Electronic Supplementary Material (ESI) for ChemComm.

Supporting Infomation

Atom-transfer radical addition of fluoroalkyl bromides to alkenes via photoredox/copper catalytic system

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Content

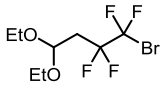
General methods

All reactions were performed under an argon atmosphere. DMSO was distilled from CaH_2 and stored over MS 4Å. Acetonitrile was distilled from CaH_2 and stored over MS 3Å. Dichloromethane was distilled from CaH_2 prior to use. Column chromatography was carried out employing silica gel (230−400 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or acidic aq. $KMnO_4$ solution. High resolution mass-spectra (HRMS) were measured using electrospray ionization (ESI) and a time-of-flight (TOF) mass analyzer (Bruker MicrOTOF II). The measurements were done in a positive-ion mode (interface capillary voltage −4500 V) or in a negative-ion mode (3200 V); the mass ranged from m/z 50 to m/z 3000. Photo-induced reactions were performed in Duran culture tubes (Roth cat. no K248.1, outside diameter = 12 mm). For irradiation, a strip of 455 nm light-emitting diodes (SMD 2835−120 LED 1 M Blue, 12 V, 24 W/m; 50 cm strip length) or 400 nm COB LED matrix Hontiey (29-32V, 3000mA, 100W; operated at 60W) were used. The distance between the reaction vessel and diodes was about 5 mm. The reaction tube was placed in a glass jacket and cooled with water at room temperature. The reaction setup was used as previously described: for LED strip,[1] for LED matrix.[2]

Starting materials

Compounds 1-bromo-1,1,2,2-tetrafluorobutane (**1a**), 4-bromo-3,3,4,4-tetrafluorobutan-1-ol (**1s**), 1,4-dibromo-1,1,2,2-tetrafluorobutane (**1t**), perfluoro-1-bromobutane (**1γ**) were purchased from P&M Invest and used without further purification. Alkenes 4-phenylbut-1-ene (**2a**), pent-4-en-1-ol (**2h**), cyclopentene (**2q**), *tert*-butylethylene (**2u**), 1-heptene (**2v**) were purchased from Acros Organics or ABCR and distilled prior to use.

Reagents shown below were synthesized according to literature procedures:



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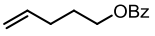
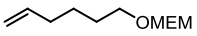


2b[4]



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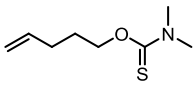

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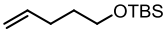

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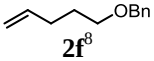

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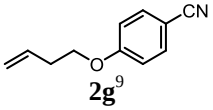

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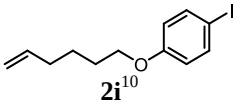

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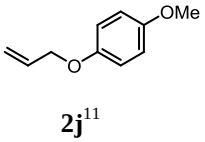

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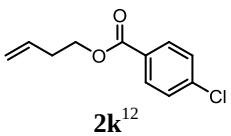

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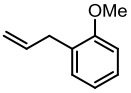

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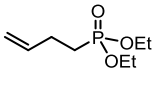

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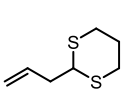

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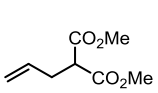

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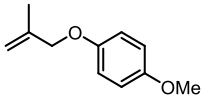

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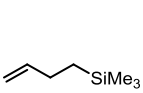

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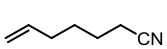

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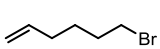

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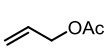

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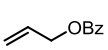

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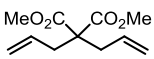

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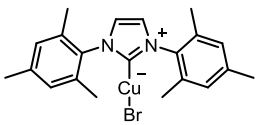
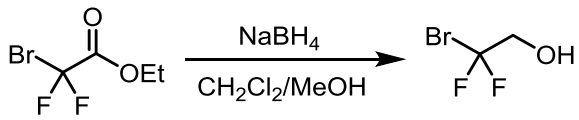


IMesCuBr[24]

2-Bromo-2,2-difluoroethan-1-ol.[25]



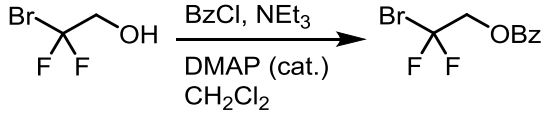
A solution of ethyl bromodifluoroacetate (12.8 mL, 100 mmol) in methanol (8 mL) was added dropwise to a refluxed suspension of sodium borohydride (2.66 g, 70 mmol) in CH_2Cl_2 (40 mL). The reaction mixture was refluxed for additional 4 hours until complete homogenization. The mixture was cooled to 0-5°C with an ice/water bath and quenched by dropwise addition of diluted (10 % *wt.*) sulphuric acid (138 mL). The reaction vessel was equipped with a distilling head and all volatile compounds were distilled with steam until the temperature of the vapor reached 100°C. The distillate was transferred into a separatory funnel, the aqueous phase was separated. The organic phase was stirred with solid ammonium chloride (*ca.* 1g), filtered, and subjected to distilled with a Vigreux column (under ambient pressure, fraction with bp 97-108 °C was collected), affording 13.2 g of crude 2-bromo-2,2-difluoroethan-1-ol in a mixture with EtOH (10 % *wt.*). Then, the obtained materials was mixed with concentrated sulfuric acid (6.6 mL) and concentrated hydrochloric acid (6.6 mL), the resulting mixture was stirred for 30 minutes at room temperature and 15 minutes at 80 °C. The emulsion was extracted with CH_2Cl_2 (3×5 mL), the combined organic phases were shaken with solid $NaHCO_3$ (*ca.* 1g) and filtered. The solvent was evaporated at room pressure with Vigreux column, the residue was distilled using a Hickman distilling head (oil bath temperature 120 – 140 °C). Yield 10.9 g (68 %).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 4.03 (t, J = 11.5 Hz, 2H), 3.18 – 2.82 (m, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 121.6 (t, J = 307.1 Hz), 68.6 (t, J = 27.0 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -58.50 – -58.69 (m).

2-(2-Bromo-2,2-difluoroethoxy)-2,3,3-trimethylbutane (1u).



Triethylamine (1.67 mL, 12 mmol), 4-(dimethylamino)pyridine (244 mg, 2 mmol) and benzoyl chloride (1.39 mL, 12 mmol) were added to a stirred solution of 2-bromo-2,2-difluoroethan-1-ol (1.61 g, 10 mmol) in CH_2Cl_2 at 0°C. The mixture was stirred overnight at room temperature, then diluted with water (15 mL), the organic phase was separated, the aqueous phase was extracted with hexane (3×5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure (100 Torr). The residue was distilled under vacuum (10

Torr) using a Hickman distilling head (oil bath temperature 120 – 140°C). The product was obtained as a colourless oil. Yield 2.39 g (90 %).

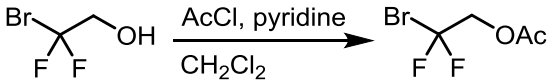
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.10 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (ddd, *J* = 8.4, 7.4, 1.4 Hz, 2H), 4.84 (t, *J* = 11.5 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 164.9, 133.9, 130.1, 128.7, 118.4 (t, *J* = 305.9 Hz), 67.5 (t, *J* = 27.8 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -56.04 (t, *J* = 11.5 Hz).

HRMS (ESI-TOF): calcd for $C_9H_7{}^{79}BrF_2O_2Ag$ [M+Ag]: 370.8643; found 370.8730.

2-(2-Bromo-2,2-difluoroethoxy)-2,3,3-trimethylbutane (1*α*).



Pyridine (1.05 mL, 13 mmol) and acetyl chloride (0.92 mL, 13 mmol) were added to a stirred solution of 2-bromo-2,2-difluoroethan-1-ol (1.61 g, 10 mmol) in CH_2Cl_2 at 0°C. The mixture was stirred overnight at room temperature, then diluted with water (15 mL), the organic phase was separated, the aqueous phase was extracted with pentane (3×5 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4 and concentrated at room pressure. The residue was distilled under vacuum (200 Torr) using a Hickman distilling head (oil bath temperature 80 – 100°C). The product was obtained as colourless oil. Yield 1.60 g (79 %).

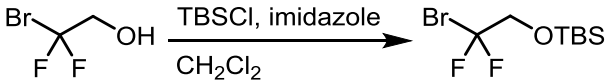
^{1}H NMR (300 MHz, $CDCl_3$), δ: 4.55 (t, *J* = 11.7 Hz, 1H), 2.12 (s, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 169.2, 118.2 (t, *J* = 305.8 Hz), 67.0 (t, *J* = 27.3 Hz), 20.3.

^{19}F NMR (282 MHz, $CDCl_3$), δ: -56.53 (t, *J* = 11.7 Hz).

MS (EI): calcd for $C_2H_2{}^{79}BrF_2$: 142.93 (M-OAc), 123.03 (M-Br); found 142.88, 122.95.

***O*-(*tert*-Butyldimethylsilyl)-2-bromo-2,2-difluoroethanol (1β).**[26]



Imidazole (0.82 g, 12 mmol) and *tert*-butylchlorodimethylsilane (1.81 g, 12 mmol) were added to a stirred solution of 2-bromo-2,2-difluoroethan-1-ol (1.61 g, 10 mmol) in CH_2Cl_2 at 0 °C. The mixture was stirred overnight at room temperature, then diluted with water (15 mL), the organic phase was separated, the aqueous phase was extracted with pentane (3×5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure (400 Torr). The

residue was distilled under vacuum (10 torr) using a Hickman distilling head (oil bath temperature 90 – 110°C). The product was obtained as colourless oil. Yield 2.34 (85 %).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 4.05 (t, *J* = 11.6 Hz, 2H), 0.93 (s, 9H), 0.13 (s, 6H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 121.8 (t, *J* = 307.6 Hz), 69.3 (t, *J* = 26.9 Hz), 25.7, 18.4, -5.3.

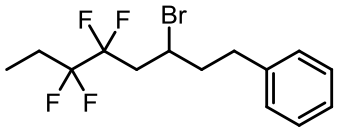
^{19}F NMR (282 MHz, $CDCl_3$), δ: -57.82 (t, *J* = 11.6 Hz).

HRMS (ESI-TOF): calcd for $C_8H_{17}{}^{79}BrF_2OSiAg$ [M+Ag]: 380.9246; found 380.9245.

General procedure for the reaction of bromides 1a-α,γ with alkenes and 1-pentyne in DMSO.

A mixture of tetrabutylammonium bromide (32 mg, 0.1 mmol), IMesCuBr (22 mg, 0.05 mmol) and *fac*-Ir(ppy)$_3$ (0.8 mg, 0.00125 mmol) was evacuated, filled with argon, and dissolved in DMSO (1 mL). The reaction tube was connected to vacuum for 2 minutes upon intensive stirring at room temperature and refilled with argon. Then, bromide (0.6 mmol in case of **1a,p,s,t,α**; 0.75 mmol in case of **1γ**; 0.5 mmol in case of **1u**) and alkene (0.5 mmol in case of **2a-o,r, 8**; 0.65 mmol in case of **2q,u,v,w-z**) [or 1-pentyne (59μL, 0.6 mmol)] were added, the tube was screw-capped and irradiated with 455 nm (12 W) LED strip (for **3a-j,m,o,p,s,γ-ε**) or 400 nm (60 W) LED matrix (for **3k-l,n,q,r,t-β** and 1-pentyne) for 16 hours. The reaction was quenched with water (5 mL) and extracted with hexane (3×3 mL). The combined organic phases were filtered through a short pad of Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified by column chromatography.

(3-Bromo-5,5,6,6-tetrafluorooctyl)benzene (3a).



Yield 159 mg (93%). Yellow oil. Chromatography: CH_2Cl_2. R_f 0.80 (CH_2Cl_2).

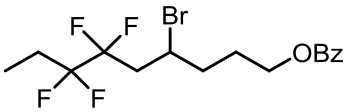
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.37 – 7.28 (m, 2H), 7.28 – 7.18 (m, 3H), 4.29 (dtd, *J* = 9.5, 6.5, 3.9 Hz, 1H), 3.09 – 2.59 (m, 4H), 2.44 – 1.96 (m, 4H), 1.16 (t, *J* = 7.5 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 140.6, 128.66, 128.65, 126.4, 119.2 (tt, *J* = 249.1, 35.6 Hz), 118.3 (tt, *J* = 251.7, 36.5 Hz), 45.61 – 45.44 (m), 40.9, 39.4 (t, *J* = 21.6 Hz), 33.6, 23.2 (t, *J* = 23.5 Hz), 4.9 (t, *J* = 5.1 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -113.7 (ddt, *J* = 264.7, 27.8, 9.2 Hz), -115.7 (ddt, *J* = 264.7, 26.6, 9.2 Hz), -118.1 (tt, *J* = 18.6, 9.2 Hz).

Calcd for $C_{14}H_{17}BrF_4$ (341.19): C 49.28, H 5.02; found: C 49.09, H 5.11.

4-Bromo-6,6,7,7-tetrafluorononyl benzoate (3b).



Yield 166 mg (83%). Pale-yellow oil. Chromatography: hexane/EtOAc (15/1). R_f 0.26 (hexane/EtOAc, 15/1).

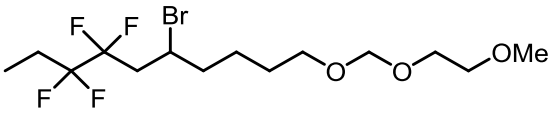
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.04 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 4.45 – 4.31 (m, 3H), 2.93 – 2.51 (m, 2H), 2.24 – 1.89 (m, 6H), 1.09 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.6, 133.1, 130.4, 129.7, 128.5, 120.2 (tt, *J* = 249.0, 35.5 Hz), 118.2 (tt, *J* = 251.7, 36.6 Hz), 64.1, 45.4, 39.5 (t, *J* = 21.7 Hz), 36.02 – 35.64 (m), 26.9, 23.3 (t, *J* = 23.5 Hz), 4.9 (t, *J* = 5.1 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -113.72 (ddt, *J* = 265.4, 27.5, 9.1 Hz), -115.72 (ddt, *J* = 265.4, 26.2, 9.1 Hz), -118.06 (tt, *J* = 18.1, 9.1 Hz).

HRMS (ESI-TOF): calcd for $C_{16}H_{23}{}^{81}BrF_4NO_2$ [M+NH_4]: 418.0823; found 418.0823.

5-Bromo-7,7,8,8-tetrafluoro-1-(methoxymethoxy)decane (3c).



Yield 145 mg (73%). Pale-yellow oil. Chromatography: hexane/EtOAc (15/1). R_f 0.23 (hexane/EtOAc, 15/1).

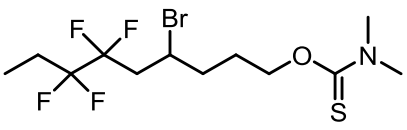
^{1}H NMR (300 MHz, $CDCl_3$), δ: 4.70 (s, 2H), 4.36 – 4.21 (m, 1H), 3.73 – 3.64 (m, 2H), 3.62 – 3.51 (m, 4H), 3.38 (s, 3H), 2.87 – 2.47 (m, 2H), 2.14 – 1.80 (m, 4H), 1.72 – 1.44 (m, 4H), 1.08 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 119.2 (tt, *J* = 249.0, 35.5 Hz), 118.3 (tt, *J* = 251.4, 36.3 Hz), 95.7, 72.0, 67.6, 66.9, 59.1, 46.0 (t, *J* = 2.9 Hz), 39.5 (t, *J* = 21.6 Hz), 39.1, 29.0, 24.2, 23.3 (t, *J* = 23.6 Hz), 4.9 (t, *J* = 5.1 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -114.0 (ddt, *J* = 265.0, 28.9, 9.5 Hz), -115.8 (ddt, *J* = 265.0, 24.7, 9.5 Hz), -118.2 (tt, *J* = 18.1, 9.5 Hz).

HRMS (ESI-TOF): calcd for $C_{14}H_{29}{}^{81}BrF_4NO_3$ [M+NH_4]: 416.1242; found 416.1242.

***O*-(4-Bromo-6,6,7,7-tetrafluorononyl)-dimethylcarbamothioate (3d).**



Yield 157 mg (82%). Yellow oil. Chromatography: hexane/EtOAc (8/1). R_f 0.22 (hexane/EtOAc, 8/1).

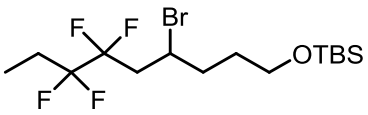
^{1}H NMR (300 MHz, $CDCl_3$), δ: 4.44 (t, *J* = 5.6 Hz, 2H), 4.36 – 4.23 (m, 1H), 3.31 (s, 3H), 3.06 (s, 3H), 2.86 – 2.44 (m, 2H), 2.13 – 1.78 (m, 6H), 1.04 (t, *J* = 7.5 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 188.1, 119.0 (tt, *J* = 249.0, 35.5 Hz), 118.1 (tt, *J* = 251.9, 251.1, 36.3 Hz), 70.4, 45.4 (t, *J* = 2.5 Hz), 42.7, 39.3 (t, *J* = 21.6 Hz), 37.7, 35.7, 26.7, 23.1 (t, *J* = 23.5 Hz), 4.8 (t, *J* = 5.1 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –113.8 (ddt, *J* = 264.9, 27.5, 8.6 Hz), –115.9 (ddt, *J* = 264.9, 25.9, 8.6 Hz), –118.2 (tt, *J* = 17.4, 8.6 Hz).

HRMS (ESI-TOF): calcd for $C_{12}H_{21}{}^{79}BrF_4NOS$ [M+H]: 382.0458; found 382.0448.

[4-Bromo-6,6,7,7-tetrafluorononyl)oxy](*tert*-butyl)dimethylsilane (3e).



Yield 170 mg (83%). Colorless oil. Chromatography: hexane/EtOAc (50/1). R_f 0.37 (hexane/EtOAc, 50/1).

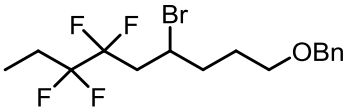
^{1}H NMR (300 MHz, $CDCl_3$), δ: 4.42 – 4.27 (m, 1H), 3.65 (t, *J* = 5.8 Hz, 2H), 2.89 – 2.48 (m, 2H), 2.17 – 1.59 (m, 6H), 1.09 (t, *J* = 7.5 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 6H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 119.2 (tt, *J* = 249.3, 35.5 Hz), 118.3 (tt, *J* = 251.4, 36.4 Hz), 62.2, 46.2 (t, *J* = 2.8 Hz), 39.6 (t, *J* = 21.6 Hz), 36.0, 30.6, 26.0, 23.3 (t, *J* = 23.5 Hz), 18.4, 4.9 (t, *J* = 5.1 Hz), -5.3.

^{19}F NMR (282 MHz, $CDCl_3$), δ: –114.1 (ddt, *J* = 265.1, 27.7, 9.1 Hz), –115.6 (ddt, *J* = 265.1, 25.7, 9.1 Hz), –118.2 (tt, *J* = 18.1, 9.1 Hz).

HRMS (ESI-TOF): calcd for $C_{15}H_{30}{}^{81}BrF_4OSi$ [M+H]: 411.1160; found 411.1154.

{[(4-Bromo-6,6,7,7-tetrafluorononyl)oxy]methyl}benzene (3f).



Yield 164 mg (85%). Colorless oil. Chromatography: hexane/EtOAc (10/1). R_f 0.48 (hexane/EtOAc, 10/1).

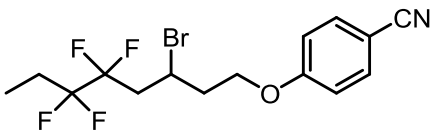
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.44 – 7.25 (m, 5H), 4.53 (s, 2H), 4.37 (dtd, *J* = 8.7, 6.6, 3.8 Hz, 1H), 3.54 (td, *J* = 6.0, 1.0 Hz, 2H), 2.93 – 2.52 (m, 2H), 2.23 – 1.91 (m, 5H), 1.95 – 1.71 (m, 1H), 1.12 (t, *J* = 7.5 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 138.5, 128.5, 127.7, 127.62, 119.2 (tt, *J* = 249.1, 35.5 Hz), 118.2 (tt, *J* = 251.5, 36.2 Hz), 73.0, 69.3, 46.0, 39.5 (t, *J* = 21.6 Hz), 36.2, 27.7, 23.3 (t, *J* = 23.6 Hz), 4.9 (t, *J* = 5.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -114.2 (ddt, *J* = 265.1, 28.5, 9.2 Hz), -115.8 (ddt, *J* = 265.1, 25.4, 9.2 Hz), -118.29 (t, *J* = 18.7, 9.2 Hz).

HRMS (ESI-TOF): calcd for $C_{16}H_{25}{}^{79}BrF_4NO$ [M+NH_4]: 402.1050; found 402.1051.

4-[(3-Bromo-5,5,6,6-tetrafluorooctyl)oxy]benzonitrile (3g).



Yield 141 mg (74%). Pale-yellow oil. Chromatography: hexane/EtOAc (6/1). R_f 0.25 (hexane/EtOAc, 6/1).

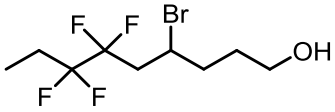
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.57 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.54 (dtd, *J* = 9.8, 6.5, 3.2 Hz, 1H), 4.31 – 4.15 (m, 2H), 2.97 – 2.59 (m, 2H), 2.52 (dddd, *J* = 14.7, 8.4, 6.2, 3.2 Hz, 1H), 2.23 (ddt, *J* = 14.7, 9.8, 4.6 Hz, 1H), 2.03 (tq, *J* = 18.9, 7.6 Hz, 2H), 1.09 (t, *J* = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 161.9, 134.1, 119.2, 119.1 (tt, *J* = 249.1, 35.4 Hz), 118.1 (tt, *J* = 251.6, 36.9 Hz), 115.3, 104.4, 66.0, 42.0 (t, *J* = 3.1 Hz), 39.6 (t, *J* = 21.7 Hz), 38.3, 23.2 (t, *J* = 23.5 Hz), 4.8 (t, *J* = 5.1 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -113.6 (ddt, *J* = 265.1, 28.0, 9.0 Hz), -115.5 (ddt, *J* = 265.1, 25.5, 9.0 Hz), -118.0 (tt, *J* = 17.9, 9.0 Hz).

HRMS (ESI-TOF): calcd for $C_{15}H_{20}{}^{81}BrF_4N_2O$ [M+NH_4]: 401.0670; found 401.0667.

4-Bromo-6,6,7,7-tetrafluorononan-1-ol (3h).



Yield 109 mg (74%). Colorless oil. Chromatography: hexane/EtOAc (3/1). R_f 0.15 (hexane/EtOAc, 3/1).

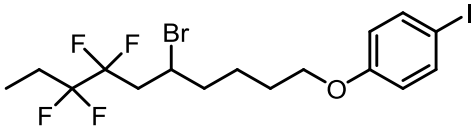
^{1}H NMR (300 MHz, $CDCl_3$), δ: 4.33 (dtd, *J* = 9.7, 6.5, 3.7 Hz, 1H), 3.69 (t, *J* = 6.2 Hz, 2H), 2.90 – 2.49 (m, 2H), 2.19 – 1.61 (m, 6H), 1.53 (s, 1H), 1.08 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 119.1 (tt, *J* = 249.1, 35.3 Hz), 118.2 (tt, *J* = 251.5, 36.5 Hz), 62.0, 45.7 (t, *J* = 2.5 Hz), 39.4 (t, *J* = 21.6 Hz), 35.6, 29.9, 23.2 (t, *J* = 23.5 Hz), 4.93 – 4.69 (m).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -114.1 (ddt, *J* = 264.7, 28.1, 8.5 Hz), -115.8 (ddt, *J* = 264.7, 25.7, 8.5 Hz), -118.2 (tt, *J* = 18.0, 8.5 Hz).

HRMS (ESI-TOF): calcd for $C_9H_{14}{}^{79}BrF_4$ [M-OH]: 277.0210; found 277.0216.

1-[(5-Bromo-7,7,8,8-tetrafluorodecyl)oxy]-4-iodobenzene (3i).



Yield 225 mg (88%). Pale-yellow oil. Chromatography: hexane/EtOAc (20/1). R_f 0.29 (hexane/EtOAc, 20/1). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 8 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 5% water; t_R = 18.1 min).

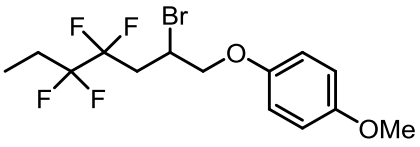
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.55 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.89 Hz, 2H), 4.36 – 4.29 (m, 1H), 3.94 (t, *J* = 6.0 Hz, 2H), 2.70 (m, 2H), 2.16 – 1.56 (m, 8H), 1.10 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 158.9, 138.3, 119.1 (tt, *J* = 249.0, 35.5 Hz), 118.2 (tt, *J* = 251.9, 36.4 Hz), 117.0, 82.7, 67.7, 45.9 (t, *J* = 2.6 Hz), 39.4 (t, *J* = 21.6 Hz), 38.9, 28.4, 24.1, 23.2 (t, *J* = 23.5 Hz), 4.9 (t, *J* = 5.1 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -114.0 (ddt, *J* = 264.9, 28.2, 9.1 Hz), -115.7 (ddt, *J* = 264.9, 26.0, 9.1 Hz), -118.1 (tt, *J* = 18.5, 9.1 Hz).

HRMS (ESI-TOF): calcd for $C_{16}H_{24}{}^{79}BrF_4INO$ [M+NH_4]: 528.0017; found 528.0033.

1-[(2-Bromo-4,4,5,5-tetrafluoroheptyl)oxy]-4-methoxybenzene (3j).



Yield 136 mg (74%). Colorless oil. Chromatography: hexane/EtOAc (20/1). R_f 0.29 (hexane/EtOAc, 20/1).

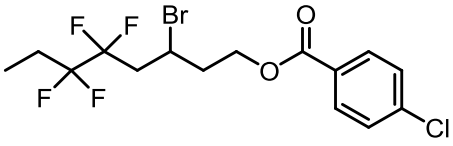
^{1}H NMR (300 MHz, $CDCl_3$), δ: 6.93 – 6.80 (m, 4H), 4.50 (p, *J* = 5.6 Hz, 1H), 4.25 (dd, *J* = 10.4, 5.8 Hz, 1H), 4.18 (dd, *J* = 10.4, 5.8 Hz, 1H), 3.78 (s, 3H), 3.02 (tdd, *J* = 17.4, 17.1, 5.8 Hz, 1H), 2.69 (tdd, *J* = 18.2, 17.1, 5.8 Hz, 1H), 2.06 (tq, *J* = 18.8, 7.6 Hz, 2H), 1.12 (t, *J* = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 154.8, 152.3, 119.2 (tt, *J* = 248.9, 35.3 Hz), 118.3 (tt, *J* = 251.4, 36.3 Hz), 116.4, 114.9, 72.7, 55.8, 40.6 (t, *J* = 3.0 Hz), 35.9 (t, *J* = 21.9 Hz), 23.3 (t, *J* = 23.5 Hz), 4.9 (t, *J* = 5.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -114.7 – -115.2 (m), -117.8 – -118.3 (m).

HRMS (ESI-TOF): calcd for $C_{14}H_{17}{}^{81}BrF_4O_2Na$ [M+Na]: 397.0220; found 397.0218.

3-Bromo-5,5,6,6-tetrafluorooctyl 4-chlorobenzoate (3k).



Yield 157 mg (75%). Pale-yellow oil. Chromatography: hexane/EtOAc (15/1). R_f 0.31 (hexane/EtOAc, 15/1). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 6 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 15% water; t_R = 29.5 min).

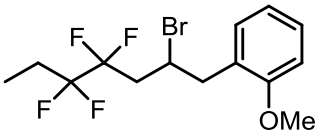
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.95 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 4.65 – 4.40 (m, 3H), 2.99 – 2.35 (m, 3H), 2.33 – 2.15 (m, 1H), 2.03 (tq, *J* = 18.9, 7.5 Hz, 2H), 1.09 (t, *J* = 7.5 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 165.5, 139.7, 131.1, 128.9, 128.5, 119.2 (tt, *J* = 249.1, 35.4 Hz), 118.2 (tt, *J* = 251.7, 37.0 Hz), 63.0, 41.8 (t, *J* = 2.9 Hz), 39.6 (t, *J* = 21.6 Hz), 37.9, 23.2 (t, *J* = 23.5 Hz), 4.9 (t, *J* = 5.1 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -113.2 (ddt, *J* = 265.0, 27.9, 9.0 Hz), -115.6 (ddt, *J* = 265.0, 25.5, 9.0 Hz), -117.9 (tt, *J* = 18.9, 9.0 Hz).

HRMS (ESI-TOF): calcd for $C_{15}H_{16}{}^{81}Br^{37}ClF_4O_2Na$ [M+Na]: 444.9801; found 444.9803.

1-(2-Bromo-4,4,5,5-tetrafluoroheptyl)-2-methoxybenzene (3l).



Yield 161 mg (90%). Colorless oil. Chromatography: hexane/EtOAc (20/1). R_f 0.43 (hexane/EtOAc, 20/1). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 8 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 10% water; t_R = 14.0 min).

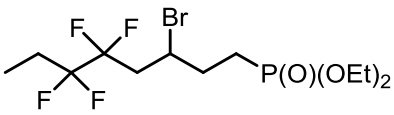
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.35 – 7.35 (m, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 6.99 – 6.86 (m, 2H), 4.67 (p, *J* = 6.1 Hz, 1H), 3.85 (s, 3H), 3.40 (dd, *J* = 14.0, 5.9 Hz, 1H), 3.16 (dd, *J* = 14.0, 6.1 Hz, 1H), 2.77 (dd, *J* = 18.0, 6.1 Hz, 1H), 2.71 (dd, *J* = 18.0, 6.1 Hz, 1H), 2.04 (tq, *J* = 18.7, 7.6 Hz, 2H), 1.11 (t, *J* = 7.6 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 157.7, 131.5, 128.7, 126.4, 120.5, 119.3 (tt, *J* = 248.9, 35.4 Hz), 118.3 (tt, *J* = 251.4, 36.1 Hz), 110.6, 55.3, 44.3 (t, *J* = 2.7 Hz), 41.4, 38.9 (t, *J* = 21.7 Hz), 23.3 (t, *J* = 23.6 Hz), 4.9 (t, *J* = 5.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -115.2 (s), -118.5 (s).

HRMS (ESI-TOF): calcd for $C_{14}H_{21}{}^{81}BrF_4NO$ [M+NH_4]: 376.0717; found 376.0719.

Diethyl (3-bromo-5,5,6,6-tetrafluorooctyl)phosphonate (3m).



Yield 162 mg (81%). Pale-yellow oil. Chromatography: hexane/EtOAc (1/1). R_f 0.15 (hexane/EtOAc, 1/1).

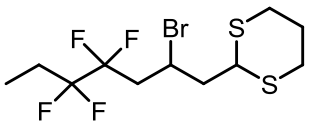
^{1}H NMR (300 MHz, $CDCl_3$), δ: 4.40 – 4.26 (m, 1H), 4.21 – 3.99 (m, 4H), 2.88 – 2.45 (m, 2H), 2.38 – 2.18 (m, 1H), 2.17 – 1.76 (m, 5H), 1.31 (t, *J* = 7.1 Hz, 6H), 1.07 (t, *J* = 7.5 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 118.9 (tt, *J* = 249.0, 35.5 Hz), 117.9 (tt, *J* = 252.2, 36.5 Hz), 61.6 (dd, *J* = 6.6, 3.6 Hz), 45.54 (dt, *J* = 19.2, 2.9 Hz), 38.9 (t, *J* = 21.7 Hz), 32.3 (t, *J* = 2.9 Hz), 24.7, 23.0 (t, *J* = 23.5 Hz), 22.8, 16.3, 16.2, 4.6 (t, *J* = 5.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -114.0 (ddt, *J* = 264.8, 27.6, 10.1 Hz), -115.6 (dt, *J* = 264.8, 25.3, 10.1 Hz), -118.1 (tt, *J* = 18.6, 10.1 Hz).

HRMS (ESI-TOF): calcd for $C_{12}H_{22}{}^{81}BrF_4O_3PNa$ [M+Na]: 425.0298; found 425.0290.

2-(2-Bromo-4,4,5,5-tetrafluoroheptyl)-1,3-dithiane (3n).



Yield 129 mg (70%). Yellow oil. Chromatography: hexane/EtOAc (8/1). R_f 0.45 (hexane/EtOAc, 8/1). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 6 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 10% water; t_R = 16.6 min).

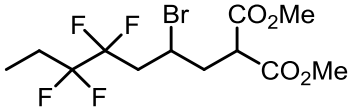
^{1}H NMR (300 MHz, $CDCl_3$), δ: 4.55 (dddd, *J* = 10.8, 8.3, 5.7, 3.0 Hz, 1H), 4.22 (dd, *J* = 10.8, 3.7 Hz, 1H), 2.97 – 2.49 (m, 6H), 2.48 – 2.36 (m, 1H), 2.28 – 1.82 (m, 5H), 1.07 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 119.1 (tt, *J* = 249.3, 35.6 Hz), 118.1 (tt, *J* = 251.8, 36.7, 36.7 Hz), 44.7, 44.2, 42.6 (t, *J* = 2.5 Hz), 39.5 (t, *J* = 21.6 Hz), 29.7, 28.9, 25.9, 23.2 (t, *J* = 23.4 Hz), 4.9 (t, *J* = 5.1 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -112.0 (ddt, *J* = 265.6, 28.6, 9.0 Hz), -114.5 (ddt, *J* = 265.6, 26.2, 9.0 Hz), -117.2 (tt, *J* = 18.1, 9.0 Hz).

HRMS (ESI-TOF): calcd for $C_{11}H_{18}{}^{81}BrF_4S_2$ [M+H]: 370.9943; found 370.9946.

Dimethyl 2-(2-bromo-4,4,5,5-tetrafluoroheptyl)malonate (3o).



Yield 154 mg (81%). Colorless oil. Chromatography: hexane/EtOAc (10/1). R_f 0.17 (hexane/EtOAc, 10/1).

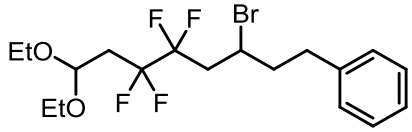
^{1}H NMR (300 MHz, $CDCl_3$), δ: 4.35 – 4.22 (m, 1H), 3.82 (dd, *J* = 10.4, 3.9 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 2.91 – 2.51 (m, 3H), 2.29 (ddd, *J* = 15.0, 11.2, 3.9 Hz, 1H), 2.02 (tq, *J* = 18.9, 7.6 Hz, 2H), 1.08 (t, *J* = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 169.0, 168.8, 119.1 (tt, *J* = 248.9, 35.5 Hz), 118.80 (tt, *J* = 251.7, 36.7 Hz), 52.85, 52.79, 50.3, 43.0 (t, *J* = 2.6 Hz), 39.6 (t, *J* = 21.7 Hz), 38.1, 23.1 (t, *J* = 23.4 Hz), 4.8 (t, *J* = 5.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -113.6 (ddt, *J* = 265.0, 27.2, 10.4 Hz), -115.3 (ddt, *J* = 265.0, 25.8, 10.4 Hz), -117.9 – -118.2 (m).

HRMS (ESI-TOF): calcd for $C_{12}H_{21}{}^{81}BrF_4NO_4$ [M+NH_4]: 400.0565; found 400.0567.

(3-Bromo-8,8-diethoxy-5,5,6,6-tetrafluorooctyl)benzene (3p).



Yield 176 mg (82%). Colorless oil. Chromatography: hexane/EtOAc (20/1). R_f 0.21 (hexane/EtOAc, 20/1).

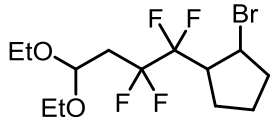
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.37 – 7.26 (m, 2H), 7.26 – 7.16 (m, 3H), 4.90 (t, *J* = 5.3 Hz, 1H), 4.33 – 4.20 (m, 1H), 3.70 (dq, *J* = 9.1, 7.1 Hz, 2H), 3.57 (dq, *J* = 9.0, 7.1 Hz, 2H), 3.02 – 2.53 (m, 4H), 2.48 – 2.07 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 140.4, 128.62, 128.58, 126.3, 117.9 (tt, *J* = 250.6, 35.4 Hz), 117.7 (tt, *J* = 250.6, 35.4 Hz), 97.3 (t, *J* = 3.6 Hz), 61.70, 61.67, 45.2 (t, *J* = 2.8 Hz), 40.8, 39.0 (t, *J* = 21.3 Hz), 34.6 (t, *J* = 21.1 Hz), 33.5, 15.2.

^{19}F NMR (282 MHz, $CDCl_3$), δ: -113.7 (ddt, *J* = 266.2, 28.4, 9.5 Hz), -114.77 – -115.16 (m), -115.6 (ddt, *J* = 266.2, 26.1, 9.5 Hz).

HRMS (ESI-TOF): calcd for $C_{18}H_{25}{}^{79}BrF_4O_2Na$ [M+Na]: 451.0866; found 451.0861.

1-Bromo-2-(4,4-diethoxy-1,1,2,2-tetrafluorobutyl)cyclopentane (3q).



Yield 82 mg (45%). Pale-yellow oil. Chromatography: hexane/EtOAc (20/1). R_f 0.33 (hexane/EtOAc, 20/1). Mixture of isomers in a ratio of 88:12 detected by GC-MS analysis.

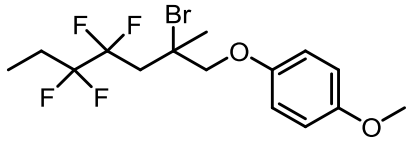
^{1}H NMR (300 MHz, $CDCl_3$), δ: 4.89 (t, *J* = 5.1 Hz, 1H), 4.54 (q, *J* = 4.6 Hz, 1H), 3.66 (dq, *J* = 9.3, 7.1 Hz, 2H), 3.54 (dq, *J* = 9.1, 7.1 Hz, 2H), 3.24 – 3.01 (m, 1H), 2.38 (td, *J* = 19.1, 5.1 Hz, 2H), 2.17 – 1.99 (m, 2H), 1.99 – 1.64 (m, 4H), 1.21 (t, *J* = 7.1 Hz, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 118.8 (tt, *J* = 252.4, 34.8 Hz), 118.4 (tt, *J* = 251.8, 36.2 Hz), 97.4 (t, *J* = 3.7 Hz), 61.76, 61.75, 51.8 (dd, *J* = 22.5, 20.3 Hz), 48.1 (tt, *J* = 3.6, 1.3 Hz), 39.1, 35.4 (t, *J* = 21.3 Hz), 26.76 – 26.31 (m), 24.6, 15.3.

^{19}F NMR (282 MHz, $CDCl_3$), δ: -113.0 (dd, *J* = 19.1, 8.7 Hz), -113.2 (dd, *J* = 19.1, 8.7 Hz), -116.7 (ddd, *J* = 270.9, 12.8, 8.7 Hz), -121.0 (ddd, *J* = 270.9, 20.2, 8.7 Hz).

HRMS (ESI-TOF): calcd for $C_{13}H_{25}{}^{81}BrF_4NO_2$ [M+NH_4]: 384.0979; found 384.0983.

1-[(2-Bromo-4,4,5,5-tetrafluoro-2-methylheptyl)oxy]-4-methoxybenzene (3r).



Yield 114 mg (59%). Colorless oil. Chromatography: hexane/EtOAc (20/1). R_f 0.25 (hexane/EtOAc, 20/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 6.97 – 6.77 (m, 4H), 4.20 (d, *J*

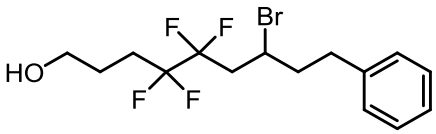
= 9.9 Hz, 1H), 4.13 (d, *J* = 9.9 Hz, 1H), 3.78 (s, 3H), 3.20 – 2.89 (m, 1H), 2.95 – 2.70 (m, 1H), 2.04 (s, 3H), 2.16 – 1.90 (m, 2H), 1.10 (t, *J* = 7.5 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 154.6, 152.6, 119.1 (tt, *J* = 250.0, 35.5 Hz), 118.9 (tt, *J* = 253.1, 35.3 Hz), 116.3, 114.9, 77.44 (t, *J* = 2.1 Hz), 59.6, 55.8, 39.9 (t, *J* = 20.5 Hz), 29.2 (t, *J* = 2.5 Hz), 23.1 (t, *J* = 23.6 Hz), 4.9 (t, *J* = 5.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -114.1 (s), -118.4 (s).

HRMS (ESI-TOF): calcd for $C_{15}H_{19}{}^{81}BrF_4O_2$ $[M^+]$: 388.0479; found 388.0475.

6-Bromo-3,3,4,4-tetrafluoro-8-phenyloctan-1-ol (3s).



Yield 169 mg (91%). Colorless solid. Mp 39 – 42°C. Chromatography: hexane/EtOAc (3/1). R_f 0.33 (hexane/EtOAc, 3/1).

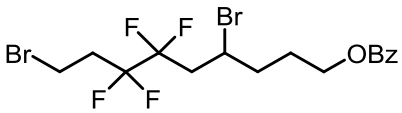
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.43 – 7.32 (m, 2H), 7.32 – 7.22 (m, 3H), 4.31 (dtd, *J* = 9.6, 6.5, 3.7 Hz, 1H), 3.72 (t, *J* = 6.2 Hz, 2H), 3.08 – 2.58 (m, 4H), 2.43 – 2.05 (m, 4H), 1.95 – 1.80 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 140.5, 128.62, 128.60, 126.3, 119.1 (tt, *J* = 249.2, 35.7 Hz), 118.1 (tt, *J* = 251.5, 36.0 Hz), 61.7, 45.4 (t, *J* = 2.8 Hz), 40.8, 39.3 (t, *J* = 21.3 Hz), 33.5, 26.3 (t, *J* = 22.8 Hz), 23.8 (t, *J* = 3.6 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -112.7 (ddt, *J* = 264.4, 28.8, 8.3 Hz), -114.4 (ddt, *J* = 264.4, 26.6, 8.3 Hz), -115.2 (tt, *J* = 17.9, 8.3 Hz).

HRMS (ESI-TOF): calcd for $C_{15}H_{23}{}^{81}BrF_4NO$ $[M+NH_4]$: 390.0874; found 390.0874.

4,9-Dibromo-6,6,7,7-tetrafluorononyl benzoate (3t).



Yield 182 mg (76%). Pale-yellow oil. Chromatography: hexane/EtOAc (15/1). R_f 0.17 (hexane/EtOAc, 15/1).

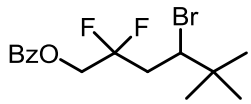
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.08 – 7.99 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (dd, *J* = 7.3, 6.9 Hz, 2H), 4.42 – 4.28 (m, 3H), 3.47 (dd, *J* = 8.8, 7.5 Hz, 2H), 2.92 – 2.50 (m, 4H), 2.22 – 1.88 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 166.6, 133.1, 130.3, 129.7, 128.5, 117.9 (tt, *J* = 251.1, 35.5 Hz), 117.8 (tt, *J* = 251.3, 36.3 Hz), 64.0, 44.8 (t, *J* = 2.8 Hz), 39.1 (t, *J* = 21.3 Hz), 35.9, 34.1 (t, *J* = 22.4 Hz), 26., 21.4 (tt, *J* = 5.4, 1.8 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -113.4 (ddt, *J* = 265.9, 27.8, 9.1 Hz), -115.3 (ddt, *J* = 265.9, 25.0, 9.1 Hz), -115.7 (t, *J* = 19.9, 9.1 Hz).

HRMS (ESI-TOF): calcd for $C_{16}H_{18}{}^{81}Br_2F_4O_2Na$ [M+Na]: 502.9462; found 502.9460.

4-Bromo-2,2-difluoro-5,5-dimethylhexyl benzoate (3u).



Yield 127 mg (73%). Colorless oil. Chromatography: hexane/EtOAc (15/1). R_f 0.26 (hexane/EtOAc, 15/1).

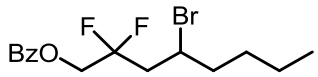
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.07 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 7.6, 7.2 Hz, 1H), 4.68 (dd, *J* = 11.3, 3.0 Hz, 1H), 4.63 (dd, *J* = 11.3, 5.3 Hz, 1H), 4.04 (d, *J* = 9.0 Hz, 1H), 2.86 – 2.52 (m, 2H), 1.09 (s, 9H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 165.5, 133.6, 129.9, 129.2, 128.6, 121.1 (t, *J* = 243.7 Hz), 64.0 (dd, *J* = 34.8, 30.9 Hz), 58.5 (dd, *J* = 6.4, 3.2 Hz), 40.0 (dd, *J* = 24.9, 23.5 Hz), 36.2, 27.1.

^{19}F NMR (282 MHz, $CDCl_3$), δ: -101.2 (dtt, *J* = 257.4, 15.5, 11.3 Hz), -105.7 (dtt, *J* = 257.4, 15.5, 11.3 Hz).

HRMS (ESI-TOF): calcd for $C_{15}H_{23}{}^{81}BrF_2NO_2$ [M+NH_4]: 368.0855; found 368.0855.

4-Bromo-2,2-difluorooctyl benzoate (3v).



Yield 143 mg (82%). Colorless oil. Chromatography: hexane/EtOAc (20/1). R_f 0.30 (hexane/EtOAc, 20/1).

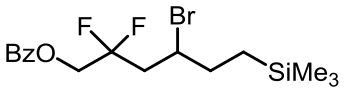
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.07 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.47 (dd, *J* = 7.6, 7.2 Hz, 2H), 4.57 (dd, *J* = 13.2, 12.1 Hz, 2H), 4.27 (p, *J* = 6.3 Hz, 1H), 2.88 – 2.48 (m, 2H), 2.04 – 1.79 (m, 2H), 1.66 – 1.20 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 165.5, 133.7, 130.0, 129.1, 128.7, 120.7 (t, *J* = 244.3 Hz), 64.3 (dd, *J* = 34.4, 32.2 Hz), 47.0 (t, *J* = 4.1 Hz), 43.6 (t, *J* = 23.6 Hz), 39.3 (d, *J* = 1.5 Hz), 29.5, 22.0, 14.0.

^{19}F NMR (282 MHz, $CDCl_3$), δ: -100.9 (dm, *J* = 258.9 Hz), -106.1 (dm, *J* = 258.9 Hz).

HRMS (ESI-TOF): calcd for $C_{15}H_{19}{}^{79}BrF_2O_2Na$ [M+Na]: 371.0429; found 371.0422.

4-Bromo-2,2-difluoro-6-(trimethylsilyl)hexyl benzoate (3w).



Yield 157 mg (80%). Colorless oil. Chromatography: hexane/EtOAc (20/1). R_f 0.28 (hexane/EtOAc, 20/1).

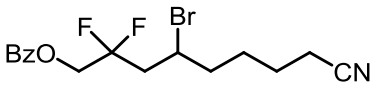
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.07 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 7.6, 7.2 Hz, 2H), 4.58 (dd, *J* = 13.8, 11.6 Hz, 2H), 4.25 (p, *J* = 6.2 Hz, 1H), 2.85 – 2.52 (m, 2H), 2.03 – 1.77 (m, 2H), 0.92 – 0.54 (m, 2H), 0.01 (s, 9H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 165.5, 133.7, 130.0, 129.1, 128.7, 120.8 (t, *J* = 244.1 Hz), 64.3 (dd, *J* = 34.4, 32.2 Hz), 50.3 (t, *J* = 4.1 Hz), 42.7 (t, *J* = 23.7 Hz), 34.4, 14.2, -1.7.

^{19}F NMR (282 MHz, $CDCl_3$), δ: -101.7 (dm, *J* = 257.8 Hz), -106.7 (dm, *J* = 257.8 Hz).

HRMS (ESI-TOF): calcd for $C_{16}H_{27}{}^{81}BrF_2NO_2Si$ [M+NH_4]: 412.0937; found 412.0922.

4-Bromo-8-cyano-2,2-difluorooctyl benzoate (3x).



Yield 138 mg (74%). Pale-yellow oil. Chromatography: hexane/EtOAc (4/1). R_f 0.26 (hexane/EtOAc, 4/1).

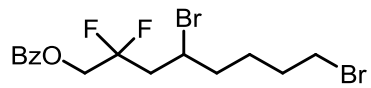
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.11 – 8.01 (m, 2H), 7.67 – 7.55 (m, 1H), 7.53 – 7.41 (m, 2H), 4.55 (dd, *J* = 13.4, 11.4 Hz, 2H), 4.26 (dtd, *J* = 8.6, 6.5, 3.9 Hz, 1H), 2.89 – 2.47 (m, 2H), 2.39 – 2.32 (m, 2H), 2.07 – 1.82 (m, 2H), 1.82 – 1.55 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 165.4, 133.8, 129.9, 129.0, 128.7, 120.6 (t, *J* = 244.5 Hz), 119.4, 64.3 (t, *J* = 33.4 Hz), 46.0 (t, *J* = 3.9 Hz), 43.4 (t, *J* = 23.5 Hz), 38.4, 26.6, 24.7, 17.2.

^{19}F NMR (282 MHz, $CDCl_3$), δ: -102.0 (ddtd, *J* = 257.4, 21.2, 12.1, 10.9 Hz), -107.2 (ddtd, *J* = 257.4, 20.2, 12.1, 11.0 Hz).

HRMS (ESI-TOF): calcd for $C_{16}H_{22}{}^{79}BrF_2N_2O_2$ [M+NH_4]: 391.0827; found 391.0822.

4,8-Dibromo-2,2-difluorooctyl benzoate (3y).



Yield 150 mg (70%). Colorless oil. Chromatography: hexane/EtOAc (15/1). R_f 0.25 (hexane/EtOAc, 15/1). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 8 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 20% water; t_R = 23.7 min).

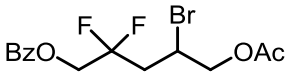
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.06 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.48 (dd, *J* = 7.7, 7.3 Hz, 2H), 4.56 (dd, *J* = 13.4, 11.5 Hz, 2H), 4.27 (dtd, *J* = 12.9, 6.5, 4.2 Hz, 1H), 3.41 (t, *J* = 6.6 Hz, 2H), 2.89 – 2.48 (m, 2H), 2.07 – 1.51 (m, 6H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 165.4, 133.8, 130.0, 129.0, 128.7, 120.7 (t, *J* = 244.3 Hz), 64.3 (dd, *J* = 34.5, 32.3 Hz), 46.3 (t, *J* = 4.0 Hz), 43.5 (t, *J* = 23.4 Hz), 38.5, 33.2, 31.9, 26.1.

^{19}F NMR (282 MHz, $CDCl_3$), δ: -102.1 (ddtd, *J* = 257.8, 23.2, 12.8, 11.7 Hz), -107.1 (ddtd, *J* = 257.8, 22.4, 12.8, 11.6 Hz).

HRMS (ESI-TOF): calcd for $C_{15}H_{22}{}^{79}Br_2F_2NO_2$ [M+NH_4]: 443.9980; found 443.9994.

5-Acetoxy-4-bromo-2,2-difluoropentyl benzoate (3z).



Yield 128 mg (70%). Colorless oil. Chromatography: hexane/EtOAc (6/1). R_f 0.20 (hexane/EtOAc, 6/1).

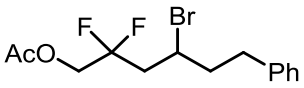
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.05 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 4.56 (dd, *J* = 13.5, 11.5 Hz, 2H), 4.42 – 4.31 (m, 3H), 2.80 – 2.58 (m, 2H), 2.07 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 170.2, 165.3, 133.8, 129.9, 128.9, 128.7, 120.4 (t, *J* = 244.5 Hz), 67.3, 64.1 (dd, *J* = 34.2, 32.7 Hz), 40.6 (t, *J* = 4.2 Hz), 39.9 (t, *J* = 24.0 Hz), 20.7.

^{19}F NMR (282 MHz, $CDCl_3$), δ: -102.7 (ddtd, *J* = 258.2, 19.8, 12.9, 12.9, Hz), -106.3 (ddtd, *J* = 258.2, 19.1, 12.9, 12.0 Hz).

HRMS (ESI-TOF): calcd for $C_{14}H_{15}{}^{81}BrF_2O_4Na$ [M+Na]: 388.9994; found 388.9999.

4-Bromo-2,2-difluoro-6-phenylhexyl acetate (3α).



Yield 134 mg (80%). Colorless oil. Chromatography: hexane/EtOAc (10/1). R_f 0.23 (hexane/EtOAc, 10/1).

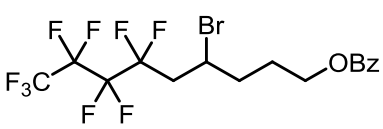
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.37 – 7.27 (m, 2H), 7.27 – 7.18 (m, 3H), 4.28 (dd, *J* = 14.3, 11.2 Hz, 2H), 4.24 – 4.12 (m, 1H), 3.02 – 2.44 (m, 4H), 2.33 – 2.15 (m, 2H), 2.13 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 169.8, 140.5, 128.7, 128.6, 126.4, 120.5 (t, *J* = 244.3 Hz), 64.0 (dd, *J* = 34.0, 32.2 Hz), 46.2 (t, *J* = 4.2 Hz), 43.4 (t, *J* = 23.5 Hz), 41.0, 33.6, 20.6.

^{19}F NMR (282 MHz, $CDCl_3$), δ: -101.1 (ddtd, *J* = 259.4, 21.1, 12.4. 11.8 Hz), -107.02 (ddtd, *J* = 259.4, 13.5, 12.4, 12.1 Hz).

HRMS (ESI-TOF): calcd for $C_{14}H_{17}{}^{81}BrF_2O_2Na$ [M+Na]: 359.0252; found 359.0261.

4-Bromo-6,6,7,7,8,8,9,9,9-nonafluorononyl benzoate (3γ).



Yield 225 mg (92%). Colorless oil. Chromatography: hexane/EtOAc (10/1). R_f 0.13 (hexane/EtOAc, 10/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.07 – 8.01 (m, 2H), 7.61 – 7.52

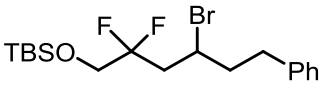
(m, 1H), 7.49 – 7.40 (m, 2H), 4.43 – 4.31 (m, 3H), 2.98 – 2.58 (m, 2H), 2.22 – 1.89 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 166.6, 133.1, 130.2, 129.7, 128.5, 117.4 (qt, *J* = 288.4, 33.4 Hz), 117.3 (tt, *J* = 257.5, 31.1 Hz), 110.2 (ttt, *J* = 265.7, 37.1, 31.1 Hz), 110.2 (tqt, *J* = 269.0, 37.1, 33.4 Hz), 63.9, 43.6 (t, *J* = 2.8 Hz), 40.0 (t, *J* = 20.9 Hz), 35.8, 26.8.

^{19}F NMR (282 MHz, $CDCl_3$), δ: -81.9 (s, 3F), -113.2 (ddd, *J* = 271.8, 26.2, 12.6 Hz, 1F), -115.0 (ddd, *J* = 273.7, 22.1, 10.8 Hz, 1F), -125.3 (s, 2F), -126.7 (s, 2F).

HRMS (ESI-TOF): calcd for $C_{16}H_{18}{}^{81}BrF_9NO_2$ [M+NH_4]: 508.0351; found 508.0358.

[(4-Bromo-2,2-difluoro-6-phenylhexyl)oxy](tert-butyl)dimethylsilane (3β).



Tetrabutylammonium bromide (53 mg, 0.165 mmol), triphenylphosphine (26 mg, 0.1 mmol), IMesCuBr (22 mg, 0.05 mmol) and *fac*-Ir(ppy)$_3$ (0.8 mg, 0.00125 mmol) were dissolved in DMSO (1 mL). The reaction tube was connected to vacuum for 2 minutes upon intensive stirring at room temperature and refilled with argon. Then, bromide **1β** (165 mg, 0.6 mmol) and alkene **2b** (66 mg, 0.5 mmol) were added, the tube was screw-capped and irradiated with 400 nm (60 W) LED matrix for 24 hours. The reaction was quenched with water (5 mL) and extracted with hexane (3×3 mL). The combined organic phases were filtered through a short pad of Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified by column chromatography.

Yield 196 mg (96%). Pale-yellow oil. Chromatography: hexane/EtOAc (50/1). R_f 0.25 (hexane/EtOAc, 50/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.38 – 7.30 (m, 2H), 7.29 – 7.23 (m, 3H), 4.27 (dtd, *J* = 9.9, 6.6, 3.7 Hz, 1H), 3.76 (dd, *J* = 14.5, 10.3 Hz, 2H), 3.04 – 2.47 (m, 4H), 2.37 – 2.11 (m, 2H), 0.95 (s, 9H), 0.12 (s, 6H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 140.8, 128.7, 126.3, 122.3 (t, *J* = 244.6 Hz), 64.7 (dd, *J* = 34.7, 33.2 Hz), 47.2 (t, *J* = 4.2 Hz), 42.7 (t, *J* = 23.5 Hz), 41.0, 33.7, 25.8, 18.3, -5.4.

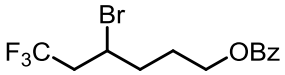
^{19}F NMR (282 MHz, $CDCl_3$), δ: -103.0 (ddtd, *J* = 252.5, 22.2, 12.2, 12.1 Hz), -107.5 (ddq, *J* = 251.4, 20.8, 12.2, 11.7 Hz).

HRMS (ESI-TOF): calcd for $C_{18}H_{29}{}^{79}BrF_2OSiNa$ [M+Na]: 429.1031; found 429.1021.

General procedure for the reaction of CF_3Br with alkenes in acetonitrile.

A mixture of triphenylphosphine (26 mg, 0.1 mmol), IMesCuBr (22 mg, 0.05 mmol) and *fac*-$Ir(ppy)_3$ (0.8 mg, 0.00125 mmol) was evacuated, filled with argon, and dissolved in acetonitrile (1 mL). The reaction tube was cooled to –20 °C, briefly connected to vacuum (2×30 seconds) upon intensive stirring and refilled with argon. Then alkene (**2b** or **2ε**, 0.5 mmol) was added. The mixture was cooled to –92 °C (acetone/liq. nitrogen) and gaseous bromotrifluoromethane (*ca.* 24 mL, 1 mmol) was gradually injected to the frozen mixture via cannula. Then, the tube was screw-capped and irradiated with a 455 nm LED strip (12 W) for 16 hours. The reaction was quenched with water (5 mL) and extracted with hexane (3×3 mL). The combined organic phases were filtered through a short pad of Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified by column chromatography.

4-Bromo-6,6,6-trifluorohexyl benzoate (3δ).



Yield 148 mg (87%). Colorless oil. Chromatography: hexane/EtOAc (10/1). R_f 0.31 (hexane/EtOAc, 10/1).

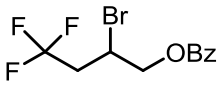
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.04 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 4.35 (dd, *J* = 6.3, 4.5 Hz, 2H), 4.22 (qd, *J* = 6.9, 3.2 Hz, 1H), 2.91 – 2.60 (m, 2H), 2.16 – 1.85 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.5, 133.1, 130.2, 129.6, 128.5, 125.3 (q, *J* = 278.2 Hz), 63.8, 44.3 (q, *J* = 3.4 Hz), 43.2 (q, *J* = 28.5 Hz), 35.2, 26.7.

^{19}F NMR (282 MHz, $CDCl_3$), δ: -64.7 (t, *J* = 10.2 Hz).

HRMS (ESI-TOF): calcd for $C_{13}H_{18}{}^{79}BrF_3NO_2$ [M+NH_4]: 356.0468; found 356.0474.

2-Bromo-4,4,4-trifluorobutyl benzoate (3ε).



Yield 109 mg (70%). Colorless oil. Chromatography: hexane/EtOAc (15/1). R_f 0.31 (hexane/EtOAc, 15/1).

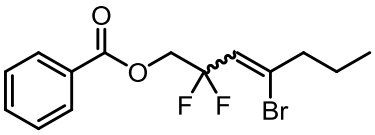
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.07 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (dd, *J* = 8.3, 7.0 Hz, 2H), 4.63 (dd, *J* = 12.2, 6.0 Hz, 1H), 4.57 (dd, *J* = 12.5, 6.1 Hz, 1H), 4.47 – 4.36 (m, 1H), 3.03 – 2.71 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 165.8, 133.7, 129.9, 129.3, 128.7, 125.2 (q, *J* = 277.7 Hz), 67.1, 40.0 (q, *J* = 29.5 Hz), 39.3 (q, *J* = 3.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -64.1 (t, *J* = 9.9 Hz).

HRMS (ESI-TOF): calcd for $C_{11}H_{10}{}^{81}BrF_3O_2Na$ [M+Na]: 334.9688; found 334.9684.

4-Bromo-2,2-difluorohept-3-en-1-yl benzoate (5). Two isomers were separated in a combined yield of 21%.



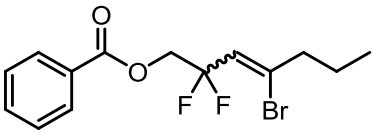
Major isomer. Yield 22 mg (13%). Colorless oil. Chromatography: hexane/EtOAc (25/1). R_f 0.14 (hexane/EtOAc, 25/1). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 6 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 10% water; t_R = 17.8 min).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.10 – 8.03 (m, 2H), 7.66 – 7.55 (m, 1H), 7.52 – 7.42 (m, 2H), 6.13 (t, *J* = 12.8 Hz, 1H), 4.54 (t, *J* = 12.8 Hz, 2H), 2.67 (tt, *J* = 7.3, 1.7 Hz, 2H), 1.67 (h, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 165.6, 140.0, 133.8, 130.1, 129.1, 128.7, 124.5 (t, *J* = 25.7 Hz), 119.4 (d, *J* = 243.9 Hz), 64.9 (t, *J* = 33.1 Hz), 39.4, 21.9, 13.1.

^{19}F NMR (282 MHz, $CDCl_3$), δ: -98.0 (qt, *J* = 12.8, 1.7 Hz).

HRMS (ESI-TOF): calcd for $C_{14}H_{15}{}^{79}BrF_2O_2Na$ [M+Na]: 355.0116; found 355.0119.



Minor isomer. Yield 13 mg (8%). Colorless oil. Chromatography: hexane/EtOAc (25/1). R_f 0.19 (hexane/EtOAc, 25/1). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 6 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 10% water; t_R = 21.0 min).

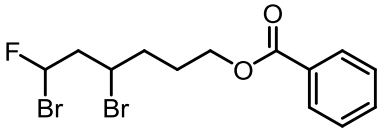
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.11 – 8.03 (m, 2H), 7.65 – 7.55 (m, 1H), 7.52 – 7.40 (m, 2H), 6.10 (t, *J* = 11.7 Hz, 1H), 4.75 (t, *J* = 13.1 Hz, 2H), 2.51 (t, *J* = 7.5 Hz, 2H), 1.63 (h, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 165.7, 135.5 (t, *J* = 9.4 Hz), 133.6, 130.1, 129.3, 128.6, 122.4 (t, *J* = 29.5 Hz), 119.2 (d, *J* = 242.1 Hz), 64.0 (t, *J* = 32.2 Hz), 44.9, 21.2, 12.8.

^{19}F NMR (282 MHz, $CDCl_3$), δ: -99.1 (tdt, *J* = 13.1, 11.7, 2.0 Hz).

HRMS (ESI-TOF): calcd for $C_{14}H_{15}{}^{79}BrF_2O_2Na$ [M+Na]: 355.0116; found 355.0111.

4,6-Dibromo-6-fluorohexyl benzoate (6). Mixture of isomers in a ratio of 1.5 : 1.



Triphenylphosphine (26 mg, 0.1 mmol), IMesCuBr (22 mg, 0.05 mmol) and *fac*-Ir(ppy)$_3$ (0.8 mg, 0.00125 mmol) were dissolved in acetonitrile (1 mL). The reaction tube was cooled to –20 °C, briefly connected to vacuum (2×30 seconds) upon intensive stirring and refilled with argon.

Then, dibromofluoromethane (60 μL, 0.75 mmol) and alkene **2b** (95 mg, 0.5 mmol) were added, the tube was screw-capped and irradiated with 400 nm (60 W) LED matrix for 16 hours. The reaction was quenched with water (5 mL) and extracted with hexane (3×3 mL). The combined organic phases were filtered through a short pad of Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified by column chromatography.

Yield 112 mg (59%). Colorless oil. Chromatography: hexane/EtOAc (15/1). R_f 0.22 (hexane/EtOAc, 15/1). Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 6 mL·min^{-1}; mobile phase: isocratic, acetonitrile/water, 10% water; t_R = 16.4 min).

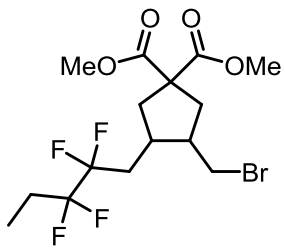
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.07 – 8.00 (m, 2H, both isomers), 7.62 – 7.53 (m, 1H, both isomers), 7.50 – 7.40 (m, 2H, both isomers), 6.74 (ddd, *J* = 51.1, 9.3, 2.2 Hz, 1H, major), 6.72 (ddd, *J* = 49.4, 7.9, 4.0 Hz, minor), 4.44 – 4.30 (m, 2H, both isomers), 4.24 – 4.08 (m, 1H, both isomers), 2.91 – 2.46 (m, 2H, both isomers), 2.14 – 1.89 (m, 4H, both isomers).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.6 (both isomers), 133.2 (both isomers), 130.2 (both isomers), 129.69 (minor), 129.68 (major), 128.5 (both isomers), 95.1 (d, *J* = 250.8 Hz, minor), 92.0 (d, *J* = 252.1 Hz, major), 64.04 (minor), 64.01 (major), 50.55 – 50.47 (m, both isomers), 50.3 (d, *J* = 16.9 Hz, major), 48.5 (d, *J* = 20.9 Hz, minor), 35.7 (major), 35.5 (minor), 26.9 (minor), 26.7 (major).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -132.8 (ddd, *J* = 49.4, 12.7, 9.2 Hz, minor), -138.5 (ddd, *J* = 51.1, 34.9, 10.6 Hz, major).

HRMS (ESI-TOF): calcd for $C_{13}H_{15}{}^{81}Br_2FO_2Na$ [M+Na]: 406.9275; found 406.9265.

Dimethyl 3-(bromomethyl)-4-(2,2,3,3-tetrafluoropentyl)cyclopentane-1,1-dicarboxylate (9).



Yield 169 mg (80%). Colorless oil. Chromatography: hexane/EtOAc (10/1). R_f 0.23 (hexane/EtOAc, 10/1). Mixture of isomers in a ratio of 93:7 detected by GC-MS analysis.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.69 (s, 6H), 3.39 (dd, *J* = 10.4, 4.9 Hz, 1H), 3.21 (dd, *J* = 10.4, 8.2 Hz, 1H), 2.61 – 2.41 (m, 4H), 2.37 – 2.28 (m, 1H), 2.23 – 1.83 (m, 5H), 1.04 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 172.7, 172.6, 119.2 (tt, *J* = 249.7, 36.0 Hz), 58.4, 52.9, 44.5, 39.2, 38.3, 35.3, 33.4, 29.1 (t, *J* = 22.5 Hz), 23.3 (t, *J* = 23.6 Hz), 4.8 (t, *J* = 5.1 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -113.9 (dd, *J* = 263.5, 30.4 Hz), -116.5 (dd, *J* = 263.5, 29.4 Hz), -118.2 (t, *J* = 18.3 Hz).

HRMS (ESI-TOF): calcd for $C_{15}H_{25}{}^{79}BrF_4NO_4$ [M+NH_4]: 438.0898; found 438.0894.

Stern-Volmer study

Experiments were performed in a screw-capped quartz vial (10×10 mm). The solvent was degassed, and the vial was filled with argon. The concentration of *fac*-Ir(ppy)$_3$ was 10^{-2} mmol/L for the quenching experiments with $EtCF_2CF_2Br$ (**1a**) and $TBSOCH_2CF_2Br$ (**1β**), and 10^{-3} mmol/L for the quenching experiment with IMesCuBr.

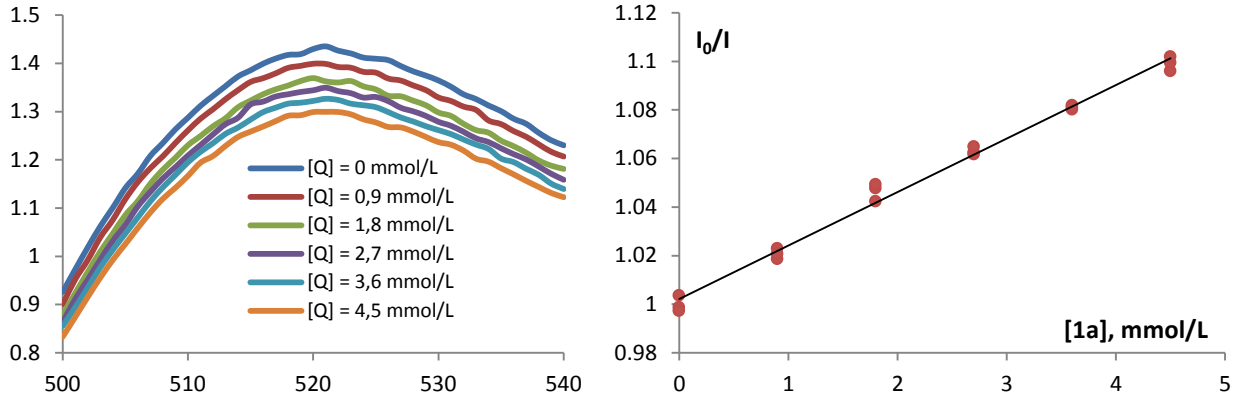


Figure S1. Quenching of fluorescence of *fac*-Ir(ppy)$_3$ by **1a** in DMSO at room temperature. Excitation wavelength 370 nm, fluorescence wavelength 520 nm.

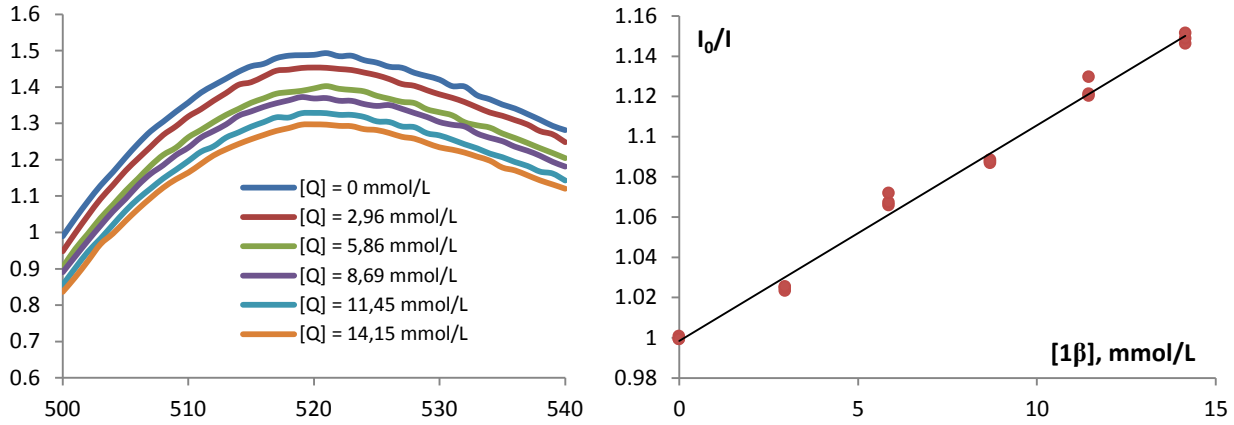


Figure S2. Quenching of fluorescence of *fac*-Ir(ppy)$_3$ by **1β** in DMSO at room temperature. Excitation wavelength 370 nm, fluorescence wavelength 520 nm.

