Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Fluoroalkyl sulfides as photoredox-active coupling reagents for alkene difunctionalization

Mikhail D. Kosobokov, Mikhail O. Zubkov, Vitalij V. Levin, Vladimir A. Kokorekin, Alexander D. Dilman*

N. D. Zelinsky Institute of Organic Chemistry, 119991 Moscow, Leninsky prosp. 47, Russian Federation.

Content

General methods

All reactions were performed under an argon atmosphere. DMSO was distilled from CaH_2 under vacuum and stored over MS 4Å. 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 basic 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, setup described on Figure S1 was used.

Reaction setup

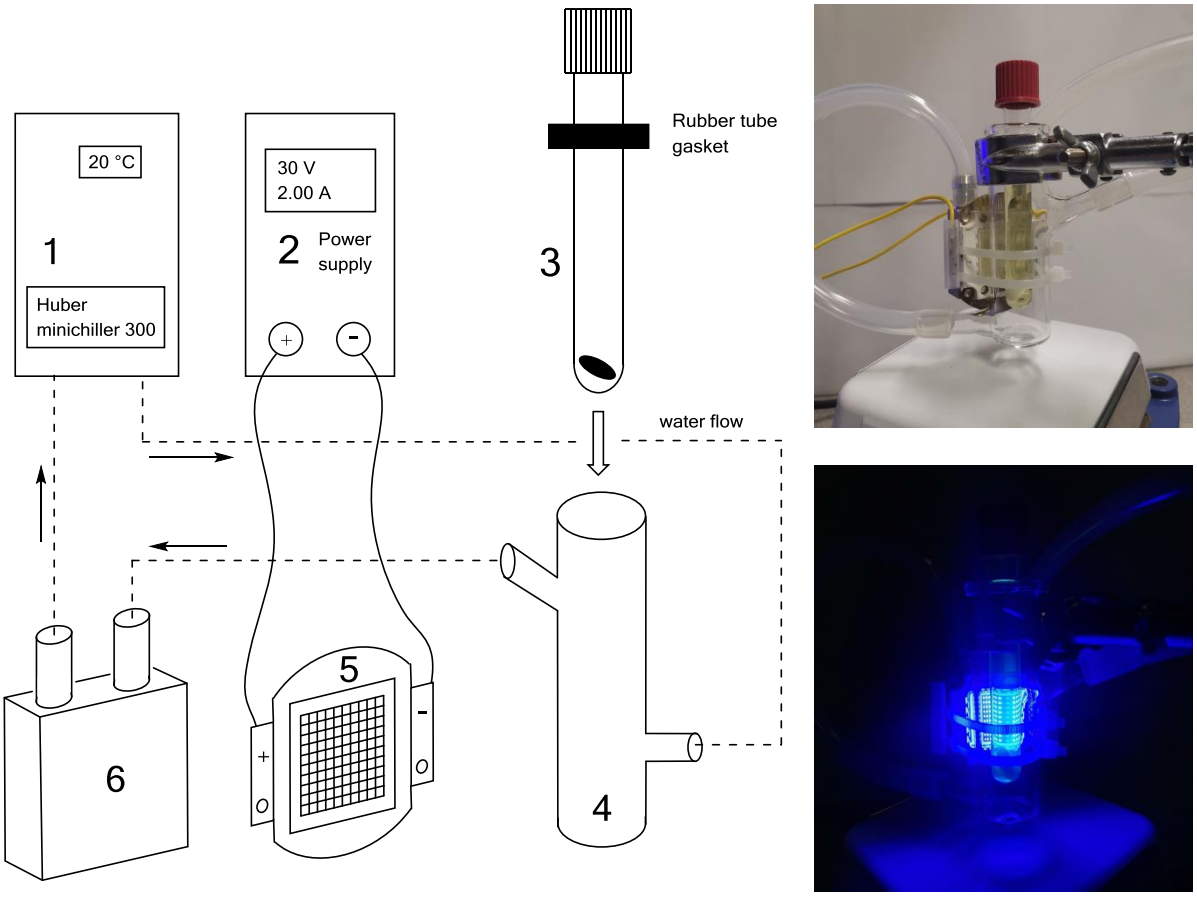


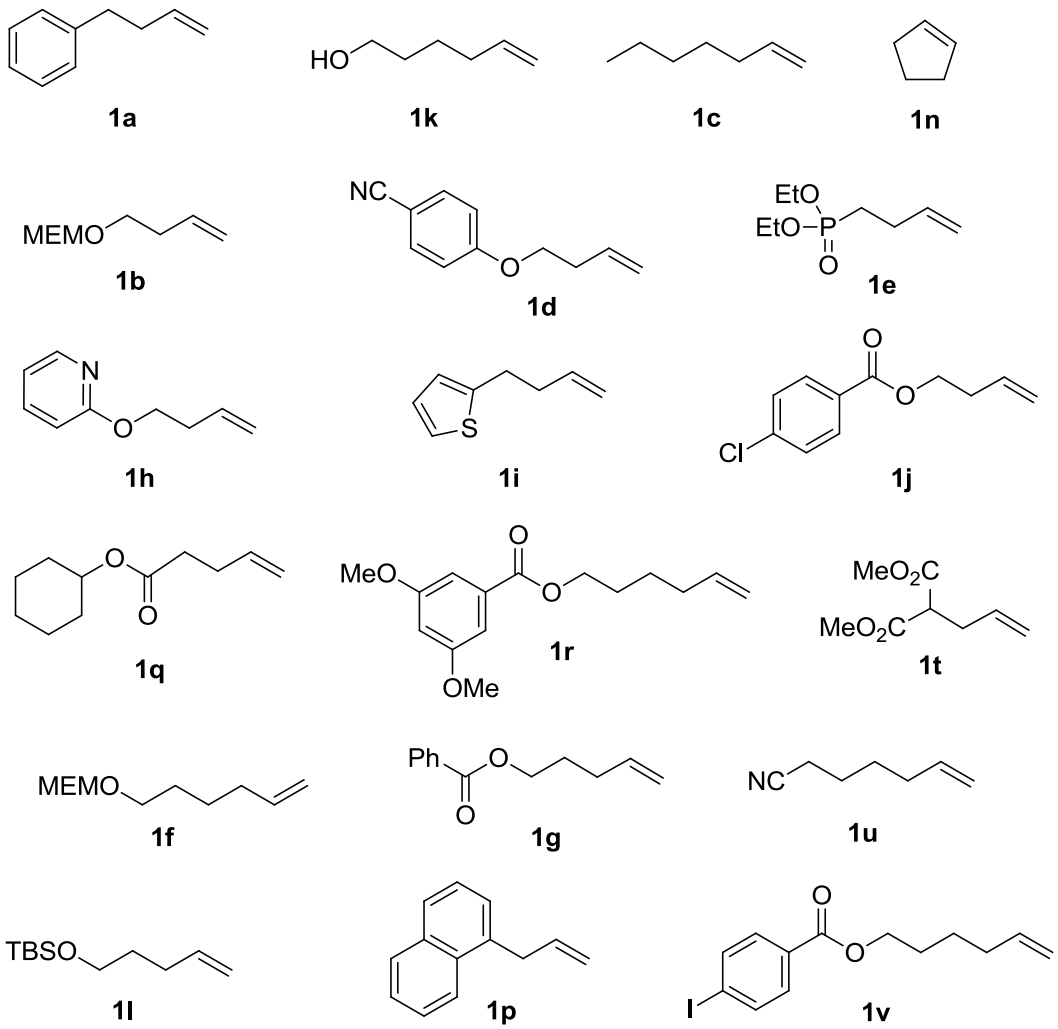
Figure S1. Photoreaction setup:

1. Flow thermostat (Huber Minichiller OLE 300)
2. Power supply (31V/3A)
3. Duran screw cap culture tube (cat #261351258)
4. Glassware jacket
5. LED chip Hontiey 100 W/455 nm
6. Water liquid cooling block (40×40×12 mm).

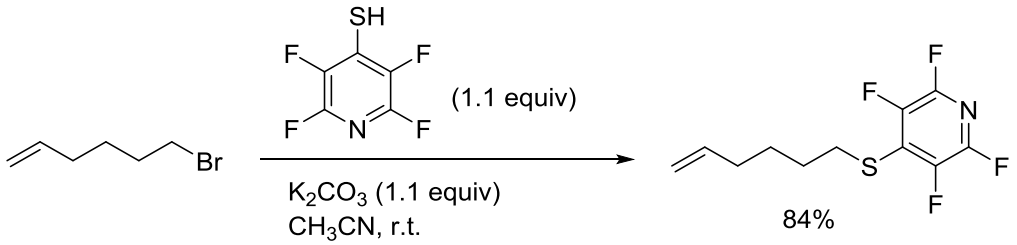
   Water block (6) and LED chip (5) should be connected with heat conductive glue.

Starting materials

Compounds **1a**, **1k, 1c** and **1n** were purchased from Acros Organics or ABCR and distilled before use. Compounds **1b**[1], **1d**[2], **1g**[2], **1e**[3], **1f**[4], **1h**[5], **1i**[6], **1j**[7], **1l**[8], **1p**[9], **1q**[10], **1t**[11], **1u**[12], **1v**[13], **1w**[15] were prepared according to literature procedures.



2,3,5,6-Tetrafluoro-4-(hex-5-en-1-ylthio)pyridine (1m).



2,3,5,6-Tetrafluoropyridine-4-thiol (2.0 g, 11 mmol) was added dropwise to the mixture of dry potassium carbonate (1.52 g, 11 mmol), 6-bromohex-1-ene (1.63 g, 10 mmol) and anhydrous acetonitrile (20 mL) at room temperature. The reaction mixture was stirred for 18 h at room temperature.

For the workup, the mixture was quenched with water (60 mL) and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was distilled in a Hickman distillation head T_{bath} = 140 – 150 °C (0.89 Torr).

Yield 2.23 g (84%). Colorless liquid.

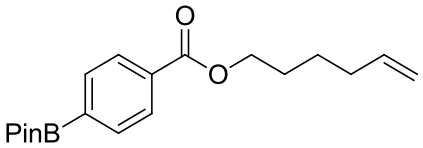
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.76 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.06 – 4.93 (m, 2H), 3.18 (t, *J* = 7.2 Hz, 2H), 2.08 (q, *J* = 7.2 Hz, 2H), 1.75 – 1.61 (m, 2H), 1.61 – 1.47 (m, 2H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.6 (dm, *J* = 245.7 Hz), 141.1 (dm, *J* = 255.8 Hz), 138.0, 132.4 – 131.2 (m), 115.3, 33.2 – 33.0 (m), 33.1, 29.3, 27.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -92.4 (td, *J* = 29.6, 13.6 Hz, 2F), -139.5 (td, *J* = 29.6, 13.6 Hz, 2F).

HRMS (ESI): calcd for $C_{11}H_{12}F_4NS$ (M+H) 266.0621, found 266.0611.

Hex-5-en-1-yl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (1o).



Compound **1o** was prepared according to modified literature procedure.[16]

Round-bottom flask was charged with $[Pd(dppf)Cl_2]\times 2CH_2Cl_2$ (49 mg, 3 mol%), KOAc (588 mg, 6 mmol), Pin_2B_2 (610 mg, 2.4 mmol), DMSO (20 mL) and compound **1r** (660 mg, 2 mmol). The mixture was stirred at 110 °C for 18 h under argon, then cooled to room temperature and diluted with water (50 mL). The mixture was extracted with methyl *tert*-butyl ether (4×10 mL). The combined organic phases were filtered through Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel.

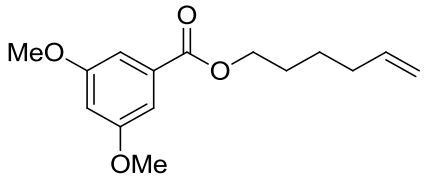
Yield 317 mg (48%). Colorless oil. Chromatography: EtOAc/Hexane, 1/5. R_f 0.48 (EtOAc/Hexane, 1/5).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 8.1 Hz, 2H), 5.82 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.12 – 4.93 (m, 2H), 4.33 (t, *J* = 6.9 Hz, 2H), 2.13 (q, *J* = 6.9 Hz, 2H), 1.88 – 1.71 (m, 2H), 1.63 – 1.48 (m, 2H), 1.35 (s, *J* = 13.6 Hz, 12H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 166.6, 138.3, 134.7, 132.7, 128.6, 114.9, 84.2, 65.0, 33.4, 28.2, 25.3, 24.9.

HRMS (ESI): calcd for $C_{19}H_{28}BO_4$ (M+H) 331.2079, found 331.2082.

Hex-5-en-1-yl 3,5-dimethoxybenzoate (1r).



Compound **1r** was prepared according to modified literature procedure.[14]

Oxalyl chloride (1.02 mL, 12 mmol) was added dropwise to a solution of 3,5-dimethoxybenzoic acid (1.84 g, 10 mmol) and DMF (39 μL, 0.5 mmol) in dichloromethane (20 mL) at room temperature. The reaction was stirred for 24 h at room temperature and the solvent was evaporated. The residue was diluted with dichloromethane (10 mL), and the solution was added dropwise to a solution of hex-5-en-1-ol (1.20 mL, 10 mmol) and Et_3N (2.09 mL, 15 mmol) in dichloromethane (10 mL), and the mixture was vigorously stirred at room temperature for 1 h.

For the work-up, water (30 mL) was added, and the mixture was extracted with dichloromethane (3×10 mL). The combined organic phases were filtered through Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel.

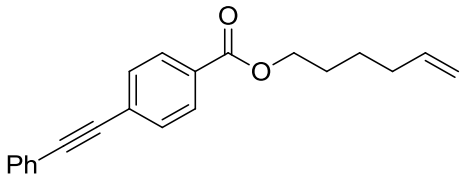
Yield 1.85 g (70%). Colorless oil. Chromatography: EtOAc/Hexane, 1/5. R_f 0.39 (EtOAc/Hexane, 1/5).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, *J* = 2.4 Hz, 2H), 6.63 (t, *J* = 2.4 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.09 – 4.92 (m, 2H), 4.30 (t, *J* = 6.7 Hz, 2H), 3.81 (s, 6H), 2.18 – 2.05 (m, 2H), 1.84 – 1.71 (m, 2H), 1.60 – 1.48 (m, 2H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 166.5, 160.7, 138.4, 132.5, 115.0, 107.3, 105.5, 65.2, 55.6, 33.4, 28.2, 25.4.

HRMS (ESI): calcd for $C_{15}H_{21}O_4$ (M+H) 265.1434, found 265.1434.

Hex-5-en-1-yl 4-(phenylethynyl)benzoate (1s).



Compound **1s** was prepared according to modified literature procedure.[17]

CuI (53 mg, 0.28 mmol, 0.14 equiv), $PdCl_2(PPh_3)_2$ (84 mg, 0.12 mmol, 0.06 equiv), and NEt_3 (1.08 mL, 7.8 mmol, 3.9 equiv) were successively added to a solution of phenyl acetylene (1.5 mL, 2.6 mmol, 1.3 equiv) and compound **1r** (660 mg, 2 mmol, 1.0 equiv) in anhydrous THF (18 mL). Upon addition of NEt_3, the reaction mixture turned dark black. The mixture was stirred at room temperature until the solution was no longer dark (*ca.* 2 h), at which point the reaction was quenched with methanol (5 mL), evaporated to dryness, and purified by silica gel chromatography.

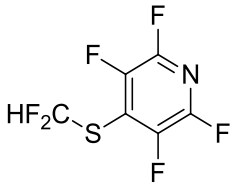
Yield 517 mg (85%). Yellow oil. Chromatography: EtOAc/Hexane, 1/10. R_f 0.29 (EtOAc/Hexane, 1/10).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.52 (m, 2H), 7.40 – 7.34 (m, 3H), 5.83 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.11 – 4.94 (m, 2H), 4.34 (t, *J* = 6.9 Hz, 2H), 2.14 (q, *J* = 6.9 Hz, 2H), 1.87 – 1.73 (m, 2H), 1.63 – 1.50 (m, 2H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 166.3, 138.5, 131.9, 131.6, 130.0, 129.6, 128.9, 128.6, 128.1, 122.9, 115.1, 92.4, 88.8, 65.2, 33.5, 28.3, 25.5.

HRMS (ESI): calcd for $C_{21}H_{21}O_2$ (M+H) 305.1536, found 305.1537.

4-[(Difluoromethyl)thio]-2,3,5,6-tetrafluoropyridine (2a).



Compound **2a** was prepared according to modified literature procedure.[18]

2,3,5,6-Tetrafluoropyridine-4-thiol (9.16 g, 50 mmol, 1 equiv) was added to a stirred suspension of K_2CO_3 (7.59 g, 55 mmol, 1.10 equiv) in dry methanol (30.0 mL). After gas evolution ceased (around 15 min), the reaction flask was immersed into ice/water bath. $TMSCF_2Br$ (15.23 g, 75 mmol, 1.5 equiv) was added dropwise keeping the temperature below 5 °C (internal temperature). The mixture was stirred for additional 5 min at 0 °C, and then at room temperature for 1 h. For the workup, the mixture was diluted with water (100 mL), and crude product was separated as a bottom layer. The aqueous phase was extracted with small amount of DCM (3×3 mL), the combined organics were dried over Na_2SO_4 and product was fractionally distilled under reduced pressure.

Yield 9.33 g (80%). Colorless liquid. Bp = 105 – 107 °C (130 Torr).

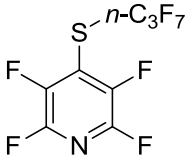
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (t, *J* = 56.4 Hz, 1H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.8 (dm, *J* = 246.9 Hz), 142.3 (dm, *J* = 262.1 Hz) 117.5 (tt, *J* = 281.5, 3.5 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -88.9 – -89.3 (m, 2F), -91.2 (d, *J* = 56.4 Hz, 2F), -133.9 – -134.3 (m, 2F).

Calcd for C_6HF_6NS (233.13): C 30.91, H 0.43, N 6.01; found: C 30.85, H 0.27, N 6.35

2,3,5,6-Tetrafluoro-4-[(perfluoropropyl)thio]pyridine (2b).



n-Perfluoropropyl iodide (5.92 g, 20 mmol, 1 equiv) was added to a stirred suspension of PyfSK (5.31 g, 24 mmol, 1.2 equiv) in dry acetonitrile (20.0 mL). The reaction flask was immersed into ice/water bath and mixture was irradiated with 60 W 400 nm LED chip for 15 min. Abundant precipitate of KI was instantly formed. For the workup, reaction mixture was diluted with 100 ml of water and bottom heavy organic layer was collected. The aqueous phase was extracted with small amount of DCM (3×3 mL), the combined organics were dried over Na_2SO_4 and product was fractionally distilled under reduced pressure. B.P. = 101 – 102 °C (118 Torr).

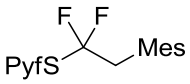
Yield 5.48 g (78%). Colorless liquid.

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 146.0 – 145.2 (m), 142.6 – 141.7 (m), 121.8 (tt, *J* = 311.4, 41.9 Hz), 117.6 (qt, *J* = 294.8, 36.9 Hz), 117.7 – 116.8 (m), 108.6 (tm, *J* = 266.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 – -81.3 (m, 3F), -85.7 – -86.1 (m, 2F), -87.9 – -88.4 (m, 2F), -124.6 – -125.0 (m, 2F), -131.1 – -131.7 (m, 2F).

MS (EI): calcd for $C_8F_{11}NS$ (M+) 350.96, found 351.02.

4-[(1,1-Difluoro-2-mesitylethyl)thio]-2,3,5,6-tetrafluoropyridine (2c).[20]



Yield 2.26 g (62%). White crystals. Mp = 120-122 °C. Chromatography: CH_2Cl_2/Hexane, 1/3. R_f 0.6 (CH_2Cl_2/Hexane, 1/3).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (s, 2H), 3.69 (t, *J* = 15.4 Hz, 2H), 2.38 (s, 6H), 2.30 (s, 3H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.8 – 144.8 (m), 142.4 – 141.4 (m), 138.6, 138.1, 129.7 (t, *J* = 288.3 Hz), 129.6, 125.2, 121.8 – 120.2 (m), 38.9 (t, *J* = 23.0 Hz), 21.0, 20.7.

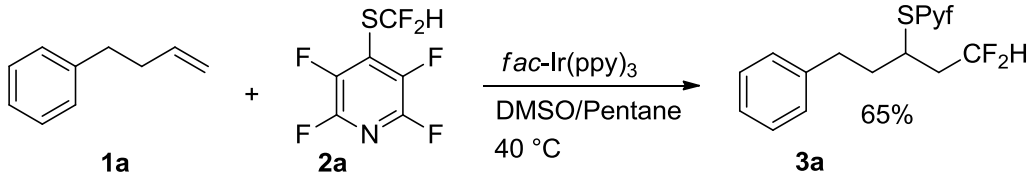
^{19}F NMR (282 MHz, $CDCl_3$) δ -63.7 – -64.1 (m, 2F), -89.4 – -89.9 (m, 2F), -132.3 – -132.8 (m, 2F).

HRMS (ESI): calcd for $C_{16}H_{14}F_6NS$ (M+H) 366.0746, found 366.0732.

Radical difunctionalization (General procedure)

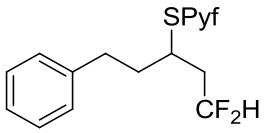
Alkene **1** (0.5 mmol, 1 equiv) and compound **2a** (140 mg, 0.6 mmol, 1.2 equiv) were successively added to a solution of *fac*-Ir(ppy)$_3$ (0.8 mg, 0.25 mol %) in DMSO (4 mL). The mixture was irradiated in a setup shown in Figure S1 (60W/455 nm/20 °C) for 18 h. For the work-up, the mixture was diluted with water (3 mL) and extracted with methyl *tert*-butyl ether (3×3 mL) The combined organic phases were filtered through Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel.

Large scale procedure for the synthesis of 3a



A solution of **1a** (1.32 g, 10 mmol, 1 equiv) and **2a** (2.8 g, 12 mmol, 1.2 equiv) in DMSO (20 mL) was placed in a 100 mL Erlenmeyer flask equipped with stirring bar and efficient condenser. Photocatalyst *fac*-Ir(ppy)$_3$ (3 mg, 0.01 mmol) was added followed by addition of pentane (20 mL). Biphasic reaction mixture was irradiated with (60W/455 nm/20 °C). Due to irradiation, the temperature of the reaction mixture increased to 36 °C, which was maintained by refluxing pentane. After 24 h, additional portions of **2a** (0.5 g, 2.15 mmol, 0.215 equiv) and *fac*-Ir(ppy)$_3$ (3 mg, 0.01 mmol) were added, and irradiation was continued for additional 48 hours to achieve full conversion. For the work-up, the mixture was diluted with water (100 mL) and extracted with methyl *tert*-butyl ether (3×30 mL). The combined organic phases were filtered through Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel. Yield 2.37 g (65%).

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



Yield 135 mg (74%). Yellow oil. Chromatography: CH_2Cl_2/Hexane, 1/5. R_f 0.12 (CH_2Cl_2/Hexane, 1/5).

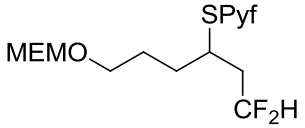
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 3H), 7.20 – 7.13 (m, 2H), 6.08 (tt, *J* = 56.0, 4.5, 1H), 3.81 – 3.68 (m, 1H), 2.96 – 2.75 (m, 2H), 2.42 – 1.92 (m, 4H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.7 (dm, *J* = 247.0 Hz), 141.9 (dm, *J* = 257.1 Hz), 140.1, 129.4 – 128.7 (m), 128.8, 128.4, 126.6, 115.4 (t, *J* = 240.3 Hz), 43.2 – 42.9 (m), 39.9 (t, *J* = 22.3 Hz), 37.6, 32.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.8 (td, *J* = 29.7, 13.3 Hz, 2F), -116.00 (ddt, *J* = 287.8, 56.0, 14.4 Hz, 1F)-117.6 (dddd, *J* = 287.8, 56.0, 19.9, 15.5 Hz, 1F), -136.5 (td, *J* = 29.7, 13.3 Hz, 2F).

HRMS (ESI): calcd for $C_{16}H_{14}F_6NS$ (M+H) 366.0746, found 366.0743.

4-[{1,1-difluoro-6-((2-methoxyethoxy)methoxy)hexan-3-yl}thio]-2,3,5,6-tetrafluoropyridine (3b).



Yield 151 mg (74%). Colorless oil. Chromatography: EtOAc/Hexane, 1/3. R_f 0.17 (EtOAc/Hexane, 1/3).

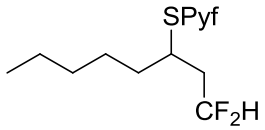
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (tdd, *J* = 56.1, 5.3, 3.9 Hz, 1H), 4.65 (s, 2H), 3.81 – 3.68 (m, 1H), 3.67 – 3.58 (m, 2H), 3.58 – 3.47 (m, 4H), 3.36 (s, 3H), 2.34 – 1.99 (m, 2H), 1.90 – 1.59 (m, 4H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.7 (dm, *J* = 247.5 Hz), 141.9 (dm, *J* = 257.0 Hz), 129.7 – 128.8 (m) 115.3 (t, *J* = 240.2 Hz), 95.6, 71.9, 67.0, 59.1, 43.7 – 43.2 (m), 39.9 (t, *J* = 22.2 Hz), 32.7, 26.5.

^{19}F NMR (282 MHz, $CDCl_3$) δ -91.0 (td, *J* = 29.8, 13.4 Hz, 2F), -116.3 (ddt, *J* = 287.7, 56.1, 14.6 Hz, 1F), -117.8 (dddd, *J* = 287.8, 56.1, 19.3, 15.7 Hz, 1F), -136.8 (td, *J* = 29.8, 13.4 Hz, 2F).

HRMS (ESI): calcd for $C_{15}H_{23}F_6N_2O_3S$ (M+NH_4) 425.1328, found 425.1322.

4-[(1,1-Difluorooctan-3-yl)thio]-2,3,5,6-tetrafluoropyridine (3c).



Yield 124 mg (75%). Colorless oil. Chromatography: EtOAc/Hexane, 1/20. R_f 0.4 (EtOAc/Hexane, 1/20). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 10 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 10% water; t_R = 12.3 min).

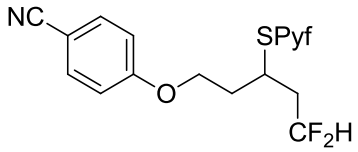
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.03 (tdd, *J* = 56.2, 5.3, 3.9 Hz, 1H), 3.81 – 3.63 (m, 1H), 2.36 – 1.96 (m, 2H), 1.82 – 1.60 (m, 2H), 1.59 – 1.40 (m, 2H), 1.39 – 1.20 (m, 4H), 0.89 (t, *J* = 6.7 Hz, 3H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.7 (dm, *J* = 246.0 Hz), 141.9 (dm, *J* = 256.7 Hz), 129.9 – 129.3 (m), 115.5 (t, *J* = 240.1 Hz), 43.9 – 43.5 (m), 39.9 (t, *J* = 22.2 Hz), 35.9, 31.4, 26.1, 22.5, 14.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ -91.1 (td, *J* = 29.6, 13.4 Hz, 2F), -116.3 (ddt, *J* = 287.7, 56.2, 14.7 Hz, 1F), -117.7 (dddd, *J* = 287.7, 56.2, 20.4, 14.8 Hz, 1F), -137.0 (td, *J* = 29.6, 13.4 Hz, 2F).

HRMS (ESI): calcd for $C_{13}H_{16}F_6NS$ (M+H) 332.0902, found 332.0893.

4-{[5,5-difluoro-3-((perfluoropyridin-4-yl)thio)pentyl]oxy}benzonitrile (3d).



Yield 122 mg (60%). Colorless crystals. Mp 126–128 °C (MeCN). Chromatography: EtOAc/Hexane, 1/2. R_f 0.22 (EtOAc/Hexane, 1/2).

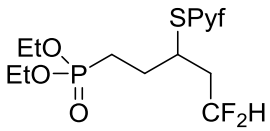
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.15 (tt, *J* = 56.0, 4.0, 1H), 4.29 – 4.10 (m, 2H), 4.07 – 3.93 (m, 1H), 2.45 – 2.16 (m, 3H), 2.16 – 1.96 (m, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 161.2, 143.6 (dm, *J* = 244.4 Hz), 142.0 (dm, *J* = 257.9 Hz), 129.0 – 128.2 (m), 134.2, 119.0, 115.2 (t, *J* = 240.2 Hz), 114.9 (s), 104.9, 64.4, 41.2 – 40.8 (m), 40.2 (t, *J* = 22.6 Hz), 35.5.

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.3 (td, *J* = 29.8, 13.2 Hz, 2F), -116.3 (ddt, *J* = 288.4, 56.0, 14.0 Hz, 1F), -117.8 (dddd, *J* = 288.4, 56.0, 20.6, 14.9 Hz, 1F), -136.2 (td, *J* = 29.8, 13.2 Hz, 2F).

HRMS (ESI): calcd for $C_{17}H_{13}F_6N_2OS$ (M+H) 407.0647, found 407.0640.

Diethyl {5,5-difluoro-3-[(perfluoropyridin-4-yl)thio]pentyl}phosphonate (3e).



Yield 153 mg (72%). Colorless oil. Chromatography: EtOAc/Hexane, 3/1. R_f 0.27 (EtOAc/Hexane, 3/1).

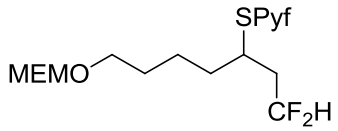
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.01 (tdd, *J* = 56.0, 4.6, 4.1 Hz, 1H) 4.19 – 3.91 (m, 4H), 3.78 – 3.67 (m, 1H), 2.29 – 1.75 (m, 6H), 1.26 (t, *J* = 7.1 Hz, 6H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.6 (dm, *J* = 246.4 Hz), 141.9 (dm, *J* = 257.4 Hz), 128.7 – 127.87 (m), 115.1 (t, *J* = 240.3 Hz), 61.9 (d, *J* = 6.5 Hz), 44.2 – 43.5 (m), 39.5 (t, *J* = 22.5 Hz), 28.8 (d, *J* = 3.8 Hz), 22.6 (d, *J* = 143.1 Hz), 16.4 (d, *J* = 5.9 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.6 (td, *J* = 29.6, 13.3 Hz, 2F), -116.4 (ddt, *J* = 288.2, 56.0, 14.3 Hz, 1F), -117.9 (dddd, *J* = 288.2, 56.0, 20.3, 15.0 Hz, 1F), -136.3 (td, *J* = 29.6, 13.3 Hz, 2F).

HRMS (ESI): calcd for $C_{14}H_{19}F_6NO_3PS$ (M+H) 426.0722, found 426.0712.

4-{[1,1-Difluoro-6-((2-methoxyethoxy)methoxy)hexan-3-yl]thio}-2,3,5,6-tetrafluoropyridine (3f).



Yield 162 mg (77%). Colorless oil. Chromatography: EtOAc/Hexane, 1/3. R_f 0.25 (EtOAc/Hexane, 1/3).

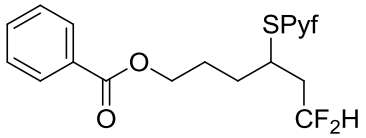
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.01 (tdd, *J* = 56.2, 5.2, 4.0 Hz, 1H), 4.66 (s, 2H), 3.78 – 3.60 (m, 3H), 3.58 – 3.46 (m, 4H), 3.36 (s, 3H), 2.32 – 1.95 (m, 2H), 1.85 – 1.63 (m, 2H), 1.65 – 1.38 (m, 4H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.6 (dm, *J* = 246.2 Hz), 141.8 (dm, *J* = 256.7 Hz), 129.8 – 129.0 (m), 115.3 (t, *J* = 240.2 Hz), 95.6, 71.9, 67.3, 66.9, 59.1, 43.7 – 43.4 (m), 39.8 (t, *J* = 22.2 Hz), 35.6, 29.2, 23.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ -91.0 (td, *J* = 29.2, 13.2 Hz, 2F), -116.3 (ddt, *J* = 287.7, 56.2, 14.3 Hz, 1F), -117.7 (dddd, *J* = 70.5, 56.2, 20.2, 14.6 Hz, 1F), -136.9 (td, *J* = 29.2, 13.2 Hz, 2F).

HRMS (ESI): calcd for $C_{16}H_{22}F_6NO_3S$ (M+H) 422.1219, found 422.1210.

6,6-Difluoro-4-[(perfluoropyridin-4-yl)thio]hexyl benzoate (3g).



Yield 165 mg (78%). Light yellow oil. Chromatography: EtOAc/Hexane, 1/5. R_f 0.31 (EtOAc/Hexane, 1/5).

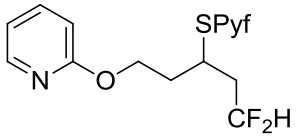
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 6.06 (tdd, *J* = 56.0, 5.3, 3.8 Hz, 1H), 4.36 (t, *J* = 6.0 Hz, 2H), 3.88 – 3.72 (m, 1H), 2.42 – 1.68 (m, 6H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 166.5, 143.7 (dm, *J* = 246.3 Hz), 141.9 (dm, *J* = 256.9 Hz) 133.2, 130.1, 129.5, 129.2 – 128.5 (m), 128.5, 115.3 (t, *J* = 240.3 Hz), 63.9, 43.7 – 43.0 (m), 39.8 (t, *J* = 22.3 Hz), 32.4, 25.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.5 (td, *J* = 29.6, 13.2 Hz, 2F), -116.2 (ddt, *J* = 288.0, 56.0, 14.2 Hz, 1F), -117.8 (dddd, *J* = 288.0, 56.0, 21.1, 15.0 Hz, 1F), -136.7 (td, *J* = 29.6, 13.2 Hz, 2F).

HRMS (ESI): calcd for $C_{18}H_{16}F_6NO_2S$ (M+H) 424.0800, found 424.0800.

4-{[1,1-Difluoro-5-(pyridin-2-yloxy)pentan-3-yl]thio}-2,3,5,6-tetrafluoropyridine (3h).



Yield 69 mg (36%). Colorless oil. Chromatography: EtOAc/Hexane, 1/5. R_f 0.26 (EtOAc/Hexane, 1/5).

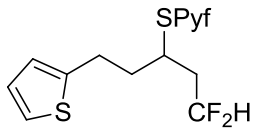
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 5.2, 1.4 Hz, 1H), 7.55 (ddd, *J* = 8.5, 6.9, 1.9 Hz, 1H), 6.87 (dd, *J* = 6.9, 5.5 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 6.14 (tdd, *J* = 56.2, 5.6, 3.6 Hz, 1H), 4.53 – 4.32 (m, 2H), 4.09 – 3.95 (m, 1H), 2.47 – 2.14 (m, 3H), 2.14 – 1.96 (m, 1H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.0, 146.9, 143.5 (dm, *J* = 245.7 Hz), 141.8 (dm, *J* = 257.0 Hz), 138.9, 129.7 – 128.6 (m), 117.4, 115.4 (t, *J* = 240.1 Hz), 110.7, 61.8, 41.1 – 40.7 (m), 40.1 (t, *J* = 22.7 Hz), 35.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ -91.0 (td, *J* = 30.1, 13.2 Hz, 2F), -116.3 (ddt, *J* = 288.1, 56.0, 13.9 Hz, 1F), -117.7 (dddd, *J* = 288.1, 56.0, 22.0, 16.0 Hz, 1F), -136.4 (td, *J* = 30.1, 13.2 Hz, 2F).

HRMS (ESI): calcd for $C_{15}H_{13}F_6N_2OS$ (M+H) 383.0647, found 383.0648.

4-{[1,1-Difluoro-5-(thiophen-2-yl)pentan-3-yl]thio}-2,3,5,6-tetrafluoropyridine (3i).



Yield 72 mg (39%). Yellow oil. Chromatography: EtOAc/Hexane, 1/10. R_f 0.25 (EtOAc/Hexane, 1/10).

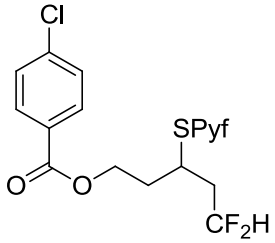
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 5.1, 1.0 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.78 (dd, *J* = 3.4, 1.0 Hz, 1H), 6.06 (tdd, *J* = 56.1, 5.4, 4.0 Hz, 1H), 3.72 (tt, *J* = 7.7, 5.4 Hz, 1H), 3.07 (t, *J* = 7.7 Hz, 2H), 2.36 – 1.93 (m, 4H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.7 (dm, *J* = 250.7 Hz) 142.51 (s), 142.0 (dm, *J* = 257.5 Hz), 129.1 – 128.4 (m), 127.1, 125.1, 123.9, 115.3 (t, *J* = 240.3 Hz), 43.1 – 42.5 (m), 39.9 (t, *J* = 22.4 Hz), 37.8, 26.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.6 (td, *J* = 29.5, 13.7 Hz, 2F), -116.0 (ddt, *J* =288.1, 56.1, 14.3 Hz, 1F) -117.6 (dddd, *J* = 288.1, 56.1, 20.6, 14.6 Hz, 1F), -136.3 (td, *J* = 29.5, 13.7 Hz, 2F).

HRMS (ESI): calcd for $C_{14}H_{12}F_6NS_2$ (M+H) 372.0310, found 372.0298.

5,5-Difluoro-3-[(perfluoropyridin-4-yl)thio]pentyl 4-chlorobenzoate (3j).



Yield 162 mg (73%). Colorless crystals. Mp 44–46 °C. Chromatography: EtOAc/Hexane, 1/5. R_f 0.23 (EtOAc/Hexane, 1/5).

Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 10 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 25% water; t_R = 26.55 min).

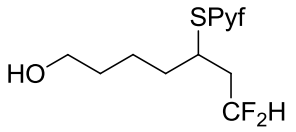
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 6.11 (tdd, *J* = 56.0, 5.3, 3.7 Hz, 1H), 4.59 – 4.43 (m, 2H), 3.92 (tt, *J* = 8.3, 5.7 Hz, 1H), 2.44 – 1.99 (m, 4H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 165.4, 143.7 (dm, *J* = 246.5 Hz), 141.8 (dm, *J* = 257.5 Hz), 139.9, 130.9, 129.0, 129.1 – 128.2 (m), 128.1, 115.2 (t, *J* = 240.4 Hz), 61.6, 40.9 – 40.4 (m), 40.0 (t, *J* = 22.5 Hz), 34.9.

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.3 (td, *J* = 29.4, 13.3 Hz, 2F), -116.4 (ddt, *J* = 288.6, 56.0, 14.3 Hz, 1F), -118.0 (dddd, *J* = 288.6, 56.0, 21.0, 15.3 Hz, 1F),-136.4 (td, *J* = 29.4, 13.3 Hz, 2F).

HRMS (ESI): calcd for $C_{17}H_{16}{}^{35}ClF_6N_2O_2S$ (M+NH_4) 461.0520, found 461.0512; calcd for $C_{17}H_{16}{}^{37}ClF_6N_2O_2S$ (M+NH_4) 463.0491, found 463.0492.

7,7-Difluoro-5-[(perfluoropyridin-4-yl)thio]heptan-1-ol (3k).



Yield 122 mg (73%). Colorless oil. Chromatography: EtOAc/Hexane, 1/1. R_f 0.46 (EtOAc/Hexane, 1/1).

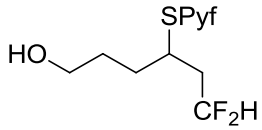
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (tdd, *J* = 56.2, 5.3, 3.8 Hz, 1H), 3.78 – 3.66 (m, 1H), 3.66 – 3.58 (m, 2H), 2.33 – 2.00 (m, 2H), 1.99 – 1.85 (broad s, 1H), 1.84 – 1.64 (m, 2H), 1.64 – 1.48 (m, 4H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.7 (dm, *J* = 245.9 Hz), 141.8 (dm, *J* = 256.9 Hz), 129.71 – 128.97 (m), 115.4 (t, *J* = 240.1 Hz), 62.4, 43.8 – 43.4 (m), 39.8 (t, *J* = 22.2 Hz), 35.6, 32.1, 22.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ -91.1 (td, *J* = 29.4, 13.6 Hz, 2F), -116.3 (ddt, *J* = 287.7, 56.2, 14.6 Hz, 1F), -117.8 (dddd, *J* = 287.7, 56.2, 20.7, 14.5 Hz, 1F), -136.9 (td, *J* = 29.4, 13.6 Hz, 2F).

HRMS (ESI): calcd for $C_{12}H_{14}F_6NOS$ (M+H) 334.0695, found 334.0699.

6,6-Difluoro-4-[(perfluoropyridin-4-yl)thio]hexan-1-ol (3l).



Yield 99 mg (62%). Yellow oil. Chromatography: EtOAc/Hexane, 1/1. R_f 0.34 (EtOAc/Hexane, 1/1).

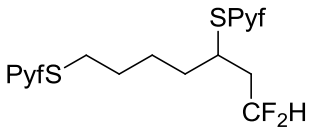
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.04 (tdd, *J* = 56.2, 5.3, 3.8 Hz, 1H), 3.82 – 3.70 (m, 1H), 3.67 (t, *J* = 5.7 Hz, 2H), 2.34 – 2.01 (m, 2H), 1.96 – 1.69 (m, 4H), 1.70 – 1.56 (br s, 1H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.7 (dm, *J* = 245.8 Hz), 141.9 (dm, *J* = 256.9 Hz), 129.66 – 128.78 (m), 115.4 (t, *J* = 240.2 Hz), 62.0, 43.8 – 43.3 (m), 39.9 (t, *J* = 22.2 Hz), 32.3, 29.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.9 (td, *J* = 29.8, 13.3 Hz, 2F), -116.3 (ddt, *J* = 287.8, 56.2, 14.7 Hz, 1F), -117.8 (dddd, *J* = 287.8, 56.2, 19.6, 15.6 Hz, 1F), -136.8 (td, *J* = 29.8, 13.3 Hz, 2F).

HRMS (ESI): calcd for $C_{11}H_{12}F_6NOS$ (M+H) 320.0538, found 320.0533.

4,4'-[(7,7-Difluoroheptane-1,5-diyl)bis(thio)]bis(tetrafluoropyridine) (3m).



Yield 199 mg (80%). Colorless oil. Chromatography: EtOAc/Hexane, 1/10. R_f 0.21 (EtOAc/Hexane, 1/10).

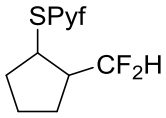
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (tdd, *J* = 56.0, 5.2, 3.8 Hz, 1H), 3.77 – 3.63 (m, 1H), 3.27 – 3.11 (m, 2H), 2.33 – 2.01 (m, 2H), 1.87 – 1.56 (m, 6H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.8 (dm, *J* = 246.4 Hz), 143.6 (dm, *J* = 245.9, Hz), 141.9 (dm, *J* = 256.8 Hz), 141.1 (dm, *J* = 255.9 Hz) 131.5 – 130.7 (m), 129.4 – 128.6 (m), 115.3 (t, *J* = 240.3 Hz), 43.9 – 43.0 (m), 39.8 (t, *J* = 22.2 Hz), 35.1, 32.9 (t, *J* = 4.8 Hz), 29.4, 25.2.

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.8 (td, *J* = 29.8, 13.2 Hz, 2F), -92.3 (td, *J* = 29.9, 13.3 Hz, 2F), -116.3 (ddt, *J* = 287.9, 56.0, 14.2 Hz ,1F), -118.0 (dddd, *J* = 287.9, 56.0, 20.0, 15.7 Hz, 1F), -136.9 (td, *J* = 29.7, 13.1 Hz, 2F), -139.4 (td, *J* = 29.8, 13.2 Hz, 2F).

HRMS (ESI): calcd for $C_{17}H_{16}F_{10}N_3S_2$ (M+NH_4) 516.0620, found 516.0609.

4-{[2-(Difluoromethyl)cyclopentyl]thio}-2,3,5,6-tetrafluoropyridine (3n).



Mixture of isomers, ratio 7 : 1**).** Yield 69 mg (46%). Colorless oil. Chromatography: Crude material was passed through 1 cm silica pad eluting with EtOAc/Hexane, 1/20. R_f 0.26 (EtOAc/Hexane, 1/20).

Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 10 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 15% water; t_R = 10.5 min).

Major isomer:

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 (td, *J* = 56.4, 3.6 Hz, 1H), 4.02 (dd, *J* = 12.5, 6.0 Hz, 1H), 2.46 – 1.61 (m, 7H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.7 (dm, *J* = 246.4 Hz), 141.5 (dm, *J* = 256.6, Hz), 130.7 – 130.0 (m), 116.6 (t, *J* = 242.6 Hz), 50.6 (t, *J* = 20.4 Hz), 45.5 – 45.2 (m), 35.4, 25.7 (t, *J* = 4.0 Hz), 24.5.

^{19}F NMR (282 MHz, $CDCl_3$) δ -91.6 (td, *J* = 30.0, 13.5 Hz, 2F), -121.7 (ddd, *J* = 281.9, 56.4, 15.6 Hz, 1F), -123.1 (ddd, *J* = 281.9, 56.4, 15.8 Hz, 1F), -137.8 (td, *J* = 30.0, 13.5 Hz).

Minor isomer selected signals:

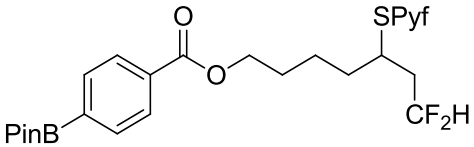
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.97 (td, *J* = 56.0, 5.7 Hz, 1H), 4.12 (dd, *J* = 12.1, 6.2 Hz, 1H), 2.69 – 2.48 (m, 1H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 117.8 (t, *J* = 240.7 Hz), 48.4 – 48.1 (m), 47.5 (t, *J* = 21.1 Hz), 34.3, 24.1 (dd, *J* = 5.8, 2.0 Hz), 22.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -116.2 (ddd, *J* = 288.5, 56.0, 9.8 Hz, 1F), -121.7 (ddd, *J* = 287.7, 56.0, 16.8 Hz, 1F)

HRMS (ESI): calcd for $C_{11}H_{10}F_6NS$ (M+H) 302.0433, found 302.0433.

7,7-Difluoro-5-[(perfluoropyridin-4-yl)thio]heptyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (3o).



Yield 163 mg (58%). Colorless oil. [The product has limited stability on silica gel and attempts of regular separation were unsuccessful. However it is stable on C18 modified silica.] Crude product was passed through 1×1 cm silica pad eluting with ethyl acetate and then purified by preparative HPLC (reversed-phase column

C18, 21×250 mm, 5 μm), flow rate 10 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 5% water; t_R = 10.7 min).

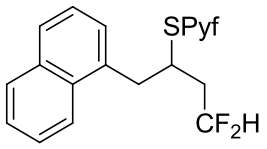
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 6.03 (tt, *J* = 56.1, 4.4 Hz, 1H), 4.34 (t, *J* = 6.1 Hz, 2H), 3.81 – 3.64 (m, 1H), 2.37 – 2.02 (m, 2H), 1.96 – 1.53 (m, 6H), 1.35 (s, 12H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 166.7, 143.7 (dm, *J* = 246.2 Hz), 141.8 (dm, *J* = 257.0 Hz) 134.8, 132.5, 129.6 – 128.4 (m) 128.7, 115.3 (t, *J* = 240.3 Hz), 84.3, 64.5, 43.8 – 43.4 (m), 39.9 (t, *J* = 22.2 Hz), 35.5, 28.5, 25.0, 23.2.

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.7 (td, *J* = 29.5, 13.5 Hz, 2F), -116.2 (ddt, *J* = 288.0, 56.1, 14.5 Hz, 1F), -117.7 (dddd, *J* = 288.0, 56.1, 20.3, 15.2 Hz, 1F), -136.8 (td, *J* = 29.5, 13.5 Hz, 2F).

HRMS (ESI): calcd for $C_{25}H_{29}BF_6NO_4S$ (M+H) 564.1813, found 564.1802.

4-{[4,4-Difluoro-1-(naphthalen-1-yl)butan-2-yl]thio}-2,3,5,6-tetrafluoropyridine (3p).



Yield 90 mg (45%). Colorless crystals. Mp 94 – 96°C. Chromatography: EtOAc/Hexane, 1/10. R_f 0.36 (EtOAc/Hexane, 1/10).

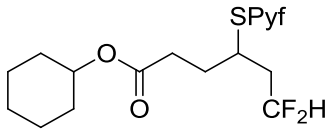
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.58 – 7.42 (m, 2H), 7.41 – 7.29 (m, 2H), 6.19 (tdd, *J* = 56.2, 5.9, 3.3 Hz, 1H), 4.53 – 4.41 (m, 1H), 3.75 (dd, *J* = 14.1, 4.9 Hz, 1H), 3.17 (dd, *J* = 14.1, 10.7 Hz, 1H), 2.55 – 2.18 (m, 2H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.9 (dm, *J* = 245.7 Hz), 140.5 (dm, *J* = 256.6 Hz), 133.2, 133.0, 131.4, 129.0, 128.9, 128.5, 128.7 – 128.0 (m), 126.8, 126.1, 125.2, 122.5, 115.3 (t, *J* = 240.6 Hz), 43.7 – 43.2 (m), 41.8, 40.0 (t, *J* = 22.8 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -92.2 (td, *J* = 30.2, 13.3 Hz, 2F), -116.0 (ddt, *J* = 287.3, 56.2, 13.3 Hz, 1F), -117.6 (dddd, *J* = 287.3, 56.2, 21.8, 15.1 Hz, 1F), -135.2 (td, *J* = 30.2, 13.3 Hz, 2F).

HRMS (ESI): calcd for $C_{19}H_{14}F_6NS$ (M+H) 402.0746, found 402.0755.

Cyclohexyl 6,6-difluoro-4-[(perfluoropyridin-4-yl]thio)hexanoate (3q).



Yield 145 mg (70%). Colorless oil. Chromatography: EtOAc/Hexane, 1/10. R_f 0.2 (EtOAc/Hexane, 1/10).

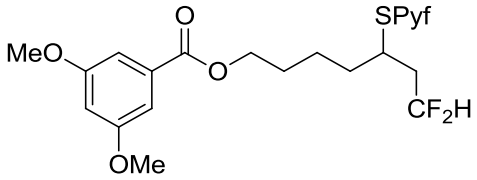
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 (tdd, *J* = 56.1, 5.3, 3.9 Hz, 1H), 4.82 – 4.65 (m, 1H), 3.81 – 3.67 (m, 1H), 2.54 (t, *J* = 6.9 Hz, 2H), 2.33 – 2.00 (m, 3H), 1.99 – 1.60 (m, 5H), 1.60 – 1.46 (m, 1H), 1.45 – 1.12 (m, 5H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 171.6, 143.7 (dm, *J* = 247.8 Hz), 142.0 (dm, *J* = 257.4 Hz), 129.1 – 128.3 (m), 115.2 (t, *J* = 240.3 Hz), 73.4, 43.5 – 43.1 (m), 40.1 (t, *J* = 22.4 Hz), 31.7, 31.3, 30.9, 25.4, 23.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.6 (td, *J* = 29.7, 13.3 Hz, 2F), -116.3 (ddt, *J* = 288.2, 56.1, 14.5 Hz, 1F), -117.8 (dddd, *J* = 288.2, 56.1, 20.2, 14.9 Hz, 1F), -136.4 (td, *J* = 29.7, 13.3 Hz, 2F).

HRMS (ESI): calcd for $C_{17}H_{20}F_6NO_2S$ (M+H) 416.1113, found 416.1099.

7,7-Difluoro-5-[(perfluoropyridin-4-yl)thio]heptyl 3,5-dimethoxybenzoate (3r).



Yield 149 mg (60%). Colorless oil. Chromatography: EtOAc/Hexane, 1/5. R_f 0.27 (EtOAc/Hexane, 1/5).

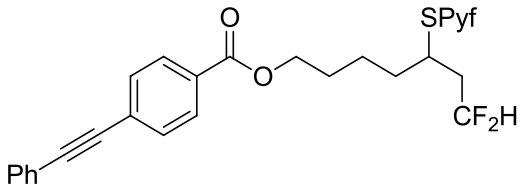
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (d, *J* = 2.3 Hz, 2H), 6.62 (t, *J* = 2.3 Hz, 1H), 6.03 (tdd, *J* = 56.1, 5.3, 3.8 Hz, 1H), 4.30 (t, *J* = 6.2 Hz, 2H), 3.81 (s, 6H), 3.77 – 3.66 (m, 1H), 2.34 – 1.99 (m, 2H), 1.90 – 1.51 (m, 6H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 166.3, 160.8, 143.7 (dm, *J* = 248.1 Hz), 141.8 (dm, *J* = 257.0 Hz), 132.1, 129.6 – 128.7 (m), 115.3 (t, *J* = 240.2 Hz), 107.2, 105.6, 64.5, 55.6, 43.8 – 43.3 (m), 39.8 (t, *J* = 22.2 Hz), 35.4, 28.4, 23.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -92.1 (td, *J* = 29.9, 13.5 Hz, 2F), -116.7 (ddt, *J* = 287.0, 56.1, 14.8 Hz, 1F), -118.1 (dddd, *J* = 287.0, 56.1, 19.9, 15.3 Hz, 1F), -137.3 (td, *J* = 29.9, 13.5 Hz, 2F).

HRMS (ESI): calcd for $C_{21}H_{22}F_6NO_4S$ (M+H) 498.1168, found 498.1164.

7,7-Difluoro-5-[(perfluoropyridin-4-yl)thio]heptyl 4-(phenylethynyl)benzoate (3s).



Yield 107 mg (40%). Colorless crystals. Mp = 79 – 81 °C. Chromatography: EtOAc/Hexane, 1/3. R_f 0.46 (EtOAc/Hexane, 1/3). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 10 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 10% water; t_R = 25.5 min).

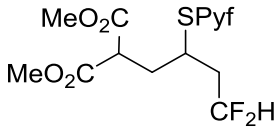
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.57 – 7.49 (m, 2H), 7.42 – 7.30 (m, 3H), 6.05 (tt, *J* = 56.0, 4.5 Hz, 1H), 4.34 (t, *J* = 6.0 Hz, 2H), 3.82 – 3.66 (m, 1H), 2.36 – 1.99 (m, 2H), 1.96 – 1.58 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 143.7 (dm, *J* = 246.1 Hz), 141.8 (dm, *J* = 256.8 Hz) 131.9, 131.6, 129.6, 129.6, 130.3 – 129.3 (m), 128.9, 128.6, 128.2, 122.8, 115.3 (t, *J* = 240.3 Hz), 92.6, 88.7, 64.6, 43.7 – 43.3 (m), 39.9 (t, *J* = 22.3 Hz), 35.5, 28.4, 23.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.1 (td, *J* = 29.5, 13.5 Hz, 2F), -115.7 (ddt, *J* = 287.8, 56.0 Hz, 14.7 Hz, 1F), -117.3 (dddd, *J* = 288.0, 56.0, 20.3, 15.0 Hz, 1F), -136.3 (td, *J* = 29.5, 13.5 Hz, 2F).

HRMS (ESI): calcd for $C_{27}H_{22}F_6NO_2S$ (M+H) 538.1270, found 538.1265.

Dimethyl 2-{4,4-difluoro-2-[(perfluoropyridin-4-yl)thio]butyl}malonate (3t).



Yield 150 mg (74%). Colorless oil. Chromatography: EtOAc/Hexane, 1/5. R_f 0.15 (EtOAc/Hexane, 1/5).

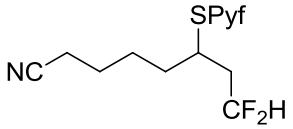
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.04 (tt, *J* = 55.6, 4.5 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.81 – 3.59 (m, 2H), 2.47 – 2.30 (m, 1H), 2.31 – 2.03 (m, 3H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 168.8, 168.8, 143.7 (dm, *J* = 246.4 Hz), 142.0 (dm, *J* = 257.4 Hz), 128.4 – 127.7 (m), 115.0 (t, *J* = 240.4 Hz), 53.1, 53.0, 48.9, 42.1 – 41.7 (m), 40.3 (t, *J* = 22.6 Hz), 34.7.

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.6 (td, *J* = 29.7, 12.9 Hz, 2F), -116.6 (ddt, *J* = 288.9, 55.6, 14.9 Hz, 1F), -118.0 (dddd, *J* = 288.9, 55.6, 19.4, 14.8 Hz, 1F) -136.3 (td, *J* = 29.7, 12.9 Hz, 2F).

HRMS (ESI): calcd for $C_{14}H_{14}F_6NO_4S$ (M+H) 406.0542, found 406.0544.

8,8-Difluoro-6-[(perfluoropyridin-4-yl)thio]octanenitrile (3u).



Yield 96 mg (56%). Colorless oil. Chromatography: EtOAc/Hexane, 1/3. Rf 0.25 (EtOAc/Hexane, 1/3).

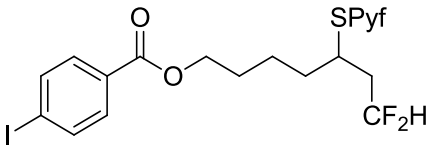
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.03 (tdd, *J* = 56.0, 5.2, 3.7 Hz, 1H), 3.79 – 3.62 (m, 1H), 2.44 – 2.33 (m, 2H), 2.30 – 2.03 (m, 2H), 1.86 – 1.60 (m, 6H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.7 (dm, *J* = 246.2 Hz), 141.9 (dm, *J* = 257.2 Hz), 129.3 – 128.2 (m), 119.3, 115.3 (t, *J* = 240.3 Hz), 43.5 – 43.1 (m), 39.8 (t, *J* = 22.2 Hz), 35.0, 25.6, 25.0, 17.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.7 (td, *J* = 29.4, 13.5 Hz, 2F), -116.3 (ddt, *J* = 288.0, 56.0, 14.6 Hz, 1F), -117.9 (dddd, *J* = 288.0, 56.0, 20.3, 15.4 Hz, 1F), -136.8 (td, *J* = 29.4, 13.5 Hz, 2F).

HRMS (ESI): calcd for $C_{13}H_{13}F_6N_2S$ (M+H) 343.0698, found 343.0685.

7,7-Difluoro-5-[(perfluoropyridin-4-yl)thio]heptyl 4-iodobenzoate (3v).



Yield 175 mg (62%). Light yellow oil. Chromatography: EtOAc/Hexane, 1/5. R_f 0.34 (EtOAc/Hexane, 1/5).

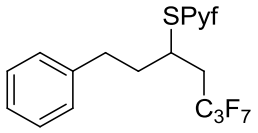
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 6.03 (tdd, *J* = 56.1, 5.2, 3.8 Hz, 1H), 4.31 (t, *J* = 6.3 Hz, 2H), 3.80 – 3.63 (m, 1H), 2.35 – 1.99 (m, 2H), 1.93 – 1.50 (m, 6H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 166.1, 143.7 (dm, *J* = 246.4 Hz), 141.8 (dm, *J* = 256.6 Hz), 137.8, 131.0, 129.8, 129.5 – 128.7, 115.3 (t, *J* = 240.3 Hz), 100.9, 64.6, 43.8 – 43.3 (m), 39.8 (t, *J* = 22.2 Hz), 35.4, 28.4, 23.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.7 (td, *J* = 29.5, 13.5 Hz, 2F), -116.1 (ddt, *J* = 287.8, 56.1, 14.6 Hz, 1F), -117.7 (dddd, *J* = 287.8, 56.1, 20.3, 15.4 Hz, 1F), -136.8 (td, *J* = 29.5, 13.5 Hz, 2F).

HRMS (ESI): calcd for $C_{19}H_{17}F_6INO_2S$ (M+H) 563.9923, found 563.9918.

2,3,5,6-Tetrafluoro-4-[(5,5,6,6,7,7,7-heptafluoro-1-phenylheptan-3-yl)thio]pyridine (4b).



Reaction was performed according to General procedure using compound **2d** (211 mg, 0.6 mmol, 1.2 equiv) instead of **2a**.

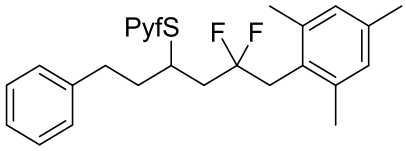
Yield 177 mg (73%). Colorless oil. Chromatography: CH_2Cl_2/Hexane, 1/5. R_f 0.38 (CH_2Cl_2/Hexane, 1/5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 3H), 7.22 – 7.12 (m, 2H), 3.98 (dt, *J* = 12.5, 6.4 Hz, 1H), 3.02 – 2.76 (m, 2H), 2.65 – 2.42 (m, 2H), 2.34 – 2.17 (m, 1H), 2.13 – 1.95 (m, 1H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.7 (dm, *J* = 246.2 Hz), 141.8 (dm, *J* = 254.1 Hz) 139.8, 132.5 – 131.7 (m), 128.8, 128.4), 126.7), 117.8 (qt, *J* = 287.2, 33.8 Hz), 116.9 (tt, *J* = 256.1, 31.2 Hz), 108.7 (tm, *J* = 264.1 Hz), 40.9, 37.5, 36.7 (t, *J* = 21.3 Hz), 32.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -81.2 (t, *J* = 9.4 Hz, 3F), -90.7 (td, *J* = 29.5, 13.3 Hz, 2F), -113.7 (dm, *J* = 277.5 Hz, 1F), -115.3 (dm, *J* = 277.5 Hz, 1F), -128.3 – -128.7 (m, 2F), -136.6 – -136.9 (m, 2F).

HRMS (ESI): calcd for $C_{18}H_{13}F_{11}NS$ (M+H) 484.0588, found 484.0598.

4-[(5,5-Difluoro-6-mesityl-1-phenylhexan-3-yl)thio]-2,3,5,6-tetrafluoropyridine (4c).



Reaction was performed according to General procedure using compound **2c** (183 mg, 0.6 mmol, 1.2 equiv) instead of **2a.**

Yield 139 mg (56%). Colorless oil. Chromatography: EtOAc/Hexane, 1/20. R_f 0.29 (EtOAc/Hexane, 1/20). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 10 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 5% water; t_R = 14.7 min).

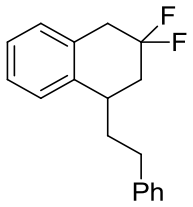
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.14 (m, 5H), 6.90 (s, 2H), 4.04 – 3.88 (m, 1H), 3.38 – 3.12 (m, 2H), 3.01 – 2.74 (m, 2H), 2.57 – 2.13 (m, 3H), 2.31 (s, 3H), 2.29 (s, 6H), 2.13 – 1.87 (m, 1H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.6 (dm, *J* = 246.8 Hz), 141.9 (dm, *J* = 256.7 Hz), 140.4, 138.1, 137.1, 130.1 – 129.4 (m), 129.4, 128.7, 128.4, 126.7 – 126.6 (m), 126.5, 124.0 (t, *J* = 245.2 Hz), 43.0 (t, *J* = 24.9 Hz), 42.7 – 42.4 (m), 37.5, 36.8 (t, *J* = 25.5 Hz), 32.7, 21.0, 20.8 (t, *J* = 2.7 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -91.2 (td, *J* = 29.9, 13.5 Hz, 2F), -94.2 (dm, *J* = 242.3 Hz, 1F), -96.8 (dm, *J* = 242.3 Hz, 1F), -136.6 (td, *J* = 29.9, 13.5 Hz, 2F).

HRMS (ESI): calcd for $C_{26}H_{29}F_6N_2S$ (M+NH_4) 515.1950, found 515.1953.

3,3-Difluoro-1-phenethyl-1,2,3,4-tetrahydronaphthalene (5).



Reaction was performed according to General procedure using compound **2d**[20] instead of **2a**; anhydrous $Zn(OAc)_2$ (92 mg, 0.5 mmol, 1 equiv) was added before irradiation.

Yield 103 mg (76%). Yellow oil. Chromatography: CH_2Cl_2/Hexane, 1/5. R_f 0.23 (CH_2Cl_2/Hexane, 1/5).

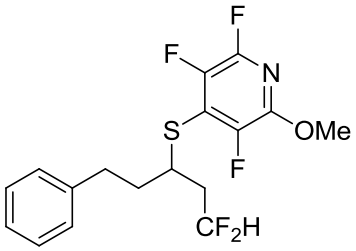
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.14 (m, 9H), 3.52 – 3.15 (m, 3H), 2.97 – 2.65 (m, 2H), 2.61 – 2.40 (m, 1H), 2.38 – 2.03 (m, 3H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 141.9, 138.2, 131.9 (dd, *J* = 7.0, 4.1 Hz), 129.3, 128.6, 128.5, 127.4, 127.0, 126.7, 126.1, 123.5 (dd, *J* = 240.4, 239.6 Hz) 38.7 (t, *J* = 26.8 Hz), 37.1 (d, *J* = 1.9 Hz), 36.7 (t, *J* = 4.6 Hz), 35.9 (dd, *J* = 24.1, 22.5 Hz), 33.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.5 (dm, *J* = 237.0 Hz), -94.2 (dm, *J* = 237.0 Hz).

HRMS (ESI): calcd for $C_{18}H_{22}F_2N$ (M+NH_4) 290.1715, found 290.1719.

4-[(1,1-Difluoro-5-phenylpentan-3-yl)thio]-2,3,5-trifluoro-6-methoxypyridine (6).



Compound **3a** (183 mg, 0.5 mmol, 1 equiv) was dissolved in methanol (1 mL) and then solid K_2CO_3 (69 mg, 0.5 mmol, 1 equiv) was added. The mixture was stirred for 18 h at room temperature, then diluted with water (5 mL). Product was extracted with methyl *tert*-butyl ether (3×3 mL). The combined organic phases were filtered through Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel.

Yield 149 mg (79%). Colorless oil. Chromatography: EtOAc/Hexane, 1/10. R_f 0.39 (EtOAc/Hexane, 1/10).

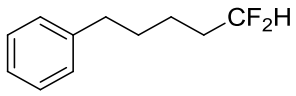
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.14 (m, 5H), 6.11 (tdd, *J* = 56.2, 5.4, 3.8 Hz, 1H), 4.02 (s, 3H), 3.71 – 3.54 (m, 1H), 2.98 – 2.74 (m, 2H), 2.36 – 1.88 (m, 4H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 146.9 – 146.1 (m), 144.3 (ddd, *J* = 239.7, 17.2, 3.3 Hz), 143.6 (dd, *J* = 256.2, 5.7 Hz), 140.5, 138.3 (dd, *J* = 250.6, 29.1 Hz), 128.7, 128.5, 126.5, 125.4 – 124.8 (m) 115.7 (t, *J* = 240.0 Hz), 54.9, 43.3 – 42.9 (m), 39.8 (t, *J* = 22.3 Hz), 37.5, 32.7.

^{19}F NMR (282 MHz, $CDCl_3$) δ -94.0 (dd, *J* = 28.9, 23.1 Hz, 1F), -116.0 (ddt, *J* = 287.4, 56.2, 13.9 Hz, 1F), -117.7 (dddd, *J* = 287.4, 56.2, 20.9, 14.9 Hz, 1F), -136.0 (d, *J* = 28.9 Hz, 1F), -146.1 (d, *J* = 23.1 Hz, 1F).

HRMS (ESI): calcd for $C_{17}H_{17}F_5NOS$ (M+H) 378.0946, found 378.0945.

(5,5-Difluoropentyl)benzene (7).[19]



A solution of compound **3a** (183 mg, 0.5 mmol, 1 equiv), Hantzsch ester (253 mg, 1 mmol, 2 equiv) and EtN(*i*-Pr)$_2$ (129 mg, 1 mmol, 2 equiv) in *N*,*N*-dimethylacetamide (1 mL) was irradiated using setup shown in Figure S1 (60W/455 nm/20 °C) for 18 h. The mixture was diluted with water (5 mL) and extracted with diethyl ether/pentane (1/20, 3×1 mL), and then directly passed through 1 g of silica gel eluting with diethyl ether/pentane (1/20, 5 mL). The solvent was carefully evaporated at atmospheric pressure, and the crude product was distilled in Hickman head T_{bath} = 160 -170 °C (9 Torr).

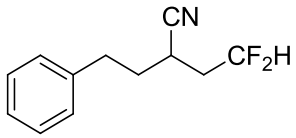
Yield 58 mg (63%) [84% NMR yield]. Colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 5.81 (tt, *J* = 56.9, 4.5 Hz, 1H), 2.66 (t, *J* = 7.6 Hz, 2H), 1.99 – 1.77 (m, 2H), 1.78 – 1.64 (m, 2H), 1.59 – 1.45 (m, 2H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.1, 128.5, 126.0, 117.5 (t, *J* = 238.8 Hz), 35.8, 34.1 (t, *J* = 20.7 Hz), 31.0, 21.9 (t, *J* = 5.5 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -116.5 (dt, *J* = 56.9, 17.5 Hz).

4,4-Difluoro-2-phenethylbutanenitrile (8).



Dry potassium acetate (1 mmol, 2 equiv), CuCN (0.55 mmol, 1.1 equiv) and DMSO (2 mL) were placed in a screw cap culture tube under inert atmosphere. TMSCN (1 mmol, 2 equiv) was added and the mixture was stirred at room temperature for about 15 min, at which point copper cyanide precipitate dissolved and the mixture has turned deep red. Then, compound **3a** (183 mg, 0.5 mmol, 1 equiv) was added followed by *fac*-Ir(ppy)$_3$ (0.8 mg, 0.25 mol%). The mixture was irradiated using setup shown in Figure S1 (60W/455 nm/20 °C) for 3 h. For the workup, the mixture was diluted with water (3 mL) and extracted with methyl *tert*-butyl ether (3×3 mL). The combined organic phases were filtered through Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel.

