



Supporting Information

for

Synthesis of tetrafluorinated piperidines from nitrones via a visible-light-promoted annelation reaction

Vyacheslav I. Supranovich, Igor A. Dmitriev and Alexander D. Dilman

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Full experimental details, compound characterization, X-ray data, and copies of NMR spectra

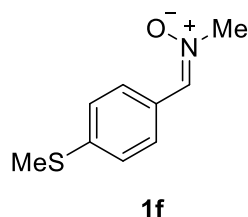
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General methods. DMF was distilled from MgSO_4 . Acetonitrile was distilled from P_2O_5 and stored over 3 Å molecular sieves. Column chromatography was carried out employing silica gel (230–400 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography and visualizing with UV and/or acidic aq. KMnO_4 solution. NMR spectra were recorded on a Bruker Avance II 300 spectrometer. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and a time-of-flight (TOF) mass analyzer. The measurements were done in the positive ion mode (interface capillary voltage –4500 V) or in the negative ion mode (3200 V); mass range from m/z 50 to m/z 3000. Melting points were measured with a Stuart SMP30.

Reagents. Nitrones were prepared according to literature procedures: *N*-(benzylidene)methylamine *N*-oxide (**1a**),¹ *N*-(4-isopropylbenzylidene)methanamine *N*-oxide (**1b**),² *N*-(4-chlorobenzylidene)methanamine *N*-oxide (**1c**),³ *N*-(2,4-dichlorobenzylidene)-1-benzylamine *N*-oxide (**1d**),² *N*-(3,4,5-trimethoxybenzylidene)-methanamine *N*-oxide (**1e**),⁴ *N*-(2-methoxybenzylidene)methanamine *N*-oxide (**1g**),⁵ *N*-[4-(methoxycarbonyl)benzylidene]methanamine *N*-oxide (**1h**),⁶ *N*-(4-(trifluoromethyl)benzylidene)methanamine *N*-oxide (**1i**),⁷ *N*-(4-cyanobenzylidene)methanamine *N*-oxide (**1j**),⁸ *N*-(2-pyridyl)-methylamine *N*-oxide (**1k**),⁵ 3,4-dihydroisoquinoline *N*-oxide (**1l**),⁹ *N*-ethylidenebenzylamine *N*-oxide (**1m**),¹⁰ *N*-butylidenebenzylamine *N*-oxide (**1n**),¹¹ *N*-(3-methylbutylidene)benzylamine *N*-oxide (**1o**),¹¹ *N*-(3-phenylpropylidene)methanamine *N*-oxide (**1q**).¹²

***N*-[4-(Methylthio)benzylidene]methylamine *N*-oxide (**1f**).¹³**

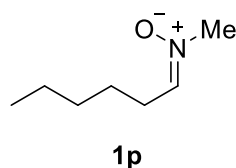


4-(Methylthio)benzaldehyde (304 mg, 2.0 mmol), *N*-methyl hydroxylamine hydrochloride (252 mg, 3.0 mmol, 1.5 equiv), and NaHCO_3 (252 mg, 3.0 mmol, 1.5 equiv) were stirred in dichloromethane (5 mL) at room temperature overnight. The mixture was poured into water (30 mL), the organic phase was separated, and the aqueous layer was additionally extracted with dichloromethane (2×5 mL). The combined organic phases were dried with MgSO_4 , filtered, and evaporated, and the residue was washed on a filter with hot hexanes affording the product as colorless crystals (295 mg, 82%). Mp 106–107 °C.

^1H NMR (300 MHz, CDCl_3) δ : 8.10 (d, J = 8.6 Hz, 2H), 7.27 (s, 1H), 7.20 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 2.45 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 141.8, 134.7, 128.6, 127.0, 125.3, 54.1, 14.9.

***N*-Hexylidenebenzylamine *N*-oxide (**1p**).¹⁴**



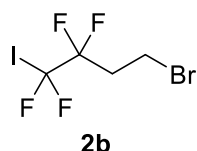
Hexanal (180 mg, 1.8 mmol) was added to a stirred mixture of *N*-benzylhydroxylamine hydrochloride (240 mg, 1.5 mmol) and NaHCO_3 (252 mg, 3.0 mmol) in dichloromethane (5 mL), and the mixture was stirred for 24 hours at room temperature. The mixture was poured into water (50 mL), the organic phase was separated,

and the aqueous layer was additionally extracted with dichloromethane (3 × 5 mL). The combined organic phases were dried with MgSO₄ and evaporated. The crude product was recrystallized from hexanes to afford 200 mg of colorless crystals (65 %). Mp 84–85 °C.

¹H NMR (300 MHz, CDCl₃) δ: 7.39–7.29 (m, 5H), 6.62 (t, *J* = 5.9 Hz, 1H), 4.81 (s, 2H), 2.42 (td, *J* = 7.4, 5.9 Hz, 2H), 1.48–1.38 (m, 2H), 1.30–1.20 (m, 4H), 0.83 (t, *J* = 6.9 Hz, 3H).

¹³C{¹H} NMR (75 MHz, CDCl₃) δ: 139.4, 133.0, 129.0, 128.7, 128.6, 68.9, 31.5, 26.5, 25.0, 22.1, 13.8.

4-Bromo-1,1,2,2-tetrafluoro-1-iodobutane (2b).



A Schlenk tube containing zinc dust (2.60 g, 40.0 mmol) and a magnetic stirrer was dried under vacuum with a heat gun and allowed to cool under argon atmosphere. Acetonitrile (5 mL) and two drops of chlorotrimethylsilane were added and the tube was heated in a 60 °C bath for 15 minutes while stirring. The heating bath was removed, and the tube was cooled in a water/ice bath. Then, 1,4-dibromo-1,1,2,2-tetrafluorobutane (5.86 g, 20.3 mmol) in acetonitrile (17 mL) was added in small portions in about 45 minutes. The bath was allowed to warm to room temperature and the reaction mixture was stirred overnight (around 16 hours). The mixture was filtered from excess of zinc through a cotton plug, and the resulting clear solution was handled open to air atmosphere without special precautions. The mixture was cooled with an ice/water bath. A solution of iodine monochloride (6.48 g, 40 mmol) in dichloromethane (10 mL) was added dropwise with a syringe in about 10 min, and the cooling bath was removed. After stirring for 24 hours at room temperature, the mixture was poured into a separatory funnel containing water (300 mL). Sodium thiosulfate hydrate (7.5 g) was added in portions and the mixture was shaken until complete discoloration occurred. The mixture was extracted with pentane (3 × 20 mL), the combined organic phases were dried over MgSO₄, and carefully evaporated at atmospheric pressure (40 °C water bath). The residue was distilled (bp 63–64 °C/20 Torr) to yield a slightly pink-colored liquid (4.61 g, 68%).

¹H NMR (300 MHz, CDCl₃) δ: 3.53 (t, *J* = 7.9 Hz, 2H), 2.71 (tt, *J* = 16.5, 8.1 Hz, 2H).

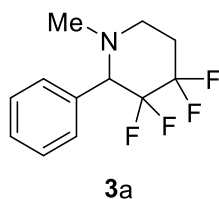
¹³C {¹H} NMR (75 MHz, CDCl₃) δ: 116.3 (tt, *J* = 254.7, 31.2 Hz), 96.9 (tt, *J* = 317.5, 42.6 Hz), 33.5 (t, *J* = 22.6 Hz), 20.9 (tt, *J* = 4.7, 1.2 Hz).

¹⁹F NMR (282 MHz, CDCl₃) δ: -61.1 (t, *J* = 4.9 Hz, 2F), -108.5 (tt, *J* = 16.8, 4.9 Hz, 2F).

Calcd for C₄H₄BrF₄I (334.88): C, 14.35; H, 1.20. Found: C, 14.51; H, 1.28.

Reaction of nitrones with 2b (general procedure). Nitrone **1** (0.50 mmol), ascorbic acid (220 mg, 1.25 mmol, 2.5 equiv), [Ir(ppy)₂(dtbbpy)][PF₆] (2.3 mg, 0.0025 mmol, 0.5 mol %) were placed in a tube (Duran, cat. # 261351258, Roth cat. no PY94.1, outside diameter 13 mm). The tube was evacuated and filled with argon and DMF (2.0 mL) was added. The tube was briefly evacuated and refilled with argon. Then, iodide **2b** (for **3a–m,o–q**, 251 mg, 0.75 mmol, 1.5 equiv; for **3n**, 168 mg, 0.5 mmol, 1.0 equiv) and 2,4,6-collidine (212 mg, 1.75 mmol, 3.5 equiv) were added. The tube was closed with a screw cap and irradiated for 1.5 hours by a 450 nm LED chip (Hontiey royal blue 100W, operated at 60 Watt). The distance between the LED chip and the reaction tube was 1 cm. During the reaction, the bath temperature was maintained in a range of 15–20 °C. The reaction mixture was poured into water (15 mL) and extracted with hexanes (3 × 4 mL). The combined organic phases were dried over Na₂SO₄, filtered, evaporated, and the residue was purified by column chromatography on silica gel.

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



Yield 104 mg (84 %). Colorless oil.

Chromatography: hexanes/EtOAc, from 5/1 to 1/1. R_f 0.18 (hexanes/EtOAc, 7/1).

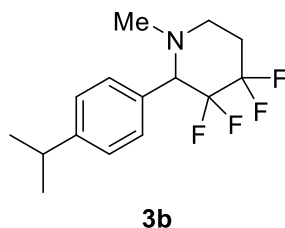
^1H NMR (300 MHz, CDCl_3) δ : 7.49–7.37 (m, 5H), 3.40 (dddd, $J = 21.7, 5.0, 3.7, 1.1$ Hz, 1H), 3.13–2.99 (m, 1H), 2.62–2.18 (m, 3H), 2.10 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 132.9, 130.3 (d, $J = 1.7$ Hz), 129.1, 128.5, 115.9 (dddd, $J = 260.5, 244.3, 32.4, 21.4$ Hz), 113.4 (dddd, $J = 254.4, 252.3, 30.2, 20.6$ Hz), 71.1 (dddd, $J = 24.9, 18.9, 3.2, 1.3$ Hz), 51.4 (d, $J = 10.5$ Hz), 43.2 (t, $J = 1.4$ Hz), 31.3 (dddd, $J = 21.2, 19.9, 3.4, 1.4$ Hz).

^{19}F NMR (282 MHz, CDCl_3) δ : -119.3 (dm, $J = 248.9$ Hz, 1F), -122.1 (dm, $J = 248.9$ Hz, 1F), -126.2 (ddtd, $J = 256.5, 21.4, 16.3, 4.4$ Hz, 1F), -130.1 (ddtd, $J = 256.5, 16.4, 14.6, 5.0$ Hz).

HRMS (ESI): calcd for $\text{C}_{12}\text{H}_{14}\text{F}_4\text{N}$ ($\text{M}+\text{H}$) 248.1057, found 248.1050.

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



Yield 102 mg (70 %). Colorless crystals. Mp 49–50 °C.

Chromatography: hexanes/EtOAc, 5/1. R_f 0.25 (hexanes/EtOAc, 5/1).

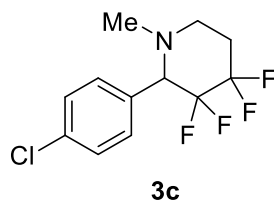
^1H NMR (300 MHz, CDCl_3) δ : 7.37 (dd, $J = 8.3, 1.7$ Hz, 2H), 7.26 (d, $J = 8.3$ Hz, 2H), 3.38 (dt, $J = 21.9, 4.6$ Hz, 1H), 3.11–3.01 (m, 1H), 2.95 (sept, $J = 6.9$ Hz, 1H), 2.60–2.18 (m, 3H), 2.11 (s, 3H), 1.30 (d, $J = 6.9$ Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 149.7, 130.2 (d, $J = 1.7$ Hz), 130.2, 126.5, 116.0 (dddd, $J = 260.5, 244.2, 32.4, 21.4$ Hz), 113.5 (dddd, $J = 254.5, 251.9, 29.8, 20.1$ Hz), 70.8 (dddd, $J = 25.1, 19.1, 3.2, 1.3$ Hz), 51.3 (d, $J = 10.5$ Hz), 43.2 (t, $J = 1.4$ Hz), 34.0, 31.3 (tdd, $J = 20.8, 3.1, 1.4$ Hz), 24.04, 24.00.

^{19}F NMR (282 MHz, CDCl_3) δ : -119.2 (dm, $J = 248.2$, 1F), -122.0 (dm, $J = 248.2$ Hz, 1F), -126.2 (ddtd, $J = 256.9, 21.3, 16.8, 15.7, 4.2$ Hz, 1F), -130.1 (ddtd, $J = 257.0, 19.1, 14.7, 4.7$ Hz, 1F).

HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{20}\text{F}_4\text{N}$ ($\text{M}+\text{H}$) 290.1526, found 290.1521.

2-(4-Chlorophenyl)-3,3,4,4-tetrafluoro-1-methylpiperidine (3c).



Yield 98 mg (70 %). Yellowish crystals. Mp 52–53 °C.

Chromatography: hexanes/EtOAc, from 5/1 to 1/1. R_f 0.25 (hexanes/EtOAc, 4/1).

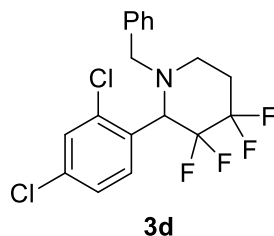
^1H NMR (300 MHz, CDCl_3) δ : 7.39 (s, 4H), 3.39 (dt, $J = 21.3, 4.5$ Hz, 1H), 3.10–3.01 (m, 1H), 2.61–2.17 (m, 3H), 2.09 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 134.99, 131.53 (d, $J = 1.8$ Hz), 131.42, 128.67, 115.70 (dddd, $J = 260.7, 244.2, 32.2, 21.3$ Hz), 113.14 (dddd, $J = 254.8, 252.3, 30.3, 20.7$ Hz), 70.34 (dddd, $J = 25.0, 19.1, 3.3, 1.3$ Hz), 51.16 (d, $J = 10.5$ Hz), 43.08 (t, $J = 1.3$ Hz), 31.15 (dddd, $J = 21.2, 19.9, 3.4, 1.3$ Hz).

^{19}F NMR (282 MHz, CDCl_3) δ : -119.6 (dm, $J = 249.0$ Hz, 1F), -122.2 (dm, $J = 249.0$ Hz, 1F), -126.2 (dm, $J = 257.0$ Hz, 1F), -130.1 (dddt, $J = 257.0, 17.5, 14.1, 4.9$ Hz, 1F).

HRMS (ESI): calcd for $\text{C}_{12}\text{H}_{13}^{35}\text{ClF}_4\text{N}$ (M+H) 282.0667, found 282.0666; calcd for $\text{C}_{12}\text{H}_{13}^{37}\text{ClF}_4\text{N}$ (M+H) 284.0638, found 284.0641.

1-Benzyl-2-(2,4-dichlorophenyl)-3,3,4,4-tetrafluoropiperidine (3d).



Yield 121 mg (62 %). Colorless crystals. Mp 113–114°C.

Chromatography: hexanes/EtOAc, 20/1. R_f 0.30 (hexanes/EtOAc, 20/1). Product isolated by chromatography was recrystallized from hexanes.

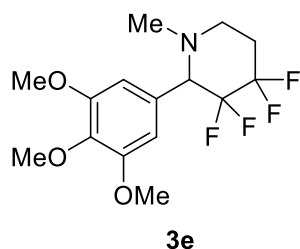
^1H NMR (300 MHz, CDCl_3) δ : 7.79 (dd, $J = 8.5, 3.2$ Hz, 1H), 7.43 (s, 1H), 7.35–7.06 (m, 6H), 4.42 (d, $J = 21.1$ Hz, 1H), 3.61 (d, $J = 13.6$ Hz, 1H), 2.96 (d, $J = 13.7$ Hz, 2H), 2.49–2.00 (m, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 137.3 (d, $J = 0.9$ Hz), 136.7, 135.5, 132.6, 132.5, 129.7, 129.5 (d, $J = 1.1$ Hz), 128.7, 128.5, 127.7, 115.9 (dddd, $J = 260.1, 244.5, 32.3, 20.9$ Hz), 113.8 (dddd, $J = 257.4, 252.8, 30.9, 21.2$ Hz), 63.9 (ddd, $J = 24.6, 17.7, 2.7$ Hz), 58.0 (t, $J = 1.2$ Hz), 47.4 (d, $J = 10.4$ Hz), 31.0 (td, $J = 21.5, 0.9$ Hz).

^{19}F NMR (282 MHz, CDCl_3) δ : -119.7 (dm, $J = 249.1$ Hz, 1F), -122.2 (dt, $J = 249.1, 15.2$ Hz, 1F), -124.9 (dq, $J = 257.8, 17.4$ Hz, 1F), -130.2 (dt, $J = 257.8, 13.9$ Hz, 1F).

HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{16}^{35}\text{Cl}_2\text{F}_4\text{N}$ (M+H) 392.0590, found 392.0578; calcd for $\text{C}_{18}\text{H}_{16}^{37}\text{Cl}^{35}\text{ClF}_4\text{N}$ (M+H) 394.0562, found 394.0552.

3,3,4,4-Tetrafluoro-1-methyl-2-(3,4,5-trimethoxyphenyl)piperidine (3e).



Yield 147 mg (87 %). Colorless crystals. Mp 97.8–98.5°C.

Chromatography: hexanes/EtOAc, 1/1. R_f 0.25 (hexanes/EtOAc, 1/1).

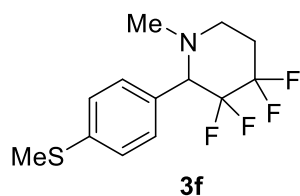
^1H NMR (300 MHz, CDCl_3) δ : 6.64 (d, J = 1.4 Hz, 2H), 3.86 (s, 9H), 3.28 (dt, J = 21.5, 4.3 Hz, 1H), 3.10–2.96 (m, 1H), 2.55–2.16 (m, 3H), 2.10 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 153.2, 138.6, 128.2, 115.8 (dddd, J = 260.7, 244.4, 32.4, 21.4 Hz), 113.3 (dddd, J = 254.5, 251.9, 29.8, 20.1 Hz), 107.3 (d, J = 1.9 Hz), 71.1 (dddd, J = 25.2, 18.9, 3.1, 1.4 Hz), 60.9, 56.2, 51.2 (d, J = 10.5 Hz), 43.1 (t, J = 1.4 Hz), 31.07 (tdd, J = 20.7, 3.6, 1.2 Hz).

^{19}F NMR (282 MHz, CDCl_3) δ : -119.3 (dm, J = 248.7, 1F), -122.1 (dm, J = 248.7 Hz, 1F), -126.1 (dtdd, J = 255.9, 21.4, 17.8, 14.1, 4.3 Hz, 1F), -130.3 (dddt, J = 255.9, 16.8, 15.0, 4.8 Hz, 1F).

HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{19}\text{F}_4\text{NO}_3$ ($\text{M}+\text{H}$) 338.1374, found 338.1373.

3,3,4,4-Tetrafluoro-1-methyl-2-[4-(methylthio)phenyl]piperidine (3f).



Yield 120 mg (81 %). Colorless crystals. Mp 109–110 °C.

Chromatography: hexanes/EtOAc, from 4/1 to 3/1. R_f 0.34 (hexanes/EtOAc, 3/1).

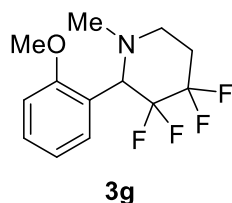
^1H NMR (300 MHz, CDCl_3) δ : 7.36 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 3.36 (dt, J = 21.5, 4.3 Hz, 1H), 3.08–3.00 (m, 1H), 2.57–2.20 (m, 3H), 2.51 (s, 3H), 2.10 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 139.7, 130.6 (d, J = 1.6 Hz), 129.5, 126.2, 115.8 (dddd, J = 260.7, 244.0, 32.5, 21.6 Hz), 113.4 (dddd, J = 254.4, 252.2, 30.4, 20.6 Hz), 70.5 (dddd, J = 25.0, 18.9, 3.1, 1.2 Hz), 51.2 (d, J = 10.5 Hz), 43.1 (t, J = 1.3 Hz), 31.2 (dddd, J = 20.9, 20.3, 3.5, 1.2 Hz), 15.5.

^{19}F NMR (282 MHz, CDCl_3) δ : -119.3 (dm, J = 249.1 Hz, 1F), -122.1 (dm, J = 249.1 Hz, 1F), -126.2 (dddd, J = 256.6, 21.6, 16.6, 3.2 Hz, 1F), -130.1 (dddt, J = 256.6, 15.8, 14.9, 4.6 Hz, 1F).

HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{16}\text{F}_4\text{NS}$ ($\text{M}+\text{H}$) 294.0934, found 294.0928.

3,3,4,4-Tetrafluoro-2-(2-methoxyphenyl)-1-methylpiperidine (3g).



Yield 83 mg (60 %). Colorless crystals. Mp 91–92 °C.

Chromatography: hexanes/EtOAc, 3/1. R_f 0.27 (hexanes/EtOAc, 3/1).

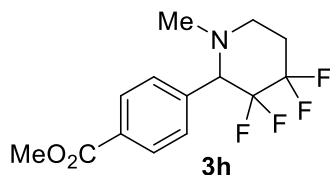
^1H NMR (300 MHz, CDCl_3) δ : 7.61 (ddd, $J = 7.7, 3.1, 1.8$ Hz, 1H), 7.35 (ddd, $J = 8.3, 7.6, 1.8$ Hz, 1H), 7.04 (ddd, $J = 7.7, 7.6, 1.1$ Hz, 1H), 6.96 (dd, $J = 8.3, 1.1$ Hz, 1H), 4.22 (d, $J = 22.9$ Hz, 1H), 3.85 (s, 3H), 3.11–3.01 (m, 1H), 2.68–2.20 (m, 3H), 2.09 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 158.7, 130.9 (d, $J = 4.2$ Hz), 129.7, 121.2, 120.8, 116.0 (dddd, $J = 260.3, 244.6, 32.9, 21.4$ Hz), 114.0 (dddd, $J = 255.8, 251.7, 29.8, 20.1$ Hz), 111.2, 61.2 (ddd, $J = 25.6, 19.0, 3.4$ Hz), 55.9, 51.6 (d, $J = 10.5$ Hz), 42.8 (t, $J = 1.4$ Hz), 31.5 (tdd, $J = 21.2, 20.2, 3.3, 1.2$ Hz).

^{19}F NMR (282 MHz, CDCl_3) δ : -119.1 (dm, $J = 247.4$ Hz, 1F), -122.3 (dm, $J = 247.4$ Hz, 1F), -125.9 (dm, $J = 256.0$ Hz), -131.6 (dddd, $J = 256.0, 16.7, 13.5, 7.3$ Hz).

HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{16}\text{F}_4\text{NO}$ ($\text{M}+\text{H}$) 278.1163, found 278.1161.

Methyl 4-(3,3,4,4-tetrafluoro-1-methylpiperidin-2-yl)benzoate (3h).



Yield 70 mg (46 %). Colorless crystals. Mp 101–102 °C.

Chromatography: hexanes/EtOAc, 2/1. R_f 0.26 (hexanes/EtOAc, 2/1).

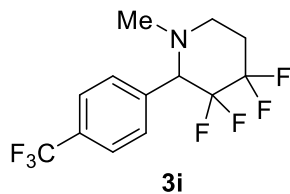
^1H NMR (300 MHz, CDCl_3) δ : 8.07 (d, $J = 8.2$ Hz, 2H), 7.53 (dd, $J = 8.2, 1.6$ Hz, 2H), 3.93 (s, 3H), 3.46 (dt, $J = 21.2, 4.5$ Hz, 1H), 3.11–2.99 (m, 1H), 2.60–2.18 (m, 3H), 2.08 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 166.76, 137.90, 130.89, 130.31 (d, $J = 1.7$ Hz), 129.57, 115.63 (dddd, $J = 260.6, 244.3, 32.2, 21.3$ Hz), 113.11 (dddd, $J = 255.2, 252.8, 30.5, 20.8$ Hz), 70.70 (dddd, $J = 25.0, 19.0, 3.3, 1.3$ Hz), 52.20, 51.16 (d, $J = 10.5$ Hz), 43.10 (t, $J = 1.4$ Hz), 31.11 (dddd, $J = 21.2, 20.0, 3.3, 1.2$ Hz).

^{19}F NMR (282 MHz, CDCl_3) δ : -119.4 (dm, $J = 249.6$ Hz, 1F), -122.4 (dm, $J = 249.6$ Hz, 1F), -125.9 (dm, $J = 257.5$ Hz, 1F), -130.04 (dddt, $J = 257.5, 18.0, 14.4, 4.9$ Hz).

HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{16}\text{F}_4\text{NO}_2$ ($\text{M}+\text{H}$) 306.1112, found 306.1120.

3,3,4,4-Tetrafluoro-1-methyl-2-[4-(trifluoromethyl)phenyl]piperidine (3i).



Yield 124 mg (78 %). Colorless crystals. Mp 69–70 °C.

Chromatography: hexanes/EtOAc, 4/1. R_f 0.25 (hexanes/EtOAc, 4/1).

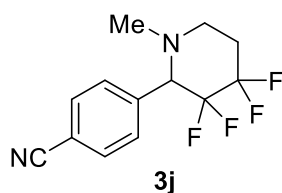
^1H NMR (300 MHz, CDCl_3) δ : 7.68 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 3.49 (dt, J = 21.0, 4.4 Hz, 1H), 3.08 (d, J = 11.1 Hz, 1H), 2.68–2.21 (m, 3H), 2.11 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 137.1, 131.4 (q, J = 32.4 Hz), 130.8 (d, J = 1.7 Hz), 125.4 (q, J = 3.8 Hz), 122.2 (q, J = 271.8 Hz), 115.7 (dddd, J = 260.8, 244.2, 32.2, 21.3 Hz), 113.2 (dddd, J = 255.0, 253.0, 30.5, 20.8 Hz), 70.7 (dddd, J = 24.9, 19.1, 3.4, 1.3 Hz), 51.2 (d, J = 10.4 Hz), 43.2 (t, J = 1.4 Hz), 31.2 (dddd, J = 21.1, 20.2, 3.3, 1.1 Hz).

^{19}F NMR (282 MHz, CDCl_3) δ : -62.5, -119.5 (dm, J = 250.4 Hz, 1F), -122.42 (dm, J = 250.4 Hz, 1F), -125.90 (ddtd, J = 257.7, 20.9, 16.6, 3.9 Hz, 1F), -130.02 (dddt, J = 257.7, 17.7, 13.3, 4.7 Hz, 1F).

HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{13}\text{F}_7\text{N}$ ($\text{M}+\text{H}$) 316.0931, found 316.0923.

4-(3,3,4,4-Tetrafluoro-1-methylpiperidin-2-yl)benzonitrile (3j).



Yield 46 mg (34 %). Colorless crystals. Mp 102–104 °C. Chromatography: hexanes/EtOAc, 2/1. R_f 0.28 (hexanes/EtOAc, 2/1).

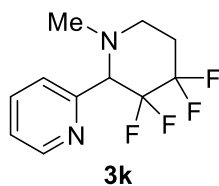
^1H NMR (300 MHz, CDCl_3) δ : 7.68 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 3.46 (dt, J = 20.8, 4.4 Hz, 1H), 3.09–3.00 (m, 1H), 2.60–2.18 (m, 3H), 2.06 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 138.3, 132.2, 131.1 (d, J = 1.7 Hz), 118.5, 113.1, 115.5 (dddd, J = 260.8, 243.7, 32.1, 21.2 Hz), 113.1 (dddd, J = 255.9, 253.4, 30.7, 20.8 Hz), 70.6 (dddd, J = 24.9, 19.0, 3.4, 1.3 Hz), 51.1 (d, J = 10.5 Hz), 43.2 (t, J = 1.3 Hz), 31.1 (dddd, J = 21.1, 20.1, 3.3, 1.3 Hz).

^{19}F NMR (282 MHz, CDCl_3) δ : -119.5 (dm, J = 249.9 Hz, 1F), -122.5 (dm, J = 249.9 Hz, 1F), -125.7 (ddd, J = 257.1, 21.5, 16.2, 4.6 Hz, 1F), -129.9 (dddd, J = 257.8, 17.0, 13.9, 5.8, 4.4 Hz, 1F).

HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{13}\text{F}_4\text{N}_2$ ($\text{M}+\text{H}$) 273.1009, found 273.1008.

2-(3,3,4,4-Tetrafluoro-1-methylpiperidin-2-yl)pyridine (3k).



Yield 92 mg (74 %). Colorless oil.

Chromatography: hexanes/EtOAc, from 1/1 to 1/2. R_f 0.22 (hexanes/EtOAc, 1/1).

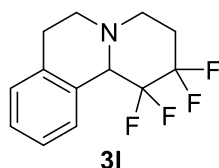
^1H NMR (300 MHz, CDCl_3) δ : 8.62 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H), 7.72 (ddd, J = 7.8, 6.8, 1.8 Hz, 1H), 7.52 (ddd, J = 7.8, 1.2, 1.0 Hz, 1H), 7.28 (ddd, J = 6.8, 4.9, 1.2 Hz, 1H), 3.68 (dt, J = 21.8, 4.7 Hz, 1H), 3.07–2.99 (m, 1H), 2.61–2.16 (m, 3H), 2.08 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 153.3, 149.4, 136.5, 125.0 (d, J = 3.2 Hz), 123.8, 115.5 (dddd, J = 260.2, 244.1, 31.9, 21.0 Hz), 113.5 (dddd, J = 256.8, 252.9, 30.7, 20.7 Hz), 72.4 (dddd, J = 24.2, 18.1, 2.7, 1.0 Hz), 51.2 (d, J = 10.5 Hz), 43.0 (t, J = 1.3 Hz), 31.2 (tdd, J = 21.0, 3.3, 1.0 Hz).

^{19}F NMR (282 MHz, CDCl_3) δ : -119.5 (dm, J = 248.7 Hz, 1F), -122.9 (dm, J = 248.7 Hz, 1F), -125.7 (dm, J = 256.6 Hz, 1F), -131.0 (dm, J = 256.6 Hz, 1F).

HRMS (ESI): calcd for $\text{C}_{11}\text{H}_{13}\text{F}_4\text{N}_2$ ($\text{M}+\text{H}$) 249.1009, found 249.1010.

1,1,2,2-Tetrafluoro-2,3,4,6,7,11b-hexahydro-1H-pyrido[2,1-a]isoquinoline (3l).



Yield 87 mg (67 %). Colorless oil.

Chromatography: hexanes/EtOAc, 3/1. R_f 0.26 (hexanes/EtOAc, 3/1).

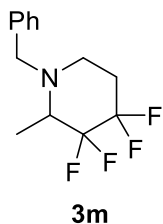
^1H NMR (300 MHz, CDCl_3) δ : 7.55 (d, J = 7.0 Hz, 1H), 7.33–7.17 (m, 3H), 4.08 (d, J = 23.7 Hz, 1H), 3.26–2.96 (m, 4H), 2.91–2.70 (m, 2H), 2.58–2.17 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 136.2, 129.3, 128.6, 128.1 (d, J = 11.0 Hz), 127.8, 126.0 (d, J = 1.5 Hz), 116.4 (dddd, J = 261.3, 244.5, 31.4, 21.8 Hz), 115.2 (dddd, J = 262.2, 257.0, 29.9, 20.7 Hz), 62.0 (dddd, J = 20.9, 19.6, 2.5, 1.2 Hz), 50.1 (d, J = 9.8 Hz), 48.4 (d, J = 1.9 Hz), 31.0 (ddd, J = 21.8, 19.0, 2.6, 1.3 Hz), 29.8.

^{19}F NMR (282 MHz, CDCl_3) δ : -116.6 (ddqd, J = 251.6, 34.9, 14.2, 4.1 Hz, 1F), -119.6 (dt, J = 251.6, 13.6 Hz, 1F), -124.0 (ddt, J = 255.3, 23.8, 15.0 Hz, 1F), -128.4 (d, J = 255.3 Hz, 1F).

HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{14}\text{F}_4\text{N}$ ($\text{M}+\text{H}$) 260.1057, found 260.1064.

1-Benzyl-3,3,4,4-tetrafluoro-2-methylpiperidine (3m).



Yield 90 mg (68 %). Colorless oil.

