Supporting Information

Copper-Catalyzed Perfluoroalkylation of Propargyl *gem*-Dichlorides

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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 Shanghai Haohong Scientific Co., Ltd, Adamas-beta, Energy Chemical, bidepharm and were used without further purification. DMSO 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. ^1H 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 Ⅰ： Preparation of $(DMPU)_2Zn(CF_2H)_2$ and $(DMPU)_2Zn(C_nF_{2n+1})_2$

$(DMPU)_2Zn(CF_2H)_2$ 2a was synthesized according to Vicic's procedure.[1]

7 mL (57.9 mmol) DMPU was cooled to -20 ℃. To this solution, 10 g (55.2 mmol) HCF_2I was added, followed by the addition of 27.6 mL hexane solution of $Zn(Et)_2$ (1 M, 27.6 mmol) and 140 mL pentane. After the whole mixture was stirred at room temperature for 2 h, white solid was precipitated and collected by filtration. The solid was washed by pentane 3 times and dried under high-vac line, to give 10.4 g $(DMPU)_2Zn(CF_2H)_2$ (89% yield). The NMR data was consistent with previous report.

Bis(perfluoroalkyl)zinc reagent $(DMPU)_2Zn(C_nF_{2n+1})_2$ 2b-2f was synthesized according to Mikami's procedure.[2]

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

To an oven-dried 50-mL two-neck round-bottomed flask equipped with a magnetic stir bar were added hexane (8 mL) and DMPU (1.3 mL, 10 mmol) under argon atmosphere. Trifluoromethyliodide (ca. g, 12.9 mmol) was bubbled into the solution at -60 °C. Diethylzinc (1.0 M in hexanes,5 mL, 5 mmol) was then added dropwise at -60 °C. After stirring at -20 °C for 48 h, unreacted trifluoromethyl iodide and hexane were removed in vacuo. The solid obtained was washed with Et_2O (15 mL) three times and dried under vacuum to give $(DMPU)_2Zn(CF_3)_2$ as a white powder (1.8 g, 78% yield).

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

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

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

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

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

To an oven-dried 50-mL two-neck round-bottomed flask equipped with a magnetic stir bar were added hexane (8 mL) and DMPU (1.3 mL, 10 mmol) under argon atmosphere. Nonafluorobutyl iodide (ca. 4.5 g,12.9 mmol) was added to the solution. Diethyl zinc solution (1.0 M in hexanes, 5 mL, 5.0 mmol) was then added dropwise at -60 °C. After the reaction mixture was stirred at 0 °C for 48 h, the precipitate was obtained. After removing the solution, the precipitate obtained was washed with hexane (15 mL) three times and dried under vacuum to give $(DMPU)_2Zn(C_4F_9)_2$ as a white powder (2.8 g, 74% yield).

Preparation of bis(tridecafluorohexyl)zinc reagent $Zn(C_6F_{13})_2(DMPU)_2$ (2f)

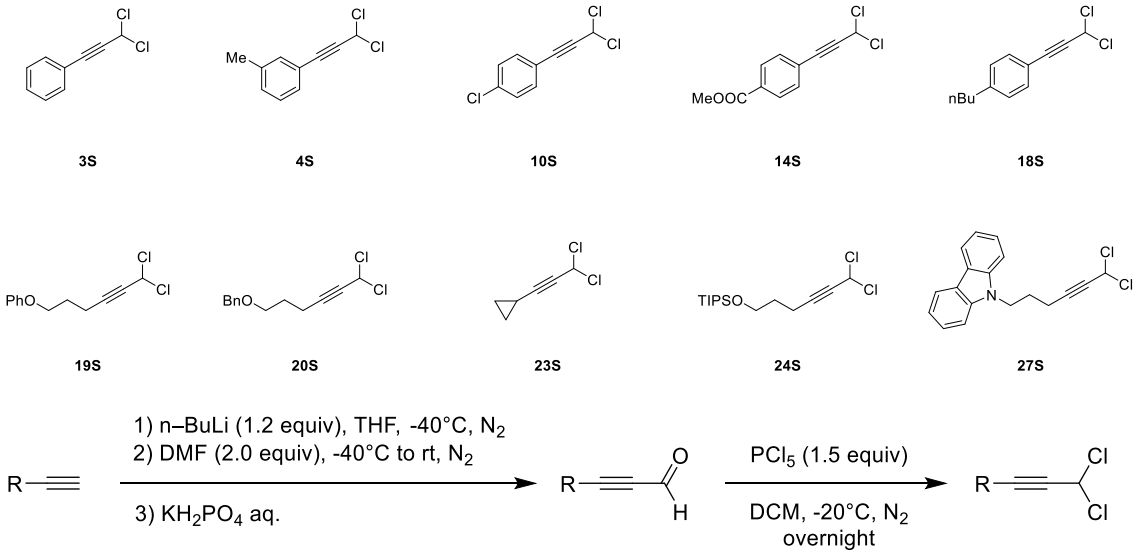
To an oven-dried 50-mL two-neck round-bottomed flask equipped with a magnetic stir bar were added hexane (8 mL) and DMPU (1.3 mL, 10 mmol) under argon atmosphere. Tridecafluorohexyl iodide (ca. 5.7 g, 12.9 mmol) was added to the solution. Diethyl zinc solution (1.0 M in hexanes, 5 mL, 5.0 mmol) was then added dropwise at -60 °C. After the reaction mixture was stirred at 0 °C for 48 h, the precipitate was obtained. After removing the solution, the precipitate obtained was washed with hexane (15 mL) three times and dried under vacuum to give $(DMPU)_2Zn(C_6F_{13})_2$ as a white powder (3.3 g, 70% yield).

3.General Procedure II：Preparation of Dichloropropargyl Substrates

All substrates were prepared according to the reported literatures.[3]

3.1 The general procedure A

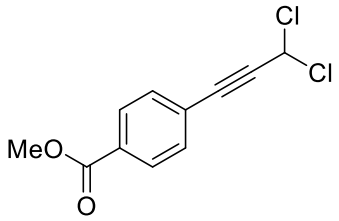
The known compounds **3S**[3a], **4S**[3a], **10S**[3a], **18S**[3a], **23S**[3a], **24S**[3b] and **27S**[3b] were prepared according to reported procedure A, and all the spectra data are in agreement with the reports.



Step 1: To a solution of 1-alkyne (2.61 mL, 5 mmol) in dry THF (5 mL) at -40 °C was added dropwise 1.6 M *n*-BuLi (3.8 mL, 6 mmol) followed by the addition of anhydrous DMF (0.8 mL, 10 mmol) in one portion. The clear reaction mixture was allowed to warmed up to room temperature and stirred until full conversion (TLC monitoring). The solution was then poured into a biphasic mixture of 30 mL 10% KH_2PO_4 aqueous solution and ether (20 mL) at 0 °C. The mixture was stirred vigorously, and layers were partitioned. The aqueous layer was extracted with ether (3 x 20 mL). The organic layers were collected, combined, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product obtained was used in the following chloration step without further purification.

Step 2: The crude product was dissolved in dry DCM (1.0 M) and cooled to -20 °C. Then, PCl_5 (1.6 g, 8 mmol) was added portion wise and the reaction mixture was stirred overnight. It was quenched by the addition of saturated $NaHCO_3$ solution at -20 °C. The mixture allowed to warm back to 25 °C, water was added to completely neutralize the solution. The aqueous phase was extracted by DCM (3 x 15 mL), the organic phases were collected, dried over Na_2SO_4, concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: petroleum ether) provided the desired compound.

The new compounds **14S, 19S, 20S** were synthesized and characterized described below.



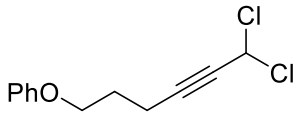
Methyl 4-(3,3-dichloroprop-1-yn-1-yl)benzoate (14S)

Colorless oil, 690 mg, 57% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 6.49 (s, 1H), 3.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 132.1, 131.1, 129.7, 125.2, 88.8, 86.5, 55.7, 52.5.

HRMS (ESI) m/z calcd for $C_{11}H_9Cl_2O_2[(M+H)^+]$: 242.9974 , found: 242.9970.



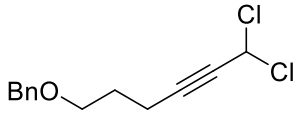
((6,6-dichlorohex-4-yn-1-yl)oxy)benzene (19S)

Colorless oil, 734 mg, 61% yield, **R**f =0.5 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.7 Hz, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.27 (s, 1H), 4.06 (t, *J* = 6.0 Hz, 2H), 2.59 – 2.54 (m, 2H), 2.04 (p, *J* = 6.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 129.6, 121.0, 114.6, 91.3, 77.0, 66.0, 56.0, 27.8, 15.8.

HRMS (ESI) m/z calcd for $C_{12}H_{13}Cl_2O[(M+H)^+]$: 243.0338 , found: 243.0339.



(((6,6-dichlorohex-4-yn-1-yl)oxy)methyl)benzene (20S)

Colorless oil, 659 mg, 52% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 30:1, v/v).

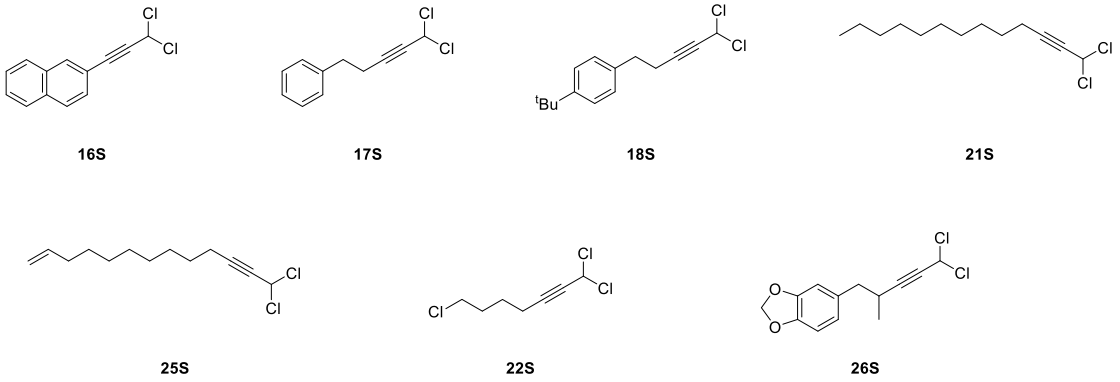
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 6.24 (s, 1H), 4.52 (s, 2H), 3.56 (t, *J* = 6.1 Hz, 2H), 2.47 (t, *J* = 7.1 Hz, 2H), 1.85 (p, *J* = 6.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 128.5, 127.8, 91.8, 76.7, 73.2, 68.5, 56.1, 28.2, 15.9.

HRMS (ESI) m/z calcd for $C_{13}H_{15}Cl_2O[(M+H)^+]$: 257.0495 , found: 257.0495.

3.2 The general procedure B

The known compounds **16S**[3b], **17S**[3b], **26S**[3b] were prepared according to reported procedure B, and all the spectra data are in agreement with the reports.



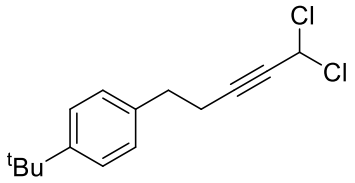
Step 1: Under nitrogen atmosphere, a solution of triphenylphosphine (4.0 equiv.) and tetrabromomethane (2.0 equiv.) in DCM (0.15 M) was stirred at 0 °C for 30 minutes. Then the corresponding aldehyde was added over a period of five minutes, and the mixture was stirred at 0 °C for one hour. After addition of water, the layers were separated, and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was dry-loaded on silica and subjected to flash chromatography (silica, DCM/PE).

Step 2: Under nitrogen atmosphere, *n*-BuLi (2.1 equiv. 1.6 M in hexane) was added over a period of 30 minutes via syringe pump to a solution of *gem*-dibromoolefine (1.0

equiv.) in dry THF (0.4 M) at -50 °C, and the mixture was stirred at -40 °C for 15 minutes. After addition of dry DMF (2.0 equiv.) at once, the mixture was allowed to warm to room temperature and stirred for one hour. The mixture was added to a stirring solution of aqueous NaH_2PO_4/Et_2O (1:1). After five minutes, the layers were separated and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic layers were dried over Na_2SO_4, the solvent was removed under reduced pressure and the crude product was subjected to flash chromatography (silica, EA/PE).

Step 3: The product was dissolved in dry DCM (1.0 M) and cooled to -20 °C. Then, PCl_5 (1.5 equiv.) was added portion wise and the reaction mixture was stirred overnight. It was quenched by the addition of saturated $NaHCO_3$ solution at -20 °C. The mixture allowed to warm back to 25 °C, water was added to completely neutralize the solution. The aqueous phase was extracted by DCM (3 x 20 mL); the organic phases were collected, dried over Na_2SO_4, concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: PE) provided the desired compound.

The new compounds **18S, 21S, 22S, 25S** were synthesized and characterized described below.



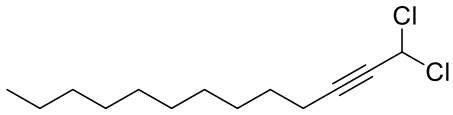
1-(tert-butyl)-4-(5,5-dichloropent-3-yn-1-yl)benzene (18S)

Colorless oil, 560 mg, 43% yield, **R**f =0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.26 (s, 1H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.64 – 2.57 (m, 2H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 137.0, 128.2, 125.5, 91.8, 77.0, 56.1, 34.6, 33.8, 31.5, 21.2.

HRMS (EI) m/z calcd for $C_{15}H_{18}Cl_2$ $[M]^+$: 268.0780, found:268.0784.



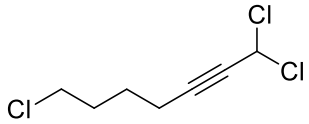
1,1-dichlorotridec-2-yne (21S)

Colorless oil, 806 mg, 66% yield, **R**f =0.7 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.26 (t, *J* = 2.0 Hz, 1H), 2.31 (td, *J* = 7.1, 2.0 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.41 – 1.34 (m, 2H), 1.38 – 1.18 (m, 12H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 92.6, 76.4, 56.2, 32.0, 29.7, 29.6, 29.4, 29.2, 28.9, 28.0, 22.8, 19.0, 14.3.

HRMS (EI) m/z calcd for $C_{13}H_{22}Cl_2$ $[M]^+$: 248.1093, found:248.1088.



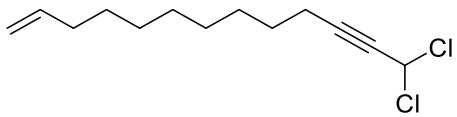
1,1,7-trichlorohept-2-yne (22S)

Yellow oil, 477 mg, 49% yield, **R**f =0.7 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (s, 1H), 3.60 – 3.52 (m, 2H), 2.37 (t, *J* = 7.1 Hz, 2H), 1.94 – 1.82 (m, 2H), 1.77 – 1.67 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 91.4, 77.0, 56.0, 44.4, 31.5, 25.1, 18.3.

HRMS (EI) m/z calcd for $C_7H_9Cl_3$ $[M]^+$: 197.9164, found: 197.9160.



13,13-dichlorotridec-1-en-11-yne (25S)

Colorless oil, 550 mg, 44% yield, **R**f =0.5 (petroleum ether).

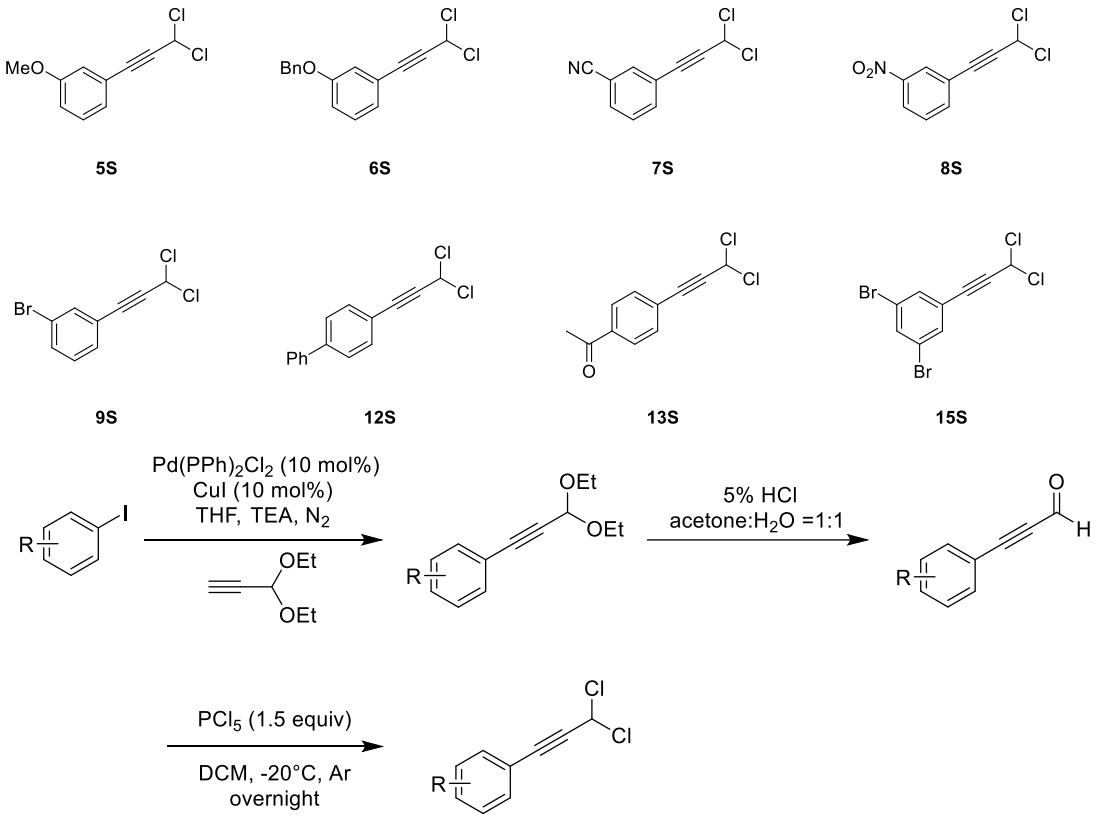
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.26 (s, 1H), 5.81 (td, *J* = 16.8, 6.9 Hz, 1H), 4.96 (dd, *J* = 24.7, 13.6 Hz, 2H), 2.31 (t, *J* = 7.2 Hz, 2H), 2.04 (q, *J* = 7.1 Hz, 2H), 1.64 – 1.47 (m, 2H), 1.45 – 1.33 (m, 4H), 1.29 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.33, 114.32, 92.63, 76.45, 56.20, 33.93, 29.40, 29.16, 29.09, 29.01, 28.88, 27.92, 18.98.

HRMS (ESI) m/z calcd for $C_{13}H_{21}Cl_2[(M+H)^+]$: 247.1015 , found: 247.1015.

3.3 The general procedure C

The known compounds **12S**[3b] was prepared according to reported procedure C, and the spectra data are in agreement with the reports.



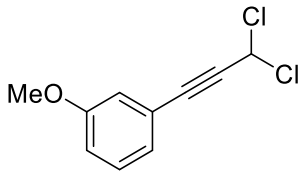
Step 1: Under nitrogen atmosphere, A mixture of Aryl iodide (5.0 mmol), 3,3-diethoxyprop-1-yne (1.0 mL, 7 mmol), triethylamine (3.0 mL), and $Pd(PPh_3)_2Cl_2$ (350 mg, 0.5 mmol), CuI (95 mg, 0.5 mmol) in 15 mL of THF was stirred at 25 °C for 4 h. The solvent was removed in vacuo, then the residue was diluted with water (15 mL) and DCM (15 mL). After extracting with DCM (3 x 20mL), the combined organic phase was dried by Na_2SO_4 and filtrated. The filtrate was evaporated.Chromatography of the residue on silica gel provided the corresponding product .

Step 2: The crude product was dissolved in mixed solvent (20 mL) of acetone and H_2O (*v:v* = 1:1), then 5 equivalents of 5% HCl (15 mL) was added to the solution, and the mixture was allowed to stand overnight at room temperature. Upon completion of the reaction, acetone was removed in vacuum, and the aqueous layer was extracted with

DCM (3 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification of the residue by column chromatography gave the crude product.

Step 3: The crude product was dissolved in dry DCM (1.0 M) and cooled to -20 °C. Then, PCl_5 (1.5 equiv.) was added portion wise and the reaction mixture was stirred overnight. It was quenched by the addition of saturated $NaHCO_3$ solution at -20 °C. The mixture allowed to warm back to 25 °C, water was added to completely neutralize the solution. The aqueous phase was extracted by DCM (3 x 20 mL); the organic phases were collected, dried over Na_2SO_4, concentrated under reduced pressure. Purification by column chromatography on silica gel (eluent: PE) provided the desired compound.

The new compounds **5S, 6S, 7S, 8S, 9S, 13S, 15S** were synthesized and characterized described below.



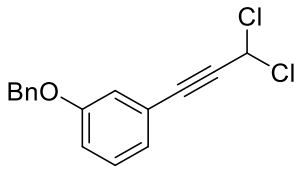
1-(3,3-dichloroprop-1-yn-1-yl)-3-methoxybenzene (5S)

Colorless oil, 784 mg, 74% yield, **R**f =0.5 (petroleum ether: ethyl acetate, 100:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 1H), 7.09 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.03 – 6.98 (m, 1H), 6.99 – 6.92 (m, 1H), 6.50 (s, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 129.7, 124.6, 121.6, 116.7, 116.7, 89.9, 83.9, 56.1, 55.5.

HRMS (ESI) m/z calcd for $C_{10}H_8Cl_2ONa[(M+Na)^+]$: 236.9844 , found: 236.9836.



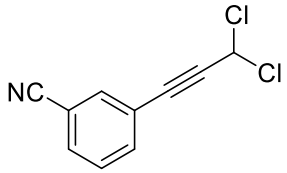
1-(benzyloxy)-3-(3,3-dichloroprop-1-yn-1-yl)benzene (6S)

White solid, 871 mg, 61% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 5H), 7.21 – 7.14 (m, 1H), 7.04 – 7.00 (m, 2H), 6.96 – 6.92 (m, 1H), 6.40 (s, 1H), 4.97 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$)δ 158.6, 136.5, 129.8, 128.8, 128.3, 127.6, 124.9, 121.7, 117.7, 117.4, 89.9, 84.0, 70.2, 56.1.

HRMS (ESI) m/z calcd for $C_{16}H_{13}Cl_2O[(M+H)^+]$: 291.0338 , found: 291.0335.



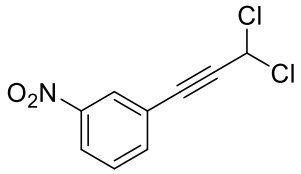
3-(3,3-dichloroprop-1-yn-1-yl)benzonitrile (7S)

Colorless oil, 592 mg, 57% yield, **R**f =0.5 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.73 – 7.65 (m, 2H), 7.54 – 7.46 (m, 1H), 6.47 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 135.4, 133.1, 129.6, 122.3, 117.7, 113.3, 86.9, 86.1, 55.4.

HRMS (ESI) m/z calcd for $C_{10}H_6Cl_2N[(M+H)^+]$: 209.9872 , found: 209.9864.



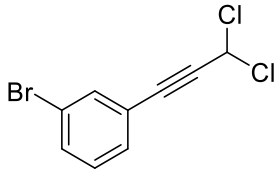
1-(3,3-dichloroprop-1-yn-1-yl)-3-nitrobenzene (8S)

Yellow oil, 611 mg, 54% yield, **R**f =0.5 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (t, *J* = 1.8 Hz, 1H), 8.30 – 8.19 (m, 1H), 7.90 – 7.67 (m, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 6.49 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 137.7, 129.8, 127.0, 124.6, 122.5, 86.9, 86.2, 55.3.

HRMS (ESI) m/z calcd for $C_9H_6Cl_2NO_2[(M+H)^+]$: 229.9770 , found: 229.9774.



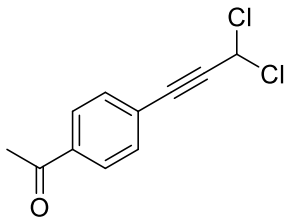
1-bromo-3-(3,3-dichloroprop-1-yn-1-yl)benzene (9S)

Yellow oil, 627 mg, 48% yield, **R**f =0.8 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (t, *J* = 1.8 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.44 – 7.37 (m, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.48 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.7, 133.1, 130.6, 130.0, 122.5, 122.4, 88.1, 85.1, 55.7.

HRMS (EI) m/z calcd for $C_9H_5BrCl_2[M]^+$: 261.8942, found: 261.8939.



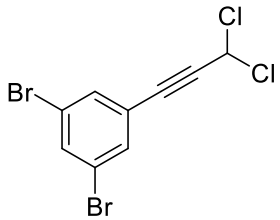
1-(4-(3,3-dichloroprop-1-yn-1-yl)phenyl)ethan-1-one (13S)

Colorless oil, 802 mg,71 % yield, **R**f =0.4 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H), 7.62 – 7.55 (m, 2H), 6.50 (s, 1H), 2.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 137.6, 132.3, 128.4, 125.3, 88.7, 86.7, 55.7, 26.8.

HRMS (ESI) m/z calcd for $C_{11}H_9Cl_2O[(M+H)^+]$: 227.0025 , found: 227.0023.



1,3-dibromo-5-(3,3-dichloroprop-1-yn-1-yl)benzene (15S)

Yellow solid, 1.05 g, 62% yield, **R**f =0.5 (petroleum ether: ethyl acetate, 100:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.57 (s, 2H), 6.44 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 133.5, 124.0, 123.0, 86.5, 86.2, 55.3.

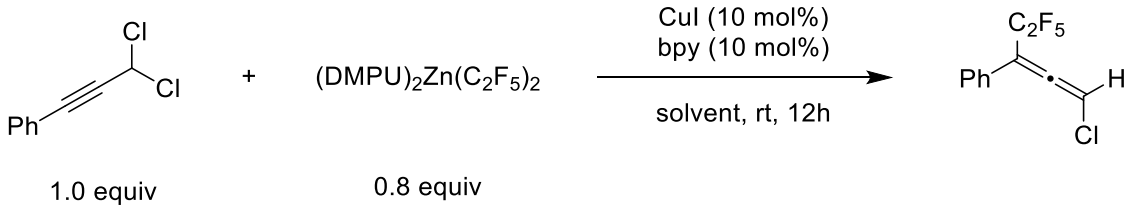
HRMS (EI) m/z calcd for $C_9H_4Br_2Cl_2[M]^+$: 339.8057, found: 339.8052.

4.Optimization studies.

4.1 Screening of reaction conditions for perfluoroalkylation of propargyl *gem*-dichlorides.

General procedure: In a nitrogen-filled glovebox, to a 8 mL vial equipped with a stir bar was added catalyst (0.02 mmol, 0.1 equiv.), ligand (0.02 mmol, 0.10 equiv.), $(DMPU)_2Zn(C_2F_5)_2$ (0.16 mmol, 0.8 equiv.), and solvent was added and stirred at rt for 10 min, then **1** (88 mg, 0.2 mmol, 1 equiv.) was added to the mixture and stirred for 12 h.

Table S1 The effects of solvent on the Perfluoroalkylation of propargyl *gem*-dichlorides.



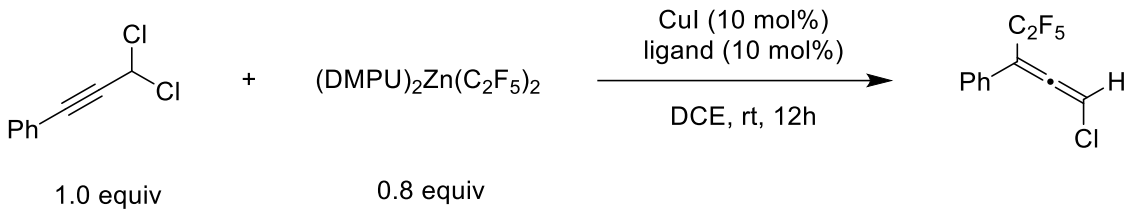
1.0 equiv 0.8 equiv

entry	solvent	Yield(%)[b]
1	Toluene	21
2	DMSO	45
3	THF	nd
4	DCM	73
5	**DCE**	**78**
6	NMP	9
7	DMA	nd
8	Dioxane	34

[a] Reaction conditions: propargyl *gem*-dichlorides **1** (0.2 mmol), Catalyst (10 mol%), Ligand (10 mol%), $(DMPU)_2Zn(C_2F_5)_2$ (0.16 mmol), solvent (1.0 mL), 12 h.

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

Table S2 The effects of ligands on the perfluoroalkylation of propargyl *gem*-dichlorides.



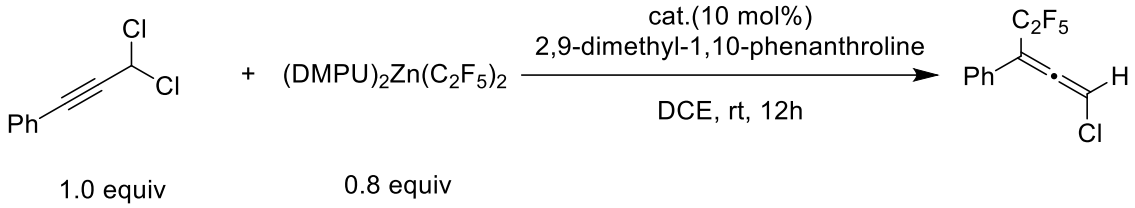
1.0 equiv 0.8 equiv

entry	catalyst	ligand	Yield(%)[b]
1	CuI	2,2':6',2''-terpyridine	23
2	CuI	4,4',4''-tri-tert-butyl-2,2':6',2''-terpyridine	26
3	CuI	1,10-phenanthroline	84
4	**CuI**	**2,9-dimethyl-1,10-phenanthroline**	**86**
5	CuI	6,6'-dimethyl-2,2'-bipyridine	78
6	CuI	4,4'-dimethyl-2,2'-bipyridine	67
7	CuI	dimethyl 2,2'-bipyridine-4,4'-dicarboxylate	60
8	CuI	RuPhos	8

[a] Reaction conditions: propargyl *gem*-dichlorides **1** (0.2 mmol), Catalyst (10 mol%), Ligand (10 mol%), $(DMPU)_2Zn(C_2F_5)_2$ (0.16 mmol), solvent (1.0 mL), 12 h.

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

Table S3 The effects of catalysts on the perfluoroalkylation of propargyl *gem*-dichlorides.



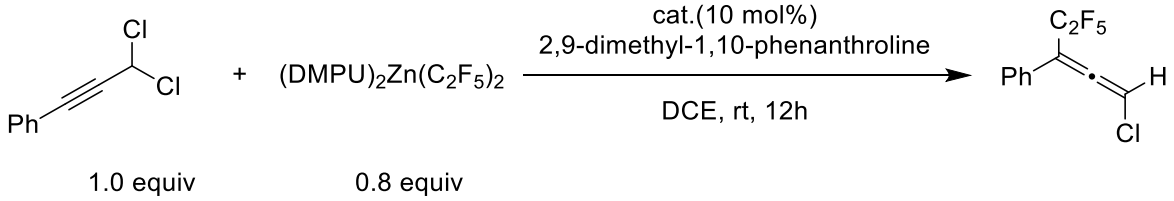
1.0 equiv 0.8 equiv

entry	catalyst	Yield(%)[b]
1	CuOTf	52
2	CuBr	82
3	**CuCl**	**92**
4	CuTc	78
5	CuCN	nd
6	CuF_2	10
7	CuOAc	77
8	$Cu(CH_3CN)_4BF_4$	69
9	$NiCl_2$ glyme	nd
10	$NiBr_2$ glyme	nd
11	No Cu cat	nd

[a] Reaction conditions: propargyl *gem*-dichlorides **1** (0.2 mmol), Catalyst (10 mol%), Ligand (10 mol%), $(DMPU)_2Zn(C_2F_5)_2$ (0.16 mmol), solvent (1.0 mL), 12 h.

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

Table S4 The effects of temperature on the perfluoroalkylation of propargyl *gem*-dichlorides.

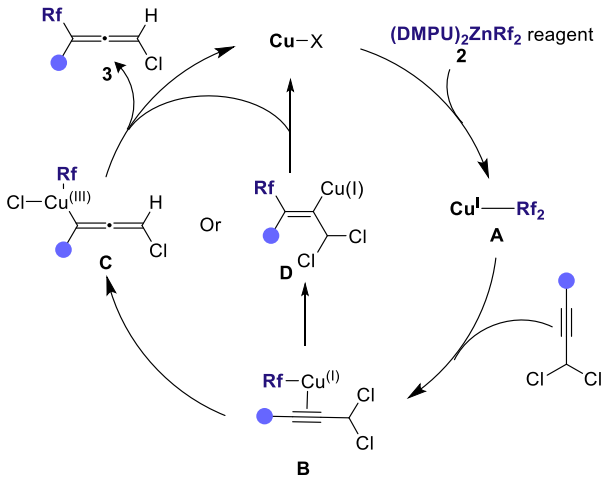


entry	temperature (℃)	yield(%)[b]
1	**25℃**	**92**
2	40℃	87
3	60℃	72
4	80℃	38
5	100℃	trace

[a] Reaction conditions: propargyl *gem*-dichlorides **1** (0.2 mmol), Catalyst (10 mol%), Ligand (10 mol%), $(DMPU)_2Zn(C_2F_5)_2$ (0.16 mmol), solvent (1.0 mL), 12 h.

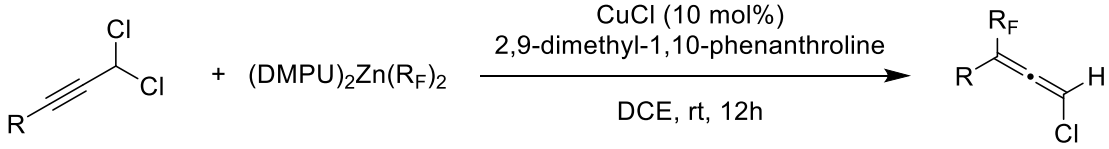
[b] Yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

5.Proposed Mechanism.



Scheme 1S Proposed mechanism

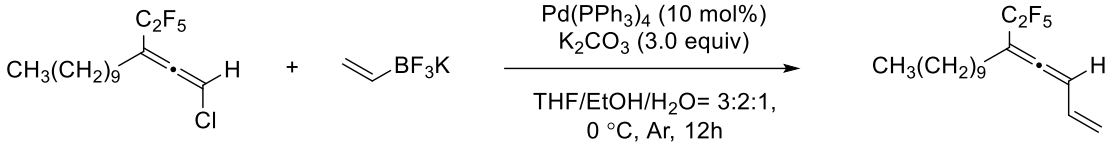
6.General Procedure for the Synthesis of Perfluoroalkyl-substituted Allenes.



In a nitrogen-filled glovebox, to a 8 mL dried screw-vial equipped with a stir bar was added CuCl (2.0 mg, 0.02 mmol, 10 mol %), 2,9-Dime-1,10-phen (4.2 mg, 0.02mmol, 10 mol %), $(DMPU)_2Zn(R_F)_2$ (0.16 mmol, 0.8 equiv.), and dry DCE (2 mL) were added into it, then removed it out of the glove box. After stirring at rt for 10 min, the dichloropropargyl Substrates (0.2 mmol, 1 equiv.) was added to the mixture and stirred at rt for 12 h. 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. Transformation of the product

5-(perfluoroethyl)pentadeca-1,3,4-triene (43)



21 **43**

A dried argon-flushed Schlenk tube was charged with K_2CO_3 (83 mg, 0.6 mmol, 3.0 equiv.), potassium vinyltrifluoroborate (107.2 mg, 0.6 mmol, 3.0 equiv.) and $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol, 10 mol %) under Ar. Then a degassed mixture of THF (1.2 mL), EtOH (0.8 mL) and H_2O (0.4 mL) was added into it under Ar. The tube was cooled to 0 ℃ for 5 minutes, 21 (66.4 mg, 0.2 mmol, 1.0 equiv.) was introduced under Ar. The Schlenk tube was sealed and the reaction mixture was stirred at 0 ℃ for 12 hours under dark environment. The final black solution was quenched by water (5 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic phases were dried over Na_2SO_4, concentrated under reduced pressure.

Colorless oil, 56.5 mg, 87% yield, **R**f =0.7 (petroleum ether).

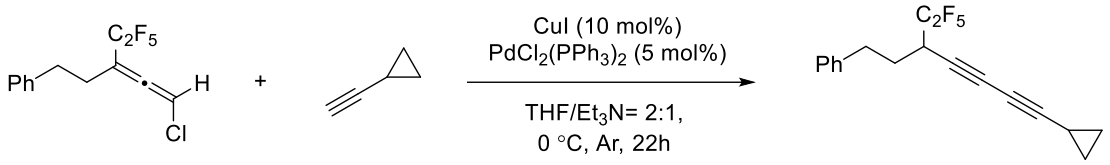
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 – 6.07 (m, 2H), 5.34 (d, *J* = 16.5 Hz, 1H), 5.16 (d, *J* = 9.7 Hz, 1H), 2.21 – 2.10 (m, 2H), 1.49 – 1.40 (m, 2H), 1.30 – 1.18 (m, 13H), 0.88 (t, *J* = 6.7 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1 (t, *J* = 7.5 Hz), 130.4, 119.3, 122.5 – 108.2 (m), 101.1, 99.1 (t, *J* = 26.2 Hz), 32.0, 29.7, 29.5, 29.5, 29.1, 27.5, 26.3, 22.8, 14.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -83.49 (s, 3F), -111.51 – -113.28 (m, 2F).

HRMS (ESI) m/z calcd for $C_{17}H_{26}F_5[(M+H)^+]$: 325.1949 , found: 325.1949.

(7-cyclopropyl-3-(perfluoroethyl)hepta-4,6-diyn-1-yl)benzene (44)



17 **44**

A dried screw-vial seal tube was charged with CuI (3.8 mg, 0.02 mmol, 10 mol %) and $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol, 5 mol %) in glove box, then moved it out of the glove box. The tube was equipped with an argon balloon, 17 (59.2 mg, 0.2 mmol, 1.0 equiv.), a dried and degassed mixture of THF (2.0 mL) and Et_3N (1.0 mL) were added into it. The atmosphere of the tube was displaced by argon for 20 minutes, then it was cooled to 0 ℃ for 10 minutes, ethynylcyclopropane (26.4 mg, 0.4 mmol, 2.0 equiv.) was introduced dropwise via syringe. The reaction mixture was stirred for 22 hours at 0 ℃ under dark environment. The tube was opened quickly at room temperature, the final black solution was filtered through celite using DCM (30 mL) under air. The filtrate was concentrated under reduced pressure to afford the crude product.

Colorless oil, 34.7 mg, 53% yield, **R**f =0.4 (petroleum ether).

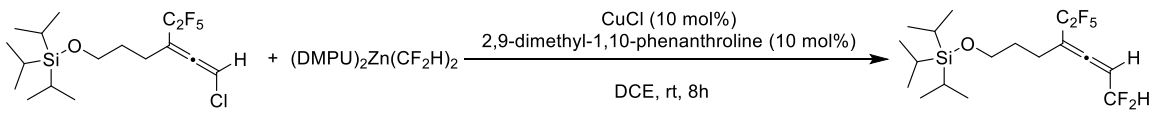
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.17 (m, 3H), 3.13 – 2.94 (m, 2H), 2.82 – 2.65 (m, 1H), 2.18 – 1.92 (m, 2H), 1.40 – 1.29 (m, 1H), 0.93 – 0.78 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 128.8, 128.6, 126.6, 83.7, 71.4, 67.4, 59.9, 35.3 (dd, J = 27.2, 22.9 Hz), 32.6, 29.0, 9.0, 0.1, *^{13}C NMR for C_2F_5 could not be assigned.*

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.68 (s, 3F), -110.60 – -131.90 (m, 2F).

HRMS (ESI) m/z calcd for $C_{18}H_{15}F_5K$ [$(M+K)^+$]: 365.1090 , found: 365.1095.

((7,7-difluoro-4-(perfluoroethyl)hepta-4,5-dien-1-yl)oxy)triisopropylsilane (45)



24 **45**

In a nitrogen-filled glovebox, to a 8 mL dried screw-vial equipped with a stir bar was added CuCl (2.0 mg, 0.02 mmol, 10 mol %), 2,9-dimethyl-1,10-phenanthroline (10

mol%) (4.2 mg, 0.02 mmol, 10 mol %), $(DMPU)_2Zn(CF_2H)_2$ (67.5 mg, 0.16 mmol, 0.8 equiv.), and dry DCE (2 mL) were added into it, then removed it out of the glove box. After stirring at rt for 10 min, 24 (81.2 mg, 0.2 mmol, 1 equiv.) was added to the mixture and stirred at rt for 12 h . 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.

Colorless oil, 58.2 mg, 69% yield, **R**f =0.5 (petroleum ether).

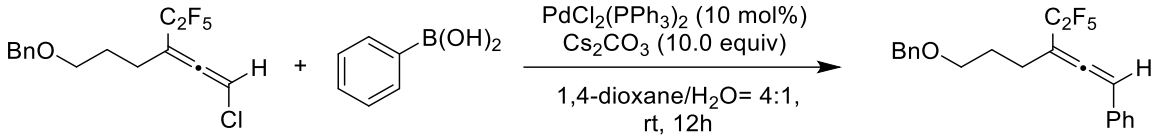
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (td, *J* = 55.7, 5.3 Hz, 1H), 5.93 – 5.79 (m, 1H), 3.74 (t, *J* = 5.9 Hz, 2H), 2.40 – 2.31 (m, 2H), 1.70 (p, *J* = 6.8 Hz, 2H), 1.08 – 1.03 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0 (t, *J* = 3.2 Hz), 112.3 (t, *J* = 239.8 Hz), 121.7 – 102.3 (m, 2C), 95.4 (t, *J* = 29.1 Hz), 61.9, 30.6, 22.6, 18.1, 12.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -83.46 (s, 3F), -108.59 – -110.72 (m, 2F), -111.94 – -114.03 (m, 2F).

HRMS (ESI) m/z calcd for $C_{18}H_{29}F_7OSiNa[(M+Na)^+]$: 445.1768 , found: 445.1770.

(6-(benzyloxy)-3-(perfluoroethyl)hexa-1,2-dien-1-yl)benzene (46)



20 **46**

Add 1,4-dioxane/H_2O=4:1 (2 mL) to a mixture of **20** (0.2 mmol, 68 mg), phenylboronic acid (0.3 mmol, 36.5 mg), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol,10 mol%) and Cs_2CO_3 (652 mg, 2 mmol). And the mixture stirred at room temperature for 12 hours. The final black solution was quenched by water (5 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic phases were dried over Na_2SO_4, concentrated under reduced pressure.

Colorless oil, 43.6 mg, 84% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 30:1, v/v).

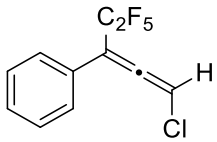
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 8H), 7.28 – 7.20 (m, 2H), 6.58 (p, *J* = 4.1 Hz, 1H), 4.45 (s, 2H), 3.57 – 3.41 (m, 2H), 2.52 – 2.25 (m, 2H), 1.90 – 1.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.3 (t, *J* = 7.4 Hz), 138.4, 131.8, 129.0, 128.5, 128.5, 127.8, 127.8, 127.4, 124.1 – 109.5 (m), 101.8, 101.2 (t, *J* = 26.3 Hz), 73.1, 69.2, 27.8, 23.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.32 (s, 3F), -101.59 – -133.32 (m, 2F).

HRMS (ESI) m/z calcd for $C_{21}H_{20}F_5O[(M+H)^+]$: 383.1429, found: 383.1436.

8.Characterization of products



(1-chloro-4,4,5,5,5-pentafluoropenta-1,2-dien-3-yl)benzene (3)

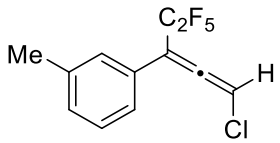
Colorless oil, 47.4 mg, 88% yield, **R**f =0.7 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.43 – 7.40 (m, 3H), 6.72 (t, *J* = 3.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.7 (t, *J* = 7.4 Hz), 129.7, 129.0, 128.8, 128.6, 121.3 – 109.2 (m, 2C), 107.6 (t, *J* = 26.9 Hz), 95.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.7 (s, 3F), -108.3 – -110.4 (m, 2F).

HRMS (EI) m/z calcd for $C_{11}H_6ClF_5[M]^+$: 268.0078 , found: 268.0073.



1-(1-chloro-4,4,5,5,5-pentafluoropenta-1,2-dien-3-yl)-3-methylbenzene (4)

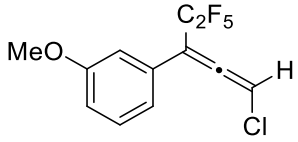
Colorless oil, 35.9 mg, 64% yield, **R**f =0.7 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.25 – 7.20 (m, 2H), 6.70 (t, *J* = 3.0 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6 (t, *J* = 7.2 Hz), 138.8, 130.5, 129.3, 128.7, 125.7, 120.7 – 108.6 (m, 2C), 107.3 (t, *J* = 26.6 Hz), 95.6, 21.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.68 (s, 3F), -108.22 – -110.23 (m, 2F).

HRMS (EI) m/z calcd for $C_{12}H_8ClF_5[M]^+$: 282.0235 , found: 282.0229.



1-(1-chloro-4,4,5,5,5-pentafluoropenta-1,2-dien-3-yl)-3-methoxybenzene (5)

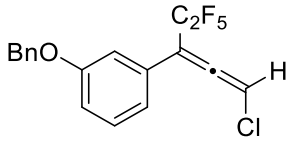
Yellow oil, 44.0 mg, 74% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 50:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 8.0 Hz, 1H), 7.10 – 7.02 (m, 1H), 6.99 – 6.97 (m, 1H), 6.97 – 6.92 (m, 1H), 6.71 (t, *J* = 2.9 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.7 (t, *J* = 7.2 Hz), 159.9, 130.0, 130.0, 121.0, 115.1, 114.4, 120.8 – 109.1 (m, 2C), 107.4 (t, *J* = 26.7 Hz), 95.8, 55.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.1 (s, 3F), -107.5 – -109.9 (m, 2F).

HRMS (ESI) m/z calcd for $C_{12}H_9ClF_5O[(M+H)^+]$: 299.0257 , found: 299.0257.



1-(benzyloxy)-3-(1-chloro-4,4,5,5,5-pentafluoropenta-1,2-dien-3-yl)benzene (6)

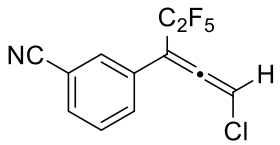
Yellow oil, 53.4 mg, 71% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 50:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4 – 7.4 (m, 4H), 7.4 – 7.3 (m, 2H), 7.1 – 7.1 (m, 2H), 7.0 – 7.0 (m, 1H), 6.7 (t, *J* = 2.9 Hz, 1H), 5.1 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.7 (t, *J* = 7.2 Hz), 159.0, 136.6, 130.1, 130.0, 128.8, 128.3, 127.7, 121.2, 116.0, 115.4, 120.8 – 109.2 (m, 2C), 107.4 (t, J = 26.7 Hz), 95.8, 70.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.7 (s, 3F), -108.3 – -110.1 (m, 2F).

HRMS (ESI) m/z calcd for $C_{18}H_{13}ClF_5O[(M+H)^+]$: 375.0570 , found: 375.0574.



3-(1-chloro-4,4,5,5,5-pentafluoropenta-1,2-dien-3-yl)benzonitrile (7)

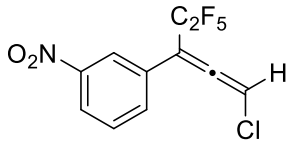
White solid, 39.2 mg, 67% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 50:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.72 – 7.67 (m, 2H), 7.58 – 7.52 (m, 1H), 6.83 (t, *J* = 2.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.3 (t, *J* = 7.0 Hz), 133.0, 132.6, 132.0, 130.2, 129.9, 117.9, 113.5, 121.5 – 108.1 (m, 2C), 105.8 (t, *J* = 27.3 Hz), 97.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -82.7 (s, 3F), -107.9 – -111.0 (m, 2F).

HRMS (ESI) m/z calcd for $C_{12}H_6ClF_5N[(M+H)^+]$: 294.0104 , found: 294.0113.



1-(1-chloro-4,4,5,5,5-pentafluoropenta-1,2-dien-3-yl)-3-nitrobenzene (8)

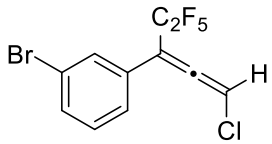
Yellow oil, 34.6 mg, 55% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.26 (m, 2H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.65 – 7.60 (m, 1H), 6.86 (t, *J* = 2.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5 (t, *J* = 7.0 Hz), 148.6, 134.4, 130.6, 130.2, 124.5, 123.7, 105.8 (t, *J* = 27.6 Hz), 97.5, ^{13}C NMR for C_2F_5 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.7 (s, 3F), -107.6 – -111.7 (m, 2F).

HRMS (ESI) m/z calcd for $C_{11}H_6ClF_5NO_2[(M+H)^+]$: 314.0002 , found: 313.9993.



1-bromo-3-(1-chloro-4,4,5,5,5-pentafluoropenta-1,2-dien-3-yl)benzene (9)

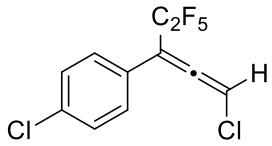
Yellow oil, 57.2 mg, 83% yield, **R**f =0.7 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.50 (m, 2H), 7.44 – 7.38 (m, 1H), 7.34 – 7.27 (m, 1H), 6.76 (t, *J* = 2.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.0 (t, *J* = 7.0 Hz), 132.8, 131.5, 130.7, 130.5, 127.2, 123.0, 121.3 – 108.5 (m, 2C), 106.3 (t, J = 26.8 Hz), 96.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.7 (s, 3F), -108.1 – -110.9 (m, 2F).

HRMS (EI) m/z calcd for $C_{11}H_5BrClF_5[M]^+$: 345.9178 , found:345.9174.



1-chloro-4-(1-chloro-4,4,5,5,5-pentafluoropenta-1,2-dien-3-yl)benzene (10)

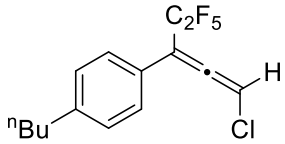
Yellow oil, 42.8 mg, 73% yield, **R**f =0.7 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 4H), 6.74 (t, *J* = 2.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.7, 136.0, 129.9, 129.3, 127.2, 121.2 – 108.8 (m, 2C), 106.7 (t, *J* = 27.0 Hz), 96.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.71 (s, 3F), -108.27 – -111.29 (m, 2F).

HRMS (EI) m/z calcd for $C_{11}H_5Cl_2F_5[M]^+$: 301.9683, found: 301.9680.



1-butyl-4-(1-chloro-4,4,5,5,5-pentafluoropenta-1,2-dien-3-yl)benzene (11)

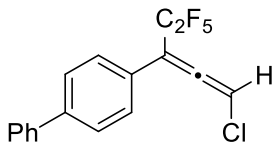
Colorless oil, 37.5 mg, 58% yield, **R**f =0.7 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 6.69 (t, *J* = 2.9 Hz, 1H), 2.65 – 2.60 (m, 2H), 1.65 – 1.59 (m, 2H), 1.39 – 1.33 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.4 (t, *J* = 7.4 Hz), 145.0, 129.1, 128.5, 125.9, 121.6 – 109.1 (m, 2C), 107.6 (t, *J* = 26.6 Hz), 95.6, 35.5, 33.5, 22.5, 14.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.7 (s, 3F), -108.3 – -110.5 (m, 2F).

HRMS (EI) m/z calcd for $C_{15}H_{14}ClF_5[M]^+$: 324.0699, found: 324.0697.



4-(1-chloro-4,4,5,5,5-pentafluoropenta-1,2-dien-3-yl)-1,1'-biphenyl (12)

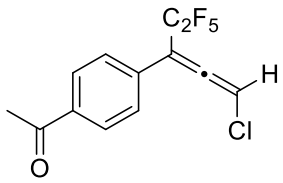
White solid, 45.1 mg, 66% yield, **R**f =0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 4H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.42 – 7.37 (m, 1H), 6.76 (t, *J* = 2.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.7 (t, *J* = 7.2 Hz), 142.6, 140.1, 129.1, 129.0, 128.1, 127.7, 127.5, 127.2, 122.8 – 108.4 (m, 2C), 107.4 (t, *J* = 26.8 Hz), 96.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.65 (s, 3F), -108.22 – -110.27 (m, 2F).

HRMS (EI) m/z calcd for $C_{17}H_{10}ClF_5[M]^+$: 344.0386 , found: 344.0381.



1-(4-(1-chloro-4,4,5,5,5-pentafluoropenta-1,2-dien-3-yl)phenyl)ethan-1-one (13)

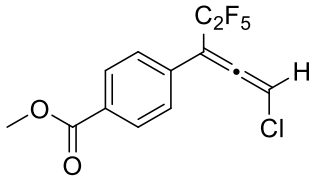
Colorless oil, 44.9 mg, 72% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.92 (m, 2H), 7.62 – 7.47 (m, 2H), 6.80 (t, *J* = 2.9 Hz, 1H), 2.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4 (t, *J* = 7.0 Hz), 197.4, 137.7, 133.3, 128.9, 128.8, 124.0 – 108.8 (m), 106.8 (t, *J* = 27.1 Hz), 96.7, 26.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.71 (s, 3F), -107.87 – -111.28 (m, 2F).

HRMS (ESI) m/z calcd for $C_{13}H_9ClF_5O[(M+H)^+]$: 311.0257 , found: 311.0261.



Methyl 4-(1-chloro-4,4,5,5,5-pentafluoropenta-1,2-dien-3-yl)benzoate (14)

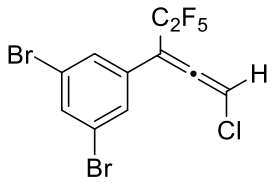
Colorless oil, 39.9 mg, 61% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 6.79 (t, *J* = 2.9 Hz, 1H), 3.94 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4 (t, *J* = 7.3 Hz), 166.4, 133.2, 131.2, 130.2, 128.6, 121.3 – 108.8 (m, 2C), 106.9 (t, *J* = 27.1 Hz), 96.6, 52.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.71 (s, 3F), -105.92 – -112.91 (m, 2F).

HRMS (ESI) m/z calcd for $C_{13}H_9ClF_5O_2[(M+H)^+]$: 327.0206 , found: 327.0205.



1,3-dibromo-5-(1-chloro-4,4,5,5,5-pentafluoropenta-1,2-dien-3-yl)benzene (15)

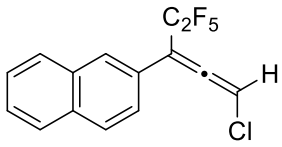
Yellow solid, 61.6 mg, 74% yield, **R**f =0.7 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (t, *J* = 1.7 Hz, 1H), 7.56 – 7.50 (m, 2H), 6.80 (t, *J* = 2.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.3 (t, *J* = 6.9 Hz), 135.3, 132.1, 130.2, 123.5, 121.5 – 108.0 (m, 2C), 105.3 (t, *J* = 27.3 Hz), 97.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.70 (s, 3F), -108.19 – -110.30 (m, 2F).

HRMS (EI) m/z calcd for $C_{11}H_4Br_2ClF_5[M]^+$: 423.8288, found: 423.8283.



