Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Novel photoredox-active group for the generation of fluorinated radicals from difluorostyrenes

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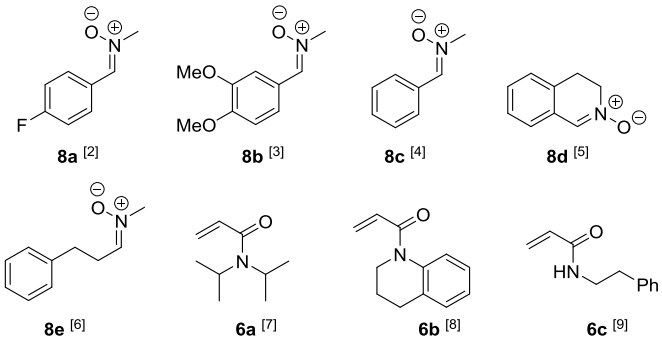
Experimental Procedures

General methods

All reactions were performed under an argon atmosphere. MeCN was distilled twice: from P_2O_5 and CaH_2 and stored over MS 3Å. Column chromatography was carried out employing silica gel (230–400 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or acidic aq $KMnO_4$ solution. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and time-of-flight (TOF) mass analyzer. The measurements were done in a positive ion mode (interface capillary voltage – 4500 V) or in a negative ion mode (3200 V); mass range from m/z 50 to m/z 3000. For irradiation, a strip of light emitting diodes (2835-120LED 1M-Blue, 12V) was used.

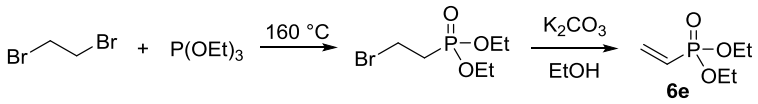
Starting compounds

Silyl enol ethers **4** were prepared according to a literature procedure[1] and were used without purification. Acrylonitrile **6d** and *tert*-butyl acrylate **6f** were purchased from Acros Organics. Nitrones **8a-e**[2-6], acrylamides **6a-c**[7-9] were prepared according to literature procedures:



8a [2] **8b** [3] **8c** [4] **8d** [5] **8e** [6] **6a** [7] **6b** [8] **6c** [9]

Diethyl vinylphosphonate (**6e**) was prepared according to modified literature procedure.[10]

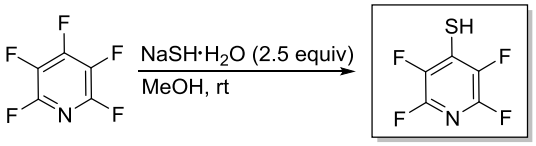


6e

(a) Triethylphosphite (10 mL, 84.8 mmol) was mixed with 1,2-dibromoethane (30 mL, 340 mmol) in a round-bottom flask equipped with a reflux condenser, heated at 160 °C and stirred for 4 h at 160 °C. The reaction mixture was cooled to room temperature, and the product was purified by distillation at reduced pressure affording 8.8 g (42%) of diethyl 2-bromoethylphosphonate as a colorless liquid. Bp 92–95 °C (1.2 Torr).

(b) Diethyl 2-bromoethylphosphonate (8.8 g, 35.9 mmol) was slowly added to a solution of K_2CO_3 (5.45 g, 39.5 mmol) in ethanol (50 mL, ethanol contains 4% of water). The reaction mixture was stirred at room temperature for 6 h. The formed solid was filtered off and washed with ethanol. The solvent was removed under vacuum and the remaining oil was distilled under reduced pressure affording 3.71 g (63%) of diethyl vinylphosphonate **6e** as a colorless liquid. Bp 46–48 °C (0.22 Torr).

Synthesis of 2,3,5,6-tetrafluoropyridine-4-thiol (2) [11]



PyfSH, 2

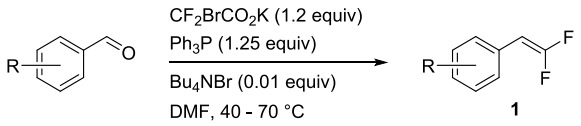
A flask containing a solution of sodium hydrosulfide hydrate NaSH·H_2O (109 g, 1.47 mol) in 200 mL of MeOH was immersed into a room temperature water bath. Pentafluoropyridine (100 g, 0.59 mol) was added dropwise, maintaining the temperature below 30 °C. The resulting cloudy viscous solution was stirred for 20 minutes and volatile components were evaporated under reduced pressure. The solid residue was carefully quenched with concentrated HCl (150 mL) (***Caution: H_2S evolution***). The product was extracted with petroleum ether (100 mL and twice 50 mL). The combined organic phases were evaporated under ambient pressure, and the residue was distilled at 56 Torr collecting the fraction boiling at 70-72 °C (56 Torr) to afford 104 g (96%) of colorless fluid liquid, which solidifies at room temperature. Mp 27-29 °C. Colorless crystals.

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.17 (s, 1H)

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 143.25 (dddd, *J* = 244.6 Hz, 16,6 Hz, 13.9 Hz, 2.4 Hz), 138.6 (dm, *J* = 255.1 Hz), 129.1 (tt, *J* = 19.2, 3.3 Hz)

^{19}F NMR (282 MHz, $CDCl_3$) δ -92.0 – -92.5 (m, 2F), -140.7 – -140.1 (m, 2F)

Synthesis of *gem*-difluorostyrenes 1 (General procedure)

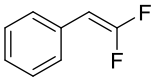


Potassium bromodifluoroacetate (2.56 g, 12 mmol) was placed in a 100 mL 2-neck round-bottom flask and dried under vacuum (ca. 0.5 Torr) at 90°C for 5 hours. The flask was cooled to room temperature, then aldehyde (10 mmol), triphenylphosphine (3.28 g, 12.5 mmol) and Bu_4NBr (32 mg, 0.1 mmol), and dry DMF (20 mL) were added successively. Thermometer and bubble counter were attached to the reaction flask. The mixture was slowly heated up until gas evolution begins (around 40-45 °C). The reaction temperature was adjusted to maintain the gas evolution rate around 1 bubble per second (in case of acceleration, the reaction mixture should be cooled a little bit with tap water bath). As reaction progresses, the bath temperature was slowly increased up to 70 °C (for **1a-i,k**) (or 45 °C for **1j**) and kept at this temperature until the gas evolution ceased (around 3 hours).

Workup for **1a,d,i,j,**: the reaction mixture was entirely re-condensed under vacuum of 1 Torr into a trap cooled with liquid nitrogen; during this, the reaction flask was slowly heated from room temperature to 70 °C. The distillate containing DMF and the product was diluted with 60 mL of water. The bottom layer of difluorostyrene was collected, and the aqueous phase was extracted with pentane (5 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed under reduced pressure. and the residue was distilled under vacuum on Hickman still.

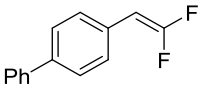
Workup for **1b,c,e,f-h,k**: the reaction mixture was cooled to room temperature, quenched with water (60 mL) and extracted with EtOAc (3×10 mL). The combined organic layers were washed with H_2O_2 (30 wt% in water, 5 mL), brine (4×10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel.

(2,2-Difluorovinyl)benzene (1a) [12,13]



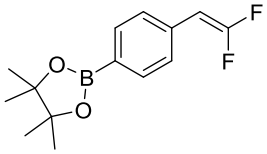
Yield 12.75 g (85%) [107 mmol scale]. Colorless liquid. Bp 114 – 116 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 4H), 7.30 – 7.22 (m, 1H), 5.30 (dd, *J* = 26.8, 3.8 Hz, 1H).
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 156.5 (dd, *J* = 298.1, 288.0 Hz), 130.5 (t, *J* = 6.3 Hz), 128.8, 127.8 (dd, *J* = 6.2, 3.5 Hz), 127.2, 82.3 (dd, *J* = 29.0, 13.6 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -.83.2 (dd, *J* = 31.1, 26.8 Hz, 1F), -85.1 (dd, *J* = 31.1, 3.8 Hz, 1F).

4-(2,2-Difluorovinyl)-1,1'-biphenyl (1b) [12]



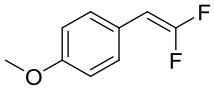
Yield 1.62 g (75%). Colorless crystals. Mp 83–85 °C.
Chromatography: hexanes/EtOAc, 20/1. R_f = 0.36 (hexanes/EtOAc, 20/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 4H), 7.51 – 7.32 (m, 5H), 5.34 (dd, *J* = 26.3, 3.7 Hz, 1H).
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 156.5 (dd, *J* = 298.5, 288.6 Hz), 140.7, 140.0 (t, *J* = 1.8 Hz), 129.5 (t, *J* = 6.4 Hz), 129.0, 128.2 (dd, *J* = 6.3, 3.6 Hz), 127.6, 127.5, 127.1, 82.1 (dd, *J* = 29.2, 13.7 Hz).

2-[4-(2,2-Difluorovinyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1c)



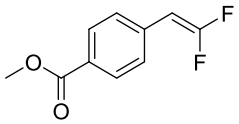
Yield 1.44 g (54%). Colorless oil.
Chromatography: hexanes/EtOAc, 20/1. R_f = 0.26 (hexanes/EtOAc, 20/1). The compound is slightly unstable on silica gel.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.29 (dd, *J* = 27.1, 3.8 Hz, 1H), 1.35 (s, 12H).
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 156.6 (dd, *J* = 299.6, 289.0 Hz), 135.2, 133.3 (t, *J* = 6.6 Hz), 127.0 (dd, *J* = 6.2, 3.5 Hz), 84.0, 82.5 (dd, *J* = 29.1, 13.3 Hz), 25.0.
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.5 (t, *J* = 27.1 Hz, 1F), -83.7 (d, *J* = 27.1 Hz, 1F).
HRMS (ESI): calcd for $C_{14}H_{18}BF_2O_2$ (M+H) 267.1365, found 267.1365; calcd for $C_{14}H_{17}BF_2O_2Na$ (M+Na) 289.1184, found 289.1179.

1-(2,2-Difluorovinyl)-4-methoxybenzene (1d) [12]



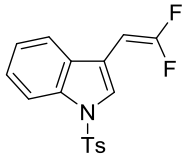
Yield 1.33 g (78%). Colorless oil. Bp 75-76 °C (15 Torr).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 5.30 (dd, *J* = 26.7, 3.9 Hz, 1H), 3.87 (s, 3H).
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 158.7, 156.0 (dd, *J* = 296.3, 286.3 Hz), 128.9 (dd, *J* = 6.2, 3.5 Hz), 122.7 (t, *J* = 6.2 Hz), 114.2, 81.6 (dd, *J* = 29.2, 14.2 Hz), 55.1.
^{19}F NMR (282 MHz, $CDCl_3$) δ -85.7 (dd, *J* = 36.8, 26.7 Hz, 1F), -87.4 (dd, *J* = 36.8, 3.9 Hz, 1F).

Methyl 4-(2,2-difluorovinyl)benzoate (1e) [12]



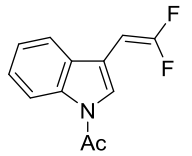
Yield 793 mg (40%). Colorless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 5.32 (dd, *J* = 26.0, 3.6 Hz, 1H), 3.91 (s, 3H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 166.6, 156.8 (dd, *J* = 300.4, 290.6 Hz), 135.1 (t, *J* = 6.7 Hz), 130.0, 128.6, 127.4 (dd, *J* = 6.4, 3.5 Hz), 82.0 (dd, *J* = 29.8, 13.1 Hz), 52.0.

3-(2,2-Difluorovinyl)-1-tosyl-1H-indole (1f) [14]



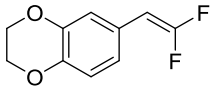
Yield 2.43 g (73%). Colorless crystals. Mp 106–108 °C.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.65 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.32 – 7.19 (m, 3H), 5.40 (d, *J* = 26.7 Hz, 1H), 2.35 (s, 3H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 156.9 (dd, *J* = 296.0, 289.9 Hz), 145.2, 135.3, 134.9, 130.0, 129.5 (d, *J* = 3.3 Hz), 127.0, 125.3, 123.5, 123.4 (dd, *J* = 9.6, 3.9 Hz), 119.2 (s), 113.9, 111.9 (dd, *J* = 6.5, 5.4 Hz), 72.52 (dd, *J* = 32.1, 18.5 Hz), 21.6 (s).

1-[3-(2,2-Difluorovinyl)-1H-indol-1-yl]ethanone (1g) [12]



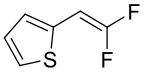
Yield 1.04 g (47%). Colorless crystals.
Chromatography: hexanes/EtOAc, 1/1. R_f = 0.5 (hexanes/EtOAc, 1/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.48 (s, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 5.47 (d, *J* = 27.0 Hz, 1H), 2.67 (s, 3H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 168.5, 156.9 (dd, *J* = 295.6, 290.2 Hz), 135.5, 129.1, 125.9, 123.9, 122.4 (dd, *J* = 9.9, 3.9 Hz), 118.5, 116.9, 111.8 (t, *J* = 5.9 Hz), 72.7 (dd, *J* = 31.7, 18.4 Hz), 24.1.

6-(2,2-Difluorovinyl)-2,3-dihydrobenzo[b][1,4]dioxine (1h) [17]



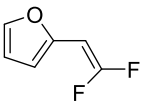
Yield 1.35 g (68%). Colorless oil. Bp (bath temperature) 160-167°C (4 Torr).
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 – 6.79 (m, 3H), 5.18 (dd, *J* = 26.1, 3.8 Hz, 1H), 4.27 (s, 3H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 156.0 (dd, *J* = 297.0, 286.8 Hz), 143.7, 142.8, 123.8 (t, *J* = 6.1 Hz), 121.1 (dd, *J* = 5.9, 3.7 Hz), 117.6, 116.5 (dd, *J* = 6.7, 3.4 Hz), 81.7 (dd, *J* = 29.5, 13.8 Hz), 64.5, 64.5.

2-(2,2-Difluorovinyl)thiophene (1i) [13]



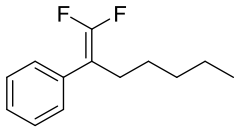
Yield 906 mg (62%). Colorless liquid. Bp 83-84 °C (183 Torr).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (t, *J* = 3.2 Hz, 1H), 7.06 – 7.00 (m, 2H), 5.58 (dd, *J* = 27.0, 2.0 Hz, 1H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 156.2 (dd, *J* = 297.2, 289.0 Hz), 132.2 (t, *J* = 6.8 Hz), 127.3, 126.1 (t, *J* = 5.3 Hz), 125.0 (dd, *J* = 6.0, 3.7 Hz), 77.7 (dd, *J* = 33.5, 17.3 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.5 (t, *J* = 27.0 Hz, 1F), -88.7 (d, *J* = 27.0 Hz, 1F).

2-(2,2-Difluorovinyl)furan (1j) [13,16]



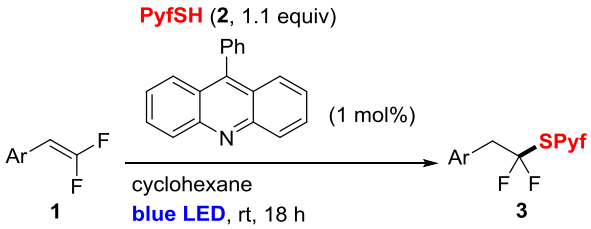
Yield 637 mg (49%). Colorless liquid. Bp 42-44 °C (170 Torr). The compound is prone to explosive polymerization in pure form. It must be kept at temperatures below –30 °C under argon atmosphere. It was used immediately after vacuum distillation (after distillation, the apparatus was filled with argon). NMR spectra were recorded immediately after distillation. The distilled product contained around 5% of pentane. Similar observations concerning the instability of **1j** were reported.[16]
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 1.8 Hz, 1H), 6.43 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.33 (d, *J* = 3.3 Hz, 1H), 5.36 (dd, *J* = 25.4, 1.8 Hz, 1H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 156.3 (dd, *J* = 297.8, 288.2 Hz), 145.6 – 144.7 (m), 142.0 – 141.8 (m), 111.5, 108.2 – 107.8 (m), 74.6 (dd, *J* = 34.7, 16.6 Hz).

(1,1-Difluorohept-1-en-2-yl)benzene (1k) [15]



Yield 1.91 g (91%). Colorless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.22 (m, 5H), 2.46 – 2.35 (m, 2H), 1.46 – 1.21 (m, 6H), 0.88 (t, *J* = 6.4 Hz, 3H).
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 153.8 (t, *J* = 288.0 Hz), 134.1, 128.5, 128.4 (t, *J* = 3.2 Hz), 127.3, 92.7 (dd, *J* = 18.0, 16.5 Hz), 31.4, 27.8, 27.6, 22.5, 14.1.

Addition of thiol 2 to the *gem*-difluorostyrenes 1 (General procedure)



A Schlenk tube containing a stirring bar and 9-phenylacridine (13 mg, 1 mol%) was evacuated and filled with argon. Then, freshly distilled cyclohexane (5 mL), difluorostyrene **1** (5 mmol) and 2,3,5,6-tetrafluoropyridine-4-thiol **2** (1 g, 5.5 mmol) were added successively. The reaction mixture was irradiated for 18 hours with 465 nm LED. For **3c,e**, another portion of 9-phenylacridine (13 mg, 1 mol%) was added, and irradiation was continued for additional 18 hours. During irradiation, the mixture was cooled with tap water (see Figure S1 for the reaction setup). For the workup, saturated aqueous solution of $Zn(OAc)_2$ (1 mL) and water (10 mL) were added. The mixture was extracted with ethyl acetate/hexane (1/3, 3×4 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under vacuum. The crude material was purified by flash column chromatography on silica gel [for **3a,b,d,f-h,j,k**] or by recrystallization [for **3e,c**] or by high vacuum distillation [for **3i**].

The procedure for synthesis of **3a** was also performed on 20 mmol scale of styrene **1a** with the same setup (5 runs). Isolated yields of **3a** were 92 – 99%.

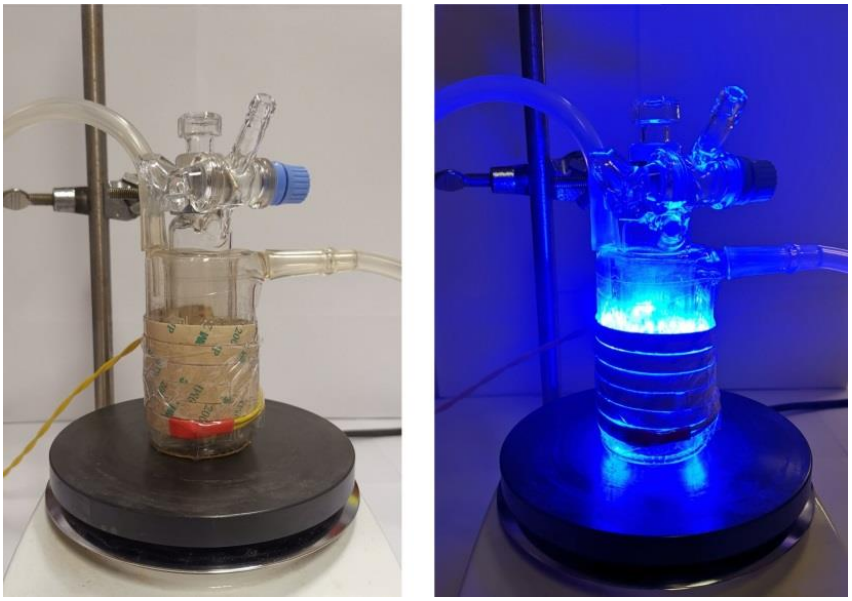
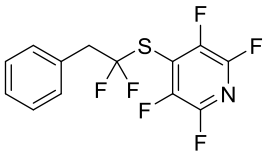


Figure S1. Setup for 5 to 20 mmol scale reactions.

4-[(1,1-Difluoro-2-phenylethyl)thio]-2,3,5,6-tetrafluoropyridine (3a)



Yield 1.53 g (95%). Colorless crystals. Mp 67-69 °C.

Chromatography: hexanes/EtOAc, 10/1. R_f = 0.5 (hexanes/EtOAc, 10/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 5H), 3.57 (t, *J* = 14.6 Hz, 2H).
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 144.8 – 144.3 (m), 142.8 – 142.2 (m), 130.6, 128.9, 128.6, 128.5 (t, *J* = 287.5 Hz), 121.1 – 120.7 (m), 45.7 (t, *J* = 22.8 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -67.4 (tt, *J* =14.6, 7.0 Hz, 2F), -89.4 – -89.8 (m, 2F), -132.24 – -132.60 (m, 2F).
HRMS (ESI): calcd for $C_{13}H_8F_6NS$ (M+H) 324.0276, found 324.0275.

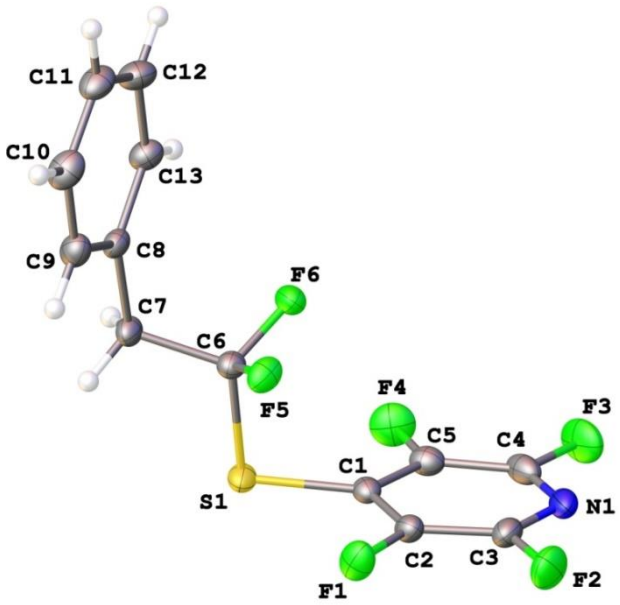
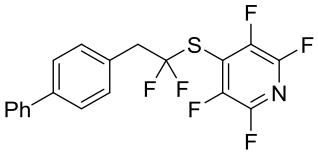


Figure S2. OLEX diagram of compound **3a** (CCDC 1947115).

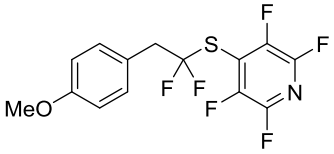
4-([2-([1,1'-Biphenyl]-4-yl)-1,1-difluoroethyl]thio)-2,3,5,6-tetrafluoropyridine (3b)



Yield 1.82 g (91%). Colorless crystals. Mp 105 – 107 °C.

Chromatography: hexanes/EtOAc, 20/1. R_f = 0.27 (hexanes/EtOAc, 20/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 4H), 7.52 – 7.34 (m, 5H), 3.62 (t, *J* = 14.5 Hz, 2H).
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 145.7 – 144.7 (m), 142.5 – 141.5 (m,), 141.5, 140.5, 131.0, 129.5 (t, *J* = 3.6 Hz), 129.0, 128.5 (t, *J* = 287.0 Hz), 127.7, 127.6, 127.2, 121.3 – 120.4 (m), 45.3 (t, *J* = 22.9 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -67.3 (tt, 14.5, 7.0 Hz, 2F), -89.3 – -89.7 (m, Hz, 2F), -132.00 – -132.54 (m, 2F).
HRMS (ESI): calcd for $C_{19}H_{12}F_6NS$ (M+H) 400.0589, found 400.0587.

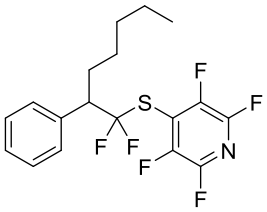
4-([1,1-Difluoro-2-(4-methoxyphenyl)ethyl]thio)-2,3,5,6-tetrafluoropyridine (3d)



Yield 1.55 g (88%). Colorless oil.

Chromatography: hexanes/EtOAc, 10/1. R_f = 0.23 (hexanes/EtOAc, 10/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H), 3.52 (t, *J* = 14.5 Hz, 2H).
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 159.9, 145.6 – 144.8 (m), 142.3 – 141.3 (m), 131.7, 128.8 (t, *J* = 287.2 Hz), 122.5 (t, *J* = 3.8 Hz), 121.5 – 120.6 (m), 114.3, 55.4, 44.9 (t, *J* = 22.9 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -67.6 (tt, *J* = 14.5, 7.0 Hz, 2F), -89.6 – -90.0. (m, 2F), -132.2 – -132.7 (m, 2F).
HRMS (ESI): calcd for $C_{14}H_{10}F_6NOS$ (M+H) 354.0382, found 354.0372.

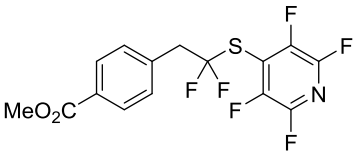
4-[(1,1-Difluoro-2-phenylheptyl)thio]-2,3,5,6-tetrafluoropyridine (3k)



Yield 1.63 g (83%). Colorless oil.

Chromatography: hexanes/CH_2Cl_2, 5/1. R_f = 0.25 (hexanes/CH_2Cl_2, 5/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 5H), 3.49 – 3.26 (m, 1H), 2.16 – 2.00 (m, 1H) 1.99 – 1.83 (m, 1H), 1.38 – 1.11 (m, 6H), 0.92 – 0.78 (m, 3H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.4 – 144.7 (m), 142.2 – 141.2 (m), 135.3 (d, *J* = 5.4 Hz), 130.6 (dd, *J* = 292.9, 289.5 Hz), 129.4, 128.8, 128.5, 121.8 – 121.1 (m), 55.1 (t, *J* = 20.6 Hz), 31.4, 29.1 (t *J* = 2.5 Hz), 26.5, 22.3, 13.9 (d, *J* = 3.5 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -70.1 (dm, *J* = 188.6 Hz, 1F), -74.3 (dm, *J* = 188.6 Hz, 1F), -89.7 – -90.1 (m, 2F), -132.3 – -132.8 (m, 2F).
HRMS (ESI): calcd for $C_{18}H_{18}F_6NS$ (M+H) 394.1059, found 394.1068.

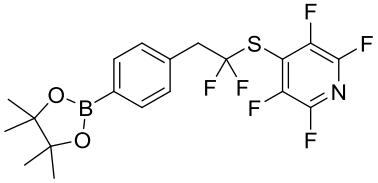
Methyl 4-(2,2-difluoro-2-[(perfluoropyridin-4-yl)thio]ethyl)benzoate (3e)



Yield 1.24 g (65%). Colorless crystals. Mp 59 – 61 °C.

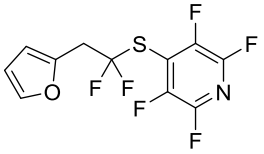
Chromatography: hexanes/EtOAc, 5/1. R_f = 0.33 (hexanes/EtOAc, 5/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 3.93 (s, 3H), 3.62 (t, *J* = 14.5 Hz, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 166.7, 145.6 – 144.8 (m), 142.3 – 141.3 (m), 135.5 (t, *J* = 3.5 Hz), 130.7, 130.5, 130.1, 128.0 (t, *J* = 287.3 Hz), 121.1 – 119.9 (m), 52.4, 45.5 (t, *J* = 23.0 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -67.5 (tt, *J* = 14.5, 7.0 Hz, 2F), -89.1 – -89.5 (m, *J* = 28.0, 12.6 Hz, 2F), -132.1 – -132.5 (m, 2F).
HRMS (ESI): calcd for $C_{15}H_9F_6NO_2SNa$ (M+Na) 404.0150, found 404.0153.

4-[(1,1-Difluoro-2-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ethyl)thio]-2,3,5,6-tetrafluoropyridine (3c)



Yield 1.64 g (73%). Colorless crystals. Mp 160 – 162 °C.
The compound was unstable on silica or alumina, purified by recrystallization from methanol.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 3.57 (t, *J* = 14.5 Hz, 3H), 1.36 (s, 12H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.6 – 144.9 (m), 142.3 – 141.4 (m), 135.3, 133.5 (t, *J* = 3.6 Hz), 129.9, 128.4 (t, *J* = 287.6 Hz), 121.3 – 120.5 (m), 84.1, 45.8 (t, *J* = 22.8 Hz), 25.0.
^{19}F NMR (282 MHz, $CDCl_3$) δ -67.2 (tt, *J* = 14.5, 7.0), -89.4 – -89.8 (m, *J* = 28.3, 12.8 Hz), -132.1 – -132.6 (m).
HRMS (ESI): calcd for $C_{19}H_{18}BF_6NO_2SNa$ (M+Na) 472.0951, found 472.0958; calcd for $C_{19}H_{18}BF_6NO_2SK$ (M+K) 488.0691, found 488.0679.

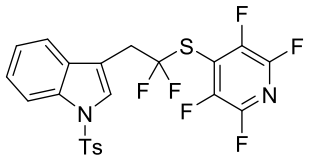
4-**([1,1-Difluoro-2-(furan-2-yl)ethyl]thio)-2,3,5,6-tetrafluoropyridine (3j)**



Yield 157 mg (10%). Colorless crystals. Mp 30 – 32 °C.

Chromatography: hexanes/EtOAc, 10/1. R_f = 0.41 (hexanes/EtOAc, 10/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 1H), 6.42 – 6.37 (m, 2H), 3.63 (t, *J* = 13.4 Hz, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.6 – 144.9 (m), 144.7 (t, *J* = 5.2 Hz), 143.5, 142.3 – 141.4 (m), 127.4 (t, *J* = 287.8 Hz), 121.0 – 120.3 (m), 111.1 (s), 111.0, 38.7 (t, *J* = 25.5 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -67.5 (tt, *J* = 13.4, 6.8 Hz, 2F), -89.3 – -89.7 (m, 2F), -132.1 – -132.6 (m, 2F).
HRMS (ESI): calcd for $C_{11}H_6F_6NOS$ (M+H) 314.0069, found 314.0074; calcd for $C_{11}H_5F_6NOSNa$ (M+Na) 335.9888, found 335.9875.

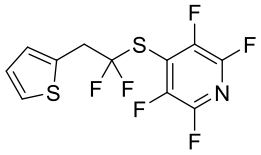
3-(2,2-Difluoro-2-[(perfluoropyridin-4-yl)thio]ethyl)-1-tosyl-1*H*-indole (3f)



Yield 2.40 g (93%). Colorless crystals. Mp 91 – 93 °C.

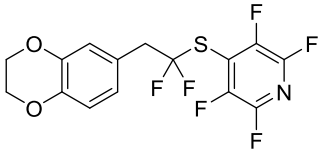
Chromatography: hexanes/EtOAc, 10/1. R_f = 0.18 (hexanes/EtOAc, 10/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.70 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.27 (m, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 3.69 (t, *J* = 14.0 Hz, 2H), 2.35 (s, 3H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.4, 145.3 – 144.9 (m), 142.3 – 141.3 (m), 135.2, 135.1, 130.3, 130.1, 128.5 (t, *J* = 287.8 Hz), 127.0, 126.8, 125.4, 123.7, 121.0 – 120.3 (m), 119.6, 113.9, 111.9 (t, *J* = 4.3 Hz), 35.6 (t, *J* = 24.9 Hz), 21.7.
^{19}F NMR (282 MHz, $CDCl_3$) δ -66.7 (tt, *J* = 14.0, 6.7 Hz, 2F), -89.2 – -89.5 (m, 2F), -132.0 – -132.7 (m, 2F).
HRMS (ESI): calcd for $C_{22}H_{14}F_6N_2O_2S_2Na$ (M+Na) 539.0293, found 539.0295; calcd for $C_{22}H_{14}F_6N_2O_2S_2K$ (M+K) 555.0032, found 555.0035.

4-([1,1-Difluoro-2-(thiophen-2-yl)ethyl]thio)-2,3,5,6-tetrafluoropyridine (3i)



Yield 971 mg (59%). Colorless crystals. Mp 26 – 28 °C.
Compound was purified by distillation on Hickman still head. Bath temperature 134 – 140°C, 0.28 Torr.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 5.0 Hz, 1H), 7.09 (d, *J* = 3.2 Hz, 1H), 7.04 (dd, *J* = 5.0, 3.2 Hz, 1H), 3.79 (t, *J* = 13.8 Hz, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.6 – 144.8 (m), 142.4 – 141.3 (m), 131.2 (t, *J* = 4.2 Hz), 129.5, 127.9 (t, *J* = 287.7 Hz), 127.4, 127.0, 121.1 – 120.3 (m), 40.0 (t, *J* = 25.1 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -68.3 (tt, *J* = 13.8, 6.6 Hz, 2F), -89.3 – -89.7 (m, 2F), -132.1 – -132.5 (m, 2F).
HRMS (ESI): calcd for $C_{11}H_5F_6NS_2Na$ (M+Na) 351.9660, found 351.9644.

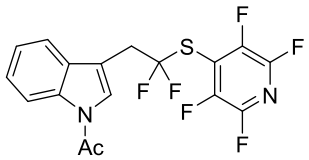
4-([2-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-1,1-difluoroethyl]thio)-2,3,5,6-tetrafluoropyridine (3h)



Yield 1.62 g (85%). Colorless crystals. Mp 84 – 86 °C.

Chromatography: hexanes/EtOAc, 5/1. R_f = 0.32 (hexanes/EtOAc, 5/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 – 6.75 (m, Hz, 3H), 4.27 (s, 4H), 3.44 (t, *J* = 14.4 Hz, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.6 – 144.8 (m), 144.0, 143.8, 142.4 – 141.1 (m), 128.7 (t, *J* = 287.8 Hz), 123.6, 123.5 (t, *J* = 4.0 Hz), 121.5 – 120.8 (m), 119.4, 117.7, 64.50, 64.46, 45.1 (t, *J* = 22.9 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -67.3 (tt, *J* = 14.4, 6.9 Hz, 2F), -89.5 – -89.9 (m, 2F), -132.1 – -132.6 (m, 2F)
HRMS (ESI): calcd for $C_{15}H_9F_6NO_2SNa$ (M+Na) 404.0150, found 404.0148.

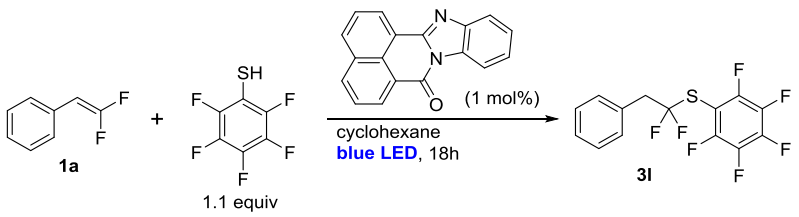
1-(3-(2,2-Difluoro-2-[(perfluoropyridin-4-yl)thio)ethyl]-1*H*-indol-1-yl)ethanone (3g)



Yield 1.09 g (54%). Colorless crystals. Mp 125 – 127 °C. Reaction was conducted in CH_2Cl_2.

Chromatography: hexanes/EtOAc, 3/1. R_f = 0.37 (hexanes/EtOAc, 3/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.51 (s, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 3.69 (t, *J* = 14.2 Hz, 2H), 2.66 (s, 3H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 168.4, 145.8 – 144.5 (m), 142.6 – 140.7 (m), 135.8, 129.9, 128.5 (t, *J* = 287.4 Hz), 126.0, 125.7, 121.0 – 120.2 (m), 119.0, 116.8, 111.8 (t, *J* = 4.1 Hz), 35.7 (t, *J* = 24.9 Hz), 24.1.
^{19}F NMR (282 MHz, $CDCl_3$) δ -66.6 (tt, *J* = 14.2, 6.8 Hz, 2F), -89.2 – -89.6 (m, 2F), -132.2 – -132.6 (m).
HRMS (ESI): calcd for $C_{17}H_{11}F_6N_2OS$ (M+H) 405.0491, found 405.0487; calcd for $C_{17}H_{10}F_6N_2OSNa$ (M+Na) 427.0310, found 427.0306.

Synthesis of (1,1-difluoro-2-phenylethyl)(perfluorophenyl)sulfane (3l).[18]



The Schlenk tube containing a stirring bar and 7*H*-benzo[de]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one (13.5 mg, 1 mol%) was evacuated and filled with argon. Then, freshly distilled cyclohexane (10 mL), difluorostyrene **1a** (701 mg, 5 mmol) and pentafluorobenzenethiol (1.1 g, 5.5 mmol) were added successively. The reaction mixture was irradiated for 18 hours with 465 nm LED; during irradiation the mixture was cooled with room temperature water (see Figure S1 for the reaction setup). For the workup, saturated aqueous solution of $Zn(OAc)_2$ (1 mL) and water (10 mL) were added. The mixture was extracted with ethyl acetate/hexane (1/3, 3×4 mL). The combined organic phases were dried with Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel. Yield 1.565 g (92%). Colorless crystals. Mp 51 – 52 °C.

Chromatography: hexanes/EtOAc, 20/1. R_f = 0.41 (hexanes/EtOAc, 20/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 5H), 3.53 (t, *J* = 14.7 Hz, 2H).
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 148.8 (dm, *J* = 243.9 Hz), 143.5 (dm, *J* = 258.8 Hz), 137.9 (dm, *J* = 256.5 Hz), 131.1 (t, *J* = 3.3 Hz), 130.6, 128.8, 128.4 (t, *J* = 284.0 Hz), 128.4, 101.5 – 100.7 (m), 45.2 (t, *J* = 23.1 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -69.9 – -70.1 (m, 2F), -129.8 (d, *J* = 21.3 Hz, 2F), -148.6 (t, *J* = 21.3 Hz, 1F), -160.9 – -161.3 (m, 2F).

Reactions of sulfides 3 with silyl enol ethers 4 (General procedure)

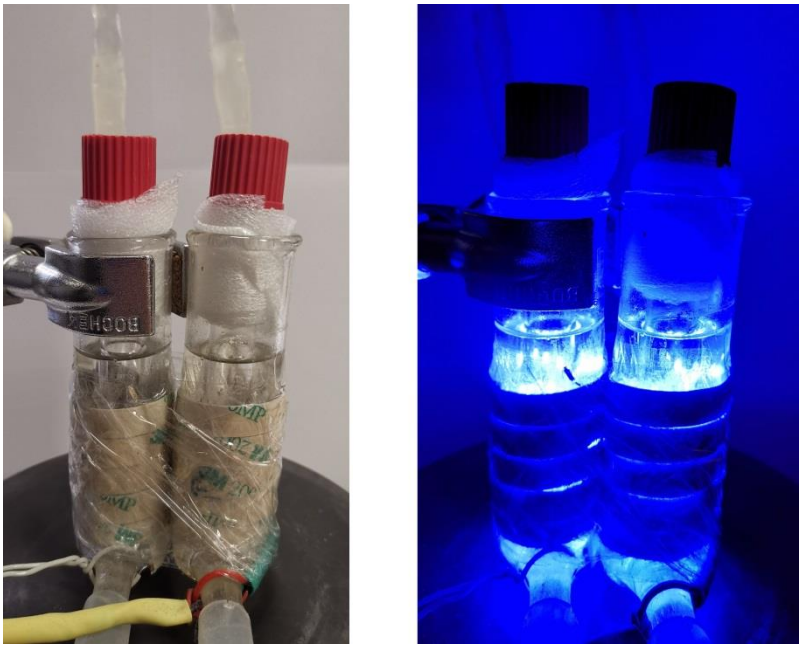
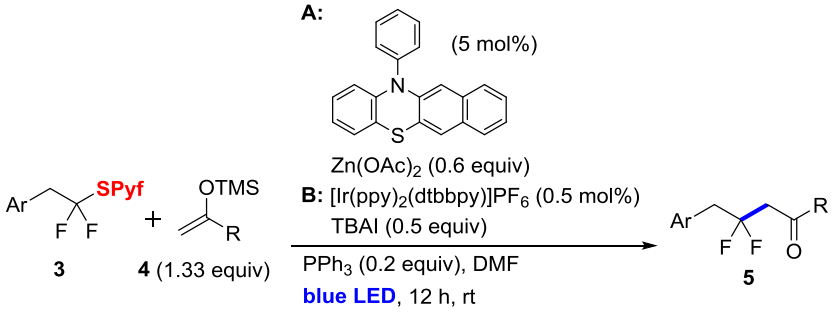


Figure S3. Setup for small scale reactions.



Method A

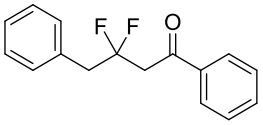
A screw capped tube containing a stirring bar, triphenylphosphine (26 mg, 0.1 mmol) and 12-phenyl-12*H*-benzo[b]phenothiazine (8 mg, 0.025 mmol, 5 mol%) was evacuated and backfilled with argon. Anhydrous DMF (1 mL) was added. The mixture was subjected to a vacuum of 10 Torr for 1 min at room temperature, and then the flask was filled with argon. Dry zinc acetate (55 mg, 0.3 mmol), sulfide **3** (0.5 mmol) and silyl enol ether **4** (0.665 mmol) were added successively. The tube was tightly closed with the screw cap and irradiated (irradiation time: 12 h for **5aa**,**ak**,**af**,**ab**; 48 h for **5ah**,**aj**) using 465 nm LED 4W; during irradiation the mixture was cooled with room temperature water (see Figure S3 for the reaction setup). For the workup, water (3 mL) was added, the mixture was

extracted with ethyl acetate/hexane (1/3, 3×3 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by chromatography (see characterization data for details).

Method B

A screw capped tube containing a stirring bar, triphenylphosphine (26 mg, 0.1 mmol), $[Ir(ppy)_2(dtbbpy)]PF_6$ (2.2 mg, 0.0025 mmol, 0.5 mol%), tetrabutylammonium iodide (92 mg, 0.25 mmol) and anhydrous DMF (1 mL). The mixture was subjected to a vacuum of 10 Torr for 1 min at room temperature, and then the flask was filled with argon. Sulfide **3** (0.5 mmol) and silyl enol ether **4** (0.665 mmol) were added, the tube was tightly closed with the screw cap and irradiated (irradiation time: 12 h for **5aa**,**ac**,**bg**,**ef**,**cf**; 48 h for **5ah**,**aj**,**ae**; 60 h for **5ab**) using 465 nm LED 4W strips; during irradiation the mixture was cooled with room temperature water (see Figure S3 for the reaction setup). For the workup, saturated aqueous solution of $Zn(OAc)_2$ (1 mL) and water (2 mL) were added, and the mixture was extracted with ethyl acetate/hexane (1/3, 3×3 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by chromatography (see characterization data for details).

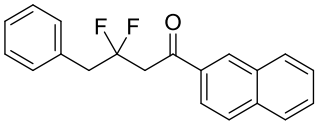
3,3-Difluoro-1,4-diphenylbutan-1-one (5aa) [19]



Method A: yield 108 mg (83%). Method B: yield 114 mg (85%). Colorless crystals. Mp 54–56 °C.

Chromatography: hexanes/EtOAc, 20/1. R_f = 0.20 (hexanes/EtOAc, 20/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.27 (m, 5H), 3.53 (t, *J* = 16.8 Hz, 2H), 3.43 (d, *J* = 14.2 Hz, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 193.9 (t, *J* = 5.8 Hz), 136.8, 133.8, 133.4 (t, *J* = 5.0 Hz), 130.5, 128.8, 128.6, 128.4, 127.5, 122.7 (t, *J* = 243.7 Hz), 43.3 (t, *J* = 26.4 Hz), 42.4 (t, *J* = 24.6 Hz).

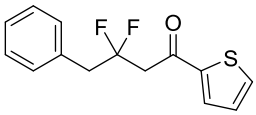
3,3-Difluoro-1-(naphthalen-2-yl)-4-phenylbutan-1-one (5ah) [20]



Method A: yield 99 mg (64%). Method B: yield 112 mg (72 %). Colorless crystals. Mp 69–71 °C.

Chromatography: hexane/EtOAc, 10/1. R_f = 0.25 (hexane/EtOAc, 10/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.00 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.96 – 7.85 (m, 3H), 7.62 (t, *J* = 7.0 Hz, 1H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.38 – 7.27 (m, 5H), 3.57 (t, *J* = 13.2 Hz, 2H), 3.54 (t, *J* = 16.7 Hz, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 193.9 (t, *J* = 6.0 Hz), 136.0, 134.3, 133.5 (t, *J* = 5.0 Hz), 132.5, 130.7, 130.6, 129.9, 129.0, 128.8, 128.7, 127.9, 127.6, 127.1, 123.8), 122.9 (t, *J* = 232.8 Hz), 43.5 (t, *J* = 26.3 Hz), 42.5 (t, *J* = 24.6 Hz).

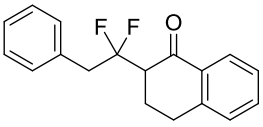
3,3-Difluoro-4-phenyl-1-(thiophen-2-yl)butan-1-one (5aj) [20]



Method A: yield 77 mg (58%). Method B: yield 32 % (^{19}F NMR). Colorless crystals. Mp 47–49 °C.

Chromatography: hexane/EtOAc, 12/1. R_f = 0.17 (hexane/EtOAc, 12/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 4.9, 0.8 Hz, 1H), 7.64 (dd, *J* = 3.8 , 0.8 Hz, 1H), 7.38 – 7.27 (m, 5H), 7.13 (dd, *J* = 4.9, 3.8 Hz, 1H), 3.46 (t, *J* = 16.7 Hz, 2H), 3.37 (t, *J* = 14.3 Hz, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 186.5 (t, *J* = 6.1 Hz), 144.4, 135.1, 133.3, 133.2 (t, *J* = 5.0 Hz), 130.7, 128.7, 128.5, 127.6, 122.3 (t, *J* = 244.2 Hz), 44.3 (t, *J* = 26.8 Hz), 42.5 (t, *J* = 24.6 Hz).

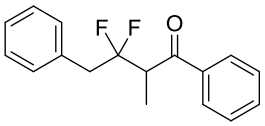
2-(1,1-Difluoro-2-phenylethyl)-3,4-dihydronaphthalen-1(2*H*)-one (5ak) [20]



Method A: yield 97 mg (68%). Pale yellow crystals. Mp 71–73 °C.

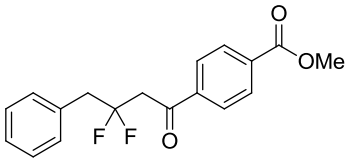
Chromatography: hexane/EtOAc, 20/1. R_f = 0.29 (hexane/EtOAc, 20/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.45 – 7.23 (m, 7H), 3.86 (dt, *J* = 27.4, 13.7 Hz, 1H), 3.64 – 3.43 (ddd, *J* = 21.3, 14.2, 8.9 Hz, 1H), 3.09 (dt, *J* = 16.9, 4.6 Hz, 1H), 3.02 – 2.83 (m, 2H), 2.49 – 2.35 (m, *J* = 13.7, 4.6 Hz, 1H), 2.31 – 2.14 (m, 1H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 194.2 (d, *J* = 6.2 Hz), 144.0, 133.9, 133.7 (d, *J* = 9.1 Hz), 132.8 (d, *J* = 3.7 Hz), 130.8, 128.8, 128.5, 127.8, 127.4, 126.9, 123.4 (t, *J* = 246.0 Hz), 51.2 (t, *J* = 25.0 Hz), 42.3 (dd, *J* = 25.9, 23.7 Hz), 28.2, 22.8 (dd, *J* = 7.9, 1.4 Hz).

3,3-Difluoro-2-methyl-1,4-diphenylbutan-1-one (5ai) [20]



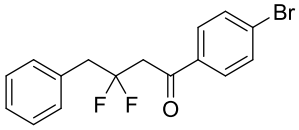
Method A: yield 121 mg (88%). Colorless oil.
The crude product was passed through 3 cm silica gel pad using hexane/EtOAc (10/1). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 12 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 17% water; t_R = 12.17 min).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.22 (m, 5H), 4.06 – 3.94 (m, 1H), 3.51 – 3.26 (m, 2H), 1.42 (d, *J* = 7.2 Hz, 3H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 198.75 (t, *J* = 4.2 Hz), 136.7, 133.6, 132.9 (t, *J* = 3.8 Hz), 130.7, 128.8, 128.6, 128.5, 127.5, 123.4 (dd, *J* = 249.2, 244.6 Hz), 45.8 (t, *J* = 24.5 Hz), 40.6 (t, *J* = 24.9 Hz), 12.4 (t, *J* = 4.8 Hz).

Methyl 4-(3,3-difluoro-4-phenylbutanoyl)benzoate (5ab)



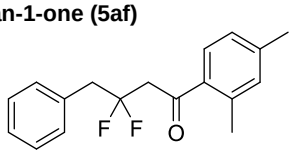
Method A: yield 40 mg (25%). Method B: yield 72 mg (45%). Colorless crystals. Mp 76–78 °C.
Chromatography: hexane/EtOAc, 7/1. R_f = 0.18 (hexane/EtOAc, 10/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.23 (m, *J* = 10.7 Hz, 5H), 3.95 (s, 3H), 3.47 (t, *J* = 16.6 Hz, 2H), 3.44 (t, *J* = 14.0 Hz, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 193.6 (t, *J* = 5.7 Hz), 166.2, 140.0, 134.6, 133.2 (t, *J* = 5.1 Hz), 130.6, 130.0, 128.8, 128.4, 127.7, 122.5 (t, *J* = 244.2 Hz), 52.7, 43.7 (t, *J* = 26.5 Hz), 42.5 (t, *J* = 24.7 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -90.7 (tt, *J* = 16.6, 14.0 Hz, 2F).
HRMS (ESI): calcd for $C_{18}H_{16}F_2O_3Na$ (M+Na) 341.0960, found 341.0960; calcd for $C_{18}H_{16}F_2O_3K$ (M+K) 357.0699, found 357.0698.

1-(4-Bromophenyl)-3,3-difluoro-4-phenylbutan-1-one (5ad)



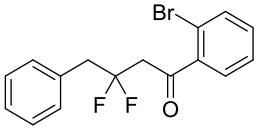
Method B: yield 118 mg (70%). Colorless crystals. Mp 60–62 °C.
Chromatography: hexane/EtOAc, 20/1. R_f = 0.24 (hexane/EtOAc, 20/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.34 – 7.27 (m, *J* = 7.4 Hz, 5H), 3.46 (t, *J* = 16.6 Hz, 2H), 3.38 (t, *J* = 14.2 Hz, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 193.0 (t, *J* = 5.8 Hz), 135.6, 133.3 (t, *J* = 5.0 Hz), 132.2, 130.6, 130.0, 129.2, 128.7, 127.7, 122.5 (t, *J* = 244.0 Hz), 43.4 (t, *J* = 26.5 Hz), 42.5 (t, *J* = 24.7 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -90.7 (tt, *J* = 16.6, 14.2 Hz, 2F).
HRMS (ESI): calcd for $C_{16}H_{14}{}^{79}BrF_2O$ (M+H) 339.0191, found 339.0188; calcd for $C_{16}H_{14}{}^{81}BrF_2O$ (M+H) 341.0171, found 341.0164; calcd for $C_{16}H_{13}{}^{79}BrF_2ONa$ (M+Na) 361.0010, found 361.0008; calcd for $C_{16}H_{13}{}^{81}BrF_2ONa$ (M+Na) 362.9990, found 362.9987.

1-(2,4-Dimethylphenyl)-3,3-difluoro-4-phenylbutan-1-one (5af)



Method A: yield 125 mg (87%). Colorless oil.
Chromatography: hexane/EtOAc, 20/1. R_f = 0.26 (hexane/EtOAc, 20/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.27 (m, 5H), 7.08 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 3.49 (t, *J* = 16.8 Hz, 2H), 3.35 (t, *J* = 14.3 Hz, 2H), 2.53 (s, 3H), 2.35 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8 (t, *J* = 5.8 Hz), 142.8, 139.3, 134.7 (t, *J* = 1.5 Hz), 133.6 (t, *J* = 5.1 Hz), 133.2, 130.6, 129.5, 128.7, 127.6, 126.5, 122.8 (t, *J* = 243.6 Hz), 45.7 (t, *J* = 26.2 Hz), 42.5 (t, *J* = 24.7 Hz), 21.7, 21.5.
^{19}F NMR (282 MHz, $CDCl_3$) δ -90.8 (tt, *J* = 16.8, 14.3 Hz, 2F).
HRMS (ESI): calcd for $C_{18}H_{19}F_2O$ (M+H) 289.1398, found 289.1404; calcd for $C_{18}H_{18}F_2ONa$ (M+Na) 311.1218, found 311.1221.

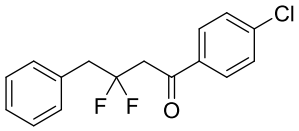
1-(2-Bromophenyl)-3,3-difluoro-4-phenylbutan-1-one (5ae)



Method B: yield 103 mg (61%) Colorless oil.
The crude product was passed through 3 cm silica gel pad using hexane/EtOAc (15/1). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 11 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 15% water; t_R = 9.05 min).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.26 (m, 8H), 3.48 (t, *J* = 16.7 Hz, 2H), 3.44 (t, *J* = 14.1 Hz, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.2 (t, *J* = 5.9 Hz), 141.1 (t, *J* = 1.6 Hz), 134.0, 133.2 (t, *J* = 5.0 Hz), 132.3, 130.6, 128.9, 128.7, 127.7, 127.7, 122.2 (t, *J* = 244.2 Hz), 118.8, 47.2 (t, *J* = 26.6 Hz), 42.5 (t, *J* = 24.6 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -91.1 (tt, *J* = 16.7, 14.1 Hz, 2F).
HRMS (ESI): calcd for $C_{16}H_{13}{}^{79}BrF_2ONa$ (M+Na) 361.0010, found 361.0003; calcd for $C_{16}H_{13}{}^{81}BrF_2ONa$ (M+Na) 362.9990, found 362.9984.

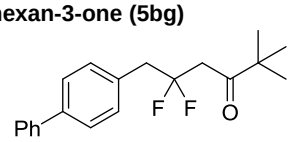
1-(4-Chlorophenyl)-3,3-difluoro-4-phenylbutan-1-one (5ac)



Method B: yield 136 mg (92%). Colorless crystals. Mp 57-59 °C.

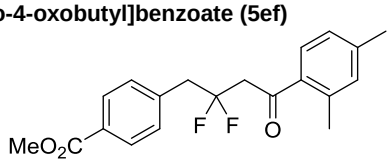
Chromatography: hexane/EtOAc, 15/1. R_f = 0.29 (hexane/EtOAc, 15/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.36 – 7.26 (m, 5H), 3.47 (t, *J* = 16.7 Hz, 2H), 3.39 (t, *J* = 14.2 Hz, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 192.8 (t, *J* = 5.8 Hz), 140.4, 135.2, 133.3 (t, *J* = 5.0 Hz), 130.6, 129.9, 129.2, 128.7, 127.7, 122.6 (t, *J* = 244.1 Hz), 43.4 (t, *J* = 26.5 Hz), 42.5 (t, *J* = 24.6 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -90.8 (tt, *J* = 16.7, 14.2 Hz, 2F).
HRMS (ESI): calcd for $C_{16}H_{14}{}^{35}ClF_2O$ (M+H) 295.0696, found 295.0703; calcd for $C_{16}H_{14}{}^{37}ClF_2O$ (M+H) 297.0630, found 297.0667; calcd for $C_{16}H_{13}{}^{35}ClF_2ONa$ (M+Na) 317.0515, found 317.0521; calcd for $C_{16}H_{13}{}^{37}ClF_2ONa$ (M+Na) 319.0487, found 319.0494.

6-([1,1'-Biphenyl]-4-yl)-5,5-difluoro-2,2-dimethylhexan-3-one (5bg)



Method B: yield 90 mg (57%). Colorless crystals. Mp 61-63 °C.
The crude product was passed through 3 cm silica gel pad using hexane/EtOAc (20/1). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 12 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 5% water; t_R = 7.64 min).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.53 (m, 4H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.32 (m, 3H), 3.53 (t, *J* = 17.0 Hz, 2H), 3.01 (t, *J* = 13.9 Hz, 2H), 1.14 (s, 9H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 209.5, 140.8, 140.4, 132.8 (t, *J* = 5.2 Hz), 131.0, 128.9, 127.5, 127.3, 127.1, 123.0 (t, *J* = 242.9 Hz), 44.9, 41.8 (t, *J* = 24.7 Hz), 41.2 (t, *J* = 26.7 Hz), 26.1.
^{19}F NMR (282 MHz, $CDCl_3$) δ -90.3 (tt, *J* = 17.0, 13.9 Hz, 2F).
HRMS (ESI): calcd for $C_{20}H_{23}F_2O$ (M+H) 317.1711, found 317.1714; calcd for $C_{20}H_{22}F_2ONa$ (M+Na) 339.1531, found 339.1529.

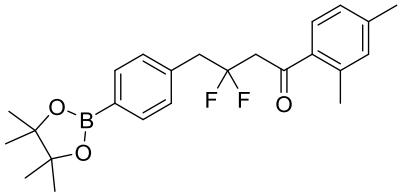
Methyl 4-[4-(2,4-dimethylphenyl)-2,2-difluoro-4-oxobutyl]benzoate (5ef)



Method B: yield 138 mg (80%). Colorless oil.

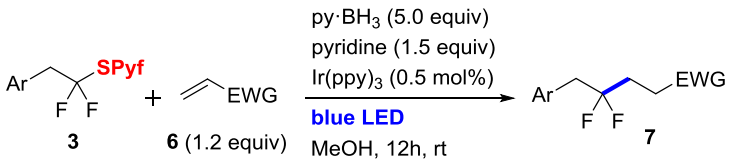
Chromatography: hexane/EtOAc, 10/1. R_f = 0.20 (hexane/EtOAc, 10/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.06 (s, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 3.89 (s, 3H) 3.54 (t, *J* = 16.8 Hz, 2H), 3.35 (t, *J* = 14.2 Hz, 2H), 2.52 (s, 3H), 2.33 (s, 3H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 196.3 (t, *J* = 5.8 Hz), 166.8, 142.9, 139.3, 138.6 (t, *J* = 4.8 Hz), 134.4, 133.2, 130.6, 129.8, 129.4, 126.5, 125.6, 122.3 (t, *J* = 243.8 Hz), 52.1, 45.6 (t, *J* = 26.0 Hz), 42.3 (t, *J* = 24.9 Hz), 21.6, 21.4.
^{19}F NMR (282 MHz, $CDCl_3$) δ -90.6 (tt, *J* = 16.8, 14.2 Hz, 2F).
HRMS (ESI): calcd for $C_{20}H_{21}F_2O_3$ (M+H), 347.1453 found, 347.1455, calcd for $C_{20}H_2F_2O_3Na$ (M+Na) 369.1273, found 369.1274.

1-(2,4-Dimethylphenyl)-3,3-difluoro-4-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]butan-1-one (5cf)



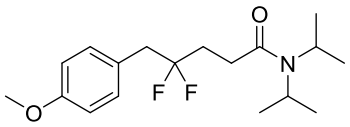
Method B: yield 83 mg (40%), ^{19}FNMR yield 76%. Colorless oil.
The crude product was passed through 3 cm silica gel pad using hexane/EtOAc (5/1). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 11 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 5% water; t_R = 10.24 min).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.07 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.51 (t, *J* = 16.7 Hz, 2H), 3.34 (t, *J* = 14.3 Hz, 2H), 2.53 (s, 3H), 2.35 (s, 3H), 1.35 (s, 12H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 196.6 (t, *J* = 5.6 Hz), 142.8, 139.2, 136.7 (t, *J* = 5.0 Hz), 135.1, 134.6, 133.2, 130.0, 129.4, 126.5, 122.7 (t, *J* = 243.7 Hz), 83.9 (s), 45.6 (t, *J* = 26.0 Hz), 42.7 (t, *J* = 24.8 Hz), 25.0, 21.7, 21.5.
^{19}F NMR (282 MHz, $CDCl_3$) δ -90.5 (tt, *J* = 16.7, 14.3 Hz, 2F).
HRMS (ESI): calcd for $C_{24}H_{30}BF_2O_3$ (M+H), 415.2255 found, 415.2262, calcd for $C_{24}H_{29}BF_2O_3Na$ (M+Na) 437.2074, found 437.2085.

Reactions of sulfides 3 with electron-withdrawing alkenes 6 (General procedure)



The tube containing a stirring bar was evacuated and filled with argon. Then, methanol (1.0 mL), sulfide **3** (0.50 mmol), alkene **6** (0.6 mmol), *fac*-Ir(ppy)$_3$ (1.6 mg, 0.0025 mmol, 0.5 mol%) and pyridine (59 mg, 0.75 mmol) were added successively. The tube was tightly closed with a screw cap and the reaction mixture was irradiated for 18 h using a strip of blue LED; during irradiation the mixture was cooled with room temperature water (see Figure S3 for the reaction setup). For the work-up, water (3 mL) was added, and the mixture was extracted with ethyl acetate (3×4 mL). The combined organic phases were dried with Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel.

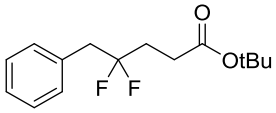
4,4-Difluoro-N,N-diisopropyl-5-(4-methoxyphenyl)pentanamide (7da)



Yield 123 mg (75%). Colorless oil.

Chromatography: hexane/EtOAc, 3/1. R_f = 0.35 (hexane/EtOAc, 3/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.03 – 3.86 (m, 1H), 3.77 (s, 3H), 3.56 – 3.34 (m, 1H), 3.09 (t, *J* = 15.9 Hz, 2H), 2.51 – 2.41 (m, 2H), 2.23 – 2.01 (m, 2H), 1.33 (d, *J* = 6.8 Hz, 6H), 1.16 (d, *J* = 6.8 Hz, 6H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 170.0, 159.0, 131.4, 125.3 (t, *J* = 5.0 Hz), 124.2 (t, *J* = 242.1 Hz), 114.0, 55.3, 48.2, 45.7, 43.0 (t, *J* = 26.2 Hz), 31.4 (t, *J* = 24.0 Hz), 27.3 (t, *J* = 3.4 Hz), 20.9, 20.7.
^{19}F NMR (282 MHz, $CDCl_3$) δ -99.4 (tt, *J* = 16.8, 15.9 Hz, 2F).
HRMS (ESI): calcd for $C_{18}H_{28}F_2NO_2$ (M+H) 328.2083, found 328.2090; calcd for $C_{18}H_{27}F_2NO_2Na$ (M+Na) 350.1902, found 350.1903.

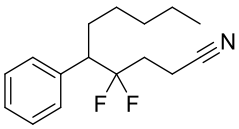
***tert*-Butyl 4,4-difluoro-5-phenylpentanoate (7af)** [20]



Yield 95 mg (70%). Colorless oil.

Chromatography: hexanes/EtOAc, 10/1. R_f = 0.29 (hexanes/EtOAc, 10/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 5H), 3.18 (t, *J* = 16.0 Hz, 2H), 2.47 (t, *J* = 7.9 Hz 2H), 2.11 (tt, *J* = 17.0, 7.9 Hz, 2H), 1.46 (s, 9H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 171.8, 133.2 (t, *J* = 4.7 Hz), 130.4, 128.6, 127.5, 123.5 (t, *J* = 242.6 Hz), 80.8, 43.5 (t, *J* = 25.9 Hz), 31.3 (t, *J* = 25.1 Hz), 28.3 (t, *J* = 4.4 Hz), 28.2.

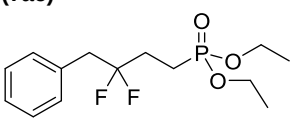
4,4-Difluoro-5-phenyldecanenitrile (7kd)



Yield 111 mg (84%). Colorless oil.

Chromatography: hexanes/EtOAc, 10/1. R_f = 0.3 (hexanes/EtOAc, 10/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 3H), 7.29 – 7.21 (m, 2H), 2.97 (dddd, *J* = 23.4, 11.7, 8.6, 3.5 Hz, 1H), 2.60 – 2.37 (m, 2H), 2.19 – 1.74 (m, 4H), 1.38 – 1.03 (m, 6H), 0.92 – 0.76 (m, 3H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 137.2 (d, *J* = 7.1 Hz), 129.1, 128.9, 127.9, 123.7 (dd, *J* = 248.3, 246.1 Hz), 118.7, 52.8 (dd, *J* = 23.4, 22.7 Hz), 31.8 (t, *J* = 25.7 Hz), 31.6, 28.1 (t, *J* = 3.9 Hz), 26.8, 22.4, 14.0, 10.4 (t, *J* = 6.3 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -103.2 (dddd, *J* = 242.3, 25.5, 8.6, 6.6 Hz, 1F), -108.5 – -114.5 (dddd, *J* = 242.3, 23.4, 9.2, 4.0 Hz, 1F).
HRMS (ESI): calcd for $C_{16}H_{21}F_2NNa$ (M+Na) 288.1534, found 288.1546; calcd for $C_{16}H_{21}F_2NK$ (M+K) 304.1274, found 304.1284.

Diethyl (3,3-difluoro-4-phenylbutyl)phosphonate (7ae) [21]

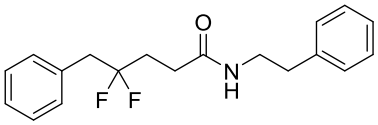


Yield 103 mg (67%). Colorless oil.

Chromatography: EtOAc, R_f = 0.22 (EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.20 (m, 5H), 4.16 – 3.97 (m, 4H), 3.16 (t, *J* = 15.9 Hz, 2H), 2.18 – 1.82 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 6H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 132.9 (t, *J* = 4.7 Hz), 130.3, 128.6, 127.6, 123.1 (dt, *J* = 243.1, 18.9 Hz), 61.9, 61.8, 43.2 (t, *J* = 25.9 Hz), 29.4 (td, *J* = 26.1, 3.8 Hz), 18.6 (dt, *J* = 145.4, 4.4 Hz), 16.5, 16.4.

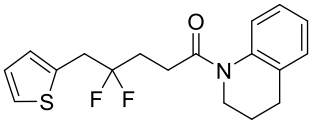
4,4-Difluoro-N-phenethyl-5-phenylpentanamide (7ac)



Yield 97 mg (61%). Pale yellow crystals. Mp 112–114°C.

Chromatography: hexanes/EtOAc, 1/1. R_f = 0.38 (hexanes/EtOAc, 1/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.22 (m, 8H), 7.19 (d, *J* = 7.0 Hz, 2H), 5.67 – 5.49 (br, 1H), 3.51 (dt, *J* = 13.1, 6.9 Hz, 2H), 3.17 (t, *J* = 16.0 Hz, 2H), 2.81 (t, *J* = 6.9 Hz, 2H), 2.39 – 2.26 (m, 2H), 2.27 – 2.04 (m, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 171.4, 138.9, 133.1 (t, *J* = 4.8 Hz), 130.4, 128.8, 128.8), 128.6, 127.5, 126.6, 123.7 (t, *J* = 242.7 Hz), 43.7 (t, *J* = 25.9 Hz), 40.8, 35.7, 31.7 (t, *J* = 24.8 Hz), 28.9 (t, *J* = 3.9 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -99.25 (tt, *J* = 16.6, 16.0Hz, 2F).
HRMS (ESI): calcd for $C_{19}H_{22}F_2NO$ (M+H) 318.1664, found 318.1664; calcd for $C_{19}H_{21}F_2NONa$ (M+Na) 340.1483, found 340.1480.

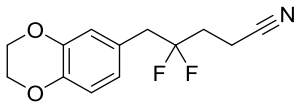
1-(3,4-Dihydroquinolin-1(2*H*)-yl)-4,4-difluoro-5-(thiophen-2-yl)pentan-1-one (7ib)



Yield 97 mg (58%). Colorless oil.

Chromatography: hexanes/EtOAc, 3/1. R_f = 0.22 (hexanes/EtOAc, 3/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.07 (m, 5H), 7.03 – 6.88 (m, 2H), 3.79 (t, *J* = 6.5 Hz, 2H), 3.37 (t, *J* = 15.4 Hz, 2H), 2.83 – 2.62 (m, 4H), 2.44 – 2.10 (m, 2H), 1.97 (pent, *J* = 6.6 Hz, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 171.0, 138.8, 134.0 (t, *J* = 5.4 Hz), 128.6, 128.0, 127.0, 126.2, 125.4, 124.6, 123.1 (t, *J* = 242.9 Hz), 44.1 – 42.6 (broad), 37.8 (t, *J* = 28.2 Hz), 31.7 (t, *J* = 24.4 Hz), 27.2 (t, *J* = 3.9 Hz), 26.8, 24.0.
^{19}F NMR (282 MHz, $CDCl_3$) δ -99.20 (tt, *J* = 16.1, 15.4 Hz, 2F).
HRMS (ESI): calcd for $C_{18}H_{20}F_2NOS$ (M+H) 336.1228, found 336.1230; calcd for $C_{18}H_{19}F_2NOSNa$ (M+Na) 358.1048, found 358.1043.

5-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-4,4-difluoropentanenitrile (7hd)



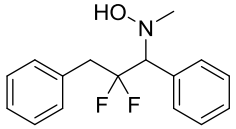
Yield 108 mg (85%). Colorless oil.

Chromatography: hexanes/EtOAc, 3/1. R_f = 0.24 (hexanes/EtOAc, 3/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (d, *J* = 8.2 Hz, 1H), 6.75 (s, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 4.24 (s, 4H), 3.06 (t, *J* = 15.8 Hz, 2H), 2.51 (t, *J* = 7.7 Hz, 2H), 2.24 – 2.00 (m, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.6, 143.3, 125.3 (t, *J* = 5.3 Hz), 123.1, 122.4 (t, *J* = 243.8 Hz), 118.9, 118.6, 117.5, 64.4, 42.5 (t, *J* = 25.5 Hz), 31.7 (t, *J* = 25.5 Hz), 10.4 (t, *J* = 6.0 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -100.17 (tt, *J* = 16.0, 15.8 Hz, 2F).
HRMS (ESI): calcd for $C_{13}H_{13}F_2NO_2Na$ (M+Na) 276.0807, found 276.0800.

Reactions of sulfides 3 with nitrones 8 (General procedure)

fac-Ir(ppy)$_3$ (1.6 mg, 0.0025 mmol, 0.5 mol%), sulfide **3** (0.5 mmol), nitrone **6** (0.75 mmol), and ascorbic acid (132 mg, 0.75 mmol) were placed in a tube containing a stirring bar. The tube was evacuated and backfilled with argon. DMSO (1 mL) was added followed by 2,4,6-collidine (91 mg, 0.75 mmol). The reaction vessel was irradiated 6 hours by a strip of blue LEDs; during irradiation the mixture was cooled with room temperature water (see Figure S3 for the reaction setup). For the work-up, the mixture was treated with water (3 mL) and extracted with EtOAc (3×4 mL). The combined organic phases were dried with Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography.

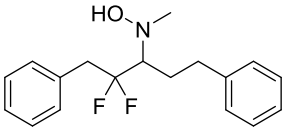
N-(2,2-Difluoro-1,3-diphenylpropyl)-N-methylhydroxylamine (9ac) [21]



Yield 111 mg (80%). Colorless crystals. Mp 138–140 °C.

Chromatography: hexanes/EtOAc, 4/1. R_f = 0.24 (hexanes/EtOAc, 4/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.17 (m, 10H), 5.62 (s, 1H), 3.82 (t, *J* = 13.6 Hz, 1H), 3.50 – 3.07 (m, 2H), 2.56 (s, 3H).
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 133.1 (t, *J* = 4.3 Hz), 132.1, 131.3, 130.8, 128.8, 128.4, 128.3, 127.4, 123.5 (t, *J* = 248.7 Hz), 74.3 (t, *J* = 23.4 Hz), 46.4, 41.9 (t, *J* = 24.9 Hz).

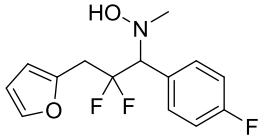
N-(2,2-Difluoro-1,5-diphenylpentan-3-yl)-N-methylhydroxylamine (9fe)



Yield 99 mg (65%). Colorless crystals. Mp 62–64°C.

Chromatography: hexanes/EtOAc, 5/1. R_f = 0.31 (hexanes/EtOAc, 5/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.17 (m, 7H), 7.13 (d, *J* = 7.0 Hz, 2H), 5.10 (s, 1H), 3.53 – 3.20 (m, 2H), 2.91 – 2.61 (m, 3H), 2.60 (s, 3H), 2.18 – 2.03 (m, 2H).
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 141.9, 133.7 (d, *J* = 8.1 Hz), 130.7, 128.7, 128.5, 128.5, 127.3, 126.0, 125.2 (dd, *J* = 266.3, 261.7 Hz), 67.0 (dd, *J* = 27.2, 22.6 Hz), 45.1 (t, *J* = 1.8 Hz), 41.3 (dd, *J* = 26.2, 23.6 Hz), 34.3 (d, *J* = 3.5 Hz), 23.7.
^{19}F NMR (282 MHz, $CDCl_3$) δ -100.7 (dt, *J* = 254.1, 20.7 Hz), -106.0 (dt, *J* = 254.1, 22.9 Hz).
HRMS (ESI): calcd for $C_{18}H_{22}F_2NO$ (M+H) 306.1664, found 306.1658.

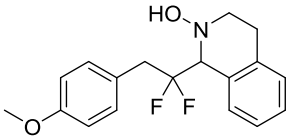
N-[2,2-Difluoro-1-(4-fluorophenyl)-3-(furan-2-yl)propyl]-N-methylhydroxylamine (9ja)



Yield 123 mg (86%). Colorless oil.

Chromatography: hexanes/EtOAc, 4/1. R_f = 0.23 (hexanes/EtOAc, 4/1).
1H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.33 (m, 3H), 7.17 – 6.96 (m, 2H), 6.44 – 6.28 (m, 1H), 6.21 (d, *J* = 3.1 Hz, 1H), 5.75 (s, 1H), 3.87 (dd, *J* = 15.3, 10.8 Hz, 1H), 3.45 (q, *J* = 15.3 Hz, 1H), 3.25 (q, *J* = 15.3 Hz, 1H), 2.53 (s, 3H).
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 163.1 (d, *J* = 247.6 Hz), 147.4 (t, *J* = 5.9 Hz), 142.4, 133.0 (d, *J* = 8.1 Hz), 127.8, 122.3 (dd, *J* = 250.4, 248.1 Hz), 115.3 (d, *J* = 21.3 Hz), 110.8, 109.6, 73.4 (dd, *J* = 24.7, 21.8 Hz), 46.4, 35.1 (t, *J* = 27.3 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -100.3 (dd, *J* = 251.1, 10.8 Hz), -102.3 (dq, *J* = 251.1, 15.3 Hz), -114.03 (s).
HRMS (ESI): calcd for $C_{14}H_{15}F_3NO_2$ (M+H) 286.1049, found 286.1053; calcd for $C_{14}H_{14}F_3NO_2Na$ (M+Na) 308.0869, found 308.0866.

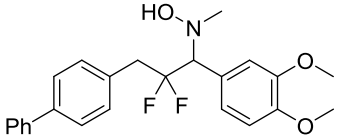
1-[1,1-Difluoro-2-(4-methoxyphenyl)ethyl]-3,4-dihydroisoquinolin-2(1*H*)-ol (9dd)



Yield 125 mg (78%). Colorless oil.

Chromatography: hexanes/EtOAc, 4/1. R_f = 0.21 (hexanes/EtOAc, 4/1).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.2 Hz, 1H), 7.33 – 7.15 (m, 5H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.20 (s, 1H), 4.52 (dd, *J* = 12.8, 9.8 Hz, 1H), 3.83 (s, 3H), 3.56 (dt, *J* = 11.4, 5.6 Hz, 1H), 3.42 – 3.20 (m, 2H), 3.10 – 2.79 (m, 3H).
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 158.9, 135.7, 131.8, 129.8, 129.3 (t, *J* = 3.7 Hz), 128.4, 127.6, 126.3, 125.1 (t, *J* = 2.9 Hz), 123.9 (t, *J* = 247.7 Hz), 113.8, 70.2 (t, *J* = 24.8 Hz), 55.3, 51.8, 38.6 (t, *J* = 24.2 Hz), 26.2.
^{19}F NMR (282 MHz, $CDCl_3$) δ -100.3 – -102.6 (m, 2F).
HRMS (ESI): calcd for $C_{18}H_{20}F_2NO_2$ (M+H) 320.1457, found 320.1458; calcd for $C_{18}H_{19}F_2NO_2Na$ (M+Na) 342.1276, found 342.1275.

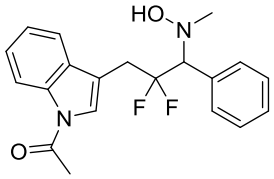
N-[3-([1,1'-Biphenyl]-4-yl)-1-(3,4-dimethoxyphenyl)-2,2-difluoropropyl]-N-methylhydroxylamine (9bb)



Yield 161 mg (78%). Colorless oil.
Crude was passed through 3 cm silica gel pad using 1/1 hexane/EtOAc mixture and final purification was performed by preparative HPLC (reversed-phase column C18, 21*250 mm, 5 µm, flow rate 12 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 5% water; t_R = 6.64 min).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.4 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.04 (s, 1H), 6.99 – 6.93 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 5.99 – 5.40 (br, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 3.82 (t, *J* = 13.7 Hz, 1H), 3.53 – 3.11 (m, 2H), 2.59 (s, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 149.4, 148.7, 140.7, 140.2, 132.1 (t, *J* = 4.1 Hz), 131.2, 128.8, 127.4, 127.0, 127.0, 124.5, 124.0, 123.5 (t, *J* = 248.9 Hz), 114.1, 110.6, 73.9 (t, *J* = 23.1 Hz), 56.0, 55.8, 46.3, 41.6 (t, *J* = 25.0 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -99.8 – -102.0 (m, 2F).
HRMS (ESI): calcd for $C_{24}H_{26}F_2NO_3$ (M+H) 414.1875, found 414.1869; calcd for $C_{24}H_{25}F_2NO_3Na$ (M+Na) 436.1695, found 436.1690.

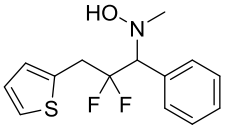
1-[3-(2,2-Difluoro-3-[hydroxy(methyl)amino]-3-phenylpropyl)-1*H*-indol-1-yl]ethanone (9gc)



Yield 145 mg (81%). White crystals. Mp 143 – 145 °C.

Chromatography: hexanes/EtOAc, 1/1. R_f = 0.35 (hexanes/EtOAc, 1/1).
^1H NMR (300 MHz, DMSO-d6) δ 8.39 – 8.30 (m, 2H), 7.72 – 7.62 (m, 2H), 7.58 – 7.48 (m, 2H), 7.41 – 7.23 (m, 5H), 4.06 (dd, *J* = 18.7, 8.4 Hz, 1H), 3.78 – 3.50 (m, 2H), 2.63 (s, 3H), 2.41 (s, 3H).
$^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d6) δ 169.1, 134.9, 133.2, 131.3, 130.9, 127.9, 127.6, 126.3, 124.6, 123.6 (dd, *J* = 250.3, 242.4 Hz), 123.1 (s), 119.8, 115.7, 113.5 (dd, *J* = 4.2, 1.3 Hz), 73.36 (dd, *J* = 28.0, 22.3 Hz), 46.3, 30.2 (t, *J* = 25.6 Hz), 23.8.
^{19}F NMR (282 MHz, DMSO-d6) δ -94.8 (d, *J* = 247.7 Hz, 1F), -100.8 (dm, *J* = 247.7 Hz, 1F).
HRMS (ESI): calcd for $C_{20}H_{21}F_2N_2O_2$ (M+H) 359.1566, found 359.1564; calcd for $C_{20}H_{20}F_2N_2O_2Na$ (M+Na) 381.1385, found 381.1381.

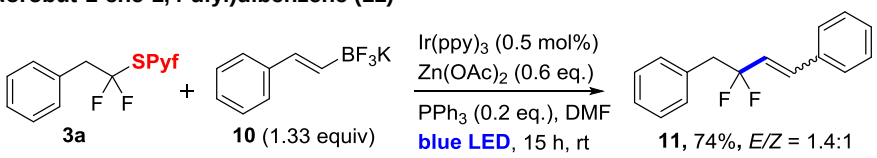
N-[2,2-Difluoro-1-phenyl-3-(thiophen-2-yl)propyl]-N-methylhydroxylamine (9ic)



Yield 113 mg (80%). White crystals. Mp 132 – 134 °C.

Chromatography: hexanes/EtOAc, 5/1. R_f = 0.18 (hexanes/EtOAc, 5/1).
^1H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.35 (m, 5H), 7.27 (d, *J* = 5.3 Hz, 1H), 7.27 (dd, *J* = 5.3, 3.1 Hz, 1H), 6.93 (d, *J* = 3.1 Hz, 1H), 5.84 – 5.47 (br, 1H), 3.92 (t, *J* = 13.7 Hz, 1H), 3.63 (td, *J* = 16.5, 15.5 Hz, 1H), 3.44 (td, *J* = 15.6, 15.5 Hz, 1H), 2.57 (s, 3H).
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 134.1 (t, *J* = 9.8 Hz), 132.0, 131.3, 128.8, 128.5, 128.3, 127.0, 125.6, 122.8 (dd, *J* = 250.0, 248.0 Hz), 73.8 (dd, *J* = 24.6, 22.0 Hz), 46.4, 36.5 (t, *J* = 27.1 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -100.7 (d, *J* = 249.7 Hz, 1F), -102.3 (dm, *J* = 249.7 Hz, 1F).
HRMS (ESI): calcd for $C_{14}H_{16}F_2NOS$ (M+H) 284.0915, found 284.0925; calcd for $C_{14}H_{15}F_2NOSNa$ (M+Na) 306.0735, found 306.0745.

Synthesis of (3,3-difluorobut-1-ene-1,4-diyl)dibenzene (11) [22]



A screw capped tube containing a stirring bar, triphenylphosphine (13 mg, 0.05 mmol), fac-Ir(ppy)$_3$ (0.82 mg, 0.00125 mmol, 0.5% mol), sulfide **3a** (81 mg, 0.25 mmol) and potassium (*E*)-trifluoro(styryl)borate 10 (70 mg,0.333 mmol) and anhydrous DMF (1 mL). The mixture was subjected to a vacuum of 10 Torr for 1 min at room temperature, and then the flask was filled with argon. Dry zinc acetate (28 mg, 0.15 mmol) was added, tube was tightly closed with the screw cap and irradiated for 15 hours using 465 nm LED; during irradiation the mixture was cooled with room temperature water (see Figure S3 for the reaction setup). For the workup, the reaction mixture was diluted with water (3 mL), and the mixture was extracted with hexane (3×3 mL). The combined organic phases were dried over Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel. Yield 45 mg (74%). Mixture of isomers, *E*:*Z* = 1.4:1. Colorless oil.

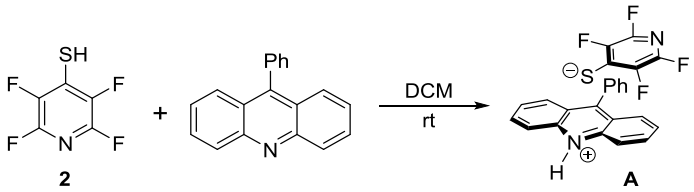
Chromatography: hexanes/EtOAc, 30/1. R_f = 0.26 (hexanes/EtOAc, 30/1).

^1H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.20 (m, 10H, Ph ***Z*+*E***), 6.88 (dt, *J* = 16.2, 2.5 Hz, 1H, ***E***), 6.78 (dt, *J* = 12.9, 1.7 Hz, 1H, ***Z***), 6.19 (dt, *J* = 16.2, 11.4 Hz, 1H, ***E***), 5.72 (dd, *J* = 27.1, 13.8 Hz, 1H, ***Z***), 3.35 (t, *J* = 14.6 Hz, 2H, ***E***), 3.25 (t, *J* = 15.9 Hz, 2H, ***Z***).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 137.4, 137.3, 136.3 (t, *J* = 7.3 Hz, ***Z***), 135.4, 135.1, 134.1 (t, *J* = 9.3 Hz, ***E***), 134.0, 133.8, 133.0 (t, *J* = 3.9 Hz, ***Z***), 132.9 (t, *J* = 4.4 Hz, ***E***), 130.7, 130.7, 129.2 (t, *J* = 3.5 Hz), 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2 (d, *J* = 2.5 Hz), 127.5, 127.5, 127.2, 125.5 (t, *J* = 28.2 Hz), 123.2 (t, *J* = 26.2 Hz, ***E***), 120.9 (t, *J* = 240.8 Hz, ***Z***), 120.8 (t, *J* = 240.6, ***E***) 44.7 (t, *J* = 28.0 Hz, ***E***), 43.7 (t, *J* = 27.0 Hz, ***Z***).

^{19}F NMR (282 MHz, $CDCl_3$) δ -85.9 (td, *J* = 15.3, 15.2 Hz, 2F, ***Z***), -94.8 (td, *J* = 14.2, 13.0 Hz, 2F, ***E***).

Synthesis of 9-phenylacridin-10-ium 2,3,5,6-tetrafluoropyridine-4-thiolate (A)



A screw capped 20 mL vial containing a stirring bar was charged with 9-phenylacridine (127.5 mg, 0.5 mmol) and dichloromethane (3 mL). Thiol **2** (91.5 mg, 0.5 mmol) was added dropwise to deliver crimson red solution. The reaction mixture was stirred for 30 min at room temperature. Then, the stirring was discontinued, and pentane (15 mL) was carefully added to form a separate layer. The reaction vial was kept in a fridge (*ca.* 5 °C) overnight for slow solvent diffusion. Red needle crystals formed were filtered off and dried under vacuum. Yield 160 mg (73 %). Mp 126-140 °C (dec).

^{1}H NMR (300 MHz, $CDCl_3$) δ 14.20 – 13.70 (broad singlet, 1H), 8.79 (d, J = 8.8 Hz, 2H), 8.07 – 7.94 (m, 2H), 7.86 (d, J = 8.7 Hz, 2H), 7.75 – 7.56 (m, 5H), 7.53 – 7.44 (m, 2H).

^{13}C{1H} NMR (75 MHz, $CDCl_3$) δ 155.0, 145.5 – 144.9 (m), 143.9 – 143.6 (m), 143.5, 142.3 – 141.6 (m), 140.7 – 140.0 (m), 134.3, 130.1, 129.8, 129.0, 127.8, 127.3, 125.4, 124.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -96.5 – -97.9 (broad singlet, 2F), -140.7 – -141.9 (broad singlet, 2F).

