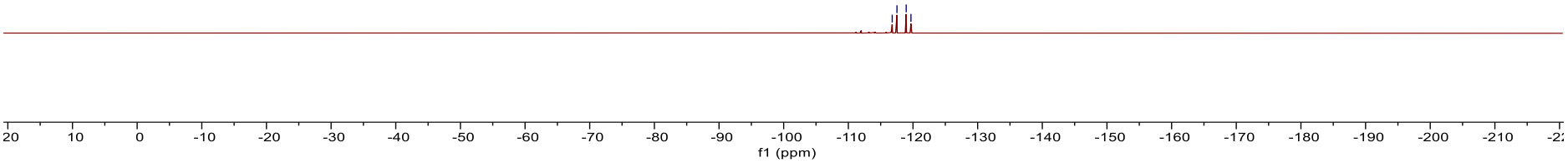
^{1}H NMR of **50S** (400 MHz, $CDCl_3$)



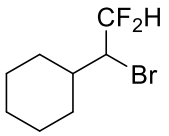
^{19}F NMR of **50S** (376 MHz, $CDCl_3$)

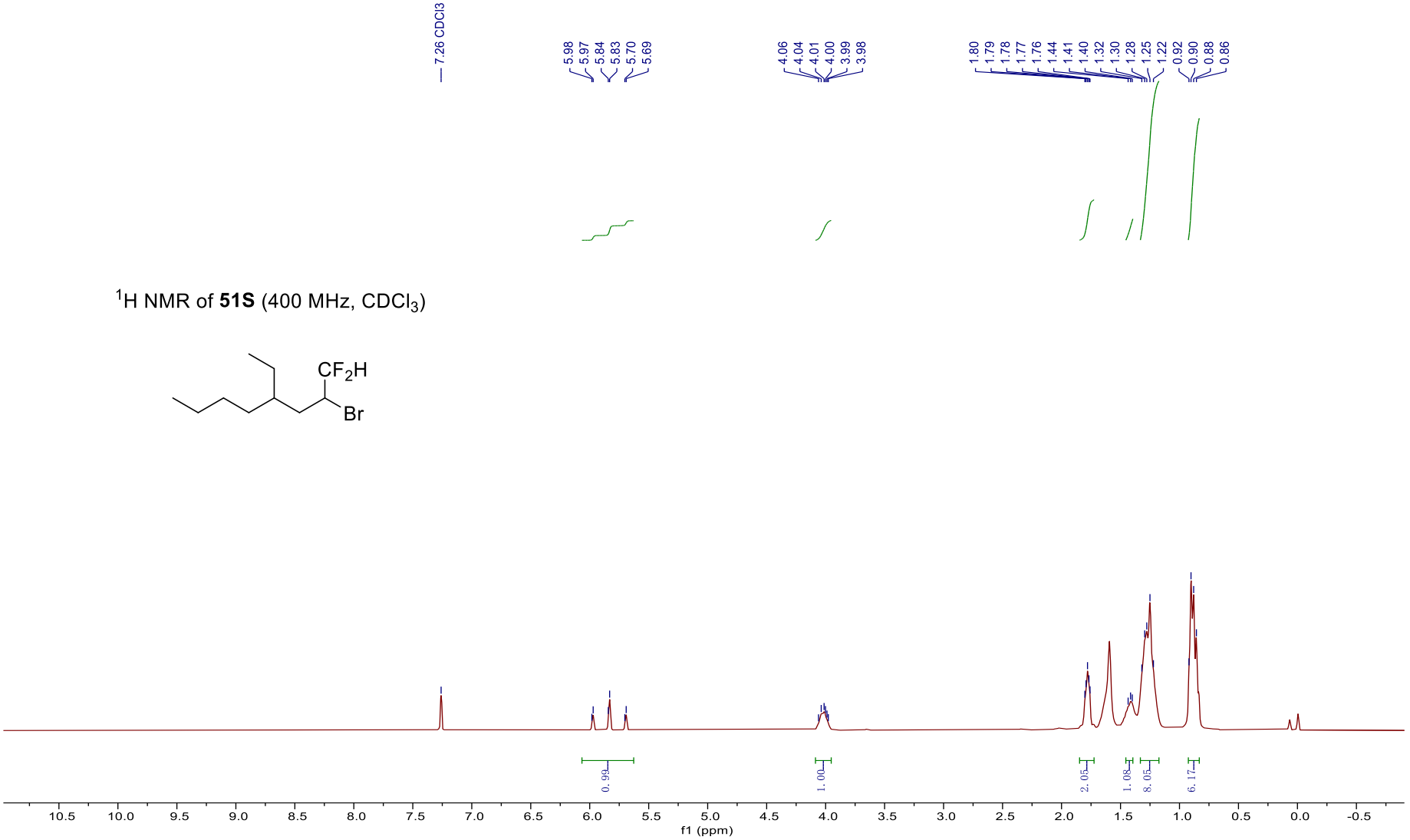






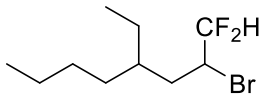
^{13}C NMR of **50S** (101 MHz, $CDCl_3$)

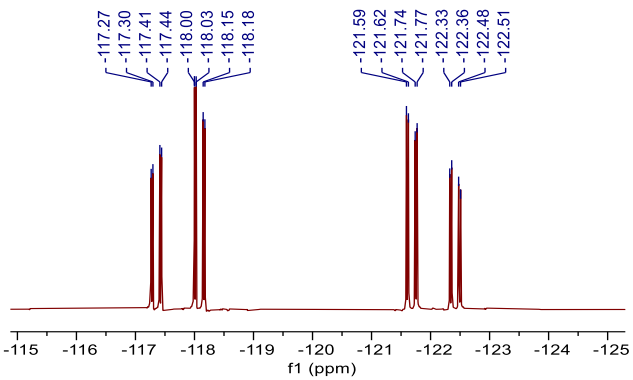


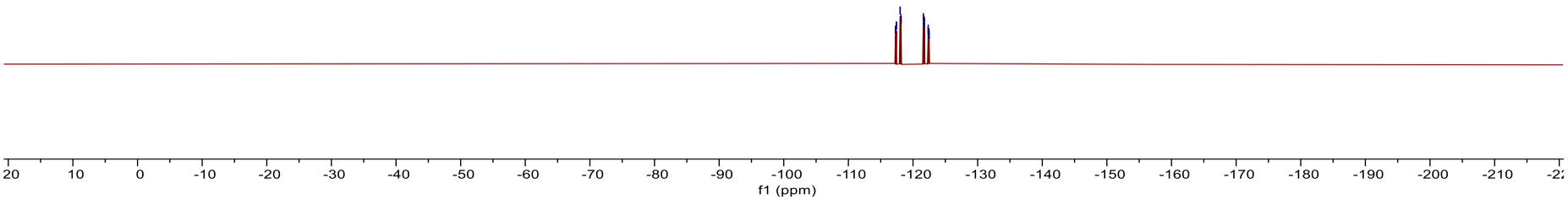


^{1}H NMR of **51S** (400 MHz, $CDCl_3$)

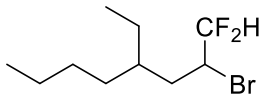
^{19}F NMR of **51S** (376 MHz, $CDCl_3$)



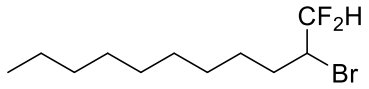


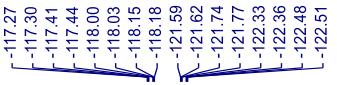


^{13}C NMR of **51S** (101 MHz, $CDCl_3$)

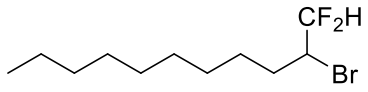


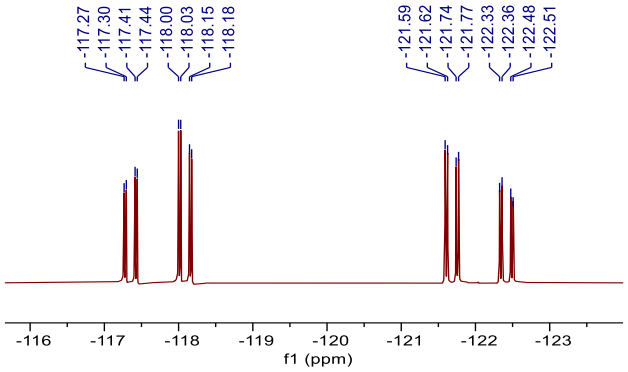
^{1}H NMR of **52S** (400 MHz, $CDCl_3$)

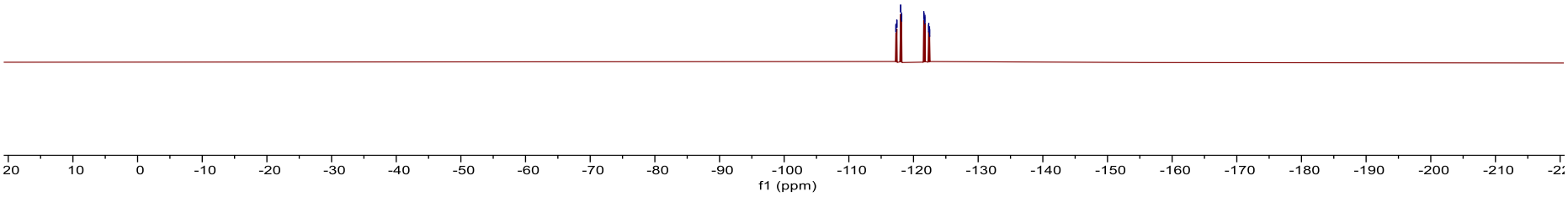




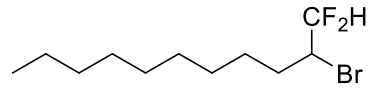
^{19}F NMR of **52S** (376 MHz, $CDCl_3$)

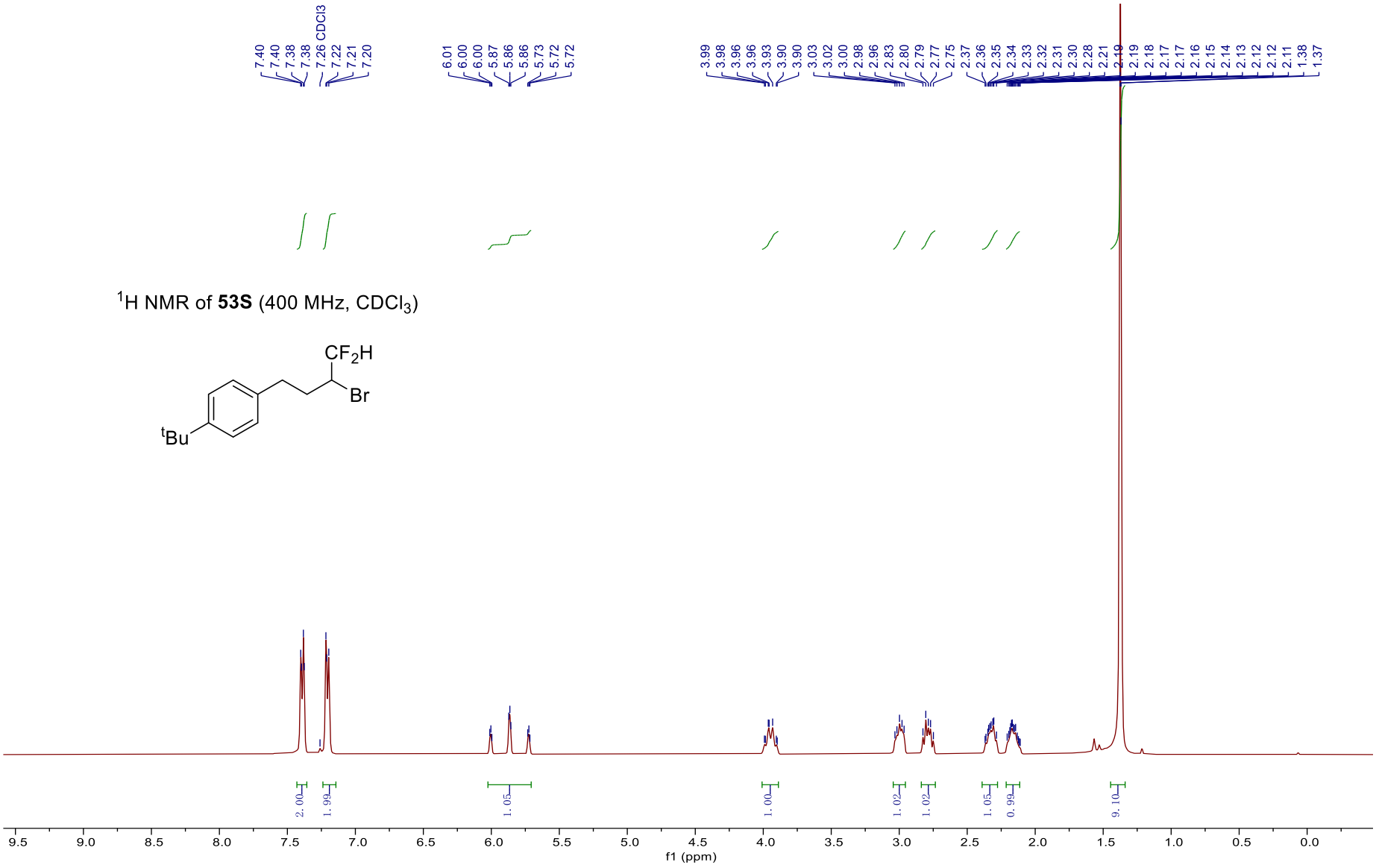






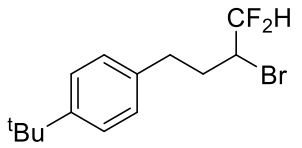
^{13}C NMR of **52S** (101 MHz, $CDCl_3$)



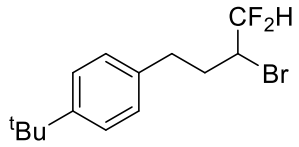


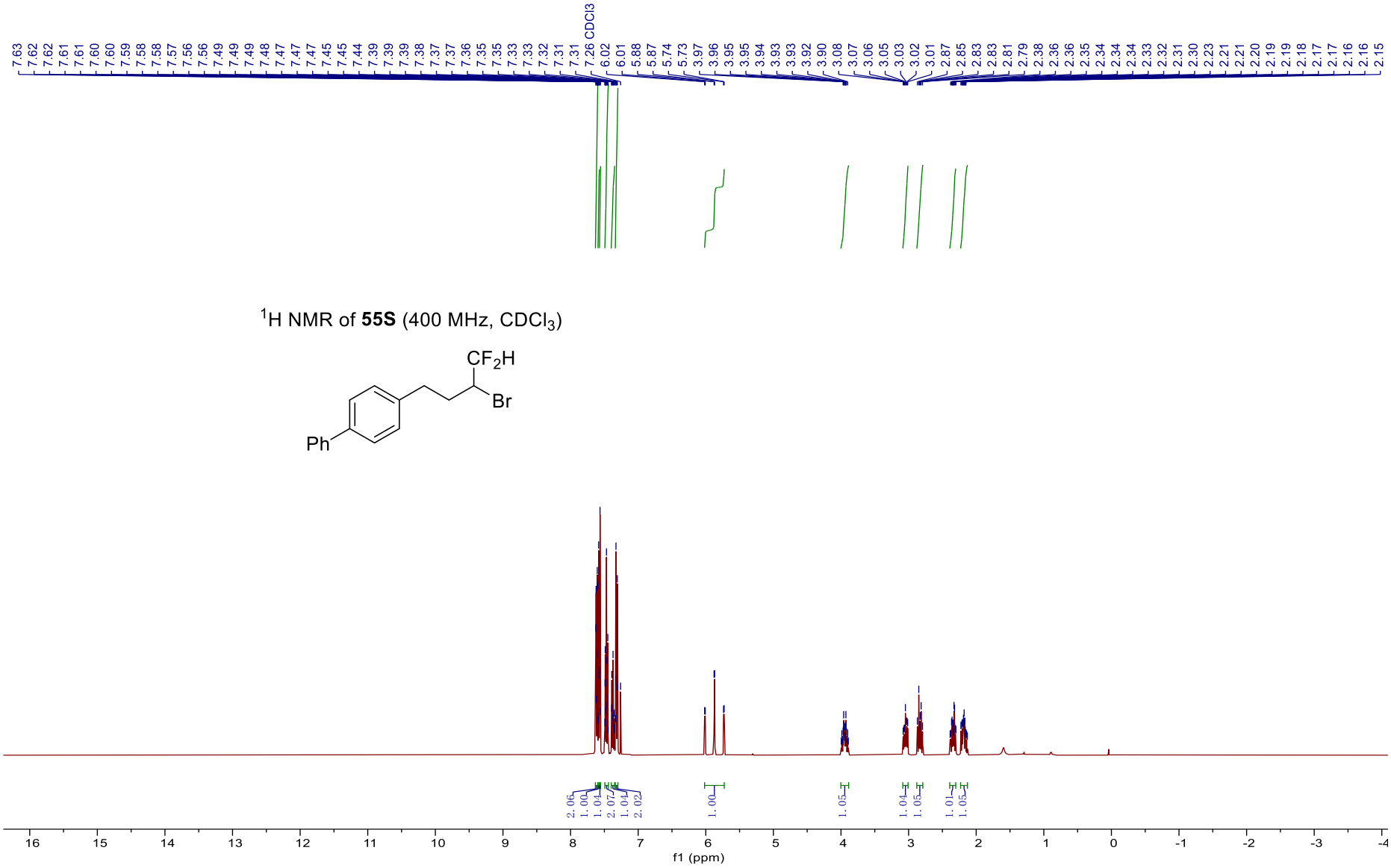
^{1}H NMR of **53S** (400 MHz, $CDCl_3$)

^{19}F NMR of **53S** (376 MHz, $CDCl_3$)

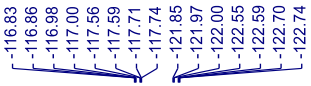


^{13}C NMR of **53S** (101 MHz, $CDCl_3$)

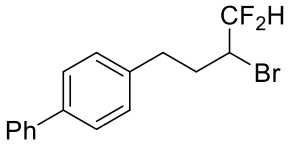


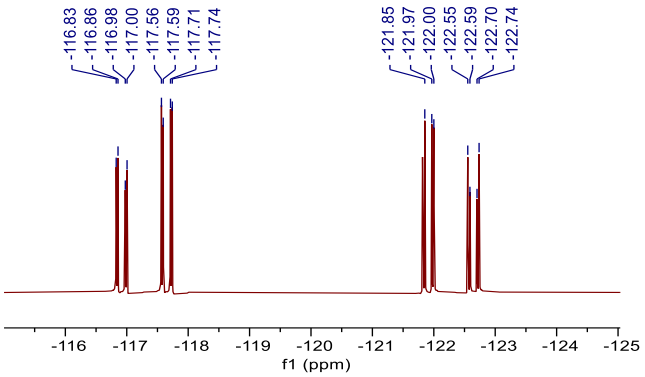


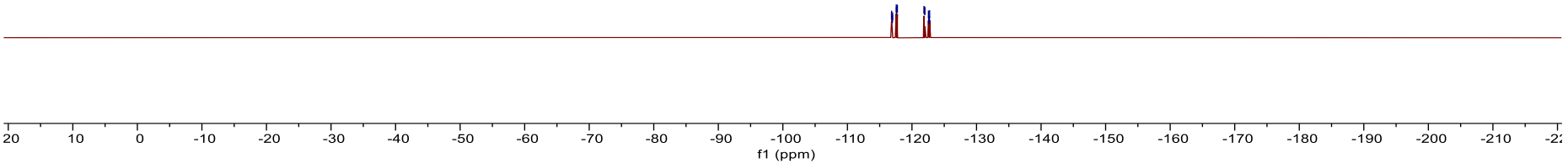
^{1}H NMR of **55S** (400 MHz, $CDCl_3$)



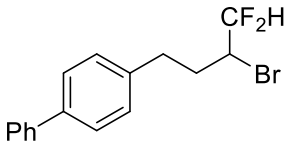
^{19}F NMR of **55S** (376 MHz, $CDCl_3$)



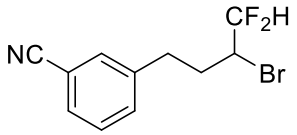




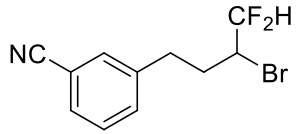
^{13}C NMR of **55S** (101 MHz, $CDCl_3$)

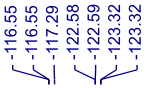


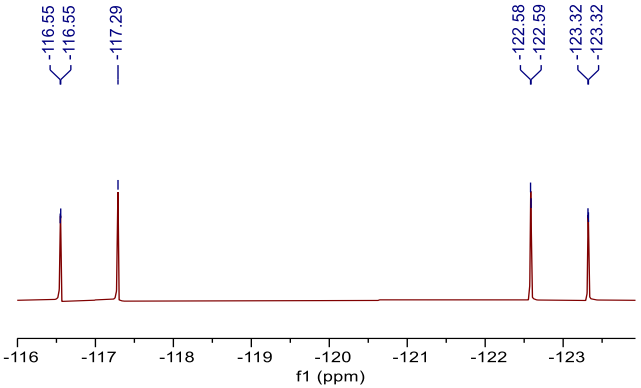
^{1}H NMR of **56S** (400 MHz, $CDCl_3$)

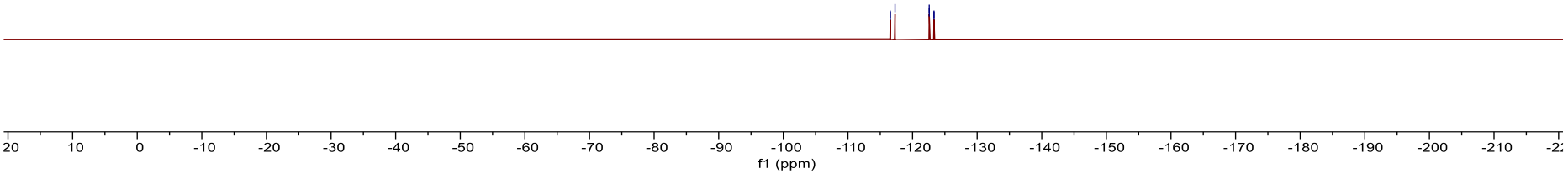


^{19}F NMR of **56S** (376 MHz, $CDCl_3$)

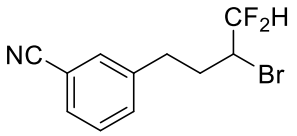


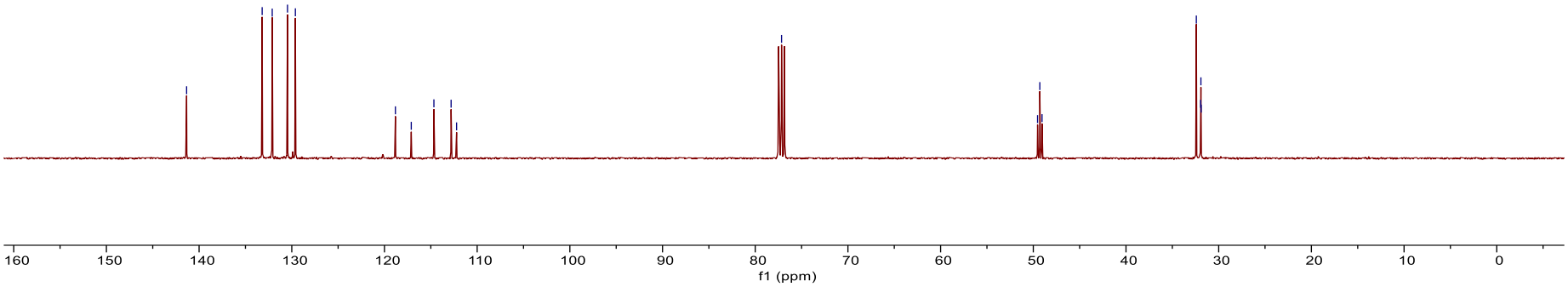


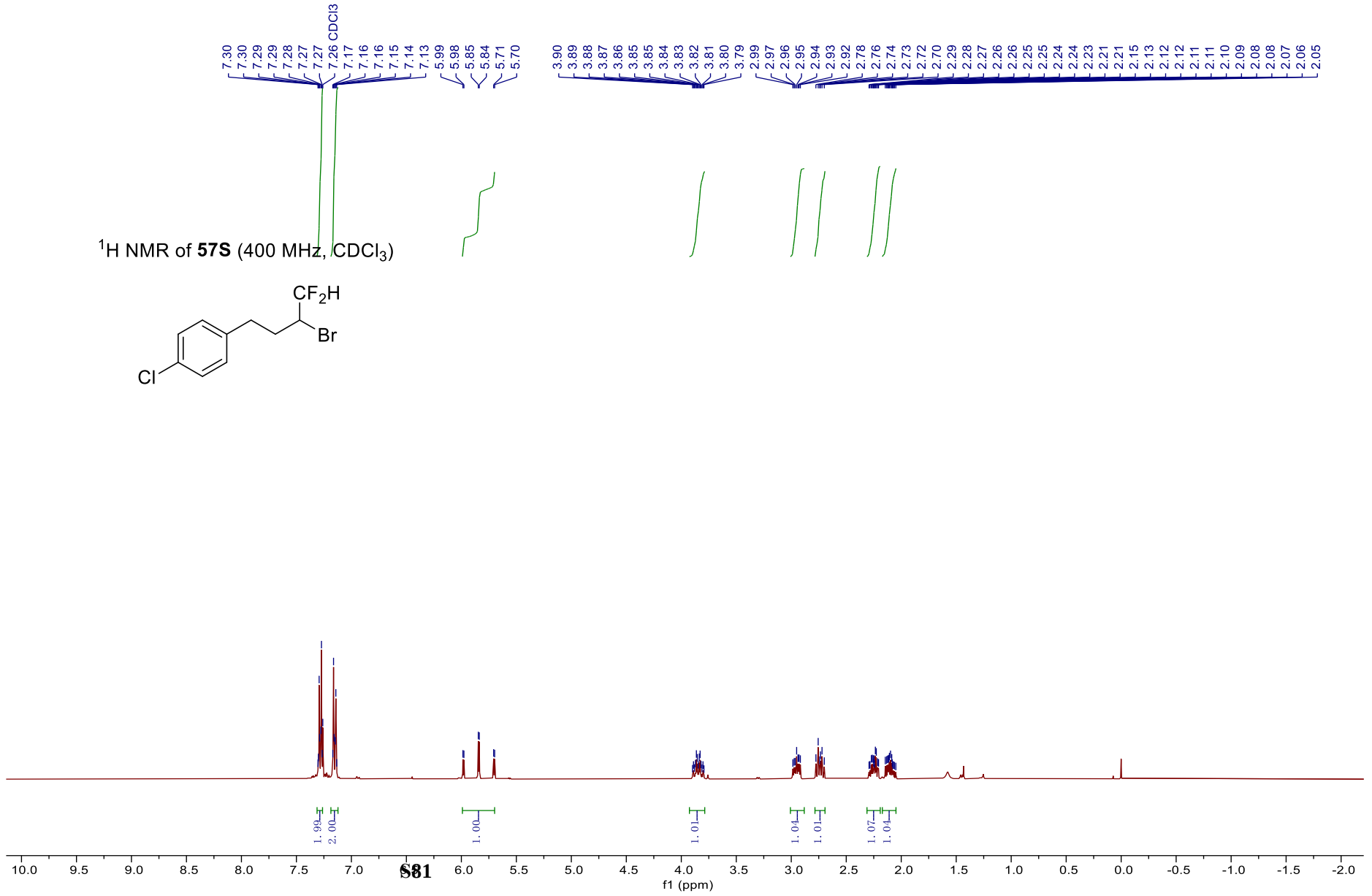


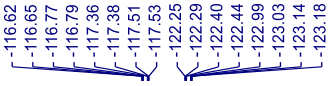


^{13}C NMR of **56S** (101 MHz, $CDCl_3$)

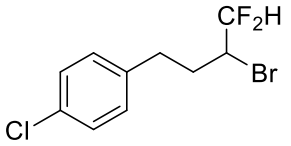


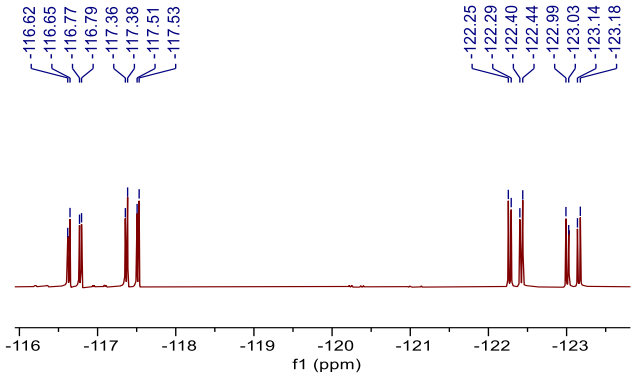


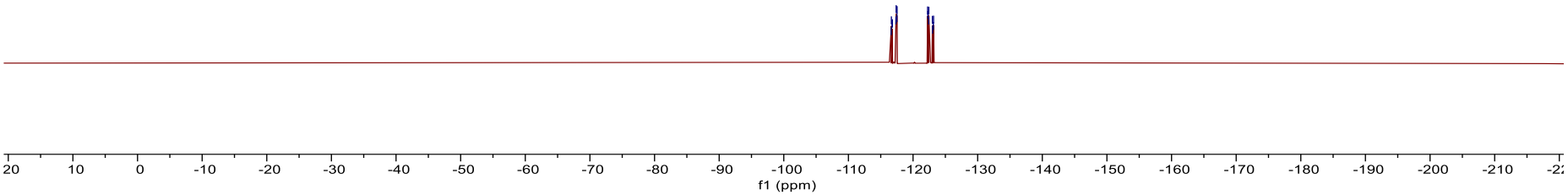

7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.26 CDCl3 7.17 7.16 7.16 7.15 7.14 7.13 5.99 5.98 5.85 5.84 5.71 5.70
3.90 3.89 3.88 3.87 3.86 3.85 3.85 3.84 3.83 3.82 3.81 3.80 3.79 2.99 2.97 2.96 2.95 2.94 2.93 2.92 2.78 2.76 2.74 2.73 2.72 2.70 2.29 2.28 2.27 2.26 2.26 2.25 2.25 2.24 2.24 2.23 2.21 2.21 2.15 2.13 2.12 2.12 2.11 2.11 2.10 2.09 2.08 2.08 2.07 2.06 2.05
1H NMR of 57S (400 MHz, CDCl3)
CF2H
Br
Cl
1.99
2.00
1.00
1.01
1.04
1.01
1.07
1.04
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 -1.5 -2.0
f1 (ppm)

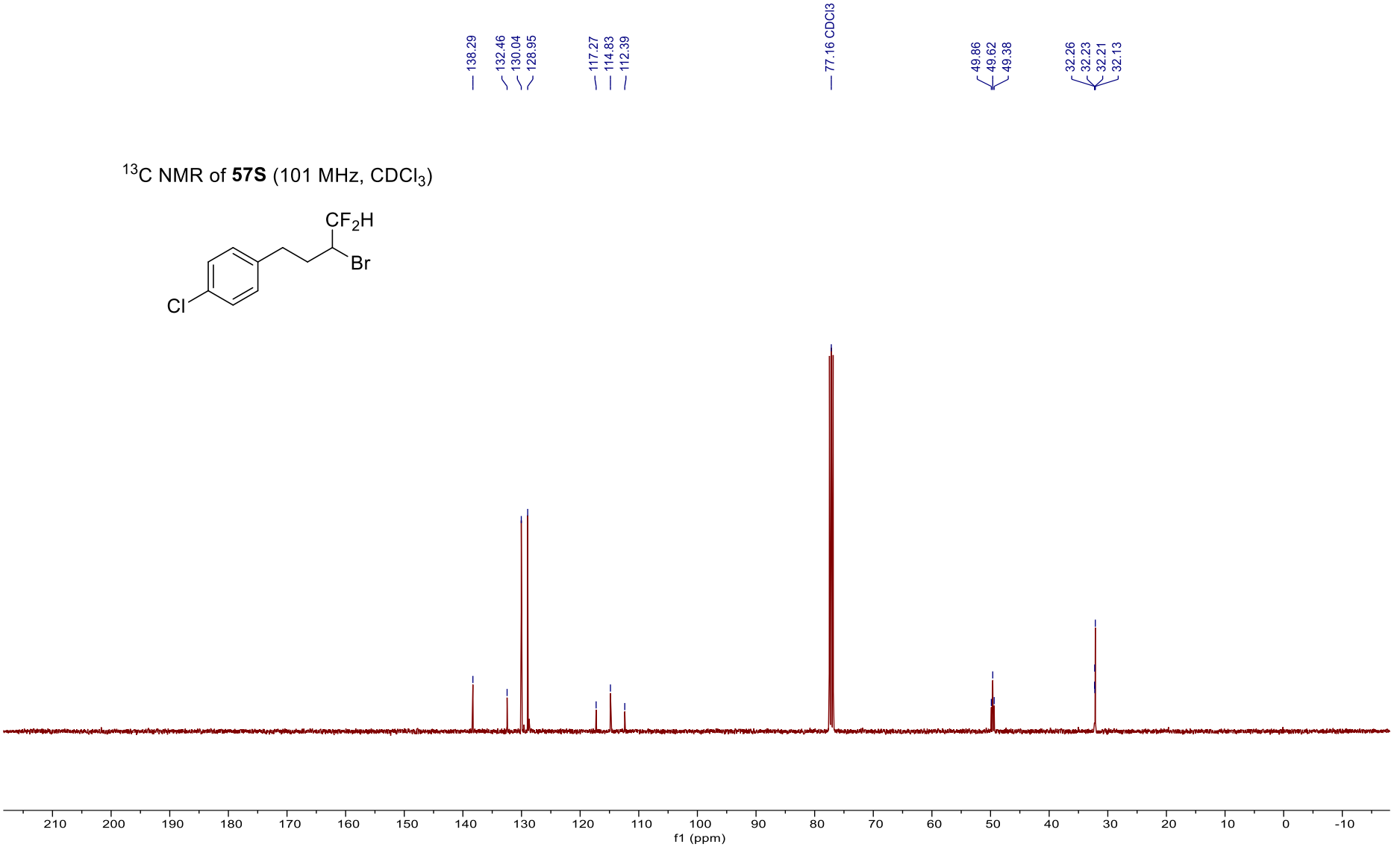


^{19}F NMR of **57S** (376 MHz, $CDCl_3$)

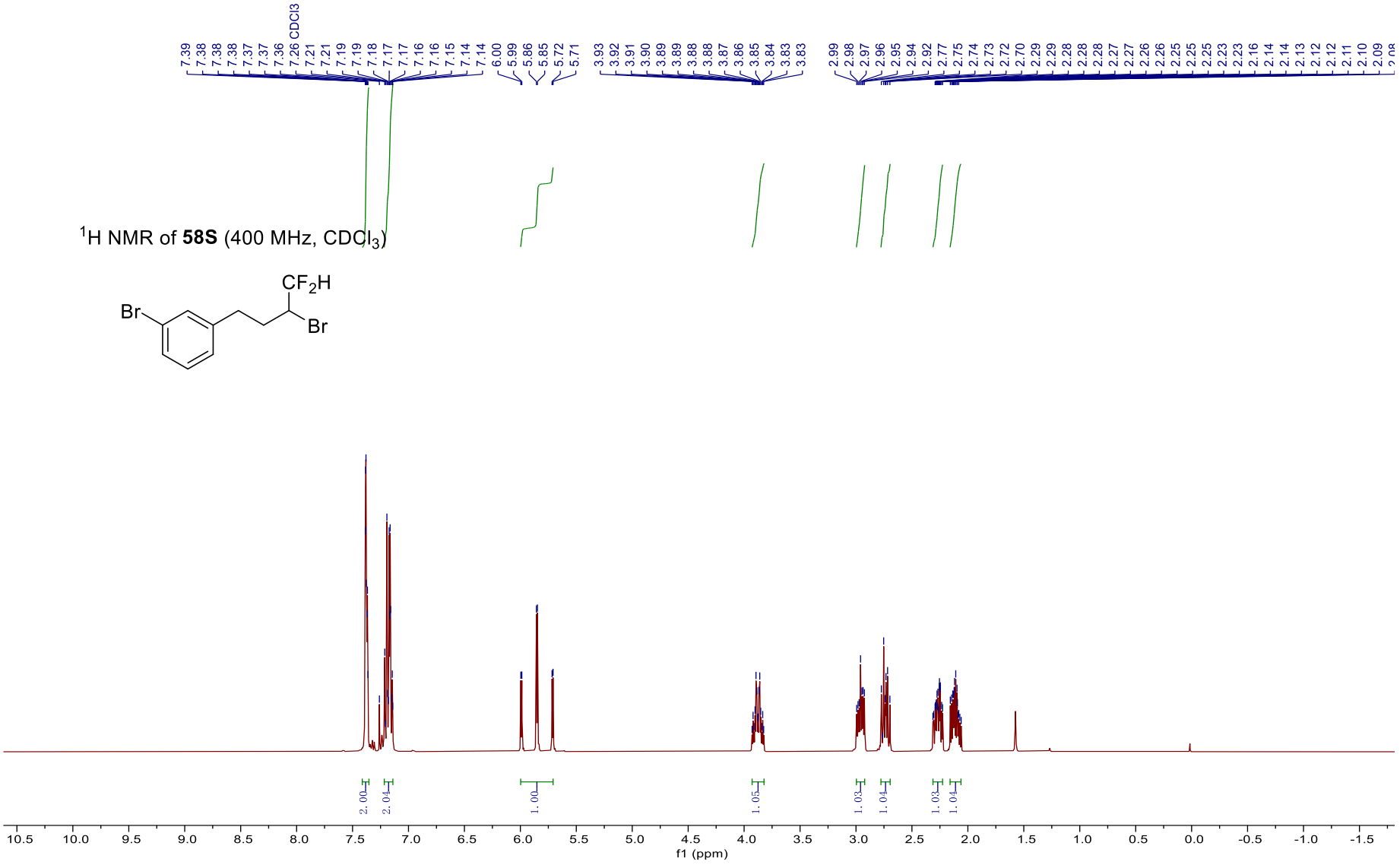




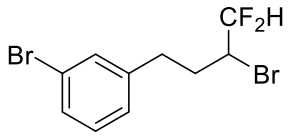


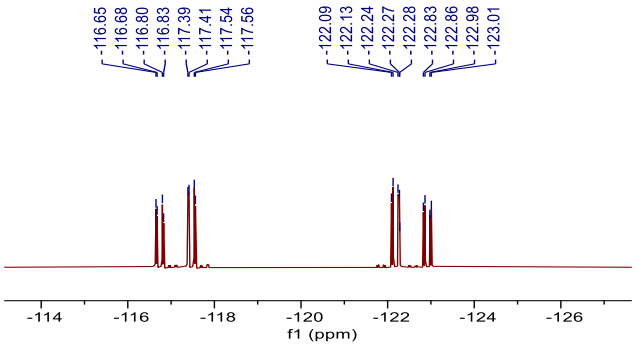


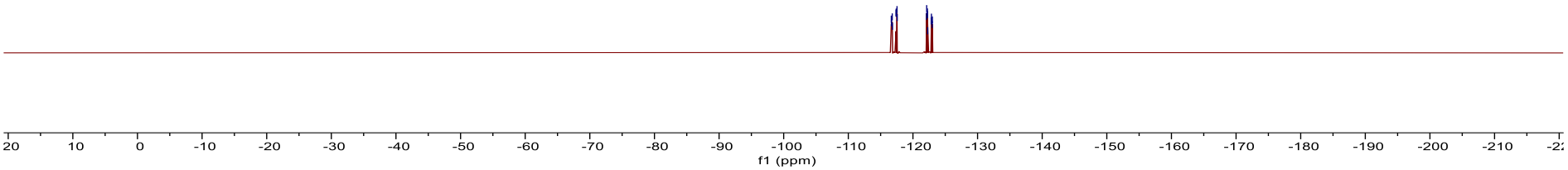
^{13}C NMR of **57S** (101 MHz, $CDCl_3$)


CDCl3
7.39 7.38 7.38 7.38 7.37 7.37 7.36 7.26 7.21 7.21 7.19 7.19 7.18 7.17 7.17 7.16 7.16 7.15 7.14 7.14
6.00 5.99 5.86 5.85 5.72 5.71
3.93 3.92 3.91 3.90 3.89 3.89 3.88 3.88 3.87 3.86 3.85 3.84 3.83 3.83
2.99 2.98 2.97 2.96 2.95 2.94 2.92 2.77 2.75 2.74 2.73 2.72 2.70 2.29 2.29 2.28 2.28 2.28 2.27 2.27 2.26 2.26 2.25 2.25 2.25 2.23 2.23 2.16 2.14 2.14 2.13 2.12 2.12 2.11 2.10 2.09
1H NMR of 58S (400 MHz, CDCl3)
CF2H
Br
Br
2.00
2.04
1.00
1.05
1.03
1.04
1.03
1.04
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 0.0 -0.5 -1.0 -1.5
f1 (ppm)

^{19}F NMR of **58S** (376 MHz, $CDCl_3$)

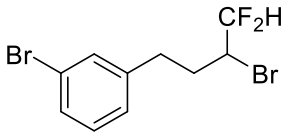


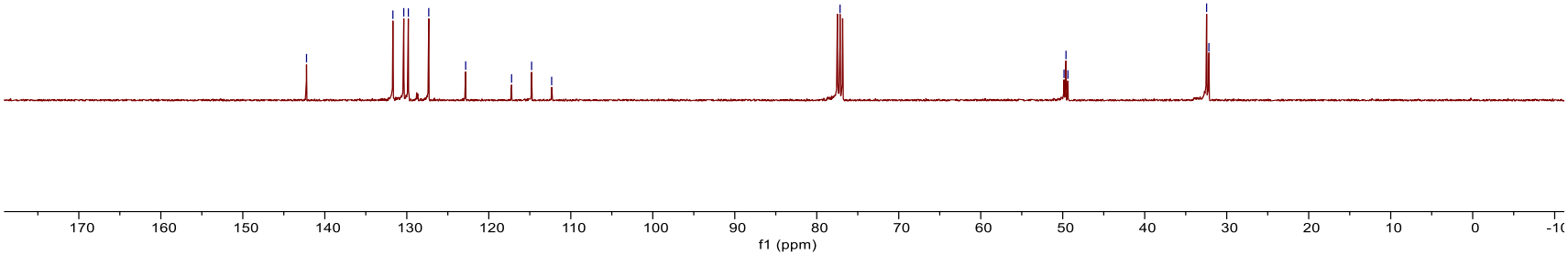


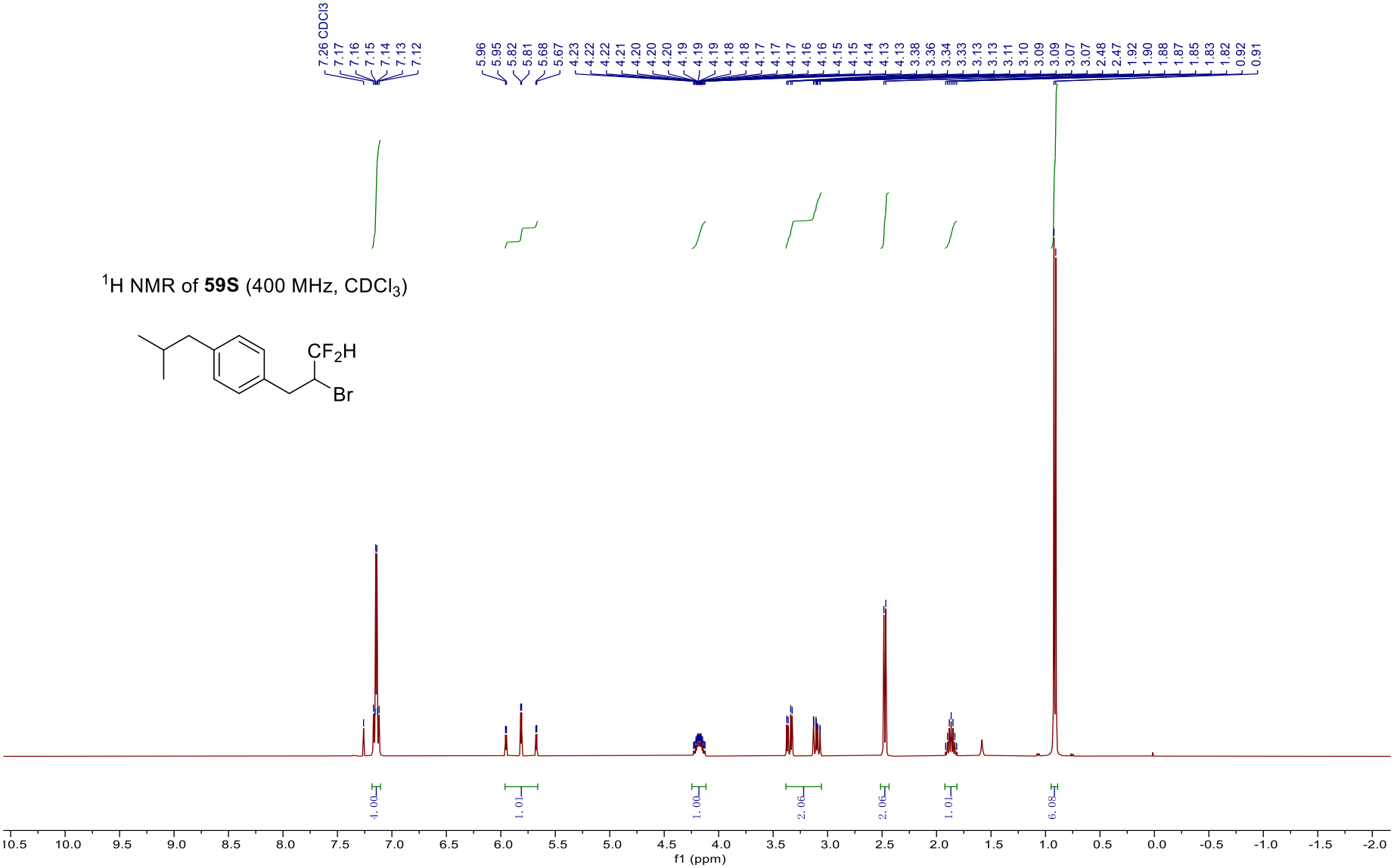


142.23
131.69
130.37
129.81
127.32
122.82
117.22
114.78
112.33
77.16 CDCl3
49.84
49.60
49.36
32.45
32.17

^{13}C NMR of **58S** (101 MHz, $CDCl_3$)

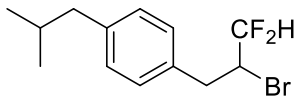


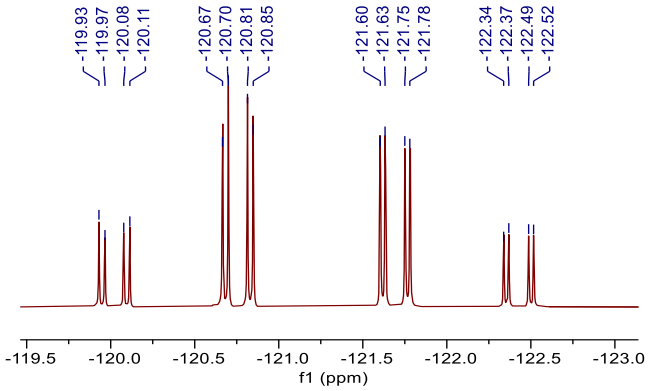


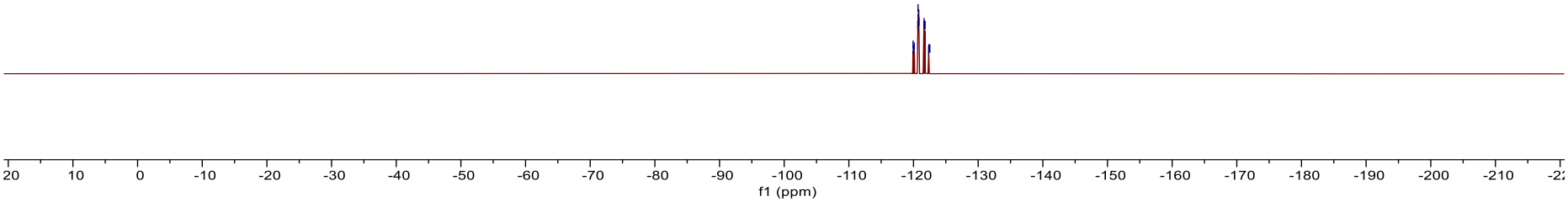


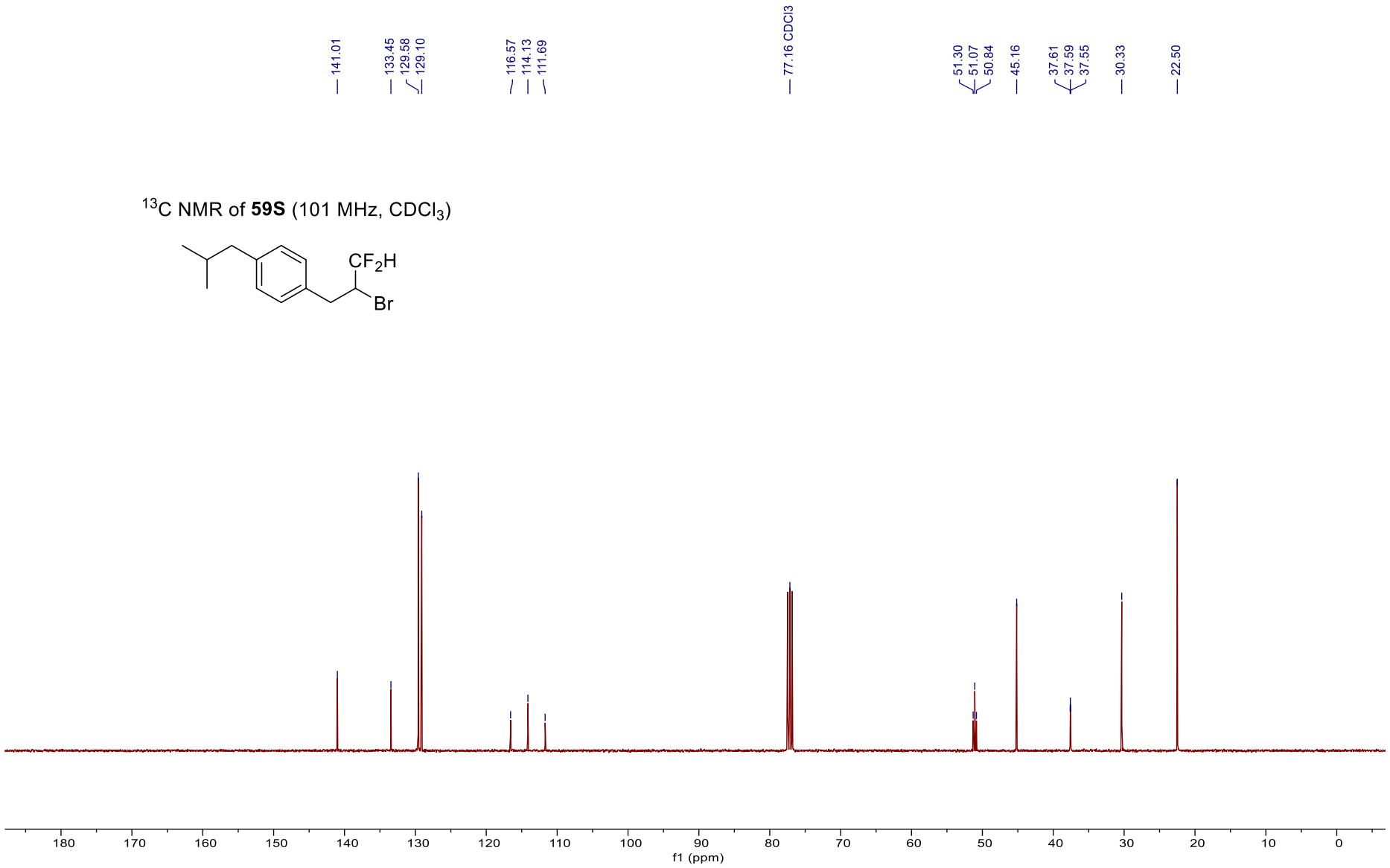
^{1}H NMR of **59S** (400 MHz, $CDCl_3$)

^{19}F NMR of **59S** ($CDCl_3$)