2-(1-chloro-4,4,5,5,5-pentafluoropenta-1,2-dien-3-yl)naphthalene (16)

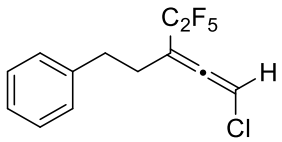
White solid, 50.2 mg, 79% yield, **R**f =0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.89 – 7.84 (m, 3H), 7.56 – 7.50 (m, 3H), 6.79 (t, *J* = 2.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.0 (t, *J* = 7.3 Hz), 133.5, 133.2, 128.8, 128.7, 128.4, 127.8, 127.5, 127.0, 125.9, 125.6, 121.1 – 111.4 (m, 2C), 107.8 (t, *J* = 26.6 Hz), 96.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -82.60 (s, 3F), -107.65 – -110.48 (m, 2F).

HRMS (EI) m/z calcd for $C_{15}H_8ClF_5[M]^+$: 318.0235, found: 318.0231.



(5-chloro-3-(perfluoroethyl)penta-3,4-dien-1-yl)benzene (17)

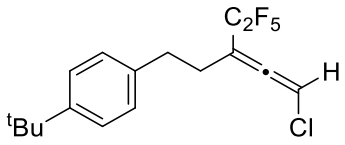
Colorless oil, 52.3 mg, 88% yield, **R**f =0.7 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.31 – 7.26 (m, 3H), 6.52 (p, *J* = 2.7 Hz, 1H), 2.88 (t, *J* = 7.5 Hz, 2H), 2.68 – 2.63 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3 (t, *J* = 7.1 Hz), 140.0, 128.7, 128.5, 126.6, 124.2 – 108.5 (m, 2C), 106.2 (t, *J* = 26.6 Hz), 96.1, 33.3, 28.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.43 (s, 3F), -112.03 – -114.37 (m, 2F).

HRMS (EI) m/z calcd for $C_{13}H_{10}ClF_5[M]^+$: 296.0386 , found: 296.0380.



1-(tert-butyl)-4-(5-chloro-3-(perfluoroethyl)penta-3,4-dien-1-yl)benzene (18)

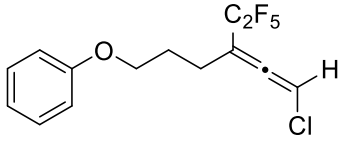
Colorless oil, 57.3 mg, 81% yield, **R**f =0.7 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.29 (m, 2H), 7.24 – 7.09 (m, 2H), 6.47 (p, *J* = 2.7 Hz, 1H), 2.87 – 2.77 (m, 2H), 2.65 – 2.55 (m, 2H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3 (t, *J* = 7.1 Hz), 149.5, 137.0, 128.2, 125.6, 124.1 – 108.5 (m, 2C), 106.3 (t, *J* = 26.5 Hz), 96.0, 34.5, 32.8, 31.5, 28.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.41 (s, 3F), -111.43 – -115.23 (m, 2F).

HRMS (EI) m/z calcd for $C_{17}H_{18}ClF_5[M]^+$: 352.1017, found: 352.1010.



((6-chloro-4-(perfluoroethyl)hexa-4,5-dien-1-yl)oxy)benzene (19)

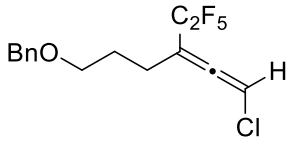
Colorless oil, 50.5 mg, 77% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 6.99 – 6.93 (m, 1H), 6.92 – 6.87 (m, 2H), 6.52 (p, *J* = 2.8 Hz, 1H), 4.04 – 4.00 (m, 2H), 2.53 – 2.46 (m, 2H), 2.04 – 1.97 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1 (t, *J* = 7.2 Hz), 158.8, 129.6, 121.0, 114.6, 120.7 – 108.5 (m, 2C), 106.4 (t, *J* = 26.7 Hz), 96.2, 66.2, 26.9, 23.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.41 (s, 3F), -111.79 – -115.84 (m, 2F).

HRMS (ESI) m/z calcd for $C_{14}H_{13}ClF_5O[(M+H)^+]$: 327.0570 , found: 327.0569.



(((6-chloro-4-(perfluoroethyl)hexa-4,5-dien-1-yl)oxy)methyl)benzene (20)

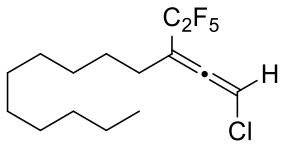
Colorless oil, 51.5 mg, 76% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 3H), 7.34 – 7.28 (m, 2H), 6.47 (p, *J* = 2.8 Hz, 1H), 4.52 (s, 2H), 3.53 (t, *J* = 6.2 Hz, 2H), 2.43 – 2.38 (m, 2H), 1.86 – 1.80 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0 (t, *J* = 7.1 Hz), 138.3, 128.6, 127.8, 123.6 – 107.9 (m, 2C), 106.6 (t, *J* = 26.5 Hz), 95.9, 73.2, 68.7, 27.3, 23.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.44 (s, 3F), -112.26 – -114.35 (m, 2F).

HRMS (EI) m/z calcd for $C_{15}H_{14}ClF_5O[M]^+$: 340.0653, found: 340.0650.



1-chloro-3-(perfluoroethyl)trideca-1,2-diene (21)

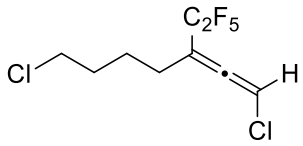
Colorless oil, 52.6 mg, 79% yield, **R**f =0.8 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (q, *J* = 2.6 Hz, 1H), 2.31 – 2.12 (m, 2H), 1.52 – 1.43 (m, 2H), 1.27 (s, 13H), 0.88 (t, *J* = 6.4 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1 (t, *J* = 7.1 Hz), 121.5 – 108.6 (m, 2C), 107.1 (t, *J* = 26.3 Hz), 95.6, 32.1, 29.7, 29.7, 29.5, 28.9, 27.0, 26.8, 25.8, 22.8, 14.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -83.48 (s, 3F), -112.14 – -114.76 (m, 2F).

HRMS (EI) m/z calcd for $C_{15}H_{22}ClF_5[M]^+$: 332.1330, found: 332.1326.



1,7-dichloro-3-(perfluoroethyl)hepta-1,2-diene (22)

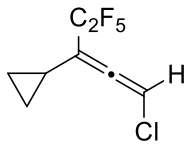
Colorless oil, 42.0 mg, 74% yield, **R**f =0.8 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (p, *J* = 2.7 Hz, 1H), 3.56 (t, *J* = 6.4 Hz, 2H), 2.30 (td, *J* = 7.4, 2.6 Hz, 2H), 1.91 – 1.79 (m, 2H), 1.75 – 1.62 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1 (t, *J* = 7.1 Hz), 121.5 – 108.4 (m, 2C), 106.4 (t, *J* = 26.6 Hz), 96.2, 44.5, 31.6, 26.1, 24.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.46 (s, 3F), -111.67 – -115.34 (m, 2F).

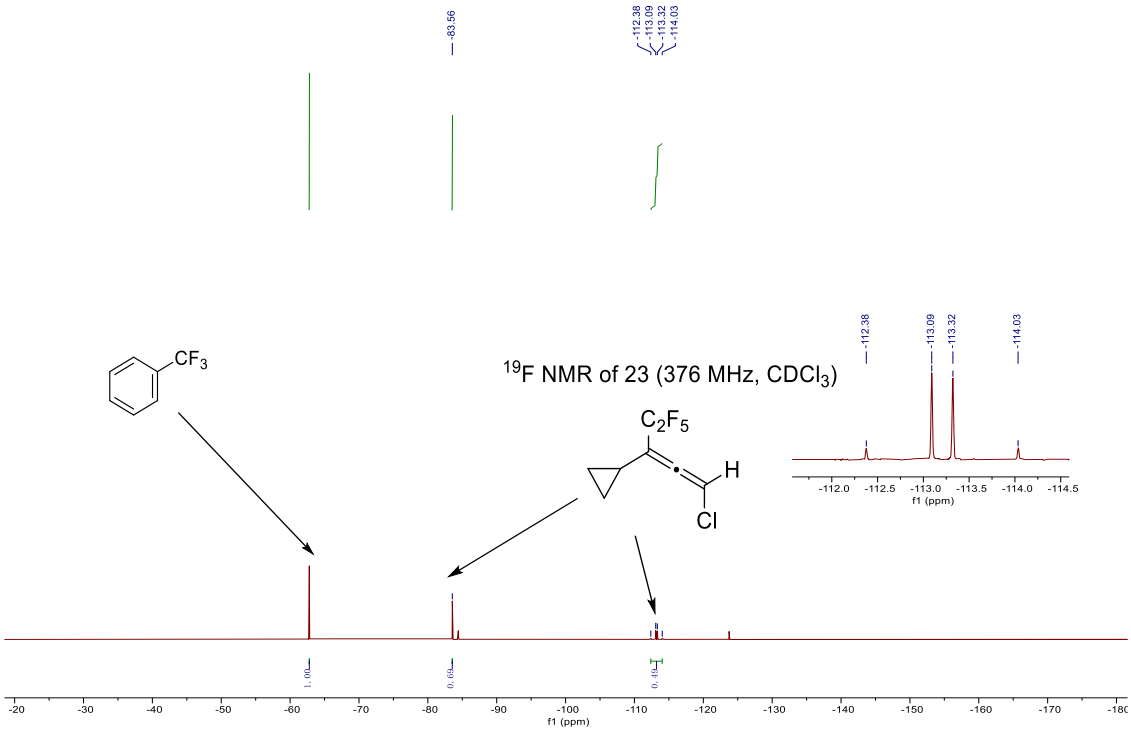
HRMS (EI) m/z calcd for $C_9H_9Cl_2F_5[M]^+$: 281.9996, found: 281.9990.

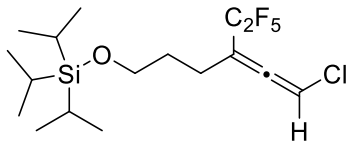


(1-chloro-4,4,5,5,5-pentafluoropenta-1,2-dien-3-yl)cyclopropane (23)

Yield was determined by ^{19}F NMR spectroscopy due to the high volatility of the desired product.

^{19}F NMR (377 MHz, $CDCl_3$) δ -83.48(s, 3F), -110.18 – -121.11 (m, 2F).





((6-chloro-4-(perfluoroethyl)hexa-4,5-dien-1-yl)oxy)triisopropylsilane (24)

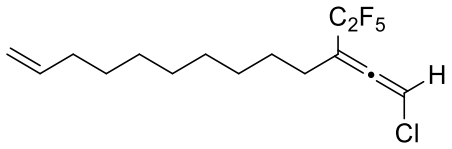
Colorless oil, 72.1 mg, 89% yield, **R**f =0.6 (petroleum ether).

^1H NMR (400 MHz, $CDCl_3$) δ 6.48 (p, *J* = 2.8 Hz, 1H), 3.77 – 3.72 (m, 2H), 2.44 – 2.36 (m, 2H), 1.77 – 1.70 (m, 2H), 1.09 – 1.03 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0 (t, *J* = 7.1 Hz), 124.7 – 108.9 (m, 2C), 107.0 (t, *J* = 26.4 Hz), 95.8, 61.9, 30.4, 23.3, 18.1, 12.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.48 (s, 3F), -112.48 – -114.41 (m, 2F).

HRMS (ESI) m/z calcd for $C_{17}H_{29}ClF_5OSi[(M+H)^+]$: 407.1591 , found: 407.1597.



1-chloro-3-(perfluoroethyl)trideca-1,2,12-triene (25)

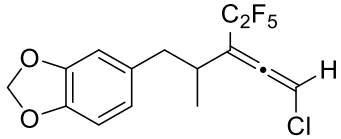
Colorless oil, 44.7 mg, 68% yield, **R**f =0.8 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (s, 1H), 5.91 – 5.70 (m, 1H), 4.99 (d, *J* = 17.1 Hz, 1H), 4.93 (d, *J* = 10.2 Hz, 1H), 2.25 (t, *J* = 7.6 Hz, 2H), 2.04 (q, *J* = 7.3 Hz, 2H), 1.52 – 1.44 (m, 2H), 1.41 – 1.26 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1 (t, *J* = 7.2 Hz), 139.3, 114.3, 121.3 – 110.9 (m, 2C), 107.0 (t, *J* = 26.4 Hz), 95.6, 33.9, 29.5, 29.4, 29.2, 29.0, 28.9, 27.0, 26.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.45 (s, 3F), -108.26 – -116.84 (m, 2F).

HRMS (ESI) m/z calcd for $C_{15}H_{21}ClF_5[(M+H)^+]$: 331.1247 , found: 331.1238.



5-(5-chloro-2-methyl-3-(perfluoroethyl)penta-3,4-dien-1-yl)benzo[d][1,3]dioxole (26)

Light yellow oil, 50.4 mg, 71% yield, *dr* = 1:1.4, **R**f =0.4 (petroleum ether: ethyl acetate, 30:1, v/v).

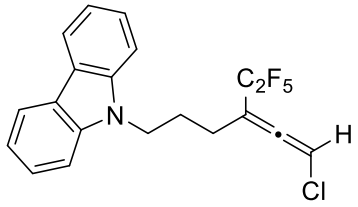
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 – 6.71 (m, 1H), 6.68 – 6.56 (m, 2H), 6.56 – 6.41 (m, 1H), 5.94 (d, *J* = 1.3 Hz, 2H), 2.91 – 2.79 (m, 1H), 2.71 – 2.58 (m, 1H), 2.55 – 2.39 (m, 1H), 1.11 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.4 (t, *J* = 7.9 Hz), 203.1 (t, *J* = 7.8 Hz), 147.7, 146.3, 146.2, 132.8, 132.7, 122.4, 122.4, 120.9 – 112.2 (m, 2C), 111.5 (t, *J* = 25.8 Hz), 109.7, 109.6, 108.3, 108.2, 101.0, 101.0, 96.5, 96.5, 42.6, 42.4, 34.7, 34.4, 20.2, 19.9. Note: The complicated spectrum due to mixture of *dr* = 10:7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.41 (d, *J* = 16.7 Hz, 3F), -110.21 – -114.77 (m, 2F).

Note: The complicated spectrum due to mixture of *dr* = 10:7.

HRMS (ESI) m/z calcd for $C_{15}H_{13}ClF_5O_2[(M+H)^+]$: 355.0519 , found: 355.0518.



9-(6-chloro-4-(perfluoroethyl)hexa-4,5-dien-1-yl)-9H-carbazole (27)

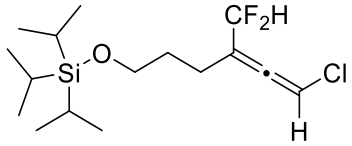
White solid, 45.3 mg, 57% yield, **R**f =0.3 (petroleum ether: ethyl acetate, 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.8 Hz, 2H), 7.51 – 7.46 (m, 2H), 7.42 – 7.38 (m, 2H), 7.29 – 7.26 (m, 1H), 7.26 – 7.23 (m, 1H), 6.56 – 6.47 (m, 1H), 4.43 – 4.36 (m, 2H), 2.40 – 2.34 (m, 2H), 2.17 – 2.08 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9 (t, *J* = 7.0 Hz), 140.4, 126.0, 123.1, 120.6, 119.3, 108.5, 106.1 (t, *J* = 26.8 Hz), 96.5, 42.0, 26.2, 24.4, ^{13}C NMR for C_2F_5 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.34 (s, 3F), -111.74 – -114.60 (m, 2F).

HRMS (ESI) m/z calcd for $C_{20}H_{16}ClF_5N[(M+H)^+]$: 400.0886 , found: 400.0890.



((6-chloro-4-(difluoromethyl)hexa-4,5-dien-1-yl)oxy)triisopropylsilane (28)

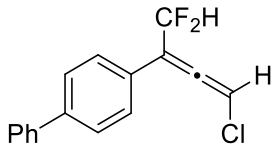
Colorless oil, 54.9 mg, 81% yield, **R**f =0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 – 6.32 (m, 1H), 6.14 (t, *J* = 56.0 Hz, 1H), 3.74 (t, *J* = 6.1 Hz, 2H), 2.43 – 2.29 (m, 2H), 1.74 (p, *J* = 6.9 Hz, 2H), 1.09 – 1.03 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8 (t, *J* = 9.3 Hz), 113.5 (t, *J* = 243.1 Hz), 110.9 (t, *J* = 25.4 Hz), 93.3, 62.2, 30.3, 22.0, 18.1, 12.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.71 (d, *J* = 56.4 Hz, 2F).

HRMS (ESI) m/z calcd for $C_{16}H_{30}ClF_2OSi[(M+H)^+]$: 339.1717 , found: 339.1726.



4-(4-chloro-1,1-difluorobuta-2,3-dien-2-yl)-1,1'-biphenyl (29)

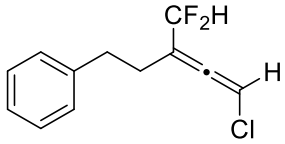
White solid, 30.5 mg, 55% yield, **R**f =0.5 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.55 (m, 5H), 7.55 – 7.29 (m, 4H), 6.74 – 6.70 (m, 1H), 6.56 (t, *J* = 52.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2 (t, *J* = 9.4 Hz), 140.6, 128.6, 128.6, 126.4, 113.6 (t, *J* = 243.1 Hz), 110.2 (t, *J* = 25.7 Hz), 93.6, 33.3, 27.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.97 – -112.60 (m, 2F).

HRMS (ESI) m/z calcd for $C_{16}H_{12}ClF_2[(M+H)^+]$: 277.0590 , found: 277.0594.



(5-chloro-3-(difluoromethyl)penta-3,4-dien-1-yl)benzene (30)

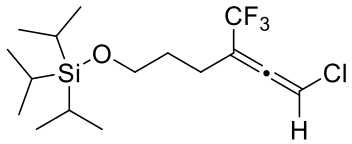
Colorless oil, 32.5 mg, 71% yield, **R**f =0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 2H), 7.25 – 7.18 (m, 3H), 6.35 – 6.27 (m, 1H), 6.14 (t, *J* = 55.9 Hz, 1H), 2.82 (t, *J* = 7.9 Hz, 2H), 2.61 – 2.52 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2 (t, *J* = 9.4 Hz), 140.6, 128.6, 128.6, 113.6 (t, *J* = 243.1 Hz), 110.2 (t, *J* = 25.7 Hz), 93.6, 33.3, 27.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.46 (dt, *J* = 57.1, 5.5 Hz,2F).

HRMS (EI) m/z calcd for $C_{12}H_{11}ClF_2[M]^+$: 228.0512 , found: 228.0506.



((6-chloro-4-(trifluoromethyl)hexa-4,5-dien-1-yl)oxy)triisopropylsilane (31)

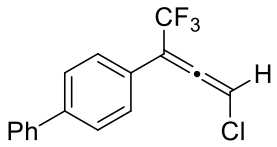
Colorless oil, 48.6 mg, 68% yield, **R**f =0.7 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$)δ 6.49 – 6.42 (m, 1H), 3.79 – 3.69 (m, 2H), 2.46 – 2.34 (m, 2H), 1.74 (p, *J* = 6.7 Hz, 2H), 1.10 – 1.02 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3 (d, *J* = 3.8 Hz), 123.7 (q, *J* = 275.7 Hz), 108.2 (q, *J* = 34.2 Hz), 95.3, 61.9, 30.2, 23.3, 18.1, 12.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -65.15 (s, 3F).

HRMS (ESI) m/z calcd for $C_{16}H_{29}ClF_3OSi[(M+H)^+]$: 357.1623 , found: 357.1630.



4-(4-chloro-1,1,1-trifluorobuta-2,3-dien-2-yl)-1,1'-biphenyl (32)

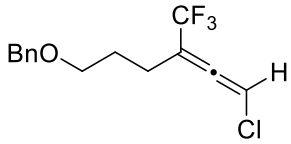
White solid, 27.7 mg, 47% yield, **R**f =0.5 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 4H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.43 (m, 2H), 7.43 – 7.35 (m, 1H), 6.80 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.7 (d, *J* = 3.6 Hz), 142.6, 140.1, 129.1, 128.2, 128.1, 127.8, 127.2, 126.9, 123.3 (q, *J* = 259.1 Hz), 109.3 (q, *J* = 52.0 Hz), 96.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -60.73 (s, 3F).

HRMS (ESI) m/z calcd for $C_{16}H_{11}ClF_3[(M+H)^+]$: 295.0496 , found: 295.0497.



(((6-chloro-4-(trifluoromethyl)hexa-4,5-dien-1-yl)oxy)methyl)benzene (33)

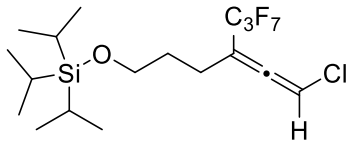
Colorless oil, 33.5 mg, 58% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 50:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 6.56 – 6.36 (m, 1H), 4.51 (s, 2H), 3.52 (t, *J* = 6.1 Hz, 2H), 2.44 – 2.35 (m, 2H), 1.86 – 1.78 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4 (d, *J* = 4.1 Hz), 138.4, 122.3 (q, *J* = 277.5 Hz), 107.9 (q, *J* = 34.6 Hz), 95.4, 73.2, 68.7, 27.2, 23.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -65.09 (s, 3F).

HRMS (ESI) m/z calcd for $C_{14}H_{15}ClF_3O[(M+H)^+]$: 291.0758 , found: 291.0756.



((4-(2-chlorovinylidene)-5,5,6,6,7,7,7-heptafluoroheptyl)oxy)triisopropylsilane (34)

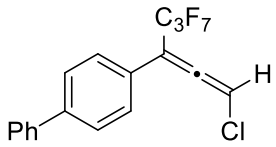
Colorless oil, 70.0 mg, 77% yield, **R**f =0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (p, *J* = 2.7 Hz, 1H), 3.91 – 3.54 (m, 2H), 2.47 – 2.34 (m, 2H), 1.82 – 1.68 (m, 2H), 1.13 – 1.01 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5 (t, *J* = 6.9 Hz), 120.07 – 108.30 (m), 107.6 (t, *J* = 26.1 Hz), 95.9, 61.9, 30.4, 23.6, 18.1, 12.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.43 (t, *J* = 9.7 Hz, 3F), -109.17 – -112.30 (m, 2F), -126.15 (s, 2F).

HRMS (ESI) m/z calcd for $C_{18}H_{29}ClF_7OSi[(M+H)^+]$: 457.1559 , found: 457.1569.



4-(1-chloro-4,4,5,5,6,6,6-heptafluorohexa-1,2-dien-3-yl)-1,1'-biphenyl (35)

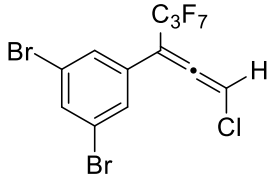
White solid, 53.7 mg, 68% yield, **R**f =0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 4H), 7.56 – 7.43 (m, 4H), 7.42 – 7.37 (m, 1H), 6.76 (t, *J* = 2.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5 (t, *J* = 6.8 Hz), 120.09 – 108.44 (m), 142.6, 140.1, 129.2, 129.1, 128.1, 127.9, 127.6, 127.3, 108.1 (t, *J* = 26.4 Hz), 95.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.13 (t, *J* = 9.8 Hz, 3F), -105.12 – -108.05 (m, 2F), -122.59 – -131.91 (m, 2F).

HRMS (EI) m/z calcd for $C_{18}H_{10}ClF_7[M]^+$: 394.0354, found: 394.0347.



1,3-dibromo-5-(1-chloro-4,4,5,5,6,6,6-heptafluorohexa-1,2-dien-3-yl)benzene (36)

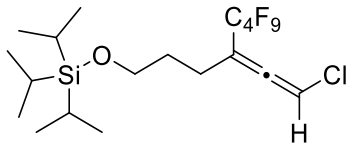
Yellow oil, 68.5 mg, 72% yield, **R**f =0.7 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (t, *J* = 1.7 Hz, 1H), 7.56 – 7.44 (m, 2H), 6.80 (t, *J* = 2.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1 (t, *J* = 6.8 Hz), 135.3, 132.4, 130.4, 123.4, 119.45 – 108.29 (m), 105.8 (t, *J* = 27.2 Hz), 97.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.07 (t, *J* = 9.8 Hz, 3F), -101.95 – -110.39 (m, 2F), -124.77 (s, 2F).

HRMS (EI) m/z calcd for $C_{12}H_4Br_2ClF_7[M]^+$: 473.8251, found: 474.8245.



((4-(2-chlorovinylidene)-5,5,6,6,7,7,8,8,8-nonafluorooctyl)oxy)triisopropylsilane (37)

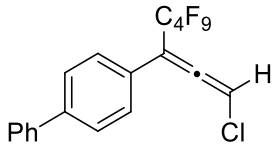
Colorless oil, 74.1 mg, 73% yield, **R**f =0.6 (petroleum ether:).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (p, *J* = 2.6 Hz, 1H), 3.81 – 3.69 (m, 2H), 2.45 – 2.35 (m, 2H), 1.73 (p, *J* = 6.9 Hz, 2H), 1.08 – 1.02 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.6 (t, *J* = 6.9 Hz), 120.00 – 109.74 (m), 107.8 (t, *J* = 26.2 Hz), 95.9, 61.8, 30.4, 23.7, 18.1, 12.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.99 (t, *J* = 10.0 Hz, 3F), -107.77 – -111.36 (m, 2F), -122.52 – -122.74 (m, 2F), -125.69 – -126.04 (m, 2F).

HRMS (ESI) m/z calcd for $C_{19}H_{29}ClF_9OSi[(M+H)^+]$: 507.1527 , found: 507.1530.



4-(1-chloro-4,4,5,5,6,6,7,7,7-nonafluorohepta-1,2-dien-3-yl)-1,1'-biphenyl (38)

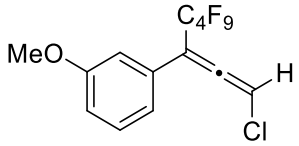
White solid, 70.3 mg, 79% yield, **R**f =0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 4H), 7.55 – 7.43 (m, 4H), 7.42 – 7.36 (m, 1H), 6.76 (t, *J* = 2.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6 (t, *J* = 7.0 Hz), 142.6, 140.1, 129.2, 129.1, 128.1, 127.9, 127.6, 127.3, 119.72 – 110.34 (m), 108.2 (t, *J* = 26.2 Hz), 95.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.88 (t, *J* = 9.7 Hz, 3F), -104.10 – -107.57 (m, 2F), -119.49 – -122.02 (m, 2F), -125.48 – -125.71 (m, 2F).

HRMS (ESI) m/z calcd for $C_{19}H_{10}ClF_9[M]^+$: 444.0322, found: 444.0317.



1-(1-chloro-4,4,5,5,6,6,7,7,7-nonafluorohepta-1,2-dien-3-yl)-3-methoxybenzene (39)

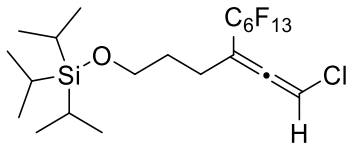
Yellow oil, 49.9 mg, 63% yield, **R**f =0.4 (petroleum ether: ethyl acetate, 30:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.8 Hz, 1H), 7.08 – 7.00 (m, 1H), 6.98 – 6.90 (m, 2H), 6.71 (t, *J* = 2.6 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6 (t, *J* = 6.9 Hz), 130.3, 130.0, 121.2, 115.0, 114.7, 108.2 (t, *J* = 26.2 Hz), 95.7, 55.5, ^{13}C NMR for C_4F_9 could not be assigned.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.90 (t, *J* = 9.8 Hz, 3F), -103.46 – -109.37 (m, 2F), -120.94 – -121.89 (m, 2F), -125.41 – -126.07 (m, 2F).

HRMS (ESI) m/z calcd for $C_{14}H_9ClF_9O[(M+H)^+]$: 399.0193 , found: 399.0194.



((4-(2-chlorovinylidene)-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)oxy)triisopropylsilane (40)

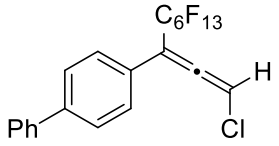
Colorless oil, 71.7 mg, 59% yield, **R**f =0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (p, *J* = 2.8 Hz, 1H), 3.80 – 3.71 (m, 2H), 2.45 – 2.36 (m, 2H), 1.74 (p, *J* = 6.4 Hz, 2H), 1.10 – 1.00 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.6 (t, *J* = 6.9 Hz), 119.80 – 110.03 (m), 107.9 (t, *J* = 26.1 Hz), 95.9, 61.8, 30.4, 23.7, 18.1, 12.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.82 (t, *J* = 10.0 Hz, 3F), -107.03 – -112.09 (m, 2F), -121.50 – -121.97 (m, 2F), -122.56 – -123.30 (m, 2F), -125.86 – -126.65 (m, 2F).

HRMS (ESI) m/z calcd for $C_{21}H_{29}ClF_{13}OSi[(M+H)^+]$: 607.1463 , found: 607.1467.



4-(1-chloro-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononona-1,2-dien-3-yl)-1,1'-biphenyl (41)

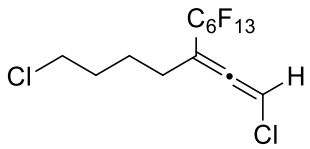
Whites solid, 74.2 mg, 68% yield, **R**f =0.6 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 4H), 7.55 – 7.44 (m, 4H), 7.43 – 7.34 (m, 1H), 6.76 (t, *J* = 2.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6 (t, *J* = 6.8 Hz), 142.5, 140.1, 129.2, 129.1, 128.1, 127.9, 127.6, 127.3, 119.47 – 109.58 (m), 108.3 (t, *J* = 26.6 Hz), 95.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.74 (t, *J* = 10.4 Hz, 3F), -104.19 – -107.18 (m, 2F), -120.19 – -120.64 (m, 2F), -121.28 – -121.71 (m, 2F), -122.53 – -123.16 (m, 2F), -125.84 – -126.44 (m, 2F).

HRMS (EI) m/z calcd for $C_{21}H_{10}ClF_{13}[M]^+$: 544.0258 , found: 544.0251.



11-chloro-7-(2-chlorovinylidene)-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoroundecane (42)

Colorless oil, 66.6 mg, 69% yield, **R**f =0.8 (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (p, *J* = 2.7 Hz, 1H), 3.56 (t, *J* = 6.4 Hz, 2H), 2.39 – 2.22 (m, 2H), 1.91 – 1.79 (m, 2H), 1.75 – 1.62 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8 (t, *J* = 7.0 Hz), 119.86 – 108.01 (m), 107.3 (t, *J* = 26.4 Hz), 96.3, 44.5, 31.6, 26.5, 24.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.82 (t, *J* = 9.8 Hz, 3F), -108.25 – -110.85 (m, 2F), -121.62 – -121.70 (m, 2F), -121.70 – -121.81 (m, 2F), -122.63 – -123.13 (m, 2F), -125.91 – -126.50 (m, 2F).

HRMS (EI) m/z calcd for $C_{13}H_9Cl_2F_{13}[M]^+$: 481.9868, found: 481.9862.

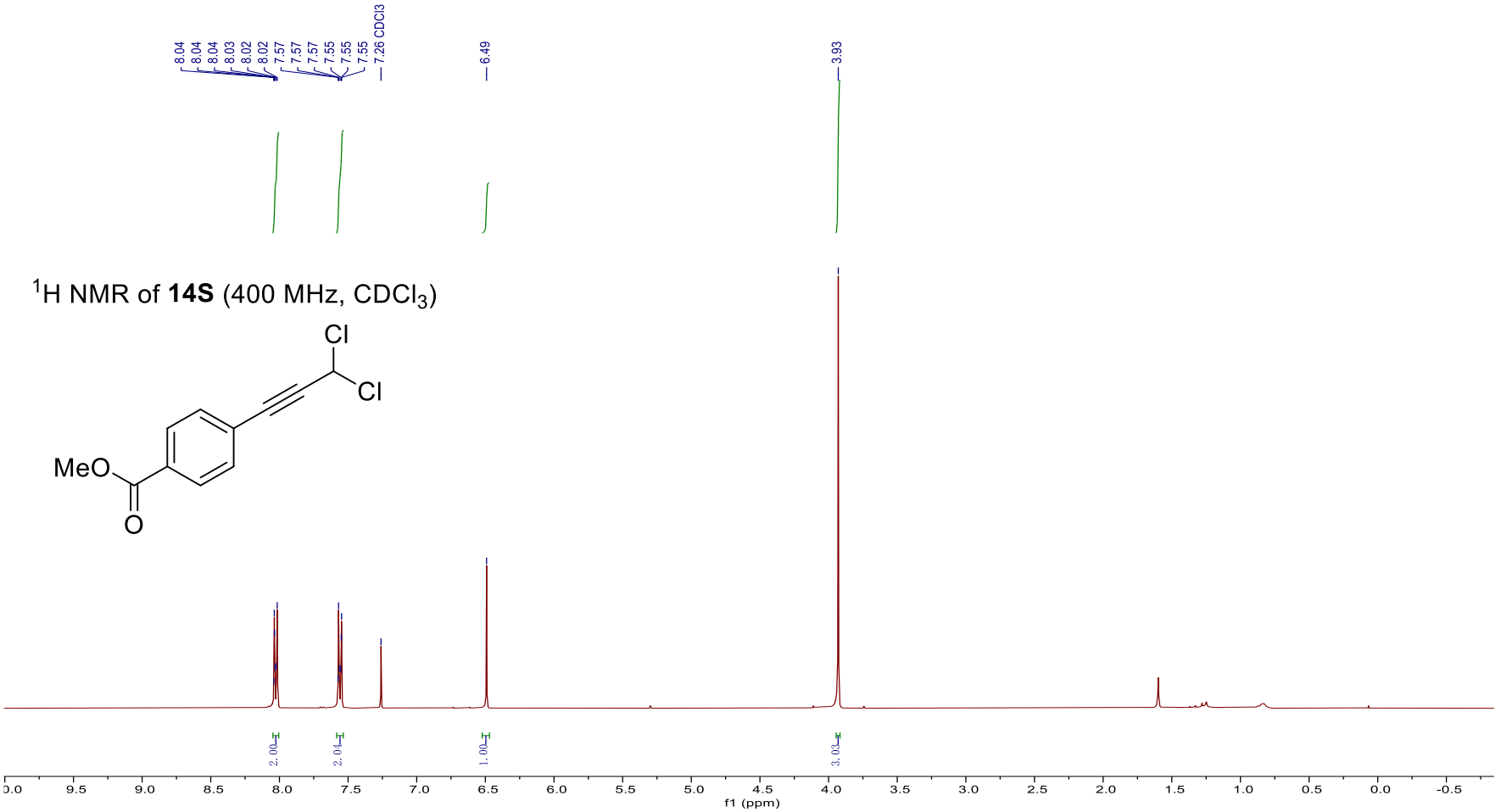
9.References

1 Xu, L.; Vicic, D. A. *J. Am. Chem.Soc.* 2016, **138**, 2536-2539.

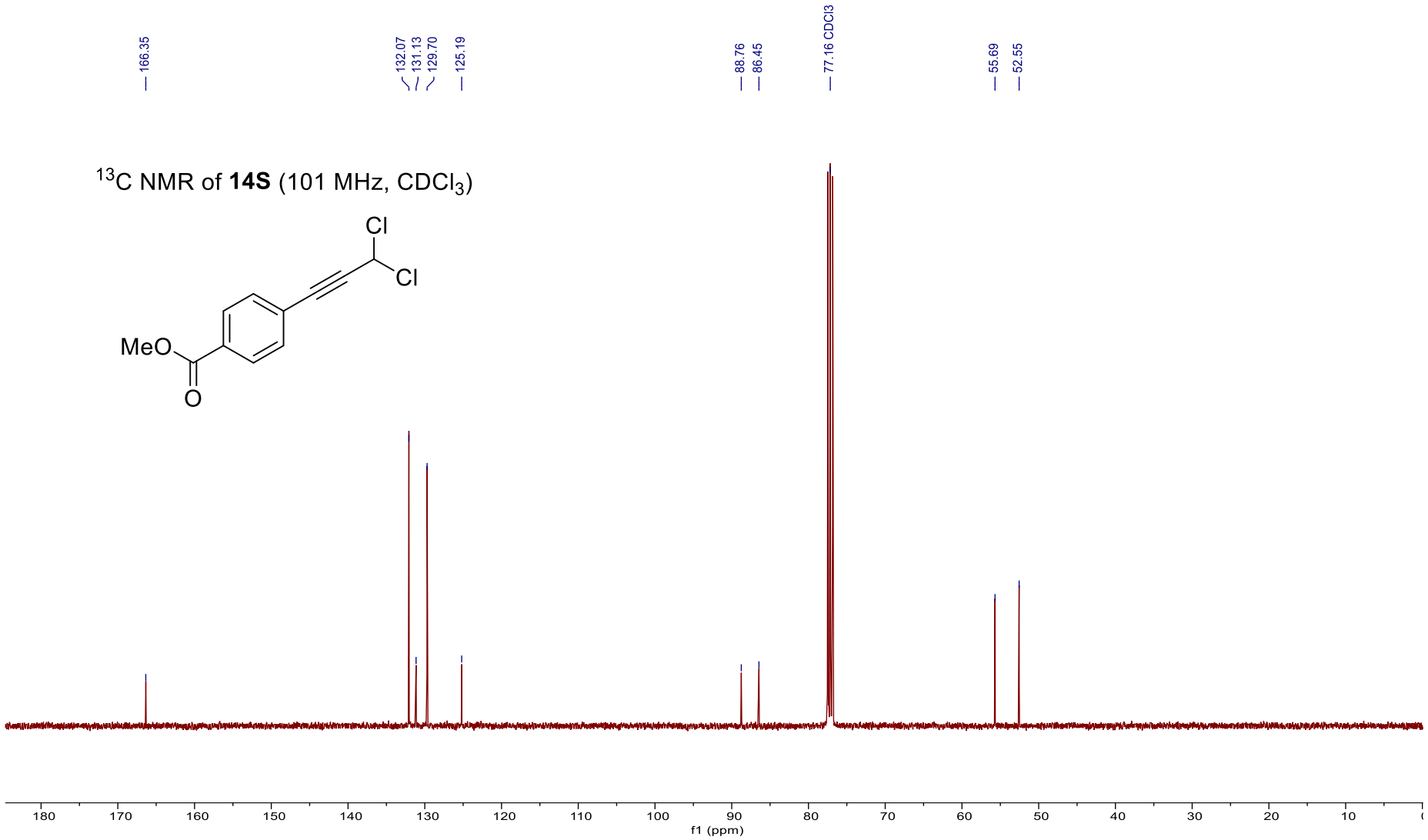
2 Aikawa, K.; Nakamura, Y.; Yokota, Y.; Toya, W.; Mikami, K. *Chem. Eur. J.* 2015, **21**, 96-100.

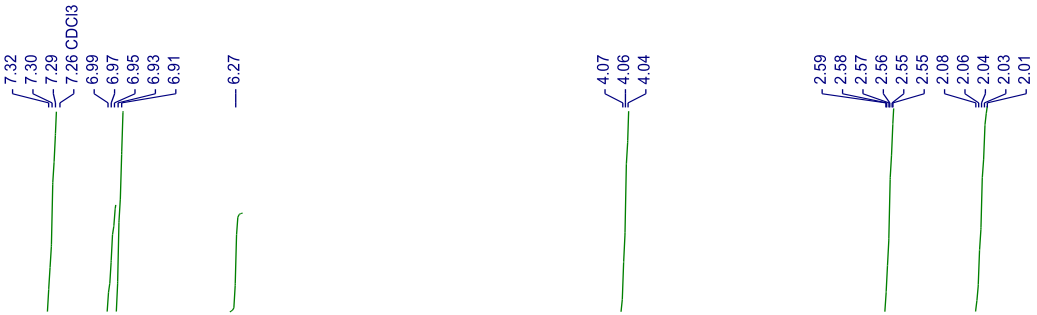
3 (a) Liu, Z.-L.; Yang, C.; Xue, Q.-Y.; Zhao, M.; Shan, C.-C.; Xu, Y.-H.; Loh, T.-P. *Angew. Chem. Int. Ed.* 2019, **58**, 16538-16542; (b) Wu, K.-F.; Dai, D.-T.; Sun, X.-Y.; Xu, Y.-H. *Org. Lett.* 2022, **24**, 2660-2664; (c) Zhou, B.; Wu, Q.; Dong, Z.; Xu, J.; Yang, Z. *Org. Lett.* 2019, **21**, 3594-3599.

NMR Spectra

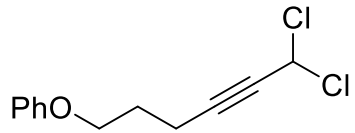


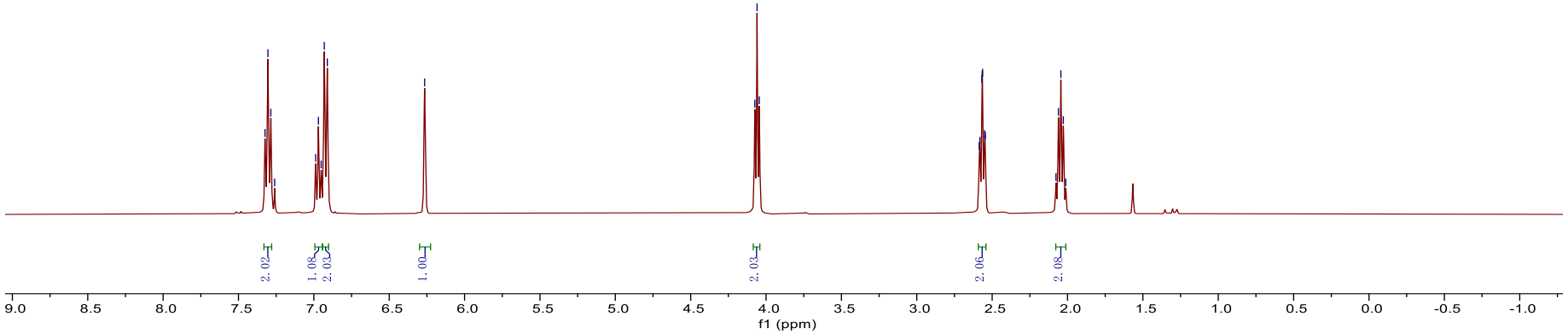
^{1}H NMR of **14S** (400 MHz, $CDCl_3$)

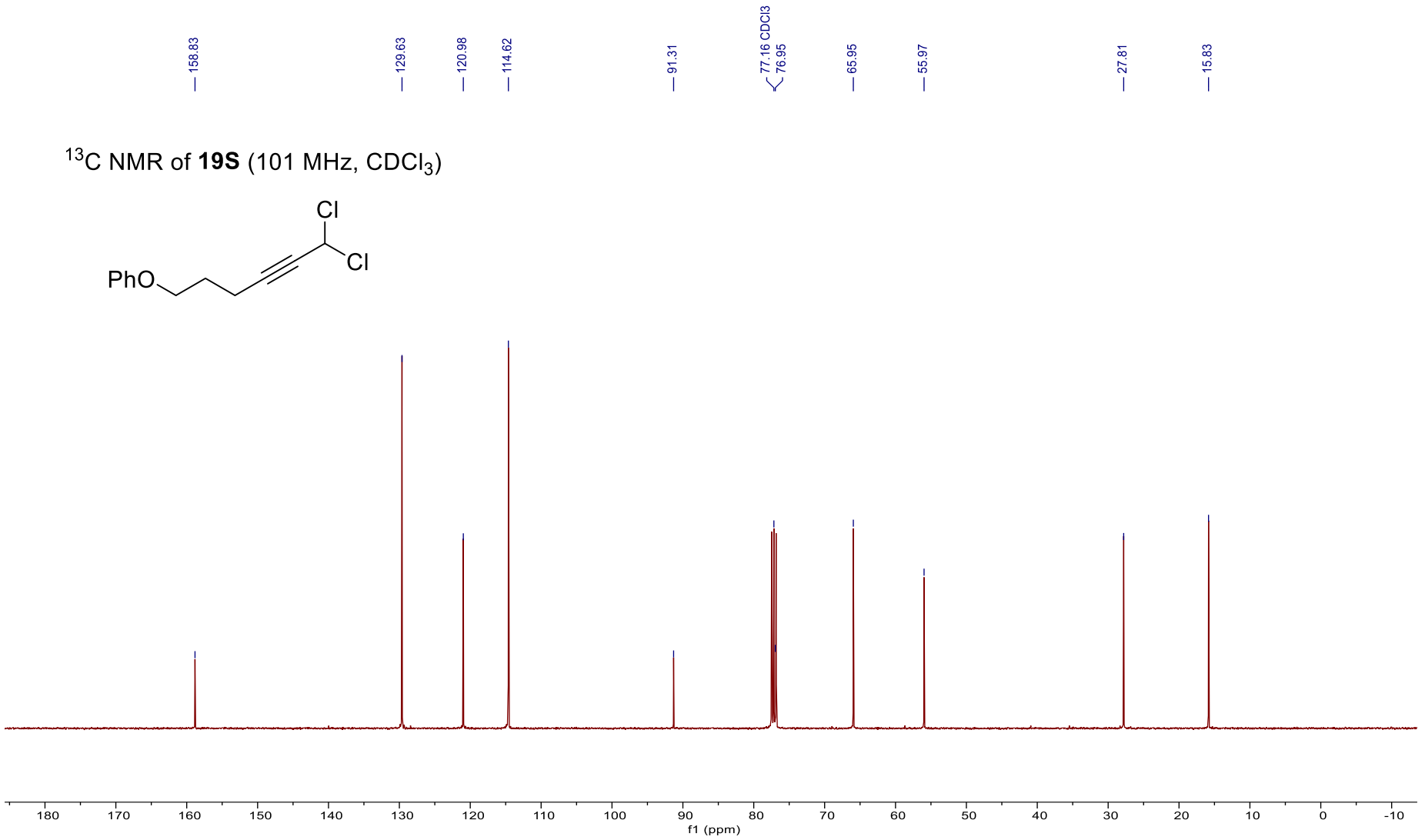

166.35
132.07
131.13
129.70
125.19
88.76
86.45
77.16 CDCl3
55.69
52.55
^{13}C NMR of **14S** (101 MHz, $CDCl_3$)
Cl
Cl
MeO
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



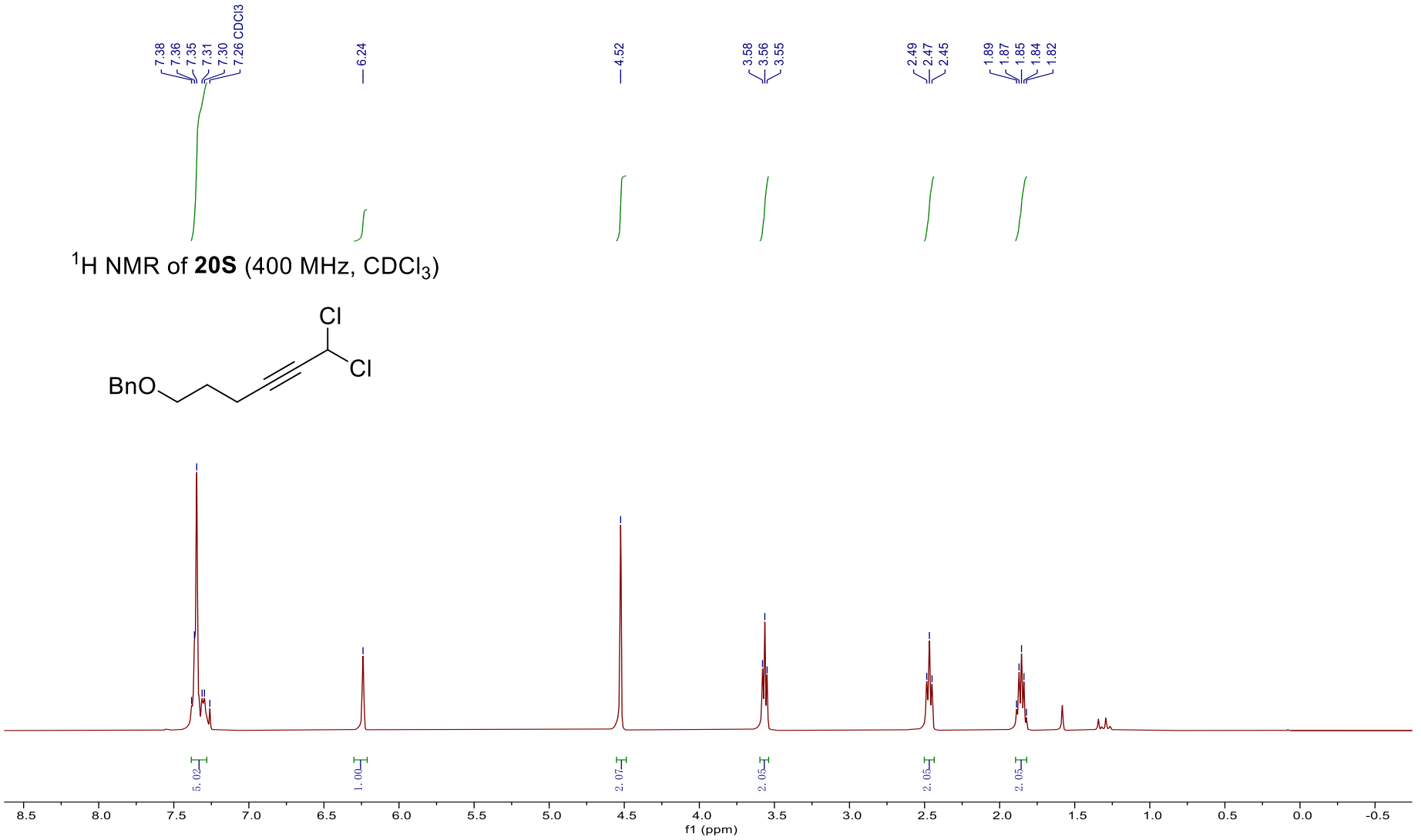
^{1}H NMR of **19S** (400 MHz, $CDCl_3$)





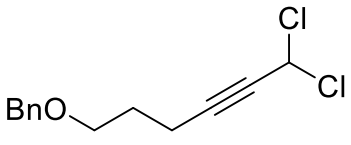


^{13}C NMR of **19S** (101 MHz, $CDCl_3$)

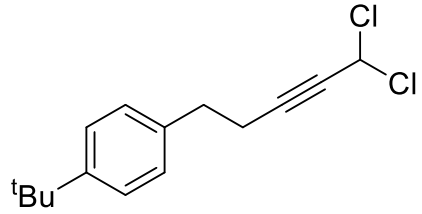


^{1}H NMR of **20S** (400 MHz, $CDCl_3$)

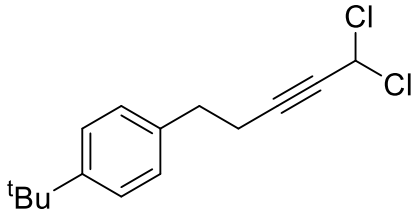
^{13}C NMR of **20S** (101 MHz, $CDCl_3$)

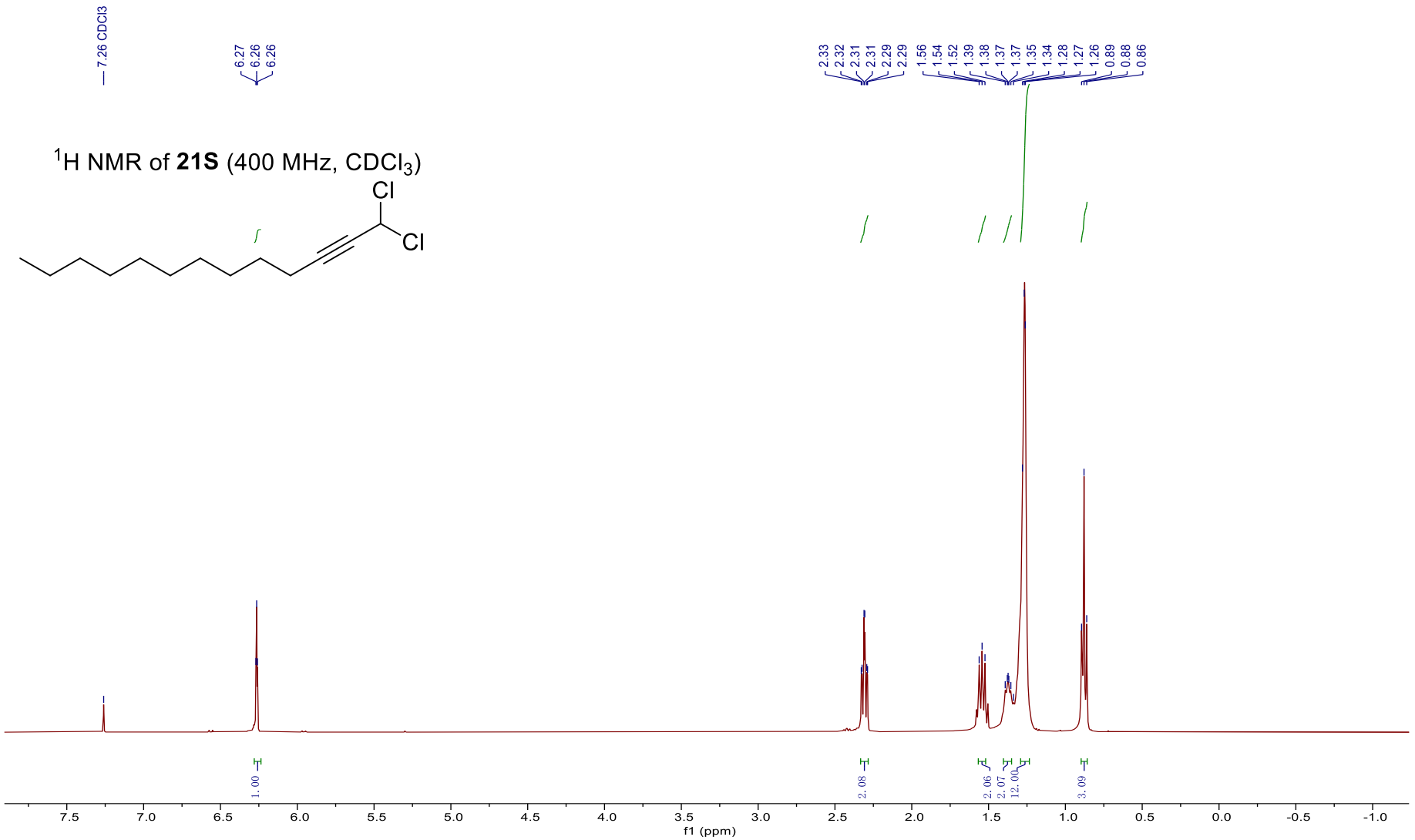


^{1}H NMR of **18S** (400 MHz, $CDCl_3$)



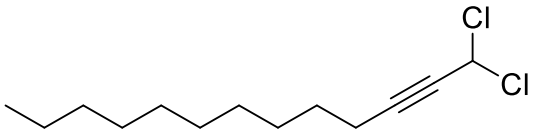
^{13}C NMR of **18S** (101 MHz, $CDCl_3$)



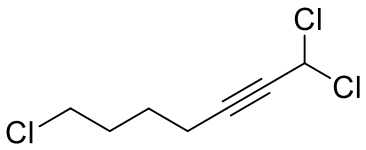


^{1}H NMR of **21S** (400 MHz, $CDCl_3$)