Yield 84 mg (80%). Colorless oil. Chromatography: EtOAc/Hexane, 1/5. R_f 0.3 (EtOAc/Hexane, 1/5).

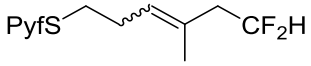
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 2H), 7.31 – 7.20 (m, 3H), 6.02 (tdd, *J* = 55.6, 5.5, 3.5 Hz, 1H), 3.03 – 2.89 (m, 1H), 2.89 – 2.70 (m, 2H), 2.38 – 1.88 (m, 4H).

^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.5, 128.9, 128.5, 126.8, 120.3, 114.9 (t, *J* = 240.6 Hz), 36.6 (t, *J* = 22.6 Hz), 34.0, 33.1, 25.2 (t, *J* = 5.6 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -116.7 (ddt, *J* = 288.5, 55.6, 14.1 Hz, 1F), -118.2 (dddd, *J* = 288.5, 55.6, 20.3, 15.5 Hz, 1F).

HRMS (ESI): calcd for $C_{12}H_{14}F_2N$ (M+H) 210.1089, found 210.1085.

4-[(6,6-Difluoro-4-methylhex-3-en-1-yl)thio]-2,3,5,6-tetrafluoropyridine (10).



Mixture of isomers: ratio 2 : 1

Yield 54 mg (34%). Colorless oil. Chromatography: EtOAc/Hexane, 1/20. R_f 0.17 (EtOAc/Hexane, 1/20). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 10 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 5% water; t_R = 6.9 min).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 – 5.59 (m, both isomers), 5.41 (t, *J* = 7.3 Hz, minor), 5.32 (t, *J* = 7.0 Hz, major), 3.29 – 3.11 (m, both isomers), 2.65 – 2.35 (m, both isomers), 1.79 (s, minor), 1.69 (s, major).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6 (dm, *J* = 245.6 Hz, both isomers), 141.1 (dm, *J* = 255.6 Hz, both isomers), 131.9 – 131.1 (m, both isomers), 130.7 (t, *J* = 5.6 Hz, major), 130.1 (t, *J* = 5.2 Hz, minor). 126.6, 126.4, 116.4 (t, *J* = 241.2 Hz, major), 115.8 (t, *J* = 241.3 Hz, minor), 44.1 (t, *J* = 21.4 Hz, major), 37.0 (t, *J* = 21.8 Hz, minor), 33.1 – 32.6 (m, both isomers), 28.8, 28.6, 24.5, 17.1.

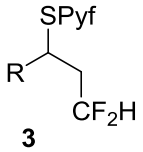
^{19}F NMR (282 MHz, $CDCl_3$) δ -91.1 – -91.9 (m, both isomers**,** 2F), -114.1 (dt, *J* = 56.6, 17.5 Hz, minor, 1F), -114.5 (dt, *J* = 56.6, 17.1 Hz, major, 1F), -138.2 – -138.7 (m, both isomers**,** 2F).

HRMS (ESI): calcd for $C_{12}H_{12}F_6NS$ (M+H) 316.0589, found 316.0582.

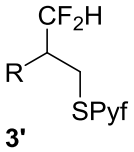
Regioselectivity

We suppose that the radical attack in our system is not completely regiospecific. However, amounts of minor isomers **3'** are small and barely enough for NMR detection. Not being able to isolate isomers **3'**, we deduce their structures from indirect evidence (GC-MS mass identity, trace signals in ^{19}F and ^{1}H NMR).

Table S1. Regioisomers in ATRA reaction.



3



3'

Compound	Ratio of isomers 3/3' (^{19}F NMR)
3a	43/1
3b	26/1
3c	24/1
3d	Minor isomer not detected
3e	28/1
3f	37/1
3g	24/1
3h	27/1
3i	Minor isomer not detected
3j	Minor isomer not detected
3k	30/1
3l	37/1
3m	32/1
3n	[a]
3o	20/1
3p	Minor isomer not detected
3q	33/1
3r	26/1
3s	Minor isomer not detected
3t	27/1
3u	23/1
3v	28/1

[a] Starting is symmetric, no regioselectivity issue.

Stern-Volmer study

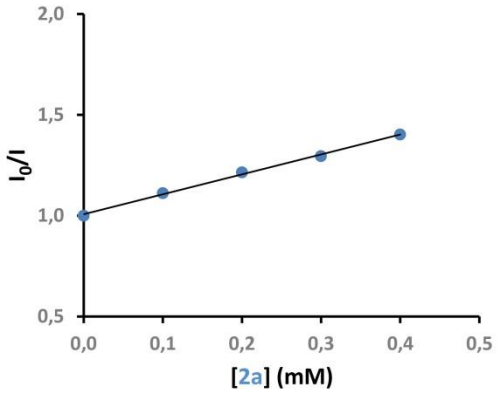


Figure S2. Plot of relative fluorescence intensities of the photoexcited *fac*-Ir(ppy)$_3$ (10^{-6} M solution in DMSO) depending on concentration of **2a** as a quencher.

UV-vis spectra

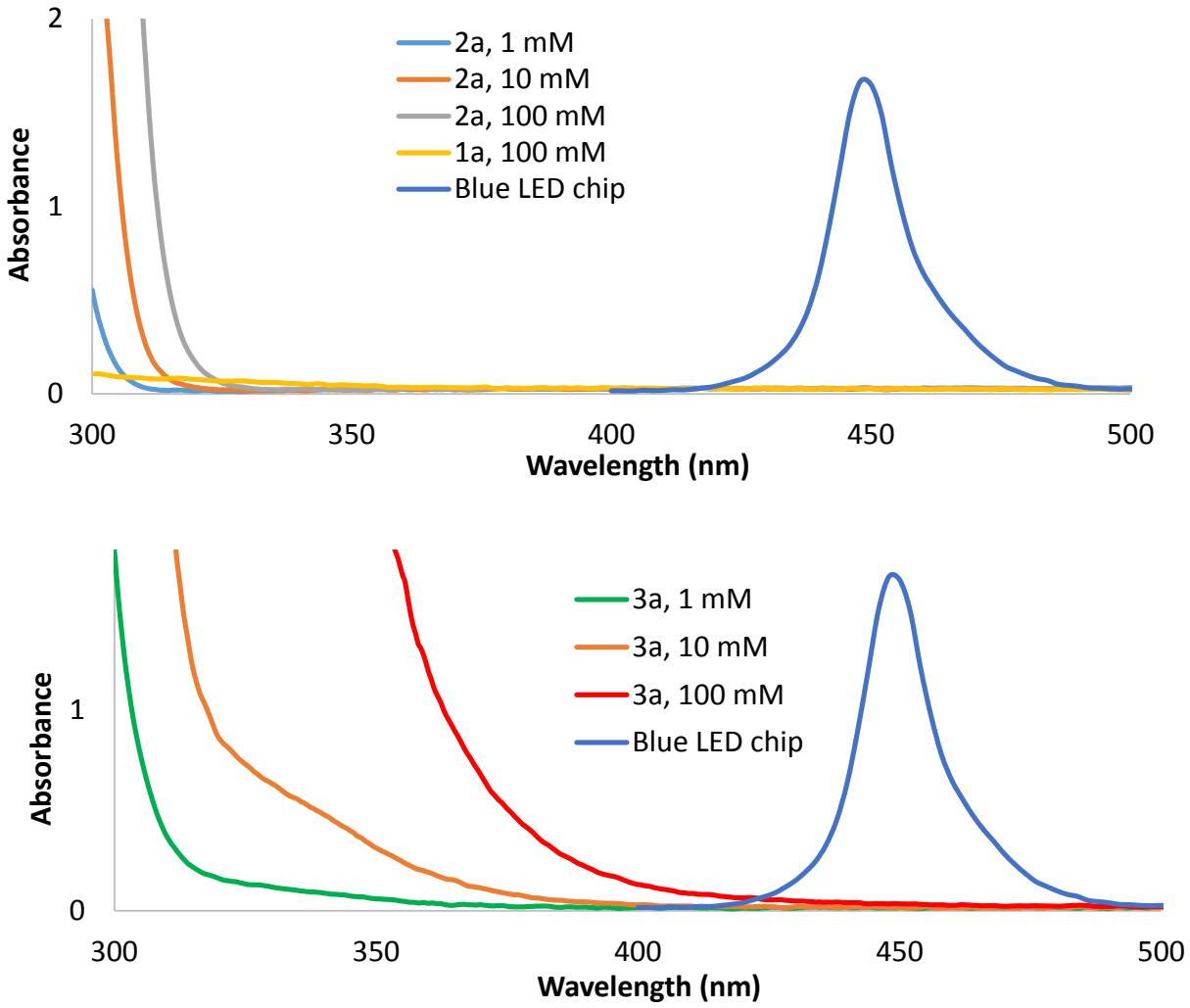


Figure S3. UV-vis spectra of compounds **1a, 2a** and **3a** in DMSO. Emission spectrum of Blue LED chip is shown on the right part.

On-off experiment

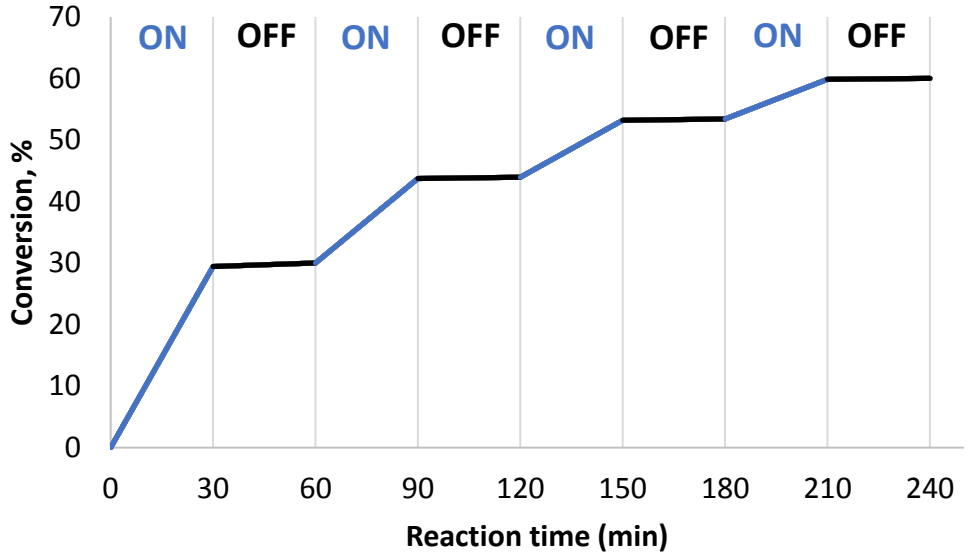


Figure S4. Intermittent light irradiation experiment. The reaction conditions are identical to general procedure for the reaction between **1a** and **2a** except 10W LED strip (2835-120LED 1M-Blue, 12V) was used for irradiation.

Quantum yield measurement[20]

Quantum yield of the reaction of 4-phenylbutene (**1a**) with PyfSCF$_2$H (**2a**) was estimated using irradiation with 50 mW blue laser (450 nm). Photon flux of the laser was measured by standard ferrioxalate actinometry -23.5 μEs/min. Mixture of 0.33 mmol of 4-phenylbutene, 0.4 mmol PyfSCHF$_2$, 0.8 μmol Ir(ppy)$_3$ and 0.33 mmol of tetraline (internal standard) in 2.5 ml DMSO was placed in square quarz cuvette (10×10 mm). Light absorption of this mixture was determined by spectrophotometry. At 450 nm reaction mixture absorption coefficient -0.913. After irradiation with laser diode for 30 min GC-analysis indicated formation of 38 μmol of ATRA-product (11.5% conversion). Using this parameters quantum yield was calculated by following equation:

$$\Phi = \frac{\text{moles of product formed}}{\text{absorbtion coeff} \cdot \text{photon flux} \cdot \text{reaction time}} = \frac{38\ \mu\text{mol}}{0.913 \cdot 23.5\ \mu\text{Es/min} \cdot 30\ \text{min}} = 0.059$$

Cyclic voltammetry

Voltammetric studies were carried out using potentiostat P30JM with a scan rate of 1.0 $V \cdot s^{-1}$ in a temperature-controlled (25 °C) glass cell (V = 10 mL) under an argon atmosphere. 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 or DMSO) 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 compound **2a** of 1 mM in MeCN or DMSO.

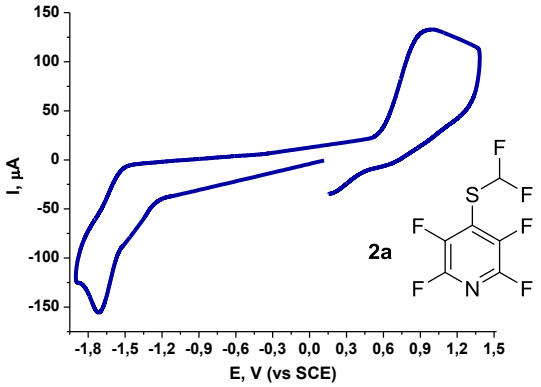


Figure S5. Compound **2a** in MeCN (initial cathodic scan). E_{onset}^{red} = -1.24 V; E_p^{red} = -1.72 V; $E_{p/2}$ = -1.48 V; i_p^{red} = 116.81 μA; E_p^{reox}= +0.96 V

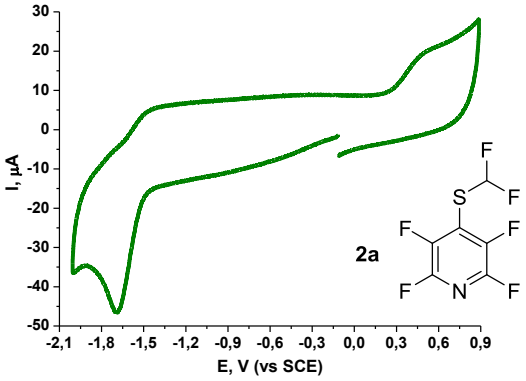


Figure S6. Compound **2a** in DMSO (initial cathodic scan). E_{onset}^{red} = -1.41 V; E_p^{red} = -1.69 V; $E_{p/2}$ = -1.55 V; i_p^{red} = 32.78 μA; E_p^{reox} = + 0.52 V

Compound **2a** has irreversible reduction peak at E_p^{red} -1.69 V (in DMSO) or -1.72 V (in MeCN), but reduction starts at more positive potentials at E_{onset}^{red} -1.24 V (in MeCN) or -1.41 V (in DMSO). A lower reduction peak current (i_p^{red}) in DMSO than in MeCN may be associated with a lower diffusion rate of the substance to the electrode surface. Presumably, after the reduction, the resulting anion-radical undergoes fragmentation into difluoromethyl radical and thiolate anion. The possible oxidation peak of the latter is registered at +0.96 V (in MeCN) or +0.49 V (in DMSO). The results are consistent with those obtained in our previous work.[21]

Free energy of single electron transfer can be estimated from the electrochemical data[22] (half-peak potential for **2a** of -1.48 V vs SCE in MeCN was used[23]) and the excited state oxidation potential of *fac*-Ir(ppy)$_3$ (-1.73 V)[24]:

$$\Delta G_{\mathrm{PET}} = -\mathcal{F}\left(E_{\mathrm{red}}(\mathbf{2a}/\mathbf{2a}^{\cdot-}) - E_{\mathrm{ox}}^{*}(\mathbf{cat}^{\cdot+}/\mathbf{cat}^{*})\right) = -23.061 \cdot (-1.48 + 1.73) \cong -5.8\ \mathrm{kcal/mol}$$

Compound **3a** has similar irreversible corresponding reduction and reoxidation peaks at more negative potentials (E_p^{red} = -1.86 V, E_{onset}^{red} = –1.52 V, E_p^{reox} = +0.46 V (in MeCN) or E_p^{red} = -1.77 V, E_{onset}^{red} = -1.51 V, E_p^{reox} = +0.44 V (in DMSO)).

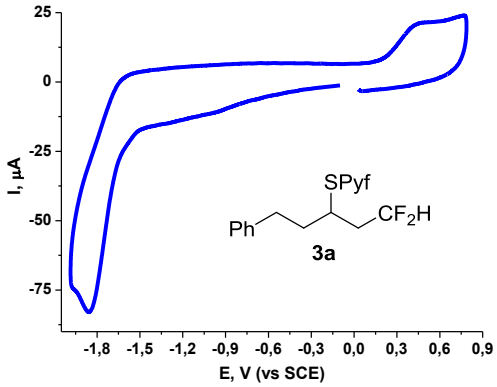


Figure S7. Compound **3a** in MeCN (initial cathodic scan)
E_{onset}^{red} = -1.52 V; E_p^{red} = -1.86 V; $E_{p/2}$ = -1.69 V;
i_p^{red} = 65.45 µA; E_p^{reox}= +0.46 V

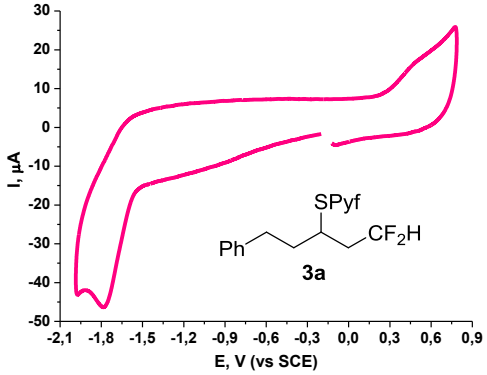


Figure S8. Compound **3a** in DMSO (initial cathodic scan)
E_{onset}^{red} = -1.51 V; E_p^{red} = -1.77 V; $E_{p/2}$ = -1.64 V;
i_p^{red} = 31.31 µA; E_p^{reox} = +0.44 V

EPR studies

Procedure: Sulfide **2a** (400 μmol) and *N*-benzylidene-*tert*-butylamine *N*-oxide (800 μmol) were added to a solution of $Ir(ppy)_3$ in DMSO (10^{-3} M, 2 mL) under argon. 300 μL of the resulting mixture was taken into an EPR tube. For the generation of radical **R2** the tube was placed under light (455 nm, 60W) for 30 seconds. The EPR spectrum was immediately recorded at 298 K on EPR spectrometer SPINSCAN X (ADANI). Radical **R2** was generated according to aforementioned procedure with addition of 4-phenyl-1-butene **1** (2000 μmol).

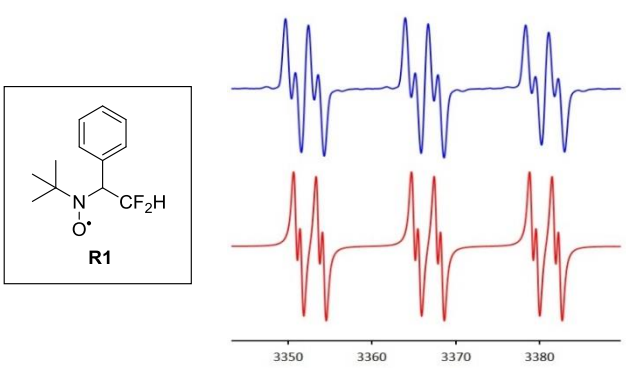


Figure S9. The X-band EPR spectrum of the radical **R1** (blue line). Simulated EPR spectrum (red line) based on hyperfine coupling constants of a_N= 14.1 G, a_H = 2.7 G and a_F = 0.7 G (*g*-factor = 2.0065).

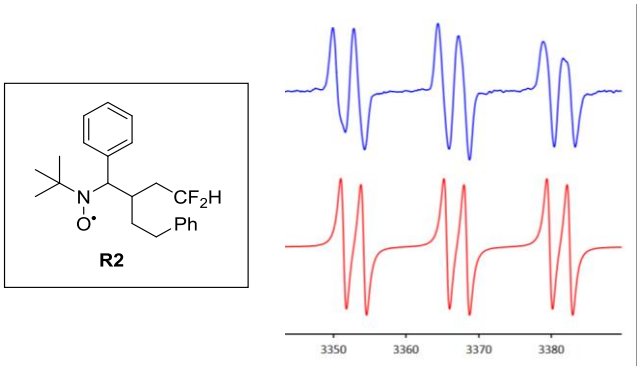


Figure S10. The X-band EPR spectrum of the radical **R2** (blue line). Simulated EPR spectrum (red line) based on hyperfine coupling constants of a_N= 14.2 G and a_H = 2.75 G (*g*-factor = 2.0065).

Experiment parameters:

Center-Field: 3360 G,
Width: 80 G
Points: 6000
Modulation Amplitude: 100 μT
Modulation Frequency: 9.432985 GHz
Microwave Power: 1.0 mW
Time constant: 0.009 s

DFT calculations

Priority of proposed group transfer was confirmed by DFT analysis of corresponding transition states. The barrier of the PyfS-group transfer from PyfSCF$_2$H (**2a**) by isopropyl radical was calculated to be lower than barriers of alternative SCF$_2$H or CF$_2$H transfer events.

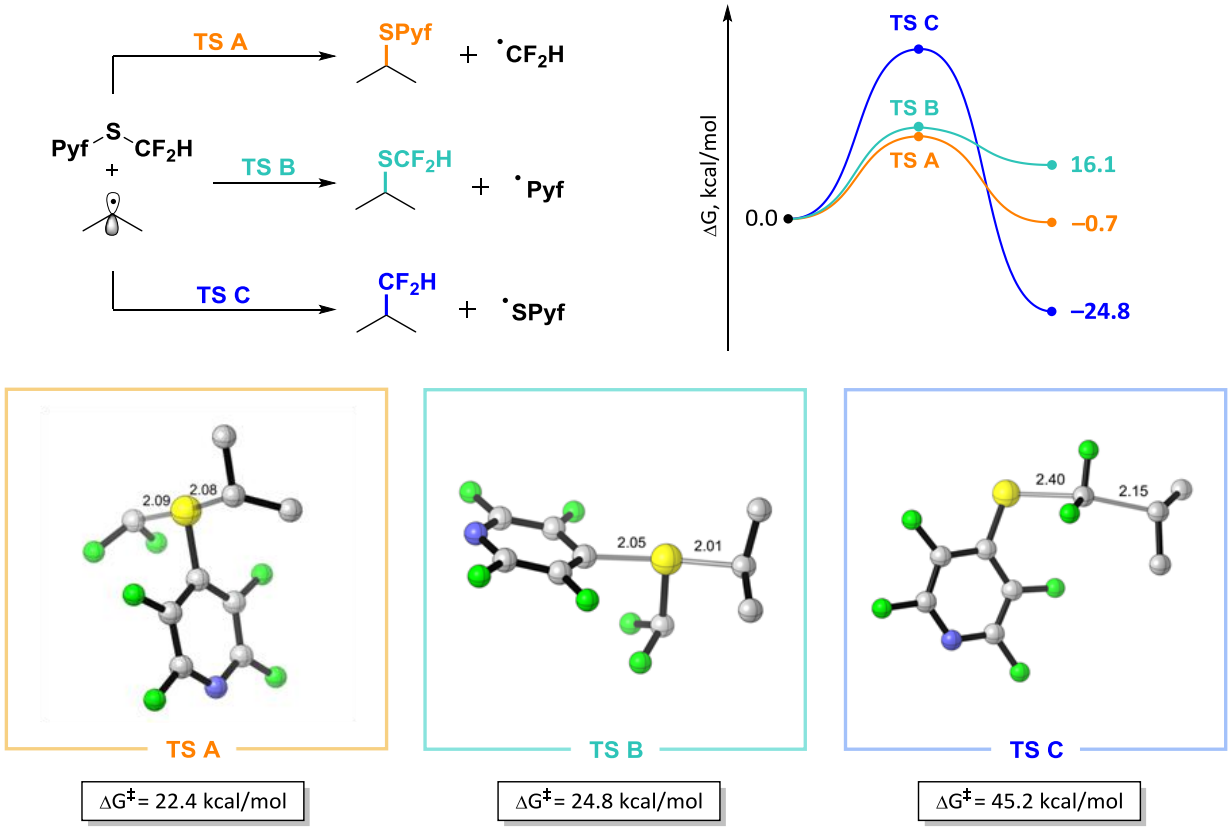
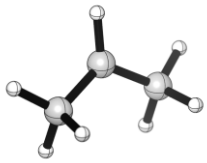


Figure S11. Energy profiles of possible homolytic substitution pathways and corresponding transition states (hydrogen atoms are omitted for clarity).

All calculations were carried out using the Gaussian09 package.[25] Geometries of stationary points were optimized using the ωB97XD functional in the 6-311++G(d,p) basis set. Stationary points were characterized as transition states or as local minima by the presence of one imaginary frequency or by their absence, respectively. Solvation effects were modeled using the IEFPCM model (DMSO).

All key structures are given in the .xyz format (visualized with CYLview[26]) with energies.

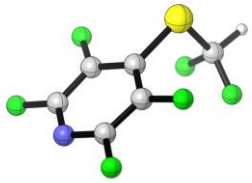
iso-Propyl radical



Energy = -118.469896480 E_h
Zero-point correction = 0.087890 E_h
Thermal correction to Energy = 0.093093 E_h
Thermal correction to Enthalpy = 0.094037 E_h
Thermal correction to Gibbs Free Energy = 0.060644 E_h
Sum of electronic and zero-point Energies = -118.382006 E_h
Sum of electronic and thermal Energies = -118.376804 E_h
Sum of electronic and thermal Enthalpies = -118.375860 E_h
Sum of electronic and thermal Free Energies = -118.409253 E_h

C	0.011133	-0.198741	1.291961
C	0.011133	0.540751	0.000000
C	0.011133	-0.198741	-1.291961
H	0.182807	0.462784	2.144117
H	-0.224175	1.600293	0.000000
H	0.182807	0.462784	-2.144117
H	0.778906	-0.982331	-1.303479
H	0.778906	-0.982331	1.303479
H	-0.949825	-0.710407	1.464966
H	-0.949825	-0.710407	-1.464966

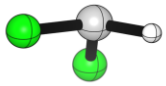
Sulfide **2a**



Energy = -1281.20586777 E_h
Zero-point correction = 0.070815 E_h
Thermal correction to Energy = 0.082849 E_h
Thermal correction to Enthalpy = 0.083793 E_h
Thermal correction to Gibbs Free Energy = 0.030592 E_h
Sum of electronic and zero-point Energies = -1281.135053 E_h
Sum of electronic and thermal Energies = -1281.123019 E_h
Sum of electronic and thermal Enthalpies = -1281.122075 E_h
Sum of electronic and thermal Free Energies = -1281.175276 E_h

S	1.799080	-0.000004	-1.159748
C	0.133389	-0.000001	-0.539721
C	-0.554522	-1.186668	-0.310002
C	-0.554518	1.186668	-0.310001
C	-1.864517	-1.122003	0.138838
C	-1.864513	1.122007	0.138839
F	0.014121	-2.365710	-0.513610
F	-2.527586	-2.248939	0.363617
F	-2.527578	2.248946	0.363621
F	0.014131	2.365708	-0.513607
N	-2.496555	0.000003	0.356370
C	2.673372	-0.000001	0.432411
H	3.742506	0.000000	0.222758
F	2.354343	-1.084121	1.179792
F	2.354341	1.084119	1.179790

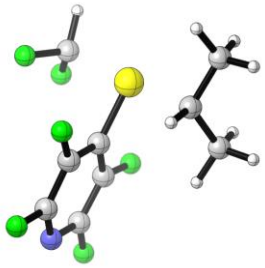
CF_2H radical



Energy = -238.324728140 E_h
Zero-point correction = 0.018993 E_h
Thermal correction to Energy = 0.022103 E_h
Thermal correction to Enthalpy = 0.023047 E_h
Thermal correction to Gibbs Free Energy = -0.006033 E_h
Sum of electronic and zero-point Energies = -238.305735 E_h
Sum of electronic and thermal Energies = -238.302625 E_h
Sum of electronic and thermal Enthalpies = -238.301681 E_h
Sum of electronic and thermal Free Energies = -238.330761 E_h

C	-0.029853	0.514142	0.000000
H	0.716474	1.306023	0.000000
F	-0.029853	-0.243937	1.092430
F	-0.029853	-0.243937	-1.092430

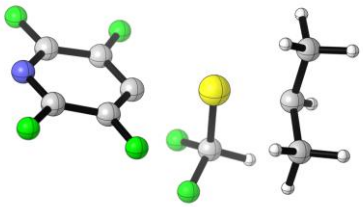
TS A



Energy = -1399.66252963 E_h
Zero-point correction = 0.161723 E_h
Thermal correction to Energy = 0.179223 E_h
Thermal correction to Enthalpy = 0.180167 E_h
Thermal correction to Gibbs Free Energy = 0.113738 E_h
Sum of electronic and zero-point Energies = -1399.500807 E_h
Sum of electronic and thermal Energies = -1399.483307 E_h
Sum of electronic and thermal Enthalpies = -1399.482363 E_h
Sum of electronic and thermal Free Energies = -1399.548791 E_h

S	1.647986	0.375962	0.020671
C	-0.085774	-0.019749	0.031147
C	-0.760137	-0.299515	1.214317
C	-0.833787	-0.073266	-1.139624
C	-2.110151	-0.605304	1.165275
C	-2.180899	-0.388972	-1.063845
F	-0.133194	-0.282214	2.385105
F	-2.756653	-0.871023	2.295081
F	-2.897538	-0.441783	-2.181268
F	-0.282190	0.158255	-2.324597
N	-2.800780	-0.647004	0.056826
C	1.801697	-2.355537	-1.081943
C	2.252073	-1.611289	0.148514
C	3.746220	-1.515286	0.327121
H	0.714433	-2.400815	-1.168839
H	1.742384	-1.933245	1.056893
H	4.013634	-0.932821	1.211058
H	4.160751	-2.521820	0.447458
H	2.166139	-3.388315	-1.024052
H	2.212918	-1.906510	-1.989775
H	4.220799	-1.064404	-0.549540
C	1.189694	2.418704	0.066884
H	2.150400	2.931635	0.062335
F	0.442563	2.775956	-0.995486
F	0.487303	2.708722	1.178818

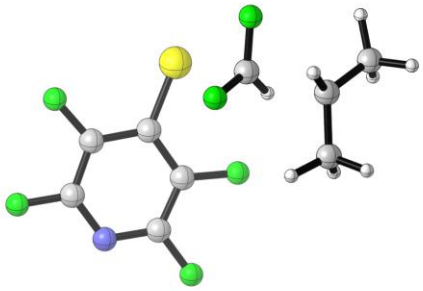
TS B



Energy = -1399.66012674 E_h
Zero-point correction = 0.162572 E_h
Thermal correction to Energy = 0.179711 E_h
Thermal correction to Enthalpy = 0.180655 E_h
Thermal correction to Gibbs Free Energy = 0.115181 E_h
Sum of electronic and zero-point Energies = -1399.497555 E_h
Sum of electronic and thermal Energies = -1399.480416 E_h
Sum of electronic and thermal Enthalpies = -1399.479471 E_h
Sum of electronic and thermal Free Energies = -1399.544945 E_h

S	1.421372	-0.531726	-0.346196
C	-0.565035	-0.116095	-0.092364
C	-1.517976	-1.089003	-0.312428
C	-0.998099	1.189312	0.011906
C	-2.849754	-0.712738	-0.392496
C	-2.355814	1.451456	-0.083461
F	-1.190185	-2.378146	-0.437745
F	-3.783651	-1.641788	-0.590341
F	-2.790842	2.705317	0.028419
F	-0.145214	2.199139	0.200381
N	-3.258090	0.525078	-0.281336
C	1.648300	-0.729146	1.447162
H	2.680321	-1.009343	1.654734
F	0.822588	-1.690555	1.923390
F	1.351330	0.404784	2.131792
C	3.750119	1.209032	-0.110889
C	3.337749	-0.093857	-0.754629
C	3.416477	-0.099498	-2.264216
H	3.682821	1.181648	0.977995
H	3.844291	-0.960794	-0.322493
H	3.084304	-1.049425	-2.687427
H	2.817024	0.708003	-2.693549
H	3.135475	2.035305	-0.476605
H	4.792361	1.420468	-0.372719
H	4.456037	0.060675	-2.566017

TS C



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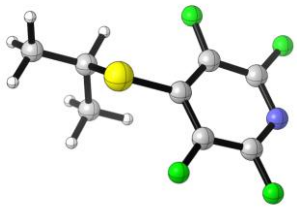
Zero-point correction = 0.160633 E_h
Thermal correction to Energy = 0.178371 E_h
Thermal correction to Enthalpy = 0.179316 E_h
Thermal correction to Gibbs Free Energy = 0.112083 E_h
Sum of electronic and zero-point Energies = -1399.463882 E_h
Sum of electronic and thermal Energies = -1399.446143 E_h
Sum of electronic and thermal Enthalpies = -1399.445199 E_h
Sum of electronic and thermal Free Energies = -1399.512432 E_h

S	0.176394	-1.713537	0.956301
C	-1.037613	-0.552271	0.490048
C	-0.867486	0.829409	0.613466
C	-2.274464	-0.943184	-0.031987
C	-1.870626	1.693234	0.223671
C	-3.209513	0.011766	-0.380986
F	0.271856	1.329258	1.110408
F	-1.680755	3.005531	0.346886
F	-4.381124	-0.381950	-0.877481
F	-2.564163	-2.234033	-0.198634
N	-3.020661	1.301841	-0.262726
C	2.055721	-0.770273	-0.204457
H	2.009495	-0.080668	0.619979
F	1.443844	-0.561991	-1.344348
F	2.745273	-1.882361	-0.172330
C	4.678855	0.296116	0.478552
C	3.728109	0.502395	-0.651038
C	3.132338	1.855008	-0.848250
H	4.942573	-0.753513	0.612033
H	3.936513	-0.061961	-1.558260
H	2.328837	1.850828	-1.585878
H	2.767706	2.280075	0.090200
H	4.289039	0.699997	1.416873
H	5.605118	0.840935	0.253291
H	3.916739	2.524729	-1.224578

i-Pr–SPyf



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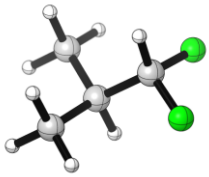
Zero-point correction = 0.142459 E_h
Thermal correction to Energy = 0.155960 E_h
Thermal correction to Enthalpy = 0.156904 E_h
Thermal correction to Gibbs Free Energy = 0.101092 E_h
Sum of electronic and zero-point Energies = -1161.213555 E_h
Sum of electronic and thermal Energies = -1161.200054 E_h
Sum of electronic and thermal Enthalpies = -1161.199110 E_h
Sum of electronic and thermal Free Energies = -1161.254922 E_h

S	1.631188	-0.598991	-0.917337
C	-0.017837	-0.192074	-0.432619
C	-0.953662	-1.193431	-0.186300
C	-0.479852	1.116978	-0.314564
C	-2.247748	-0.843959	0.161188
C	-1.794321	1.344577	0.051838
F	-0.623440	-2.478538	-0.271491
F	-3.134340	-1.804712	0.399877
F	-2.225354	2.596086	0.170596
F	0.321127	2.151575	-0.558104
N	-2.658425	0.390746	0.282016
C	2.640516	0.292857	0.358715
H	2.454478	1.357568	0.220319
C	4.094994	-0.014477	0.019685
H	4.740665	0.521680	0.719333
H	4.306236	-1.083175	0.115867
H	4.352833	0.305751	-0.992089
C	2.267980	-0.132572	1.770495
H	1.224313	0.088996	2.004619
H	2.437415	-1.203058	1.912871
H	2.891679	0.413799	2.483837

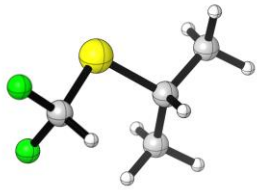
i-Pr-CF_2H



Energy = -356.949330771 E_h
Zero-point correction = 0.117295 E_h
Thermal correction to Energy = 0.124209 E_h
Thermal correction to Enthalpy = 0.125153 E_h
Thermal correction to Gibbs Free Energy = 0.086598 E_h
Sum of electronic and zero-point Energies = -356.832035 E_h
Sum of electronic and thermal Energies = -356.825122 E_h
Sum of electronic and thermal Enthalpies = -356.824178 E_h
Sum of electronic and thermal Free Energies = -356.862733 E_h

C	1.415300	-1.264244	0.058226
C	0.648543	-0.000002	-0.333833
C	1.415282	1.264254	0.058219
H	0.890134	-2.169010	-0.252424
H	0.479526	-0.000005	-1.416554
H	0.890141	2.169008	-0.252507
H	1.566847	1.307445	1.141589
H	1.566938	-1.307386	1.141588
H	2.398399	-1.261138	-0.416953
H	2.398413	1.261120	-0.416891
C	-0.717523	-0.000002	0.313191
H	-0.693459	-0.000011	1.405895
F	-1.448142	1.094439	-0.083805
F	-1.448141	-1.094445	-0.083812

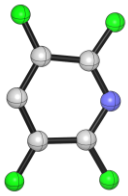
i-Pr-SCF_2H



Energy = -755.133764419 E_h
Zero-point correction = 0.118299 E_h
Thermal correction to Energy = 0.126889 E_h
Thermal correction to Enthalpy = 0.127834 E_h
Thermal correction to Gibbs Free Energy = 0.083713 E_h
Sum of electronic and zero-point Energies = -755.015465 E_h
Sum of electronic and thermal Energies = -755.006875 E_h
Sum of electronic and thermal Enthalpies = -755.005931 E_h
Sum of electronic and thermal Free Energies = -755.050052 E_h

S	0.023389	-0.784188	-0.444096
C	-1.390579	0.052298	0.399868
H	-1.187043	-0.018107	1.471350
C	-2.638658	-0.763167	0.075258
H	-3.497577	-0.317009	0.582336
H	-2.843926	-0.757475	-0.999143
H	-2.544204	-1.798534	0.408394
C	-1.536452	1.511447	-0.012186
H	-0.652838	2.100573	0.238549
H	-1.711063	1.593125	-1.088327
H	-2.392564	1.948976	0.509963
C	1.401884	0.066995	0.340842
H	1.192372	0.325281	1.379492
F	1.753501	1.214396	-0.316187
F	2.495993	-0.740536	0.291769

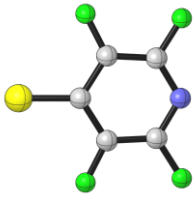
Pyf radical



Energy = -644.519859949 E_h
Zero-point correction = 0.044195 E_h
Thermal correction to Energy = 0.051555 E_h
Thermal correction to Enthalpy = 0.052500 E_h
Thermal correction to Gibbs Free Energy = 0.011031 E_h
Sum of electronic and zero-point Energies = -644.475665 E_h
Sum of electronic and thermal Energies = -644.468305 E_h
Sum of electronic and thermal Enthalpies = -644.467360 E_h
Sum of electronic and thermal Free Energies = -644.508829 E_h

C	0.000000	-1.378847	0.000000
C	0.000000	-0.734226	1.205424
C	0.000000	-0.734226	-1.205424
C	0.000000	0.655230	1.127988
C	0.000000	0.655230	-1.127988
F	0.000000	-1.364068	2.372979
F	0.000000	1.364073	2.249631
F	0.000000	1.364073	-2.249631
F	0.000000	-1.364068	-2.372979
N	0.000000	1.317278	0.000000

PyfS radical



Energy = -1042.77289466 E_h
Zero-point correction = 0.046695 E_h
Thermal correction to Energy = 0.055331 E_h
Thermal correction to Enthalpy = 0.056276 E_h
Thermal correction to Gibbs Free Energy = 0.011526 E_h
Sum of electronic and zero-point Energies = -1042.726199 E_h
Sum of electronic and thermal Energies = -1042.717563 E_h
Sum of electronic and thermal Enthalpies = -1042.716619 E_h
Sum of electronic and thermal Free Energies = -1042.761368 E_h

S	-2.619821	0.000000	-0.000029
C	-0.902284	0.000000	-0.000013
C	-0.155204	-1.192283	-0.000003
C	-0.155204	1.192283	-0.000002
C	1.227065	-1.125193	0.000013
C	1.227065	1.125194	0.000014
F	-0.753400	-2.369777	-0.000007
F	1.931954	-2.248740	0.000021
F	1.931954	2.248740	0.000021
F	-0.753401	2.369777	-0.000006
N	1.893507	0.000000	0.000020

X-Ray Crystallographic Data

Identification code	**3d**
Empirical formula	$C_{17}H_{12}F_6N_2OS$
Formula weight	406.35
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 7.1213(2) Å
	b = 9.6599(3) Å
	c = 24.5371(8) Å
Volume	1687.93(9) $Å^3$
Z	4
Density (calculated)	1.599 g/cm^3
Absorption coefficient	0.264 mm^{-1}
F(000)	824
Crystal size	0.24 x 0.20 x 0.13 mm^3
Theta range for data collection	2.684 to 33.208°.
Index ranges	-10≤h≤10, -14≤k≤14, -37≤l≤37
Reflections collected	59793
Independent reflections	6462 [R(int) = 0.0560]
Observed reflections	5749
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6843 and 0.6672
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6462 / 0 / 249
Goodness-of-fit on F^2	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0733
R indices (all data)	R1 = 0.0433, wR2 = 0.0784
Absolute structure parameter	0.12(7)
Largest diff. peak and hole	0.349 and -0.206 $e \cdot Å^{-3}$

X-ray crystallographic data and refinement details.

X-ray diffraction data were collected at 100K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (graphite monochromator, shutterless φ- and ω-scan technique), using Mo K_α-radiation (0.71073 Å). The intensity data were integrated by the SAINT program[27] and corrected for absorption and decay using SADABS.[28] The structure was solved by direct methods using SHELXS-2013[29] and refined on F^2 using SHELXL-2018.[30] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The SHELXTL program suite[27] was used for molecular graphics.

CCDC contains the supplementary crystallographic data for **3d** (# 1988907). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

Crystal structure determination was performed in the Department of Structural Studies of Zelinsky Institute of Organic Chemistry, Moscow.

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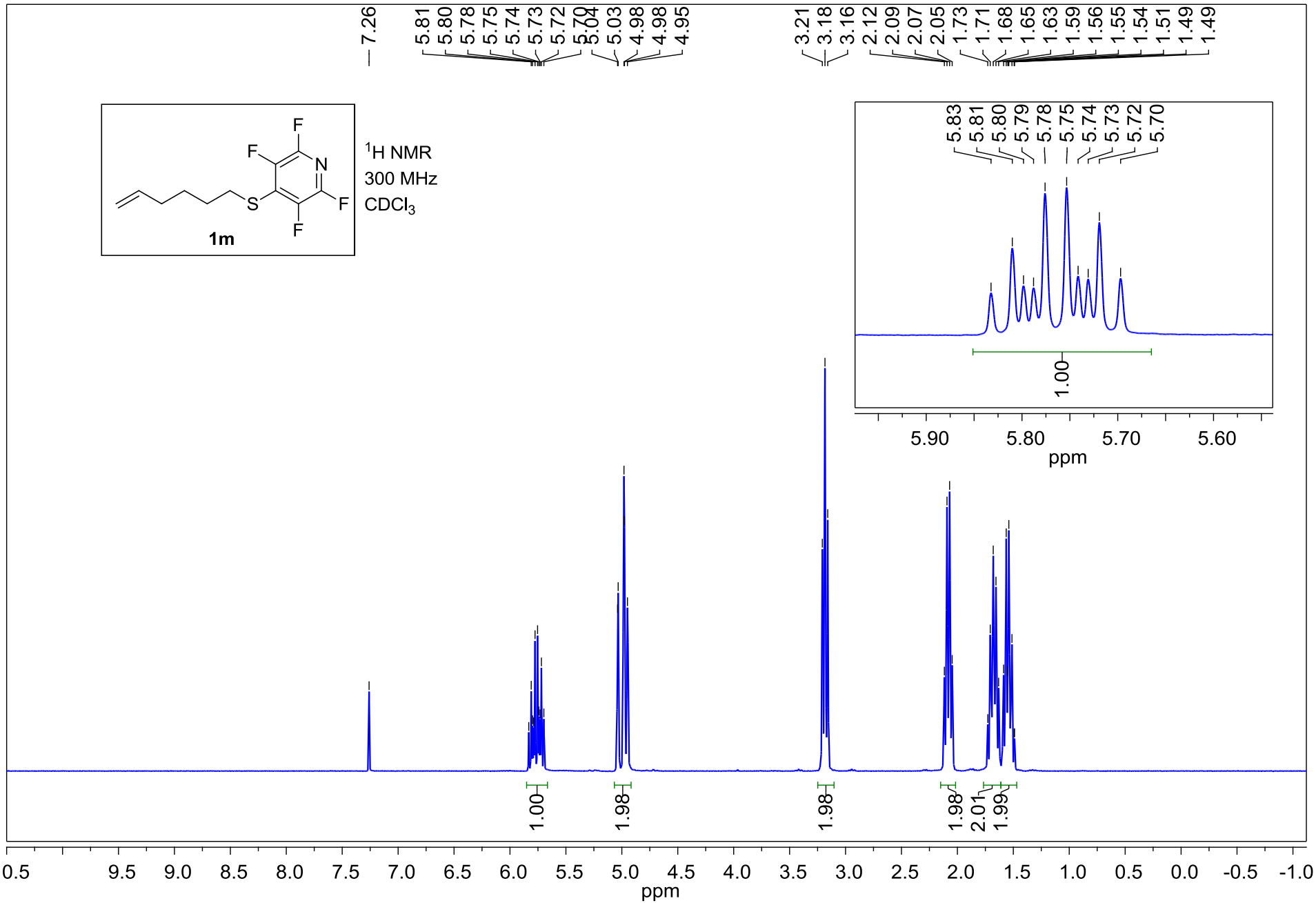
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2.05
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1.0
0.5
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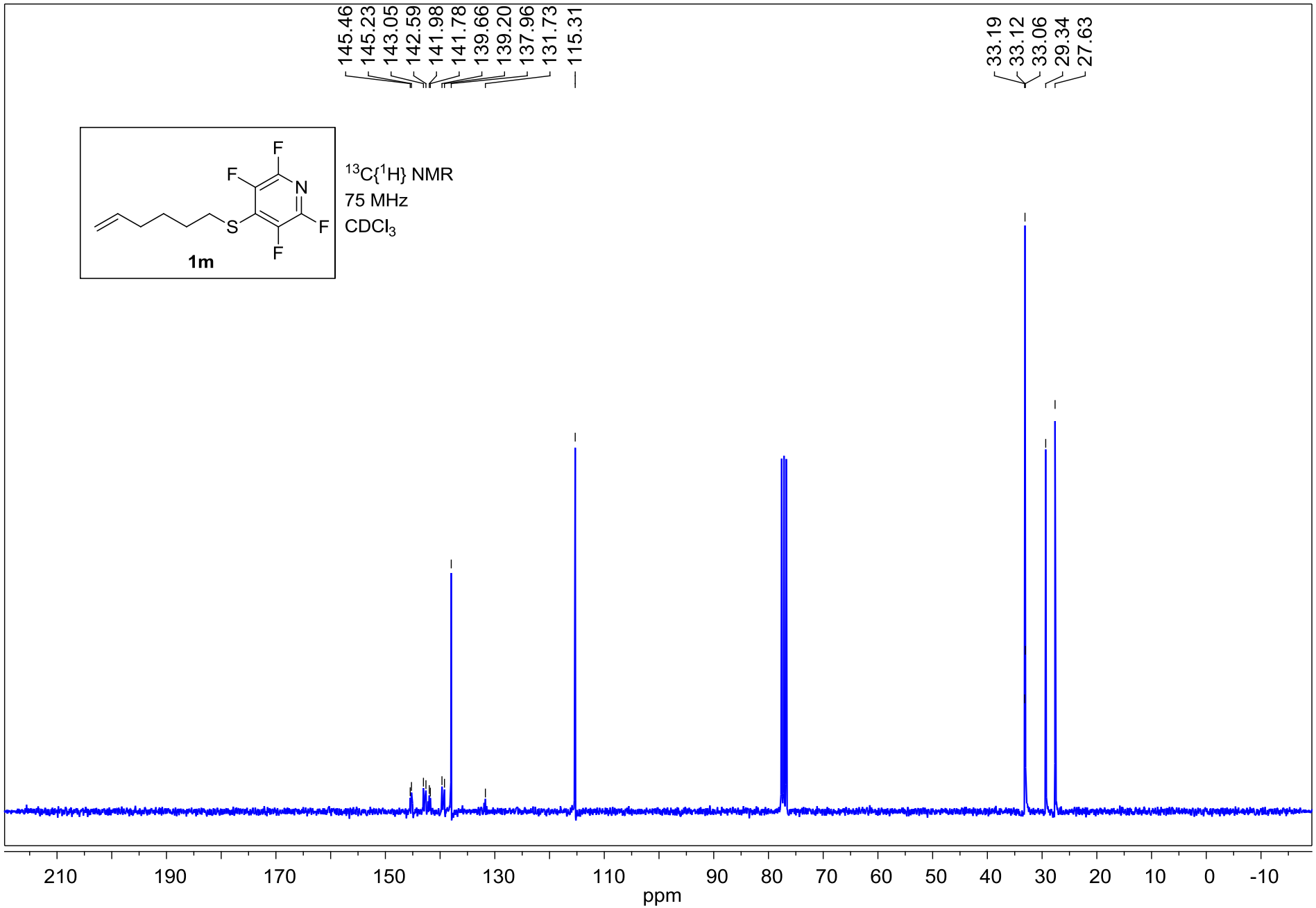
-1.0
ppm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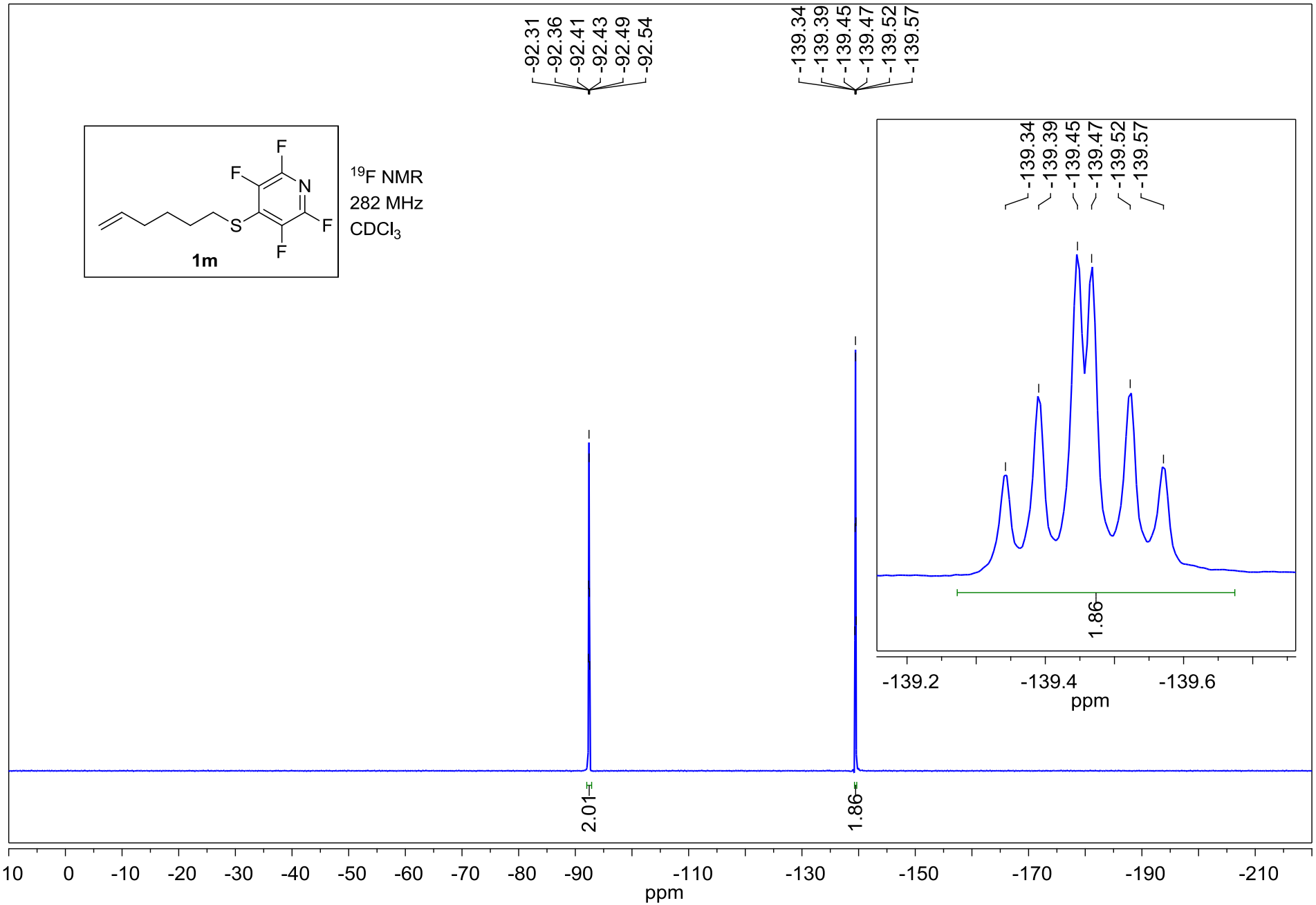
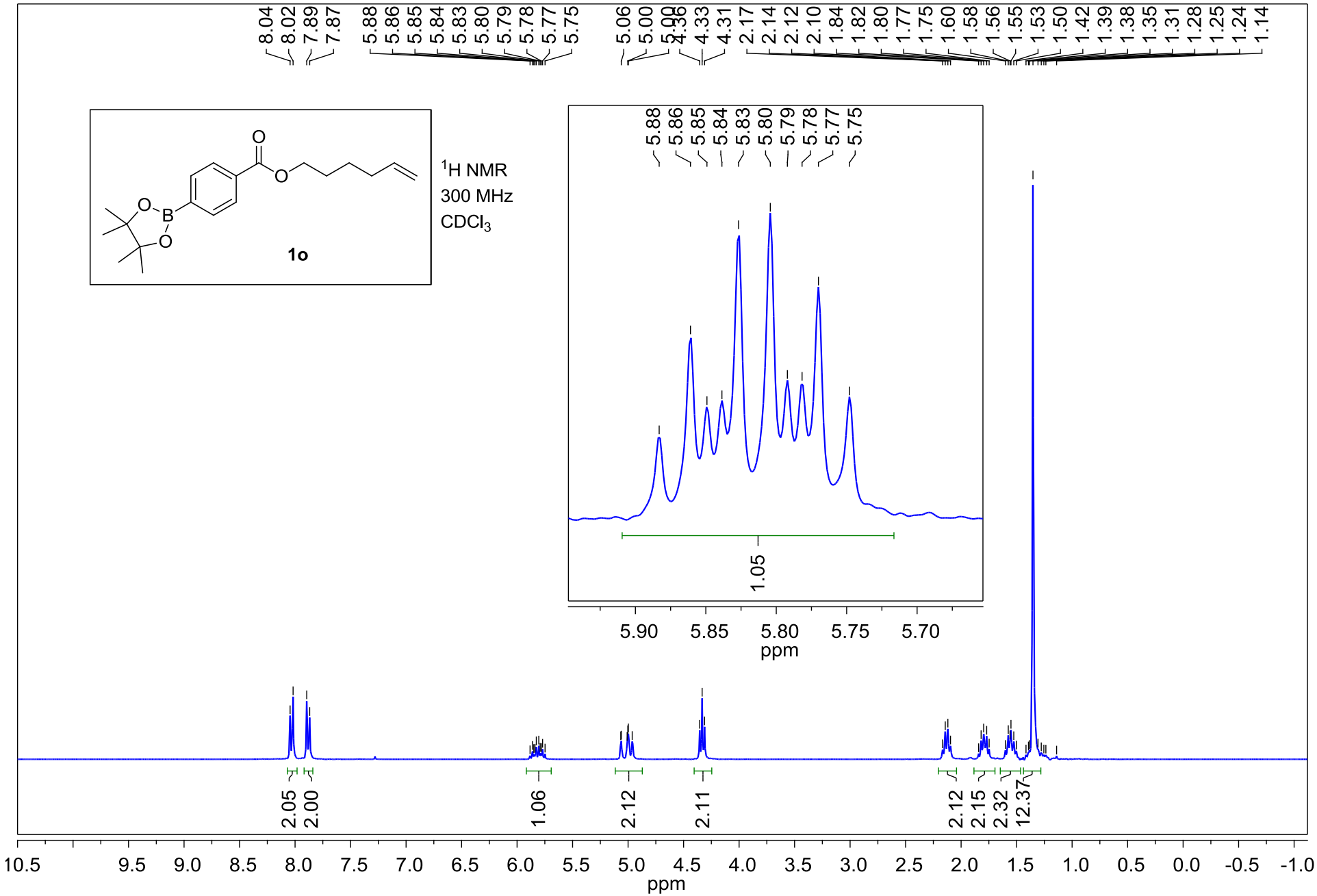
145.23
143.05
142.59
141.98
141.78
139.66
139.20
137.96
131.73
115.31
33.19
33.12
33.06
29.34
27.63
F
F
N
S
F
F
1m
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm


-92.31
-92.36
-92.41
-92.43
-92.49
-92.54
-139.34
-139.39
-139.45
-139.47
-139.52
-139.57
F
F
N
S
F
F
1m
19F NMR
282 MHz
CDCl3
1.86
-139.2
-139.4
-139.6
ppm
2.01
1.86
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm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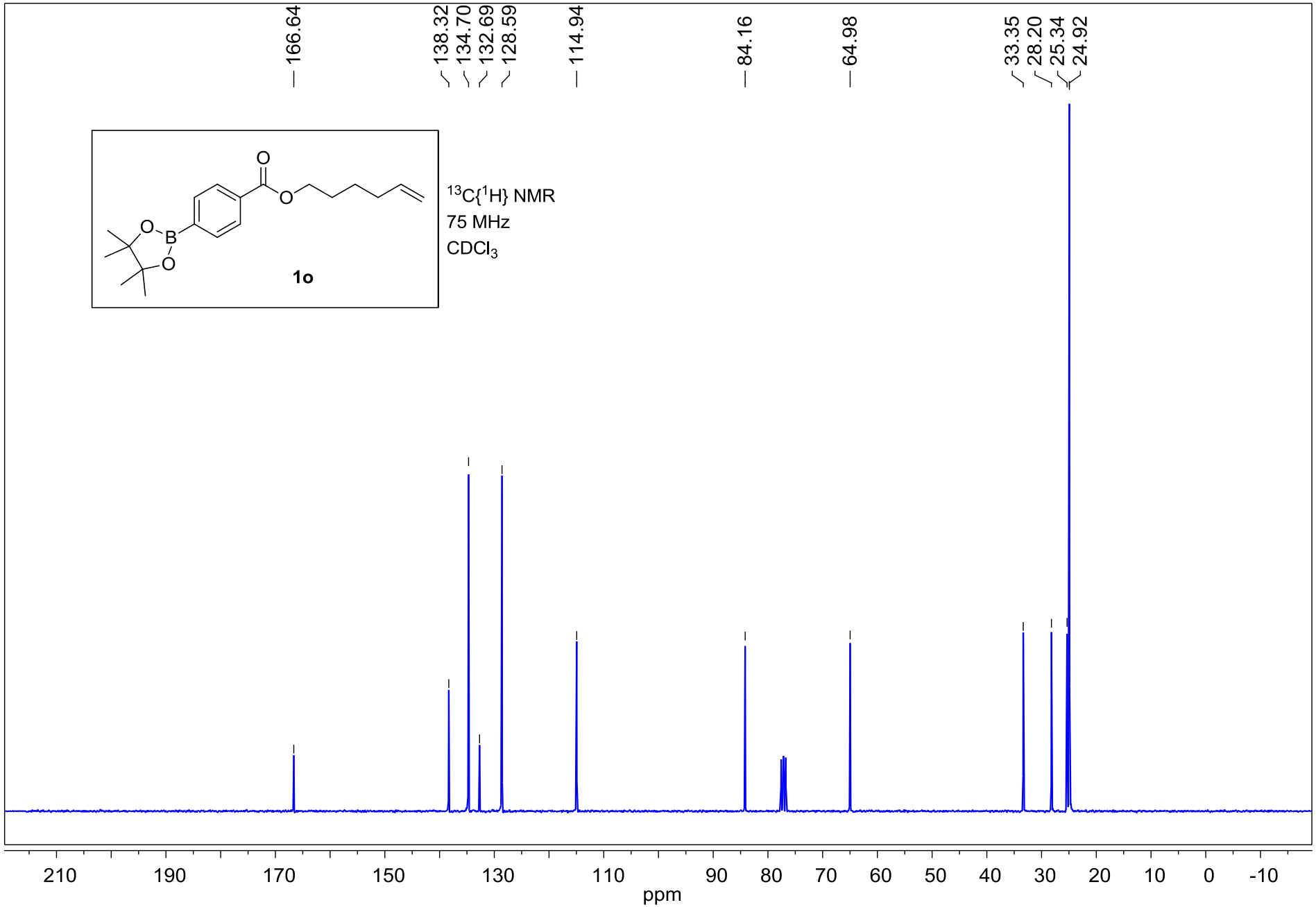
8.02
7.89
7.87
5.88
5.86
5.85
5.84
5.83
5.80
5.79
5.78
5.77
5.75
5.06
5.00
4.36
4.33
4.31
2.17
2.14
2.12
2.10
1.84
1.82
1.80
1.77
1.75
1.60
1.58
1.56
1.55
1.53
1.50
1.42
1.39
1.38
1.35
1.31
1.28
1.25
1.24
1.14
O
O
O
B
O
1o
1H NMR
300 MHz
CDCl3
1.05
5.90
5.85
5.80
5.75
5.70
ppm
2.05
2.00
1.06
2.12
2.11
2.12
2.15
2.32
12.37
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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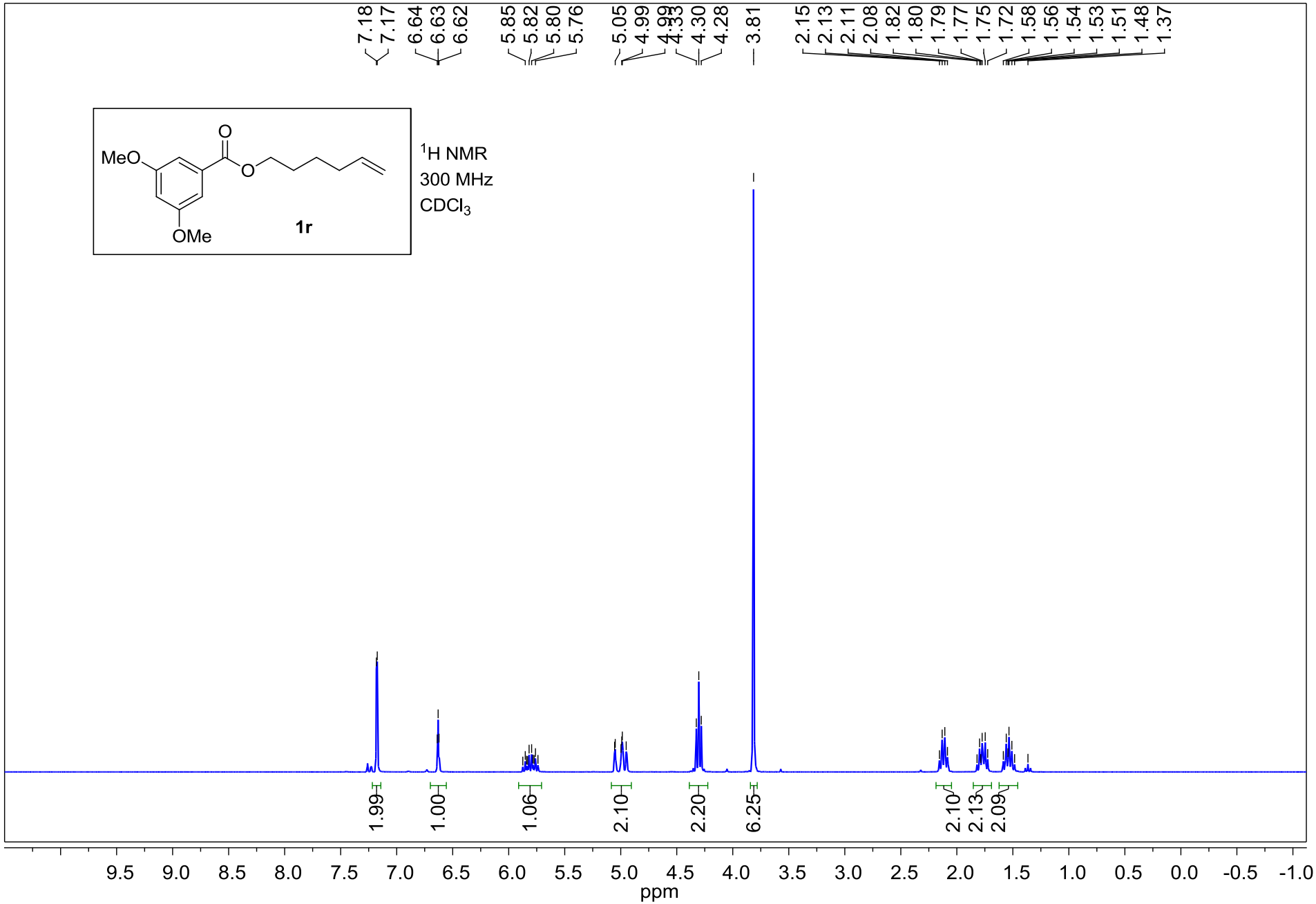
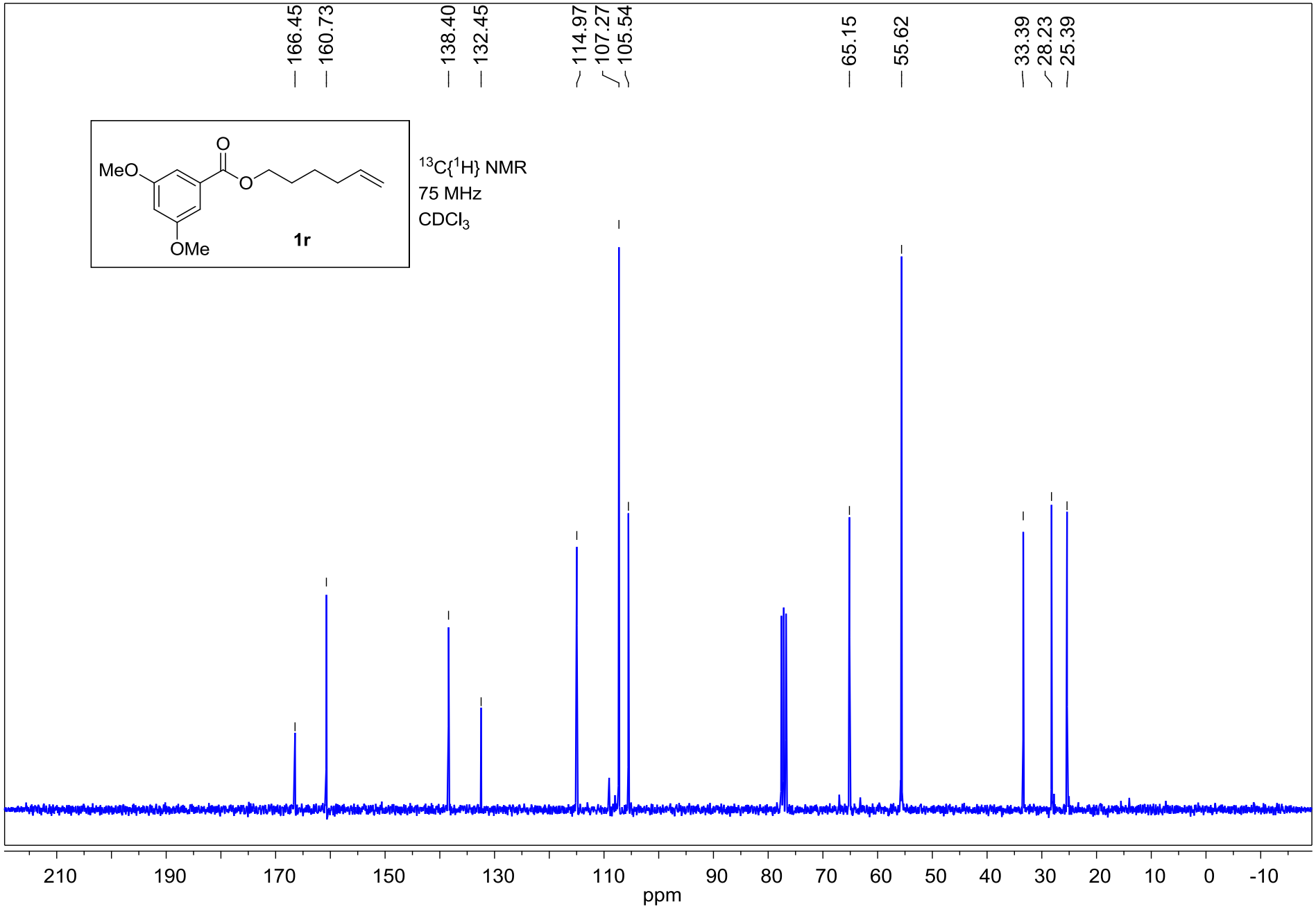
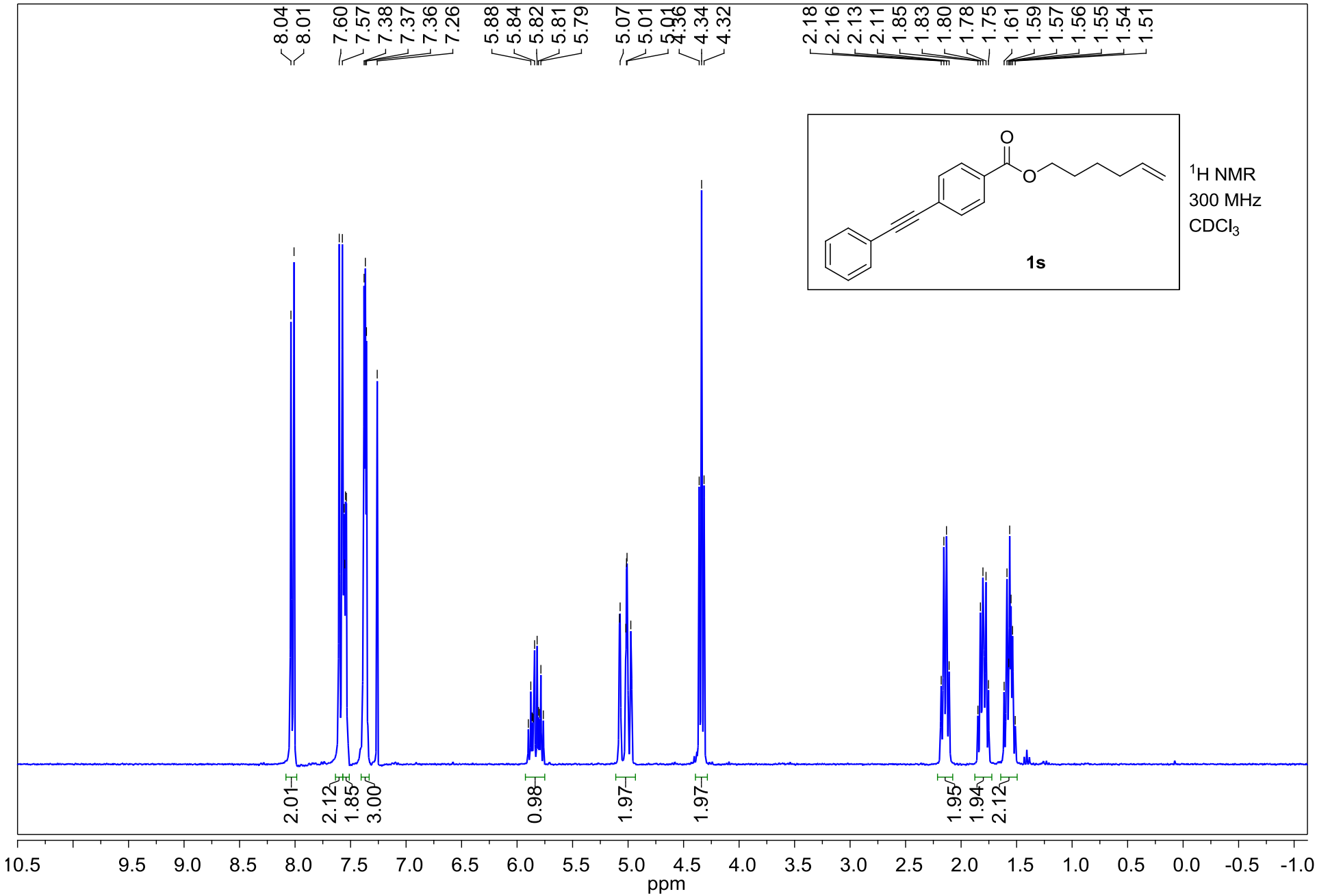
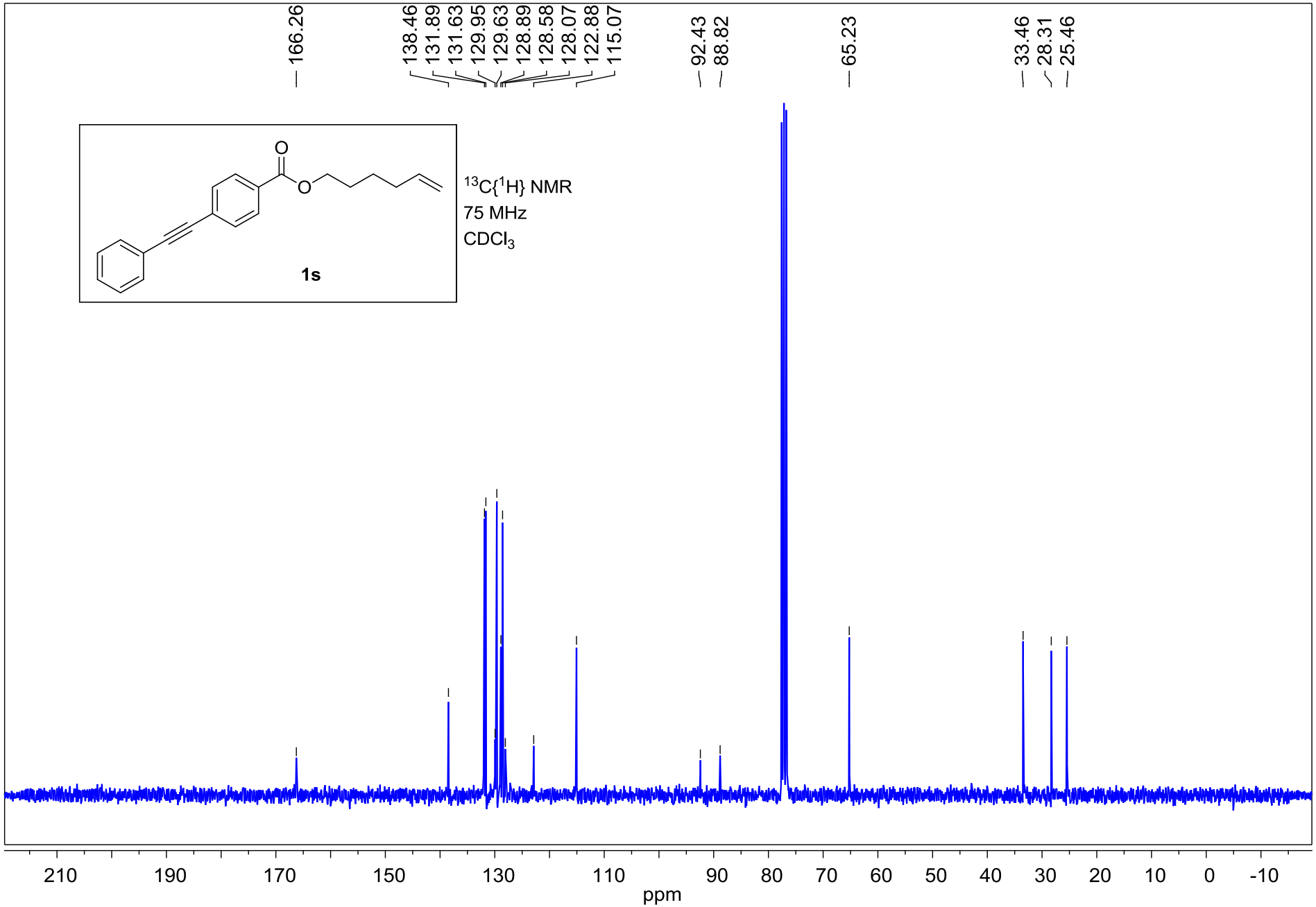
138.32
134.70
132.69
128.59
114.94
84.16
64.98
33.35
28.20
25.34
24.92
O
O
O
B
O
1o
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm


7.18
7.17
6.64
6.63
6.62
5.85
5.82
5.80
5.76
5.05
4.99
4.99
4.33
4.30
4.28
3.81
2.15
2.13
2.11
2.08
1.82
1.80
1.79
1.77
1.75
1.72
1.58
1.56
1.54
1.53
1.51
1.48
1.37
MeO
O
O
OMe
1r
1H NMR
300 MHz
CDCl3
1.99
1.00
1.06
2.10
2.20
6.25
2.10
2.13
2.09
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


166.45
160.73
138.40
132.45
114.97
107.27
105.54
65.15
55.62
33.39
28.23
25.39
MeO
OMe
O
O
1r
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm


8.04
8.01
7.60
7.57
7.38
7.37
7.36
7.26
5.88
5.84
5.82
5.81
5.79
5.07
5.01
5.01
4.36
4.34
4.32
2.18
2.16
2.13
2.11
1.85
1.83
1.80
1.78
1.75
1.61
1.59
1.57
1.56
1.55
1.54
1.51
O
O
1s
1H NMR
300 MHz
CDCl3
2.01
2.12
1.85
3.00
0.98
1.97
1.97
1.95
1.94
2.12
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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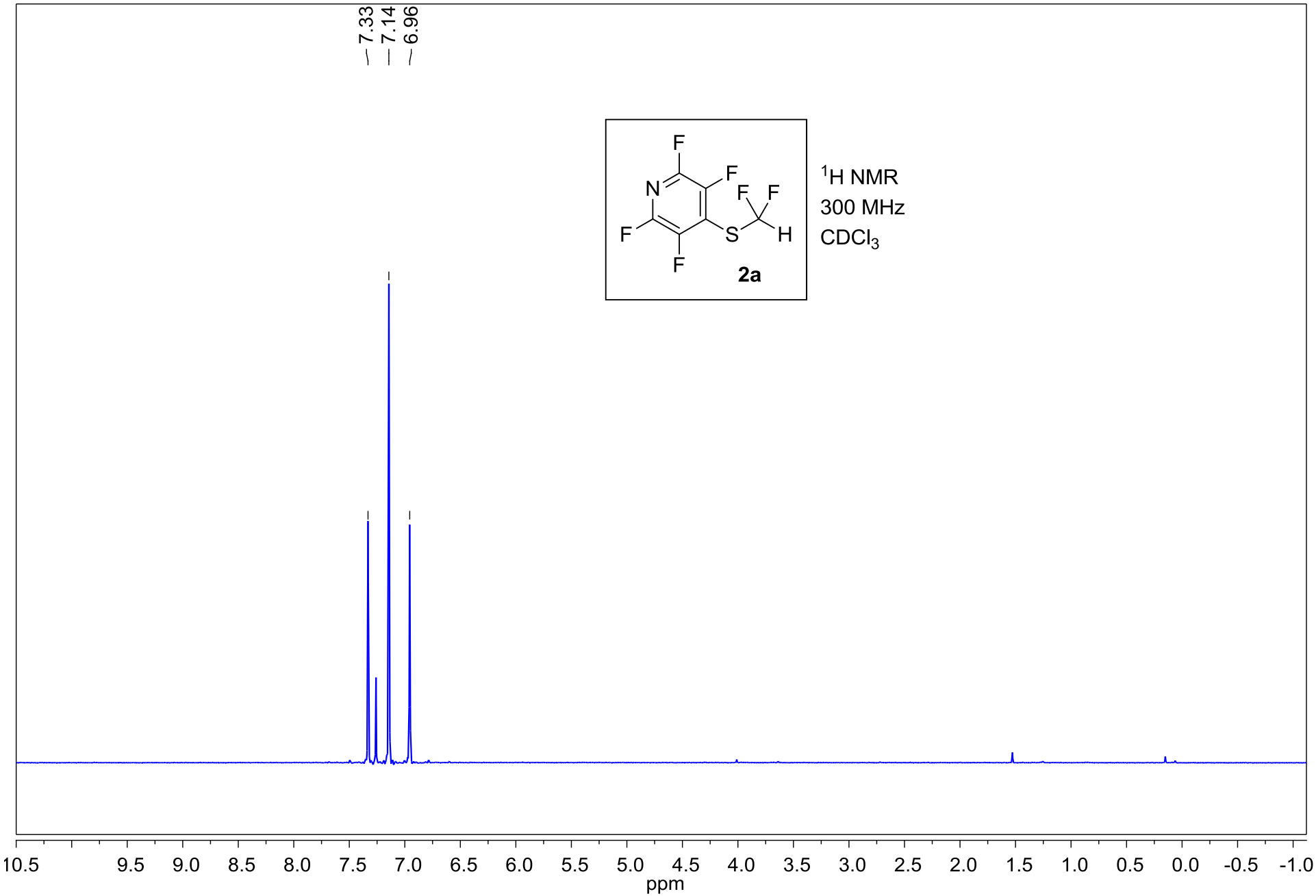
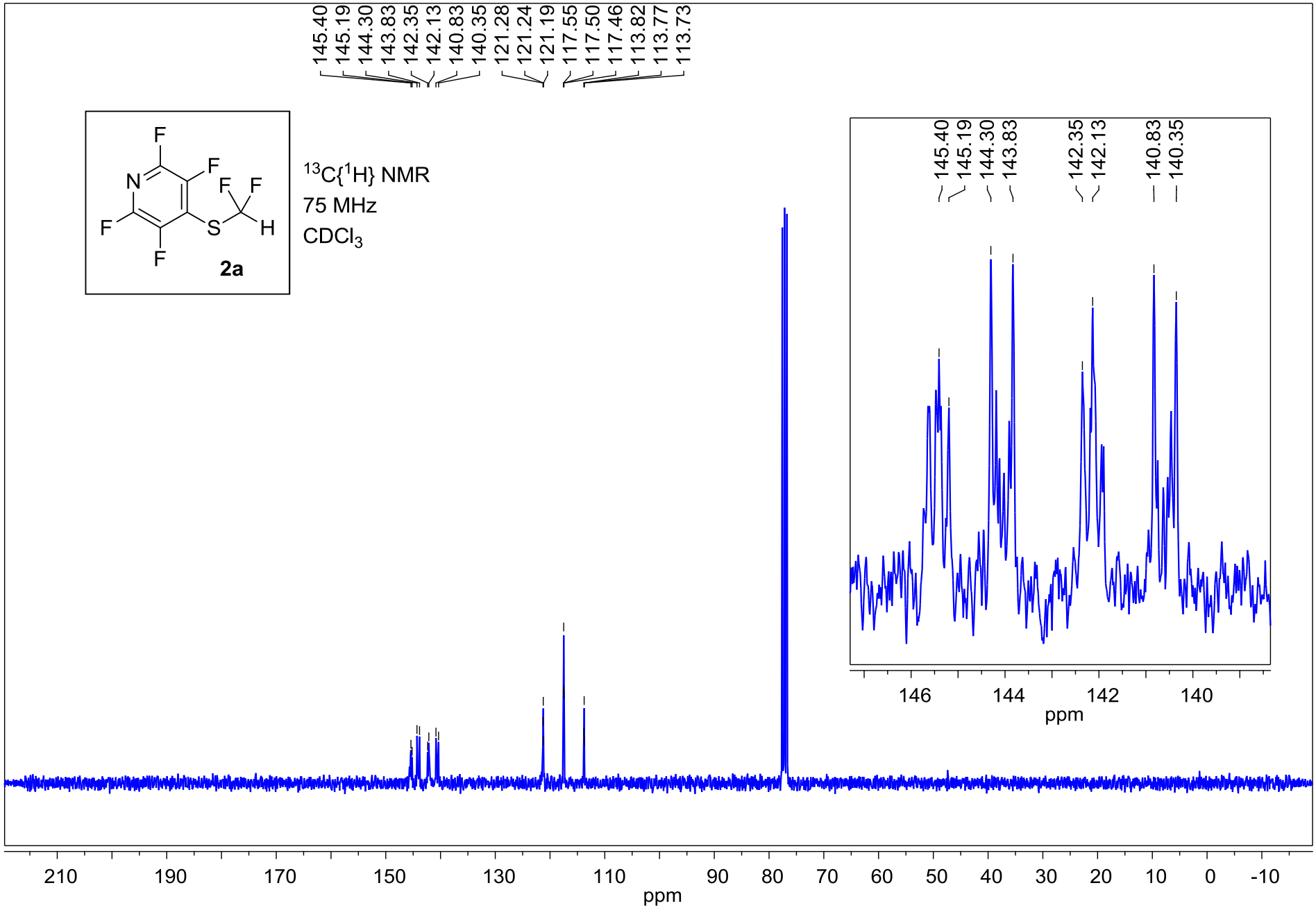
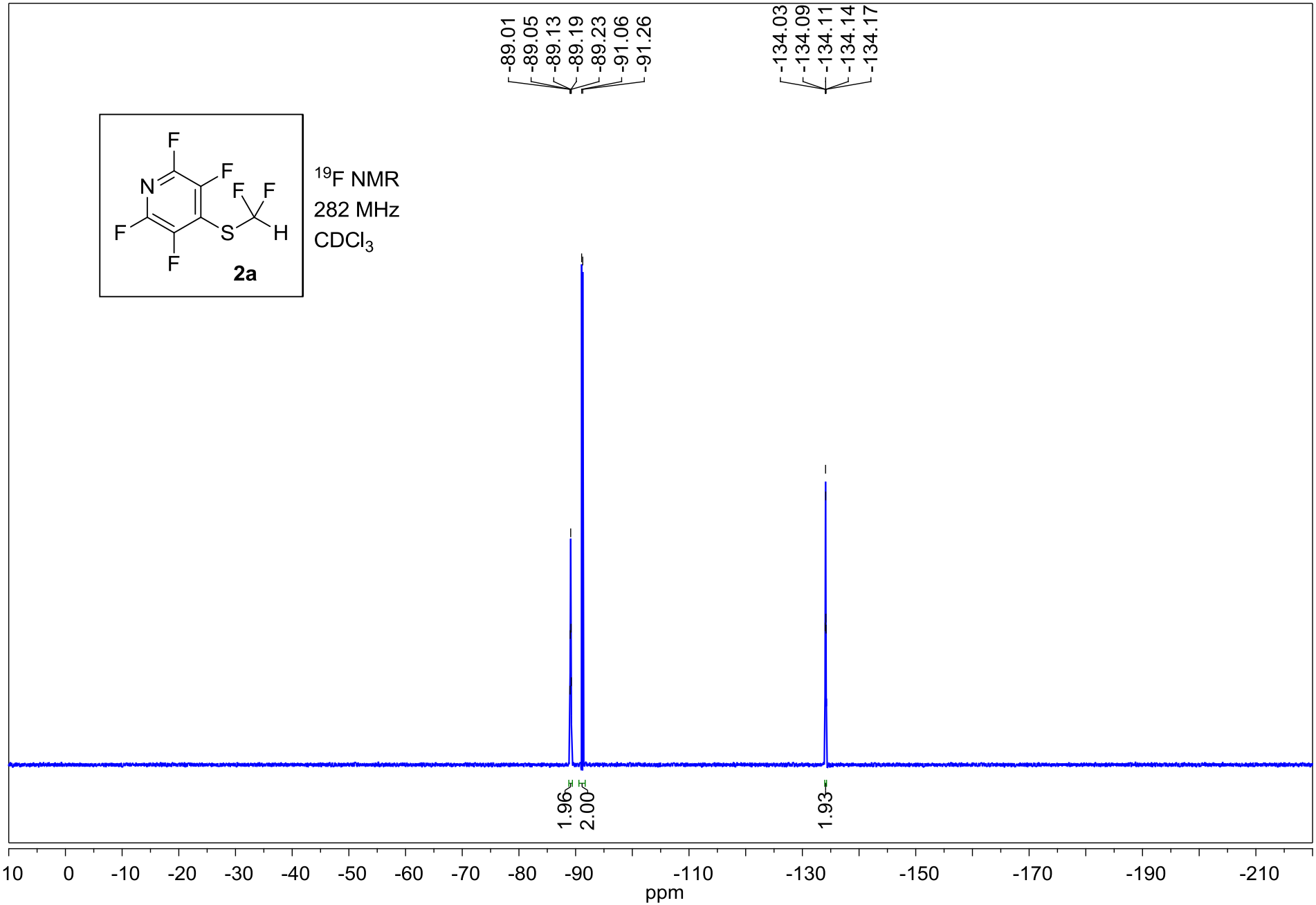
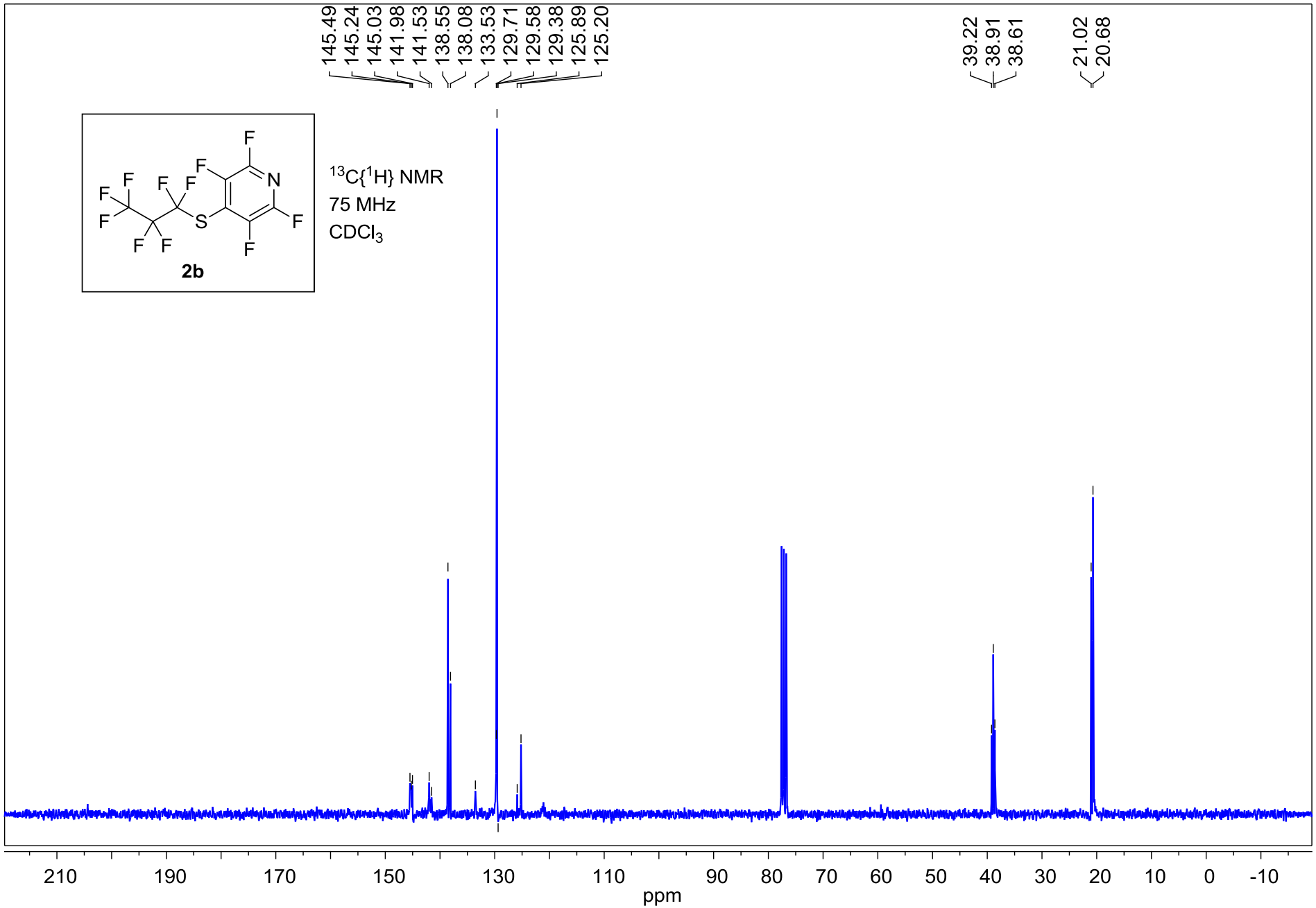
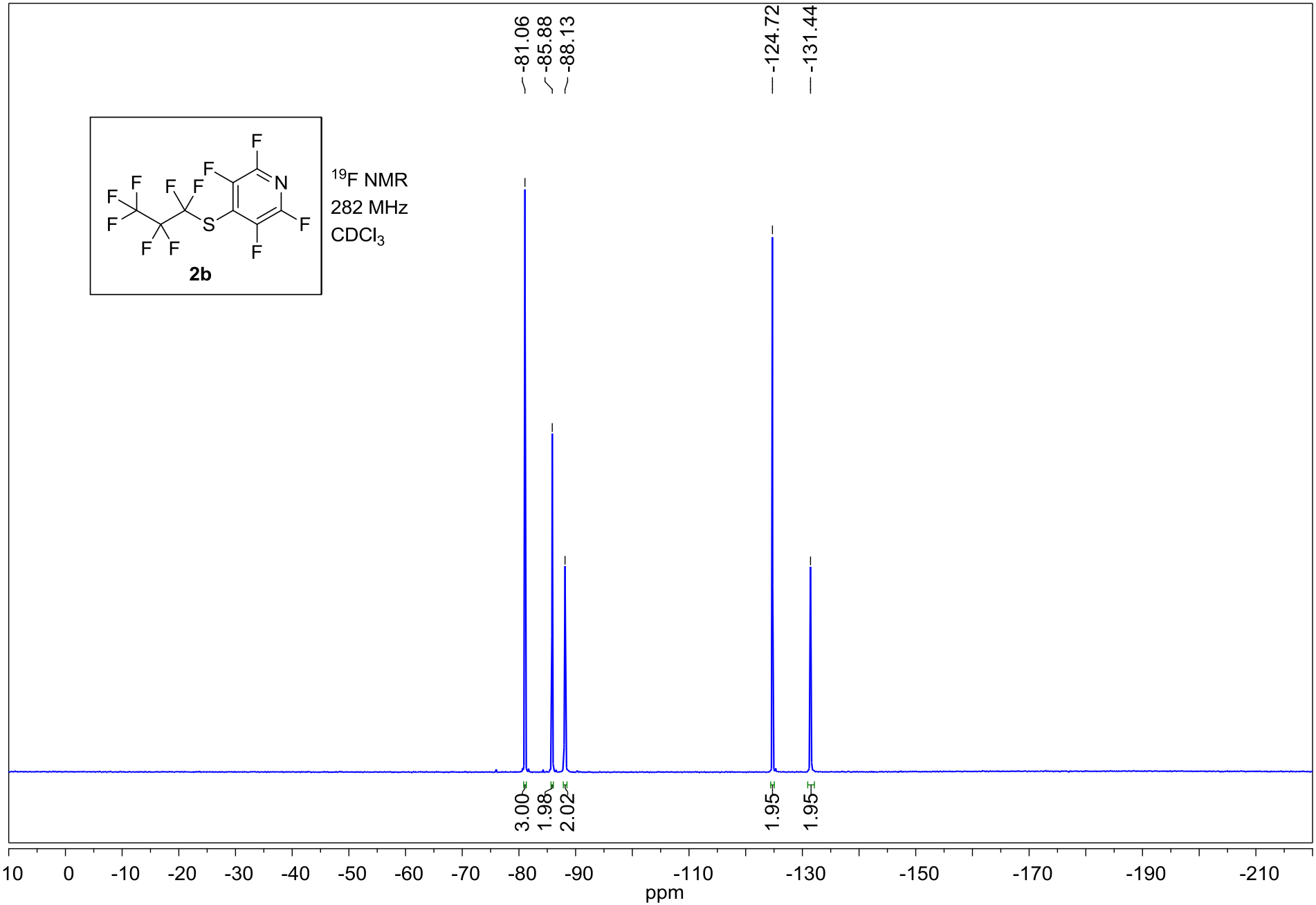
138.46
131.89
131.63
129.95
129.63
128.89
128.58
128.07
122.88
115.07
92.43
88.82
65.23
33.46
28.31
25.46
O
O
1s
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

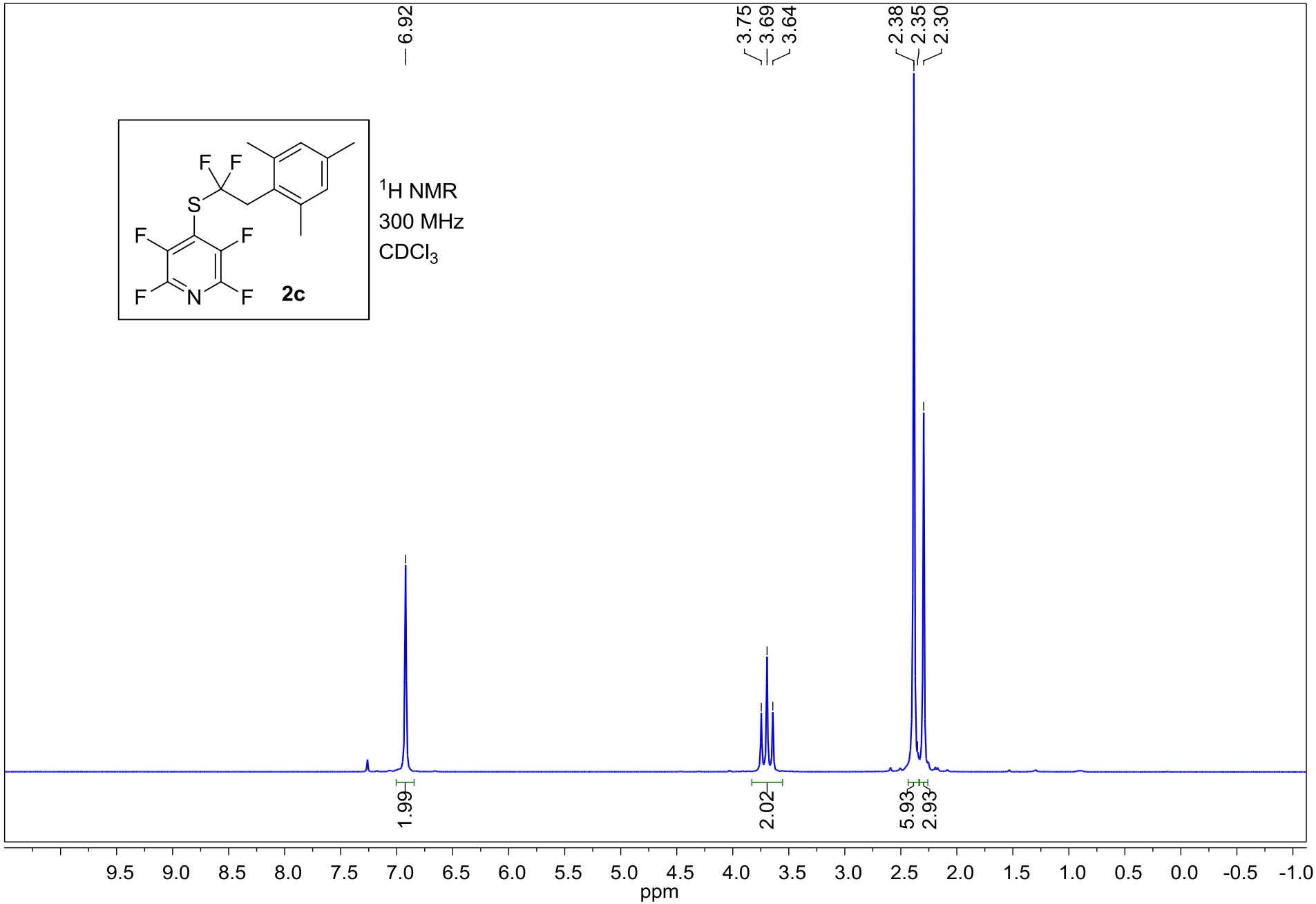

7.33
7.14
6.96
F
N
F
F
F
F
S
H
F
2a
^{1}H NMR
300 MHz
$CDCl_3$
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

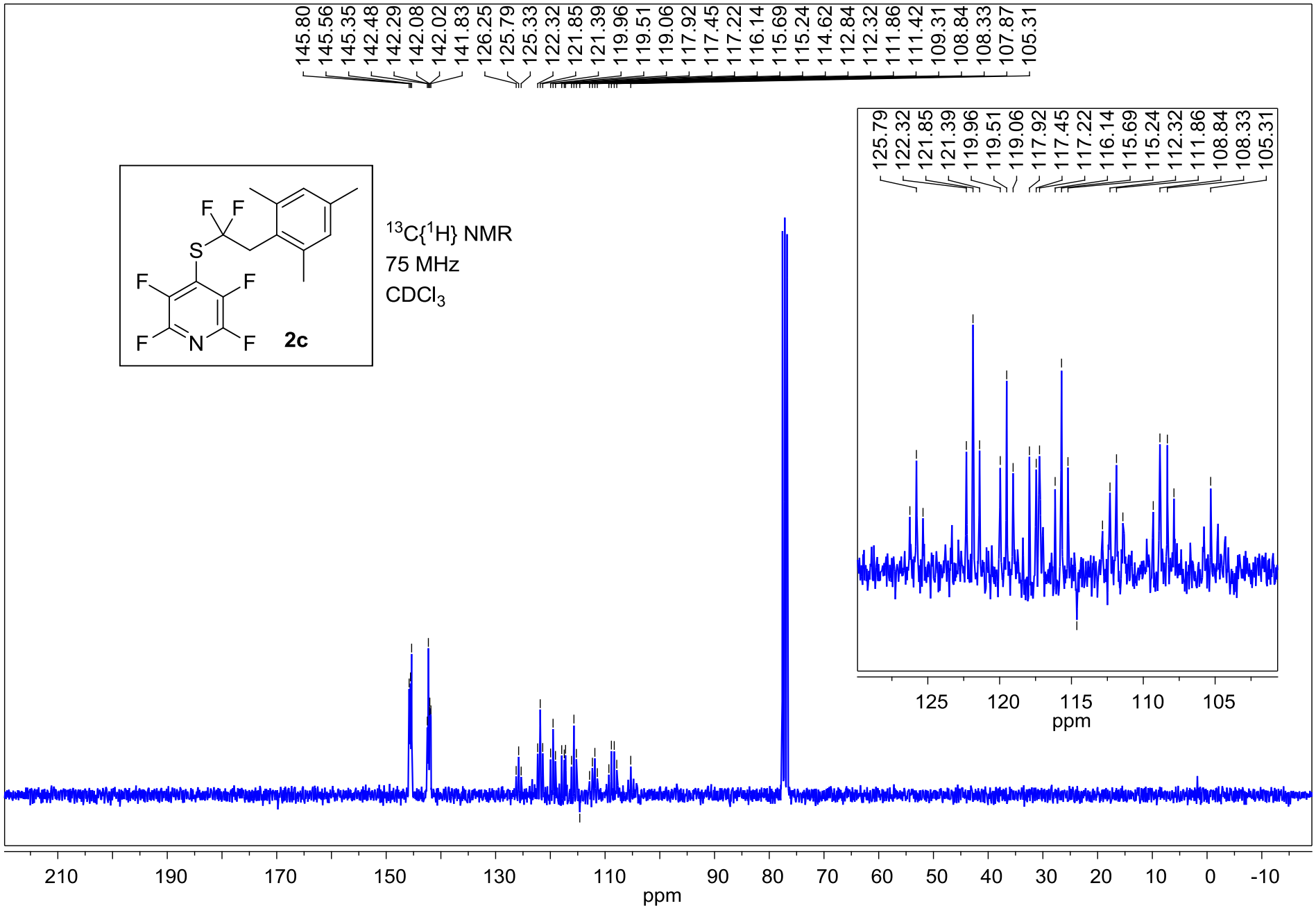

145.40
145.19
144.30
143.83
142.35
142.13
140.83
140.35
121.28
121.24
121.19
117.55
117.50
117.46
113.82
113.77
113.73
F
F
N
F
F
F
S
H
F
2a
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
145.40
145.19
144.30
143.83
142.35
142.13
140.83
140.35
146
144
142
140
ppm
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

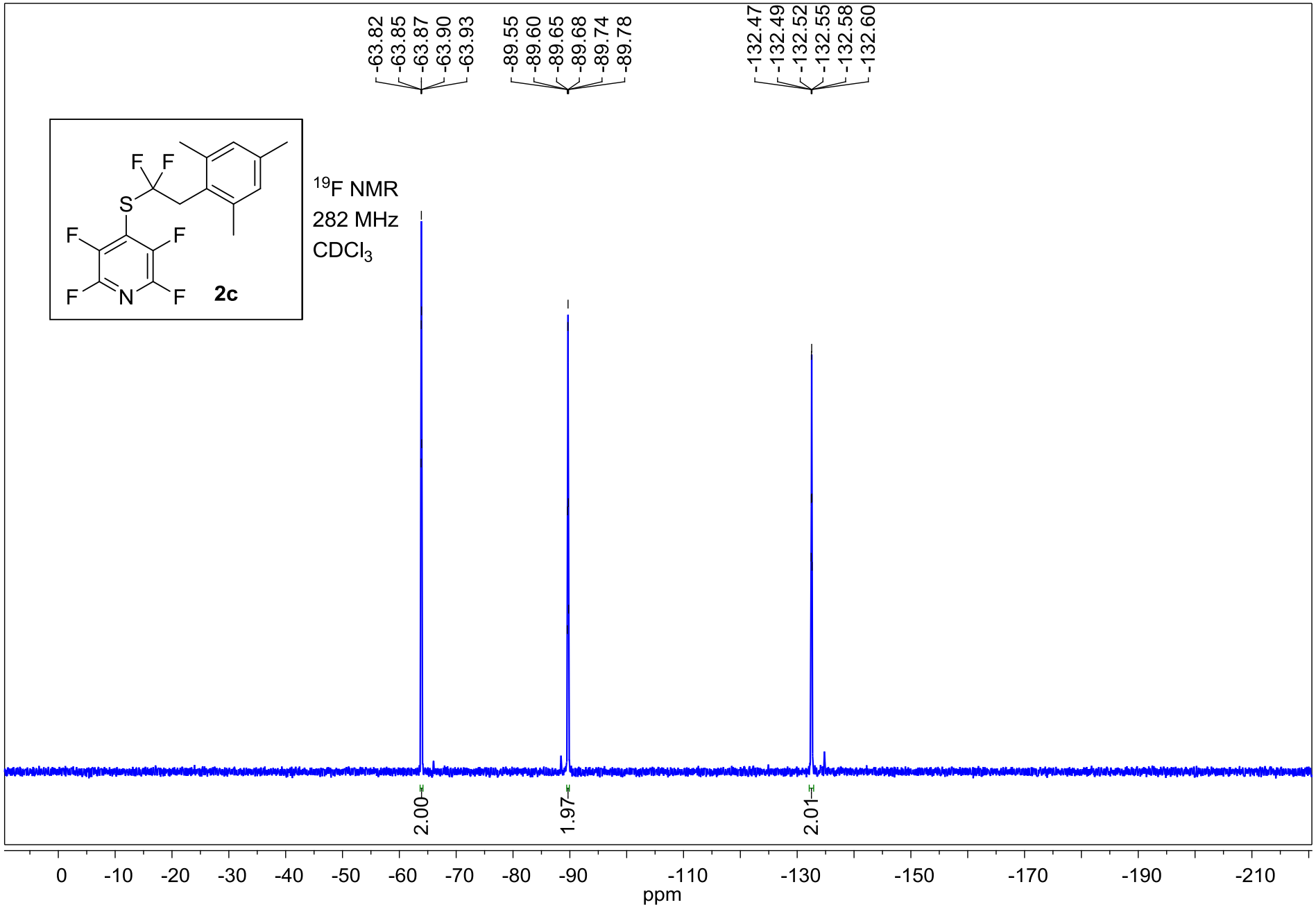

-89.01
-89.05
-89.13
-89.19
-89.23
-91.06
-91.26
-134.03
-134.09
-134.11
-134.14
-134.17
F
F
N
F
F
F
S
H
F
2a
19F NMR
282 MHz
CDCl3
1.96
2.00
1.93
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm


145.49
145.24
145.03
141.98
141.53
138.55
138.08
133.53
129.71
129.58
129.38
125.89
125.20
39.22
38.91
38.61
21.02
20.68
2b
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm


-81.06
-85.88
-88.13
-124.72
-131.44
3.00
1.98
2.02
1.95
1.95
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm
^{19}F NMR
282 MHz
$CDCl_3$
2b


6.92
3.75
3.69
3.64
2.38
2.35
2.30
F
F
S
F
F
F
N
F
2c
^{1}H NMR
300 MHz
$CDCl_3$
1.99
2.02
5.93
2.93
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


145.80
145.56
145.35
142.48
142.29
142.08
142.02
141.83
126.25
125.79
125.33
122.32
121.85
121.39
119.96
119.51
119.06
117.92
117.45
117.22
116.14
115.69
115.24
114.62
112.84
112.32
111.86
111.42
109.31
108.84
108.33
107.87
105.31
F F
S
F F
F N F
2c
13C{1H} NMR
75 MHz
CDCl3
125.79
122.32
121.85
121.39
119.96
119.51
119.06
117.92
117.45
117.22
116.14
115.69
115.24
112.32
111.86
108.84
108.33
105.31
125 120 115 110 105
ppm
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
ppm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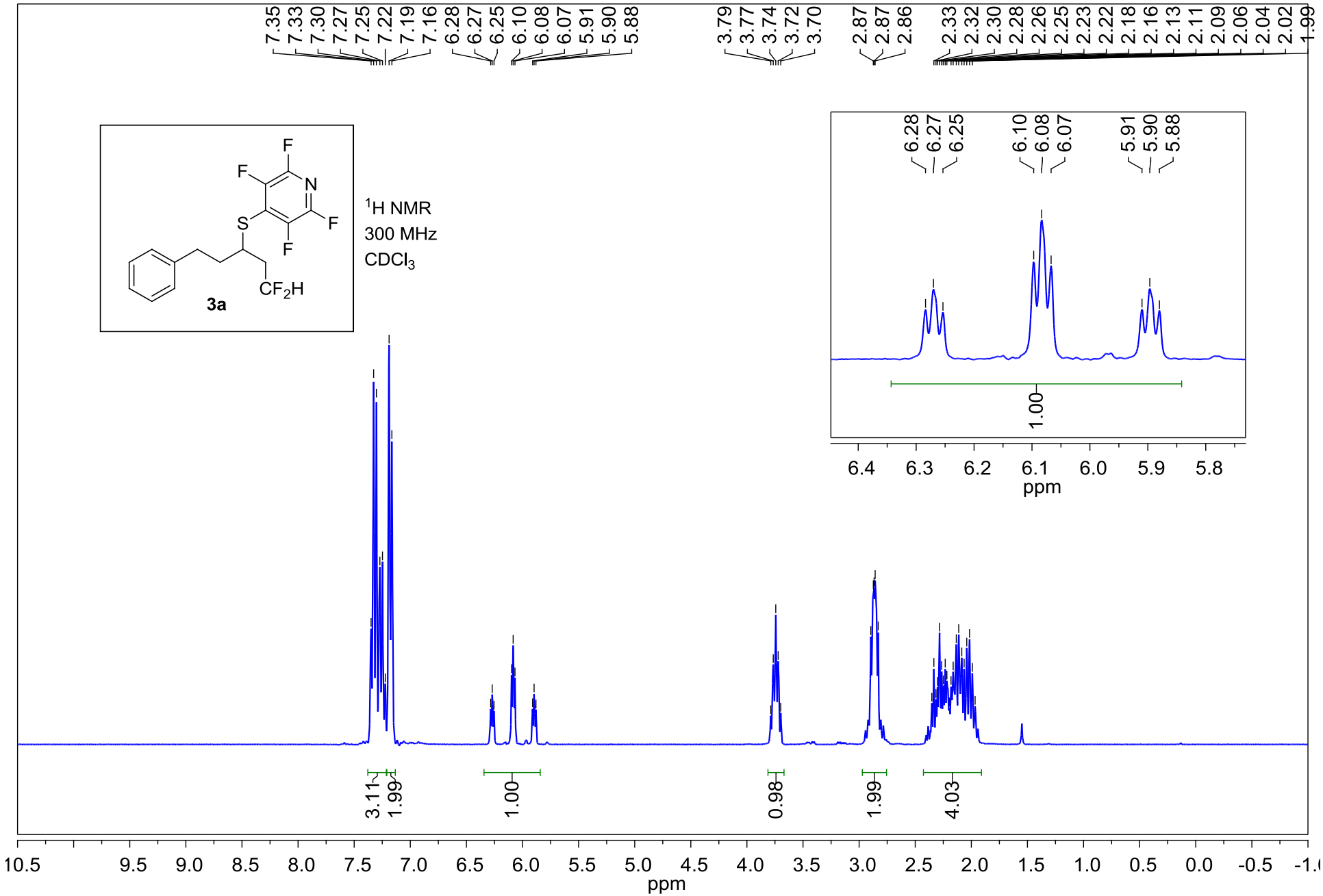
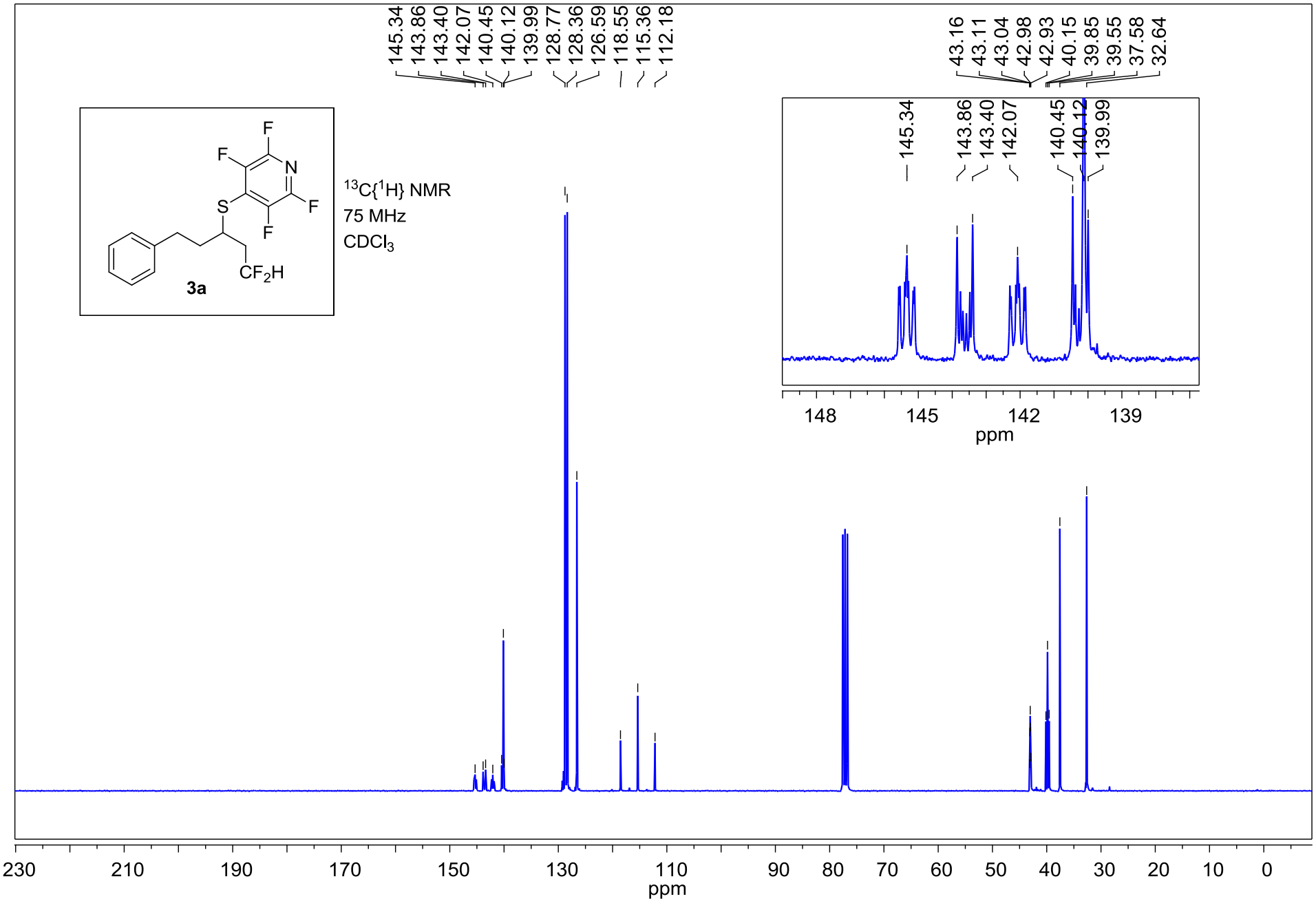
-63.85
-63.87
-63.90
-63.93
-89.55
-89.60
-89.65
-89.68
-89.74
-89.78
-132.47
-132.49
-132.52
-132.55
-132.58
-132.60
F
F
S
F
F
F
N
F
2c
19F NMR
282 MHz
CDCl3
2.00
1.97
2.01
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm


7.35 7.33 7.30 7.27 7.25 7.22 7.19 7.16 6.28 6.27 6.25 6.10 6.08 6.07 5.91 5.90 5.88 3.79 3.77 3.74 3.72 3.70 2.87 2.87 2.86 2.33 2.32 2.30 2.28 2.26 2.25 2.23 2.22 2.18 2.16 2.13 2.11 2.09 2.06 2.04 2.02 1.99
F F N S F F CF2H
3a
1H NMR
300 MHz
CDCl3
6.28 6.27 6.25 6.10 6.08 6.07 5.91 5.90 5.88
1.00
6.4 6.3 6.2 6.1 6.0 5.9 5.8
ppm
3.11 1.99 1.00 0.98 1.99 4.03
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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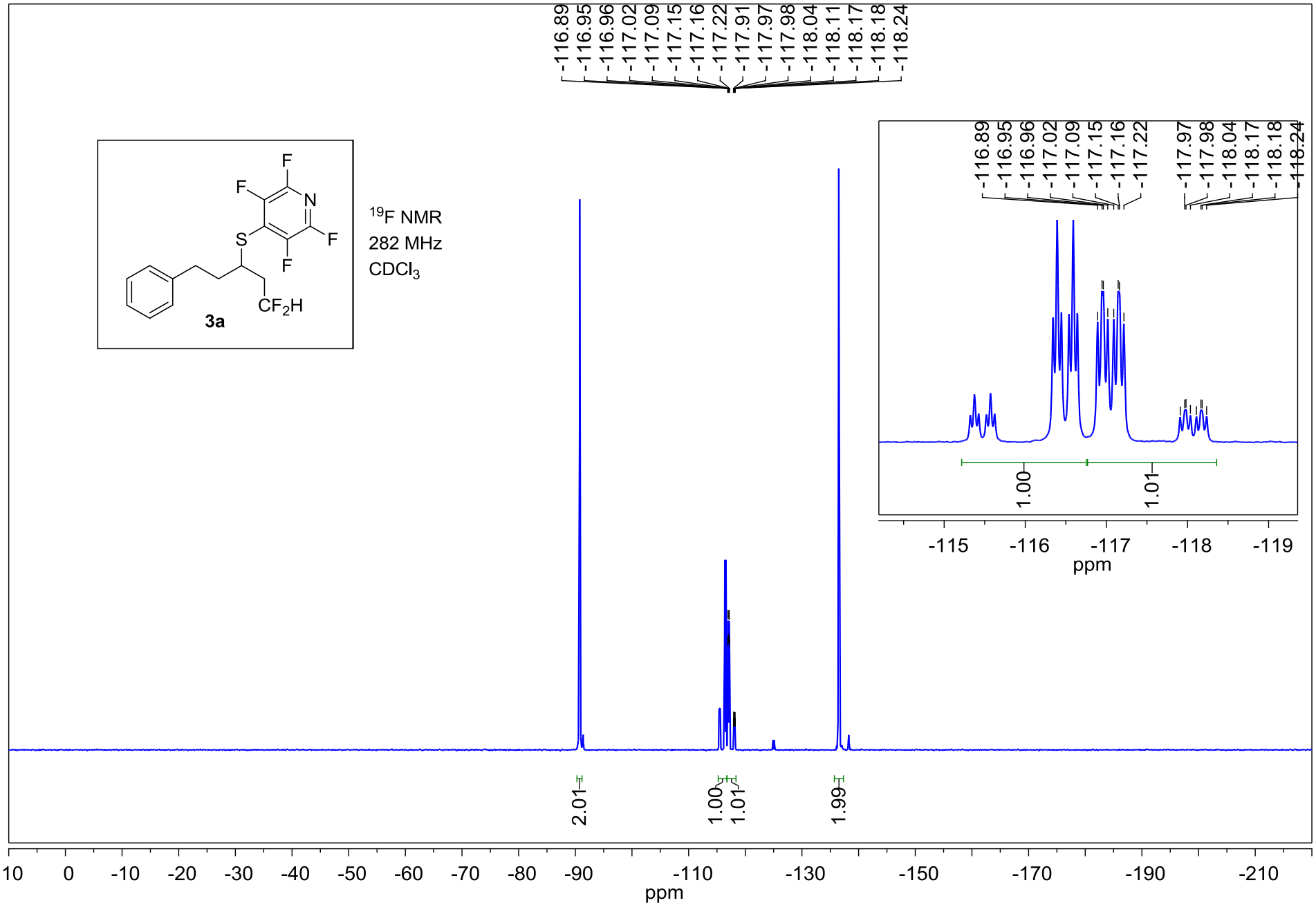
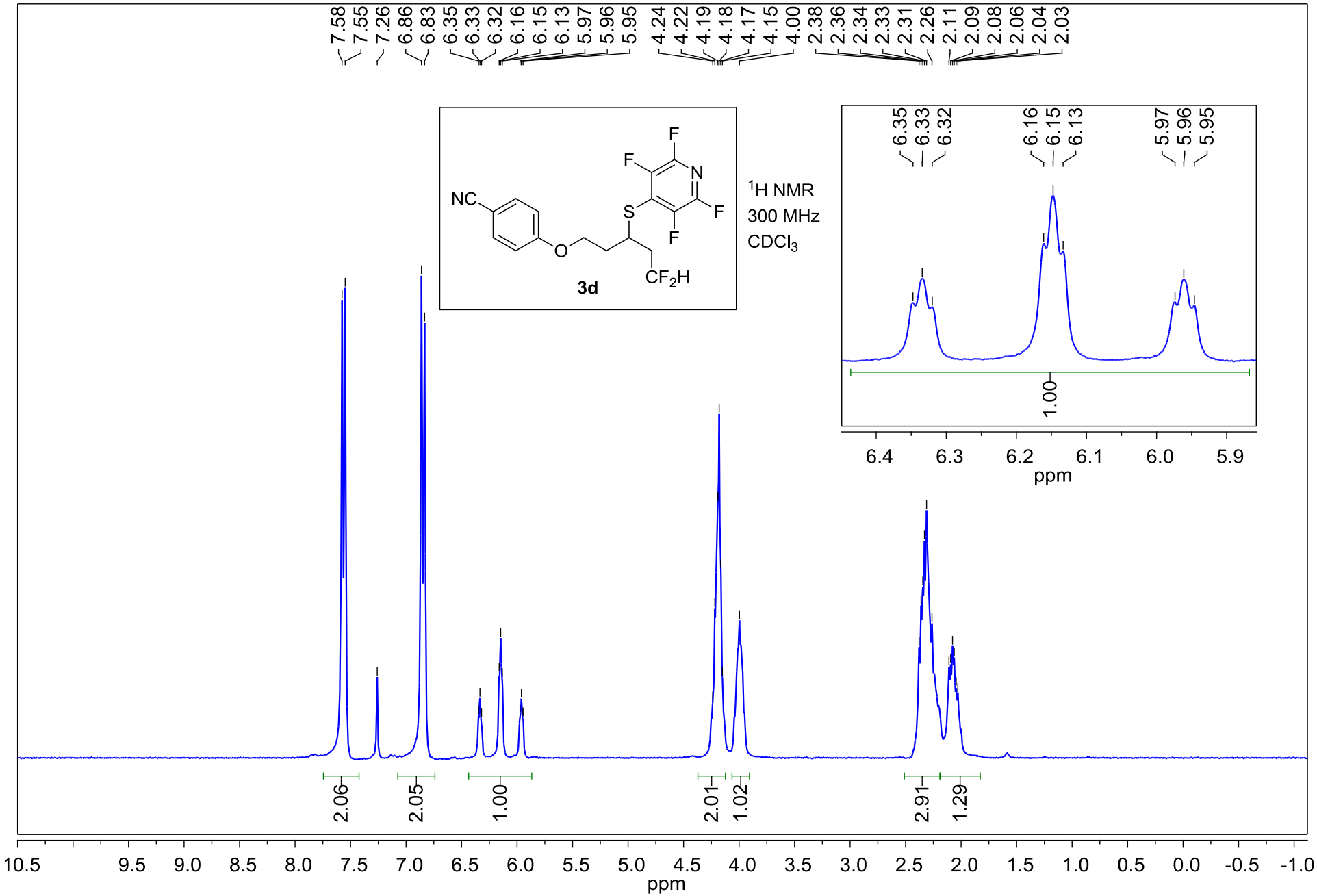
142.07
140.45
140.12
139.99
128.77
128.36
126.59
118.55
115.36
112.18
43.16
43.11
43.04
42.98
42.93
40.15
39.85
39.55
37.58
32.64
F
F
N
S
F
F
CF2H
3a
13C{1H} NMR
75 MHz
CDCl3
145.34
143.86
143.40
142.07
140.45
140.12
139.99
148
145
142
139
ppm
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
ppm


-116.89
-116.95
-116.96
-117.02
-117.09
-117.15
-117.16
-117.22
-117.91
-117.97
-117.98
-118.04
-118.11
-118.17
-118.18
-118.24
F
F
N
S
F
F
CF2H
3a
19F NMR
282 MHz
CDCl3
1.00
1.01
-115
-116
-117
-118
-119
ppm
2.01
1.00
1.01
1.99
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm


7.58
7.55
7.26
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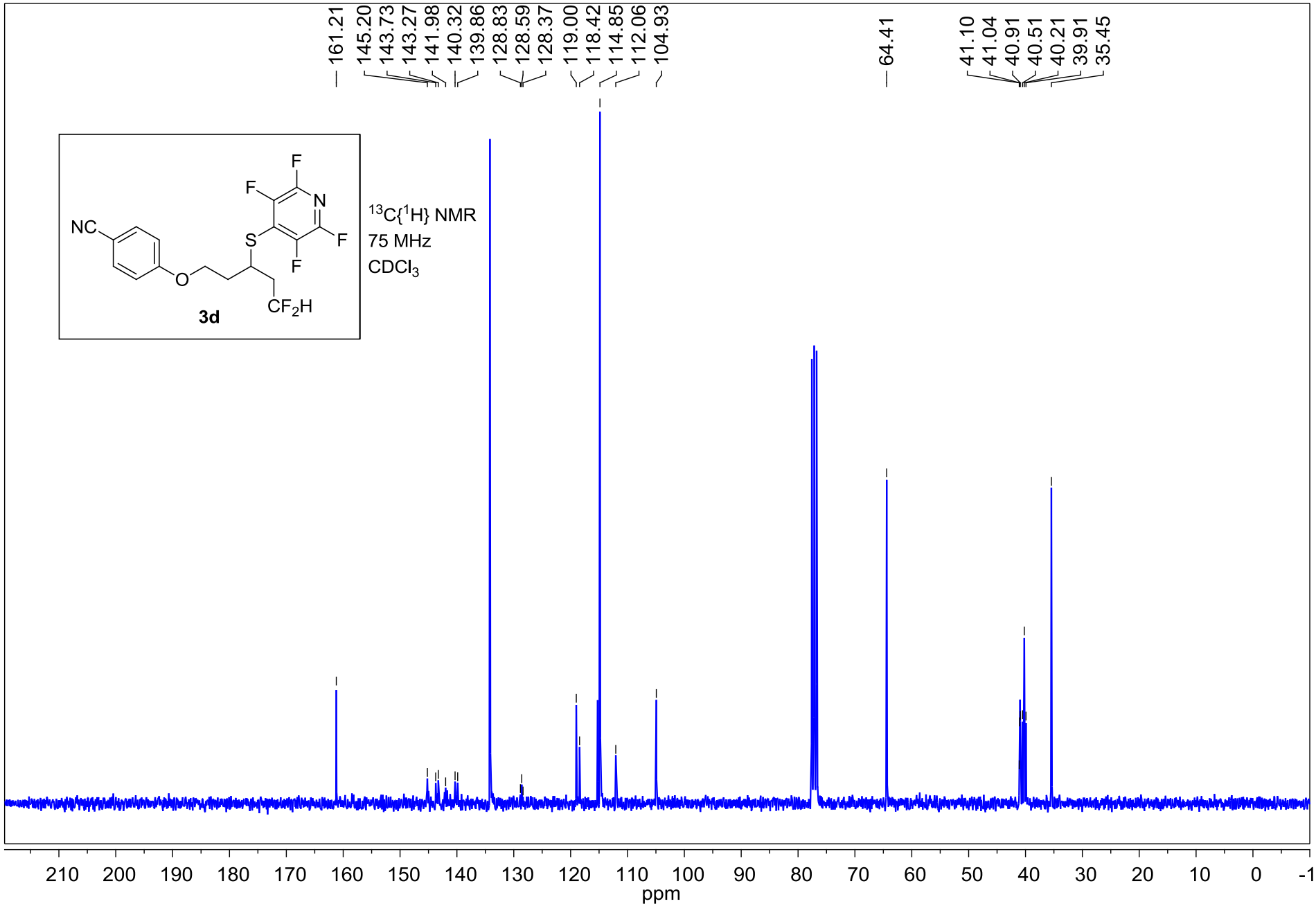
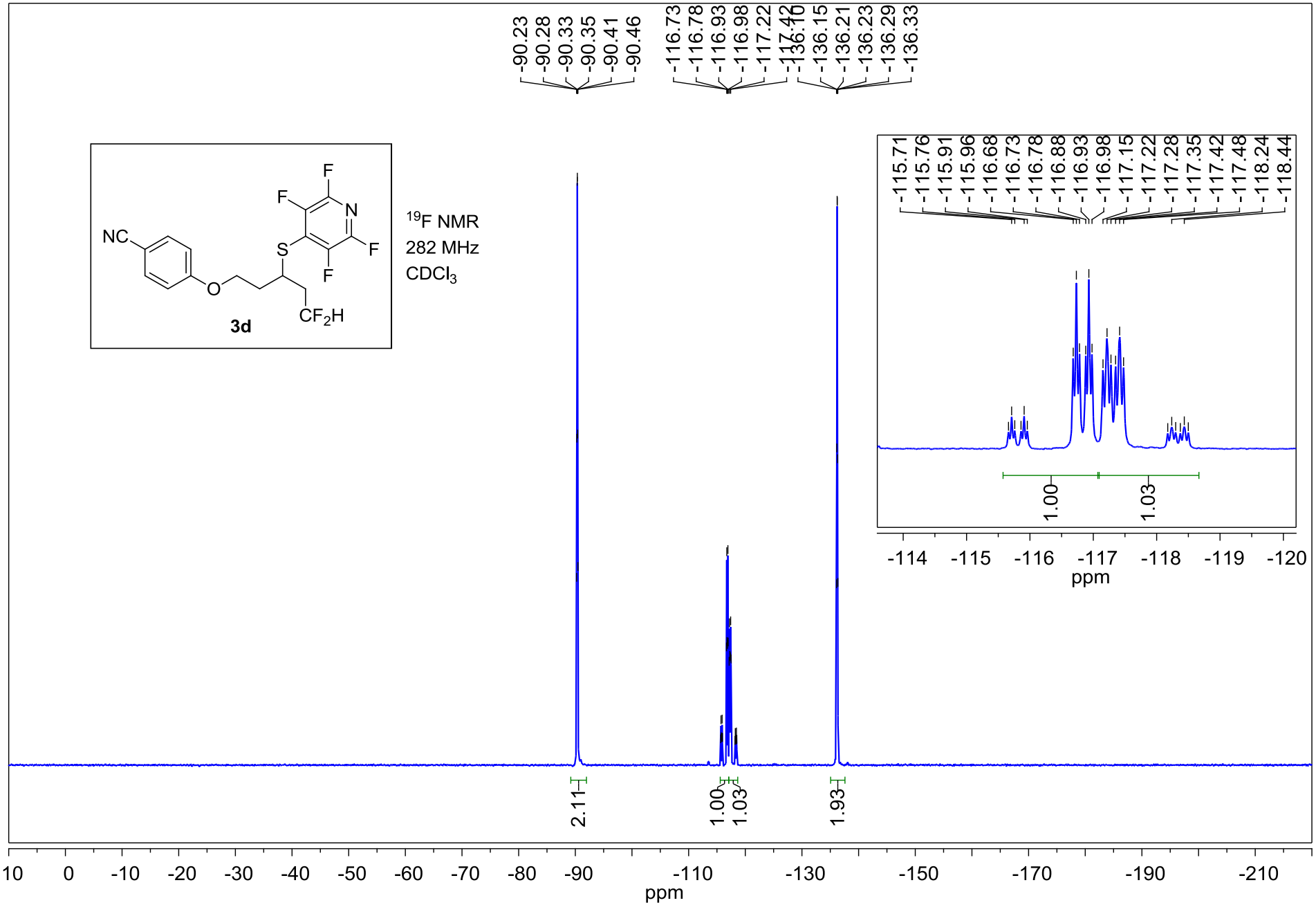
6.35
6.33
6.32
6.16
6.15
6.13
5.97
5.96
5.95
4.24
4.22
4.19
4.18
4.17
4.15
4.00
2.38
2.36
2.34
2.33
2.31
2.26
2.11
2.09
2.08
2.06
2.04
2.03
F
F
N
NC
S
F
F
O
CF2H
3d
1H NMR
300 MHz
CDCl3
1.00
6.4
6.3
6.2
6.1
6.0
5.9
ppm
2.06
2.05
1.00
2.01
1.02
2.91
1.29
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm


161.21
145.20
143.73
143.27
141.98
140.32
139.86
128.83
128.59
128.37
119.00
118.42
114.85
112.06
104.93
64.41
41.10
41.04
40.91
40.51
40.21
39.91
35.45
NC
O
S
F
F
F
N
F
CF2H
3d
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