Chromatography: hexanes/EtOAc, 20/1. R_f 0.30 (hexanes/EtOAc, 20/1).

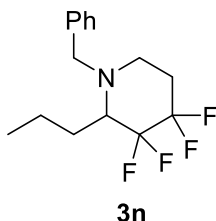
^1H NMR (300 MHz, CDCl_3) δ : 7.44–7.30 (m, 5H), 4.00 (d, $J = 13.6$ Hz, 1H), 3.44 (d, $J = 13.6$ Hz, 1H), 3.13–2.97 (m, 1H), 2.93–2.84 (m, 1H), 2.51–2.40 (m, 1H), 2.24–2.08 (m, 2H), 1.39 (d, $J = 6.6$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 138.4, 128.7, 128.6, 127.5, 116.2 (tt, $J = 252.4, 26.7$ Hz), 115.0 (tt, $J = 254.6, 25.4$ Hz), 58.8 (t, $J = 22.7$ Hz), 56.0, 45.5 (t, $J = 5.2$ Hz), 31.2 (t, $J = 20.6$ Hz), 9.8.

^{19}F NMR (282 MHz, CDCl_3) δ : -118.9 (d, $J = 255.1$ Hz, 1F), -120.0 (d, $J = 255.1$ Hz, 1F), -128.1 (br s, 1F), -131.1 (dd, $J = 252.8, 14.0$ Hz, 1F).

HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{16}\text{F}_4\text{N}$ ($\text{M}+\text{H}$) 262.1213, found 262.1213.

1-Benzyl-3,3,4,4-tetrafluoro-2-propylpiperidine (3n).



Yield 87 mg (60 %). Colorless oil.

Chromatography: hexanes/EtOAc, 40/1. R_f 0.26 (hexanes/EtOAc, 40/1).

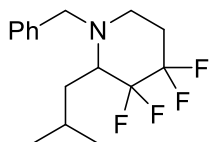
^1H NMR (300 MHz, CDCl_3) δ : 7.41–7.28 (m, 5H), 3.86 (d, $J = 14.0$ Hz, 1H), 3.78 (d, $J = 14.0$ Hz, 1H), 3.20–3.06 (m, 1H), 2.97 (dt, $J = 14.1, 5.1$ Hz, 1H), 2.69 (ddd, $J = 13.1, 8.5, 4.2$ Hz, 1H), 2.29–2.10 (m, 2H), 1.83–1.41 (m, 4H), 1.00 (t, $J = 7.2$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 139.1 (t, $J = 1.2$ Hz), 128.6, 128.5, 127.4, 116.5 (tt, $J = 252.1, 26.9$ Hz), 116.0 (tt, $J = 258.9, 25.4$ Hz), 62.6 (t, $J = 21.2$ Hz), 53.4, 43.6 (t, $J = 4.3$ Hz), 29.0 (t, $J = 20.4$ Hz), 26.4 (ddd, $J = 3.8, 2.5, 1.4$ Hz), 19.9, 14.1.

^{19}F NMR (282 MHz, CDCl_3) δ : -117.1 (s, 2F), -123.4 (br s, 1F), -127.1 (d, $J = 253.4$ Hz, 1F).

HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{20}\text{F}_4\text{N}$ ($\text{M}+\text{H}$) 290.1526, found 290.1529.

1-Benzyl-3,3,4,4-tetrafluoro-2-isobutylpiperidine (3o).



3o

Yield 92 mg (60 %). Colorless oil.

Chromatography: hexanes/EtOAc, 40/1. R_f 0.32 (hexanes/EtOAc, 40/1).

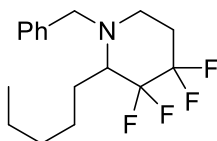
^1H NMR (300 MHz, CDCl_3) δ : 7.30–7.17 (m, 5H), 3.73 (s, 2H), 3.12 (q, $J = 11.3$ Hz, 1H), 2.87 (dt, $J = 14.3$, 5.3 Hz, 1H), 2.62 (ddd, $J = 14.4$, 8.6, 4.2 Hz, 1H), 2.19–2.01 (m, 2H), 1.81–1.60 (m, 2H), 1.42 (ddd, $J = 14.8$, 9.5, 3.8 Hz, 1H), 0.89 (d, $J = 6.6$ Hz, 3H), 0.84 (d, $J = 6.5$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 139.1, 128.6, 128.5, 127.5, 116.5 (tt, $J = 252.2$, 27.1 Hz), 116.1 (tt, $J = 259.7$, 25.4 Hz), 60.9 (t, $J = 21.1$ Hz), 53.5, 43.4 (t, $J = 4.0$ Hz), 33.1 (ddd, $J = 3.6$, 2.2, 1.5 Hz), 28.8 (t, $J = 20.4$ Hz), 25.0, 23.7, 21.4.

^{19}F NMR (282 MHz, CDCl_3) δ : -117.6 (s, 2F), -124.0 (br s, 1F), -128.0 (d, $J = 254.5$ Hz, 1F).

HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{22}\text{F}_4\text{N}$ ($\text{M}+\text{H}$) 304.1683, found 304.1676.

3,3,4,4-Tetrafluoro-1-methyl-2-pentylpiperidine (3p).



3p

Yield 87 mg (55 %). Colorless oil.

Chromatography: hexanes/EtOAc, 40/1. R_f 0.35 (hexanes/EtOAc, 40/1).

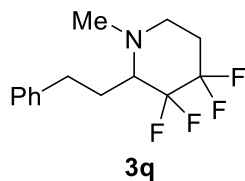
^1H NMR (300 MHz, CDCl_3) δ : 7.41–7.27 (m, 5H), 3.81 (q, $J = 11.5$ Hz, 2H), 3.17–3.02 (m, 1H), 3.01–2.92 (m, 1H), 2.73–2.62 (m, 1H), 2.29–2.10 (m, 2H), 1.79 (q, $J = 7.4$ Hz, 2H), 1.67–1.29 (m, 6H), 0.95 (t, $J = 6.8$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 139.0, 128.62, 128.56, 127.5, 116.5 (tt, $J = 252.4$, 26.8 Hz), 116.1 (tt, $J = 259.1$, 25.5 Hz), 62.9 (t, $J = 21.2$ Hz), 53.9, 43.7 (t, $J = 4.5$ Hz), 31.8, 29.1 (t, $J = 20.5$ Hz), 26.3, 24.2 (ddd, $J = 3.9$, 2.6, 1.4 Hz), 22.6, 14.1.

^{19}F NMR (282 MHz, CDCl_3) δ : -117.9 (s, 2F), -112.4 (br. s, 1F), -127.9 (d, $J = 250.5$ Hz, 1F).

HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{24}\text{F}_4\text{N}$ ($\text{M}+\text{H}$) 318.1839, found 318.1842.

3,3,4,4-Tetrafluoro-1-methyl-2-(2-phenylethyl)piperidine (3q).



Yield 94 mg (68 %). Colorless oil.

Chromatography: hexanes/EtOAc, 5/1. R_f 0.30 (hexanes/EtOAc, 5/1).

^1H NMR (300 MHz, CDCl_3) δ : 7.40-7.23 (m, 5H), 3.07-2.68 (m, 5H), 2.48 (s, 3H), 2.41-1.98 (m, 4H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 141.6, 128.6, 128.5, 126.2, 116.0 (tt, $J = 252.1, 26.7$ Hz), 115.8 (tdd, $J = 257.6, 28.4, 22.8$ Hz), 62.8 (t, $J = 21.3$ Hz), 49.6 (d, $J = 9.0$ Hz), 39.3, 32.4 (t, $J = 1.2$ Hz), 29.8 (t, $J = 20.5$ Hz), 26.6 (q, $J = 1.8$ Hz).

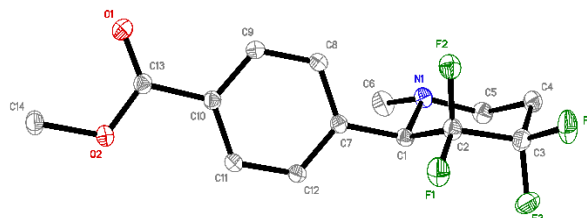
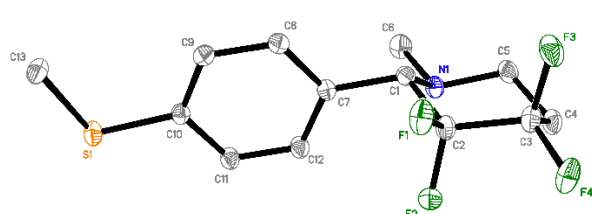
^{19}F NMR (282 MHz, CDCl_3) δ : -118.4 (dd, $J = 250.7, 23.5$ Hz, 1F), 120.4 (d, $J = 250.7$ Hz), -126.2 (d, $J = 254.5$ Hz), -128.3 (br s).

HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{18}\text{F}_4\text{N}$ ($\text{M}+\text{H}$) 276.1370, found 276.1374.

X-ray data

X-ray diffraction data were collected at 100 K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (graphite monochromator, shutterless ϕ - and ω -scan technique), using MoK α irradiation. The intensity data were integrated by the SAINT program¹⁵ and corrected for absorption and decay using SADABS.¹⁶ The structure was solved by direct methods using SHELXT¹⁷ and refined on F^2 using SHELXL-2018.¹⁸ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The tetrafluoropiperidinyl fragment is disordered over two positions with the site occupancy ratio of 0.9674(7):0.0326(7). The SHELXTL program suite¹ was used for molecular graphics. The CIF files were deposited with the Cambridge Crystallographic Data Centre (**3f**: 2032382; **3h**: 2032383).

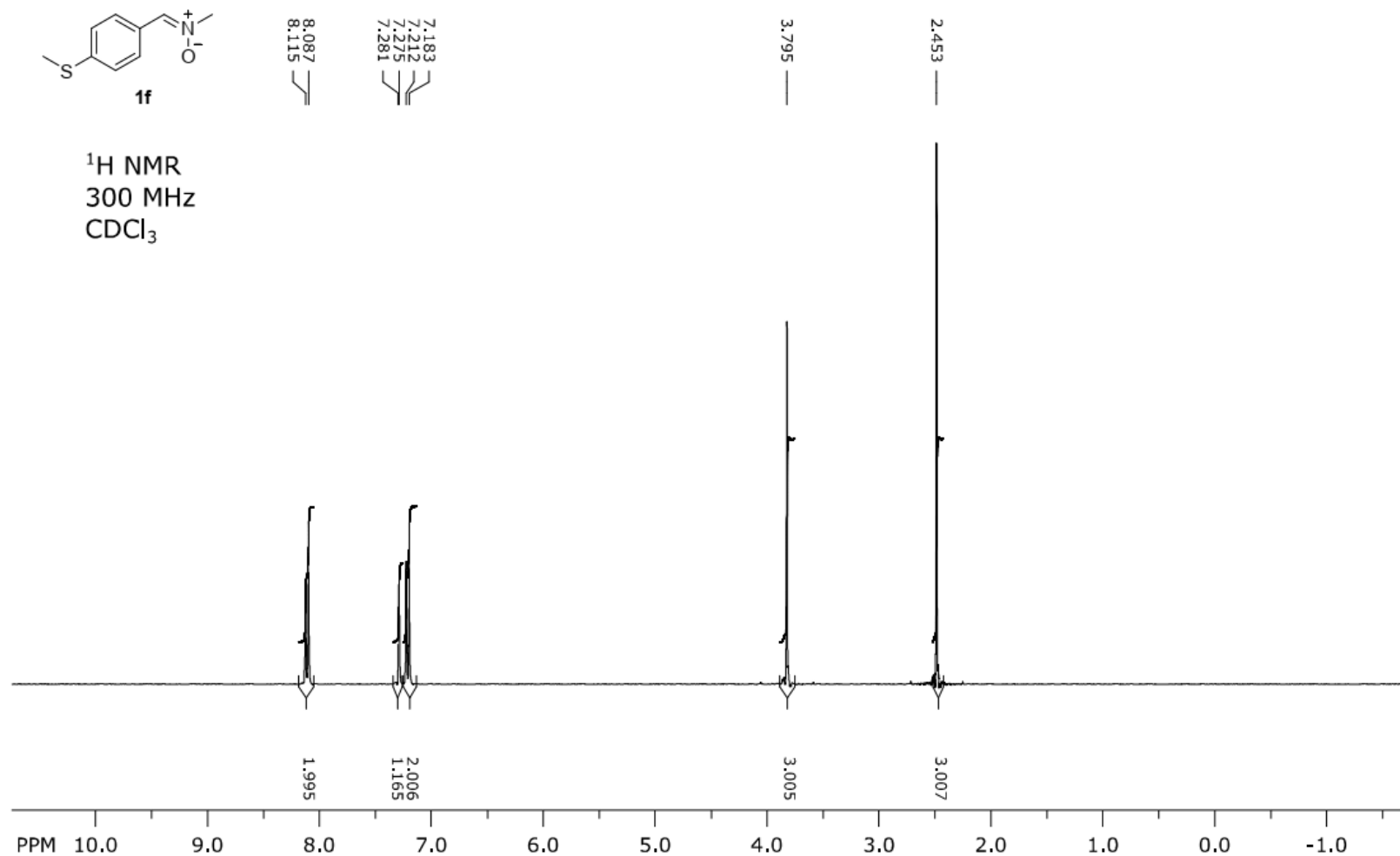
Table S1: Crystal data and structure refinement for **3f,h**.

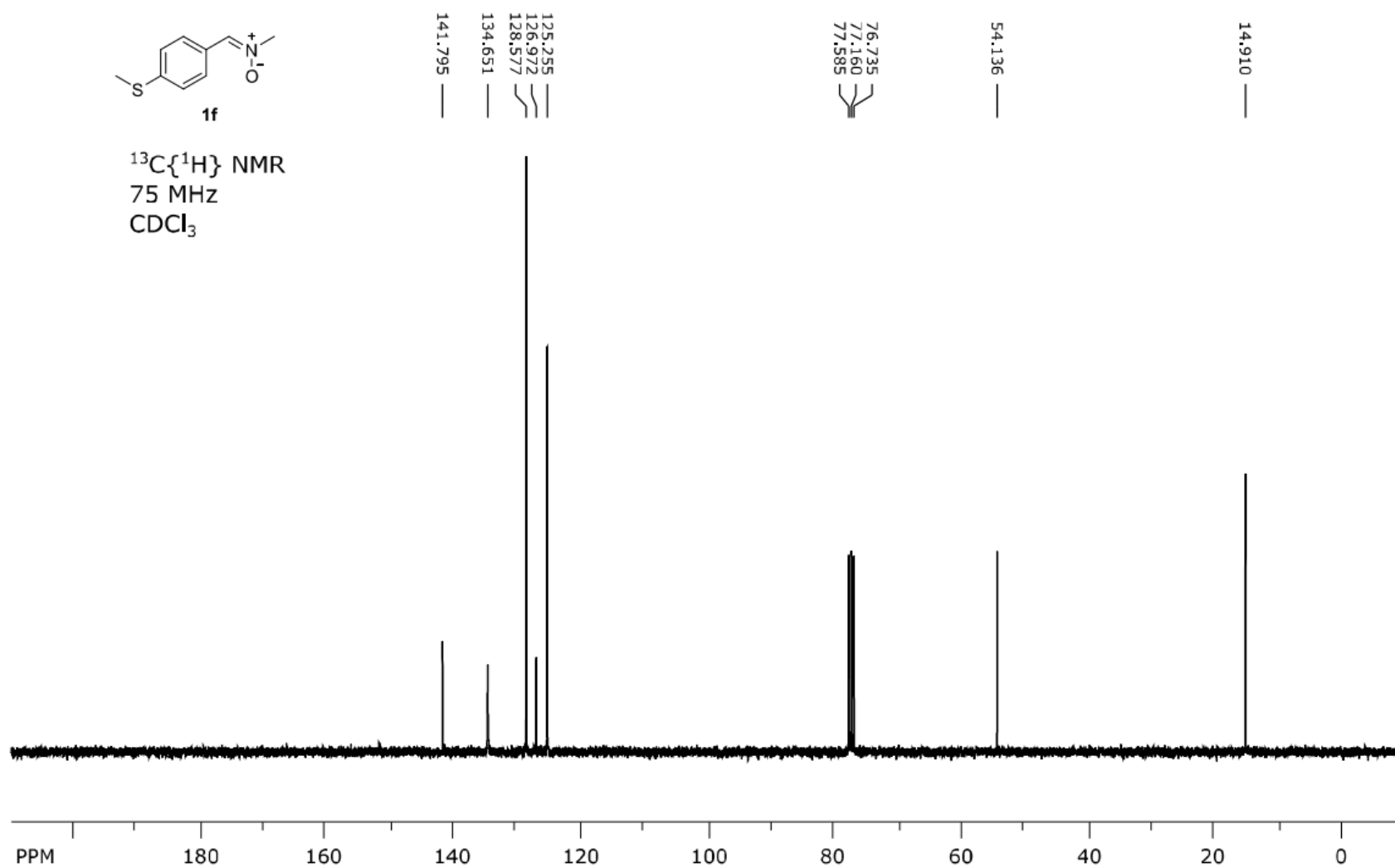


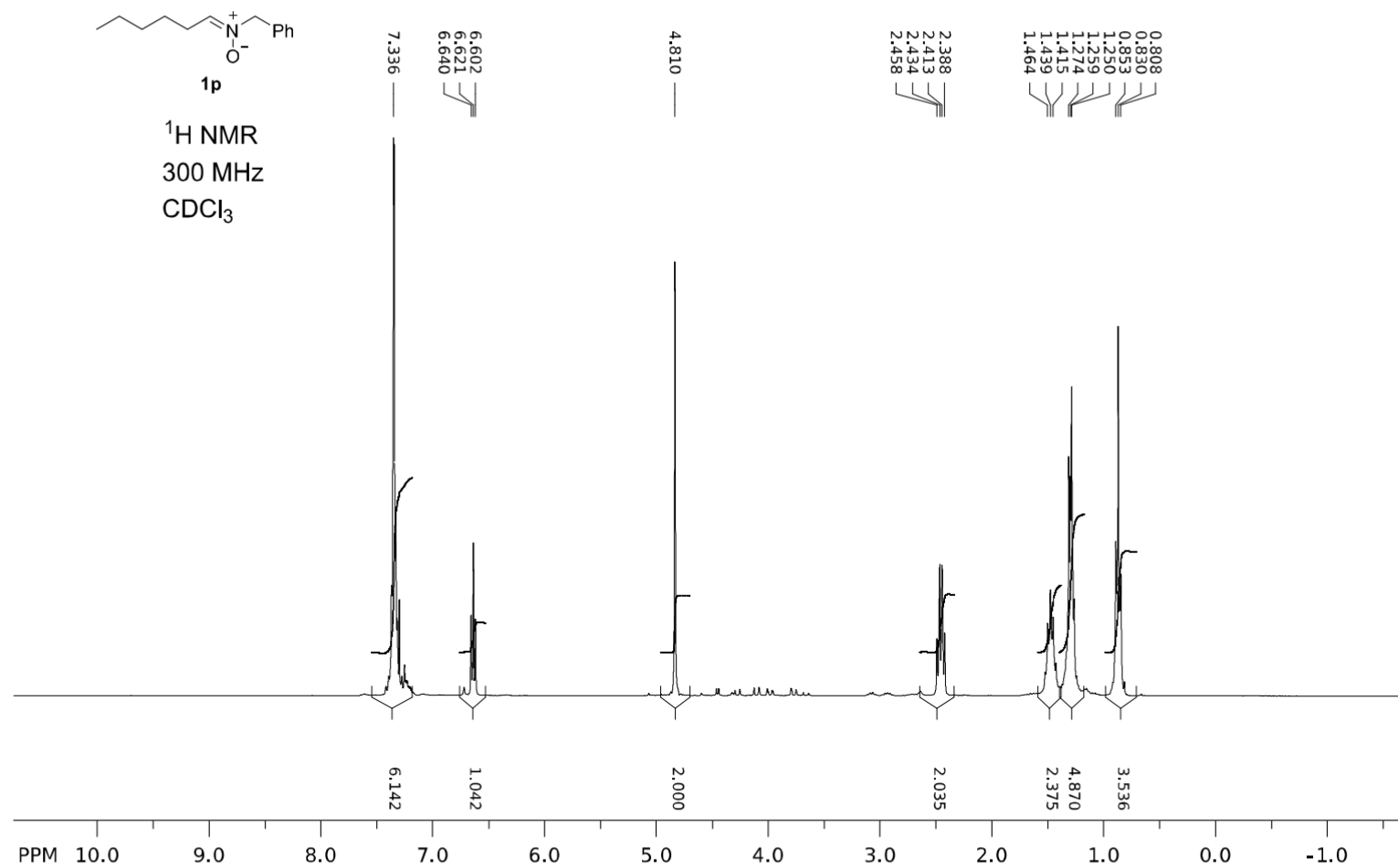
Compound	3f		3h	
Empirical formula	C ₁₃ H ₁₅ F ₄ N S		C ₁₄ H ₁₅ F ₄ N O ₂	
Formula weight	293.32		305.27	
Temperature	100(2) K		100(2) K	
Wavelength	0.71073 Å		0.71073 Å	
Crystal system	Monoclinic		Monoclinic	
Space group	P2 ₁ /c		P2 ₁ /c	
Unit cell dimensions	a = 13.2686(3) Å	$\alpha = 90^\circ$	a = 13.4130(3) Å	$\alpha = 90^\circ$
	b = 7.4126(2) Å	$\beta = 93.2710(10)^\circ$	b = 7.3746(2) Å	$\beta = 90.2570(10)^\circ$
	c = 13.3406(3) Å	$\gamma = 90^\circ$	c = 13.8840(3) Å	$\gamma = 90^\circ$
Volume	1309.97(5) Å ³		1373.33(6) Å ³	
Z	4		4	
Density (calculated)	1.487 g/cm ³		1.476 g/cm ³	
Absorption coefficient	0.280 mm ⁻¹		0.134 mm ⁻¹	
F(000)	608		632	
Crystal size	0.58 x 0.24 x 0.14 mm ³		0.59 x 0.56 x 0.15 mm ³	
Theta range for data collection	3.059 to 36.325°		2.934 to 37.060°	
Index ranges	-22 ≤ h ≤ 21, -12 ≤ k ≤ 12, -22 ≤ l ≤ 22		-22 ≤ h ≤ 22, -12 ≤ k ≤ 12, -23 ≤ l ≤ 23	
Reflections collected	59051		52704	
Independent reflections	6357 [R(int) = 0.0386]		7002 [R(int) = 0.0350]	
Observed reflections	5116		5318	
Completeness to theta = 25.242°	99.80%		99.80%	
Absorption correction	Semi-empirical from equivalents		Semi-empirical from equivalents	
Max. and min. transmission	0.6967 and 0.6461		0.7473 and 0.6996	
Refinement method	Full-matrix least-squares on F ²		Full-matrix least-squares on F ²	
Data / restraints / parameters	6357 / 12 / 205		7002 / 0 / 192	
Goodness-of-fit on F ²	1.023		1.046	
Final R indices [I > 2σ(I)]	R1 = 0.0364, wR2 = 0.0896		R1 = 0.0406, wR2 = 0.1097	
R indices (all data)	R1 = 0.0509, wR2 = 0.0984		R1 = 0.0606, wR2 = 0.1205	
Largest diff. peak and hole	0.778 and -0.392 e.Å ⁻³		0.530 and -0.285 e.Å ⁻³	

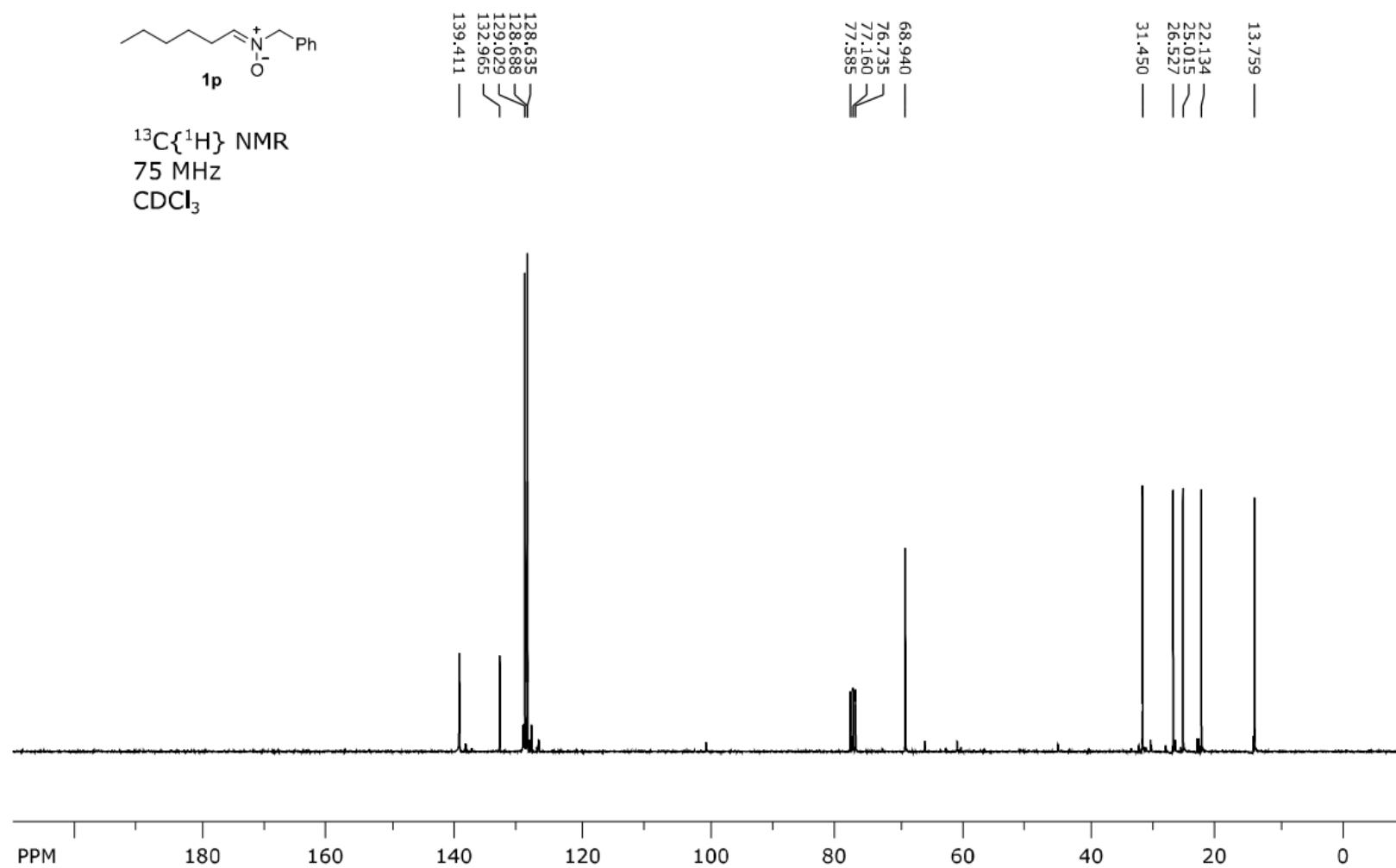
References

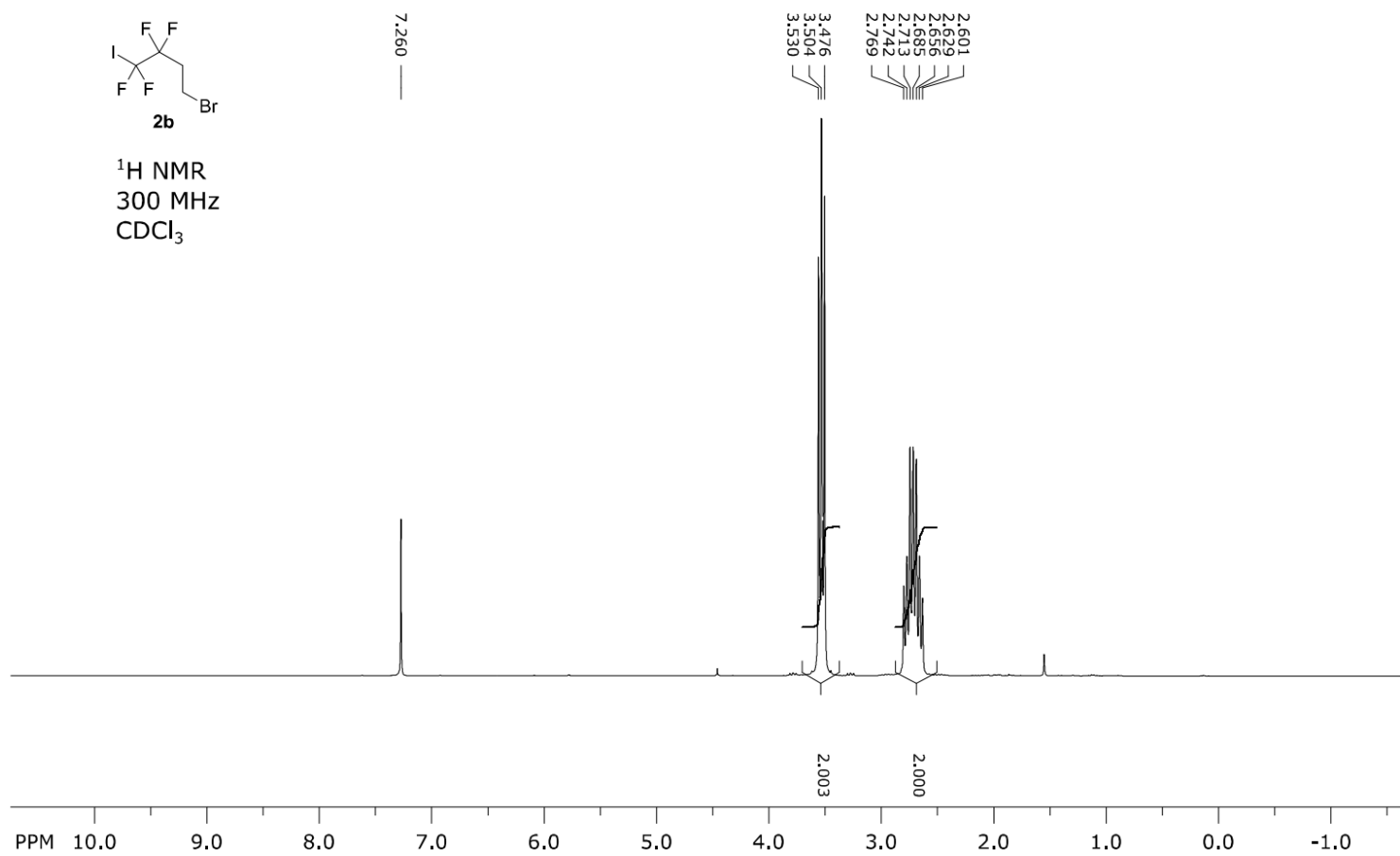
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17. Sheldrick, G. M. *Acta Cryst.* **2015**, A71, 3–8.
18. Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3–8.