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

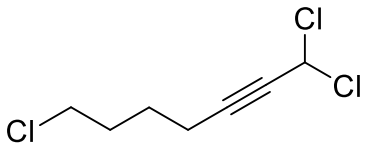


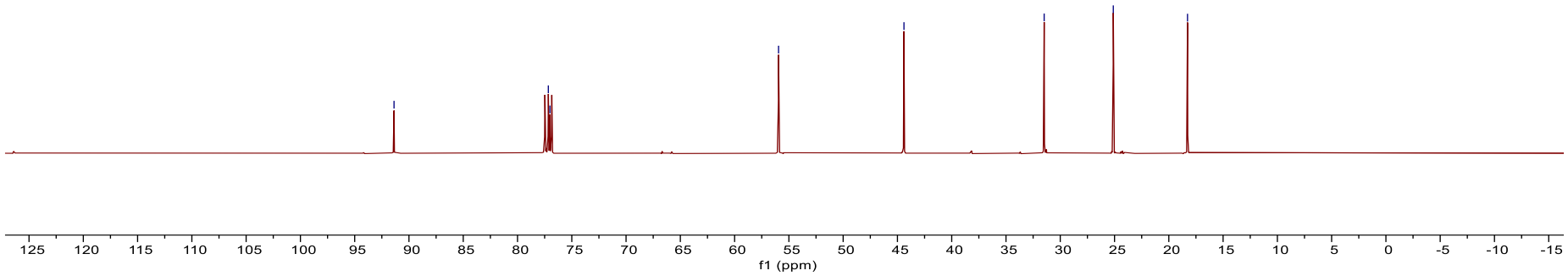
^{1}H NMR of **22S** (400 MHz, $CDCl_3$)

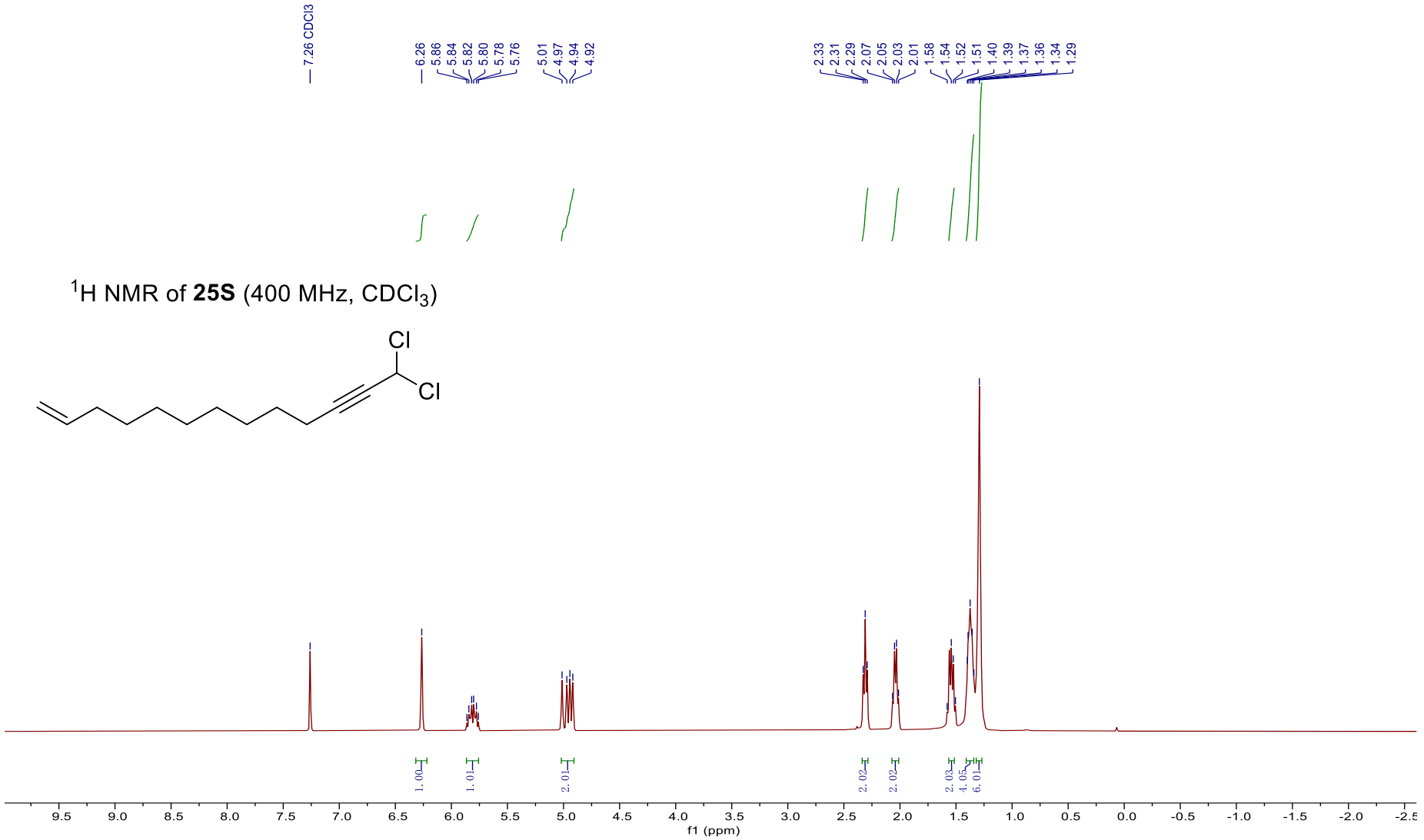


91.37
77.16 CDCl3
77.01
55.95
44.40
31.48
25.11
18.28

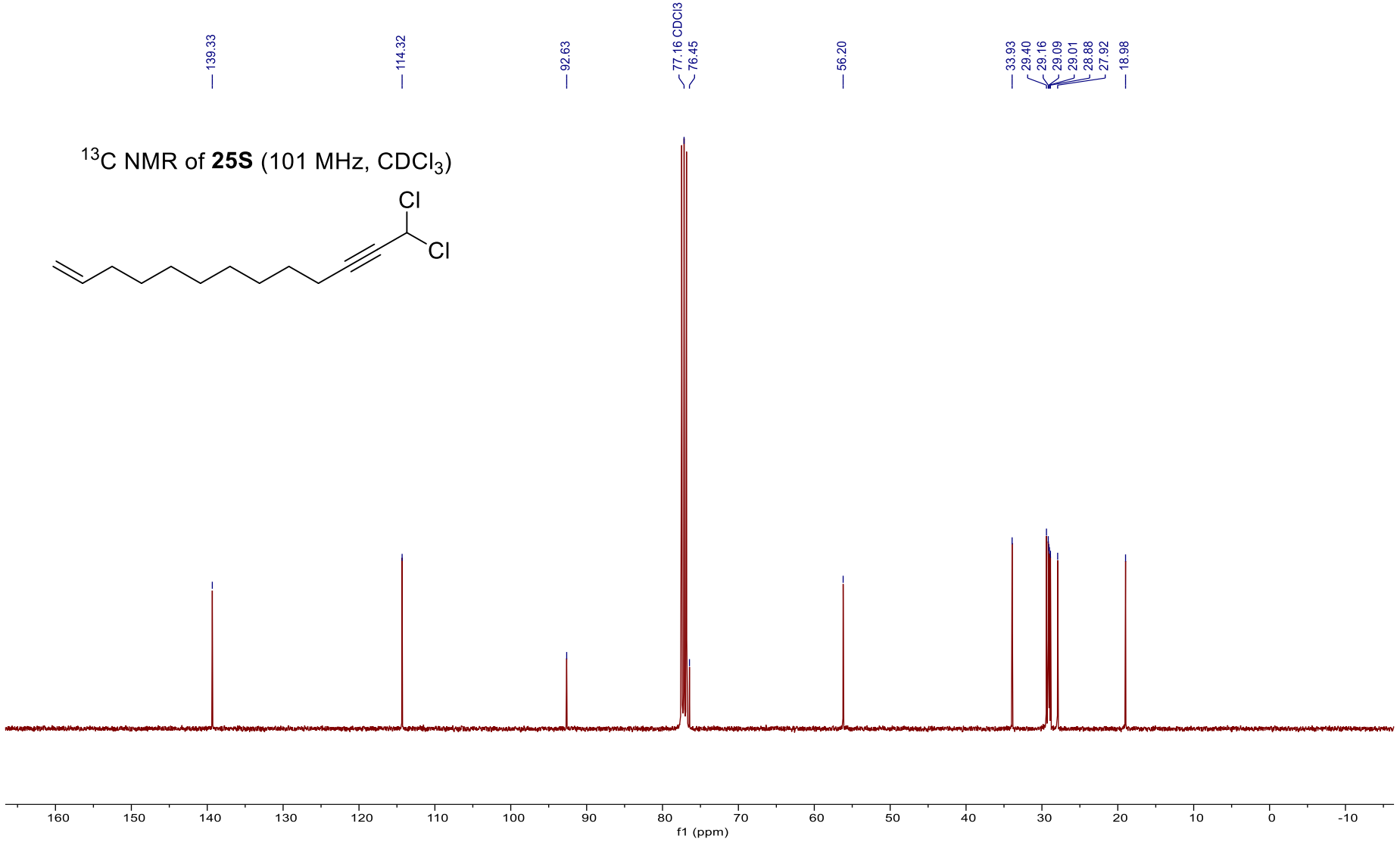
^{13}C NMR of **22S** (101 MHz, $CDCl_3$)

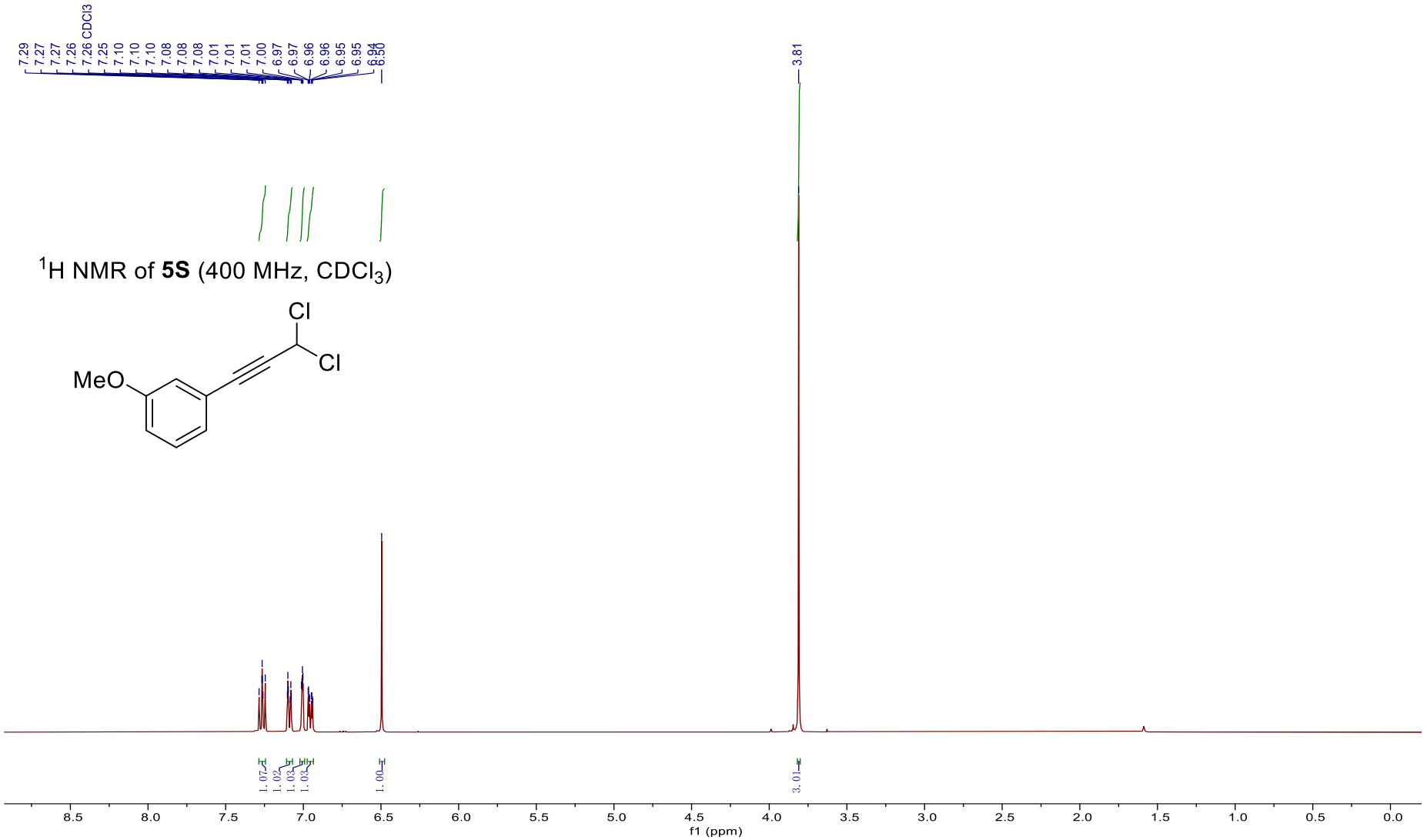






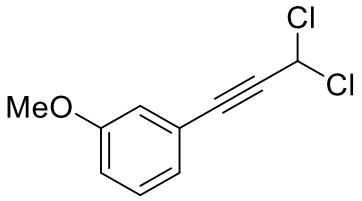
^{1}H NMR of **25S** (400 MHz, $CDCl_3$)

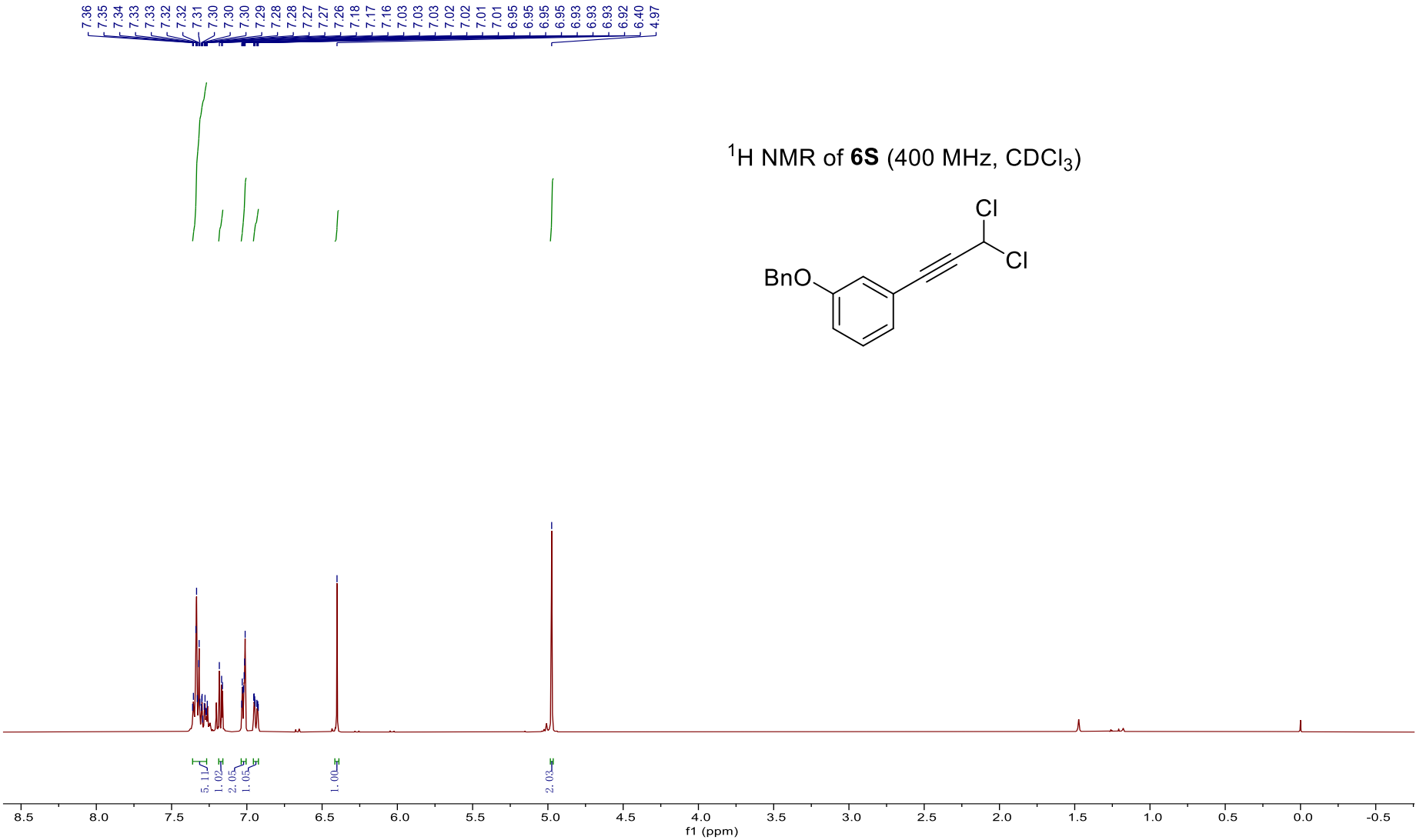

139.33
114.32
92.63
77.16 CDCl3
76.45
56.20
33.93
29.40
29.16
29.09
29.01
28.88
27.92
18.98
13C NMR of 25S (101 MHz, CDCl3)
Cl
Cl
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



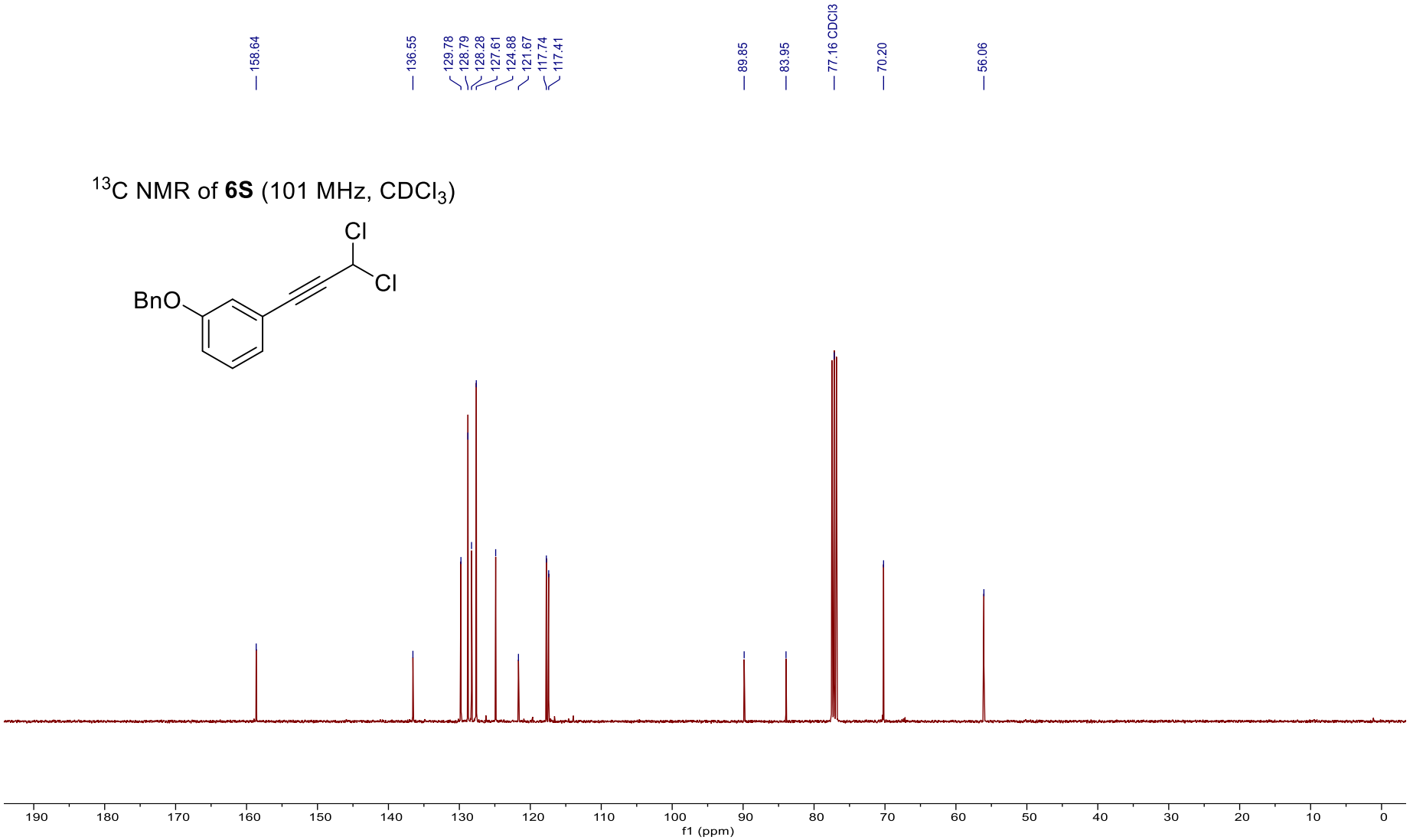
^{1}H NMR of **5S** (400 MHz, $CDCl_3$)

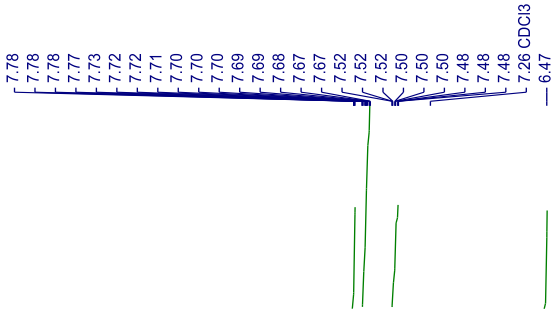
^{13}C NMR of **5S** (101 MHz, $CDCl_3$)



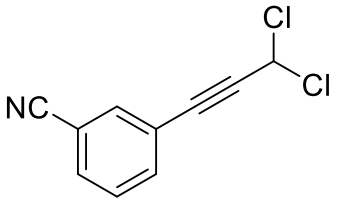


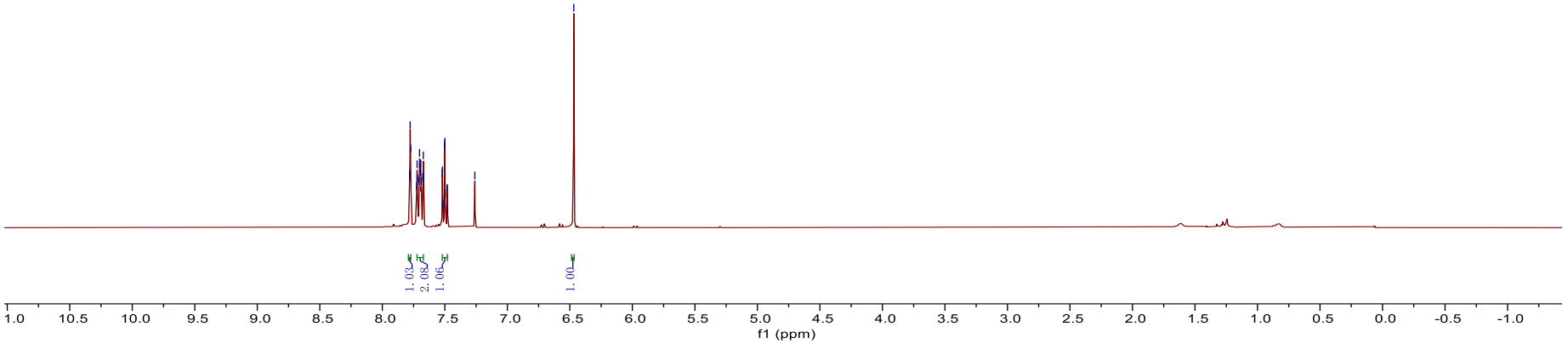
^{1}H NMR of **6S** (400 MHz, $CDCl_3$)


158.64
136.55
129.78
128.79
128.28
127.61
124.88
121.67
117.74
117.41
89.85
83.95
77.16 CDCl3
70.20
56.06
13C NMR of 6S (101 MHz, CDCl3)
Cl
Cl
BnO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

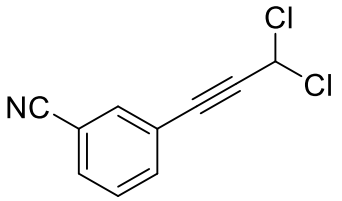


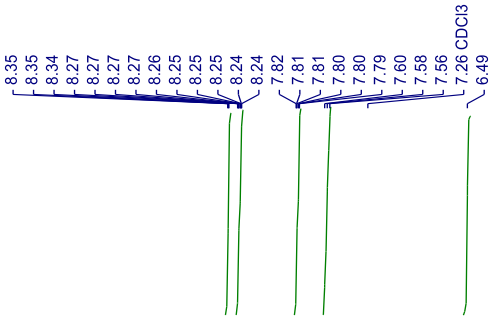
^{1}H NMR of **7S** (400 MHz, $CDCl_3$)



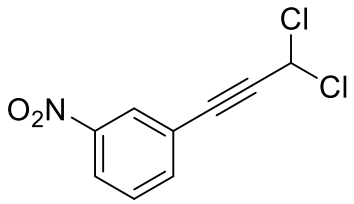


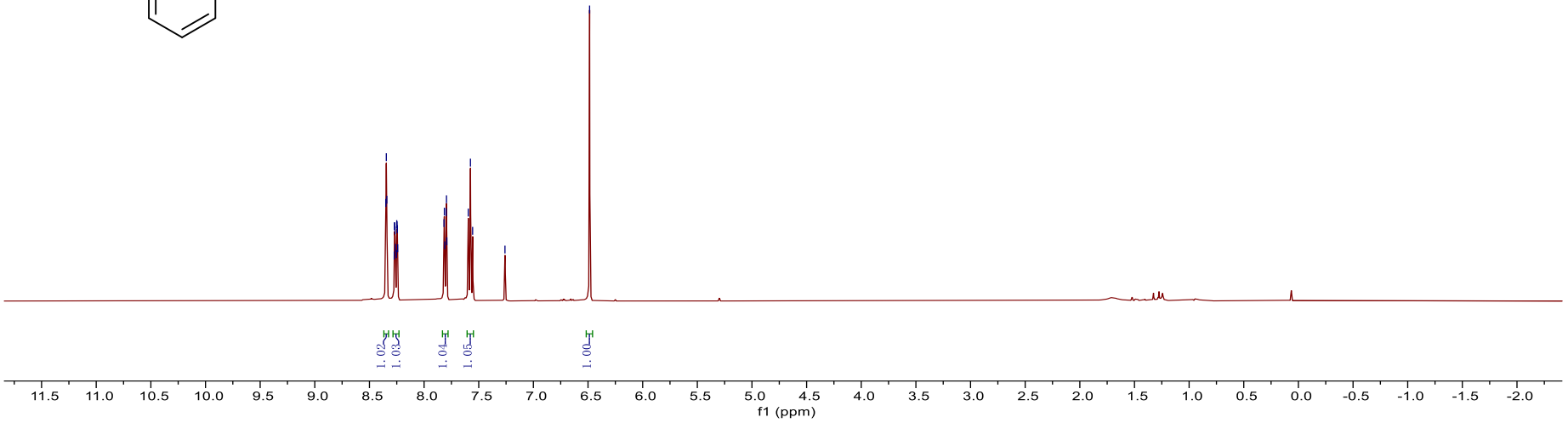
^{13}C NMR of **7S** (101 MHz, $CDCl_3$)



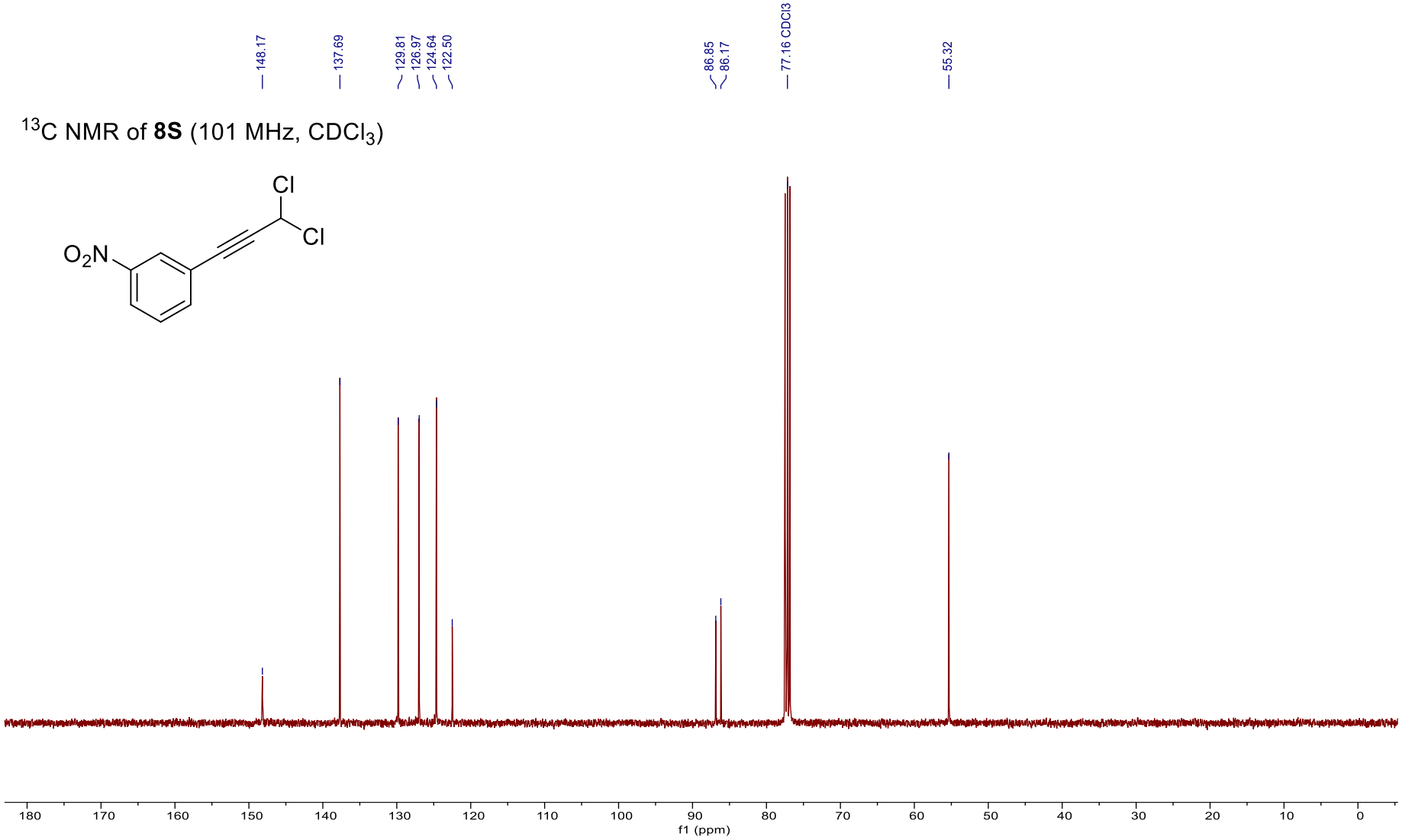


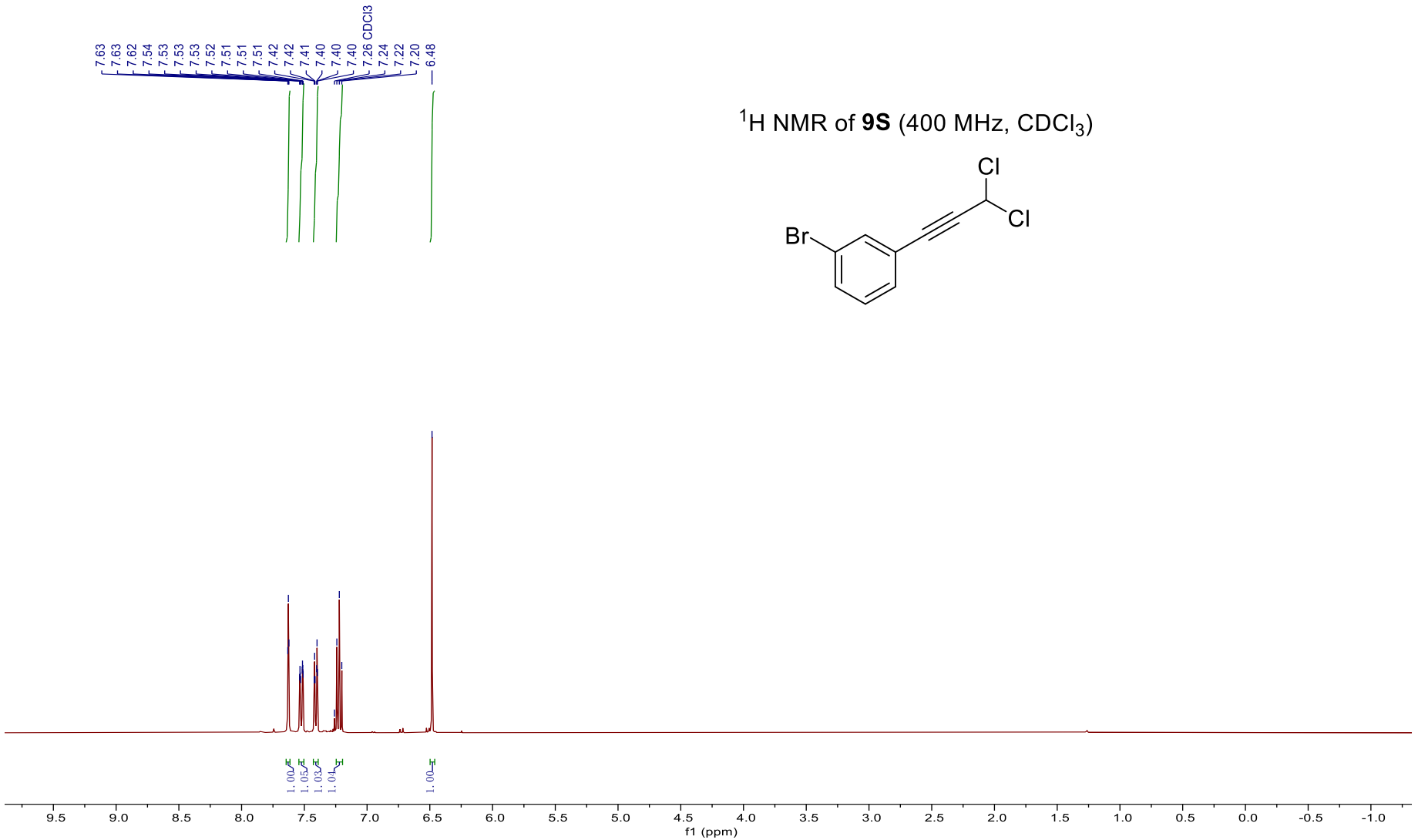
^{1}H NMR of **8S** (400 MHz, $CDCl_3$)





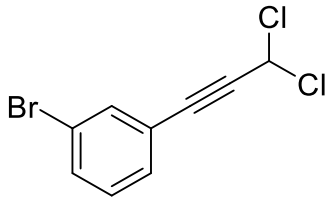
^{13}C NMR of **8S** (101 MHz, $CDCl_3$)

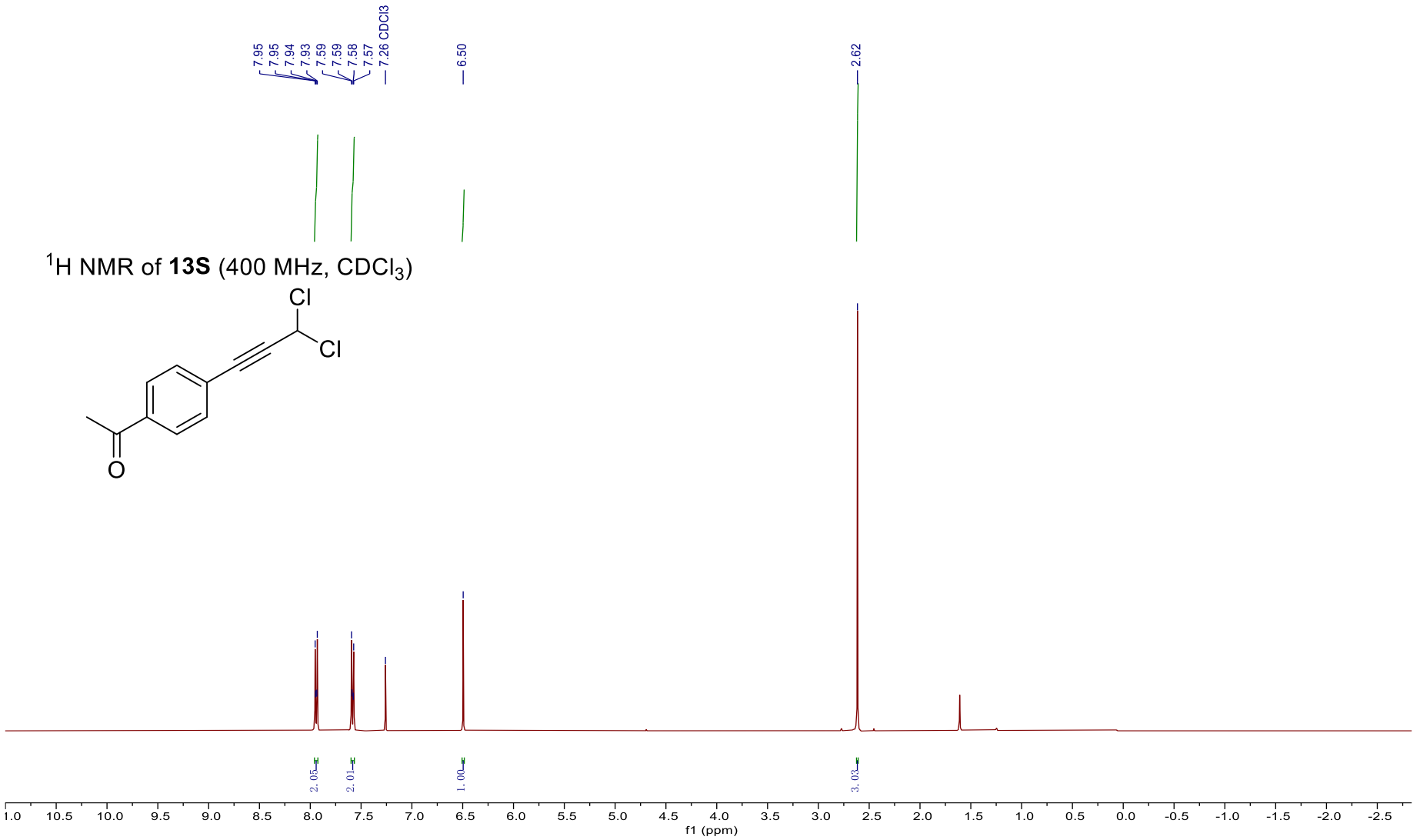




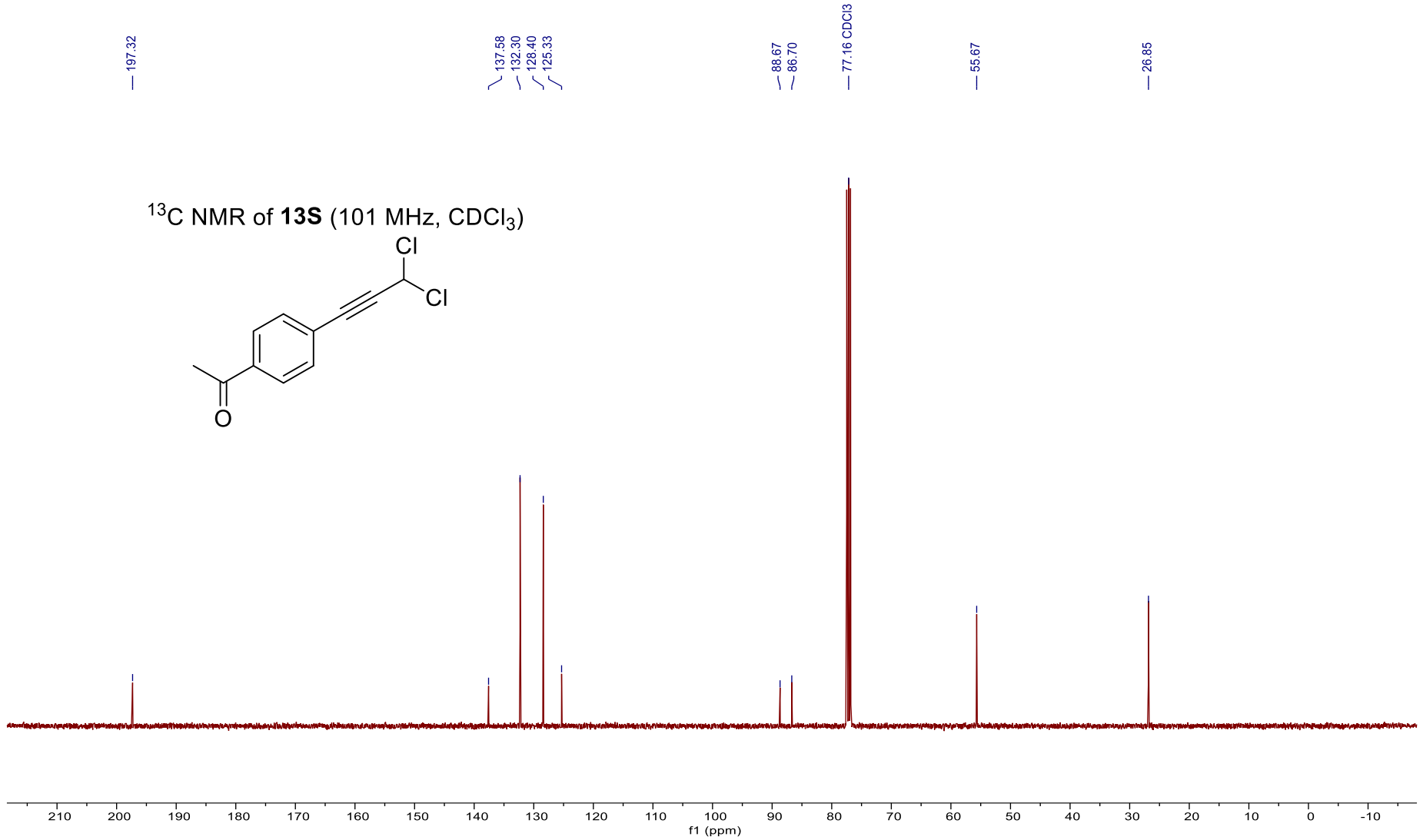
^{1}H NMR of **9S** (400 MHz, $CDCl_3$)

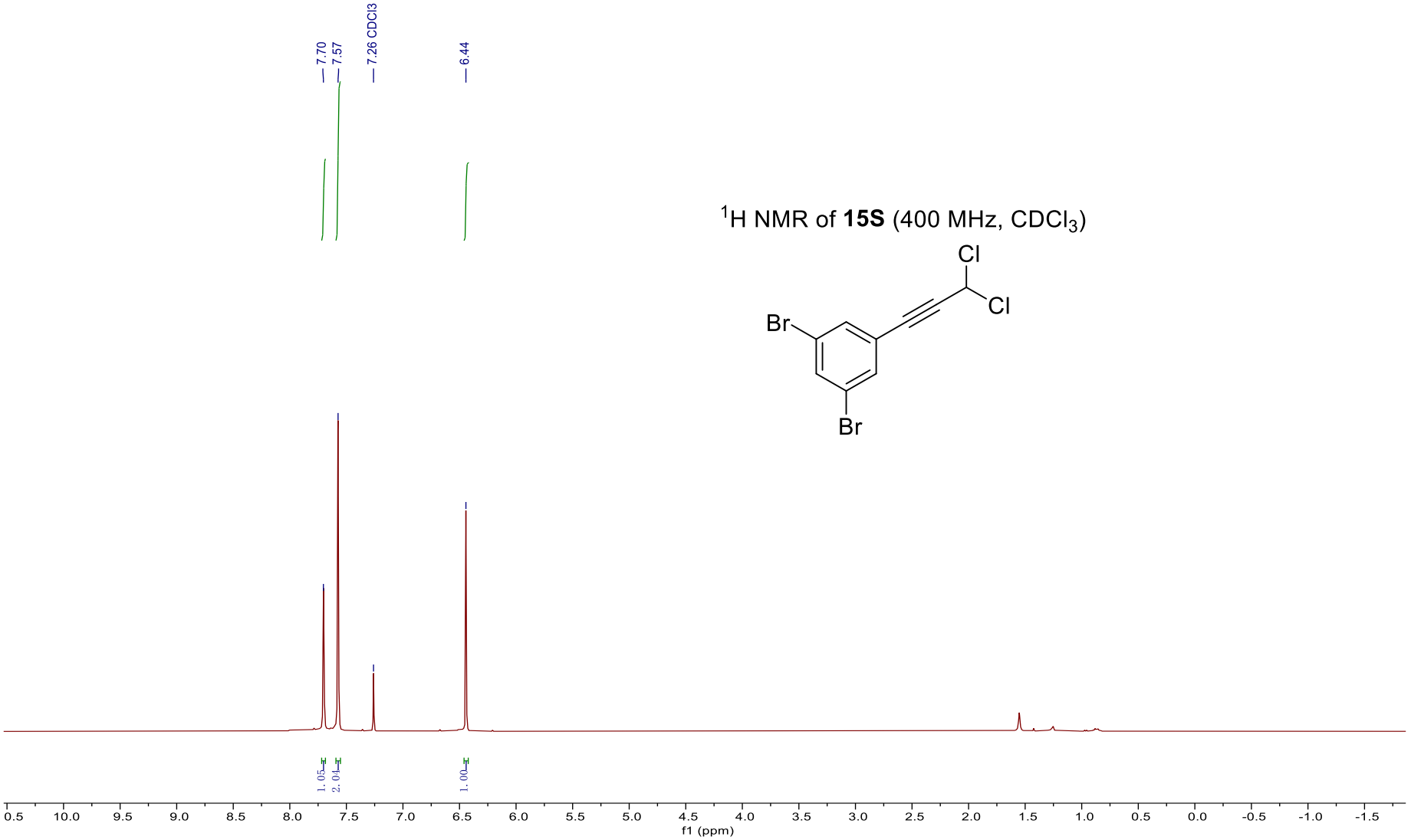
^{13}C NMR of **9S** (101 MHz, $CDCl_3$)





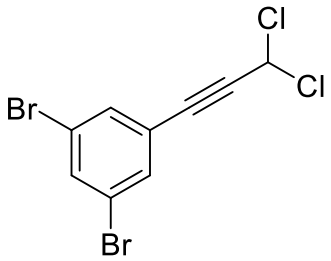
^{1}H NMR of **13S** (400 MHz, $CDCl_3$)


197.32
137.58
132.30
128.40
125.33
88.67
86.70
77.16 CDCl3
55.67
26.85
13C NMR of 13S (101 MHz, CDCl3)
Cl
Cl
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)

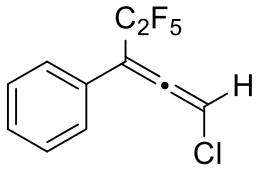


^{1}H NMR of **15S** (400 MHz, $CDCl_3$)

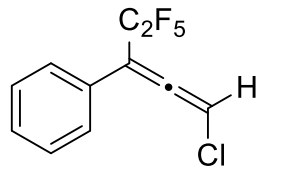
^{13}C NMR of **15S** (101 MHz, $CDCl_3$)

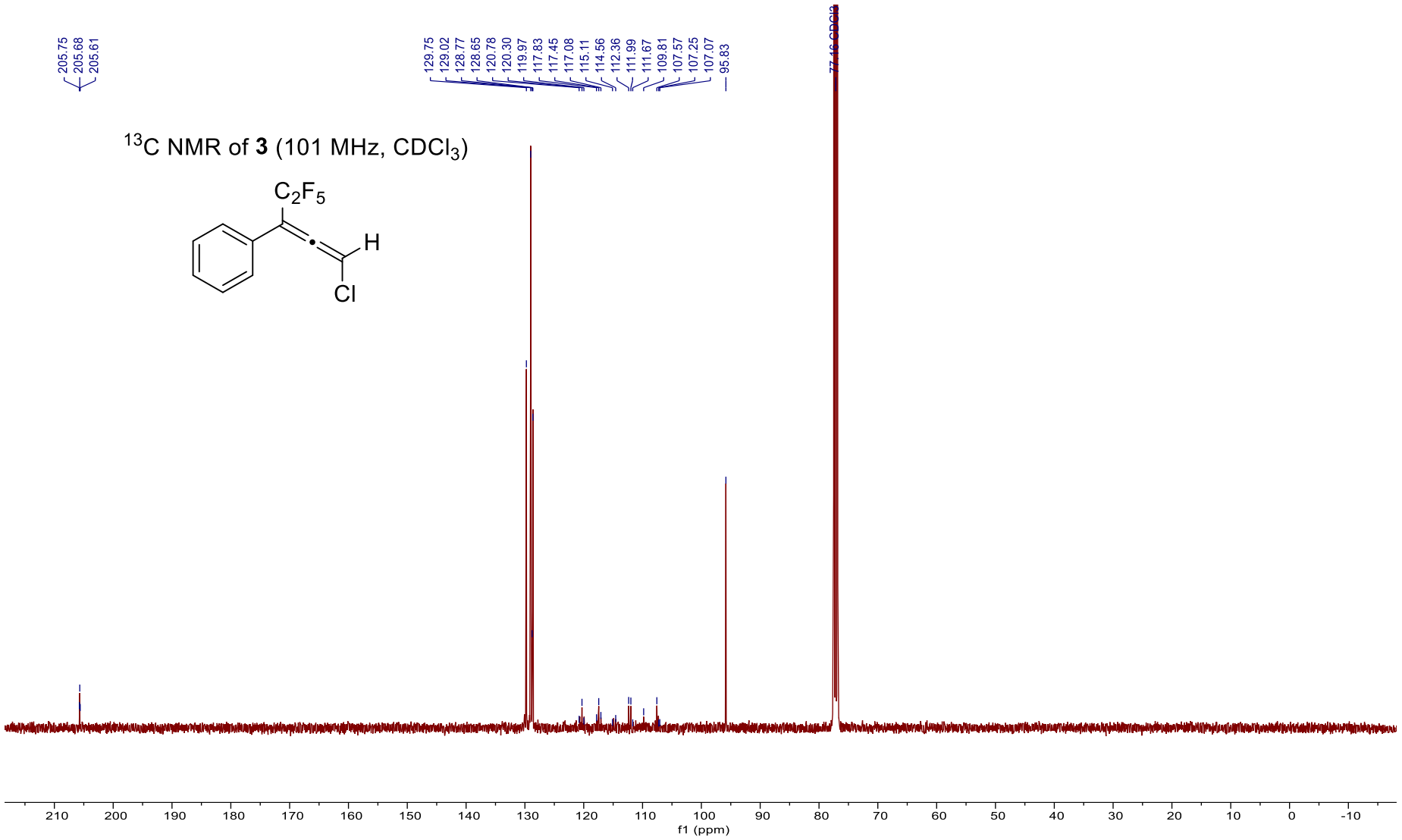


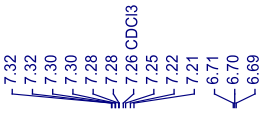
^{1}H NMR of **3** (400 MHz, $CDCl_3$)



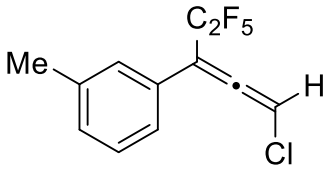
^{19}F NMR of **3** (376 MHz, $CDCl_3$)

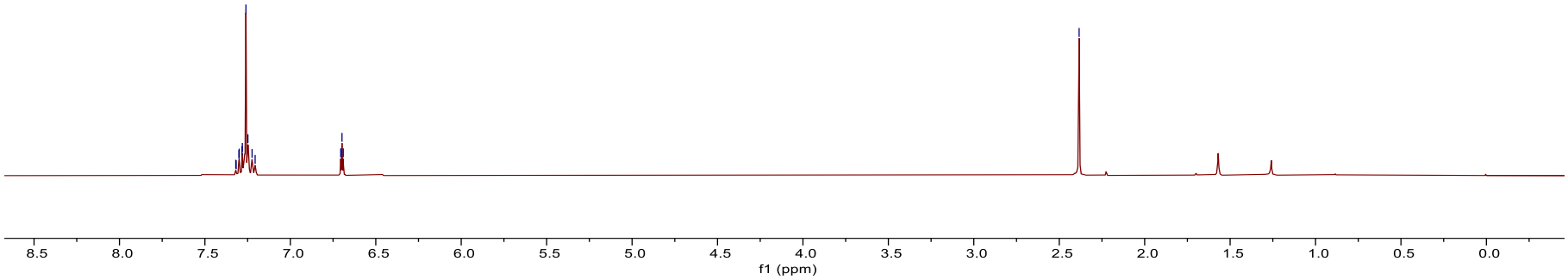



205.75
205.68
205.61
129.75
129.02
128.77
128.65
120.78
120.30
119.97
117.83
117.45
117.08
115.11
114.56
112.36
111.99
111.67
109.81
107.57
107.25
107.07
95.83
77.16 CDCl3
13C NMR of 3 (101 MHz, CDCl3)
C2F5
H
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

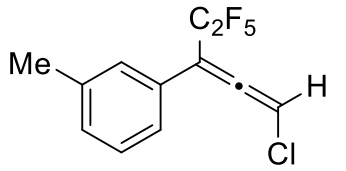


^{1}H NMR of **4** (400 MHz, $CDCl_3$)

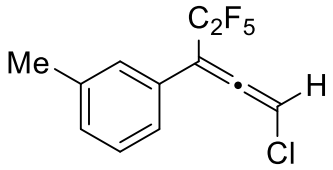




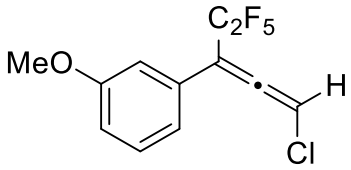
^{19}F NMR of **4** (376 MHz, $CDCl_3$)



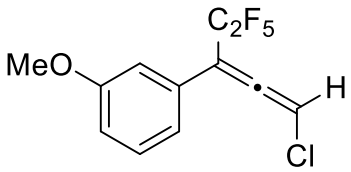
^{13}C NMR of **4** (101 MHz, $CDCl_3$)



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

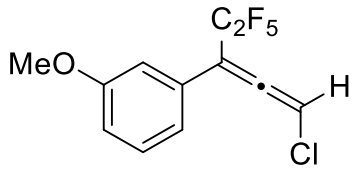


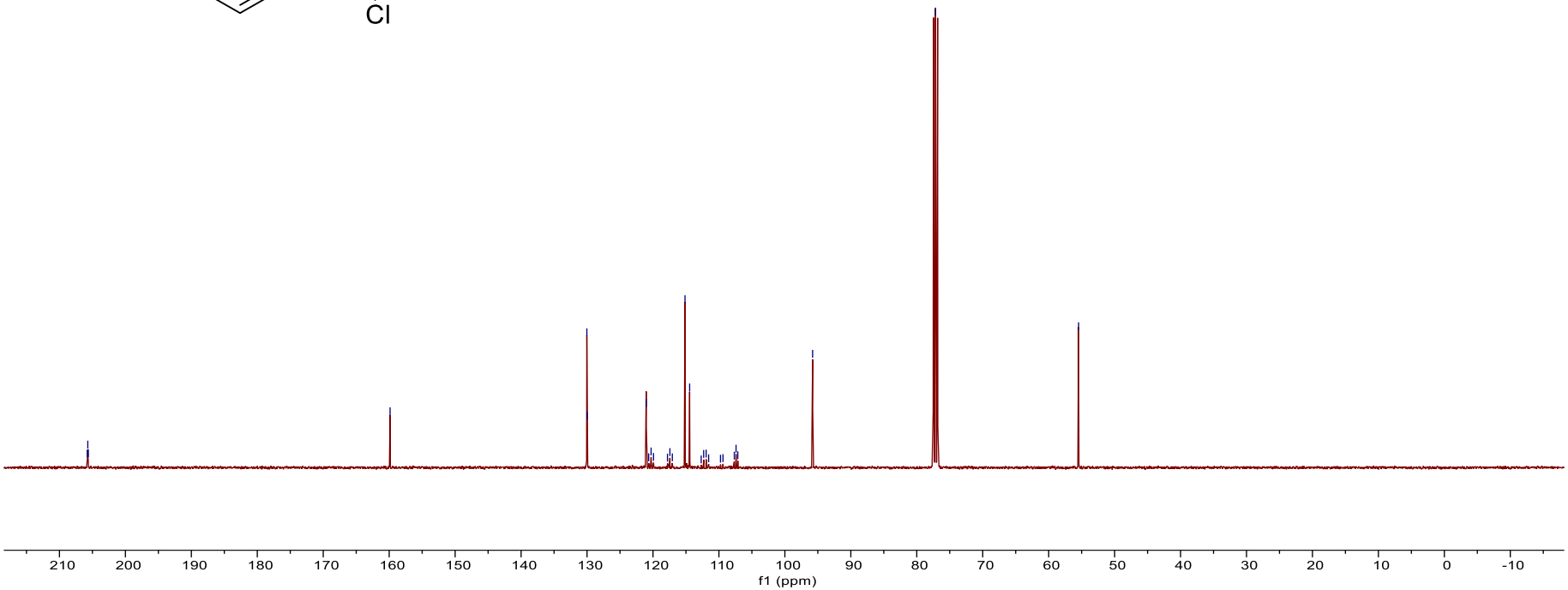
^{19}F NMR of **5** (376 MHz, $CDCl_3$)



