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Synthesis of tetrafluorinated tetrahydroquinolines *via* photoredox catalysis

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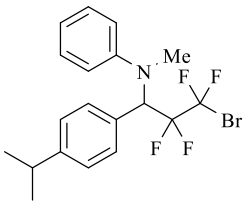
General. All reactions were performed under an argon atmosphere. Dichloromethane was distilled from P_2O_5. Dimethylformamide was distilled under vacuum from CaH_2 and stored over MS 4Å. Column chromatography was carried out employing silica gel (230-400 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or acidic aq. $KMnO_4$ solution. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and time-of-flight (TOF) mass analyzer. The measurements were done in a positive ion mode (interface capillary voltage – 4500 V) or in a negative ion mode (3200 V); mass range from m/z 50 to m/z 3000. For GC-MS analysis, Agilent DB-1MS column coupled with the electron impact ionization mass detector was used. Starting bromotetrafluoroethyl-substituted hydroxylamines and amine **1a** were obtained as reported [I. A. Dmitriev *et al*, *Adv. Synth. Cat.*, 2018, **360**, 3788].

Synthesis of amines 1b-e (General procedure). Benzoyl chloride (169 mg, 1.2 mmol) was added to a solution of bromotetrafluoroethyl-substituted hydroxylamine (1.0 mmol) and NEt_3 (152 mg, 1.5 mmol) in dry dichloromethane (2 ml). The reaction flask was immersed in 50 °C bath, and the mixture was stirred at this temperature for 4 hours. The mixture was cooled to room temperature, and then washed with brine (5 ml), and the aqueous phase was extracted with dichloromethane (3×2 ml). The combined organic phases were dried with $MgSO_4$, and the solvent was evaporated under vacuum. The residue was dissolved in dry THF (1 ml), and this solution was added to a mixture of phenylmagnesium chloride (1.0 ml of 2.0 *M* in THF, 2.0 mmol) and diethylaluminum chloride (2.3 ml of 1.1 *M* in toluene, 2.5 mmol) while cooling with ice/water bath. The cooling bath was removed, and the mixture was stirred overnight at room temperature. The mixture was carefully quenched by dropwise addition of sat. aqueous NH_4Cl (3 ml). The mixture was diluted with water (20 ml) and extracted with hexanes (3×20 ml). The combined organic phases were filtered through a pad of celite. The solvent was evaporated under vacuum, and the residue was purified by chromatography.

***N*-[3-Bromo-2,2,3,3-tetrafluoro-1-(4-isopropylphenyl)propyl]-*N*-methylaniline (1b).**



Yield 198 mg (47%). Chromatography: hexanes, R_f 0.18. Colourless oil.

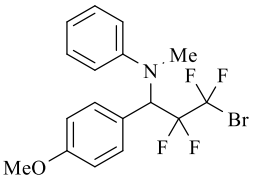
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.44-7.26 (m, 6H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.93 (t, *J* = 7.2 Hz, 1H), 5.80 (dd, *J* = 19.4, 11.6 Hz, 1H), 2.97 (sept, *J* = 6.9 Hz, 1H), 2.87 (s, 3H), 1.33 (d, *J* = 6.9 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.9, 149.3, 130.1 (d, *J* = 2.1 Hz), 129.4, 129.0 (t, *J* = 2.2 Hz), 126.7, 118.9, 114.4, 62.1 (dd, *J* = 26.7, 19.8), 33.9, 33.8, 24.0

^{19}F NMR (282 MHz, $CDCl_3$) δ: –62.8 (dd, *J* = 178.1, 4.8 Hz, 1F), -63.1 (dd, *J* = 178.1, 4.9 Hz, 1F), –105.0 (dd, *J* = 270.5, 10.8 Hz, 1F), –113.4 (ddd, *J* = 270.5, 19.3, 4.7 Hz, 1F).

HRMS (ESI): calcd for $C_{19}H_{21}{}^{79}BrF_4N$ (M+H) 418.0788 found 418.0787;
calcd for $C_{19}H_{21}{}^{81}BrF_4N$ (M+H) 420.0768 found 420.0768.

***N*-[3-Bromo-2,2,3,3-tetrafluoro-1-(4-methoxyphenyl)propyl]-*N*-methylaniline (1c).**



Chromatography (hexanes/EtOAc, 20:1, R_f 0.30) gave 241 mg of colourless oil containing an impurity. The product was dissolved in hexanes (10 ml) and washed with hydrochloric acid (6 ml sat. HCl and 10 ml water), the purity of organic phase was controlled by GC-MS analysis. Evaporation of the organic phase gave 188 mg of colourless oil (46%).

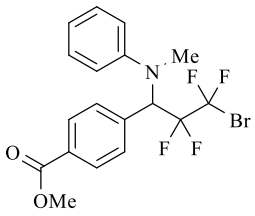
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39-7.32 (m, 4H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.93-6.89 (m, 3H), 5.72 (dd, *J* = 18.5, 12.7 Hz, 1H), 3.83 (s, 3H), 2.83 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.7, 149.2, 130.4, 129.4, 124.6, 119.1, 114.6, 114.0, 62.2 (dd, *J* = 26.3, 18,9), 55.3, 33.7.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –61.8 (dd, *J* = 177.6, 5.1 Hz, 1F), –62.1 (dd, *J* = 177.6, 5.3 Hz, 1F), –105.3 (ddd, *J* = 270.0, 12.3, 5.0 Hz, 1F), -112.1 (ddd, *J* = 270.0, 18.4, 5.0 Hz, 1F).

HRMS (ESI): calcd for $C_{17}H_{17}{}^{79}BrF_4NO$ (M+H) 406.0424 found 406.0415.
calcd for $C_{17}H_{17}{}^{81}BrF_4NO$ (M+H) 408.0404 found 408.0397.

Methyl 4-{3-bromo-2,2,3,3-tetrafluoro-1-[methyl(phenyl)amino]propyl}benzoate (1d)



Chromatography (hexanes/EtOAc, 10:1, R_f 0.28) gave 163 mg of colourless oil containing an impurity. The product was dissolved in hexanes (10 ml) and washed with hydrochloric acid (4 ml sat. HCl and 10 ml water), the purity of organic phase was controlled by GC-MS analysis. Evaporation of the organic phase gave 132 mg of colourless oil (30%).

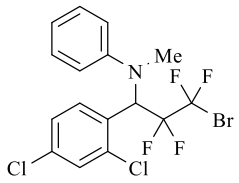
^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.31 (dd, *J* = 8.8, 7.4 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.90 (t, *J* = 7.3 Hz, 1H), 5.77 (dd, *J* = 19.4, 10.5 Hz, 1H), 3.93 (s, 3H), 2.77 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.5, 149.5, 137.5 (d, *J* = 2.3 Hz), 130.4, 130.1, 129.9, 129.5, 128.9 (t, *J* = 2.5 Hz), 128.4, 119.5, 114.7, 62.3 (dd, *J* = 27.2, 20.1), 52.3, 33.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –62.2 (dd, *J* = 179.0, 6.5 Hz, 1F), –62.7 (dd, *J* = 179.0 5.9 Hz, 1F), –104.0 (ddd, *J* = 271.5, 10.6, 5.8 Hz, 1F), –112.9 (ddd, *J* = 271.5, 19.2, 6.0 Hz, 1F).

HRMS (ESI): calcd for $C_{18}H_{17}{}^{79}BrF_4NO_2$ (M+H) 434.0373 found 434.0369.
calcd for $C_{18}H_{17}{}^{81}BrF_4NO_2$ (M+H) 436.0354 found 436.0354.

***N*-[3-Bromo-1-(2,4-dichlorophenyl)-2,2,3,3-tetrafluoropropyl]-*N*-methylaniline (1e)**



Yield 165 mg (37%). Chromatography: hexanes, R_f 0.23. Colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.74 (d, *J* = 8.6 Hz, 1H), 7.49 (d, *J* = 2.2 Hz, 1H), 7.37-7.31 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.26 (dd, *J* = 16.5, 14.1 Hz, 1H), 2.91 (s, 3H).

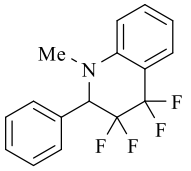
^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.6, 136.4, 135.4, 131.7, 130.3, 129.2, 126.9, 119.6, 115.1, 58.4 (dd, *J* = 23.4, 21.6), 34.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –62.0 (m, 2F), –108.1 (dd, *J* = 270.8, 13.9 Hz, 1F), –109.5 (d, *J* = 270.8, 16.8 Hz, 1F).

HRMS (ESI): calcd for $C_{16}H_{13}{}^{79}BrCl_2F_4NO$ (M+H) 443.9539 found 443.9522.
calcd for $C_{16}H_{13}{}^{81}BrCl_2F_4NO$ (M+H) 445.9518 found 445.9506.

Synthesis of compounds 2 (General procedure). Substrate **1** (0.30 mmol), *fac*-Ir(ppy)$_3$ (1.0 mg, 1.5 μmol) and sodium carbonate (38 mg, 0.37 mmol) were placed in a test tube. The tube was evacuated and filled with argon, DMF (1.5 ml) was added, and the tube was closed tightly with a screw-cap. The reaction mixture was irradiated for 24 hours by a strip of light emitting diodes (2835-120LED 1M-Blue, 12V); during the irradiation the mixture was cooled with water to maintain temperature around 23-25 °C. The mixture was then poured into water (10 ml) and extracted with hexanes (5×4 ml). The combined organic phases were dried with Na_2SO_4, concentrated under vacuum, and the residue was purified by chromatography.

3,3,4,4-Tetrafluoro-1-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2a).



Yield 65 mg (73%). Colourless oil. Chromatography (EtOAc/hexanes 1:7, R_f 0.33).

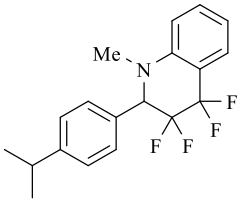
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 7.8 Hz, 1H), 7.50-7.36 (m, 6H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 4.72 (dt, *J* = 19.2, 8.3 Hz, 1H), 2.85 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 145.8 (dd, *J* = 5.8, 4.3 Hz), 133.1, 132.1, 129.5, 129.3, 128.7, 126.2 (dd, *J* =5.1, 2.5 Hz), 118.2 (d, *J* = 1.8 Hz), 116.2-115.2 (m), 114.4 (td, *J* = 23.5, 1.4 Hz), 113.0, 112.8-111.9 (m), 109.1 (ddd, *J* = 31.6, 22.7, 6.8 Hz), 66.5 (dd, *J* = 26.8, 22.1 Hz), 37.7.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –96.7 (dm, *J* = 265.1 Hz, 1F), –120.9 (dm, *J* = 265.1 Hz, 1F), –124.1 (dm, *J* = 253.7 Hz), –128.8 (d, *J* = 253.7 Hz, 1F).

HRMS (ESI): calcd for $C_{16}H_{14}F_4N$ (M+H) 296.1057 found 296.1052.

3,3,4,4-Tetrafluoro-2-(4-isopropylphenyl)-1-methyl-1,2,3,4-tetrahydroquinoline (2b).



Yield 68 mg (67%). Chromatography: hexanes/EtOAc, 20:1, R_f 0.28. Colourless oil.

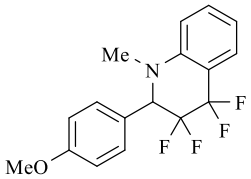
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.65 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.50-7.44 (m, 1H), 7.35-7.28 (m, 4H),6.93 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.71 (dt, *J* = 19.6, 8.4 Hz, 1H), 2.97 (sept, *J* = 6.9 Hz, 1H), 2.86 (s, 3H), 1.32 (s, 3H), 1.28 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.1, 145.9 (dd, *J* = 5.9, 4.2 Hz), 133.0 (dd, *J* = 2.5, 1.4 Hz), 129.5 (d, *J* = 1.5 Hz), 129.3, 126.8, 126.2 (d, *J* = 5.5 Hz), 118.0 (d, *J* = 1.7 Hz), 114.4 (td, *J* = 23.3, 1.6 Hz), 113.0, 66.2 (ddd, *J* = 26.9, 22.0, 1.2 Hz), 37.6, 34.0, 24.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –95.9 (ddd, *J* = 263.7 Hz, 19.7, 7.4, 1F), –121.2 (ddd, *J* = 263.9, 18.3, 8.7 Hz, 1F), –124.2 (ddt, *J* = 253.1, 19.7, 8.7 Hz), –128.7 (dt, *J* = 253.0, 19.1 Hz, 1F).

HRMS (ESI): calcd for $C_{19}H_{20}F_4N$ (M+H) 338.1526 found 338.1520.

3,3,4,4-Tetrafluoro-2-(4-methoxyphenyl)-1-methyl-1,2,3,4-tetrahydroquinoline (2c).



Yield 46 mg (47%). Chromatography: hexanes/EtOAc, 5:1, R_f 0.38.

Colourless crystals. Mp 112-115 °C.

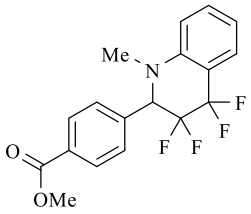
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.97-6.83 (m, 4H), 4.66 (dt, *J* = 19.8, 8.3 Hz, 1H), 3.83 (s, 3H), 2.83 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.4, 145.8 (dd, *J* = 6.1, 4.2 Hz), 133.0 (dd, *J* = 2.5, 1.3 Hz), 130.7(d, *J* = 1.6 Hz), 126.2 (dd, *J* = 5.1, 2.1 Hz), 123.8, 118.1 (d, *J* = 1.7 Hz), 114.1, 113.1, 65.8 (ddd, *J* = 26.9, 22.0, 1.3 Hz), 55.4, 37.4.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –95.4 (ddd, *J* = 264.1 Hz, 19.5, 6.7, 1F), –121.8 (ddd, *J* = 263.7, 17.5, 8.0 Hz, 1F), –124.6 (dtd, *J* = 253.2, 19.8, 8.8 Hz), –128.9 (dt, *J* = 253.0, 19.2 Hz, 1F).

HRMS (ESI): calcd for $C_{17}H_{16}F_4NO$ (M+H) 326.1163 found 326.1168.

Methyl 4-(3,3,4,4-tetrafluoro-1-methyl-1,2,3,4-tetrahydroquinolin-2-yl)benzoate (2d)



Yield 45 mg (42%). Chromatography: hexanes/EtOAc, 4:1, R_f 0.28.

Colourless crystals. Mp 119-120 °C.

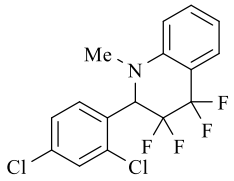
^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.50-7.43 (m, 3H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 4.77 (dt, *J* = 18.3, 8.4 Hz, 1H), 3.93 (s, 3H), 2.84 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.1, 144.9 (dd, *J* = 6.0, 4.4 Hz), 136.7, 132.6 (dd, *J* = 2.3, 1.5 Hz), 130.6, 129.3, 128.9 (d, *J* = 1.6 Hz), 125.7 (dd, *J* = 5.0, 2.5 Hz), 117.9 (d, *J* = 1.6 Hz), 112.5, 65.7 (ddd, *J* = 26.9, 22.2, 1.0 Hz), 51.8, 37.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –98.0 (ddd, *J* = 265.4 Hz, 18.3, 6.0, 1F), –119.7 (ddd, *J* = 265.0, 18.2, 7.3 Hz, 1F), –123.4 (ddt, *J* = 253.6, 19.7, 8.6 Hz), –128.9 (dt, *J* = 254.0, 18.3 Hz, 1F).

HRMS (ESI): calcd for $C_{18}H_{16}F_4NO_2$ (M+H) 354.1112 found 354.1108.

2-(2,4-Dichlorophenyl)-3,3,4,4-tetrafluoro-1-methyl-1,2,3,4-tetrahydroquinoline (2e)



Yield 69 mg (63%). Chromatography: hexanes/EtOAc, 7:1, R_f 0.36.