-90.23
-90.28
-90.33
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NC
O
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F
F
F
N
CF2H
3d
19F NMR
282 MHz
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1.03
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-115
-116
-117
-118
-119
-120
ppm
2.11
1.00
1.03
1.93
10
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-190
-210
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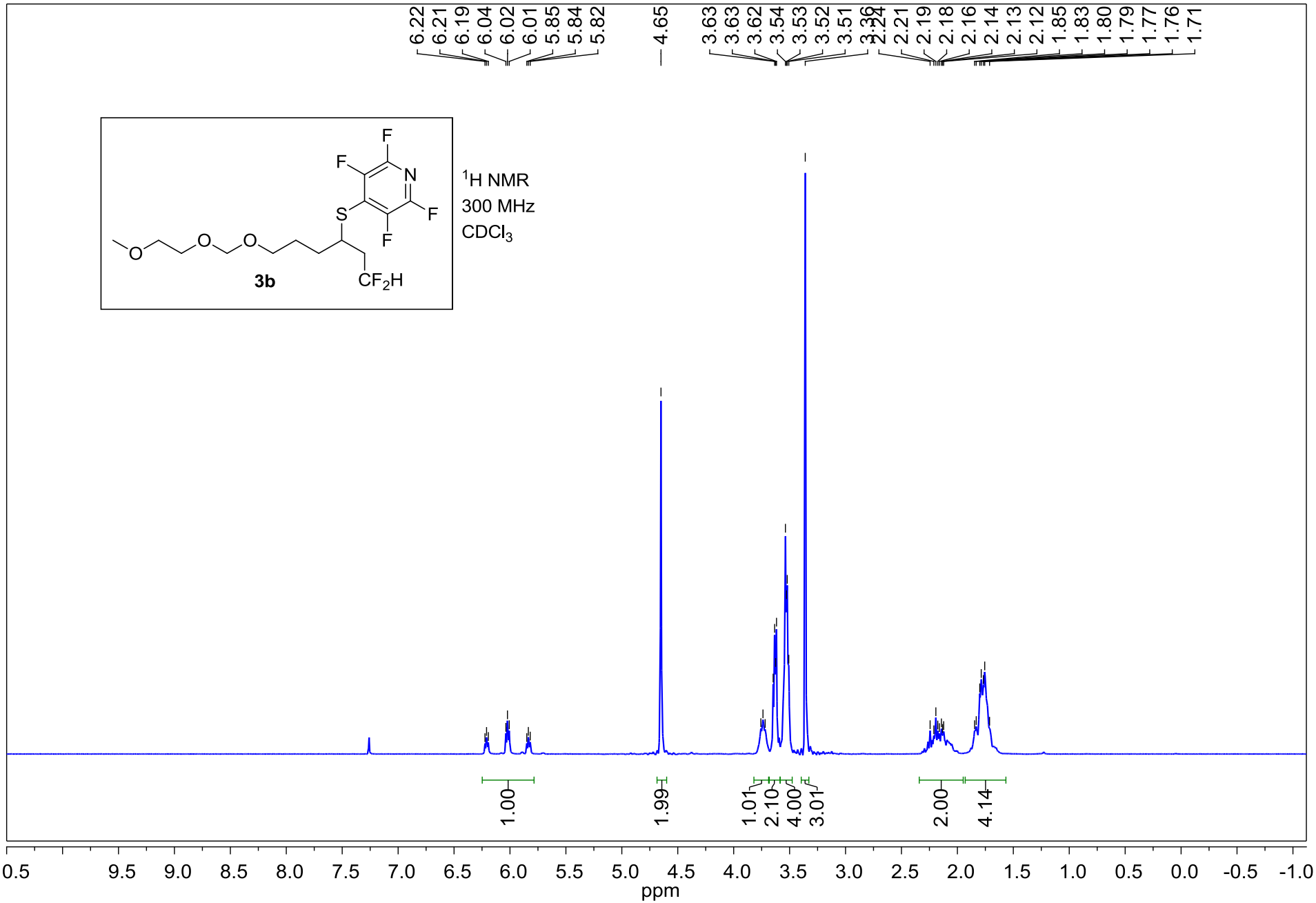
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3.54
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3.51
3.36
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F
F
N
S
F
F
O
O
O
3b
CF2H
1H NMR
300 MHz
CDCl3
1.00
1.99
1.01
2.10
4.00
3.01
2.00
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10.5
9.5
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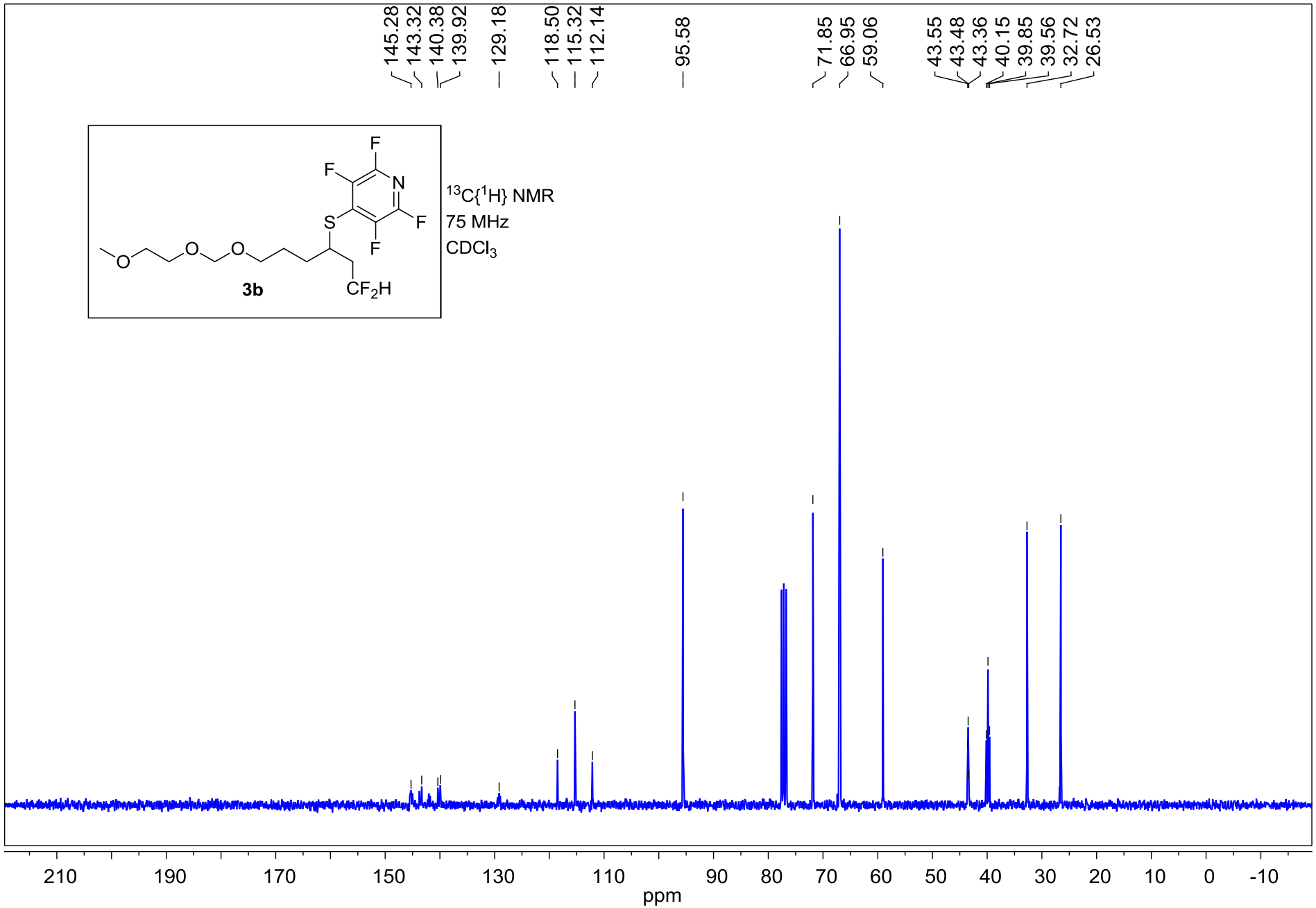
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43.48
43.36
40.15
39.85
39.56
32.72
26.53
F
F
N
S
F
F
O
O
O
CF2H
3b
13C{1H} NMR
75 MHz
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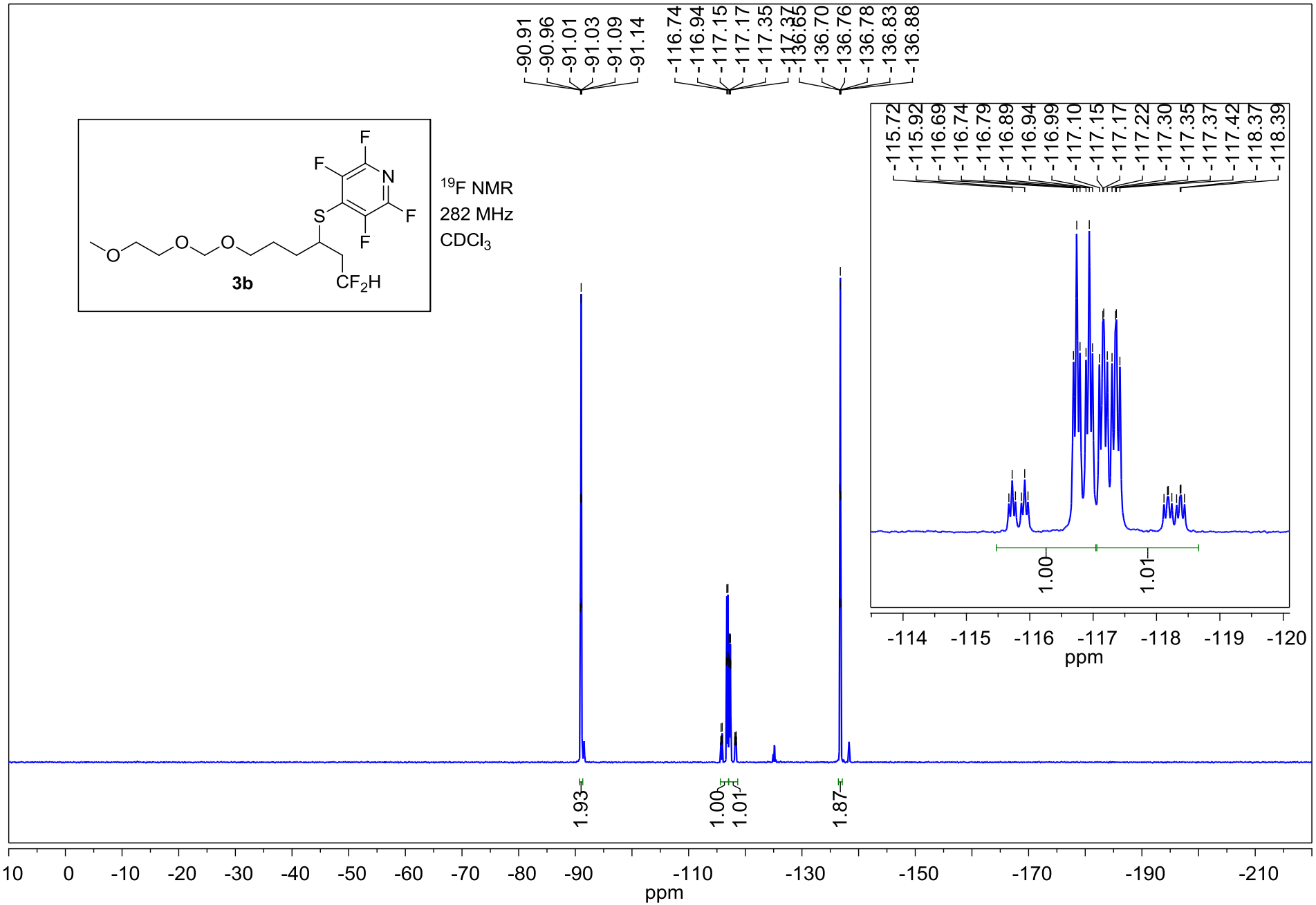
ppm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-136.76
-136.78
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F
F
N
S
F
F
O
O
O
3b
CF2H
19F NMR
282 MHz
CDCl3
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-116.89
-116.94
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1.01
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-115
-116
-117
-118
-119
-120
ppm
1.93
1.00
1.01
1.87
10
0
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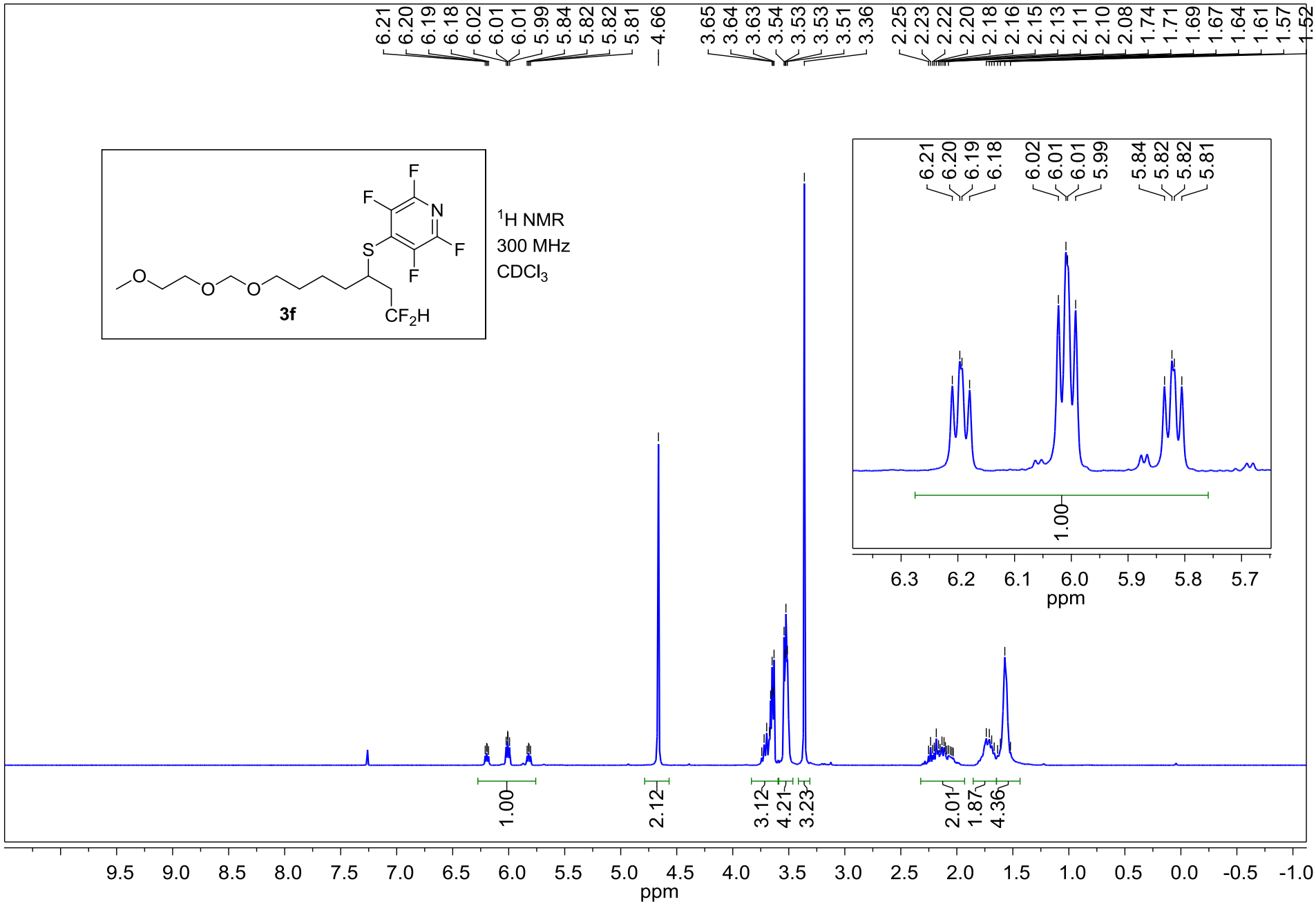
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm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3.65 3.64 3.63 3.54 3.53 3.53 3.51 3.36
2.25 2.23 2.22 2.20 2.18 2.16 2.15 2.13 2.11 2.10 2.08 1.74 1.71 1.69 1.67 1.64 1.61 1.57 1.52
F
F
N
S
F
F
O
O
O
3f
CF2H
1H NMR
300 MHz
CDCl3
1.00
6.3 6.2 6.1 6.0 5.9 5.8 5.7
ppm
1.00 2.12 3.12 4.21 3.23 2.01 1.87 4.36
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
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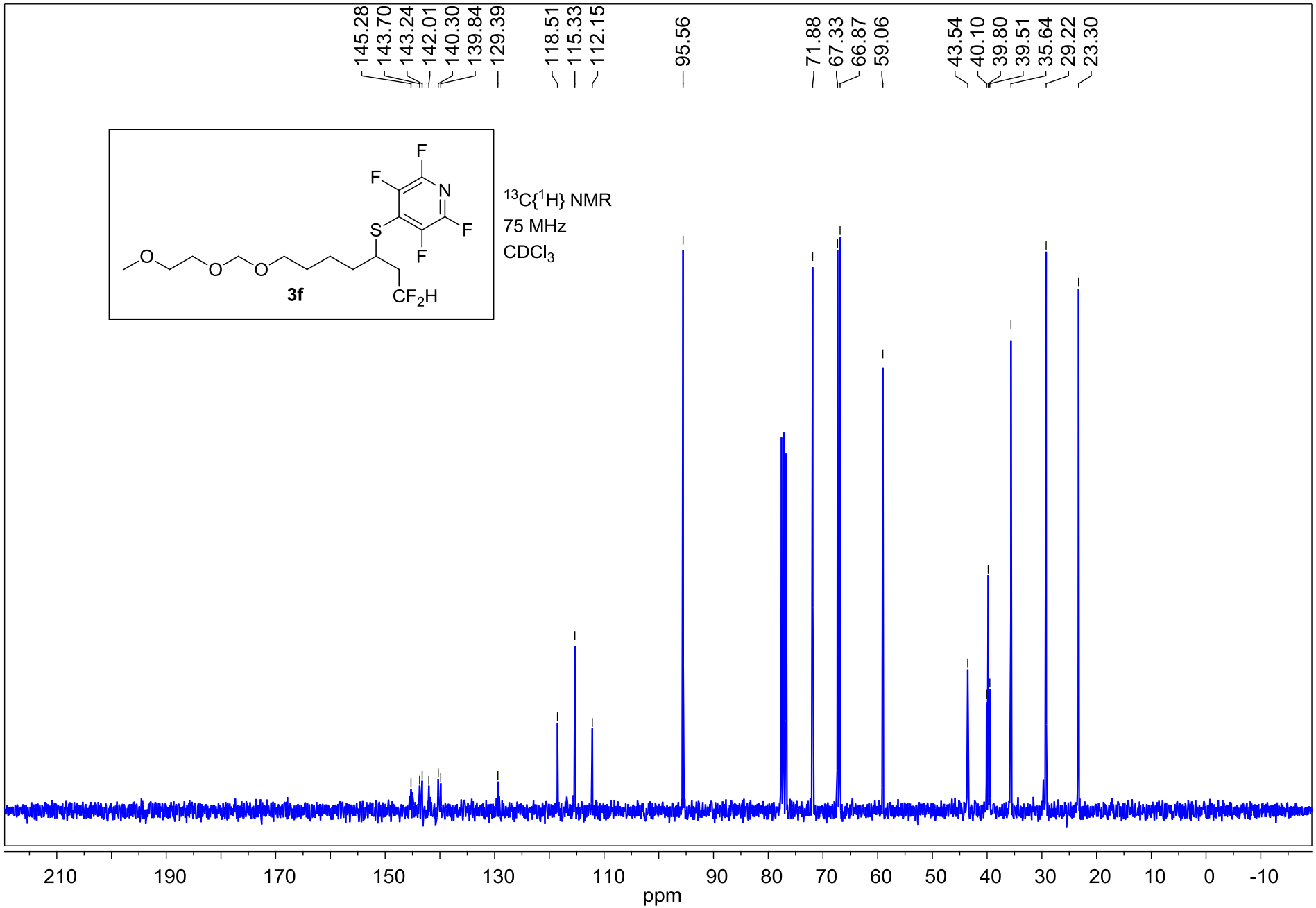
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66.87
59.06
43.54
40.10
39.80
39.51
35.64
29.22
23.30
F
F
N
S
F
F
O
O
O
3f
CF2H
13C{1H} NMR
75 MHz
CDCl3
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170
150
130
110
90
80
70
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50
40
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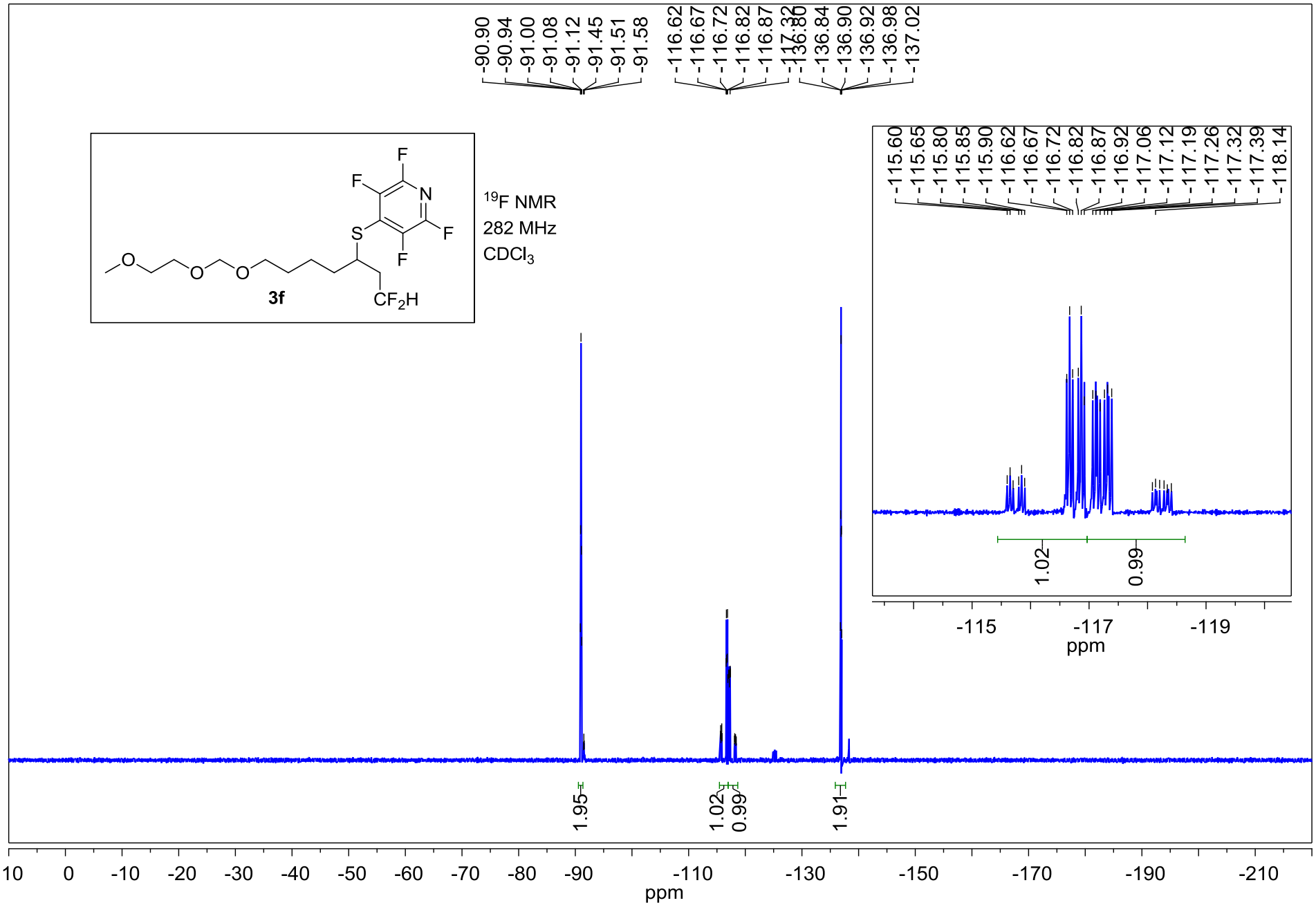
20
10
0
-10
ppm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-91.51
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-116.82
-116.87
-117.32
-136.80
-136.84
-136.90
-136.92
-136.98
-137.02
F
F
N
S
F
F
O
O
O
3f
CF2H
19F NMR
282 MHz
CDCl3
-115.60
-115.65
-115.80
-115.85
-115.90
-116.62
-116.67
-116.72
-116.82
-116.87
-116.92
-117.06
-117.12
-117.19
-117.26
-117.32
-117.39
-118.14
1.02
0.99
-115
-117
-119
ppm
1.95
1.02
0.99
1.91
10
0
-10
-20
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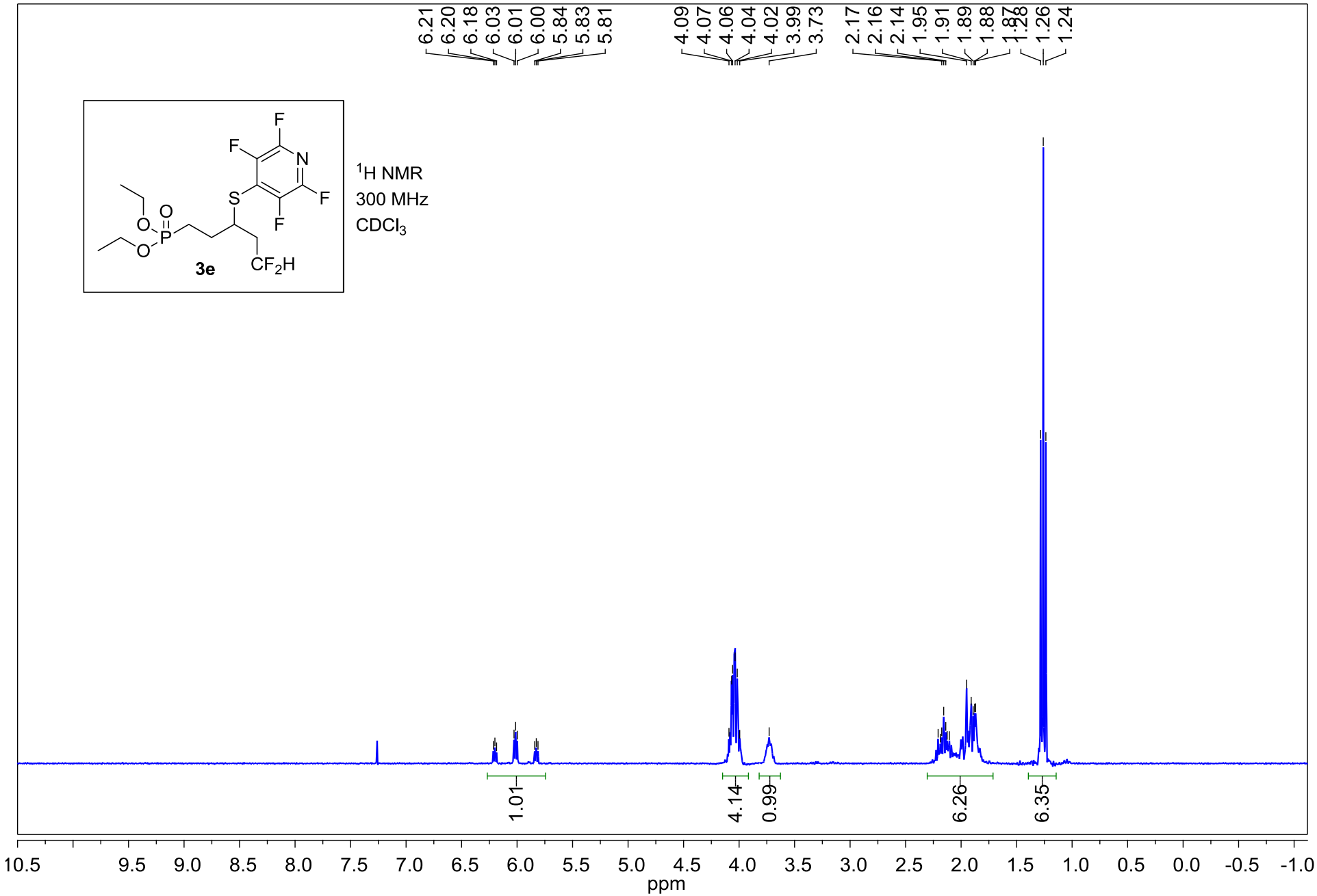
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm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6.03
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5.83
5.81
4.09
4.07
4.06
4.04
4.02
3.99
3.73
2.17
2.16
2.14
1.95
1.91
1.89
1.88
1.87
1.28
1.26
1.24
F
F
N
S
F
F
O
O
P
O
CF2H
3e
1H NMR
300 MHz
CDCl3
1.01
4.14
0.99
6.26
6.35
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
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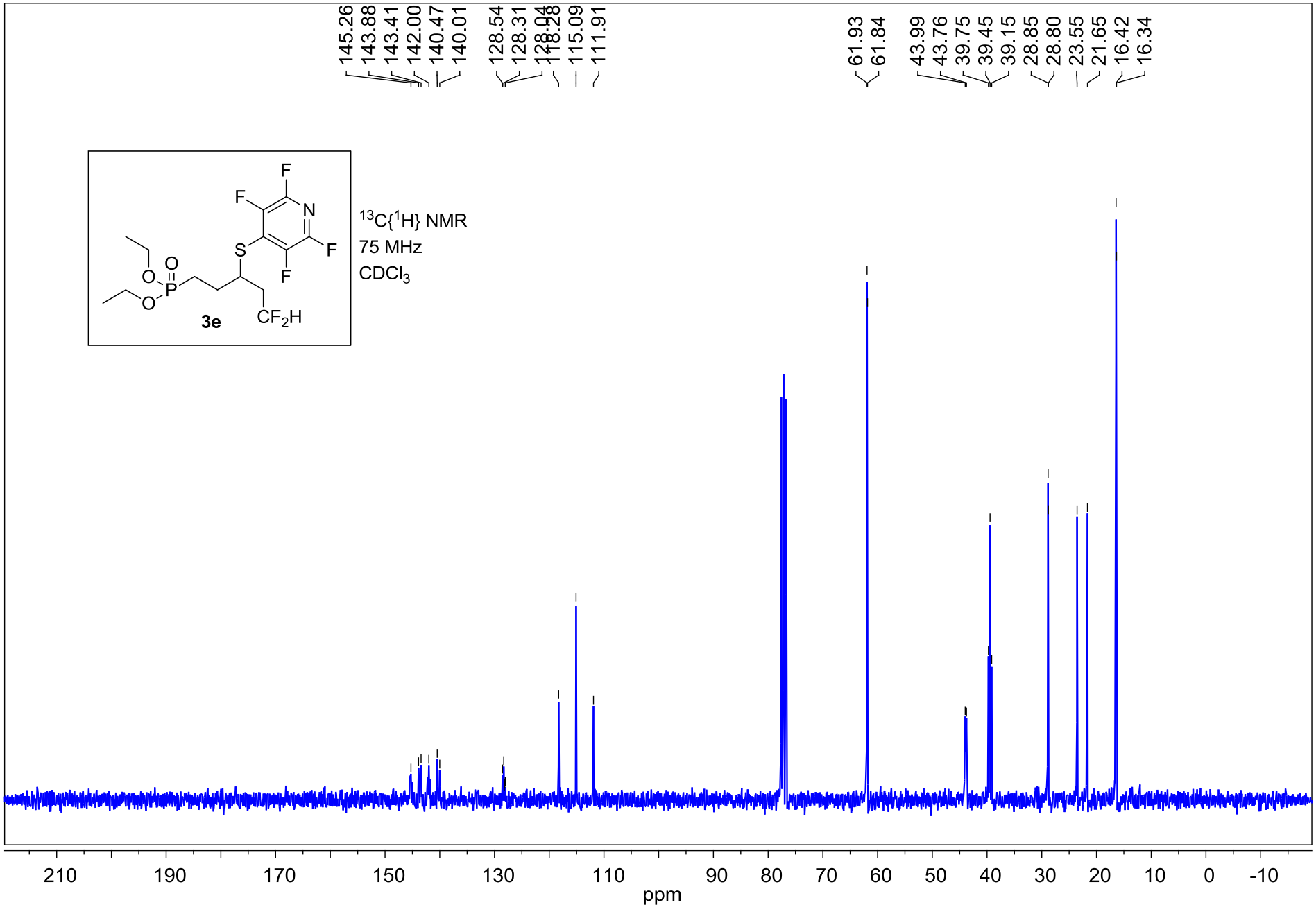
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm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115.09
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61.93
61.84
43.99
43.76
39.75
39.45
39.15
28.85
28.80
23.55
21.65
16.42
16.34
F
F
N
S
F
F
O
O
P
O
O
CF2H
3e
13C{1H} NMR
75 MHz
CDCl3
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170
150
130
110
90
80
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50
40
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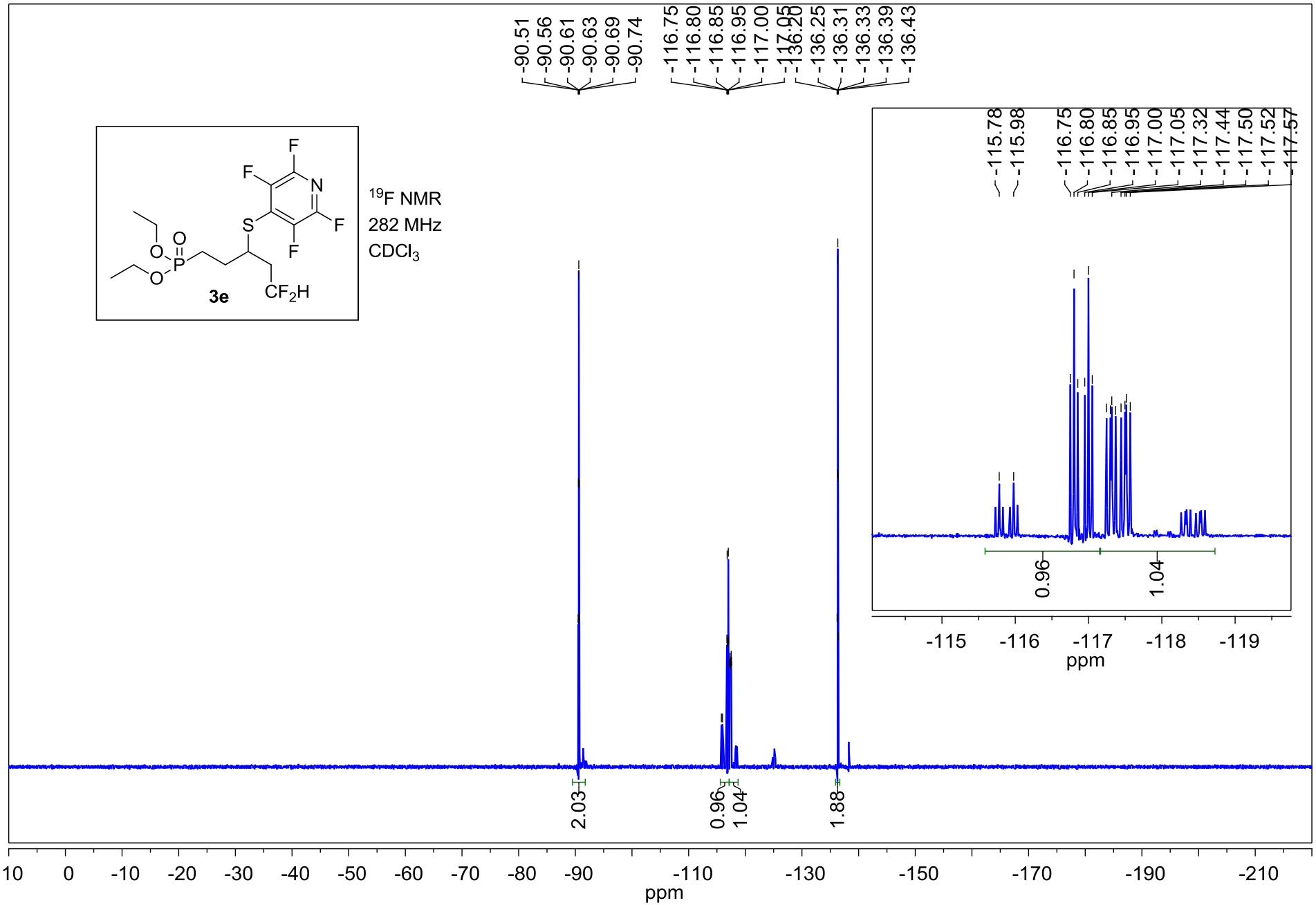
20
10
0
-10
ppm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-117.05
-136.20
-136.25
-136.31
-136.33
-136.39
-136.43
F
F
N
S
F
F
O
O
P
O
3e
CF2H
19F NMR
282 MHz
CDCl3
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-116.75
-116.80
-116.85
-116.95
-117.00
-117.05
-117.32
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1.04
-115
-116
-117
-118
-119
ppm
2.03
0.96
1.04
1.88
10
0
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-60
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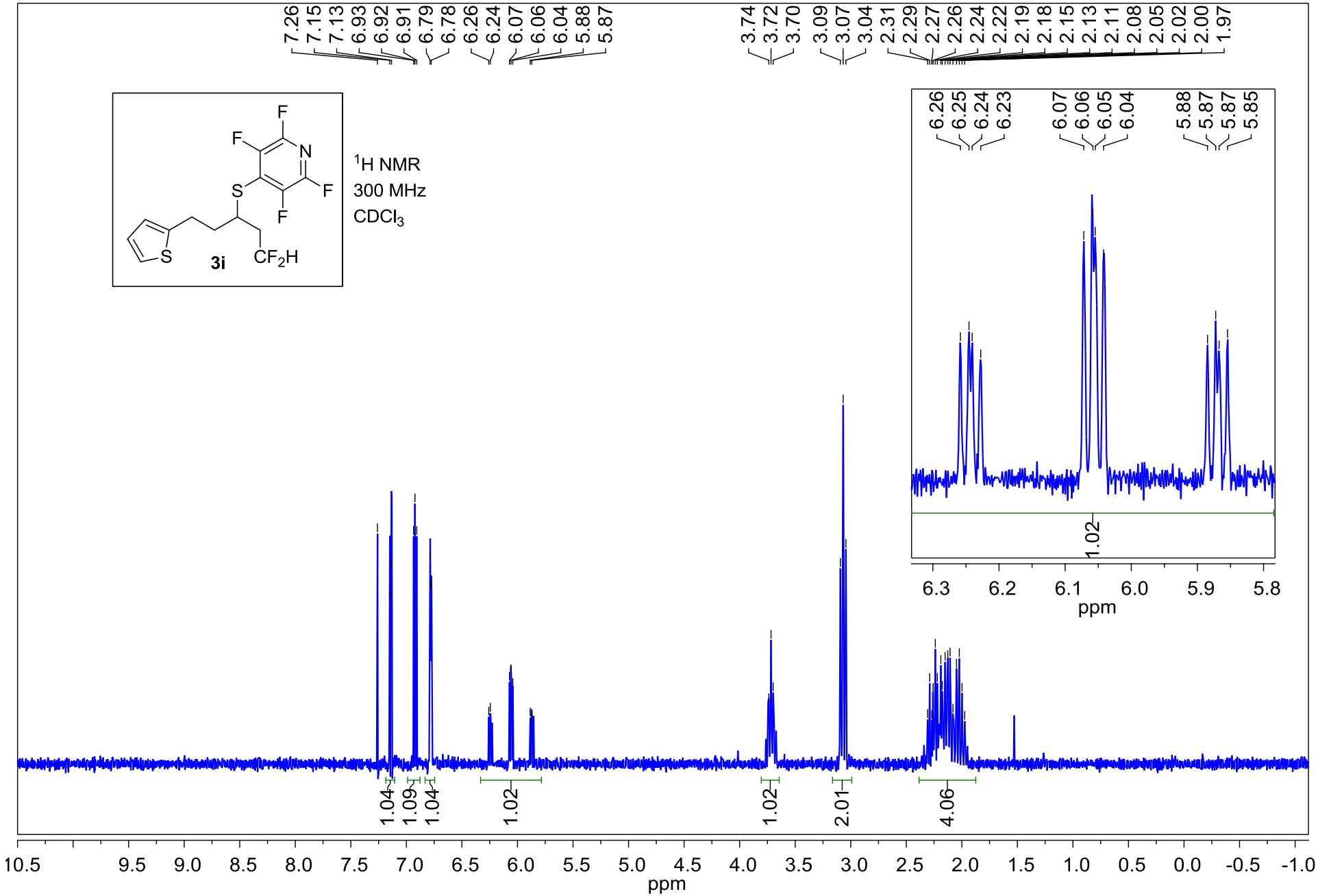
-210
ppm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6.78
6.26
6.24
6.07
6.06
6.04
5.88
5.87
3.74
3.72
3.70
3.09
3.07
3.04
2.31
2.29
2.27
2.26
2.24
2.22
2.19
2.18
2.15
2.13
2.11
2.08
2.05
2.02
2.00
1.97
F
F
N
S
F
F
S
CF2H
3i
1H NMR
300 MHz
CDCl3
6.26
6.25
6.24
6.23
6.07
6.06
6.05
6.04
5.88
5.87
5.87
5.85
1.02
6.3
6.2
6.1
6.0
5.9
5.8
ppm
1.04
1.09
1.04
1.02
1.02
2.01
4.06
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.5
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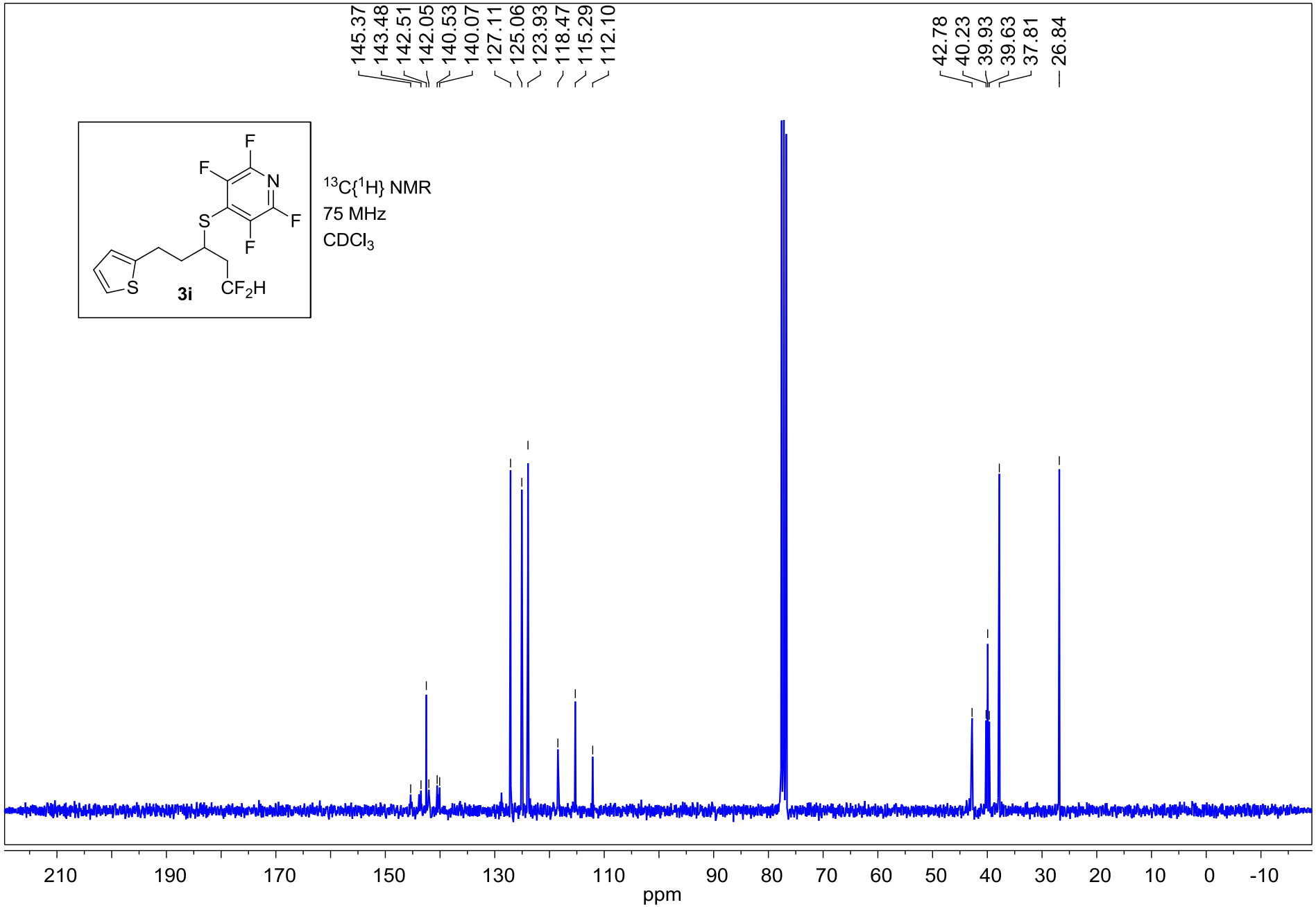
-1.0
ppm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125.06
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42.78
40.23
39.93
39.63
37.81
26.84
F
F
N
S
F
F
S
CF2H
3i
13C{1H} NMR
75 MHz
CDCl3
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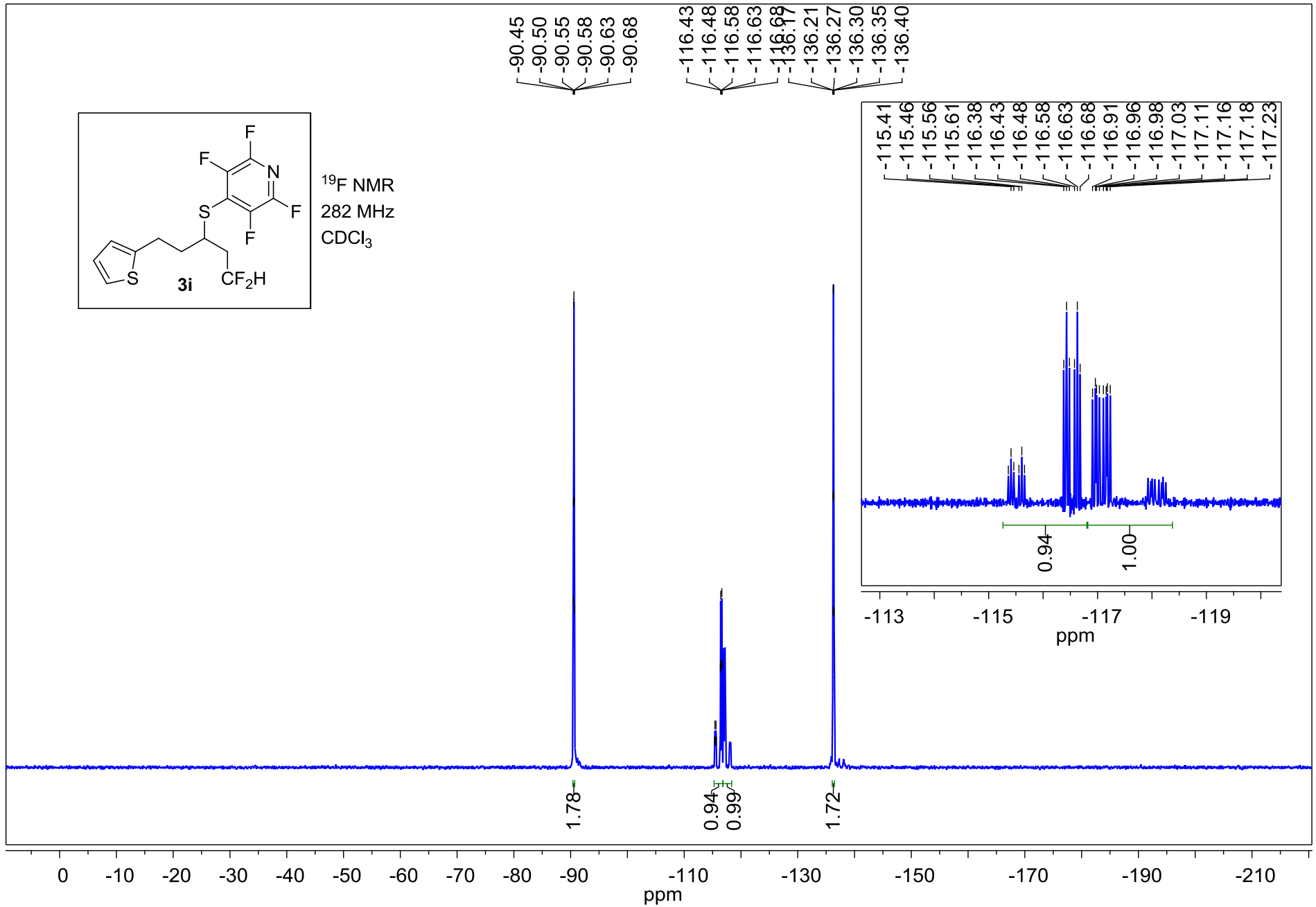
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm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-116.77
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F
F
N
S
F
F
S
CF2H
3i
19F NMR
282 MHz
CDCl3
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-115.46
-115.56
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-116.38
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-119
ppm
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0.99
1.72
0
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-50
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-190
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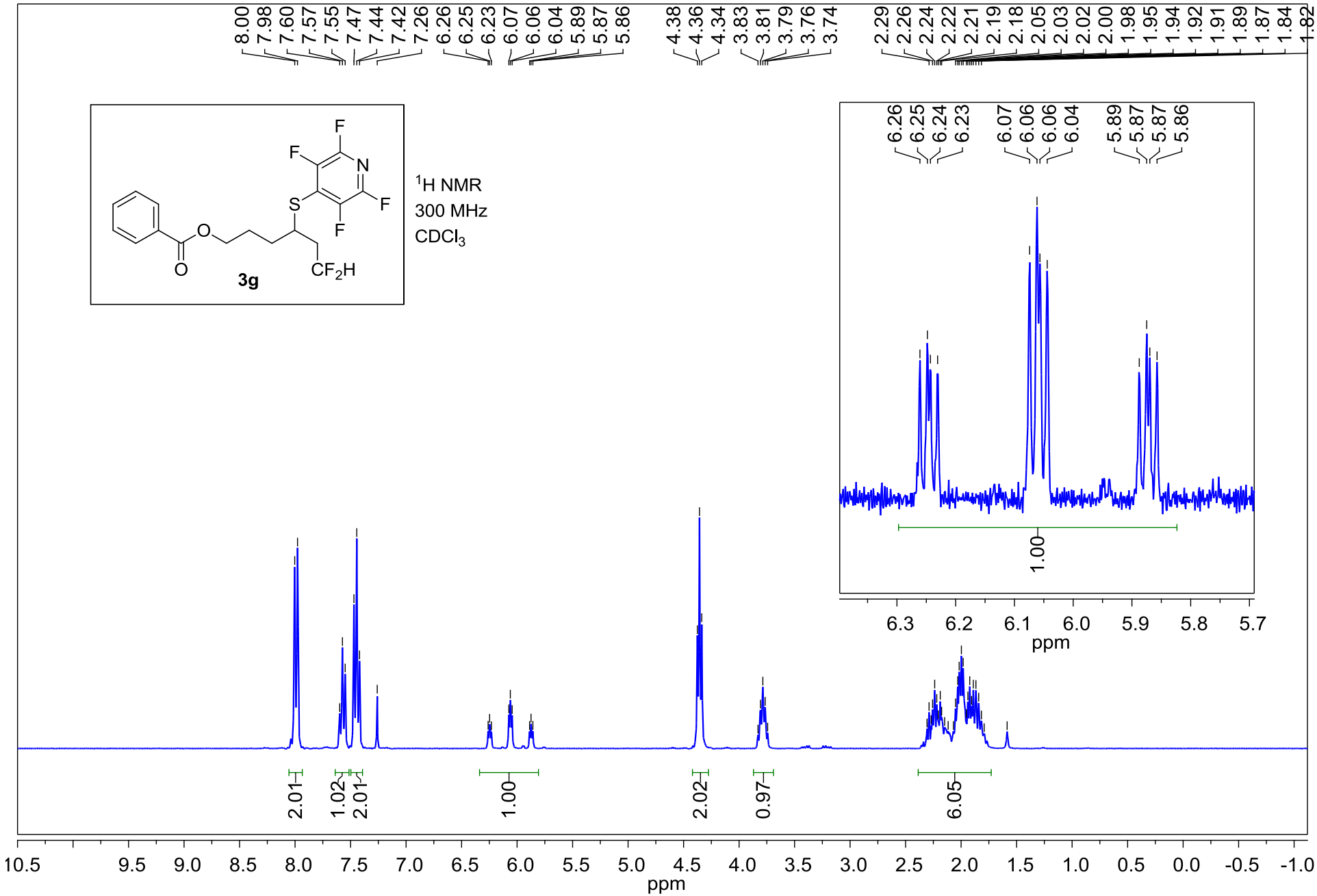
ppm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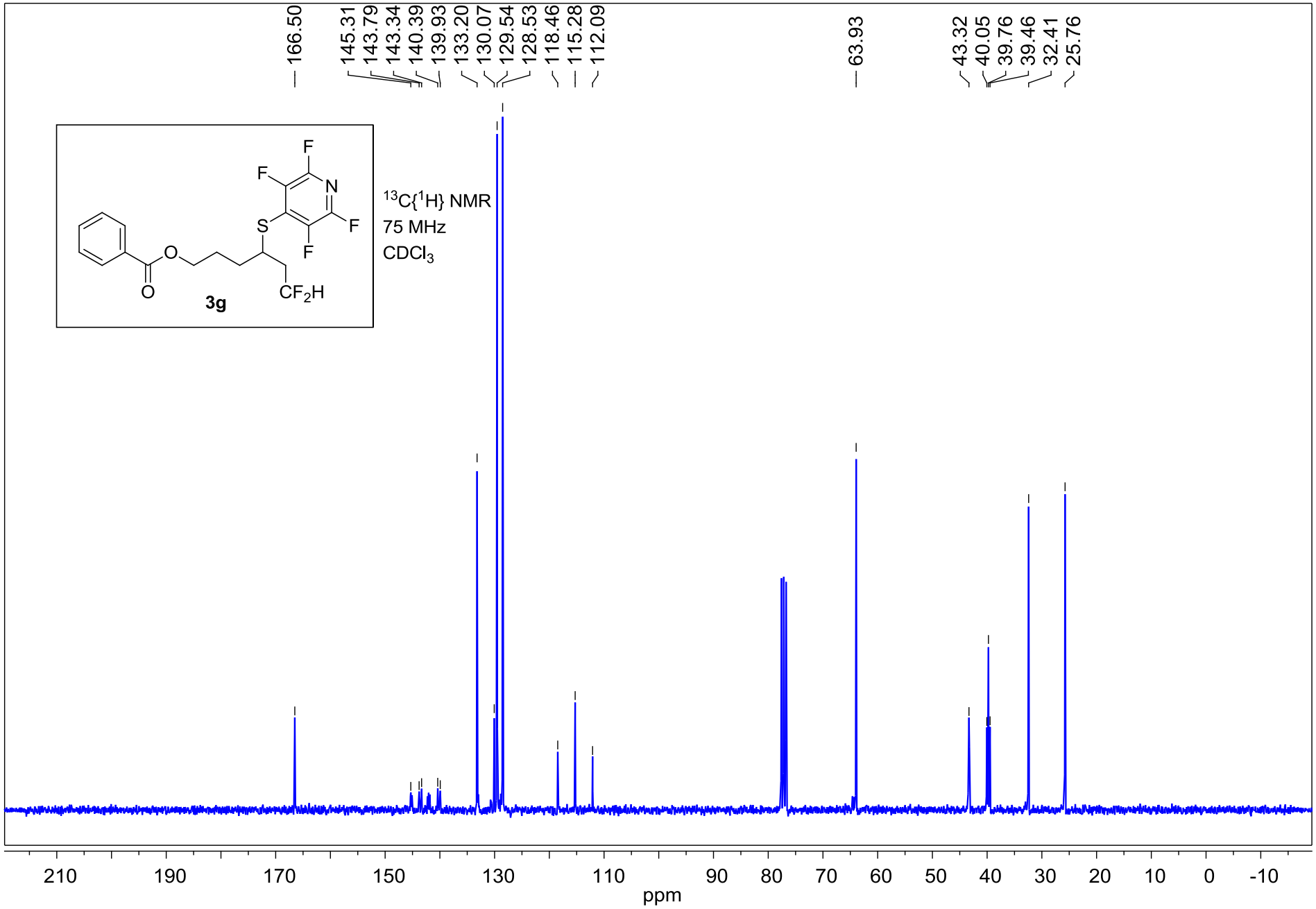
F
F
N
S
F
F
O
O
CF2H
3g
1H NMR
300 MHz
CDCl3
6.26 6.25 6.24 6.23 6.07 6.06 6.06 6.04 5.89 5.87 5.87 5.86
1.00
6.3 6.2 6.1 6.0 5.9 5.8 5.7
ppm
2.01 1.02 2.01 1.00 2.02 0.97 6.05
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm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118.46
115.28
112.09
63.93
43.32
40.05
39.76
39.46
32.41
25.76
F
F
N
S
F
F
O
O
CF2H
3g
13C{1H} NMR
75 MHz
CDCl3
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150
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90
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50
40
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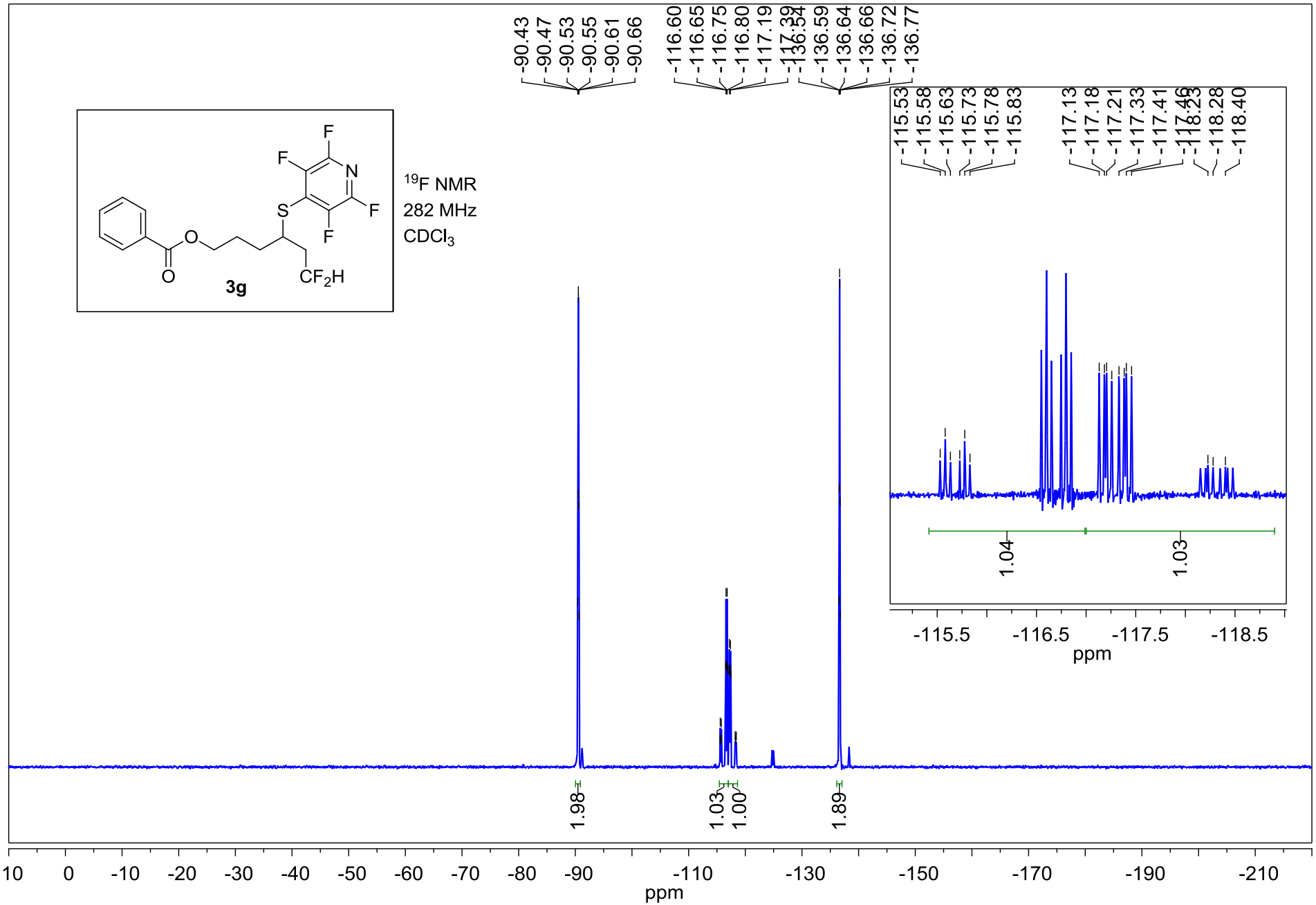
ppm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-136.72
-136.77
-115.53
-115.58
-115.63
-115.73
-115.78
-115.83
-117.13
-117.18
-117.21
-117.33
-117.41
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-118.23
-118.28
-118.40
F
F
N
S
F
F
O
O
CF2H
3g
19F NMR
282 MHz
CDCl3
1.04
1.03
-115.5
-116.5
-117.5
-118.5
ppm
1.98
1.03
1.00
1.89
10
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-80
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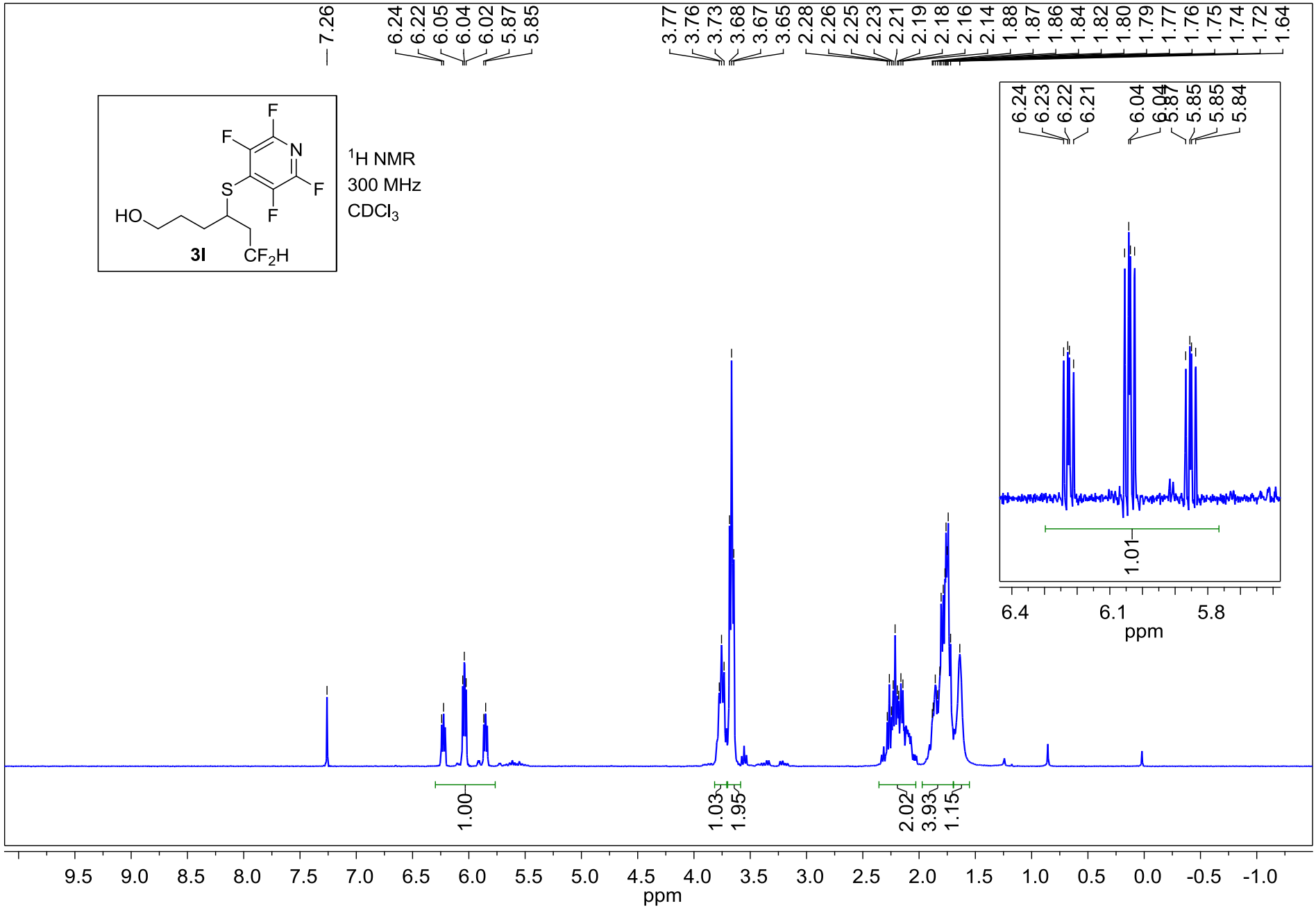
-190
-210
ppm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3.68
3.67
3.65
2.28
2.26
2.25
2.23
2.21
2.19
2.18
2.16
2.14
1.88
1.87
1.86
1.84
1.82
1.80
1.79
1.77
1.76
1.75
1.74
1.72
1.64
F
F
N
S
F
F
HO
3l
CF2H
1H NMR
300 MHz
CDCl3
6.24
6.23
6.22
6.21
6.04
6.04
5.87
5.85
5.85
5.84
1.01
6.4
6.1
5.8
ppm
1.00
1.03
1.95
2.02
3.93
1.15
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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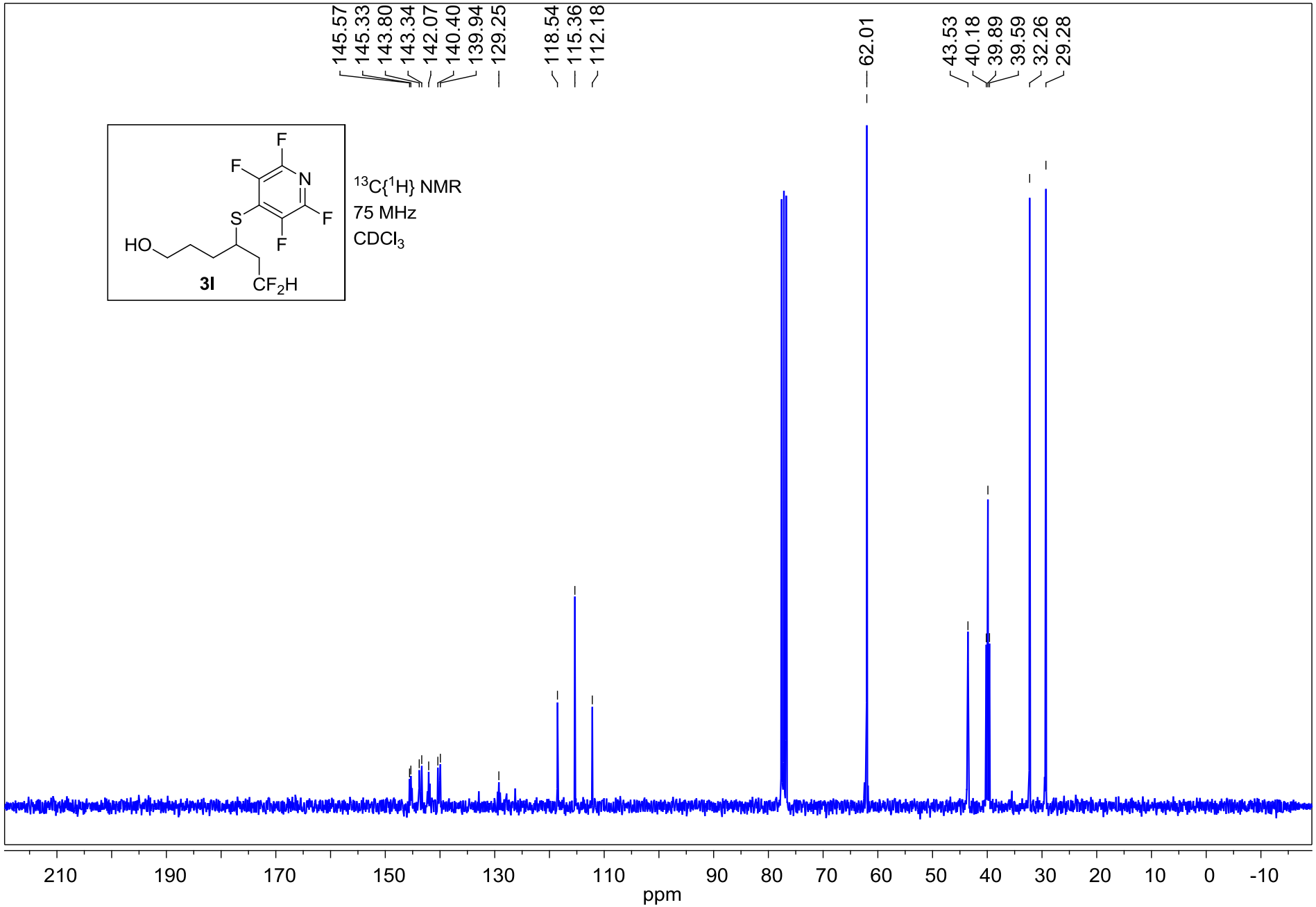
ppm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112.18
62.01
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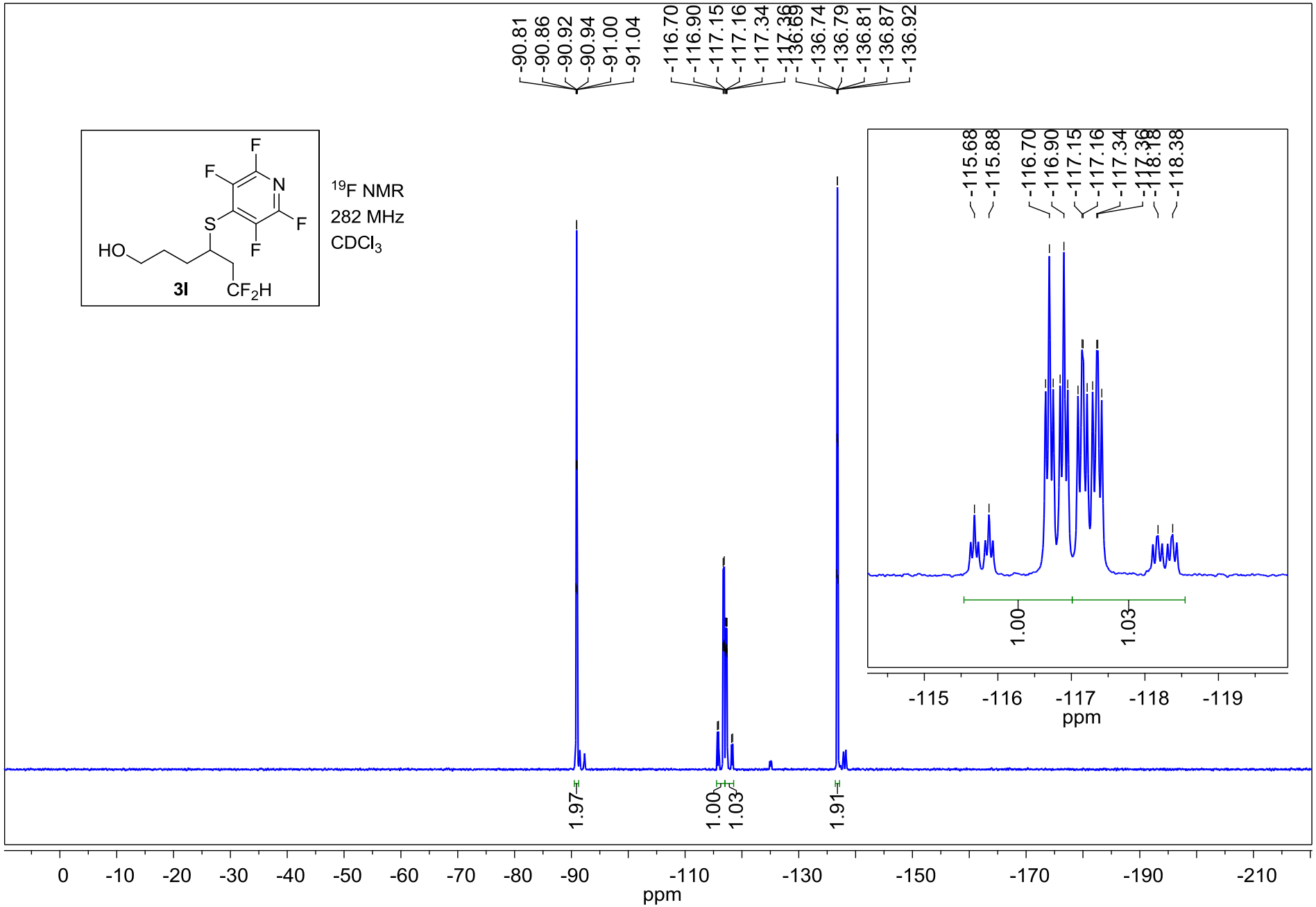
40.18
39.89
39.59
32.26
29.28
F
F
N
S
F
F
HO
3l
CF2H
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm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-91.04