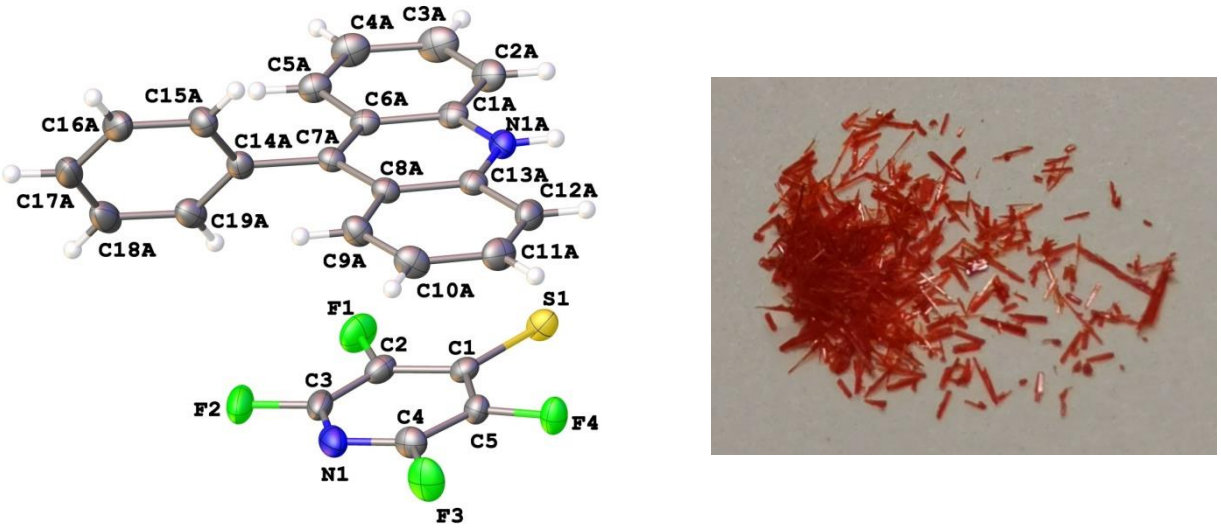


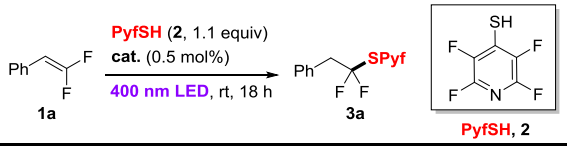
Figure S4. OLEX diagram of compound **A** (CCDC 1947116).

Results and Discussions

Optimization of Reactions Parameters

Optimization reactions were carried out on 0.50 mmol scale, unless mentioned otherwise. The reaction mixtures were analyzed by GC-FID (mesitylene as an internal standard) and/or ^{19}F NMR (trifluorotoluene as an internal standard).

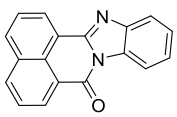
Table S1. Addition of thiol **2** to the *gem*-difluorostyrene **1a**.



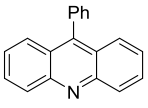
Entry	Photocatalyst	Solvent	Deviation	Yield (%)[a]
1	cat-I	MeCN	none	36
2	cat-I	DCM	none	71
3	cat-I	DCM	352 nm	52
4	cat-II	MeCN	none	17
5	cat-II	DCM	none	67
6	none	cyclohexane	none	34
7	cat-I	cyclohexane	none	99
8	cat-II	cyclohexane	none	99
9	cat-III	cyclohexane	none	92
10	cat-IV	cyclohexane	none	88
11	cat-II	cyclohexane	1 h	55
12	cat-II	cyclohexane	1 h, 465 nm	47
13	**cat-II**	**cyclohexane**	**465 nm**	**99 (95)**
14[b]	cat-II	cyclohexane	465 nm	99 (95)

[a] Determined by GC-FID. Isolated yields are shown in parenthesis.

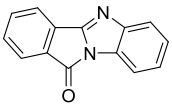
[b] 20 mmol scale.



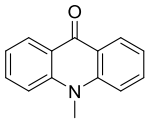
cat-I



cat-II

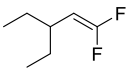


cat-III



cat-IV

Unsuccessful substrates:



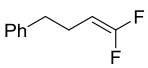
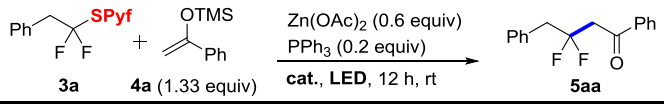


Table S2. Reactions of sulfides **3** with silyl enol ethers **4** (Method A).

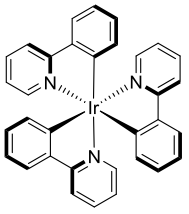


3a **4a** (1.33 equiv) **5aa**

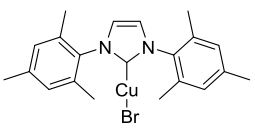
Entry	Photocatalyst	Solvent	Deviation	Wavelength	Yield (%)[a]
1	cat-V (0.5%)	MeCN	no $Zn(OAc)_2$	400 nm	14
2	cat-V (0.5%)	MeCN	none	400 nm	87
3	none	MeCN	none	400 nm	0
4	cat-VI (5%)	MeCN	none	400 nm	43
5	cat-VII (5%)	MeCN	no PPh_3	400 nm	71
6	cat-VII (5%)	MeCN	2 h	400 nm	0
7	cat-VII (5%)	MeCN	none	400 nm	85
8	cat-VII (5%)	MeCN	none	465 nm	0
9	cat-VIII (5%)	DCM	none	465 nm	49
10	cat-VIII (5%)	cyclohexane	none	465 nm	0
11	cat-VIII (5%)	DMSO	none	465 nm	86 (83)
12	**cat-VIII (5%)**	**DMF**	**none**	**465 nm**	**87 (83)**
13	none	DMF	24 h, 40W LED[b]	465 nm	33
14	cat-VIII (5%)	DMF	1.0 equiv $Zn(OAc)_2$	465 nm	74
15	cat-VIII (5%)	DMF	0.6 equiv PPh_3	465 nm	62
16	cat-VIII (5%)	DMF	ZnF_2 instead of $Zn(OAc)_2$	465 nm	80
17	cat-VIII (5%)	DMF	ZnI_2 instead of $Zn(OAc)_2$	465 nm	66
18	cat-VIII (5%)	DMF	CuF_2 instead of $Zn(OAc)_2$	465 nm	74
19	cat-VIII (5%)	DMF	MnF_2 instead of $Zn(OAc)_2$	465 nm	87
20	cat-V (0.5%)	DMF	none	465 nm	79
21	cat-IX (0.5%)	DMF	none	465 nm	48

[a] Yield determined by ^{19}F NMR. Isolated yields are shown in parentheses.

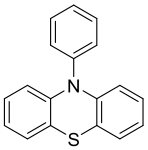
[b] 40W Blue Kessil LED lamp.



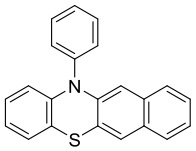
cat-V



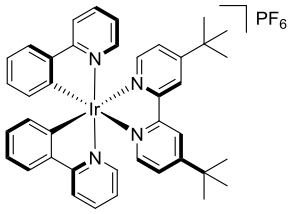
cat-VI



cat-VII

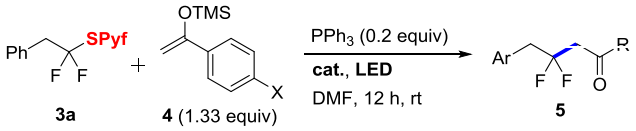


cat-VIII



cat-IX

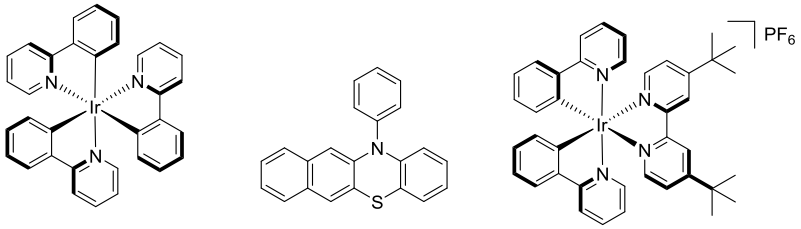
Table S3. Reactions of sulfides **3** with silyl enol ethers **4** containing EWG group (Method B).

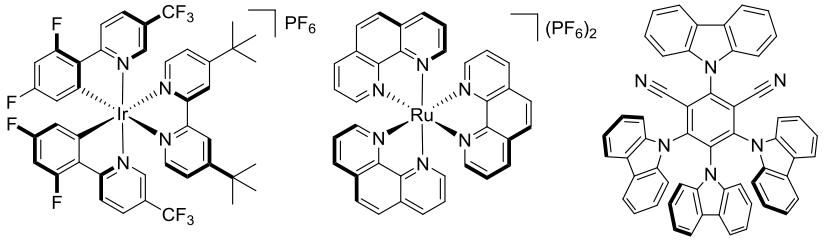


3a **4** (1.33 equiv) **5**

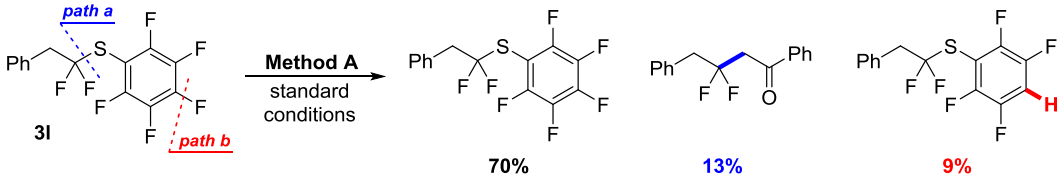
Entry	X	Photocatalyst	Deviation	Yield (%)[a]
1	CO_2Me	cat-VIII (5%)	$Zn(OAc)_2$ (0.6 equiv)	0
2	CO_2Me	cat-X (0.5%)	$Zn(OAc)_2$ (0.6 equiv)	0
3	CO_2Me	cat-XI (0.5%)	$Zn(OAc)_2$ (0.6 equiv)	0
4	CO_2Me	cat-V (0.5%)	$Zn(OAc)_2$ (0.6 equiv)	35 (25)
5	CO_2Me	cat-IX (0.5%)	0.5 equiv TBAI	31
6	CO_2Me	cat-X (0.5%)	0.5 equiv TBAI	35
7	CO_2Me	cat-XII (0.5%)	0.5 equiv TBAI	32
8	**CO_2Me**	**cat-X (0.5%)**	**0.5 equiv TBAI, 60 h**	**53 (45)**
9	Cl	cat-VIII (5%)	$Zn(OAc)_2$ (0.6 equiv)	57
10	Cl	cat-XII (0.5%)	0.5 equiv TBAI	79
11	**Cl**	**cat-IX (0.5%)**	**0.5 equiv TBAI**	**99 (92)**

[a] Yield determined by ^{19}F NMR. Isolated yields are shown in parentheses.





Reaction of sulfide **3l** with silyl enol ether **4a** under optimal conditions proceeded with low conversion. A by-product resulting from the hydrodefluorination of **3l** was also observed (**Scheme S1)**. Yields were determined by ^{19}F NMR with internal standard.



Scheme S1. Reaction of compound **3l**.

Mechanistic Studies

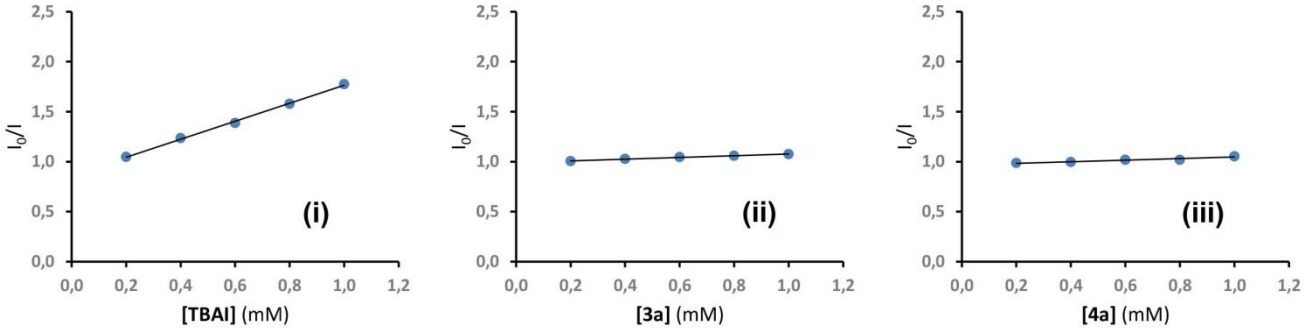


Figure S5. Stern-Volmer studies. Plots of relative fluorescence intensities of the photoexcited catalyst $[Ir(ppy)_2(dtbbpy)]PF_6$ **(cat-IX)** depending on concentration of the quencher – **(i)** Bu_4NI (TBAI), **(ii)** sulfide **3a**, **(iii)** silyl enol ether **4a**. Solvent - MeCN.

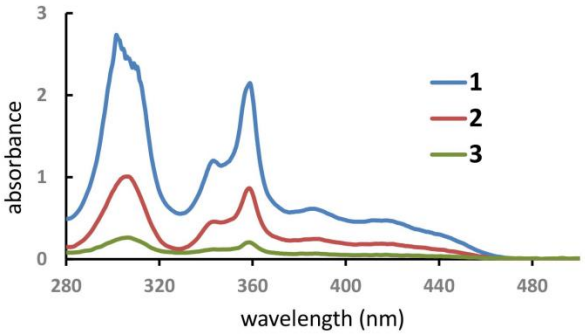


Figure S6. UV-vis spectra of solutions of compound **A** in MeCN: **1** – $5 \cdot 10^{-1}$ mM, **2** – $5 \cdot 10^{-2}$ mM, **3** – $5 \cdot 10^{-3}$ mM.

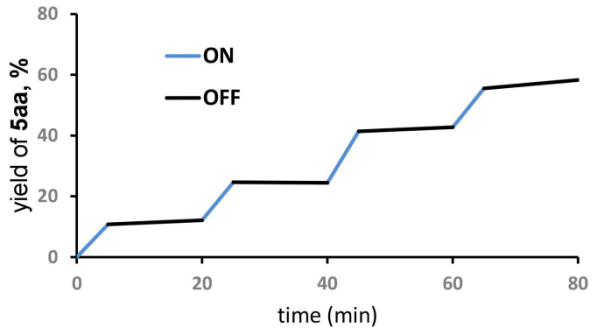


Figure S7. Intermittent light irradiation experiment. The reaction conditions are identical to Method A in Table 2 except for irradiation with 40W blue Kessil LED lamp (A160WE).

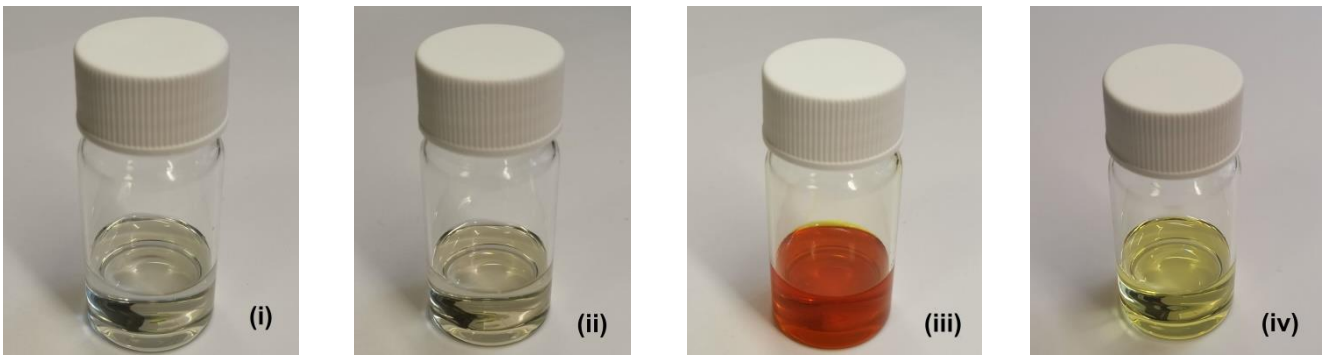


Figure S8. Comparison of the colors of cyclohexane solutions: **(i)** PyfSH, **(ii)** 9-phenylacridine (**cat-II**), **(iii)** mixture of PyfSH and **cat-II** prior to irradiation, **(iv)** reaction mixture after addition of PyfSH with 18 h irradiation.

Cyclic Voltammetry studies.

Voltammetric studies were carried out using potentiostat P30JM with a scan rates of 1.0 and 8.0 $V \cdot s^{-1}$ in a temperature-controlled (25 °C) glass cell (V = 10 mL) under a nitrogen atmosphere. Software *iR* compensation using ferrocene (R = 600 Ω) was used in all experiments. A glassy carbon disk (d = 2.9 mm) was used as the working electrode (carefully polished before each measurement). A saturated calomel electrode (SCE) separated from the solution being studied by a salt bridge filled with the supporting electrolyte (0.1 M Et_4NClO_4 in MeCN) was used as the reference electrode. A platinum plate (S = 3 cm^2) was used as the counter electrode. All experiments were performed with the concentration of a studied compounds of 1 mM in MeCN.

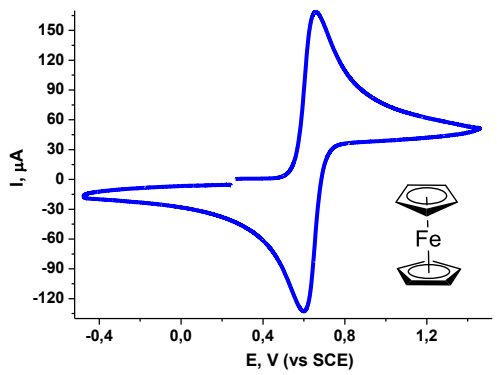


Figure S9. Ferrocene (initial anodic scan, rate 1.0 $V \cdot s^{-1}$). E_p^{ox} = +0.66 V, i_p = 167.91 μA; E_p^{rered} = +0.60 V.

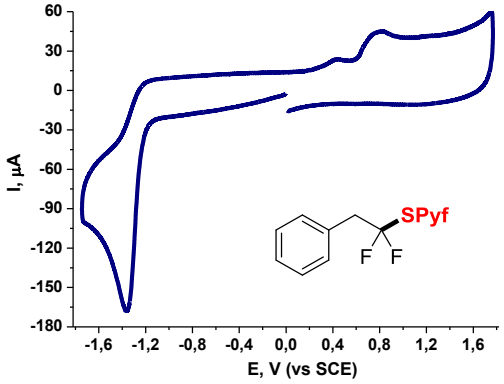


Figure S10. Compound **3a** (initial cathodic scan, rate 1.0 $V \cdot s^{-1}$). E_p^{red} = –1.36 V, i_p = 147.24 μA; E_{p1}^{reox} = + 0.45 V; E_{p2}^{reox} = +0.80 V.

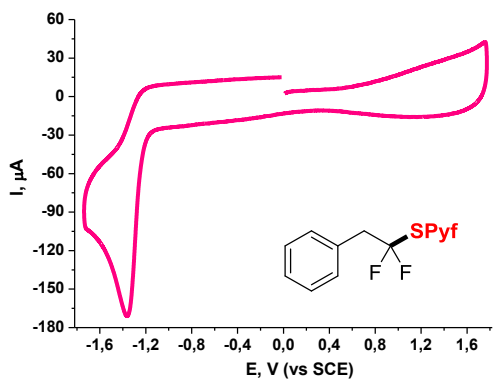


Figure S11. Compound **3a** (initial anodic scan, rate 1.0 $V \cdot s^{-1}$). E_p^{red} = –1.36 V.

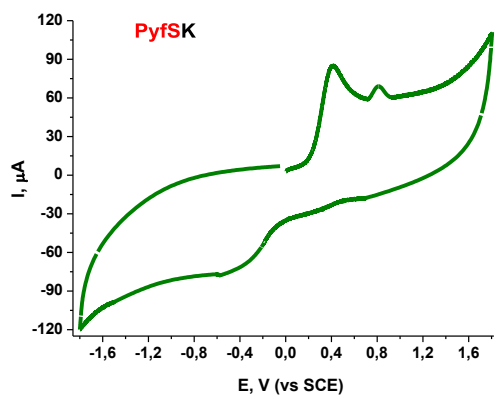


Figure S12. Compound **PyfSK** (initial anodic scan, rate 1.0 $V \cdot s^{-1}$). E_{p1}^{ox} = + 0.42 V; i_p = 84.94 μA; E_{p2}^{reox} = +0.81 V.

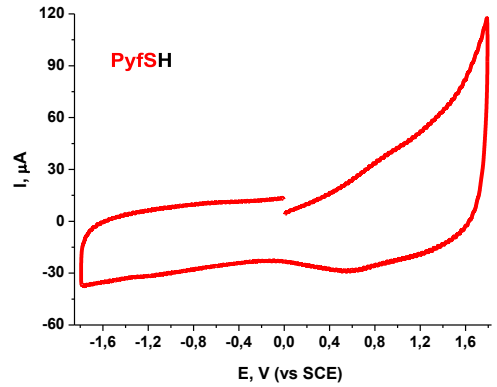


Figure S13. Compound **PyfSH** (initial anodic scan, rate 1.0 $V \cdot s^{-1}$). E_p^{ox} > 1.80 V (supporting electrolyte discharge).

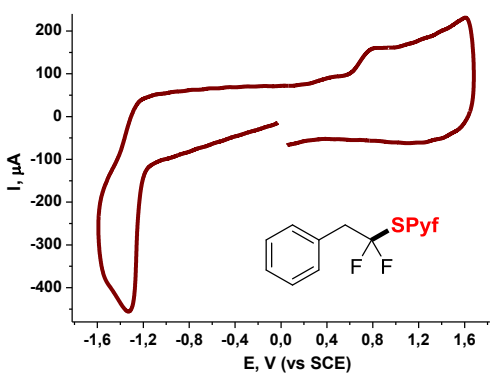


Figure S14. Compound **3a** (initial cathodic scan, rate 8.0 $V \cdot s^{-1}$). E_{red} = –1.35 V; E_{p1}^{reox} = + 0.45 V; E_{p2}^{reox} = +0.80 V.

Intensity of the cathodic peak of **3a** is comparable to that of single-electron wave of ferrocene (see Figures S9 and S10). This suggests that compound **3a** may follow single-electron reduction pathway. At scan rate of 1.0-8.0 $V \cdot s^{-1}$ (see Figures S10 and S14) the reduction of **3a** is irreversible. Presumably, after the reduction, the resulting anion-radical undergoes fragmentation with the formation of stable thiolate-anion and a radical species. On the reversed scan (scan rate of 1.0-8.0 $V \cdot s^{-1}$, see Figures S10 and S14), there are two irreversible anodic peaks at +0.45 and +0.80 V, which correspond to thiolate-anion (*cf.* with Figure S12). The first peak may relate to the oxidative transformation of thiolate-anion to the thiyl radical, the second peak – to the oxidation of thiyl radical followed by fragmentation. Corresponding thiol (see Figure S13) is electrochemically inactive in the studied potential range.

EPR experiment

Procedure: Sulfide **3a** (400 μmol) and 5,5-dimethyl-1-pyrroline-N-oxide (800 μmol) were added to the solution of $Ir(ppy)_3$ in benzene (10^{-3} M, 2 mL) under argon. 300 μL of the resulted mixture was taken into an EPR tube. The tube was placed under light (455 nm, 60W) for 15 seconds. The EPR spectrum was immediately recorded at 298 K on EPR spectrometer SPINSCAN X (ADANI).

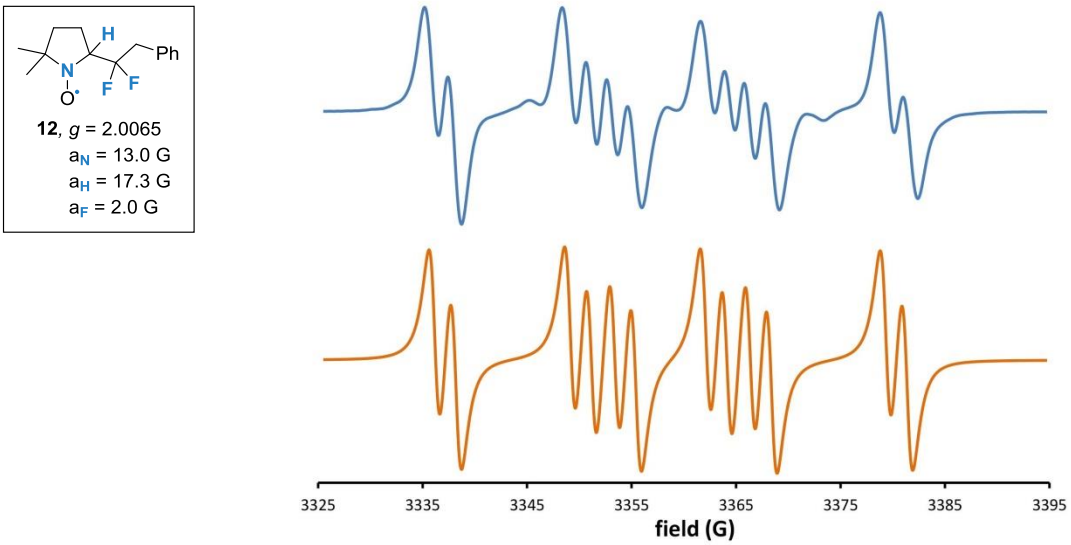


Figure S15. The X-band EPR spectrum (blue line) of the radical **12**. Simulated EPR spectrum (orange line) based on hyperfine coupling constants of a_N= 12.98 G, a_H = 17.25 G and a_F = 2.01 G (*g*-factor = 2.0065).

Experiment parameters:

Center-Field: 3360 G
Width: 100 G
Points: 5000
Scans: 5
Modulation Amplitude: 100 μT
Modulation Frequency: 9.432985 GHz
Microwave Power: 1.0 mW
Time constant: 0.009 s

X-Ray Crystallographic Data

Table S4. Crystallographic data for compounds **3a** and **A**

Compound	**3a**	**A**
Formula moiety	$C_{13}H_7F_6NS$	C_5F_4NS, $C_{19}H_{14}N$
Brutto formula	$C_{13}H_7F_6NS$	$C_{24}H_{14}F_4N_2S$
Formula weight	323.26	438.43
Diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD
Scan mode	ω and ϕ scans	ω and ϕ scans
Anode [Wavelength, Å]	MoKα [0.71073] sealed tube	MoKα [0.71073] sealed tube
Crystal dimensions, mm	0.24 × 0.29 × 0.32	0.25 × 0.25 × 0.25
Crystal color	yellow	yellow
Crystal system	monoclinic	monoclinic
a, Å	9.5947(11)	8.6198(3)
b, Å	4.8799(6)	7.7249(3)
c, Å	13.6316(16)	29.3919(11)
α, °	90	90
β, °	94.414(2)	91.2010(10)
γ, °	90	90
Volume, $Å^3$	636.35(13)	1956.69(13)
Density, gcm^{-3}	1.687	1.488
Temperature, K	120	120
T_{min}/T_{max}	0.6745/0.7465	0.6448/0.7461
μ, mm^{-1}	0.319	0.217
Space group	$P2_1$	$P2_1/c$
Z	2	4
F(000)	324	896
Reflections collected	9856	26990
Independent reflections	4591	6204
Reflections (I>2σ(I))	4107	4804
Parameters	190	280
R_{int}	0.0254	0.0349
$2\theta_{min}$ - $2\theta_{max}$, °	4.258 - 65.552	4.726 - 61.850
wR_2 (all reflections)	0.0790	0.1097
R_1(I>σ(I))	0.0352	0.0408
GOF	1.041	1.013
ρ_{min}/ρ_{max}, $eÅ^{-3}$	-0.215/0.333	-0.308/0.402
Restraints	1	0

The structures were solved by direct method and refined in anisotropic approximation for non-hydrogen atoms. Hydrogens atoms of methyl, methylene and aromatic fragments were calculated according to those idealized geometry and refined with constraints applied to C-H and N-H bond lengths and equivalent displacement parameters ($U_{eq}(H) = 1.2U_{eq}(X)$, X - central atom of XH_2 group; $U_{eq}(H) = 1.5U_{eq}(Y)$, Y - central atom of YH_3 group. All structures were solved with the ShelXT[23] program and refined with the ShelXL[24] program. Molecular graphics was drawn using OLEX2 [25] program.

CCDC contains the supplementary crystallographic data for **3a** (# 1947115) and **A** (# 1947116). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

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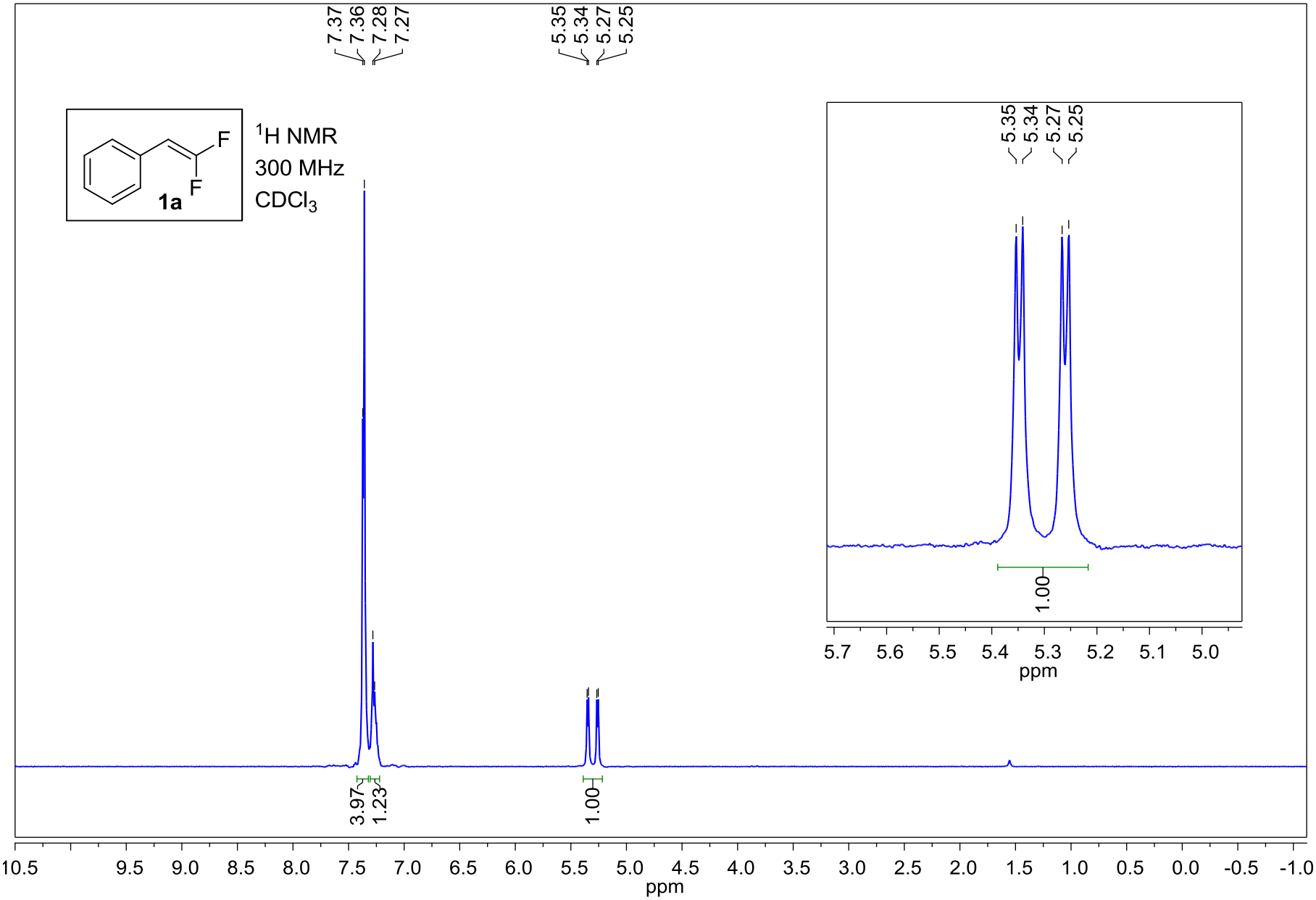
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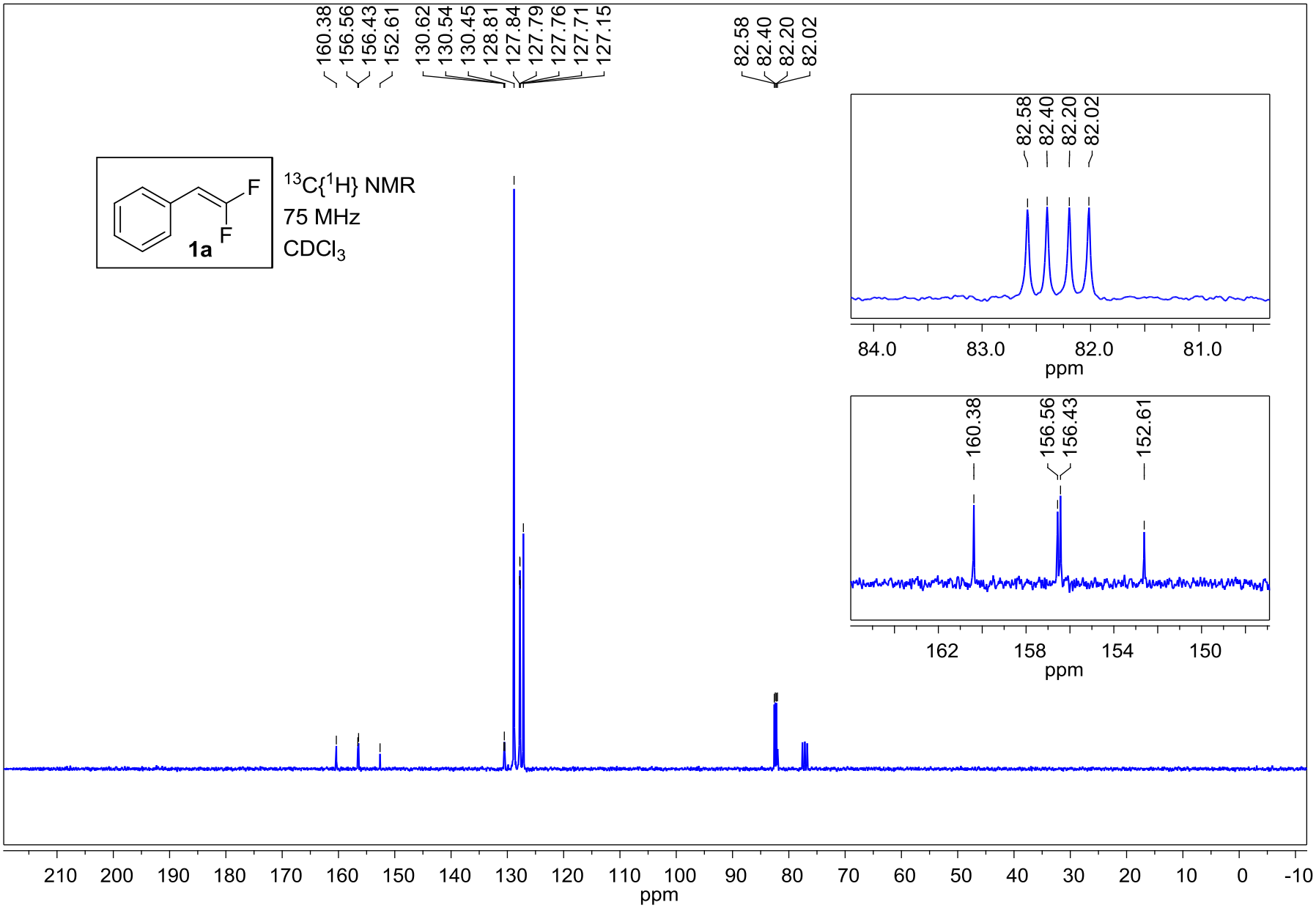
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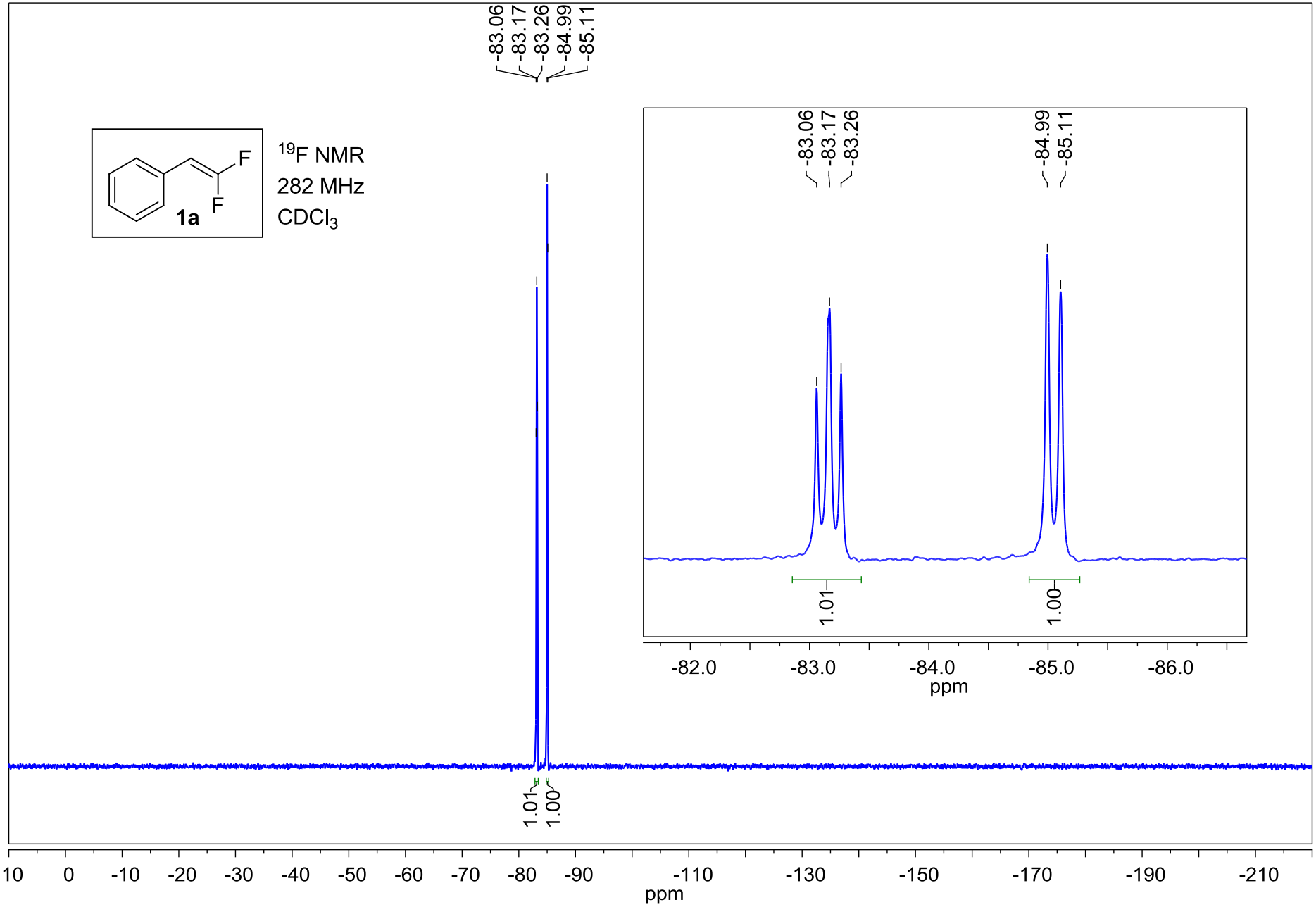
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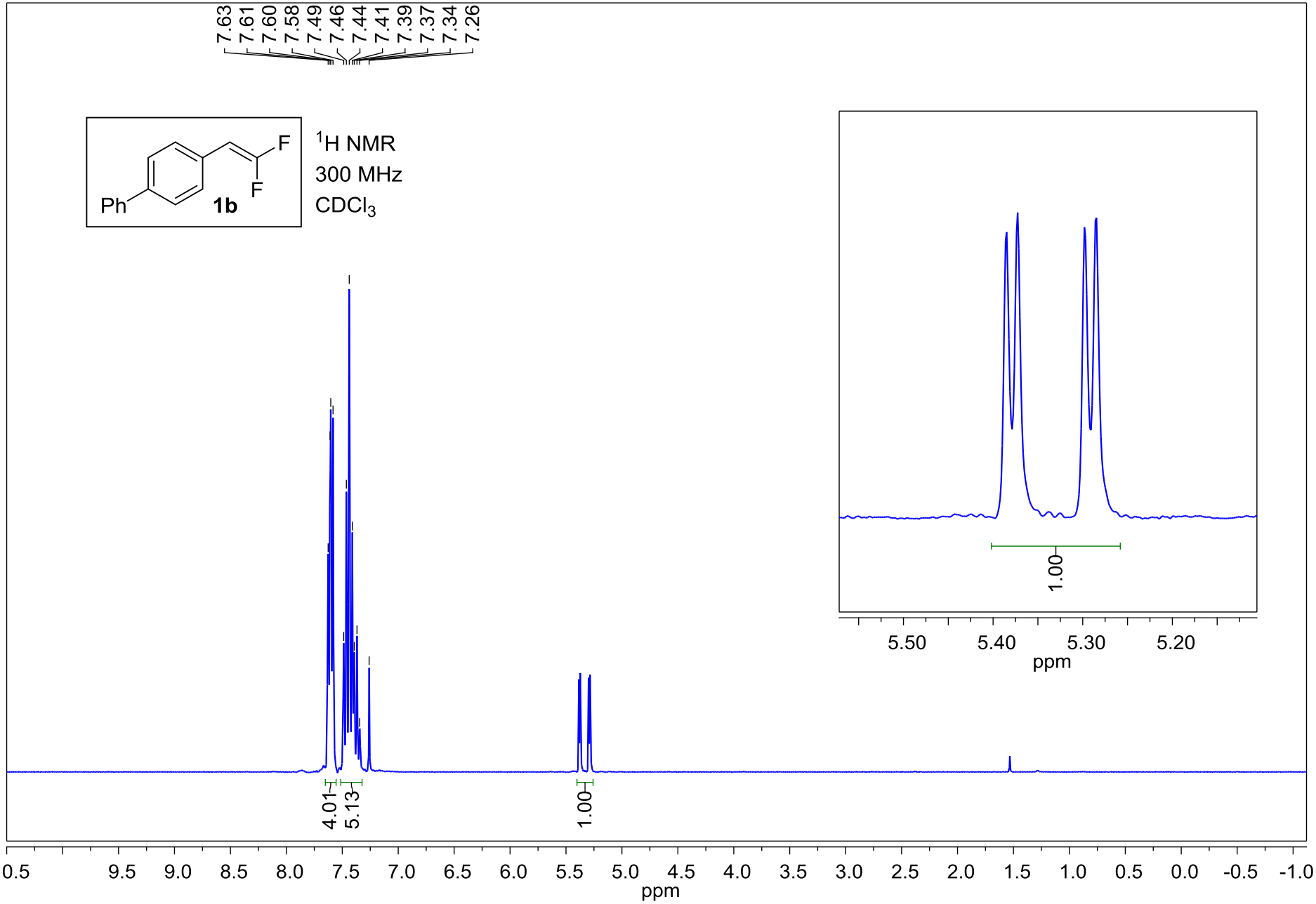
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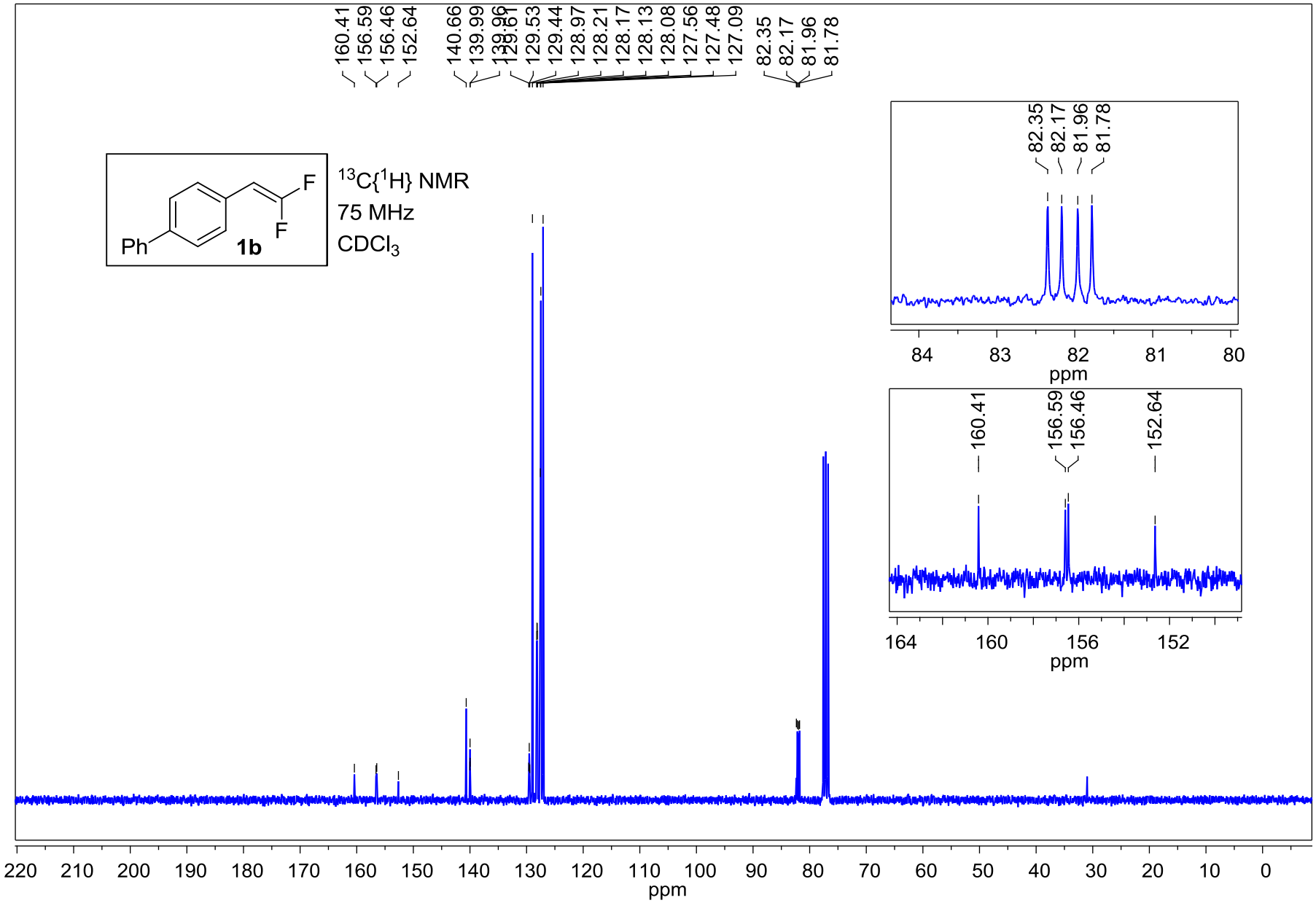
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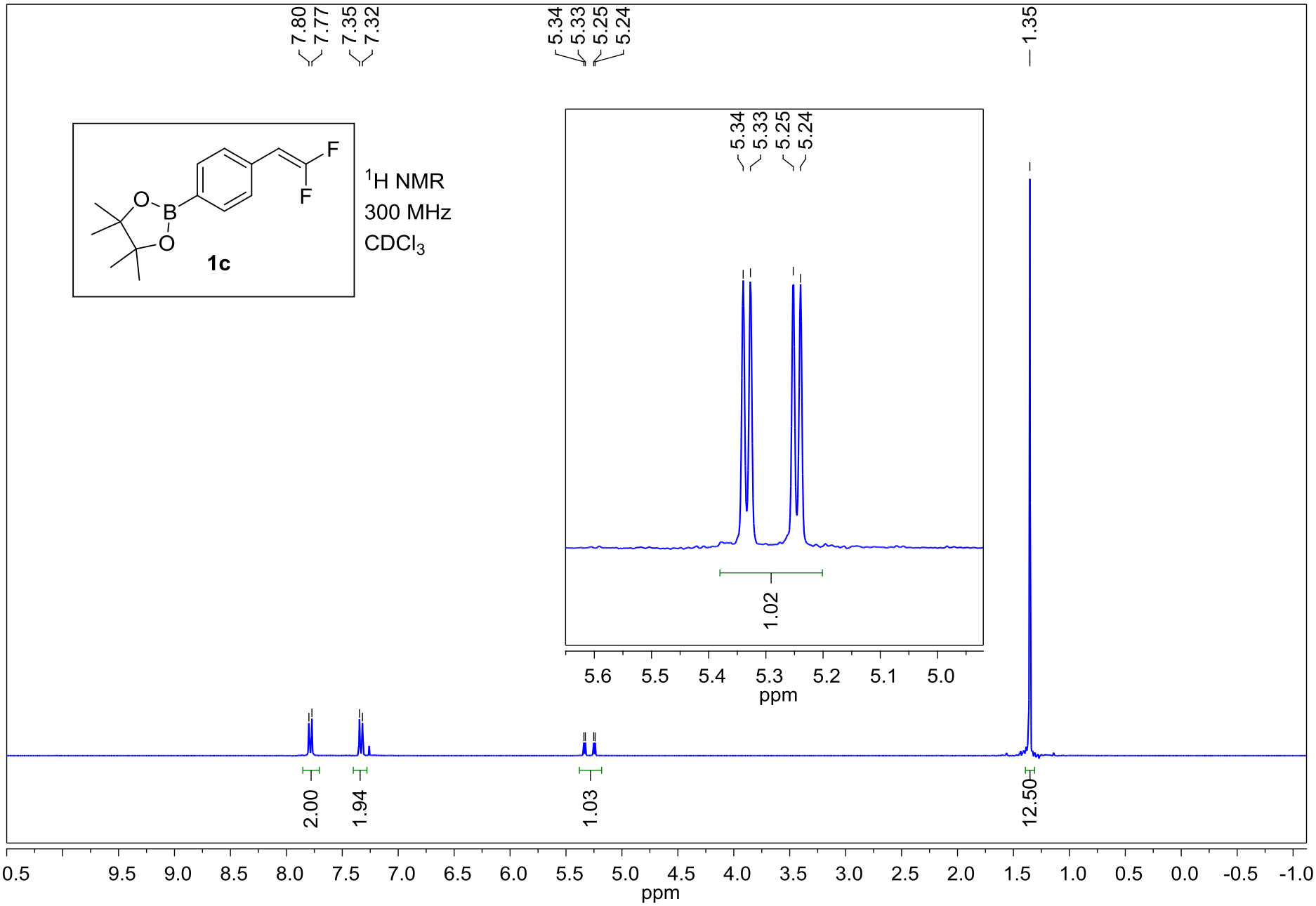
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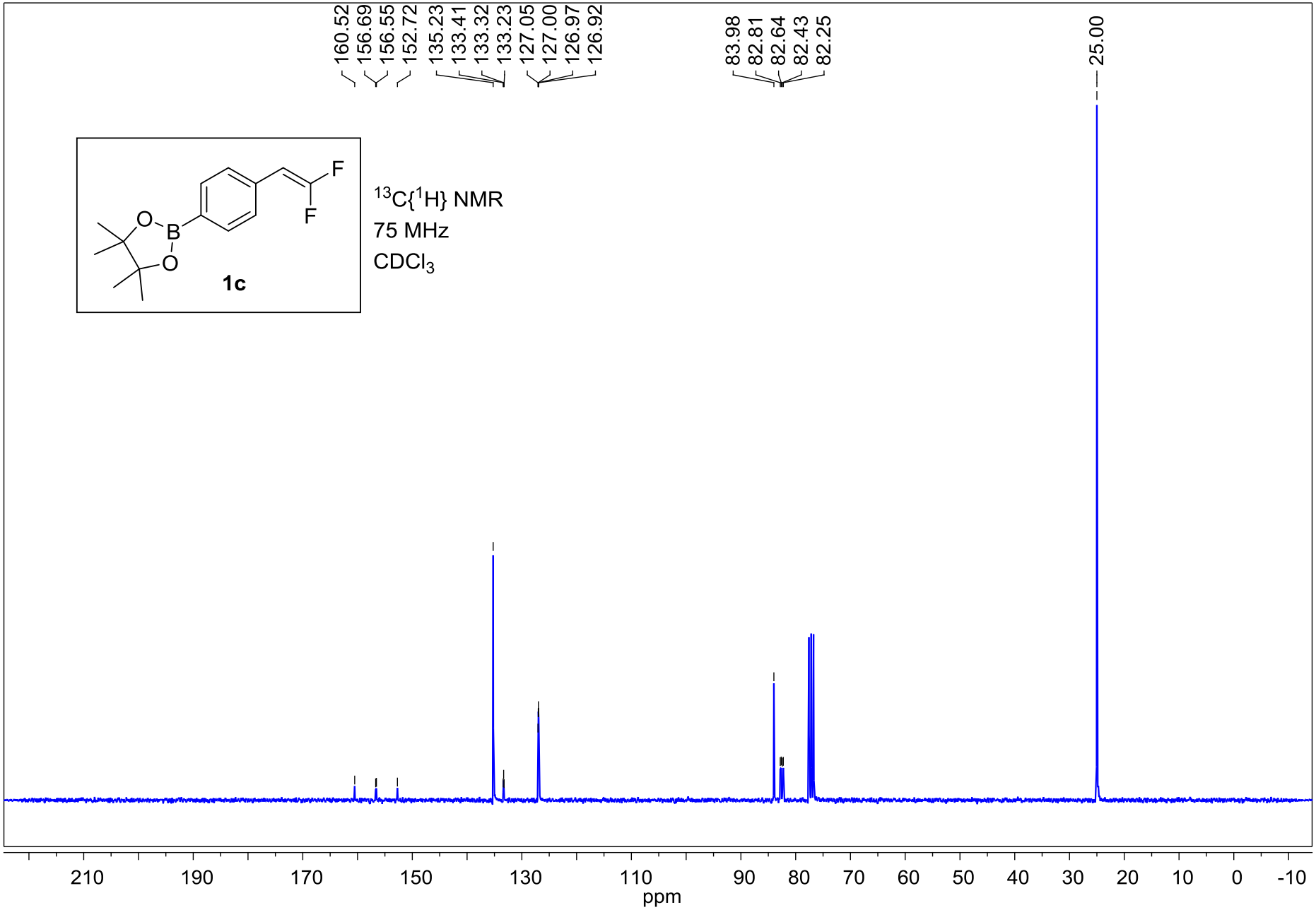
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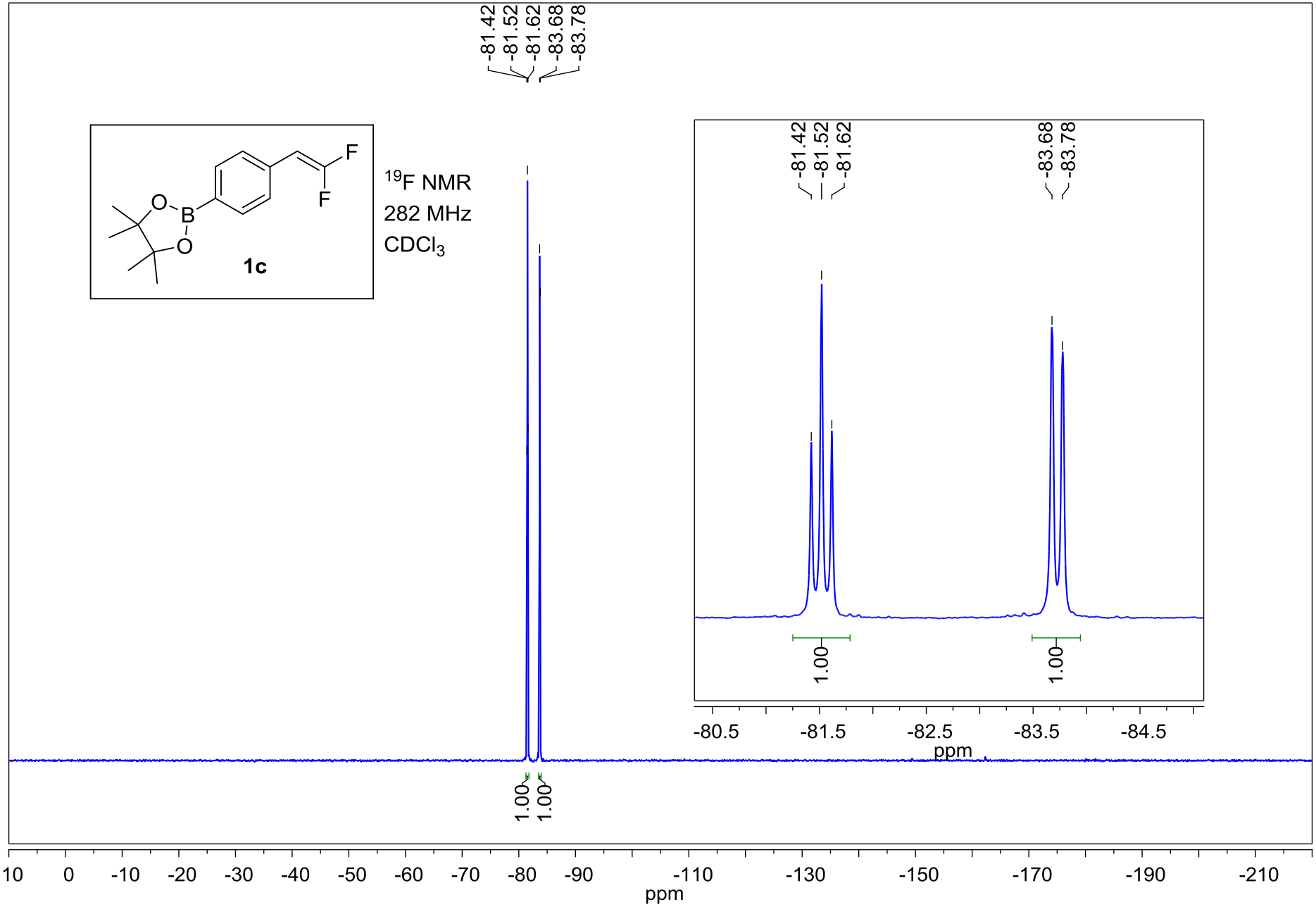
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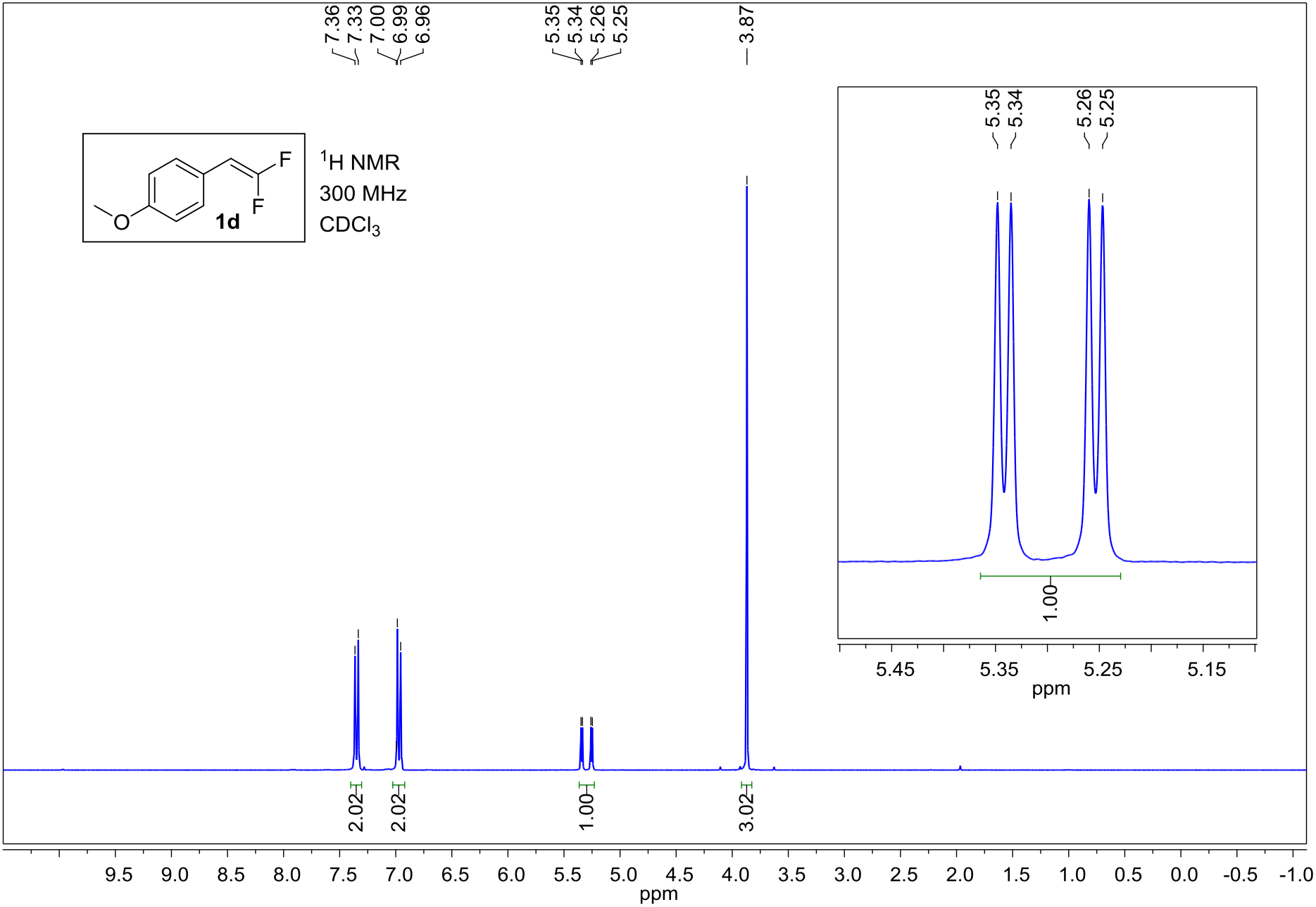
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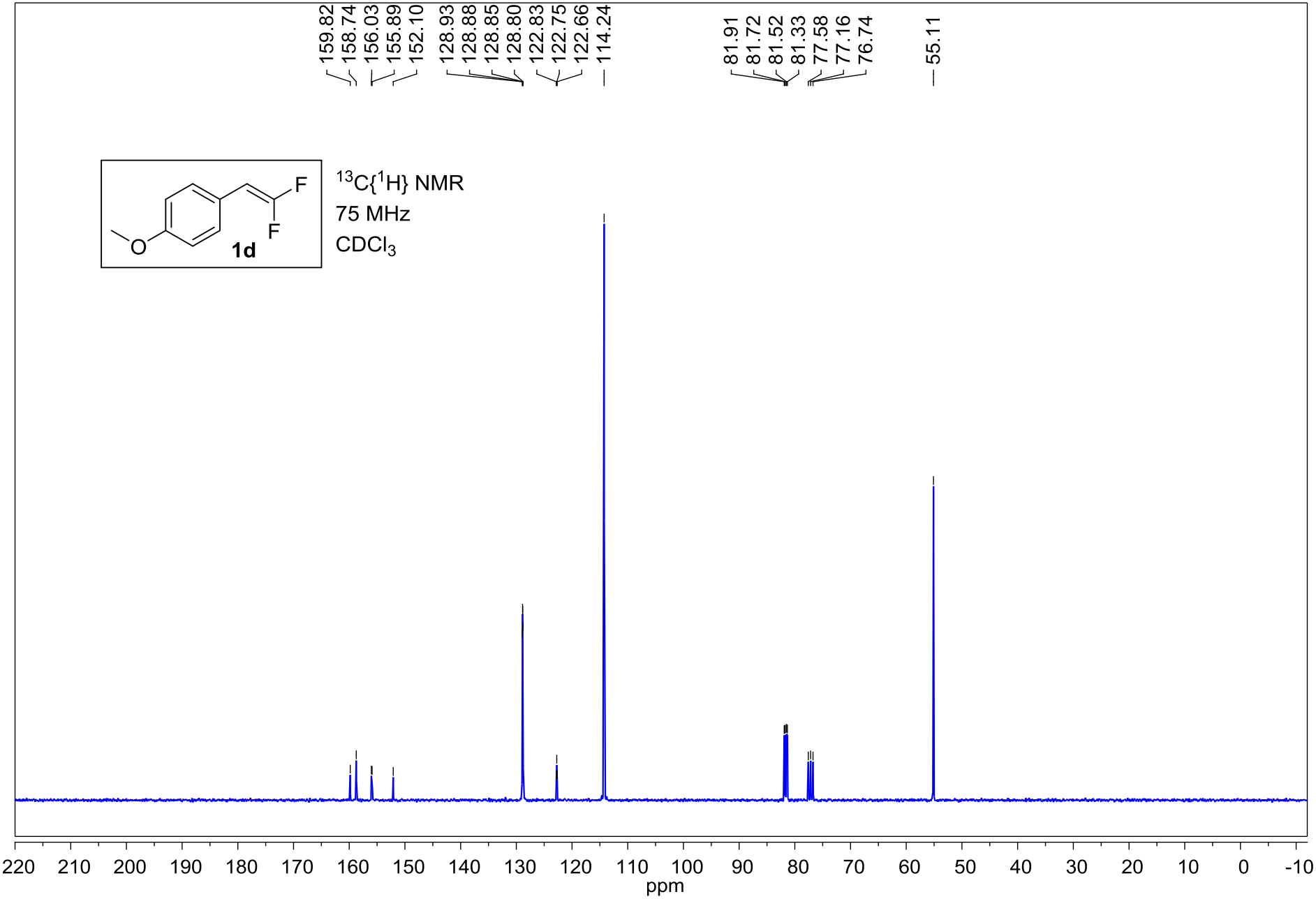
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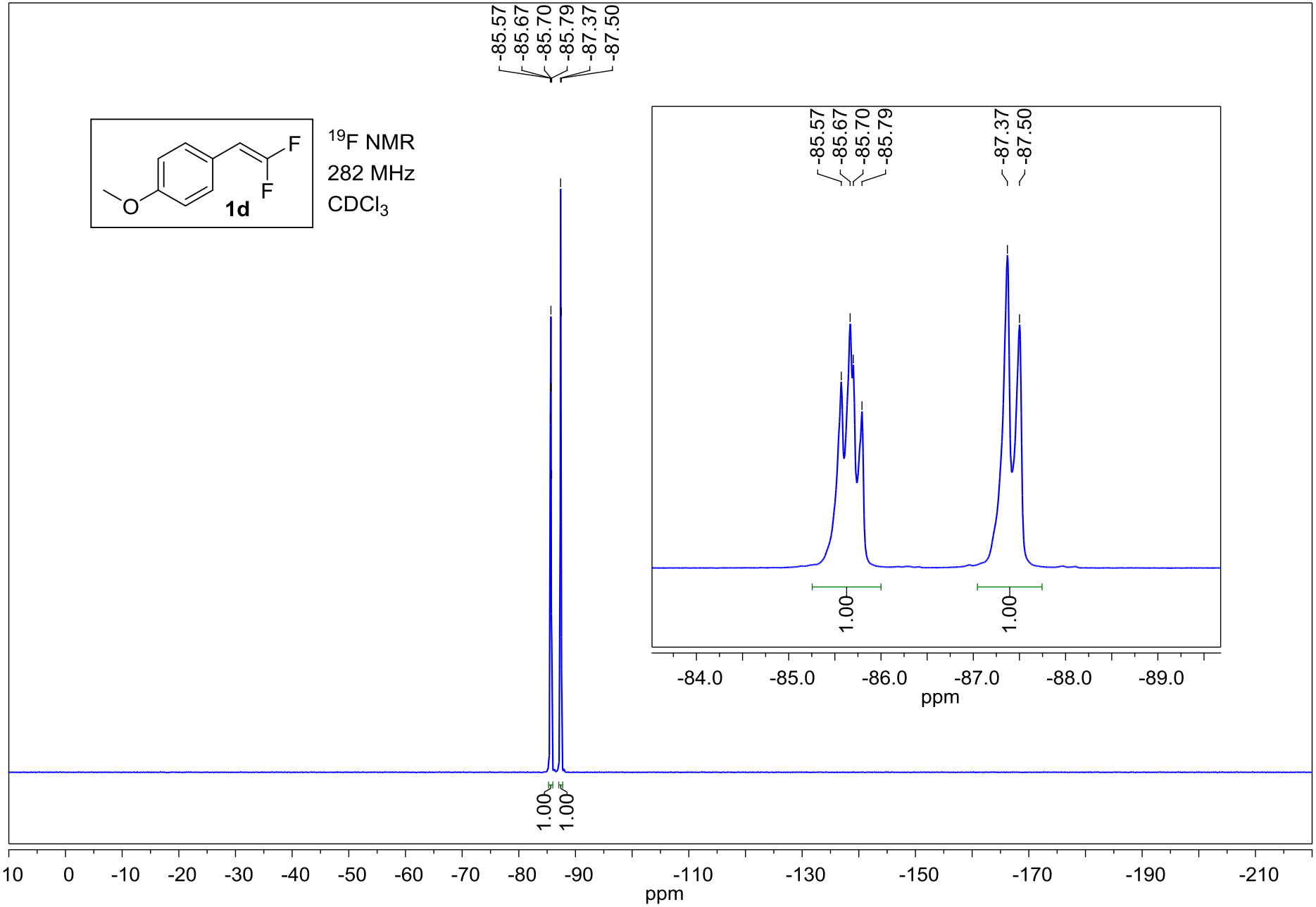
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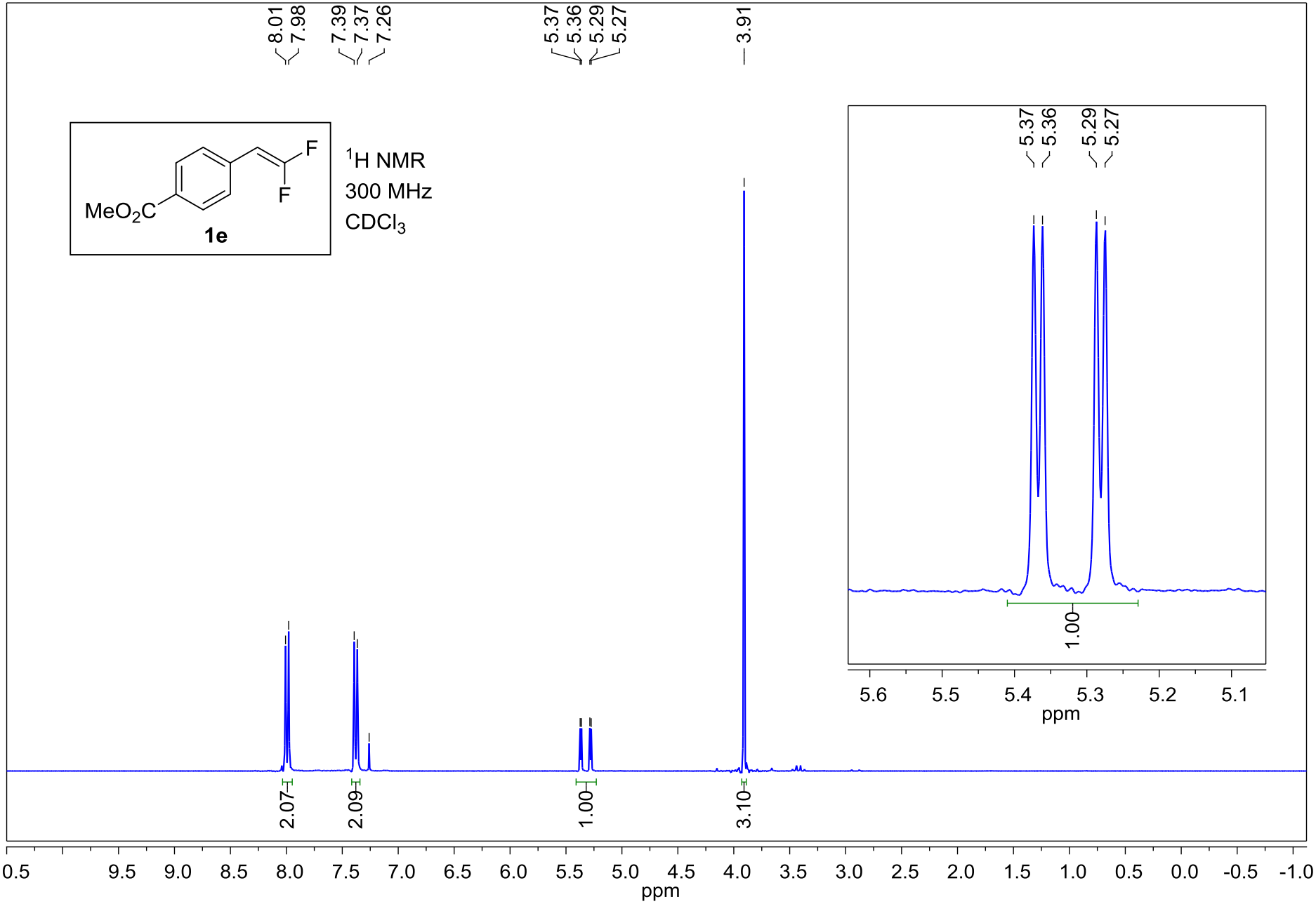
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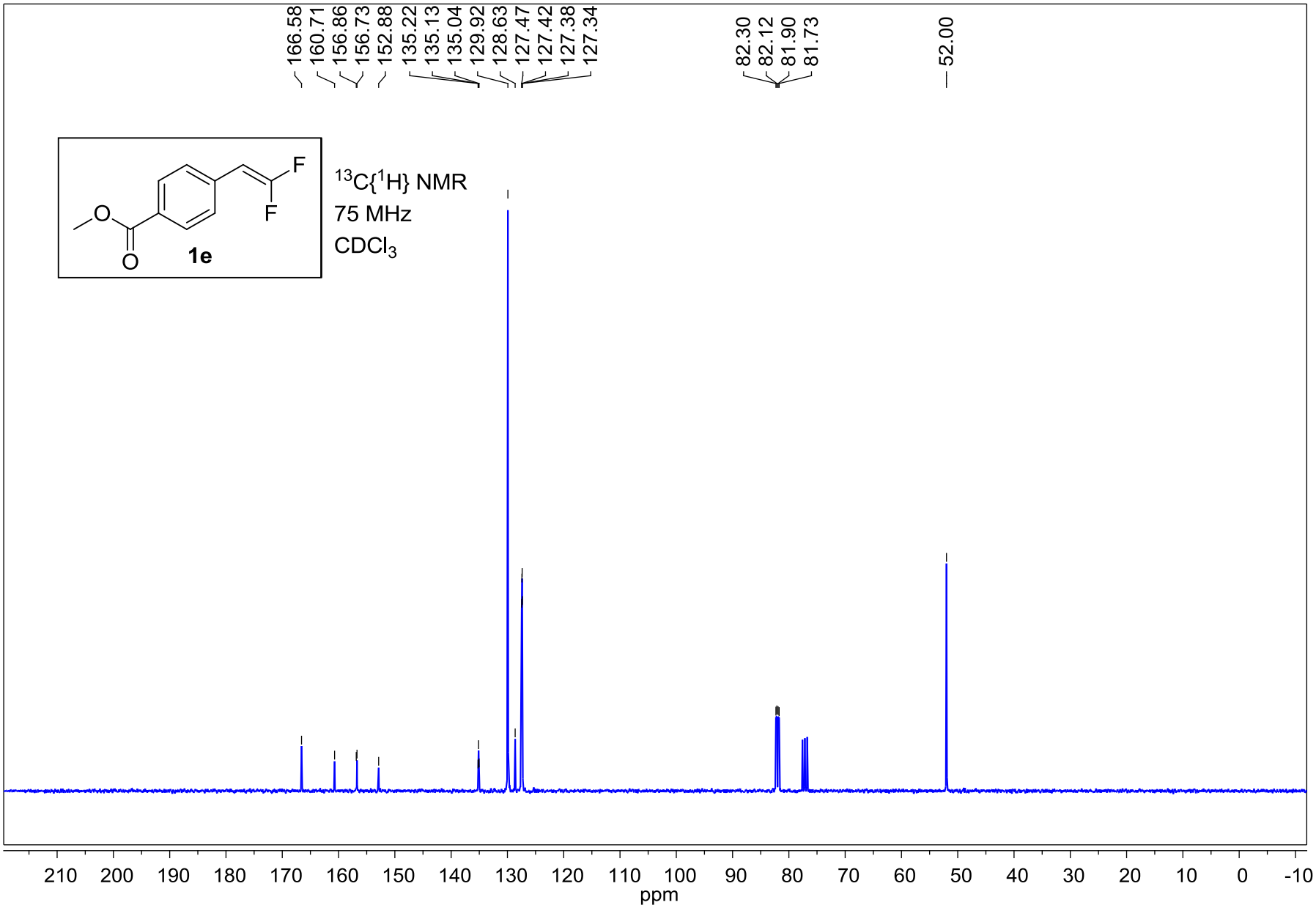
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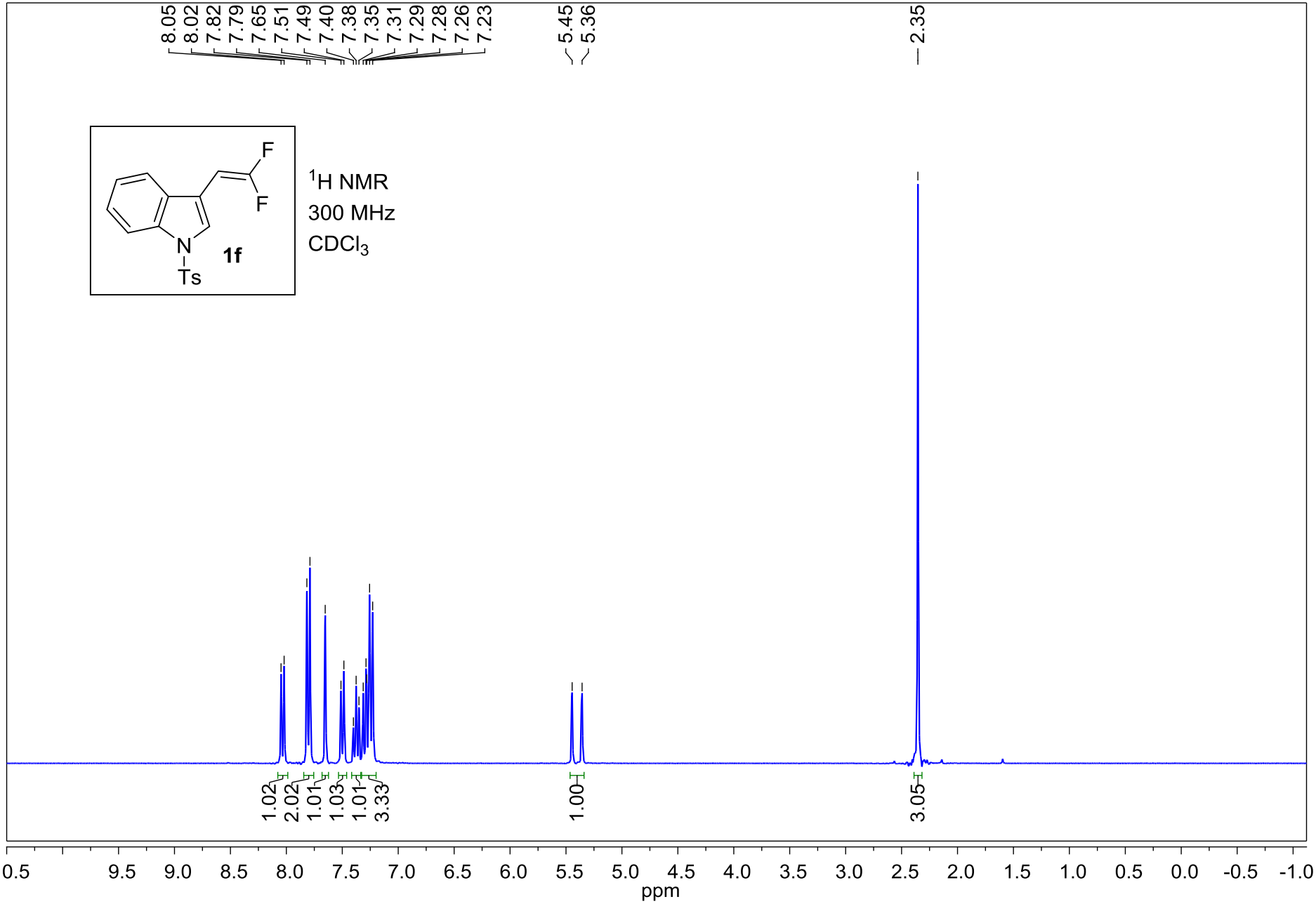
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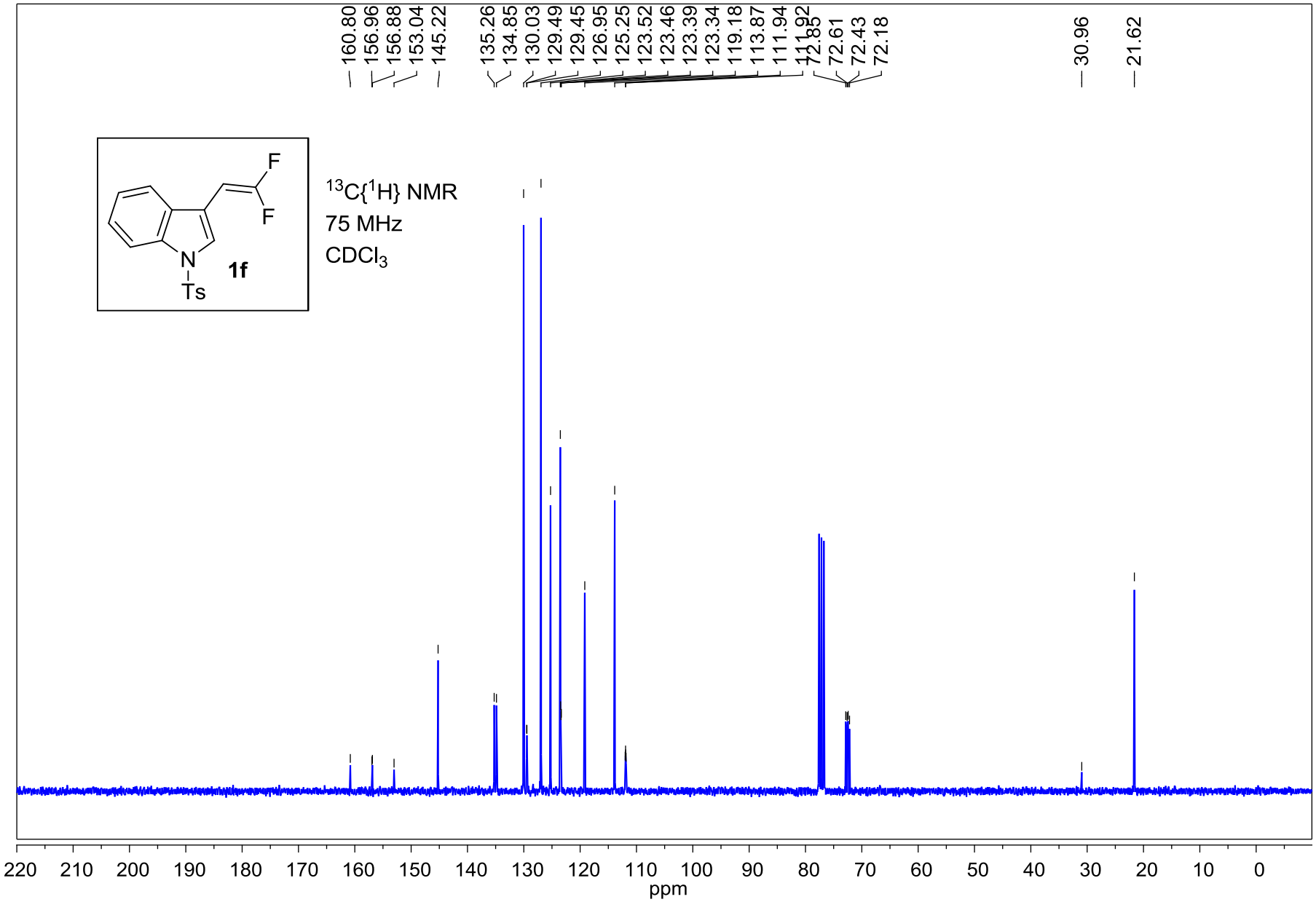
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CDCl3
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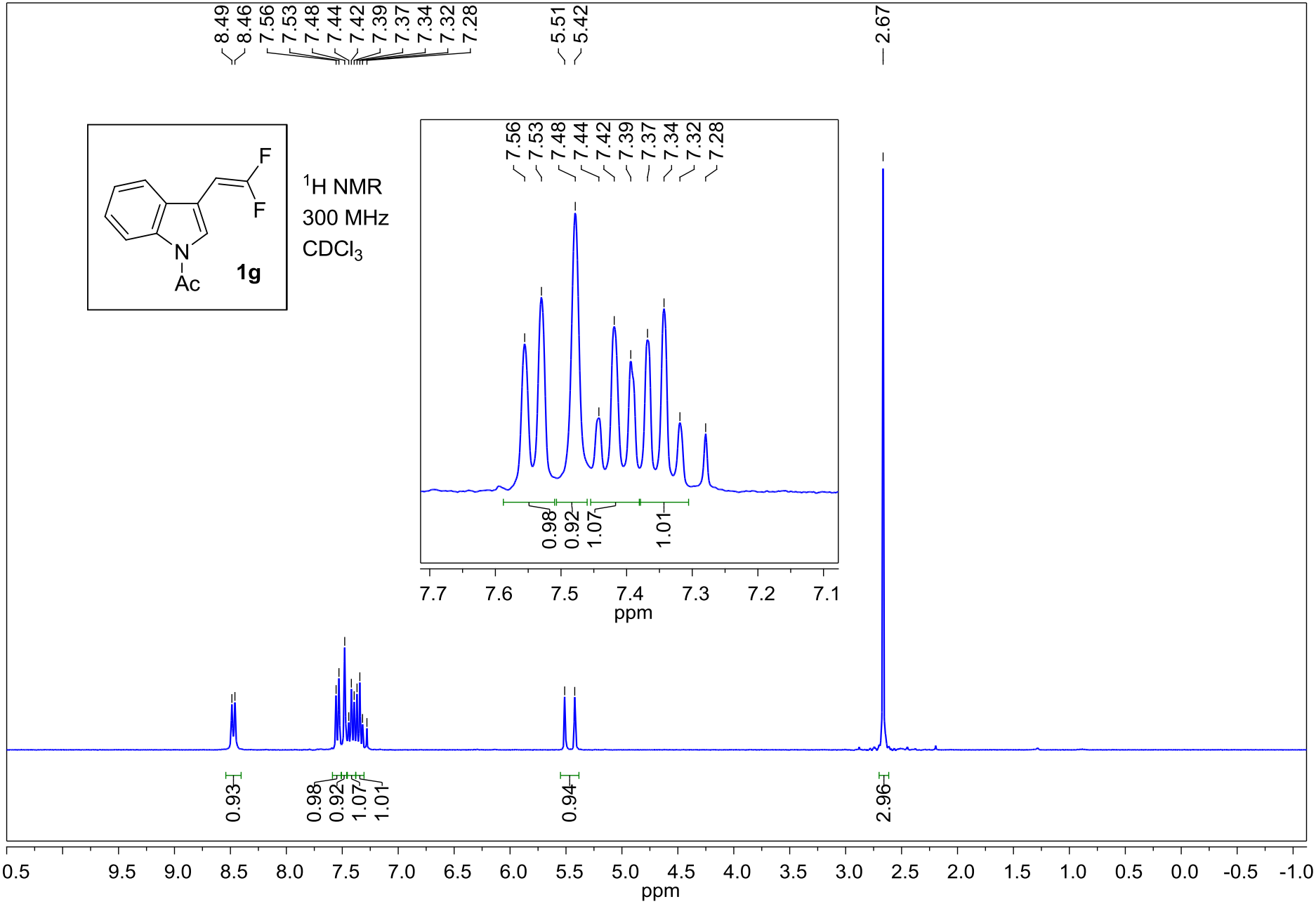
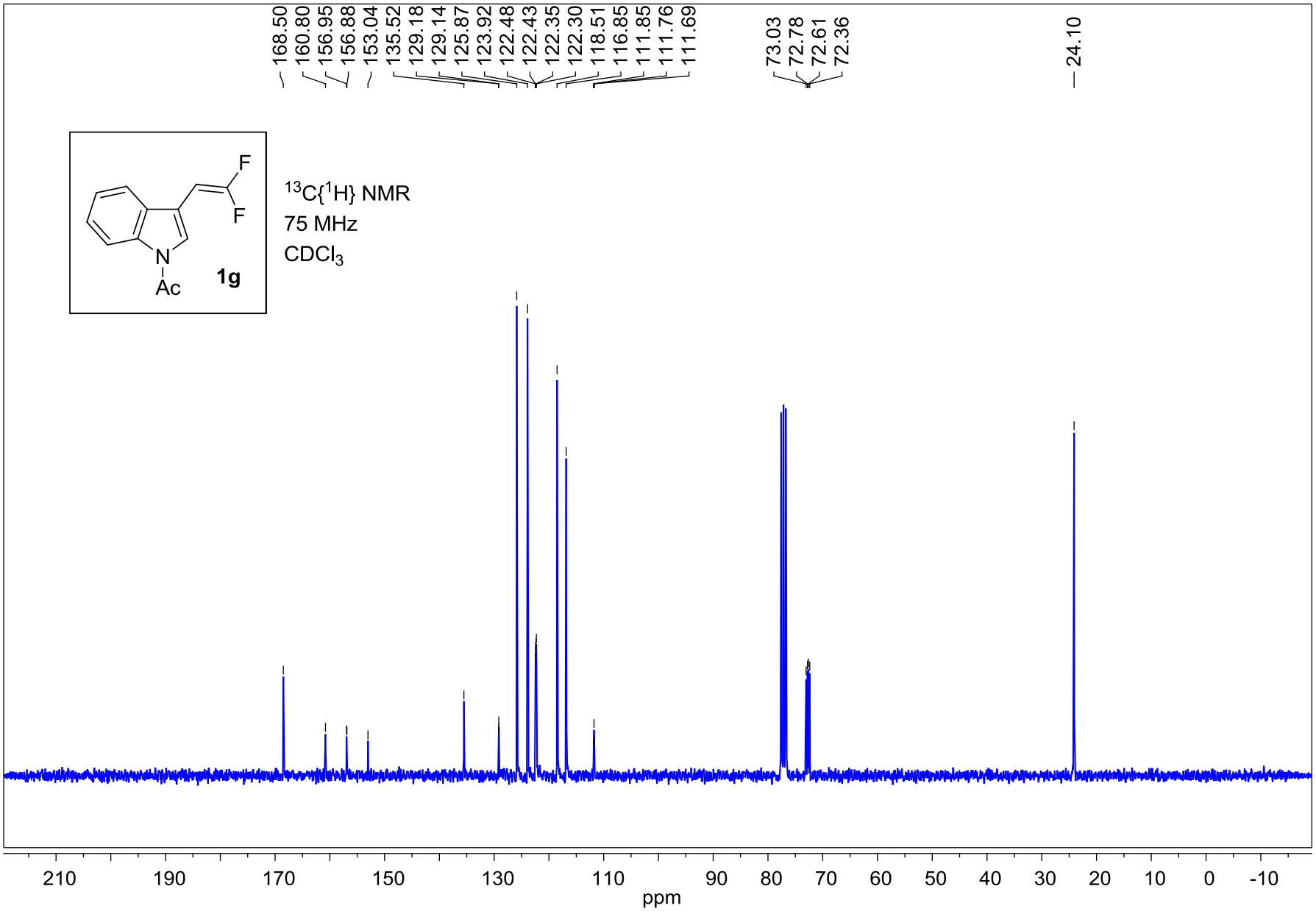
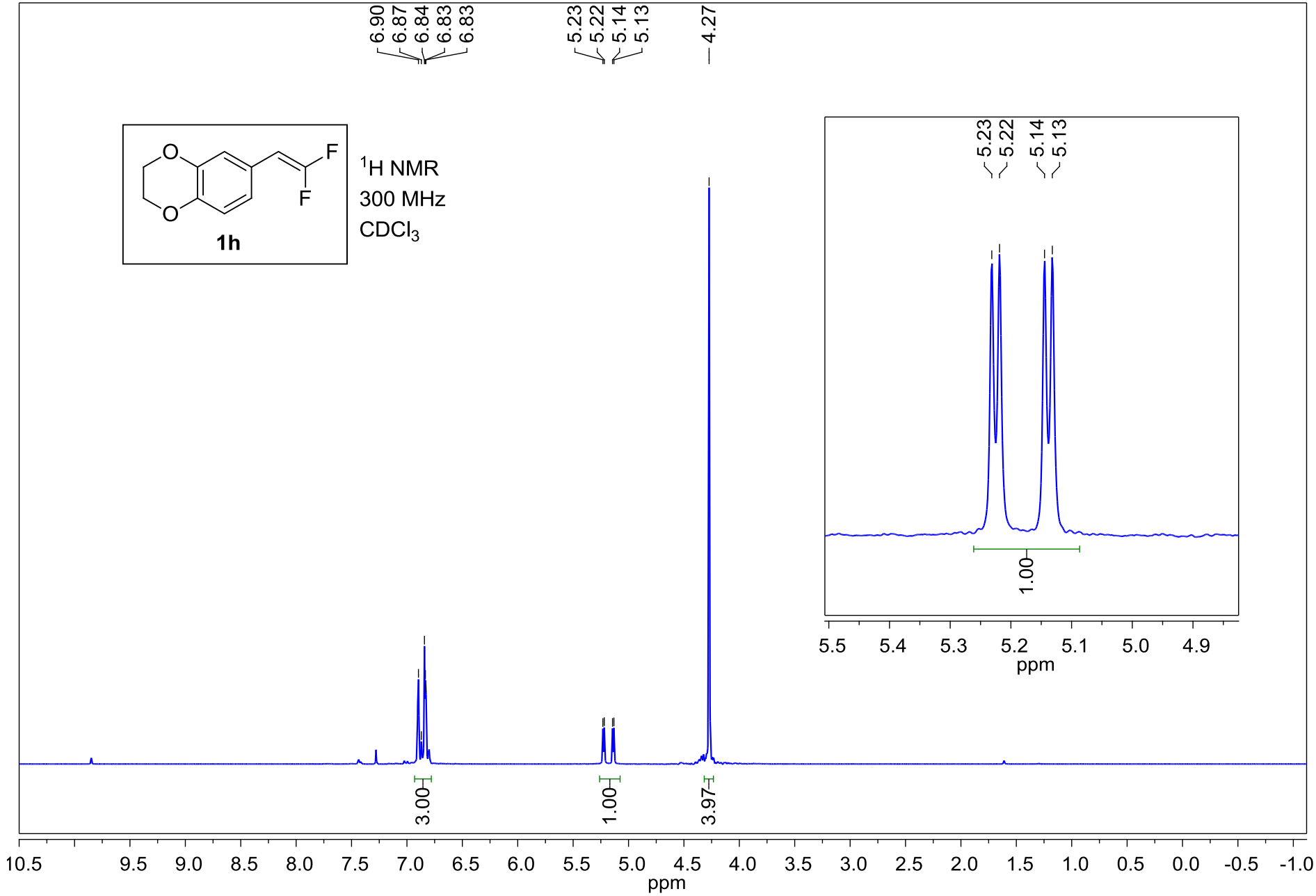
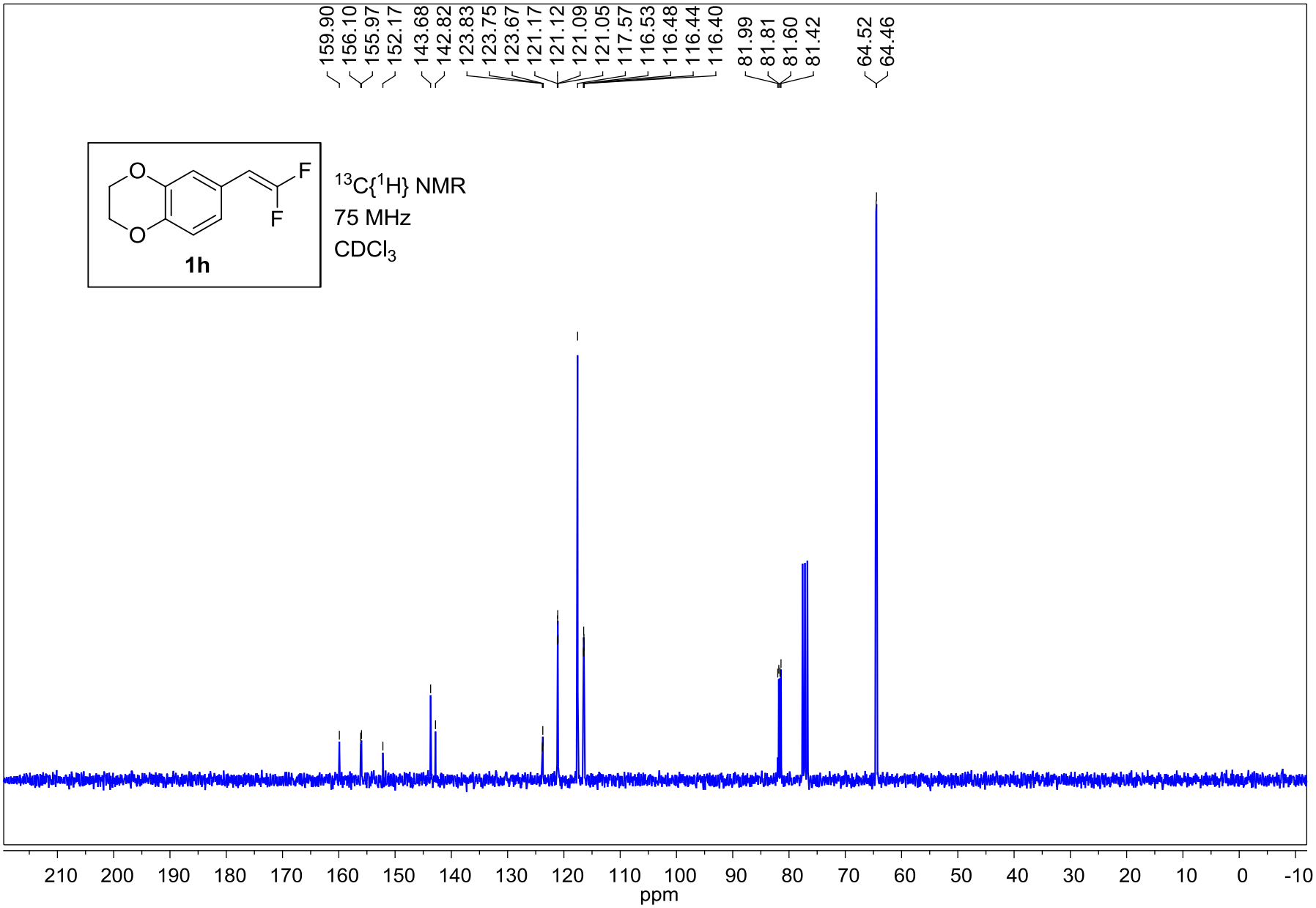
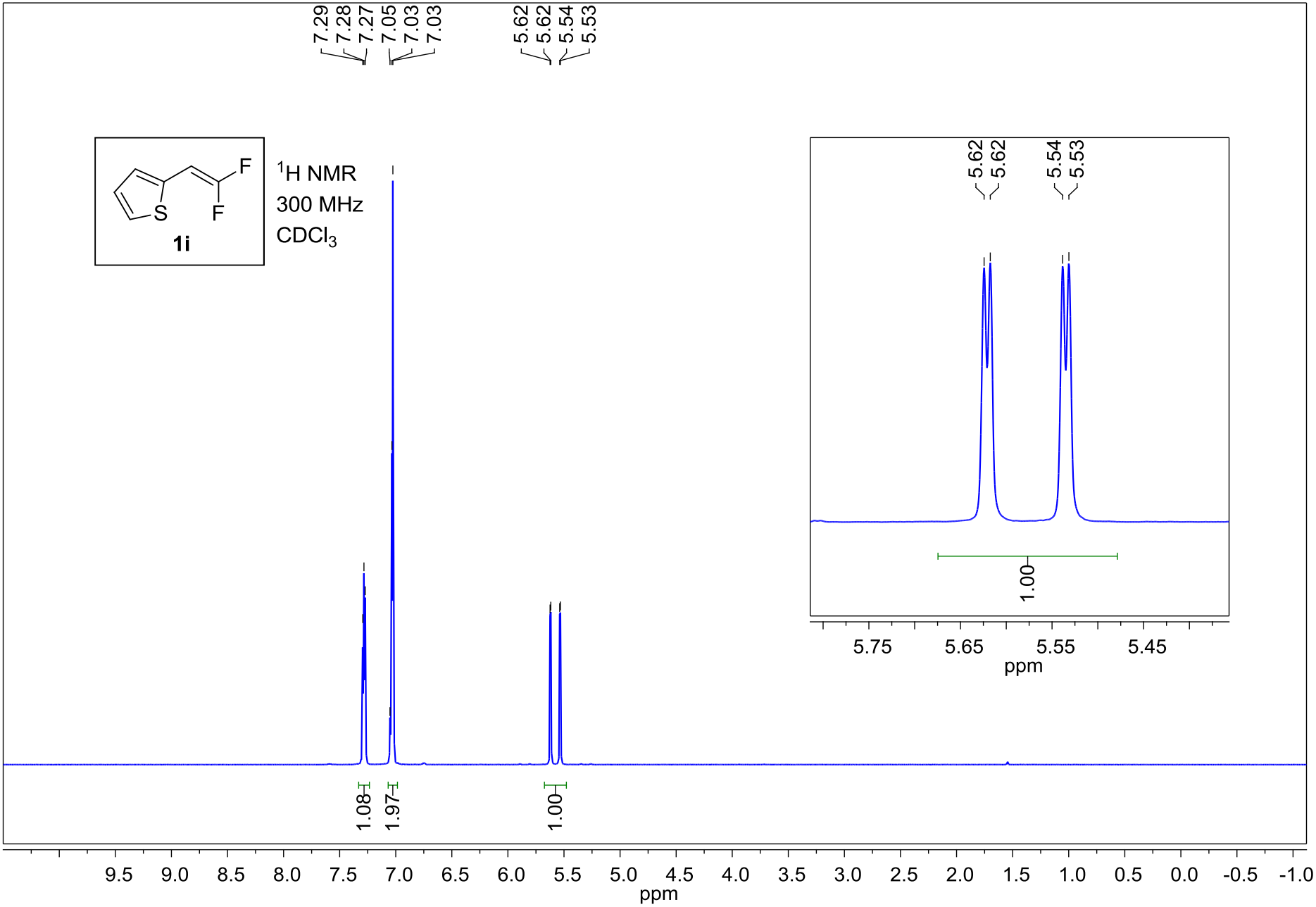
ppm