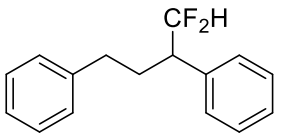




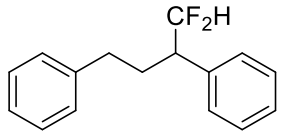


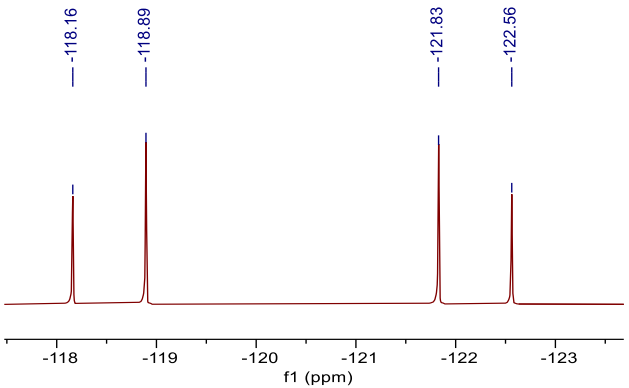
^{13}C NMR of **59S** (101 MHz, $CDCl_3$)

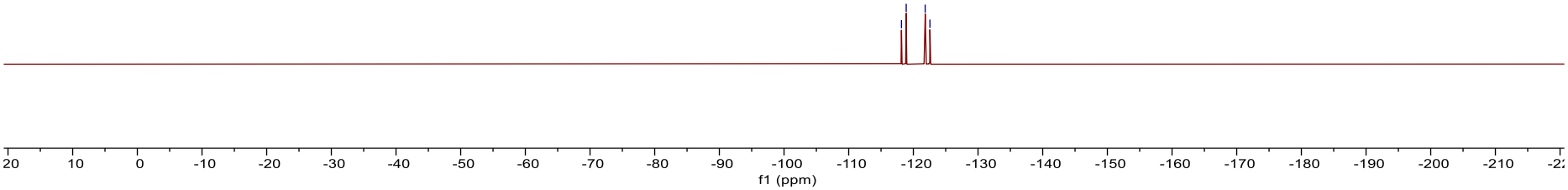
^{1}H NMR of **3** (400 MHz, $CDCl_3$)

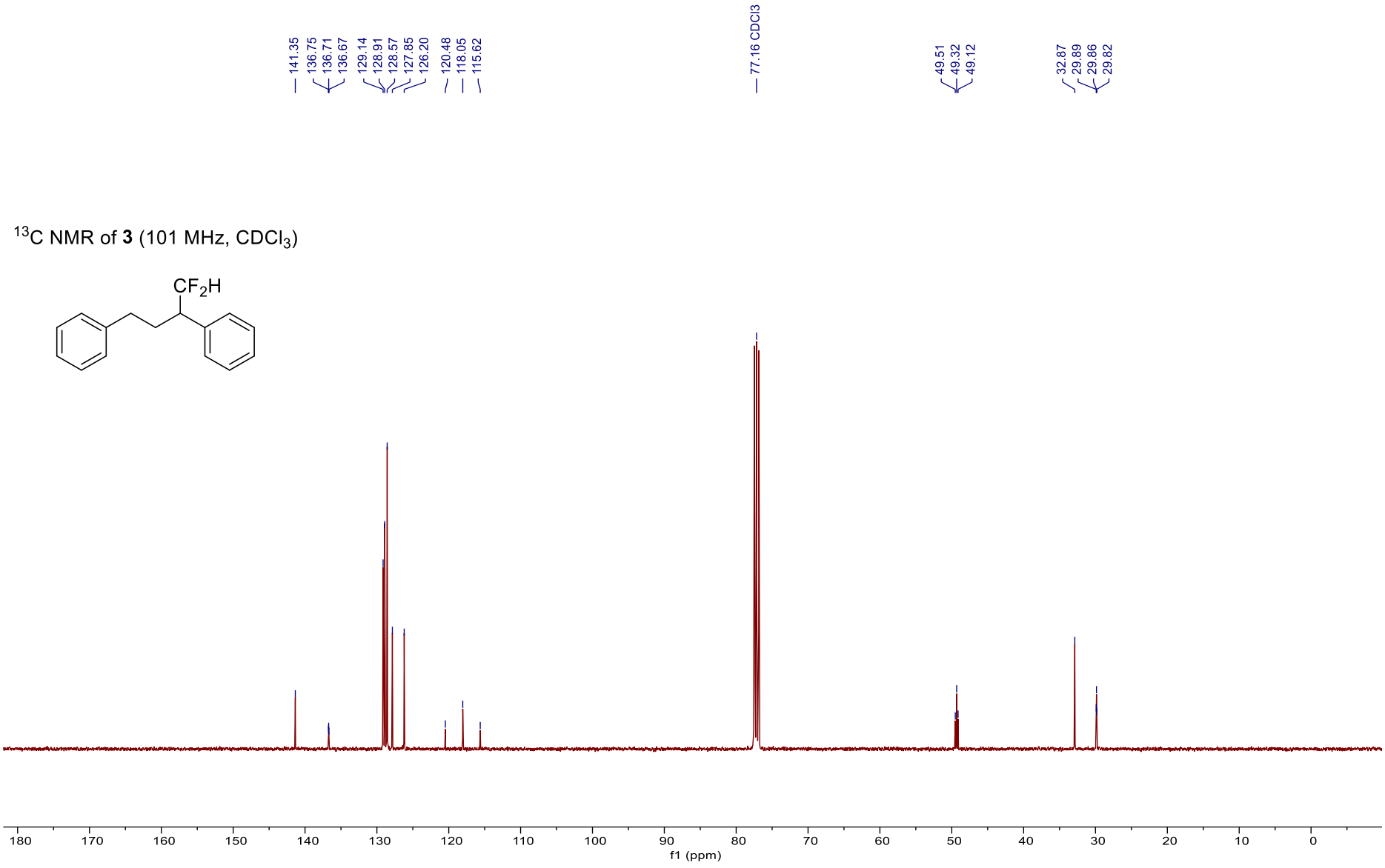


^{19}F NMR of **3** (376 MHz, $CDCl_3$)

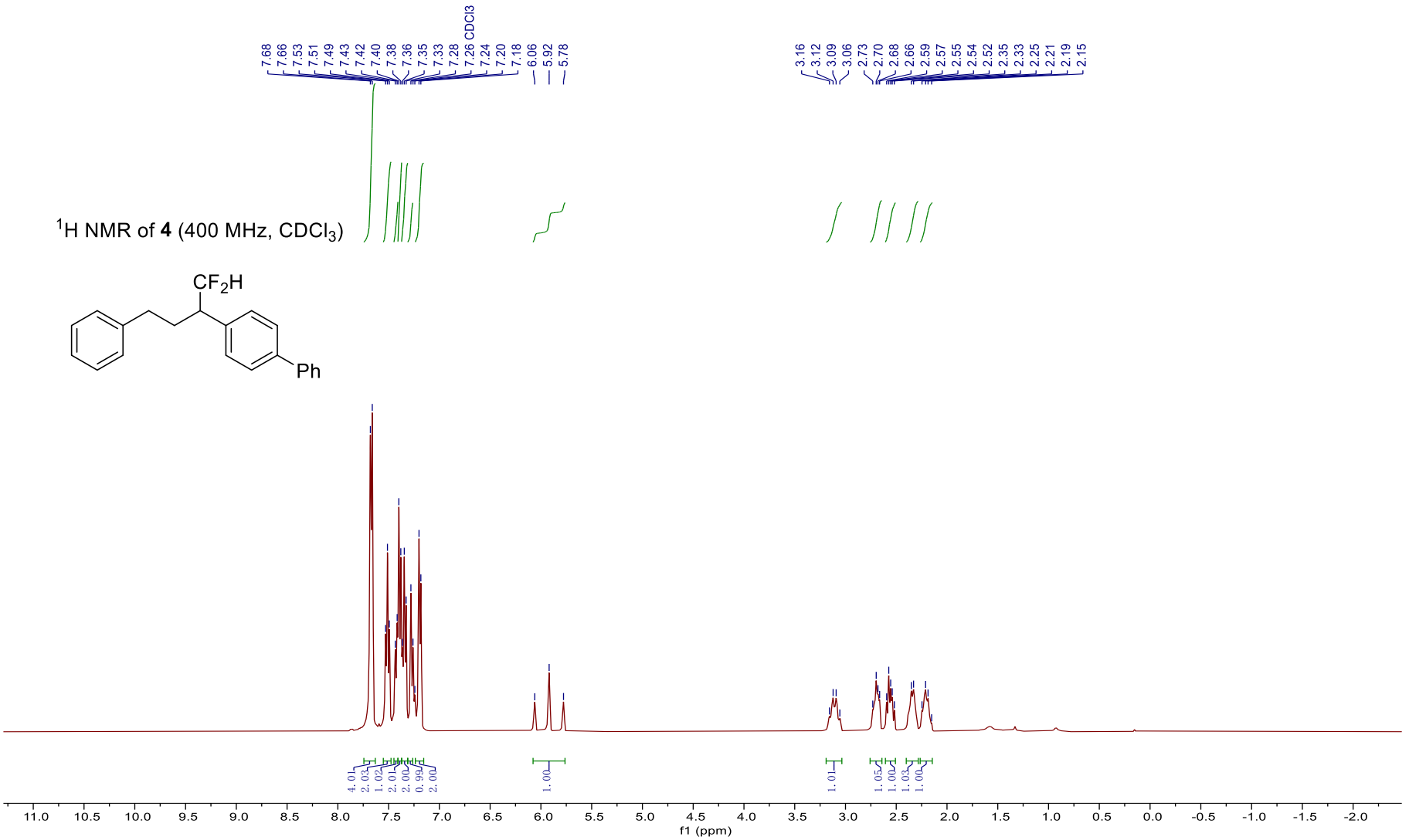




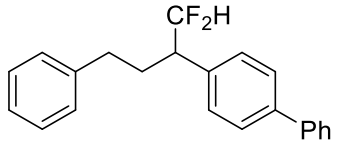


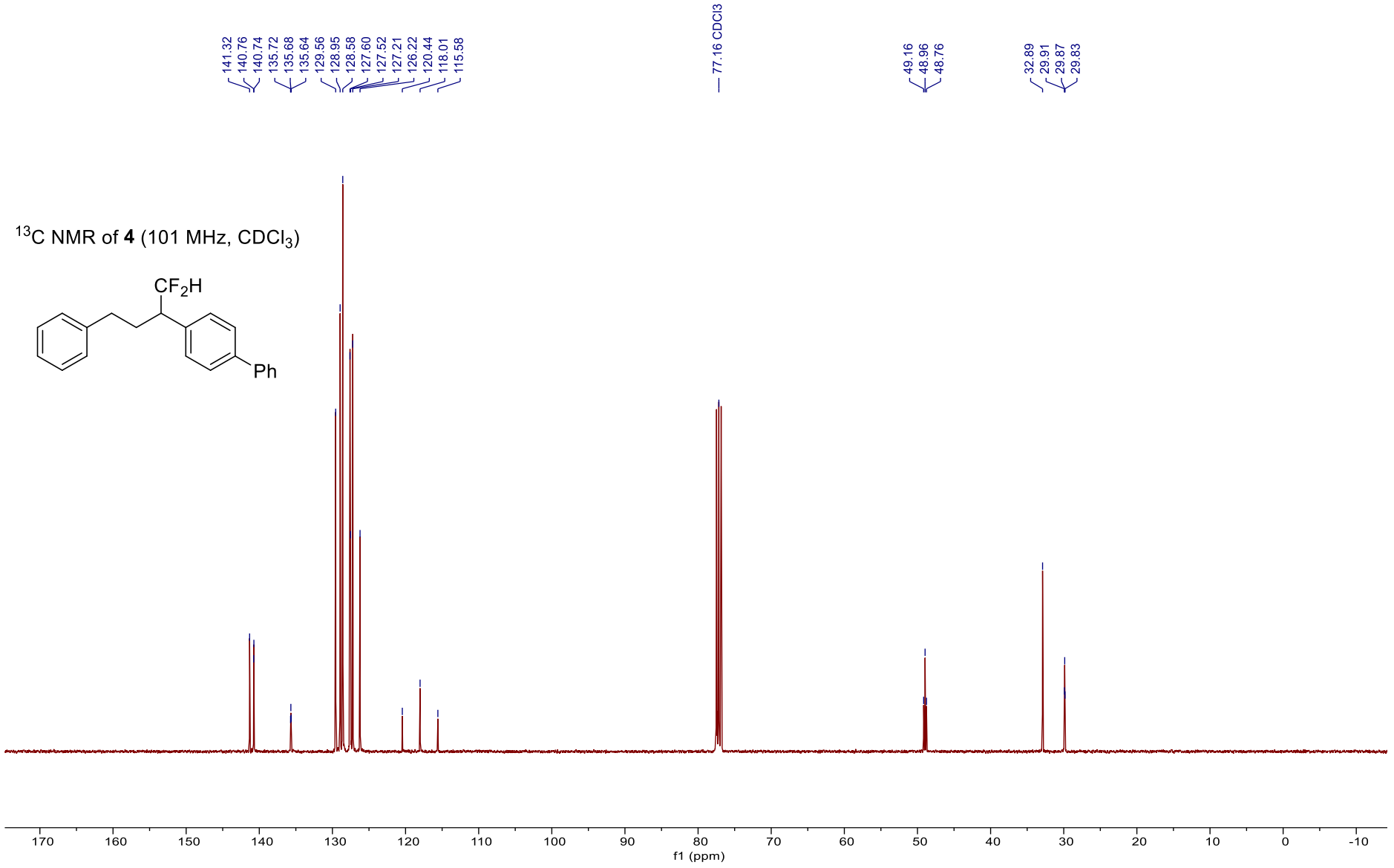


^{13}C NMR of **3** (101 MHz, $CDCl_3$)

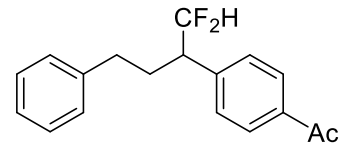

7.68
7.66
7.53
7.51
7.49
7.43
7.42
7.40
7.38
7.36
7.35
7.33
7.28
7.26 CDCl3
7.24
7.20
7.18
6.06
5.92
5.78
3.16
3.12
3.09
3.06
2.73
2.70
2.68
2.66
2.59
2.57
2.55
2.54
2.52
2.35
2.33
2.25
2.21
2.19
2.15
1H NMR of 4 (400 MHz, CDCl3)
CF2H
Ph
4.01
2.03
1.02
2.01
2.00
0.99
2.00
1.00
1.01
1.05
1.00
1.03
1.00
f1 (ppm)

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

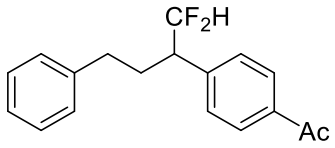


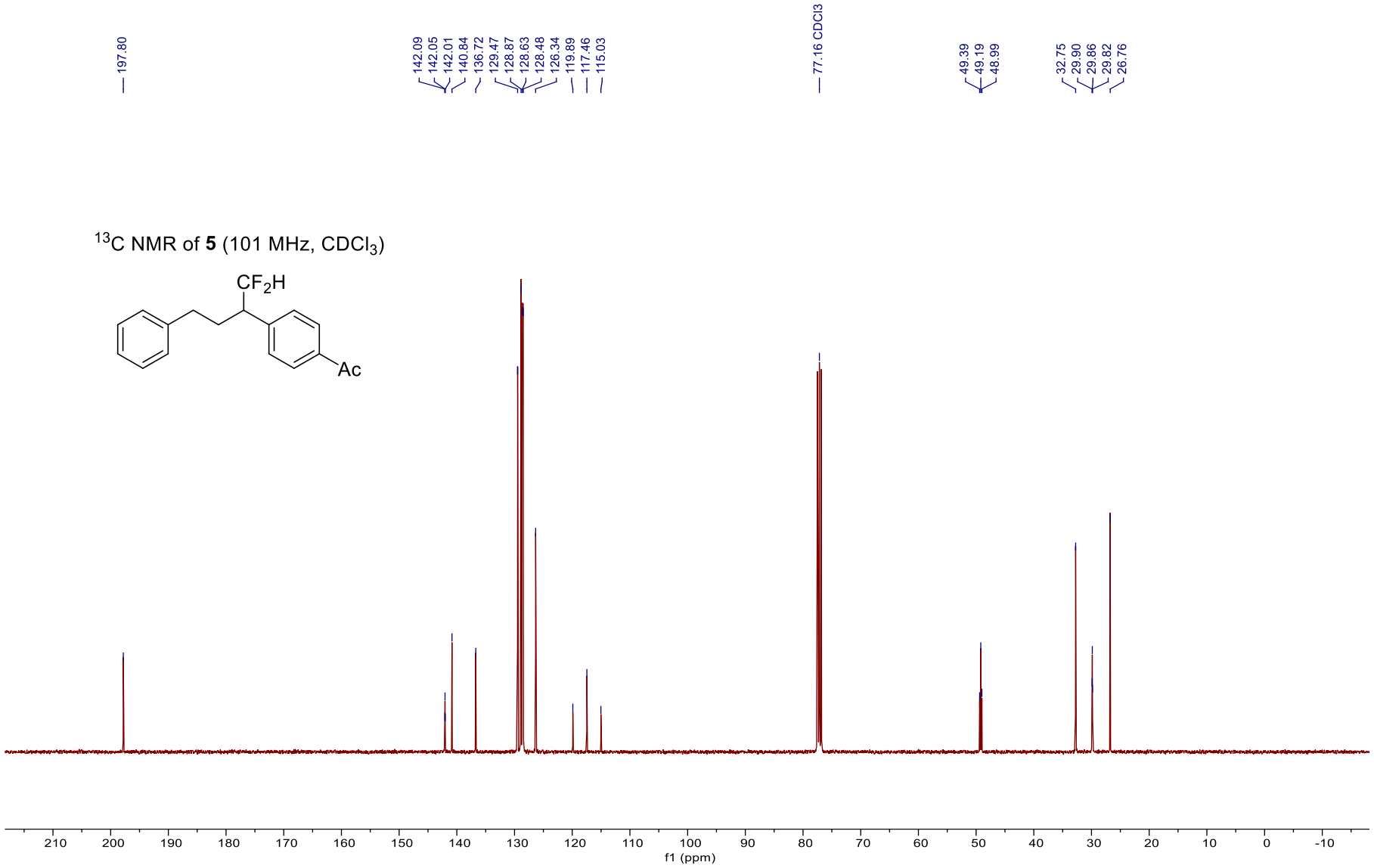

141.32
140.76
140.74
135.72
135.68
135.64
129.56
128.95
128.58
127.60
127.52
127.21
126.22
120.44
118.01
115.58
77.16 CDCl3
49.16
48.96
48.76
32.89
29.91
29.87
29.83
^{13}C NMR of **4** (101 MHz, $CDCl_3$)
CF_2H
Ph
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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

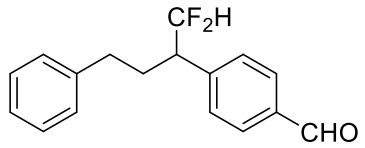


^{19}F NMR of **5** (376 MHz, $CDCl_3$)

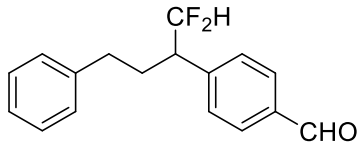



197.80
142.09
142.05
142.01
140.84
136.72
129.47
128.87
128.63
128.48
126.34
119.89
117.46
115.03
77.16 CDCl3
49.39
49.19
48.99
32.75
29.90
29.86
29.82
26.76
^{13}C NMR of **5** (101 MHz, $CDCl_3$)
CF_2H
Ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

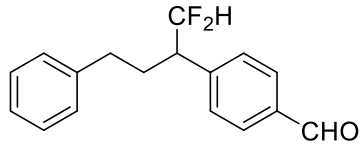
^{1}H NMR of **6** (400 MHz, $CDCl_3$)

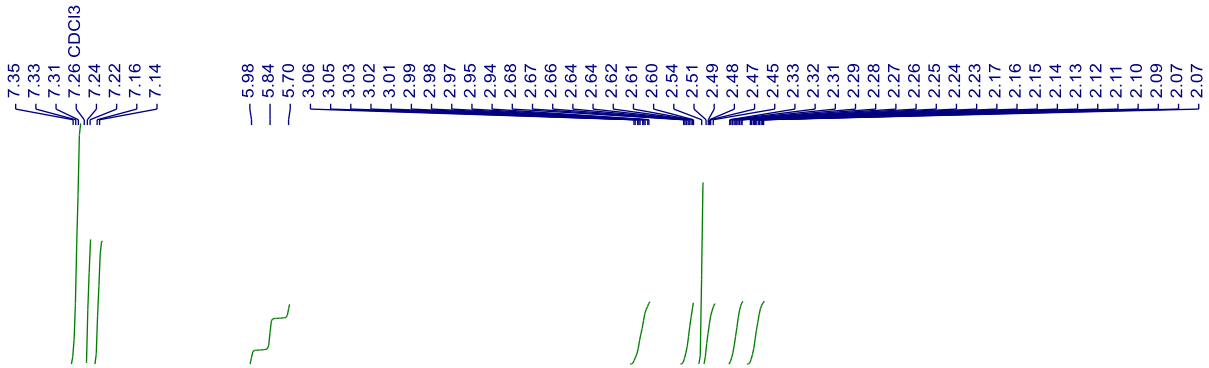


^{19}F NMR of **6** (376 MHz, $CDCl_3$)

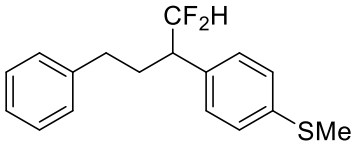


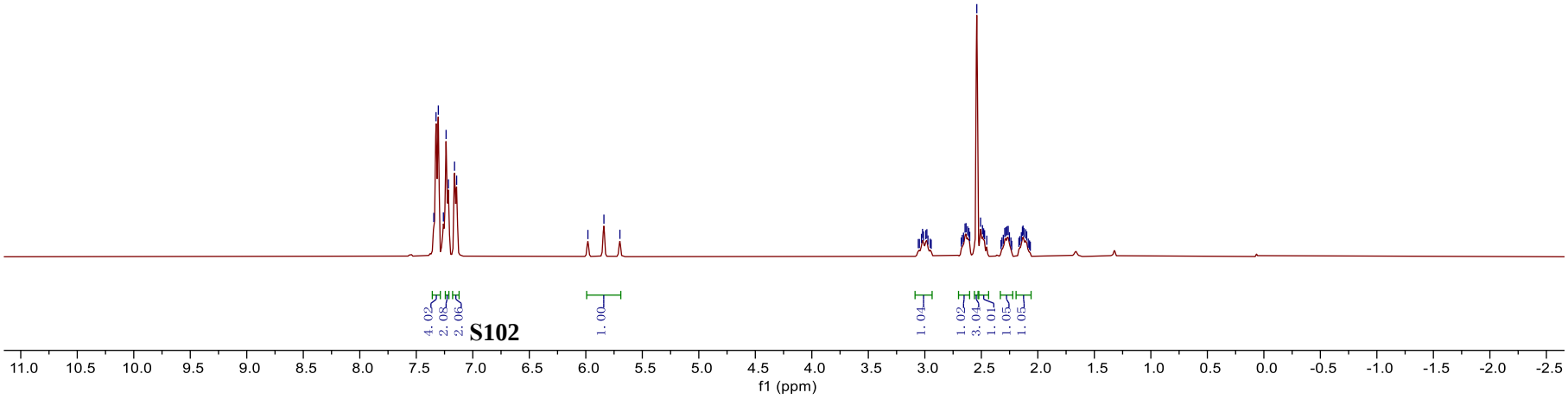
^{13}C NMR of **6** (101 MHz, $CDCl_3$)



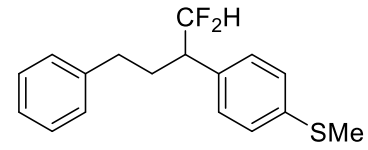


^{1}H NMR of **7** (400 MHz, $CDCl_3$)

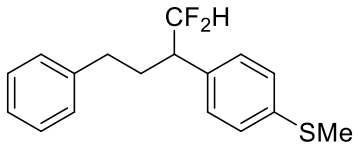




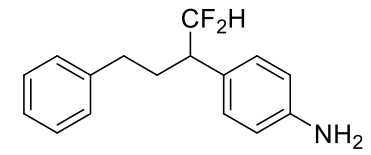
^{19}F NMR of **7** (376 MHz, $CDCl_3$)

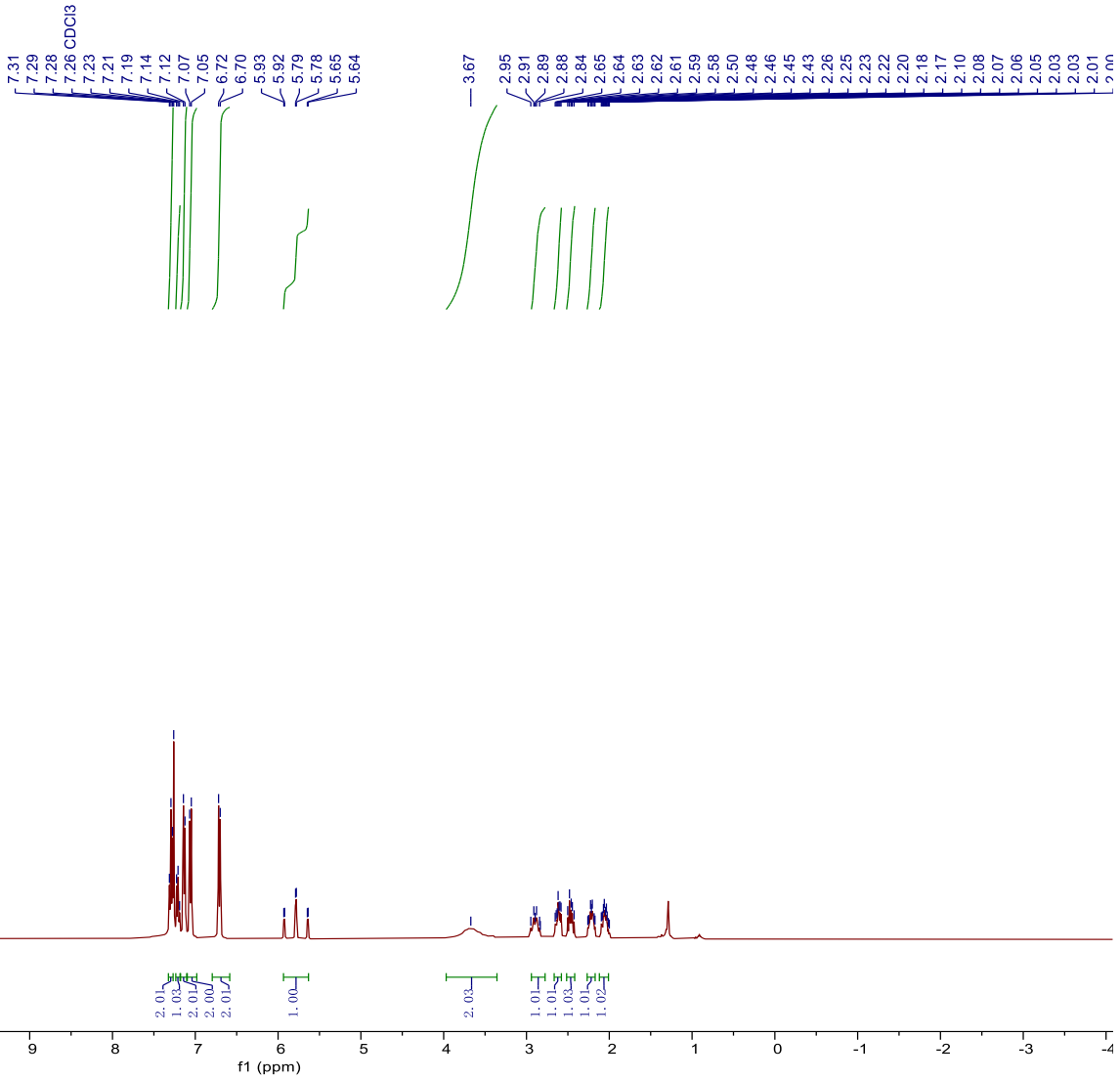


^{13}C NMR of **7** (101 MHz, $CDCl_3$)

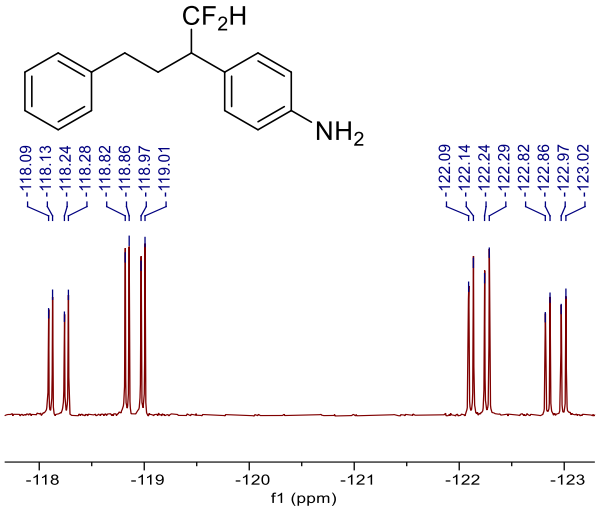


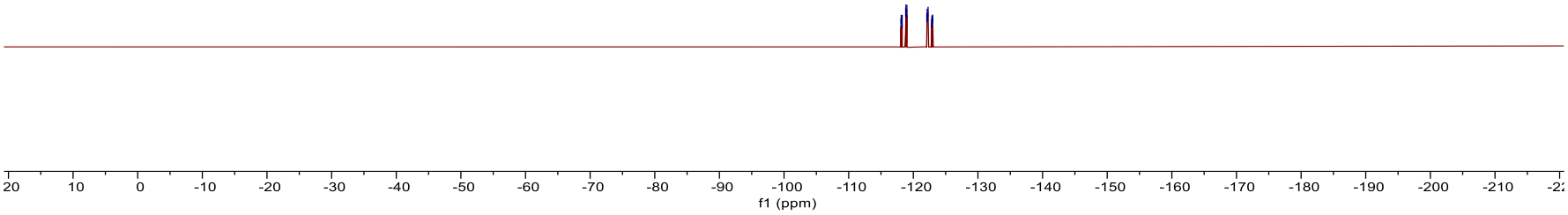
^{1}H NMR of **8** (400 MHz, $CDCl_3$)



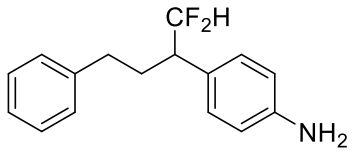


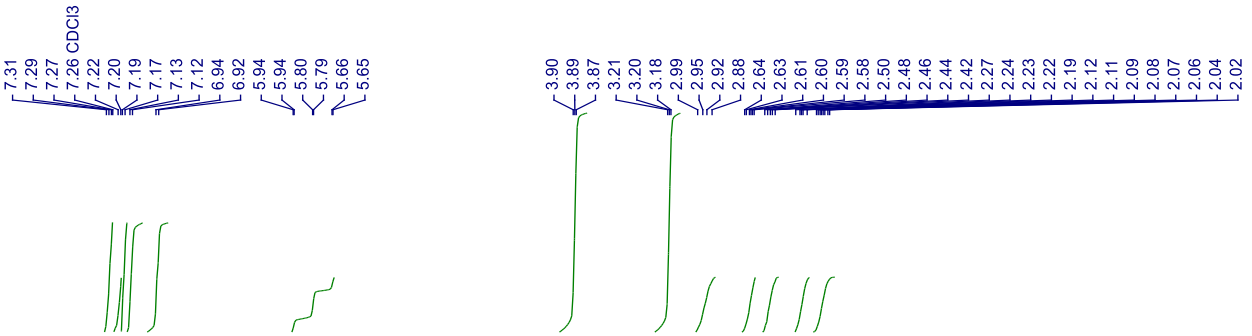
^{19}F NMR of **8** (376 MHz, $CDCl_3$)



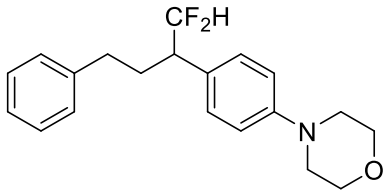


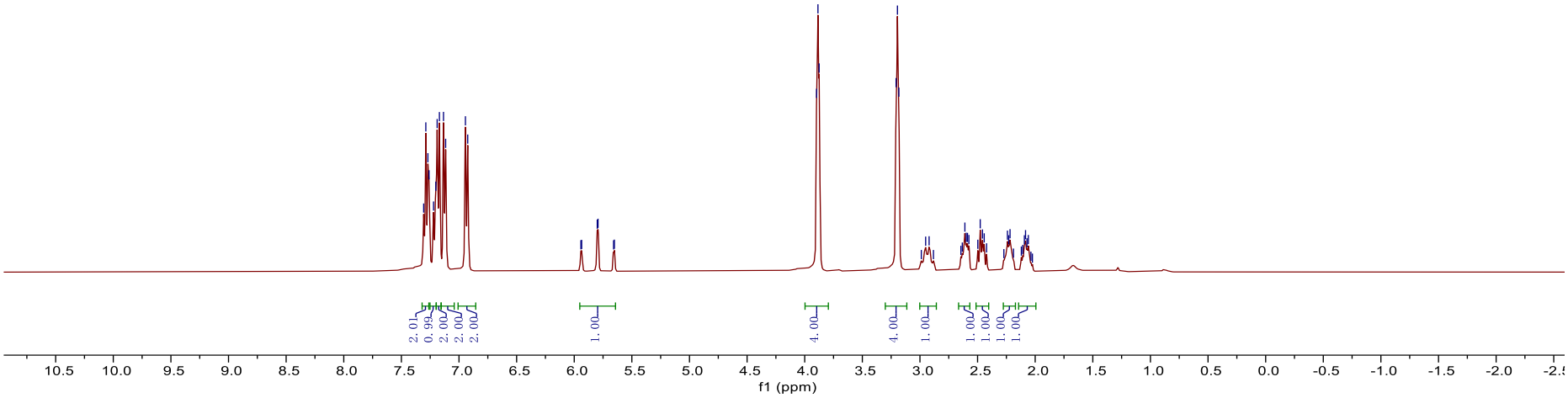
^{13}C NMR of **8** (101 MHz, $CDCl_3$)



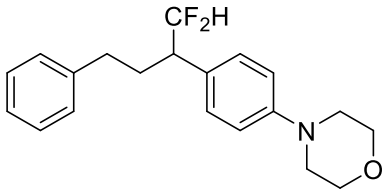


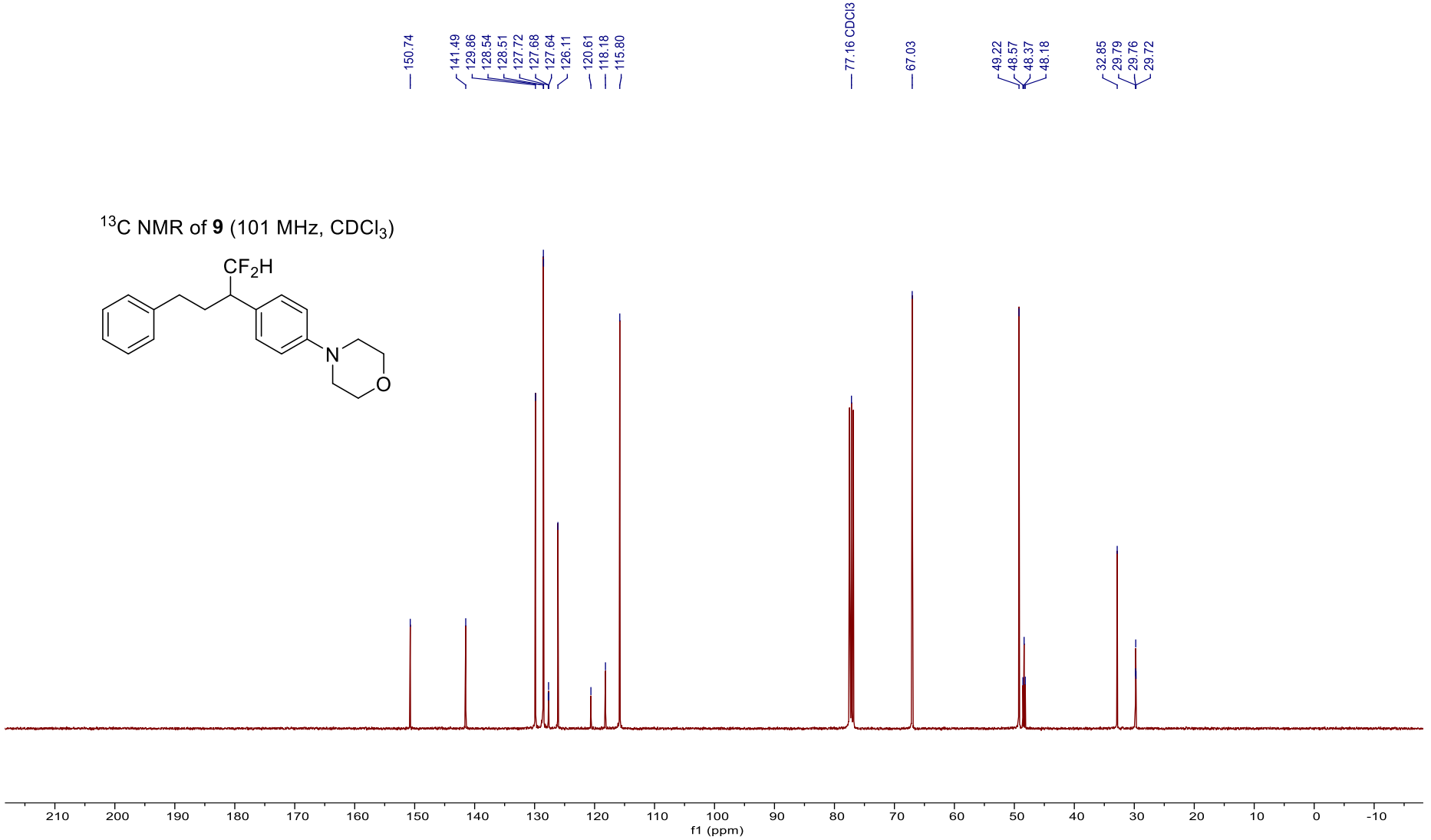
^{1}H NMR of **9** (400 MHz, $CDCl_3$)



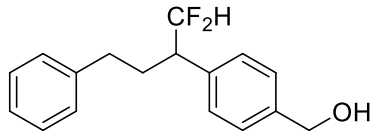


^{19}F NMR of **9** (376 MHz, $CDCl_3$)

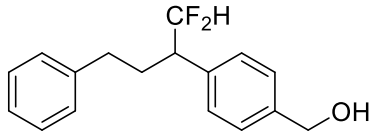



150.74
141.49
129.86
128.54
128.51
127.72
127.68
127.64
126.11
120.61
118.18
115.80
77.16 CDCl3
67.03
49.22
48.57
48.37
48.18
32.85
29.79
29.76
29.72
13C NMR of 9 (101 MHz, CDCl3)
CF2H
N
O
f1 (ppm)

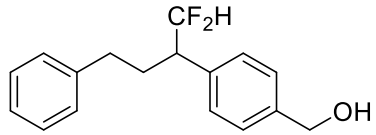
^{1}H NMR of **10** (400 MHz, $CDCl_3$)

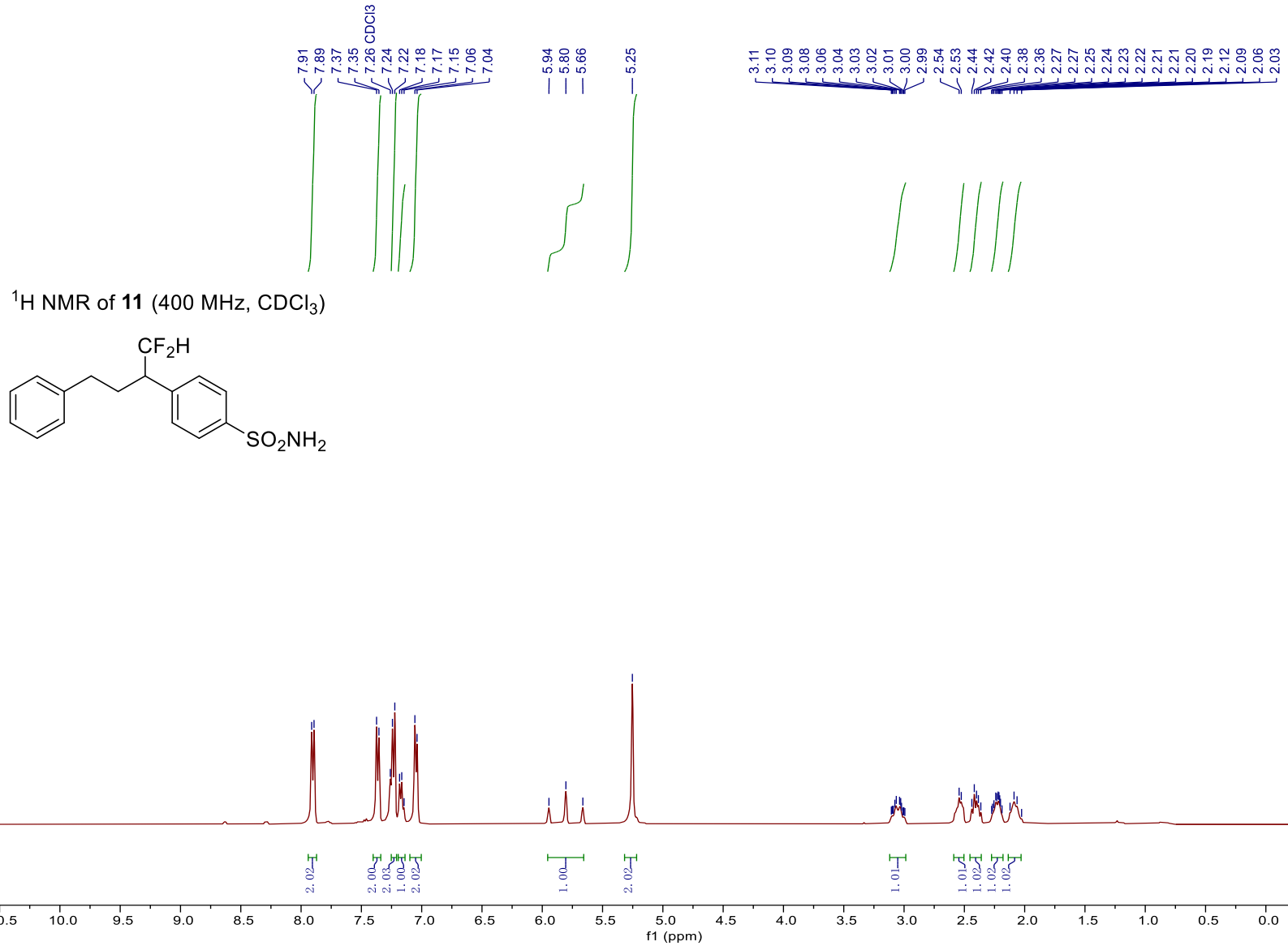


^{19}F NMR of **10** (376 MHz, $CDCl_3$)



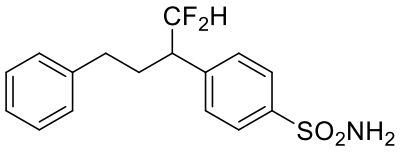
^{13}C NMR of **10** (101 MHz, $CDCl_3$)

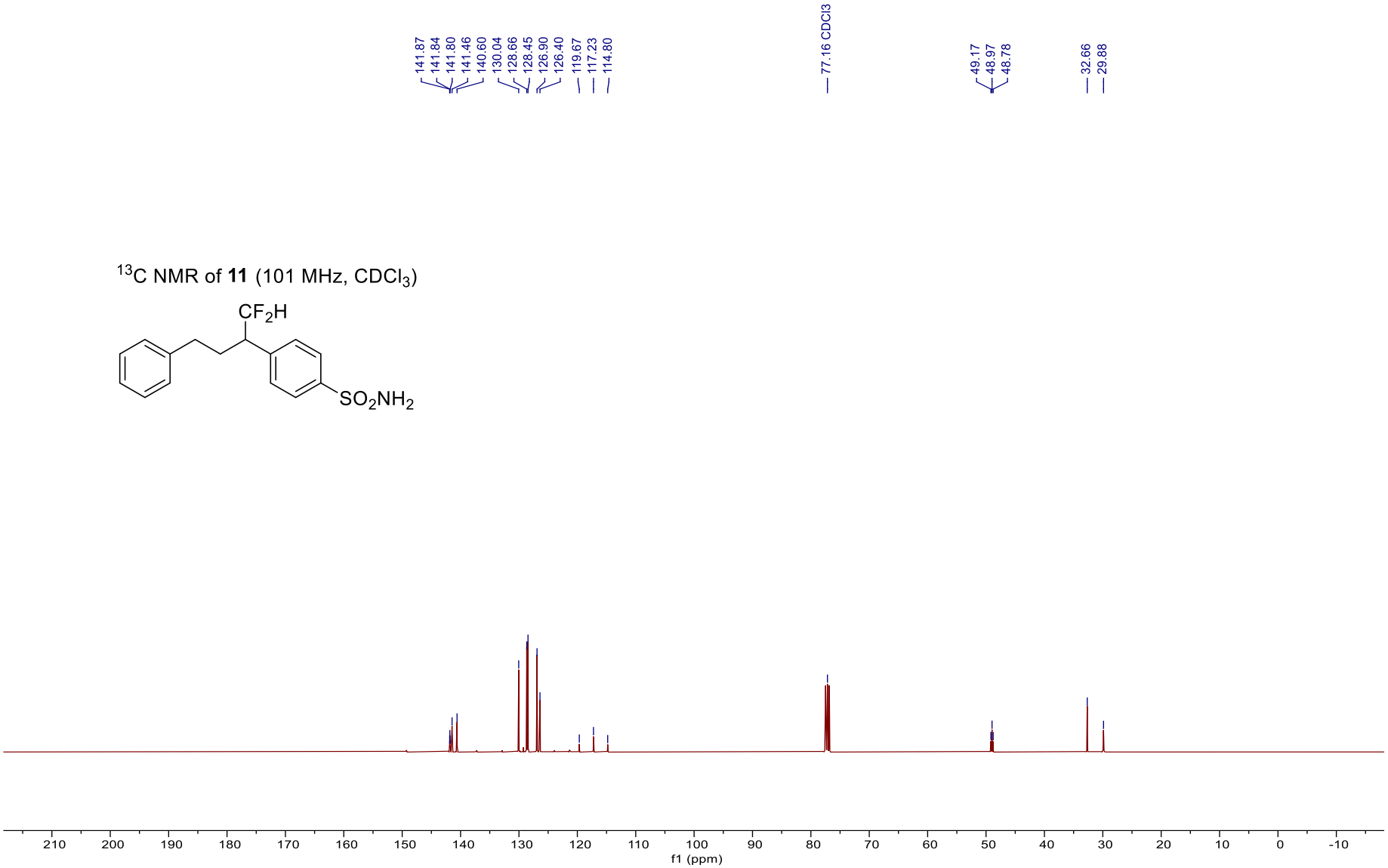




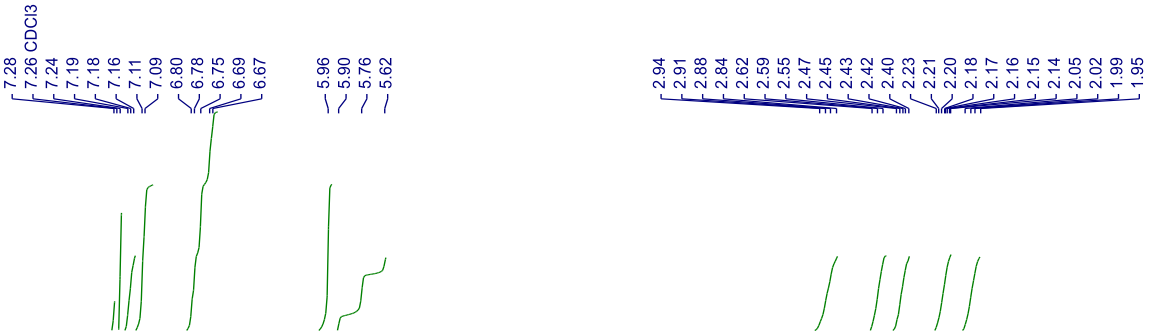
^{1}H NMR of **11** (400 MHz, $CDCl_3$)

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

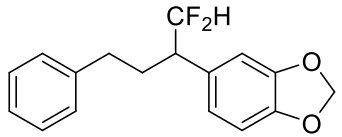


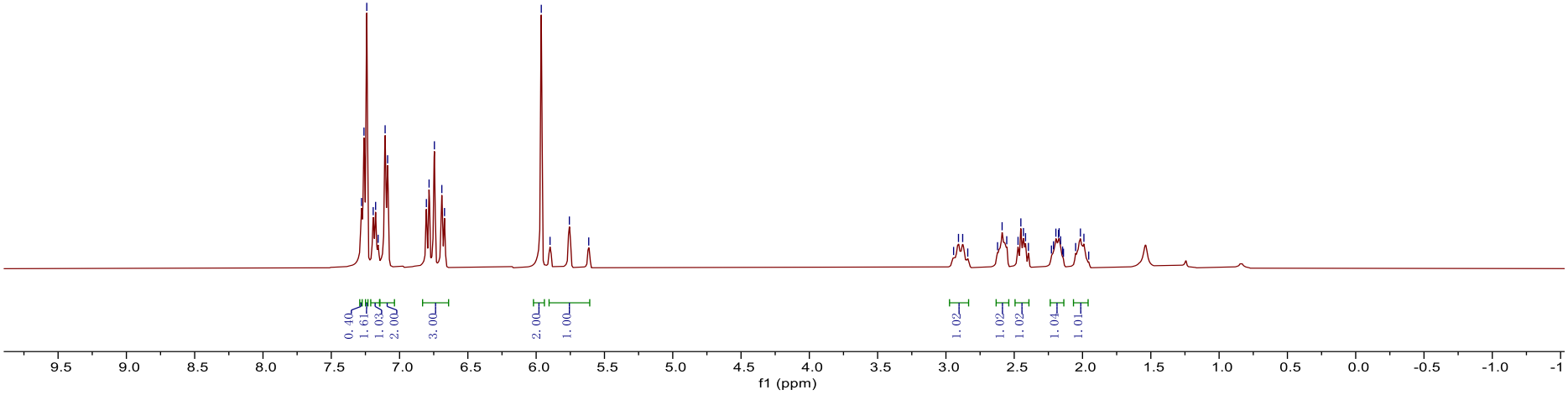


^{13}C NMR of **11** (101 MHz, $CDCl_3$)

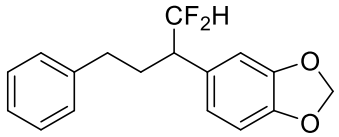


^{1}H NMR of **12** (400 MHz, $CDCl_3$)

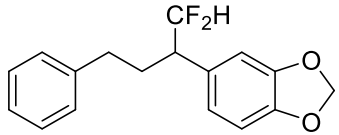




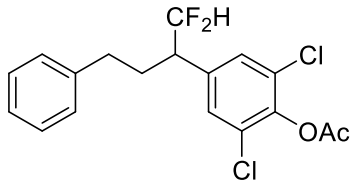
^{19}F NMR of **12** (376 MHz, $CDCl_3$)



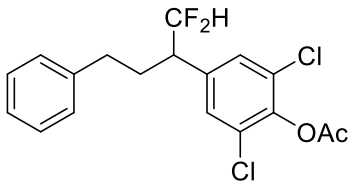
^{13}C NMR of **12** (101 MHz, $CDCl_3$)



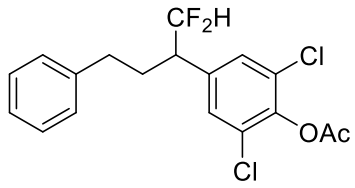
^{1}H NMR of **13** (400 MHz, $CDCl_3$)



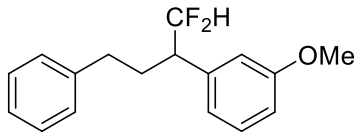
^{19}F NMR of **13** (376 MHz, $CDCl_3$)



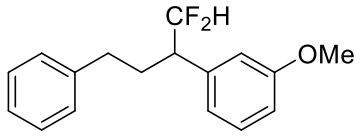
^{13}C NMR of **13** (101 MHz, $CDCl_3$)