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-136.79
-136.81
-136.87
-136.92
F
F
N
S
F
F
HO
3l
CF2H
19F NMR
282 MHz
CDCl3
-115.68
-115.88
-116.70
-116.90
-117.15
-117.16
-117.34
-118.18
-118.38
1.00
1.03
-115
-116
-117
-118
-119
ppm
1.97
1.00
1.03
1.91
0
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-60
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-190
-210
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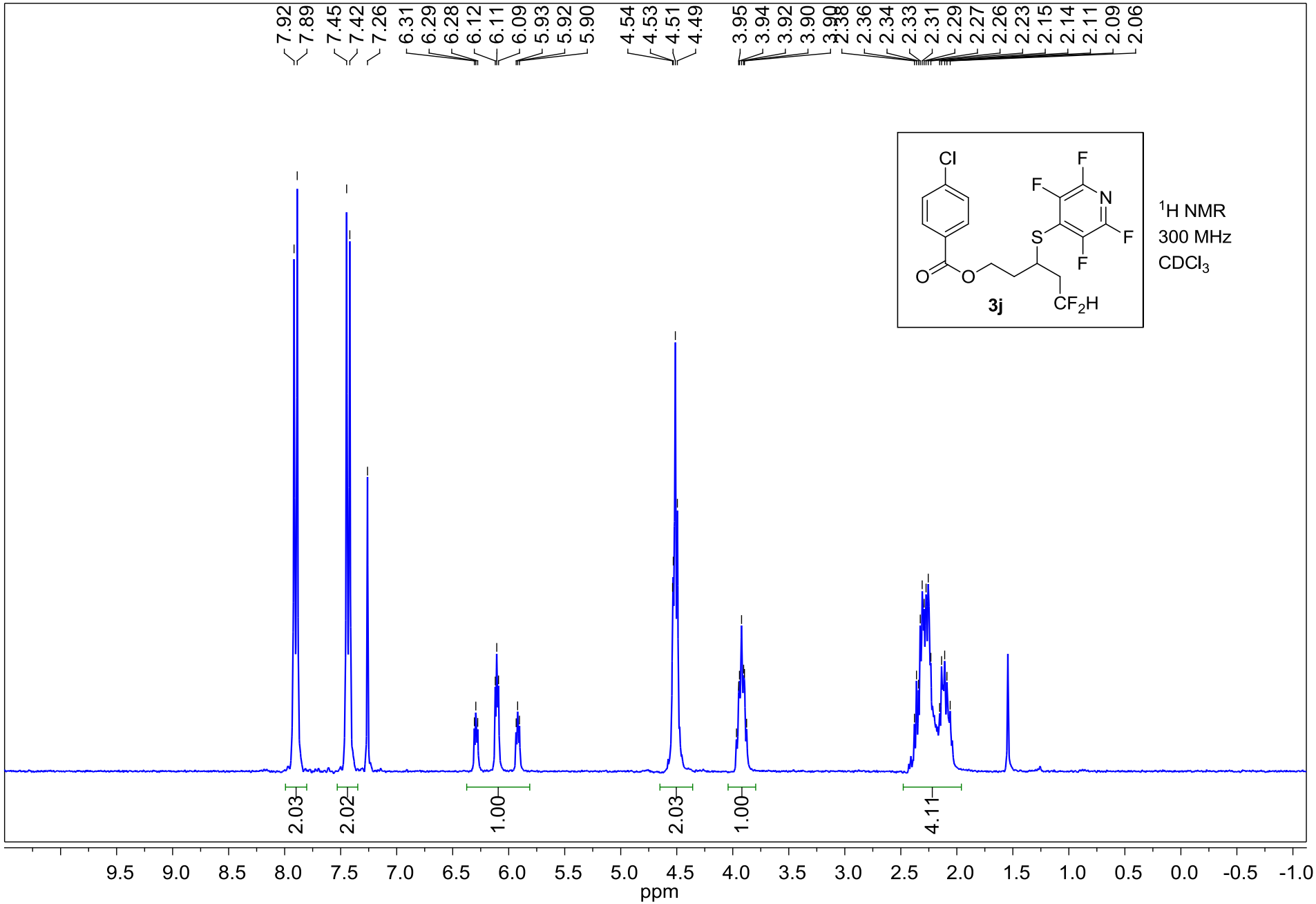
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5.92
5.90
4.54
4.53
4.51
4.49
3.95
3.94
3.92
3.90
3.38
2.36
2.34
2.33
2.31
2.29
2.27
2.26
2.23
2.15
2.14
2.11
2.09
2.06
Cl
F
F
N
S
F
F
O
O
CF2H
3j
1H NMR
300 MHz
CDCl3
2.03
2.02
1.00
2.03
1.00
4.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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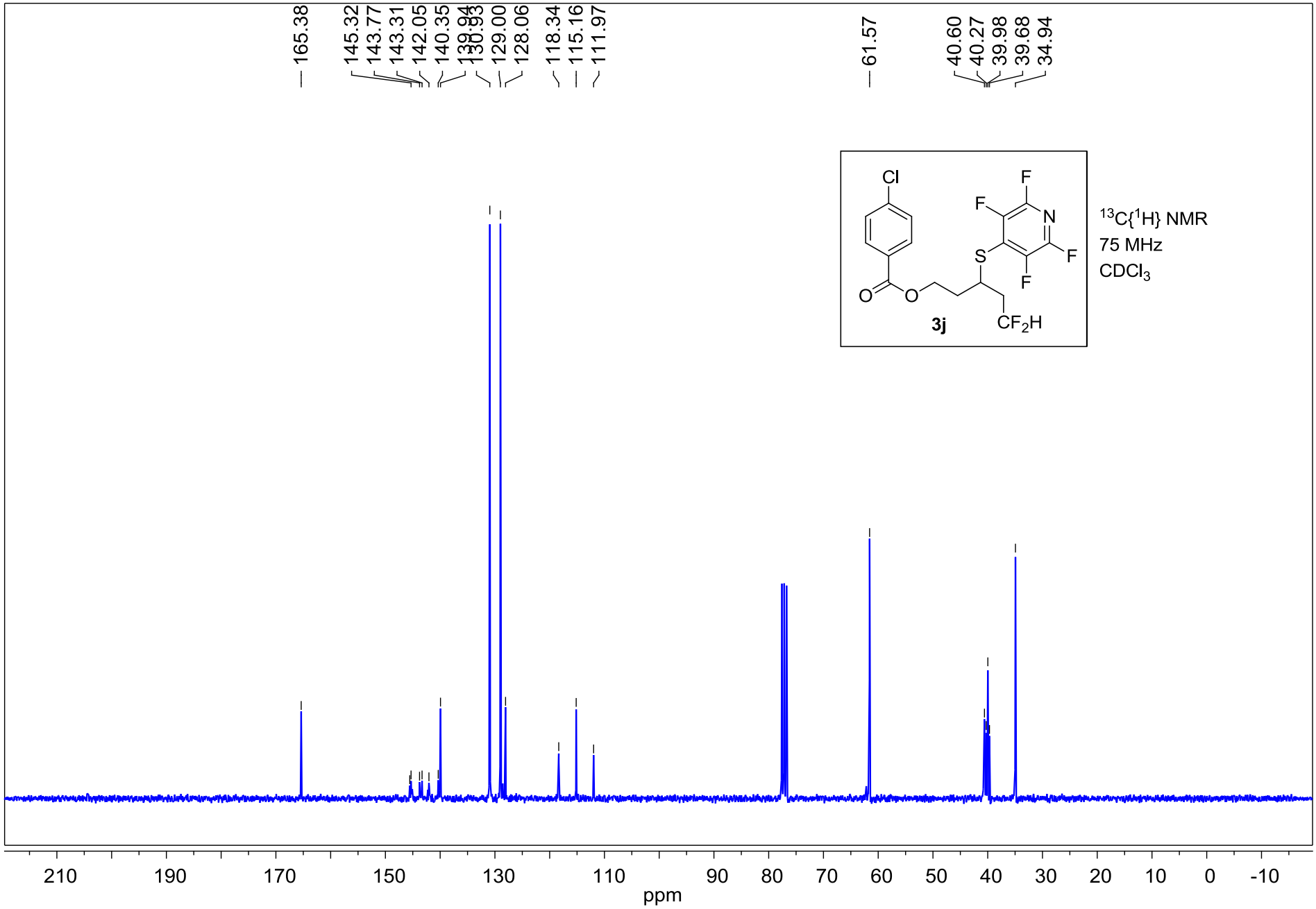
ppm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139.94
130.93
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128.06
118.34
115.16
111.97
61.57
40.60
40.27
39.98
39.68
34.94
Cl
F
F
N
F
S
F
O
O
3j
CF2H
13C{1H} NMR
75 MHz
CDCl3
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170
150
130
110
90
80
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50
40
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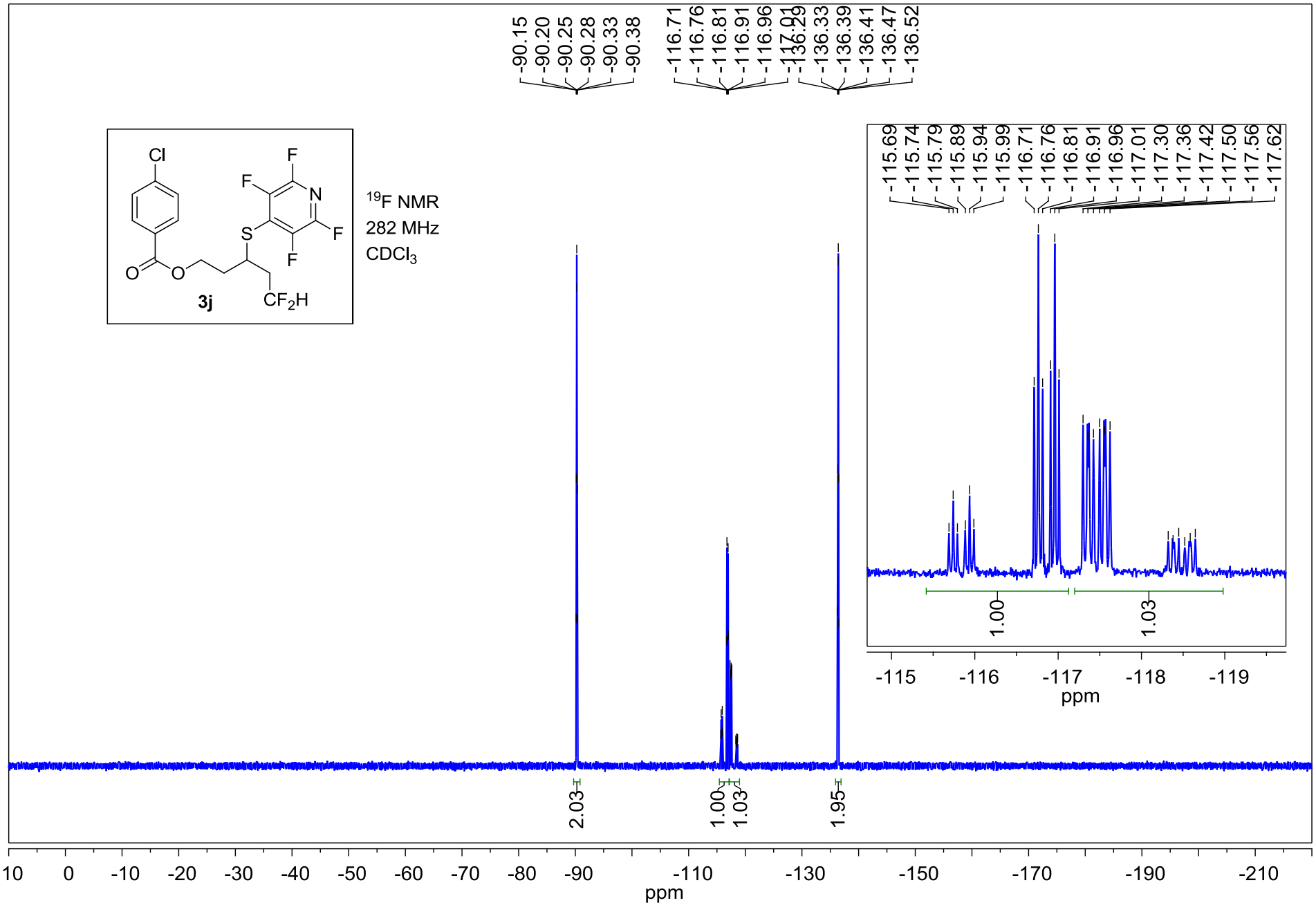
20
10
0
-10
ppm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Cl
F
F
N
S
F
F
O
O
3j
CF2H
19F NMR
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CDCl3
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-115.74
-115.79
-115.89
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-116.76
-116.81
-116.91
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-117.01
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-117.36
-117.42
-117.50
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1.03
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-116
-117
-118
-119
ppm
2.03
1.00
1.03
1.95
10
0
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-50
-60
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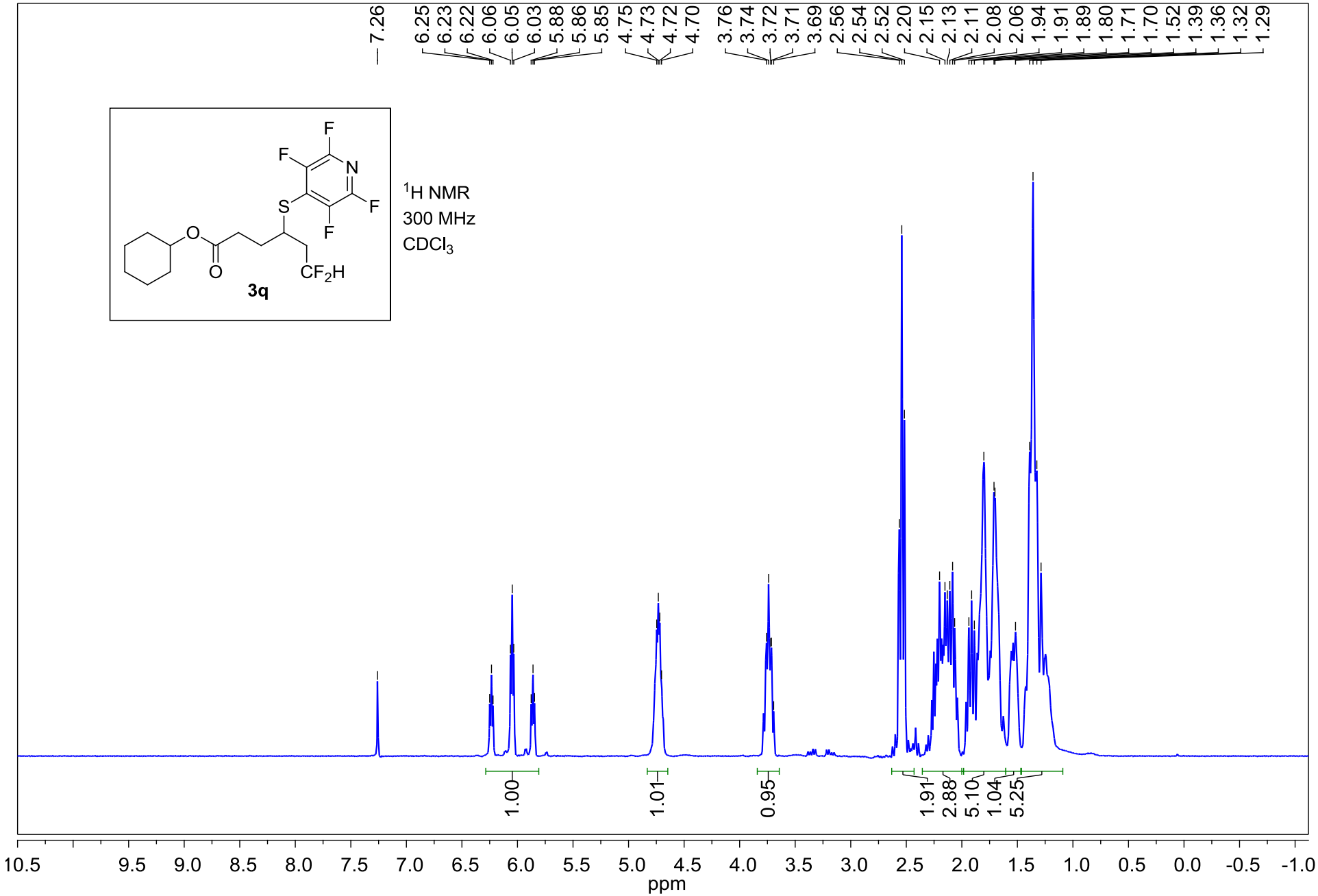
-130
-150
-170
-190
-210
ppm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5.85
4.75
4.73
4.72
4.70
3.76
3.74
3.72
3.71
3.69
2.56
2.54
2.52
2.20
2.15
2.13
2.11
2.08
2.06
1.94
1.91
1.89
1.80
1.71
1.70
1.52
1.39
1.36
1.32
1.29
F
F
N
S
F
F
O
O
CF2H
3q
1H NMR
300 MHz
CDCl3
1.00
1.01
0.95
1.91
2.88
5.10
1.04
5.25
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
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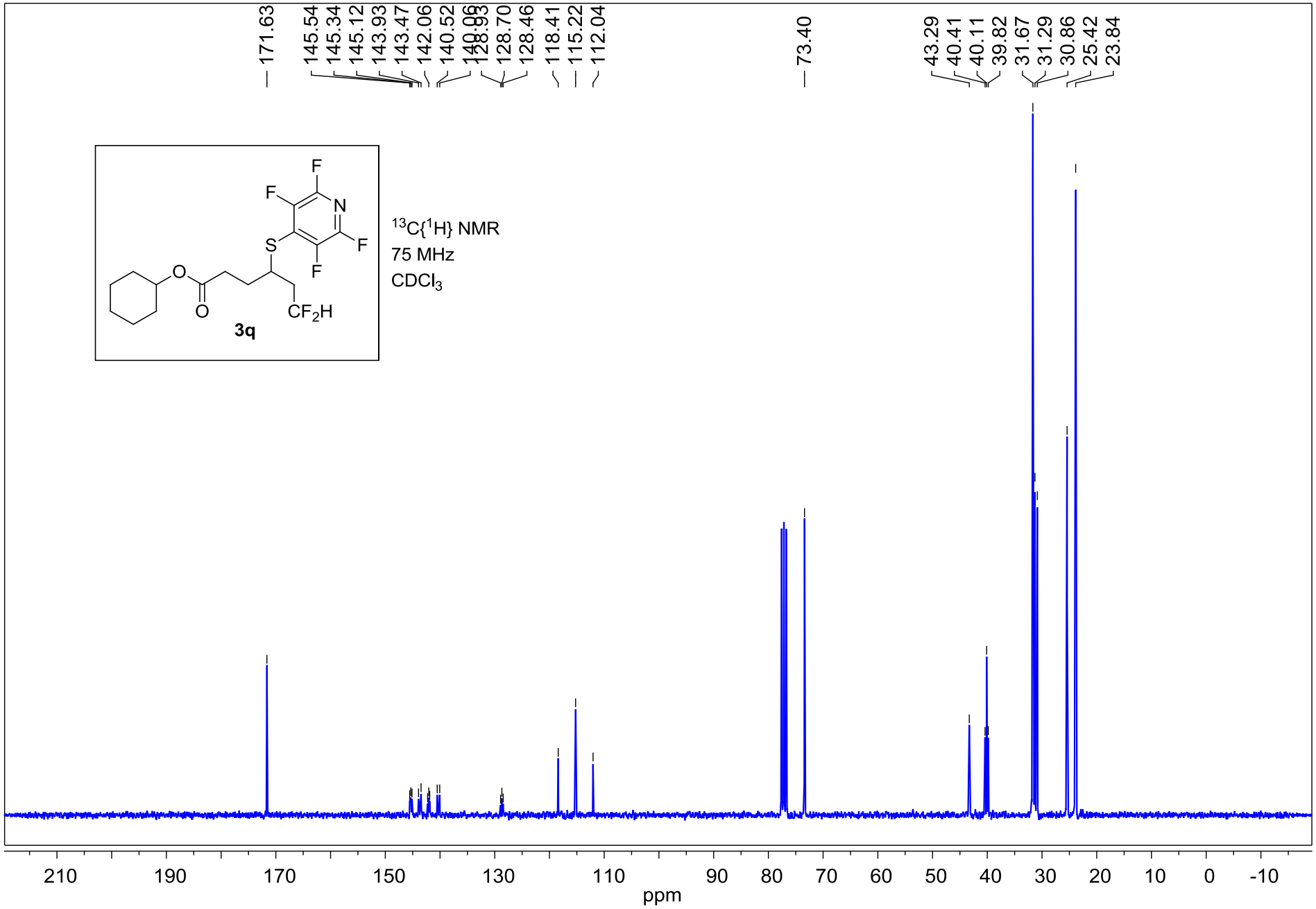
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm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145.34
145.12
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143.47
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140.52
140.06
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128.70
128.46
118.41
115.22
112.04
73.40
43.29
40.41
40.11
39.82
31.67
31.29
30.86
25.42
23.84
F
F
N
S
F
F
O
O
CF2H
3q
13C{1H} NMR
75 MHz
CDCl3
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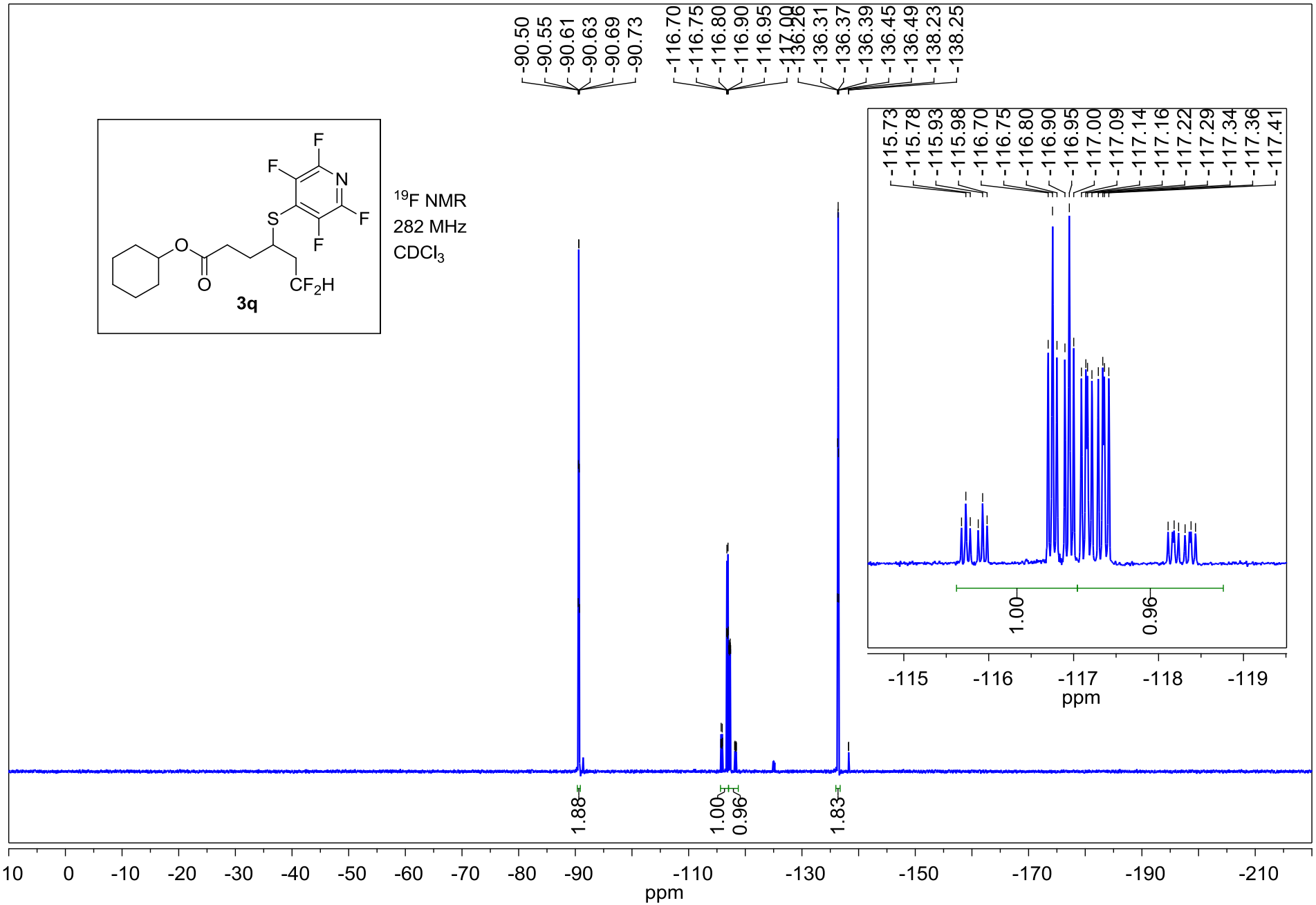
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm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-90.55
-90.61
-90.63
-90.69
-90.73
-116.70
-116.75
-116.80
-116.90
-116.95
-117.00
-136.26
-136.31
-136.37
-136.39
-136.45
-136.49
-138.23
-138.25
F
F
N
S
F
F
O
O
CF2H
3q
19F NMR
282 MHz
CDCl3
-115.73
-115.78
-115.93
-115.98
-116.70
-116.75
-116.80
-116.90
-116.95
-117.00
-117.09
-117.14
-117.16
-117.22
-117.29
-117.34
-117.36
-117.41
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0.96
-115
-116
-117
-118
-119
ppm
1.88
1.00
0.96
1.83
10
0
-10
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-60
-70
-80
-90
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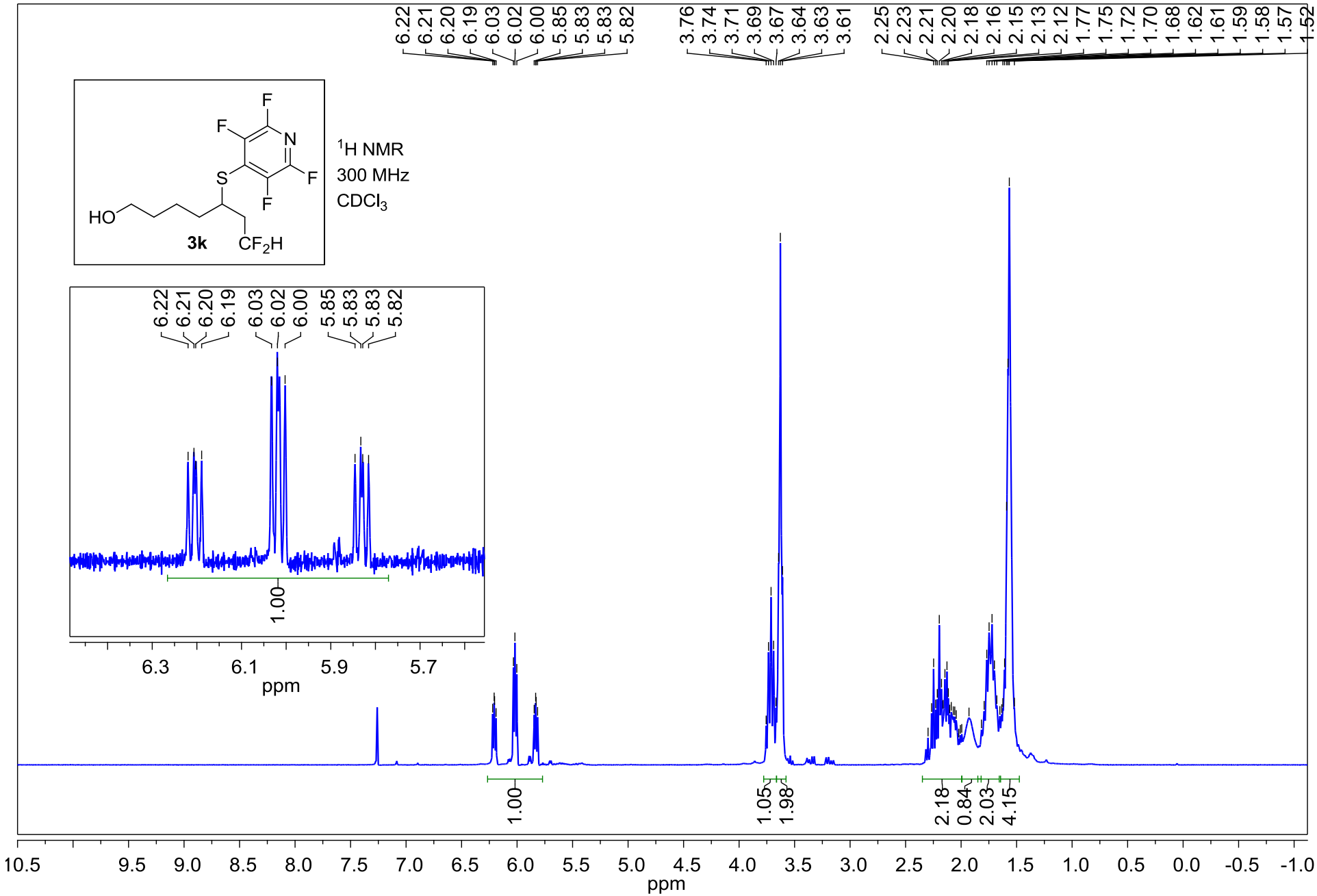
-170
-190
-210
ppm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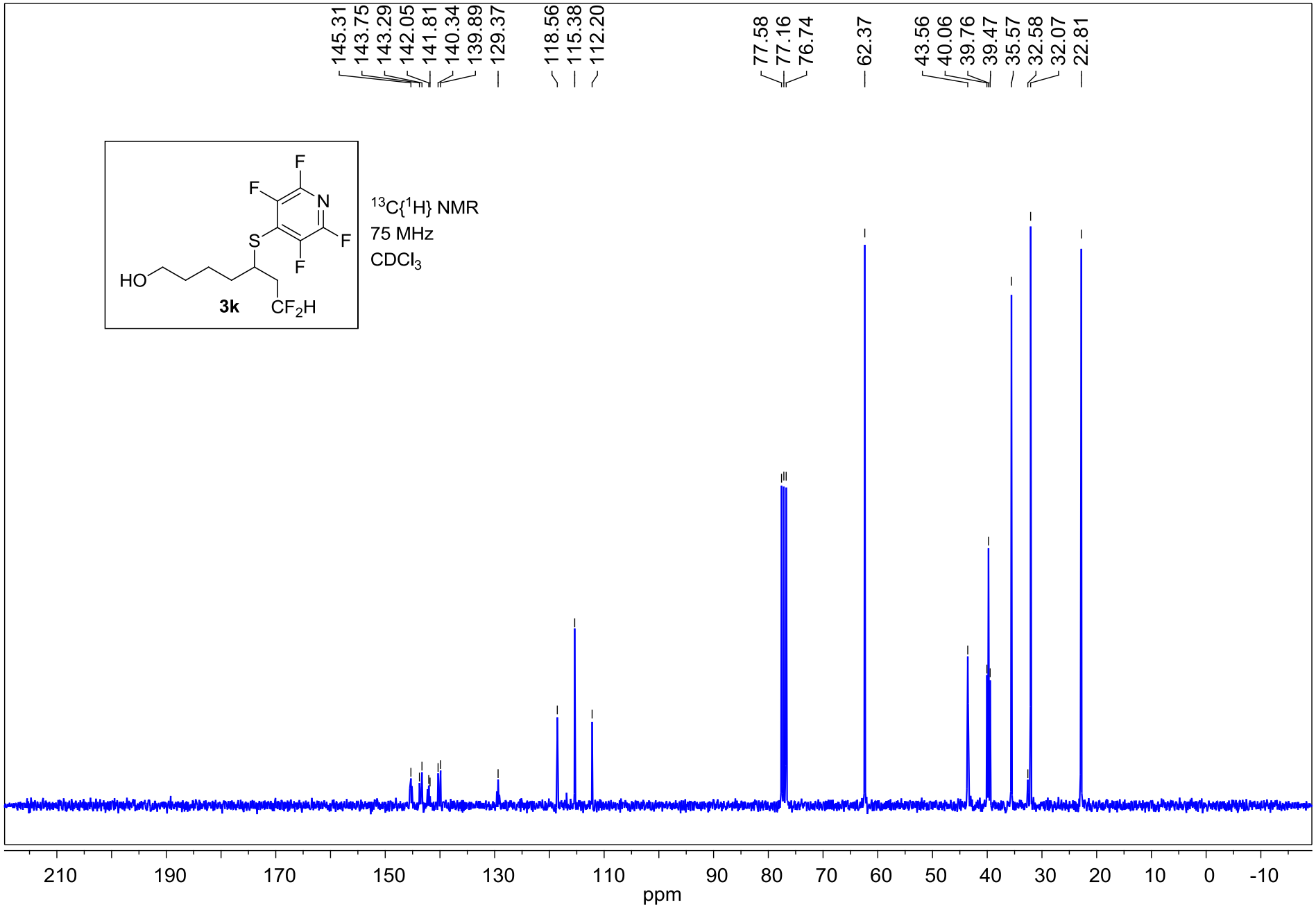
6.21
6.20
6.19
6.03
6.02
6.00
5.85
5.83
5.83
5.82
3.76
3.74
3.71
3.69
3.67
3.64
3.63
3.61
2.25
2.23
2.21
2.20
2.18
2.16
2.15
2.13
2.12
1.77
1.75
1.72
1.70
1.68
1.62
1.61
1.59
1.58
1.57
1.52
F
F
N
S
F
F
HO
3k
CF2H
1H NMR
300 MHz
CDCl3
1.00
6.3
6.1
5.9
5.7
ppm
1.00
1.05
1.98
2.18
0.84
2.03
4.15
10.5
9.5
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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141.81
140.34
139.89
129.37
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115.38
112.20
77.58
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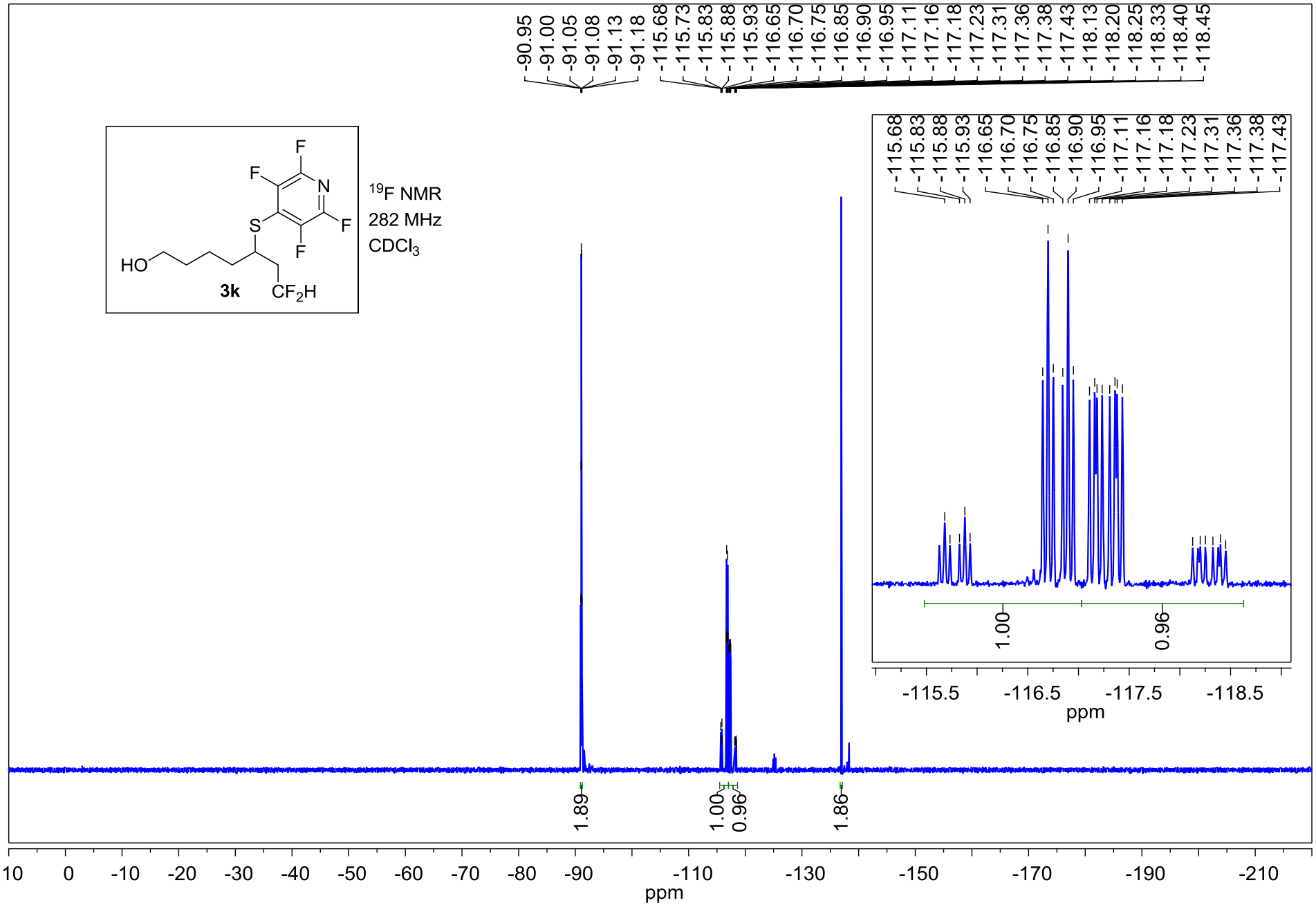
76.74
62.37
43.56
40.06
39.76
39.47
35.57
32.58
32.07
22.81
F
F
N
S
F
F
HO
3k
CF2H
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm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-91.13
-91.18
-115.68
-115.73
-115.83
-115.88
-115.93
-116.65
-116.70
-116.75
-116.85
-116.90
-116.95
-117.11
-117.16
-117.18
-117.23
-117.31
-117.36
-117.38
-117.43
-118.13
-118.20
-118.25
-118.33
-118.40
-118.45
F
F
N
S
F
F
HO
3k
CF2H
19F NMR
282 MHz
CDCl3
1.89
1.00
0.96
1.86
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm
1.00
0.96
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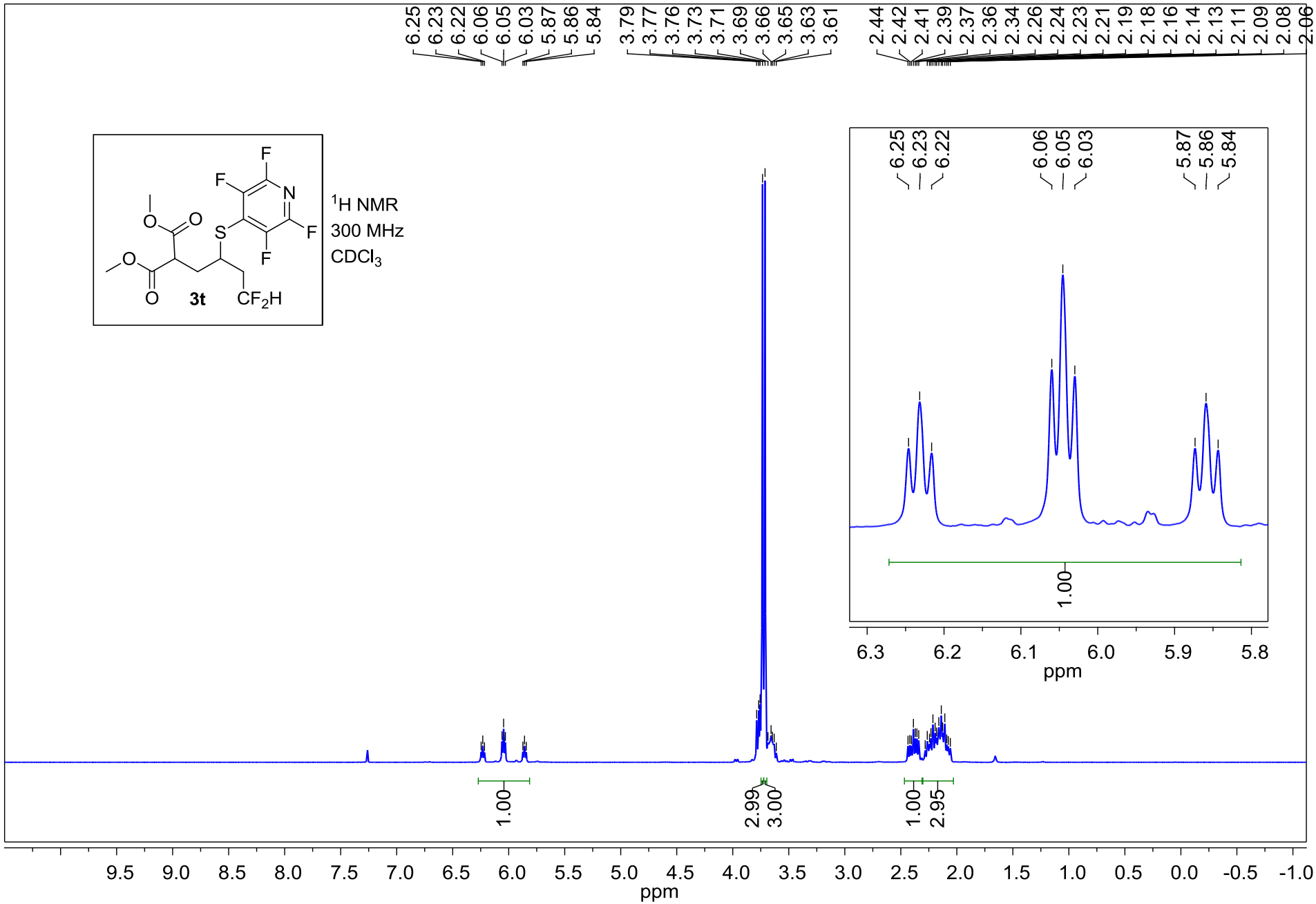
-116.5
-117.5
-118.5
ppm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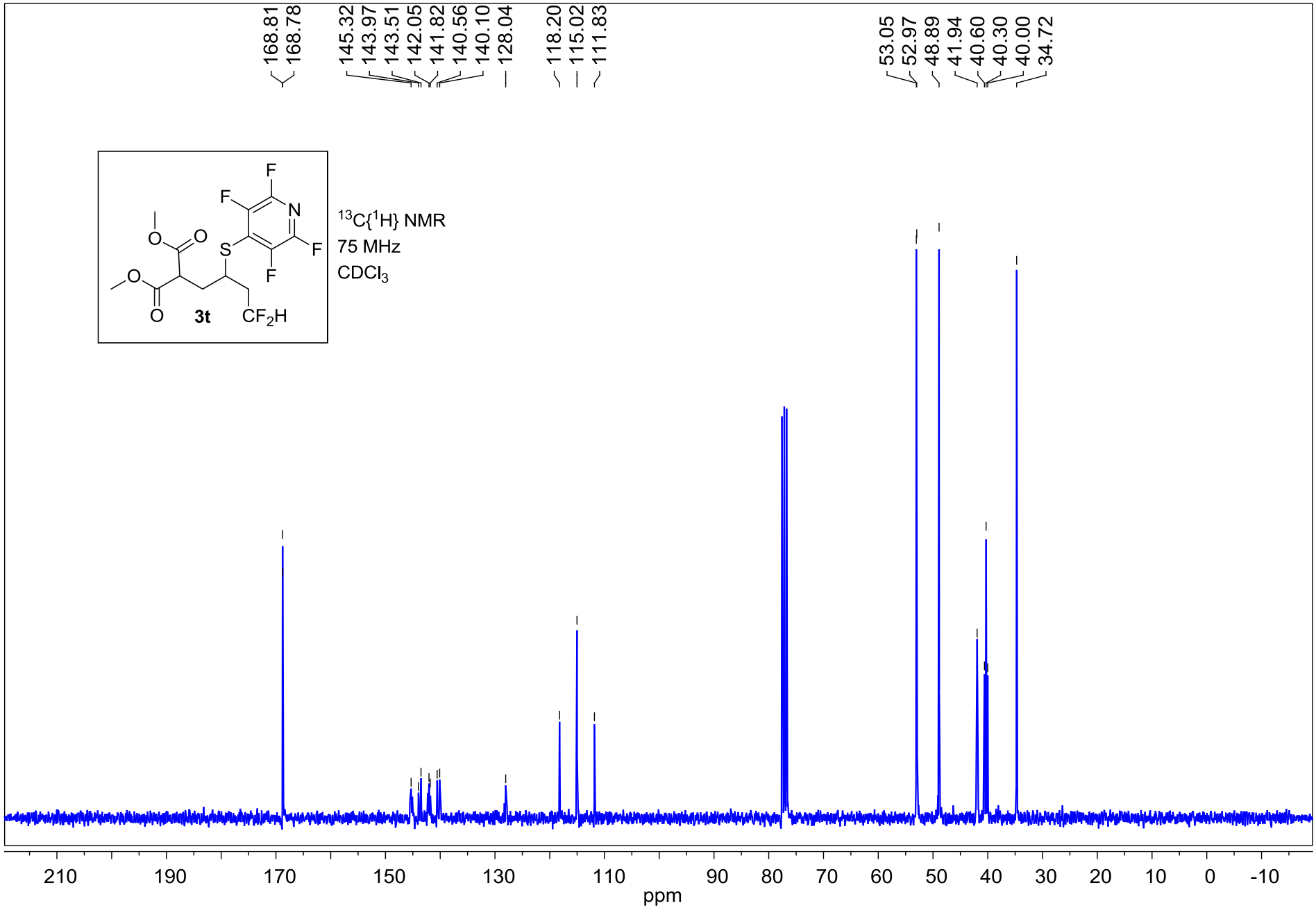
3.79 3.77 3.76 3.73 3.71 3.69 3.66 3.65 3.63 3.61
2.44 2.42 2.41 2.39 2.37 2.36 2.34 2.26 2.24 2.23 2.21 2.19 2.18 2.16 2.14 2.13 2.11 2.09 2.08 2.06
F
F
N
O
O
S
F
F
O
O
3t
CF2H
1H NMR
300 MHz
CDCl3
6.25 6.23 6.22 6.06 6.05 6.03 5.87 5.86 5.84
1.00
6.3 6.2 6.1 6.0 5.9 5.8
ppm
1.00 2.99 3.00 1.00 2.95
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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168.78
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143.51
142.05
141.82
140.56
140.10
128.04
118.20
115.02
111.83
53.05
52.97
48.89
41.94
40.60
40.30
40.00
34.72
F
F
N
O
O
S
F
F
O
O
3t
CF2H
13C{1H} NMR
75 MHz
CDCl3
210
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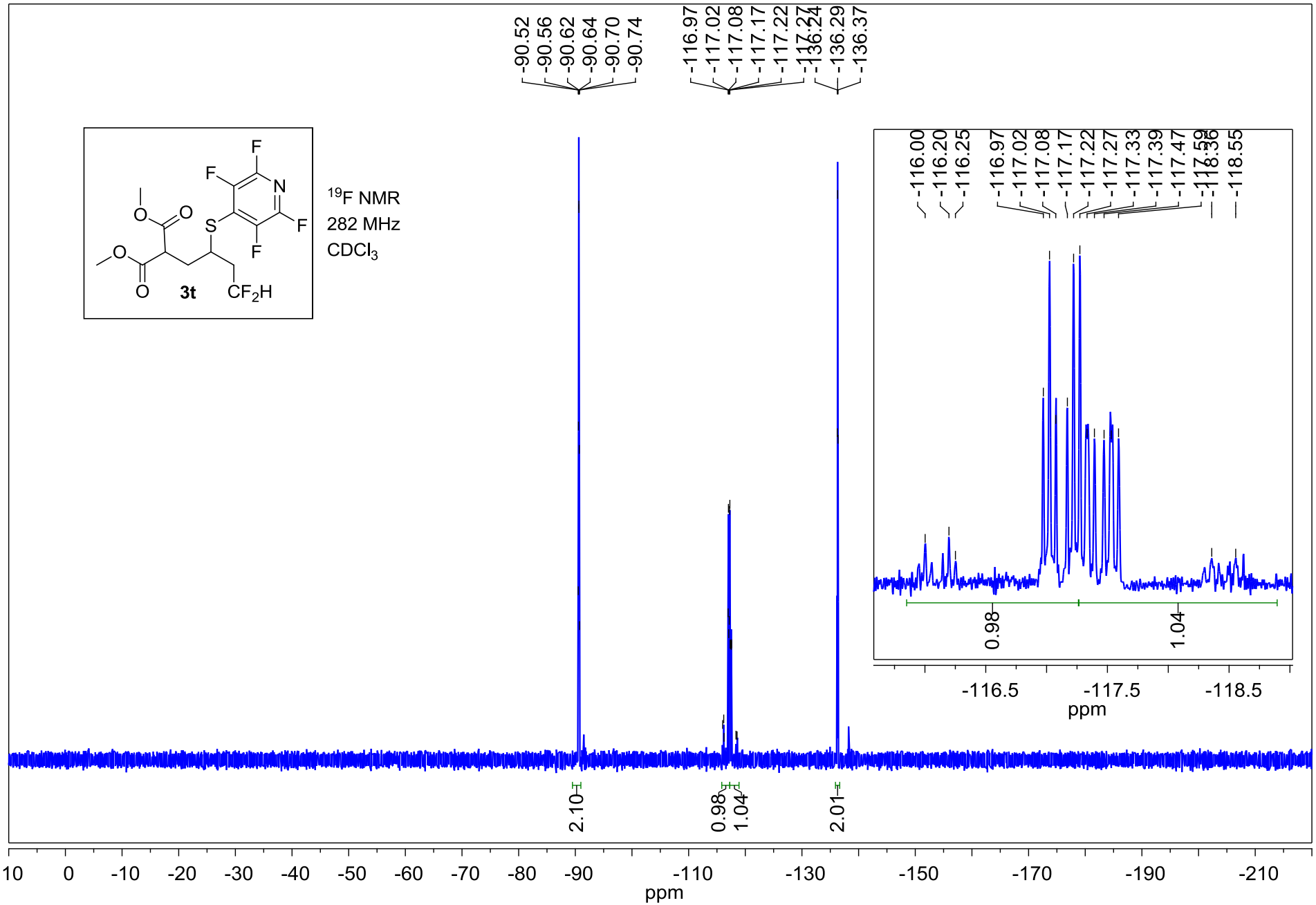
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm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-90.74
-116.97
-117.02
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-117.17
-117.22
-117.27
-136.24
-136.29
-136.37
F
F
N
O
O
S
F
F
O
O
3t
CF2H
19F NMR
282 MHz
CDCl3
-116.00
-116.20
-116.25
-116.97
-117.02
-117.08
-117.17
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-117.33
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-117.5
-118.5
ppm
2.10
0.98
1.04
2.01
10
0
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-30
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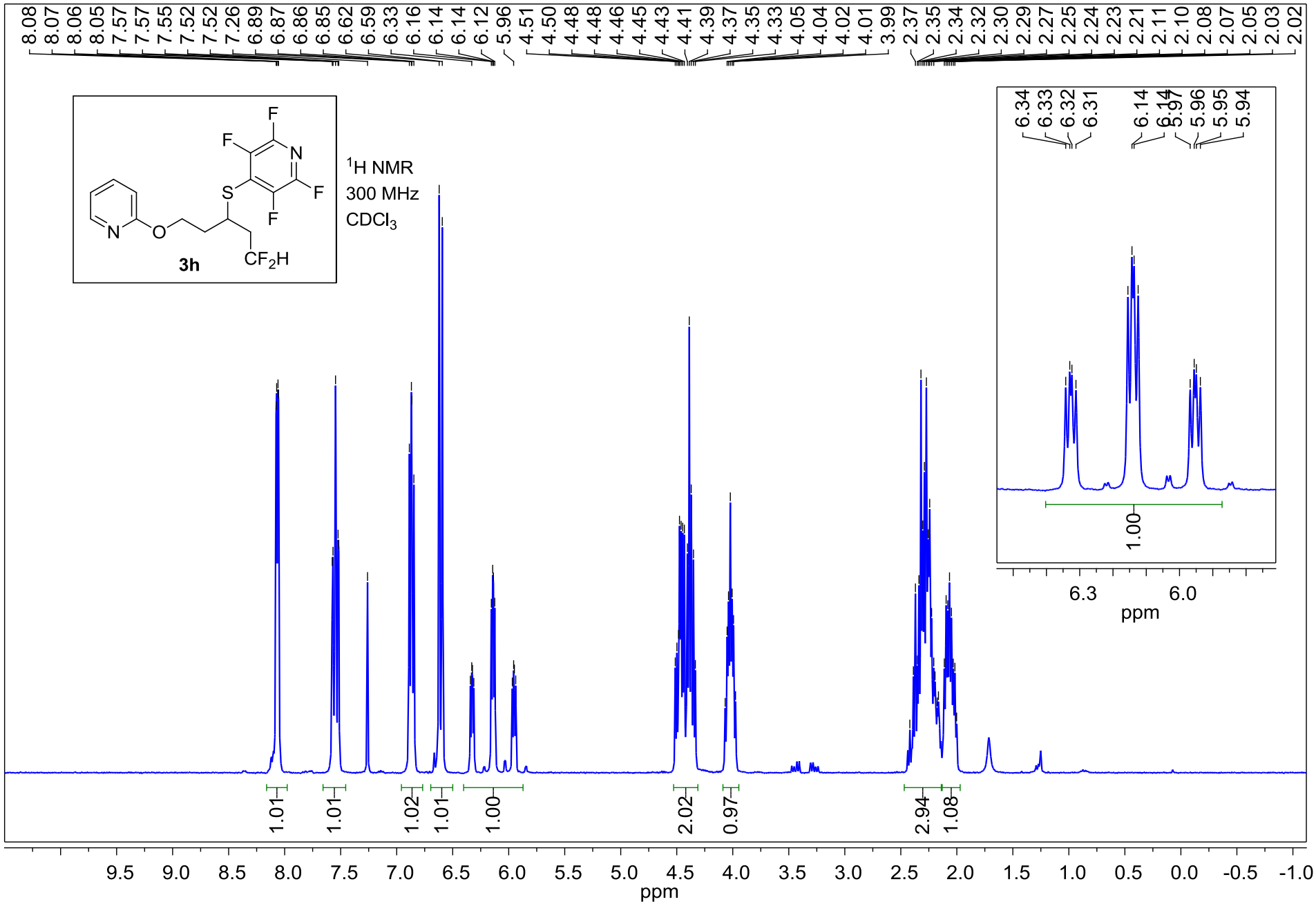
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm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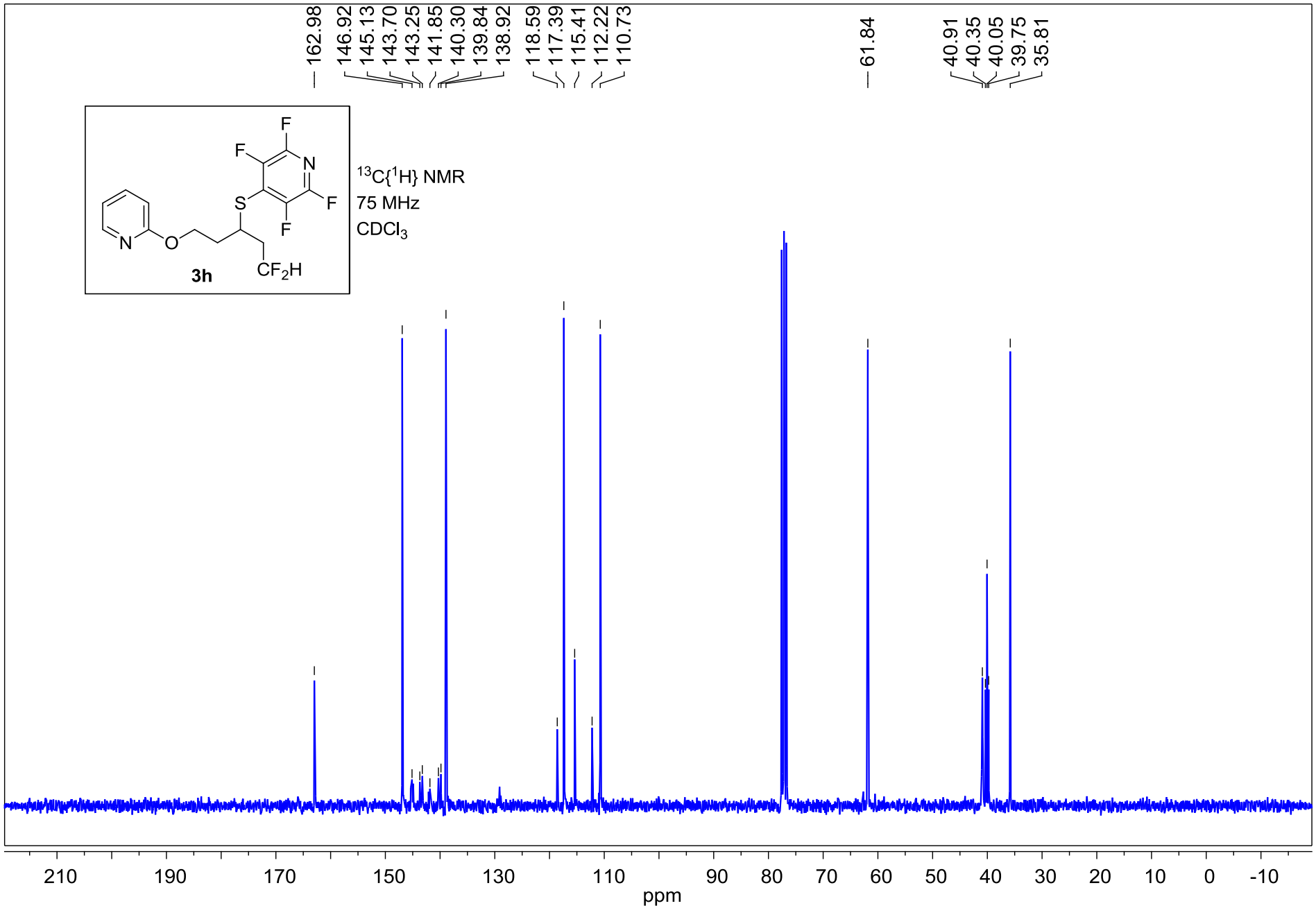
F
F
N
S
F
F
N
O
CF2H
3h
1H NMR
300 MHz
CDCl3
6.34 6.33 6.32 6.31 6.14 6.14 5.97 5.96 5.95 5.94
1.00
6.3
6.0
ppm
1.01 1.01 1.02 1.01 1.00 2.02 0.97 2.94 1.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm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139.84
138.92
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117.39
115.41
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110.73
61.84
40.91
40.35
40.05
39.75
35.81
F
F
N
S
F
F
N
O
CF2H
3h
13C{1H} NMR
75 MHz
CDCl3
210
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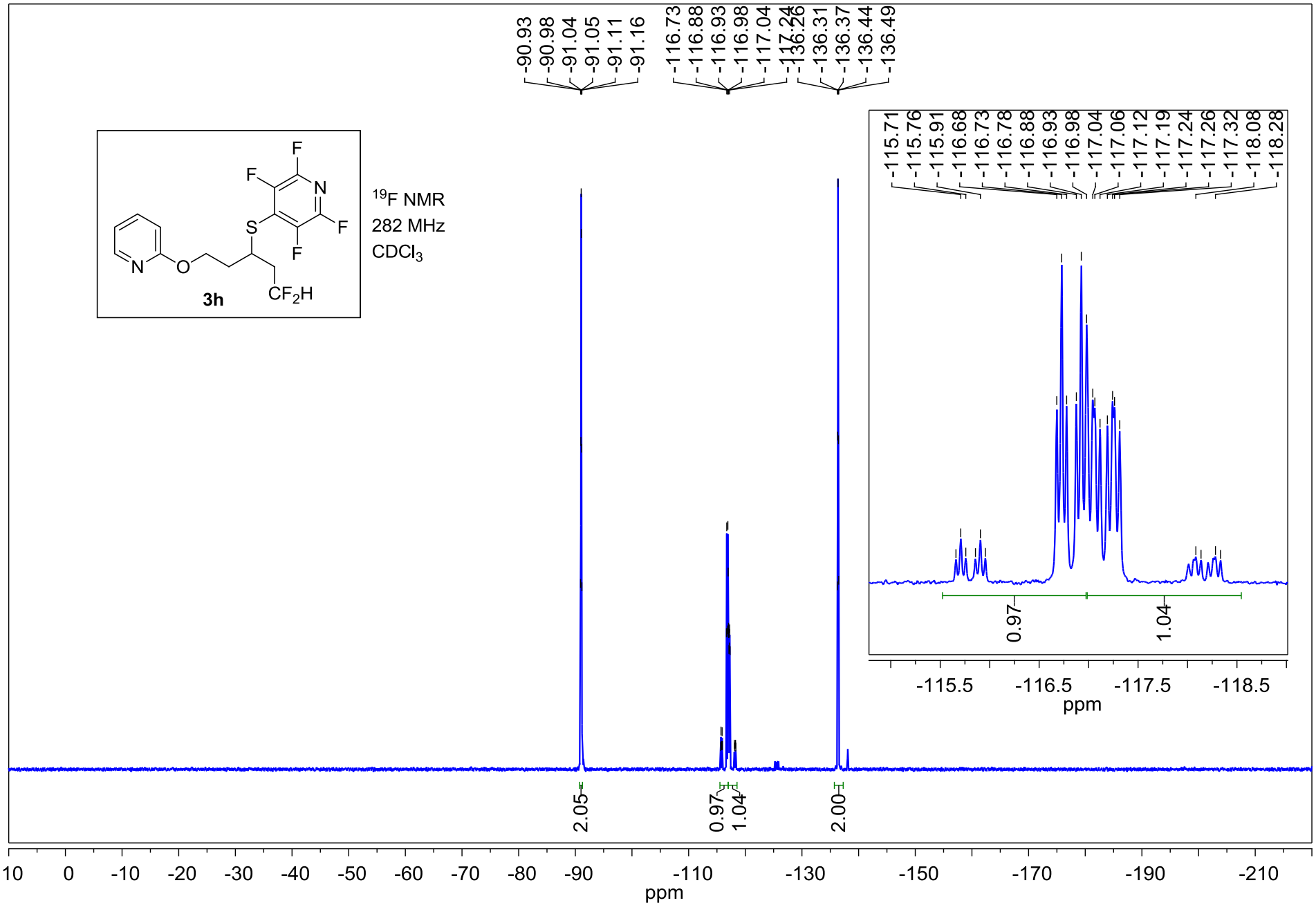
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm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-116.88
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-116.98
-117.04
-117.24
-117.26
-136.31
-136.37
-136.44
-136.49
F
F
N
S
F
F
N
O
CF2H
3h
19F NMR
282 MHz
CDCl3
-115.71
-115.76
-115.91
-116.68
-116.73
-116.78
-116.88
-116.93
-116.98
-117.04
-117.06
-117.12
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-117.24
-117.26
-117.32
-118.08
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0.97
1.04
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-116.5
-117.5
-118.5
ppm
2.05
0.97
1.04
2.00
10
0
-10
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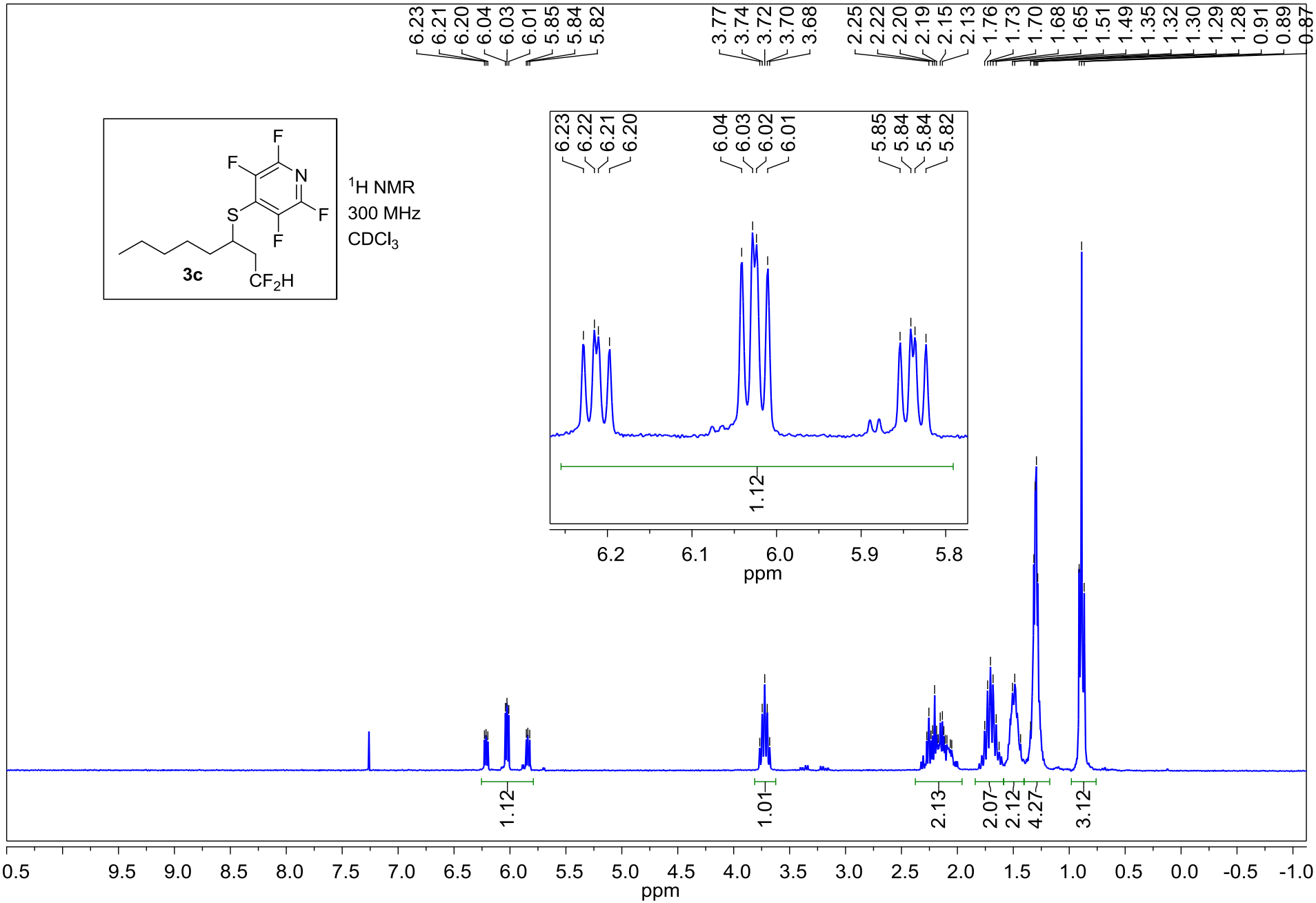
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm


6.23
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6.03
6.01
5.85
5.84
5.82
3.77
3.74
3.72
3.70
3.68
2.25
2.22
2.20
2.19
2.15
2.13
1.76
1.73
1.70
1.68
1.65
1.51
1.49
1.35
1.32
1.30
1.29
1.28
0.91
0.89
0.87
F
F
N
S
F
F
3c
CF2H
1H NMR
300 MHz
CDCl3
6.23
6.22
6.21
6.20
6.04
6.03
6.02
6.01
5.85
5.84
5.84
5.82
1.12
6.2
6.1
6.0
5.9
5.8
ppm
1.12
1.01
2.13
2.07
2.12
4.27
3.12
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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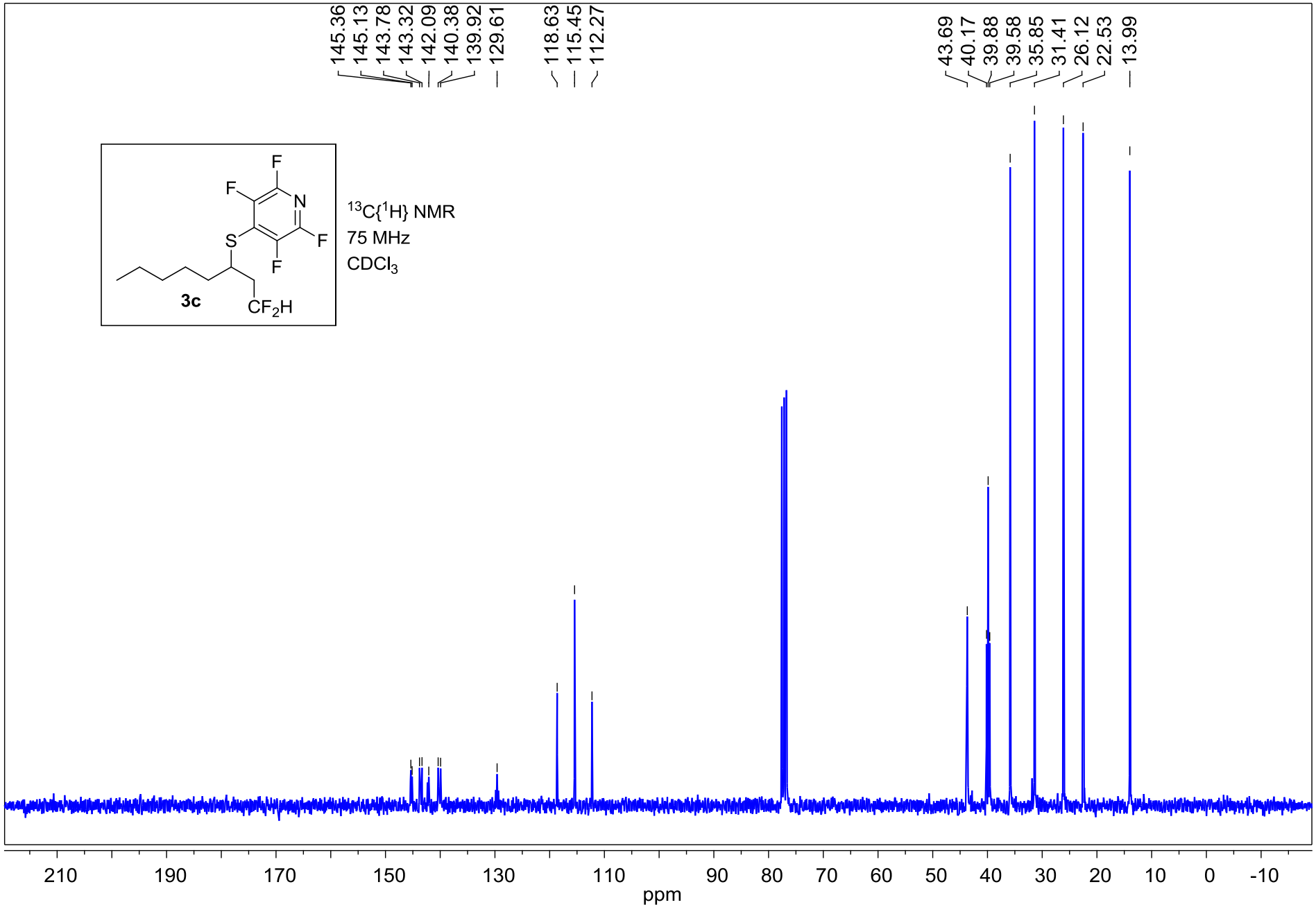
-1.0
ppm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143.32
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140.38
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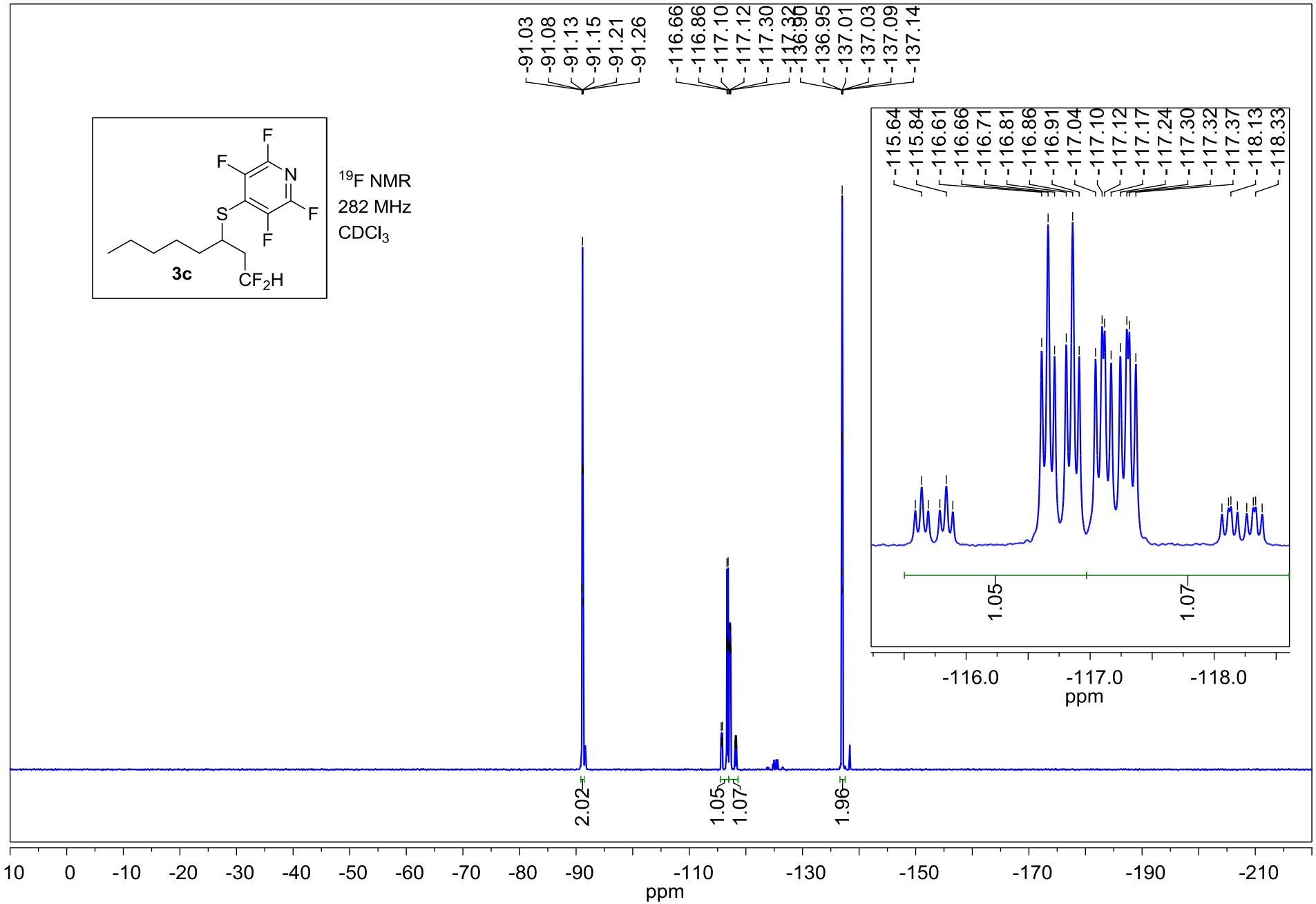
129.61
118.63
115.45
112.27
43.69
40.17
39.88
39.58
35.85
31.41
26.12
22.53
13.99
F
F
N
S
F
F
3c
CF2H
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm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-91.13
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-116.66
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-117.10
-117.12
-117.30
-117.32
-136.90
-136.95
-137.01
-137.03
-137.09
-137.14
-115.64
-115.84
-116.61
-116.66
-116.71
-116.81
-116.86
-116.91
-117.04
-117.10
-117.12
-117.17
-117.24
-117.30
-117.32
-117.37
-118.13
-118.33
F
F
N
S
F
F
3c
CF2H
19F NMR
282 MHz
CDCl3
1.05
1.07
-116.0
-117.0
-118.0
ppm
2.02
1.05
1.07
1.96
10
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-60
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-80
-90
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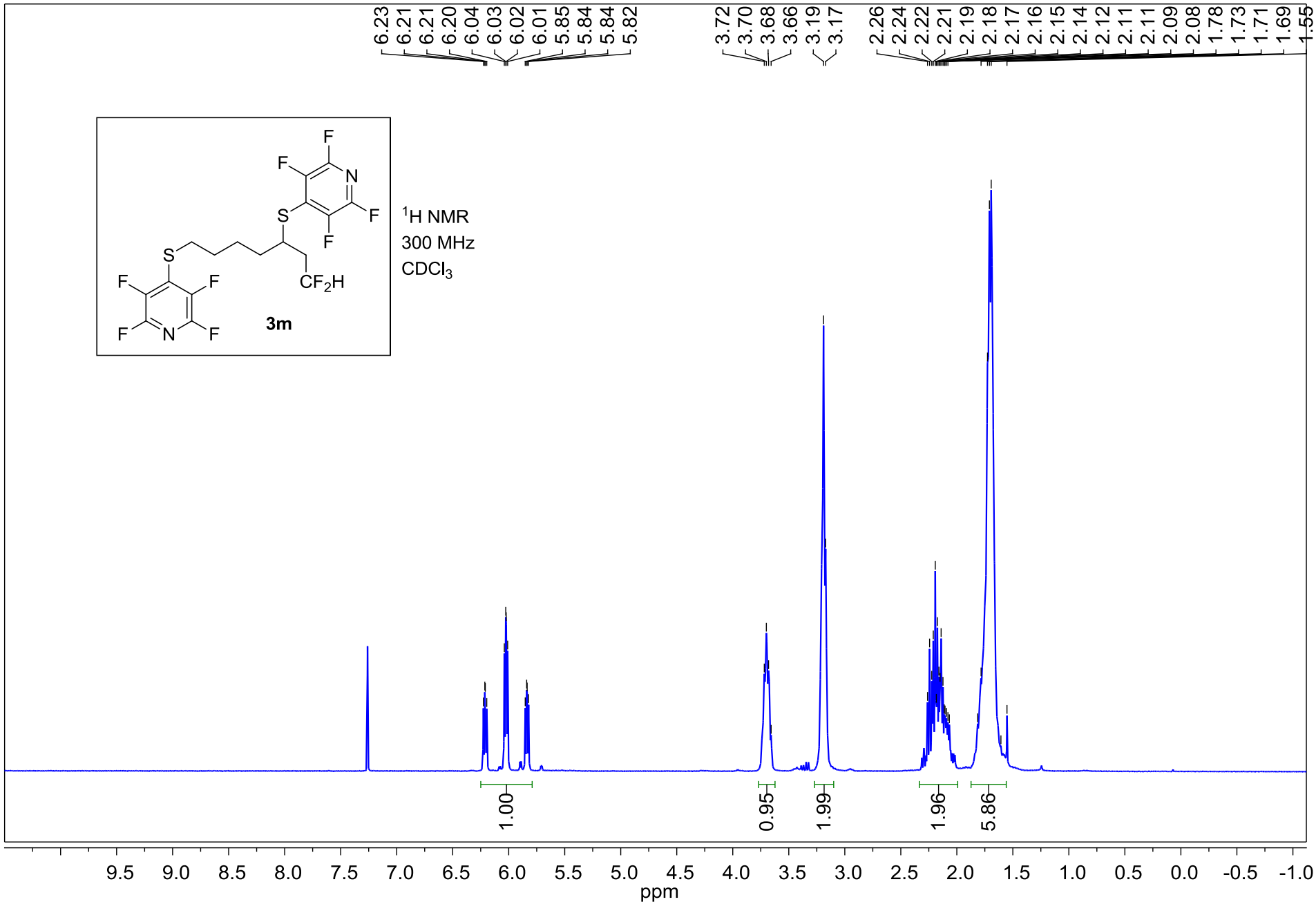
-130
-150
-170
-190
-210
ppm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6.01
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5.84
5.82
3.72
3.70
3.68
3.66
3.19
3.17
2.26
2.24
2.22
2.21
2.19
2.18
2.17
2.16
2.15
2.14
2.12
2.11
2.11
2.09
2.08
1.78
1.73
1.71
1.69
1.55
F
F
N
F
S
F
S
F
F
F
N
F
CF2H
3m
1H NMR
300 MHz
CDCl3
1.00
0.95
1.99
1.96
5.86
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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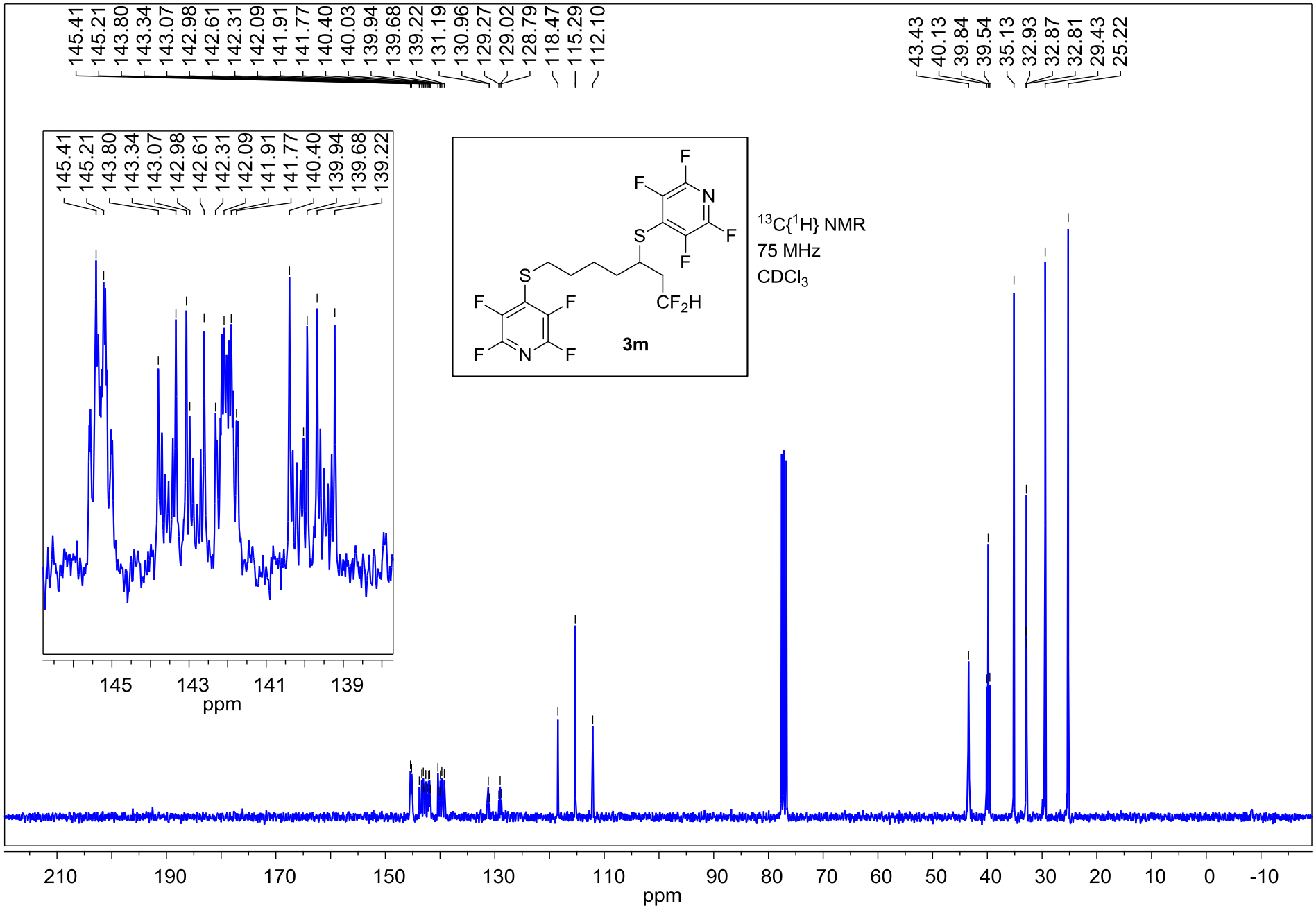
ppm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140.03
139.94
139.68
139.22
131.19
130.96
129.27
129.02
128.79
118.47
115.29
112.10
43.43
40.13
39.84
39.54
35.13
32.93
32.87
32.81
29.43
25.22
F
F
N
F
S
F
S
F
F
F
N
F
CF2H
3m
13C{1H} NMR
75 MHz
CDCl3
ppm
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170
150
130
110
90
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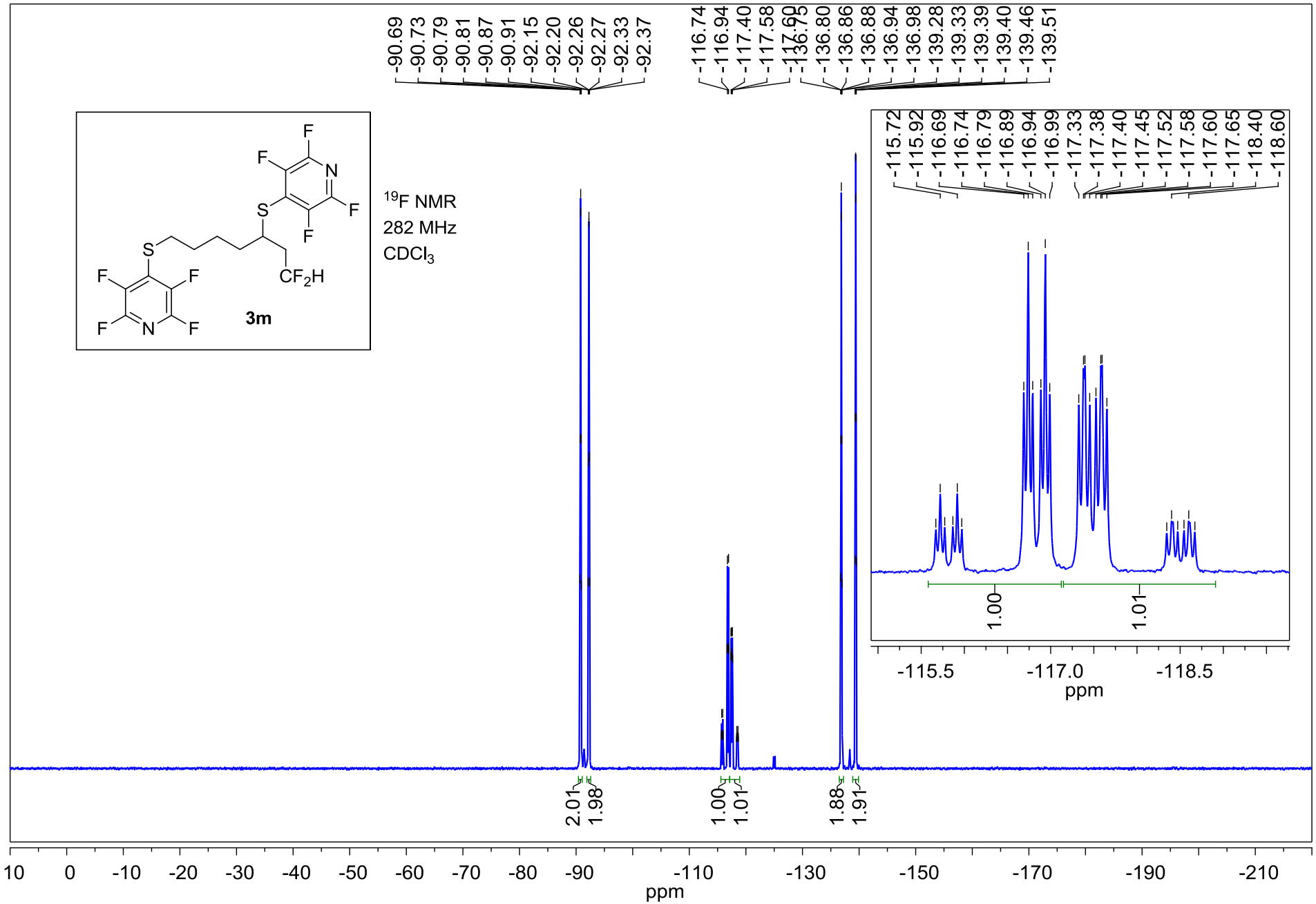
60
50
40
30
20
10
0
-10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-92.15
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-136.80
-136.86
-136.88
-136.94
-136.98
-139.28
-139.33
-139.39
-139.40
-139.46
-139.51
19F NMR
282 MHz
CDCl3
3m
-115.72
-115.92
-116.69
-116.74
-116.79
-116.89
-116.94
-116.99
-117.33
-117.38
-117.40
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-117.58
-117.60
-117.65
-118.40
-118.60
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1.01
-115.5
-117.0
-118.5
ppm
2.01
1.98
1.00
1.01
1.88
1.91
10
0
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-20
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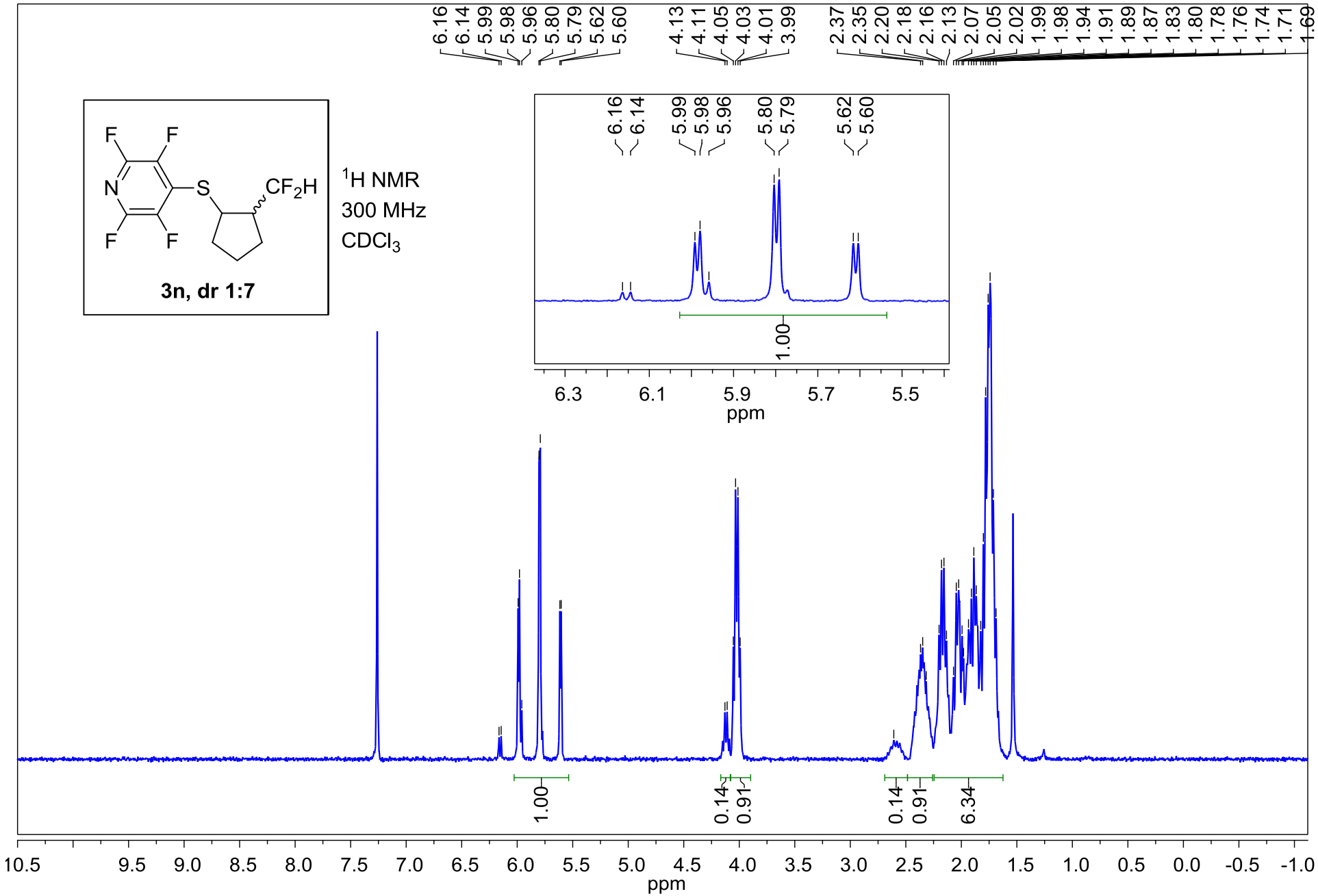
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm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6.14
5.99
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5.79
5.62
5.60
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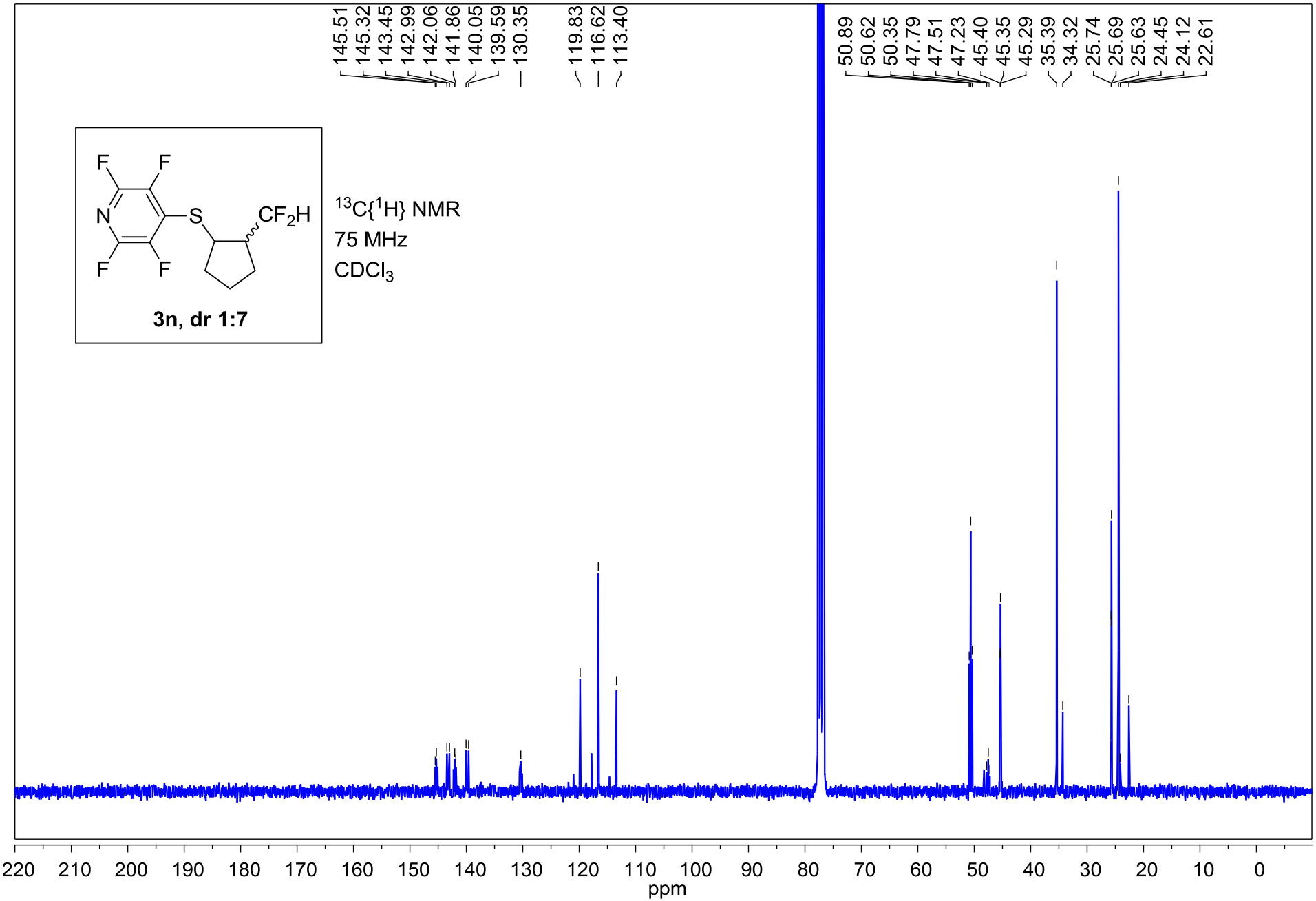
4.11
4.05
4.03
4.01
3.99
2.37
2.35
2.20
2.18
2.16
2.13
2.07
2.05
2.02
1.99
1.98
1.94
1.91
1.89
1.87
1.83
1.80
1.78
1.76
1.74
1.71
1.69
F
F
N
S
CF2H
F
F
3n, dr 1:7
1H NMR
300 MHz
CDCl3
1.00
6.3
6.1
5.9
5.7
5.5
ppm
1.00
0.14
0.91
0.14
0.91
6.34
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm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140.05
139.59
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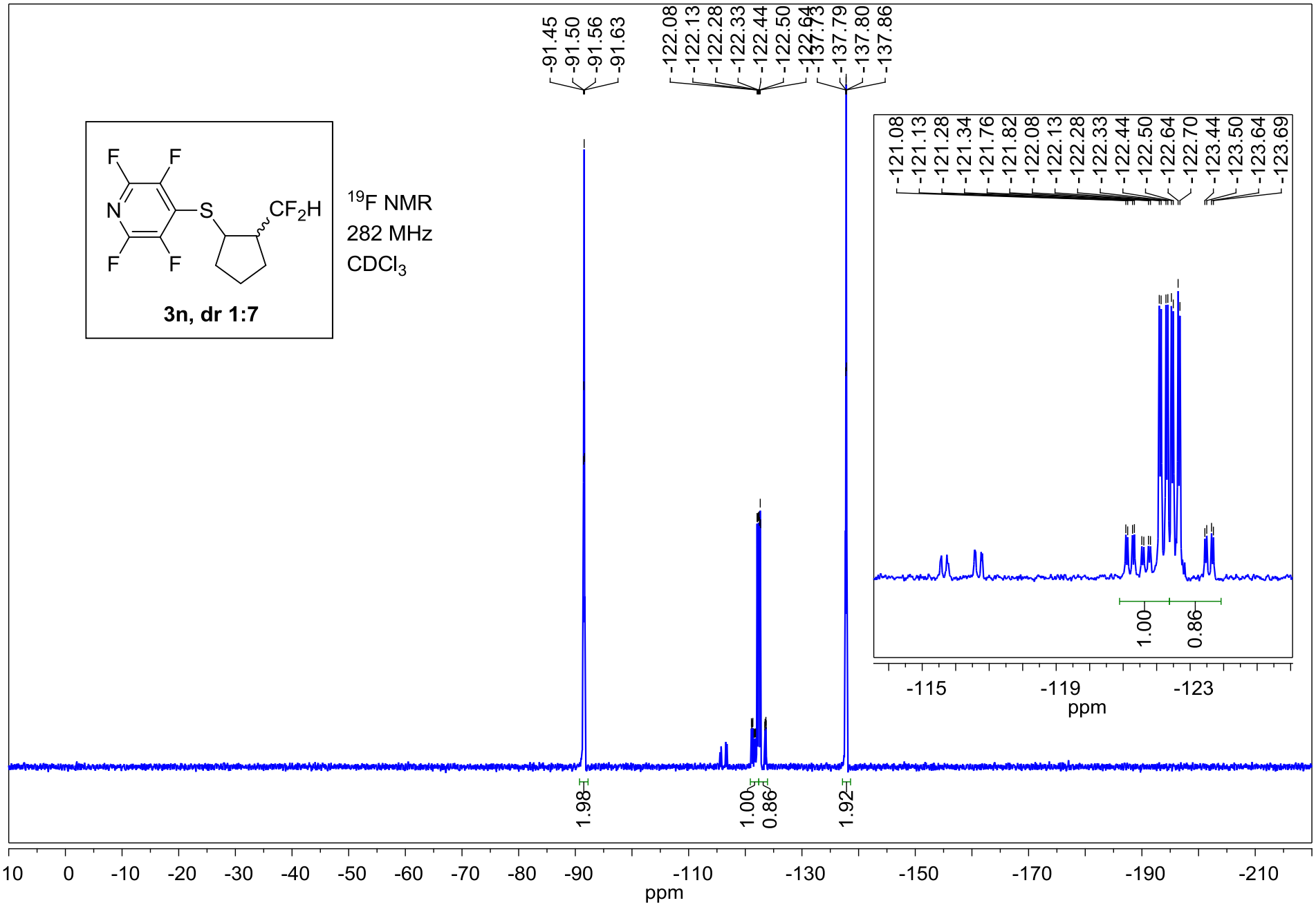
119.83
116.62
113.40
50.89
50.62
50.35
47.79
47.51
47.23
45.40
45.35
45.29
35.39
34.32
25.74
25.69
25.63
24.45
24.12
22.61
F
F
N
S
CF2H
F
F
3n, dr 1:7
13C{1H} NMR
75 MHz
CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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-122.28
-122.33
-122.44
-122.50
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-137.73
-137.79
-137.80
-137.86
F
F
N
S
CF2H
F
F
3n, dr 1:7
19F NMR
282 MHz
CDCl3
-121.08
-121.13
-121.28
-121.34
-121.76
-121.82
-122.08
-122.13
-122.28
-122.33
-122.44
-122.50
-122.64
-122.70
-123.44
-123.50
-123.64
-123.69
1.00
0.86
-115
-119
-123
ppm
1.98
1.00
0.86
1.92
10
0
-10
-20
-30
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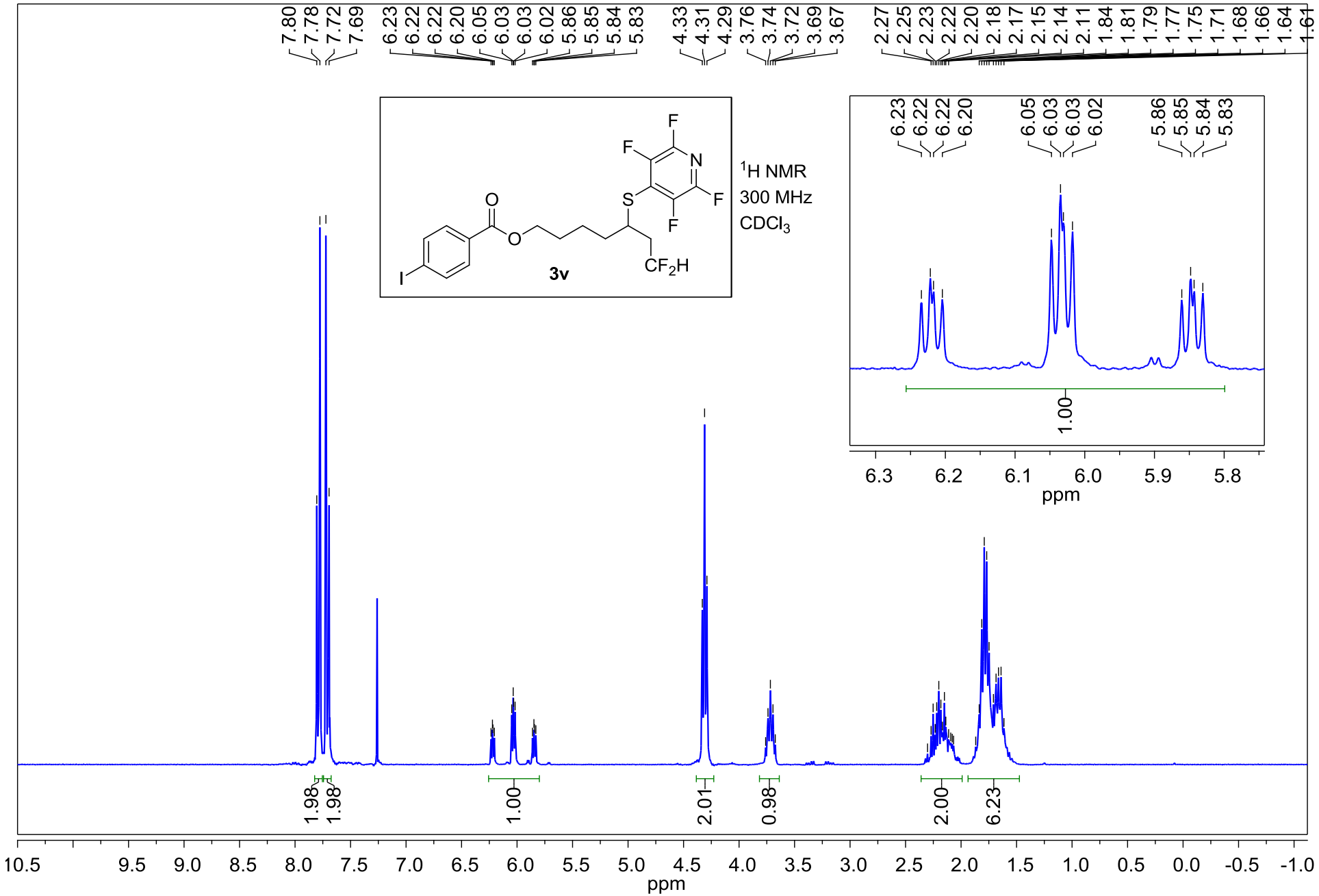
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm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7.78
7.72
7.69
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6.22
6.22
6.20
6.05
6.03
6.03
6.02
5.86
5.85
5.84
5.83
4.33
4.31
4.29
3.76
3.74
3.72
3.69
3.67
2.27
2.25
2.23
2.22
2.20
2.18
2.17
2.15
2.14
2.11
1.84
1.81
1.79
1.77
1.75
1.71
1.68
1.66
1.64
1.61
F
F
N
F
S
F
O
O
I
3v
CF2H
1H NMR
300 MHz
CDCl3
1.00
6.3
6.2
6.1
6.0
5.9
5.8
ppm
1.98
1.98
1.00
2.01
0.98
2.00
6.23
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
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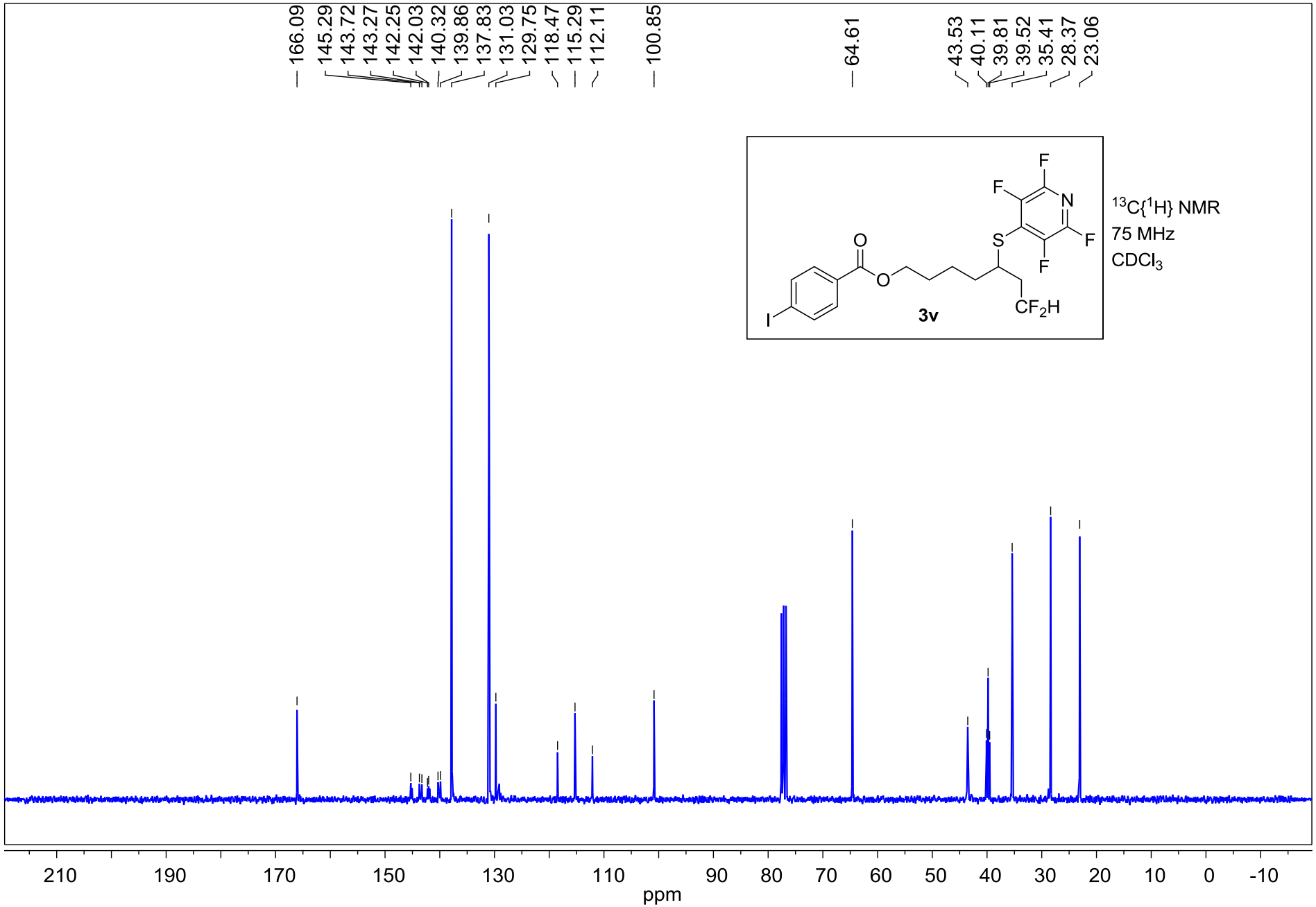
-0.5
-1.0
ppm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143.27
142.25
142.03
140.32
139.86
137.83
131.03
129.75
118.47
115.29
112.11
100.85
64.61
43.53
40.11
39.81
39.52
35.41
28.37
23.06
F
F
N
F
S
F
O
O
I
CF2H
3v
13C{1H} NMR
75 MHz
CDCl3
210
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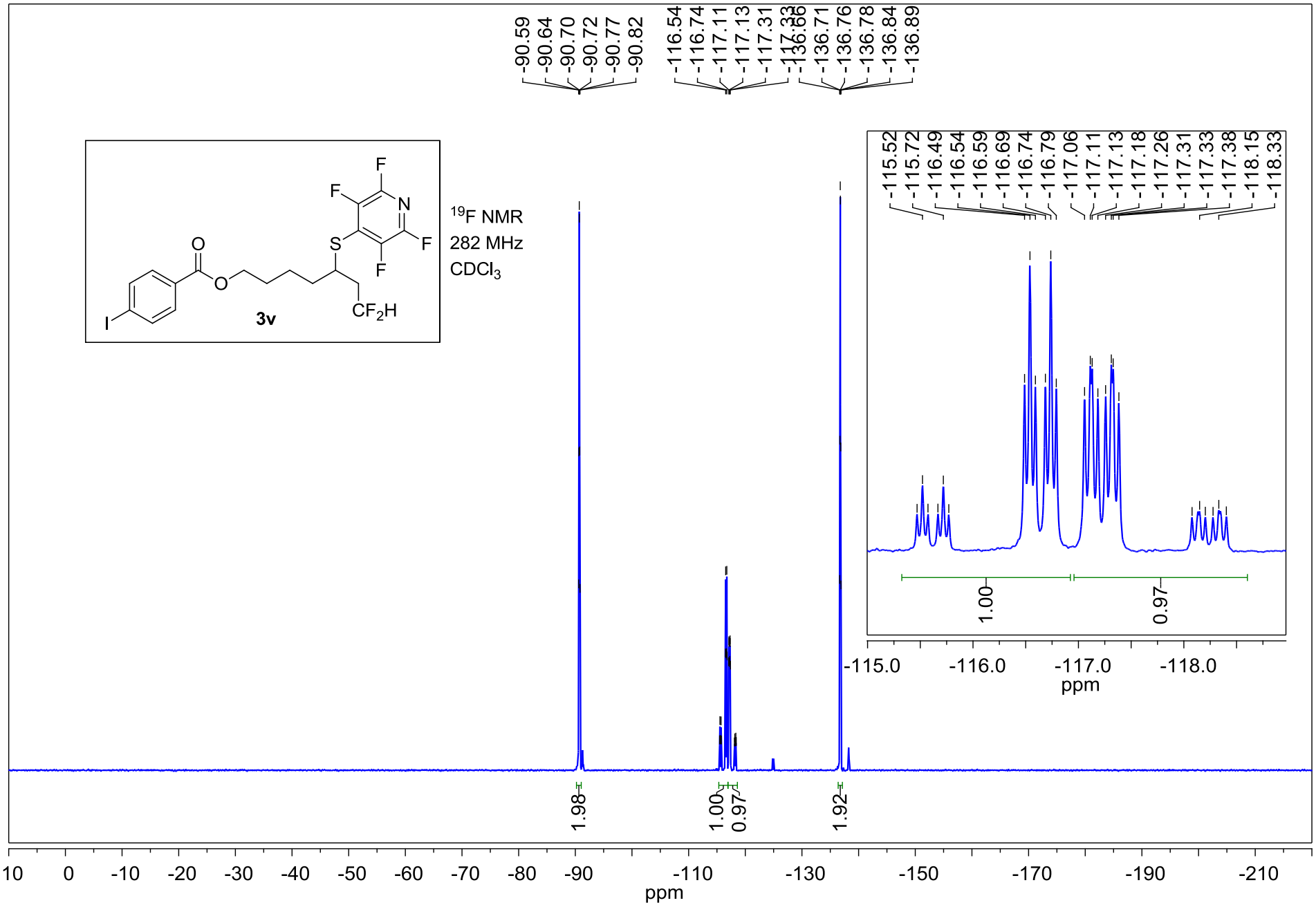
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm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-90.64
-90.70
-90.72
-90.77
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-116.54
-116.74
-117.11
-117.13
-117.31
-117.33
-136.71
-136.76
-136.78
-136.84
-136.89
F
F
N
S
F
F
O
O
I
3v
CF2H
19F NMR
282 MHz
CDCl3
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-116.59
-116.69
-116.74
-116.79
-117.06
-117.11
-117.13
-117.18
-117.26
-117.31
-117.33
-117.38
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-118.33
1.00
0.97
-115.0
-116.0
-117.0
-118.0
ppm
1.98
1.00
0.97
1.92
10
0
-10
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-30
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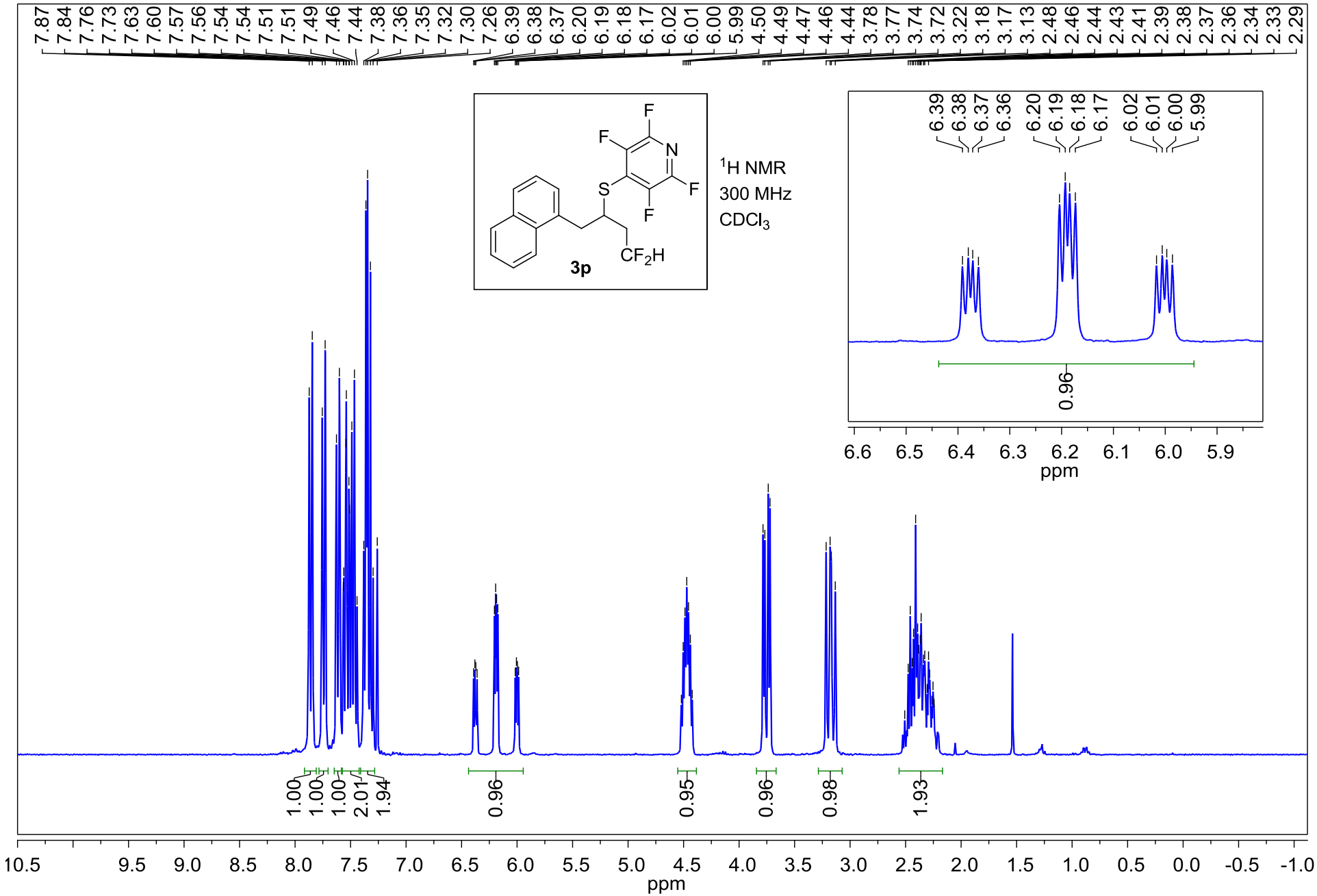
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm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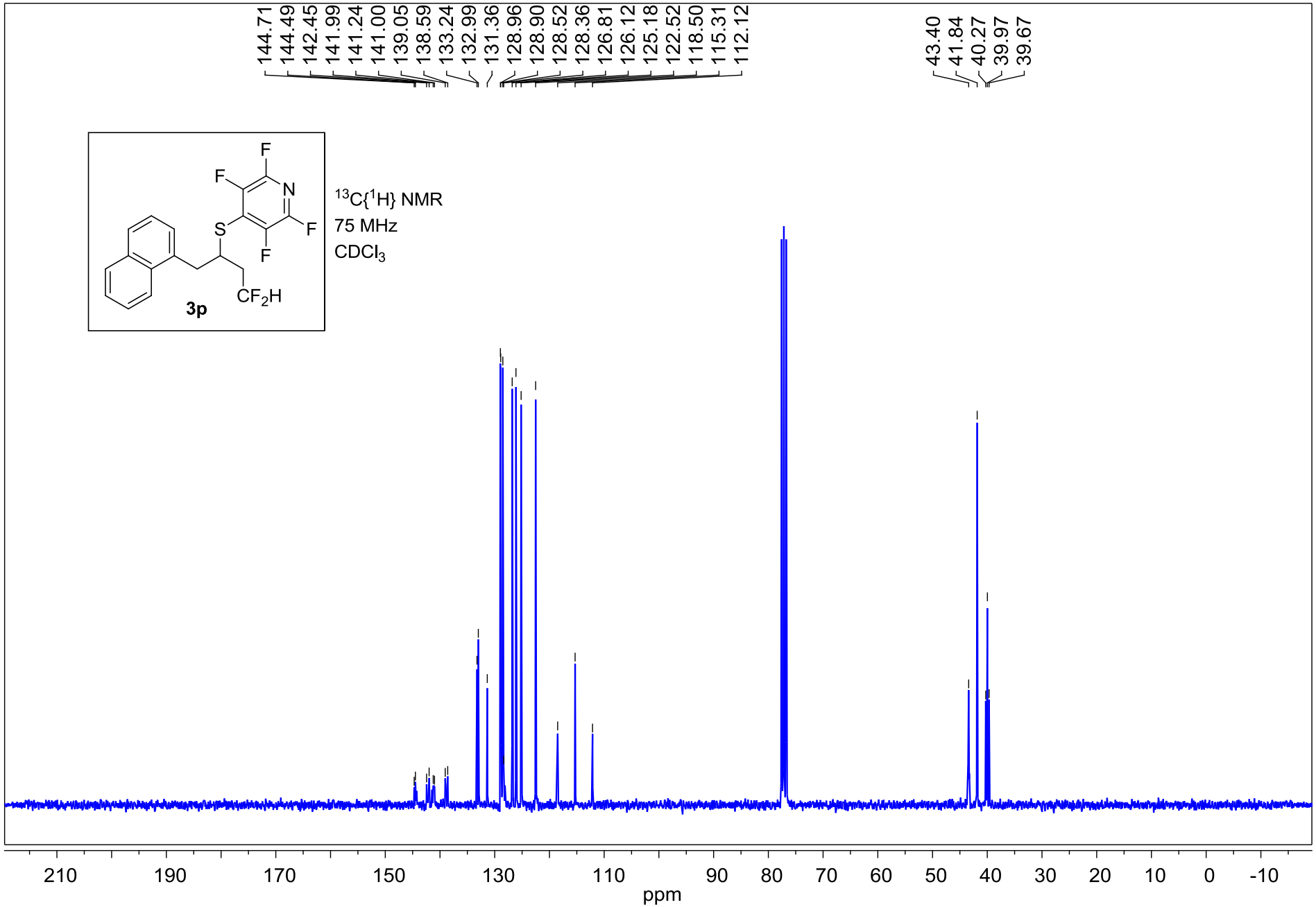
F
F
N
S
F
F
CF2H
3p
1H NMR
300 MHz
CDCl3
6.39 6.38 6.37 6.36 6.20 6.19 6.18 6.17 6.02 6.01 6.00 5.99
0.96
6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9
ppm
1.00 1.00 1.00 2.01 1.94 0.96 0.95 0.96 0.98 1.93
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm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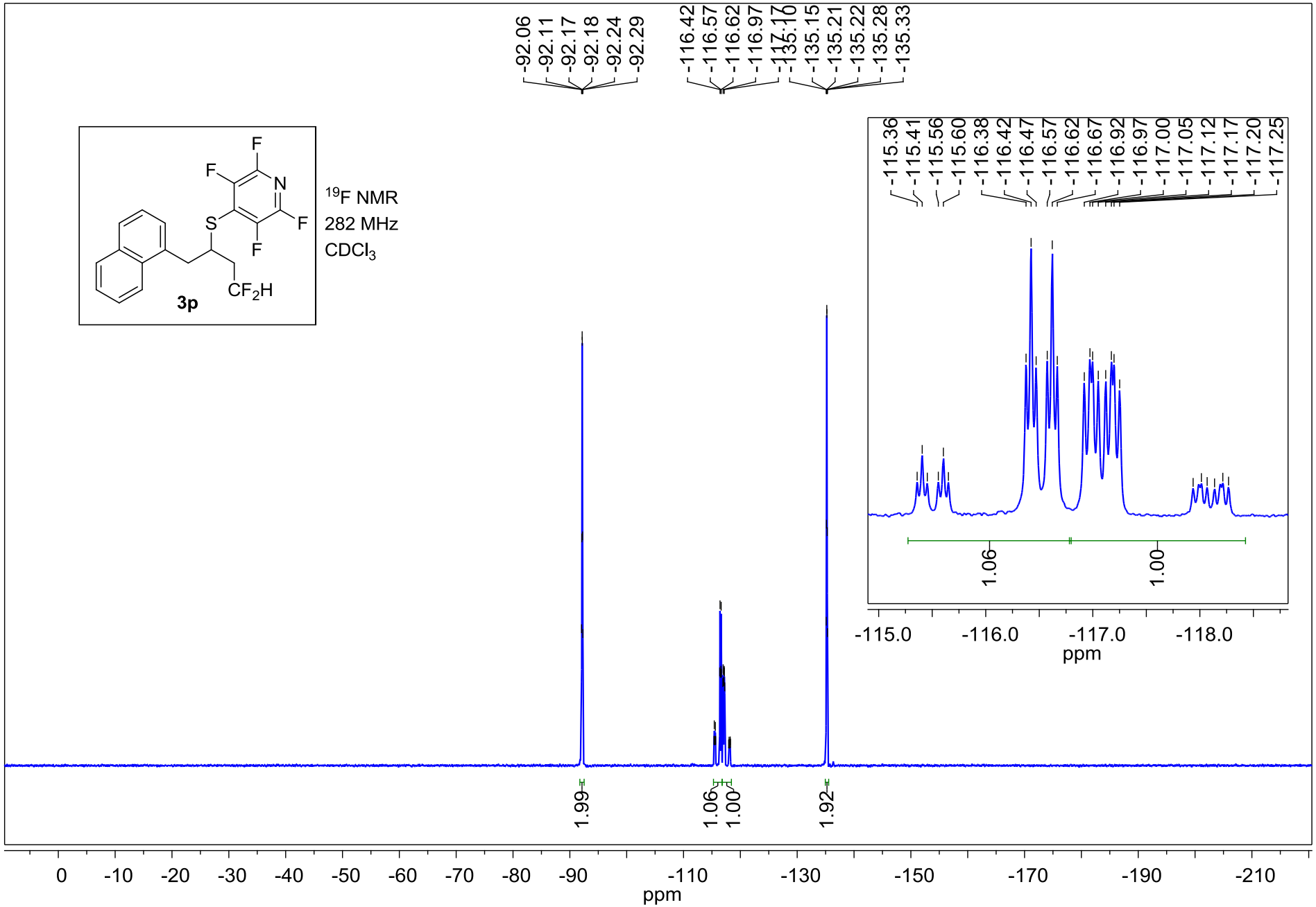
132.99
131.36
128.96
128.90
128.52
128.36
126.81
126.12
125.18
122.52
118.50
115.31
112.12
43.40
41.84
40.27
39.97
39.67
F
F
N
S
F
F
CF2H
3p
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm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-92.11
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-116.62
-116.97
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-135.10
-135.15
-135.21
-135.22
-135.28
-135.33
F
F
N
S
F
F
CF2H
3p
19F NMR
282 MHz
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-116.47
-116.57
-116.62
-116.67
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-116.97
-117.00
-117.05
-117.12
-117.17
-117.20
-117.25
1.06
1.00
-115.0
-116.0
-117.0
-118.0
ppm
1.99
1.06
1.00
1.92
0
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-30
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-50
-60
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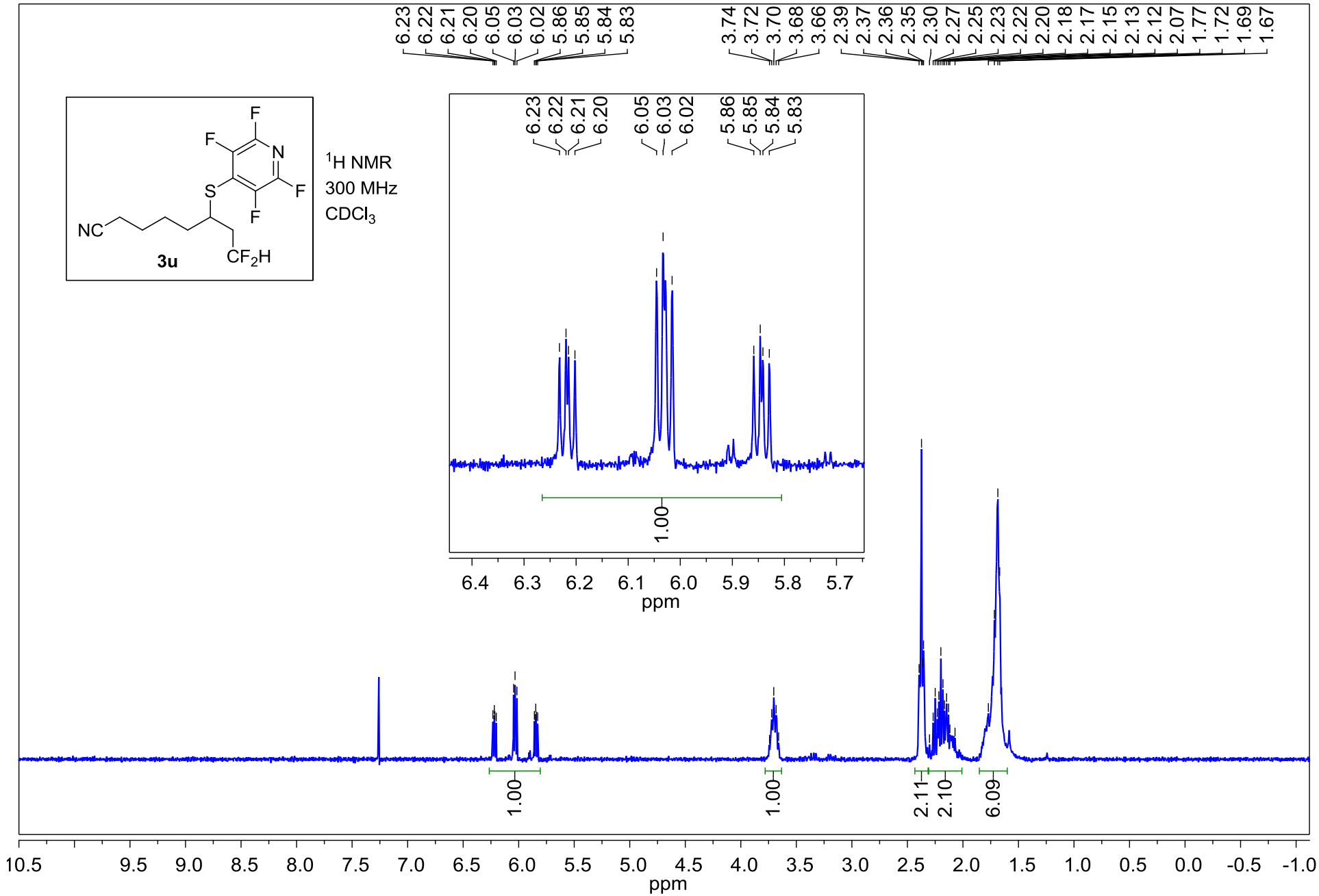
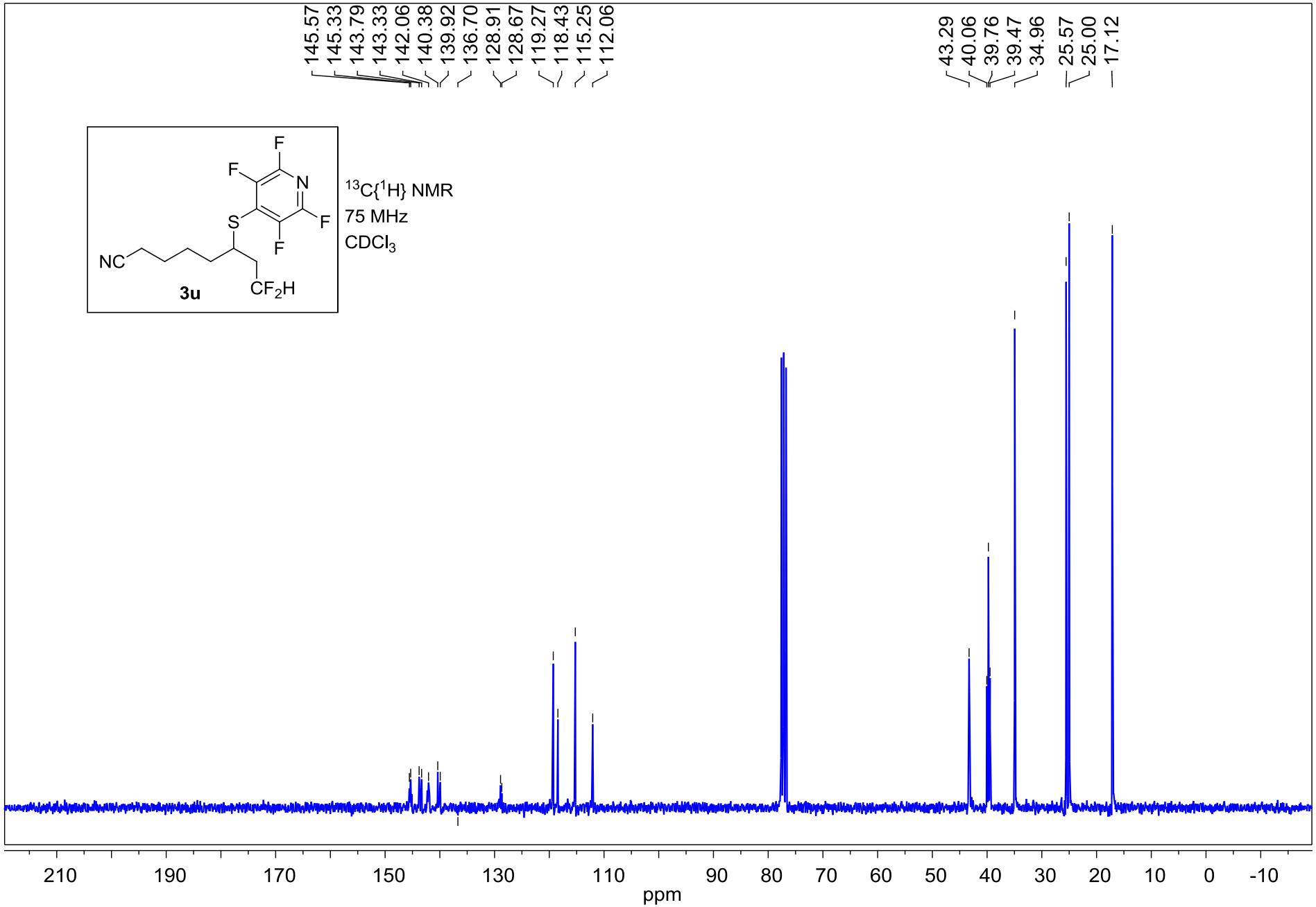
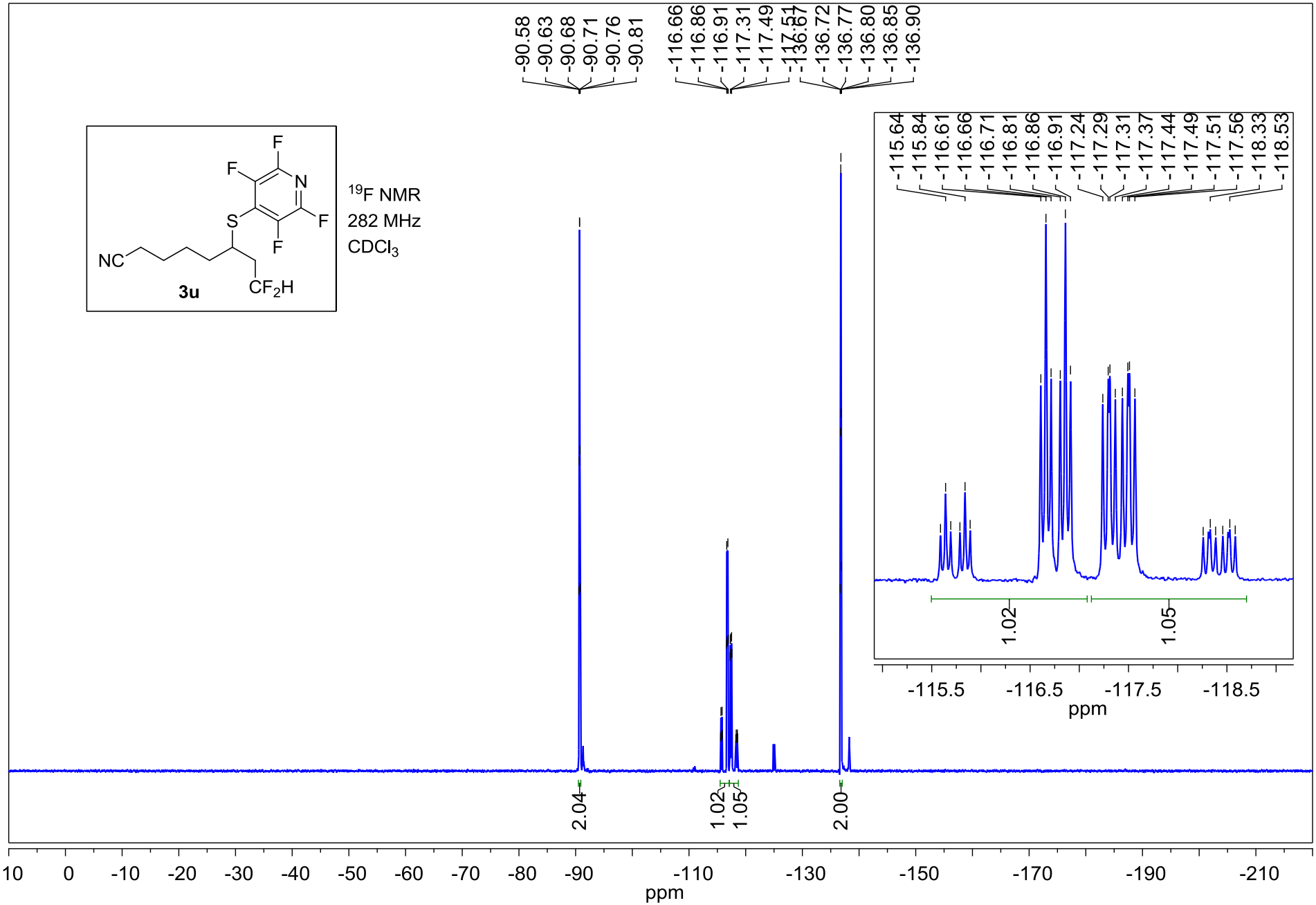
-80
-90
-110
-130
-150
-170
-190
-210
ppm