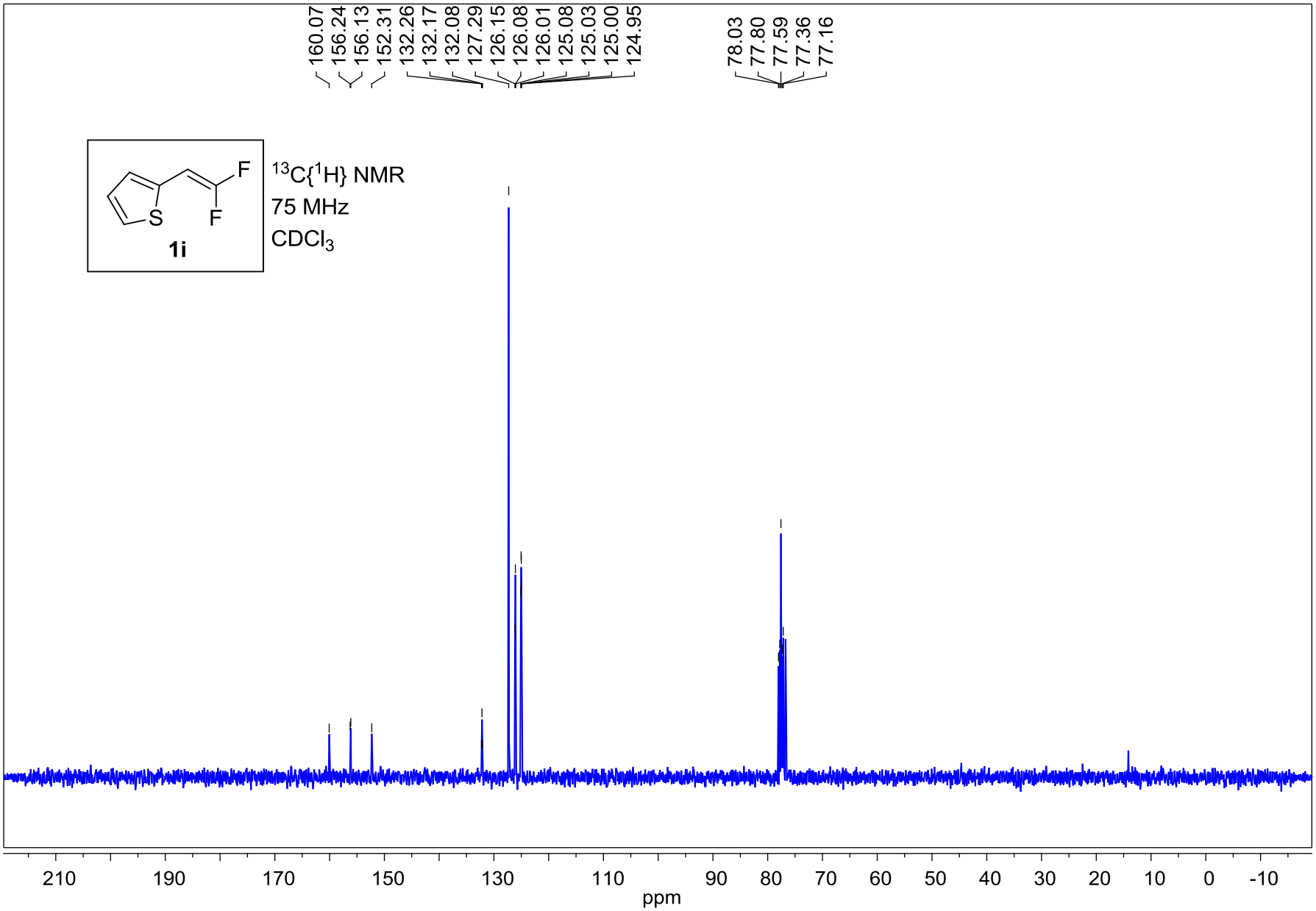

8.49
8.46
7.56
7.53
7.48
7.44
7.42
7.39
7.37
7.34
7.32
7.28
5.51
5.42
2.67
F
F
N
Ac
1g
1H NMR
300 MHz
CDCl3
0.98
0.92
1.07
1.01
7.7
7.6
7.5
7.4
7.3
7.2
7.1
ppm
0.93
0.98
0.92
1.07
1.01
0.94
2.96
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

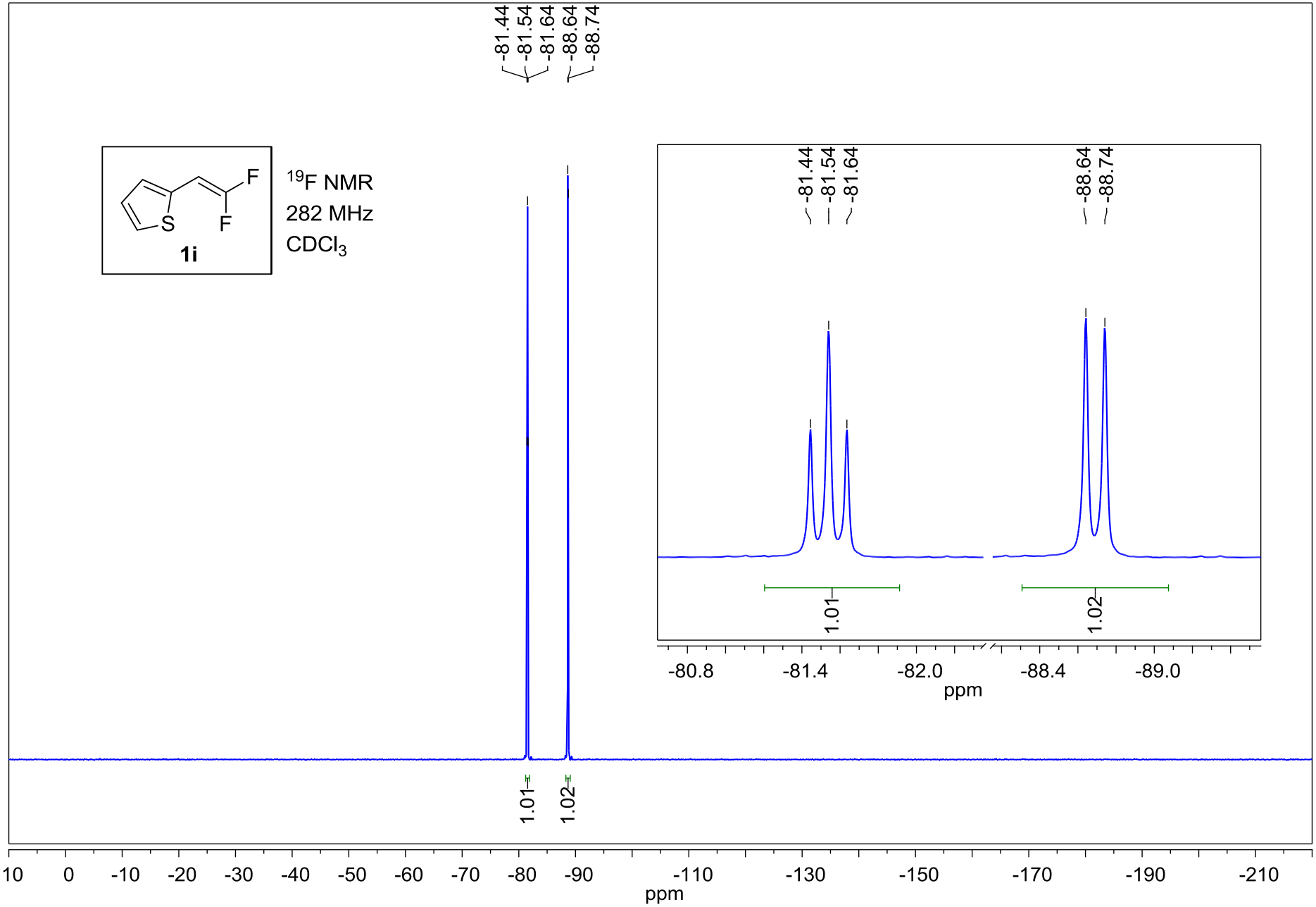

168.50
160.80
156.95
156.88
153.04
135.52
129.18
129.14
125.87
123.92
122.48
122.43
122.35
122.30
118.51
116.85
111.85
111.76
111.69
73.03
72.78
72.61
72.36
24.10
F
F
N
Ac
1g
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

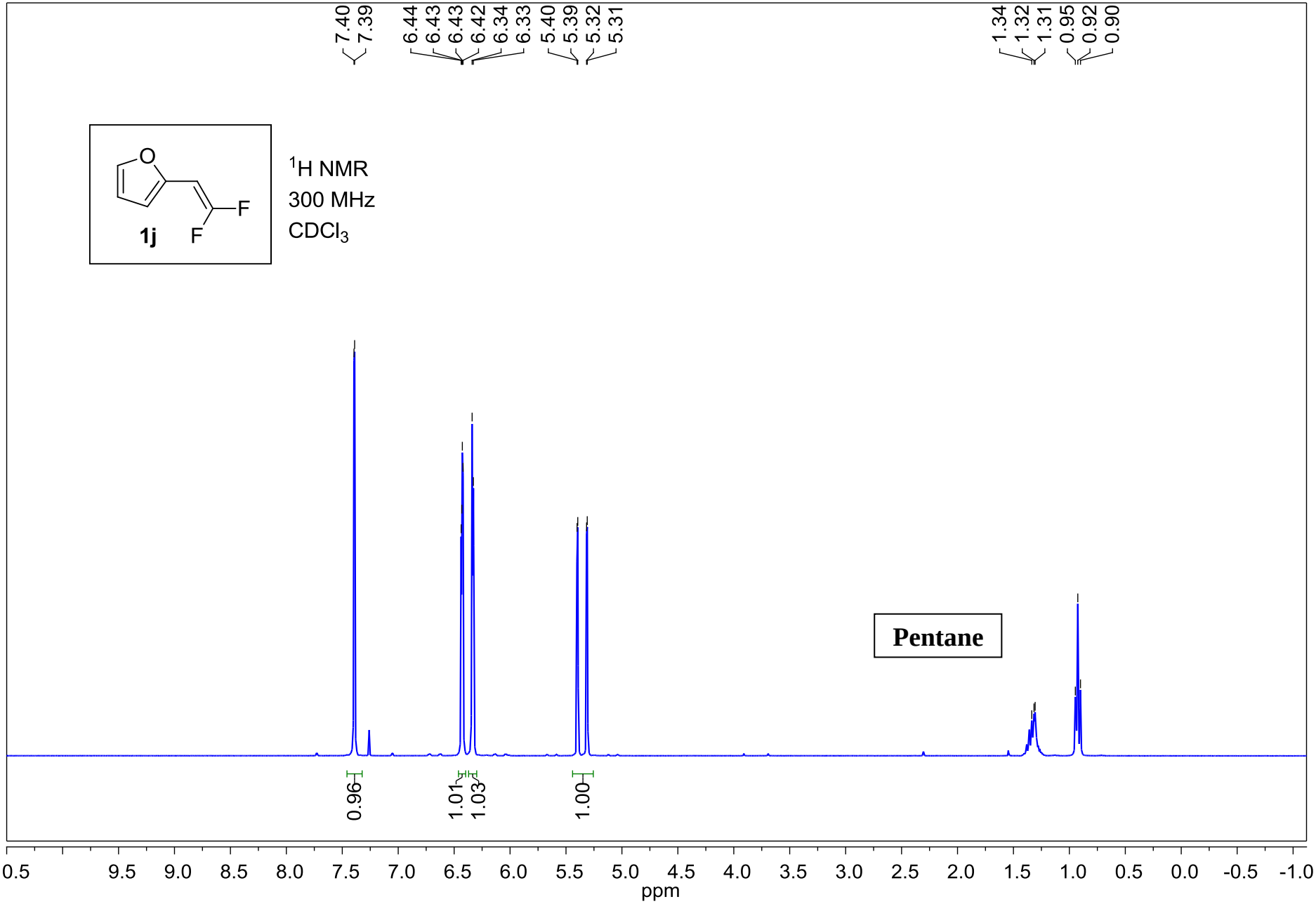

6.90
6.87
6.84
6.83
6.83
5.23
5.22
5.14
5.13
4.27
O
O
F
F
1h
1H NMR
300 MHz
CDCl3
5.23
5.22
5.14
5.13
1.00
5.5 5.4 5.3 5.2 5.1 5.0 4.9
ppm
3.00
1.00
3.97
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

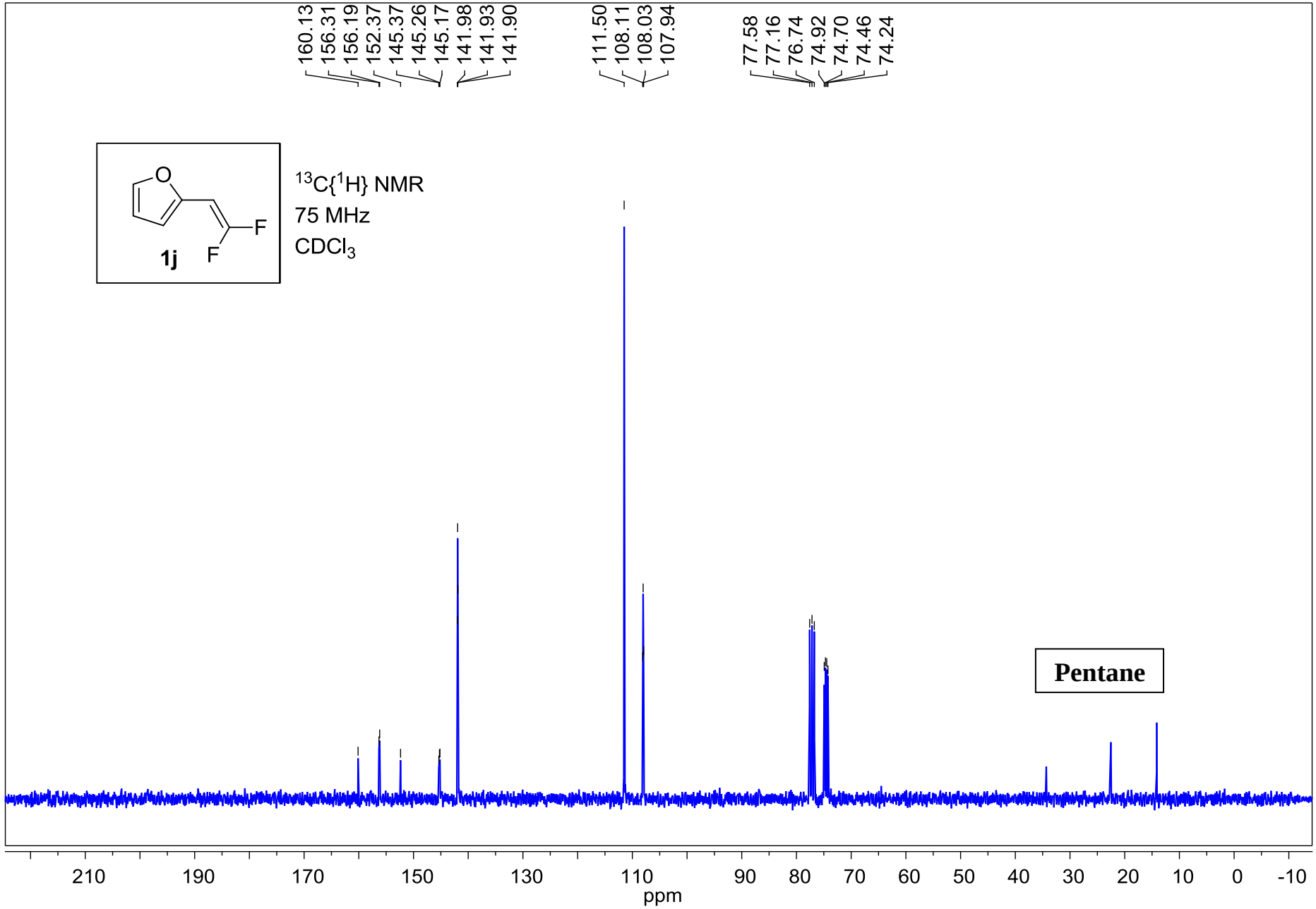

159.90
156.10
155.97
152.17
143.68
142.82
123.83
123.75
123.67
121.17
121.12
121.09
121.05
117.57
116.53
116.48
116.44
116.40
81.99
81.81
81.60
81.42
64.52
64.46
O
O
F
F
1h
13C{1H} NMR
75 MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

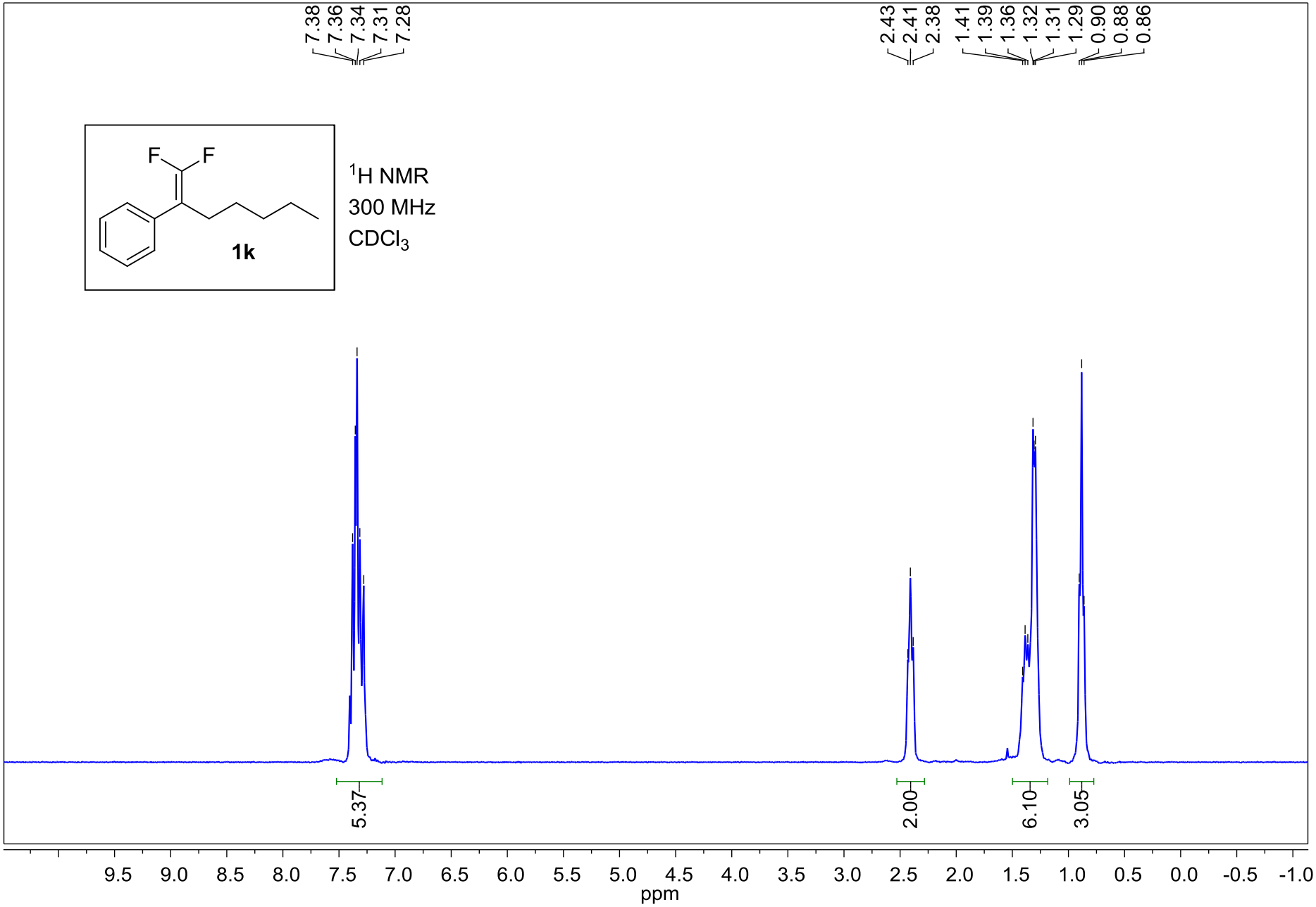

7.29
7.28
7.27
7.05
7.03
7.03
5.62
5.62
5.54
5.53
F
S
F
1i
1H NMR
300 MHz
CDCl3
5.62
5.62
5.54
5.53
1.00
5.75
5.65
5.55
5.45
ppm
1.08
1.97
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

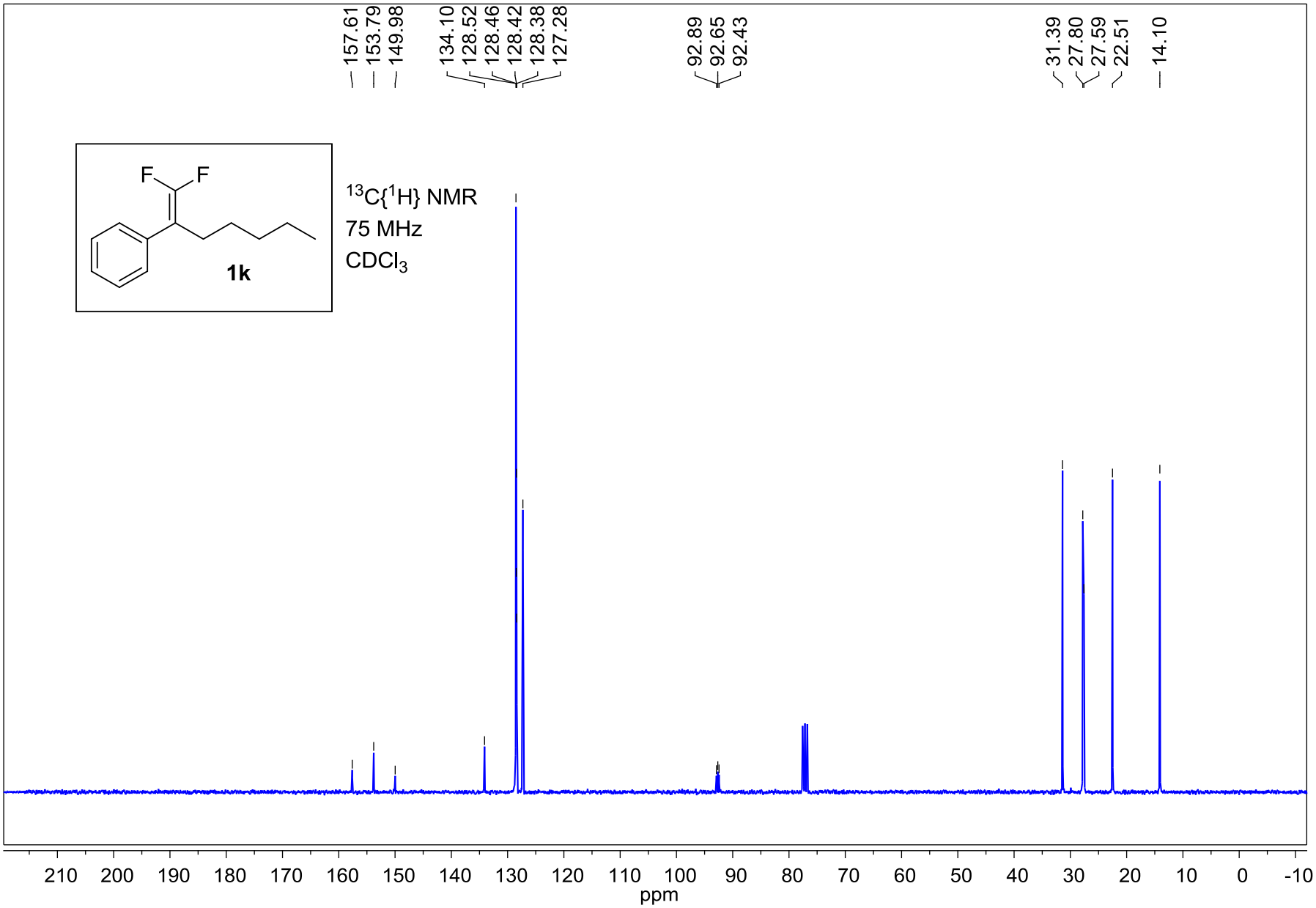

160.07
156.24
156.13
152.31
132.26
132.17
132.08
127.29
126.15
126.08
126.01
125.08
125.03
125.00
124.95
78.03
77.80
77.59
77.36
77.16
F
S
F
1i
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

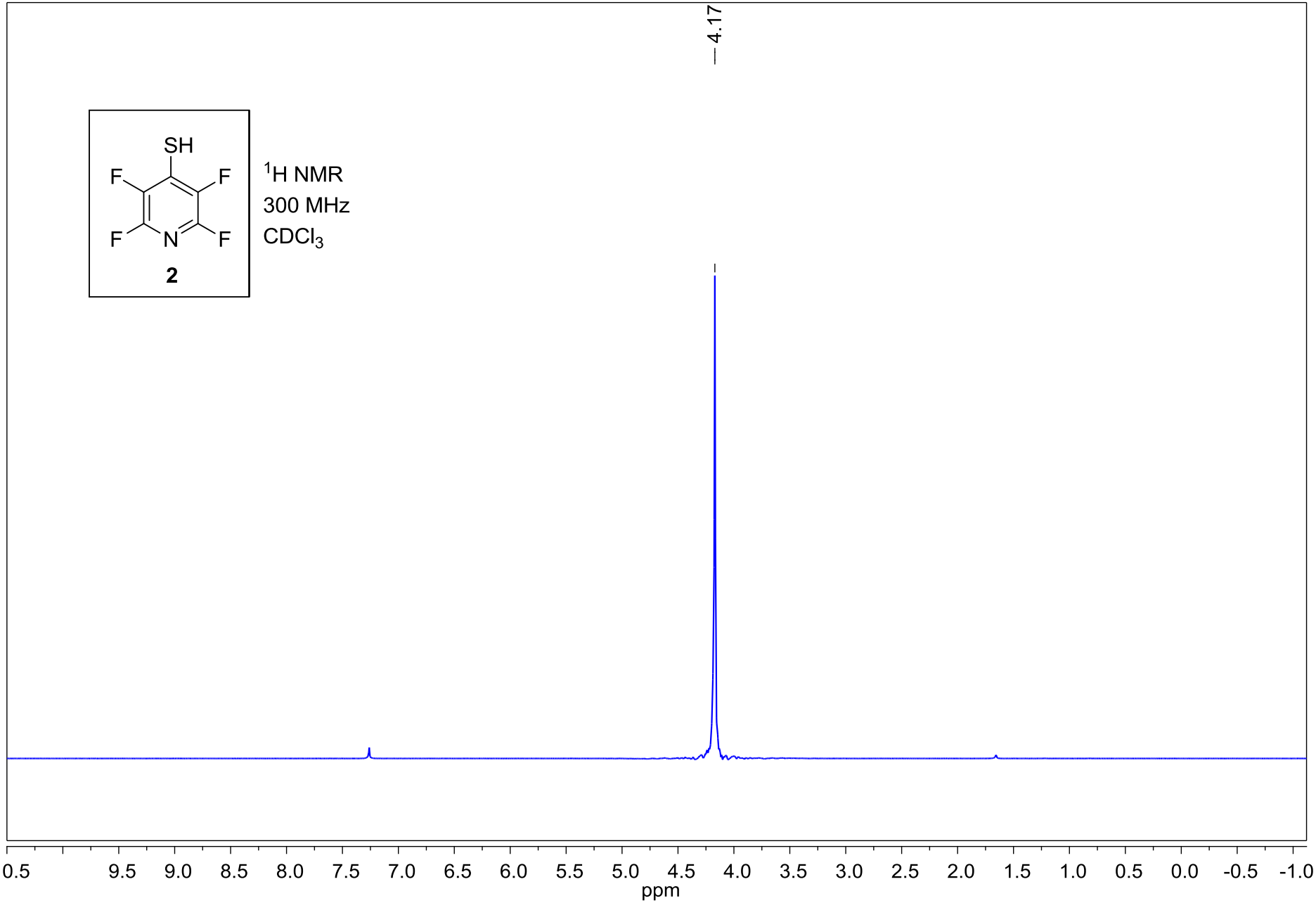

-81.44
-81.54
-81.64
-88.64
-88.74
F
S
F
1i
19F NMR
282 MHz
CDCl3
1.01
1.02
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
ppm
-80.8 -81.4 -82.0 -88.4 -89.0
ppm

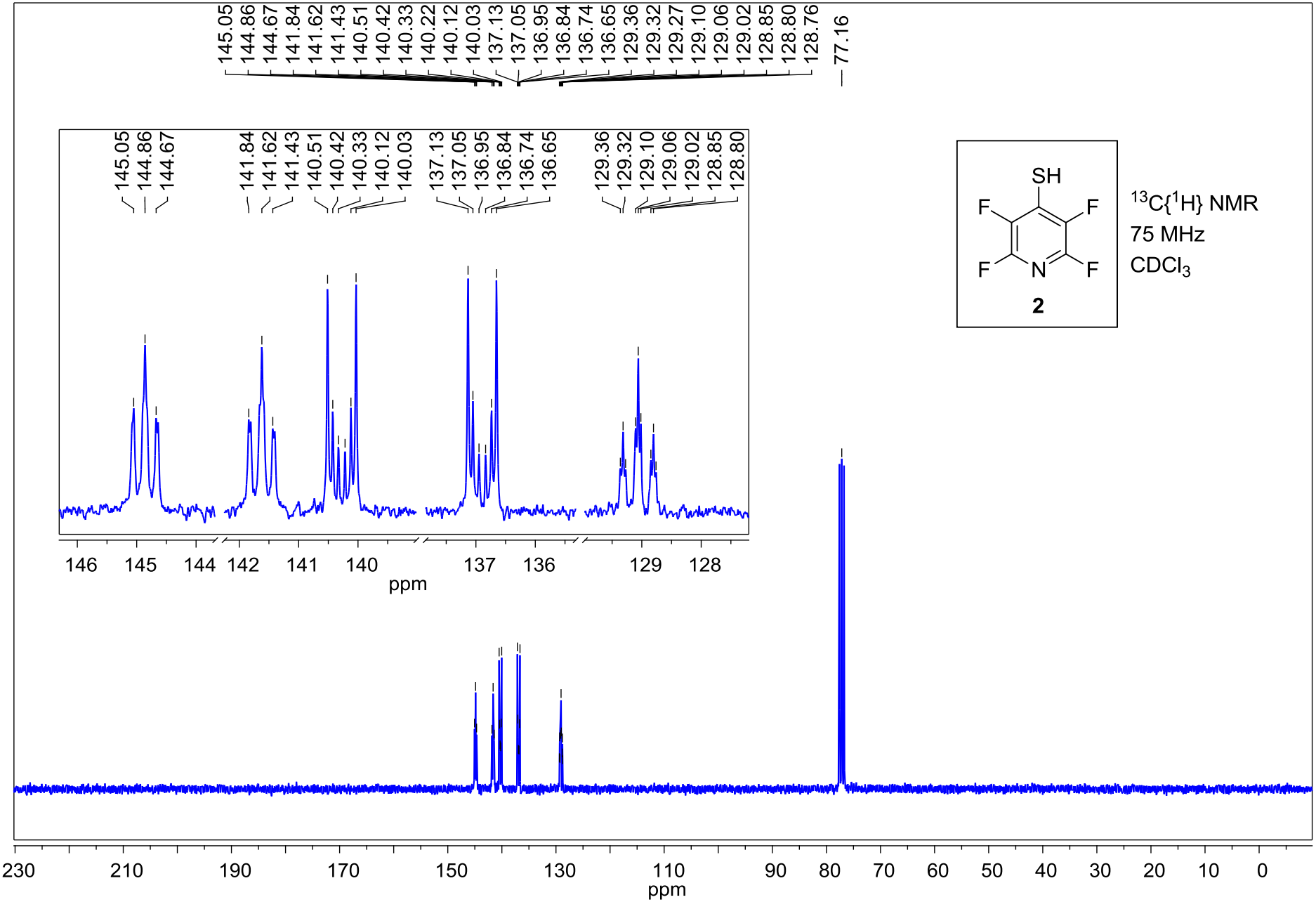

7.40
7.39
6.44
6.43
6.43
6.42
6.34
6.33
5.40
5.39
5.32
5.31
1.34
1.32
1.31
0.95
0.92
0.90
O
F
F
1j
1H NMR
300 MHz
CDCl3
Pentane
0.96
1.01
1.03
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

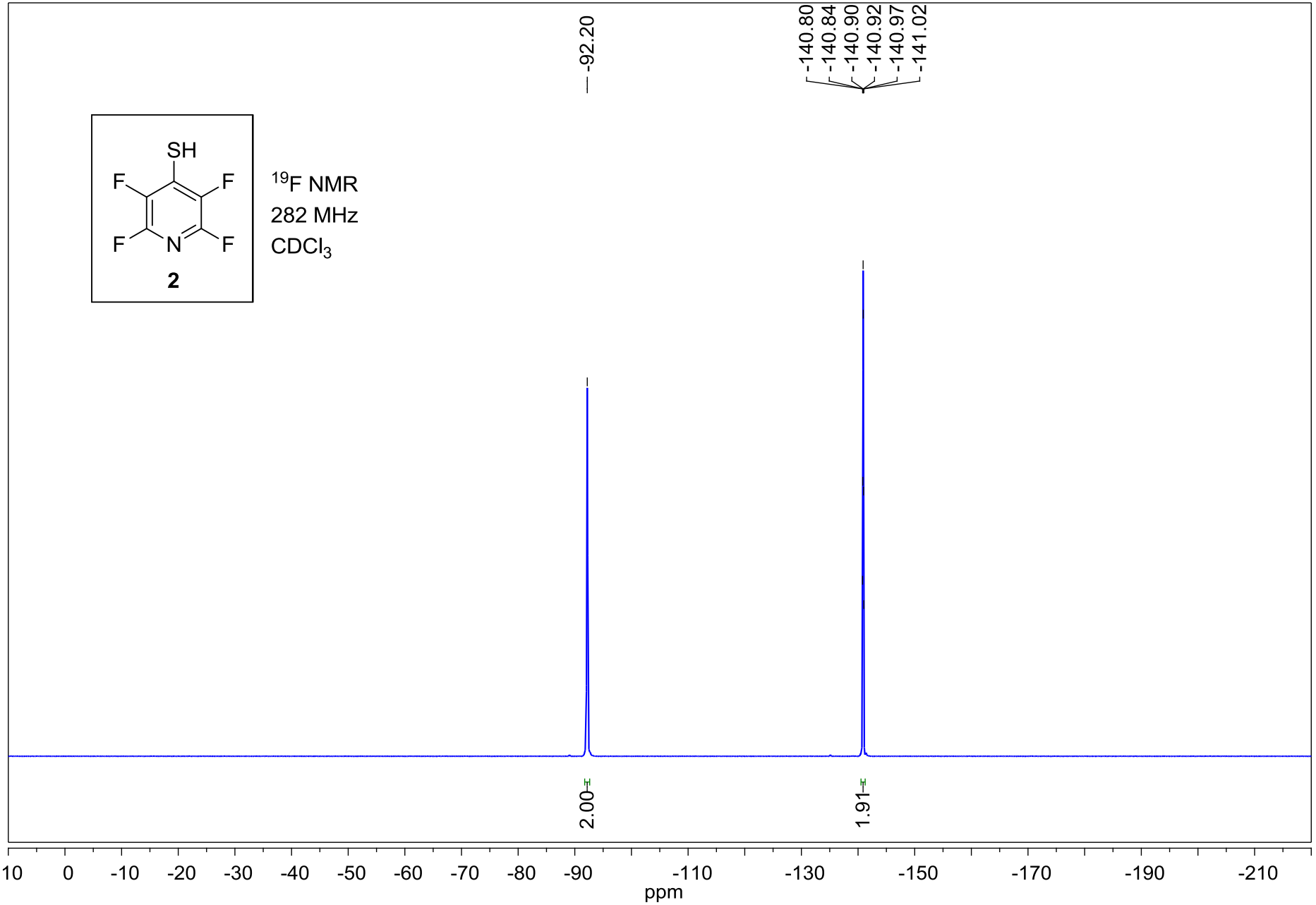

160.13
156.31
156.19
152.37
145.37
145.26
145.17
141.98
141.93
141.90
111.50
108.11
108.03
107.94
77.58
77.16
76.74
74.92
74.70
74.46
74.24
O
F
F
1j
13C{1H} NMR
75 MHz
CDCl3
Pentane
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

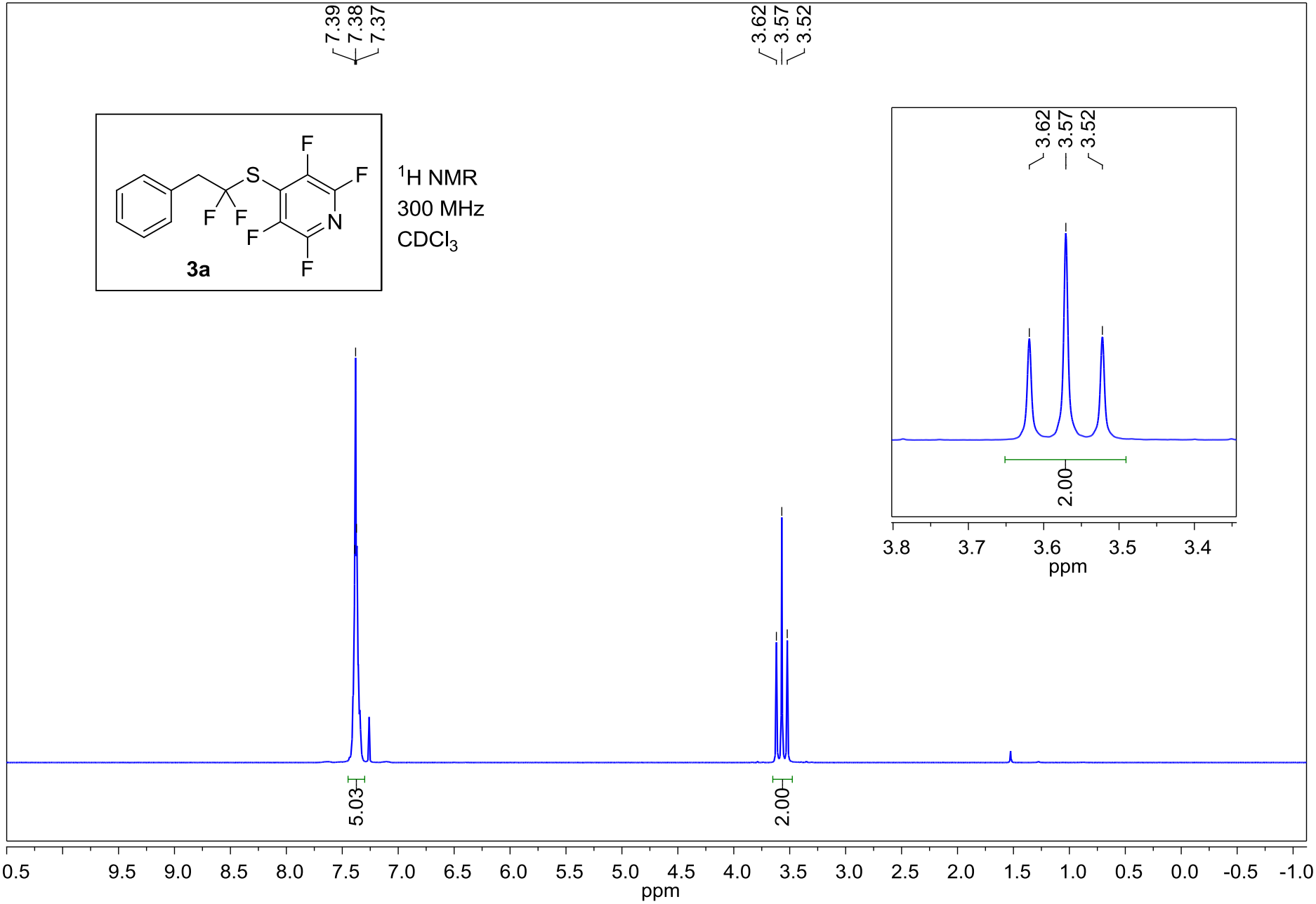

7.38
7.36
7.34
7.31
7.28
2.43
2.41
2.38
1.41
1.39
1.36
1.32
1.31
1.29
0.90
0.88
0.86
F
F
1k
1H NMR
300 MHz
CDCl3
5.37
2.00
6.10
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

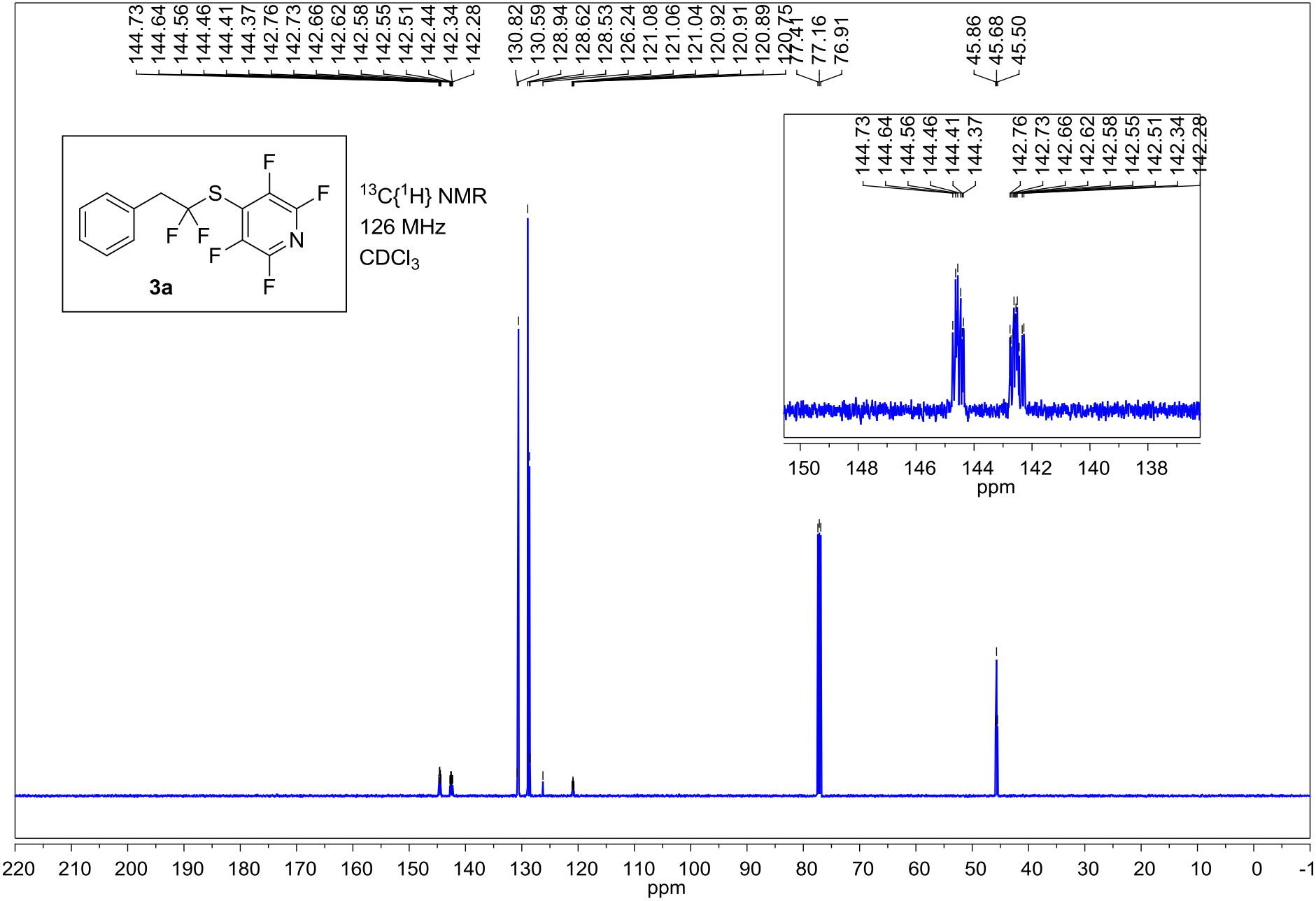

157.61
153.79
149.98
134.10
128.52
128.46
128.42
128.38
127.28
92.89
92.65
92.43
31.39
27.80
27.59
22.51
14.10
F
F
1k
13C{1H} NMR
75 MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

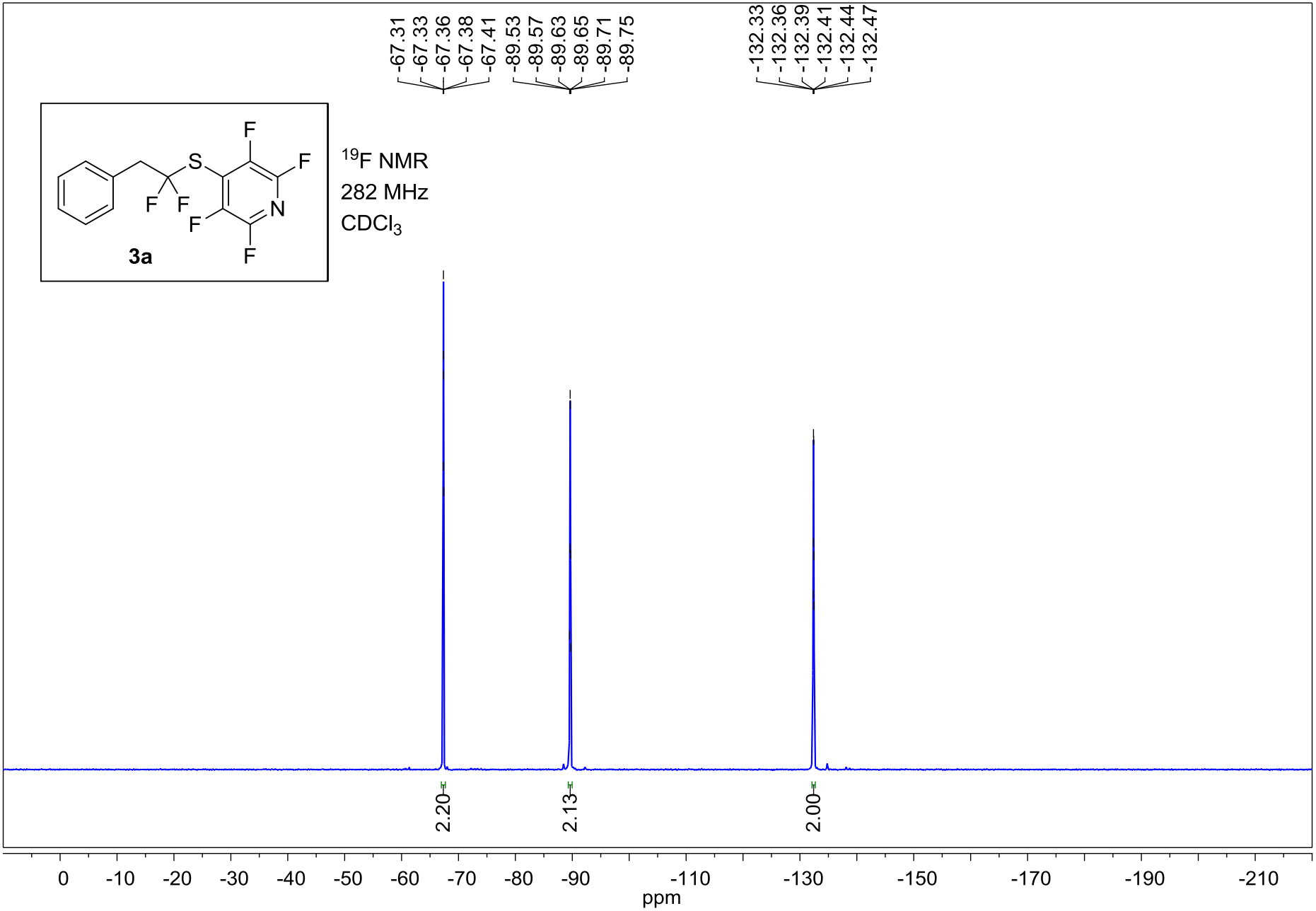

4.17
SH
F
F
F
N
F
2
1H NMR
300 MHz
CDCl3
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

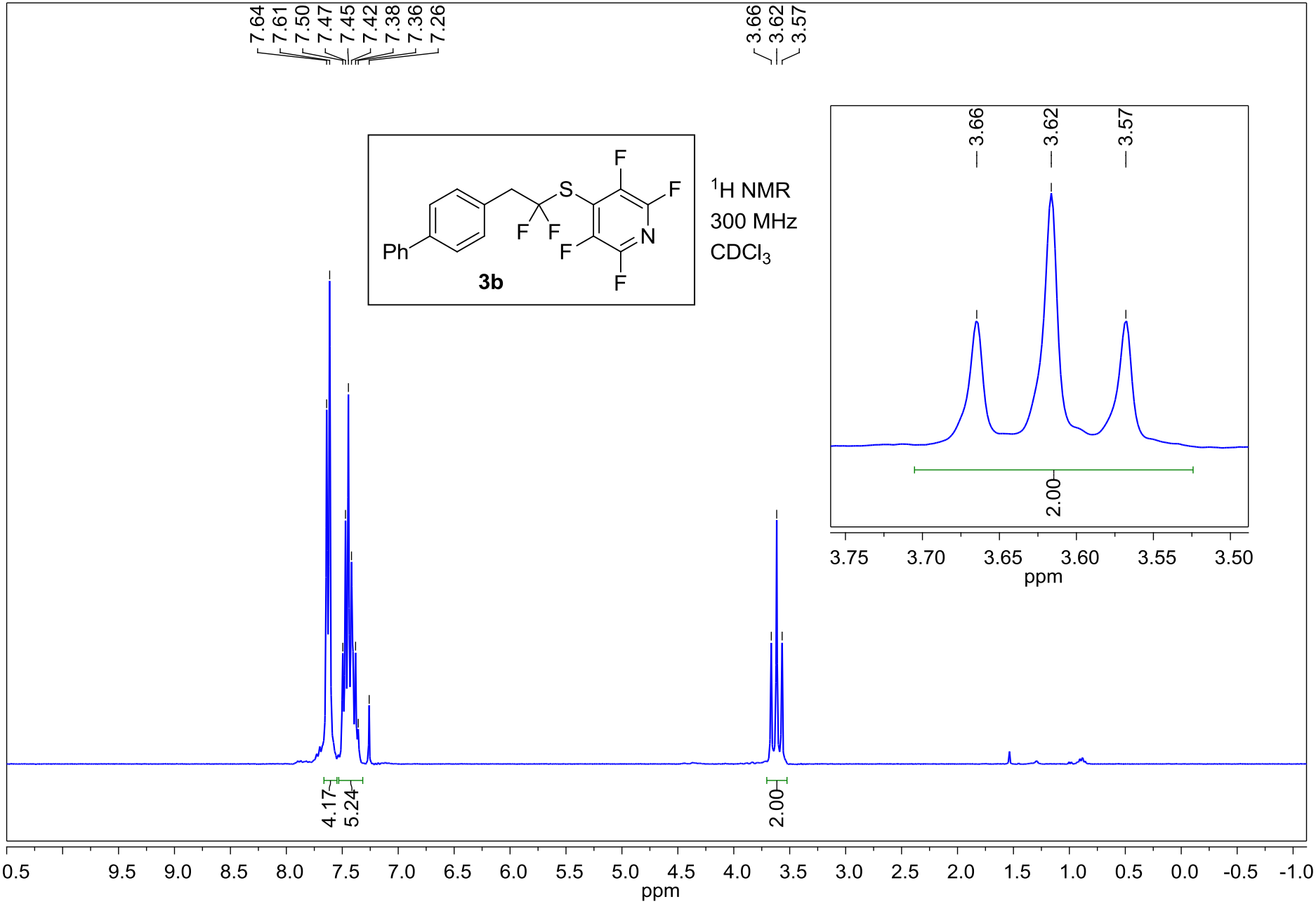

145.05
144.86
144.67
141.84
141.62
141.43
140.51
140.42
140.33
140.22
140.12
140.03
137.13
137.05
136.95
136.84
136.74
136.65
129.36
129.32
129.27
129.10
129.06
129.02
128.85
128.80
128.76
77.16
146
145
144
142
141
140
137
136
129
128
ppm
SH
F
F
F
N
F
2
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
ppm

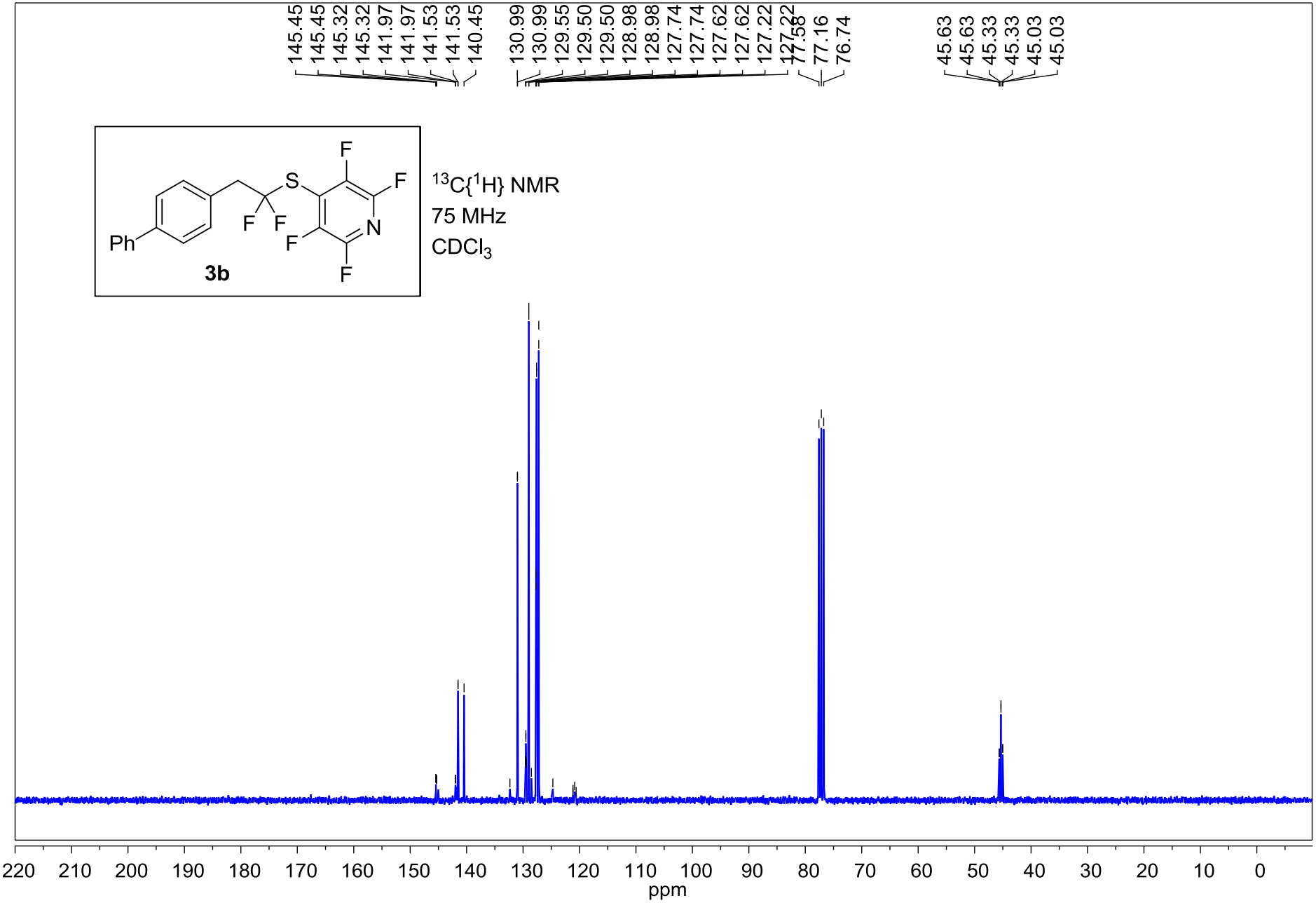

-92.20
-140.80
-140.84
-140.90
-140.92
-140.97
-141.02
SH
F
F
F
N
F
2
19F NMR
282 MHz
CDCl3
2.00
1.91
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

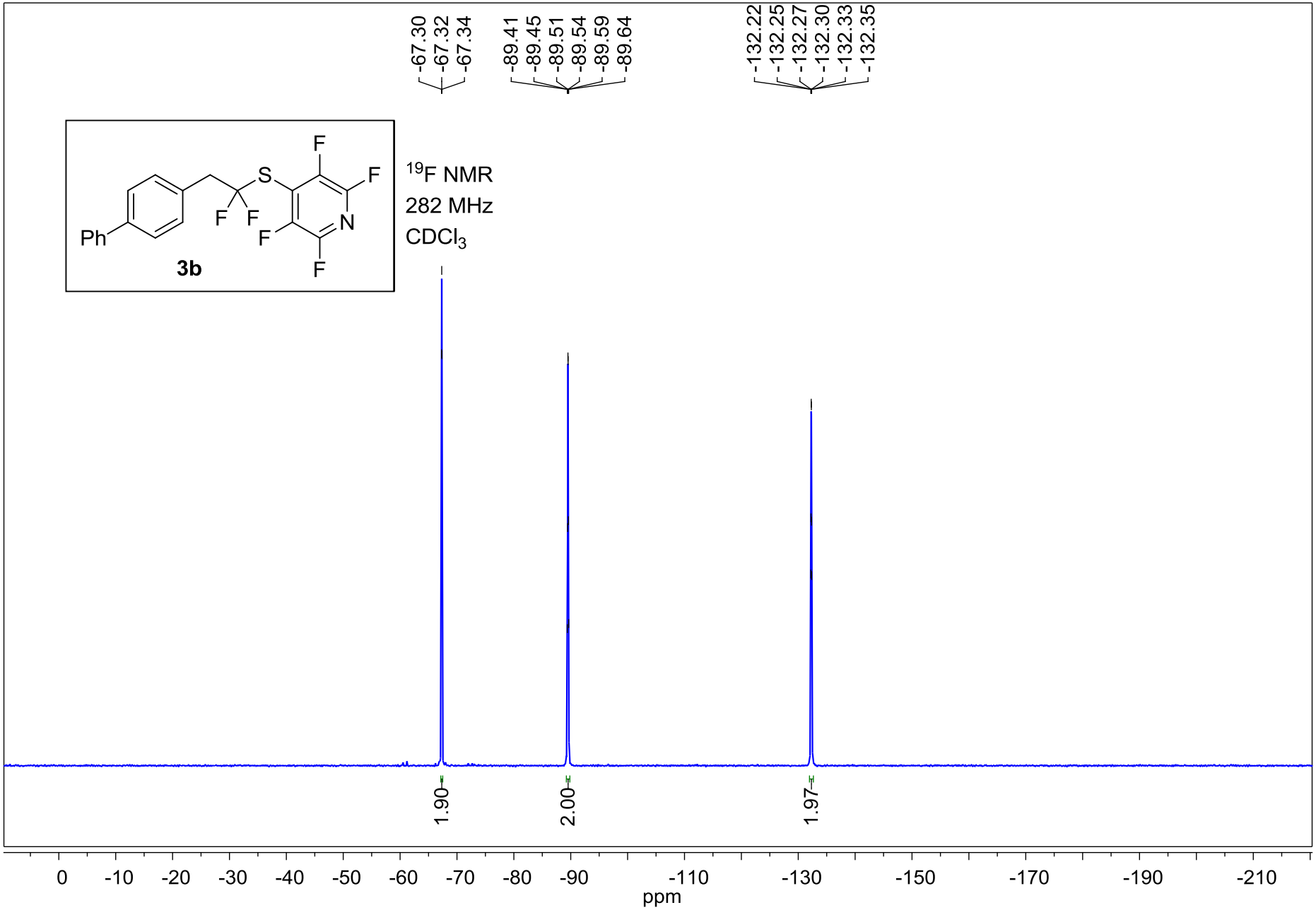

7.39
7.38
7.37
3.62
3.57
3.52
F
S
F
F
F
F
N
F
3a
^{1}H NMR
300 MHz
$CDCl_3$
3.62
3.57
3.52
2.00
3.8
3.7
3.6
3.5
3.4
ppm
5.03
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

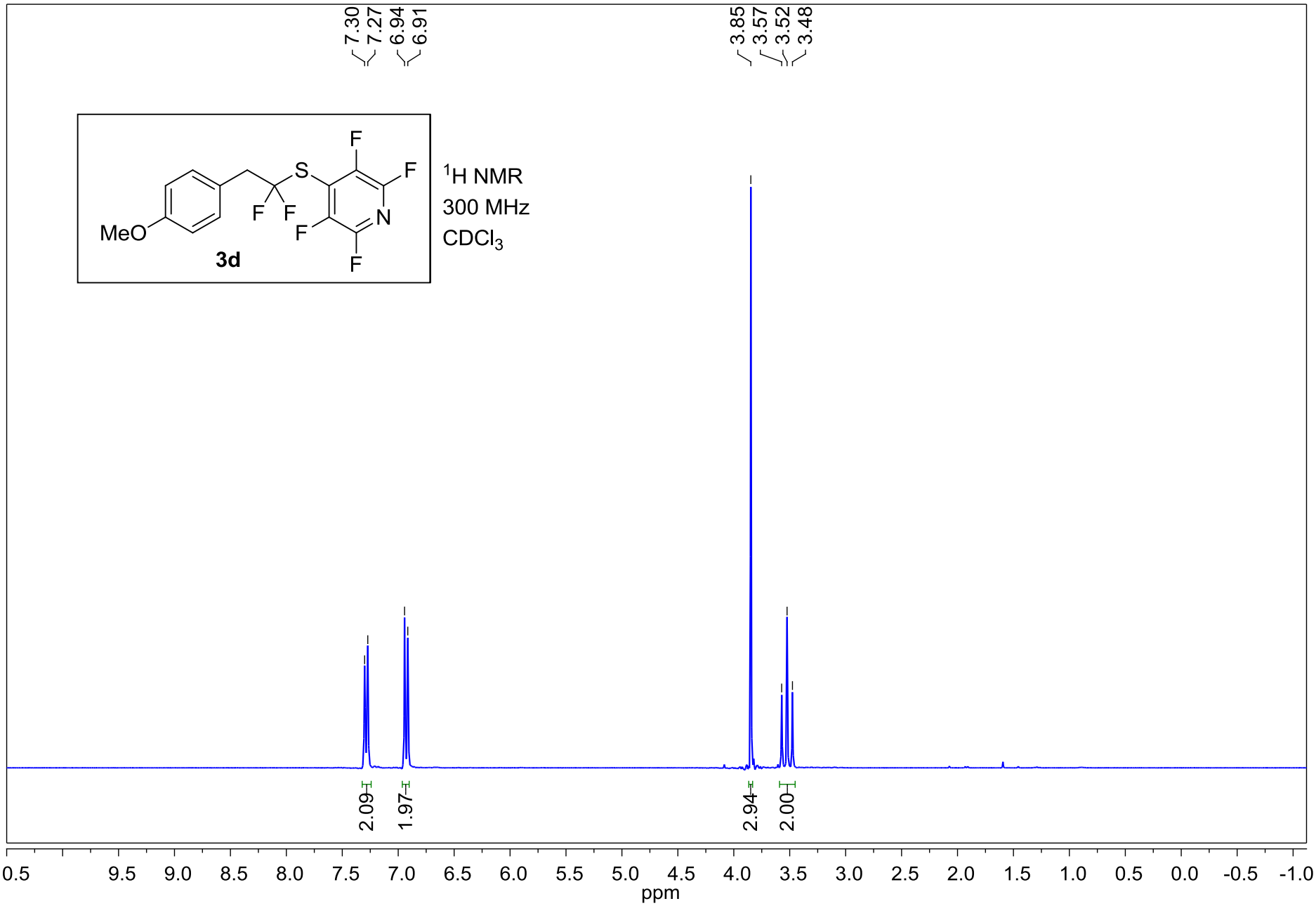

144.73
144.64
144.56
144.46
144.41
144.37
142.76
142.73
142.66
142.62
142.58
142.55
142.51
142.44
142.34
142.28
130.82
130.59
128.94
128.62
128.53
126.24
121.08
121.06
121.04
120.92
120.91
120.89
120.75
77.41
77.16
76.91
45.86
45.68
45.50
F
S
F
F
F
F
N
F
3a
$^{13}C\{^{1}H\}$ NMR
126 MHz
$CDCl_3$
150
148
146
144
142
140
138
ppm
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

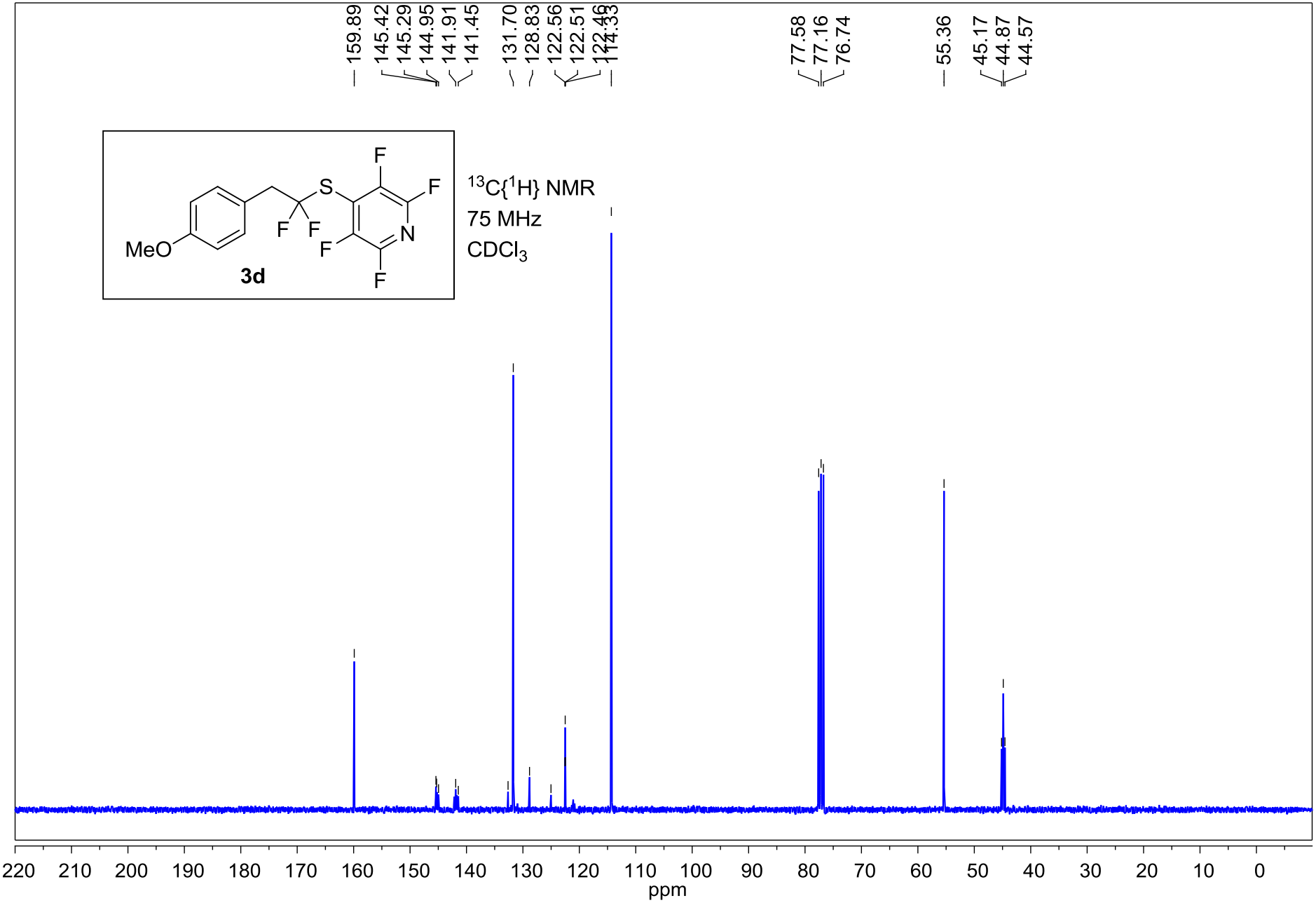

-67.31
-67.33
-67.36
-67.38
-67.41
-89.53
-89.57
-89.63
-89.65
-89.71
-89.75
-132.33
-132.36
-132.39
-132.41
-132.44
-132.47
F
S
F
F
F
F
N
F
3a
19F NMR
282 MHz
CDCl3
2.20
2.13
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

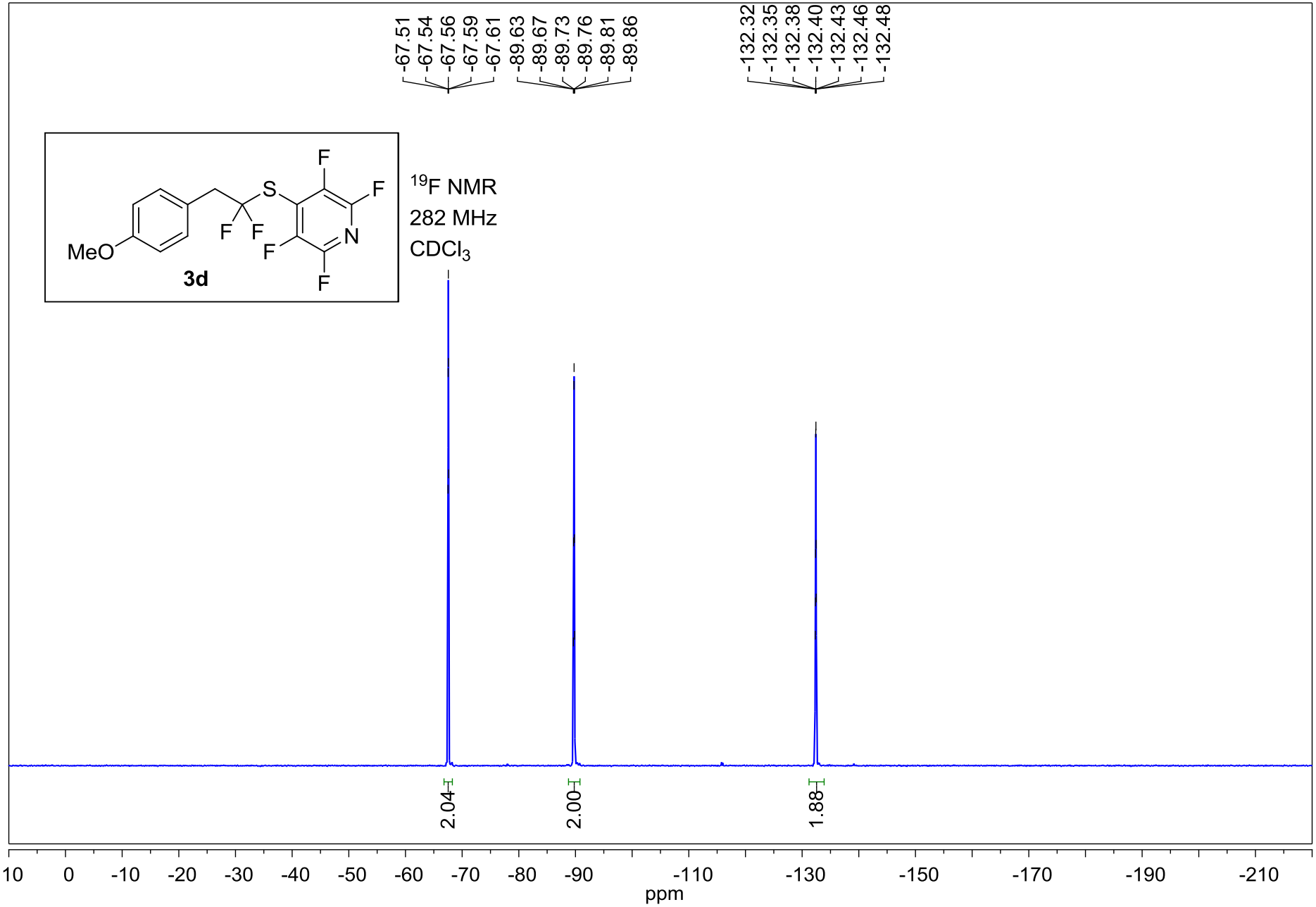

7.64
7.61
7.50
7.47
7.45
7.42
7.38
7.36
7.26
3.66
3.62
3.57
Ph
S
F
F
F
F
F
F
N
3b
1H NMR
300 MHz
CDCl3
4.17
5.24
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm
3.75
3.70
3.65
3.60
3.55
3.50
ppm