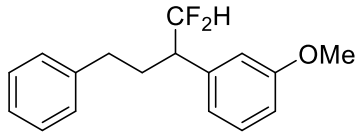
^{1}H NMR of **14** (400 MHz, $CDCl_3$)

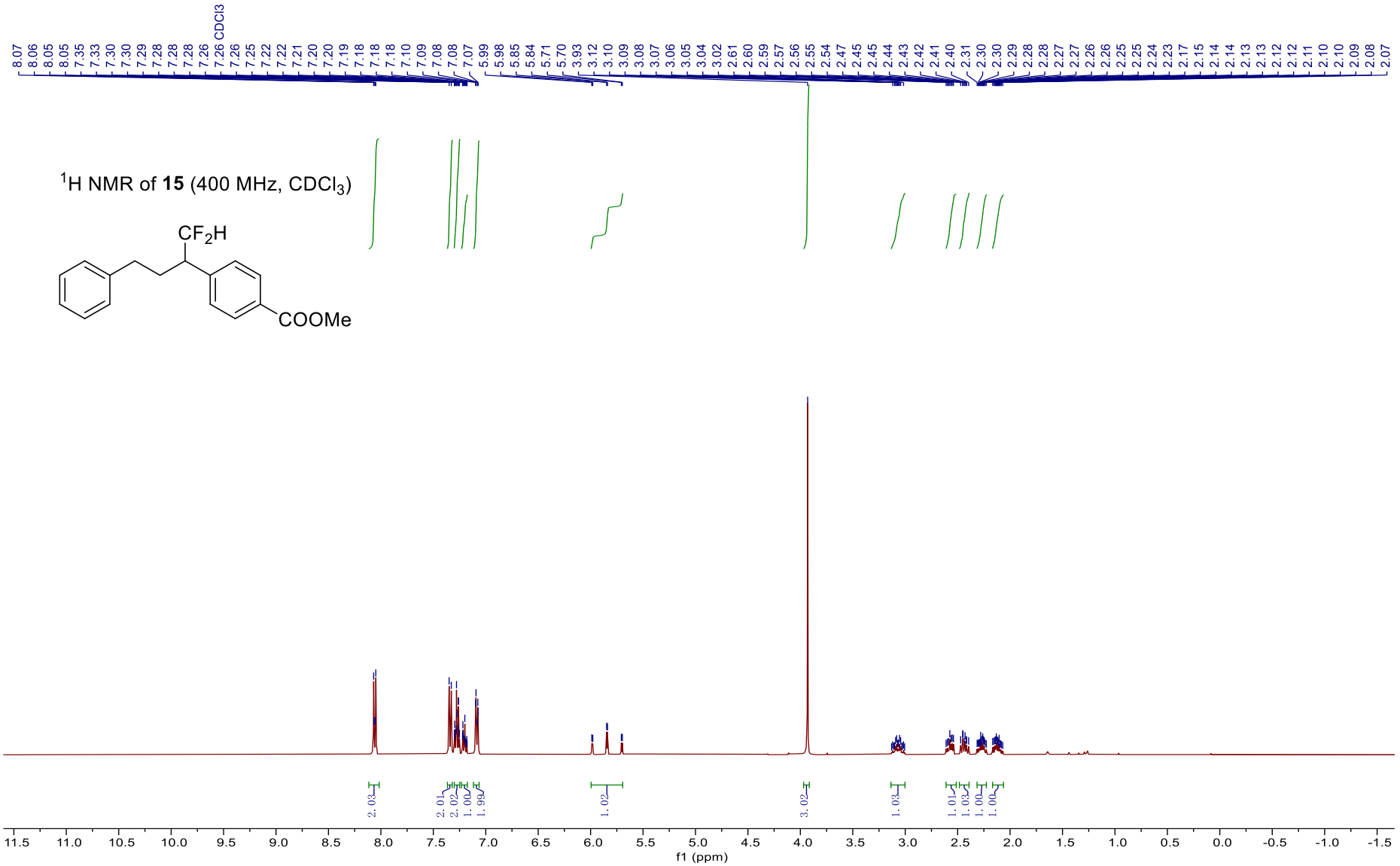


^{19}F NMR of **14** (376 MHz, $CDCl_3$)

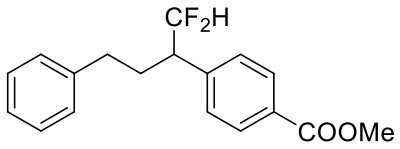


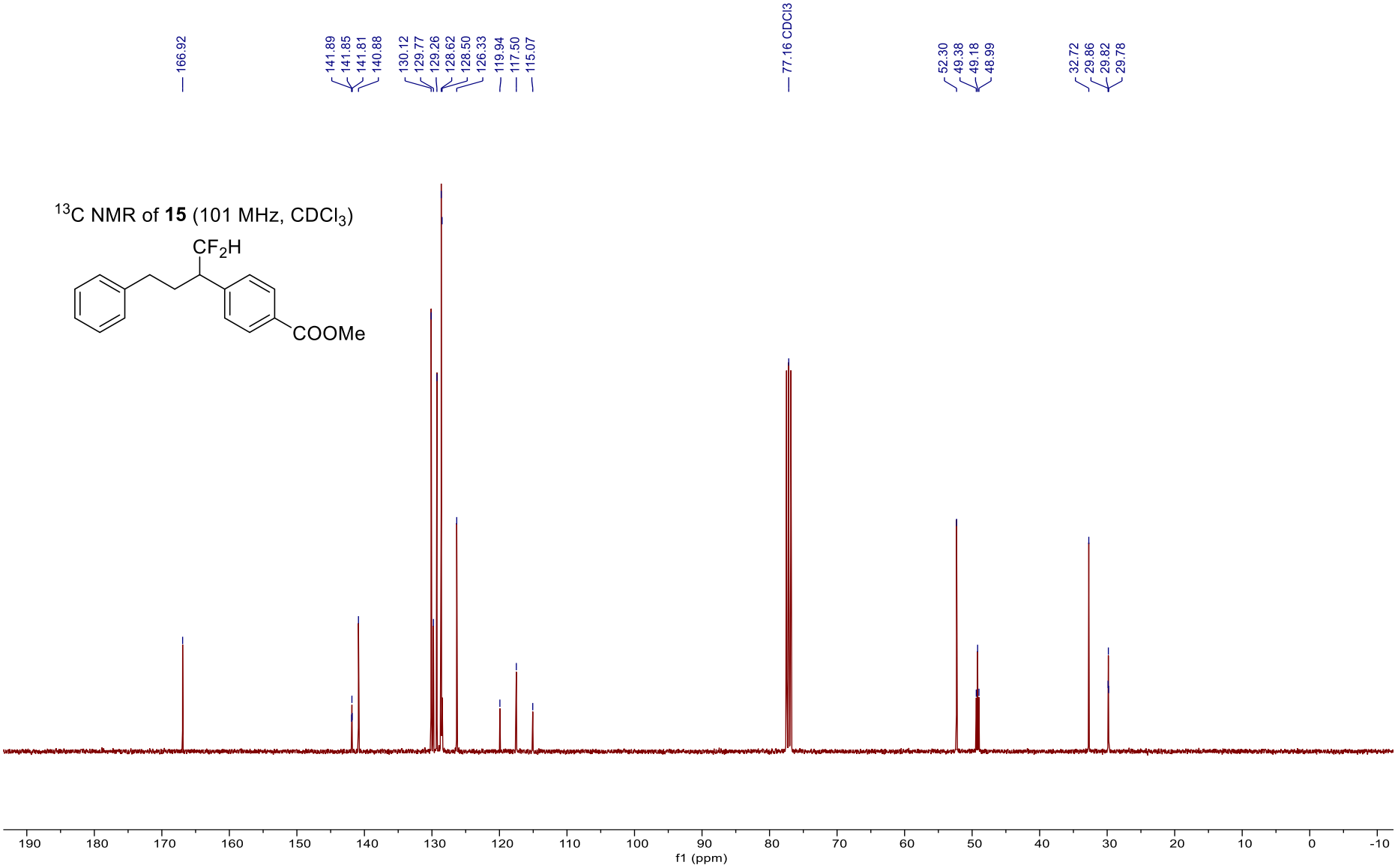
^{13}C NMR of **14** (101 MHz, $CDCl_3$)



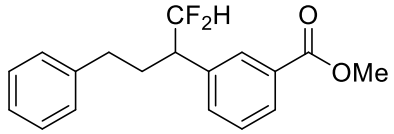

8.07 8.06 8.05 8.05 7.35 7.33 7.30 7.30 7.29 7.28 7.28 7.28 7.26 7.26 CDCl3 7.26 7.25 7.22 7.22 7.21 7.20 7.20 7.19 7.18 7.18 7.18 7.10 7.09 7.08 7.08 7.07 5.99 5.98 5.85 5.84 5.71 5.70 3.93 3.12 3.10 3.09 3.08 3.07 3.06 3.05 3.04 3.02 2.61 2.60 2.59 2.57 2.56 2.55 2.54 2.47 2.45 2.44 2.43 2.42 2.41 2.40 2.31 2.30 2.30 2.29 2.28 2.28 2.27 2.27 2.26 2.26 2.25 2.25 2.24 2.23 2.17 2.15 2.14 2.14 2.13 2.13 2.12 2.12 2.11 2.10 2.10 2.09 2.08 2.07
1H NMR of 15 (400 MHz, CDCl3)
CF2H
COOMe
2.03 2.01 2.02 1.00 1.99 1.02 3.02 1.03 1.01 1.03 1.00 1.00
11.5 11.0 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 0.0 -0.5 -1.0 -1.5
f1 (ppm)

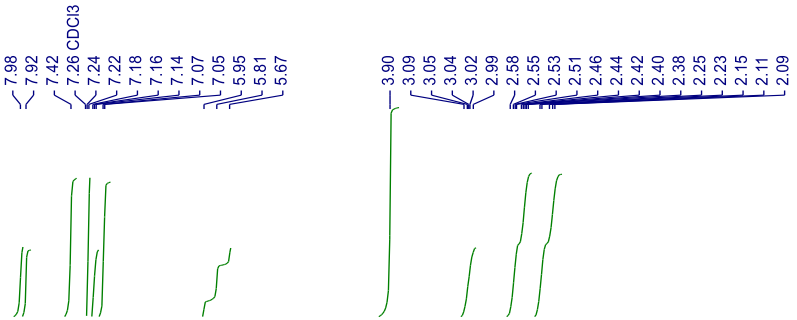
^{19}F NMR of **15** (376 MHz, $CDCl_3$)

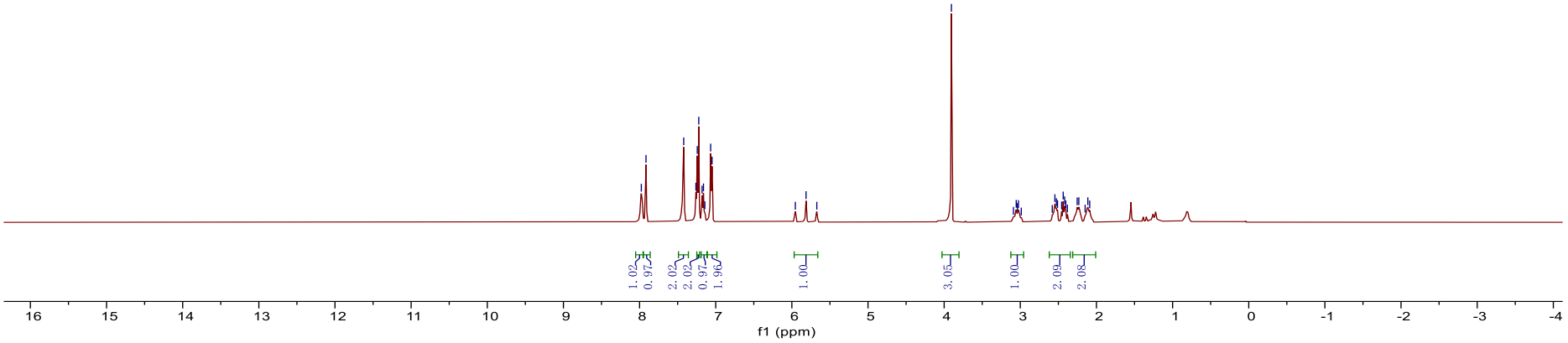



166.92
141.89
141.85
141.81
140.88
130.12
129.77
129.26
128.62
128.50
126.33
119.94
117.50
115.07
77.16 CDCl3
52.30
49.38
49.18
48.99
32.72
29.86
29.82
29.78
13C NMR of 15 (101 MHz, CDCl3)
CF2H
COOMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

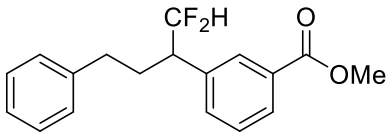
^{1}H NMR of **16** (400 MHz, $CDCl_3$)

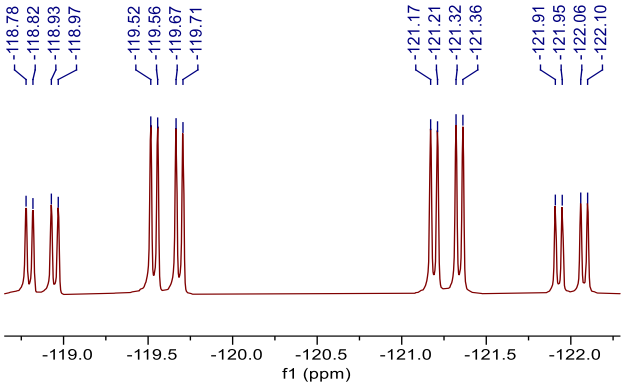


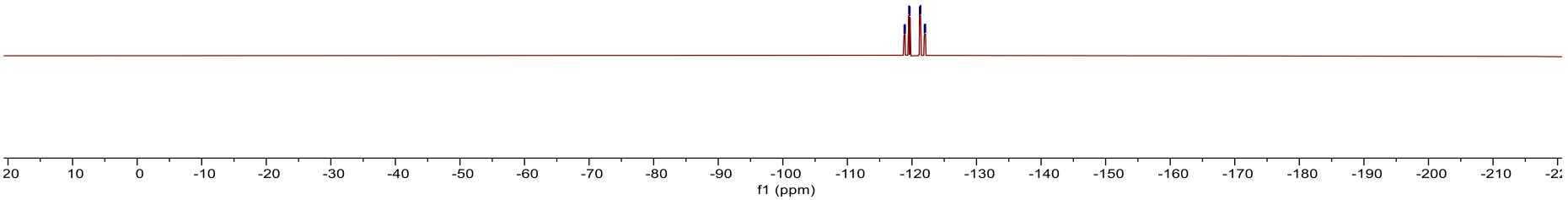


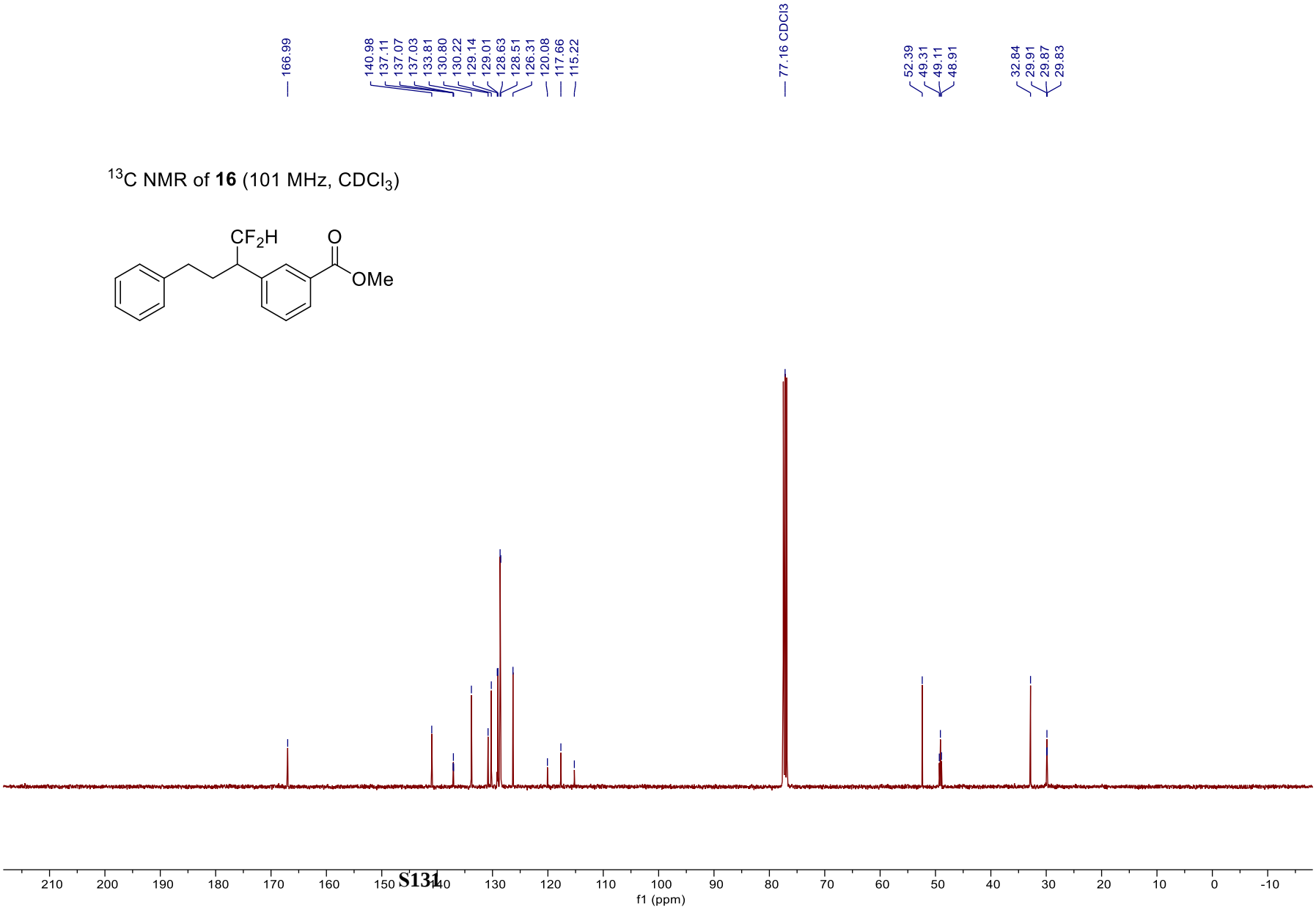


^{19}F NMR of **16** ($CDCl_3$)

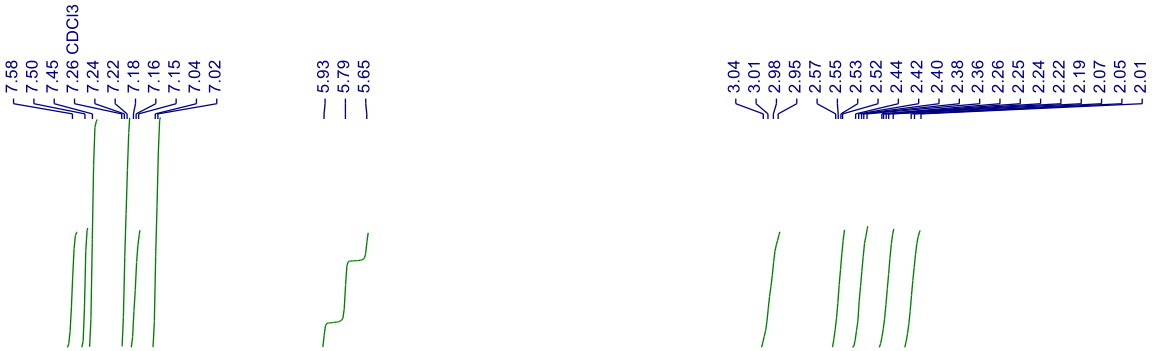




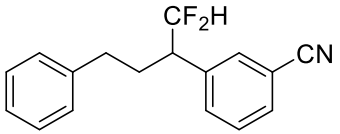


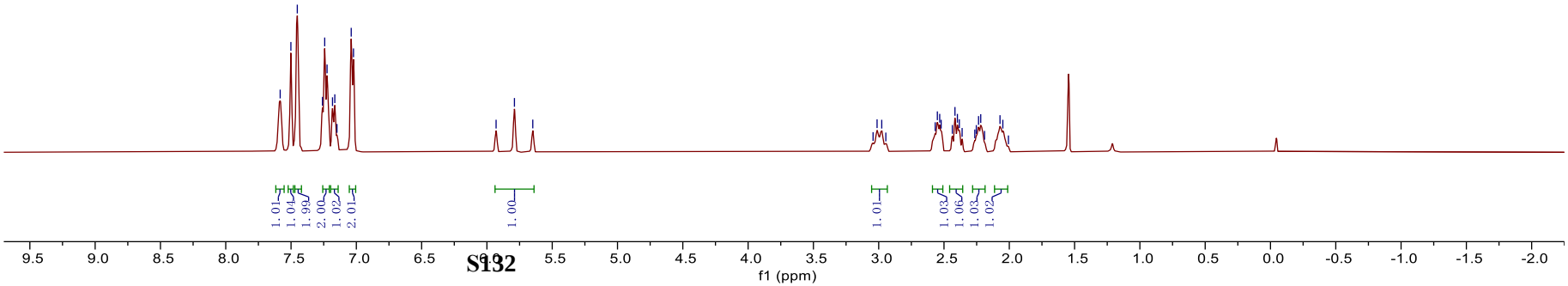


^{13}C NMR of **16** ($CDCl_3$)

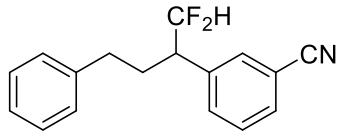


^{1}H NMR of **17** (400 MHz, $CDCl_3$)

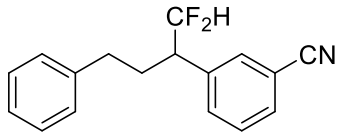


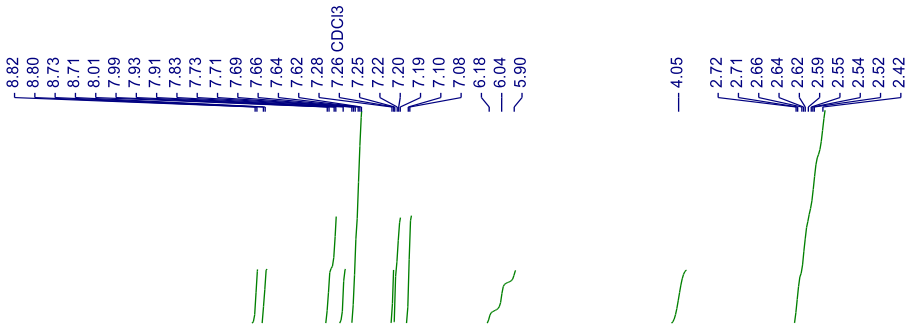


^{19}F NMR of **17** (376 MHz, $CDCl_3$)

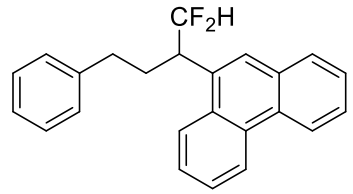


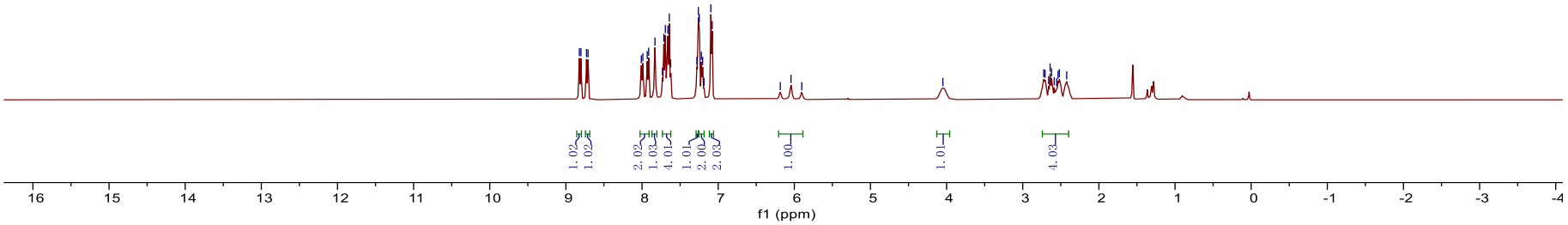
^{13}C NMR of **17** (101 MHz, $CDCl_3$)



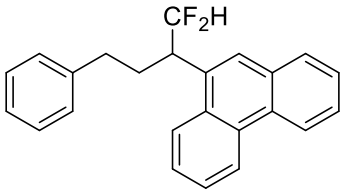


^{1}H NMR of **18** (400 MHz, $CDCl_3$)

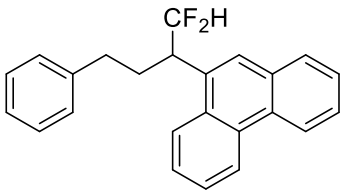




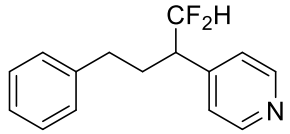
^{19}F NMR of **18** (376 MHz, $CDCl_3$)

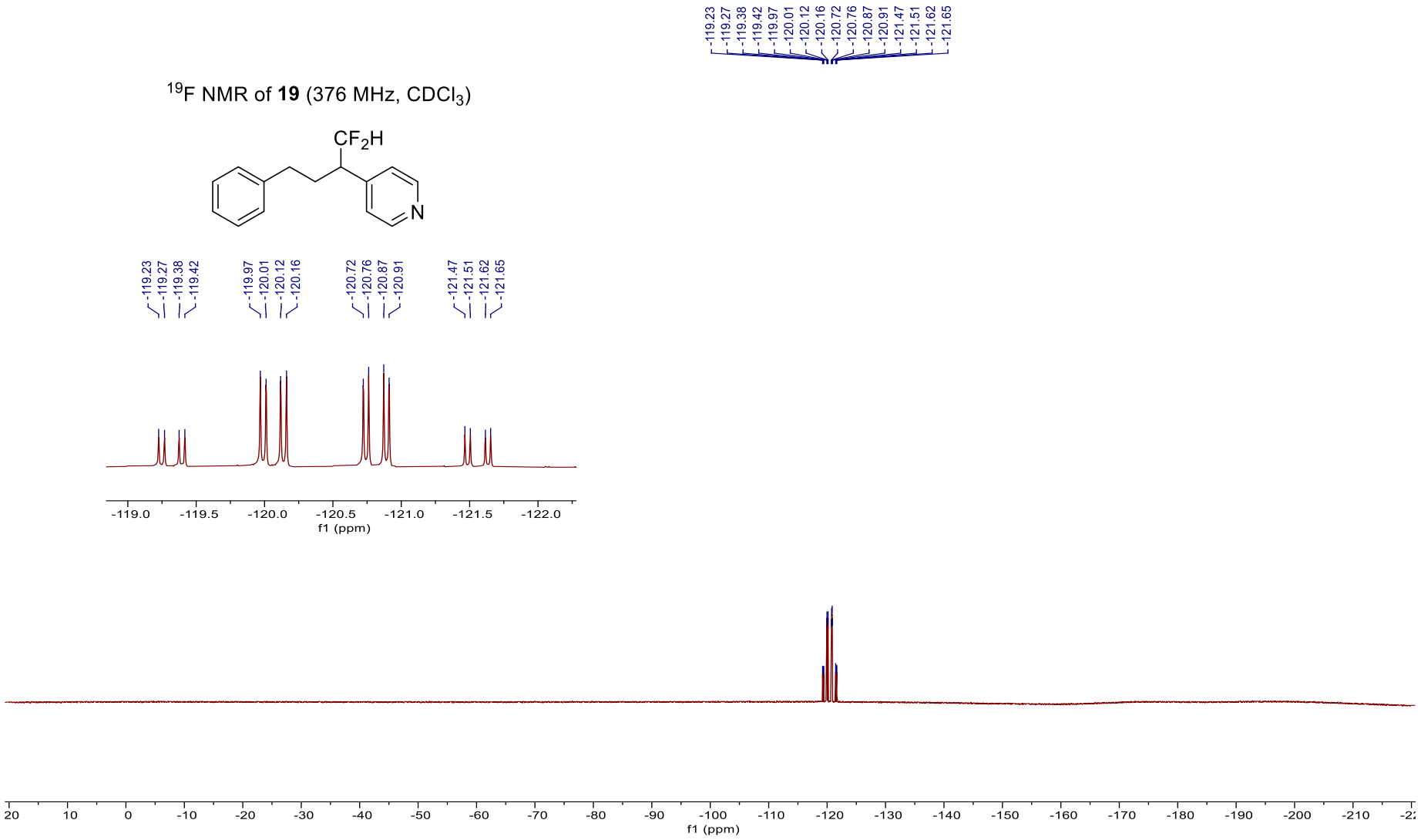


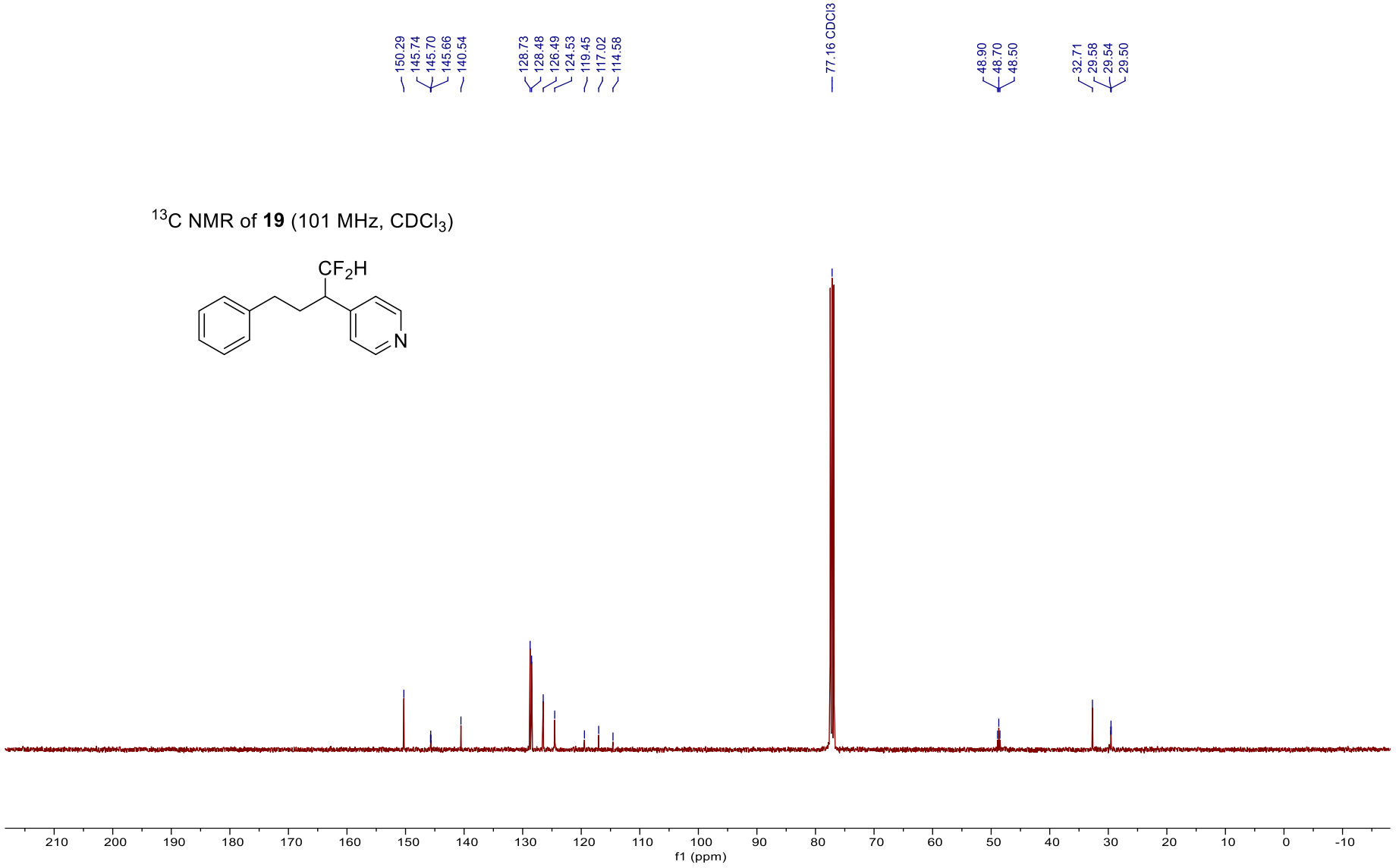
^{13}C NMR of **18** (101 MHz, $CDCl_3$)



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

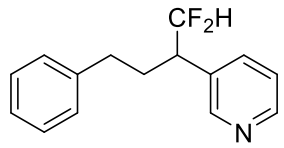


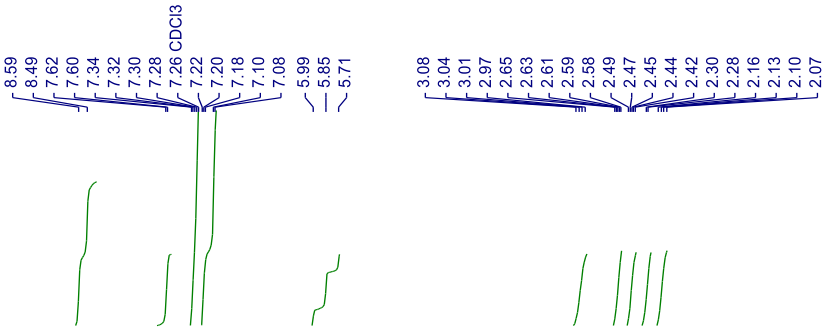

-119.23
-119.27
-119.38
-119.42
-119.97
-120.01
-120.12
-120.16
-120.72
-120.76
-120.87
-120.91
-121.47
-121.51
-121.62
-121.65
19F NMR of 19 (376 MHz, CDCl3)
CF2H
N
-119.0
-119.5
-120.0
-120.5
-121.0
-121.5
-122.0
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

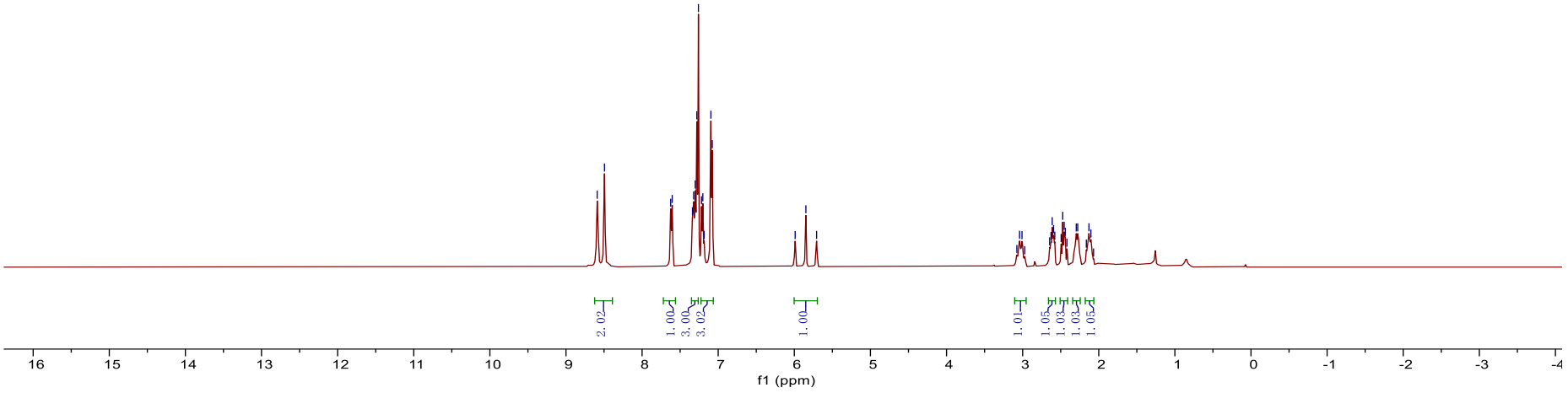


^{13}C NMR of **19** (101 MHz, $CDCl_3$)

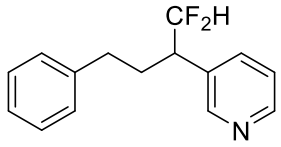
^{1}H NMR of **20** (400 MHz, $CDCl_3$)

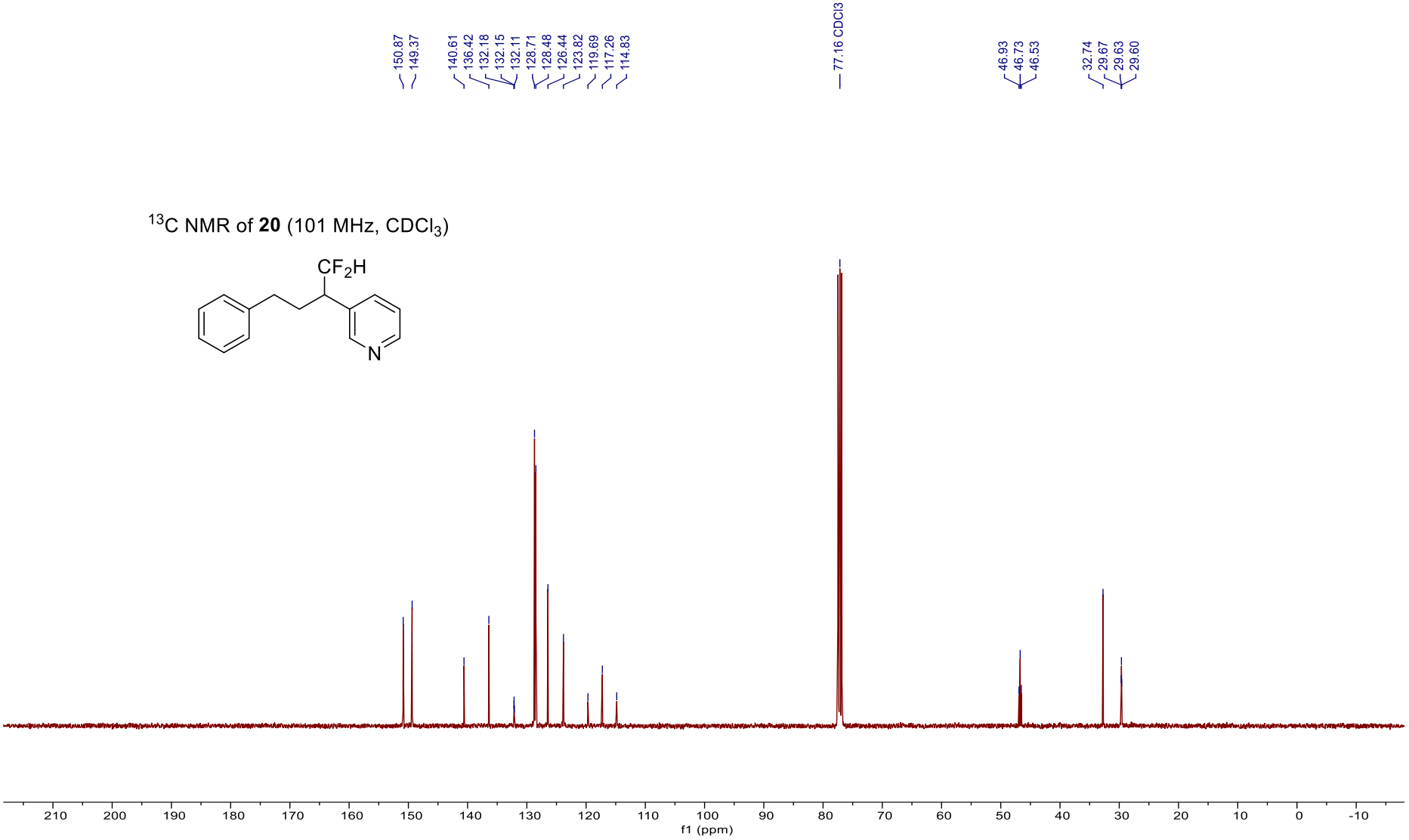




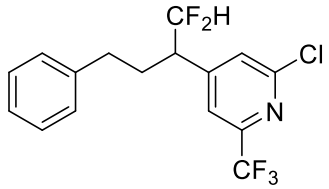


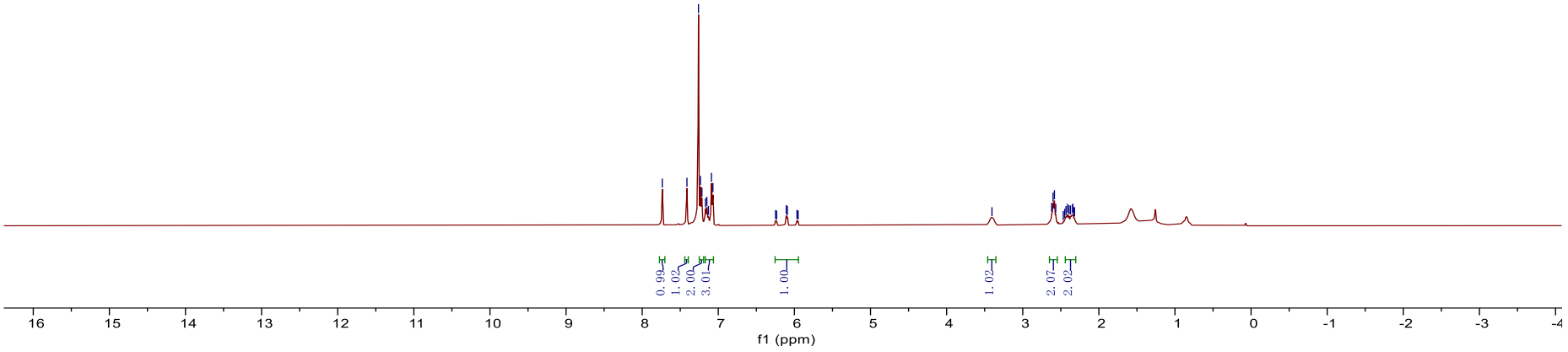
^{19}F NMR of **20** (376 MHz, $CDCl_3$)



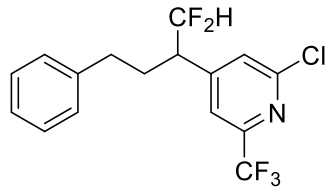

150.87
149.37
140.61
136.42
132.18
132.15
132.11
128.71
128.48
126.44
123.82
119.69
117.26
114.83
77.16 CDCl3
46.93
46.73
46.53
32.74
29.67
29.63
29.60
^{13}C NMR of **20** (101 MHz, $CDCl_3$)
CF_2H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

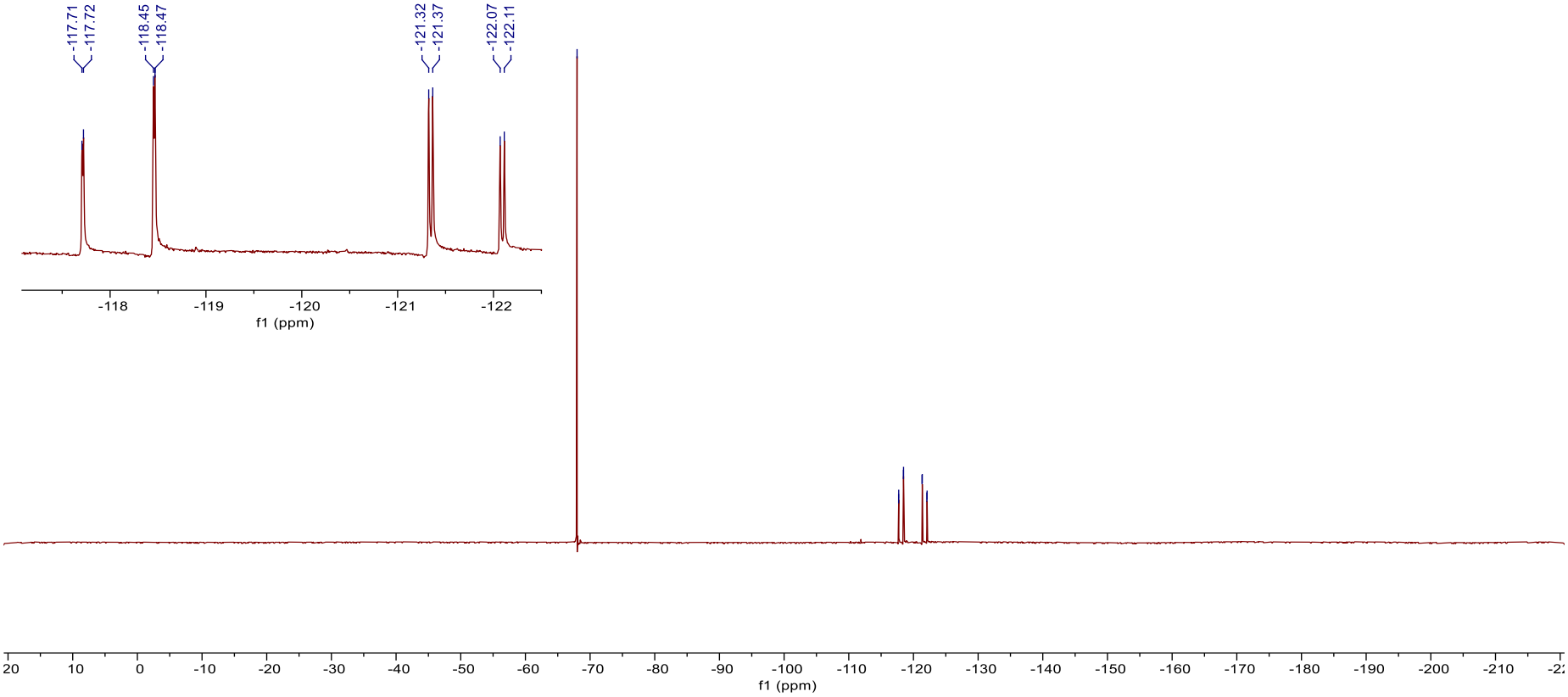
^{1}H NMR of **21** (400 MHz, $CDCl_3$)

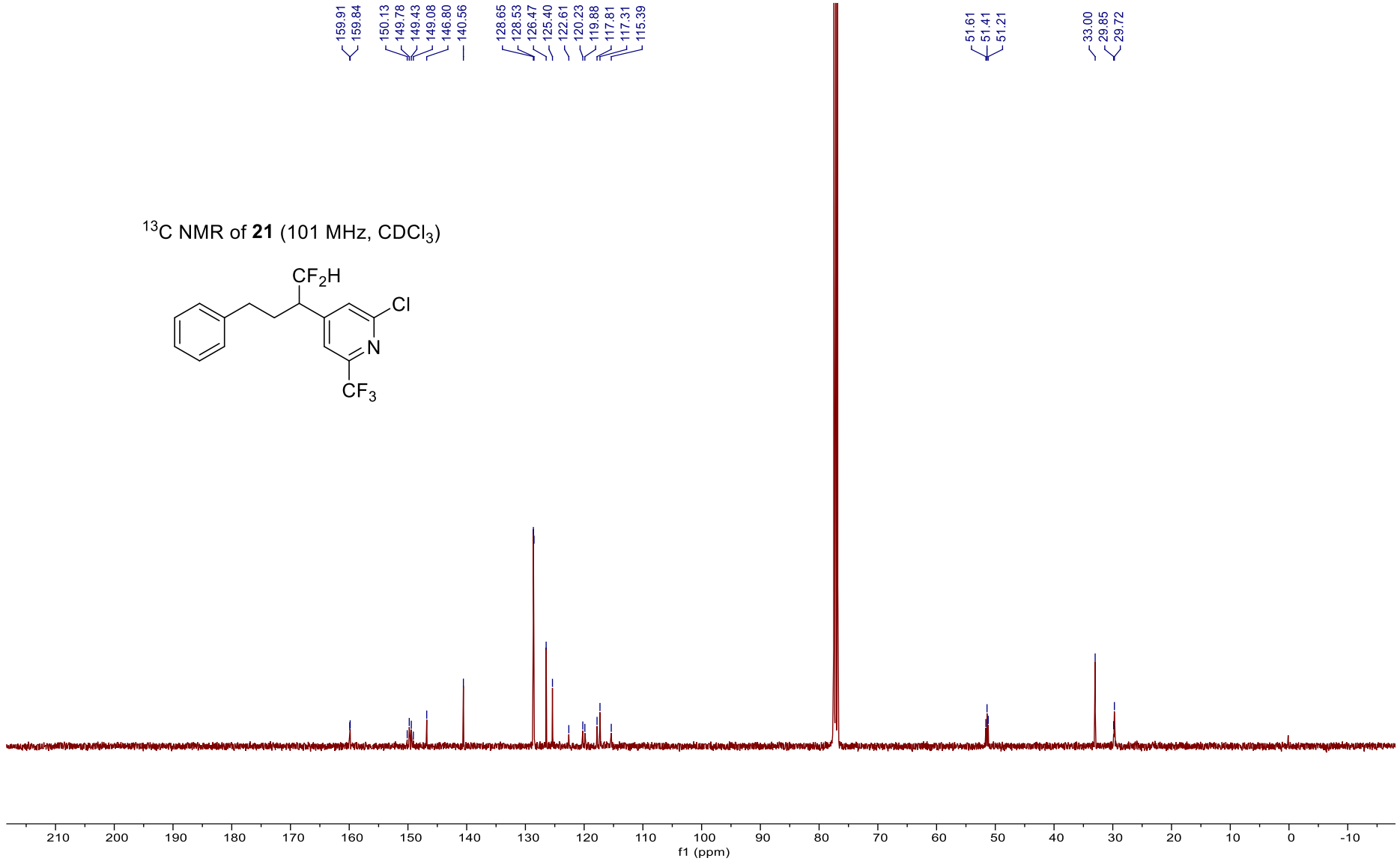




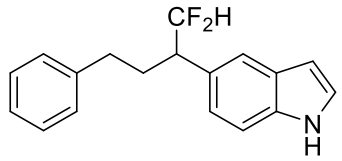
^{19}F NMR of **21** (376 MHz, $CDCl_3$)



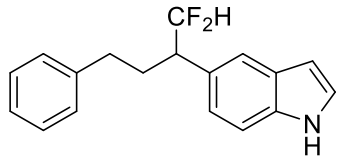



159.91
159.84
150.13
149.78
149.43
149.08
146.80
140.56
128.65
128.53
126.47
125.40
122.61
120.23
119.88
117.81
117.31
115.39
51.61
51.41
51.21
33.00
29.85
29.72
^{13}C NMR of **21** (101 MHz, $CDCl_3$)
CF_2H
Cl
N
CF_3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

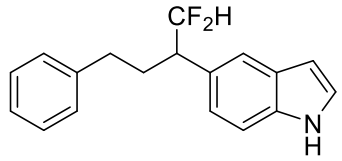
^{1}H NMR of **22** (400 MHz, $CDCl_3$)



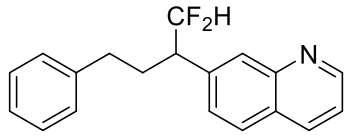
^{19}F NMR of **22** (376 MHz, $CDCl_3$)



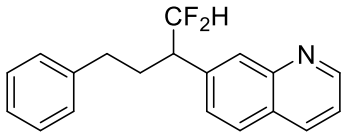
^{13}C NMR of **22** (101 MHz, $CDCl_3$)