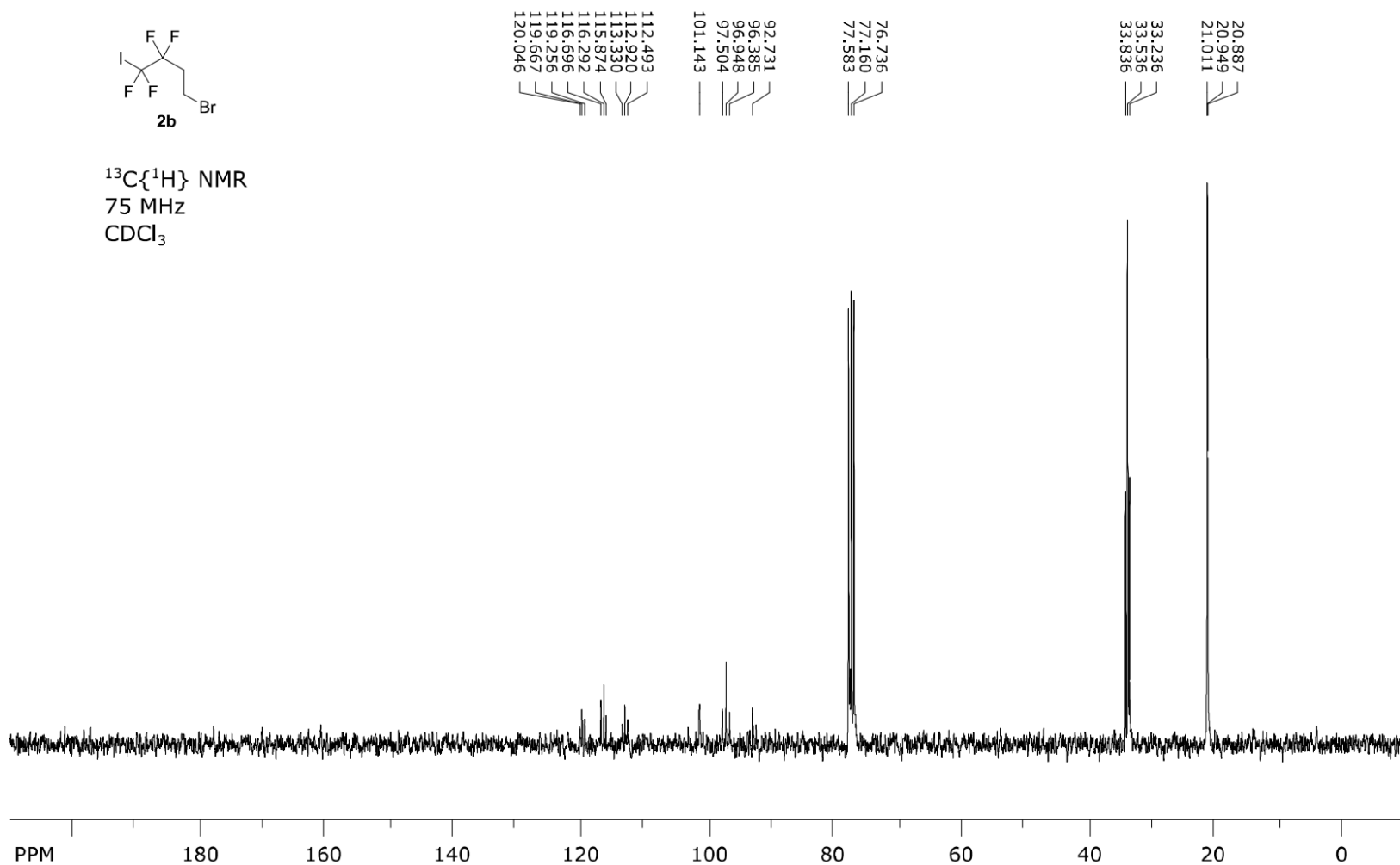


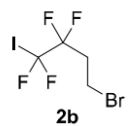




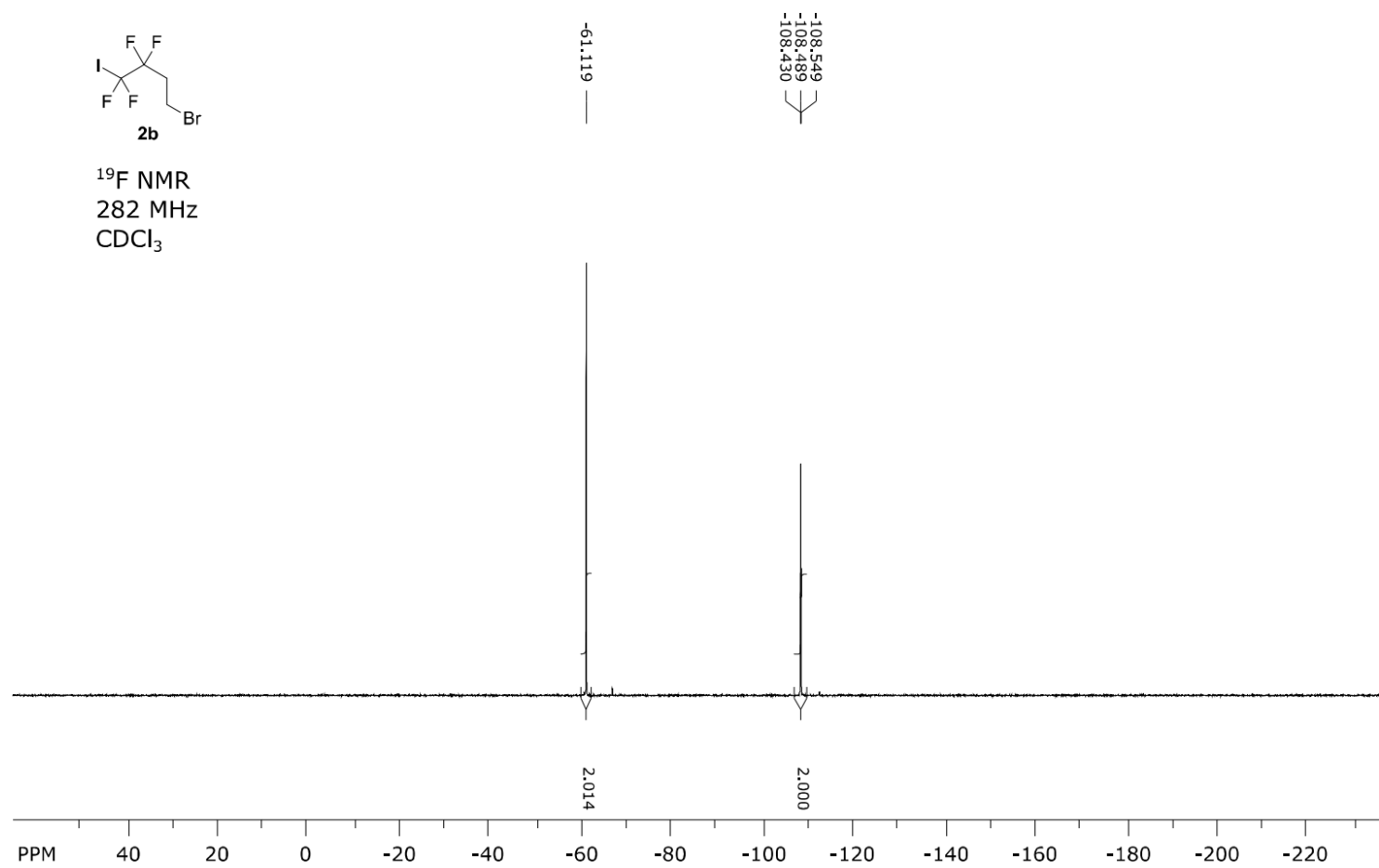


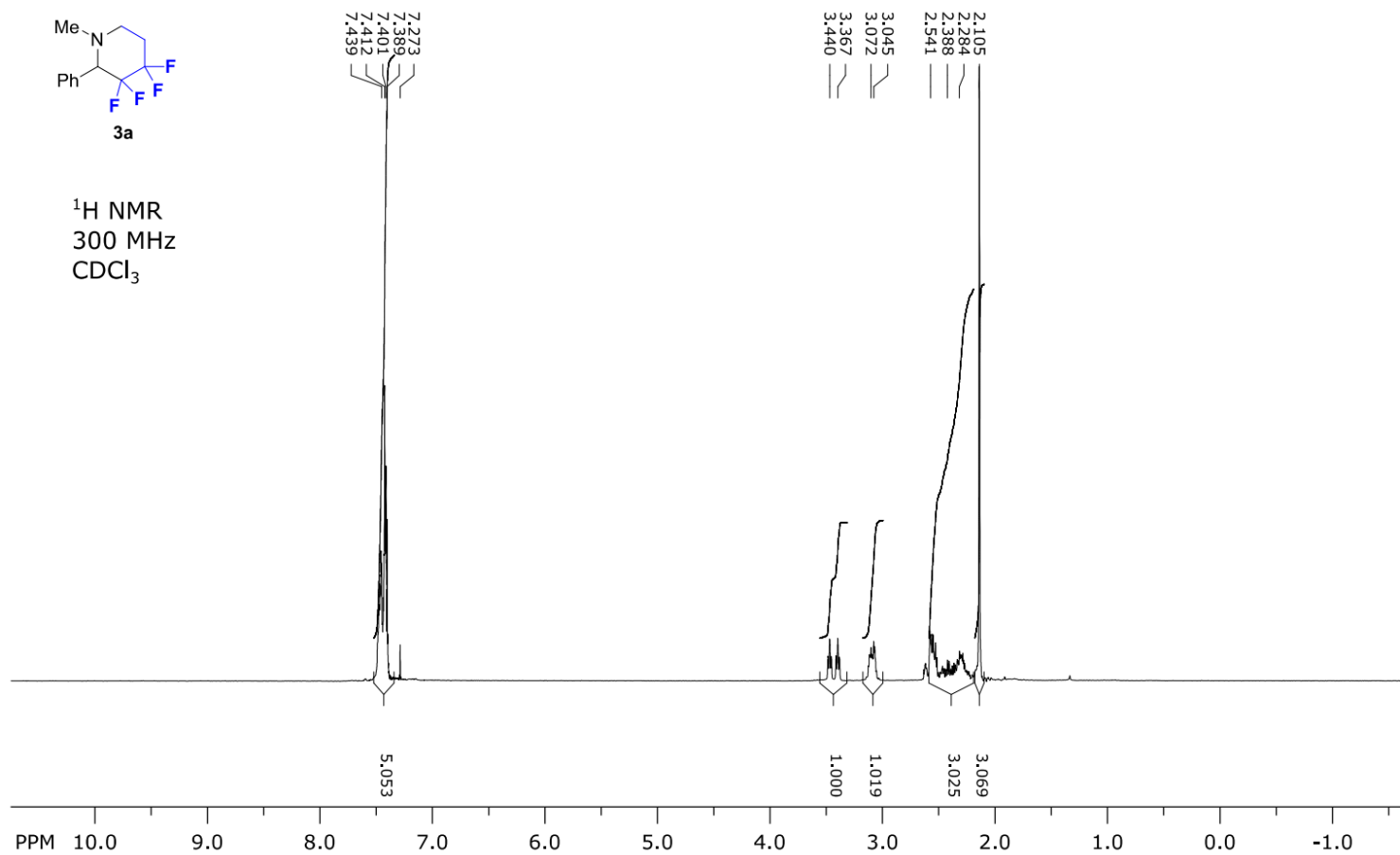
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75 MHz
 CDCl_3

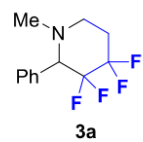




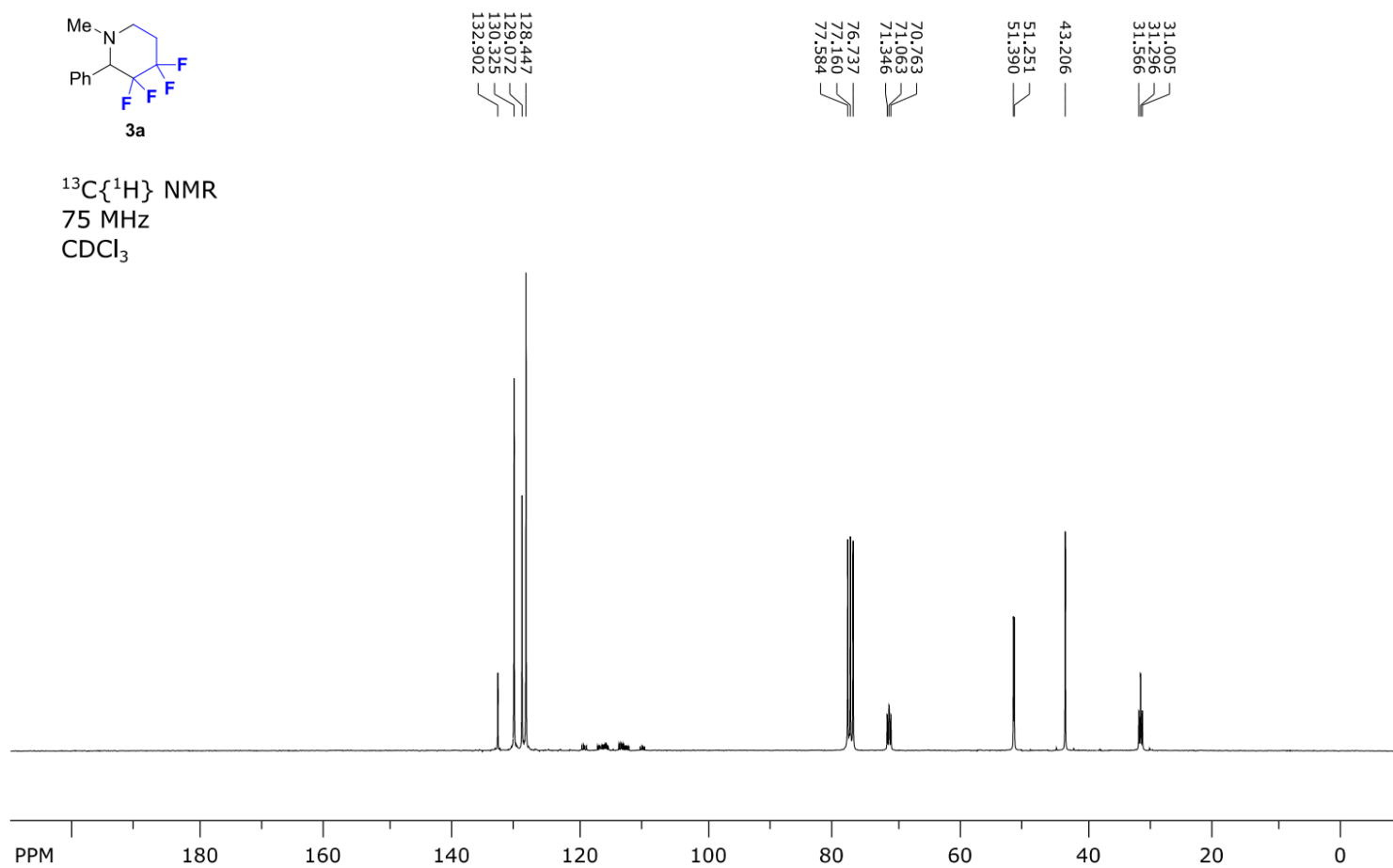
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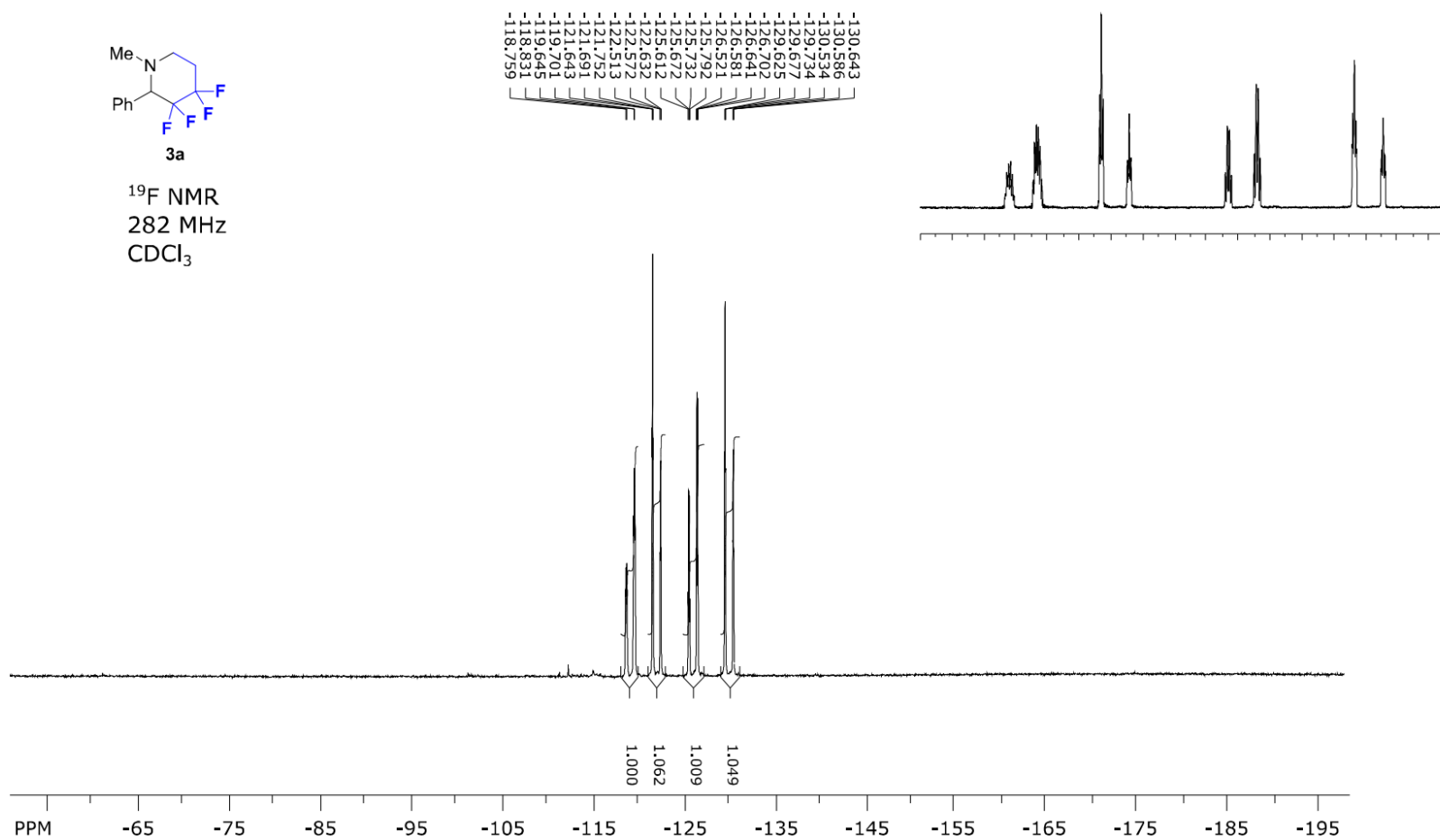






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75 MHz
 CDCl_3

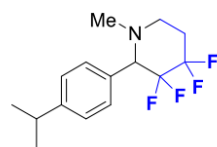






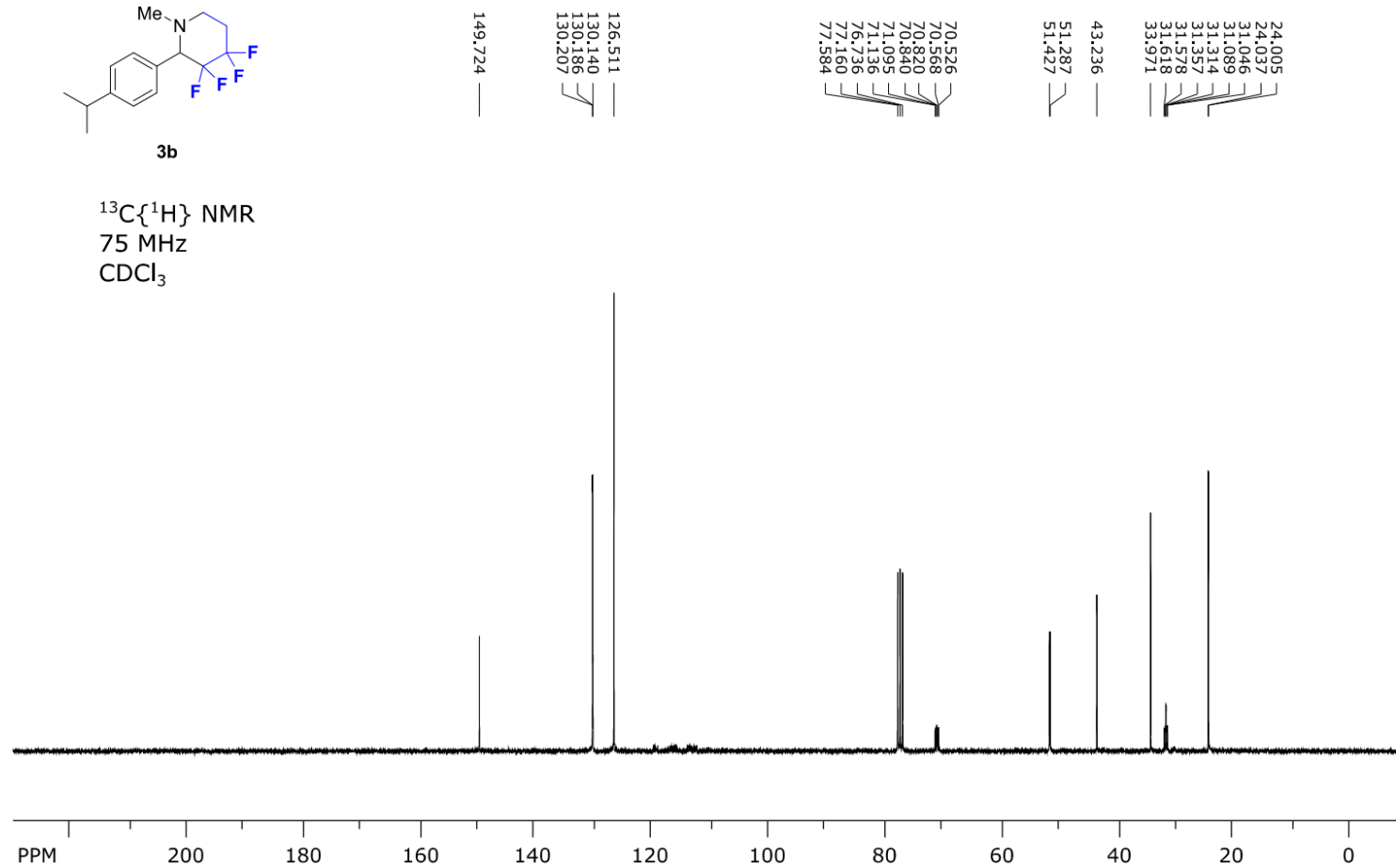
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7.276	—
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7.379	—

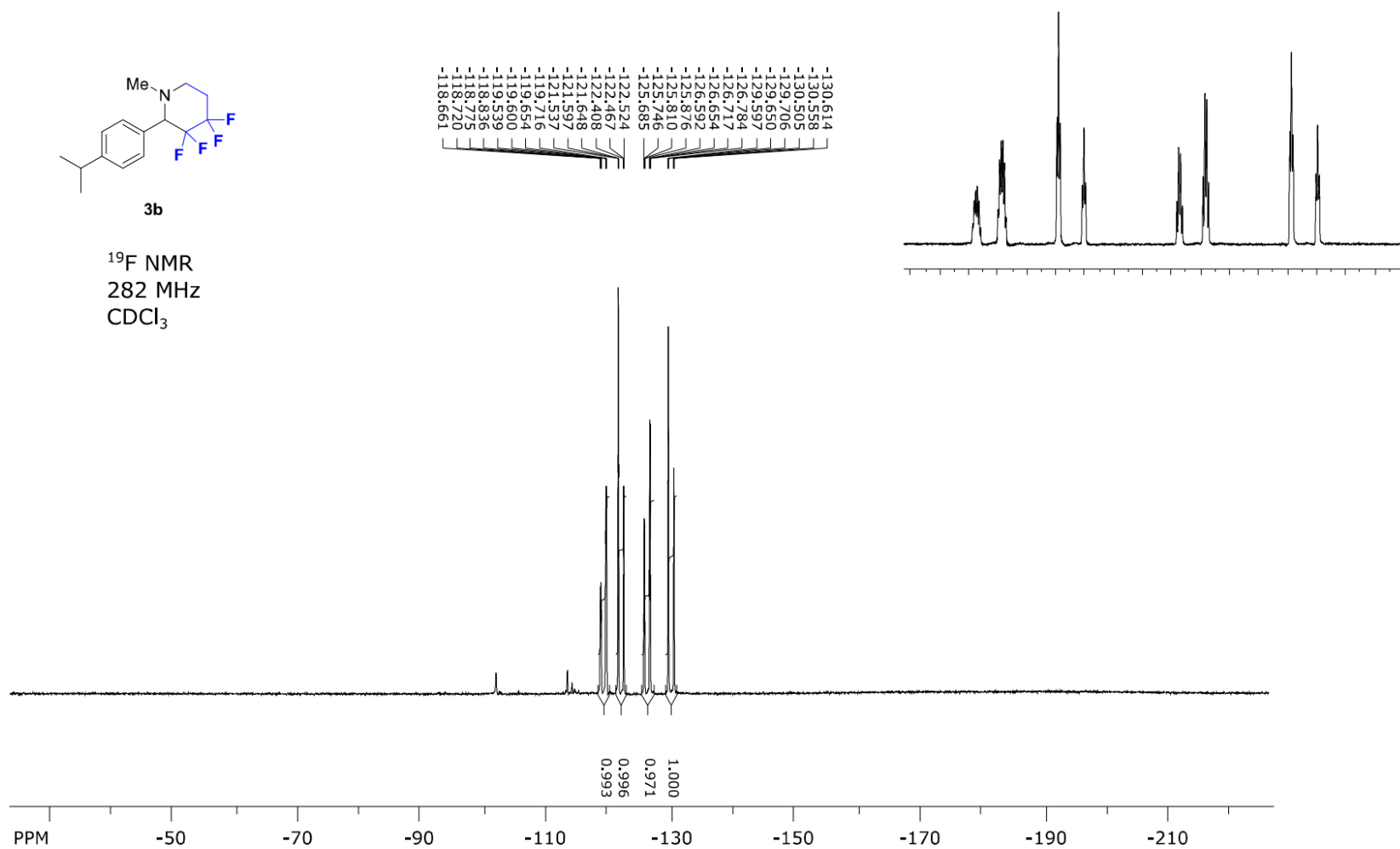


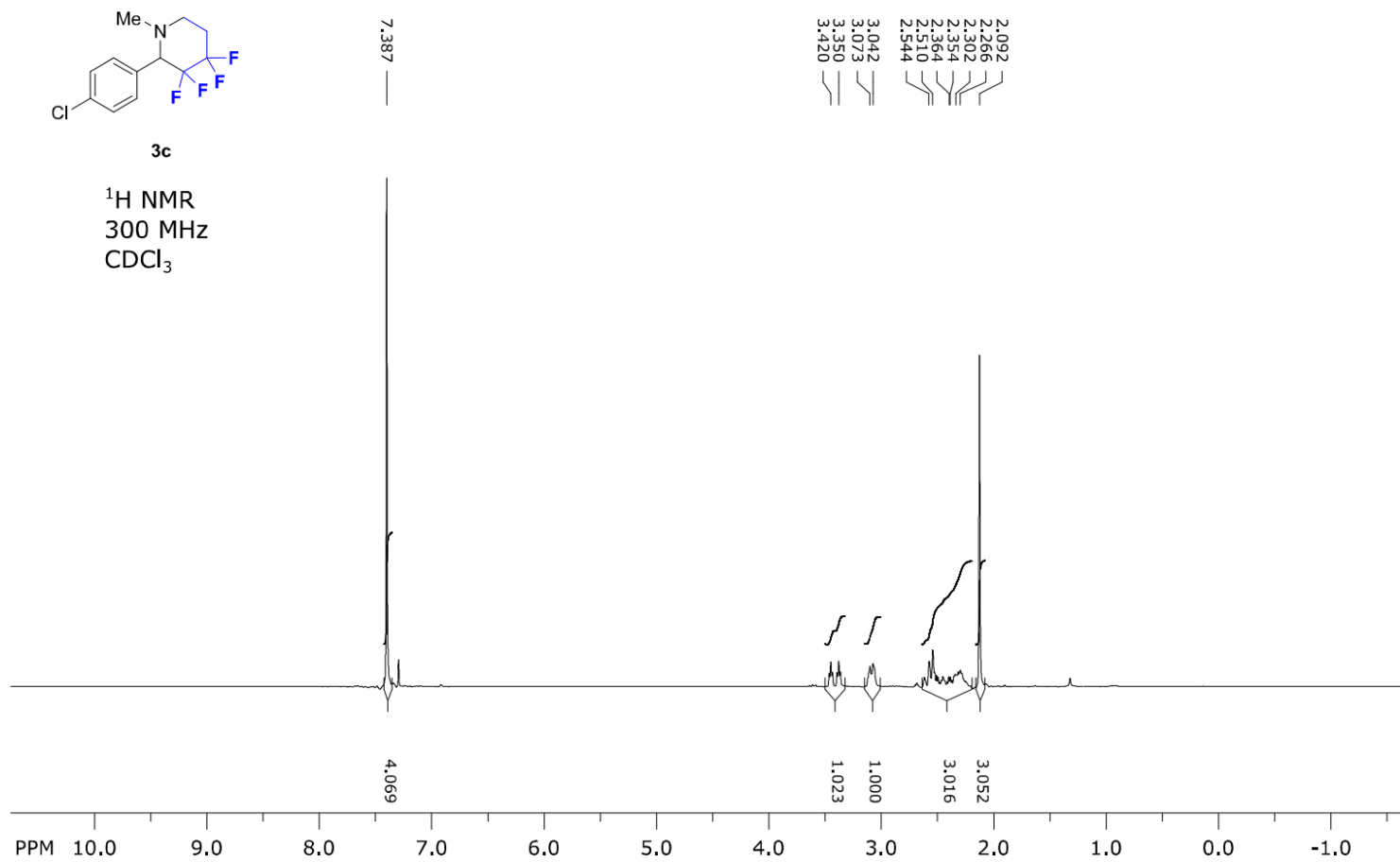


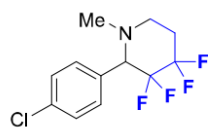
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$^{13}\text{C}\{^1\text{H}\}$ NMR
75 MHz
 CDCl_3