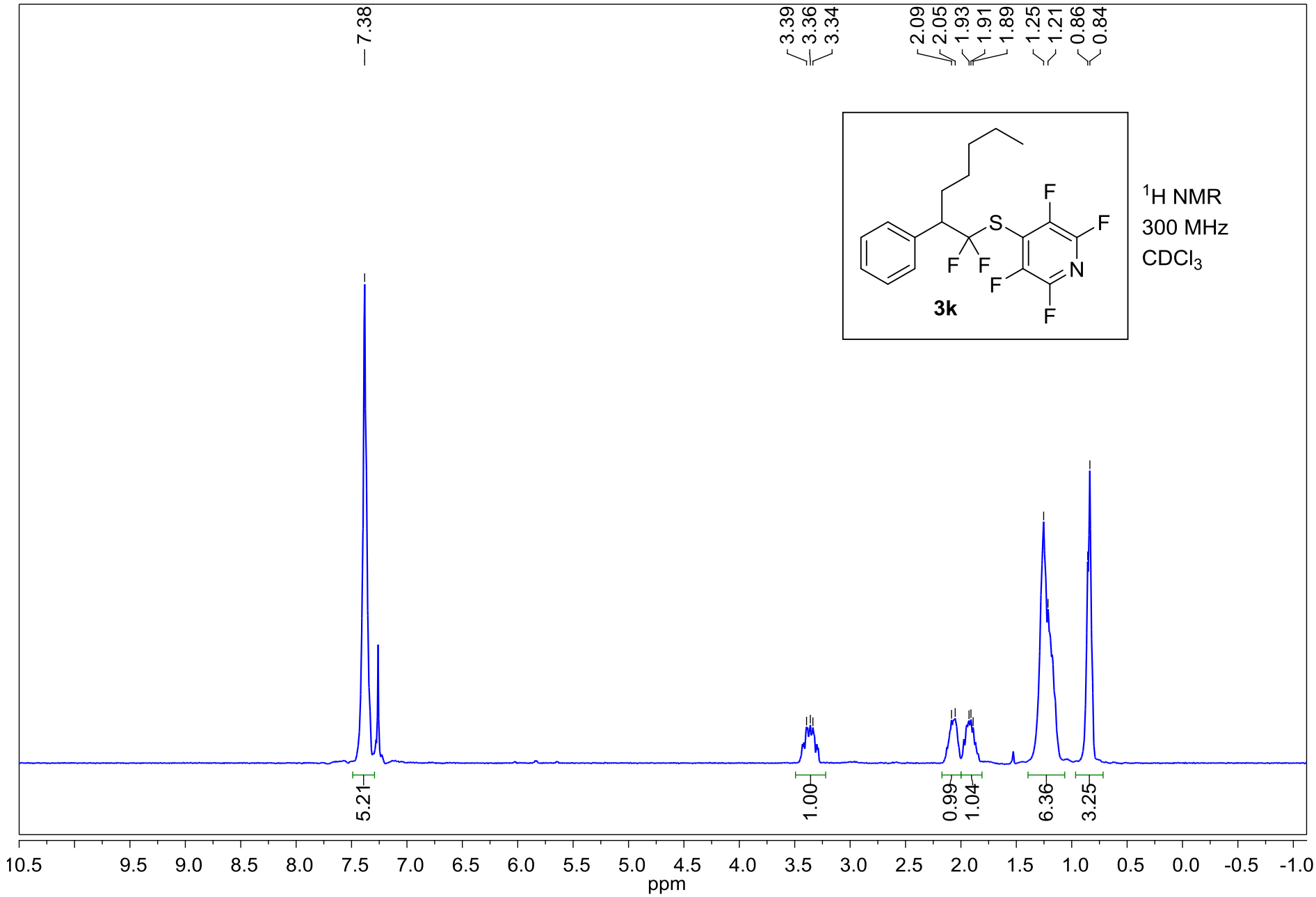

145.45
145.45
145.32
145.32
141.97
141.97
141.53
141.53
140.45
130.99
130.99
129.55
129.50
129.50
128.98
128.98
127.74
127.74
127.62
127.62
127.22
127.22
77.58
77.16
76.74
45.63
45.63
45.33
45.33
45.03
45.03
F
S
F
F
F
F
N
F
Ph
3b
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

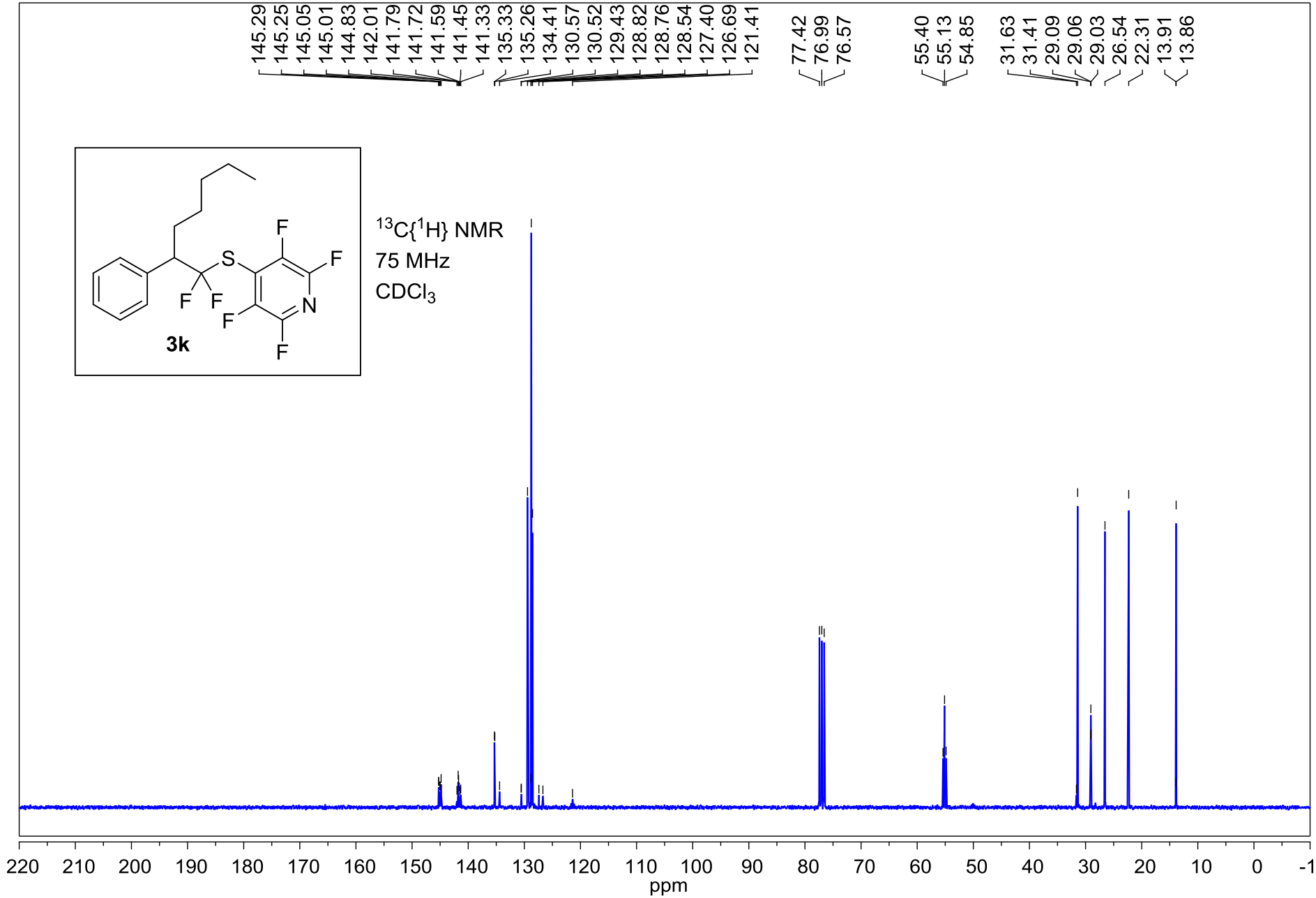

-67.30
-67.32
-67.34
-89.41
-89.45
-89.51
-89.54
-89.59
-89.64
-132.22
-132.25
-132.27
-132.30
-132.33
-132.35
F
S
F
F
F
F
N
F
Ph
3b
19F NMR
282 MHz
CDCl3
1.90
2.00
1.97
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

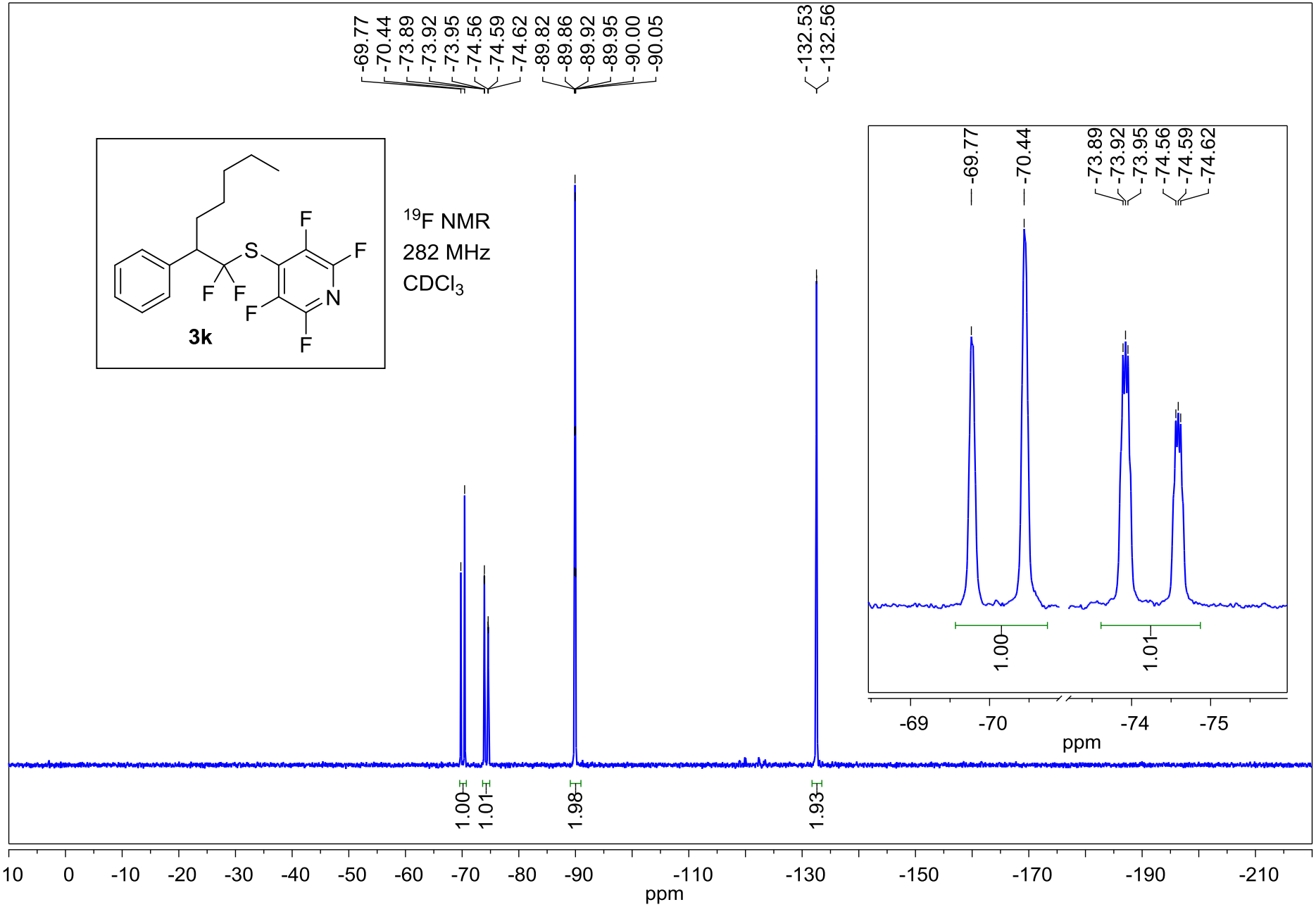

7.30
7.27
6.94
6.91
3.85
3.57
3.52
3.48
MeO
S
F
F
F
F
F
N
F
3d
^{1}H NMR
300 MHz
$CDCl_3$
2.09
1.97
2.94
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

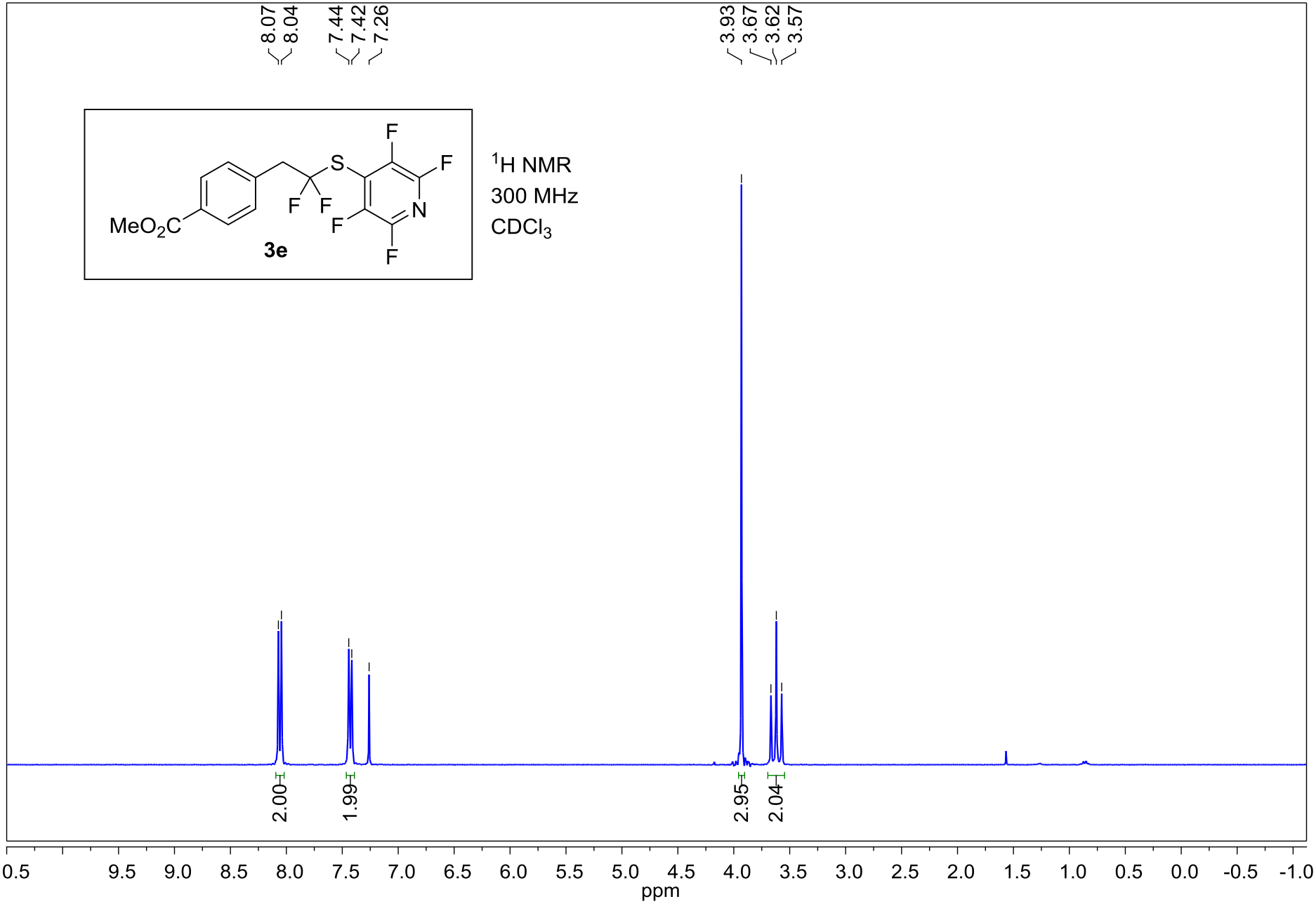

159.89
145.42
145.29
144.95
141.91
141.45
131.70
128.83
122.56
122.51
122.46
114.33
77.58
77.16
76.74
55.36
45.17
44.87
44.57
MeO
S
F
F
F
F
F
F
N
3d
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

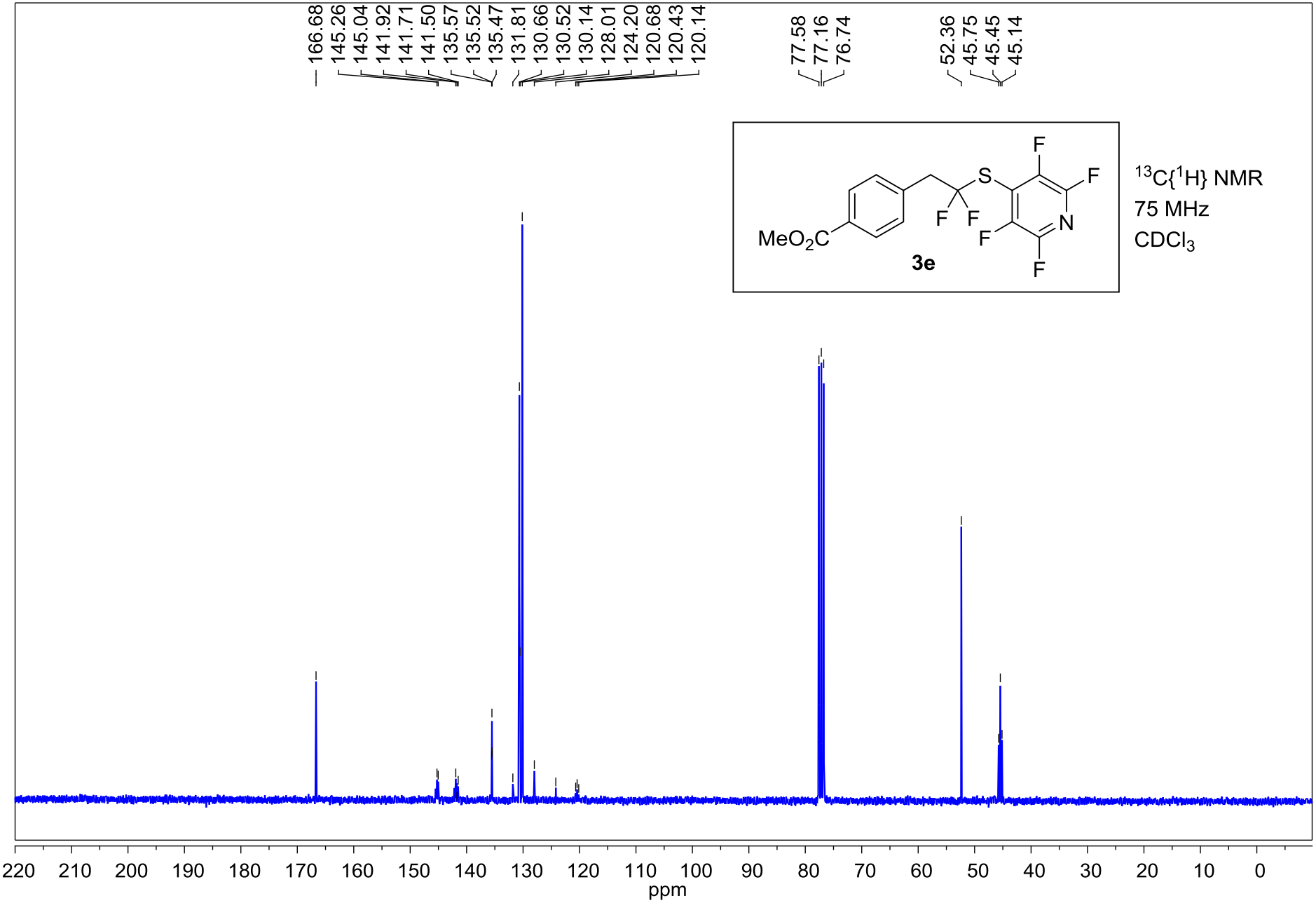

-67.51
-67.54
-67.56
-67.59
-67.61
-89.63
-89.67
-89.73
-89.76
-89.81
-89.86
-132.32
-132.35
-132.38
-132.40
-132.43
-132.46
-132.48
MeO
S
F
F
F
F
F
F
N
3d
19F NMR
282 MHz
CDCl3
2.04
2.00
1.88
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

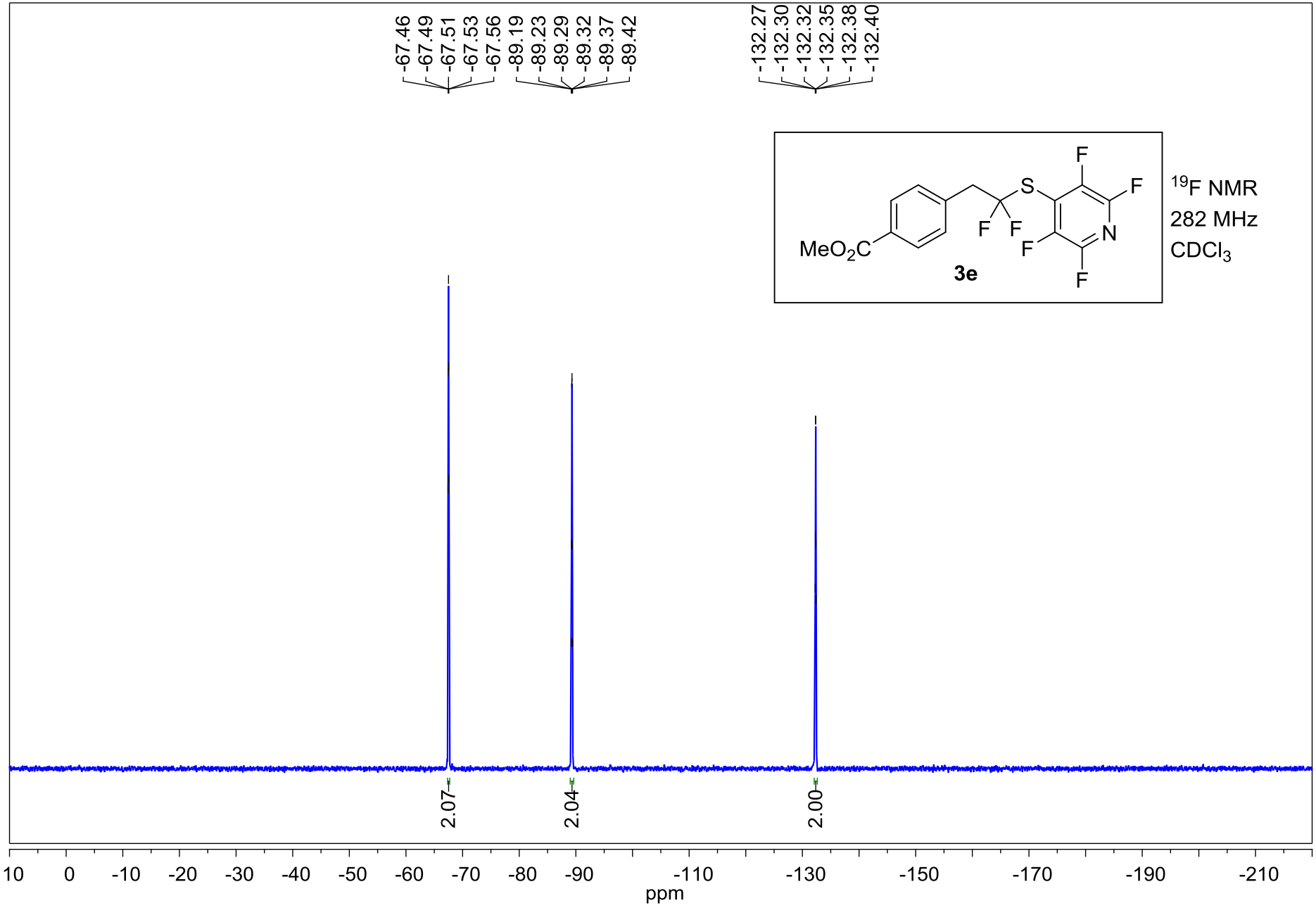

7.38
3.39
3.36
3.34
2.09
2.05
1.93
1.91
1.89
1.25
1.21
0.86
0.84
F
S
F
F
F
F
N
F
3k
^{1}H NMR
300 MHz
$CDCl_3$
5.21
1.00
0.99
1.04
6.36
3.25
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

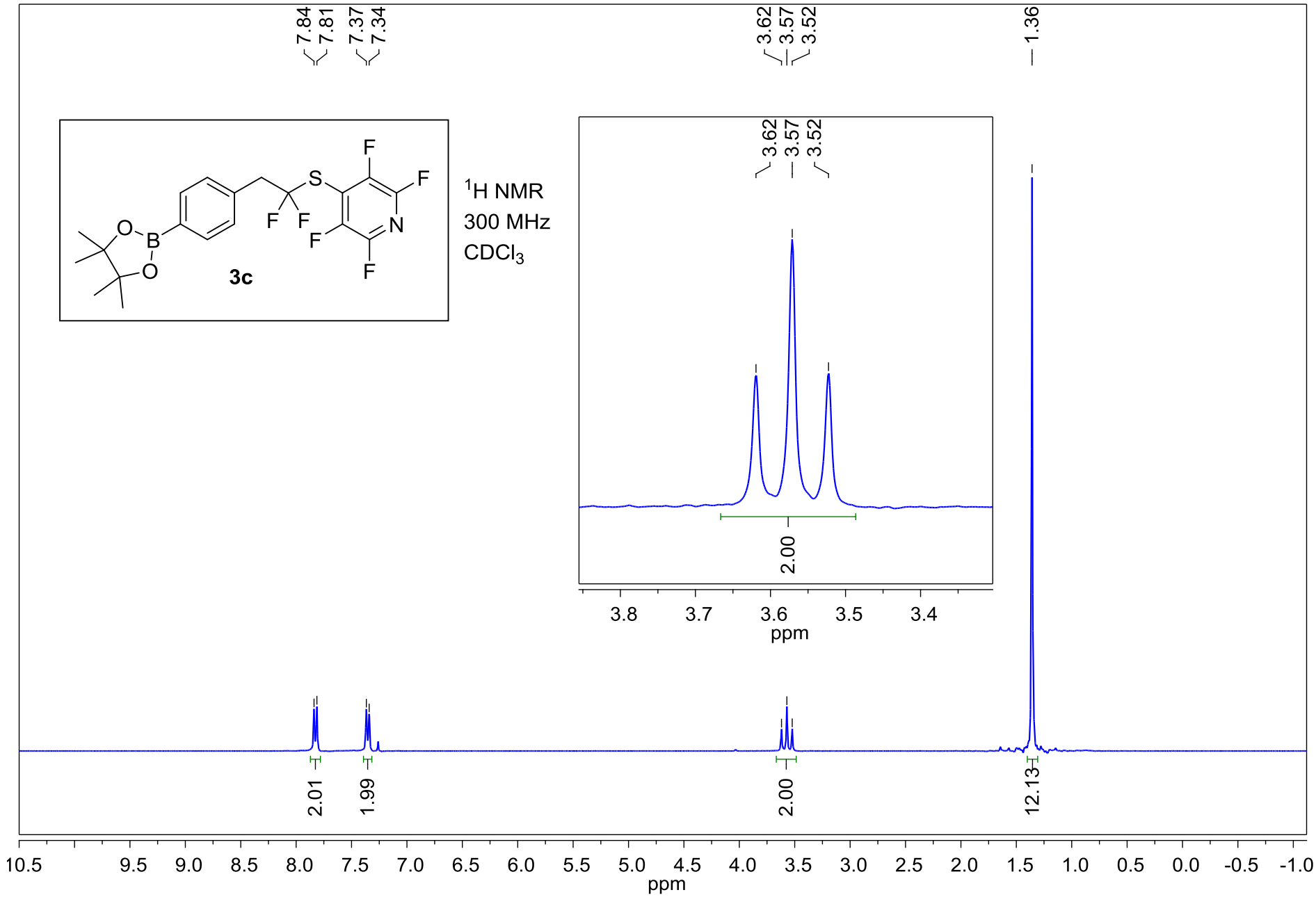

145.29
145.25
145.05
145.01
144.83
142.01
141.79
141.72
141.59
141.45
141.33
135.33
135.26
134.41
130.57
130.52
129.43
128.82
128.76
128.54
127.40
126.69
121.41
77.42
76.99
76.57
55.40
55.13
54.85
31.63
31.41
29.09
29.06
29.03
26.54
22.31
13.91
13.86
F
S
F
F
F
F
N
F
3k
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

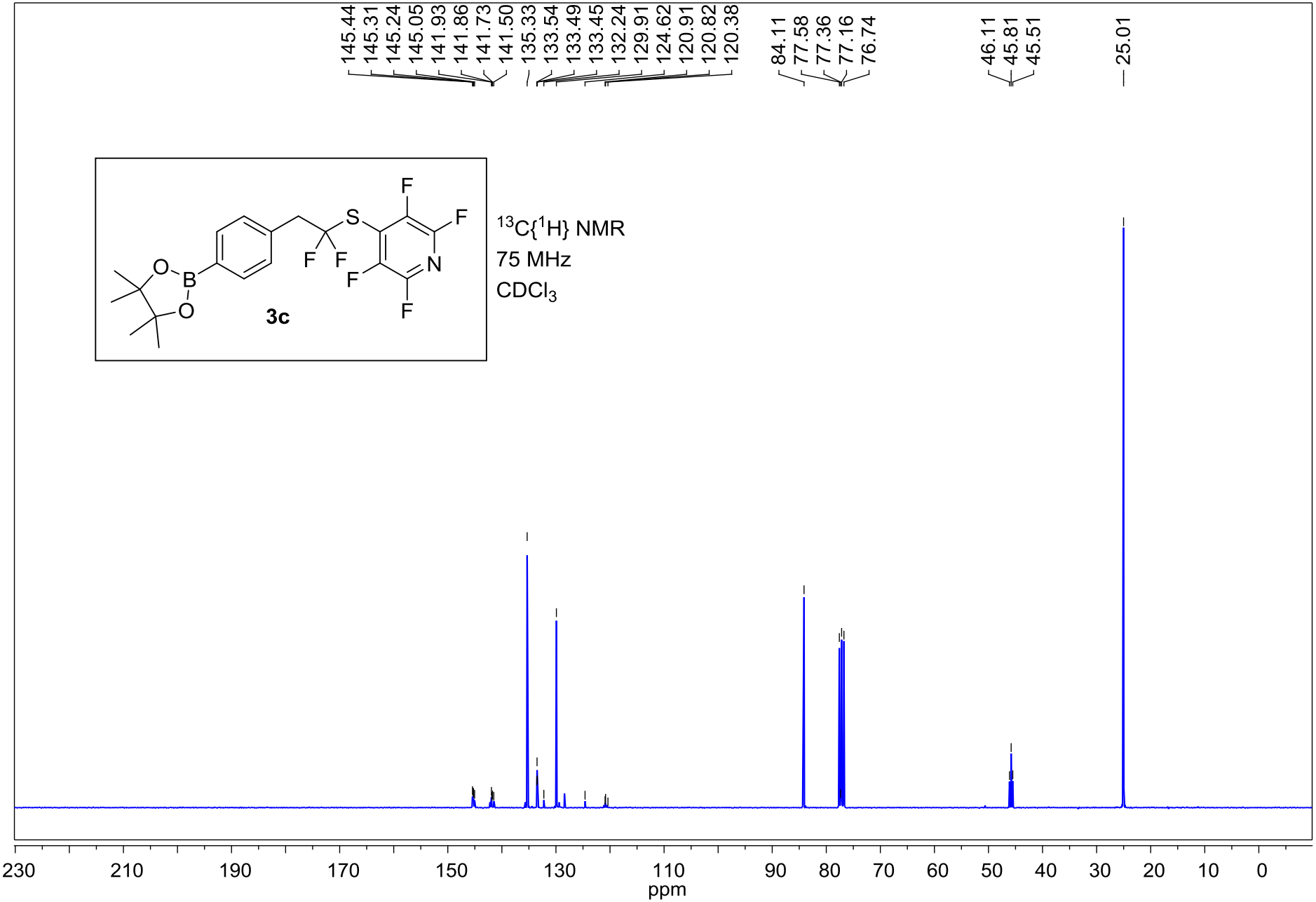

-69.77
-70.44
-73.89
-73.92
-73.95
-74.56
-74.59
-74.62
-89.82
-89.86
-89.92
-89.95
-90.00
-90.05
-132.53
-132.56
3k
^{19}F NMR
282 MHz
$CDCl_3$
1.00
1.01
1.98
1.93
ppm

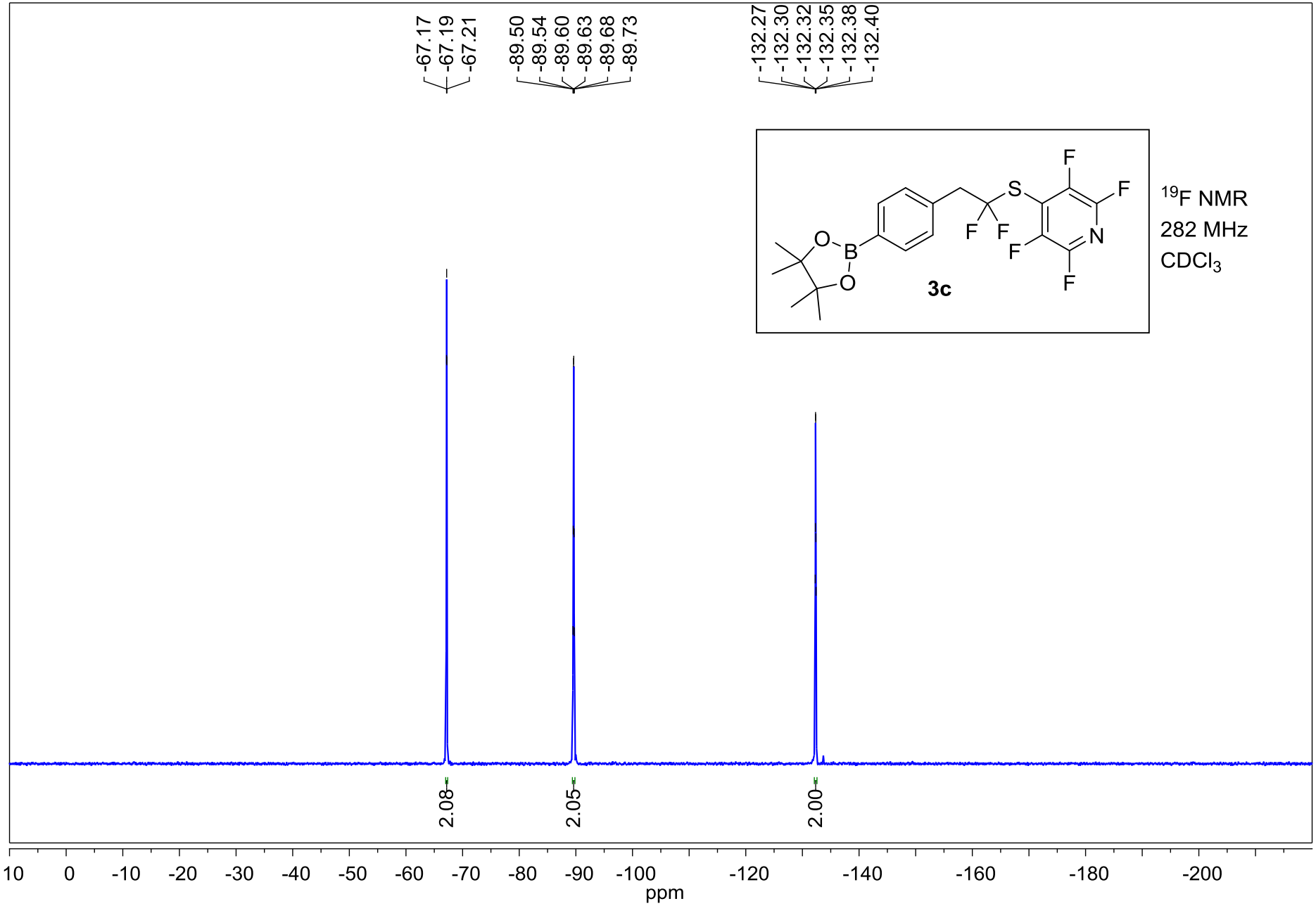

8.07
8.04
7.44
7.42
7.26
3.93
3.67
3.62
3.57
MeO2C
S
F
F
F
F
F
N
F
3e
1H NMR
300 MHz
CDCl3
2.00
1.99
2.95
2.04
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

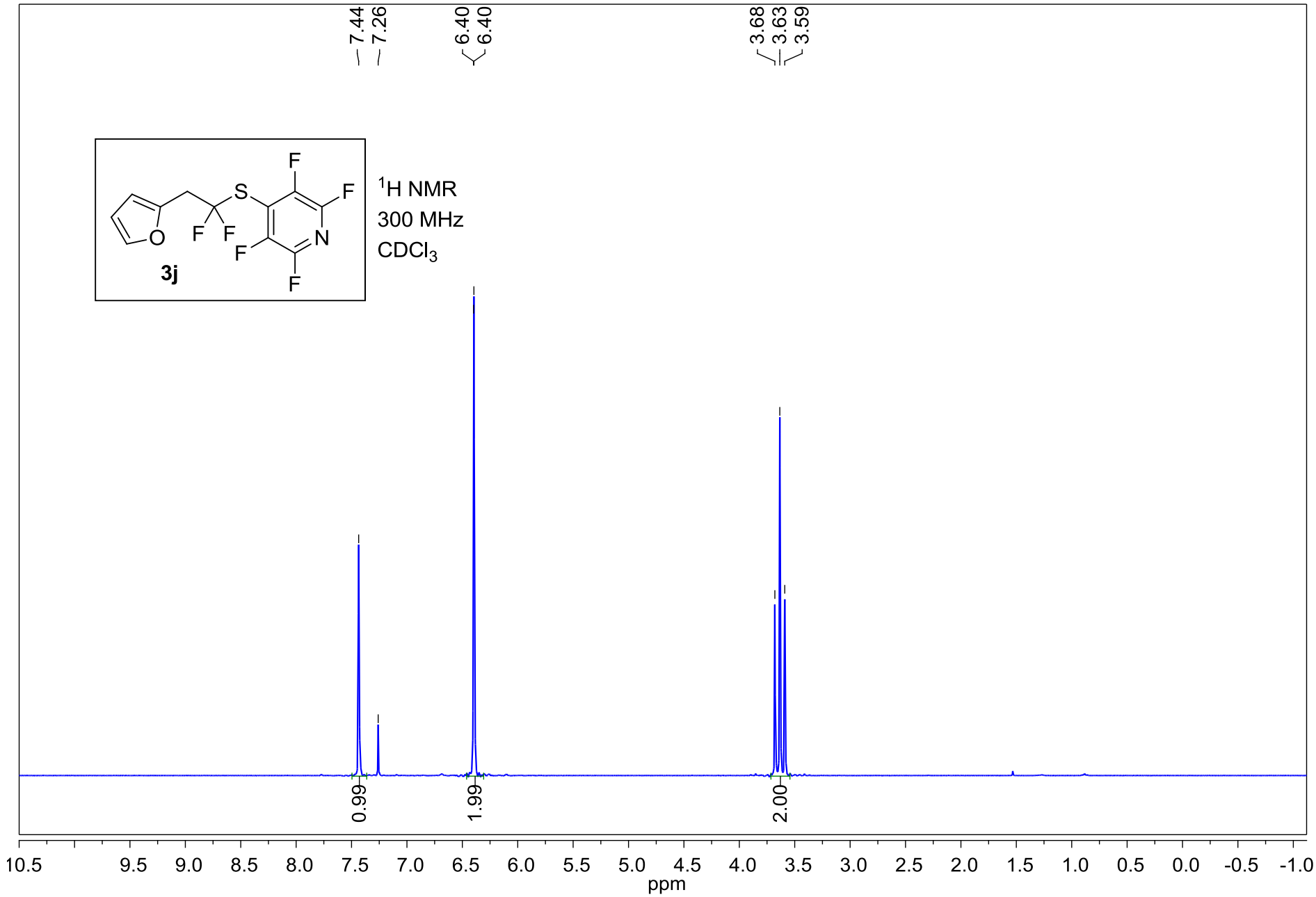

166.68
145.26
145.04
141.92
141.71
141.50
135.57
135.52
135.47
131.81
130.66
130.52
130.14
128.01
124.20
120.68
120.43
120.14
77.58
77.16
76.74
52.36
45.75
45.45
45.14
MeO2C
S
F
F
F
F
F
N
F
3e
13C{1H} NMR
75 MHz
CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

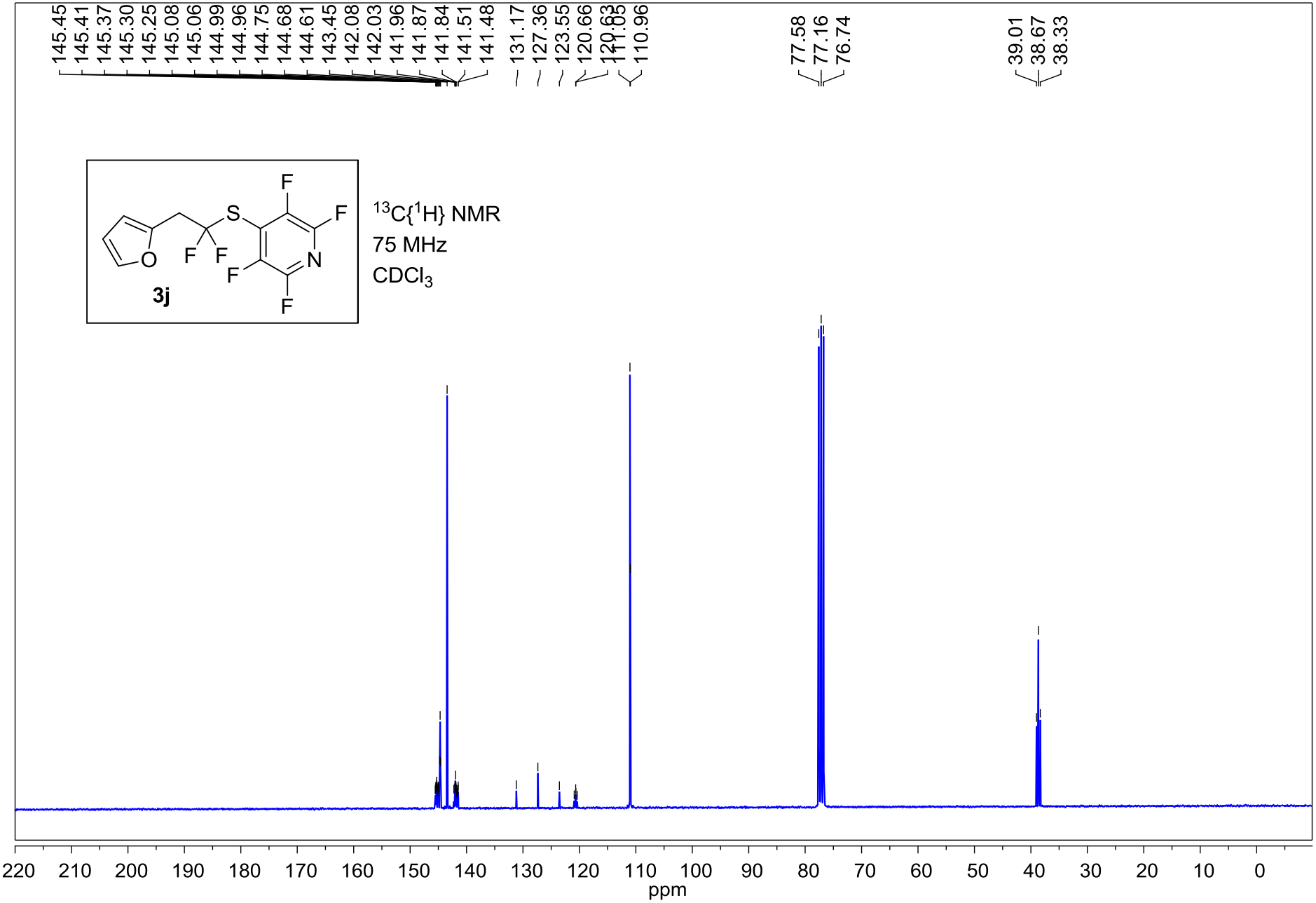

-67.46
-67.49
-67.51
-67.53
-67.56
-89.19
-89.23
-89.29
-89.32
-89.37
-89.42
-132.27
-132.30
-132.32
-132.35
-132.38
-132.40
MeO2C
S
F
F
F
F
F
N
F
3e
19F NMR
282 MHz
CDCl3
2.07
2.04
2.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

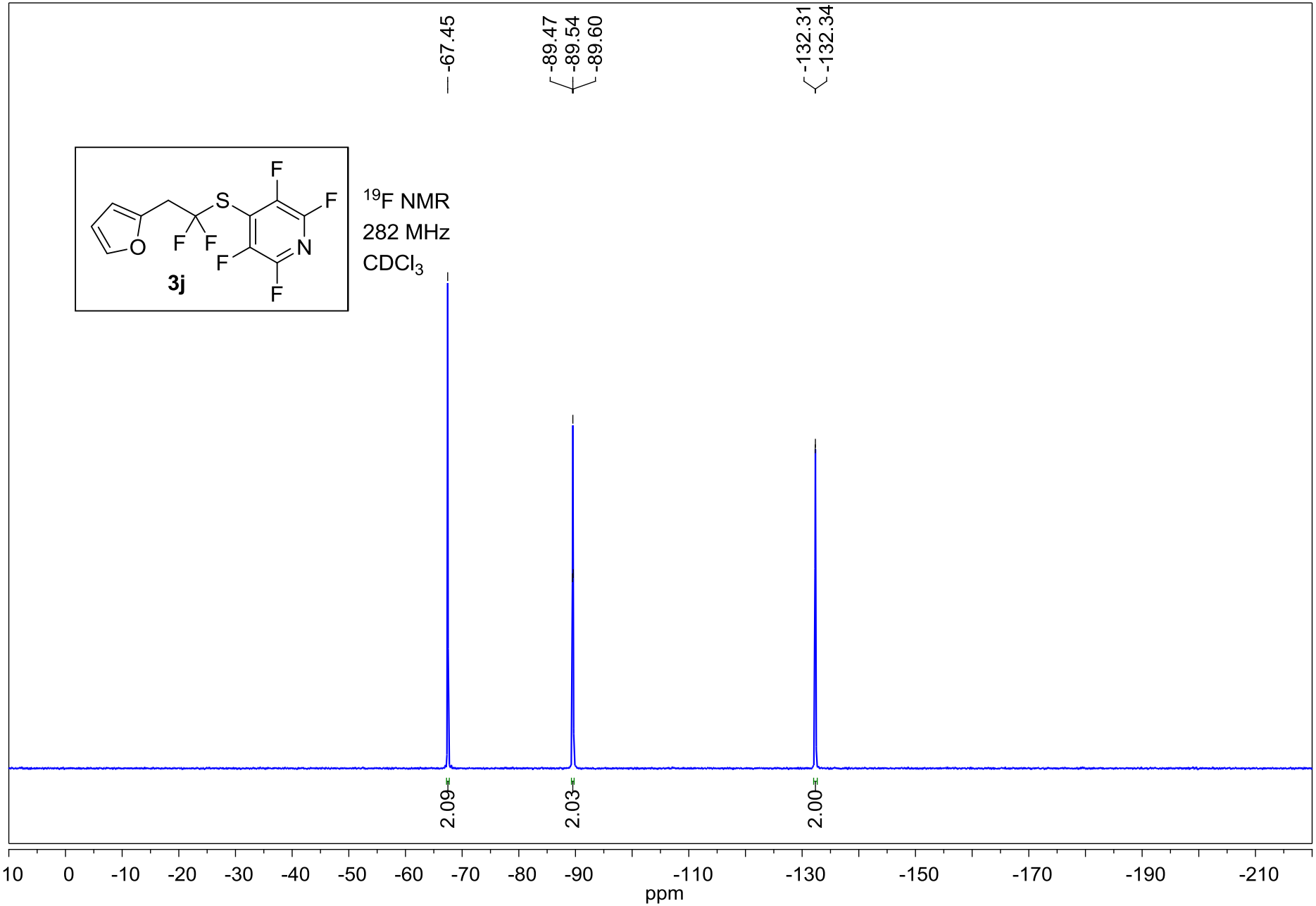

7.84
7.81
7.37
7.34
3.62
3.57
3.52
1.36
3c
^{1}H NMR
300 MHz
$CDCl_3$
2.00
2.01
1.99
2.00
12.13
ppm

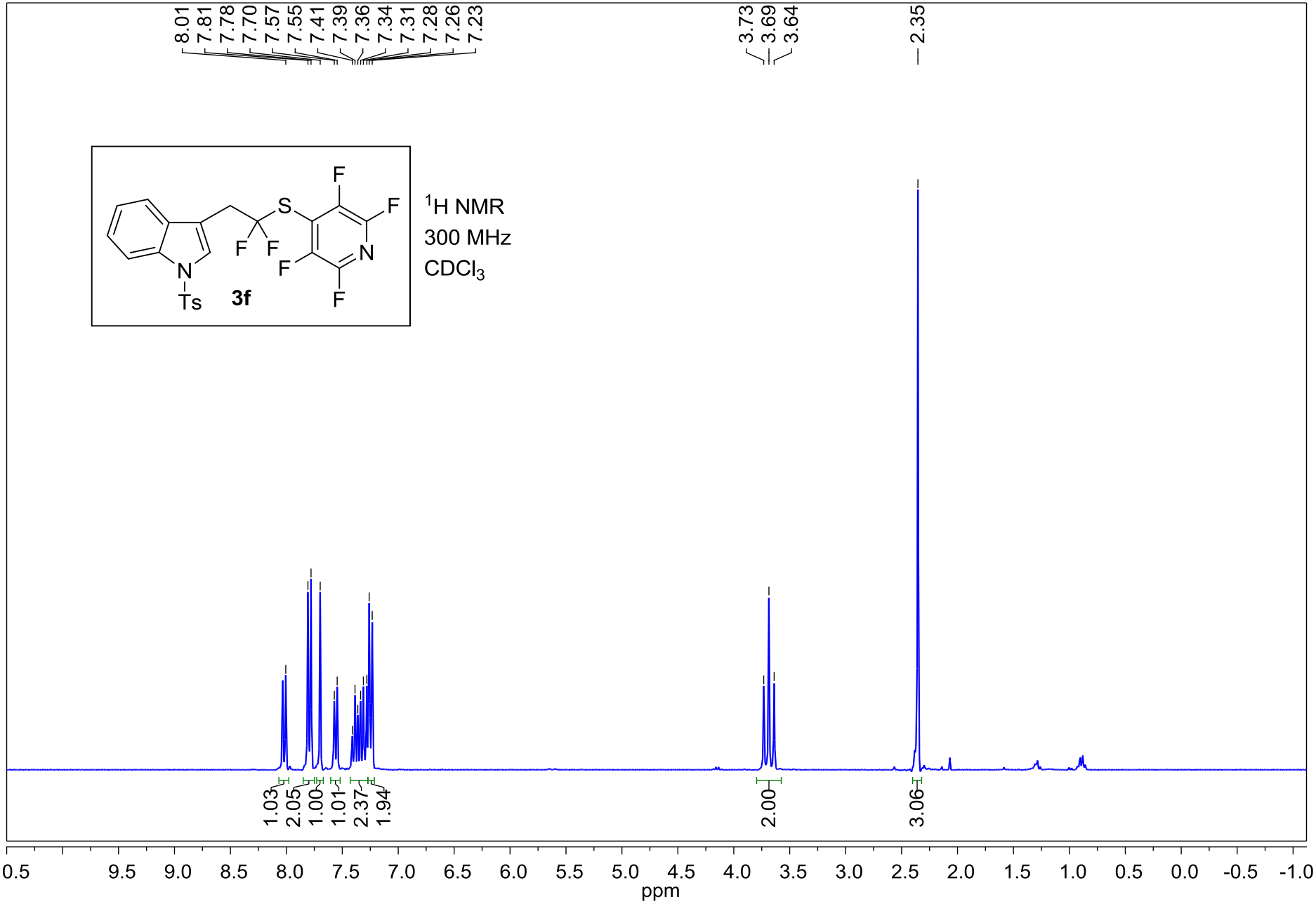

145.44
145.31
145.24
145.05
141.93
141.86
141.73
141.50
135.33
133.54
133.49
133.45
132.24
129.91
124.62
120.91
120.82
120.38
84.11
77.58
77.36
77.16
76.74
46.11
45.81
45.51
25.01
3c
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
ppm

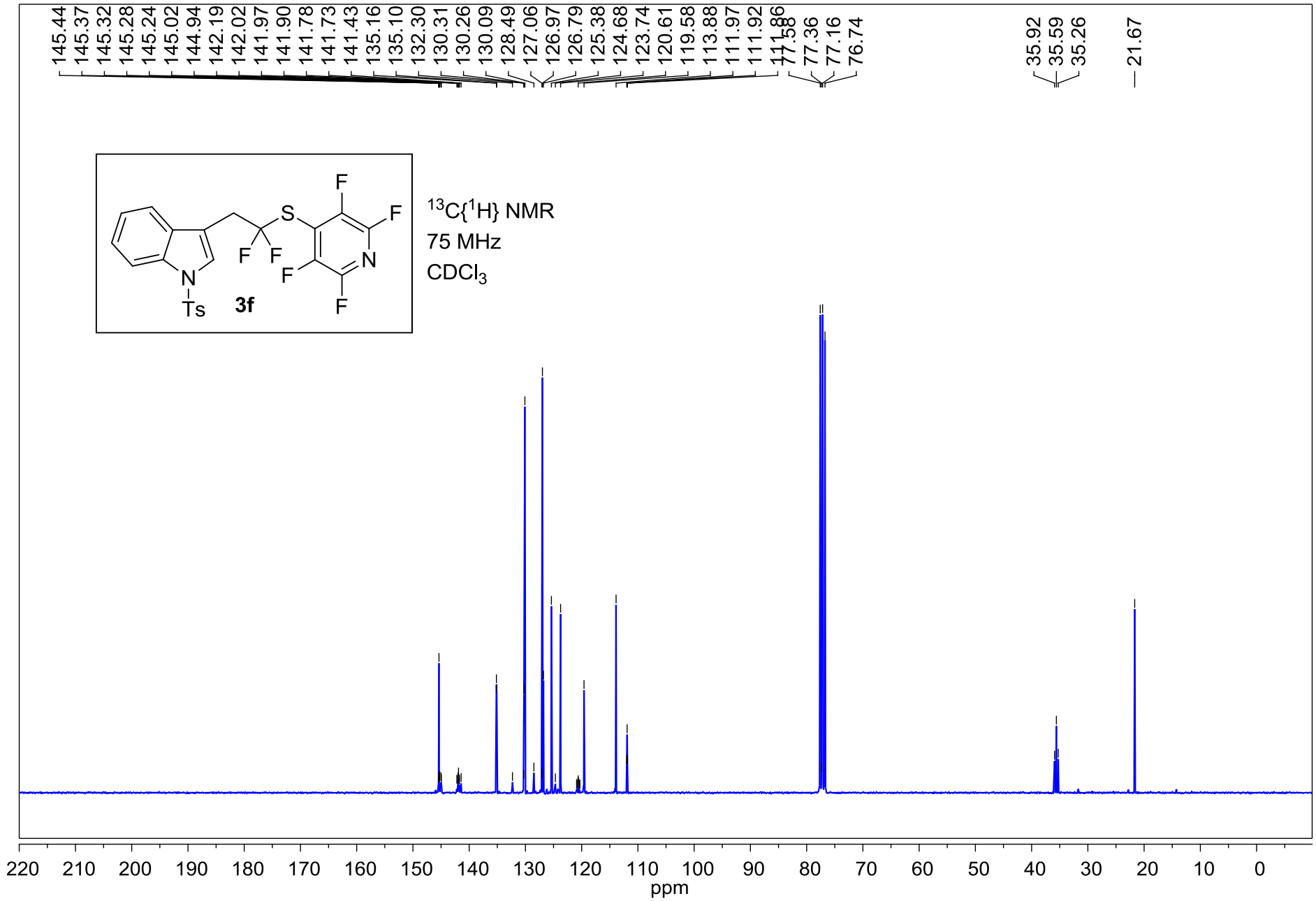

-67.17
-67.19
-67.21
-89.50
-89.54
-89.60
-89.63
-89.68
-89.73
-132.27
-132.30
-132.32
-132.35
-132.38
-132.40
3c
^{19}F NMR
282 MHz
$CDCl_3$
2.08
2.05
2.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
ppm

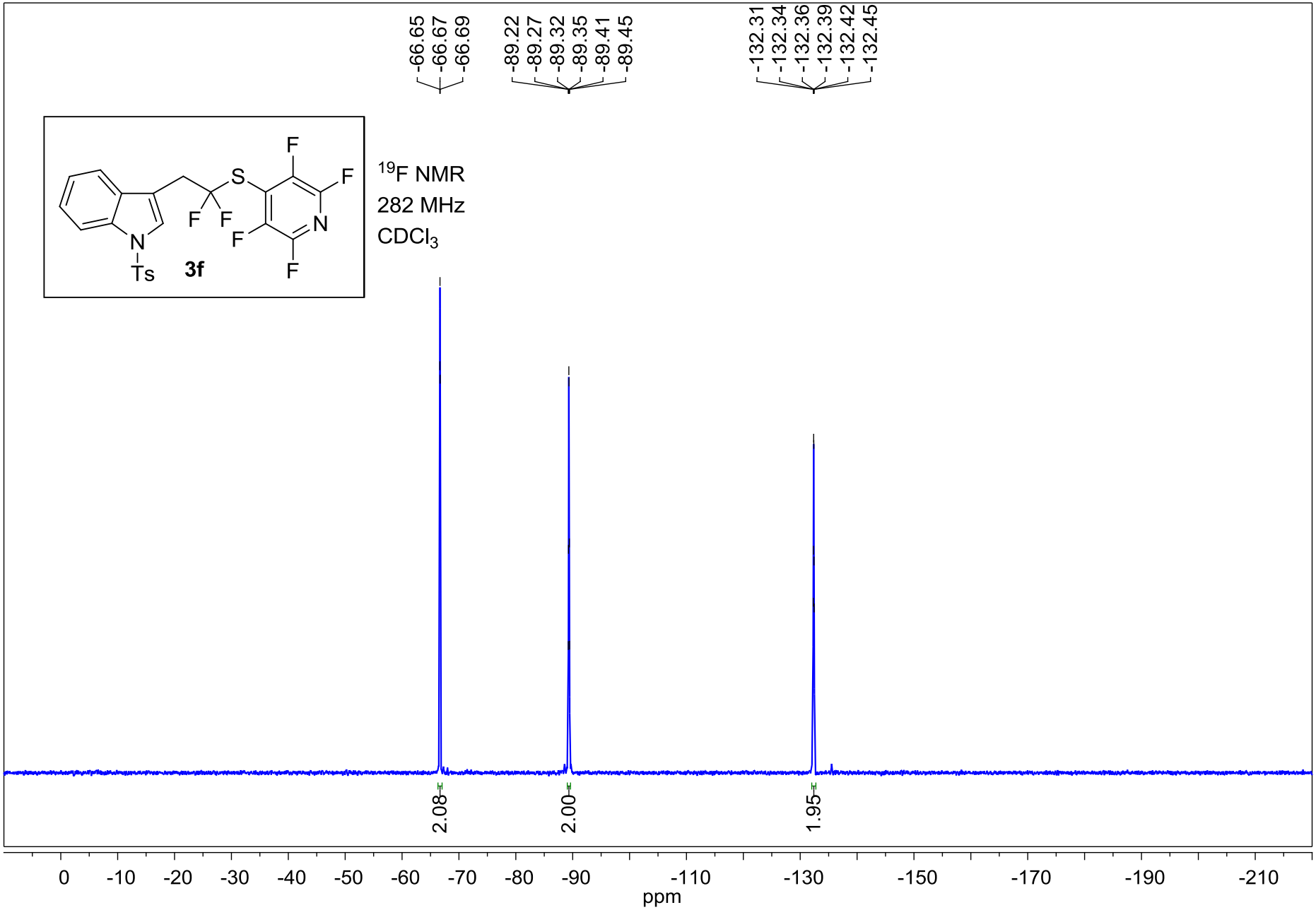

7.44
7.26
6.40
6.40
3.68
3.63
3.59
F
S
F
O
F
F
F
N
F
F
3j
1H NMR
300 MHz
CDCl3
0.99
1.99
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

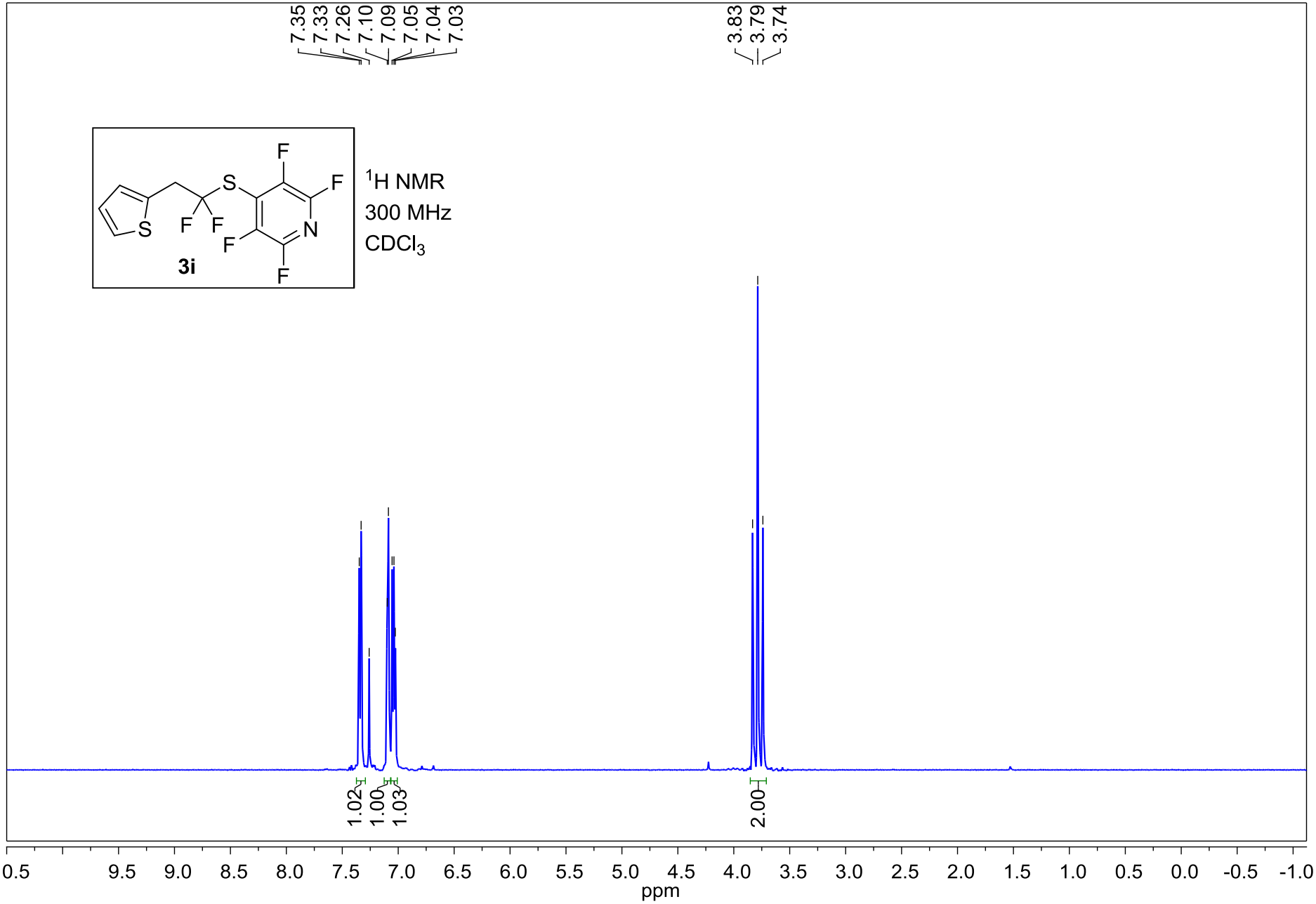

145.45
145.41
145.37
145.30
145.25
145.08
145.06
144.99
144.96
144.75
144.68
144.61
143.45
142.08
142.03
141.96
141.87
141.84
141.51
141.48
131.17
127.36
123.55
120.66
120.63
111.05
110.96
77.58
77.16
76.74
39.01
38.67
38.33
F
S
F
O
F
F
F
N
F
F
3j
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

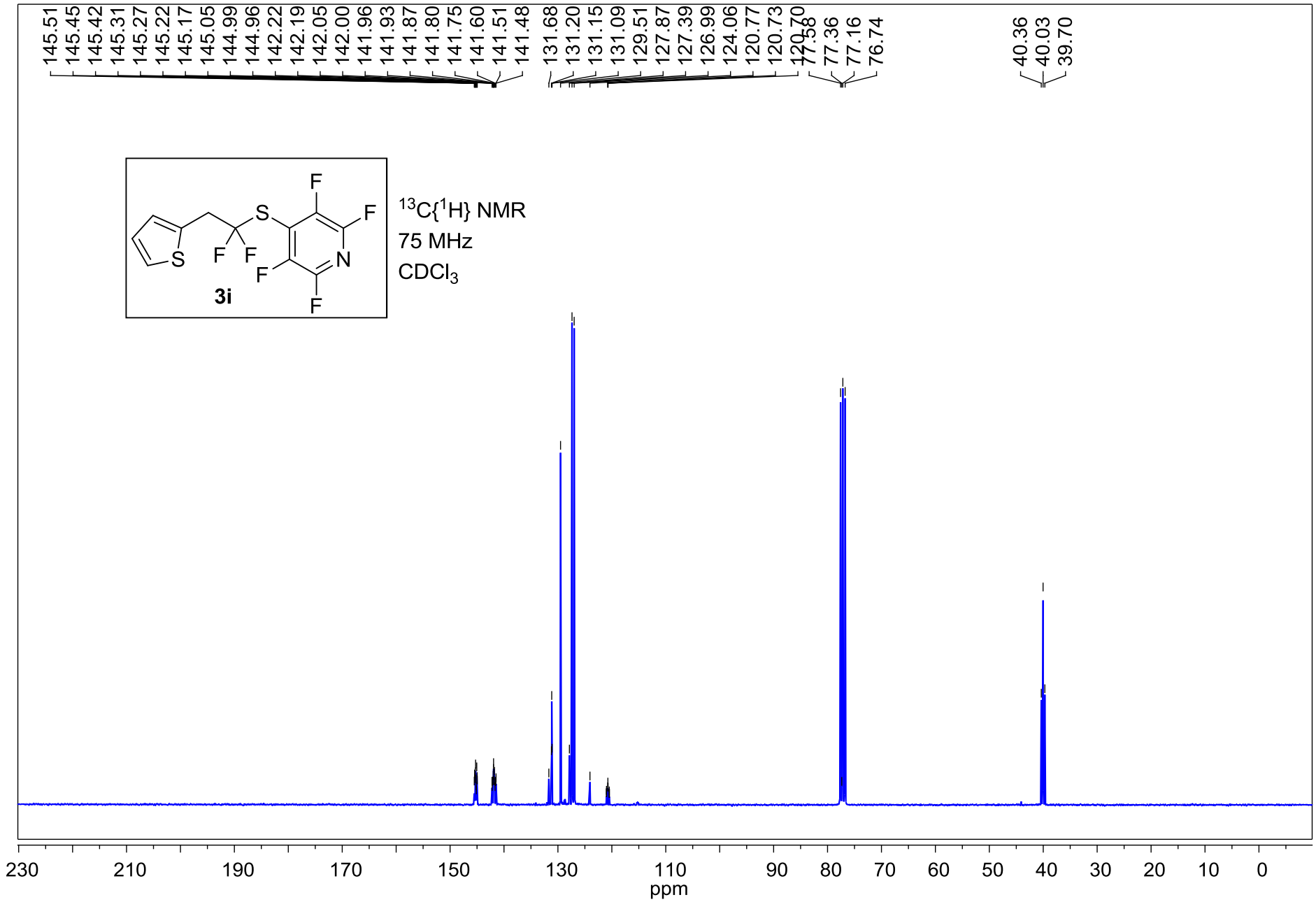

-67.45
-89.47
-89.54
-89.60
-132.31
-132.34
3j
^{19}F NMR
282 MHz
$CDCl_3$
2.09
2.03
2.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
ppm


8.01
7.81
7.78
7.70
7.57
7.55
7.41
7.39
7.36
7.34
7.31
7.28
7.26
7.23
3.73
3.69
3.64
2.35
F
S
F
F
F
F
N
N
Ts
3f
^{1}H NMR
300 MHz
$CDCl_3$
1.03
2.05
1.00
1.01
2.37
1.94
2.00
3.06
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm


145.44
145.37
145.32
145.28
145.24
145.02
144.94
142.19
142.02
141.97
141.90
141.78
141.73
141.43
135.16
135.10
132.30
130.31
130.26
130.09
128.49
127.06
126.97
126.79
125.38
124.68
123.74
120.61
119.58
113.88
111.97
111.92
111.86
77.58
77.36
77.16
76.74
35.92
35.59
35.26
21.67
F
S
F
F
F
F
N
N
Ts
3f
13C{1H} NMR
75 MHz
CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-66.65
-66.67
-66.69
-89.22
-89.27
-89.32
-89.35
-89.41
-89.45
-132.31
-132.34
-132.36
-132.39
-132.42
-132.45
F
S
F
F
F
F
N
N
Ts
3f
19F NMR
282 MHz
CDCl3
2.08
2.00
1.95
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm


7.35
7.33
7.26
7.10
7.09
7.05
7.04
7.03
3.83
3.79
3.74
F
S
F
F
S
F
F
N
F
3i
^{1}H NMR
300 MHz
$CDCl_3$
1.02
1.00
1.03
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm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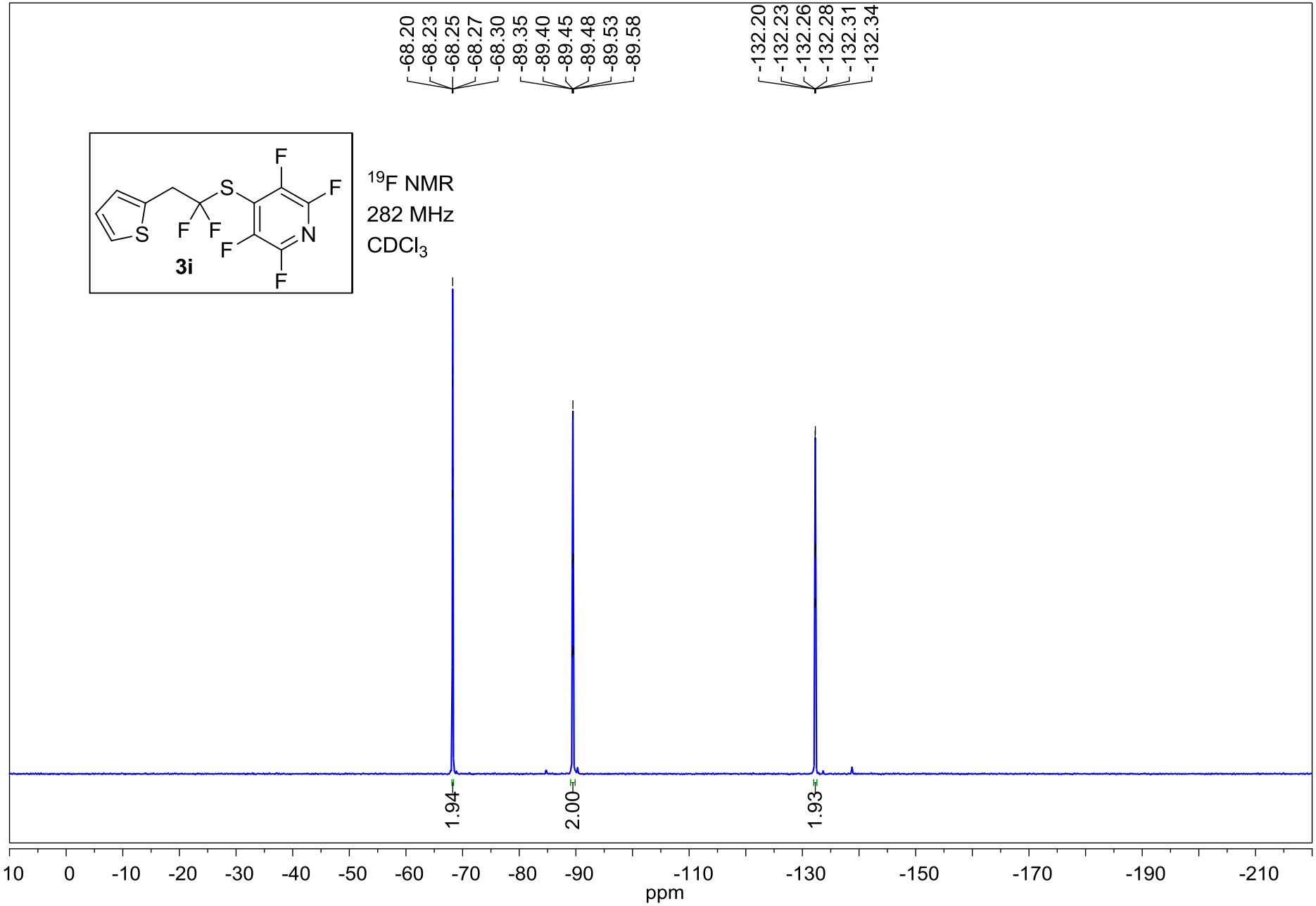
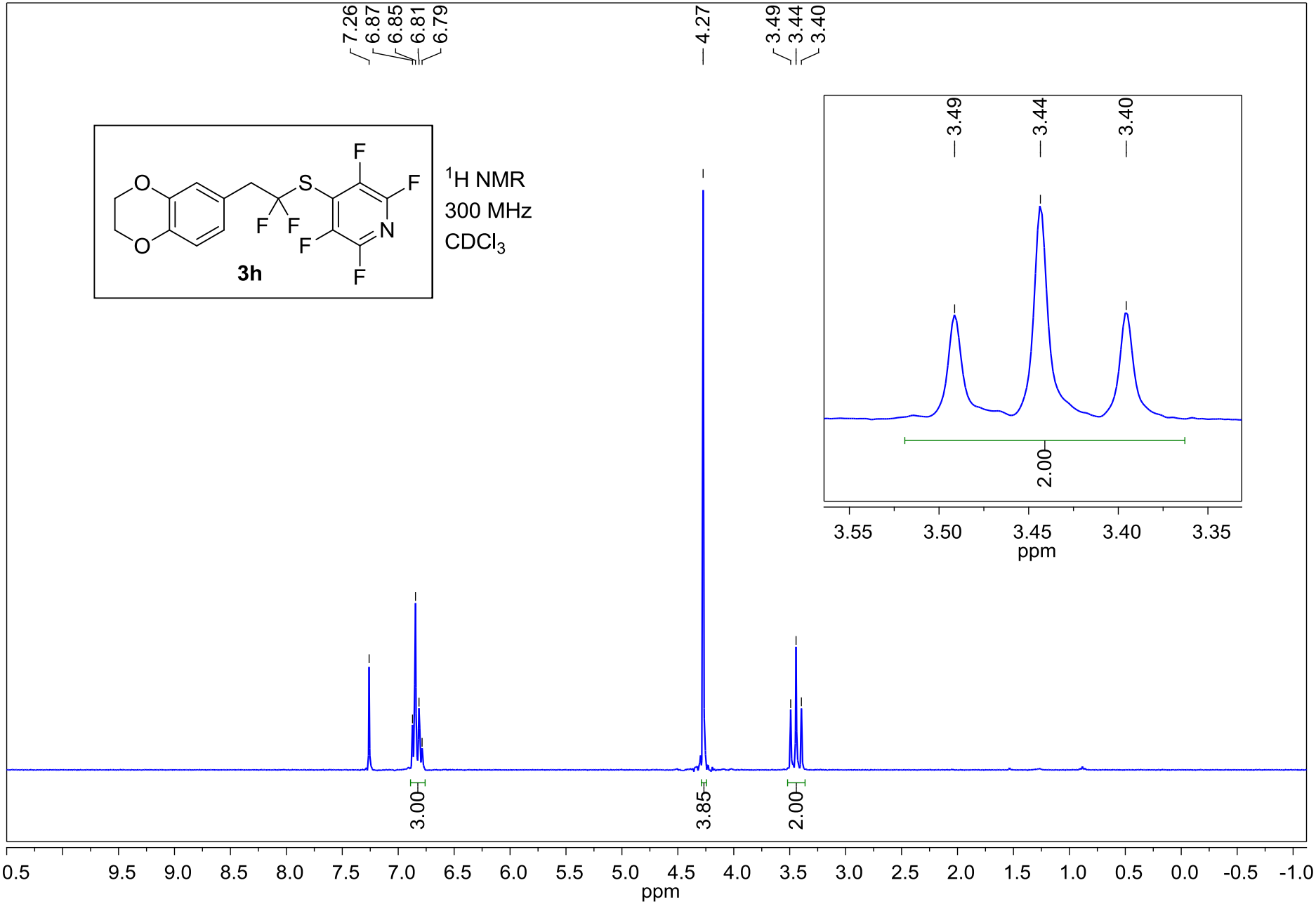
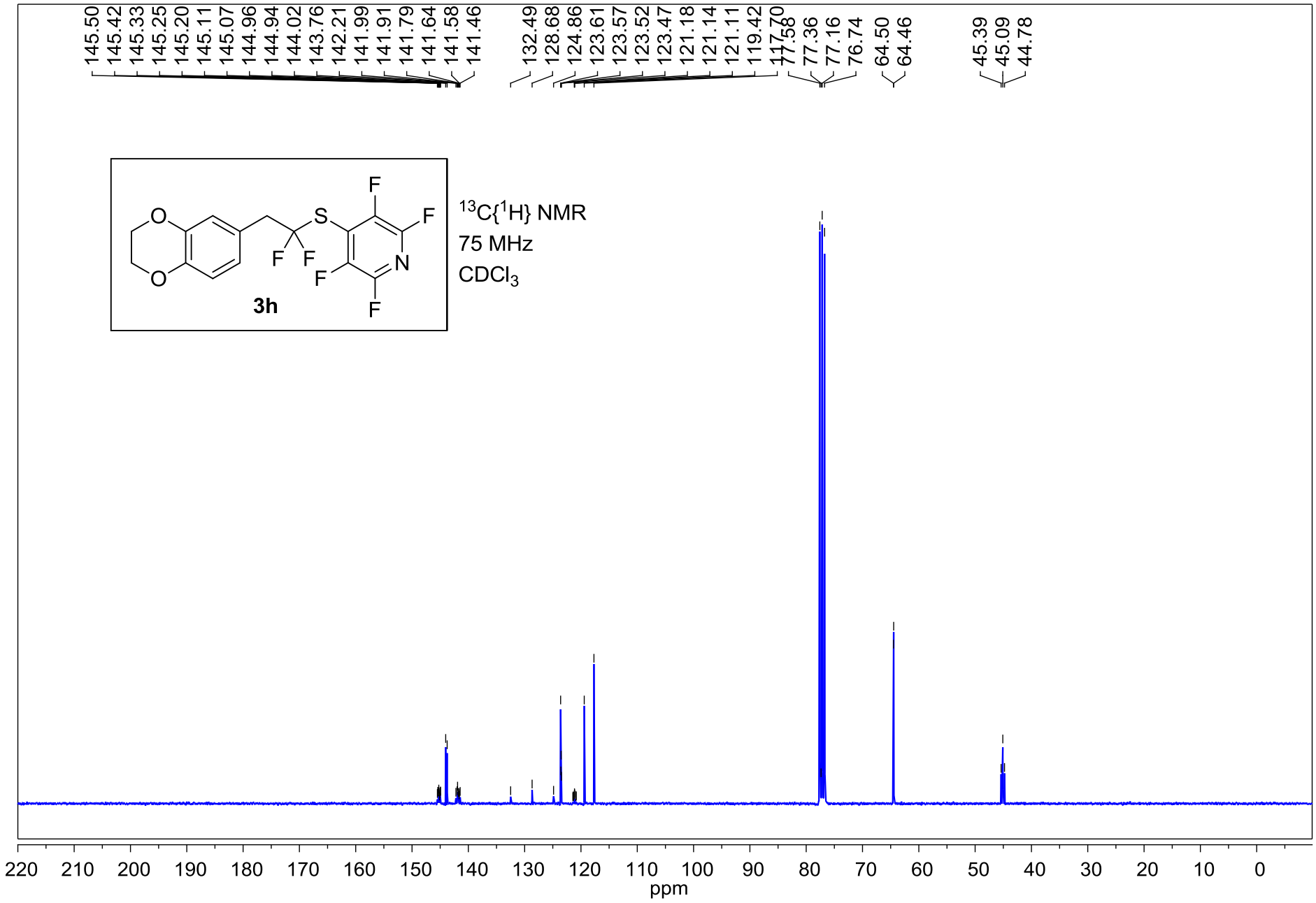
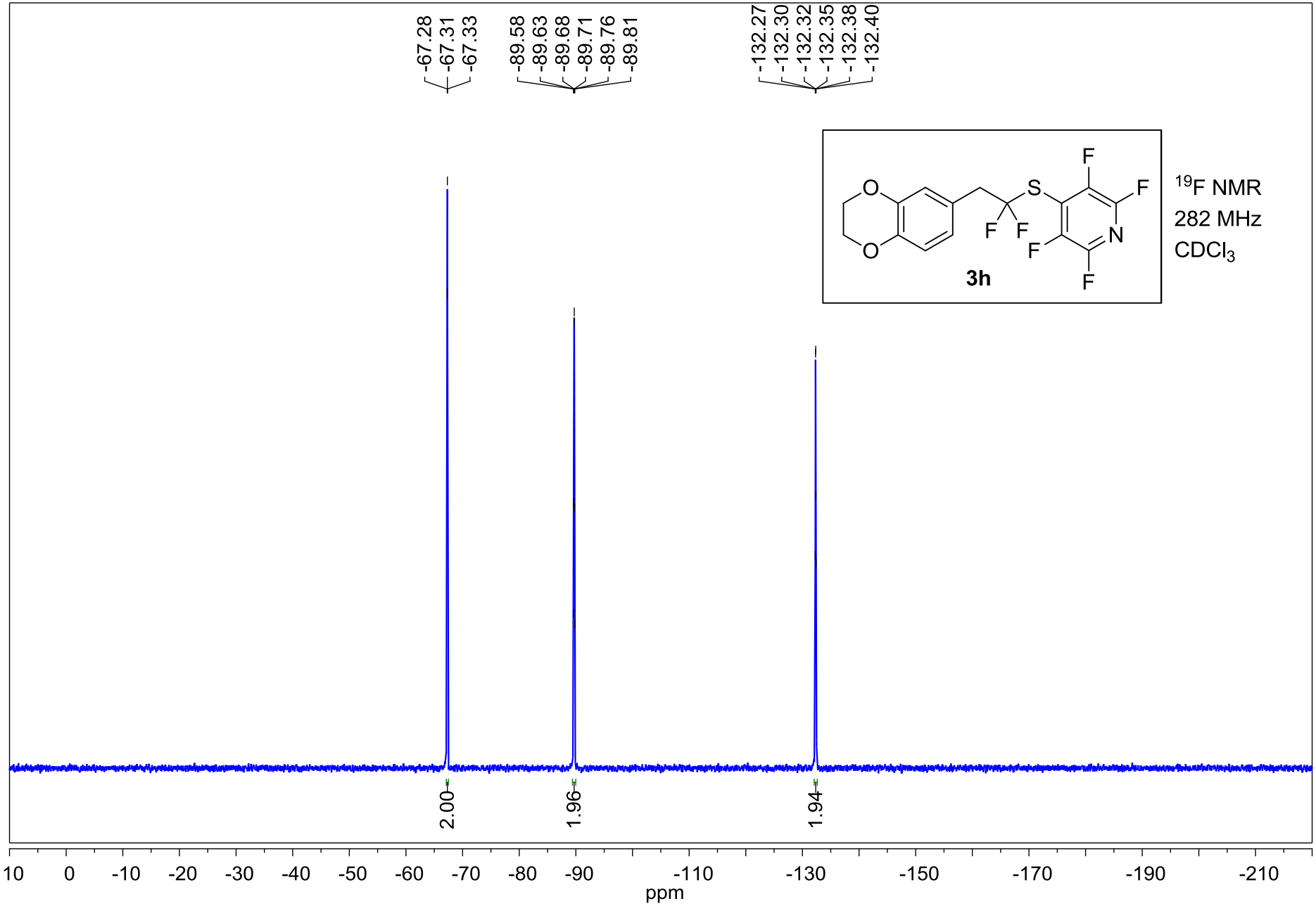
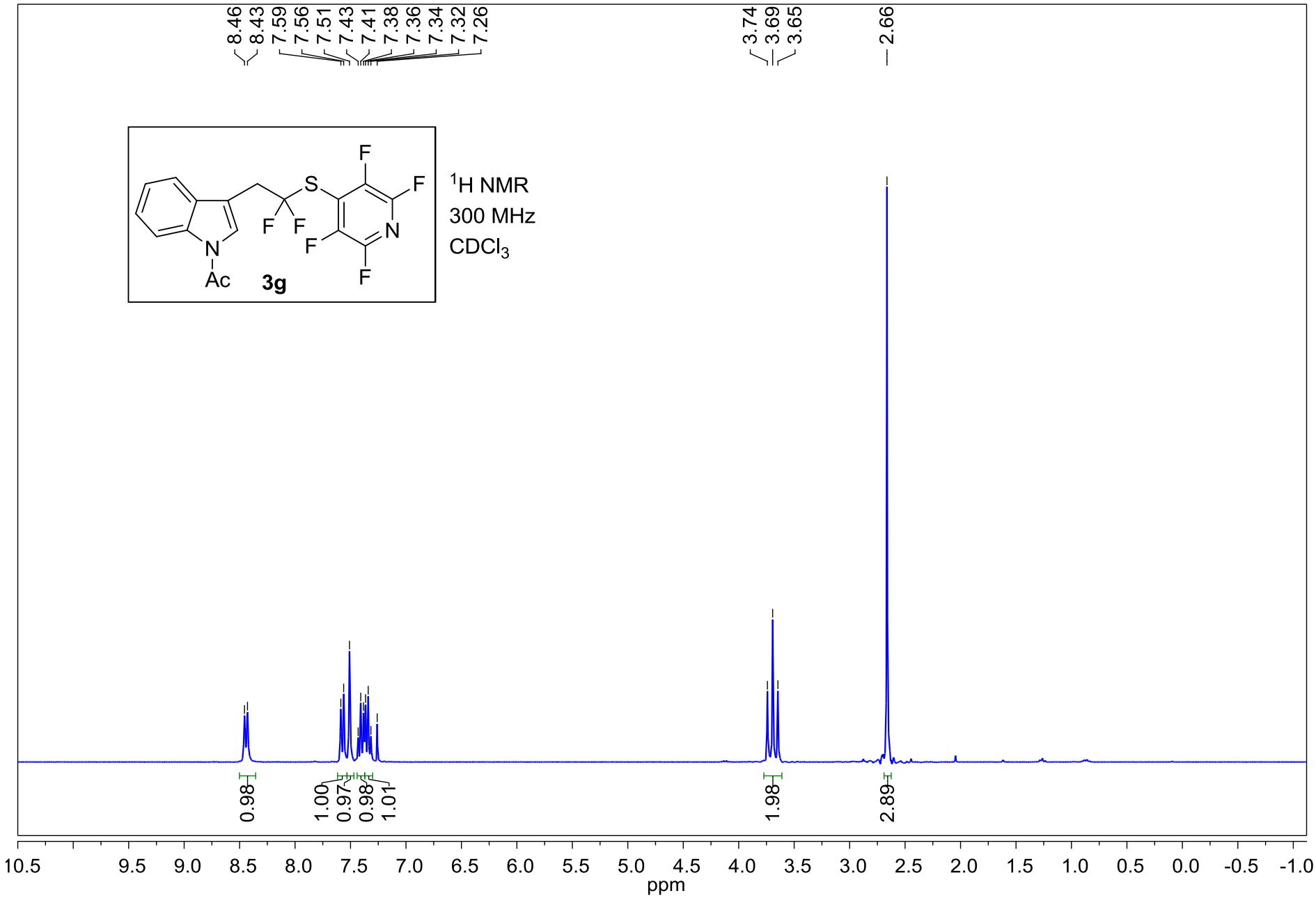
145.45
145.42
145.31
145.27
145.22
145.17
145.05
144.99
144.96
142.22
142.19
142.05
142.00
141.96
141.93
141.87
141.80
141.75
141.60
141.51
141.48
131.68
131.20
131.15
131.09
129.51
127.87
127.39
126.99
124.06
120.77
120.73
120.70
77.58
77.36
77.16
76.74
40.36
40.03
39.70
F
S
F
F
F
S
F
N
F
3i
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
ppm