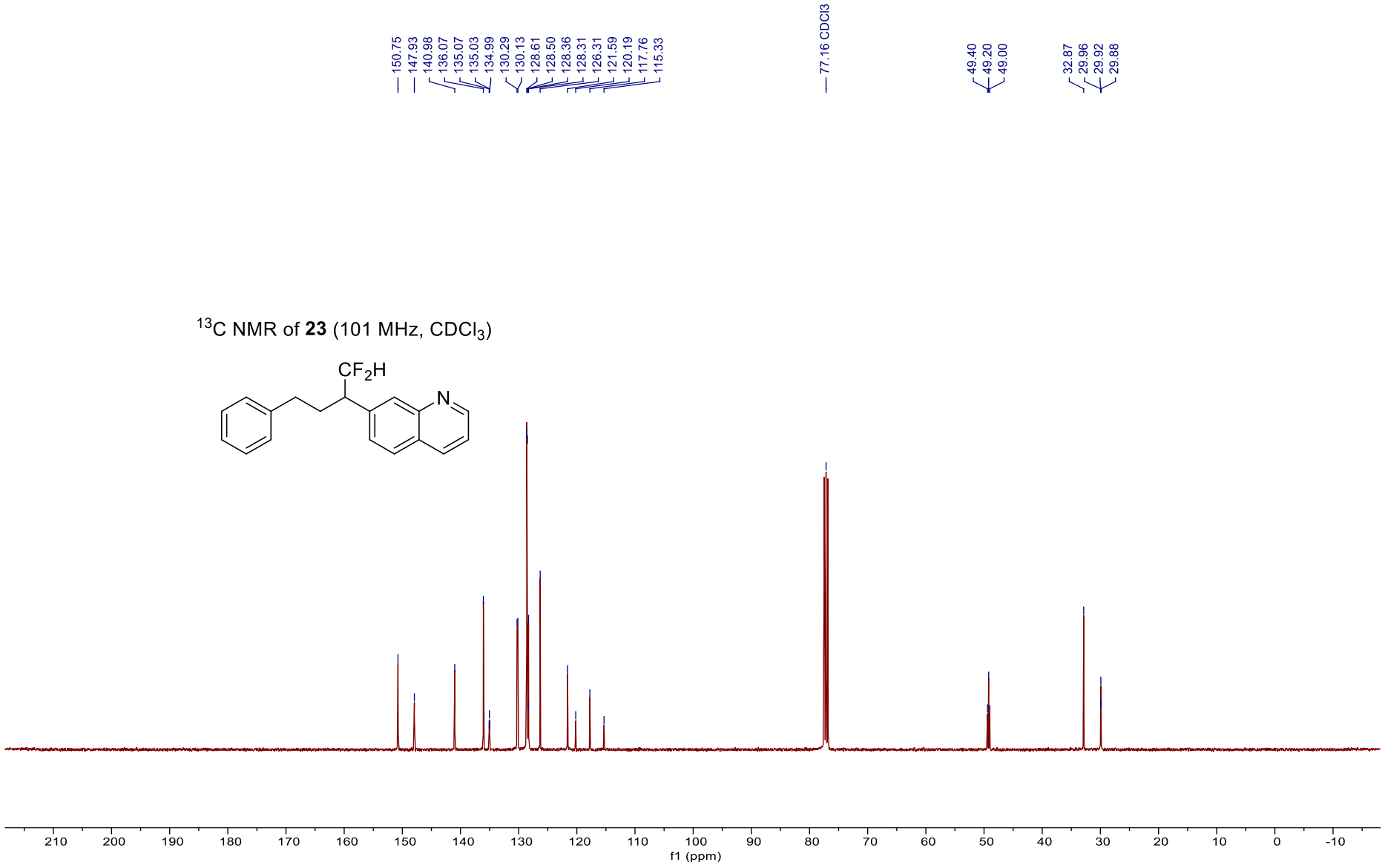


^{1}H NMR of **23** (400 MHz, $CDCl_3$)

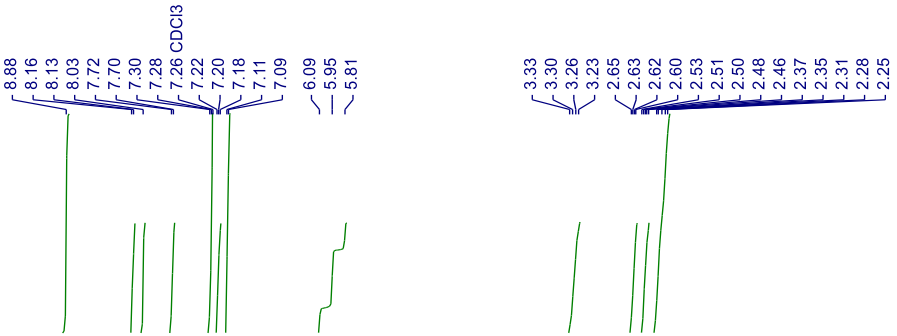


^{19}F NMR of **23** (376 MHz, $CDCl_3$)

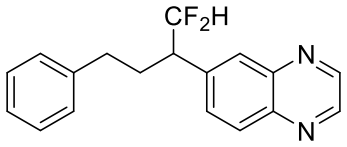


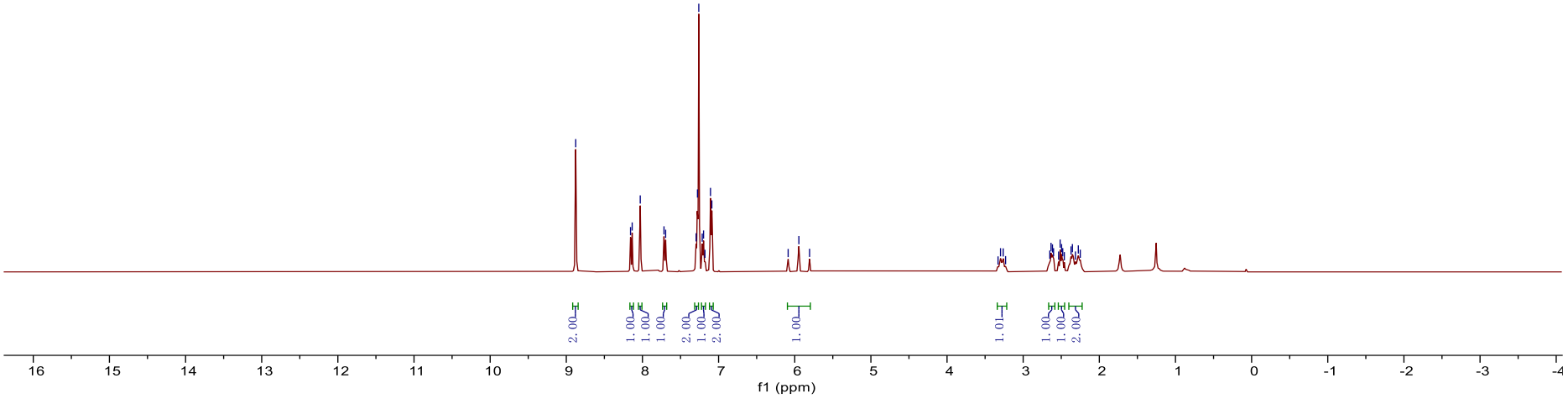


^{13}C NMR of **23** (101 MHz, $CDCl_3$)

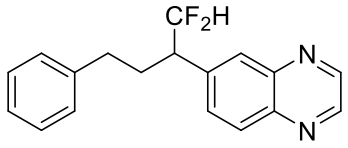


^{1}H NMR of **24** (400 MHz, $CDCl_3$)

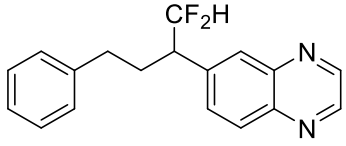


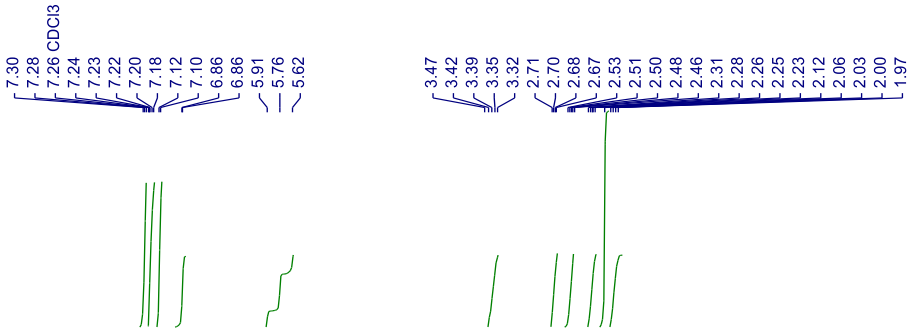


^{19}F NMR of **24** (376 MHz, $CDCl_3$)

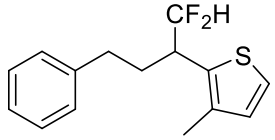


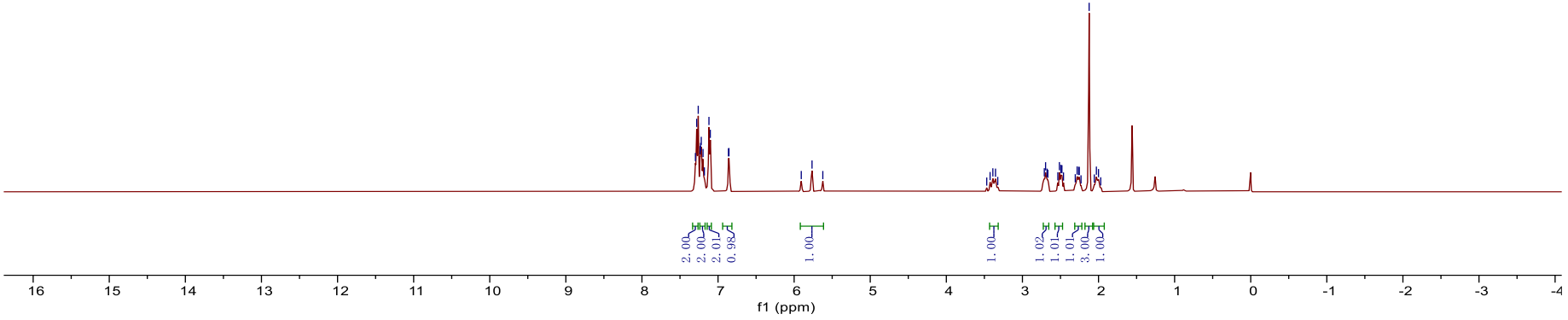
^{13}C NMR of **24** (101 MHz, $CDCl_3$)



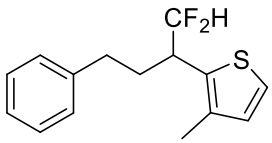


^{1}H NMR of **25** (400 MHz, $CDCl_3$)

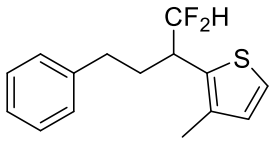




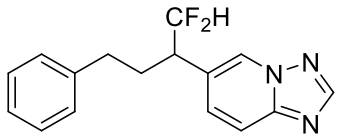
^{19}F NMR of **25** (376 MHz, $CDCl_3$)



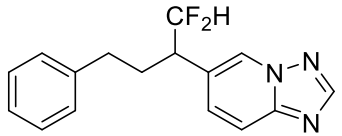
^{13}C NMR of **25** (101 MHz, $CDCl_3$)



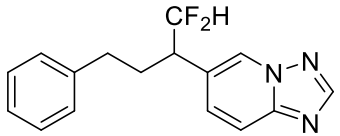
^{1}H NMR of **26** (400 MHz, $CDCl_3$)

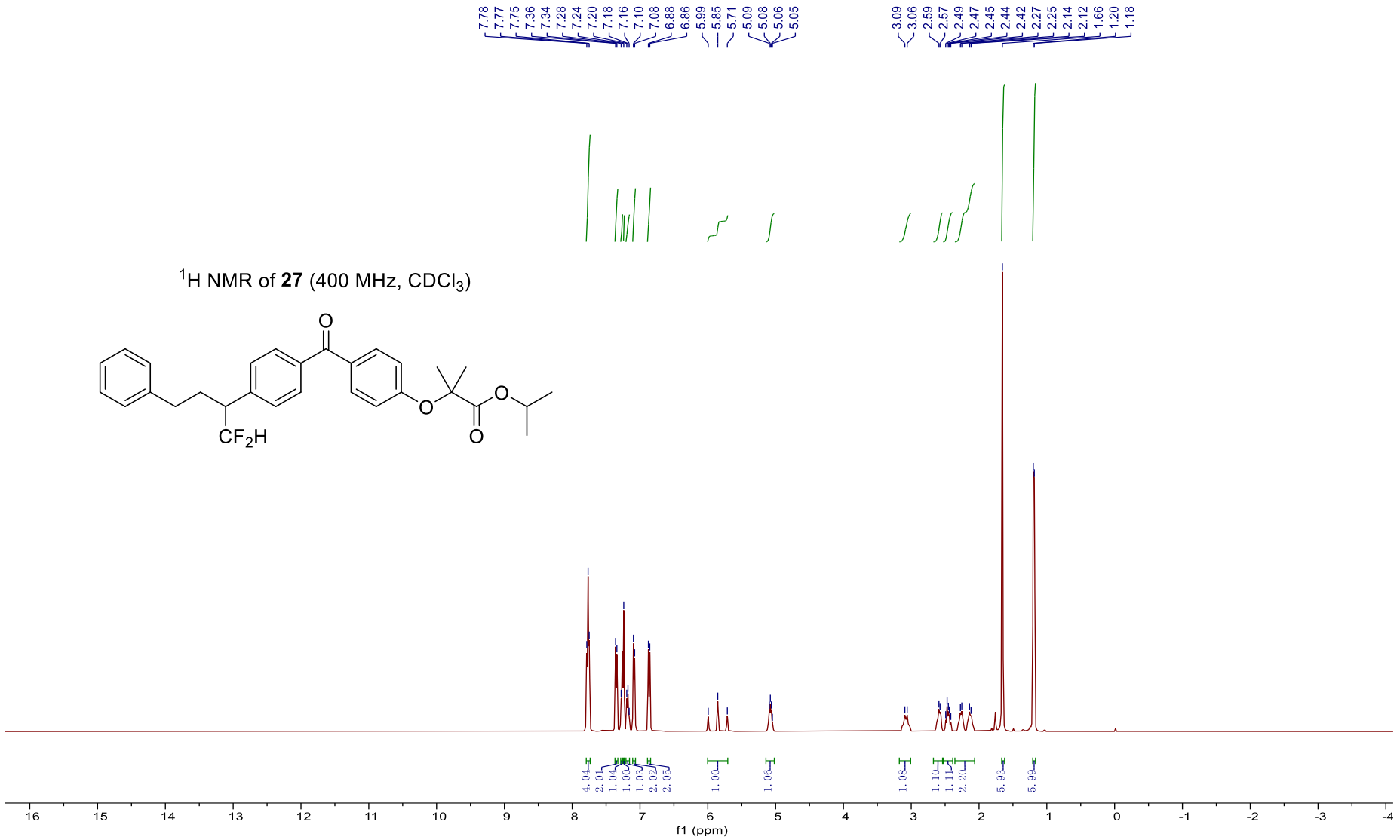


^{19}F NMR of **26** (376 MHz, $CDCl_3$)



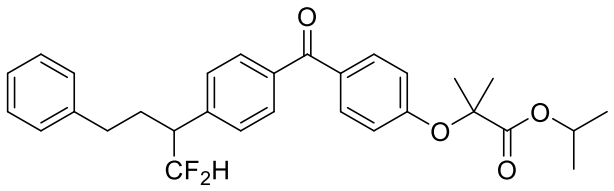
^{13}C NMR of **26** (101 MHz, $CDCl_3$)

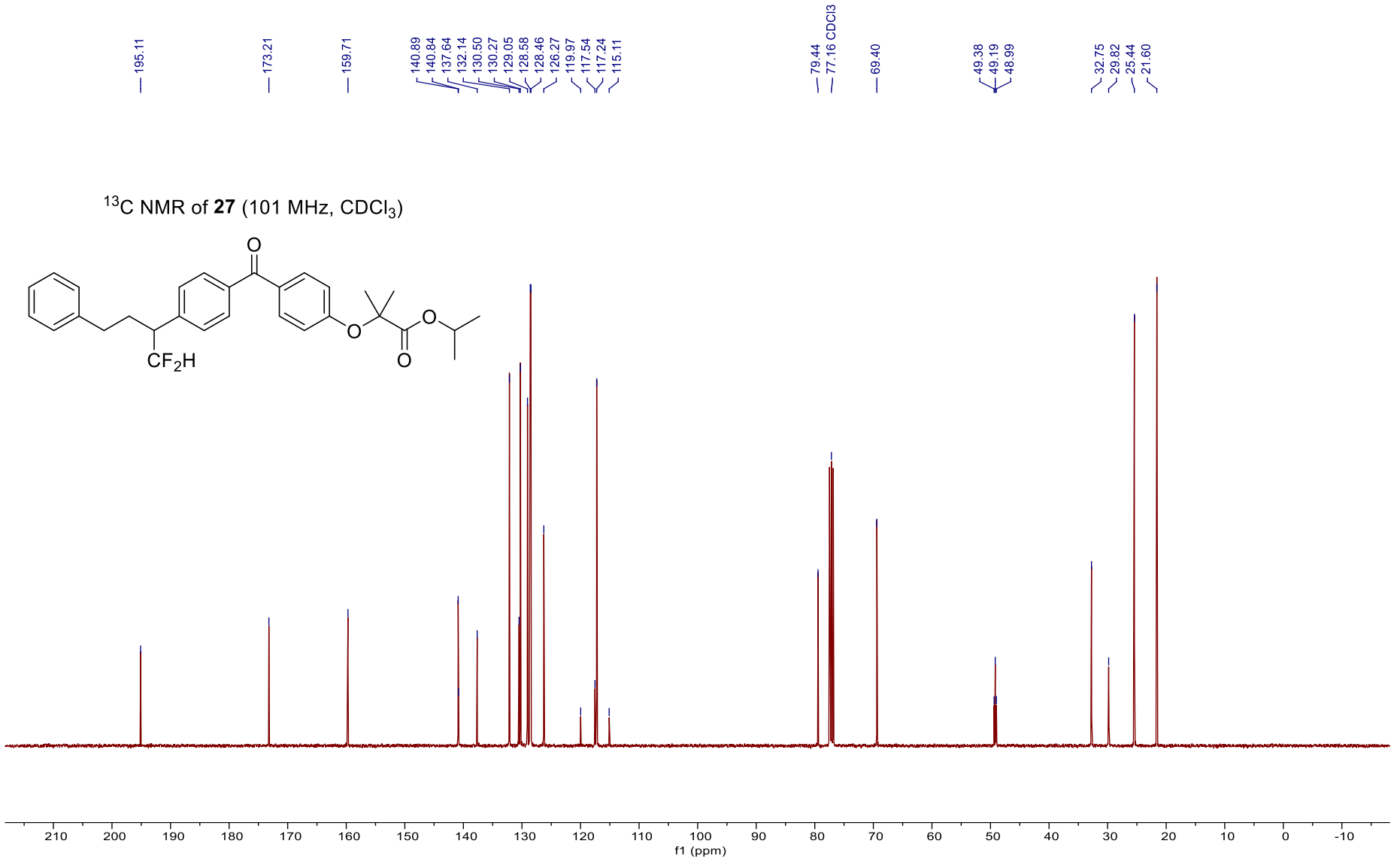


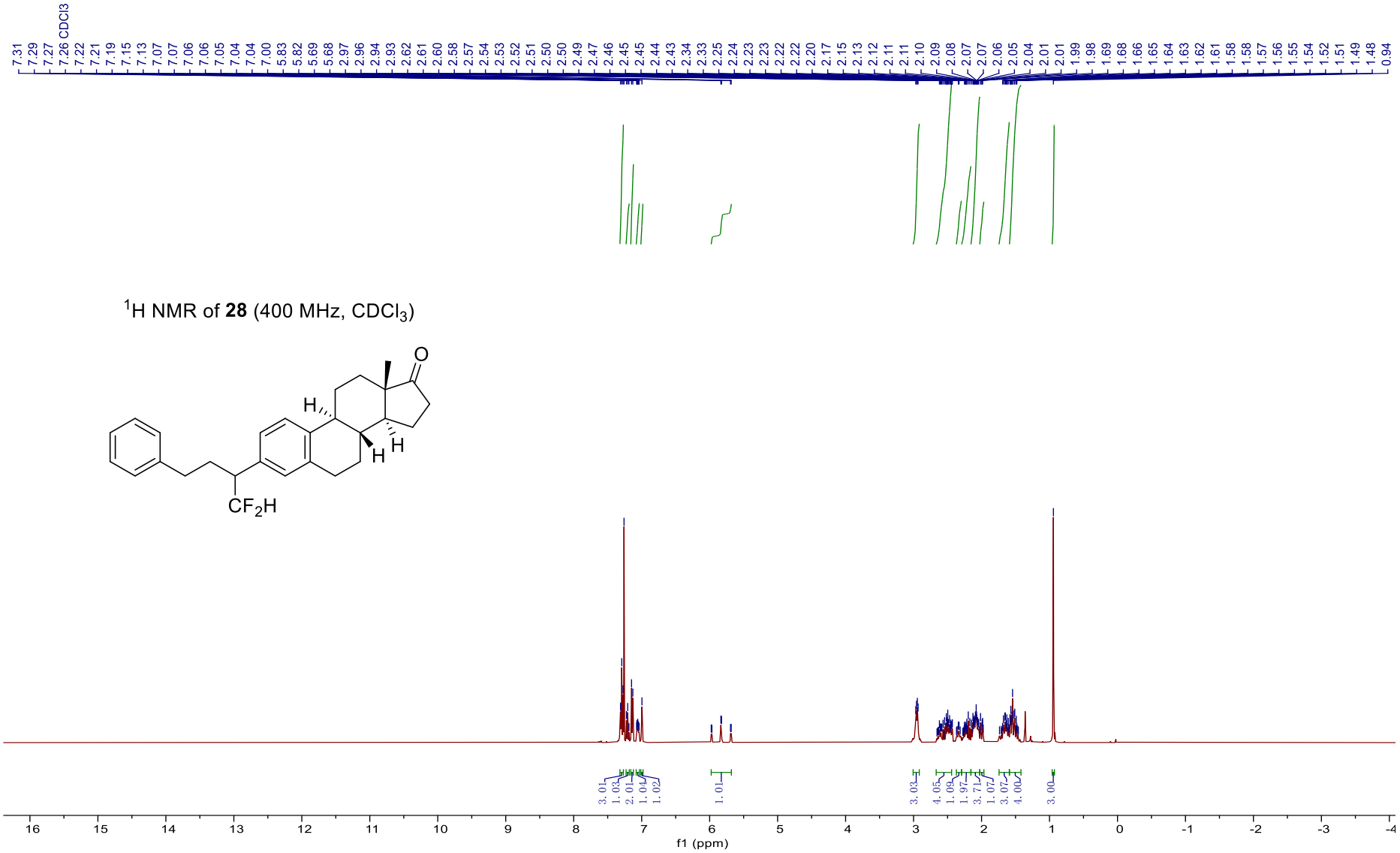


^{1}H NMR of **27** (400 MHz, $CDCl_3$)

^{19}F NMR of **27** (376 MHz, $CDCl_3$)

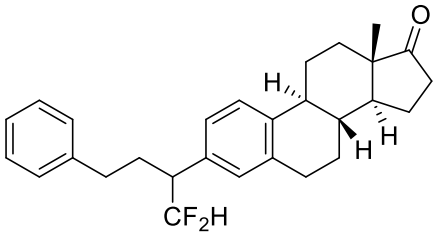


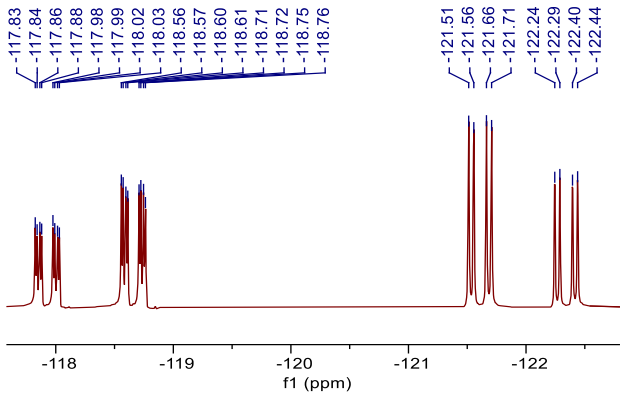

195.11
173.21
159.71
140.89
140.84
137.64
132.14
130.50
130.27
129.05
128.58
128.46
126.27
119.97
117.54
117.24
115.11
79.44
77.16 CDCl3
69.40
49.38
49.19
48.99
32.75
29.82
25.44
21.60
^{13}C NMR of **27** (101 MHz, $CDCl_3$)
O
O
O
O
CF_2H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

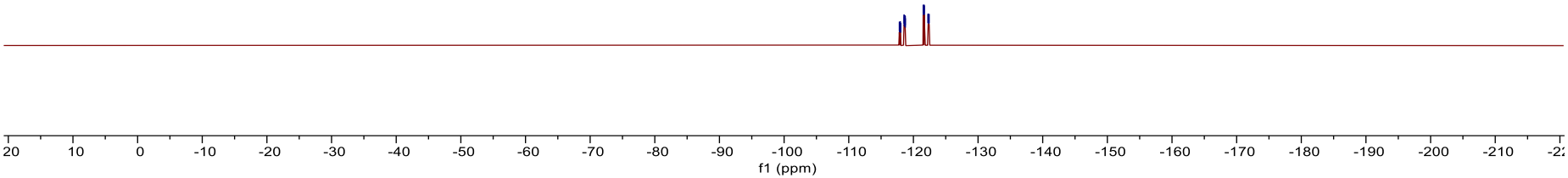


^{1}H NMR of **28** (400 MHz, $CDCl_3$)

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





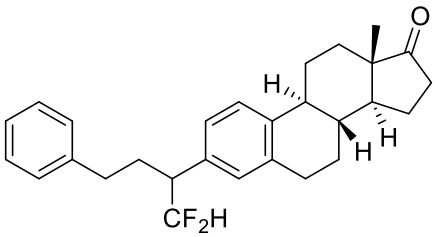


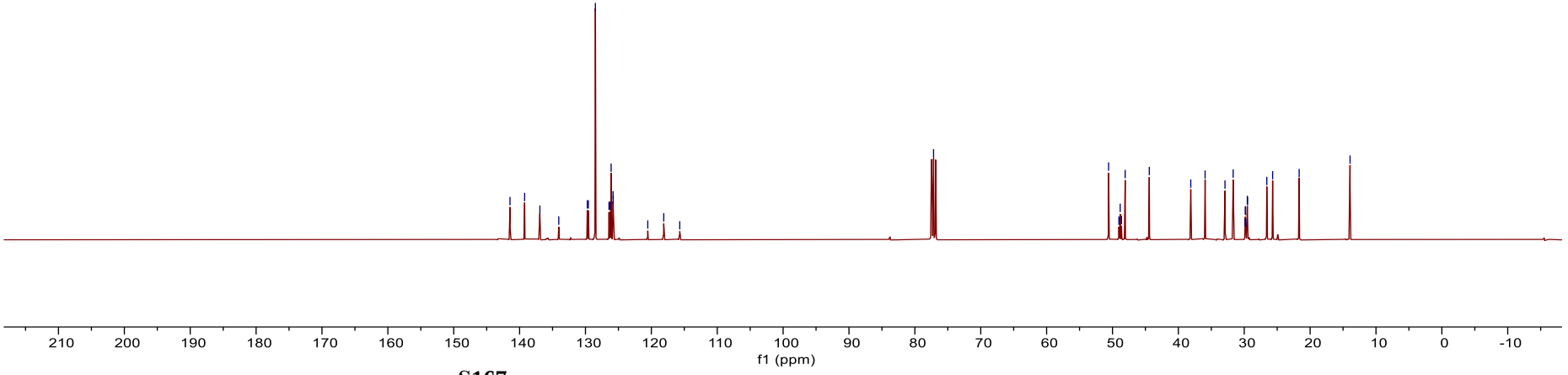
141.46
139.24
136.92
134.05
129.73
129.55
128.50
126.43
126.27
126.10
125.81
125.79
120.54
118.12
115.69

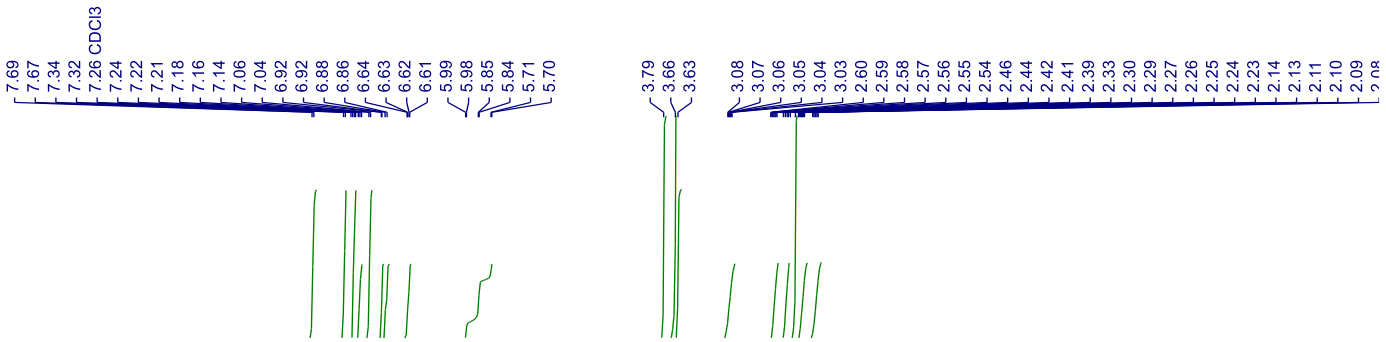
77.16 CDCl3

50.59
49.03
48.83
48.64
48.07
44.41
38.12
35.94
32.92
31.68
29.87
29.83
29.80
29.76
29.53
29.50
26.57
25.69
21.66
13.94

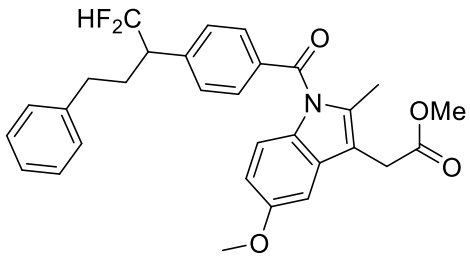
^{13}C NMR of **28** (101 MHz, $CDCl_3$)

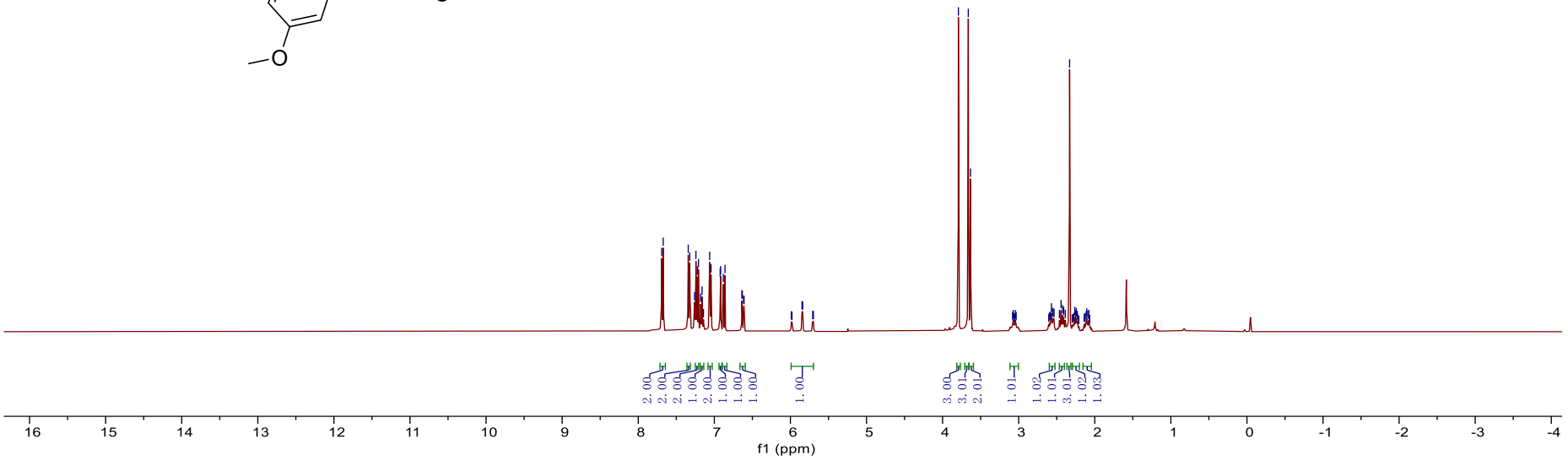




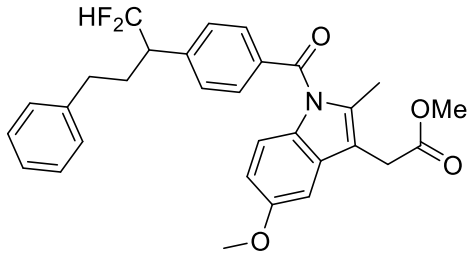


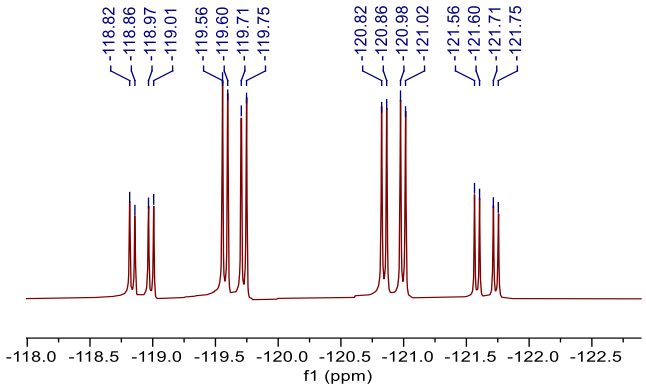
^{1}H NMR of **29** (400 MHz, $CDCl_3$)

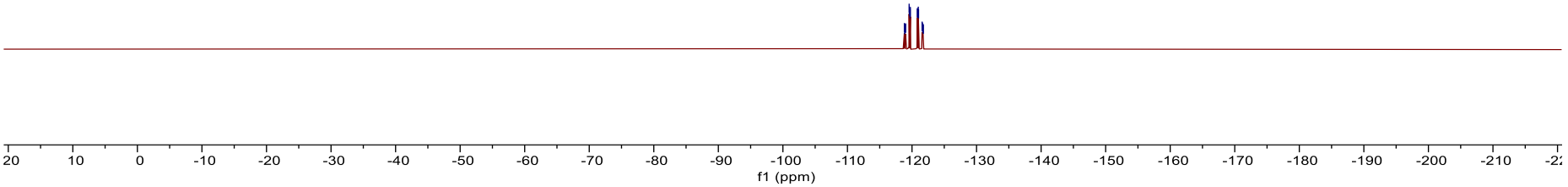


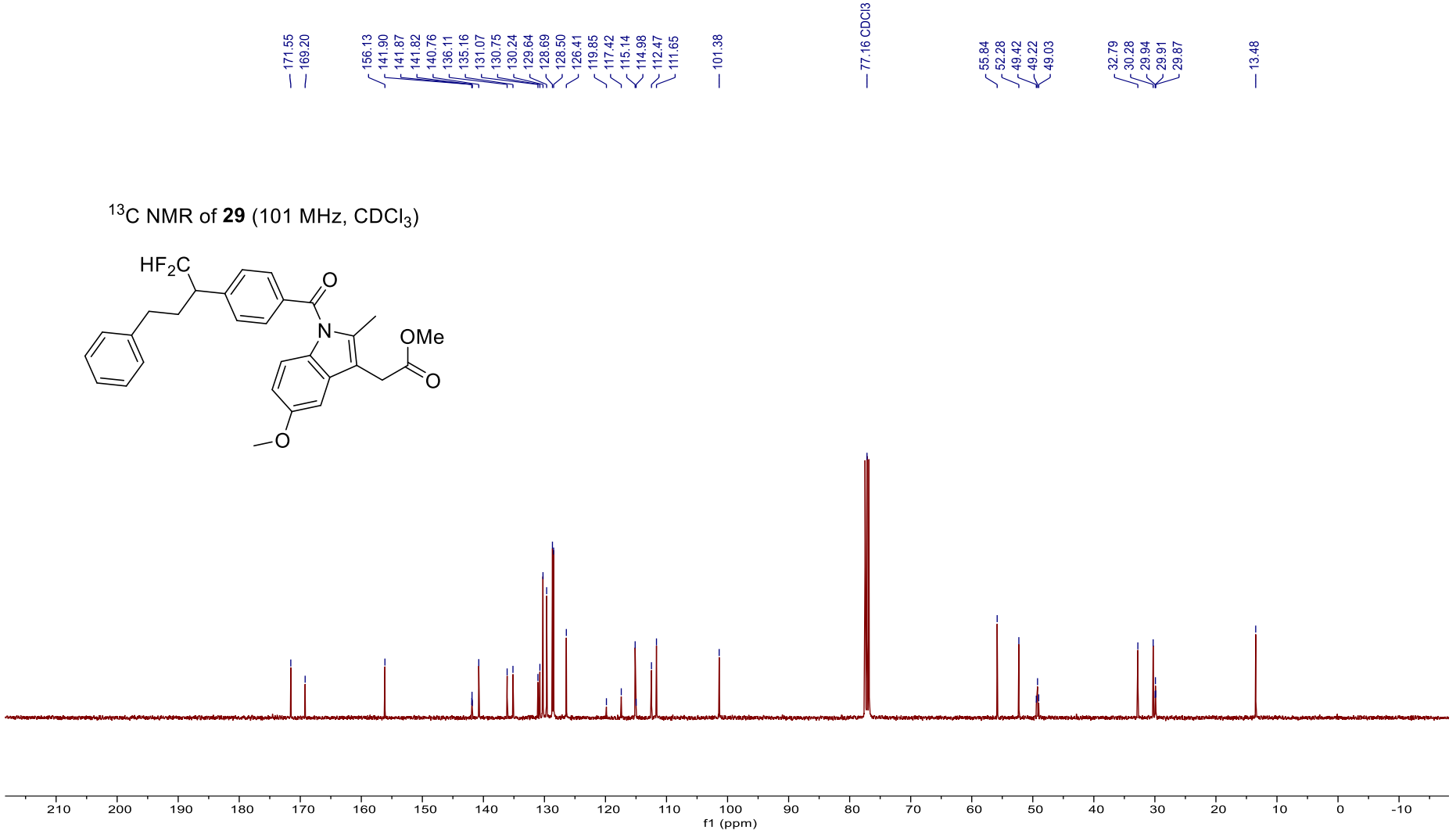


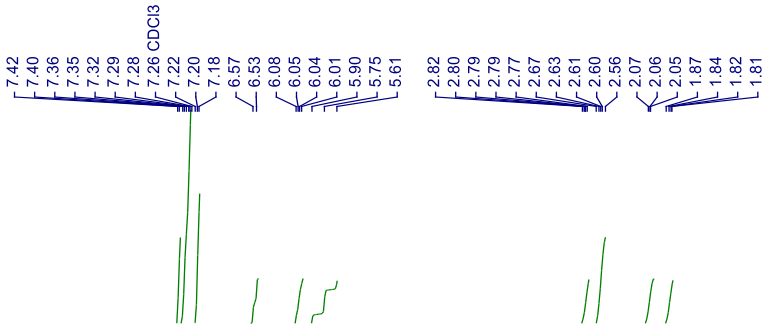
^{19}F NMR of **29** (376 MHz, $CDCl_3$)



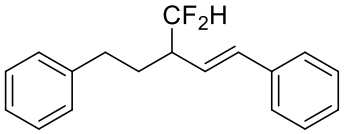


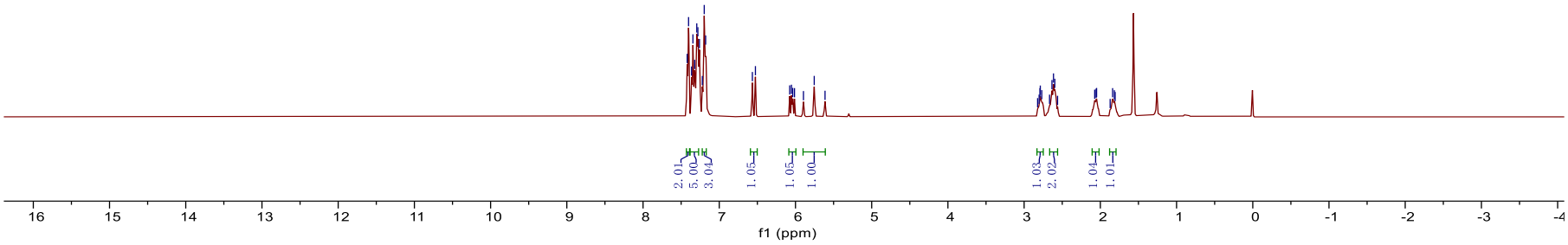


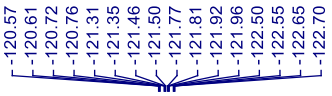

171.55
169.20
156.13
141.90
141.87
141.82
140.76
136.11
135.16
131.07
130.75
130.24
129.64
128.69
128.50
126.41
119.85
117.42
115.14
114.98
112.47
111.65
101.38
77.16 CDCl3
55.84
52.28
49.42
49.22
49.03
32.79
30.28
29.94
29.91
29.87
13.48
^{13}C NMR of **29** (101 MHz, $CDCl_3$)
HF_2C
O
N
OMe
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



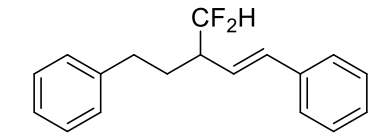
^{1}H NMR of **30** (400 MHz, $CDCl_3$)

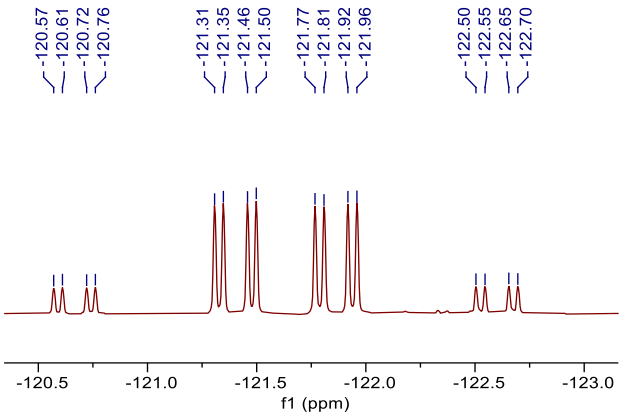


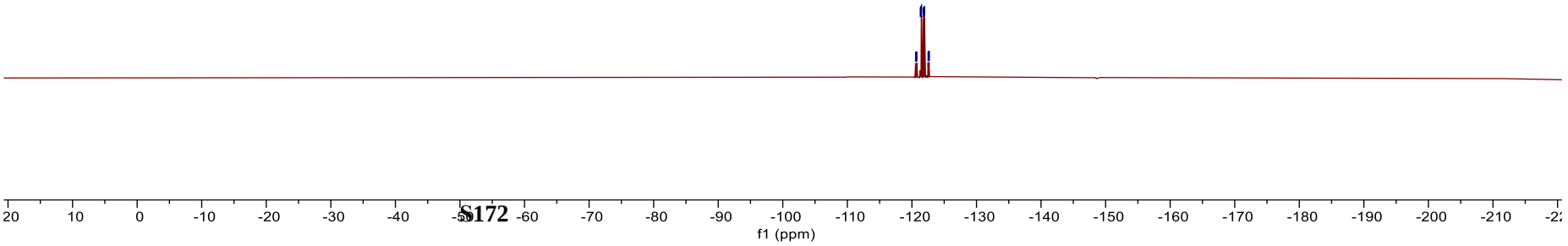




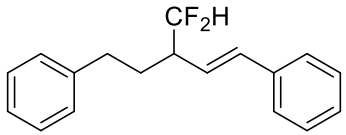
^{19}F NMR of **30** ($CDCl_3$)

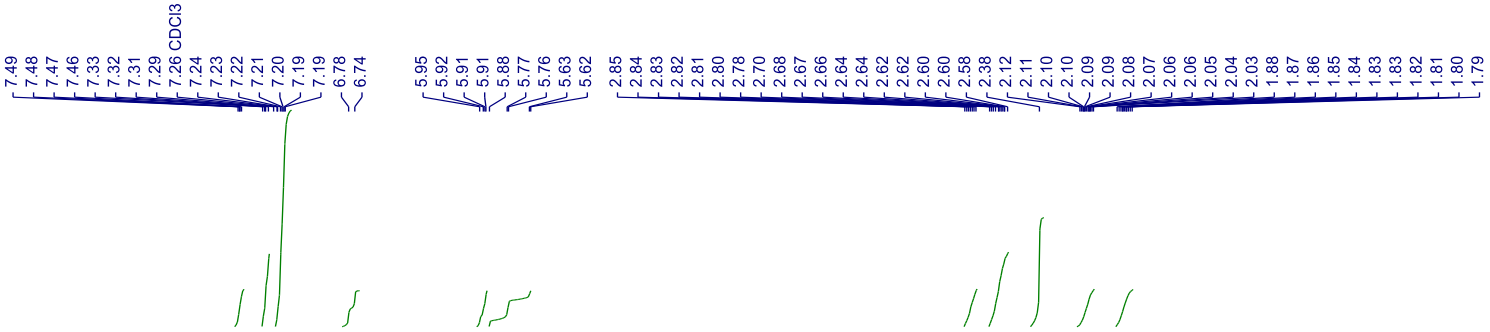




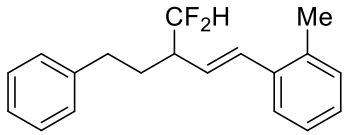


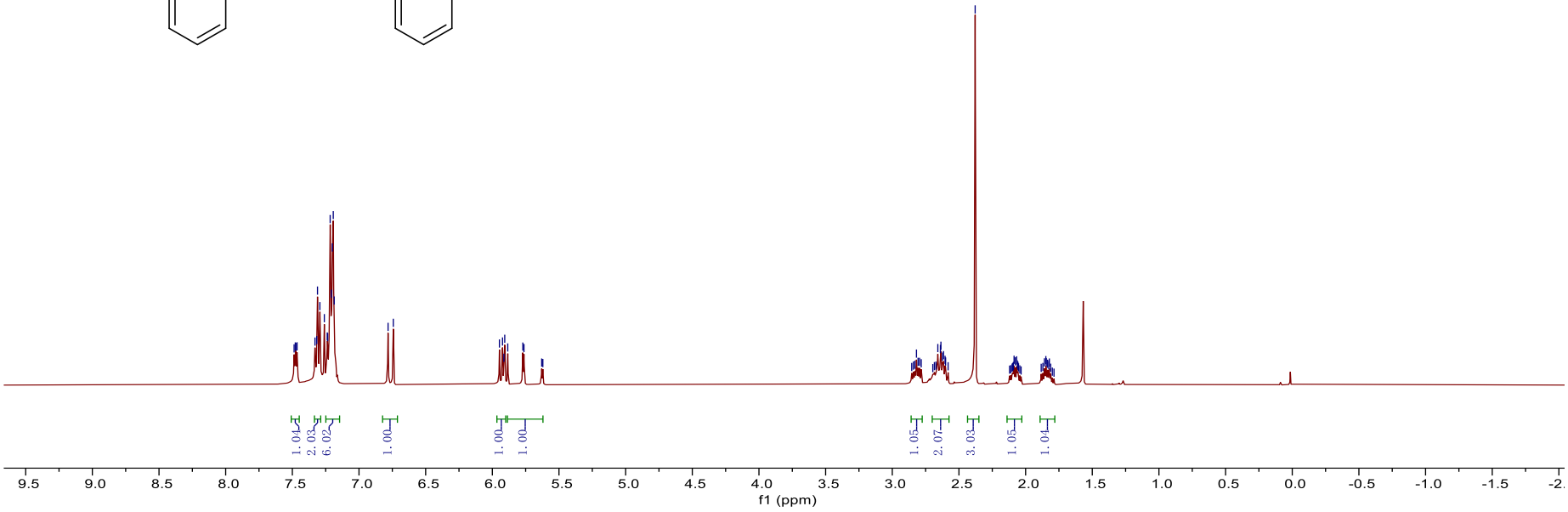
^{13}C NMR of **30** (101 MHz, $CDCl_3$)



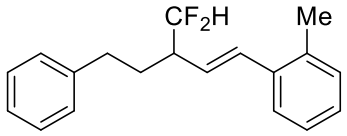


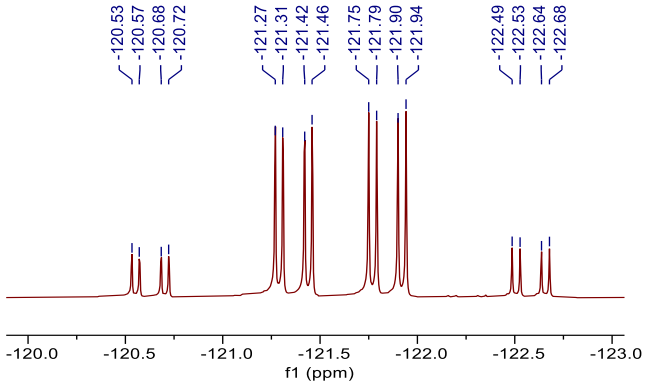
^{1}H NMR of **31** (400 MHz, $CDCl_3$)

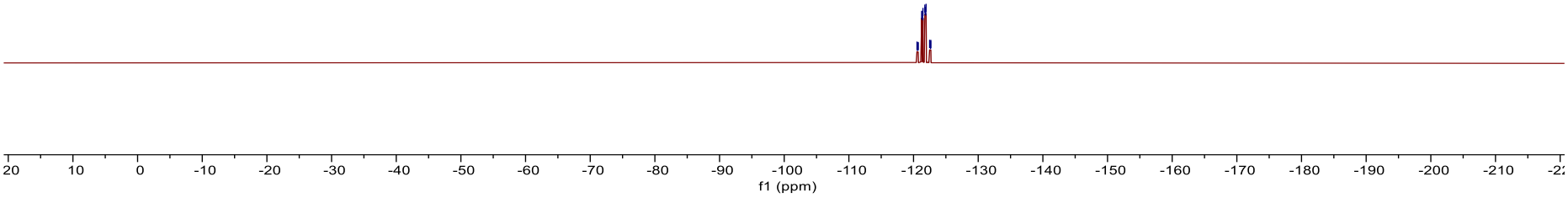




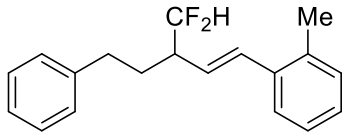
^{19}F NMR of **31** (376 MHz, $CDCl_3$)



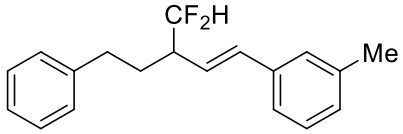




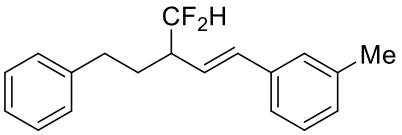
^{13}C NMR of **31** (101 MHz, $CDCl_3$)

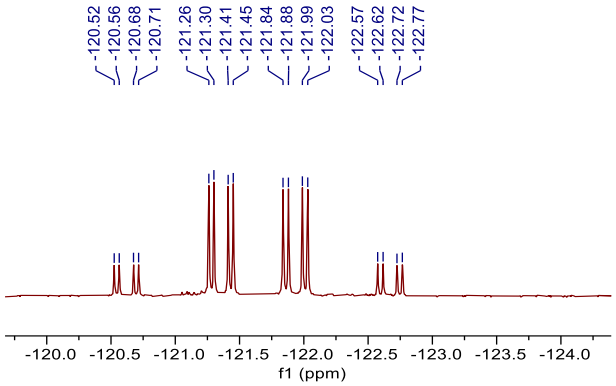


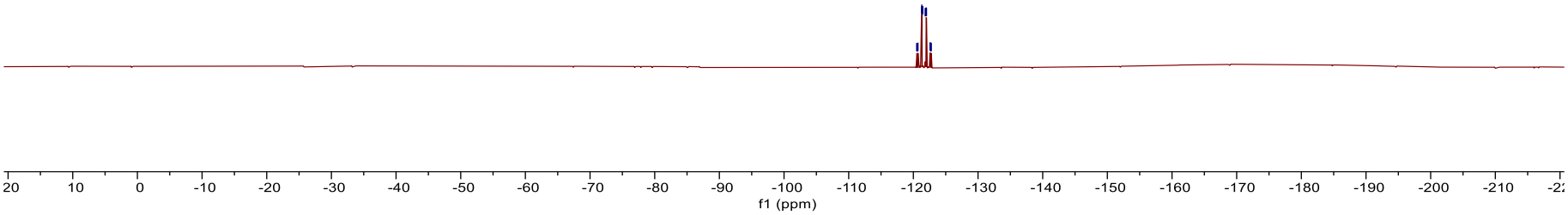
^{1}H NMR of **32** (400 MHz, $CDCl_3$)



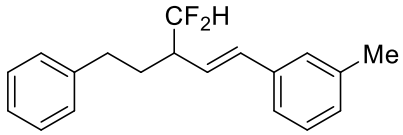
^{19}F NMR of **32** (376 MHz, $CDCl_3$)