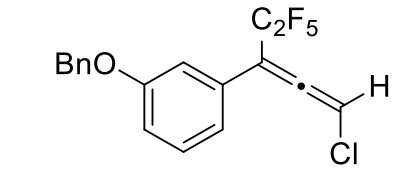
205.77
205.70
205.63
159.87
130.03
129.97
121.04
120.65
120.29
119.92
117.80
117.43
117.07
115.14
114.44
112.69
112.31
111.94
111.56
109.76
109.38
107.67
107.40
107.14
95.79
77.16 CDCl3
55.46

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

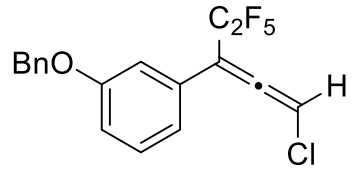




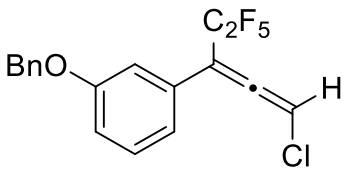
^{1}H NMR of **6** (400 MHz, $CDCl_3$)

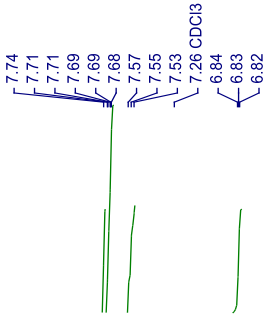


^{19}F NMR of **6** (376 MHz, $CDCl_3$)

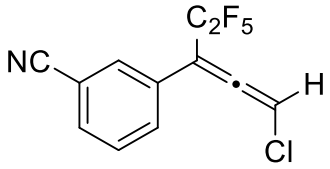


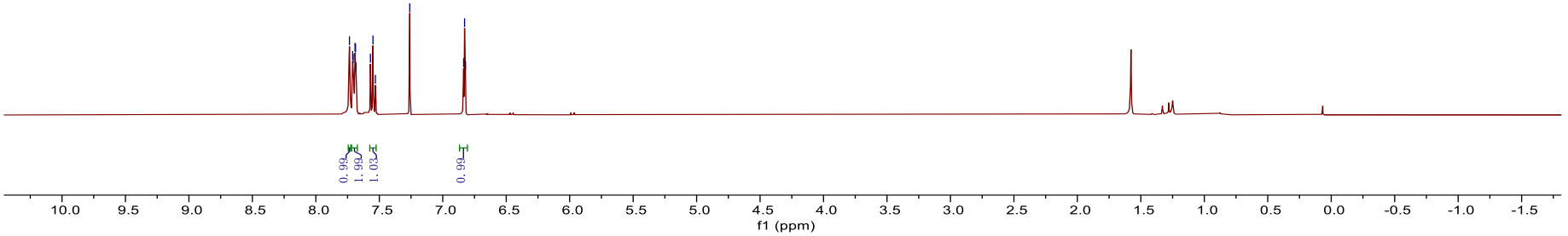
^{13}C NMR of **6** (101 MHz, $CDCl_3$)



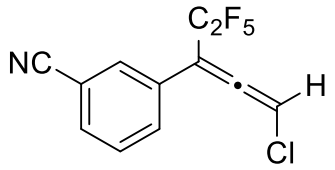


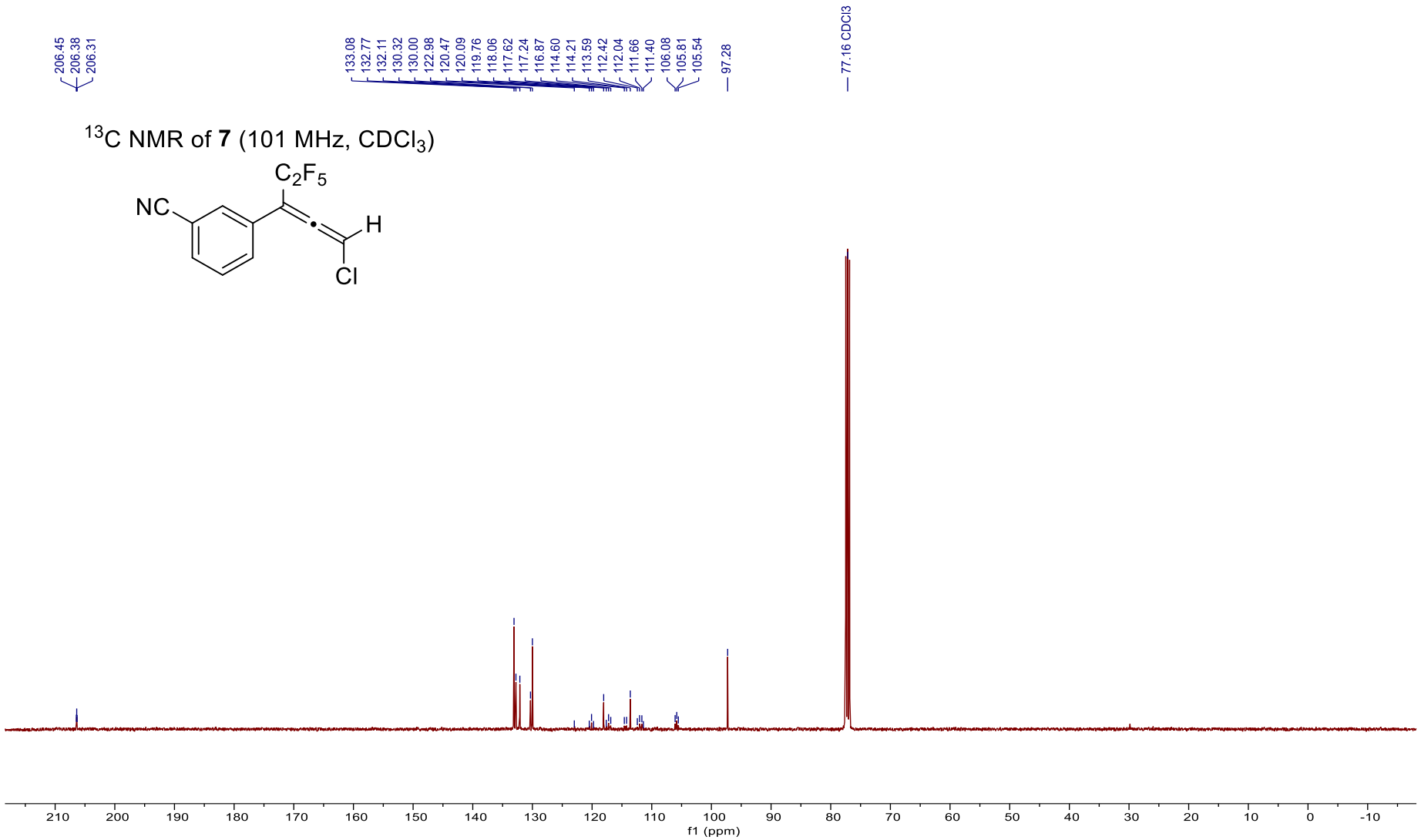
^{1}H NMR of **7** (400 MHz, $CDCl_3$)

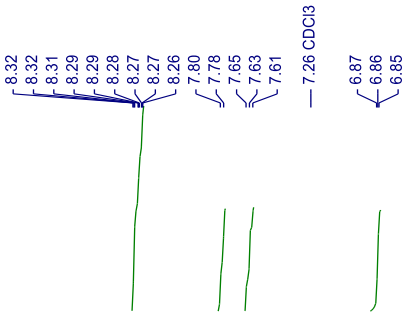




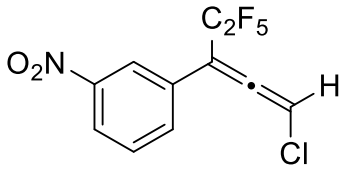
^{19}F NMR of **7** (376 MHz, $CDCl_3$)

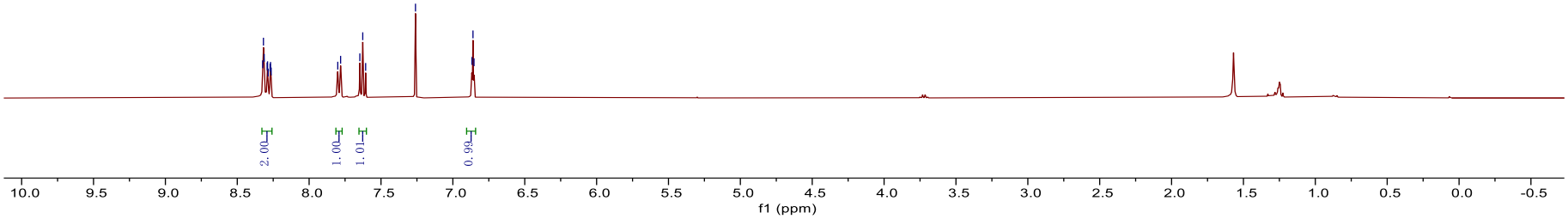



206.45
206.38
206.31
133.08
132.77
132.11
130.32
130.00
122.98
120.47
120.09
119.76
118.06
117.62
117.24
116.87
114.60
114.21
113.59
112.42
112.04
111.66
111.40
106.08
105.81
105.54
97.28
77.16 CDCl3
^{13}C NMR of **7** (101 MHz, $CDCl_3$)
C_2F_5
NC
H
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

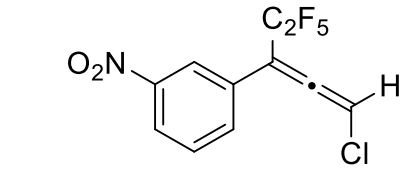


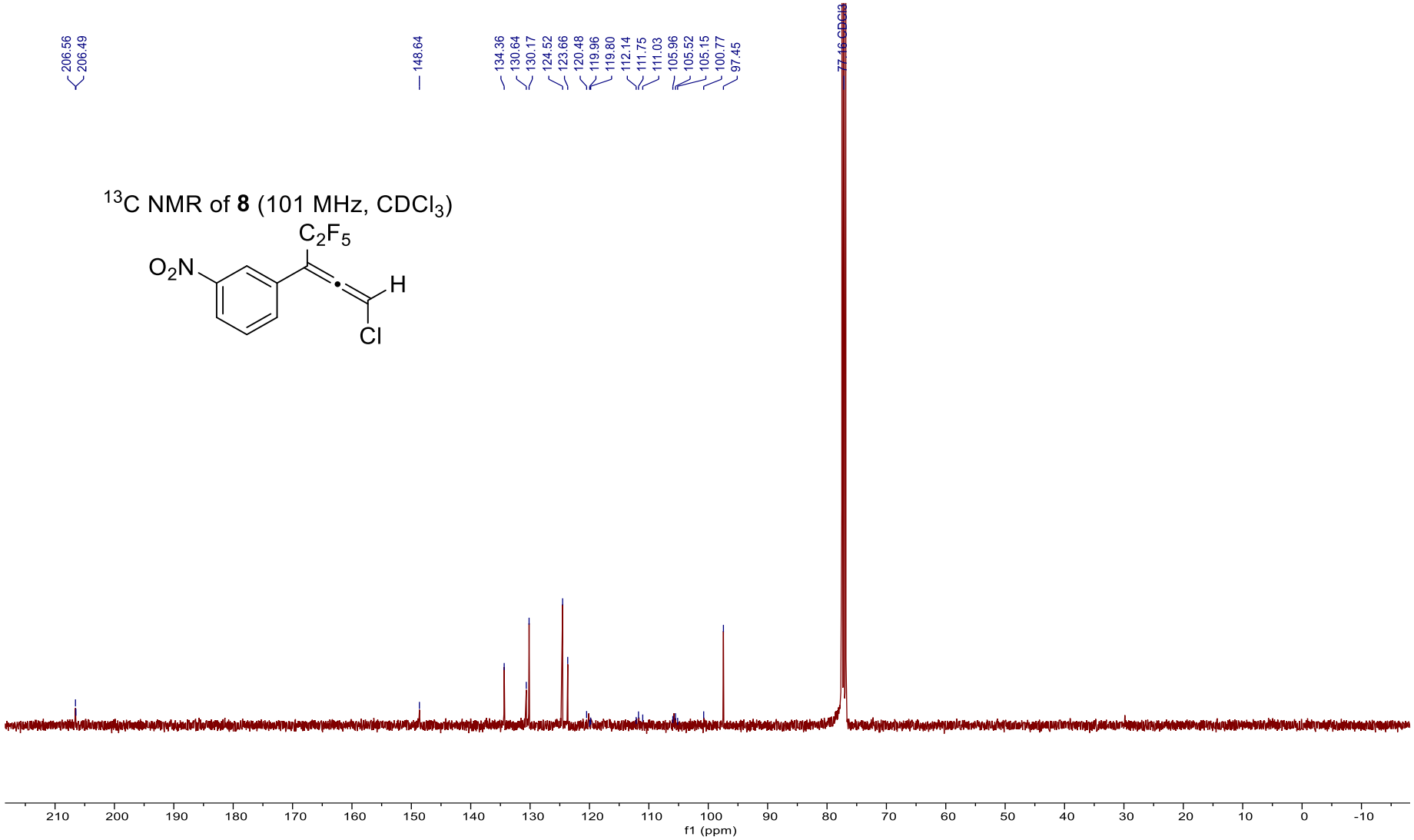
^{1}H NMR of **8** (400 MHz, $CDCl_3$)

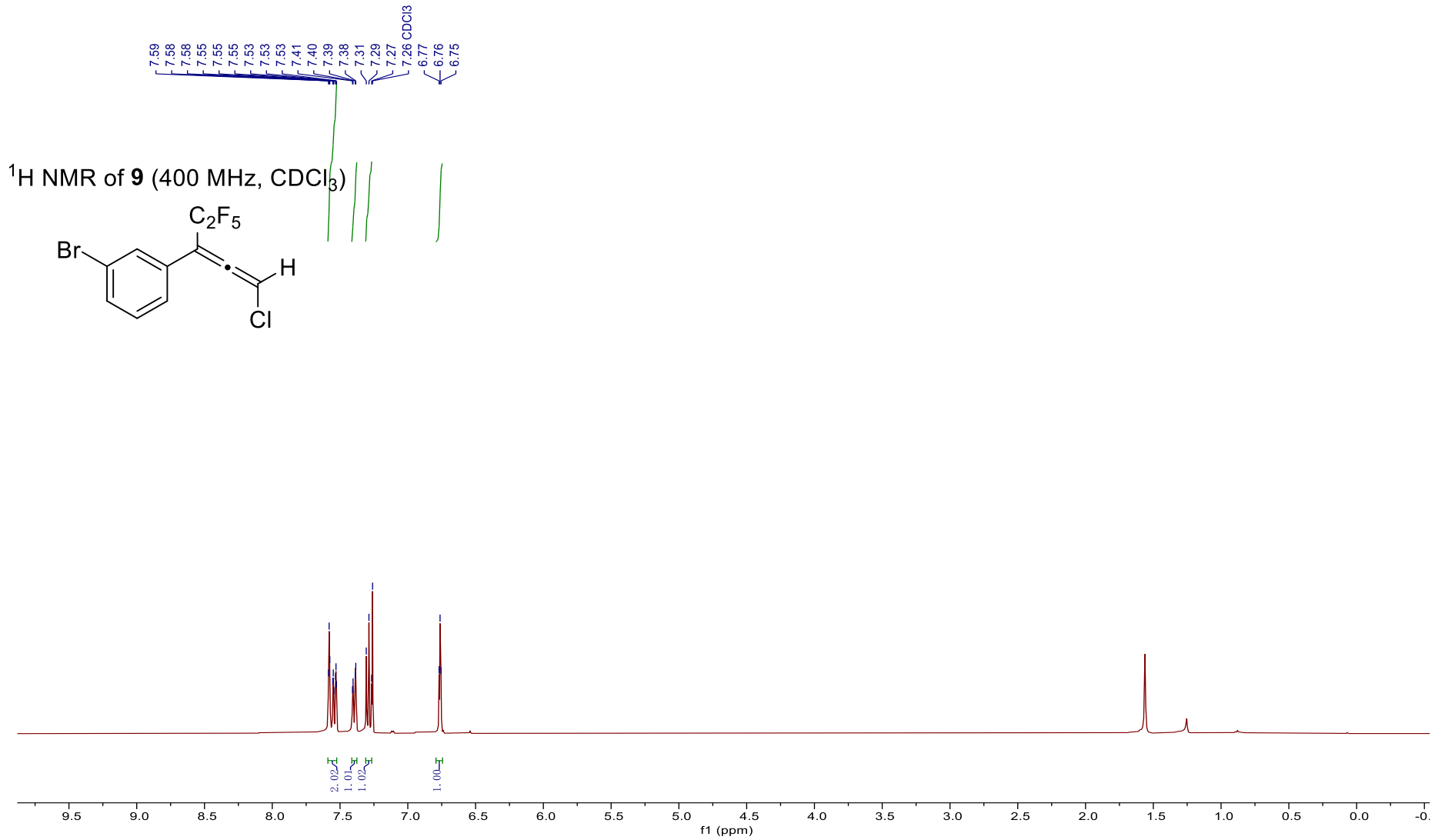




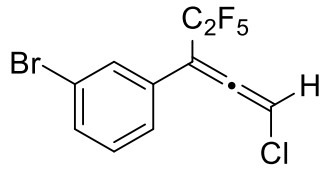
^{19}F NMR of **8** (376 MHz, $CDCl_3$)

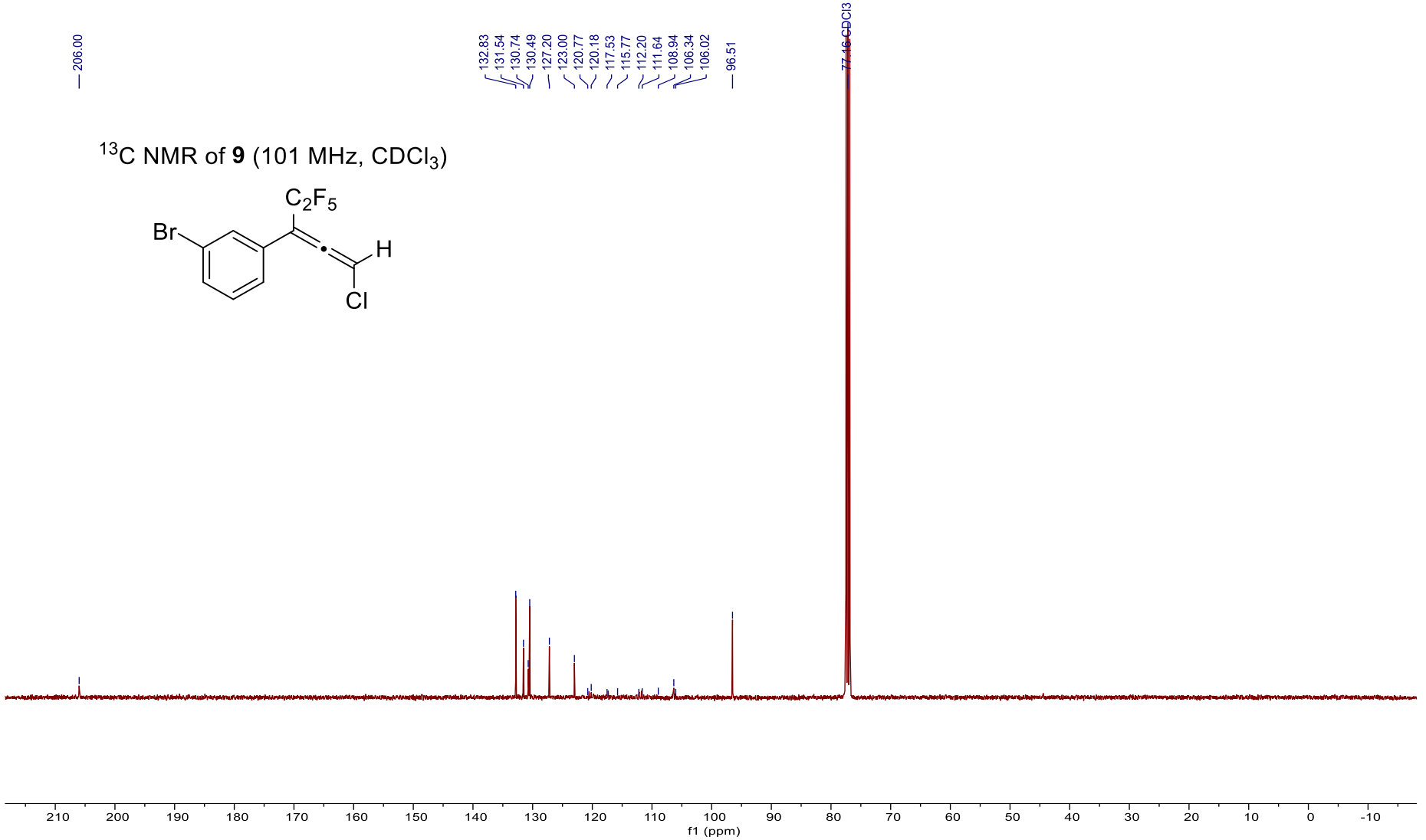



206.56
206.49
148.64
134.36
130.64
130.17
124.52
123.66
120.48
119.96
119.80
112.14
111.75
111.03
105.96
105.52
105.15
100.77
97.45
77.16 CDCl3
13C NMR of 8 (101 MHz, CDCl3)
C2F5
O2N
H
Cl
f1 (ppm)

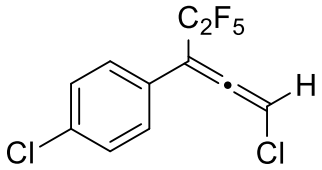

7.59
7.58
7.58
7.55
7.55
7.55
7.53
7.53
7.53
7.41
7.40
7.39
7.38
7.31
7.29
7.27
7.26 CDCl3
6.77
6.76
6.75
1H NMR of 9 (400 MHz, CDCl3)
C2F5
Br
H
Cl
2.02
1.01
1.02
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

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

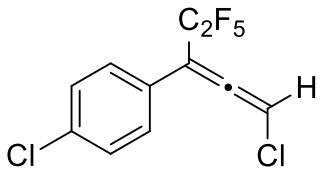


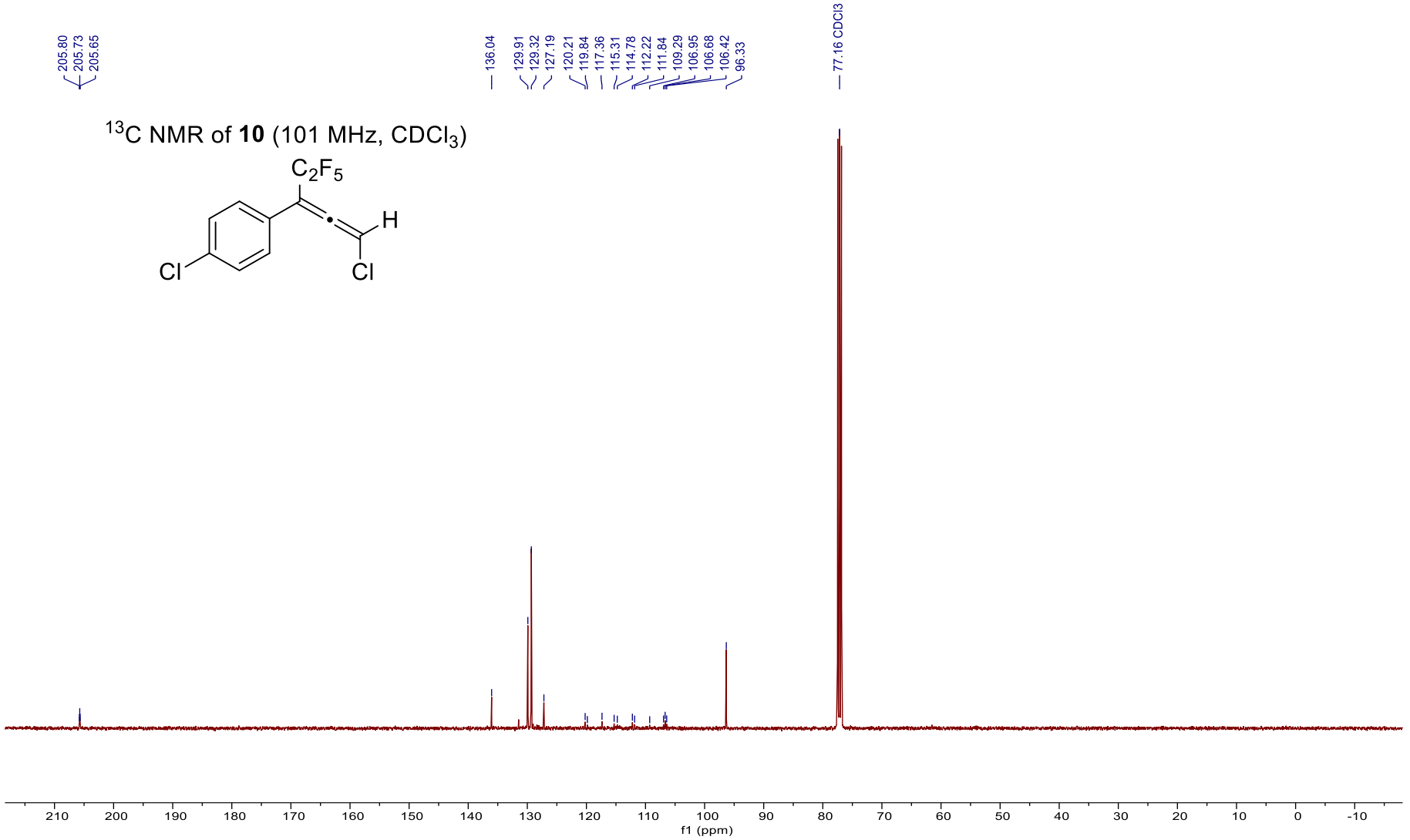

206.00
132.83
131.54
130.74
130.49
127.20
123.00
120.77
120.18
117.53
115.77
112.20
111.64
108.94
106.34
106.02
96.51
77.16 CDCl3
13C NMR of 9 (101 MHz, CDCl3)
C2F5
Br
H
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

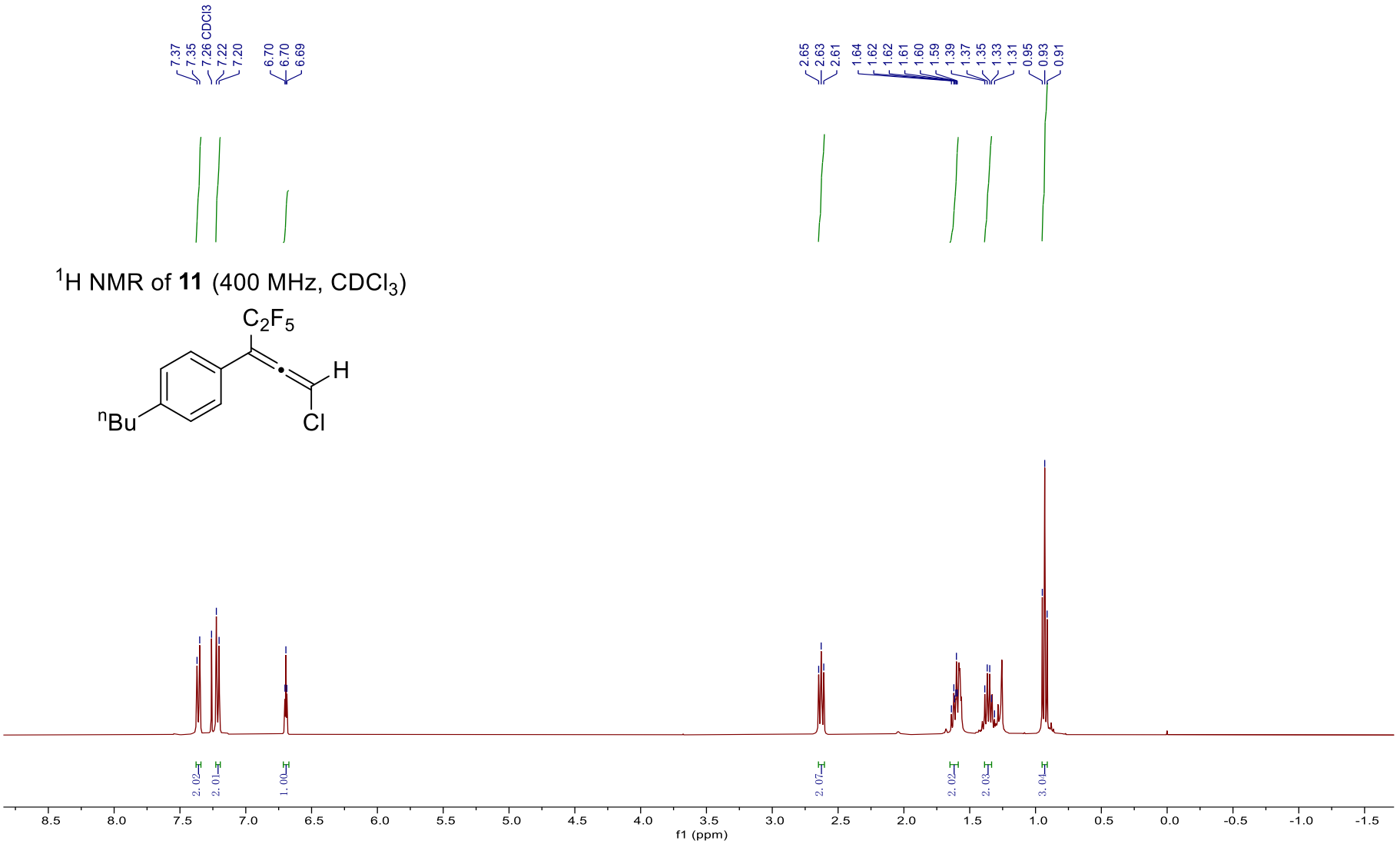
^{1}H NMR of **10** (400 MHz, $CDCl_3$)



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

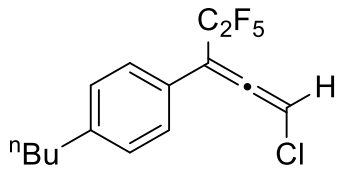


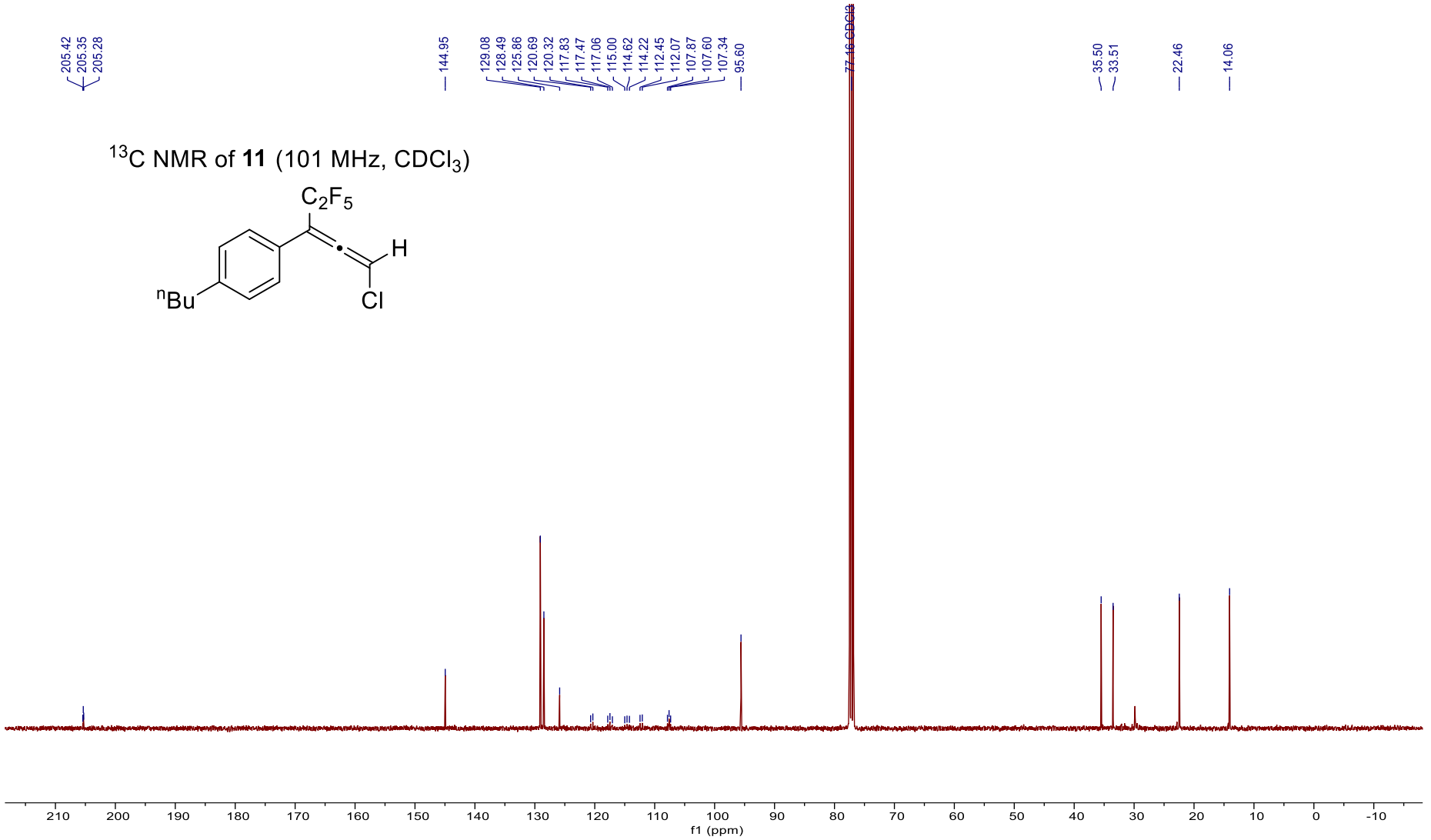

205.80
205.73
205.65
136.04
129.91
129.32
127.19
120.21
119.84
117.36
115.31
114.78
112.22
111.84
109.29
106.95
106.68
106.42
96.33
77.16 CDCl3
^{13}C NMR of **10** (101 MHz, $CDCl_3$)
C_2F_5
H
Cl
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

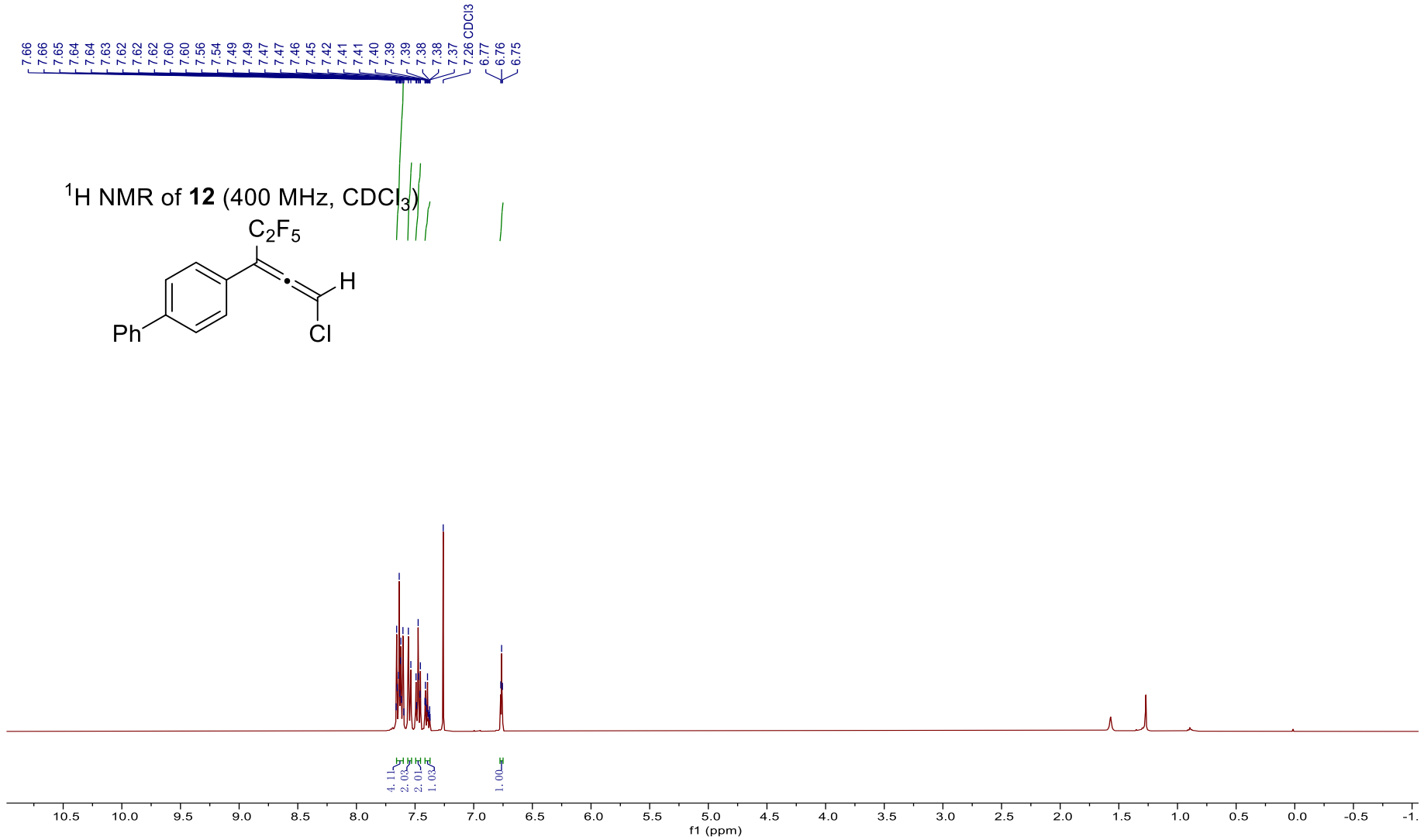


^{1}H NMR of **11** (400 MHz, $CDCl_3$)

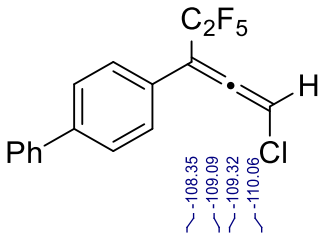
^{19}F NMR of **11** (376 MHz, $CDCl_3$)




205.42
205.35
205.28
144.95
129.08
128.49
125.86
120.69
120.32
117.83
117.47
117.06
115.00
114.62
114.22
112.45
112.07
107.87
107.60
107.34
95.60
77.16 CDCl3
35.50
33.51
22.46
14.06
13C NMR of 11 (101 MHz, CDCl3)
C2F5
H
nBu
Cl
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)


7.66
7.66
7.65
7.64
7.64
7.63
7.62
7.62
7.62
7.60
7.60
7.56
7.54
7.49
7.49
7.47
7.47
7.46
7.45
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.26 CDCl3
6.77
6.76
6.75
1H NMR of 12 (400 MHz, CDCl3)
C2F5
H
Ph
Cl
4.11
2.03
2.01
1.03
1.00
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.
f1 (ppm)

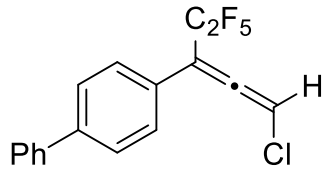
^{19}F NMR of **12** (376 MHz, $CDCl_3$)

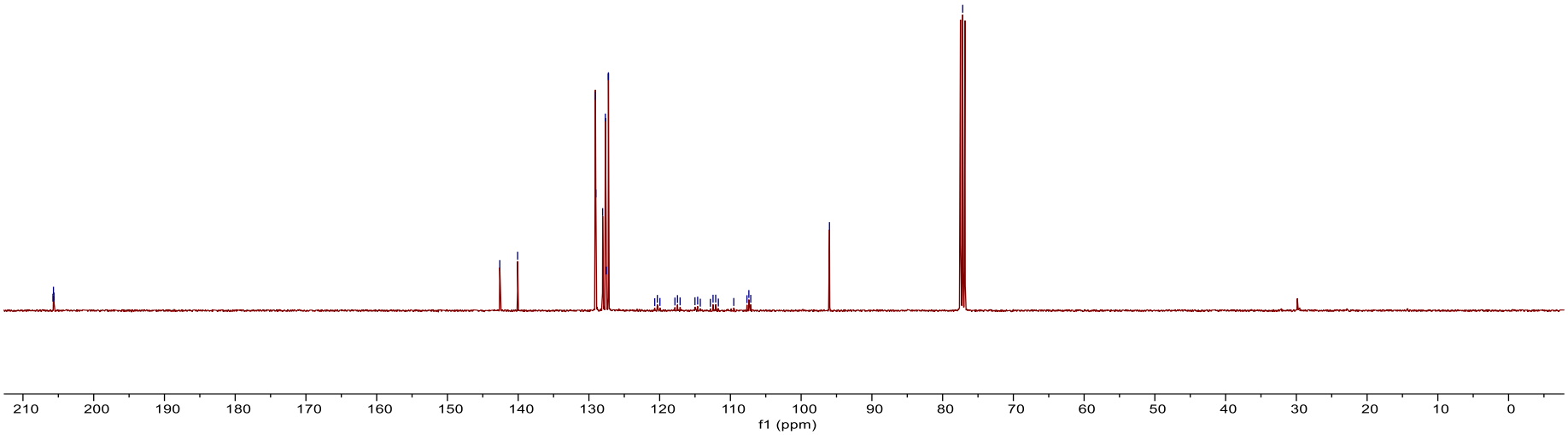


205.76
205.69
205.62

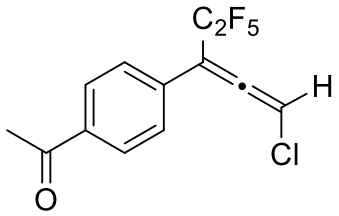
142.60
140.08
129.08
129.02
128.06
127.68
127.51
127.24
120.70
120.33
119.96
117.84
117.48
117.11
115.01
114.63
114.26
112.83
112.45
112.08
111.70
109.52
107.66
107.39
107.12
96.00
77.16 CDCl3

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

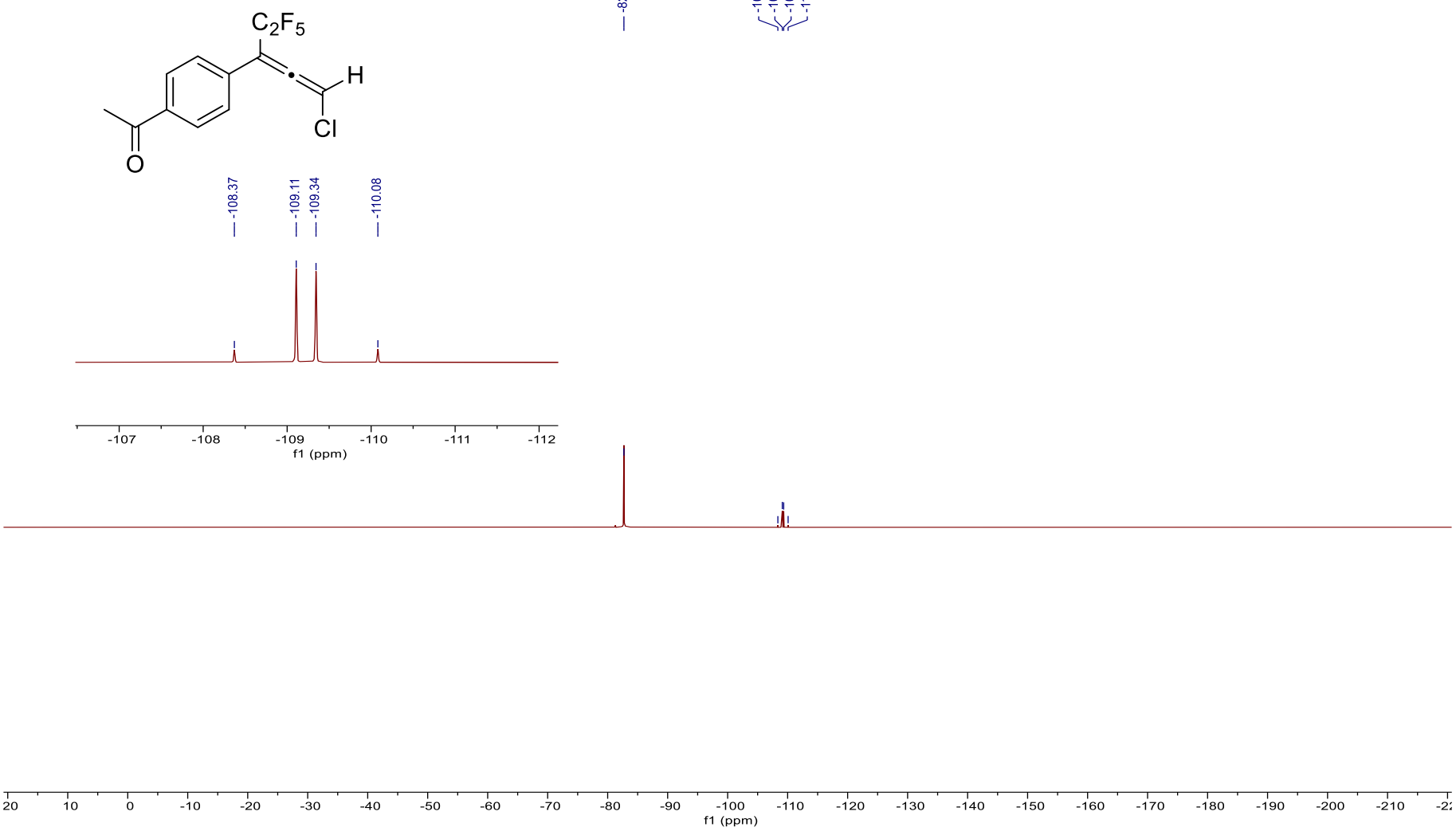




^{1}H NMR of **13** (400 MHz, $CDCl_3$)

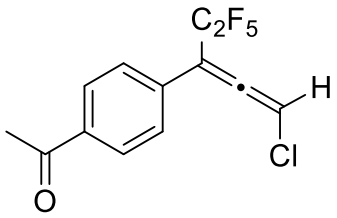


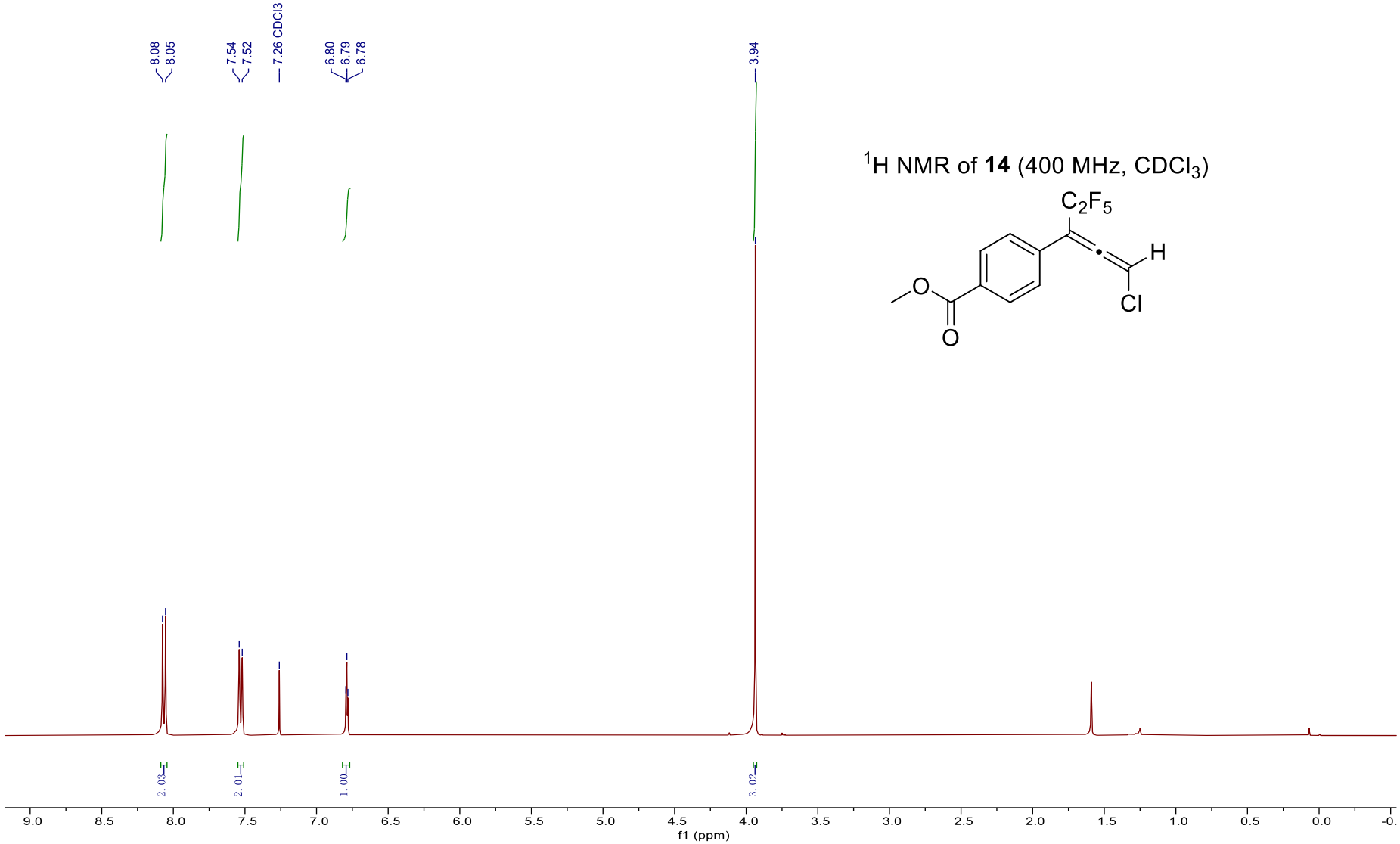
^{19}F NMR of **13** (376 MHz, $CDCl_3$)



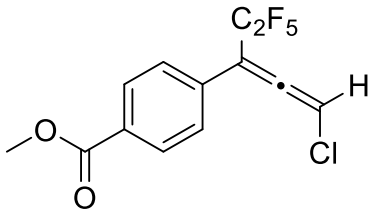
206.49
206.42
206.35
197.37
137.69
133.30
128.88
128.84
123.41
123.04
123.00
120.56
120.19
119.82
117.71
117.34
116.97
114.38
112.21
111.83
107.10
106.83
106.56
96.71
77.16 CDCl3
26.84

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



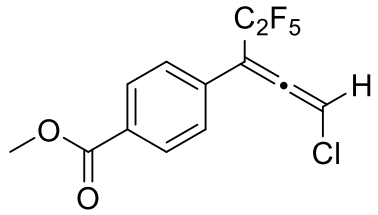

8.08
8.05
7.54
7.52
7.26 CDCl3
6.80
6.79
6.78
3.94
2.03
2.01
1.00
3.02
f1 (ppm)
^{1}H NMR of **14** (400 MHz, $CDCl_3$)
C_2F_5
H
Cl
O
O

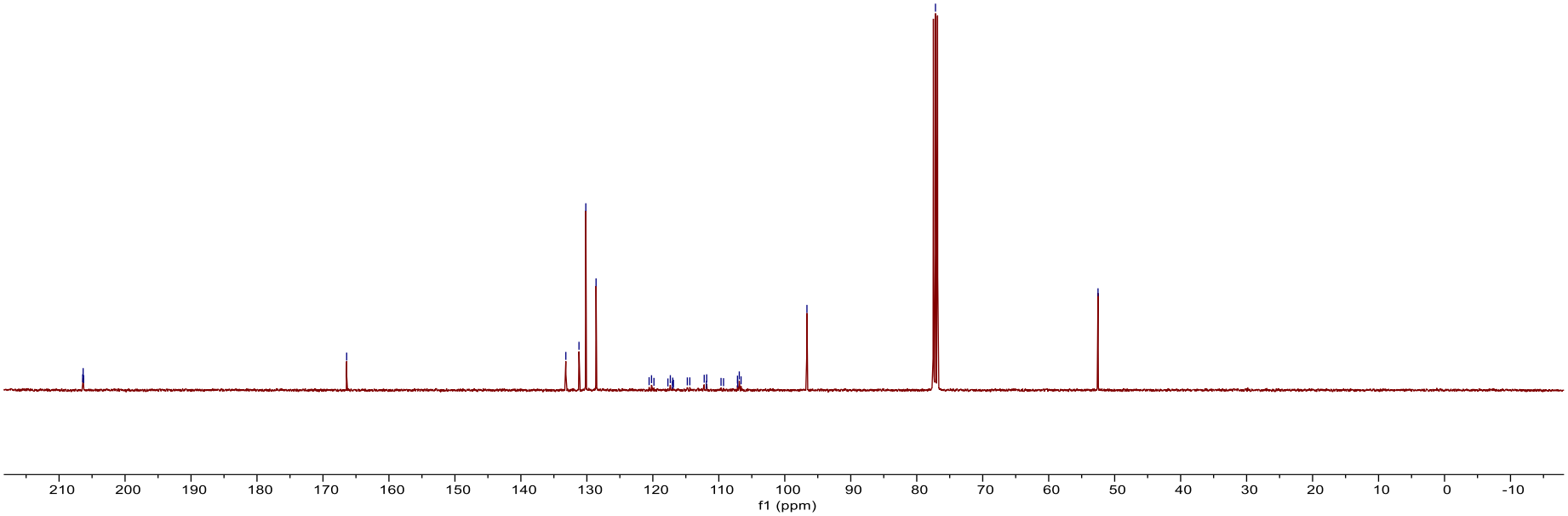
^{19}F NMR of **14** (376 MHz, $CDCl_3$)



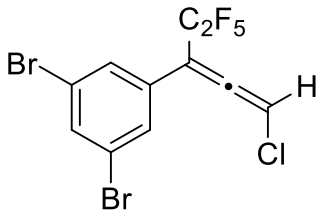
206.42
206.35
206.28
166.41
133.19
131.19
130.16
128.61
120.57
120.20
119.83
117.72
117.35
117.02
116.98
116.88
114.77
114.39
112.22
111.89
111.84
109.66
109.28
107.17
107.14
106.90
106.63
96.64
77.16 CDCl3
52.52