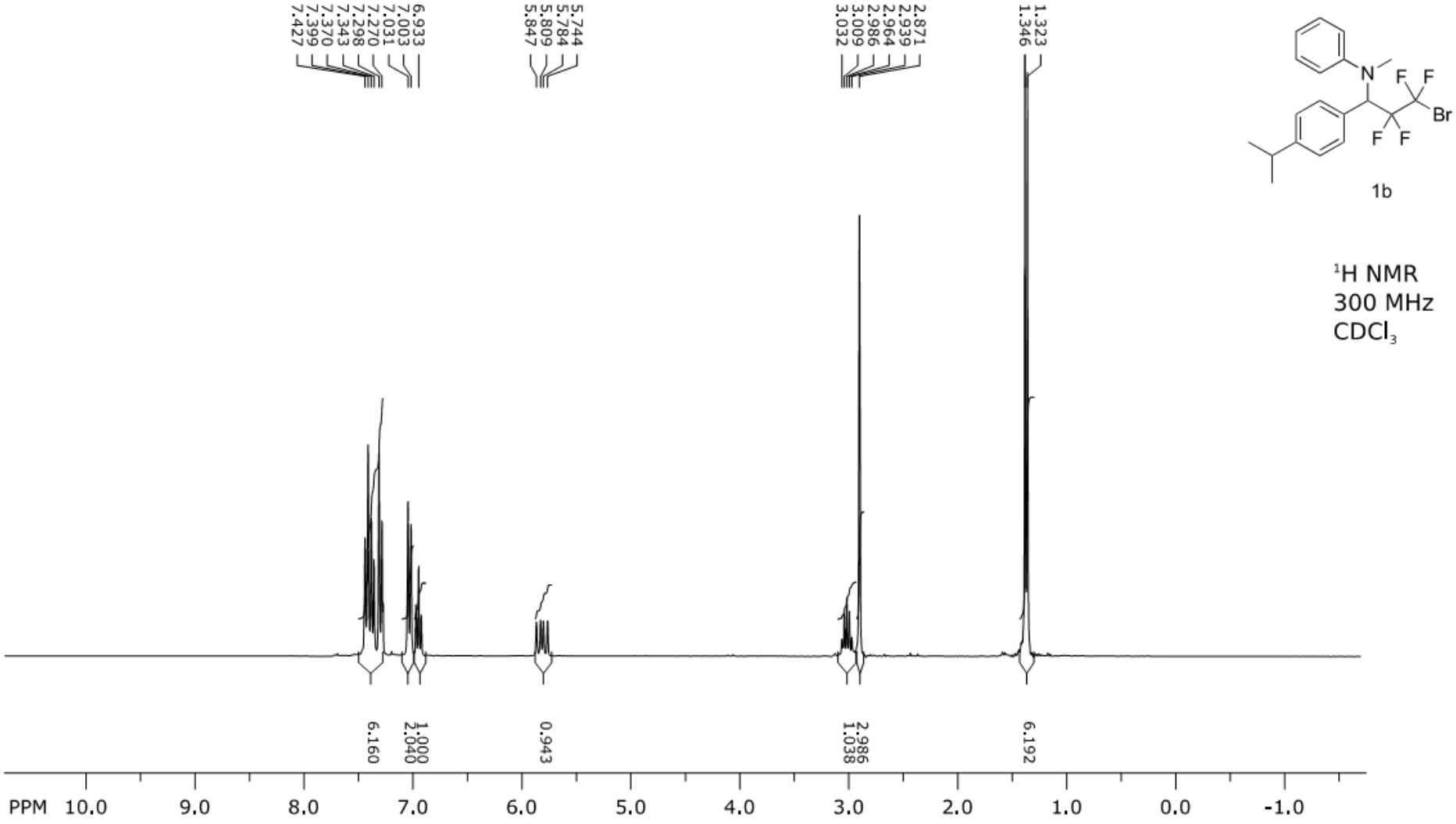
Colourless crystals. Mp 104-106°C.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.66 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 8.5, 1.7 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 5.42 (dt, *J* = 17.9, 8.0 Hz, 1H), 2.80 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 145.6 (dd, *J* = 5.9, 4.4 Hz), 136.5, 135.9, 133.2 (dd, *J* = 2.4, 1.4 Hz), 131.5 (dd, *J* = 3.0, 1.4 Hz), 130.0, 128.8 (t, *J* = 2.7 Hz), 127.6, 126.3 (dd, *J* = 5.2, 2.6 Hz), 118.7 (d, *J* = 1.7 Hz), 113.3, 61.7 (ddd, *J* = 28.0, 21.8, 1.2 Hz), 37.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –97.8 (ddd, *J* = 264.6 Hz, 19.1, 5.0, 1F), –120.2 (dd, *J* = 264.1, 11.5 Hz, 1F), –124.6 (ddt, *J* = 255.2, 19.2, 8.2 Hz), –128.9 (dt, *J* = 255.0, 18.0 Hz, 1F).