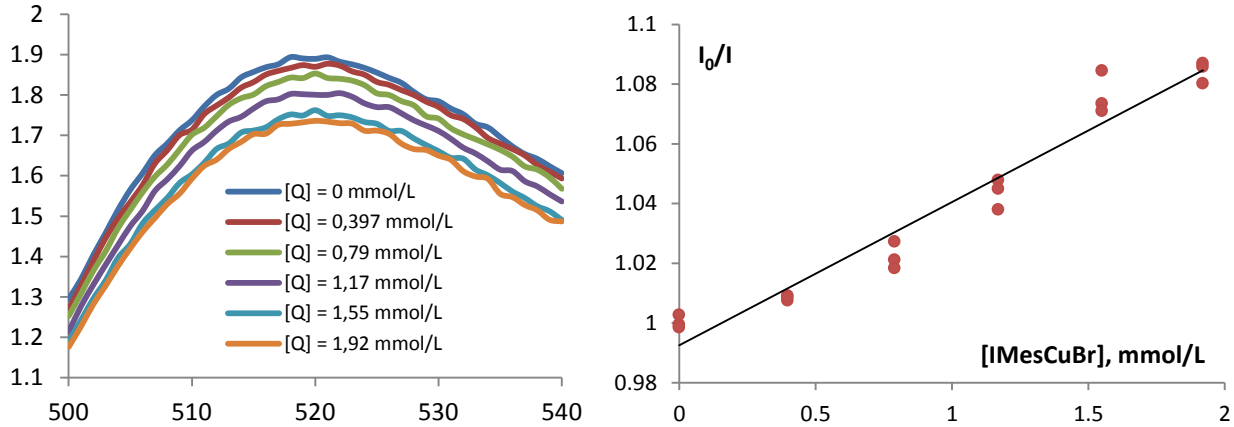


Figure S3. Quenching of fluorescence of *fac*-Ir(ppy)$_3$ by IMesCuBr in DMSO at room temperature. Excitation wavelength 370 nm, fluorescence wavelength 520 nm.

Quantum yield measurement[27]

Quantum yield for the reaction of 4-phenyl-1-butene **1a** with $EtCF_2CF_2Br$ **2a** was estimated using irradiation with a 380 mW blue laser (400 nm). Photon flux of the laser was measured by standard ferrioxalate actinometry – 6,1 μEs/min. A mixture of **1a** (132 mg, 1.0 mmol), **2a** (170 μl, 1.2 mmol), PPh_3 (52 mg, 0.2 mmol), IMesCuBr (44 mg, 0.1 mmol), *fac*-$Ir(ppy)_3$ (1.6 mg, 2.5 μmol) and 67 mg of tetralin (internal standard) in MeCN (2 mL) was placed in a square quartz cuvette (10×10 mm). At 400 nm, the reaction mixture completely absorbs the laser light. The cuvette was irradiated for 4 hours, and every 60 minutes the mixture was analyzed by GC. The quantum yield Φ was calculated by the following equation:

$$\phi = \frac{moles\ of\ product\ formed}{photon\ flux \cdot reaction\ time}/Q = \frac{0{,}126}{0{,}239} = 0{,}527$$

$$Q = quenching\ fraction = \frac{I_0 - I}{I_0} = 0{,}239$$

Measurement and calculation of *Q*-factor was essential because strong fluorescence of the reaction mixture was observed. The fluorescence of *fac*-$Ir(ppy)_3$ (1.6 mg, 2.5 μmol) in CH_3CN (2 mL) was taken as I_0 and the fluorescence of a mixture of **1a** (132 mg, 1 mmol), **2a** (159 μl, 1.2 mmol), PPh_3 (52 mg, 0.2 mmol), IMesCuBr (44 mg, 0,1 mmol) and *fac*-$Ir(ppy)_3$ (1.6 mg, 2.5 μmol) was taken as *I*. The excitation wavelength was 400 nm, the registration wavelength was 520 nm.

Cyclic voltammetry

Voltammetric studies were carried out using potentiostat P30JM with a scan rate of 0.1 $V \cdot s^{-1}$ 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 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 of 1 mM in DMSO.

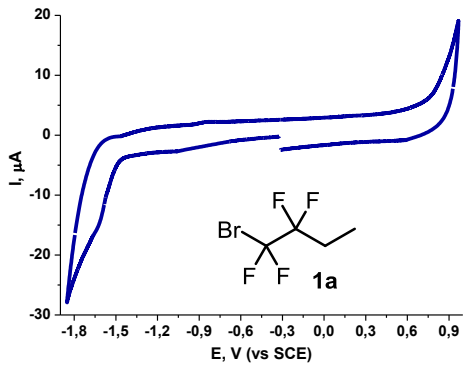


Figure S4. Compound **1a** (initial cathodic scan) E_{onset}^{red} = -1.48 V; E_p^{red} = -1.62 V; i_p^{red} = 11.02 μA

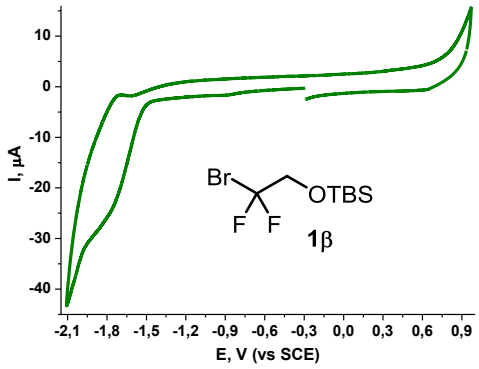


Figure S5. Compound **1β** (initial cathodic scan) E_{onset}^{red} = -1.50 V; E_p^{red} = -1.74 V; i_p^{red} = 21.92 μA

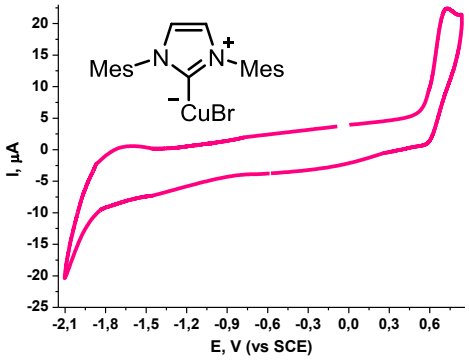


Figure S6. Compound IMesCuBr (initial anodic scan). E_{onset}^{ox} = +0.44 V; E_p^{ox} = +0.72 V; i_p^{ox} = 17.48 μA

Compounds **1a** and **1β** have only corresponding irreversible reduction waves at E_p^{red} = -1.62 V and -1.74 V, respectively, but reduction starts earlier at E_{onset}^{red} = -1.48 V and -1.50 V. Presumably, after the reduction, the resulting anion-radical undergoes fragmentation into alkyl radical and bromide ion. IMesCuBr have only oxidation wave at E_p^{ox} = +0.72 V, but oxidation starts earlier at E_{onset}^{ox} = + 0.44 V.

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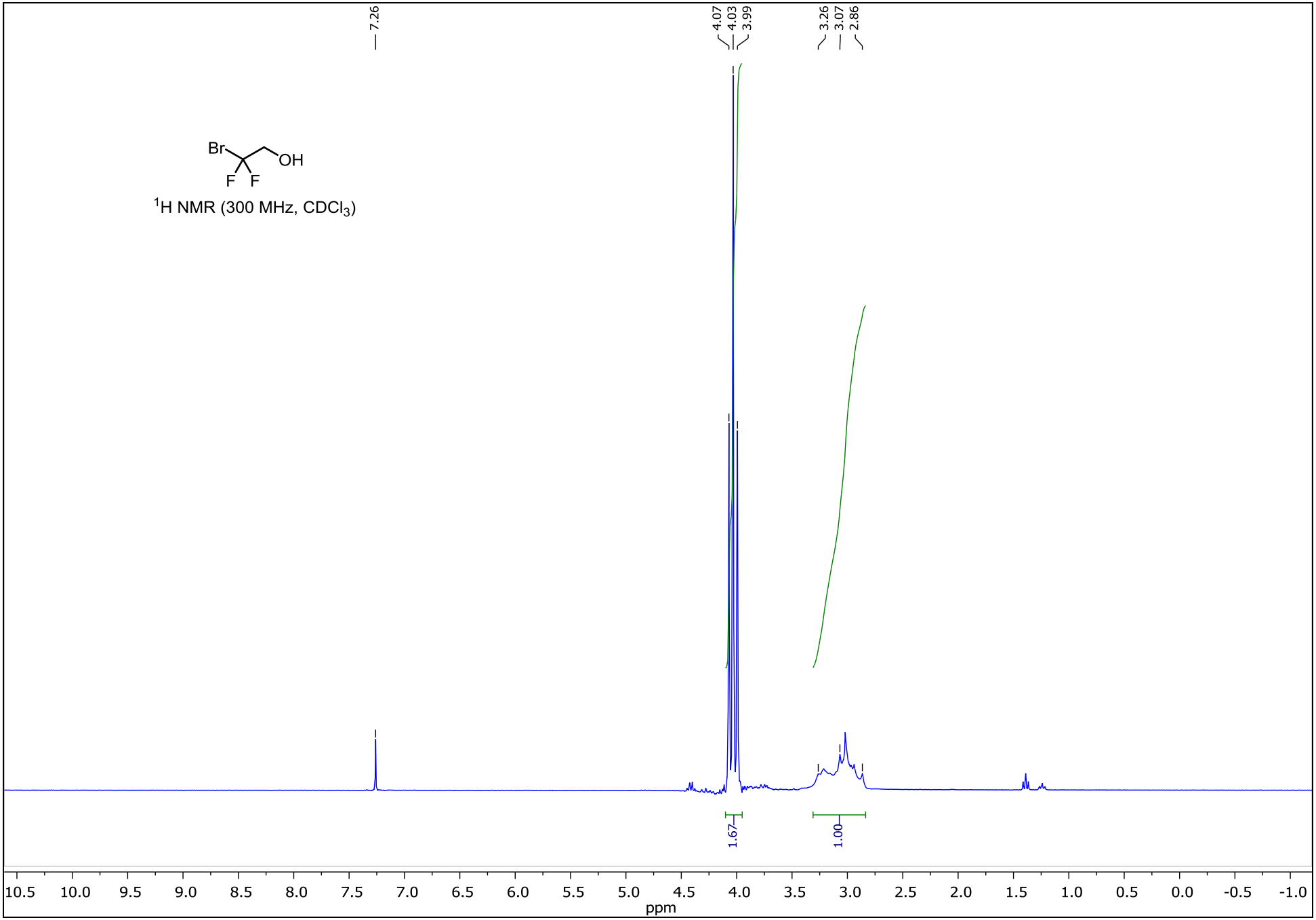
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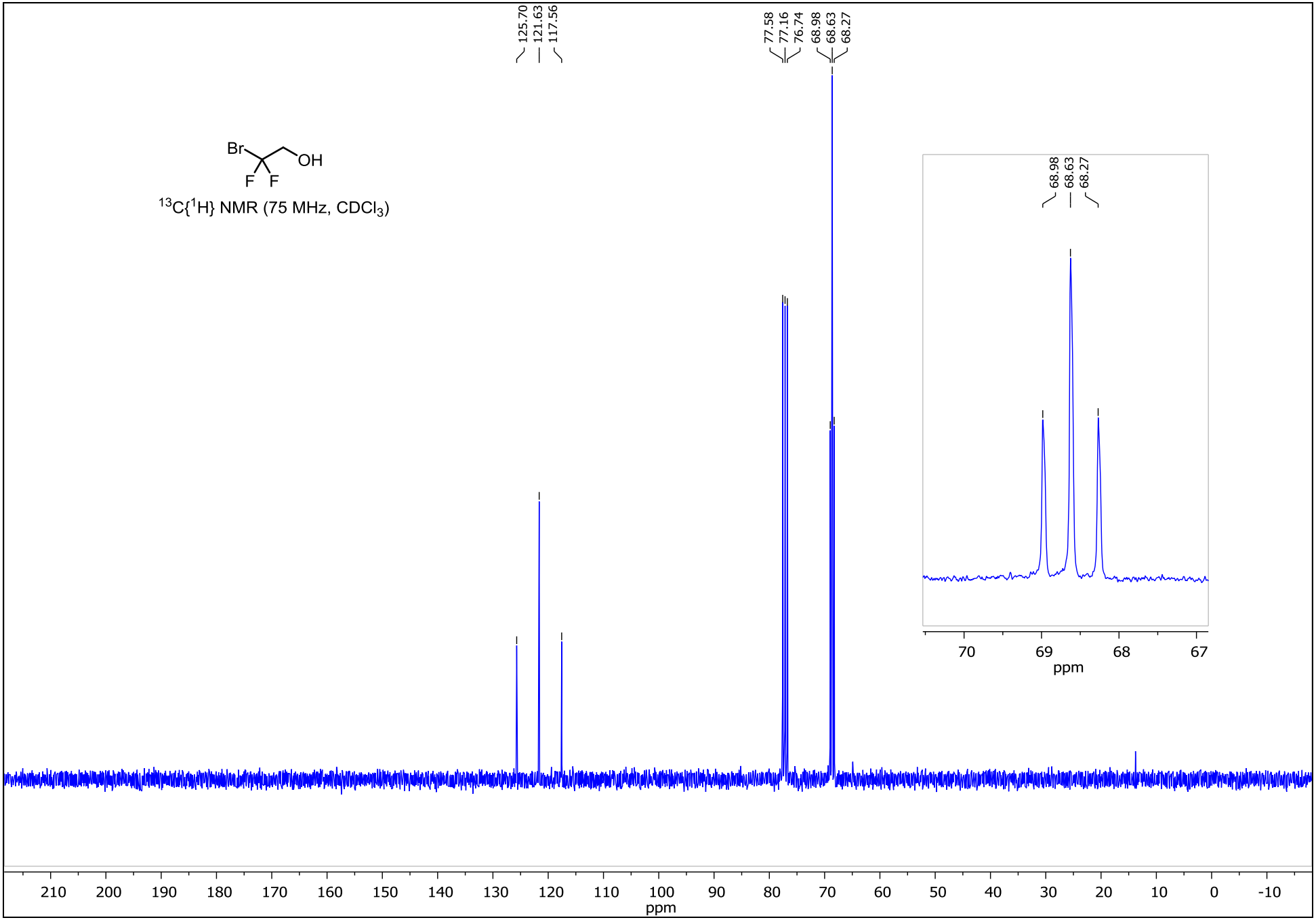
4.07
4.03
3.99
3.26
3.07
2.86
Br
OH
F F
^{1}H NMR (300 MHz, CDCl$_3$)
1.67
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm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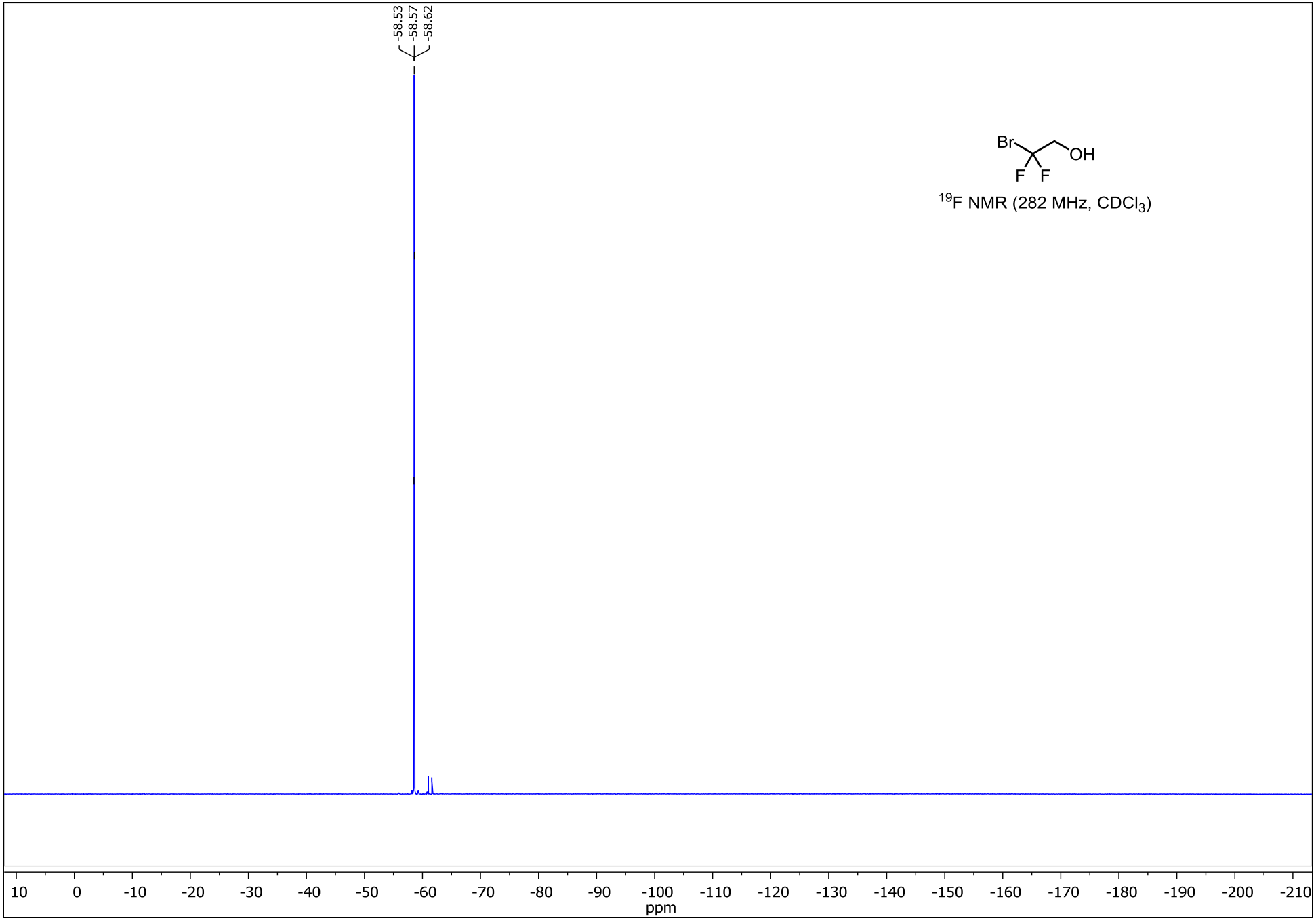
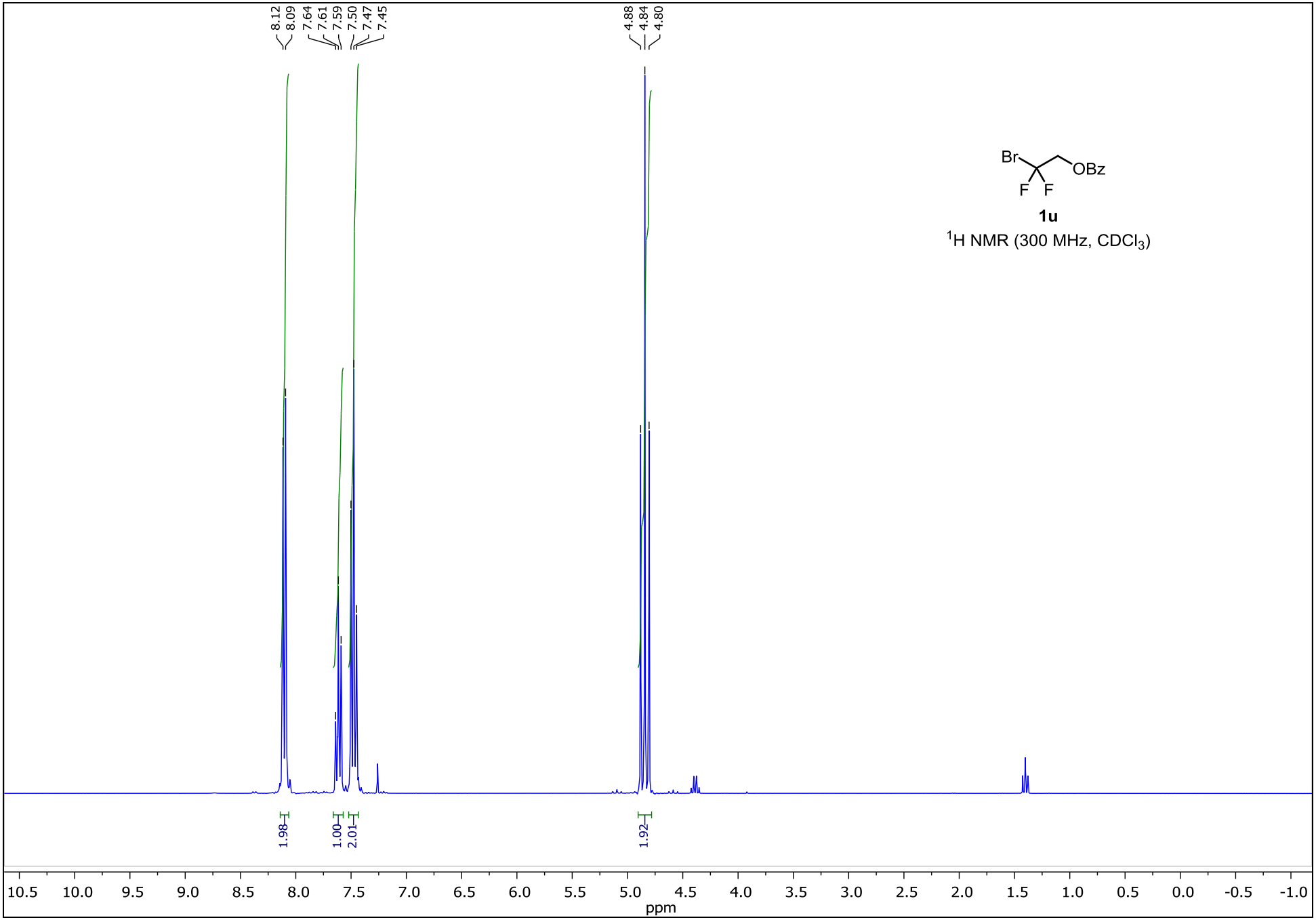
121.63
117.56
77.58
77.16
76.74
68.98
68.63
68.27
Br
OH
F F
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
68.98
68.63
68.27
70
69
68
67
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm



^{19}F NMR (282 MHz, $CDCl_3$)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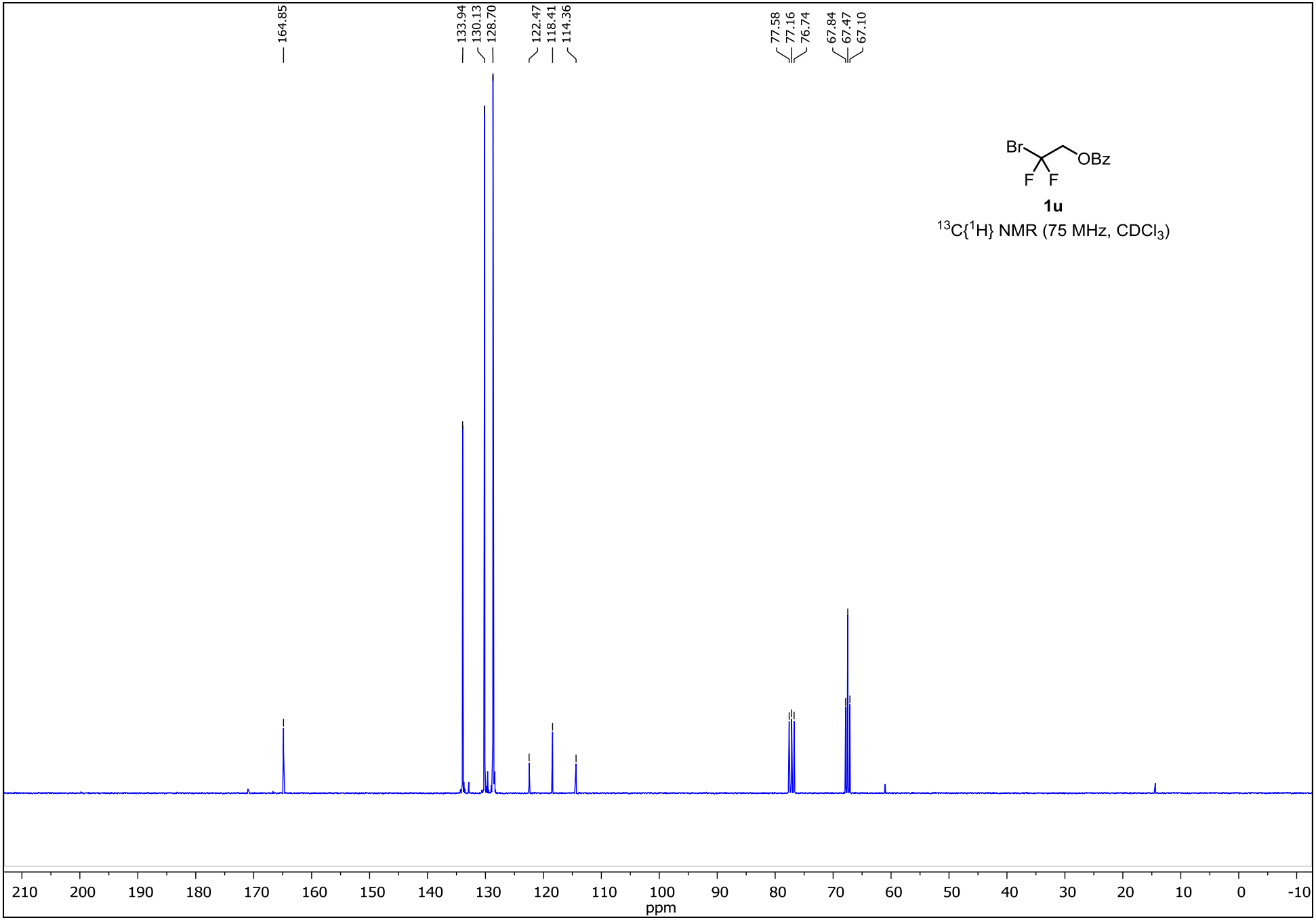
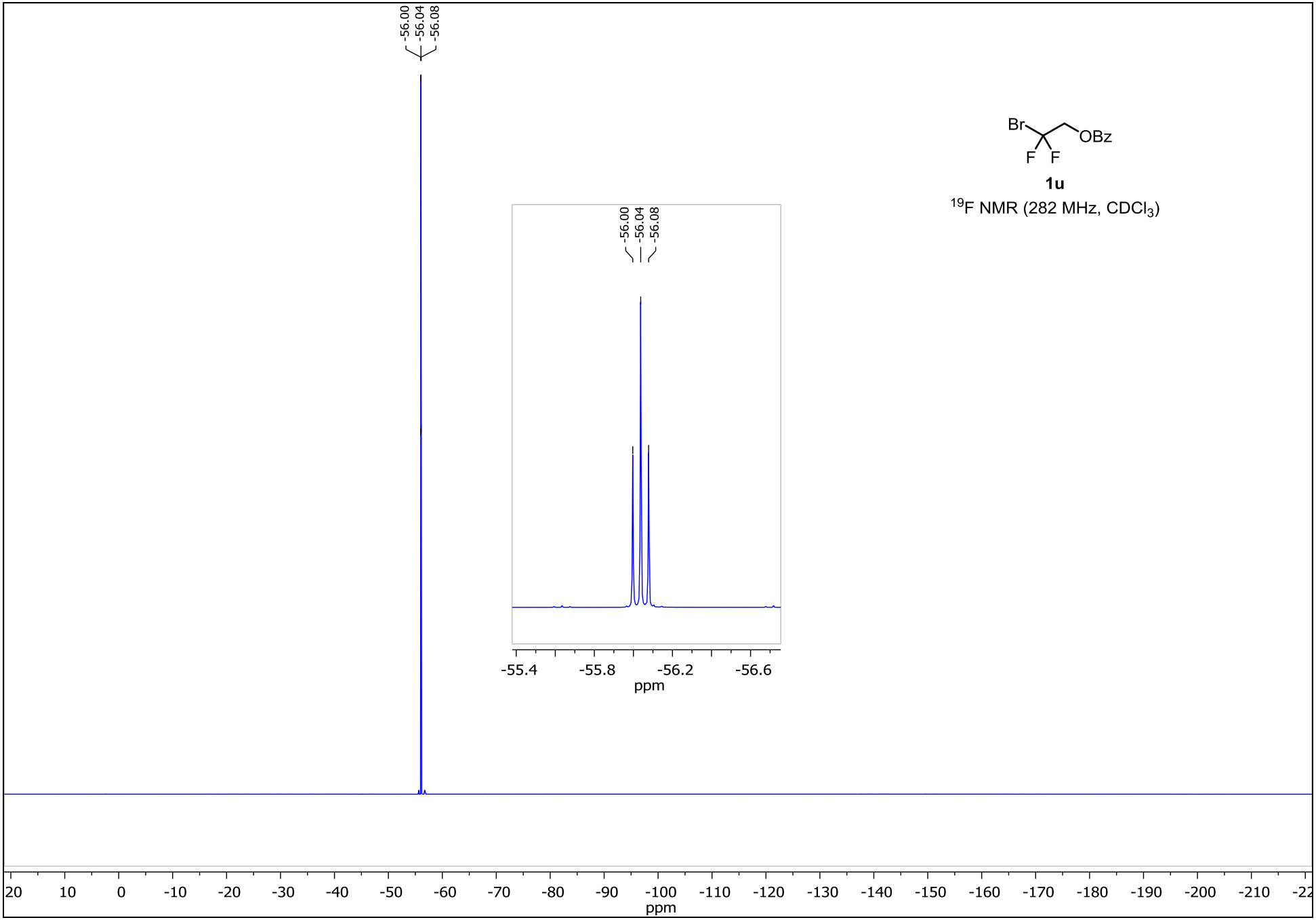
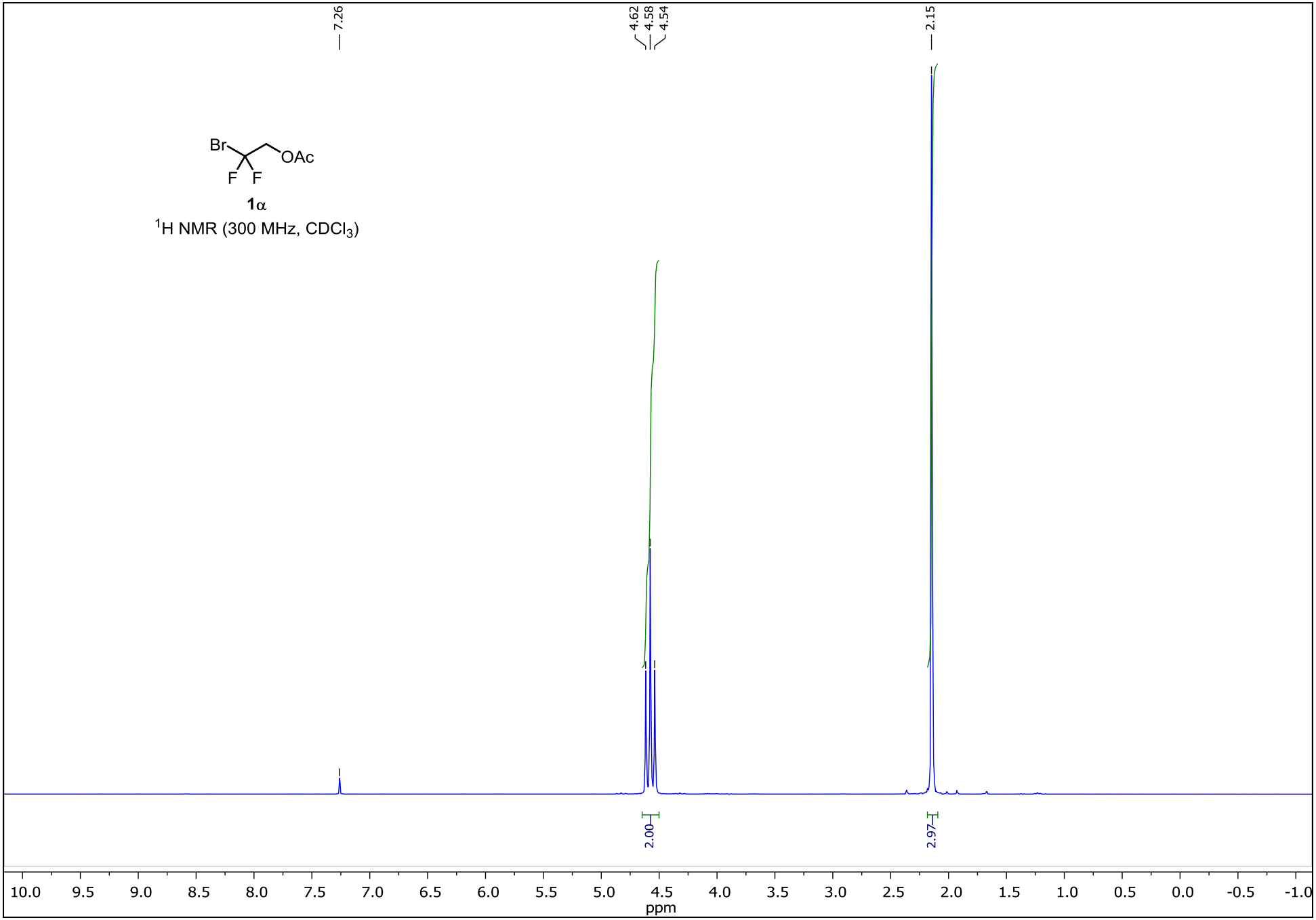
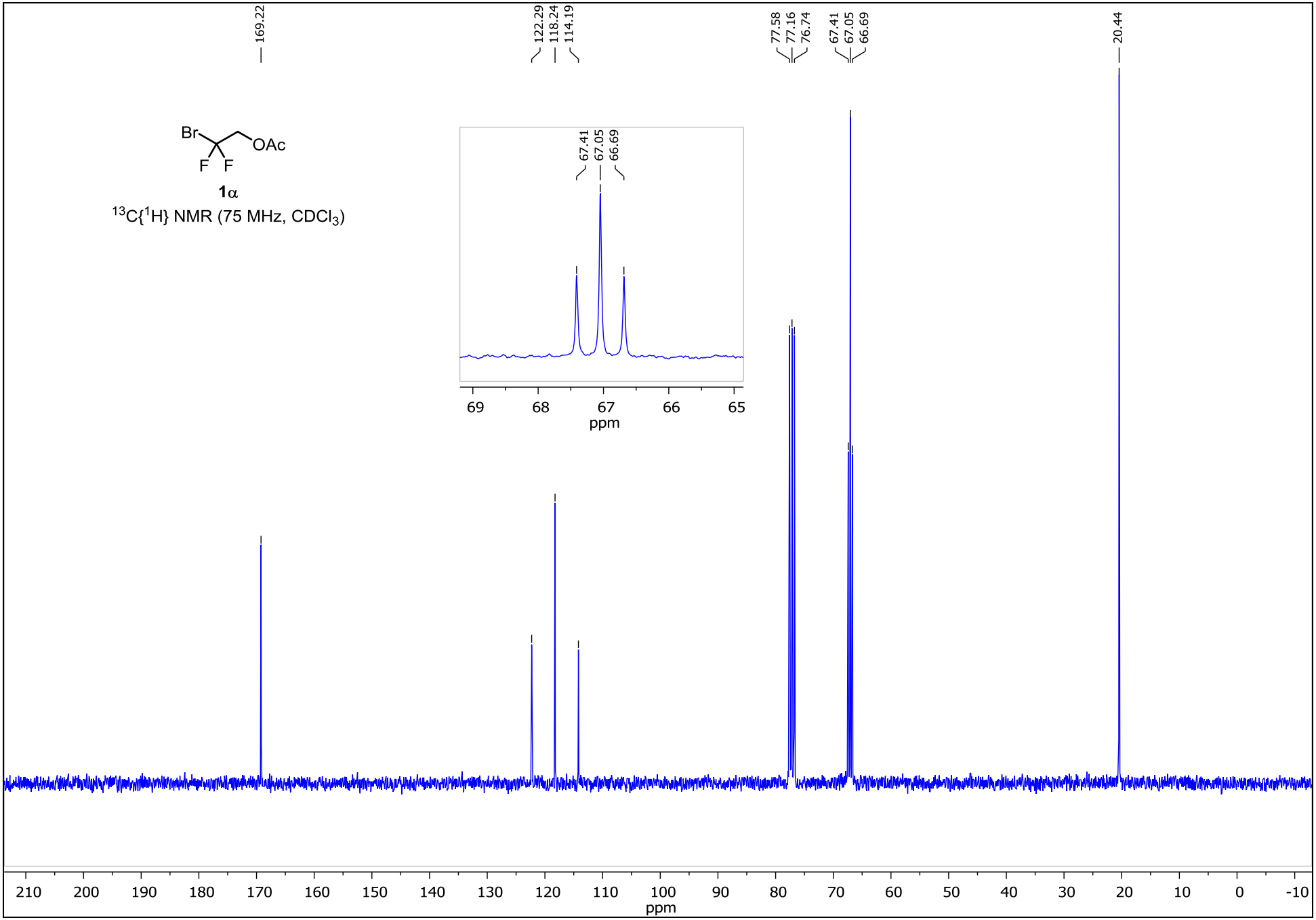
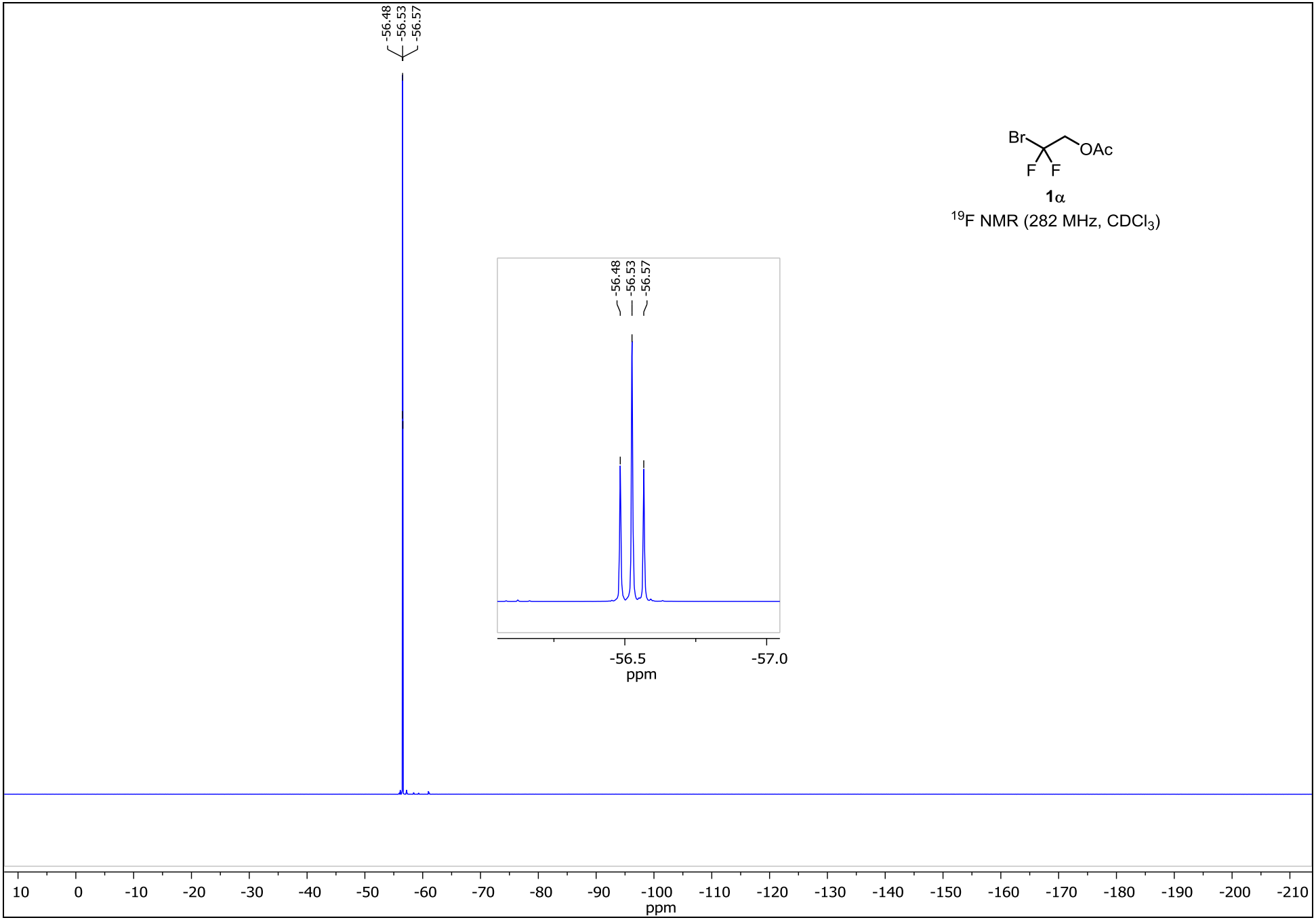
8.09
7.64
7.61
7.59
7.50
7.47
7.45
4.88
4.84
4.80
Br
OBz
F F
1u
1H NMR (300 MHz, CDCl3)
1.98
1.00
2.01
1.92
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


164.85
133.94
130.13
128.70
122.47
118.41
114.36
77.58
77.16
76.74
67.84
67.47
67.10
Br
OBz
F F
1u
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


-56.00
-56.04
-56.08
Br
OBz
F F
1u
^{19}F NMR (282 MHz, $CDCl_3$)
-55.4
-55.8
-56.2
-56.6
ppm
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
ppm


7.26
4.62
4.58
4.54
2.15
Br
OAc
F F
1α
1H NMR (300 MHz, CDCl3)
2.00
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


169.22
122.29
118.24
114.19
77.58
77.16
76.74
67.41
67.05
66.69
20.44
Br
OAc
F F
1α
13C{1H} NMR (75 MHz, CDCl3)
67.41
67.05
66.69
69
68
67
66
65
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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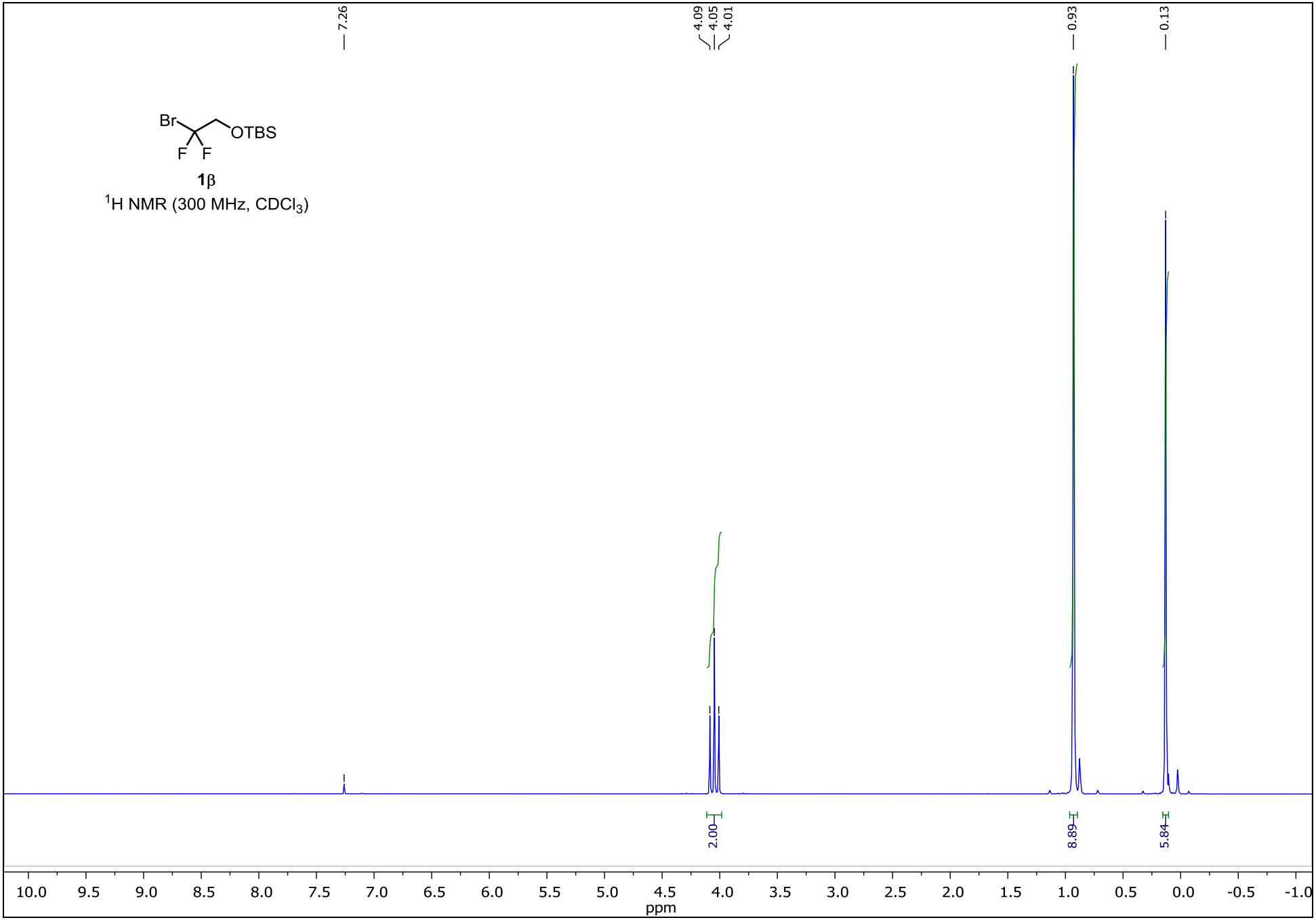
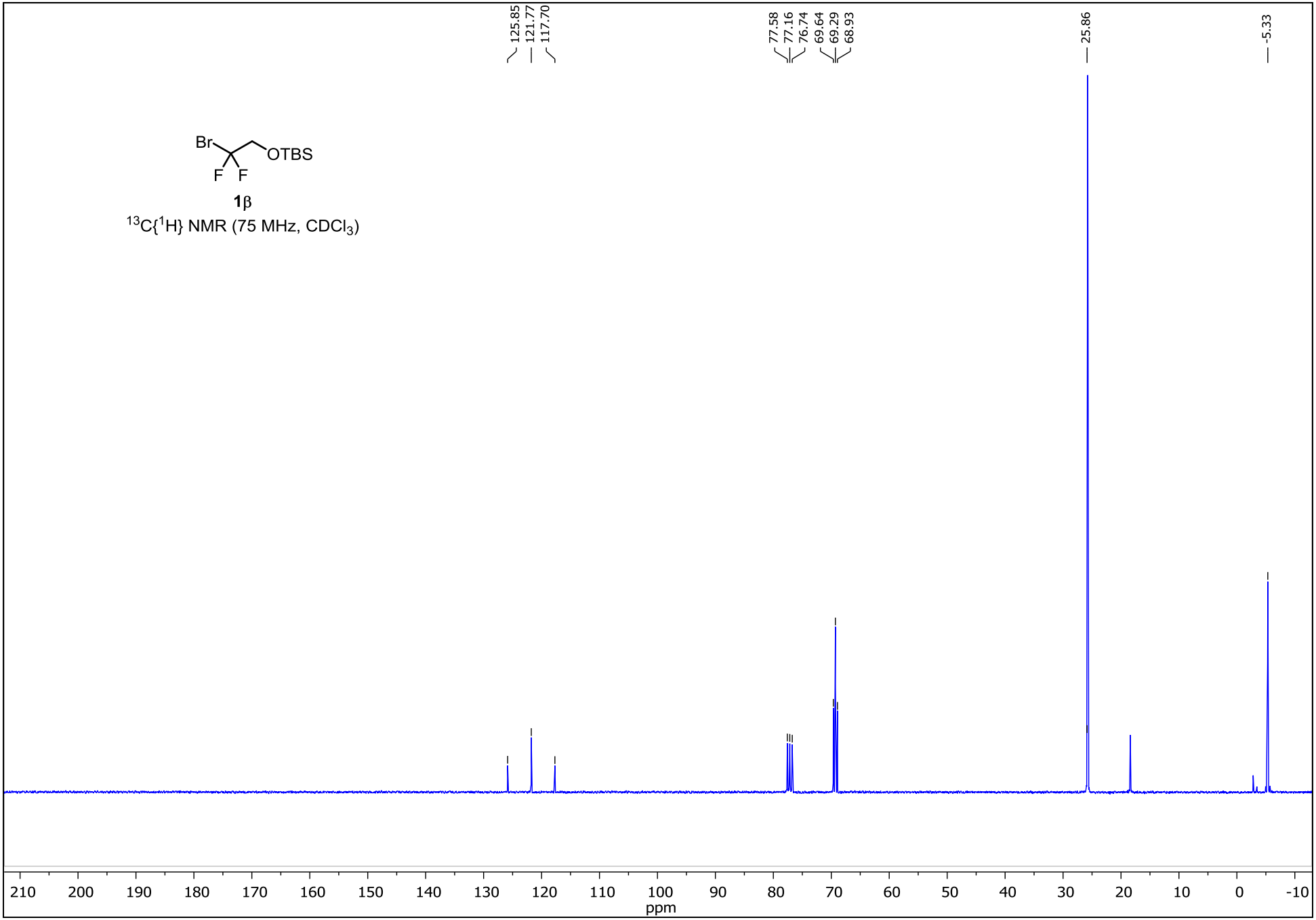
-56.53
-56.57
Br
OAc
F F
1α
19F NMR (282 MHz, CDCl3)
-56.48
-56.53
-56.57
-56.5
-57.0
ppm
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
ppm


7.26
4.09
4.05
4.01
0.93
0.13
Br
OTBS
F F
1β
1H NMR (300 MHz, CDCl3)
2.00
8.89
5.84
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm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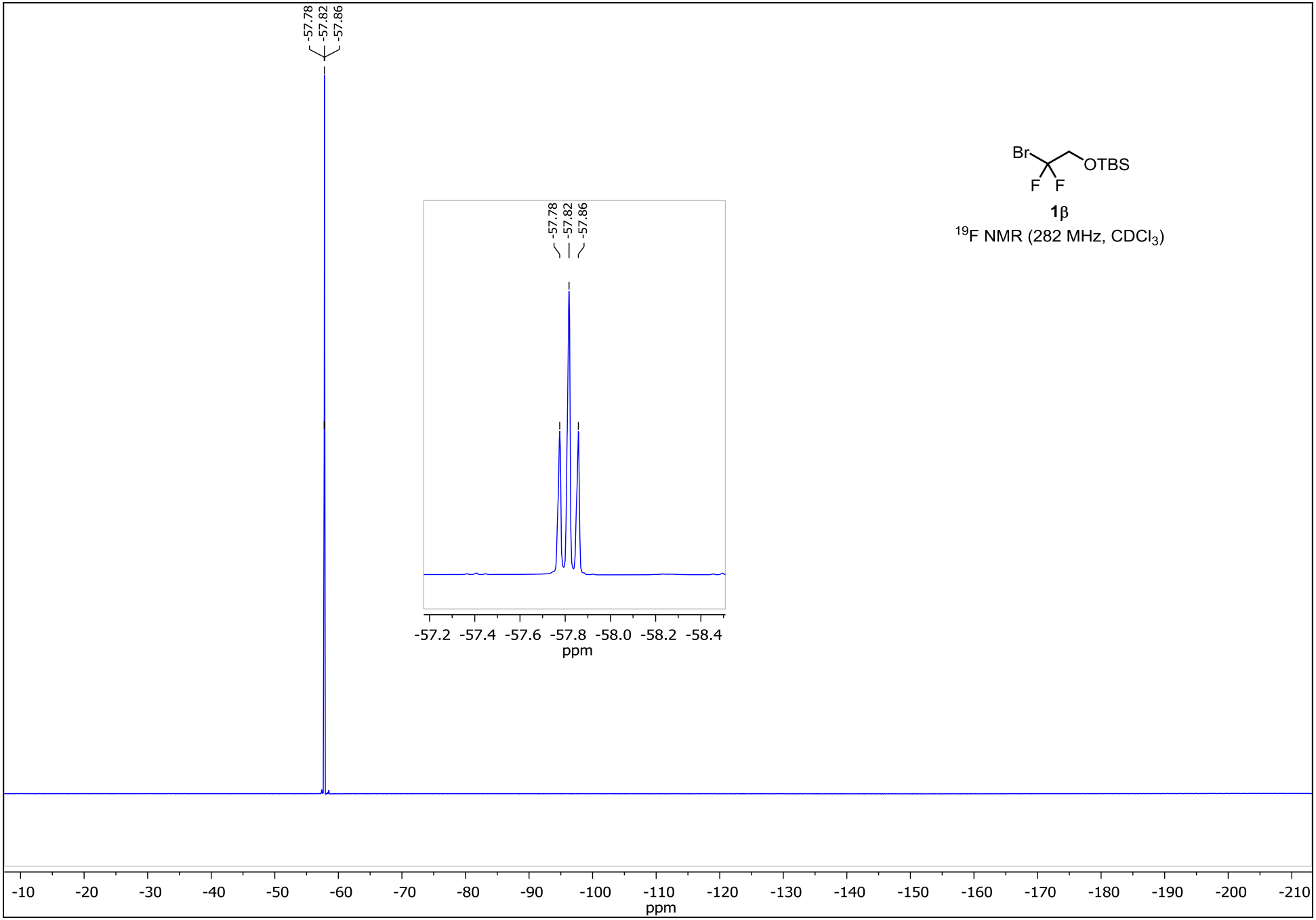
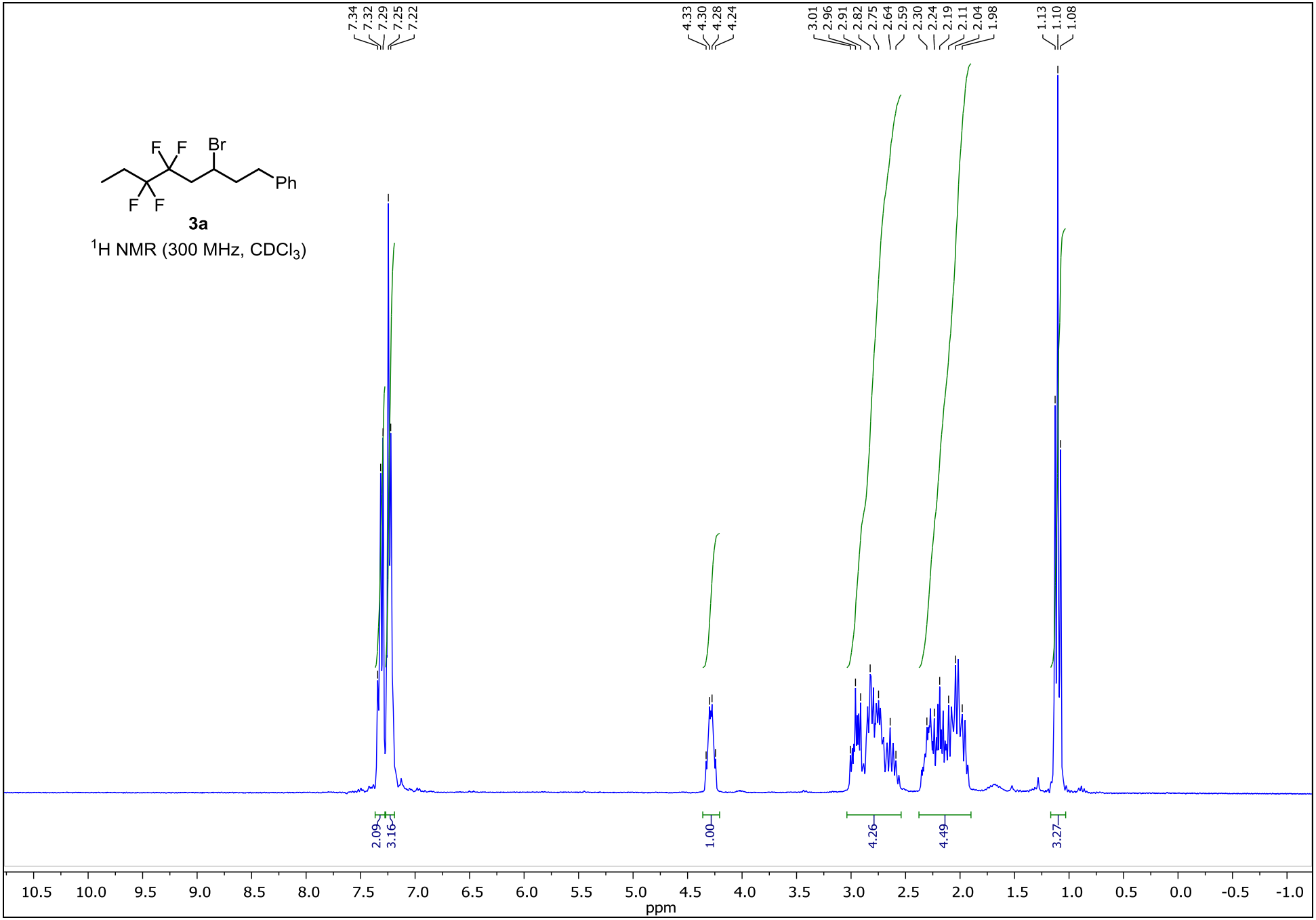
121.77
117.70
77.58
77.16
76.74
69.64
69.29
68.93
25.86
-5.33
Br
OTBS
F F
1β
13C{1H} NMR (75 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



1β

^{19}F NMR (282 MHz, $CDCl_3$)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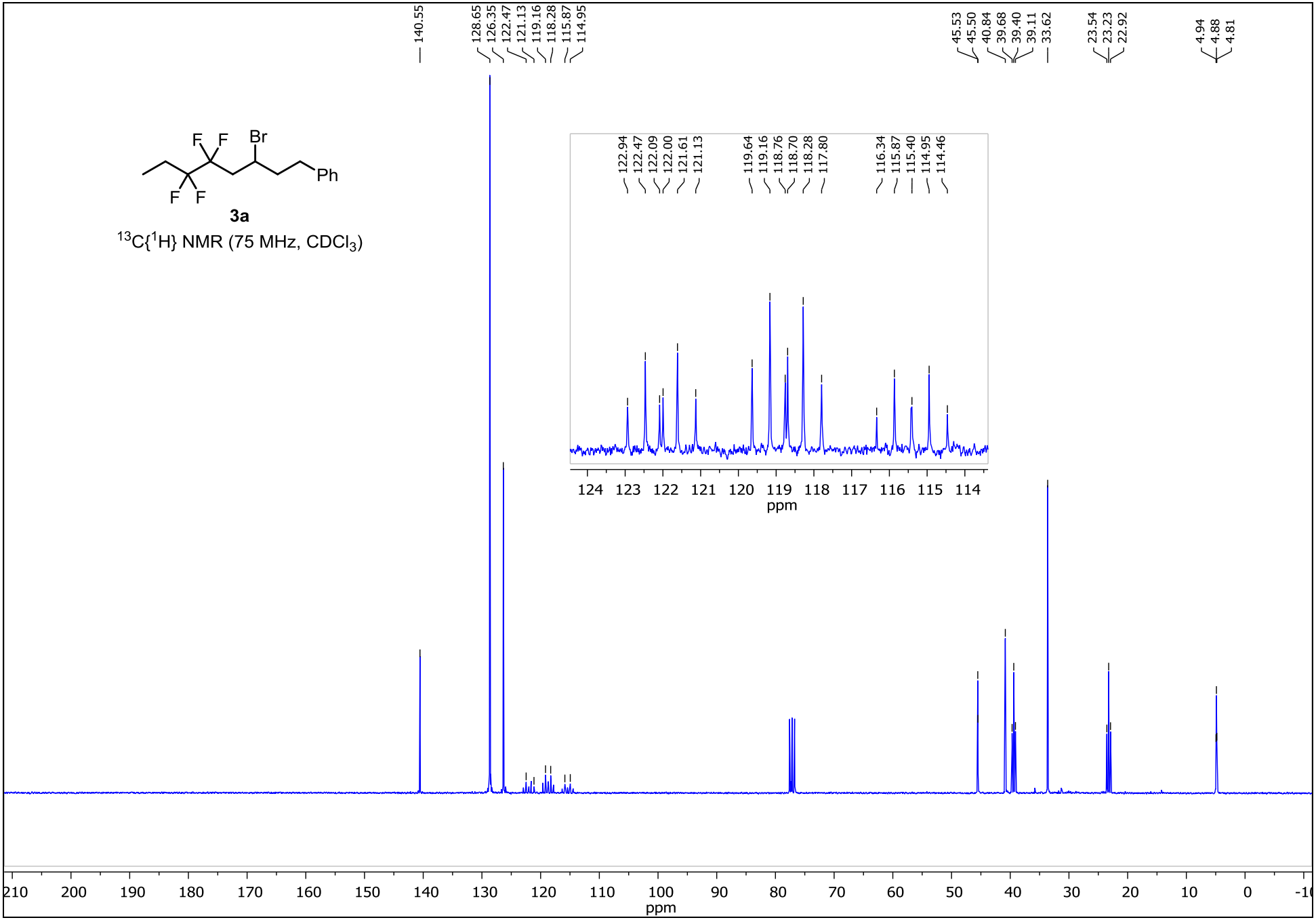
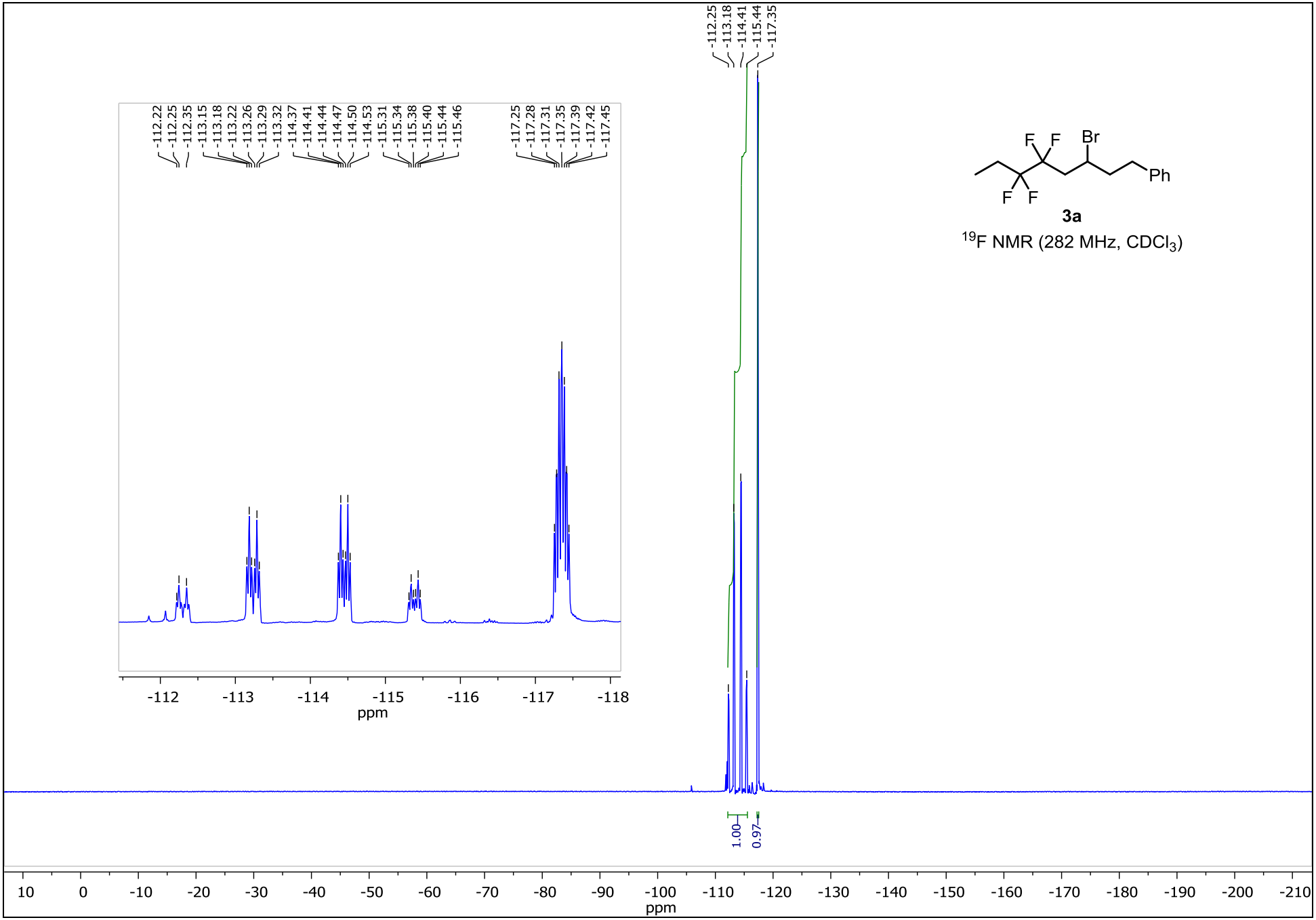
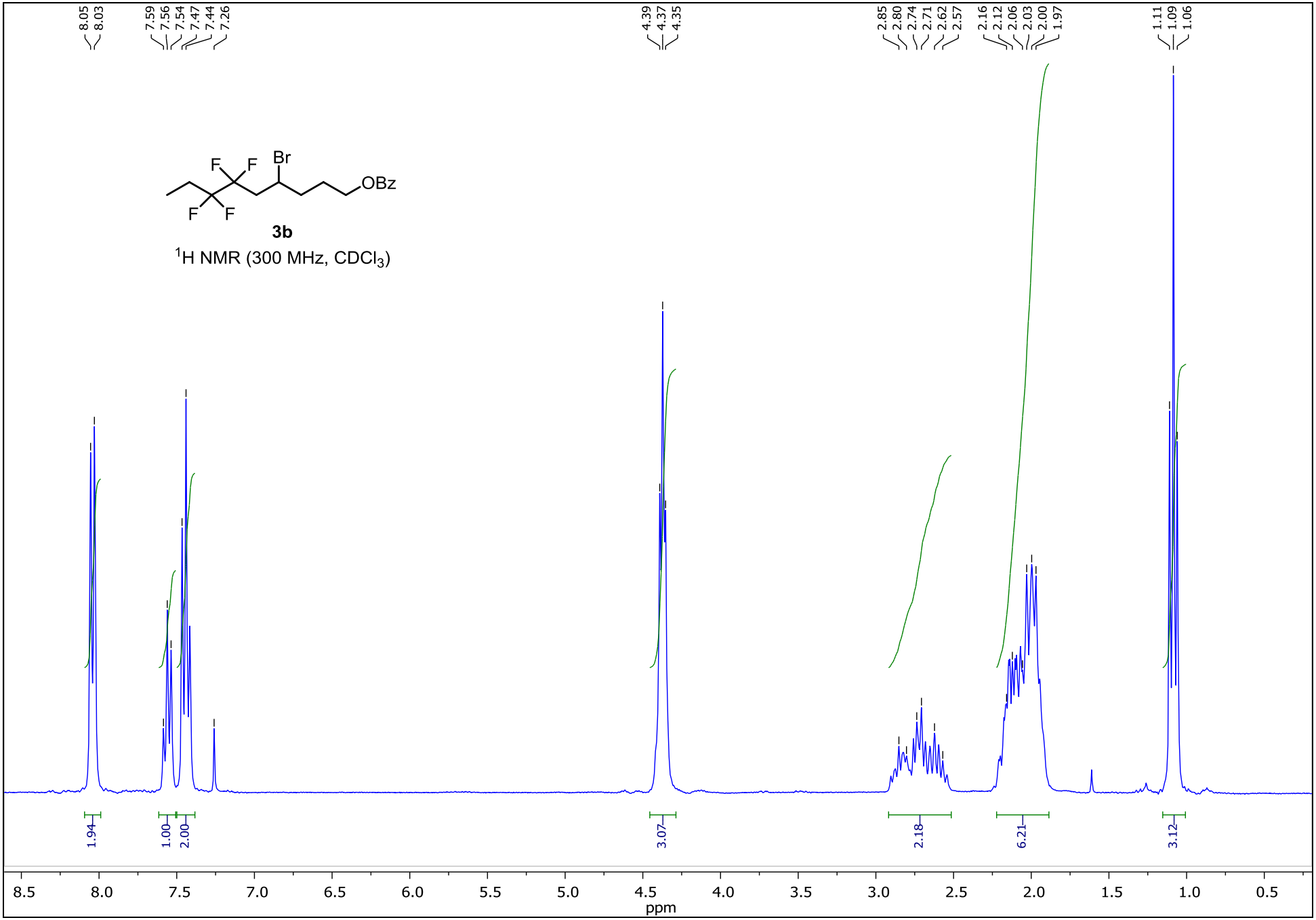
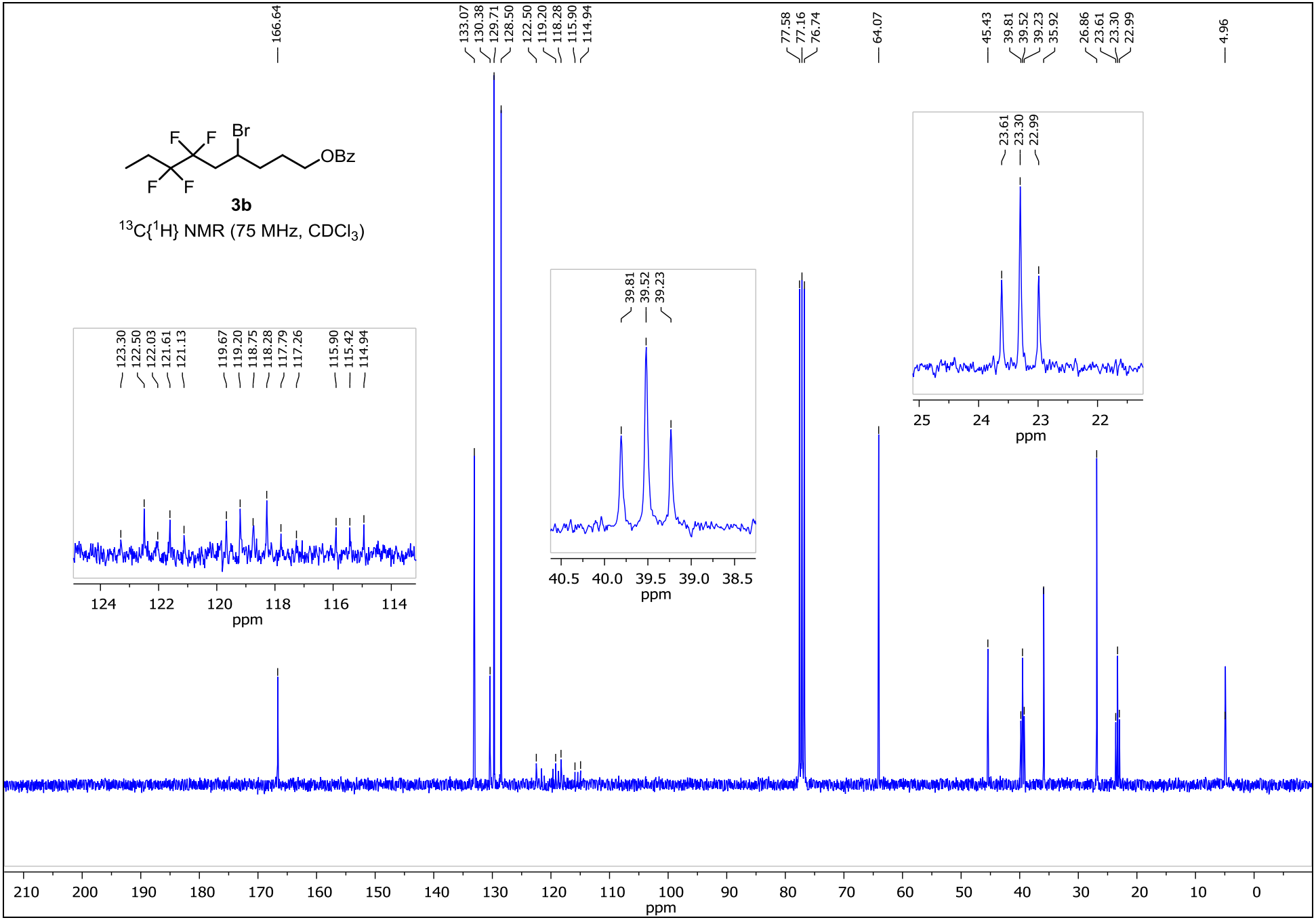
7.32
7.29
7.25
7.22
4.33
4.30
4.28
4.24
3.01
2.96
2.91
2.82
2.75
2.64
2.59
2.30
2.24
2.19
2.11
2.04
1.98
1.13
1.10
1.08
F F Br
Ph
F F
3a
1H NMR (300 MHz, CDCl3)
2.09
3.16
1.00
4.26
4.49
3.27
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