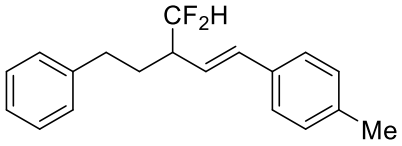




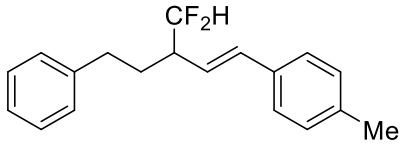
^{13}C NMR of **32** (101 MHz, $CDCl_3$)

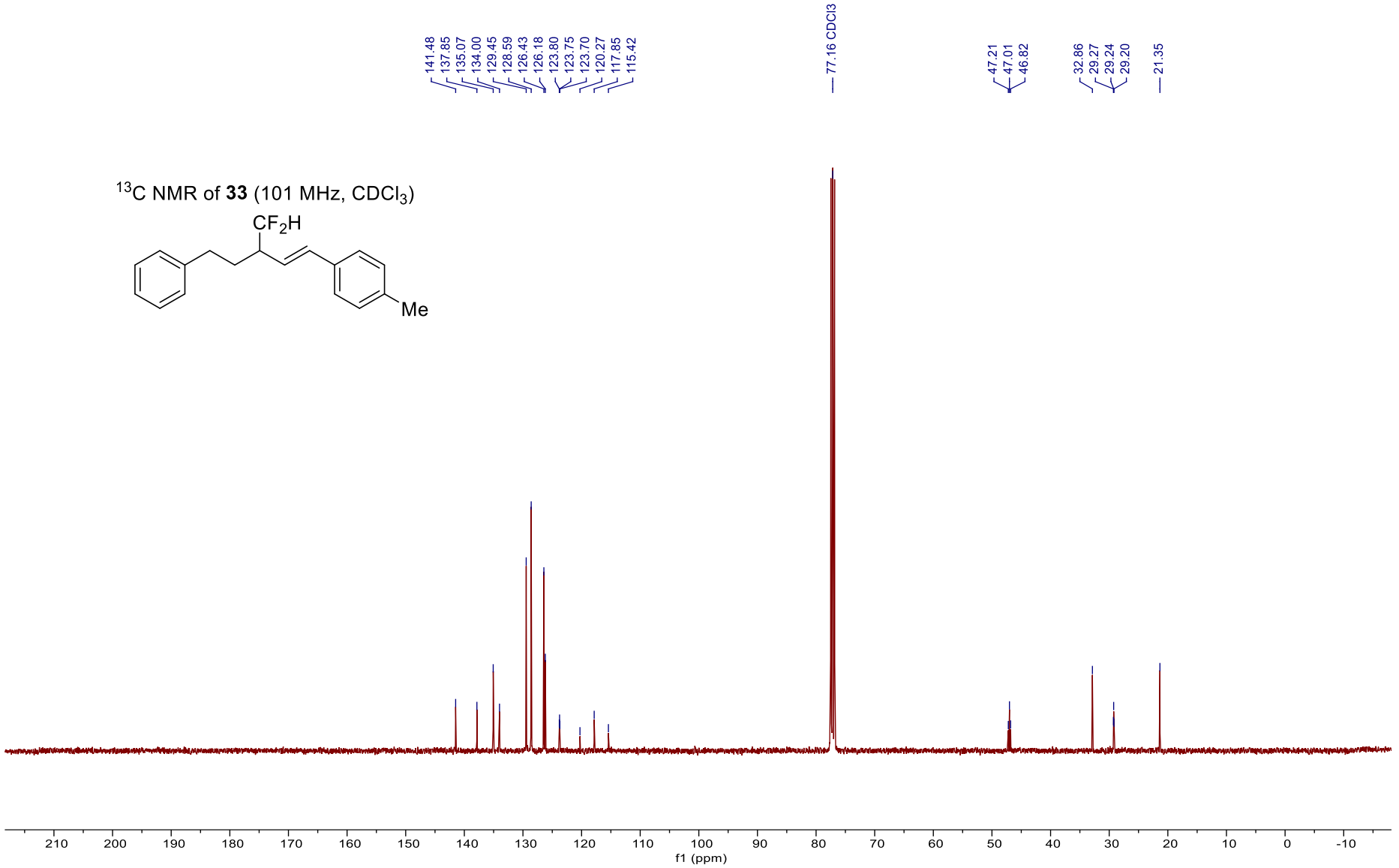


^{1}H NMR of **33** (400 MHz, $CDCl_3$)

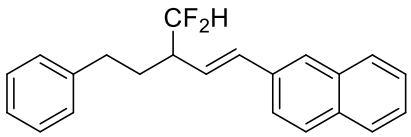


^{19}F NMR of **33** (376 MHz, $CDCl_3$)

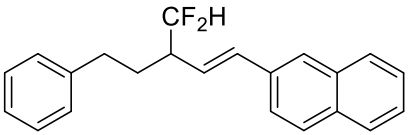


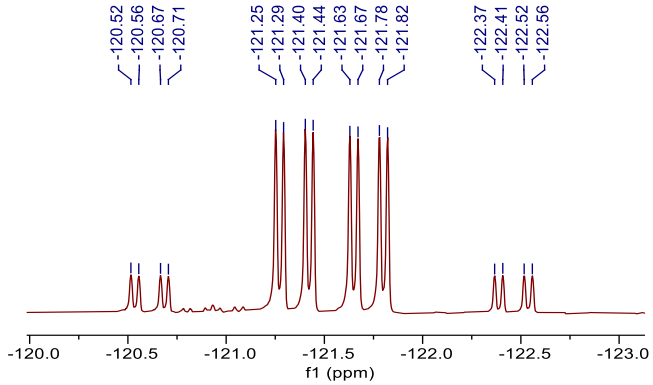

141.48
137.85
135.07
134.00
129.45
128.59
126.43
126.18
123.80
123.75
123.70
120.27
117.85
115.42
77.16 CDCl3
47.21
47.01
46.82
32.86
29.27
29.24
29.20
21.35
13C NMR of 33 (101 MHz, CDCl3)
CF2H
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

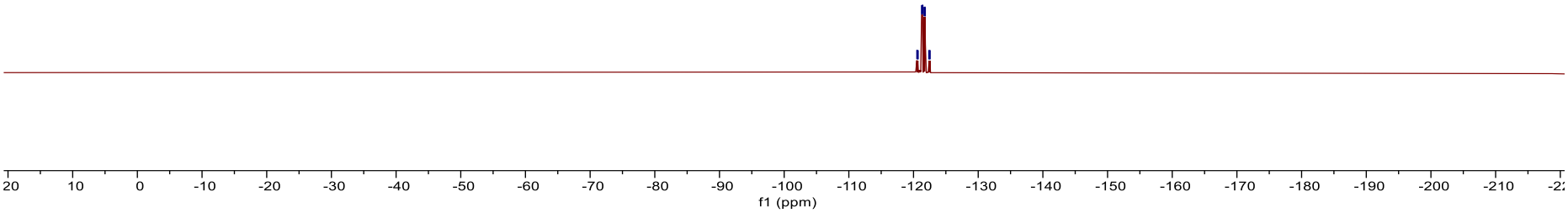
^{1}H NMR of **34** (400 MHz, $CDCl_3$)

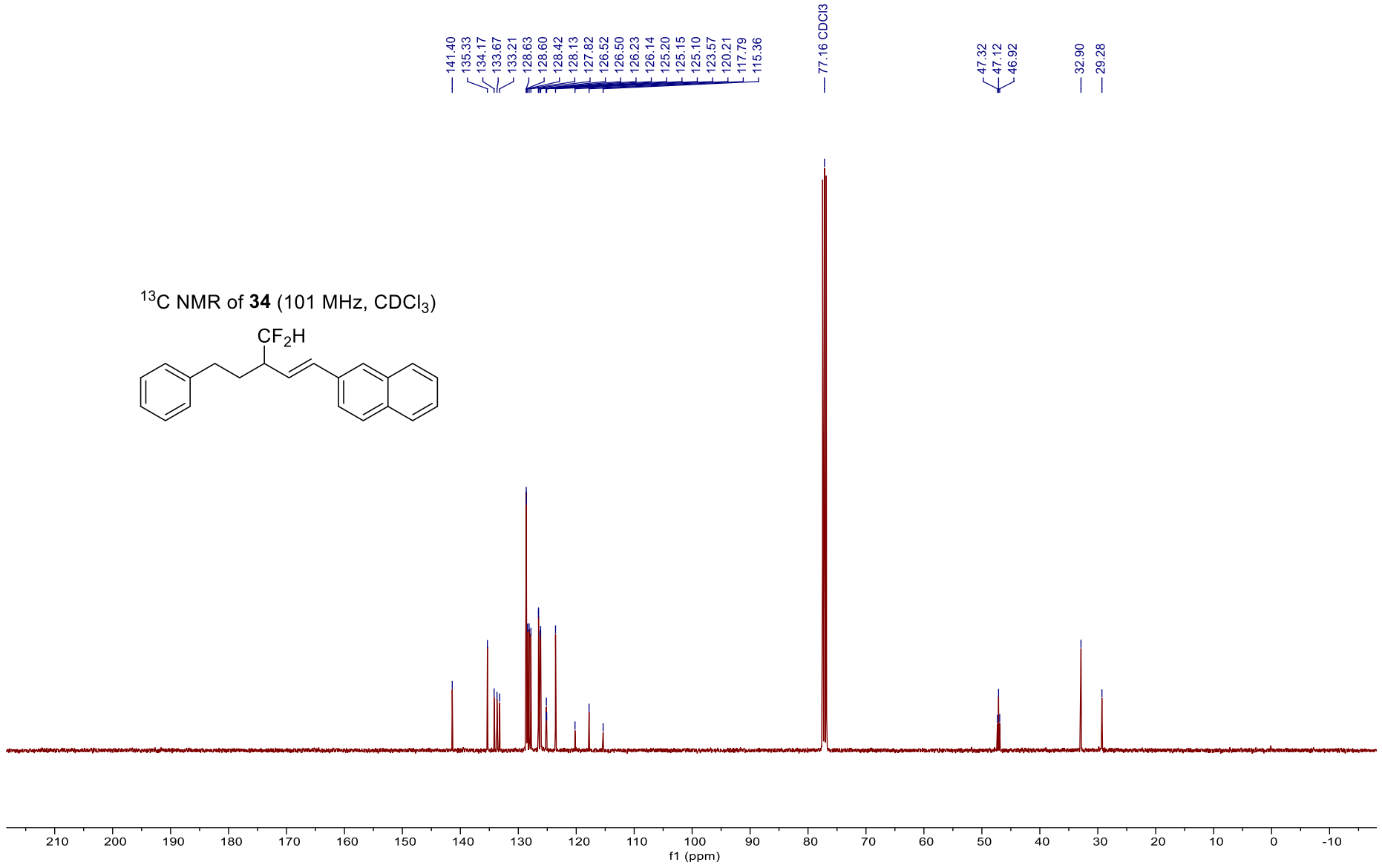


^{19}F NMR of **34** (376 MHz, $CDCl_3$)

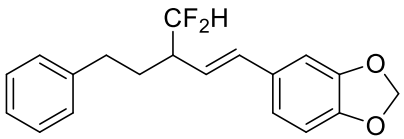




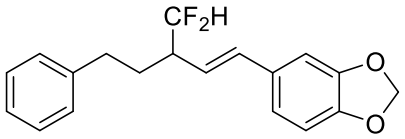


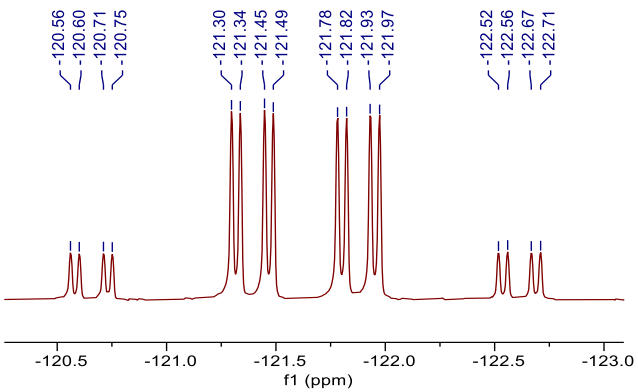

141.40
135.33
134.17
133.67
133.21
128.63
128.60
128.42
128.13
127.82
126.52
126.50
126.23
126.14
125.20
125.15
125.10
123.57
120.21
117.79
115.36
77.16 CDCl3
47.32
47.12
46.92
32.90
29.28
^{13}C NMR of **34** (101 MHz, $CDCl_3$)
CF_2H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

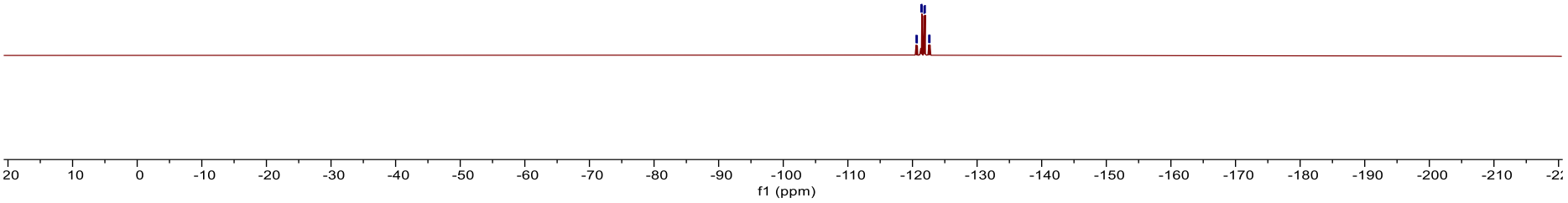
^{1}H NMR of **35** (400 MHz, $CDCl_3$)



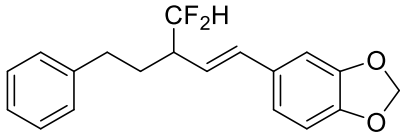
^{19}F NMR of **35** (376 MHz, $CDCl_3$)



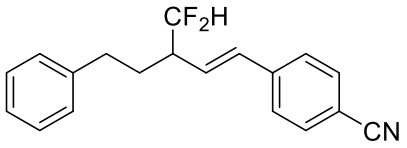




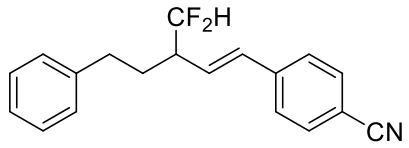
^{13}C NMR of **35** (101 MHz, $CDCl_3$)

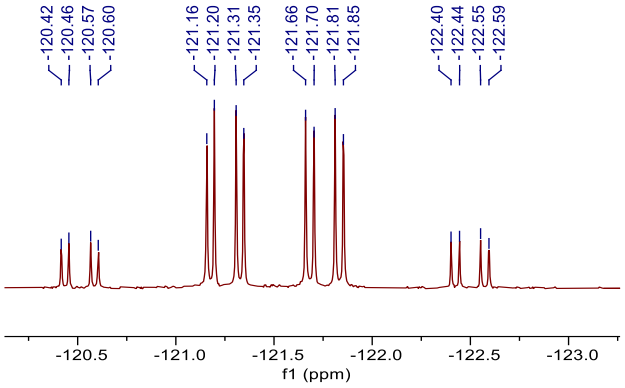


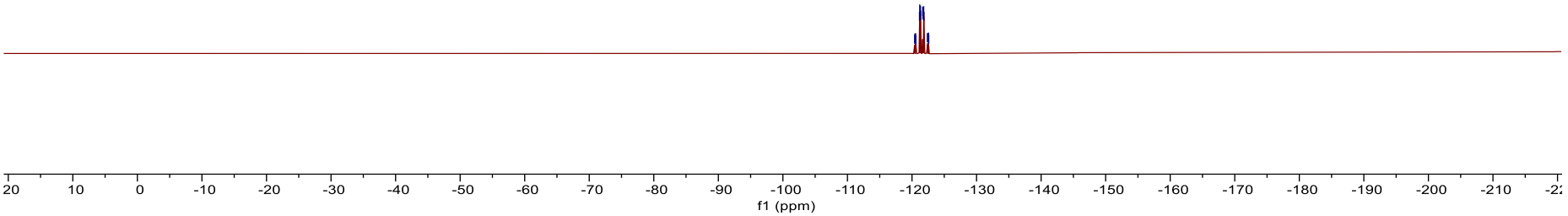
^{1}H NMR of **36** (400 MHz, $CDCl_3$)

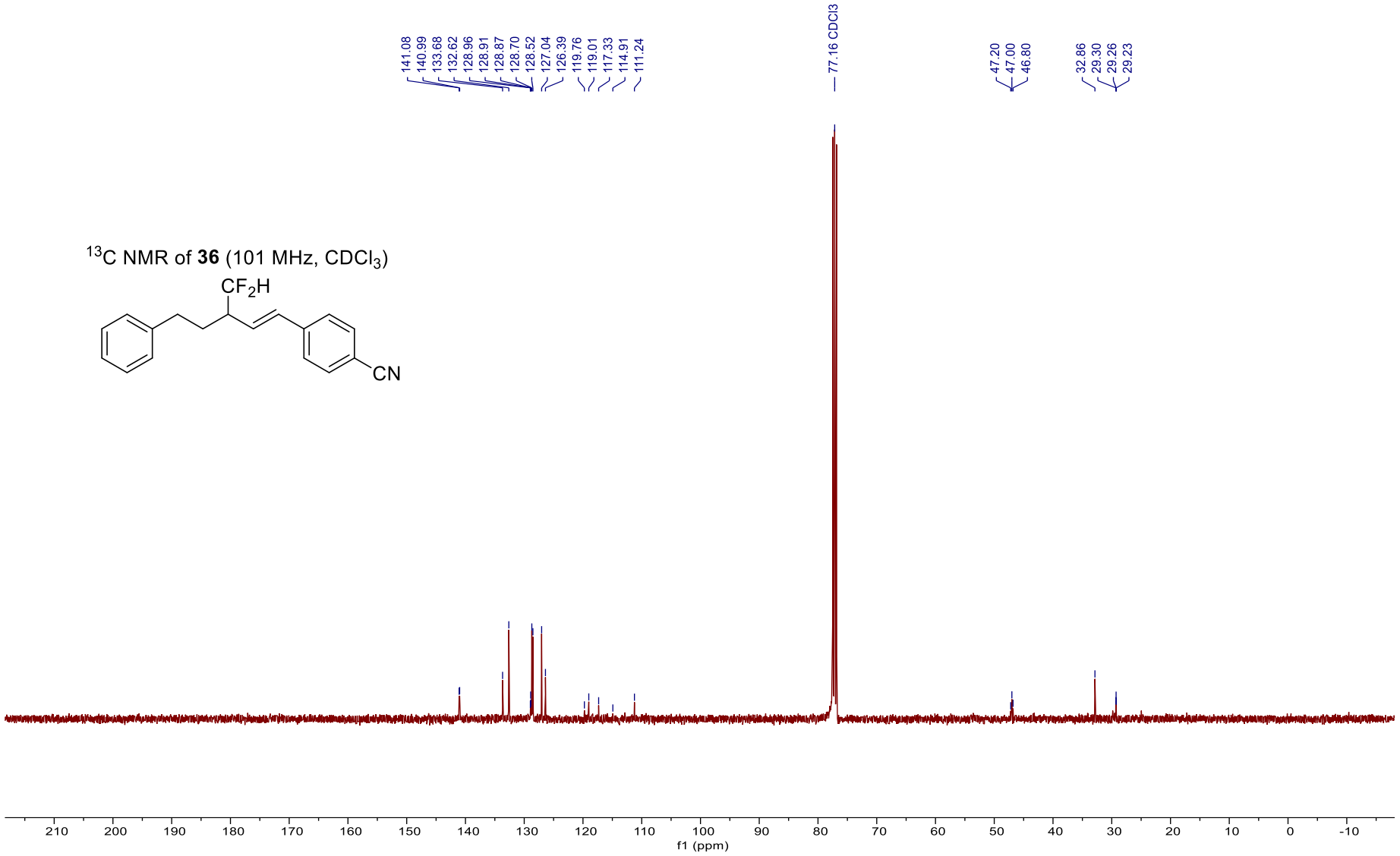


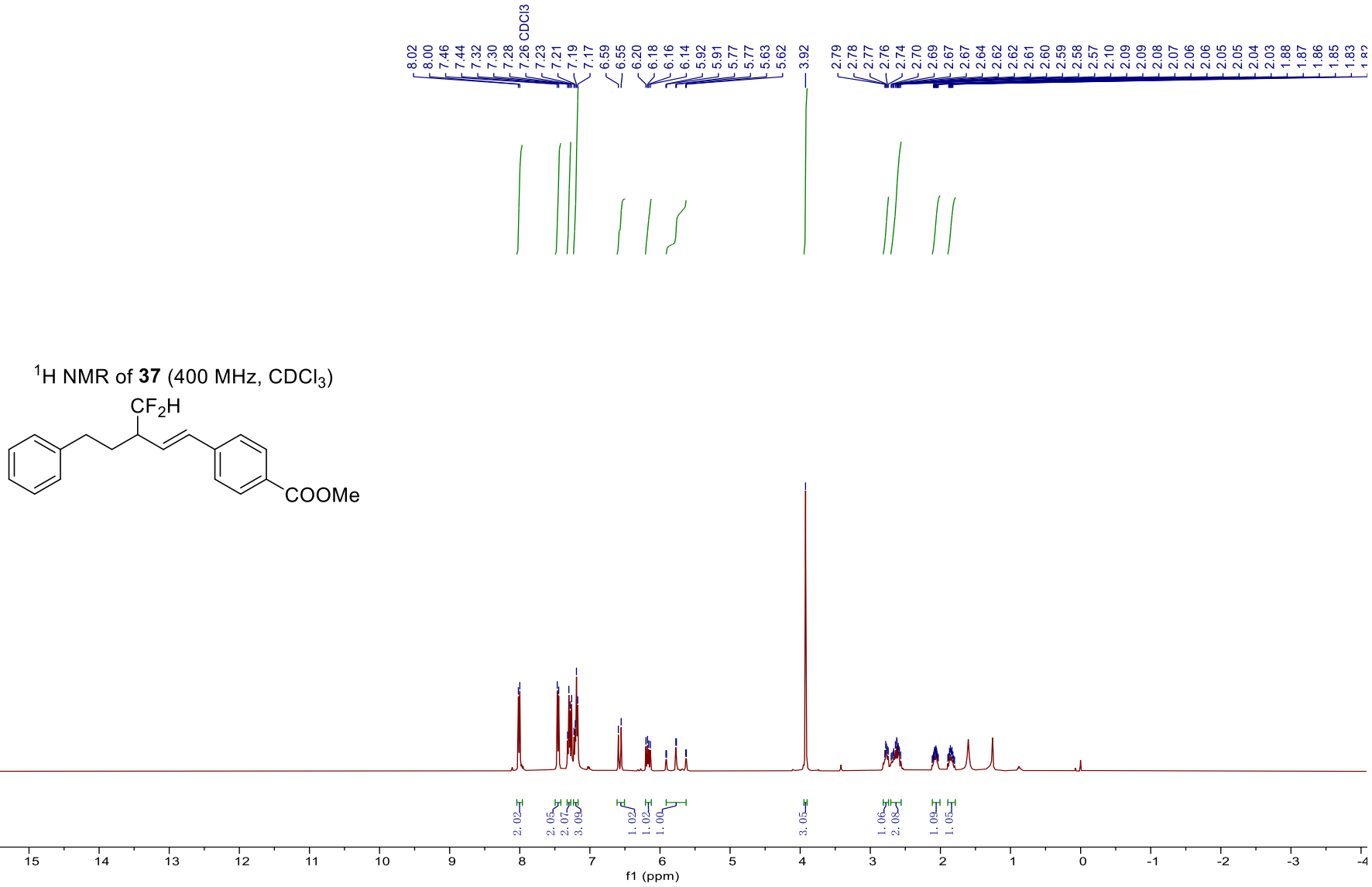
^{19}F NMR of **36** (376 MHz, $CDCl_3$)





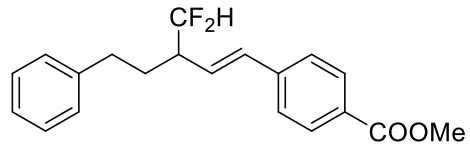


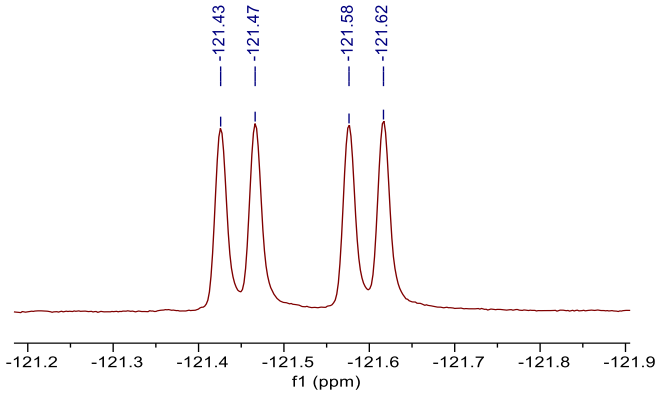

141.08
140.99
133.68
132.62
128.96
128.91
128.87
128.70
128.52
127.04
126.39
119.76
119.01
117.33
114.91
111.24
77.16 CDCl3
47.20
47.00
46.80
32.86
29.30
29.26
29.23
^{13}C NMR of **36** (101 MHz, $CDCl_3$)
CF_2H
CN
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

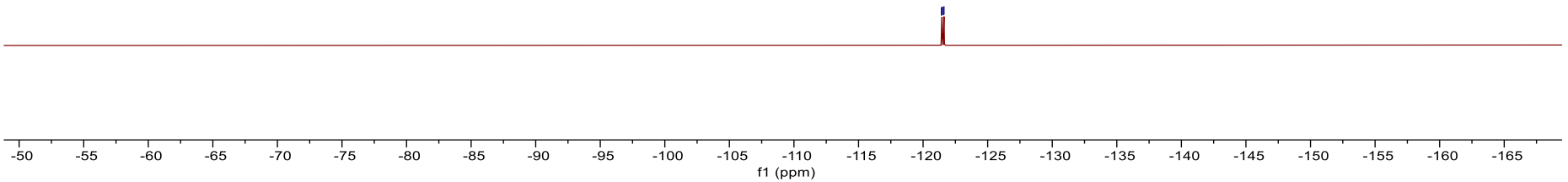


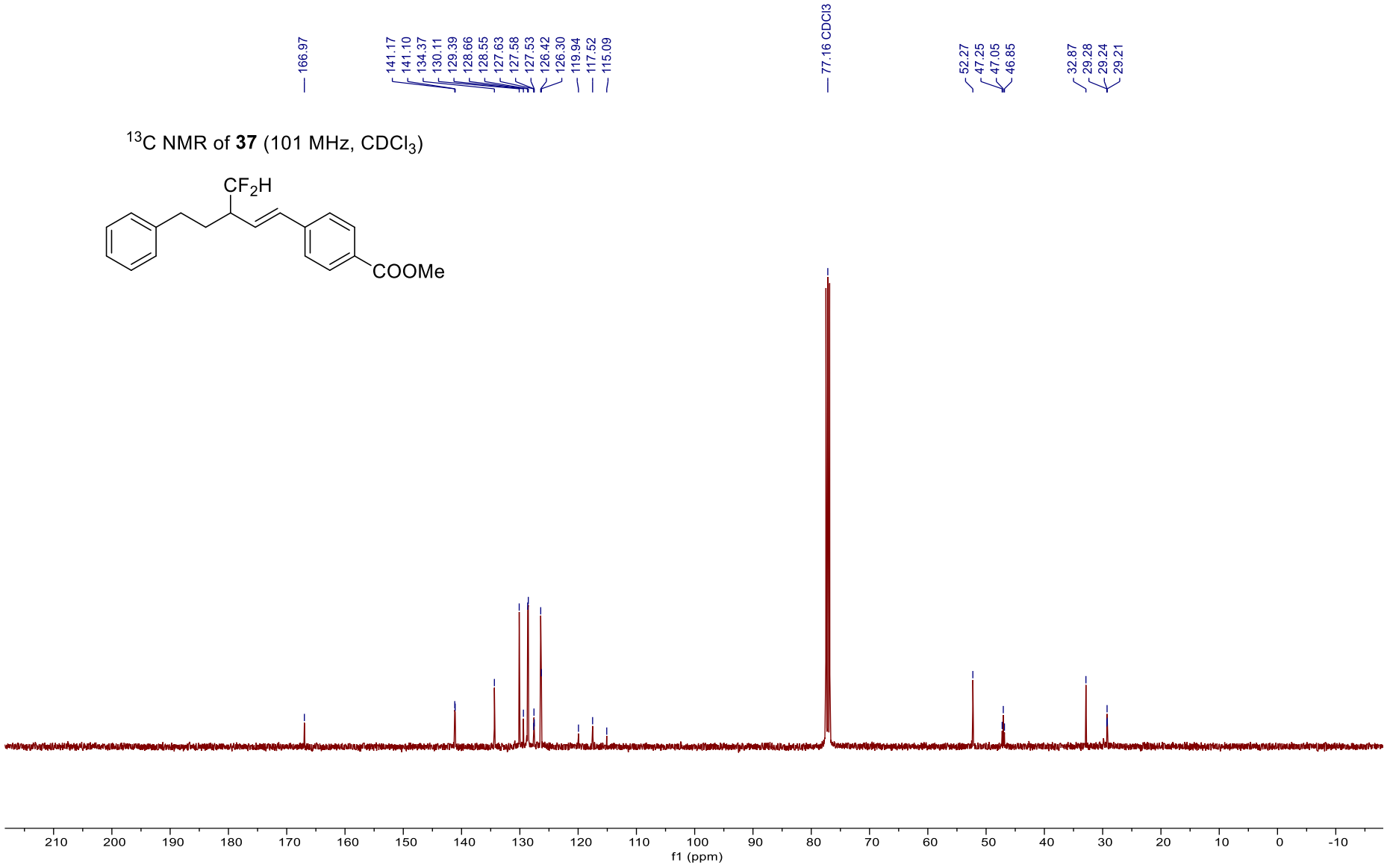
^{1}H NMR of **37** (400 MHz, $CDCl_3$)

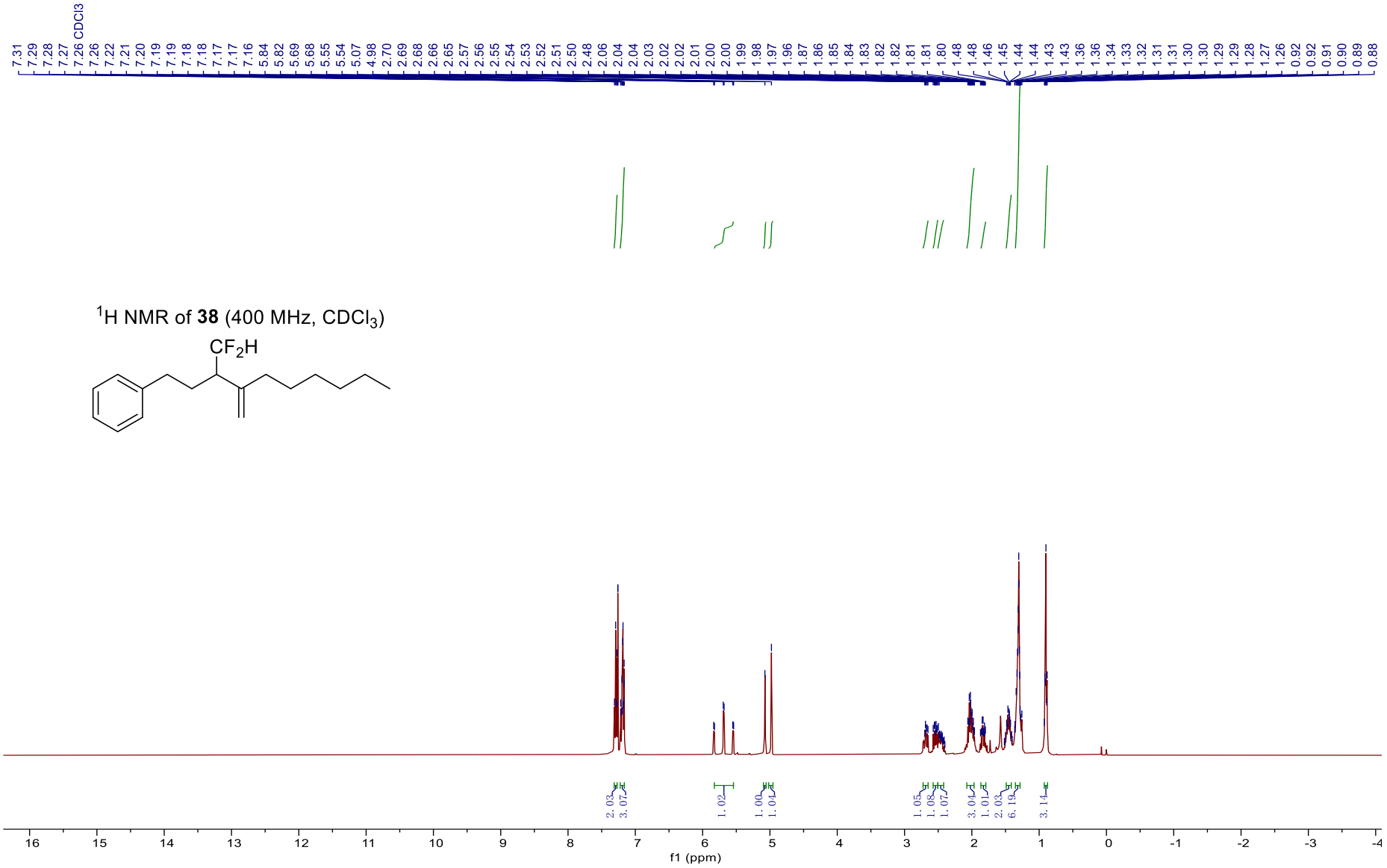
^{19}F NMR of **37** (376 MHz, $CDCl_3$)





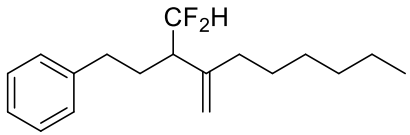


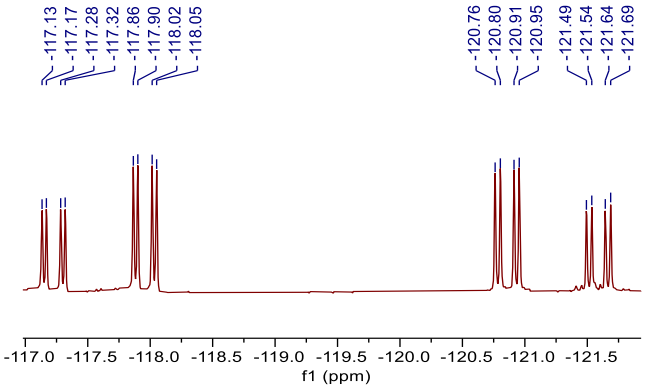

166.97
141.17
141.10
134.37
130.11
129.39
128.66
128.55
127.63
127.58
127.53
126.42
126.30
119.94
117.52
115.09
77.16 CDCl3
52.27
47.25
47.05
46.85
32.87
29.28
29.24
29.21
^{13}C NMR of **37** (101 MHz, $CDCl_3$)
CF_2H
COOMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

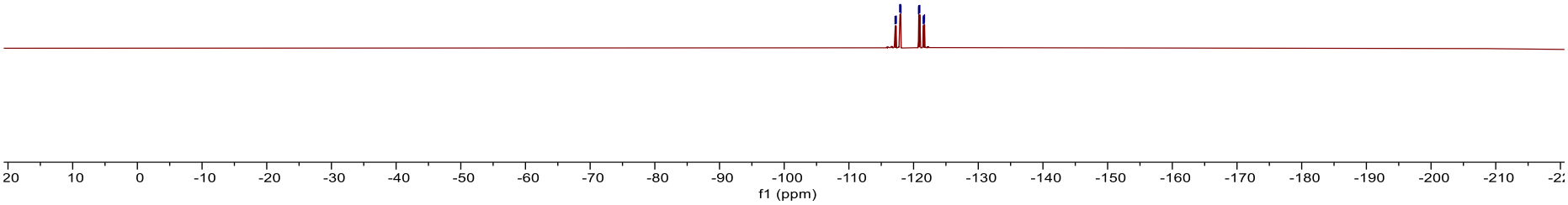


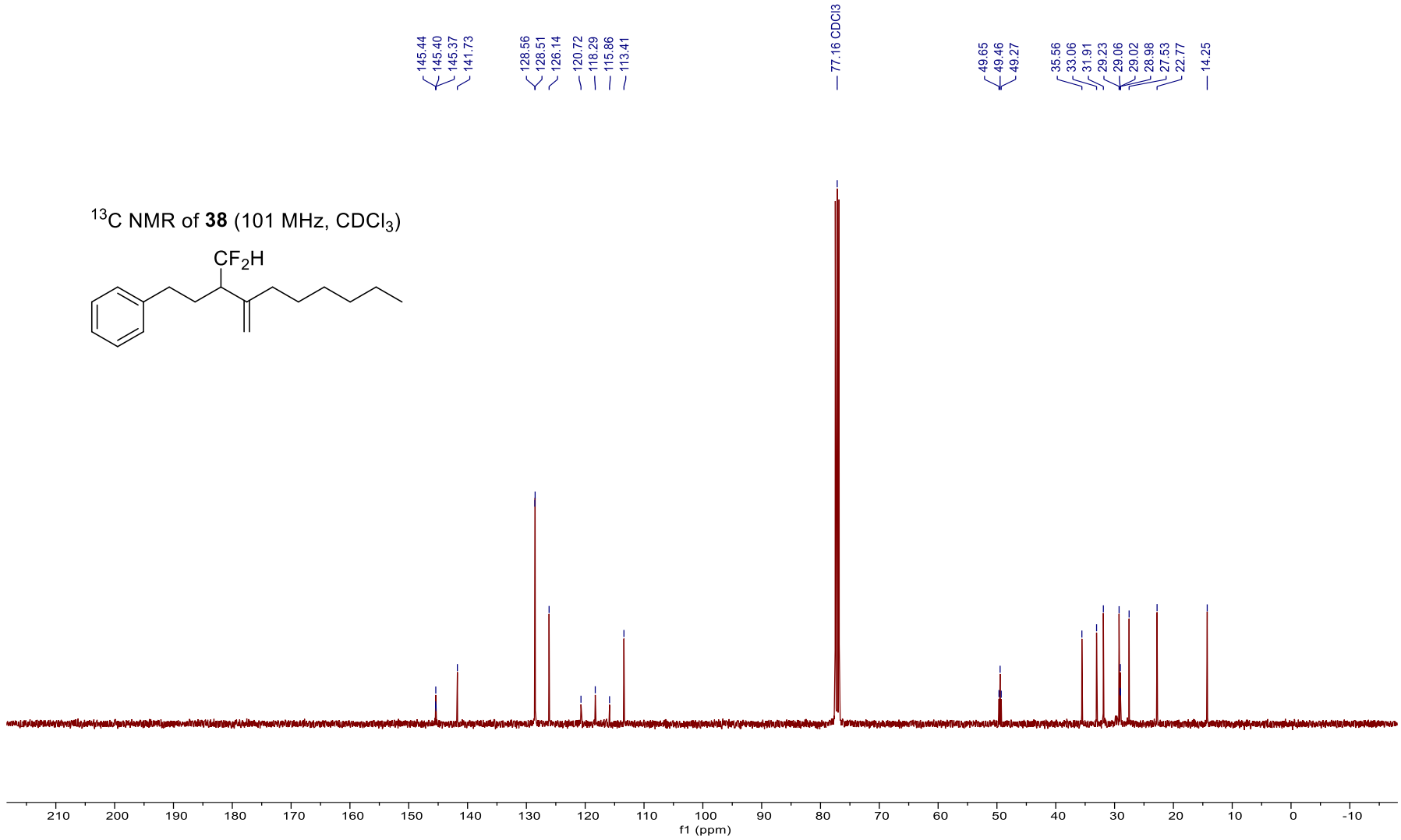
^{1}H NMR of **38** (400 MHz, $CDCl_3$)

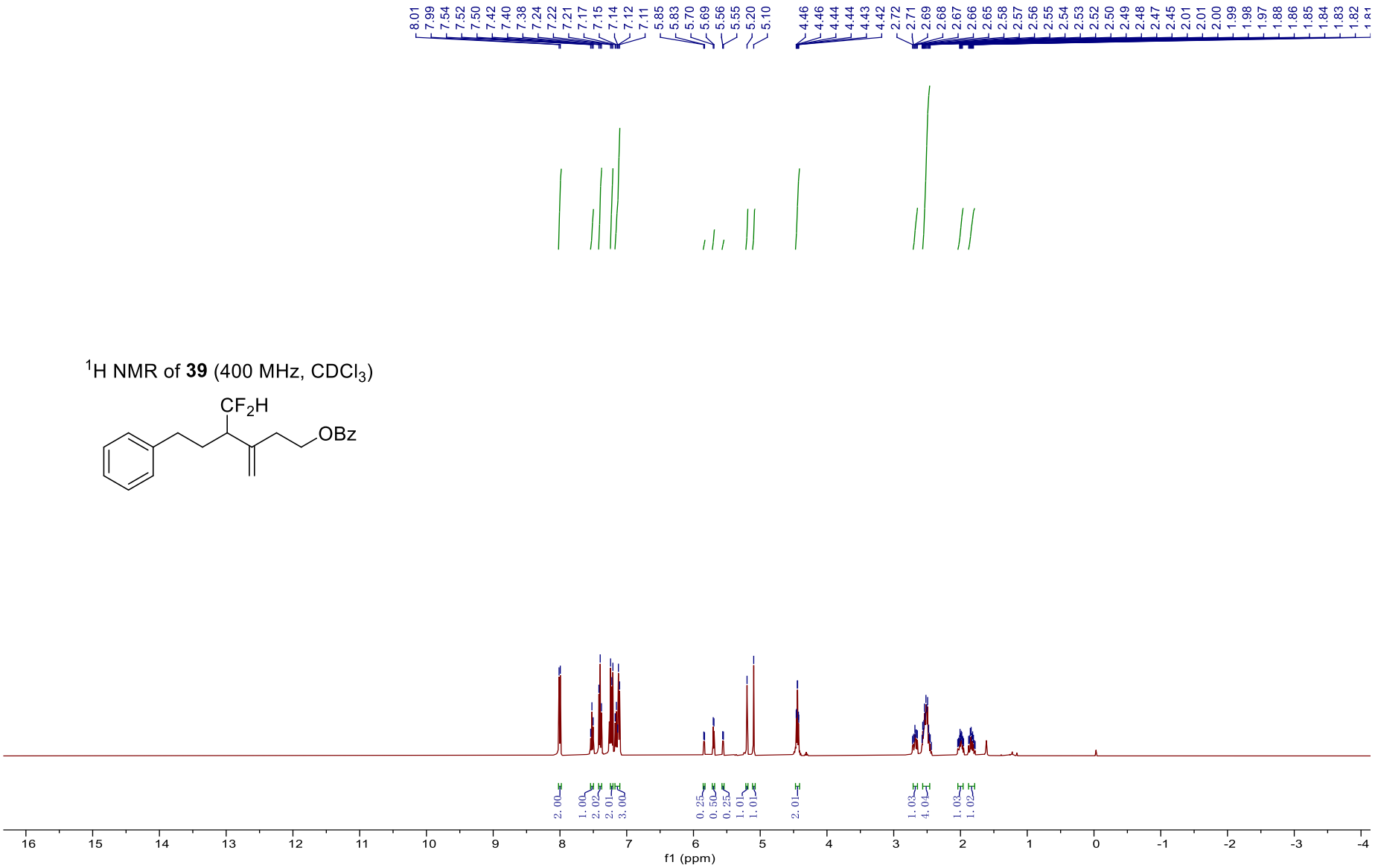
^{19}F NMR of **38** (376 MHz, $CDCl_3$)





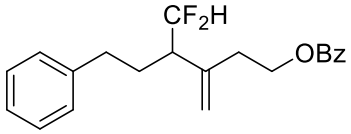


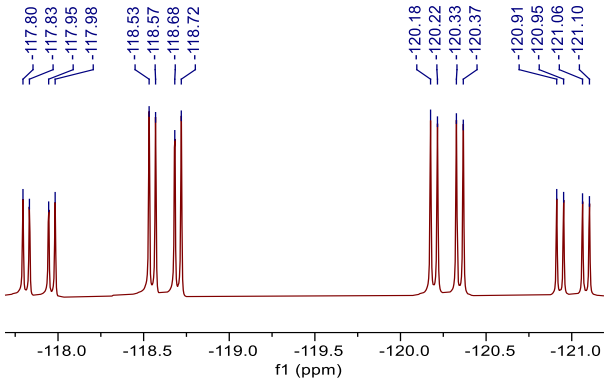

145.44
145.40
145.37
141.73
128.56
128.51
126.14
120.72
118.29
115.86
113.41
77.16 CDCl3
49.65
49.46
49.27
35.56
33.06
31.91
29.23
29.06
29.02
28.98
27.53
22.77
14.25
^{13}C NMR of **38** (101 MHz, $CDCl_3$)
CF_2H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

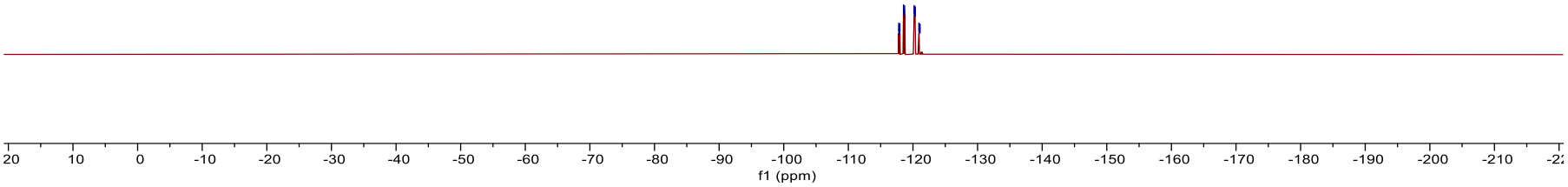


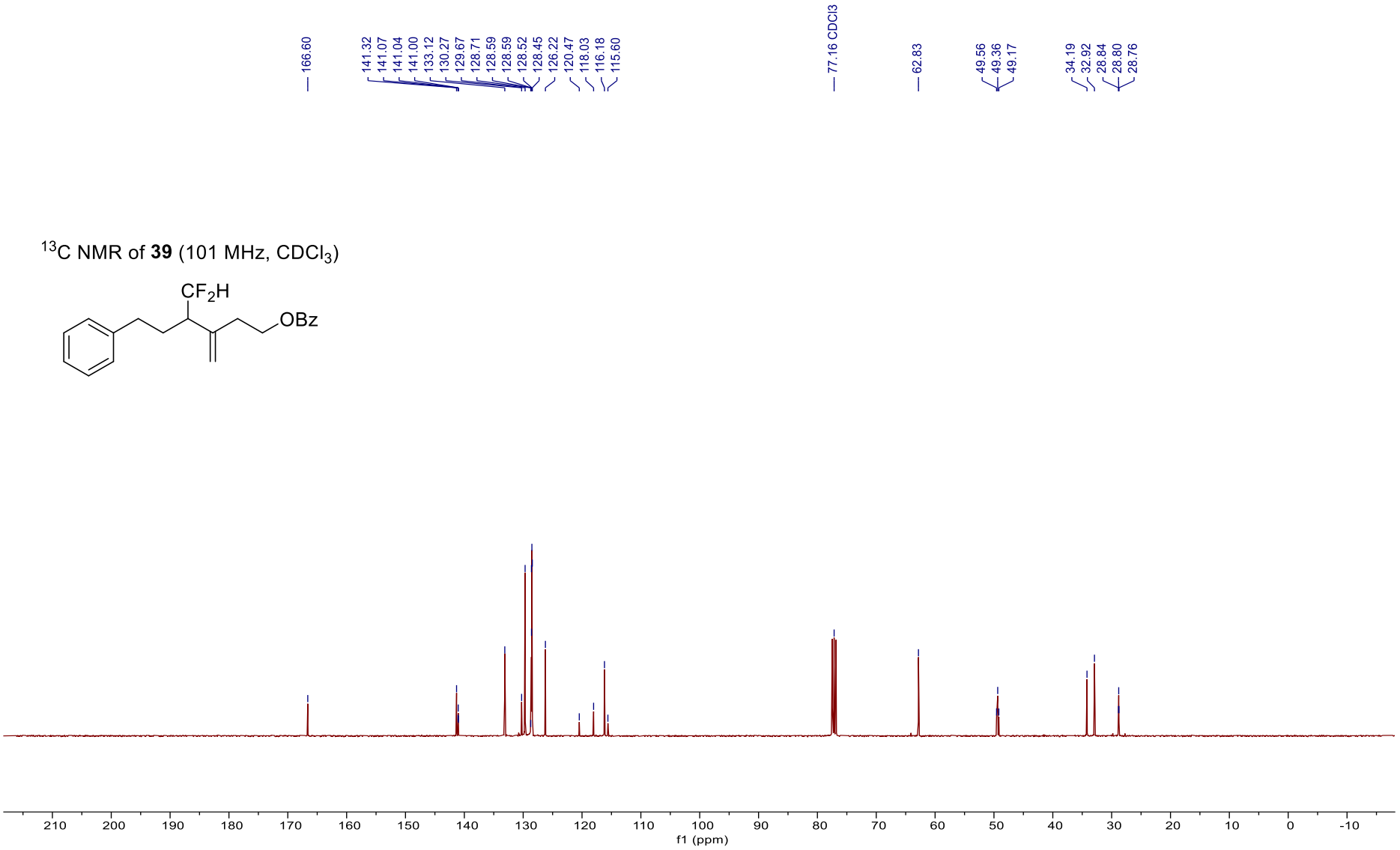
^{1}H NMR of **39** (400 MHz, $CDCl_3$)

^{19}F NMR of **39** (376 MHz, $CDCl_3$)



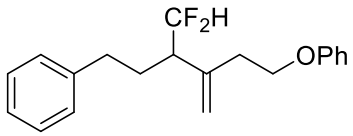


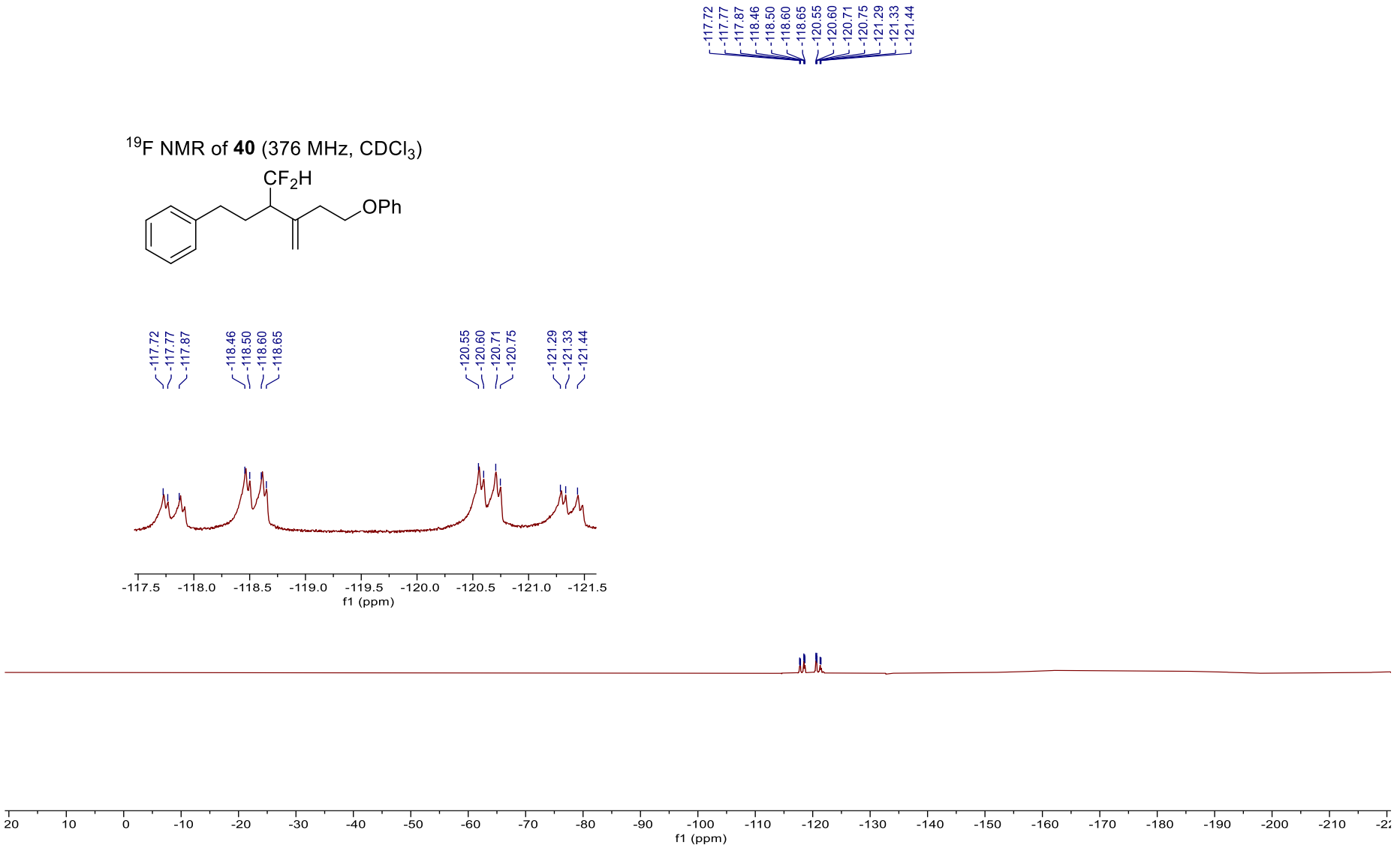




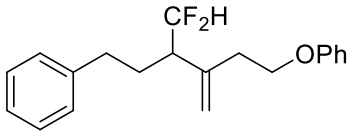
^{13}C NMR of **39** (101 MHz, $CDCl_3$)