HRMS (ESI): calcd for $C_{16}H_{12}Cl_2F_4N$ (M+H) 364.0277 found 364.0268.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3.009
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1.000
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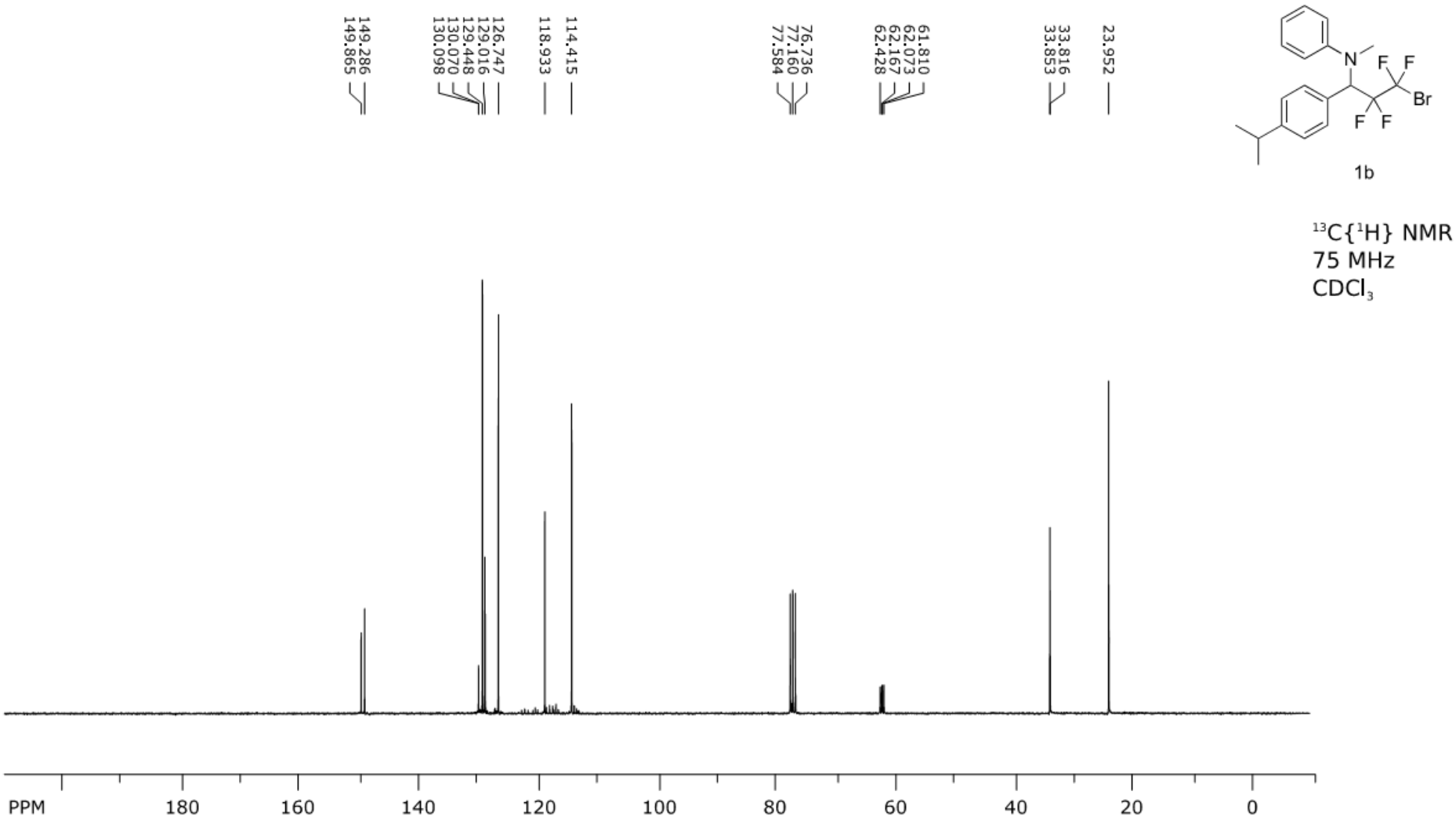
2.986
1.038
6.192
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
N
F F
Br
F F
1b
^{1}H NMR
300 MHz
$CDCl_3$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61.810
62.073
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33.816
33.853
23.952
N
F
F
Br
F
F
1b
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140
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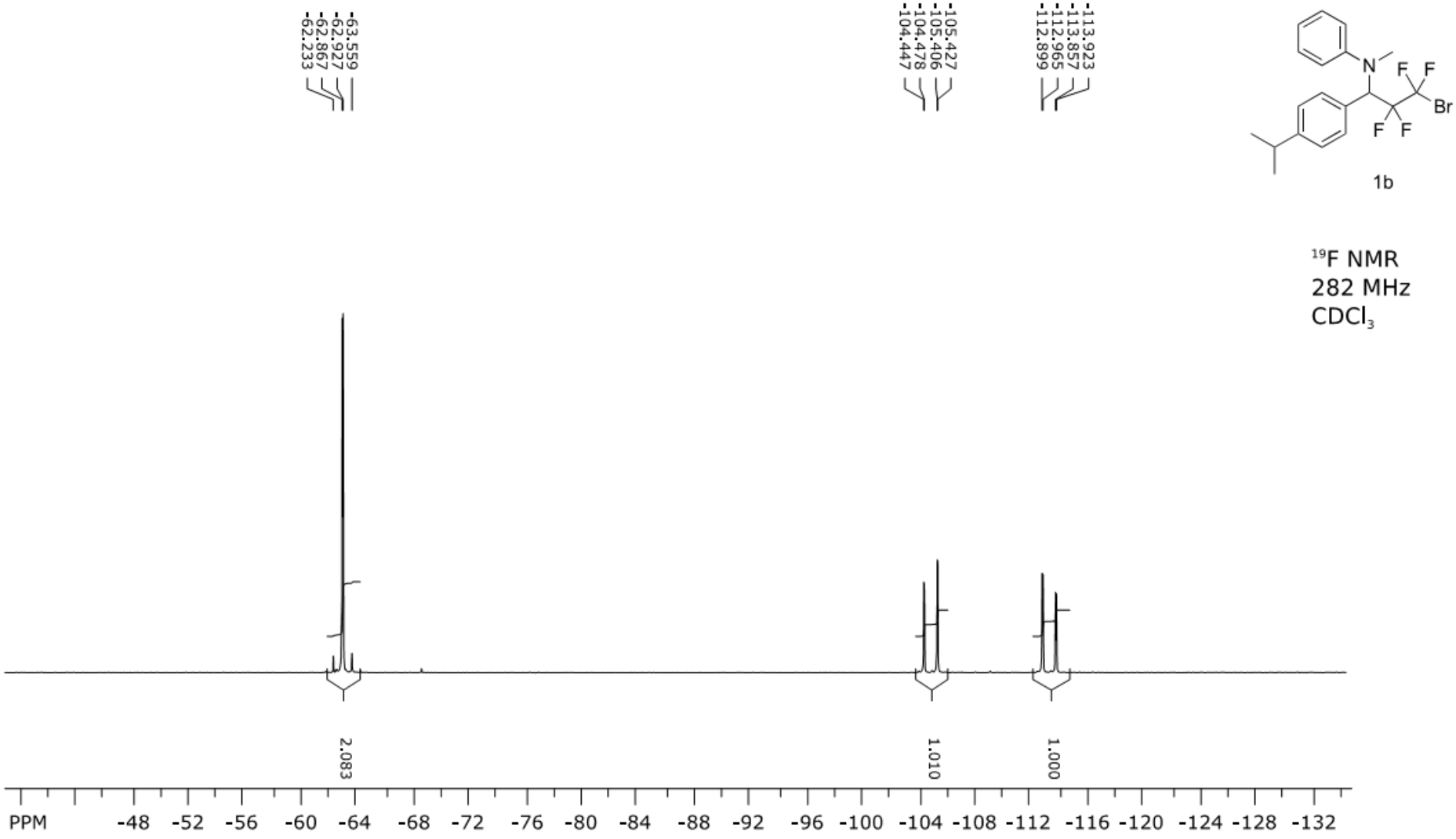
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F
F
F
F
Br
1b
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282 MHz
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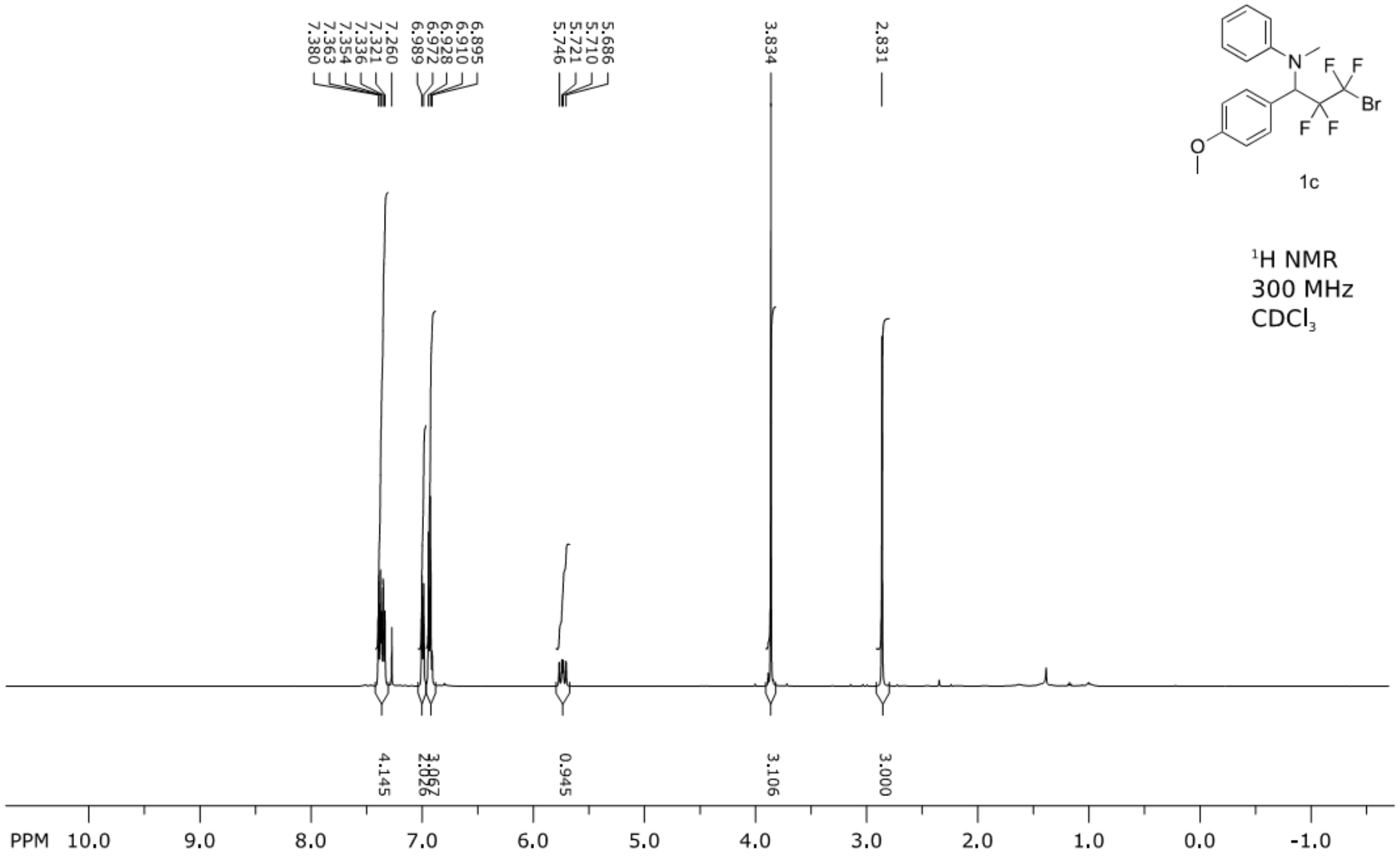
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7.321
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6.910
6.895
5.746
5.721
5.710
5.686
3.834
2.831
N
F
F
Br
F
F
O
1c
^{1}H NMR
300 MHz
$CDCl_3$
4.145
2.026
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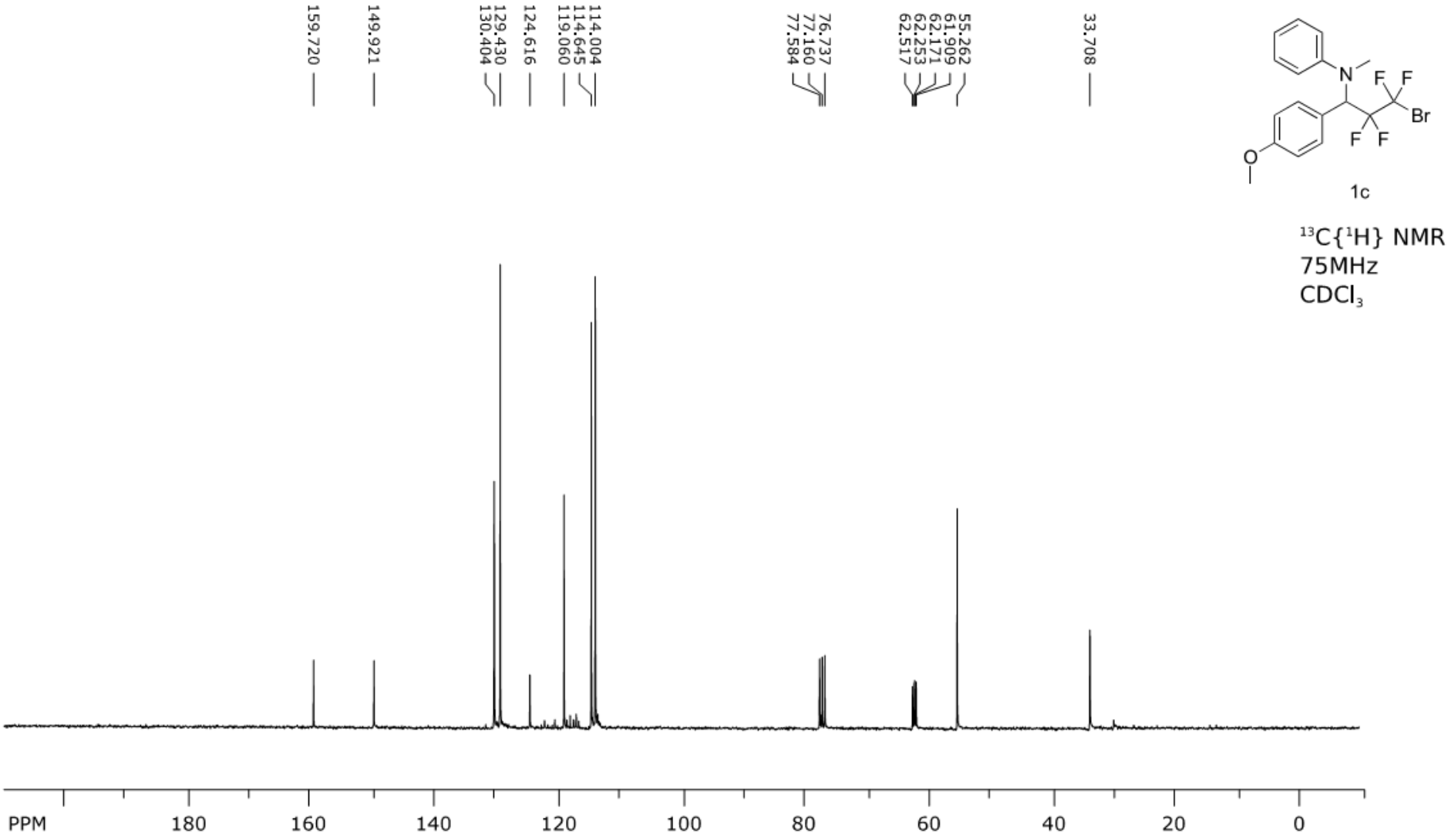
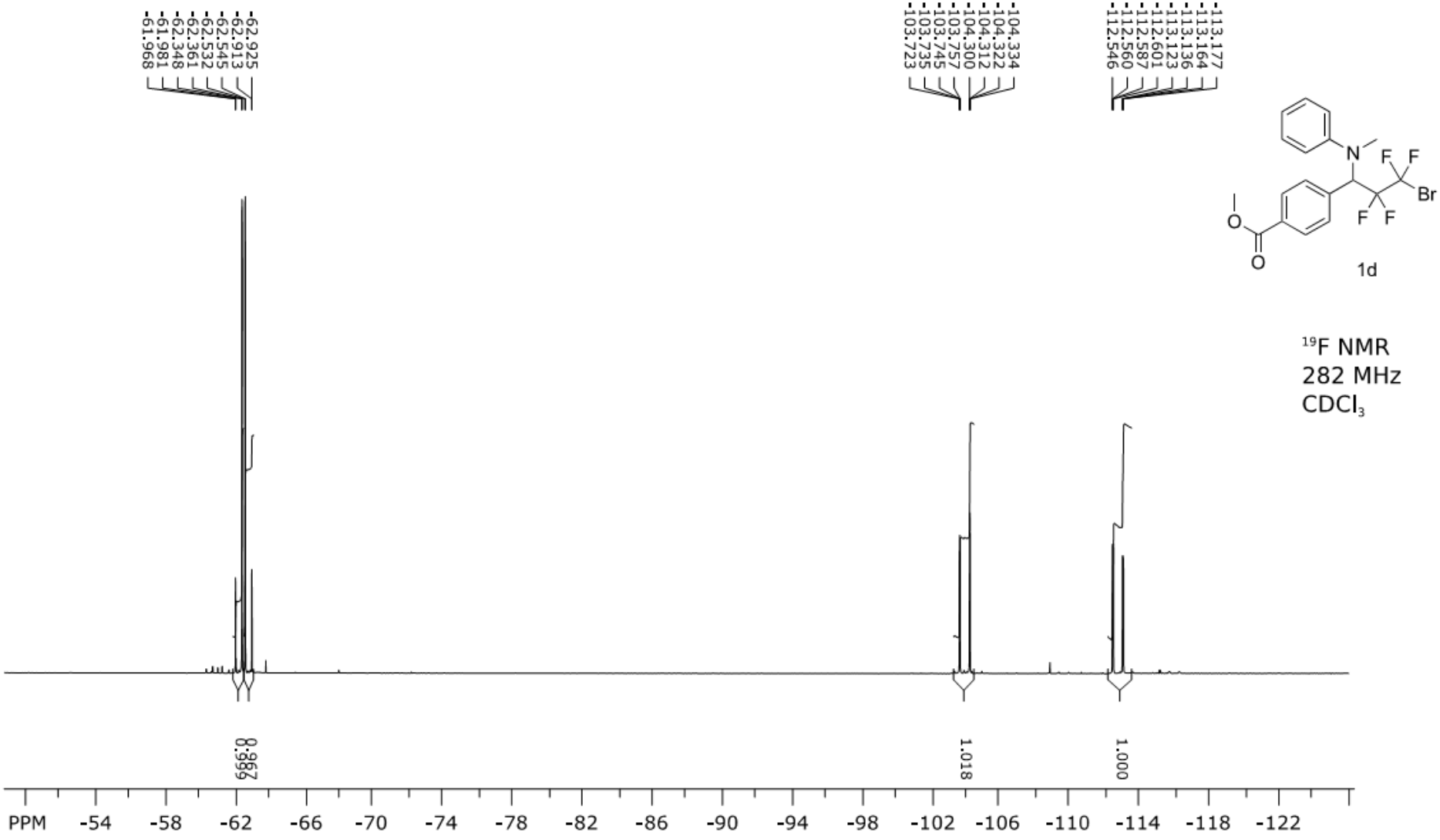
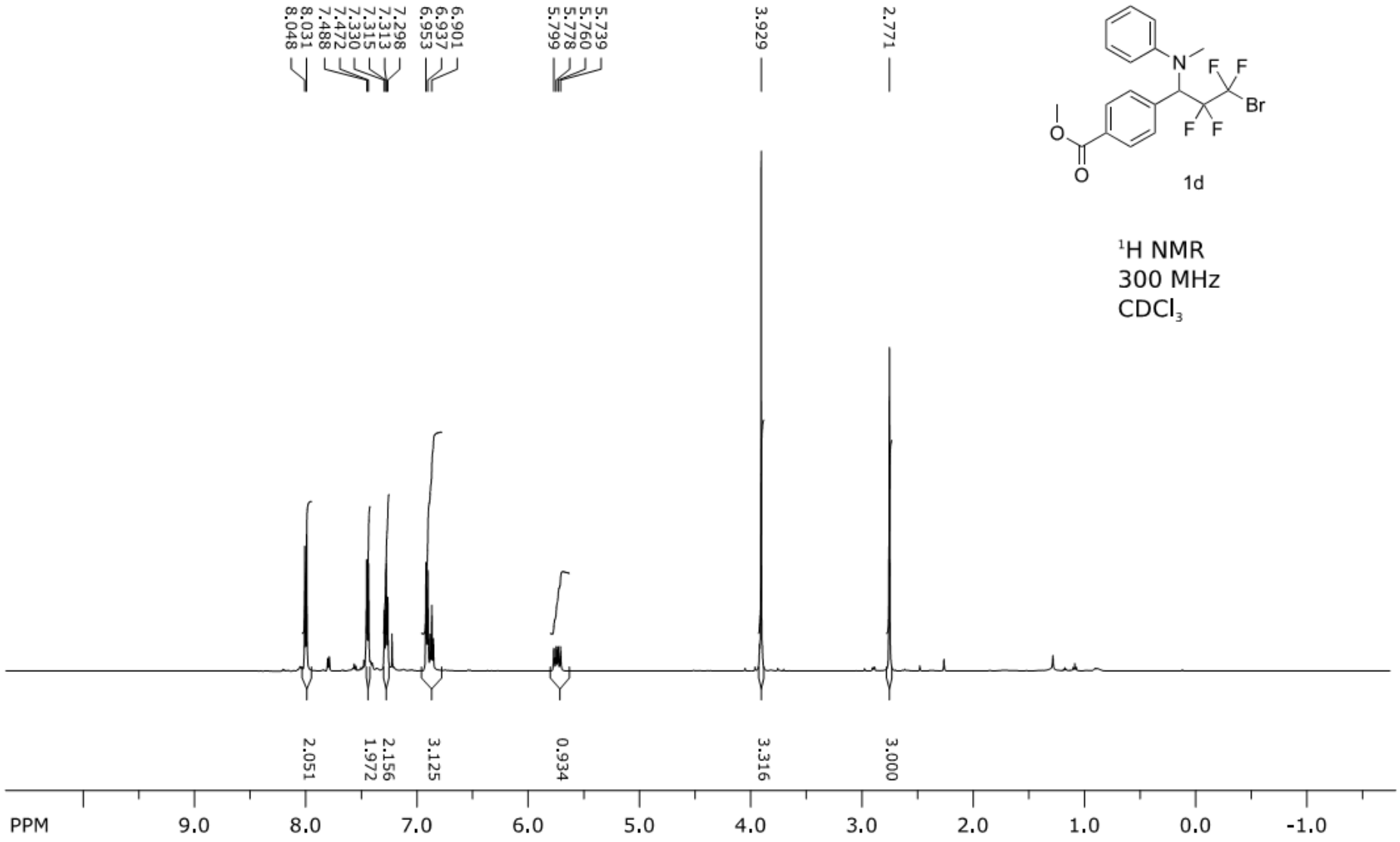
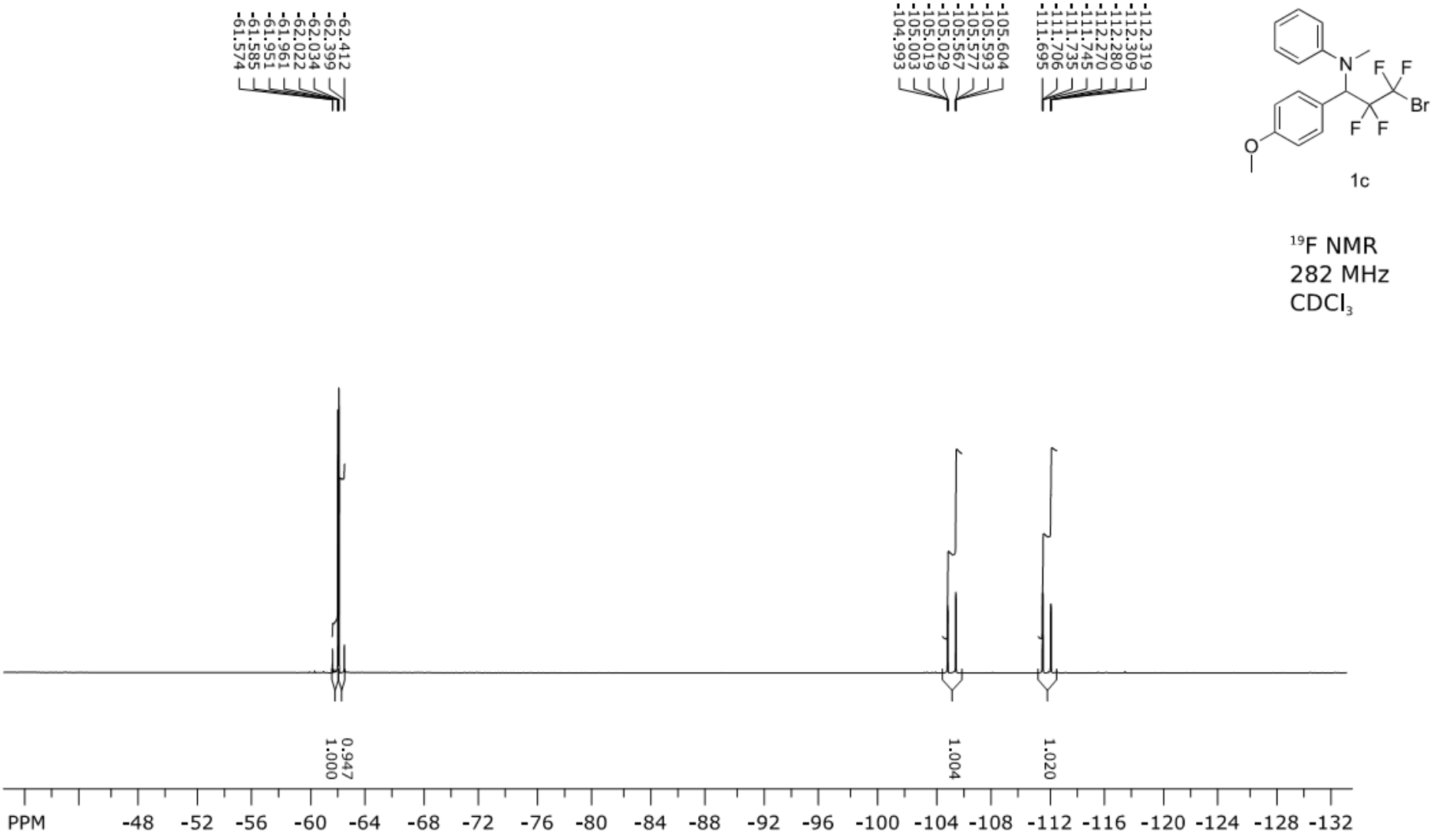
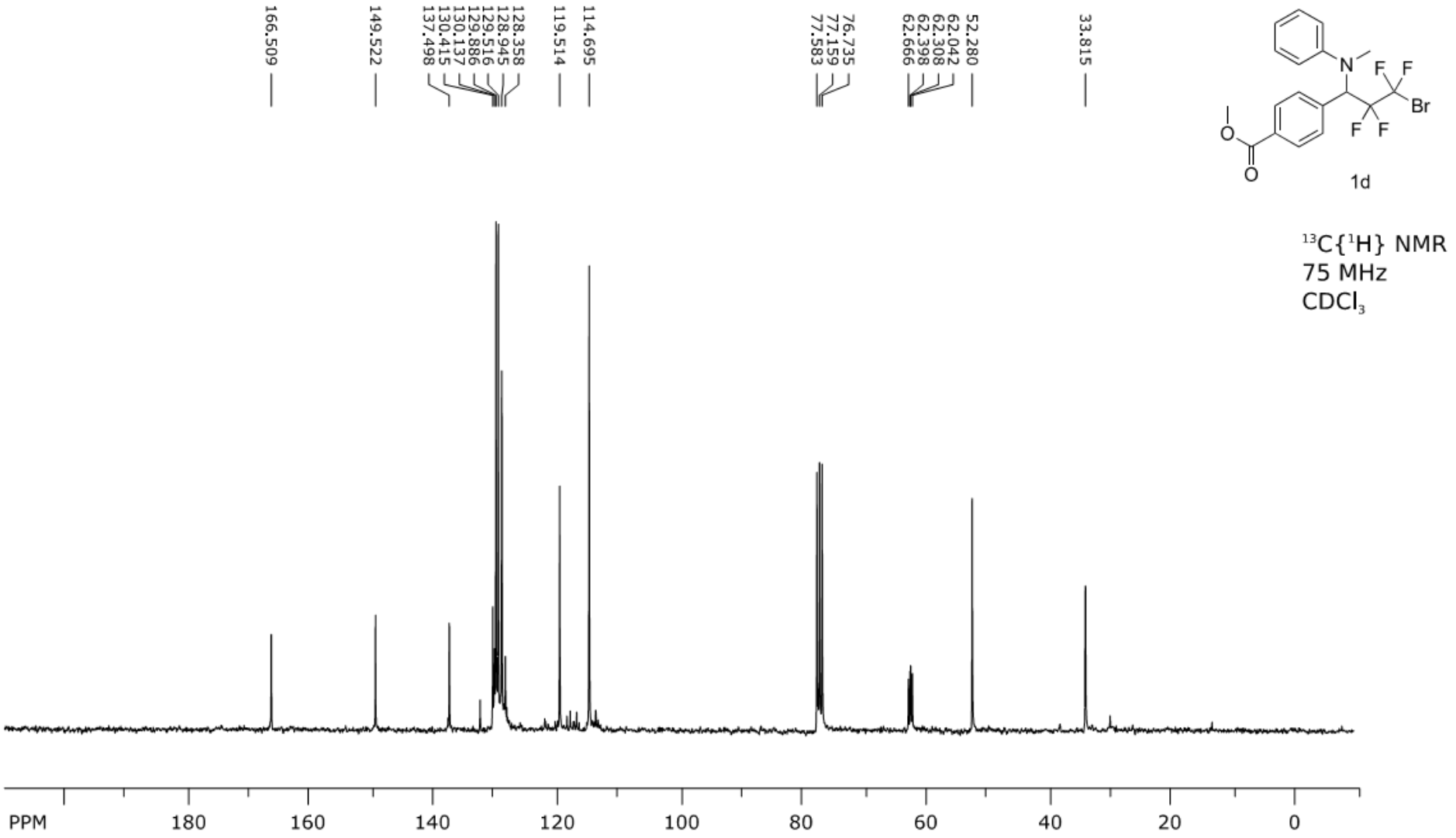
3.106
3.000
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0