F F Br
Ph
F F
3a
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
140.55
128.65
126.35
122.47
121.13
119.16
118.28
115.87
114.95
45.53
45.50
40.84
39.68
39.40
39.11
33.62
23.54
23.23
22.92
4.94
4.88
4.81
122.94
122.47
122.09
122.00
121.61
121.13
119.64
119.16
118.76
118.70
118.28
117.80
116.34
115.87
115.40
114.95
114.46
124 123 122 121 120 119 118 117 116 115 114
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


-112.25
-113.18
-114.41
-115.44
-117.35
-112.22
-112.25
-112.35
-113.15
-113.18
-113.22
-113.26
-113.29
-113.32
-114.37
-114.41
-114.44
-114.47
-114.50
-114.53
-115.31
-115.34
-115.38
-115.40
-115.44
-115.46
-117.25
-117.28
-117.31
-117.35
-117.39
-117.42
-117.45
F F Br
Ph
F F
3a
19F NMR (282 MHz, CDCl3)
1.00
0.97
ppm
ppm


8.05
8.03
7.59
7.56
7.54
7.47
7.44
7.26
4.39
4.37
4.35
2.85
2.80
2.74
2.71
2.62
2.57
2.16
2.12
2.06
2.03
2.00
1.97
1.11
1.09
1.06
F
F
Br
OBz
F
F
3b
1H NMR (300 MHz, CDCl3)
1.94
1.00
2.00
3.07
2.18
6.21
3.12
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
ppm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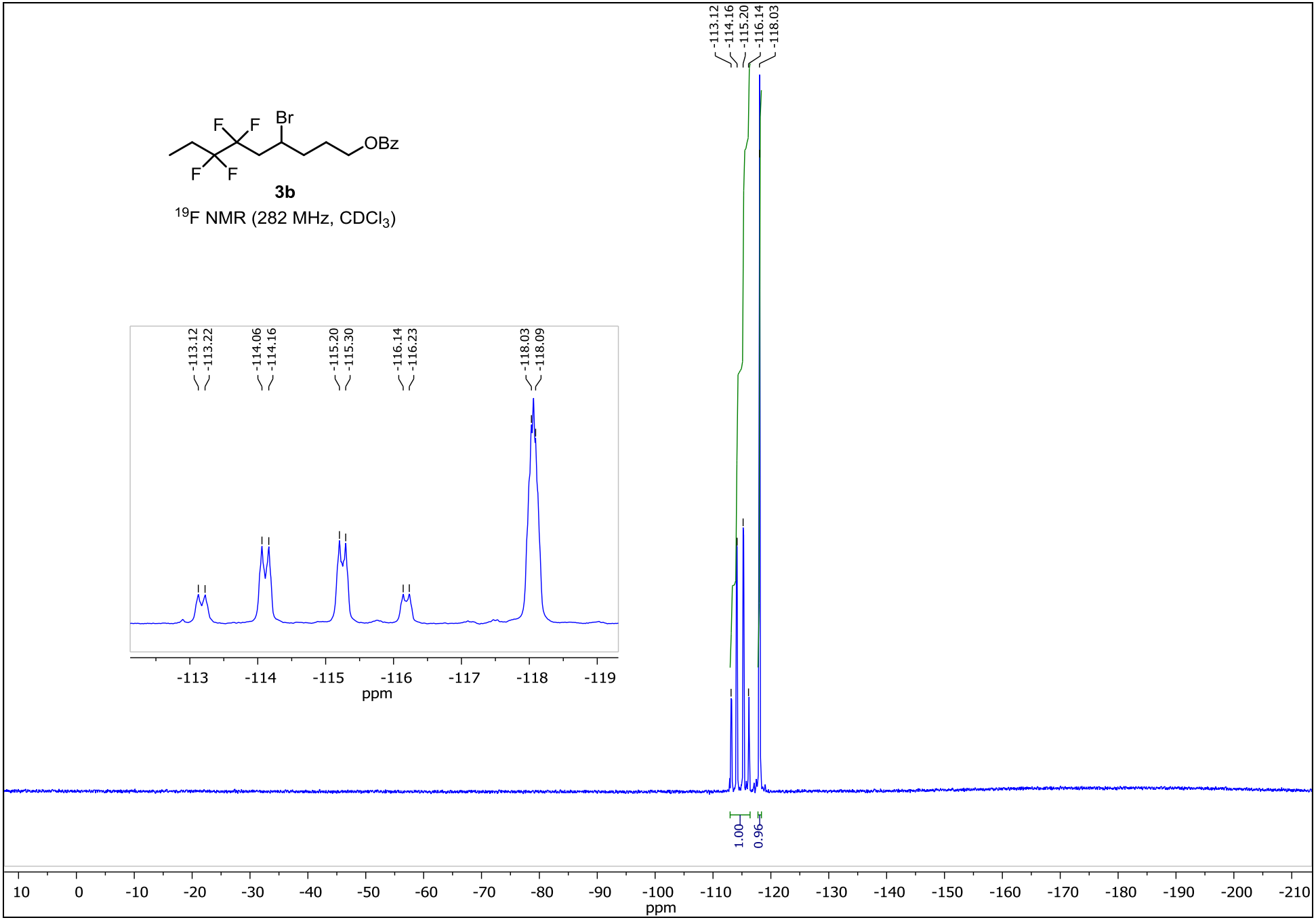
130.38
129.71
128.50
122.50
119.20
118.28
115.90
114.94
77.58
77.16
76.74
64.07
45.43
39.81
39.52
39.23
35.92
26.86
23.61
23.30
22.99
4.96
F
F
Br
OBz
F
F
3b
13C{1H} NMR (75 MHz, CDCl3)
123.30
122.50
122.03
121.61
121.13
119.67
119.20
118.75
118.28
117.79
117.26
115.90
115.42
114.94
124
122
120
118
116
114
ppm
39.81
39.52
39.23
40.5
40.0
39.5
39.0
38.5
ppm
23.61
23.30
22.99
25
24
23
22
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


F
F
Br
OBz
F
F
3b
19F NMR (282 MHz, CDCl3)
-113.12
-114.16
-115.20
-116.14
-118.03
-113.12
-113.22
-114.06
-114.16
-115.20
-115.30
-116.14
-116.23
-118.03
-118.09
-113
-114
-115
-116
-117
-118
-119
ppm
1.00
0.96
10
0
-10
-20
-30
-40
-50
-60
-70
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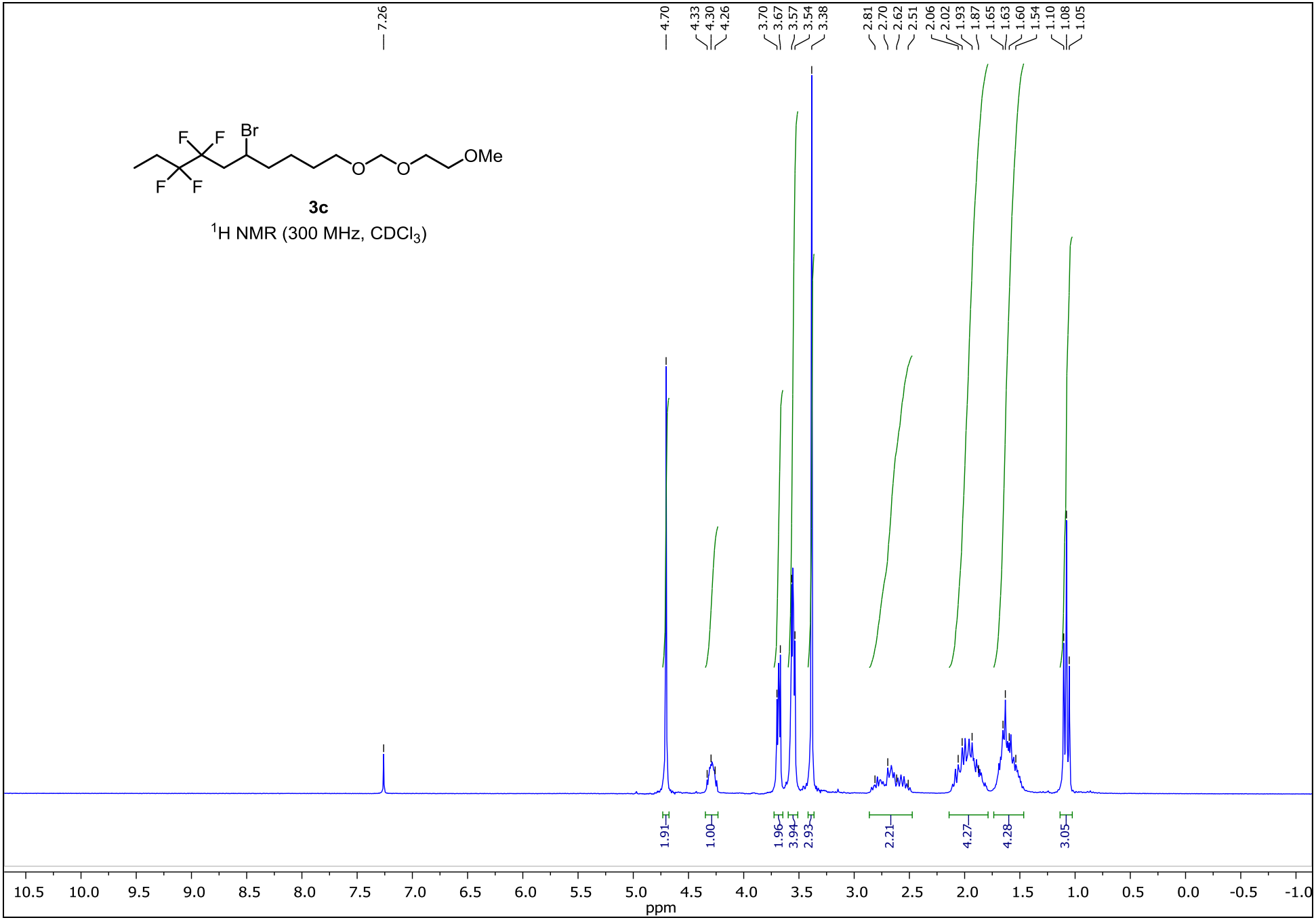
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm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4.70
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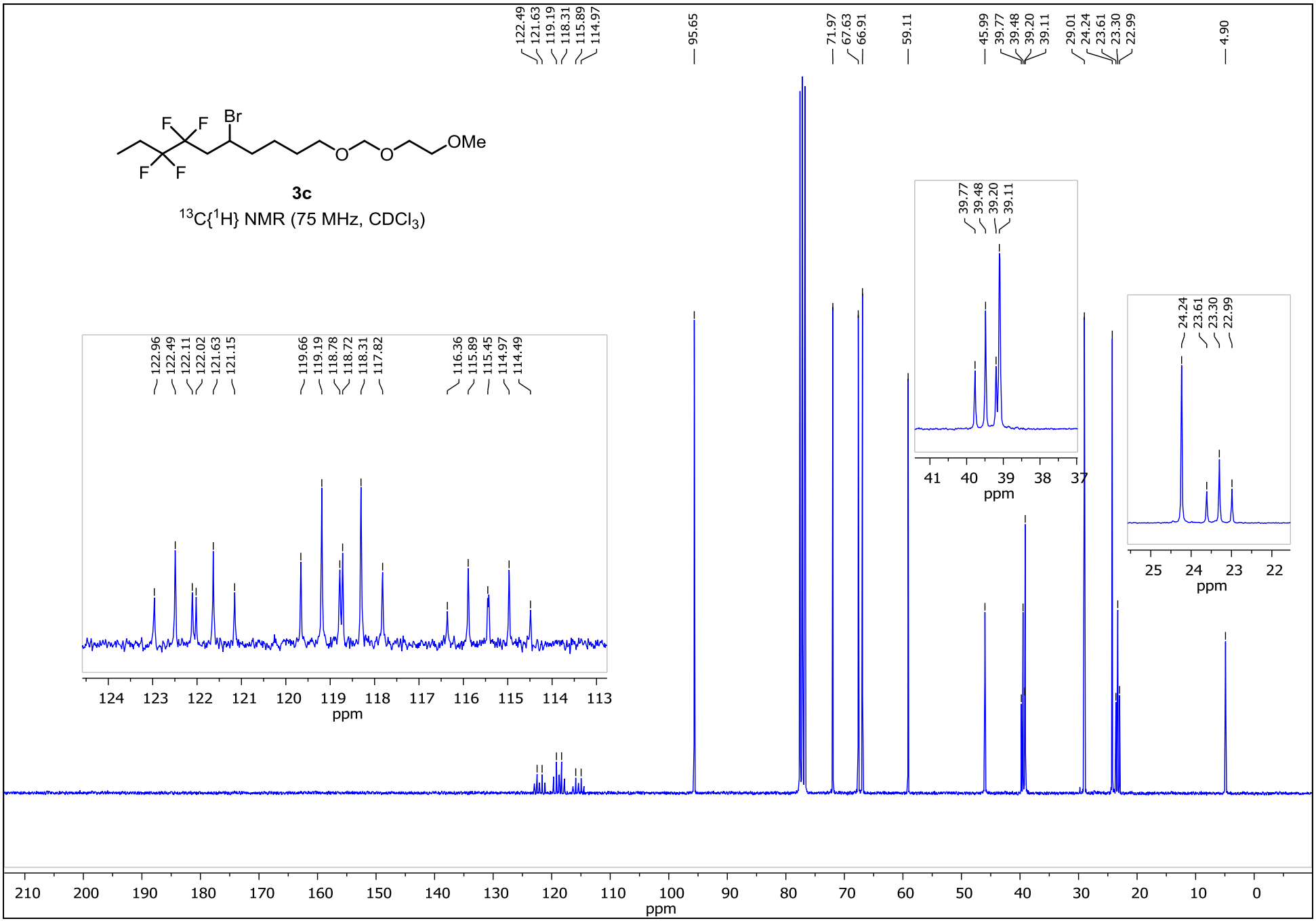
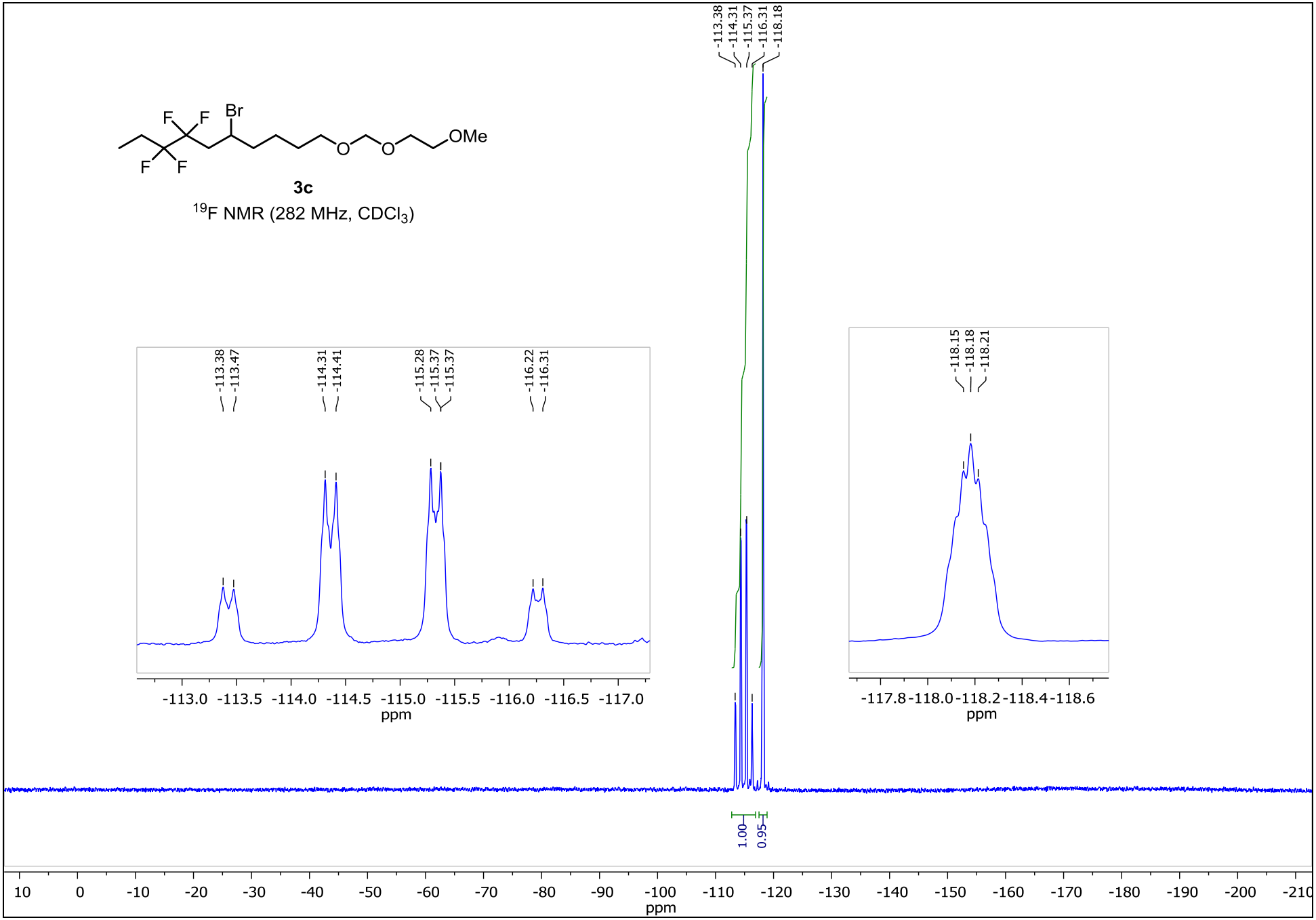
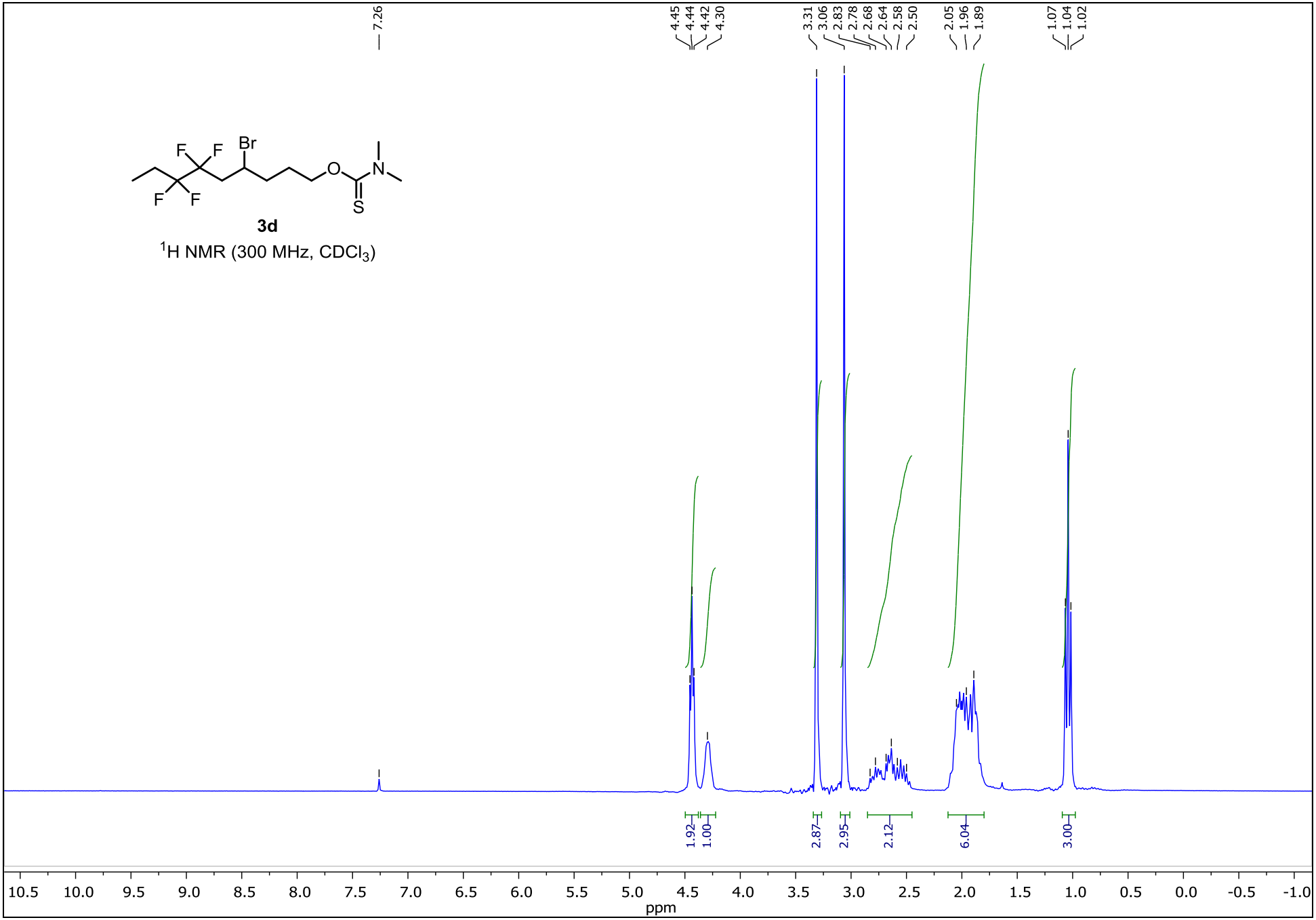
4.26
3.70
3.67
3.57
3.54
3.38
2.81
2.70
2.62
2.51
2.06
2.02
1.93
1.87
1.65
1.63
1.60
1.54
1.10
1.08
1.05
F
F
Br
F
F
O
O
OMe
3c
1H NMR (300 MHz, CDCl3)
1.91
1.00
1.96
3.94
2.93
2.21
4.27
4.28
3.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

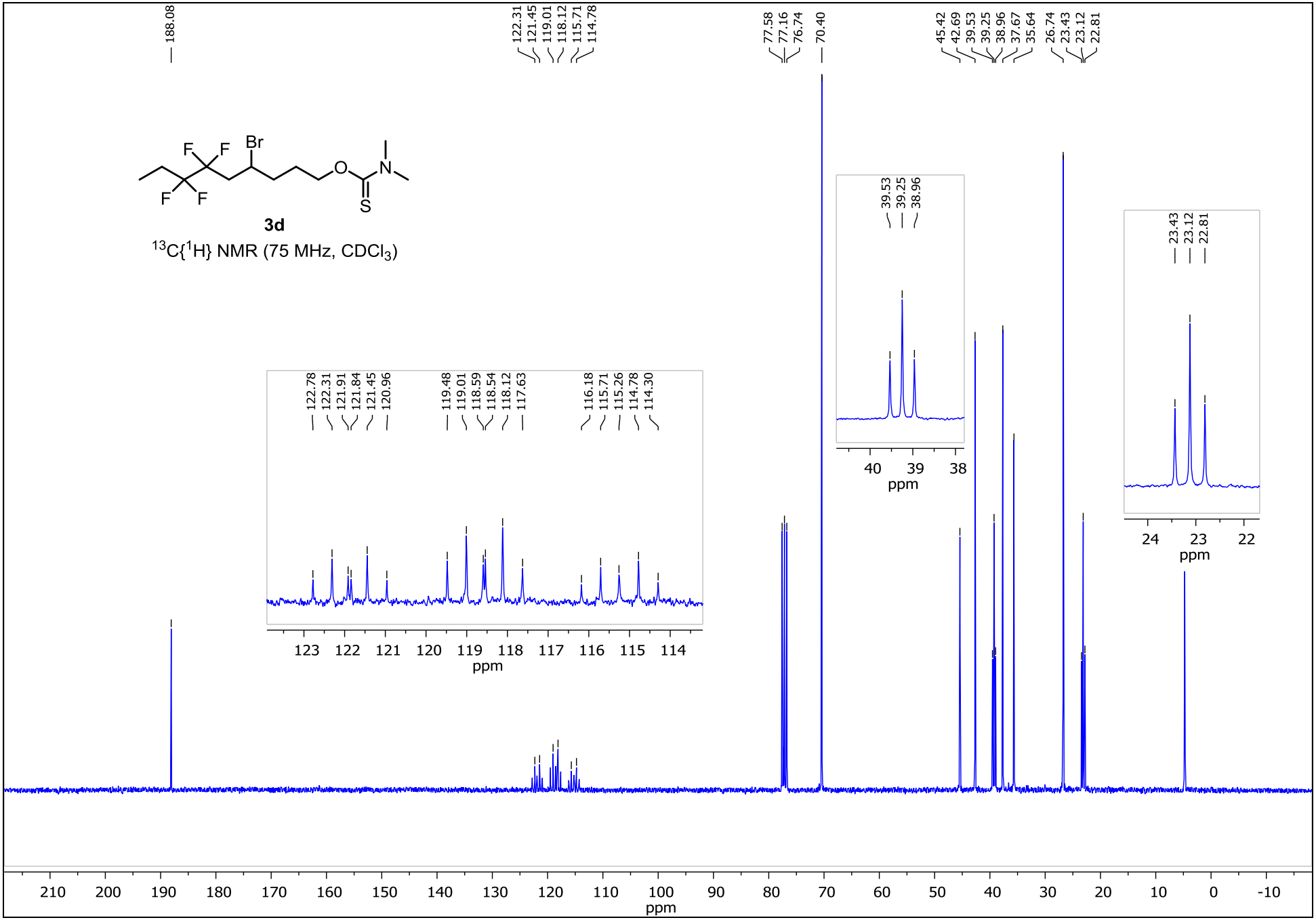

122.49
121.63
119.19
118.31
115.89
114.97
95.65
71.97
67.63
66.91
59.11
45.99
39.77
39.48
39.20
39.11
29.01
24.24
23.61
23.30
22.99
4.90
F
F
Br
F
F
O
O
OMe
3c
13C{1H} NMR (75 MHz, CDCl3)
122.96
122.49
122.11
122.02
121.63
121.15
119.66
119.19
118.78
118.72
118.31
117.82
116.36
115.89
115.45
114.97
114.49
124 123 122 121 120 119 118 117 116 115 114 113
ppm
41 40 39 38 37
ppm
25 24 23 22
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

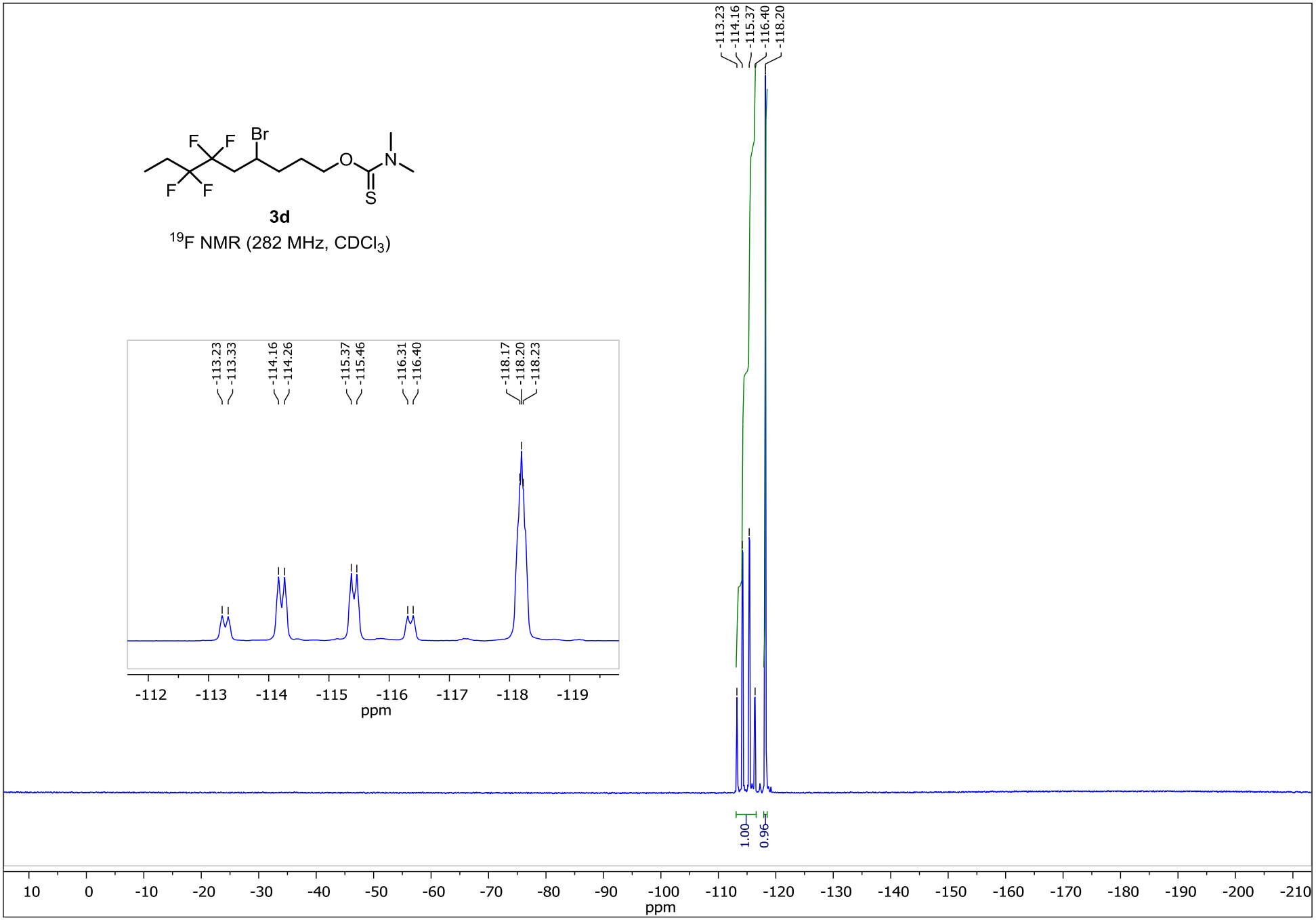

F
F
Br
F
F
O
O
OMe
3c
19F NMR (282 MHz, CDCl3)
-113.38
-114.31
-115.37
-116.31
-118.18
-113.38
-113.47
-114.31
-114.41
-115.28
-115.37
-115.37
-116.22
-116.31
-118.15
-118.18
-118.21
-113.0 -113.5 -114.0 -114.5 -115.0 -115.5 -116.0 -116.5 -117.0
ppm
-117.8 -118.0 -118.2 -118.4 -118.6
ppm
1.00
0.95
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
ppm

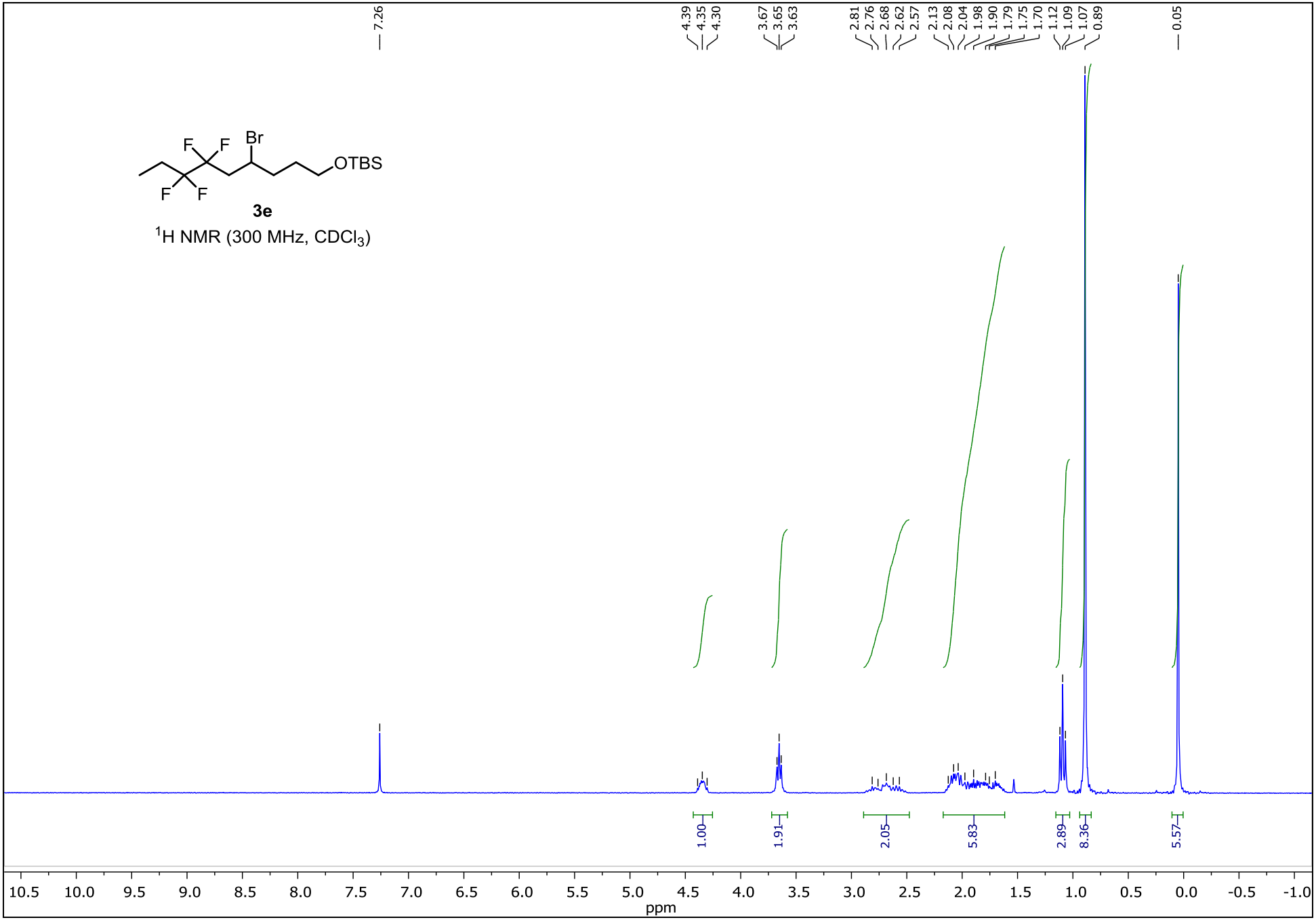


3d

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

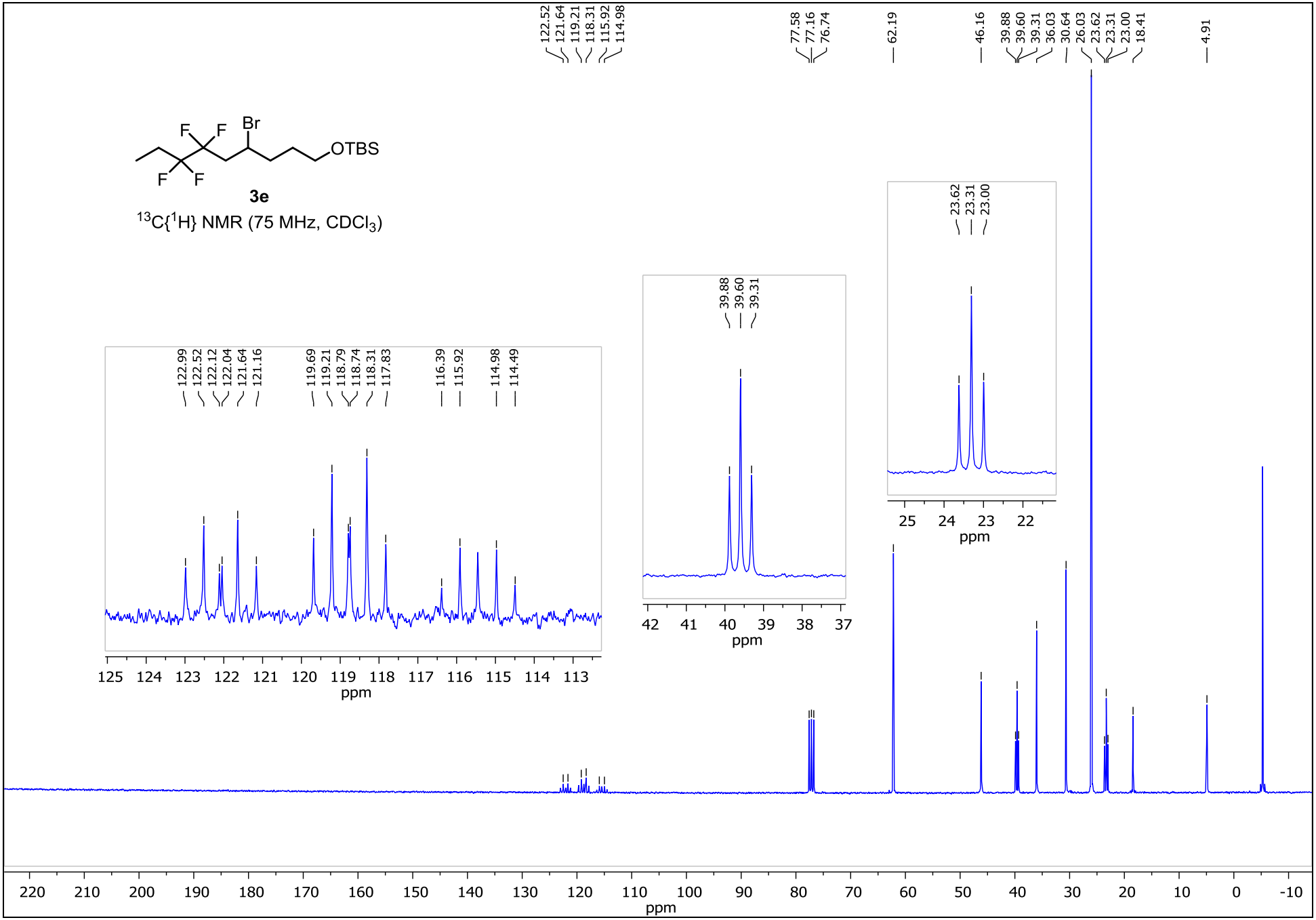

188.08
122.31
121.45
119.01
118.12
115.71
114.78
77.58
77.16
76.74
70.40
45.42
42.69
39.53
39.25
38.96
37.67
35.64
26.74
23.43
23.12
22.81
F
F
Br
F
F
O
N
S
3d
13C{1H} NMR (75 MHz, CDCl3)
122.78
122.31
121.91
121.84
121.45
120.96
119.48
119.01
118.59
118.54
118.12
117.63
116.18
115.71
115.26
114.78
114.30
123 122 121 120 119 118 117 116 115 114
ppm
39.53
39.25
38.96
40 39 38
ppm
23.43
23.12
22.81
24 23 22
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

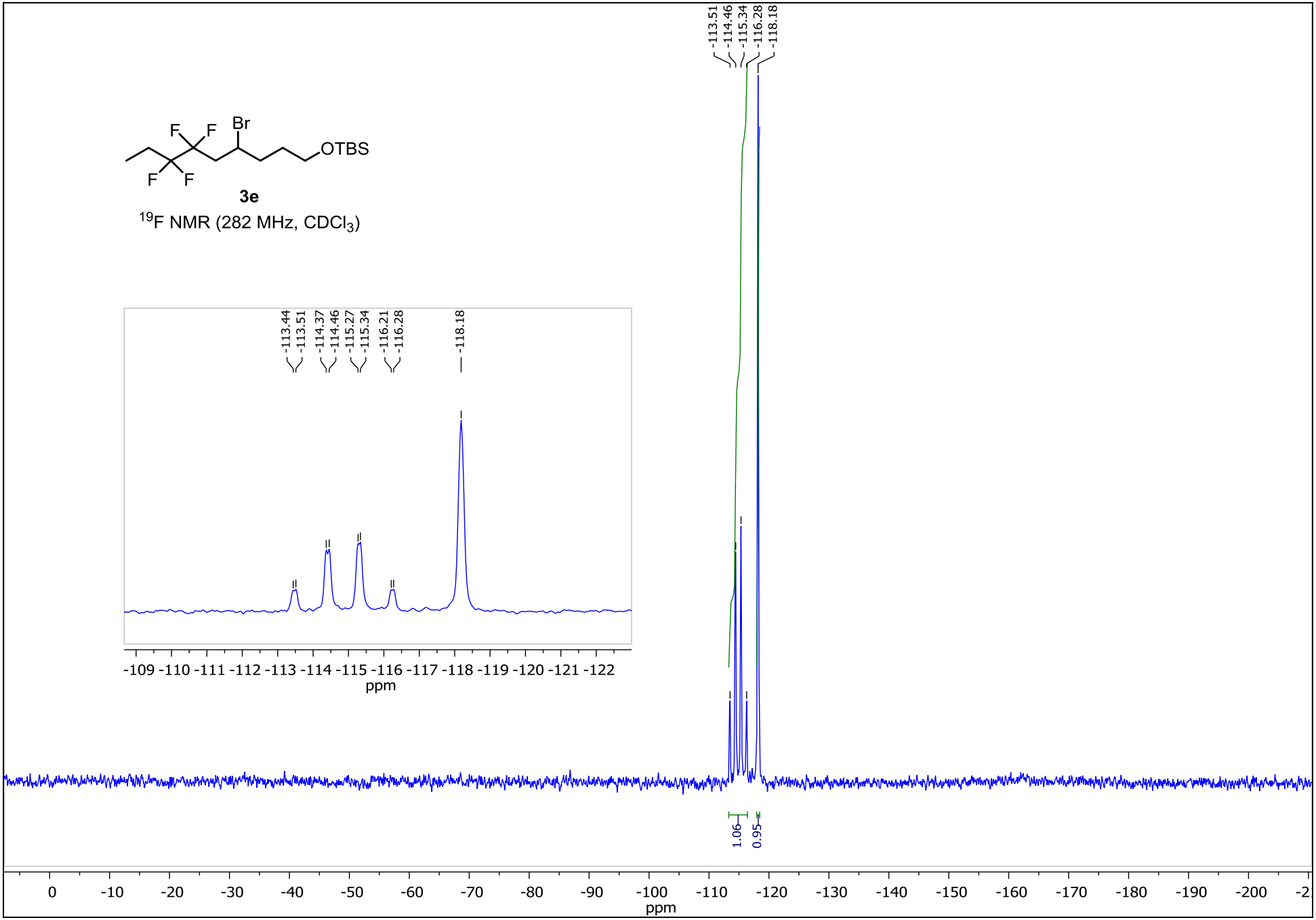

F
F
Br
O
N
F
F
S
3d
^{19}F NMR (282 MHz, $CDCl_3$)
-113.23
-114.16
-115.37
-116.40
-118.20
-113.23
-113.33
-114.16
-114.26
-115.37
-115.46
-116.31
-116.40
-118.17
-118.20
-118.23
-112
-113
-114
-115
-116
-117
-118
-119
ppm
1.00
0.96
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

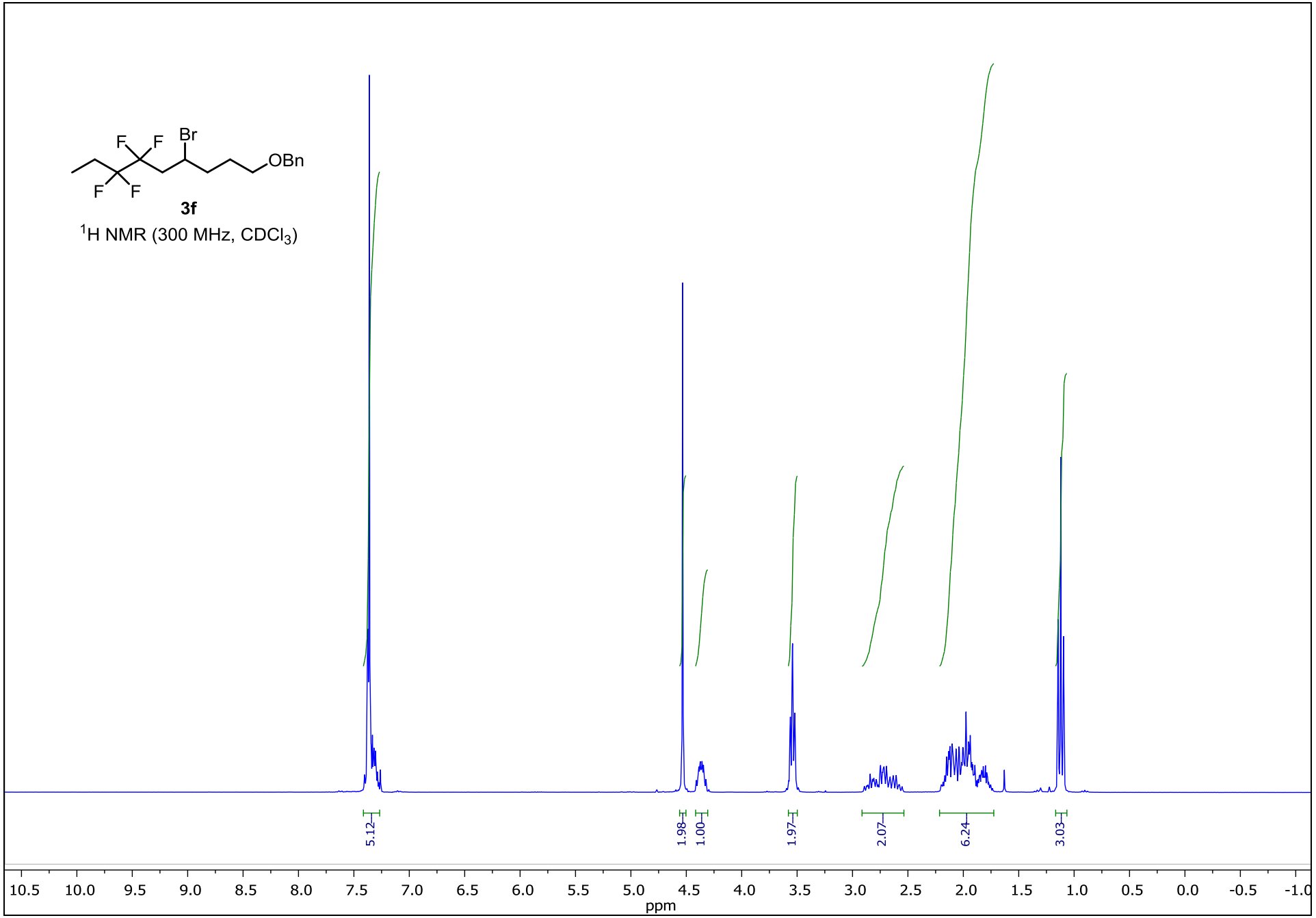


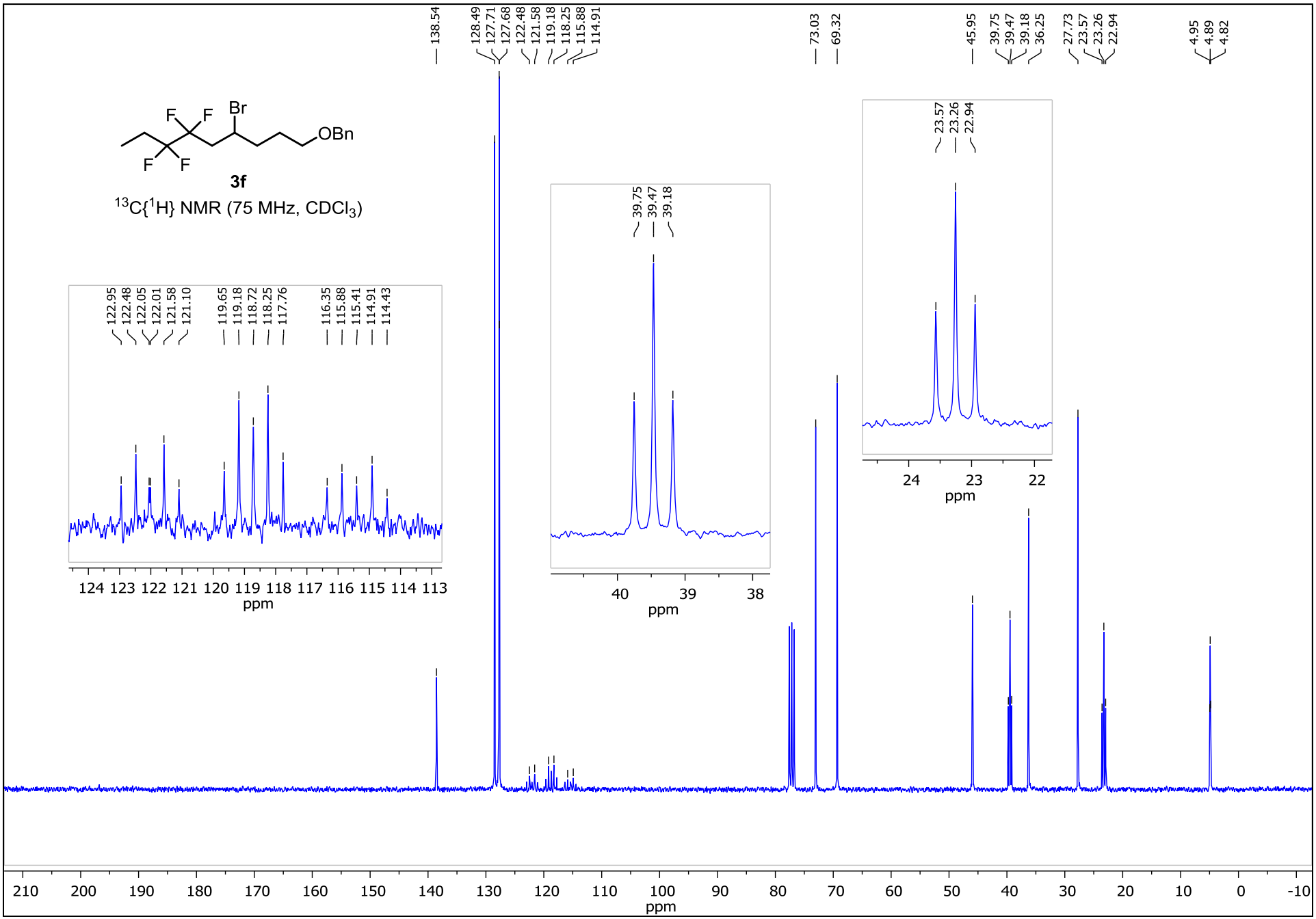
3e

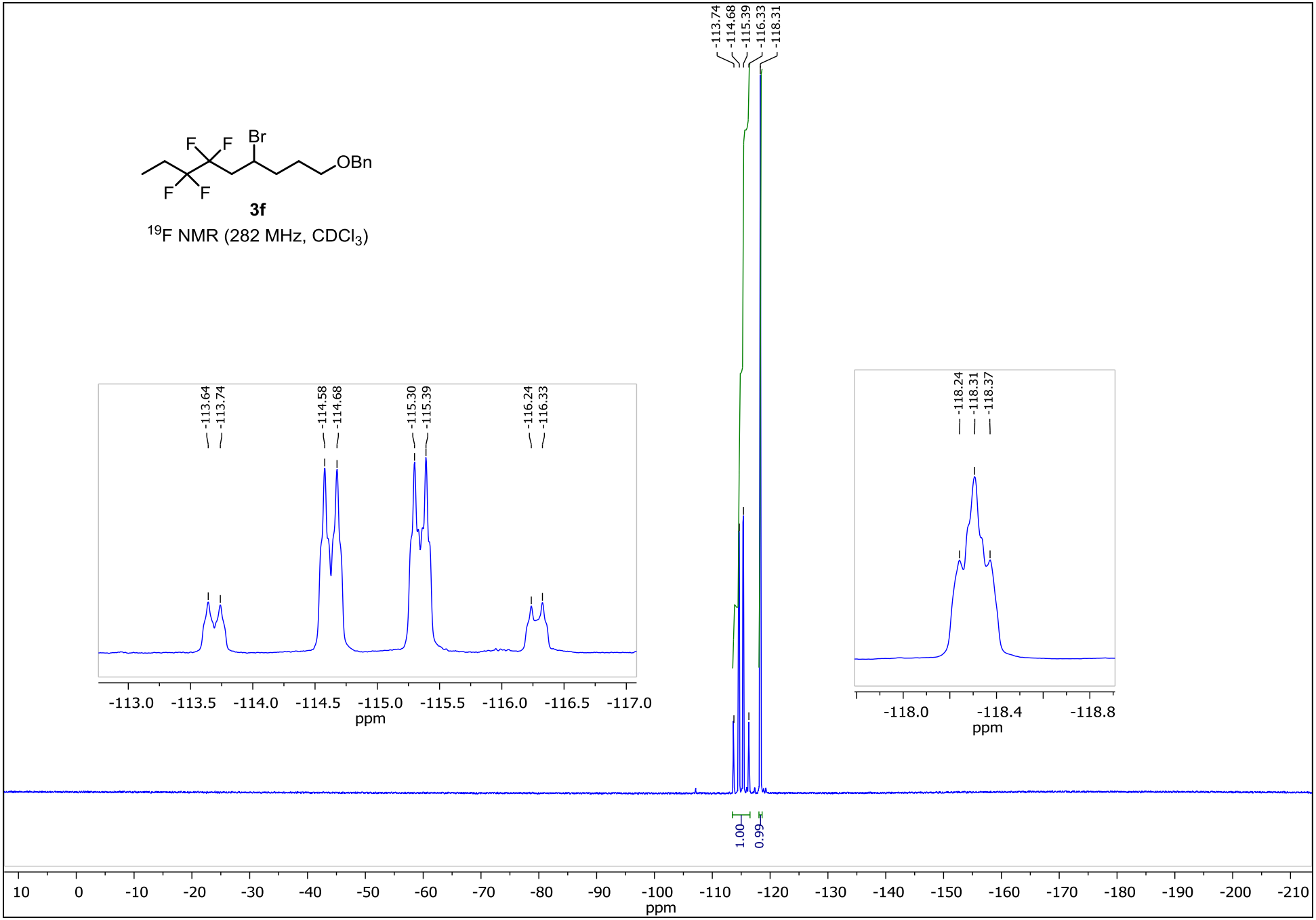
^{1}H NMR (300 MHz, $CDCl_3$)

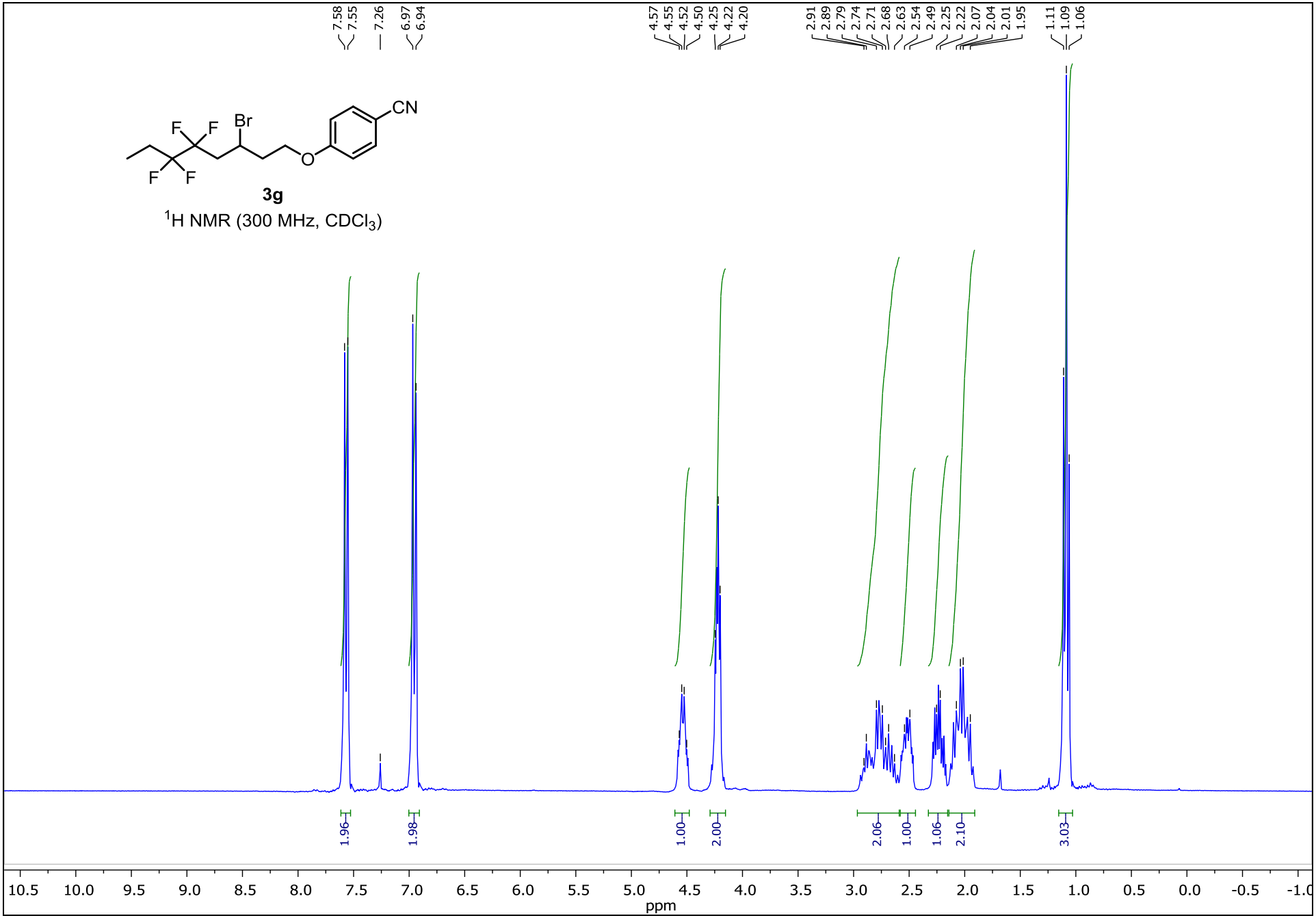

F
F
Br
OTBS
F
F
3e
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
122.52
121.64
119.21
118.31
115.92
114.98
77.58
77.16
76.74
62.19
46.16
39.88
39.60
39.31
36.03
30.64
26.03
23.62
23.31
23.00
18.41
4.91
122.99
122.52
122.12
122.04
121.64
121.16
119.69
119.21
118.79
118.74
118.31
117.83
116.39
115.92
114.98
114.49
125 124 123 122 121 120 119 118 117 116 115 114 113
ppm
39.88
39.60
39.31
42 41 40 39 38 37
ppm
23.62
23.31
23.00
25 24 23 22
ppm
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

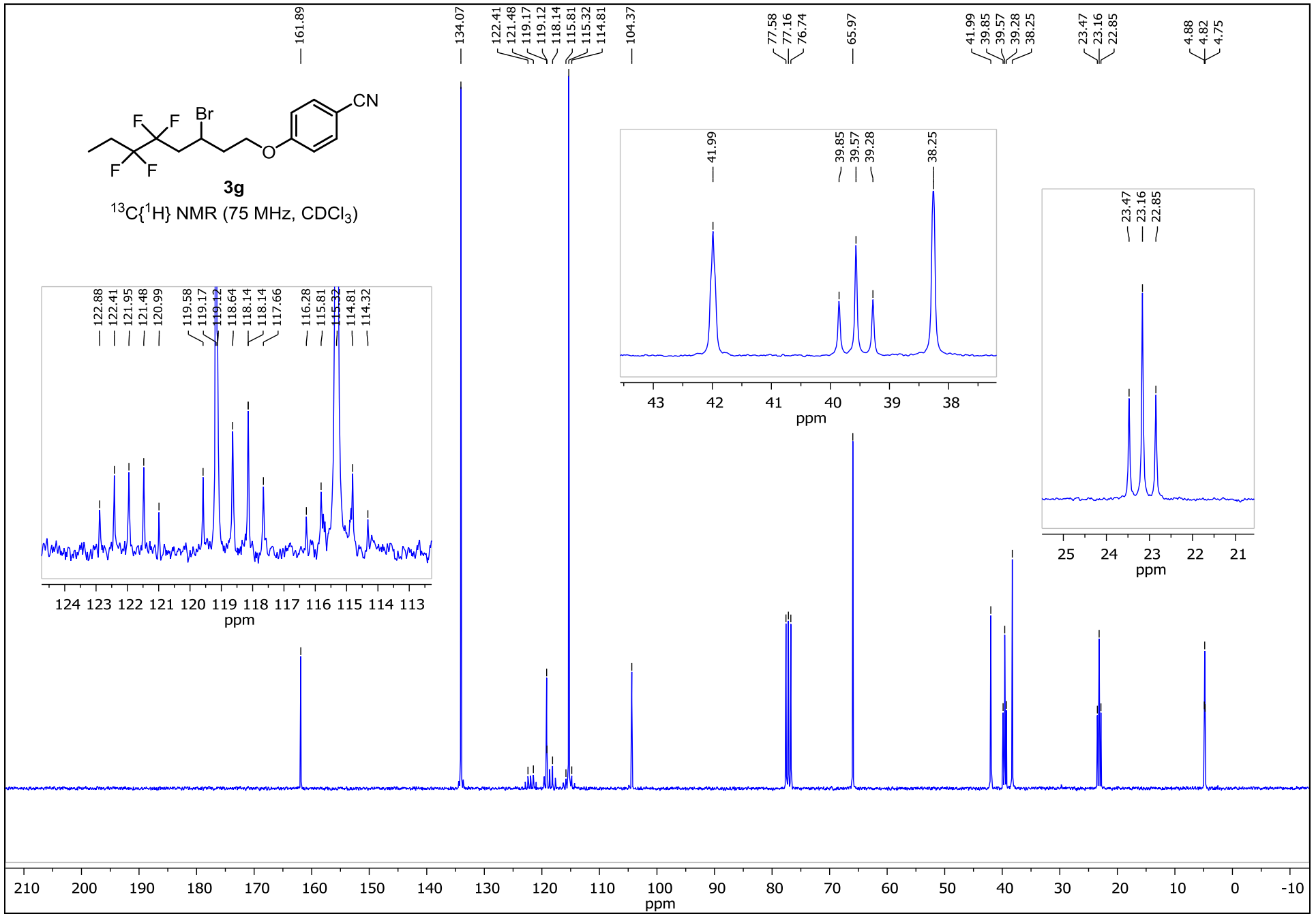

F
F
Br
OTBS
F
F
3e
19F NMR (282 MHz, CDCl3)
-113.51
-114.46
-115.34
-116.28
-118.18
-113.44
-113.51
-114.37
-114.46
-115.27
-115.34
-116.21
-116.28
-118.18
-109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122
ppm
1.06
0.95
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
ppm

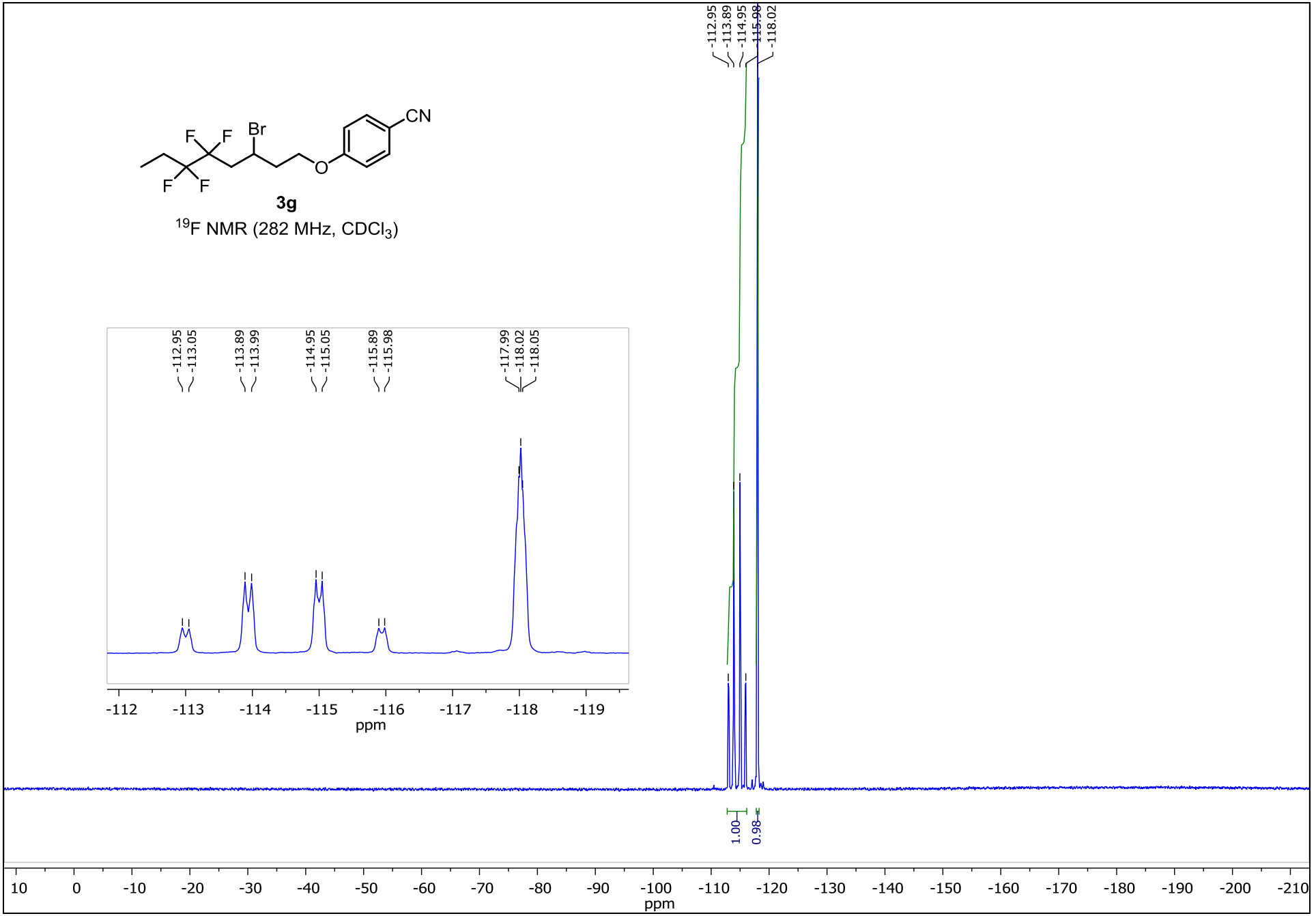

F
F
Br
OBn
F
F
3f
1H NMR (300 MHz, CDCl3)
5.12
1.98
1.00
1.97
2.07
6.24
3.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

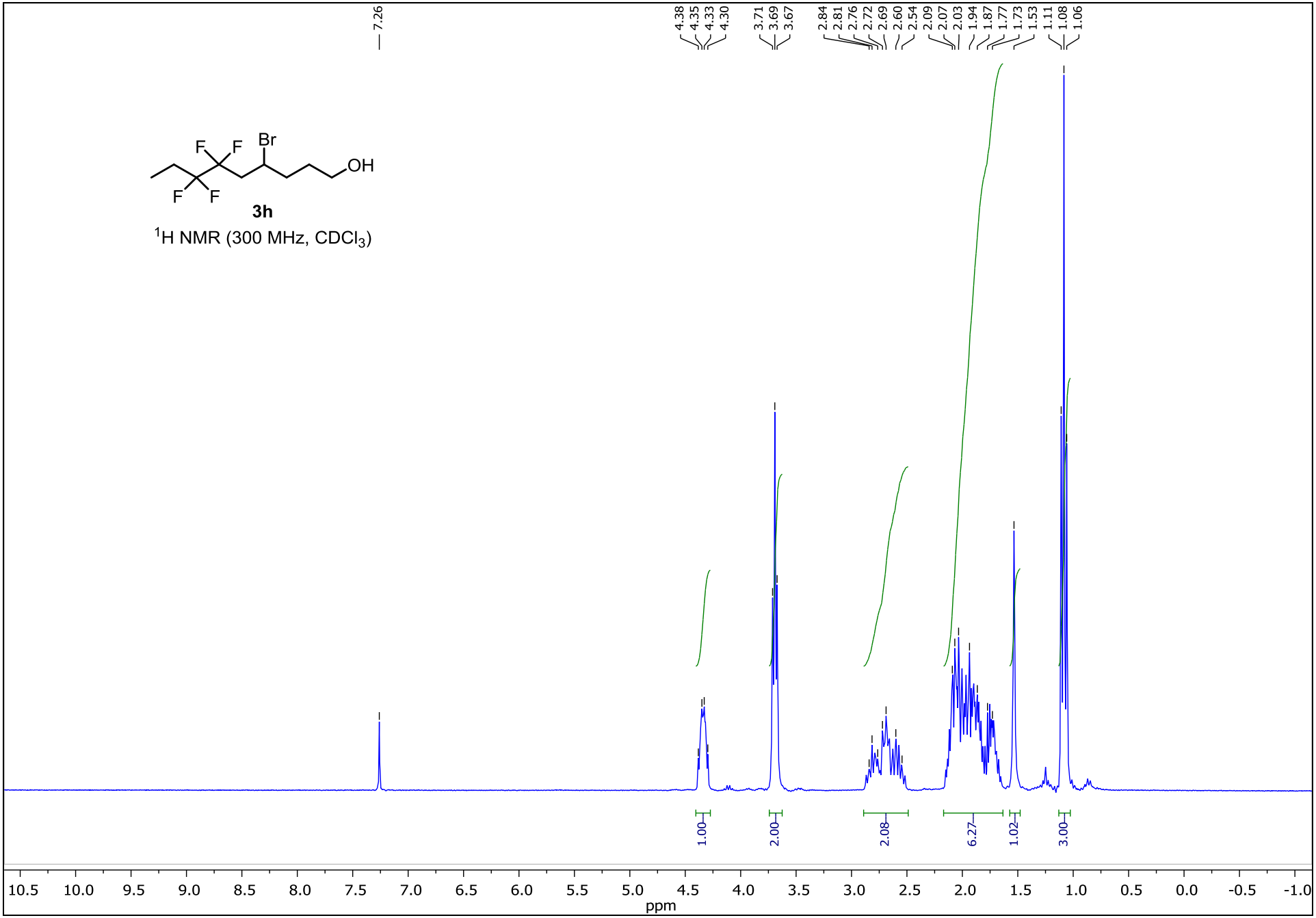

F
F
Br
OBn
F
F
3f
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
138.54
128.49
127.71
127.68
122.48
121.58
119.18
118.25
115.88
114.91
73.03
69.32
45.95
39.75
39.47
39.18
36.25
27.73
23.57
23.26
22.94
4.95
4.89
4.82
122.95
122.48
122.05
122.01
121.58
121.10
119.65
119.18
118.72
118.25
117.76
116.35
115.88
115.41
114.91
114.43
124 123 122 121 120 119 118 117 116 115 114 113
ppm
39.75
39.47
39.18
40 39 38
ppm
23.57
23.26
22.94
24 23 22
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