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

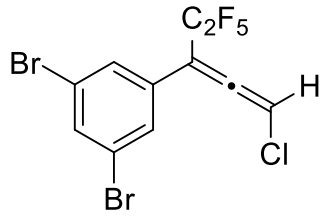


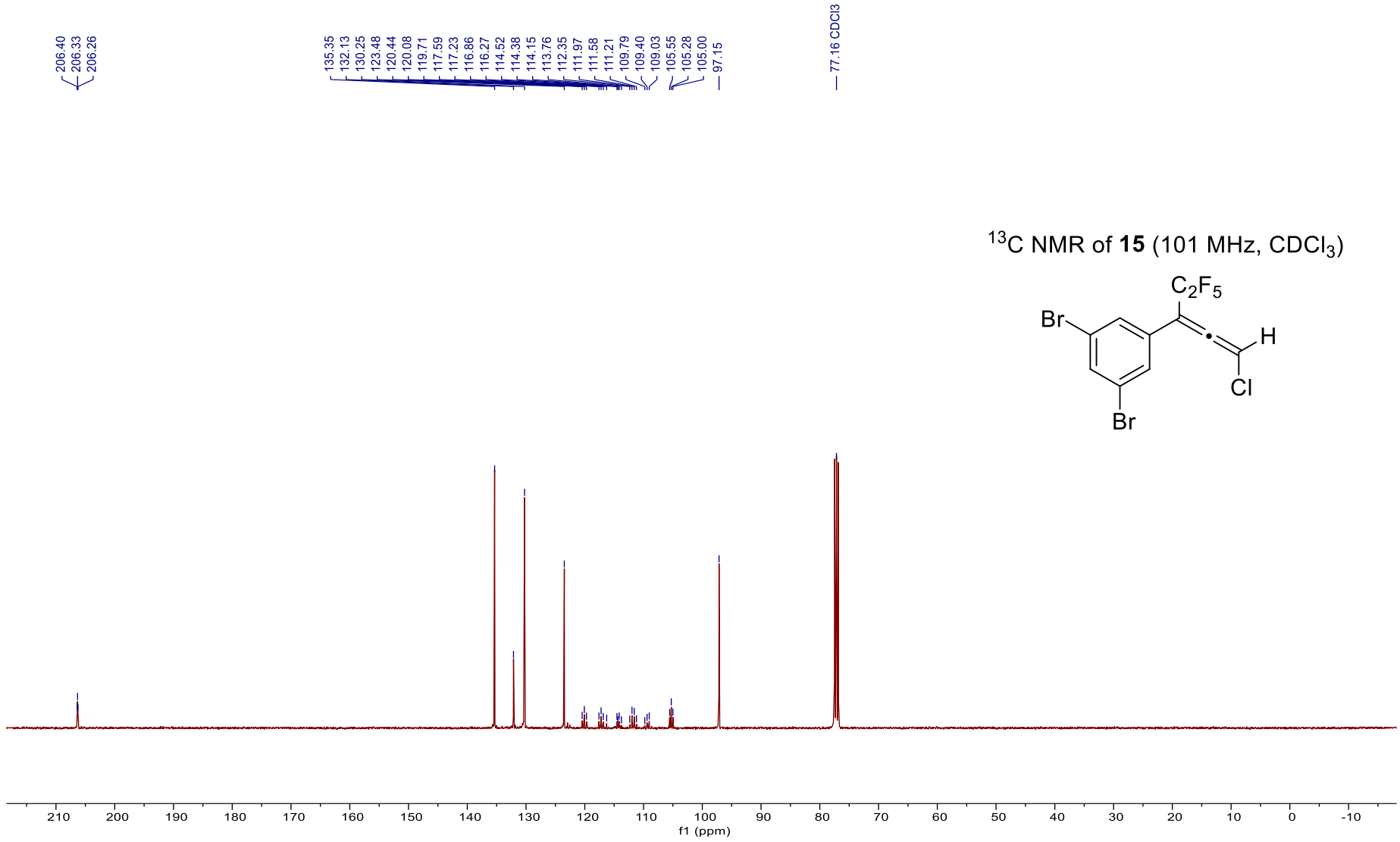


^{1}H NMR of **15** (400 MHz, $CDCl_3$)

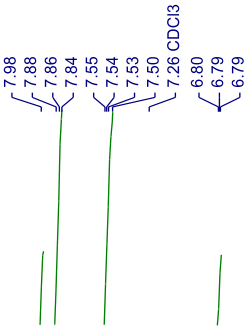


^{19}F NMR of **15** (376 MHz, $CDCl_3$)

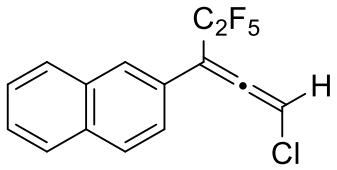


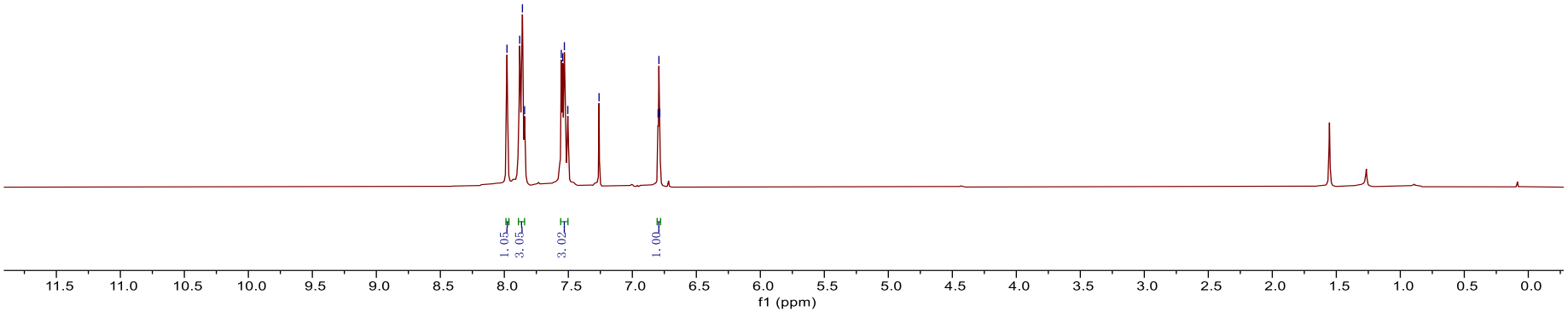


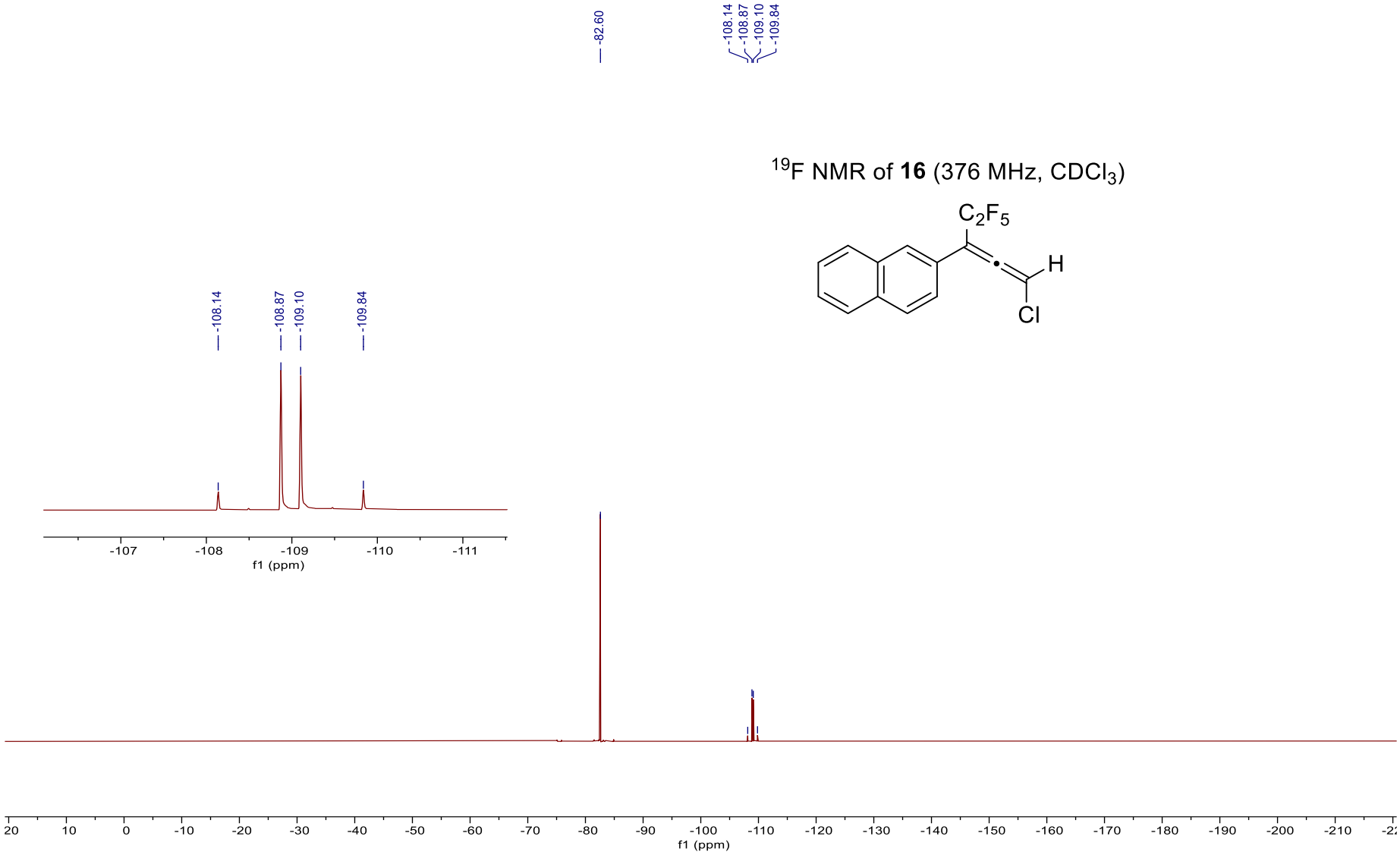
^{13}C NMR of **15** ($CDCl_3$)

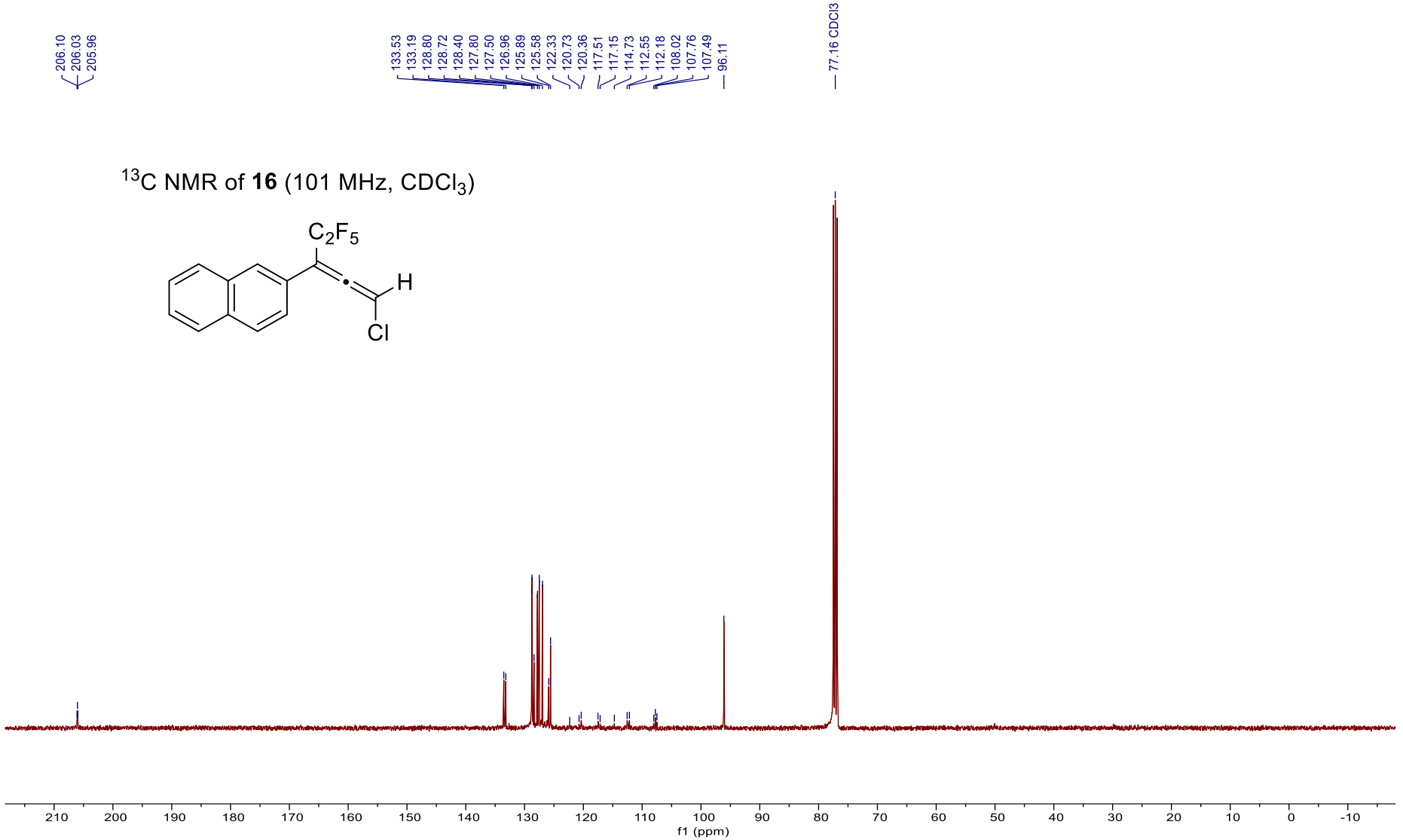


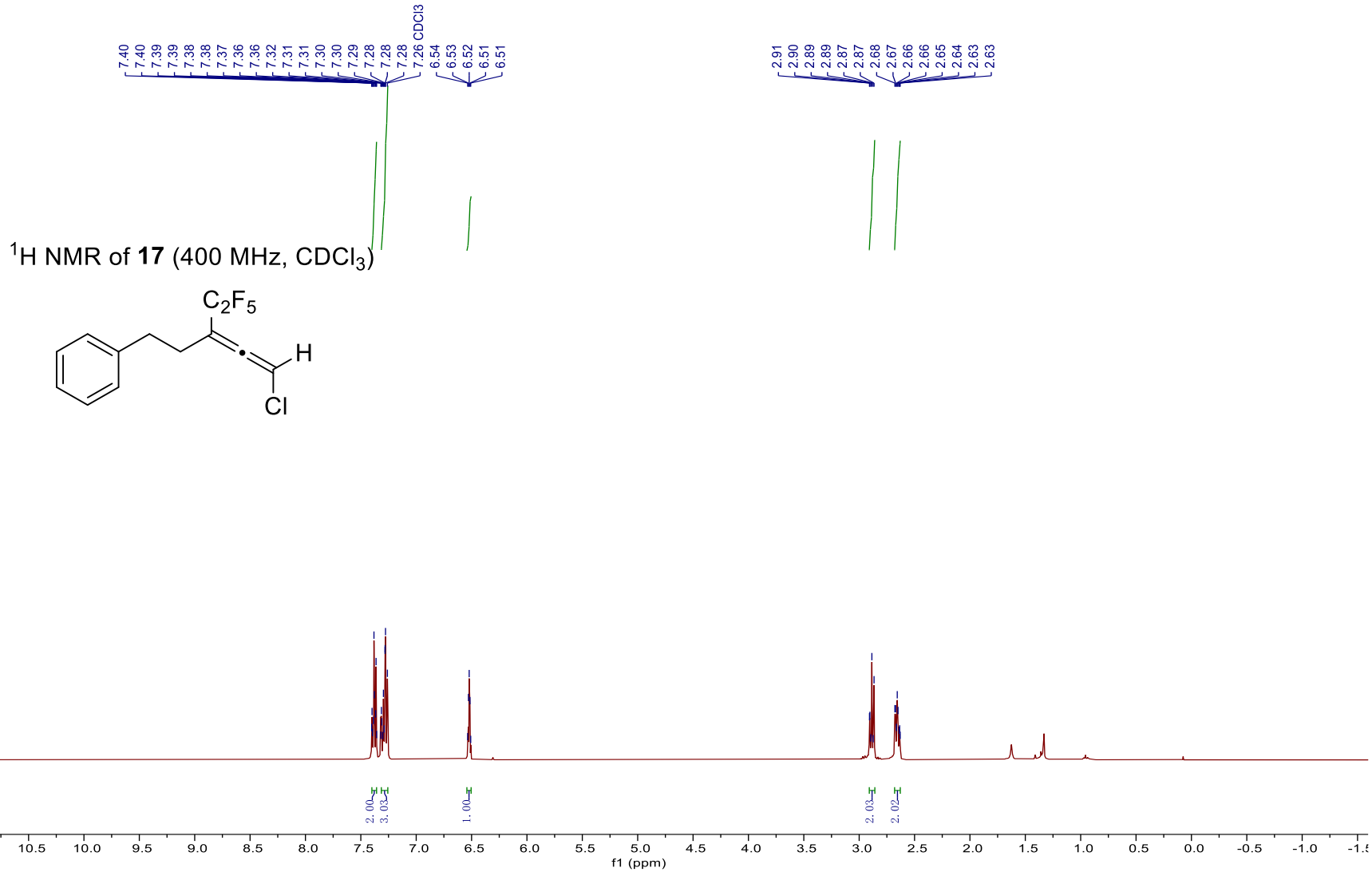
^{1}H NMR of **16** (400 MHz, $CDCl_3$)

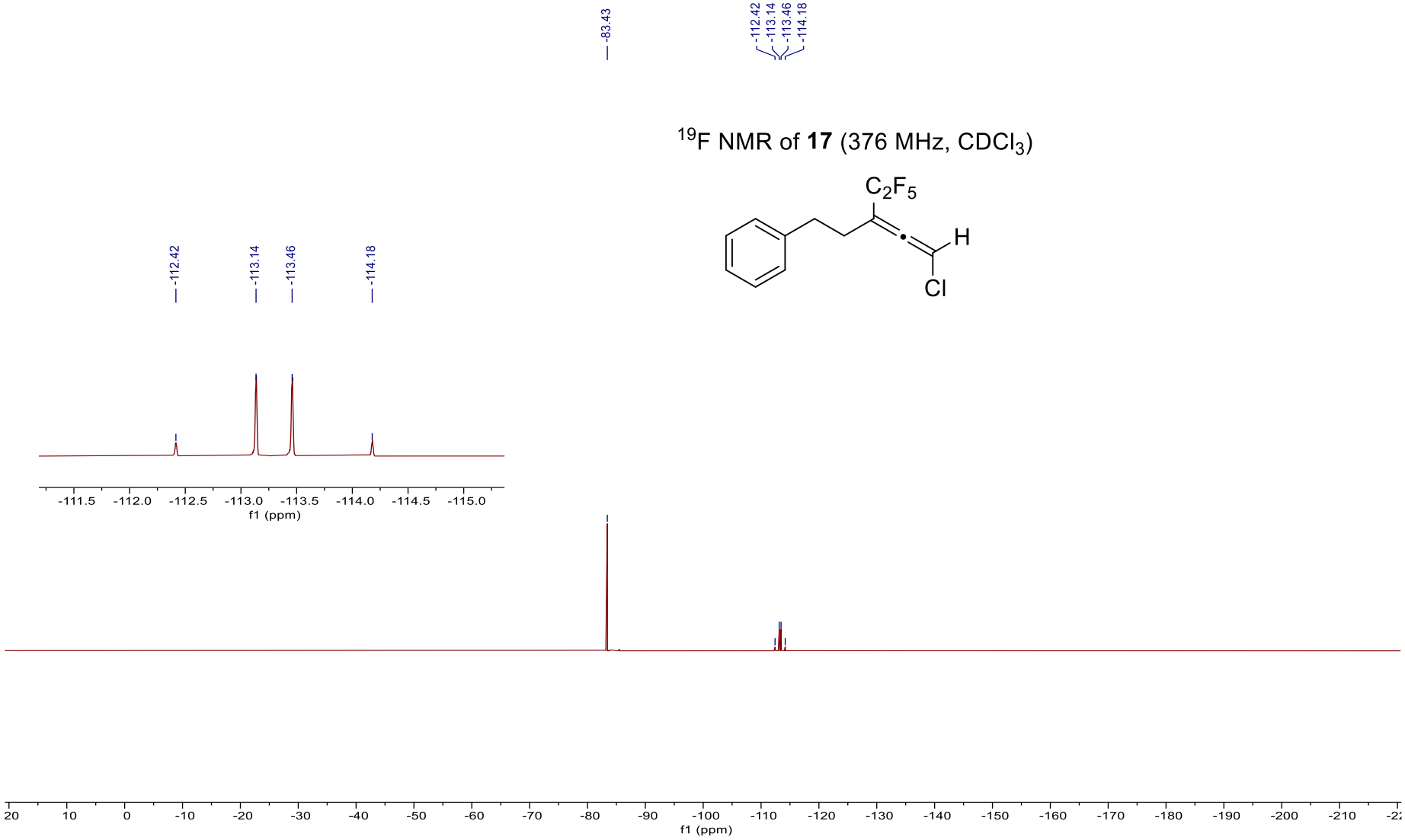


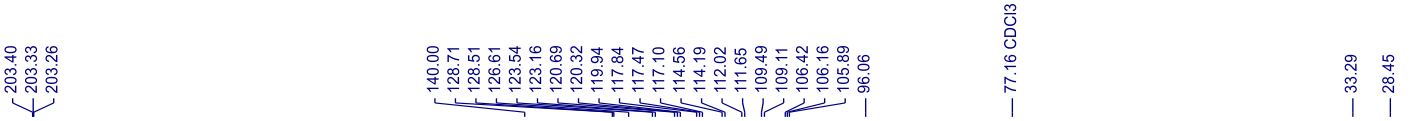



-82.60
-108.14
-108.87
-109.10
-109.84
^{19}F NMR of **16** (376 MHz, $CDCl_3$)
C_2F_5
H
Cl
-108.14
-108.87
-109.10
-109.84
-107
-108
-109
-110
-111
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

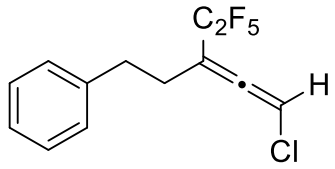

206.10
206.03
205.96
133.53
133.19
128.80
128.72
128.40
127.80
127.50
126.96
125.89
125.58
122.33
120.73
120.36
117.51
117.15
114.73
112.55
112.18
108.02
107.76
107.49
96.11
77.16 CDCl3
^{13}C NMR of **16** (101 MHz, $CDCl_3$)
C_2F_5
H
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

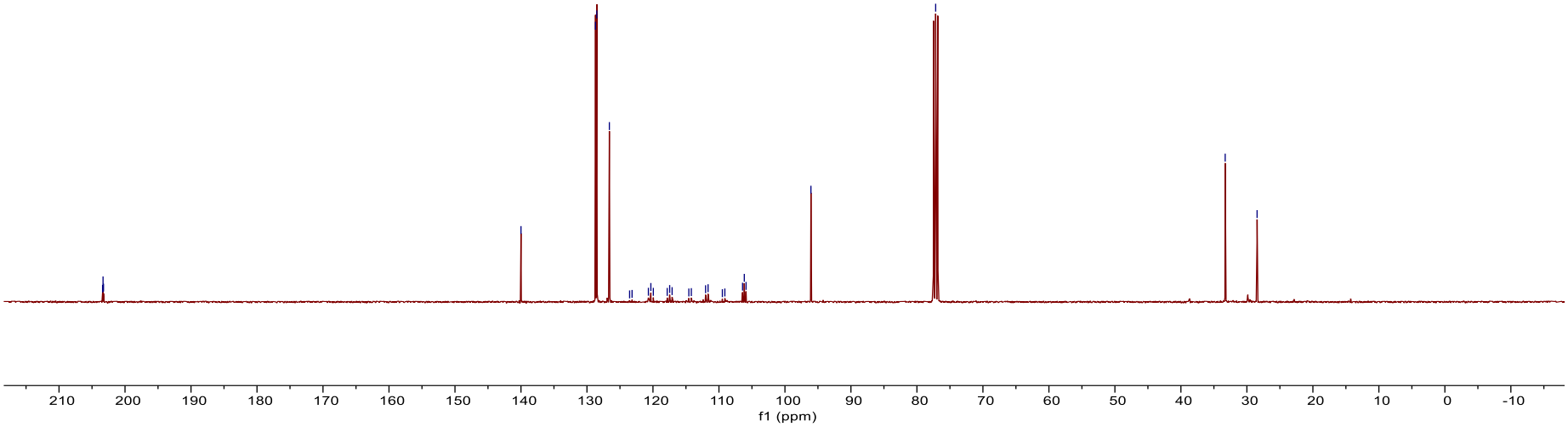

7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.28
7.26 CDCl3
6.54
6.53
6.52
6.51
6.51
2.91
2.90
2.89
2.89
2.87
2.87
2.68
2.67
2.66
2.66
2.65
2.64
2.63
2.63
^{1}H NMR of **17** (400 MHz, $CDCl_3$)
C_2F_5
H
Cl
2.00
3.03
1.00
2.03
2.02
f1 (ppm)


-83.43
-112.42
-113.14
-113.46
-114.18
19F NMR of 17 (376 MHz, CDCl3)
C2F5
H
Cl
-112.42
-113.14
-113.46
-114.18
-111.5 -112.0 -112.5 -113.0 -113.5 -114.0 -114.5 -115.0
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)

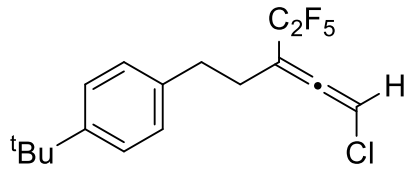


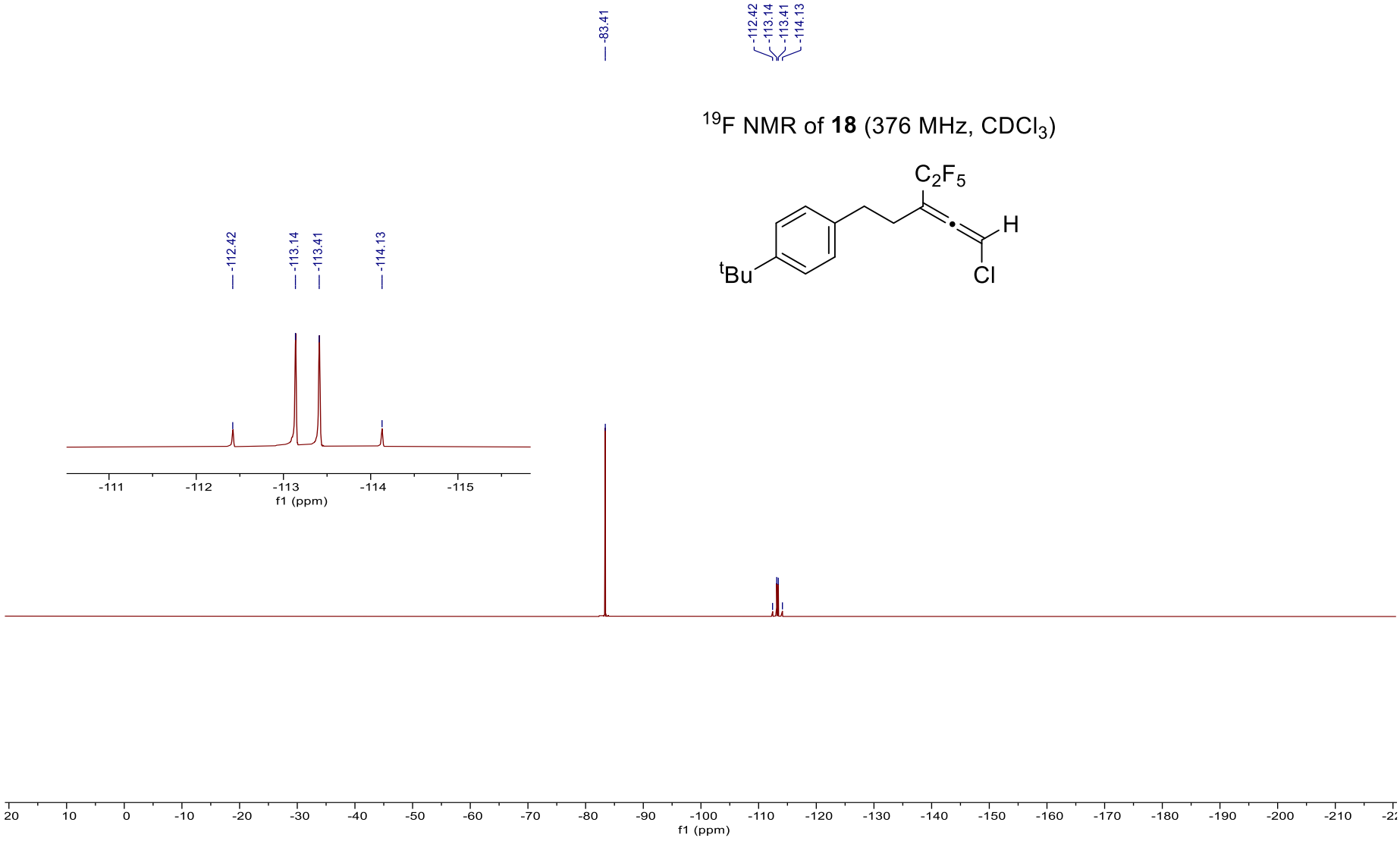
^{13}C NMR of **17** (101 MHz, $CDCl_3$)

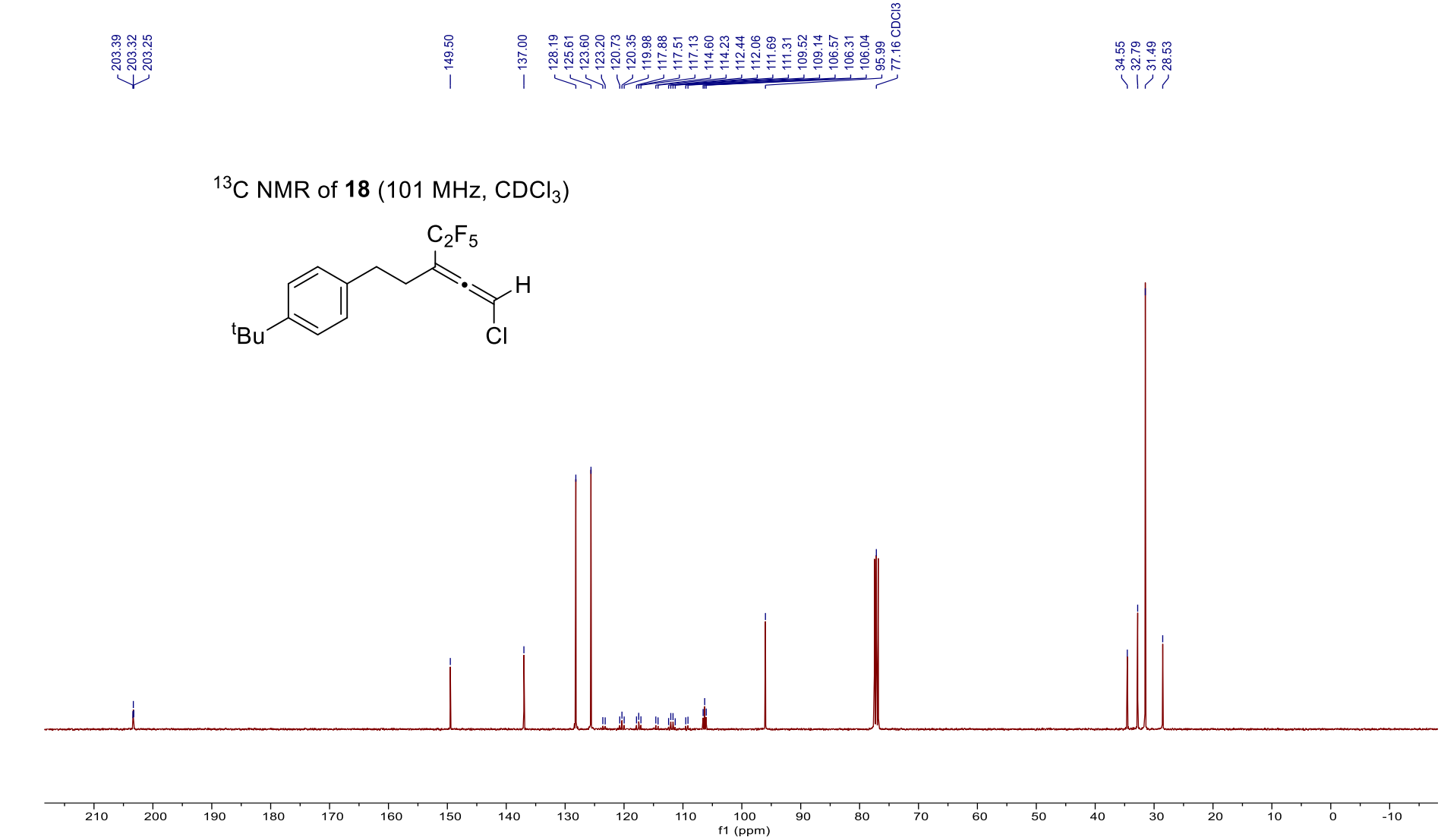




^{1}H NMR of **18** (400 MHz, $CDCl_3$)

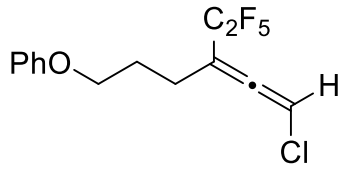


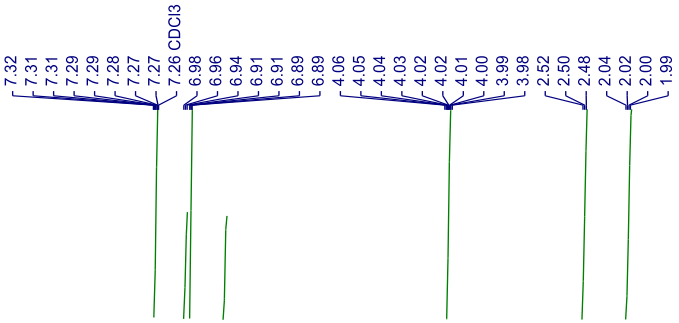

-83.41
-112.42
-113.14
-113.41
-114.13
^{19}F NMR of **18** (376 MHz, $CDCl_3$)
C_2F_5
H
Cl
^{t}Bu
-112.42
-113.14
-113.41
-114.13
-111
-112
-113
-114
-115
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

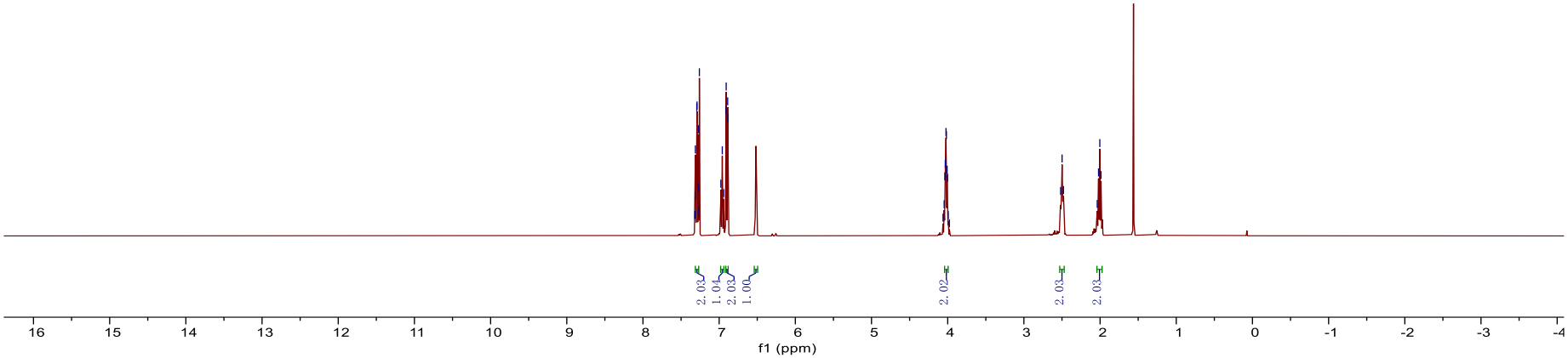


^{13}C NMR of **18** (101 MHz, $CDCl_3$)

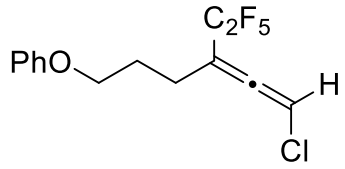
^{1}H NMR of **19** (400 MHz, $CDCl_3$)

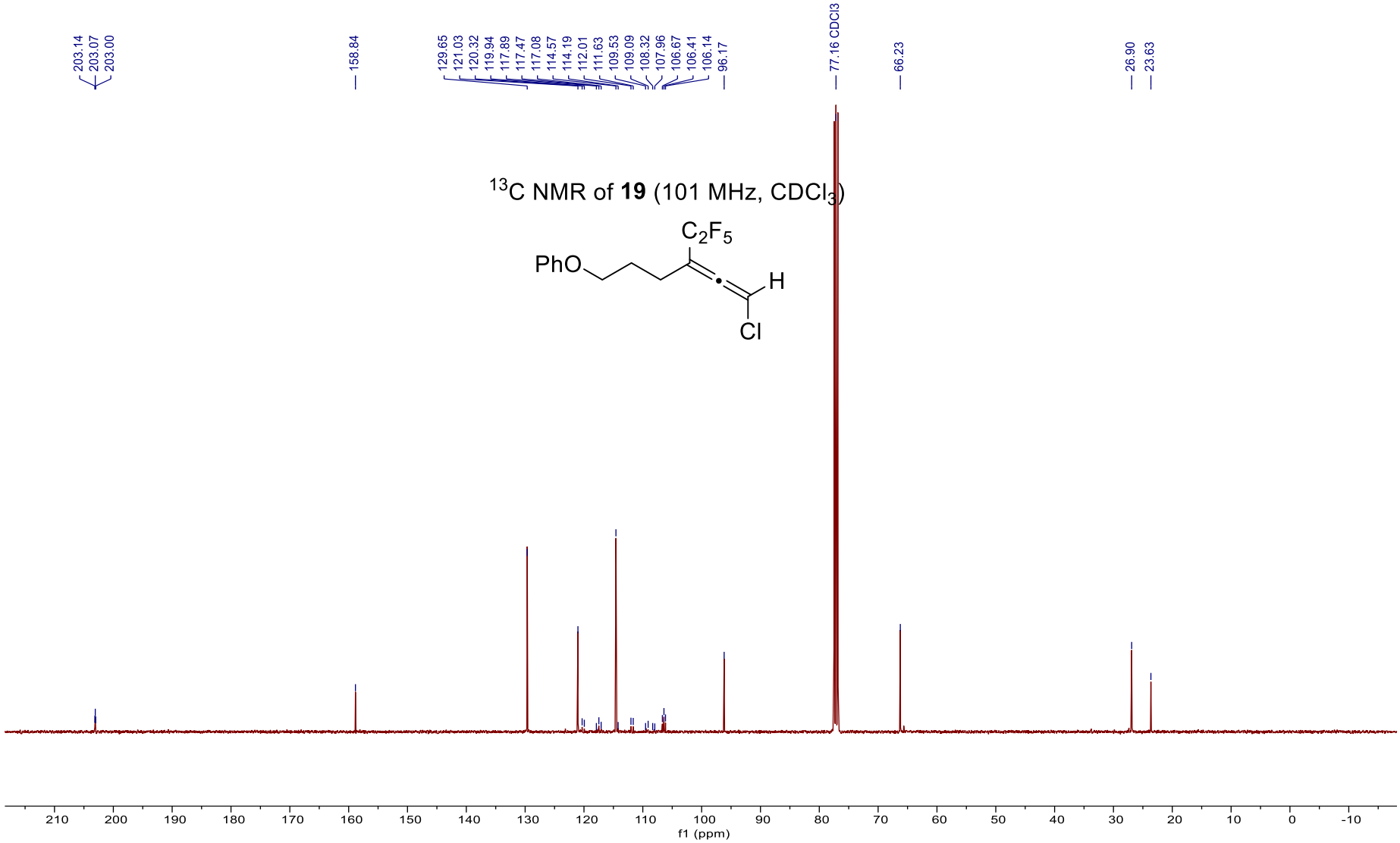


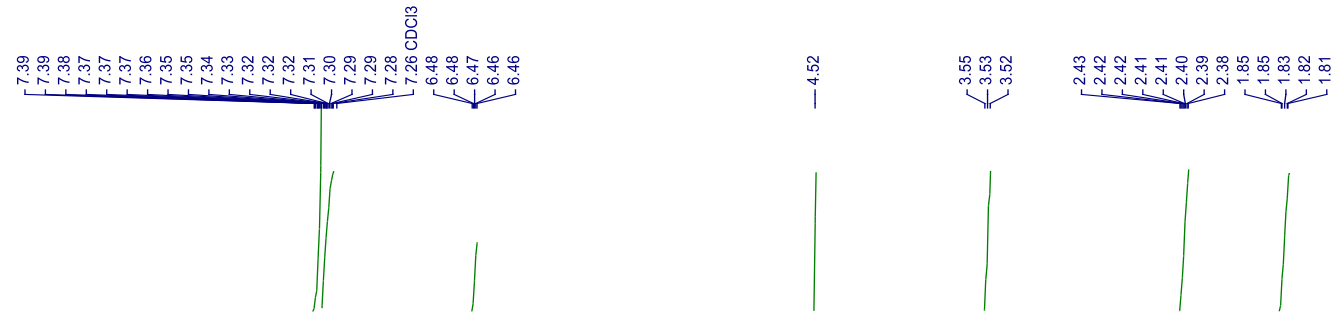




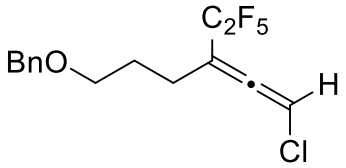
^{19}F NMR of **19** (376 MHz, $CDCl_3$)

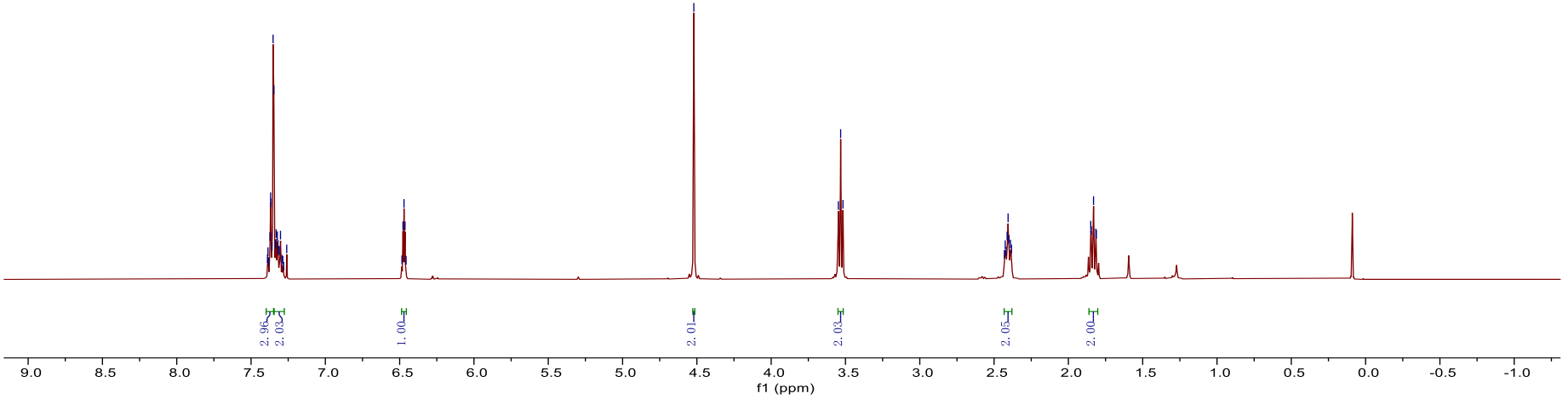



203.14
203.07
203.00
158.84
129.65
121.03
120.32
119.94
117.89
117.47
117.08
114.57
114.19
112.01
111.63
109.53
109.09
108.32
107.96
106.67
106.41
106.14
96.17
77.16 CDCl3
66.23
26.90
23.63
^{13}C NMR of **19** (101 MHz, $CDCl_3$)
C_2F_5
PhO
H
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

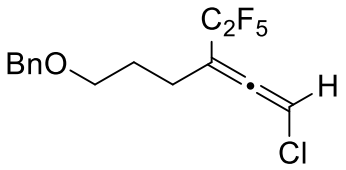


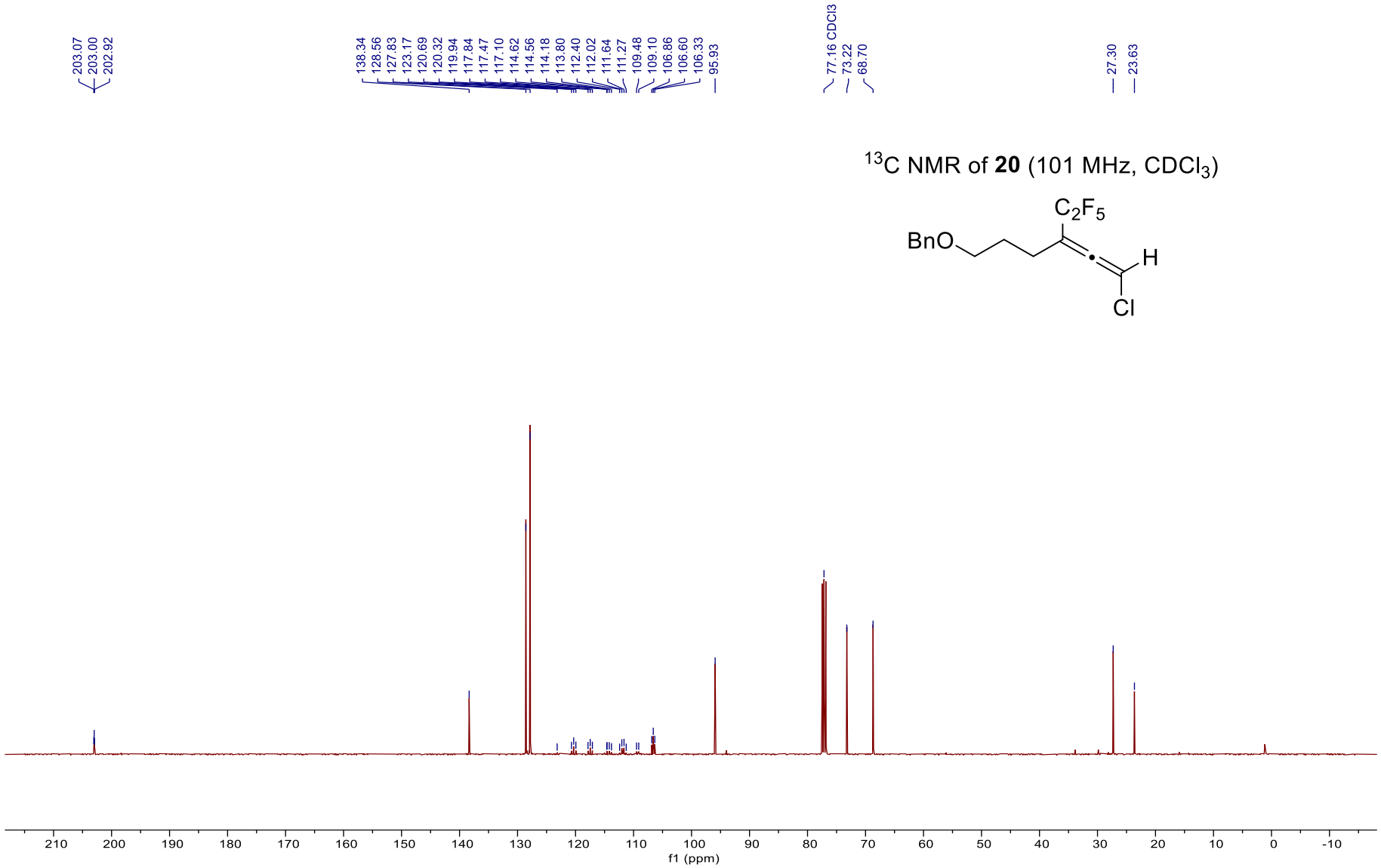
^{1}H NMR of **20** (400 MHz, $CDCl_3$)

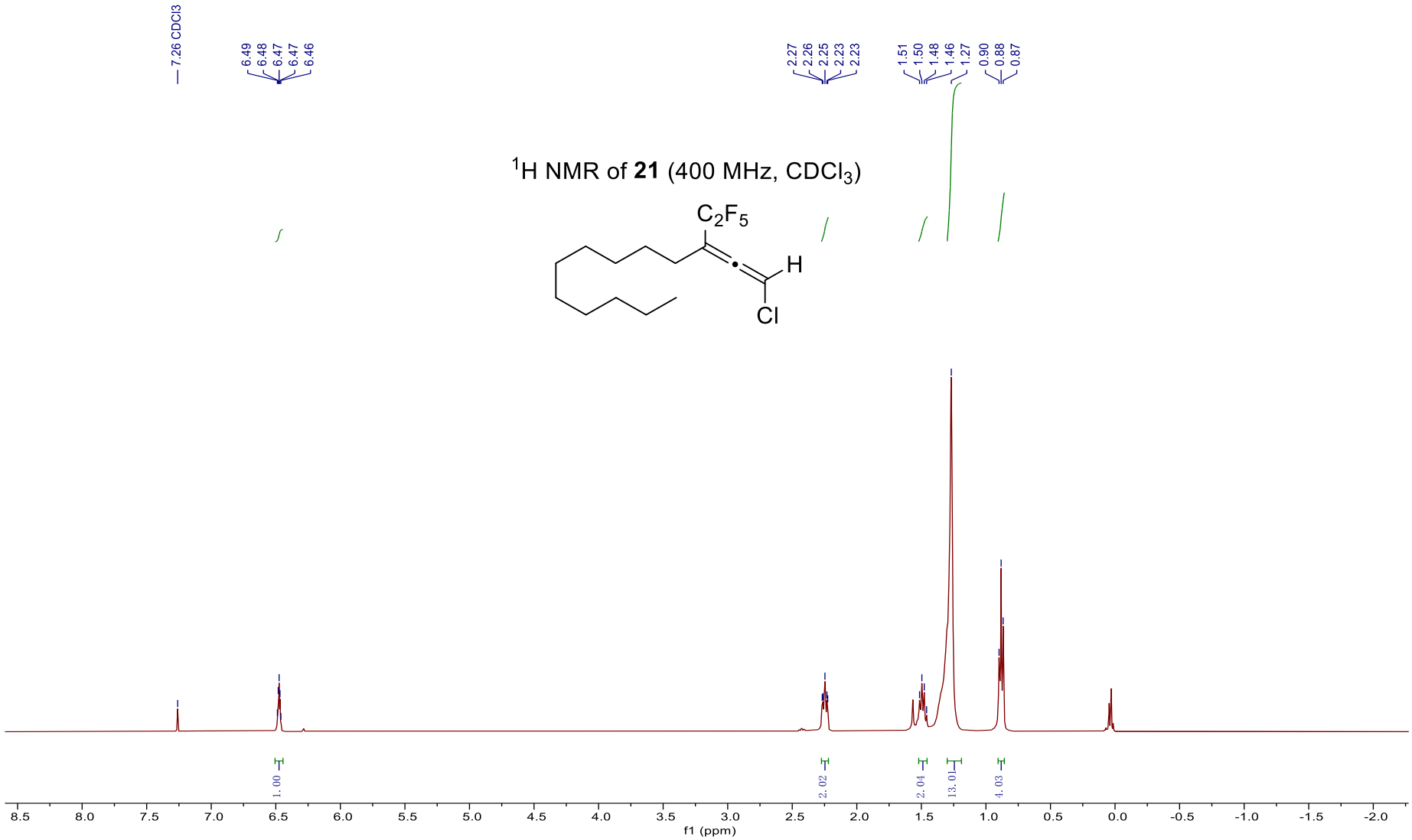


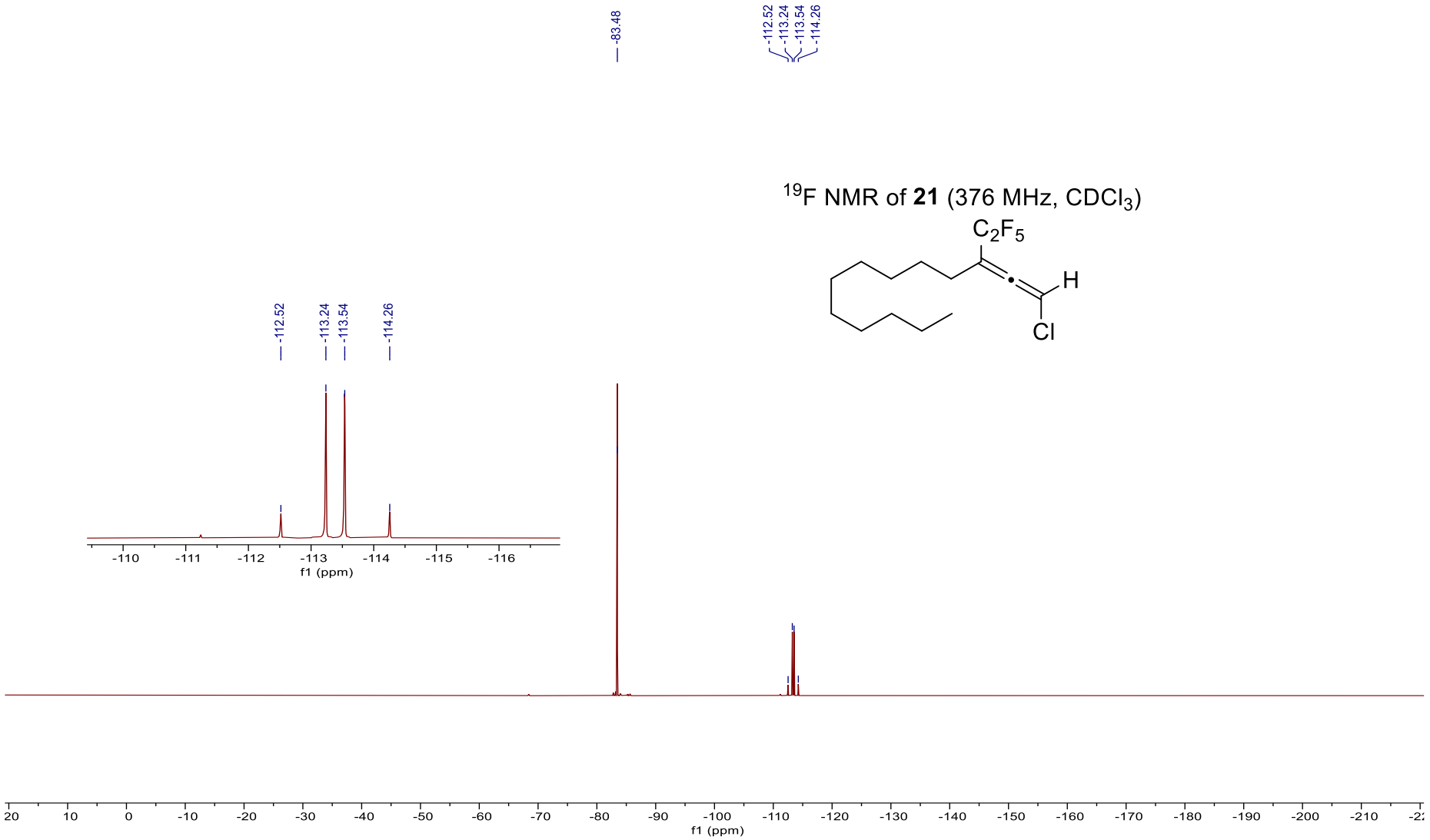


^{19}F NMR of **20** (376 MHz, $CDCl_3$)