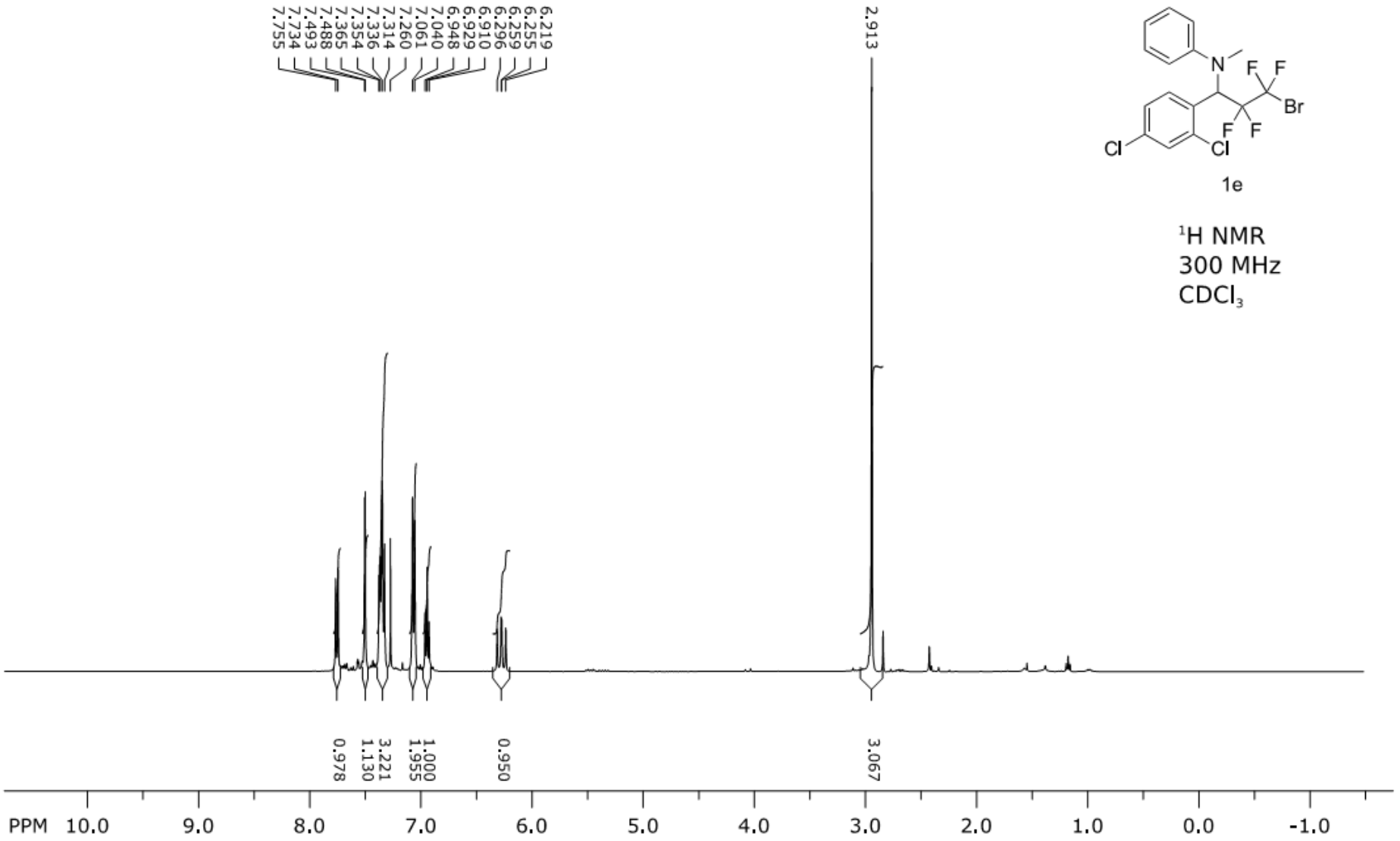

159.720
149.921
130.404
129.430
124.616
119.060
114.645
114.004
77.584
77.160
76.737
62.517
62.253
62.171
61.909
55.262
33.708
N
F
F
Br
F
F
O
1c
$^{13}C\{^{1}H\}$ NMR
75MHz
$CDCl_3$
PPM
180
160
140
120
100
80
60
40
20
0

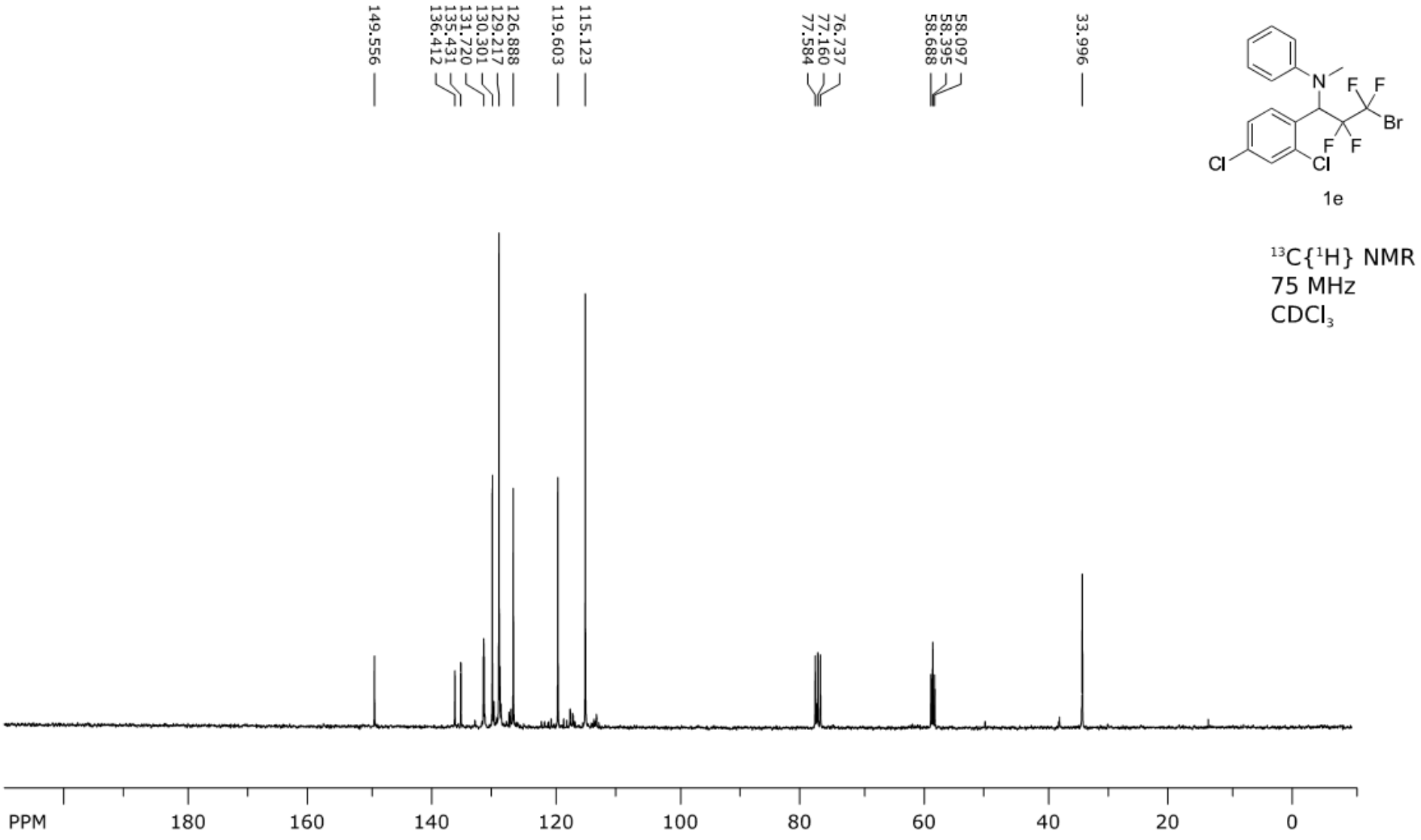

-61.968
-61.981
-62.348
-62.361
-62.532
-62.545
-62.913
-62.925
-103.723
-103.735
-103.745
-103.757
-104.300
-104.312
-104.322
-104.334
-112.546
-112.560
-112.587
-112.601
-113.123
-113.136
-113.164
-113.177
N
F
F
Br
F
F
O
O
1d
^{19}F NMR
282 MHz
$CDCl_3$
8.966
1.018
1.000
PPM
-54
-58
-62
-66
-70
-74
-78
-82
-86
-90
-94
-98
-102
-106
-110
-114
-118
-122

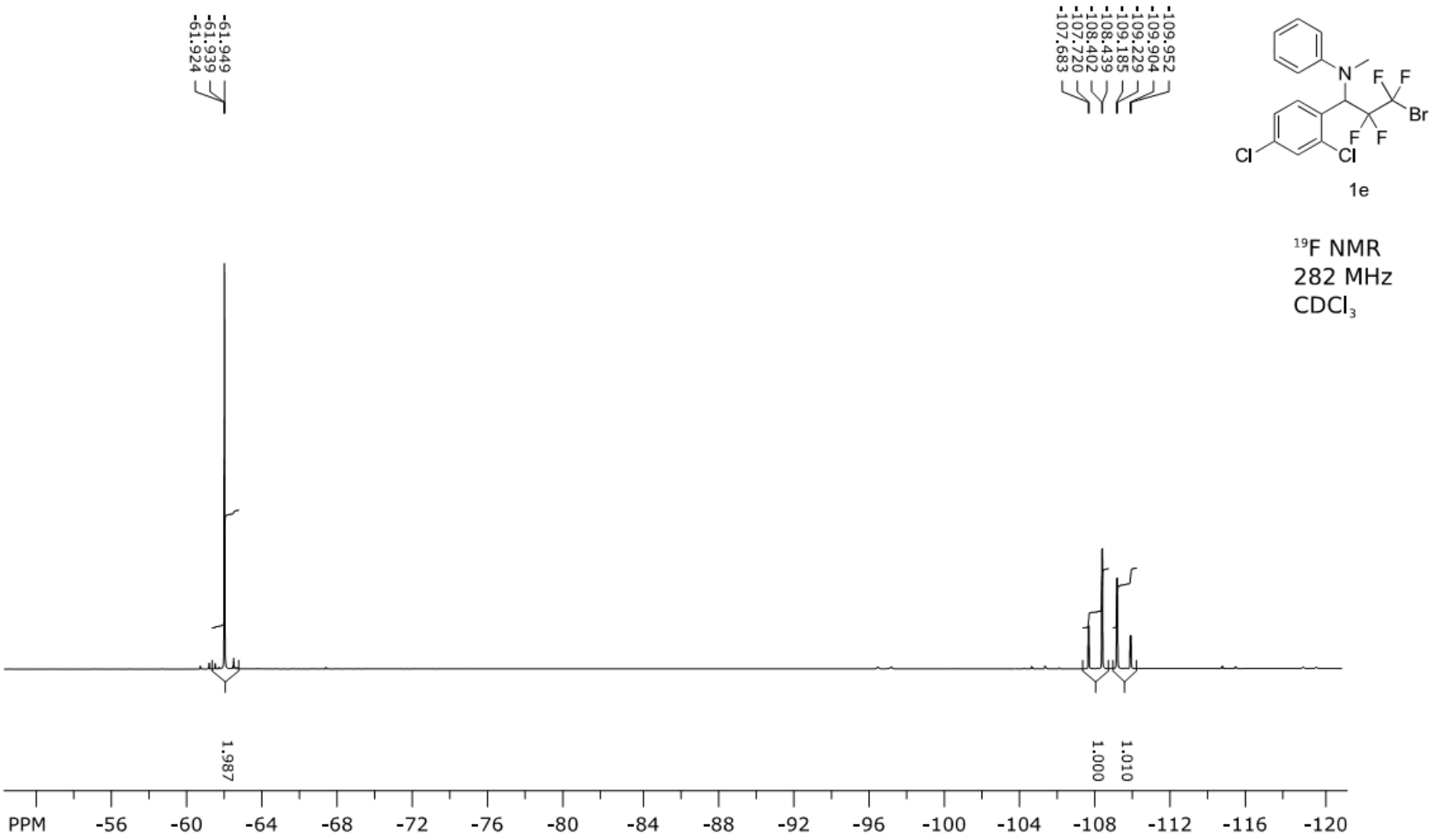

8.048
8.031
7.488
7.472
7.330
7.315
7.313
7.298
6.953
6.937
6.901
5.799
5.778
5.760
5.739
3.929
2.771
N
F
F
Br
F
F
O
O
1d
1H NMR
300 MHz
CDCl3
2.051
2.156
1.972
3.125
0.934
3.316
3.000
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0