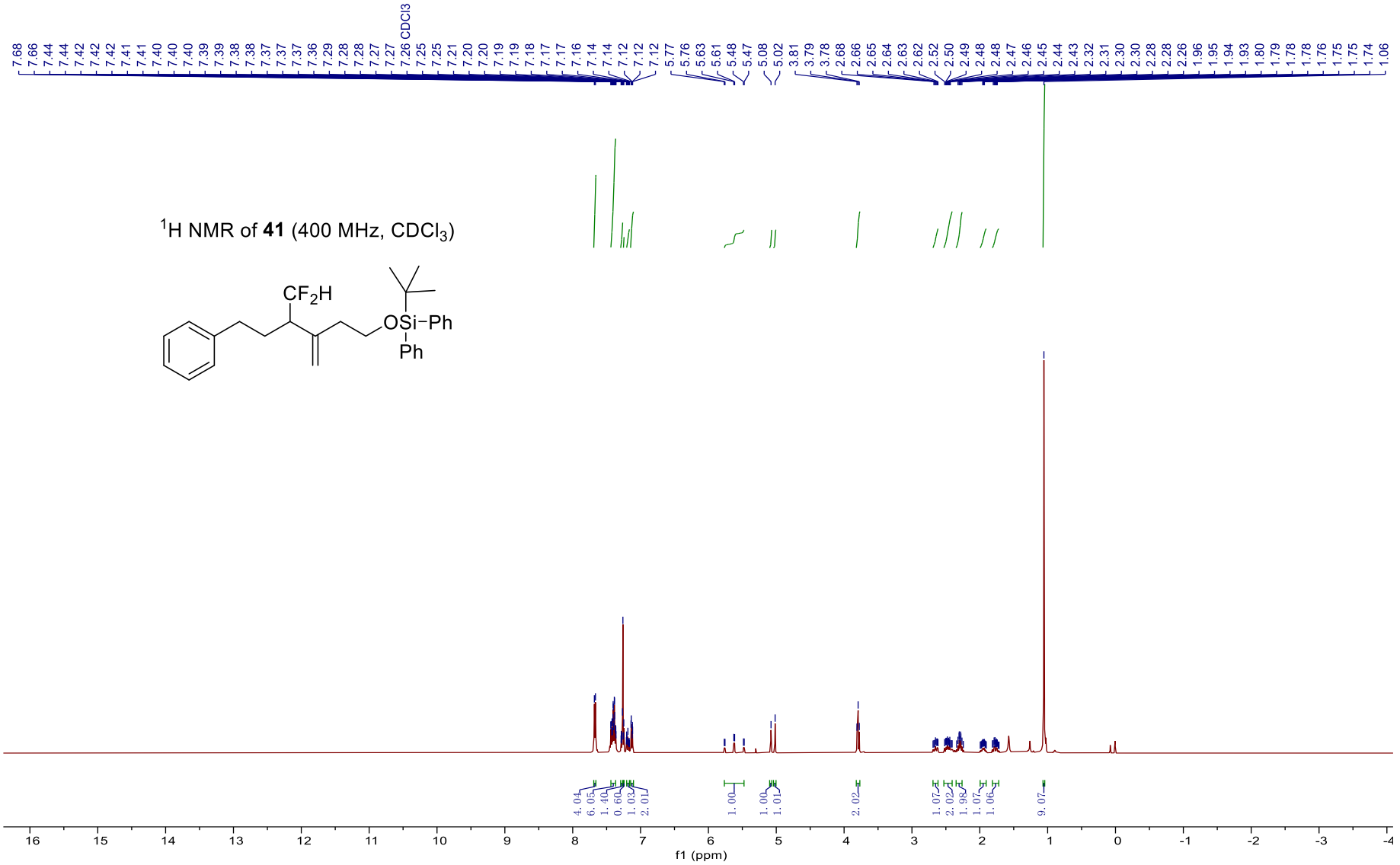
^{1}H NMR of **40** (400 MHz, $CDCl_3$)



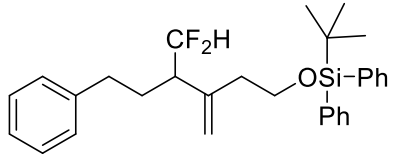

-117.72
-117.77
-117.87
-118.46
-118.50
-118.60
-118.65
-120.55
-120.60
-120.71
-120.75
-121.29
-121.33
-121.44
19F NMR of 40 (376 MHz, CDCl3)
CF2H
OPh
-117.5
-118.0
-118.5
-119.0
-119.5
-120.0
-120.5
-121.0
-121.5
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

^{13}C NMR of **40** (101 MHz, $CDCl_3$)

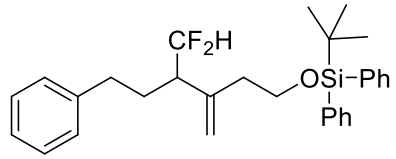


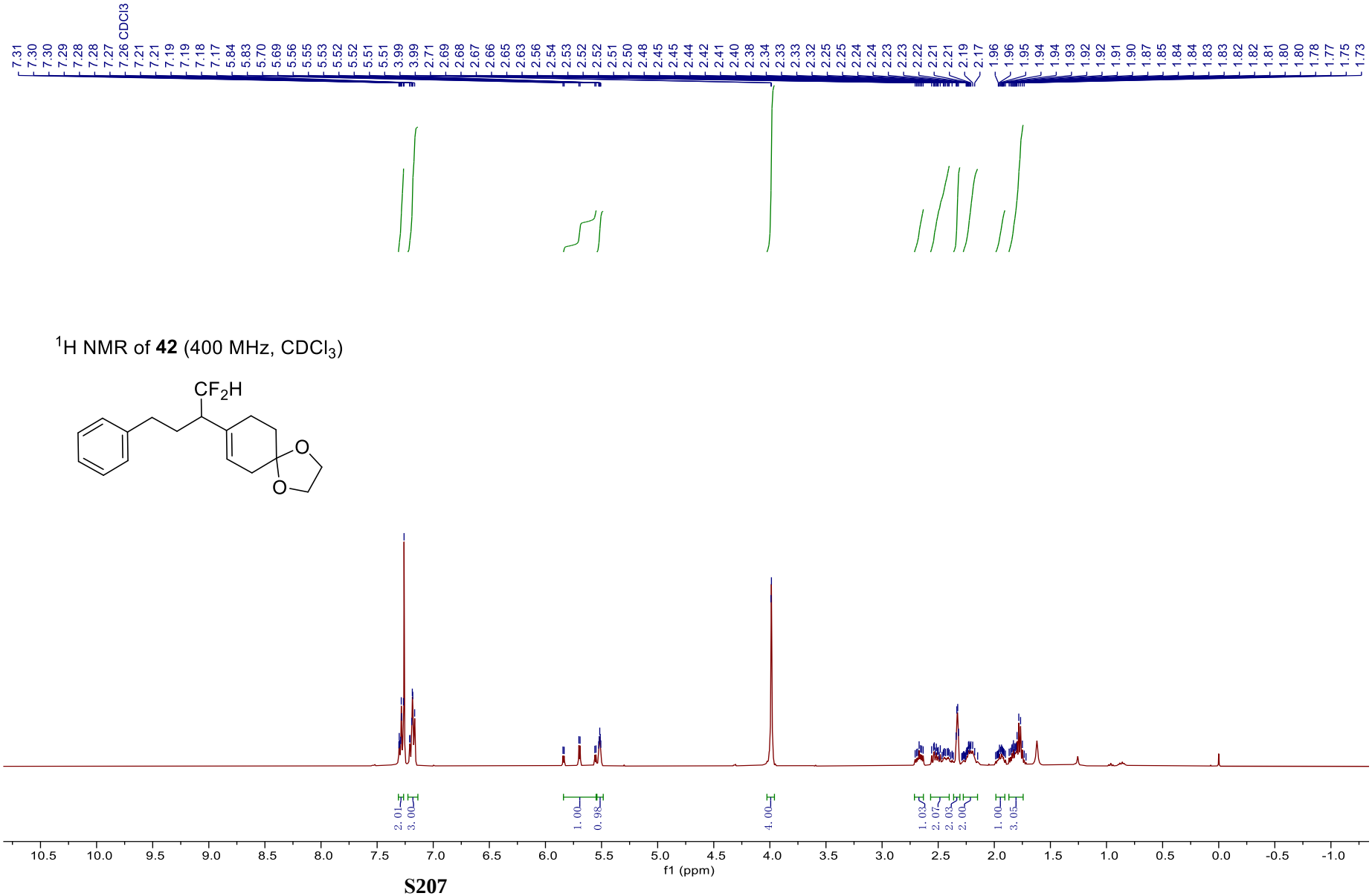

7.68 7.66 7.44 7.44 7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.29 7.28 7.28 7.27 7.27 7.26 CDCl3 7.25 7.25 7.21 7.20 7.20 7.19 7.19 7.18 7.17 7.17 7.16 7.14 7.14 7.12 7.12 7.12 5.77 5.76 5.63 5.61 5.48 5.47 5.08 5.02 3.81 3.79 3.78 2.68 2.66 2.65 2.64 2.63 2.62 2.52 2.50 2.49 2.48 2.48 2.47 2.46 2.45 2.44 2.43 2.32 2.31 2.30 2.30 2.28 2.28 2.26 1.96 1.95 1.94 1.93 1.80 1.79 1.78 1.78 1.76 1.75 1.75 1.74 1.06
^{1}H NMR of **41** (400 MHz, $CDCl_3$)
CF_2H
OSi−Ph
Ph
4.04 6.05 1.40 0.60 1.03 2.01 1.00 1.00 1.01 2.02 1.07 2.02 1.98 1.07 1.06 9.07
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

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



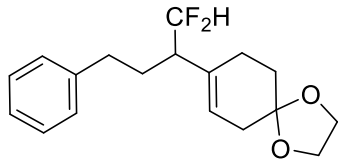
^{13}C NMR of **41** (101 MHz, $CDCl_3$)

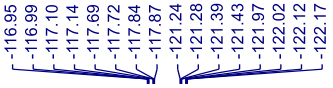


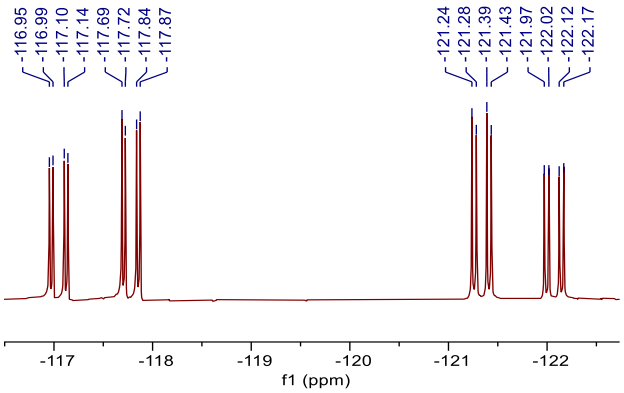


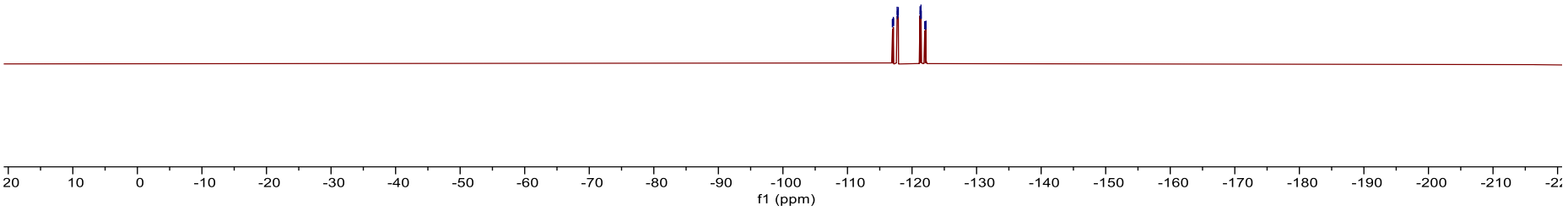
^{1}H NMR of **42** (400 MHz, $CDCl_3$)

^{19}F NMR of **42** (376 MHz, $CDCl_3$)

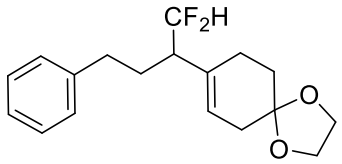


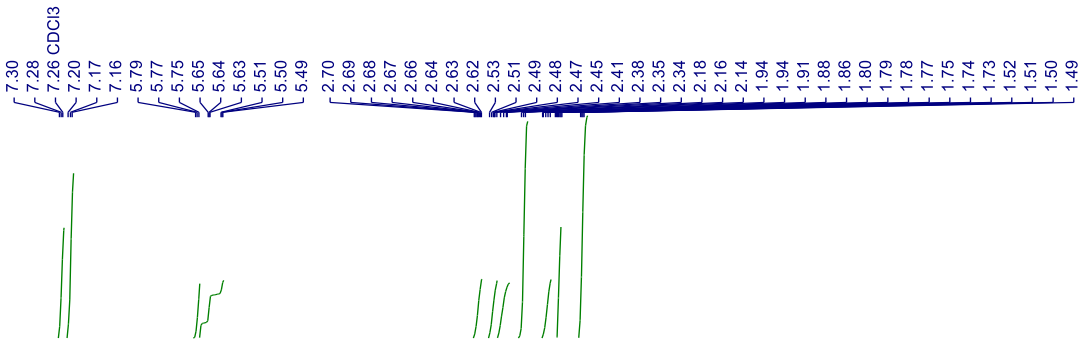




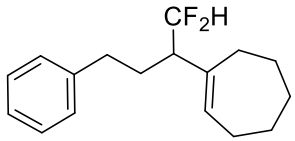


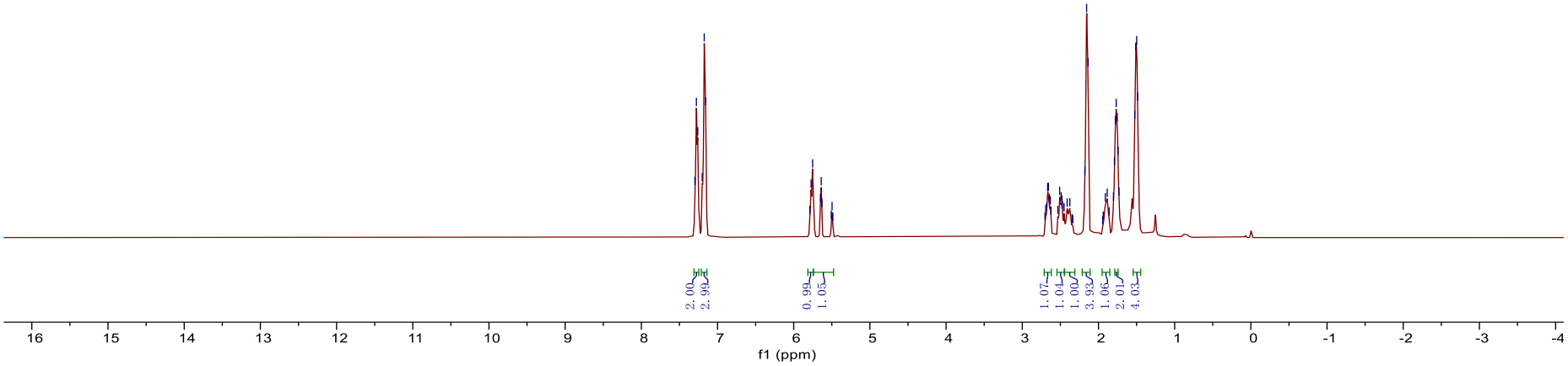
^{13}C NMR of **42** (101 MHz, $CDCl_3$)



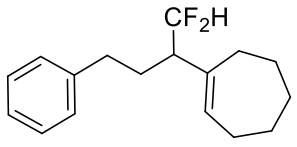


^{1}H NMR of **43** (400 MHz, $CDCl_3$)

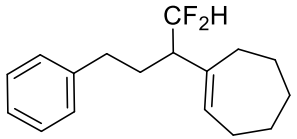


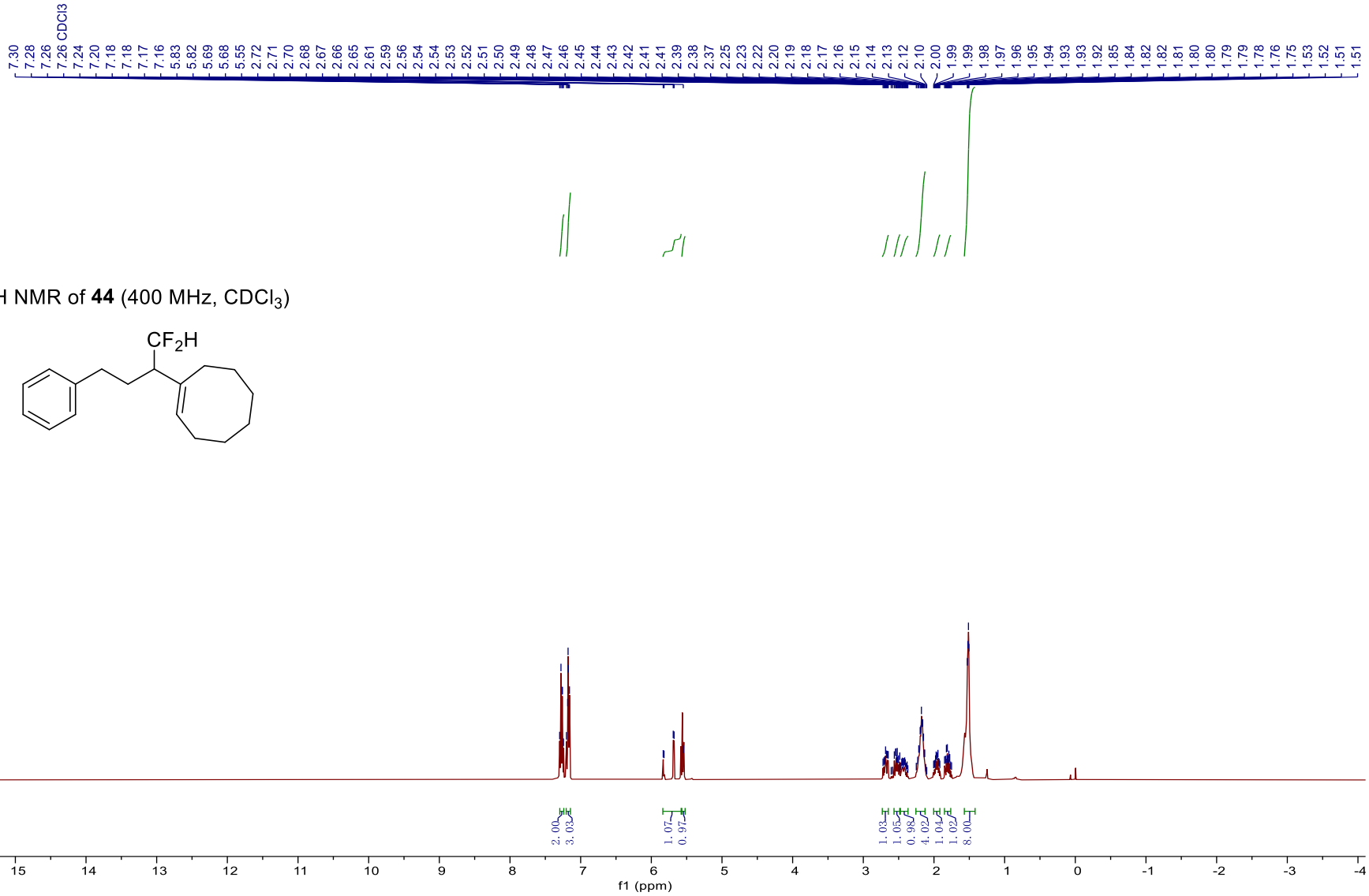


^{19}F NMR of **43** (376 MHz, $CDCl_3$)



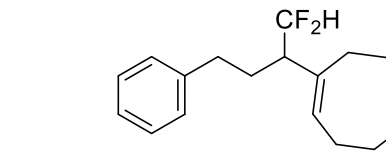
^{13}C NMR of **43** (101 MHz, $CDCl_3$)

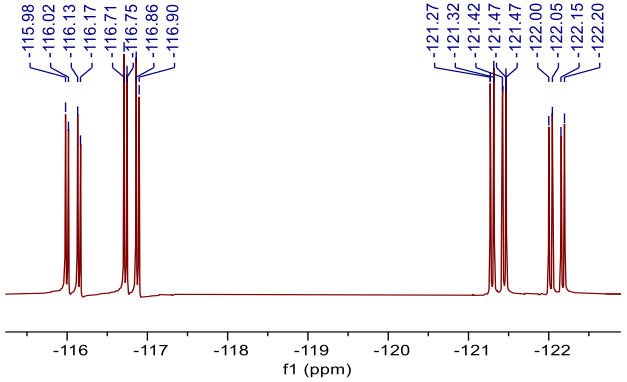


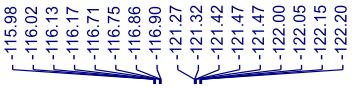


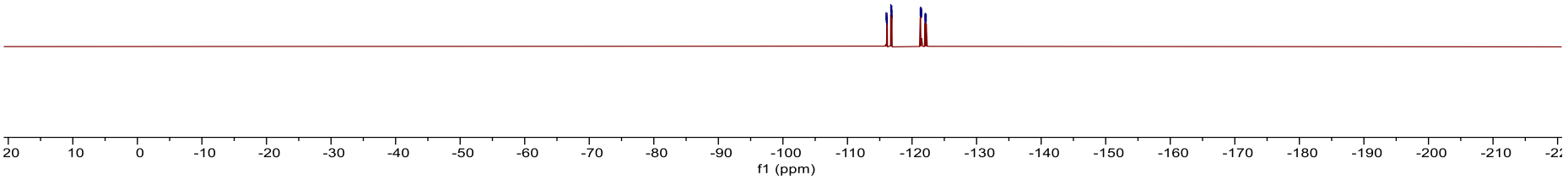
^{1}H NMR of **44** (400 MHz, $CDCl_3$)

^{19}F NMR of **44** (376 MHz, $CDCl_3$)

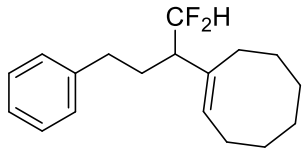


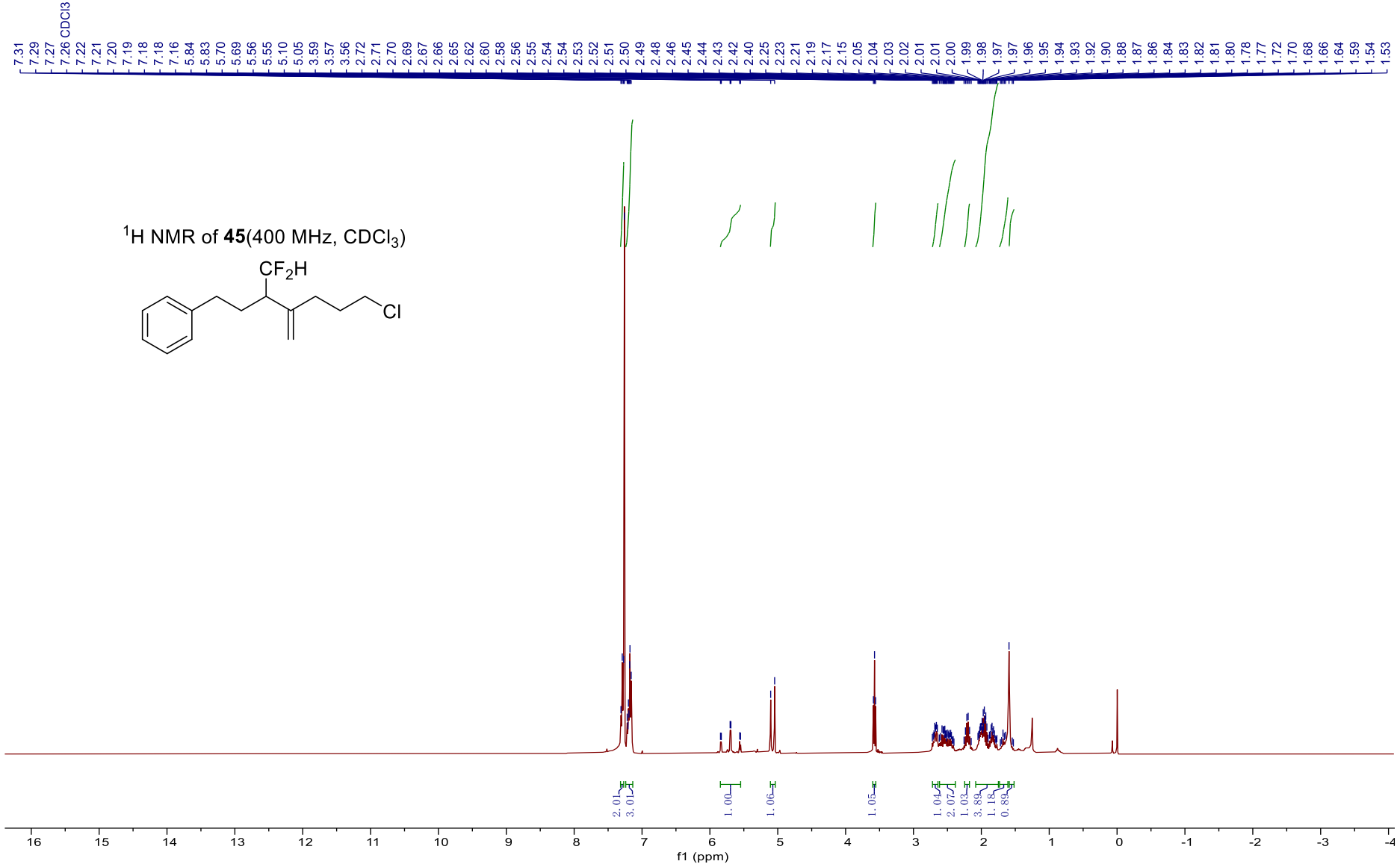




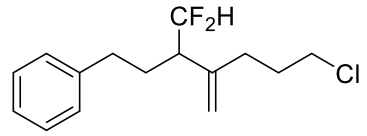


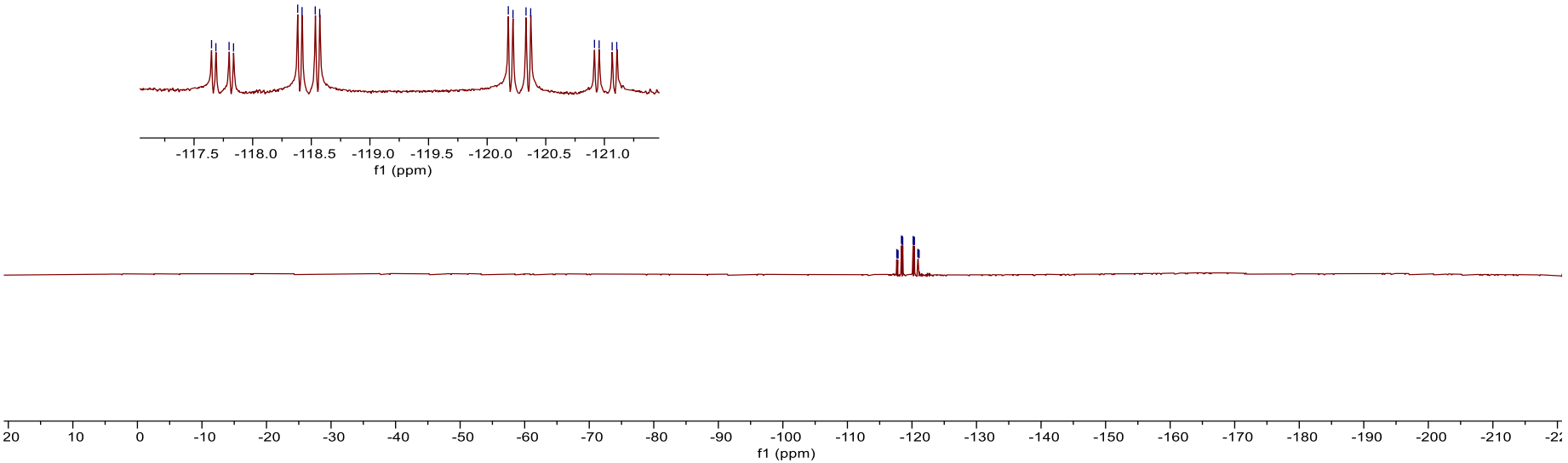
^{13}C NMR of **44** (101 MHz, $CDCl_3$)



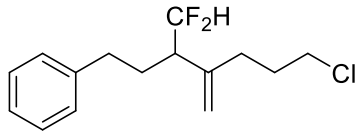

7.31 7.29 7.27 7.26 CDCl3 7.22 7.21 7.20 7.19 7.18 7.18 7.16 5.84 5.83 5.70 5.69 5.56 5.55 5.10 5.05 3.59 3.57 3.56 2.72 2.71 2.70 2.69 2.67 2.66 2.65 2.62 2.60 2.58 2.56 2.55 2.54 2.54 2.53 2.52 2.51 2.50 2.49 2.48 2.46 2.45 2.44 2.43 2.42 2.40 2.25 2.23 2.21 2.19 2.17 2.15 2.05 2.04 2.03 2.02 2.01 2.01 2.00 1.99 1.98 1.97 1.97 1.96 1.95 1.94 1.93 1.92 1.90 1.88 1.87 1.86 1.84 1.83 1.82 1.81 1.80 1.78 1.77 1.72 1.70 1.68 1.66 1.64 1.59 1.54 1.53
^{1}H NMR of **45**(400 MHz, $CDCl_3$)
CF_2H
Cl
2.01 3.01 1.00 1.06 1.05 1.04 2.07 1.03 3.89 1.18 0.89
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

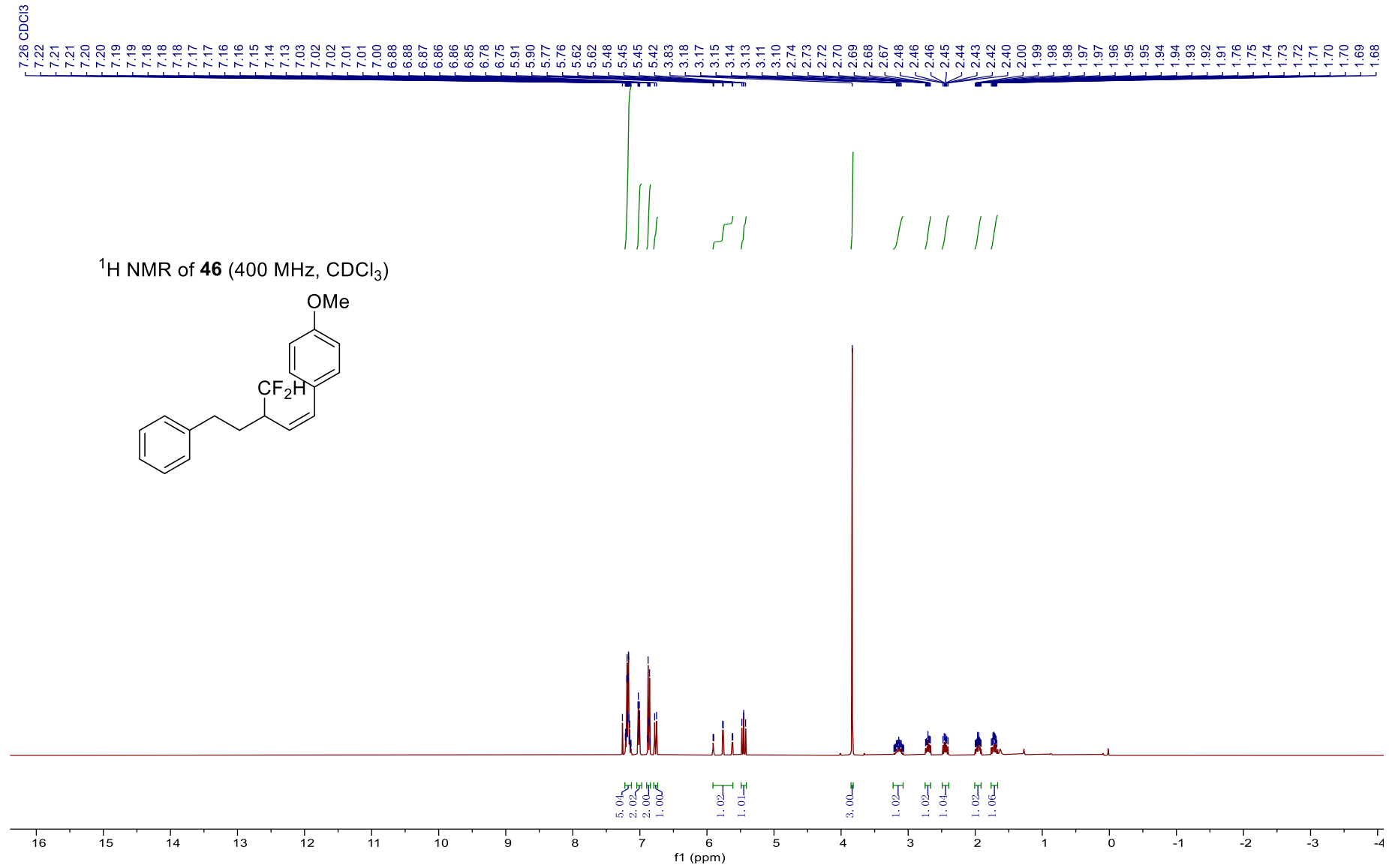
^{19}F NMR of **45** (376 MHz, $CDCl_3$)





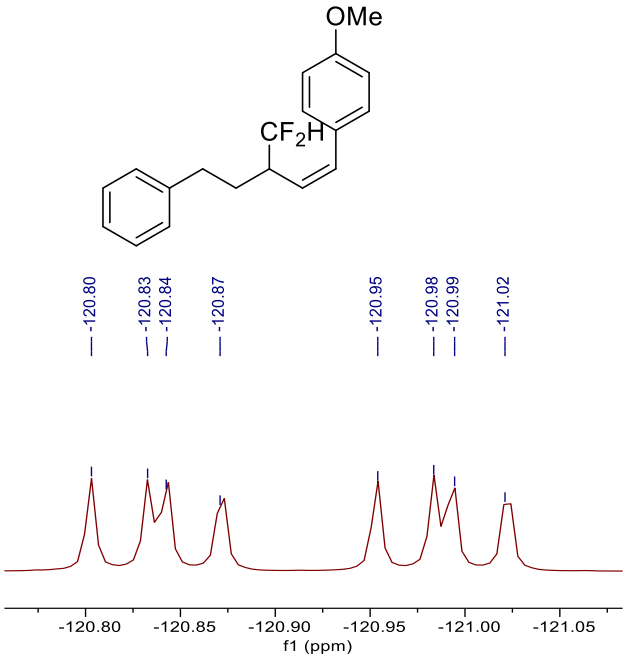
^{13}C NMR of **45** (101 MHz, $CDCl_3$)

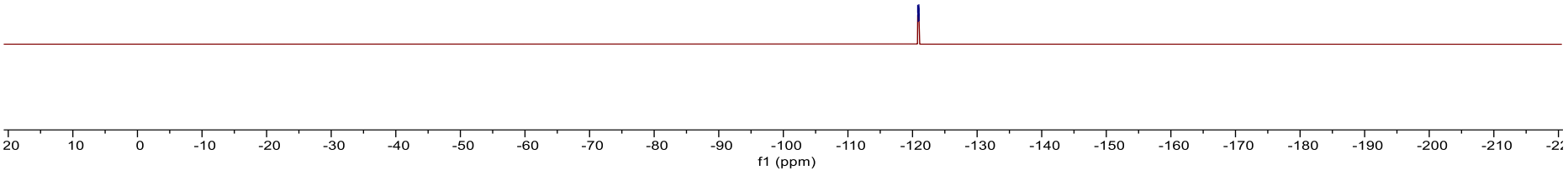


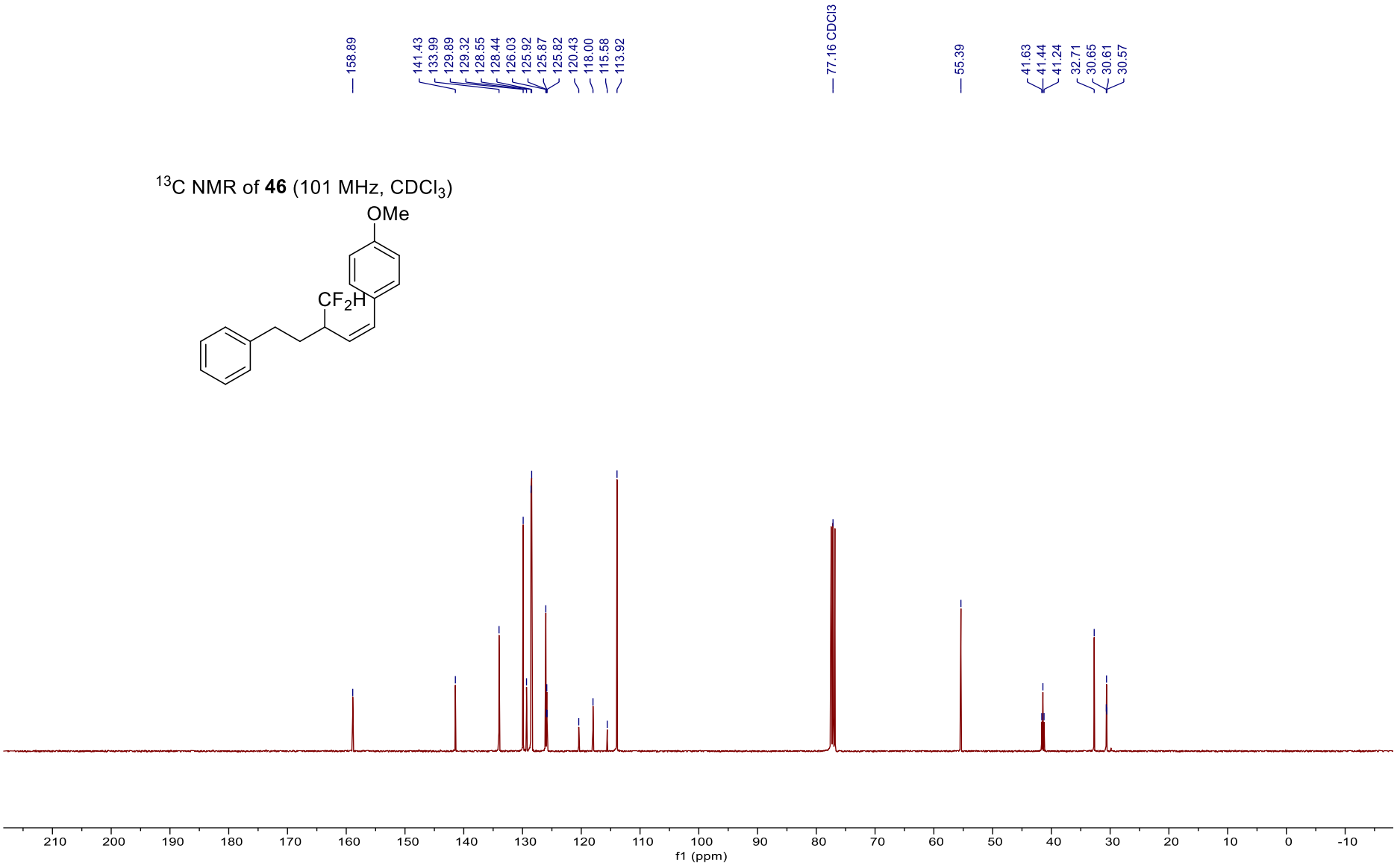


^{1}H NMR of **46** (400 MHz, $CDCl_3$)

^{19}F NMR of **46** (376 MHz, $CDCl_3$)

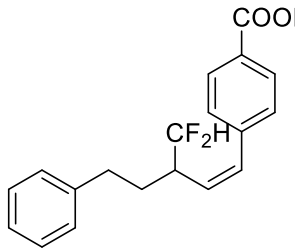




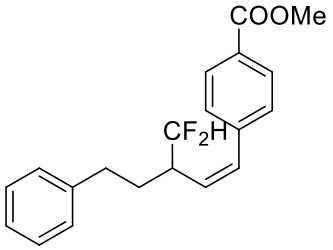


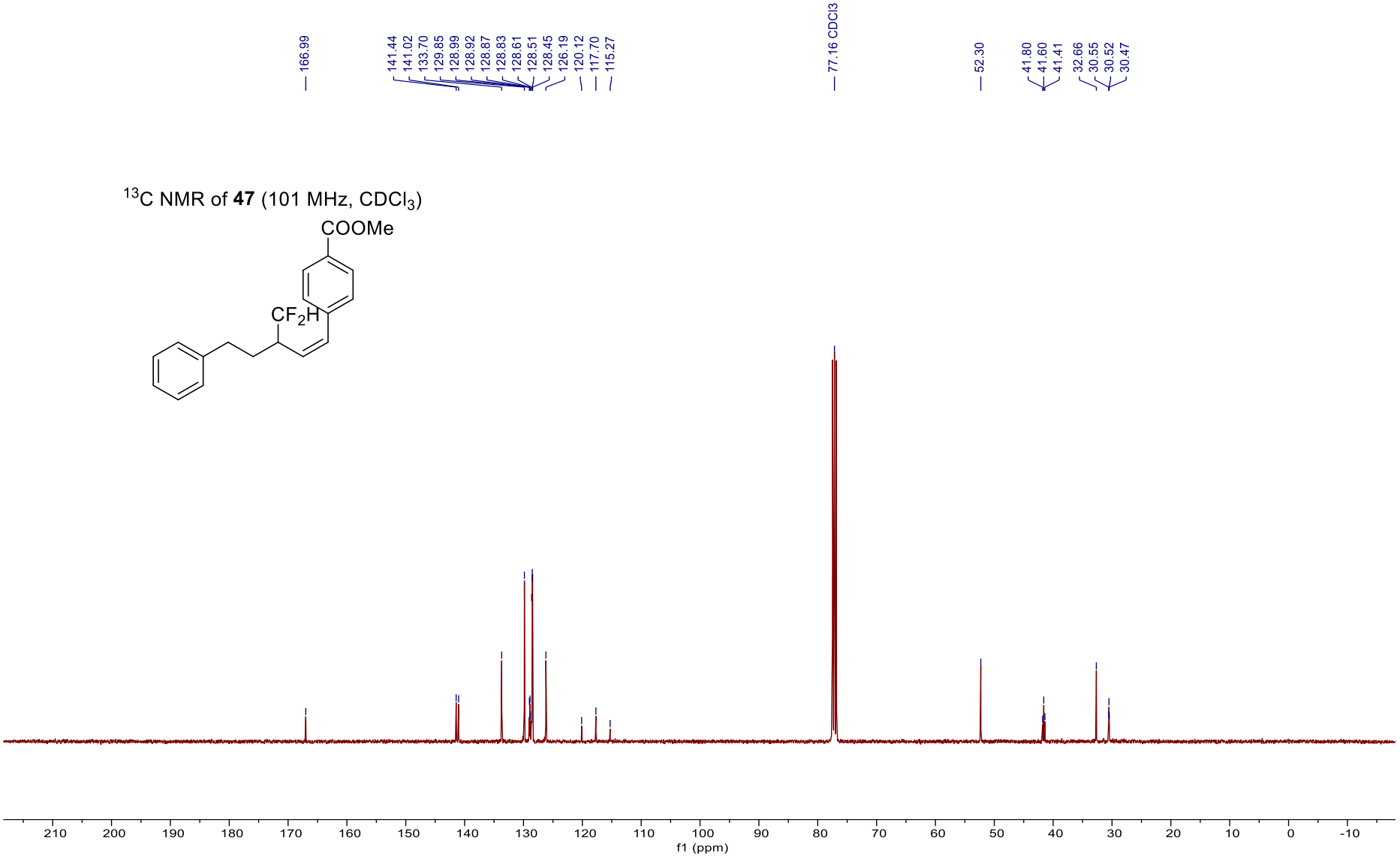
^{13}C NMR of **46** (101 MHz, $CDCl_3$)

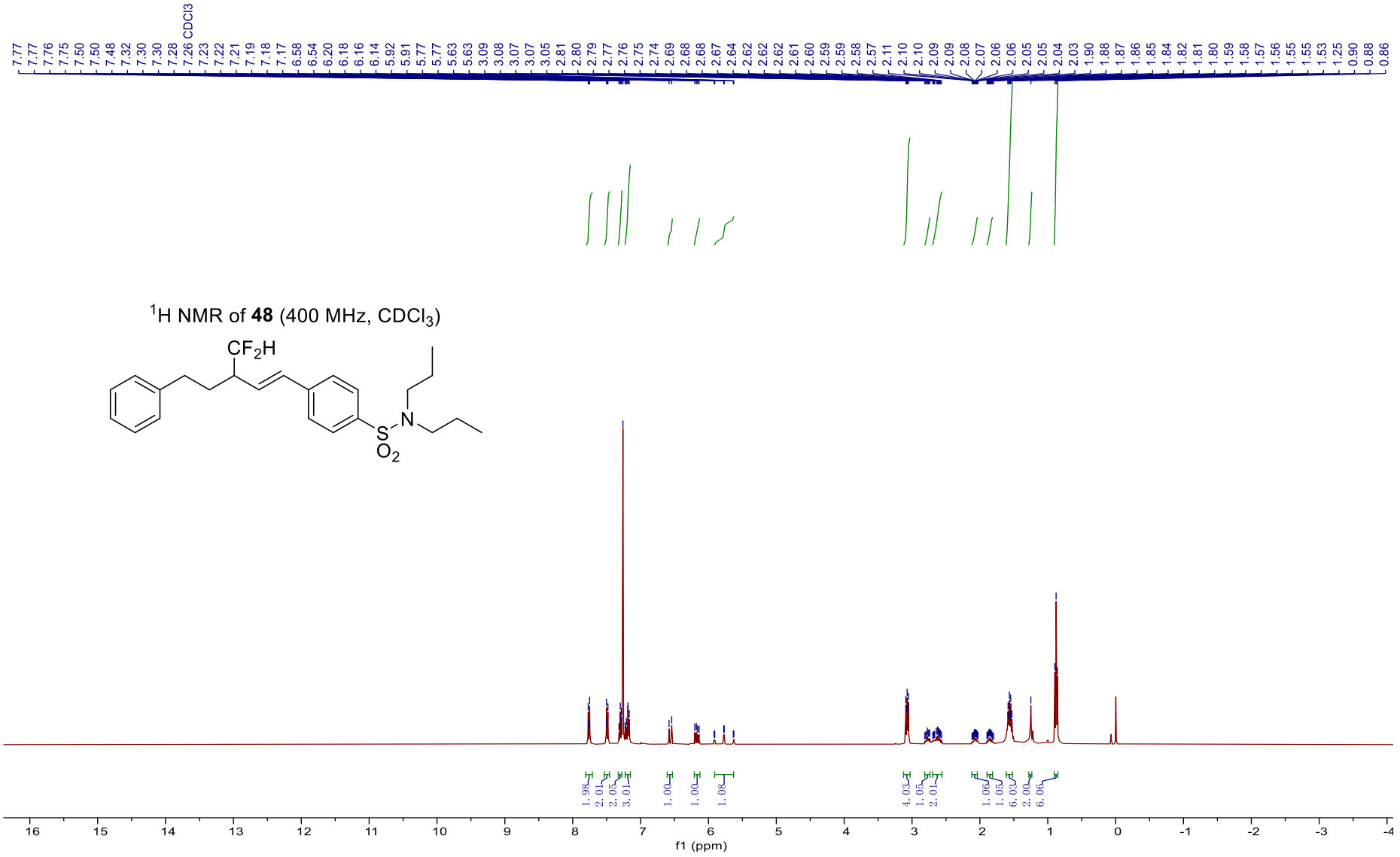
^{1}H NMR of **47** (400 MHz, $CDCl_3$)