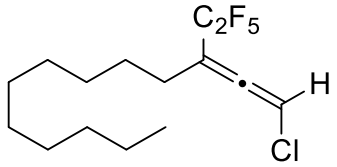


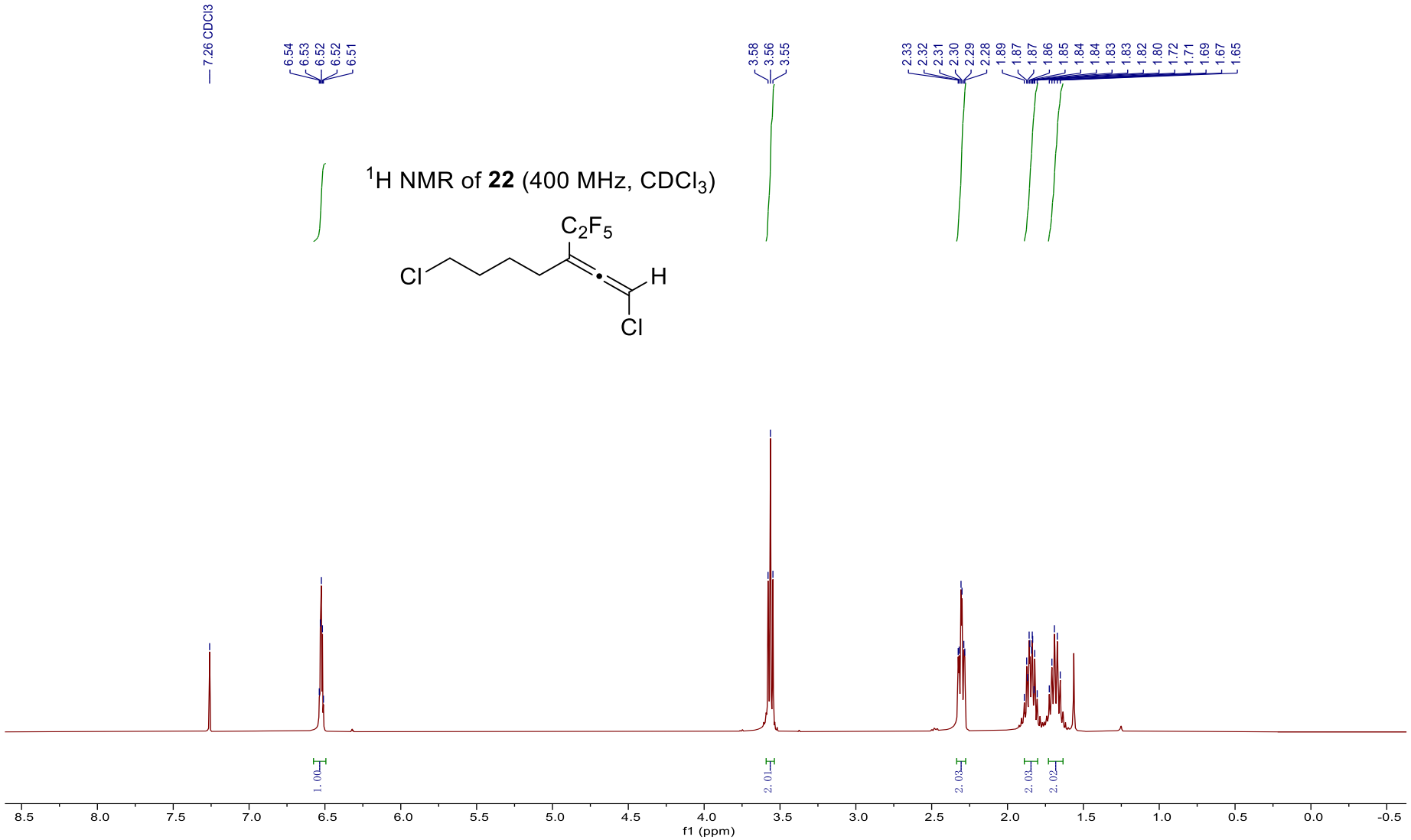

203.07
203.00
202.92
138.34
128.56
127.83
123.17
120.69
120.32
119.94
117.84
117.47
117.10
114.62
114.56
114.18
113.80
112.40
112.02
111.64
111.27
109.48
109.10
106.86
106.60
106.33
95.93
77.16 CDCl3
73.22
68.70
27.30
23.63
^{13}C NMR of **20** (101 MHz, $CDCl_3$)
C_2F_5
BnO
H
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

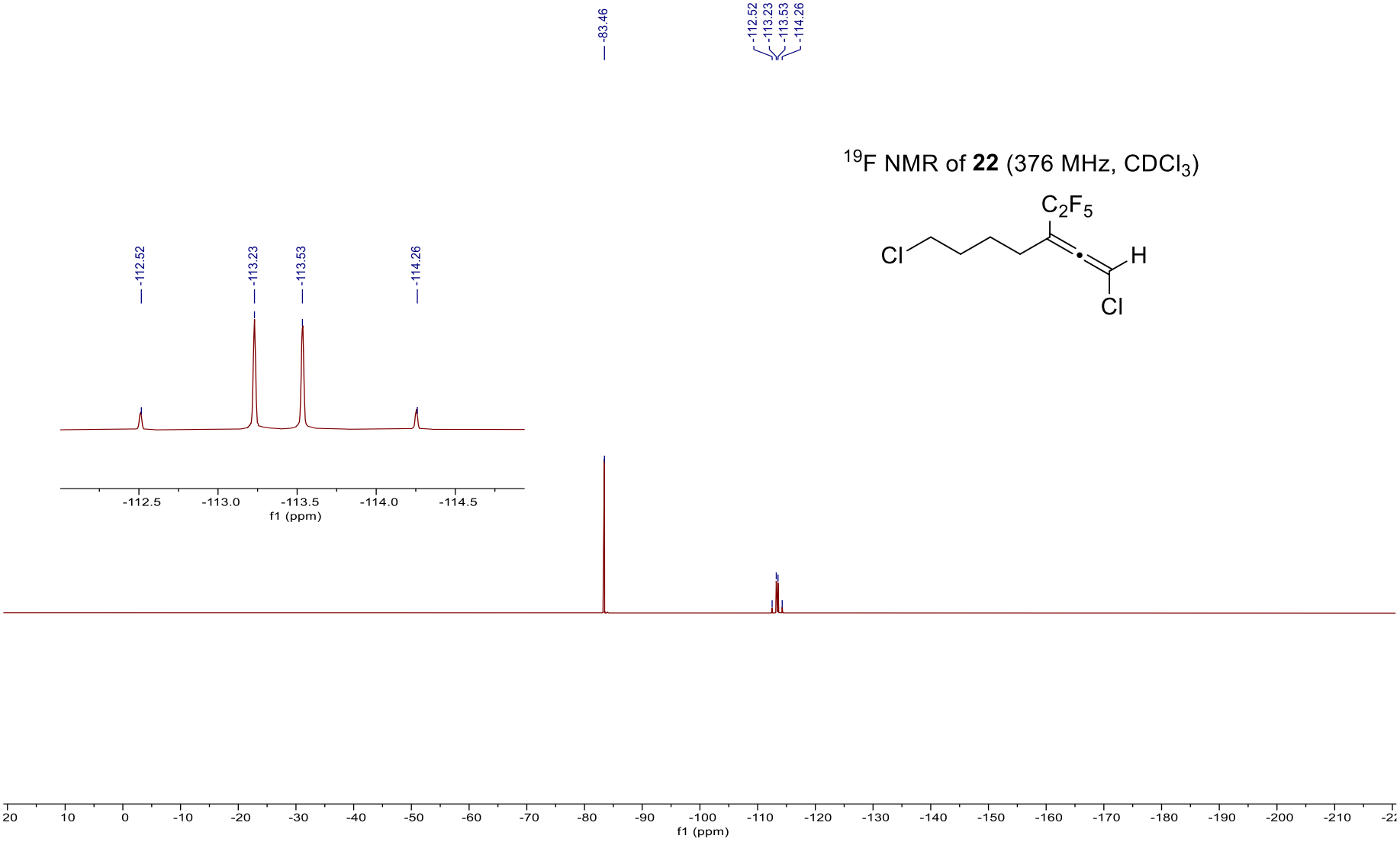

7.26 CDCl3
6.49
6.48
6.47
6.47
6.46
2.27
2.26
2.25
2.23
2.23
1.51
1.50
1.48
1.46
1.27
0.90
0.88
0.87
^{1}H NMR of **21** (400 MHz, $CDCl_3$)
C_2F_5
H
Cl
1.00
2.02
2.04
13.01
4.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
f1 (ppm)


-83.48
-112.52
-113.24
-113.54
-114.26
^{19}F NMR of **21** (376 MHz, $CDCl_3$)
C_2F_5
H
Cl
-112.52
-113.24
-113.54
-114.26
-110
-111
-112
-113
-114
-115
-116
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)

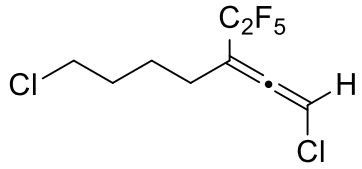
^{13}C NMR of **21** (101 MHz, $CDCl_3$)



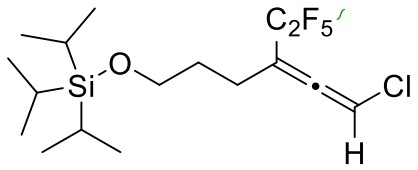

7.26 CDCl3
6.54
6.53
6.52
6.52
6.51
3.58
3.56
3.55
2.33
2.32
2.31
2.30
2.29
2.28
1.89
1.87
1.87
1.86
1.85
1.84
1.84
1.83
1.83
1.82
1.80
1.72
1.71
1.69
1.67
1.65
1H NMR of 22 (400 MHz, CDCl3)
C2F5
Cl
H
Cl
1.00
2.01
2.03
2.03
2.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

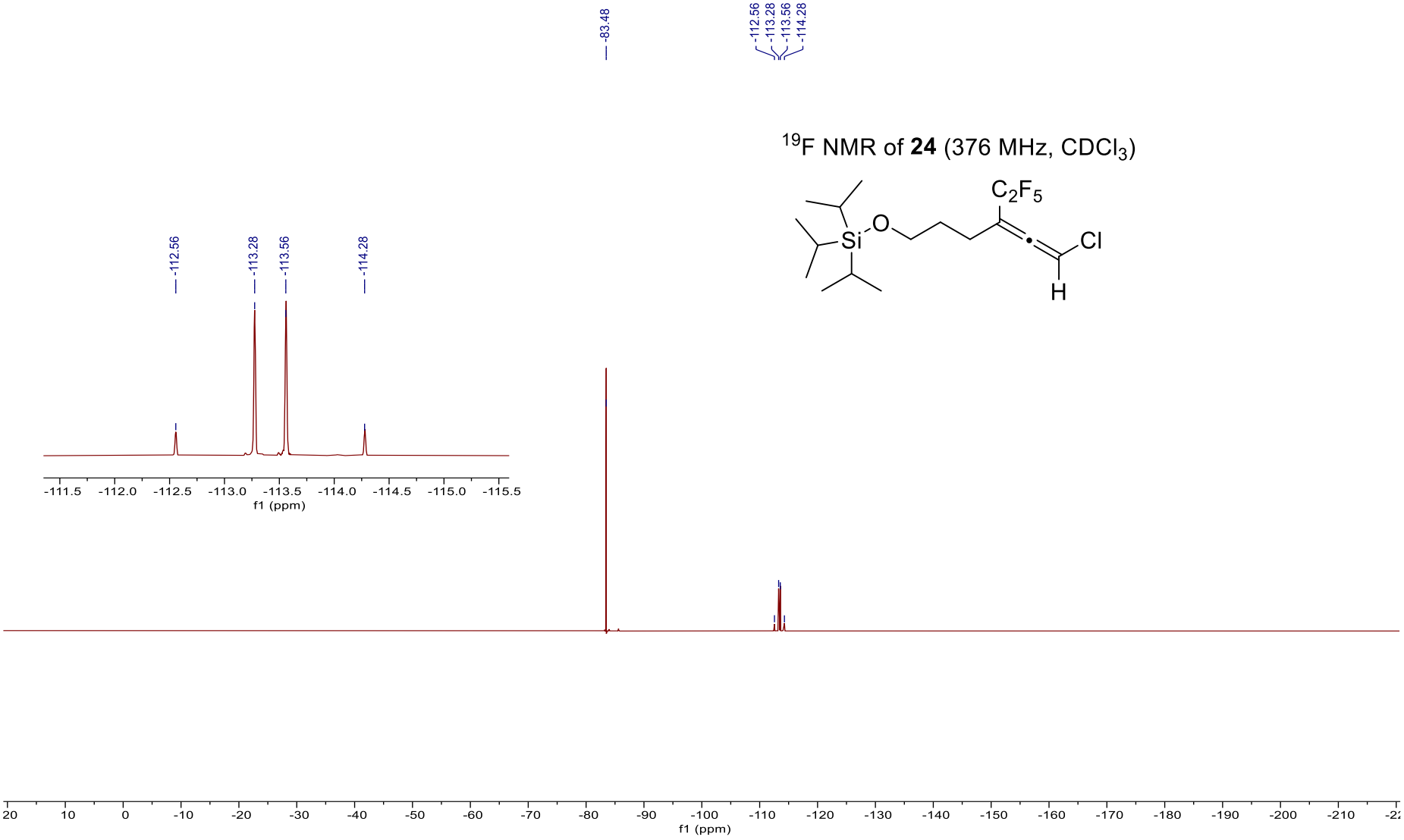

-83.46
-112.52
-113.23
-113.53
-114.26
^{19}F NMR of **22** (376 MHz, $CDCl_3$)
C_2F_5
Cl
H
Cl
-112.52
-113.23
-113.53
-114.26
-112.5
-113.0
-113.5
-114.0
-114.5
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

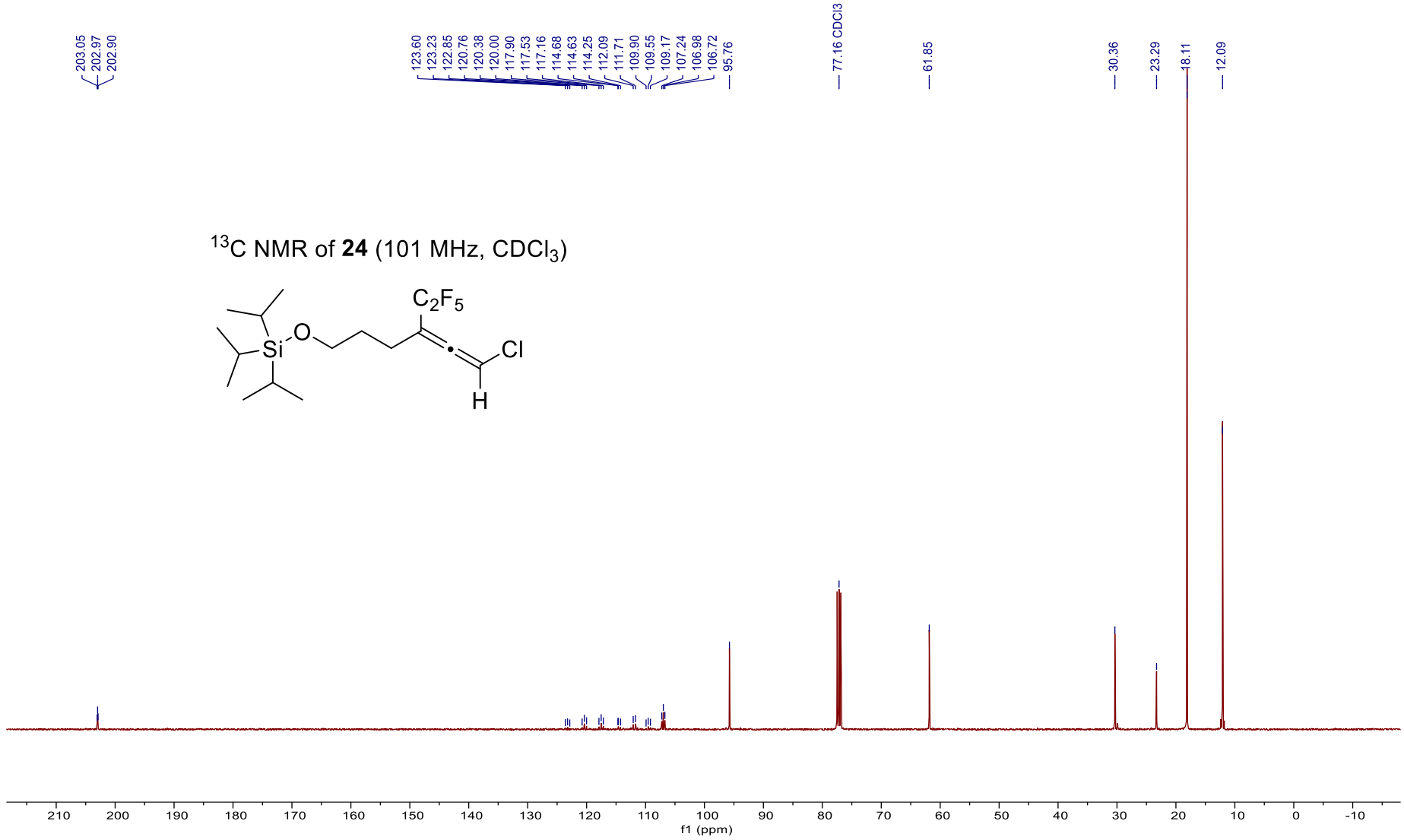
^{13}C NMR of **22** (101 MHz, $CDCl_3$)



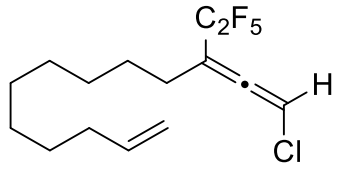
^{1}H NMR of **24** (400 MHz, $CDCl_3$)

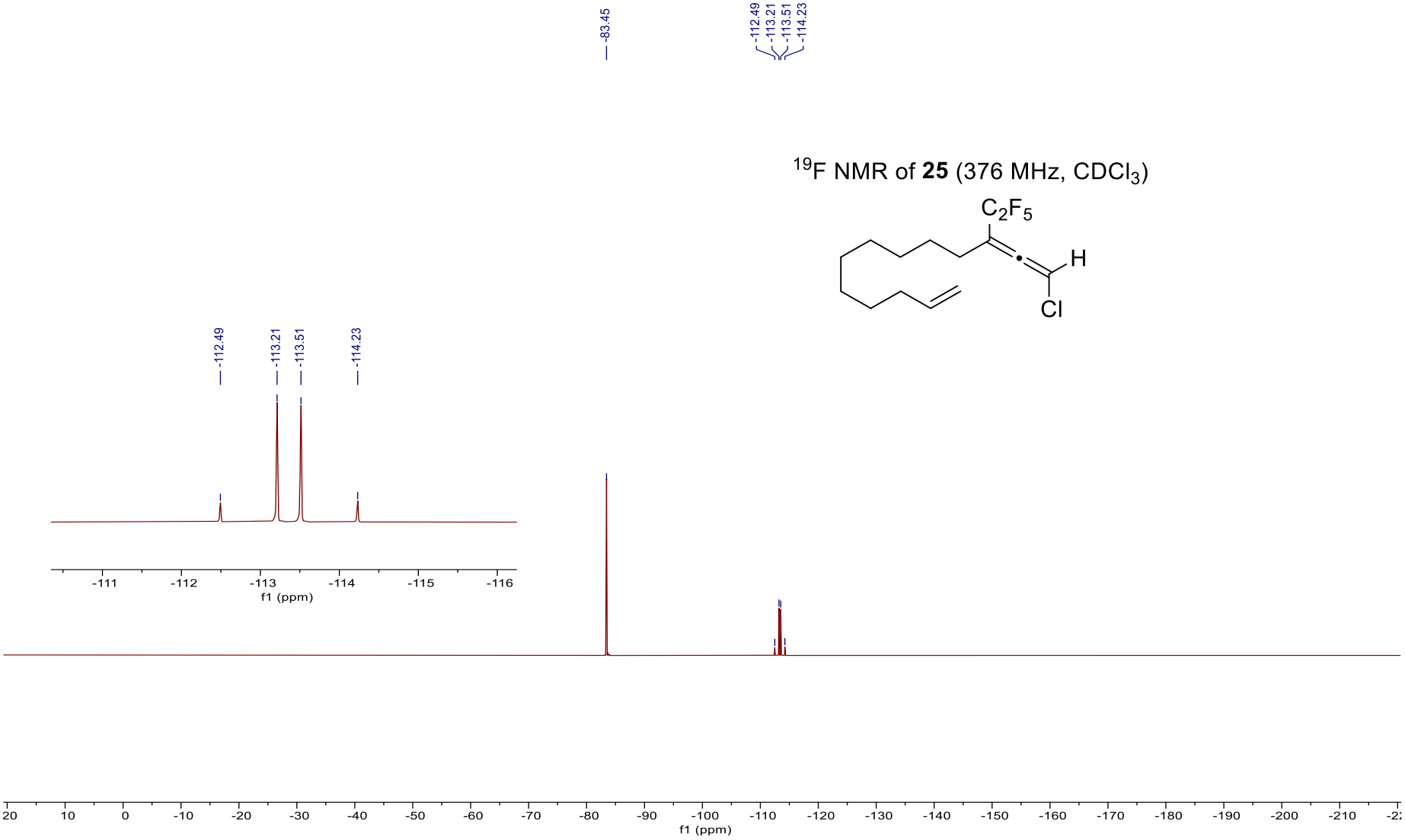


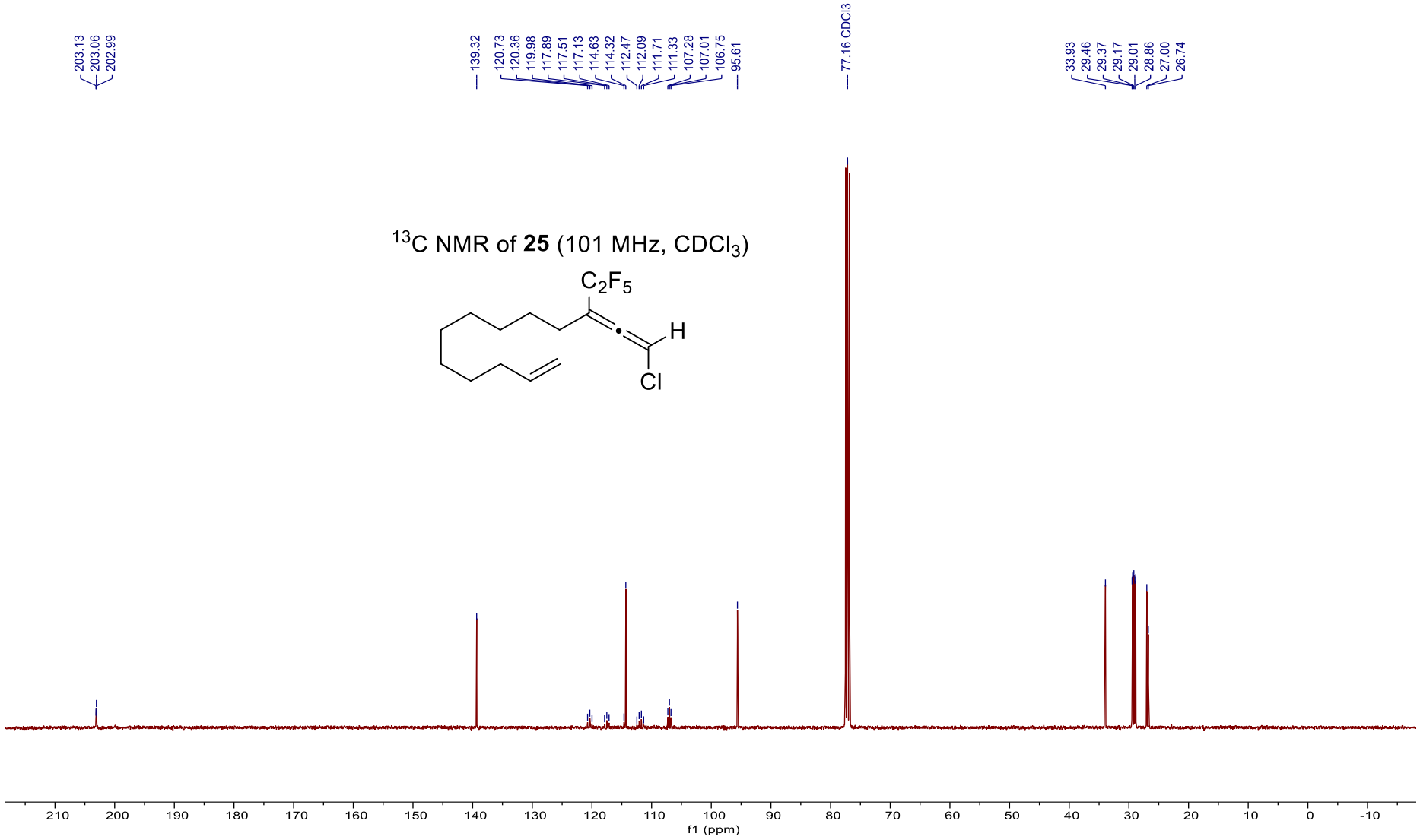

-83.48
-112.56
-113.28
-113.56
-114.28
19F NMR of 24 (376 MHz, CDCl3)
C2F5
Si
O
Cl
H
-112.56
-113.28
-113.56
-114.28
-111.5 -112.0 -112.5 -113.0 -113.5 -114.0 -114.5 -115.0 -115.5
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

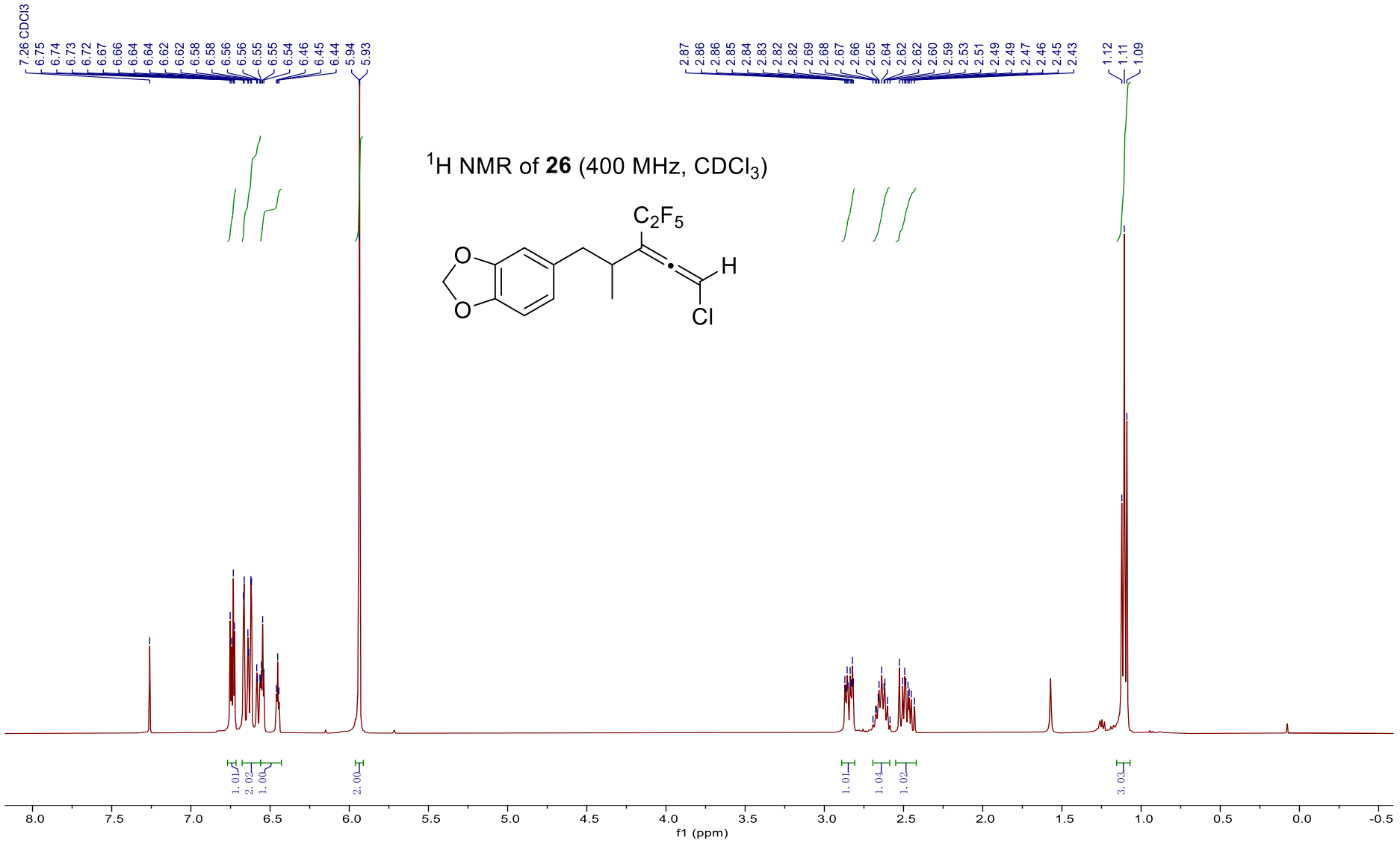

203.05
202.97
202.90
123.60
123.23
122.85
120.76
120.38
120.00
117.90
117.53
117.16
114.68
114.63
114.25
112.09
111.71
109.90
109.55
109.17
107.24
106.98
106.72
95.76
77.16 CDCl3
61.85
30.36
23.29
18.11
12.09
^{13}C NMR of **24** (101 MHz, $CDCl_3$)
C_2F_5
Si
O
Cl
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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

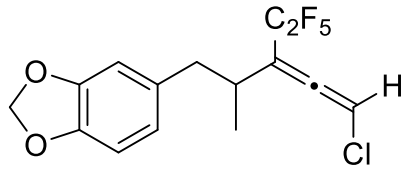



-83.45
-112.49
-113.21
-113.51
-114.23
^{19}F NMR of **25** (376 MHz, $CDCl_3$)
C_2F_5
H
Cl
-112.49
-113.21
-113.51
-114.23
-111
-112
-113
-114
-115
-116
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

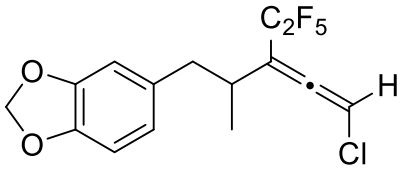

203.13
203.06
202.99
139.32
120.73
120.36
119.98
117.89
117.51
117.13
114.63
114.32
112.47
112.09
111.71
111.33
107.28
107.01
106.75
95.61
77.16 CDCl3
33.93
29.46
29.37
29.17
29.01
28.86
27.00
26.74
13C NMR of 25 (101 MHz, CDCl3)
C2F5
H
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

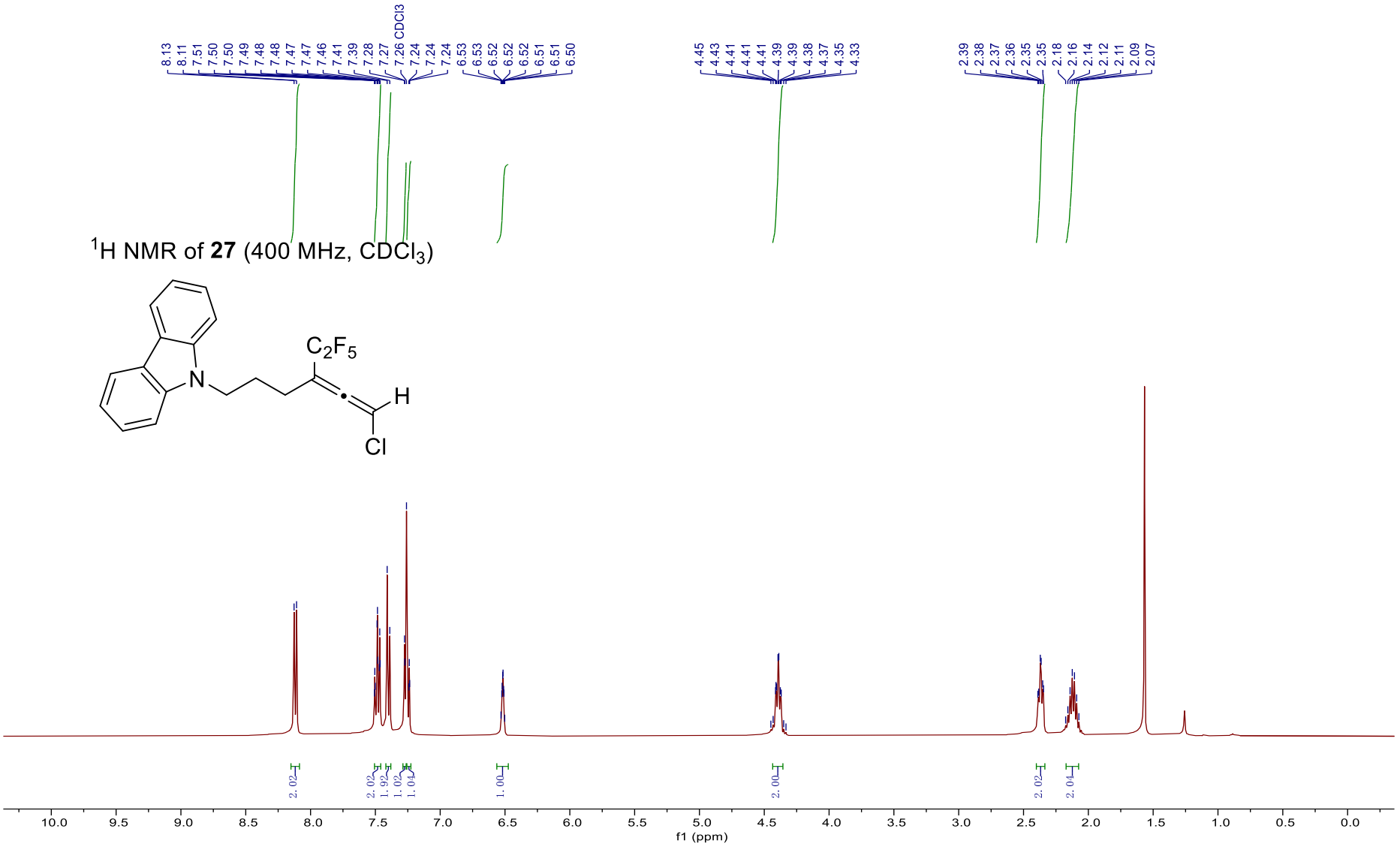

7.26 CDCl3
6.75
6.74
6.73
6.72
6.67
6.66
6.64
6.64
6.62
6.62
6.58
6.58
6.56
6.56
6.55
6.55
6.54
6.46
6.45
6.44
5.94
5.93
2.87
2.86
2.86
2.85
2.84
2.83
2.82
2.82
2.69
2.68
2.67
2.66
2.65
2.64
2.62
2.62
2.60
2.59
2.53
2.51
2.49
2.49
2.47
2.46
2.45
2.43
1.12
1.11
1.09
1H NMR of 26 (400 MHz, CDCl3)
C2F5
O
O
H
Cl
1.01
2.02
1.00
2.00
1.01
1.04
1.02
3.03
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
f1 (ppm)

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

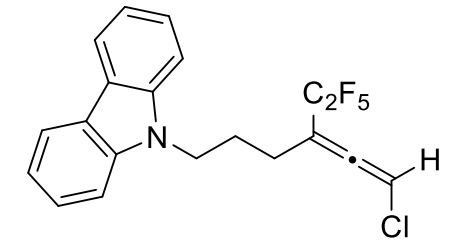


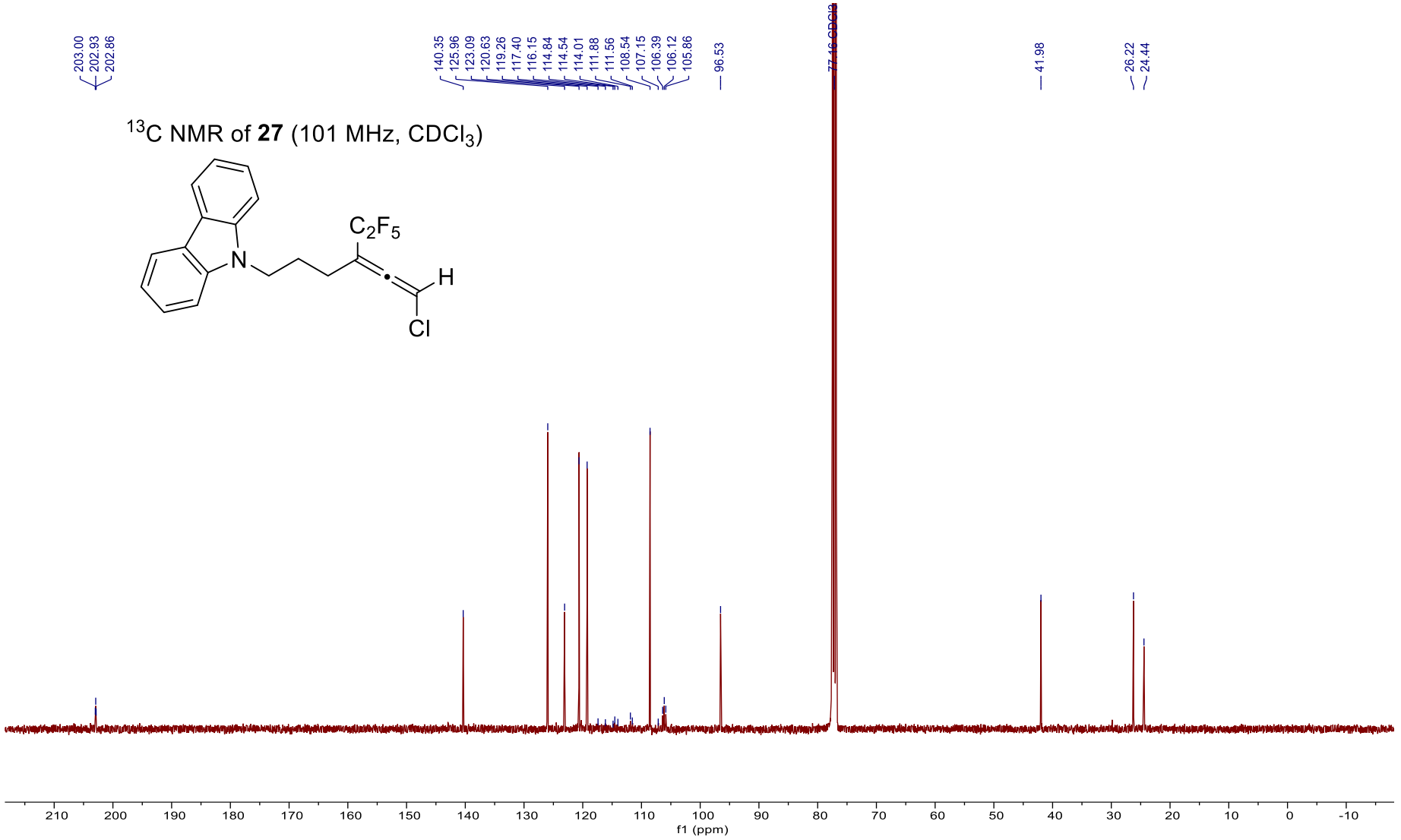
^{13}C NMR of **26** (101 MHz, $CDCl_3$)



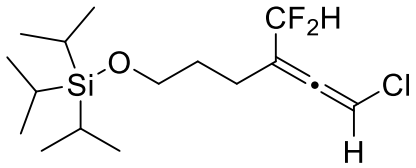

8.13
8.11
7.51
7.50
7.50
7.49
7.48
7.48
7.47
7.47
7.46
7.41
7.39
7.28
7.27
7.26 CDCl3
7.24
7.24
7.24
6.53
6.53
6.52
6.52
6.52
6.51
6.51
6.50
4.45
4.43
4.41
4.41
4.41
4.39
4.39
4.38
4.37
4.35
4.33
2.39
2.38
2.37
2.36
2.35
2.35
2.18
2.16
2.14
2.12
2.11
2.09
2.07
1H NMR of 27 (400 MHz, CDCl3)
C2F5
N
H
Cl
2.02
2.02
1.92
1.02
1.04
1.00
2.00
2.02
2.04
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
f1 (ppm)

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

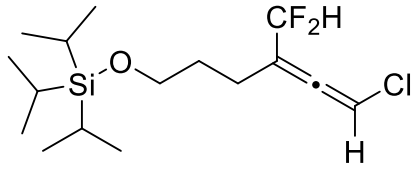


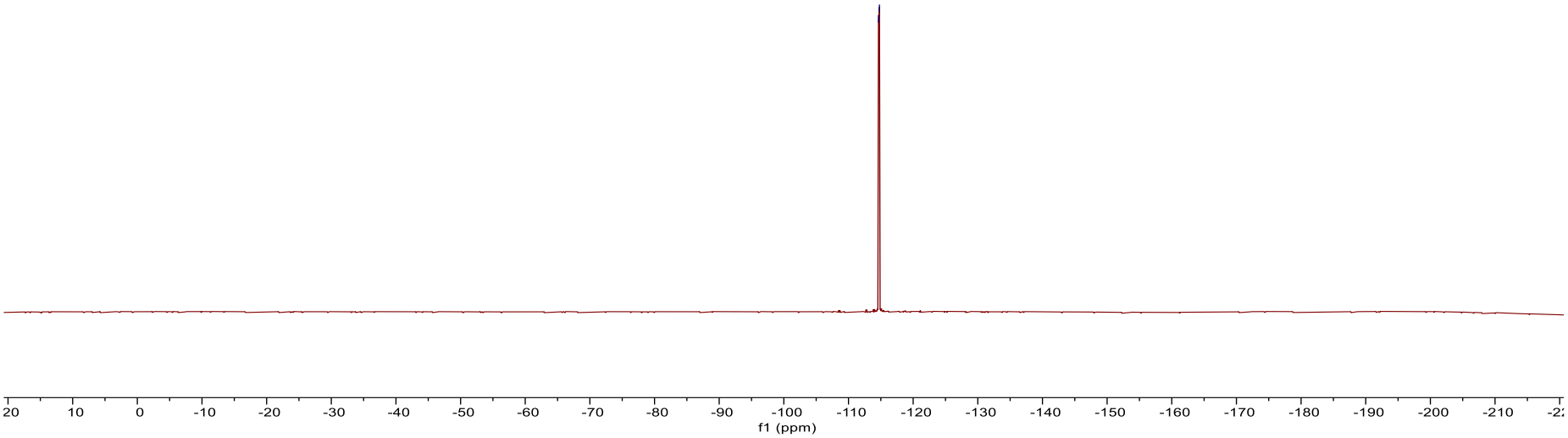

203.00
202.93
202.86
140.35
125.96
123.09
120.63
119.26
117.40
116.15
114.84
114.54
114.01
111.88
111.56
108.54
107.15
106.39
106.12
105.86
96.53
77.16 CDCl3
41.98
26.22
24.44
13C NMR of 27 (101 MHz, CDCl3)
C2F5
N
H
Cl
f1 (ppm)

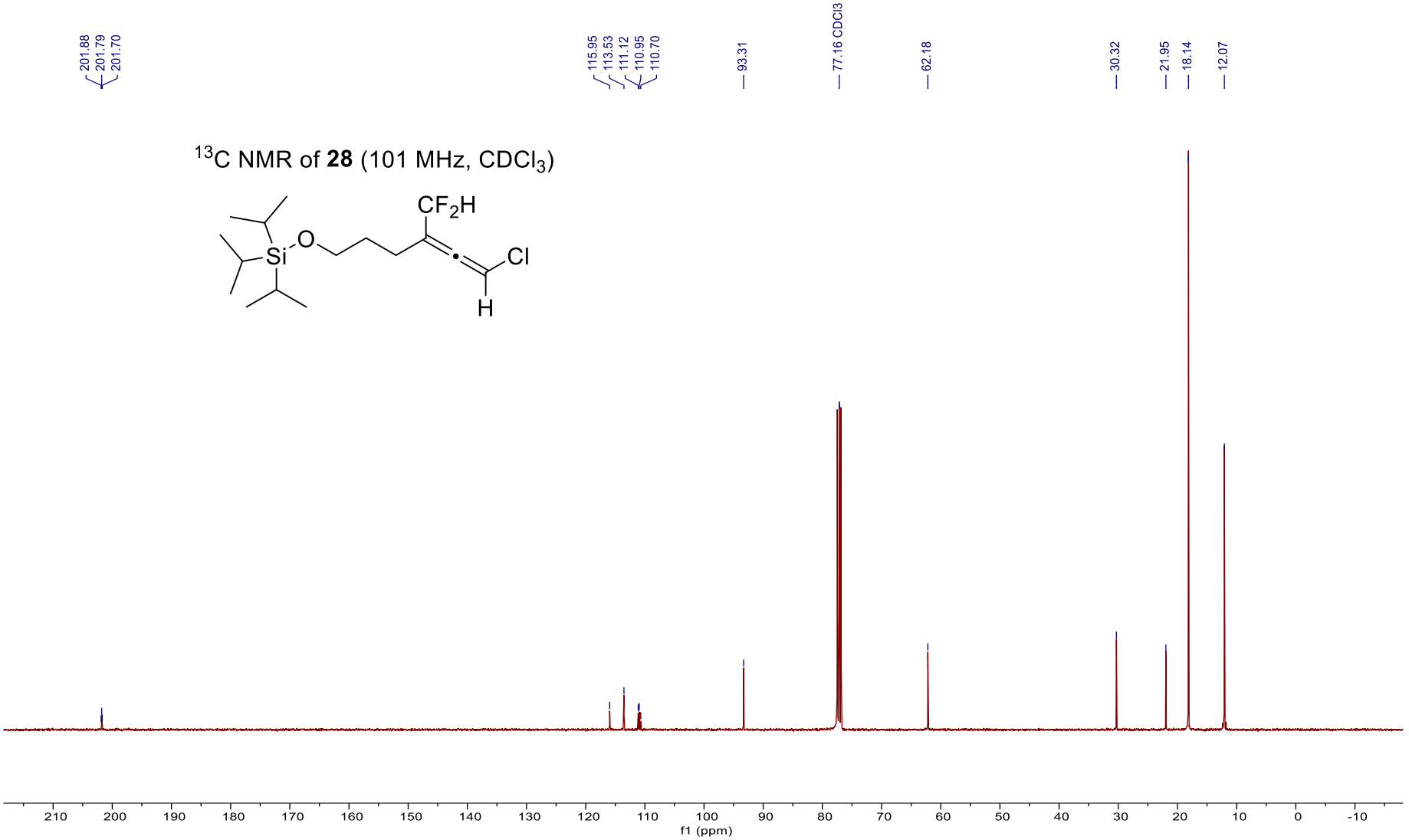
^{1}H NMR of **28** (400 MHz, $CDCl_3$)

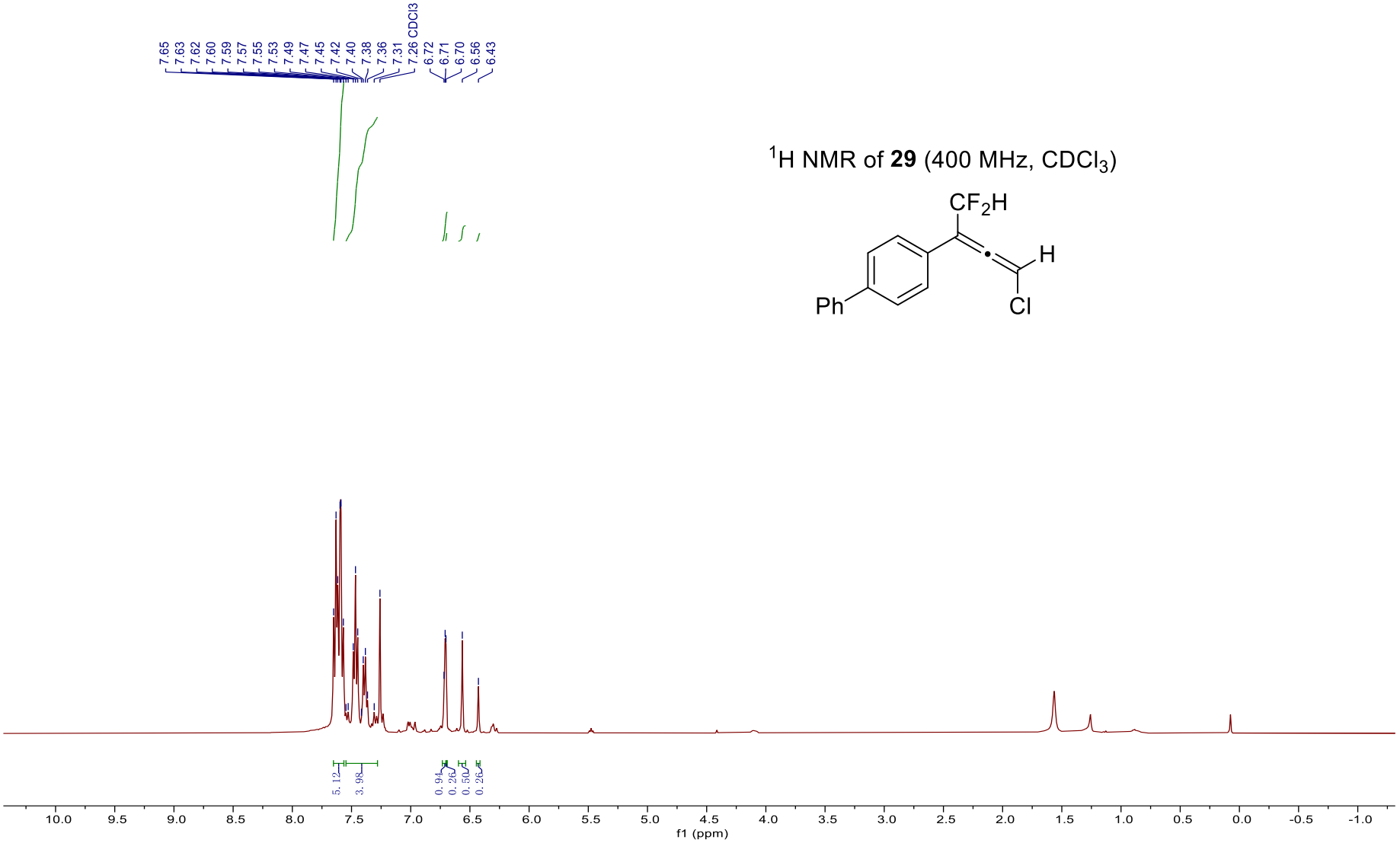


^{19}F NMR of **28** (376 MHz, $CDCl_3$)



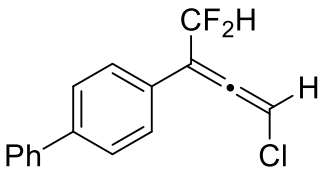


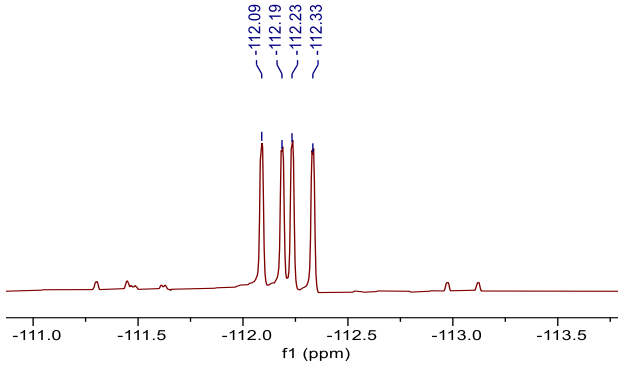

201.88
201.79
201.70
115.95
113.53
111.12
110.95
110.70
93.31
77.16 CDCl3
62.18
30.32
21.95
18.14
12.07
13C NMR of 28 (101 MHz, CDCl3)
CF2H
Si
O
Cl
H
f1 (ppm)

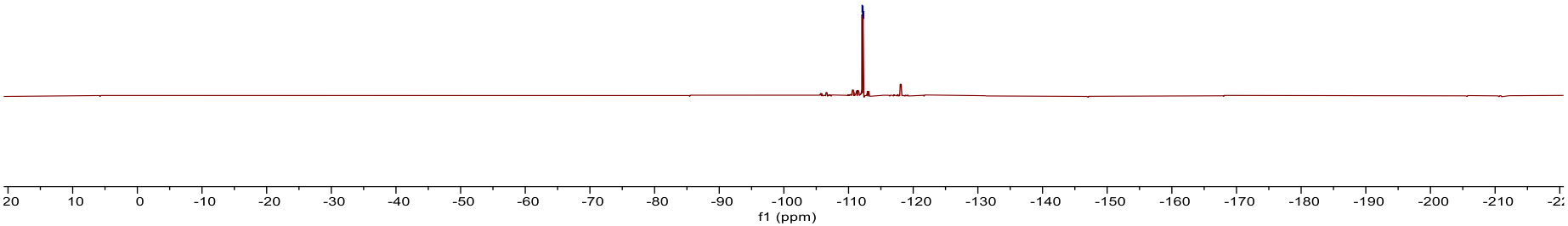


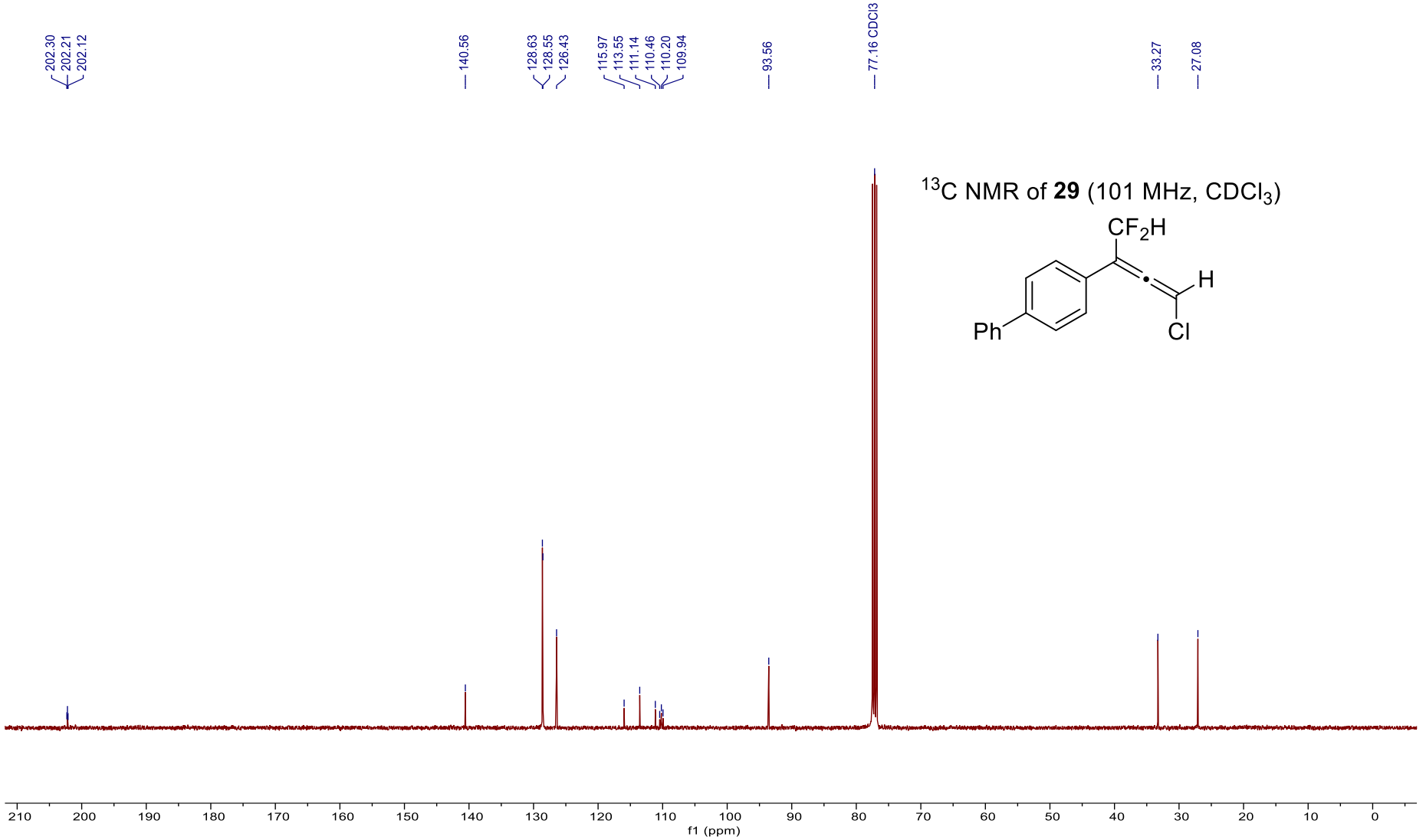
^{1}H NMR of **29** (400 MHz, $CDCl_3$)