6.23 6.22 6.21 6.20 6.05 6.03 6.02 5.86 5.85 5.84 5.83
3.74 3.72 3.70 3.68 3.66 2.39 2.37 2.36 2.35 2.30 2.27 2.25 2.23 2.22 2.20 2.18 2.17 2.15 2.13 2.12 2.07 1.77 1.72 1.69 1.67
F
F
N
S
F
F
NC
CF2H
3u
1H NMR
300 MHz
CDCl3
1.00
6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7
ppm
1.00
1.00
2.11
2.10
6.09
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


145.57
145.33
143.79
143.33
142.06
140.38
139.92
136.70
128.91
128.67
119.27
118.43
115.25
112.06
43.29
40.06
39.76
39.47
34.96
25.57
25.00
17.12
F
F
N
S
F
F
NC
CF2H
3u
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm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-90.63
-90.68
-90.71
-90.76
-90.81
-116.66
-116.86
-116.91
-117.31
-117.49
-117.51
-136.72
-136.77
-136.80
-136.85
-136.90
F
F
N
S
F
F
NC
CF2H
3u
19F NMR
282 MHz
CDCl3
-115.64
-115.84
-116.61
-116.66
-116.71
-116.81
-116.86
-116.91
-117.24
-117.29
-117.31
-117.37
-117.44
-117.49
-117.51
-117.56
-118.33
-118.53
1.02
1.05
-115.5
-116.5
-117.5
-118.5
ppm
2.04
1.02
1.05
2.00
10
0
-10
-20
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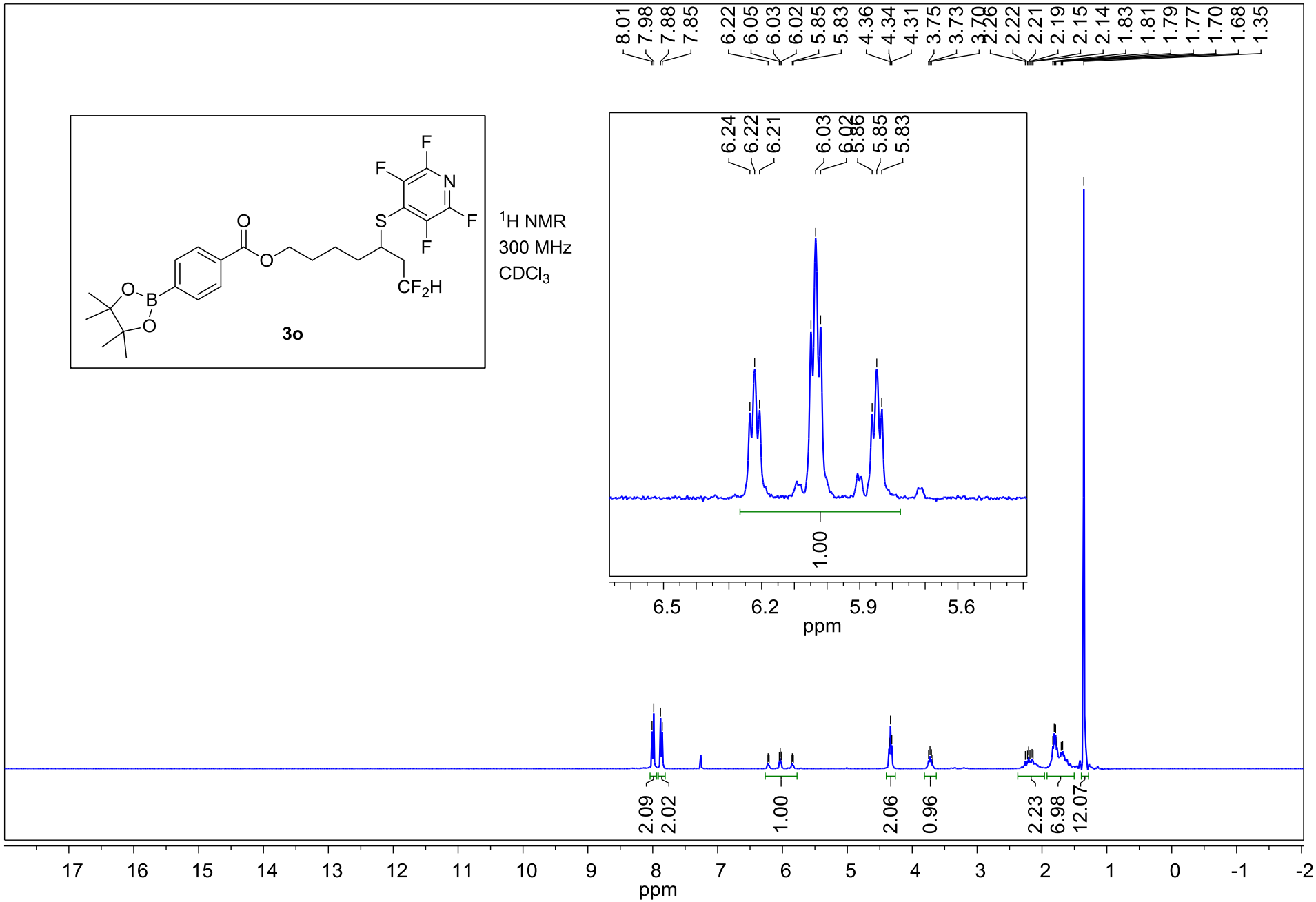
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm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7.98
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7.85
6.22
6.05
6.03
6.02
5.85
5.83
4.36
4.34
4.31
3.75
3.73
3.70
2.26
2.22
2.21
2.19
2.15
2.14
1.83
1.81
1.79
1.77
1.70
1.68
1.35
F
F
N
S
F
F
O
O
O
B
O
CF2H
3o
1H NMR
300 MHz
CDCl3
6.24
6.22
6.21
6.03
6.02
5.86
5.85
5.83
1.00
6.5
6.2
5.9
5.6
ppm
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2.02
1.00
2.06
0.96
2.23
6.98
12.07
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
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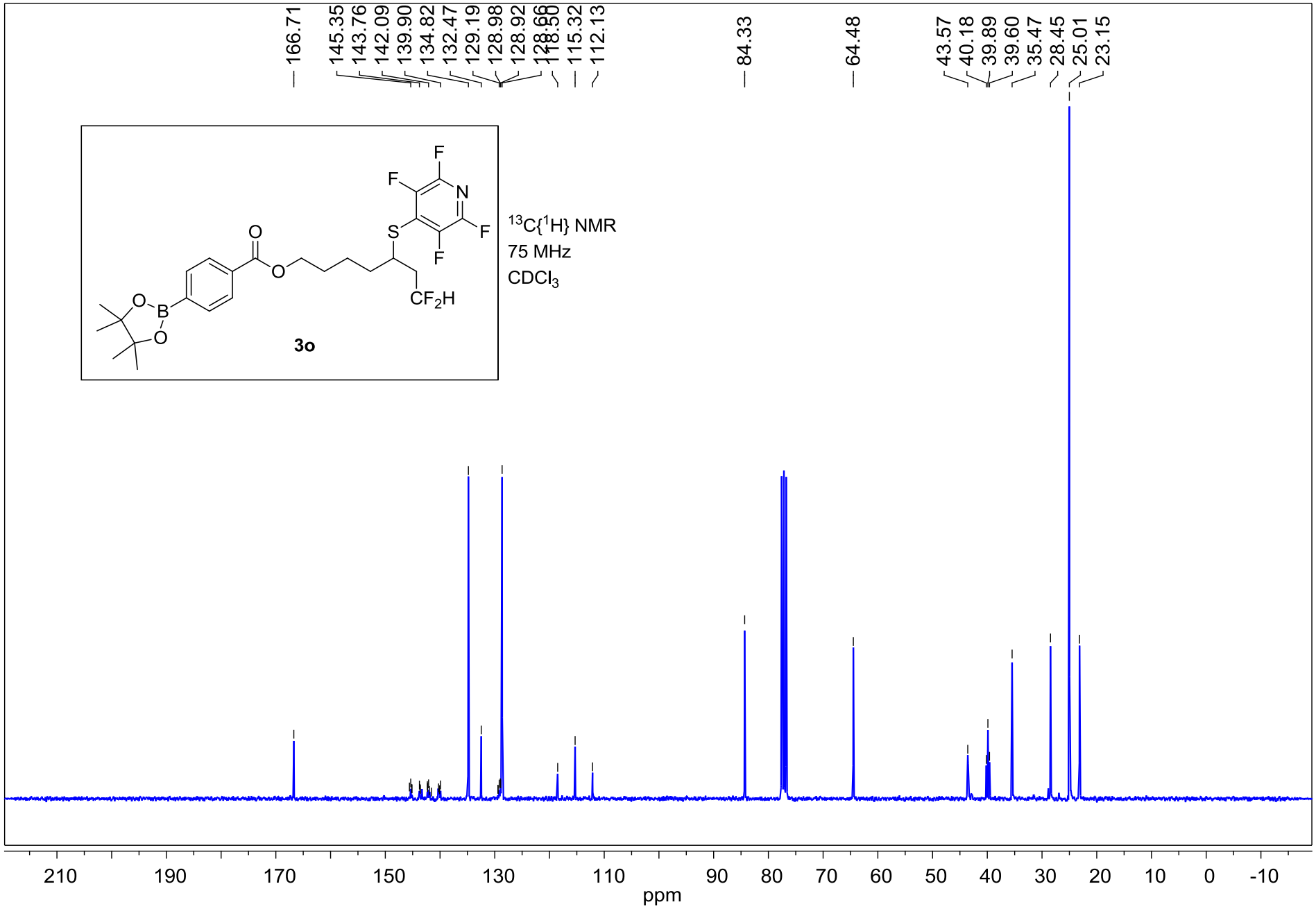
-2
ppm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145.35
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142.09
139.90
134.82
132.47
129.19
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128.92
128.66
118.50
115.32
112.13
84.33
64.48
43.57
40.18
39.89
39.60
35.47
28.45
25.01
23.15
F
F
N
F
S
F
O
O
O
B
O
CF2H
3o
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
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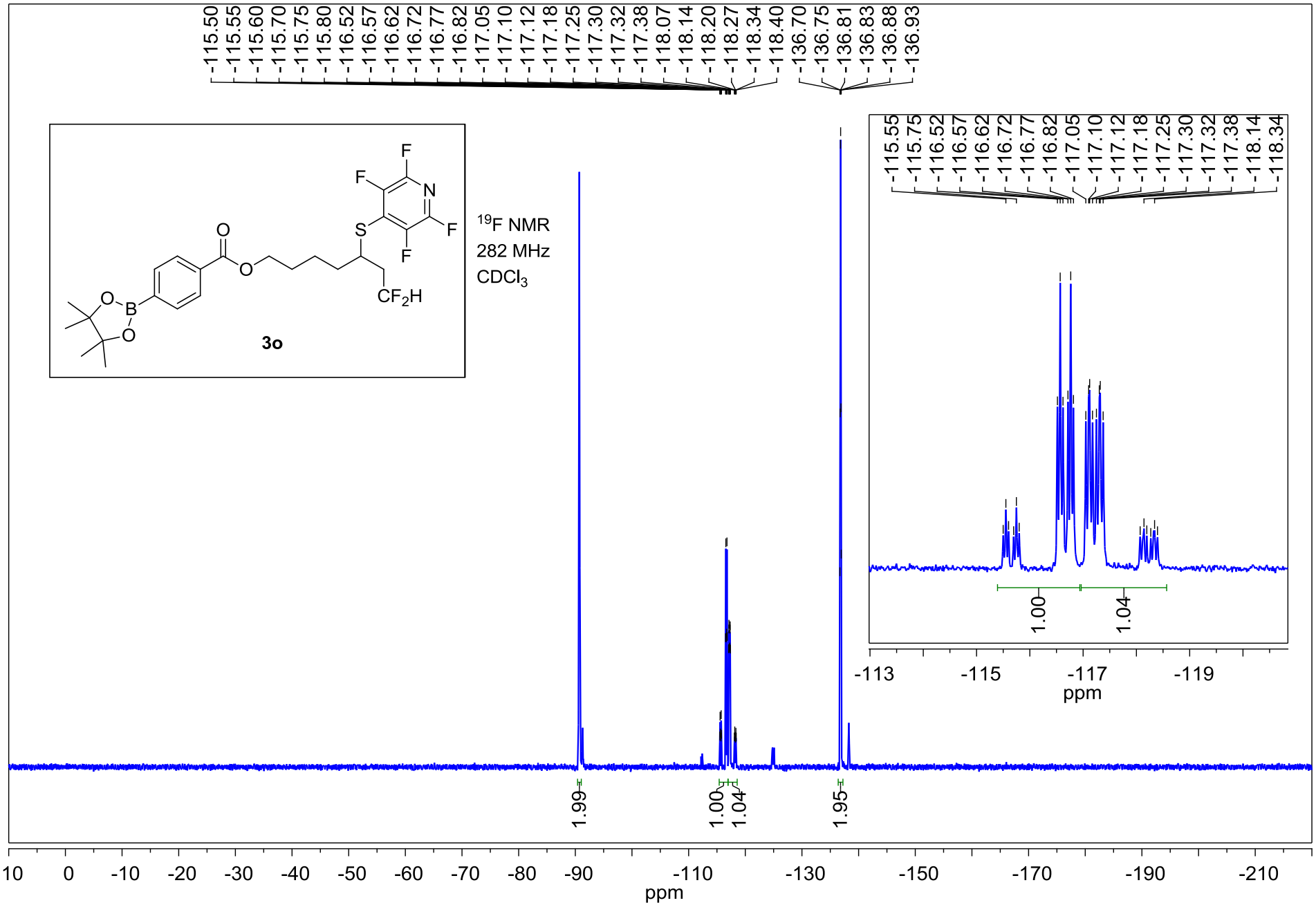
50
40
30
20
10
0
-10
ppm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-115.55
-115.60
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-116.52
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-116.62
-116.72
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-116.82
-117.05
-117.10
-117.12
-117.18
-117.25
-117.30
-117.32
-117.38
-118.07
-118.14
-118.20
-118.27
-118.34
-118.40
-136.70
-136.75
-136.81
-136.83
-136.88
-136.93
F
F
N
F
S
F
O
O
O
B
O
CF2H
3o
19F NMR
282 MHz
CDCl3
1.99
1.00
1.04
1.95
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm
-115.55
-115.75
-116.52
-116.57
-116.62
-116.72
-116.77
-116.82
-117.05
-117.10
-117.12
-117.18
-117.25
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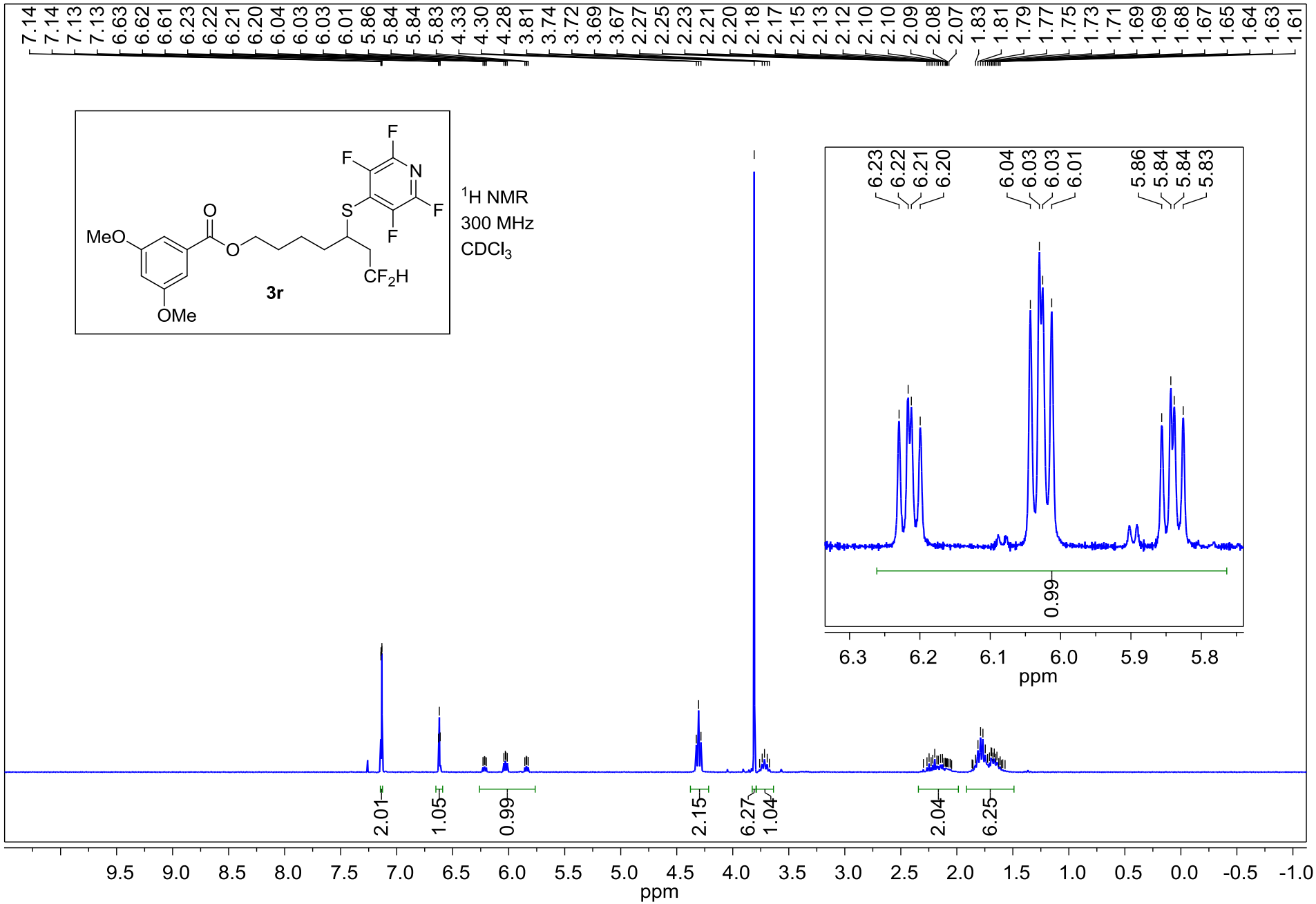
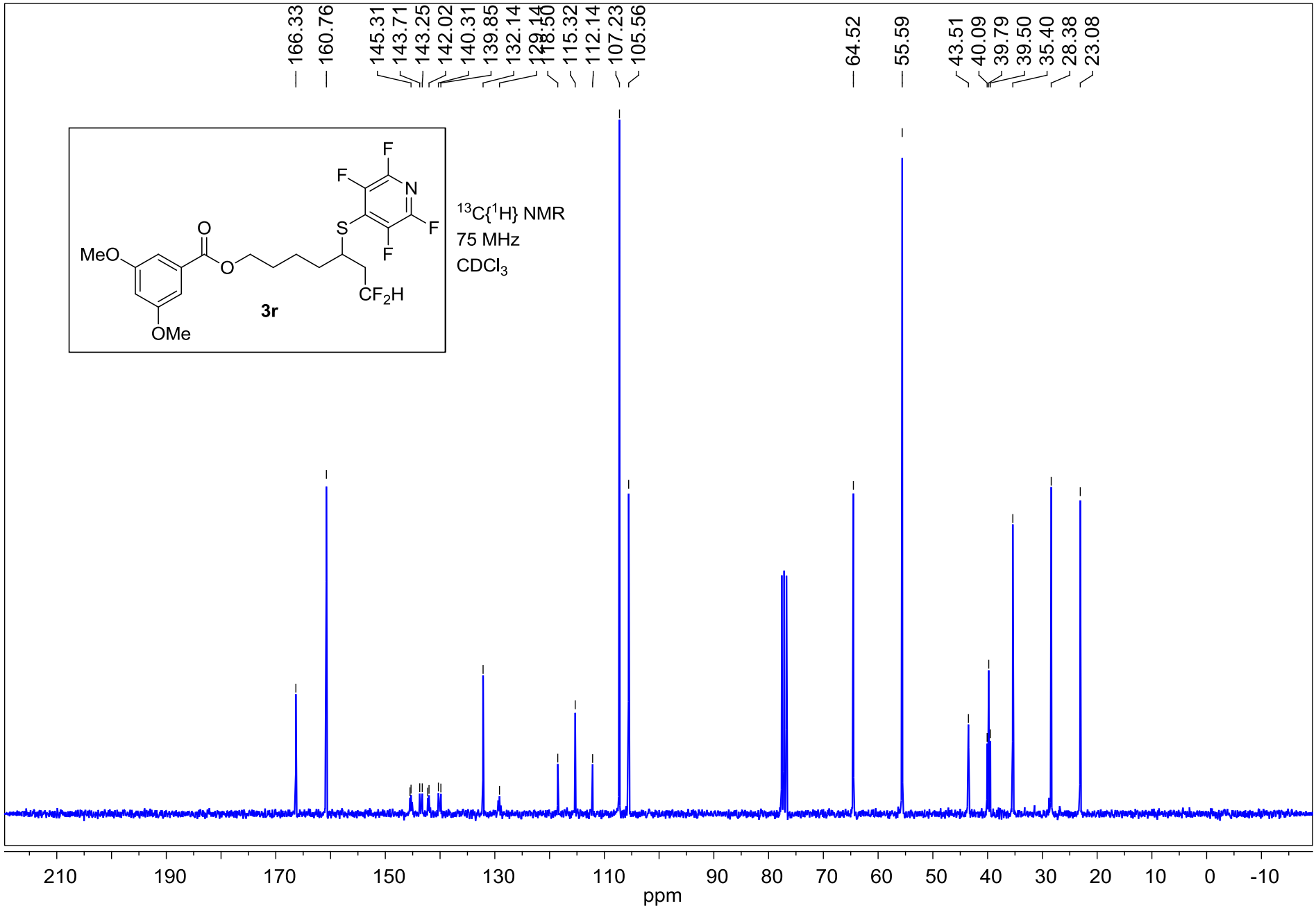
-118.14
-118.34
1.00
1.04
-113
-115
-117
-119
ppm


7.14 7.14 7.13 7.13 6.63 6.62 6.61 6.23 6.22 6.21 6.20 6.04 6.03 6.03 6.01 5.86 5.84 5.84 5.83 4.33 4.30 4.28 3.81 3.74 3.72 3.69 3.67 2.27 2.25 2.23 2.21 2.20 2.18 2.17 2.15 2.13 2.12 2.10 2.10 2.09 2.08 2.07 1.83 1.81 1.79 1.77 1.75 1.73 1.71 1.69 1.69 1.68 1.67 1.65 1.64 1.63 1.61
F
F
N
S
F
F
O
MeO
O
CF2H
OMe
3r
1H NMR
300 MHz
CDCl3
6.23 6.22 6.21 6.20 6.04 6.03 6.03 6.01 5.86 5.84 5.84 5.83
0.99
6.3 6.2 6.1 6.0 5.9 5.8
ppm
2.01 1.05 0.99 2.15 6.27 1.04 2.04 6.25
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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160.76
145.31
143.71
143.25
142.02
140.31
139.85
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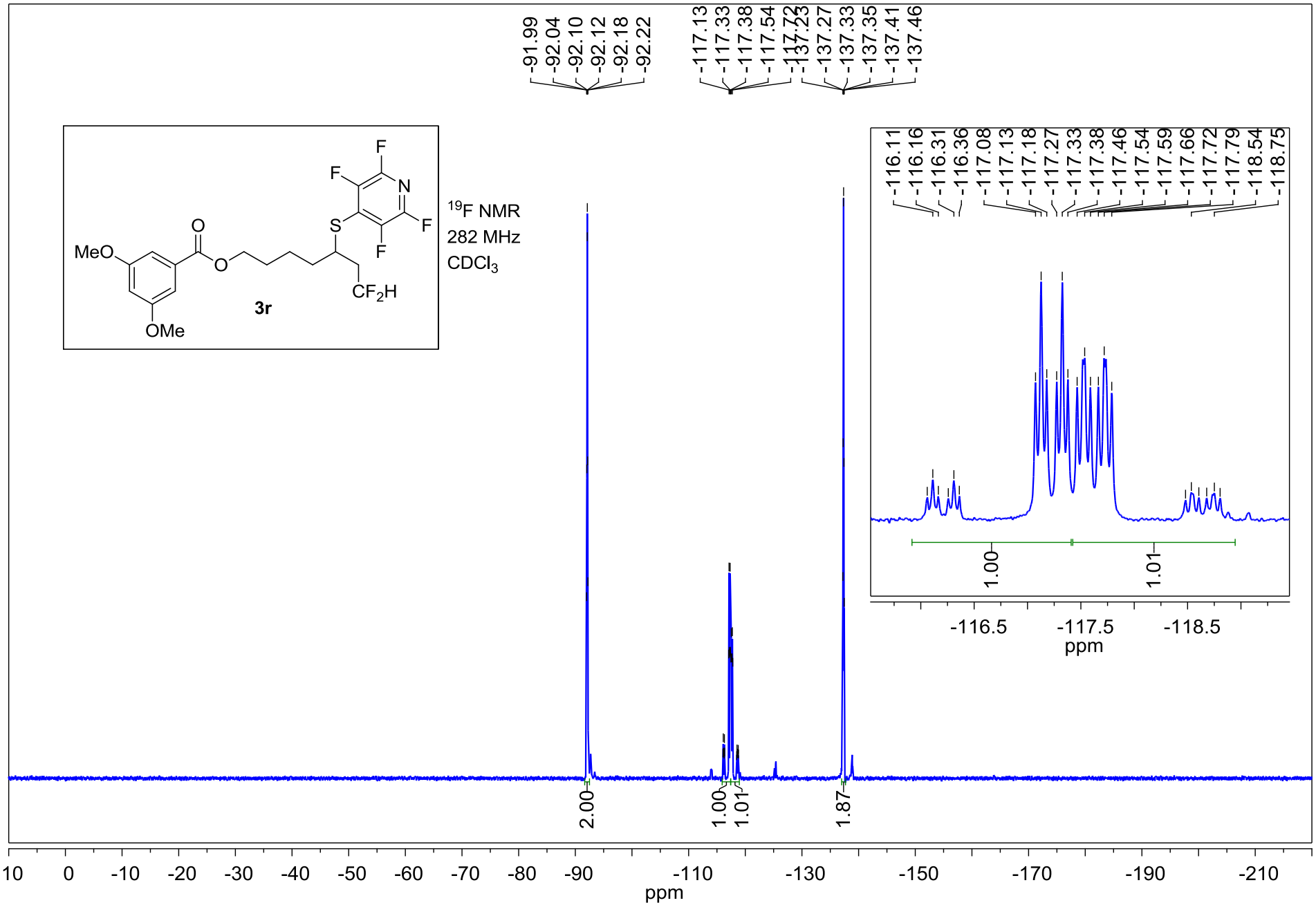
129.14
128.50
115.32
112.14
107.23
105.56
64.52
55.59
43.51
40.09
39.79
39.50
35.40
28.38
23.08
F
F
N
F
S
F
MeO
O
O
CF2H
OMe
3r
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm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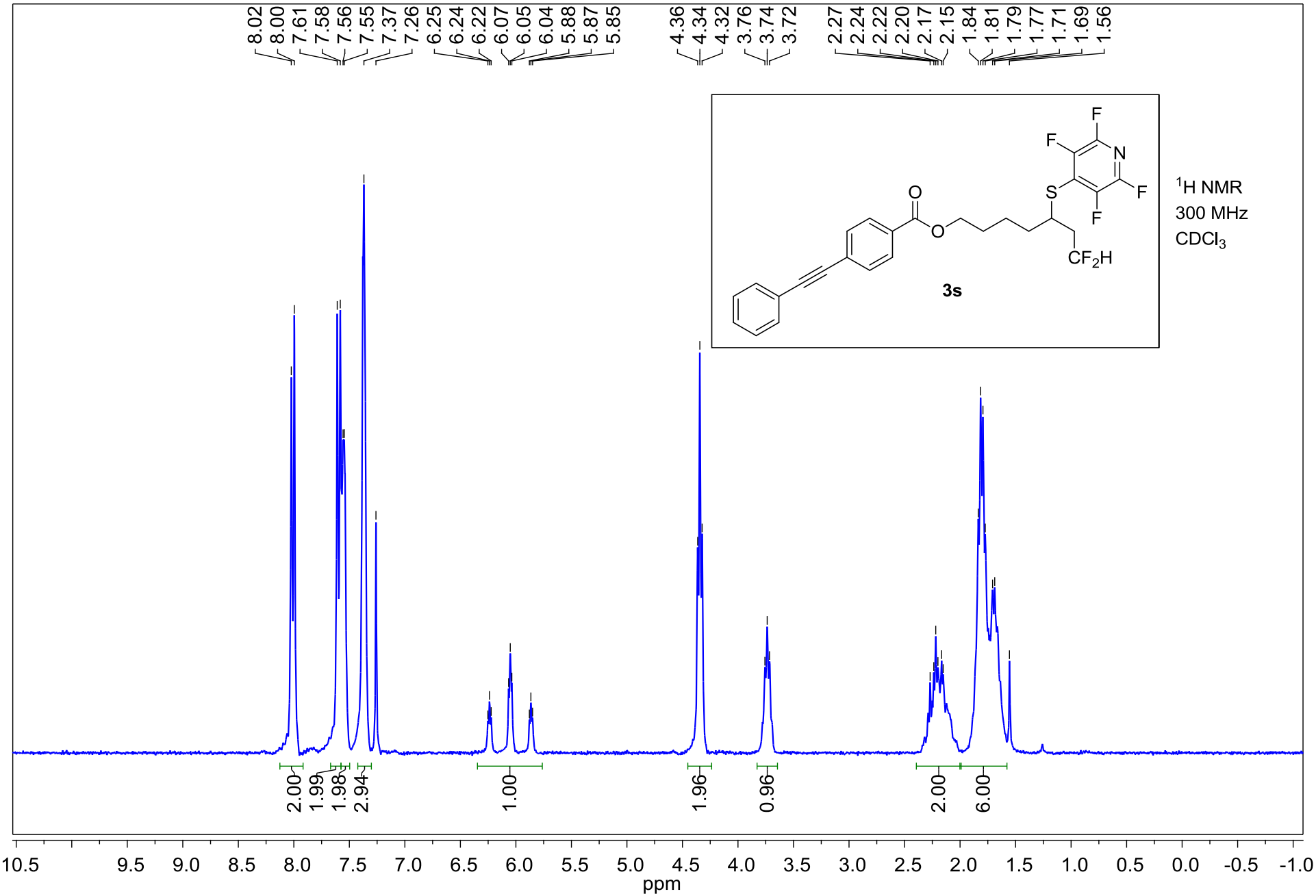
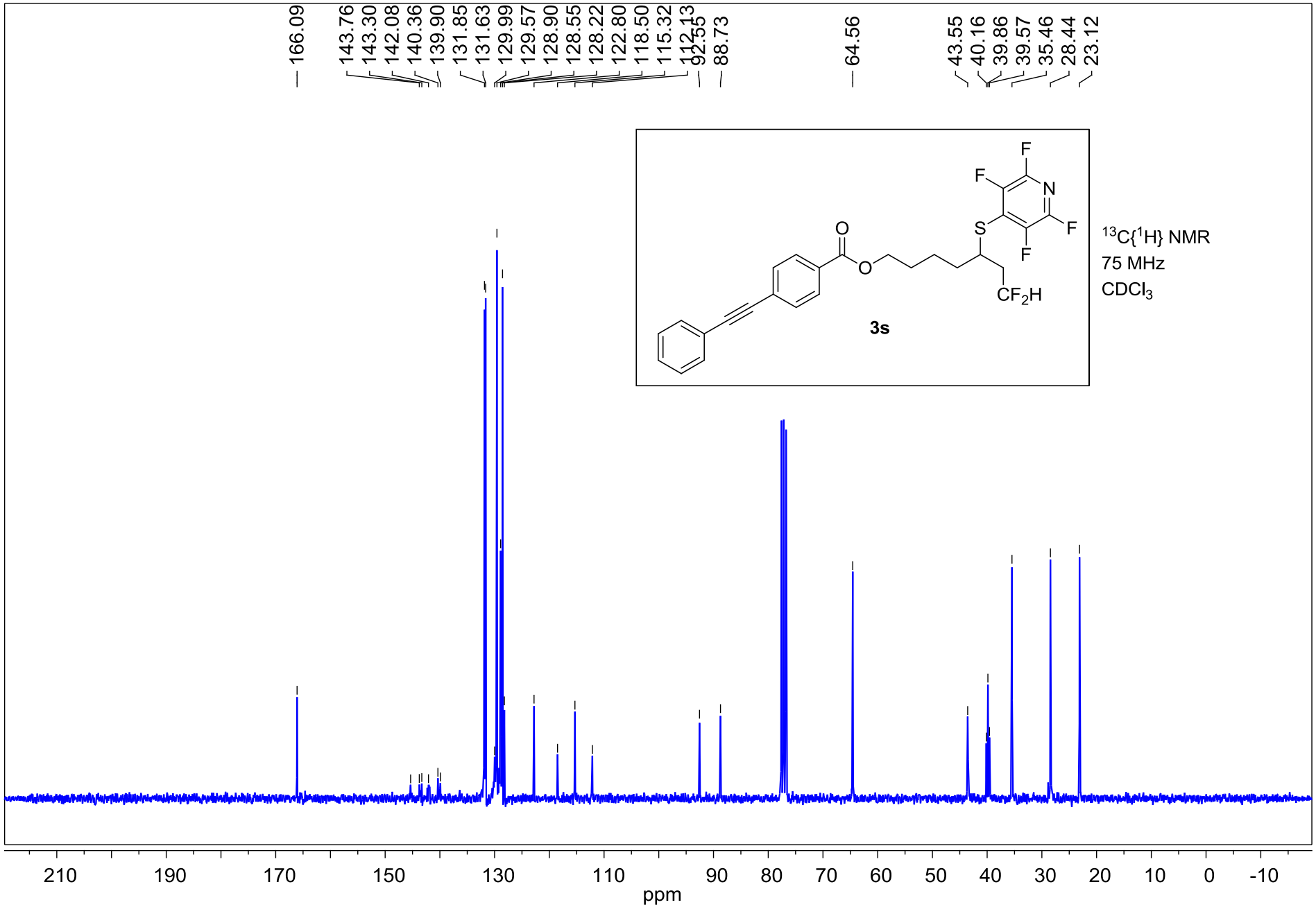
-92.04
-92.10
-92.12
-92.18
-92.22
-117.13
-117.33
-117.38
-117.54
-137.27
-137.33
-137.35
-137.41
-137.46
F
F
N
F
S
F
MeO
O
O
CF2H
OMe
3r
19F NMR
282 MHz
CDCl3
-116.11
-116.16
-116.31
-116.36
-117.08
-117.13
-117.18
-117.27
-117.33
-117.38
-117.46
-117.54
-117.59
-117.66
-117.72
-117.79
-118.54
-118.75
1.00
1.01
-116.5
-117.5
-118.5
ppm
2.00
1.00
1.01
1.87
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm


8.02
8.00
7.61
7.58
7.56
7.55
7.37
7.26
6.25
6.24
6.22
6.07
6.05
6.04
5.88
5.87
5.85
4.36
4.34
4.32
3.76
3.74
3.72
2.27
2.24
2.22
2.20
2.17
2.15
1.84
1.81
1.79
1.77
1.71
1.69
1.56
F
F
N
F
S
F
O
O
CF2H
3s
1H NMR
300 MHz
CDCl3
2.00
1.99
1.98
2.94
1.00
1.96
0.96
2.00
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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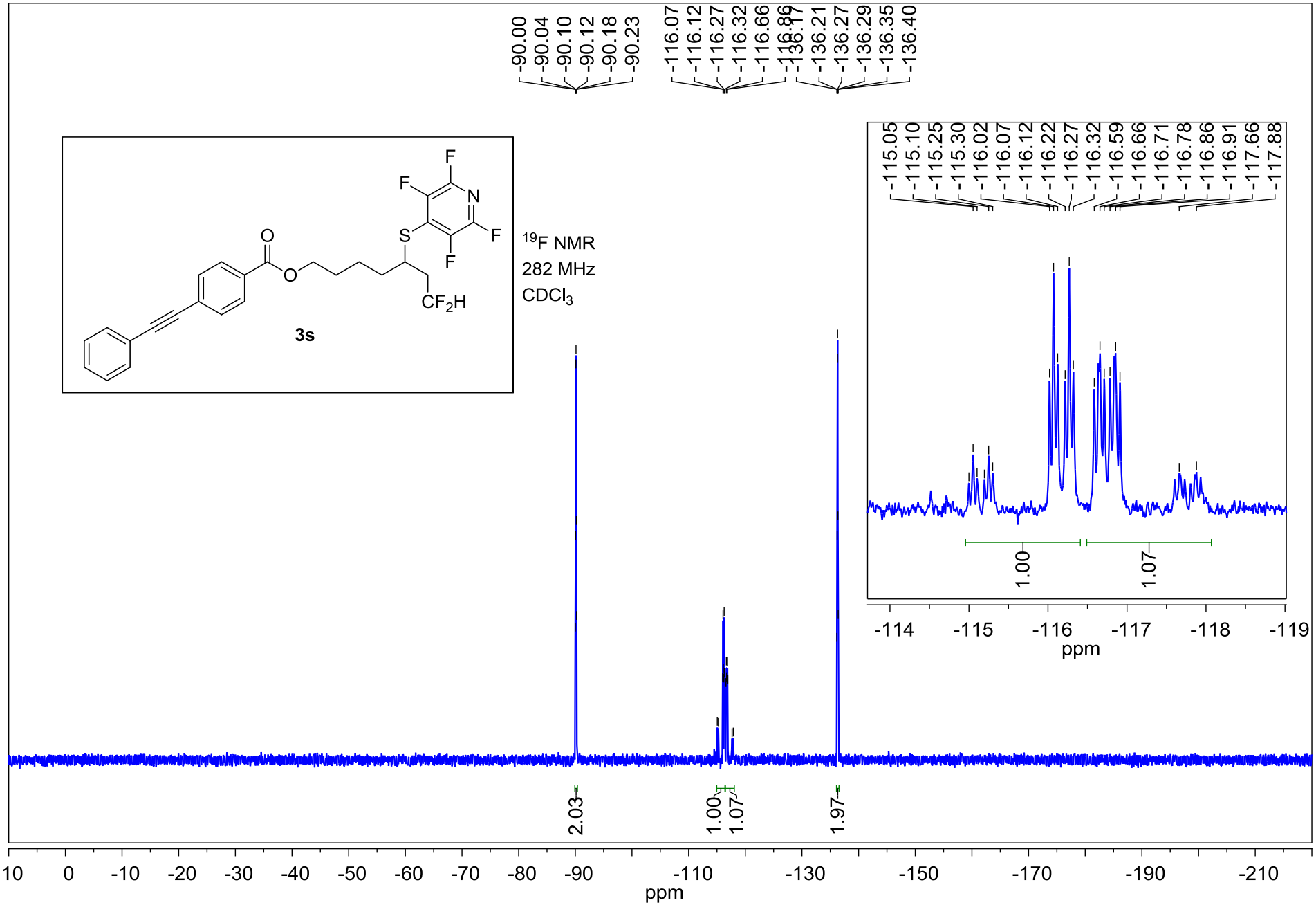
143.76
143.30
142.08
140.36
139.90
131.85
131.63
129.99
129.57
128.90
128.55
128.22
122.80
118.50
115.32
112.13
92.55
88.73
64.56
43.55
40.16
39.86
39.57
35.46
28.44
23.12
F
F
N
F
S
F
O
O
CF2H
3s
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm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-90.04
-90.10
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-90.18
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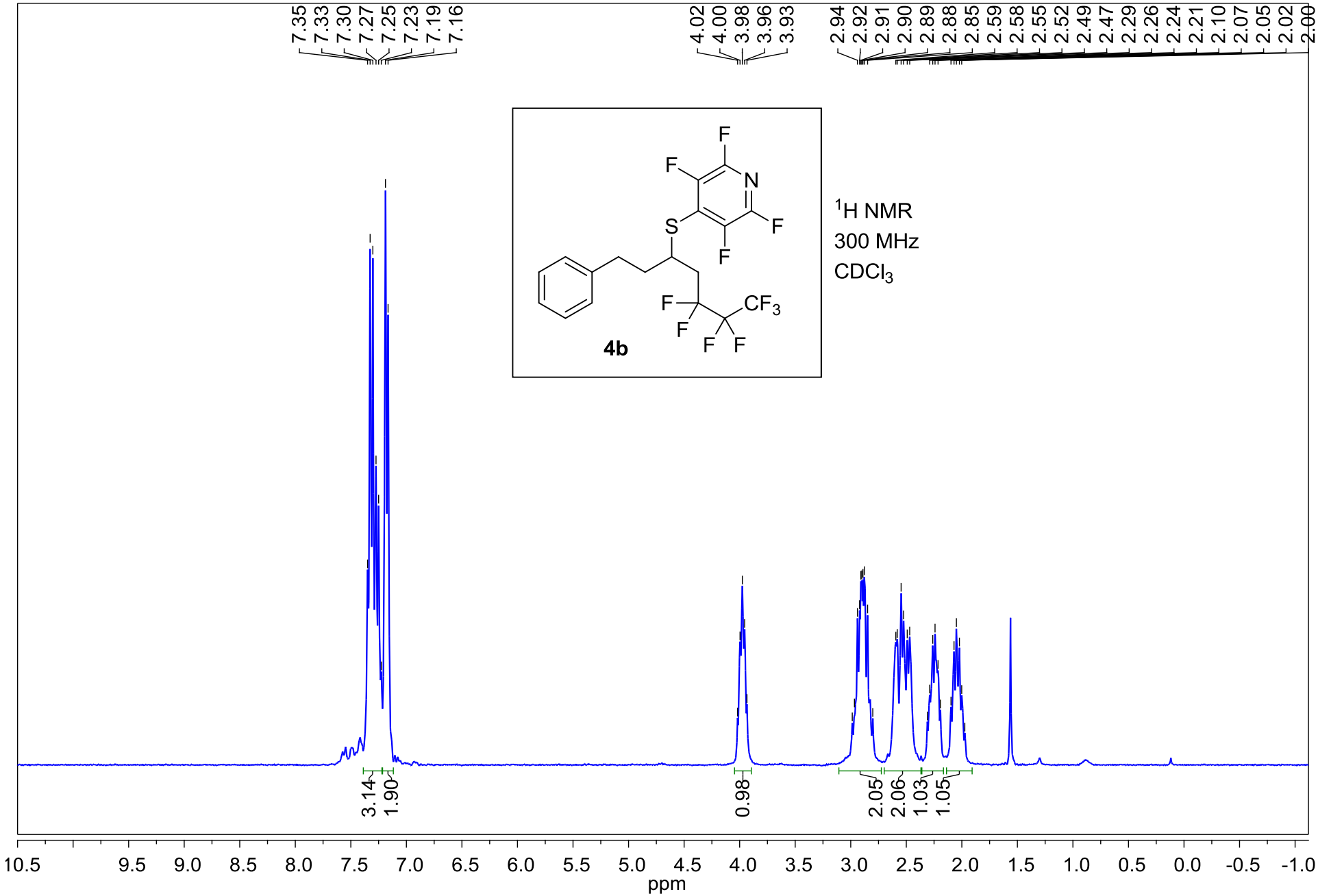
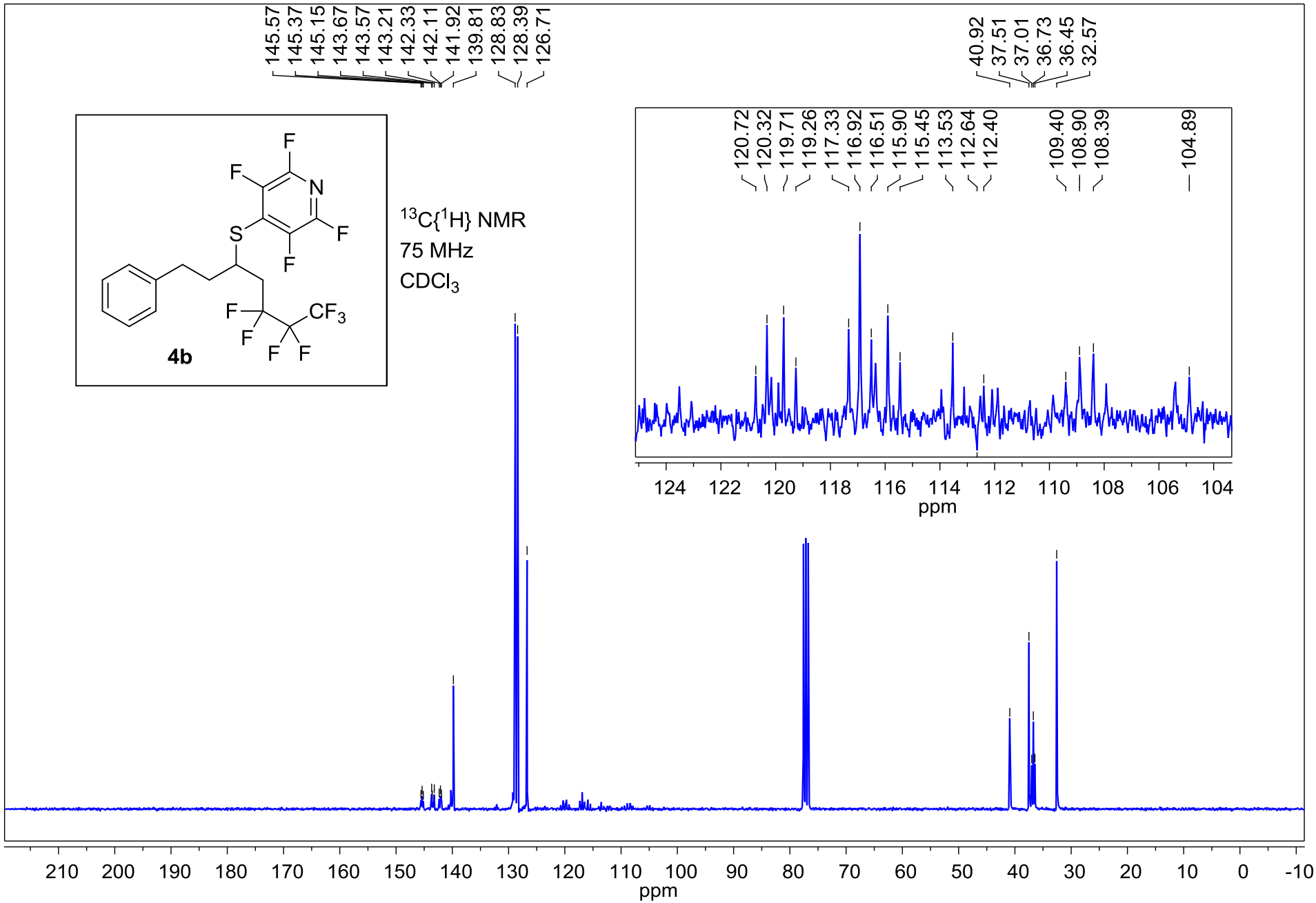
-116.07
-116.12
-116.27
-116.32
-116.66
-116.86
-116.97
-136.21
-136.27
-136.29
-136.35
-136.40
F
F
N
F
S
F
O
O
CF2H
3s
19F NMR
282 MHz
CDCl3
-115.05
-115.10
-115.25
-115.30
-116.02
-116.07
-116.12
-116.22
-116.27
-116.32
-116.59
-116.66
-116.71
-116.78
-116.86
-116.91
-117.66
-117.88
1.00
1.07
-114
-115
-116
-117
-118
-119
ppm
2.03
1.00
1.07
1.97
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm


7.35
7.33
7.30
7.27
7.25
7.23
7.19
7.16
4.02
4.00
3.98
3.96
3.93
2.94
2.92
2.91
2.90
2.89
2.88
2.85
2.59
2.58
2.55
2.52
2.49
2.47
2.29
2.26
2.24
2.21
2.10
2.07
2.05
2.02
2.00
F
F
N
S
F
F
F
CF3
F
F
F
4b
1H NMR
300 MHz
CDCl3
3.14
1.90
0.98
2.05
2.06
1.03
1.05
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


145.57
145.37
145.15
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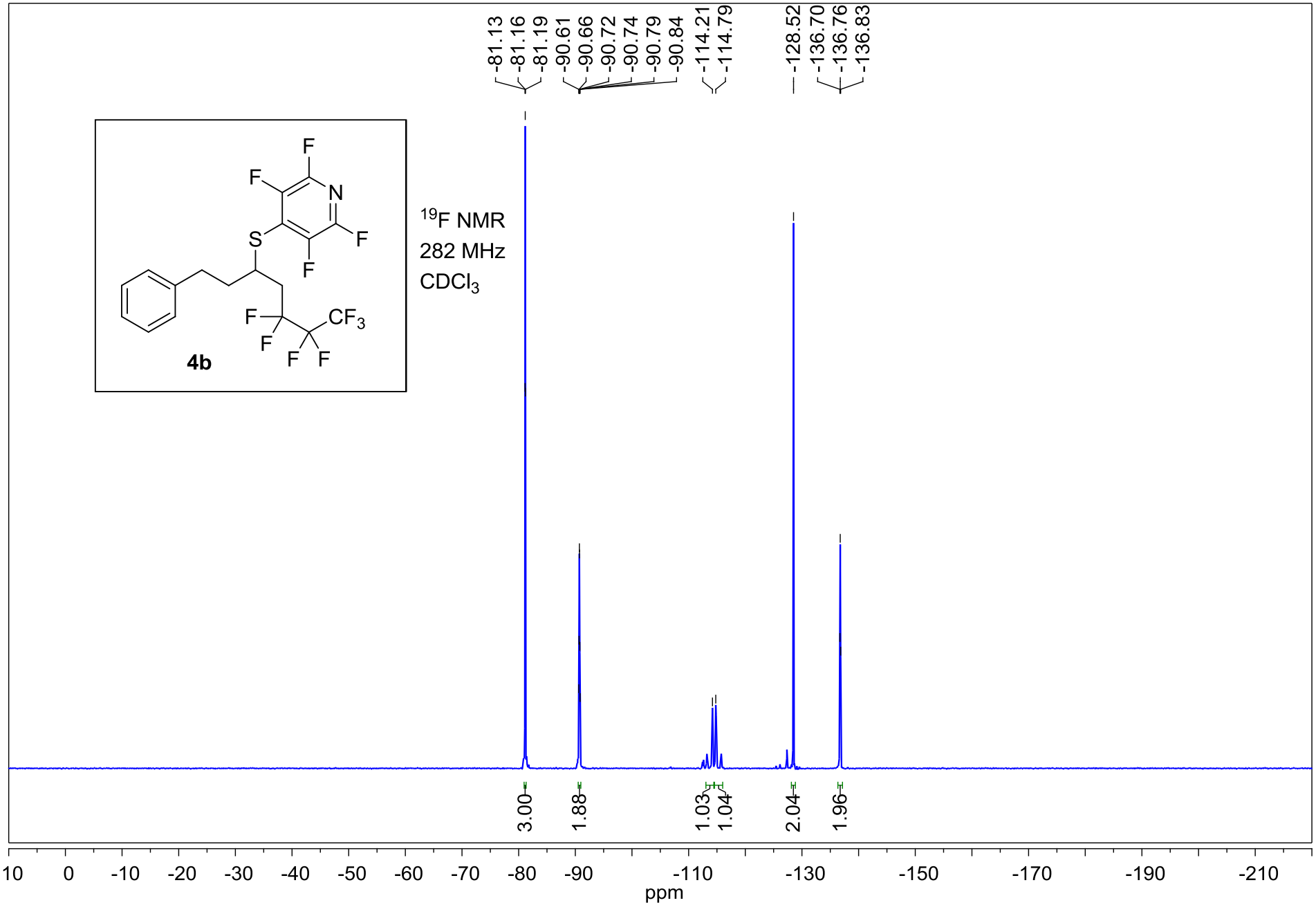
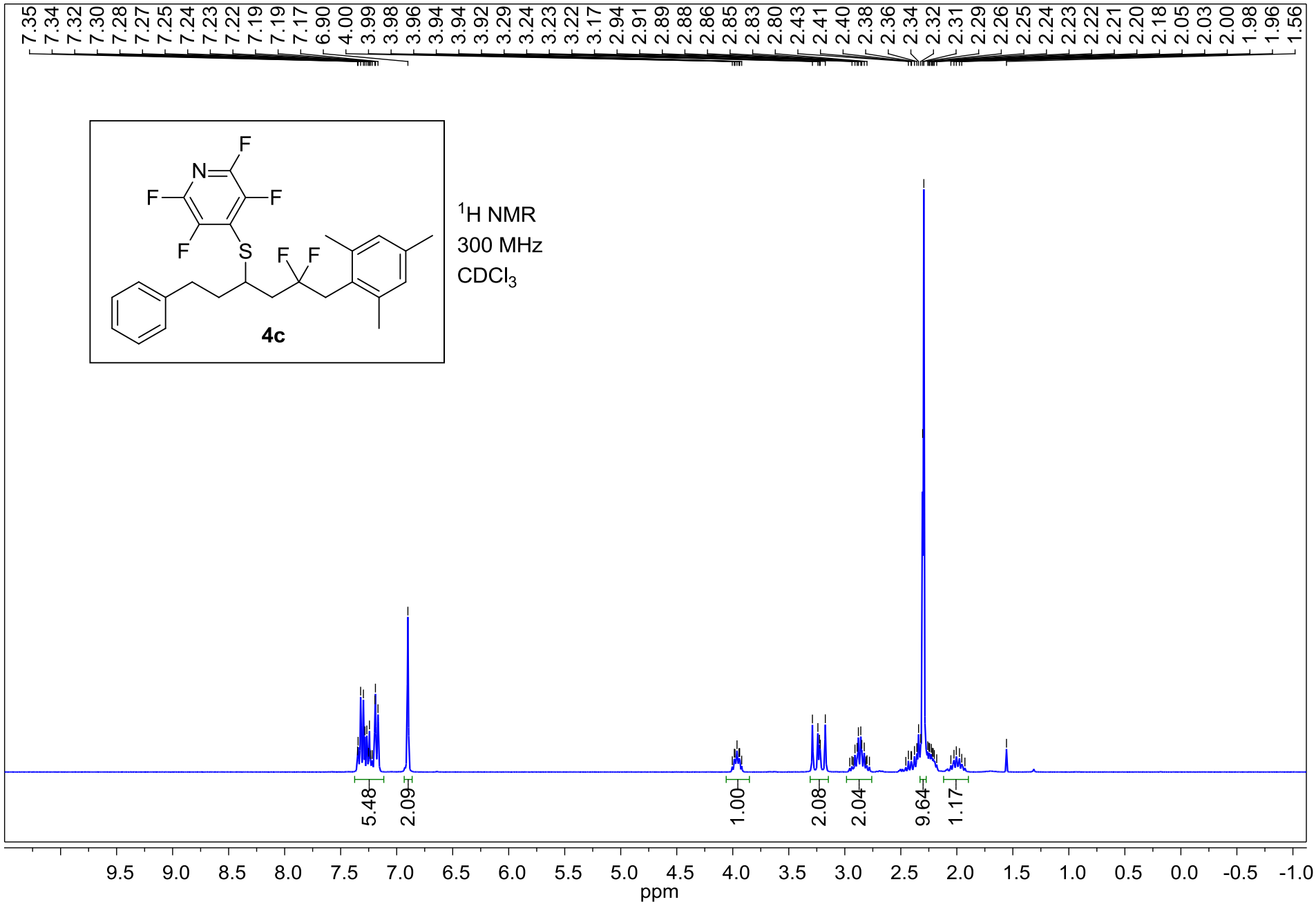
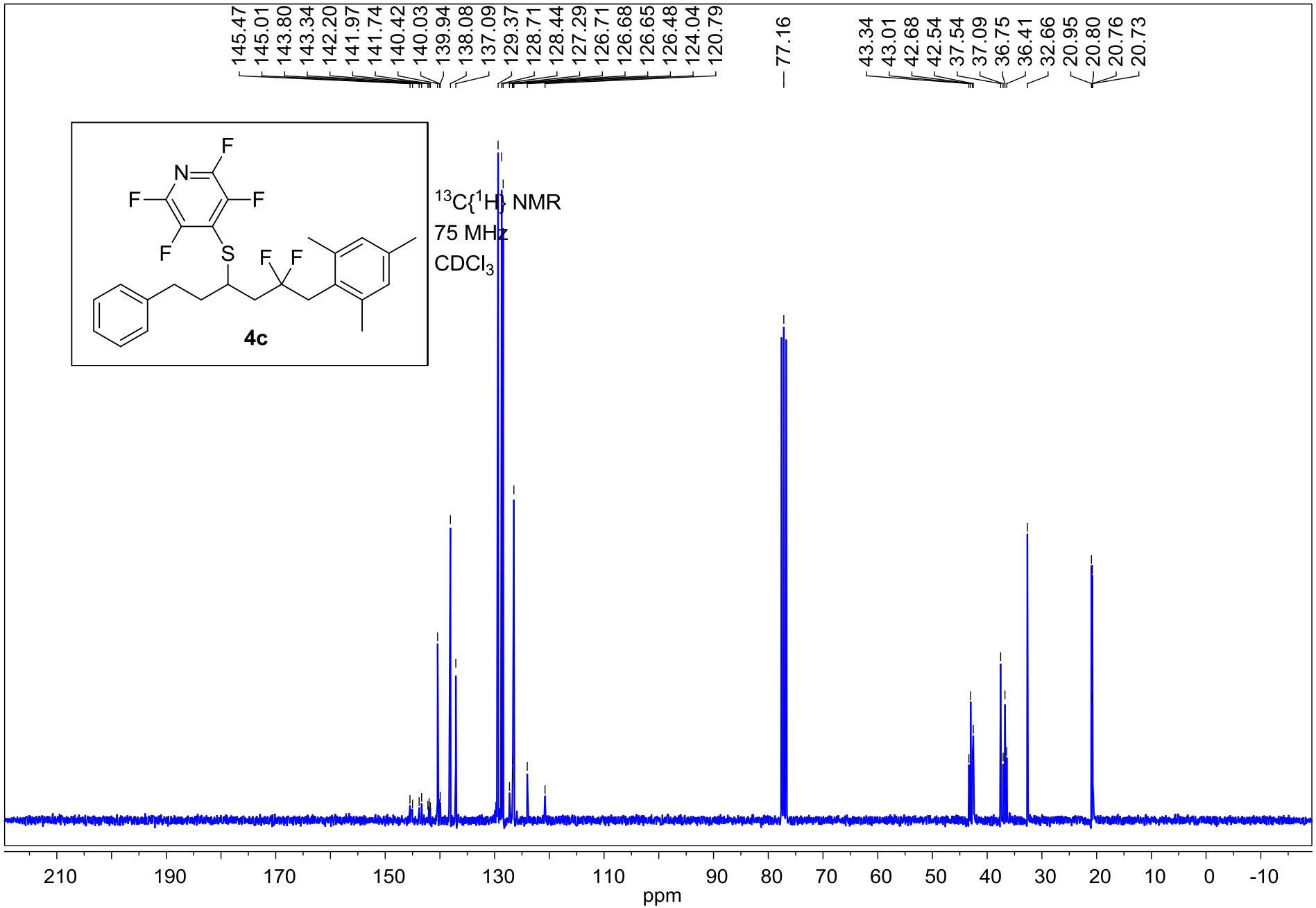
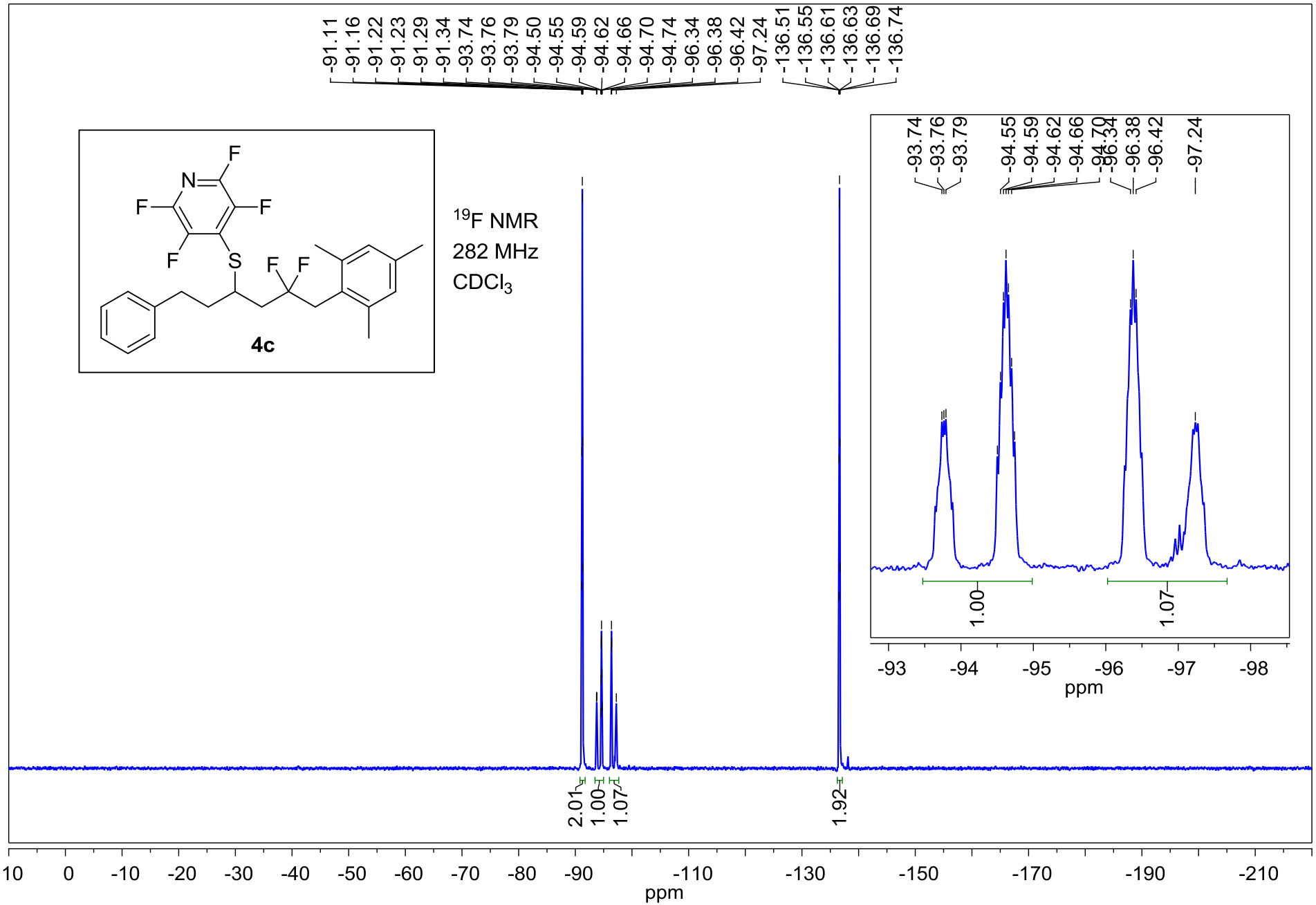
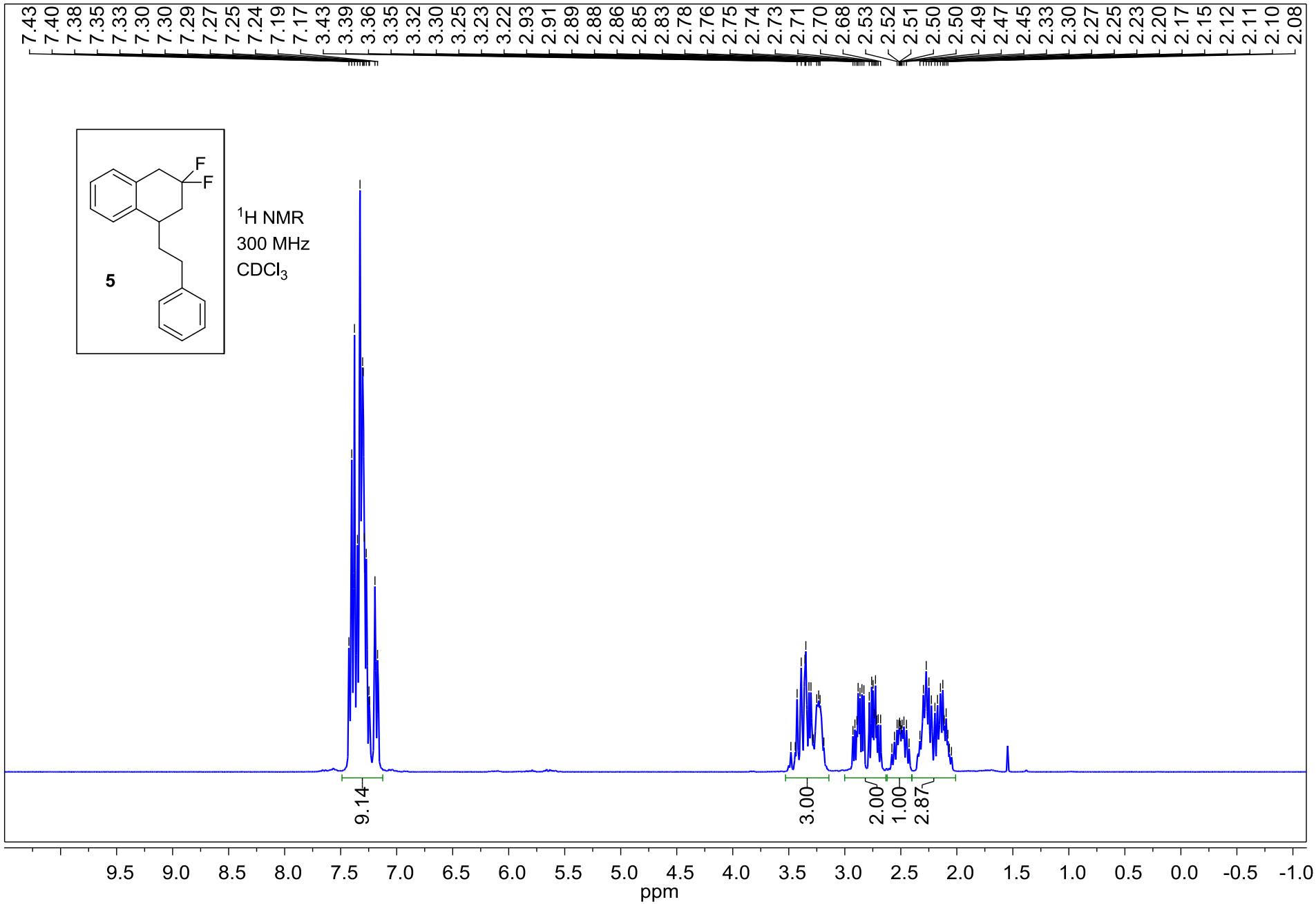
143.57
143.21
142.33
142.11
141.92
139.81
128.83
128.39
126.71
40.92
37.51
37.01
36.73
36.45
32.57
F
F
N
S
F
F
F
CF3
F
F
F
4b
13C{1H} NMR
75 MHz
CDCl3
120.72
120.32
119.71
119.26
117.33
116.92
116.51
115.90
115.45
113.53
112.64
112.40
109.40
108.90
108.39
104.89
124 122 120 118 116 114 112 110 108 106 104
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

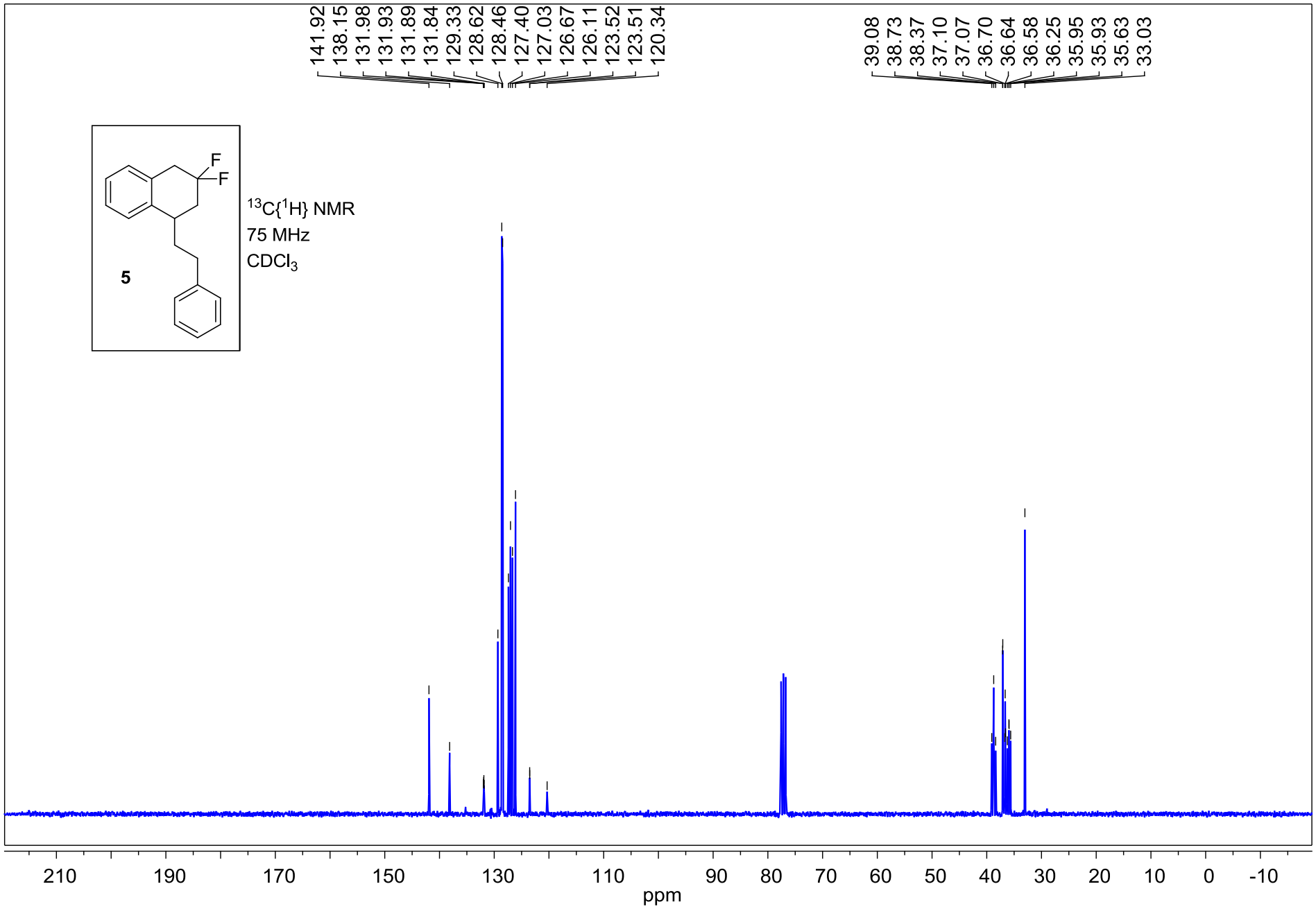

-81.13
-81.16
-81.19
-90.61
-90.66
-90.72
-90.74
-90.79
-90.84
-114.21
-114.79
-128.52
-136.70
-136.76
-136.83
F
F
N
S
F
F
F
F
F
F
F
CF3
4b
19F NMR
282 MHz
CDCl3
3.00
1.88
1.03
1.04
2.04
1.96
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