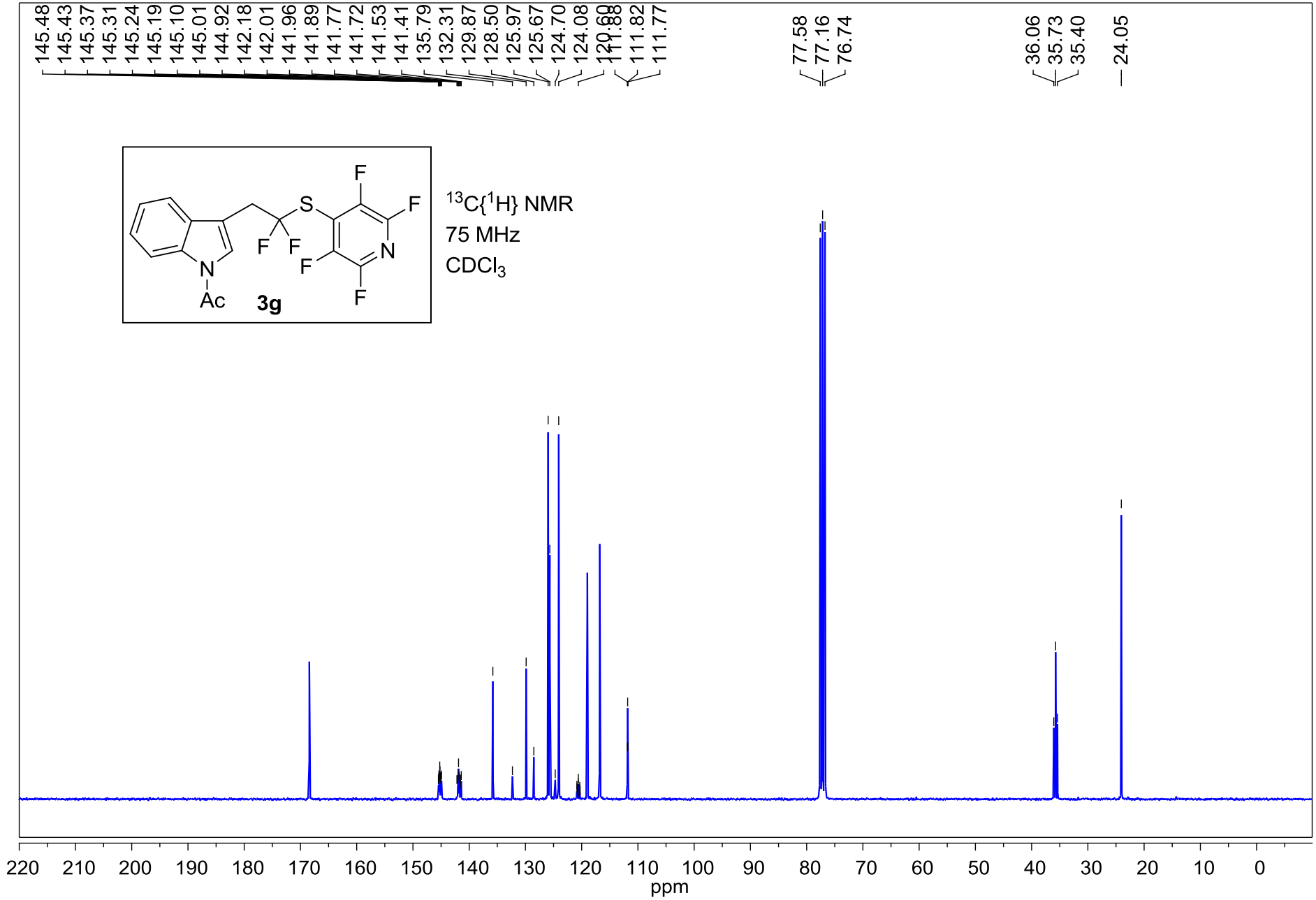

-68.20
-68.23
-68.25
-68.27
-68.30
-89.35
-89.40
-89.45
-89.48
-89.53
-89.58
-132.20
-132.23
-132.26
-132.28
-132.31
-132.34
F
S
F
F
F
F
S
F
N
F
3i
^{19}F NMR
282 MHz
$CDCl_3$
1.94
2.00
1.93
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

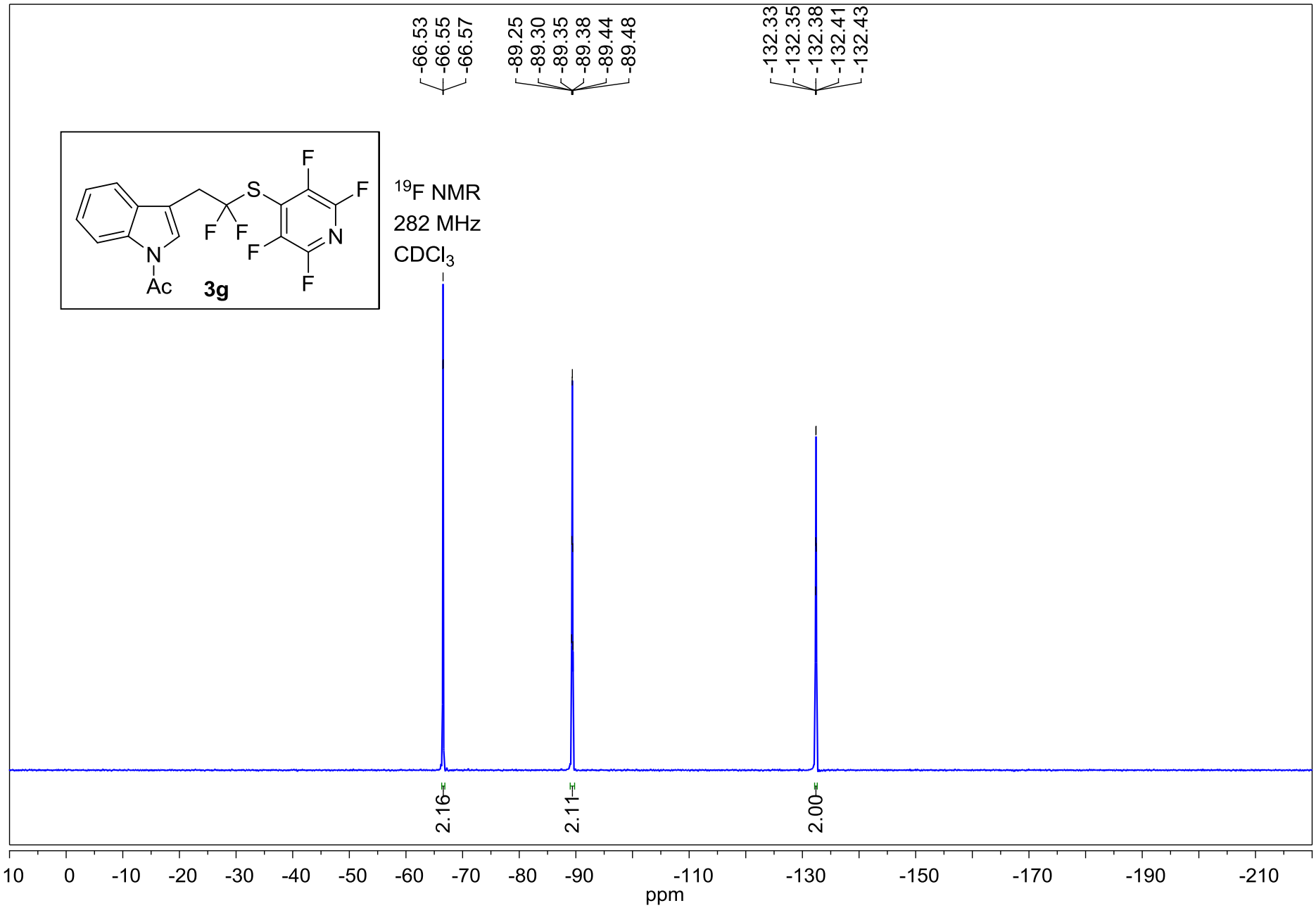

7.26
6.87
6.85
6.81
6.79
4.27
3.49
3.44
3.40
3h
^{1}H NMR
300 MHz
$CDCl_3$
3.00
3.85
2.00
ppm

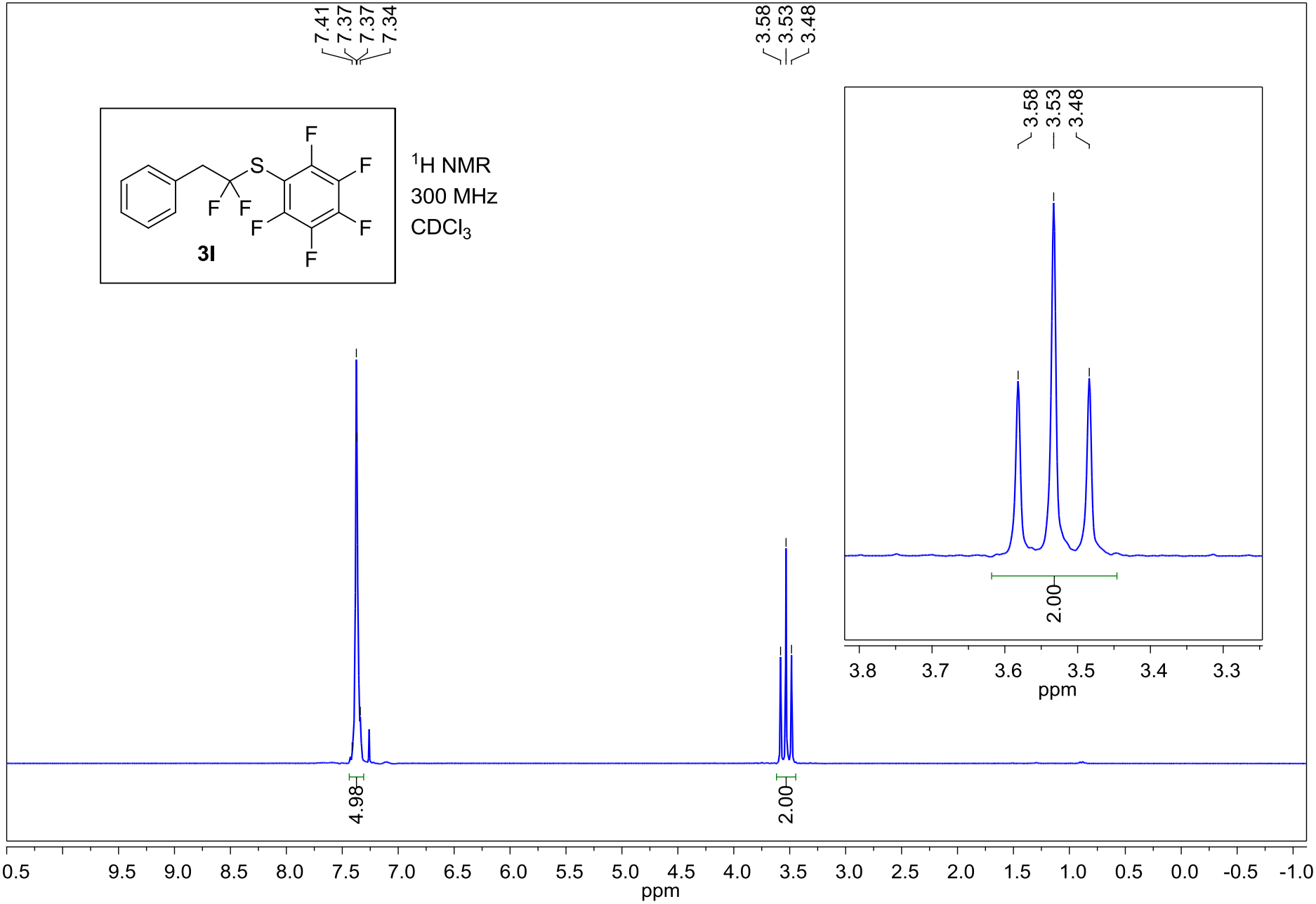

145.50
145.42
145.33
145.25
145.20
145.11
145.07
144.96
144.94
144.02
143.76
142.21
141.99
141.91
141.79
141.64
141.58
141.46
132.49
128.68
124.86
123.61
123.57
123.52
123.47
121.18
121.14
121.11
119.42
117.70
77.58
77.36
77.16
76.74
64.50
64.46
45.39
45.09
44.78
O
O
S
F
F
F
F
F
F
N
3h
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

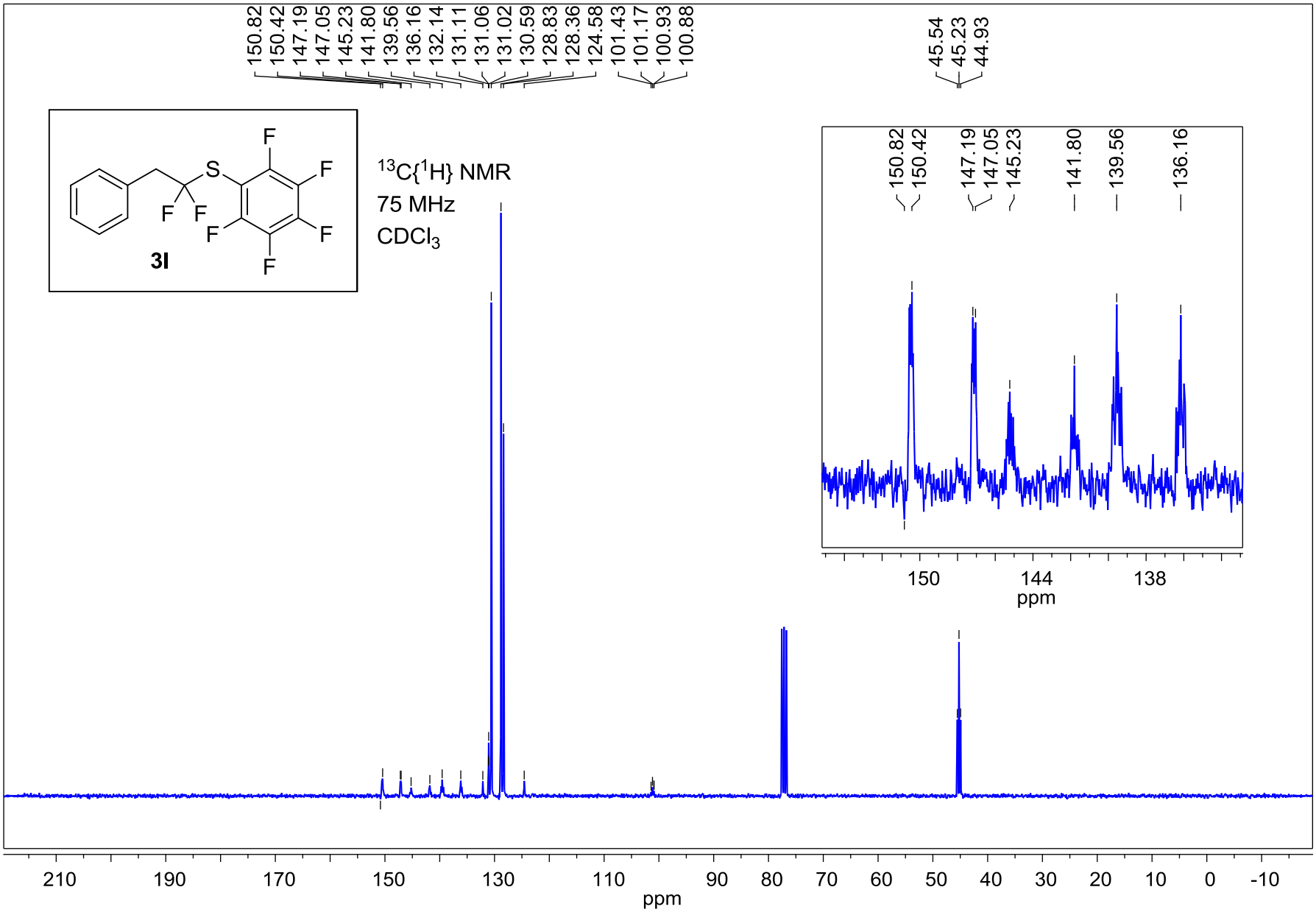

-67.28
-67.31
-67.33
-89.58
-89.63
-89.68
-89.71
-89.76
-89.81
-132.27
-132.30
-132.32
-132.35
-132.38
-132.40
O
O
S
F
F
F
F
F
N
F
3h
^{19}F NMR
282 MHz
$CDCl_3$
2.00
1.96
1.94
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

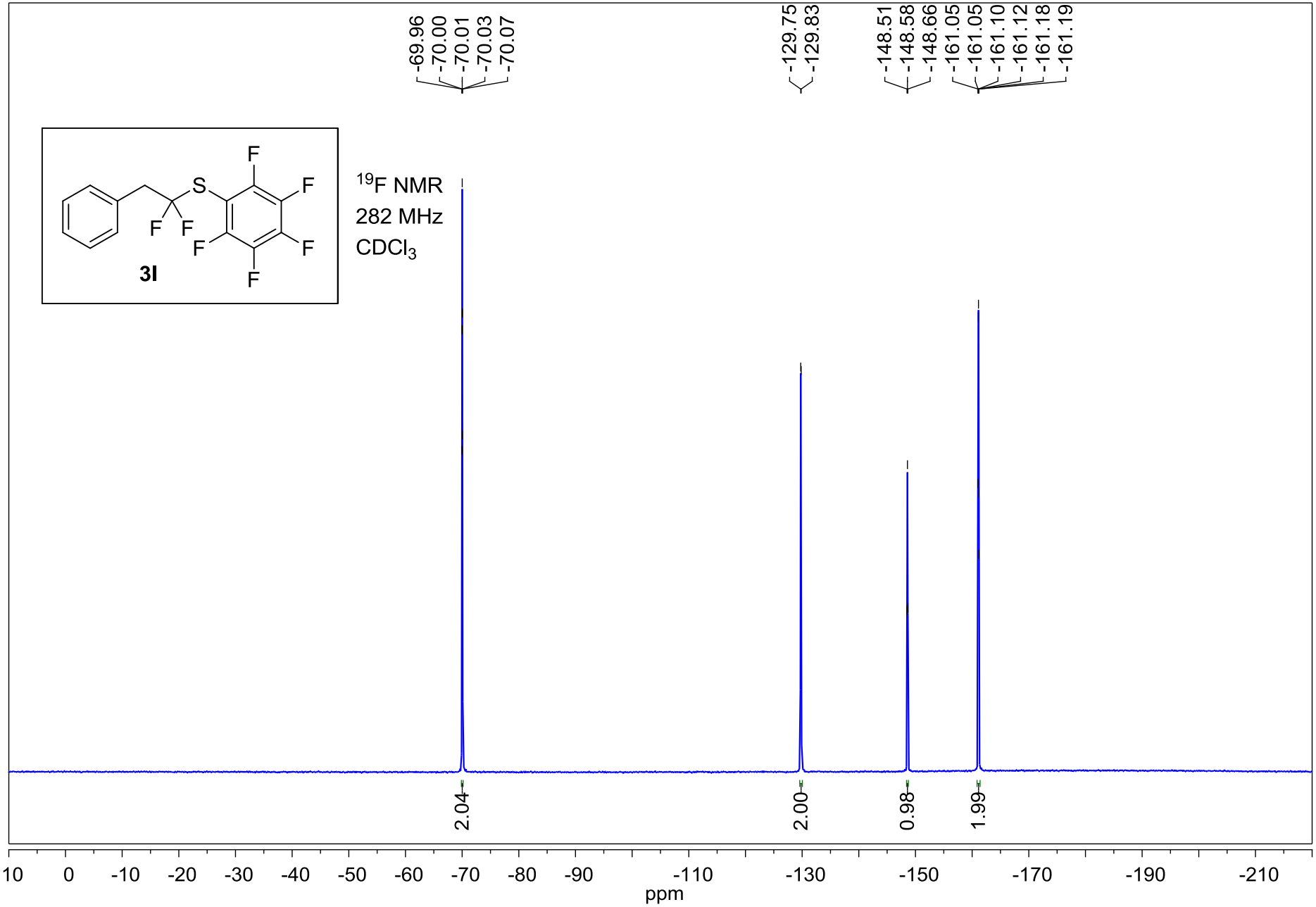

8.46
8.43
7.59
7.56
7.51
7.43
7.41
7.38
7.36
7.34
7.32
7.26
3.74
3.69
3.65
2.66
F
S
F
F
F
F
N
N
Ac
3g
^{1}H NMR
300 MHz
$CDCl_3$
0.98
1.00
0.97
0.98
1.01
1.98
2.89
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

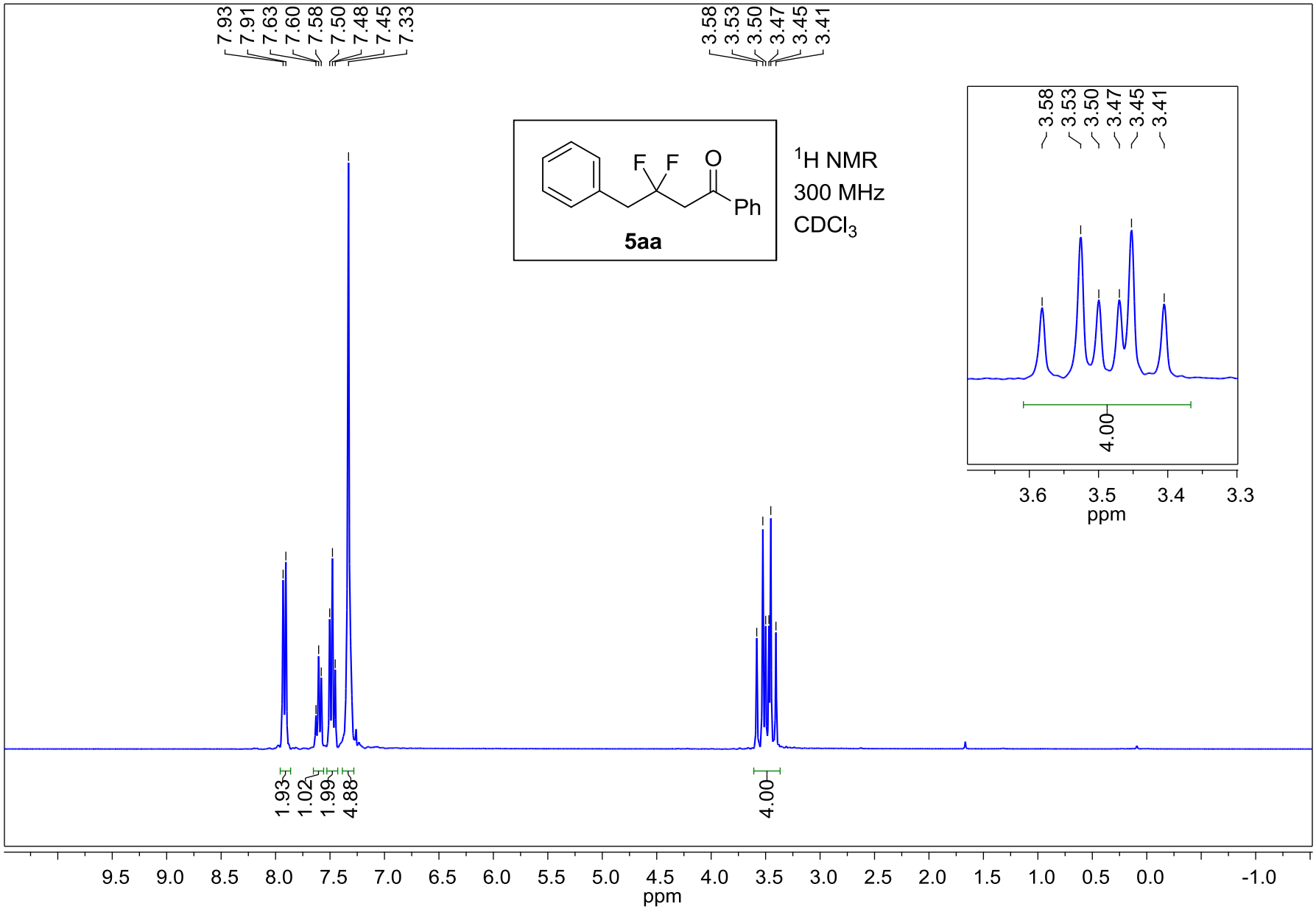

145.48
145.43
145.37
145.31
145.24
145.19
145.10
145.01
144.92
142.18
142.01
141.96
141.89
141.77
141.72
141.53
141.41
135.79
132.31
129.87
128.50
125.97
125.67
124.70
124.08
120.60
111.88
111.82
111.77
77.58
77.16
76.74
36.06
35.73
35.40
24.05
F
S
F
F
F
F
N
N
Ac
3g
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

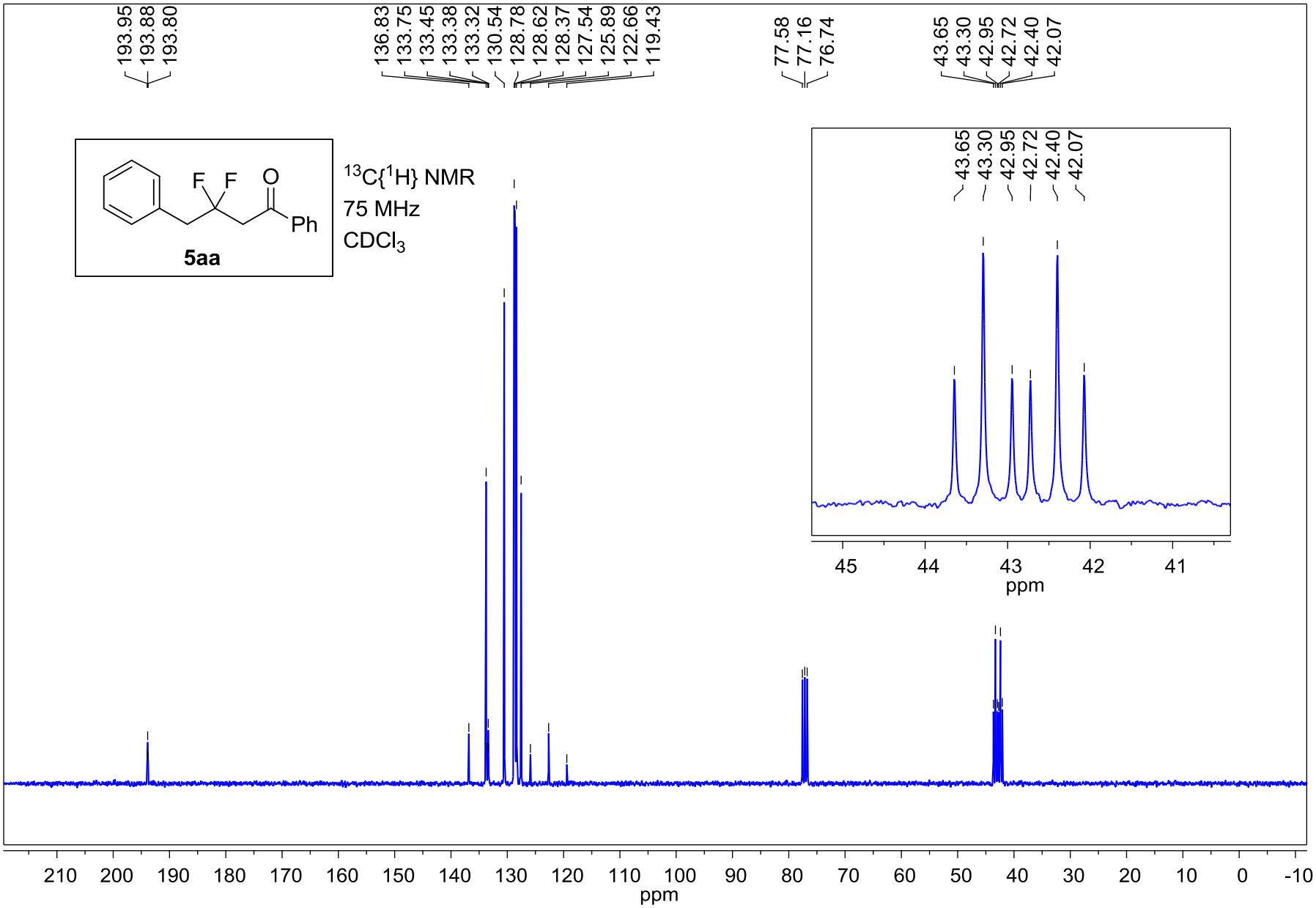

-66.53
-66.55
-66.57
-89.25
-89.30
-89.35
-89.38
-89.44
-89.48
-132.33
-132.35
-132.38
-132.41
-132.43
F
S
F
F
F
F
N
N
Ac
3g
19F NMR
282 MHz
CDCl3
2.16
2.11
2.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

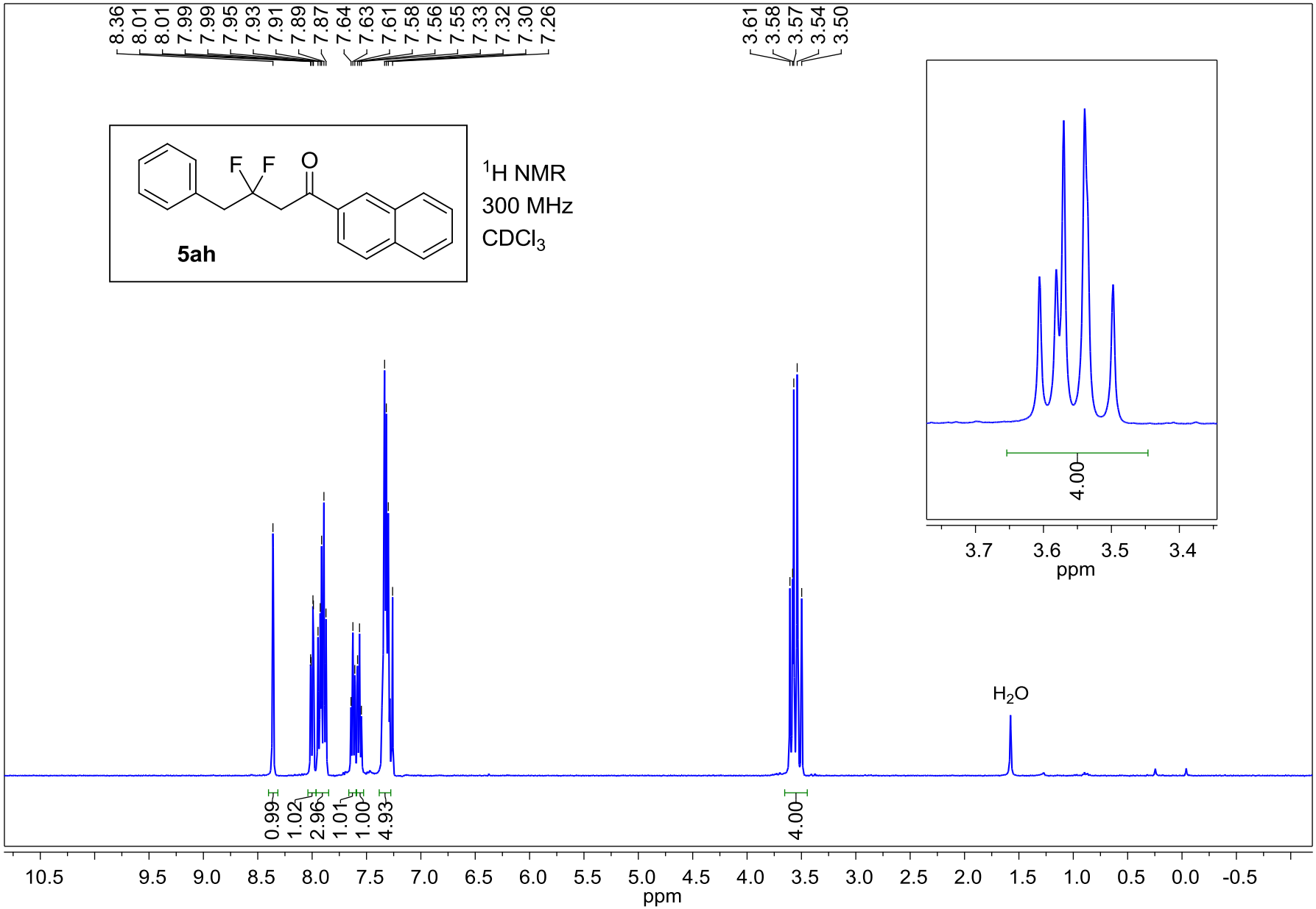

7.41
7.37
7.37
7.34
3.58
3.53
3.48
F
S
F
F
F
F
F
F
3I
^{1}H NMR
300 MHz
$CDCl_3$
3.58
3.53
3.48
2.00
3.8
3.7
3.6
3.5
3.4
3.3
ppm
4.98
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

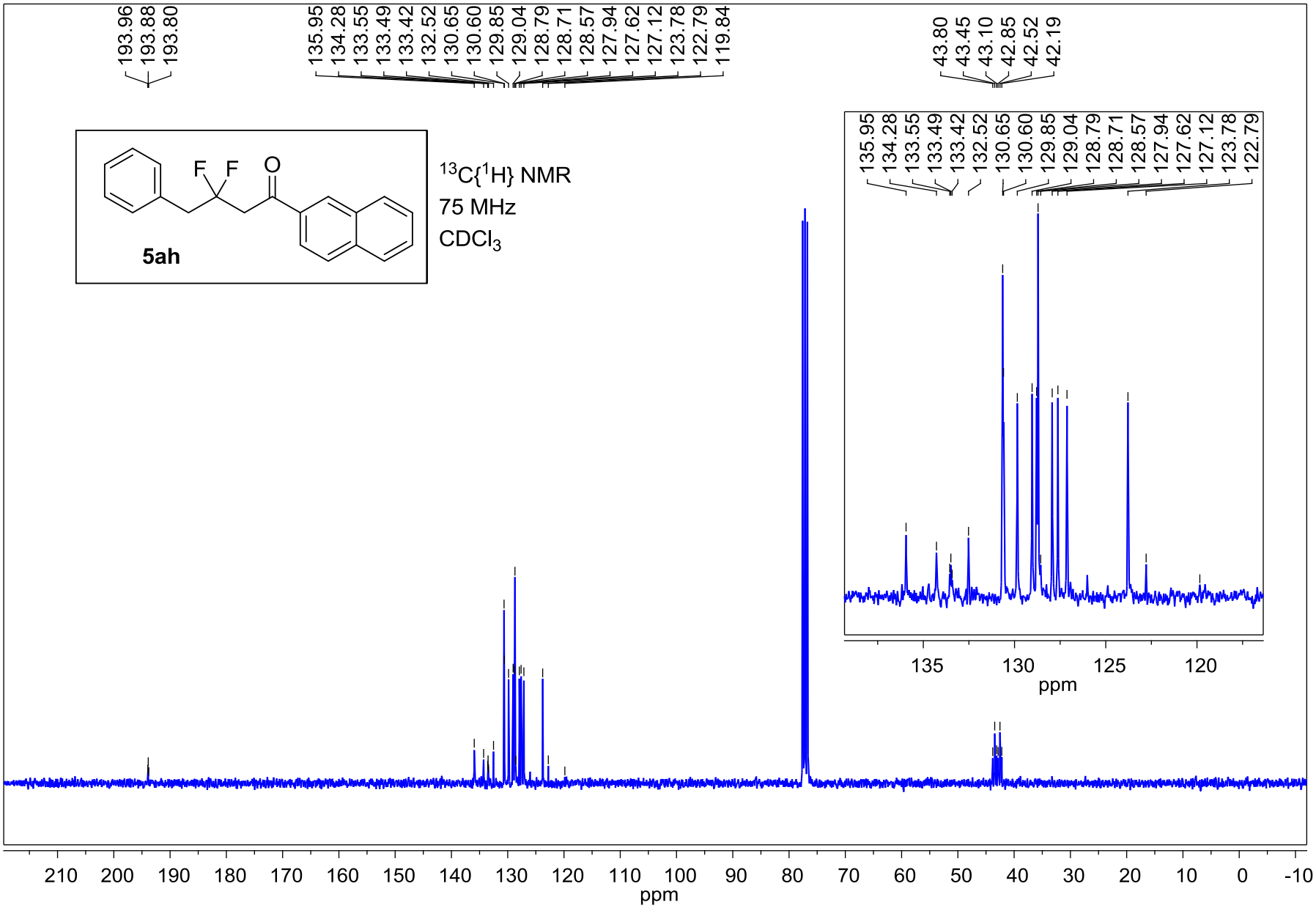

150.82
150.42
147.19
147.05
145.23
141.80
139.56
136.16
132.14
131.11
131.06
131.02
130.59
128.83
128.36
124.58
101.43
101.17
100.93
100.88
45.54
45.23
44.93
3l
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
ppm
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
144
138

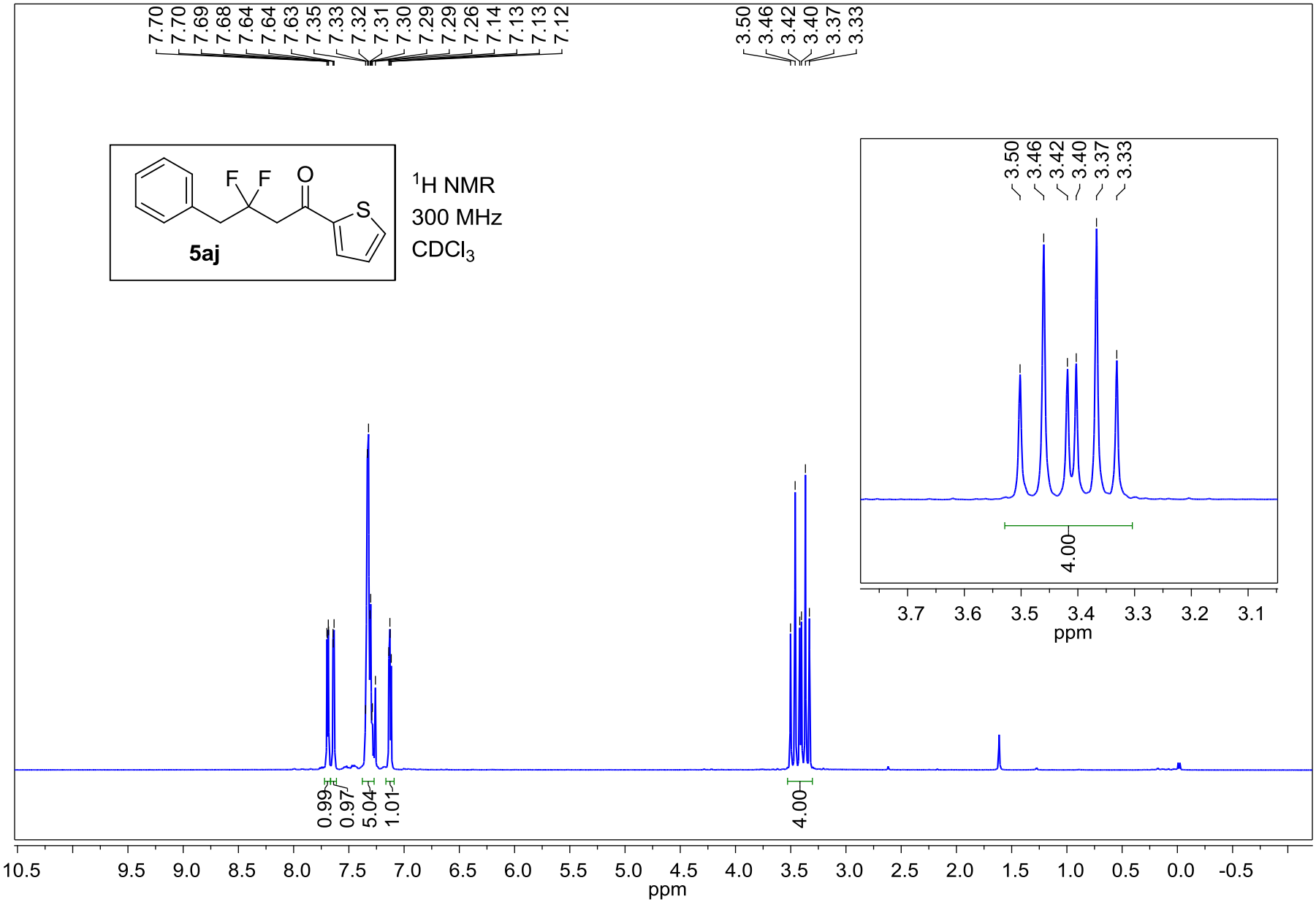

-69.96
-70.00
-70.01
-70.03
-70.07
-129.75
-129.83
-148.51
-148.58
-148.66
-161.05
-161.05
-161.10
-161.12
-161.18
-161.19
F
S
F
F
F
F
F
F
3l
19F NMR
282 MHz
CDCl3
2.04
2.00
0.98
1.99
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

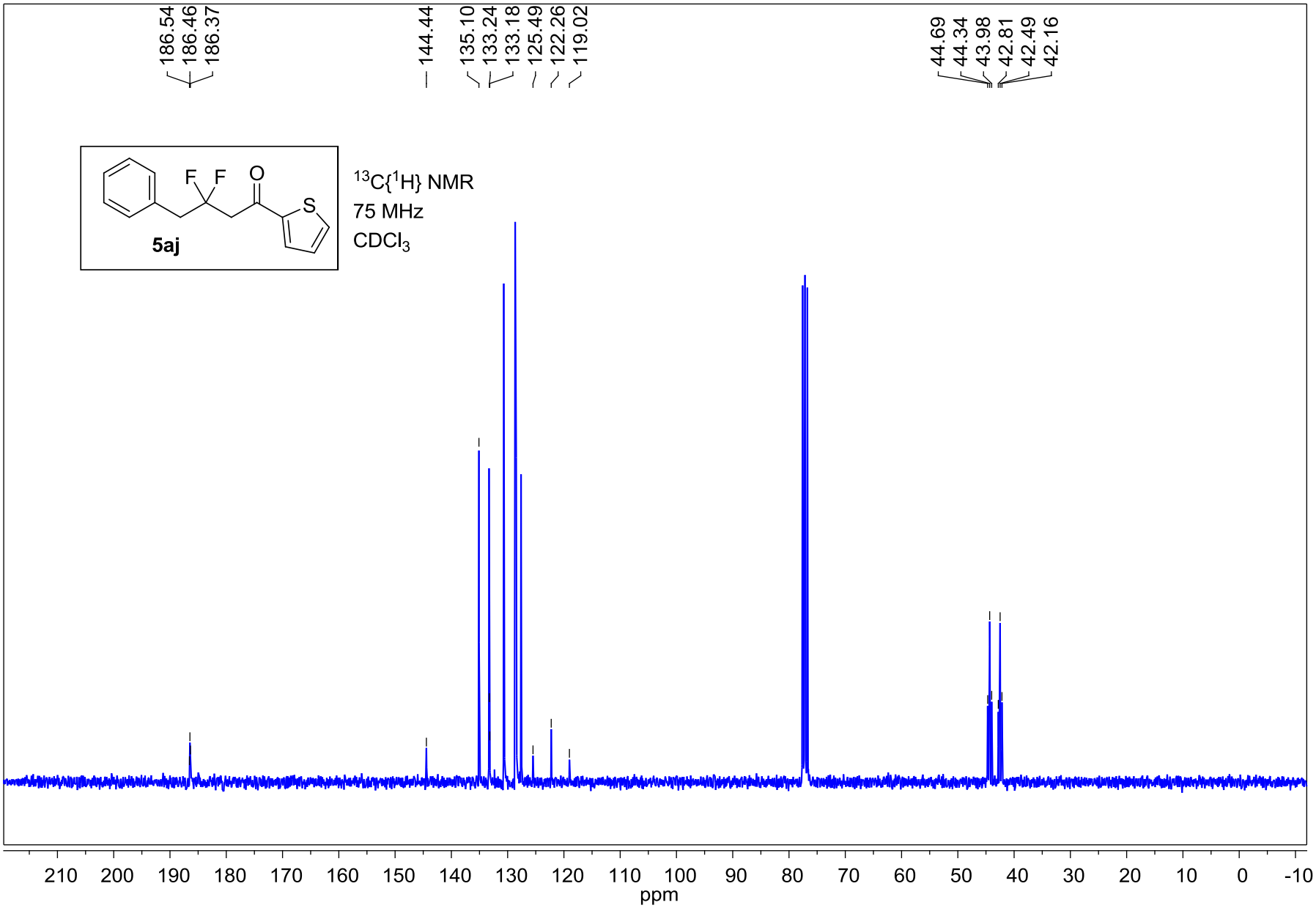

7.93
7.91
7.63
7.60
7.58
7.50
7.48
7.45
7.33
3.58
3.53
3.50
3.47
3.45
3.41
F F O
Ph
5aa
1H NMR
300 MHz
CDCl3
4.00
3.6
3.5
3.4
3.3
ppm
1.93
1.02
1.99
4.88
4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
ppm

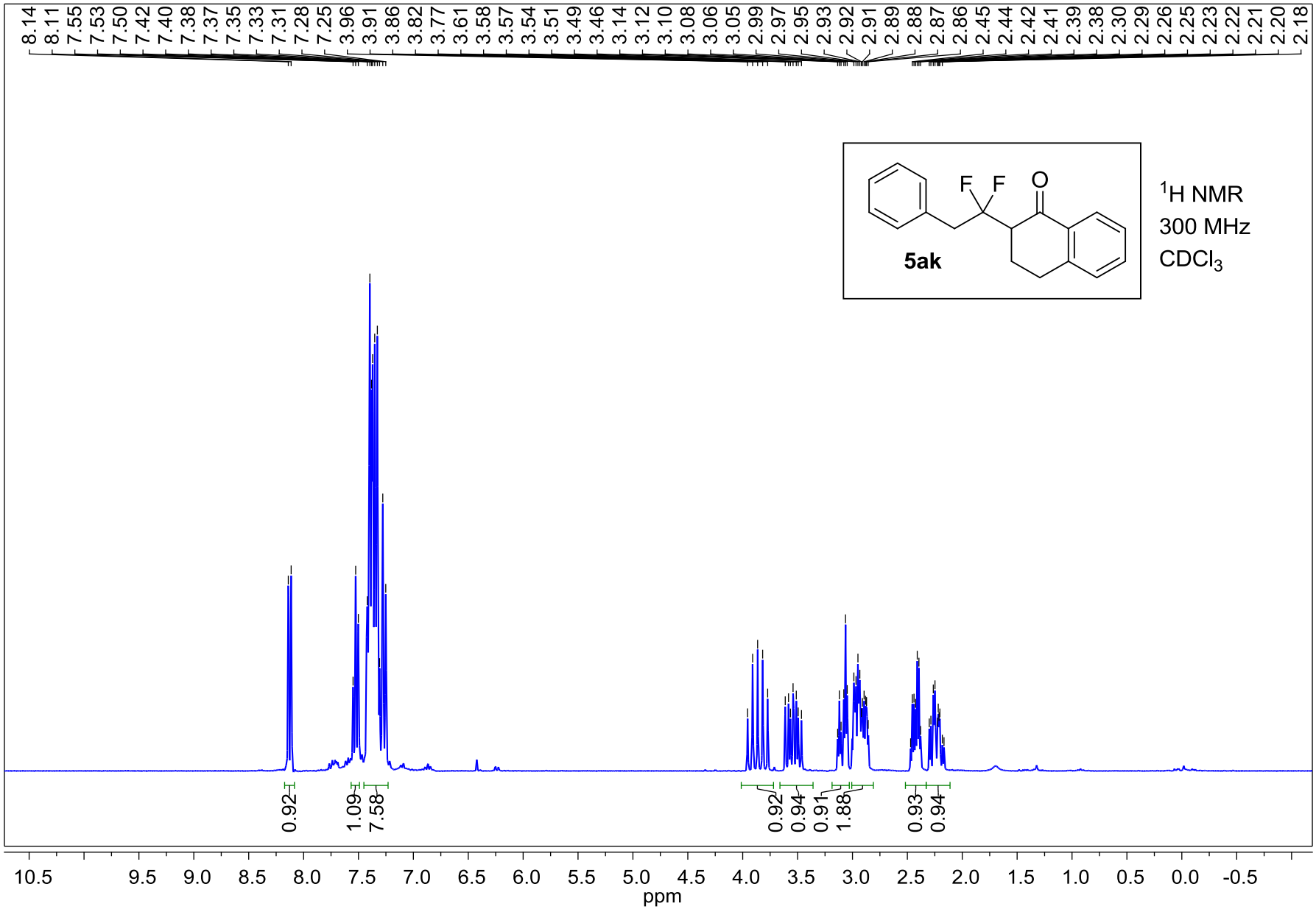

193.95
193.88
193.80
136.83
133.75
133.45
133.38
133.32
130.54
128.78
128.62
128.37
127.54
125.89
122.66
119.43
77.58
77.16
76.74
43.65
43.30
42.95
42.72
42.40
42.07
F F O
Ph
5aa
13C{1H} NMR
75 MHz
CDCl3
45
44
43
42
41
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

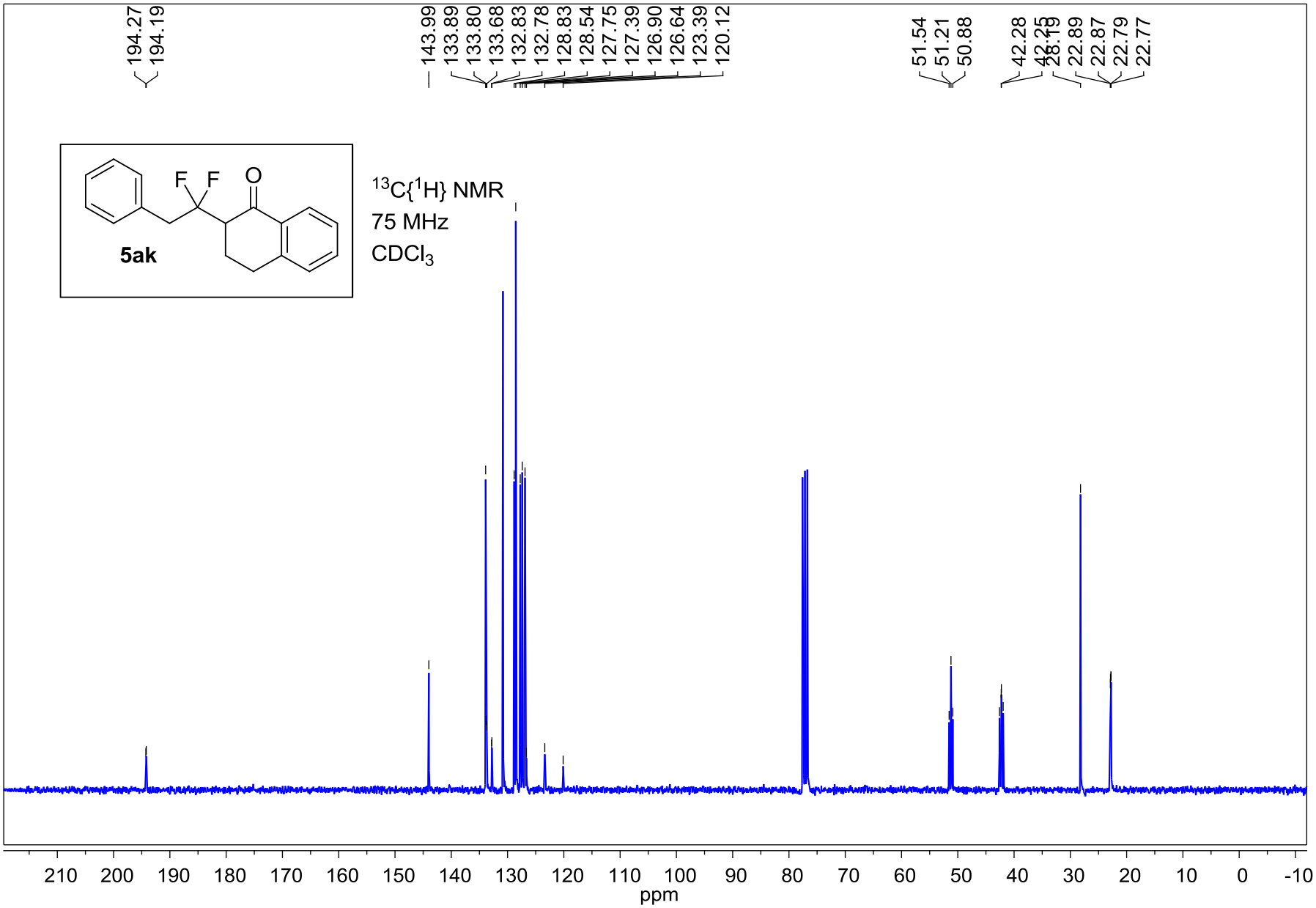

8.36
8.01
8.01
7.99
7.99
7.95
7.93
7.91
7.89
7.87
7.64
7.63
7.61
7.58
7.56
7.55
7.33
7.32
7.30
7.26
3.61
3.58
3.57
3.54
3.50
F F O
5ah
1H NMR
300 MHz
CDCl3
4.00
3.7
3.6
3.5
3.4
ppm
H2O
0.99
1.02
2.96
1.01
1.00
4.93
4.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm

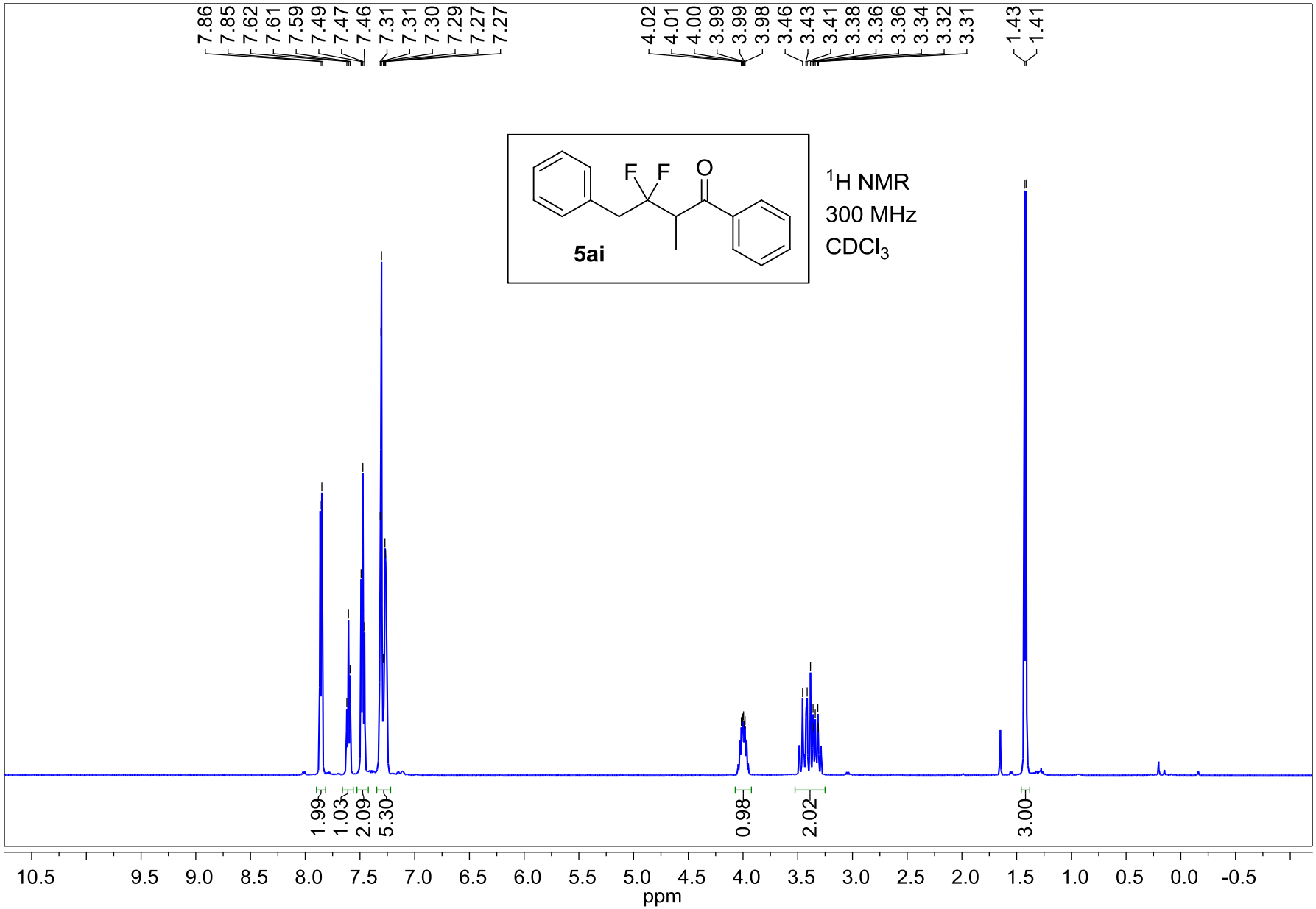

193.96
193.88
193.80
135.95
134.28
133.55
133.49
133.42
132.52
130.65
130.60
129.85
129.04
128.79
128.71
128.57
127.94
127.62
127.12
123.78
122.79
119.84
43.80
43.45
43.10
42.85
42.52
42.19
F
F
O
5ah
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
ppm
ppm

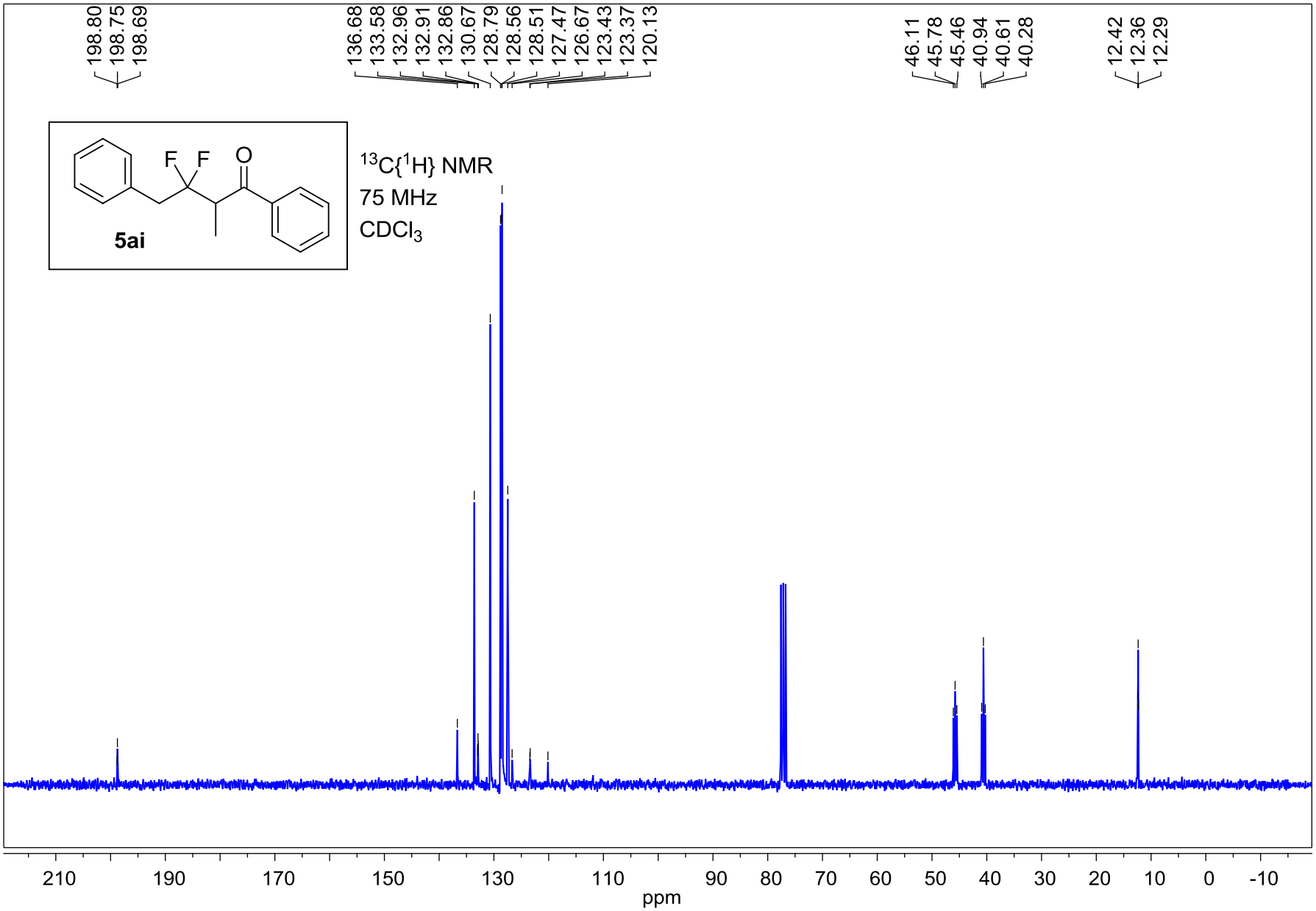

7.70
7.70
7.69
7.68
7.64
7.64
7.63
7.35
7.33
7.32
7.31
7.30
7.29
7.29
7.26
7.14
7.13
7.13
7.12
3.50
3.46
3.42
3.40
3.37
3.33
F F O
S
5aj
1H NMR
300 MHz
CDCl3
4.00
ppm
0.99
0.97
5.04
1.01
4.00
ppm

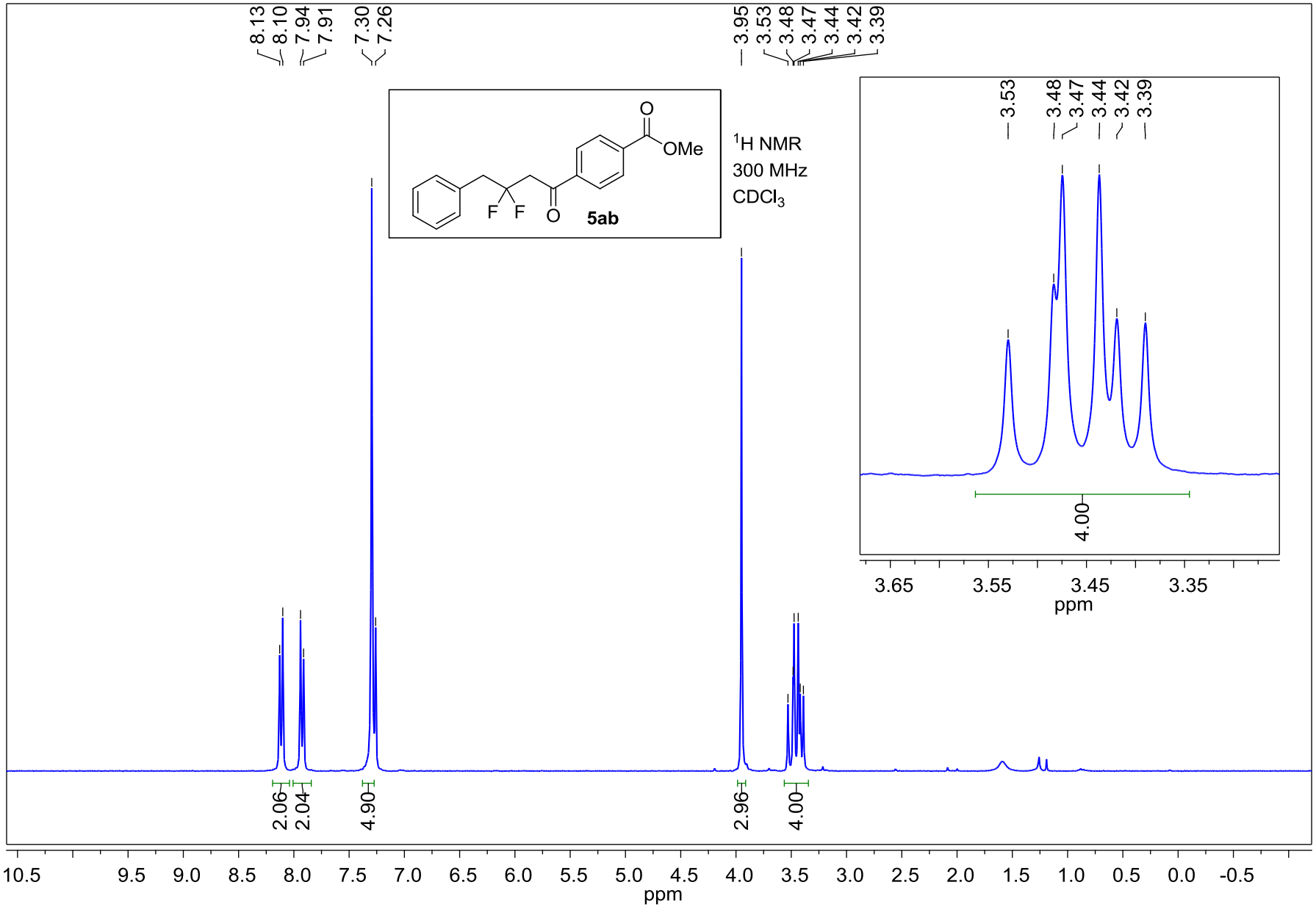

186.54
186.46
186.37
144.44
135.10
133.24
133.18
125.49
122.26
119.02
44.69
44.34
43.98
42.81
42.49
42.16
F
F
O
S
5aj
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

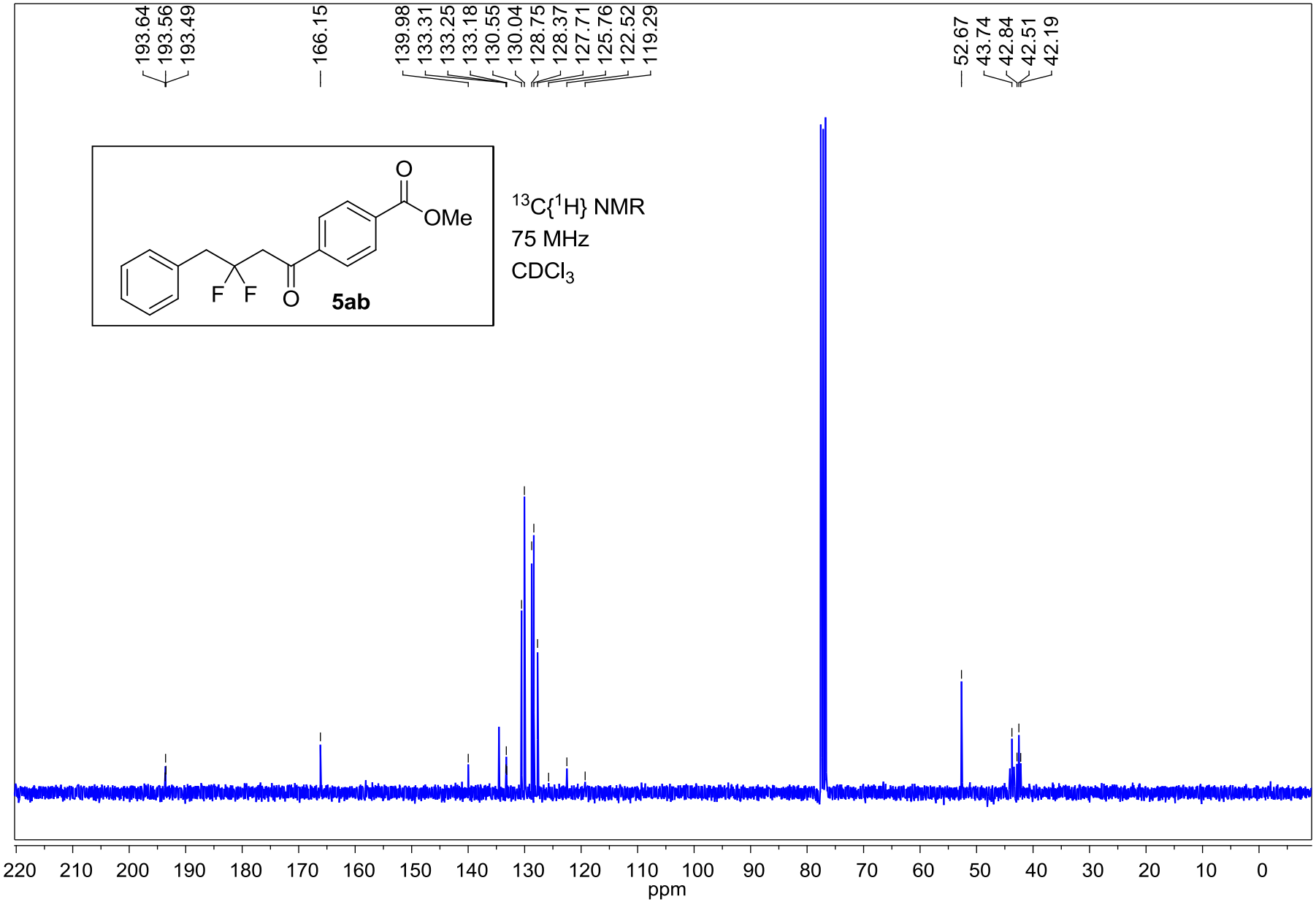

8.14 8.11 7.55 7.53 7.50 7.42 7.40 7.38 7.37 7.35 7.33 7.31 7.28 7.25 3.96 3.91 3.86 3.82 3.77 3.61 3.58 3.57 3.54 3.51 3.49 3.46 3.14 3.12 3.10 3.08 3.06 3.05 2.99 2.97 2.95 2.93 2.92 2.91 2.89 2.88 2.87 2.86 2.45 2.44 2.42 2.41 2.39 2.38 2.30 2.29 2.26 2.25 2.23 2.22 2.21 2.20 2.18
F F O
5ak
^{1}H NMR
300 MHz
$CDCl_3$
0.92 1.09 7.58 0.92 0.94 0.91 1.88 0.93 0.94
10.5 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
ppm

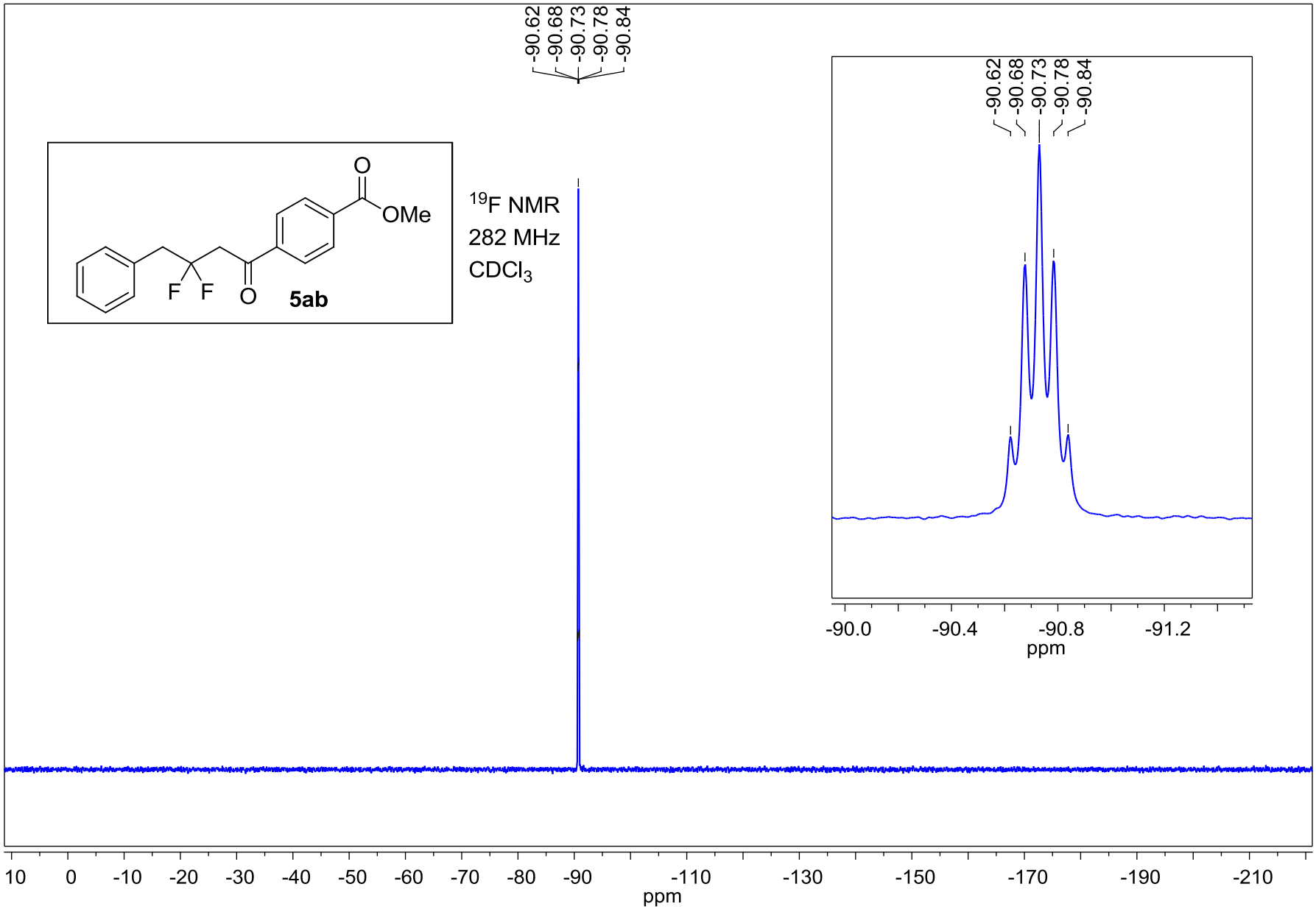

194.27
194.19
143.99
133.89
133.80
133.68
132.83
132.78
128.83
128.54
127.75
127.39
126.90
126.64
123.39
120.12
51.54
51.21
50.88
42.28
42.25
28.19
22.89
22.87
22.79
22.77
F
F
O
5ak
13C{1H} NMR
75 MHz
CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

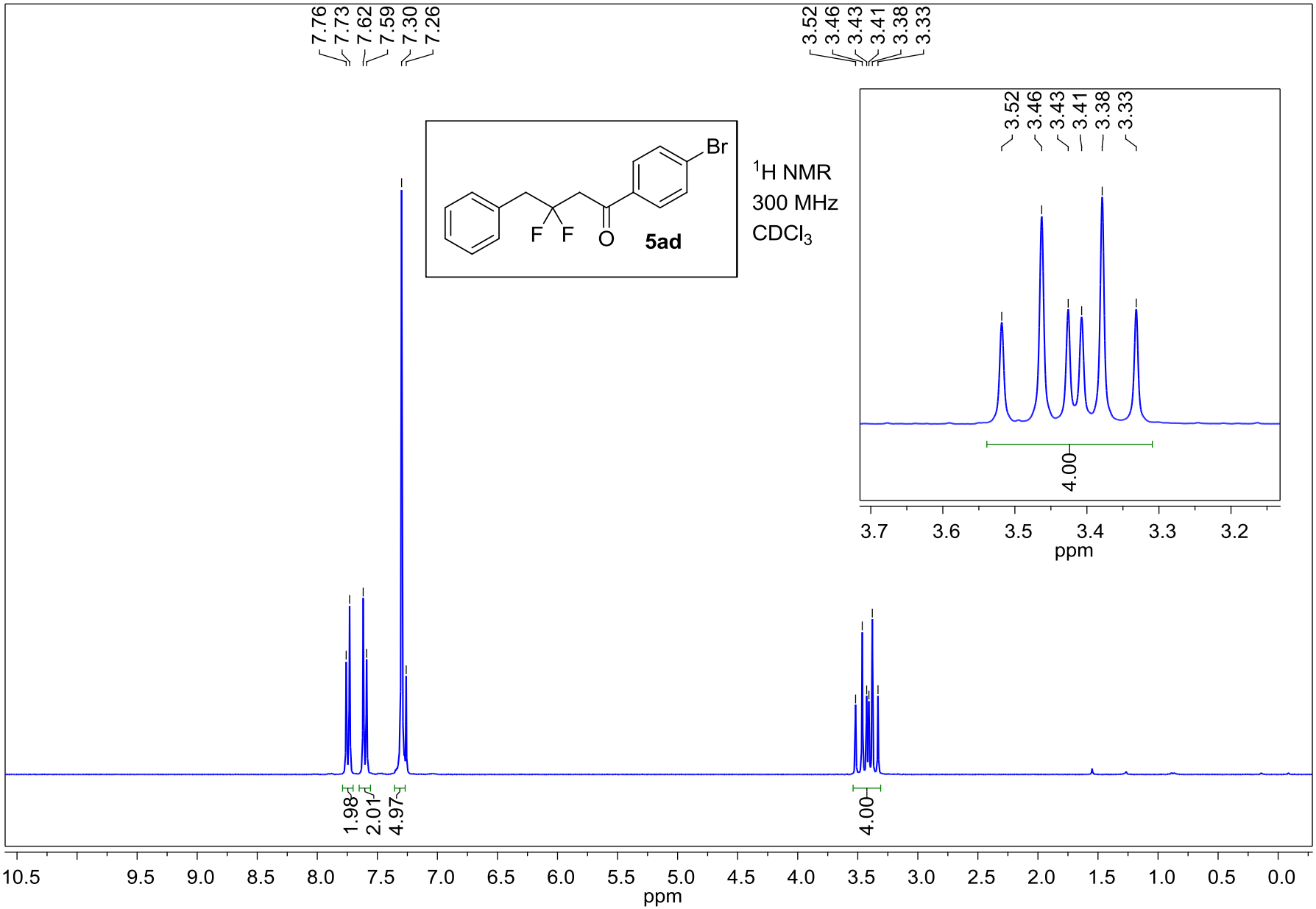

7.86
7.85
7.62
7.61
7.59
7.49
7.47
7.46
7.31
7.31
7.30
7.29
7.27
7.27
4.02
4.01
4.00
3.99
3.99
3.98
3.46
3.43
3.41
3.38
3.36
3.36
3.34
3.32
3.31
1.43
1.41
F
F
O
5ai
1H NMR
300 MHz
CDCl3
1.99
1.03
2.09
5.30
0.98
2.02
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm

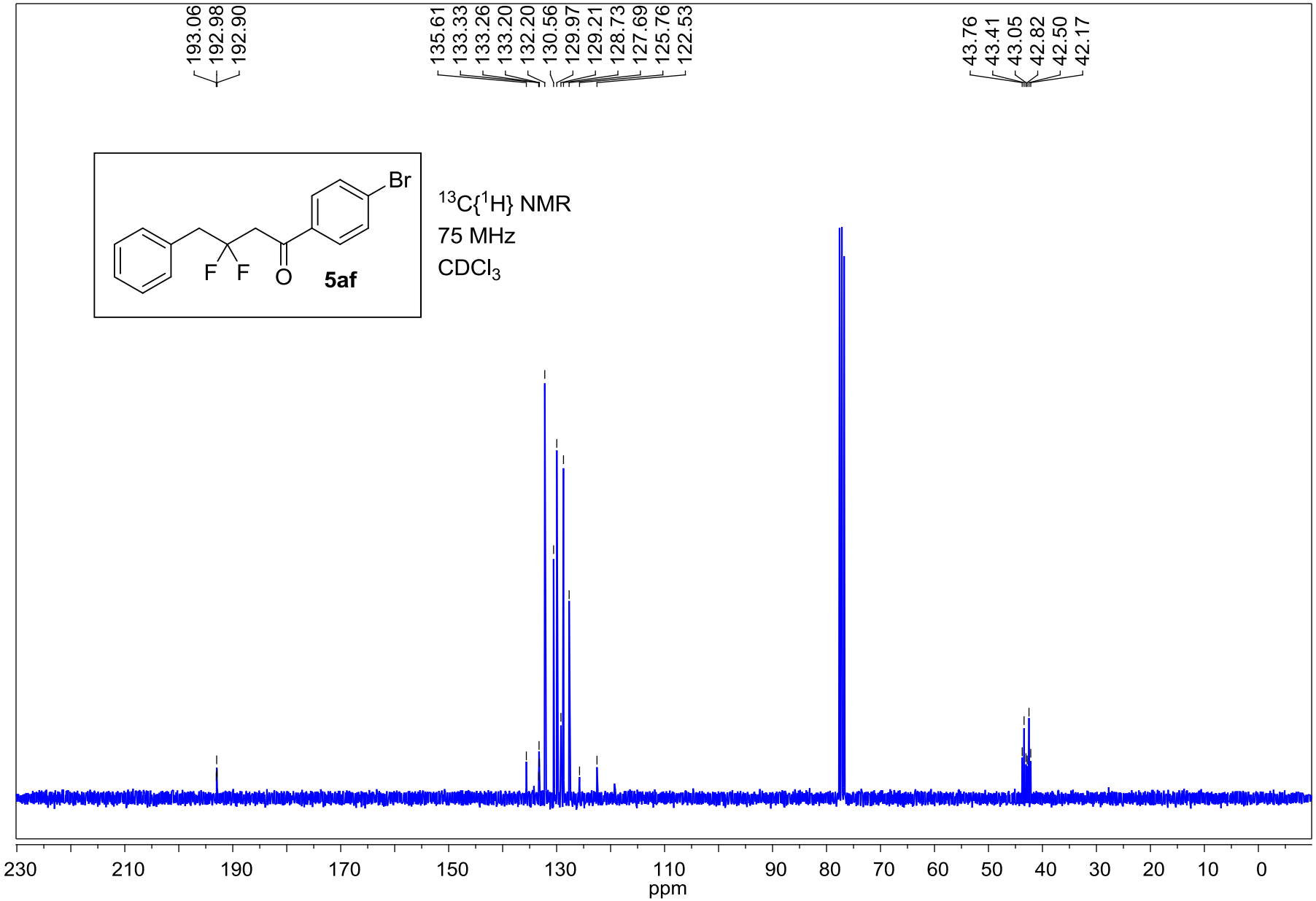

198.80
198.75
198.69
136.68
133.58
132.96
132.91
132.86
130.67
128.79
128.56
128.51
127.47
126.67
123.43
123.37
120.13
46.11
45.78
45.46
40.94
40.61
40.28
12.42
12.36
12.29
F
F
O
5ai
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm


8.13
8.10
7.94
7.91
7.30
7.26
3.95
3.53
3.48
3.47
3.44
3.42
3.39
O
OMe
F F O
5ab
1H NMR
300 MHz
CDCl3
4.00
3.65
3.55
3.45
3.35
ppm
2.06
2.04
4.90
2.96
4.00
10.5
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
ppm


193.64
193.56
193.49
166.15
139.98
133.31
133.25
133.18
130.55
130.04
128.75
128.37
127.71
125.76
122.52
119.29
52.67
43.74
42.84
42.51
42.19
O
OMe
F F
O
5ab
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


-90.62
-90.68
-90.73
-90.78
-90.84
O
OMe
F F O
5ab
^{19}F NMR
282 MHz
$CDCl_3$
-90.0
-90.4
-90.8
-91.2
ppm
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
ppm