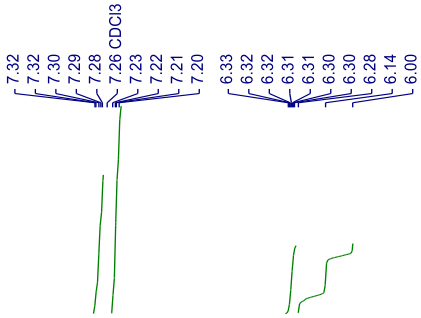
^{19}F NMR of **29** (376 MHz, $CDCl_3$)

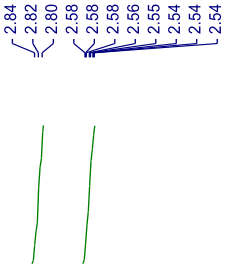




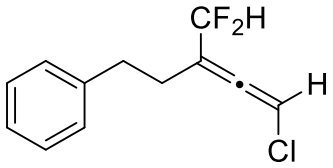


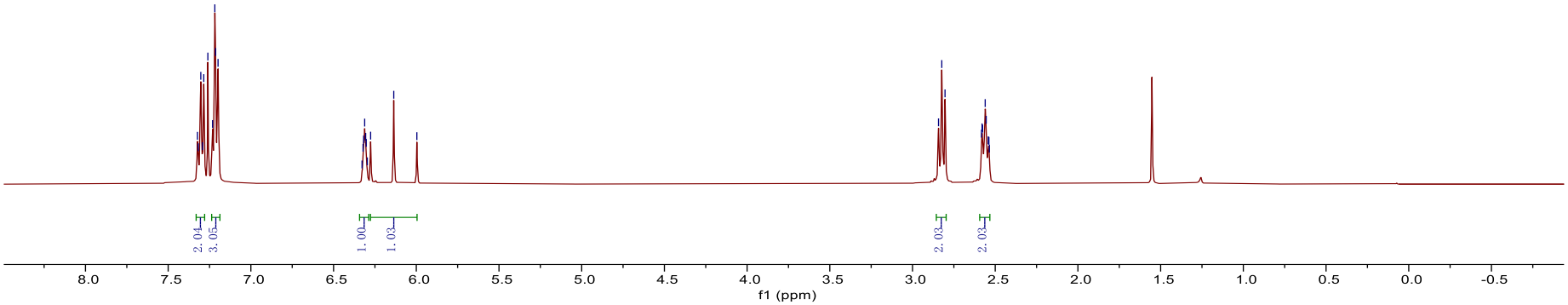

202.30
202.21
202.12
140.56
128.63
128.55
126.43
115.97
113.55
111.14
110.46
110.20
109.94
93.56
77.16 CDCl3
33.27
27.08
13C NMR of 29 (101 MHz, CDCl3)
CF2H
H
Ph
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



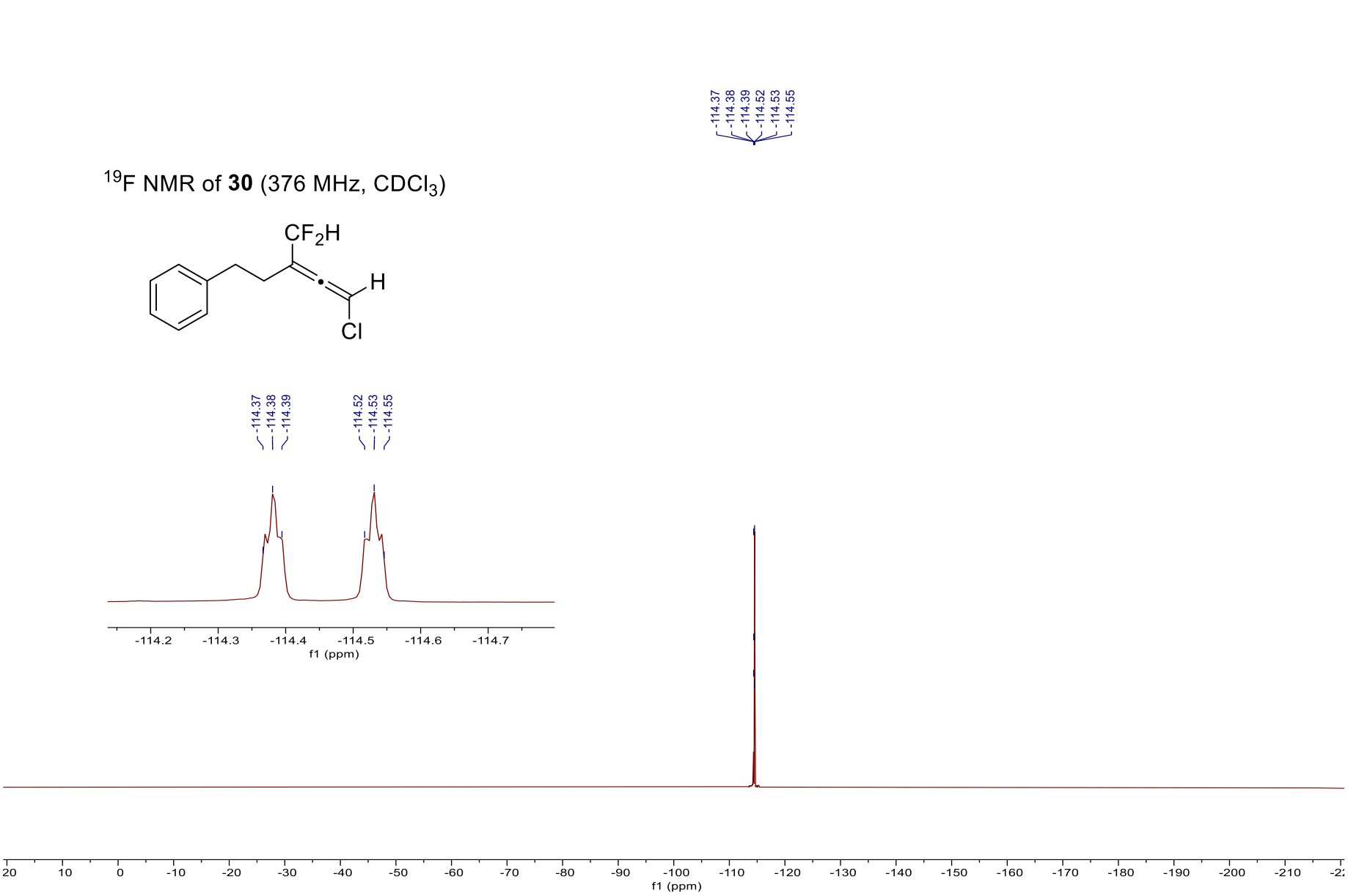


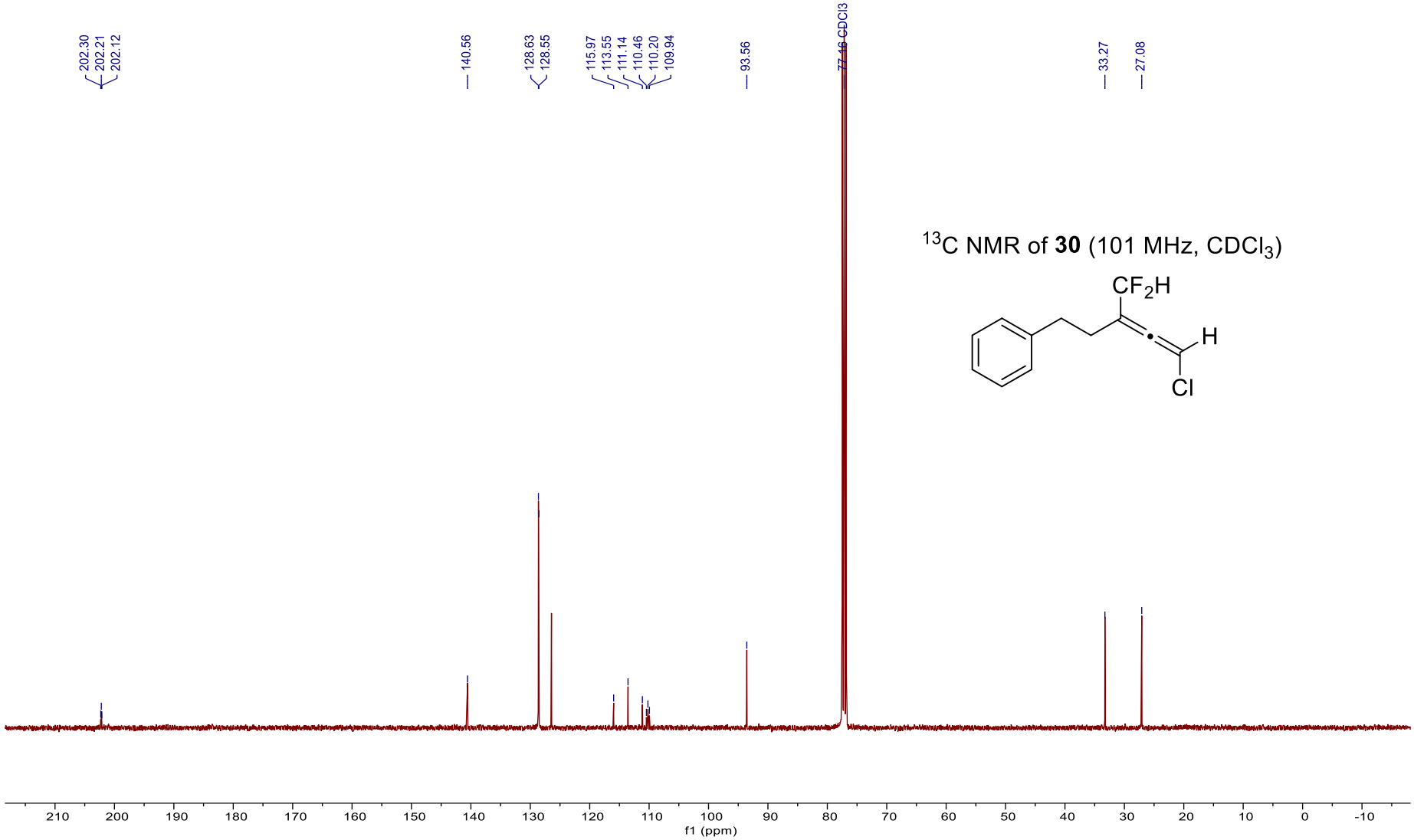
^{1}H NMR of **30** (400 MHz, $CDCl_3$)



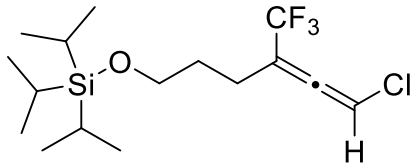


^{19}F NMR of **30** (376 MHz, $CDCl_3$)

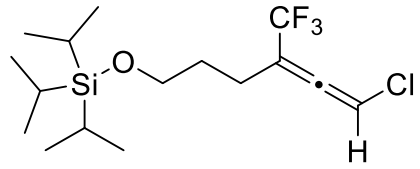


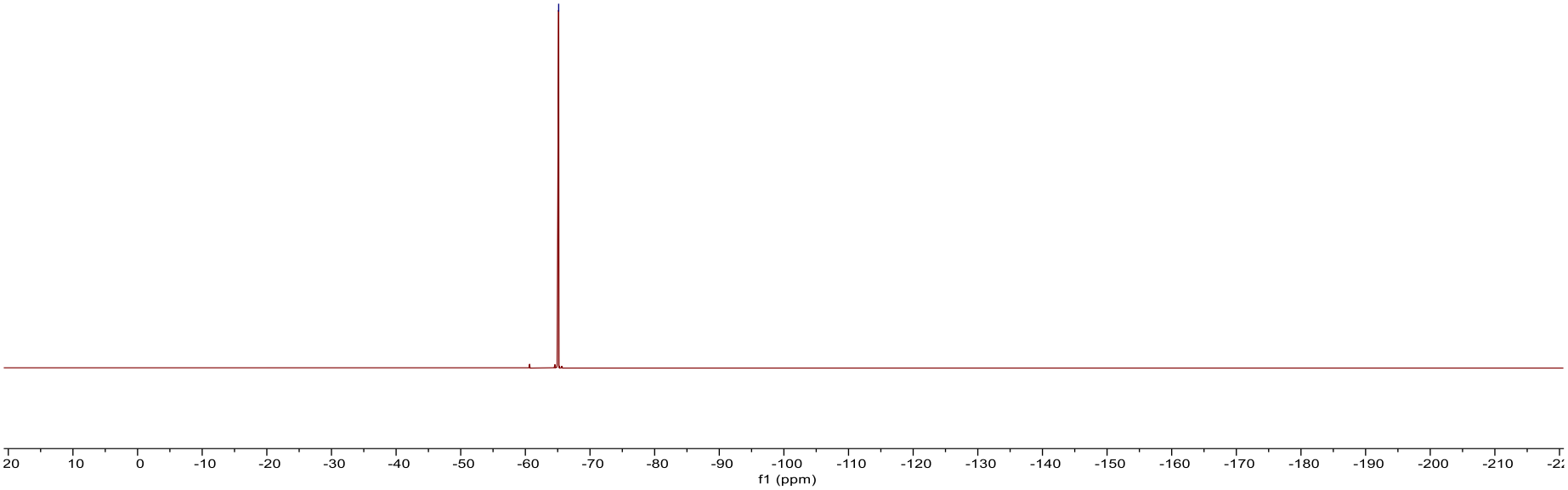

202.30
202.21
202.12
140.56
128.63
128.55
115.97
113.55
111.14
110.46
110.20
109.94
93.56
77.16 CDCl3
33.27
27.08
13C NMR of 30 (101 MHz, CDCl3)
CF2H
H
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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

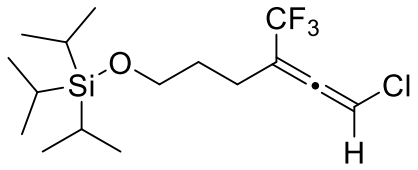


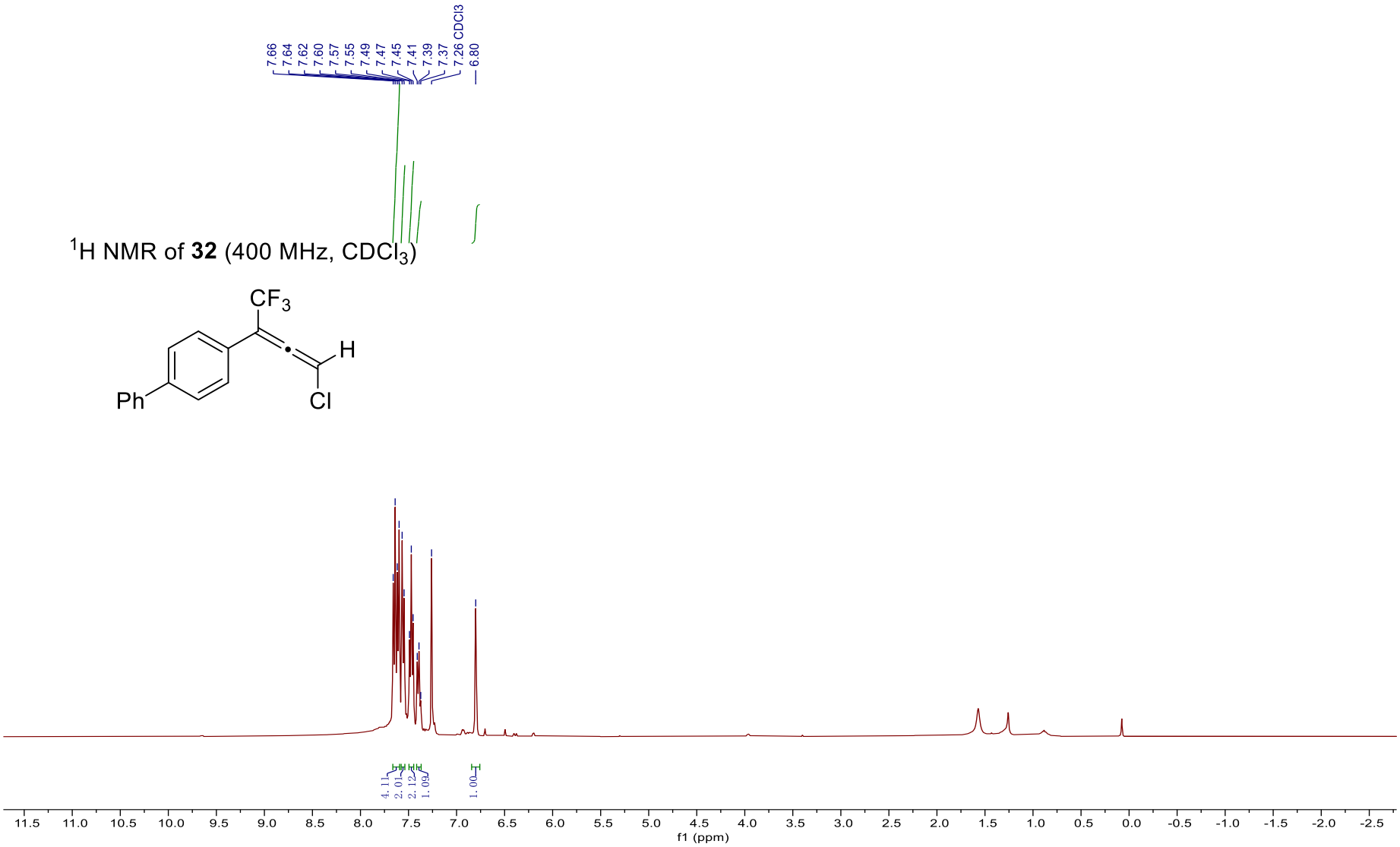
^{19}F NMR of **31** (376 MHz, $CDCl_3$)





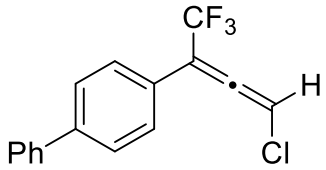
^{13}C NMR of **31** (101 MHz, $CDCl_3$)



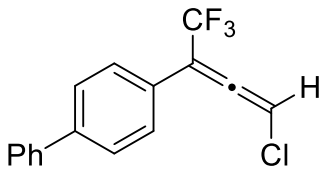


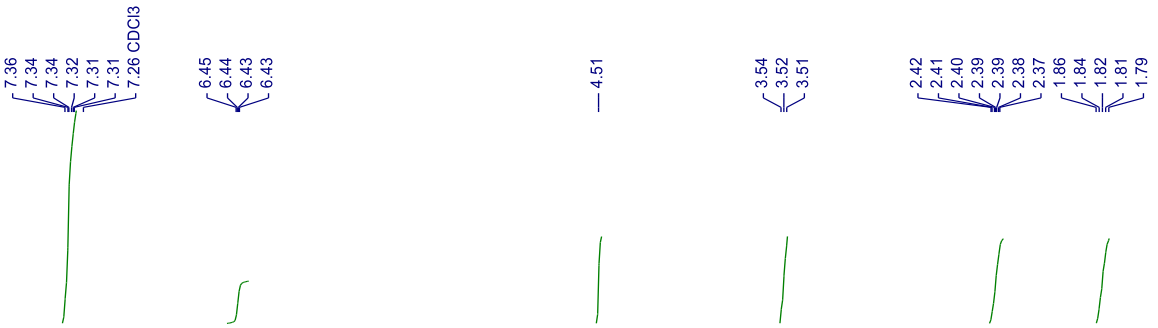
^{1}H NMR of **32** (400 MHz, $CDCl_3$)

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

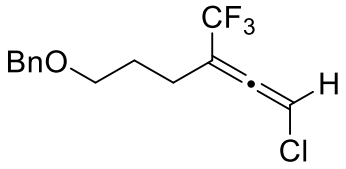


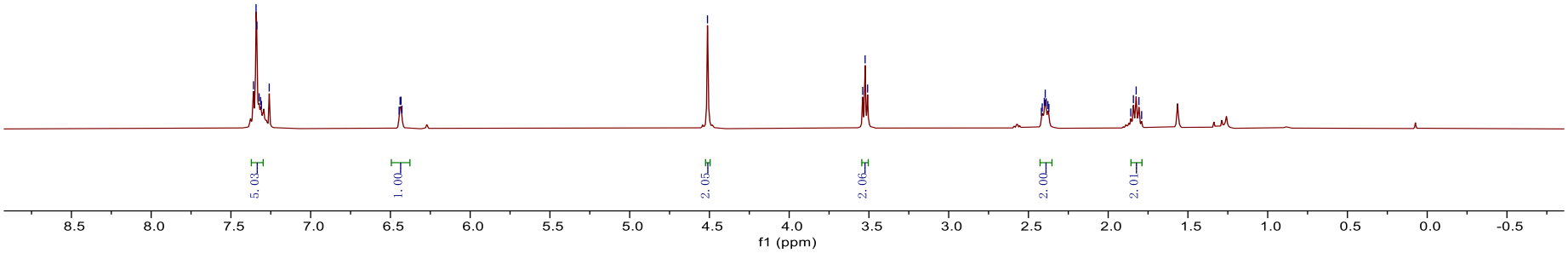
^{13}C NMR of **32** (101 MHz, $CDCl_3$)



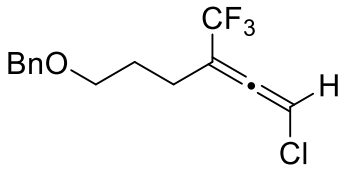


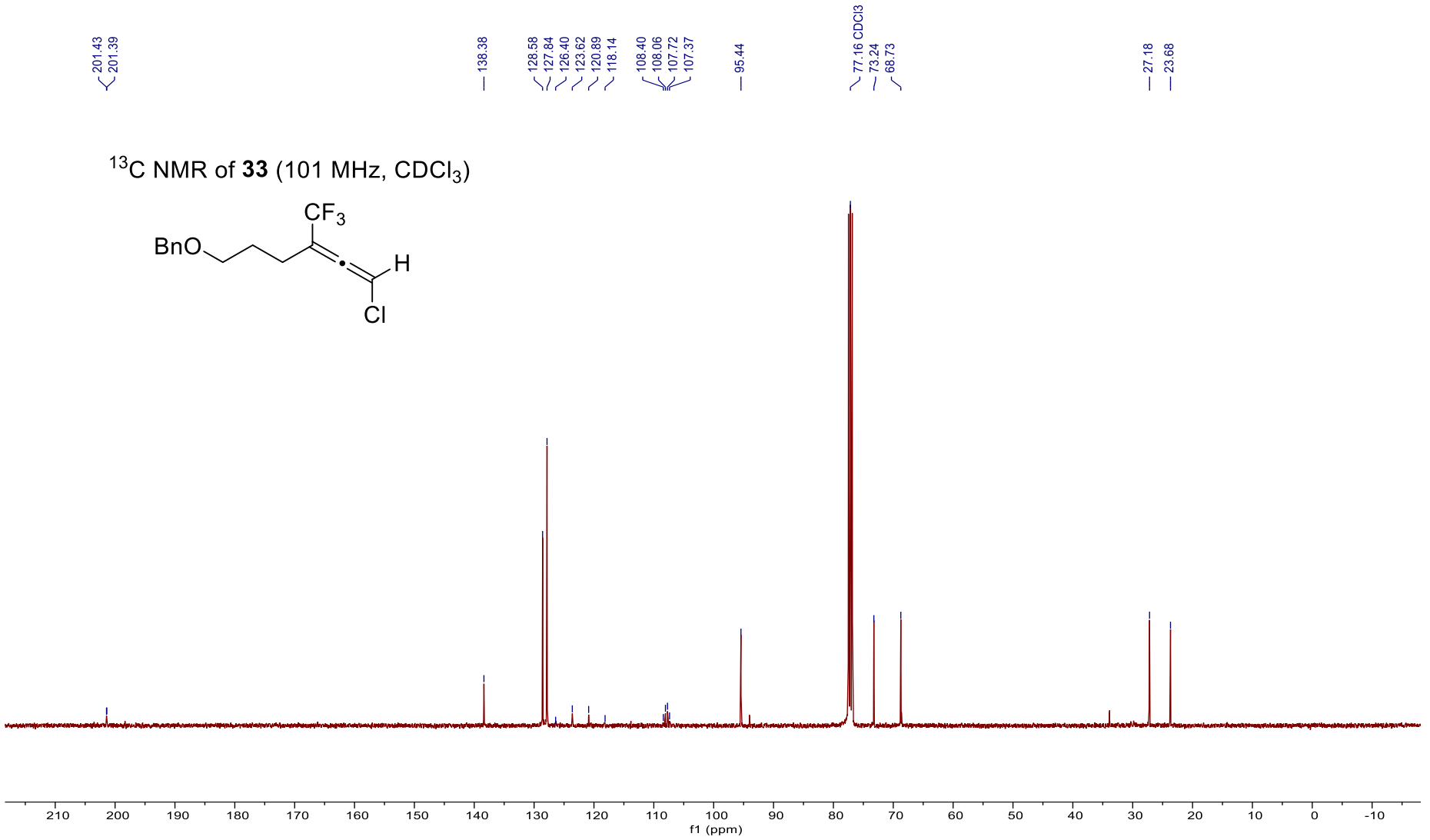
^{1}H NMR of **33** (400 MHz, $CDCl_3$)



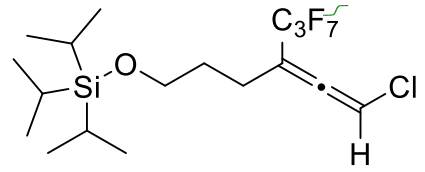


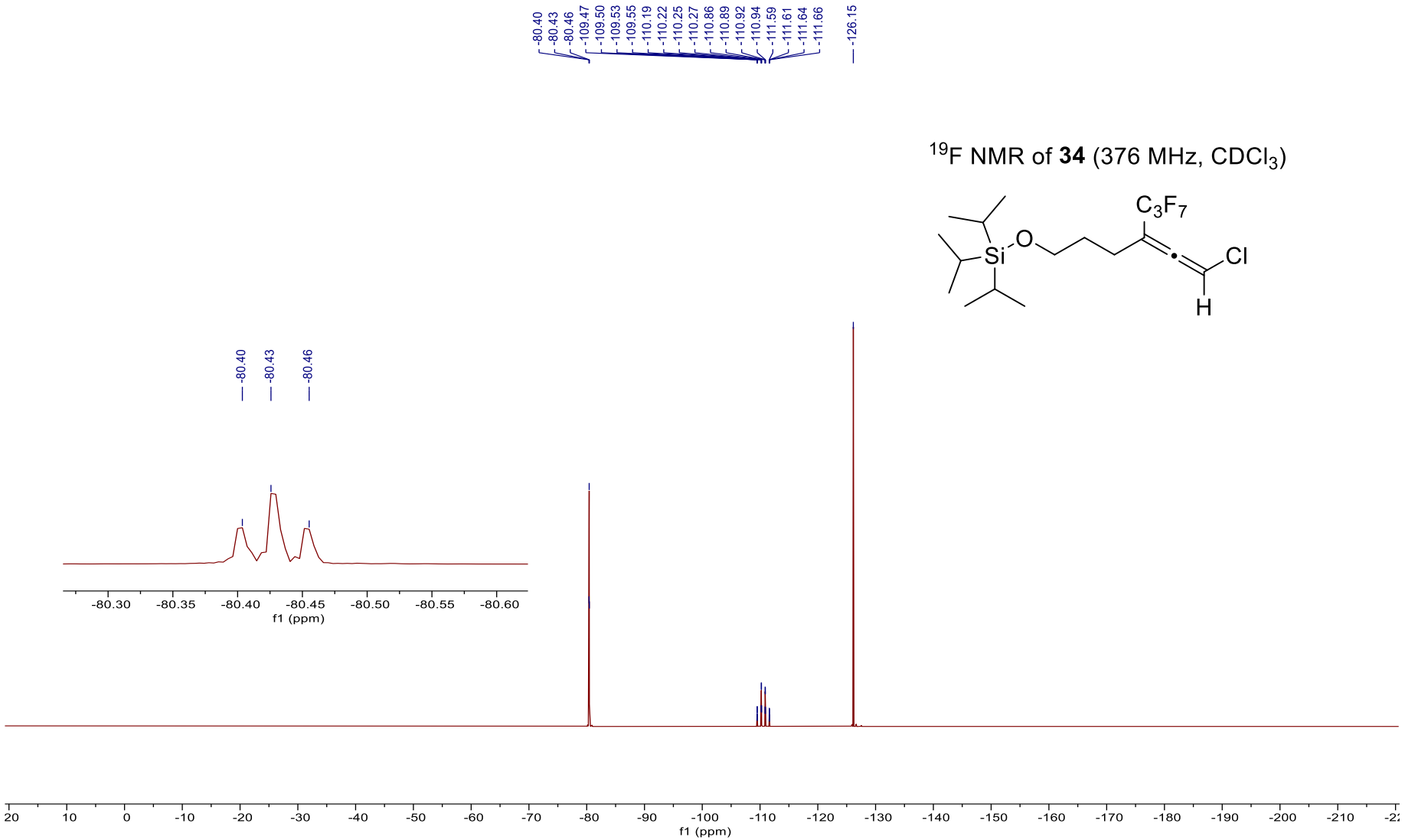
^{19}F NMR of **33** (376 MHz, $CDCl_3$)

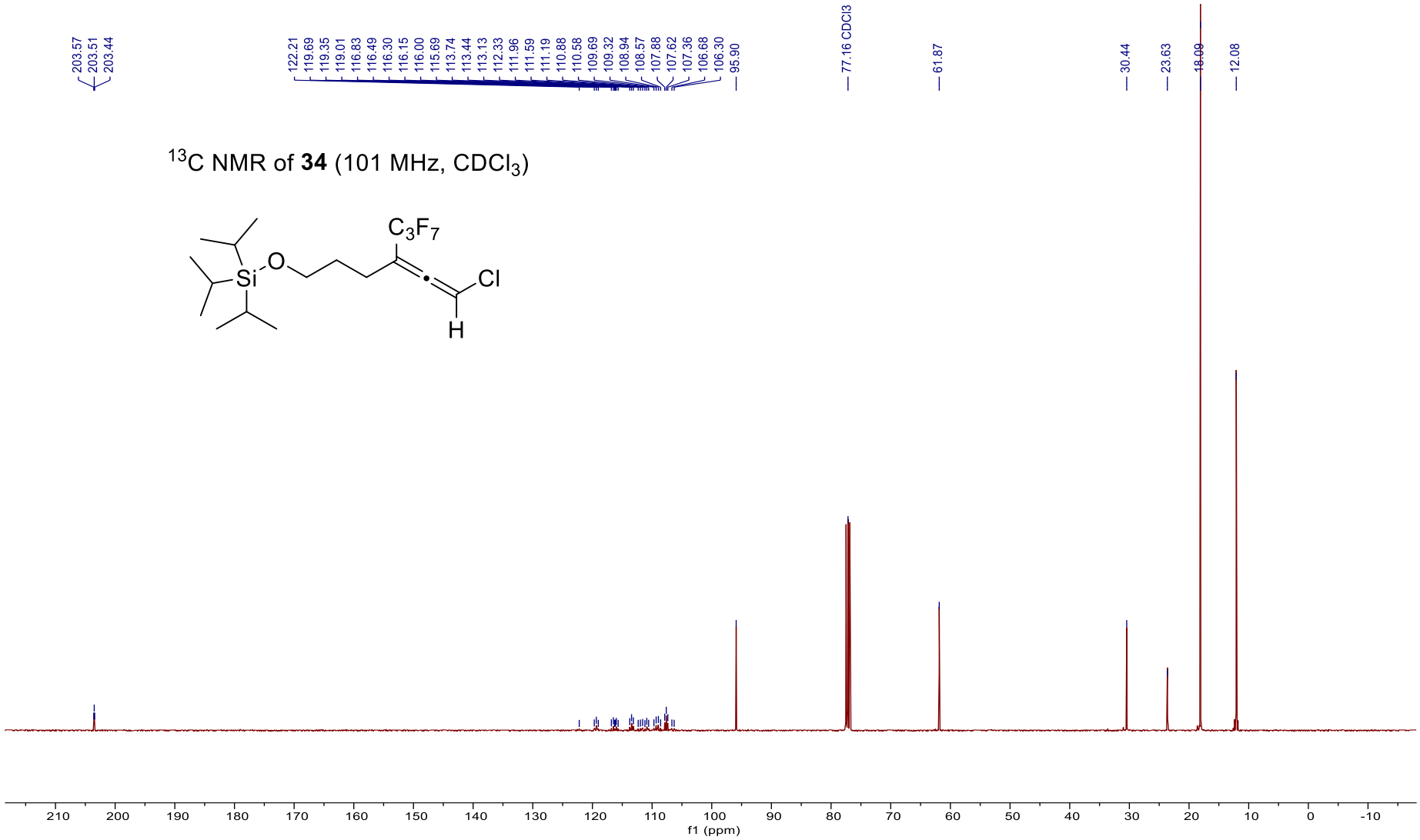


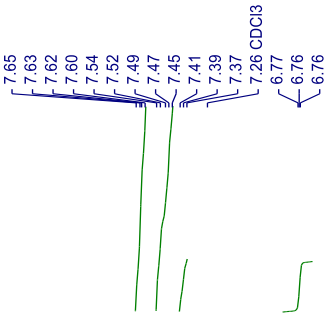

201.43
201.39
138.38
128.58
127.84
126.40
123.62
120.89
118.14
108.40
108.06
107.72
107.37
95.44
77.16 CDCl3
73.24
68.73
27.18
23.68
13C NMR of 33 (101 MHz, CDCl3)
CF3
BnO
H
Cl
f1 (ppm)

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

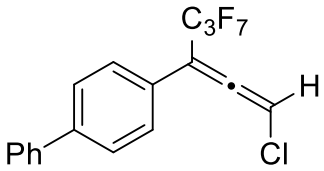


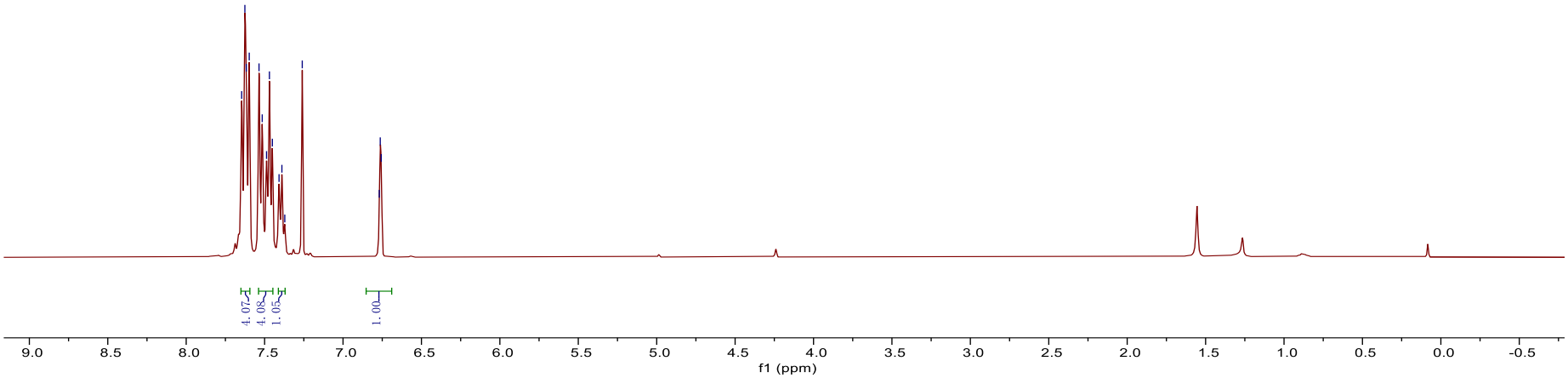

-80.40
-80.43
-80.46
-109.47
-109.50
-109.53
-109.55
-110.19
-110.22
-110.25
-110.27
-110.86
-110.89
-110.92
-110.94
-111.59
-111.61
-111.64
-111.66
-126.15
19F NMR of 34 (376 MHz, CDCl3)
C3F7
Si
O
Cl
H
-80.40
-80.43
-80.46
-80.30
-80.35
-80.40
-80.45
-80.50
-80.55
-80.60
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

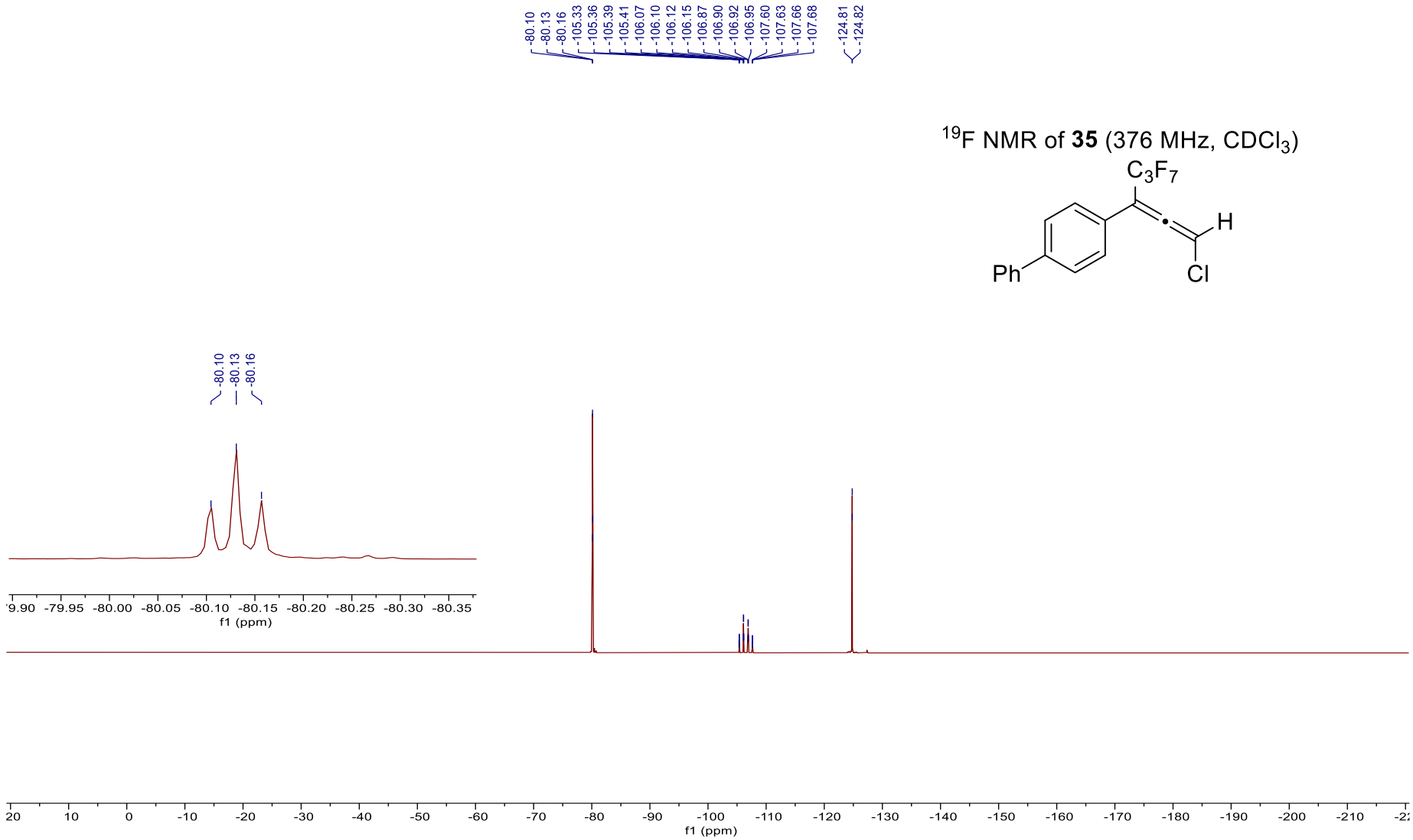

203.57
203.51
203.44
122.21
119.69
119.35
119.01
116.83
116.49
116.30
116.15
116.00
115.69
113.74
113.44
113.13
112.33
111.96
111.59
111.19
110.88
110.58
109.69
109.32
108.94
108.57
107.88
107.62
107.36
106.68
106.30
95.90
77.16 CDCl3
61.87
30.44
23.63
18.09
12.08
^{13}C NMR of **34** (101 MHz, $CDCl_3$)
C_3F_7
Si
O
Cl
H
f1 (ppm)

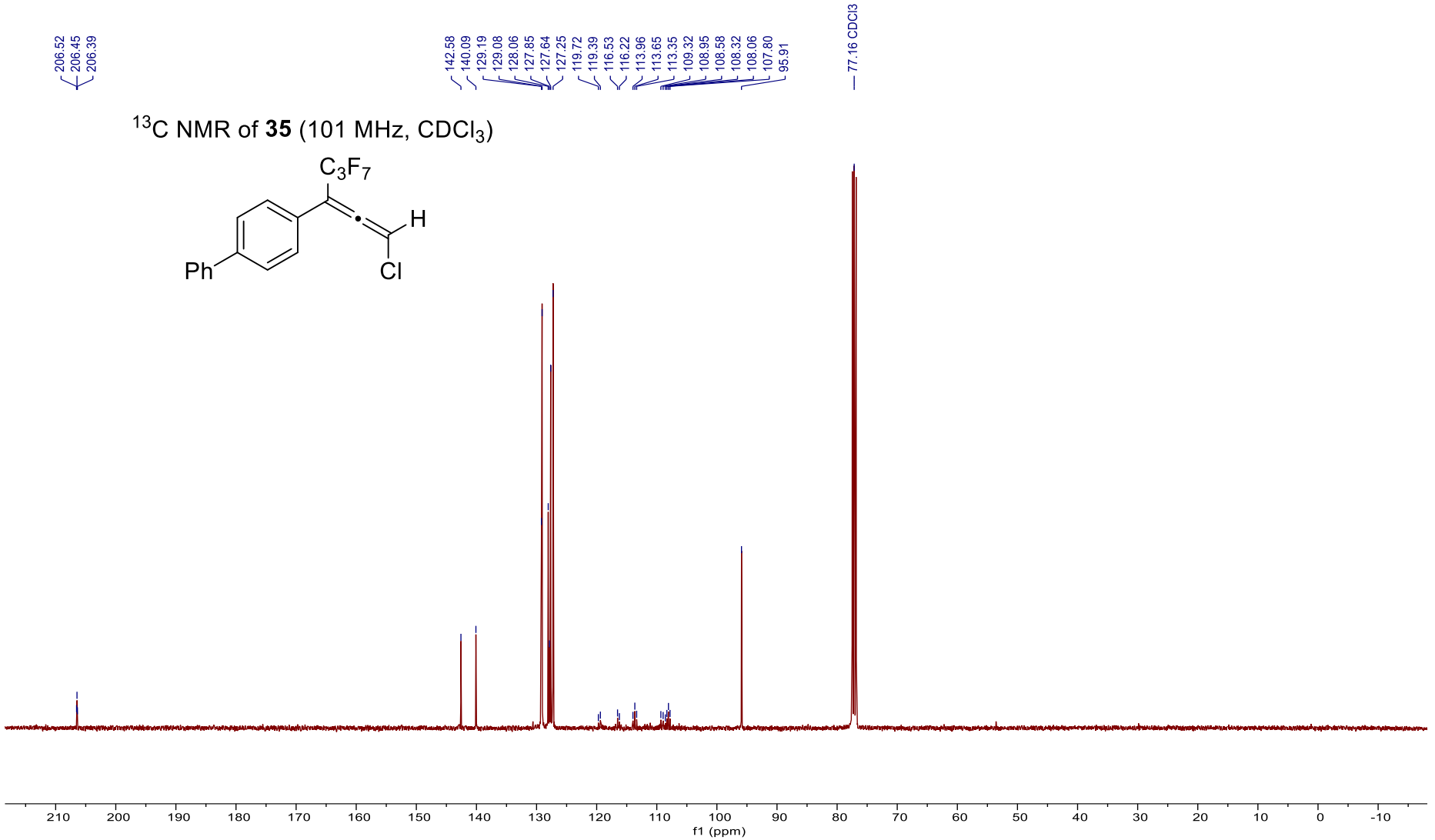


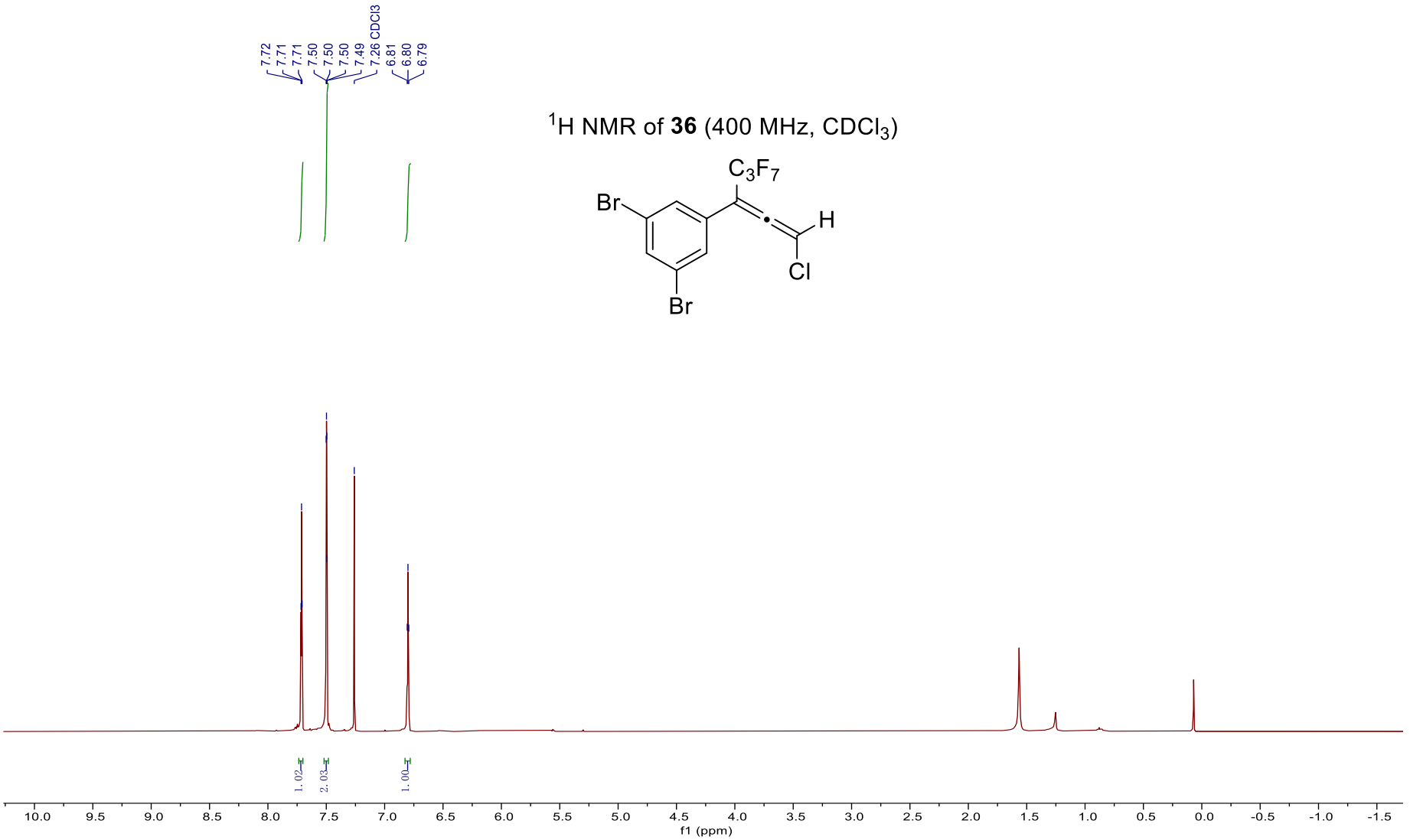
^{1}H NMR of **35** (400 MHz, $CDCl_3$)





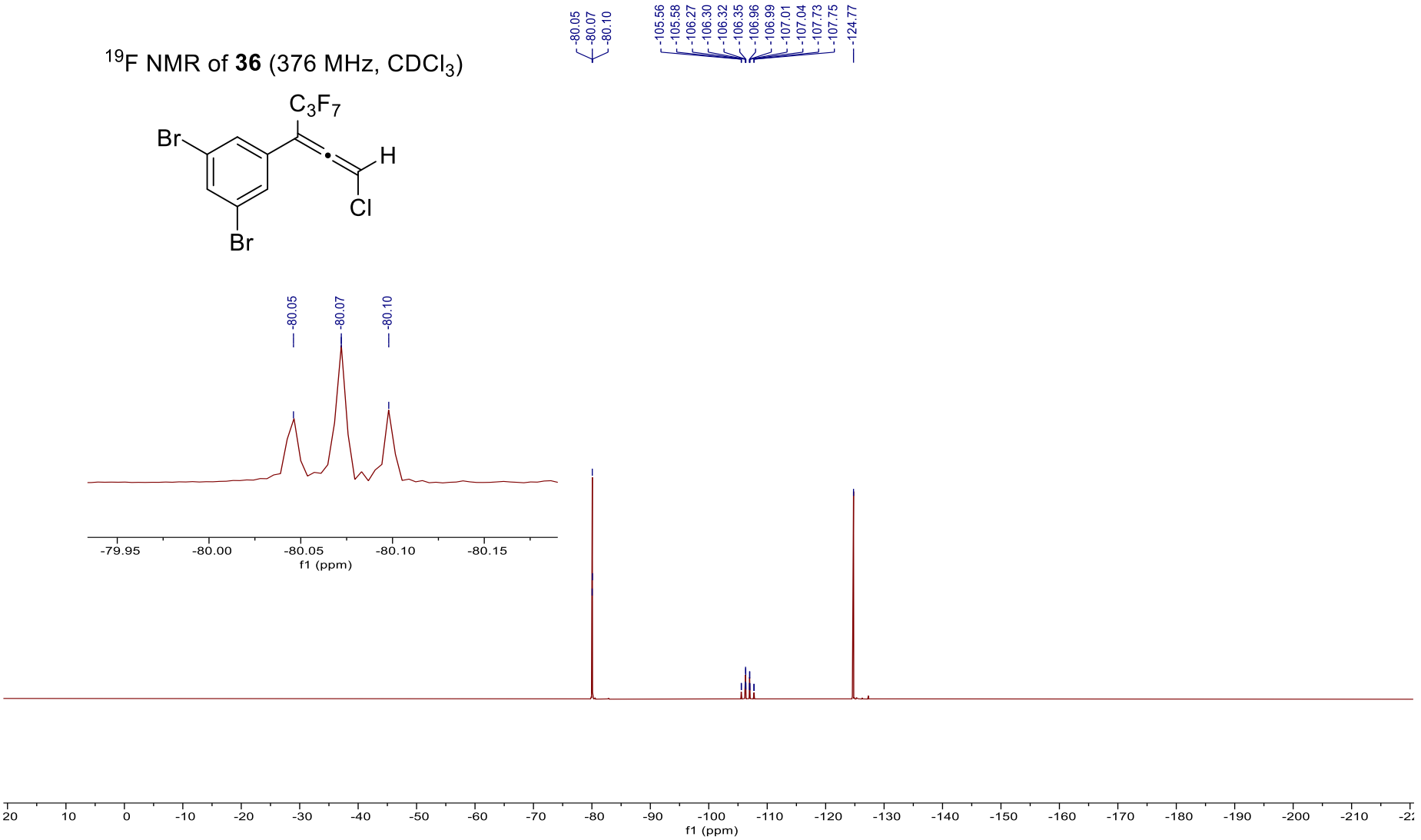

-80.10
-80.13
-80.16
-105.33
-105.36
-105.39
-105.41
-106.07
-106.10
-106.12
-106.15
-106.87
-106.90
-106.92
-106.95
-107.60
-107.63
-107.66
-107.68
-124.81
-124.82
19F NMR of 35 (376 MHz, CDCl3)
C3F7
H
Cl
Ph
-80.10
-80.13
-80.16
9.90 -79.95 -80.00 -80.05 -80.10 -80.15 -80.20 -80.25 -80.30 -80.35
f1 (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)