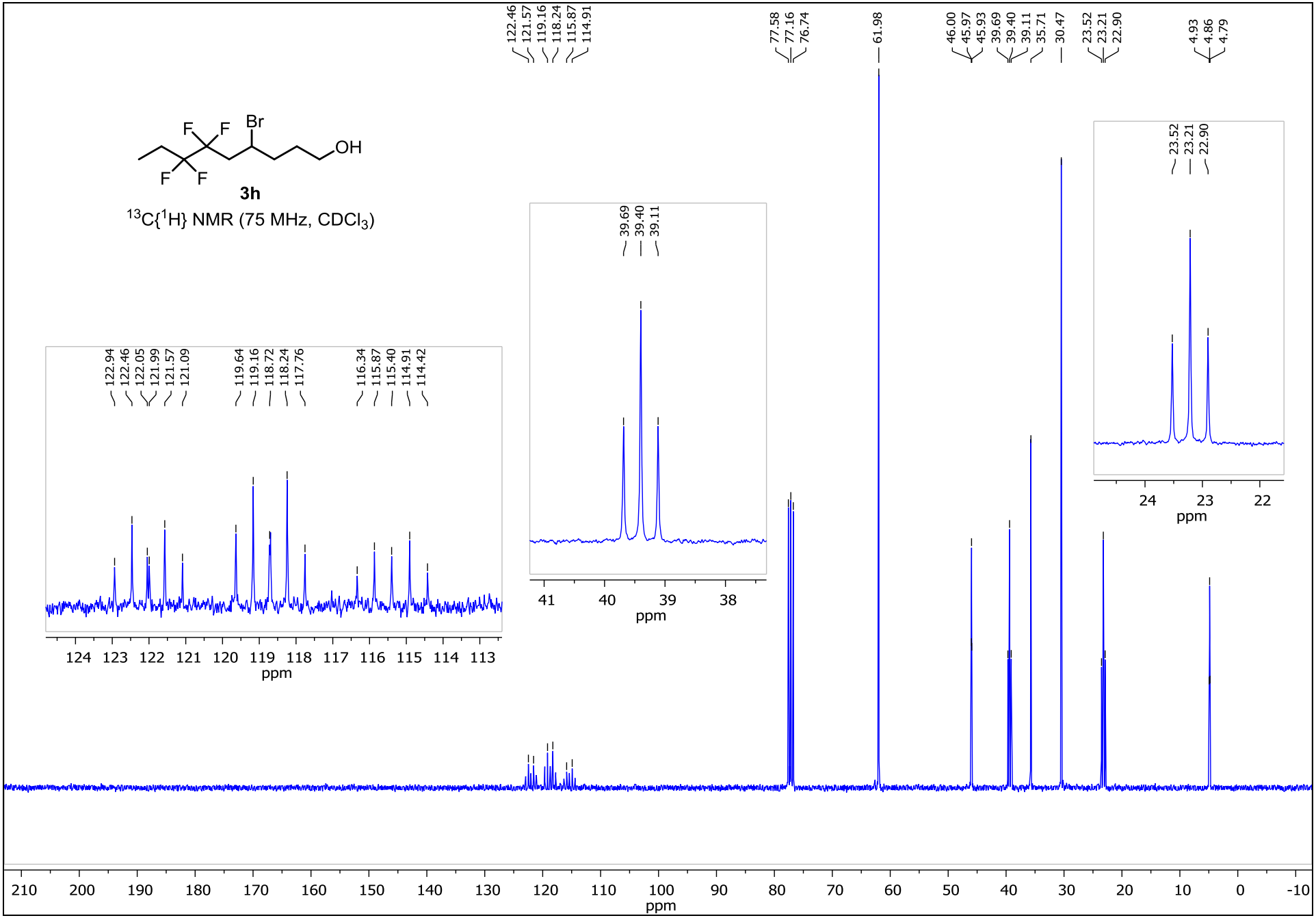

F
F
Br
OBn
F
F
3f
19F NMR (282 MHz, CDCl3)
-113.74
-114.68
-115.39
-116.33
-118.31
-113.64
-113.74
-114.58
-114.68
-115.30
-115.39
-116.24
-116.33
-113.0
-113.5
-114.0
-114.5
-115.0
-115.5
-116.0
-116.5
-117.0
ppm
-118.24
-118.31
-118.37
-118.0
-118.4
-118.8
ppm
1.00
0.99
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

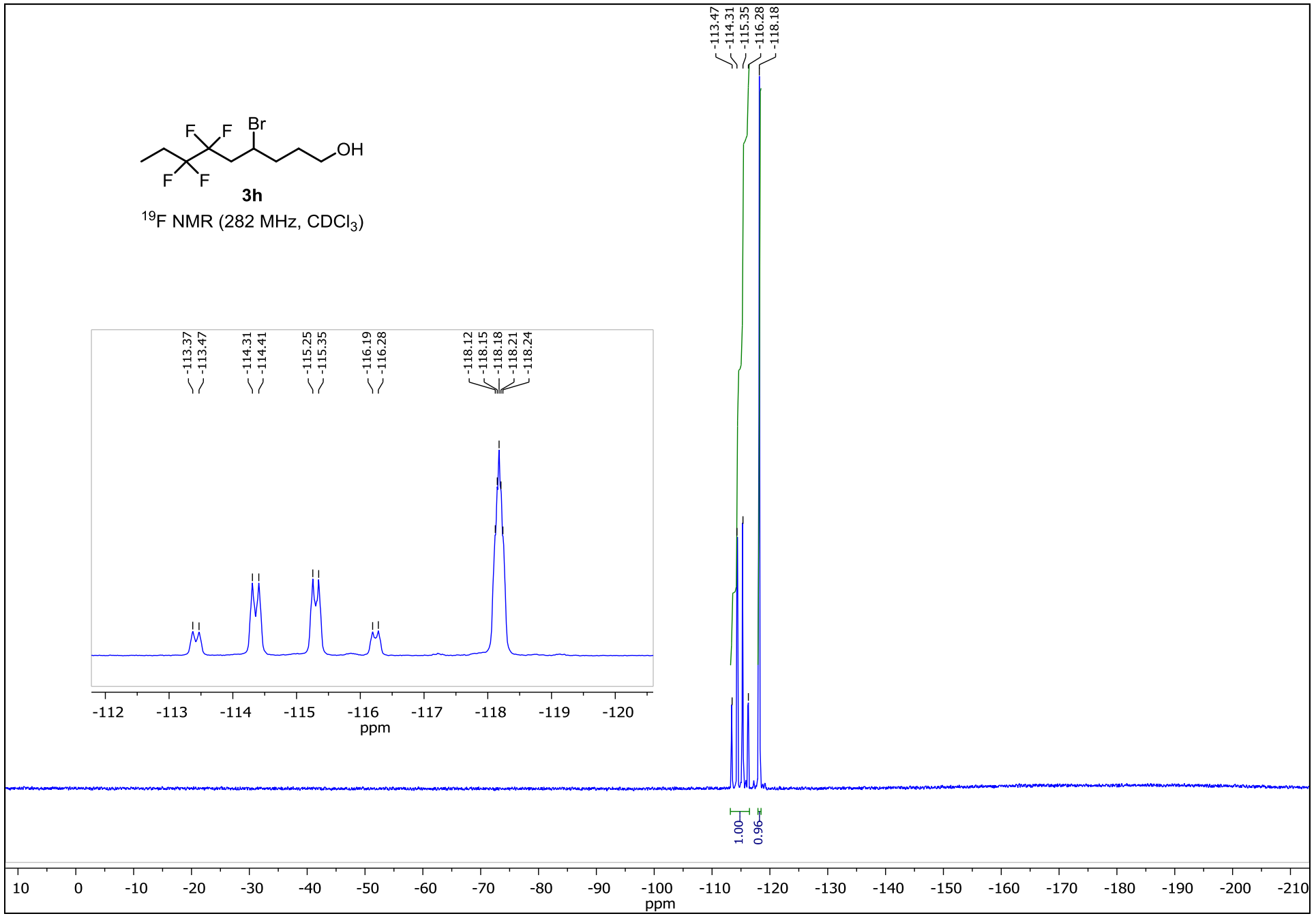

7.58
7.55
7.26
6.97
6.94
4.57
4.55
4.52
4.50
4.25
4.22
4.20
2.91
2.89
2.79
2.74
2.71
2.68
2.63
2.54
2.49
2.25
2.22
2.07
2.04
2.01
1.95
1.11
1.09
1.06
F
F
Br
CN
O
F
F
3g
1H NMR (300 MHz, CDCl3)
1.96
1.98
1.00
2.00
2.06
1.00
1.06
2.10
3.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

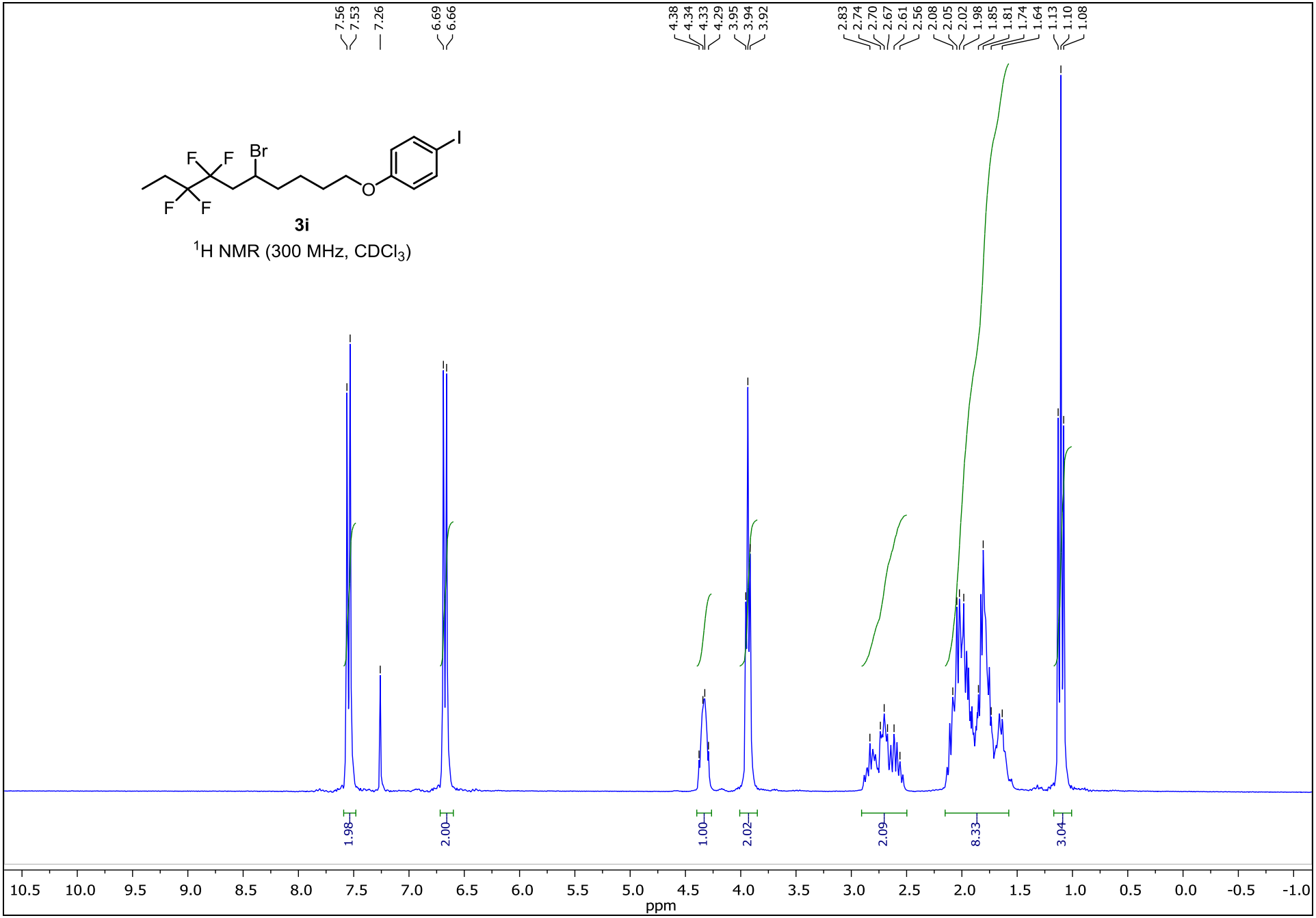

161.89
134.07
122.41
121.48
119.17
119.12
118.14
115.81
115.32
114.81
104.37
77.58
77.16
76.74
65.97
41.99
39.85
39.57
39.28
38.25
23.47
23.16
22.85
4.88
4.82
4.75
F
F
Br
CN
O
F
F
3g
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
122.88
122.41
121.95
121.48
120.99
119.58
119.17
119.12
118.64
118.14
118.14
117.66
116.28
115.81
115.32
114.81
114.32
124 123 122 121 120 119 118 117 116 115 114 113
ppm
43 42 41 40 39 38
ppm
25 24 23 22 21
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


F
F
Br
CN
O
F
F
3g
19F NMR (282 MHz, CDCl3)
-112.95
-113.89
-114.95
-115.98
-118.02
-112.95
-113.05
-113.89
-113.99
-114.95
-115.05
-115.89
-115.98
-117.99
-118.02
-118.05
-112
-113
-114
-115
-116
-117
-118
-119
ppm
1.00
0.98
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm


7.26
4.38
4.35
4.33
4.30
3.71
3.69
3.67
2.84
2.81
2.76
2.72
2.69
2.60
2.54
2.09
2.07
2.03
1.94
1.87
1.77
1.73
1.53
1.11
1.08
1.06
F
F
Br
OH
F
F
3h
1H NMR (300 MHz, CDCl3)
1.00
2.00
2.08
6.27
1.02
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

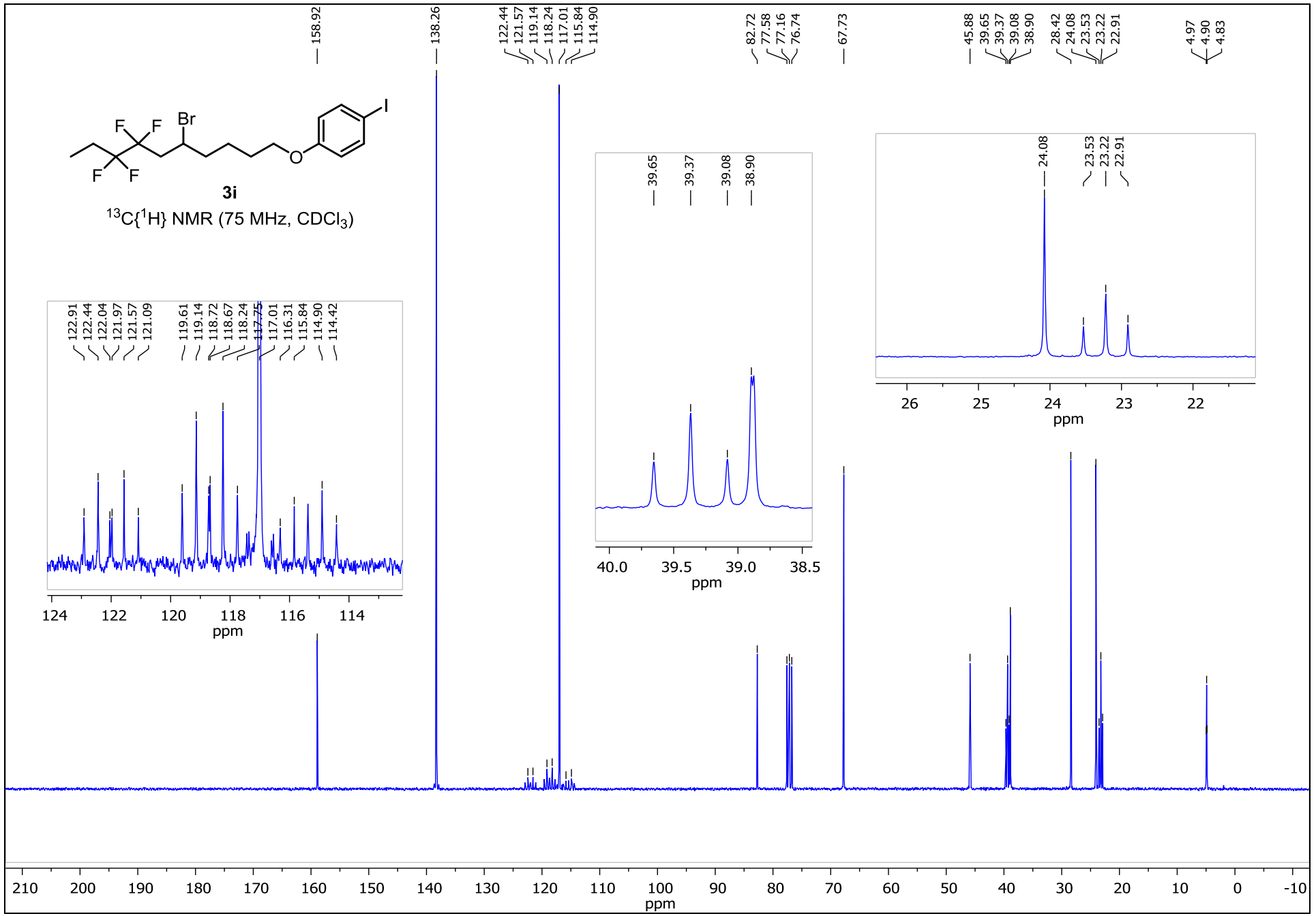

F
F
Br
OH
F
F
3h
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
122.46
121.57
119.16
118.24
115.87
114.91
77.58
77.16
76.74
61.98
46.00
45.97
45.93
39.69
39.40
39.11
35.71
30.47
23.52
23.21
22.90
4.93
4.86
4.79
122.94
122.46
122.05
121.99
121.57
121.09
119.64
119.16
118.72
118.24
117.76
116.34
115.87
115.40
114.91
114.42
124 123 122 121 120 119 118 117 116 115 114 113
ppm
41 40 39 38
ppm
24 23 22
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

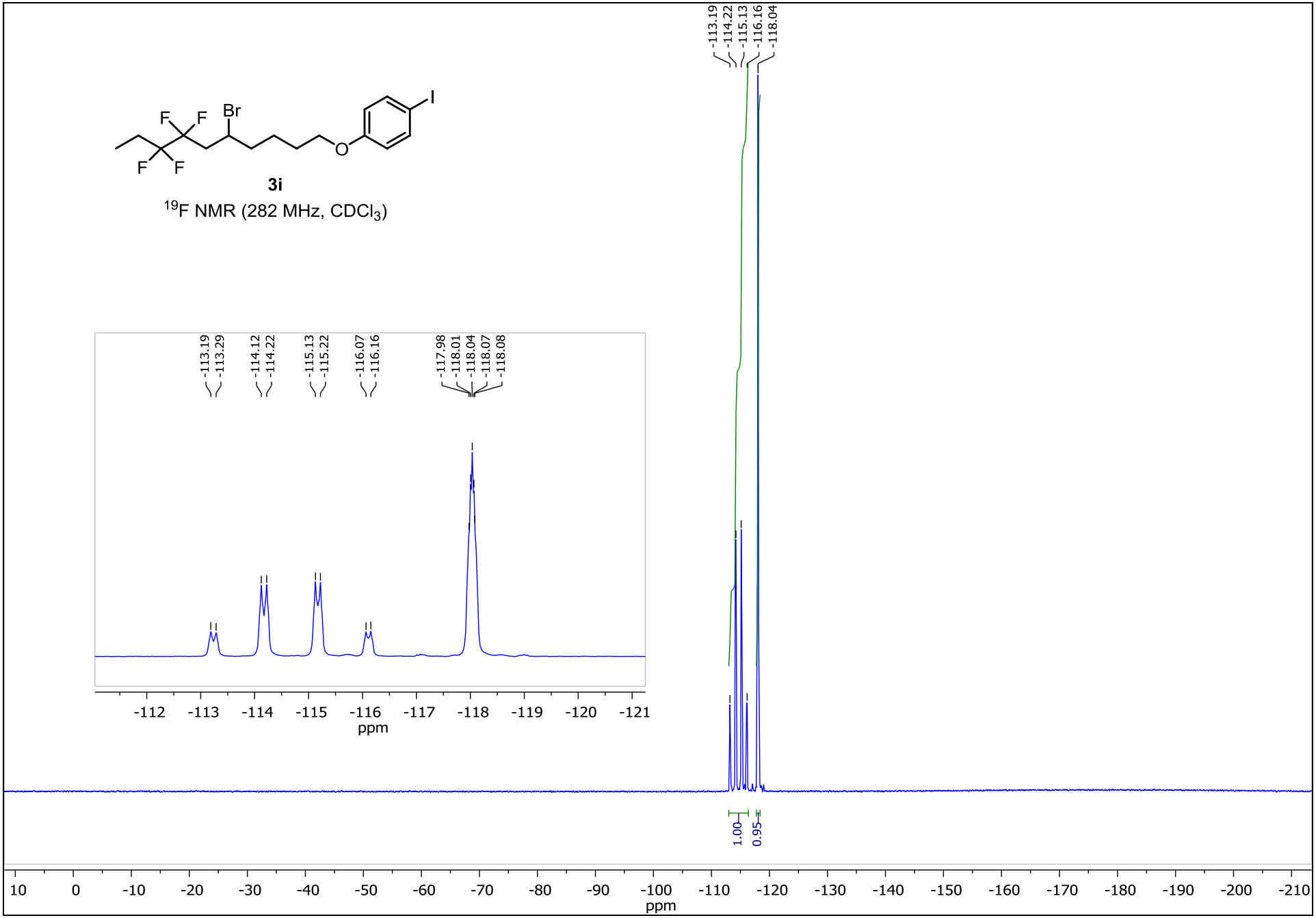

F
F
Br
OH
F
F
3h
19F NMR (282 MHz, CDCl3)
-113.47
-114.31
-115.35
-116.28
-118.18
-113.37
-113.47
-114.31
-114.41
-115.25
-115.35
-116.19
-116.28
-118.12
-118.15
-118.18
-118.21
-118.24
-112
-113
-114
-115
-116
-117
-118
-119
-120
ppm
1.00
0.96
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

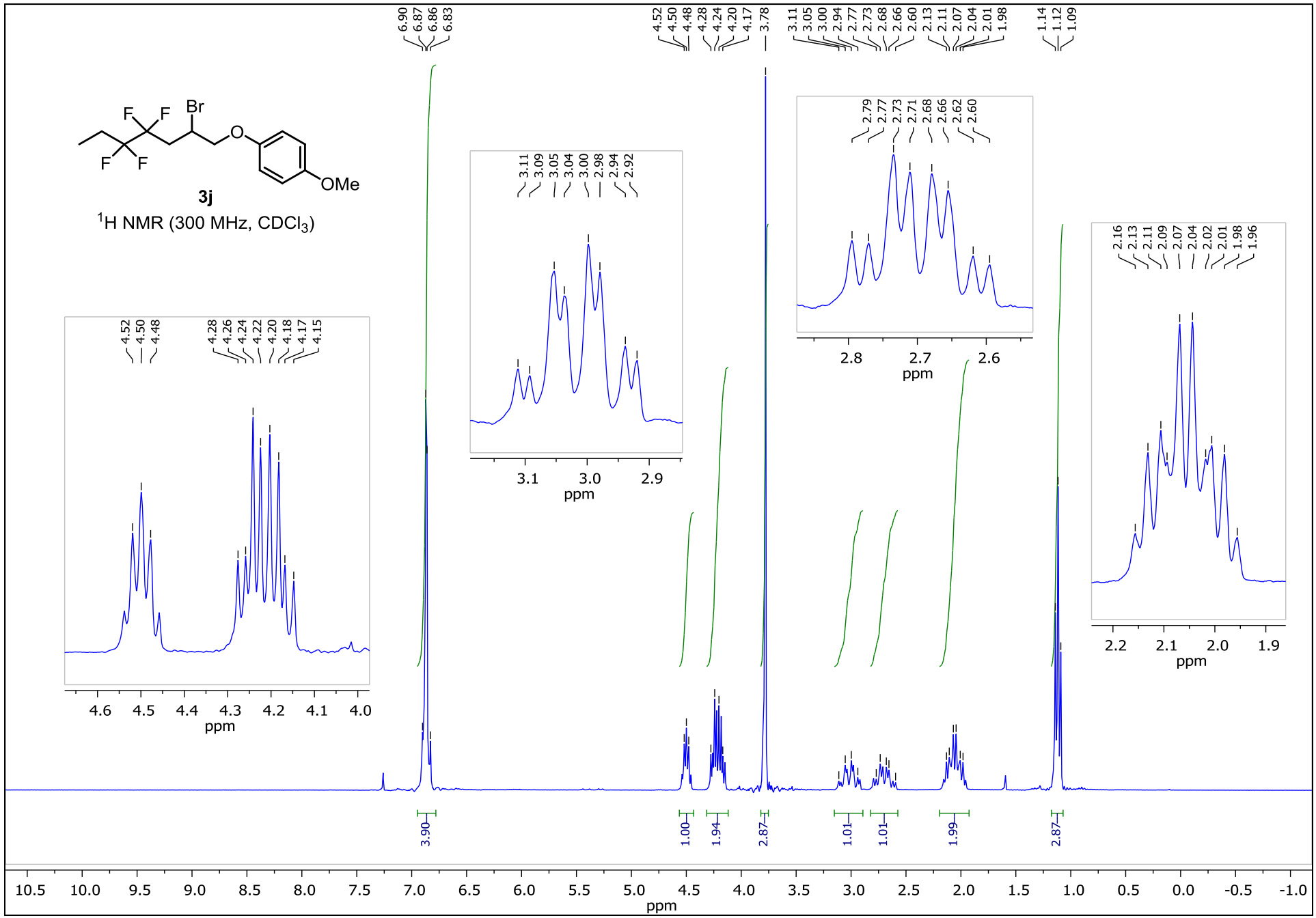


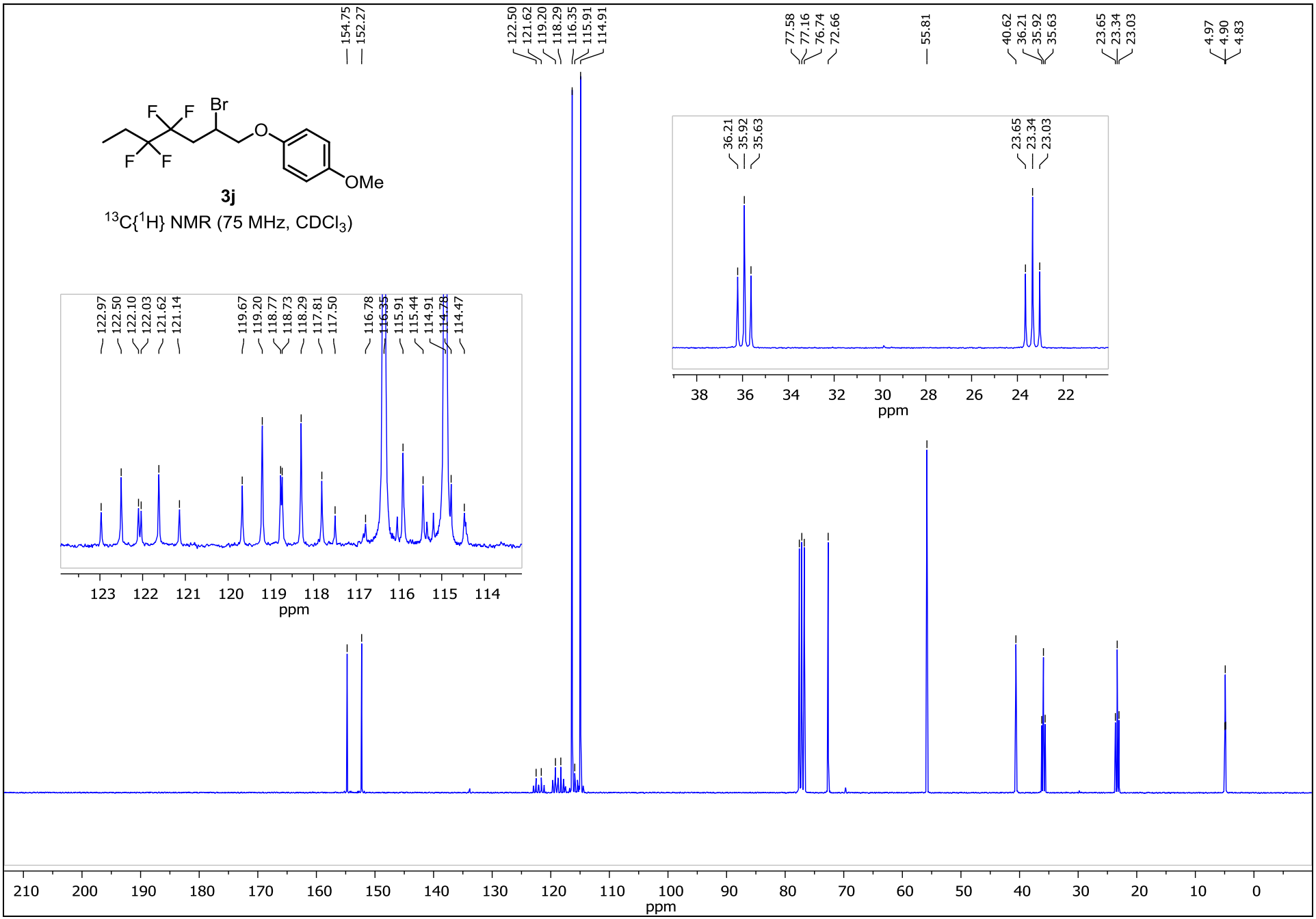
3i

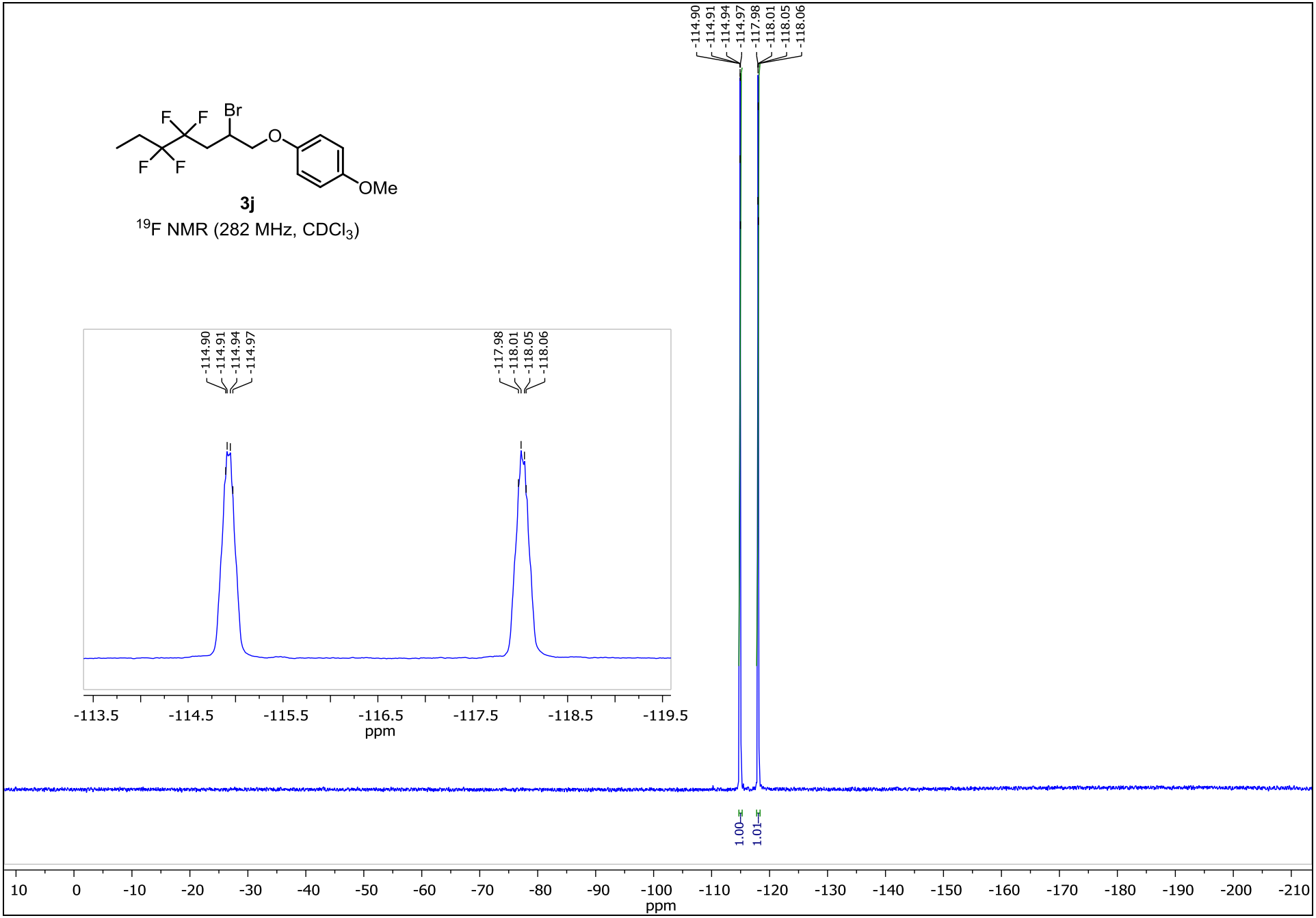
^{1}H NMR (300 MHz, $CDCl_3$)

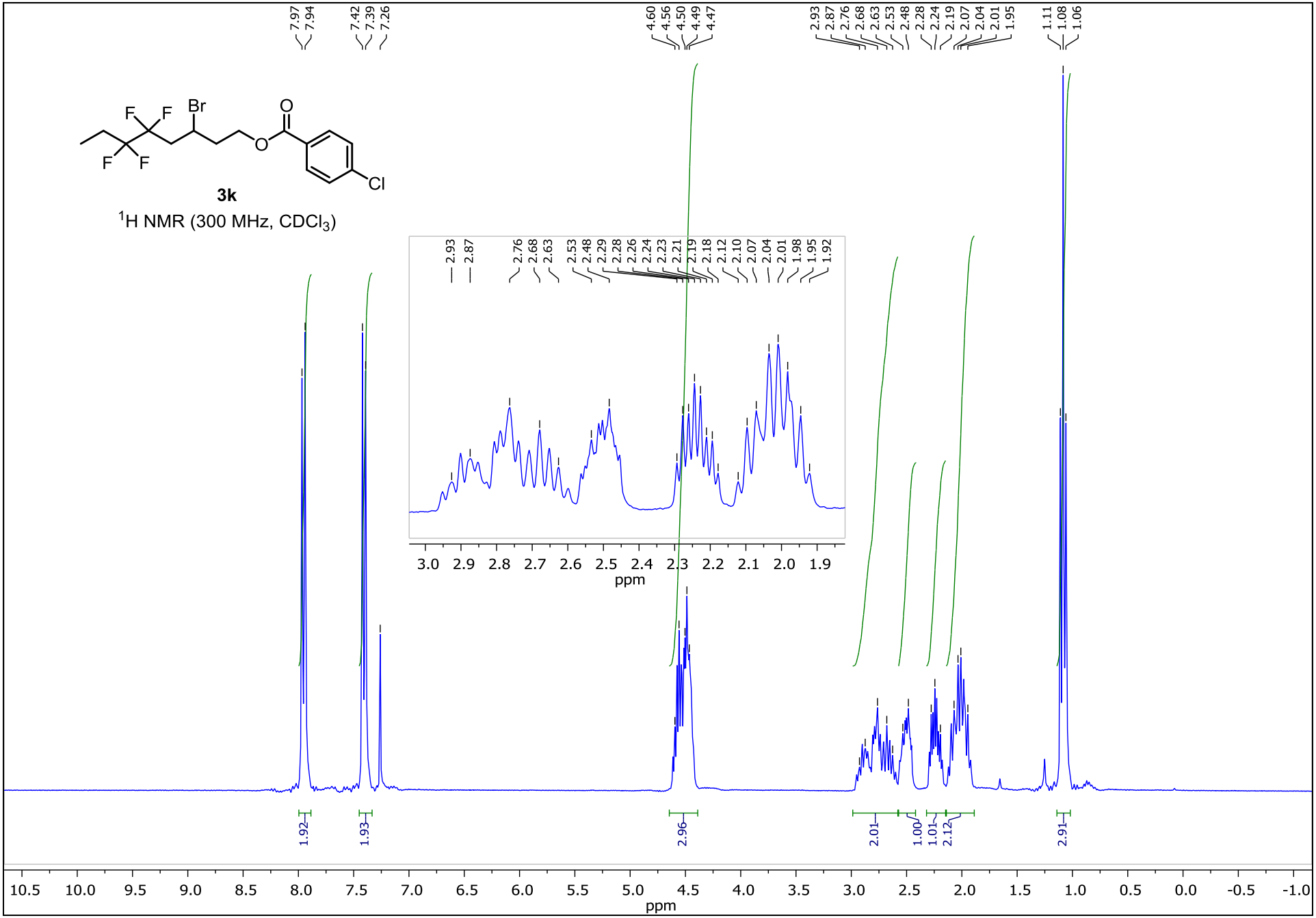

158.92
138.26
122.44
121.57
119.14
118.24
117.01
115.84
114.90
82.72
77.58
77.16
76.74
67.73
45.88
39.65
39.37
39.08
38.90
28.42
24.08
23.53
23.22
22.91
4.97
4.90
4.83
F
F
Br
F
F
O
I
3i
13C{1H} NMR (75 MHz, CDCl3)
122.91
122.44
122.04
121.97
121.57
121.09
119.61
119.14
118.72
118.67
118.24
117.75
117.01
116.31
115.84
114.90
114.42
124
122
120
118
116
114
ppm
39.65
39.37
39.08
38.90
40.0
39.5
39.0
38.5
ppm
24.08
23.53
23.22
22.91
26
25
24
23
22
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

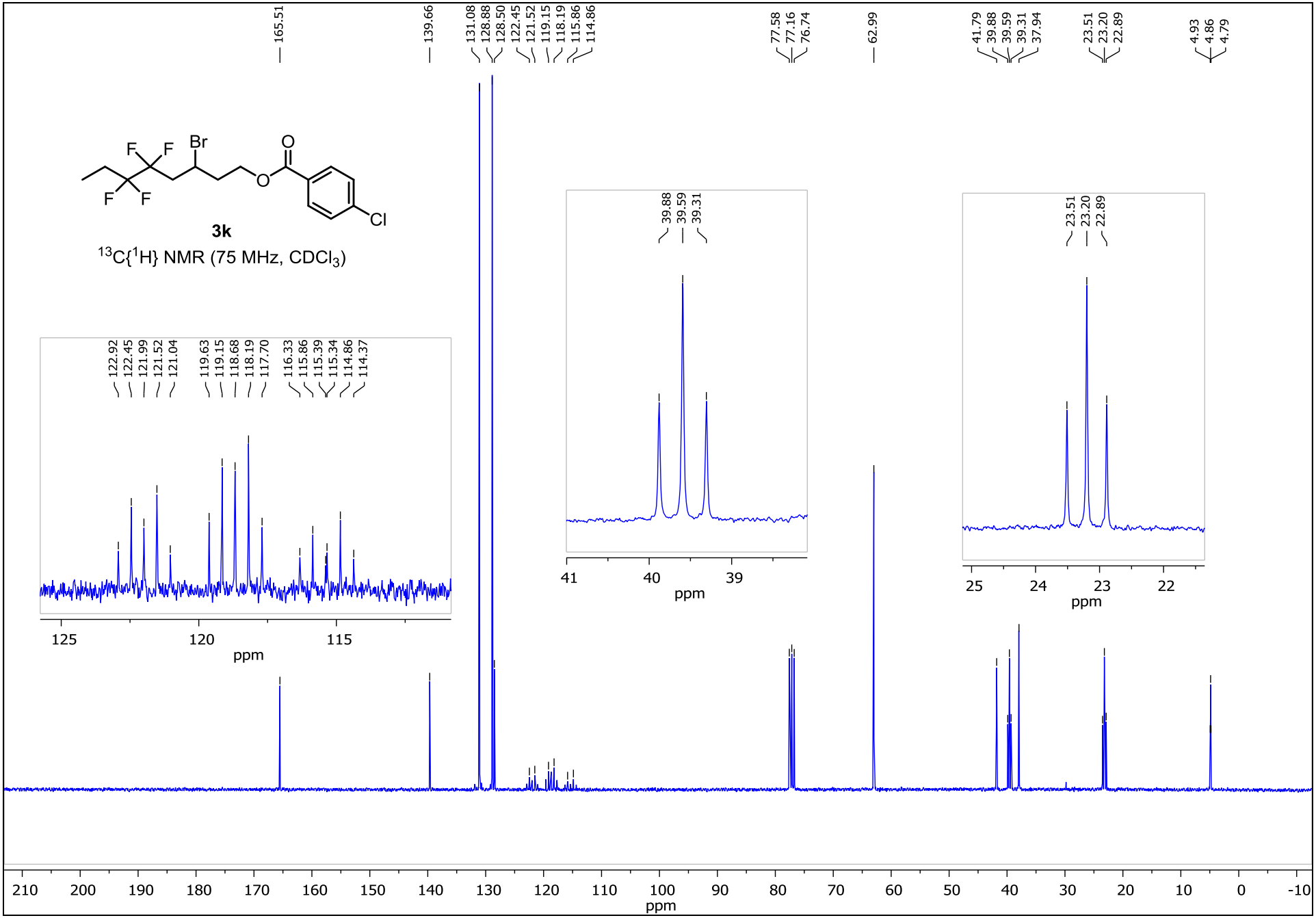

F
F
Br
I
O
F
F
3i
19F NMR (282 MHz, CDCl3)
-113.19
-114.22
-115.13
-116.16
-118.04
-113.19
-113.29
-114.12
-114.22
-115.13
-115.22
-116.07
-116.16
-117.98
-118.01
-118.04
-118.07
-118.08
-112
-113
-114
-115
-116
-117
-118
-119
-120
-121
ppm
1.00
0.95
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

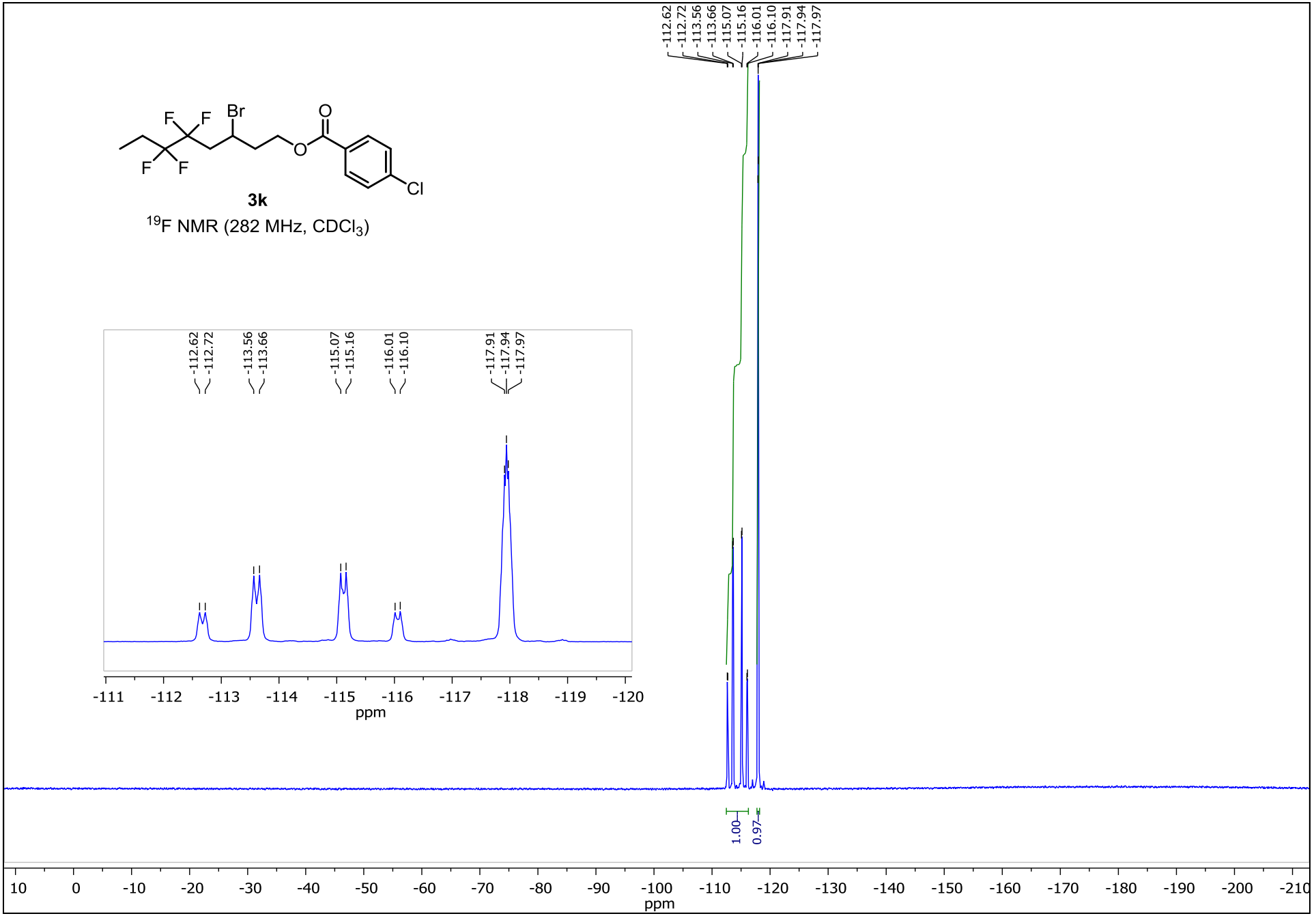

F
F
Br
O
F
F
OMe
3j
^{1}H NMR (300 MHz, $CDCl_3$)
6.90
6.87
6.86
6.83
4.52
4.50
4.48
4.28
4.24
4.20
4.17
3.78
3.11
3.05
3.00
2.94
2.77
2.73
2.68
2.66
2.60
2.13
2.11
2.07
2.04
2.01
1.98
1.14
1.12
1.09
3.90
1.00
1.94
2.87
1.01
1.01
1.99
2.87
ppm

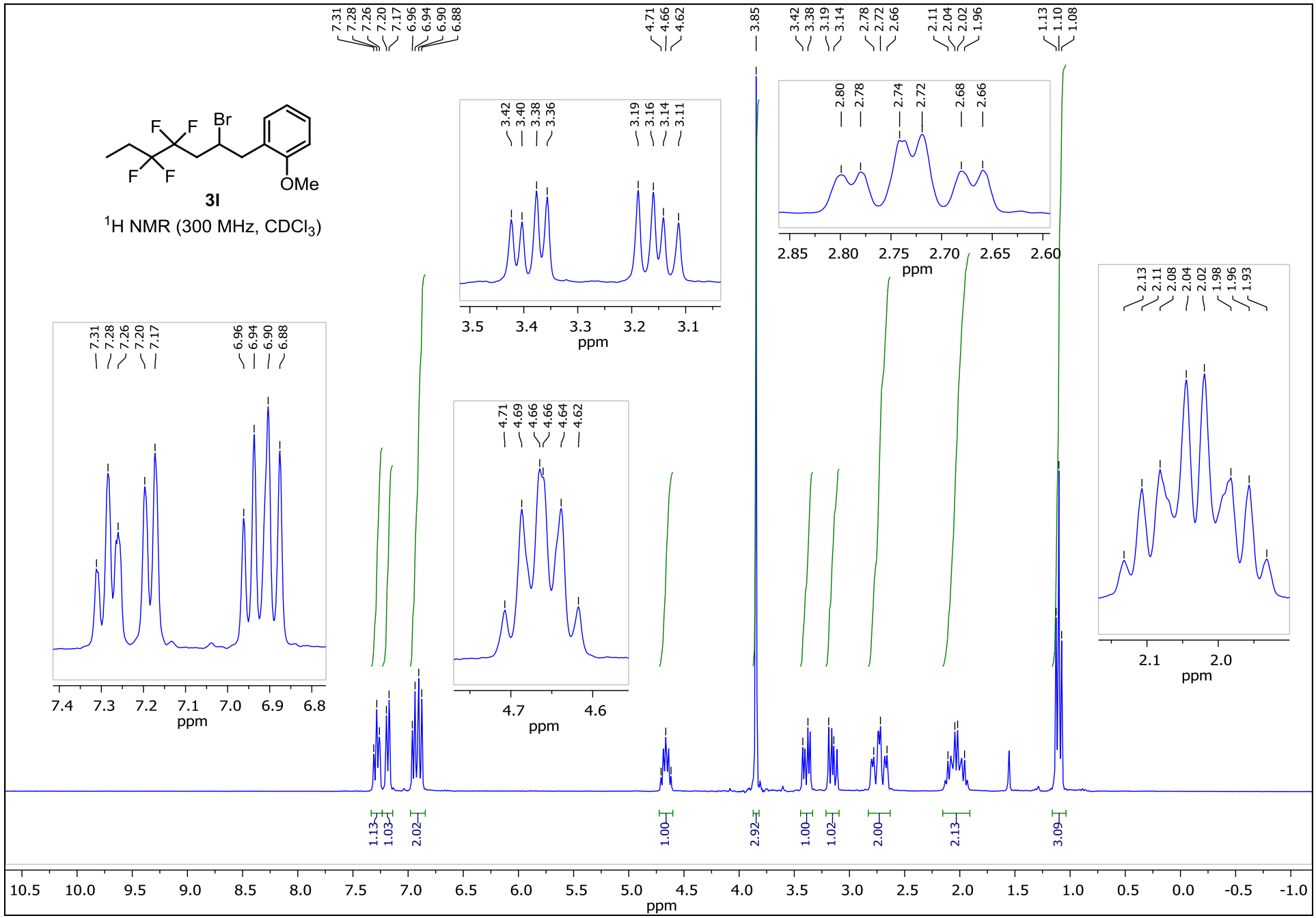

154.75
152.27
122.50
121.62
119.20
118.29
116.35
115.91
114.91
77.58
77.16
76.74
72.66
55.81
40.62
36.21
35.92
35.63
23.65
23.34
23.03
4.97
4.90
4.83
F
F
Br
O
F
F
OMe
3j
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
122.97
122.50
122.10
122.03
121.62
121.14
119.67
119.20
118.77
118.73
118.29
117.81
117.50
116.78
116.35
115.91
115.44
114.91
114.78
114.47
123 122 121 120 119 118 117 116 115 114
ppm
36.21
35.92
35.63
23.65
23.34
23.03
38 36 34 32 30 28 26 24 22
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

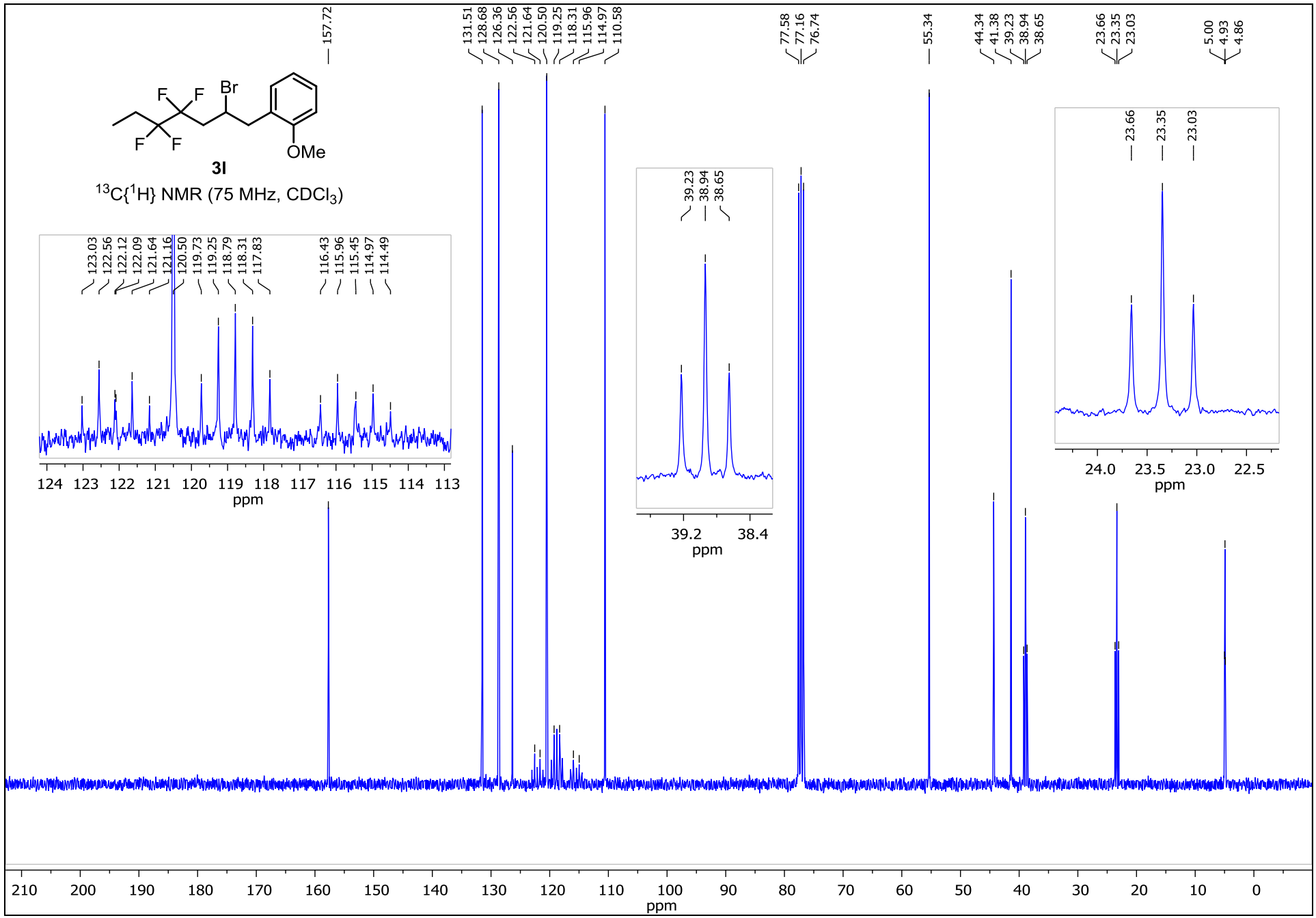

F
F
Br
O
F
F
OMe
3j
19F NMR (282 MHz, CDCl3)
-114.90
-114.91
-114.94
-114.97
-117.98
-118.01
-118.05
-118.06
1.00
1.01
-113.5
-114.5
-115.5
-116.5
-117.5
-118.5
-119.5
ppm
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

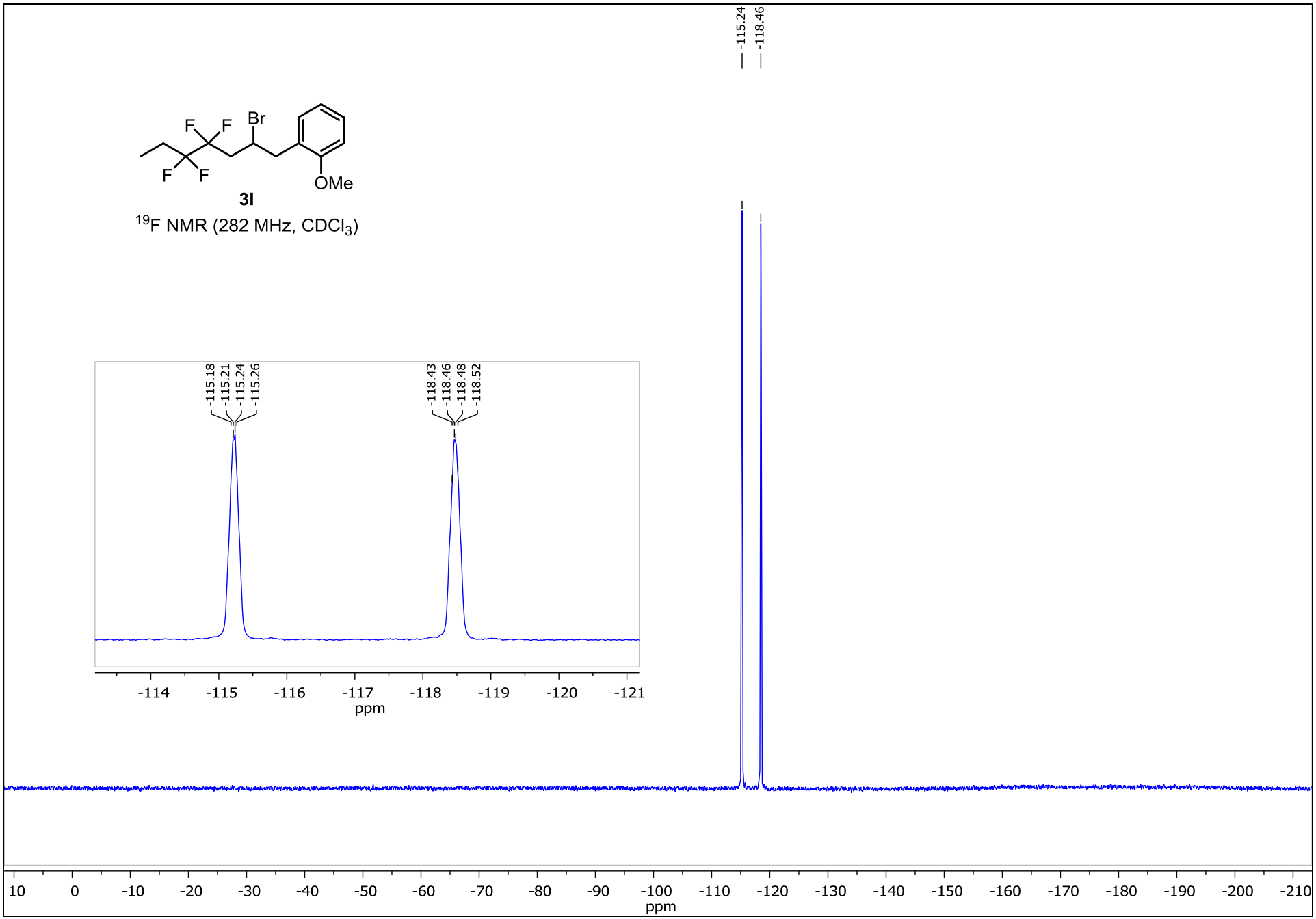

7.97
7.94
7.42
7.39
7.26
4.60
4.56
4.50
4.49
4.47
2.93
2.87
2.76
2.68
2.63
2.53
2.48
2.28
2.24
2.19
2.07
2.04
2.01
1.95
1.11
1.08
1.06
F
F
Br
O
O
F
F
Cl
3k
1H NMR (300 MHz, CDCl3)
2.93
2.87
2.76
2.68
2.63
2.53
2.48
2.29
2.28
2.26
2.24
2.23
2.21
2.19
2.18
2.12
2.10
2.07
2.04
2.01
1.98
1.95
1.92
3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9
ppm
1.92
1.93
2.96
2.01
1.00
1.01
2.12
2.91
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

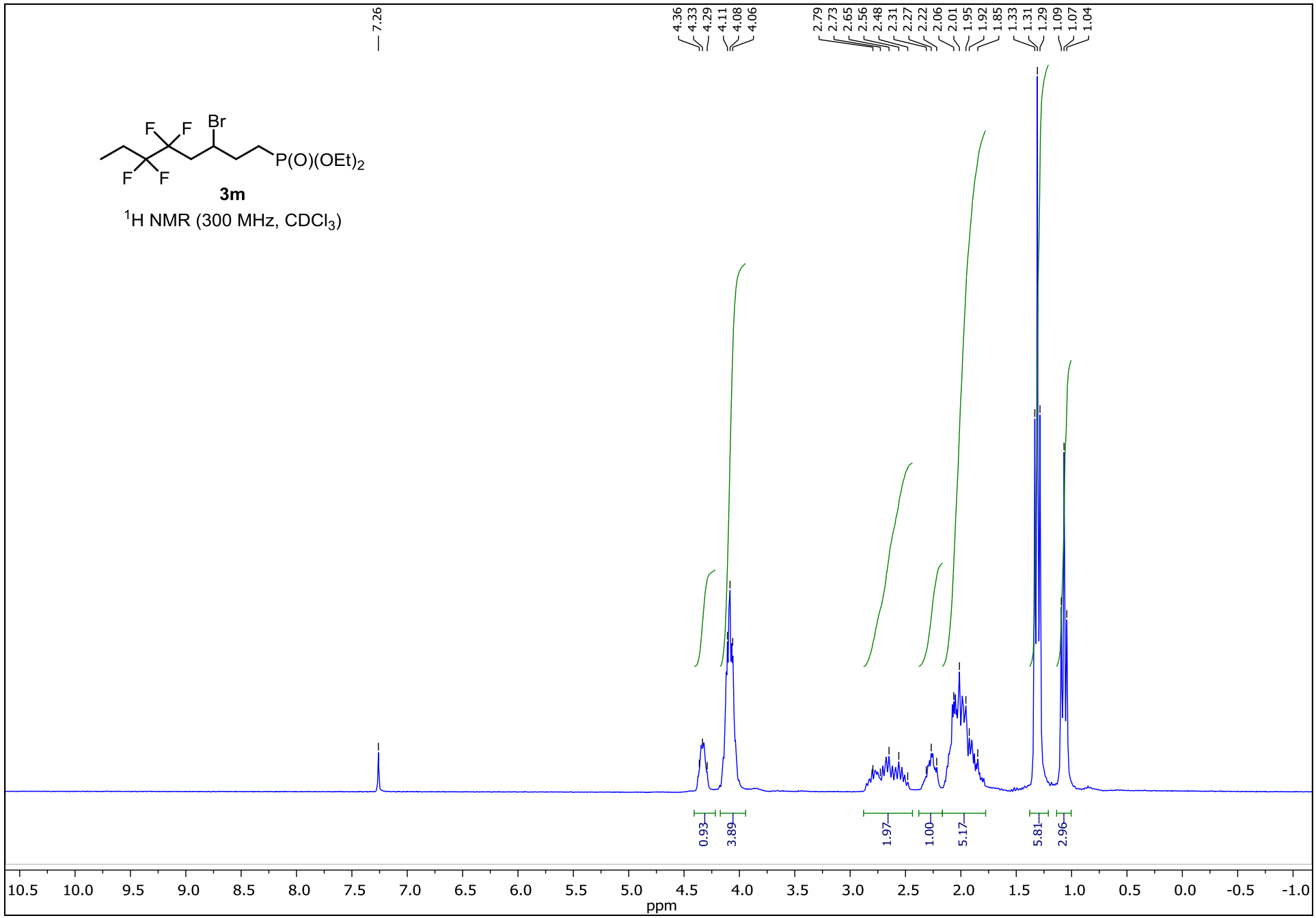

165.51
139.66
131.08
128.88
128.50
122.45
121.52
119.15
118.19
115.86
114.86
77.58
77.16
76.74
62.99
41.79
39.88
39.59
39.31
37.94
23.51
23.20
22.89
4.93
4.86
4.79
F
F
Br
O
O
F
F
Cl
3k
13C{1H} NMR (75 MHz, CDCl3)
122.92
122.45
121.99
121.52
121.04
119.63
119.15
118.68
118.19
117.70
116.33
115.86
115.39
115.34
114.86
114.37
125
120
115
ppm
39.88
39.59
39.31
41
40
39
ppm
23.51
23.20
22.89
25
24
23
22
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

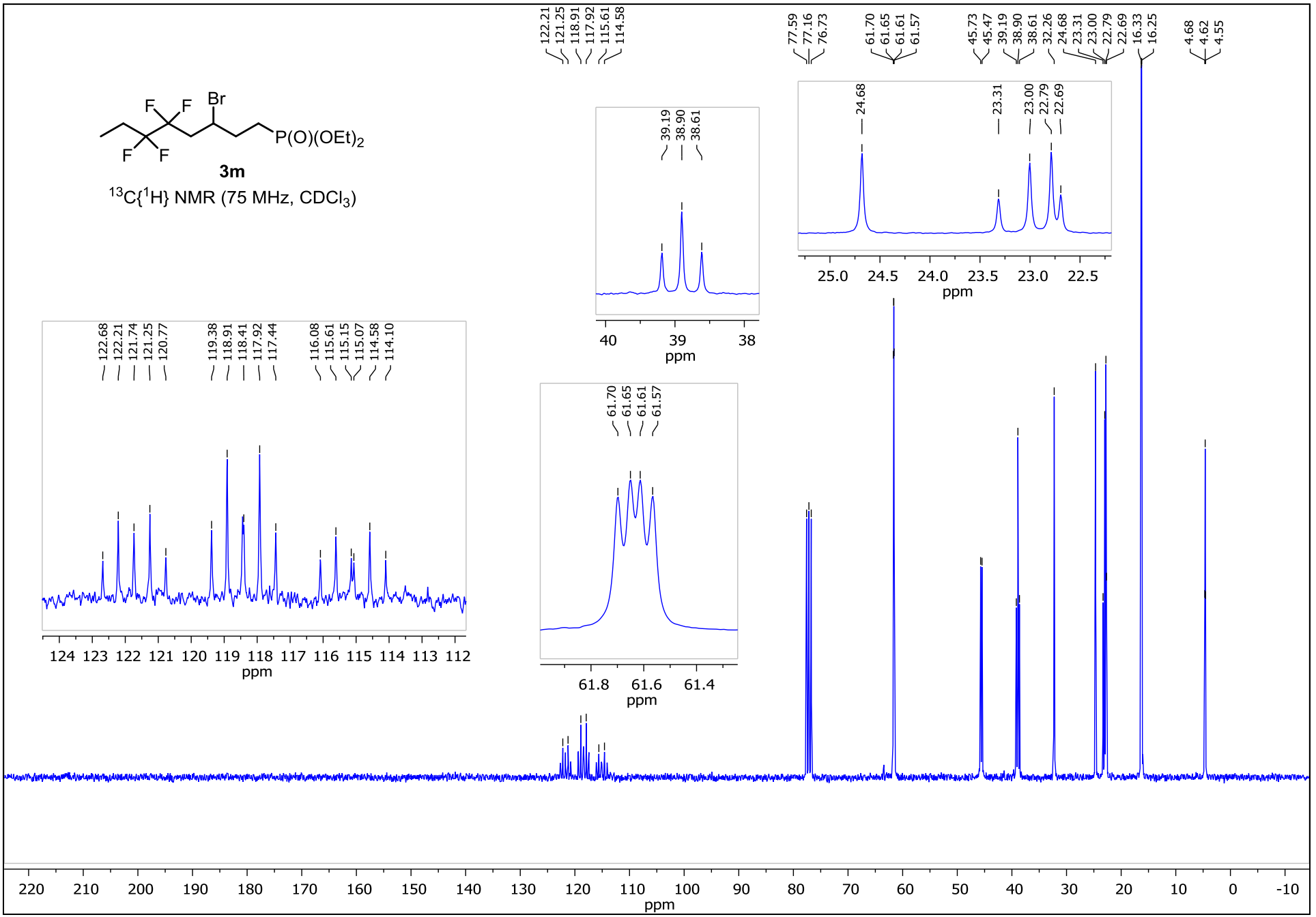

F
F
Br
O
F
F
O
Cl
3k
19F NMR (282 MHz, CDCl3)
-112.62
-112.72
-113.56
-113.66
-115.07
-115.16
-116.01
-116.10
-117.91
-117.94
-117.97
1.00
0.97
ppm

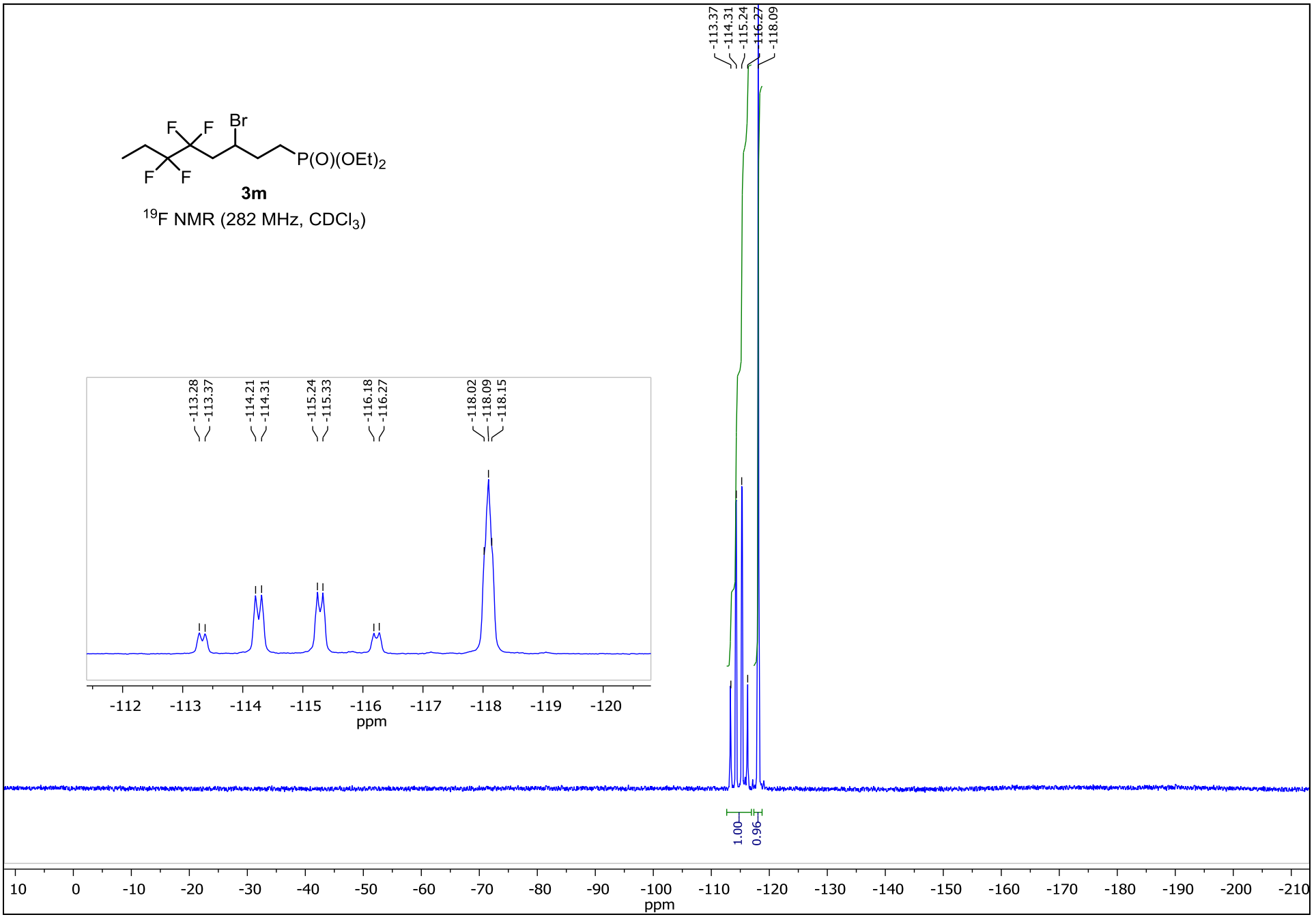

F
F
Br
F
F
OMe
3l
^{1}H NMR (300 MHz, $CDCl_3$)
7.31 7.28 7.26 7.20 7.17 6.96 6.94 6.90 6.88
4.71 4.66 4.62
3.85
3.42 3.38 3.19 3.14
2.78 2.72 2.66
2.11 2.04 2.02 1.96
1.13 1.10 1.08
1.13 1.03 2.02 1.00 2.92 1.00 1.02 2.00 2.13 3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

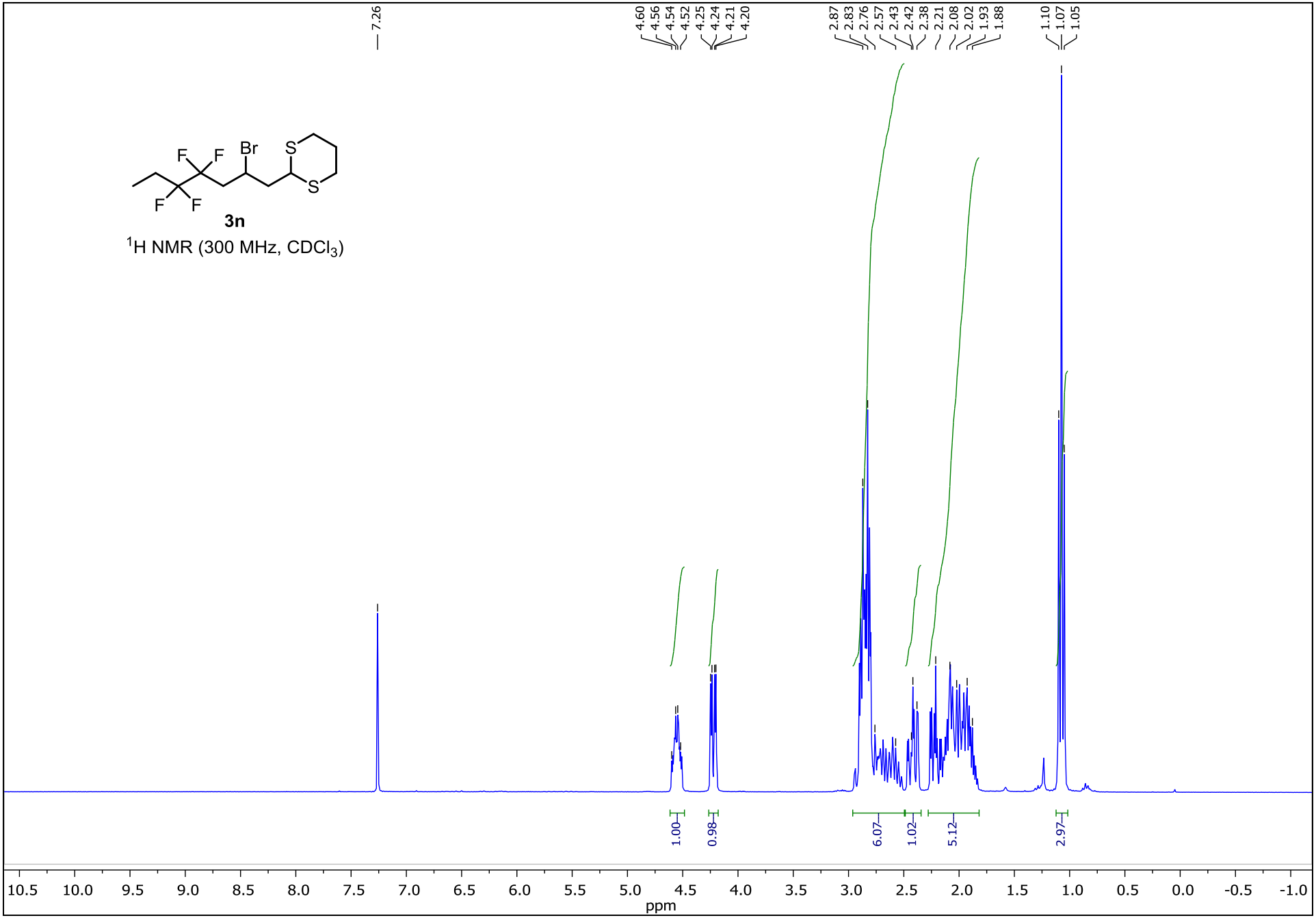

157.72
131.51
128.68
126.36
122.56
121.64
120.50
119.25
118.31
115.96
114.97
110.58
77.58
77.16
76.74
55.34
44.34
41.38
39.23
38.94
38.65
23.66
23.35
23.03
5.00
4.93
4.86
F
F
Br
F
F
OMe
3l
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
123.03
122.56
122.12
122.09
121.64
121.16
120.50
119.73
119.25
118.79
118.31
117.83
116.43
115.96
115.45
114.97
114.49
124 123 122 121 120 119 118 117 116 115 114 113
ppm
39.23
38.94
38.65
39.2 38.4
ppm
23.66
23.35
23.03
24.0 23.5 23.0 22.5
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

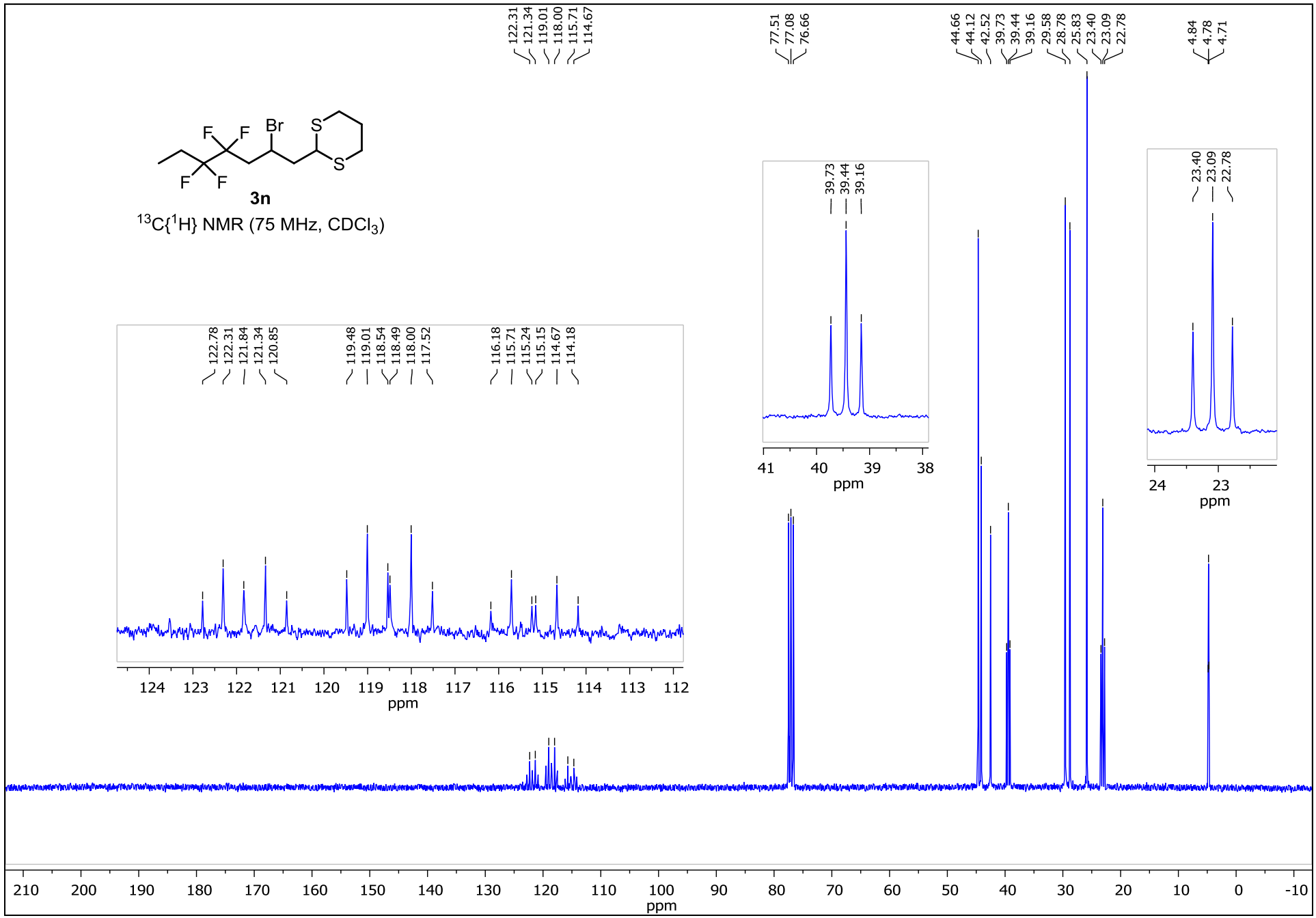

-115.24
-118.46
F
F
Br
F
F
OMe
3l
19F NMR (282 MHz, CDCl3)
-115.18
-115.21
-115.24
-115.26
-118.43
-118.46
-118.48
-118.52
-114
-115
-116
-117
-118
-119
-120
-121
ppm
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

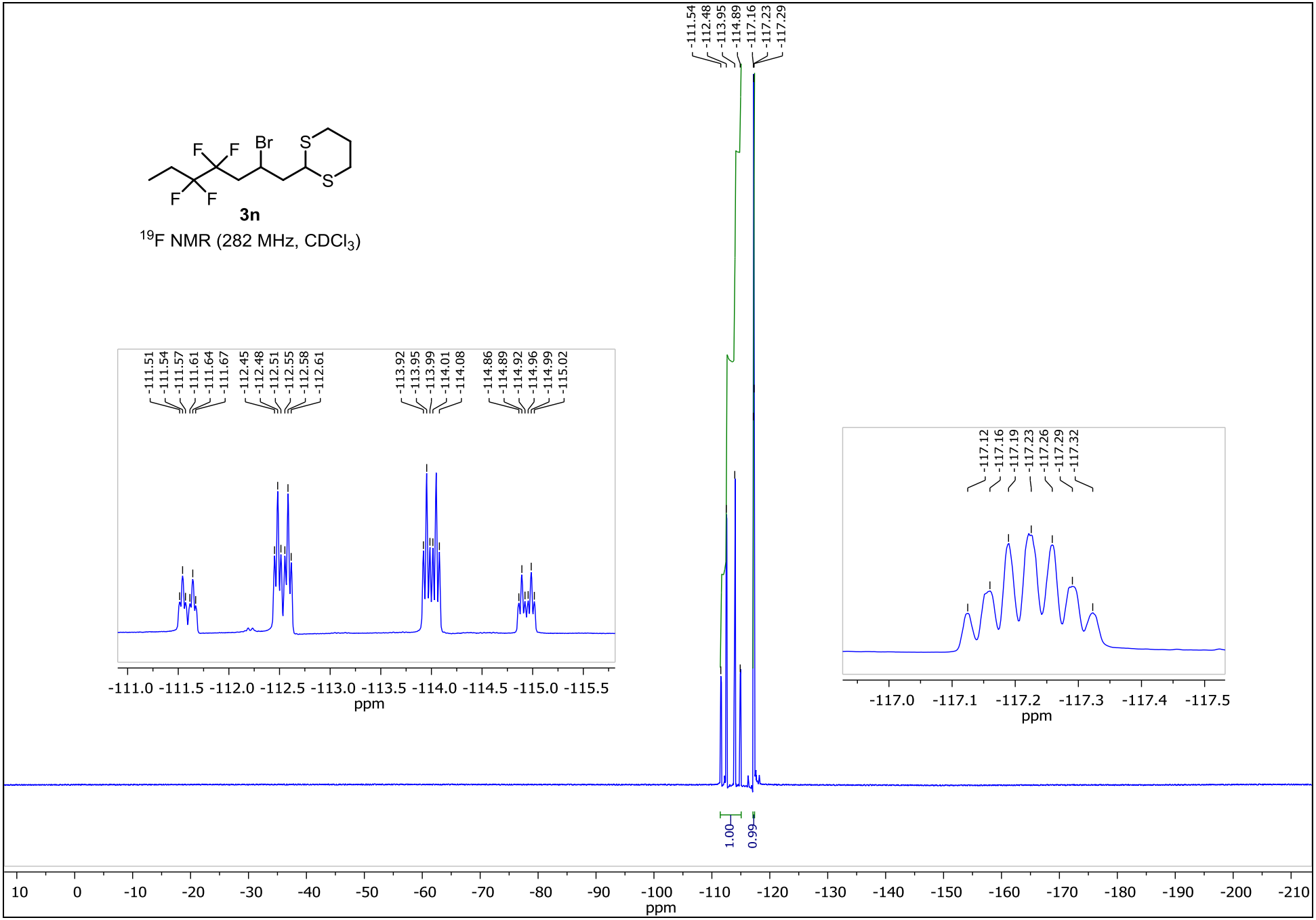

7.26
4.36
4.33
4.29
4.11
4.08
4.06
2.79
2.73
2.65
2.56
2.48
2.31
2.27
2.22
2.06
2.01
1.95
1.92
1.85
1.33
1.31
1.29
1.09
1.07
1.04
F
F
Br
F
F
P(O)(OEt)2
3m
1H NMR (300 MHz, CDCl3)
0.93
3.89
1.97
1.00
5.17
5.81
2.96
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

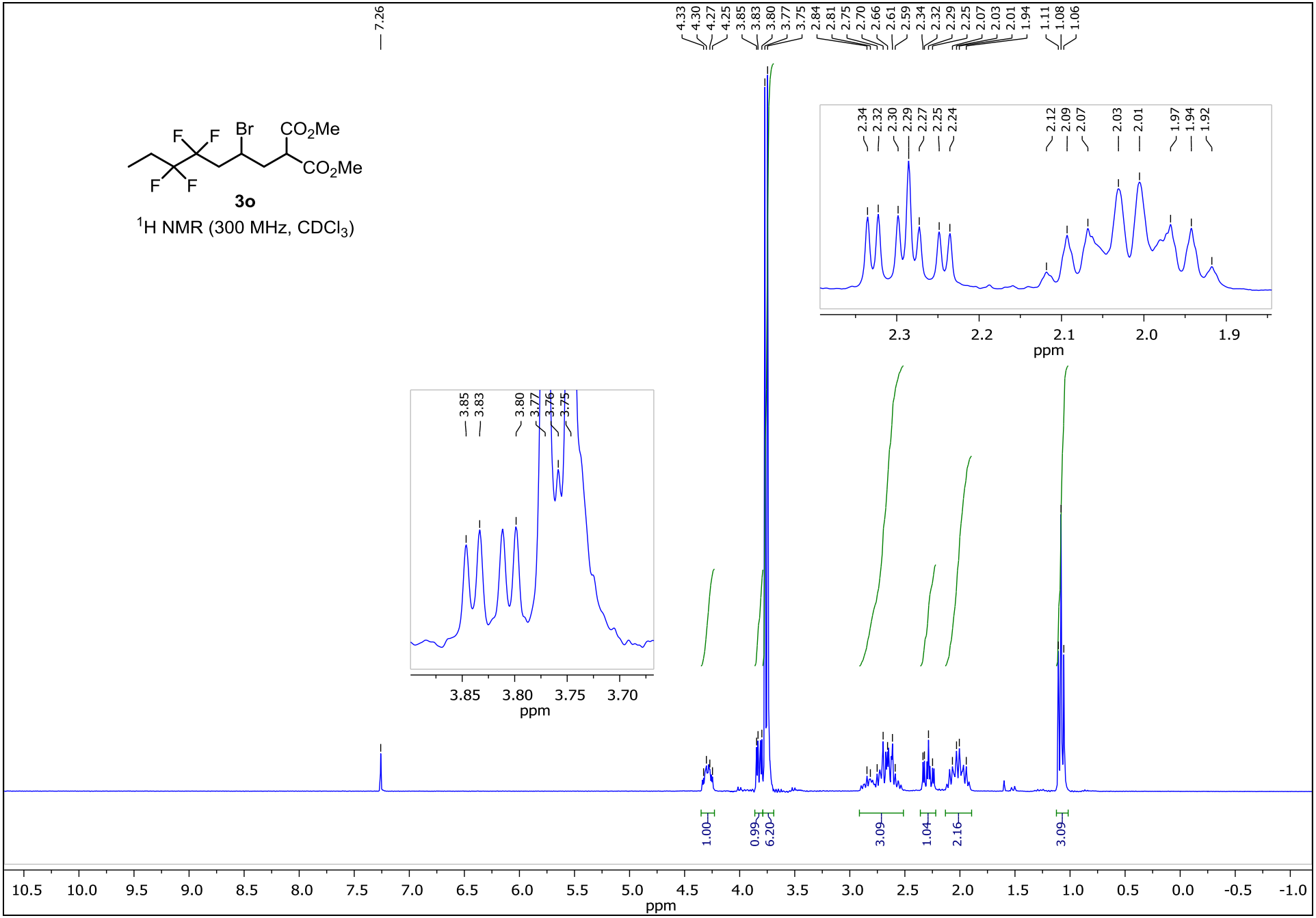

F
F
Br
F
F
P(O)(OEt)2
3m
13C{1H} NMR (75 MHz, CDCl3)
122.21
121.25
118.91
117.92
115.61
114.58
77.59
77.16
76.73
61.70
61.65
61.61
61.57
45.73
45.47
39.19
38.90
38.61
32.26
24.68
23.31
23.00
22.79
22.69
16.33
16.25
4.68
4.62
4.55
39.19
38.90
38.61
40
39
38
ppm
24.68
23.31
23.00
22.79
22.69
25.0
24.5
24.0
23.5
23.0
22.5
ppm
122.68
122.21
121.74
121.25
120.77
119.38
118.91
118.41
117.92
117.44
116.08
115.61
115.15
115.07
114.58
114.10
124 123 122 121 120 119 118 117 116 115 114 113 112
ppm
61.70
61.65
61.61
61.57
61.8
61.6
61.4
ppm
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

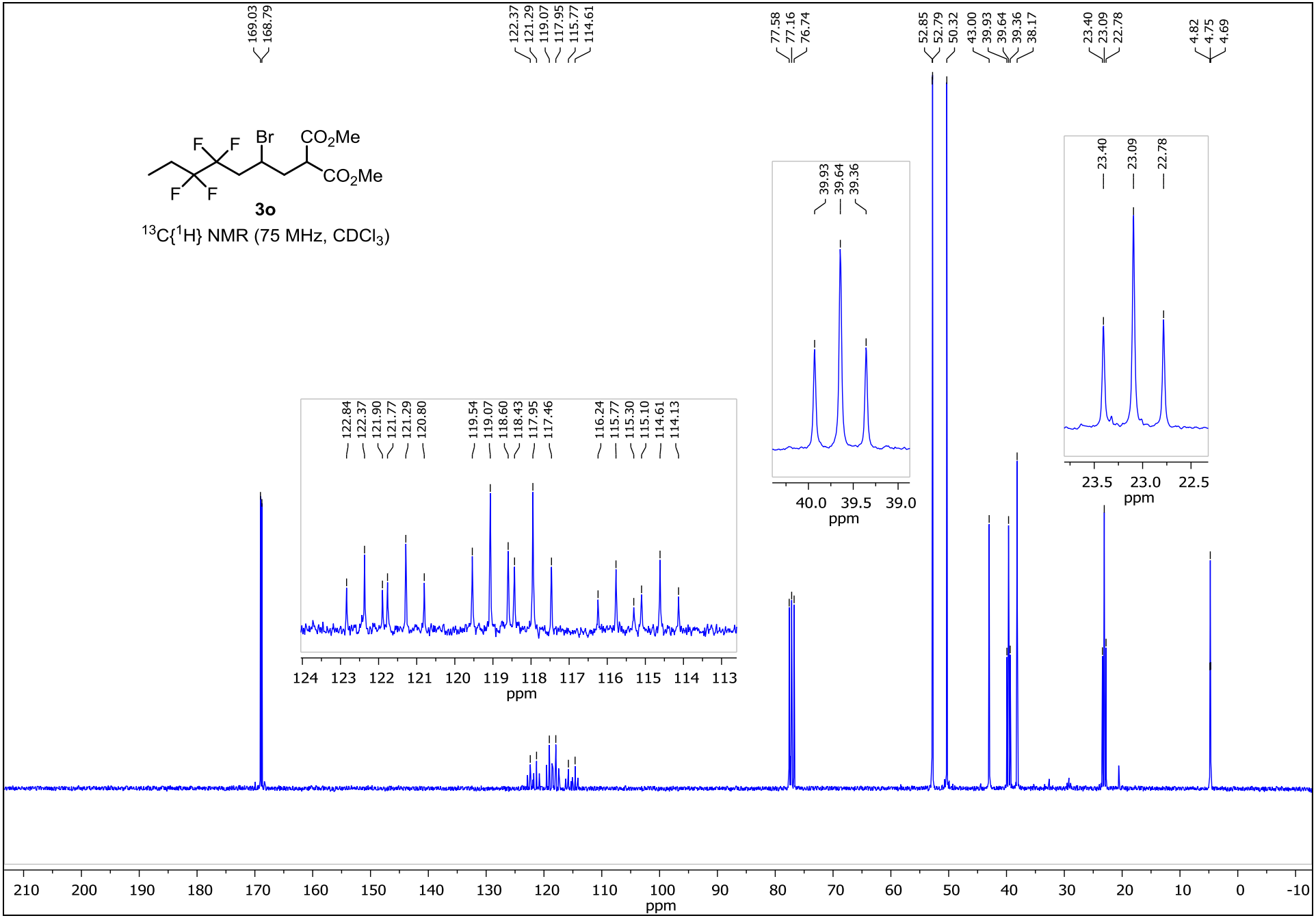

F
F
Br
P(O)(OEt)2
F
F
3m
19F NMR (282 MHz, CDCl3)
-113.37
-114.31
-115.24
-116.27
-118.09
-113.28
-113.37
-114.21
-114.31
-115.24
-115.33
-116.18
-116.27
-118.02
-118.09
-118.15
-112
-113
-114
-115
-116
-117
-118
-119
-120
ppm
1.00
0.96
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

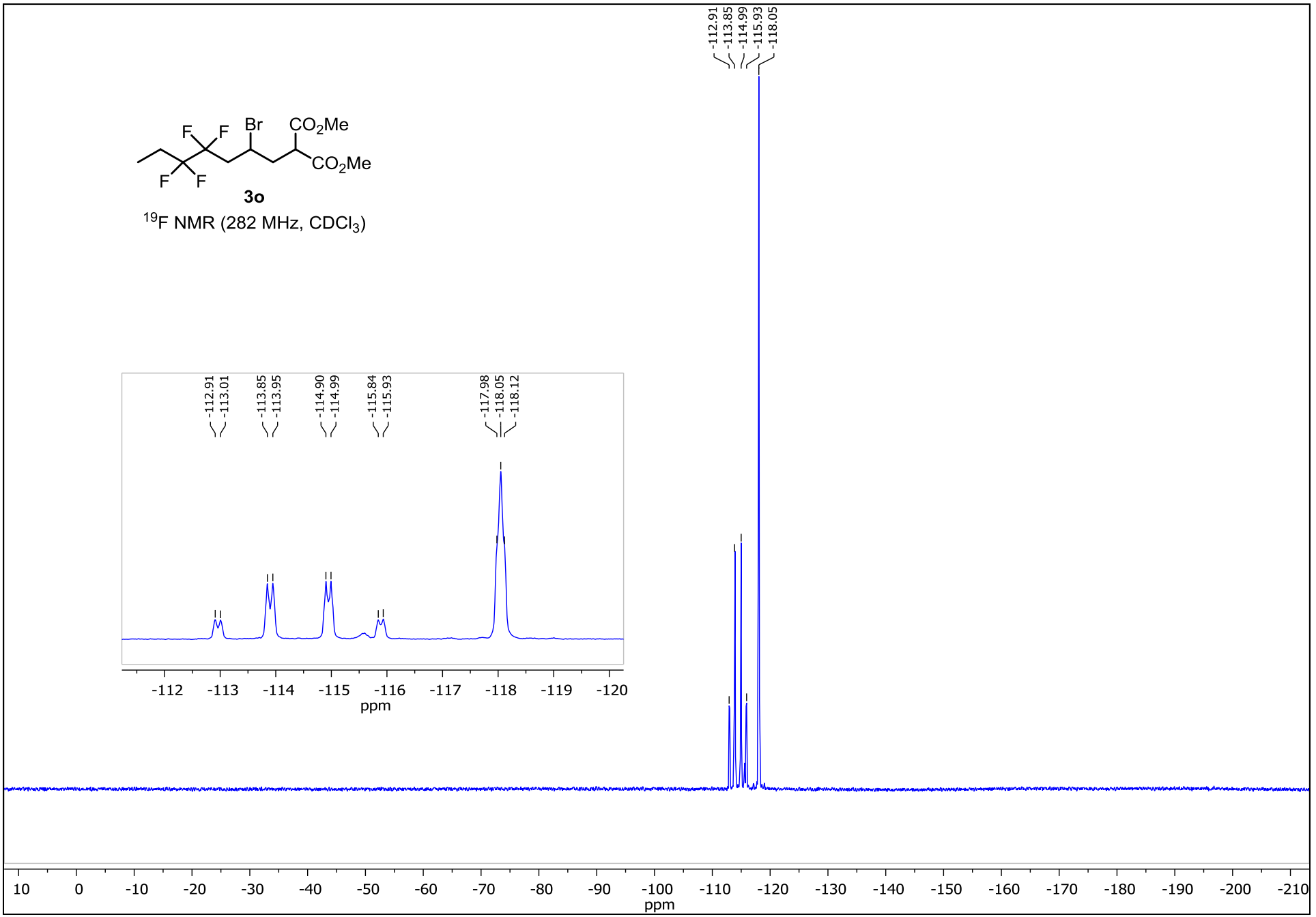

7.26
4.60
4.56
4.54
4.52
4.25
4.24
4.21
4.20
2.87
2.83
2.76
2.57
2.43
2.42
2.38
2.21
2.08
2.02
1.93
1.88
1.10
1.07
1.05
F
F
Br
S
S
F
F
3n
1H NMR (300 MHz, CDCl3)
1.00
0.98
6.07
1.02
5.12
2.97
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

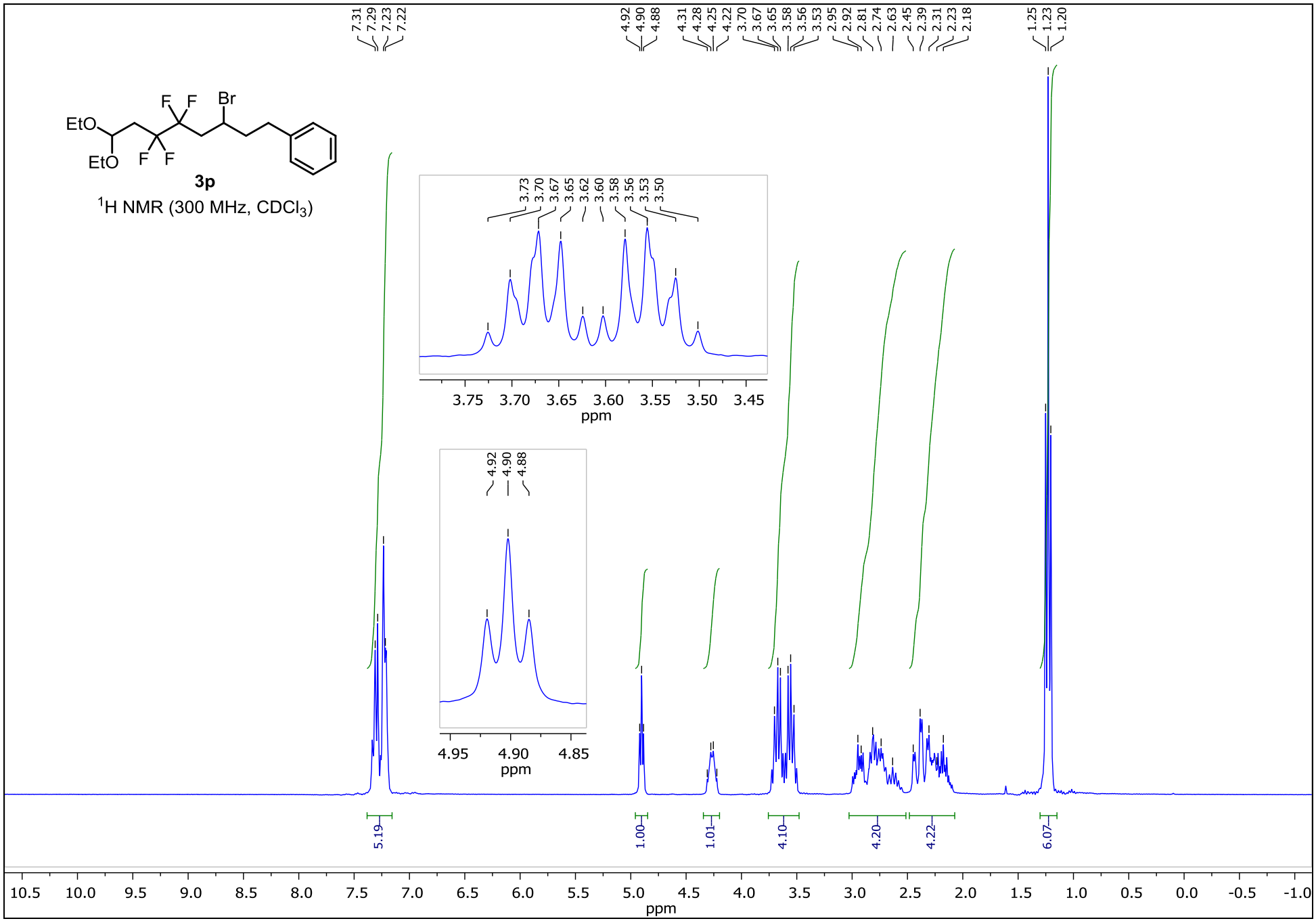

122.31
121.34
119.01
118.00
115.71
114.67
77.51
77.08
76.66
44.66
44.12
42.52
39.73
39.44
39.16
29.58
28.78
25.83
23.40
23.09
22.78
4.84
4.78
4.71
F
F
Br
S
S
F
F
3n
13C{1H} NMR (75 MHz, CDCl3)
122.78
122.31
121.84
121.34
120.85
119.48
119.01
118.54
118.49
118.00
117.52
116.18
115.71
115.24
115.15
114.67
114.18
124 123 122 121 120 119 118 117 116 115 114 113 112
ppm
39.73
39.44
39.16
41 40 39 38
ppm
23.40
23.09
22.78
24 23
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

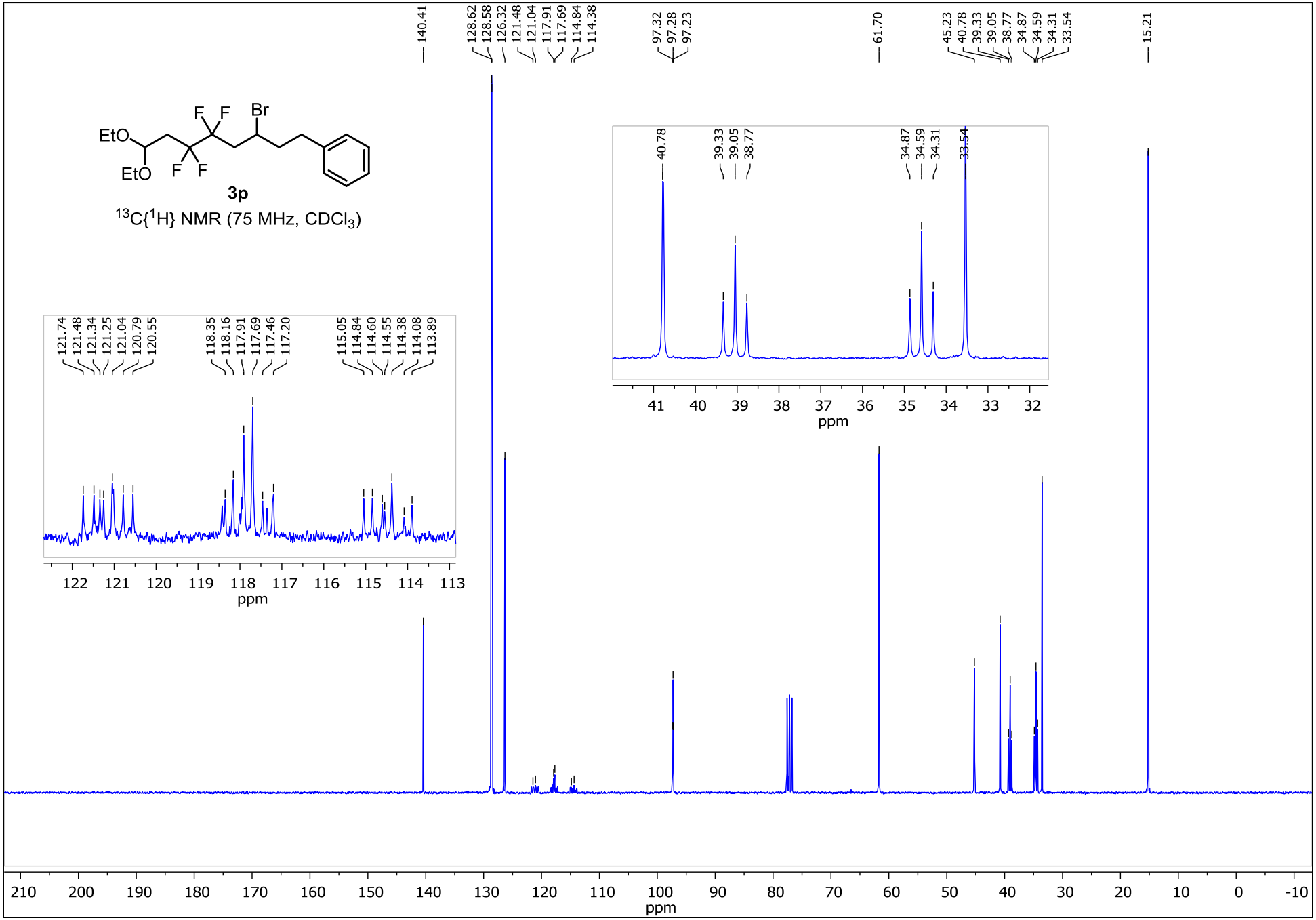

F
F
Br
S
S
F
F
3n
19F NMR (282 MHz, CDCl3)
-111.54
-112.48
-113.95
-114.89
-117.16
-117.23
-117.29
-111.51
-111.54
-111.57
-111.61
-111.64
-111.67
-112.45
-112.48
-112.51
-112.55
-112.58
-112.61
-113.92
-113.95
-113.99
-114.01
-114.08
-114.86
-114.89
-114.92
-114.96
-114.99
-115.02
-111.0 -111.5 -112.0 -112.5 -113.0 -113.5 -114.0 -114.5 -115.0 -115.5
ppm
-117.12
-117.16
-117.19
-117.23
-117.26
-117.29
-117.32
-117.0 -117.1 -117.2 -117.3 -117.4 -117.5
ppm
1.00
0.99
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
ppm

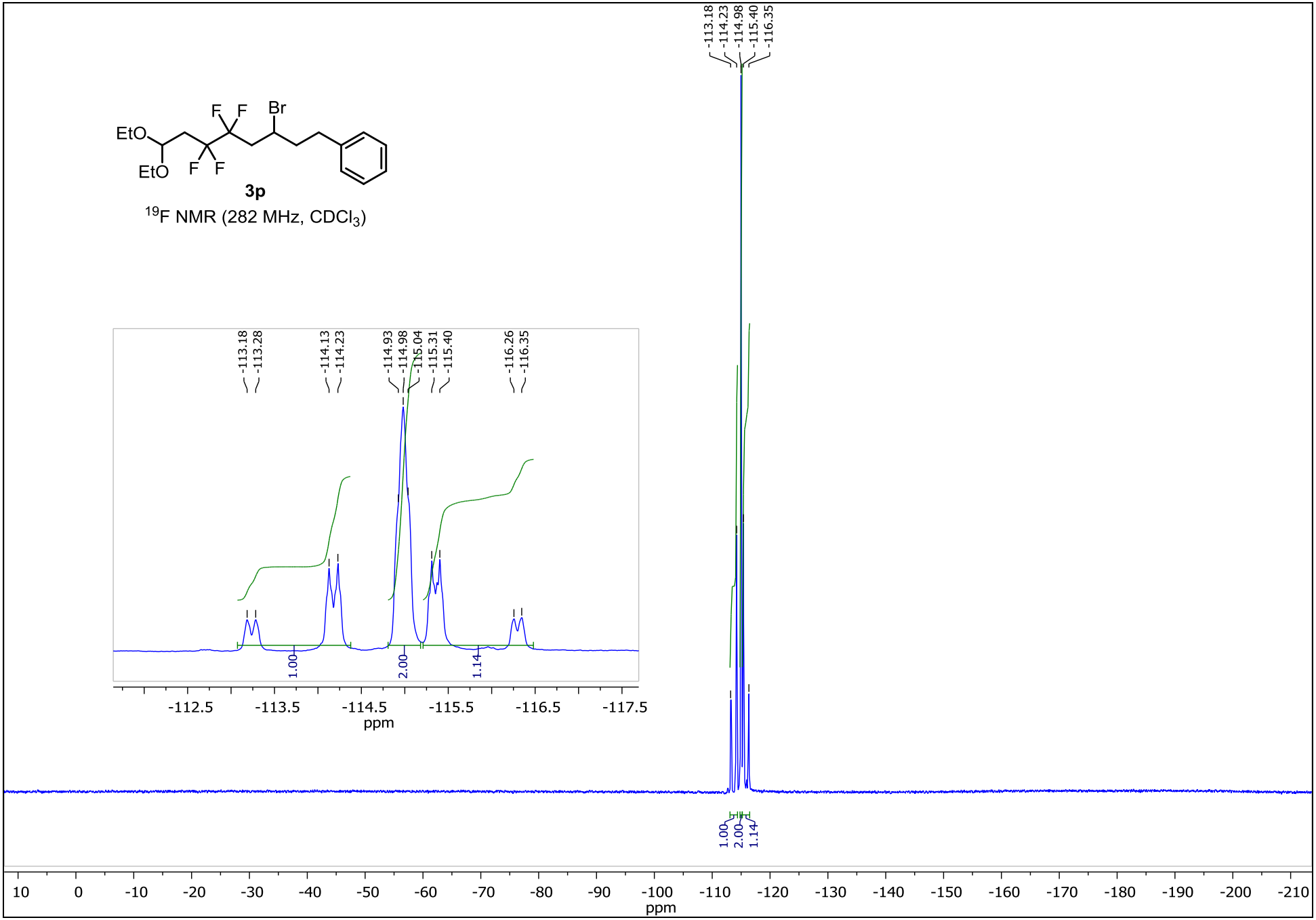

F
F
Br
CO2Me
F
F
CO2Me
3o
1H NMR (300 MHz, CDCl3)
7.26
4.33
4.30
4.27
4.25
3.85
3.83
3.80
3.77
3.75
2.84
2.81
2.75
2.70
2.66
2.61
2.59
2.34
2.32
2.29
2.25
2.07
2.03
2.01
1.94
1.11
1.08
1.06
2.34
2.32
2.30
2.29
2.27
2.25
2.24
2.12
2.09
2.07
2.03
2.01
1.97
1.94
1.92
2.3
2.2
2.1
2.0
1.9
ppm
3.85
3.83
3.80
3.77
3.76
3.75
3.85
3.80
3.75
3.70
ppm
1.00
0.99
6.20
3.09
1.04
2.16
3.09
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

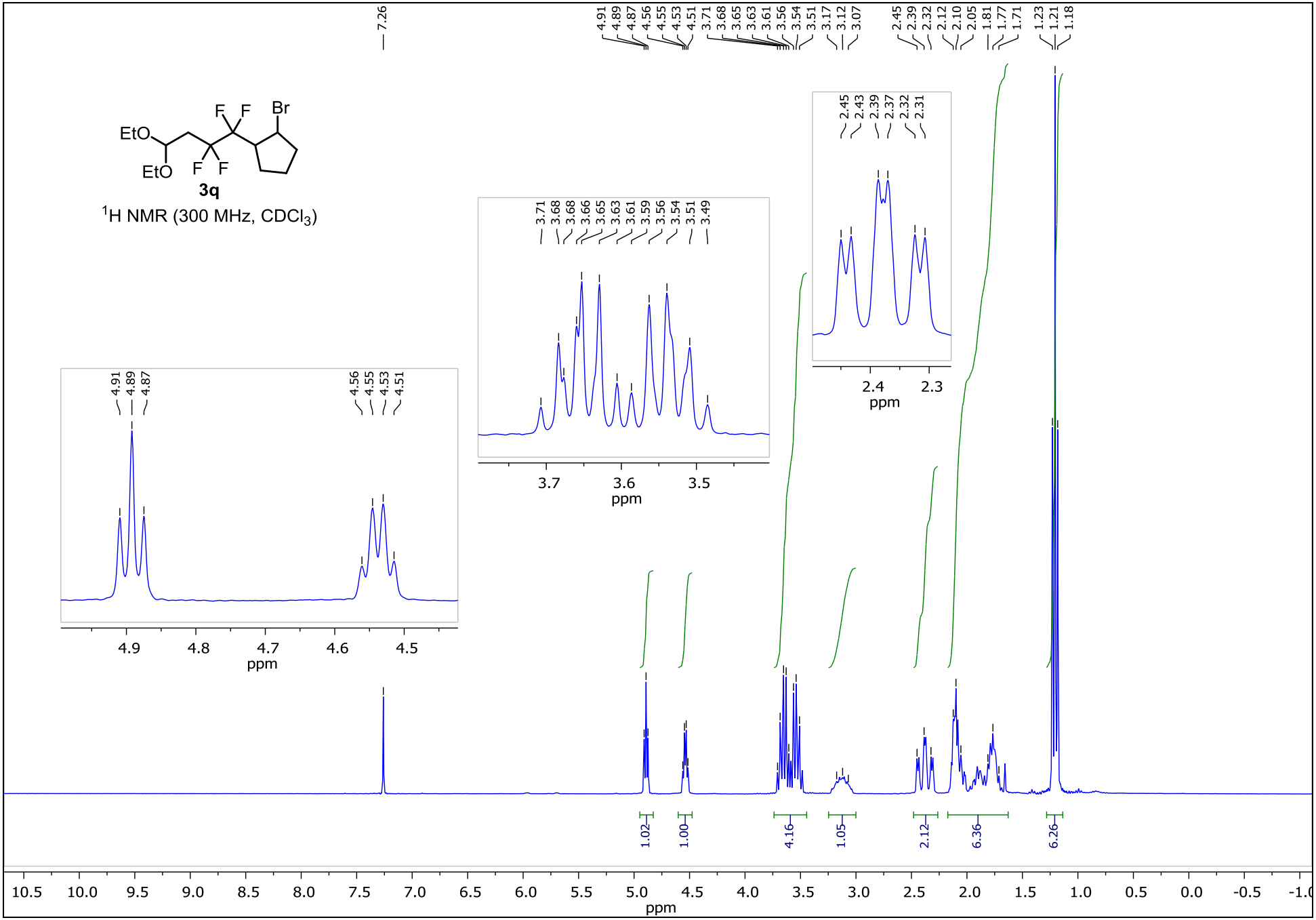

169.03
168.79
122.37
121.29
119.07
117.95
115.77
114.61
77.58
77.16
76.74
52.85
52.79
50.32
43.00
39.93
39.64
39.36
38.17
23.40
23.09
22.78
4.82
4.75
4.69
F
F
Br
CO2Me
CO2Me
F
F
3o
13C{1H} NMR (75 MHz, CDCl3)
122.84
122.37
121.90
121.77
121.29
120.80
119.54
119.07
118.60
118.43
117.95
117.46
116.24
115.77
115.30
115.10
114.61
114.13
124 123 122 121 120 119 118 117 116 115 114 113
ppm
39.93
39.64
39.36
40.0 39.5 39.0
ppm
23.40
23.09
22.78
23.5 23.0 22.5
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

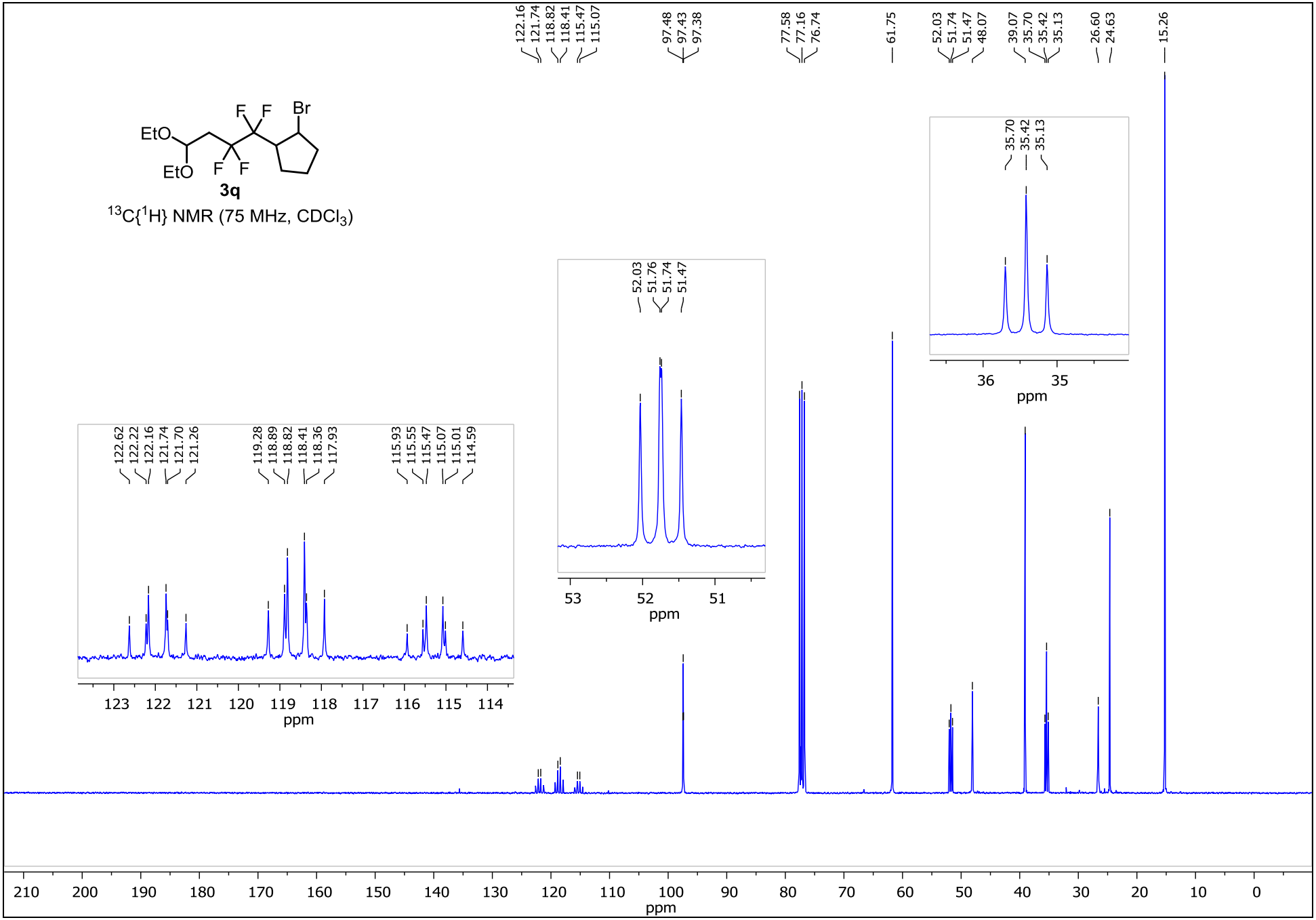

F
F
Br
CO2Me
CO2Me
F
F
3o
19F NMR (282 MHz, CDCl3)
-112.91
-113.85
-114.99
-115.93
-118.05
-112.91
-113.01
-113.85
-113.95
-114.90
-114.99
-115.84
-115.93
-117.98
-118.05
-118.12
-112
-113
-114
-115
-116
-117
-118
-119
-120
ppm
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

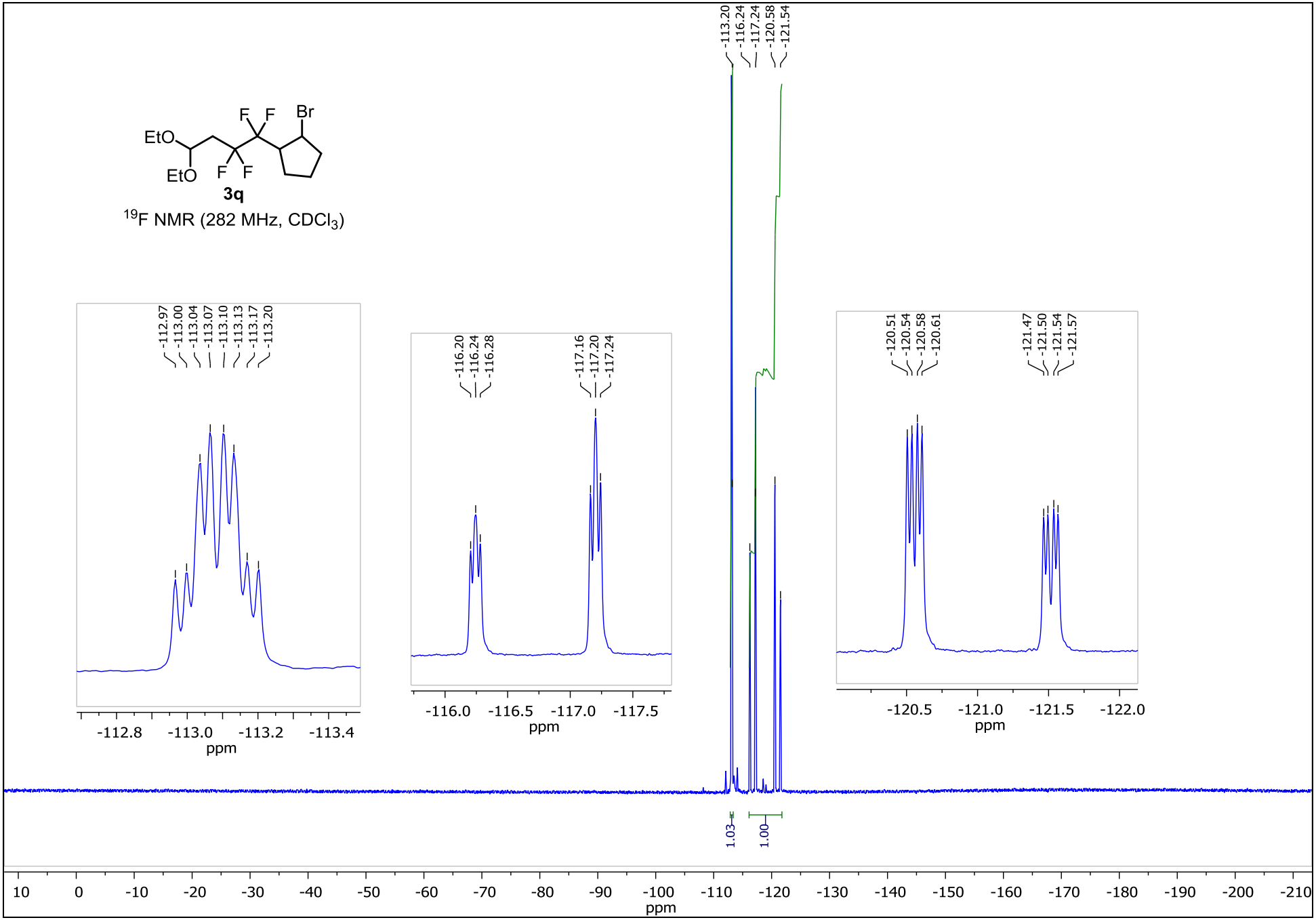

EtO
EtO
F F
F F
Br
3p
^{1}H NMR (300 MHz, $CDCl_3$)
7.31 7.29 7.23 7.22
4.92 4.90 4.88
4.31 4.28 4.25 4.22
3.70 3.67 3.65 3.58 3.56 3.53
2.95 2.92 2.81 2.74 2.63 2.45 2.39 2.31 2.23 2.18
1.25 1.23 1.20
3.73 3.70 3.67 3.65 3.62 3.60 3.58 3.56 3.53 3.50
3.75 3.70 3.65 3.60 3.55 3.50 3.45
ppm
4.92 4.90 4.88
4.95 4.90 4.85
ppm
5.19
1.00
1.01
4.10
4.20
4.22
6.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

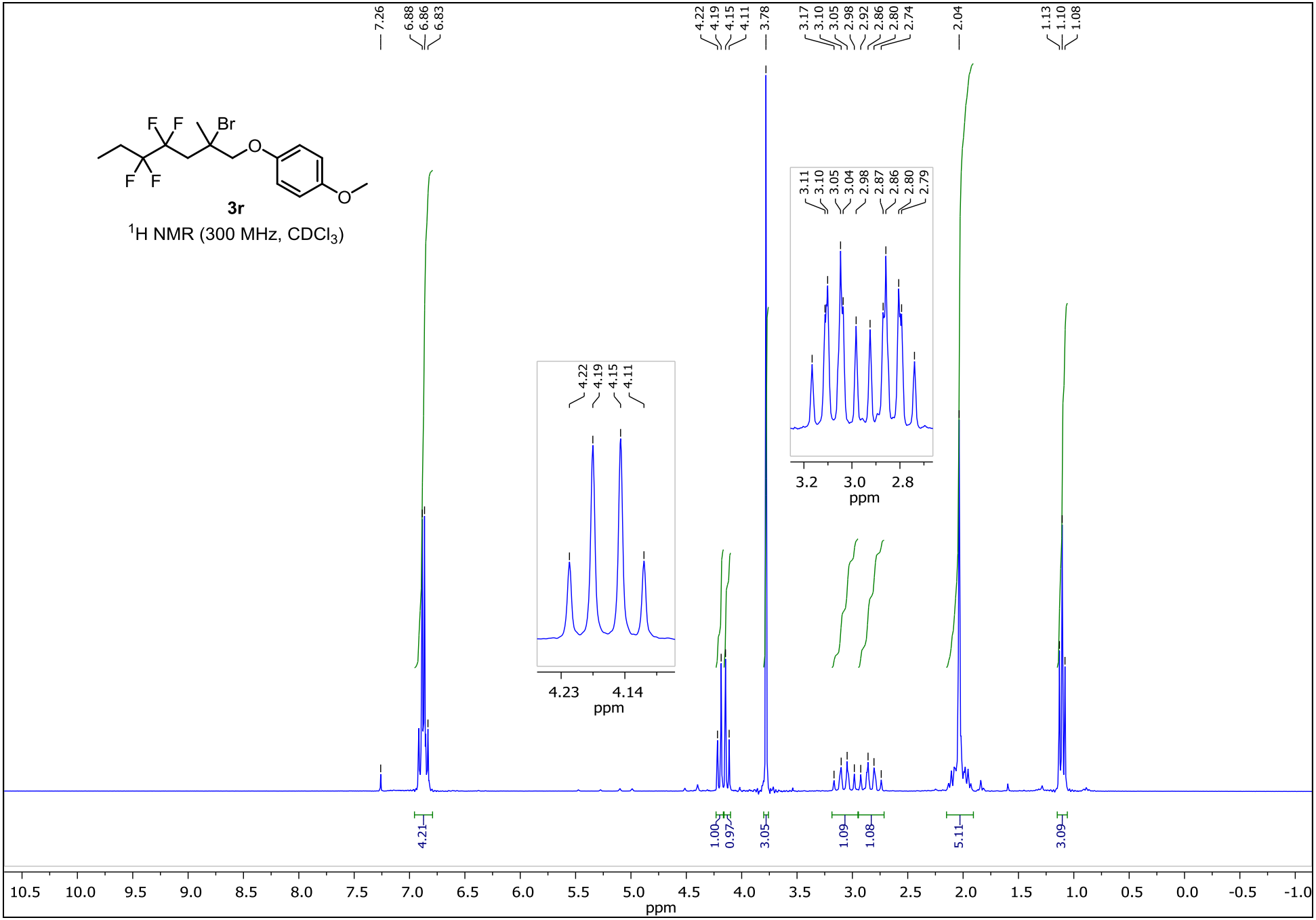

EtO
EtO
F F
F F
Br
3p
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
140.41
128.62
128.58
126.32
121.48
121.04
117.91
117.69
114.84
114.38
97.32
97.28
97.23
61.70
45.23
40.78
39.33
39.05
38.77
34.87
34.59
34.31
33.54
15.21
121.74
121.48
121.34
121.25
121.04
120.79
120.55
118.35
118.16
117.91
117.69
117.46
117.20
115.05
114.84
114.60
114.55
114.38
114.08
113.89
ppm
ppm
ppm

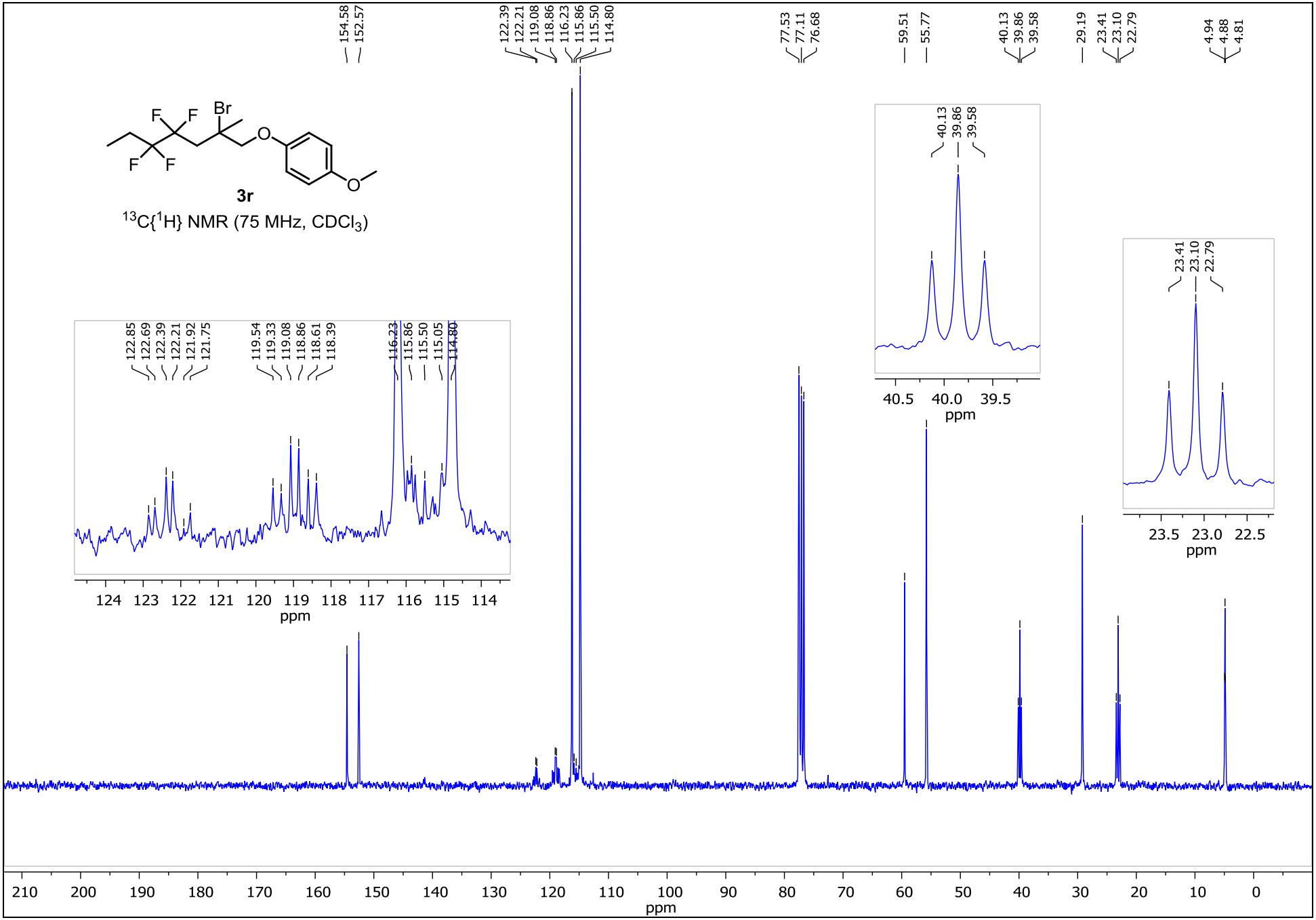

EtO
EtO
F F
F F
Br
3p
^{19}F NMR (282 MHz, CDCl$_3$)
-113.18
-114.23
-114.98
-115.40
-116.35
-113.18
-113.28
-114.13
-114.23
-114.93
-114.98
-115.04
-115.31
-115.40
-116.26
-116.35
1.00
2.00
1.14
-112.5
-113.5
-114.5
-115.5
-116.5
-117.5
ppm
1.00
2.00
1.14
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

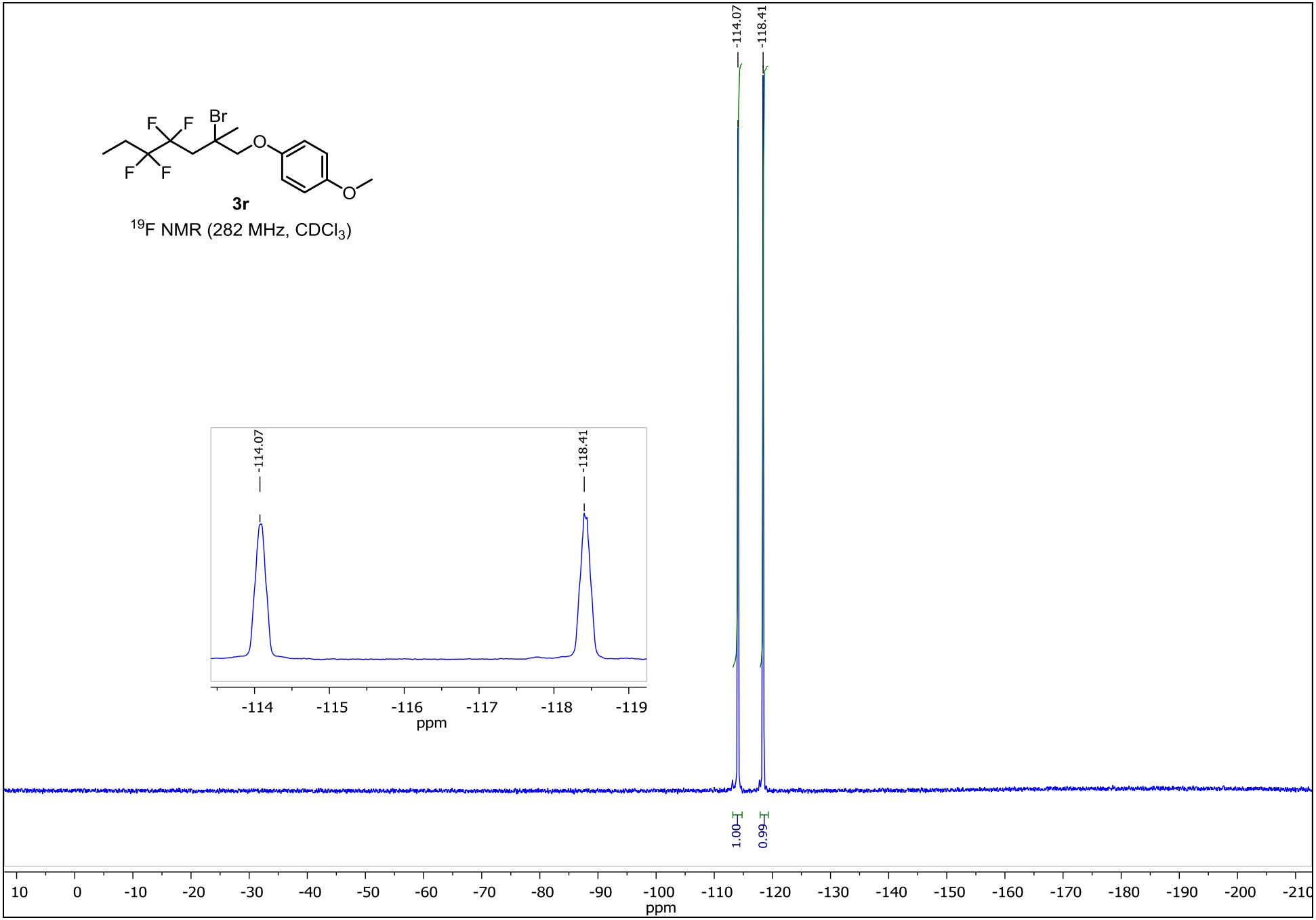

EtO
EtO
F F
F F
Br
3q
^{1}H NMR (300 MHz, $CDCl_3$)
ppm

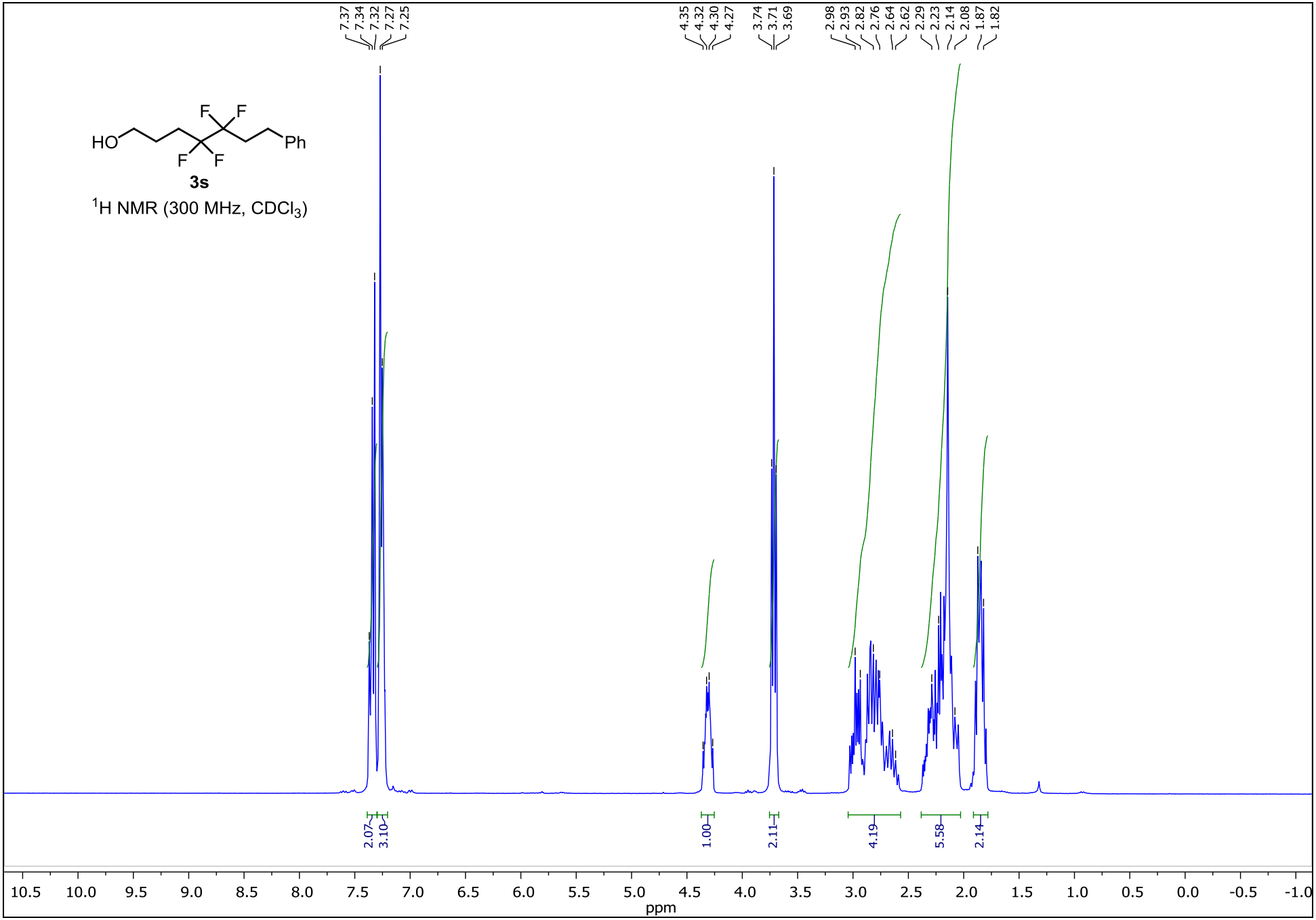

122.16
121.74
118.82
118.41
115.47
115.07
97.48
97.43
97.38
77.58
77.16
76.74
61.75
52.03
51.74
51.47
48.07
39.07
35.70
35.42
35.13
26.60
24.63
15.26
EtO
EtO
F
F
F
F
Br
3q
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
122.62
122.22
122.16
121.74
121.70
121.26
119.28
118.89
118.82
118.41
118.36
117.93
115.93
115.55
115.47
115.07
115.01
114.59
123 122 121 120 119 118 117 116 115 114
ppm
52.03
51.76
51.74
51.47
53 52 51
ppm
35.70
35.42
35.13
36 35
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

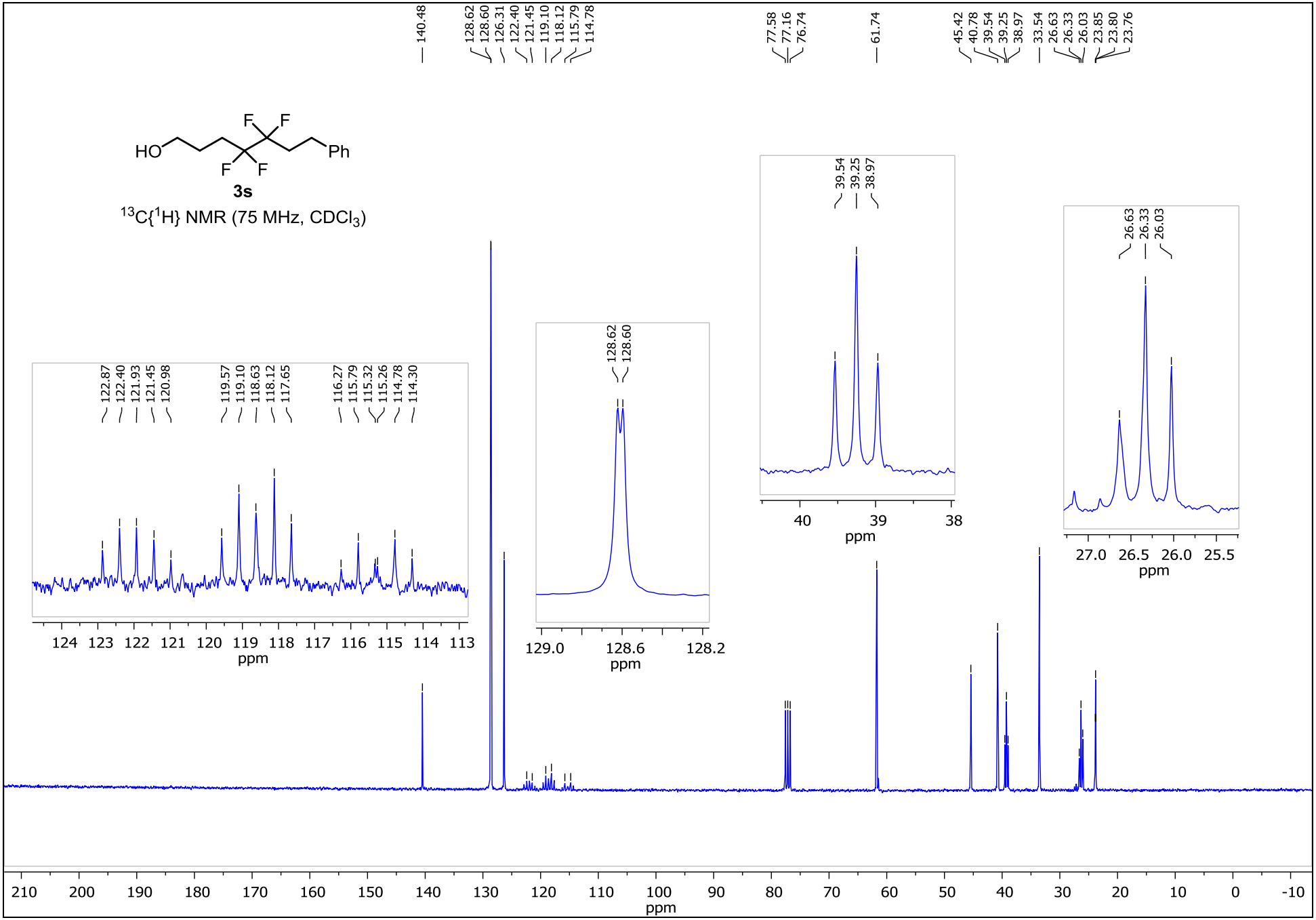

EtO
EtO
F F
F F
Br
3q
19F NMR (282 MHz, CDCl3)
-113.20
-116.24
-117.24
-120.58
-121.54
-112.97
-113.00
-113.04
-113.07
-113.10
-113.13
-113.17
-113.20
-112.8
-113.0
-113.2
-113.4
ppm
-116.20
-116.24
-116.28
-117.16
-117.20
-117.24
-116.0
-116.5
-117.0
-117.5
ppm
-120.51
-120.54
-120.58
-120.61
-121.47
-121.50
-121.54
-121.57
-120.5
-121.0
-121.5
-122.0
ppm
1.03
1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

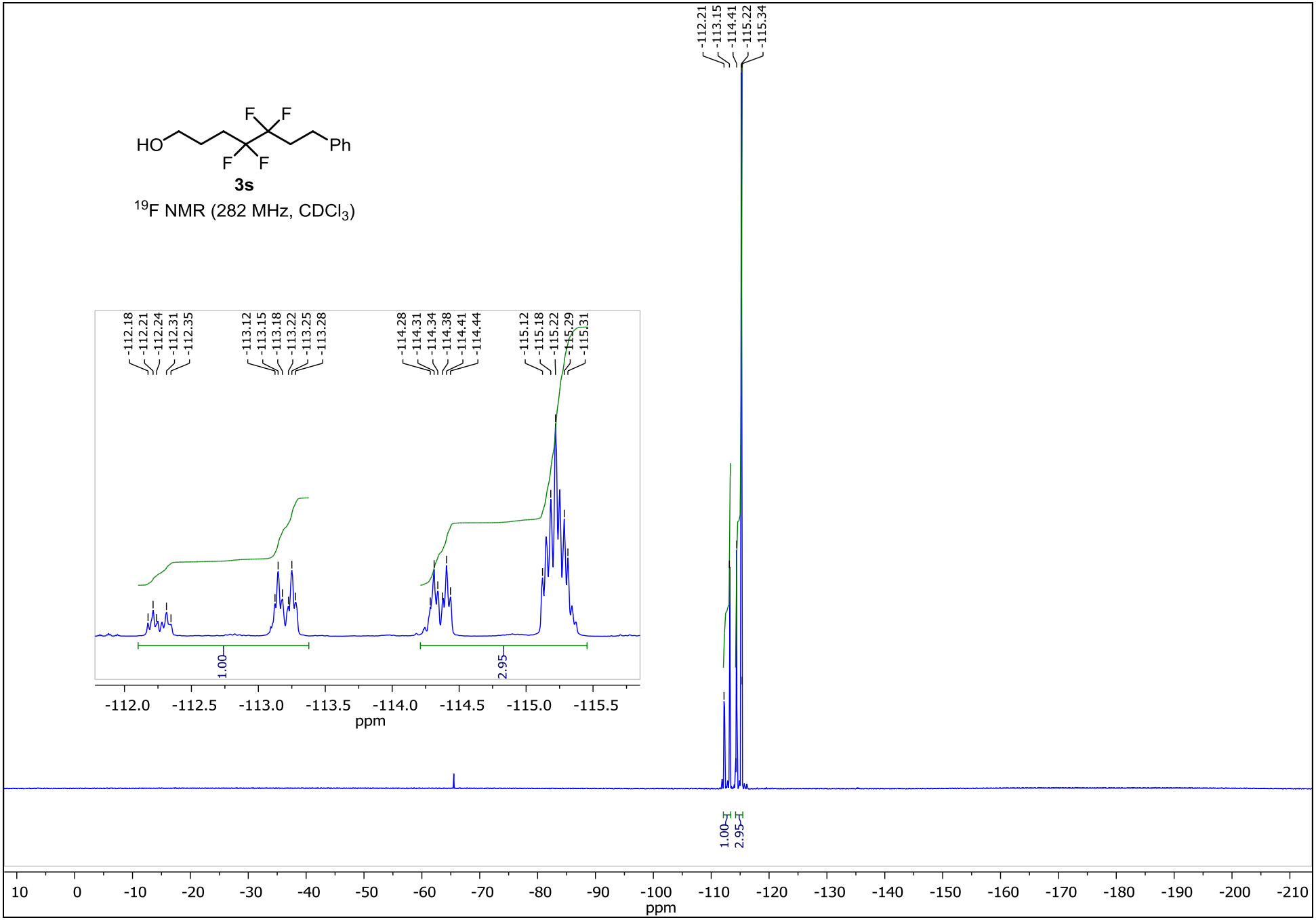

F F Br
F F
O
O
3r
1H NMR (300 MHz, CDCl3)
7.26
6.88
6.86
6.83
4.22
4.19
4.15
4.11
3.78
3.17
3.10
3.05
2.98
2.92
2.86
2.80
2.74
2.04
1.13
1.10
1.08
3.11
3.10
3.05
3.04
2.98
2.87
2.86
2.80
2.79
3.2
3.0
2.8
ppm
4.23
4.14
ppm
4.21
1.00
0.97
3.05
1.09
1.08
5.11
3.09
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

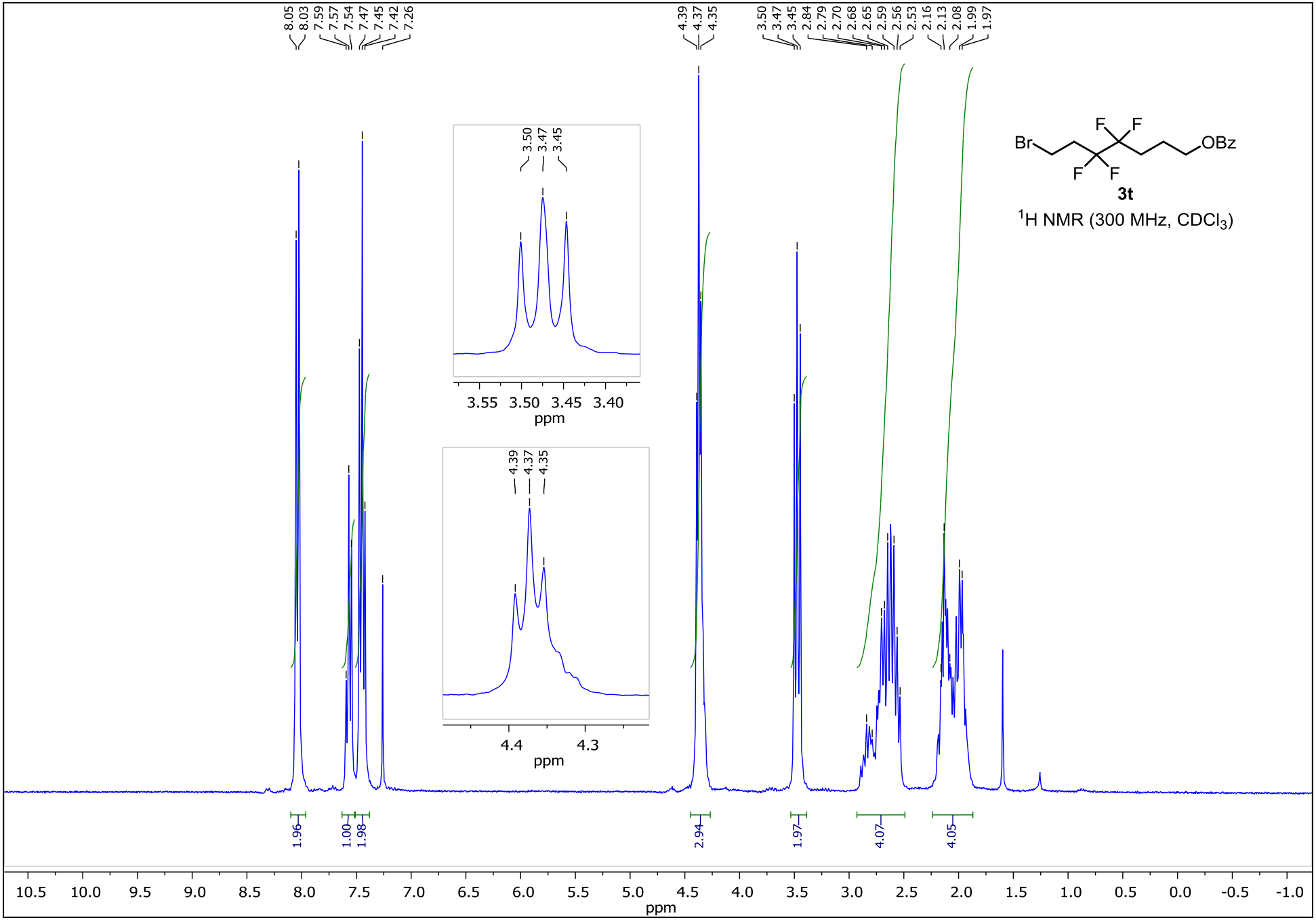

154.58
152.57
122.39
122.21
119.08
118.86
116.23
115.86
115.50
114.80
77.53
77.11
76.68
59.51
55.77
40.13
39.86
39.58
29.19
23.41
23.10
22.79
4.94
4.88
4.81
F
F
Br
O
F
F
O
3r
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
122.85
122.69
122.39
122.21
121.92
121.75
119.54
119.33
119.08
118.86
118.61
118.39
116.23
115.86
115.50
115.05
114.80
124 123 122 121 120 119 118 117 116 115 114
ppm
40.13
39.86
39.58
40.5 40.0 39.5
ppm
23.41
23.10
22.79
23.5 23.0 22.5
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

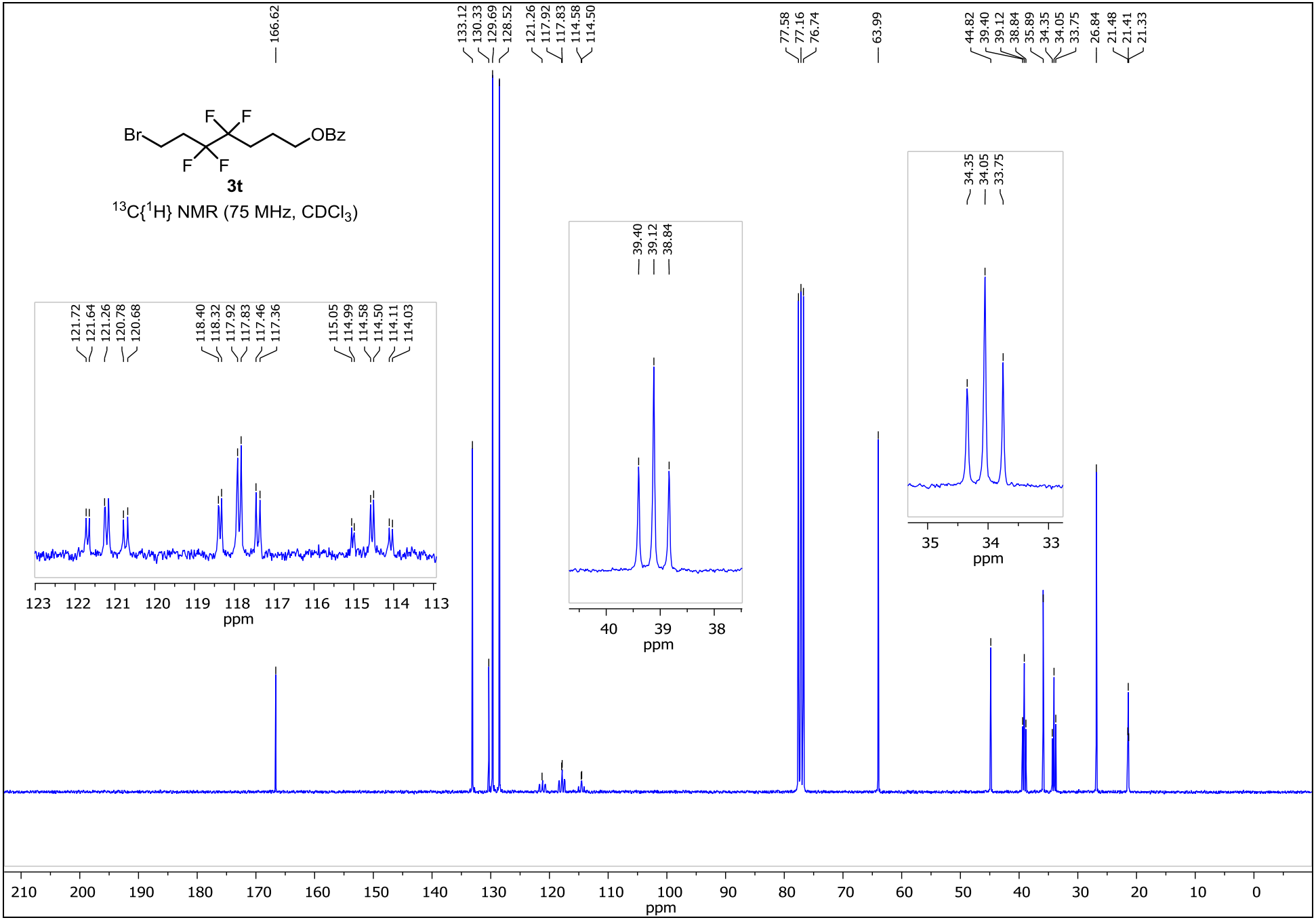

F
F
Br
O
F
F
O
3r
^{19}F NMR (282 MHz, CDCl$_3$)
-114.07
-118.41
-114.07
-118.41
-114
-115
-116
-117
-118
-119
ppm
1.00
0.99
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

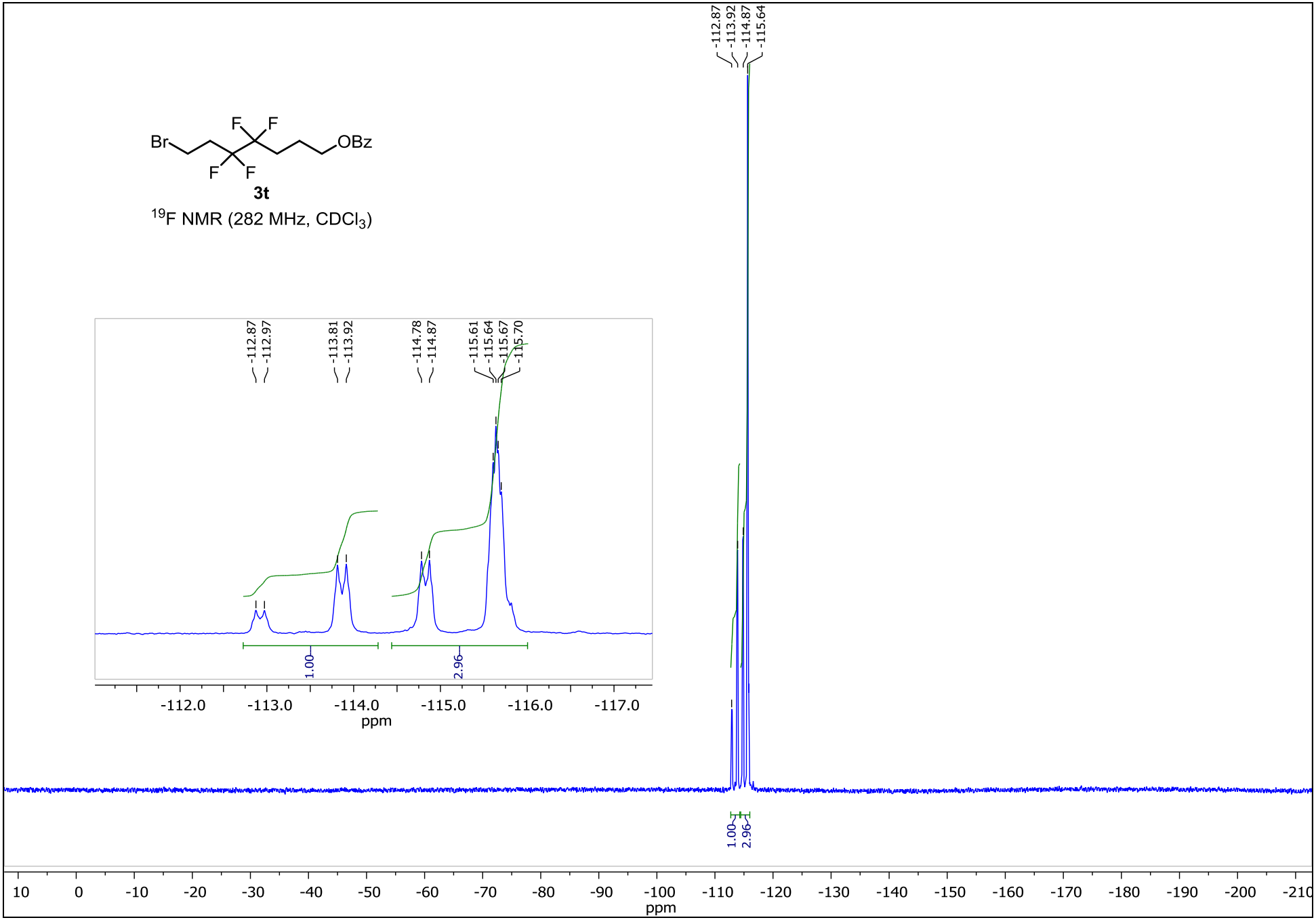

7.37
7.34
7.32
7.27
7.25
4.35
4.32
4.30
4.27
3.74
3.71
3.69
2.98
2.93
2.82
2.76
2.64
2.62
2.29
2.23
2.14
2.08
1.87
1.82
HO
F
F
F
F
Ph
3s
1H NMR (300 MHz, CDCl3)
2.07
3.10
1.00
2.11
4.19
5.58
2.14
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

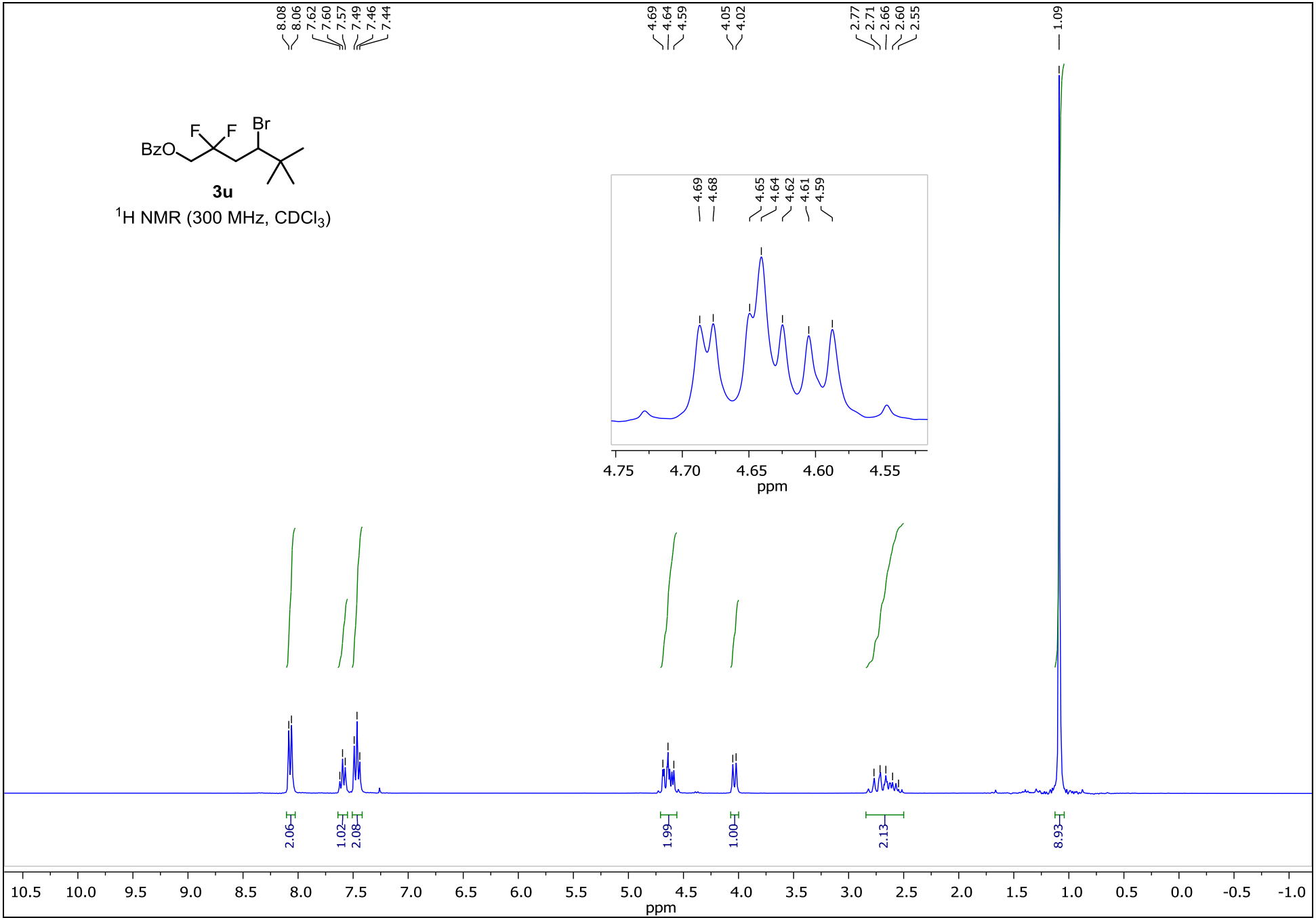

HO
F
F
F
F
Ph
3s
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
140.48
128.62
128.60
126.31
122.40
121.45
119.10
118.12
115.79
114.78
77.58
77.16
76.74
61.74
45.42
40.78
39.54
39.25
38.97
33.54
26.63
26.33
26.03
23.85
23.80
23.76
122.87
122.40
121.93
121.45
120.98
119.57
119.10
118.63
118.12
117.65
116.27
115.79
115.32
115.26
114.78
114.30
124 123 122 121 120 119 118 117 116 115 114 113
ppm
128.62
128.60
129.0 128.6 128.2
ppm
39.54
39.25
38.97
40 39 38
ppm
26.63
26.33
26.03
27.0 26.5 26.0 25.5
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

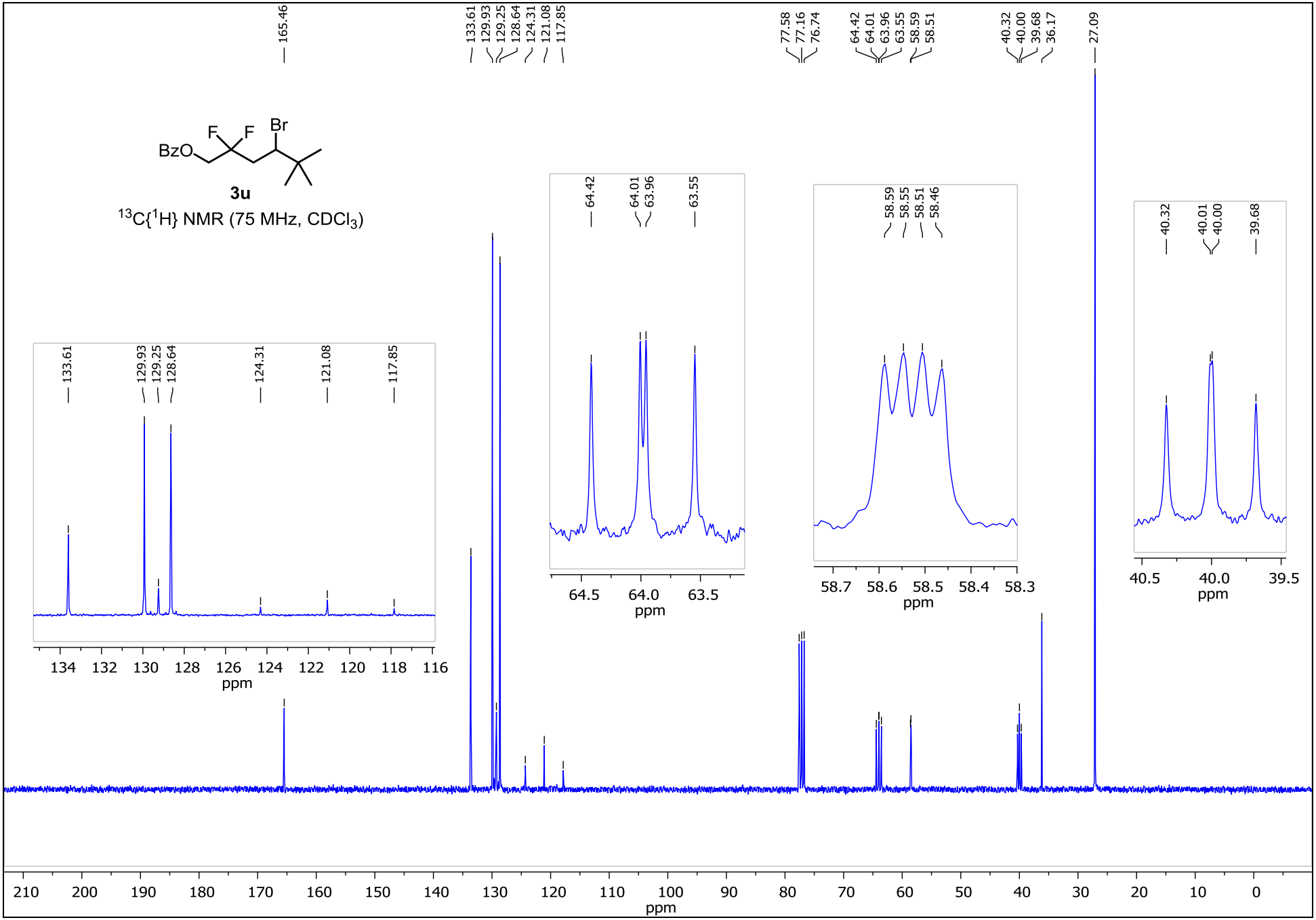

HO
F
F
F
F
Ph
3s
^{19}F NMR (282 MHz, $CDCl_3$)
-112.21
-113.15
-114.41
-115.22
-115.34
-112.18
-112.21
-112.24
-112.31
-112.35
-113.12
-113.15
-113.18
-113.22
-113.25
-113.28
-114.28
-114.31
-114.34
-114.38
-114.41
-114.44
-115.12
-115.18
-115.22
-115.29
-115.31
1.00
2.95
-112.0
-112.5
-113.0
-113.5
-114.0
-114.5
-115.0
-115.5
ppm
1.00
2.95
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

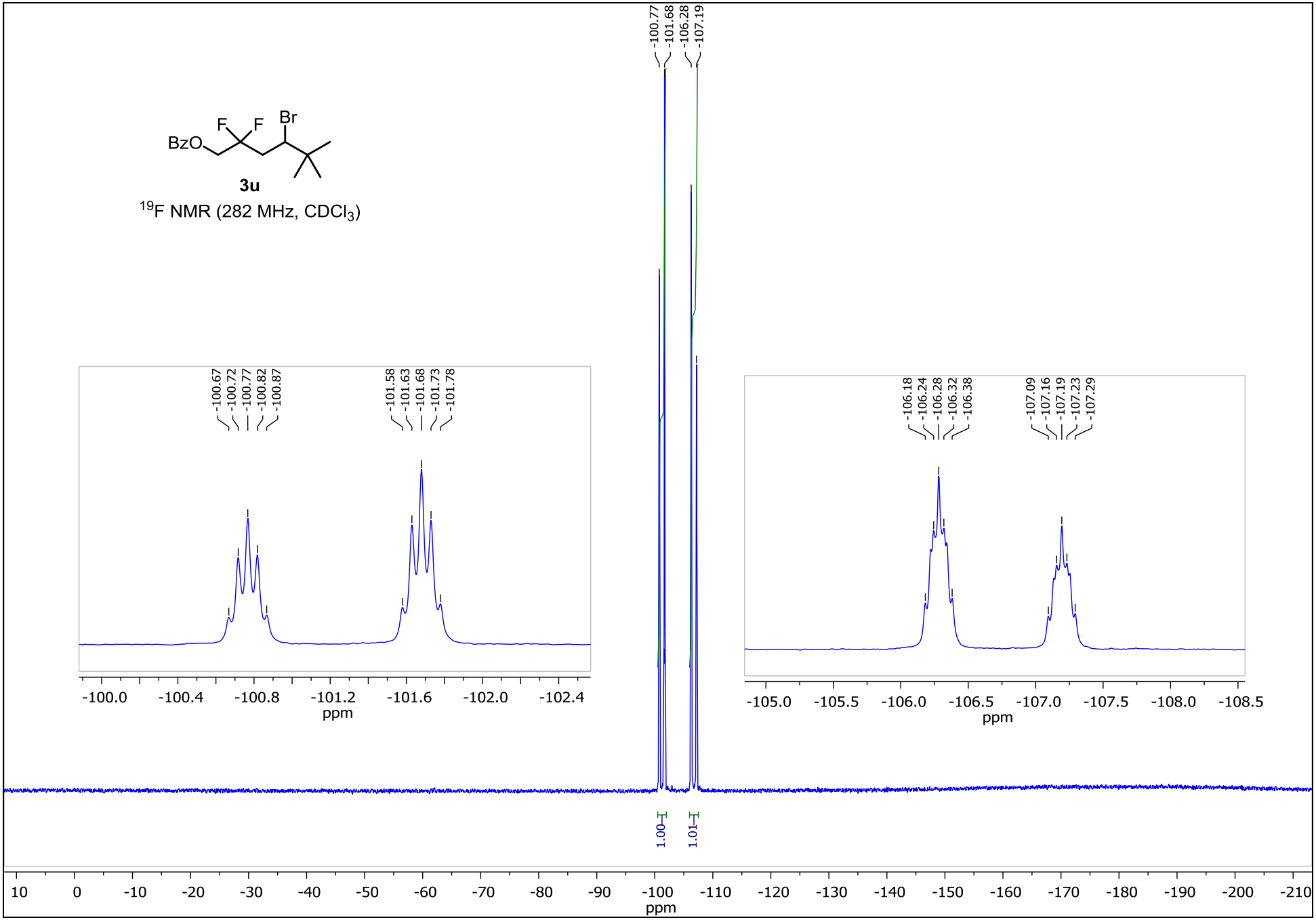

8.05
8.03
7.59
7.57
7.54
7.47
7.45
7.42
7.26
4.39
4.37
4.35
3.50
3.47
3.45
2.84
2.79
2.70
2.68
2.65
2.59
2.56
2.53
2.16
2.13
2.08
1.99
1.97
3.55 3.50 3.45 3.40
ppm
4.4 4.3
ppm
1.96
1.00
1.98
2.94
1.97
4.07
4.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm
Br
F
F
F
F
OBz
3t
1H NMR (300 MHz, CDCl3)

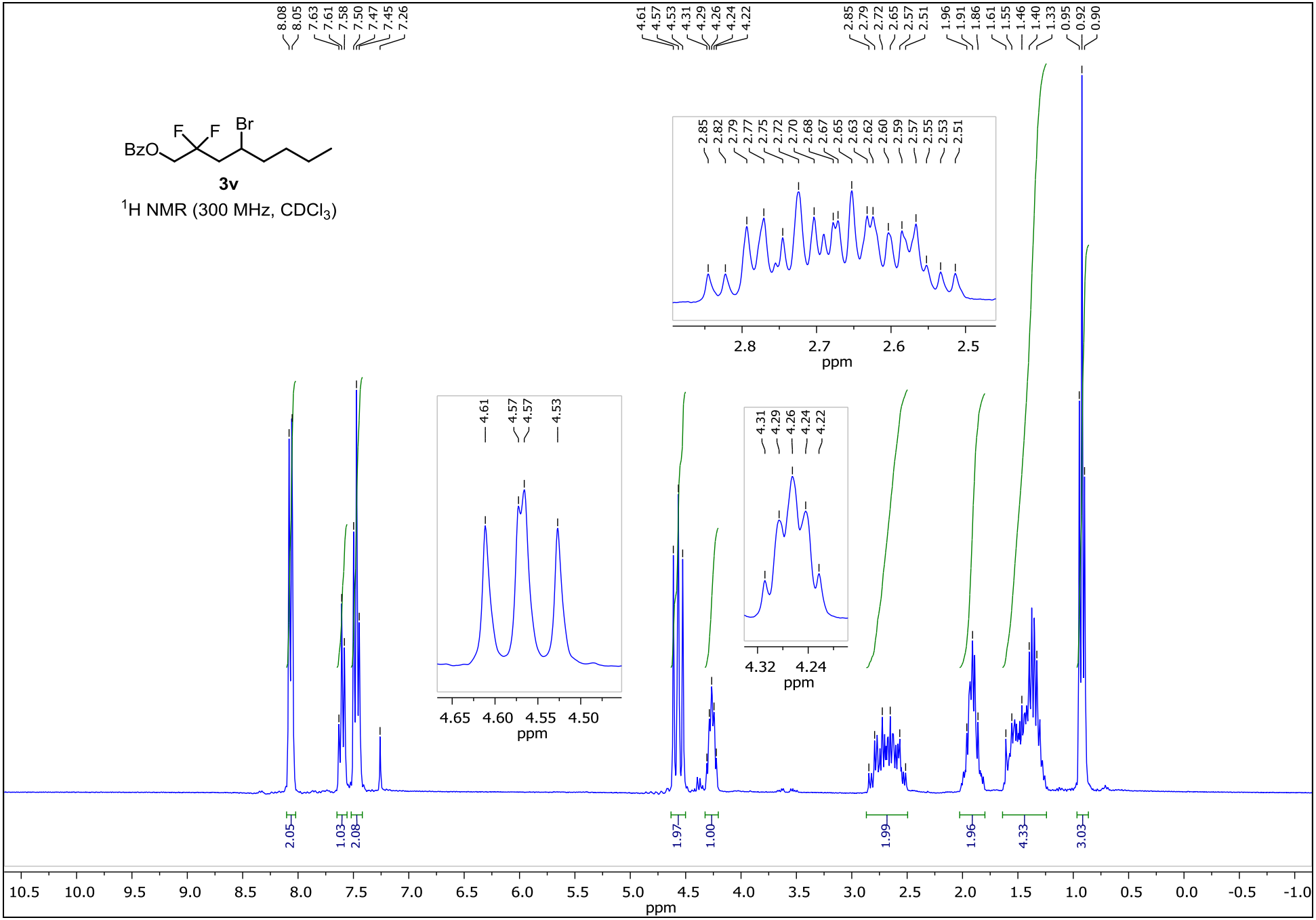

166.62
133.12
130.33
129.69
128.52
121.26
117.92
117.83
114.58
114.50
77.58
77.16
76.74
63.99
44.82
39.40
39.12
38.84
35.89
34.35
34.05
33.75
26.84
21.48
21.41
21.33
Br
F
F
F
F
OBz
3t
13C{1H} NMR (75 MHz, CDCl3)
121.72
121.64
121.26
120.78
120.68
118.40
118.32
117.92
117.83
117.46
117.36
115.05
114.99
114.58
114.50
114.11
114.03
123 122 121 120 119 118 117 116 115 114 113
ppm
39.40
39.12
38.84
40 39 38
ppm
34.35
34.05
33.75
35 34 33
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

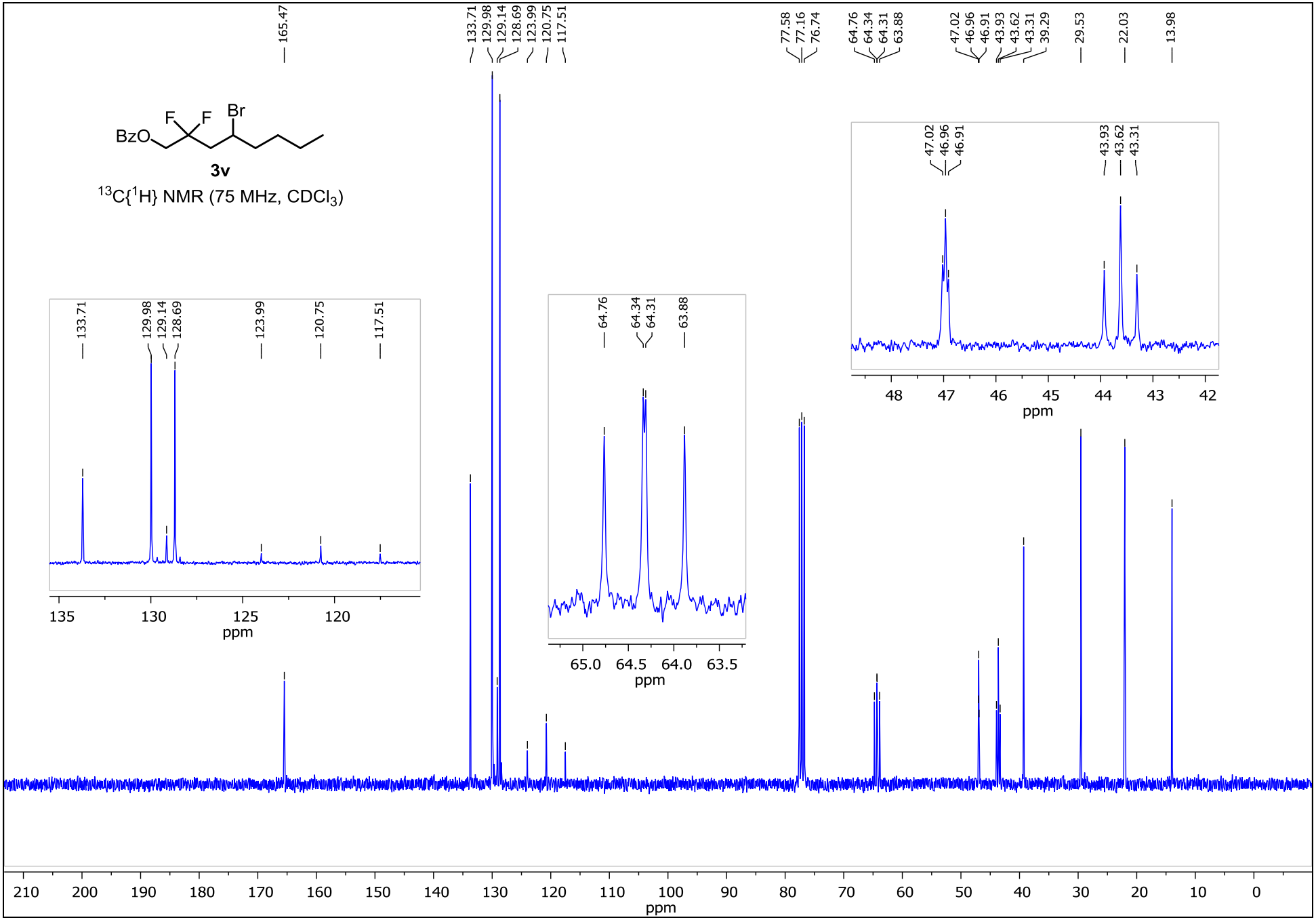

F F
Br OBz
F F
3t
19F NMR (282 MHz, CDCl3)
-112.87
-113.92
-114.87
-115.64
-112.87
-112.97
-113.81
-113.92
-114.78
-114.87
-115.61
-115.64
-115.67
-115.70
1.00
2.96
-112.0
-113.0
-114.0
-115.0
-116.0
-117.0
ppm
1.00
2.96
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

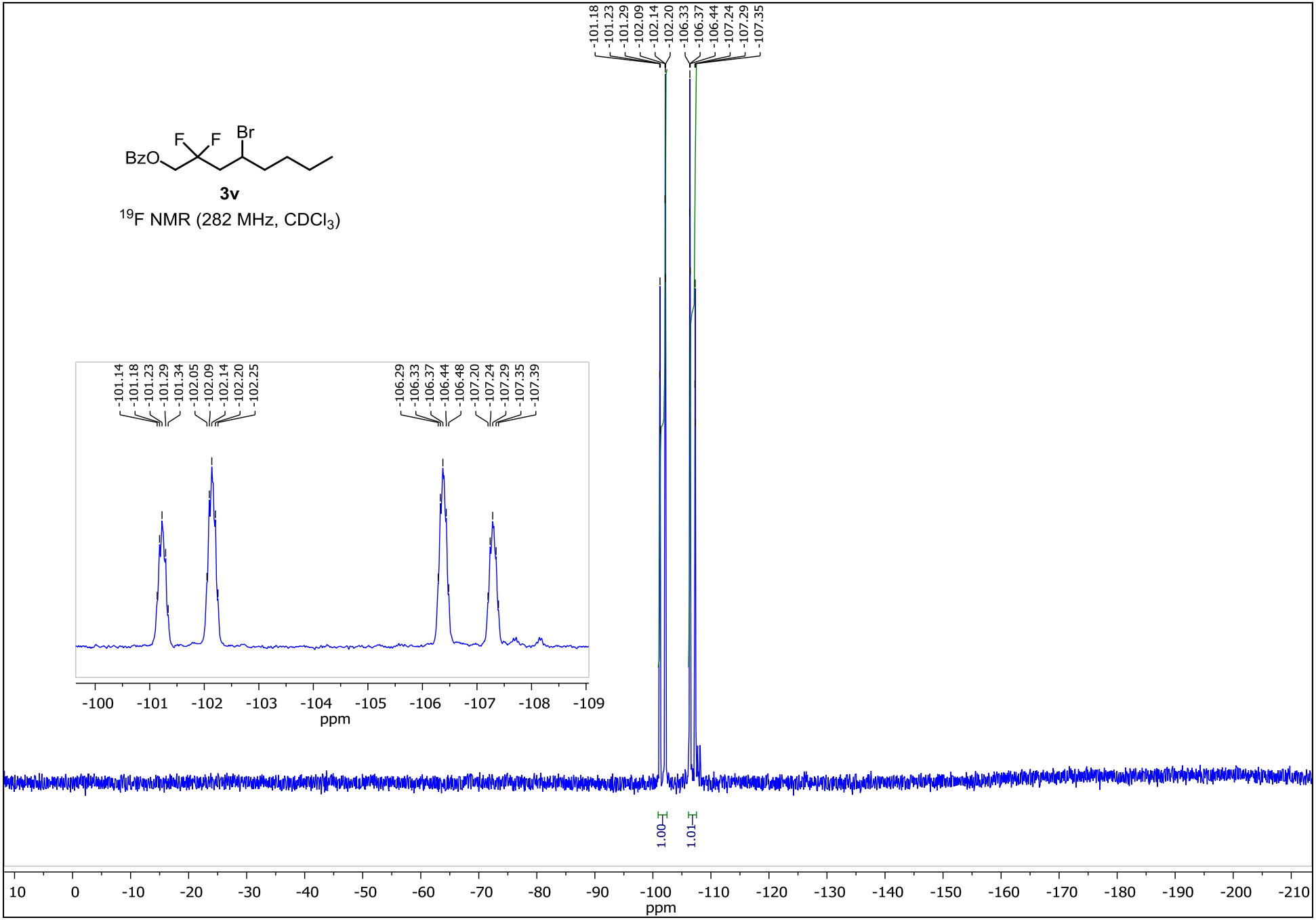

8.08
8.06
7.62
7.60
7.57
7.49
7.46
7.44
4.69
4.64
4.59
4.05
4.02
2.77
2.71
2.66
2.60
2.55
1.09
F
F
Br
BzO
3u
1H NMR (300 MHz, CDCl3)
4.69
4.68
4.65
4.64
4.62
4.61
4.59
4.75
4.70
4.65
4.60
4.55
ppm
2.06
1.02
2.08
1.99
1.00
2.13
8.93
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

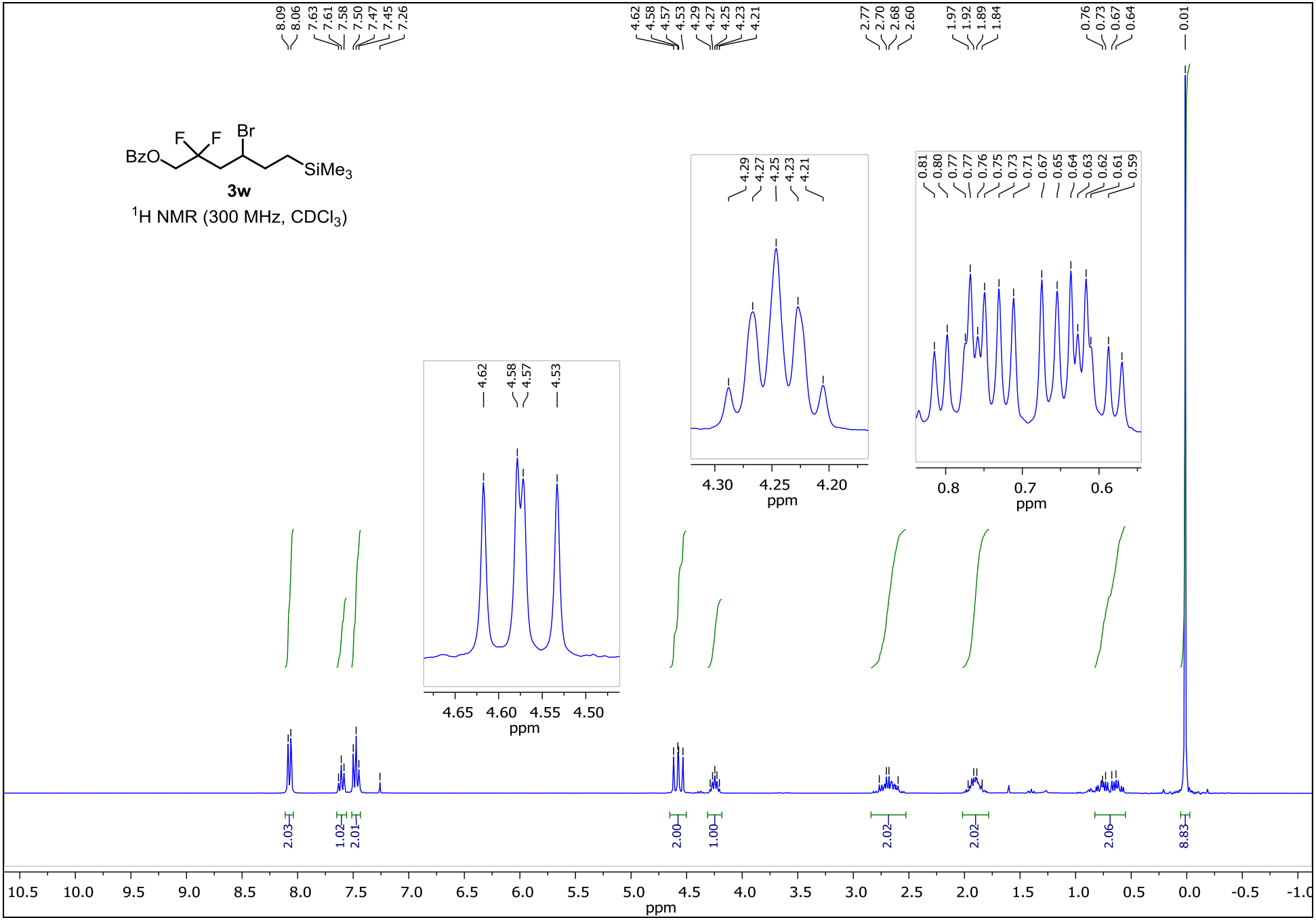

165.46
133.61
129.93
129.25
128.64
124.31
121.08
117.85
77.58
77.16
76.74
64.42
64.01
63.96
63.55
58.59
58.51
40.32
40.00
39.68
36.17
27.09
F
F
Br
BzO
3u
13C{1H} NMR (75 MHz, CDCl3)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
134 132 130 128 126 124 122 120 118 116
64.5 64.0 63.5
58.7 58.6 58.5 58.4 58.3
40.5 40.0 39.5

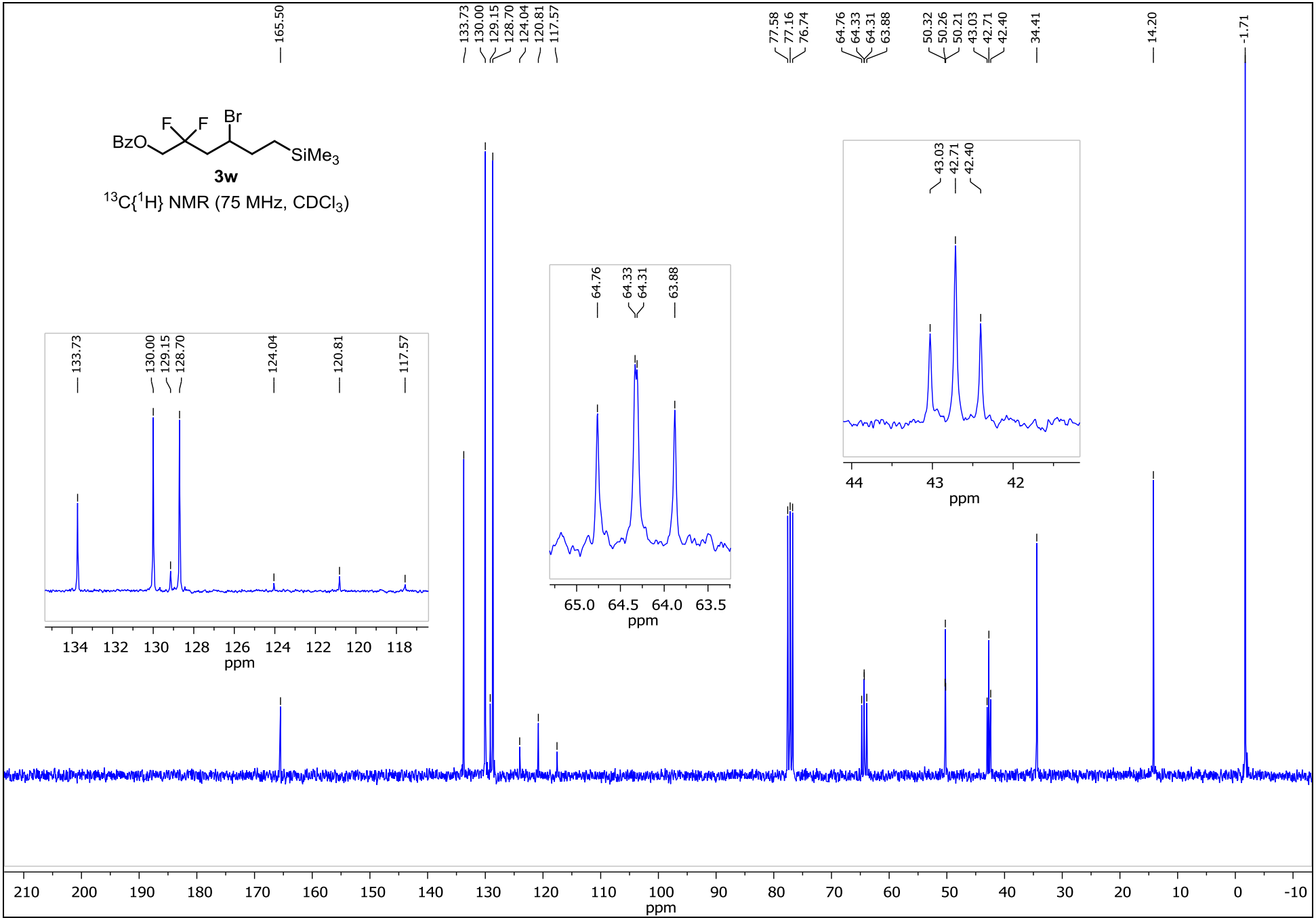

-100.77
-101.68
-106.28
-107.19
F
F
Br
BzO
3u
^{19}F NMR (282 MHz, CDCl$_3$)
-100.67
-100.72
-100.77
-100.82
-100.87
-101.58
-101.63
-101.68
-101.73
-101.78
-100.0
-100.4
-100.8
-101.2
-101.6
-102.0
-102.4
ppm
-106.18
-106.24
-106.28
-106.32
-106.38
-107.09
-107.16
-107.19
-107.23
-107.29
-105.0
-105.5
-106.0
-106.5
-107.0
-107.5
-108.0
-108.5
ppm
1.00
1.01
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

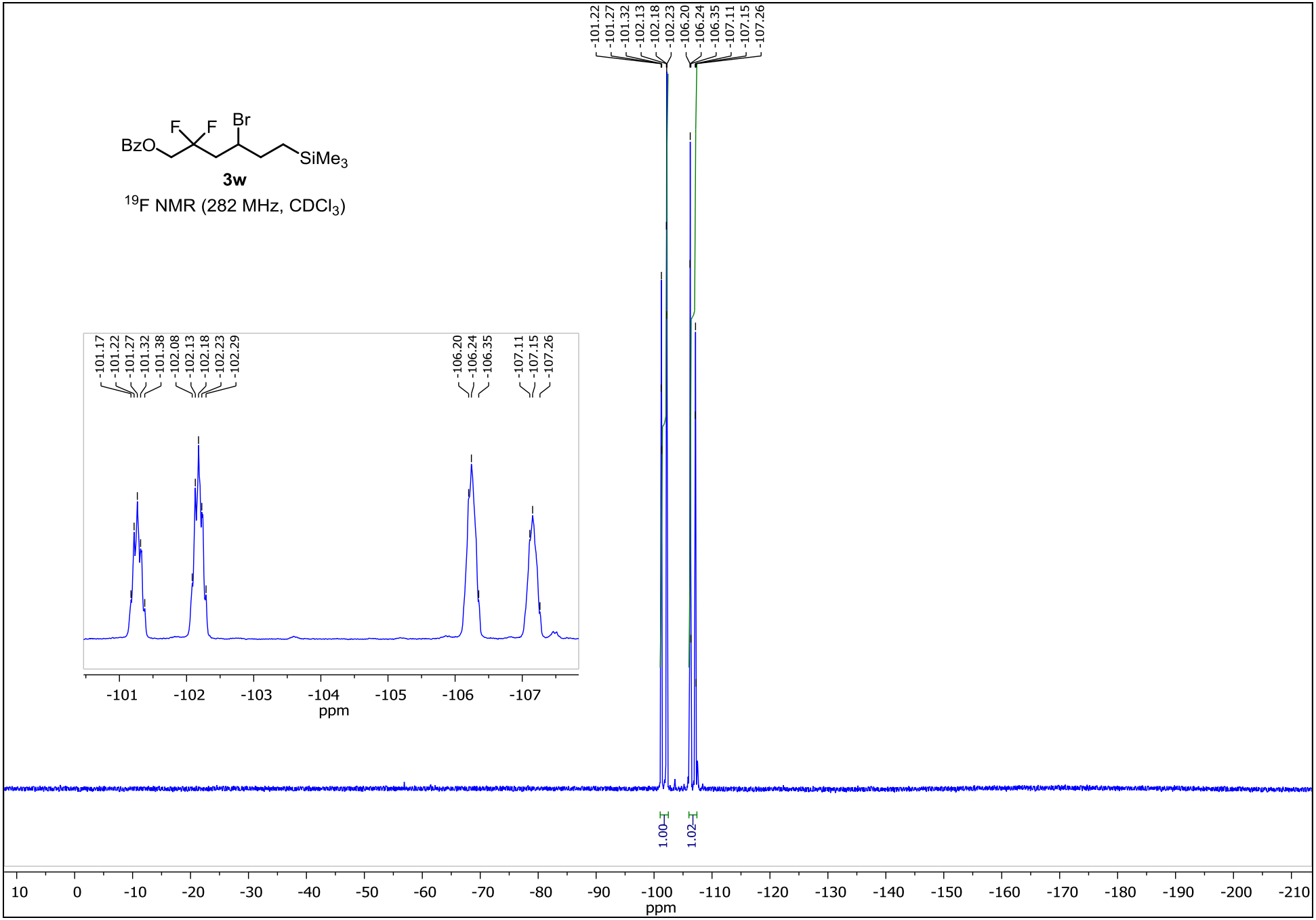

8.08
8.05
7.63
7.61
7.58
7.50
7.47
7.45
7.26
4.61
4.57
4.53
4.31
4.29
4.26
4.24
4.22
2.85
2.79
2.72
2.65
2.57
2.51
1.96
1.91
1.86
1.61
1.55
1.46
1.40
1.33
0.95
0.92
0.90
F
F
Br
BzO
3v
1H NMR (300 MHz, CDCl3)
2.85
2.82
2.79
2.77
2.75
2.72
2.70
2.68
2.67
2.65
2.63
2.62
2.60
2.59
2.57
2.55
2.53
2.51
2.8
2.7
2.6
2.5
ppm
4.61
4.57
4.57
4.53
4.65
4.60
4.55
4.50
ppm
4.31
4.29
4.26
4.24
4.22
4.32
4.24
ppm
2.05
1.03
2.08
1.97
1.00
1.99
1.96
4.33
3.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

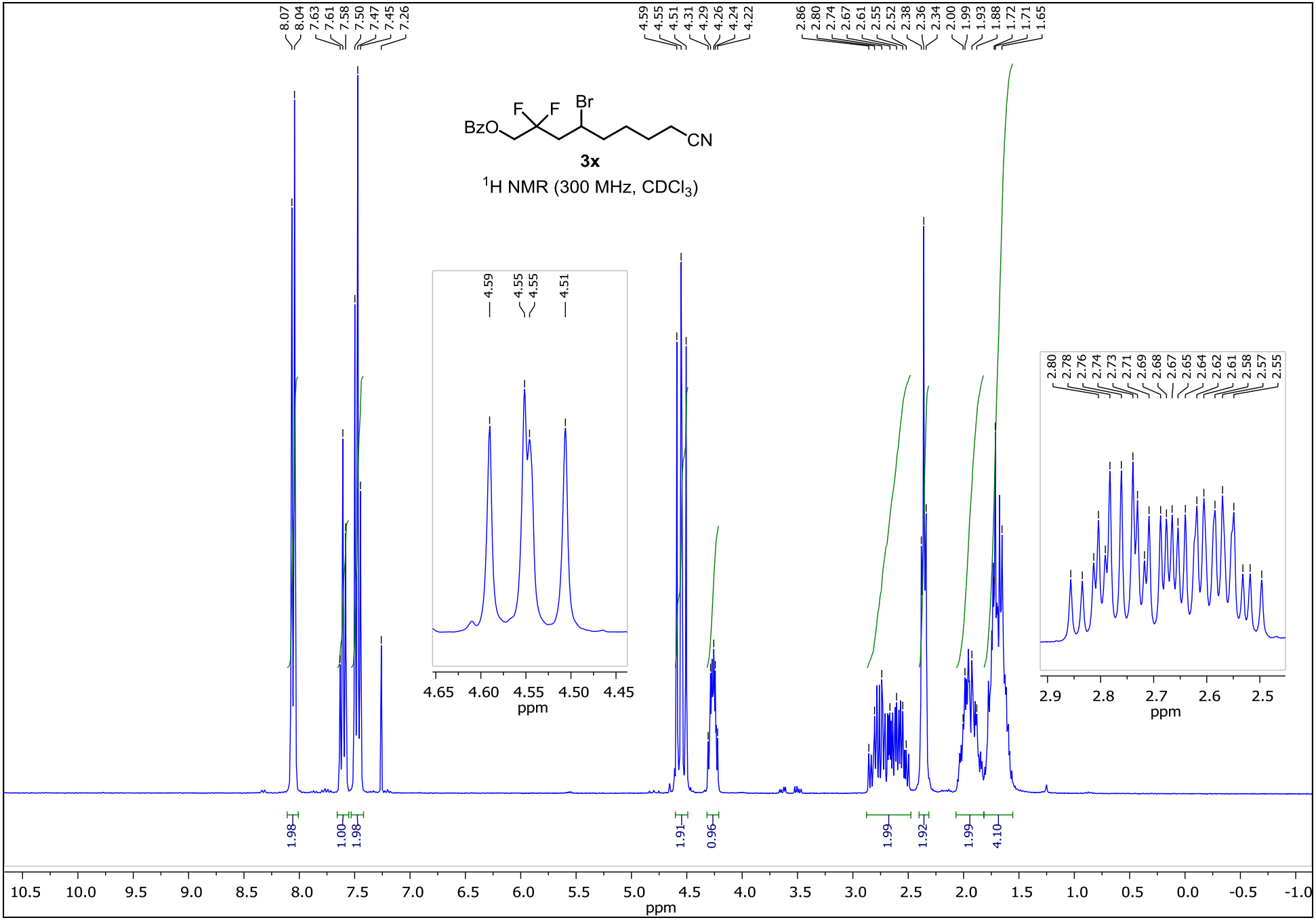

165.47
133.71
129.98
129.14
128.69
123.99
120.75
117.51
77.58
77.16
76.74
64.76
64.34
64.31
63.88
47.02
46.96
46.91
43.93
43.62
43.31
39.29
29.53
22.03
13.98
F
F
Br
BzO
3v
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
ppm

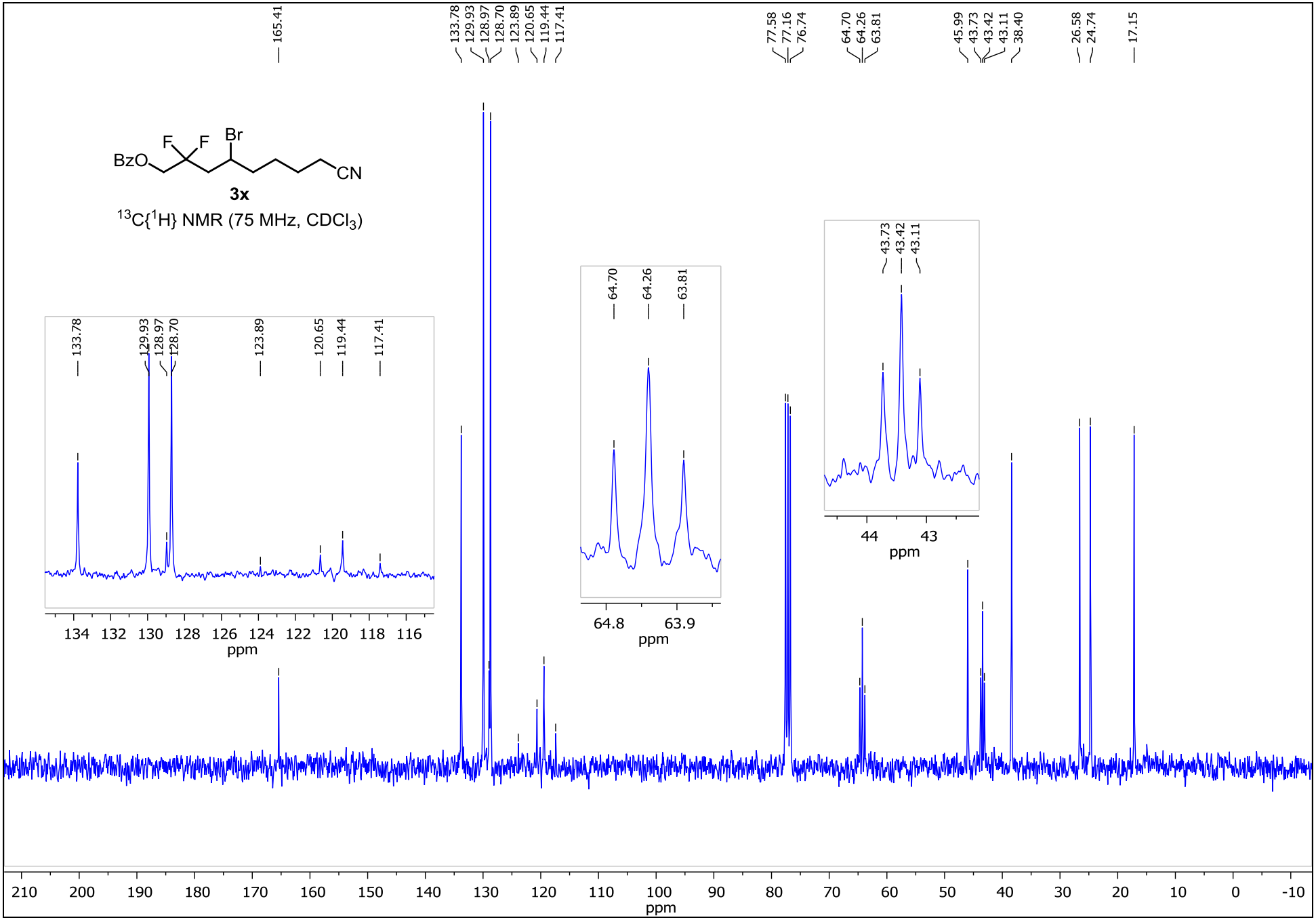

F
F
Br
BzO
3v
19F NMR (282 MHz, CDCl3)
-101.18
-101.23
-101.29
-102.09
-102.14
-102.20
-106.33
-106.37
-106.44
-107.24
-107.29
-107.35
-101.14
-101.18
-101.23
-101.29
-101.34
-102.05
-102.09
-102.14
-102.20
-102.25
-106.29
-106.33
-106.37
-106.44
-106.48
-107.20
-107.24
-107.29
-107.35
-107.39
-100 -101 -102 -103 -104 -105 -106 -107 -108 -109
ppm
1.00
1.01
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
ppm

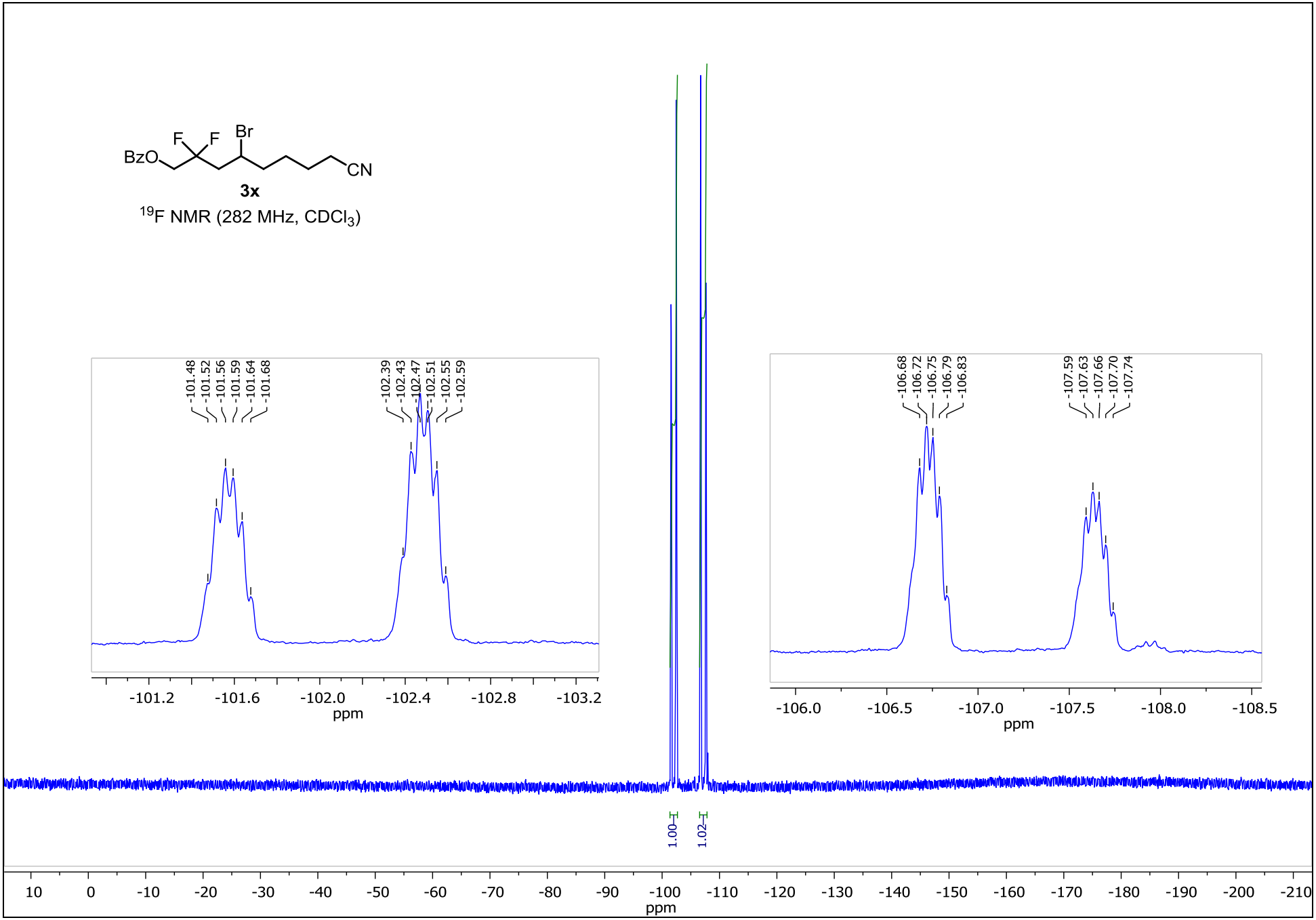

8.09
8.06
7.63
7.61
7.58
7.50
7.47
7.45
7.26
4.62
4.58
4.57
4.53
4.29
4.27
4.25
4.23
4.21
2.77
2.70
2.68
2.60
1.97
1.92
1.89
1.84
0.76
0.73
0.67
0.64
0.01
F
F
Br
BzO
SiMe3
3w
1H NMR (300 MHz, CDCl3)
0.81
0.80
0.77
0.77
0.76
0.75
0.73
0.71
0.67
0.65
0.64
0.63
0.62
0.61
0.59
4.30
4.25
4.20
ppm
0.8
0.7
0.6
ppm
4.65
4.60
4.55
4.50
ppm
2.03
1.02
2.01
2.00
1.00
2.02
2.02
2.06
8.83
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

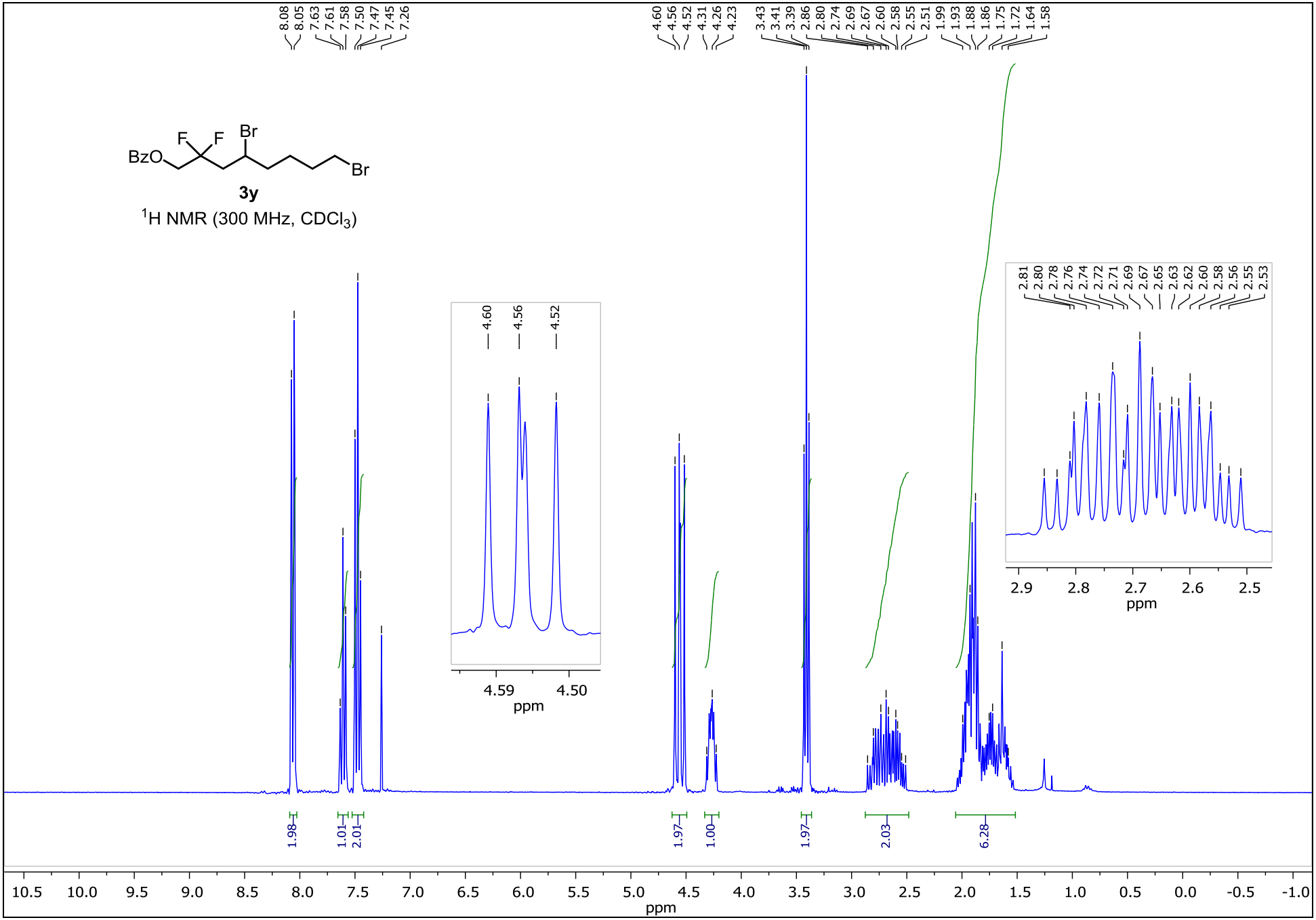

165.50
133.73
130.00
129.15
128.70
124.04
120.81
117.57
77.58
77.16
76.74
64.76
64.33
64.31
63.88
50.32
50.26
50.21
43.03
42.71
42.40
34.41
14.20
-1.71
F
F
Br
BzO
SiMe3
3w
13C{1H} NMR (75 MHz, CDCl3)
ppm

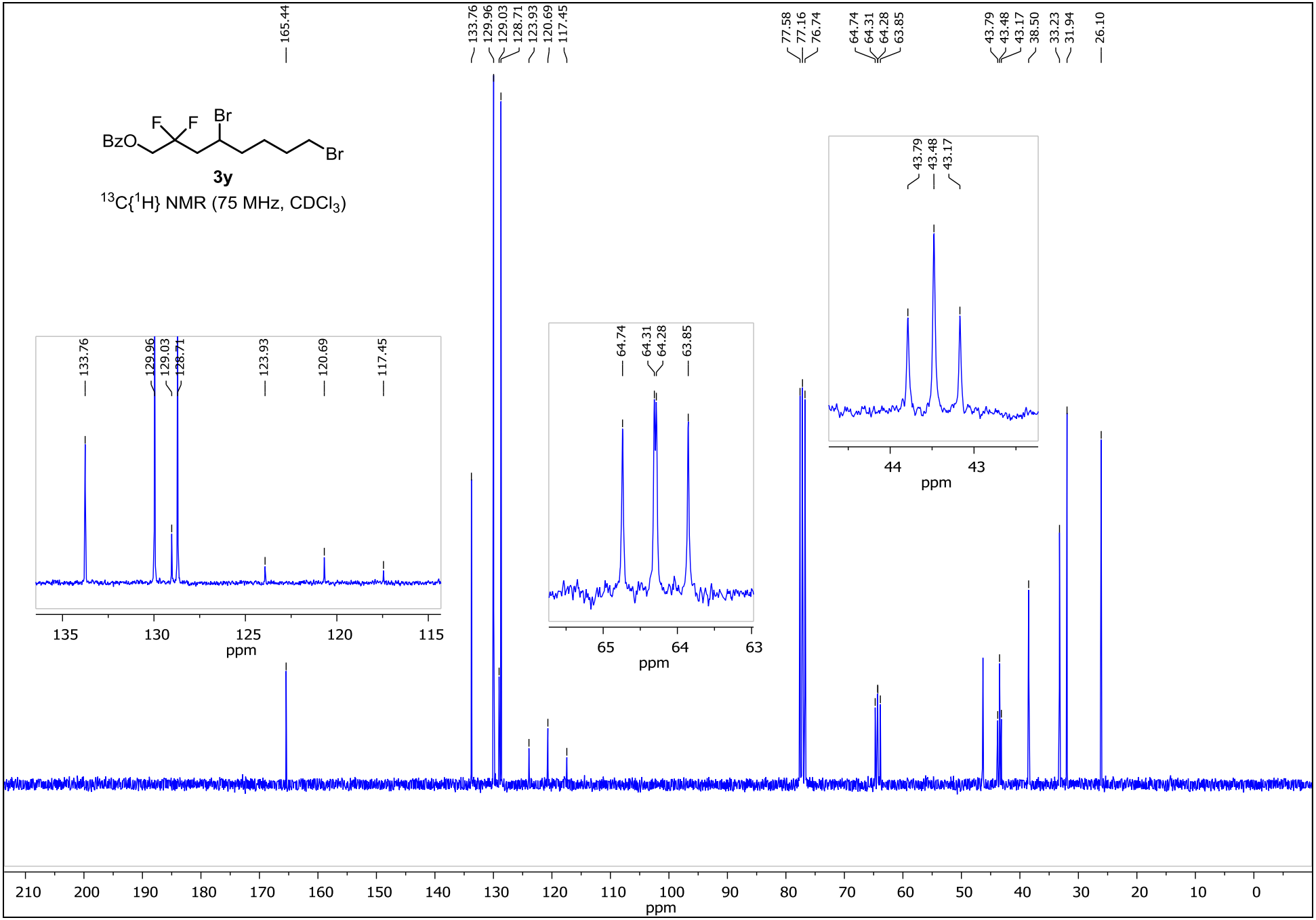

F
F
Br
BzO
SiMe3
3w
19F NMR (282 MHz, CDCl3)
-101.22
-101.27
-101.32
-102.13
-102.18
-102.23
-106.20
-106.24
-106.35
-107.11
-107.15
-107.26
-101.17
-101.22
-101.27
-101.32
-101.38
-102.08
-102.13
-102.18
-102.23
-102.29
-106.20
-106.24
-106.35
-107.11
-107.15
-107.26
-101
-102
-103
-104
-105
-106
-107
ppm
1.00
1.02
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

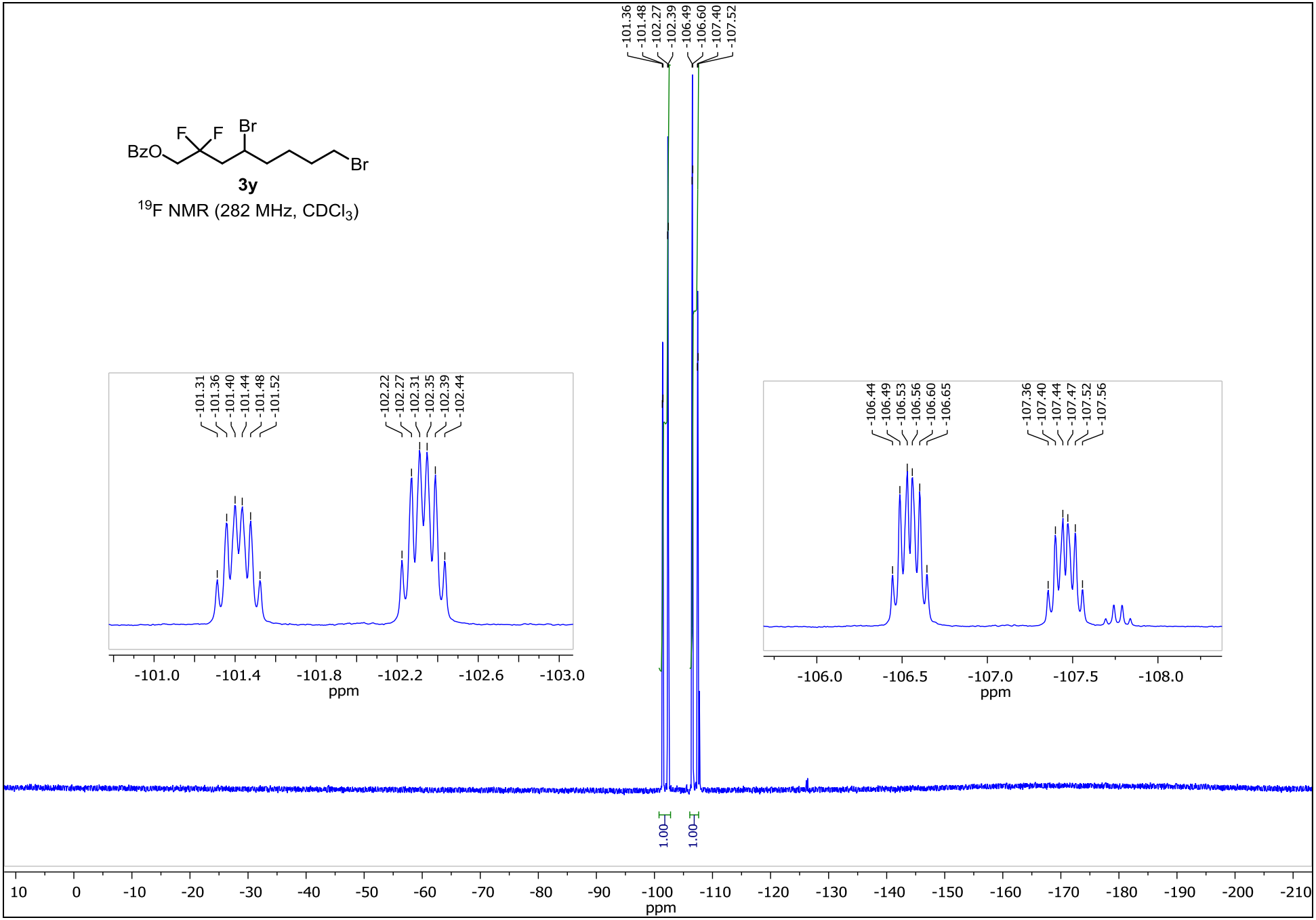

8.07
8.04
7.63
7.61
7.58
7.50
7.47
7.45
7.26
4.59
4.55
4.51
4.31
4.29
4.26
4.24
4.22
2.86
2.80
2.74
2.67
2.61
2.55
2.52
2.38
2.36
2.34
2.00
1.99
1.93
1.88
1.72
1.71
1.65
F
F
Br
BzO
CN
3x
1H NMR (300 MHz, CDCl3)
4.65 4.60 4.55 4.50 4.45
ppm
2.9 2.8 2.7 2.6 2.5
ppm
1.98
1.00
1.98
1.91
0.96
1.99
1.92
1.99
4.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

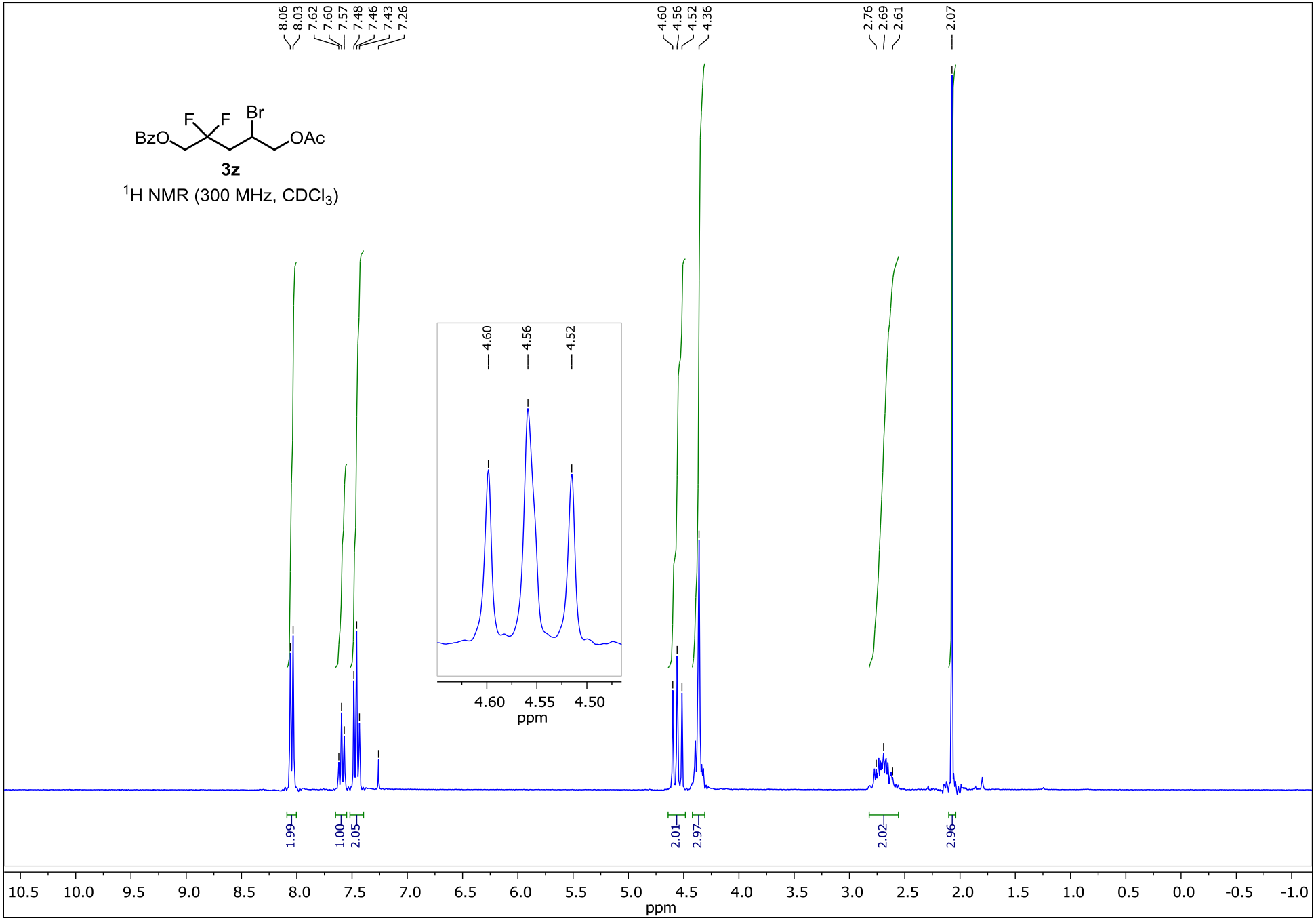

165.41
133.78
129.93
128.97
128.70
123.89
120.65
119.44
117.41
77.58
77.16
76.74
64.70
64.26
63.81
45.99
43.73
43.42
43.11
38.40
26.58
24.74
17.15
F
F
Br
BzO
CN
3x
13C{1H} NMR (75 MHz, CDCl3)
ppm
ppm
ppm
ppm

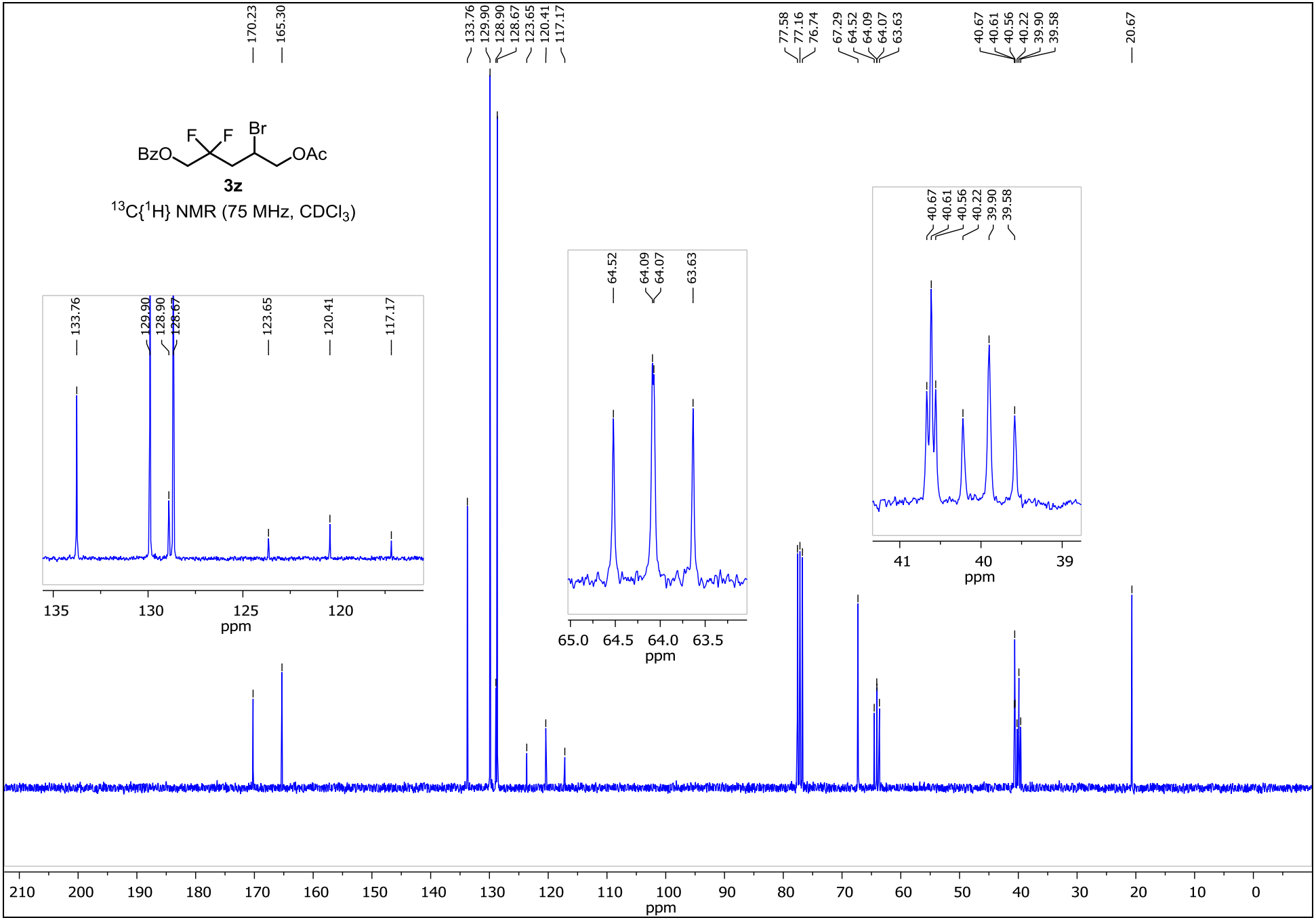

F
F
Br
BzO
CN
3x
19F NMR (282 MHz, CDCl3)
-101.48
-101.52
-101.56
-101.59
-101.64
-101.68
-102.39
-102.43
-102.47
-102.51
-102.55
-102.59
-101.2
-101.6
-102.0
-102.4
-102.8
-103.2
ppm
-106.68
-106.72
-106.75
-106.79
-106.83
-107.59
-107.63
-107.66
-107.70
-107.74
-106.0
-106.5
-107.0
-107.5
-108.0
-108.5
ppm
1.00
1.02
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

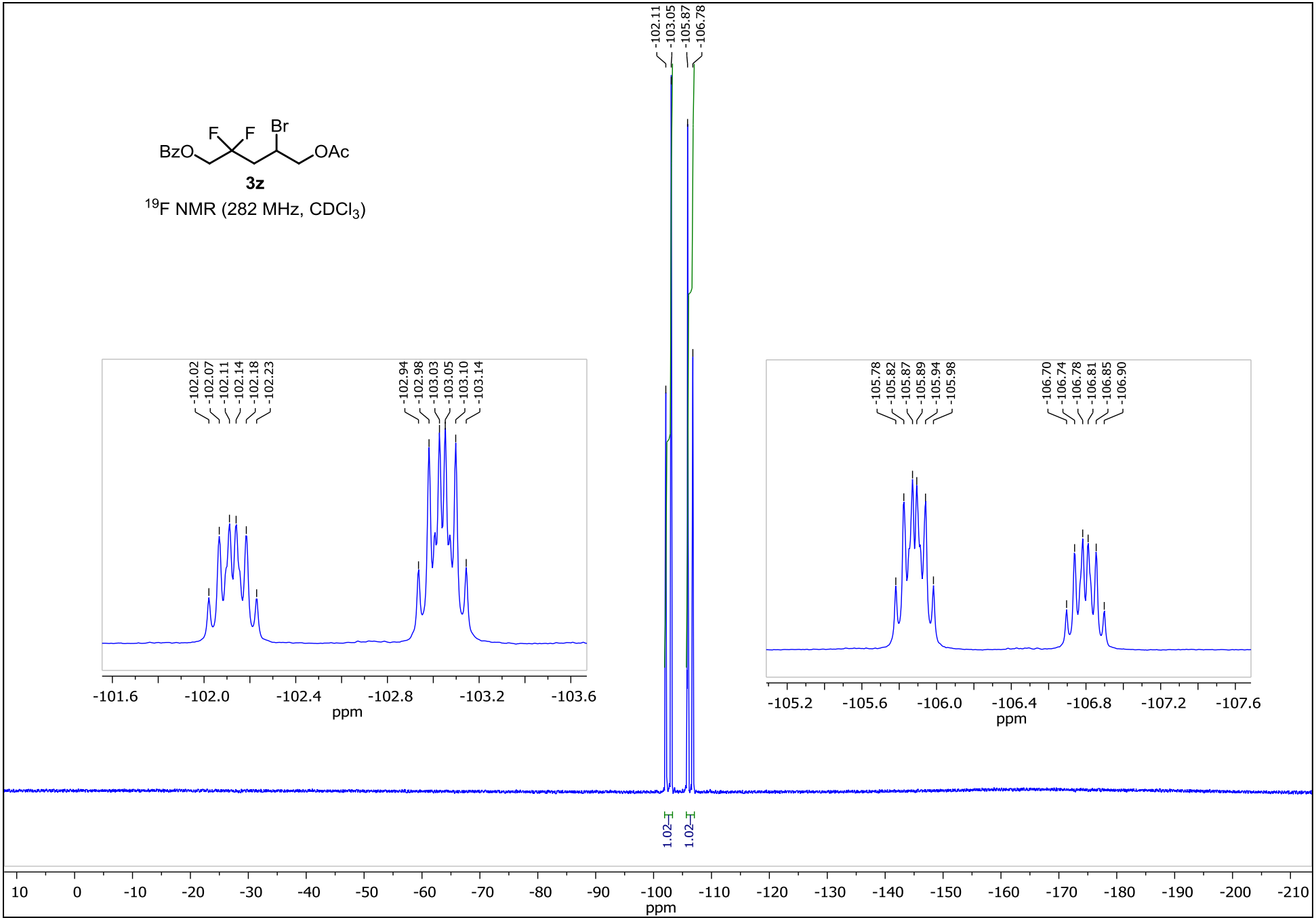

8.08
8.05
7.63
7.61
7.58
7.50
7.47
7.45
7.26
4.60
4.56
4.52
4.31
4.26
4.23
3.43
3.41
3.39
2.86
2.80
2.74
2.69
2.67
2.60
2.58
2.55
2.51
1.99
1.93
1.88
1.86
1.75
1.72
1.64
1.58
F
F
Br
BzO
Br
3y
1H NMR (300 MHz, CDCl3)
4.60
4.56
4.52
4.59
4.50
ppm
2.81
2.80
2.78
2.76
2.74
2.72
2.71
2.69
2.67
2.65
2.63
2.62
2.60
2.58
2.56
2.55
2.53
2.9
2.8
2.7
2.6
2.5
ppm
1.98
1.01
2.01
1.97
1.00
1.97
2.03
6.28
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

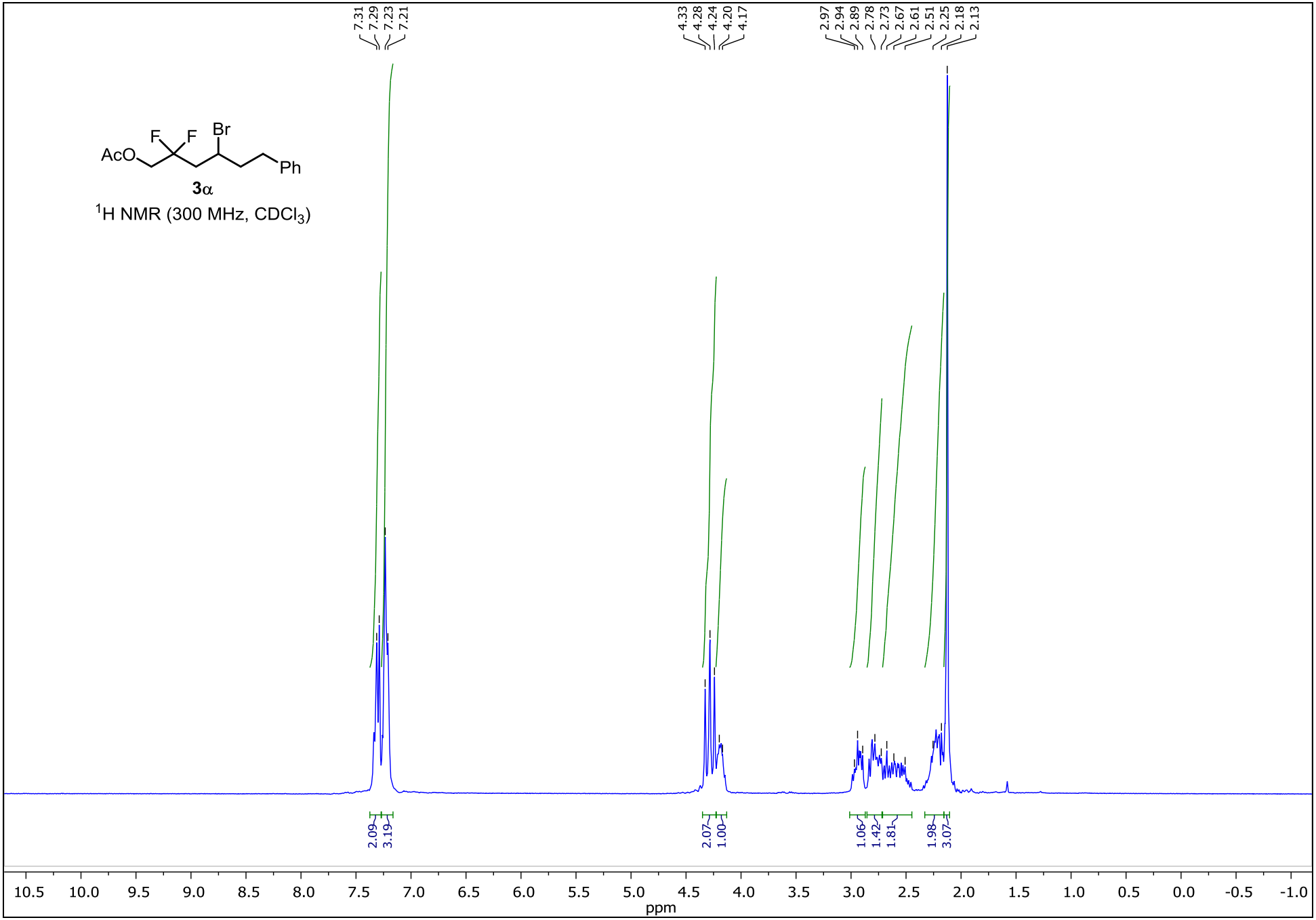

165.44
133.76
129.96
129.03
128.71
123.93
120.69
117.45
77.58
77.16
76.74
64.74
64.31
64.28
63.85
43.79
43.48
43.17
38.50
33.23
31.94
26.10
F
F
Br
BzO
Br
3y
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
ppm

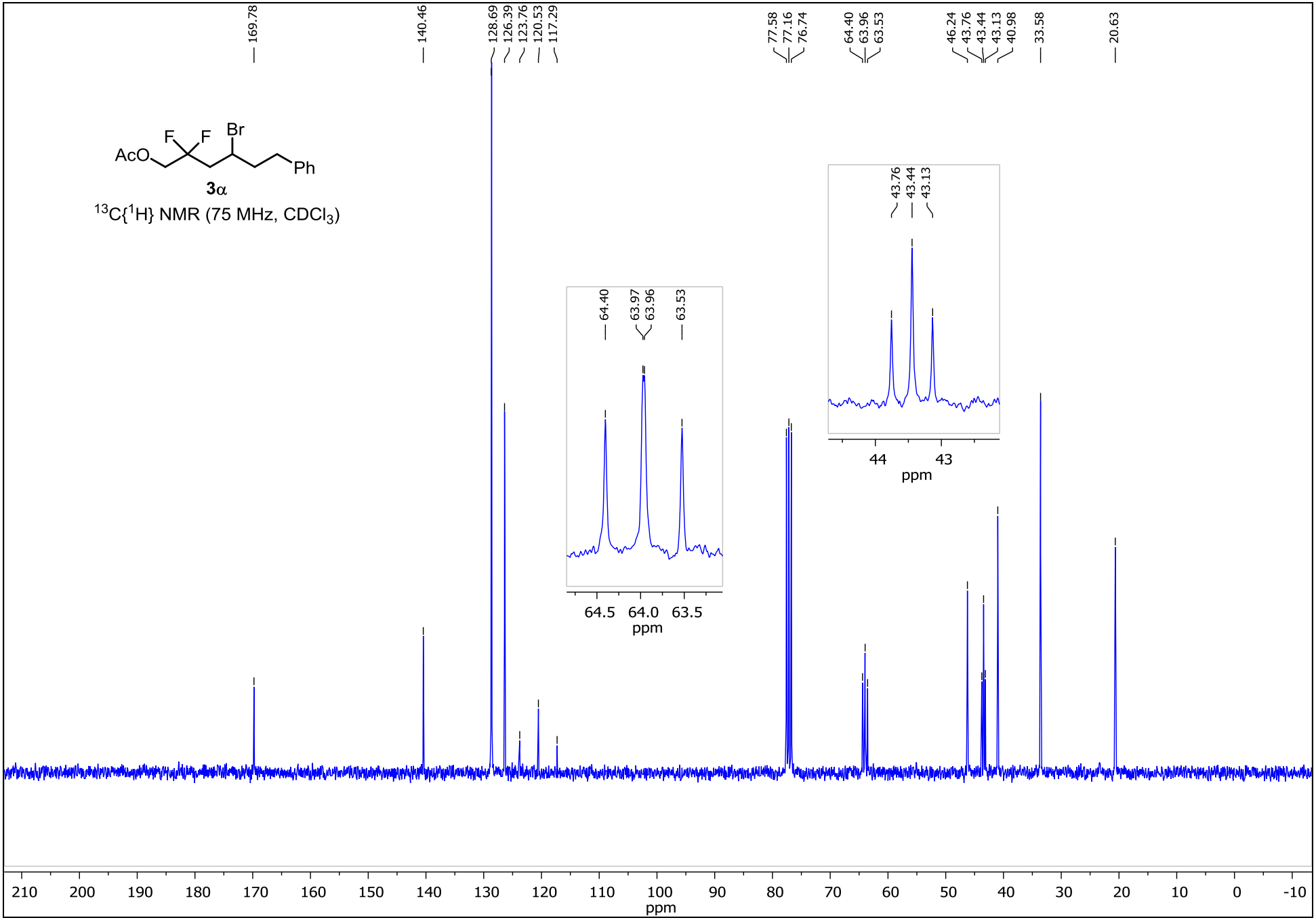

F
F
Br
BzO
Br
3y
19F NMR (282 MHz, CDCl3)
-101.36
-101.48
-102.27
-102.39
-106.49
-106.60
-107.40
-107.52
-101.31
-101.36
-101.40
-101.44
-101.48
-101.52
-102.22
-102.27
-102.31
-102.35
-102.39
-102.44
-101.0
-101.4
-101.8
-102.2
-102.6
-103.0
ppm
-106.44
-106.49
-106.53
-106.56
-106.60
-106.65
-107.36
-107.40
-107.44
-107.47
-107.52
-107.56
-106.0
-106.5
-107.0
-107.5
-108.0
ppm
1.00
1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

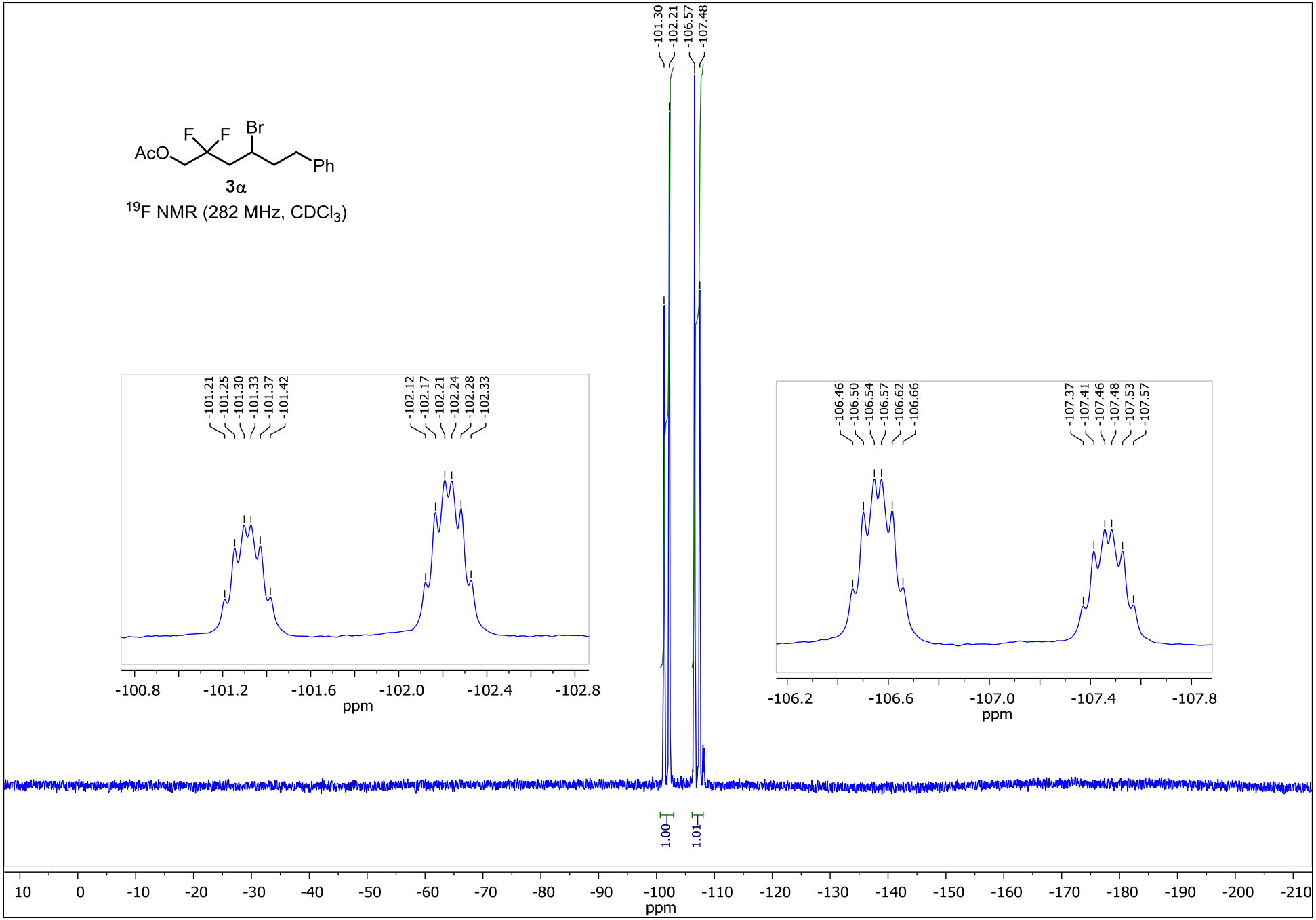

8.06
8.03
7.62
7.60
7.57
7.48
7.46
7.43
7.26
4.60
4.56
4.52
4.36
2.76
2.69
2.61
2.07
F
F
Br
BzO
OAc
3z
1H NMR (300 MHz, CDCl3)
4.60
4.56
4.52
4.60
4.55
4.50
ppm
1.99
1.00
2.05
2.01
2.97
2.02
2.96
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

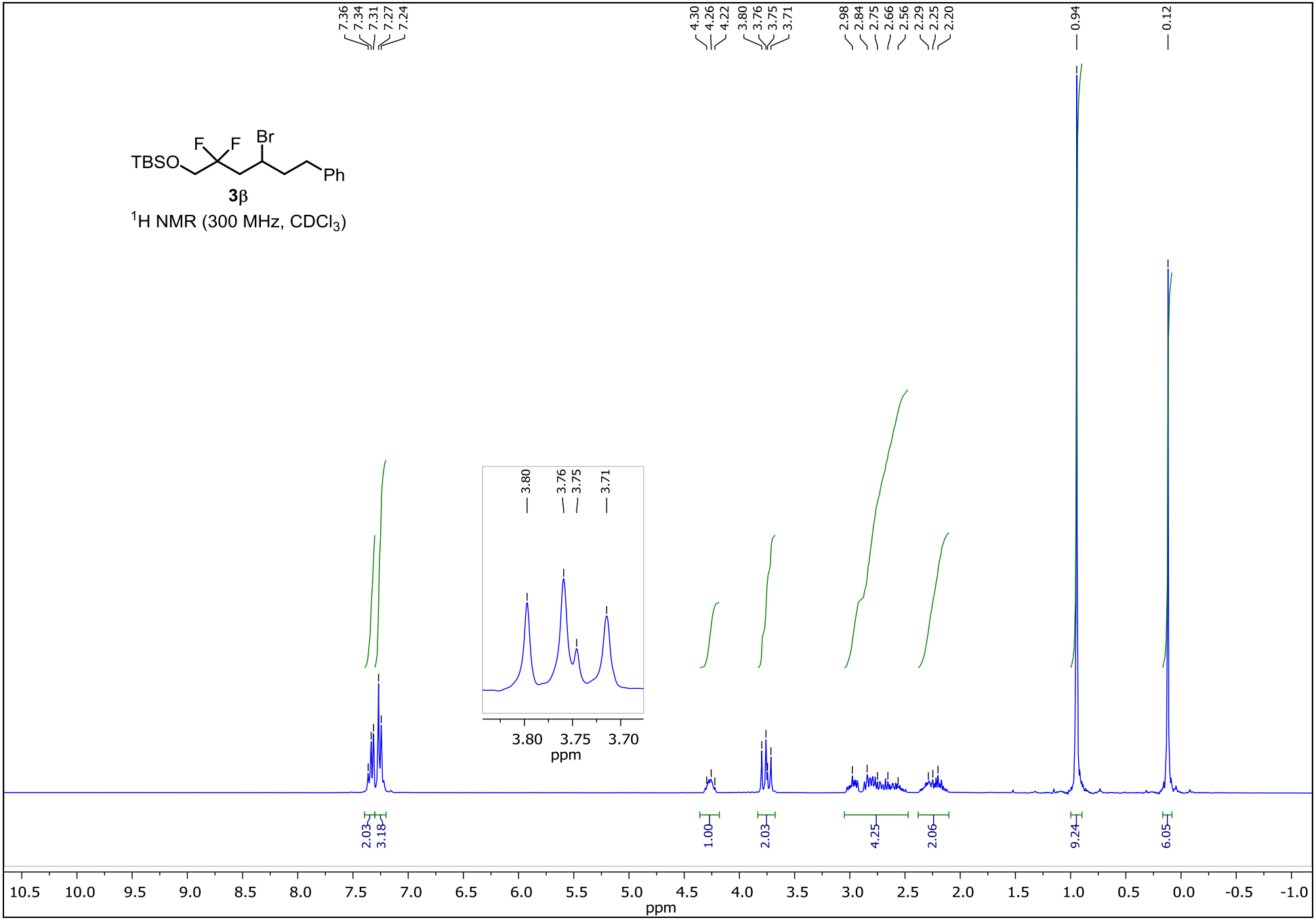

170.23
165.30
133.76
129.90
128.90
128.67
123.65
120.41
117.17
77.58
77.16
76.74
67.29
64.52
64.09
64.07
63.63
40.67
40.61
40.56
40.22
39.90
39.58
20.67
F
F
Br
BzO
OAc
3z
13C{1H} NMR (75 MHz, CDCl3)
ppm

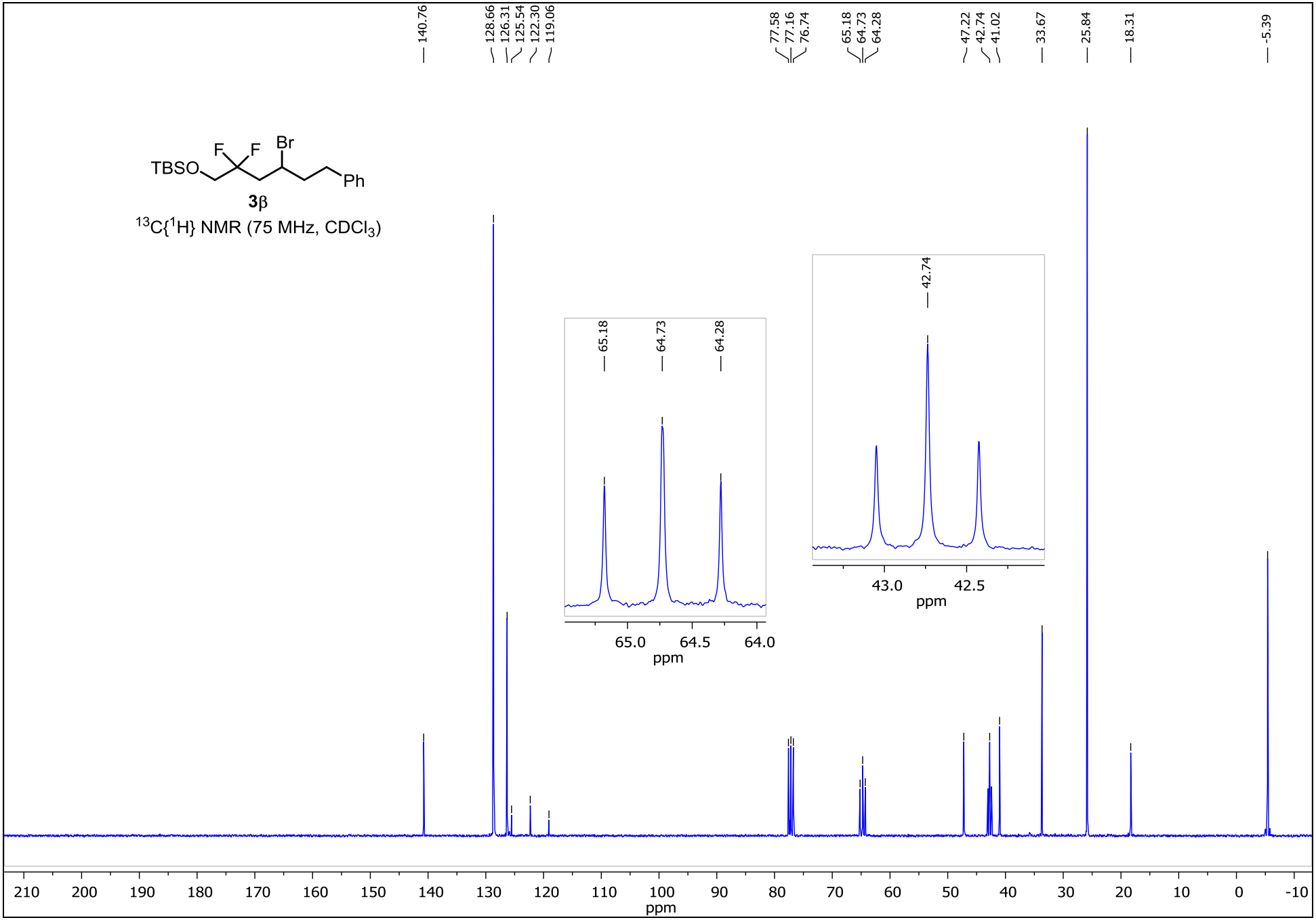

F
F
Br
BzO
OAc
3z
^{19}F NMR (282 MHz, $CDCl_3$)
-102.11
-103.05
-105.87
-106.78
-102.02
-102.07
-102.11
-102.14
-102.18
-102.23
-102.94
-102.98
-103.03
-103.05
-103.10
-103.14
-101.6
-102.0
-102.4
-102.8
-103.2
-103.6
ppm
-105.78
-105.82
-105.87
-105.89
-105.94
-105.98
-106.70
-106.74
-106.78
-106.81
-106.85
-106.90
-105.2
-105.6
-106.0
-106.4
-106.8
-107.2
-107.6
ppm
1.02
1.02
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

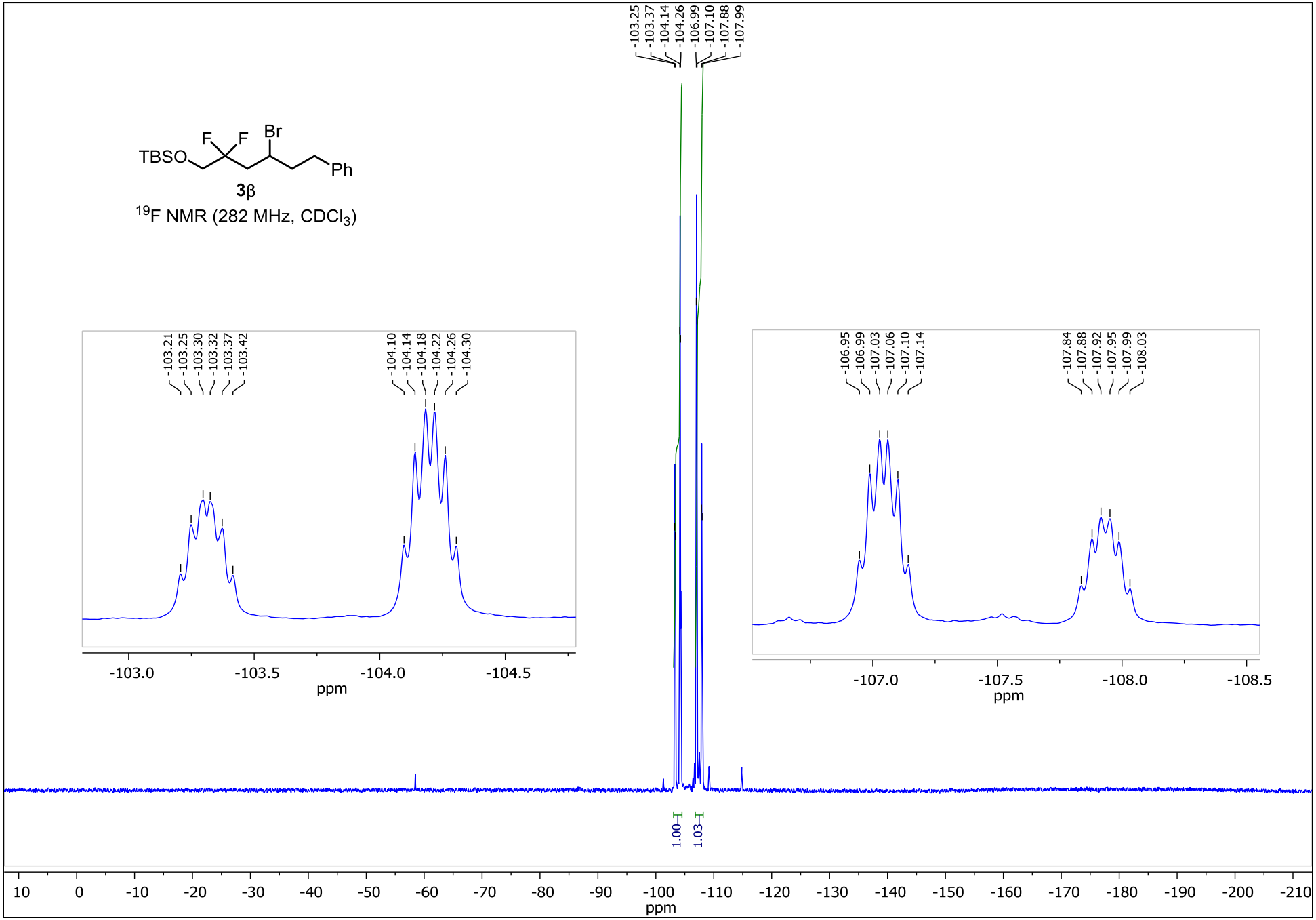

7.31
7.29
7.23
7.21
4.33
4.28
4.24
4.20
4.17
2.97
2.94
2.89
2.78
2.73
2.67
2.61
2.51
2.25
2.18
2.13
F
F
Br
AcO
Ph
3α
1H NMR (300 MHz, CDCl3)
2.09
3.19
2.07
1.00
1.06
1.42
1.81
1.98
3.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

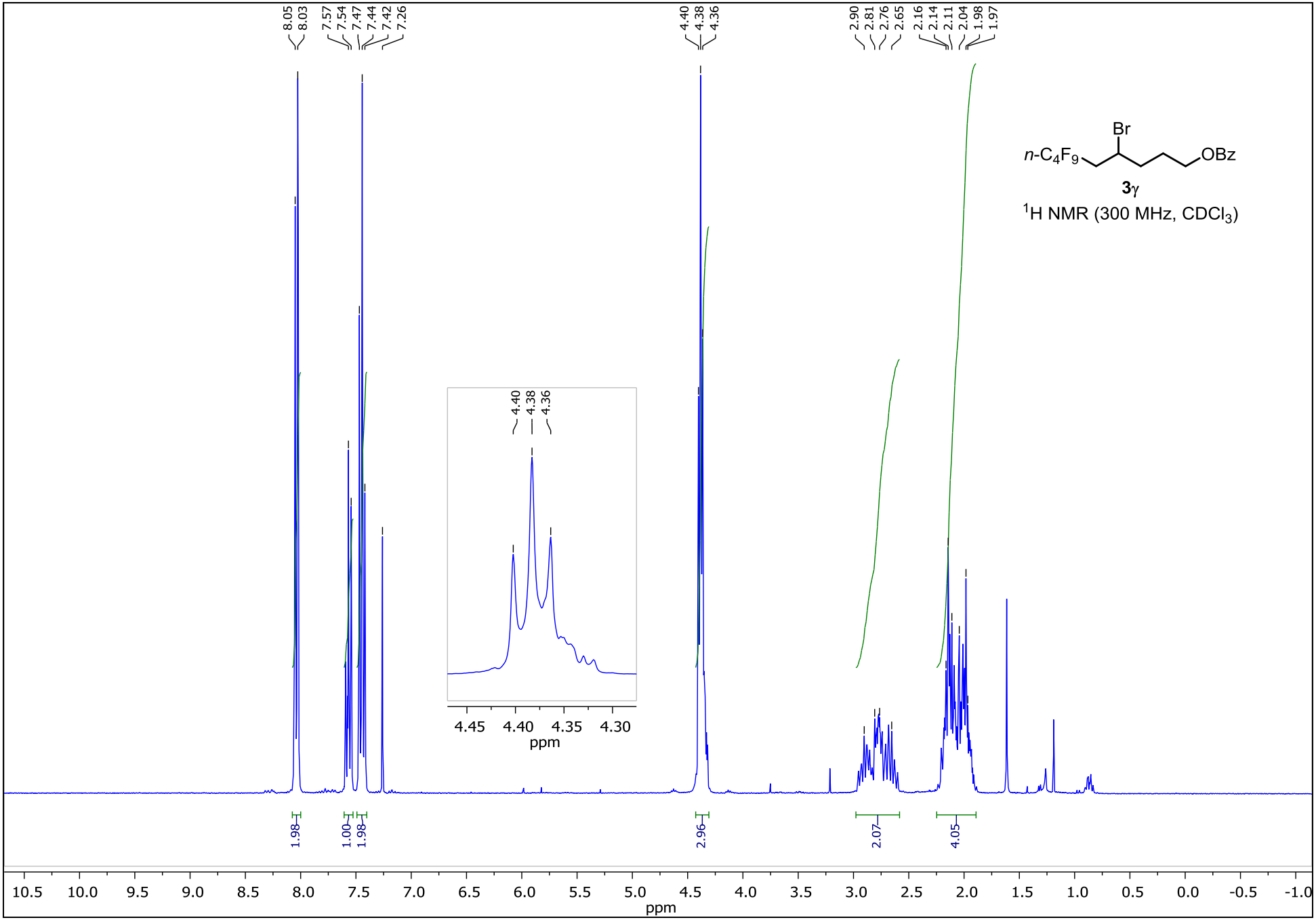

169.78
140.46
128.69
126.39
123.76
120.53
117.29
77.58
77.16
76.74
64.40
63.96
63.53
46.24
43.76
43.44
43.13
40.98
33.58
20.63
F
F
Br
AcO
Ph
3α
13C{1H} NMR (75 MHz, CDCl3)
64.40
63.97
63.96
63.53
64.5
64.0
63.5
ppm
43.76
43.44
43.13
44
43
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

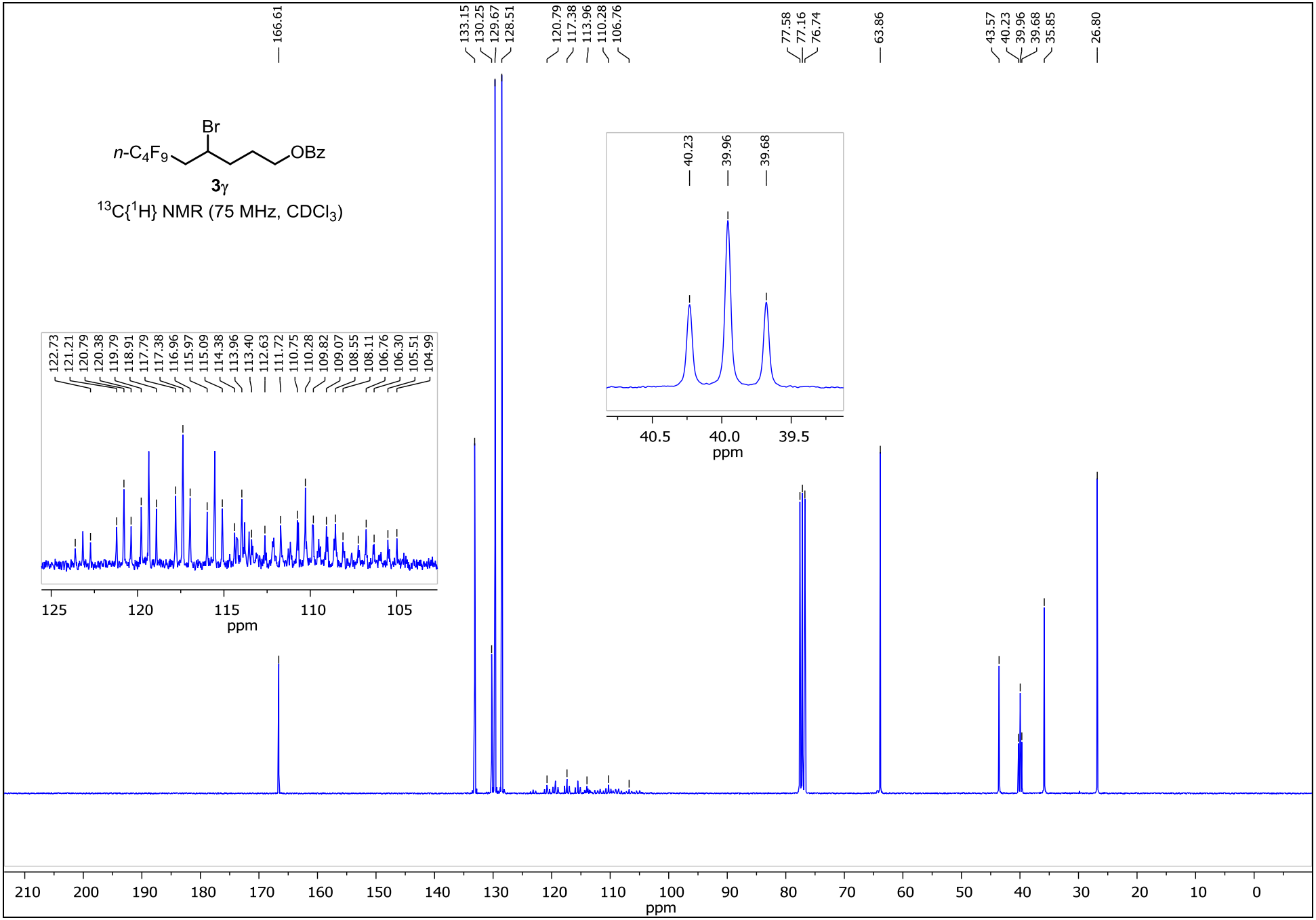

F
F
Br
AcO
Ph
3α
19F NMR (282 MHz, CDCl3)
-101.30
-102.21
-106.57
-107.48
-101.21
-101.25
-101.30
-101.33
-101.37
-101.42
-102.12
-102.17
-102.21
-102.24
-102.28
-102.33
-100.8
-101.2
-101.6
-102.0
-102.4
-102.8
ppm
-106.46
-106.50
-106.54
-106.57
-106.62
-106.66
-107.37
-107.41
-107.46
-107.48
-107.53
-107.57
-106.2
-106.6
-107.0
-107.4
-107.8
ppm
1.00
1.01
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

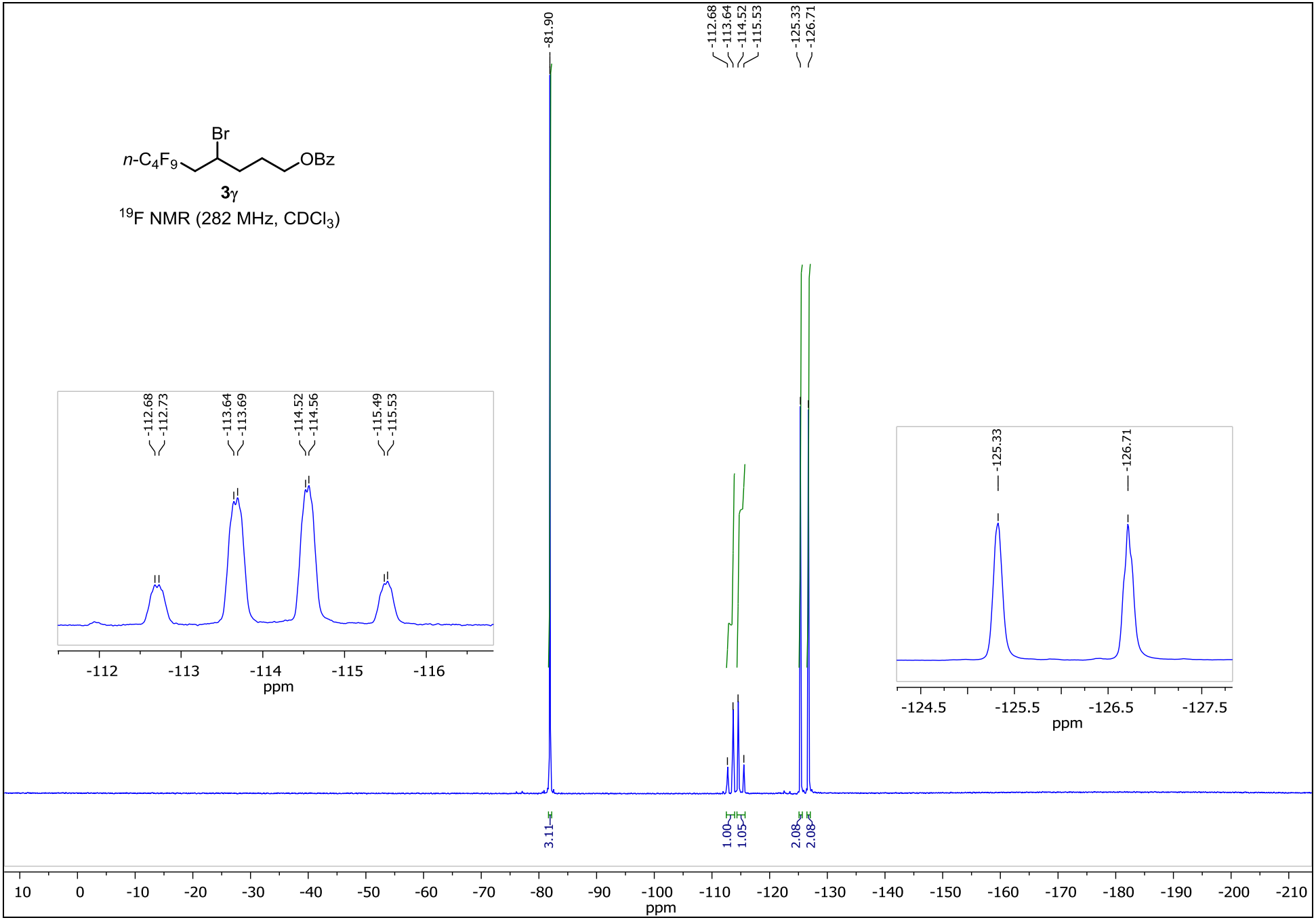

7.36
7.34
7.31
7.27
7.24
4.30
4.26
4.22
3.80
3.76
3.75
3.71
2.98
2.84
2.75
2.66
2.56
2.29
2.25
2.20
0.94
0.12
F
F
Br
TBSO
Ph
3β
1H NMR (300 MHz, CDCl3)
3.80
3.76
3.75
3.71
3.80 3.75 3.70
ppm
2.03
3.18
1.00
2.03
4.25
2.06
9.24
6.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

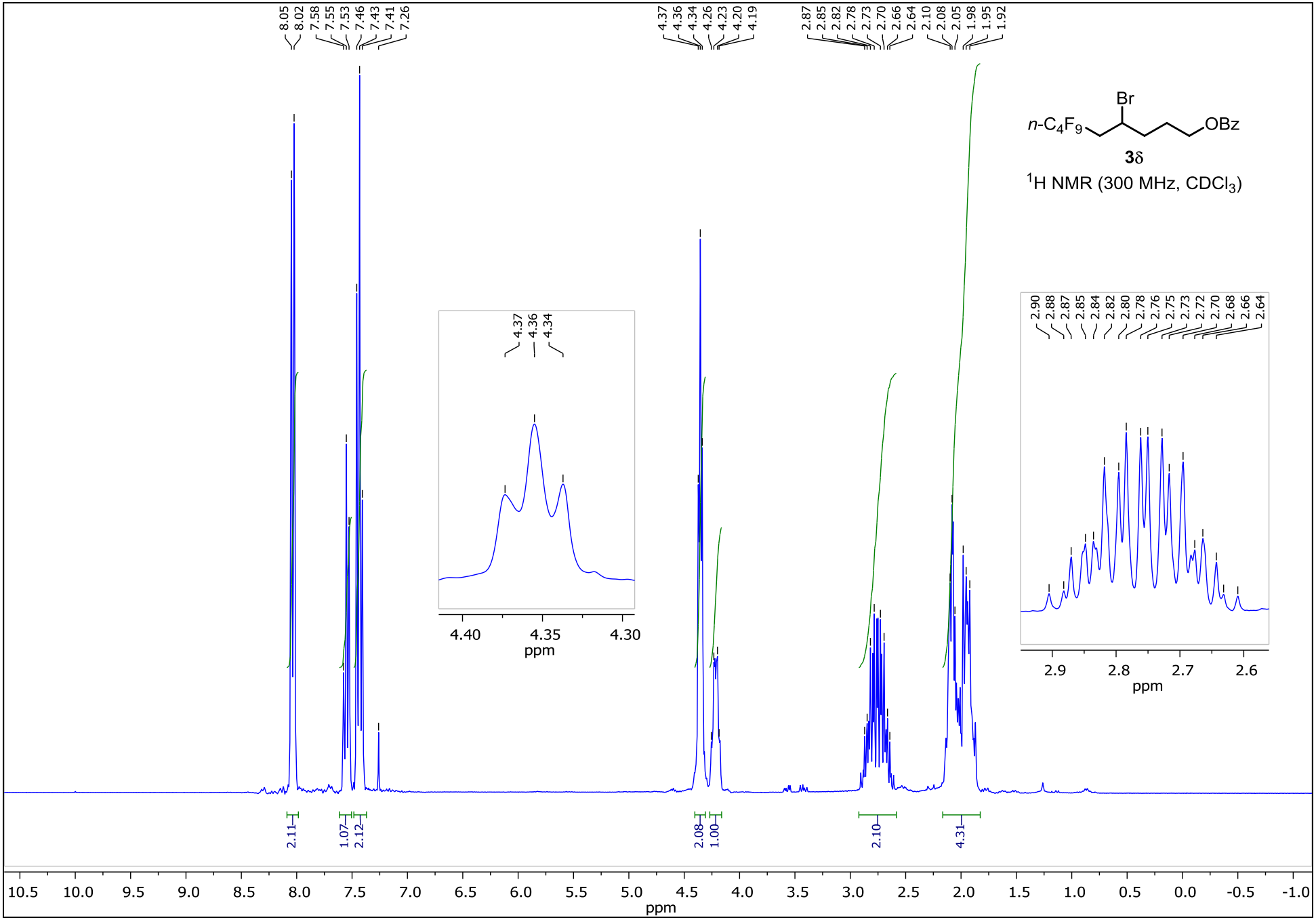

140.76
128.66
126.31
125.54
122.30
119.06
77.58
77.16
76.74
65.18
64.73
64.28
47.22
42.74
41.02
33.67
25.84
18.31
-5.39
TBSO
F
F
Br
Ph
3β
13C{1H} NMR (75 MHz, CDCl3)
65.18
64.73
64.28
65.0
64.5
64.0
ppm
42.74
43.0
42.5
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