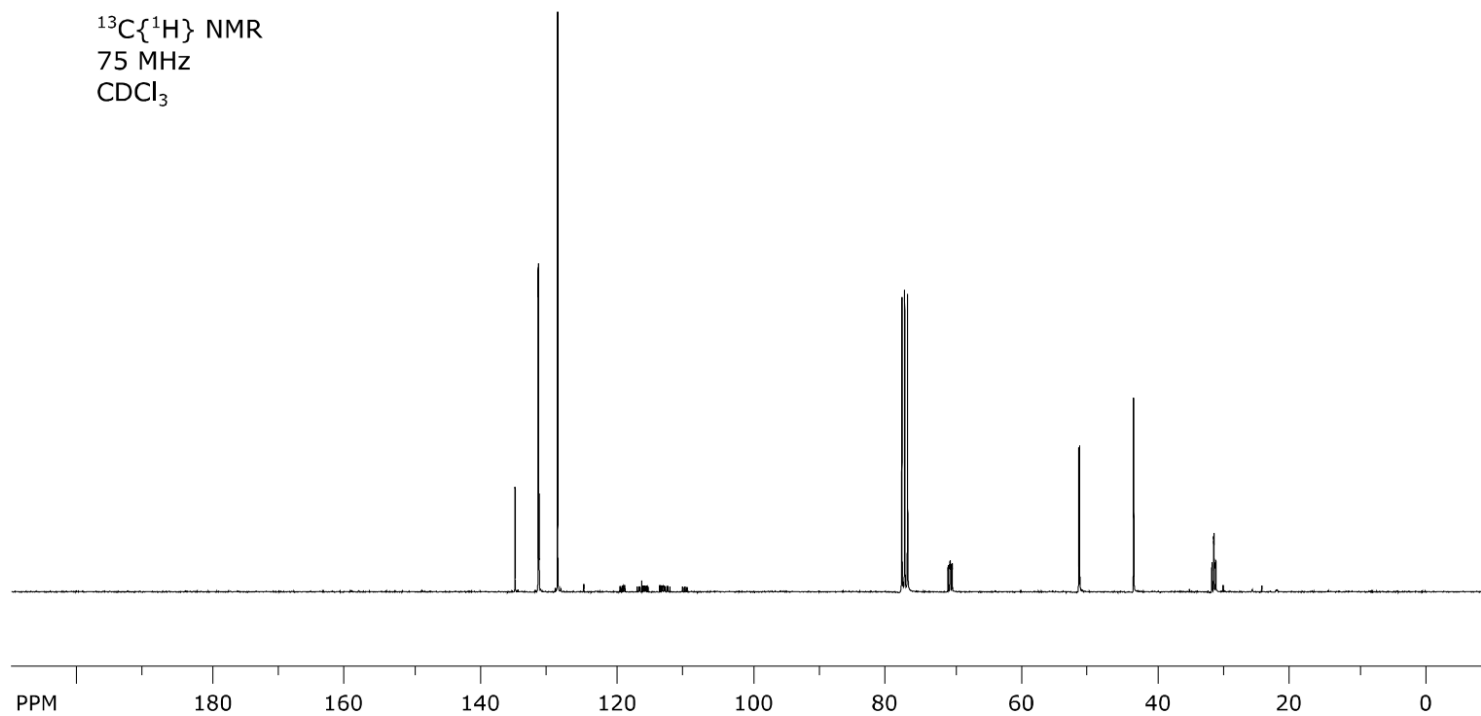


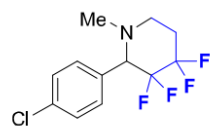




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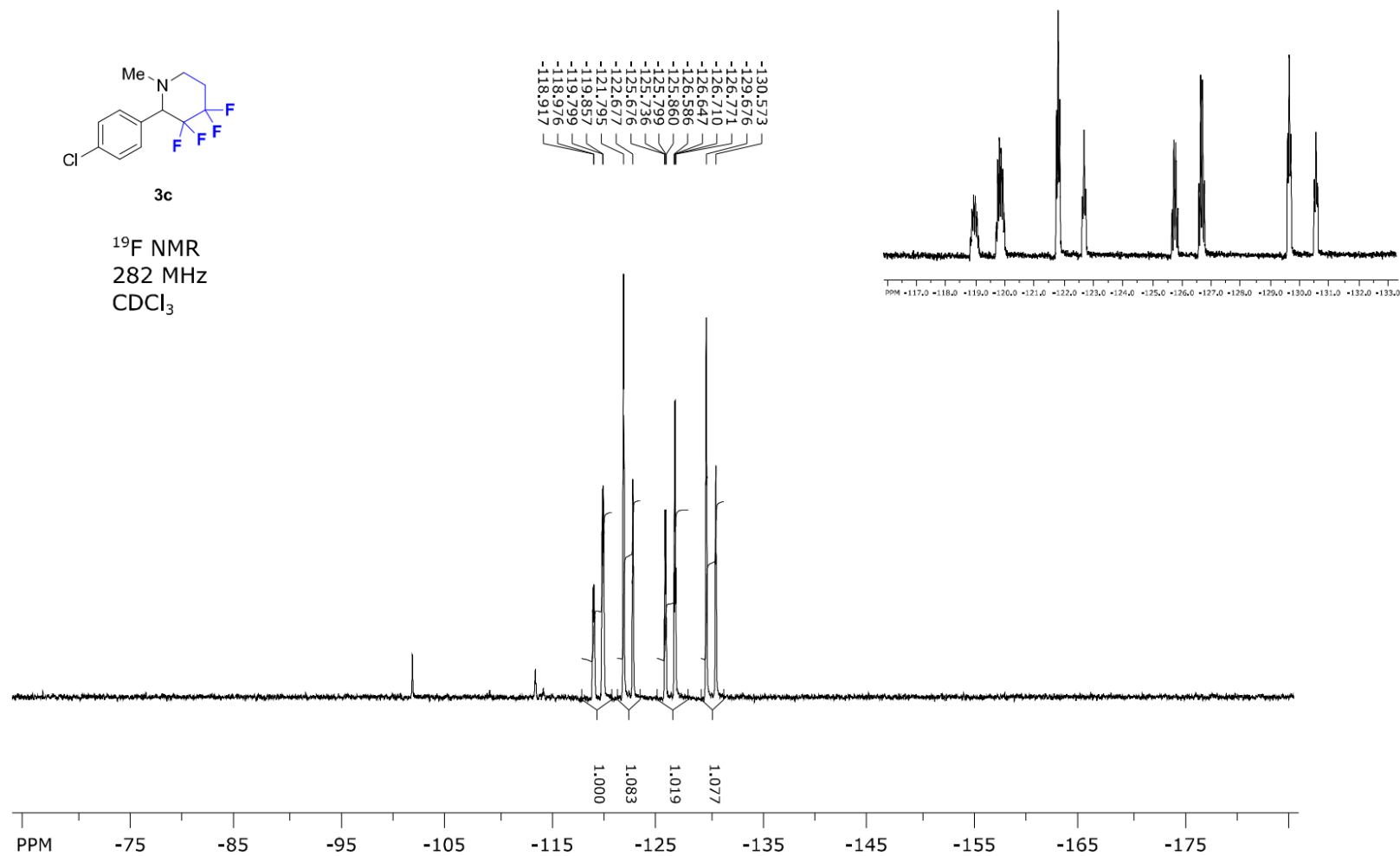
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75 MHz
 CDCl_3

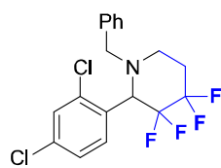




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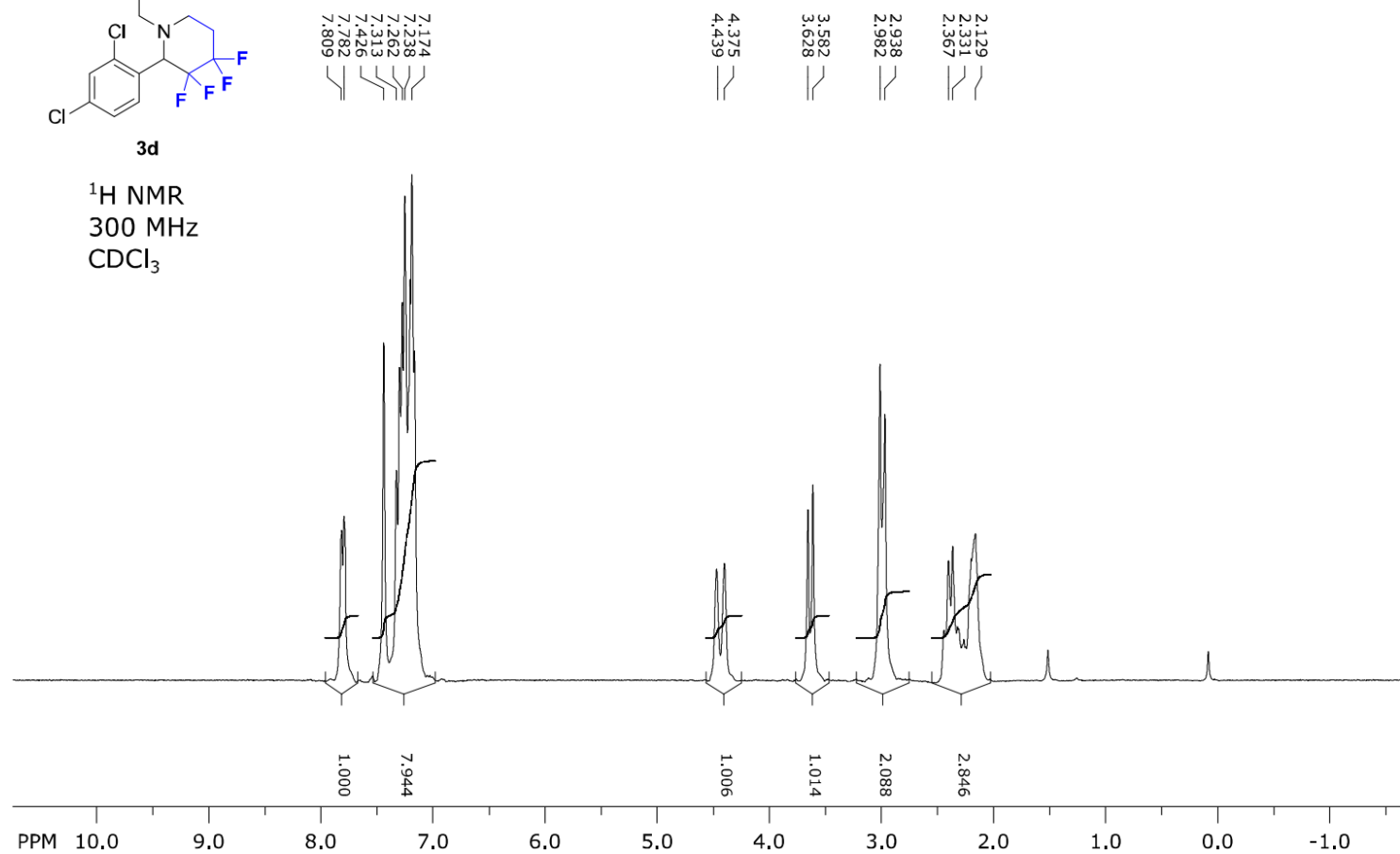
¹⁹F NMR
282 MHz
CDCl₃

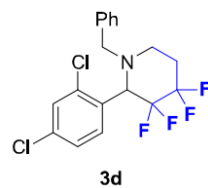




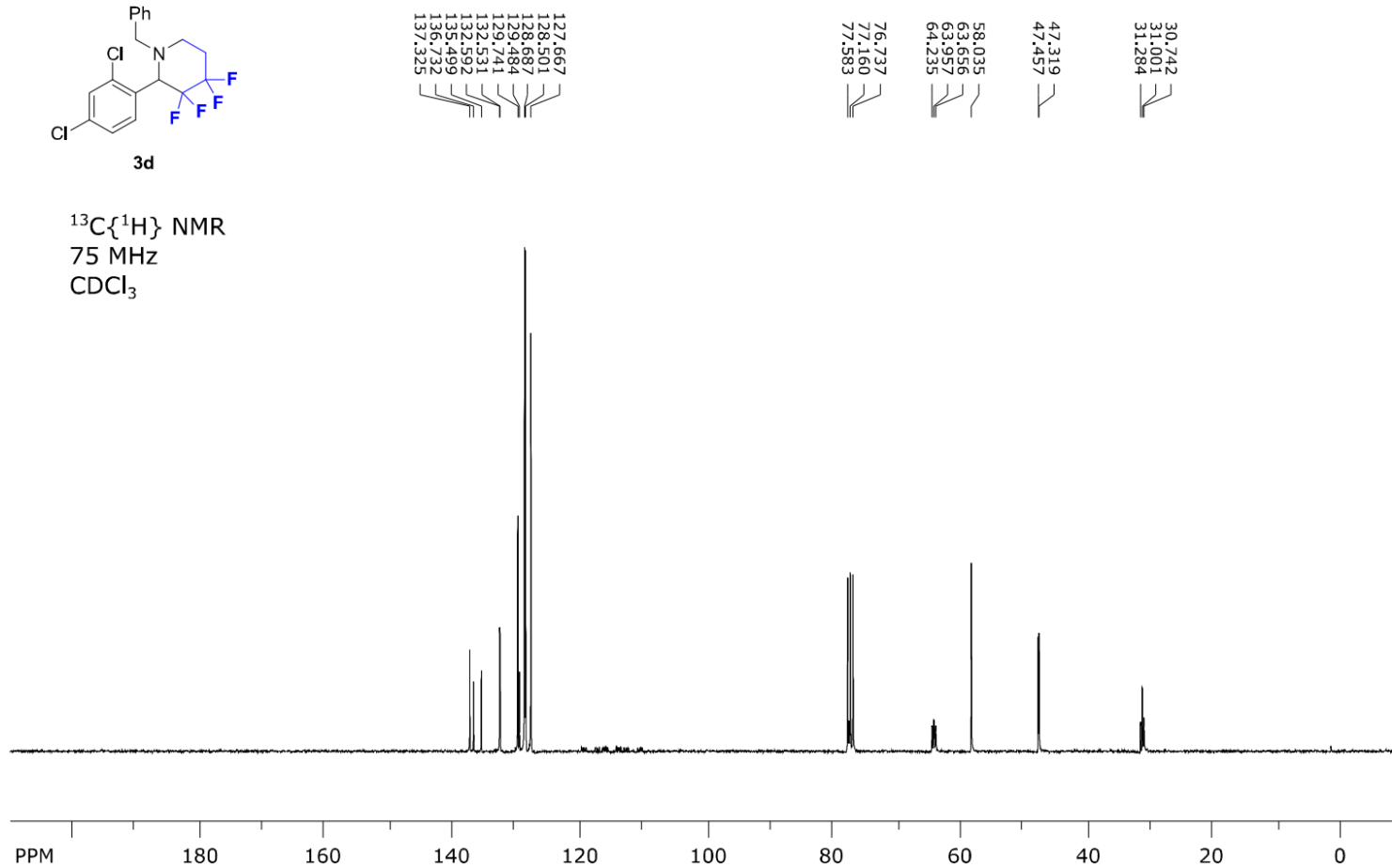
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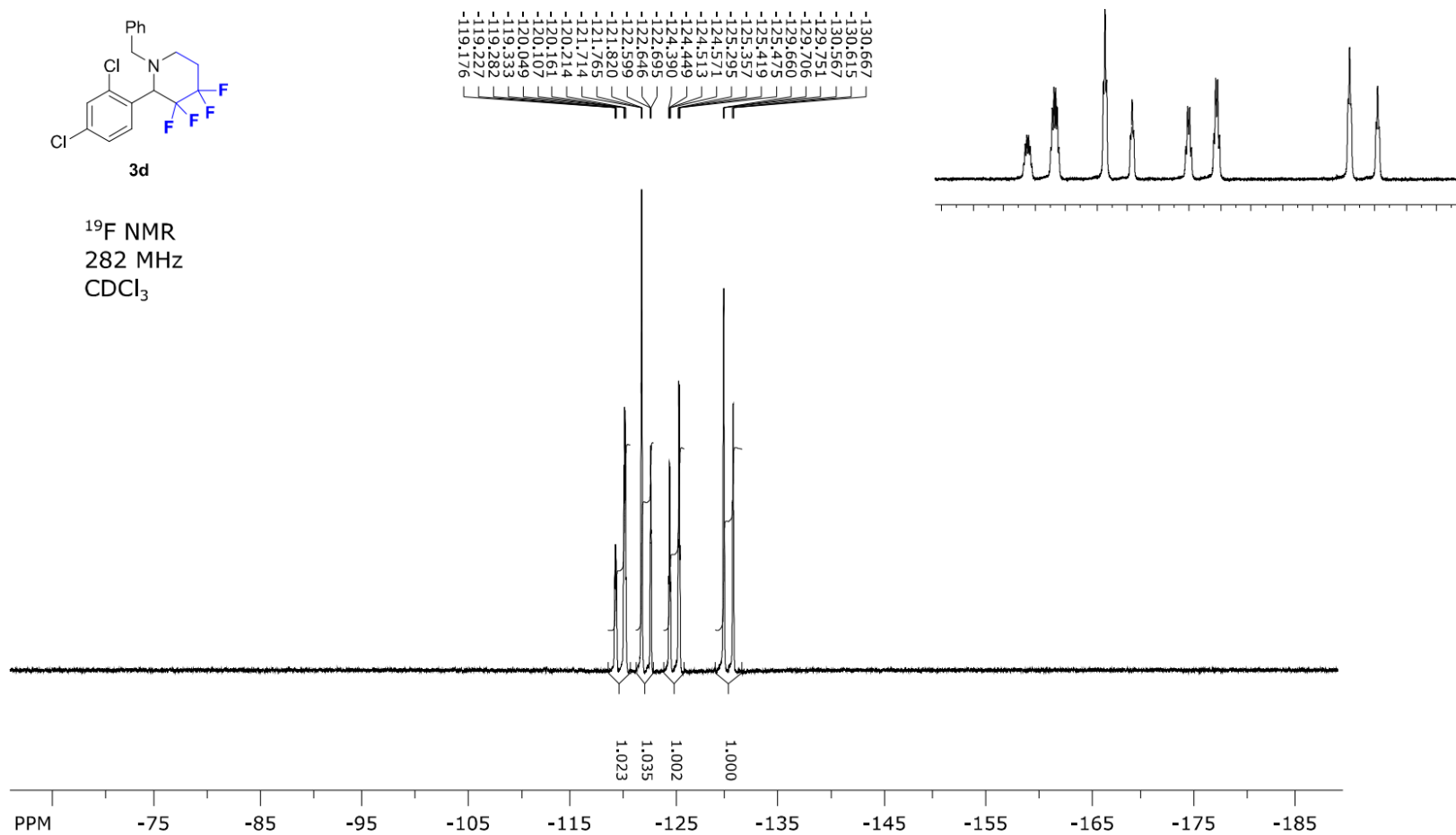
^1H NMR
300 MHz
 CDCl_3

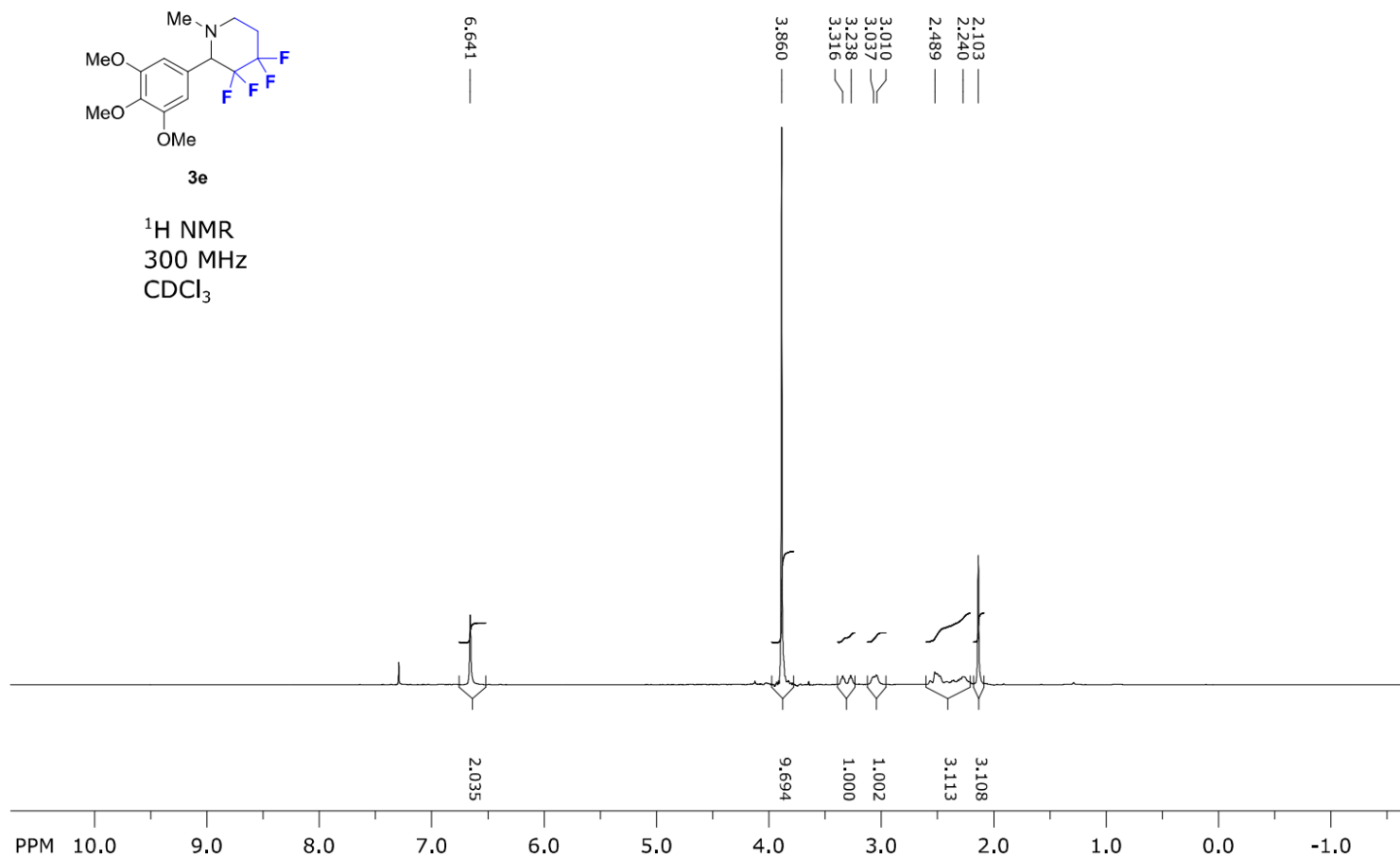


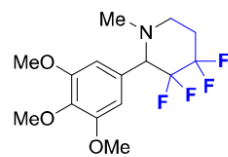


$^{13}\text{C}\{^1\text{H}\}$ NMR
75 MHz
 CDCl_3



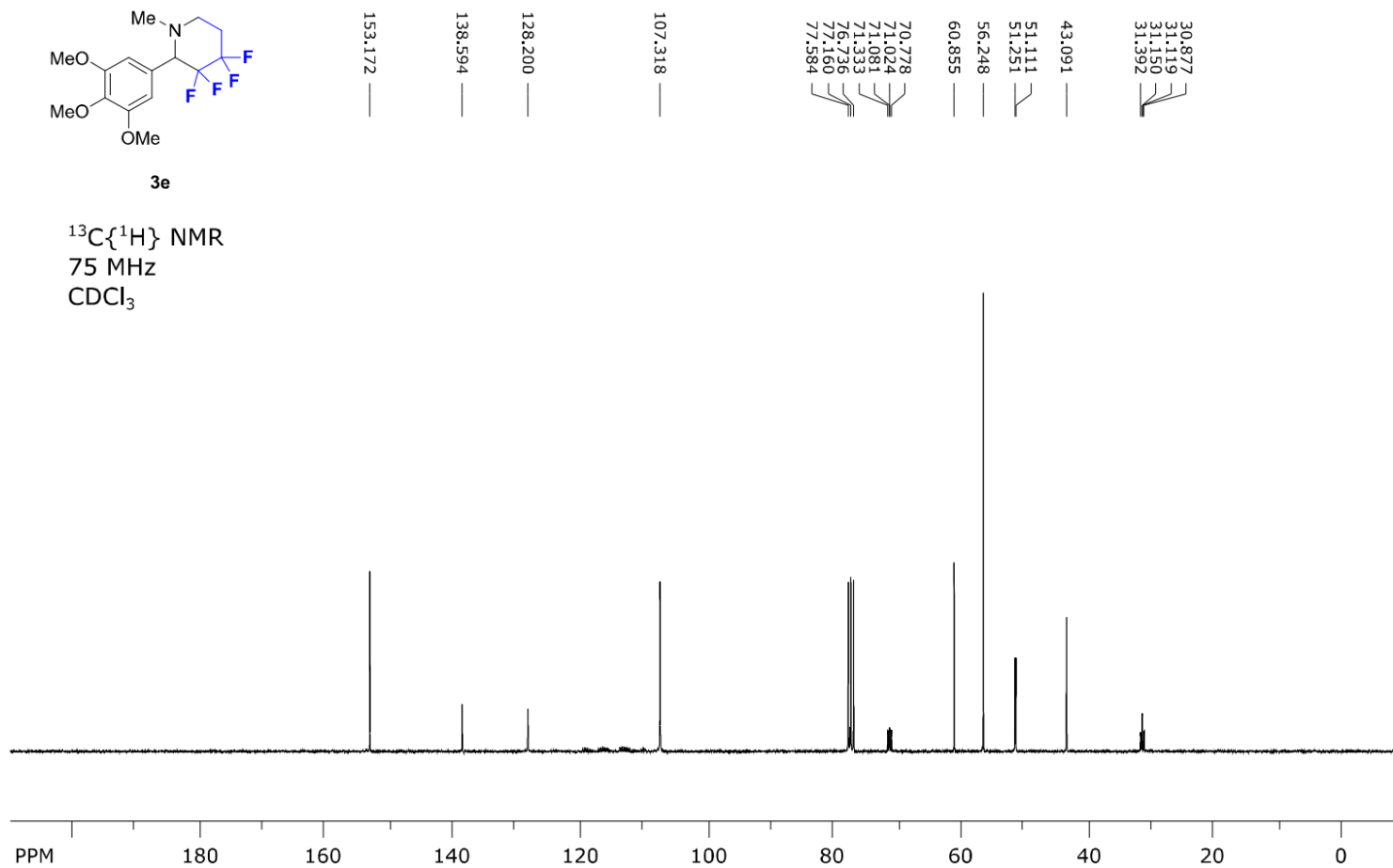


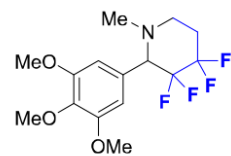




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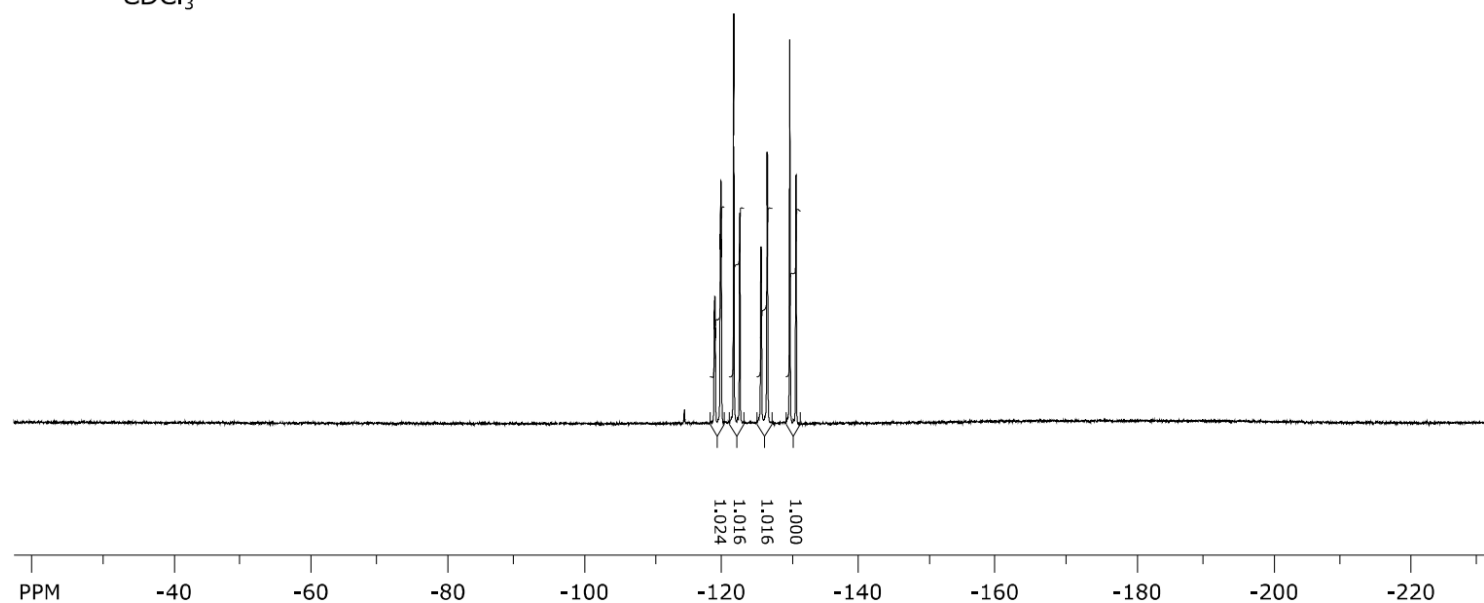
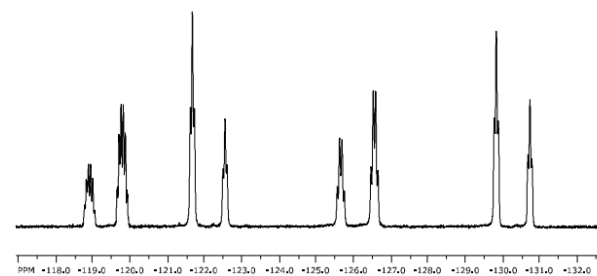
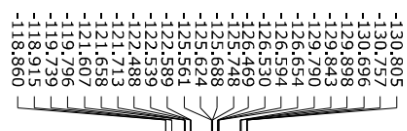
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75 MHz
 CDCl_3

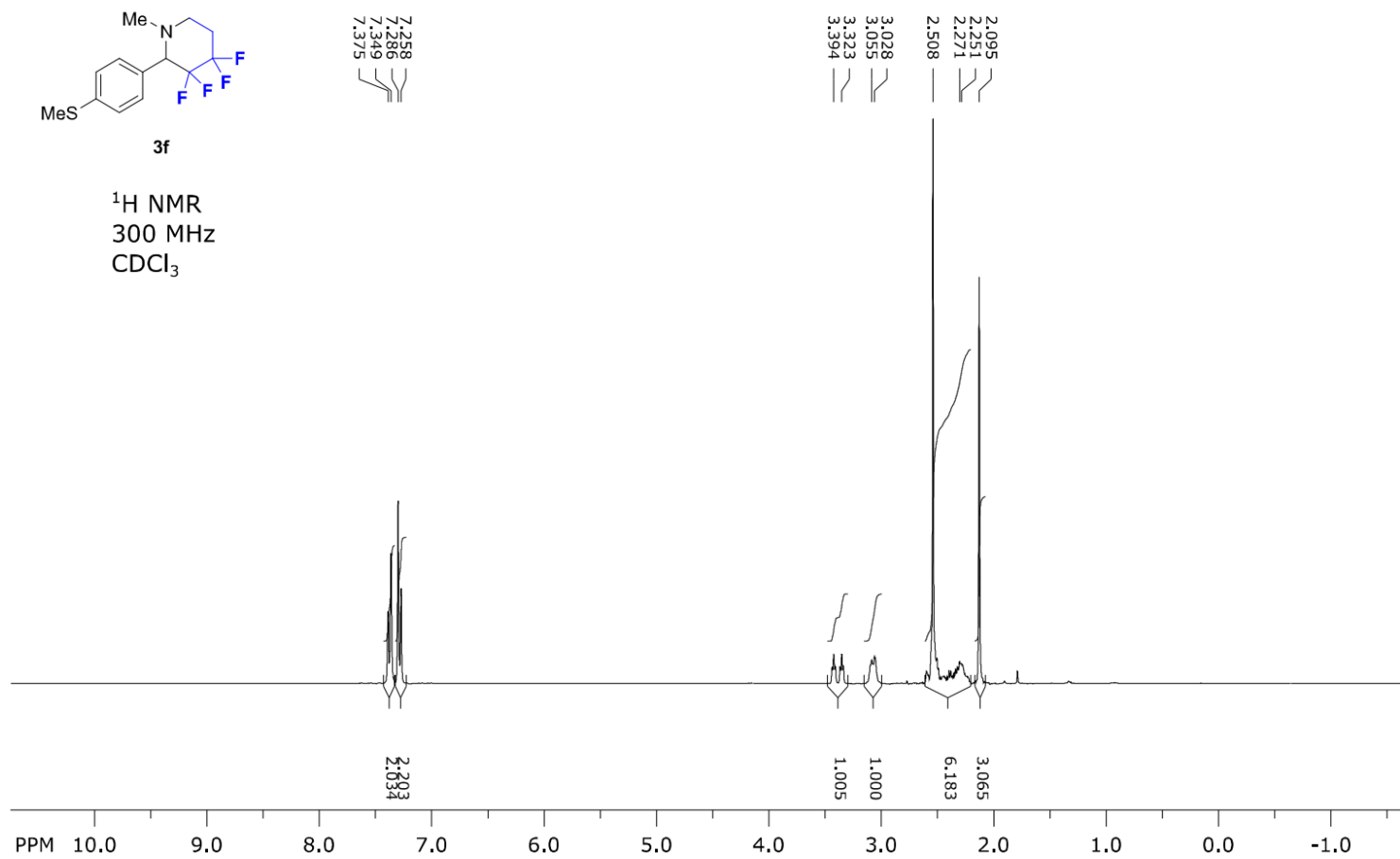


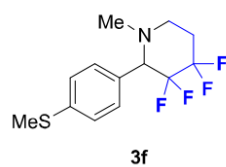


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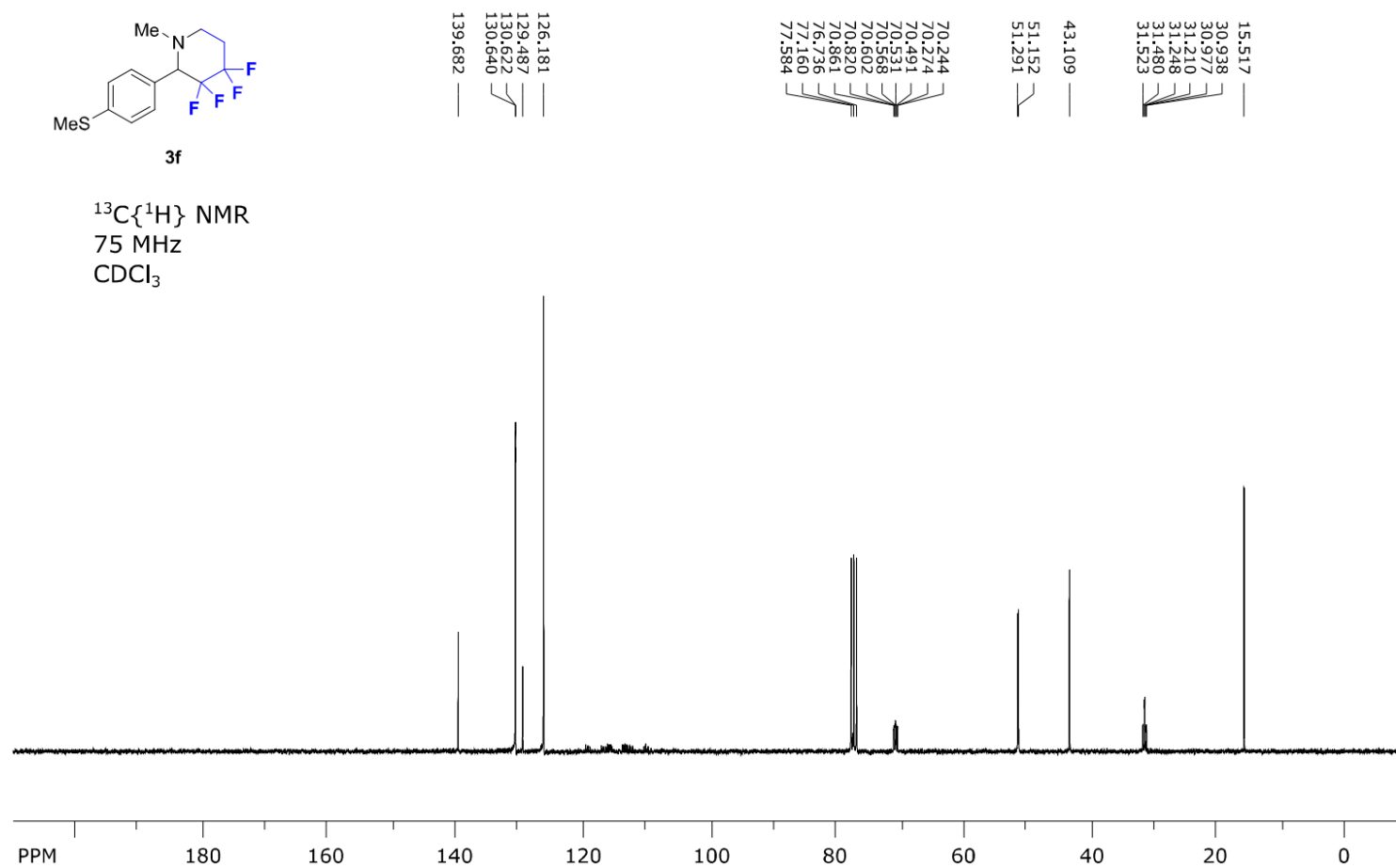
^{19}F NMR
282 MHz
 CDCl_3

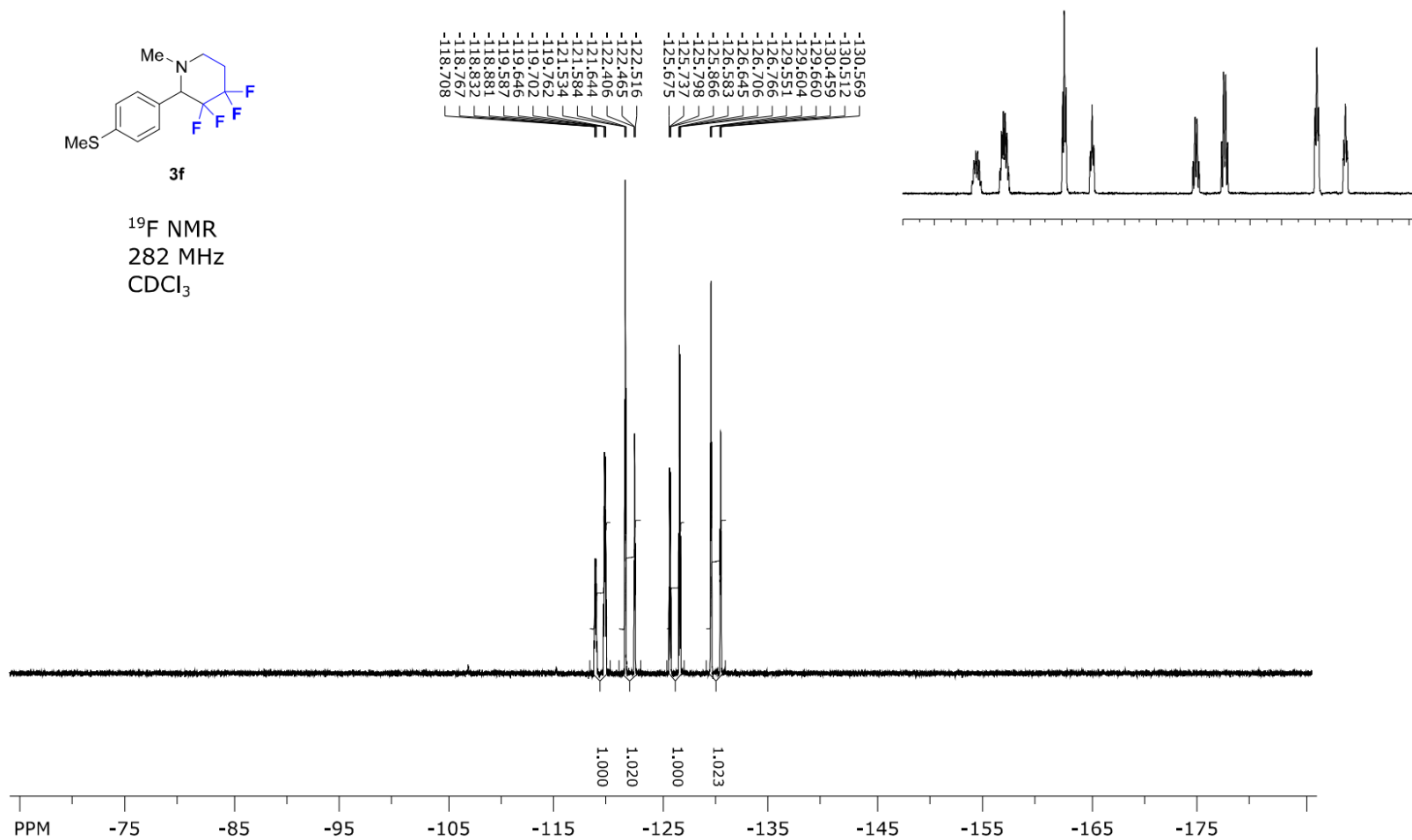


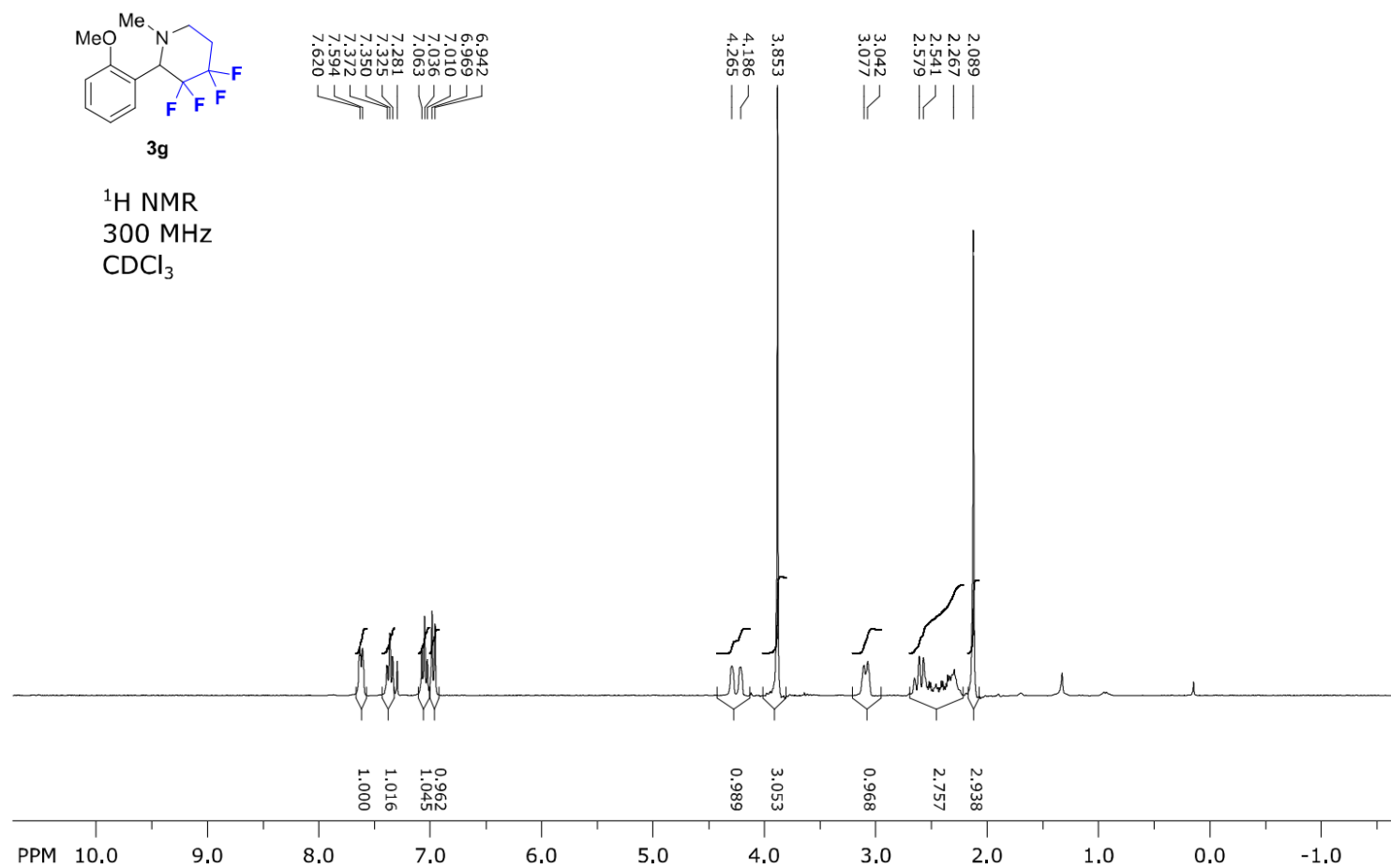


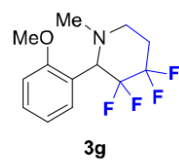


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75 MHz
 CDCl_3

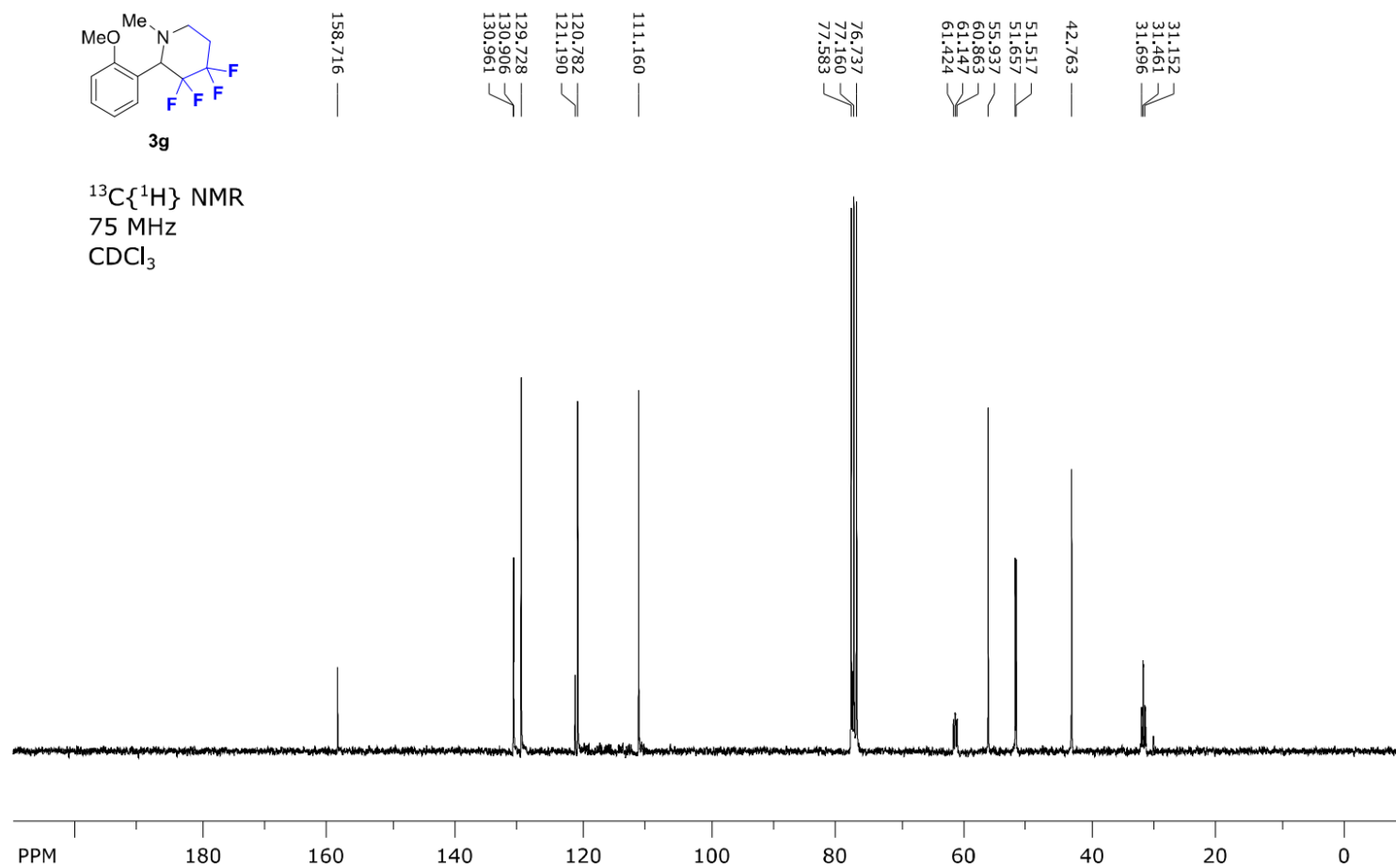


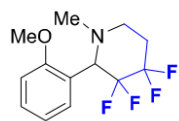






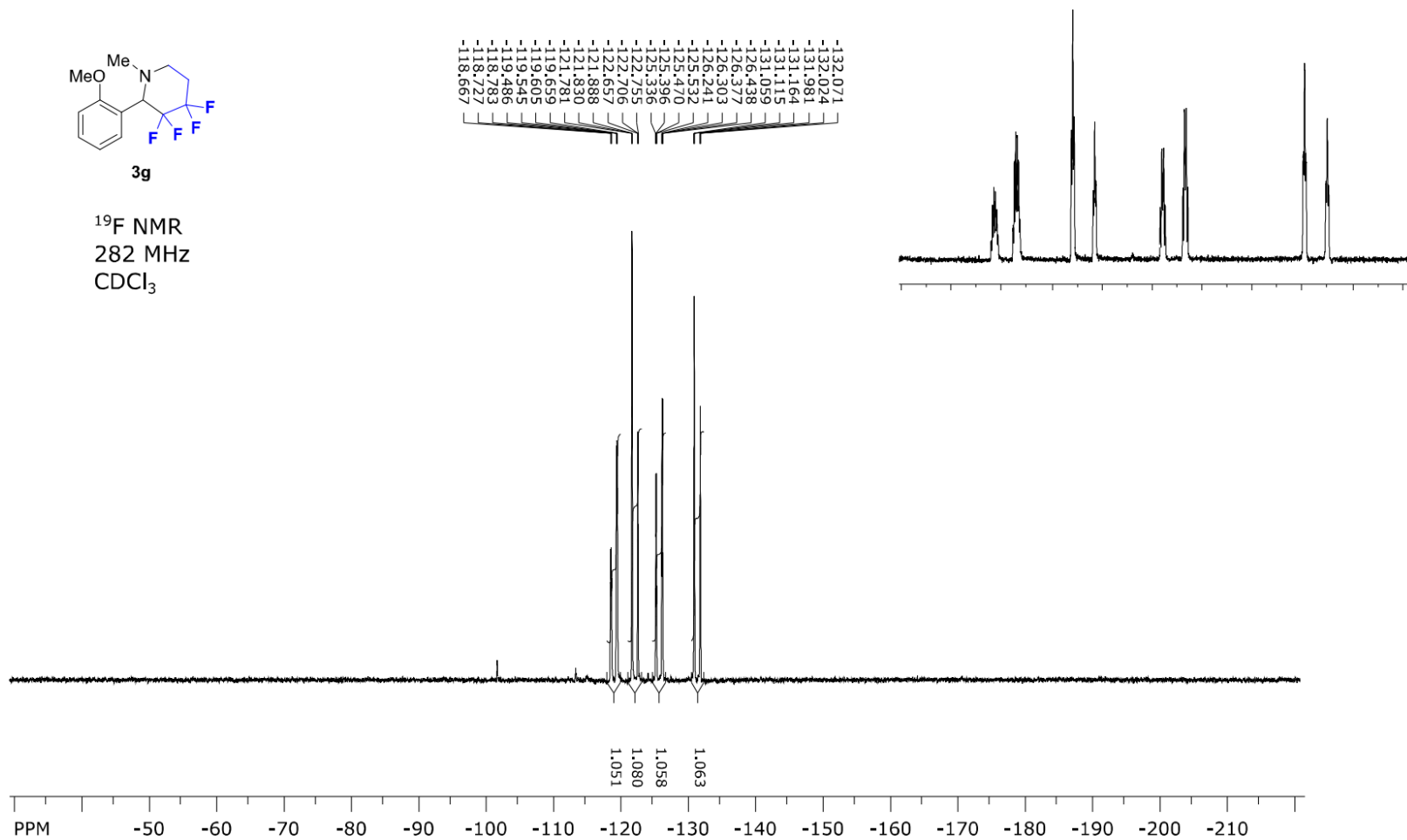
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75 MHz
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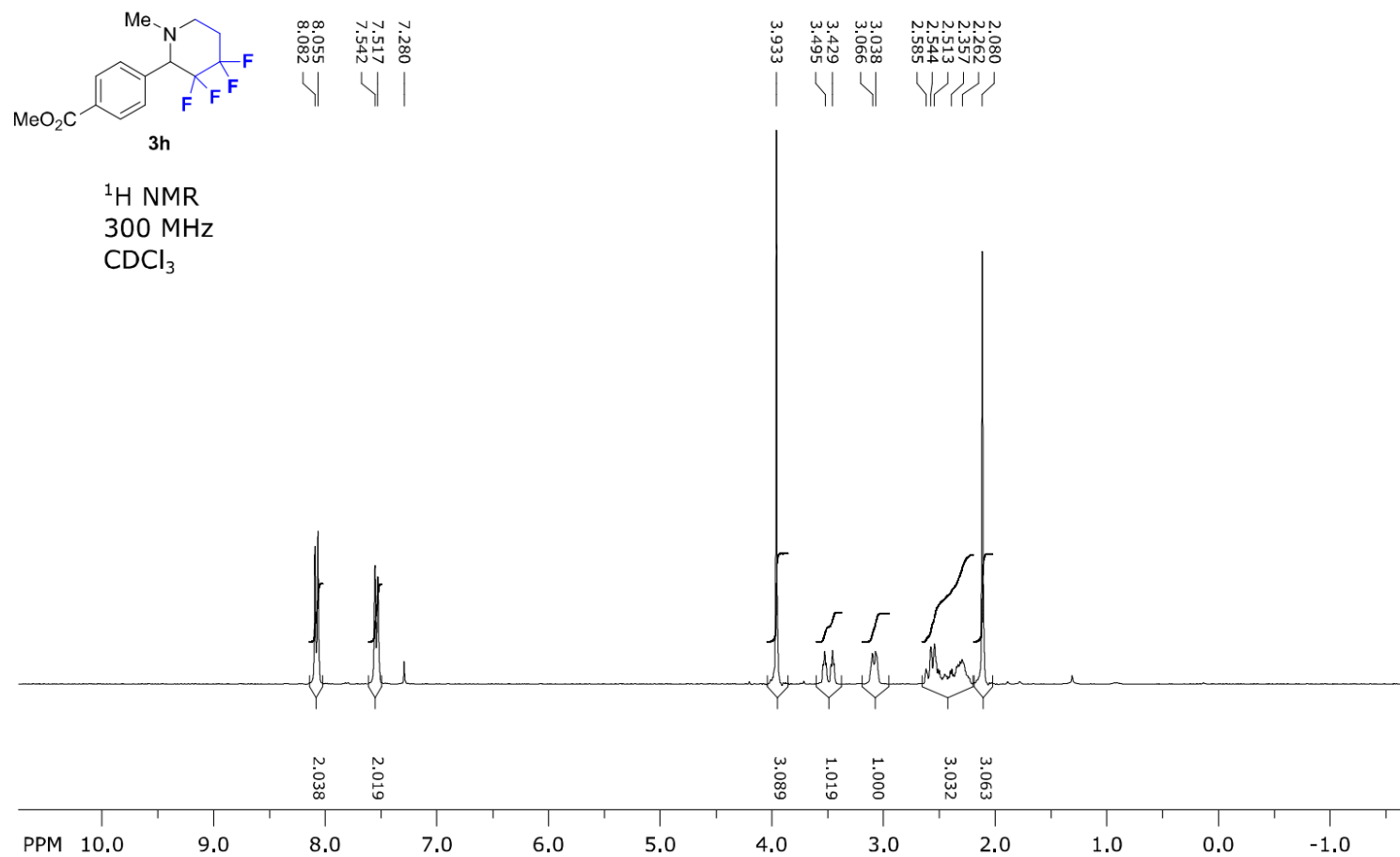


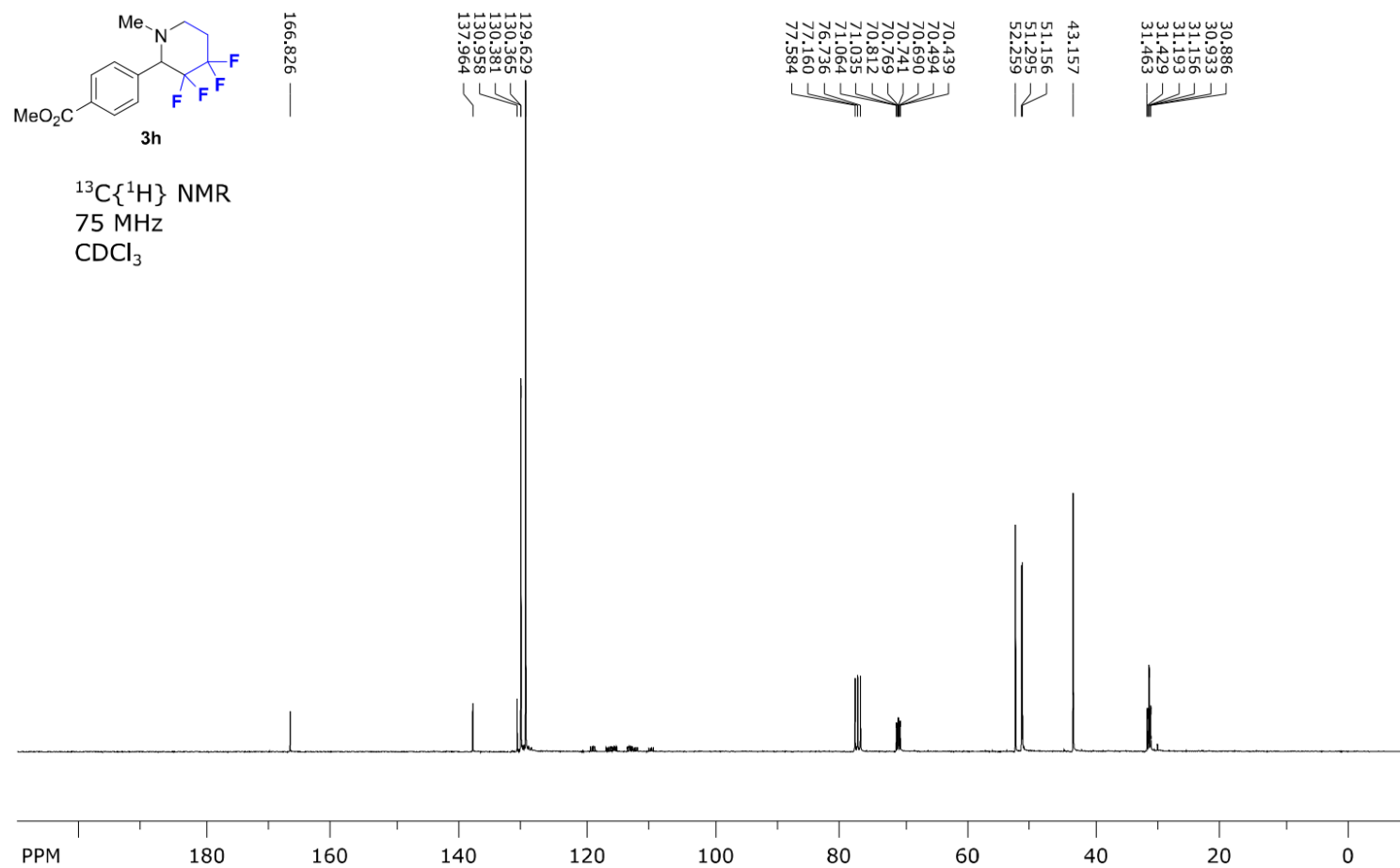


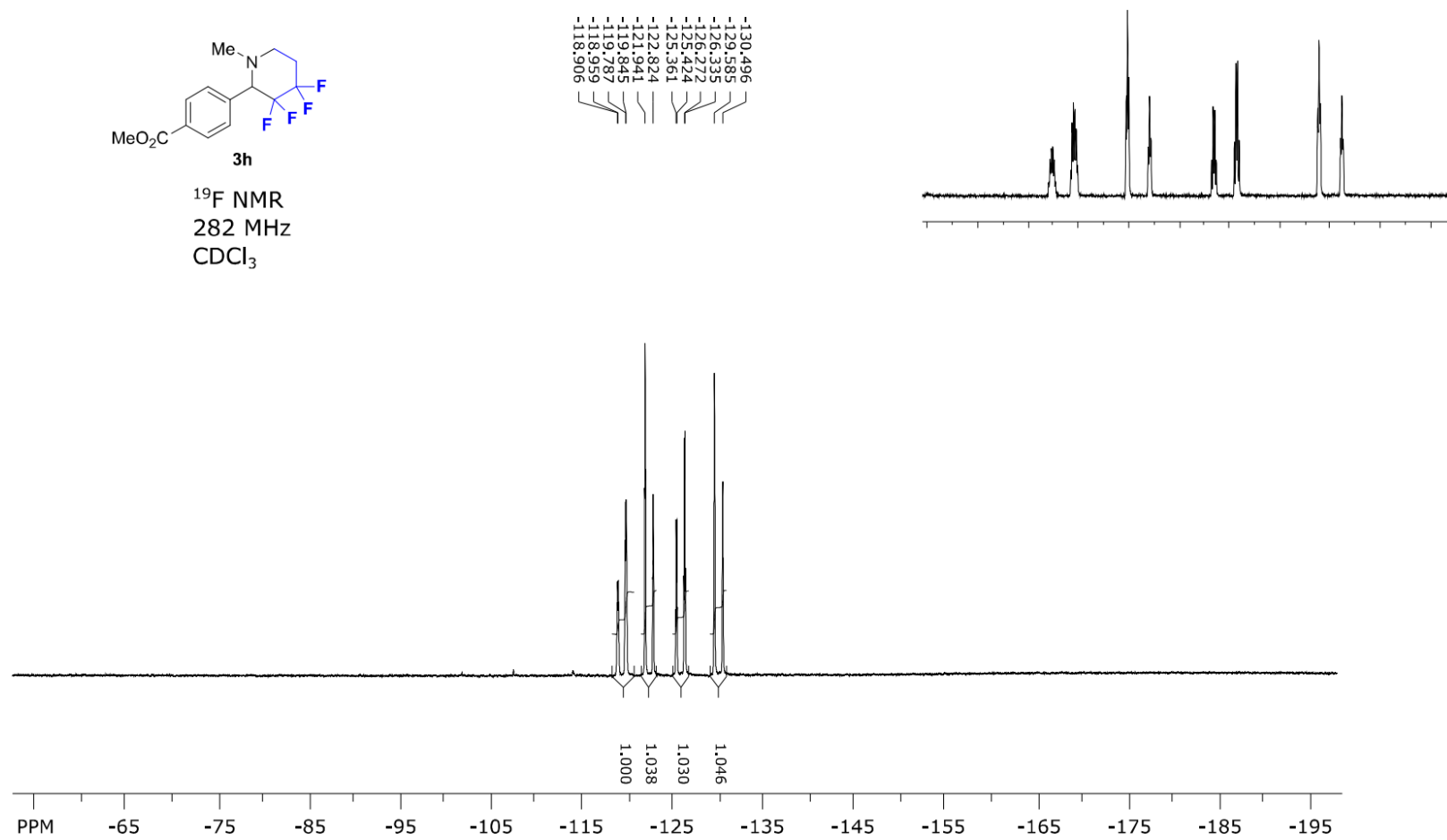
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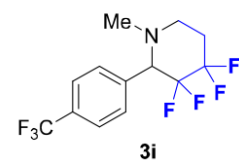
¹⁹F NMR
282 MHz
CDCl₃



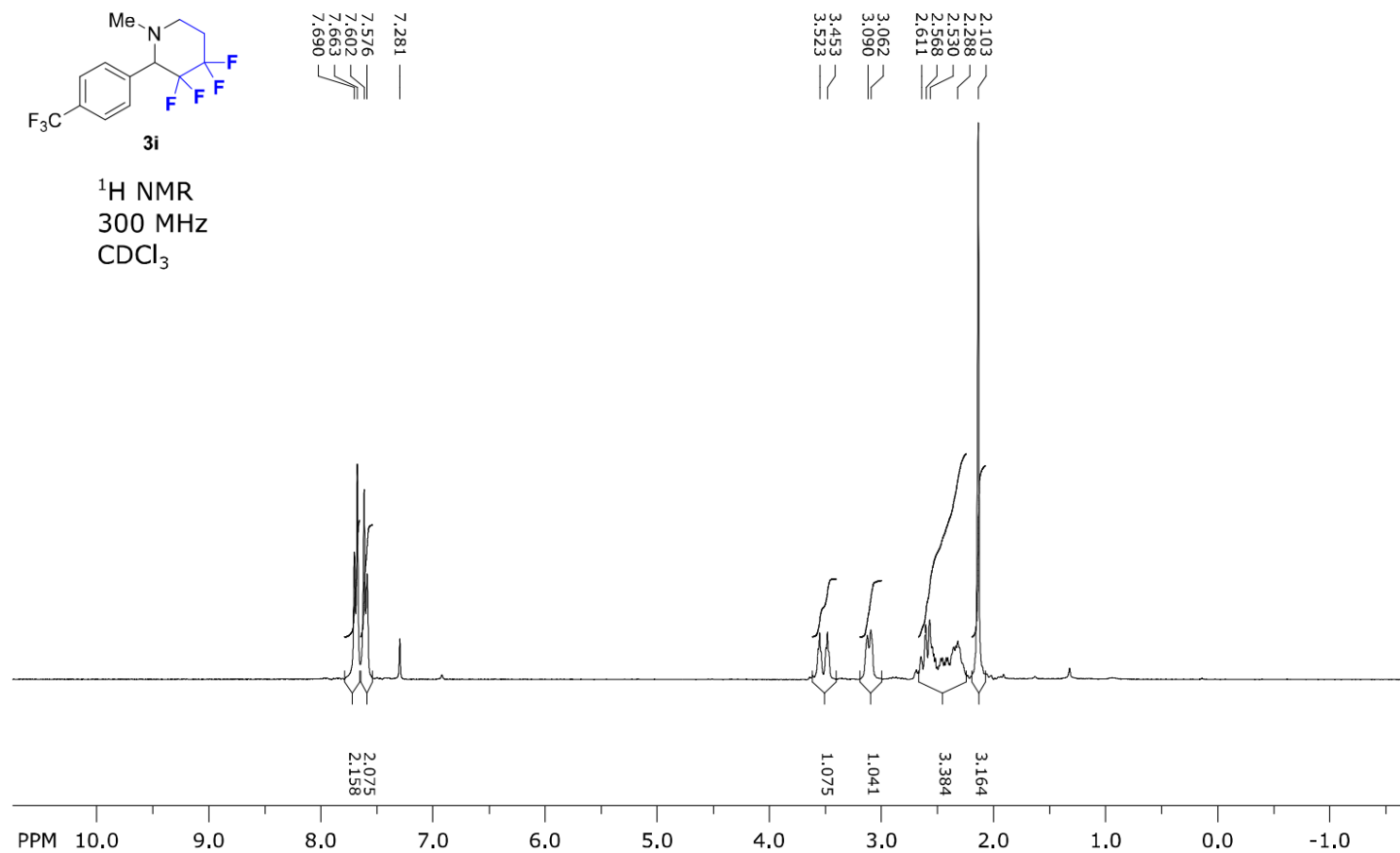


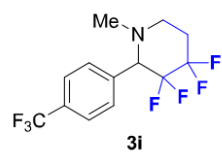




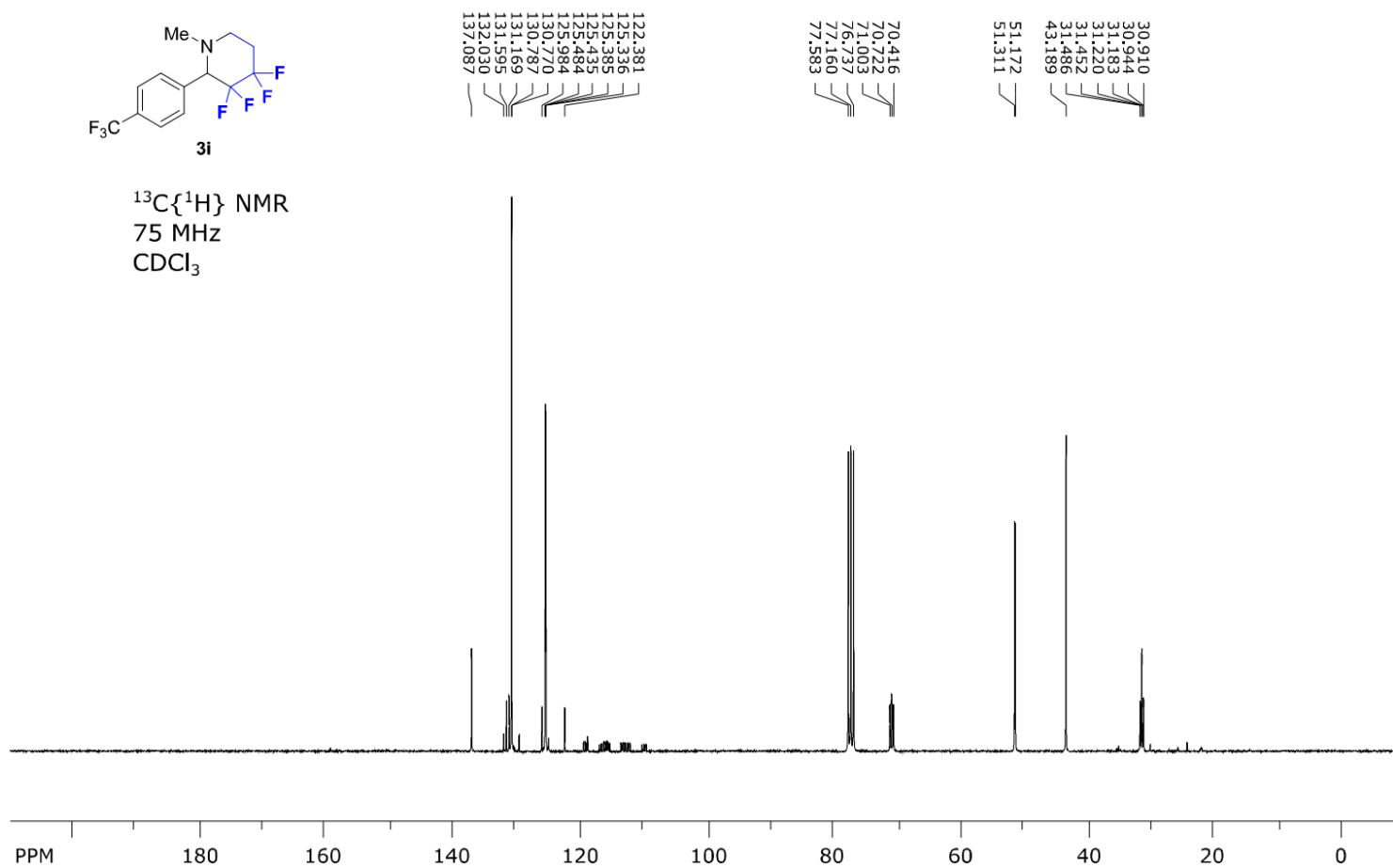


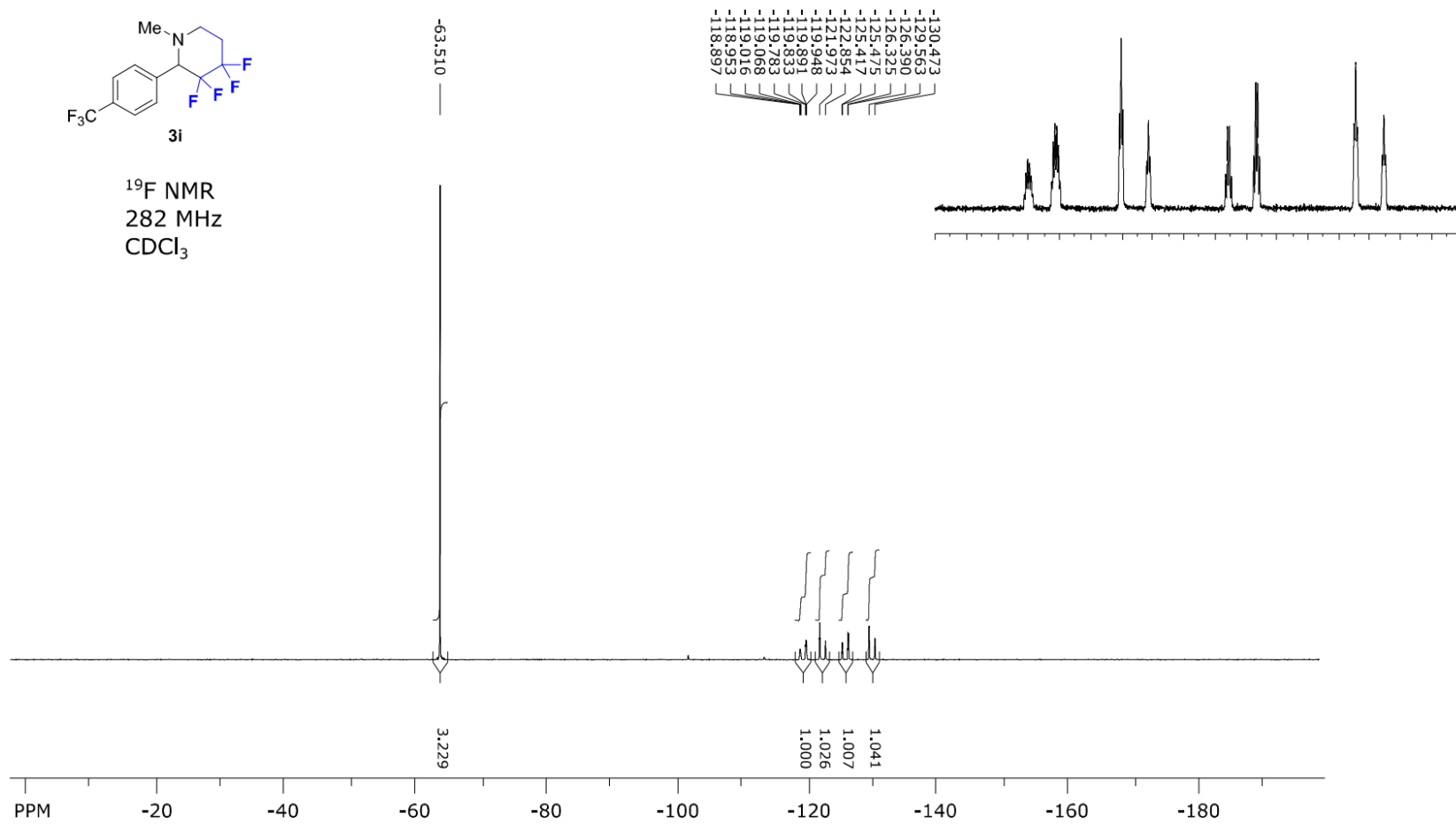
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 300 MHz
 CDCl₃

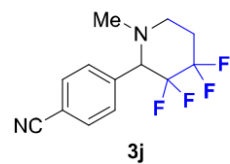




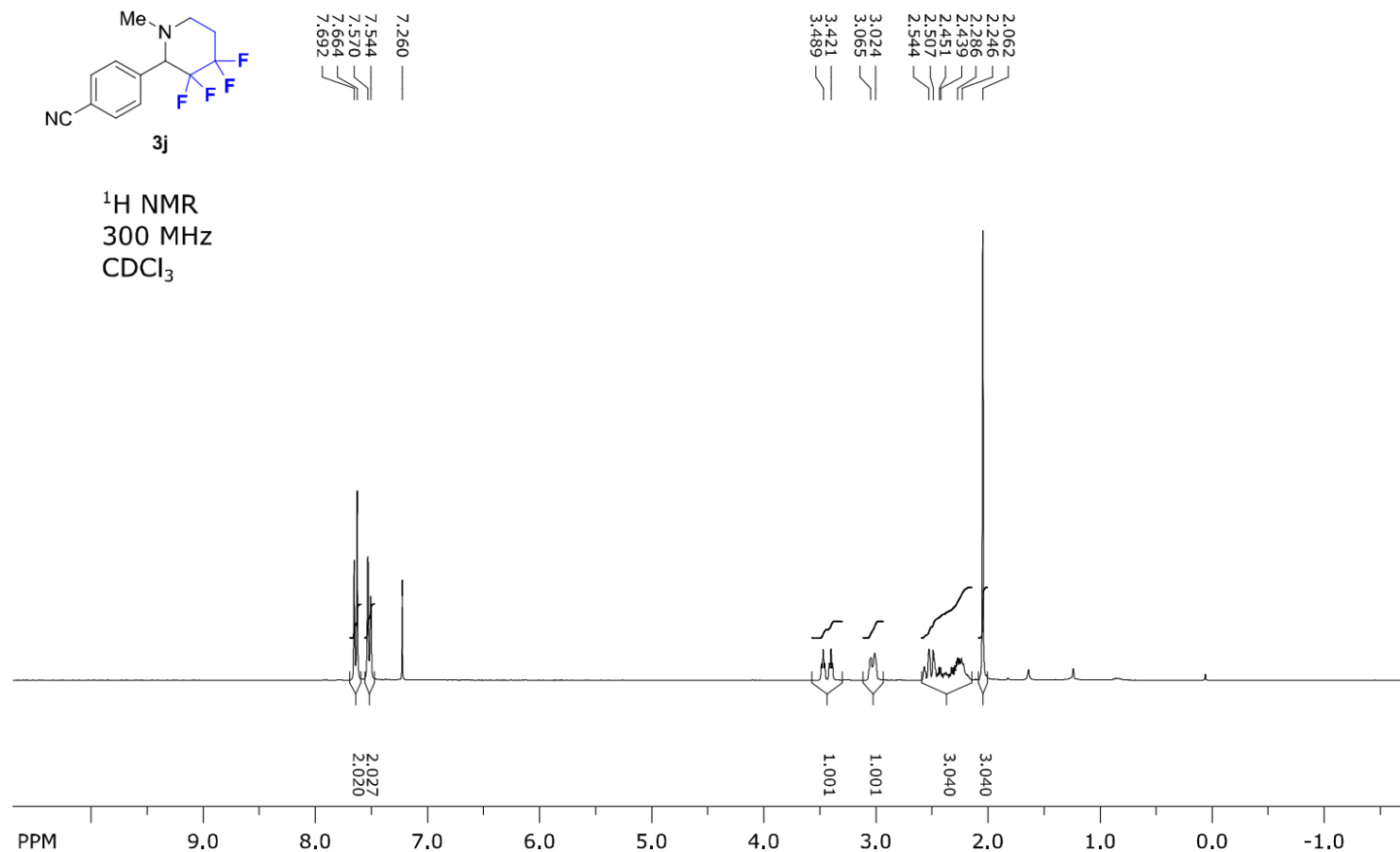
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 75 MHz
 CDCl_3

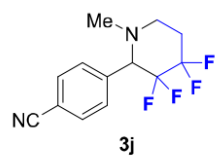




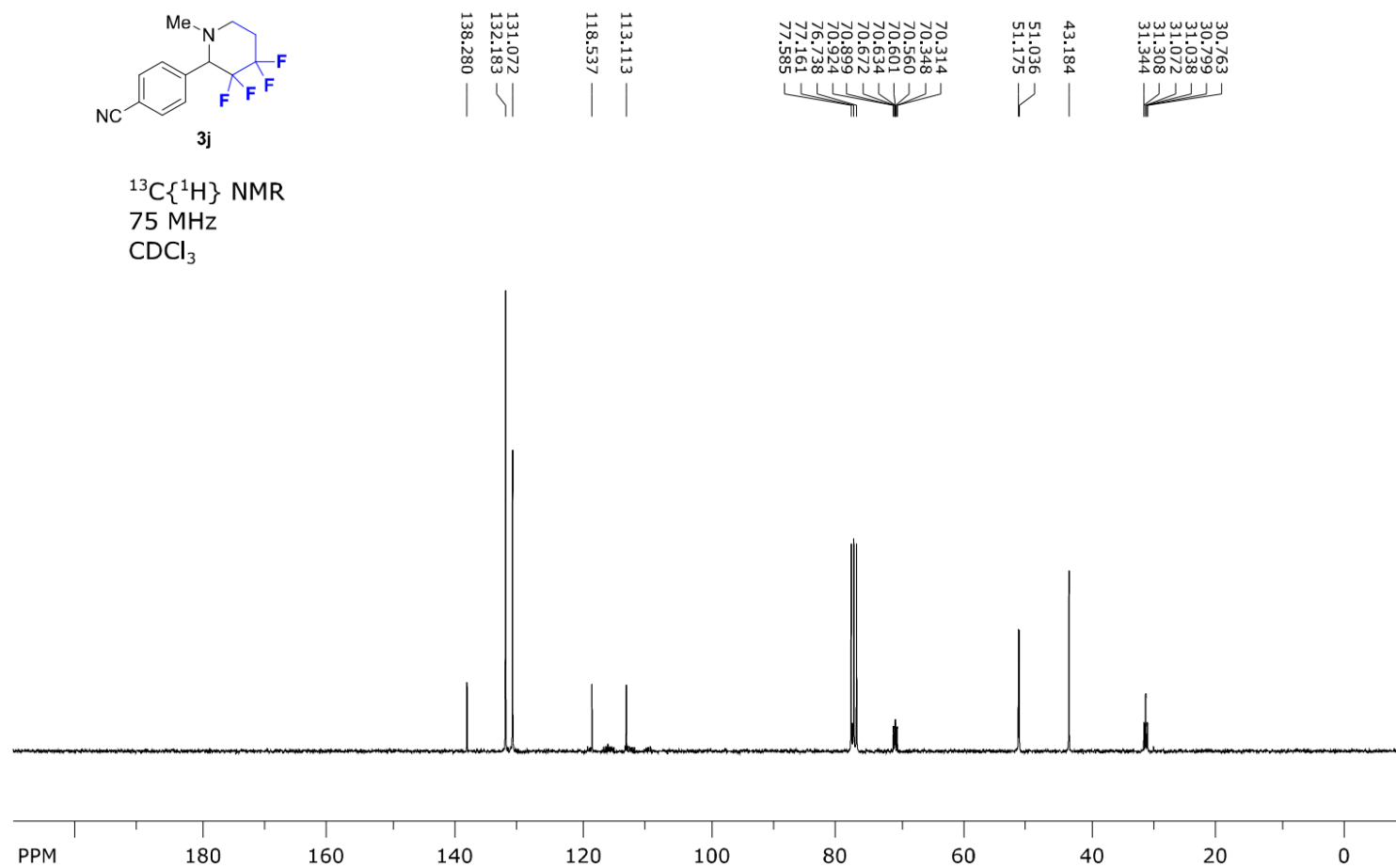


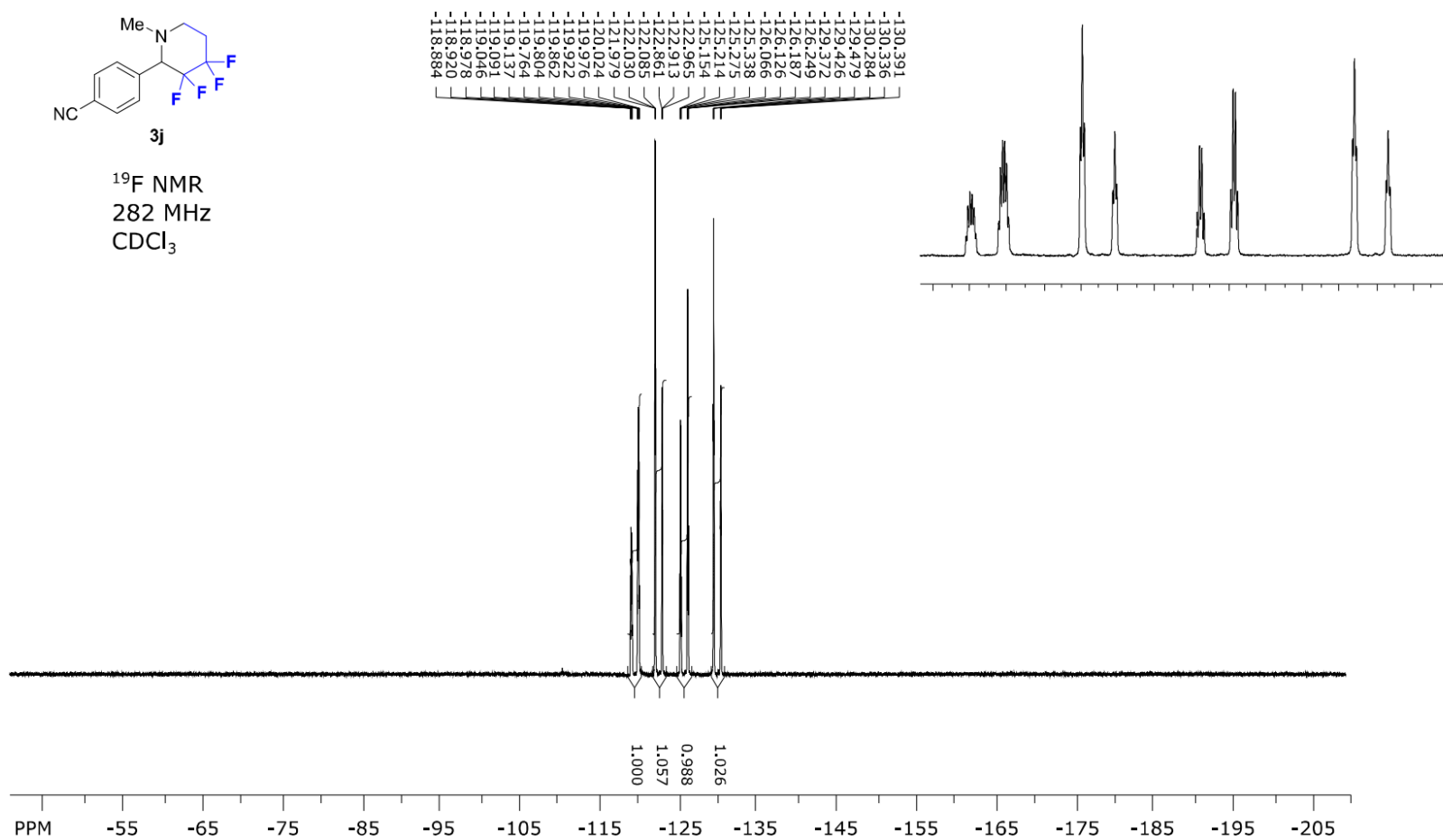
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 300 MHz
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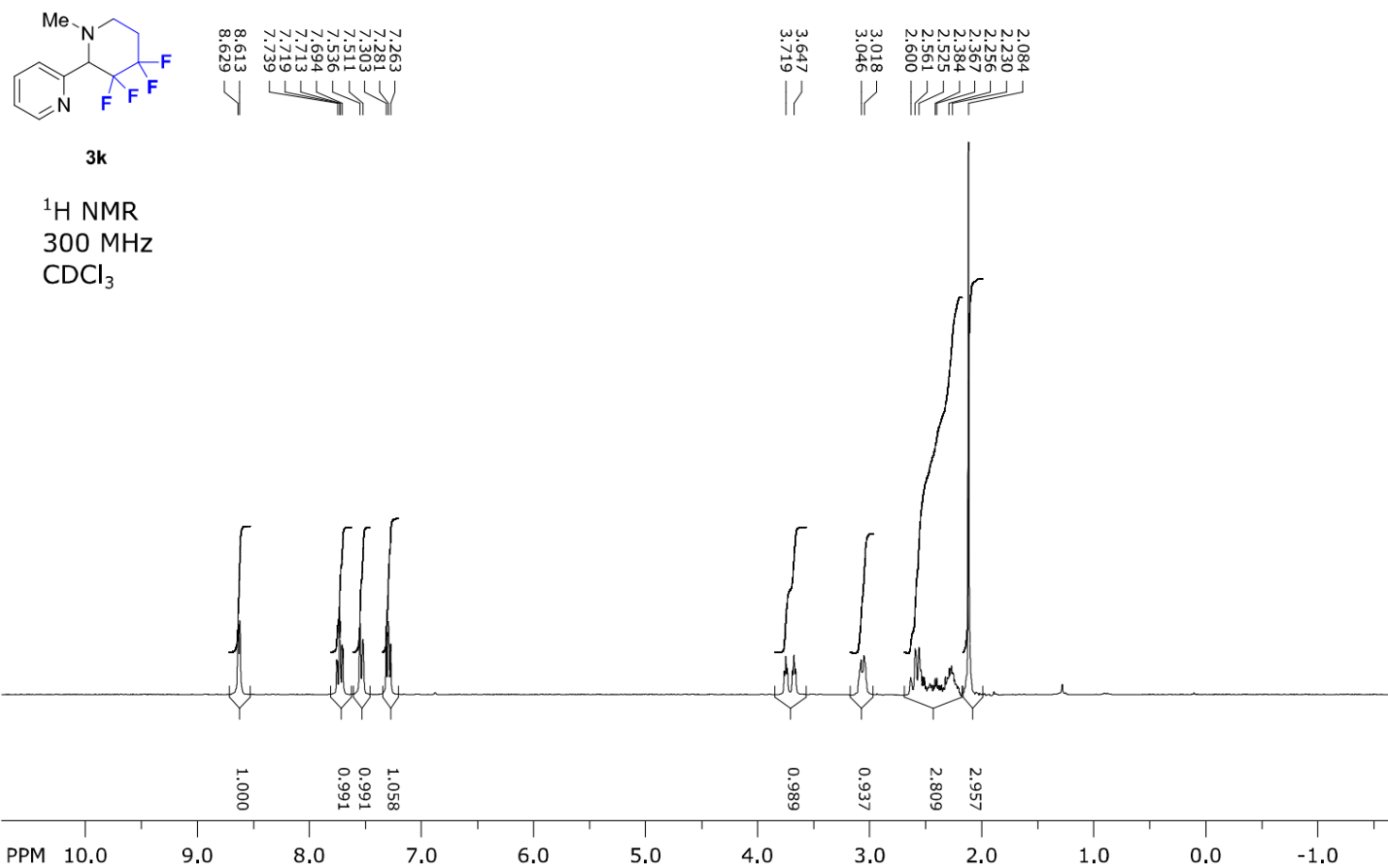


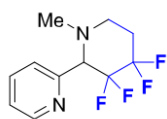


$^{13}\text{C}\{^1\text{H}\}$ NMR
75 MHz
 CDCl_3



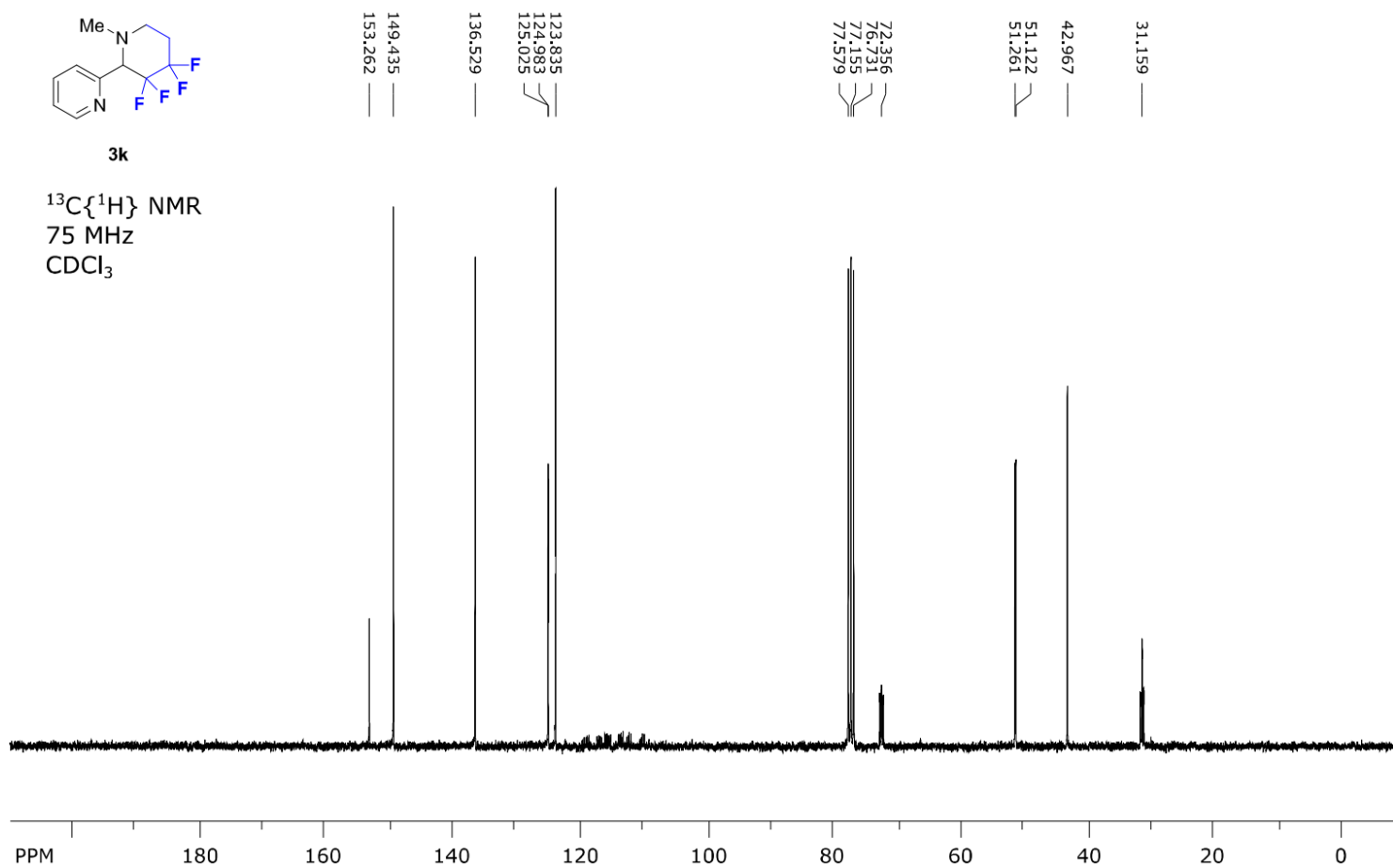


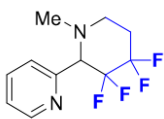




3k

$^{13}\text{C}\{^1\text{H}\}$ NMR
75 MHz
 CDCl_3

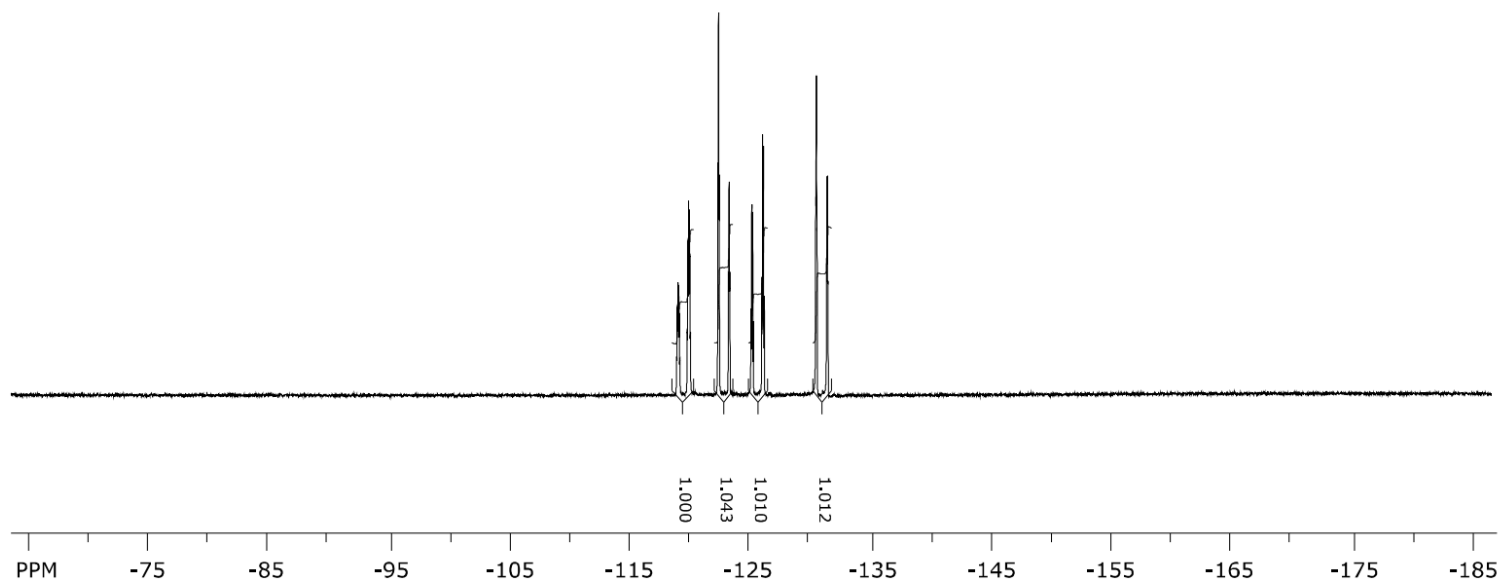
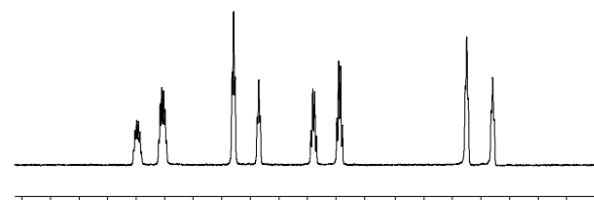


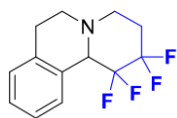


3k

^{19}F NMR
282 MHz
 CDCl_3

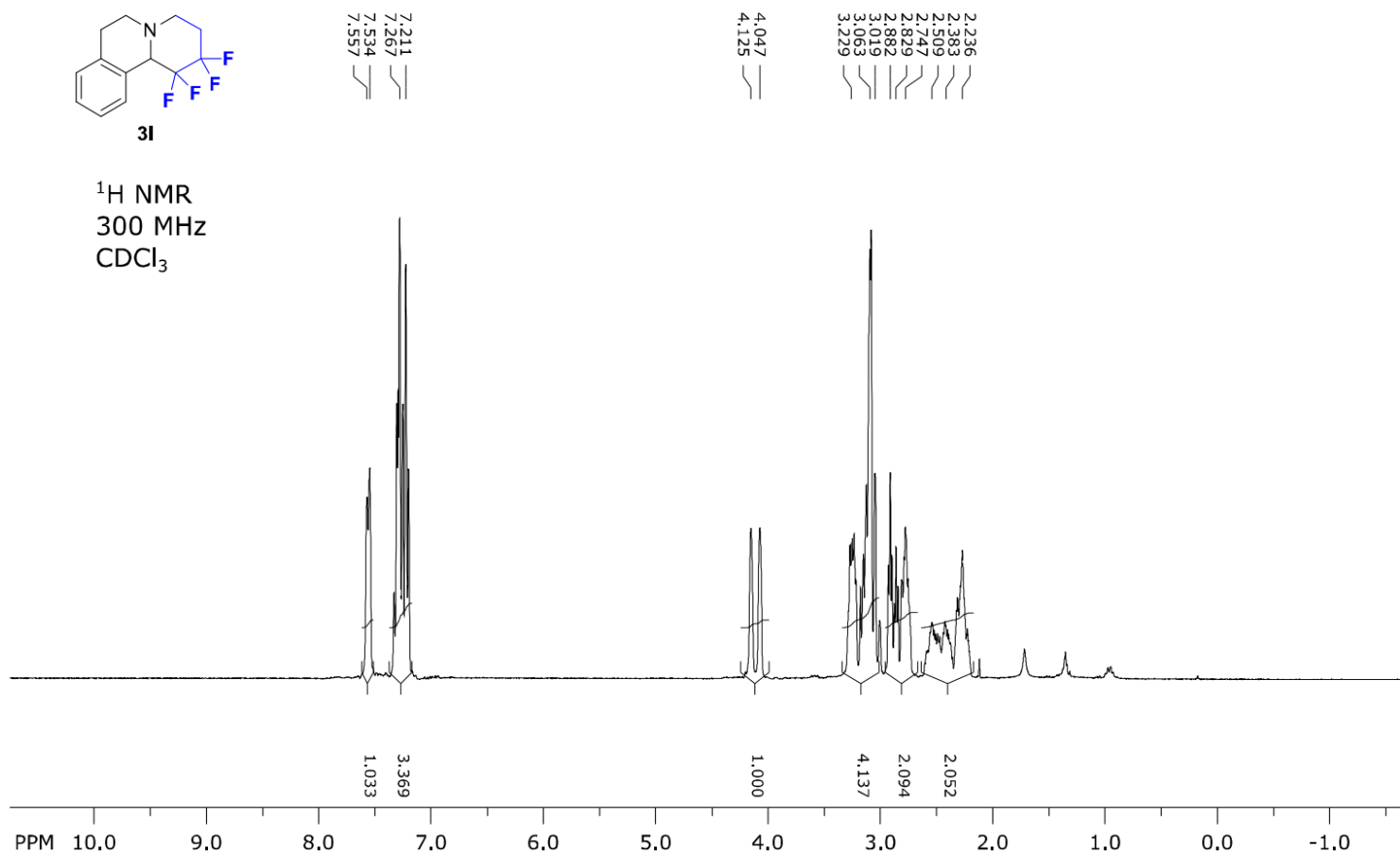
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-126.134
-126.070
-126.007
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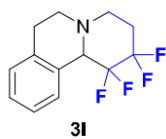




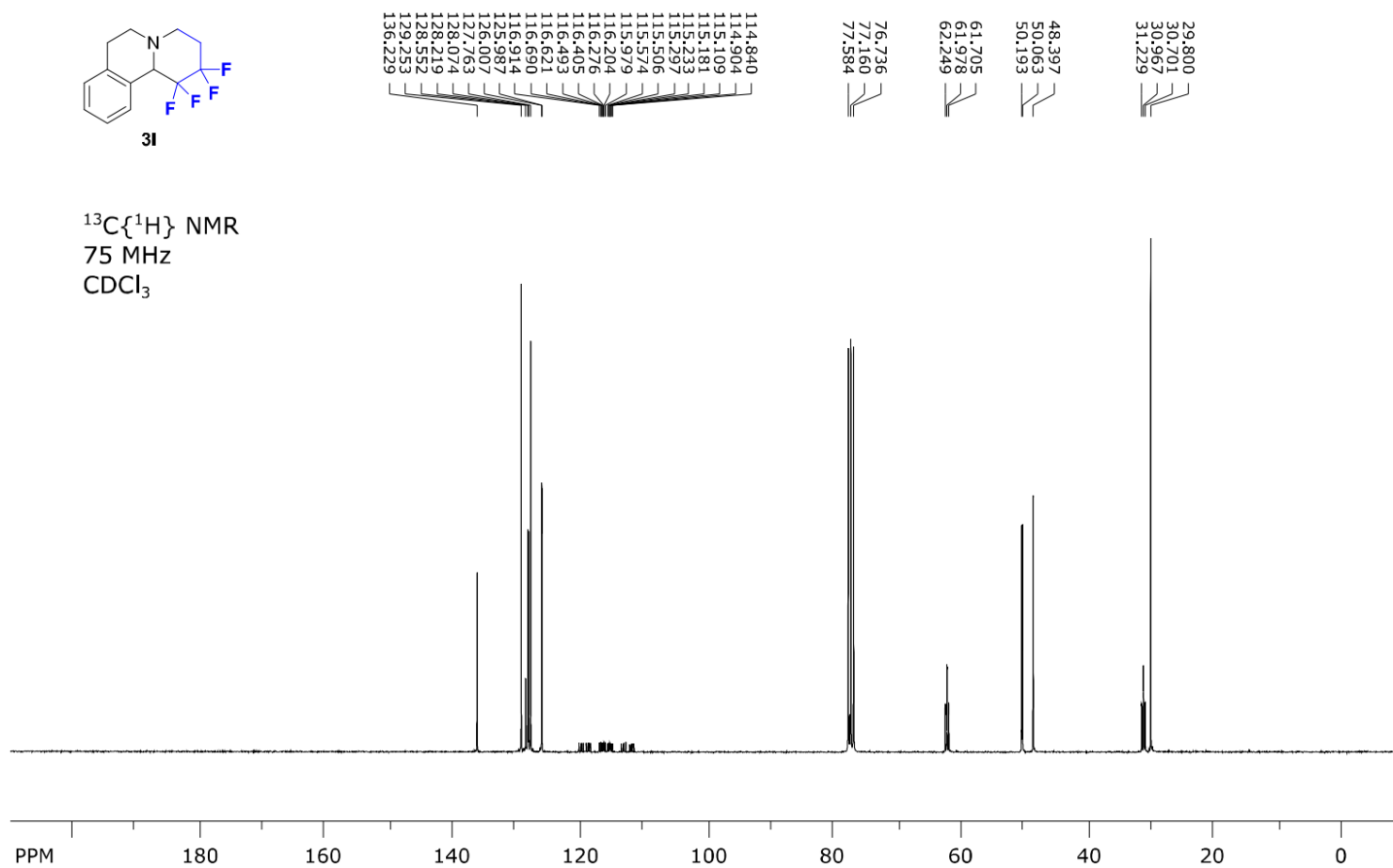
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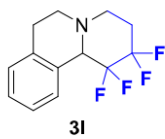
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300 MHz
 CDCl_3



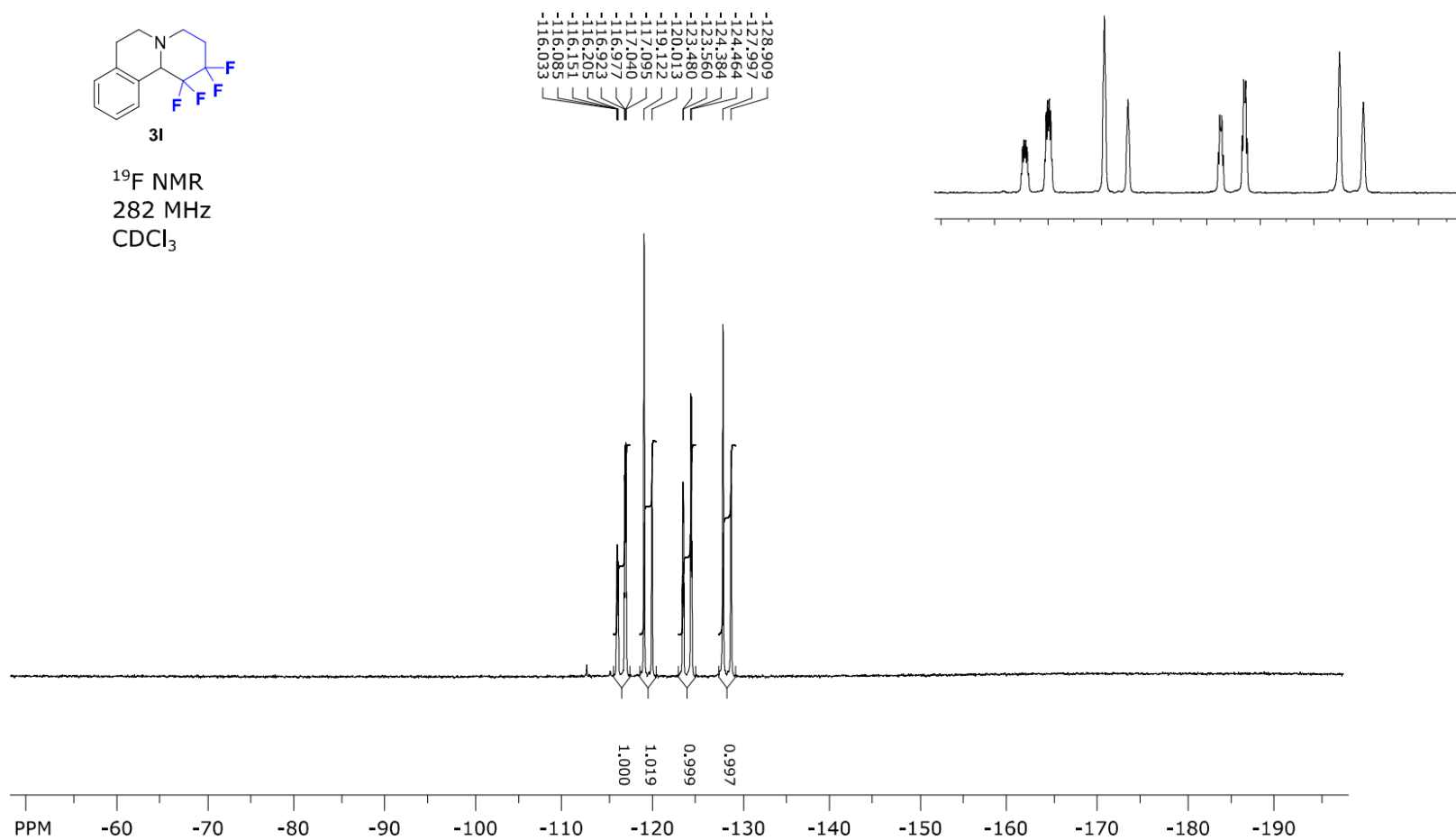


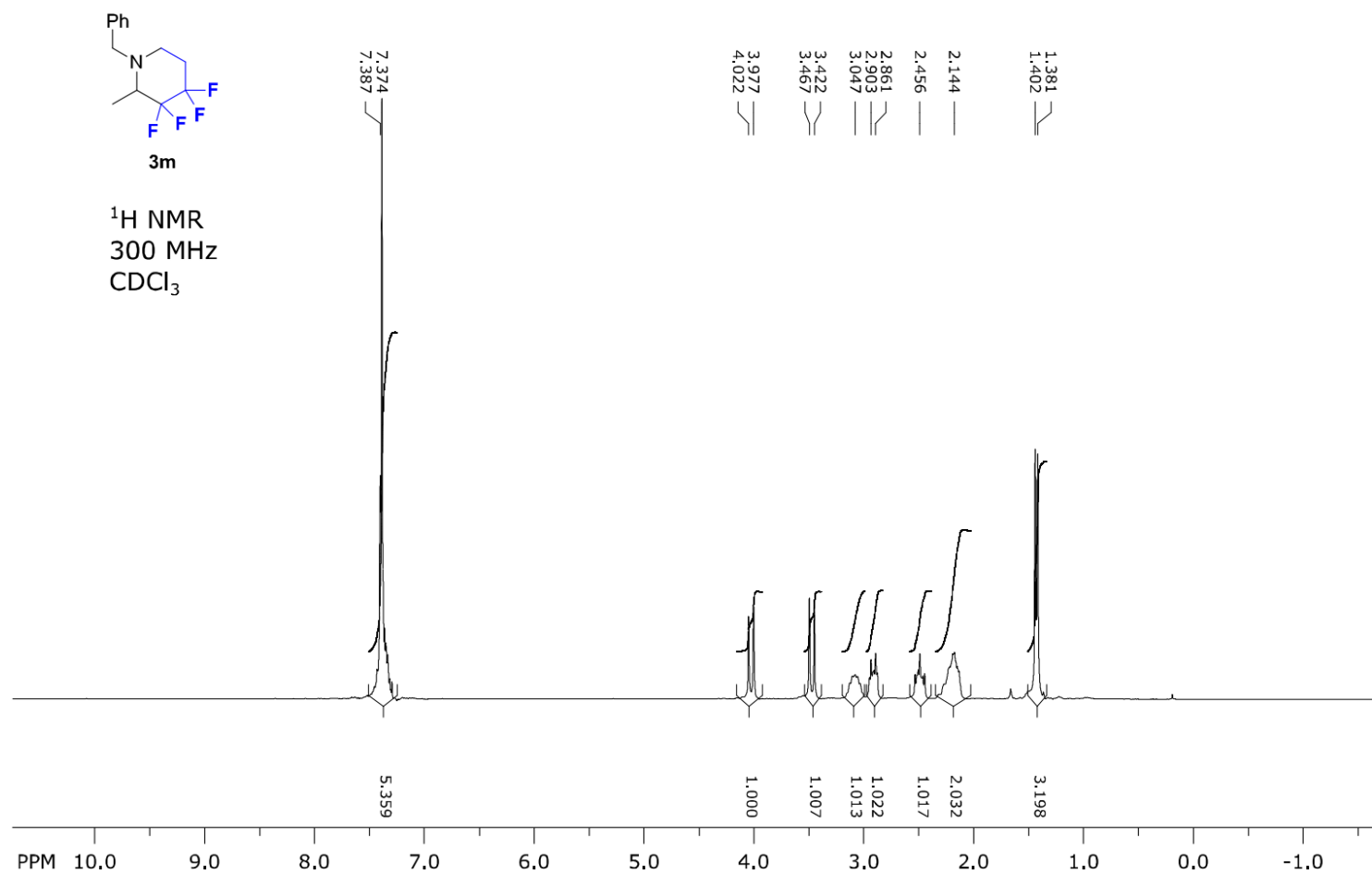
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75 MHz
 CDCl_3

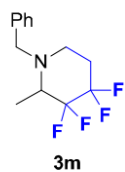




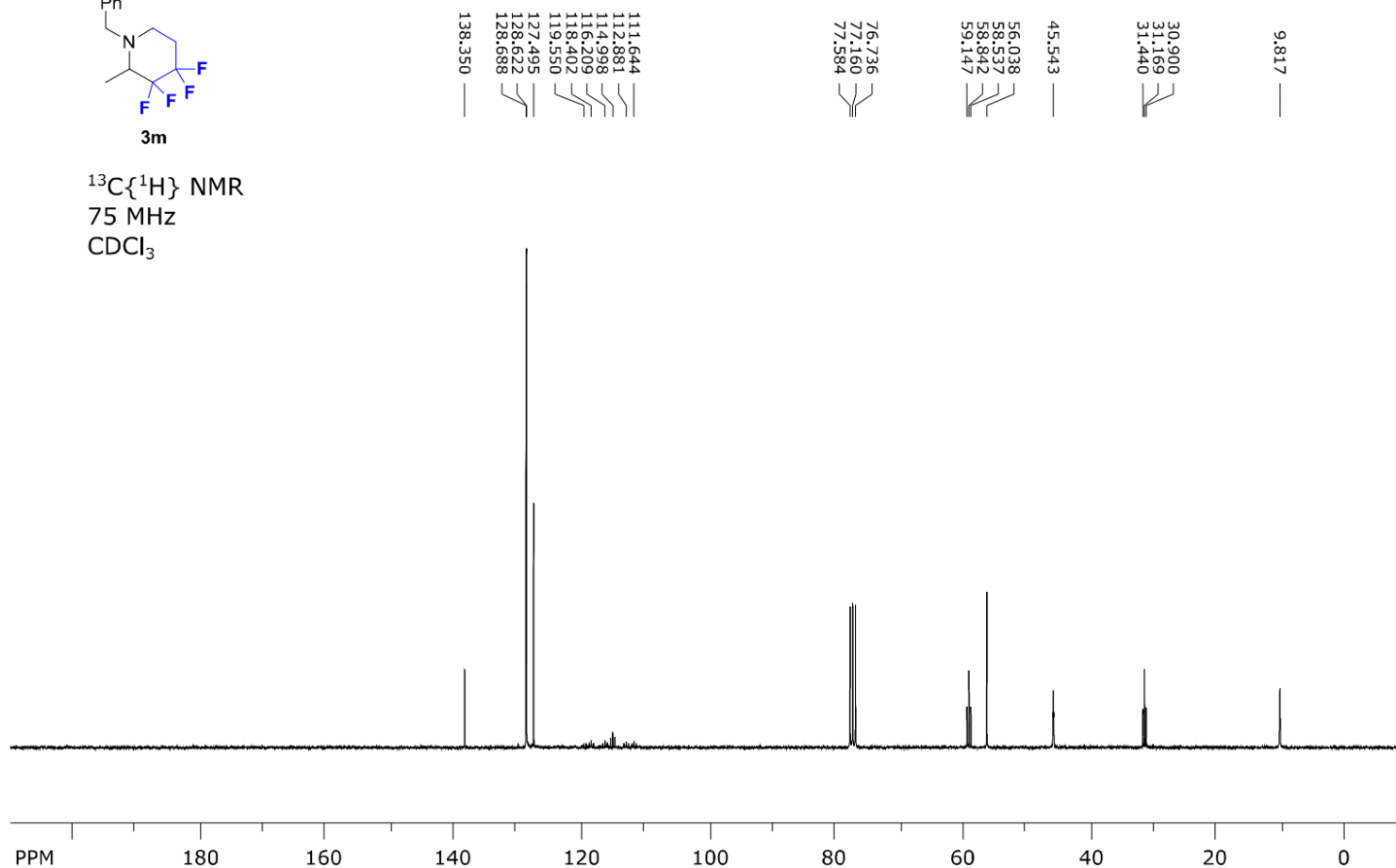
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282 MHz
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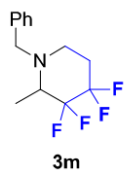






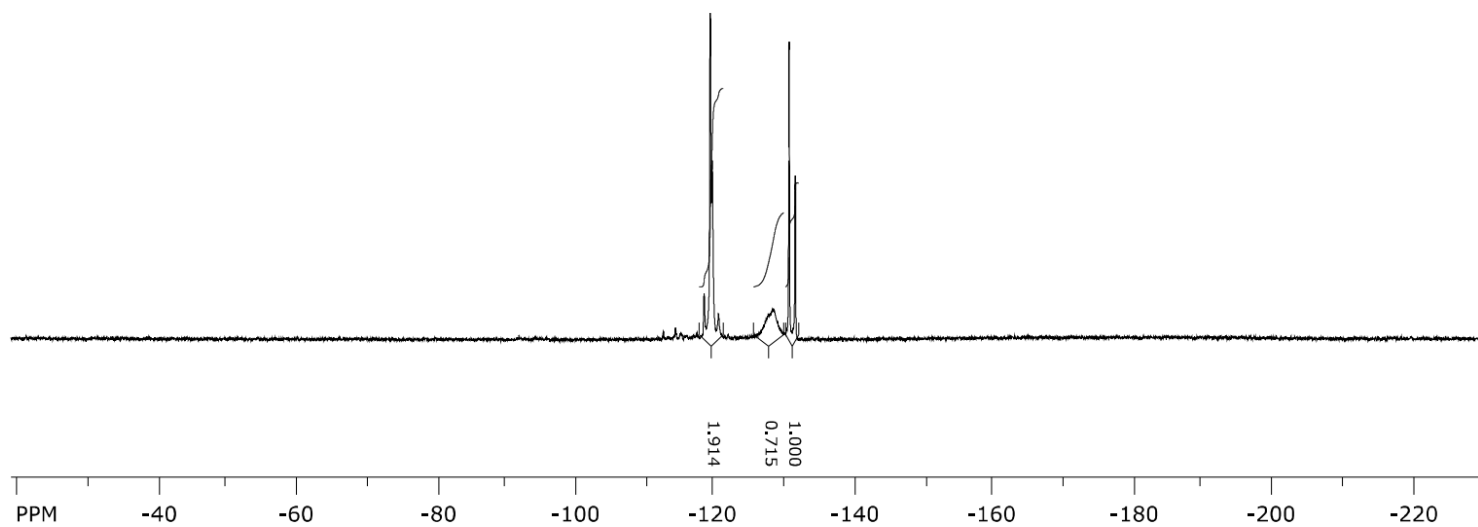
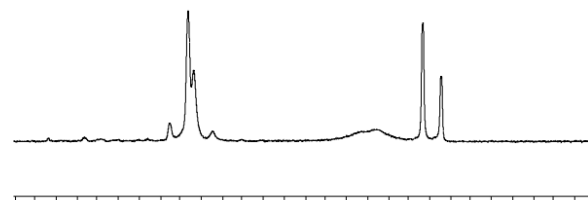
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 75 MHz
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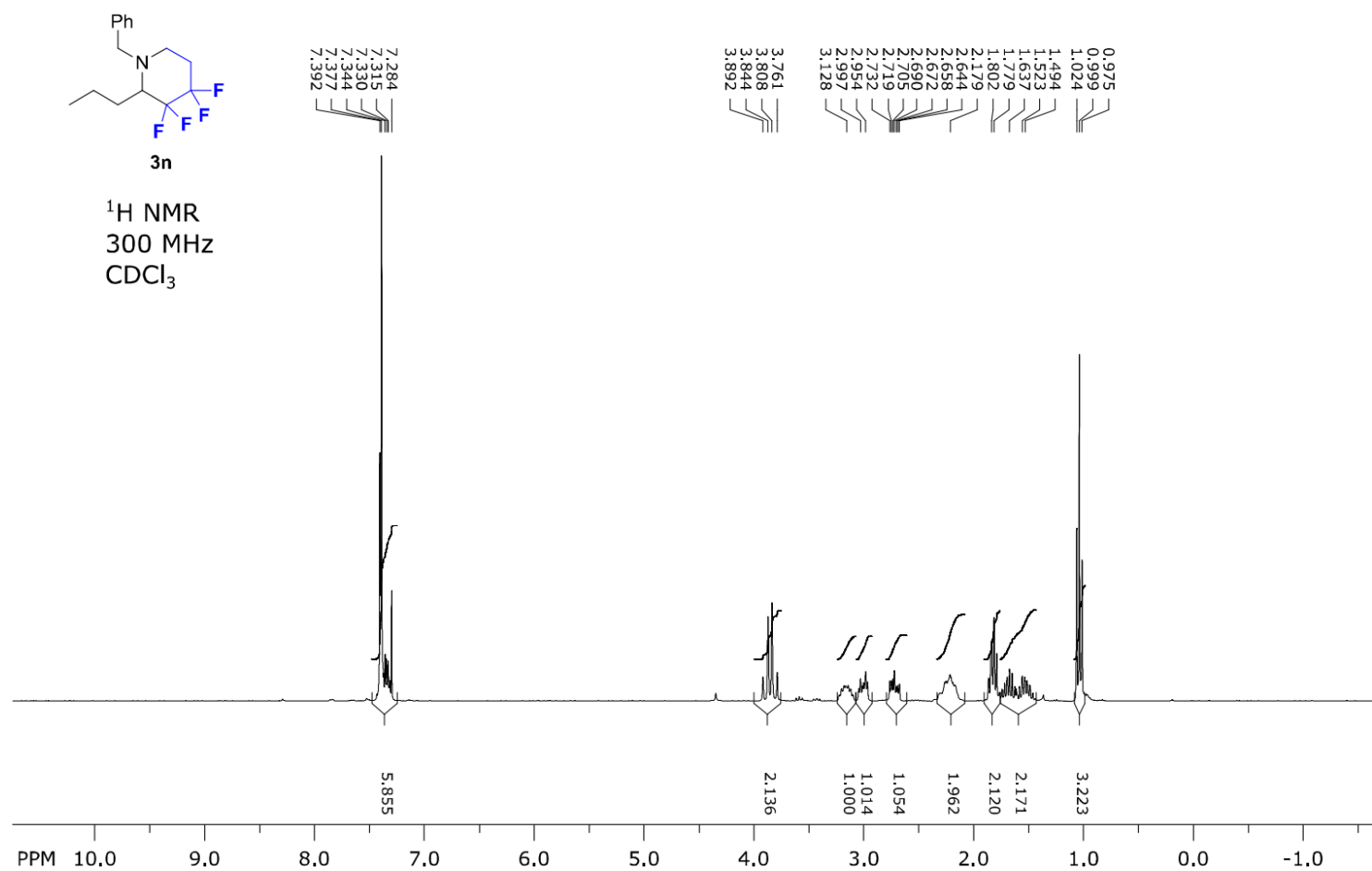


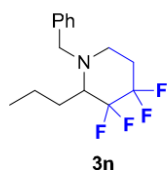


¹⁹F NMR
 282 MHz
 CDCl₃

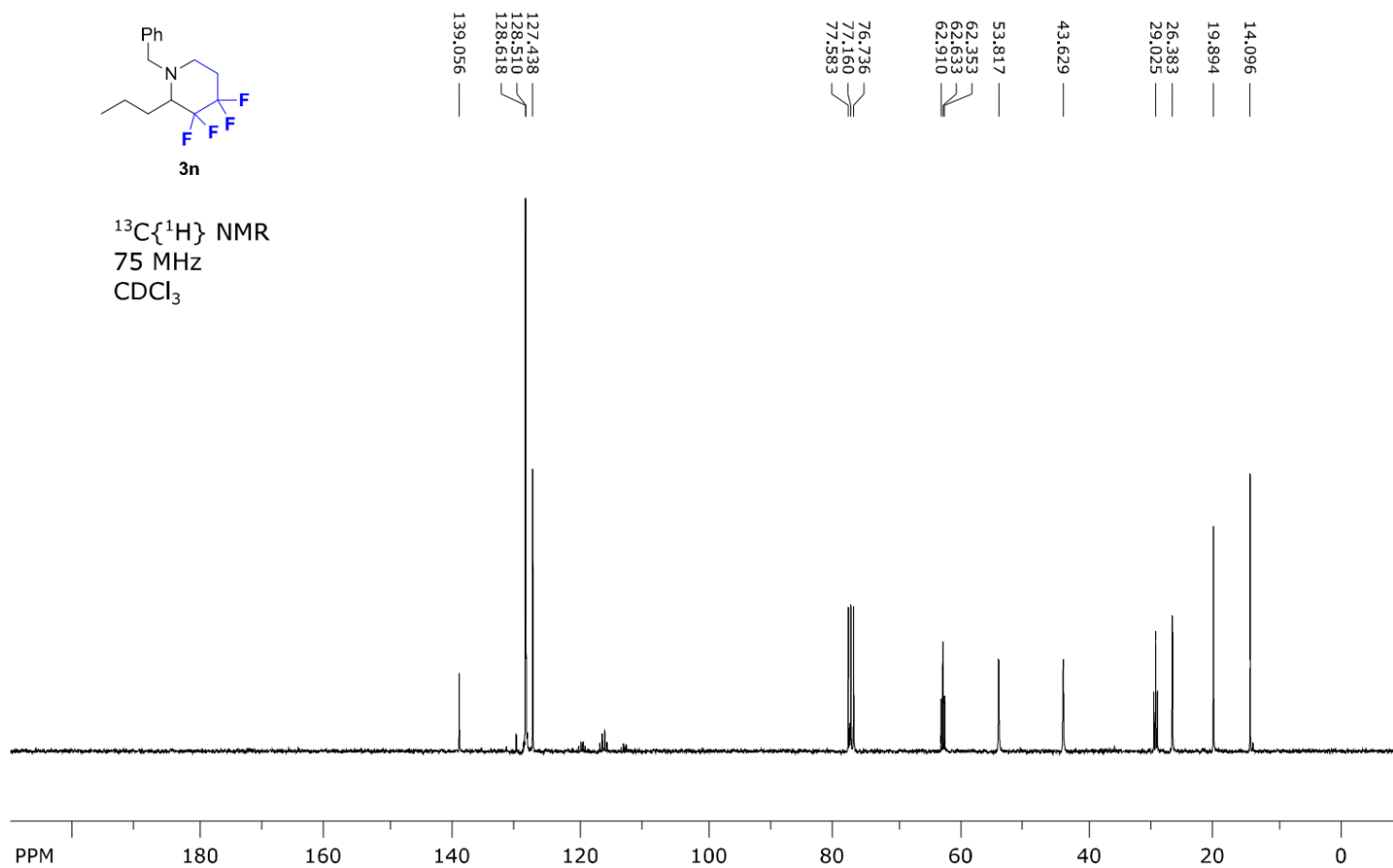
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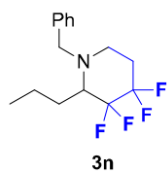




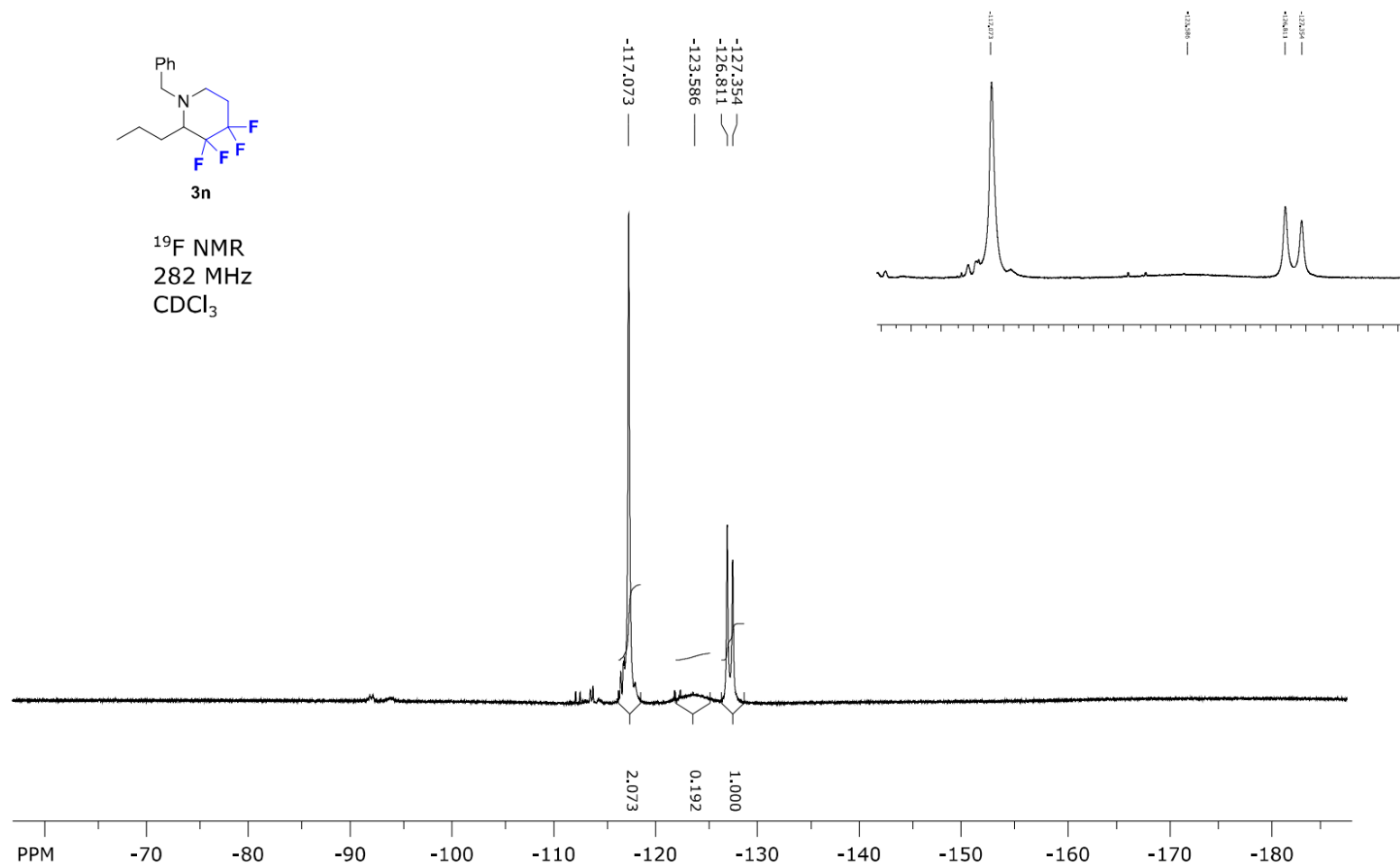


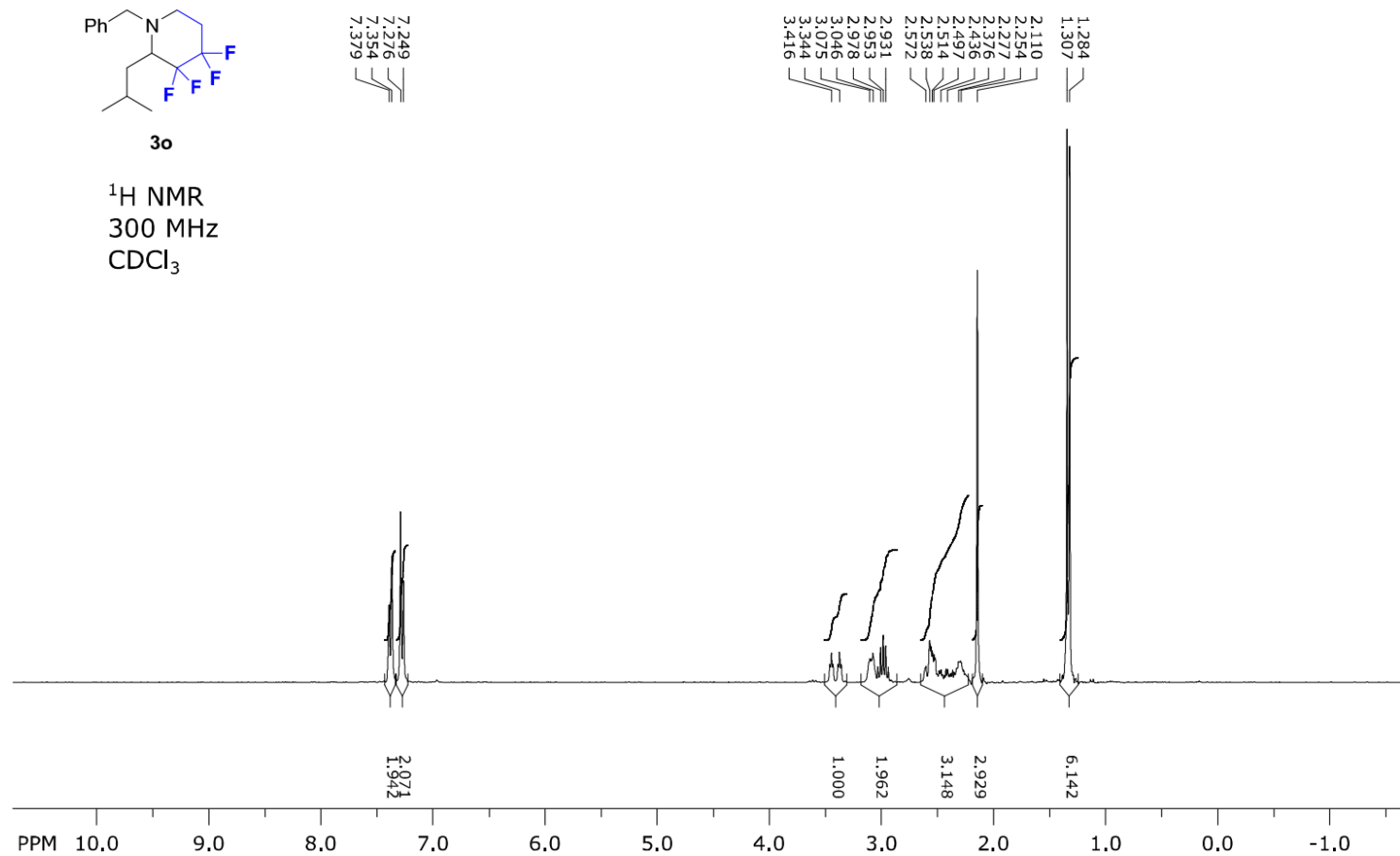
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 75 MHz
 CDCl_3

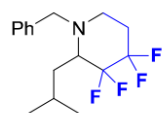




¹⁹F NMR
282 MHz
CDCl₃

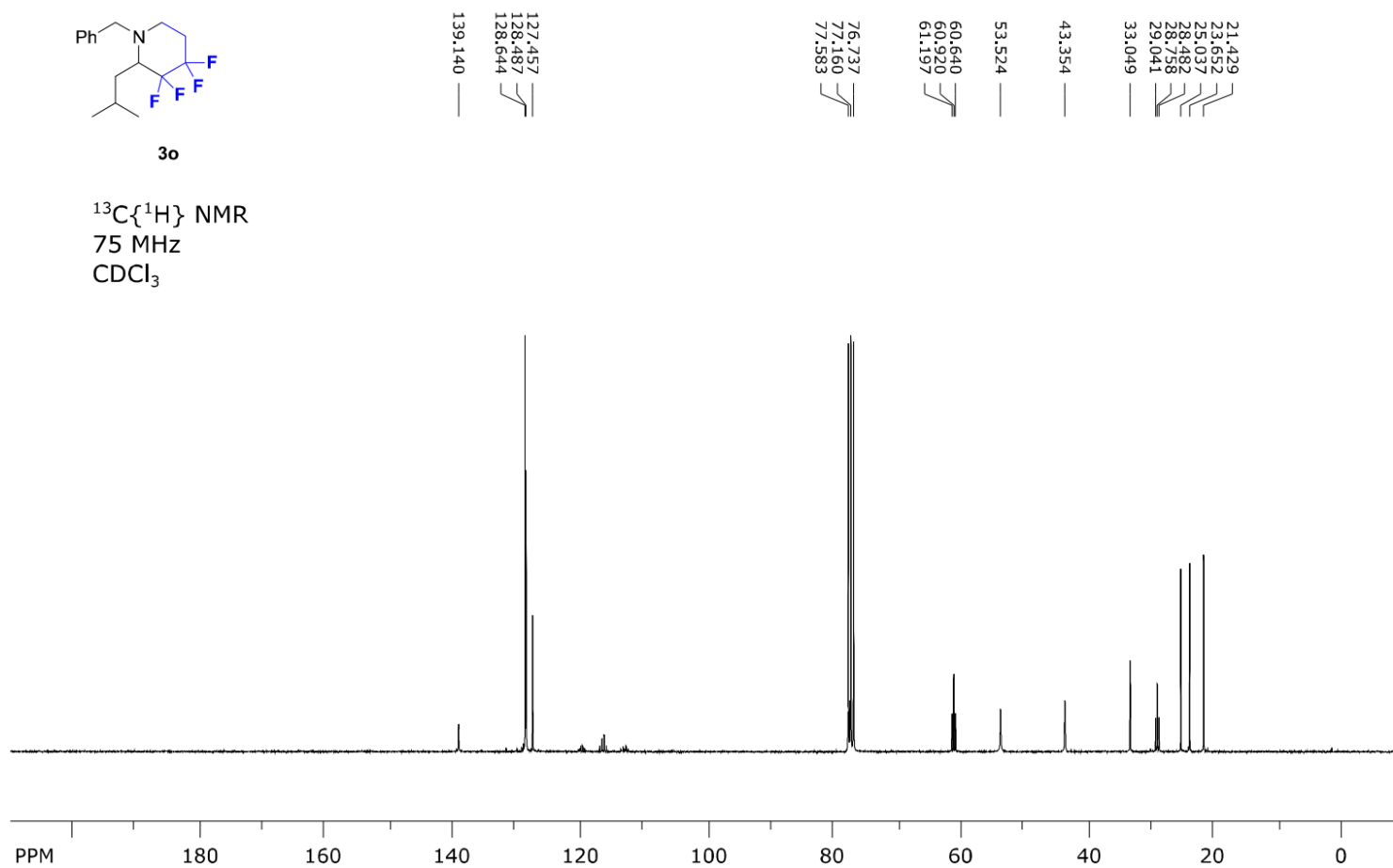


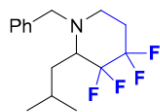




3o

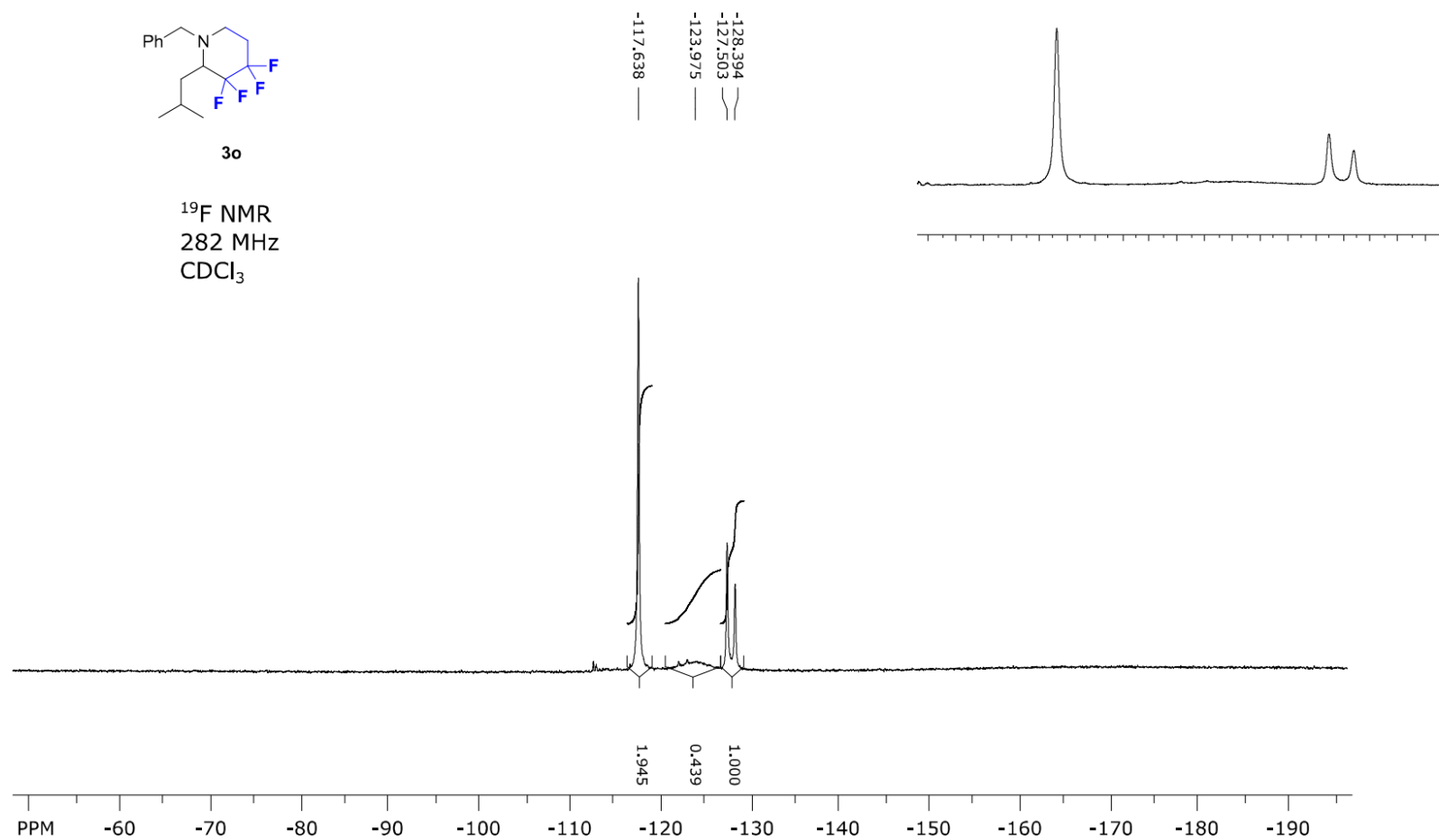
$^{13}\text{C}\{^1\text{H}\}$ NMR
75 MHz
 CDCl_3

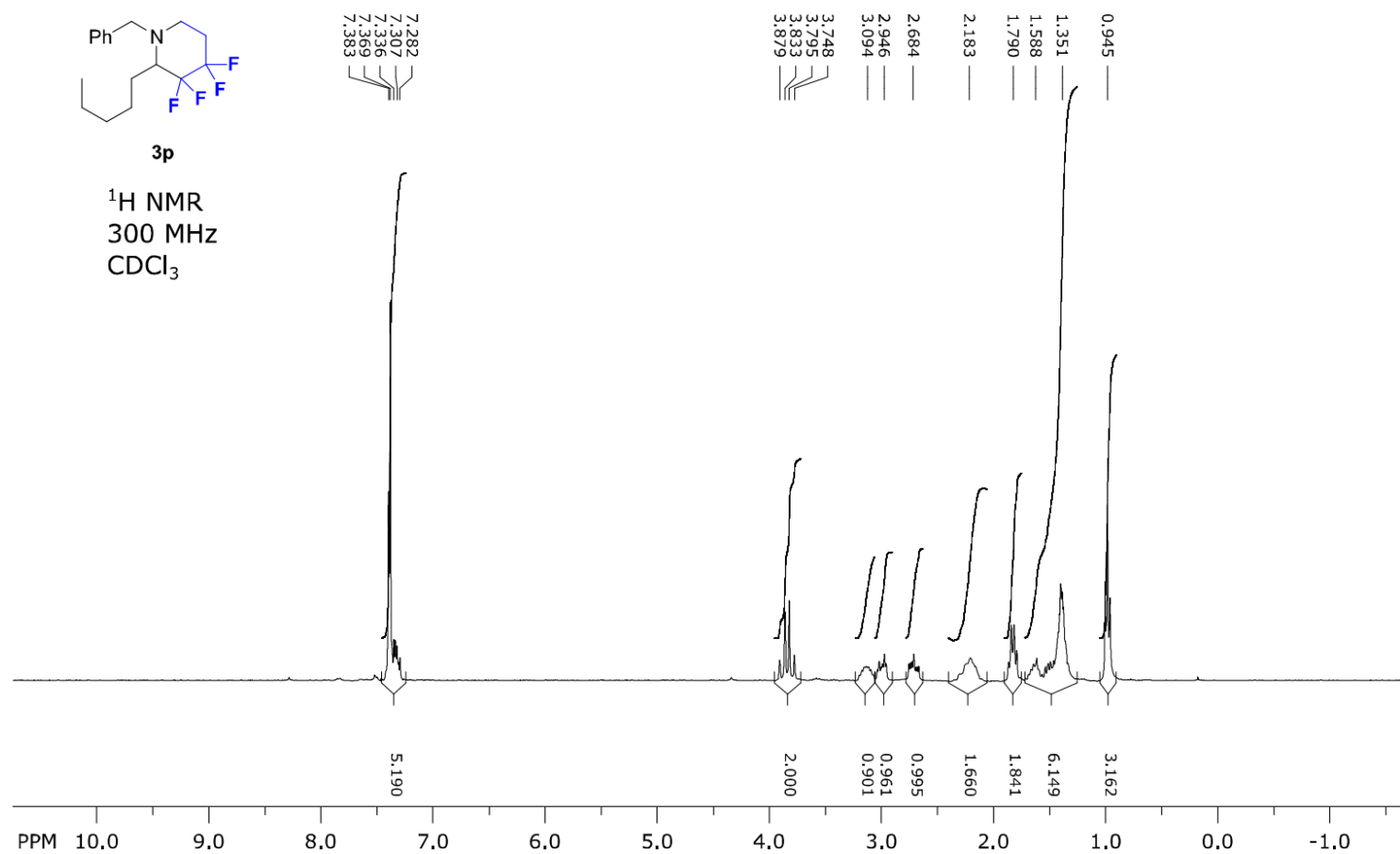


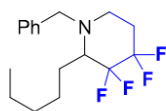


3o

^{19}F NMR
282 MHz
 CDCl_3

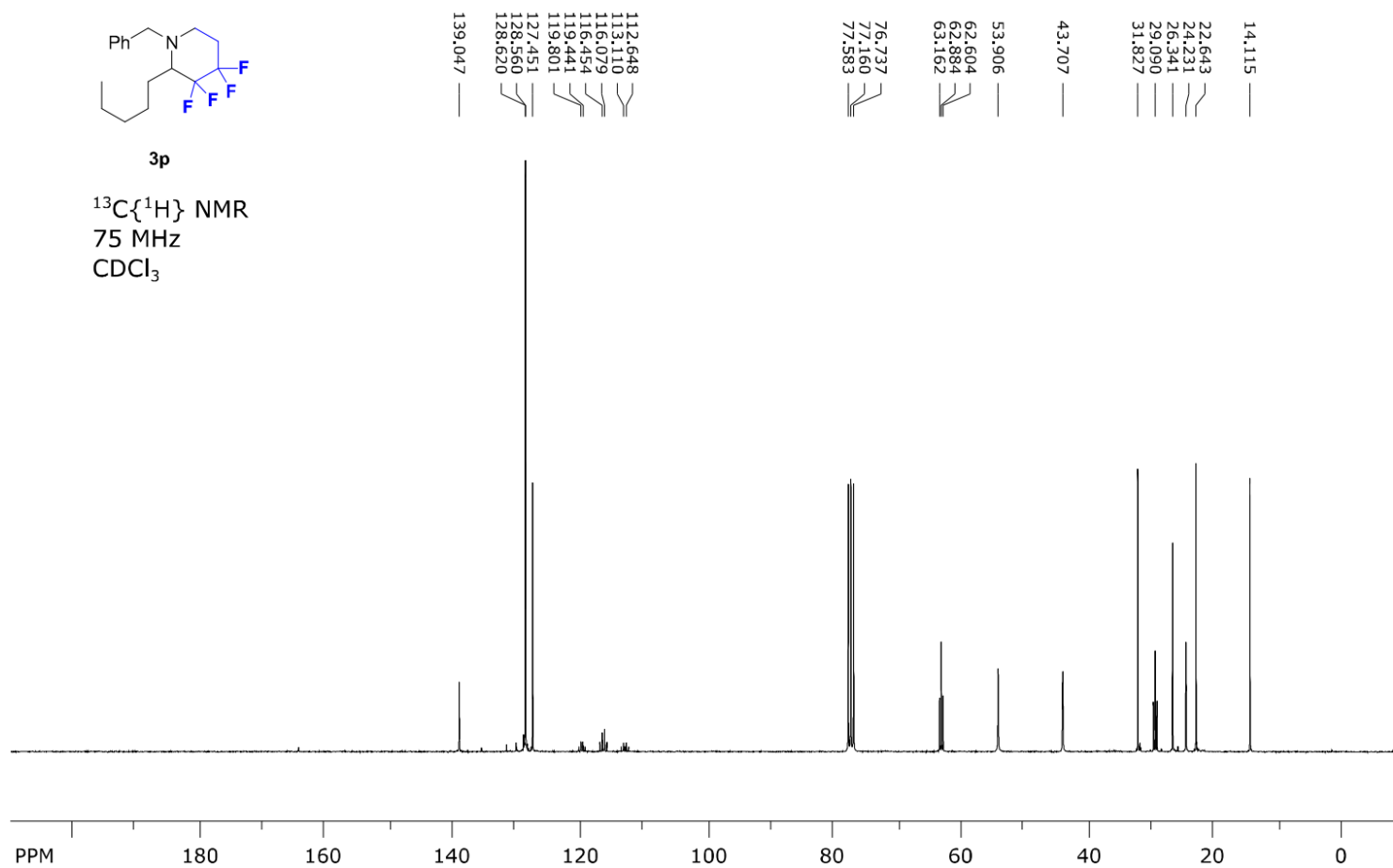


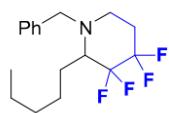




3p

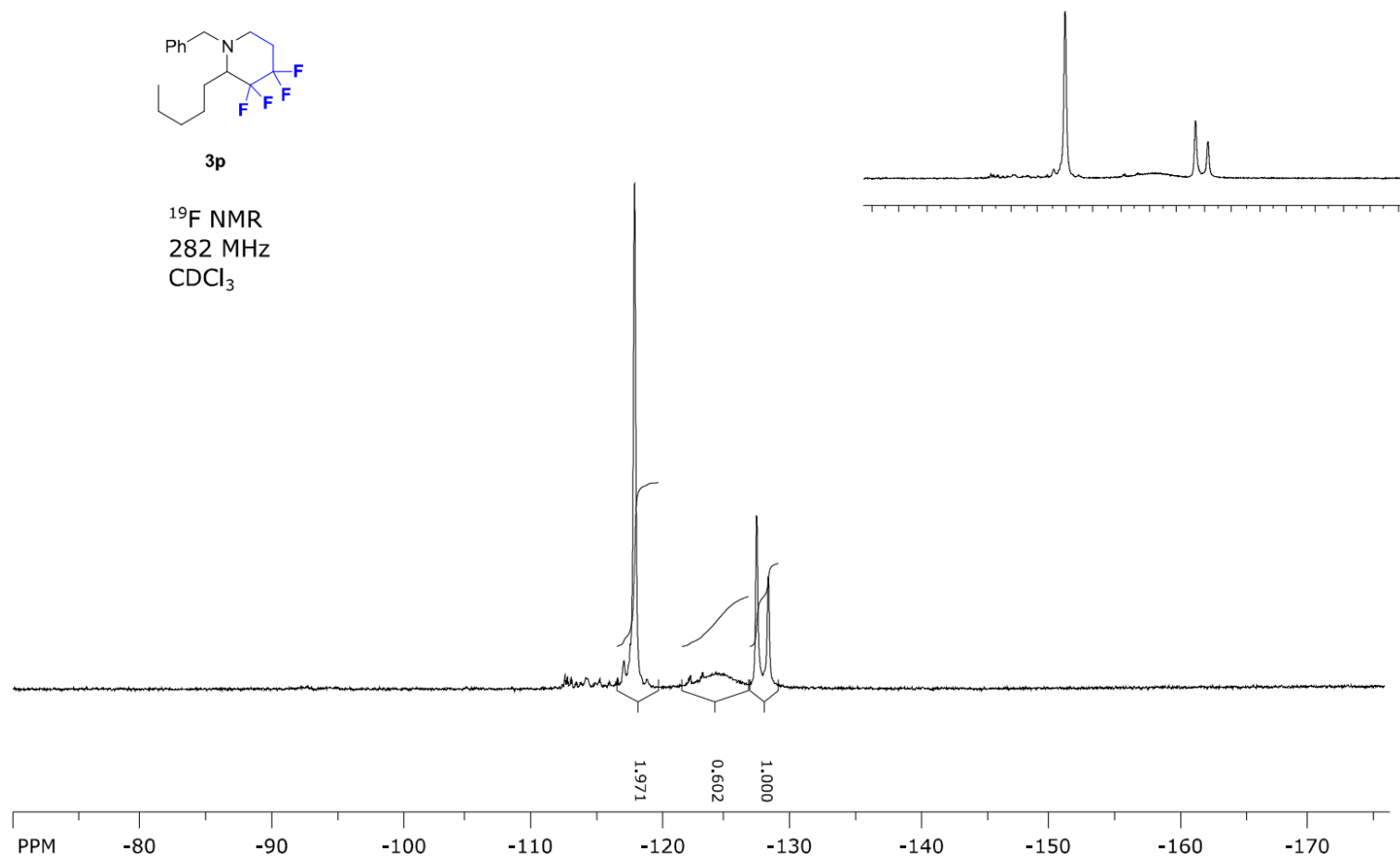
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75 MHz
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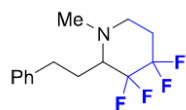




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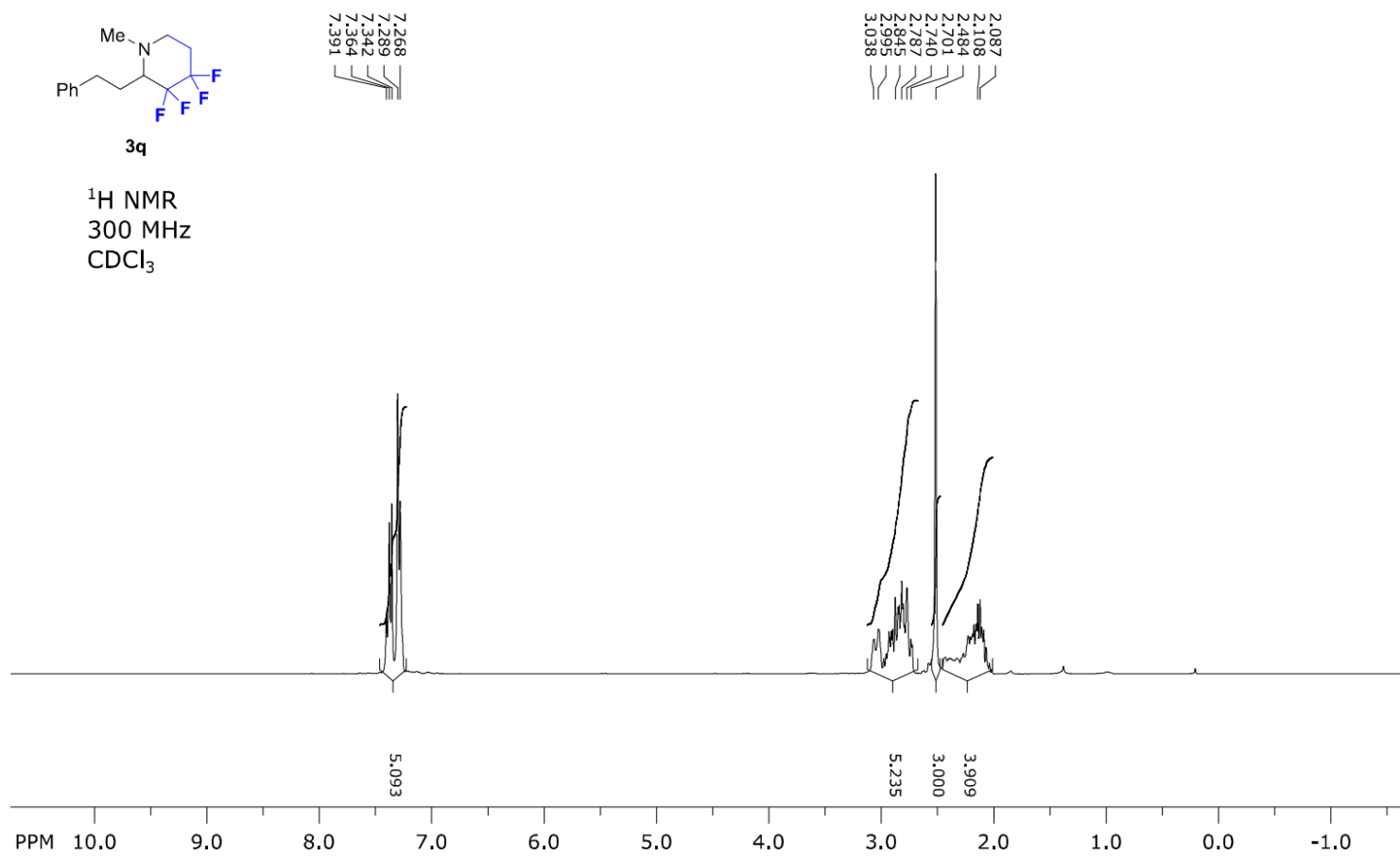
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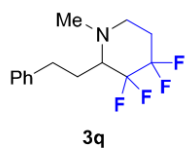




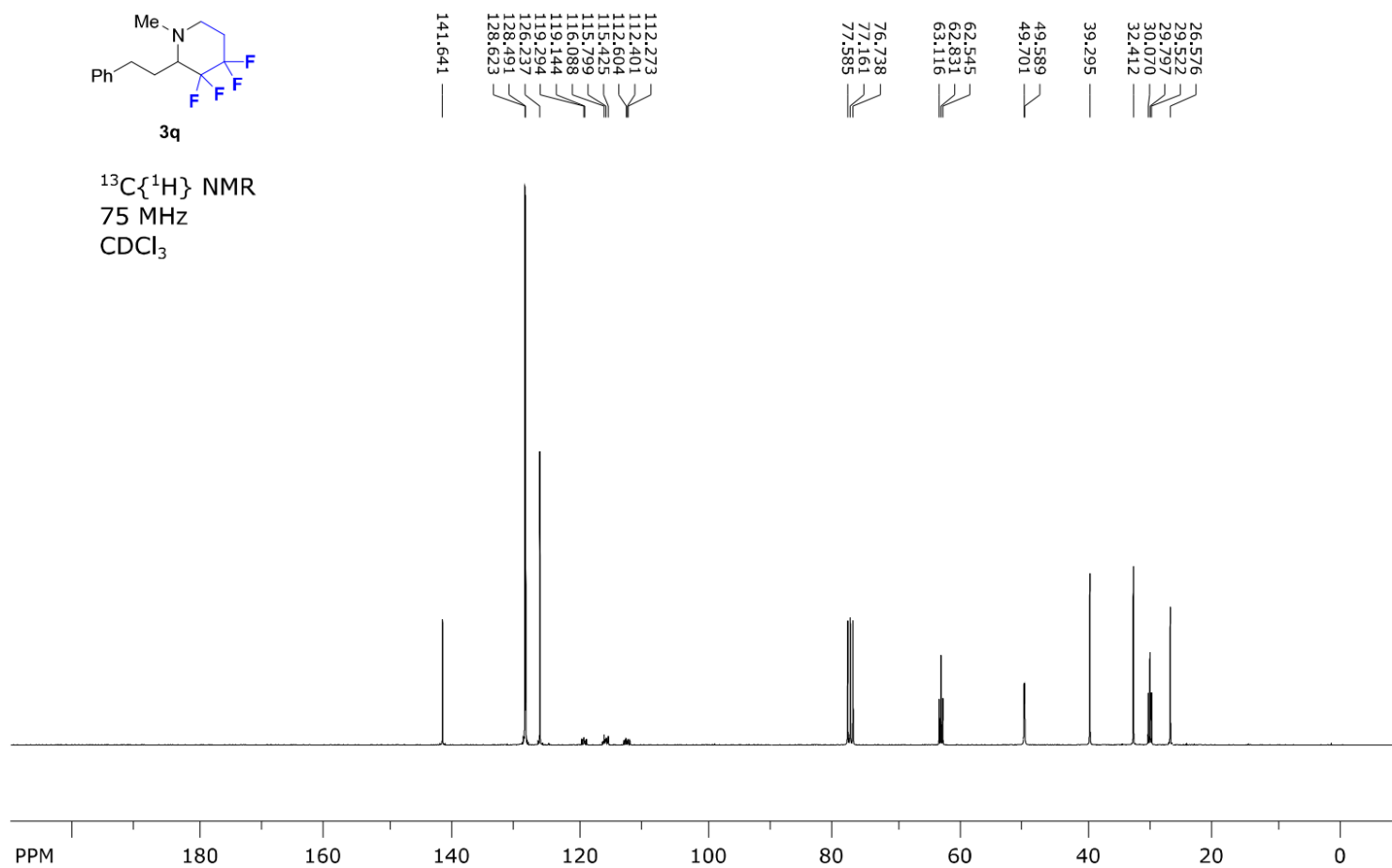
3q

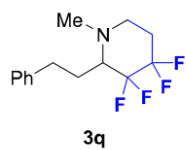
¹H NMR
300 MHz
CDCl₃





$^{13}\text{C}\{^1\text{H}\}$ NMR
75 MHz
 CDCl_3





¹⁹F NMR
282 MHz
CDCl₃