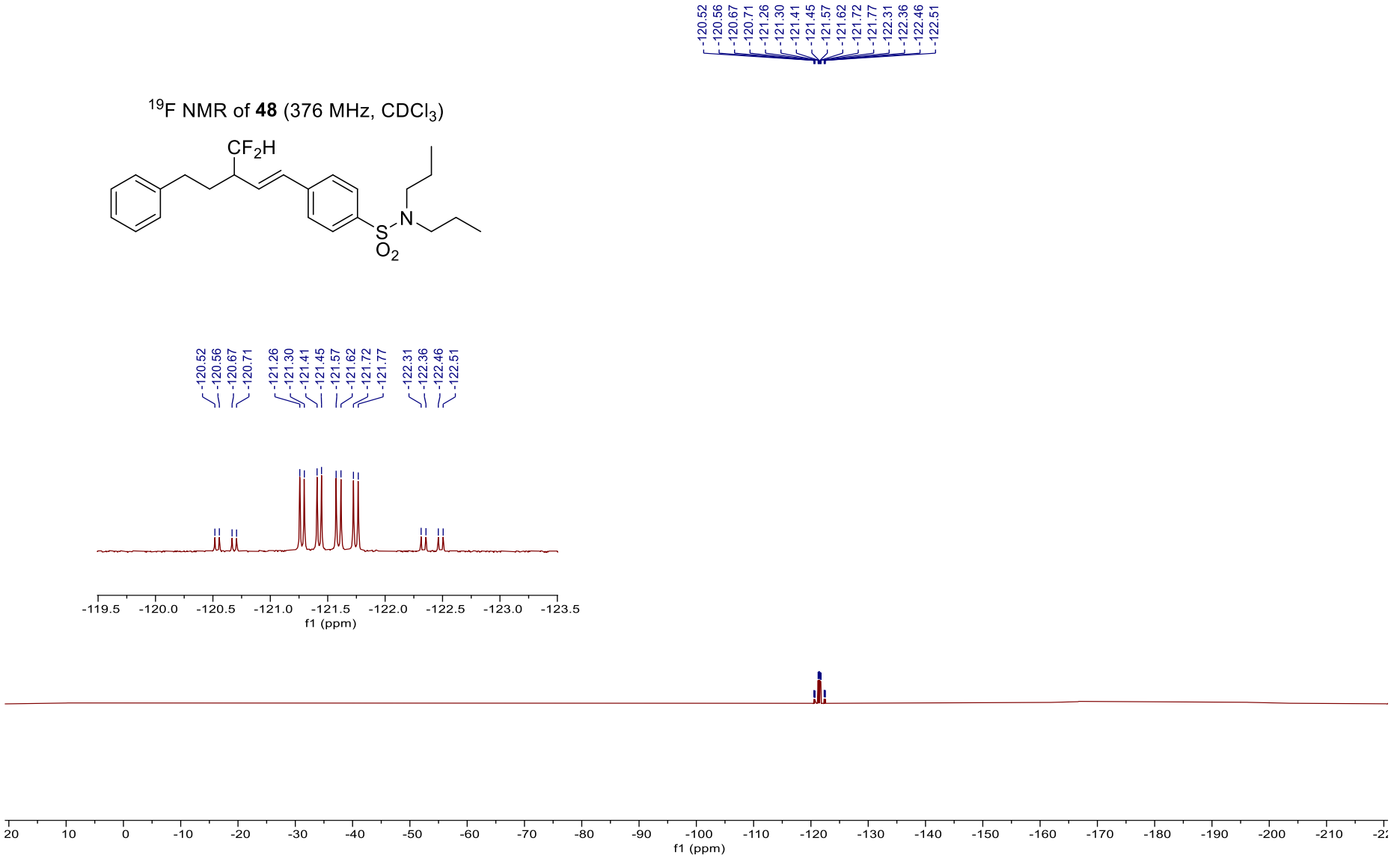


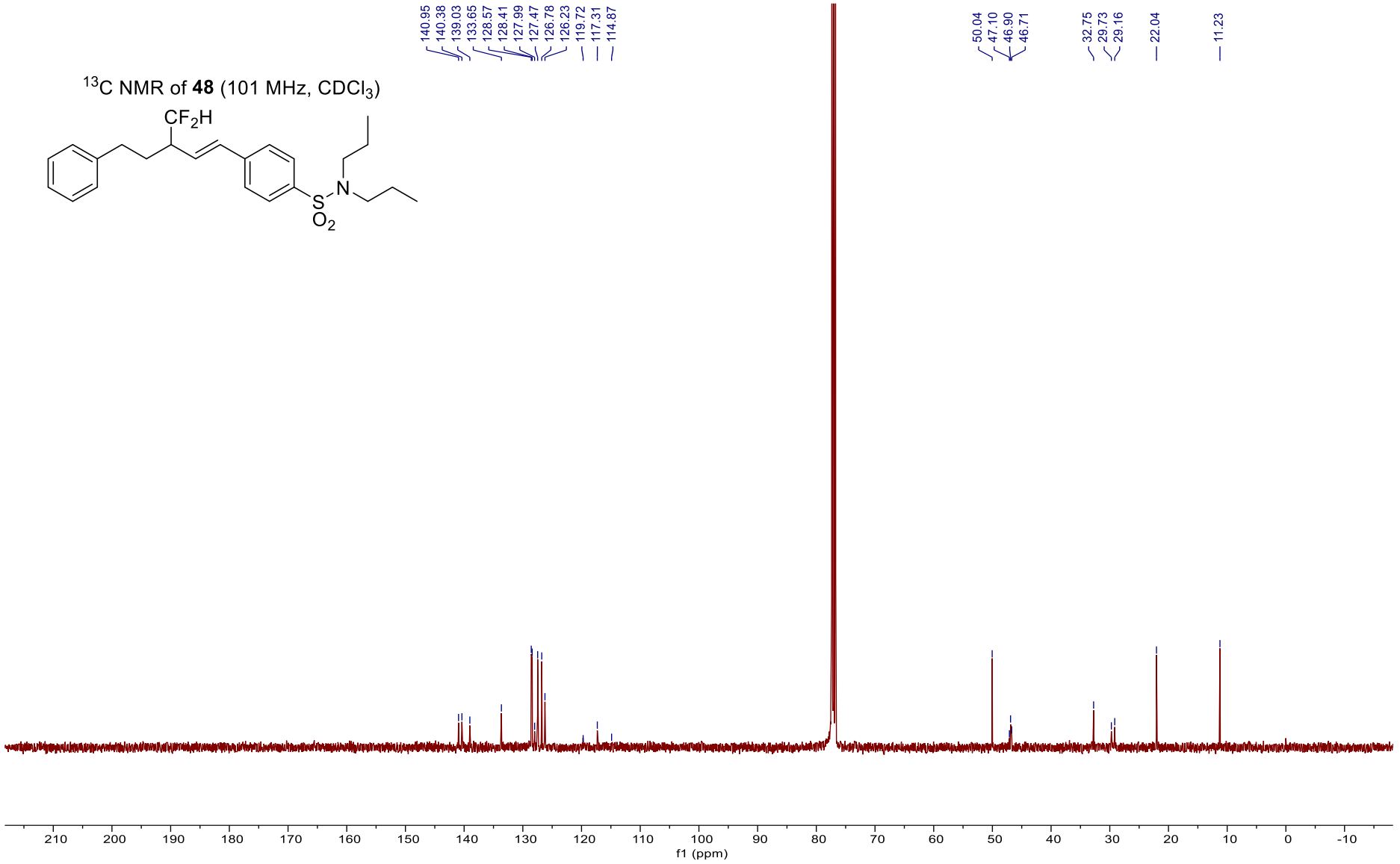
^{19}F NMR of **47** (376 MHz, $CDCl_3$)



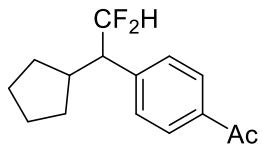

166.99
141.44
141.02
133.70
129.85
128.99
128.92
128.87
128.83
128.61
128.51
128.45
126.19
120.12
117.70
115.27
77.16 CDCl3
52.30
41.80
41.60
41.41
32.66
30.55
30.52
30.47
^{13}C NMR of **47** (101 MHz, $CDCl_3$)
COOMe
CF_2H
f1 (ppm)


7.77 7.77 7.76 7.75 7.50 7.50 7.48 7.32 7.30 7.30 7.28 7.26 CDCl3 7.23 7.22 7.21 7.19 7.18 7.17 6.58 6.54 6.20 6.18 6.16 6.14 5.92 5.91 5.77 5.77 5.63 5.63 3.09 3.08 3.07 3.07 3.05 2.81 2.80 2.79 2.77 2.76 2.75 2.74 2.69 2.68 2.68 2.67 2.64 2.62 2.62 2.62 2.61 2.60 2.59 2.59 2.58 2.57 2.11 2.10 2.10 2.09 2.09 2.08 2.07 2.06 2.06 2.05 2.05 2.04 2.03 1.90 1.88 1.87 1.86 1.85 1.84 1.82 1.81 1.80 1.59 1.58 1.57 1.56 1.55 1.55 1.53 1.25 0.90 0.88 0.86
1H NMR of 48 (400 MHz, CDCl3)
CF2H
S
O2
N
1.98 2.01 2.05 3.01 1.00 1.00 1.08 4.03 1.05 2.01 1.06 1.05 6.03 2.00 6.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

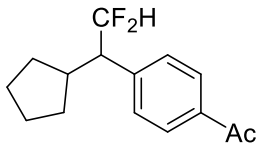

-120.52
-120.56
-120.67
-120.71
-121.26
-121.30
-121.41
-121.45
-121.57
-121.62
-121.72
-121.77
-122.31
-122.36
-122.46
-122.51
19F NMR of 48 (376 MHz, CDCl3)
CF2H
S
O2
N
-119.5
-120.0
-120.5
-121.0
-121.5
-122.0
-122.5
-123.0
-123.5
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

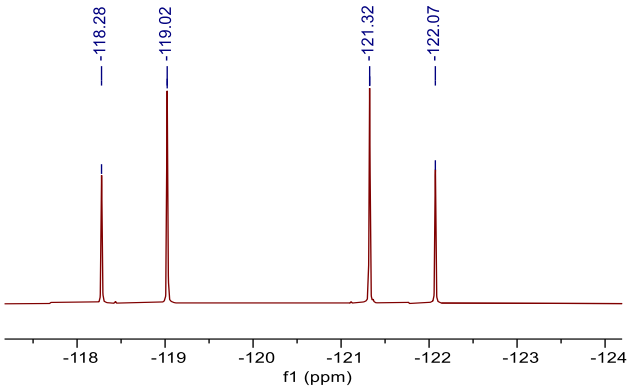

^{13}C NMR of **48** (101 MHz, $CDCl_3$)
CF_2H
S
N
O_2
140.95
140.38
139.03
133.65
128.57
128.41
127.99
127.47
126.78
126.23
119.72
117.31
114.87
50.04
47.10
46.90
46.71
32.75
29.73
29.16
22.04
11.23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

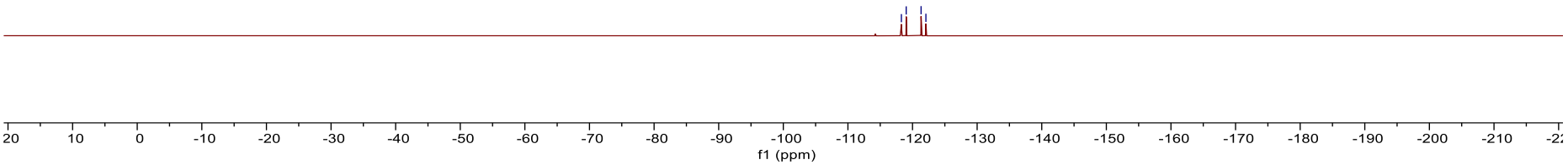
^{1}H NMR of **49** (400 MHz, $CDCl_3$)

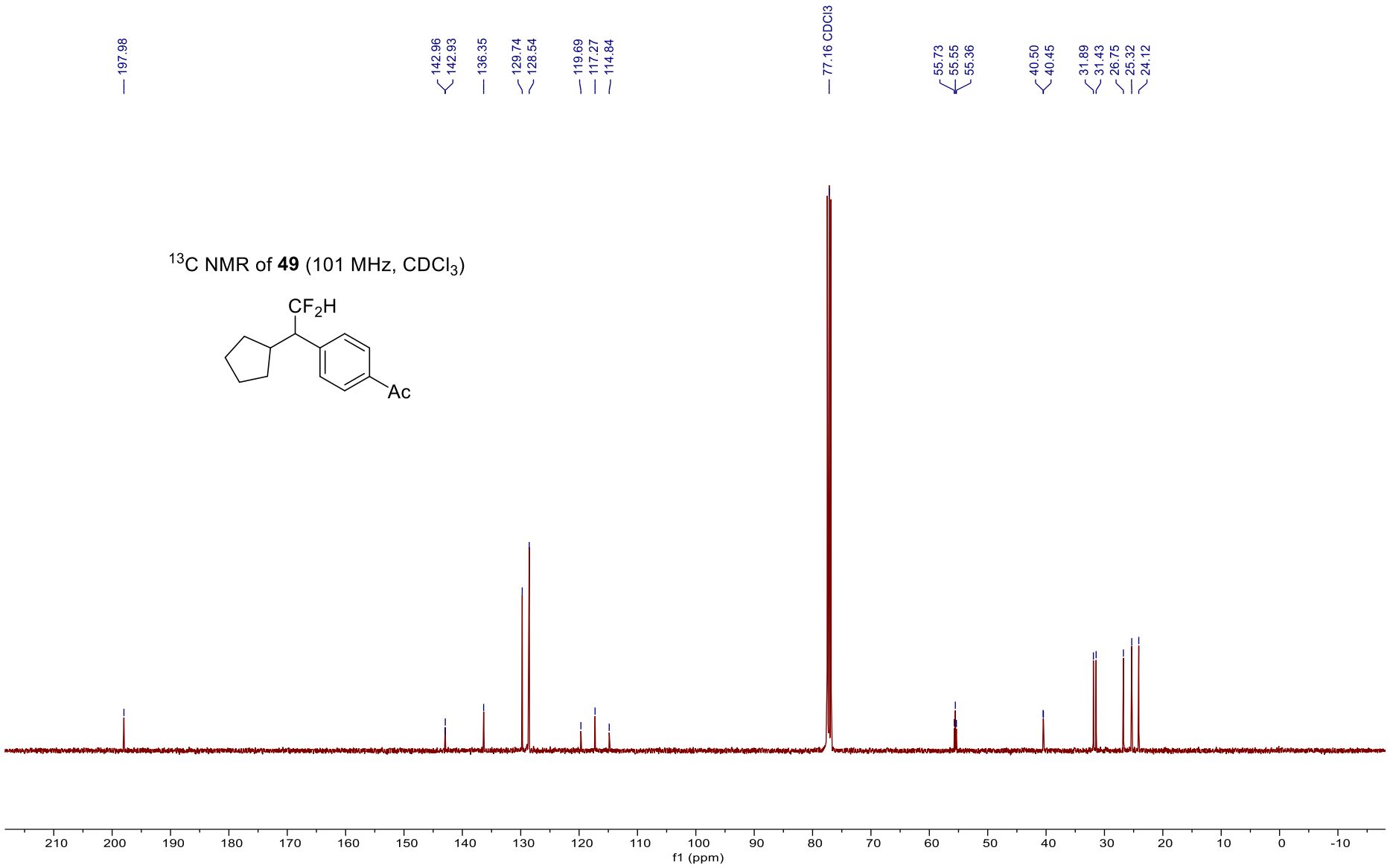


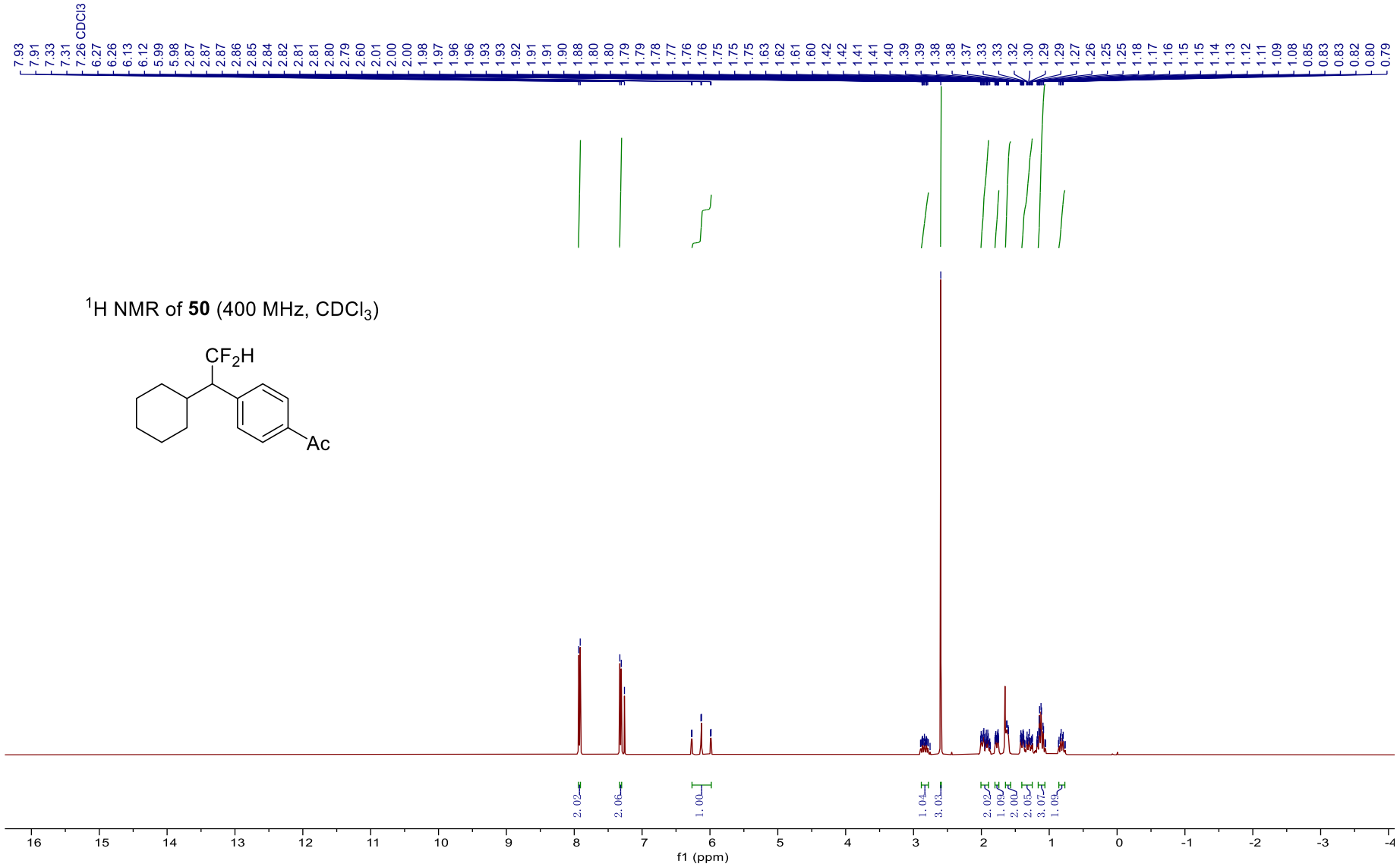
^{19}F NMR of **49** (376 MHz, $CDCl_3$)



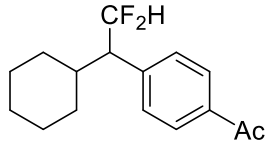


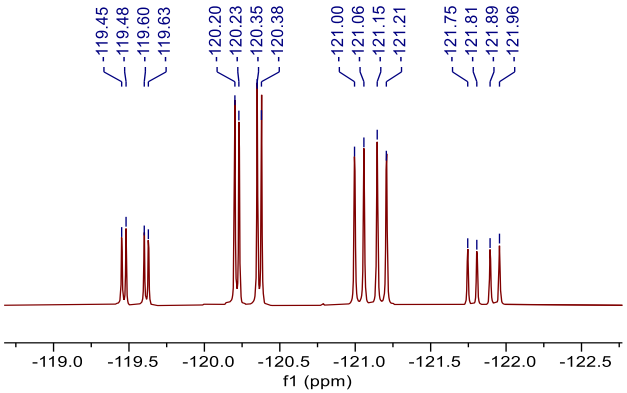


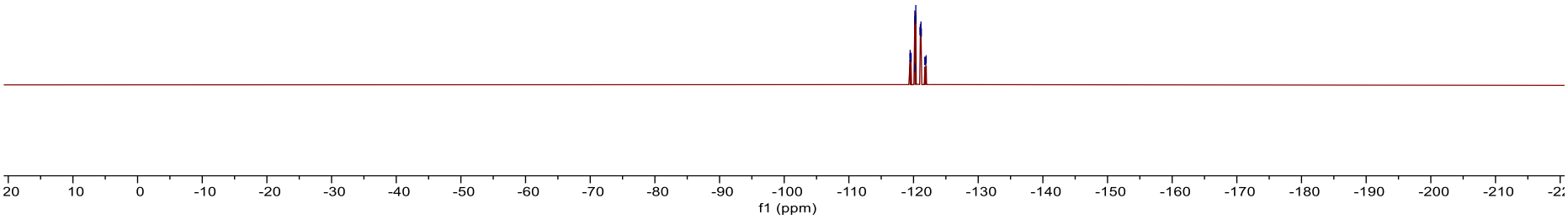

197.98
142.96
142.93
136.35
129.74
128.54
119.69
117.27
114.84
77.16 CDCl3
55.73
55.55
55.36
40.50
40.45
31.89
31.43
26.75
25.32
24.12
^{13}C NMR of **49** (101 MHz, $CDCl_3$)
CF_2H
Ac
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

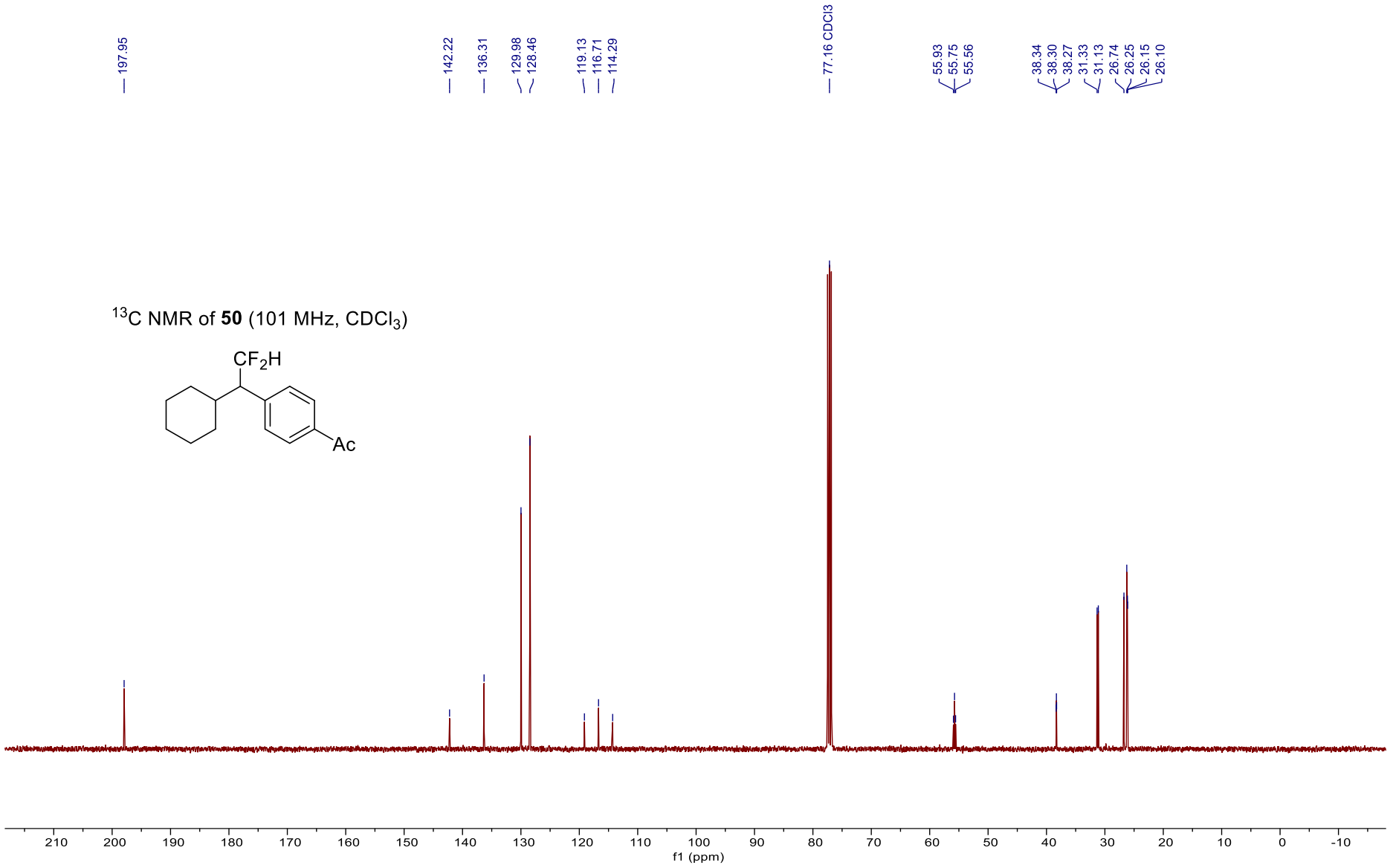

7.93
7.91
7.33
7.31
7.26 CDCl3
6.27
6.26
6.13
6.12
5.99
5.98
2.87
2.87
2.87
2.86
2.85
2.84
2.82
2.81
2.81
2.80
2.79
2.60
2.01
2.00
2.00
1.98
1.97
1.96
1.96
1.93
1.93
1.92
1.91
1.91
1.90
1.88
1.80
1.80
1.79
1.79
1.78
1.77
1.76
1.76
1.75
1.75
1.75
1.63
1.62
1.61
1.60
1.42
1.42
1.41
1.41
1.40
1.39
1.39
1.38
1.38
1.37
1.33
1.33
1.32
1.30
1.29
1.29
1.27
1.26
1.25
1.25
1.18
1.17
1.16
1.15
1.15
1.14
1.13
1.12
1.11
1.09
1.08
0.85
0.83
0.83
0.82
0.80
0.79
^{1}H NMR of **50** (400 MHz, $CDCl_3$)
CF_2H
Ac
2.02
2.06
1.00
1.04
3.03
2.02
1.09
2.00
2.05
3.07
1.09
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

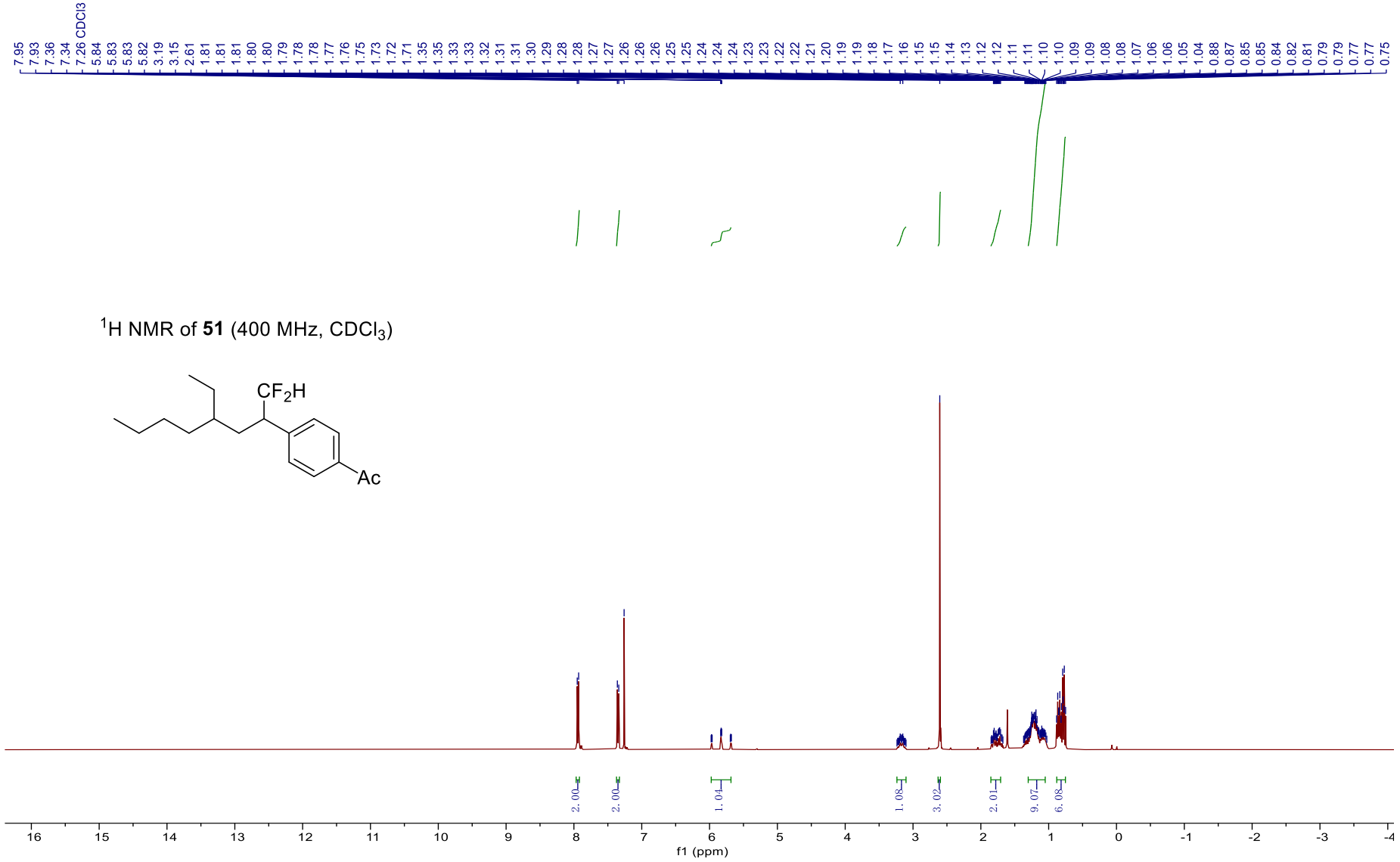
^{19}F NMR of **50** ($CDCl_3$)





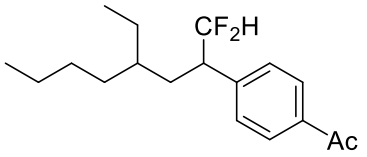


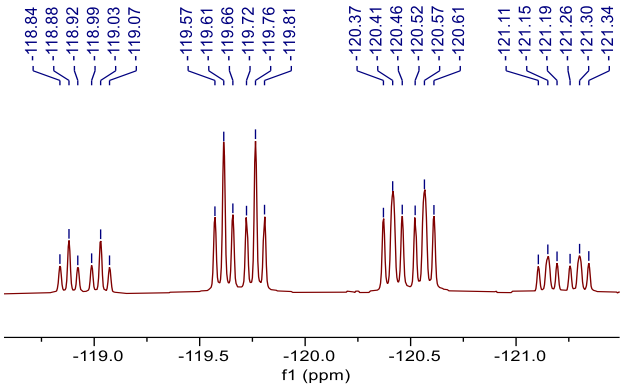

197.95
142.22
136.31
129.98
128.46
119.13
116.71
114.29
77.16 CDCl3
55.93
55.75
55.56
38.34
38.30
38.27
31.33
31.13
26.74
26.25
26.15
26.10
13C NMR of 50 (101 MHz, CDCl3)
CF2H
Ac
f1 (ppm)

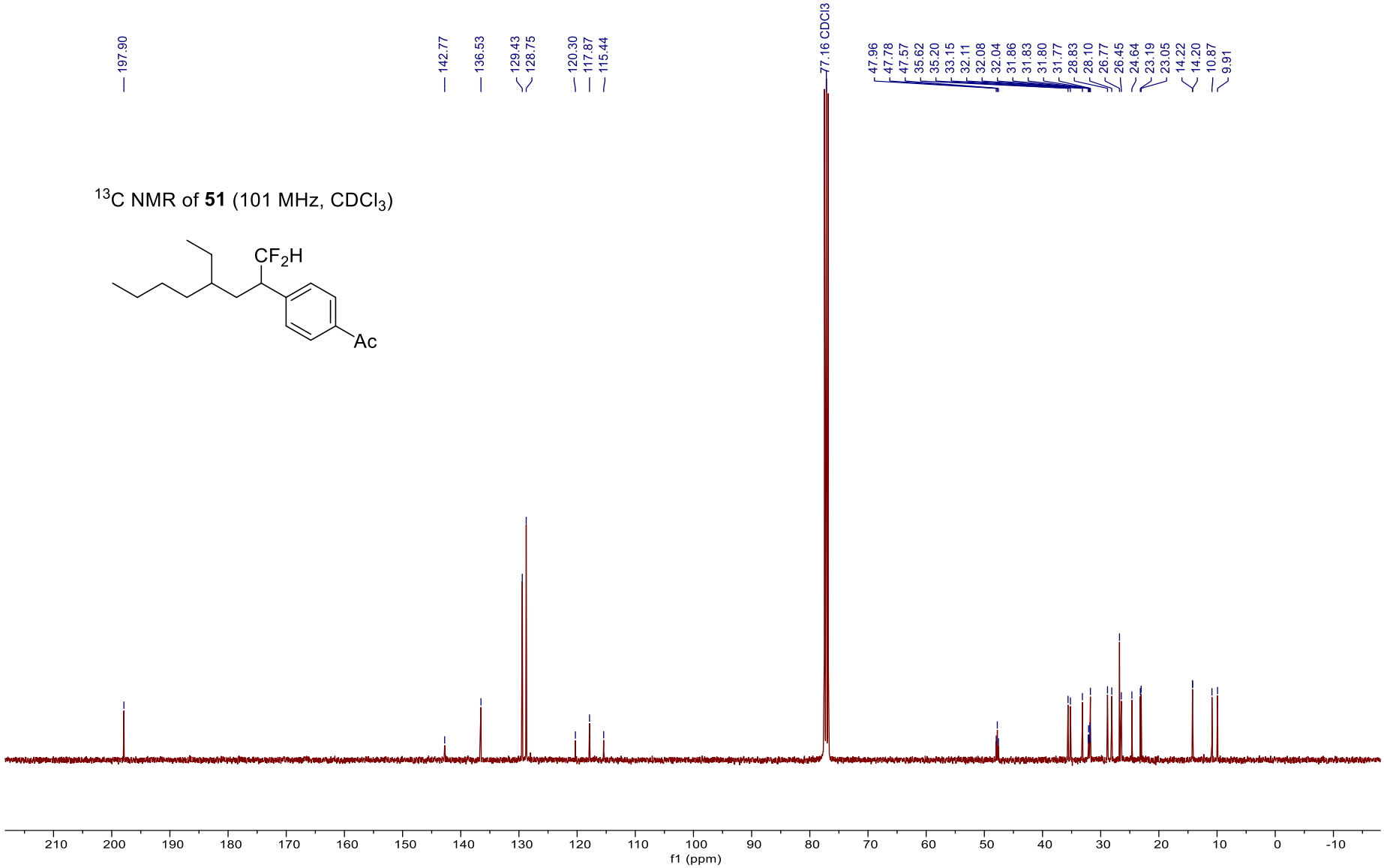


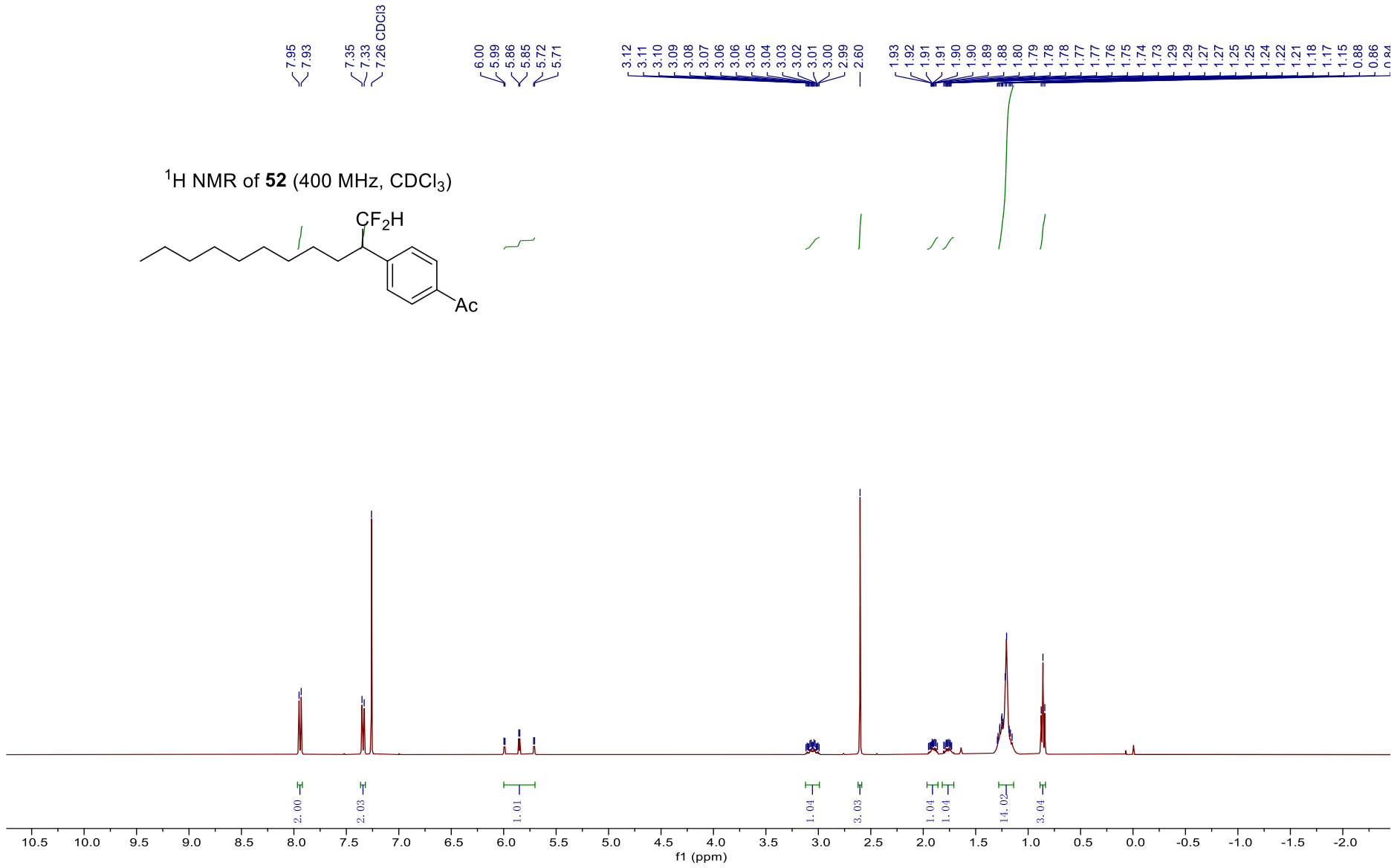
^{1}H NMR of **51** (400 MHz, $CDCl_3$)

^{19}F NMR of **51** (376 MHz, $CDCl_3$)

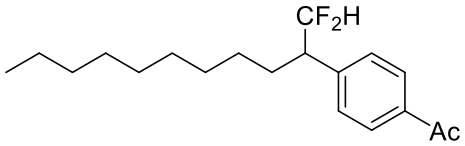


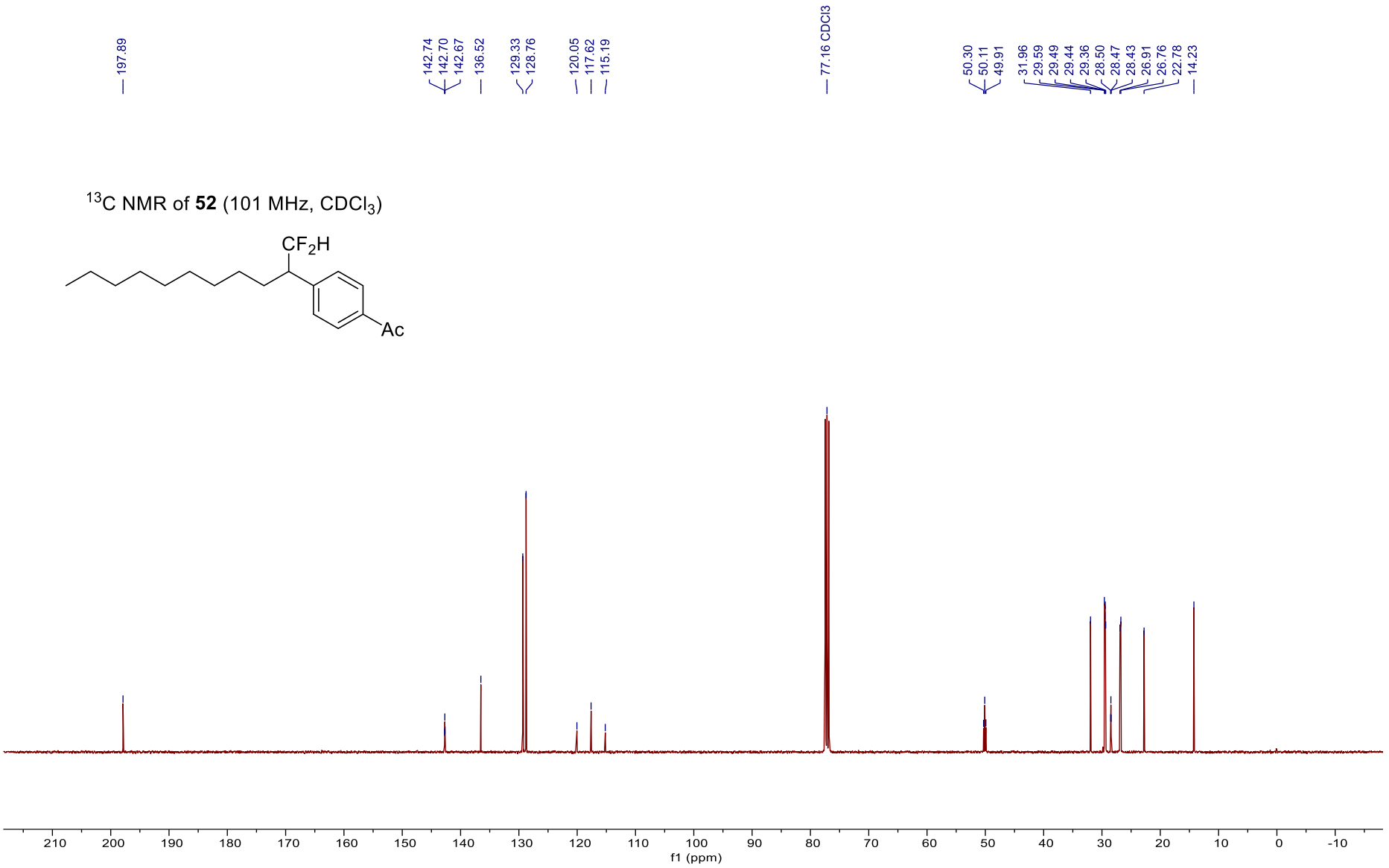



197.90
142.77
136.53
129.43
128.75
120.30
117.87
115.44
77.16 CDCl3
47.96
47.78
47.57
35.62
35.20
33.15
32.11
32.08
32.04
31.86
31.83
31.80
31.77
28.83
28.10
26.77
26.45
24.64
23.19
23.05
14.22
14.20
10.87
9.91
^{13}C NMR of **51** (101 MHz, $CDCl_3$)
CF_2H
Ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

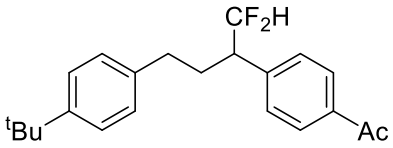

7.95
7.93
7.35
7.33
7.26 CDCl3
6.00
5.99
5.86
5.85
5.72
5.71
3.12
3.11
3.10
3.09
3.08
3.07
3.06
3.06
3.05
3.04
3.03
3.02
3.01
3.00
2.99
2.60
1.93
1.92
1.91
1.91
1.90
1.90
1.89
1.88
1.80
1.79
1.78
1.78
1.77
1.77
1.76
1.75
1.74
1.73
1.29
1.29
1.27
1.27
1.25
1.25
1.24
1.22
1.21
1.18
1.17
1.15
0.88
0.86
1H NMR of 52 (400 MHz, CDCl3)
CF2H
Ac
2.00
2.03
1.01
1.04
3.03
1.04
1.04
14.02
3.04
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
0.0
-0.5
-1.0
-1.5
-2.0
f1 (ppm)

^{19}F NMR of **52** (376 MHz, $CDCl_3$)

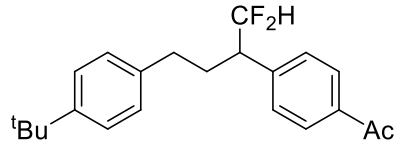


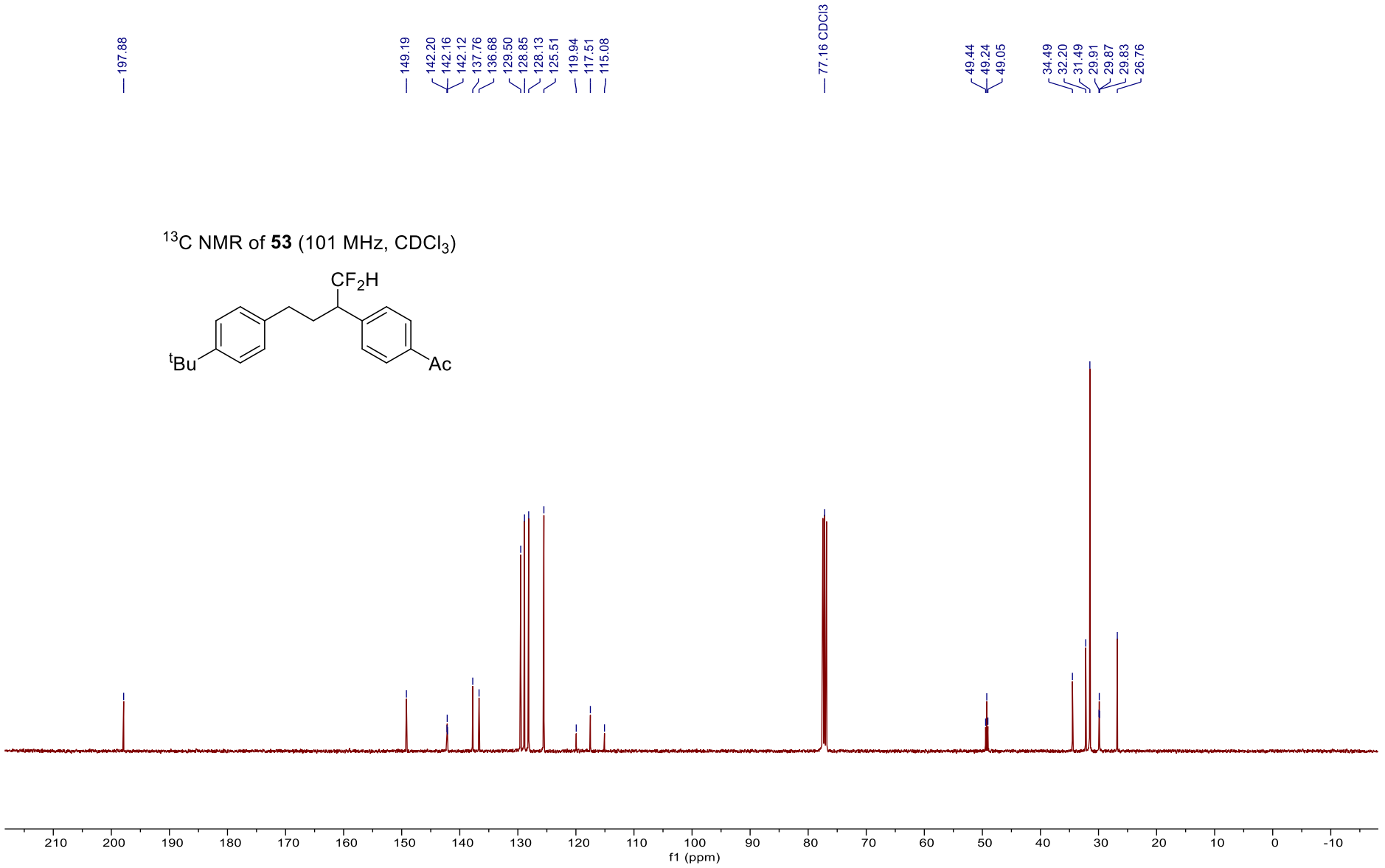

197.89
142.74
142.70
142.67
136.52
129.33
128.76
120.05
117.62
115.19
77.16 CDCl3
50.30
50.11
49.91
31.96
29.59
29.49
29.44
29.36
28.50
28.47
28.43
26.91
26.76
22.78
14.23
^{13}C NMR of **52** (101 MHz, $CDCl_3$)
CF_2H
Ac
f1 (ppm)

^{1}H NMR of **53** (400 MHz, $CDCl_3$)

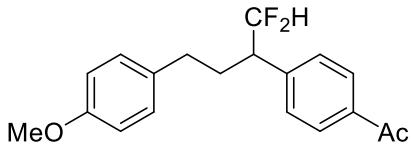


^{19}F NMR of **53** (376 MHz, $CDCl_3$)

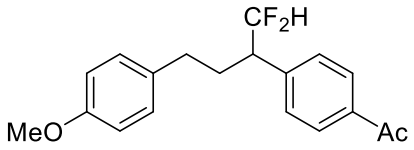


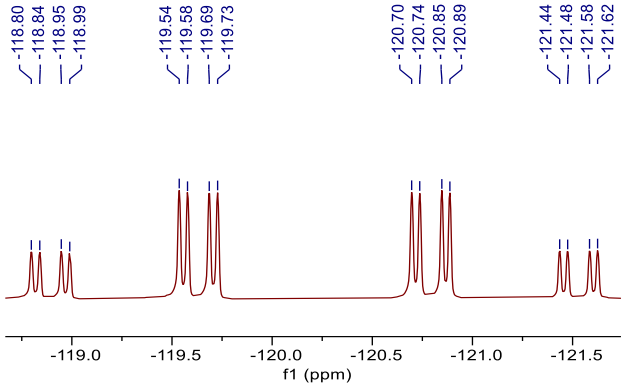

197.88
149.19
142.20
142.16
142.12
137.76
136.68
129.50
128.85
128.13
125.51
119.94
117.51
115.08
77.16 CDCl3
49.44
49.24
49.05
34.49
32.20
31.49
29.91
29.87
29.83
26.76
^{13}C NMR of **53** (101 MHz, $CDCl_3$)
CF_2H
^{t}Bu
Ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

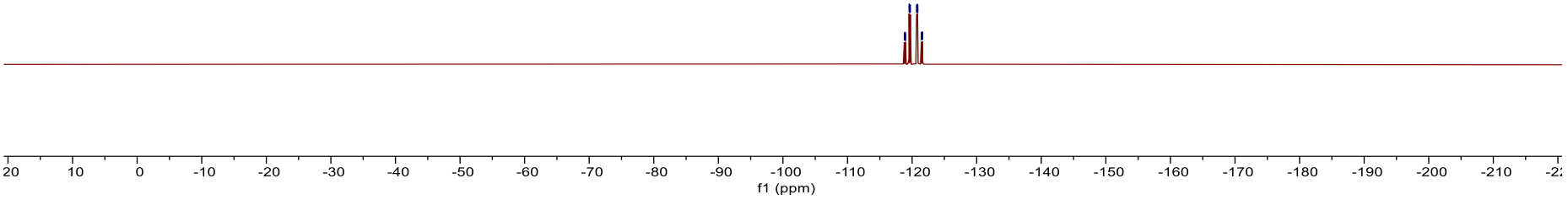
^{1}H NMR of **54** (400 MHz, $CDCl_3$)

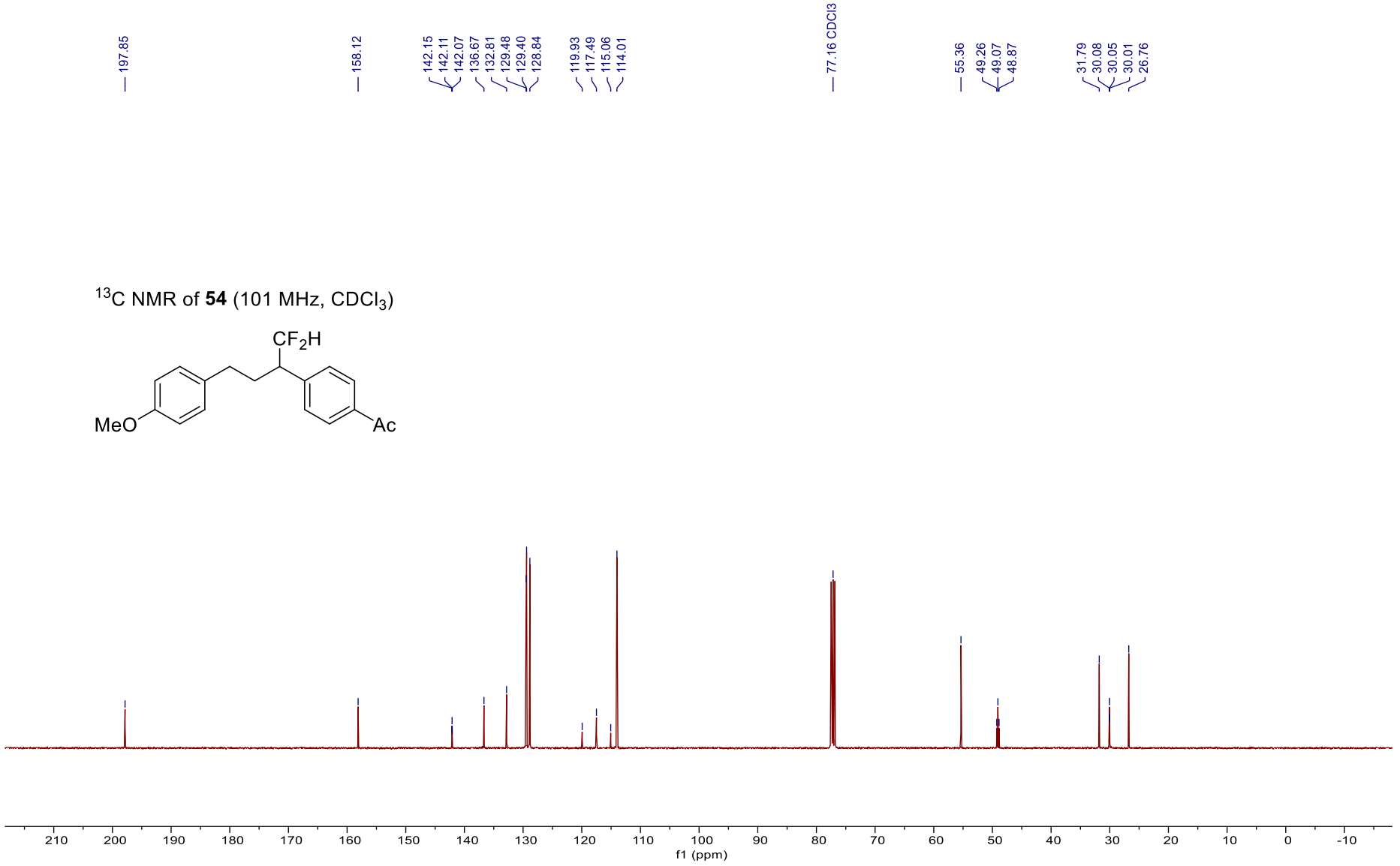


^{19}F NMR of **54** (376 MHz, $CDCl_3$)