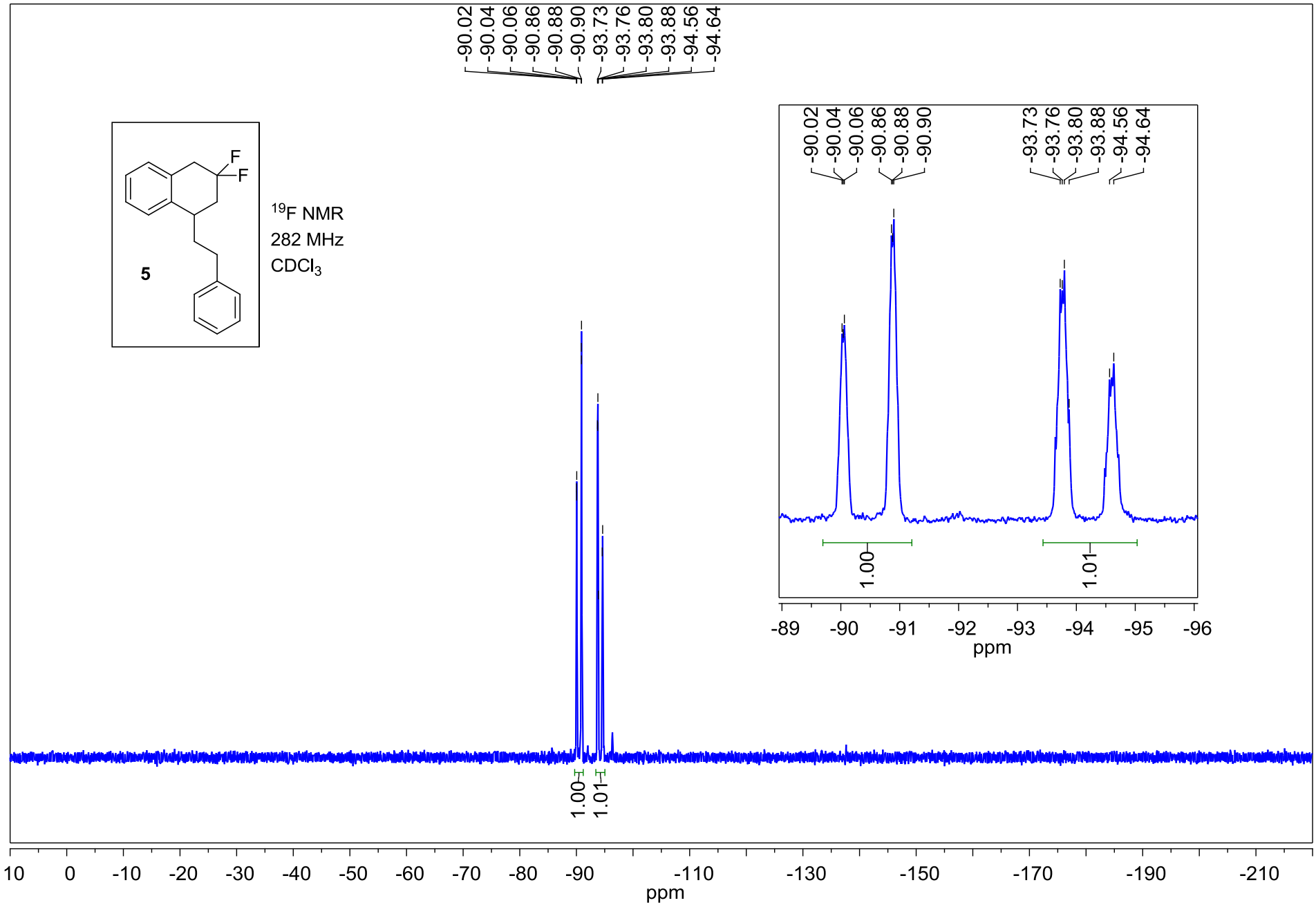

7.35 7.34 7.32 7.30 7.28 7.27 7.25 7.24 7.23 7.22 7.19 7.19 7.17 6.90 4.00 3.99 3.98 3.96 3.94 3.94 3.92 3.29 3.24 3.23 3.22 3.17 2.94 2.91 2.89 2.88 2.86 2.85 2.83 2.80 2.43 2.41 2.40 2.38 2.36 2.34 2.32 2.31 2.29 2.26 2.25 2.24 2.23 2.22 2.21 2.20 2.18 2.05 2.03 2.00 1.98 1.96 1.56
F
N
F
F
F
S
F
F
4c
1H NMR
300 MHz
CDCl3
5.48
2.09
1.00
2.08
2.04
9.64
1.17
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

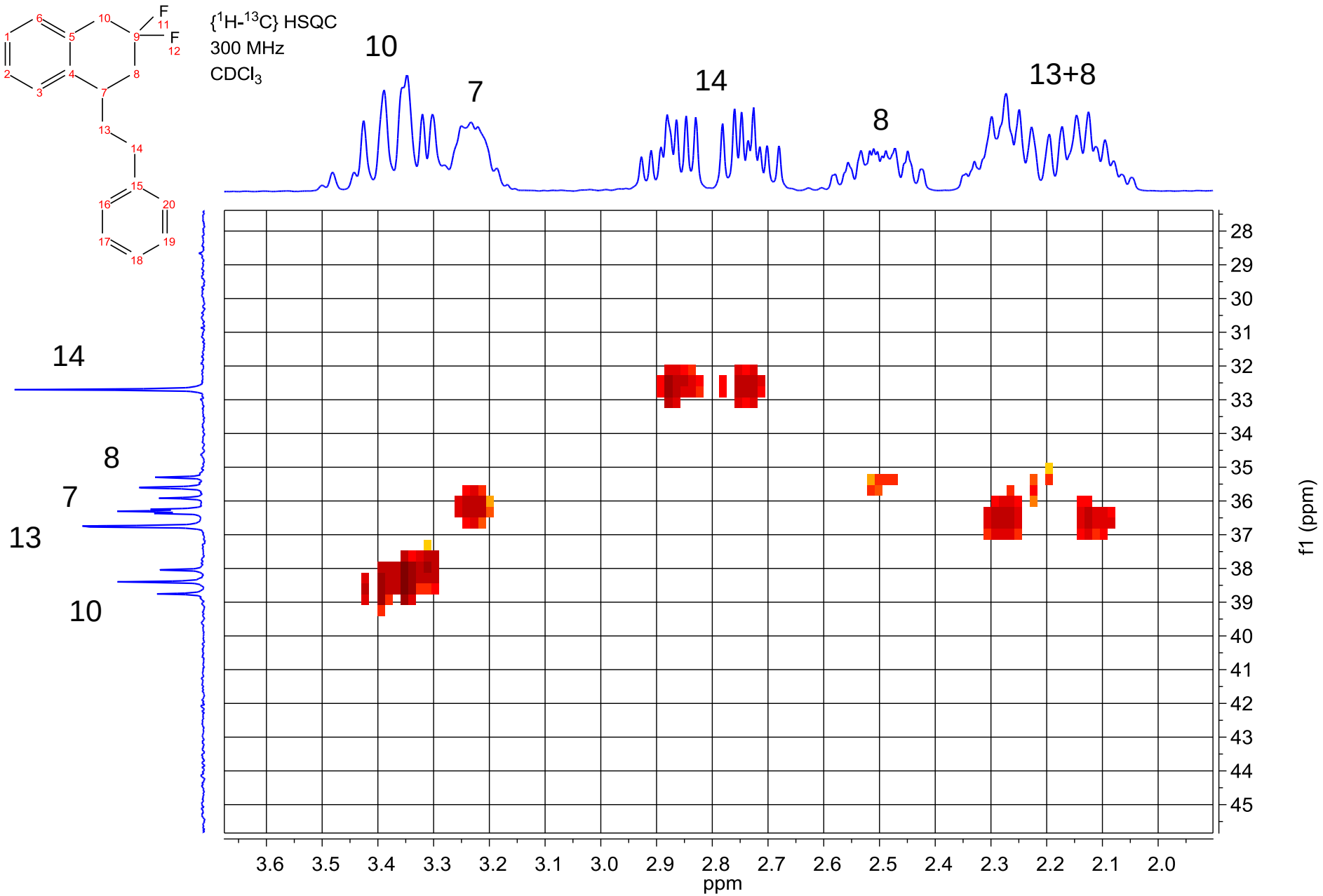

145.47
145.01
143.80
143.34
142.20
141.97
141.74
140.42
140.03
139.94
138.08
137.09
129.37
128.71
128.44
127.29
126.71
126.68
126.65
126.48
124.04
120.79
77.16
43.34
43.01
42.68
42.54
37.54
37.09
36.75
36.41
32.66
20.95
20.80
20.76
20.73
F
N
F
F
F
S
F
F
4c
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

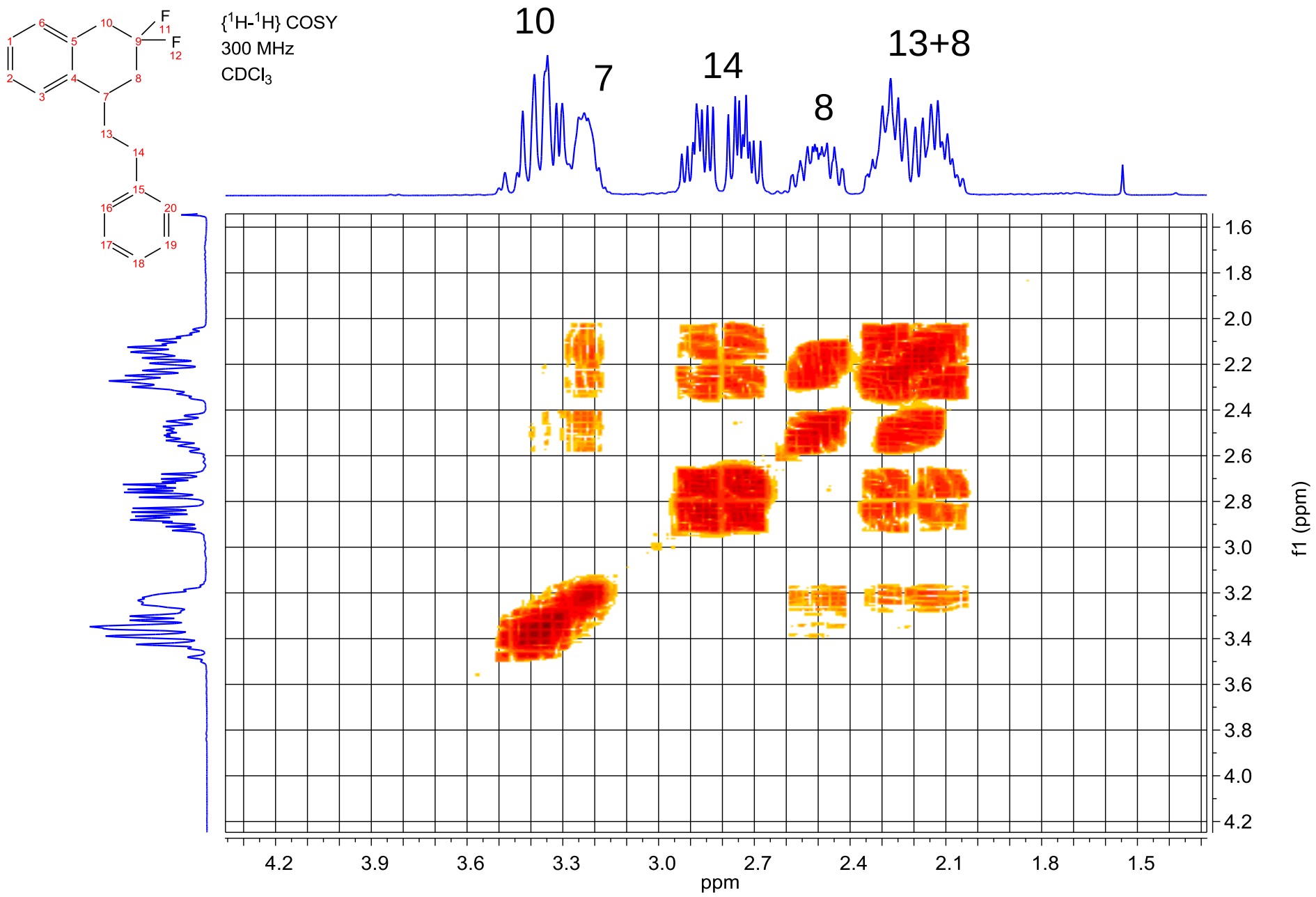

-91.11
-91.16
-91.22
-91.23
-91.29
-91.34
-93.74
-93.76
-93.79
-94.50
-94.55
-94.59
-94.62
-94.66
-94.70
-94.74
-96.34
-96.38
-96.42
-97.24
-136.51
-136.55
-136.61
-136.63
-136.69
-136.74
F
N
F
F
F
S
F
F
4c
19F NMR
282 MHz
CDCl3
2.01
1.00
1.07
1.92
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm
-93.74
-93.76
-93.79
-94.55
-94.59
-94.62
-94.66
-94.70
-96.34
-96.38
-96.42
-97.24
1.00
1.07
-93
-94
-95
-96
-97
-98
ppm

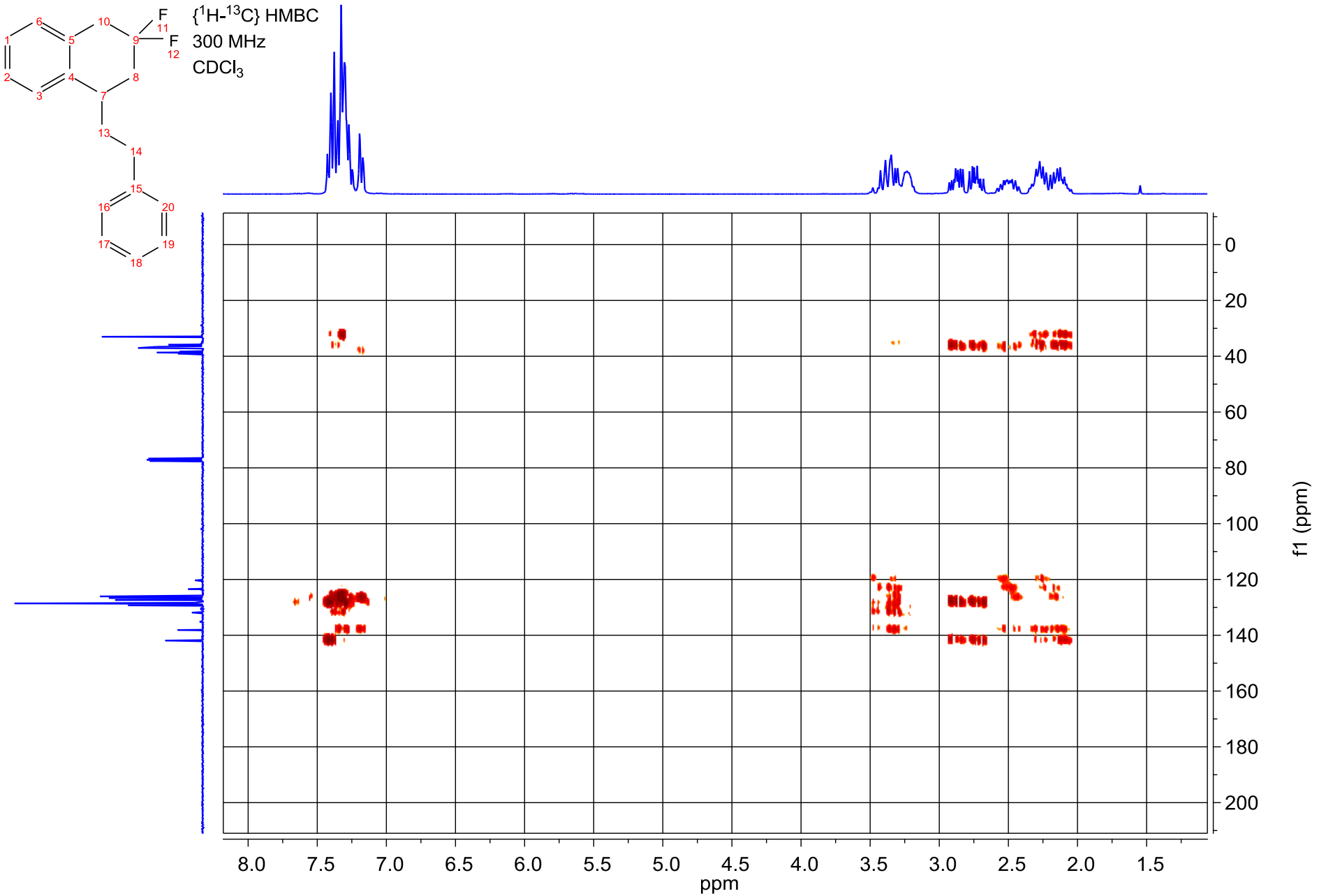

7.43 7.40 7.38 7.35 7.33 7.30 7.30 7.29 7.27 7.25 7.24 7.19 7.17 3.43 3.39 3.36 3.35 3.32 3.30 3.25 3.23 3.22 2.93 2.91 2.89 2.88 2.86 2.85 2.83 2.78 2.76 2.75 2.74 2.73 2.71 2.70 2.68 2.53 2.52 2.51 2.50 2.50 2.49 2.47 2.45 2.33 2.30 2.27 2.25 2.23 2.20 2.17 2.15 2.12 2.11 2.10 2.08
F
F
5
1H NMR
300 MHz
CDCl3
9.14
3.00
2.00
1.00
2.87
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

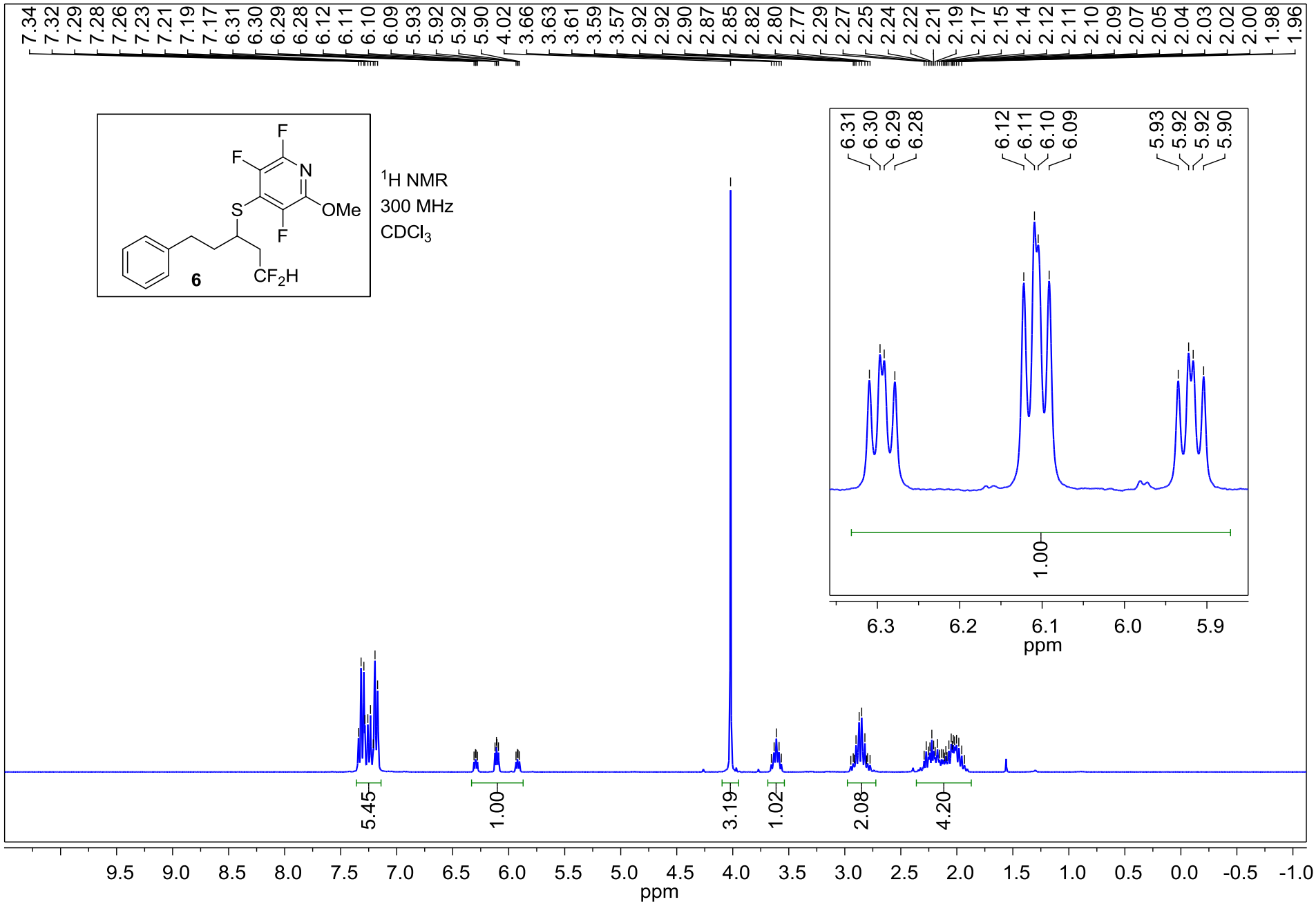

141.92
138.15
131.98
131.93
131.89
131.84
129.33
128.62
128.46
127.40
127.03
126.67
126.11
123.52
123.51
120.34
39.08
38.73
38.37
37.10
37.07
36.70
36.64
36.58
36.25
35.95
35.93
35.63
33.03
F
F
5
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

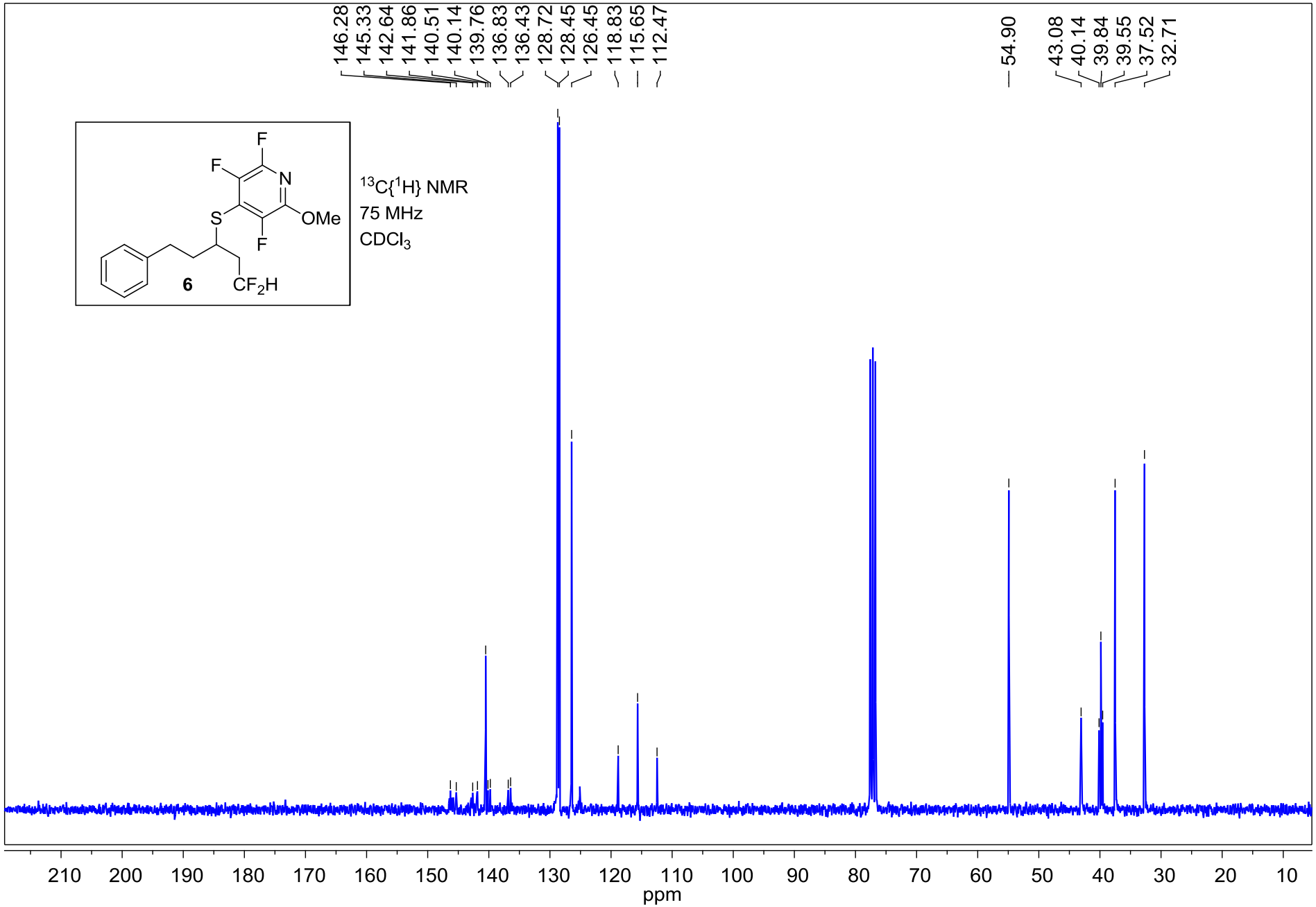

-90.02
-90.04
-90.06
-90.86
-90.88
-90.90
-93.73
-93.76
-93.80
-93.88
-94.56
-94.64
F
F
5
19F NMR
282 MHz
CDCl3
1.00
1.01
-89
-90
-91
-92
-93
-94
-95
-96
ppm
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

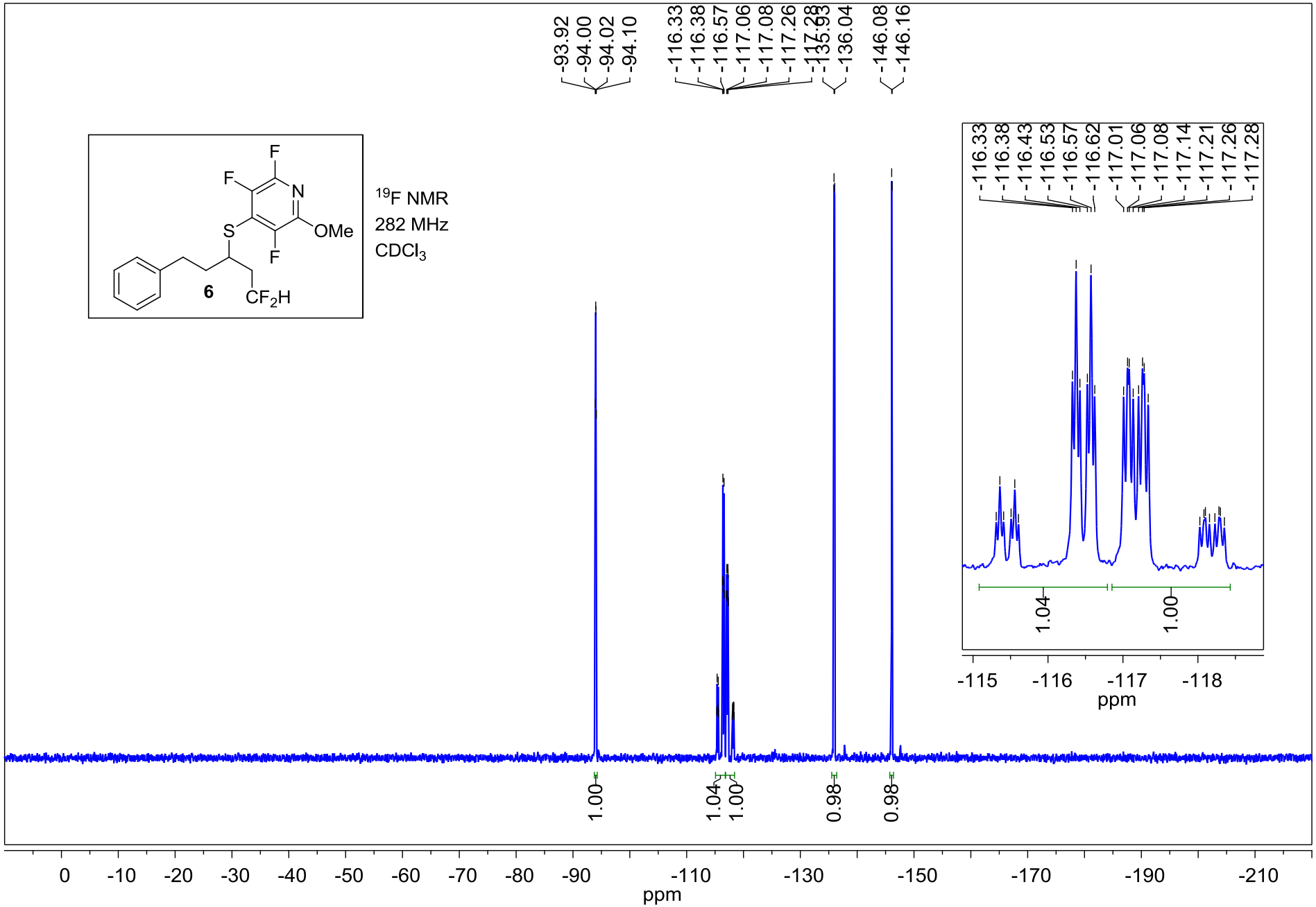

{1H-13C} HSQC
300 MHz
CDCl3
10
7
14
8
13+8
14
8
7
13
10
f1 (ppm)
ppm
3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0
28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45

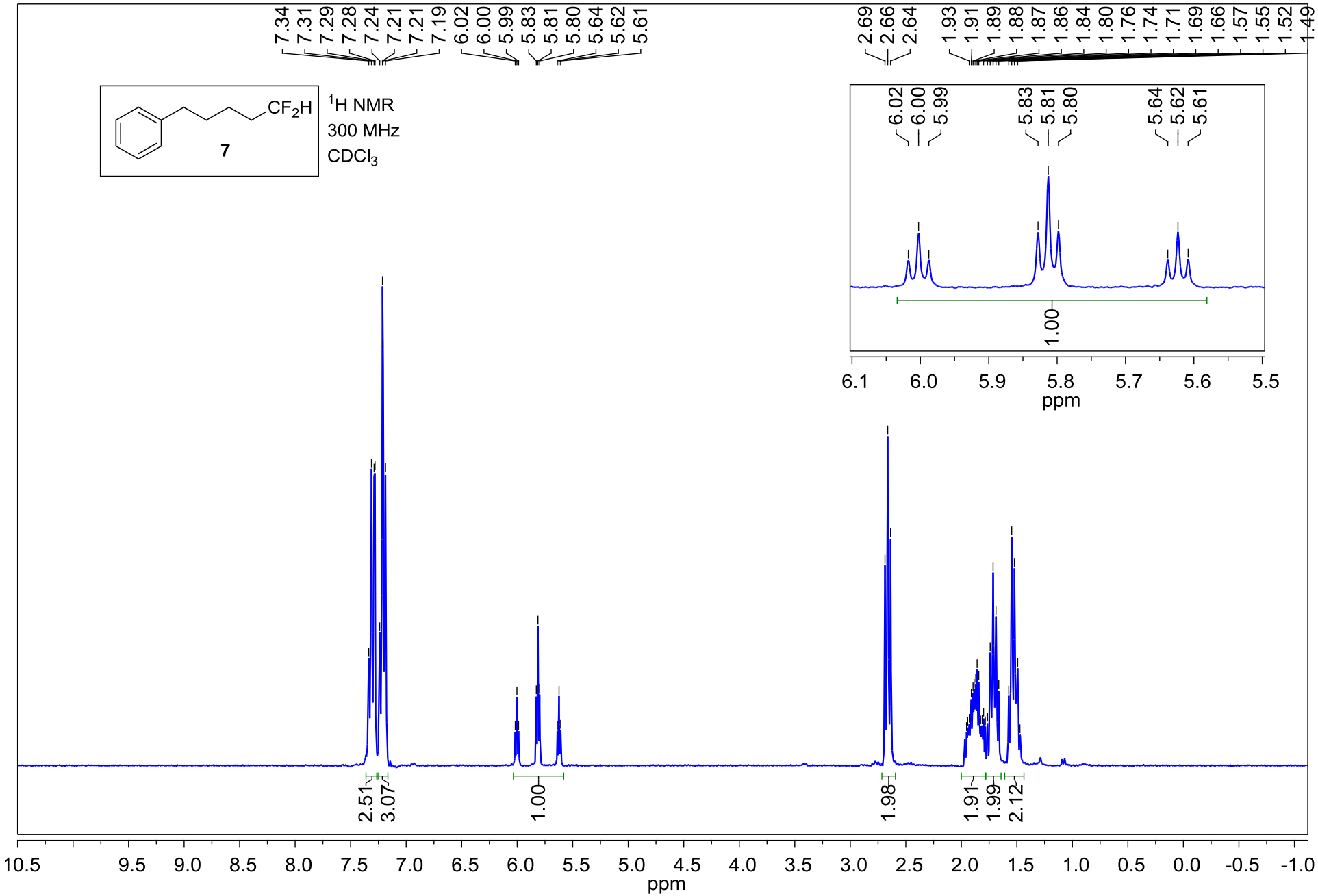

{1H-1H} COSY
300 MHz
CDCl3
10
7
14
8
13+8
F
F
ppm
f1 (ppm)

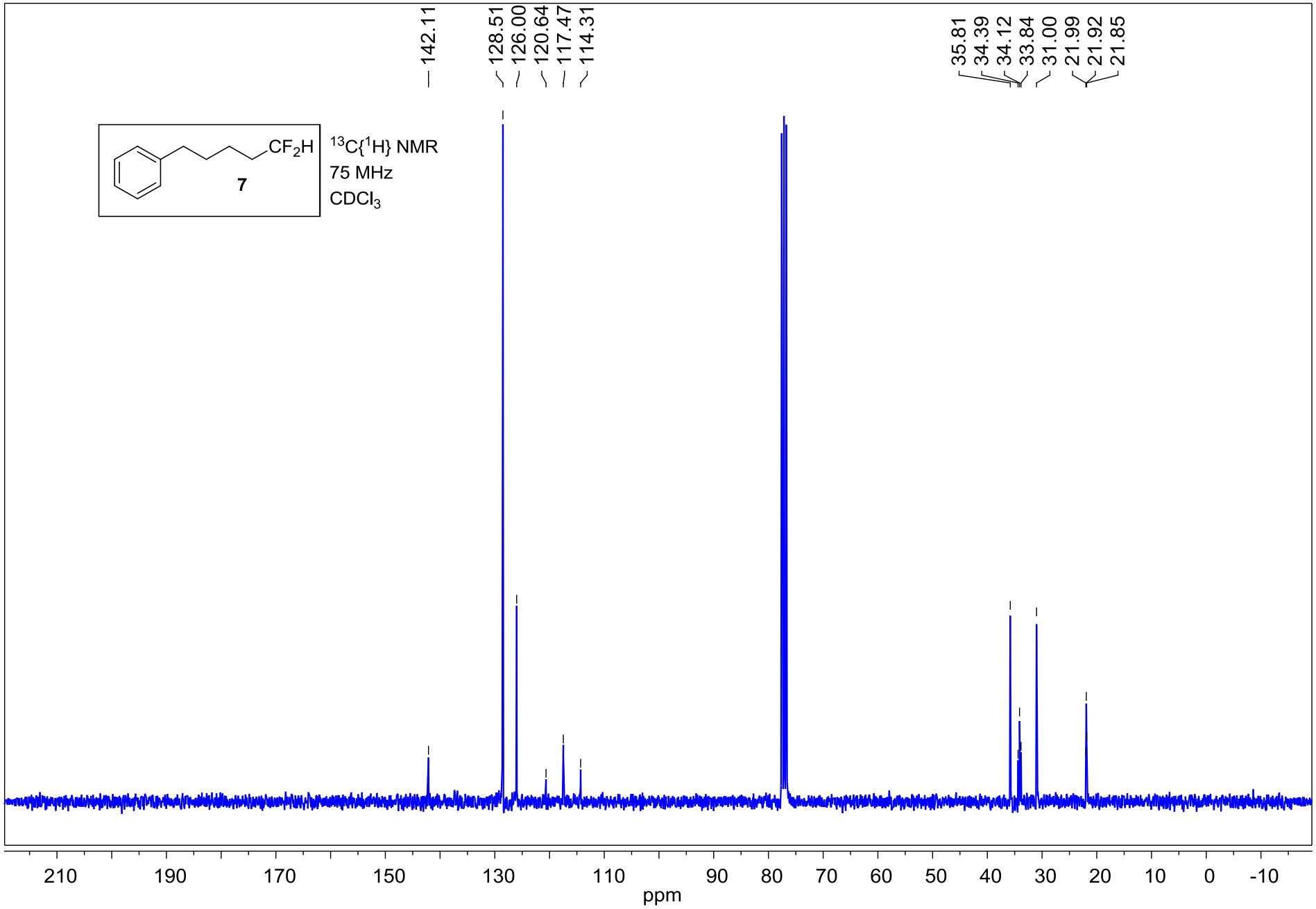

{1H-13C} HMBC
300 MHz
CDCl3
F
F
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)

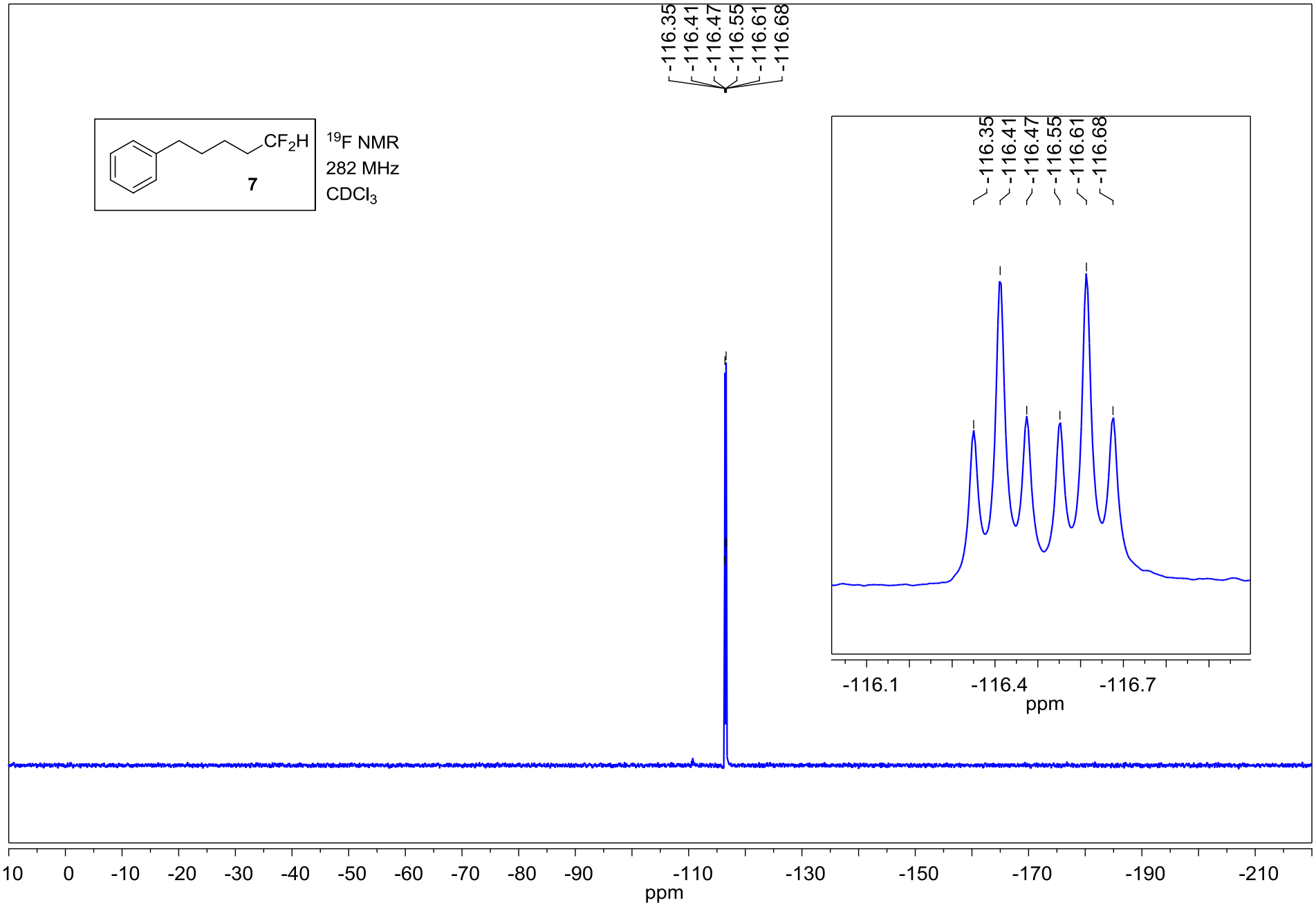

7.34 7.32 7.29 7.28 7.26 7.23 7.21 7.19 7.17 6.31 6.30 6.29 6.28 6.12 6.11 6.10 6.09 5.93 5.92 5.92 5.90 4.02 3.66 3.63 3.61 3.59 3.57 2.92 2.92 2.90 2.87 2.85 2.82 2.80 2.77 2.29 2.27 2.25 2.24 2.22 2.21 2.19 2.17 2.15 2.14 2.12 2.11 2.10 2.09 2.07 2.05 2.04 2.03 2.02 2.00 1.98 1.96
F
F
N
S
OMe
F
CF2H
6
1H NMR
300 MHz
CDCl3
6.31 6.30 6.29 6.28 6.12 6.11 6.10 6.09 5.93 5.92 5.92 5.90
1.00
6.3 6.2 6.1 6.0 5.9
ppm
5.45 1.00 3.19 1.02 2.08 4.20
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

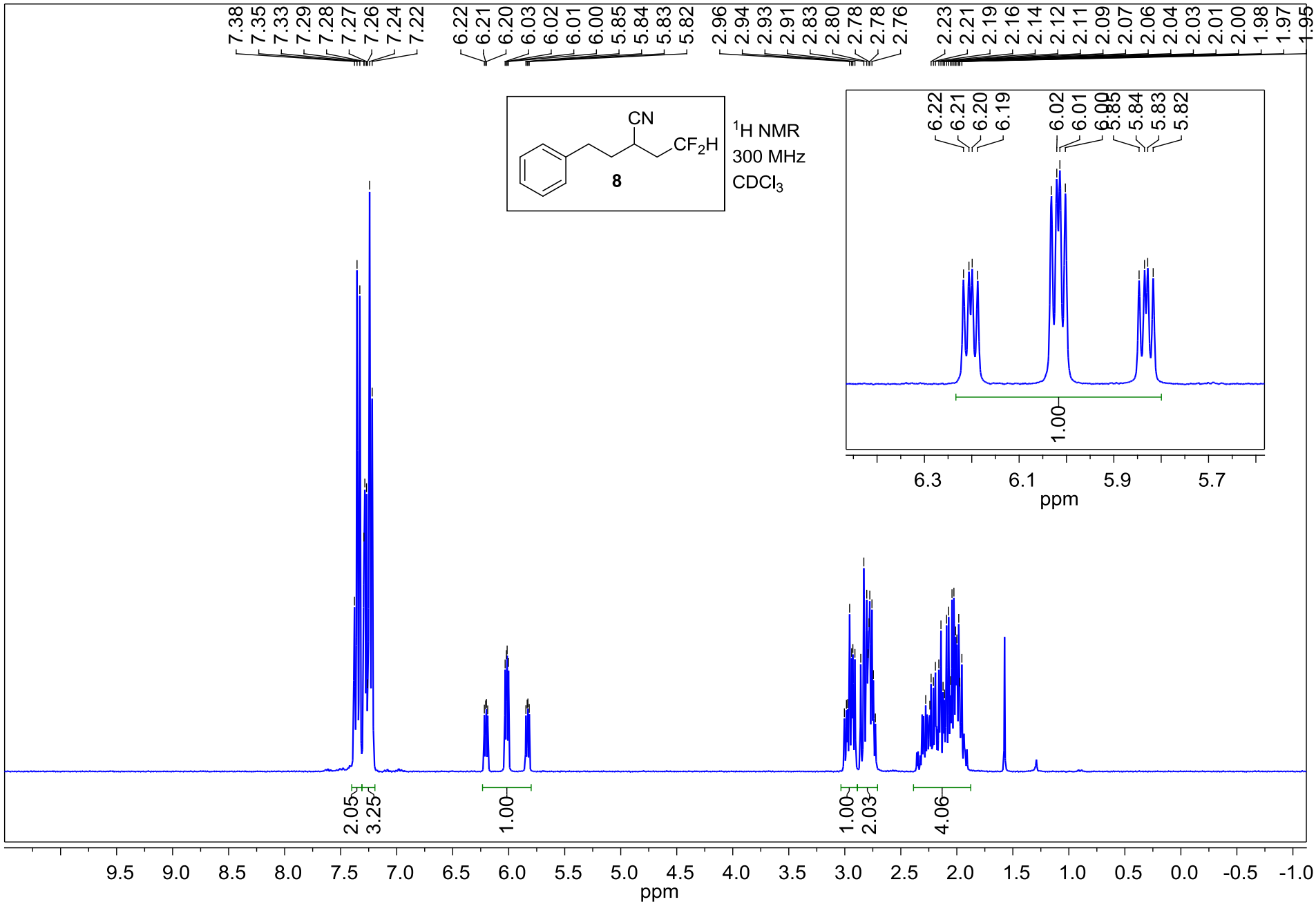

146.28
145.33
142.64
141.86
140.51
140.14
139.76
136.83
136.43
128.72
128.45
126.45
118.83
115.65
112.47
54.90
43.08
40.14
39.84
39.55
37.52
32.71
F
F
N
S
OMe
F
6
CF2H
13C{1H} NMR
75 MHz
CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

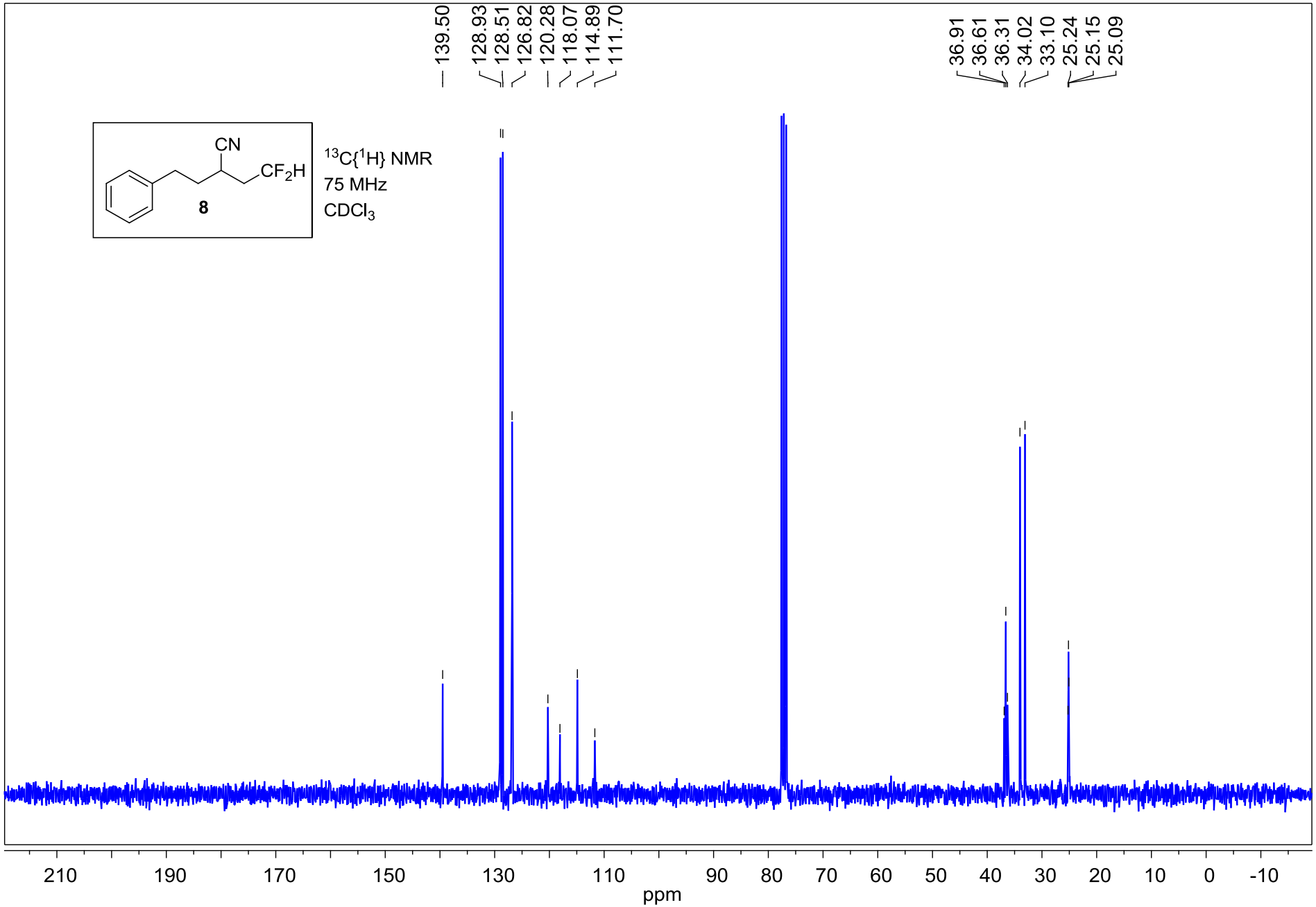

-93.92
-94.00
-94.02
-94.10
-116.33
-116.38
-116.57
-117.06
-117.08
-117.26
-117.28
-135.93
-136.04
-146.08
-146.16
F
F
N
S
OMe
F
6
CF2H
19F NMR
282 MHz
CDCl3
-116.33
-116.38
-116.43
-116.53
-116.57
-116.62
-117.01
-117.06
-117.08
-117.14
-117.21
-117.26
-117.28
1.04
1.00
-115
-116
-117
-118
ppm
1.00
1.04
1.00
0.98
0.98
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

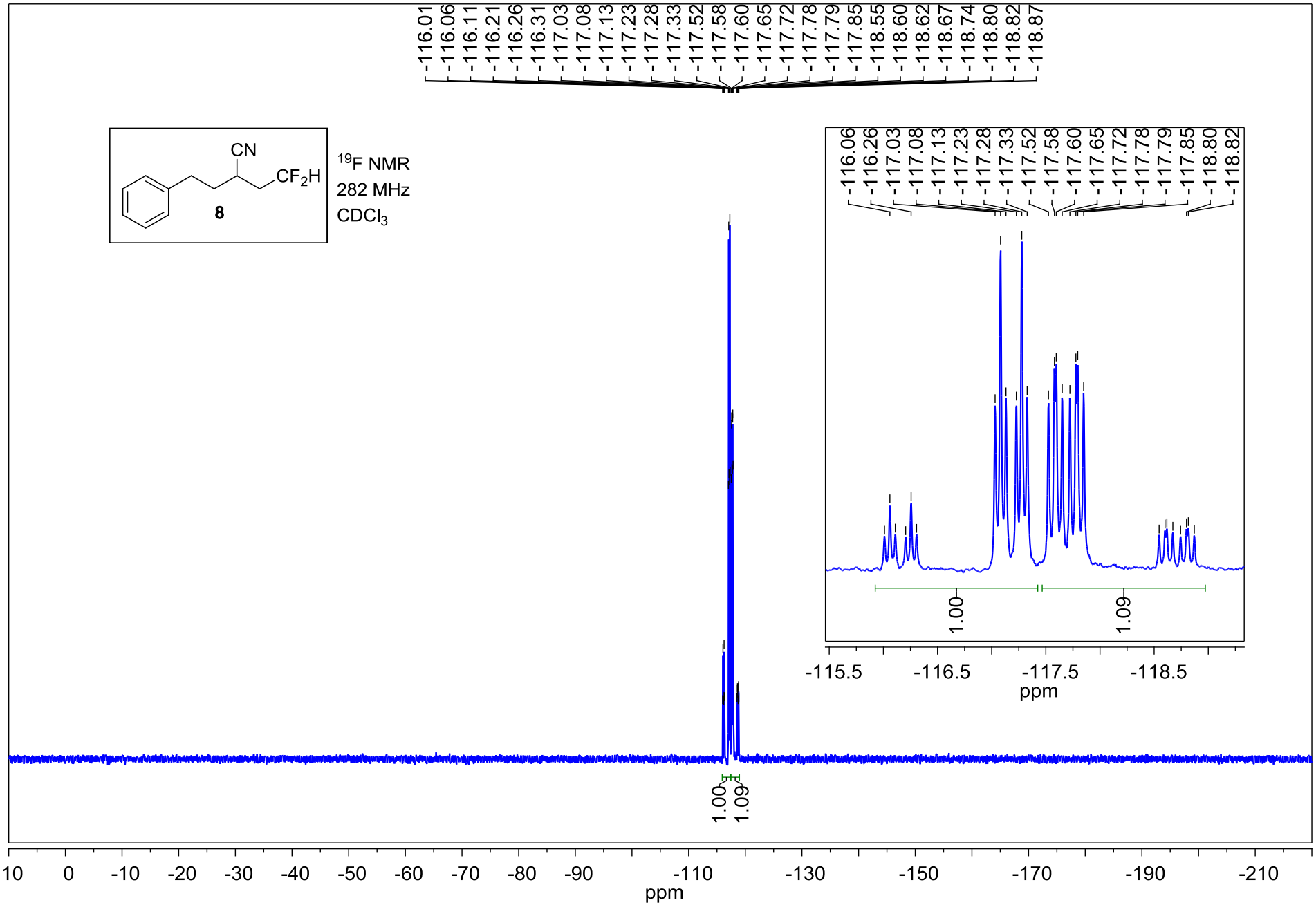

7.34
7.31
7.29
7.28
7.24
7.21
7.21
7.19
6.02
6.00
5.99
5.83
5.81
5.80
5.64
5.62
5.61
2.69
2.66
2.64
1.93
1.91
1.89
1.88
1.87
1.86
1.84
1.80
1.76
1.74
1.71
1.69
1.66
1.57
1.55
1.52
1.49
CF2H
7
1H NMR
300 MHz
CDCl3
1.00
6.1
6.0
5.9
5.8
5.7
5.6
5.5
ppm
2.51
3.07
1.00
1.98
1.91
1.99
2.12
10.5
9.5
9.0
8.5
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

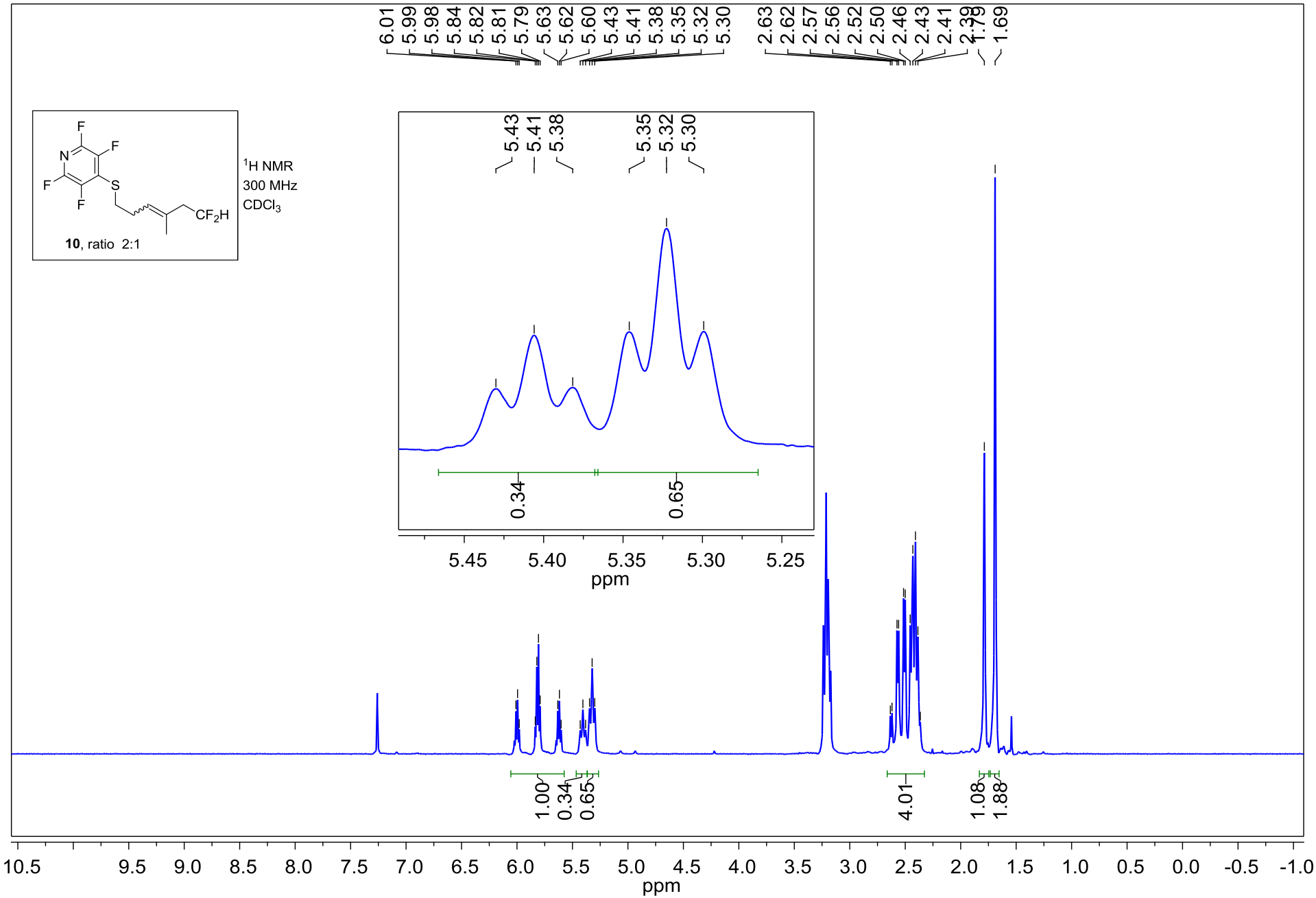

142.11
128.51
126.00
120.64
117.47
114.31
35.81
34.39
34.12
33.84
31.00
21.99
21.92
21.85
CF2H
7
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm

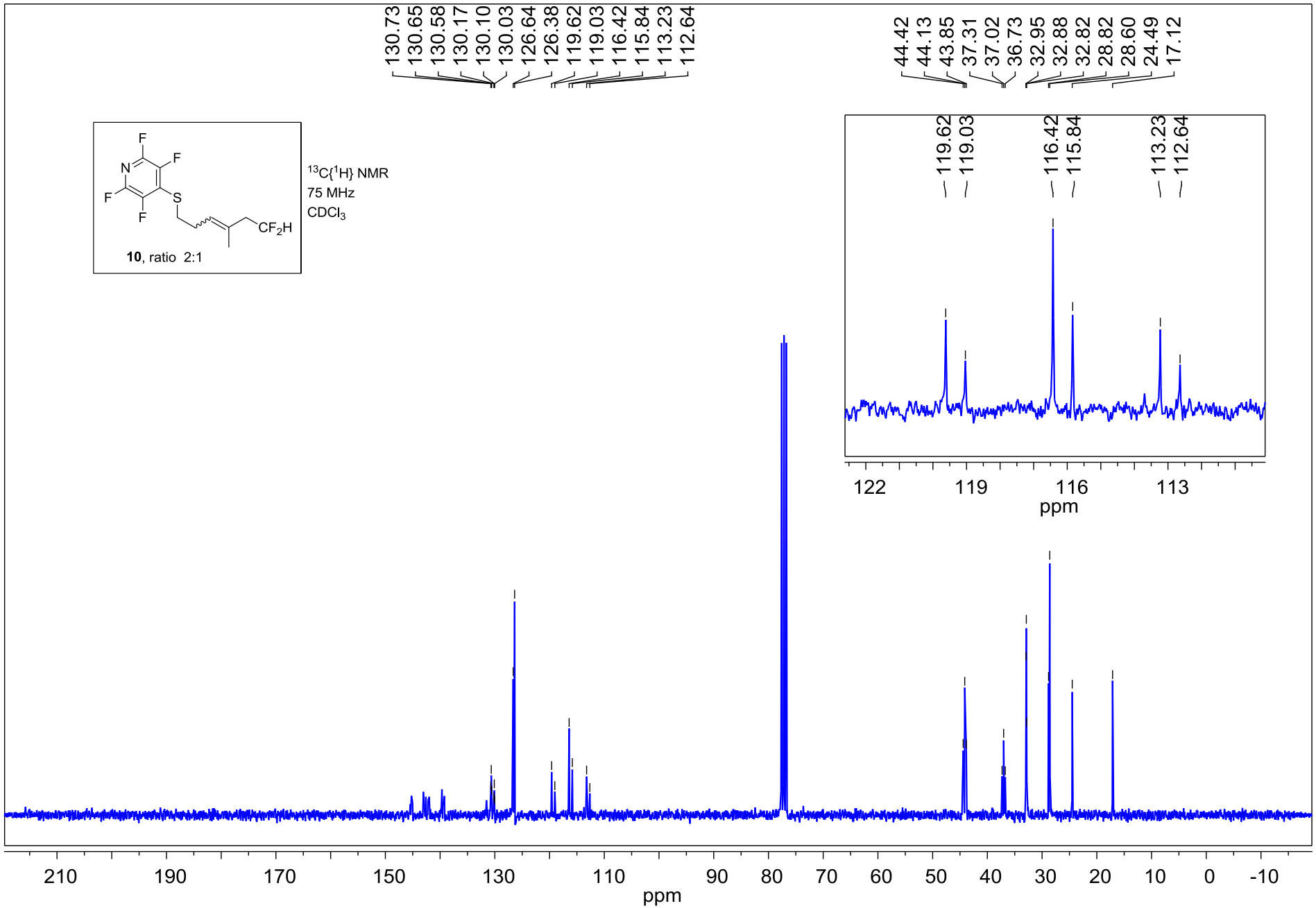

-116.35
-116.41
-116.47
-116.55
-116.61
-116.68
CF2H
7
19F NMR
282 MHz
CDCl3
-116.35
-116.41
-116.47
-116.55
-116.61
-116.68
-116.1
-116.4
-116.7
ppm
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm

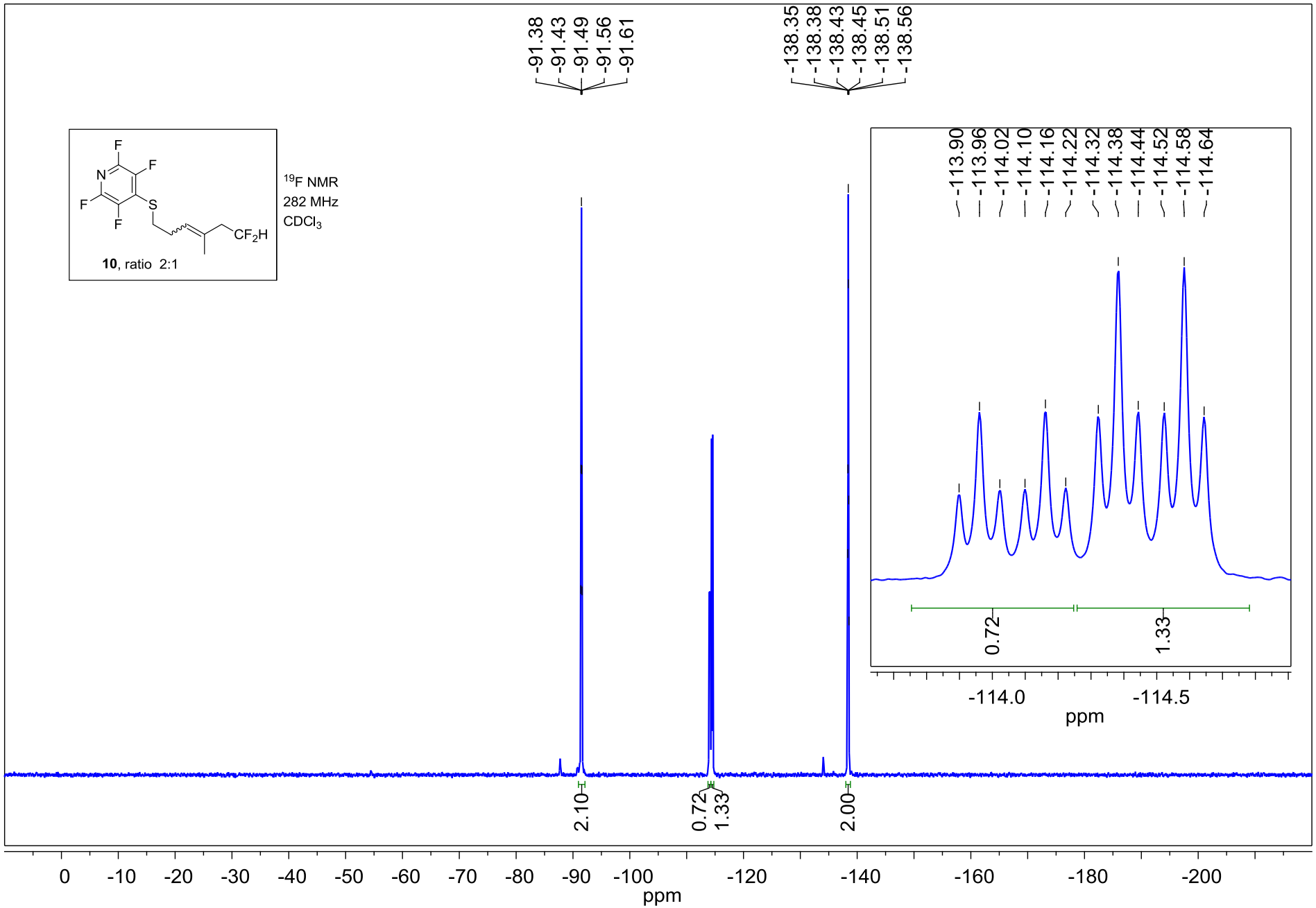

7.38 7.35 7.33 7.29 7.28 7.27 7.26 7.24 7.22
6.22 6.21 6.20 6.03 6.02 6.01 6.00 5.85 5.84 5.83 5.82
2.96 2.94 2.93 2.91 2.83 2.80 2.78 2.78 2.76
2.23 2.21 2.19 2.16 2.14 2.12 2.11 2.09 2.07 2.06 2.04 2.03 2.01 2.00 1.98 1.97 1.95
CN
CF2H
8
1H NMR
300 MHz
CDCl3
6.22 6.21 6.20 6.19
6.02 6.01 6.00 5.85 5.84 5.83 5.82
1.00
6.3 6.1 5.9 5.7
ppm
2.05 3.25 1.00 1.00 2.03 4.06
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


139.50
128.93
128.51
126.82
120.28
118.07
114.89
111.70
36.91
36.61
36.31
34.02
33.10
25.24
25.15
25.09
CN
CF2H
8
13C{1H} NMR
75 MHz
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm


-116.01
-116.06
-116.11
-116.21
-116.26
-116.31
-117.03
-117.08
-117.13
-117.23
-117.28
-117.33
-117.52
-117.58
-117.60
-117.65
-117.72
-117.78
-117.79
-117.85
-118.55
-118.60
-118.62
-118.67
-118.74
-118.80
-118.82
-118.87
CN
CF2H
8
19F NMR
282 MHz
CDCl3
-116.06
-116.26
-117.03
-117.08
-117.13
-117.23
-117.28
-117.33
-117.52
-117.58
-117.60
-117.65
-117.72
-117.78
-117.79
-117.85
-118.80
-118.82
1.00
1.09
-115.5
-116.5
-117.5
-118.5
ppm
1.00
1.09
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
ppm


6.01
5.99
5.98
5.84
5.82
5.81
5.79
5.63
5.62
5.60
5.43
5.41
5.38
5.35
5.32
5.30
2.63
2.62
2.57
2.56
2.52
2.50
2.46
2.43
2.41
2.39
1.79
1.69
F
N
F
F
F
S
CF2H
10, ratio 2:1
1H NMR
300 MHz
CDCl3
5.43
5.41
5.38
5.35
5.32
5.30
0.34
0.65
5.45
5.40
5.35
5.30
5.25
ppm
1.00
0.34
0.65
4.01
1.08
1.88
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


130.73
130.65
130.58
130.17
130.10
130.03
126.64
126.38
119.62
119.03
116.42
115.84
113.23
112.64
44.42
44.13
43.85
37.31
37.02
36.73
32.95
32.88
32.82
28.82
28.60
24.49
17.12
F
N
F
F
F
S
CF2H
10, ratio 2:1
13C{1H} NMR
75 MHz
CDCl3
119.62
119.03
116.42
115.84
113.23
112.64
122
119
116
113
ppm
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
ppm


-91.38
-91.43
-91.49
-91.56
-91.61
-138.35
-138.38
-138.43
-138.45
-138.51
-138.56
F
N
F
F
S
F
CF2H
10, ratio 2:1
19F NMR
282 MHz
CDCl3
-113.90
-113.96
-114.02
-114.10
-114.16
-114.22
-114.32
-114.38
-114.44
-114.52
-114.58
-114.64
0.72
1.33
-114.0
-114.5
ppm
2.10
0.72
1.33
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
ppm