7.76
7.73
7.62
7.59
7.30
7.26
3.52
3.46
3.43
3.41
3.38
3.33
Br
F F O
5ad
1H NMR
300 MHz
CDCl3
4.00
3.7
3.6
3.5
3.4
3.3
3.2
ppm
1.98
2.01
4.97
4.00
10.5
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
ppm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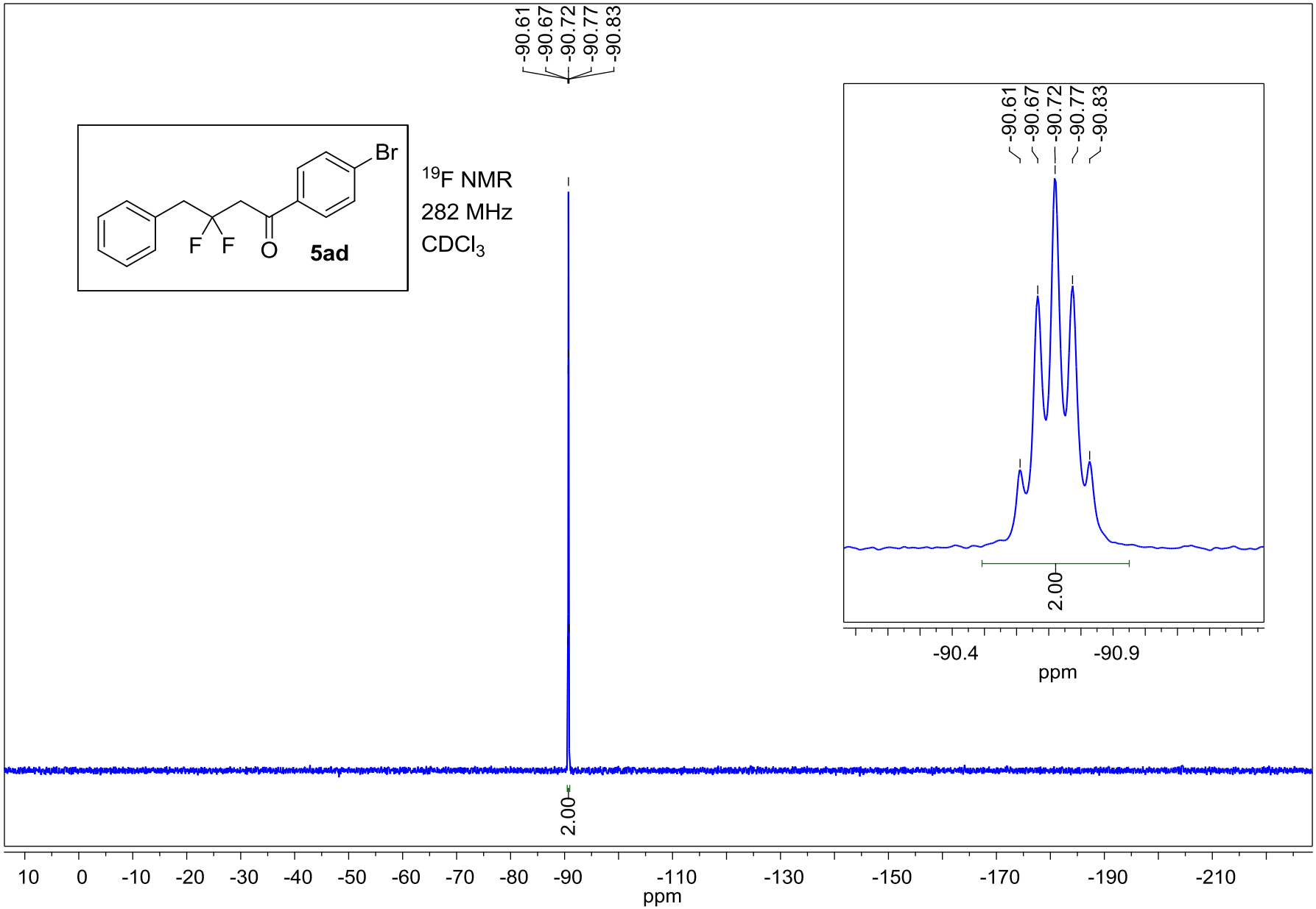
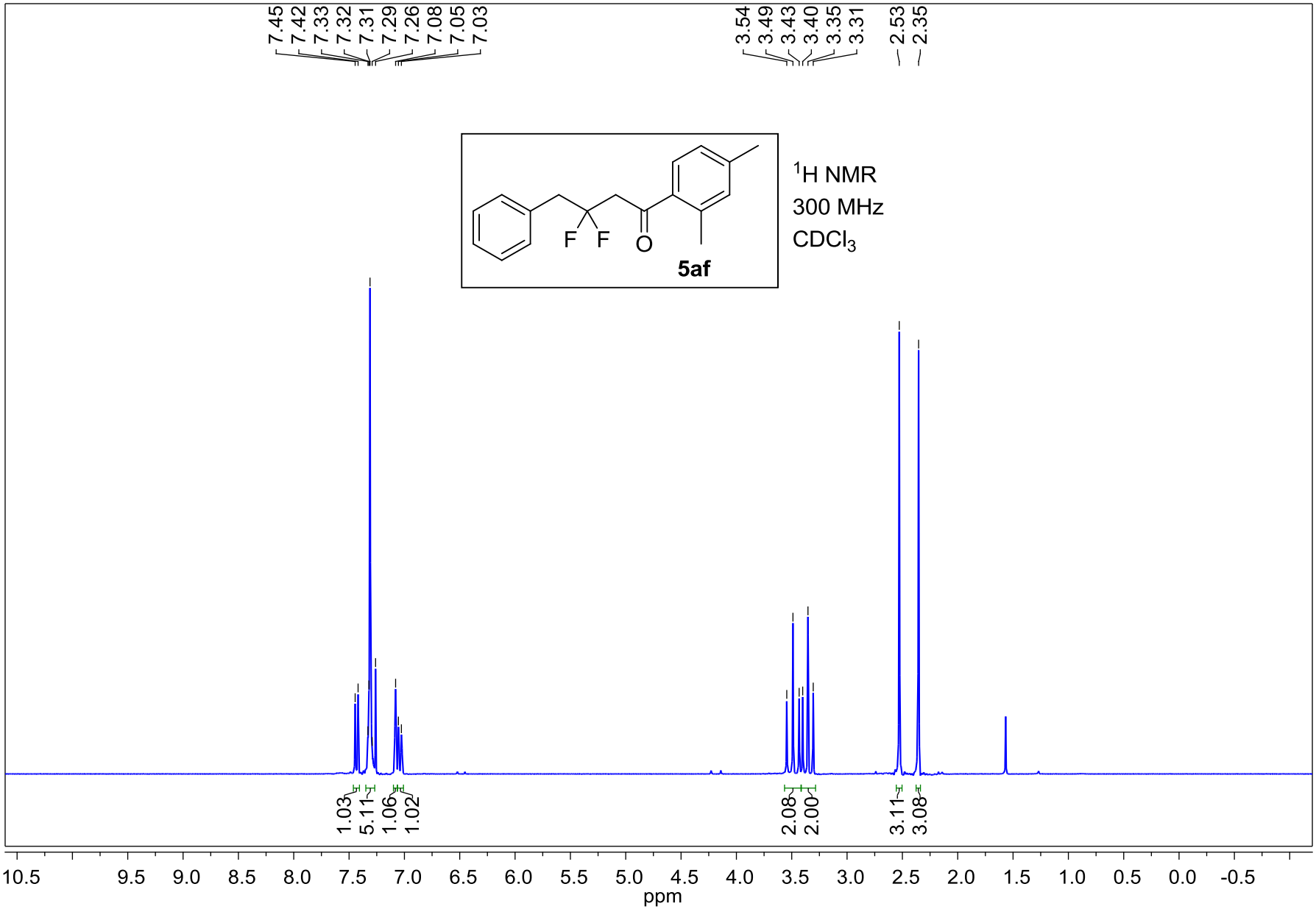
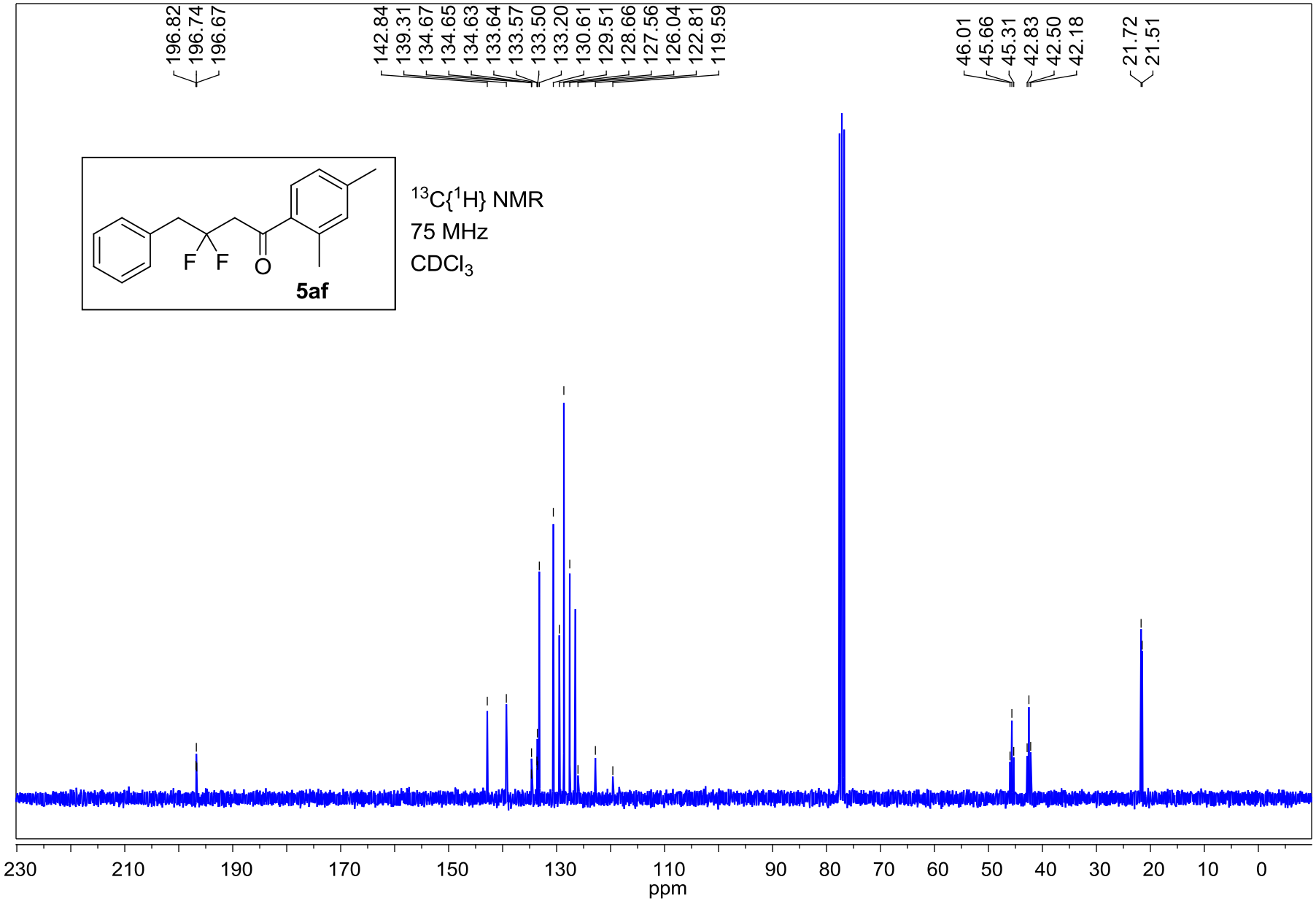
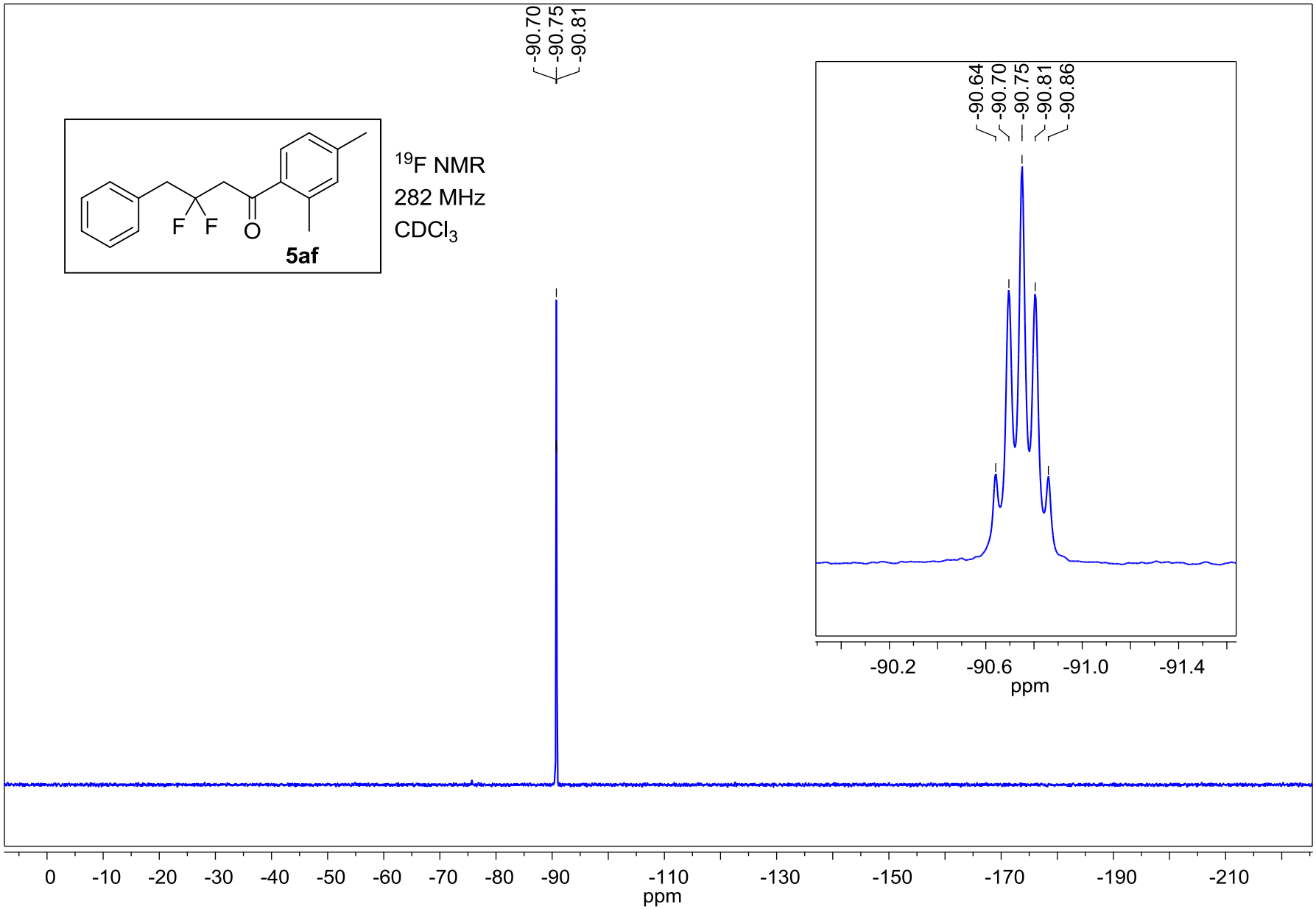
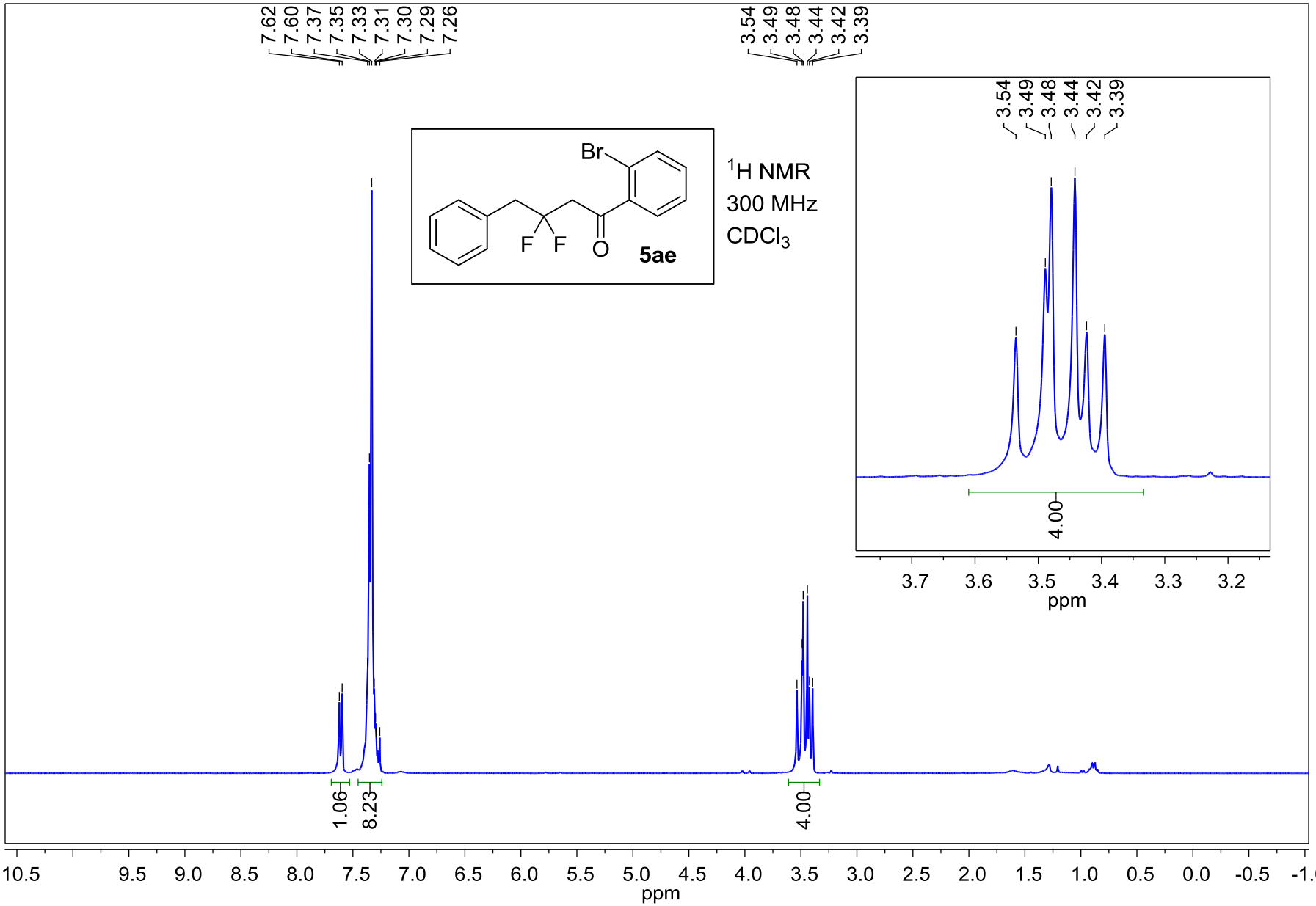
192.98
192.90
135.61
133.33
133.26
133.20
132.20
130.56
129.97
129.21
128.73
127.69
125.76
122.53
43.76
43.41
43.05
42.82
42.50
42.17
Br
F F O
5af
13C{1H} NMR
75 MHz
CDCl3
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
ppm

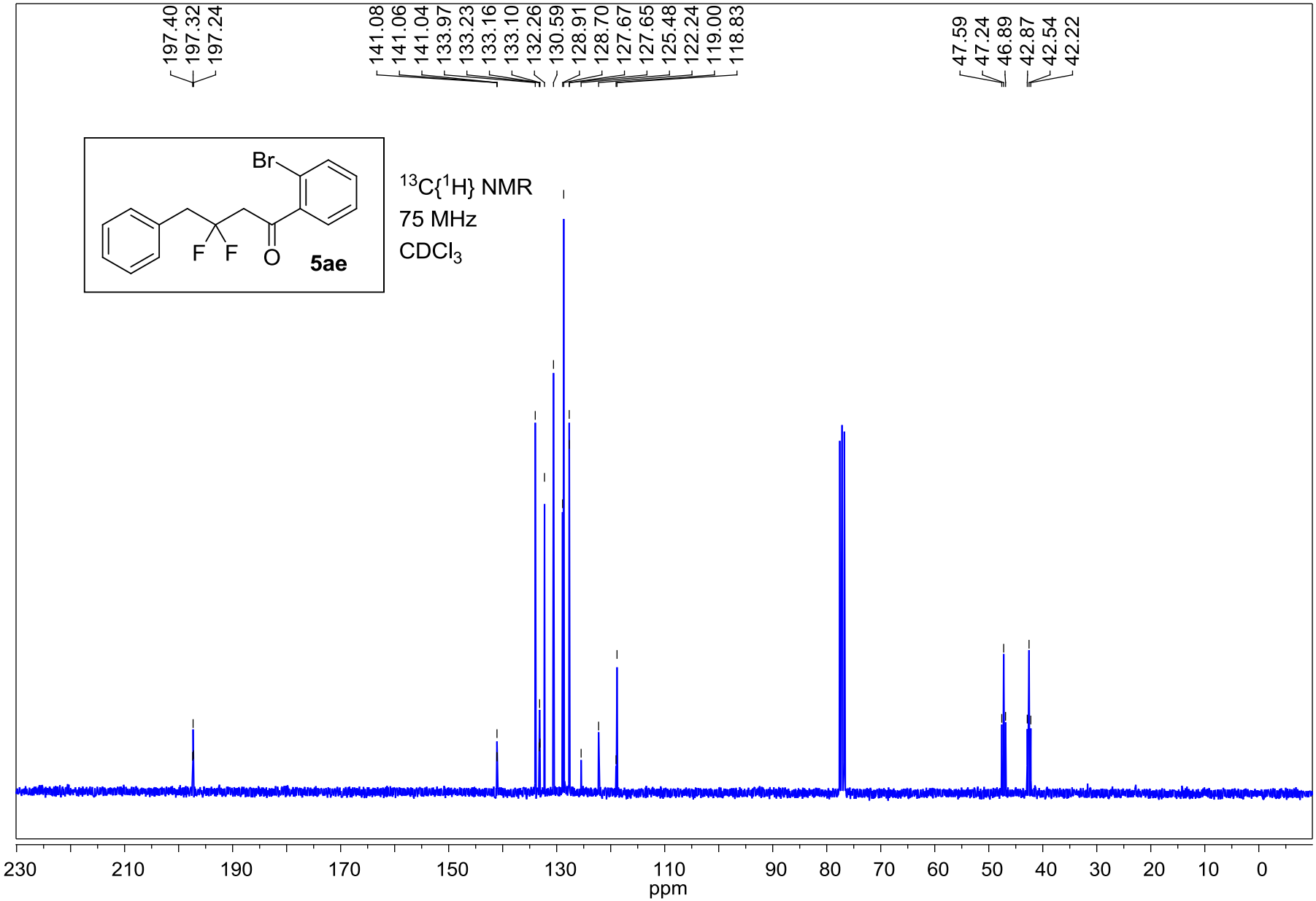

-90.61
-90.67
-90.72
-90.77
-90.83
Br
F F O
5ad
19F NMR
282 MHz
CDCl3
2.00
-90.4
-90.9
ppm
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
ppm

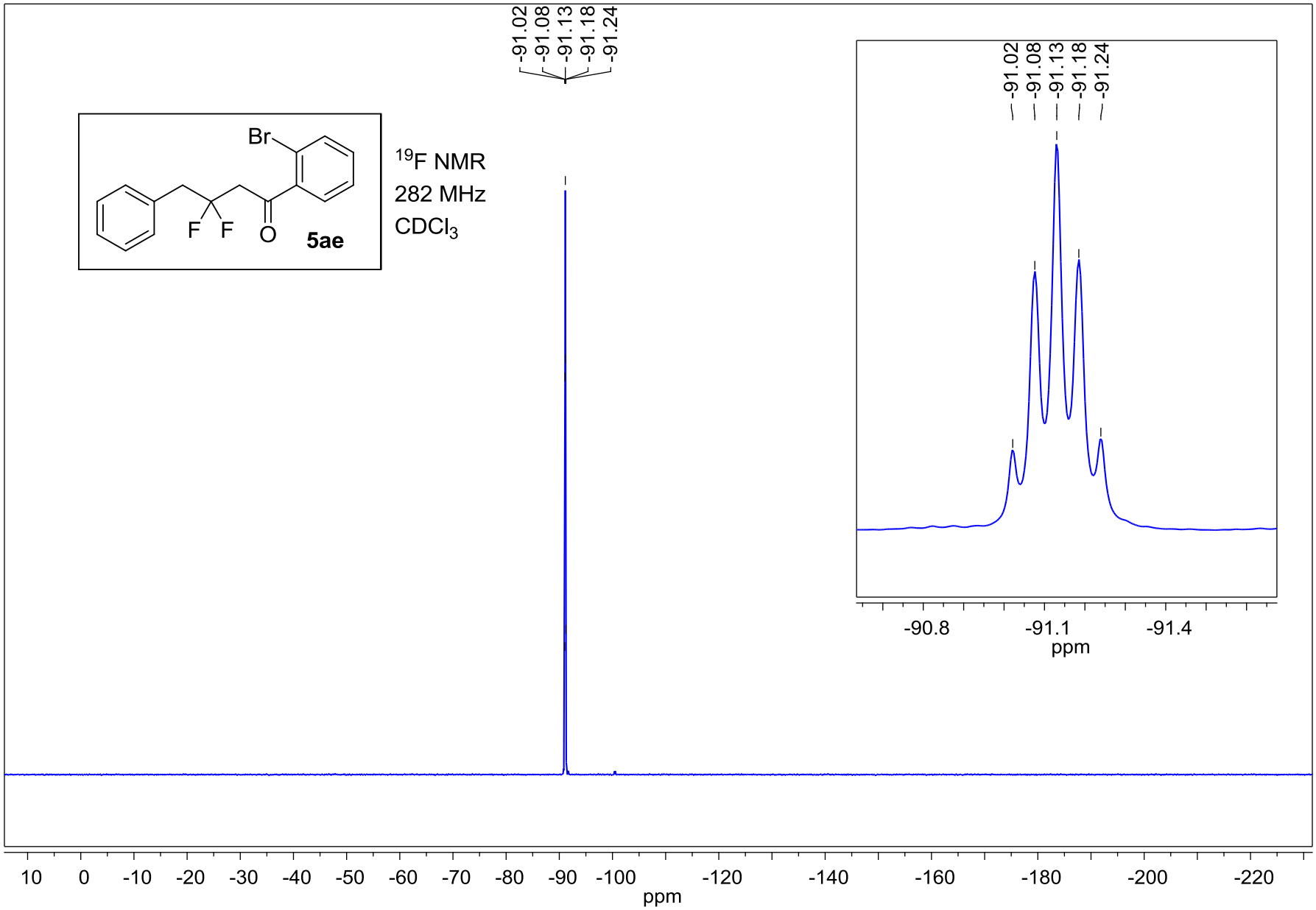

7.45
7.42
7.33
7.32
7.31
7.29
7.26
7.08
7.05
7.03
3.54
3.49
3.43
3.40
3.35
3.31
2.53
2.35
F F O
5af
1H NMR
300 MHz
CDCl3
1.03
5.11
1.06
1.02
2.08
2.00
3.11
3.08
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

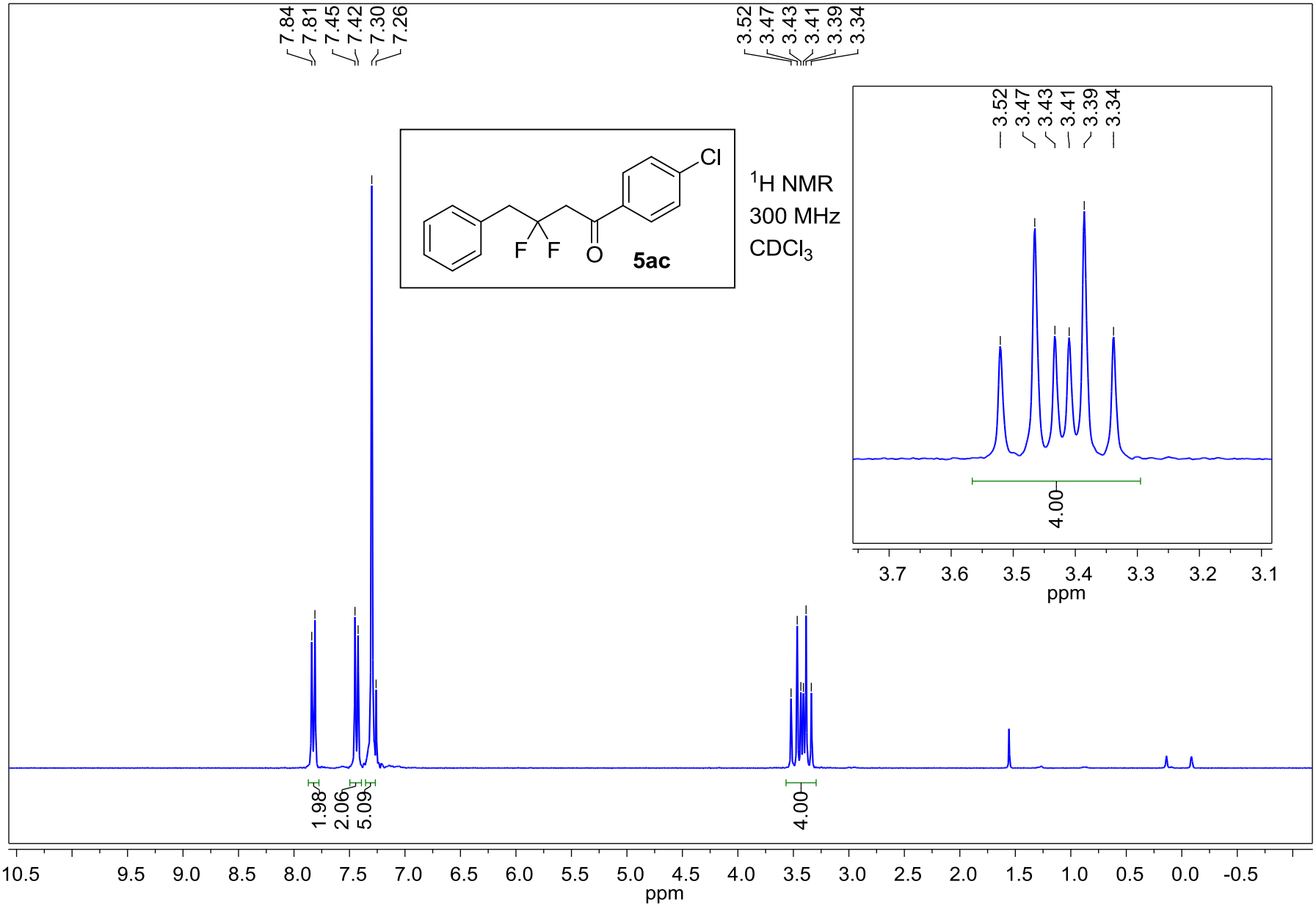

196.82
196.74
196.67
142.84
139.31
134.67
134.65
134.63
133.64
133.57
133.50
133.20
130.61
129.51
128.66
127.56
126.04
122.81
119.59
46.01
45.66
45.31
42.83
42.50
42.18
21.72
21.51
F
F
O
5af
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
ppm

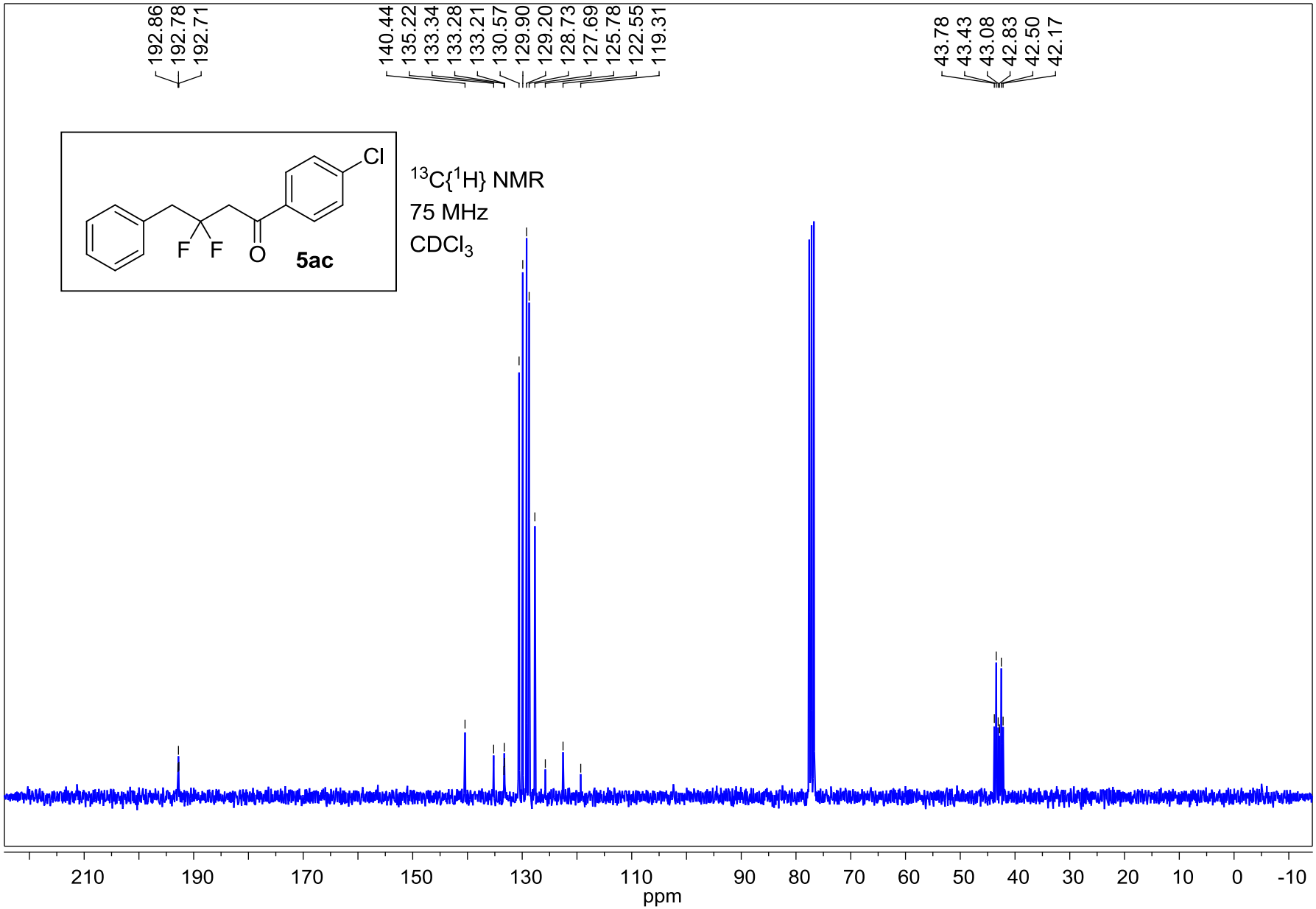

-90.70
-90.75
-90.81
F F O
5af
^{19}F NMR
282 MHz
$CDCl_3$
-90.64
-90.70
-90.75
-90.81
-90.86
-90.2
-90.6
-91.0
-91.4
ppm
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

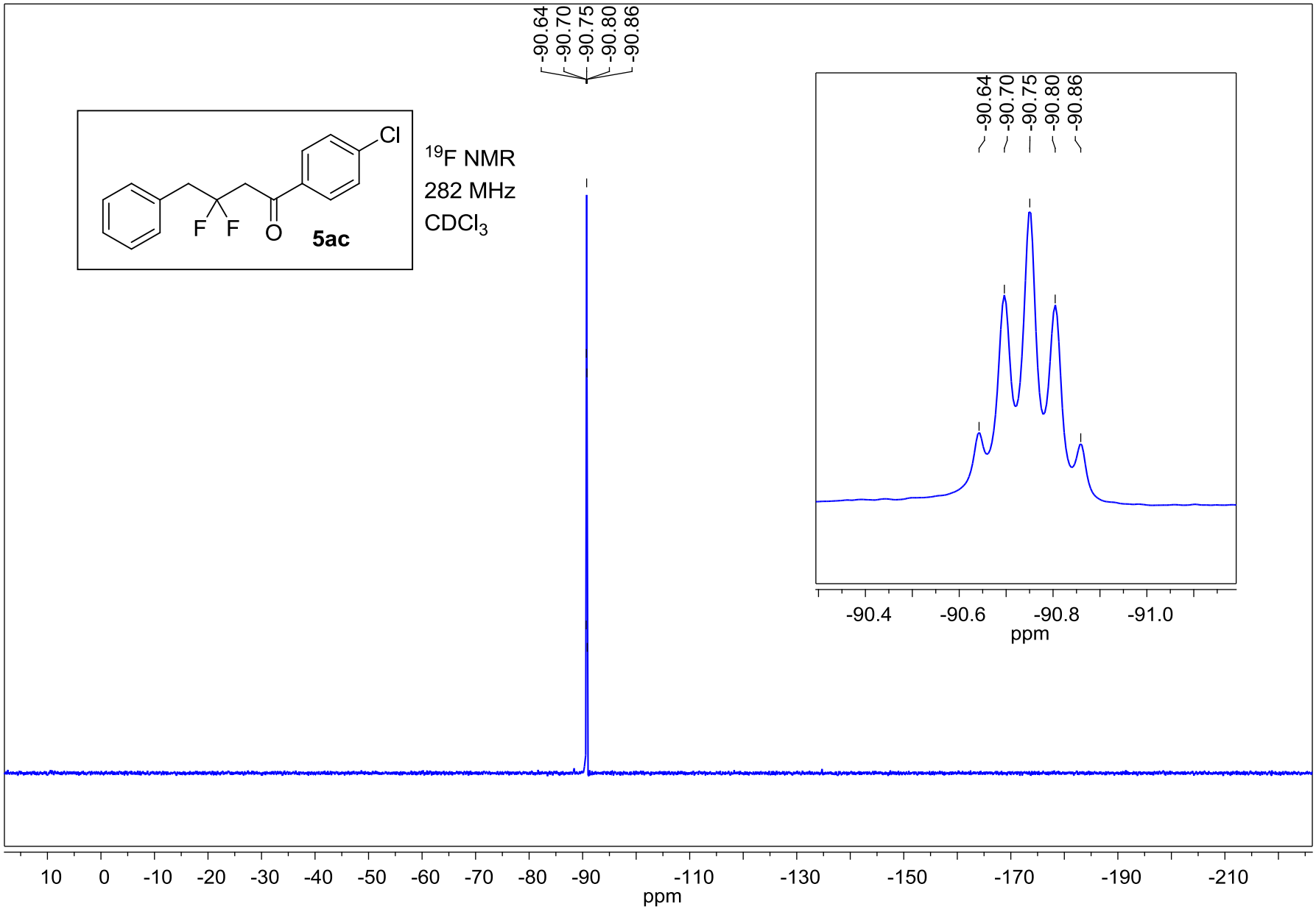

7.62
7.60
7.37
7.35
7.33
7.31
7.30
7.29
7.26
3.54
3.49
3.48
3.44
3.42
3.39
Br
F F O
5ae
1H NMR
300 MHz
CDCl3
1.06
8.23
4.00
4.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm
3.7 3.6 3.5 3.4 3.3 3.2
ppm

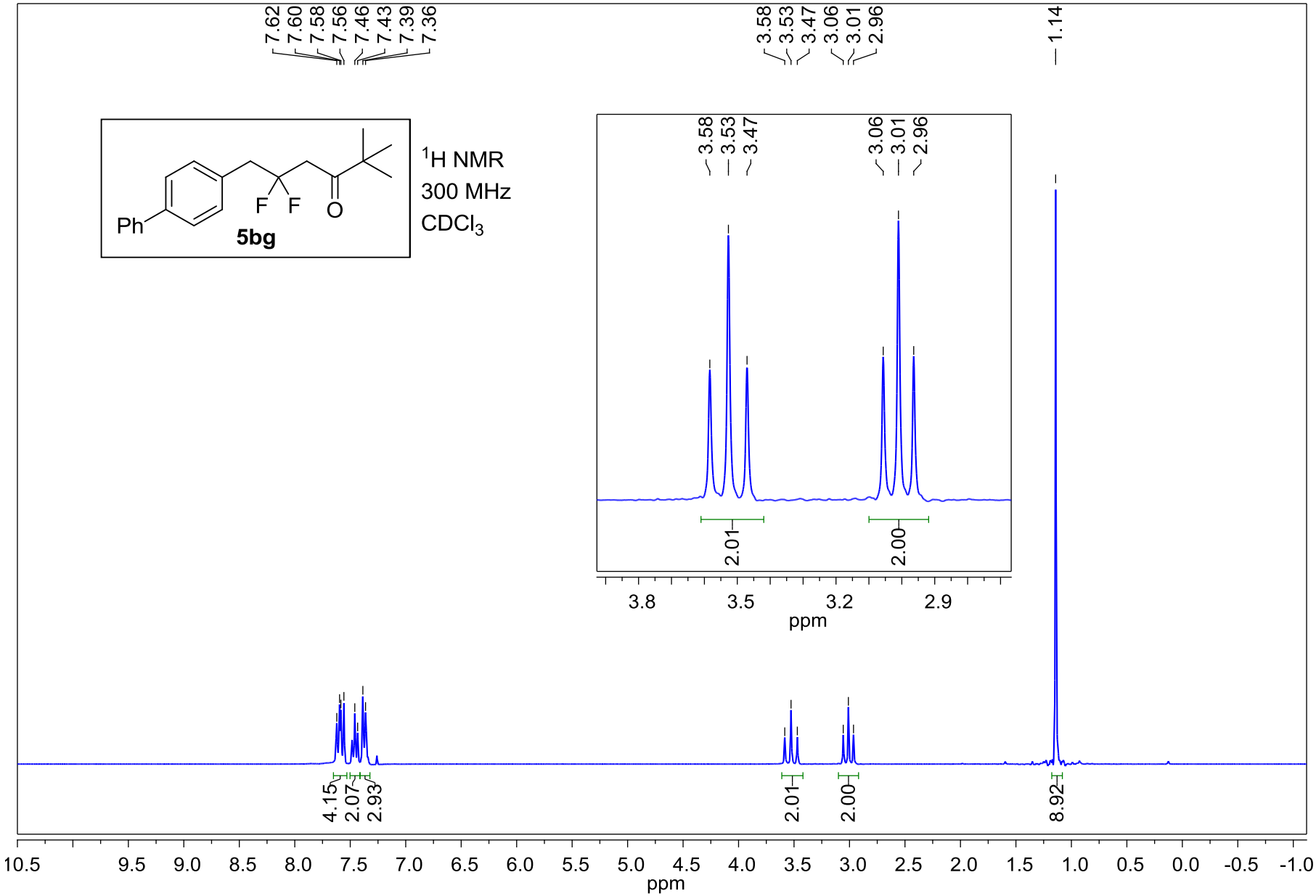

197.40
197.32
197.24
141.08
141.06
141.04
133.97
133.23
133.16
133.10
132.26
130.59
128.91
128.70
127.67
127.65
125.48
122.24
119.00
118.83
47.59
47.24
46.89
42.87
42.54
42.22
Br
F
F
O
5ae
13C{1H} NMR
75 MHz
CDCl3
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
ppm

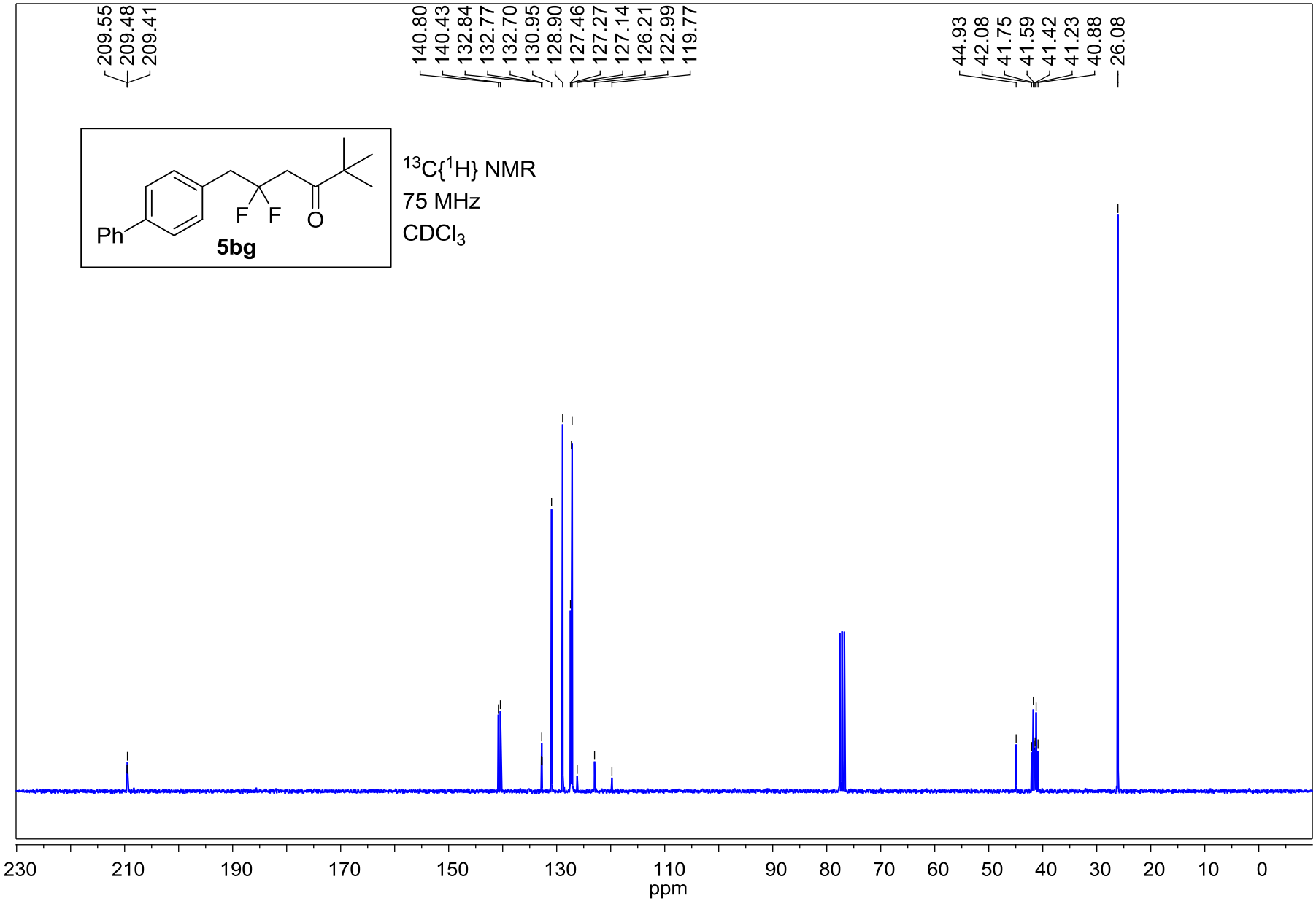

-91.02
-91.08
-91.13
-91.18
-91.24
Br
F F O
5ae
19F NMR
282 MHz
CDCl3
-90.8
-91.1
-91.4
ppm
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220
ppm

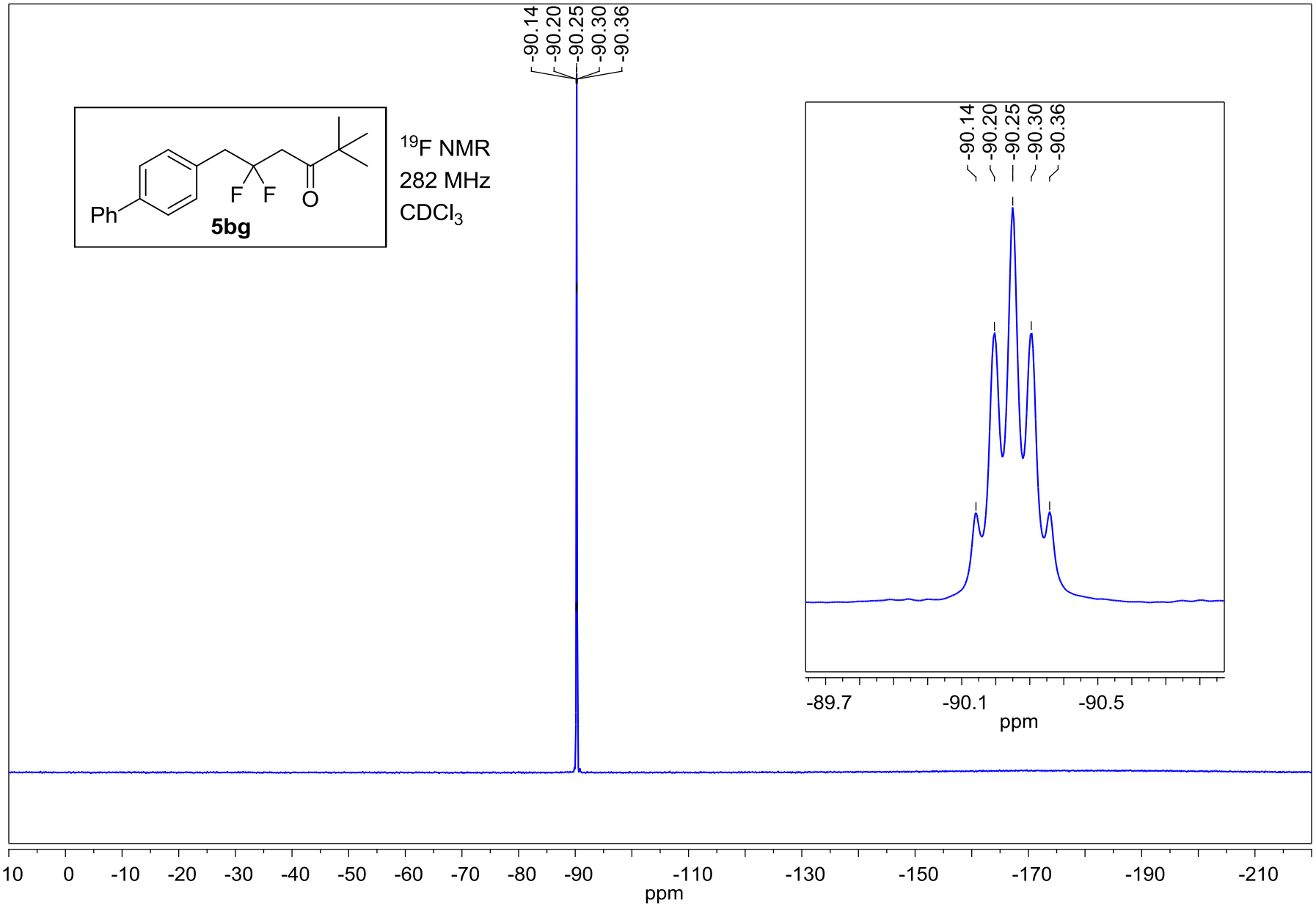

7.84
7.81
7.45
7.42
7.30
7.26
3.52
3.47
3.43
3.41
3.39
3.34
Cl
F F O
5ac
1H NMR
300 MHz
CDCl3
1.98
2.06
5.09
4.00
ppm
4.00
3.7 3.6 3.5 3.4 3.3 3.2 3.1
ppm
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

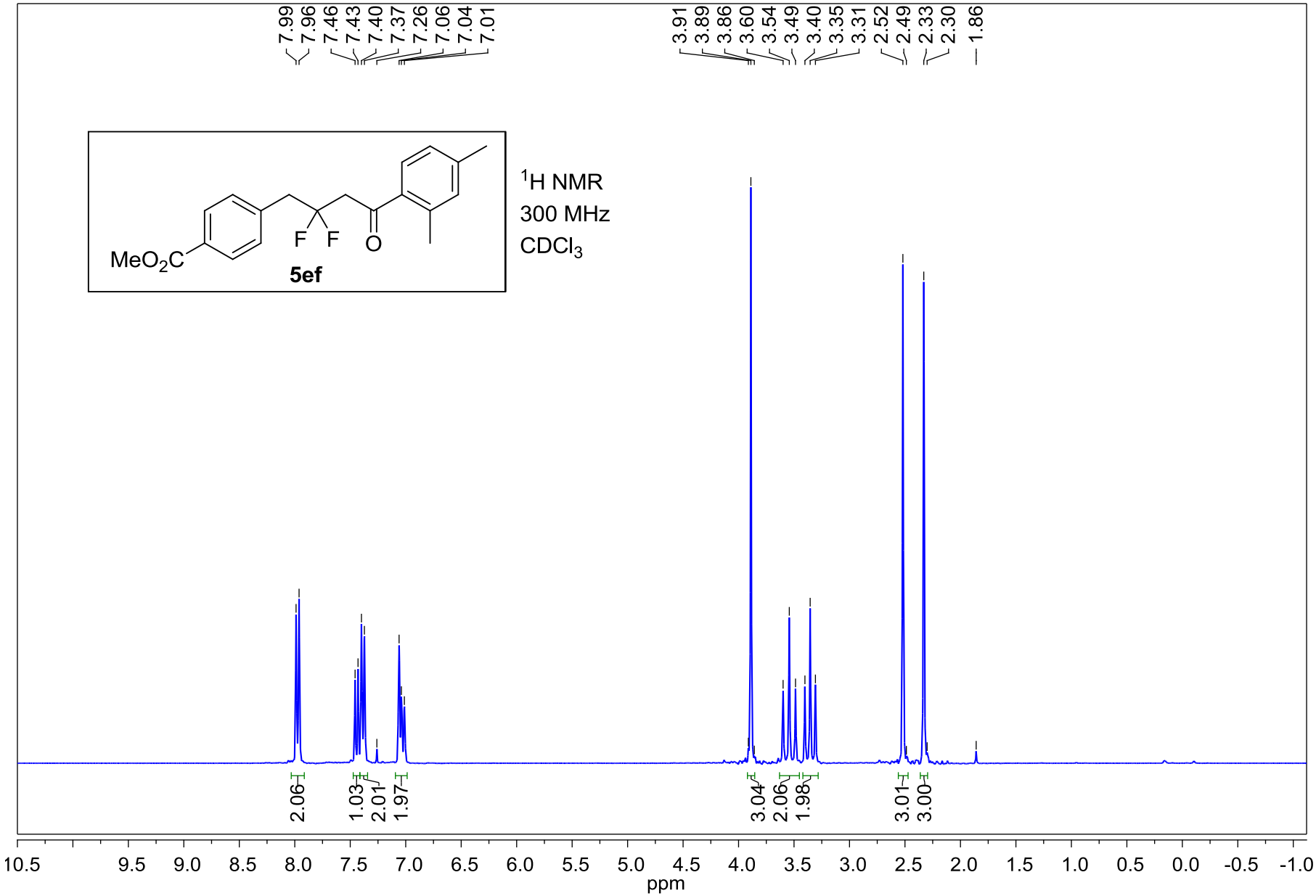

192.86
192.78
192.71
140.44
135.22
133.34
133.28
133.21
130.57
129.90
129.20
128.73
127.69
125.78
122.55
119.31
43.78
43.43
43.08
42.83
42.50
42.17
Cl
F F O
5ac
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

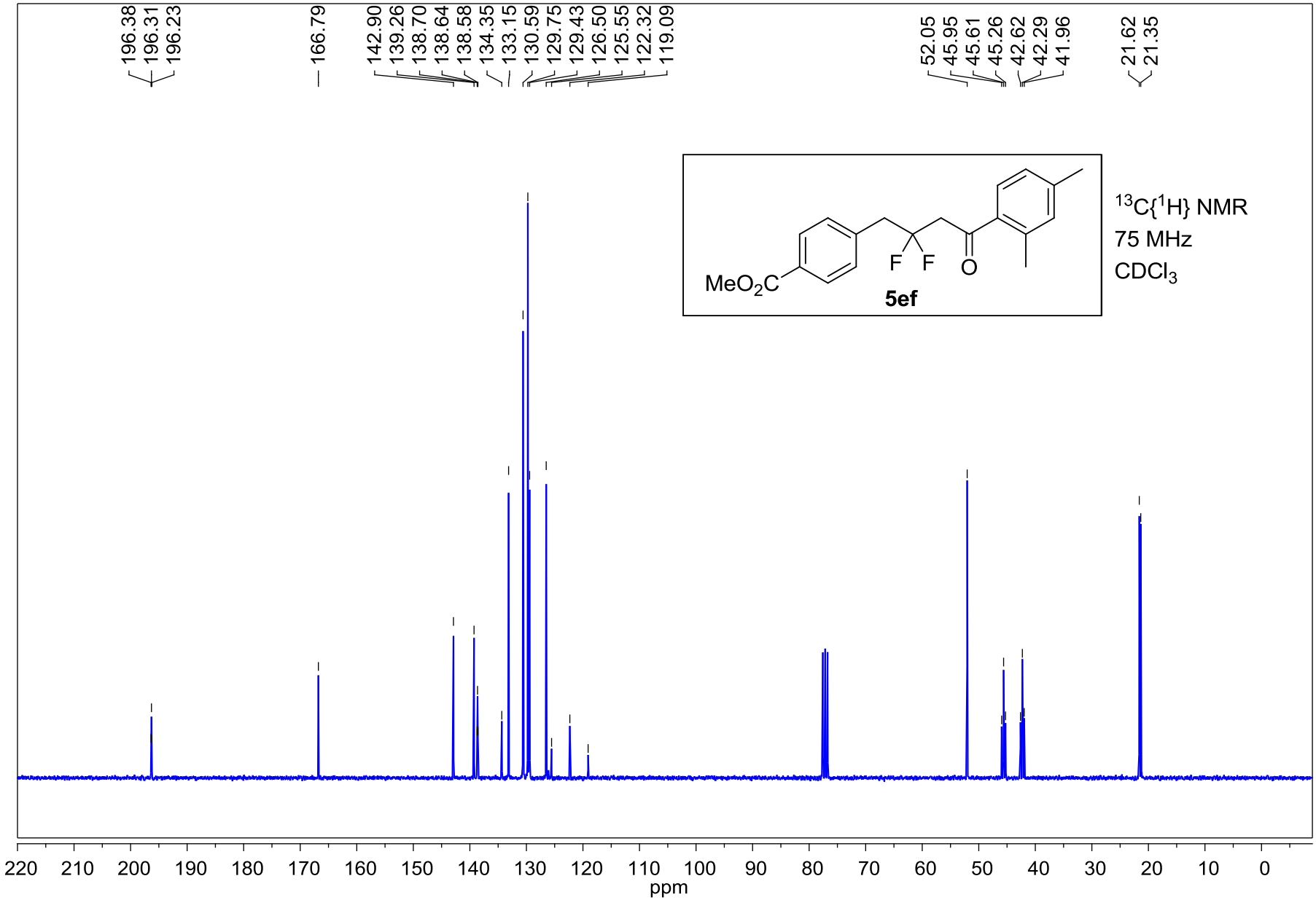

-90.64
-90.70
-90.75
-90.80
-90.86
Cl
F F O
5ac
19F NMR
282 MHz
CDCl3
-90.64
-90.70
-90.75
-90.80
-90.86
-90.4
-90.6
-90.8
-91.0
ppm
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
ppm

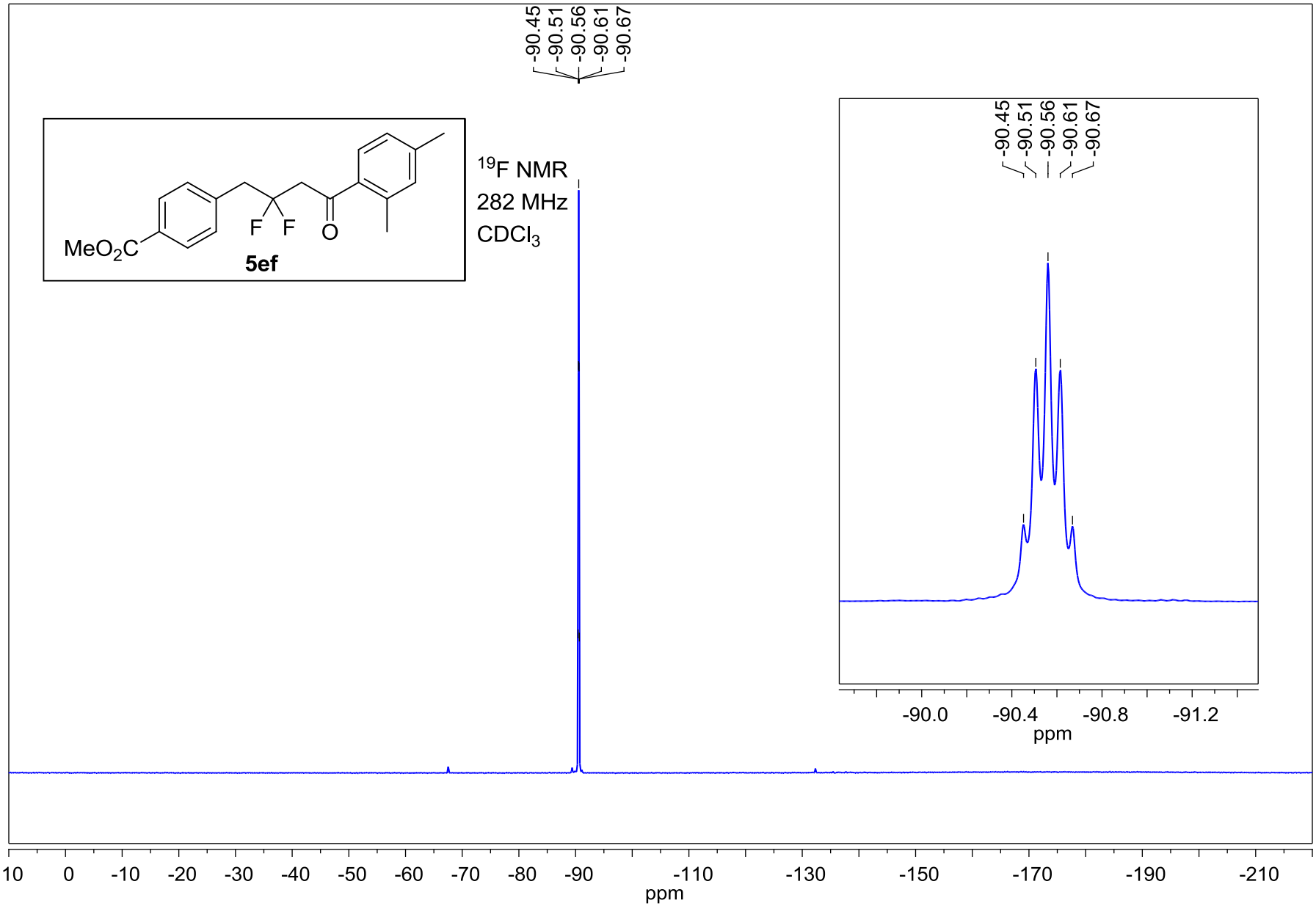

7.62
7.60
7.58
7.56
7.46
7.43
7.39
7.36
3.58
3.53
3.47
3.06
3.01
2.96
1.14
Ph
F
F
O
5bg
^{1}H NMR
300 MHz
$CDCl_3$
2.01
2.00
3.8
3.5
3.2
2.9
ppm
4.15
2.07
2.93
2.01
2.00
8.92
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

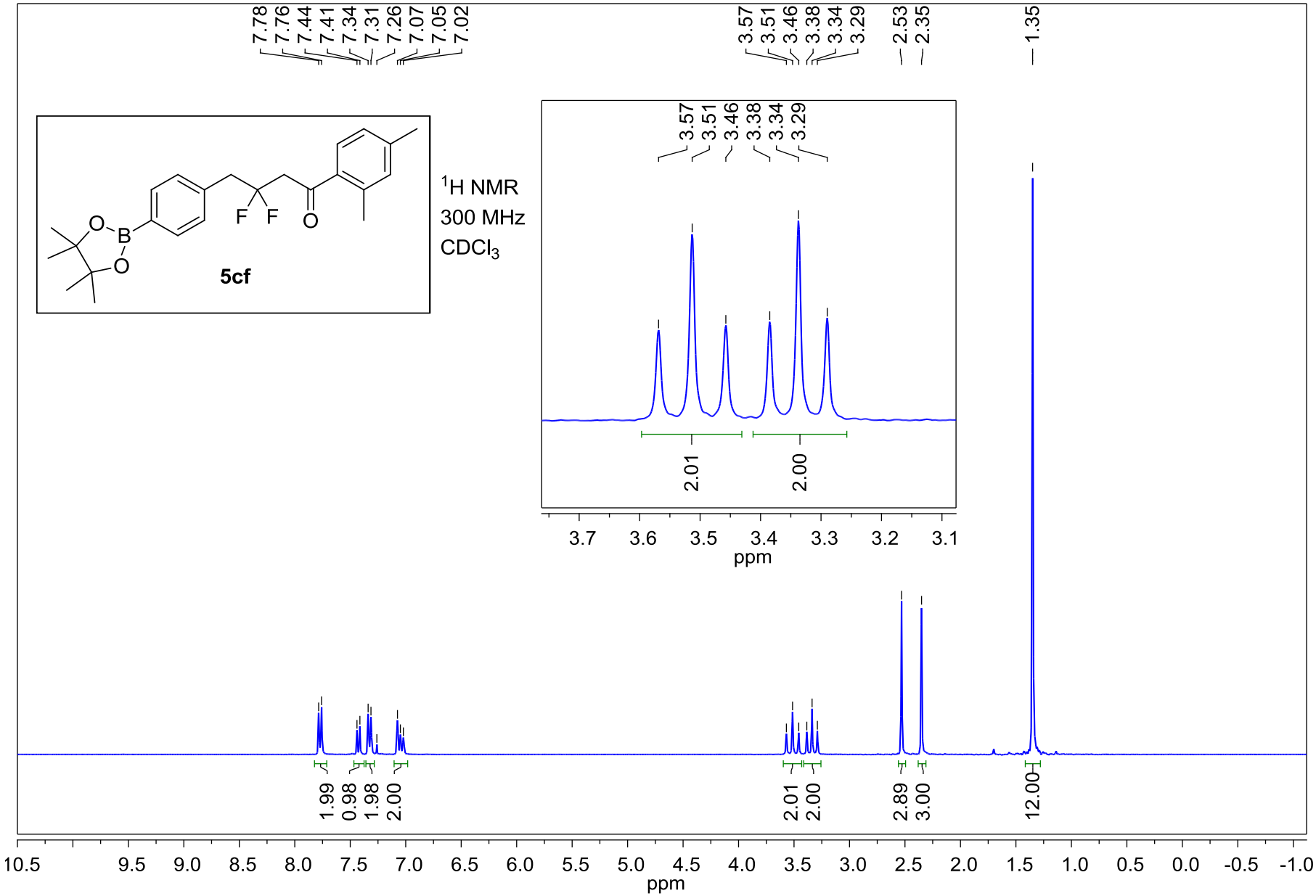

209.55
209.48
209.41
140.80
140.43
132.84
132.77
132.70
130.95
128.90
127.46
127.27
127.14
126.21
122.99
119.77
44.93
42.08
41.75
41.59
41.42
41.23
40.88
26.08
Ph
F
F
O
5bg
13C{1H} NMR
75 MHz
CDCl3
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
ppm

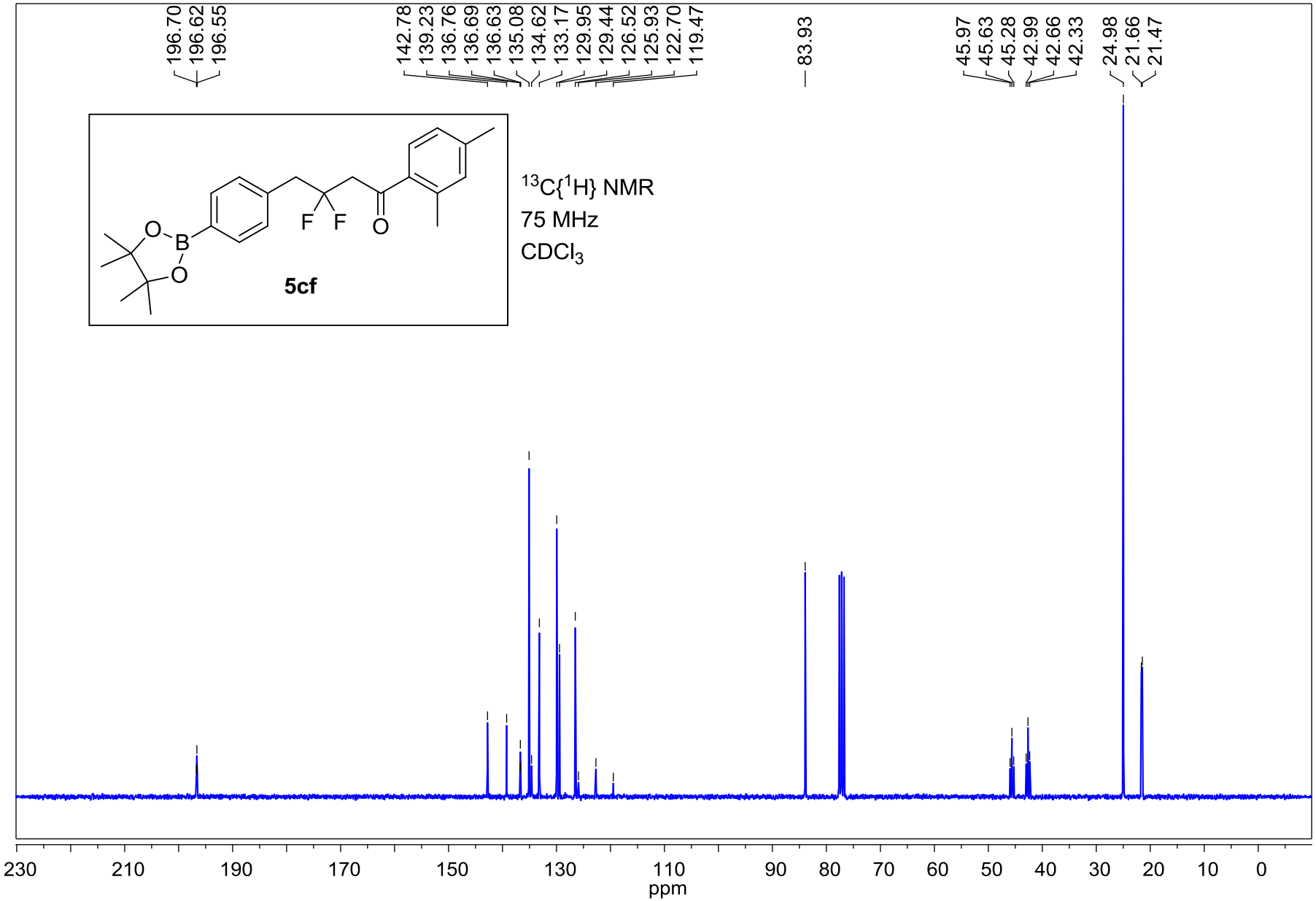

-90.14
-90.20
-90.25
-90.30
-90.36
Ph
F
F
O
5bg
19F NMR
282 MHz
CDCl3
-89.7
-90.1
-90.5
ppm
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

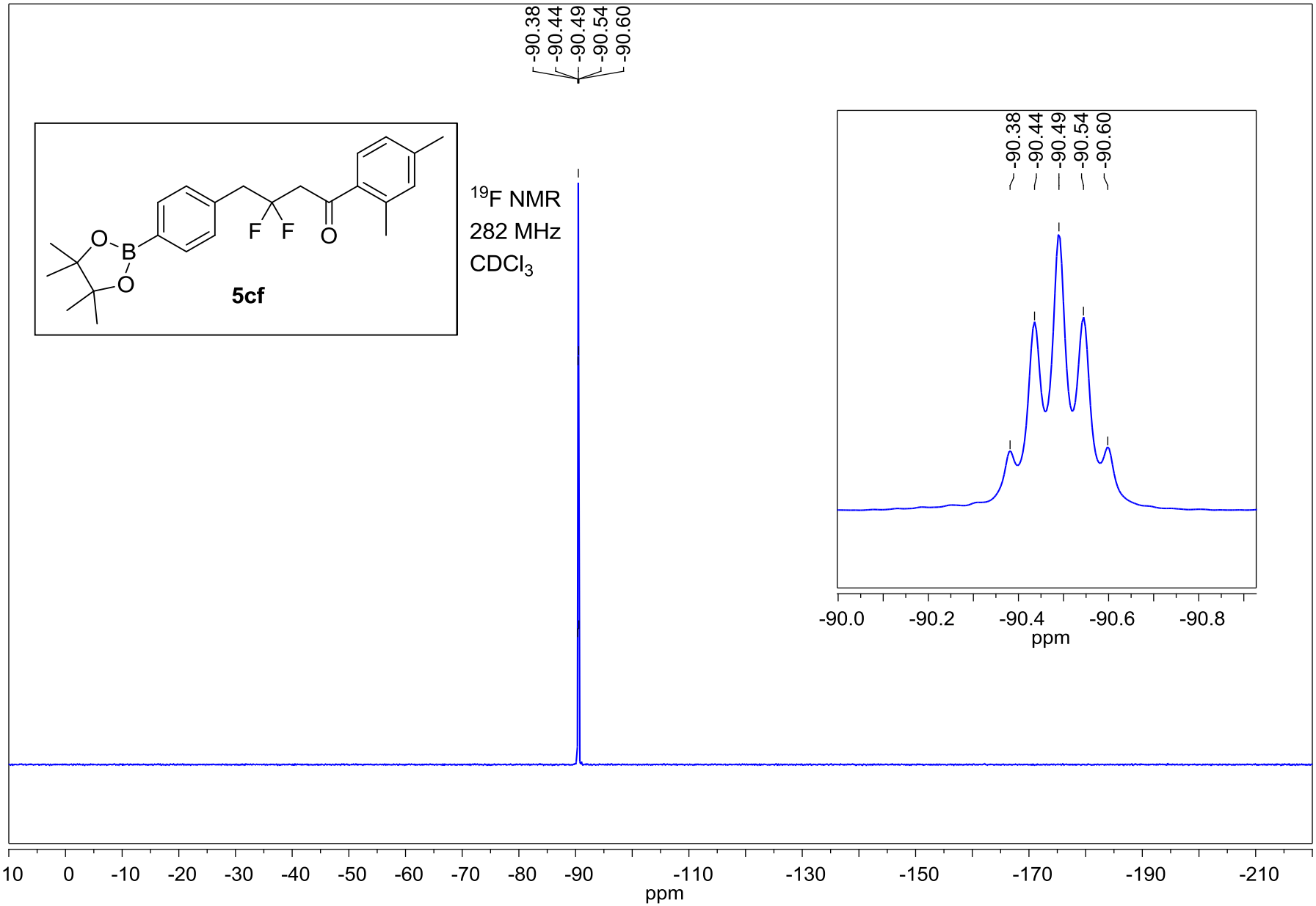

7.99
7.96
7.46
7.43
7.40
7.37
7.26
7.06
7.04
7.01
3.91
3.89
3.86
3.60
3.54
3.49
3.40
3.35
3.31
2.52
2.49
2.33
2.30
1.86
MeO2C
F F
O
5ef
1H NMR
300 MHz
CDCl3
2.06
1.03
2.01
1.97
3.04
2.06
1.98
3.01
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

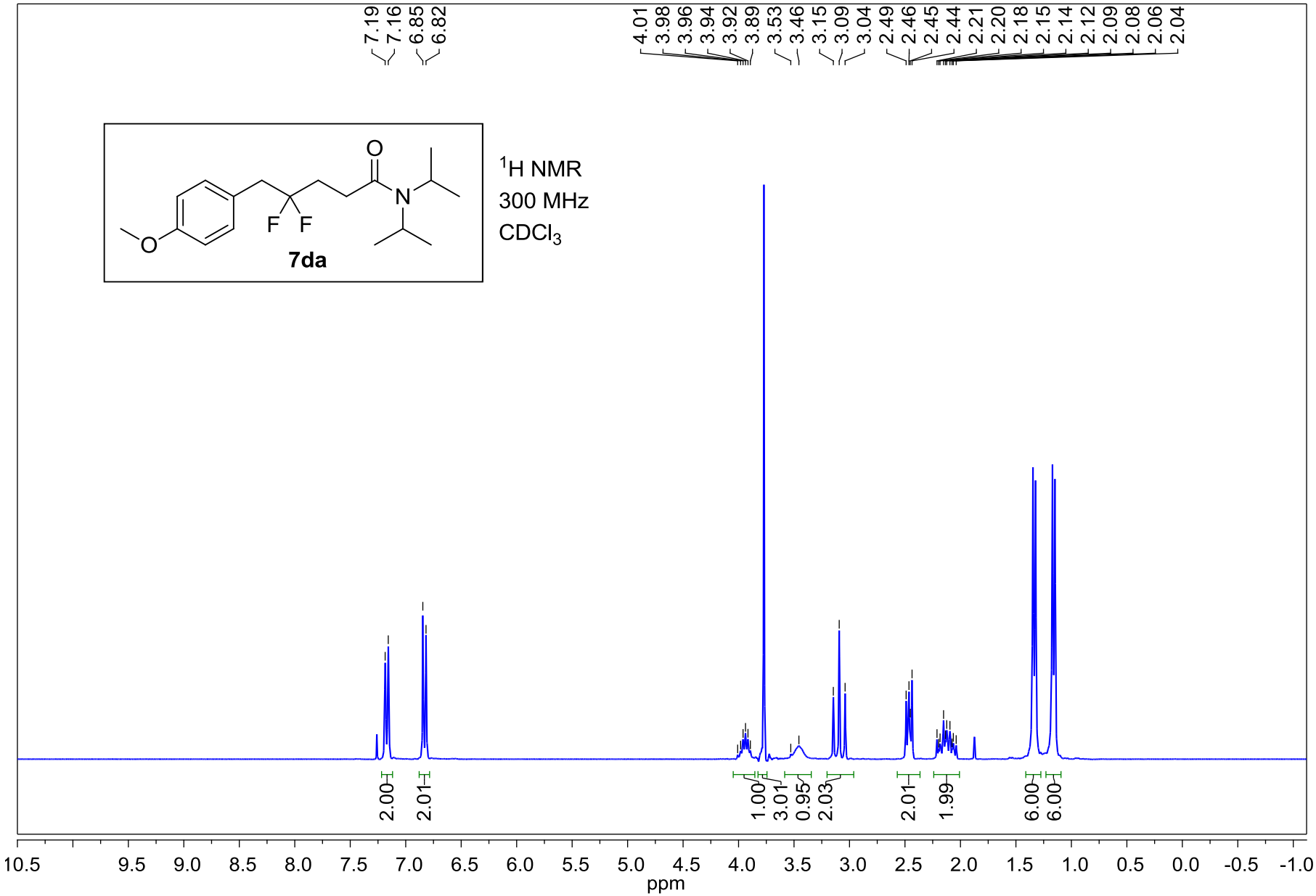

196.38
196.31
196.23
166.79
142.90
139.26
138.70
138.64
138.58
134.35
133.15
130.59
129.75
129.43
126.50
125.55
122.32
119.09
52.05
45.95
45.61
45.26
42.62
42.29
41.96
21.62
21.35
MeO2C
F F
O
5ef
13C{1H} NMR
75 MHz
CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

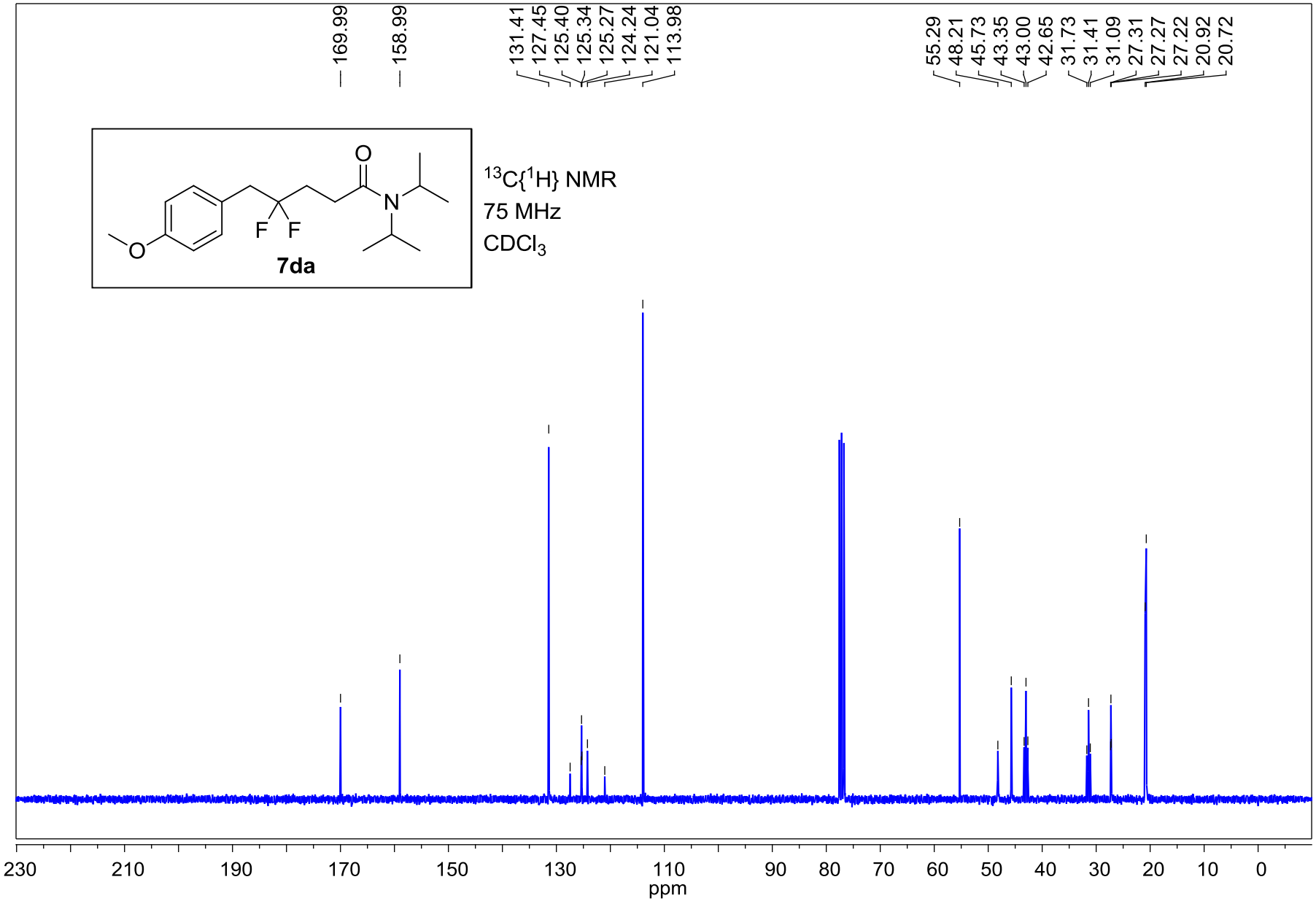

-90.45
-90.51
-90.56
-90.61
-90.67
MeO2C
F F
O
5ef
19F NMR
282 MHz
CDCl3
-90.45
-90.51
-90.56
-90.61
-90.67
-90.0
-90.4
-90.8
-91.2
ppm
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

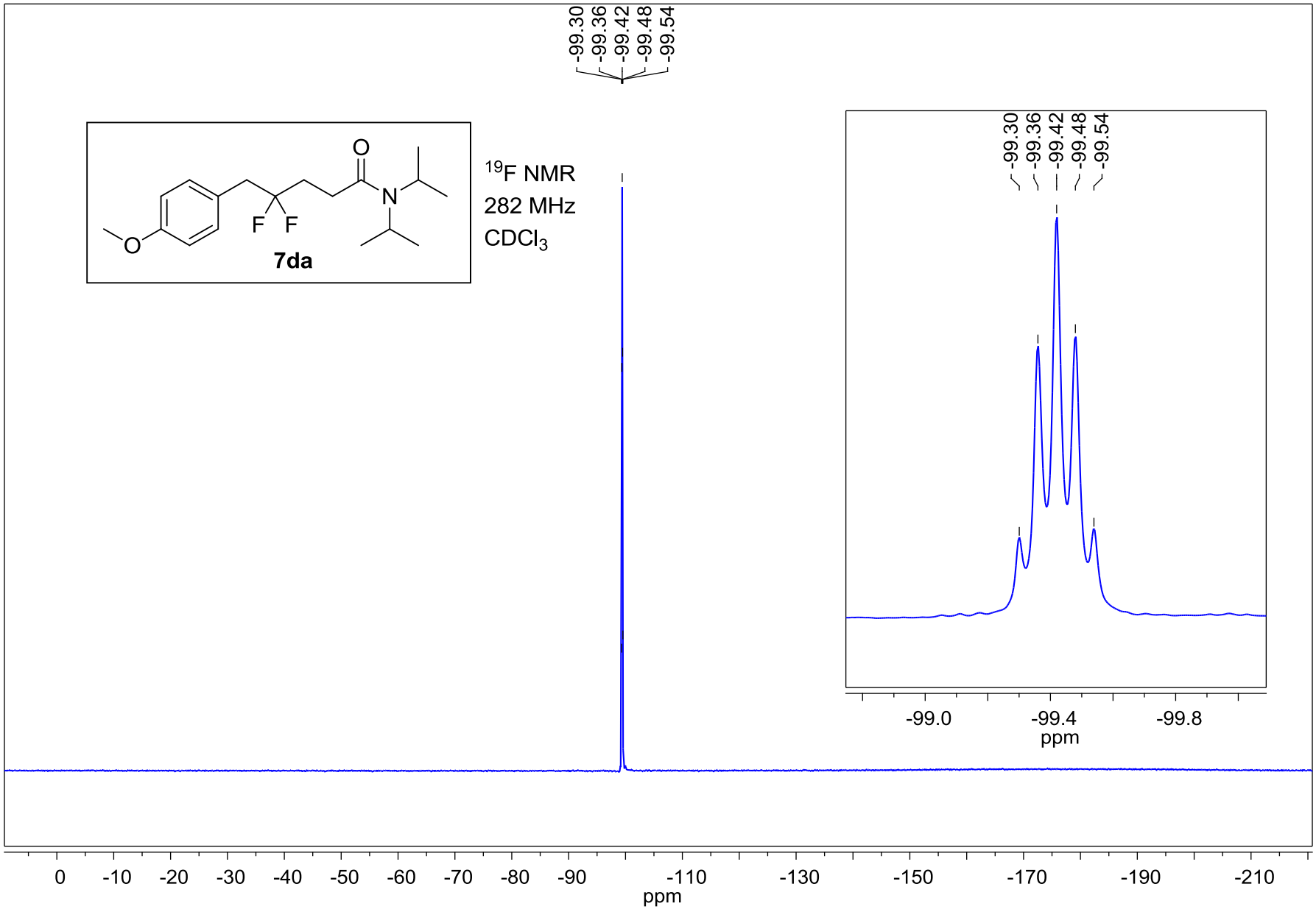

7.78
7.76
7.44
7.41
7.34
7.31
7.26
7.07
7.05
7.02
3.57
3.51
3.46
3.38
3.34
3.29
2.53
2.35
1.35
5cf
^{1}H NMR
300 MHz
$CDCl_3$
2.01
2.00
ppm
1.99
0.98
1.98
2.00
2.01
2.00
2.89
3.00
12.00
ppm