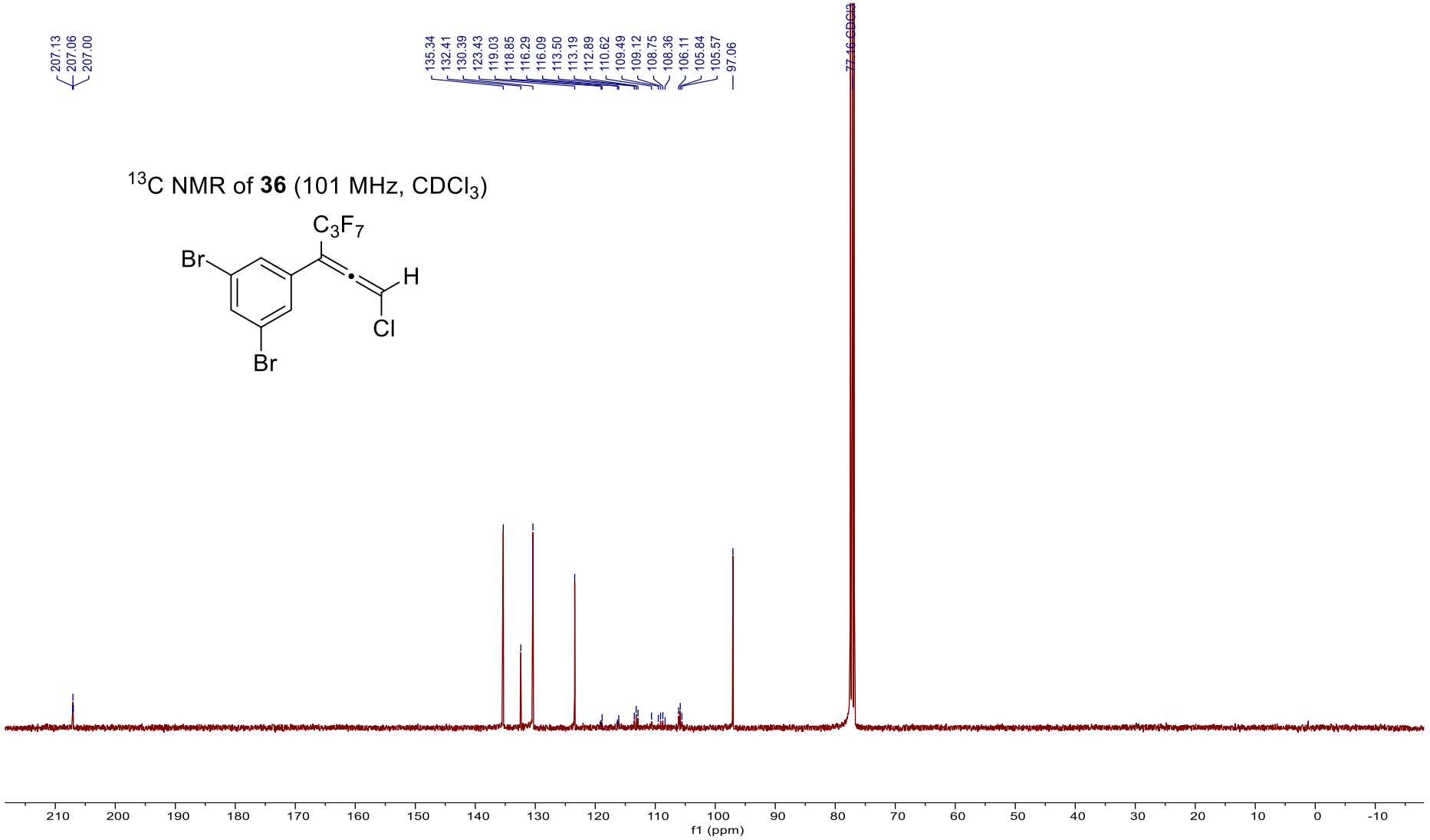

206.52
206.45
206.39
142.58
140.09
129.19
129.08
128.06
127.85
127.64
127.25
119.72
119.39
116.53
116.22
113.96
113.65
113.35
109.32
108.95
108.58
108.32
108.06
107.80
95.91
77.16 CDCl3
^{13}C NMR of **35** (101 MHz, $CDCl_3$)
C_3F_7
H
Ph
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



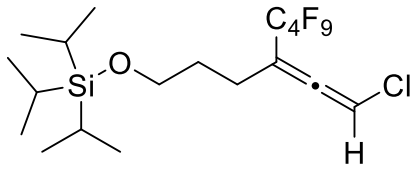
^{1}H NMR of **36** (400 MHz, $CDCl_3$)

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

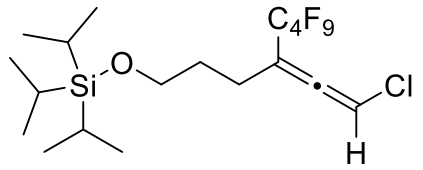


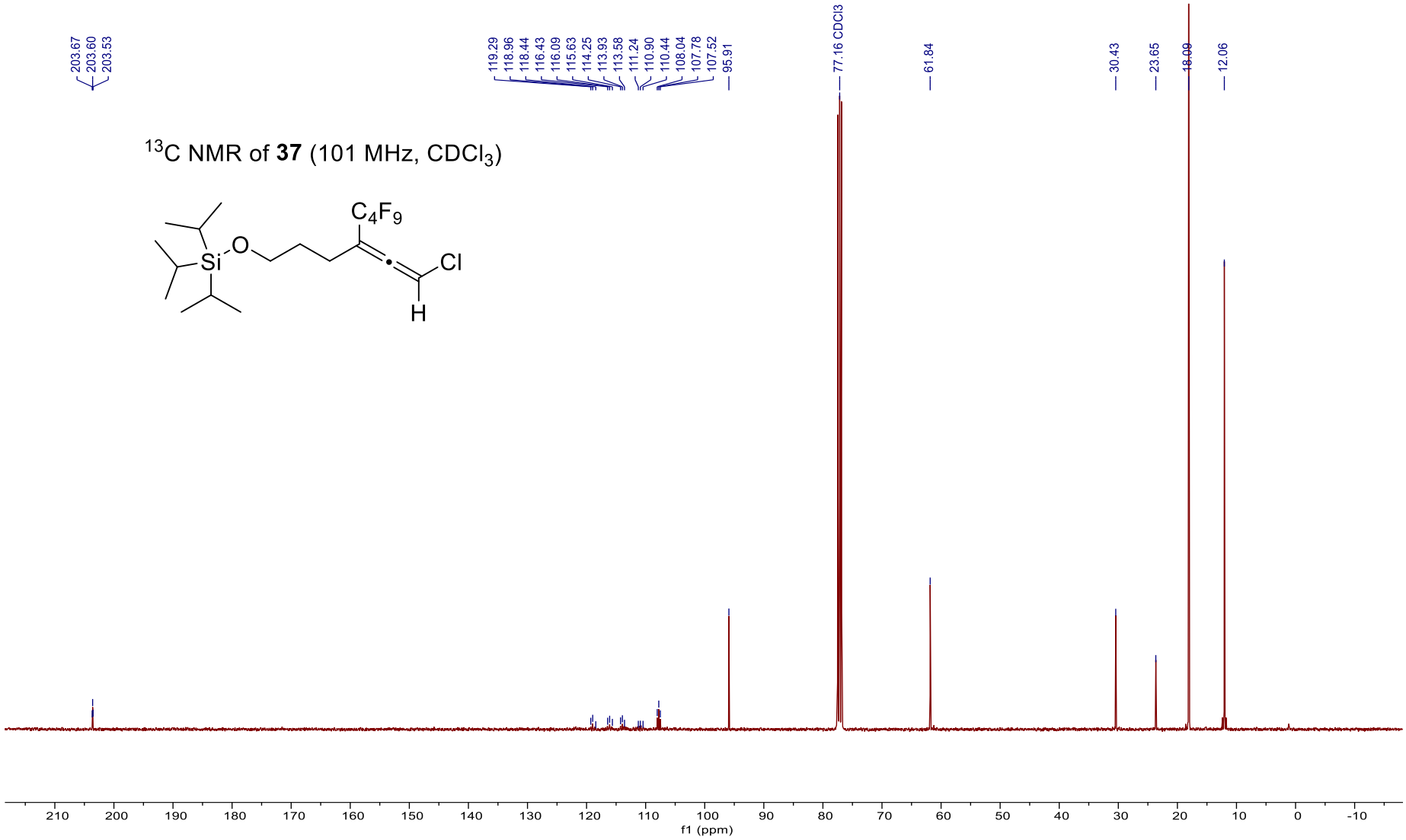

207.13
207.06
207.00
135.34
132.41
130.39
123.43
119.03
118.85
116.29
116.09
113.50
113.19
112.89
110.62
109.49
109.12
108.75
108.36
106.11
105.84
105.57
97.06
77.46 CDCl3
13C NMR of 36 (101 MHz, CDCl3)
C3F7
Br
H
Cl
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

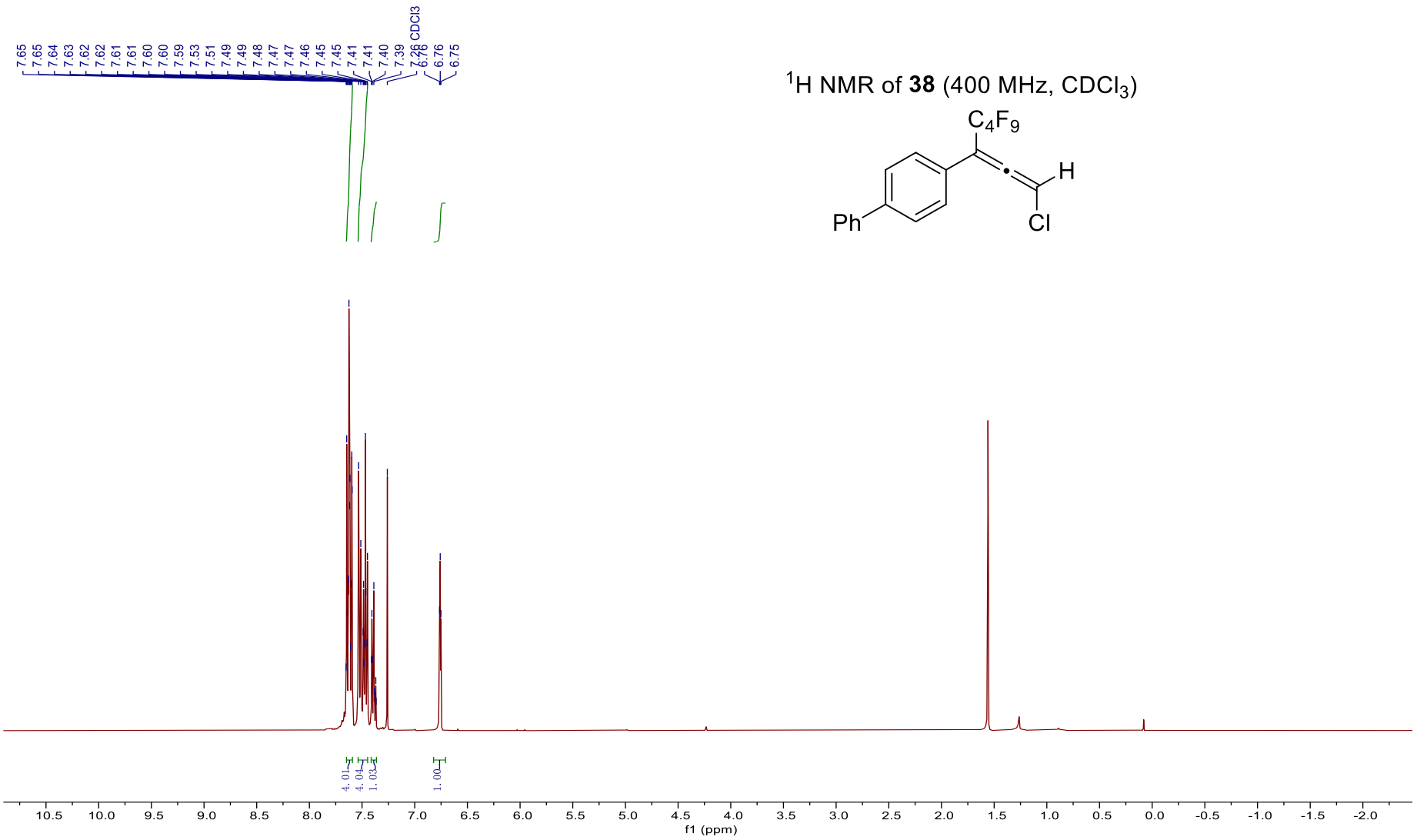
^{1}H NMR of **37** (400 MHz, $CDCl_3$)



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

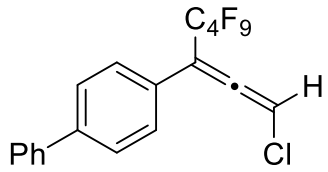


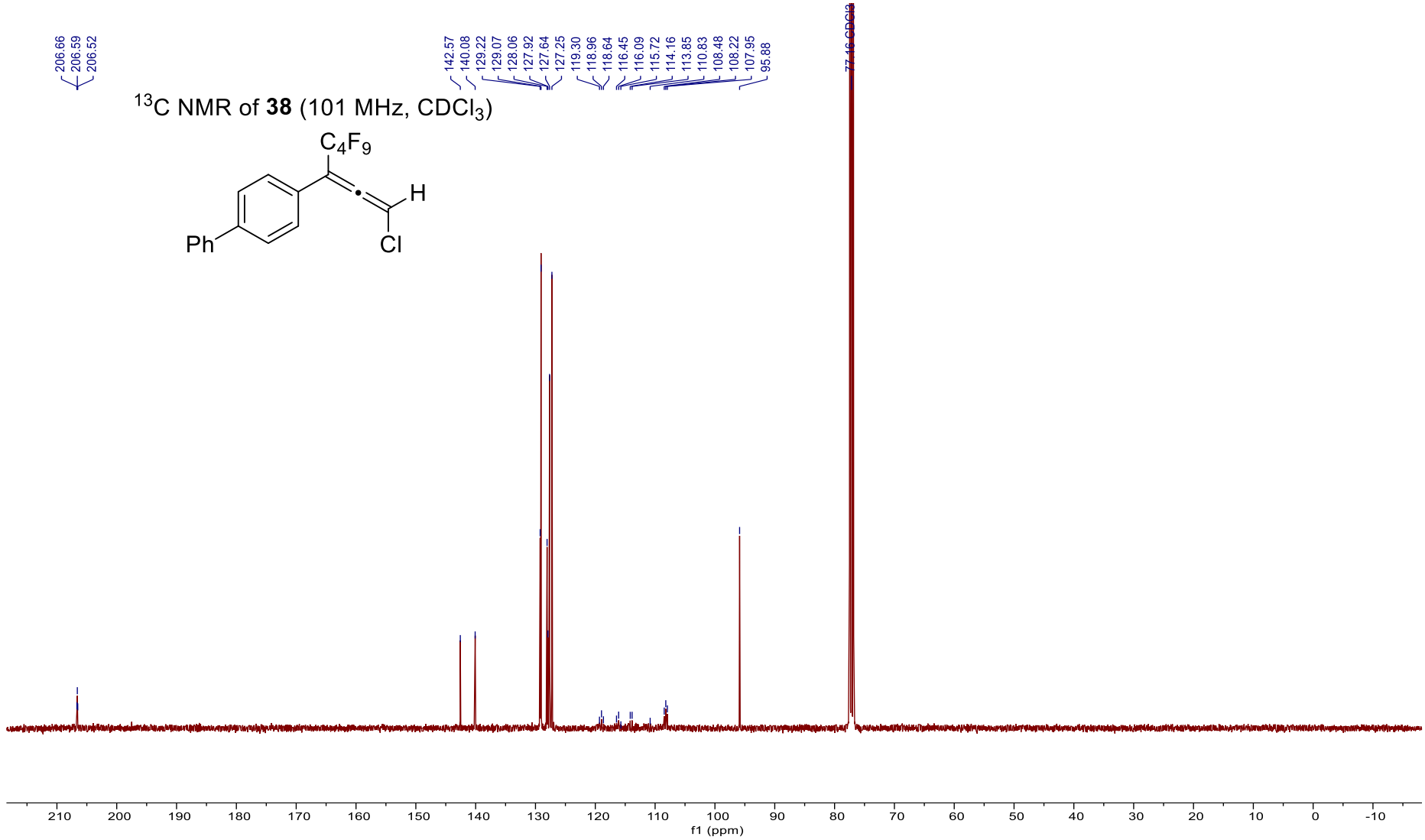

203.67
203.60
203.53
119.29
118.96
118.44
116.43
116.09
115.63
114.25
113.93
113.58
111.24
110.90
110.44
108.04
107.78
107.52
95.91
77.16 CDCl3
61.84
30.43
23.65
18.99
12.06
13C NMR of 37 (101 MHz, CDCl3)
C4F9
Si
O
Cl
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

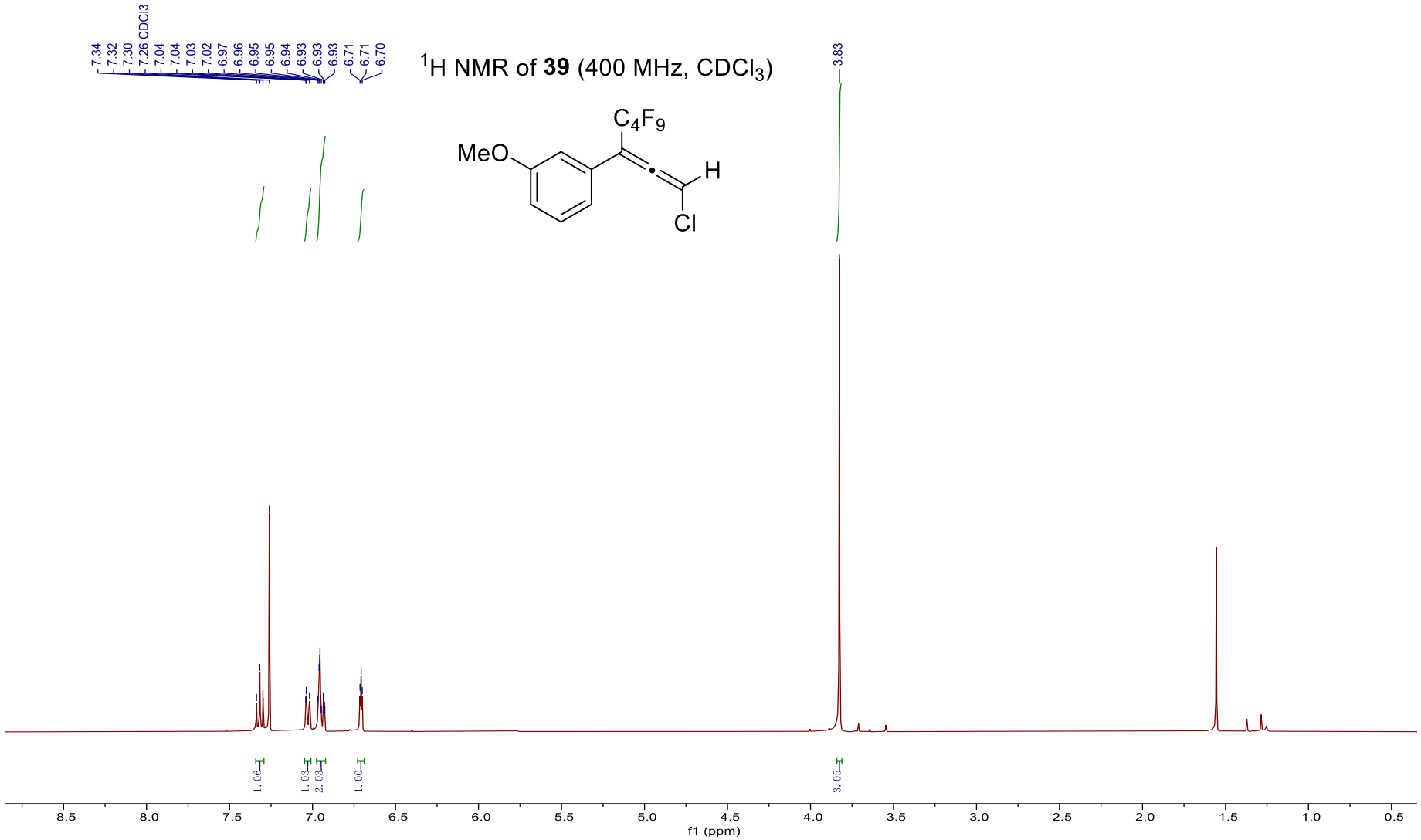


^{1}H NMR of **38** (400 MHz, $CDCl_3$)

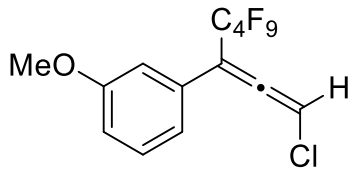
^{19}F NMR of **38** (376 MHz, $CDCl_3$)

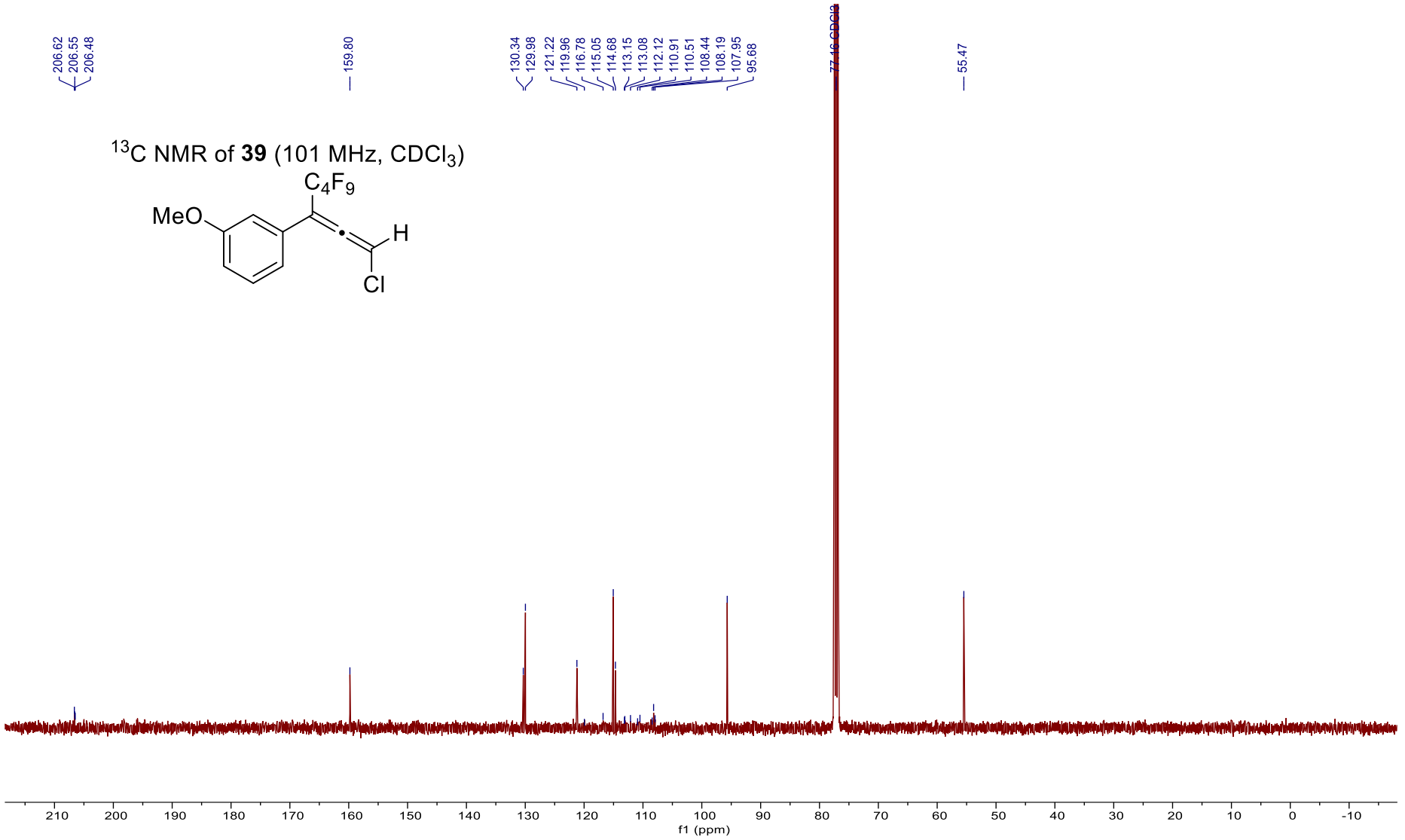


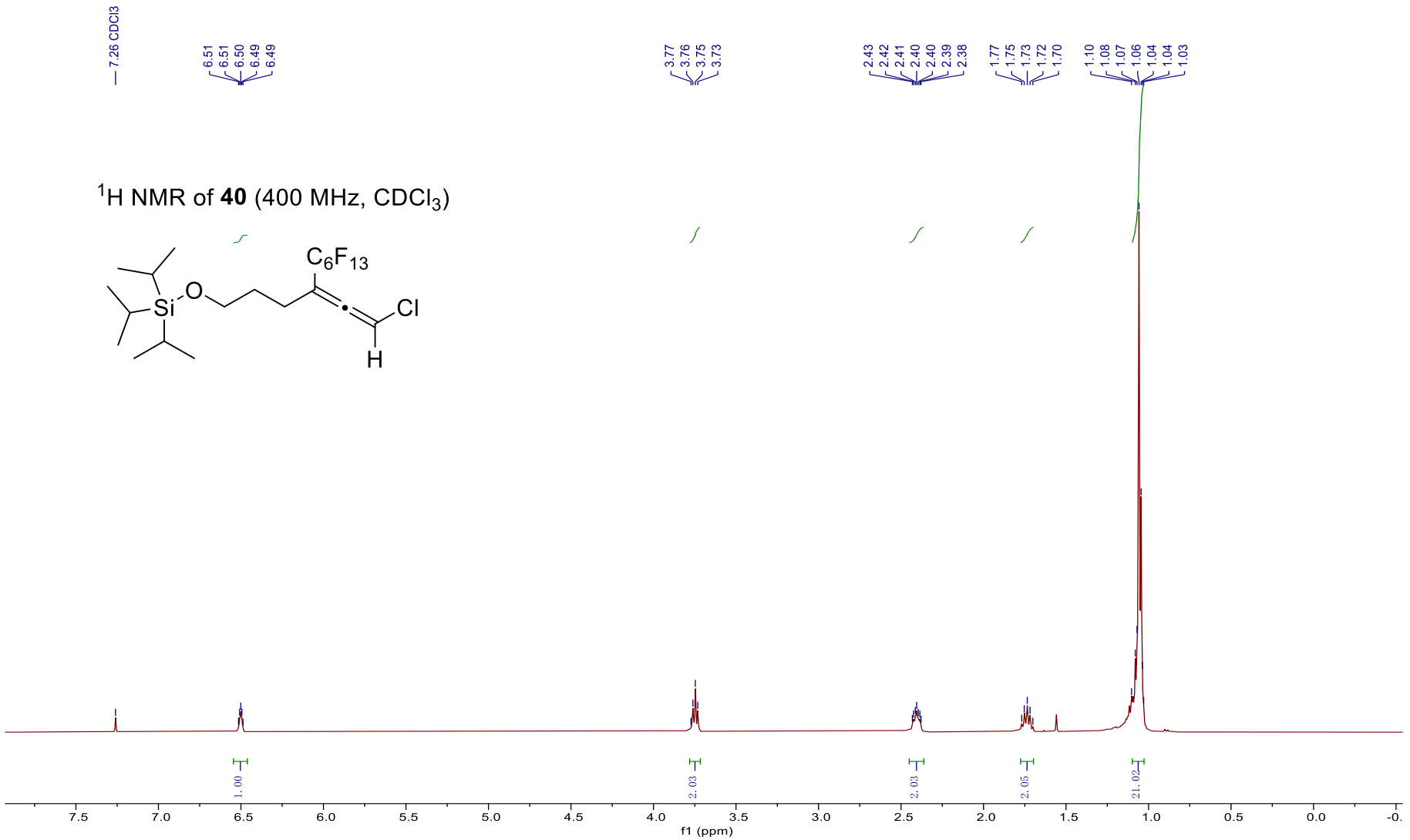

206.66
206.59
206.52
142.57
140.08
129.22
129.07
128.06
127.92
127.64
127.25
119.30
118.96
118.64
116.45
116.09
115.72
114.16
113.85
110.83
108.48
108.22
107.95
95.88
77.16 CDCl3
13C NMR of 38 (101 MHz, CDCl3)
C4F9
H
Ph
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


^{1}H NMR of **39** (400 MHz, $CDCl_3$)
C_4F_9
MeO
H
Cl
7.34
7.32
7.30
7.26 CDCl3
7.04
7.04
7.03
7.02
6.97
6.96
6.95
6.95
6.94
6.93
6.93
6.93
6.71
6.71
6.70
3.83
1.06
1.03
2.03
1.00
3.05
f1 (ppm)

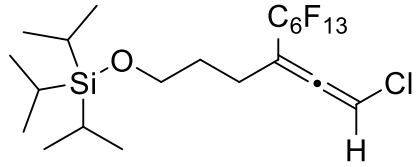
^{19}F NMR of **39** (376 MHz, $CDCl_3$)

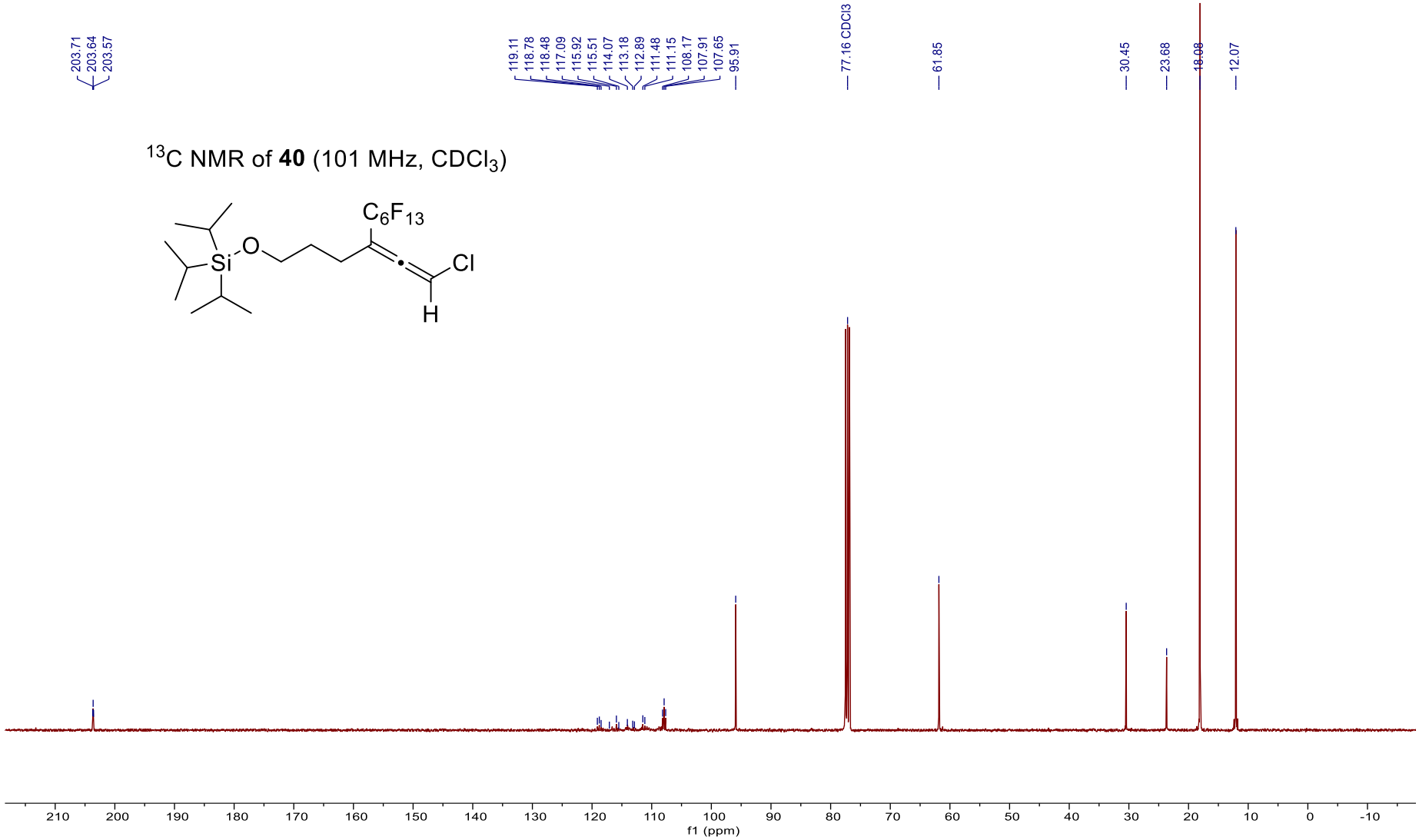


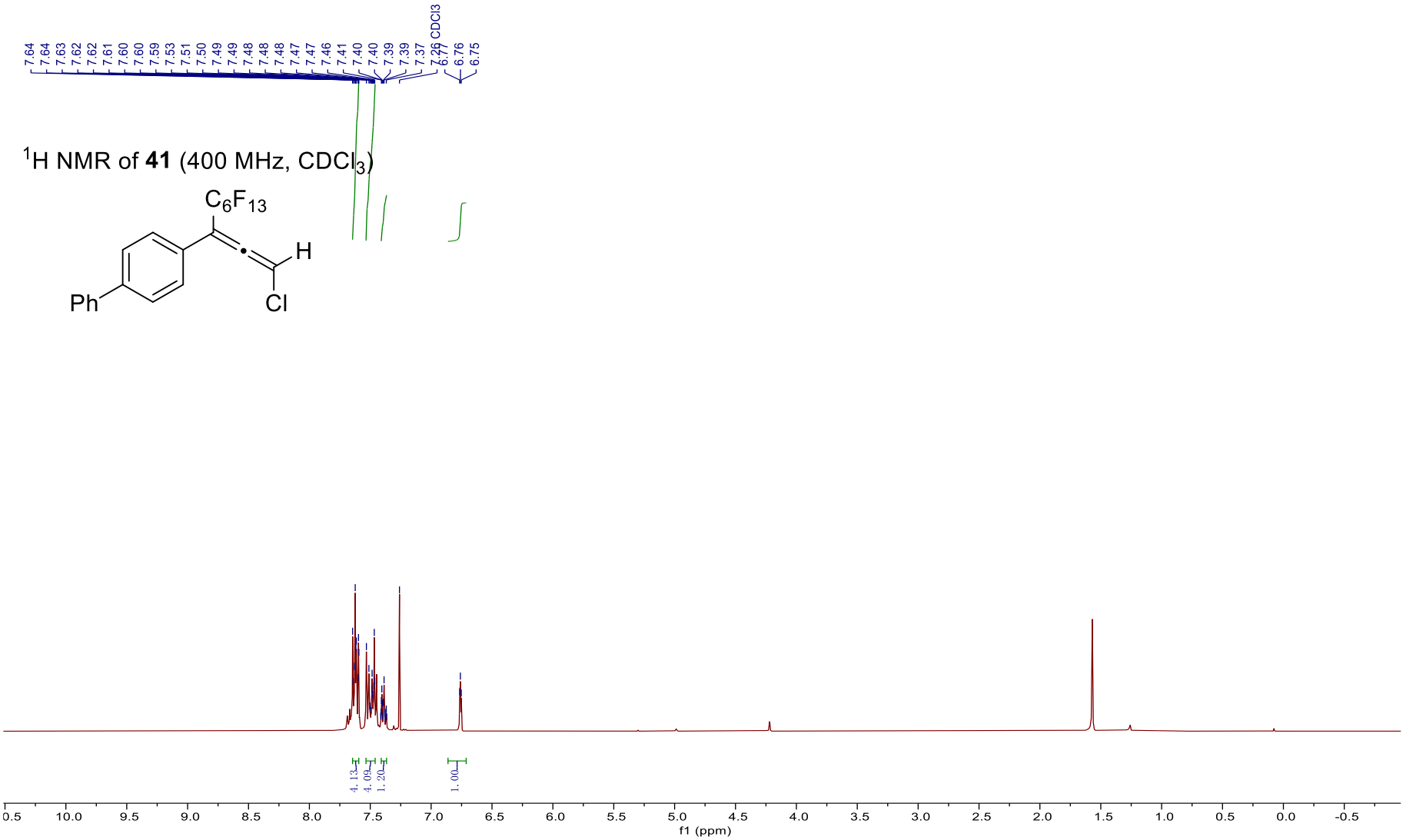

206.62
206.55
206.48
159.80
130.34
129.98
121.22
119.96
116.78
115.05
114.68
113.15
113.08
112.12
110.91
110.51
108.44
108.19
107.95
95.68
77.46 CDCl3
55.47
13C NMR of 39 (101 MHz, CDCl3)
C4F9
MeO
H
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

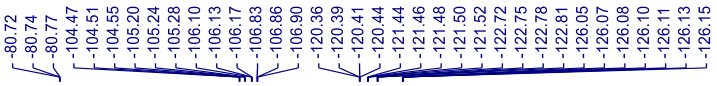

7.26 CDCl3
6.51
6.51
6.50
6.49
6.49
3.77
3.76
3.75
3.73
2.43
2.42
2.41
2.40
2.40
2.39
2.38
1.77
1.75
1.73
1.72
1.70
1.10
1.08
1.07
1.06
1.04
1.04
1.03
1H NMR of 40 (400 MHz, CDCl3)
C6F13
Si
O
Cl
H
1.00
2.03
2.03
2.05
21.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

^{19}F NMR of **40** (376 MHz, $CDCl_3$)

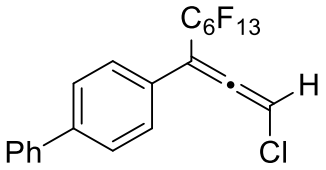


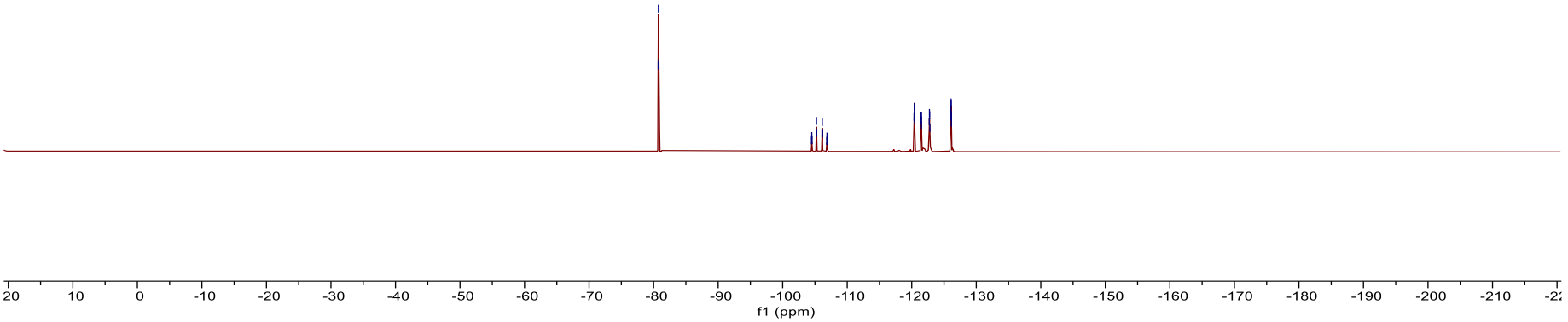

203.71
203.64
203.57
119.11
118.78
118.48
117.09
115.92
115.51
114.07
113.18
112.89
111.48
111.15
108.17
107.91
107.65
95.91
77.16 CDCl3
61.85
30.45
23.68
18.08
12.07
^{13}C NMR of **40** (101 MHz, $CDCl_3$)
C_6F_{13}
Si
O
Cl
H
f1 (ppm)

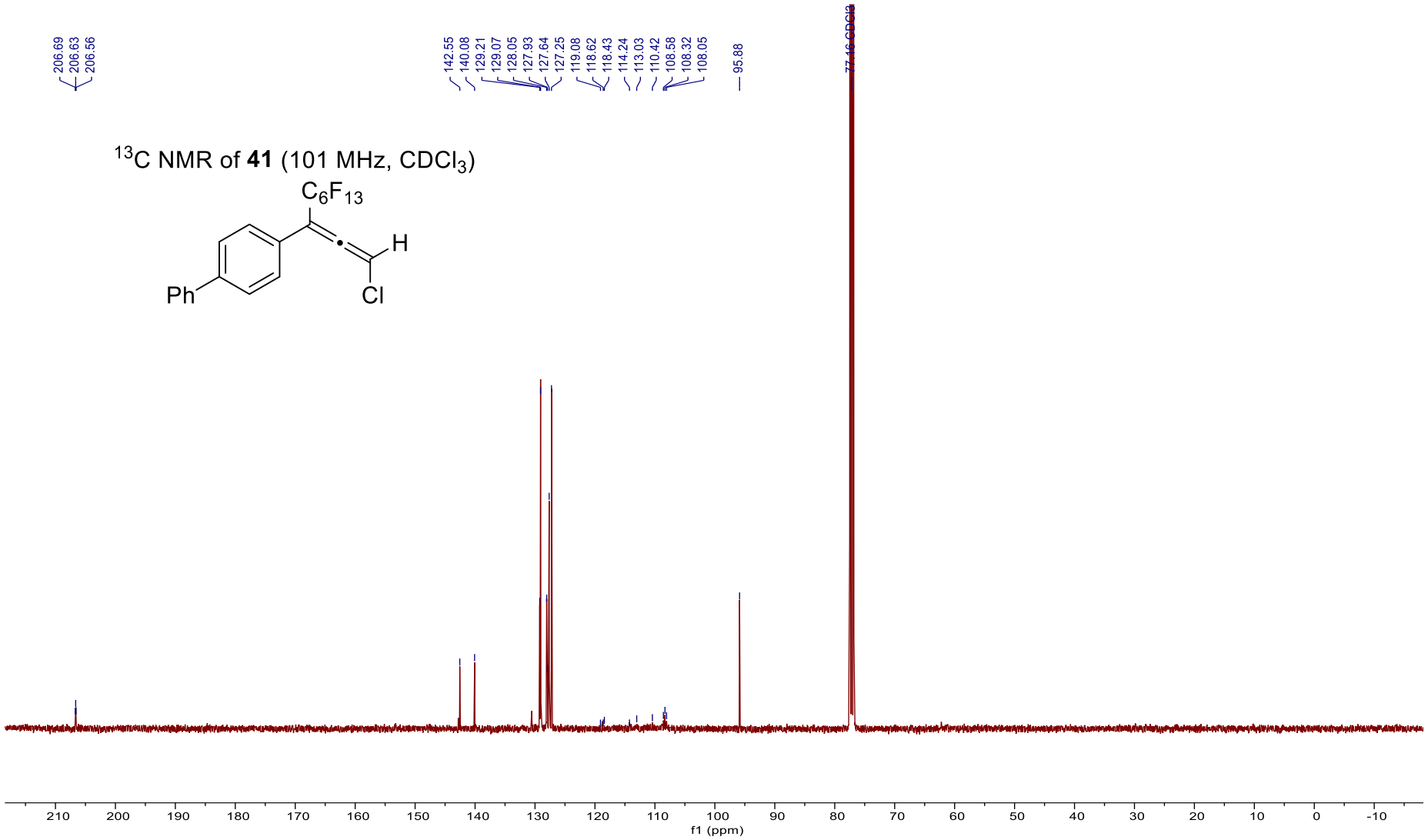

7.64
7.64
7.63
7.62
7.62
7.61
7.60
7.60
7.59
7.53
7.51
7.50
7.49
7.49
7.48
7.48
7.48
7.47
7.47
7.46
7.41
7.40
7.40
7.39
7.39
7.37
7.26 CDCl3
6.77
6.76
6.75
1H NMR of 41 (400 MHz, CDCl3)
C6F13
H
Ph
Cl
4.13
4.09
1.20
1.00
f1 (ppm)



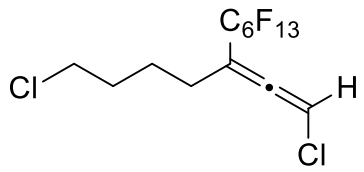
^{19}F NMR of **41** (376 MHz, $CDCl_3$)



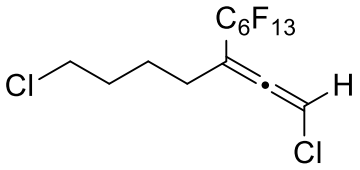


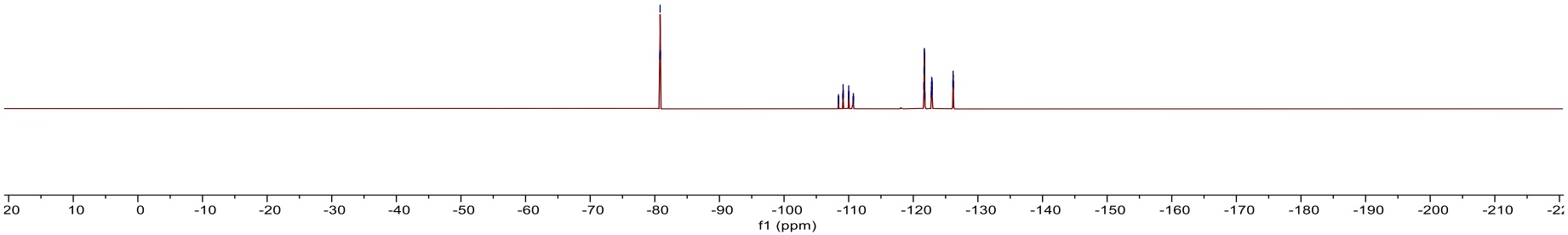

206.69
206.63
206.56
142.55
140.08
129.21
129.07
128.05
127.93
127.64
127.25
119.08
118.62
118.43
114.24
113.03
110.42
108.58
108.32
108.05
95.88
77.16 CDCl3
13C NMR of 41 (101 MHz, CDCl3)
C6F13
H
Ph
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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

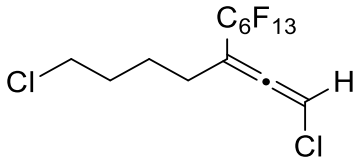


^{19}F NMR of **42** (376 MHz, $CDCl_3$)

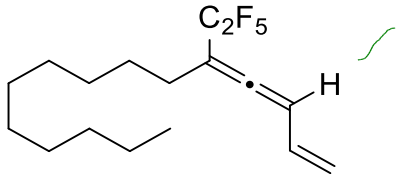




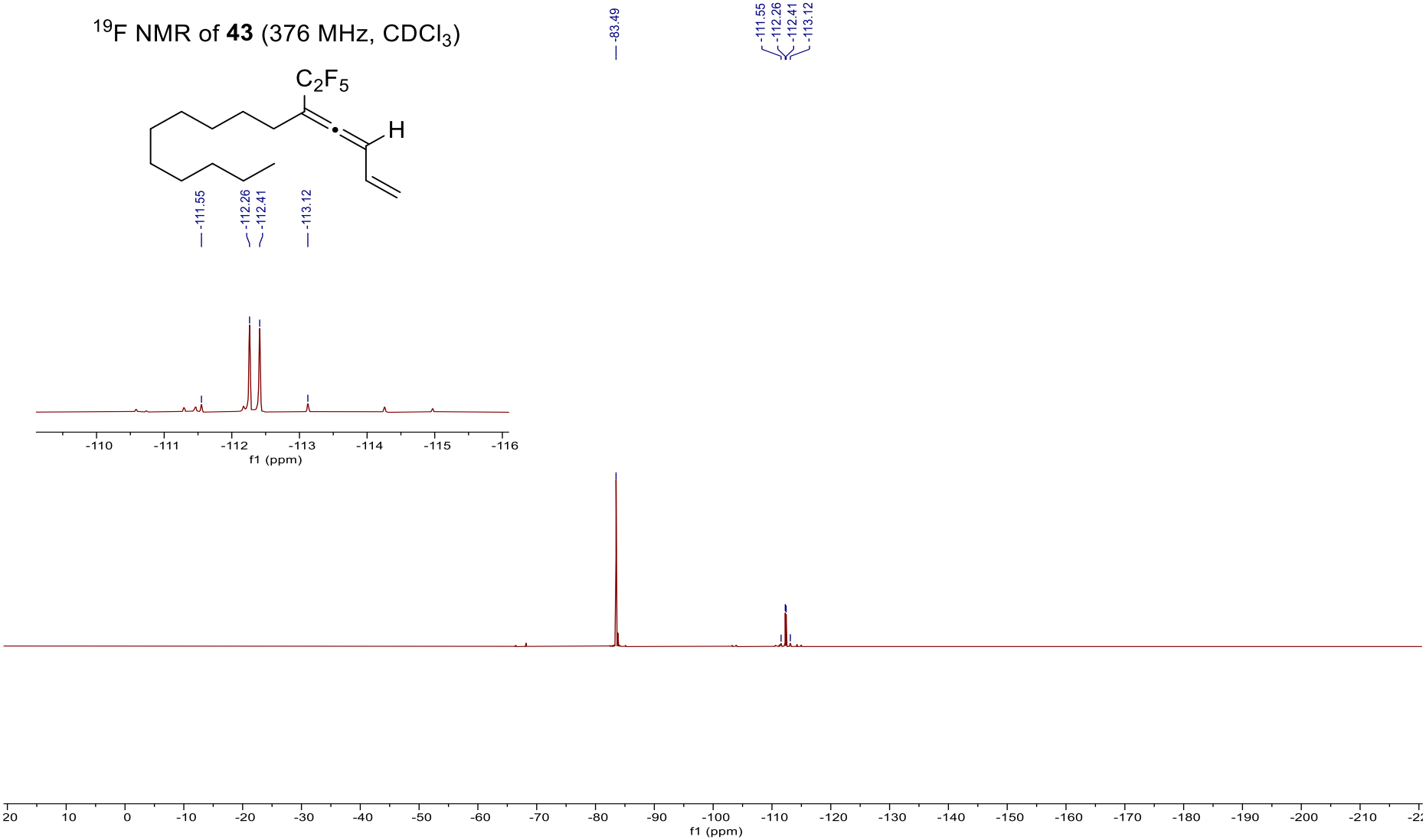
^{13}C NMR of **42** (101 MHz, $CDCl_3$)



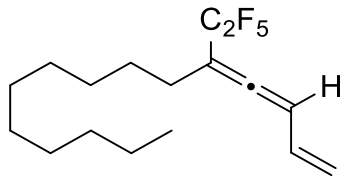
^{1}H NMR of **43** (101 MHz, $CDCl_3$)



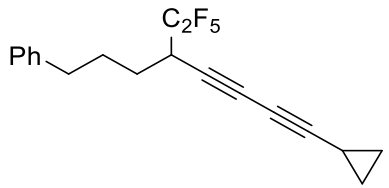
^{19}F NMR of **43** (376 MHz, $CDCl_3$)



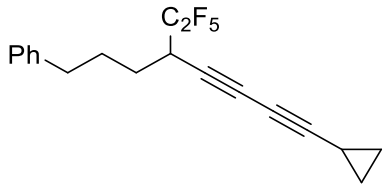
^{13}C NMR of **43** (101 MHz, $CDCl_3$)



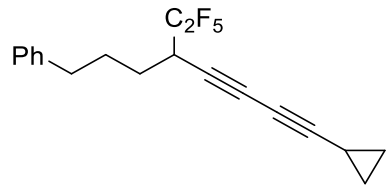
^{1}H NMR of **44** (101 MHz, $CDCl_3$)



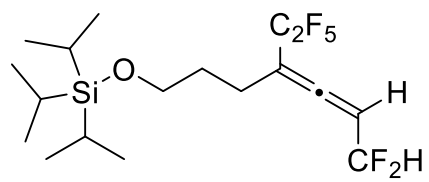
^{19}F NMR of **44** (376 MHz, $CDCl_3$)



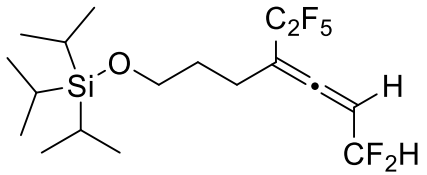
^{13}C NMR of **44** (101 MHz, $CDCl_3$)



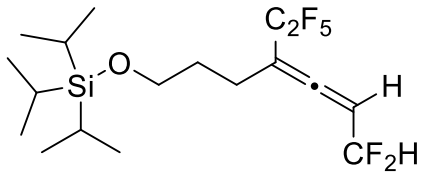
^{1}H NMR of **45** (400 MHz, $CDCl_3$)

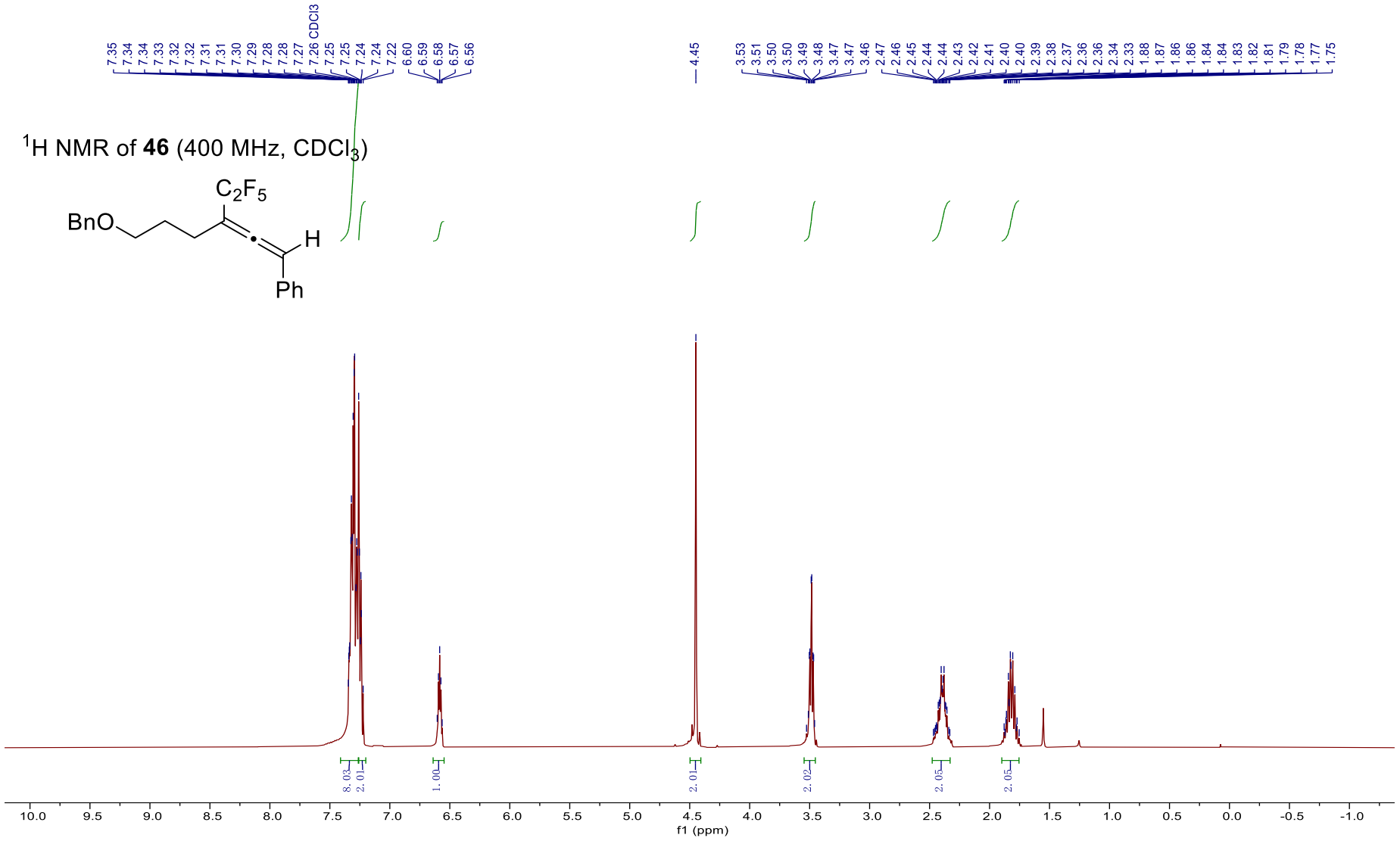


^{19}F NMR of **45** (376 MHz, $CDCl_3$)

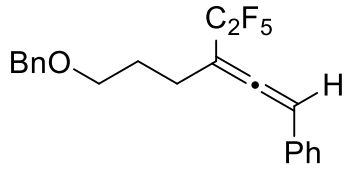


^{13}C NMR of **45** (101 MHz, $CDCl_3$)




^{1}H NMR of **46** (400 MHz, $CDCl_3$)
C_2F_5
BnO
H
Ph
f1 (ppm)

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



205.35
205.28
205.20
138.45
131.82
129.03
128.53
128.45
127.79
127.75
127.44
123.89
123.50
123.12
121.03
120.65
120.27
118.19
117.81
117.42
115.68
115.31
114.95
113.53
113.15
112.78
112.41
110.63
110.25
101.85
101.50
101.24
100.98
77.16 CDCl3
73.15
69.20
27.77
23.40

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