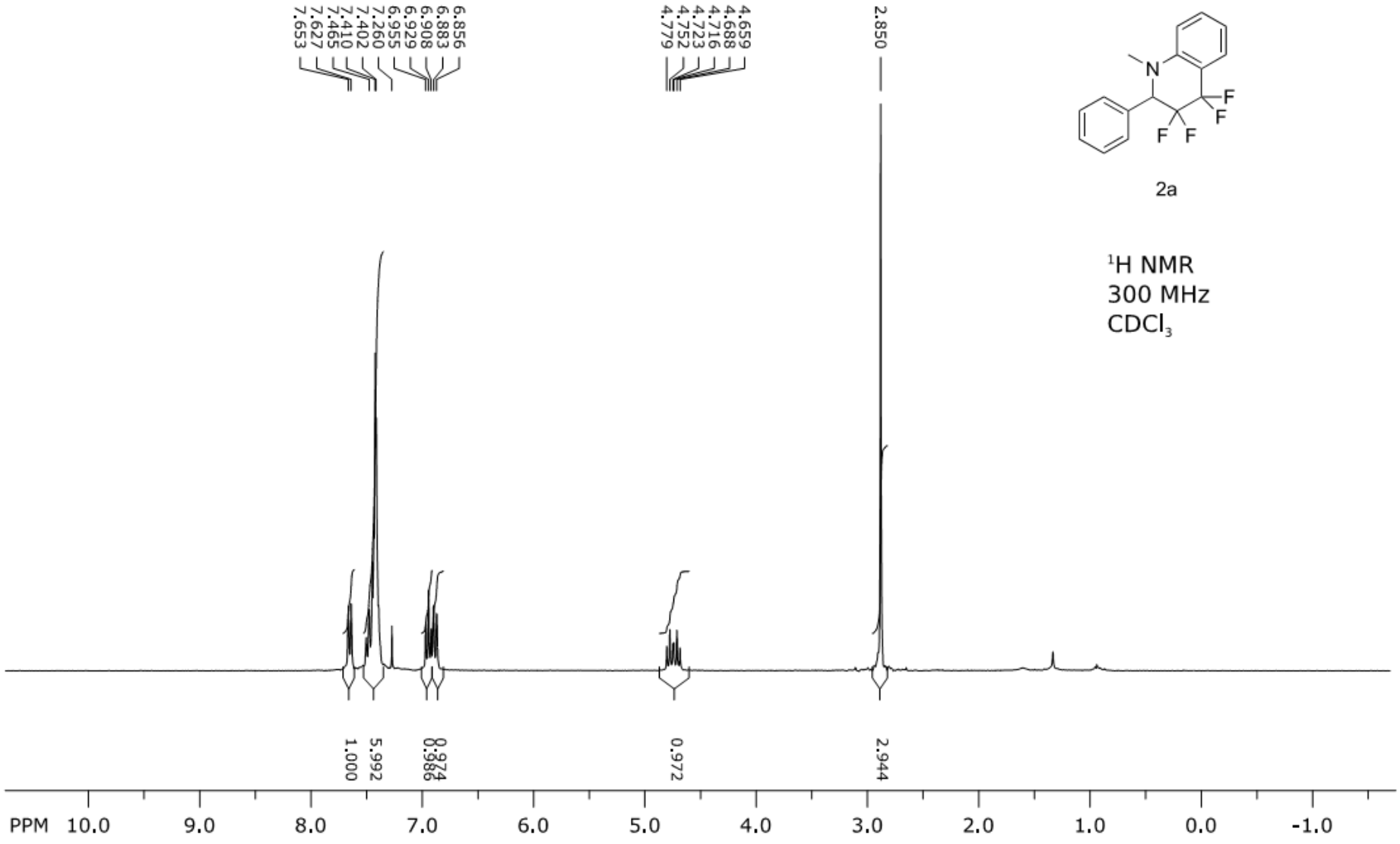

-61.574
-61.585
-61.951
-61.961
-62.022
-62.034
-62.399
-62.412
-104.993
-105.003
-105.019
-105.029
-105.567
-105.577
-105.593
-105.604
-111.695
-111.706
-111.735
-111.745
-112.270
-112.280
-112.309
-112.319
N
F
F
Br
F
F
O
1c
19F NMR
282 MHz
CDCl3
0.947
1.000
1.004
1.020
PPM
-48
-52
-56
-60
-64
-68
-72
-76
-80
-84
-88
-92
-96
-100
-104
-108
-112
-116
-120
-124
-128
-132

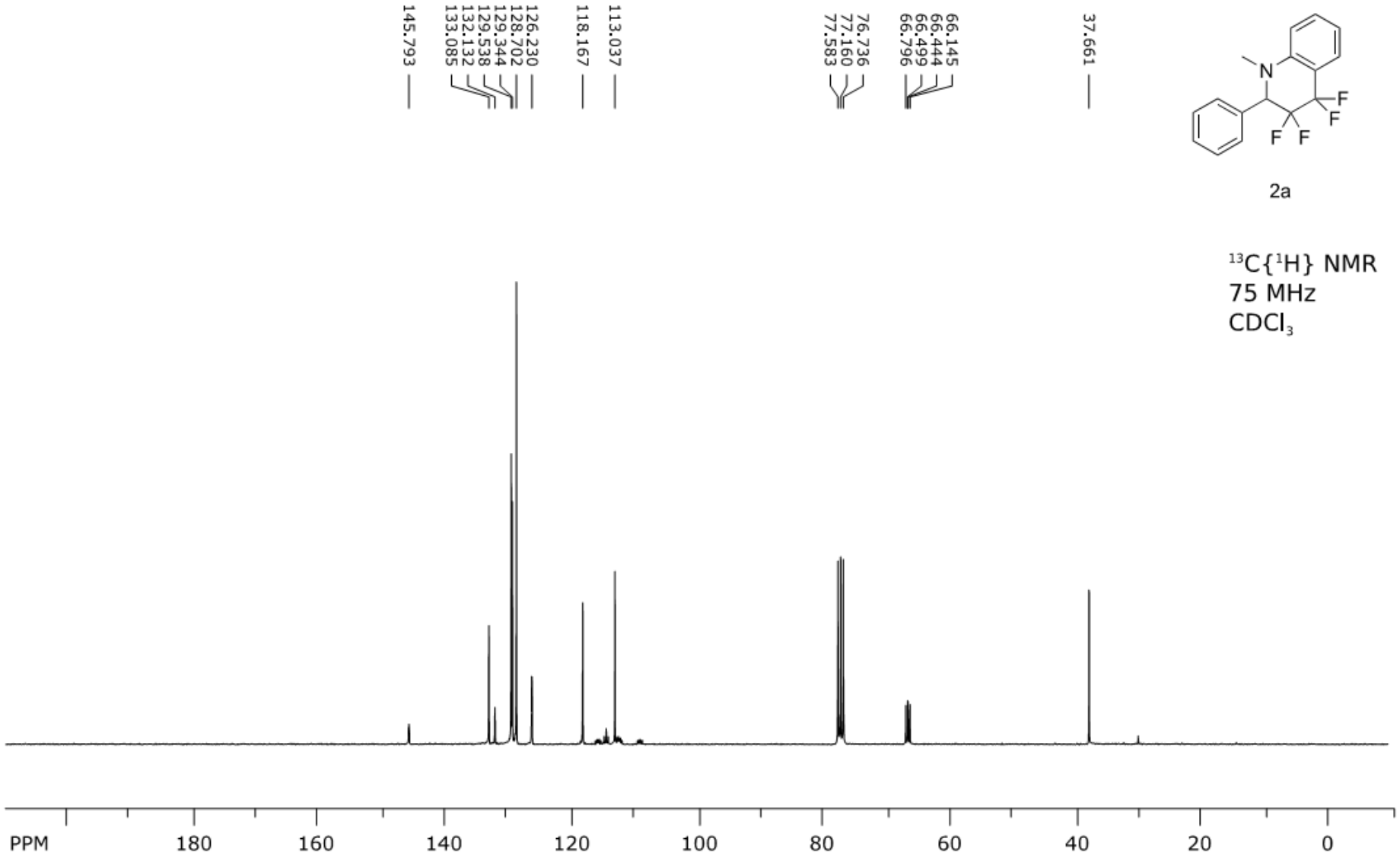

166.509
149.522
137.498
130.415
130.137
129.886
129.516
128.945
128.358
119.514
114.695
77.583
77.159
76.735
62.666
62.398
62.308
62.042
52.280
33.815
N
F
F
Br
F
F
O
O
1d
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
PPM
180
160
140
120
100
80
60
40
20
0

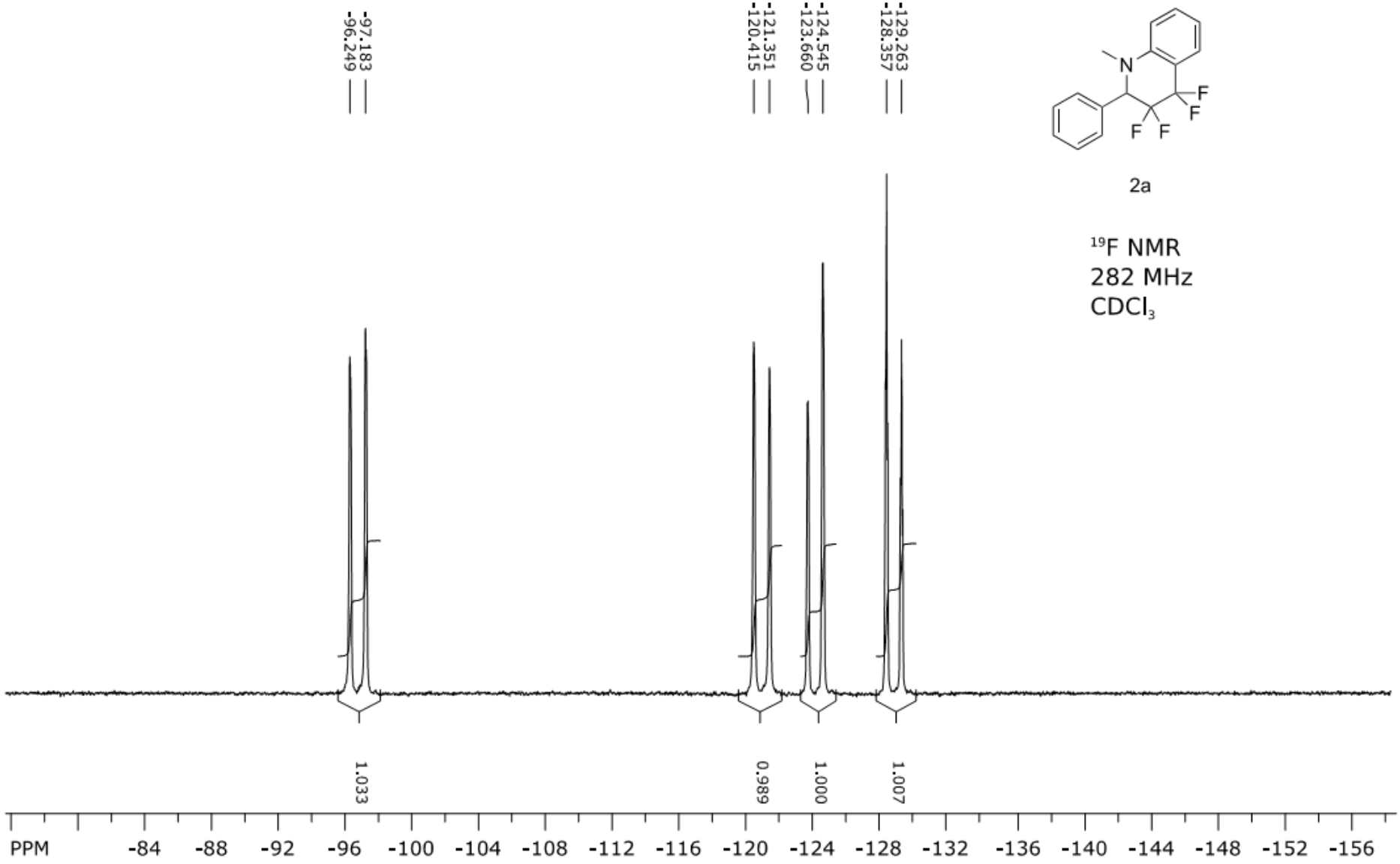

7.755
7.734
7.493
7.488
7.365
7.354
7.336
7.314
7.260
7.061
7.040
6.948
6.929
6.910
6.296
6.259
6.255
6.219
2.913
0.978
3.221
1.130
1.000
1.955
0.950
3.067
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
N
F F
Br
F F
Cl
Cl
1e
^{1}H NMR
300 MHz
$CDCl_3$

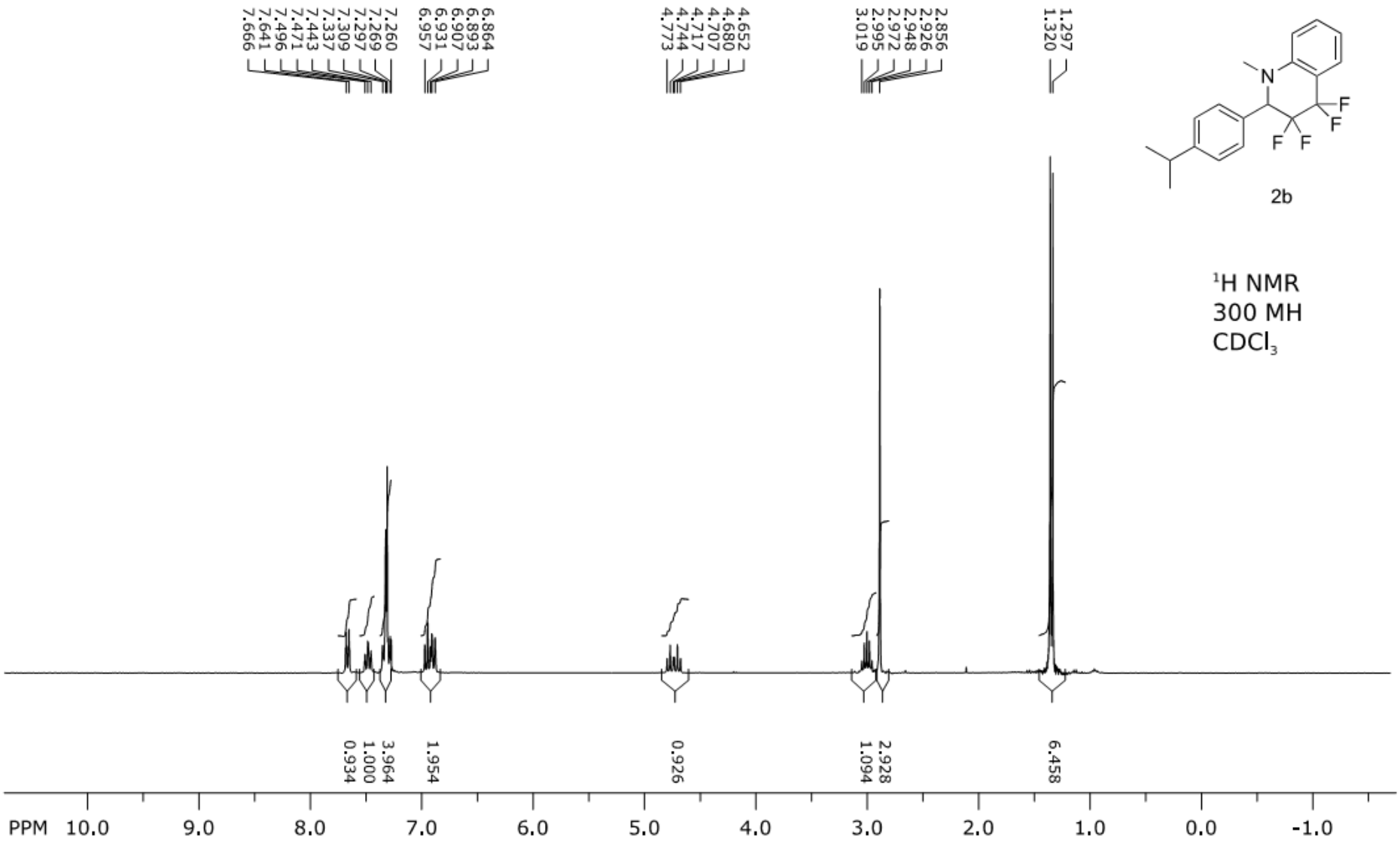

149.556
136.412
135.431
131.720
130.301
129.217
126.888
119.603
115.123
77.584
77.160
76.737
58.688
58.395
58.097
33.996
N
F
F
Br
F
F
Cl
Cl
1e
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
PPM
180
160
140
120
100
80
60
40
20
0