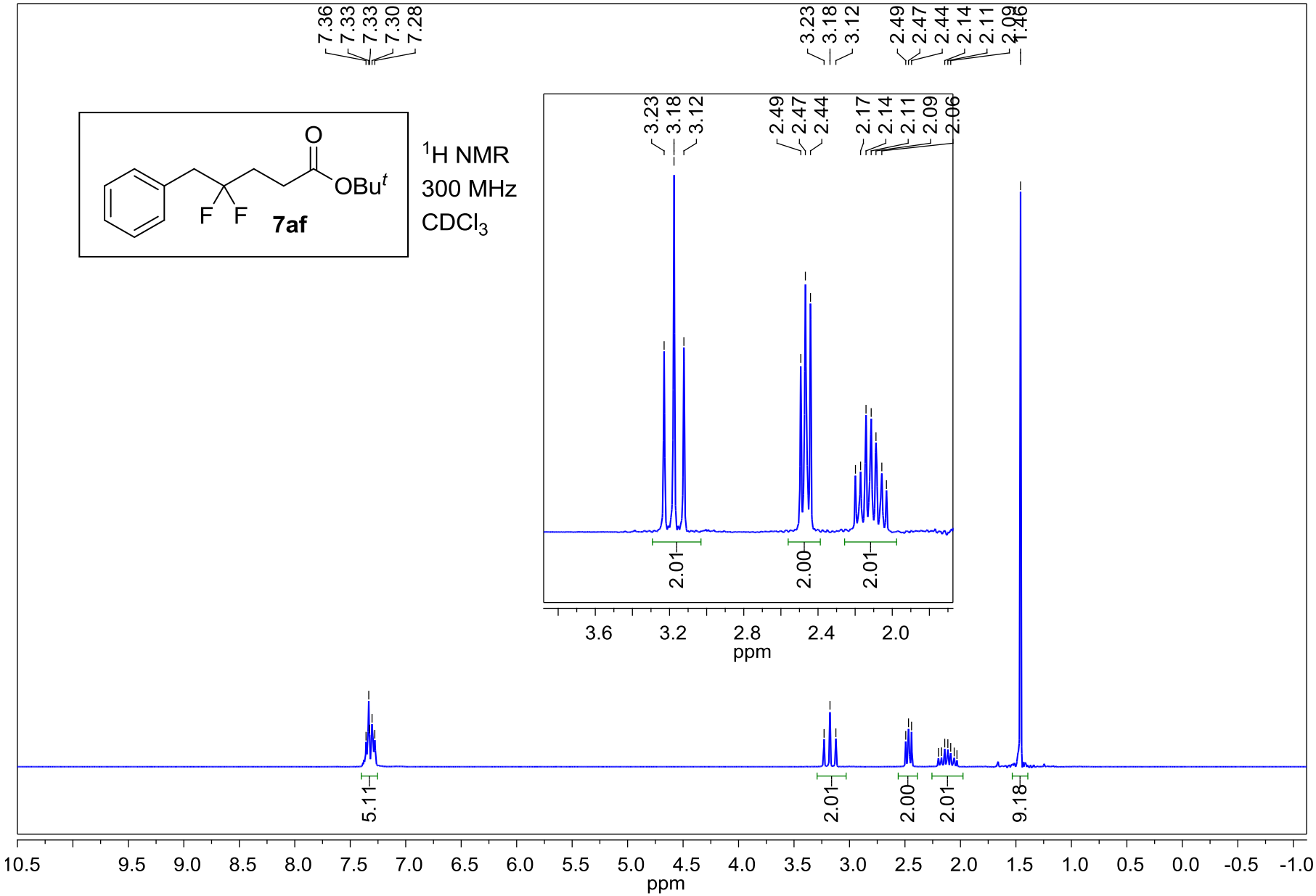

196.70
196.62
196.55
142.78
139.23
136.76
136.69
136.63
135.08
134.62
133.17
129.95
129.44
126.52
125.93
122.70
119.47
83.93
45.97
45.63
45.28
42.99
42.66
42.33
24.98
21.66
21.47
F F O
O B O
5cf
13C{1H} NMR
75 MHz
CDCl3
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
ppm

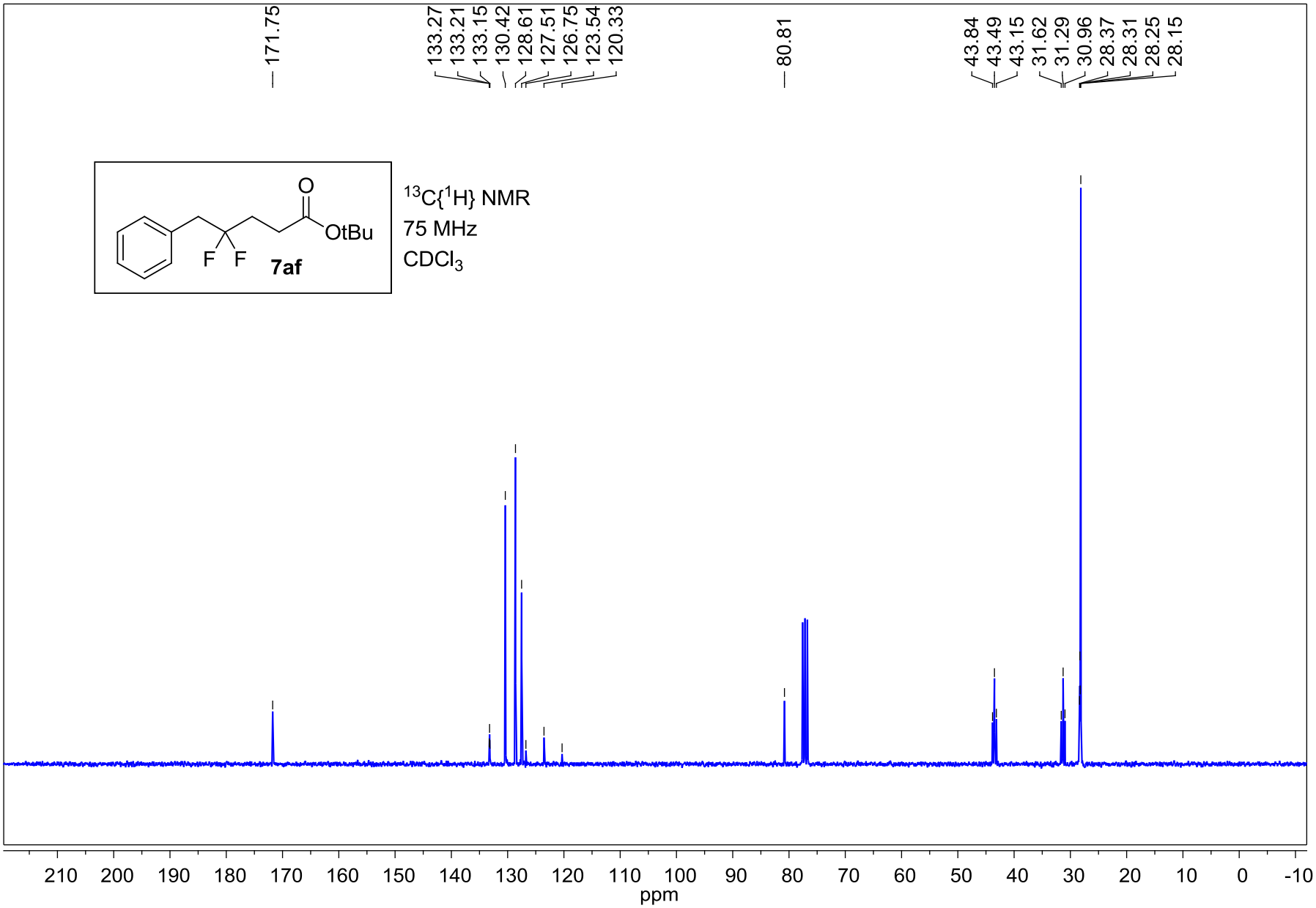

-90.38
-90.44
-90.49
-90.54
-90.60
5cf
^{19}F NMR
282 MHz
$CDCl_3$
-90.0
-90.2
-90.4
-90.6
-90.8
ppm
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

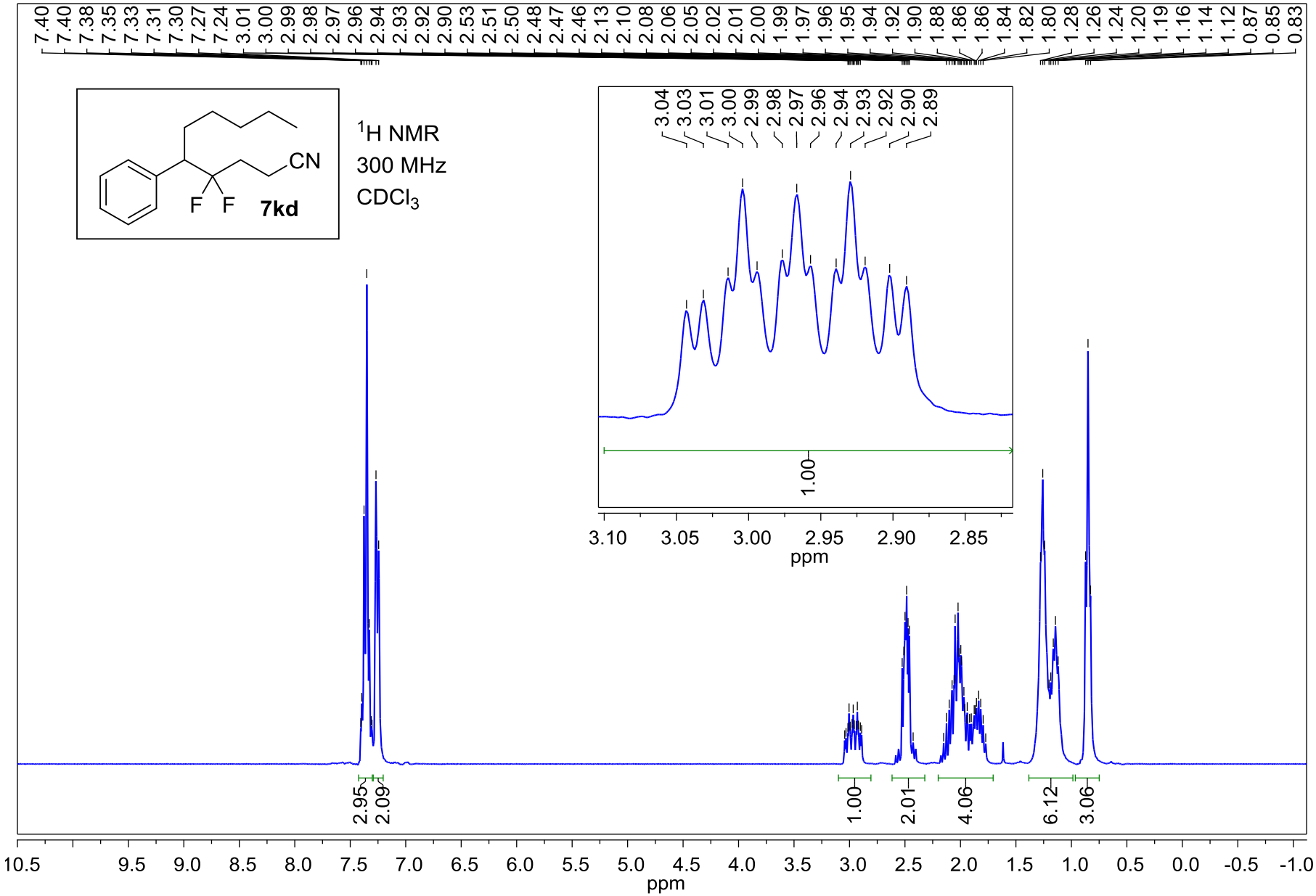

7.19
7.16
6.85
6.82
4.01
3.98
3.96
3.94
3.92
3.89
3.53
3.46
3.15
3.09
3.04
2.49
2.46
2.45
2.44
2.21
2.20
2.18
2.15
2.14
2.12
2.09
2.08
2.06
2.04
O
N
F F
O
7da
1H NMR
300 MHz
CDCl3
2.00
2.01
1.00
3.01
0.95
2.03
2.01
1.99
6.00
6.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

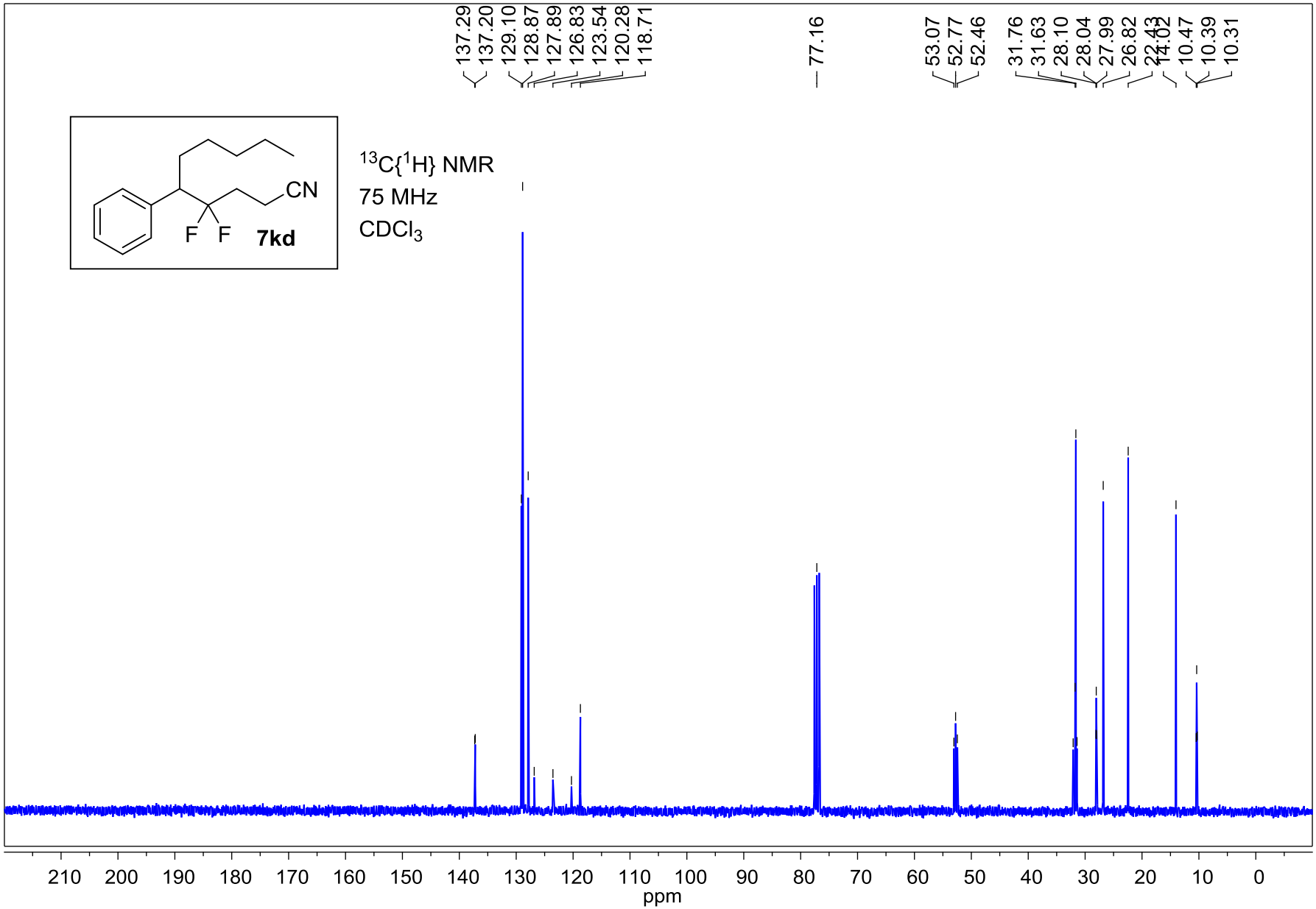

169.99
158.99
131.41
127.45
125.40
125.34
125.27
124.24
121.04
113.98
55.29
48.21
45.73
43.35
43.00
42.65
31.73
31.41
31.09
27.31
27.27
27.22
20.92
20.72
O
N
F F
O
7da
13C{1H} NMR
75 MHz
CDCl3
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
ppm

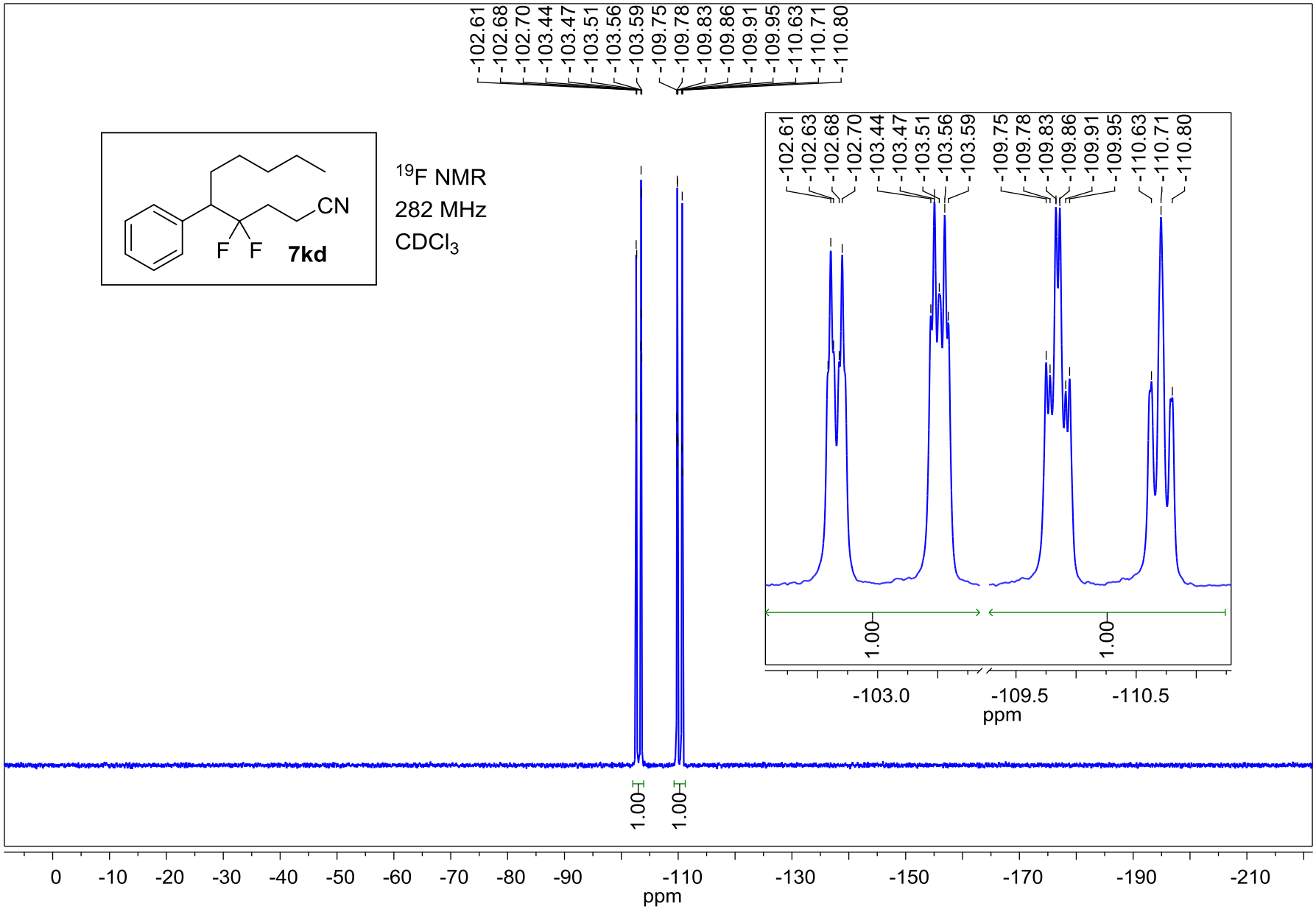

-99.30
-99.36
-99.42
-99.48
-99.54
O
N
F F
O
7da
^{19}F NMR
282 MHz
$CDCl_3$
-99.30
-99.36
-99.42
-99.48
-99.54
-99.0
-99.4
-99.8
ppm
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

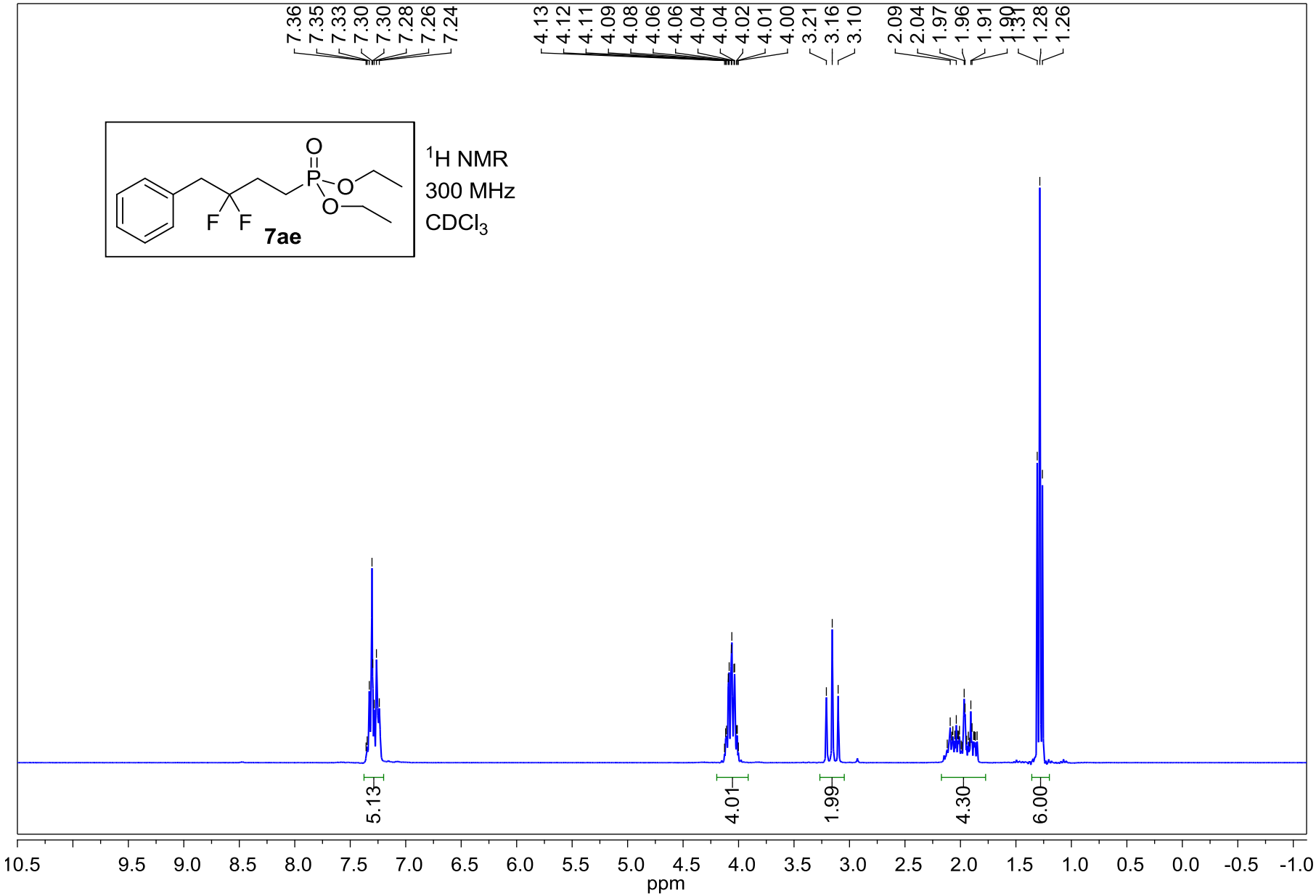

7.36
7.33
7.33
7.30
7.28
3.23
3.18
3.12
2.49
2.47
2.44
2.14
2.11
2.09
1.46
O
OBu^t
F F
7af
^{1}H NMR
300 MHz
$CDCl_3$
2.17
2.06
2.01
2.00
2.01
3.6
3.2
2.8
2.4
2.0
ppm
5.11
2.01
2.00
2.01
9.18
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm


171.75
133.27
133.21
133.15
130.42
128.61
127.51
126.75
123.54
120.33
80.81
43.84
43.49
43.15
31.62
31.29
30.96
28.37
28.31
28.25
28.15
O
OtBu
F F
7af
13C{1H} NMR
75 MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


7.40 7.40 7.38 7.35 7.33 7.31 7.30 7.27 7.24 3.01 3.00 2.99 2.98 2.97 2.96 2.94 2.93 2.92 2.90 2.53 2.51 2.50 2.48 2.47 2.46 2.13 2.10 2.08 2.06 2.05 2.02 2.01 2.00 1.99 1.97 1.96 1.95 1.94 1.92 1.90 1.88 1.86 1.86 1.84 1.82 1.80 1.28 1.26 1.24 1.20 1.19 1.16 1.14 1.12 0.87 0.85 0.83
CN
F F
7kd
1H NMR
300 MHz
CDCl3
3.04 3.03 3.01 3.00 2.99 2.98 2.97 2.96 2.94 2.93 2.92 2.90 2.89
1.00
3.10 3.05 3.00 2.95 2.90 2.85
ppm
2.95 2.09 1.00 2.01 4.06 6.12 3.06
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


137.29
137.20
129.10
128.87
127.89
126.83
123.54
120.28
118.71
77.16
53.07
52.77
52.46
31.76
31.63
28.10
28.04
27.99
26.82
22.43
14.02
10.47
10.39
10.31
CN
F F
7kd
13C{1H} NMR
75 MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


-102.61
-102.68
-102.70
-103.44
-103.47
-103.51
-103.56
-103.59
-109.75
-109.78
-109.83
-109.86
-109.91
-109.95
-110.63
-110.71
-110.80
CN
F F
7kd
19F NMR
282 MHz
CDCl3
-102.63
1.00
1.00
-103.0
-109.5
-110.5
ppm
1.00
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm


7.36
7.35
7.33
7.30
7.30
7.28
7.26
7.24
4.13
4.12
4.11
4.09
4.08
4.06
4.06
4.04
4.04
4.02
4.01
4.00
3.21
3.16
3.10
2.09
2.04
1.97
1.96
1.91
1.90
1.31
1.28
1.26
O
P
O
O
F
F
7ae
1H NMR
300 MHz
CDCl3
5.13
4.01
1.99
4.30
6.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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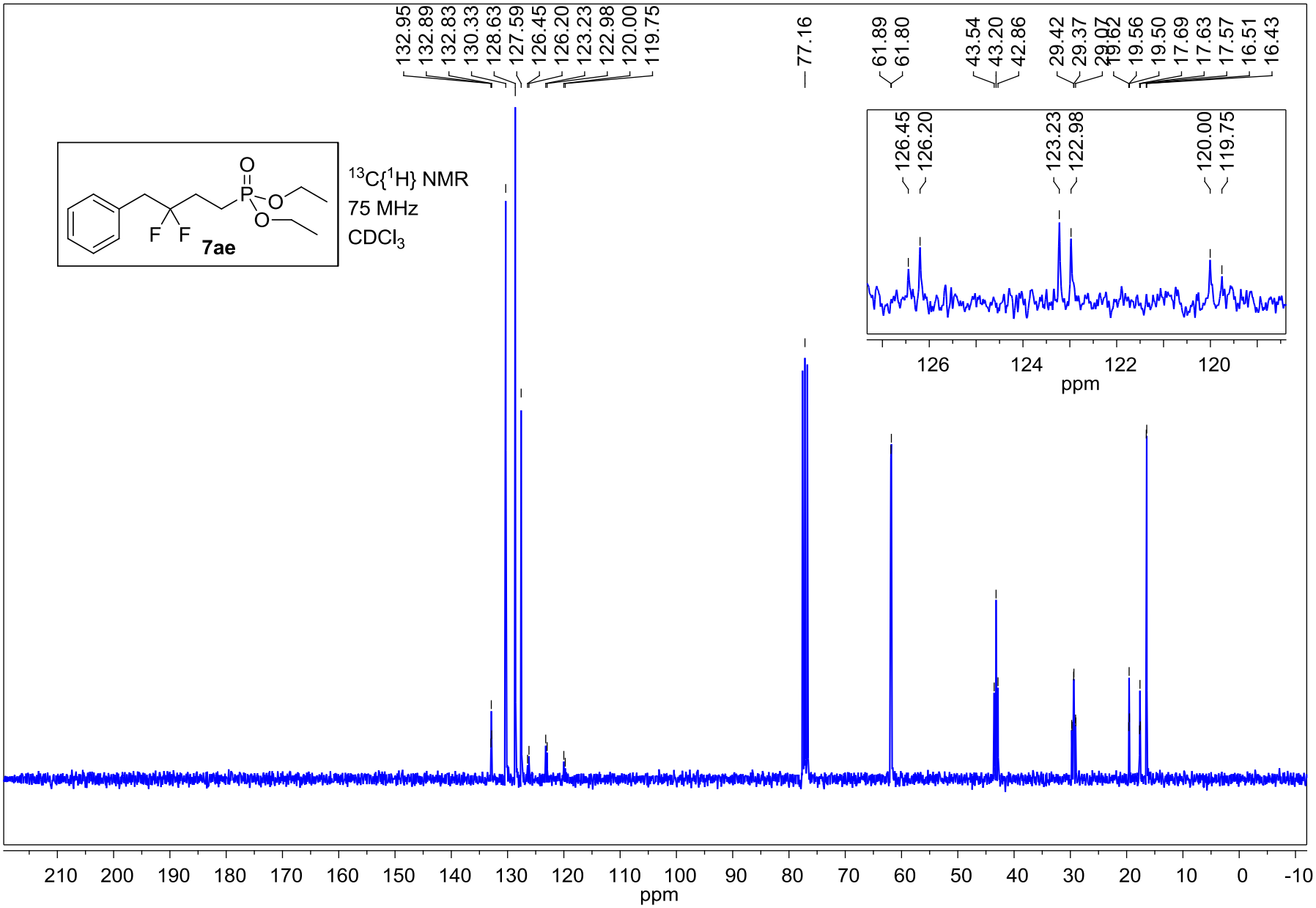
ppm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77.16
61.89
61.80
43.54
43.20
42.86
29.42
29.37
19.62
19.56
19.50
17.69
17.63
17.57
16.51
16.43
126.45
126.20
123.23
122.98
120.00
119.75
126
124
122
120
ppm
O
P
O
O
F
F
7ae
13C{1H} NMR
75 MHz
CDCl3
210
200
190
180
170
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150
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130
120
110
100
90
80
70
60
50
40
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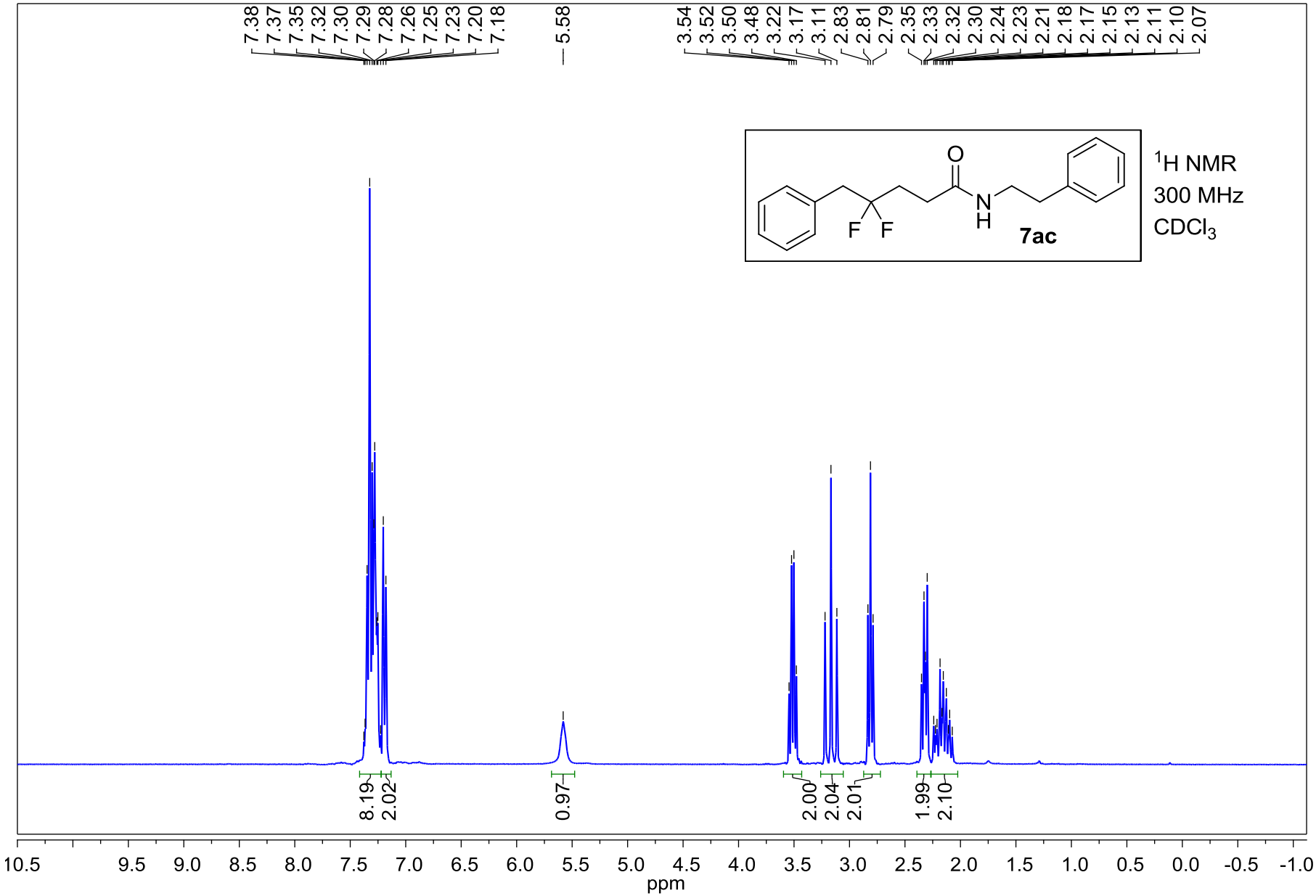
20
10
0
-10
ppm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5.58
3.54
3.52
3.50
3.48
3.22
3.17
3.11
2.83
2.81
2.79
2.35
2.33
2.32
2.30
2.24
2.23
2.21
2.18
2.17
2.15
2.13
2.11
2.10
2.07
O
N
H
F F
7ac
1H NMR
300 MHz
CDCl3
8.19
2.02
0.97
2.00
2.04
2.01
1.99
2.10
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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0.5
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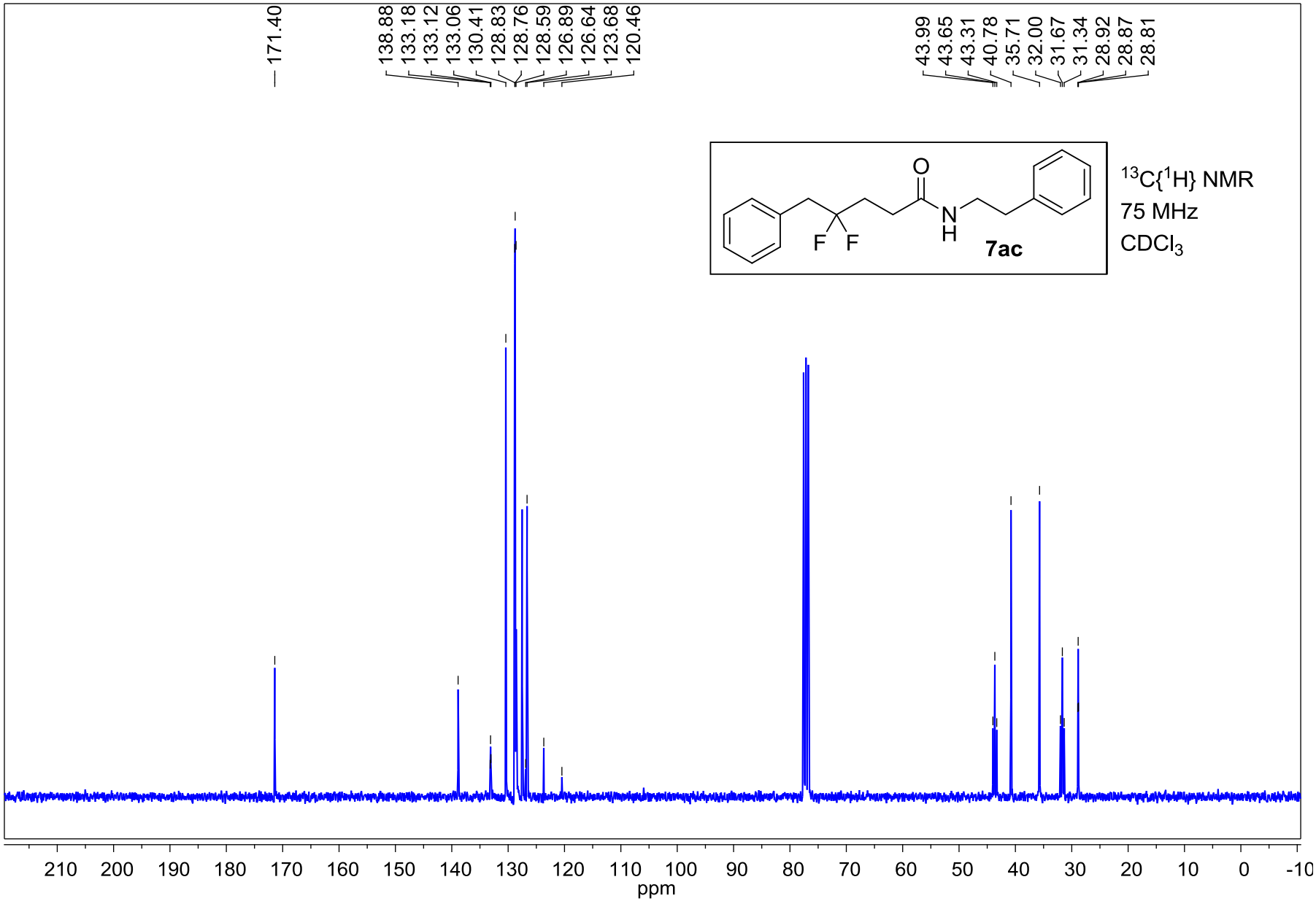
-1.0
ppm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133.12
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130.41
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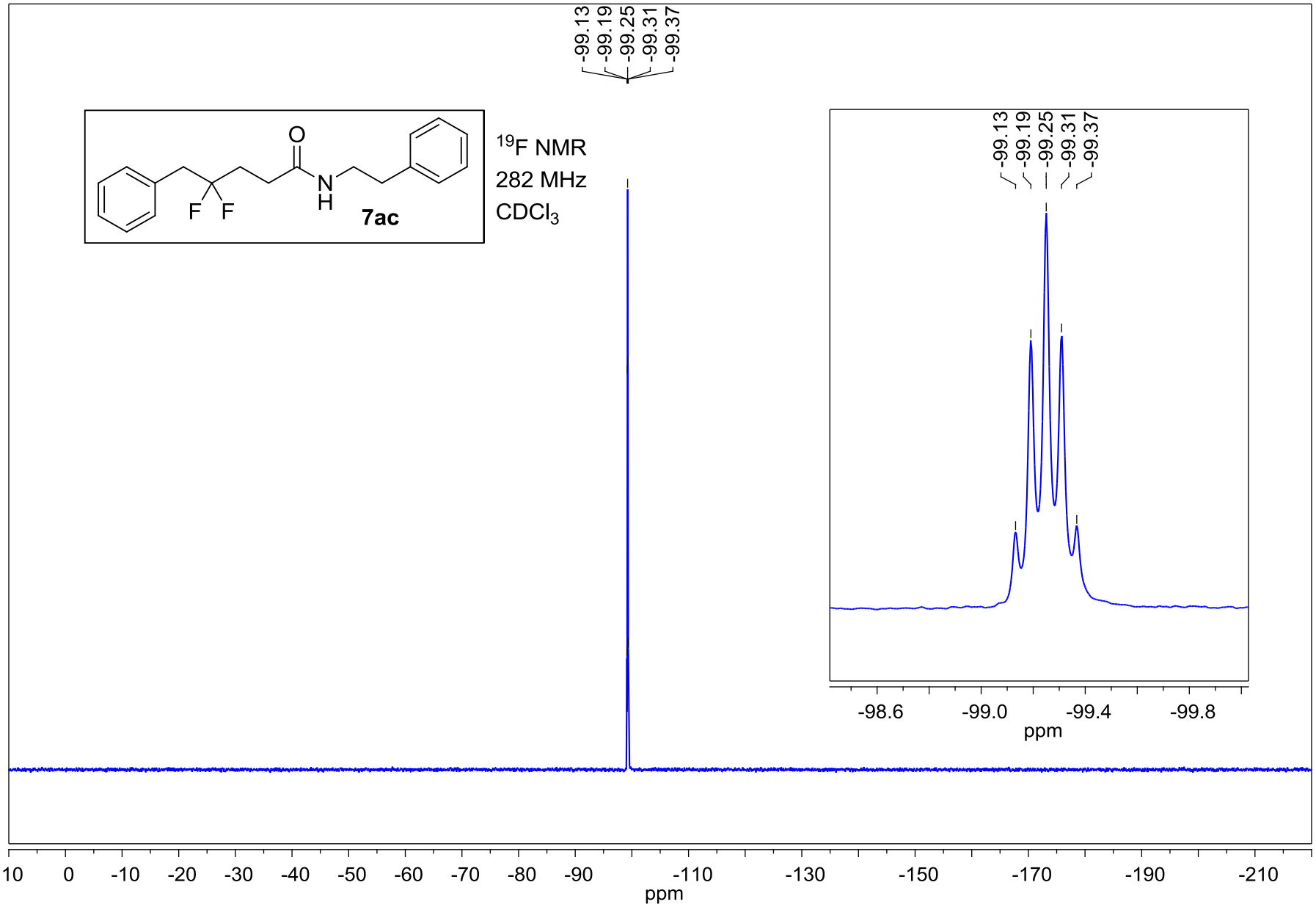
128.76
128.59
126.89
126.64
123.68
120.46
43.99
43.65
43.31
40.78
35.71
32.00
31.67
31.34
28.92
28.87
28.81
O
N
H
F F
7ac
13C{1H} NMR
75 MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm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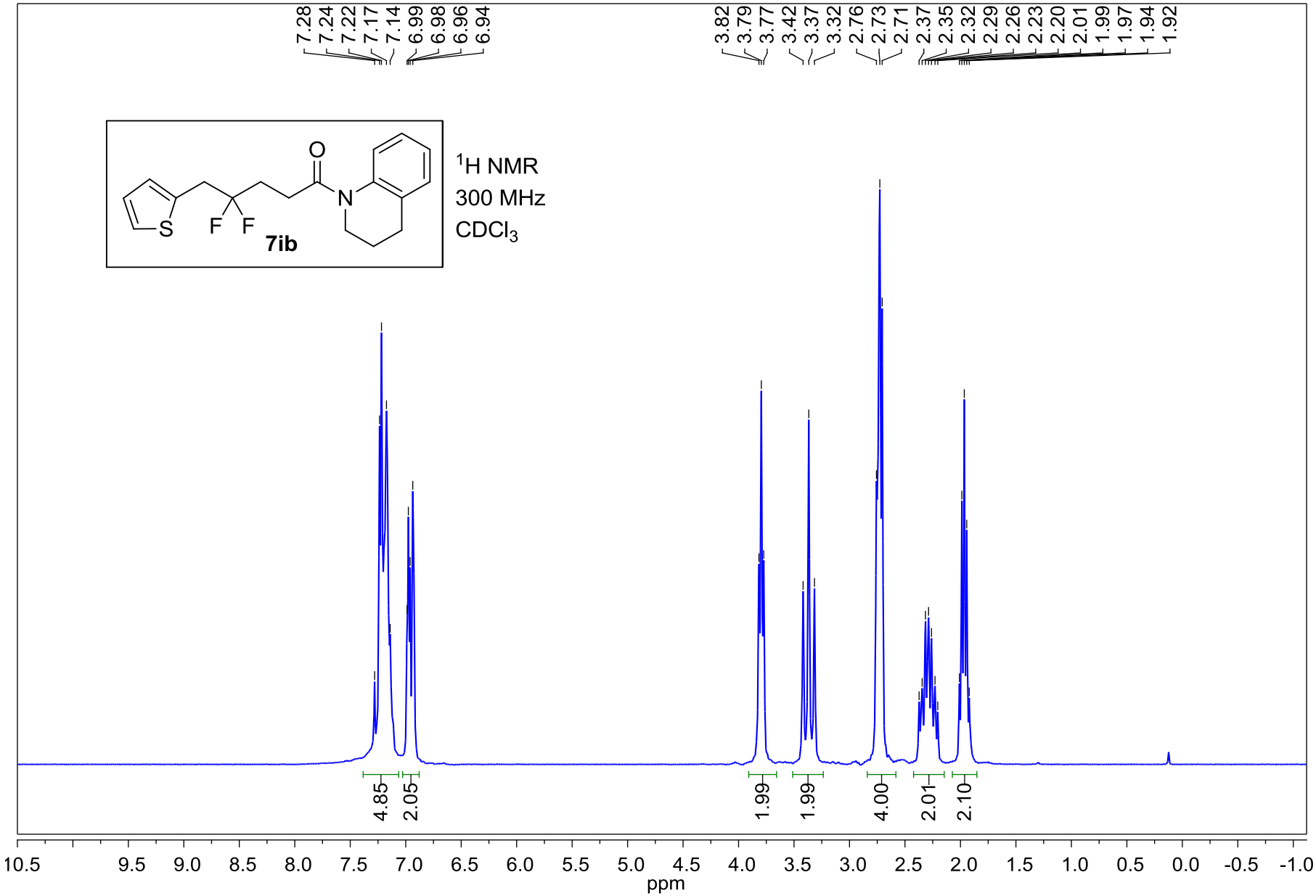
-99.19
-99.25
-99.31
-99.37
O
N
H
F F
7ac
19F NMR
282 MHz
CDCl3
-98.6
-99.0
-99.4
-99.8
ppm
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
ppm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3.79
3.77
3.42
3.37
3.32
2.76
2.73
2.71
2.37
2.35
2.32
2.29
2.26
2.23
2.20
2.01
1.99
1.97
1.94
1.92
O
N
S
F F
7ib
1H NMR
300 MHz
CDCl3
4.85
2.05
1.99
1.99
4.00
2.01
2.10
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
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1.0
0.5
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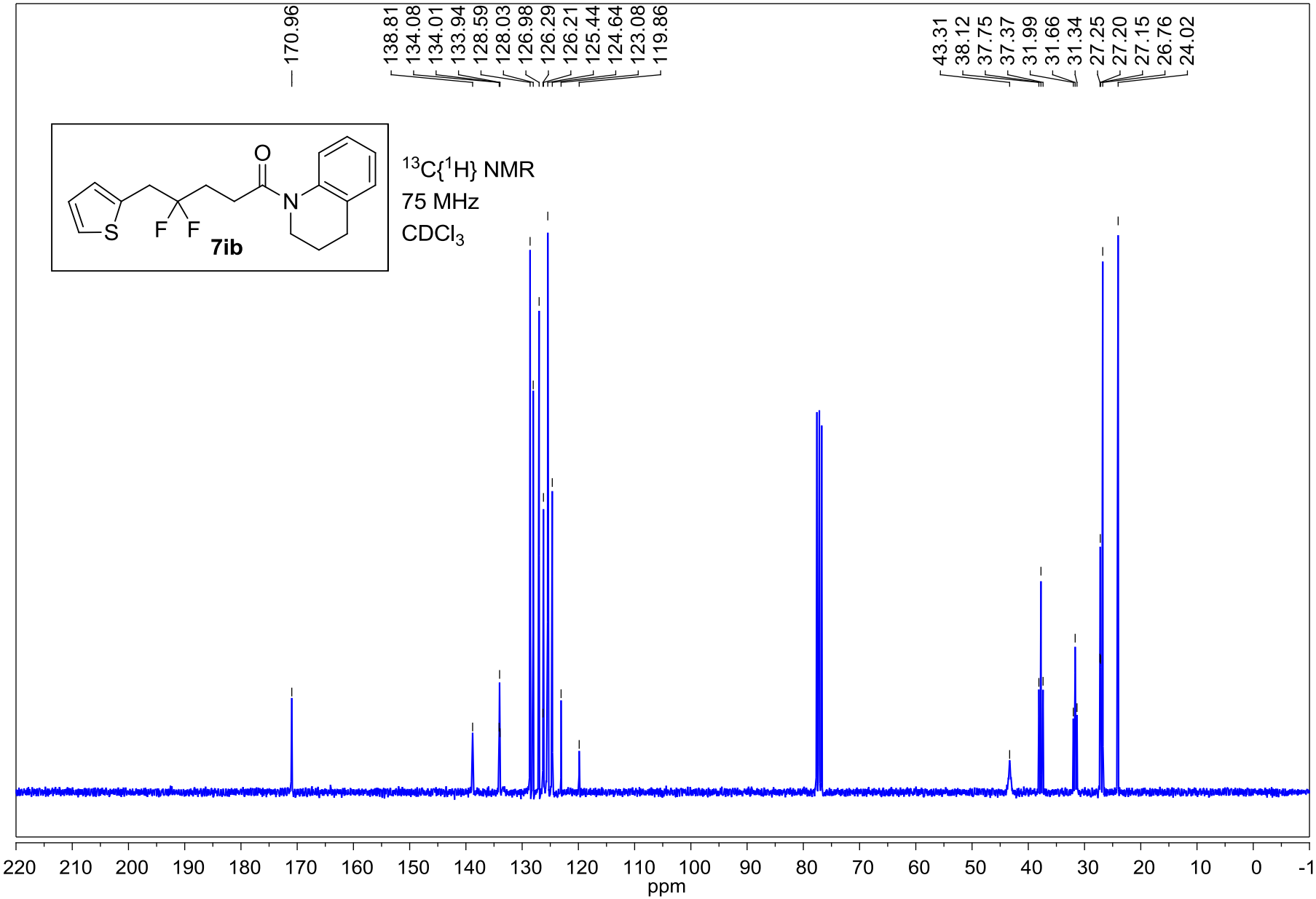
-0.5
-1.0
ppm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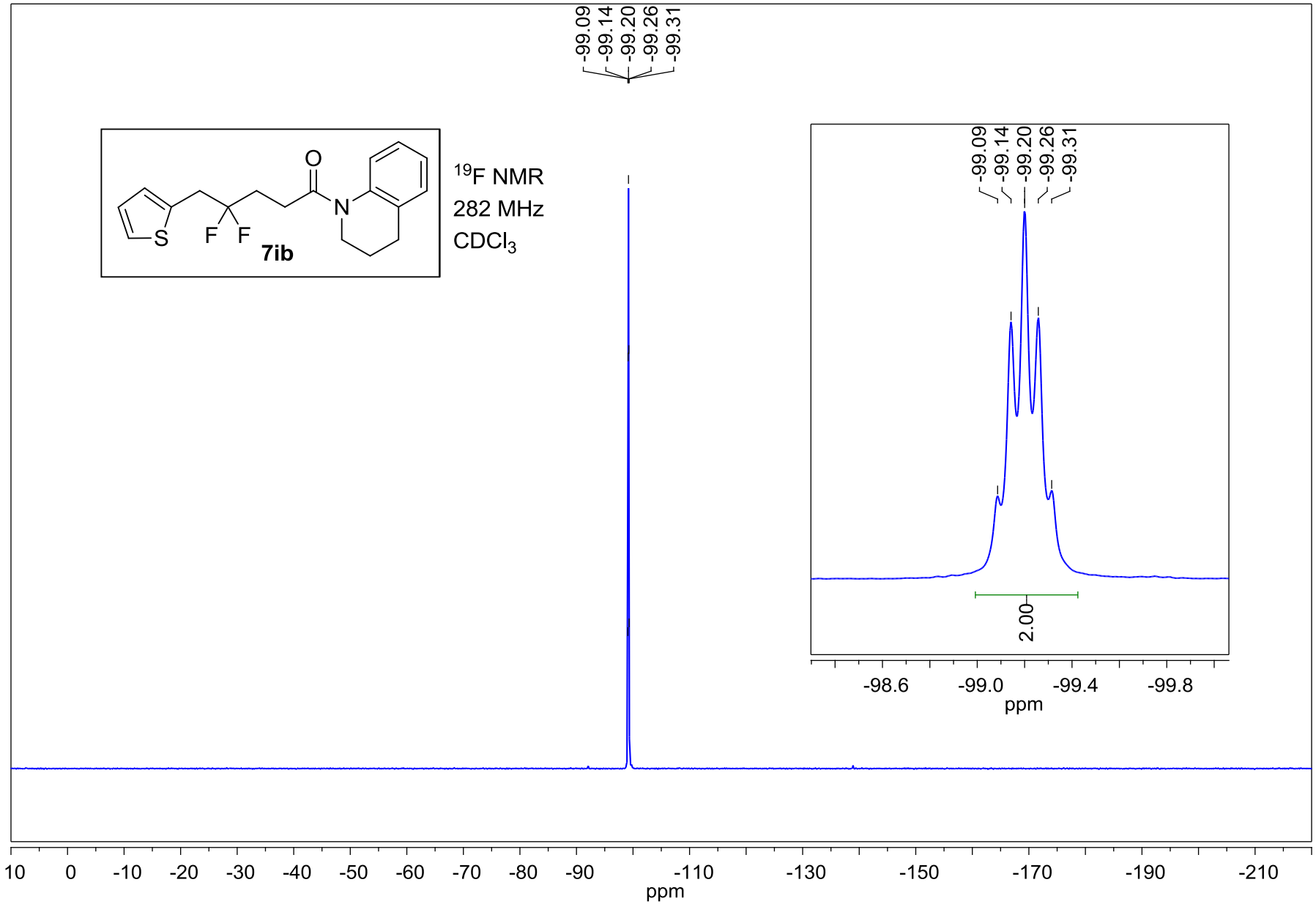
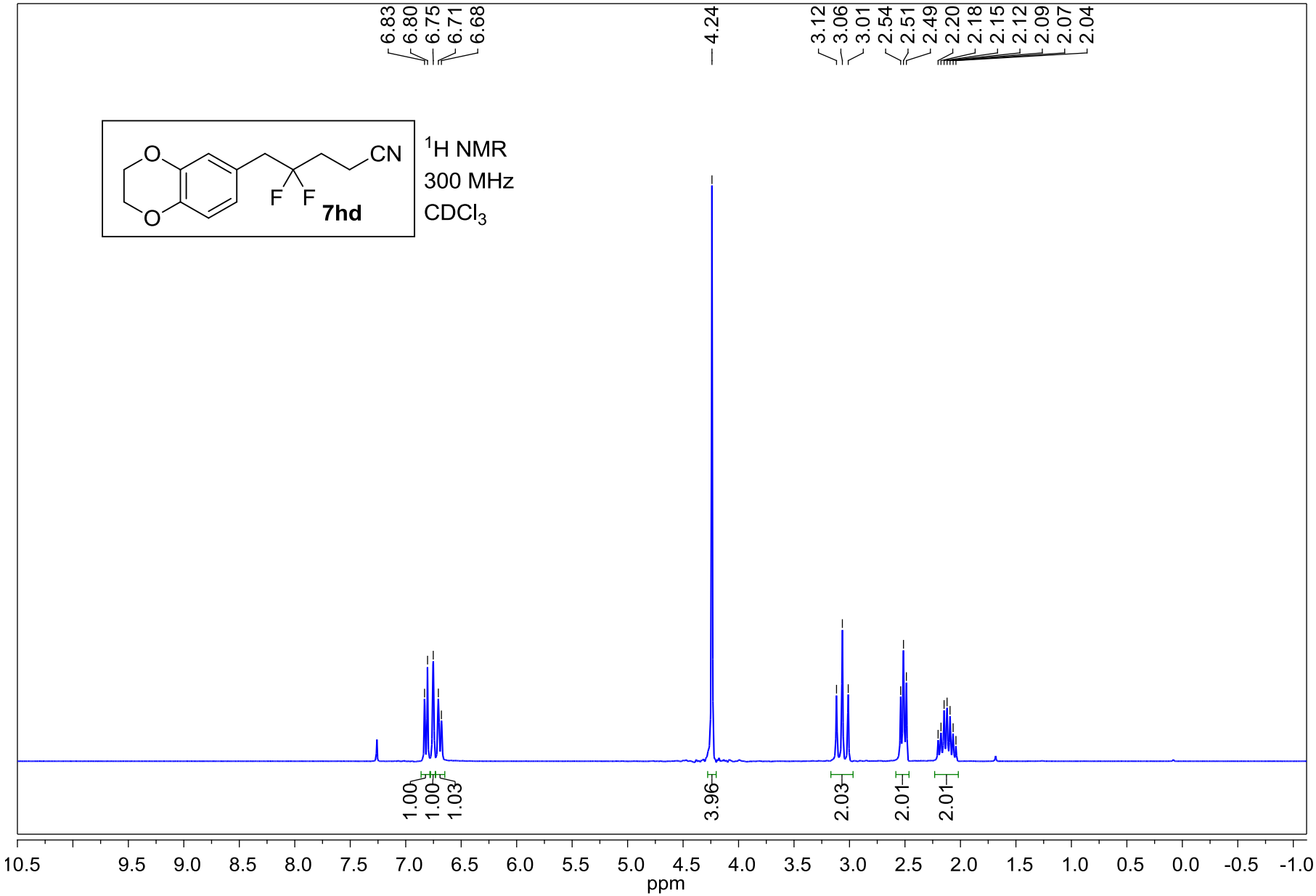
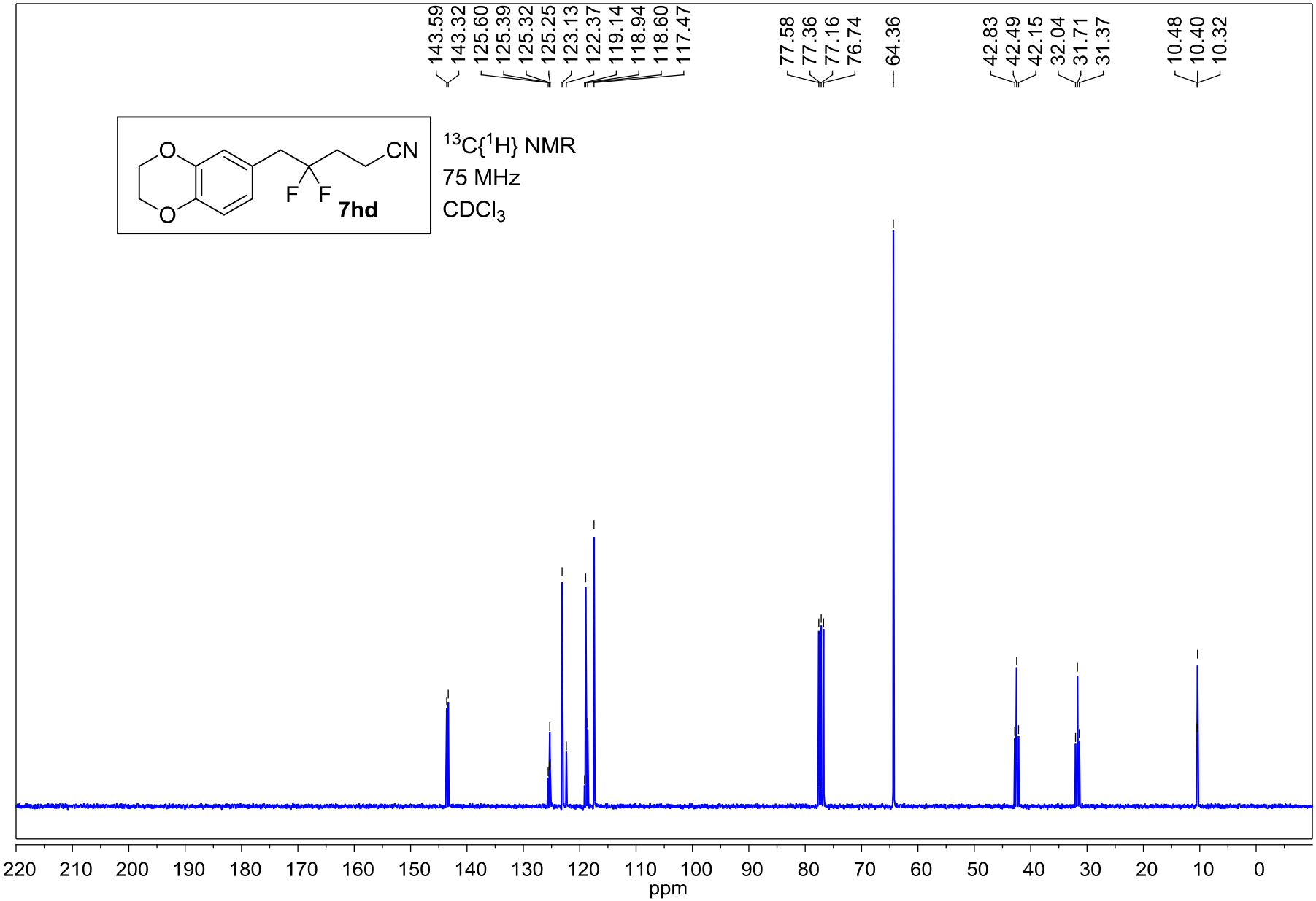
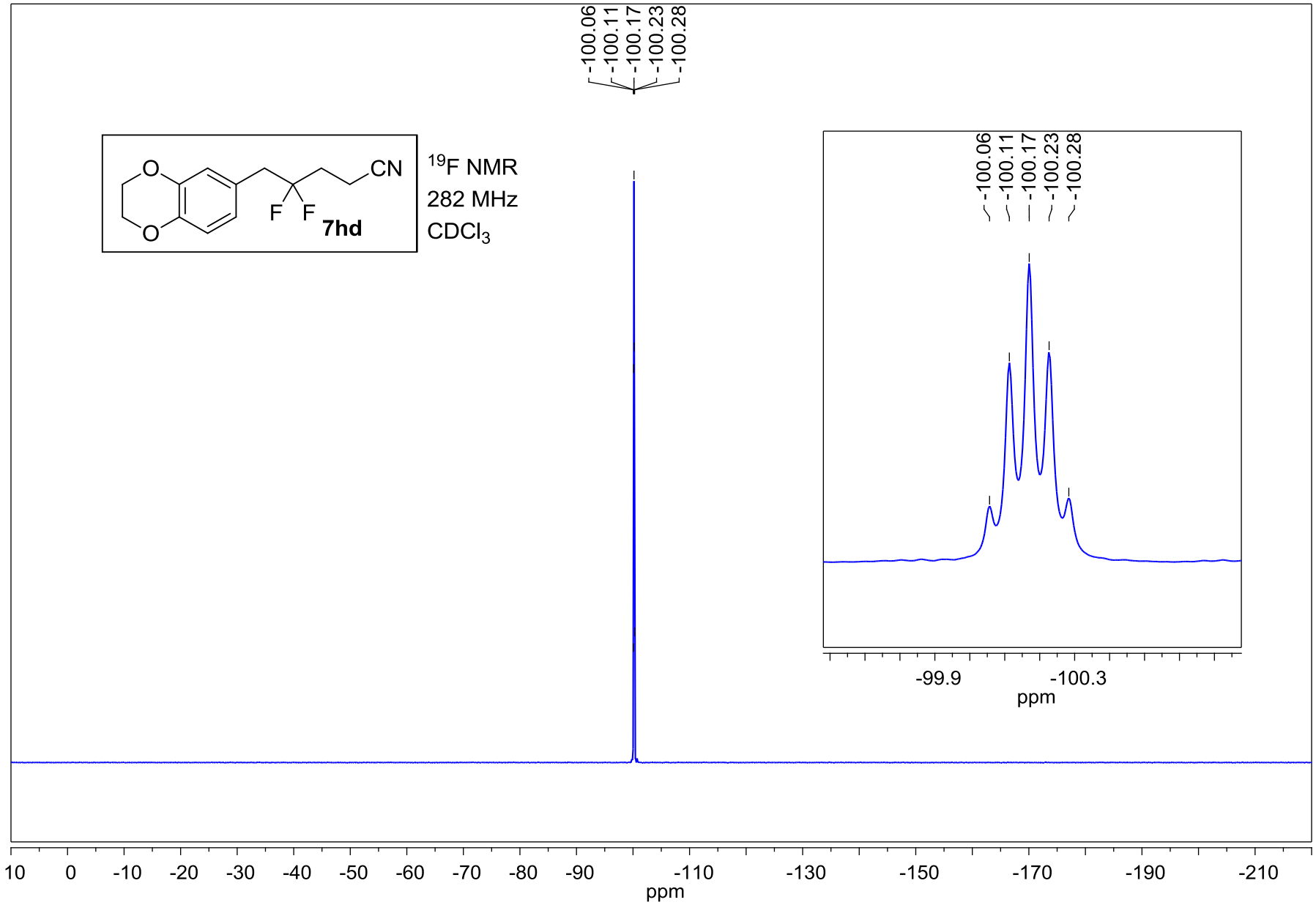
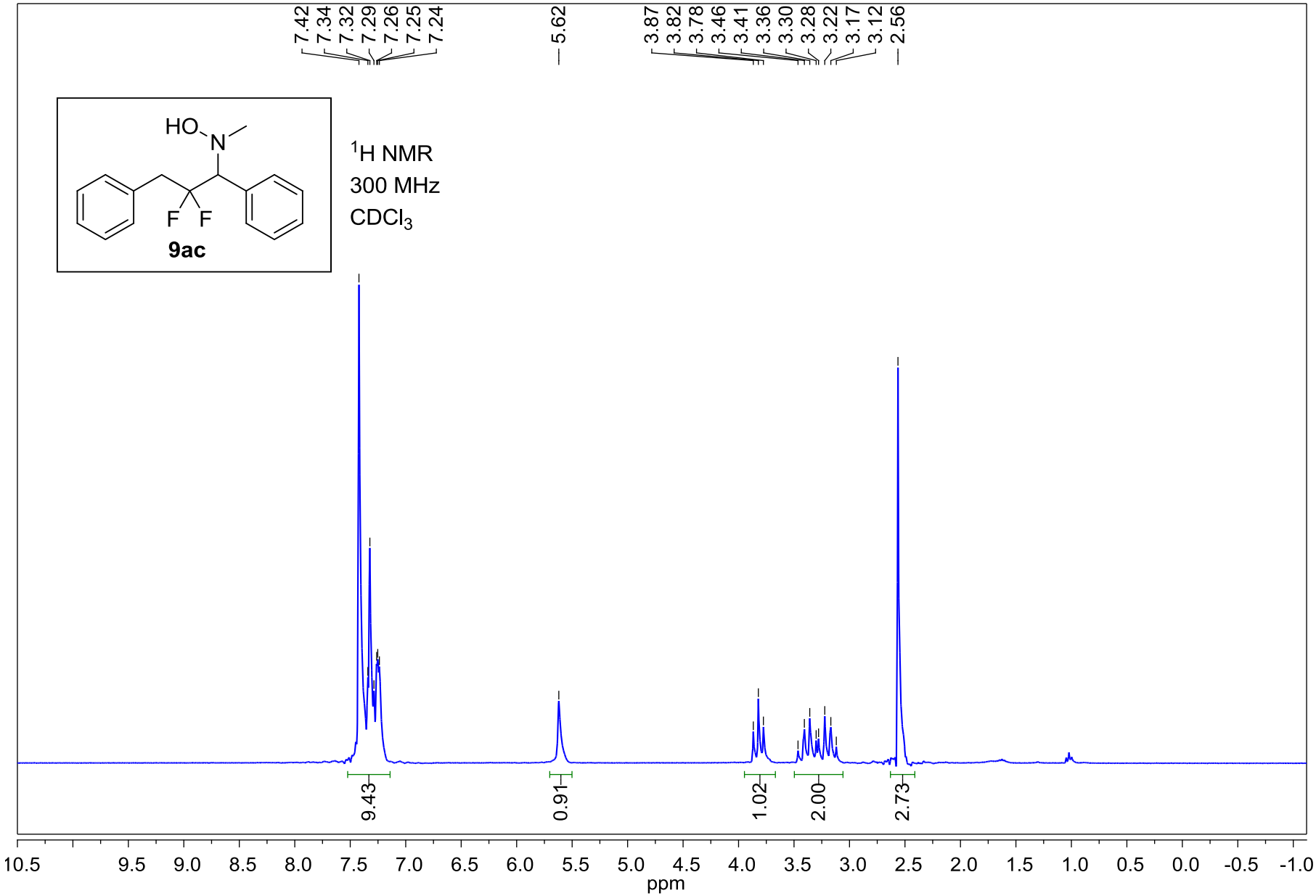
138.81
134.08
134.01
133.94
128.59
128.03
126.98
126.29
126.21
125.44
124.64
123.08
119.86
43.31
38.12
37.75
37.37
31.99
31.66
31.34
27.25
27.20
27.15
26.76
24.02
O
N
S
F
F
7ib
13C{1H} NMR
75 MHz
CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


-99.09
-99.14
-99.20
-99.26
-99.31
O
N
S
F F
7ib
19F NMR
282 MHz
CDCl3
2.00
-98.6
-99.0
-99.4
-99.8
ppm
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
ppm


6.83
6.80
6.75
6.71
6.68
4.24
3.12
3.06
3.01
2.54
2.51
2.49
2.20
2.18
2.15
2.12
2.09
2.07
2.04
O
O
F
F
CN
7hd
1H NMR
300 MHz
CDCl3
1.00
1.00
1.03
3.96
2.03
2.01
2.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm


143.59
143.32
125.60
125.39
125.32
125.25
123.13
122.37
119.14
118.94
118.60
117.47
77.58
77.36
77.16
76.74
64.36
42.83
42.49
42.15
32.04
31.71
31.37
10.48
10.40
10.32
O
O
F
F
CN
7hd
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


