

Novel Convenient 2-Step Synthesis of Pyrido[1,2-*a*]indoles from Ppyrilium Salts and *o*-Bromoanilines

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General information

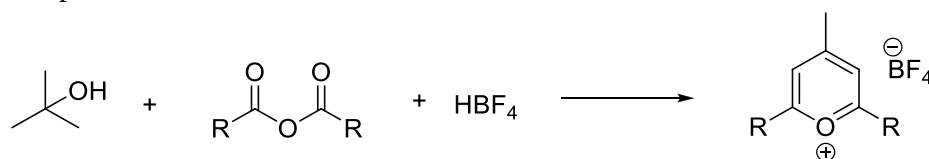
Solvents were purchased from commercial sources and were absolutized before use. Thin layer chromatography was performed using pre-coated plates obtained from E. Merck (TLC silica gel 60 F254). TLC plates were visualized by exposure to ultraviolet light (UV). Silica gel chromatography purifications were performed by flash chromatography using EM Science silica gel 60 (230-400 mesh). All other reagents were commercially available and were used without further purification.

All new compounds were characterized by ^1H NMR, ^{13}C NMR, ^{19}F NMR, B^{11} NMR, ^1H - ^{13}C HSQC NMR, ^1H - ^{15}N HMBC NMR, FTIR and High Resolution Mass Spectrometry (HRMS). NMR spectra were obtained on a Bruker "Ascend™ 400" (400 MHz ^1H , 101 MHz ^{13}C , 376 MHz ^{19}F). Coupling constants J are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as "s", "d", "t" or "m" for singlet, doublet, triplet or multiplet, respectively. The analysis was performed on an "Agilent 1260" Infinity liquid chromatograph combined with a Bruker MaXis Impact mass spectrometer with electrospray ionization method (ESI). Eluents used: 80% MeCN, 20% H_2O and direct injection of the sample (no chromatography column) were performed.

Preparation of pyrylium salts

General Procedure 1 (GP-1)

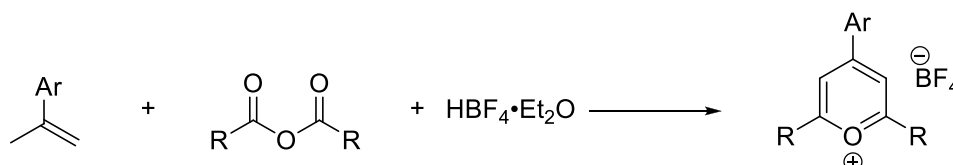
A published procedure with minor modifications.¹



To a mixture of *tert*-butanol (7.4 g, 0.1 mol, 1 eq) and carboxylic acid anhydride (1.3 mol, 13 eq.) a 48% aqueous solution of HBF_4 (12.5 ml, 17.4 g, 0.095 mol, 0.95 eq) was added dropwise at such rate that the temperature of the reaction mixture was about 80 °C (cooling with water bath). After addition the reaction mixture was allowed to stir overnight at room temperature, then cooled to -20 °C and diluted with diethyl ether. The precipitate was filtered, washed with diethyl ether and dried in vacuum.

General Procedure 2 (GP-2)

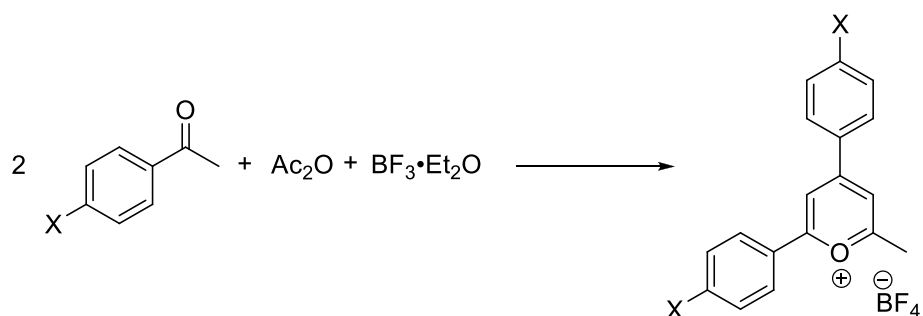
A published procedure with minor modifications.²



To a solution of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (1 eq) in carboxylic acid anhydride (1 ml per 1 mmol of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$) 2-aryl-propene-1 (1 eq) was added dropwise at 0 °C. The reaction mixture was allowed to stir at room temperature overnight. The reaction mixture was cooled to -20 °C and diethyl ether (1.5 ml per 1 mmol of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$) was added. The precipitate was filtered, washed with diethyl ether. The product can be purified by dissolution in acetone and precipitation with diethyl ether.