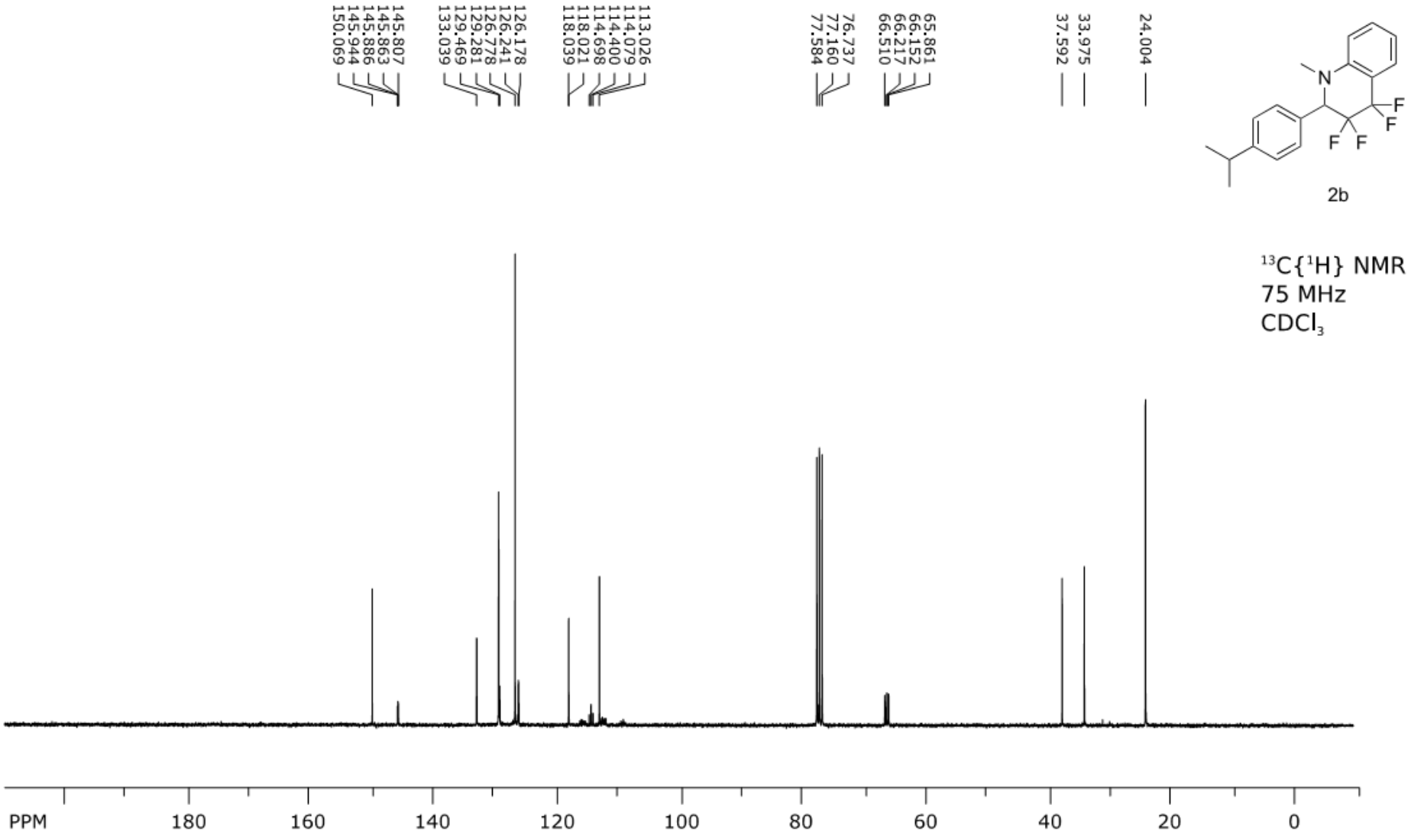

-61.949
-61.939
-61.924
-107.683
-107.720
-108.402
-108.439
-109.185
-109.229
-109.904
-109.952
N
F
F
Br
F
F
Cl
Cl
1e
19F NMR
282 MHz
CDCl3
1.987
1.000
1.010
PPM
-56
-60
-64
-68
-72
-76
-80
-84
-88
-92
-96
-100
-104
-108
-112
-116
-120

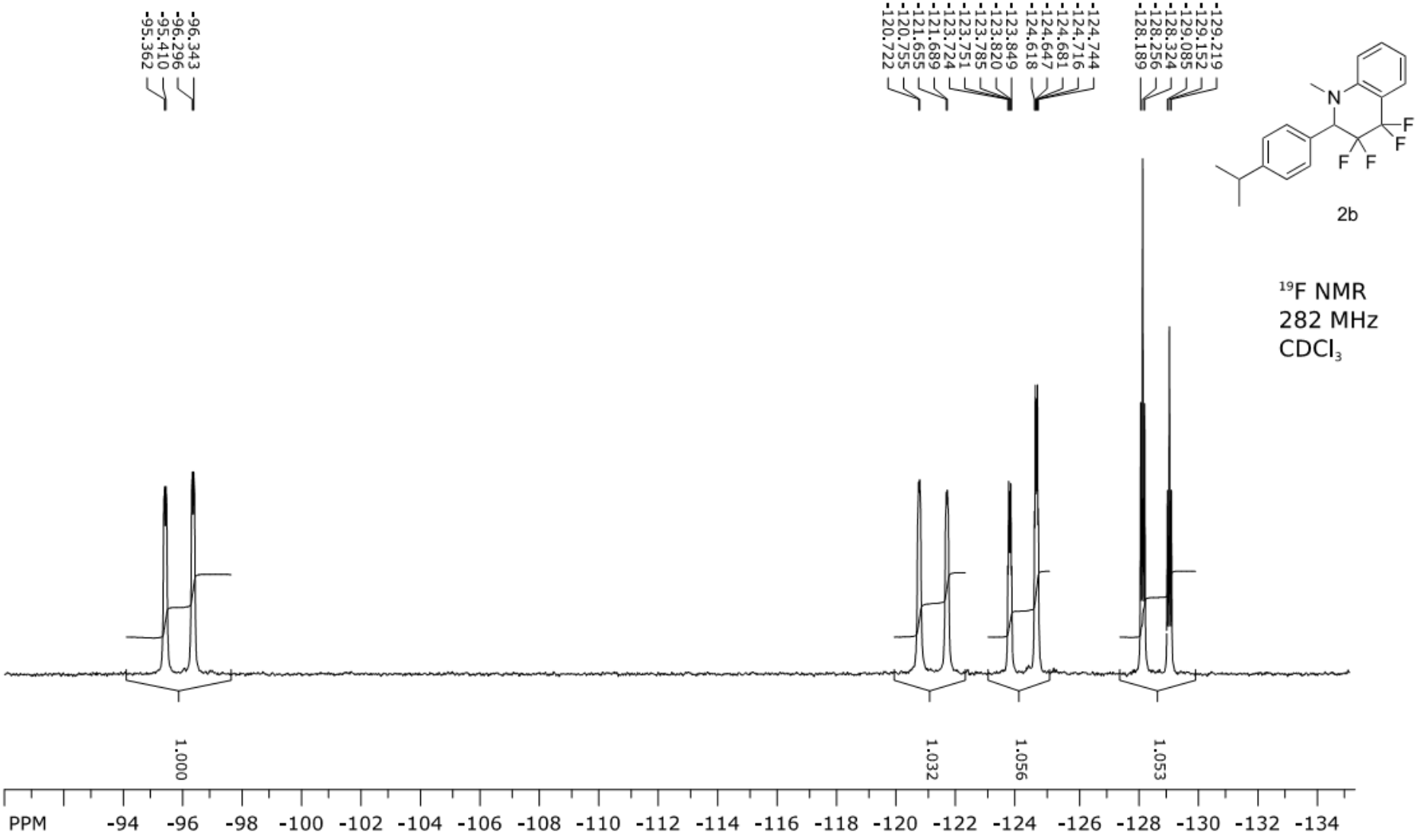

7.653
7.627
7.465
7.410
7.402
7.260
6.955
6.929
6.908
6.883
6.856
4.779
4.752
4.723
4.716
4.688
4.659
2.850
N
F
F
F
F
2a
1H NMR
300 MHz
CDCl3
1.000
5.992
0.974
0.986
0.972
2.944
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0

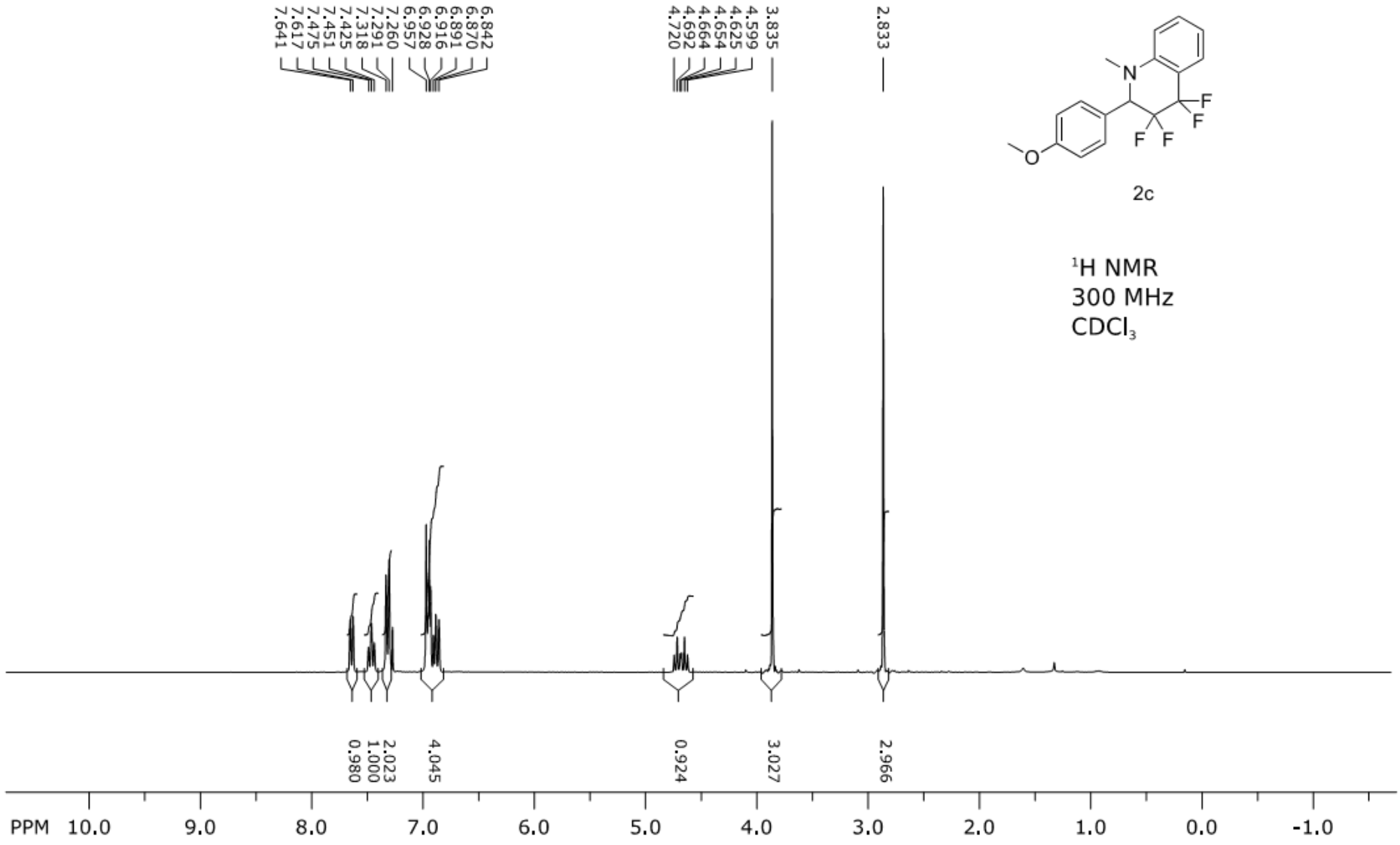

145.793
133.085
132.132
129.538
129.344
128.702
126.230
118.167
113.037
77.583
77.160
76.736
66.796
66.499
66.444
66.145
37.661
N
F
F
F
F
2a
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
PPM
180
160
140
120
100
80
60
40
20
0

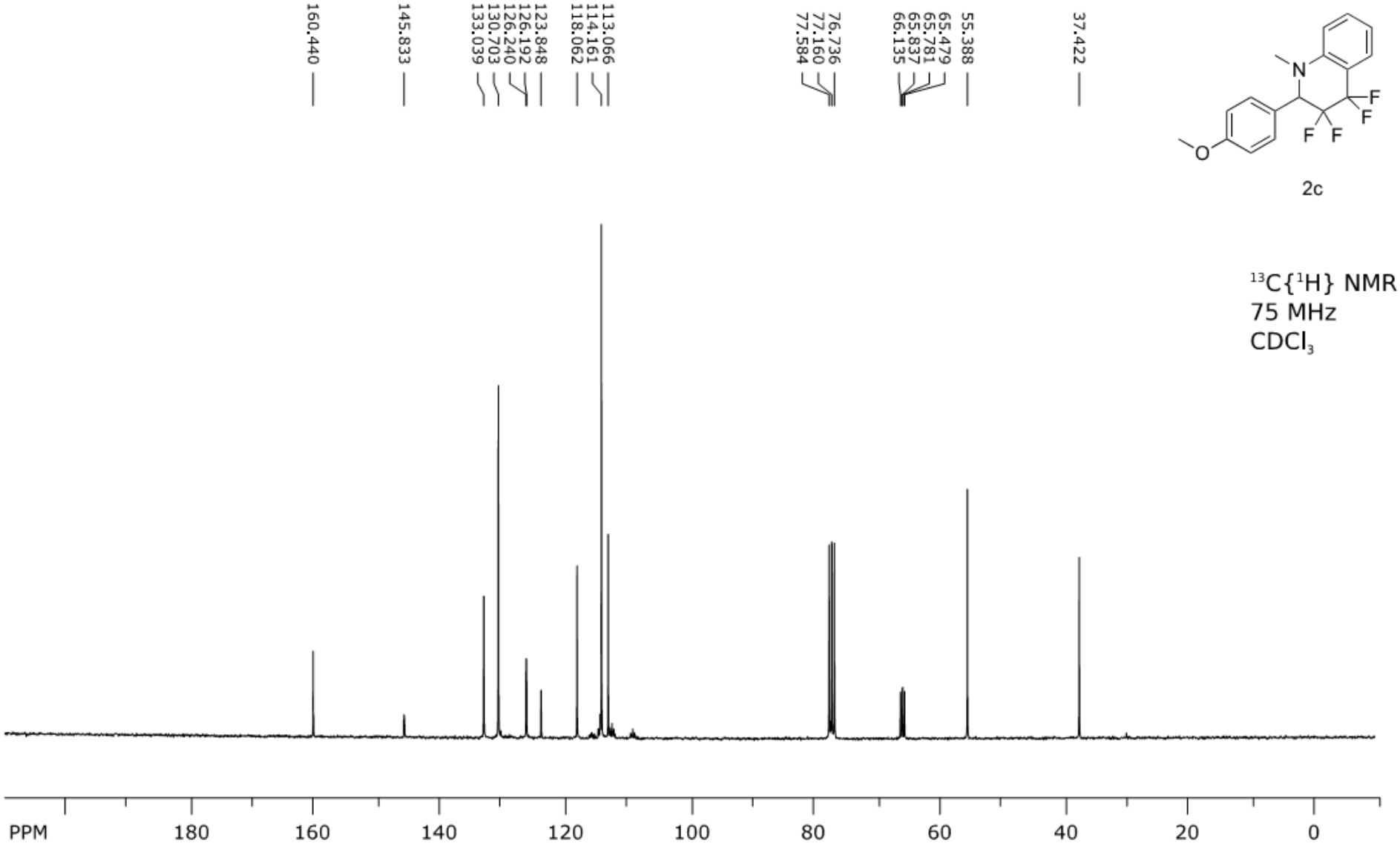

-97.183
-96.249
-121.351
-120.415
-124.545
-123.660
-129.263
-128.357
N
F
F
F
F
2a
^{19}F NMR
282 MHz
$CDCl_3$
1.033
0.989
1.000
1.007
PPM
-84
-88
-92
-96
-100
-104
-108
-112
-116
-120
-124
-128
-132
-136
-140
-144
-148
-152
-156