-100.06
-100.11
-100.17
-100.23
-100.28
O
O
F
F
CN
7hd
19F NMR
282 MHz
CDCl3
-100.06
-100.11
-100.17
-100.23
-100.28
-99.9
-100.3
ppm
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm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7.34
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7.26
7.25
7.24
5.62
3.87
3.82
3.78
3.46
3.41
3.36
3.30
3.28
3.22
3.17
3.12
2.56
HO
N
F
F
9ac
1H NMR
300 MHz
CDCl3
9.43
0.91
1.02
2.00
2.73
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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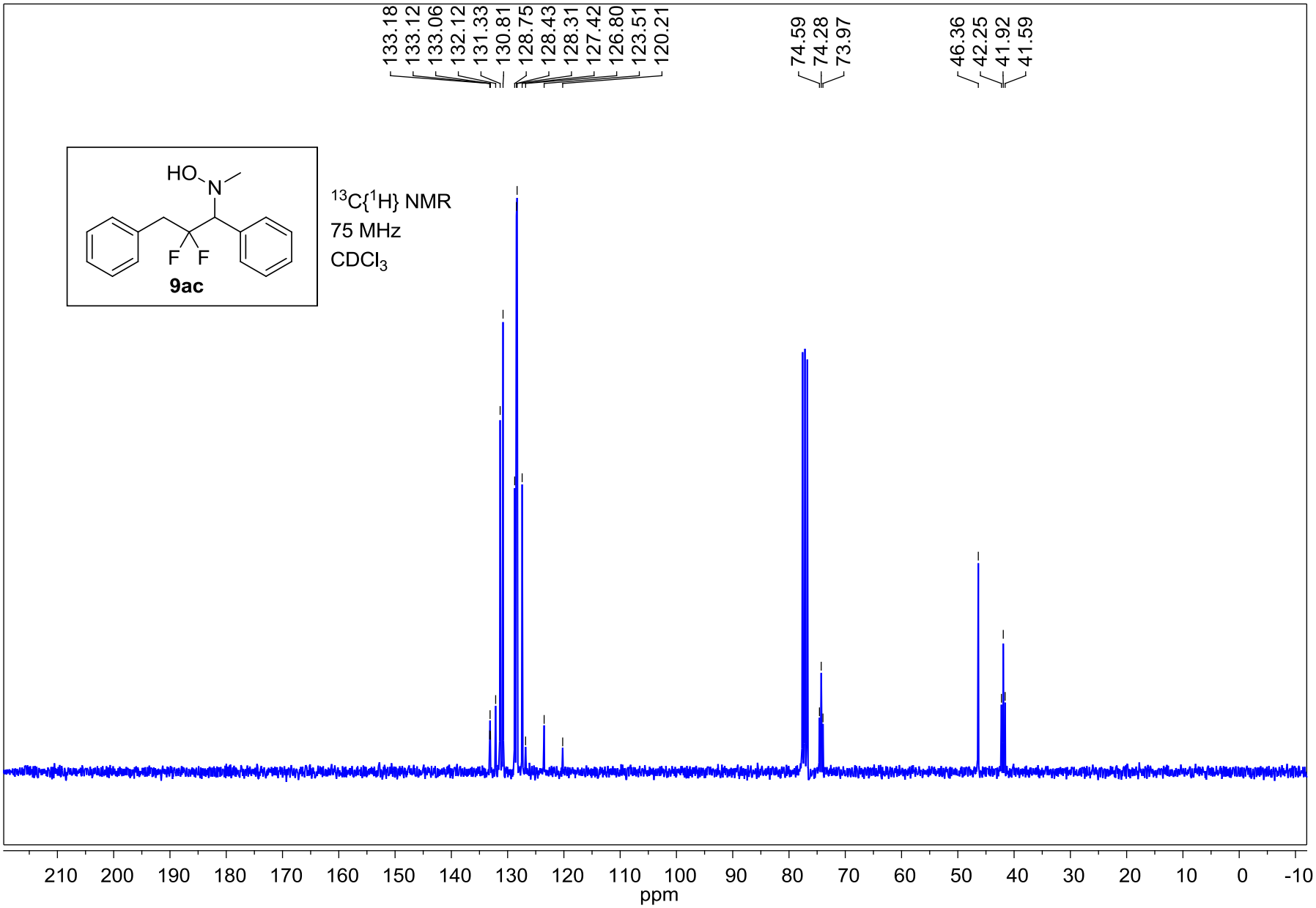
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm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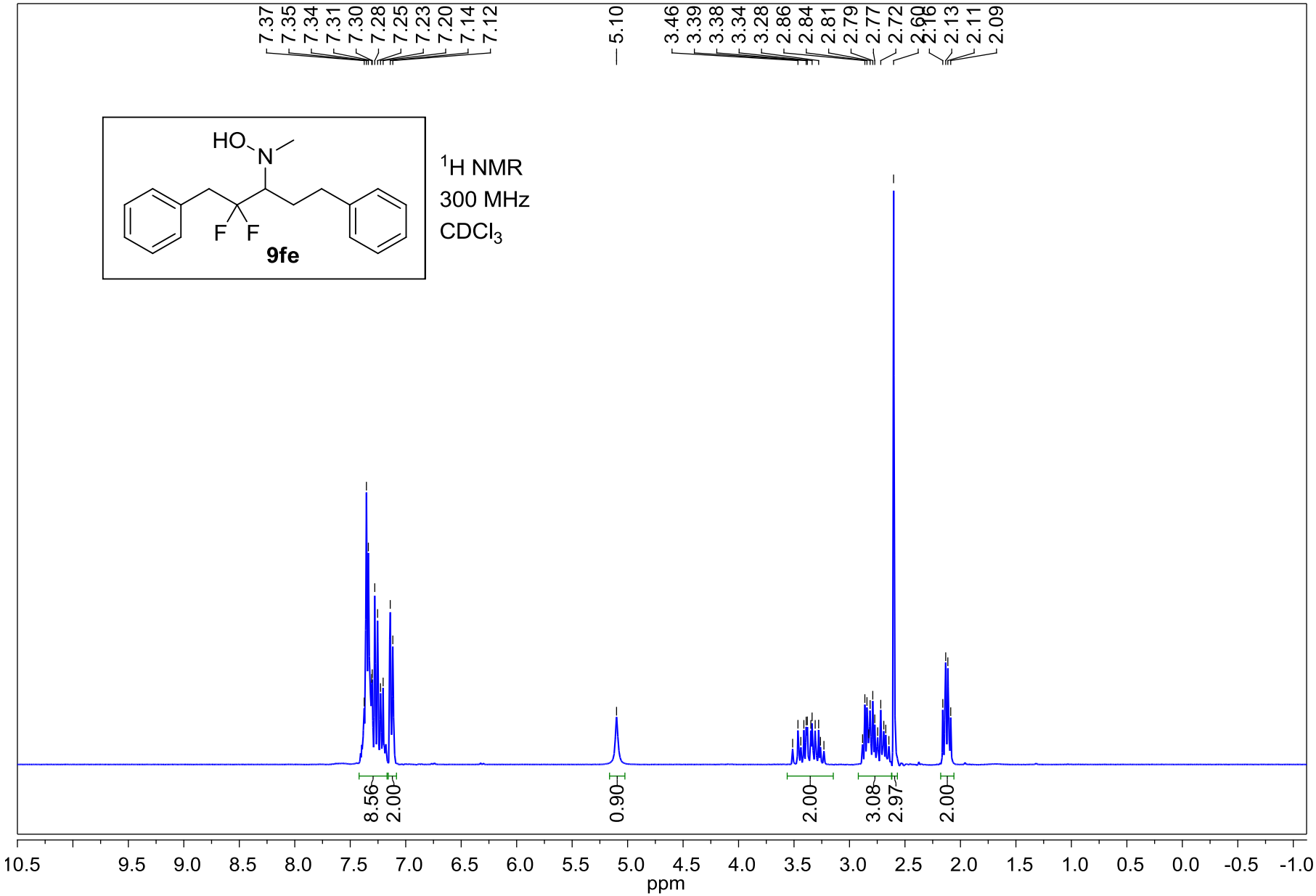
133.12
133.06
132.12
131.33
130.81
128.75
128.43
128.31
127.42
126.80
123.51
120.21
74.59
74.28
73.97
46.36
42.25
41.92
41.59
HO
N
F F
9ac
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm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7.35
7.34
7.31
7.30
7.28
7.25
7.23
7.20
7.14
7.12
5.10
3.46
3.39
3.38
3.34
3.28
2.86
2.84
2.81
2.79
2.77
2.72
2.60
2.16
2.13
2.11
2.09
HO
N
F
F
9fe
1H NMR
300 MHz
CDCl3
8.56
2.00
0.90
2.00
3.08
2.97
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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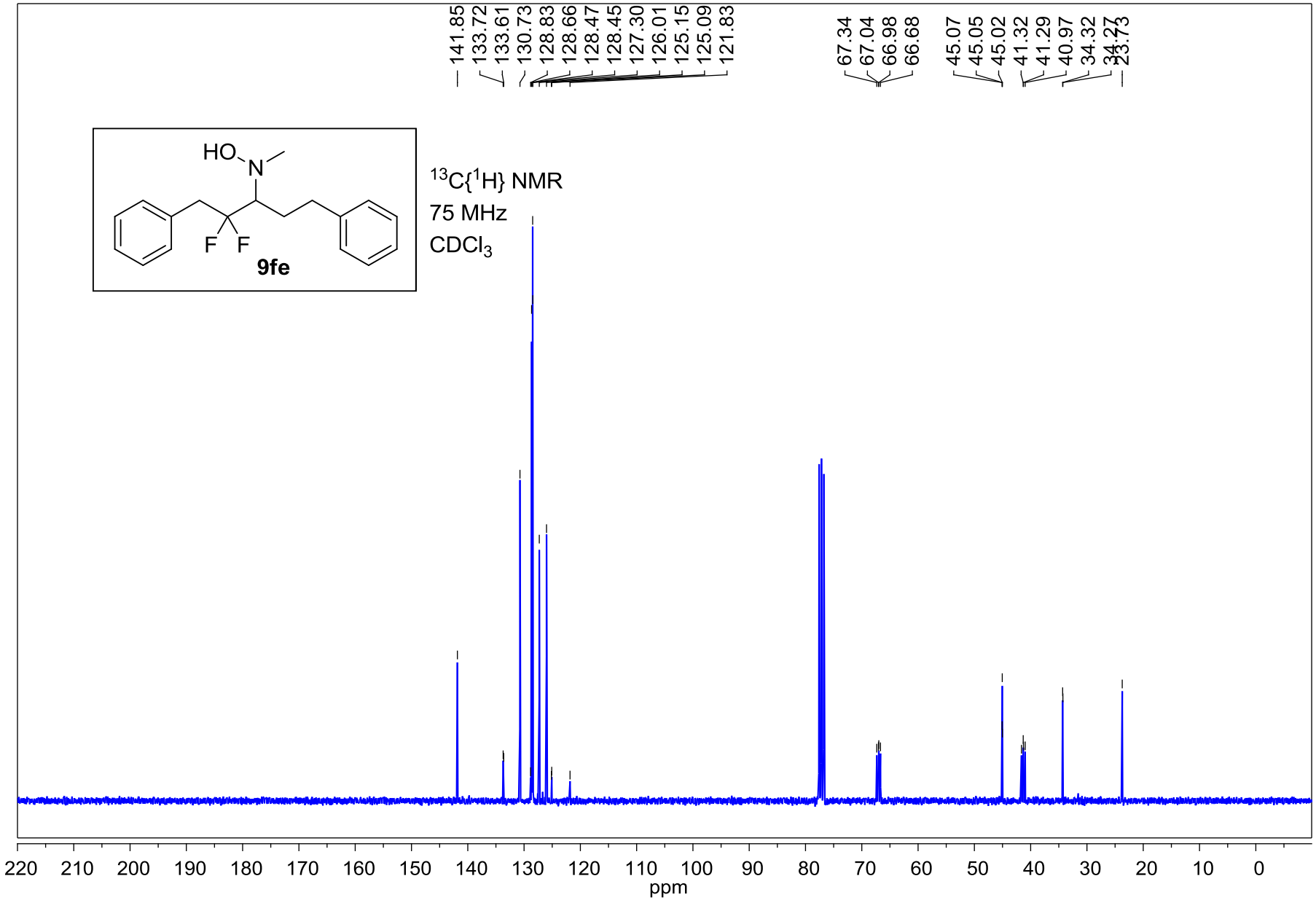
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm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128.66
128.47
128.45
127.30
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125.15
125.09
121.83
67.34
67.04
66.98
66.68
45.07
45.05
45.02
41.32
41.29
40.97
34.32
34.27
23.73
HO
N
F
F
9fe
13C{1H} NMR
75 MHz
CDCl3
220
210
200
190
180
170
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150
140
130
120
110
100
90
80
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60
50
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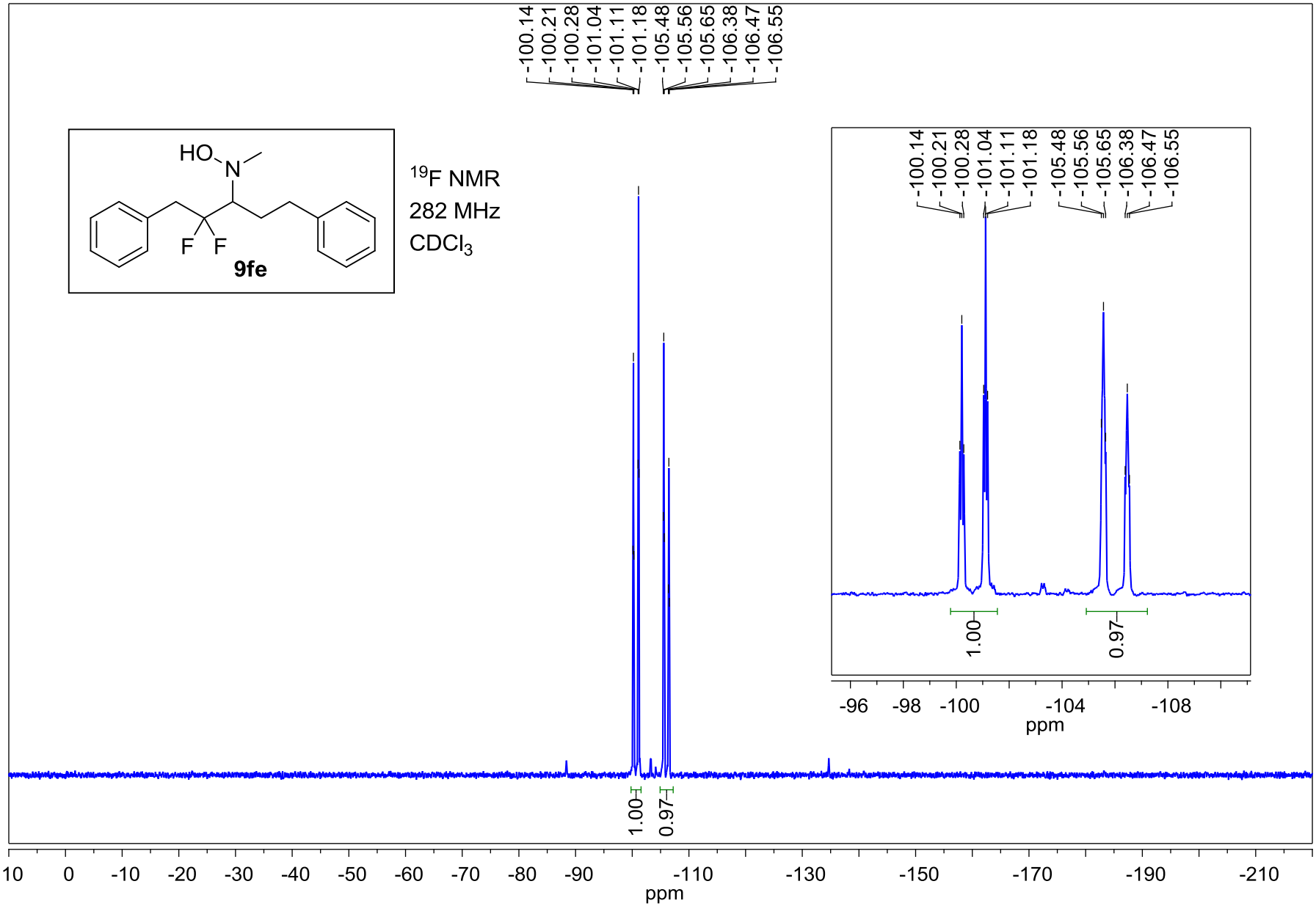
20
10
0
ppm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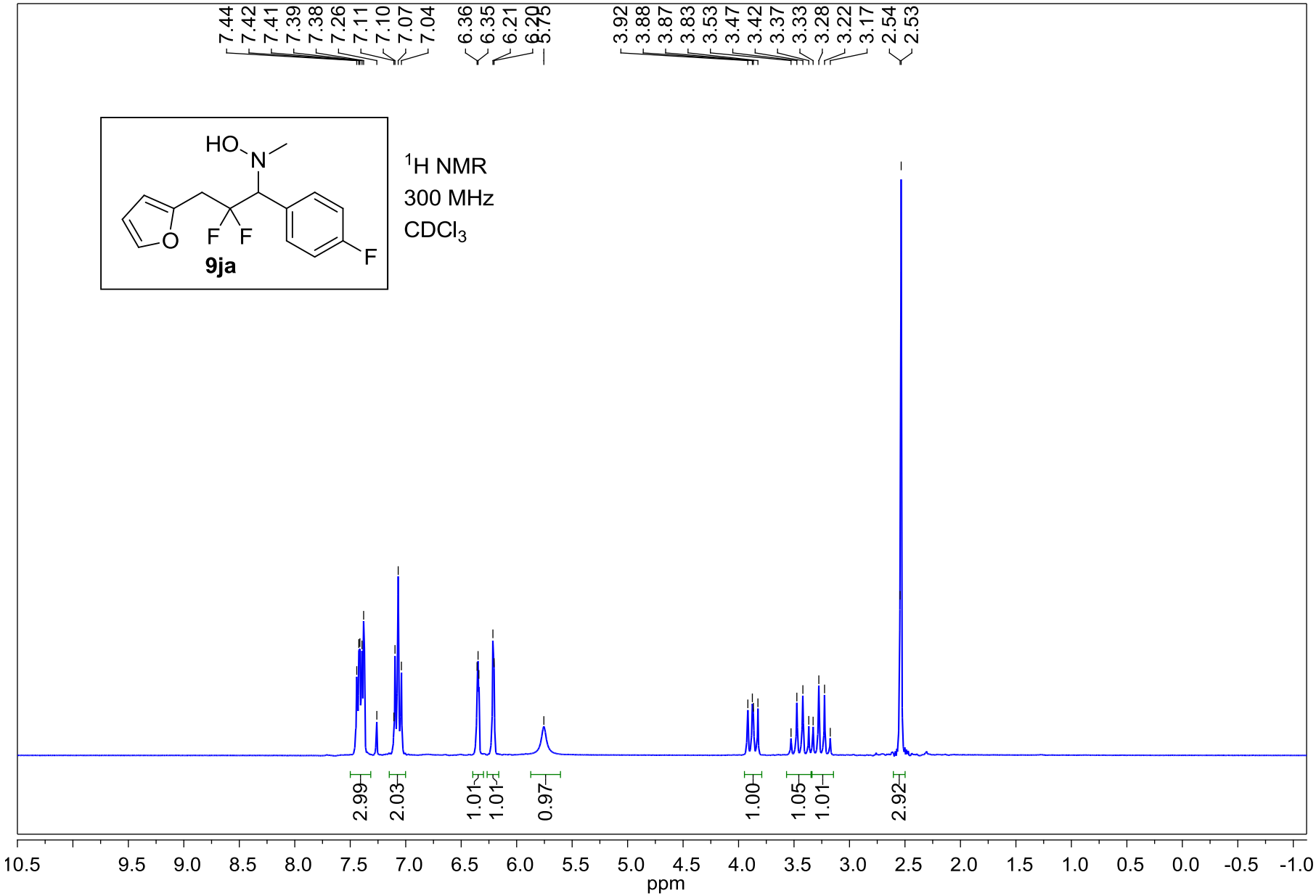
-100.21
-100.28
-101.04
-101.11
-101.18
-105.48
-105.56
-105.65
-106.38
-106.47
-106.55
HO
N
F F
9fe
19F NMR
282 MHz
CDCl3
1.00
0.97
-96 -98 -100 -104 -108
ppm
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
ppm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7.42
7.41
7.39
7.38
7.26
7.11
7.10
7.07
7.04
6.36
6.35
6.21
6.20
5.75
3.92
3.88
3.87
3.83
3.53
3.47
3.42
3.37
3.33
3.28
3.22
3.17
2.54
2.53
HO
N
O
F
F
F
9ja
1H NMR
300 MHz
CDCl3
2.99
2.03
1.01
1.01
0.97
1.00
1.05
1.01
2.92
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
1.0
0.5
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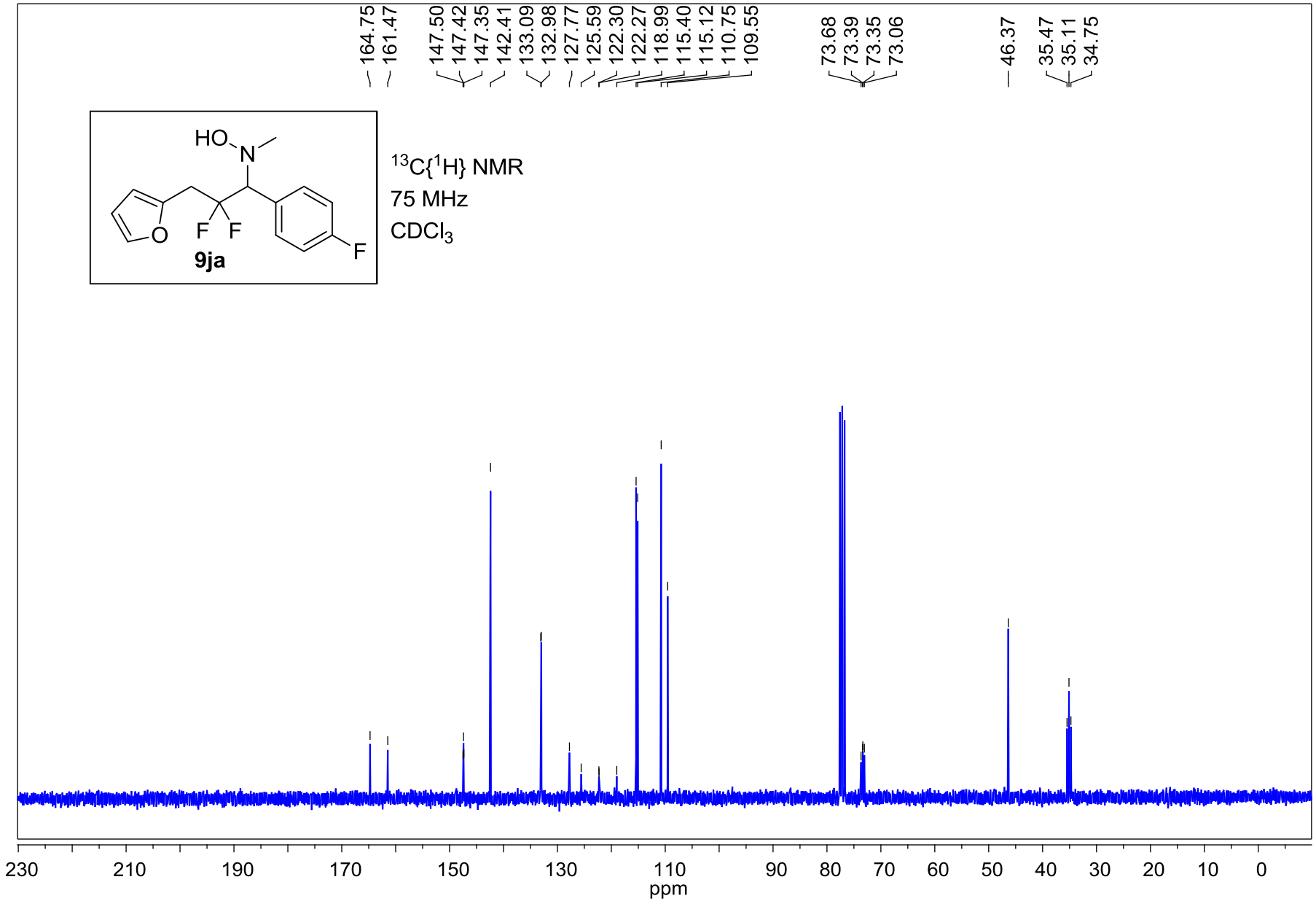
-0.5
-1.0
ppm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142.41
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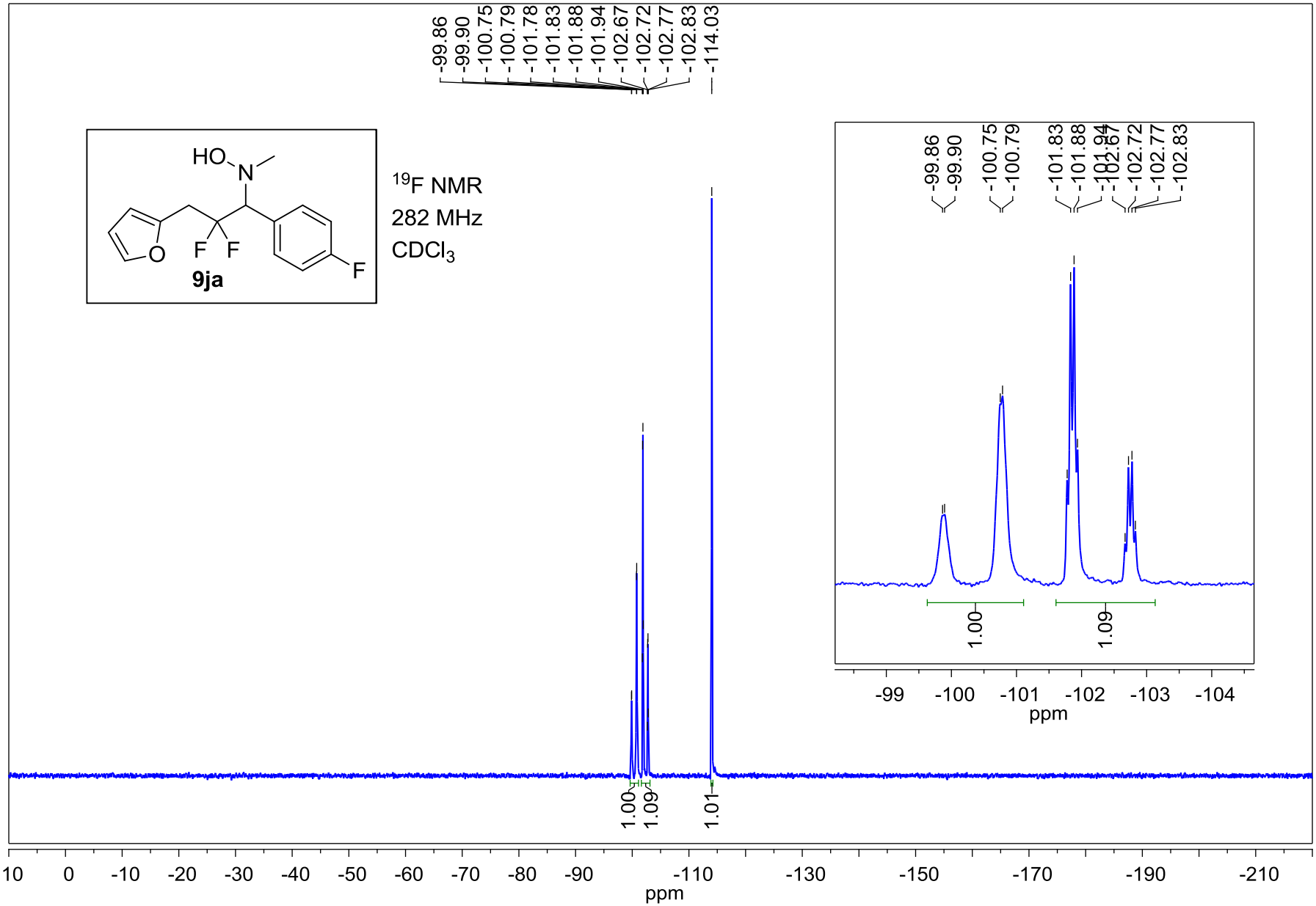
132.98
127.77
125.59
122.30
122.27
118.99
115.40
115.12
110.75
109.55
73.68
73.39
73.35
73.06
46.37
35.47
35.11
34.75
HO
N
O
F
F
F
9ja
13C{1H} NMR
75 MHz
CDCl3
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
ppm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-100.79
-101.78
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-101.88
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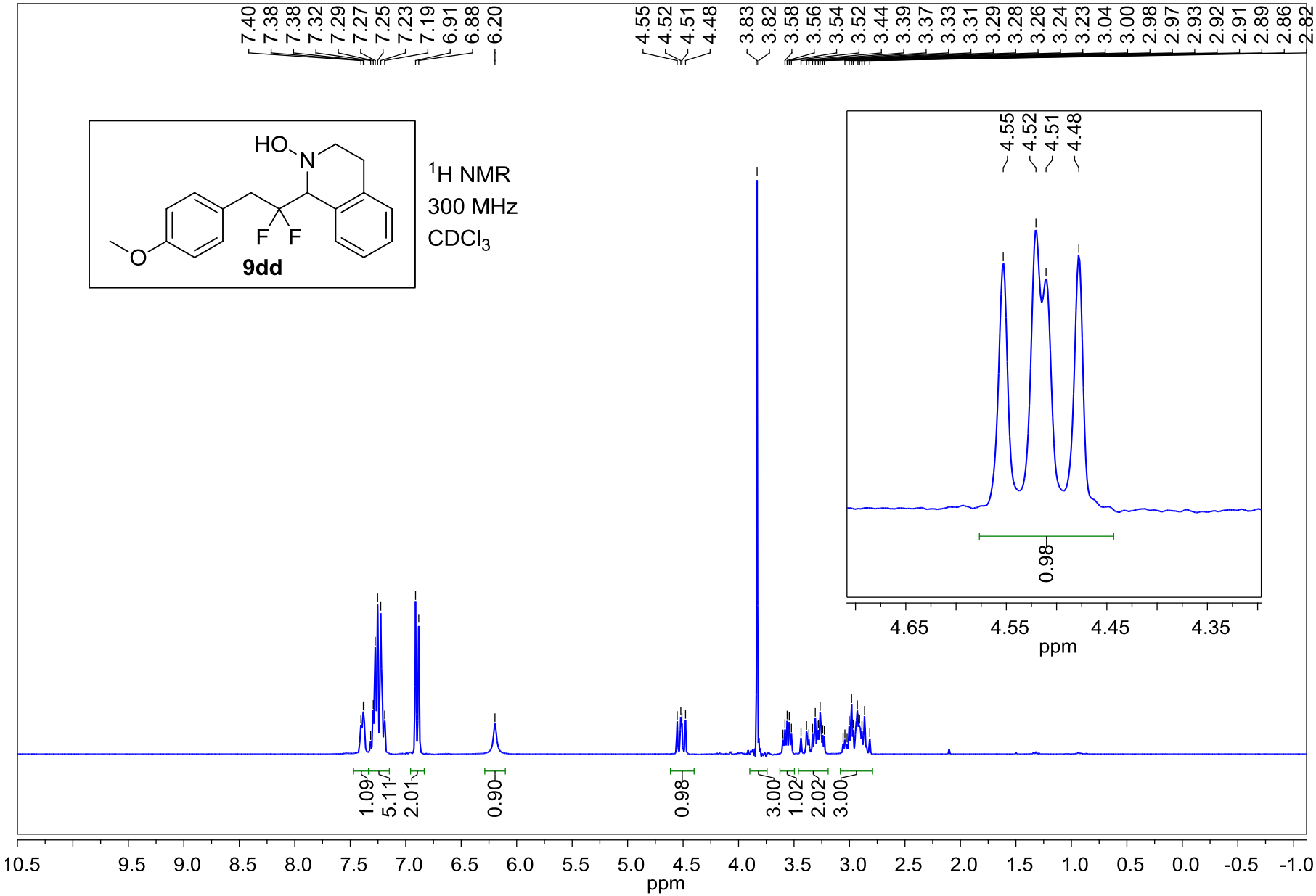
-102.72
-102.77
-102.83
-114.03
HO
N
O
F F
F
9ja
19F NMR
282 MHz
CDCl3
1.00
1.09
1.01
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
ppm
-99 -100 -101 -102 -103 -104
ppm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7.38
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7.25
7.23
7.19
6.91
6.88
6.20
4.55
4.52
4.51
4.48
3.83
3.82
3.58
3.56
3.54
3.52
3.44
3.39
3.37
3.33
3.31
3.29
3.28
3.26
3.24
3.23
3.04
3.00
2.98
2.97
2.93
2.92
2.91
2.89
2.86
2.82
HO
N
F
F
O
9dd
1H NMR
300 MHz
CDCl3
4.65
4.55
4.45
4.35
ppm
0.98
1.09
5.11
2.01
0.90
0.98
3.00
1.02
2.02
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.5
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1.5
1.0
0.5
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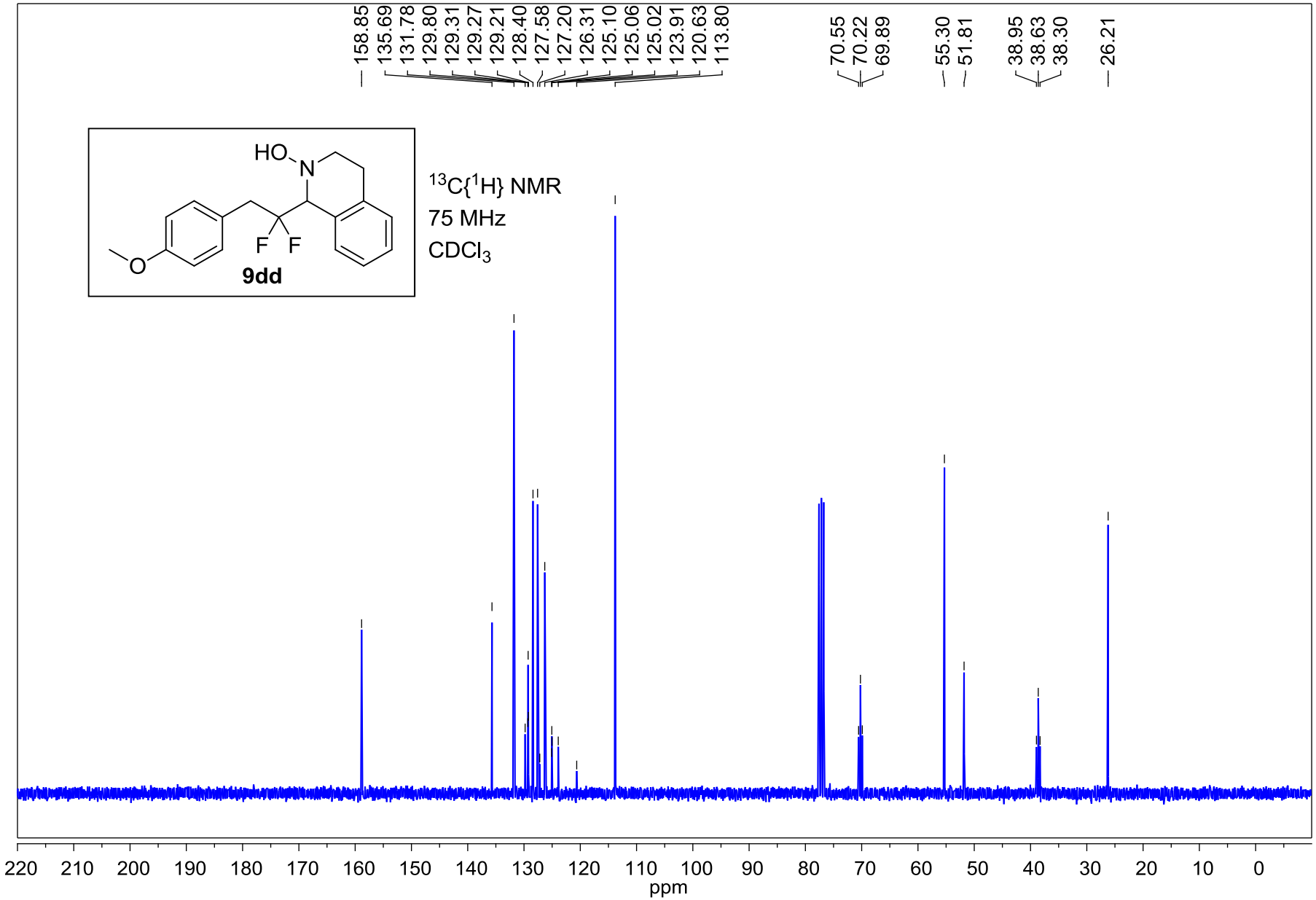
-0.5
-1.0
ppm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129.21
128.40
127.58
127.20
126.31
125.10
125.06
125.02
123.91
120.63
113.80
70.55
70.22
69.89
55.30
51.81
38.95
38.63
38.30
26.21
HO
N
F
F
O
9dd
13C{1H} NMR
75 MHz
CDCl3
220
210
200
190
180
170
160
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140
130
120
110
100
90
80
70
60
50
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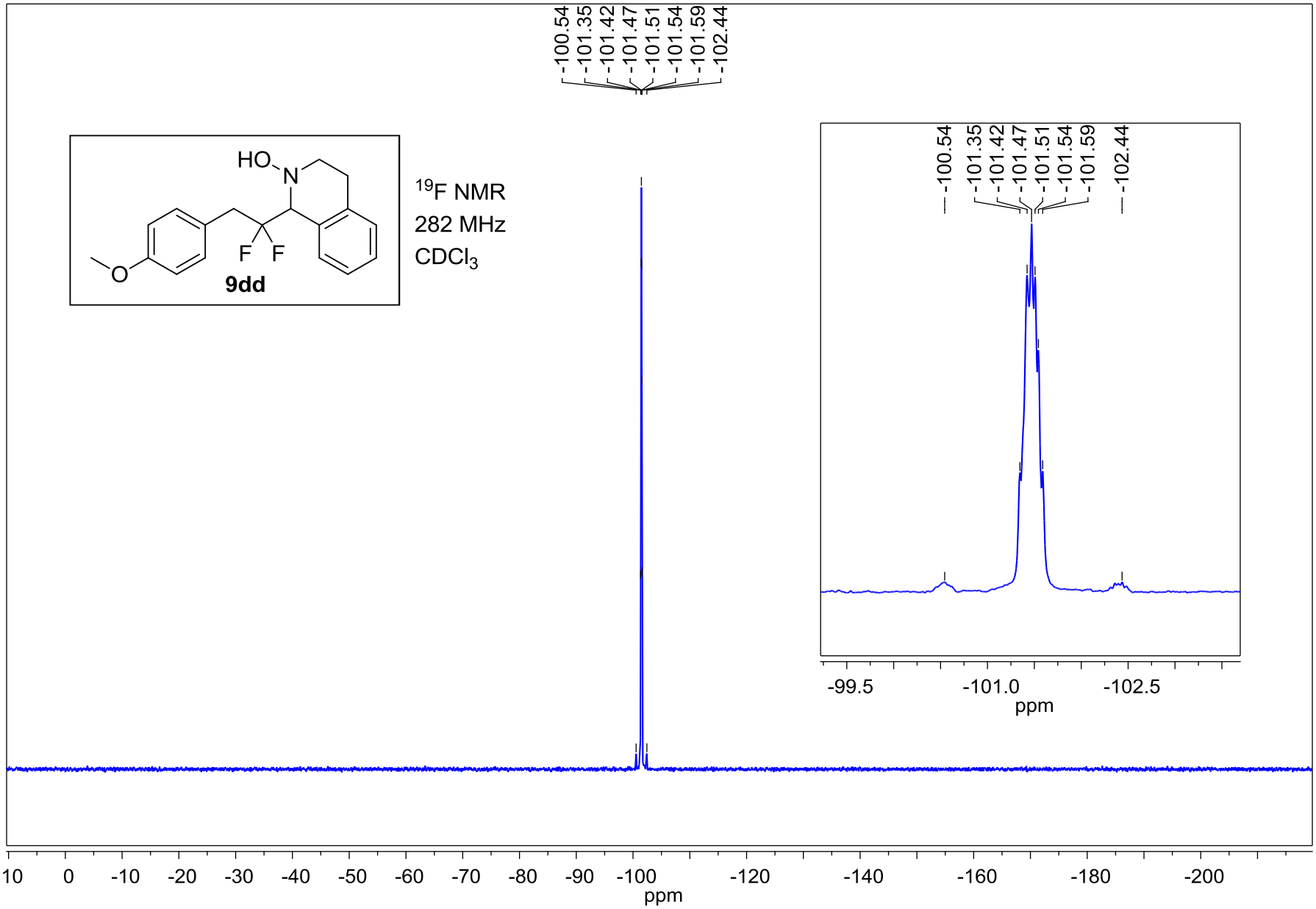
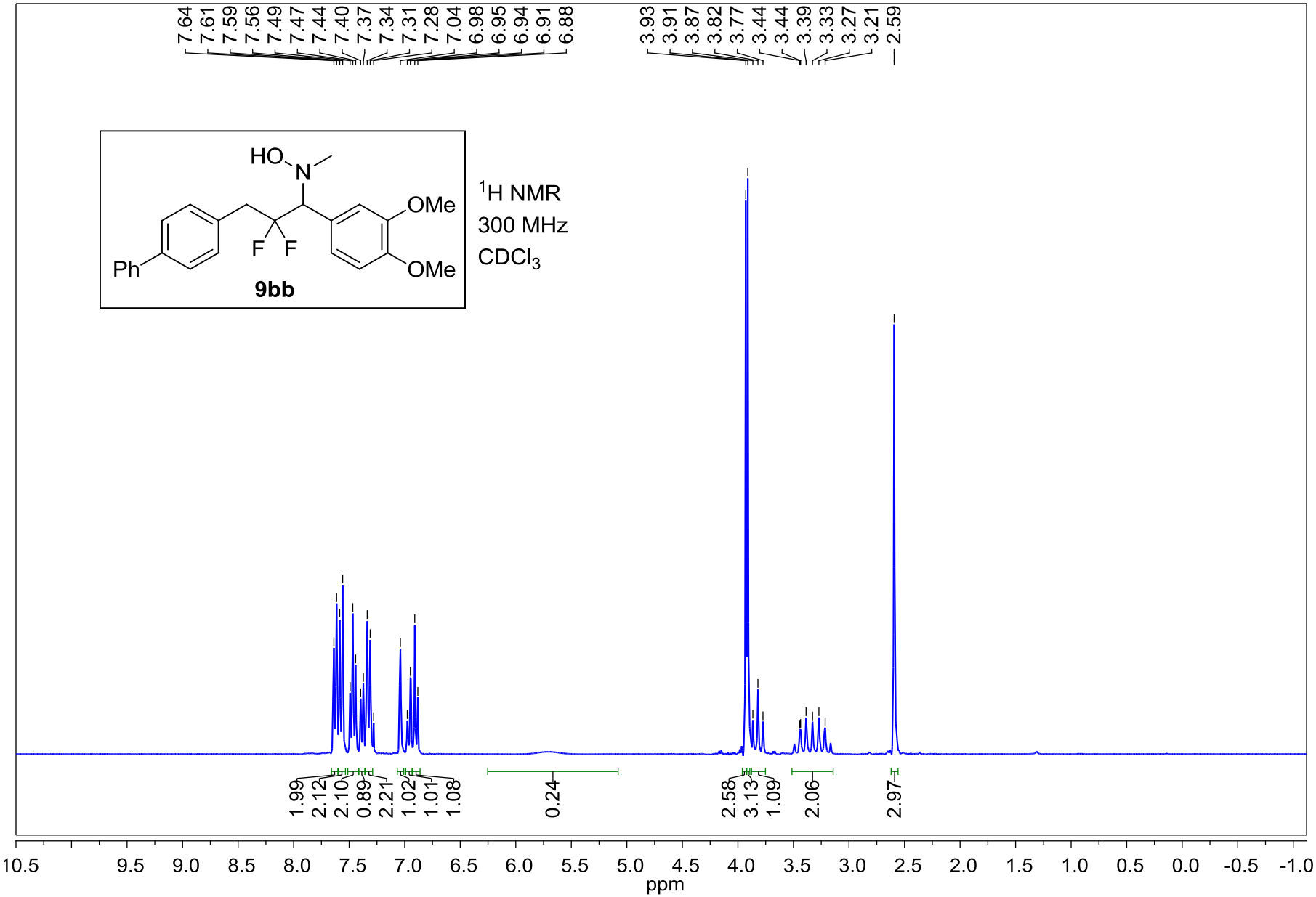
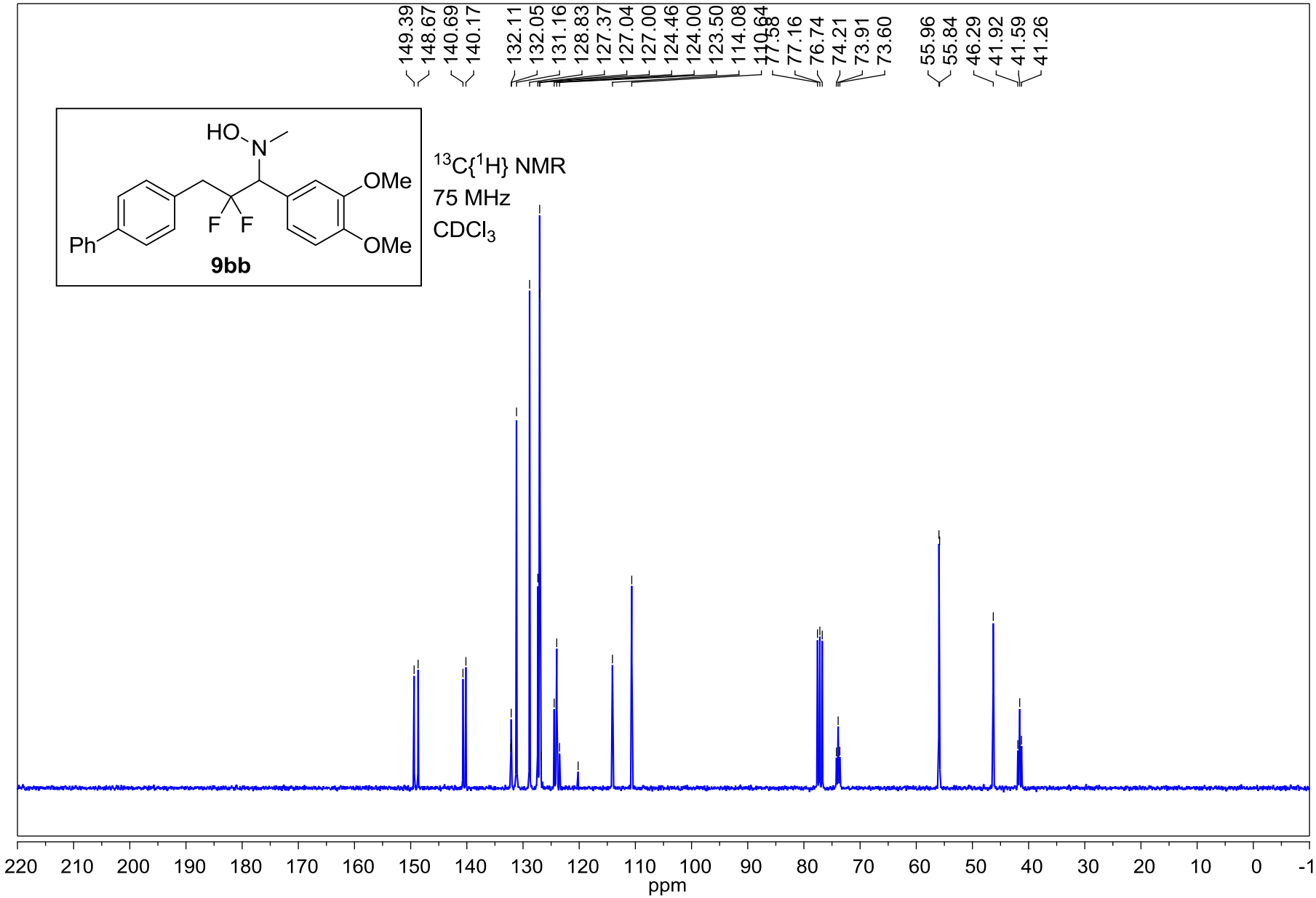
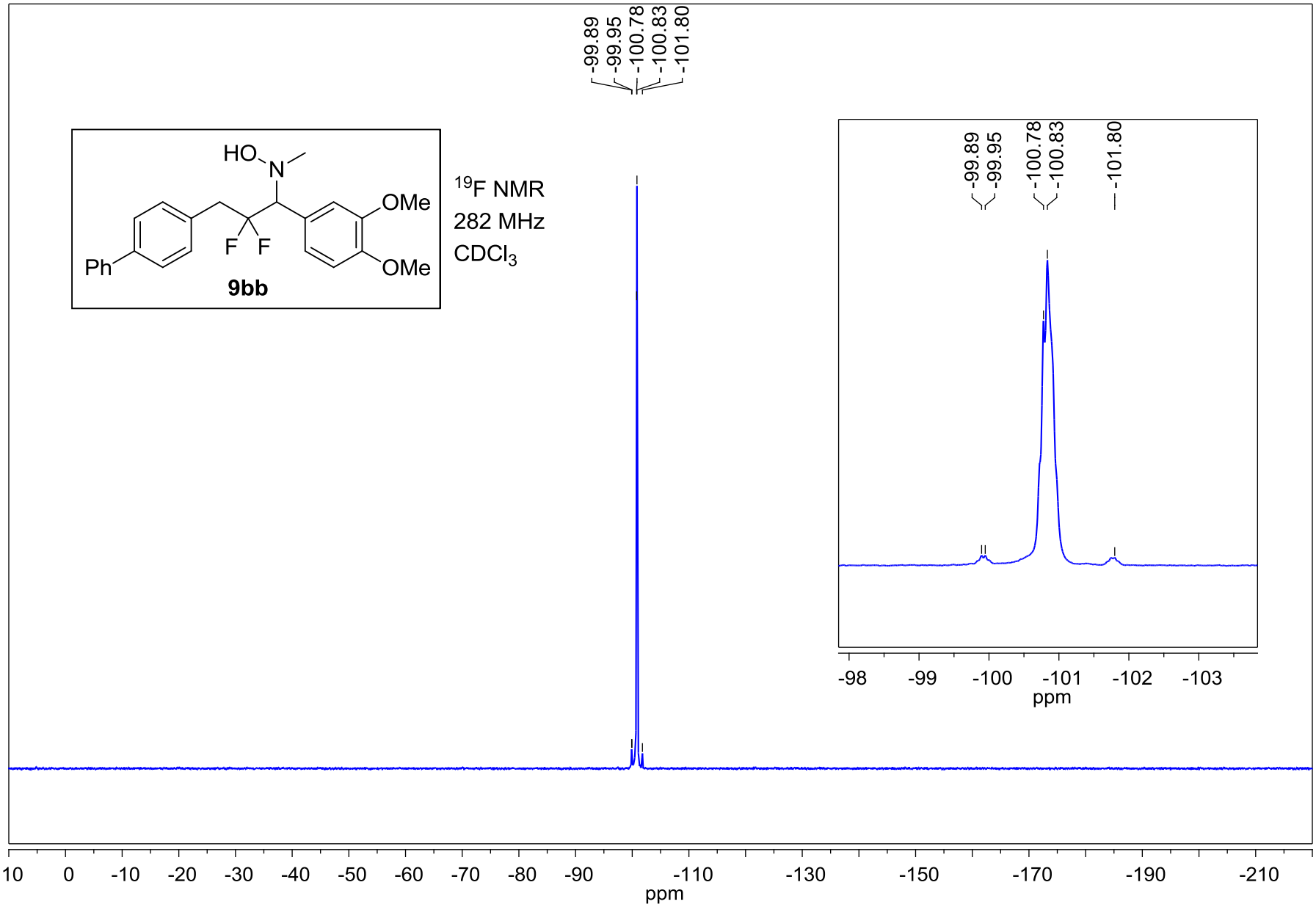
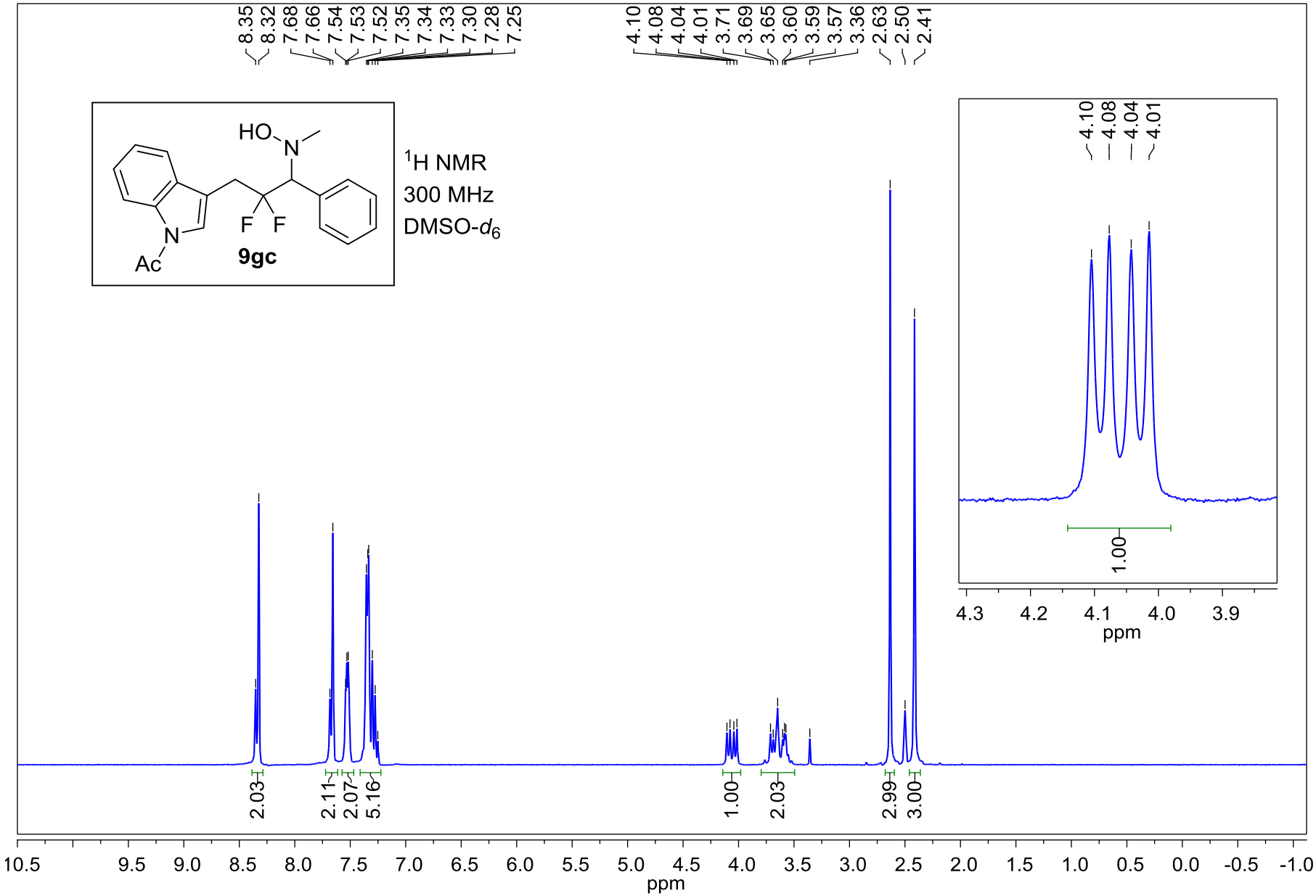
30
20
10
0
ppm

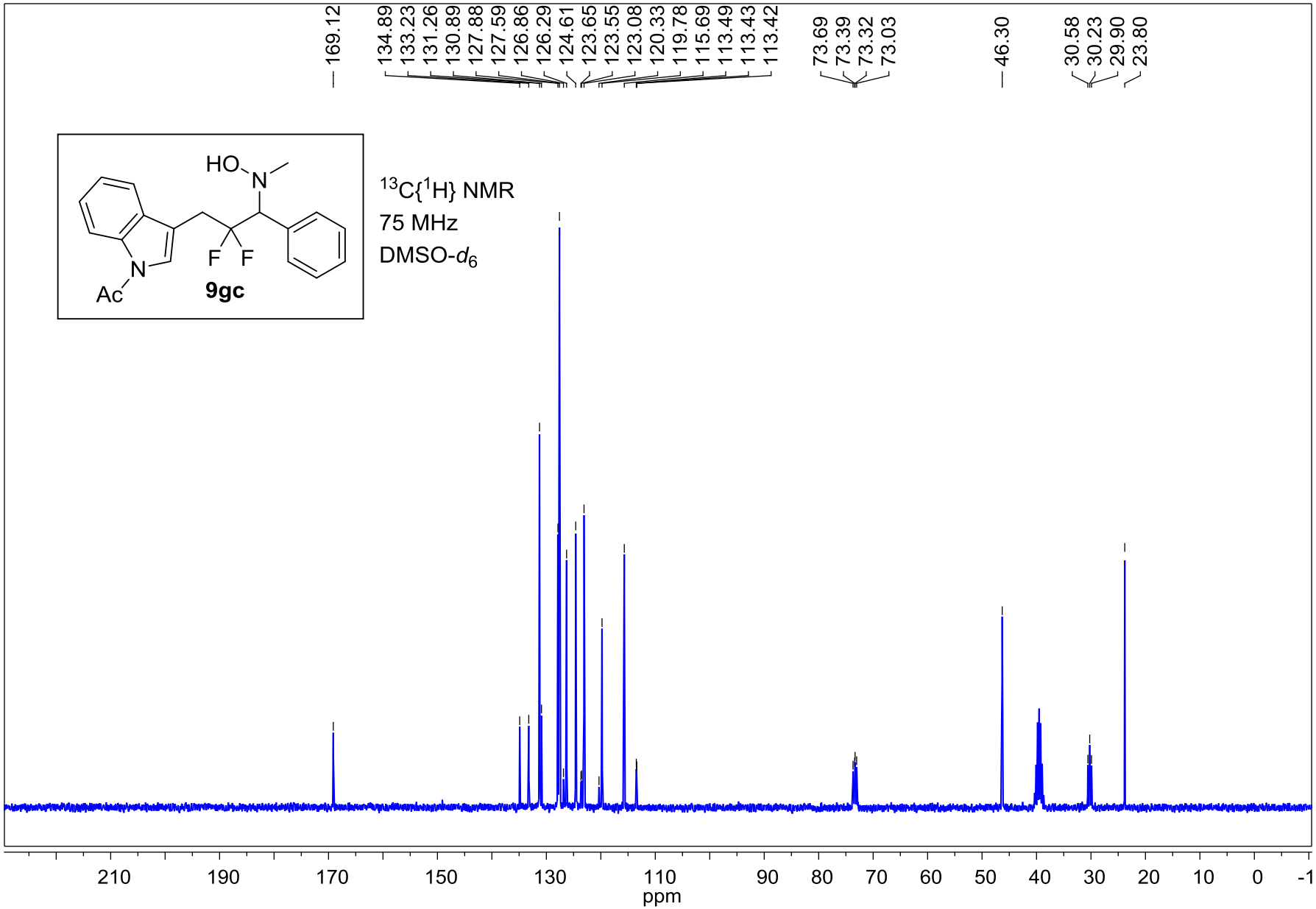

-100.54
-101.35
-101.42
-101.47
-101.51
-101.54
-101.59
-102.44
HO
N
F F
O
9dd
^{19}F NMR
282 MHz
$CDCl_3$
-99.5
-101.0
-102.5
ppm
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
ppm

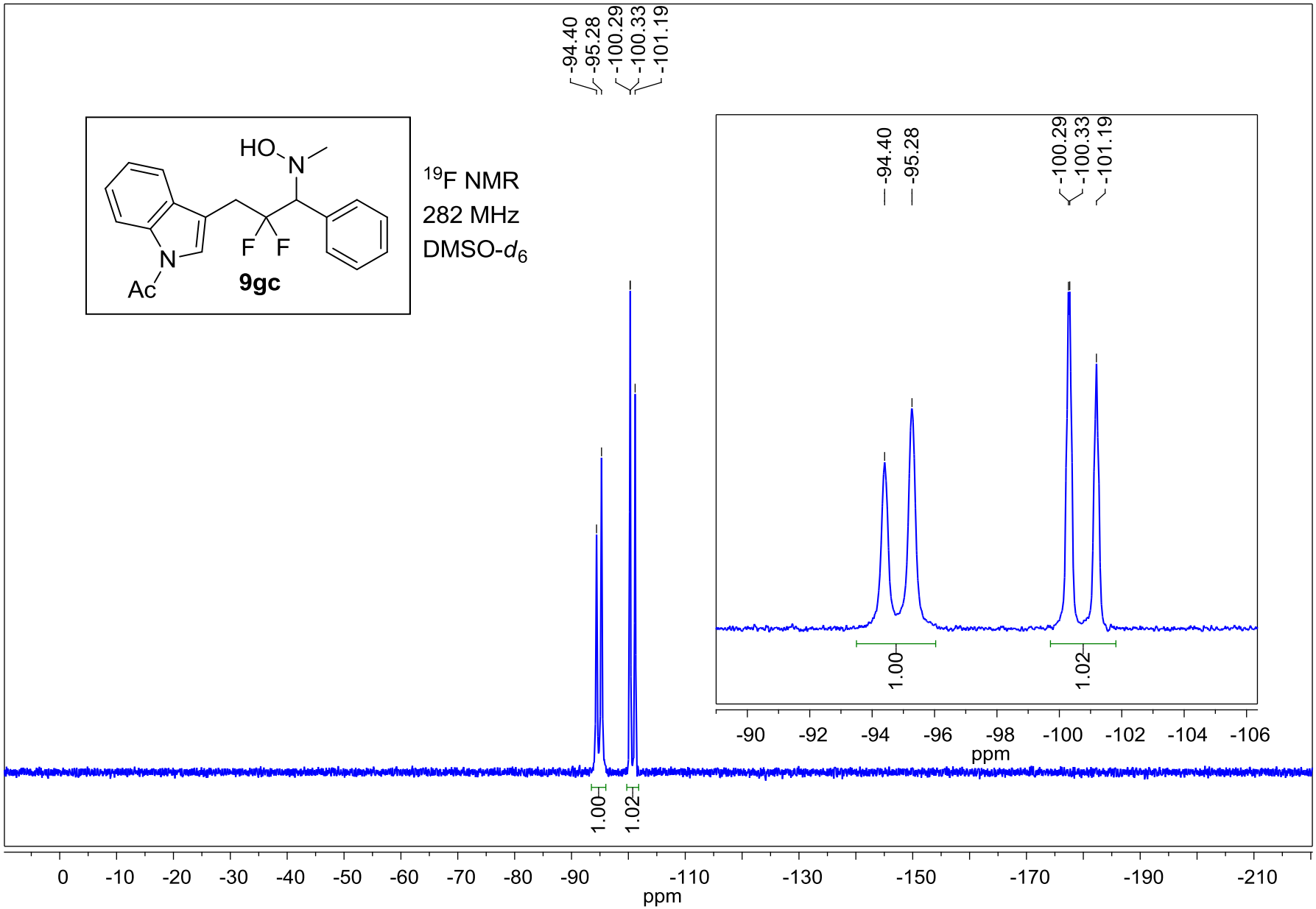

7.64
7.61
7.59
7.56
7.49
7.47
7.44
7.40
7.37
7.34
7.31
7.28
7.04
6.98
6.95
6.94
6.91
6.88
3.93
3.91
3.87
3.82
3.77
3.44
3.44
3.39
3.33
3.27
3.21
2.59
HO
N
OMe
OMe
F
F
Ph
9bb
1H NMR
300 MHz
CDCl3
1.99
2.12
2.10
0.89
2.21
1.02
1.01
1.08
0.24
2.58
3.13
1.09
2.06
2.97
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

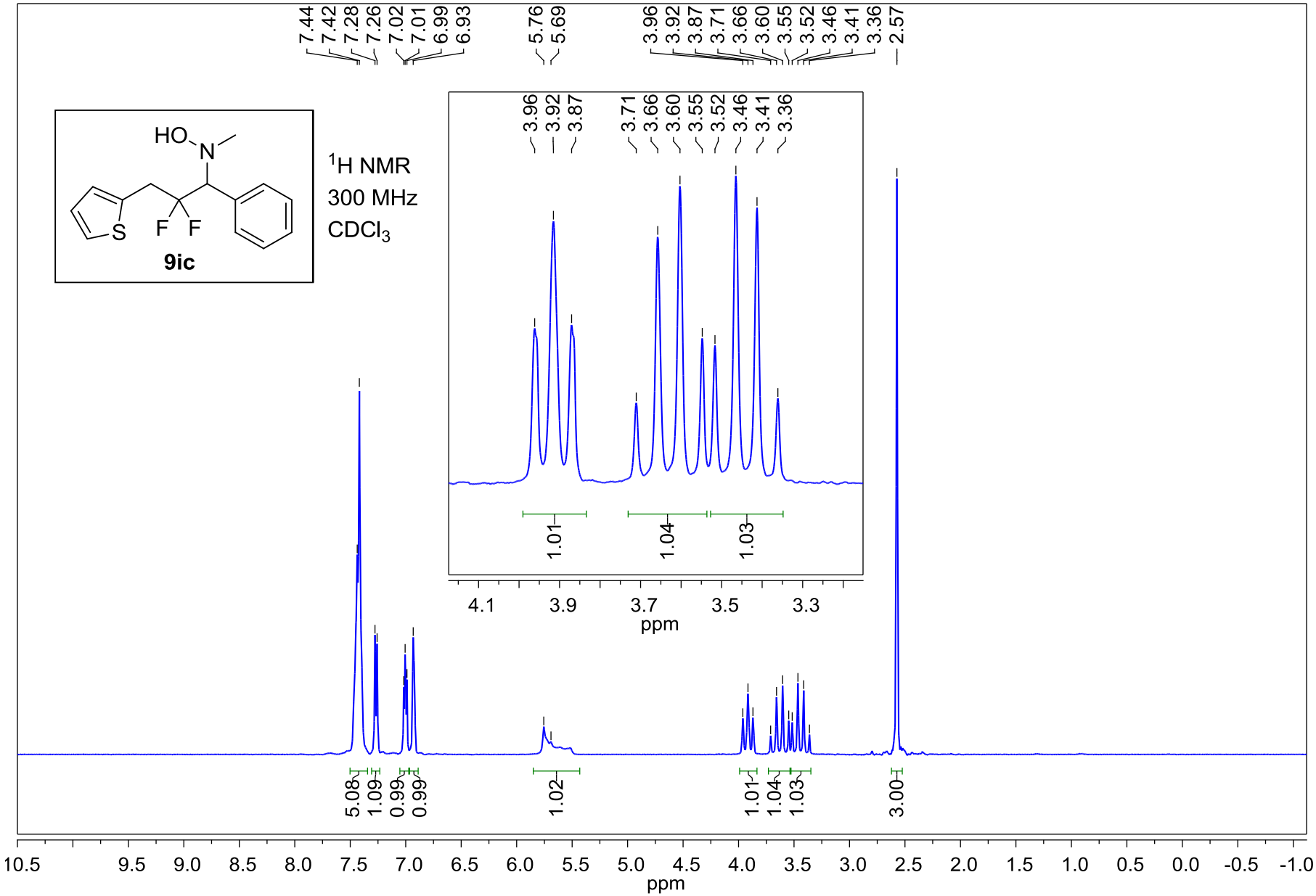

149.39
148.67
140.69
140.17
132.11
132.05
131.16
128.83
127.37
127.04
127.00
124.46
124.00
123.50
114.08
110.64
77.58
77.16
76.74
74.21
73.91
73.60
55.96
55.84
46.29
41.92
41.59
41.26
HO
N
OMe
F F
OMe
Ph
9bb
13C{1H} NMR
75 MHz
CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

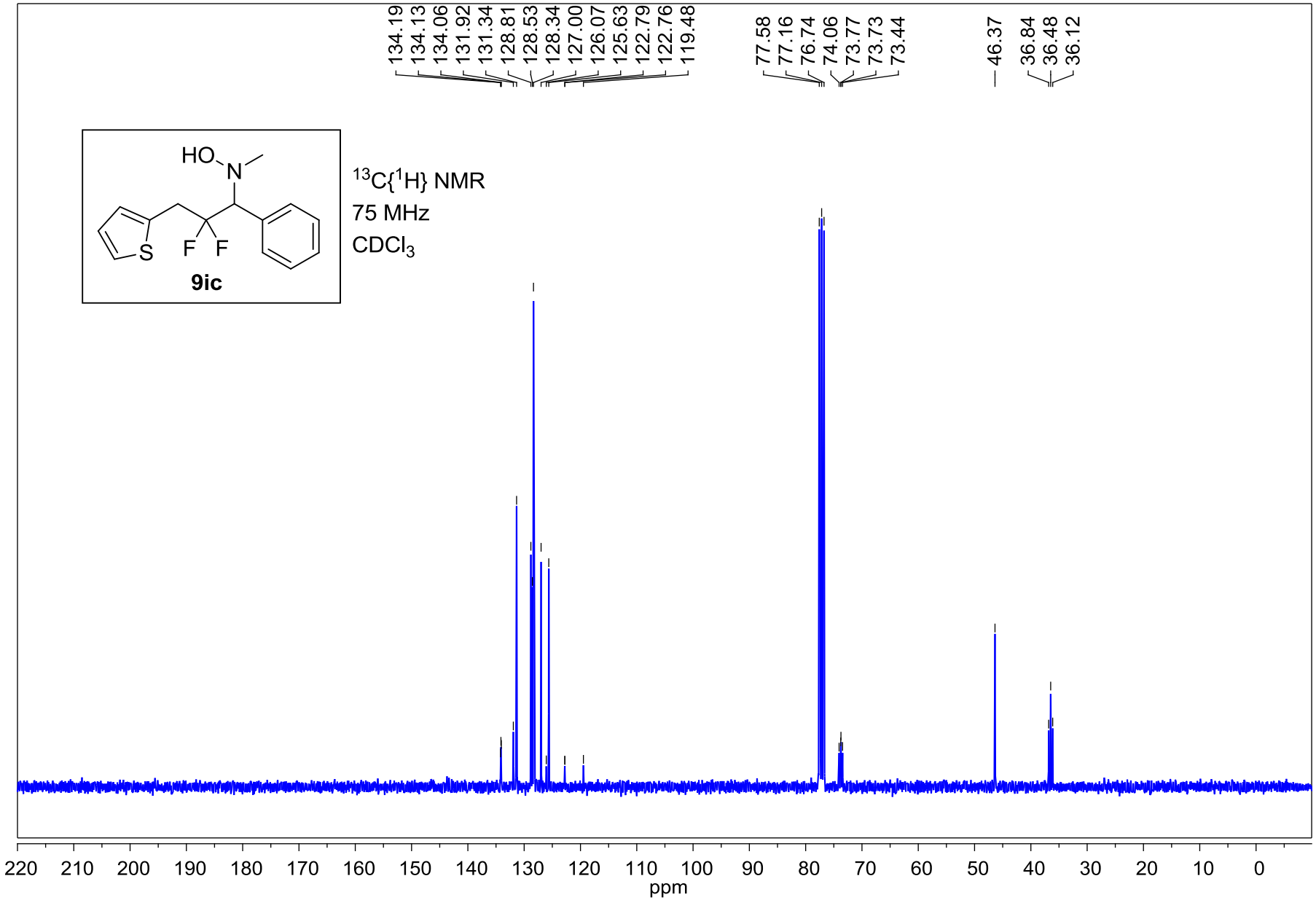

-99.89
-99.95
-100.78
-100.83
-101.80
HO
N
OMe
F F
OMe
Ph
9bb
19F NMR
282 MHz
CDCl3
-98
-99
-100
-101
-102
-103
ppm
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

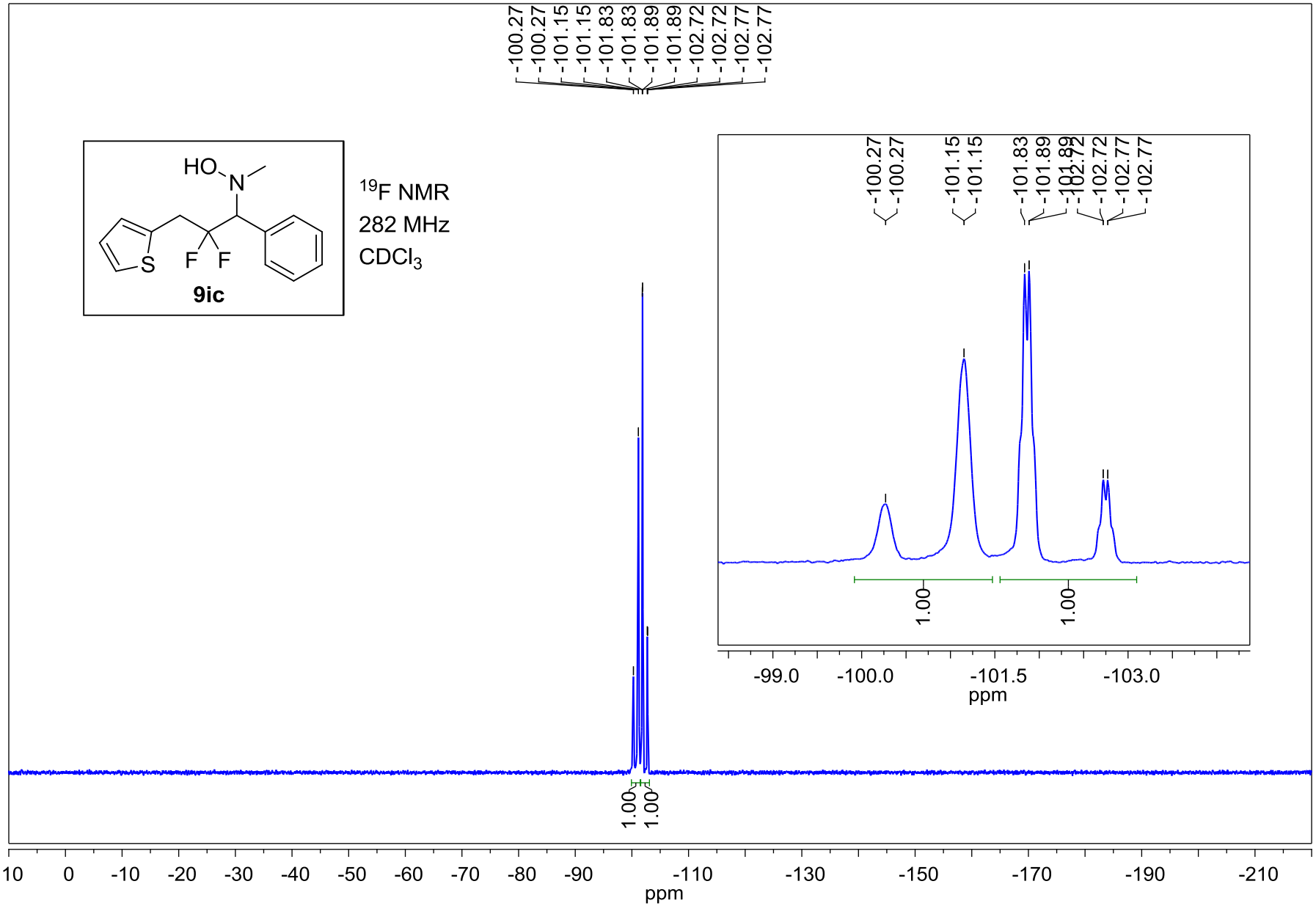

8.35
8.32
7.68
7.66
7.54
7.53
7.52
7.35
7.34
7.33
7.30
7.28
7.25
4.10
4.08
4.04
4.01
3.71
3.69
3.65
3.60
3.59
3.57
3.36
2.63
2.50
2.41
HO
N
F F
N
Ac
9gc
1H NMR
300 MHz
DMSO-d6
2.03
2.11
2.07
5.16
1.00
2.03
2.99
3.00
1.00
ppm
ppm

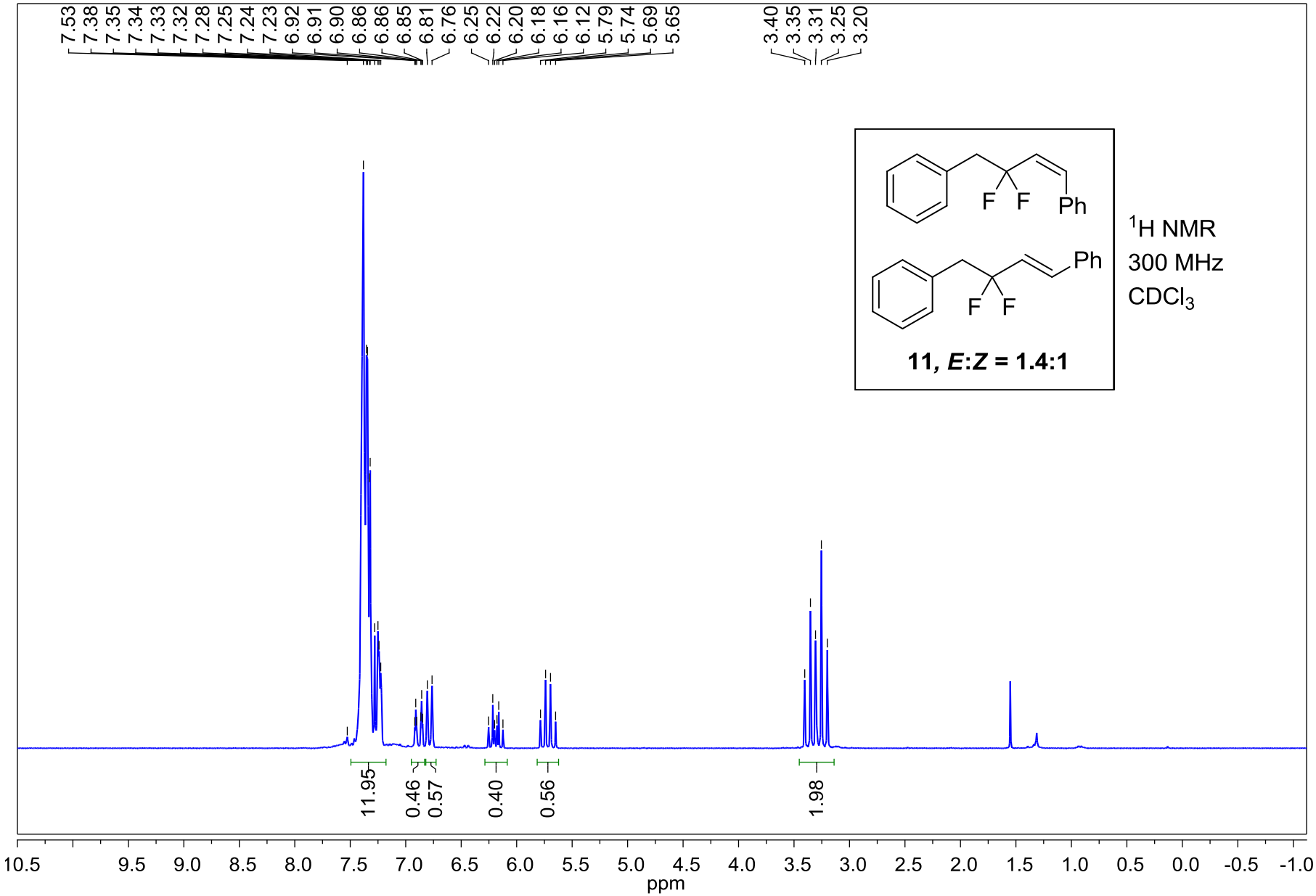

169.12
134.89
133.23
131.26
130.89
127.88
127.59
126.86
126.29
124.61
123.65
123.55
123.08
120.33
119.78
115.69
113.49
113.43
113.42
73.69
73.39
73.32
73.03
46.30
30.58
30.23
29.90
23.80
HO
N
F F
N
Ac
9gc
13C{1H} NMR
75 MHz
DMSO-d6
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

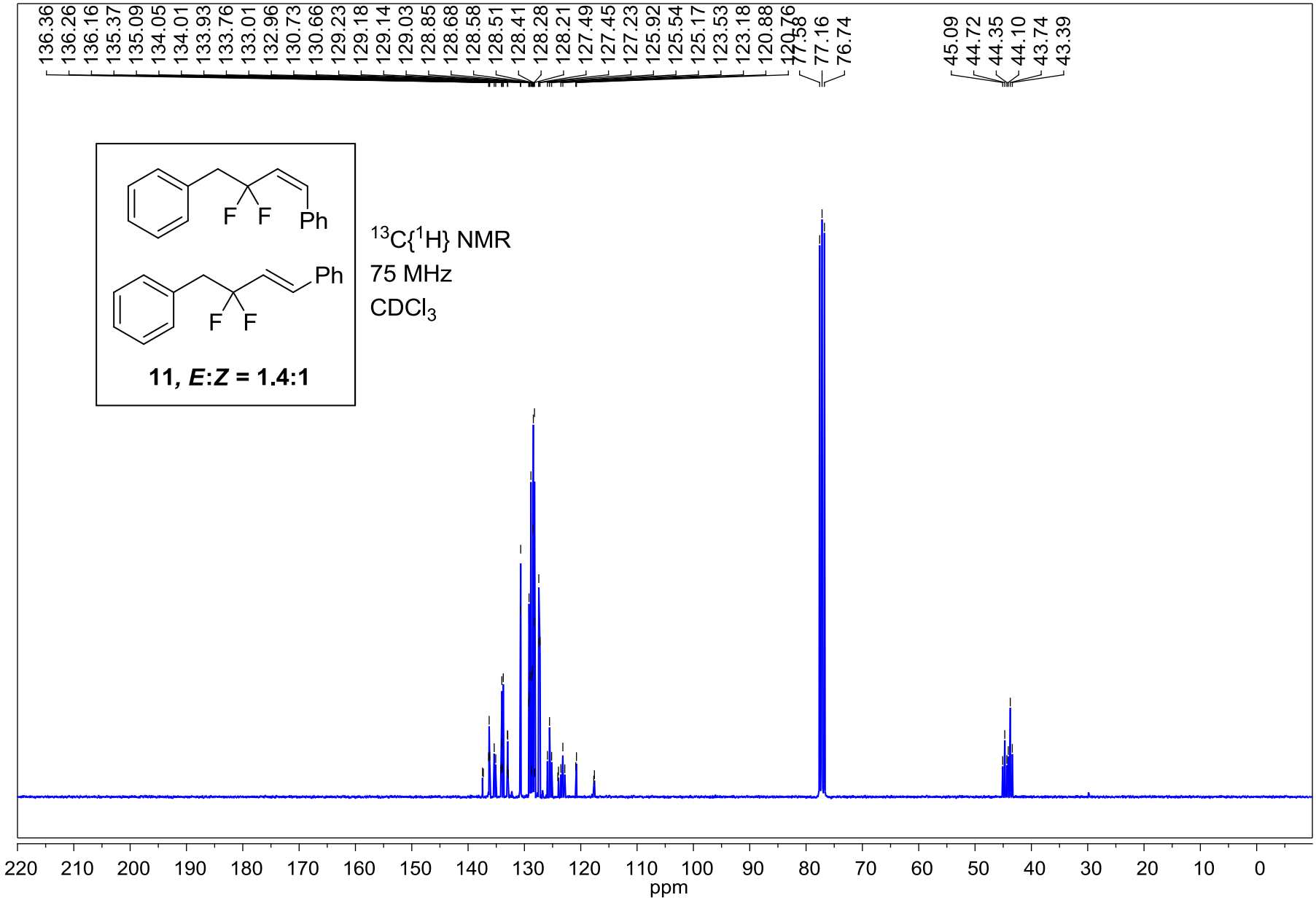

-94.40
-95.28
-100.29
-100.33
-101.19
HO
N
F F
N
Ac
9gc
^{19}F NMR
282 MHz
DMSO-d_6
1.00
1.02
ppm
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
-90 -92 -94 -96 -98 -100 -102 -104 -106

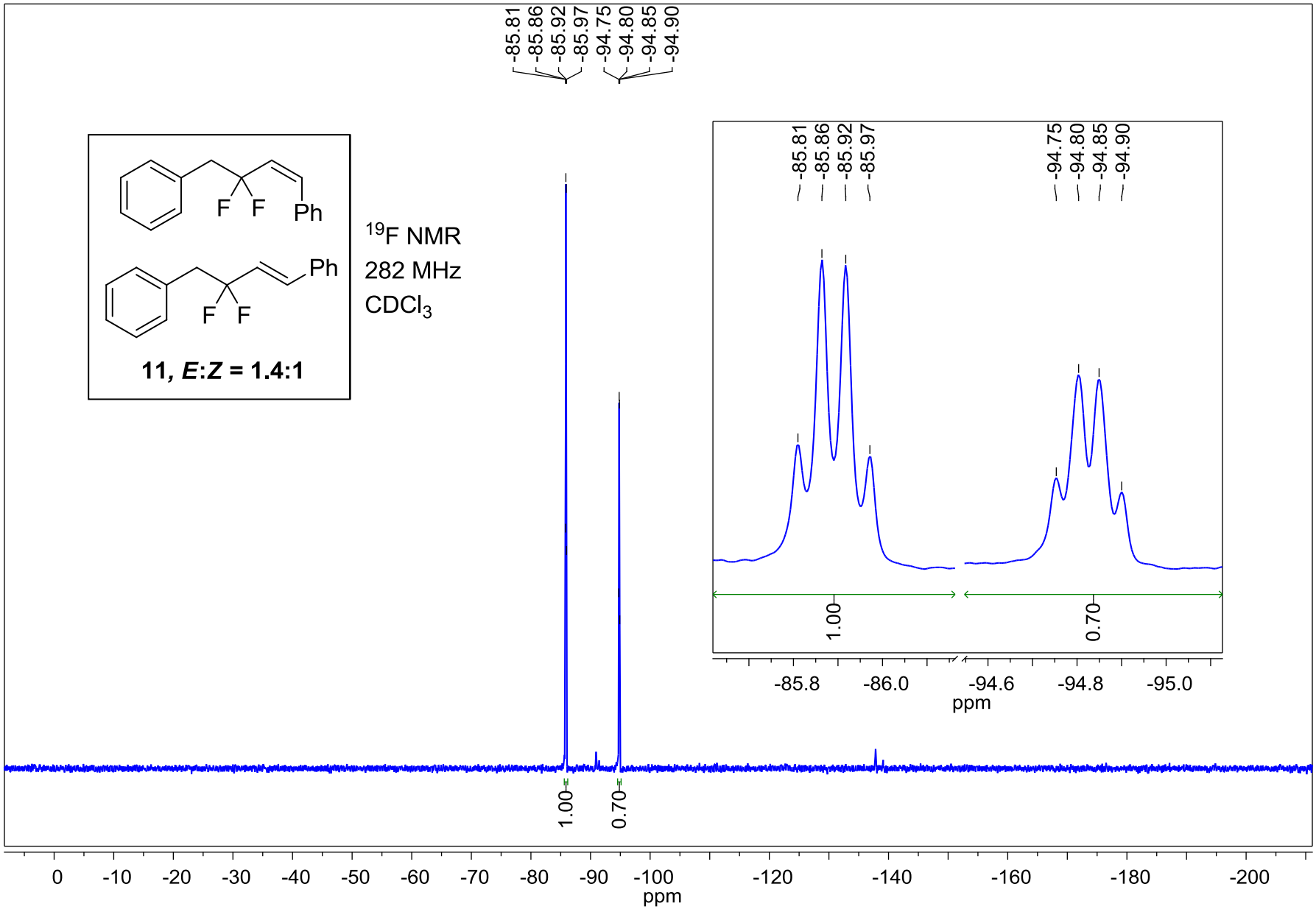

7.44
7.42
7.28
7.26
7.02
7.01
6.99
6.93
5.76
5.69
3.96
3.92
3.87
3.71
3.66
3.60
3.55
3.52
3.46
3.41
3.36
2.57
HO
N
S
F
F
9ic
1H NMR
300 MHz
CDCl3
1.01
1.04
1.03
4.1
3.9
3.7
3.5
3.3
ppm
5.08
1.09
0.99
0.99
1.02
1.01
1.04
1.03
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

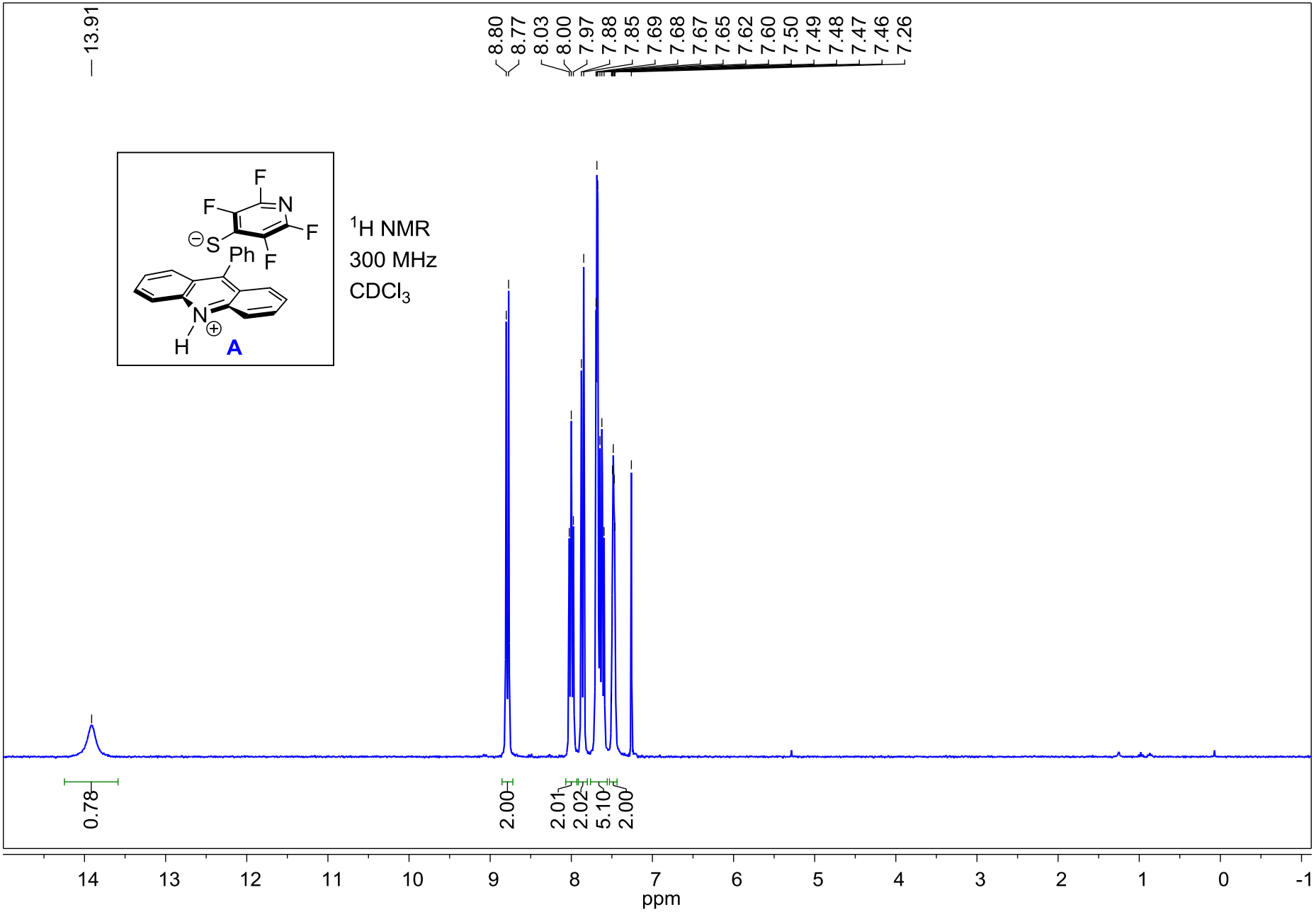

134.19
134.13
134.06
131.92
131.34
128.81
128.53
128.34
127.00
126.07
125.63
122.79
122.76
119.48
77.58
77.16
76.74
74.06
73.77
73.73
73.44
46.37
36.84
36.48
36.12
HO
N
S
F
F
9ic
13C{1H} NMR
75 MHz
CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

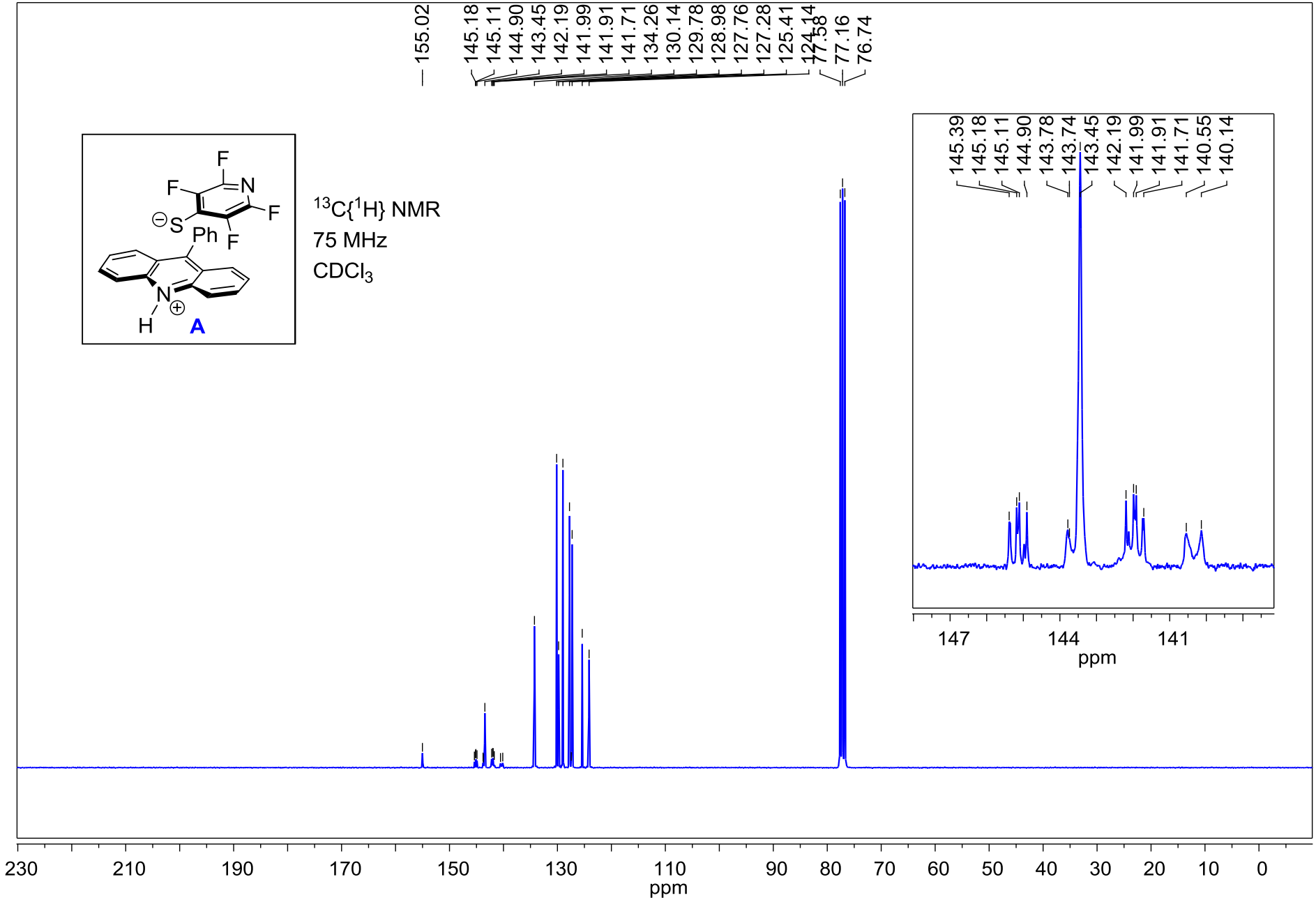

-100.27
-100.27
-101.15
-101.15
-101.83
-101.83
-101.89
-101.89
-102.72
-102.72
-102.77
-102.77
HO
N
S
F
F
9ic
^{19}F NMR
282 MHz
$CDCl_3$
1.00
1.00
-99.0
-100.0
-101.5
-103.0
ppm
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm


7.53
7.38
7.35
7.34
7.33
7.32
7.28
7.25
7.24
7.23
6.92
6.91
6.90
6.86
6.86
6.85
6.81
6.76
6.25
6.22
6.20
6.18
6.16
6.12
5.79
5.74
5.69
5.65
3.40
3.35
3.31
3.25
3.20
F F Ph
Ph
F F
11, E:Z = 1.4:1
1H NMR
300 MHz
CDCl3
11.95
0.46
0.57
0.40
0.56
1.98
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm


136.36
136.26
136.16
135.37
135.09
134.05
134.01
133.93
133.76
133.01
132.96
130.73
130.66
129.23
129.18
129.14
129.03
128.85
128.68
128.58
128.51
128.41
128.28
128.21
127.49
127.45
127.23
125.92
125.54
125.17
123.53
123.18
120.88
120.76
77.58
77.16
76.74
45.09
44.72
44.35
44.10
43.74
43.39
F F Ph
Ph
F F
11, E:Z = 1.4:1
13C{1H} NMR
75 MHz
CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


-85.81
-85.86
-85.92
-85.97
-94.75
-94.80
-94.85
-94.90
F F Ph
Ph
F F
11, E:Z = 1.4:1
19F NMR
282 MHz
CDCl3
1.00
0.70
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
ppm
-85.8
-86.0
-94.6
-94.8
-95.0


13.91
8.80
8.77
8.03
8.00
7.97
7.88
7.85
7.69
7.68
7.67
7.65
7.62
7.60
7.50
7.49
7.48
7.47
7.46
7.26
F
F
N
F
S
Ph
F
N
H
A
1H NMR
300 MHz
CDCl3
0.78
2.00
2.01
2.02
5.10
2.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm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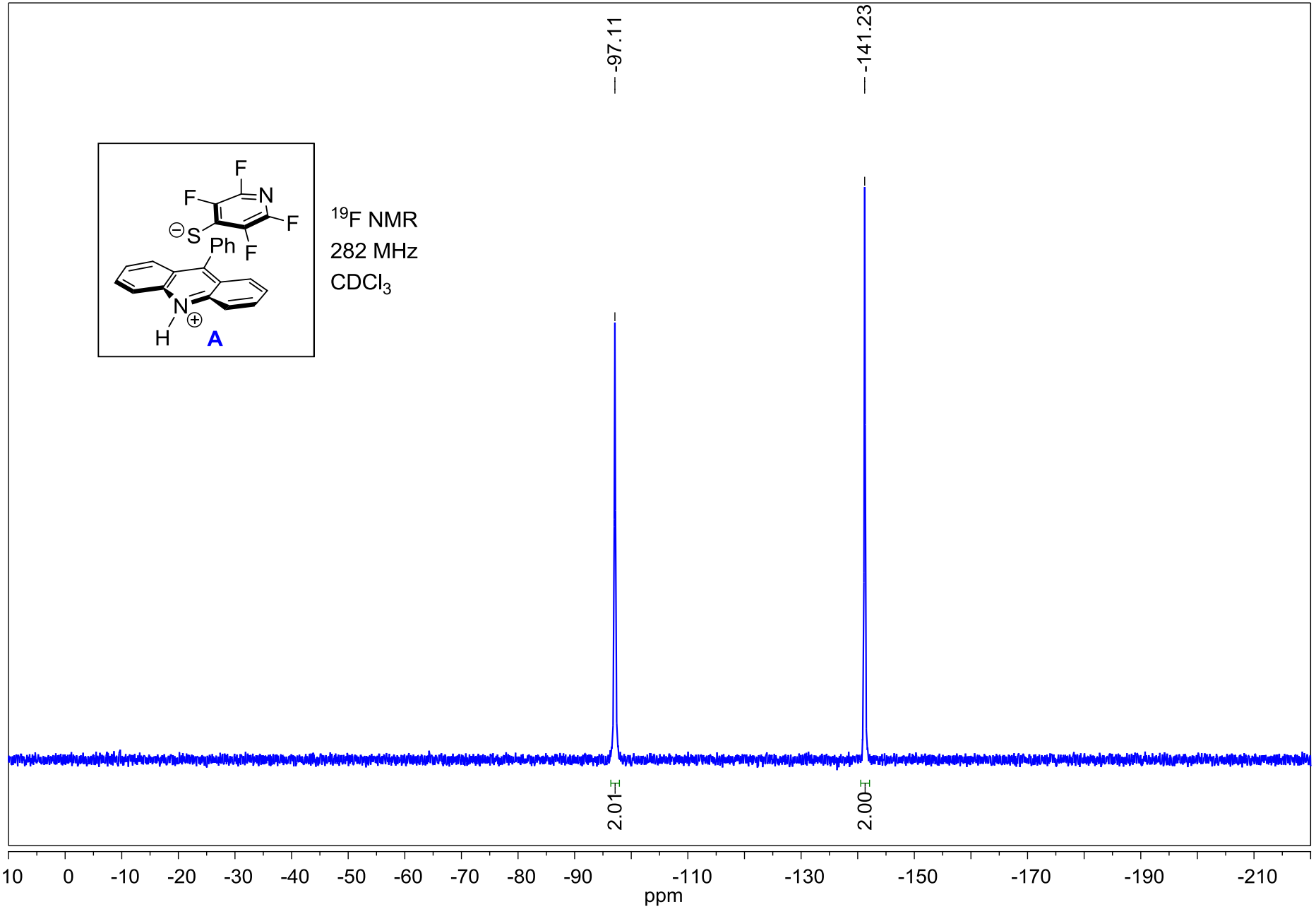
145.18
145.11
144.90
143.45
142.19
141.99
141.91
141.71
134.26
130.14
129.78
128.98
127.76
127.28
125.41
124.14
77.58
77.16
76.74
F
F
N
F
S
Ph
F
N
H
A
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
145.39
145.18
145.11
144.90
143.78
143.74
143.45
142.19
141.99
141.91
141.71
140.55
140.14
147
144
141
ppm
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
ppm


-97.11
-141.23
F
F
N
F
S
Ph
F
N
H
A
^{19}F NMR
282 MHz
$CDCl_3$
2.01
2.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm