Supporting Information

Aminals as powerful XAT-reagents: activation of fluorinated alkyl chlorides

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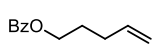
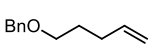
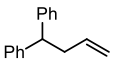
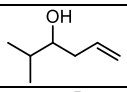
General methods

All reactions were performed under an argon atmosphere. Acetonitrile was distilled from CaH_2 and stored over MS 3Å. Column chromatography was carried out employing silica gel (230−400 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or acidic aq. $KMnO_4$ solution. High resolution mass-spectra (HRMS) were measured using electrospray ionization (ESI) and 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 455 nm COB LED matrix Hontiey (29-32V, 3000mA, 100W; operated at 30W) 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.[1]

Starting materials

All commercially available reagents were purchased from Acros Organics, ABCR or P&M Invest. Alkenes were distilled prior to use. Reagents shown below were synthesized according to literature procedures: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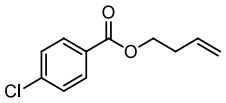	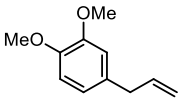	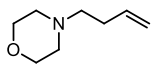	
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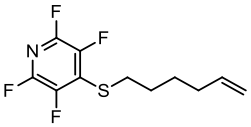	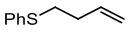	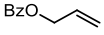	
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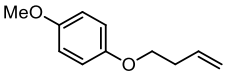			
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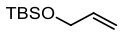	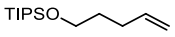	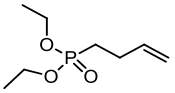	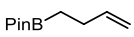	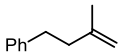
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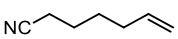	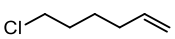	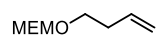	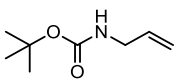	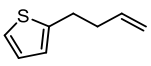
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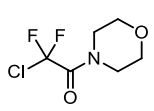
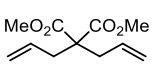
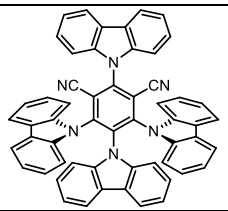
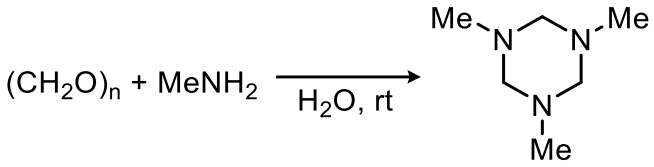
				
2b[25]	**1z**[26]	4CzIPN[27]		

1,3,5-Trimethyl-1,3,5-triazinane (N1).[28]



In a round-bottom flask, methylamine (380 mL of 38% aqueous solution, 3.49 mol) and acetic acid (0.1 mL) were added. Then, paraform (104.6 g, 3.49 mol) was added partially at such a rate to maintain internal temperature below 35 °C. The mixture was stirred overnight at room temperature, then it was diluted with methyl *tert*-butyl ether (150 mL). Solid sodium hydroxide (100 g) was gradually added with vigorous stirring. The organic layer was separated, and the aqueous phase was extracted with methyl *tert*-butyl ether (3×70 mL). The combined organic layers were dried with solid NaOH, filtered. The volatile components were evaporated under atmospheric pressure. The solvent was distilled off under ambient pressure, and the residue was distilled under reduced pressure, the fraction boiling at 44-49 °C (11 Torr) was collected. Yield 128 g (86%). Colorless liquid.

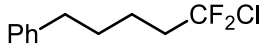
^{1}H NMR (300 MHz, Chloroform-*d*) δ 2.94 (br s, 6H), 2.03 (s, 9H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 76.9, 39.9.

Hydrofluoroalkylation of alkenes with Freon-12 (General procedure A).

A test tube was evacuated and filled with argon. Then, acetonitrile (1 mL), triazinane **N1** (129 g, 1 mmol), alkene (0.5 mmol), 2-methylpropane-2-thiol (6 μL, 0.05 mmol), and 4CzIPN (2 mg, 0.0025 mmol) were added. The mixture was cooled to –40 °C (acetone/liq. nitrogen) and gaseous dichlorodifluoromethane (**2a**) (ca. 36 mL, 1.5 mmol) was gradually injected into the frozen mixture via a syringe (the syringe needle was inserted into the reaction mixture). The tube was sealed with a screw-cap, the cooling bath was removed, and the mixture was irradiated with a strip of blue light (455 nm, 10W) for 5 hours. The mixture was quenched with water (5 mL) and extracted with hexane (3×1.5mL). 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.

(5-Chloro-5,5-difluoropentyl)benzene (3a)



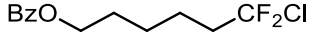
Yield 101 mg (92%). Colorless oil. Chromatography: hexanes.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.42 – 7.20 (m, 5H), 2.72 (t, *J* = 7.0 Hz, 2H), 2.48 – 2.30 (m, 2H), 1.87 – 1.64 (m, 4H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 141.9, 130.1 (t, *J* = 291.8 Hz), 128.6, 128.5, 126.1, 41.9 (t, *J* = 23.9 Hz), 35.7, 30.5, 23.1 (t, *J* = 3.0 Hz).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -51.29 (t, *J* = 13.1 Hz).

6-Chloro-6,6-difluorohexyl benzoate (3b)



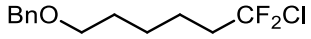
Yield 116 mg (84%). Colorless oil. Chromatography: hexanes/EtOAc, 20/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 7.4 Hz, 2H), 7.61 – 7.48 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 4.33 (t, *J* = 6.5 Hz, 2H), 2.41 – 2.21 (m, 2H), 1.88 – 1.72 (m, 2H), 1.77 – 1.61 (m, 2H), 1.61 – 1.45 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 166.6, 133.0, 130.4, 130.0 (t, *J* = 291.7 Hz), 129.6, 128.4, 64.6, 41.8 (t, *J* = 23.9 Hz), 28.5, 25.2, 23.1 (t, *J* = 3.1 Hz).

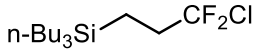
^{19}F NMR (282 MHz, Chloroform-*d*) δ -51.36 (t, *J* = 12.9 Hz, 2F).
HRMS (ESI): calcd for $C_{13}H_{15}{}^{35}ClF_2O_2Na$ (M+Na) 299.0621, found 299.0620.

(((6-Chloro-6,6-difluorohexyl)oxy)methyl)benzene (3c)



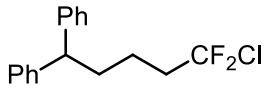
Yield 95 mg (72%). Colorless oil. Chromatography: hexanes/EtOAc, 30/1.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.30 – 7.17 (m, 5H), 4.43 (s, 2H), 3.40 (t, *J* = 6.3 Hz, 2H), 2.30 – 2.10 (m, 2H), 1.70 – 1.48 (m, 4H), 1.47 – 1.30 (m, 2H).
^{13}C{^{1}H} NMR (75 MHz, Chloroform-d) δ 138.6, 130.1 (t, *J* = 291.7 Hz), 128.5, 127.70, 127.65, 73.0, 70.0, 41.9 (t, J = 23.8 Hz), 29.5, 25.4, 23.2 (t, *J* = 3.0 Hz).
^{19}F NMR (282 MHz, Chloroform-*d*) δ -51.26 (t, *J* = 13.2 Hz, 2F).
HRMS (ESI): calcd for $C_{13}H_{17}{}^{35}ClF_2ONa$ (M+Na) 285.0828, found 285.0832.

Tributyl(3-chloro-3,3-difluoropropyl)silane (3d)



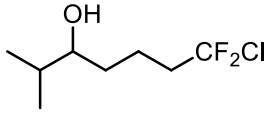
Modified General procedure A: amounts of the reagents, **N1** (194 mg, 1.5 mmol), **2a** (48 mL, 2 mmol) and 4CzIPN (4 mg, 0.005 mmol).
Yield 144 mg (92%). Colorless oil. Chromatography: hexanes.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 2.32 – 2.11 (m, 2H), 1.43 – 1.19 (m, 12H), 0.90 (t, *J* = 6.9 Hz, 9H), 0.86 – 0.75 (m, 2H), 0.64 – 0.49 (m, 6H).
^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 131.4 (t, *J* = 292.3 Hz), 37.4 (t, *J* = 25.0 Hz), 26.9, 26.1, 13.9, 12.0, 5.9.
^{19}F NMR (282 MHz, Chloroform-*d*) δ -53.77 (t, *J* = 12.7 Hz).
Anal. Calcd for $C_{17}H_{17}ClF_2$: C, 57.57; H 9.98. Found: C 58.00, H 9.90.

(5-Chloro-5,5-difluoropentane-1,1-diyl)dibenzene (3e)



Yield 113 mg (77%). Colorless oil. Chromatography: hexanes.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.45 – 7.24 (m, 10H), 4.01 (t, *J* = 7.9 Hz, 1H), 2.50 – 2.30 (m, 2H), 2.22 (q, *J* = 7.9 Hz, 2H), 1.79 – 1.62 (m, 2H).
^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 144.5, 130.0 (t, *J* = 291.9 Hz), 128.7, 127.9, 126.5, 51.2, 41.8 (t, *J* = 23.9 Hz), 34.7, 22.0 (t, *J* = 3.0 Hz).
^{19}F NMR (282 MHz, Chloroform-*d*) δ -51.08 (t, *J* = 13.1 Hz).
Anal. Calcd for $C_{17}H_{17}ClF_2$: C, 69.27; H 5.81. Found: C 69.20, H 6.00.

7-Chloro-7,7-difluoro-2-methylheptan-3-ol (3f)



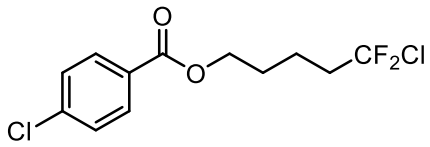
Yield 79 mg (79%). Pale-yellow oil. Chromatography: DCM/pentane, 5/1 with gradient elution to DCM.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 3.35 (ddd, *J* = 8.8, 5.2, 3.5 Hz, 1H), 2.30 (tt, *J* = 13.1, 7.9 Hz, 2H), 1.94 – 1.74 (m, 1H), 1.73 – 1.33 (m, 5H), 1.01 (d, *J* = 6.8 Hz, 6H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, Chloroform-*d*) δ 130.12 (t, *J* = 291.7 Hz), 76.4, 42.0 (t, *J* = 23.8 Hz), 33.8, 32.9, 20.2 (t, *J* = 3.2 Hz), 18.8, 17.3.

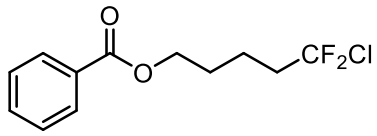
^{19}F NMR (282 MHz, Chloroform-*d*) δ -51.40 (t, *J* = 13.1 Hz).

HRMS (ESI): calcd for $C_8H_{15}{}^{35}ClF_2ONa$ (M+Na) 223.0672, found 223.0662.

5-Chloro-5,5-difluoropentyl 4-chlorobenzoate (3g)



3g



3g-H

Yield 125 mg (84%). Colorless oil. Chromatography: hexanes/EtOAc, 20/1. According to GC-MS analysis, the compound contains ca. 2% of impurity, which can be ascribed to the protodechlorinated product **3g-H** (MS peaks: m/z, 105, 262, 264).

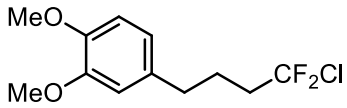
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 4.34 (t, *J* = 6.0 Hz, 2H), 2.46 – 2.27 (m, 2H), 1.93 – 1.67 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, Chloroform-*d*) δ 165.7, 139.6, 131.0, 129.8 (t, J = 291.8 Hz), 128.8, 128.7, 64.45, 41.5 (t, *J* = 24.1 Hz), 27.8, 20.2 (t, *J* = 3.2 Hz); Impurity: δ 133.1, 130.7, 129.6, 128.5.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -51.50 (t, *J* = 12.9 Hz).

HRMS (ESI): calcd for $C_{12}H_{12}{}^{35}Cl_2F_2O_2Na$ (M+Na) 319.0075, found 319.0074.

4-(4-Chloro-4,4-difluorobutyl)-1,2-dimethoxybenzene (3h)



Yield 107 mg (81%). Colorless oil. Chromatography: hexanes/EtOAc, 10/1.

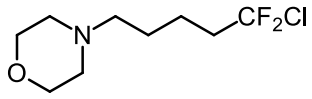
^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.84 – 6.74 (m, 1H), 6.74 – 6.60 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.36 – 2.16 (m, 2H), 2.00 – 1.82 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, Chloroform-*d*) δ 149.0, 147.5, 133.3, 130.0 (t, *J* = 291.7 Hz), 120.3, 111.6, 111.4, 55.9, 55.8, 41.1 (t, *J* = 23.9 Hz), 34.1, 25.0 (t, *J* = 2.8 Hz).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -51.13 (t, *J* = 13.2 Hz, 2F).

HRMS (ESI): calcd for $C_{12}H_{15}{}^{35}ClF_2O_2Na$ (M+Na) 287.0621, found 287.0632.

4-(5-Chloro-5,5-difluoropentyl)morpholine (3i)



Yield 89 mg (78%). Colorless oil. Chromatography: hexanes/EtOAc, 1/1 with gradient elution to MeOH.

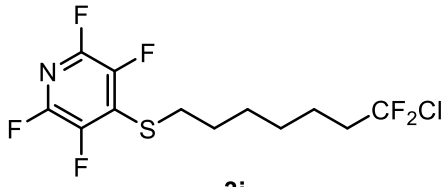
^{1}H NMR (300 MHz, Chloroform-*d*) δ 3.69 (t, *J* = 4.5 Hz, 4H), 2.40 (t, *J* = 4.5 Hz, 4H), 2.37 – 2.19 (m, 4H), 1.69 – 1.48 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, Chloroform-*d*) δ 130.0 (t, *J* = 291.8 Hz), 67.1, 58.5, 53.8, 41.8 (t, *J* = 23.9 Hz), 25.6, 21.4 (t, *J* = 3.1 Hz).

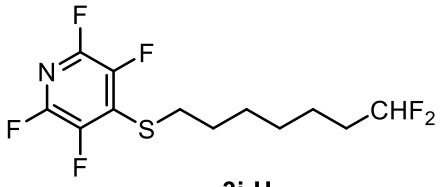
^{19}F NMR (282 MHz, Chloroform-*d*) δ -51.40 (t, *J* = 12.9 Hz).

HRMS (ESI): calcd for $C_{19}H_{17}{}^{35}ClF_2NO$ (M+H) 228.0961, found 228.0964.

4-((7-Chloro-7,7-difluoroheptyl)thio)-2,3,5,6-tetrafluoropyridine (3j)



3j



3j-H

Yield 109 mg (62%). Colorless oil. Chromatography: hexanes/EtOAc, 50/1. According to GC-MS analysis, the compound contains ca. 2% of impurity, which can be ascribed to the protodechlorinated product **3j-H** (MS peak: m/z, 317).

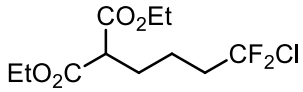
^{1}H NMR (300 MHz, Chloroform-*d*) δ 3.18 (t, *J* = 7.3 Hz, 2H), 2.37 – 2.13 (m, 2H), 1.76 – 1.55 (m, 4H), 1.55 – 1.31 (m, 4H). Impurity: δ 5.78 (tt, *J* = 56.9, 4.3 Hz)

^{13}C NMR (75 MHz, Chloroform-*d*) δ 143.6 (dm, *J* = 245.5 Hz), 141.3 (dm, *J* = 255.4 Hz), 131.6 (t, *J* = 17.3 Hz), 130.1 (t, *J* = 291.7 Hz), 41.8 (t, *J* = 23.9 Hz), 33.1 (t, *J* = 4.9 Hz), 29.7, 28.1, 28.1, 23.2 (t, *J* = 3.0 Hz). Impurity: δ 117.4 (t, *J* = 238.7 Hz)

^{19}F NMR (282 MHz, Chloroform-*d*) δ -51.48 (t, *J* = 12.9 Hz, 2F), -91.92 – -92.86 (m, 2F), -139.22 – -139.96 (m, 2F). Impurity: δ -116.77 (dt, *J* = 56.9, 17.5 Hz)

HRMS (ESI): calcd for $C_{11}H_{11}{}^{35}ClF_6NSNa$ (M+Na) 374.0175, found 374.0167.

Diethyl 2-(4-chloro-4,4-difluorobutyl)malonate (3k)



Modified General procedure A: amounts of the reagents, **N1** (194 mg, 1.5 mmol), **2a** (48 mL, 2 mmol) and 4CzIPN (4 mg, 0.005 mmol).

Yield 123 mg (86%). Colorless oil. Chromatography: hexanes/EtOAc, 12/1.

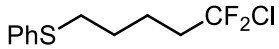
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.18 (q, *J* = 7.1 Hz, 4H), 3.31 (t, *J* = 7.4 Hz, 1H), 2.39 – 2.20 (m, 2H), 1.94 (q, *J* = 7.8 Hz, 2H), 1.77 – 1.58 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 169.0, 129.6 (t, *J* = 291.8 Hz), 61.56, 51.6, 41.5 (t, *J* = 24.2 Hz), 27.6, 21.3 (t, *J* = 3.2 Hz), 14.1.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -51.60 (t, *J* = 12.8 Hz).

HRMS (ESI): calcd for $C_{11}H_{17}ClF_2O_4Na$ (M+Na) 309.0676, found 309.0666.

(5-Chloro-5,5-difluoropentyl)(phenyl)sulfane (3l)



Modified General procedure A: amount of the reagent, 2-methylpropane-2-thiol (12 μL, 0.1 mmol).

Yield 89 mg (71%). Colorless oil. Chromatography: hexanes/EtOAc, 50/1.

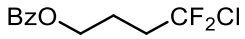
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.41 – 7.26 (m, 4H), 7.21 (t, *J* = 7.1 Hz, 1H), 2.95 (t, *J* = 6.6 Hz, 2H), 2.40 – 2.21 (m, 2H), 1.87 – 1.64 (m, 4H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 136.3, 129.9 (t, *J* = 291.7 Hz), 129.6, 129.1, 126.3, 41.5 (t, *J* = 24.1 Hz), 33.5, 28.2, 22.5 (t, *J* = 3.0 Hz).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -51.35 (t, *J* = 13.0 Hz).

HRMS (ESI): calcd for $C_{11}H_{13}{}^{35}ClF_2S{}^{107}Ag$ (M+Ag) 356.9440, found 356.9434.

4-Chloro-4,4-difluorobutyl benzoate (3m)



Modified General procedure A: amounts of the reagents, **N1** (194 mg, 1.5 mmol), **2a** (48 mL, 2 mmol) and 4CzIPN (4 mg, 0.005 mmol).

Yield 80 mg (64%). Colorless oil. Chromatography: hexanes/EtOAc, 20/1. According to GC-MS analysis, ^{1}H NMR and ^{19}F NMR, the compound contains ca. 2% of impurity, which can be ascribed to the regioisomeric product (3,3,3-trifluoro-2-methylpropyl benzoate).

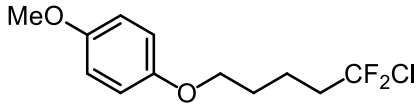
^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.09 – 8.00 (m, 2H), 7.64 – 7.52 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.40 (t, *J* = 6.3 Hz, 2H), 2.59 – 2.39 (m, 2H), 2.19 – 2.04 (m, 2H); impurity: δ 1.31 (d, *J* = 6.9 Hz).

^{13}C NMR (76 MHz, Chloroform-*d*) δ 166.5, 133.3, 130.0, 129.69, 129.67 (t, *J* = 291.4 Hz), 128.6, 63.2, 39.0 (t, *J* = 24.8 Hz), 23.2 (t, *J* = 3.3 Hz).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -51.67 (t, *J* = 12.8 Hz); impurity: δ -55.24 (d, *J* = 9.4 Hz).

HRMS (ESI): calcd for $C_{11}H_{11}{}^{35}ClF_2O_2Na$ (M+Na) 271.0308, found 271.0299.

1-((5-Chloro-5,5-difluoropentyl)oxy)-4-methoxybenzene (3n)



Yield 69 mg (52%). Colorless solid. Mp 37-40 °C. Chromatography: hexanes/EtOAc, 15/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.85 (s, 4H), 3.95 (t, *J* = 5.6 Hz, 2H), 3.78 (s, 3H), 2.48 – 2.28 (m, 2H), 1.92 – 1.75 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 154.1, 153.1, 130.0(t, *J* = 291.8 Hz), 115.56, 114.8, 68.0, 55.8, 41.7 (t, *J* = 23.9 Hz), 28.4, 20.4 (t, *J* = 3.2 Hz).

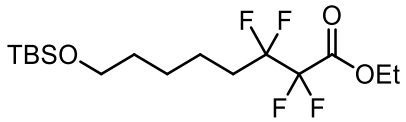
^{19}F NMR (282 MHz, Chloroform-*d*) δ -51.40 (t, *J* = 12.8 Hz).

HRMS (ESI): calcd for $C_{12}H_{15}{}^{35}ClF_2O_2$ (M) 264.0723, found 264.0721.

Fluoroalkylation of alkenes (General procedure B).

A test tube was evacuated and filled with argon. Then, acetonitrile (1 mL), triazinane **N1** (129 g, 1 mmol), alkene (0.5 mmol), fluoroalkyl chloride (0.875 mmol) or chloroform (160 μL, 2 mmol), 2-methylpropane-2-thiol (6 μL, 0.05 mmol), 4CzIPN (2 mg, 0.0025 mmol) were added. The tube was screw-capped and irradiated with 455 nm (10W) strip for 5 hours. The reaction was quenched with water (5 mL) and extracted with hexane (3×1.5mL). 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.

Ethyl 8-((*tert*-butyldimethylsilyl)oxy)-2,2,3,3-tetrafluorooctanoate (4a)



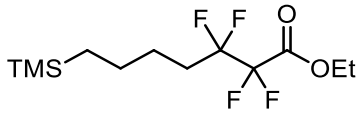
Yield 169 mg (90%). Colorless oil. Chromatography: hexanes/EtOAc, 20/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.39 (q, *J* = 7.1 Hz, 2H), 3.61 (t, *J* = 6.2 Hz, 2H), 2.04 (tt, *J* = 18.4, 8.0 Hz, 2H), 1.66 – 1.43 (m, 4H), 1.48 – 1.31 (m, 5H), 0.89 (s, 9H), 0.04 (s, 6H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 160.8 (t, *J* = 30.4 Hz), 118.1 (tt, *J* = 251.6, 31.6 Hz), 109.7 (tt, *J* = 261.4, 37.0 Hz), 63.8, 62.9, 32.5, 30.7 (t, *J* = 22.4 Hz), 26.1, 25.7, 20.3 (t, *J* = 3.7 Hz), 18.5, 14.0, -5.2.

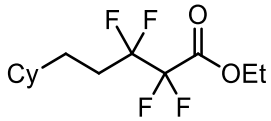
^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.62 (t, *J* = 18.8 Hz), -120.92 (s, 2F).
HRMS (ESI): calcd for $C_{16}H_{30}F_4O_3SiNa$ (M+Na) 397.1793, found 397.1791.

Ethyl 2,2,3,3-tetrafluoro-7-(trimethylsilyl)heptanoate (4b)



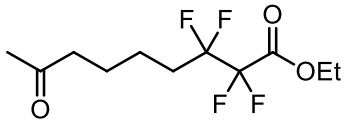
Yield 130 mg (86%). Colorless oil. Chromatography: hexanes/EtOAc, 50/1.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.39 (q, *J* = 7.2 Hz, 2H), 2.16 – 1.92 (m, 2H), 1.65 – 1.54 (m, 2H), 1.46 – 1.29 (m, 5H), 0.57 – 0.45 (m, 2H), -0.02 (s, 9H).
^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 160.8 (t, *J* = 30.3 Hz), 118.5 (tt, *J* = 251.4, 31.7 Hz), 109.7 (tt, *J* = 261.2, 37.2 Hz), 63.8, 30.3 (t, *J* = 22.4 Hz), 24.1 (t, *J* = 3.4 Hz), 23.8, 16.6, 14.0, -1.6.
^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.51 (t, *J* = 19.1 Hz, 2F), -120.93 (s, 2F).
HRMS (ESI): calcd for $C_{12}H_{22}F_4O_2SiNa$ (M+Na) 325.1217, found 325.1219.

Ethyl 5-cyclohexyl-2,2,3,3-tetrafluoropentanoate (4c)



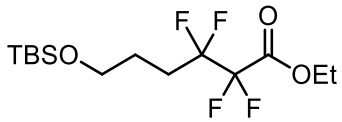
Yield 125 mg (88%). Colorless oil. Chromatography: hexanes/EtOAc, 30/1.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.39 (q, *J* = 7.2 Hz, 2H), 2.16 – 1.92 (m, 2H), 1.76 – 1.61 (m, 5H), 1.54 – 1.41 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.31 – 1.03 (m, 4H), 1.00 – 0.82 (m, 2H).
^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 160.8 (t, *J* = 30.4 Hz), 118.6 (tt, *J* = 251.9, 31.7 Hz), 109.74 (tt, *J* = 261.0, 37.1 Hz), 63.8, 37.4, 33.1, 28.2 (t, *J* = 22.4 Hz), 27.5 (t, *J* = 3.3 Hz), 26.6, 26.3, 14.0.
^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.89 (t, *J* = 19.0 Hz, 2F), -120.89 (s, 2F).
HRMS (ESI): calcd for $C_{13}H_{20}F_4O_2Na$ (M+Na) 307.1292, found 307.1291.

Ethyl 2,2,3,3-tetrafluoro-8-oxononanoate (4d)



Yield 118 mg (87%). Pale-yellow oil. Chromatography: hexanes/EtOAc, 4/1.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.33 (q, *J* = 7.1 Hz, 2H), 2.42 (t, *J* = 6.8 Hz, 2H), 2.08 (s, 3H), 2.05 – 1.88 (m, 2H), 1.68 – 1.43 (m, 4H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 208.1, 160.5 (t, *J* = 30.2 Hz), 118.1 (tt, *J* = 251.9, 31.6 Hz), 109.5 (tt, *J* = 261.3, 36.8 Hz), 63.8, 43.1, 30.5 (t, *J* = 22.5 Hz), 29.8, 23.2, 20.0 (t, *J* = 3.9 Hz), 13.8.
^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.61 (t, *J* = 18.8 Hz, 2F), -120.93 (s, 2F).
HRMS (ESI): calcd for $C_{11}H_{16}F_4O_3Na$ (M+Na) 295.0928, found 295.0936.

Ethyl 6-((*tert*-butyldimethylsilyl)oxy)-2,2,3,3-tetrafluorohexanoate (4e)



Yield 142 mg (82%). Colorless oil. Chromatography: hexanes/EtOAc, 20/1.

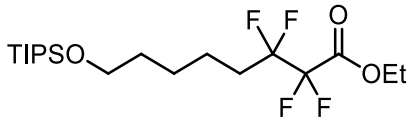
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.45 – 4.31 (m, 2H), 3.66 (t, *J* = 5.8 Hz, 2H), 2.26 – 1.99 (m, 2H), 1.85 – 1.70 (m, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 160.7 (t, *J* = 30.4 Hz), 118.6 (tt, *J* = 251.8, 31.6 Hz), 109.7 (tt, *J* = 261.2, 36.9 Hz), 63.8, 61.9, 27.5 (t, *J* = 22.4 Hz), 26.0, 24.0 (t, *J* = 3.4 Hz), 13.9, -5.3.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.49 (t, *J* = 19.1 Hz, 2F), -120.98 (s, 2F).

HRMS (ESI): calcd for $C_{14}H_{26}F_4O_3SiNa$ (M+Na) 369.1480, found 369.1486.

Ethyl 2,2,3,3-tetrafluoro-8-((triisopropylsilyl)oxy)octanoate (4e)



Yield 173 mg (83%). Colorless oil. Chromatography: hexanes/EtOAc, 30/1.

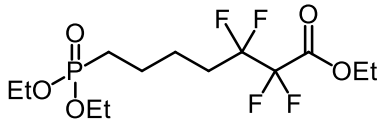
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.39 (q, *J* = 7.2 Hz, 2H), 3.69 (t, *J* = 6.1 Hz, 2H), 2.05 (tt, *J* = 18.8, 7.9 Hz, 2H), 1.69 – 1.51 (m, 4H), 1.51 – 1.40 (m, 2H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.10 – 1.00 (m, 21H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 160.7 (t, *J* = 30.4 Hz), 118.4 (tt, *J* = 251.7, 31.7 Hz), 109.7 (tt, *J* = 261.2, 37.1 Hz), 63.8, 63.2, 32.7, 30.7 (t, *J* = 22.4 Hz), 25.8, 20.3 (t, *J* = 3.7 Hz), 18.1, 14.0, 12.2.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.65 (t, *J* = 18.8 Hz, 2F), -120.95 (s, 2F).

HRMS (ESI): calcd for $C_{19}H_{36}F_4O_3SiNa$ (M+Na) 439.2262, found 439.2275.

Ethyl 7-(diethoxyphosphoryl)-2,2,3,3-tetrafluoroheptanoate (4g)



Yield 159 mg (87%). Colorless oil. Chromatography: EtOAc /EtOH, 20/1.

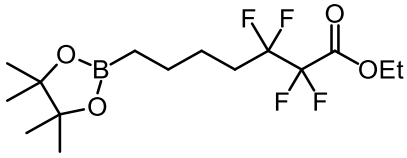
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.34 (q, *J* = 7.1 Hz, 2H), 4.16 – 3.94 (m, 4H), 2.16 – 1.88 (m, 2H), 1.82 – 1.50 (m, 6H), 1.41 – 1.17 (m, 9H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 160.4 (t, *J* = 30.3 Hz), 118.1 (tt, *J* = 251.9, 31.7 Hz), 109.5 (tt, *J* = 261.4, 36.9 Hz), 63.8, 61.5 (d, *J* = 6.4 Hz), 30.1 (t, *J* = 22.6 Hz), 25.5 (d, *J* = 141.8 Hz), 22.2 (d, *J* = 5.0 Hz), 21.3 (dt, *J* = 17.1, 3.8 Hz), 16.4 (d, *J* = 6.0 Hz), 13.8.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.65 (t, *J* = 18.6 Hz, 2F), -120.98 (s, 2F).

HRMS (ESI): calcd for $C_{13}H_{23}F_4O_5PNa$ (M+Na) 389.1111, found 389.1114.

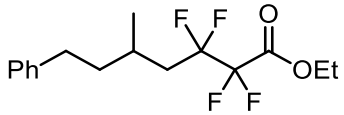
Ethyl 2,2,3,3-tetrafluoro-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanoate (4h)



Yield 119 mg (67%). Colorless oil. Chromatography: hexanes/EtOAc, 12/1.

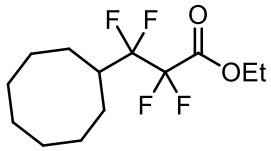
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.35 (q, *J* = 7.2 Hz, 2H), 2.11 – 1.88 (m, 2H), 1.63 – 1.40 (m, 4H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.20 (s, 12H), 0.77 (t, *J* = 7.5 Hz, 2H).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 160.7 (t, *J* = 30.3 Hz), 118.4 (tt, *J* = 251.6, 31.7 Hz), 109.7 (tt, *J* = 261.3, 37.1 Hz), 83.1, 63.7, 30.5 (t, *J* = 22.4 Hz), 24.9, 23.8, 22.8 (t, *J* = 3.7 Hz), 13.9, 11.0.
^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.63 (t, *J* = 18.9 Hz, 2F), -120.99 (s, 2F).
HRMS (ESI): calcd for $C_{15}H_{25}BF_4O_4Na$ (M+Na) 379.1677, found 379.1673.

Ethyl 2,2,3,3-tetrafluoro-5-methyl-7-phenylheptanoate (4i)



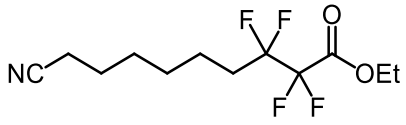
Yield 131 mg (82%). Colorless oil. Chromatography: hexanes/EtOAc, 30/1.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.36 – 7.26 (m, 2H), 7.26 – 7.16 (m, 3H), 4.41 (q, *J* = 7.2 Hz, 2H), 2.78 – 2.54 (m, 2H), 2.31 – 1.69 (m, 4H), 1.69 – 1.51 (m, 1H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.13 (d, *J* = 6.3 Hz, 3H).
^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 160.7 (t, *J* = 30.3 Hz), 142.2, 128.52, 128.45, 126.0, 118.8 (tt, *J* = 253.0, 31.4 Hz), 109.6 (tt, *J* = 261.5, 37.1 Hz), 63.9, 39.4, 36.6 (t, *J* = 21.3 Hz), 33.2, 26.6 (t, *J* = 2.1 Hz), 20.6 (d, *J* = 2.1 Hz), 14.0.
^{19}F NMR (282 MHz, Chloroform-*d*) δ -112.93 (ddd, *J* = 266.4, 31.0, 9.8 Hz, 1F), -114.68 (ddd, *J* = 266.4, 29.3, 9.8 Hz, 1F), -121.01 (s, 2F).
HRMS (ESI): calcd for $C_{16}H_{20}F_4O_2Na$ (M+Na) 343.1292, found 343.1292.

Ethyl 3-cyclooctyl-2,2,3,3-tetrafluoropropanoate (4j)



Modified General procedure B: 1 mmol of fluoroalkylchloride was used.
Yield 118 mg (83%). Colorless oil. Chromatography: hexanes/EtOAc, 40/1.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.39 (q, *J* = 7.1 Hz, 2H), 2.44 – 2.30 (m, 1H), 1.98 – 1.76 (m, 2H), 1.79 – 1.62 (m, 2H), 1.67 – 1.41 (m, 10H), 1.37 (t, *J* = 7.1 Hz, 3H).
^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 161.0 (t, *J* = 30.8 Hz), 119.6 (tt, *J* = 254.7, 30.4 Hz), 110.8 (tt, *J* = 262.8, 39.2 Hz), 63.7, 39.9 (t, *J* = 20.0 Hz), 26.8, 26.5, 25.4, 25.0 (tt, *J* = 4.2, 1.9 Hz), 13.9.
^{19}F NMR (282 MHz, Chloroform-*d*) δ -116.64 (d, *J* = 16.6 Hz, 2F), -117.40 (s, 2F).
HRMS (ESI): calcd for $C_{13}H_{20}F_4O_2Na$ (M+Na) 307.1292, found 307.1290.

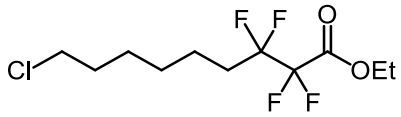
Ethyl 9-cyano-2,2,3,3-tetrafluorononanoate (4k)



Yield 113 mg (80%). Colorless oil. Chromatography: hexanes/EtOAc, 4/1.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.35 (q, *J* = 7.2 Hz, 2H), 2.31 (t, *J* = 7.0 Hz, 2H), 2.13 – 1.89 (m, 2H), 1.72 – 1.50 (m, 4H), 1.49 – 1.26 (m, 7H).
^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 160.4 (t, *J* = 30.2 Hz), 119.6, 118.2 (tt, *J* = 251.8, 31.7 Hz), 109.5 (tt, *J* = 261.3, 36.8 Hz), 63.8, 30.3 (t, *J* = 22.4 Hz), 28.27, 28.25, 25.1, 20.1 (t, *J* = 3.8 Hz), 16.9, 13.7.

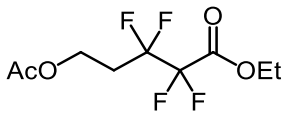
^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.72 (t, *J* = 18.9 Hz, 2F), -121.01 (s, 2F).
HRMS (ESI): calcd for $C_{12}H_{17}F_4NO_2Na$ (M+Na) 306.1088, found 306.1094.

Ethyl 9-chloro-2,2,3,3-tetrafluorononanoate (4l)



Yield 116 mg (79%). Colorless oil. Chromatography: hexanes/EtOAc, 25/1.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.38 (q, *J* = 7.1 Hz, 2H), 3.52 (t, *J* = 6.6 Hz, 2H), 2.16 – 1.92 (m, 2H), 1.78 (p, *J* = 6.8 Hz, 2H), 1.67 – 1.53 (m, 2H), 1.53 – 1.29 (m, 7H).
^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 160.7 (t, *J* = 30.3 Hz), 118.3 (tt, *J* = 251.8, 31.7 Hz), 109.6 (tt, *J* = 261.4, 37.0 Hz), 63.9, 44.9, 32.4, 30.5 (t, *J* = 22.4 Hz), 28.6, 26.6, 20.3 (t, *J* = 3.8 Hz), 13.9.
^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.65 (t, *J* = 19.1 Hz, 2F), -120.95 (s, 2F).
HRMS (ESI): calcd for $C_{11}H_{17}{}^{35}ClF_4O_2Na$ (M+Na) 315.0745, found 315.0736.

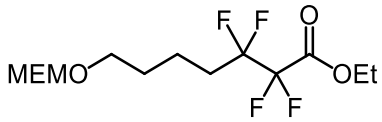
Ethyl 5-acetoxy-2,2,3,3-tetrafluoropentanoate (4m)



Modified General procedure B: irradiation time 10 hours.
Yield 81 mg (62%). Colorless oil. Chromatography: DCM. Compare to the general procedure,

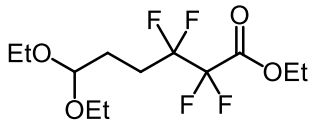
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.44 – 4.26 (m, 4H), 2.44 (tt, *J* = 18.3, 6.7 Hz, 2H), 2.04 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.7, 160.2 (t, *J* = 30.1 Hz), 117.3 (tt, *J* = 253.2, 32.1 Hz), 109.2 (tt, *J* = 261.8, 36.2 Hz), 64.1, 56.7 (t, *J* = 4.8 Hz), 30.3 (t, *J* = 21.8 Hz), 20.7, 13.9.
^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.00 (t, *J* = 18.3 Hz, 2F), -121.07 (s, 2F).
HRMS (ESI): calcd for $C_9H_{12}F_4O_4Na$ (M+Na) 283.0564, found 283.0575.

Ethyl 2,2,3,3-tetrafluoro-7-((2-methoxyethoxy)methoxy)heptanoate (4n)



Yield 135 mg (81%). Colorless oil. Chromatography: hexanes/EtOAc, 3/1.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.67 (s, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.70 – 3.61 (m, 2H), 3.59 – 3.48 (m, 4H), 3.36 (s, 3H), 2.03 (tt, *J* = 18.8, 7.1 Hz, 2H), 1.73 – 1.55 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 3H).
^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 160.6 (t, *J* = 30.3 Hz), 118.3 (tt, *J* = 251.8, 31.8 Hz), 109.6 (tt, *J* = 261.4, 37.0 Hz), 95.6, 71.9, 67.2, 66.9, 63.8, 59.0, 30.4 (t, *J* = 22.4 Hz), 29.3, 17.5 (t, *J* = 4.0 Hz), 13.9.
^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.75 (t, *J* = 18.8 Hz), -120.97.
HRMS (ESI): calcd for $C_{13}H_{22}F_4O_5Na$ (M+Na) 357.1296, found 357.1290.

Ethyl 6,6-diethoxy-2,2,3,3-tetrafluorohexanoate (4o)



Yield 99 mg (65%). Colorless oil. Chromatography: hexanes/EtOAc, 12/1.

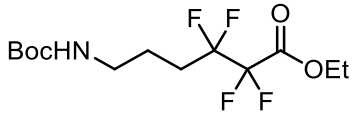
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.50 (t, *J* = 5.4 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.62 (dq, *J* = 9.2, 7.1 Hz, 2H), 3.47 (dq, *J* = 9.4, 7.1 Hz, 2H), 2.24 – 2.00 (m, 2H), 1.91 – 1.72 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 160.5 (t, *J* = 30.3 Hz), 118.4 (tt, *J* = 251.8, 31.6 Hz), 109.6 (tt, *J* = 261.3, 36.8 Hz), 101.7, 63.8, 61.7, 26.0 (t, *J* = 22.4 Hz), 25.0 (t, *J* = 3.5 Hz), 15.3, 13.8.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.60 (t, *J* = 18.9 Hz, 2F), -120.94 (s, 2F).

HRMS (ESI): calcd for $C_{12}H_{20}F_4O_4Na$ (M+Na) 327.1190, found 327.1194.

Ethyl 6-((*tert*-butoxycarbonyl)amino)-2,2,3,3-tetrafluorohexanoate (4p)



Yield 134 mg (81%). Colorless oil. Chromatography: hexanes/EtOAc, 5/1.

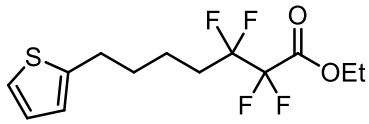
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.57 (brs, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.20 (q, *J* = 7.0 Hz, 2H), 2.21 – 1.98 (m, 2H), 1.78 (p, *J* = 7.0 Hz, 2H), 1.44 (s, 9H), 1.37 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 160.51 (t, *J* = 30.4 Hz), 156.09, 118.23 (tt, *J* = 252.1, 31.8 Hz), 109.50 (tt, *J* = 261.4, 36.8 Hz), 79.48, 63.90, 39.89, 28.42, 28.03 (t, *J* = 22.7 Hz), 21.51 (t, *J* = 3.6 Hz), 13.87.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.33 (t, *J* = 19.1 Hz), -120.79 (s, 2F).

HRMS (ESI): calcd for $C_{13}H_{21}F_4NO_2Na$ (M+Na) 354.1299, found 354.1295.

Ethyl 2,2,3,3-tetrafluoro-7-(thiophen-2-yl)heptanoate (4q)



Yield 103 mg (66%). Colorless oil. Chromatography: hexanes/EtOAc, 25/1. Compare to the general procedure, 1.25 mmol of fluoroalkylchloride was used.

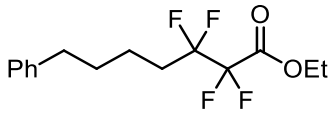
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.13 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.94 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.81 (dq, *J* = 3.4, 1.1 Hz, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 2.89 (td, *J* = 7.0, 1.1 Hz, 2H), 2.23 – 1.98 (m, 2H), 1.87 – 1.60 (m, 4H), 1.38 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 160.6 (t, *J* = 30.3 Hz), 144.6, 126.9, 124.34, 123.2, 118.3 (tt, *J* = 251.9, 31.7 Hz), 109.6 (tt, *J* = 261.3, 37.0 Hz), 63.9, 31.4, 30.4 (t, *J* = 22.4 Hz), 29.6, 20.0 (t, *J* = 3.8 Hz), 13.9.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.52 (t, *J* = 18.9 Hz, 2F), -120.85 (s, 2F).

HRMS (ESI): calcd for $C_{13}H_{16}F_4O_2SNa$ (M+Na) 335.0699, found 335.0693.

Ethyl 2,2,3,3-tetrafluoro-7-phenylheptanoate (4r)



Yield 130 mg (85%). Colorless oil. Chromatography: hexanes/EtOAc, 25/1.

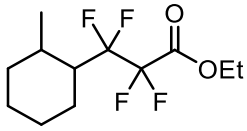
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.38 – 7.27 (m, 2H), 7.27 – 7.14 (m, 3H), 4.41 (q, *J* = 7.2 Hz, 2H), 2.68 (t, *J* = 7.2 Hz, 2H), 2.23 – 1.99 (m, 2H), 1.82 – 1.58 (m, 4H), 1.39 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 160.7 (t, *J* = 30.4 Hz), 141.9, 128.49, 128.47, 126.0, 118.3 (tt, *J* = 251.7, 31.7 Hz), 109.4 (tt, *J* = 261.4, 261.3, 37.0 Hz), 63.9, 35.7, 31.1, 30.5 (t, *J* = 22.4 Hz), 20.1 (t, *J* = 3.8 Hz), 13.9.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.54 (t, *J* = 19.0 Hz, 2F), -120.88 (s, 2F).

HRMS (ESI): calcd for $C_{15}H_{18}F_4O_2Na$ (M+Na) 329.1135, found 329.1134.

Ethyl 2,2,3,3-tetrafluoro-3-(2-methylcyclohexyl)propanoate (4s)



Modified General procedure B: 1.25 mmol of fluoroalkylchloride was used, irradiation time 10 hours.

Yield 96 mg (71%). Colorless oil. Chromatography: hexanes/EtOAc, 35/1.

Mixture of isomers, 7.9:1.

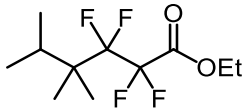
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.38 (q, *J* = 7.1 Hz, 2H), 2.39 – 2.12 (m, 1H), 1.90 – 1.15 (m, 12H), 1.03 (dt, *J* = 7.0, 1.7 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*), major isomer: δ 160.89 (t, *J* = 30.4 Hz), 123.23 – 105.96 (m), 63.74, 42.58 (t, *J* = 20.1 Hz), 33.78, 27.14 (t, *J* = 3.3 Hz), 26.04, 19.84, 19.24 (dd, *J* = 4.9, 2.7 Hz), 13.93, 13.53; minor isomer: δ 47.31 (t, *J* = 19.6 Hz), 36.06, 31.95, 29.84, 25.51, 25.44, 21.55 (dd, *J* = 5.5, 1.1 Hz).

^{19}F NMR (282 MHz, Chloroform-*d*), major isomer: δ -113.76 (ddd, *J* = 276.6, 20.9, 7.4 Hz), -117.71 (dm, *J* = 275.8 Hz), -118.74 (dt, *J* = 267.0, 6.4 Hz), -119.71 (dd, *J* = 267.2, 6.6 Hz); minor isomer: δ -103.17 (d, *J* = 279.0 Hz), -116.45 (ddt, *J* = 278.6, 19.9, 9.8 Hz). -115.72 (dt, *J* = 268.4, 9.7 Hz), -119.57 (dd, *J* = 268.6, 10.9 Hz)

HRMS (ESI): calcd for $C_{12}H_{18}F_4O_2Na$ (M+Na) 293.1135, found 293.1134.

Ethyl 2,2,3,3-tetrafluoro-4,4,5-trimethylhexanoate (4t)



Modified General procedure B: amount of methylpropane-2-thiol (12 μL, 0.1 mmol), irradiation time 10 hours.

Yield 45 mg (35%). Colorless oil. Chromatography: DCM/pentane, 30/1.

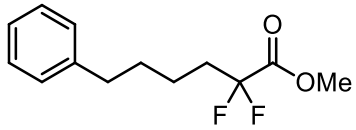
^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.38 (q, *J* = 7.1 Hz, 2H), 2.05 (hept, *J* = 6.8 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.09 (s, 6H), 0.95 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (76 MHz, Chloroform-*d*) δ 161.2 (t, *J* = 30.8 Hz), 120.7 (tt, *J* = 258.6, 31.3 Hz), 112.0 (tt, *J* = 264.1, 41.7 Hz), 63.8, 44.2 (tt, *J* = 18.6, 2.0 Hz), 32.4 (p, *J* = 2.0 Hz), 18.8 (tt, *J* = 5.4, 2.8 Hz), 18.6 (t, *J* = 2.7 Hz), 14.0.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -110.31 – -110.37 (m, 2F), -114.59 – -114.66 (m, 2F).

HRMS (ESI): calcd for $C_{11}H_9F_{13}O_2Na$ (M+Na) 281.1135, found 281.1144.

Methyl 2,2-difluoro-6-phenylhexanoate (5a)



Modified General procedure B: irradiation time 10 hours.

Yield 105 mg (87%). Colorless oil. Chromatography: hexanes/EtOAc, 20/1.

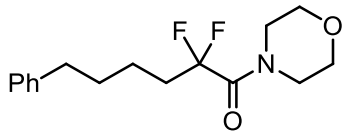
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.39 – 7.27 (m, 2H), 7.27 – 7.15 (m, 3H), 3.87 (s, 3H), 2.72 – 2.61 (m, 2H), 2.24 – 2.02 (m, 2H), 1.80 – 1.64 (m, 2H), 1.69 – 1.47 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 164.9 (t, *J* = 33.3 Hz), 141.9, 128.5, 126.0, 116.5 (t, *J* = 250.0 Hz), 53.3, 35.6, 34.5 (t, *J* = 23.2 Hz), 30.9, 21.2 (t, *J* = 4.3 Hz).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -106.35 (t, *J* = 16.9 Hz).

HRMS (ESI): calcd for $C_{13}H_{16}F_2O_2Na$ (M+Na) 265.1011, found 265.1008.

2,2-Difluoro-1-morpholino-6-phenylhexan-1-one (5b)



Modified General procedure B: irradiation time 10 hours.

Yield 128 mg (86%). Colorless oil. Chromatography: hexanes/EtOAc, 4/1.

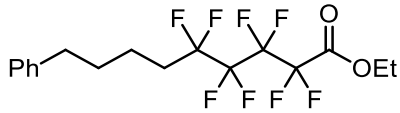
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.42 – 7.15 (m, 5H), 3.82 – 3.66 (m, 8H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.25 (tt, *J* = 17.9, 7.8 Hz, 2H), 1.89 – 1.56 (m, 4H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 162.2 (t, *J* = 29.8 Hz), 142.2, 128.42, 128.37, 125.8, 119.6 (t, *J* = 253.9 Hz), 66.84, 66.77, 46.6 (t, *J* = 6.4 Hz), 43.4, 35.7, 34.5 (t, *J* = 22.9 Hz), 31.2, 21.2 (t, *J* = 4.6 Hz).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -100.20 (t, *J* = 18.4 Hz).

HRMS (ESI): calcd for $C_{16}H_{21}F_2NO_2Na$ (M+Na) 320.1433, found 320.1423.

Ethyl 2,2,3,3,4,4,5,5-octafluoro-9-phenylnonanoate (5c)



Yield 179 mg (88%). Colorless oil. Chromatography: hexanes/EtOAc, 30/1.

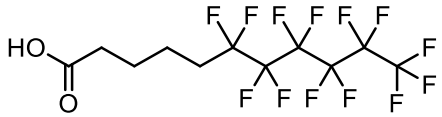
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.39 – 7.28 (m, 2H), 7.28 – 7.17 (m, 3H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H), 2.23 – 1.99 (m, 2H), 1.83 – 1.65 (m, 4H), 1.40 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 159.0 (t, *J* = 29.5 Hz), 141.9, 128.53, 128.48, 126.1, 118.5 (tt, *J* = 254.3, 30.9 Hz), 111.4 (ttt, J = 264.5, 34.3, 30.7 Hz), 111.0 (ttt, J = 266.8, 34.3, 30.7 Hz), 108.3 (tt, *J* = 266.7, 32.2 Hz), 64.5, 35.7, 31.0, 30.9 (t, *J* = 22.4 Hz), 20.0 (t, *J* = 3.8 Hz), 13.7.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.22 (p, *J* = 16.8 Hz, 2F), -119.71 (t, *J* = 11.6 Hz, 2F), -123.62 (s, 2F), -124.35 (s, 2F).

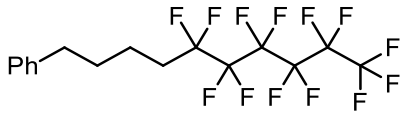
HRMS (ESI): calcd for $C_{17}H_{18}F_8O_2Na$ (M+Na) 429.1071, found 429.1054.

6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoroundecanoic acid (5d)



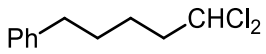
Modified General procedure B: 2,4,6-trimethylpyridine (73 μL, 0.55 mmol) was added before the irradiation. After irradiation, the reaction was quenched with 3 mL of 2M hydrochloric acid.
Yield 183 mg (87%). Pale-green solid. Mp 55-57 °C. Chromatography: DCM/i-PrOH, 12/1.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 11.78 (s, 1H), 2.41 (t, *J* = 6.8 Hz, 2H), 2.20 – 1.92 (m, 2H), 1.82 – 1.66 (m, 4H).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 180.90, 124.3 – 104.0 (m), 33.8, 30.8 (t, *J* = 22.5 Hz), 24.2, 19.9 (t, *J* = 4.1 Hz).
^{19}F NMR (282 MHz, Chloroform-*d*) δ -82.13 (t, *J* = 10.9 Hz, 3F), -115.50 (p, *J* = 17.0 Hz, 2F), -123.01 (s, 2F), -123.98 (s, 2F), -124.67 (s, 2F), -127.31 (t, *J* = 16.0 Hz, 2F).
HRMS (ESI): calcd for $C_{11}H_9F_{13}O_2Na$ (M+Na) 443.0287, found 443.0287.

(5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluorodecyl)benzene (5e)



Yield 199 mg (88%). Colorless oil. Chromatography: hexanes.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.40 – 7.19 (m, 5H), 2.71 (t, *J* = 7.1 Hz, 2H), 2.24 – 2.01 (m, 2H), 1.85 – 1.62 (m, 4H).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 141.9, 128.6, 128.5, 126.2, 124.1 – 103.3 (m), 35.7, 31.1, 31.0 (t, *J* = 22.4 Hz), 20.0 (t, *J* = 3.7 Hz).
^{19}F NMR (282 MHz, Chloroform-*d*) δ -81.87 (t, *J* = 10.4 Hz, 3F), -115.28 (p, *J* = 17.0 Hz, 2F), -122.82 (t, *J* = 14.8 Hz, 2F), -123.79, -124.49 (t, *J* = 16.0 Hz, 2F), -127.10 (t, *J* = 16.0 Hz, 2F).
HRMS (ESI): calcd for $C_{16}H_{13}F_{13}Na$ (M+Na) 475.0702, found 475.0711.

(5,5-Dichloropentyl)benzene (5f)



Modified General procedure B: amounts of the reagents **N1** (194 mg, 1.5 mmol) and 4CzIPN (4 mg, 0.005 mmol); irradiation time 10 hours.
Yield 73 mg (67%). Colorless oil. Chromatography: hexanes. Compare to the general procedure,
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 2H), 7.26 – 7.17 (m, 3H), 5.76 (t, *J* = 6.1 Hz, 1H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.33 – 2.19 (m, 2H), 1.79 – 1.54 (m, 4H).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 142.1, 128.5, 128.5, 126.0, 73.6, 43.6, 35.8, 30.5, 25.7.

Gram-scale synthesis of (5-chloro-5,5-difluoropentyl)benzene (3a).
A 100 mL thick wall screw-cap glass flask was evacuated and filled with argon. Then, acetonitrile (20 mL), triazinane **N1** (5.16 g, 40 mmol), 4-phenylbut-1-ene (2.64 g, 20 mmol), 4CzIPN (40 mg, 0.05 mmol), and 2-methylpropane-2-thiol (240μL, 2 mmol) were added. The flask was placed into the dish-shaped Dewar vessel and cooled to –40 °C (acetone/liq. nitrogen), and gaseous dichlorodifluoromethane (*ca.* 1.44 L, 60 mmol) was gradually injected into the frozen mixture via a syringe (the syringe needle was inserted into the reaction mixture). Then, the tube was screw-capped, placed into a beaker, cooled with water flow at room temperature, and irradiated for 5 h with a 455 nm 30 W

LED matrix placed under the bottom of the beaker. The reaction was quenched with water (10 mL) and extracted with hexane (3×6 mL). The combined organic phases were filtered through a short pad of Na_2SO_4 and concentrated on a rotary evaporator. The residue was distilled under vacuum using a Hickmann distilling head. Boiling point 65−73 °C (bath temperature) at 0.6 Torr. Yield 3.41 g (78%).

Gram-scale synthesis of methyl 2,2-difluoro-6-phenylhexanoate (5a).

A 50 mL flat-bottom flask was flushed with argon using a crooked needle. Then, acetonitrile (10 mL), triazinane **N1** (2.58g, 420 mmol), 4-phenylbut-1-ene (1.32 g, 10 mmol), 4CzIPN (20 mg, 0.025 mmol), methyl 2-chloro-2,2-difluoroacetate (1.86 mL, 17.5 mmol) and 2-methylpropane-2-thiol (120μL, 1 mmol) were added. The flask was closed with a stopper, placed into a beaker, cooled with water flow at room temperature, and irradiated for 3 h with a 455 nm 30 W LED matrix placed under the bottom of the beaker. The reaction was quenched with water (10 mL) and extracted with hexane (3×6 mL). The combined organic phases were filtered through a short pad of Na_2SO_4 and concentrated on a rotary evaporator. The residue was distilled under vacuum using a Hickmann distilling head. Boiling point 133−143 °C (bath temperature) at 1.7 Torr. Yield 1.94 g (80%).

Synthesis of 2,2-difluoro-6-phenylhexan-1-ol (6)

Methyl 2,2-difluoro-6-phenylhexanoate (242 mg, 1 mmol) and methanol (44 μL) were added dropwise to a stirring suspension of sodium borohydride (32 mg, 0.85 mmol) in diethyl ether (0.75 mL). After refluxing in water bath for 3 hours, the reaction tube was immersed into an ice/water bath and quenched with 1 mL of 4M HCl solution. The organic layer was separated, and the aqueous layer was extracted with hexane (4×2 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 (hexanes/EtOAc, 3/1). Colorless oil. Yield 184 mg (86%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.27 – 7.17 (m, 2H), 7.17 – 7.07 (m, 3H), 3.63 (td, *J* = 12.9, 5.5 Hz, 2H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.45 – 2.02 (m, 1H), 1.98 – 1.75 (m, 2H), 1.68 – 1.56 (m, 2H), 1.60 – 1.43 (m, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 142.18, 128.43, 128.41, 125.87, 123.36 (t, *J* = 241.6 Hz), 63.95 (t, *J* = 31.8 Hz), 35.70, 33.15 (t, *J* = 24.0 Hz), 31.22, 21.52 (t, *J* = 4.6 Hz).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -103.92 (t, *J* = 17.9 Hz).

HRMS (ESI): calcd for $C_{16}H_{21}F_2NONa$ (M+Na) 304.1483, found 304.1490.

Synthesis of 2,2-difluoro-6-phenyl-1-(pyrrolidin-1-yl)hexan-1-one (7)

Pyrrolidine (123 μL, 1.5 mmol, 1.5 equiv) was added dropwise to a stirring solution of methyl 2,2-difluoro-6-phenylhexanoate (242 mg, 1 mmol) in methanol (1 mL). The mixture was stirred overnight at room temperature. All volatile components were evaporated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc, 3/1). Colorless oil. Yield 239 mg (85%)

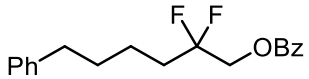
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.40 – 7.29 (m, 2H), 7.27 – 7.14 (m, 3H), 3.73 (t, *J* = 6.8 Hz, 2H), 3.58 (t, *J* = 7.0 Hz, 2H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.36 – 2.13 (m, 2H), 2.06 – 1.80 (m, 4H), 1.86 – 1.58 (m, 4H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 162.22 (t, *J* = 30.2 Hz), 142.04, 128.28, 128.20, 125.65, 119.08 (t, *J* = 252.6 Hz), 47.21, 46.45 (t, *J* = 6.4 Hz), 35.55, 34.07 (t, *J* = 23.2 Hz), 31.04, 26.39 (t, *J* = 1.8 Hz), 23.15, 21.17 (t, *J* = 4.5 Hz).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -109.08 (p, *J* = 15.0 Hz).

HRMS (ESI): calcd for $C_{12}H_{16}F_2ONa$ (M+Na) 237.1061, found 237.1062.

2,2-Difluoro-6-phenylhexyl benzoate (5g)[29]



Prepared from 4-phenyl-1-butene (**1a**) and 2-bromo-2,2-difluoroethyl benzoate (**8**)[30] (1.75 equiv) according to General Procedure B.

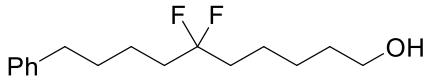
Yield 131 mg (82%). Colorless oil. Chromatography: hexanes/EtOAc, 8/1.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 – 8.03 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.25 (m, 2H), 7.24 – 7.14 (m, 3H), 4.49 (t, *J* = 12.4 Hz, 2H), 2.66 (t, *J* = 7.4 Hz, 2H), 2.14 – 1.91 (m, 2H), 1.80 – 1.54 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 142.1, 133.6, 130.0, 129.3, 128.7, 128.5, 126.0, 121.9 (t, *J* = 242.0 Hz), 64.3 (t, *J* = 34.0 Hz), 35.8, 34.1 (t, *J* = 23.8 Hz), 31.2, 21.5 (t, *J* = 4.5 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -106.06 (p, *J* = 15.0 Hz).

6,6-Difluoro-10-phenyldecan-1-ol (10)



A test tube was evacuated and filled with argon. Then, acetonitrile (1 mL), triazinane **N1** (129 mg, 1 mmol), pent-4-en-1-ol (43 mg, 0.5 mmol), compound **3a** (191 mg, 0.875 mmol), 2-methylpropane-2-thiol (6 μL, 0.05 mmol), 3DPA2FBN (3.2 mg, 0.005 mmol) were added. The tube was screw-capped and irradiated with 400 nm (60W) matrix for 15 hours. The reaction was quenched with water (5 mL) and extracted with hexane (3×1.5 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 (hexanes/EtOAc, 3/1). Yield 64 mg (47%). Pale-yellow oil. According to ^{1}H NMR, ^{13}C NMR and HRMS data, the compound contains ca. 15% of impurity, which can be ascribed to the alkene hydrothiolation product 5-(*tert*-butylthio)pentan-1-ol.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 – 7.18 (m, 2H), 7.18 – 7.07 (m, 3H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.89 – 1.29 (m, 15H); impurity: δ 2.50 (t, *J* = 7.2 Hz), 1.28 (s).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 128.50, 128.47, 125.9, 125.3 (t, *J* = 240.5 Hz), 62.8, 36.43 (t, *J* = 25.5 Hz), 36.36 (t, *J* = 25.6 Hz), 35.8, 32.6, 31.3, 25.7, 22.3 (t, *J* = 4.8 Hz), 22.2 (t, *J* = 4.7 Hz); impurity: δ 62.9, 32.5, 31.1, 29.8, 28.4, 25.5.

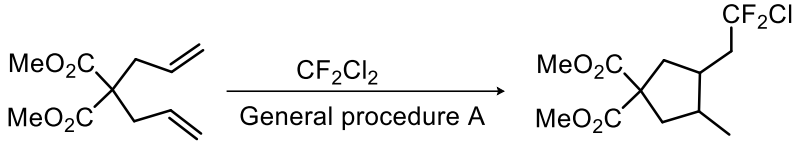
^{19}F NMR (282 MHz, $CDCl_3$) δ -98.57 (p, *J* = 16.7 Hz).

HRMS (ESI): calcd for $C_{16}H_{24}F_2ONa$ (M+Na) 293.1687, found 293.1687; calcd for $C_9H_{20}OS^{107}Ag$ (M+Ag) 283.0280, found 283.0282.

Mechanistic studies

A. Radical clock experiment

Dimethyl 3-(2-chloro-2,2-difluoroethyl)-4-methylcyclopentane-1,1-dicarboxylate (11)



1α **11**, 90%

Following the General procedure A, the cyclized product was obtained in 90 % yield (134 mg). Colorless oil. Chromatography: hexanes/EtOAc, 10/1.

Mixture of isomers, 8.3:1.

^{1}H NMR (300 MHz, Chloroform-*d*), major isomer: δ 3.71 (s, 6H), 2.56 – 2.18 (m, 6H), 2.18 – 1.97 (m, 2H), 0.85 (d, *J* = 6.9 Hz, 3H); minor isomer: δ 1.01 (d, *J* = 6.2 Hz).

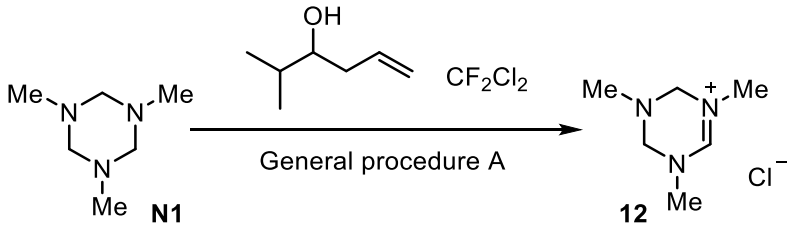
^{13}C NMR (75 MHz, Chloroform-*d*), major isomer: δ 173.11, 173.06, 130.9 (t, *J* = 292.4 Hz), 58.6, 53.0, 52.9, 42.2 (t, *J* = 23.7 Hz), 41.4, 38.2, 37.8 (t, *J* = 2.0 Hz), 36.1, 15.1; minor isomer: δ 45.6 (t, *J* = 23.6 Hz), 40.5, 39.9, 31.0, 17.3.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -49.37 (dt, *J* = 160.4, 12.4 Hz, 1F), -50.56 (dt, *J* = 160.4, 13.5 Hz, 1F).

HRMS (ESI): calcd for $C_{12}H_{17}{}^{35}ClF_2O_4Na$ (M+Na) 321.0676, found 321.0673.

B. Isolation of iminium salt

1,3,5-Trimethyl-2,3,4,5-tetrahydro-1,3,5-triazin-1-ium chloride (12)[31]



N1 **12**

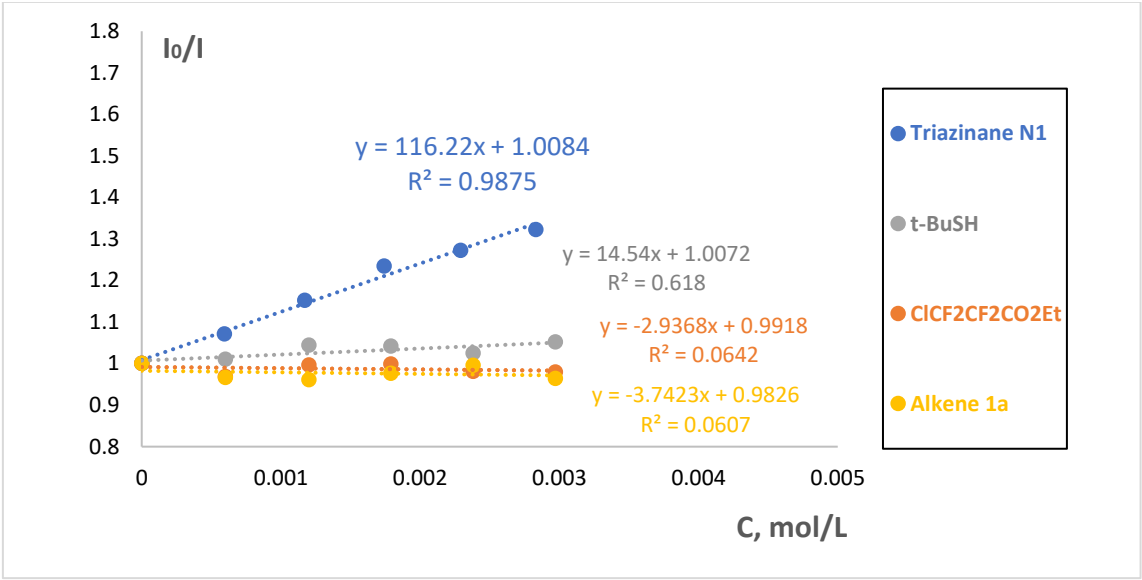
The reaction was performed according to the General procedure A using 2-methylhex-5-en-3-ol. After irradiation, the mixture was diluted with 2 mL of methyl *tert*-butyl ether, then the precipitate was separated from solution by centrifugation, washed with methyl *tert*-butyl ether (3×1 mL), and dried under vacuum to obtain white powder (160 mg, yield 98%). Mp 199-200 °C.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.66 (s, 1H), 4.21 (s, 4H), 3.22 (s, 6H), 2.49 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 154.2, 66.9, 40.23, 39.5.

Stern-Volmer study

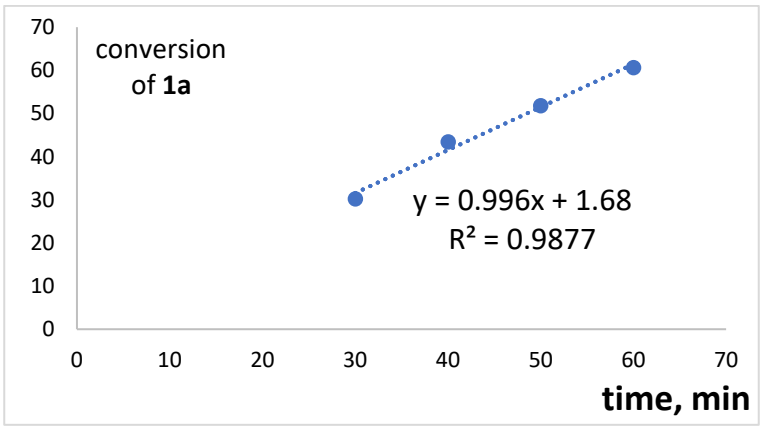
Experiments were performed in a screw-capped quartz vial (10×10 mm). The solvent was degassed, and the vial was filled with argon. The concentration of 4CzIPN was 0.1 mmol/L. Excitation wavelength 435 nm, fluorescence wavelength 548 nm. Measurements were performed at room temperature.



C. Quantum yield measurement

Quantum yield for the reaction of 4-phenyl-1-butene (**1a**) with $Cl(CF_2)_2CO_2Et$ was estimated using irradiation with a 870 mW purple LED strip (400 nm), setup and reaction tube were used as for the reactions in General procedures A and B. Photon flux of the LED strip was measured by standard ferrioxalate actinometry – 11,203μEs/min. A mixture of **1a** (66 mg, 0.5 mmol), triazinane **N1** (129 mg, 1 mmol), $Cl(CF_2)_2CO_2Et$ (144 mg, 0.875 mmol), 4CzIPN (2 mg, 5μmol) and 37 mg of tetralin (internal standard) in acetonitrile (1 mL) was placed in a reaction tube. At 400 nm, the reaction mixture completely absorbs the laser light. The tube was irradiated for 60minutes, and every 10 minutes the mixture was analyzed by GC. The quantum yield Φ was calculated by the following equation:

$$\phi = \frac{conversion(\%) \cdot n_0(\mathbf{1a})}{t \cdot photon\ flux \cdot 100\%} = \frac{0{,}996 \cdot 0{,}5 \cdot 10^{-3}}{1 \cdot 11{,}203 \cdot 10^{-6} \cdot 100} = 0{,}44$$



Quantum chemical calculations

General

Calculations were carried out using the Gaussian09 package[32] using uwB97XD/def2svp method. For calculations in solution, CPCM model[33,34] (acetonitrile) was used.

All stationary points were verified by vibrational analysis; Gibbs free energies from the frequency calculations with the CPCM model were used uncorrected. Transition states were subjected to IRC calculations in forward and reverse directions.

NBO analysis[35] was used to analyze interactions via second-order perturbation theory; for open-shell systems, $CHOOSE keylist was used with LONE and BOND specifications for both alpha and beta spins.

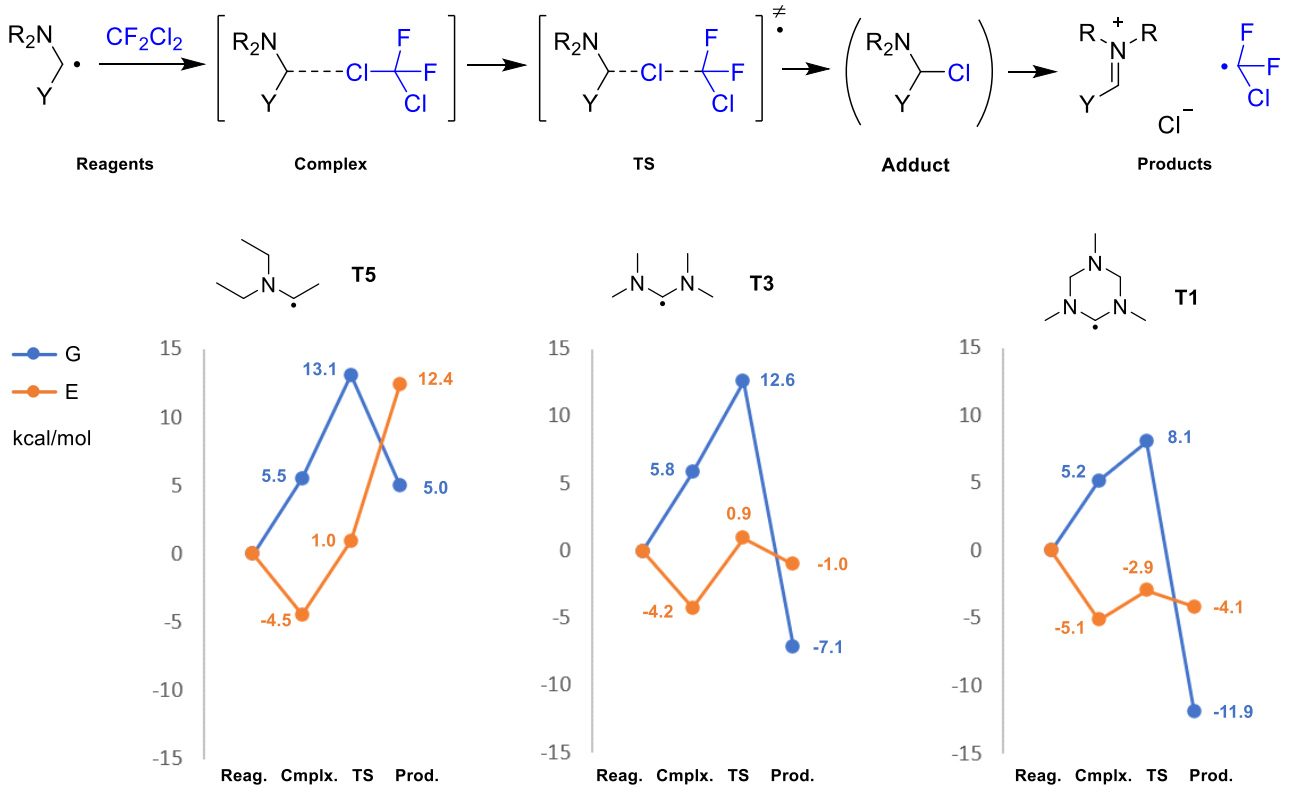
Discussion

For reactions of amino-substituted radicals **T5**, **T3** and **T1**, the reaction paths from TS to reagents and products were analyzed.

On potential energy surfaces, pre-activation complexes were identified with very long C…Cl bond (2.95 – 3.0 Å) with virtually unperturbed geometries of amino-alkyl radicals and CF_2Cl_2. However, these complexes were not the minima on Gibbs free energy surfaces (Figures S1).

Optimization of final adducts in acetonitrile solution for reactions of **T3** and **T1** was problematic, resulting in dissociation of the C-Cl bond and formation of iminium ions (this is the same as was observed in the literature[36,37]). Correspondingly, for direct comparison, iminium ions were calculated to allow the direct comparison of reactions of **T5**, **T3** and **T1**.

Figure S1. Gibbs free energy (G) and potential energy (E) surfaces, in kcal/mol.



For radical **T3**, the rotation around the C-N bonds was evaluated. Relaxed potential energy scan was performed by variation of the dihedral angle C3 N18 N17 C1 (Figure S1, Table S1). Energies of interactions of nitrogen lone pairs with the adjacent carbon orbital derived from second order perturbation theory analysis are given (Figure S2, Table S1). For NBO calculations, $CHOOSE keylist was used with specifications: LONE for nitrogens and central carbon; BOND (S) for all single bonds.

Figure S1. Relaxed potential energy scan.

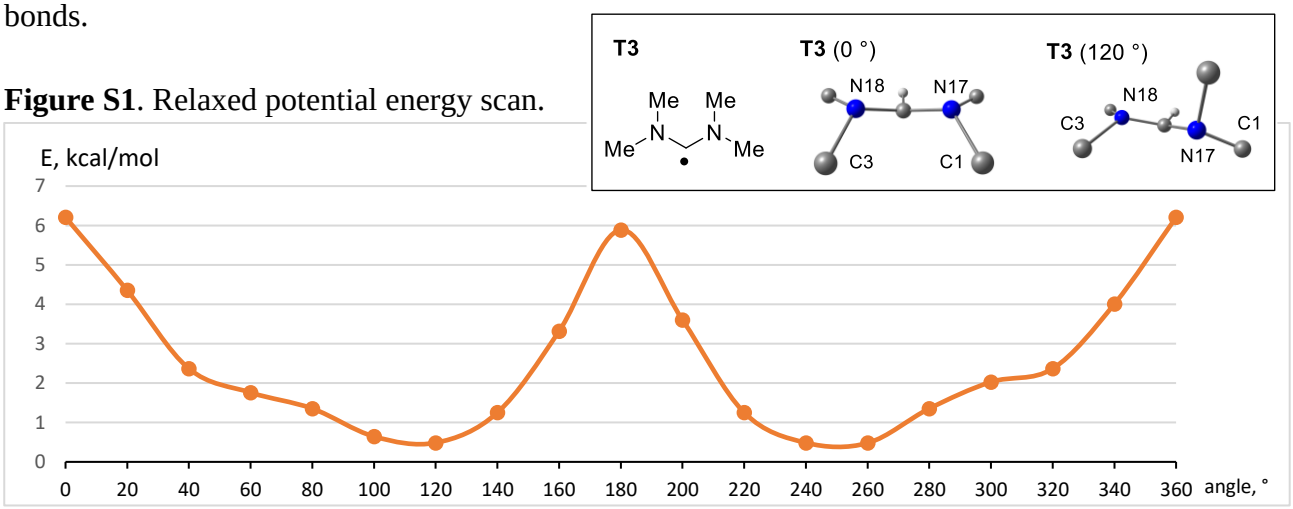


Figure S2.

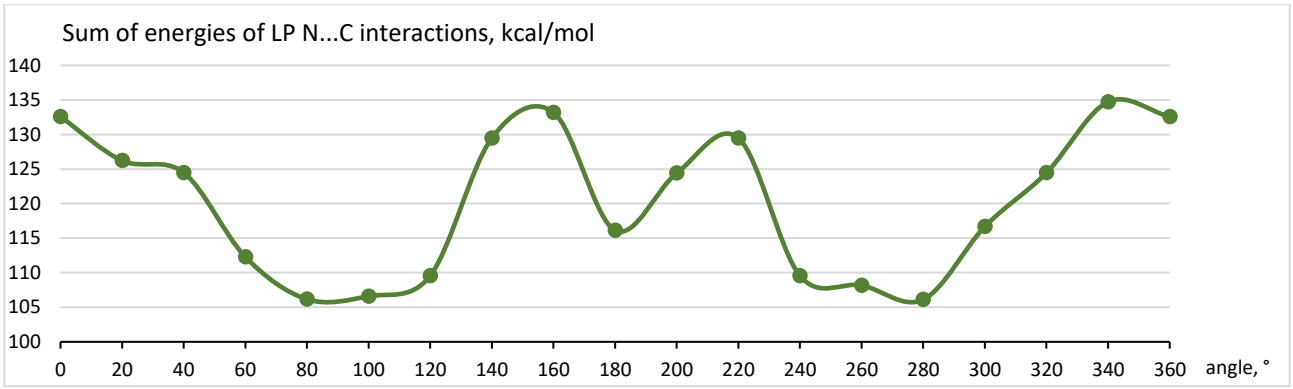


Table S1. Energies of conformers, and energies obtained from NBO analysis.

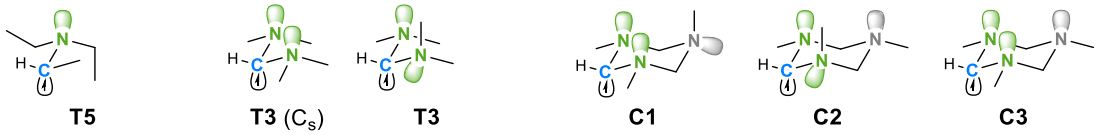
Angle, °	E,[a] kcal/mol	E, a.u.	Energy (kcal/mol) LP (N18)...LP*(C2)	Energy (kcal/mol) LP (N17)...LP*(C2)	Sum of lone pair interactions, kcal/mol
0	5.8	-307.4636585	65.7	66.9	132.6
20	3.9	-307.4666111	77.5	48.7	126.2
40	1.9	-307.4697777	91.1	33.3	124.5
60	1.3	-307.4707451	104.2	8.1	112.3
80	0.9	-307.4713916	104.8	1.4	106.2
100	0.2	-307.4725205	97.5	9.1	106.6
120	0.0	-307.4727755	92.8	16.8	109.6
140	0.8	-307.4715545	89.3	40.2	129.5
160	2.9	-307.4682631	86.3	46.9	133.2
180	5.4	-307.4641652	46.8	69.3	116.1
200	3.2	-307.4678062	44.4	80.0	124.4
220	0.8	-307.4715545	40.3	89.2	129.5
240	0.0	-307.4727755	16.7	92.8	109.6
260	0.0	-307.4727859	13.0	95.2	108.2
280	0.9	-307.4713916	1.4	104.7	106.1
300	1.6	-307.4703166	15.3	101.4	116.7
320	1.9	-307.4697777	33.4	91.1	124.5
340	3.6	-307.4671631	35.5	99.2	134.7
360	5.8	-307.4636585	65.7	66.9	132.6
Optimized structure, **T3**					
114	**0.0**	**-307.4728318**	93.9	14.6	108.5

[a] Energies of conformers are given relative to that of the optimized structure **T3**.

NBO analysis

To evaluate interaction of nitrogen lone pair(s) with the adjacent carbon orbital NBO analysis was performed. For optimized geometries, $CHOOSE keylist was used with specifications (using pop=nboread keyword): LONE for nitrogen and carbon; BOND (S) for all single bonds.
Energies obtained from second order perturbation theory analysis are summarized in Table S2.

Table S2. Energies of N…C interactions, in kcal/mol



Structure	Energy LP (N1)…LP*(C)	Energy LP (N2)…LP*(C)	Sum of lone pair interactions
T5	104.7	-	**104.7**
T3 (C_s)[a]	66.5	66.5	**133.1**
T3	93.9	14.6	**108.5**
C1	70.5	70.5	**141.0**
C2	89.2	31.8	**121.1**
C3	70.1	70.1	**140.3**

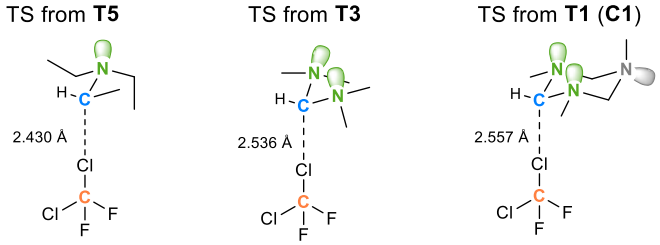
[a] Constrained with C_s symmetry.

The following conclusions can be drawn concerning the nitrogen lone pair and a carbon radical:

a. Triazinane conformer **C1** has the strongest stabilization by nitrogen lone pairs.
b. From **T5** to **T3** interaction energy increases insignificantly.
c. Interaction is maximized when nitrogen lone pair and singly occupied orbital have *anti-periplanar* arrangement – cf. **T3**-C_s vs **T3**, and **C1** vs **C2**

For analysis of transition states, the following $CHOOSE specification was used: LONE for N, C adjacent to nitrogen(s), Cl, F; BOND (S) for all single bonds and breaking C-Cl bond. This gave energies of interaction of nitrogen lone pair(s) with the adjacent carbon orbital and energies of interaction of carbon orbital with the breaking C-Cl bond Energies are summarized in Table S3.

Table S3. Energies of N…C interactions, in kcal/mol



TS	Energy LP (N1)…LP*(C)	Energy LP (N2)…LP*(C)	Sum of lone pair interactions	Energy LP (C) … BD* (Cl-C)
From **T5**	154.8	-	154.8	**95.2**
From **T3**	113.8	63.2	177.0	**47.9**
From **T1 (C1)**	89.2	89.1	178.2	**40.9**

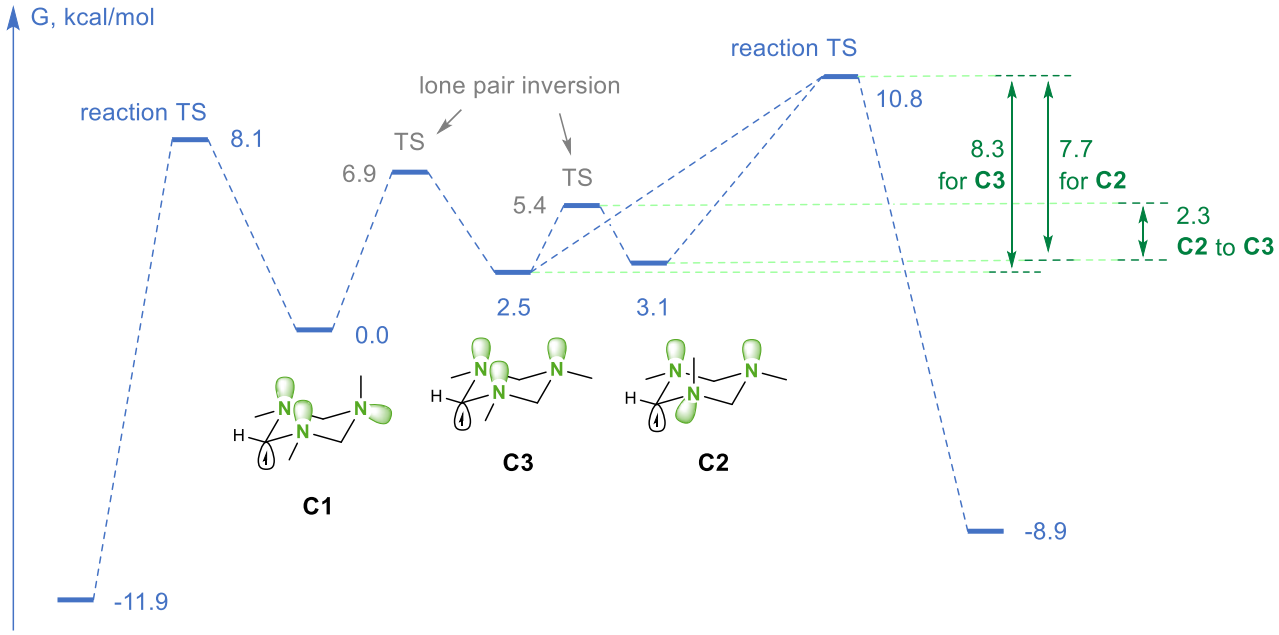
The following conclusions can be drawn:

a. Triazinane **T1** has the strongest TS stabilization by nitrogen lone pairs.
b. Lone pair interactions in transition states from **T3** and **T1** differ insignificantly.
c. The interaction between the carbon singly occupied orbital with the C-Cl bond is strongest in **T5** and weakest in **T1**. This stands in accord with the bond distances of forming C…Cl bond (shown in the drawing), thereby reflecting the latest TS for **T5** and earliest TS for **T1**.

Analysis of reactivities of conformers C1, C2 and C3 of triazinane T1.

Conformers **C1**, **C2** and **C3** may intercovert into each other via lone pair inversion (Figure S3). Activation energy for conversion **C1** to **C3** is 6.9 kcal/mol. The less stable **C3** conformer reacts slower (activation energy 8.3 kcal) compared to **C1** (activation energy 8.1). When attempted search for TS for the reaction of **C2**, the nitrogen lone pair inversion proceeded earlier, which is in accord with the lone pair inversion activation energy of only 2.3 kcal/mol. As a result, for the reaction of **C2**, the same TS as for that of **C3** was located.

Figure S3. Free energy profile of the reaction of conformers **C1-C3**. Relative energies are given with respect to **C1** (taken as 0.0). Energies are given in kcal/mol.

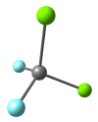


Energies and coordinates

CF_2Cl_2

Gas phase

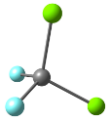
SCF Done: E(RwB97XD)	-1157.634001
Zero-point correction	0.013661
Thermal correction to Energy	0.018328
Thermal correction to Enthalpy	0.019272
Thermal correction to Gibbs Free Energy	-0.015432
Sum of electronic and zero-point Energies	-1157.62034
Sum of electronic and thermal Energies	-1157.615673
Sum of electronic and thermal Enthalpies	-1157.614729
Sum of electronic and thermal Free Energies	-1157.649433



6	-0.000287000	0.345473000	0.000000000
9	-0.000201000	1.119597000	-1.070913000
9	-0.000200000	1.119595000	1.070915000
17	1.462023000	-0.653530000	-0.000001000
17	-1.461710000	-0.653857000	0.000000000

In MeCN

SCF Done: E(RwB97XD)	-1157.634714
Zero-point correction	0.013410
Thermal correction to Energy	0.018096
Thermal correction to Enthalpy	0.01904
Thermal correction to Gibbs Free Energy	-0.015692
Sum of electronic and zero-point Energies	-1157.621305
Sum of electronic and thermal Energies	-1157.616618
Sum of electronic and thermal Enthalpies	-1157.615674
Sum of electronic and thermal Free Energies	-1157.650406

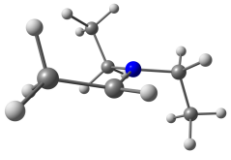


6	-0.000287000	0.345473000	0.000000000
9	-0.000200000	1.119597000	-1.070913000
9	-0.000199000	1.119595000	1.070915000
17	1.462023000	-0.653530000	-0.000001000
17	-1.461710000	-0.653856000	0.000000000

Et_2NCHMe radical (**T5**)

Gas phase

SCF Done: E(UwB97XD)	-291.468625
Zero-point correction	0.193305
Thermal correction to Energy	0.202886
Thermal correction to Enthalpy	0.20383
Thermal correction to Gibbs Free Energy	0.158125
Sum of electronic and zero-point Energies	-291.27532
Sum of electronic and thermal Energies	-291.265739
Sum of electronic and thermal Enthalpies	-291.264795
Sum of electronic and thermal Free Energies	-291.3105

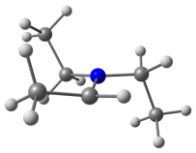


7	-0.133093000	-0.053150000	-0.203693000
6	0.465745000	1.024361000	0.562608000

1	-0.334398000	1.707771000	0.891475000
1	0.908904000	0.624647000	1.490015000
6	-1.497318000	0.132778000	-0.650794000
1	-1.599954000	1.159891000	-1.039745000
1	-1.669922000	-0.535474000	-1.510317000
6	0.345220000	-1.355214000	-0.099003000
1	-0.210173000	-2.070606000	-0.714459000
6	1.511264000	1.813362000	-0.220518000
1	1.917600000	2.636761000	0.387110000
1	2.346376000	1.165853000	-0.524566000
1	1.069979000	2.243602000	-1.132321000
6	-2.554626000	-0.128452000	0.421747000
1	-3.568357000	0.005133000	0.014455000
1	-2.463574000	-1.155526000	0.805228000
1	-2.438436000	0.560980000	1.272439000
6	1.794886000	-1.625789000	0.134233000
1	1.952813000	-2.703453000	0.284154000
1	2.439718000	-1.317130000	-0.716207000
1	2.190048000	-1.116680000	1.028944000

In MeCN

SCF Done: E(UwB97XD)	-291.4706986
Zero-point correction	0.193004
Thermal correction to Energy	0.202558
Thermal correction to Enthalpy	0.203502
Thermal correction to Gibbs Free Energy	0.158199
Sum of electronic and zero-point Energies	-291.277695
Sum of electronic and thermal Energies	-291.268141
Sum of electronic and thermal Enthalpies	-291.267197
Sum of electronic and thermal Free Energies	-291.312499



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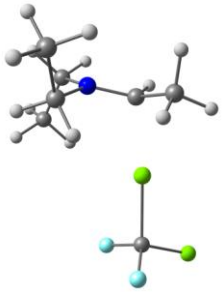
1	0.928826000	0.630240000	1.485754000
6	-1.493473000	0.114850000	-0.650545000
1	-1.597191000	1.140708000	-1.040937000
1	-1.658276000	-0.557447000	-1.508176000
6	0.362894000	-1.359537000	-0.090199000
1	-0.181891000	-2.076217000	-0.715152000
6	1.472738000	1.840035000	-0.227955000
1	1.867311000	2.670544000	0.377274000
1	2.319904000	1.214404000	-0.545751000
1	1.005993000	2.264563000	-1.129913000
6	-2.556511000	-0.145711000	0.415837000
1	-3.566173000	-0.006497000	0.001031000
1	-2.475441000	-1.175464000	0.795428000
1	-2.442721000	0.542379000	1.267905000
6	1.820432000	-1.610833000	0.128776000
1	1.996103000	-2.686979000	0.272048000
1	2.451978000	-1.289514000	-0.726853000
1	2.217960000	-1.097227000	1.019726000

Et_2NCHMe radical (**T5**) + CF_2Cl_2, transition state

Gas phase

SCF Done: E(UwB97XD)	-1449.09595
Zero-point correction	0.208805
Thermal correction to Energy	0.224225
Thermal correction to Enthalpy	0.22517
Thermal correction to Gibbs Free Energy	0.162934
Sum of electronic and zero-point Energies	-1448.887146
Sum of electronic and thermal Energies	-1448.871725
Sum of electronic and thermal Enthalpies	-1448.870781
Sum of electronic and thermal Free Energies	-1448.933016



7	2.390743000	0.145430000	-0.349846000
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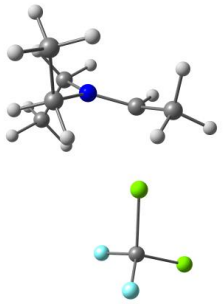
1	2.824539000	0.894401000	1.539058000
1	1.998101000	-0.650211000	1.544293000
6	2.540338000	1.499126000	-0.867978000
1	3.563190000	1.836615000	-0.630770000
1	2.480859000	1.442892000	-1.965442000
6	1.575061000	-0.728431000	-0.990056000
1	1.373453000	-0.445295000	-2.027346000
6	4.141765000	-0.774229000	1.166057000
1	4.411288000	-0.887541000	2.226475000
1	4.125461000	-1.774247000	0.710220000
1	4.932718000	-0.189735000	0.672495000
6	1.516576000	2.501719000	-0.341240000
1	1.684368000	3.484211000	-0.806511000
1	0.492940000	2.170408000	-0.560839000
1	1.599976000	2.629890000	0.748403000
6	1.673506000	-2.202549000	-0.733854000
1	0.851836000	-2.719028000	-1.244821000
1	2.629850000	-2.594284000	-1.123401000
1	1.609300000	-2.448737000	0.334957000
6	-2.527893000	0.129154000	0.460135000
17	-0.572748000	-0.353460000	-0.300347000
17	-3.823648000	-0.402717000	-0.620406000
9	-2.556590000	1.442370000	0.612013000
9	-2.647264000	-0.438930000	1.646658000

In MeCN

SCF Done: E(UwB97XD)	-1449.103853
Zero-point correction	0.208191
Thermal correction to Energy	0.223713
Thermal correction to Enthalpy	0.224657
Thermal correction to Gibbs Free Energy	0.161802
Sum of electronic and zero-point Energies	-1448.895662
Sum of electronic and thermal Energies	-1448.880141
Sum of electronic and thermal Enthalpies	-1448.879197
Sum of electronic and thermal Free Energies	-1448.942052



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6	2.964057000	-0.092687000	1.005402000
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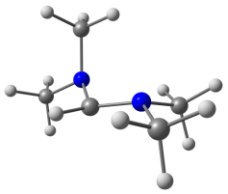
1	2.263621000	-0.707773000	1.589163000
6	2.554677000	1.476637000	-0.878978000
1	3.592147000	1.802016000	-0.701542000

1	2.430738000	1.403230000	-1.969116000
6	1.607079000	-0.760536000	-0.931268000
1	1.353735000	-0.496100000	-1.961589000
6	4.348405000	-0.728934000	0.970046000
1	4.744296000	-0.834469000	1.990498000
1	4.317799000	-1.726648000	0.509827000
1	5.048948000	-0.106343000	0.393852000
6	1.575911000	2.497426000	-0.306406000
1	1.740688000	3.475599000	-0.781036000
1	0.537438000	2.186607000	-0.484162000
1	1.714262000	2.624063000	0.777951000
6	1.670923000	-2.221554000	-0.615135000
1	0.841572000	-2.741361000	-1.110552000
1	2.616006000	-2.654737000	-0.988488000
1	1.606638000	-2.428169000	0.462186000
6	-2.571275000	0.129226000	0.445085000
17	-0.678818000	-0.332197000	-0.226689000
17	-3.858800000	-0.404169000	-0.668728000
9	-2.634287000	1.445367000	0.601642000
9	-2.747799000	-0.435195000	1.632176000

$Me_2NCHNMe_2$ radical (**T3**)

Gas phase



SCF Done: E(UwB97XD)	-307.4706471
Zero-point correction	0.181301
Thermal correction to Energy	0.190764
Thermal correction to Enthalpy	0.191708
Thermal correction to Gibbs Free Energy	0.147151
Sum of electronic and zero-point Energies	-307.289346
Sum of electronic and thermal Energies	-307.279883
Sum of electronic and thermal Enthalpies	-307.278939
Sum of electronic and thermal Free Energies	-307.323496

6	0.001472000	-0.694317000	-0.026445000
1	-0.026070000	-1.642101000	0.541099000
6	-2.293355000	-0.661829000	-0.674812000
1	-2.680711000	-1.440923000	0.019803000
1	-3.124170000	0.026629000	-0.896623000
1	-1.996950000	-1.157536000	-1.609713000
6	-1.518384000	0.855197000	1.042810000
1	-0.627644000	1.392800000	1.395844000
1	-2.295536000	1.595376000	0.793852000
1	-1.895053000	0.227915000	1.880010000
6	2.368274000	-0.737271000	0.457984000
1	2.126125000	-1.453212000	1.256419000
1	2.797179000	-1.302524000	-0.395209000
1	3.146406000	-0.056510000	0.836675000
6	1.434774000	1.088717000	-0.845185000
1	0.483509000	1.584997000	-1.072411000
1	2.131810000	1.823771000	-0.412927000
1	1.868380000	0.717706000	-1.796546000
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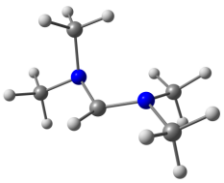
7	1.194503000	0.013674000	0.092833000

In MeCN

SCF Done: E(UwB97XD)	-307.4728318
Zero-point correction	0.180798
Thermal correction to Energy	0.190325
Thermal correction to Enthalpy	0.19127

Thermal correction to Gibbs Free Energy	0.146546
Sum of electronic and zero-point Energies	-307.292034
Sum of electronic and thermal Energies	-307.282506
Sum of electronic and thermal Enthalpies	-307.281562
Sum of electronic and thermal Free Energies	-307.326285



6	-0.003016000	-0.690772000	-0.035434000
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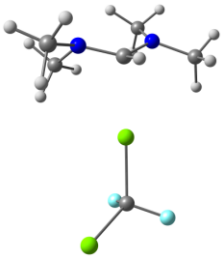
6	-2.307588000	-0.686575000	-0.635679000
1	-2.659794000	-1.446833000	0.096599000
1	-3.154515000	-0.016244000	-0.849962000
1	-2.039169000	-1.210439000	-1.564137000
6	-1.506862000	0.893921000	1.006768000
1	-0.620703000	1.463595000	1.318443000
1	-2.307263000	1.607575000	0.755996000
1	-1.846193000	0.284882000	1.872349000
6	2.360816000	-0.755921000	0.460762000
1	2.108579000	-1.477378000	1.250707000
1	2.788902000	-1.315320000	-0.395911000
1	3.141835000	-0.084220000	0.848011000
6	1.452685000	1.088777000	-0.834566000
1	0.515693000	1.614618000	-1.053510000
1	2.169527000	1.801245000	-0.398528000
1	1.874627000	0.717695000	-1.791016000
7	-1.179460000	0.075907000	-0.152416000
7	1.193187000	0.008910000	0.094236000

$Me_2NCHNMe_2$ radical (**T3**) + CF_2Cl_2, transition state

Gas phase

SCF Done: E(UwB97XD)	-1465.098621
Zero-point correction	0.196631
Thermal correction to Energy	0.212369
Thermal correction to Enthalpy	0.213313
Thermal correction to Gibbs Free Energy	0.150027
Sum of electronic and zero-point Energies	-1464.90199
Sum of electronic and thermal Energies	-1464.886252
Sum of electronic and thermal Enthalpies	-1464.885308
Sum of electronic and thermal Free Energies	-1464.948594

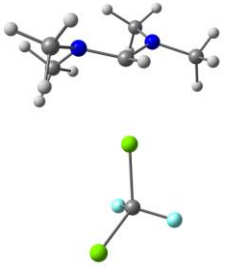


6	2.465013000	-0.419352000	0.179719000
9	2.587028000	-0.630408000	1.480695000
9	2.884668000	-1.498548000	-0.460118000
17	3.431080000	0.993613000	-0.300700000
17	0.427067000	-0.167807000	-0.235405000
6	-1.954960000	0.109638000	-0.631121000
1	-1.756514000	0.167149000	-1.705423000
6	-1.812842000	1.565718000	1.337350000
1	-0.796354000	1.997557000	1.343951000
1	-2.506074000	2.263802000	1.831185000
1	-1.769913000	0.640974000	1.919917000
6	-2.087303000	2.474380000	-0.881263000
1	-2.604526000	2.327560000	-1.839029000
1	-2.529691000	3.353356000	-0.391042000
1	-1.018247000	2.685850000	-1.077822000
6	-2.073606000	-2.270672000	-0.875810000
1	-1.811750000	-2.072086000	-1.924721000
1	-1.169048000	-2.657211000	-0.373391000
1	-2.859450000	-3.039460000	-0.852550000
6	-3.218025000	-1.214187000	1.020211000

1	-3.771867000	-0.298203000	1.264287000
1	-3.938948000	-2.041775000	0.949161000
1	-2.516950000	-1.445391000	1.845431000
7	-2.254729000	1.313084000	-0.027814000
7	-2.558710000	-1.060706000	-0.251598000

In MeCN

SCF Done: E(UwB97XD)	-1465.106057
Zero-point correction	0.195903
Thermal correction to Energy	0.211571
Thermal correction to Enthalpy	0.212516
Thermal correction to Gibbs Free Energy	0.149448
Sum of electronic and zero-point Energies	-1464.910154
Sum of electronic and thermal Energies	-1464.894486
Sum of electronic and thermal Enthalpies	-1464.893542
Sum of electronic and thermal Free Energies	-1464.956609

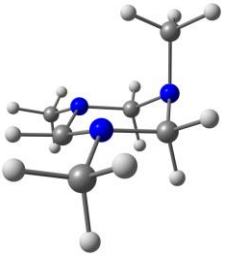


6	2.456129000	-0.407527000	0.177604000
9	2.612540000	-0.619748000	1.477790000
9	2.885377000	-1.484826000	-0.466489000
17	3.433179000	1.005472000	-0.311486000
17	0.524457000	-0.165885000	-0.195664000
6	-1.959888000	0.099833000	-0.630367000
1	-1.738039000	0.155252000	-1.701105000
6	-1.866495000	1.572325000	1.333074000
1	-0.851729000	2.011163000	1.353993000
1	-2.564404000	2.277152000	1.809401000
1	-1.840002000	0.655134000	1.929683000
6	-2.162494000	2.466264000	-0.891697000
1	-2.666994000	2.295578000	-1.852009000
1	-2.637042000	3.331652000	-0.407465000
1	-1.102097000	2.722024000	-1.086847000
6	-2.071227000	-2.287376000	-0.873555000
1	-1.781198000	-2.086761000	-1.914759000
1	-1.187720000	-2.692423000	-0.346806000
1	-2.861826000	-3.051116000	-0.874233000
6	-3.259327000	-1.228384000	0.996396000
1	-3.824075000	-0.314300000	1.221607000
1	-3.972012000	-2.060985000	0.909484000
1	-2.582643000	-1.450644000	1.844088000
7	-2.290444000	1.303506000	-0.033790000
7	-2.562623000	-1.076985000	-0.256768000

Triazinane radical (**T1**), structure **C1**

Gas phase

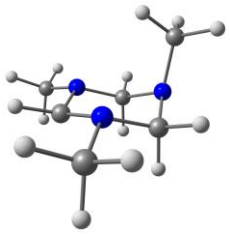
SCF Done: E(UwB97XD)	-400.8345676
Zero-point correction	0.208238
Thermal correction to Energy	0.217813
Thermal correction to Enthalpy	0.218757
Thermal correction to Gibbs Free Energy	0.173829
Sum of electronic and zero-point Energies	-400.626329
Sum of electronic and thermal Energies	-400.616755
Sum of electronic and thermal Enthalpies	-400.61581
Sum of electronic and thermal Free Energies	-400.660739



6	-0.145415000	0.927929000	1.174509000
6	-0.605226000	-1.112644000	0.000000000
6	-0.145415000	0.927929000	-1.174509000
1	-0.618700000	-2.209676000	0.000000000
1	-1.185253000	1.322749000	1.192452000
1	0.367890000	1.290082000	2.079121000
1	0.367890000	1.290082000	-2.079121000
1	-1.185253000	1.322749000	-1.192452000
6	-0.657461000	-1.115080000	2.404467000
1	-0.513087000	-2.205793000	2.383490000
1	-0.105547000	-0.719670000	3.270911000
1	-1.738481000	-0.918066000	2.562527000
6	-0.657461000	-1.115080000	-2.404467000
1	-0.105547000	-0.719670000	-3.270911000
1	-0.513087000	-2.205793000	-2.383490000
1	-1.738481000	-0.918066000	-2.562527000
7	0.510626000	1.439402000	0.000000000
7	-0.145415000	-0.529012000	1.193009000
7	-0.145415000	-0.529012000	-1.193009000
6	1.947919000	1.226355000	0.000000000
1	2.387624000	1.703603000	-0.888413000
1	2.387624000	1.703603000	0.888413000
1	2.232183000	0.157768000	0.000000000

In MeCN

SCF Done: E(UwB97XD)	-400.8389468
Zero-point correction	0.207911
Thermal correction to Energy	0.217506
Thermal correction to Enthalpy	0.21845
Thermal correction to Gibbs Free Energy	0.17348
Sum of electronic and zero-point Energies	-400.631036
Sum of electronic and thermal Energies	-400.621441
Sum of electronic and thermal Enthalpies	-400.620496
Sum of electronic and thermal Free Energies	-400.665467

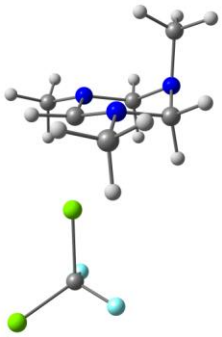


6	-0.142747000	0.924939000	1.176993000
6	-0.610409000	-1.112219000	0.000000000
6	-0.142747000	0.924939000	-1.176993000
1	-0.639394000	-2.209288000	0.000000000
1	-1.183513000	1.316333000	1.198543000
1	0.371161000	1.285614000	2.081119000
1	0.371161000	1.285614000	-2.081119000
1	-1.183513000	1.316333000	-1.198543000
6	-0.659213000	-1.117095000	2.406841000
1	-0.523858000	-2.208699000	2.385267000
1	-0.106461000	-0.723440000	3.272854000
1	-1.738027000	-0.910194000	2.563616000
6	-0.659213000	-1.117095000	-2.406841000
1	-0.106461000	-0.723440000	-3.272854000
1	-0.523858000	-2.208699000	-2.385267000
1	-1.738027000	-0.910194000	-2.563616000
7	0.509851000	1.441247000	0.000000000
7	-0.142747000	-0.533239000	1.192780000
7	-0.142747000	-0.533239000	-1.192780000
6	1.949811000	1.239744000	0.000000000
1	2.386883000	1.716967000	-0.889497000
1	2.386883000	1.716967000	0.889497000
1	2.243634000	0.173465000	0.000000000

Triazinane radical (**T1**) [structure **C1**] + CF_2Cl_2, transition state

Gas phase

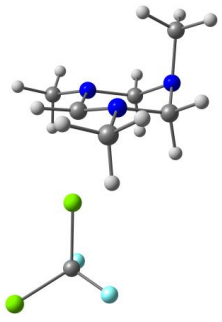
SCF Done: E(UwB97XD)	-1558.470883
Zero-point correction	0.222566
Thermal correction to Energy	0.238556
Thermal correction to Enthalpy	0.2395
Thermal correction to Gibbs Free Energy	0.176256
Sum of electronic and zero-point Energies	-1558.248318
Sum of electronic and thermal Energies	-1558.232327
Sum of electronic and thermal Enthalpies	-1558.231383
Sum of electronic and thermal Free Energies	-1558.294628



6	2.241759000	-1.191710000	0.767532000
6	1.393942000	0.040608000	-1.102167000
6	2.233521000	1.155184000	0.844440000
1	1.091707000	0.074392000	-2.152770000
1	1.308579000	-1.246142000	1.361574000
1	2.829765000	-2.101200000	0.959996000
1	2.816704000	2.053815000	1.094531000
1	1.301353000	1.165445000	1.442590000
6	1.334298000	-2.361989000	-1.201724000
1	1.216494000	-2.262045000	-2.289920000
1	2.009089000	-3.208117000	-1.006510000
1	0.342083000	-2.579765000	-0.765866000
6	1.313538000	2.443591000	-1.043965000
1	1.978123000	3.281594000	-0.788167000
1	1.201601000	2.417026000	-2.137109000
1	0.317151000	2.621108000	-0.599181000
7	2.985142000	-0.027237000	1.159246000
7	1.909009000	-1.153641000	-0.657929000
7	1.898911000	1.207434000	-0.580300000
17	-0.934569000	-0.000974000	-0.274626000
6	-2.825150000	-0.065253000	0.537451000
9	-2.905240000	0.883313000	1.456701000
9	-2.970104000	-1.237970000	1.133335000
17	-4.095359000	0.159709000	-0.684161000
6	4.350149000	-0.005265000	0.662107000
1	4.874605000	0.868338000	1.075661000
1	4.878745000	-0.905829000	1.006725000
1	4.417106000	0.037896000	-0.441662000

In MeCN

SCF Done: E(UwB97XD)	-1558.478337
Zero-point correction	0.221739
Thermal correction to Energy	0.237786
Thermal correction to Enthalpy	0.238731
Thermal correction to Gibbs Free Energy	0.175316
Sum of electronic and zero-point Energies	-1558.256599
Sum of electronic and thermal Energies	-1558.240551
Sum of electronic and thermal Enthalpies	-1558.239607
Sum of electronic and thermal Free Energies	-1558.303021



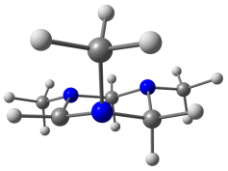
6	2.275157000	-1.193733000	0.763624000
6	1.390264000	0.040500000	-1.093774000
6	2.267707000	1.157711000	0.840790000
1	1.087497000	0.074520000	-2.145011000
1	1.354041000	-1.250322000	1.377938000

1	2.865748000	-2.102877000	0.947023000
1	2.854285000	2.056102000	1.081712000
1	1.347906000	1.169831000	1.459671000
6	1.356086000	-2.369249000	-1.195819000
1	1.215566000	-2.263520000	-2.280600000
1	2.047274000	-3.205551000	-1.018299000
1	0.377815000	-2.615568000	-0.741964000
6	1.335194000	2.450591000	-1.037294000
1	2.013532000	3.281093000	-0.795115000
1	1.205303000	2.419563000	-2.128189000
1	0.349845000	2.652217000	-0.576418000
7	3.023679000	-0.027021000	1.148481000
7	1.919531000	-1.154813000	-0.654034000
7	1.909977000	1.208571000	-0.576139000
17	-1.014159000	-0.003584000	-0.224454000
6	-2.822359000	-0.065531000	0.528871000
9	-2.931877000	0.880884000	1.451103000
9	-2.994489000	-1.238389000	1.122996000
17	-4.086163000	0.163417000	-0.709143000
6	4.381011000	-0.004544000	0.625496000
1	4.912235000	0.870594000	1.026556000
1	4.915461000	-0.906584000	0.956510000
1	4.425602000	0.039269000	-0.479086000

Triazinane radical (**T1**), structure **C2**

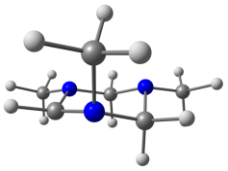
Gas phase

SCF Done: E(UwB97XD)	-400.8287094
Zero-point correction	0.208021
Thermal correction to Energy	0.217499
Thermal correction to Enthalpy	0.218444
Thermal correction to Gibbs Free Energy	0.173688
Sum of electronic and zero-point Energies	-400.620689
Sum of electronic and thermal Energies	-400.61121
Sum of electronic and thermal Enthalpies	-400.610266
Sum of electronic and thermal Free Energies	-400.655022



6	1.185706000	0.477854000	0.688181000
6	-0.184091000	-1.295409000	-0.082277000
6	-1.120142000	0.862931000	0.485462000
1	-0.298531000	-2.066257000	-0.863115000
1	1.093265000	0.115556000	1.737507000
1	2.174861000	0.947776000	0.576210000
1	-1.971208000	1.546529000	0.399136000
1	-0.226275000	-1.823819000	0.911460000
7	0.153833000	1.451564000	0.453390000
7	1.084203000	-0.629135000	-0.252858000
7	-1.283428000	-0.360703000	-0.189204000
6	0.408995000	2.330491000	-0.679759000
1	0.457804000	1.781325000	-1.639121000
1	-0.392324000	3.080612000	-0.747072000
1	1.359503000	2.866427000	-0.531768000
6	2.194504000	-1.544268000	-0.181935000
1	2.091930000	-2.326275000	-0.949920000
1	3.135589000	-1.007417000	-0.374376000
1	2.287979000	-2.049520000	0.806185000
6	-2.581668000	-0.977327000	-0.092133000
1	-3.363457000	-0.226846000	-0.278336000
1	-2.679715000	-1.765823000	-0.854104000
1	-2.771506000	-1.429980000	0.902779000

In MeCN

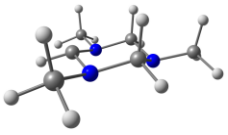


SCF Done: E(UwB97XD)	-400.8339684
Zero-point correction	0.207824
Thermal correction to Energy	0.217305
Thermal correction to Enthalpy	0.21825
Thermal correction to Gibbs Free Energy	0.173485
Sum of electronic and zero-point Energies	-400.626145
Sum of electronic and thermal Energies	-400.616663
Sum of electronic and thermal Enthalpies	-400.615719
Sum of electronic and thermal Free Energies	-400.660484

6	1.191168000	0.472023000	0.681029000
6	-0.187098000	-1.298517000	-0.073149000
6	-1.120489000	0.865573000	0.479875000
1	-0.308503000	-2.081562000	-0.839417000
1	1.104279000	0.103644000	1.728755000
1	2.180076000	0.940739000	0.567612000
1	-1.965553000	1.554839000	0.374074000
1	-0.224192000	-1.809429000	0.927925000
7	0.158032000	1.451737000	0.456243000
7	1.081104000	-0.632817000	-0.261577000
7	-1.284640000	-0.359905000	-0.188996000
6	0.415618000	2.341556000	-0.669837000
1	0.464151000	1.801432000	-1.634550000
1	-0.384774000	3.092827000	-0.734211000
1	1.368225000	2.872253000	-0.519375000
6	2.191904000	-1.553183000	-0.184453000
1	2.083608000	-2.342201000	-0.943782000
1	3.133955000	-1.020132000	-0.380765000
1	2.281623000	-2.047197000	0.808113000
6	-2.588351000	-0.972753000	-0.093663000
1	-3.367067000	-0.220044000	-0.282373000
1	-2.685539000	-1.763834000	-0.852039000
1	-2.778270000	-1.422624000	0.901532000

Triazinane radical (**T1**), structure **C3**

Gas phase



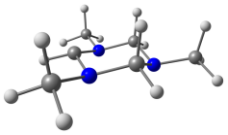
SCF Done: E(UwB97XD)	-400.8276441
Zero-point correction	0.207322
Thermal correction to Energy	0.217054
Thermal correction to Enthalpy	0.217998
Thermal correction to Gibbs Free Energy	0.172714
Sum of electronic and zero-point Energies	-400.620322
Sum of electronic and thermal Energies	-400.61059
Sum of electronic and thermal Enthalpies	-400.609646
Sum of electronic and thermal Free Energies	-400.654931

6	0.432594000	0.543622000	1.188199000
6	0.432594000	0.543622000	-1.188199000
6	-0.579510000	-1.273005000	0.000000000
1	0.257301000	1.176858000	-2.073096000
1	1.479265000	0.133795000	1.271389000
1	0.257301000	1.176858000	2.073096000
1	-1.312591000	-2.088482000	0.000000000
1	1.479265000	0.133795000	-1.271389000

7	-0.530012000	-0.531125000	1.189484000
7	0.288917000	1.348097000	0.000000000
7	-0.530012000	-0.531125000	-1.189484000
6	-0.530012000	-1.310324000	2.401079000
1	-0.708697000	-0.653565000	3.266147000
1	-1.342753000	-2.050422000	2.367357000
1	0.422278000	-1.856181000	2.568099000
6	1.161026000	2.494844000	0.000000000
1	0.966411000	3.113586000	-0.888827000
1	0.966411000	3.113586000	0.888827000
1	2.242664000	2.228788000	0.000000000
6	-0.530012000	-1.310324000	-2.401079000
1	-1.342753000	-2.050422000	-2.367357000
1	-0.708697000	-0.653565000	-3.266147000
1	0.422278000	-1.856181000	-2.568099000

In MeCN

SCF Done: E(UwB97XD)	-400.8340324
Zero-point correction	0.207155
Thermal correction to Energy	0.216871
Thermal correction to Enthalpy	0.217815
Thermal correction to Gibbs Free Energy	0.172595
Sum of electronic and zero-point Energies	-400.626878
Sum of electronic and thermal Energies	-400.617162
Sum of electronic and thermal Enthalpies	-400.616217
Sum of electronic and thermal Free Energies	-400.661437

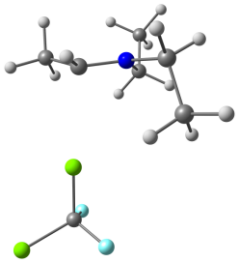


6	0.440027000	0.538474000	1.186782000
6	0.440027000	0.538474000	-1.186782000
6	-0.594469000	-1.265311000	0.000000000
1	0.288060000	1.168377000	-2.077404000
1	1.477952000	0.109407000	1.254609000
1	0.288060000	1.168377000	2.077404000
1	-1.323979000	-2.084292000	0.000000000
1	1.477952000	0.109407000	-1.254609000
7	-0.543789000	-0.521627000	1.190336000
7	0.296095000	1.349998000	0.000000000
7	-0.543789000	-0.521627000	-1.190336000
6	-0.543789000	-1.306172000	2.403070000
1	-0.711007000	-0.650465000	3.270409000
1	-1.359843000	-2.042302000	2.370650000
1	0.406997000	-1.855279000	2.561737000
6	1.195387000	2.481645000	0.000000000
1	1.015844000	3.102280000	-0.890133000
1	1.015844000	3.102280000	0.890133000
1	2.267987000	2.187417000	0.000000000
6	-0.543789000	-1.306172000	-2.403070000
1	-1.359843000	-2.042302000	-2.370650000
1	-0.711007000	-0.650465000	-3.270409000
1	0.406997000	-1.855279000	-2.561737000

Et_2NCHMe radical (**T5**) + CF_2Cl_2, complex

In MeCN

SCF Done: E(UwB97XD)	-1449.112516
Zero-point correction	0.207129
Thermal correction to Energy	0.22351
Thermal correction to Enthalpy	0.224454
Thermal correction to Gibbs Free Energy	0.158447
Sum of electronic and zero-point Energies	-1448.905386
Sum of electronic and thermal Energies	-1448.889005
Sum of electronic and thermal Enthalpies	-1448.888061
Sum of electronic and thermal Free Energies	-1448.954068

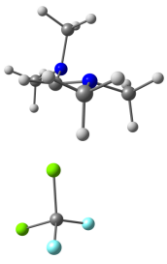


7	2.576591000	0.136377000	-0.294191000
6	2.593925000	-0.263160000	1.103608000
1	2.553742000	0.645956000	1.725157000
1	1.674810000	-0.823172000	1.340392000
6	2.904458000	1.517792000	-0.590176000
1	3.749243000	1.813772000	0.052976000
1	3.275838000	1.570976000	-1.626524000
6	1.869887000	-0.594181000	-1.235800000
1	1.903323000	-0.154588000	-2.238699000
6	3.824194000	-1.081774000	1.482093000
1	3.813573000	-1.324589000	2.555654000
1	3.859775000	-2.024891000	0.917137000
1	4.746453000	-0.520730000	1.266825000
6	1.746097000	2.497199000	-0.408741000
1	2.072798000	3.526422000	-0.620157000
1	0.917346000	2.248662000	-1.087940000
1	1.357972000	2.467534000	0.621249000
6	1.781193000	-2.084353000	-1.142552000
1	1.093375000	-2.465463000	-1.911356000
1	2.759511000	-2.584590000	-1.299057000
1	1.400794000	-2.431474000	-0.167702000
6	-2.490875000	0.131094000	0.432862000
17	-0.889480000	-0.129429000	-0.296531000
17	-3.791952000	-0.455895000	-0.621320000
9	-2.666519000	1.424396000	0.659053000
9	-2.556107000	-0.500358000	1.595068000

$Me_2NCHNMe_2$ radical (**T3**) + CF_2Cl_2, complex

In MeCN

SCF Done: E(UwB97XD)	-1465.114267
Zero-point correction	0.195141
Thermal correction to Energy	0.211517
Thermal correction to Enthalpy	0.212462
Thermal correction to Gibbs Free Energy	0.146897
Sum of electronic and zero-point Energies	-1464.919126
Sum of electronic and thermal Energies	-1464.90275
Sum of electronic and thermal Enthalpies	-1464.901805
Sum of electronic and thermal Free Energies	-1464.96737



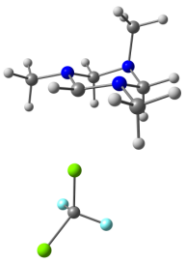
6	-2.605271000	0.236400000	0.167307000
9	-2.793886000	0.454978000	1.459231000
9	-3.036533000	1.297537000	-0.496023000
17	-3.547638000	-1.182708000	-0.325519000

17	-0.869371000	0.008918000	-0.145474000
6	2.099007000	-0.077251000	-0.569200000
1	2.042822000	-0.202942000	-1.665734000
6	2.098646000	-2.407924000	-0.084515000
1	2.334838000	-2.771930000	-1.108901000
1	2.482625000	-3.152946000	0.629259000
1	1.005120000	-2.365704000	0.016464000
6	4.128648000	-1.130501000	0.220987000
1	4.508999000	-0.128362000	0.461260000
1	4.485269000	-1.831026000	0.992098000
1	4.564978000	-1.439013000	-0.753154000
6	1.947696000	2.281842000	-1.057787000
1	2.218242000	2.020966000	-2.090774000
1	0.856769000	2.475371000	-1.023416000
1	2.466691000	3.215525000	-0.794091000
6	2.176667000	1.543345000	1.247171000
1	2.501343000	0.691538000	1.856489000
1	2.780522000	2.424590000	1.511586000
1	1.117816000	1.761085000	1.492101000
7	2.672578000	-1.111120000	0.194887000
7	2.345209000	1.226715000	-0.156168000

Triazinane radical (**T1**) [structure **C1**] + CF_2Cl_2, complex

In MeCN

SCF Done: E(UwB97XD)	-1558.481808
Zero-point correction	0.222074
Thermal correction to Energy	0.238599
Thermal correction to Enthalpy	0.239544
Thermal correction to Gibbs Free Energy	0.174195
Sum of electronic and zero-point Energies	-1558.259734
Sum of electronic and thermal Energies	-1558.243209
Sum of electronic and thermal Enthalpies	-1558.242265
Sum of electronic and thermal Free Energies	-1558.307613



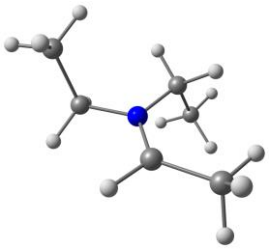
6	-2.268996000	-1.203017000	-0.739538000
6	-1.544851000	0.054286000	1.171650000
6	-2.277328000	1.149622000	-0.833732000
1	-1.364449000	0.098672000	2.252760000
1	-1.289640000	-1.245418000	-1.261937000
1	-2.825313000	-2.119530000	-0.988303000
1	-2.840221000	2.039284000	-1.154763000
1	-1.298261000	1.157195000	-1.358557000
6	-1.485301000	-2.351241000	1.269159000
1	-1.460376000	-2.273584000	2.366134000
1	-2.096338000	-3.226693000	1.003191000
1	-0.449876000	-2.530244000	0.915671000
6	-1.501130000	2.460191000	1.075903000
1	-2.120684000	3.307053000	0.745108000
1	-1.470887000	2.469977000	2.175420000
1	-0.468815000	2.619202000	0.703984000
7	-2.987696000	-0.046148000	-1.210003000
7	-2.071921000	-1.158839000	0.705730000
7	-2.080150000	1.222735000	0.610586000
17	1.228842000	0.005283000	0.173881000
6	2.877256000	-0.065194000	-0.518118000
9	3.007262000	0.875292000	-1.441067000
9	3.058982000	-1.240123000	-1.100919000
17	4.119068000	0.165749000	0.727963000
6	-4.389209000	-0.035472000	-0.823248000
1	-4.887585000	0.833597000	-1.277390000

1	-4.880522000	-0.943533000	-1.202448000
1	-4.541992000	0.010664000	0.270990000

Iminium ion from the reaction of Et_2NCHMe radical **T5**

In MeCN

SCF Done: E(RwB97XD)	-291.3680069
Zero-point correction	0.196995
Thermal correction to Energy	0.206222
Thermal correction to Enthalpy	0.207167
Thermal correction to Gibbs Free Energy	0.163011
Sum of electronic and zero-point Energies	-291.171012
Sum of electronic and thermal Energies	-291.161784
Sum of electronic and thermal Enthalpies	-291.16084
Sum of electronic and thermal Free Energies	-291.204996

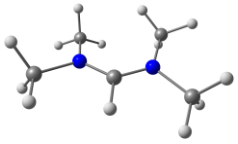


7	0.110875000	-0.149646000	0.100318000
6	-0.392107000	1.039317000	-0.617954000
1	0.488323000	1.561688000	-1.010655000
1	-0.974548000	0.703194000	-1.483859000
6	1.481033000	-0.047534000	0.645299000
1	1.570085000	0.952255000	1.091913000
1	1.571384000	-0.781305000	1.455538000
6	-0.580368000	-1.218881000	0.271683000
1	-0.085695000	-2.019458000	0.832461000
6	-1.202455000	1.947201000	0.293279000
1	-1.512804000	2.834927000	-0.273585000
1	-2.104883000	1.441903000	0.664717000
1	-0.608296000	2.281964000	1.155110000
6	2.537667000	-0.276678000	-0.422168000
1	3.530023000	-0.179231000	0.037801000
1	2.449369000	-1.284997000	-0.850114000
1	2.469272000	0.460106000	-1.234638000
6	-1.952683000	-1.473009000	-0.200608000
1	-1.931548000	-2.368470000	-0.840965000
1	-2.566352000	-1.736408000	0.674736000
1	-2.416980000	-0.641139000	-0.737876000

Iminium ion from the reaction of $Me_2NCHNMe_2$ radical **T3**

In MeCN

SCF Done: E(RwB97XD)	-307.3914322
Zero-point correction	0.186510
Thermal correction to Energy	0.195694
Thermal correction to Enthalpy	0.196638
Thermal correction to Gibbs Free Energy	0.153229
Sum of electronic and zero-point Energies	-307.204922
Sum of electronic and thermal Energies	-307.195738
Sum of electronic and thermal Enthalpies	-307.194794
Sum of electronic and thermal Free Energies	-307.238203



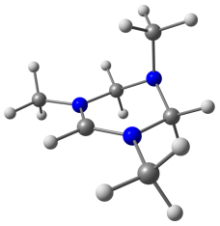
6	0.000065000	-0.654819000	-0.000095000
1	0.000085000	-1.747822000	-0.000190000
6	1.500514000	1.307198000	0.251508000
1	0.741826000	1.777510000	0.882773000
1	2.457931000	1.358200000	0.784115000
1	1.601970000	1.853356000	-0.696905000

6	2.365694000	-0.958788000	-0.166394000
1	2.057144000	-1.996480000	-0.333121000
1	2.931377000	-0.614750000	-1.043433000
1	3.012273000	-0.908866000	0.720695000
6	-2.365529000	-0.958930000	0.166466000
1	-2.056886000	-1.996485000	0.333859000
1	-2.931489000	-0.614492000	1.043167000
1	-3.011883000	-0.909559000	-0.720824000
6	-1.500772000	1.307070000	-0.251505000
1	-0.741718000	1.777939000	-0.881872000
1	-2.457677000	1.357756000	-0.785086000
1	-1.603440000	1.852910000	0.696961000
7	1.195982000	-0.102803000	0.024510000
7	-1.195888000	-0.102854000	-0.024513000

Iminium ion from the reaction of triazinane radical **C1**

In MeCN

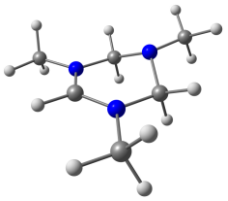
SCF Done: E(RwB97XD)	-400.7625582
Zero-point correction	0.212014
Thermal correction to Energy	0.221761
Thermal correction to Enthalpy	0.222705
Thermal correction to Gibbs Free Energy	0.177563
Sum of electronic and zero-point Energies	-400.550544
Sum of electronic and thermal Energies	-400.540798
Sum of electronic and thermal Enthalpies	-400.539853
Sum of electronic and thermal Free Energies	-400.584995



6	1.174550000	0.733483000	0.700073000
6	0.000000000	-1.168726000	-0.199477000
6	-1.174550000	0.733483000	0.700073000
1	0.000000000	-2.151327000	-0.679261000
1	1.245930000	0.599821000	1.790814000
1	2.076154000	1.253172000	0.351784000
1	-2.076154000	1.253171000	0.351785000
1	-1.245929000	0.599821000	1.790814000
6	2.425175000	-1.263321000	-0.206669000
1	2.246615000	-2.244777000	-0.660521000
1	3.022768000	-0.650920000	-0.895965000
1	2.983059000	-1.399864000	0.730292000
6	-2.425174000	-1.263322000	-0.206669000
1	-3.022768000	-0.650921000	-0.895965000
1	-2.246615000	-2.244777000	-0.660521000
1	-2.983059000	-1.399865000	0.730292000
7	0.000000000	1.471433000	0.352578000
7	1.158622000	-0.605568000	0.067243000
7	-1.158622000	-0.605568000	0.067243000
6	-0.000001000	2.011267000	-1.002503000
1	-0.888637000	2.641169000	-1.140479000
1	0.888635000	2.641169000	-1.140479000
1	-0.000001000	1.234862000	-1.790994000

Iminium ion from the reaction of triazinane radical **C3**

In MeCN



SCF Done: E(RwB97XD)	-400.757463
Zero-point correction	0.211722
Thermal correction to Energy	0.221566
Thermal correction to Enthalpy	0.22251
Thermal correction to Gibbs Free Energy	0.177208
Sum of electronic and zero-point Energies	-400.545741
Sum of electronic and thermal Energies	-400.535897
Sum of electronic and thermal Enthalpies	-400.534953
Sum of electronic and thermal Free Energies	-400.580255

6	1.184740000	-0.718823000	0.271487000
6	-1.195932000	-0.699683000	0.271981000
6	0.010733000	1.339609000	-0.100694000
1	-2.080438000	-1.107921000	-0.236303000
1	1.310880000	-0.879748000	1.363892000
1	2.062342000	-1.140972000	-0.237383000
1	0.019330000	2.414556000	-0.296869000
1	-1.323939000	-0.858430000	1.364463000
7	1.162938000	0.720096000	0.016587000
7	-0.010522000	-1.308673000	-0.267854000
7	-1.151170000	0.738555000	0.016715000
6	2.435787000	1.419082000	-0.065087000
1	3.011618000	1.050876000	-0.925330000
1	2.261835000	2.494662000	-0.179472000
1	3.009327000	1.247276000	0.856126000
6	-0.022316000	-2.756919000	-0.190256000
1	-0.913925000	-3.144507000	-0.701970000
1	0.864340000	-3.158837000	-0.699491000
1	-0.026848000	-3.136032000	0.851119000
6	-2.412672000	1.457624000	-0.065302000
1	-2.221996000	2.530326000	-0.179802000
1	-2.994160000	1.098591000	-0.925657000
1	-2.989124000	1.294968000	0.855763000

Chloride anion (Cl^-)

In MeCN

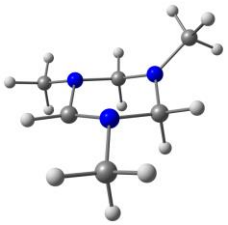
SCF Done: E(RwB97XD)	-460.1984759
Zero-point correction	0.000000
Thermal correction to Energy	0.001416
Thermal correction to Enthalpy	0.00236
Thermal correction to Gibbs Free Energy	-0.015023
Sum of electronic and zero-point Energies	-460.198476
Sum of electronic and thermal Energies	-460.19706
Sum of electronic and thermal Enthalpies	-460.196115
Sum of electronic and thermal Free Energies	-460.213499

17	0.000000000	0.000000000	0.000000000

Transition state for the interconversion of **C1** and **C3** (nitrogen lone pair inversion)

In MeCN

SCF Done: E(UwB97XD)	-400.8263268
Zero-point correction	0.206447
Thermal correction to Energy	0.215858
Thermal correction to Enthalpy	0.216802
Thermal correction to Gibbs Free Energy	0.171869
Sum of electronic and zero-point Energies	-400.61988
Sum of electronic and thermal Energies	-400.610469
Sum of electronic and thermal Enthalpies	-400.609524
Sum of electronic and thermal Free Energies	-400.654458

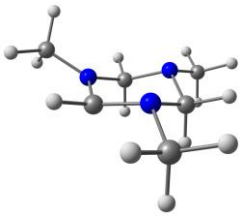


6	-1.167150000	-0.699911000	0.426895000
6	-0.060023000	1.359029000	-0.113041000
6	1.220291000	-0.597752000	0.426916000
1	-0.102241000	2.347532000	-0.587717000
1	-1.280592000	-0.529757000	1.528880000
1	-2.018540000	-1.316081000	0.101789000
1	2.120159000	-1.139122000	0.098843000
1	1.320788000	-0.422656000	1.529225000
6	-2.457376000	1.306137000	-0.028211000
1	-2.466882000	2.234591000	-0.617895000
1	-3.313476000	0.692354000	-0.346916000
1	-2.605685000	1.577554000	1.037894000
6	2.333869000	1.510703000	-0.026472000
1	3.238830000	0.973418000	-0.348228000
1	2.263405000	2.438471000	-0.612918000
1	2.460411000	1.790244000	1.040326000
7	0.056619000	-1.360285000	0.125568000
7	-1.227269000	0.587164000	-0.261249000
7	1.169184000	0.689876000	-0.259846000
6	0.126297000	-2.691014000	-0.408302000
1	0.293203000	-3.476030000	0.357081000
1	-0.812357000	-2.935808000	-0.928001000
1	0.937786000	-2.775136000	-1.150381000

Transition state for the interconversion of **C2** to **C3** (nitrogen lone pair inversion)

In MeCN

SCF Done: E(UwB97XD)	-400.8289093
Zero-point correction	0.206472
Thermal correction to Energy	0.215812
Thermal correction to Enthalpy	0.216756
Thermal correction to Gibbs Free Energy	0.171982
Sum of electronic and zero-point Energies	-400.622438
Sum of electronic and thermal Energies	-400.613097
Sum of electronic and thermal Enthalpies	-400.612153
Sum of electronic and thermal Free Energies	-400.656927



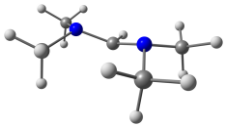
6	1.307457000	0.285162000	0.399314000
6	-0.464546000	-1.335022000	0.224225000
6	-0.919605000	1.017381000	0.040907000
1	-0.755688000	-2.358050000	-0.036695000
1	1.267449000	0.502264000	1.498612000
1	2.350597000	0.416125000	0.075726000
1	-1.551531000	1.721480000	-0.523578000

1	-1.076345000	1.236227000	1.134822000
6	1.868244000	-2.051180000	-0.243436000
1	1.387327000	-3.037310000	-0.294738000
1	2.316854000	-1.844377000	-1.233852000
1	2.688563000	-2.120492000	0.491488000
6	-2.734575000	-0.566494000	0.017274000
1	-3.354877000	0.144404000	-0.548817000
1	-3.013078000	-1.583752000	-0.294856000
1	-2.980544000	-0.461159000	1.094658000
7	0.465126000	1.224917000	-0.322702000
7	0.894135000	-1.061629000	0.134187000
7	-1.337887000	-0.332739000	-0.267121000
6	0.876149000	2.593932000	-0.105996000
1	0.247850000	3.273957000	-0.699898000
1	0.805033000	2.906551000	0.959370000
1	1.920032000	2.727624000	-0.426520000

$Me_2NCHNMe_2$ radical, C_s symmetry (**T3**-C_s)

In MeCN

SCF Done: E(UwB97XD)	-307.4636667
Zero-point correction	0.181608
Thermal correction to Energy	0.190352
Thermal correction to Enthalpy	0.191296
Thermal correction to Gibbs Free Energy	0.148015
Sum of electronic and zero-point Energies	-307.282059
Sum of electronic and thermal Energies	-307.273314
Sum of electronic and thermal Enthalpies	-307.27237
Sum of electronic and thermal Free Energies	-307.315652

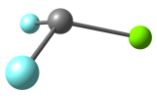


6	0.223748000	1.278251000	1.612952000
6	-0.334241000	-0.504438000	0.000000000
6	0.223748000	1.278251000	-1.612952000
1	-0.643591000	-1.554306000	0.000000000
1	-0.793248000	1.721335000	1.607803000
1	0.636204000	1.380818000	2.626586000
1	0.636204000	1.380818000	-2.626586000
1	-0.793248000	1.721335000	-1.607803000
6	-0.217502000	-0.975187000	2.330420000
1	-0.067833000	-2.034004000	2.074824000
1	0.373810000	-0.760206000	3.232341000
1	-1.288369000	-0.831556000	2.584423000
6	-0.217502000	-0.975187000	-2.330420000
1	0.373810000	-0.760206000	-3.232341000
1	-0.067833000	-2.034004000	-2.074824000
1	-1.288369000	-0.831556000	-2.584423000
7	0.223748000	-0.125776000	1.239499000
7	0.223748000	-0.125776000	-1.239499000
1	0.860235000	1.876131000	0.950867000
1	0.860235000	1.876131000	-0.950867000

CF_2Cl radical

In MeCN

SCF Done: E(UwB97XD)	-697.5192049
Zero-point correction	0.010592
Thermal correction to Energy	0.014318
Thermal correction to Enthalpy	0.015263
Thermal correction to Gibbs Free Energy	-0.017158



Sum of electronic and zero-point Energies	-697.508613
Sum of electronic and thermal Energies	-697.504886
Sum of electronic and thermal Enthalpies	-697.503942
Sum of electronic and thermal Free Energies	-697.536363

6	0.430750000	-0.000001000	0.325660000
9	1.056121000	-1.079377000	-0.079433000
9	1.056121000	1.079377000	-0.079433000
17	-1.270275000	0.000000000	-0.030833000

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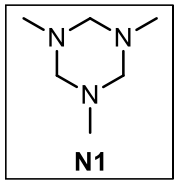
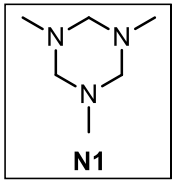


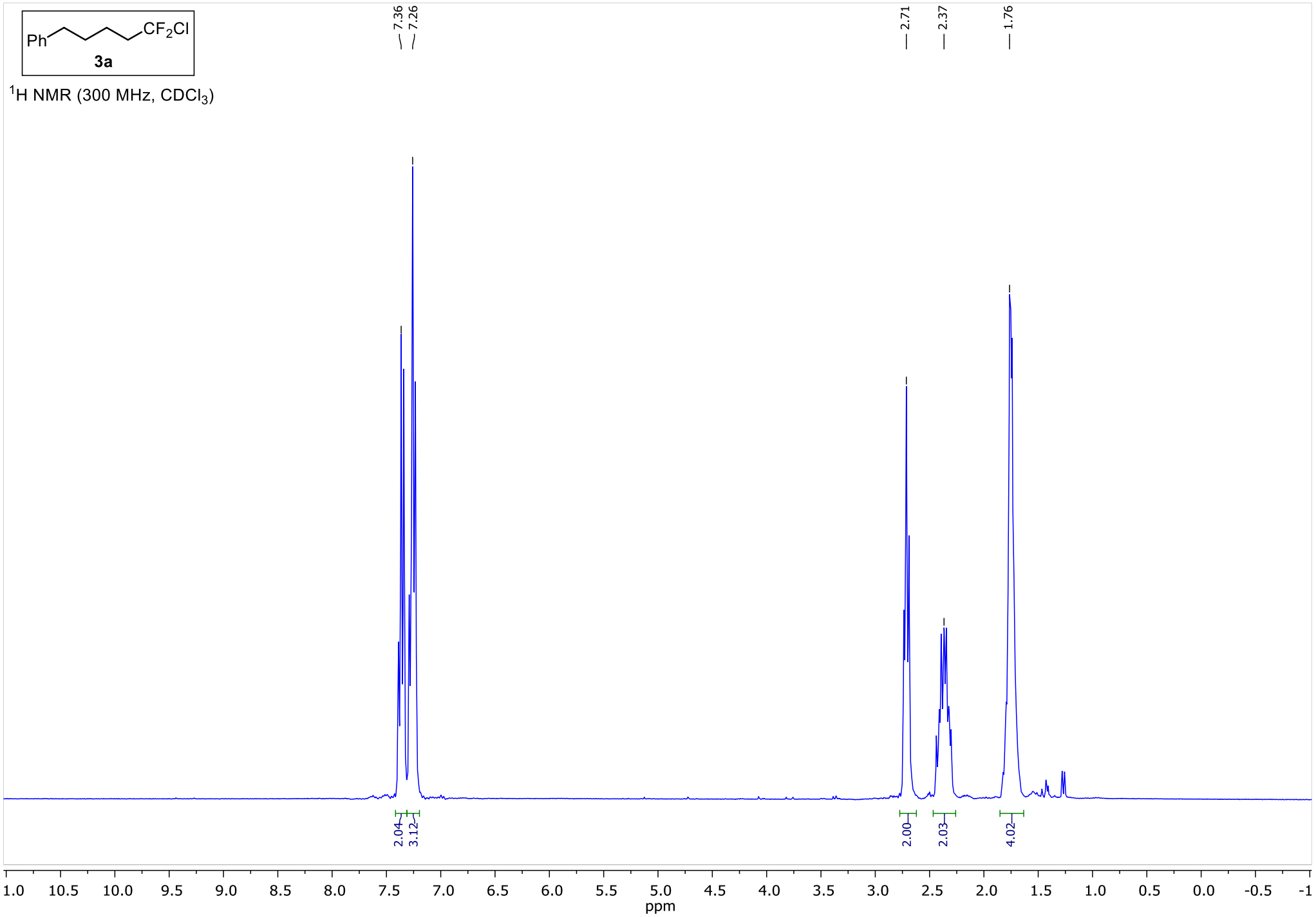
N1

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



N1

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)


Ph
CF2Cl
3a
1H NMR (300 MHz, CDCl3)
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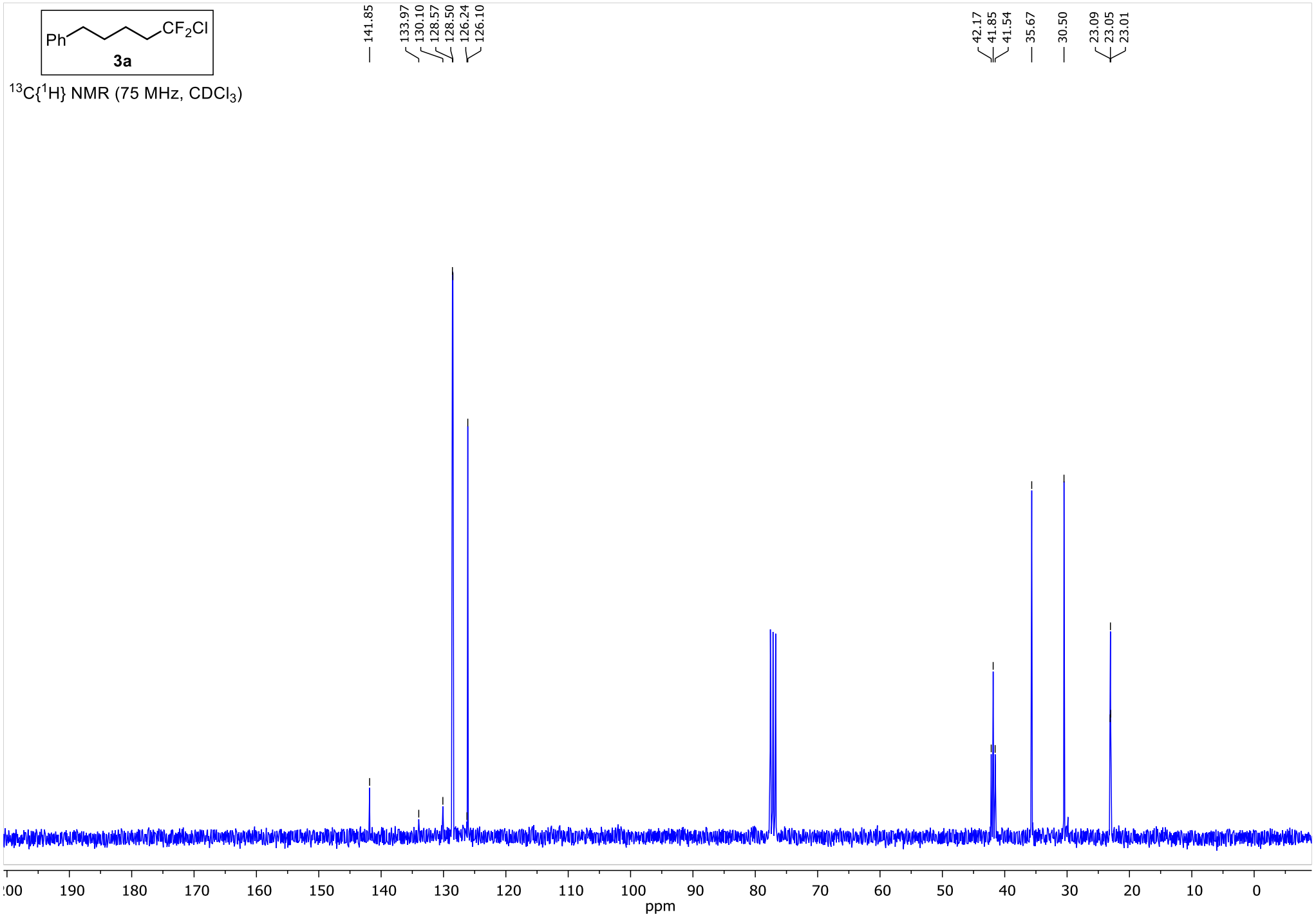
2.04
3.12
2.00
2.03
4.02
ppm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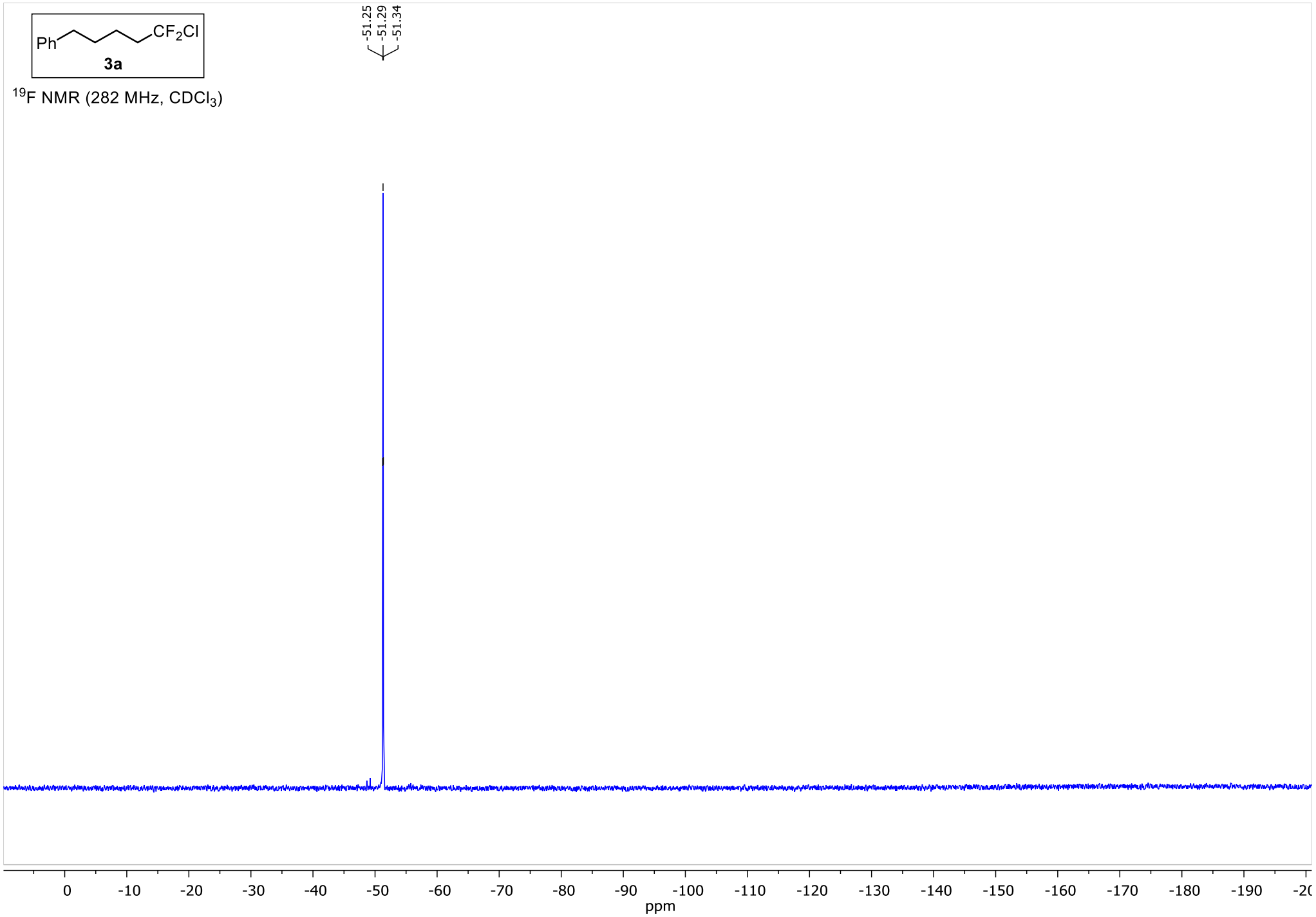
CF2Cl
3a
13C{1H} NMR (75 MHz, CDCl3)
141.85
133.97
130.10
128.57
128.50
126.24
126.10
42.17
41.85
41.54
35.67
30.50
23.09
23.05
23.01
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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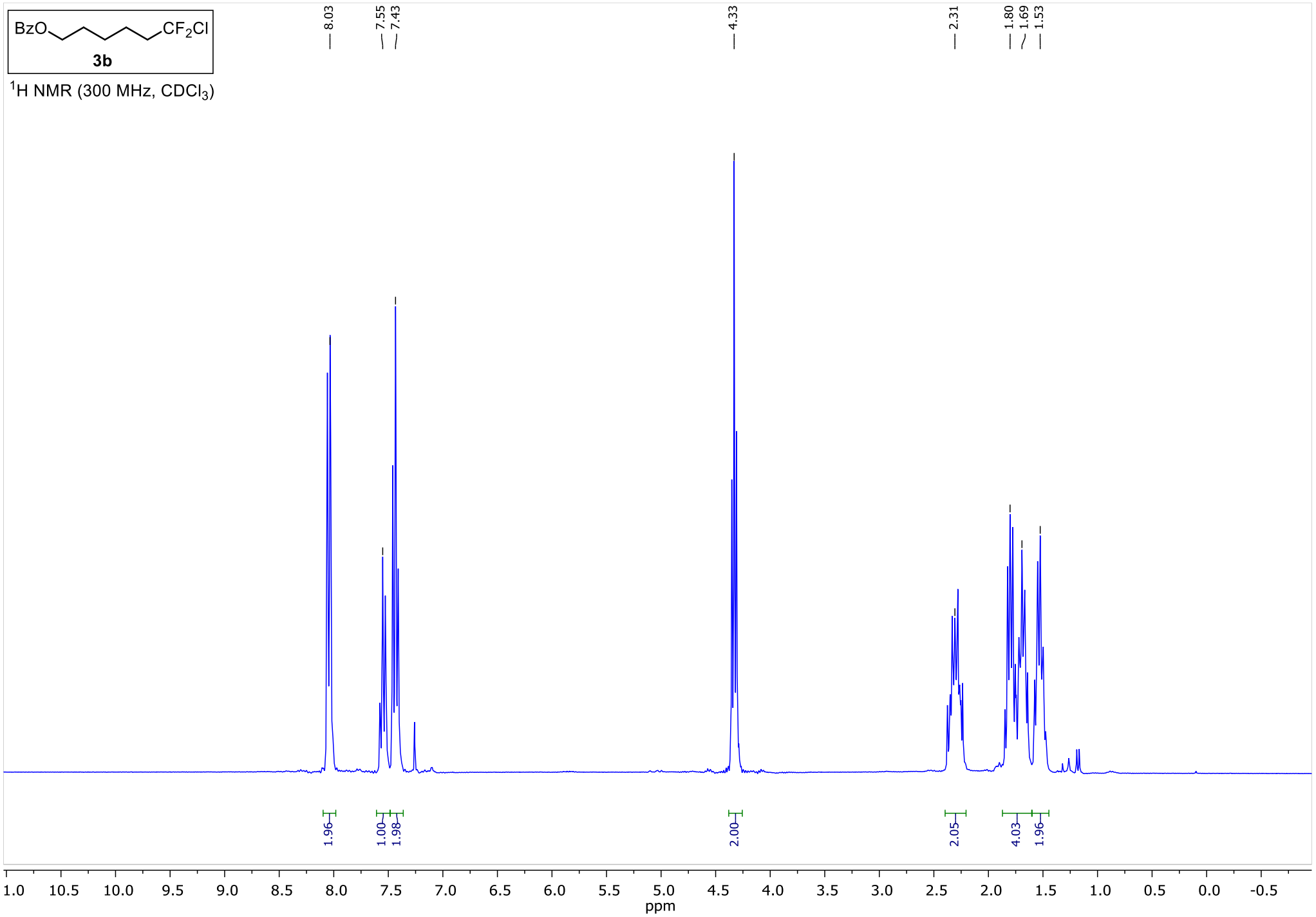
-51.29
-51.34
19F NMR (282 MHz, CDCl3)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm


BzO
CF2Cl
3b
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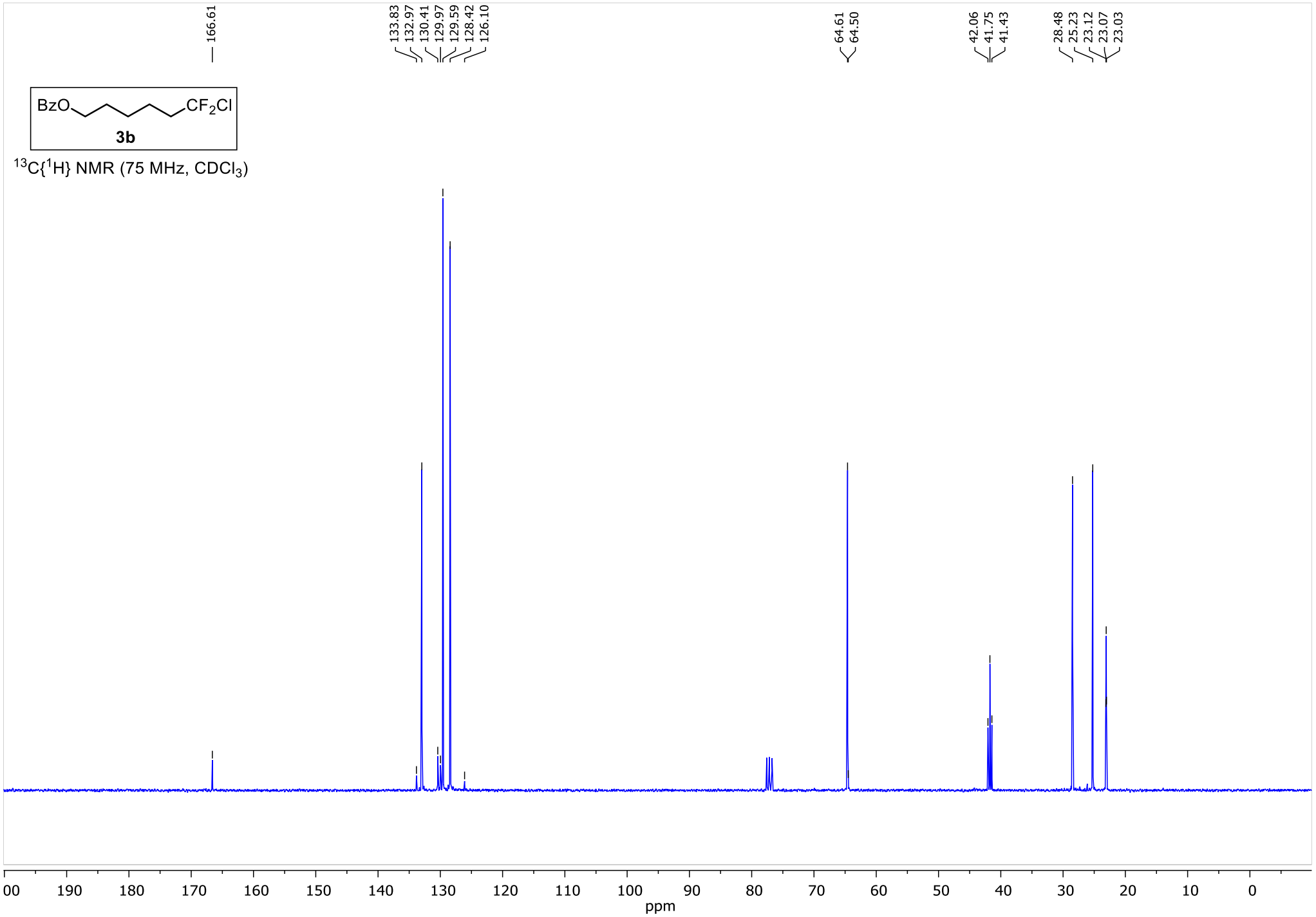
8.03
7.55
7.43
4.33
2.31
1.80
1.69
1.53
1.96
1.00
1.98
2.00
2.05
4.03
1.96
ppm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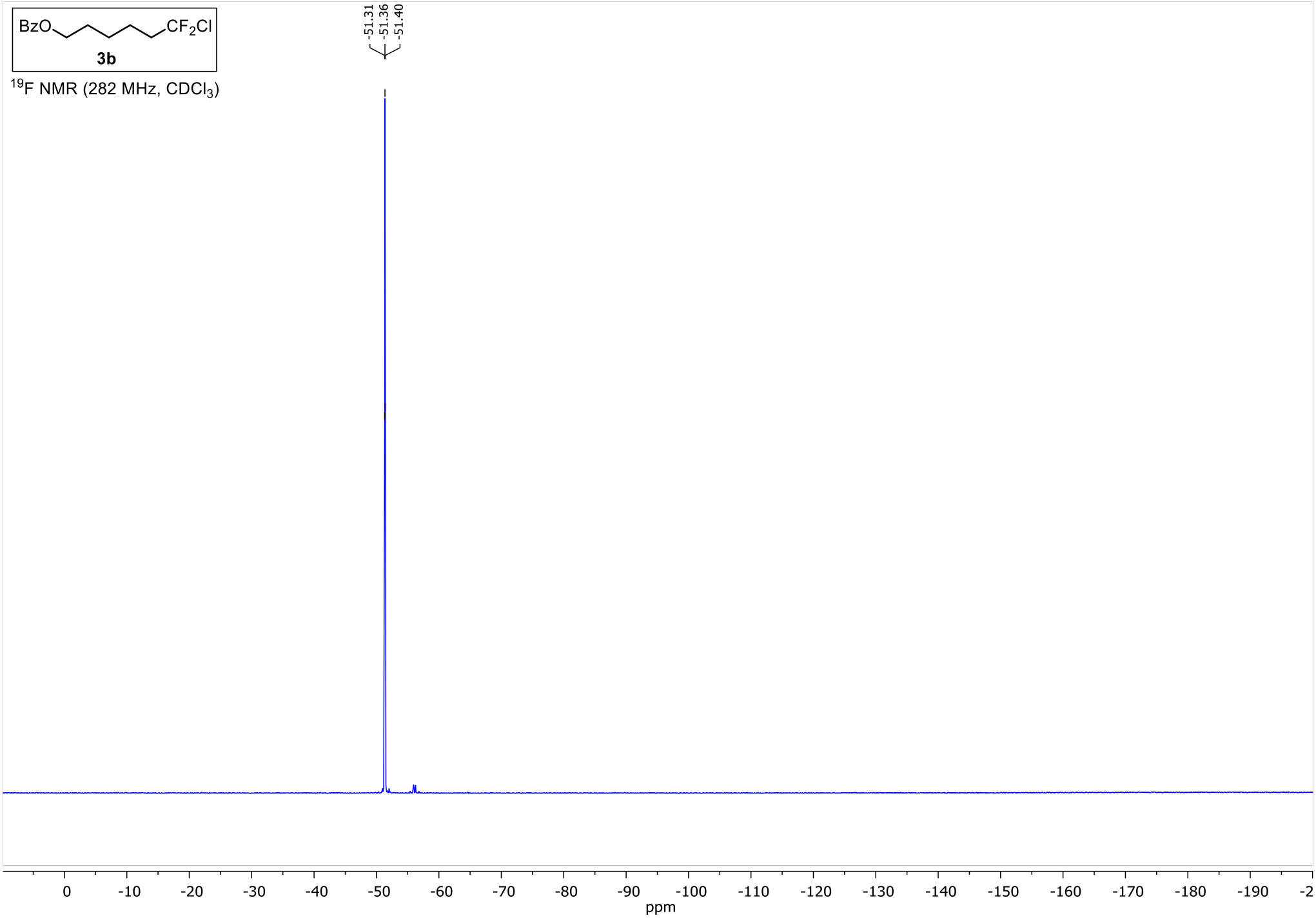
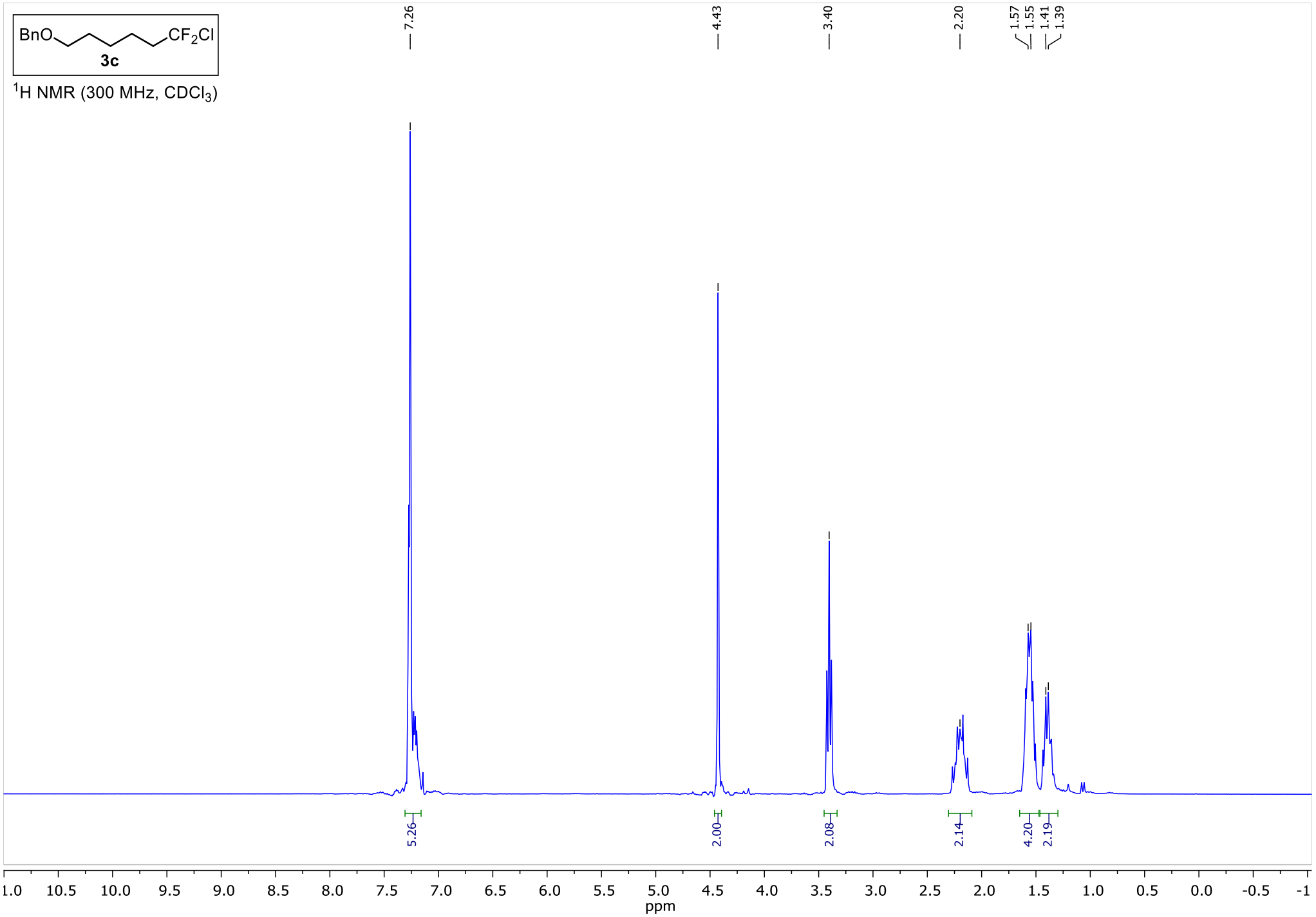
133.83
132.97
130.41
129.97
129.59
128.42
126.10
64.61
64.50
42.06
41.75
41.43
28.48
25.23
23.12
23.07
23.03
BzO
CF2Cl
3b
13C{1H} NMR (75 MHz, CDCl3)
ppm


BzO
CF2Cl
3b
19F NMR (282 MHz, CDCl3)
-51.31
-51.36
-51.40
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
ppm


BnO
CF2Cl
3c
1H NMR (300 MHz, CDCl3)
7.26
4.43
3.40
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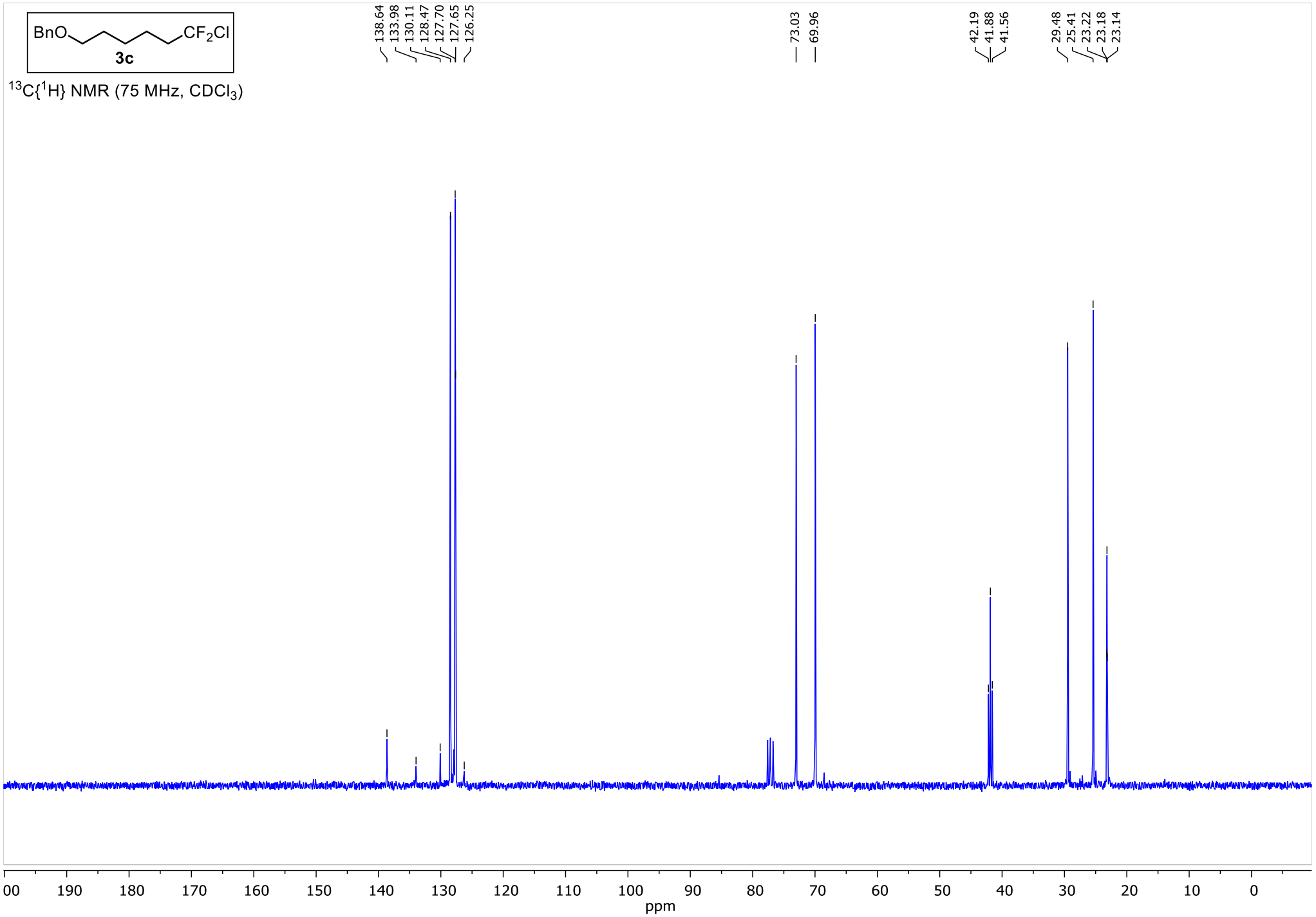
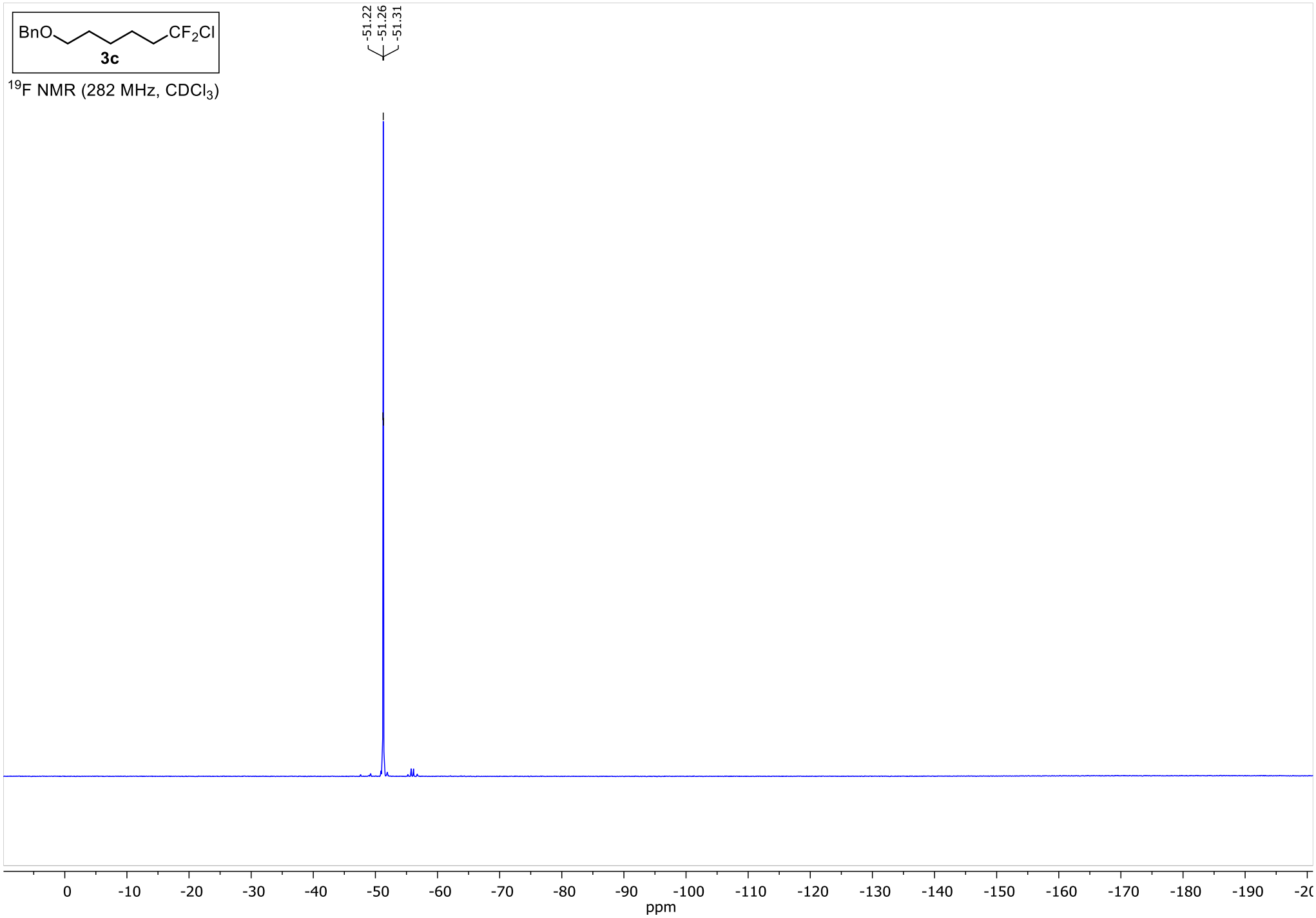
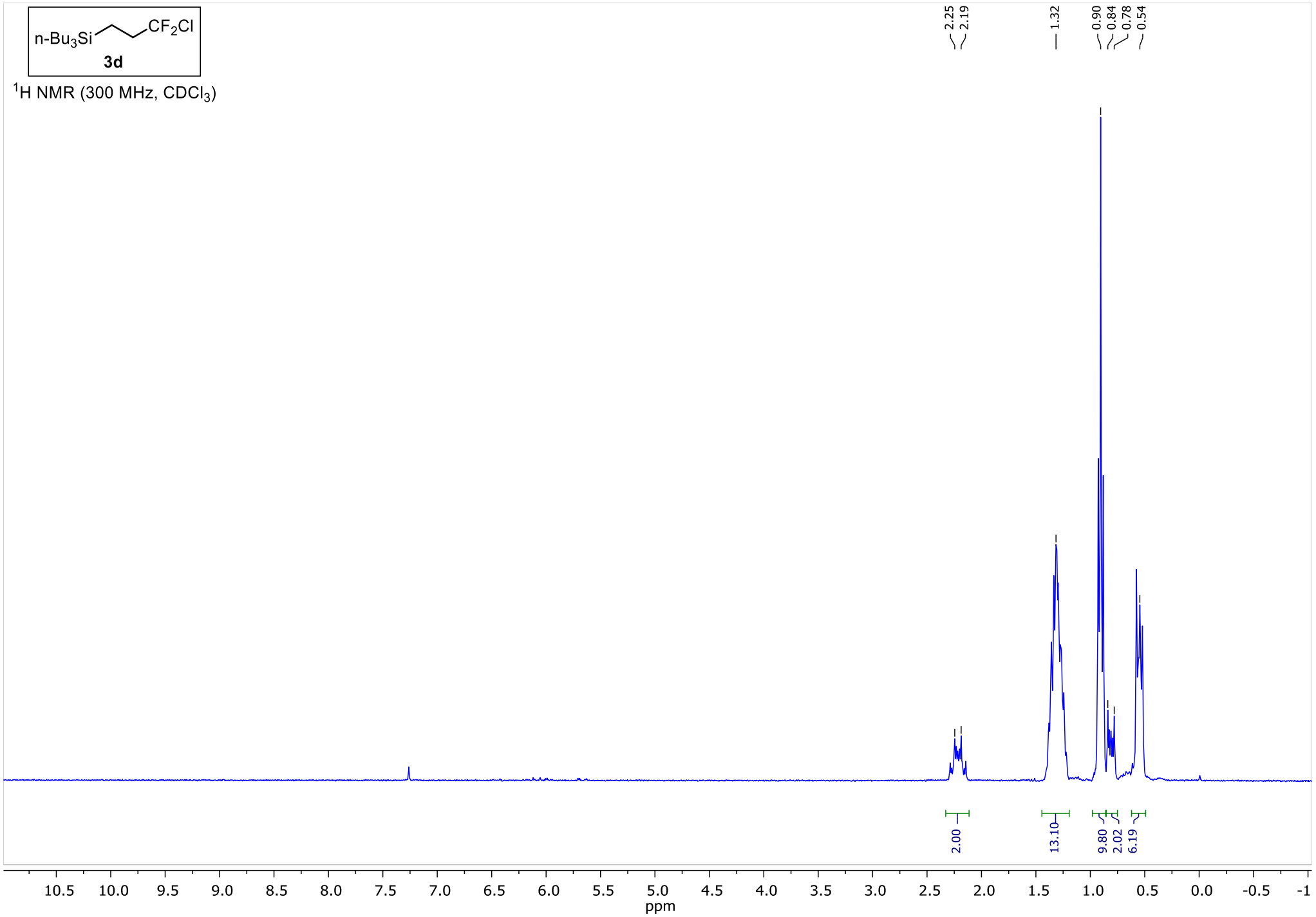
1.55
1.41
1.39
5.26
2.00
2.08
2.14
4.20
2.19
ppm


BnO
CF2Cl
3c
13C{1H} NMR (75 MHz, CDCl3)
138.64
133.98
130.11
128.47
127.70
127.65
126.25
73.03
69.96
42.19
41.88
41.56
29.48
25.41
23.22
23.18
23.14
ppm


BnO
CF2Cl
3c
19F NMR (282 MHz, CDCl3)
-51.22
-51.26
-51.31
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm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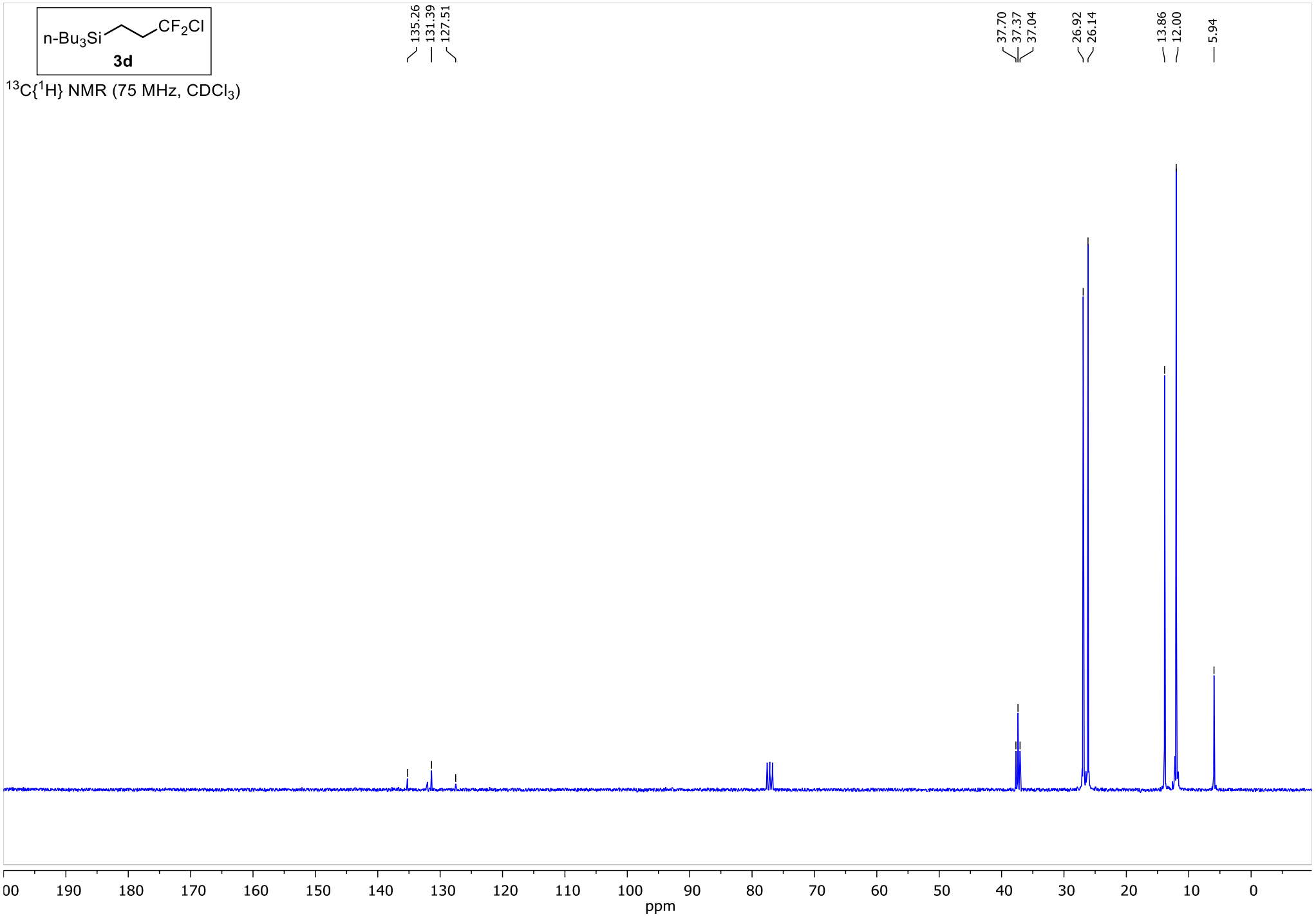
CF2Cl
3d
1H NMR (300 MHz, CDCl3)
2.25
2.19
1.32
0.90
0.84
0.78
0.54
2.00
13.10
9.80
2.02
6.19
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
ppm


n-Bu3Si
CF2Cl
3d
13C{1H} NMR (75 MHz, CDCl3)
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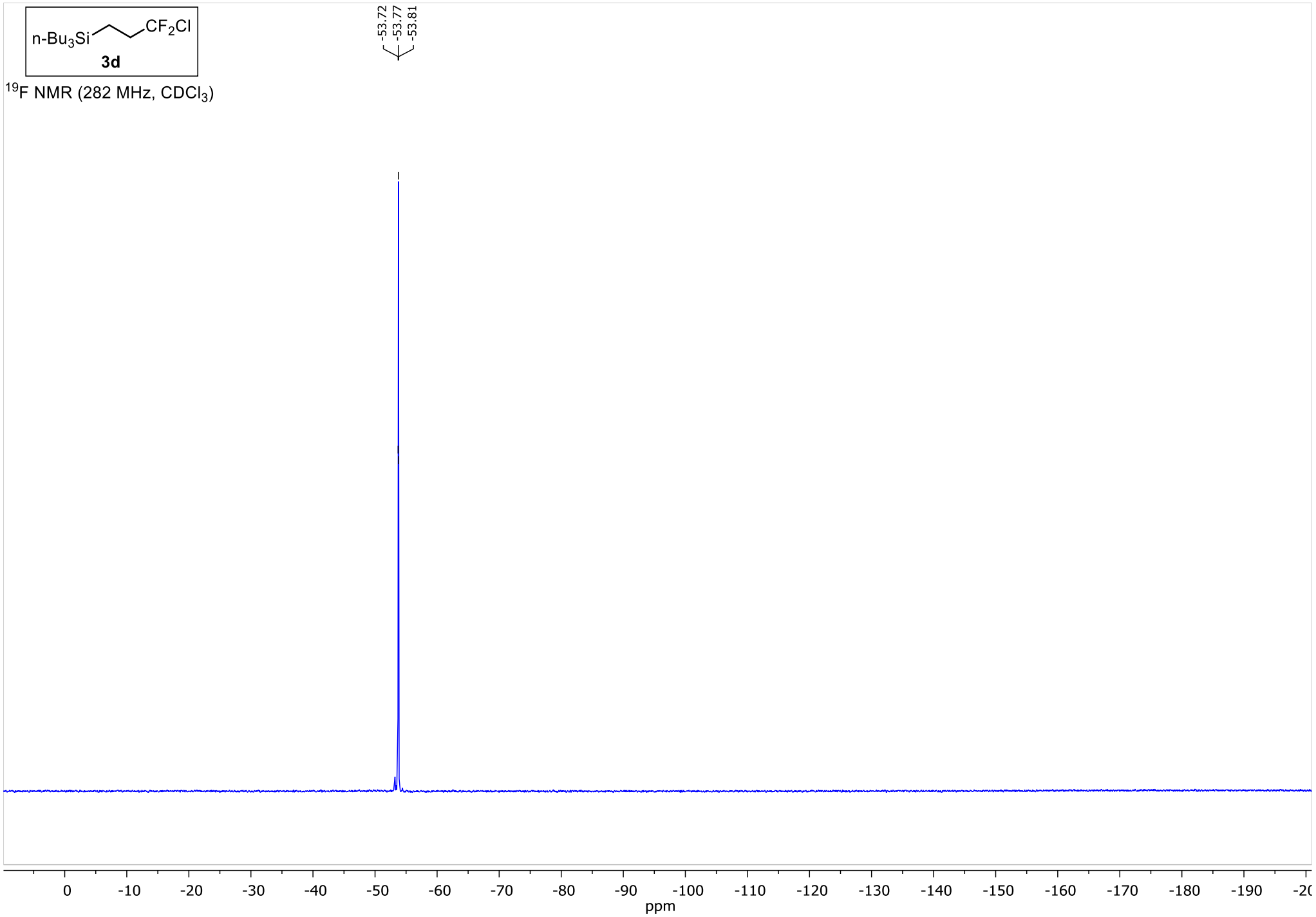
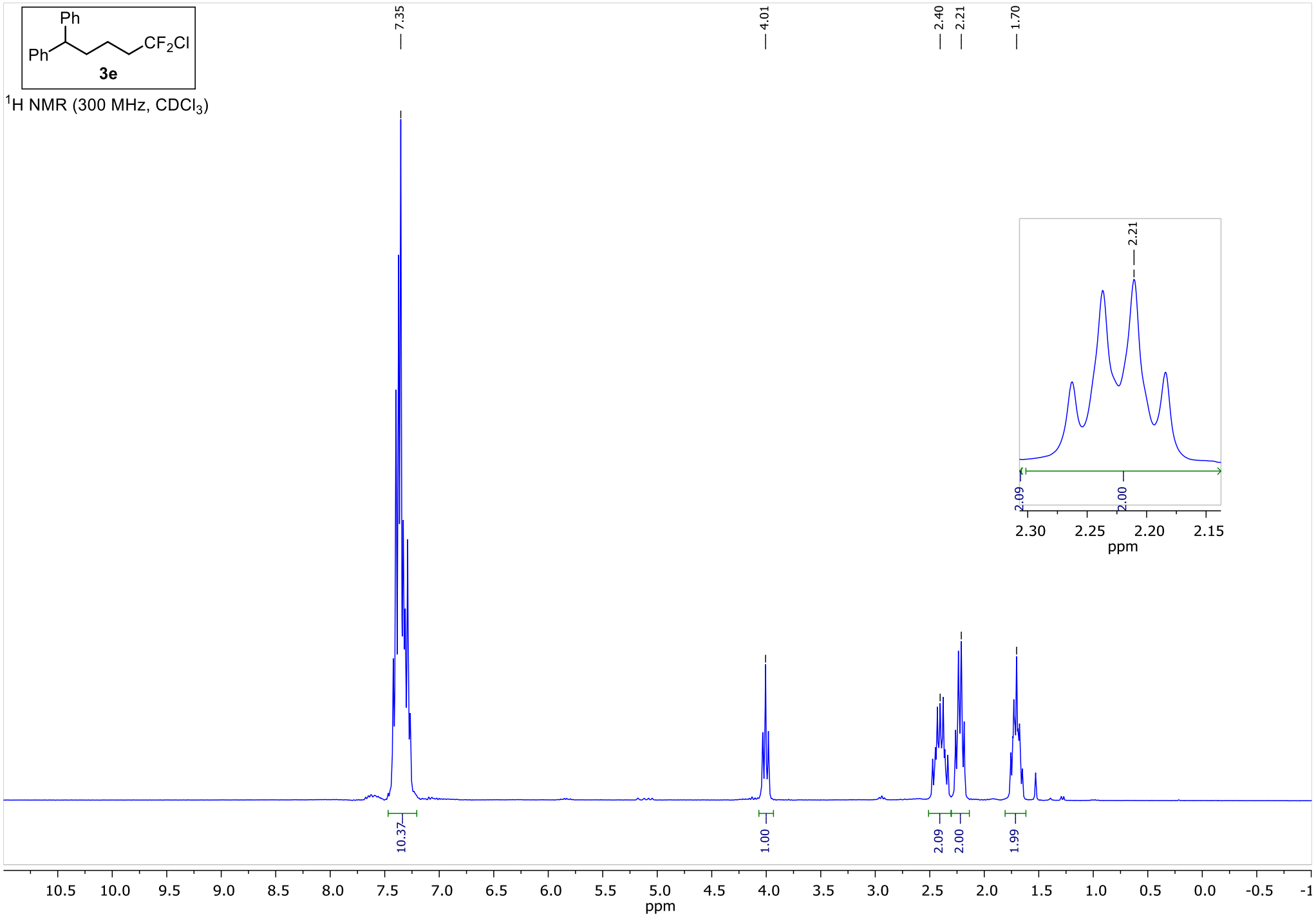
131.39
127.51
37.70
37.37
37.04
26.92
26.14
13.86
12.00
5.94
ppm


n-Bu3Si
CF2Cl
3d
19F NMR (282 MHz, CDCl3)
-53.72
-53.77
-53.81
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm


Ph
Ph
CF2Cl
3e
1H NMR (300 MHz, CDCl3)
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4.01
2.40
2.21
1.70
10.37
1.00
2.09
2.00
1.99
2.21
2.09
2.00
2.30
2.25
2.20
2.15
ppm
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
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3.0
2.5
2.0
1.5
1.0
0.5
0.0
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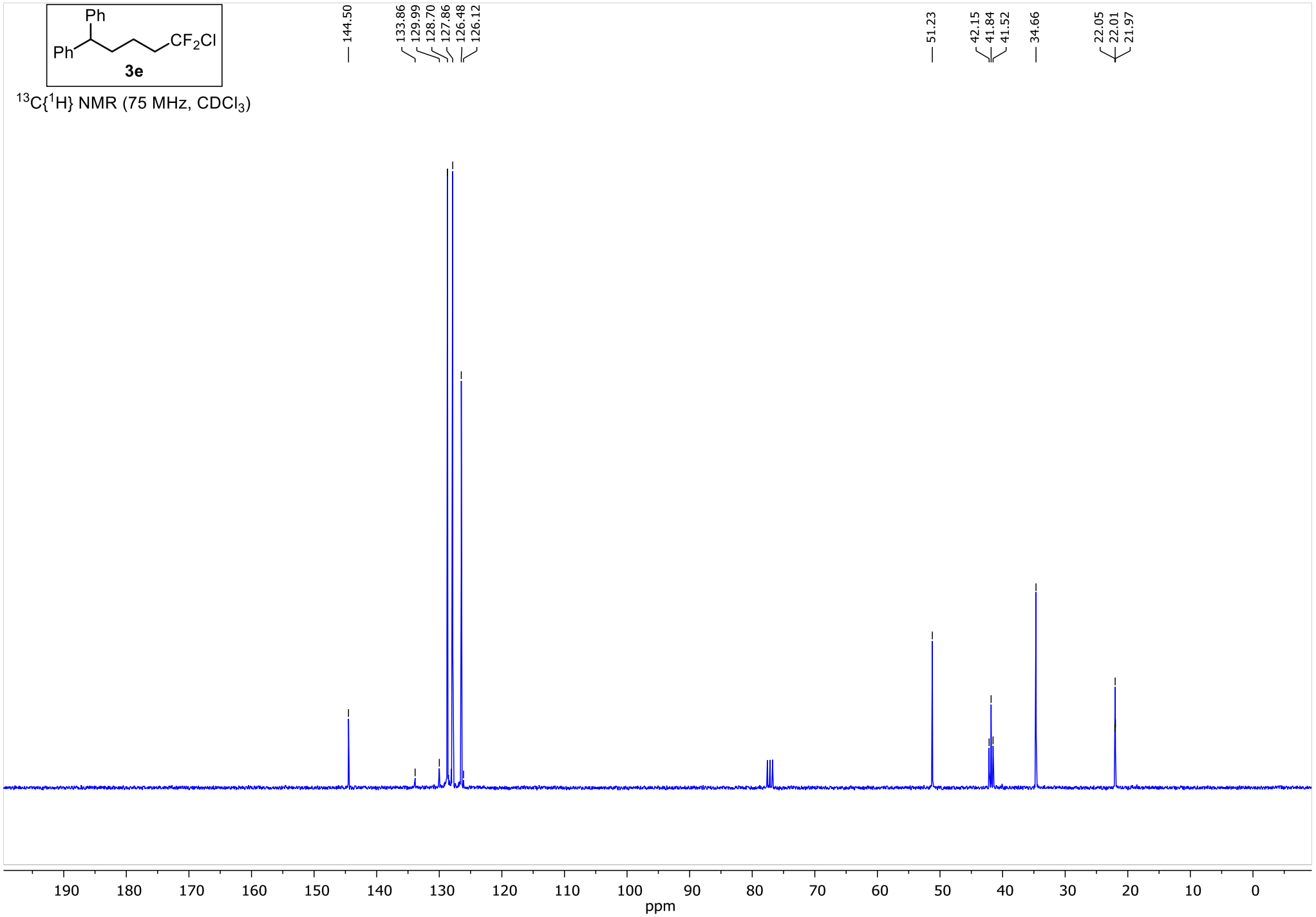
-1
ppm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Ph
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3e
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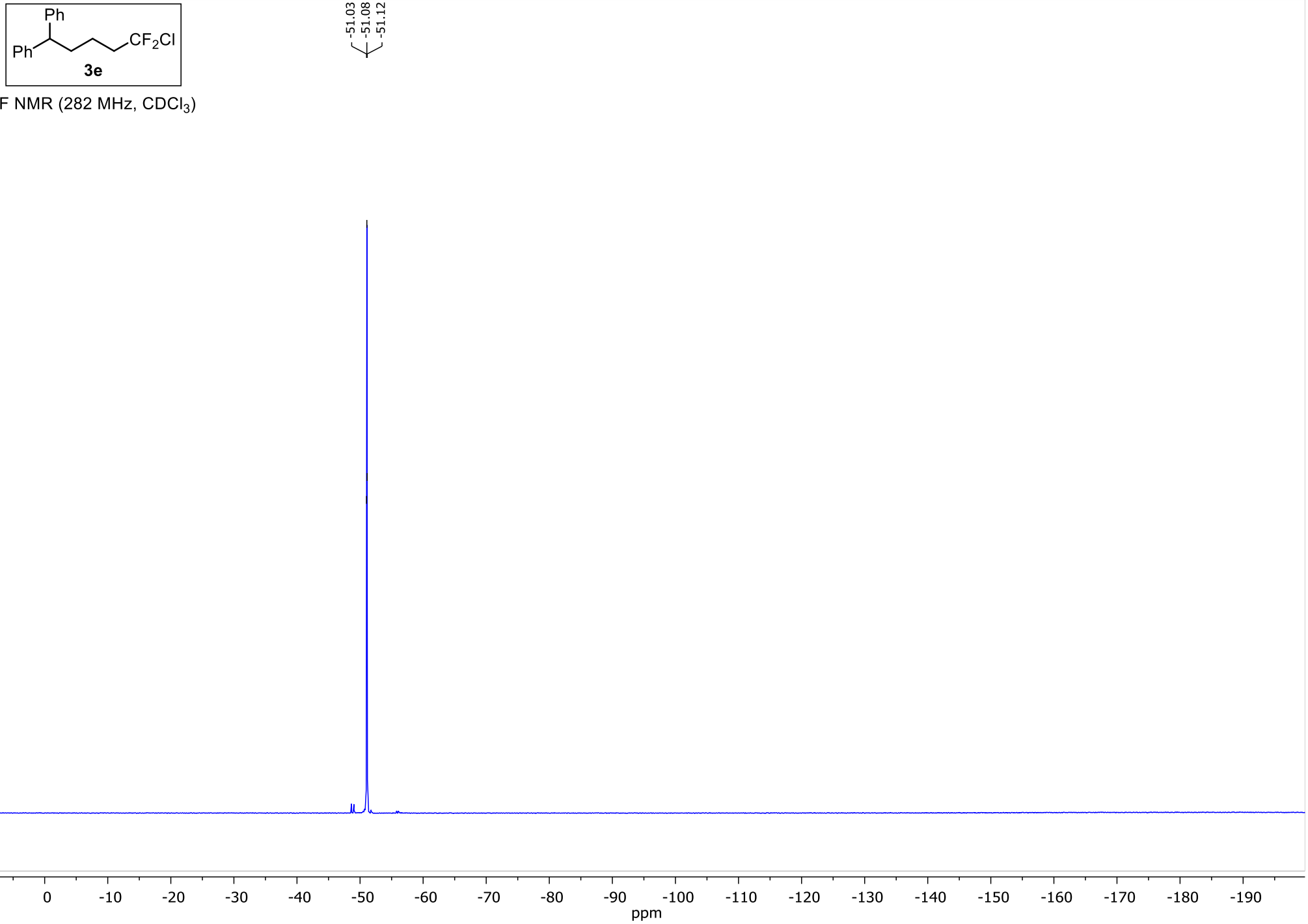
133.86
129.99
128.70
127.86
126.48
126.12
51.23
42.15
41.84
41.52
34.66
22.05
22.01
21.97
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Ph
Ph
CF_2Cl
3e
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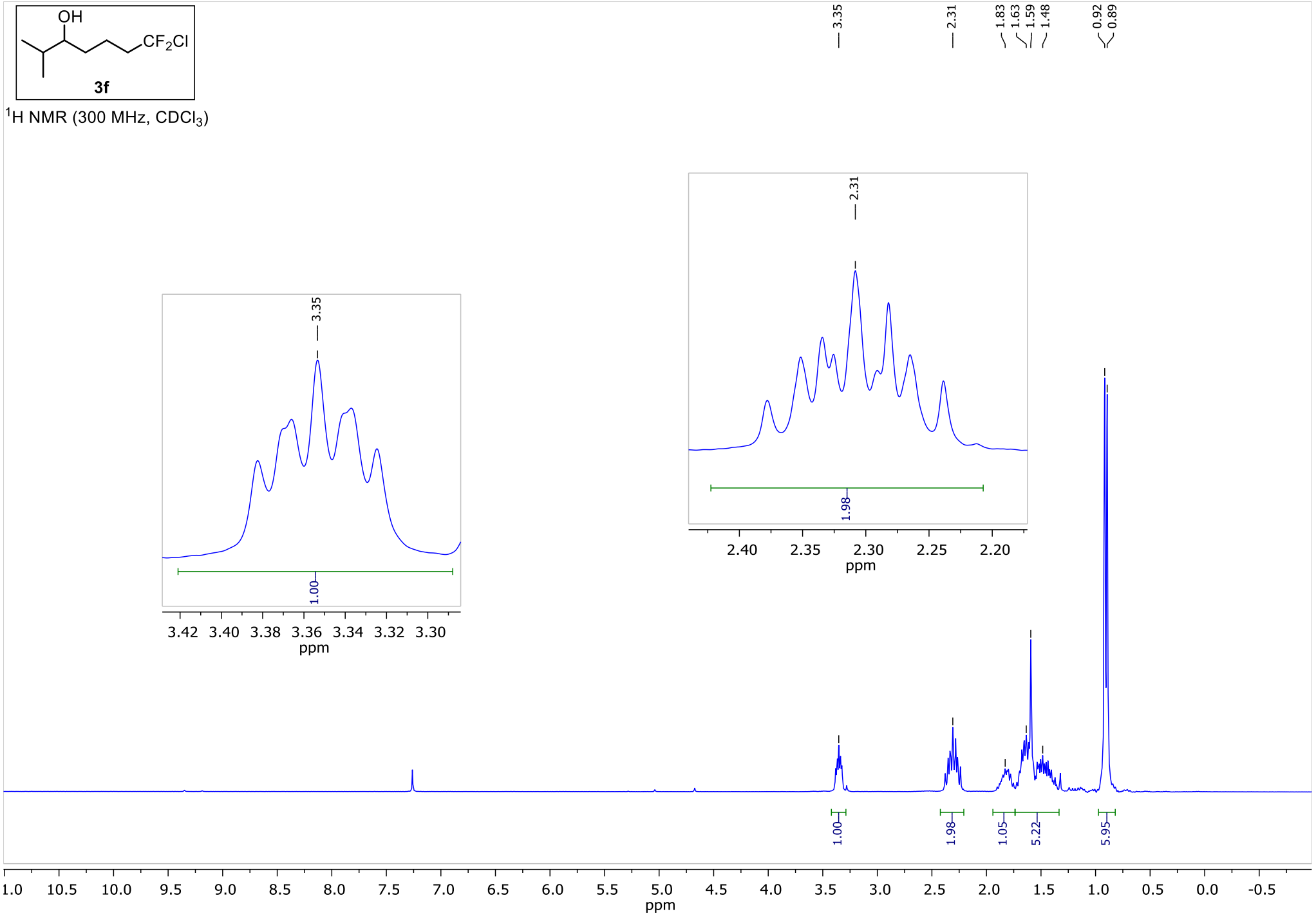
-51.08
-51.12
^{19}F NMR (282 MHz, $CDCl_3$)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm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1.59
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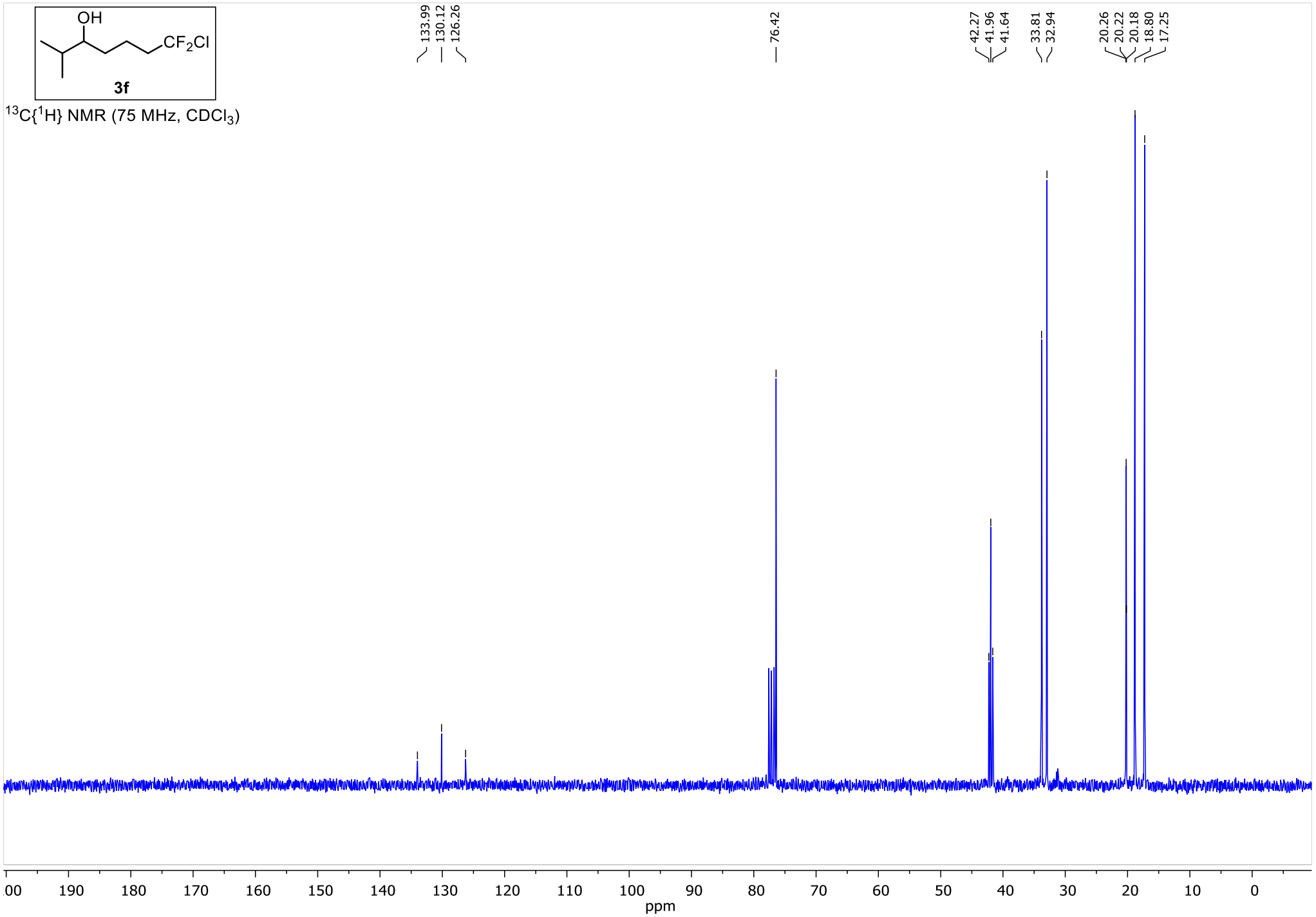
1.98
1.05
5.22
5.95
ppm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3f
133.99
130.12
126.26
76.42
42.27
41.96
41.64
33.81
32.94
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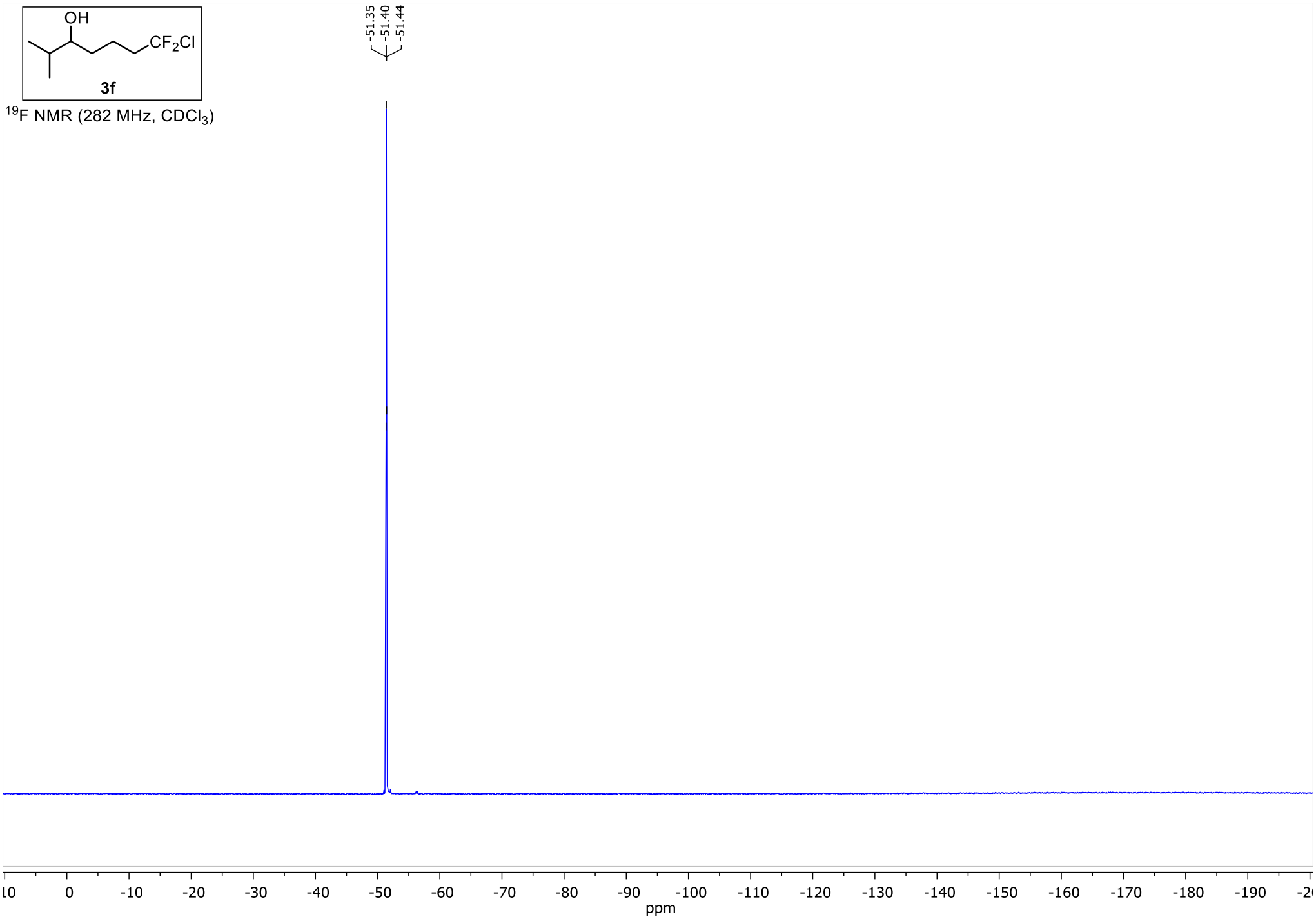
18.80
17.25
13C{1H} NMR (75 MHz, CDCl3)
ppm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CF2Cl
3f
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-51.40
-51.44
19F NMR (282 MHz, CDCl3)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
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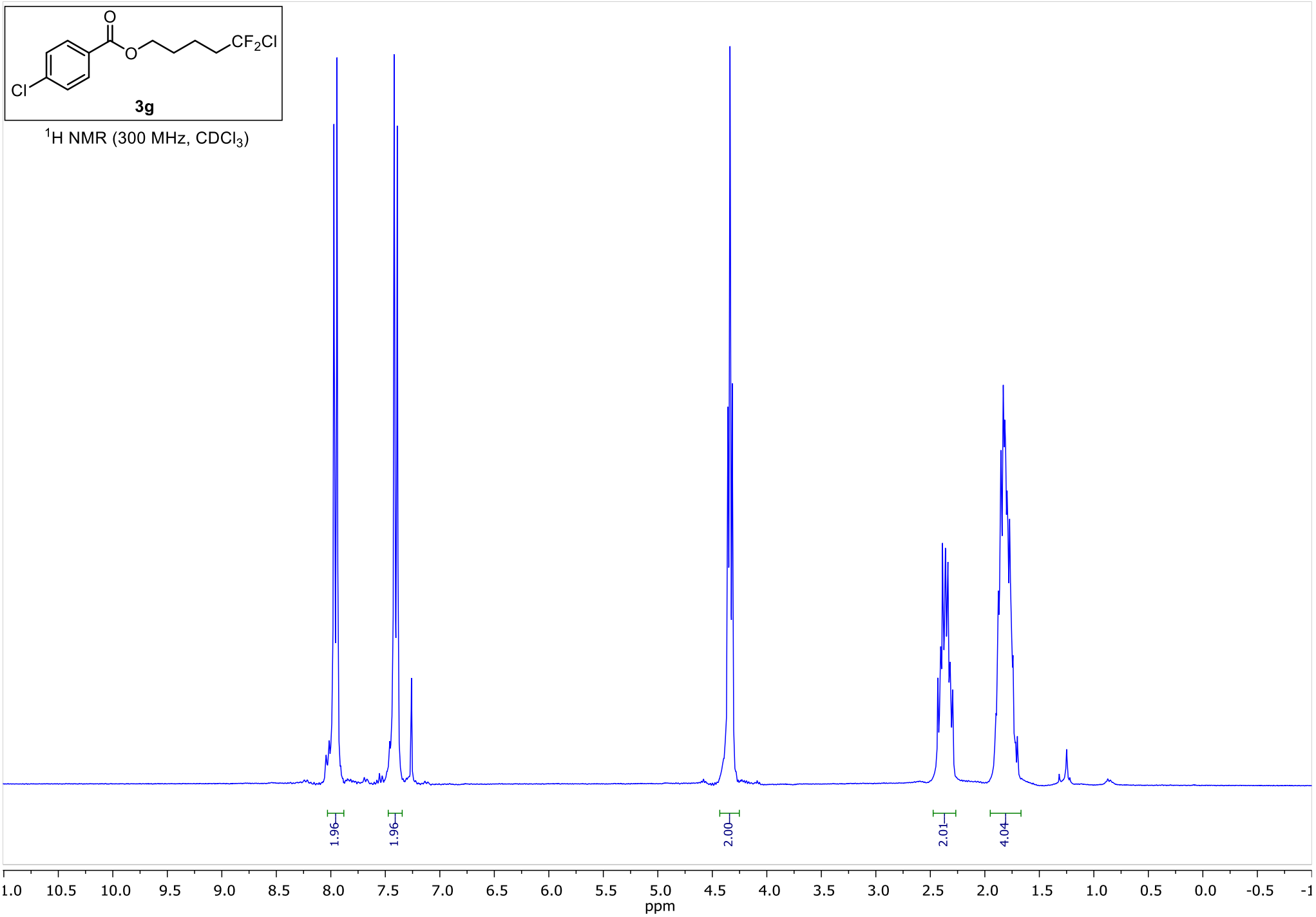
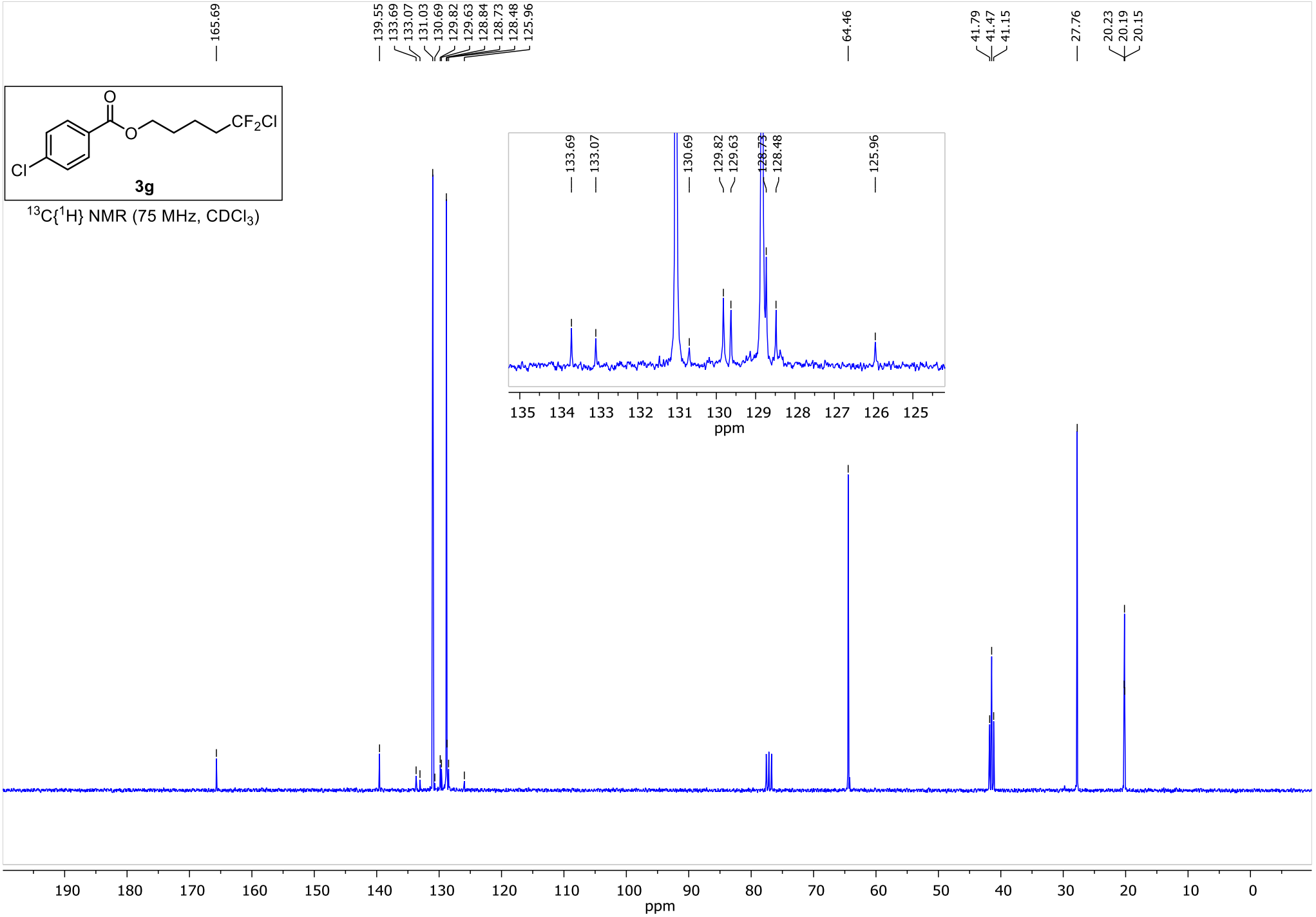
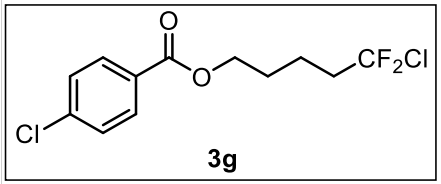
-120
-130
-140
-150
-160
-170
-180
-190
-2
ppm

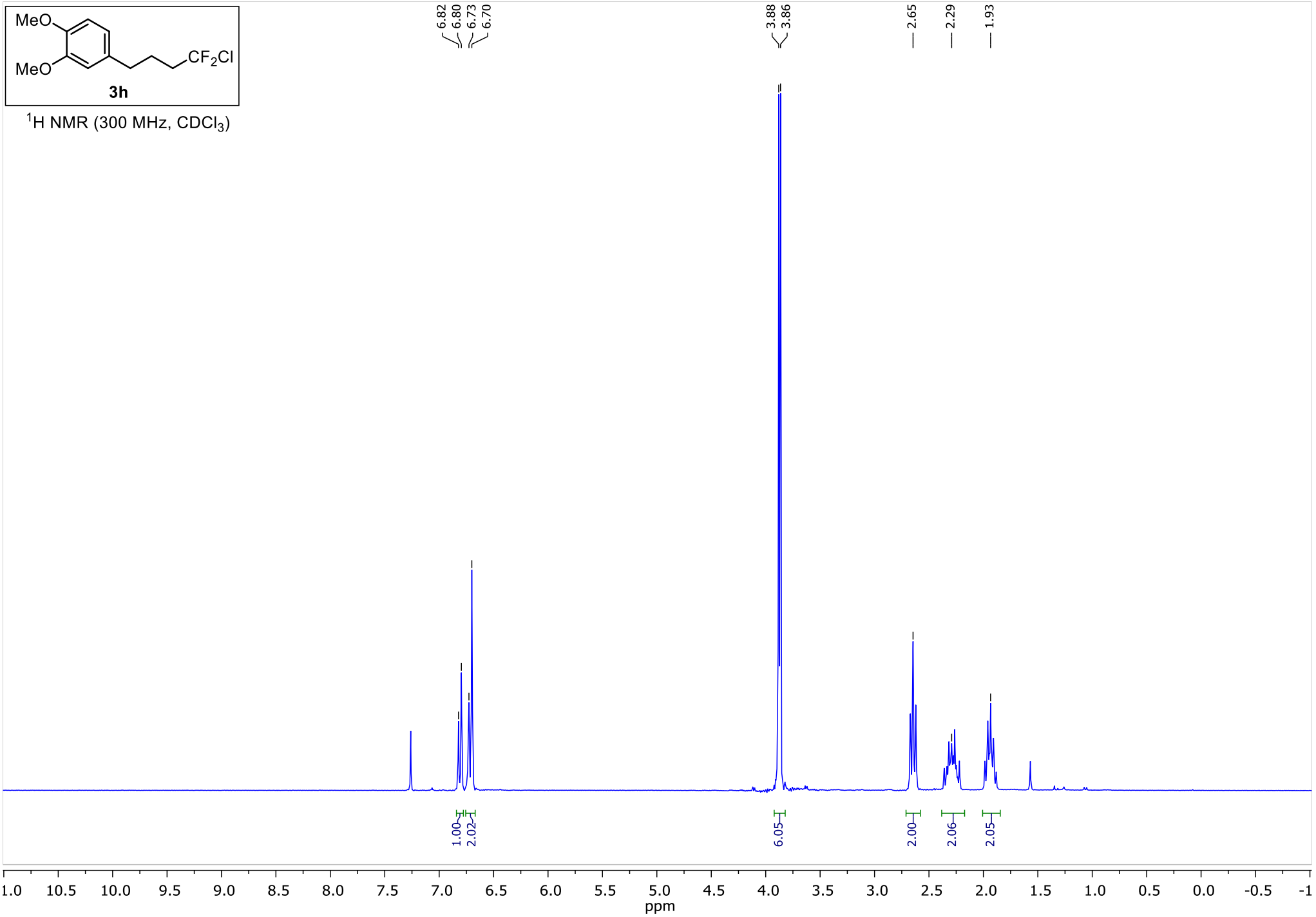

O
O
CF2Cl
Cl
3g
1H NMR (300 MHz, CDCl3)
1.96
1.96
2.00
2.01
4.04
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
ppm

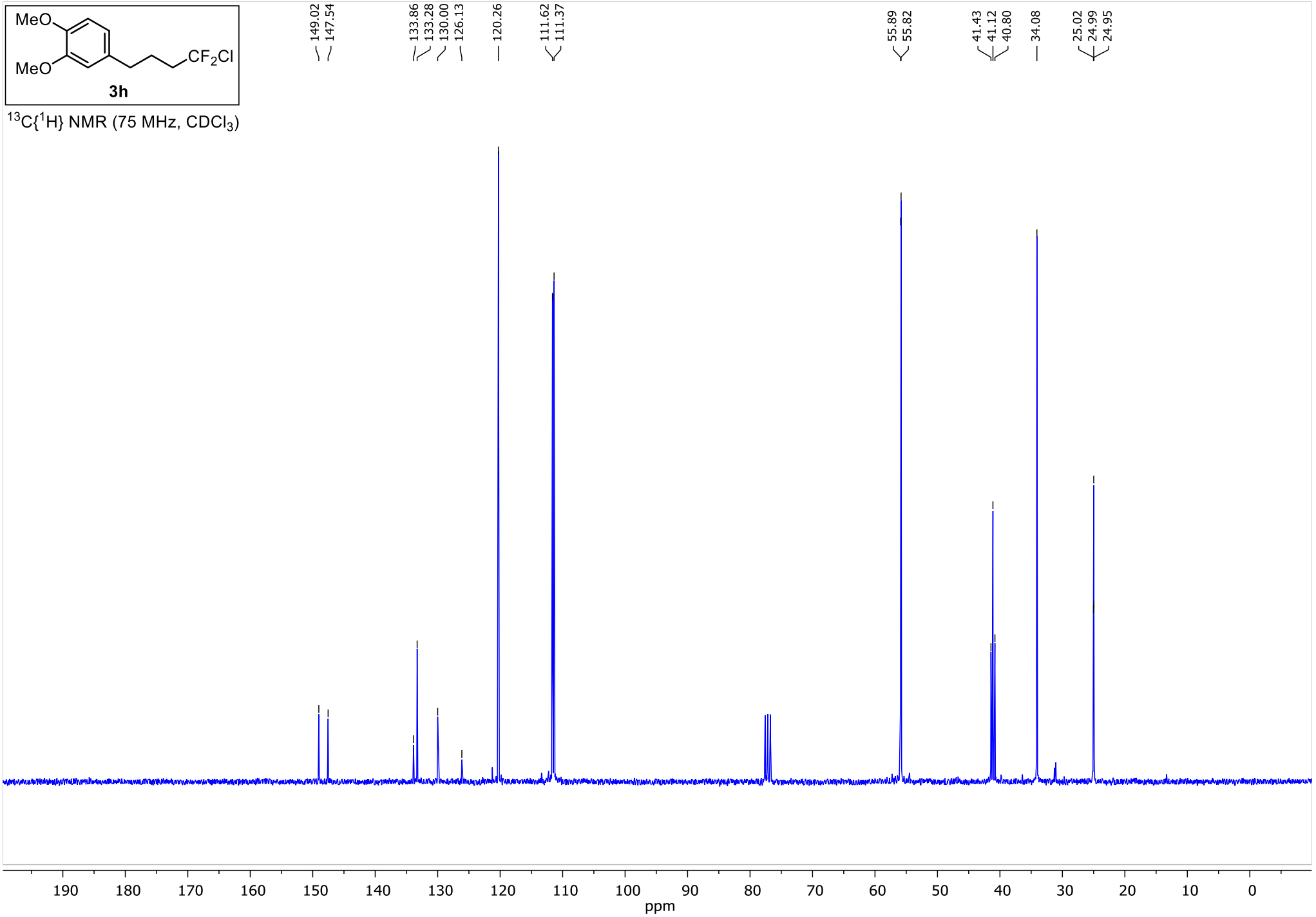

165.69
139.55
133.69
133.07
131.03
130.69
129.82
129.63
128.84
128.73
128.48
125.96
64.46
41.79
41.47
41.15
27.76
20.23
20.19
20.15
O
O
CF2Cl
Cl
3g
13C{1H} NMR (75 MHz, CDCl3)
133.69
133.07
130.69
129.82
129.63
128.73
128.48
125.96
135 134 133 132 131 130 129 128 127 126 125
ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

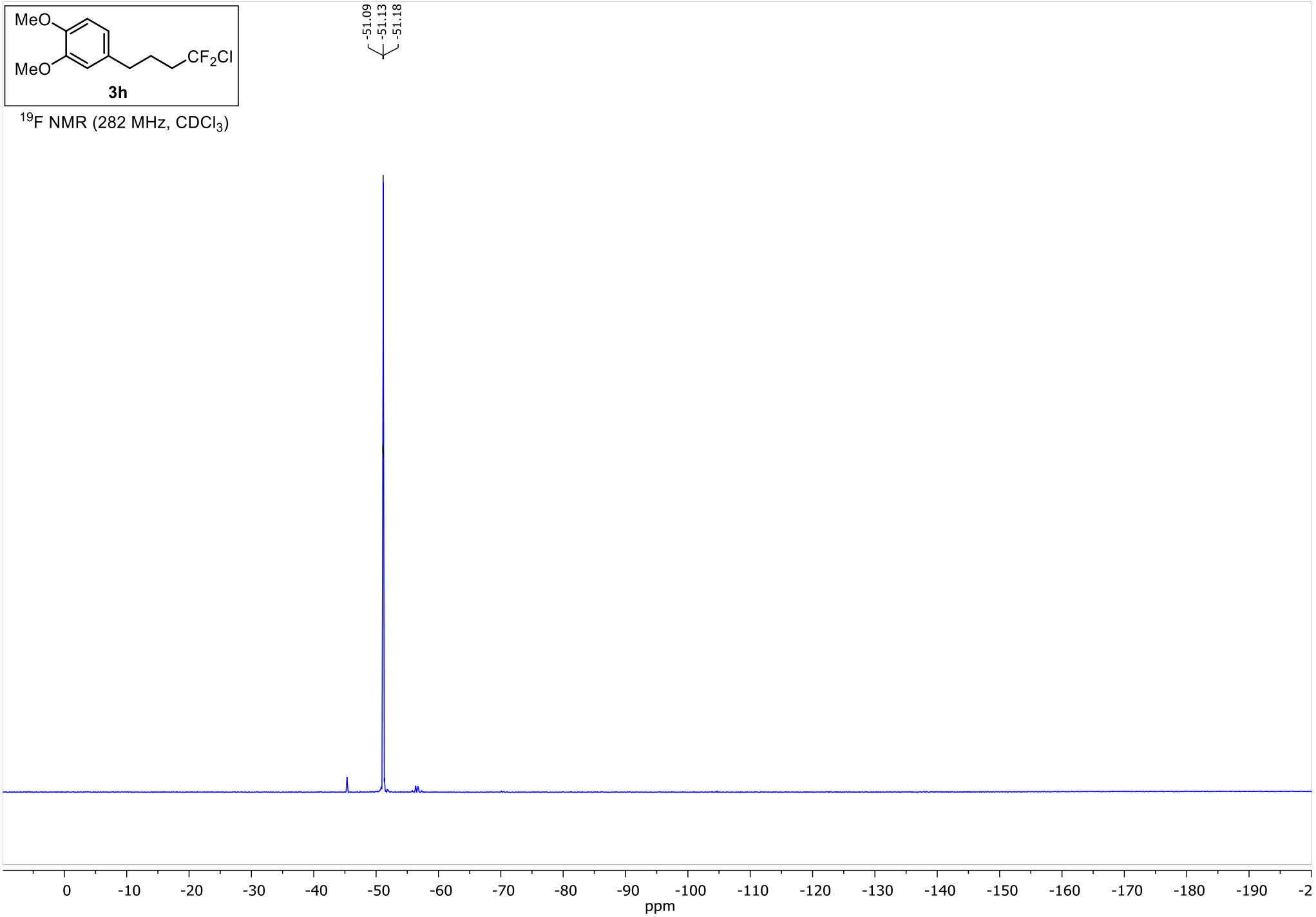


3g

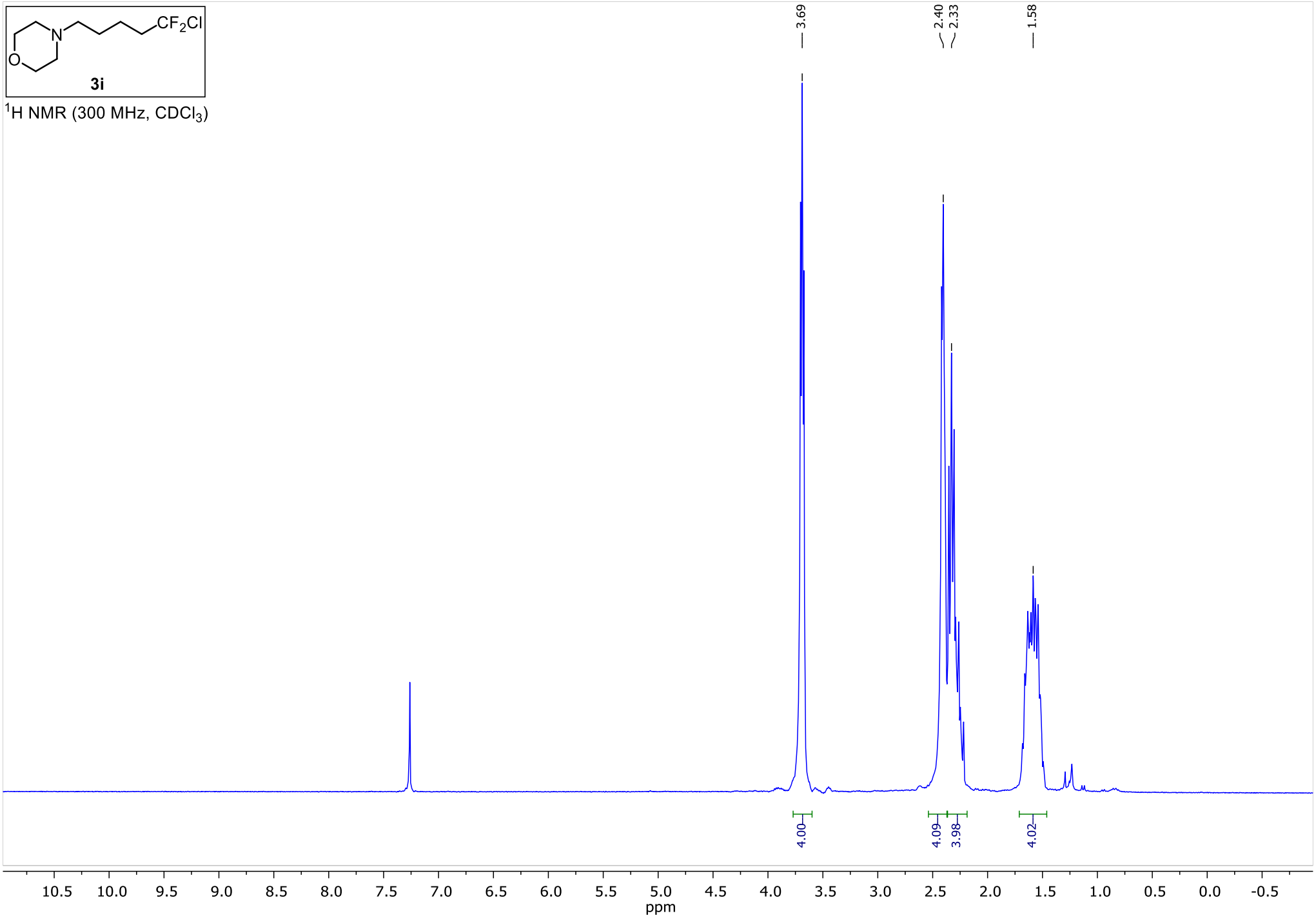
^{19}F NMR (282 MHz, $CDCl_3$)

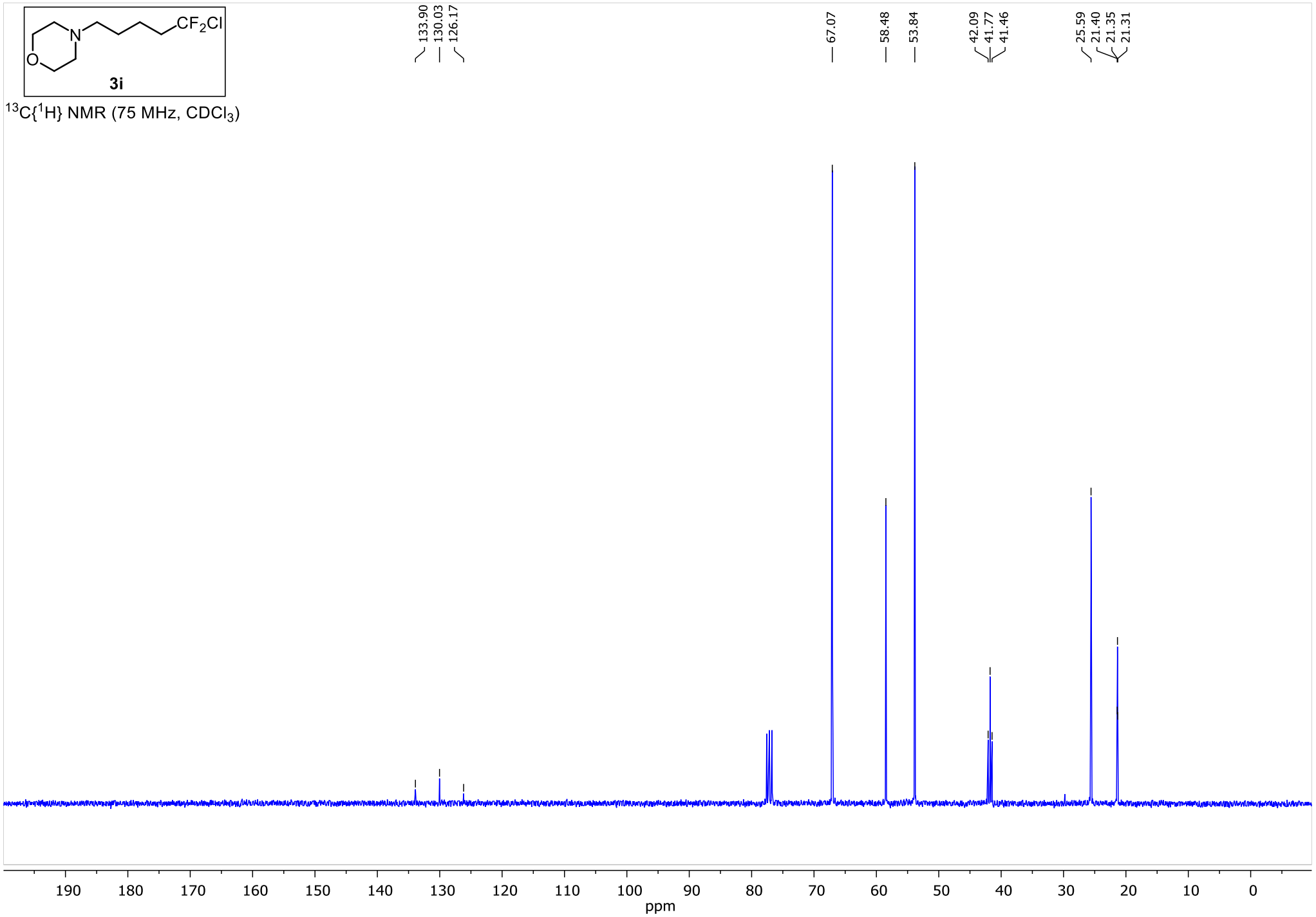

MeO
MeO
CF2Cl
3h
1H NMR (300 MHz, CDCl3)
6.82
6.80
6.73
6.70
3.88
3.86
2.65
2.29
1.93
1.00
2.02
6.05
2.00
2.06
2.05
ppm

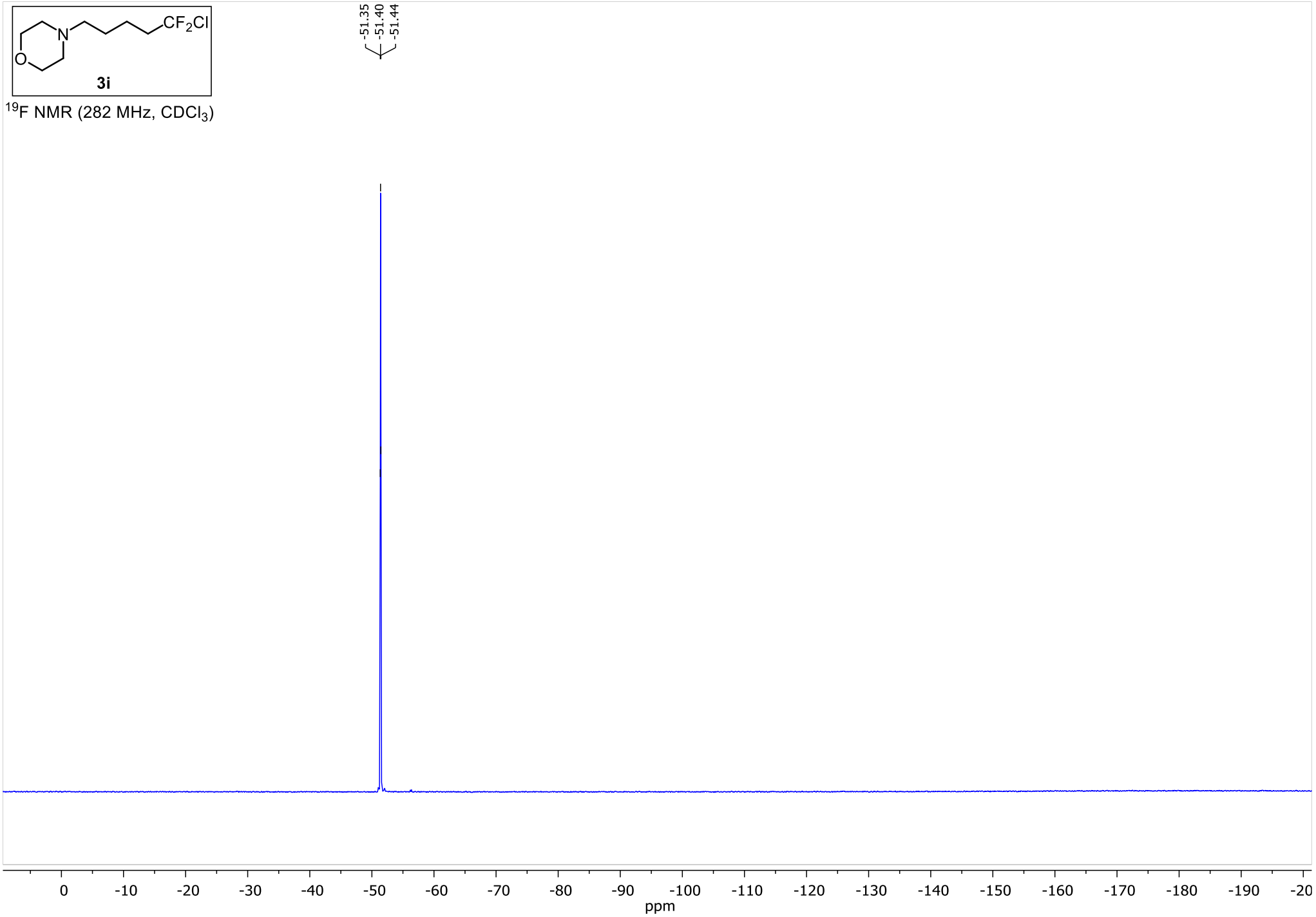

MeO
MeO
CF2Cl
3h
13C{1H} NMR (75 MHz, CDCl3)
149.02
147.54
133.86
133.28
130.00
126.13
120.26
111.62
111.37
55.89
55.82
41.43
41.12
40.80
34.08
25.02
24.99
24.95
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

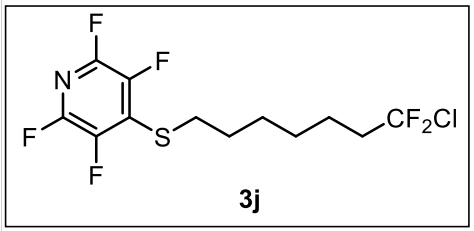


^{19}F NMR (282 MHz, $CDCl_3$)


3i
^{1}H NMR (300 MHz, $CDCl_3$)
3.69
2.40
2.33
1.58
4.00
4.09
3.98
4.02
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
ppm

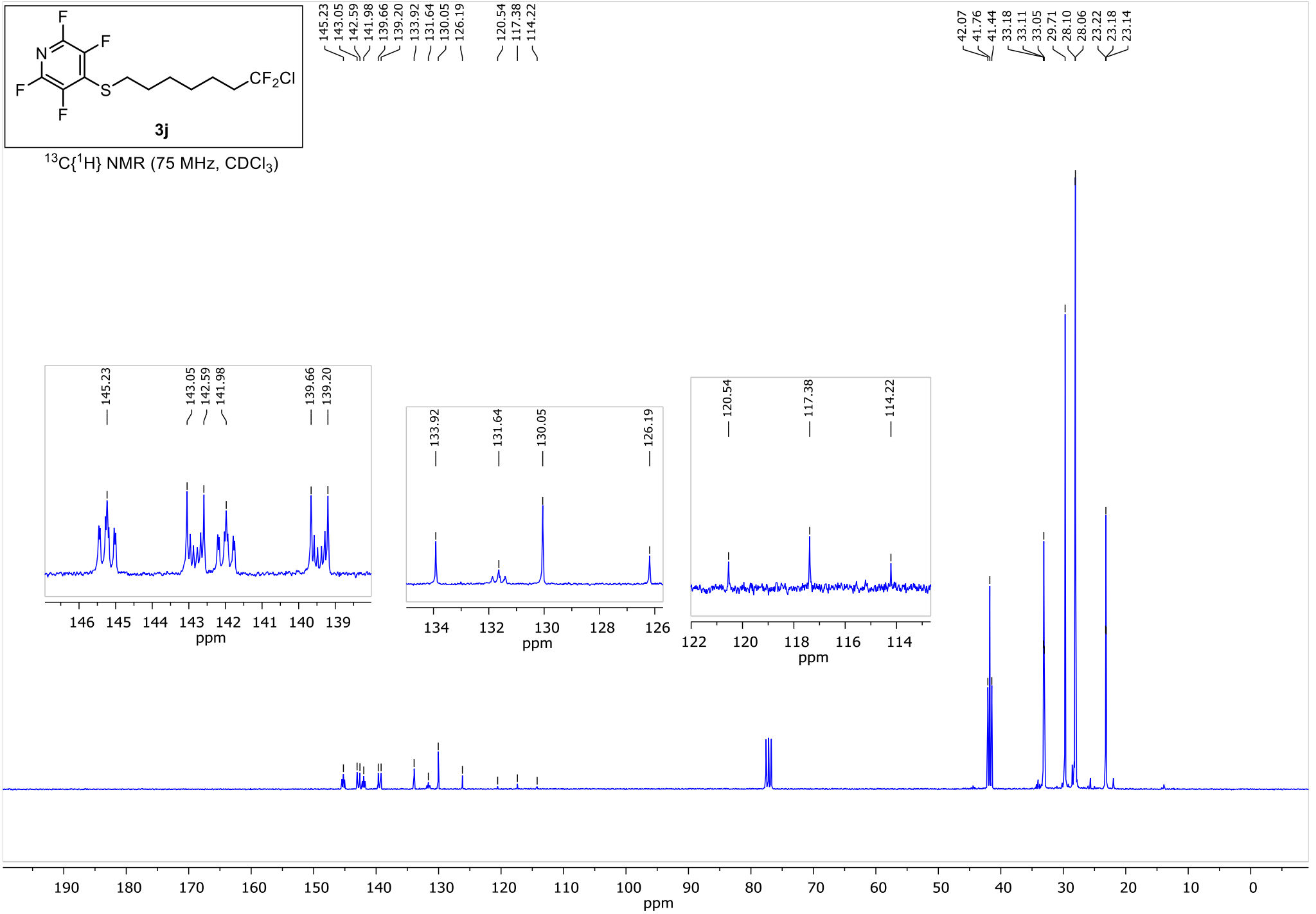

3i
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
133.90
130.03
126.17
67.07
58.48
53.84
42.09
41.77
41.46
25.59
21.40
21.35
21.31
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

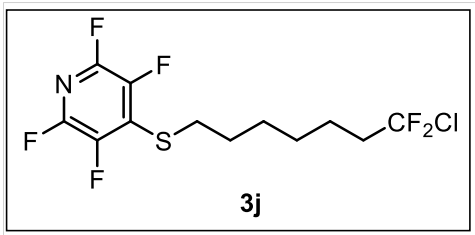

-51.35
-51.40
-51.44
3i
19F NMR (282 MHz, CDCl3)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
ppm



3j

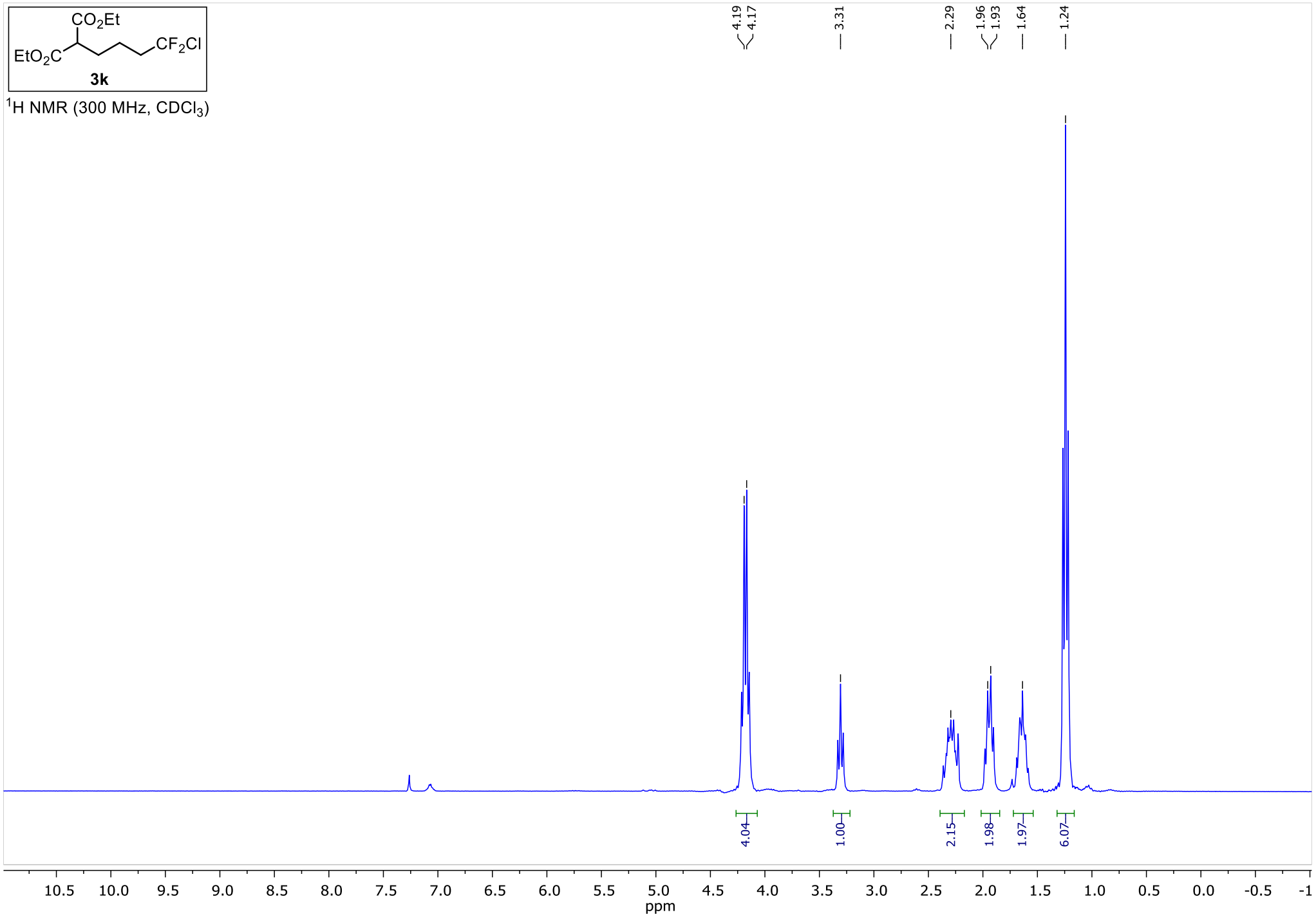
^{1}H NMR (300 MHz, $CDCl_3$)

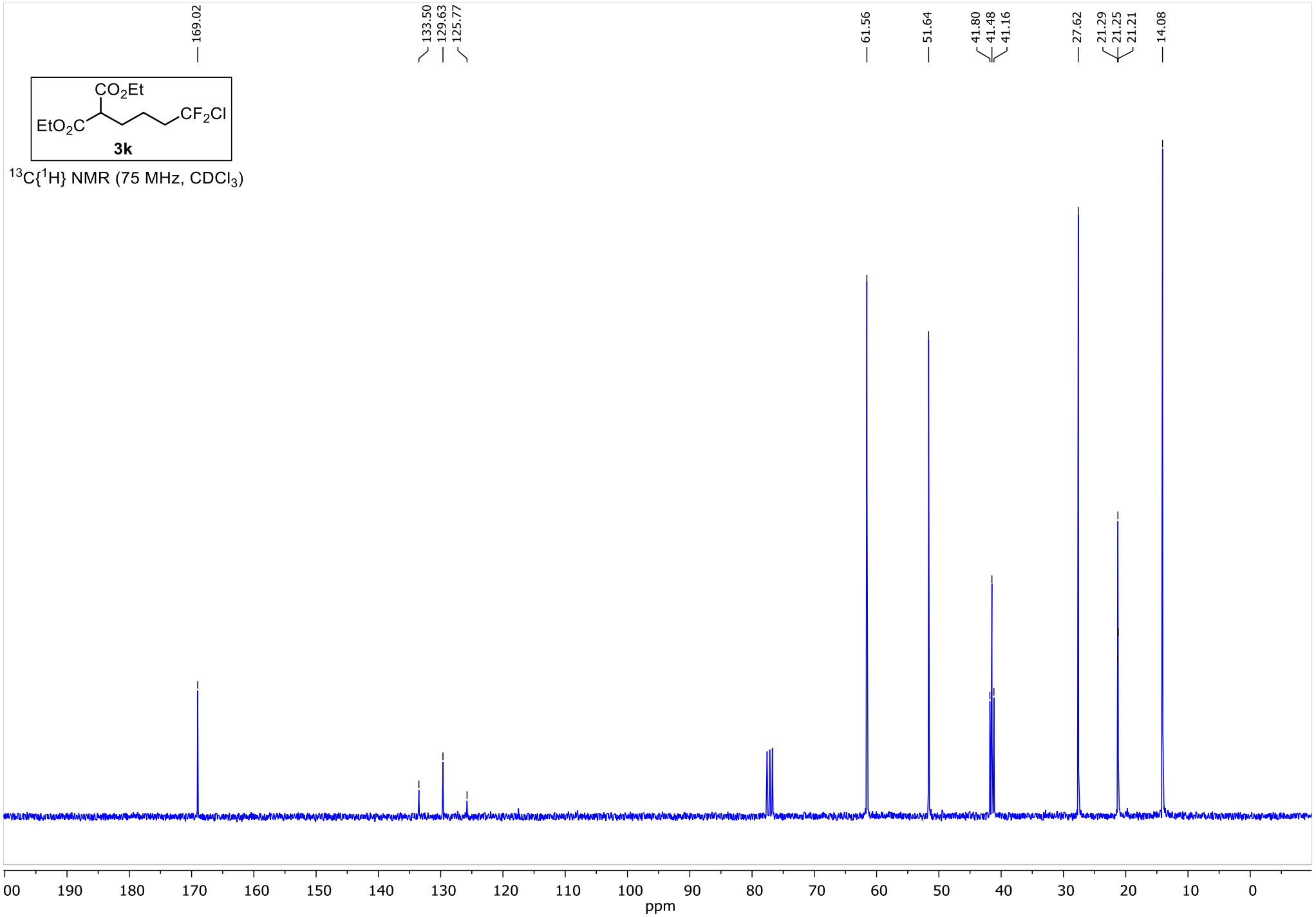

F
F
N
F
F
S
CF2Cl
3j
13C{1H} NMR (75 MHz, CDCl3)
145.23
143.05
142.59
141.98
139.66
139.20
133.92
131.64
130.05
126.19
120.54
117.38
114.22
42.07
41.76
41.44
33.18
33.11
33.05
29.71
28.10
28.06
23.22
23.18
23.14
ppm

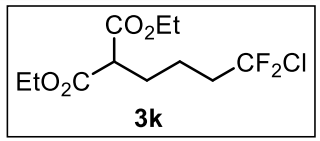


3j

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

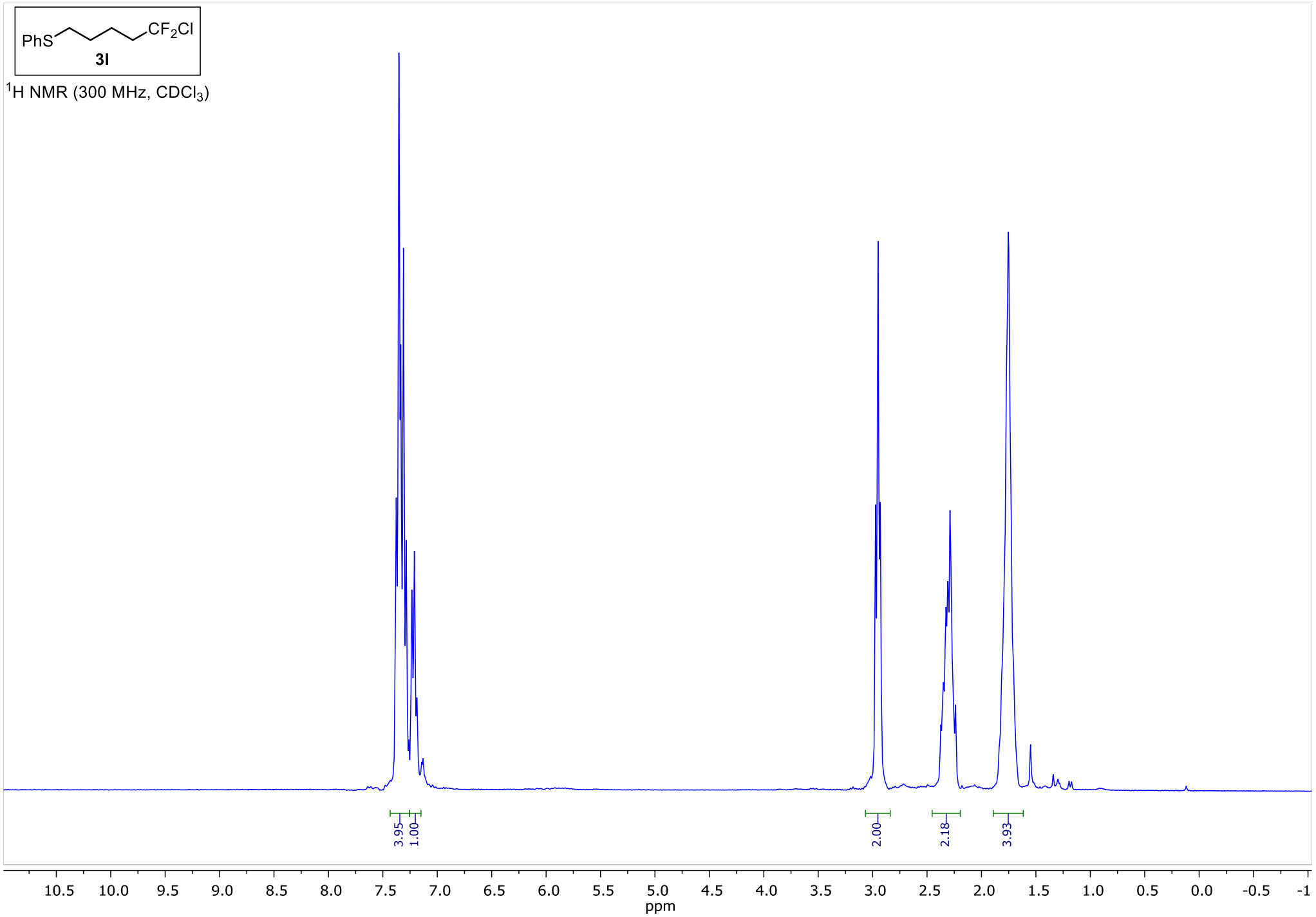

CO2Et
EtO2C
CF2Cl
3k
1H NMR (300 MHz, CDCl3)
4.19
4.17
3.31
2.29
1.96
1.93
1.64
1.24
4.04
1.00
2.15
1.98
1.97
6.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
ppm

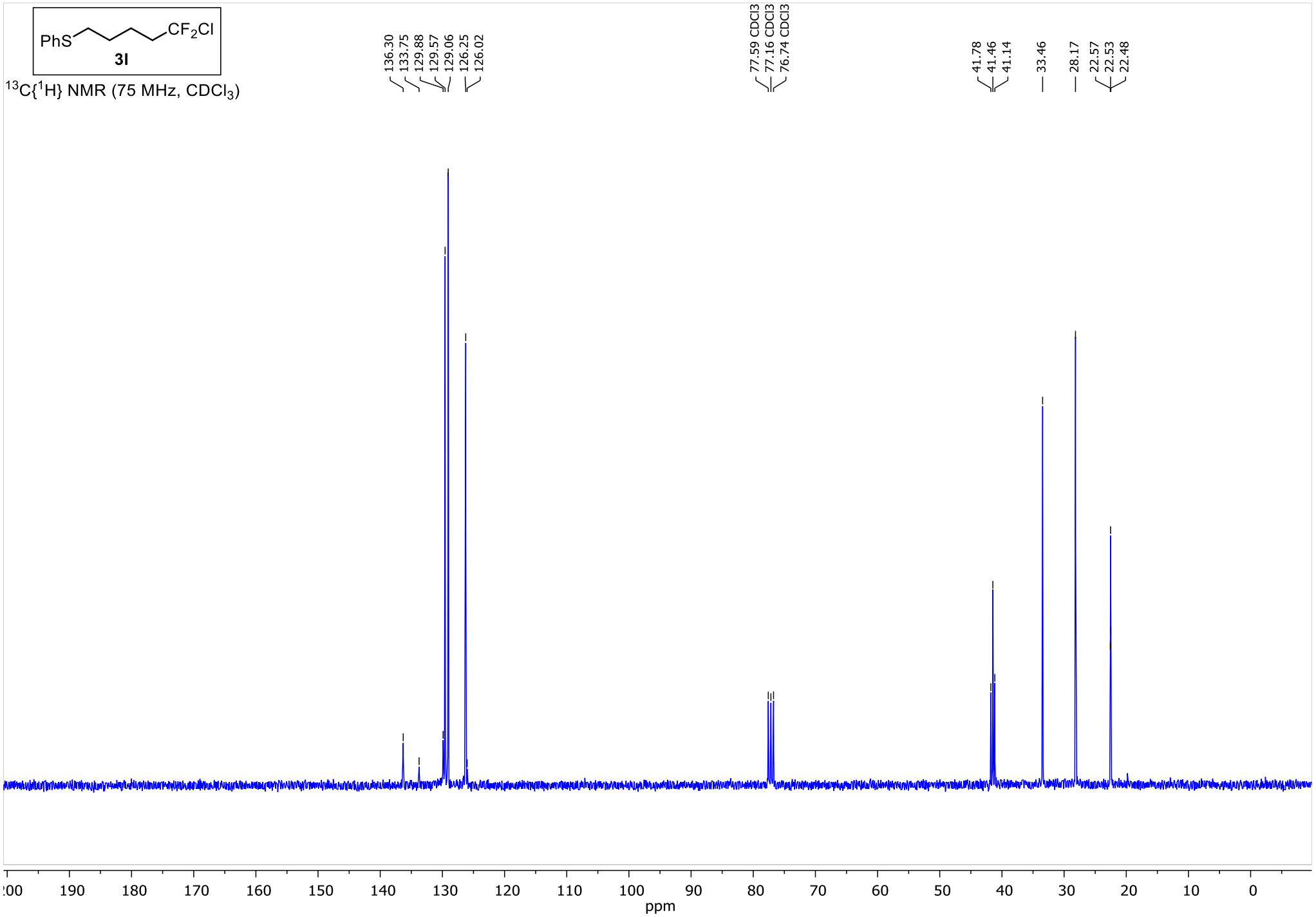

169.02
133.50
129.63
125.77
61.56
51.64
41.80
41.48
41.16
27.62
21.29
21.25
21.21
14.08
CO2Et
EtO2C
CF2Cl
3k
13C{1H} NMR (75 MHz, CDCl3)
ppm

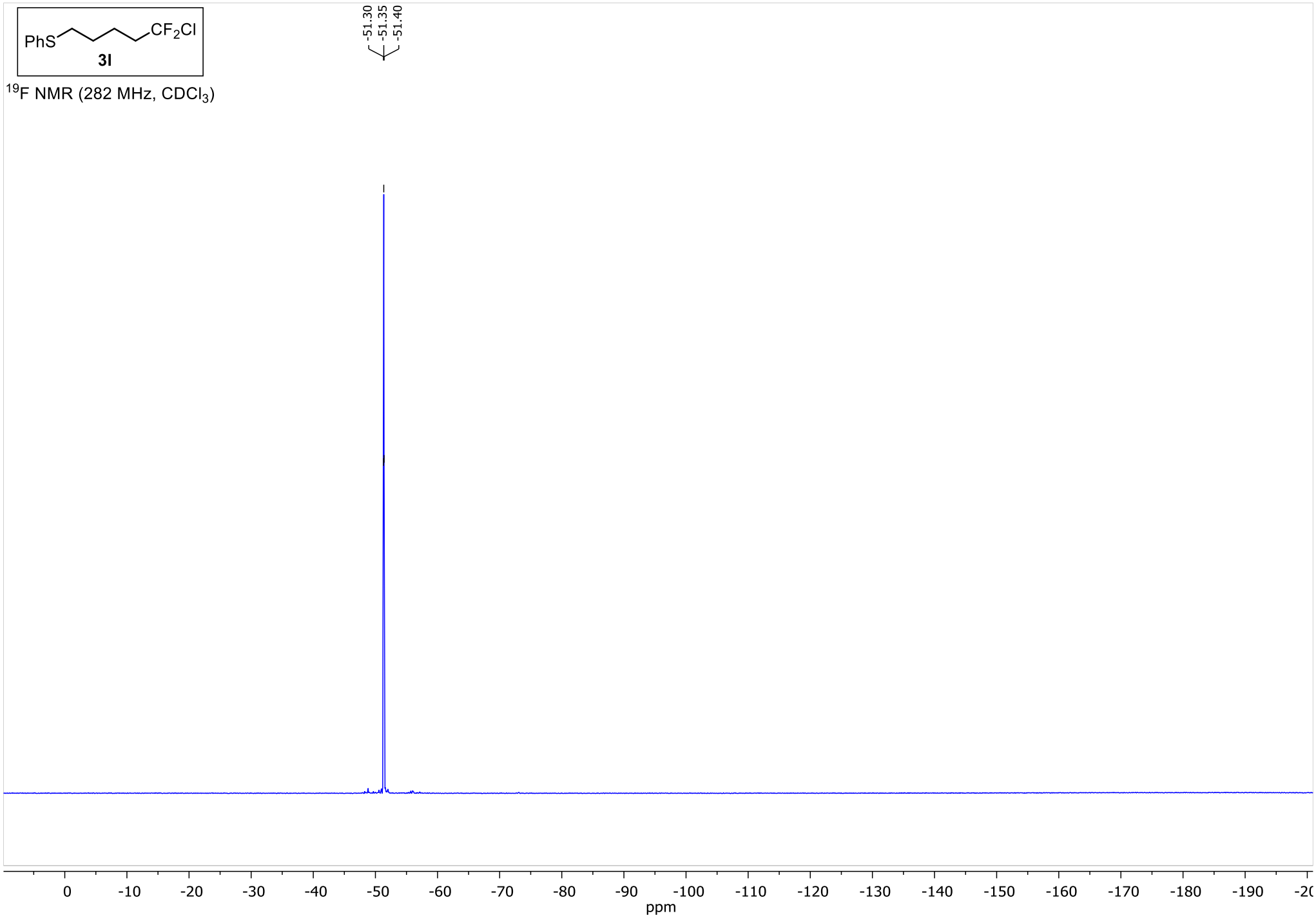


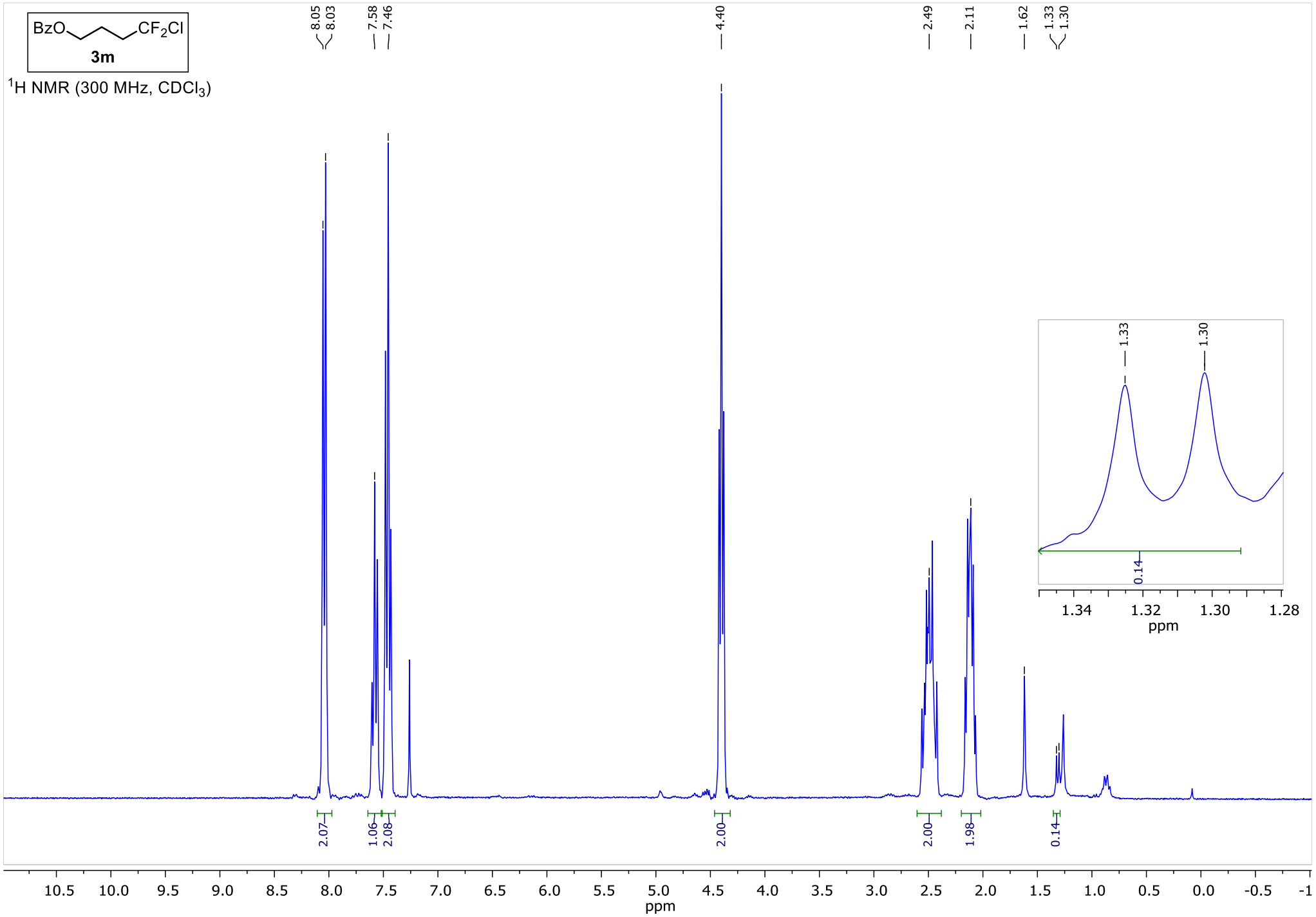
3k

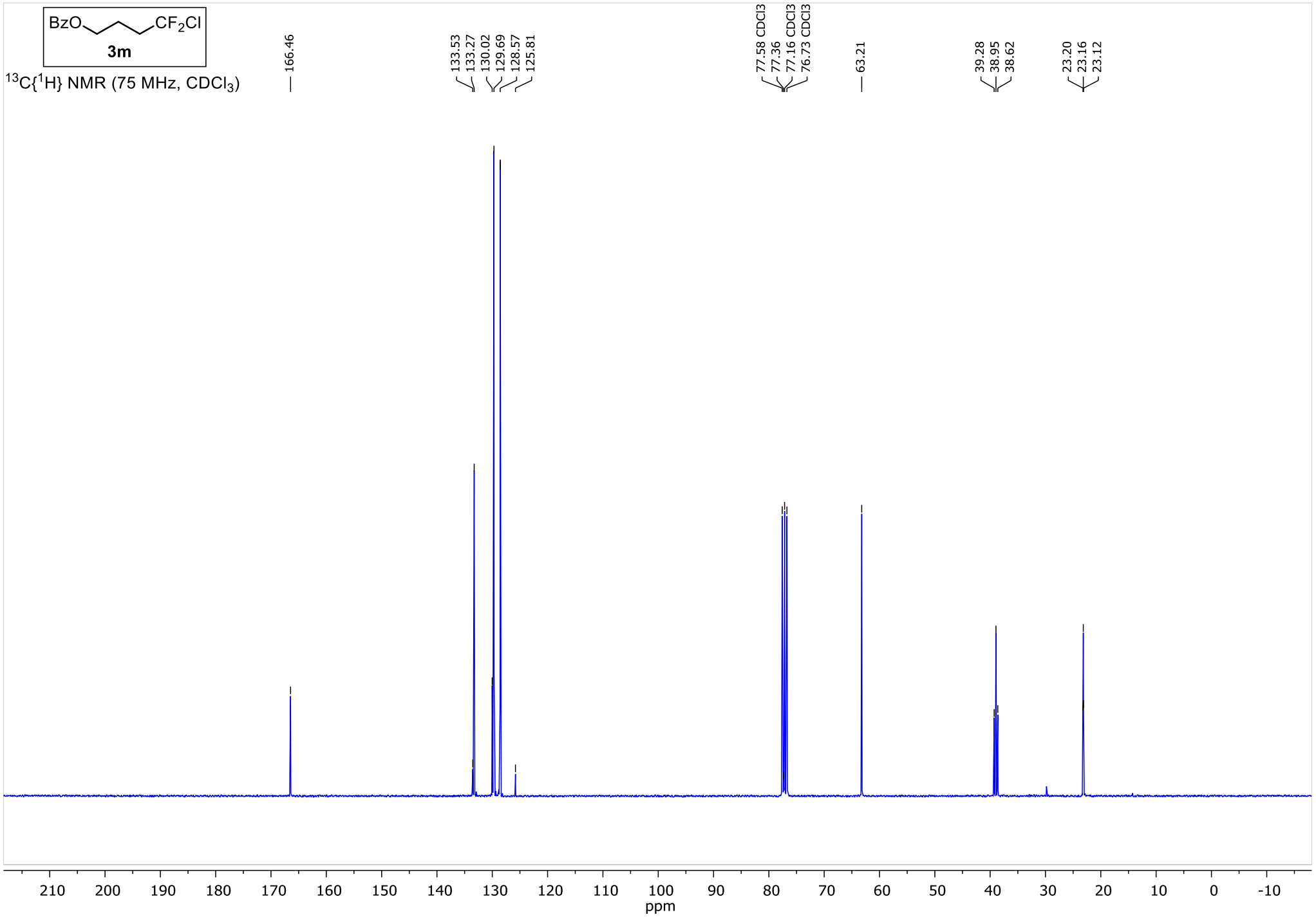
^{19}F NMR (282 MHz, $CDCl_3$)

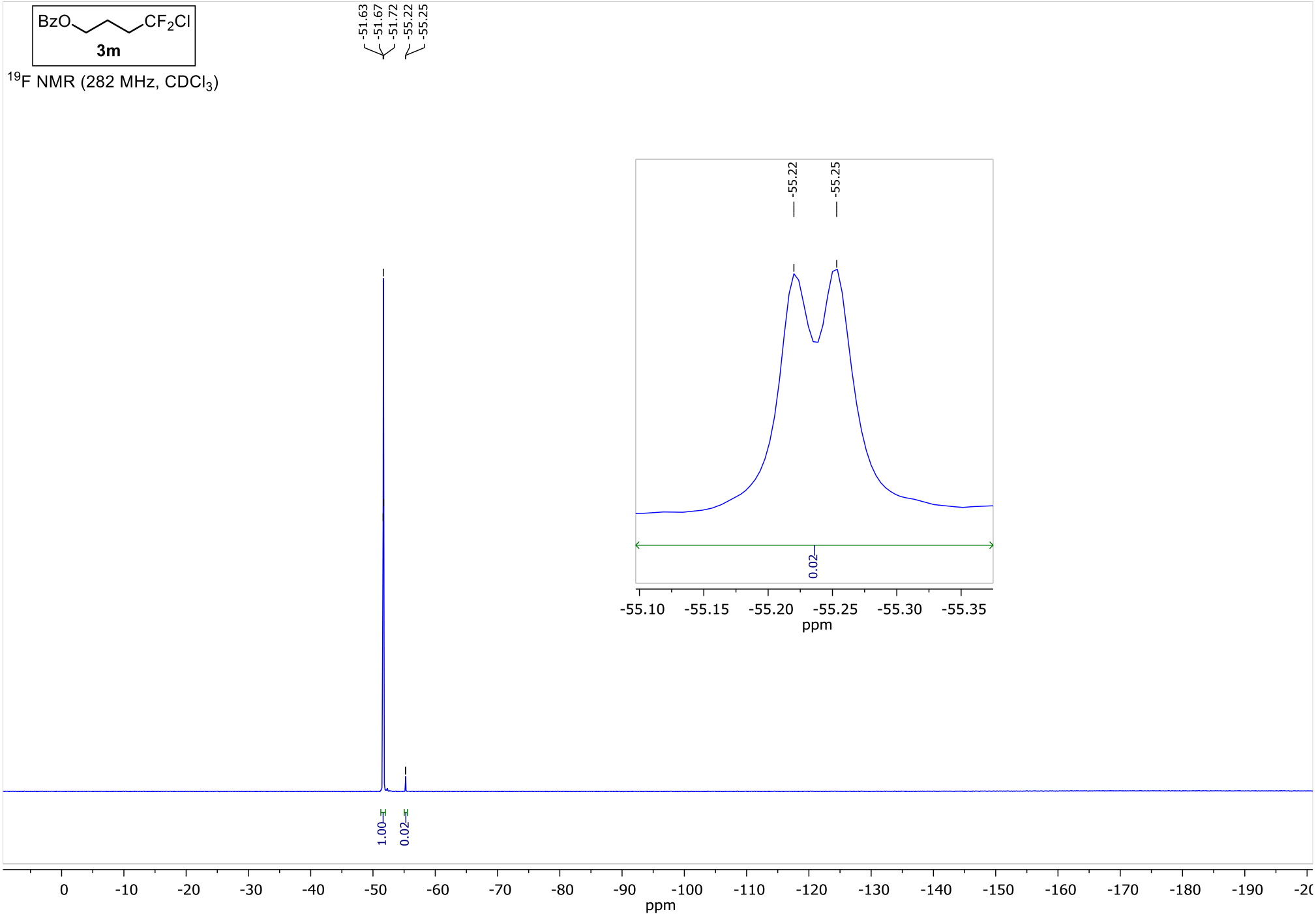

PhS
CF2Cl
3l
1H NMR (300 MHz, CDCl3)
3.95
1.00
2.00
2.18
3.93
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
ppm

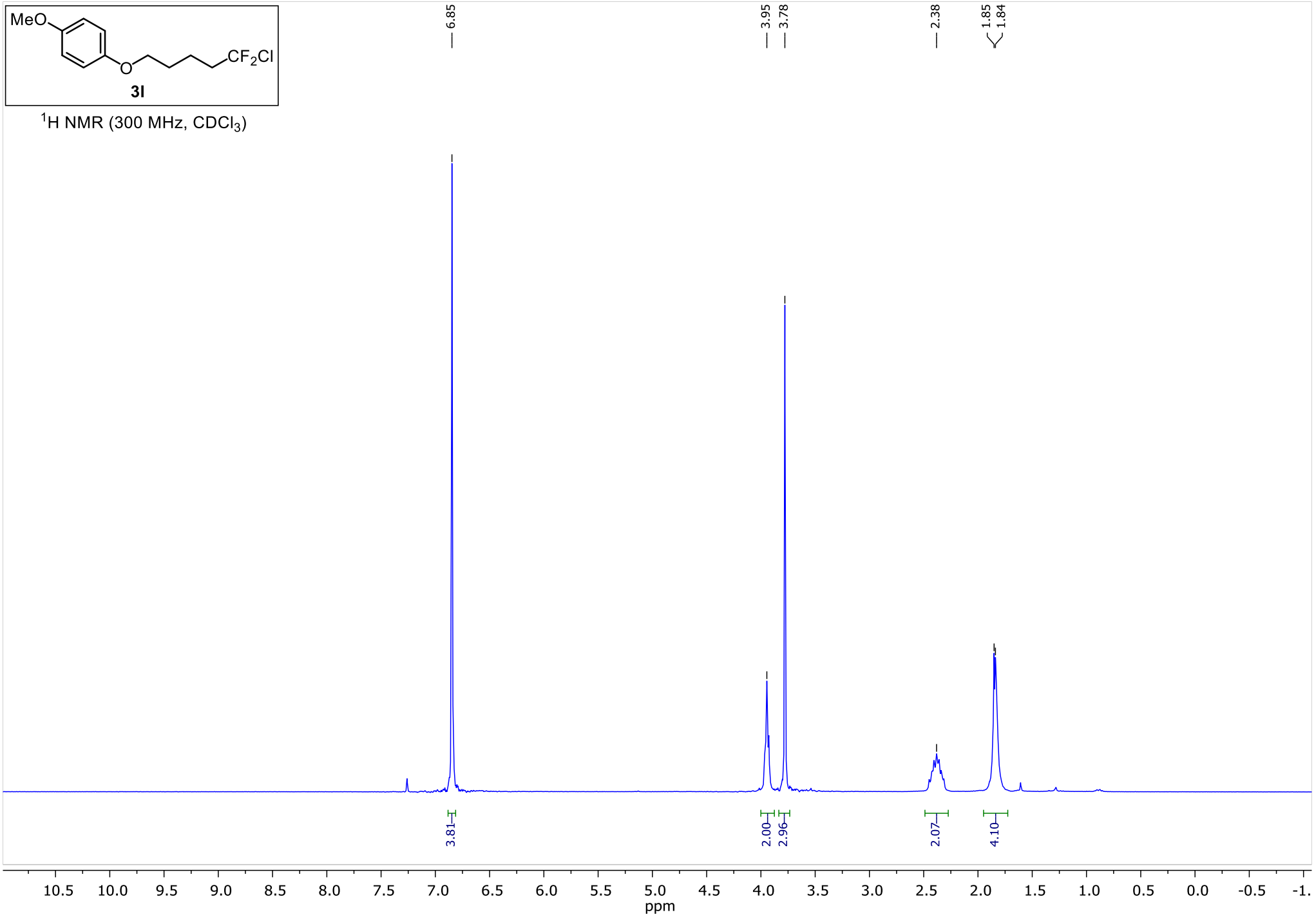

PhS
CF2Cl
3l
13C{1H} NMR (75 MHz, CDCl3)
136.30
133.75
129.88
129.57
129.06
126.25
126.02
77.59 CDCl3
77.16 CDCl3
76.74 CDCl3
41.78
41.46
41.14
33.46
28.17
22.57
22.53
22.48
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

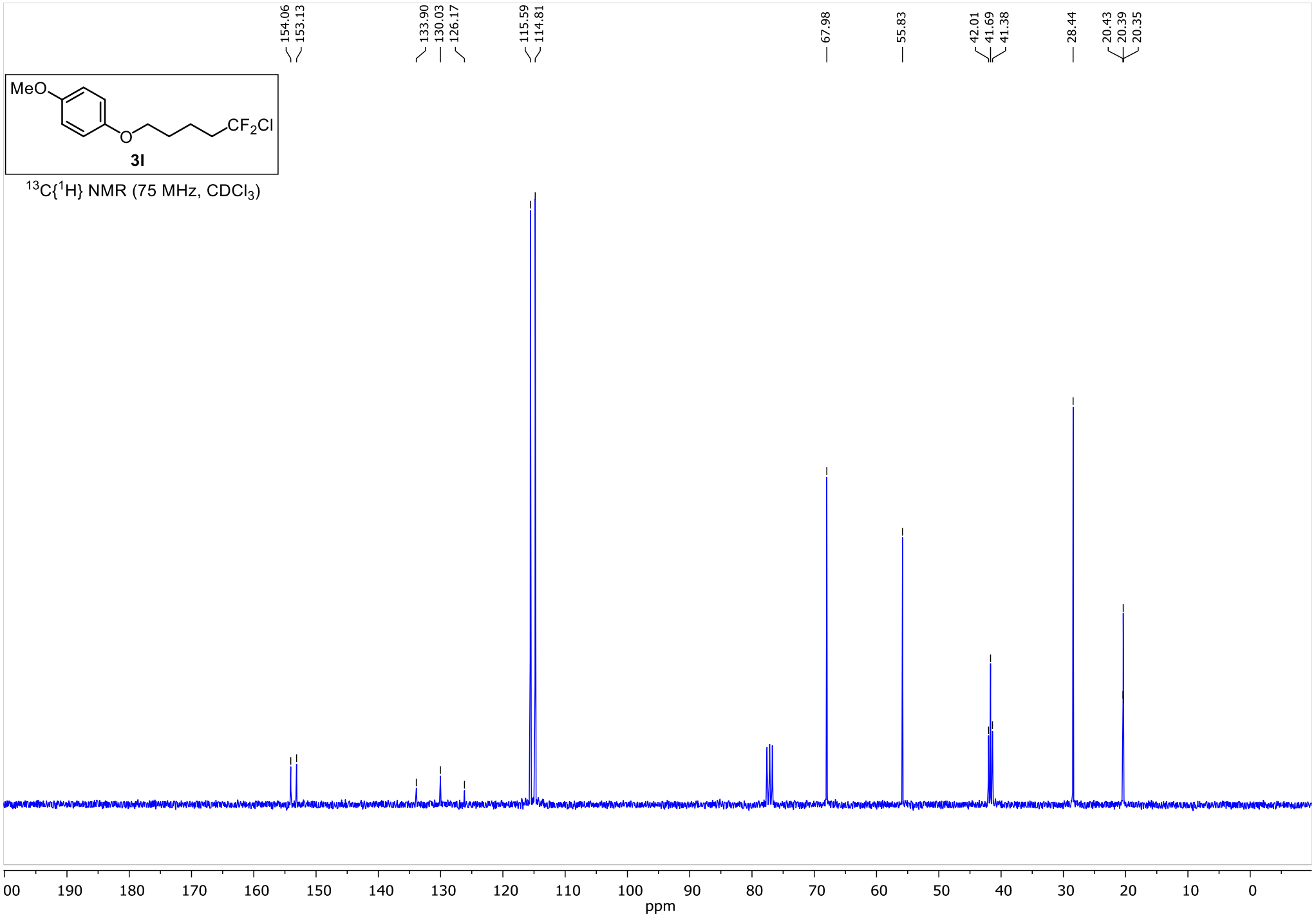

PhS
CF2Cl
3l
-51.30
-51.35
-51.40
19F NMR (282 MHz, CDCl3)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm

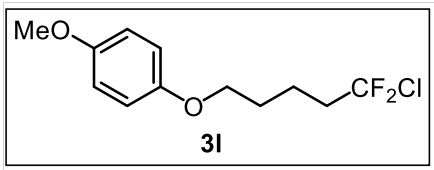

BzO
CF2Cl
3m
1H NMR (300 MHz, CDCl3)
8.05
8.03
7.58
7.46
4.40
2.49
2.11
1.62
1.33
1.30
2.07
1.06
2.08
2.00
2.00
1.98
0.14
1.33
1.30
0.14
1.34
1.32
1.30
1.28
ppm
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
ppm


BzO
CF2Cl
3m
13C{1H} NMR (75 MHz, CDCl3)
166.46
133.53
133.27
130.02
129.69
128.57
125.81
77.58 CDCl3
77.36
77.16 CDCl3
76.73 CDCl3
63.21
39.28
38.95
38.62
23.20
23.16
23.12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


BzO
CF2Cl
3m
19F NMR (282 MHz, CDCl3)
-51.63
-51.67
-51.72
-55.22
-55.25
-55.22
-55.25
0.02
-55.10
-55.15
-55.20
-55.25
-55.30
-55.35
ppm
1.00
0.02
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm

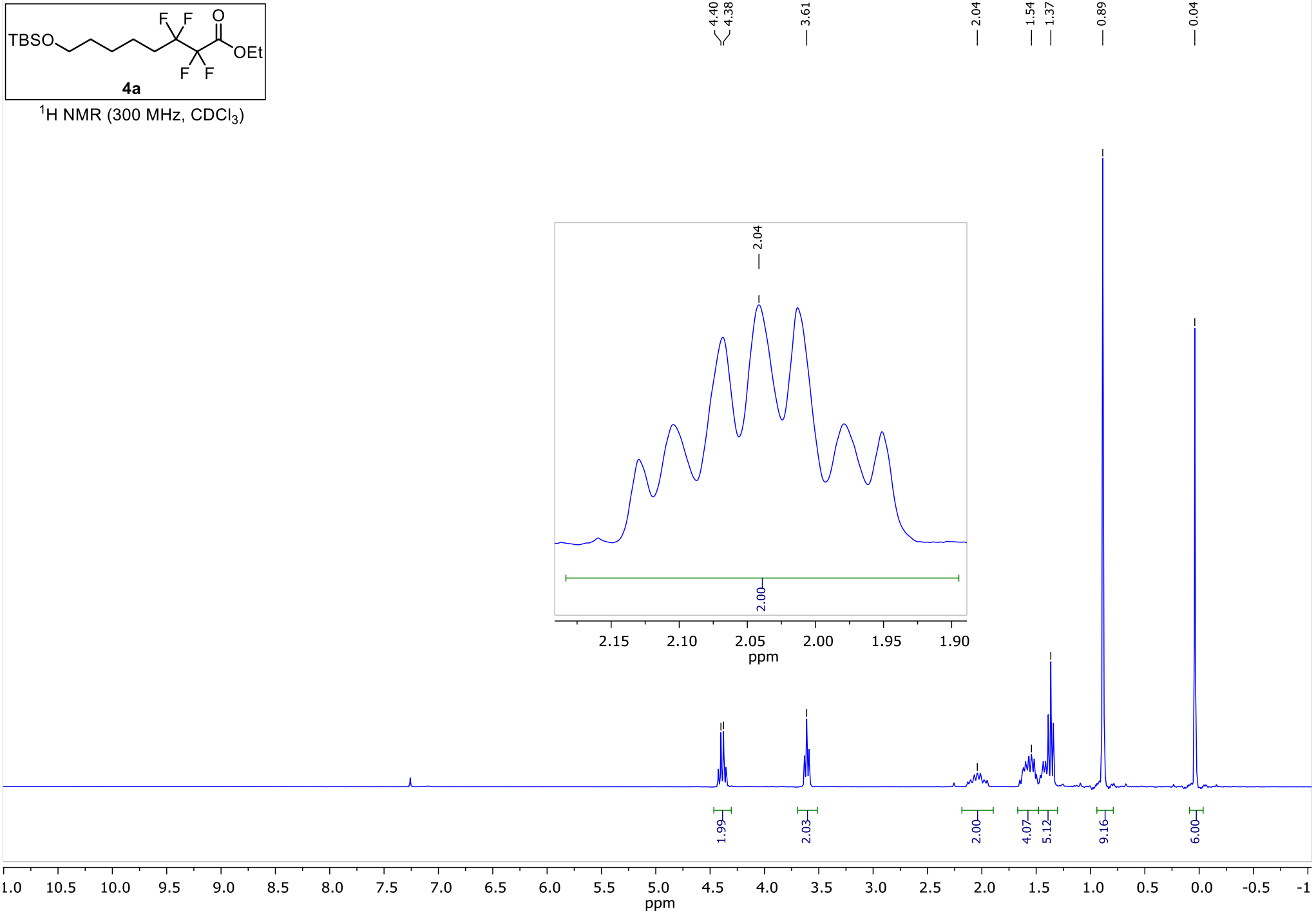

MeO
O
CF2Cl
3l
1H NMR (300 MHz, CDCl3)
6.85
3.95
3.78
2.38
1.85
1.84
3.81
2.00
2.96
2.07
4.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
ppm

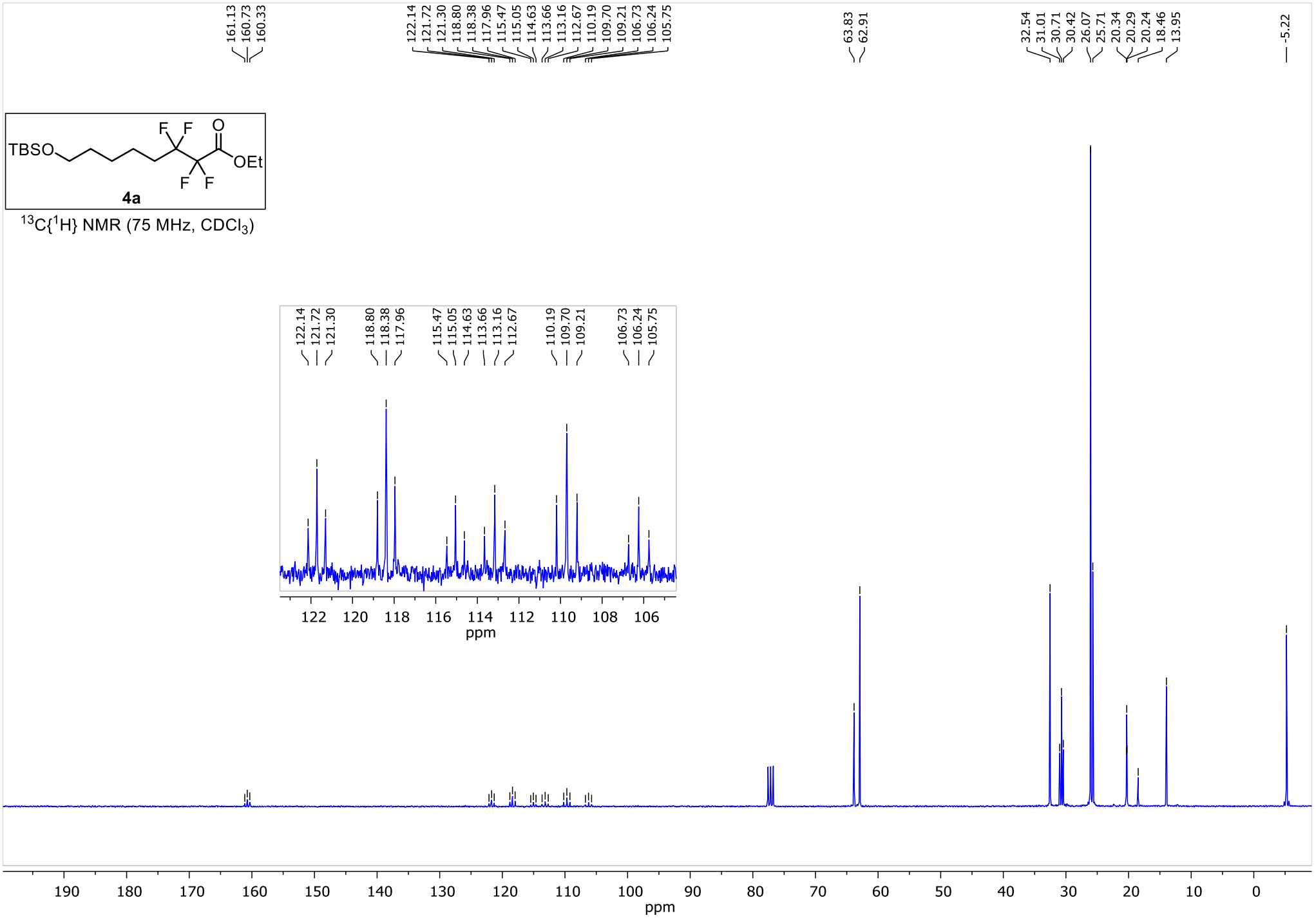

154.06
153.13
133.90
130.03
126.17
115.59
114.81
67.98
55.83
42.01
41.69
41.38
28.44
20.43
20.39
20.35
MeO
O
CF2Cl
3l
13C{1H} NMR (75 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

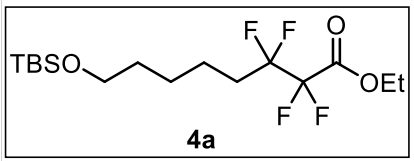


3l

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

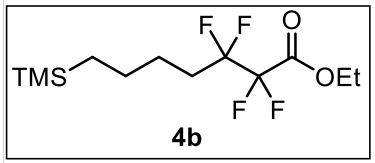

TBSO
F F O
OEt
F F
4a
1H NMR (300 MHz, CDCl3)
4.40
4.38
3.61
2.04
1.54
1.37
0.89
0.04
2.04
2.00
2.15 2.10 2.05 2.00 1.95 1.90
ppm
1.99
2.03
2.00
4.07
5.12
9.16
6.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
ppm


161.13
160.73
160.33
122.14
121.72
121.30
118.80
118.38
117.96
115.47
115.05
114.63
113.66
113.16
112.67
110.19
109.70
109.21
106.73
106.24
105.75
63.83
62.91
32.54
31.01
30.71
30.42
26.07
25.71
20.34
20.29
20.24
18.46
13.95
-5.22
TBSO
F
F
O
OEt
F
F
4a
13C{1H} NMR (75 MHz, CDCl3)
ppm
ppm



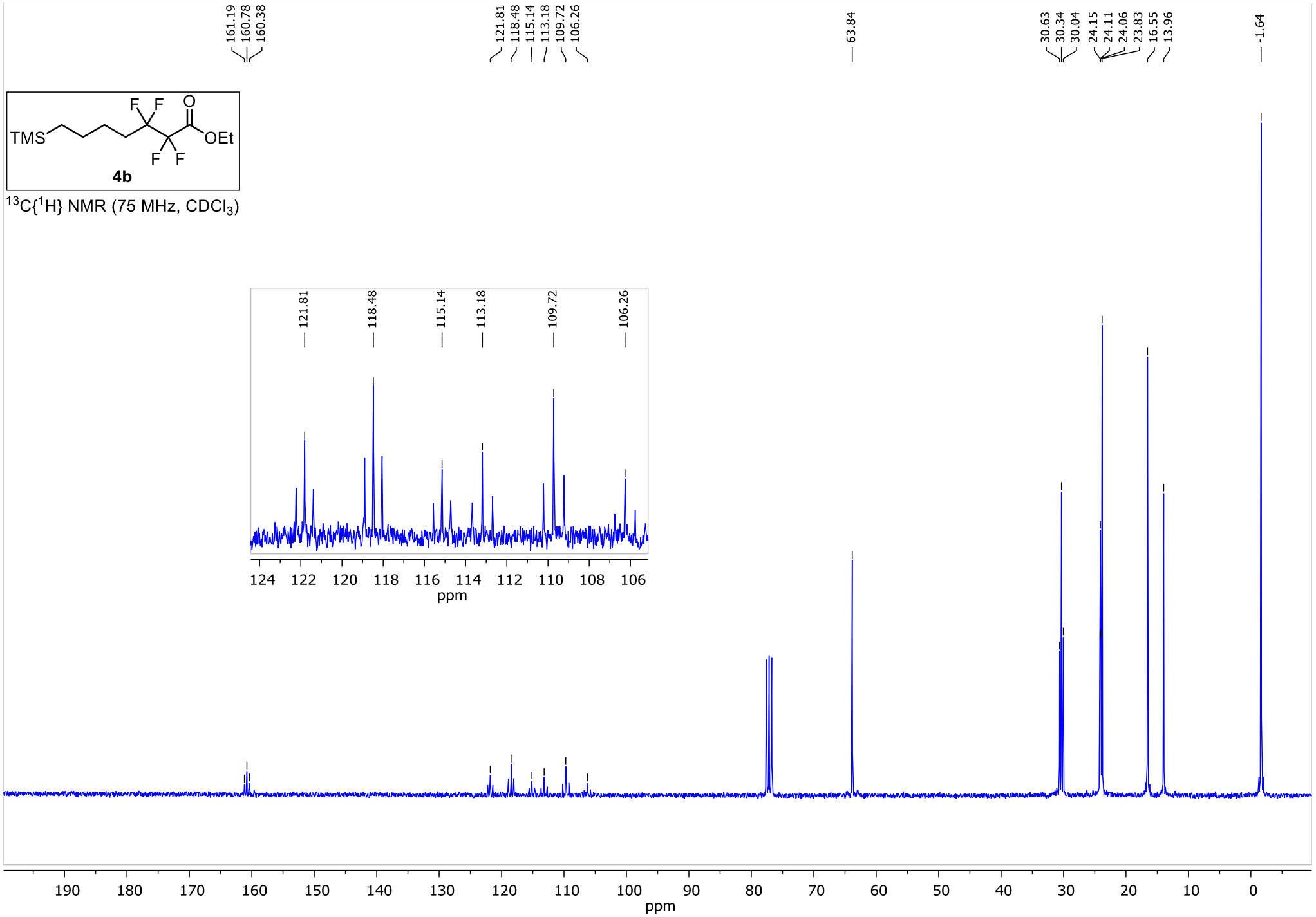
4a

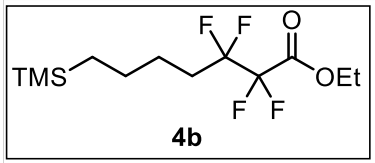
^{19}F NMR (282 MHz, $CDCl_3$)



4b

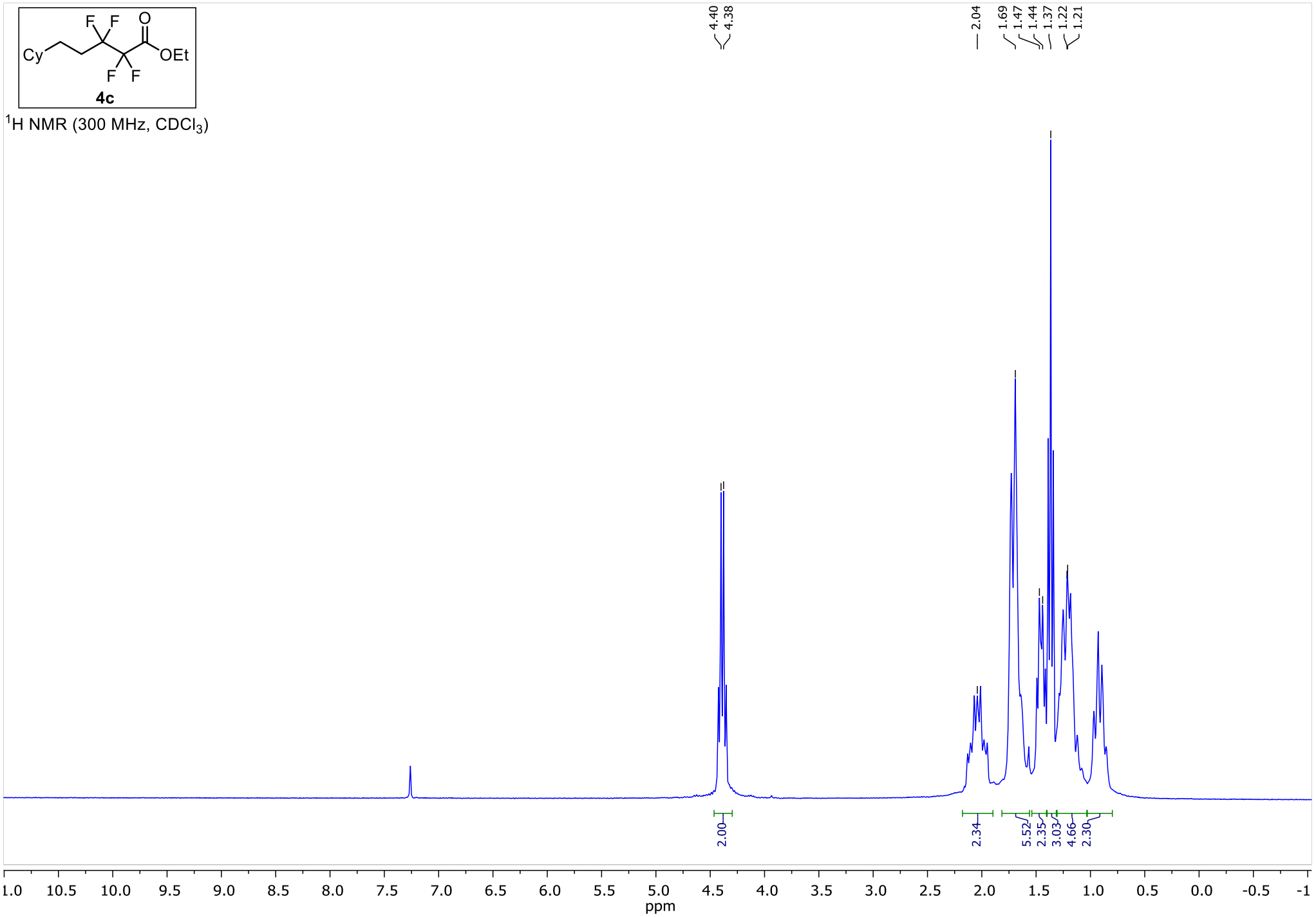
^{1}H NMR (300 MHz, $CDCl_3$)

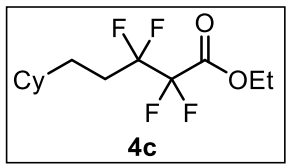

161.19
160.78
160.38
121.81
118.48
115.14
113.18
109.72
106.26
63.84
30.63
30.34
30.04
24.15
24.11
24.06
23.83
16.55
13.96
-1.64
F F O
TMS
OEt
F F
4b
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
121.81
118.48
115.14
113.18
109.72
106.26
124 122 120 118 116 114 112 110 108 106
ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



4b

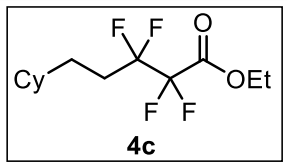
^{19}F NMR (282 MHz, $CDCl_3$)


F F O
Cy
OEt
F F
4c
1H NMR (300 MHz, CDCl3)
4.40
4.38
2.04
1.69
1.47
1.44
1.37
1.22
1.21
2.00
2.34
5.52
2.35
3.03
4.66
2.30
ppm



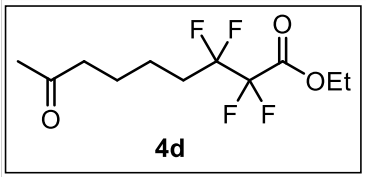
4c

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



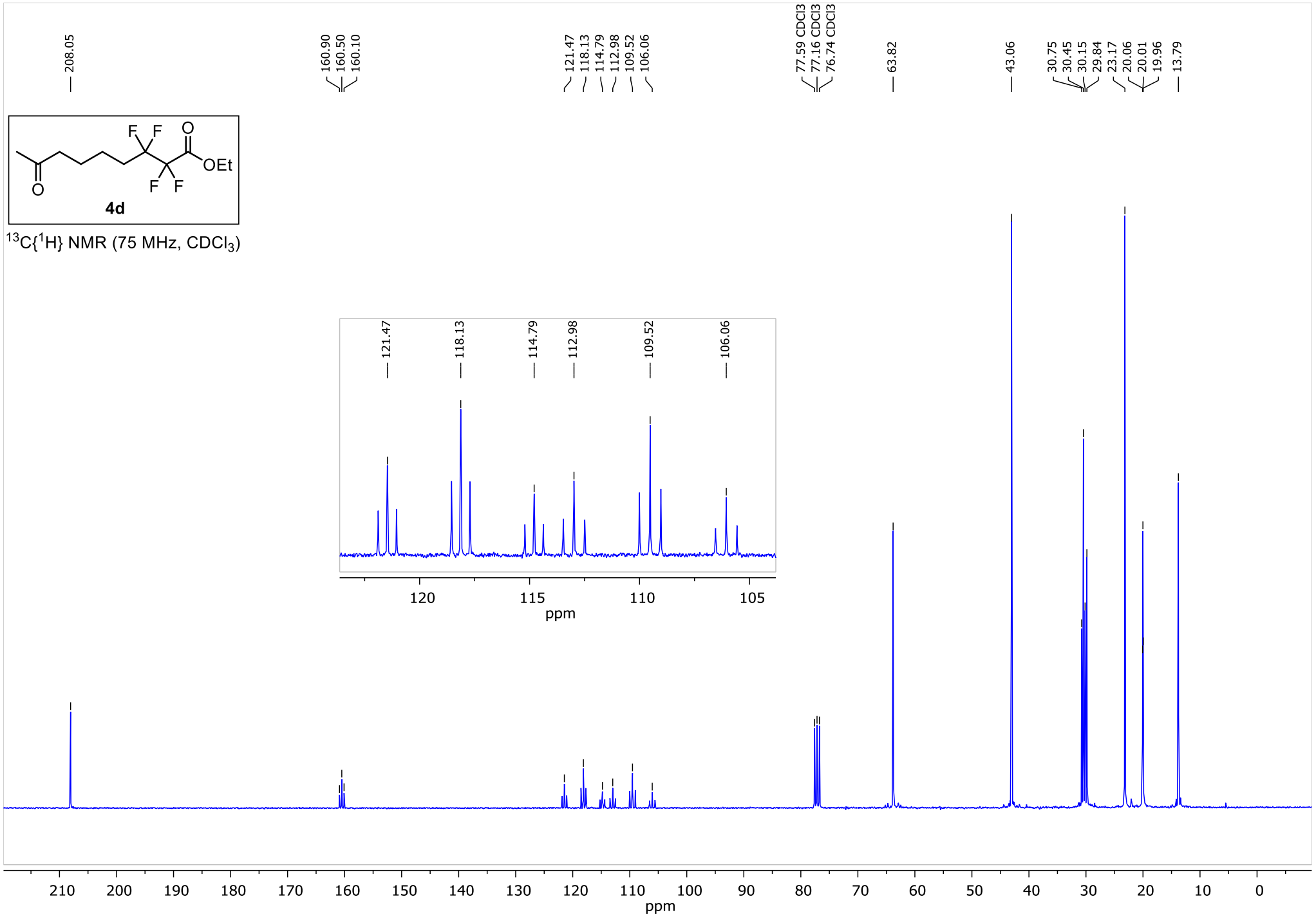
4c

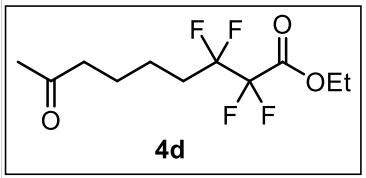
^{19}F NMR (282 MHz, $CDCl_3$)



4d

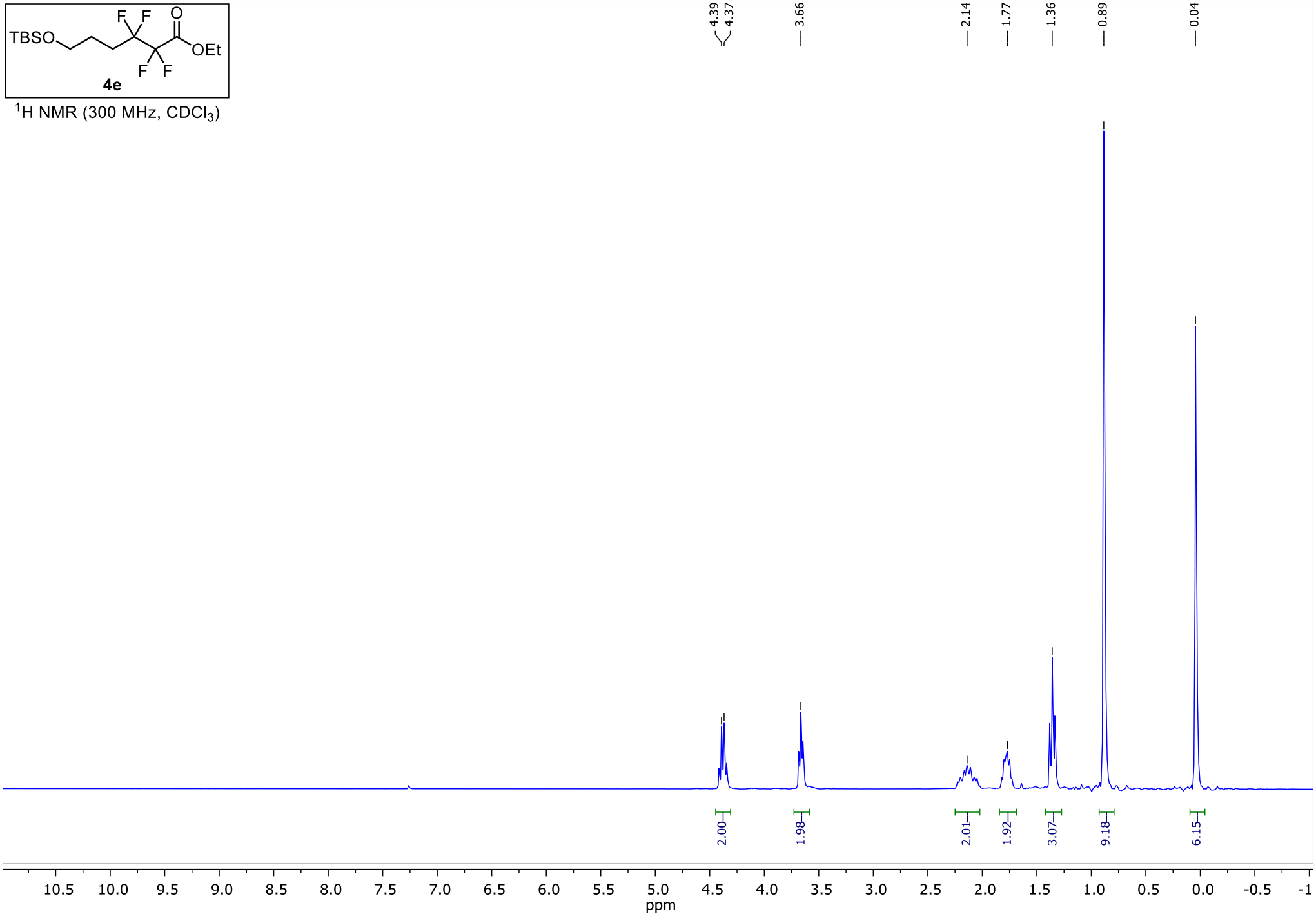
^{1}H NMR (300 MHz, $CDCl_3$)

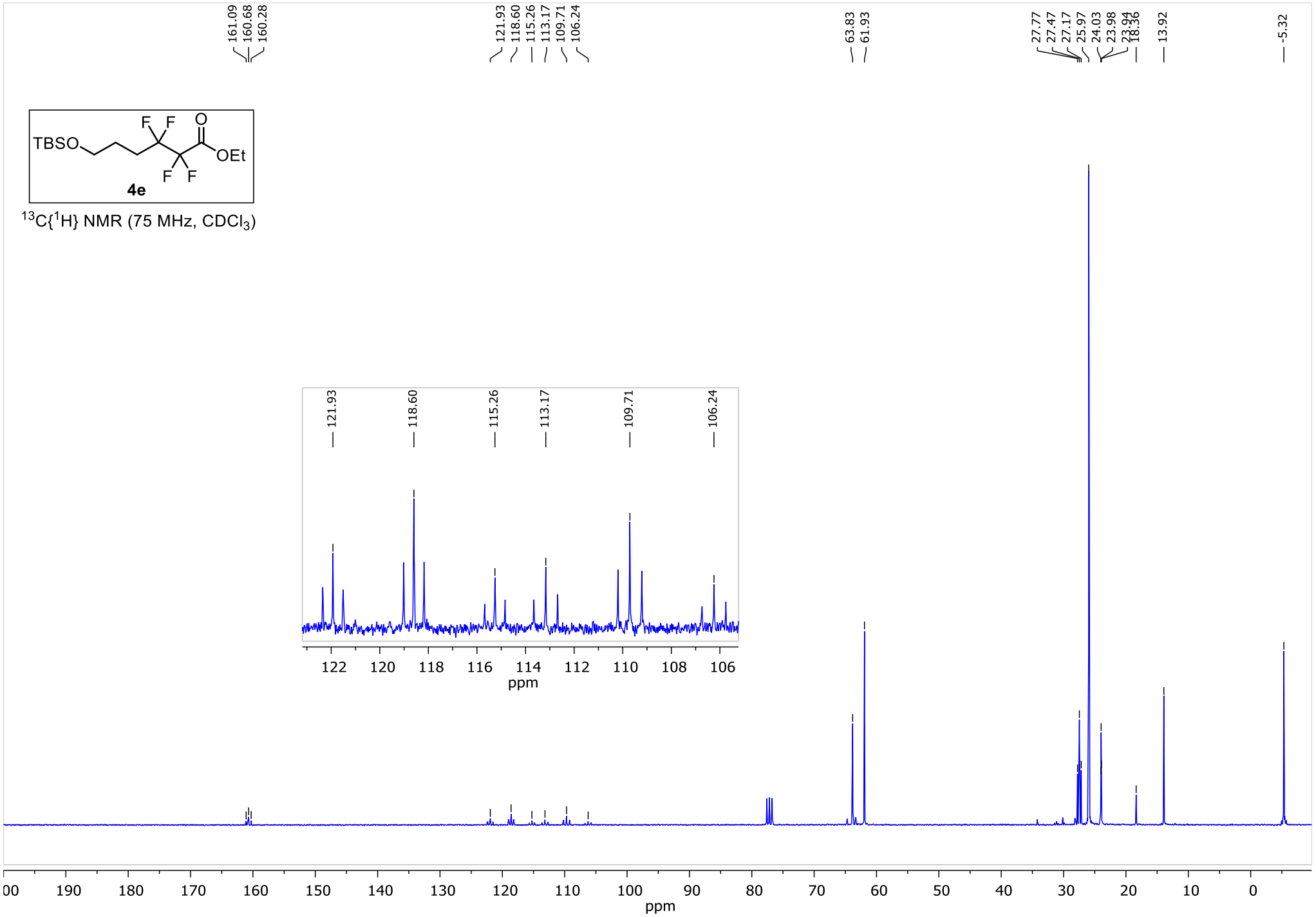

208.05
160.90
160.50
160.10
121.47
118.13
114.79
112.98
109.52
106.06
77.59 CDCl3
77.16 CDCl3
76.74 CDCl3
63.82
43.06
30.75
30.45
30.15
29.84
23.17
20.06
20.01
19.96
13.79
F F O
OEt
F F
O
4d
13C{1H} NMR (75 MHz, CDCl3)
121.47
118.13
114.79
112.98
109.52
106.06
120
115
110
105
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

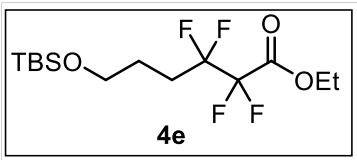


4d

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

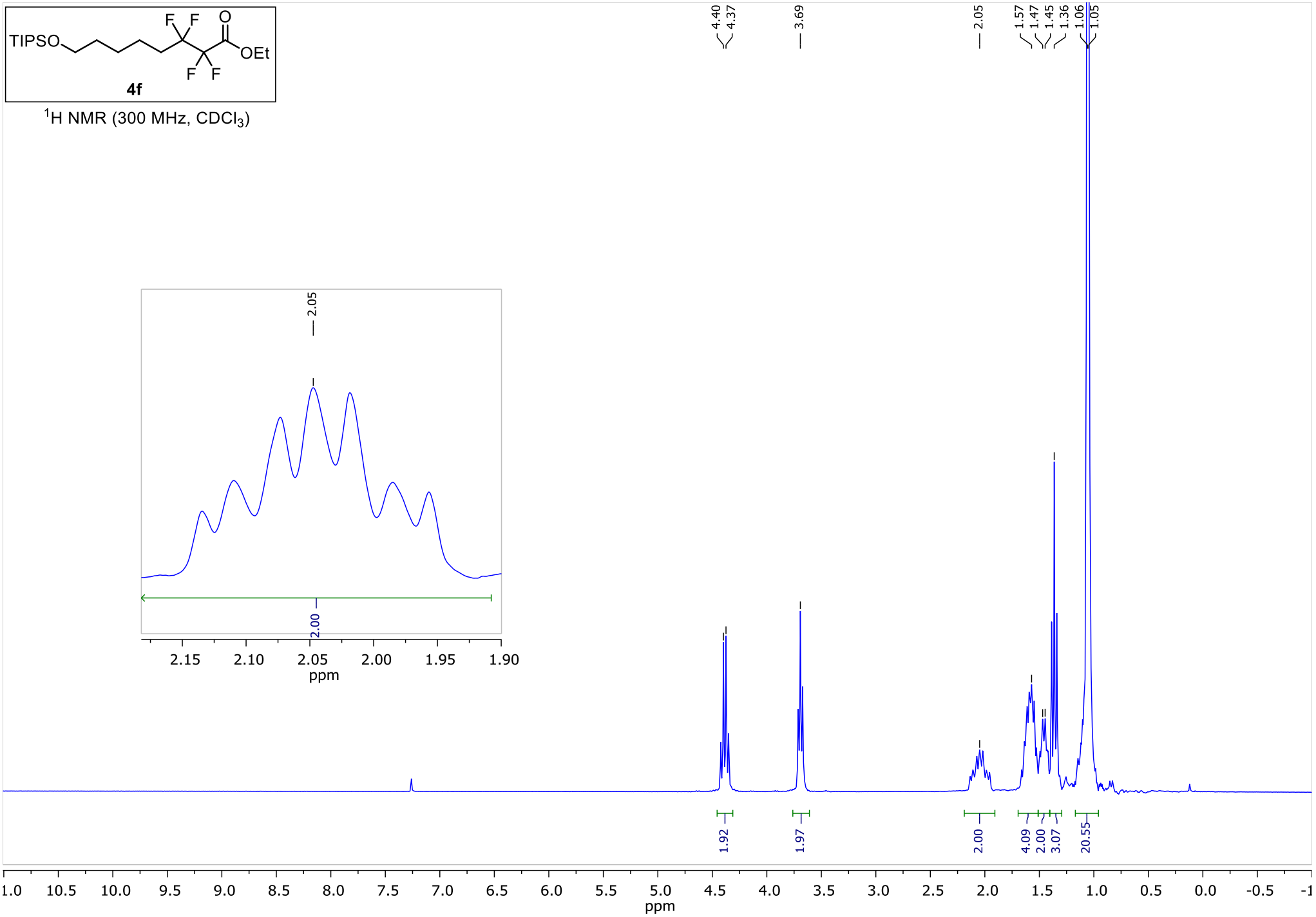

TBSO
F F
O
OEt
F F
4e
1H NMR (300 MHz, CDCl3)
4.39
4.37
3.66
2.14
1.77
1.36
0.89
0.04
2.00
1.98
2.01
1.92
3.07
9.18
6.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
ppm

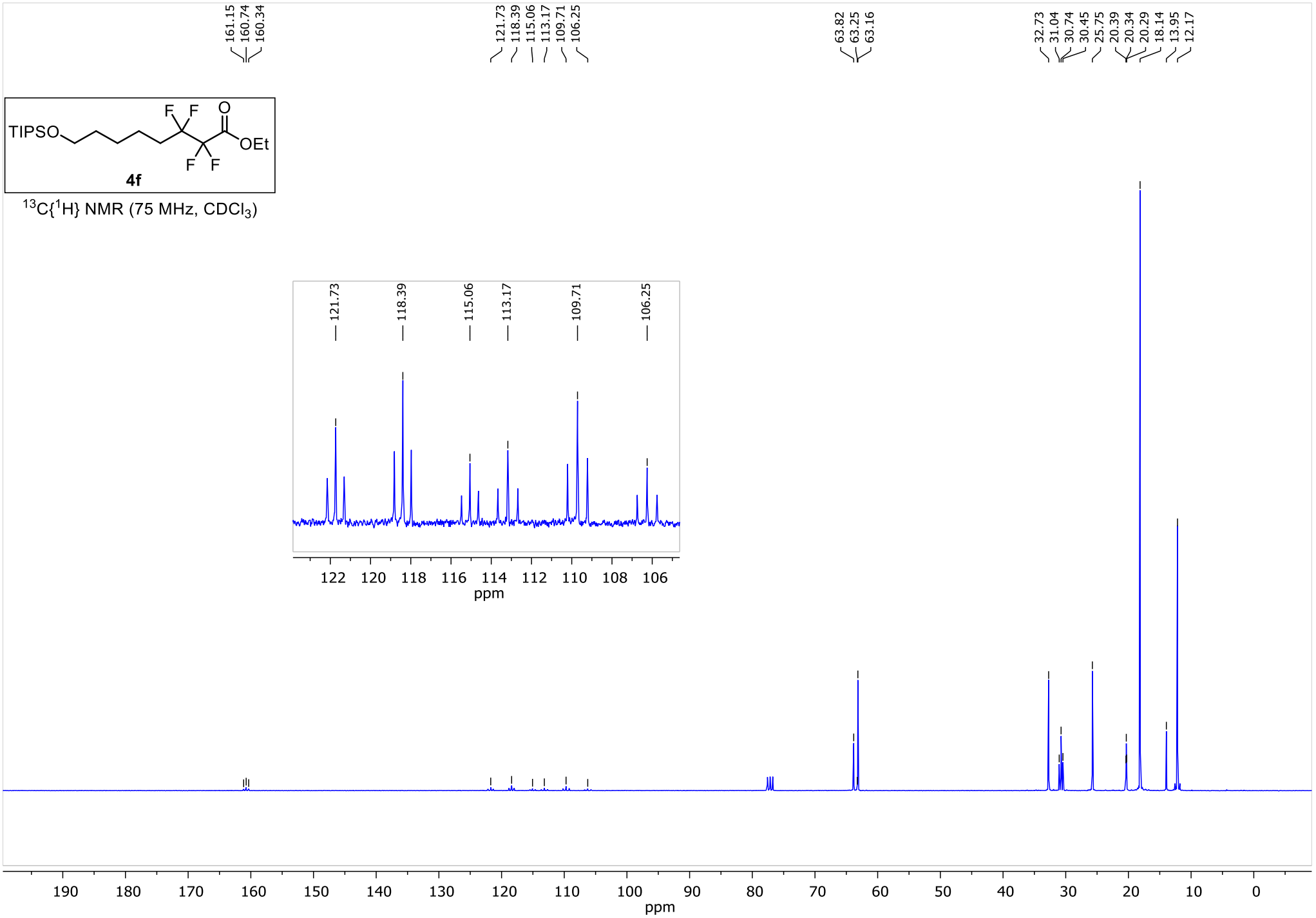

161.09
160.68
160.28
121.93
118.60
115.26
113.17
109.71
106.24
63.83
61.93
27.77
27.47
27.17
25.97
24.03
23.98
23.94
18.36
13.92
-5.32
TBSO
F F
O
OEt
F F
4e
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
122 120 118 116 114 112 110 108 106
ppm
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

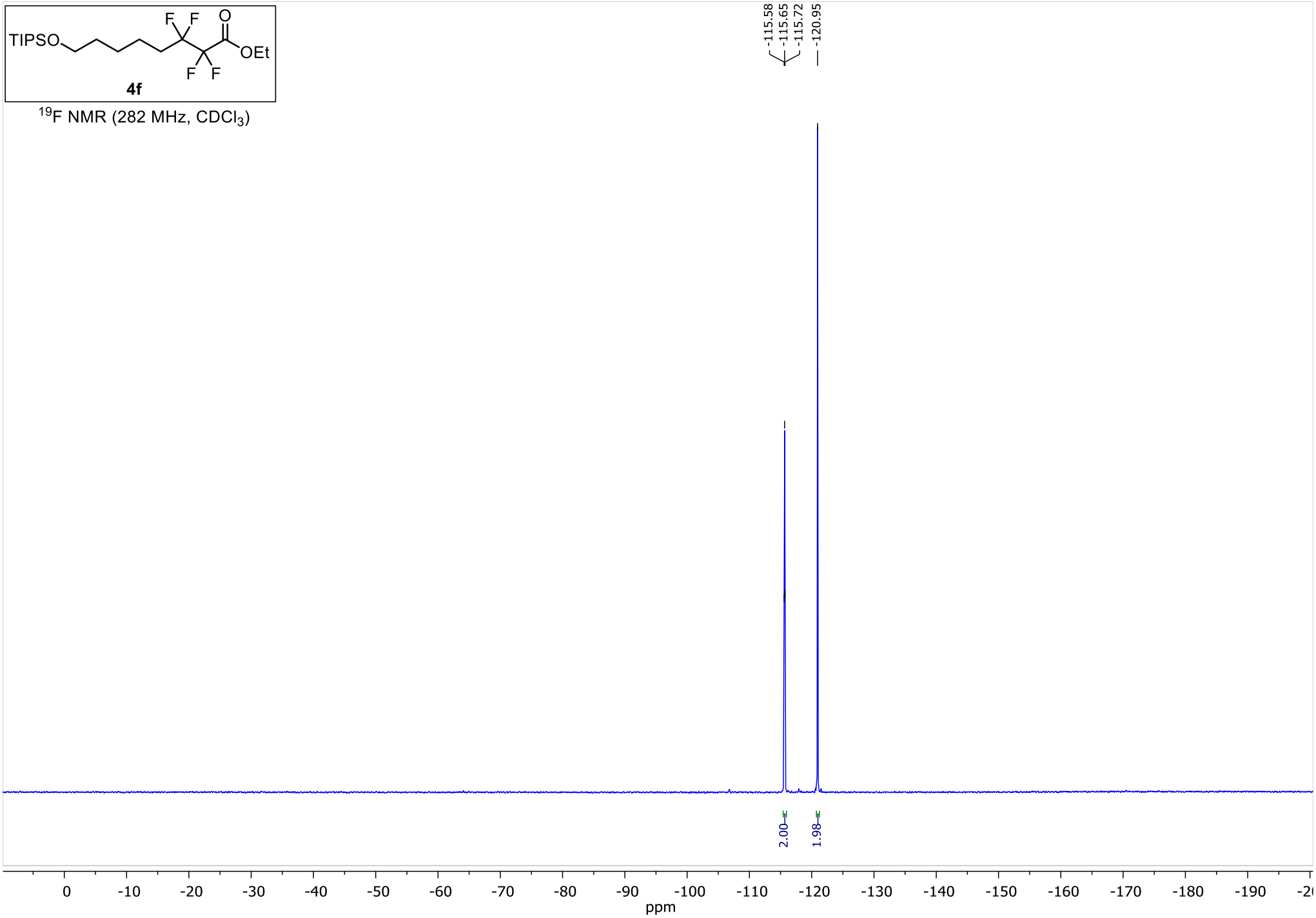


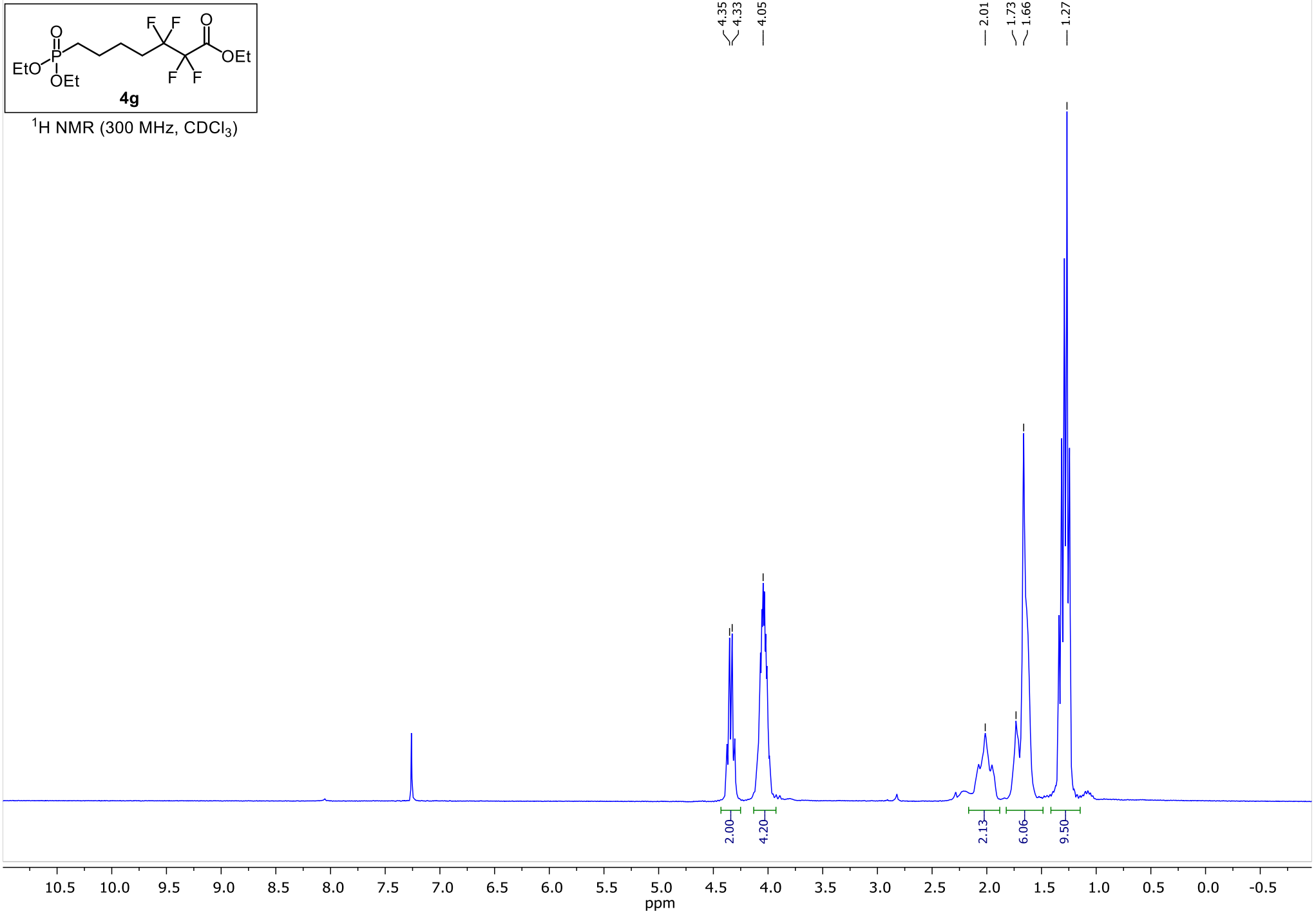
4e

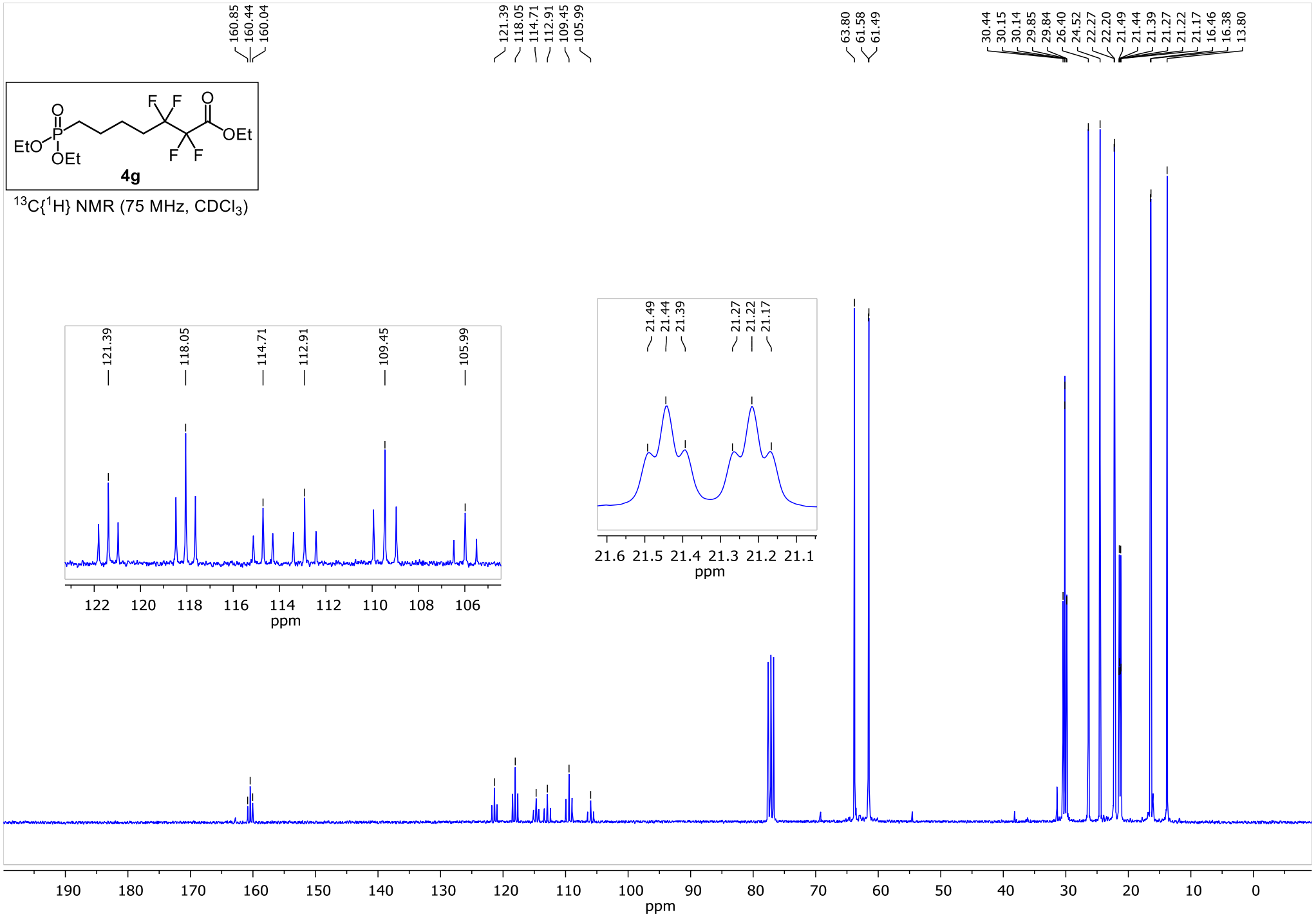
^{19}F NMR (282 MHz, $CDCl_3$)

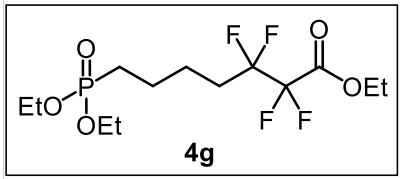

TIPSO
F F
O
OEt
F F
4f
1H NMR (300 MHz, CDCl3)
4.40
4.37
3.69
2.05
1.57
1.47
1.45
1.36
1.06
1.05
1.92
1.97
2.00
4.09
2.00
3.07
20.55
ppm


161.15
160.74
160.34
121.73
118.39
115.06
113.17
109.71
106.25
63.82
63.25
63.16
32.73
31.04
30.74
30.45
25.75
20.39
20.34
20.29
18.14
13.95
12.17
TIPSO
F F
O
OEt
F F
4f
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
ppm


TIPSO
F F
O
OEt
F F
4f
^{19}F NMR (282 MHz, $CDCl_3$)
-115.58
-115.65
-115.72
-120.95
2.00
1.98
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm

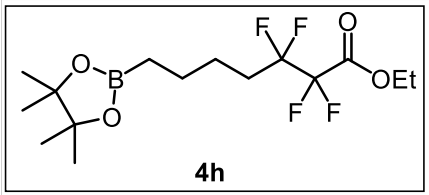

4g
1H NMR (300 MHz, CDCl3)
4.35
4.33
4.05
2.01
1.73
1.66
1.27
2.00
4.20
2.13
6.06
9.50
ppm


160.85
160.44
160.04
121.39
118.05
114.71
112.91
109.45
105.99
63.80
61.58
61.49
30.44
30.15
30.14
29.85
29.84
26.40
24.52
22.27
22.20
21.49
21.44
21.39
21.27
21.22
21.17
16.46
16.38
13.80
O
P
O
EtO
OEt
F F
O
OEt
F F
4g
13C{1H} NMR (75 MHz, CDCl3)
121.39
118.05
114.71
112.91
109.45
105.99
122 120 118 116 114 112 110 108 106
ppm
21.49
21.44
21.39
21.27
21.22
21.17
21.6 21.5 21.4 21.3 21.2 21.1
ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



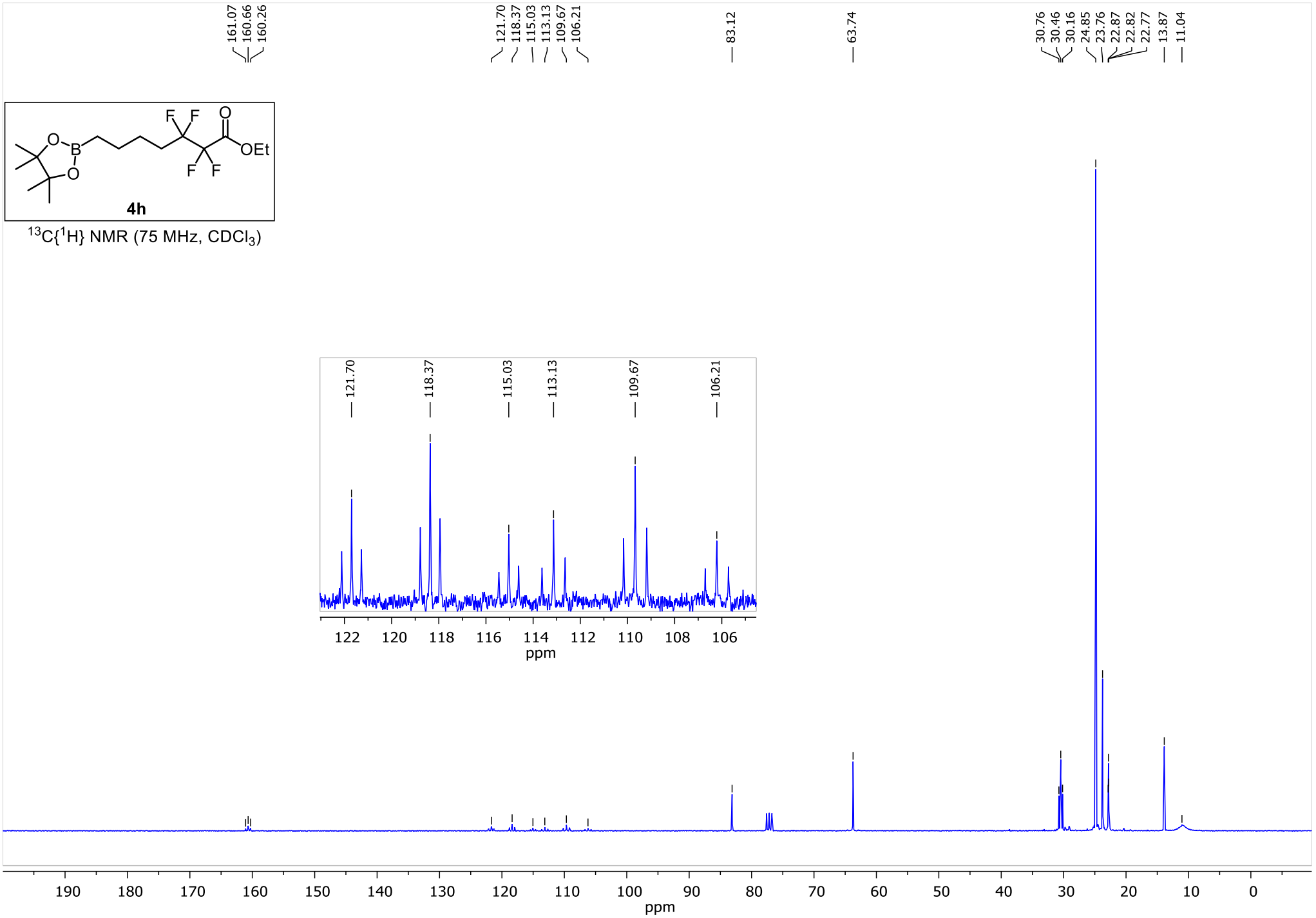
4g

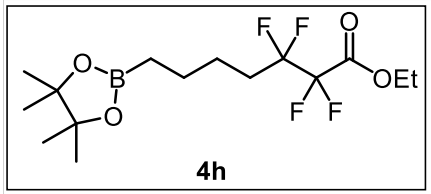
^{19}F NMR (282 MHz, $CDCl_3$)



4h

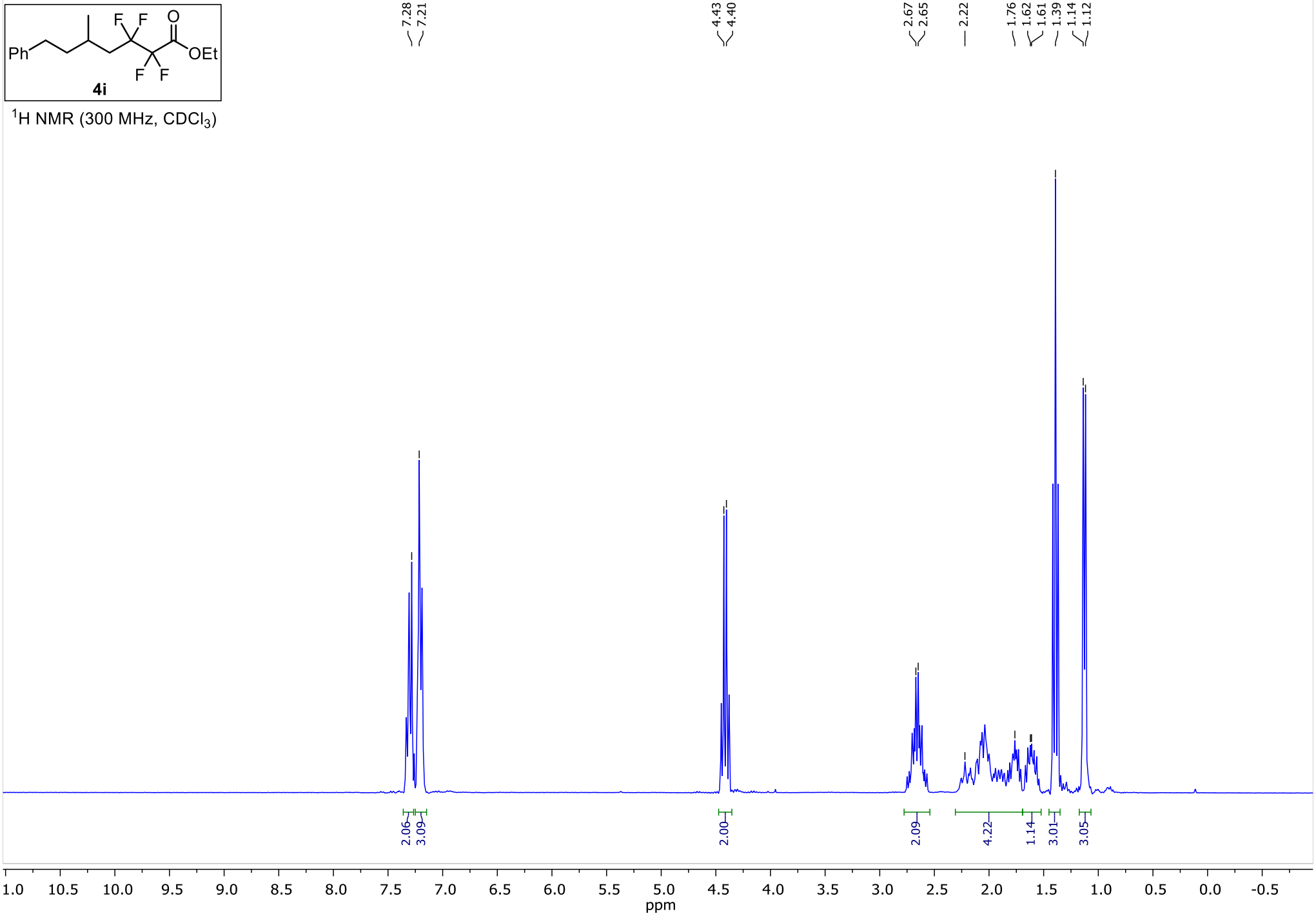
^{1}H NMR (300 MHz, $CDCl_3$)

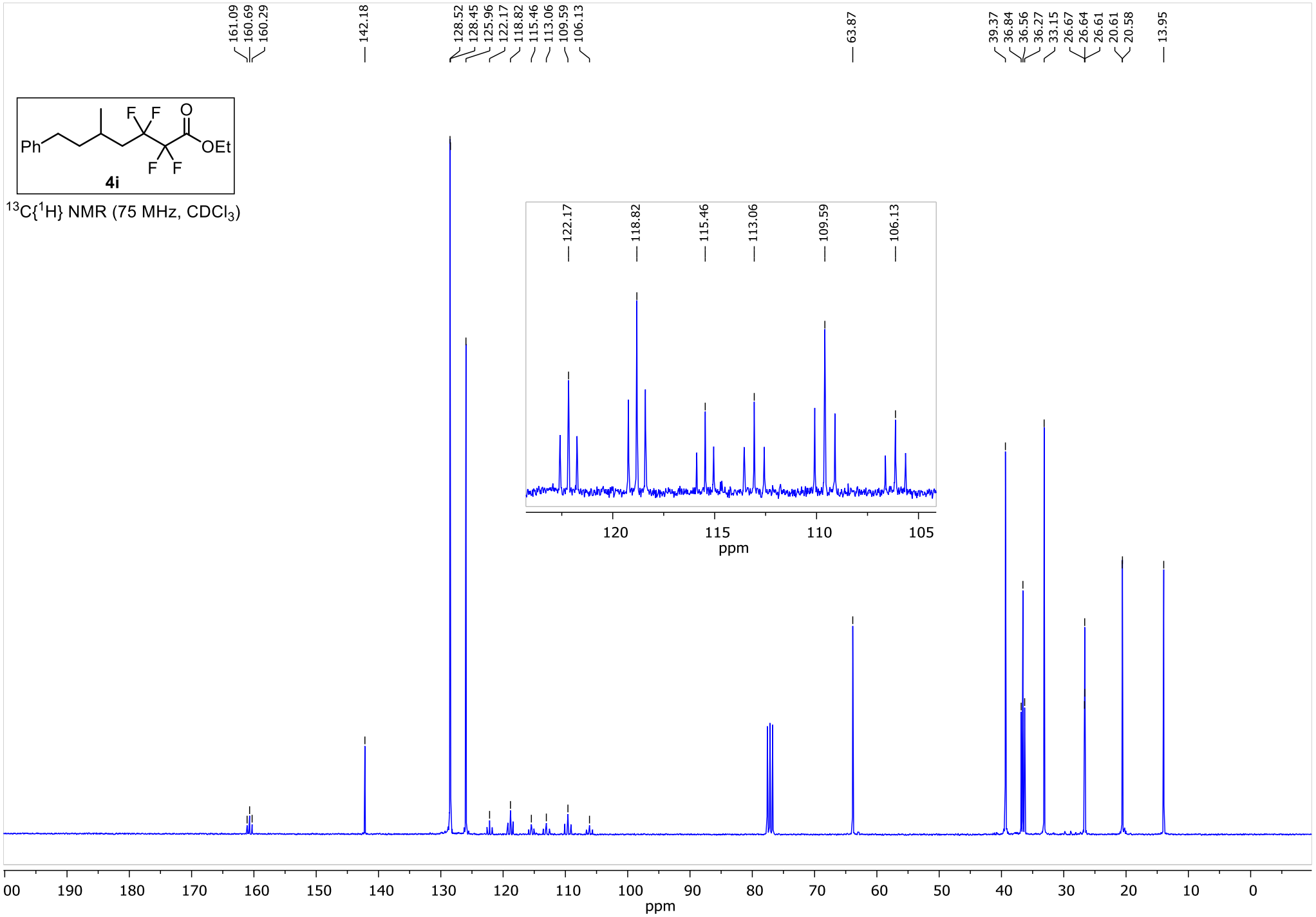

161.07
160.66
160.26
121.70
118.37
115.03
113.13
109.67
106.21
83.12
63.74
30.76
30.46
30.16
24.85
23.76
22.87
22.82
22.77
13.87
11.04
F F O
O B OEt
O
F F
4h
13C{1H} NMR (75 MHz, CDCl3)
121.70
118.37
115.03
113.13
109.67
106.21
122 120 118 116 114 112 110 108 106
ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

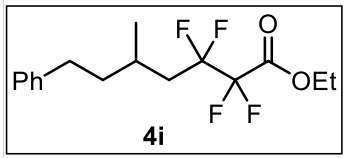


4h

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

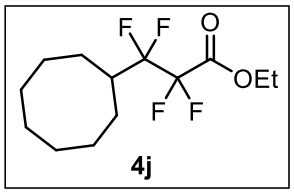

F F O
Ph
OEt
F F
4i
^{1}H NMR (300 MHz, $CDCl_3$)
7.28
7.21
4.43
4.40
2.67
2.65
2.22
1.76
1.62
1.61
1.39
1.14
1.12
2.06
3.09
2.00
2.09
4.22
1.14
3.01
3.05
ppm


161.09
160.69
160.29
142.18
128.52
128.45
125.96
122.17
118.82
115.46
113.06
109.59
106.13
63.87
39.37
36.84
36.56
36.27
33.15
26.67
26.64
26.61
20.61
20.58
13.95
F F O
Ph
OEt
F F
4i
13C{1H} NMR (75 MHz, CDCl3)
122.17
118.82
115.46
113.06
109.59
106.13
120
115
110
105
ppm
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



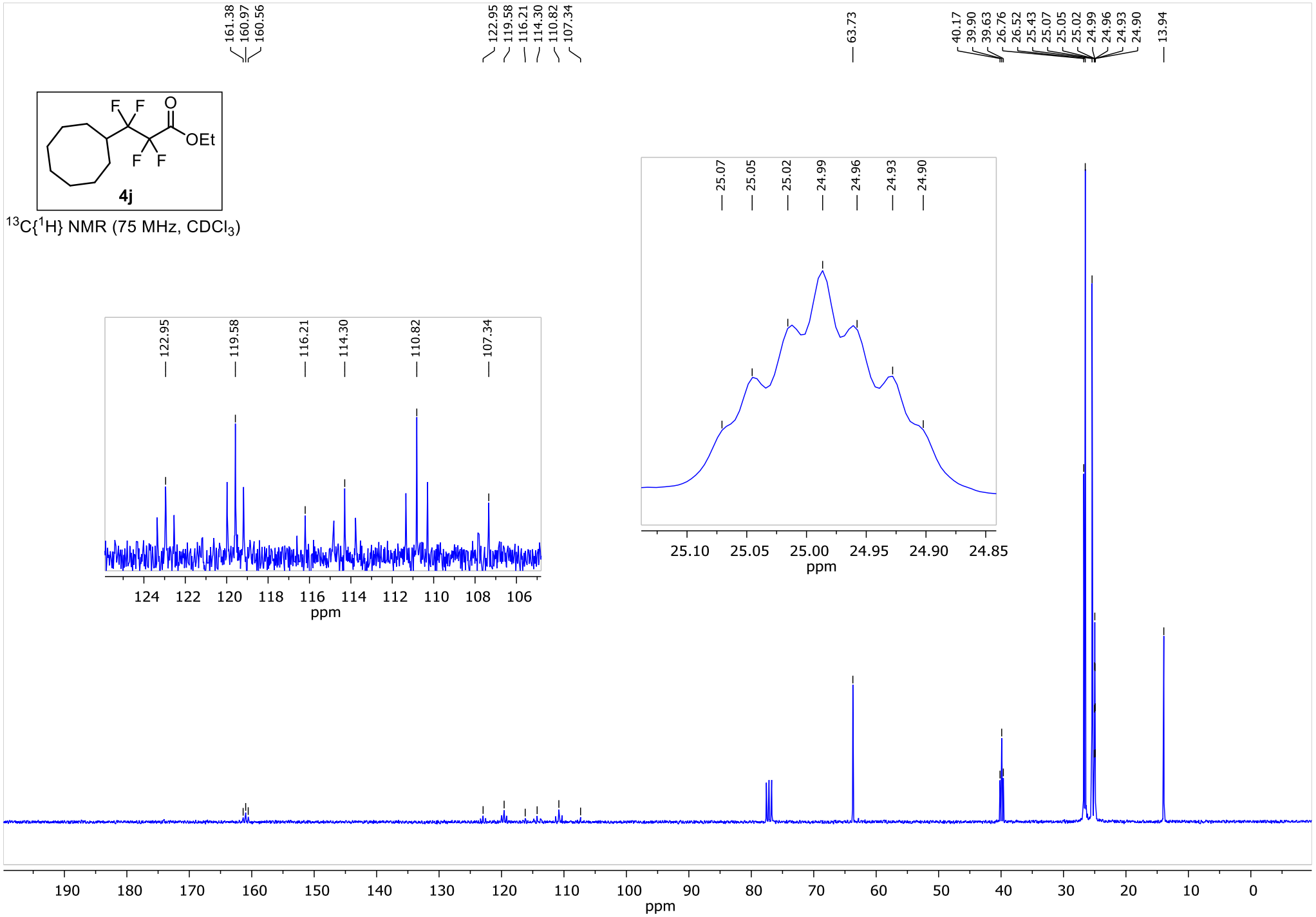
4i

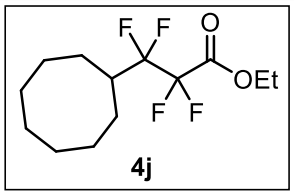
^{19}F NMR (282 MHz, $CDCl_3$)



4j

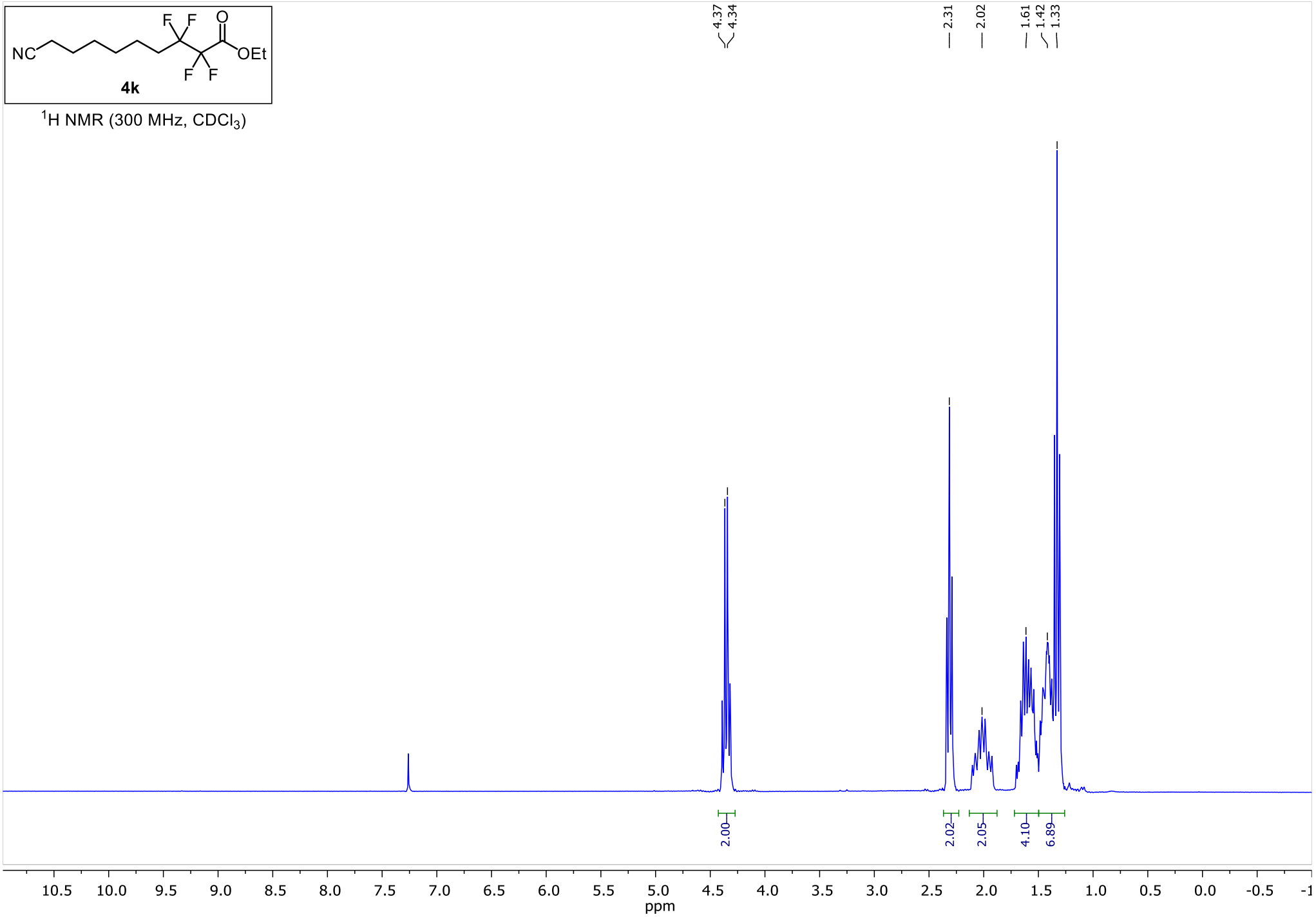
^{1}H NMR (300 MHz, $CDCl_3$)

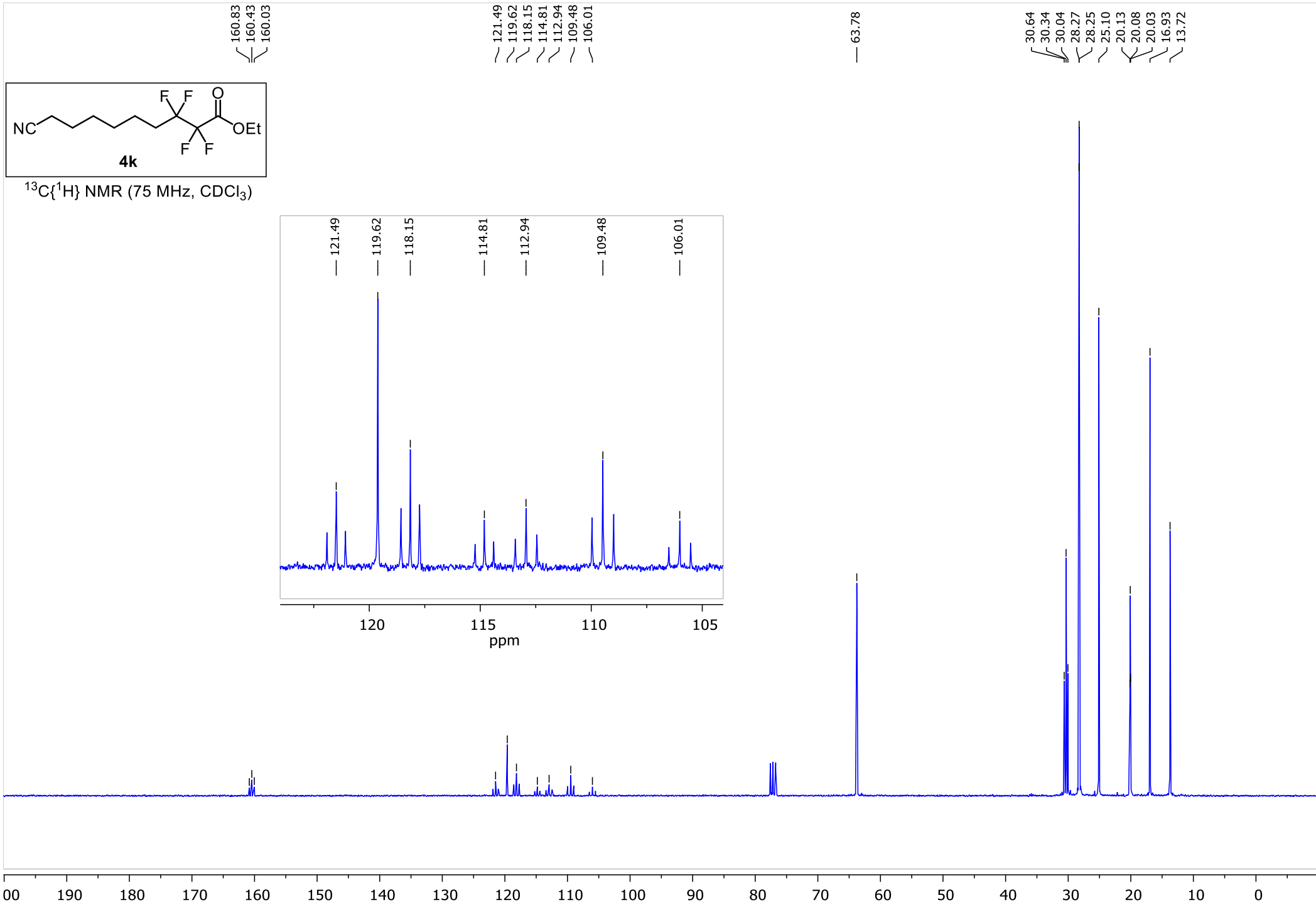

161.38
160.97
160.56
122.95
119.58
116.21
114.30
110.82
107.34
63.73
40.17
39.90
39.63
26.76
26.52
25.43
25.07
25.05
25.02
24.99
24.96
24.93
24.90
13.94
F F O
OEt
F F
4j
13C{1H} NMR (75 MHz, CDCl3)
25.07
25.05
25.02
24.99
24.96
24.93
24.90
25.10 25.05 25.00 24.95 24.90 24.85
ppm
122.95
119.58
116.21
114.30
110.82
107.34
124 122 120 118 116 114 112 110 108 106
ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

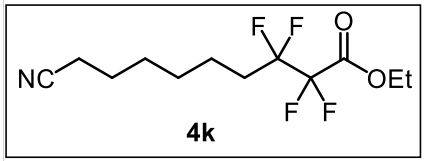


4j

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

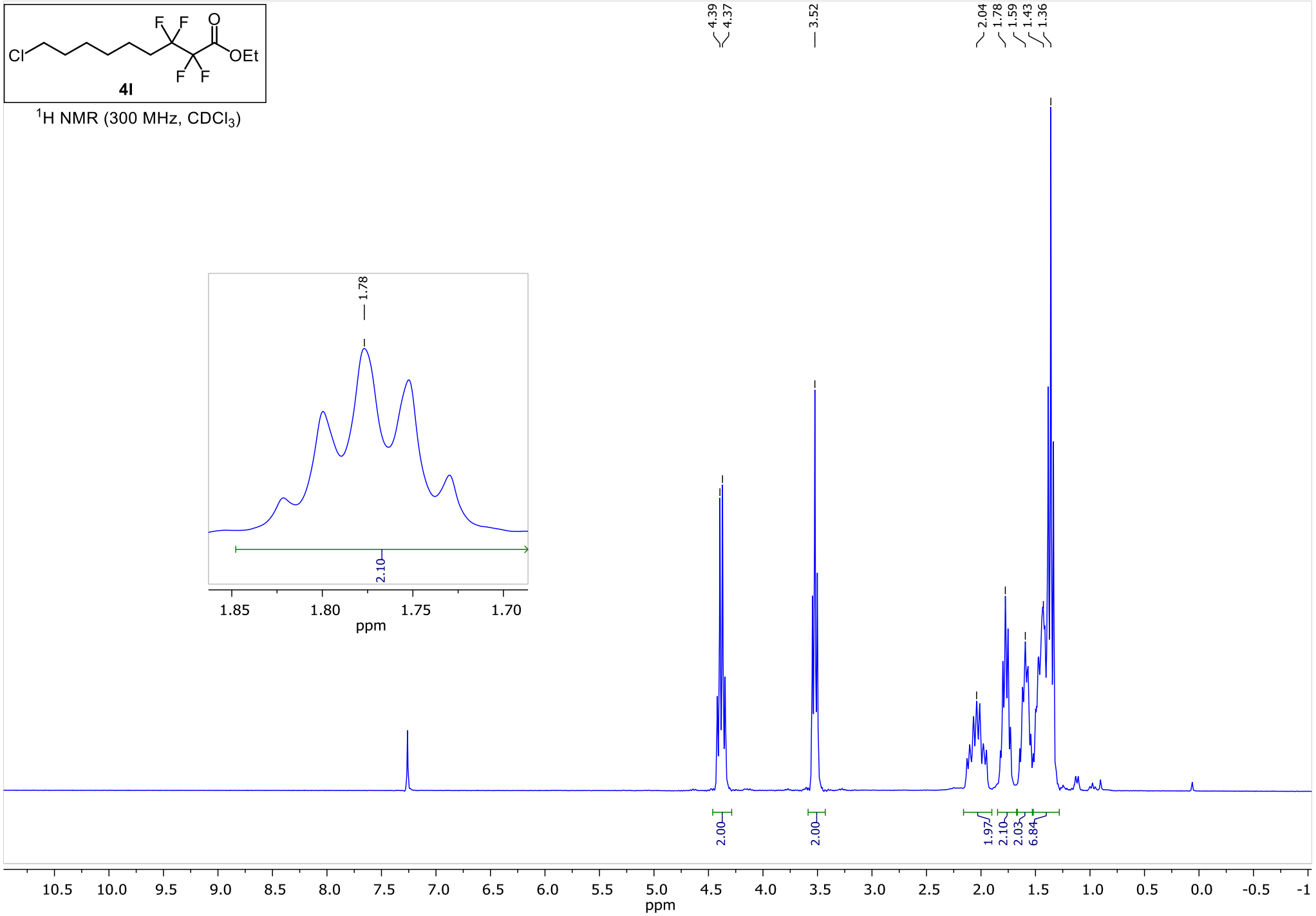

F F O
NC OEt
F F
4k
^{1}H NMR (300 MHz, $CDCl_3$)
4.37
4.34
2.31
2.02
1.61
1.42
1.33
2.00
2.02
2.05
4.10
6.89
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
ppm

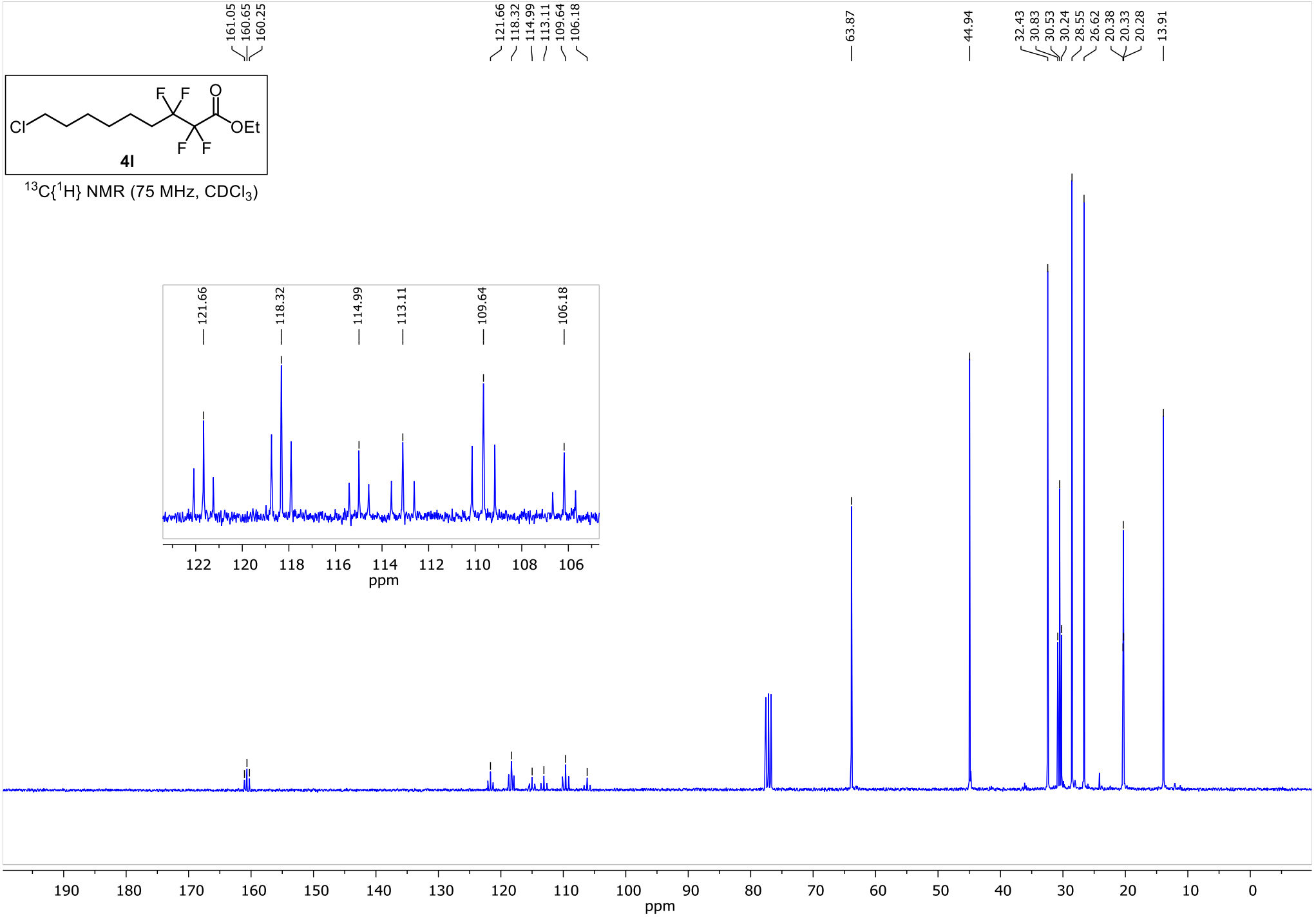

160.83
160.43
160.03
121.49
119.62
118.15
114.81
112.94
109.48
106.01
63.78
30.64
30.34
30.04
28.27
25.10
20.13
20.08
20.03
16.93
13.72
F F O
NC
OEt
F F
4k
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
121.49
119.62
118.15
114.81
112.94
109.48
106.01
120
115
110
105
ppm
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

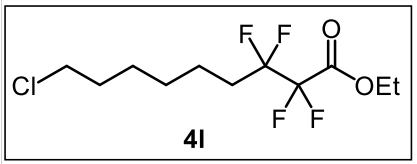


4k

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

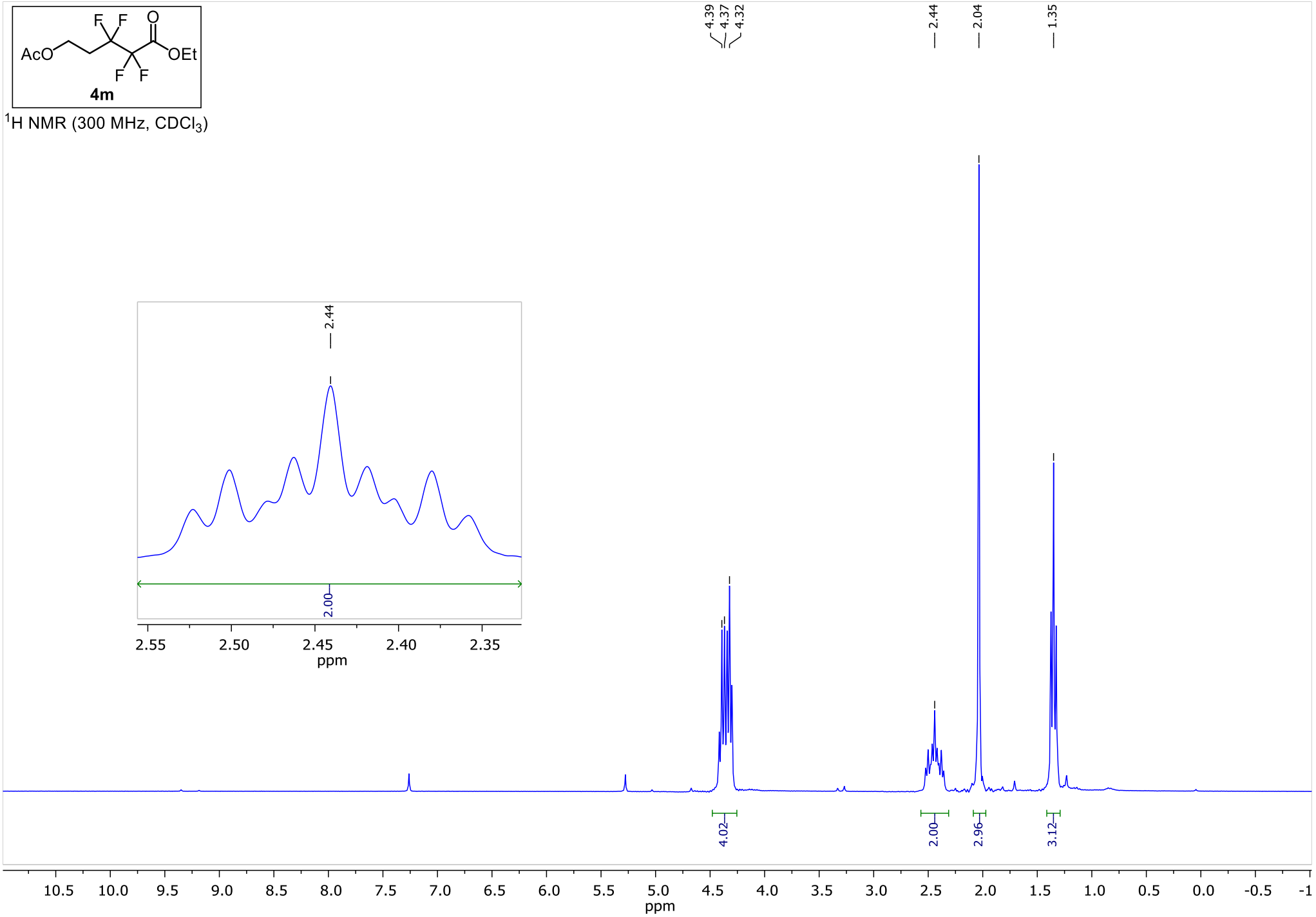

F F O
Cl
OEt
F F
4l
1H NMR (300 MHz, CDCl3)
4.39
4.37
3.52
2.04
1.78
1.59
1.43
1.36
1.78
2.10
1.85
1.80
1.75
1.70
ppm
2.00
2.00
1.97
2.10
2.03
6.84
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
ppm

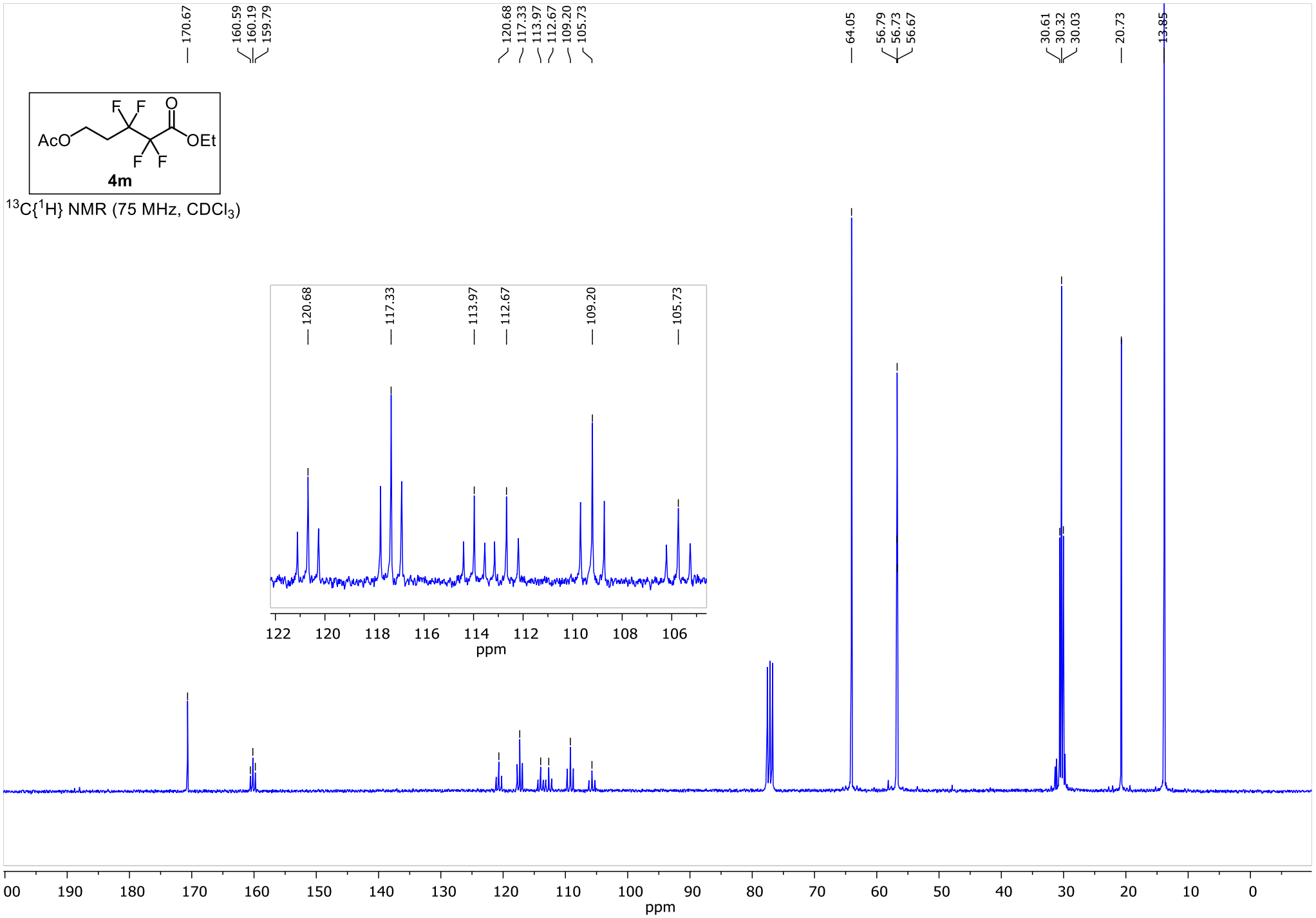

161.05
160.65
160.25
121.66
118.32
114.99
113.11
109.64
106.18
63.87
44.94
32.43
30.83
30.53
30.24
28.55
26.62
20.38
20.33
20.28
13.91
F F O
Cl
OEt
F F
4l
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
122 120 118 116 114 112 110 108 106
ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

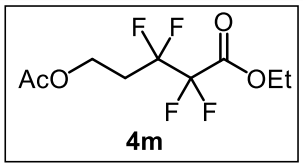


4l

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

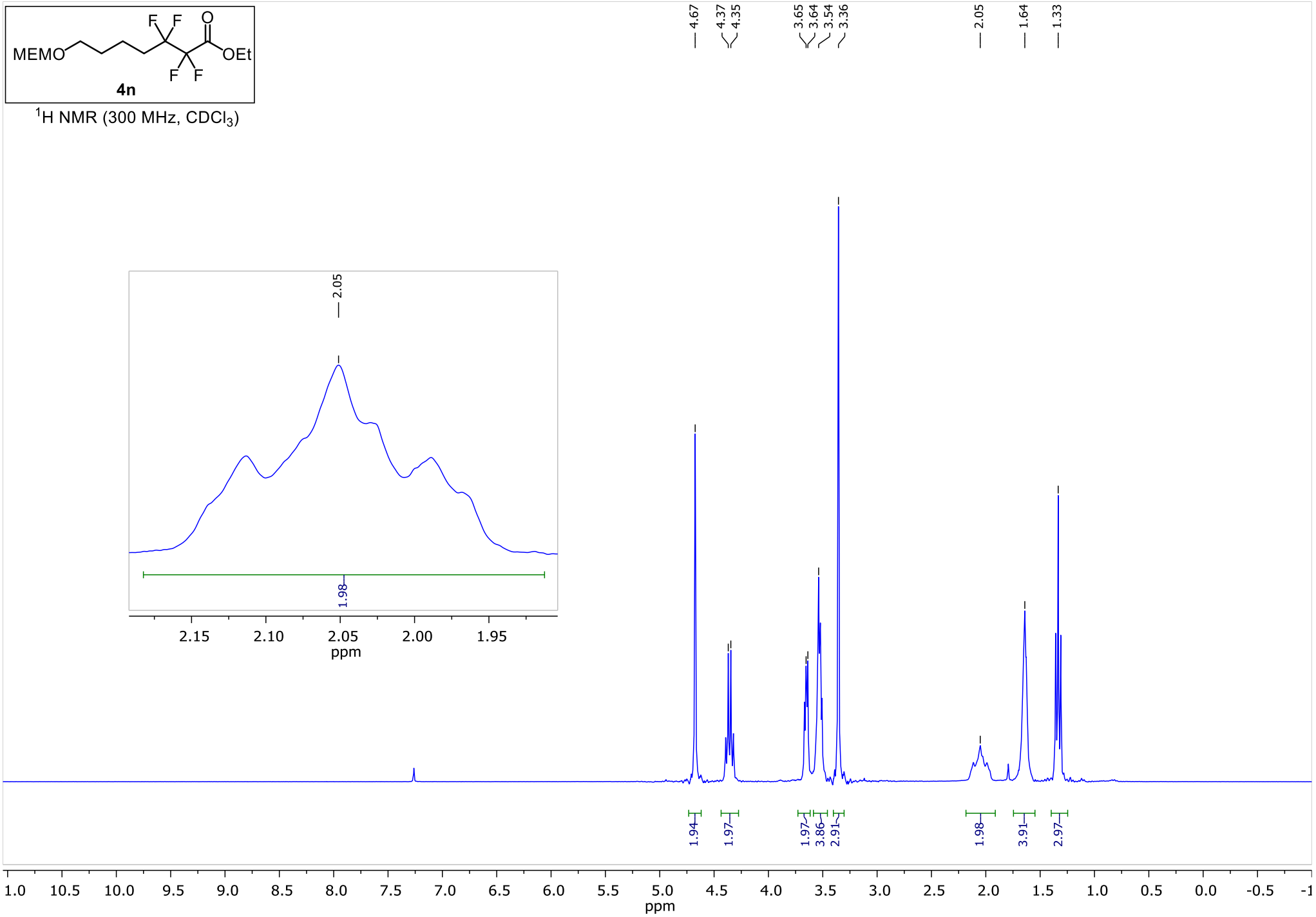

F F O
AcO OEt
F F
4m
1H NMR (300 MHz, CDCl3)
4.39
4.37
4.32
2.44
2.04
1.35
2.44
2.00
2.55 2.50 2.45 2.40 2.35
ppm
4.02
2.00
2.96
3.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
ppm

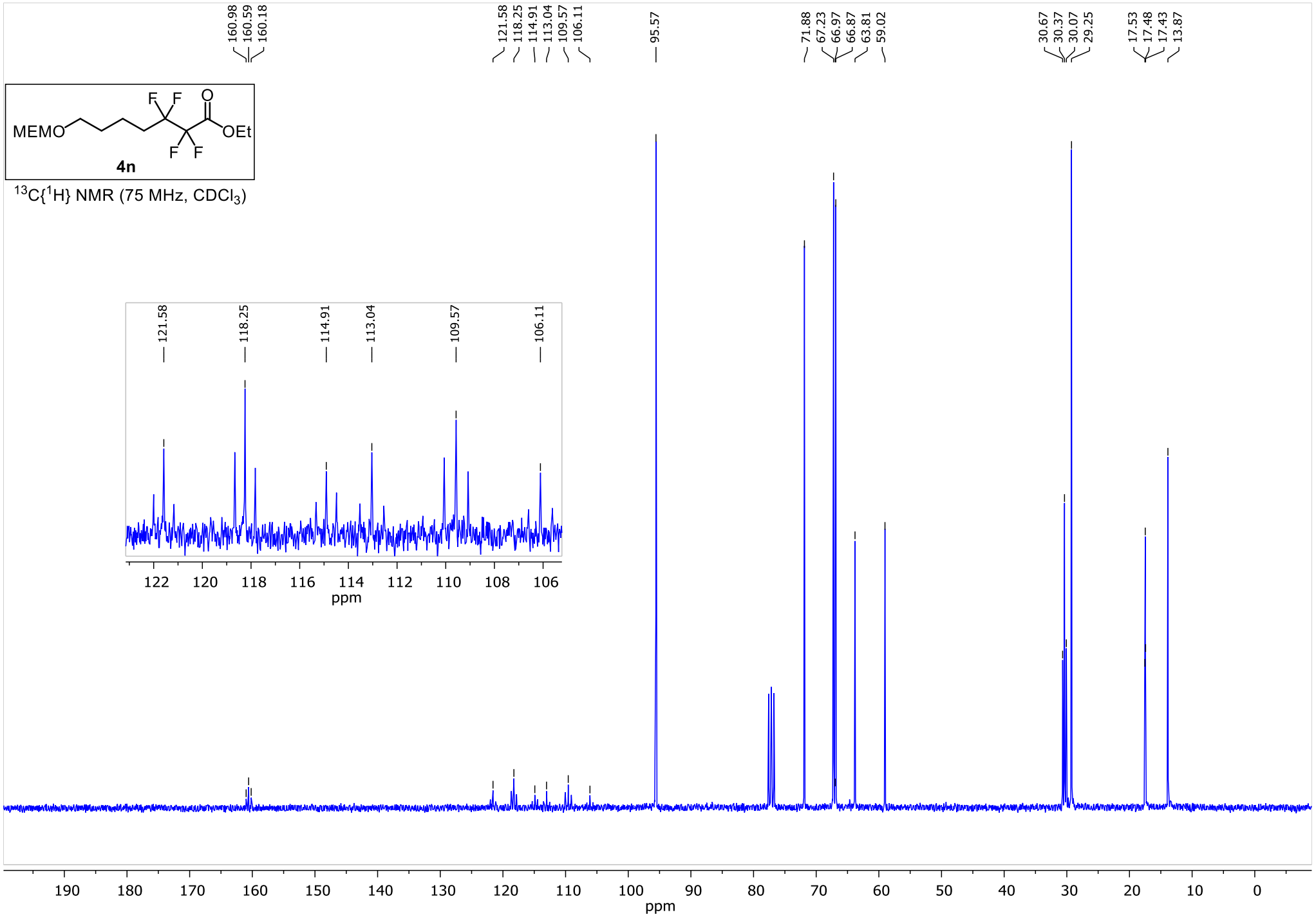

170.67
160.59
160.19
159.79
120.68
117.33
113.97
112.67
109.20
105.73
64.05
56.79
56.73
56.67
30.61
30.32
30.03
20.73
13.85
F F O
AcO
OEt
F F
4m
13C{1H} NMR (75 MHz, CDCl3)
120.68
117.33
113.97
112.67
109.20
105.73
122 120 118 116 114 112 110 108 106
ppm
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

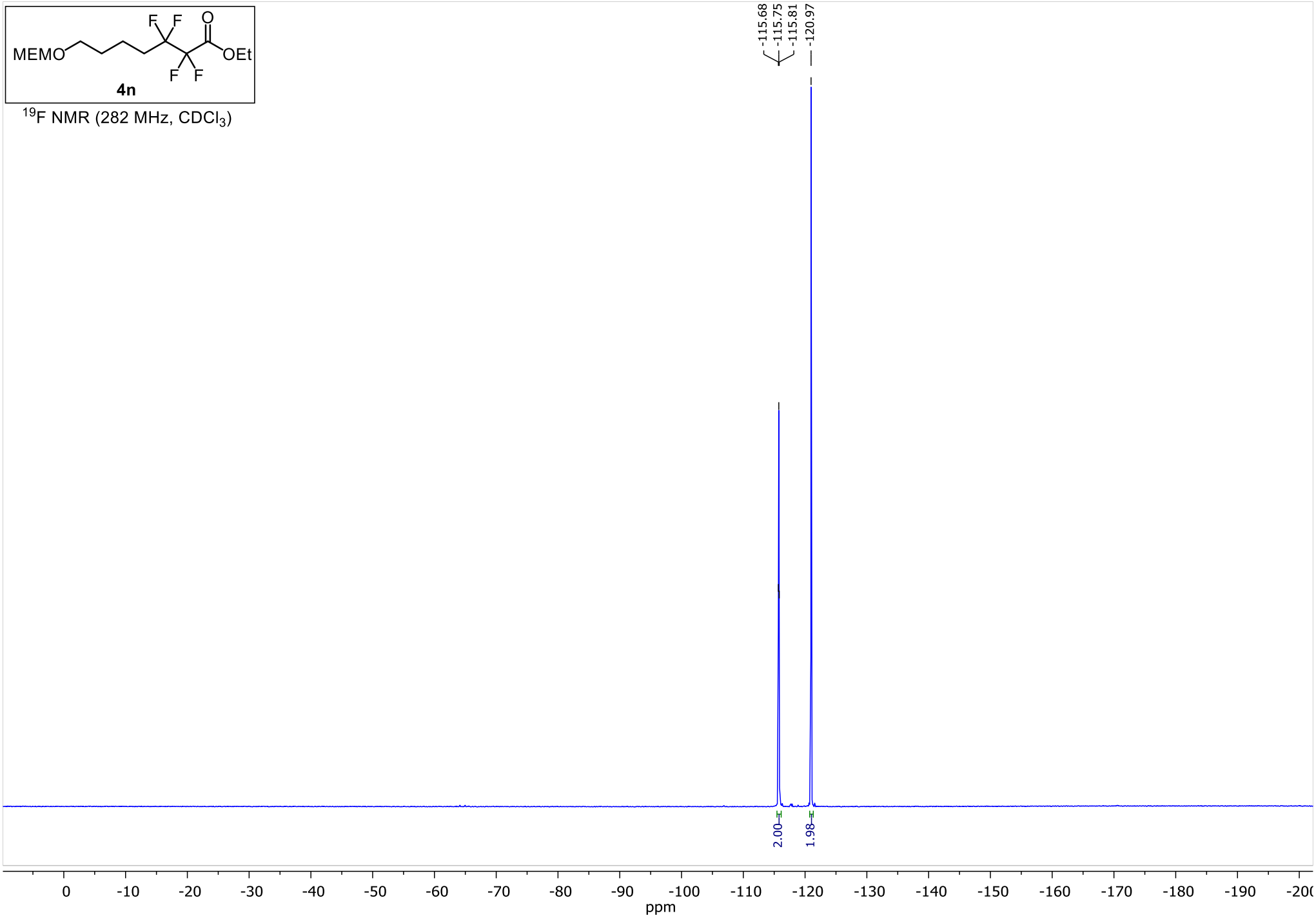


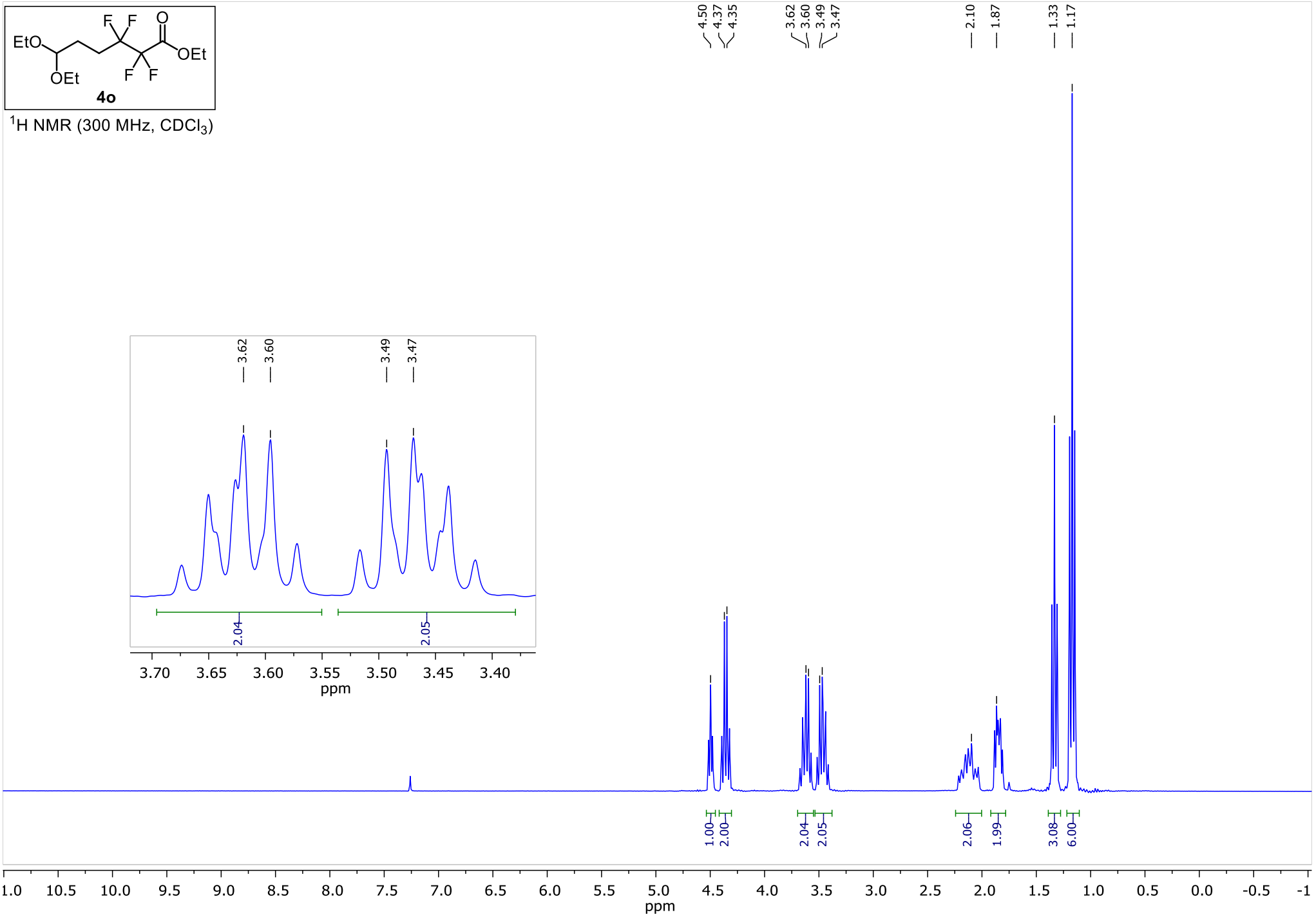
4m

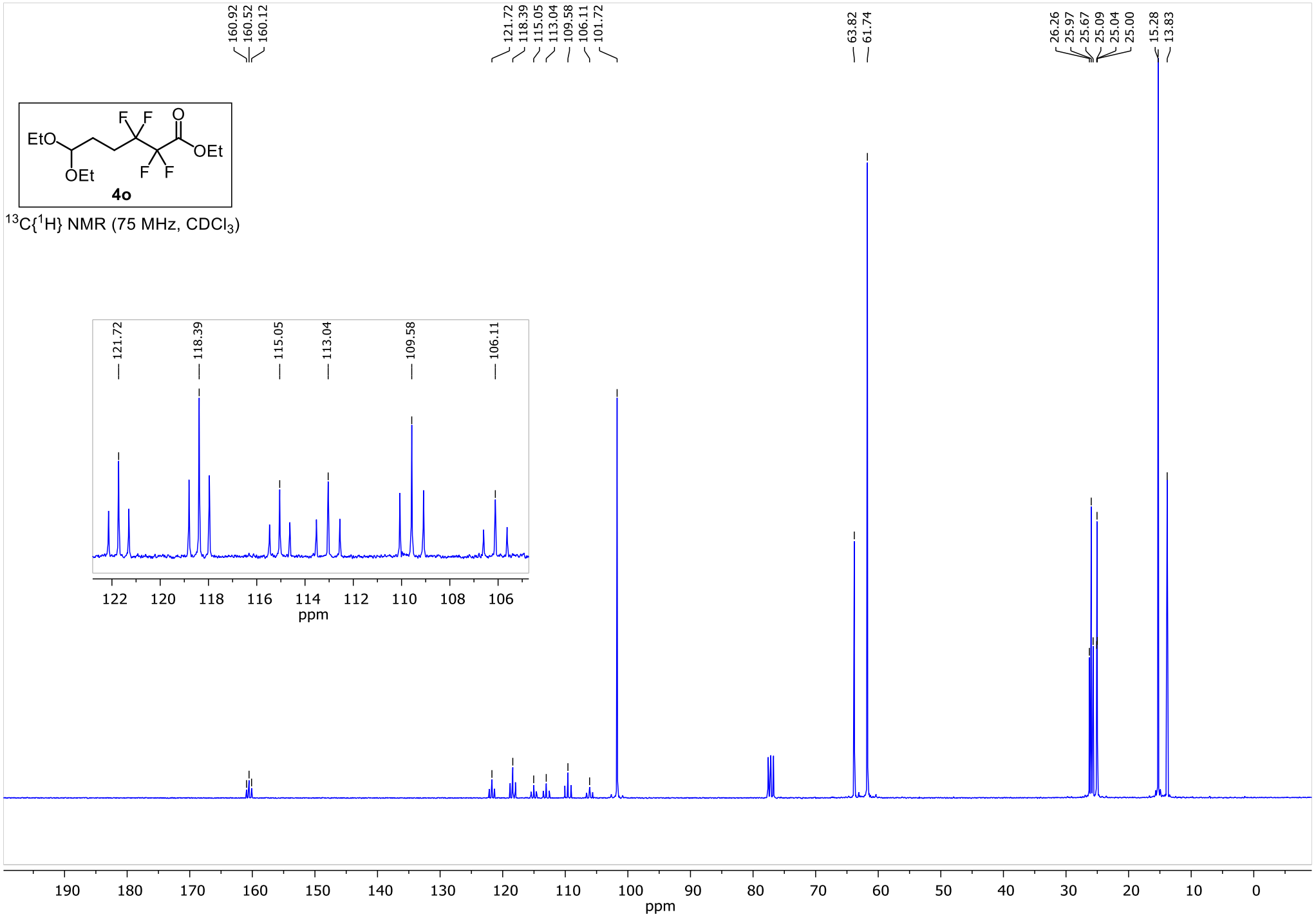
^{19}F NMR (282 MHz, $CDCl_3$)

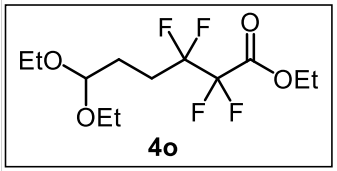

MEMO
F F
O
OEt
F F
4n
1H NMR (300 MHz, CDCl3)
4.67
4.37
4.35
3.65
3.64
3.54
3.36
2.05
1.64
1.33
1.94
1.97
1.97
3.86
2.91
1.98
3.91
2.97
2.05
1.98
2.15
2.10
2.05
2.00
1.95
ppm
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
ppm


160.98
160.59
160.18
121.58
118.25
114.91
113.04
109.57
106.11
95.57
71.88
67.23
66.97
66.87
63.81
59.02
30.67
30.37
30.07
29.25
17.53
17.48
17.43
13.87
F F O
MEMO
OEt
F F
4n
13C{1H} NMR (75 MHz, CDCl3)
121.58
118.25
114.91
113.04
109.57
106.11
122 120 118 116 114 112 110 108 106
ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


F F O
MEMO
OEt
F F
4n
19F NMR (282 MHz, CDCl3)
-115.68
-115.75
-115.81
-120.97
2.00
1.98
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
ppm

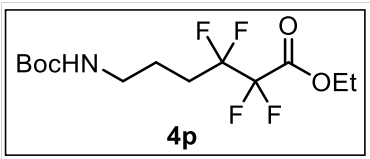

EtO
OEt
F F
F F
O
OEt
4o
1H NMR (300 MHz, CDCl3)
4.50
4.37
4.35
3.62
3.60
3.49
3.47
2.10
1.87
1.33
1.17
1.00
2.00
2.04
2.05
2.06
1.99
3.08
6.00
ppm
2.04
2.05
3.70 3.65 3.60 3.55 3.50 3.45 3.40
ppm


160.92
160.52
160.12
121.72
118.39
115.05
113.04
109.58
106.11
101.72
63.82
61.74
26.26
25.97
25.67
25.09
25.04
25.00
15.28
13.83
F F O
EtO
OEt
OEt
F F
4o
13C{1H} NMR (75 MHz, CDCl3)
121.72
118.39
115.05
113.04
109.58
106.11
122 120 118 116 114 112 110 108 106
ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



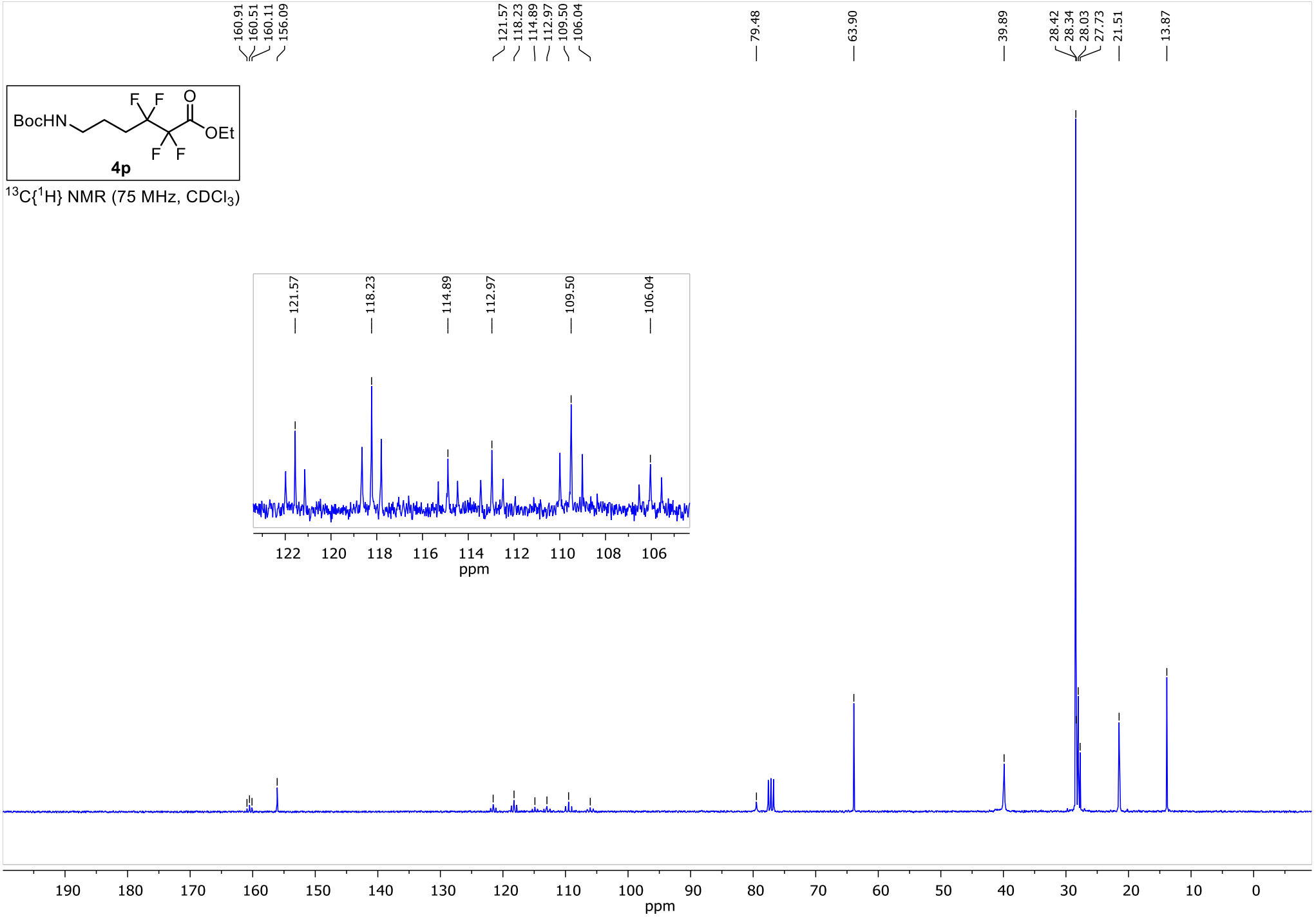
4o

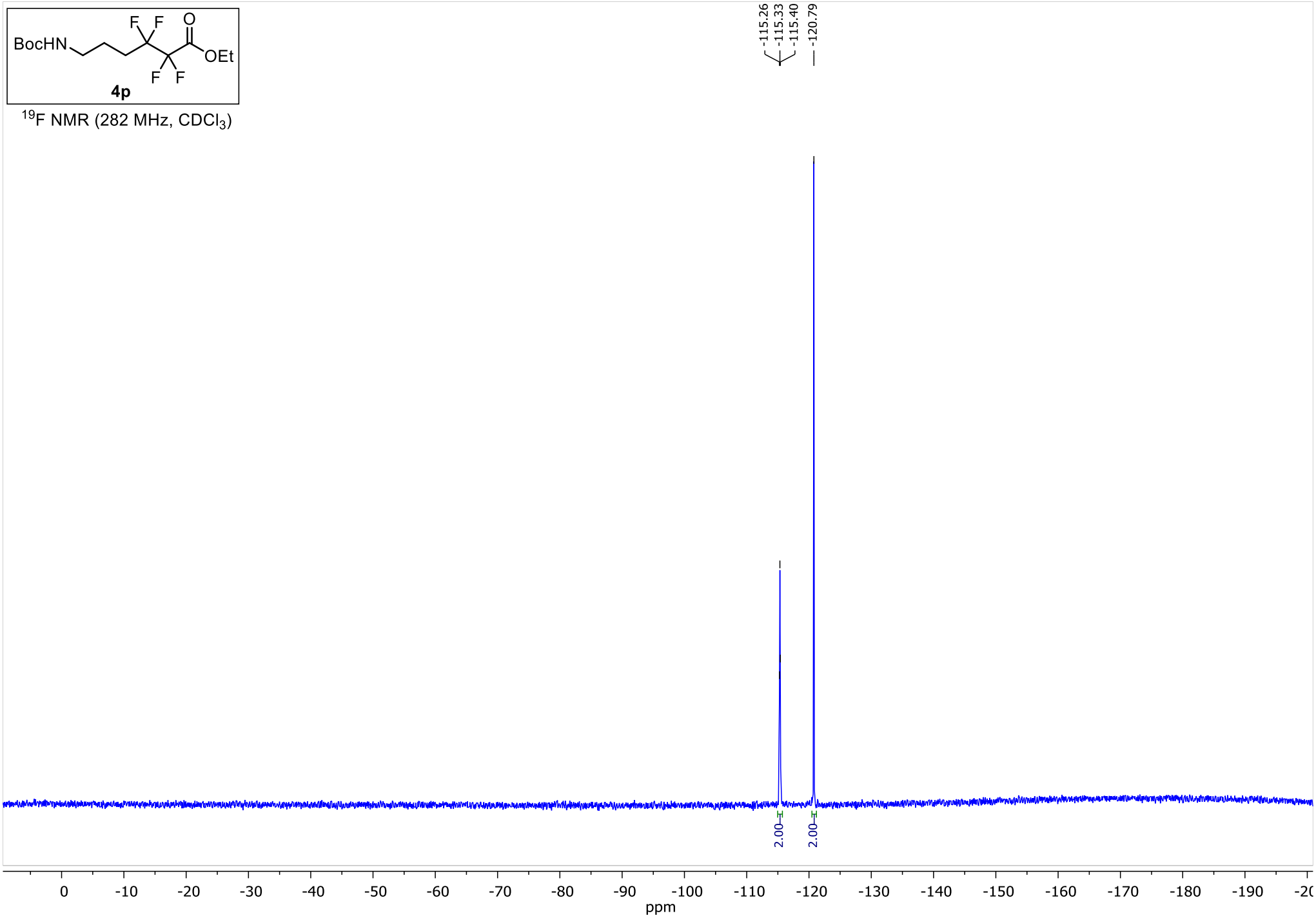
^{19}F NMR (282 MHz, $CDCl_3$)

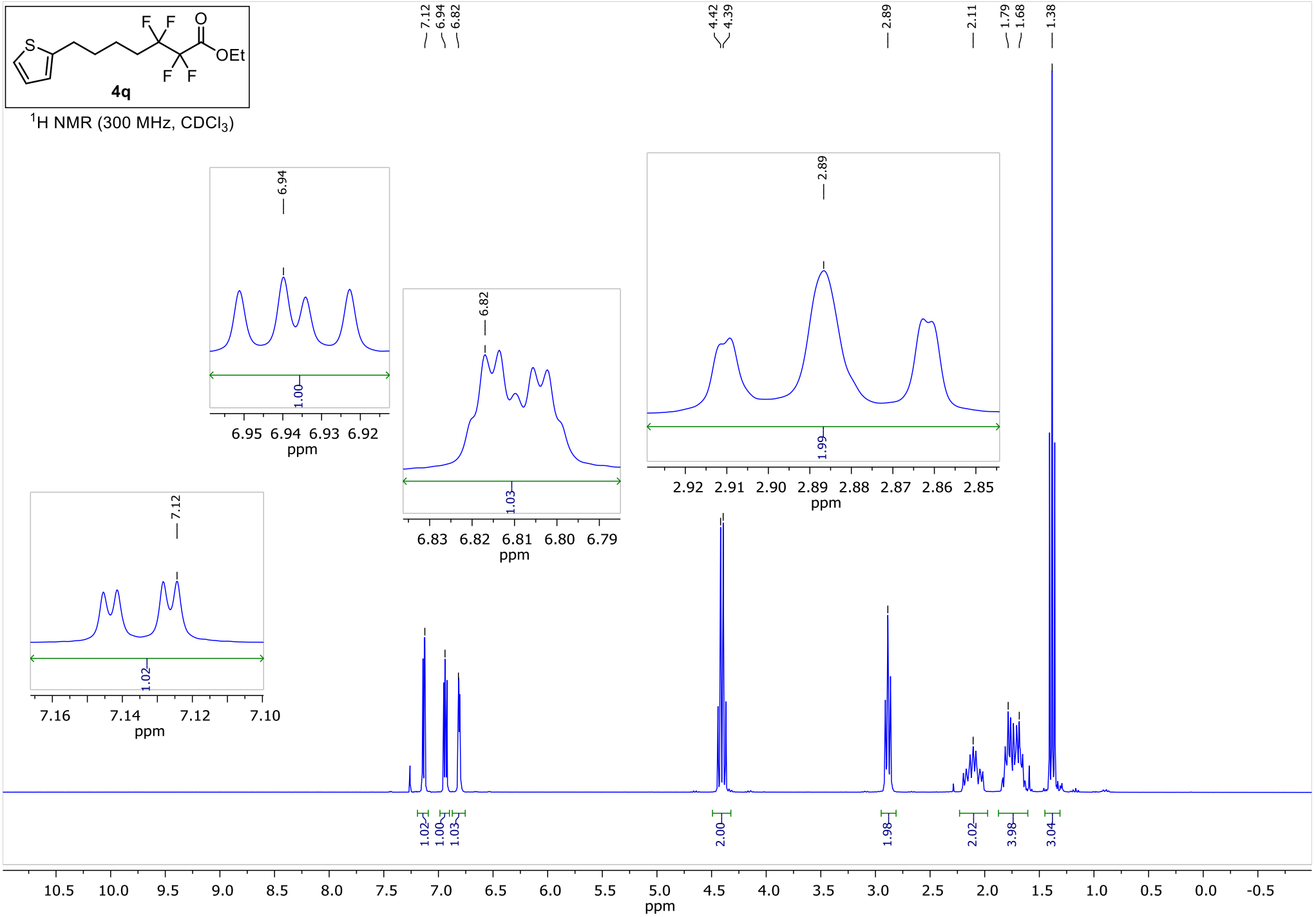


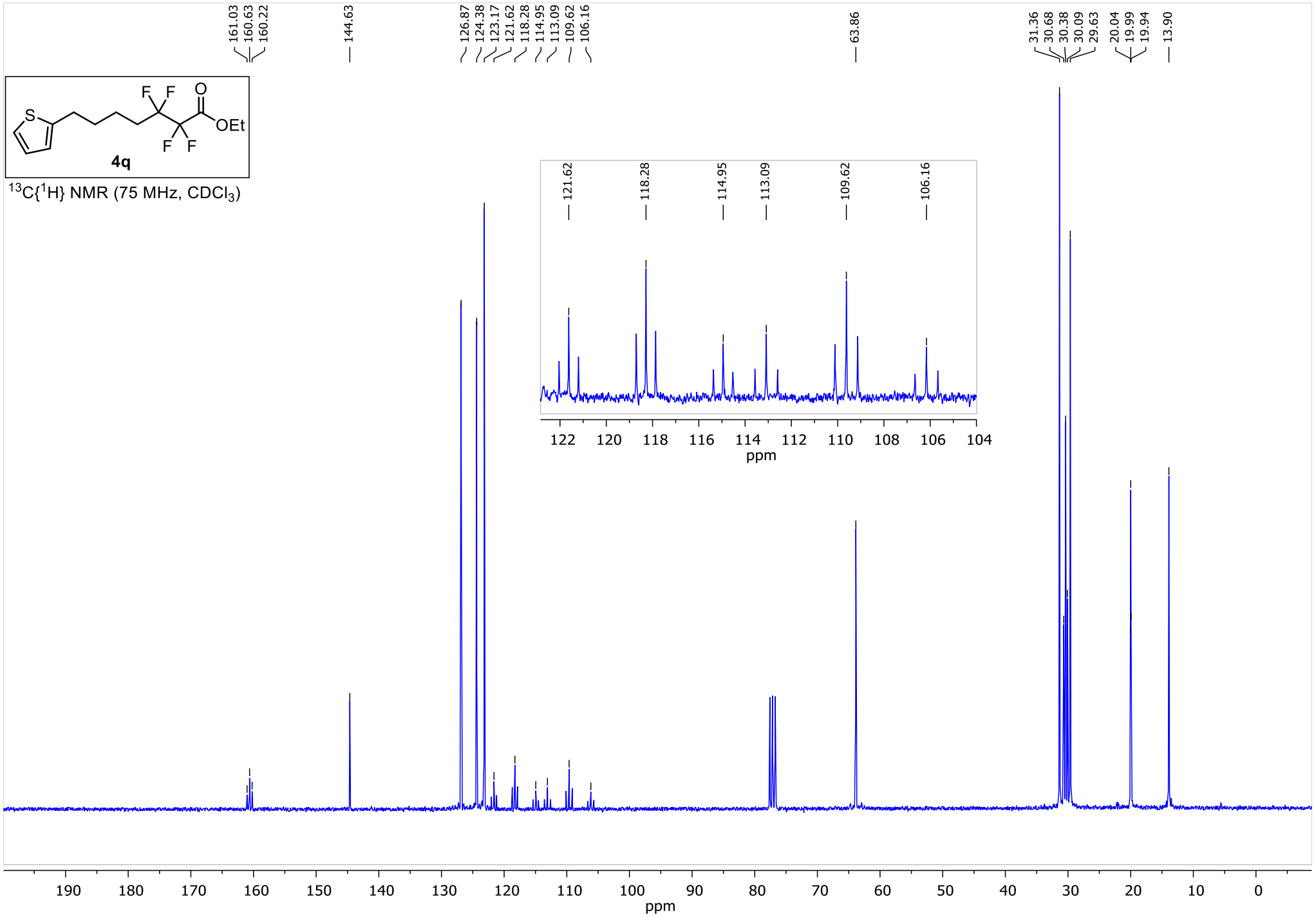
4p

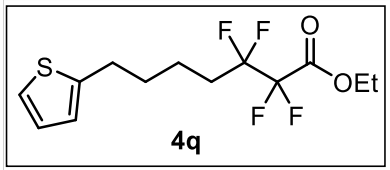
^{1}H NMR (300 MHz, $CDCl_3$)


160.91
160.51
160.11
156.09
121.57
118.23
114.89
112.97
109.50
106.04
79.48
63.90
39.89
28.42
28.34
28.03
27.73
21.51
13.87
BocHN
F F
O
OEt
F F
4p
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
ppm
ppm


BocHN
F F
O
OEt
F F
4p
^{19}F NMR (282 MHz, $CDCl_3$)
-115.26
-115.33
-115.40
-120.79
2.00
2.00
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
ppm

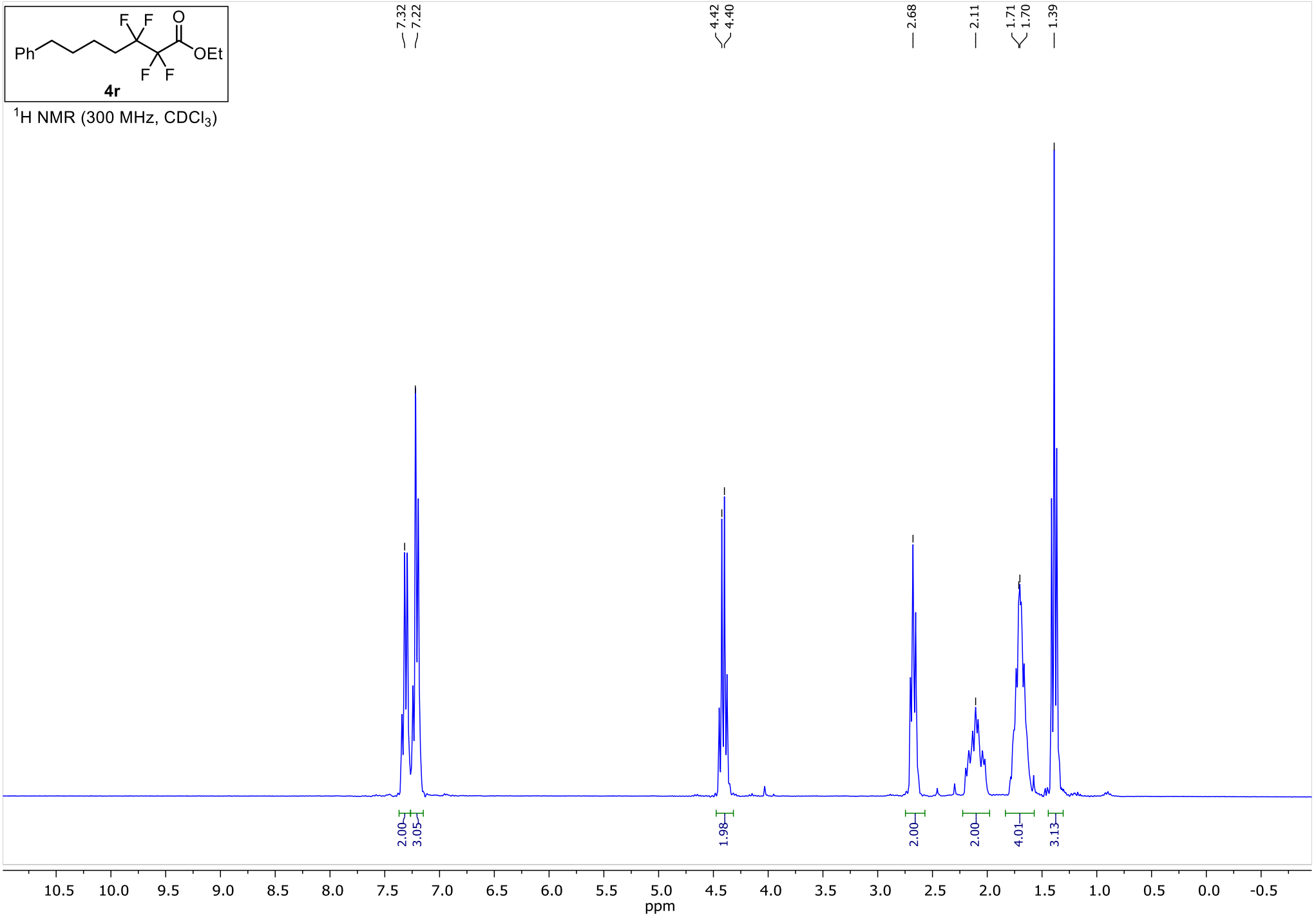

4q
^{1}H NMR (300 MHz, CDCl$_3$)
7.12
6.94
6.82
4.42
4.39
2.89
2.11
1.79
1.68
1.38
1.02
1.00
1.03
2.00
1.98
2.02
3.98
3.04
ppm

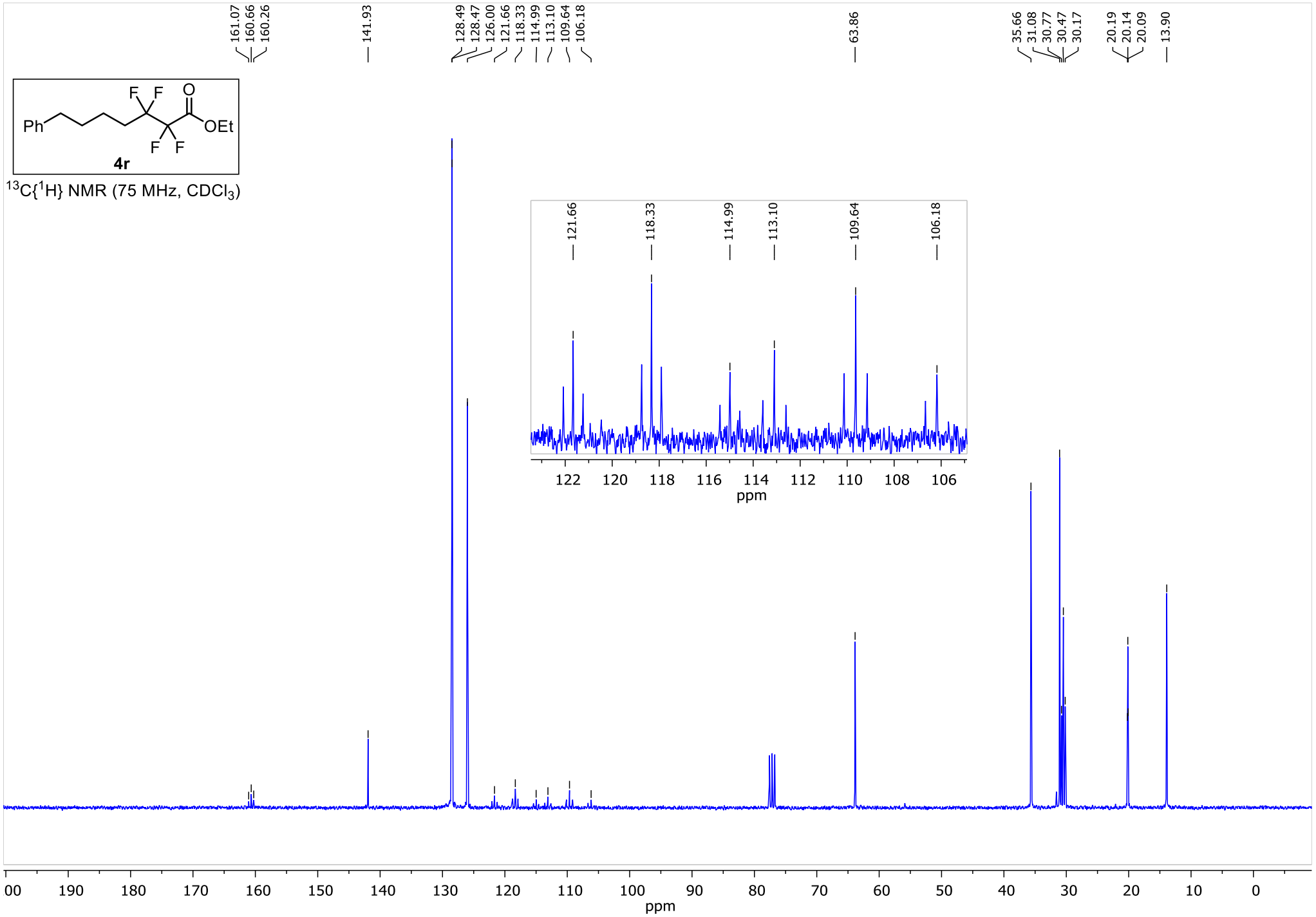

161.03
160.63
160.22
144.63
126.87
124.38
123.17
121.62
118.28
114.95
113.09
109.62
106.16
63.86
31.36
30.68
30.38
30.09
29.63
20.04
19.99
19.94
13.90
F F O
S
OEt
F F
4q
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
121.62
118.28
114.95
113.09
109.62
106.16
122 120 118 116 114 112 110 108 106 104
ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

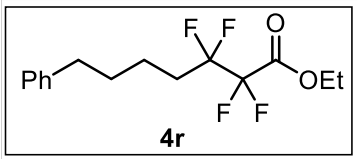


4q

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

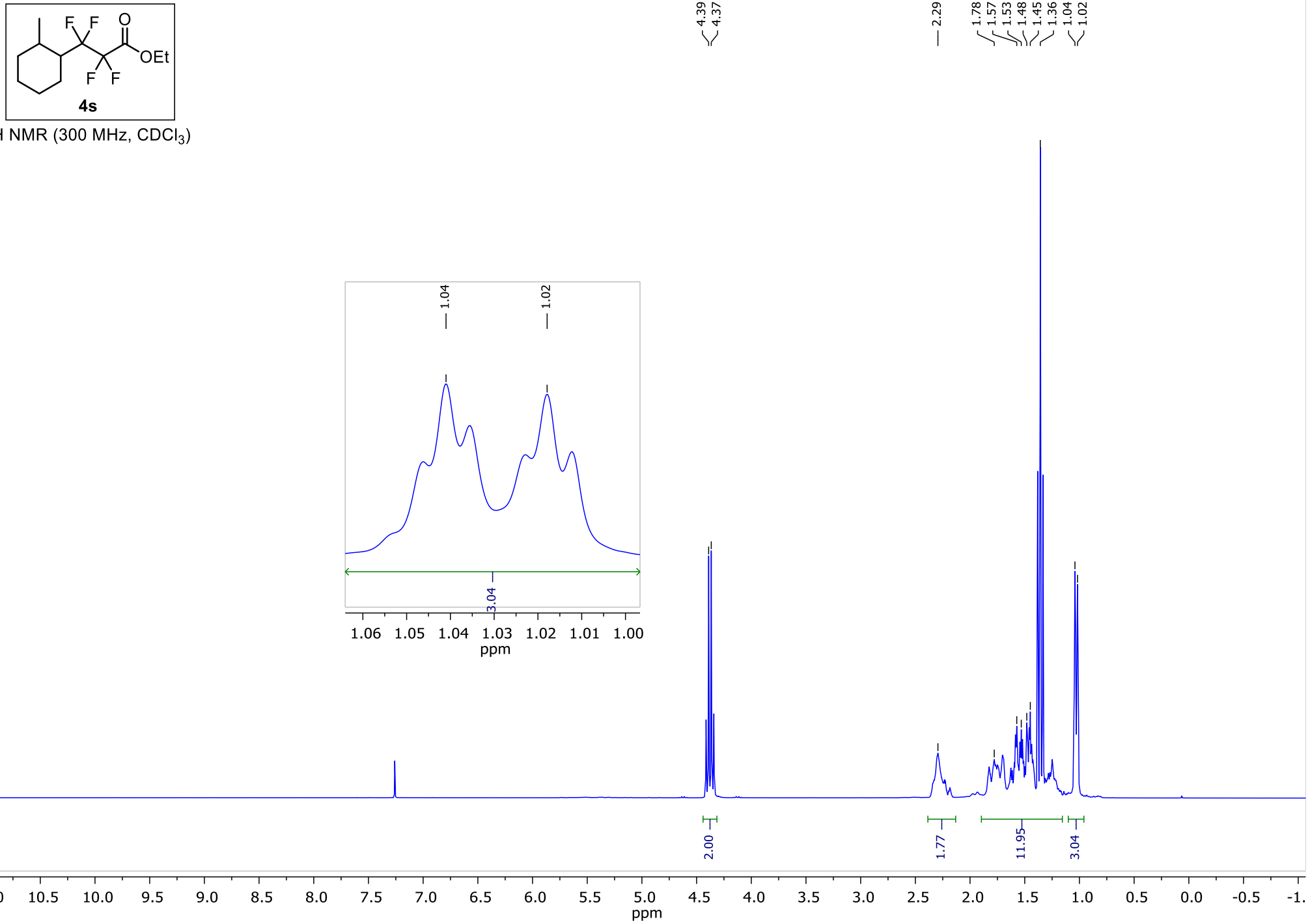

F F O
Ph
OEt
F F
4r
^{1}H NMR (300 MHz, $CDCl_3$)
7.32
7.22
4.42
4.40
2.68
2.11
1.71
1.70
1.39
2.00
3.05
1.98
2.00
2.00
4.01
3.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

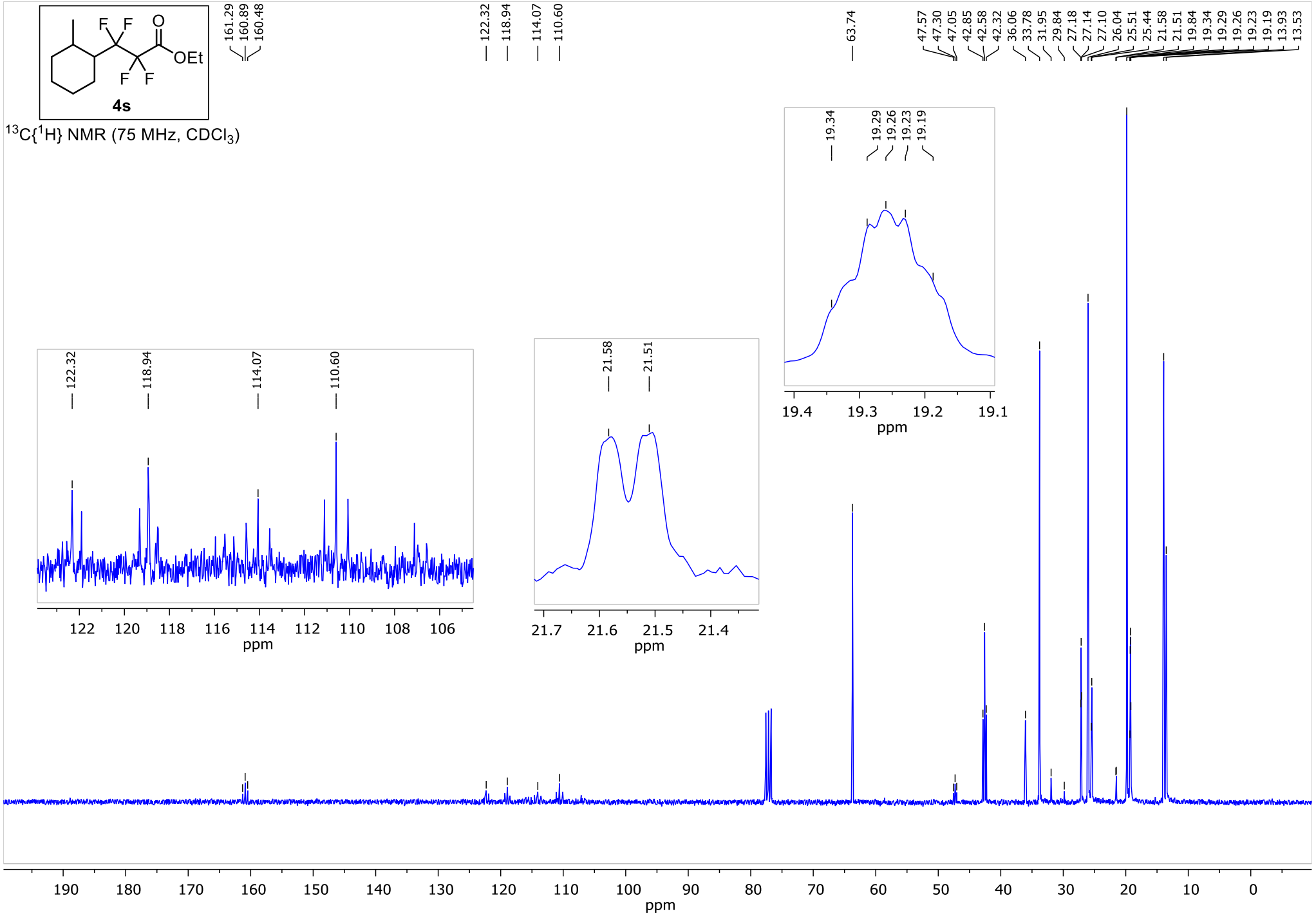

161.07
160.66
160.26
141.93
128.49
128.47
126.00
121.66
118.33
114.99
113.10
109.64
106.18
63.86
35.66
31.08
30.77
30.47
30.17
20.19
20.14
20.09
13.90
F F O
Ph
OEt
F F
4r
13C{1H} NMR (75 MHz, CDCl3)
121.66
118.33
114.99
113.10
109.64
106.18
122 120 118 116 114 112 110 108 106
ppm
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

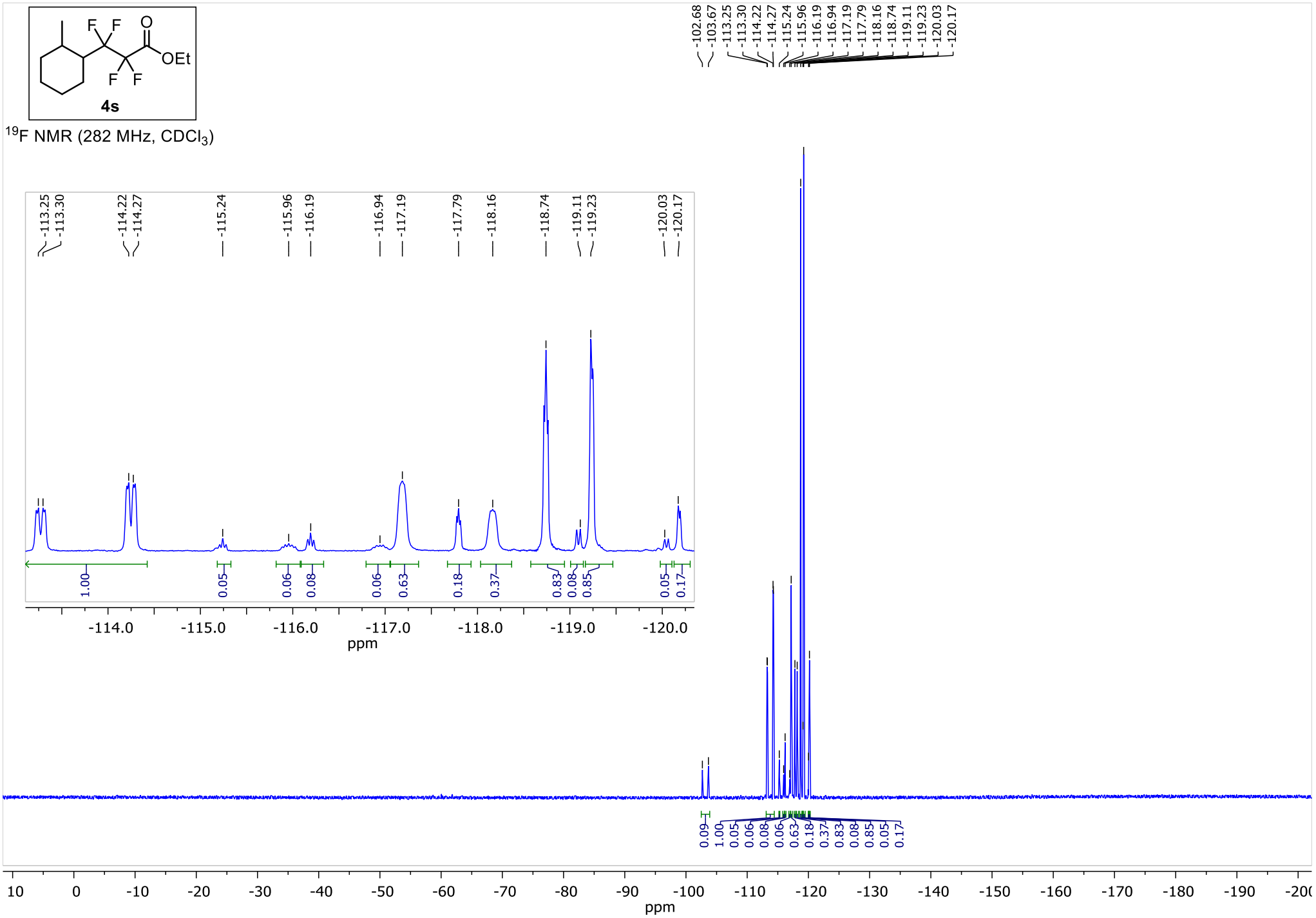


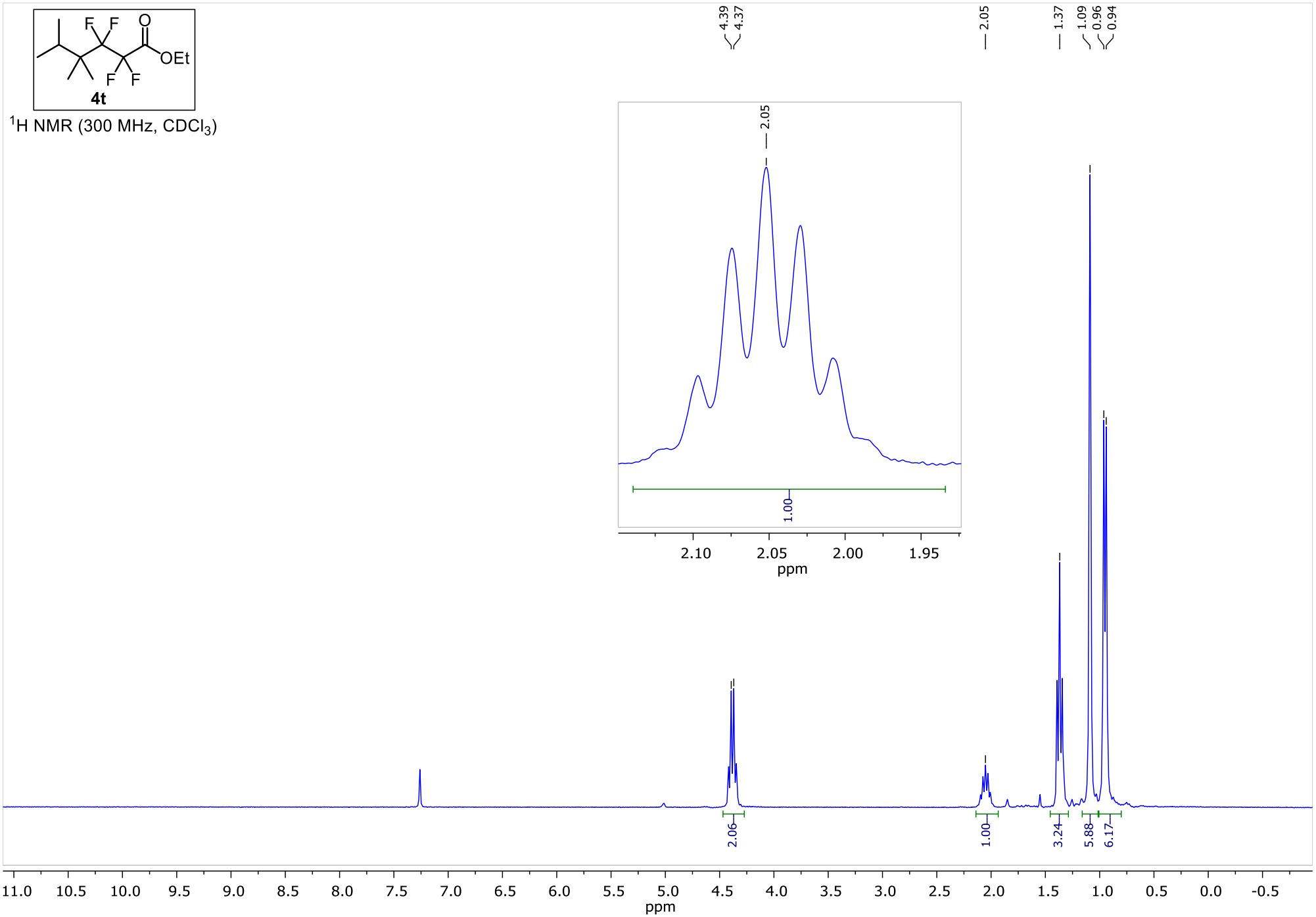
4r

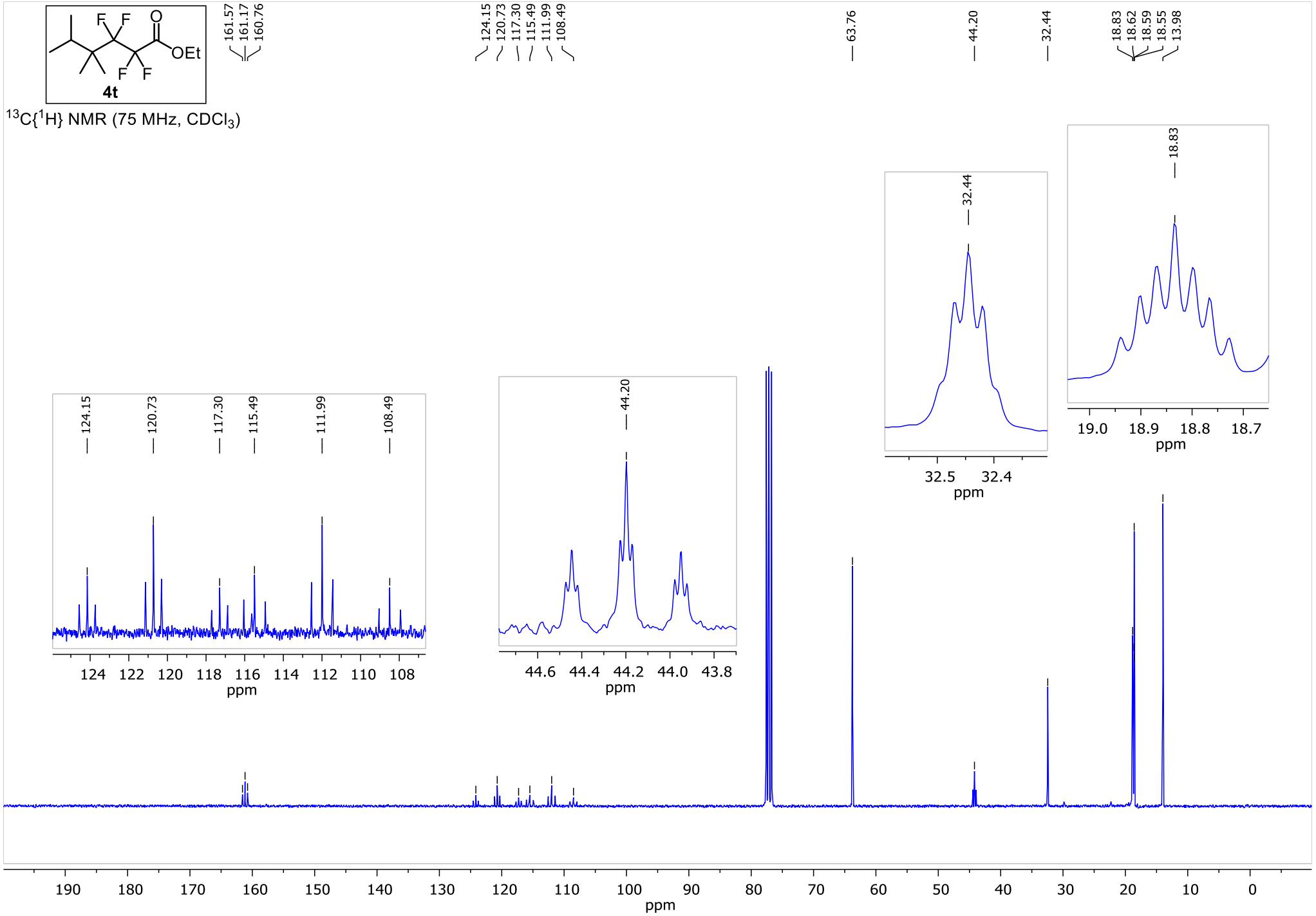
^{19}F NMR (282 MHz, $CDCl_3$)

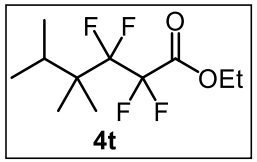

F F O
OEt
F F
4s
1H NMR (300 MHz, CDCl3)
4.39
4.37
2.29
1.78
1.57
1.53
1.48
1.45
1.36
1.04
1.02
1.04
1.02
3.04
1.06 1.05 1.04 1.03 1.02 1.01 1.00
ppm
2.00
1.77
11.95
3.04
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
ppm


F F O
OEt
F F
4s
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
161.29
160.89
160.48
122.32
118.94
114.07
110.60
63.74
47.57
47.30
47.05
42.85
42.58
42.32
36.06
33.78
31.95
29.84
27.18
27.14
27.10
26.04
25.51
25.44
21.58
21.51
19.84
19.34
19.29
19.26
19.23
19.19
13.93
13.53
19.34
19.29
19.26
19.23
19.19
19.4
19.3
19.2
19.1
ppm
122.32
118.94
114.07
110.60
122
120
118
116
114
112
110
108
106
ppm
21.58
21.51
21.7
21.6
21.5
21.4
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


F F O
OEt
F F
4s
19F NMR (282 MHz, CDCl3)
-102.68
-103.67
-113.25
-113.30
-114.22
-114.27
-115.24
-115.96
-116.19
-116.94
-117.19
-117.79
-118.16
-118.74
-119.11
-119.23
-120.03
-120.17
1.00
0.05
0.06
0.08
0.06
0.63
0.18
0.37
0.83
0.08
0.85
0.05
0.17
-114.0
-115.0
-116.0
-117.0
-118.0
-119.0
-120.0
ppm
0.09
1.00
0.05
0.06
0.08
0.06
0.63
0.18
0.37
0.83
0.08
0.85
0.05
0.17
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
ppm

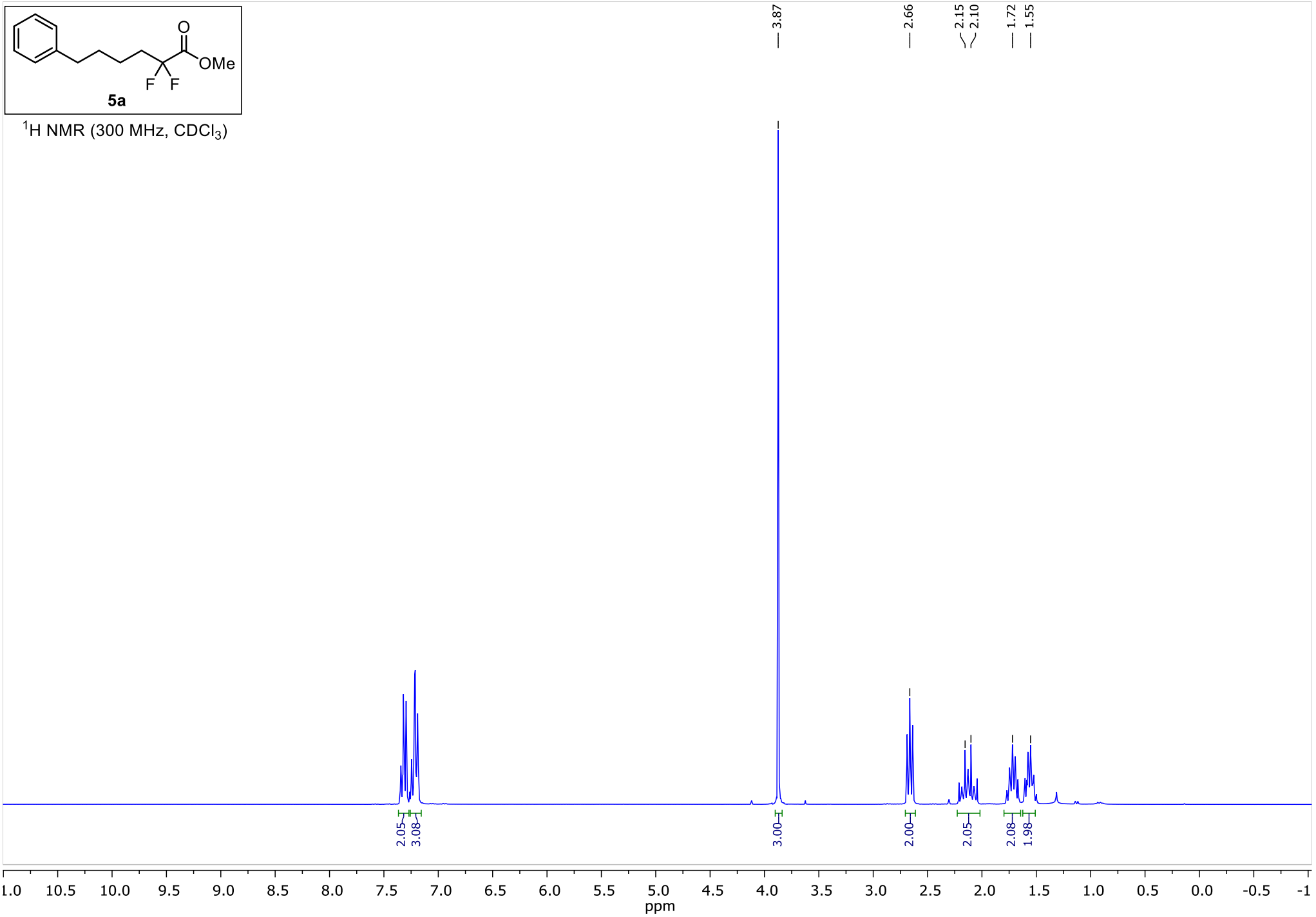

F F O
OEt
F F
4t
^{1}H NMR (300 MHz, $CDCl_3$)
4.39
4.37
2.05
1.37
1.09
0.96
0.94
2.05
1.00
2.10
2.05
2.00
1.95
ppm
2.06
1.00
3.24
5.88
6.17
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm

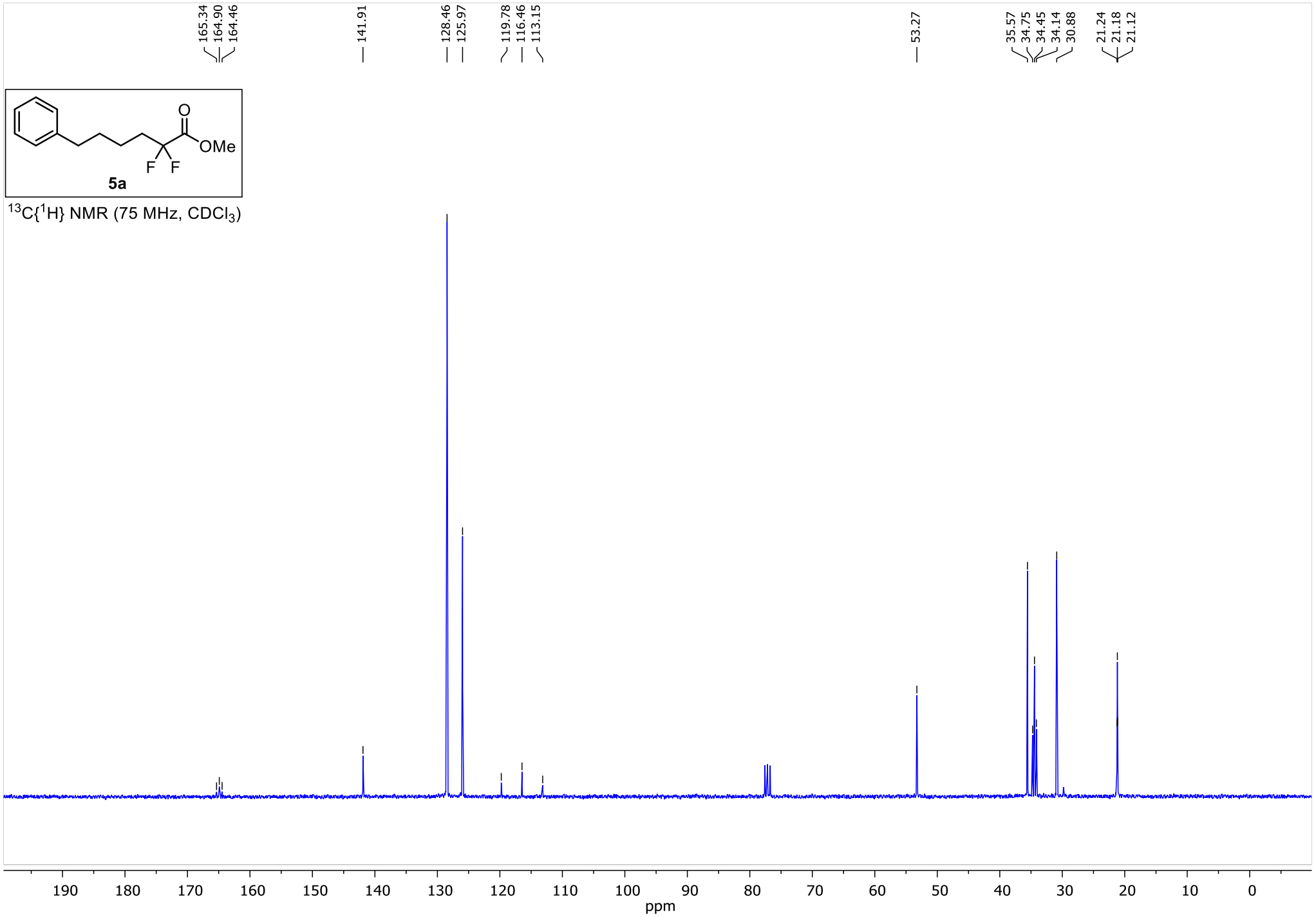

F F O
OEt
F F
4t
161.57
161.17
160.76
124.15
120.73
117.30
115.49
111.99
108.49
63.76
44.20
32.44
18.83
18.62
18.59
18.55
13.98
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
ppm

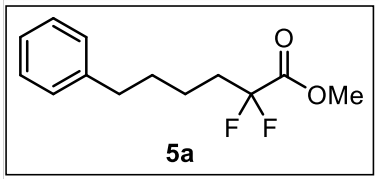


4t

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

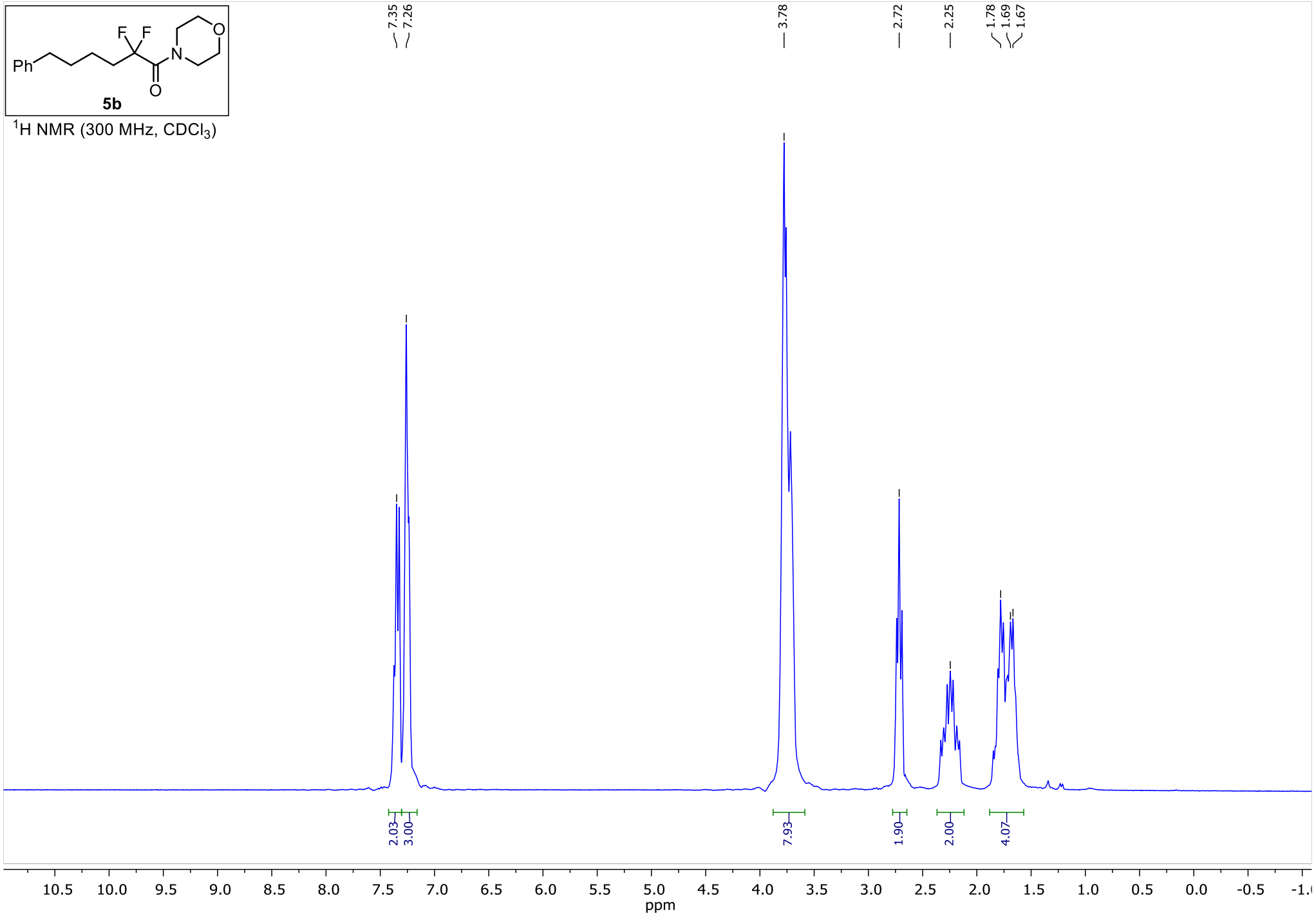

O
OMe
F F
5a
^{1}H NMR (300 MHz, $CDCl_3$)
3.87
2.66
2.15
2.10
1.72
1.55
2.05
3.08
3.00
2.00
2.05
2.08
1.98
ppm

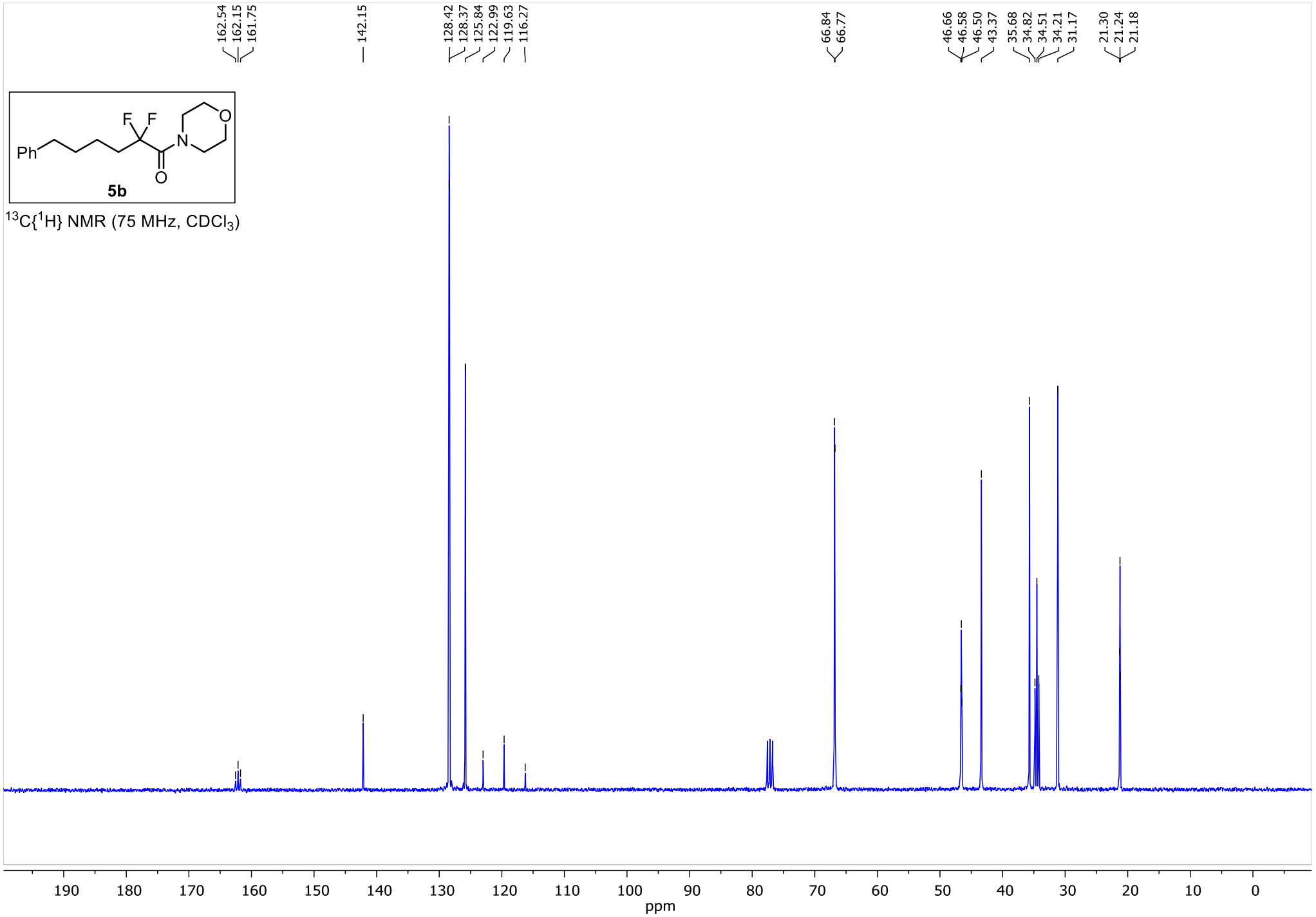

165.34
164.90
164.46
141.91
128.46
125.97
119.78
116.46
113.15
53.27
35.57
34.75
34.45
34.14
30.88
21.24
21.18
21.12
O
OMe
F F
5a
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



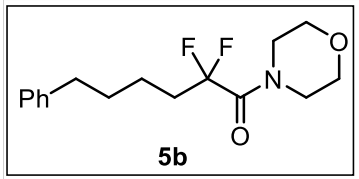
5a

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


F F
O
N
Ph
O
5b
^{1}H NMR (300 MHz, $CDCl_3$)
7.35
7.26
3.78
2.72
2.25
1.78
1.69
1.67
2.03
3.00
7.93
1.90
2.00
4.07
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
ppm

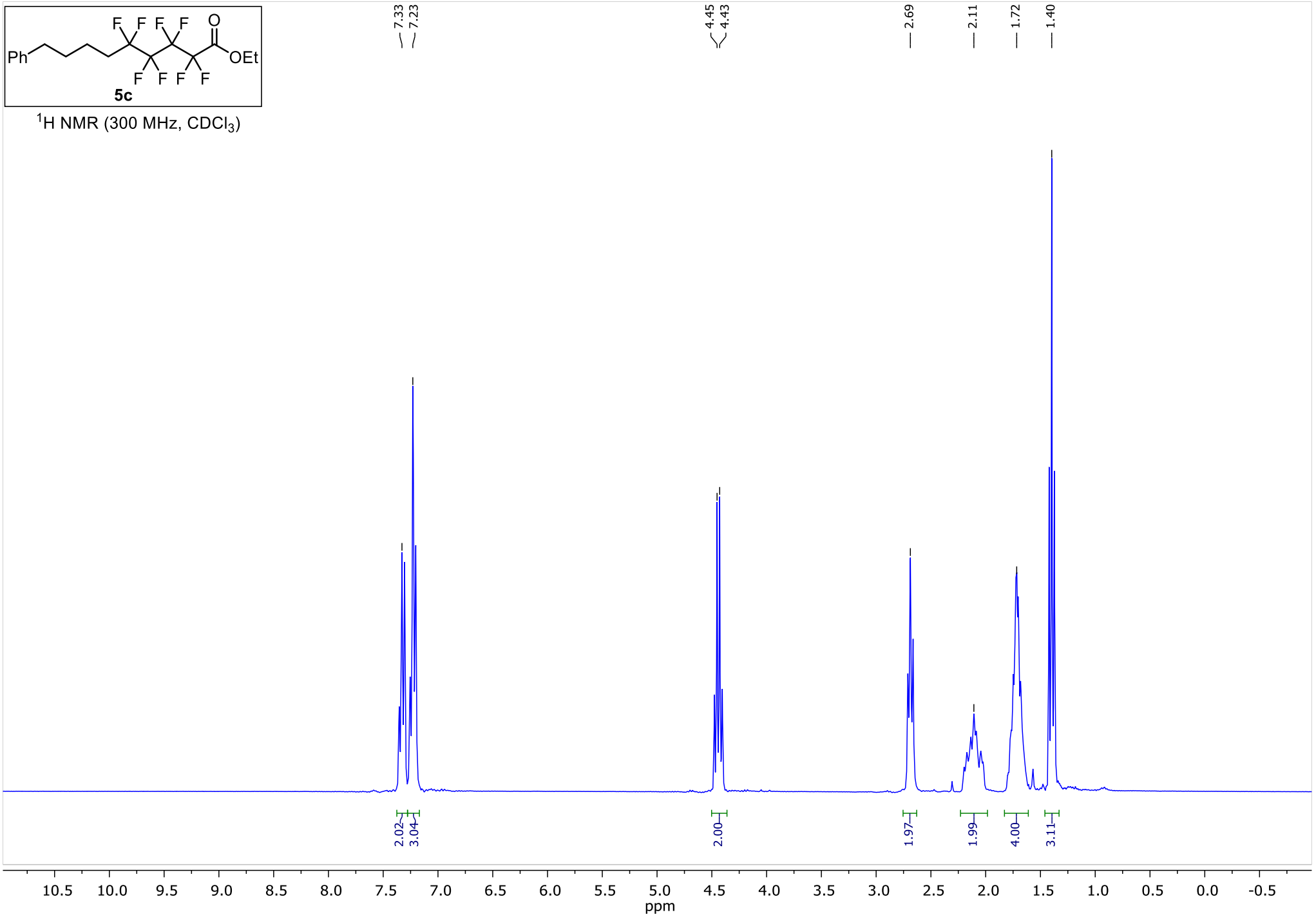


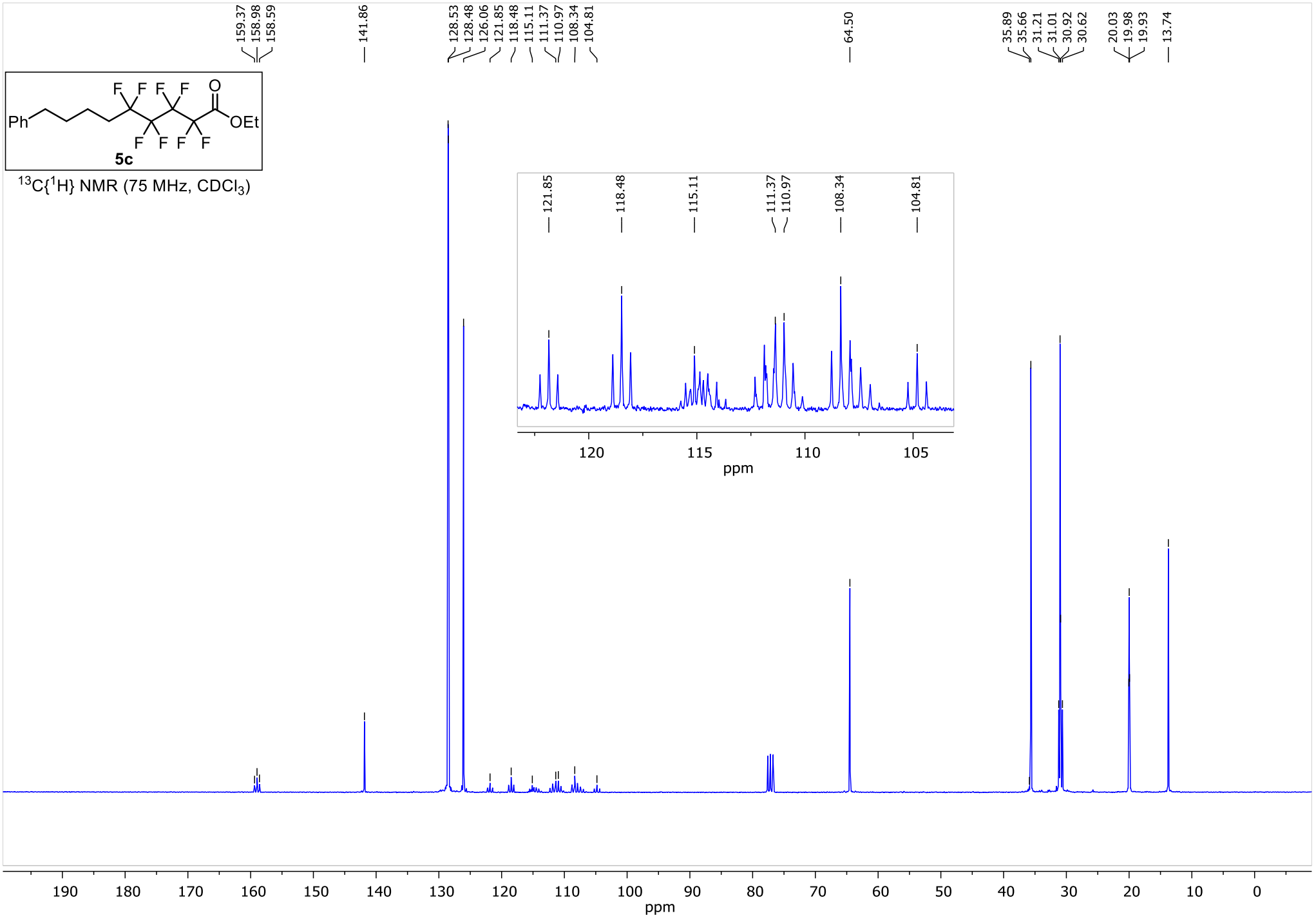
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

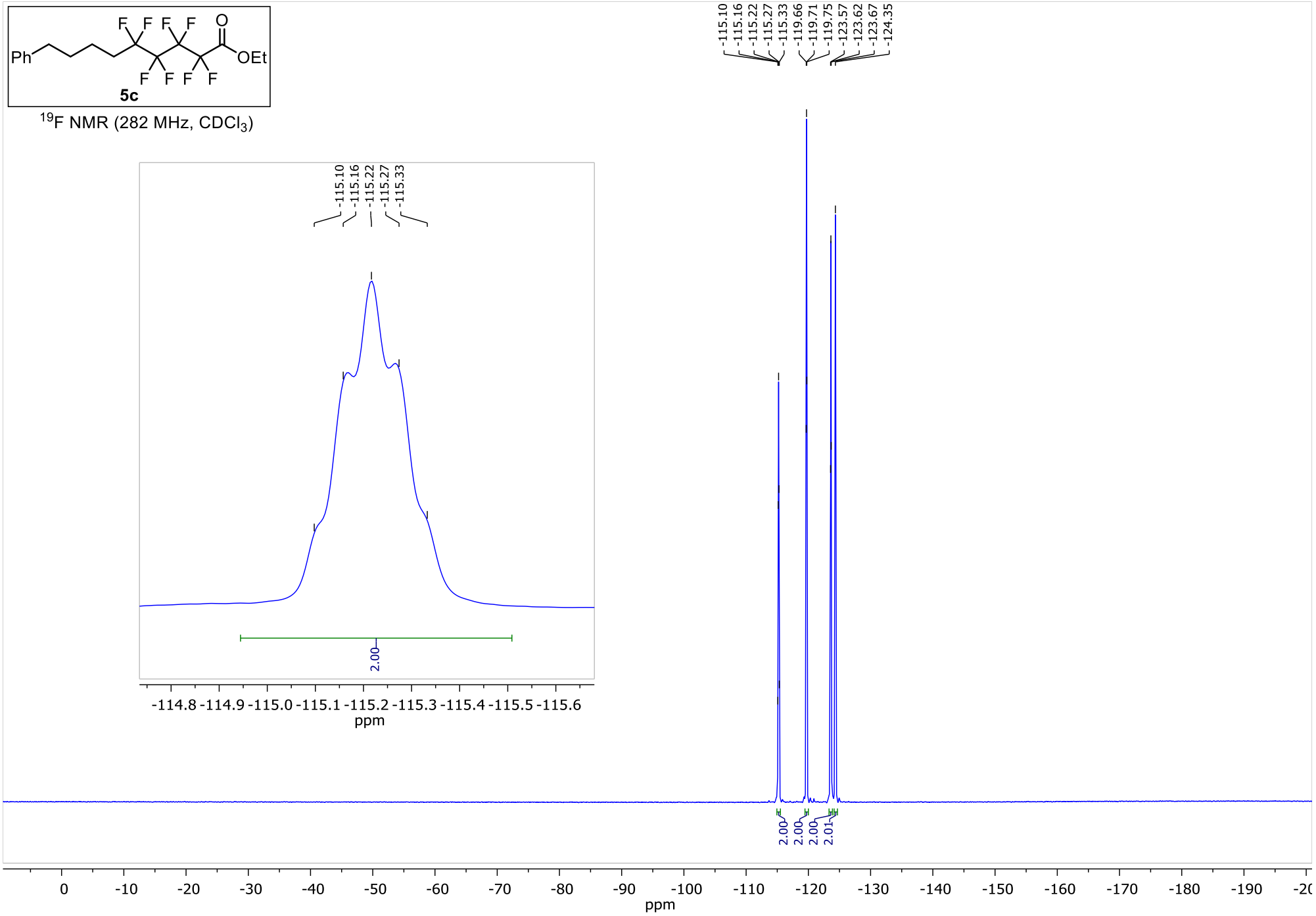


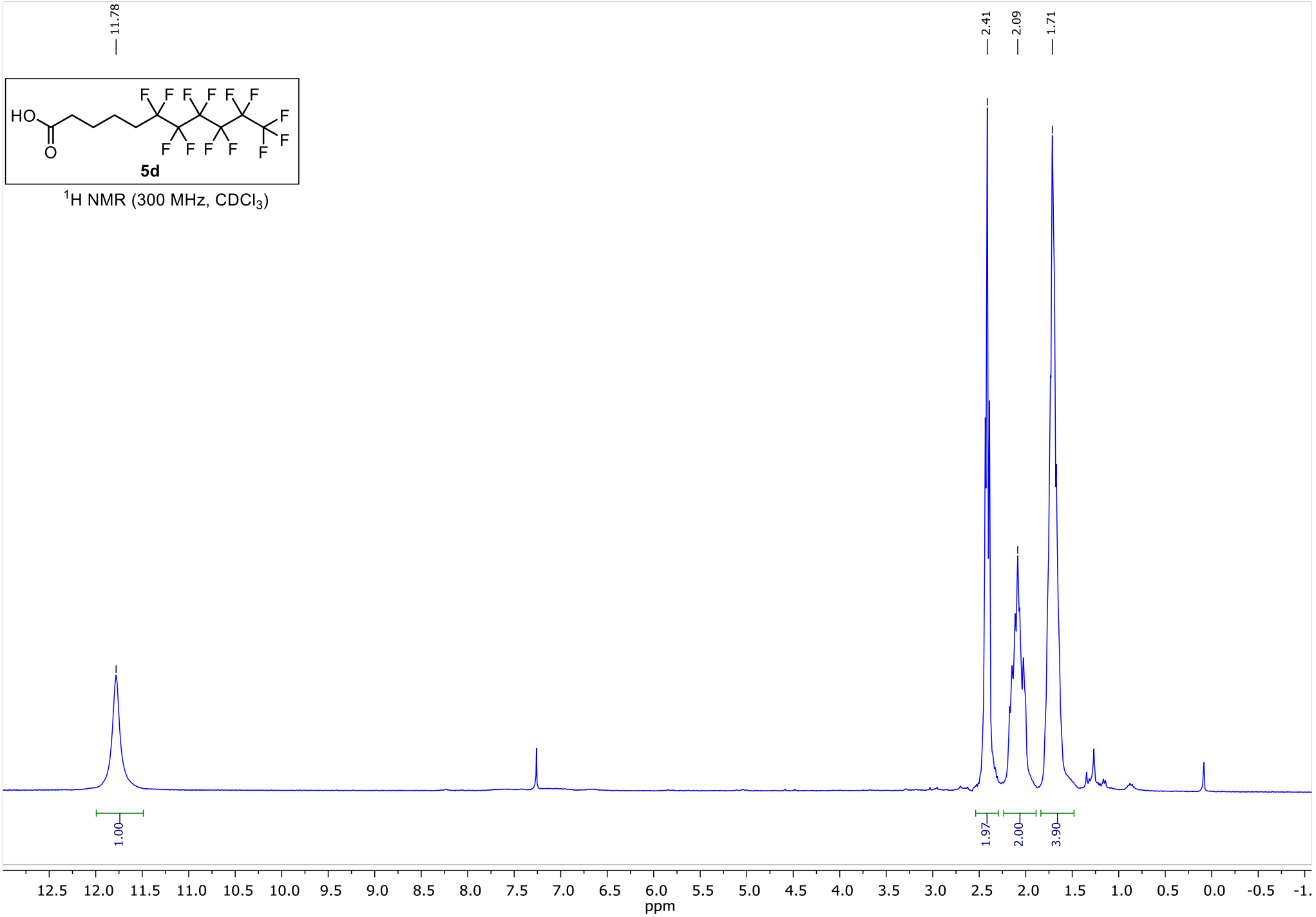
5b

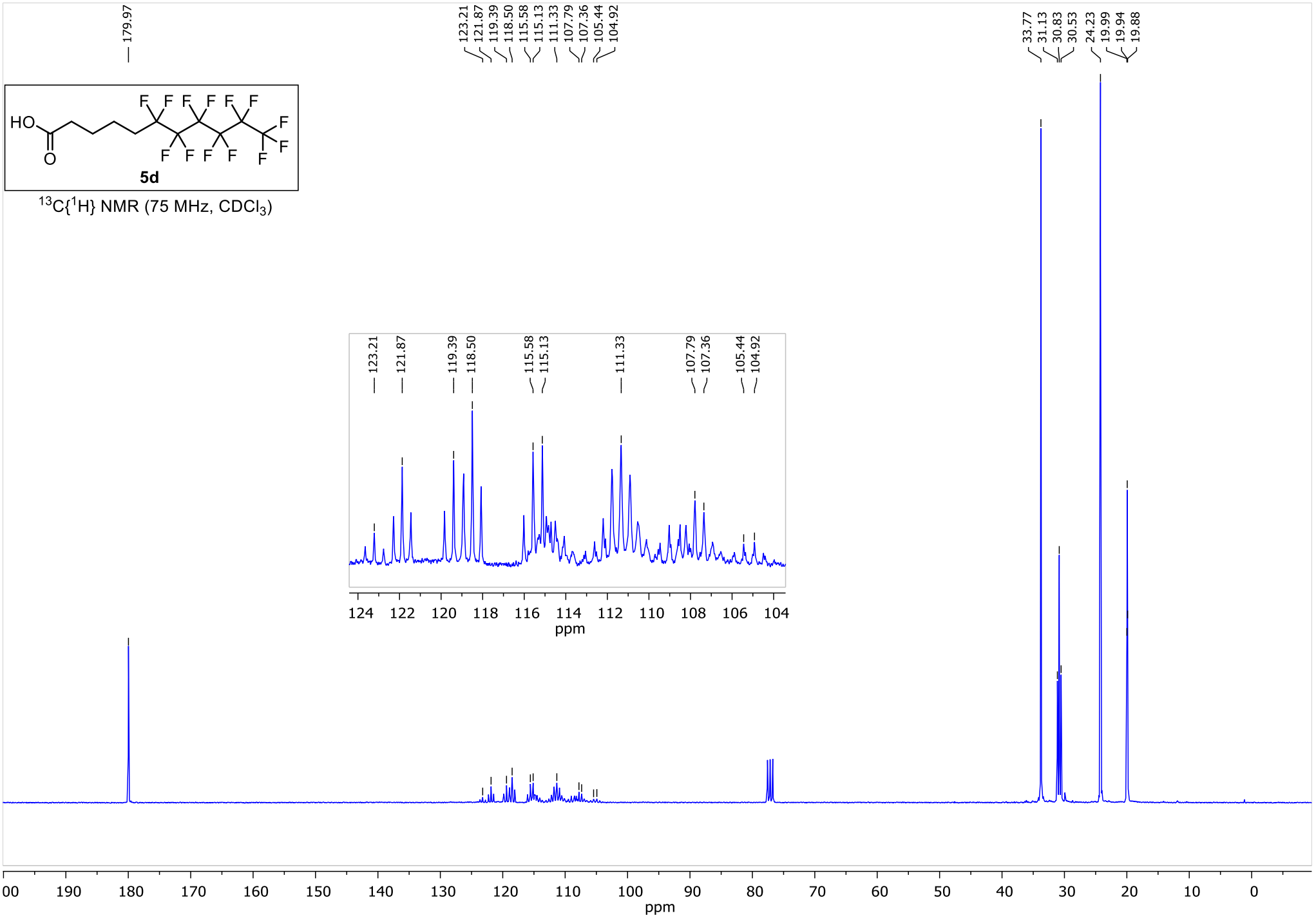
^{19}F NMR (282 MHz, $CDCl_3$)


F F F F O
Ph
OEt
F F F F
5c
1H NMR (300 MHz, CDCl3)
7.33
7.23
4.45
4.43
2.69
2.11
1.72
1.40
2.02
3.04
2.00
1.97
1.99
4.00
3.11
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
ppm

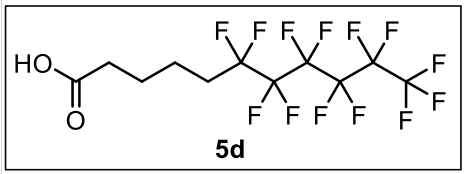

159.37
158.98
158.59
141.86
128.53
128.48
126.06
121.85
118.48
115.11
111.37
110.97
108.34
104.81
64.50
35.89
35.66
31.21
31.01
30.92
30.62
20.03
19.98
19.93
13.74
F F F F O
Ph
OEt
F F F F
5c
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
121.85
118.48
115.11
111.37
110.97
108.34
104.81
120
115
110
105
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


F F F F O
Ph
OEt
F F F F
5c
^{19}F NMR (282 MHz, $CDCl_3$)
-115.10
-115.16
-115.22
-115.27
-115.33
-119.66
-119.71
-119.75
-123.57
-123.62
-123.67
-124.35
2.00
2.00
2.00
2.01
-114.8 -114.9 -115.0 -115.1 -115.2 -115.3 -115.4 -115.5 -115.6
ppm
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
ppm

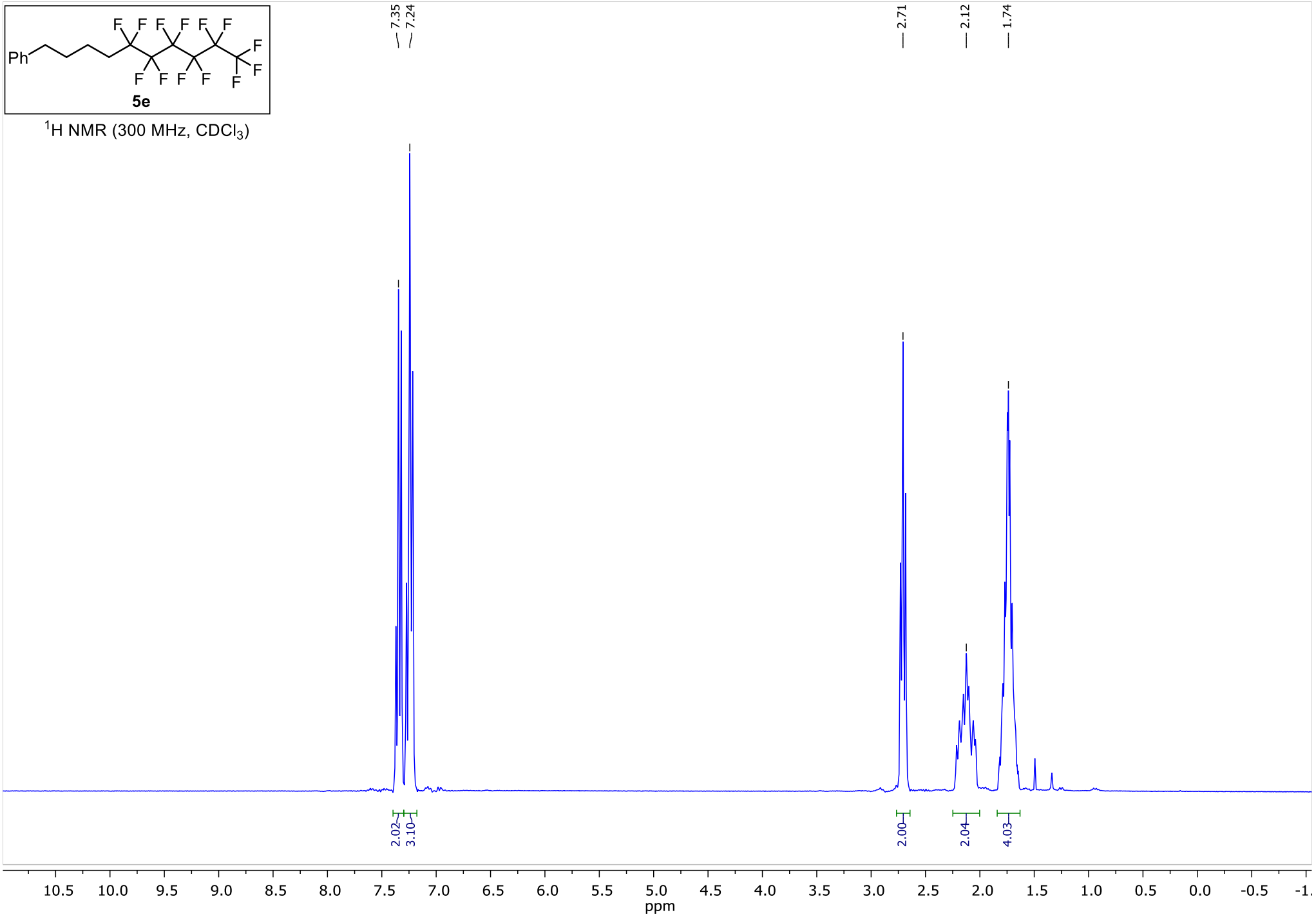

11.78
2.41
2.09
1.71
HO
O
F
5d
1H NMR (300 MHz, CDCl3)
1.00
1.97
2.00
3.90
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
ppm

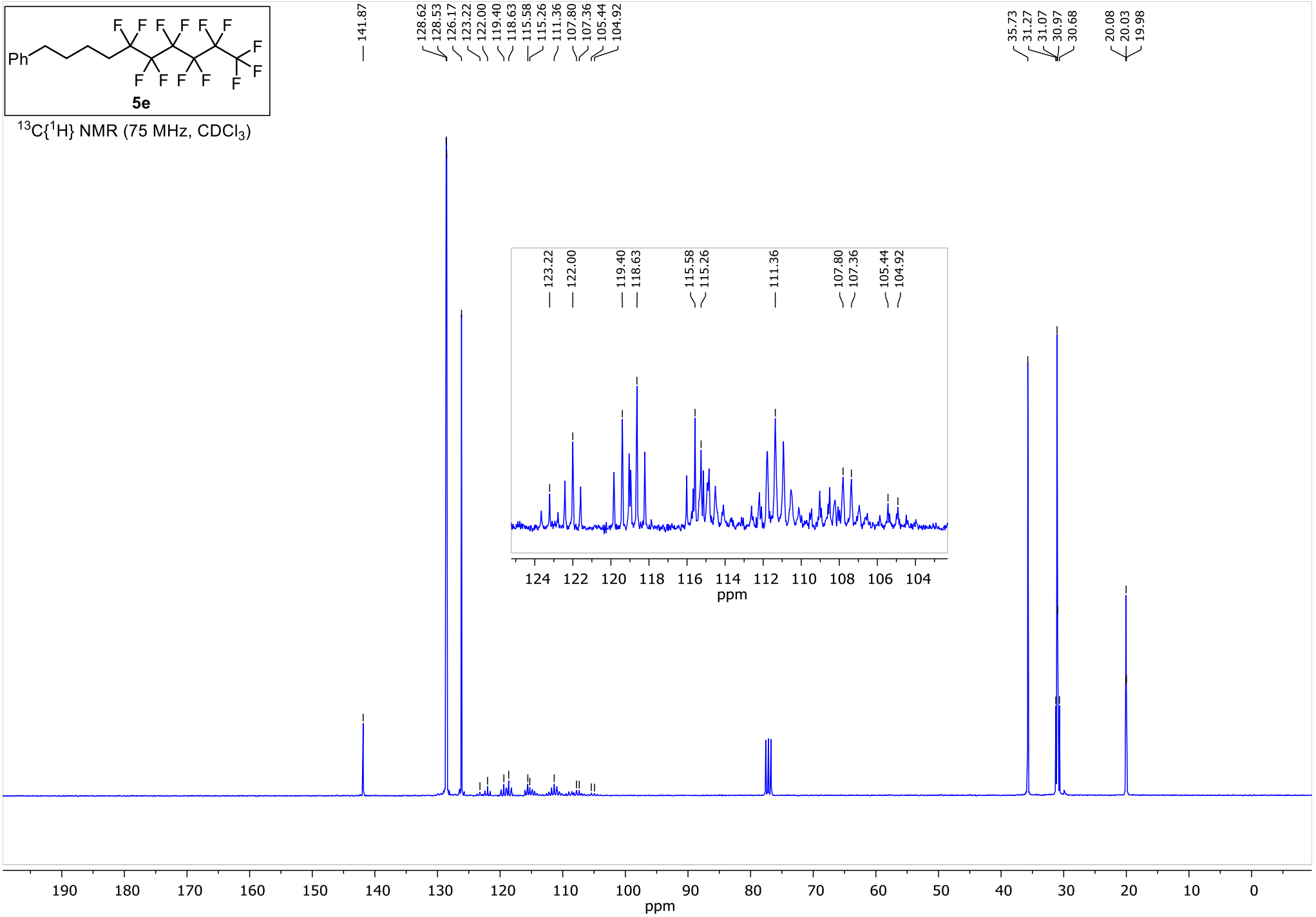


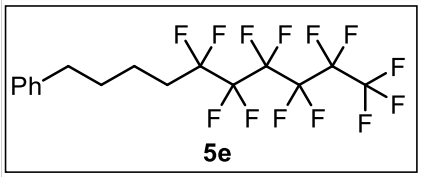
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



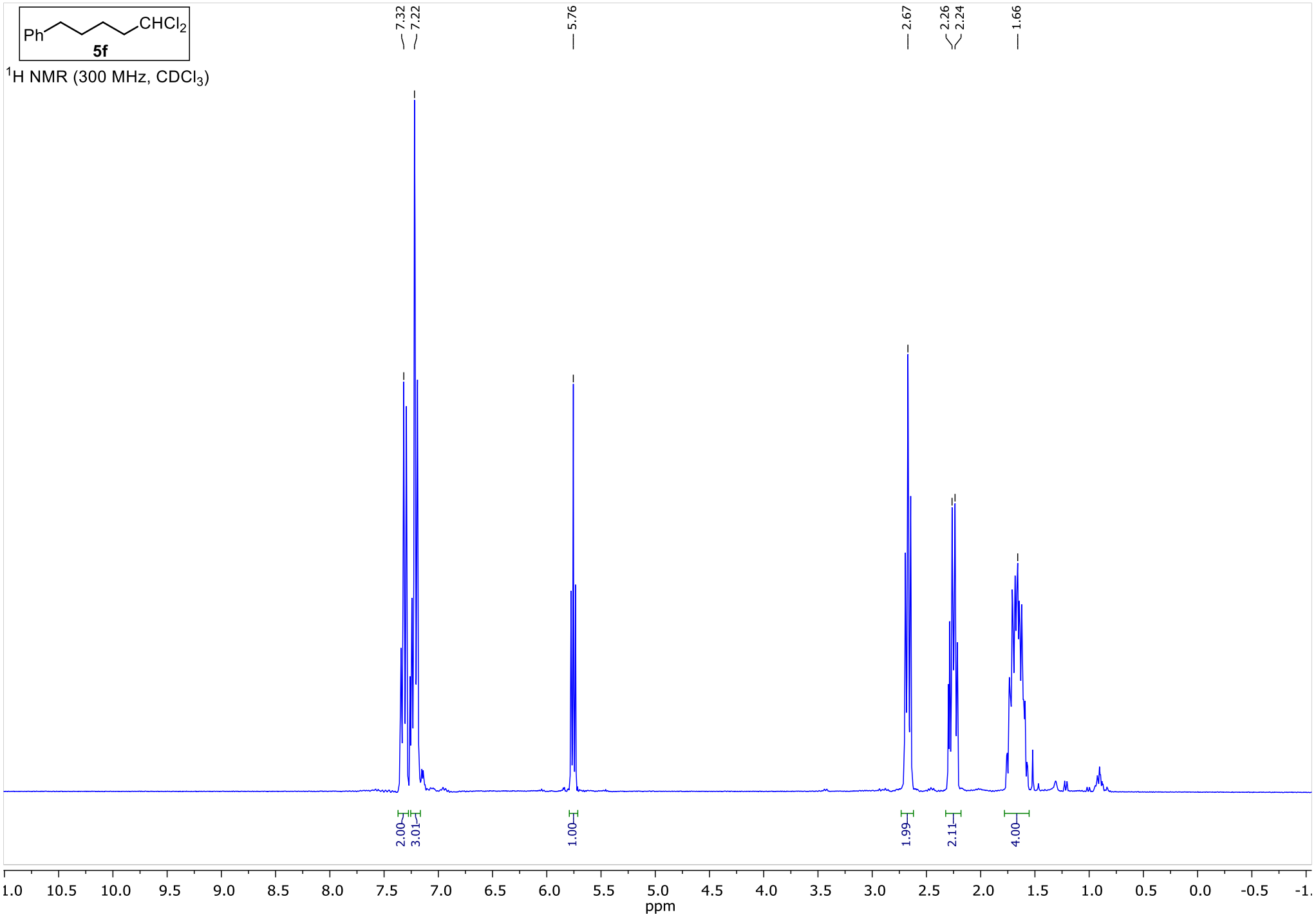
^{19}F NMR (282 MHz, $CDCl_3$)

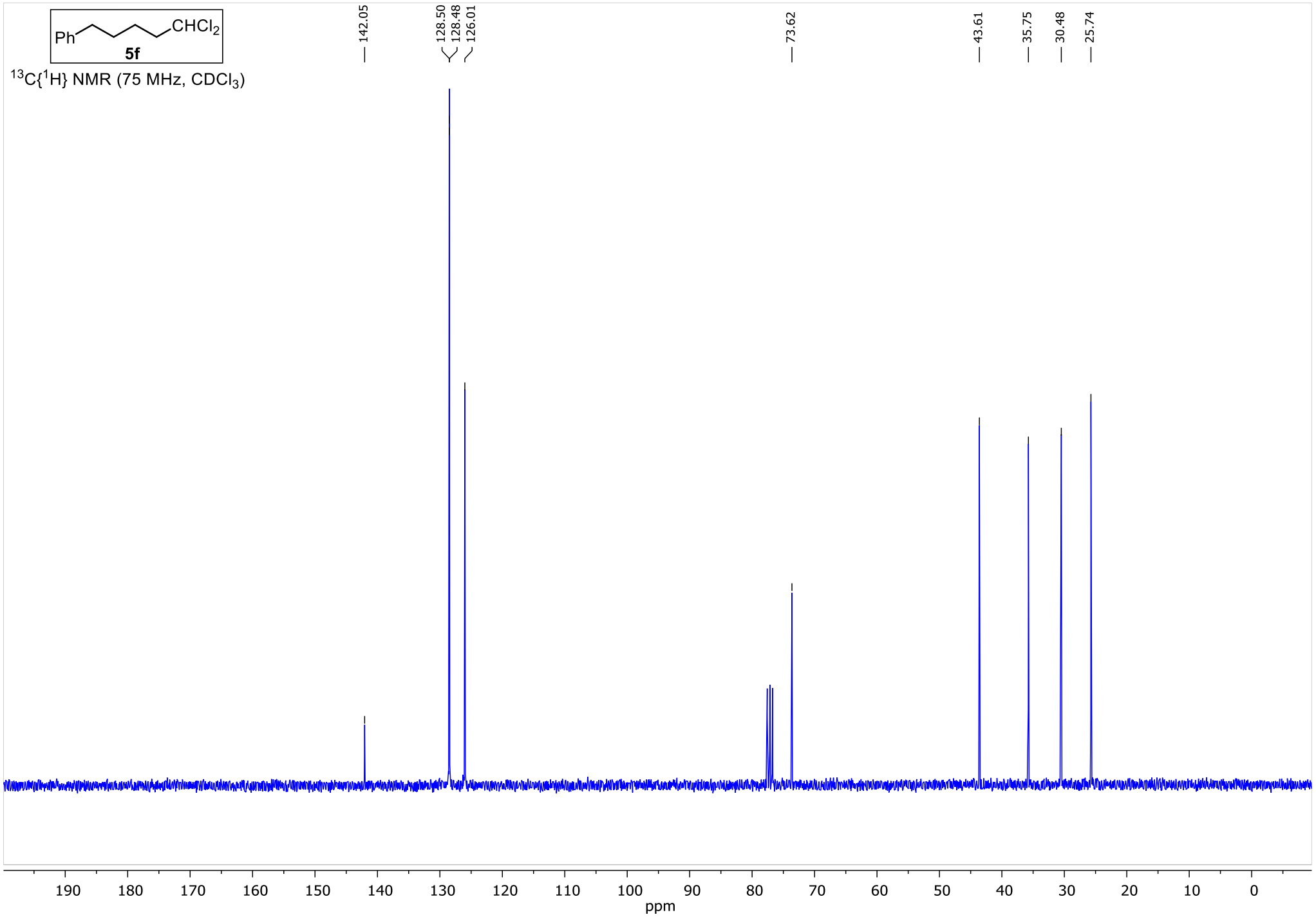

Ph
F F F F F F F F F F F F F
5e
^{1}H NMR (300 MHz, $CDCl_3$)
7.35
7.24
2.71
2.12
1.74
2.02
3.10
2.00
2.04
4.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
ppm

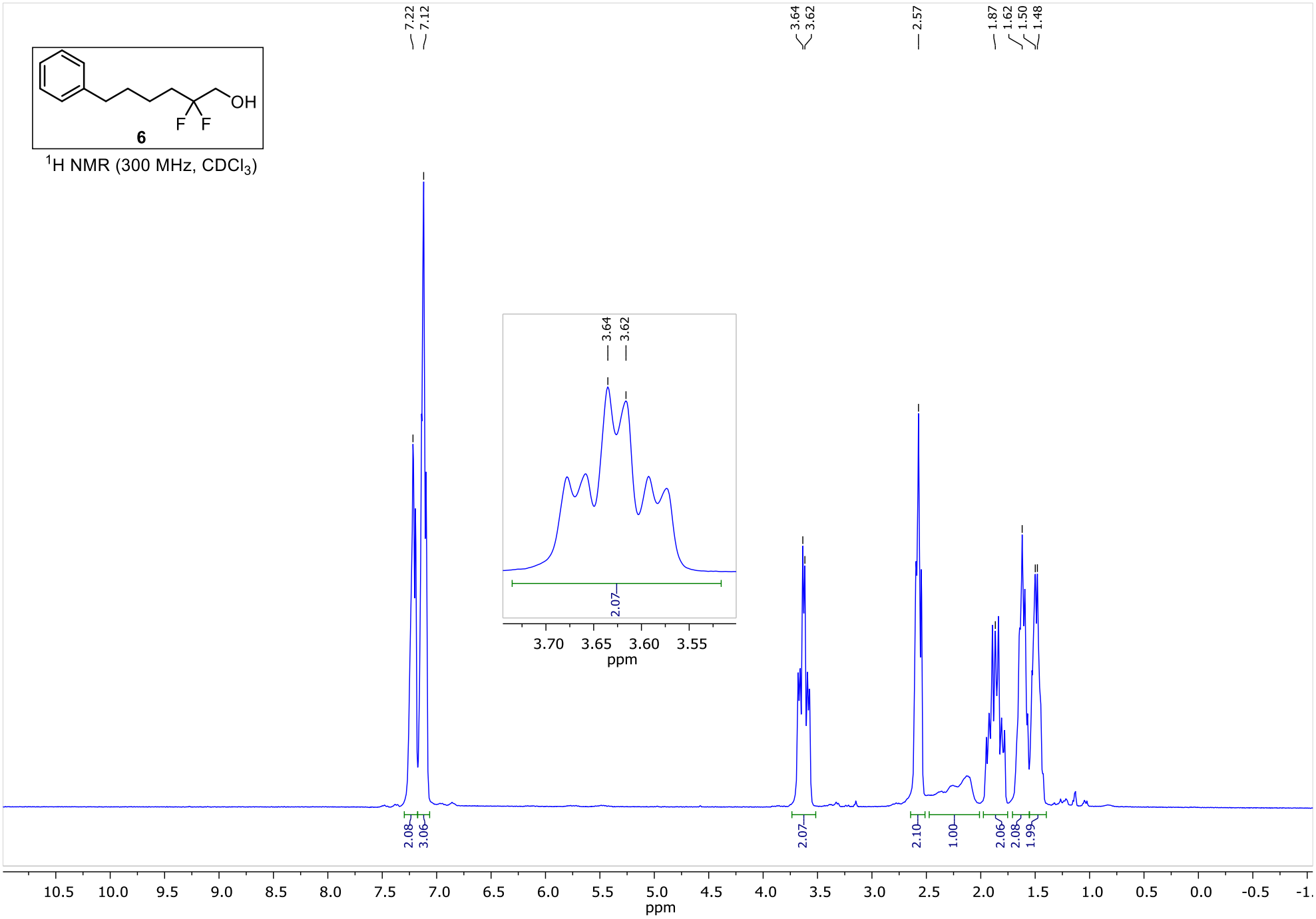

Ph
F F F F F F F F F F F F
5e
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
141.87
128.62
128.53
126.17
123.22
122.00
119.40
118.63
115.58
115.26
111.36
107.80
107.36
105.44
104.92
35.73
31.27
31.07
30.97
30.68
20.08
20.03
19.98
124 122 120 118 116 114 112 110 108 106 104
ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

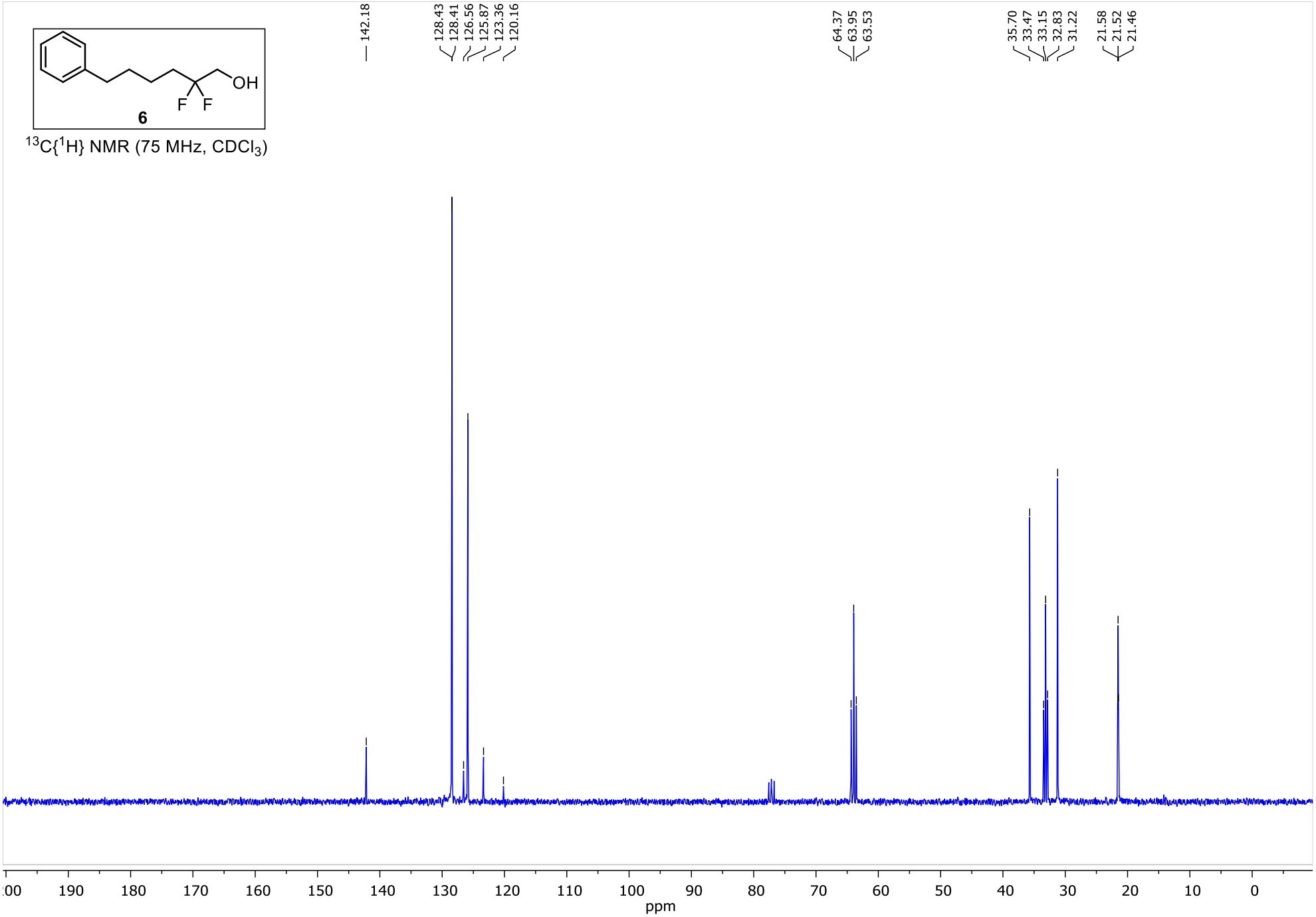


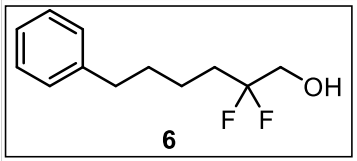
^{19}F NMR (282 MHz, $CDCl_3$)


Ph
CHCl2
5f
1H NMR (300 MHz, CDCl3)
7.32
7.22
5.76
2.67
2.26
2.24
1.66
2.00
3.01
1.00
1.99
2.11
4.00
ppm


Ph
CHCl2
5f
13C{1H} NMR (75 MHz, CDCl3)
142.05
128.50
128.48
126.01
73.62
43.61
35.75
30.48
25.74
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

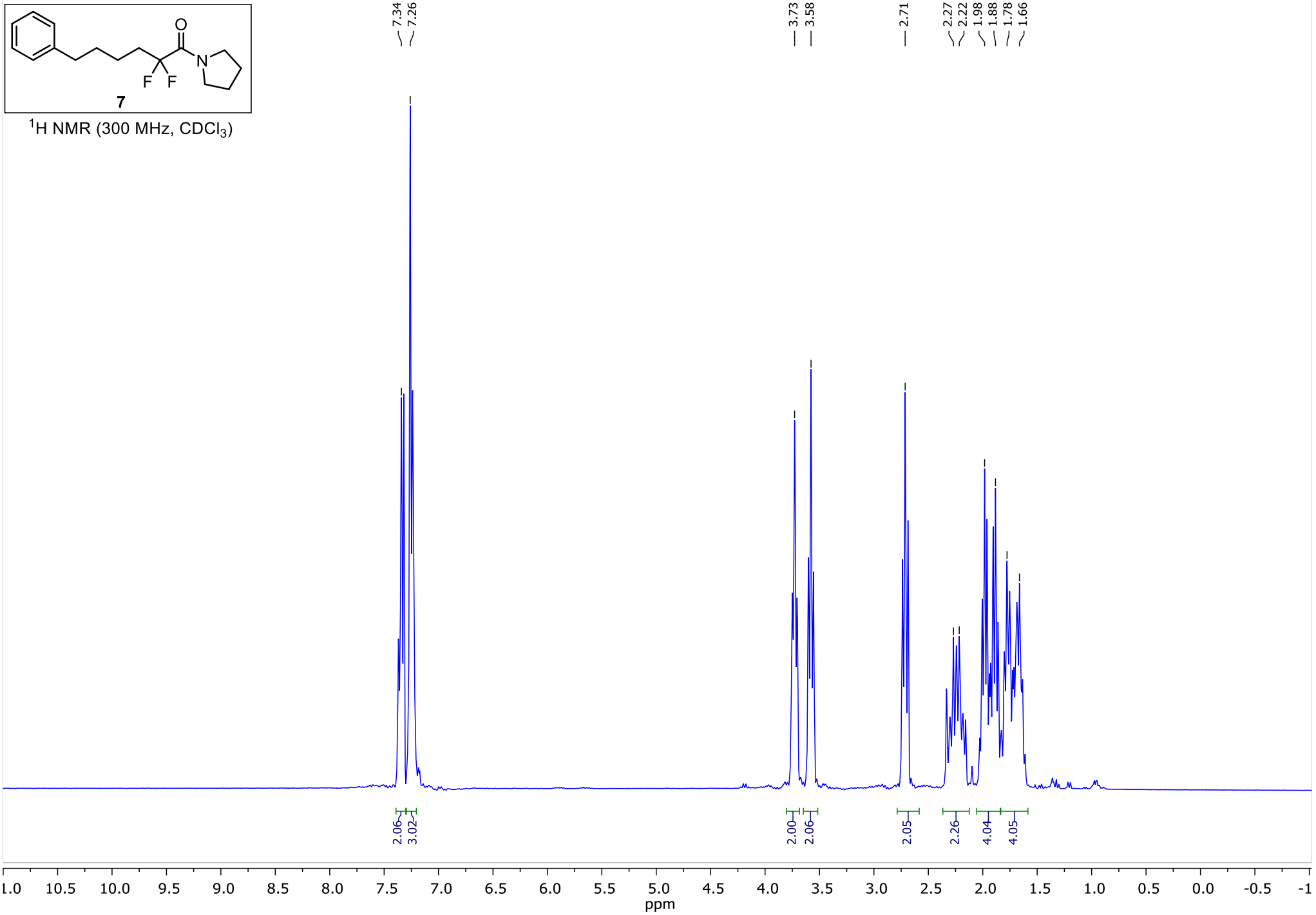

7.22
7.12
3.64
3.62
2.57
1.87
1.62
1.50
1.48
OH
F F
6
^{1}H NMR (300 MHz, $CDCl_3$)
3.64
3.62
2.07
3.70 3.65 3.60 3.55
ppm
2.08
3.06
2.07
2.10
1.00
2.06
2.08
1.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

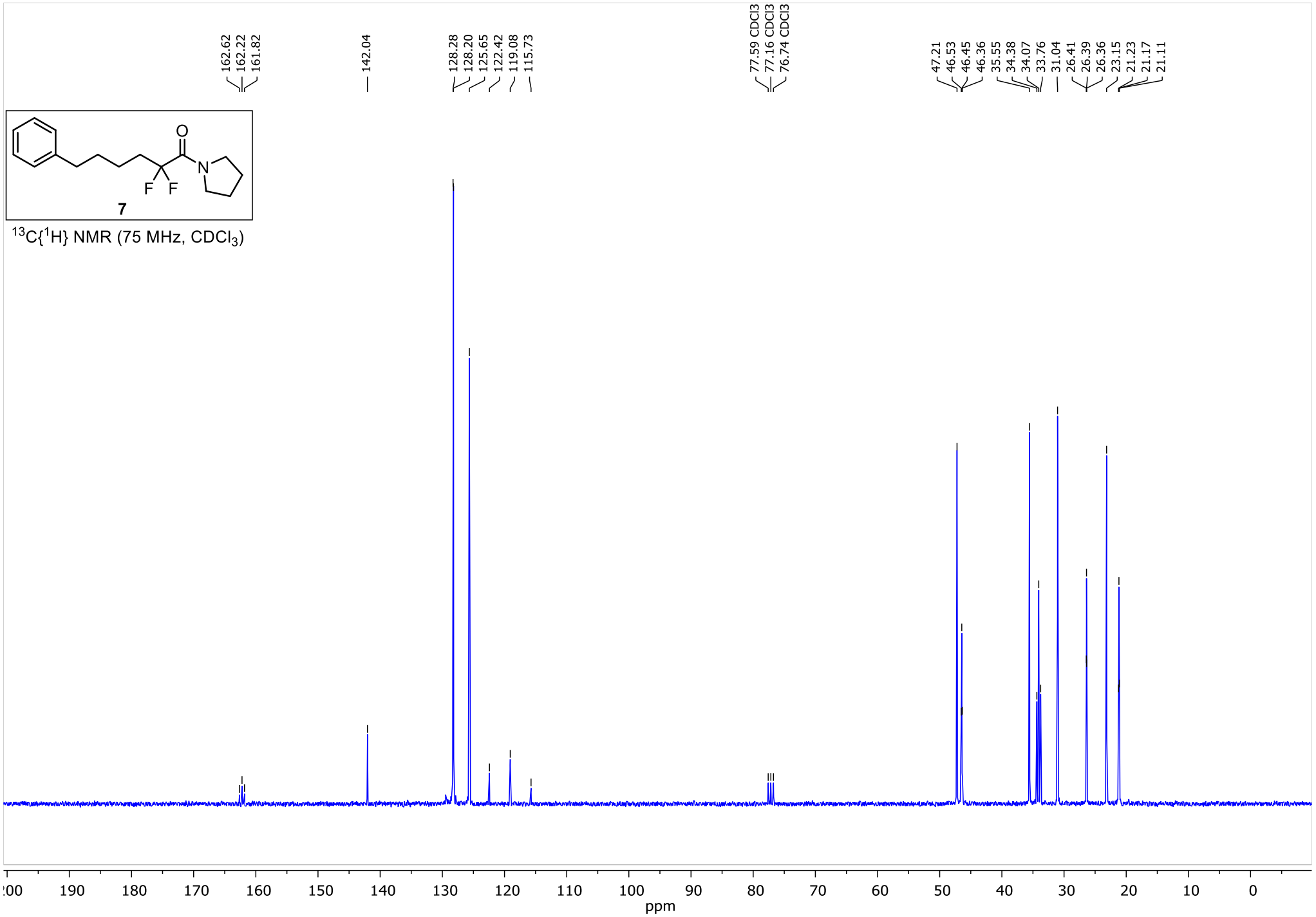

142.18
128.43
128.41
126.56
125.87
123.36
120.16
64.37
63.95
63.53
35.70
33.47
33.15
32.83
31.22
21.58
21.52
21.46
OH
F F
6
13C{1H} NMR (75 MHz, CDCl3)
ppm

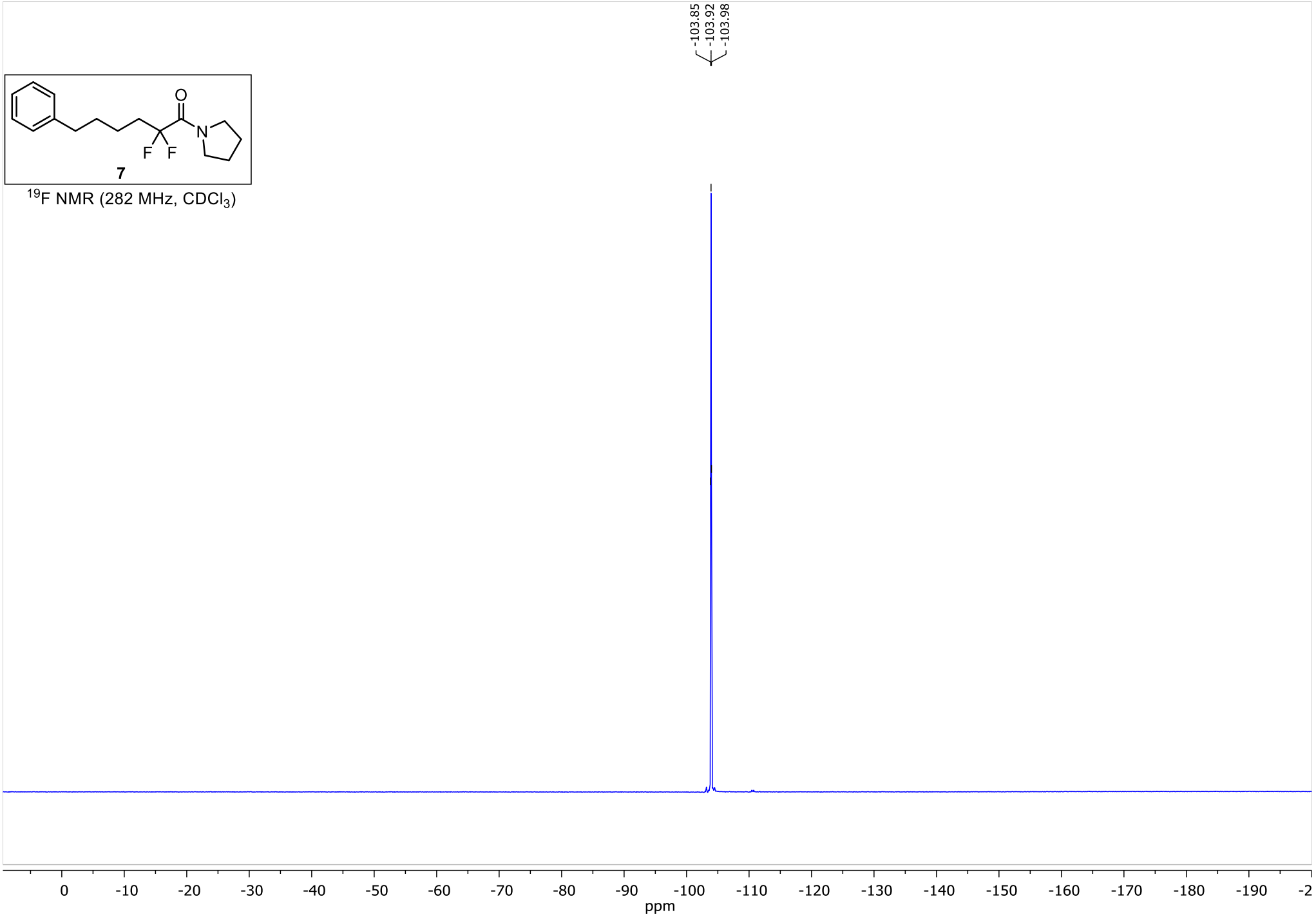


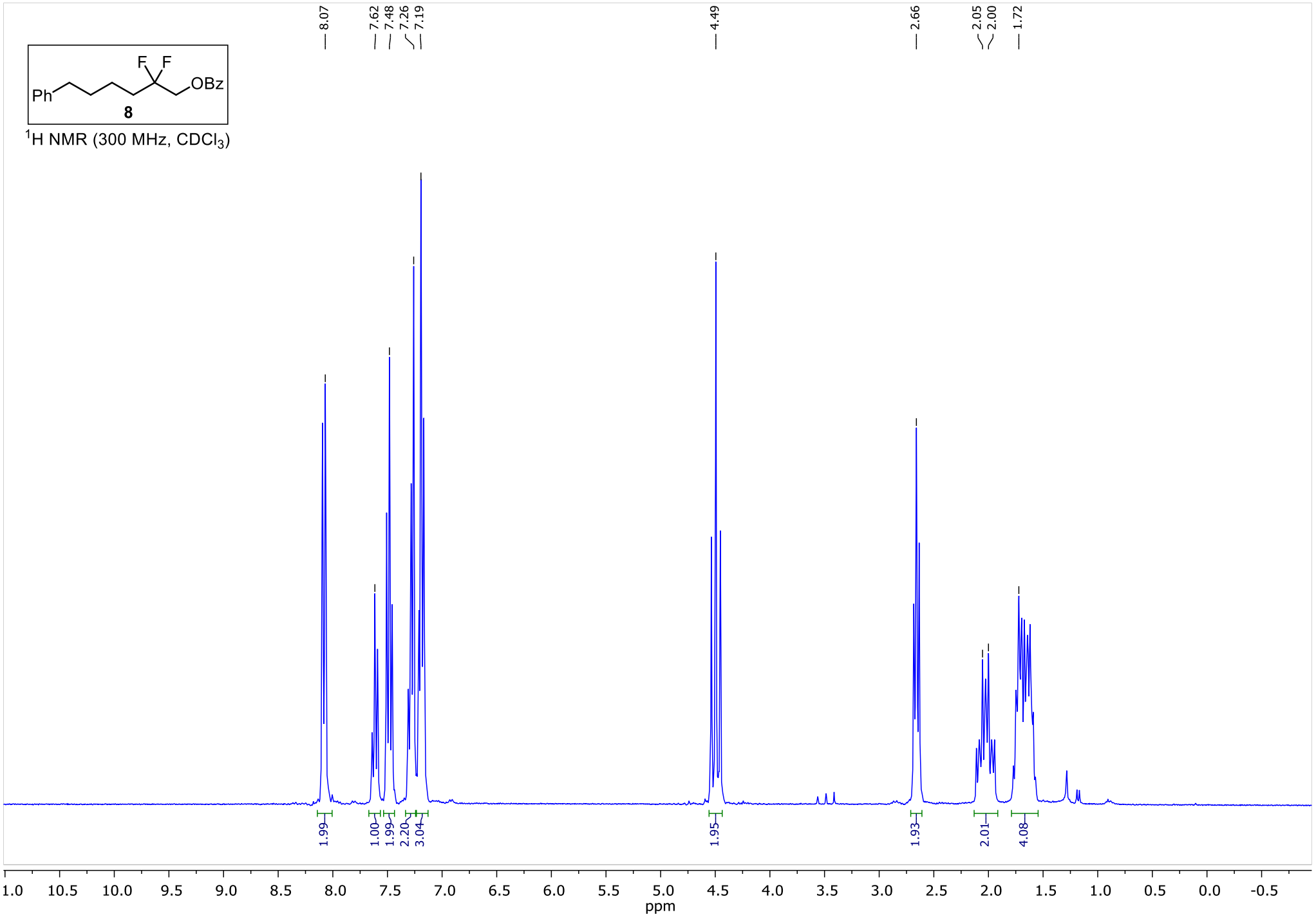
6

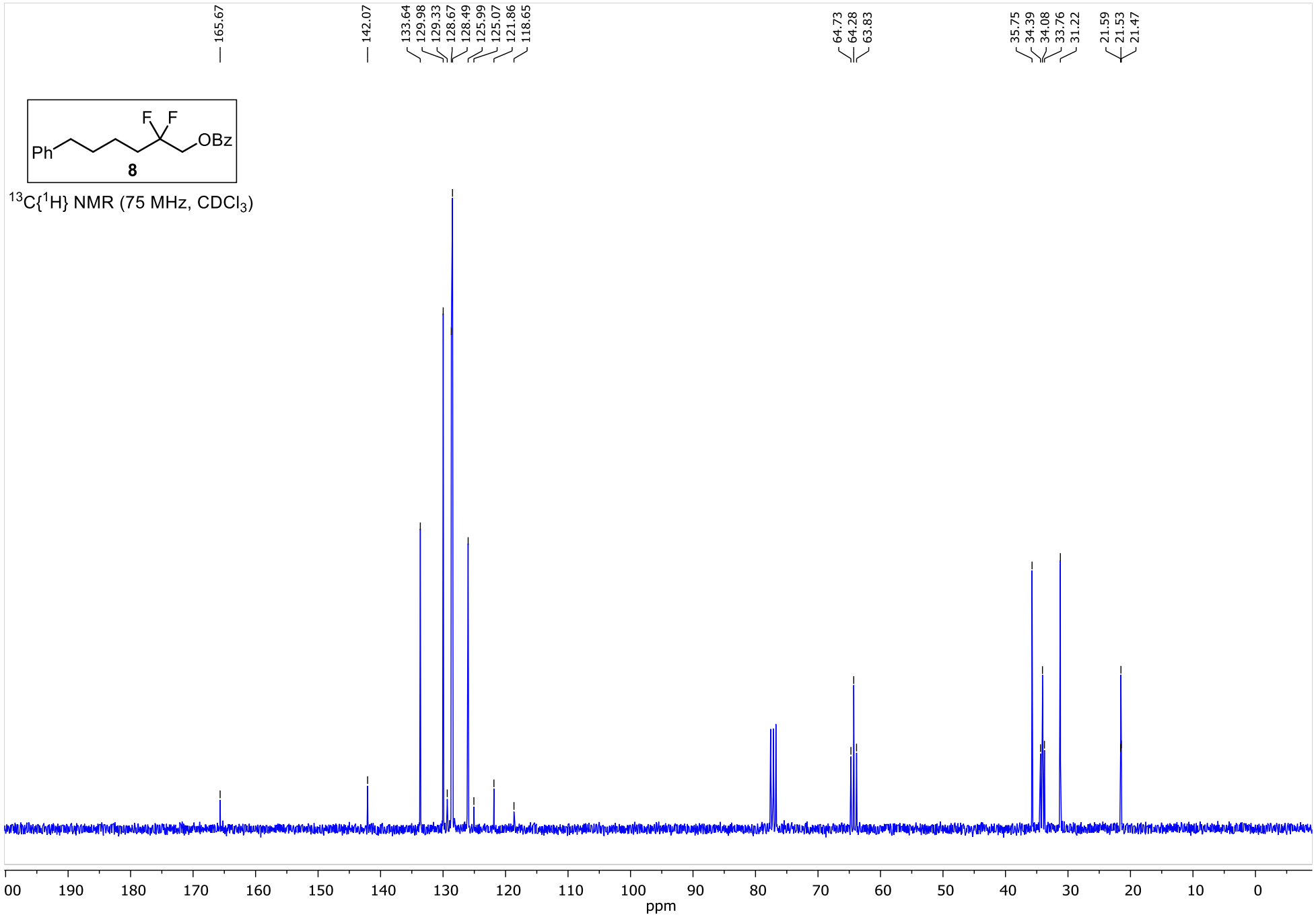
^{19}F NMR (282 MHz, $CDCl_3$)

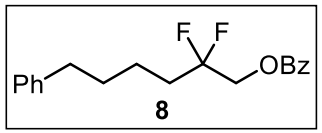

7
^{1}H NMR (300 MHz, $CDCl_3$)
7.34
7.26
3.73
3.58
2.71
2.27
2.22
1.98
1.88
1.78
1.66
2.06
3.02
2.00
2.06
2.05
2.26
4.04
4.05
ppm


162.62
162.22
161.82
142.04
128.28
128.20
125.65
122.42
119.08
115.73
77.59 CDCl3
77.16 CDCl3
76.74 CDCl3
47.21
46.53
46.45
46.36
35.55
34.38
34.07
33.76
31.04
26.41
26.39
26.36
23.15
21.23
21.17
21.11
O
N
F F
7
13C{1H} NMR (75 MHz, CDCl3)
ppm


-103.85
-103.92
-103.98
O
N
F F
7
^{19}F NMR (282 MHz, $CDCl_3$)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2
ppm

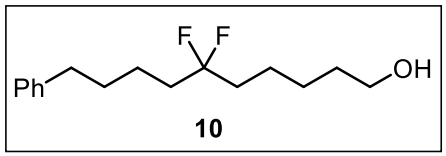

8.07
7.62
7.48
7.26
7.19
4.49
2.66
2.05
2.00
1.72
F
F
Ph
OBz
8
1H NMR (300 MHz, CDCl3)
1.99
1.00
1.99
2.20
3.04
1.95
1.93
2.01
4.08
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm


165.67
142.07
133.64
129.98
129.33
128.67
128.49
125.99
125.07
121.86
118.65
64.73
64.28
63.83
35.75
34.39
34.08
33.76
31.22
21.59
21.53
21.47
F
F
Ph
OBz
8
13C{1H} NMR (75 MHz, CDCl3)
ppm



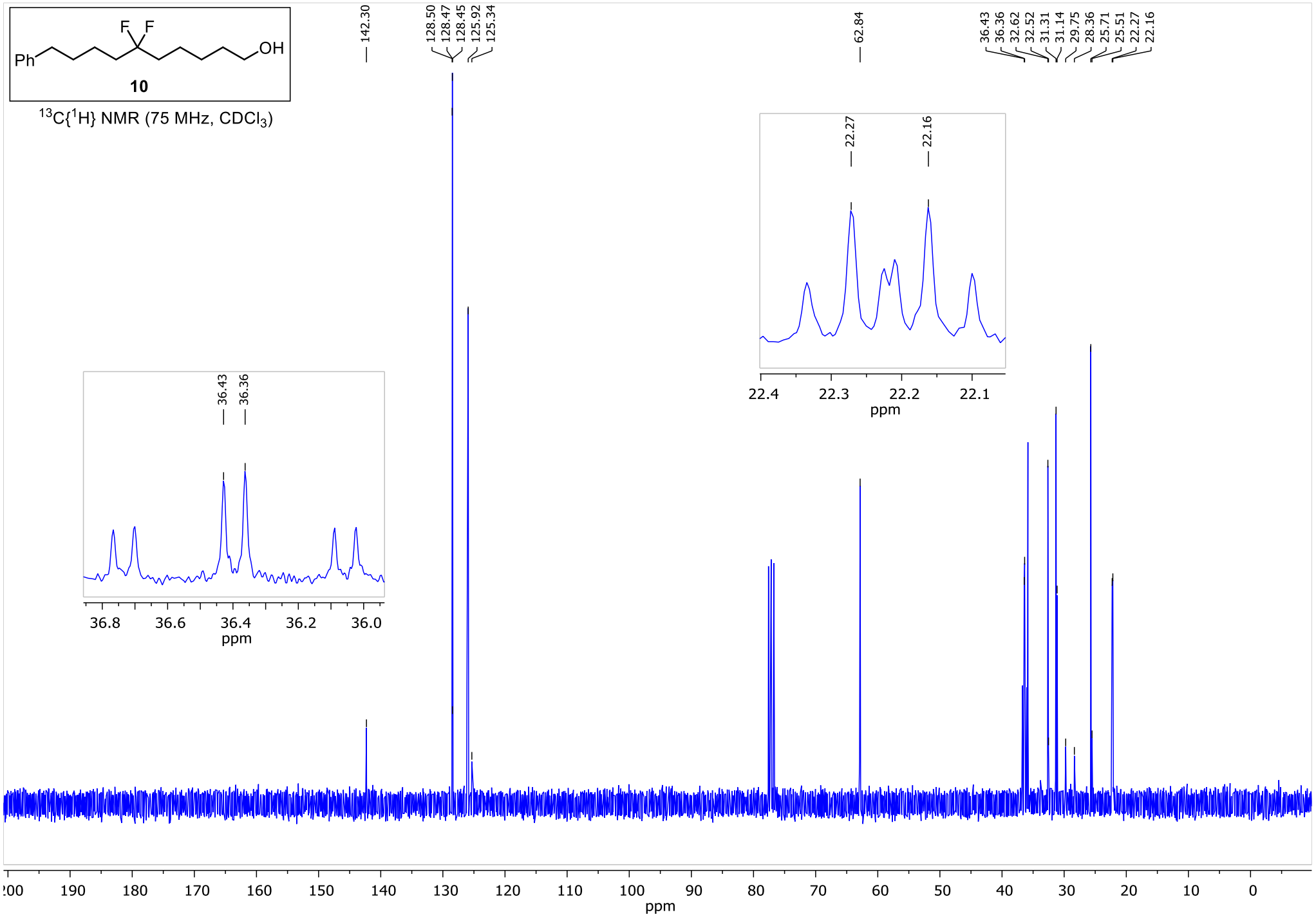
8

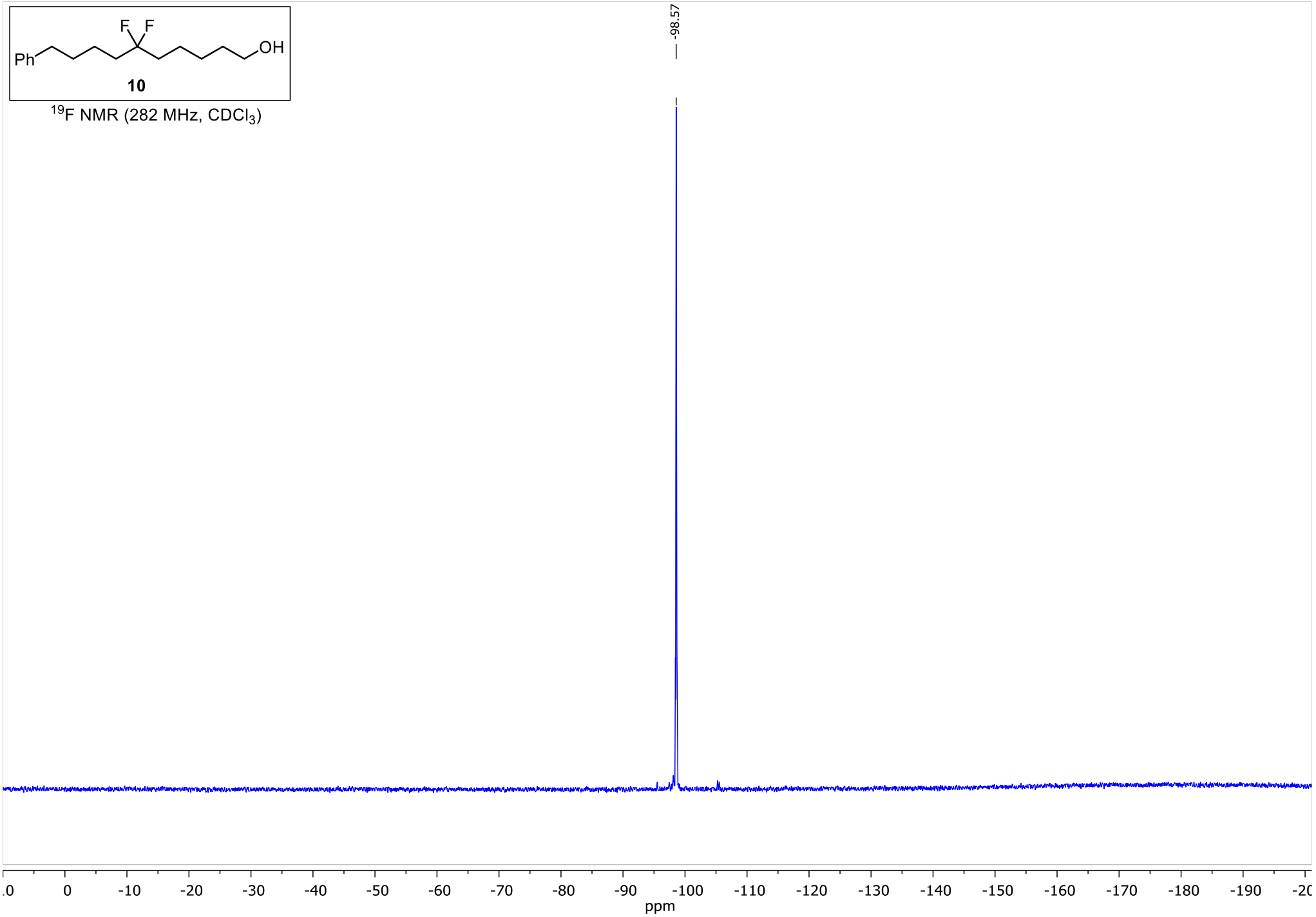
^{19}F NMR (282 MHz, $CDCl_3$)



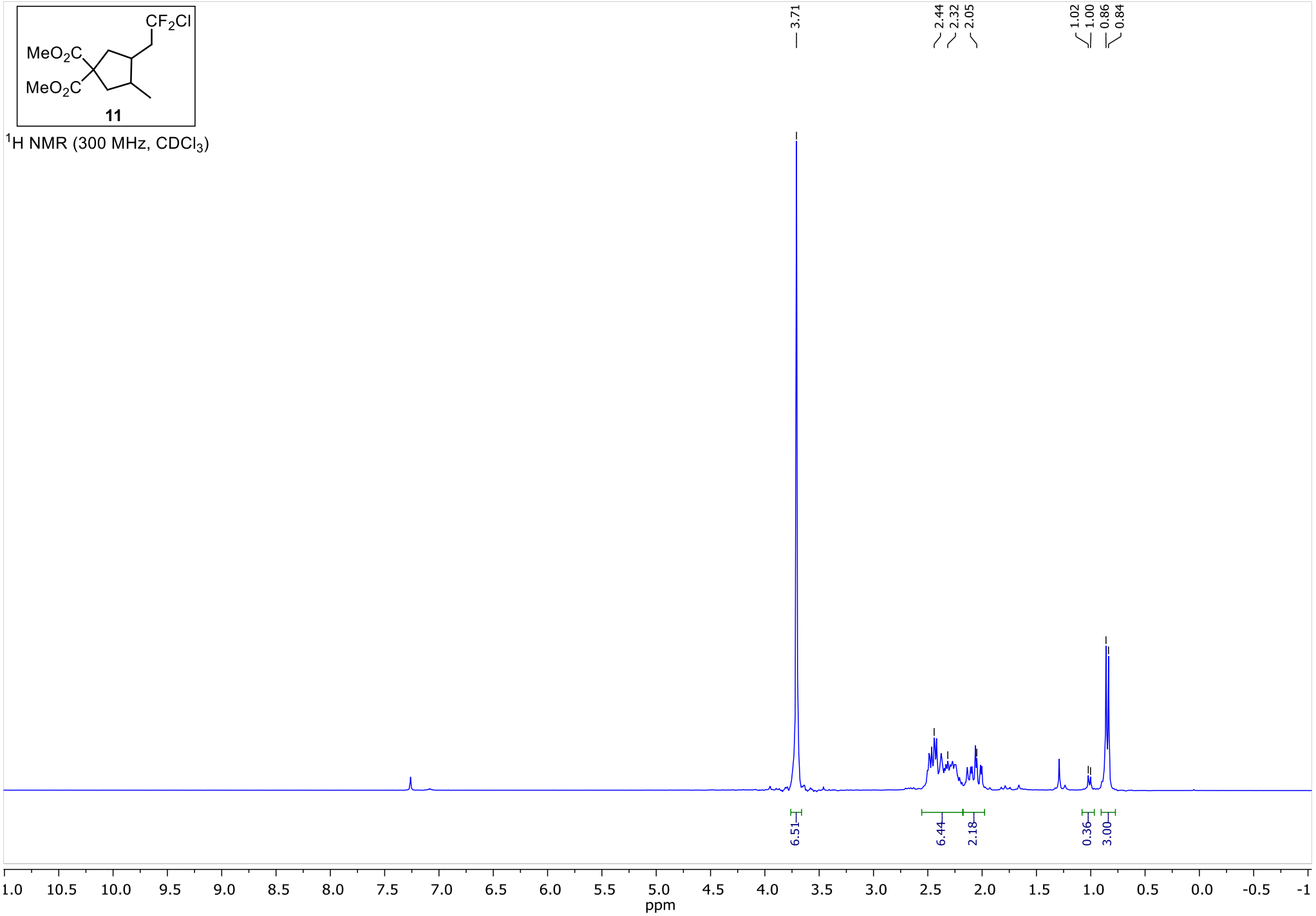
10

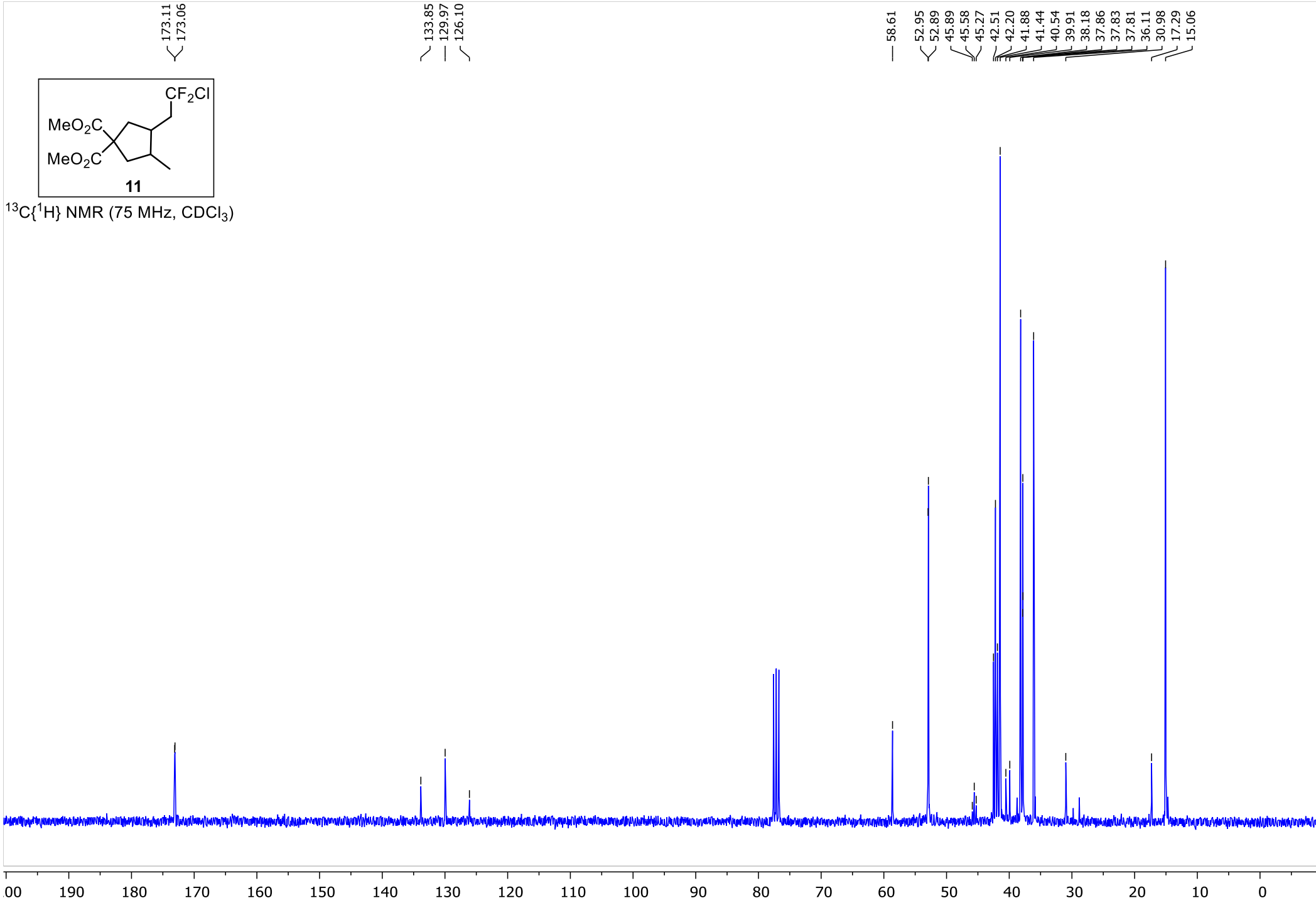
^{1}H NMR (300 MHz, $CDCl_3$)

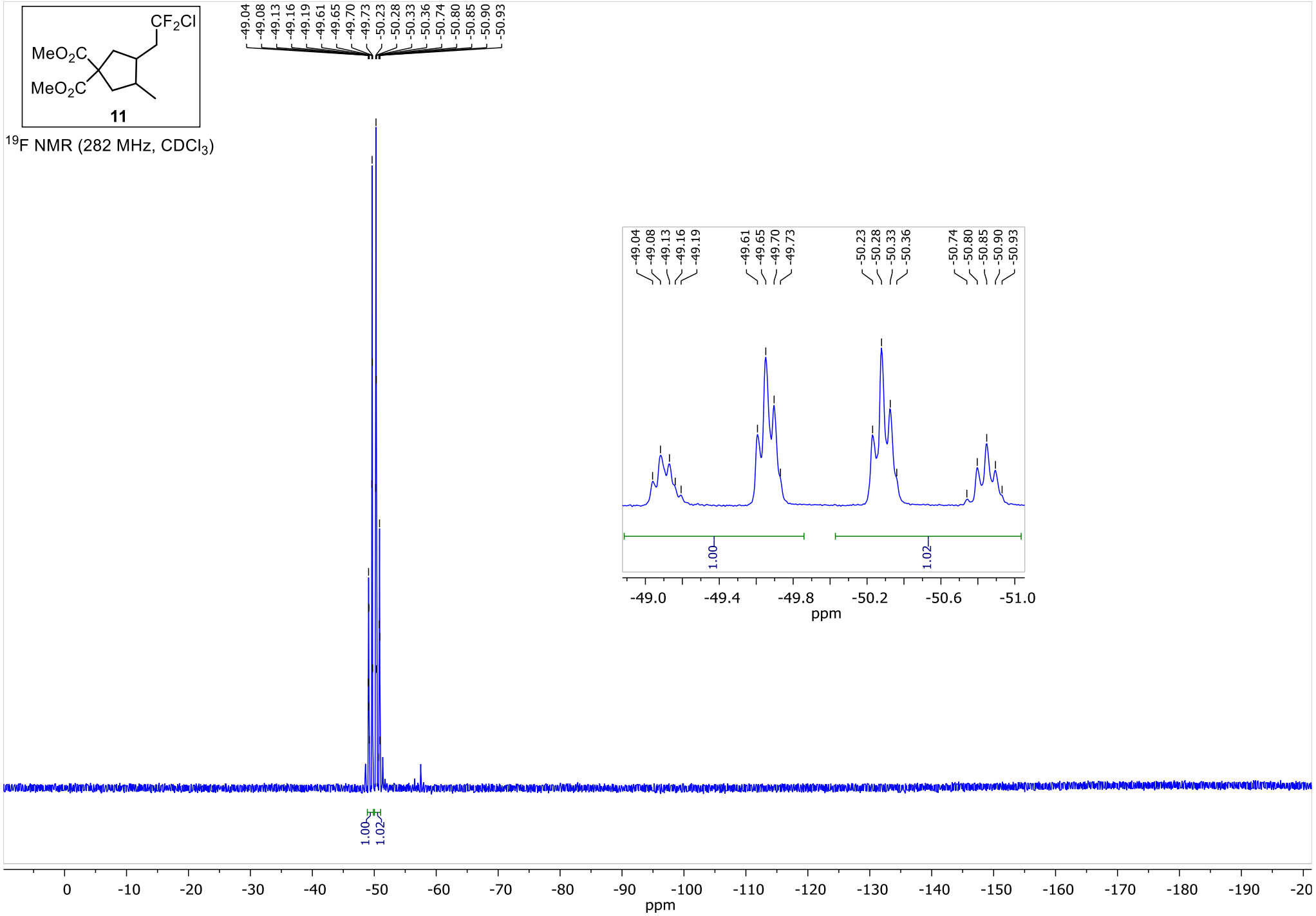

F F
Ph
OH
10
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
142.30
128.50
128.47
128.45
125.92
125.34
62.84
36.43
36.36
32.62
32.52
31.31
31.14
29.75
28.36
25.71
25.51
22.27
22.16
22.27
22.16
22.4
22.3
22.2
22.1
ppm
36.43
36.36
36.8
36.6
36.4
36.2
36.0
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

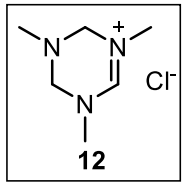


^{19}F NMR (282 MHz, $CDCl_3$)


CF2Cl
MeO2C
MeO2C
11
1H NMR (300 MHz, CDCl3)
3.71
2.44
2.32
2.05
1.02
1.00
0.86
0.84
6.51
6.44
2.18
0.36
3.00
ppm

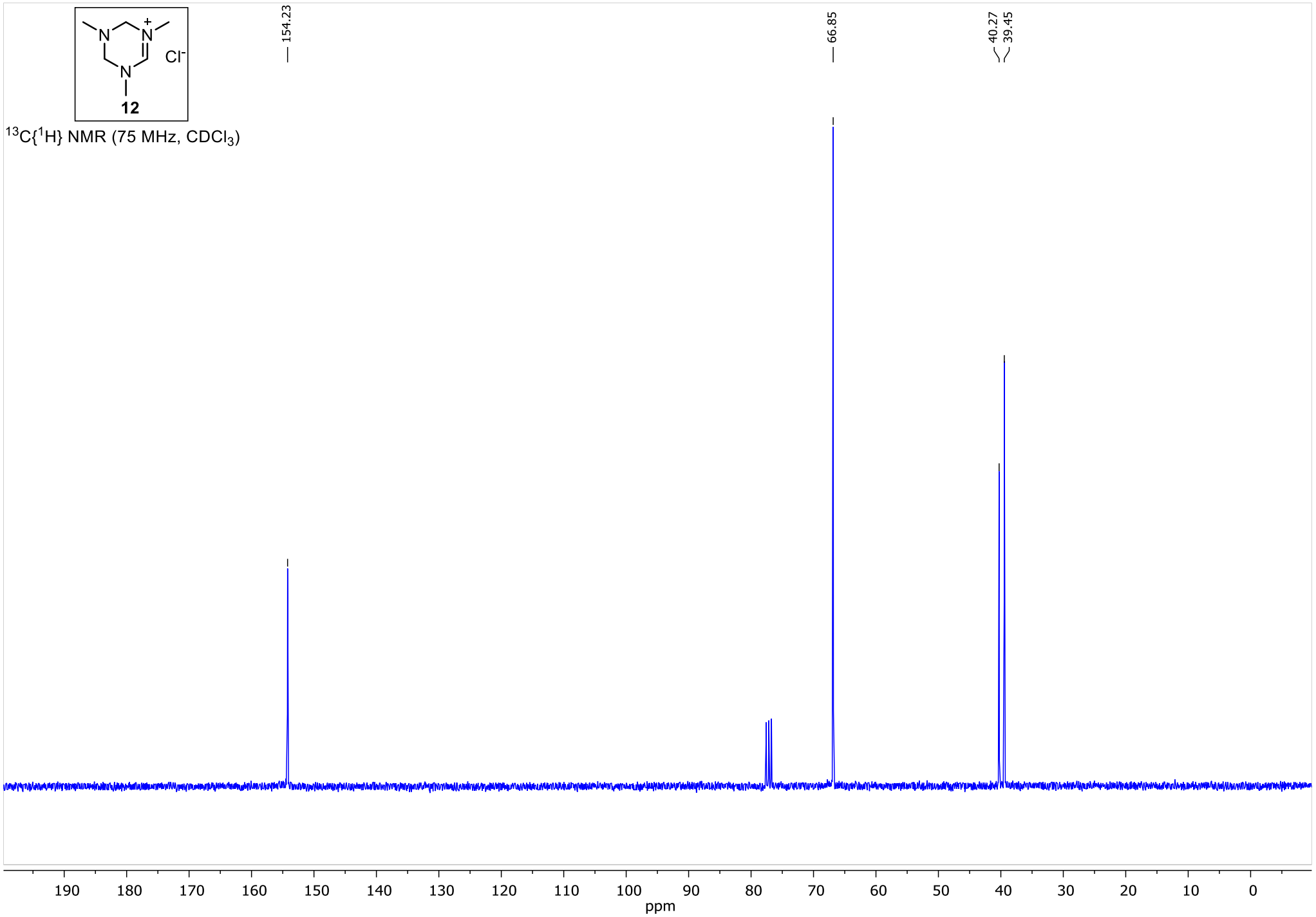

173.11
173.06
133.85
129.97
126.10
58.61
52.95
52.89
45.89
45.58
45.27
42.51
42.20
41.88
41.44
40.54
39.91
38.18
37.86
37.83
37.81
36.11
30.98
17.29
15.06
CF2Cl
MeO2C
MeO2C
11
13C{1H} NMR (75 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


CF2Cl
MeO2C
MeO2C
11
19F NMR (282 MHz, CDCl3)
-49.04
-49.08
-49.13
-49.16
-49.19
-49.61
-49.65
-49.70
-49.73
-50.23
-50.28
-50.33
-50.36
-50.74
-50.80
-50.85
-50.90
-50.93
1.00
1.02
-49.0
-49.4
-49.8
-50.2
-50.6
-51.0
ppm
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
ppm



12

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


154.23
66.85
40.27
39.45
12
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Crude product from the reaction of tetramethylethylene with ethyl 4-chloro-2,2,3,3-tetrafluoropropionate performed according to General procedure B.

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