7.666
7.641
7.496
7.471
7.443
7.337
7.309
7.297
7.269
7.260
6.957
6.931
6.907
6.893
6.864
4.773
4.744
4.717
4.707
4.680
4.652
3.019
2.995
2.972
2.948
2.926
2.856
1.320
1.297
N
F
F
F
F
2b
^{1}H NMR
300 MH
$CDCl_3$
0.934
1.000
3.964
1.954
0.926
1.094
2.928
6.458
PPM 10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0


150.069
145.944
145.886
145.863
145.807
133.039
129.469
129.281
126.778
126.241
126.178
118.039
118.021
114.698
114.400
114.079
113.026
77.584
77.160
76.737
66.510
66.217
66.152
65.861
37.592
33.975
24.004
N
F
F
F
F
2b
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
PPM
180
160
140
120
100
80
60
40
20
0


-95.362
-95.410
-96.296
-96.343
-120.722
-120.755
-121.655
-121.689
-123.724
-123.751
-123.785
-123.820
-123.849
-124.618
-124.647
-124.681
-124.716
-124.744
-128.189
-128.256
-128.324
-129.085
-129.152
-129.219
N
F
F
F
F
2b
^{19}F NMR
282 MHz
$CDCl_3$
1.000
1.032
1.056
1.053
PPM
-94
-96
-98
-100
-102
-104
-106
-108
-110
-112
-114
-116
-118
-120
-122
-124
-126
-128
-130
-132
-134


7.641
7.617
7.475
7.451
7.425
7.318
7.291
7.260
6.957
6.928
6.916
6.891
6.870
6.842
4.720
4.692
4.664
4.654
4.625
4.599
3.835
2.833
N
F
F
F
F
O
2c
1H NMR
300 MHz
CDCl3
0.980
2.023
1.000
4.045
0.924
3.027
2.966
PPM 10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0


160.440
145.833
133.039
130.703
126.240
126.192
123.848
118.062
114.161
113.066
77.584
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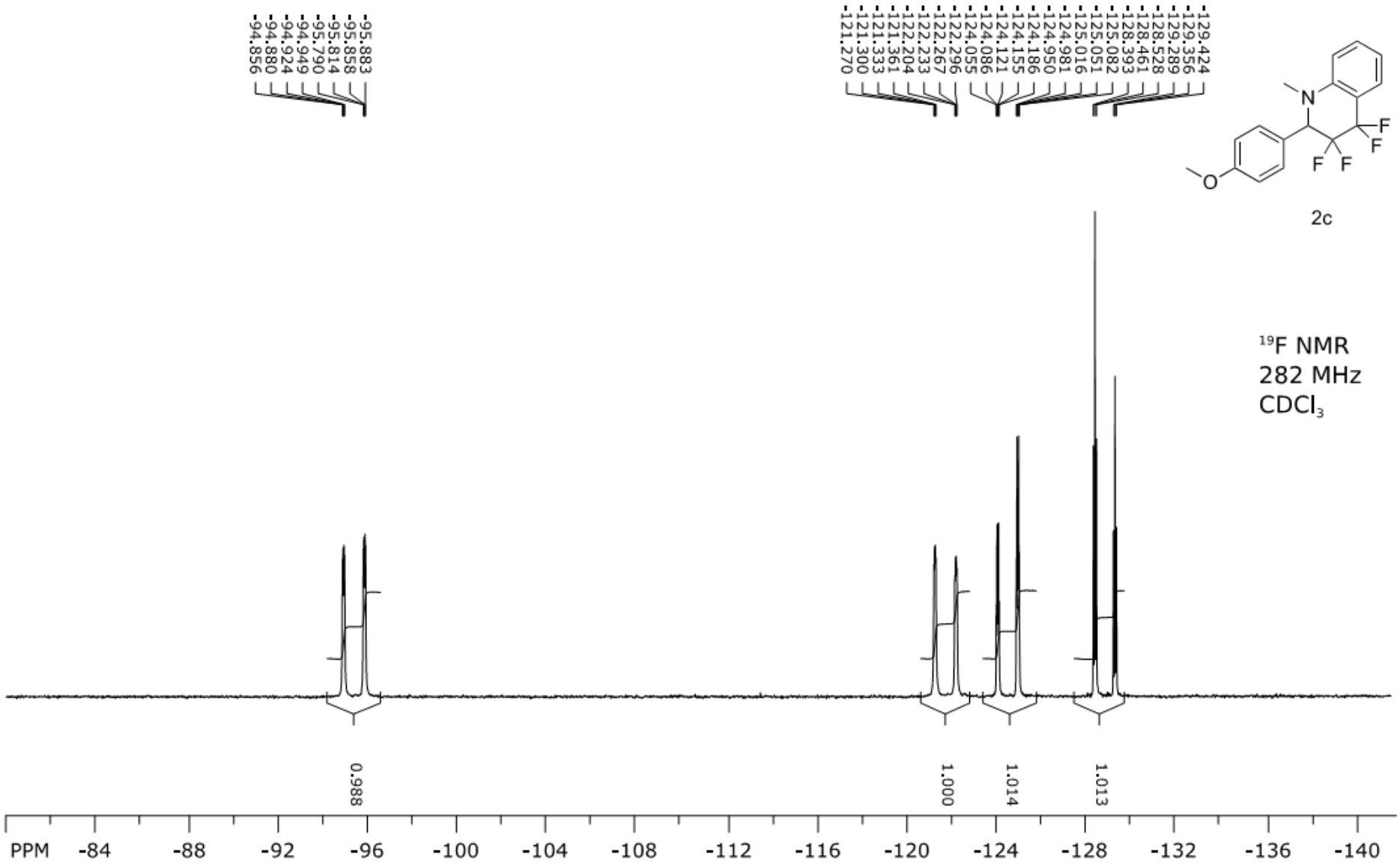
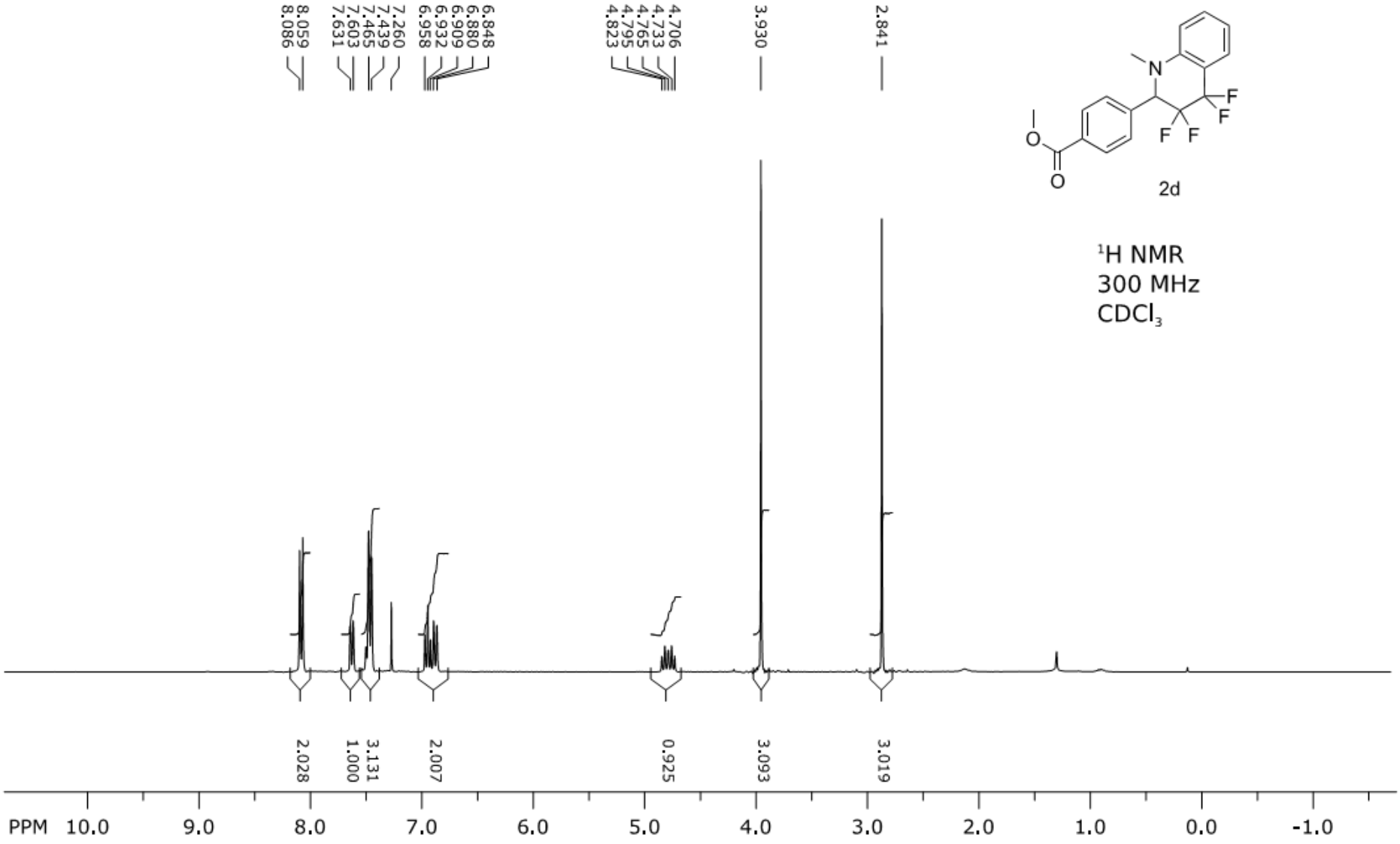
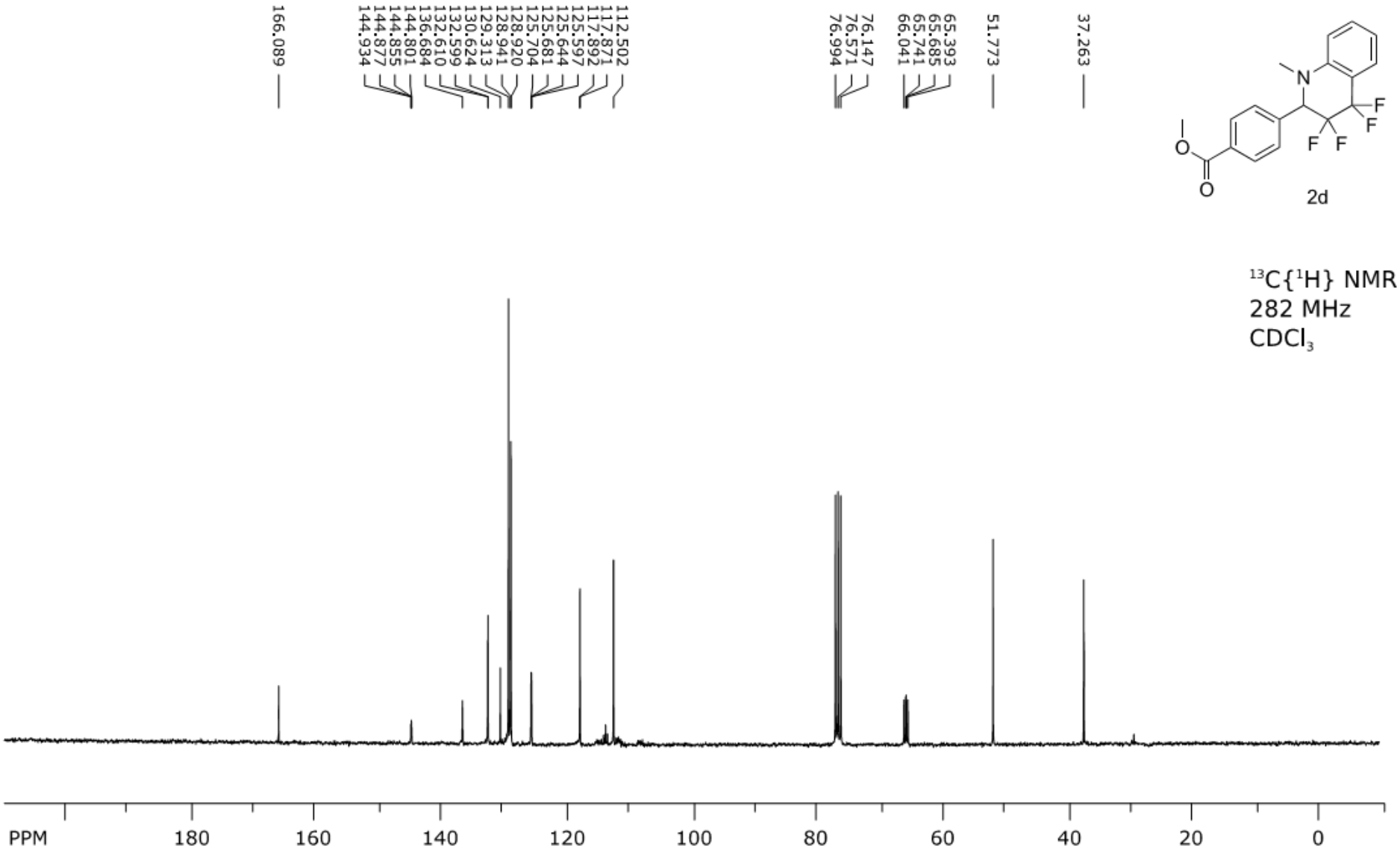
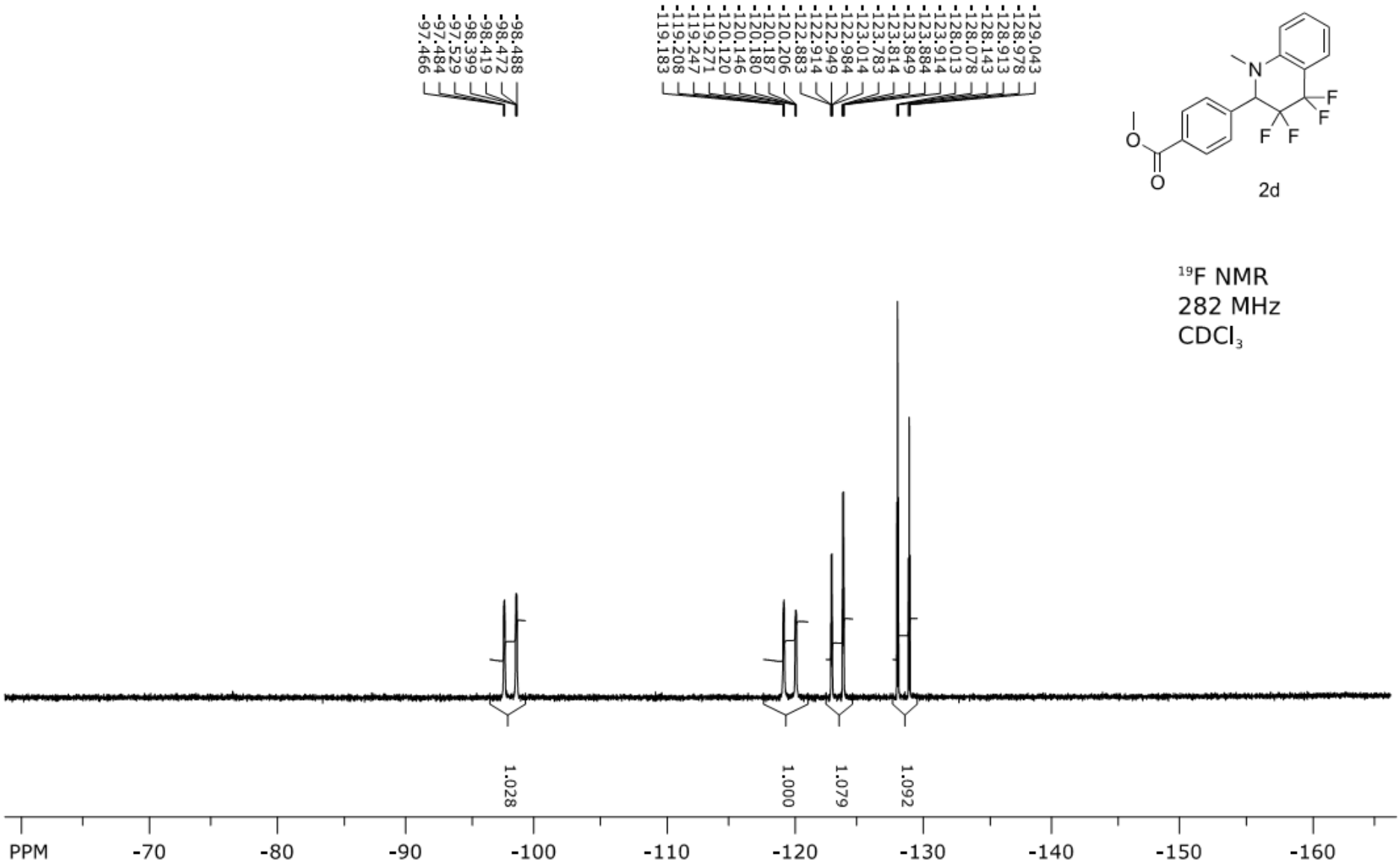
76.736
66.135
65.837
65.781
65.479
55.388
37.422
N
F
F
F
F
O
2c
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
PPM
180
160
140
120
100
80
60
40
20
0