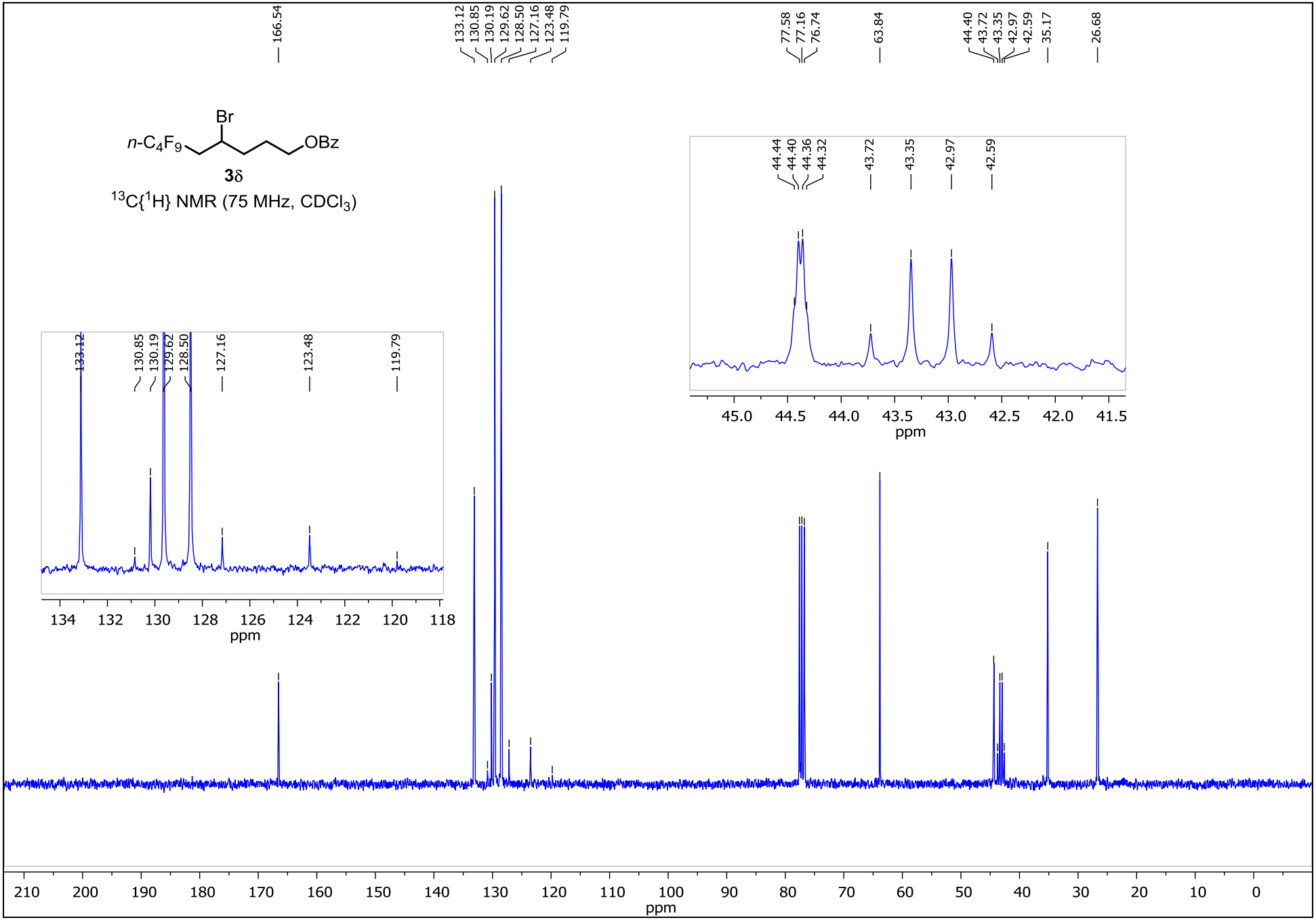

TBSO
F
F
Br
Ph
3β
19F NMR (282 MHz, CDCl3)
-103.25
-103.37
-104.14
-104.26
-106.99
-107.10
-107.88
-107.99
-103.21
-103.25
-103.30
-103.32
-103.37
-103.42
-104.10
-104.14
-104.18
-104.22
-104.26
-104.30
-103.0
-103.5
-104.0
-104.5
ppm
-106.95
-106.99
-107.03
-107.06
-107.10
-107.14
-107.84
-107.88
-107.92
-107.95
-107.99
-108.03
-107.0
-107.5
-108.0
-108.5
ppm
1.00
1.03
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

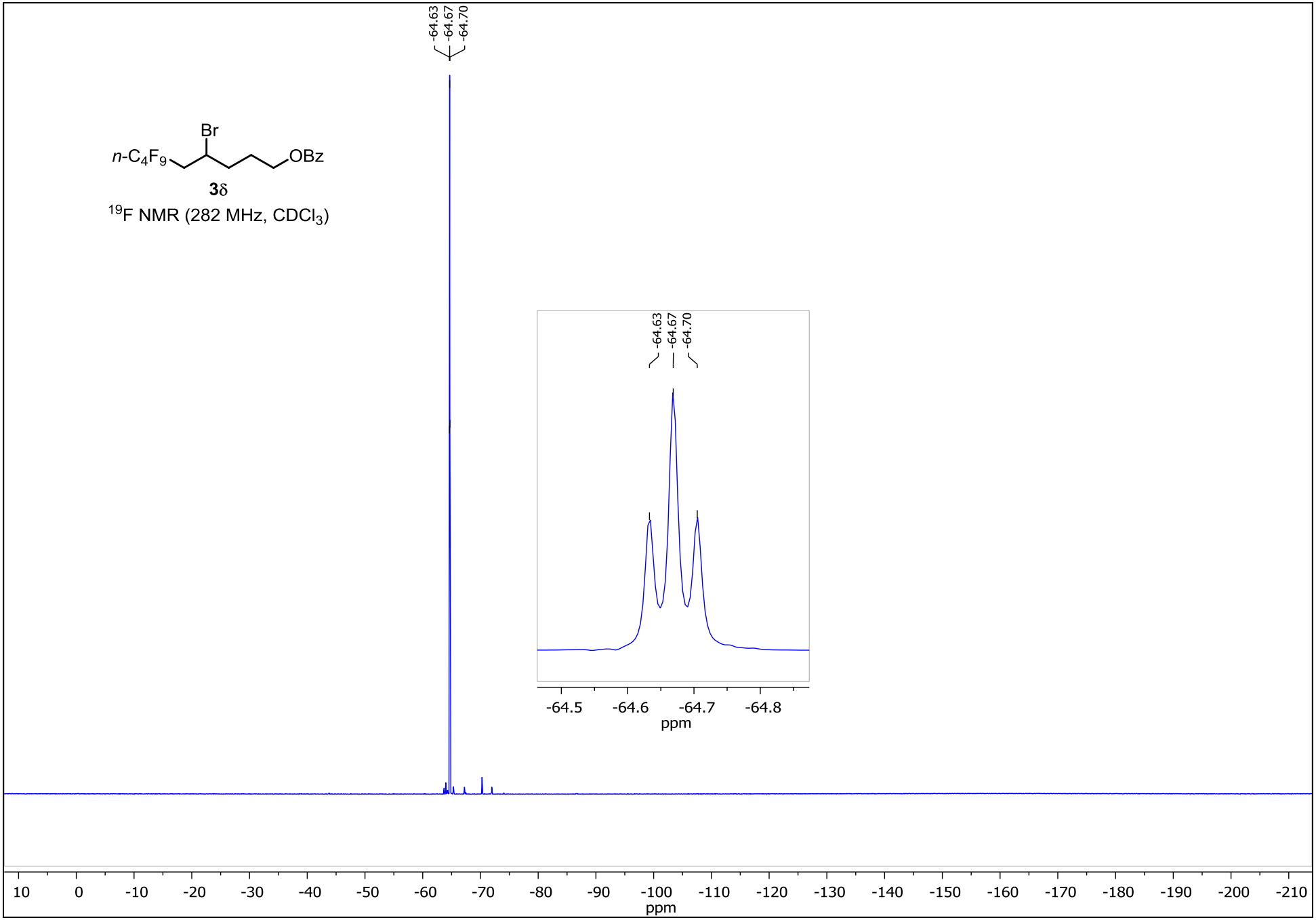

8.05
8.03
7.57
7.54
7.47
7.44
7.42
7.26
4.40
4.38
4.36
2.90
2.81
2.76
2.65
2.16
2.14
2.11
2.04
1.98
1.97
Br
n-C4F9
OBz
3γ
1H NMR (300 MHz, CDCl3)
4.45
4.40
4.35
4.30
ppm
1.98
1.00
1.98
2.96
2.07
4.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

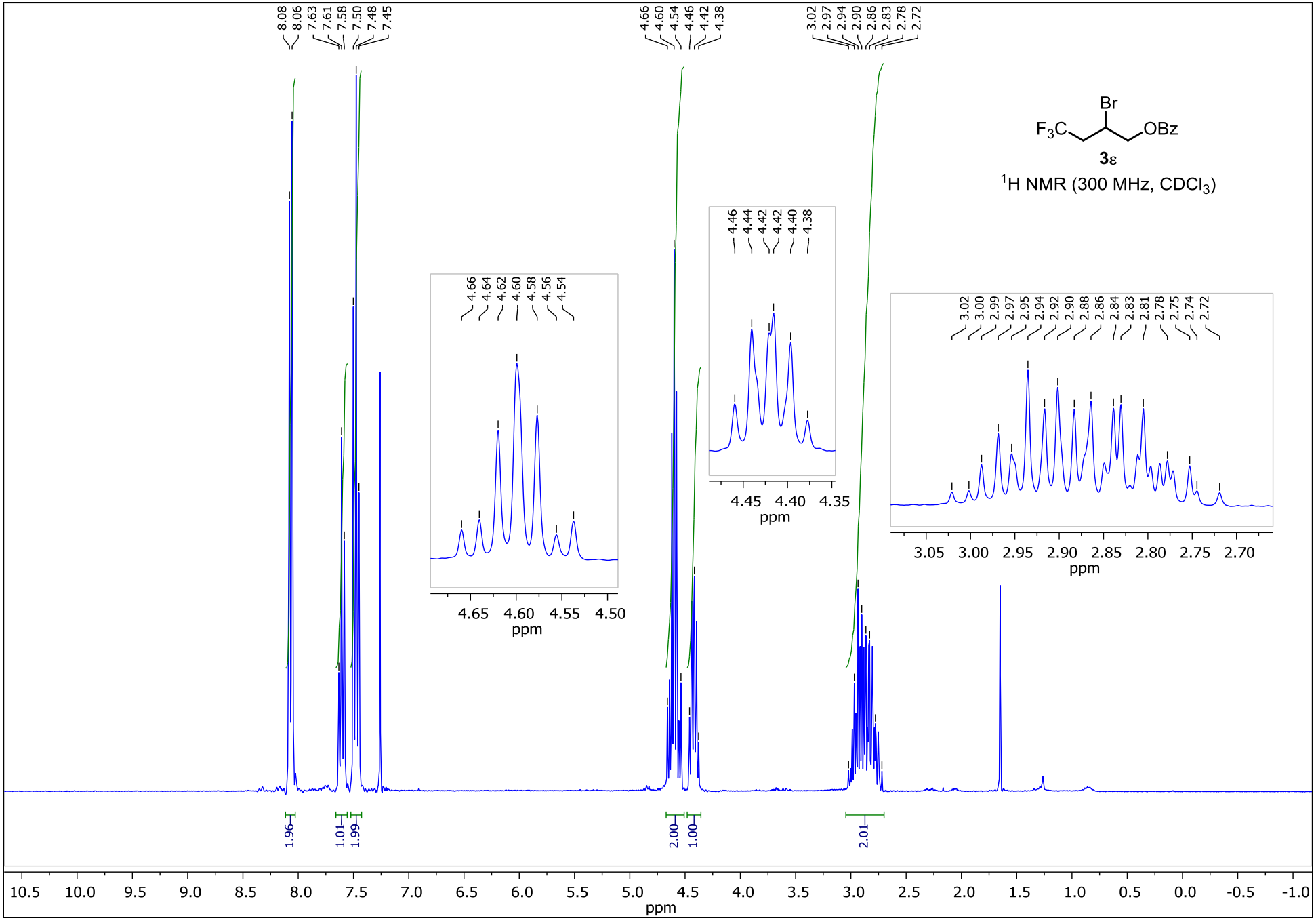

166.61
133.15
130.25
129.67
128.51
120.79
117.38
113.96
110.28
106.76
77.58
77.16
76.74
63.86
43.57
40.23
39.96
39.68
35.85
26.80
Br
n-C4F9
OBz
3γ
13C{1H} NMR (75 MHz, CDCl3)
40.23
39.96
39.68
40.5
40.0
39.5
ppm
122.73
121.21
120.79
120.38
119.79
118.91
117.79
117.38
116.96
115.97
115.09
114.38
113.96
113.40
112.63
111.72
110.75
110.28
109.82
109.07
108.55
108.11
106.76
106.30
105.51
104.99
125
120
115
110
105
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

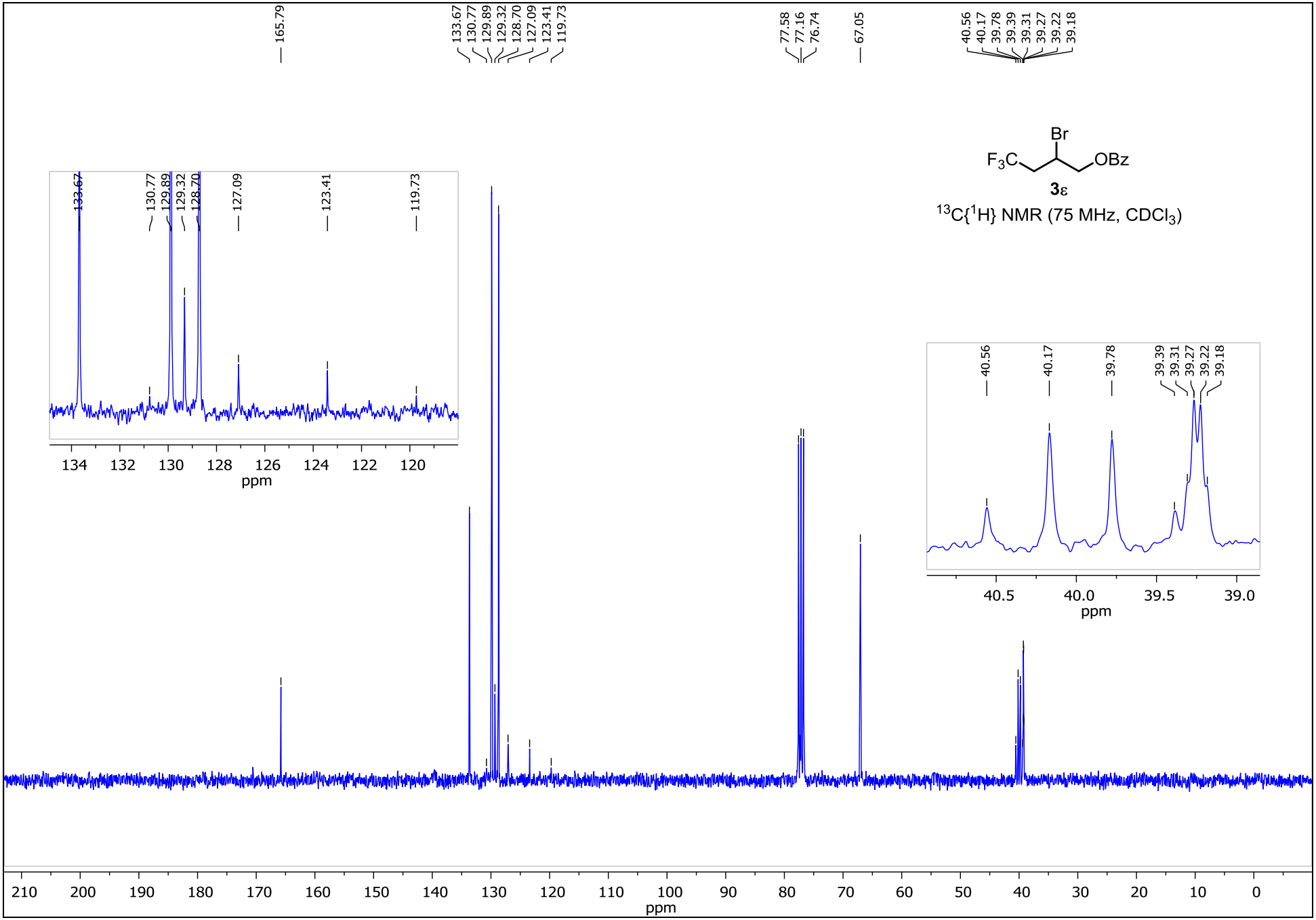

Br
n-C4F9
OBz
3γ
19F NMR (282 MHz, CDCl3)
-81.90
-112.68
-113.64
-114.52
-115.53
-125.33
-126.71
-112.68
-112.73
-113.64
-113.69
-114.52
-114.56
-115.49
-115.53
-112
-113
-114
-115
-116
ppm
-125.33
-126.71
-124.5
-125.5
-126.5
-127.5
ppm
3.11
1.00
1.05
2.08
2.08
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

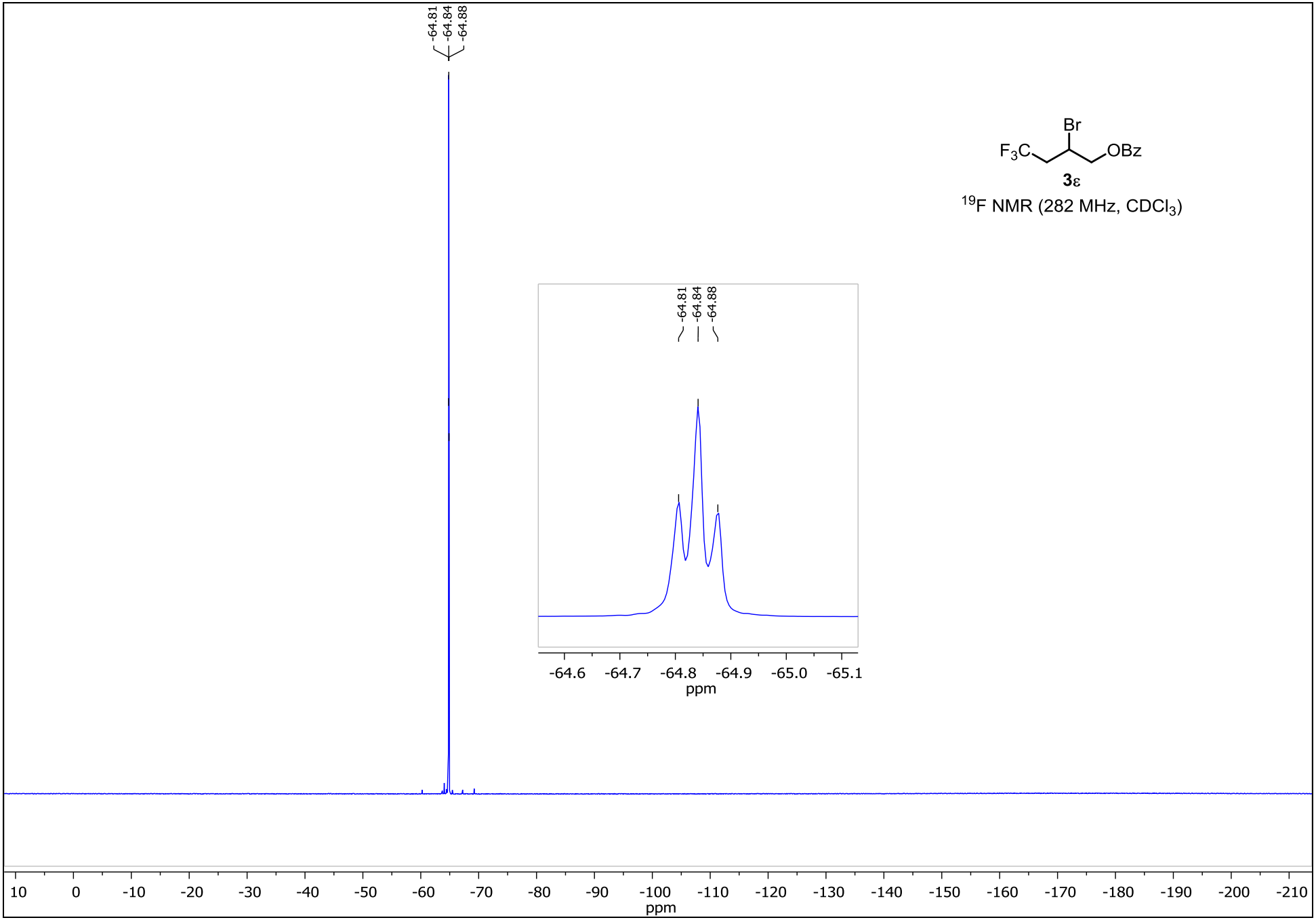

8.05
8.02
7.58
7.55
7.53
7.46
7.43
7.41
7.26
4.37
4.36
4.34
4.26
4.23
4.20
4.19
2.87
2.85
2.82
2.78
2.73
2.70
2.66
2.64
2.10
2.08
2.05
1.98
1.95
1.92
Br
n-C4F9
OBz
3δ
1H NMR (300 MHz, CDCl3)
4.40
4.35
4.30
ppm
2.90
2.88
2.87
2.85
2.84
2.82
2.80
2.78
2.76
2.75
2.73
2.72
2.70
2.68
2.66
2.64
2.9
2.8
2.7
2.6
ppm
2.11
1.07
2.12
2.08
1.00
2.10
4.31
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

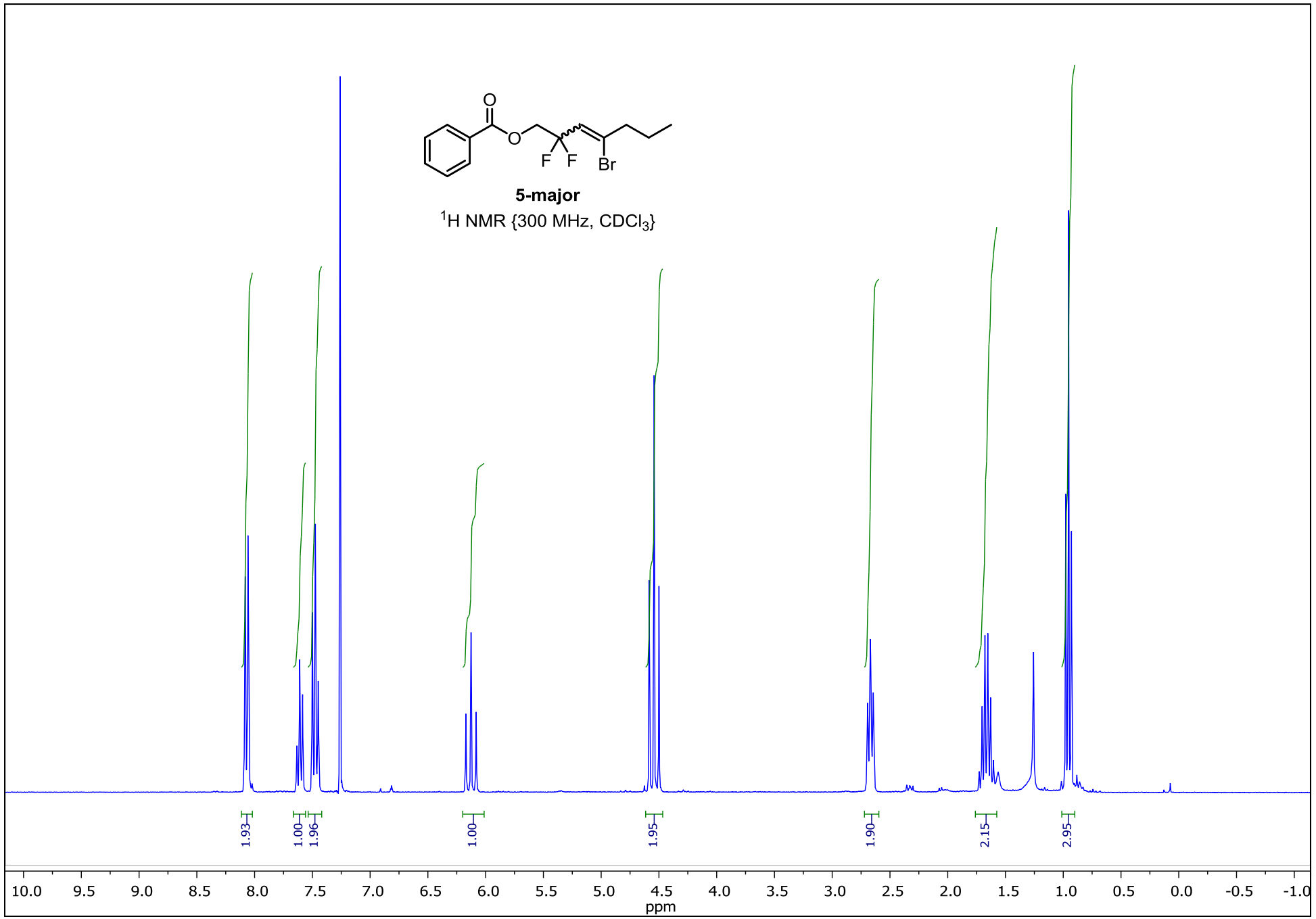

166.54
133.12
130.85
130.19
129.62
128.50
127.16
123.48
119.79
77.58
77.16
76.74
63.84
44.40
43.72
43.35
42.97
42.59
35.17
26.68
Br
n-C4F9
OBz
3δ
13C{1H} NMR (75 MHz, CDCl3)
44.44
44.40
44.36
44.32
43.72
43.35
42.97
42.59
45.0
44.5
44.0
43.5
43.0
42.5
42.0
41.5
ppm
133.12
130.85
130.19
129.62
128.50
127.16
123.48
119.79
134
132
130
128
126
124
122
120
118
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

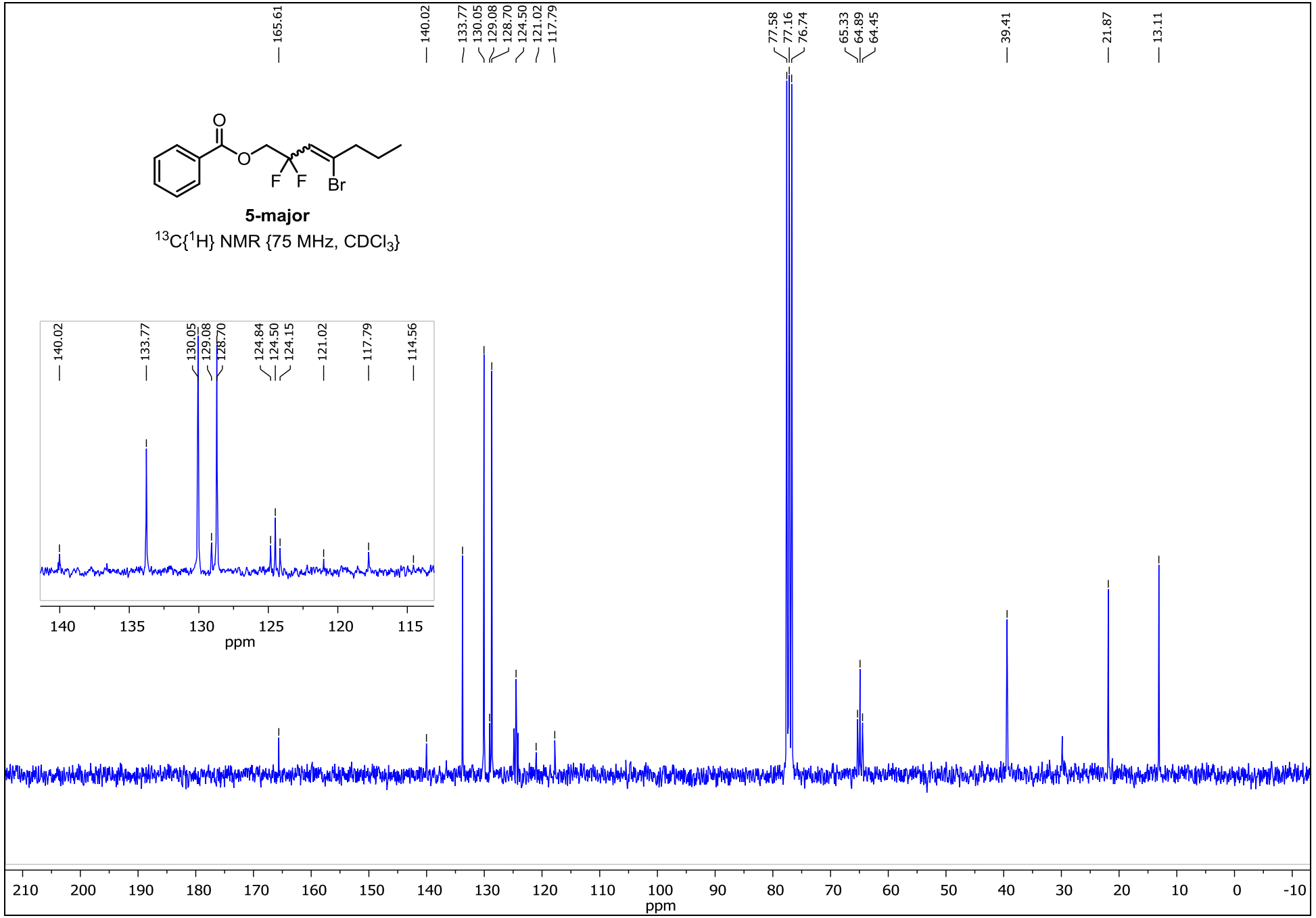

-64.63
-64.67
-64.70
Br
n-C4F9
OBz
3δ
19F NMR (282 MHz, CDCl3)
-64.5
-64.6
-64.7
-64.8
ppm
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

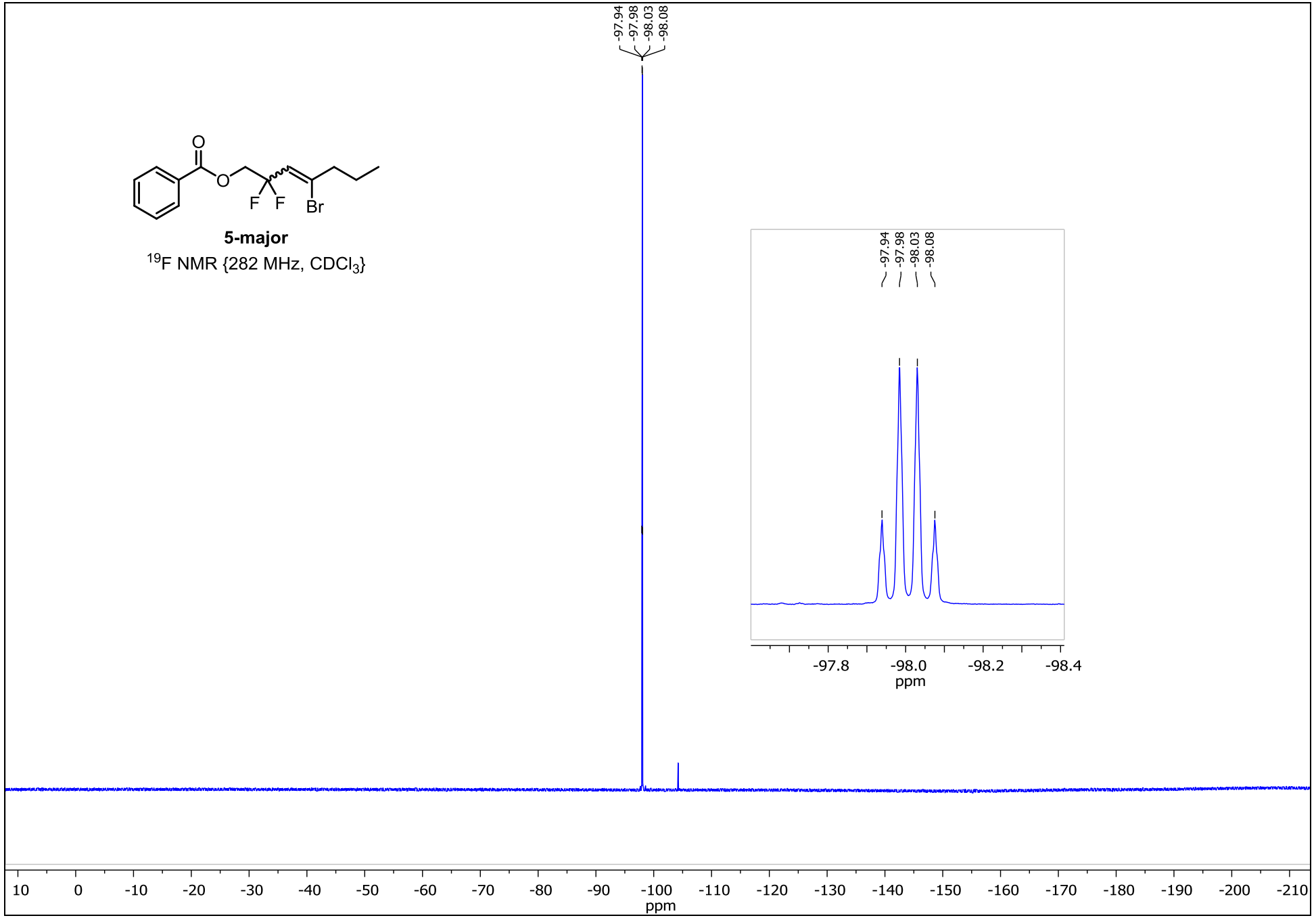

8.08
8.06
7.63
7.61
7.58
7.50
7.48
7.45
4.66
4.60
4.54
4.46
4.42
4.38
3.02
2.97
2.94
2.90
2.86
2.83
2.78
2.72
Br
F3C
OBz
3ε
1H NMR (300 MHz, CDCl3)
4.66
4.64
4.62
4.60
4.58
4.56
4.54
4.65 4.60 4.55 4.50
ppm
4.46
4.44
4.42
4.42
4.40
4.38
4.45 4.40 4.35
ppm
3.02
3.00
2.99
2.97
2.95
2.94
2.92
2.90
2.88
2.86
2.84
2.83
2.81
2.78
2.75
2.74
2.72
3.05 3.00 2.95 2.90 2.85 2.80 2.75 2.70
ppm
1.96
1.01
1.99
2.00
1.00
2.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

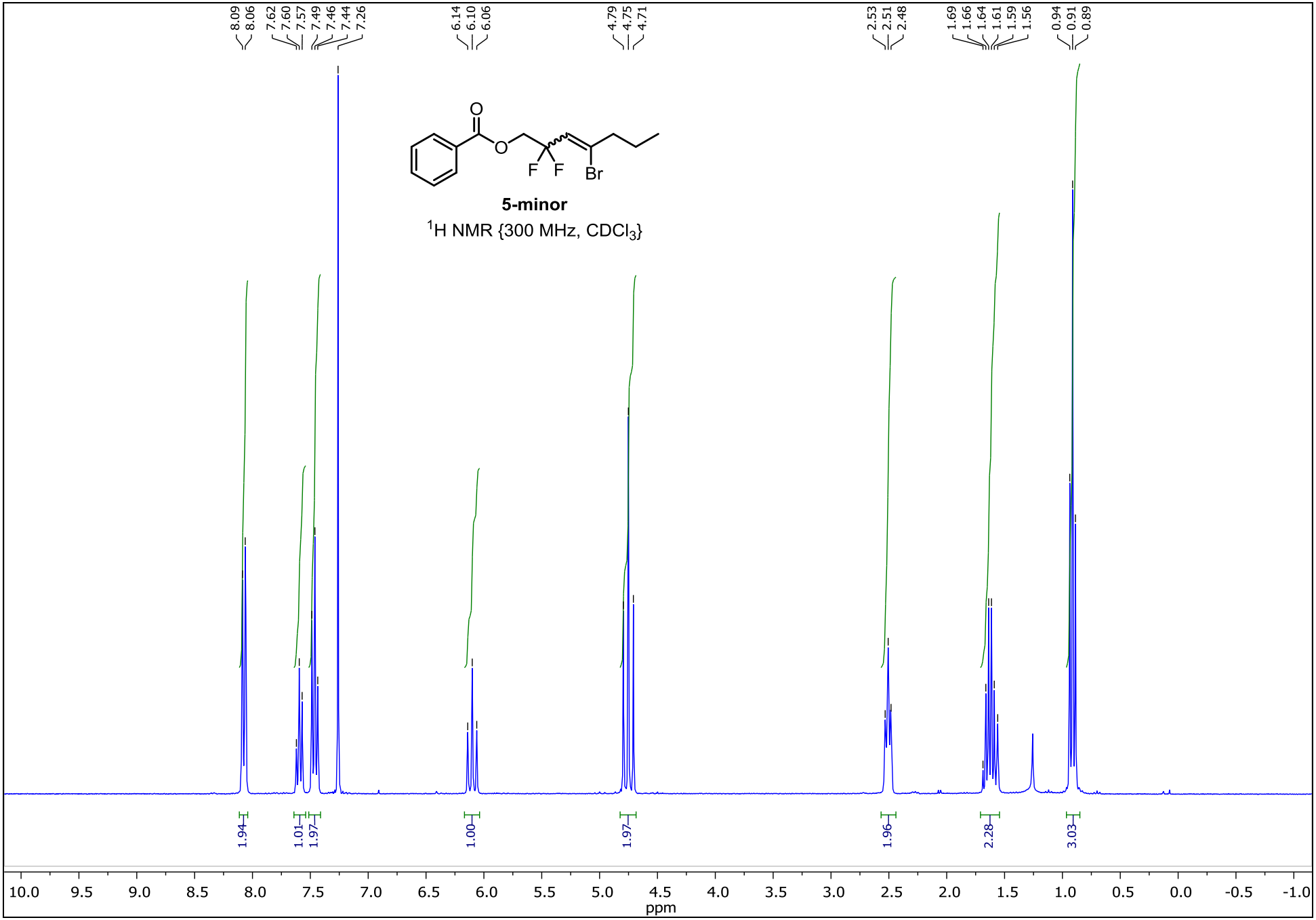

165.79
133.67
130.77
129.89
129.32
128.70
127.09
123.41
119.73
77.58
77.16
76.74
67.05
40.56
40.17
39.78
39.39
39.31
39.27
39.22
39.18
Br
F3C
OBz
3ε
13C{1H} NMR (75 MHz, CDCl3)
ppm
ppm

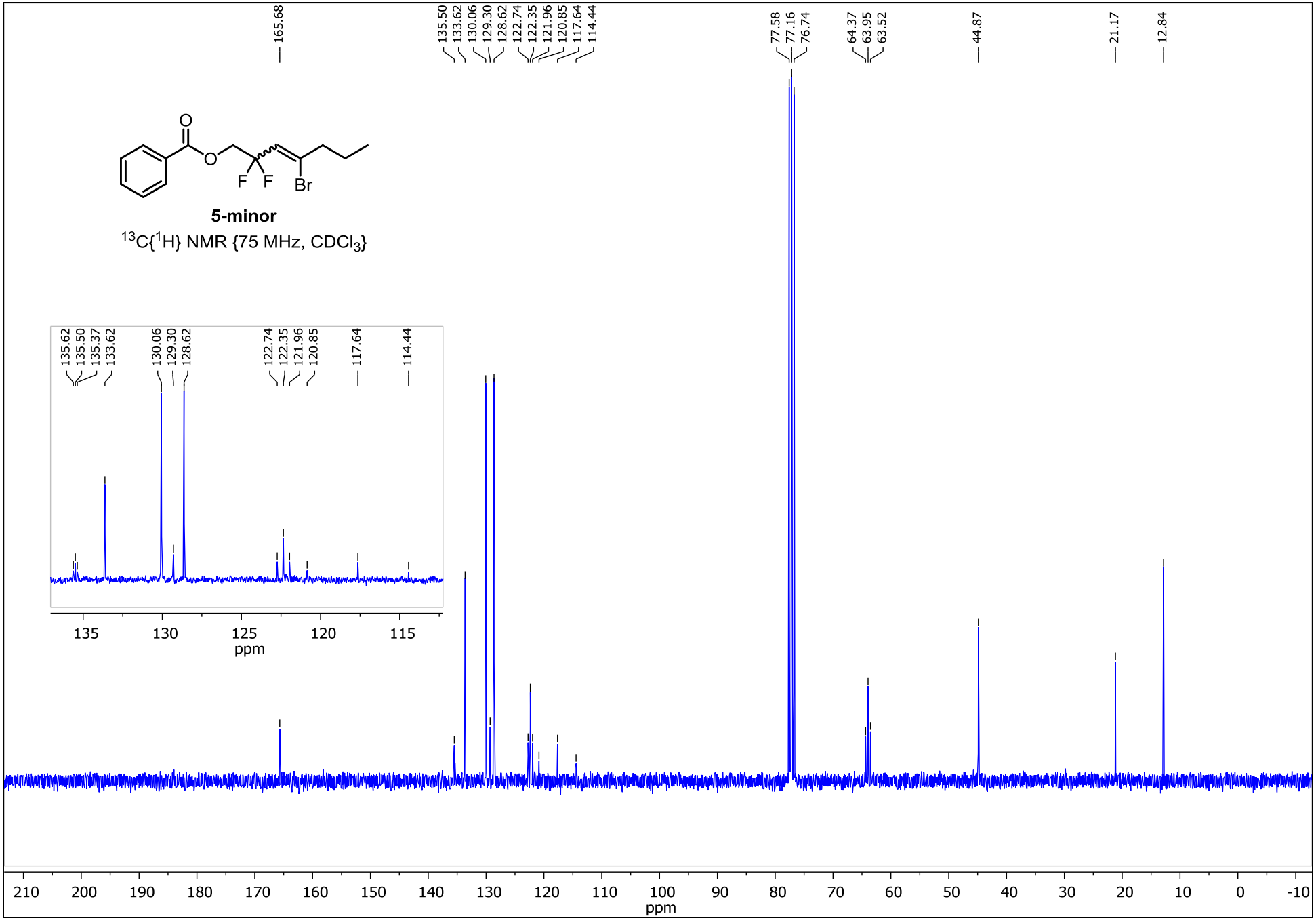

-64.81
-64.84
-64.88
Br
F3C
OBz
3ε
19F NMR (282 MHz, CDCl3)
-64.6
-64.7
-64.8
-64.9
-65.0
-65.1
ppm
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

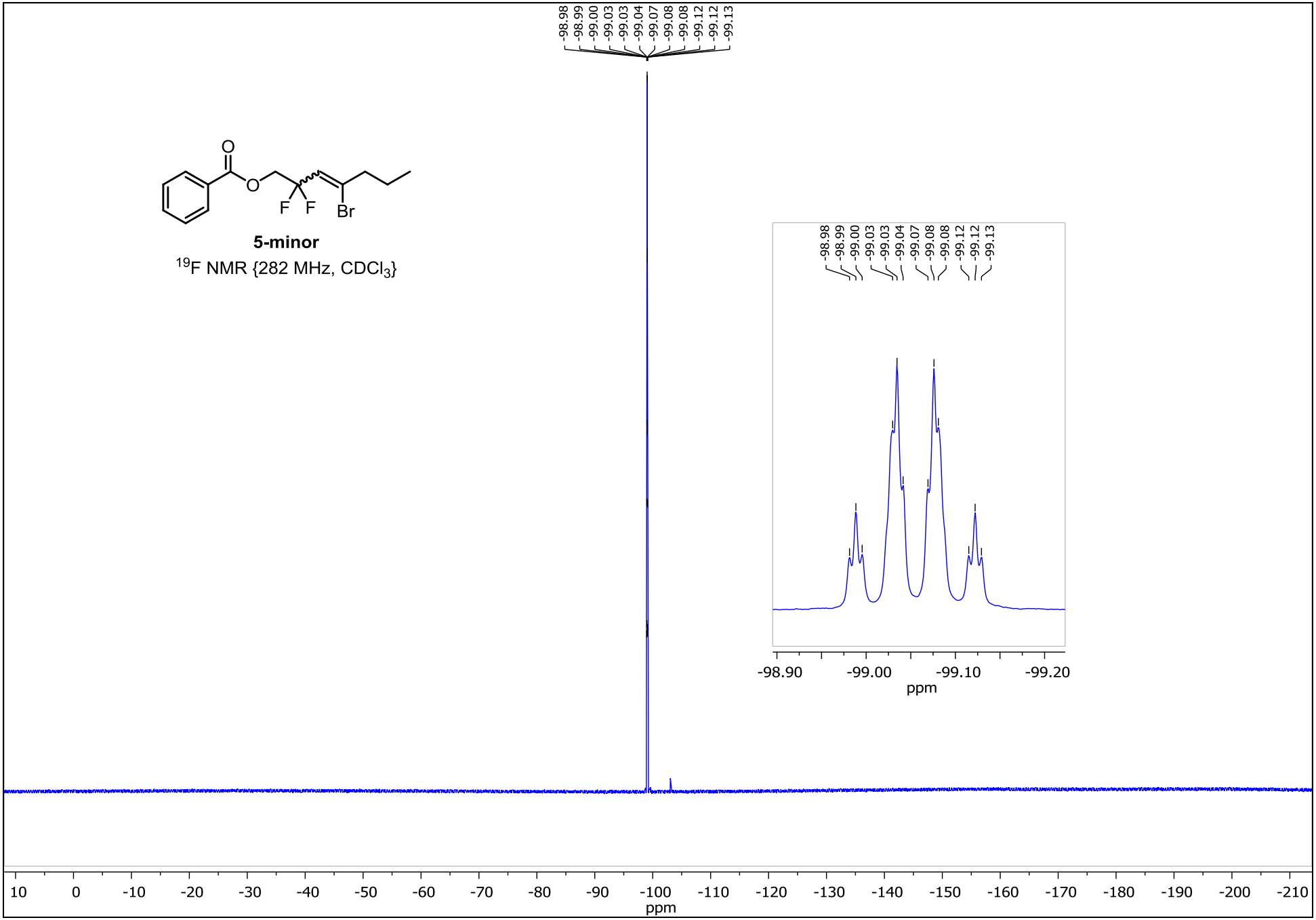

O
O
F
F
Br
5-major
1H NMR {300 MHz, CDCl3}
1.93
1.00
1.96
1.00
1.95
1.90
2.15
2.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

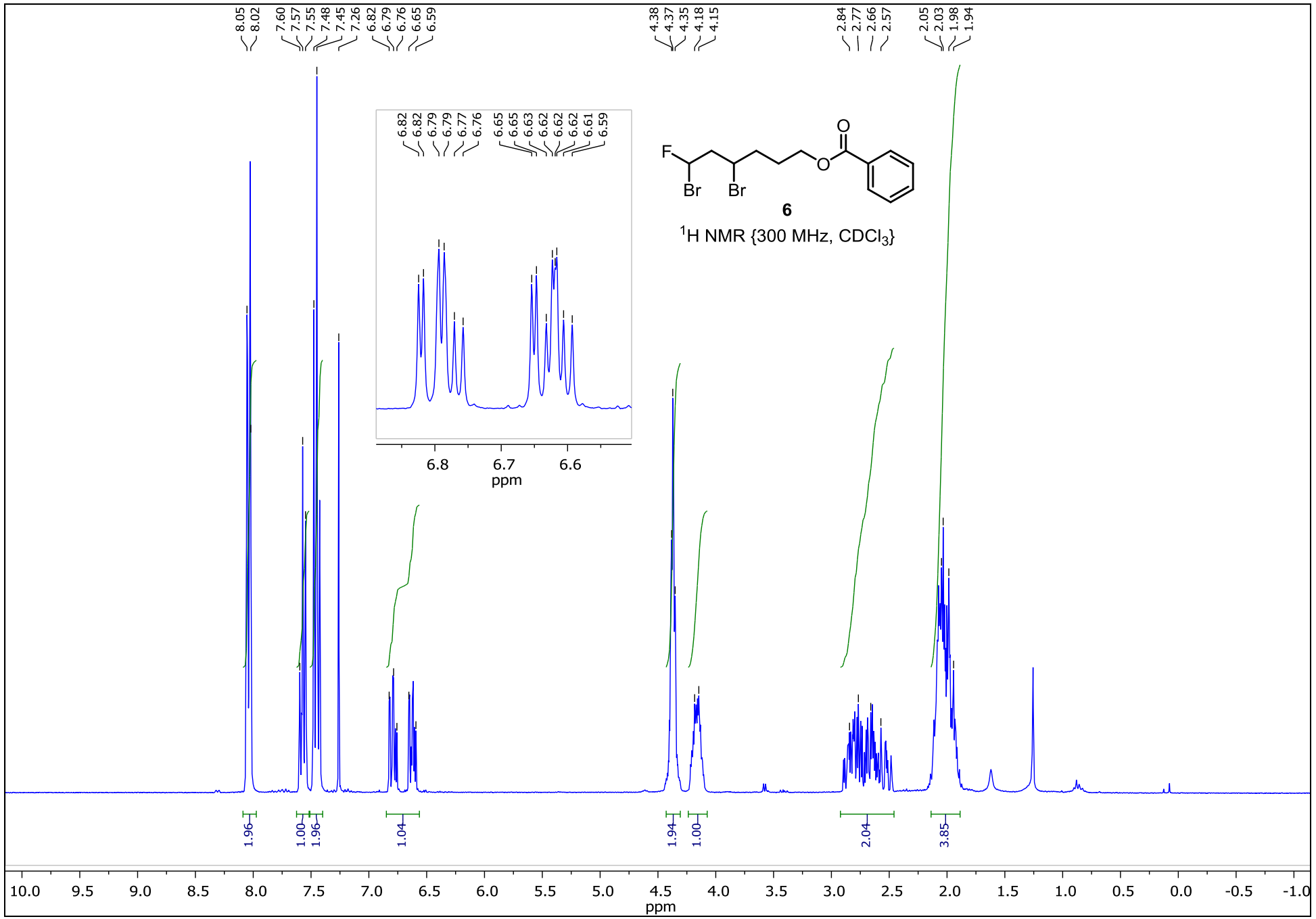

165.61
140.02
133.77
130.05
129.08
128.70
124.50
121.02
117.79
77.58
77.16
76.74
65.33
64.89
64.45
39.41
21.87
13.11
O
O
F
F
Br
5-major
13C{1H} NMR {75 MHz, CDCl3}
140.02
133.77
130.05
129.08
128.70
124.84
124.50
124.15
121.02
117.79
114.56
140
135
130
125
120
115
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

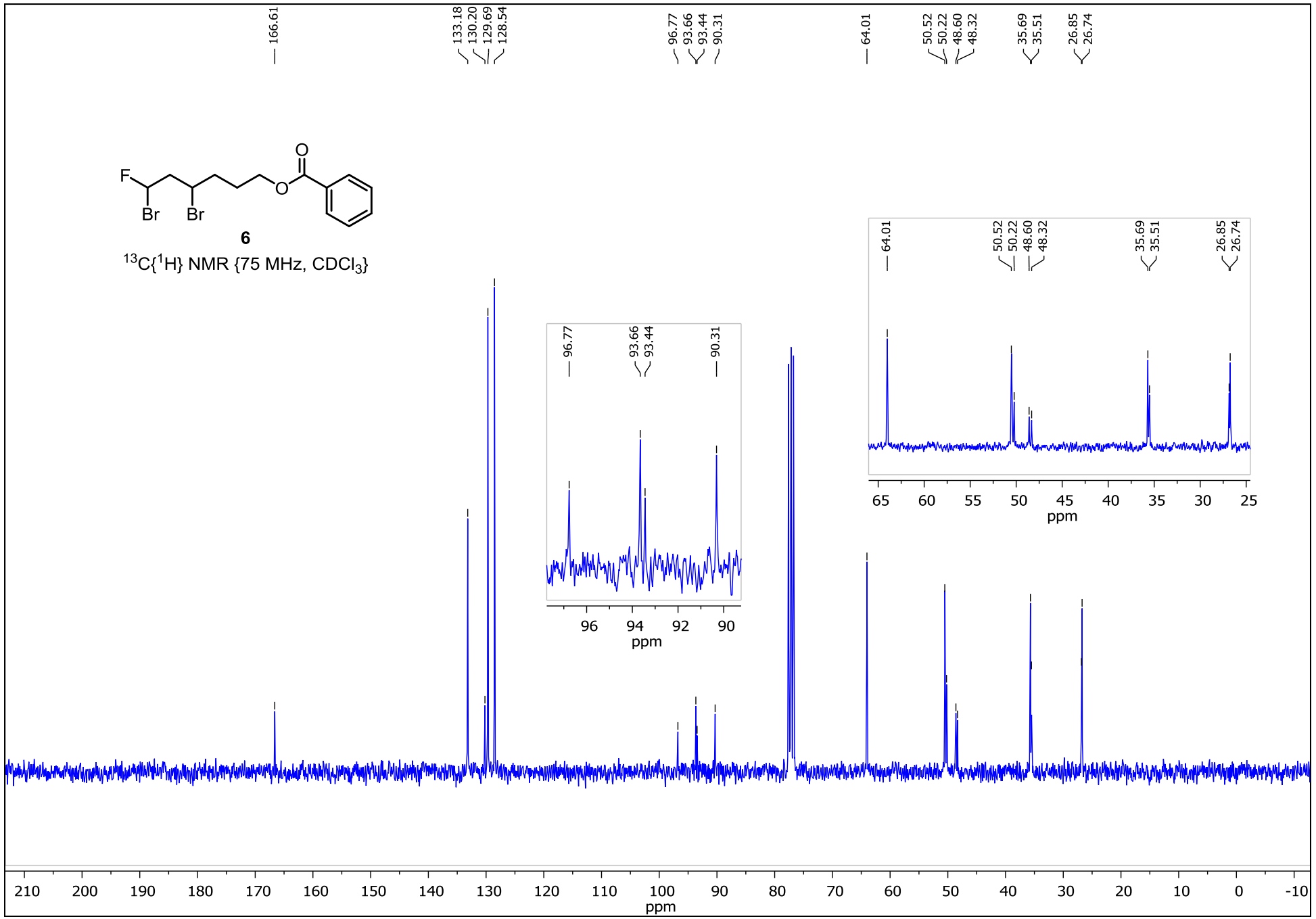

-97.94
-97.98
-98.03
-98.08
O
O
F
F
Br
5-major
19F NMR {282 MHz, CDCl3}
-97.94
-97.98
-98.03
-98.08
-97.8
-98.0
-98.2
-98.4
ppm
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

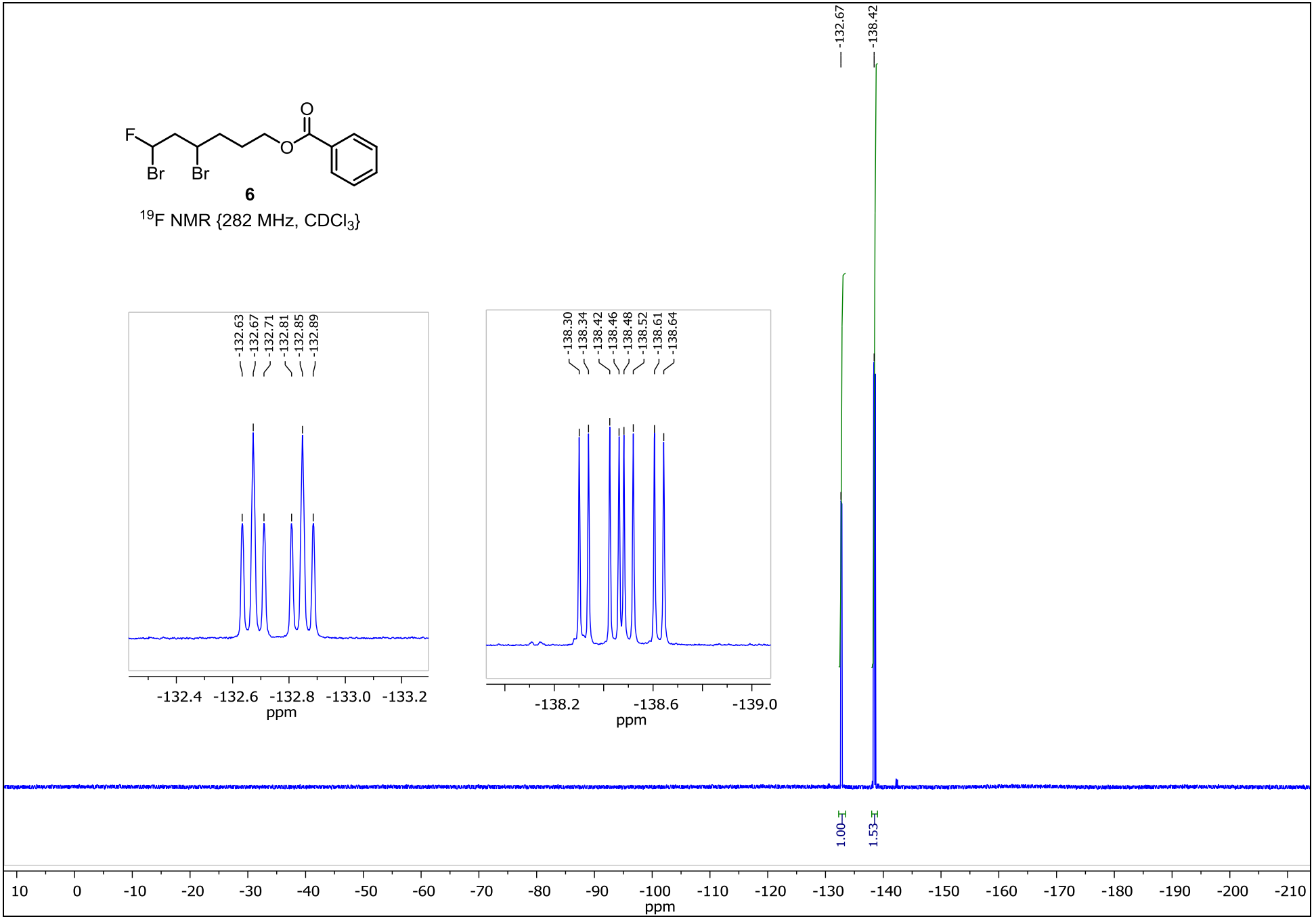

8.09
8.06
7.62
7.60
7.57
7.49
7.46
7.44
7.26
6.14
6.10
6.06
4.79
4.75
4.71
2.53
2.51
2.48
1.69
1.66
1.64
1.61
1.59
1.56
0.94
0.91
0.89
O
O
F
F
Br
5-minor
1H NMR {300 MHz, CDCl3}
1.94
1.01
1.97
1.00
1.97
1.96
2.28
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

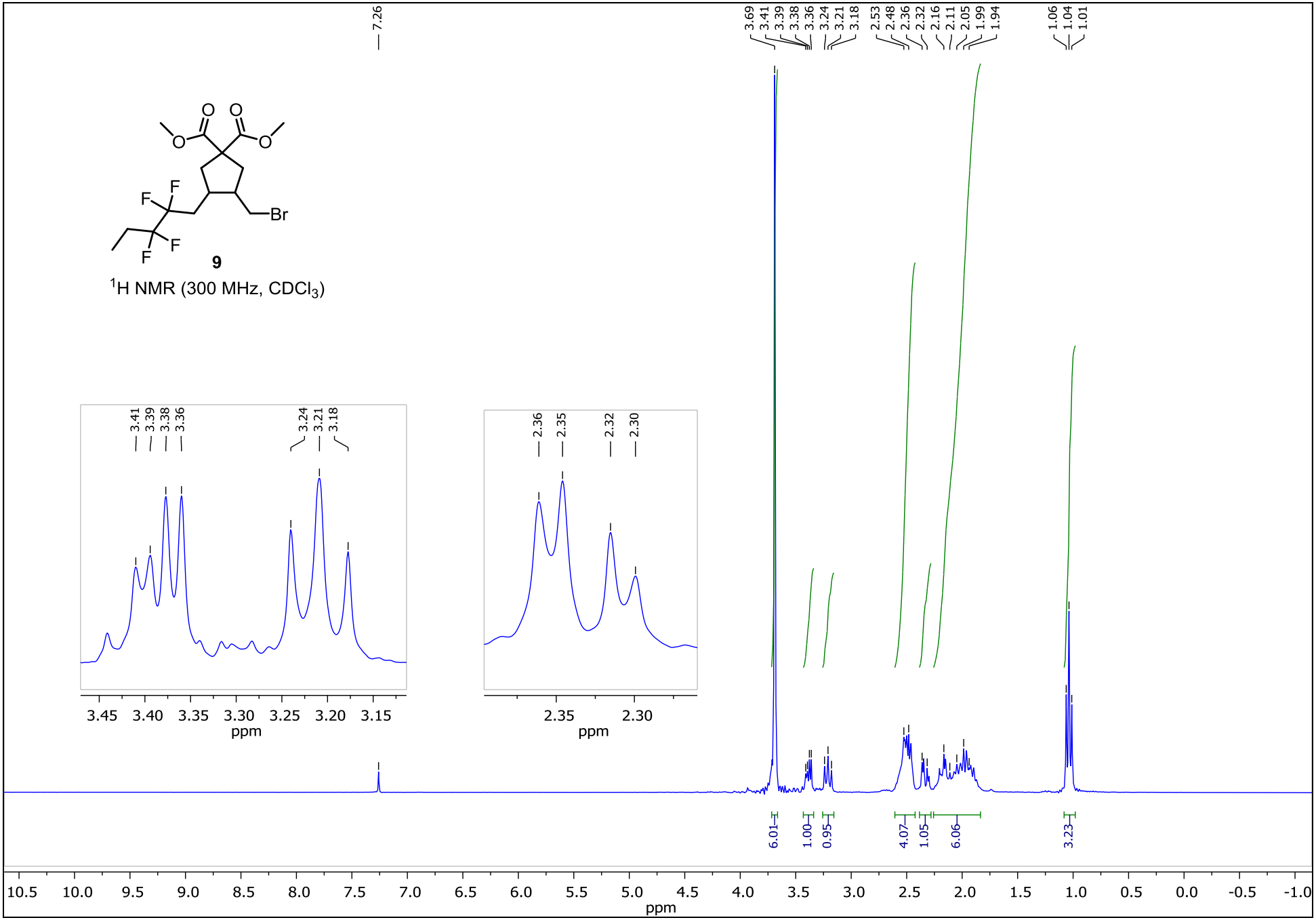

165.68
135.50
133.62
130.06
129.30
128.62
122.74
122.35
121.96
120.85
117.64
114.44
77.58
77.16
76.74
64.37
63.95
63.52
44.87
21.17
12.84
O
O
F
F
Br
5-minor
13C{1H} NMR {75 MHz, CDCl3}
135.62
135.50
135.37
133.62
130.06
129.30
128.62
122.74
122.35
121.96
120.85
117.64
114.44
135
130
125
120
115
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

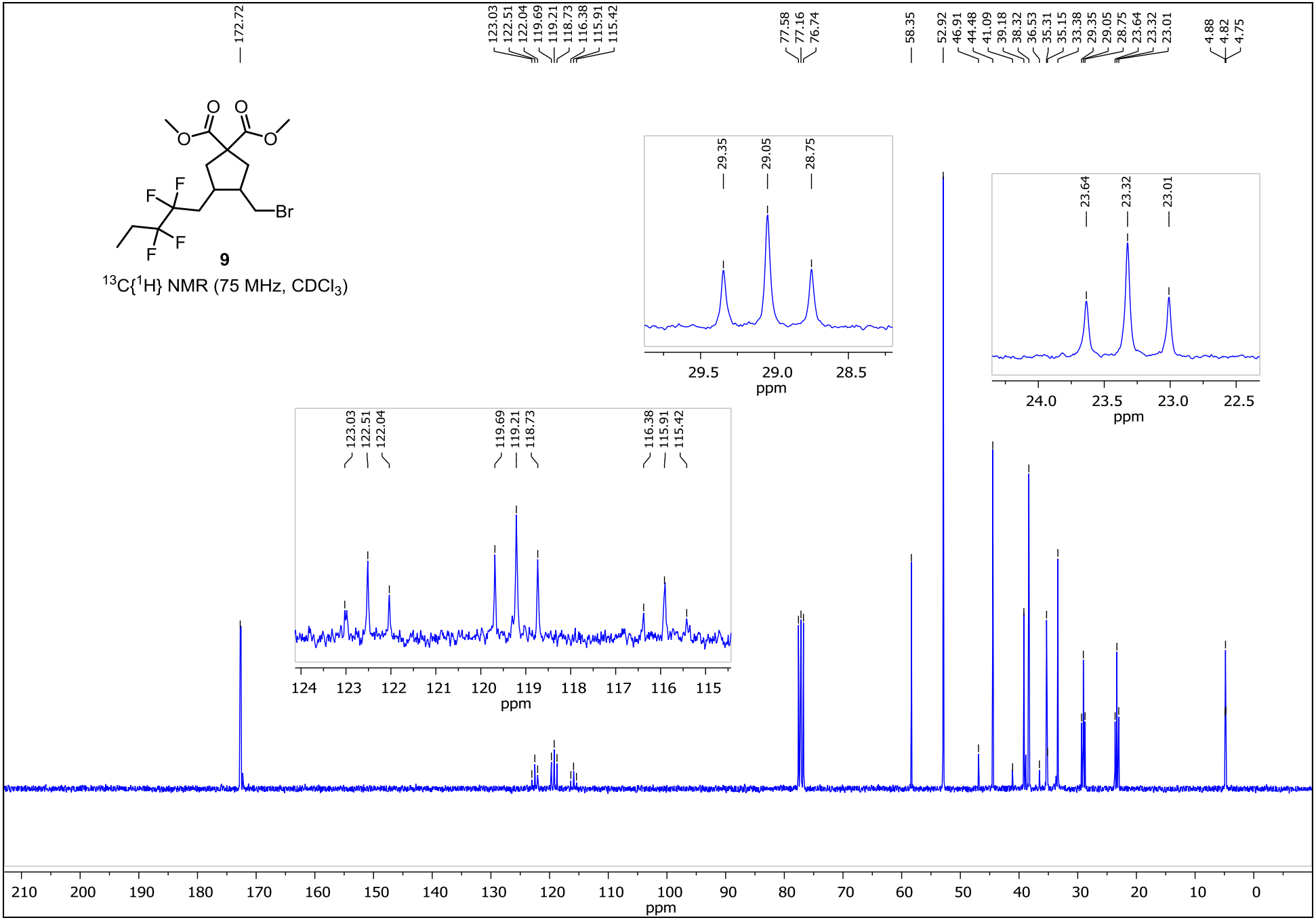

-98.98
-98.99
-99.00
-99.03
-99.03
-99.04
-99.07
-99.08
-99.08
-99.12
-99.12
-99.13
O
O
F
F
Br
5-minor
19F NMR {282 MHz, CDCl3}
-98.90
-99.00
-99.10
-99.20
ppm
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

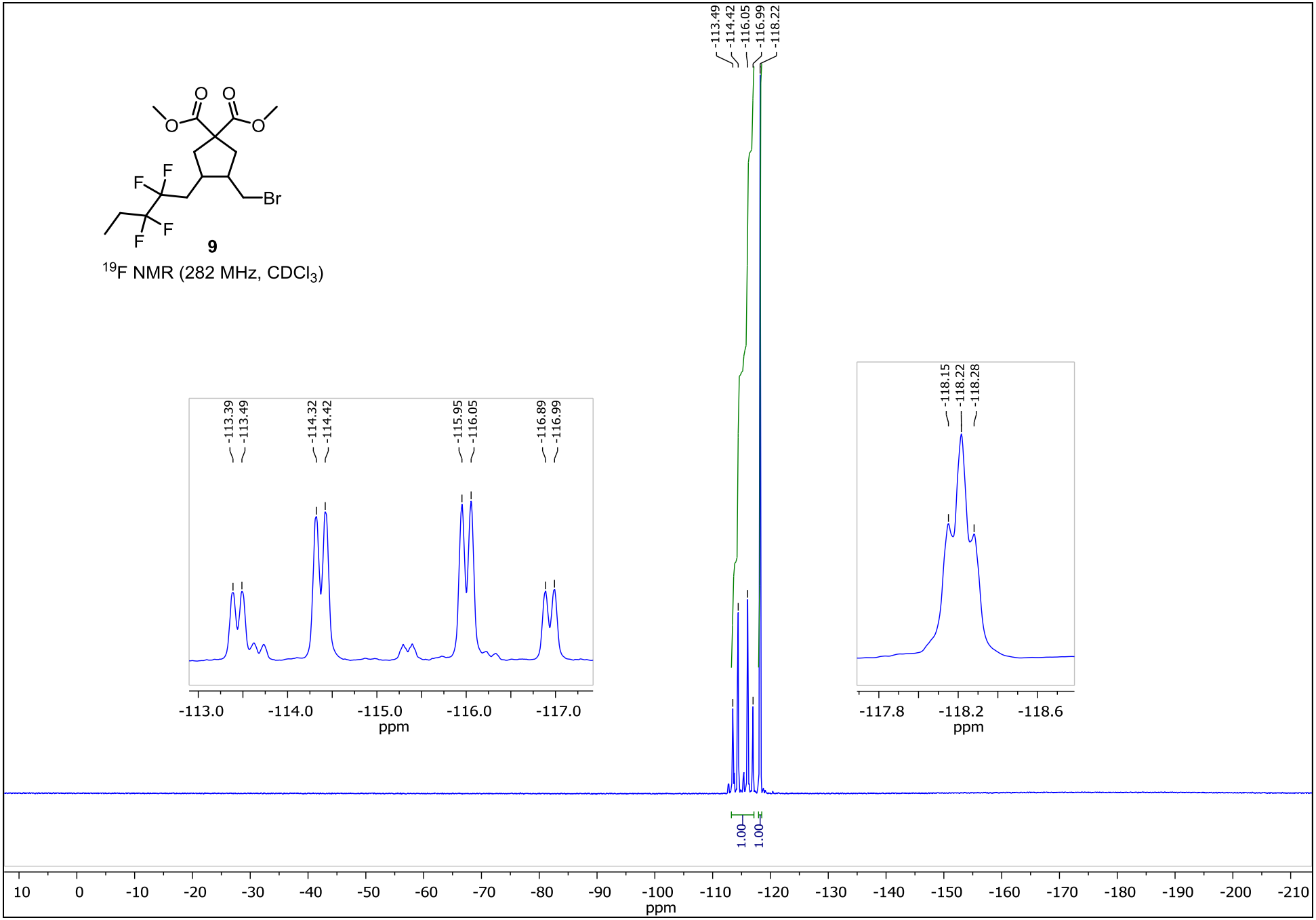

8.05
8.02
7.60
7.57
7.55
7.48
7.45
7.26
6.82
6.79
6.76
6.65
6.59
4.38
4.37
4.35
4.18
4.15
2.84
2.77
2.66
2.57
2.05
2.03
1.98
1.94
6.82
6.82
6.79
6.79
6.77
6.76
6.65
6.65
6.63
6.62
6.62
6.62
6.61
6.59
6.8
6.7
6.6
ppm
F
Br
Br
O
O
6
1H NMR {300 MHz, CDCl3}
1.96
1.00
1.96
1.04
1.94
1.00
2.04
3.85
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm


166.61
133.18
130.20
129.69
128.54
96.77
93.66
93.44
90.31
64.01
50.52
50.22
48.60
48.32
35.69
35.51
26.85
26.74
F
Br
Br
O
O
6
$^{13}C\{^{1}H\}$ NMR {75 MHz, $CDCl_3$}
ppm


F
Br
Br
O
O
6
19F NMR {282 MHz, CDCl3}
-132.63
-132.67
-132.71
-132.81
-132.85
-132.89
-132.4
-132.6
-132.8
-133.0
-133.2
ppm
-138.30
-138.34
-138.42
-138.46
-138.48
-138.52
-138.61
-138.64
-138.2
-138.6
-139.0
ppm
-132.67
-138.42
1.00
1.53
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm


7.26
3.69
3.41
3.39
3.38
3.36
3.24
3.21
3.18
2.53
2.48
2.36
2.32
2.16
2.11
2.05
1.99
1.94
1.06
1.04
1.01
O
O
O
O
F
F
F
F
Br
9
1H NMR (300 MHz, CDCl3)
3.41
3.39
3.38
3.36
3.24
3.21
3.18
3.45 3.40 3.35 3.30 3.25 3.20 3.15
ppm
2.36
2.35
2.32
2.30
2.35 2.30
ppm
6.01
1.00
0.95
4.07
1.05
6.06
3.23
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


172.72
123.03
122.51
122.04
119.69
119.21
118.73
116.38
115.91
115.42
77.58
77.16
76.74
58.35
52.92
46.91
44.48
41.09
39.18
38.32
36.53
35.31
35.15
33.38
29.35
29.05
28.75
23.64
23.32
23.01
4.88
4.82
4.75
O
O
O
O
F
F
F
F
Br
9
13C{1H} NMR (75 MHz, CDCl3)
ppm



9

^{19}F NMR (282 MHz, $CDCl_3$)