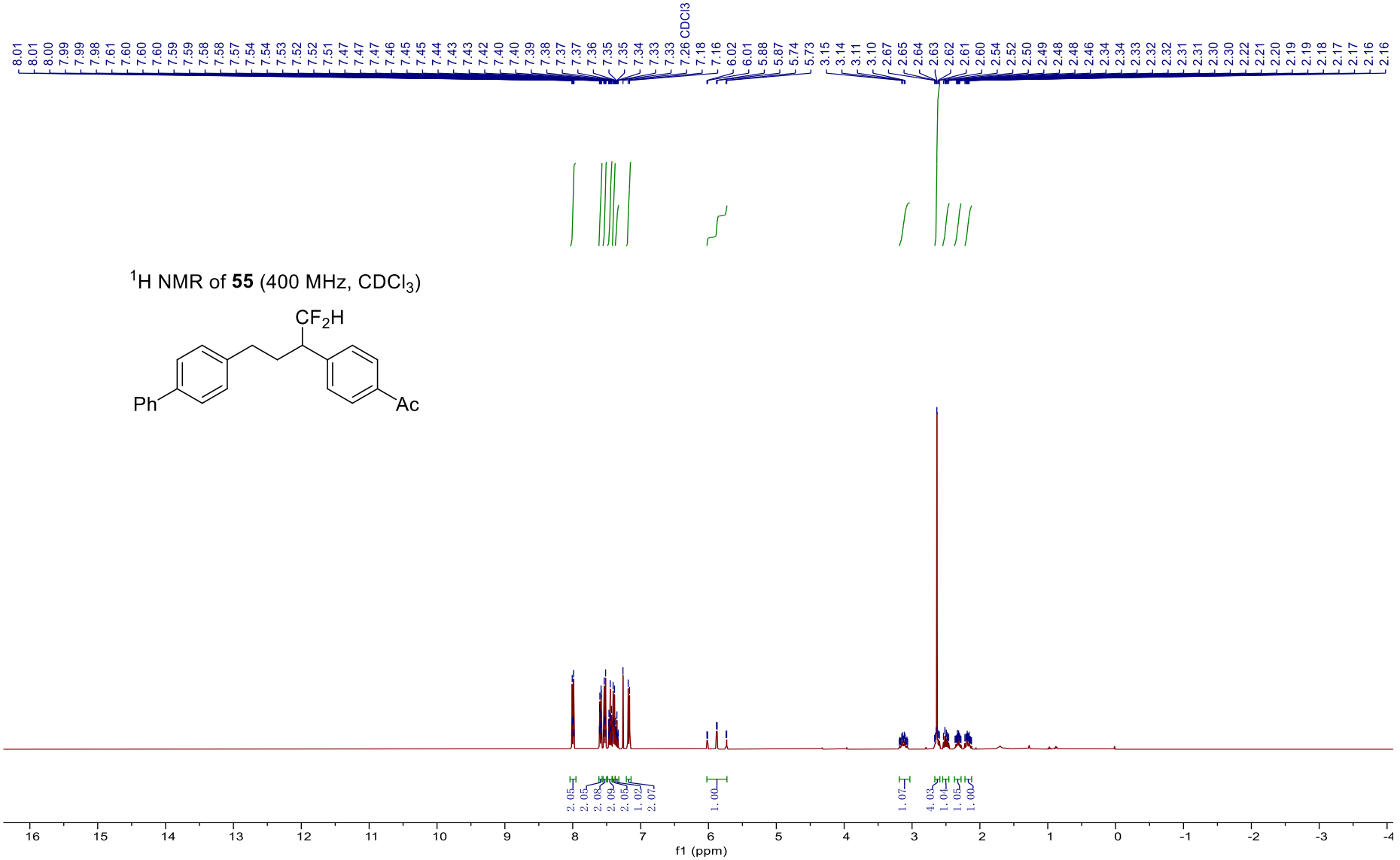






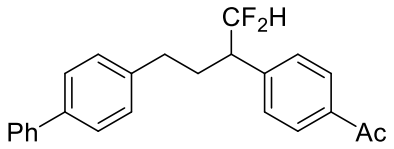


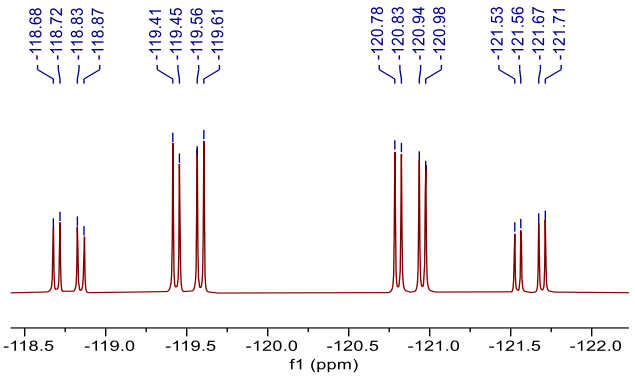
^{13}C NMR of **54** (101 MHz, $CDCl_3$)

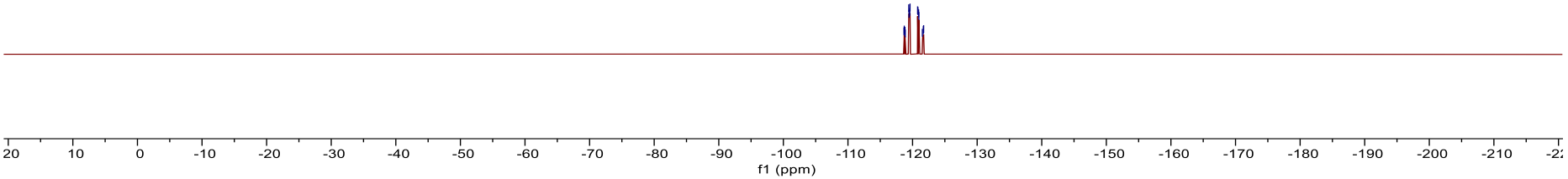


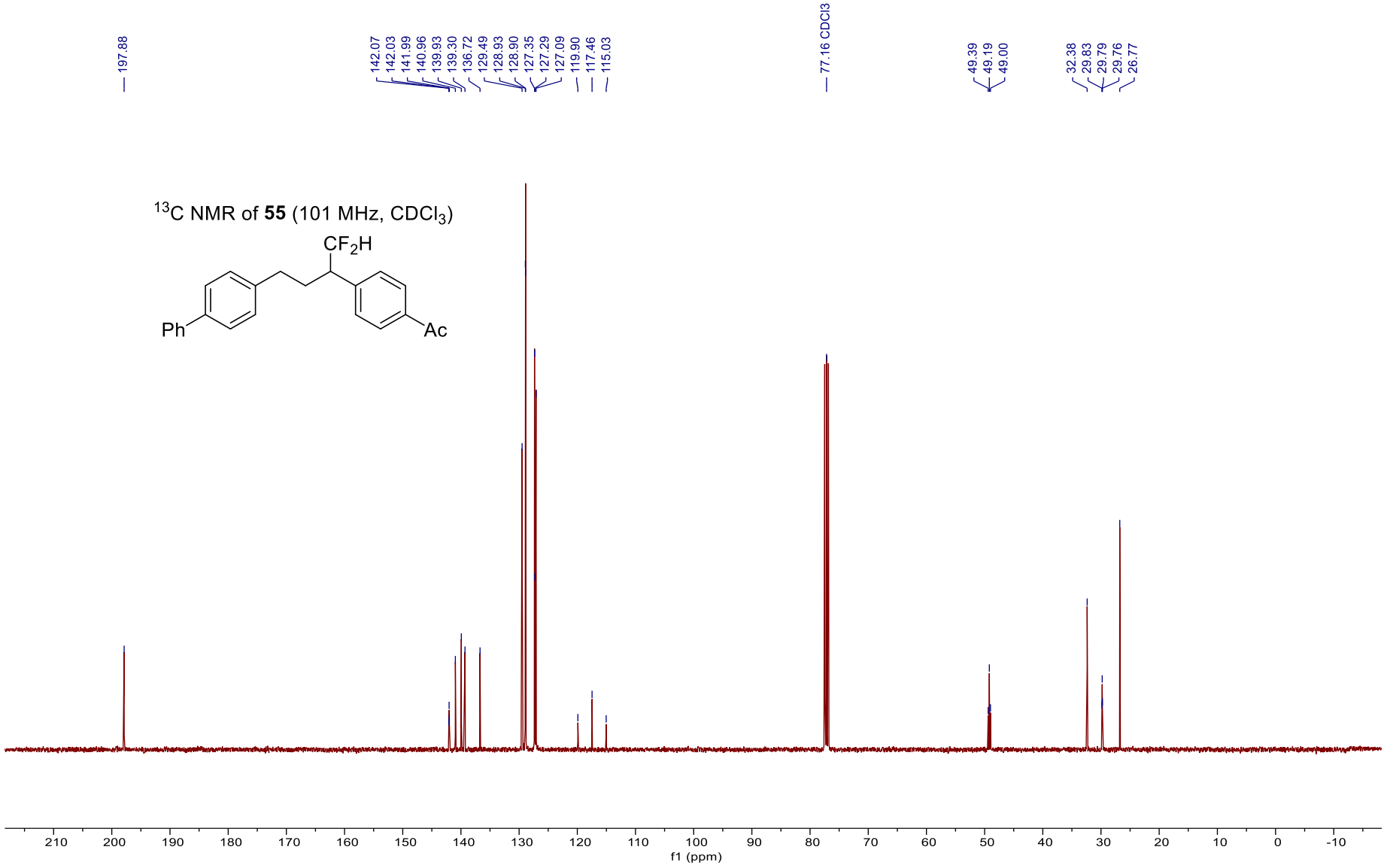
^{1}H NMR of **55** (400 MHz, $CDCl_3$)

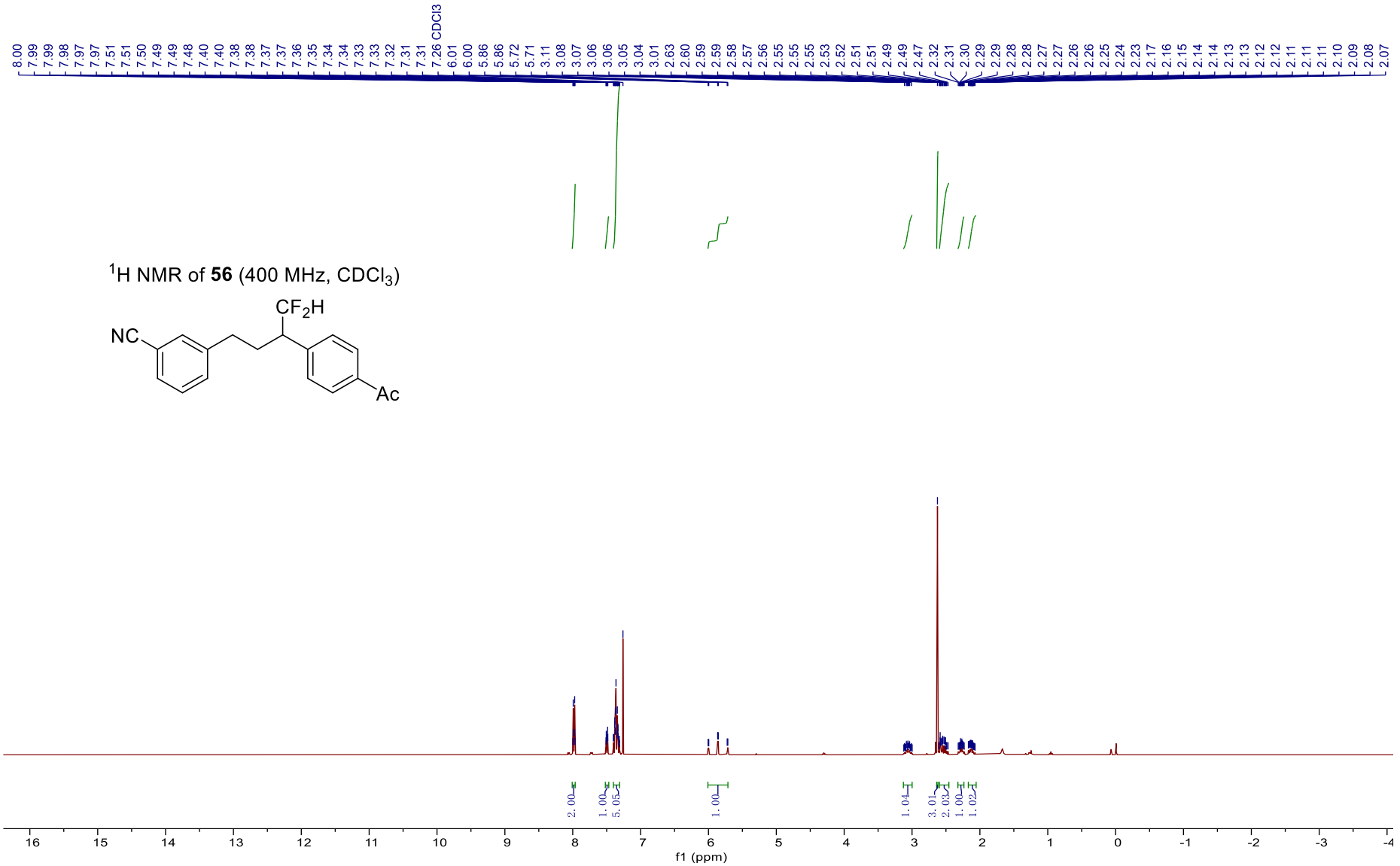
^{19}F NMR of **55** ($CDCl_3$)



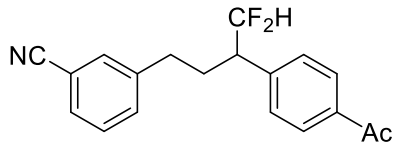


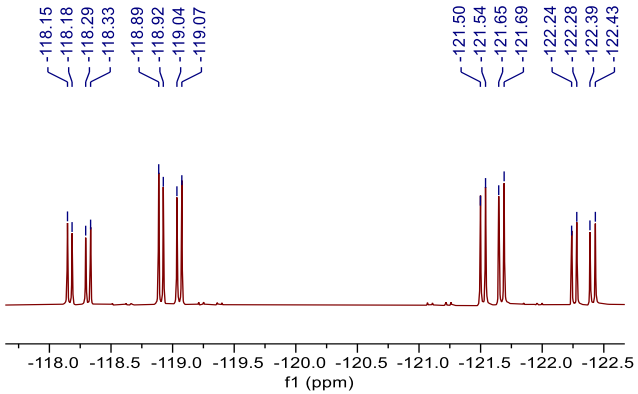


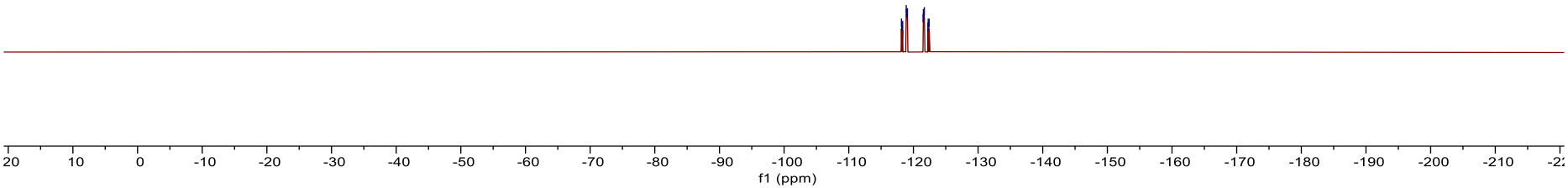

197.88
142.07
142.03
141.99
140.96
139.93
139.30
136.72
129.49
128.93
128.90
127.35
127.29
127.09
119.90
117.46
115.03
77.16 CDCl3
49.39
49.19
49.00
32.38
29.83
29.79
29.76
26.77
13C NMR of 55 (101 MHz, CDCl3)
CF2H
Ph
Ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

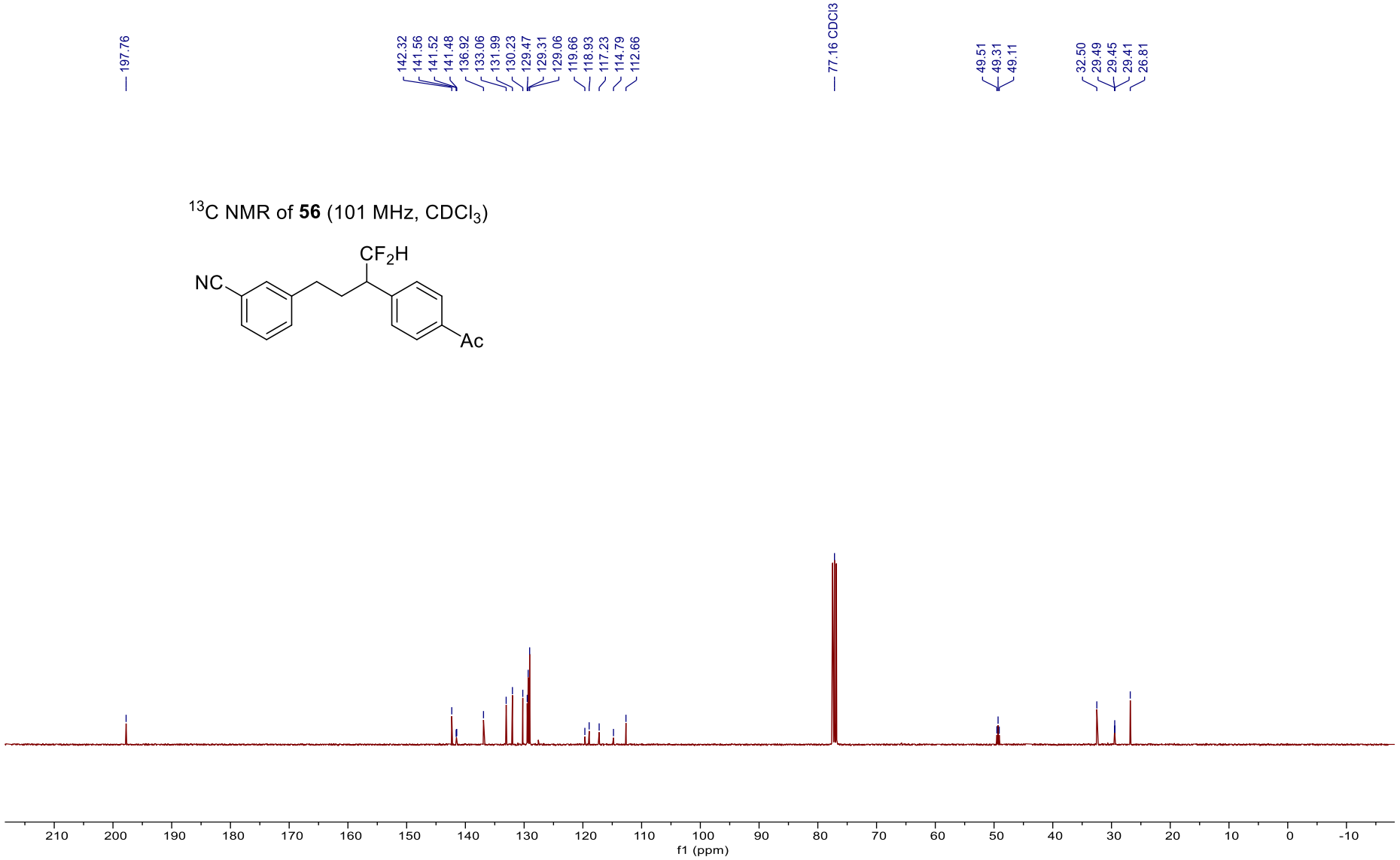

8.00 7.99 7.99 7.98 7.97 7.97 7.51 7.51 7.50 7.49 7.49 7.48 7.40 7.40 7.38 7.38 7.37 7.37 7.36 7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.26 CDCl3 6.01 6.00 5.86 5.86 5.72 5.71 3.11 3.08 3.07 3.06 3.06 3.05 3.04 3.01 2.63 2.60 2.59 2.59 2.58 2.57 2.56 2.55 2.55 2.53 2.52 2.51 2.51 2.49 2.49 2.47 2.32 2.31 2.30 2.29 2.29 2.28 2.28 2.27 2.27 2.26 2.26 2.25 2.24 2.23 2.17 2.16 2.15 2.14 2.14 2.13 2.13 2.12 2.12 2.11 2.11 2.11 2.10 2.09 2.08 2.07
^{1}H NMR of **56** (400 MHz, $CDCl_3$)
CF_2H
NC
Ac
2.00 1.00 5.05 1.00 1.04 3.01 2.03 1.00 1.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

^{19}F NMR of **56** (376 MHz, $CDCl_3$)



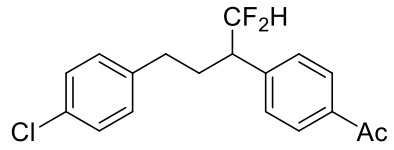


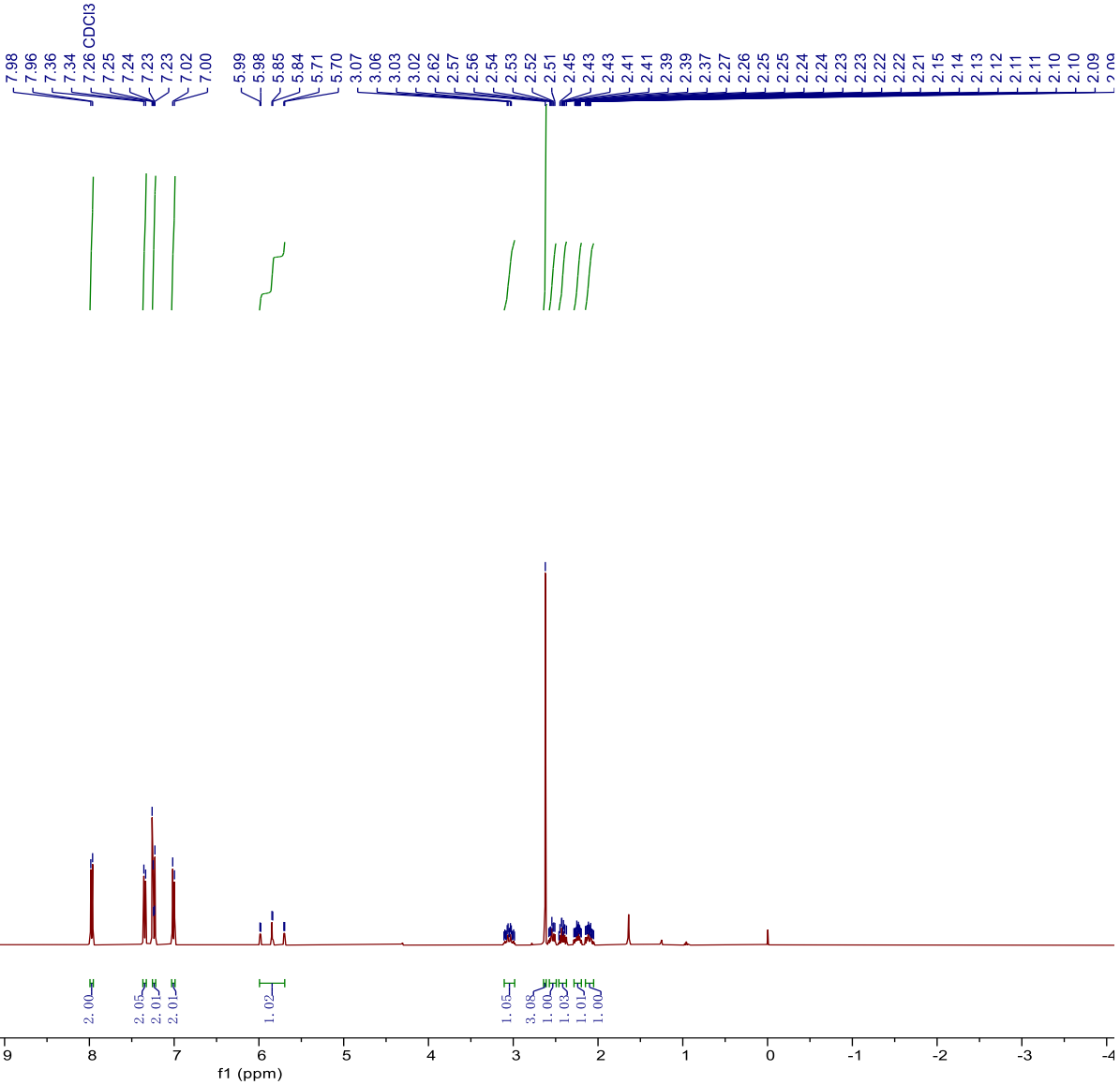




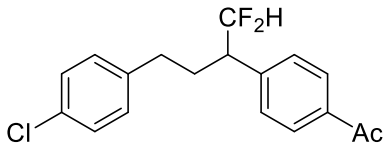
^{13}C NMR of **56** (101 MHz, $CDCl_3$)

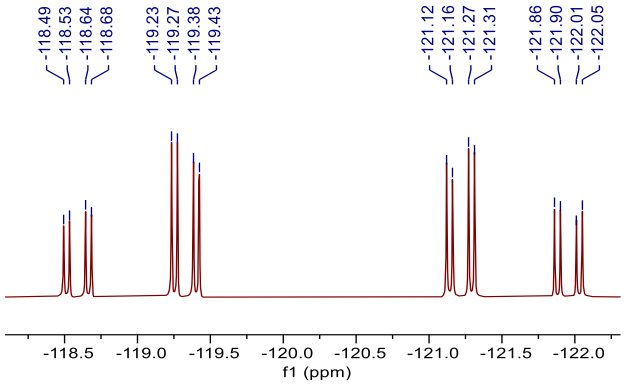
^{1}H NMR of **57** (400 MHz, $CDCl_3$)

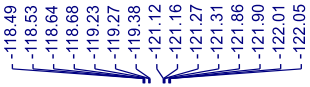


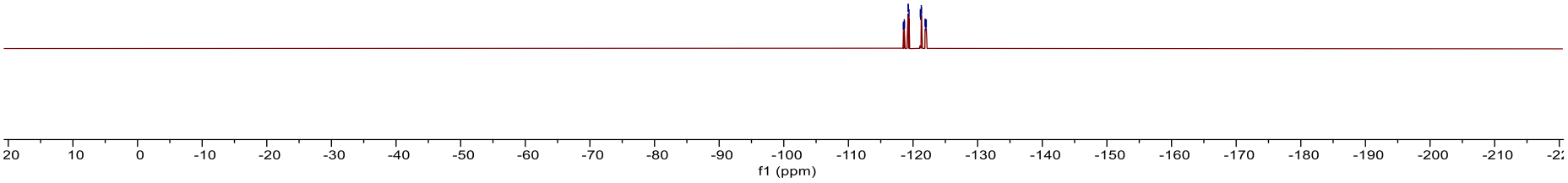


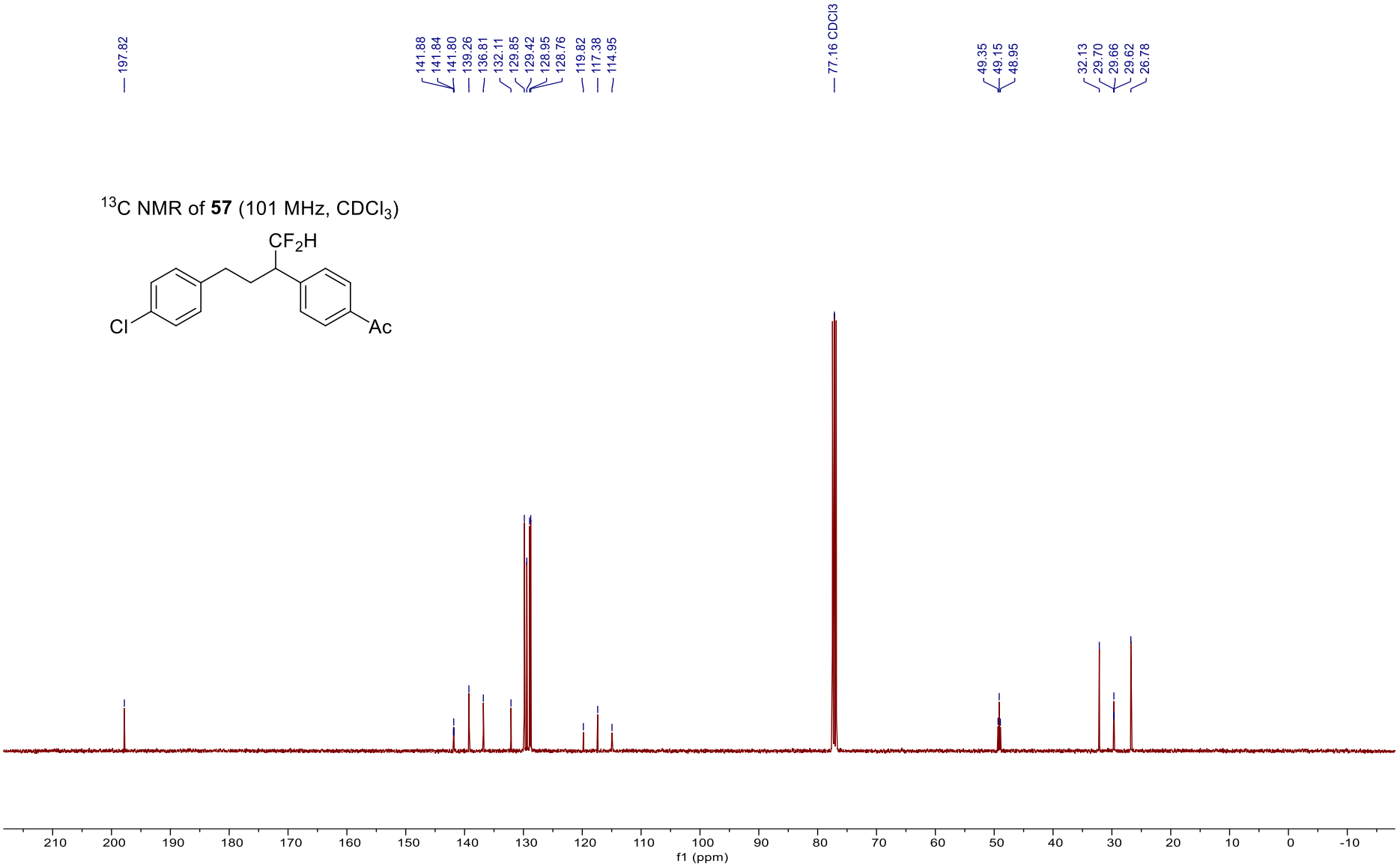
^{19}F NMR of **57** (376 MHz, $CDCl_3$)

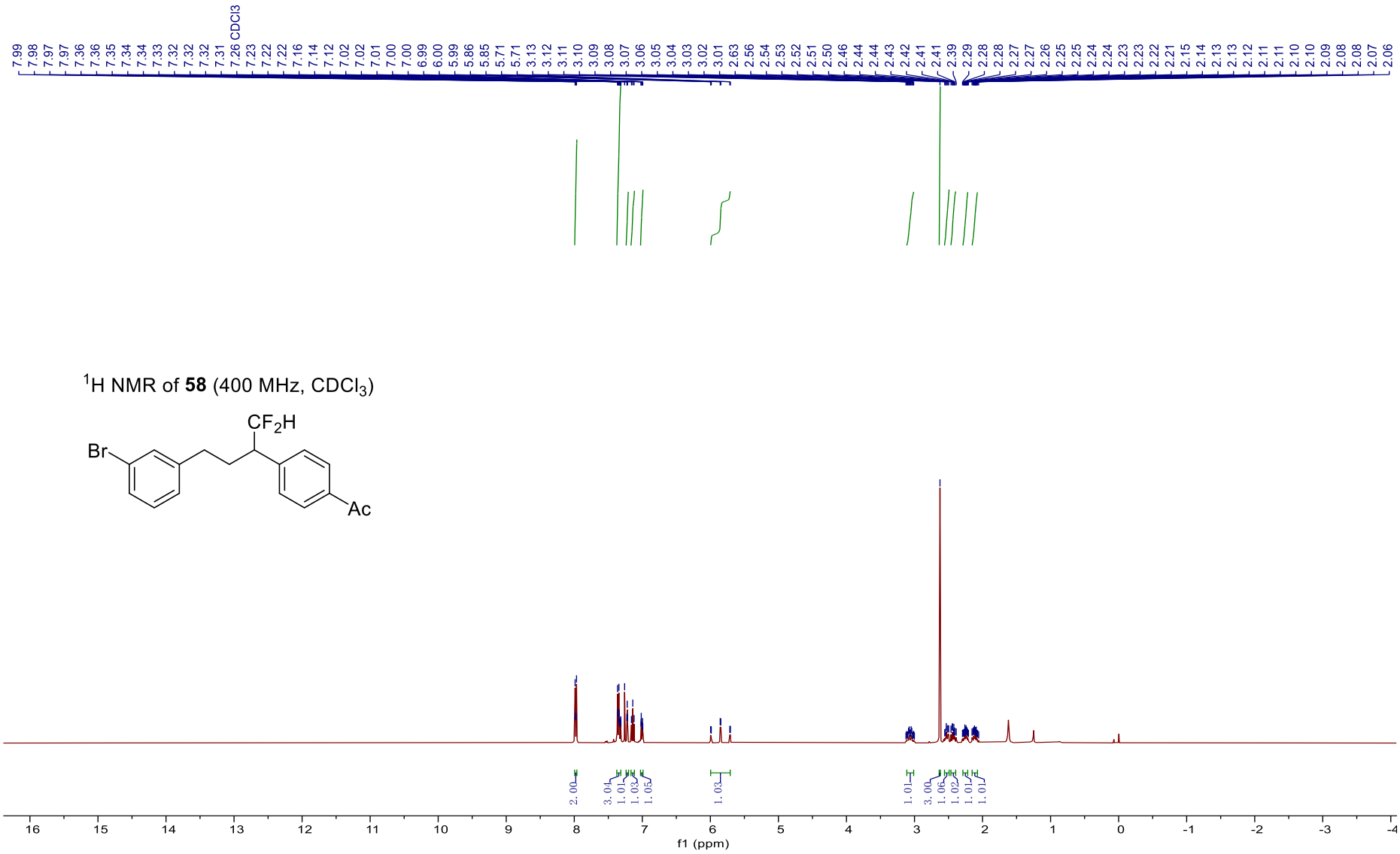






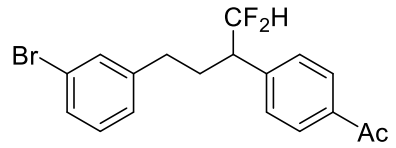


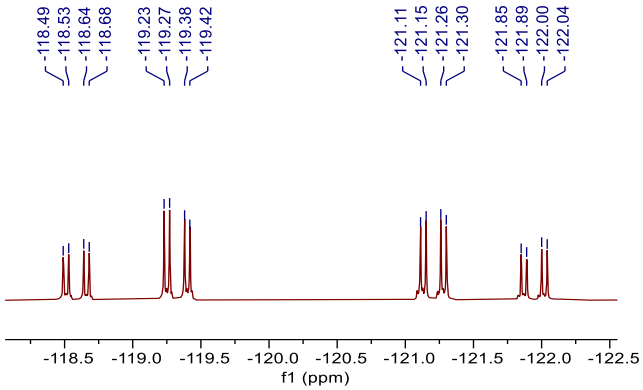

197.82
141.88
141.84
141.80
139.26
136.81
132.11
129.85
129.42
128.95
128.76
119.82
117.38
114.95
77.16 CDCl3
49.35
49.15
48.95
32.13
29.70
29.66
29.62
26.78
^{13}C NMR of **57** (101 MHz, $CDCl_3$)
CF_2H
Cl
Ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

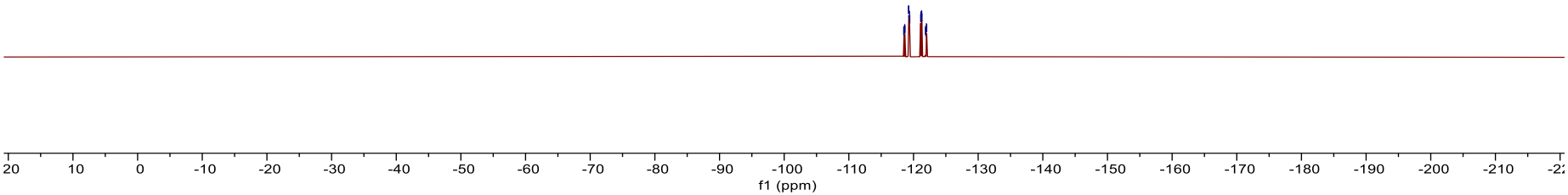


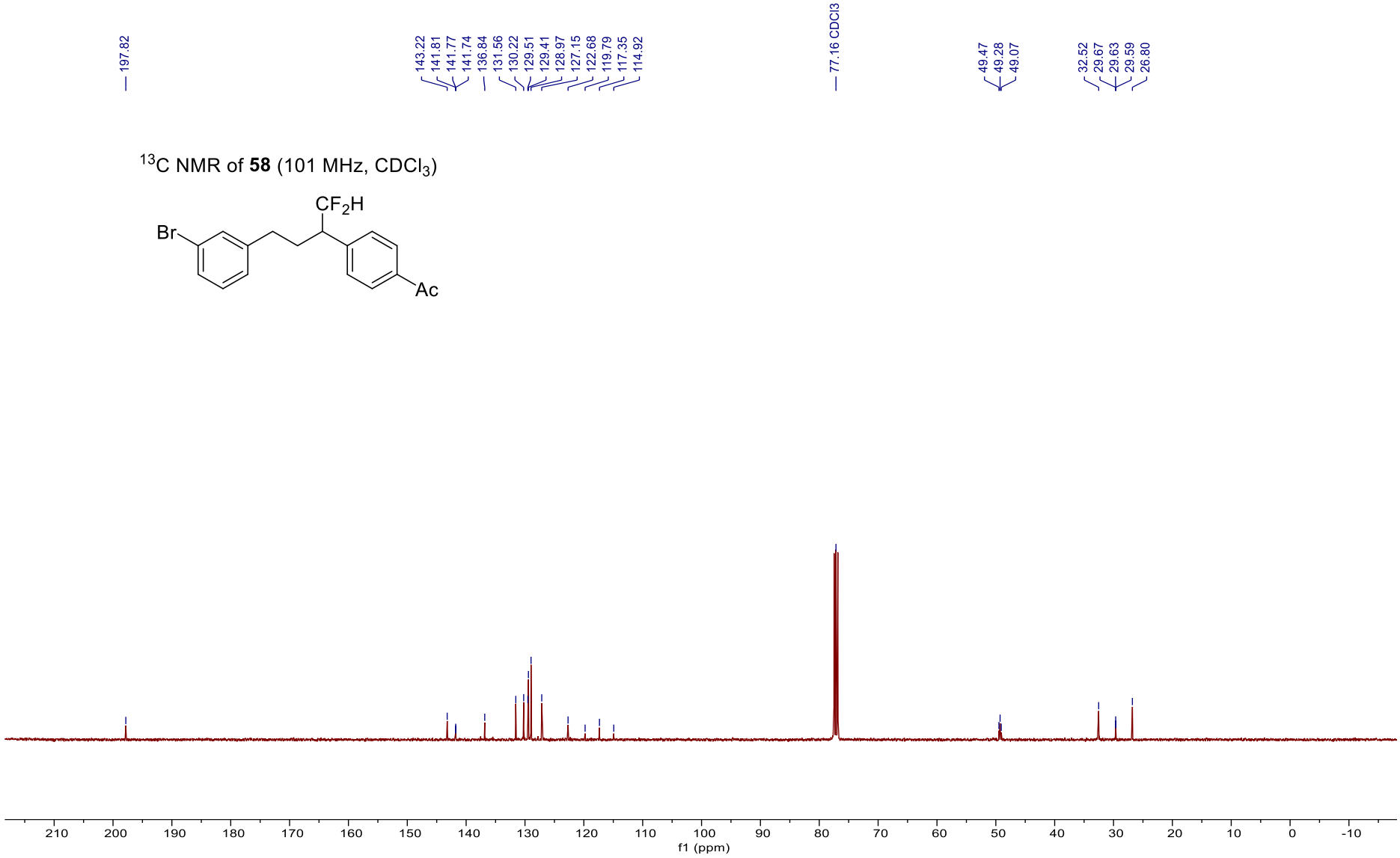
^{1}H NMR of **58** (400 MHz, $CDCl_3$)

^{19}F NMR of **58** (376 MHz, $CDCl_3$)



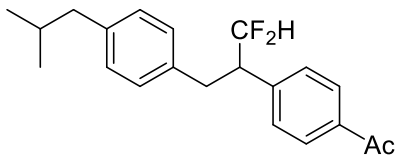




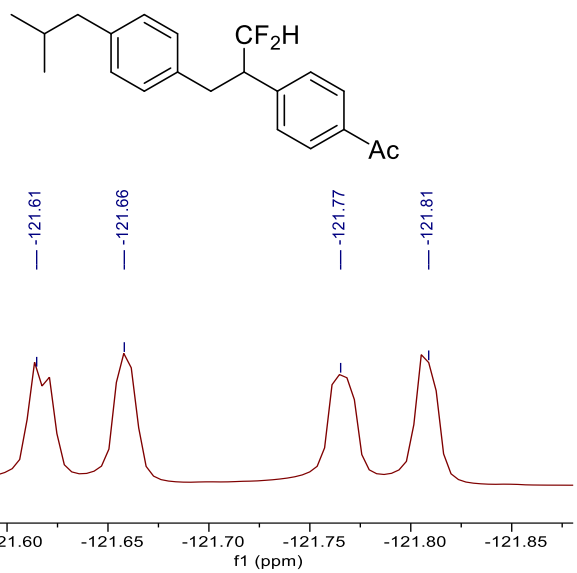


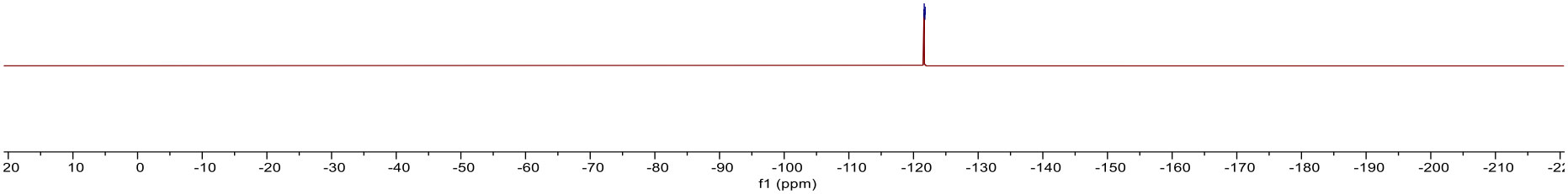
^{13}C NMR of **58** (101 MHz, $CDCl_3$)

^{1}H NMR of **59** (400 MHz, $CDCl_3$)



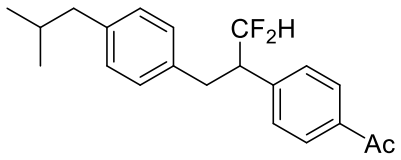
^{19}F NMR of **59** (376 MHz, $CDCl_3$)

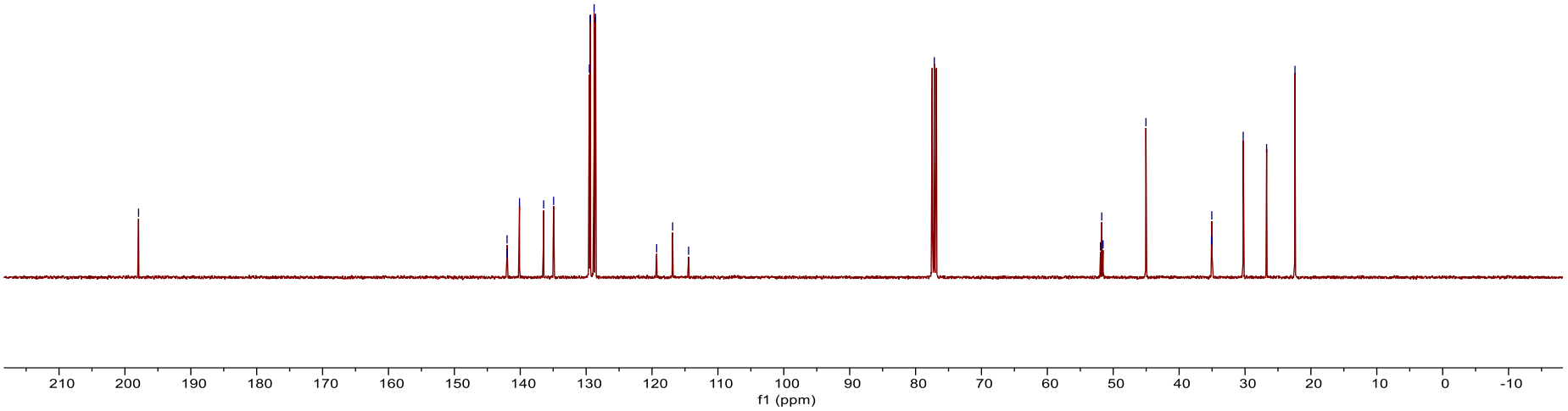


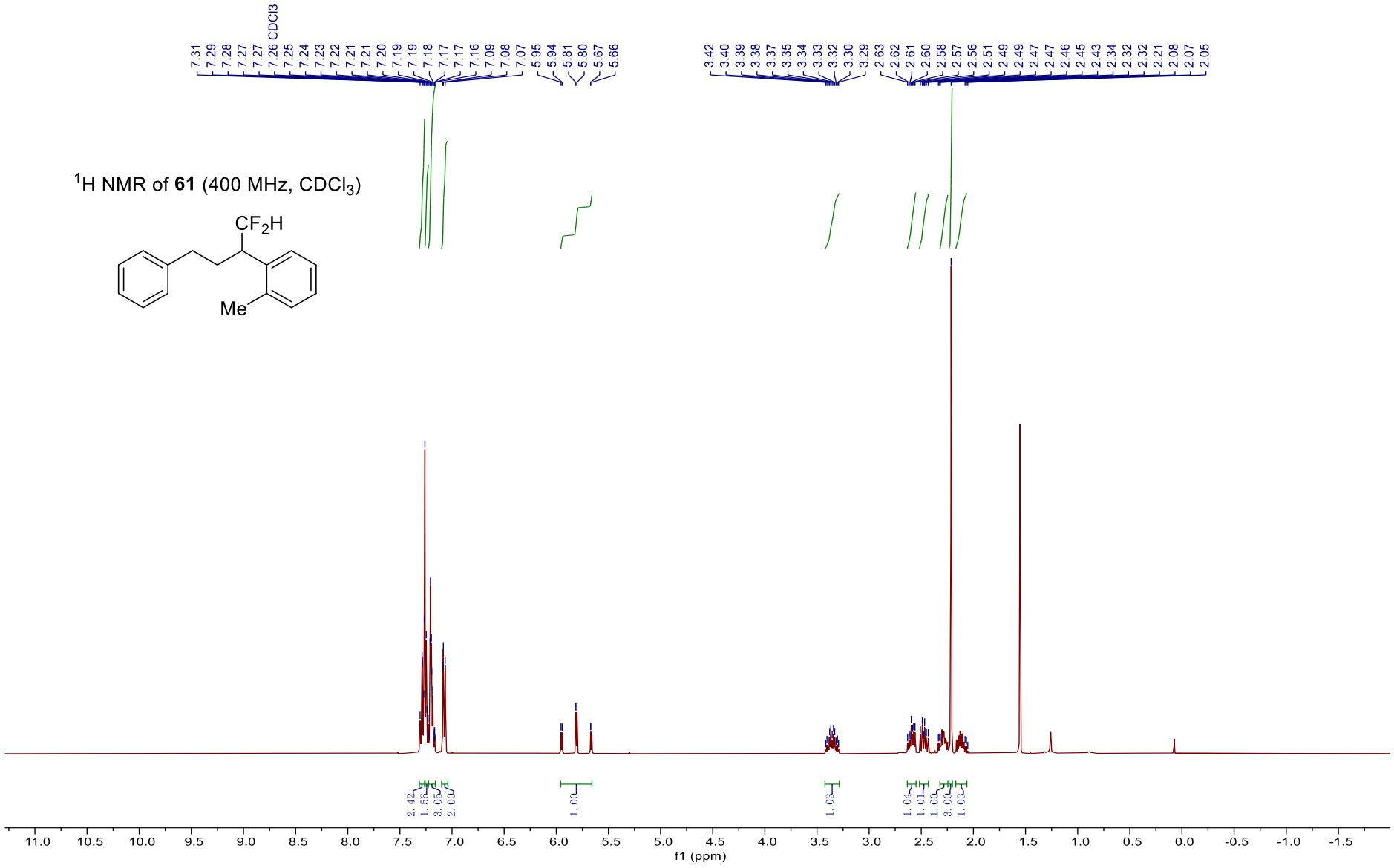


197.93
142.04
142.01
141.98
140.11
136.45
134.94
129.52
129.35
128.79
128.57
119.30
116.87
114.44
77.16 CDCl3
51.94
51.74
51.55
45.04
35.09
35.04
35.00
30.28
26.72
22.42

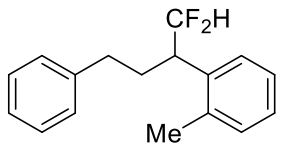
^{13}C NMR of **59** (101 MHz, $CDCl_3$)

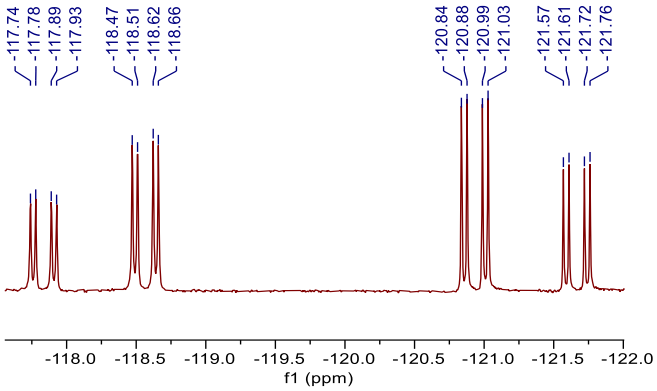


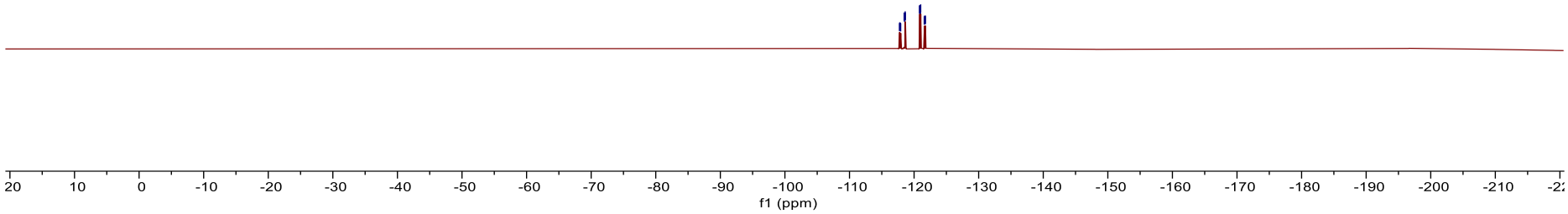



^{1}H NMR of **61** (400 MHz, $CDCl_3$)
CF_2H
Me
7.31 7.29 7.28 7.27 7.27 7.26 CDCl3 7.25 7.24 7.23 7.22 7.21 7.21 7.20 7.19 7.19 7.18 7.17 7.17 7.16 7.09 7.08 7.07 5.95 5.94 5.81 5.80 5.67 5.66
3.42 3.40 3.39 3.38 3.37 3.35 3.34 3.33 3.32 3.30 3.29 2.63 2.62 2.61 2.60 2.58 2.57 2.56 2.51 2.49 2.49 2.47 2.47 2.46 2.45 2.43 2.34 2.32 2.32 2.21 2.08 2.07 2.05
2.42 1.56 3.05 2.00 1.00 1.03 1.04 1.01 1.00 3.00 1.03
11.0 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 0.0 -0.5 -1.0 -1.5
f1 (ppm)

^{19}F NMR of **61** (376 MHz, $CDCl_3$)







^{13}C NMR of **61** (101 MHz, $CDCl_3$)