-94.856
-94.880
-94.924
-94.949
-95.790
-95.814
-95.858
-95.883
-121.270
-121.300
-121.333
-121.361
-122.204
-122.233
-122.267
-122.296
-124.055
-124.086
-124.121
-124.155
-124.186
-124.950
-124.981
-125.016
-125.051
-125.082
-128.393
-128.461
-128.528
-129.289
-129.356
-129.424
N
F
F
F
F
O
2c
^{19}F NMR
282 MHz
$CDCl_3$
0.988
1.000
1.014
1.013
PPM -84 -88 -92 -96 -100 -104 -108 -112 -116 -120 -124 -128 -132 -136 -140


8.086
8.059
7.631
7.603
7.465
7.439
7.260
6.958
6.932
6.909
6.880
6.848
4.823
4.795
4.765
4.733
4.706
3.930
2.841
2d
^{1}H NMR
300 MHz
$CDCl_3$
2.028
1.000
3.131
2.007
0.925
3.093
3.019
PPM 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0


166.089
144.934
144.877
144.855
144.801
136.684
132.610
130.624
129.313
128.941
128.920
125.704
125.681
125.644
125.597
117.892
117.871
112.502
76.994
76.571
76.147
66.041
65.741
65.685
65.393
51.773
37.263
N
F
F
F
F
O
O
2d
$^{13}C\{^{1}H\}$ NMR
282 MHz
$CDCl_3$
PPM
180
160
140
120
100
80
60
40
20
0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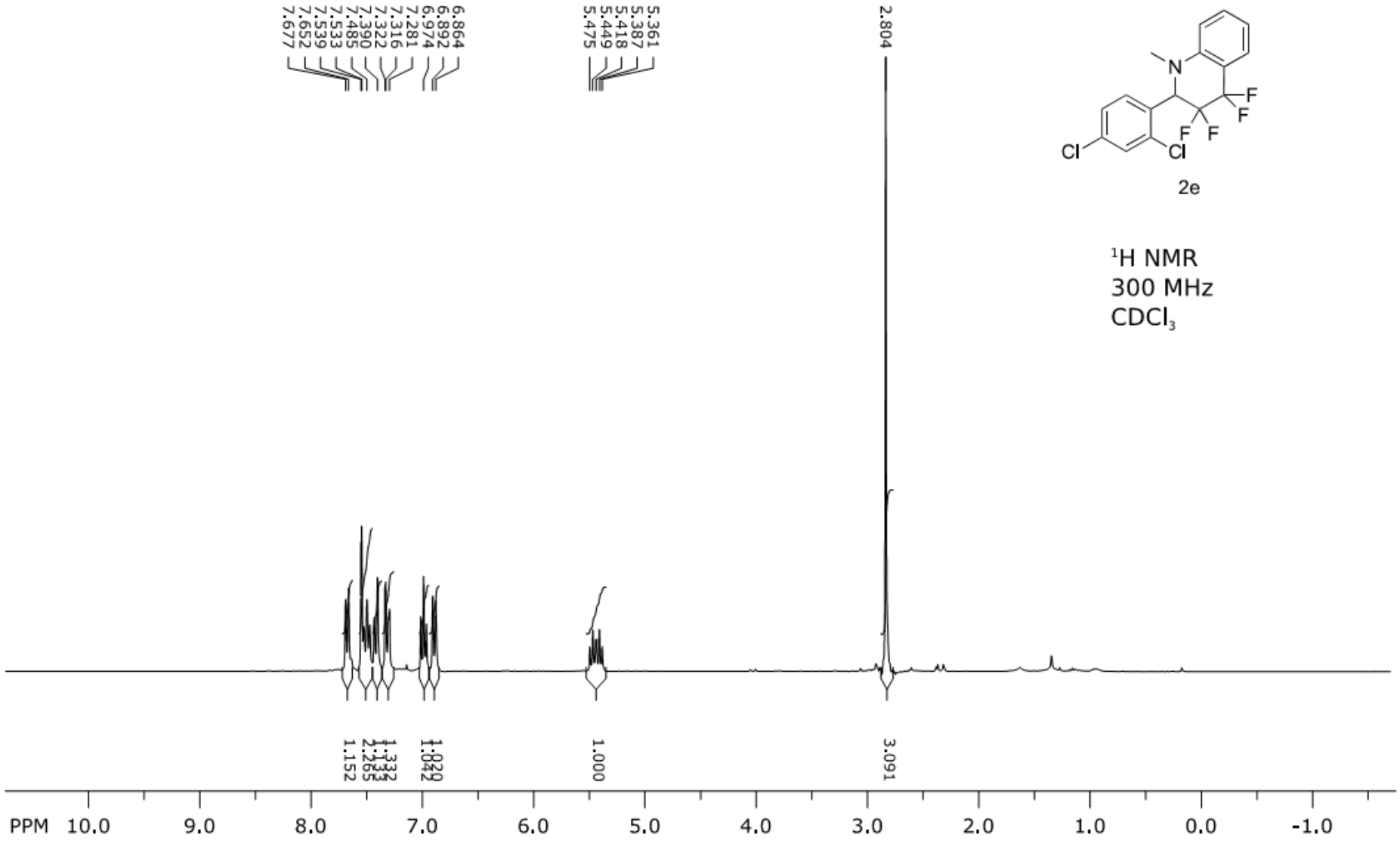
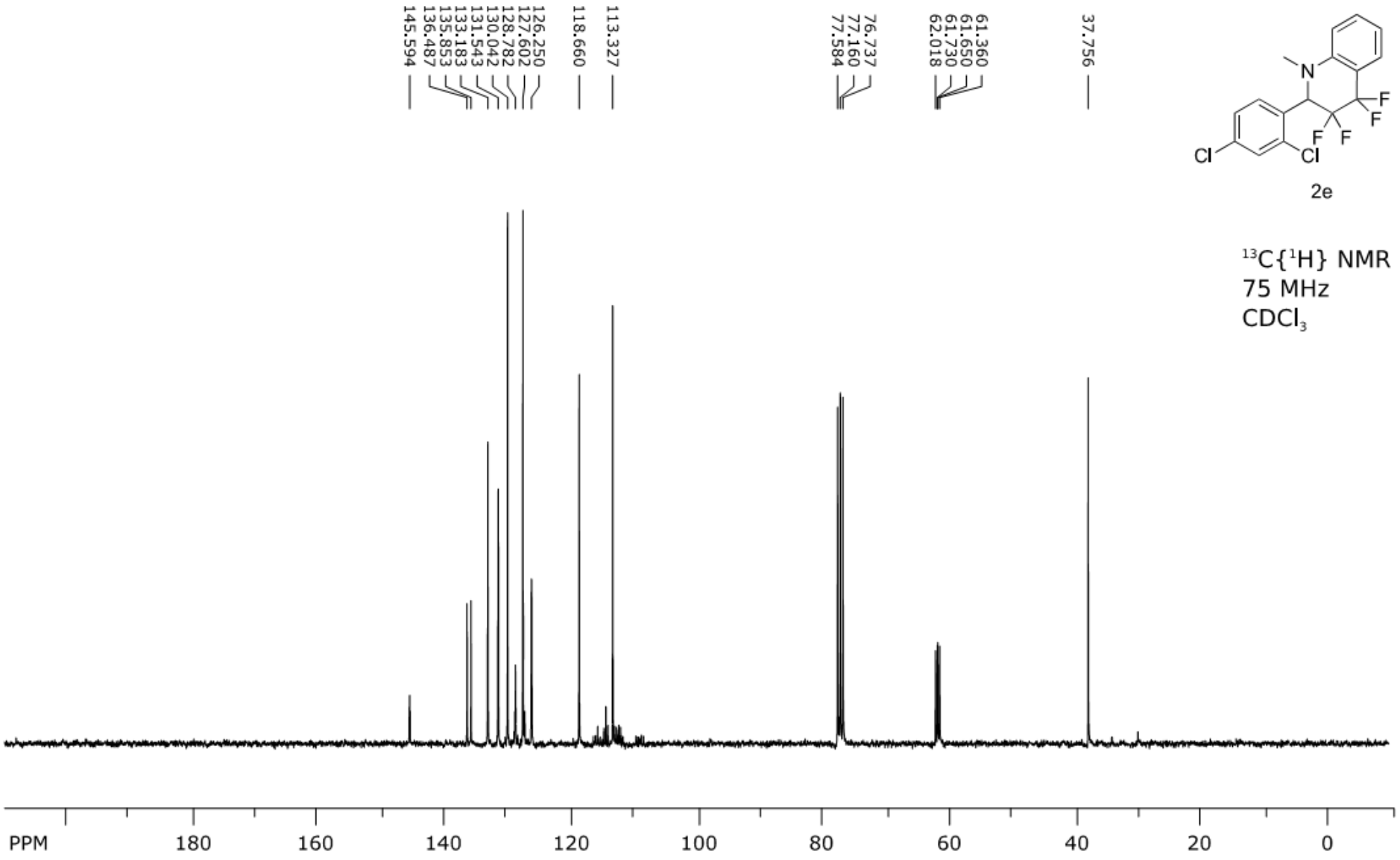
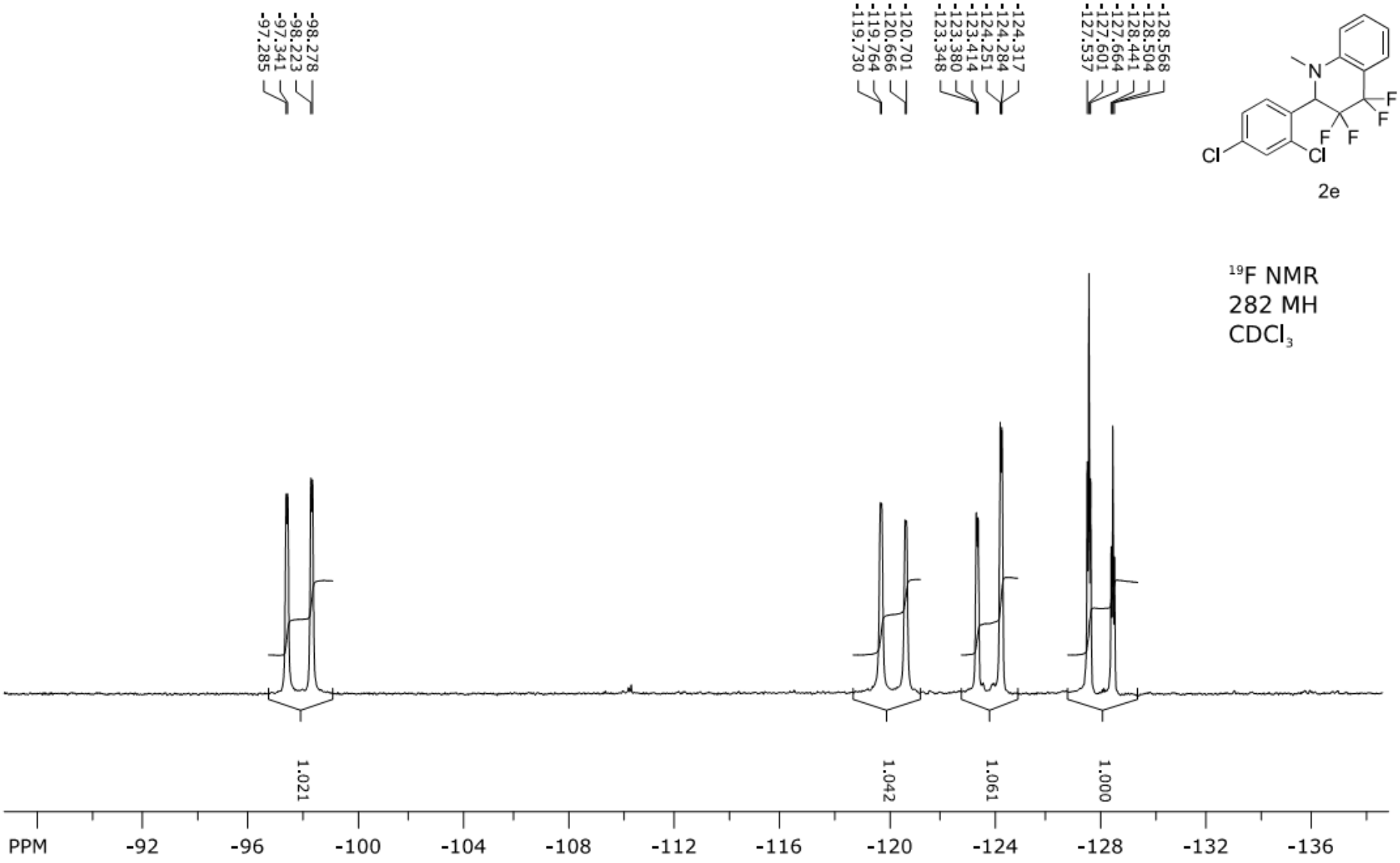
-97.484
-97.529
-98.399
-98.419
-98.472
-98.488
-119.183
-119.208
-119.247
-119.271
-120.120
-120.146
-120.180
-120.187
-120.206
-122.883
-122.914
-122.949
-122.984
-123.014
-123.783
-123.814
-123.849
-123.884
-123.914
-128.013
-128.078
-128.143
-128.913
-128.978
-129.043
N
F
F
F
F
O
O
2d
19F NMR
282 MHz
CDCl3
1.028
1.000
1.079
1.092
PPM
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160



2e

^{1}H NMR
300 MHz
$CDCl_3$


145.594
136.487
135.853
133.183
131.543
130.042
128.782
127.602
126.250
118.660
113.327
77.584
77.160
76.737
62.018
61.730
61.650
61.360
37.756
N
F
F
F
F
Cl
Cl
2e
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
PPM
180
160
140
120
100
80
60
40
20
0


-97.285
-97.341
-98.223
-98.278
-119.730
-119.764
-120.666
-120.701
-123.348
-123.380
-123.414
-124.251
-124.284
-124.317
-127.537
-127.601
-127.664
-128.441
-128.504
-128.568
N
F
F
F
F
Cl
Cl
2e
19F NMR
282 MH
CDCl3
1.021
1.042
1.061
1.000
PPM
-92
-96
-100
-104
-108
-112
-116
-120
-124
-128
-132
-136