General Procedure 3 (GP-3)

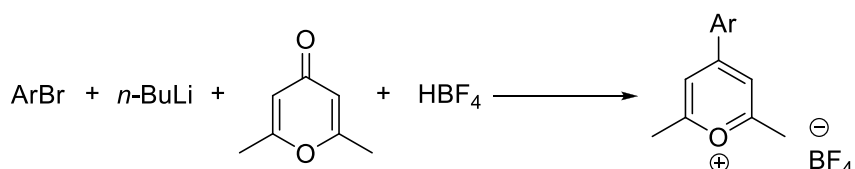
A published procedure with minor modifications.³



A mixture of substituted acetophenone (0.2 mol), acetic anhydride (0.4 mol) and boron trifluoride diethyl etherate (0.14 mol) was refluxed for 2h. The hot dark brown reaction mixture was diluted with 300 ml of ethyl acetate and refluxed for 5 min. The precipitate was filtered and washed with 3x30 ml of hot ethyl acetate. The product may be contaminated with boron difluoride β -diketonate complex, which may be removed either by washing with hot ethyl acetate either by dissolution in acetone and precipitation with diethyl ether.

General Procedure 4 (GP-4)

A published procedure with minor modifications.⁴



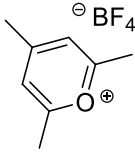
To a cooled to $-78\text{ }^\circ\text{C}$ solution of aryl bromide (10 mmol) in THF (30 ml) 2.5M solution of $n\text{-BuLi}$ in hexanes (4 ml, 10 mmol) was added dropwise at such rate that the temperature of the reaction mixture was about $(-72)\text{ }^\circ\text{C}$ – $(-80)\text{ }^\circ\text{C}$. The reaction mixture was stirred after addition for 30 minutes at this temperature, then a solution of 2,6-dimethyl-4H-pyran-4-one (1.1 g, 9 mmol) in THF was added dropwise. The reaction mixture was allowed to reach 0°C and 48% aqueous solution of HBF_4 (3 ml) was added. The reaction mixture was filtered. The precipitate was washed with diethyl ether and purified by dissolution in acetone and precipitation with diethyl ether.

Analytical data of pyridinium salts

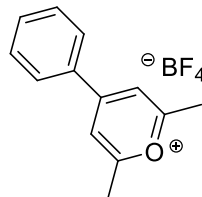
According to the literature, various deuterated solvents and their mixtures were used to acquire NMR spectra of pyrylium salts: CD_3CN , $\text{CDCl}_3/\text{CF}_3\text{COOH}$, CD_3OD . Deuterated DMSO is a less suitable solvent due to its reactivity towards pyrylium salts. We believe that acetone- d_6 is the most convenient and accessible solvent for this class of compounds. However, it should be noted that alkyl groups in the 2- and 6-positions of the pyrylium ring can be deuterated upon prolonged standing. This will lead to a decrease in the integral intensities of these groups relative to other signals and to the appearance of multiplet signals in the ^{13}C spectra due to the spin-spin coupling of carbon and deuterium atoms. Thus, to obtain undeuterated signals of alkyl groups in

the ^1H spectra of pyrylium salts, the spectra of samples should be acquired as quickly as possible after preparation.

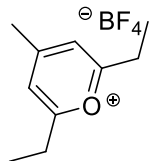
2,4,6-trimethylpyrylium tetrafluoroborate (**1a**)

 Following **GP-1**, 2,4,6-trimethylpyrylium tetrafluoroborate (**1a**) was obtained from *tert*-butanol, $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ and acetic anhydride as a beige solid, 56% yield. ^1H NMR (400 MHz, Acetone- d_6) δ 8.04 (s, 2H), 2.97 (s, 6H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, Acetone- d_6) δ 178.99, 175.44, 124.20, 23.46, 21.33. ^{11}B NMR (128 MHz, Acetone- d_6) δ -1.01. ^{19}F NMR (376 MHz, Acetone- d_6) δ -151.75, -151.80. The NMR data are in agreement with previously reported.⁵

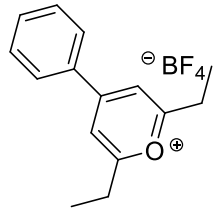
2,6-dimethyl-4-phenylpyrylium tetrafluoroborate (**1b**)

 Following **GP-2**, 2,6-dimethyl-4-phenylpyrylium tetrafluoroborate (**1b**) was obtained from 2-phenylpropene, $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ and acetic anhydride as a yellow solid, 27% yield. ^1H NMR (400 MHz, Acetone- d_6) δ 8.57 (s, 2H), 8.29 (d, J = 7.4 Hz, 2H), 7.84 (t, J = 7.4 Hz, 1H), 7.73 (t, J = 7.8 Hz, 2H), 3.07 – 3.00 (m, 5H of 6H due to fast isotopic exchange). ^{13}C NMR (101 MHz, Acetone- d_6) δ 179.71, 167.11, 136.16, 133.04, 131.05, 130.41, 119.29, 21.68, 21.66 – 21.21 (m, due to fast isotopic exchange). ^{11}B NMR (128 MHz, Acetone- d_6) δ -0.94. ^{19}F NMR (376 MHz, Acetone- d_6) δ -151.56, -151.62. The NMR data are in agreement with previously reported.²

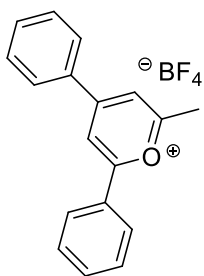
2,6-diethyl-4-methylpyrylium tetrafluoroborate (**1c**)

 Following **GP-1**, 2,6-diethyl-4-methylpyrylium tetrafluoroborate (**1c**) was obtained from *tert*-butanol, $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ and propionic anhydride as a beige solid, 48% yield. ^1H NMR (400 MHz, Acetone- d_6) δ 8.06 (s, 2H), 3.28 (q, J = 7.5 Hz, 4H), 2.81 – 2.77 (m, 3H of 4H due to fast isotopic exchange), 1.46 (t, J = 7.5 Hz, 6H). ^{13}C NMR (101 MHz, Acetone- d_6) δ 182.53, 175.70, 123.08, 28.70, 23.57, 23.53 – 23.01 (m, due to fast isotopic exchange), 10.75. ^{11}B NMR (128 MHz, Acetone- d_6) δ -1.04. ^{19}F NMR (376 MHz, Acetone- d_6) δ -151.74, -151.80. HRMS (m/z): calc. for $\text{C}_{10}\text{H}_{15}\text{O}^+ [\text{M}-\text{BF}_4]^+ = 115.1117$; found: 115.1110. The NMR data are in agreement with previously reported.⁵

2,6-diethyl-4-phenylpyrylium tetrafluoroborate (**1d**)

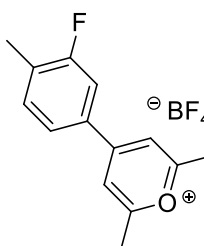
 Following **GP-2**, 2,6-diethyl-4-phenylpyrylium tetrafluoroborate (**1d**) was obtained from 2-phenylpropene, $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ and propionic anhydride as a yellowish solid, 23% yield. MP = 173-174 °C. ^1H NMR (400 MHz, Acetone- d_6) δ 8.53 (s, 2H), 8.32 (d, J = 7.5 Hz, 2H), 7.83 (t, J = 7.4 Hz, 1H), 7.72 (t, J = 7.8 Hz, 2H), 3.38 (q, J = 7.5 Hz, 4H), 1.53 (t, J = 7.5 Hz, 6H). ^{13}C NMR (101 MHz, Acetone- d_6) δ 183.37, 167.41, 136.02, 133.30, 130.96, 130.52, 118.34, 29.16, 29.12 – 28.51 (m), 11.05. ^{11}B NMR (128 MHz, Acetone- d_6) δ -0.94. ^{19}F NMR (376 MHz, Acetone- d_6) δ -151.56, -151.61. HRMS (m/z): calc. for $\text{C}_{15}\text{H}_{17}\text{O}^+ [\text{M}-\text{BF}_4]^+ = 213.1274$; found: 213.1275.

2-methyl-4,6-diphenylpyrylium tetrafluoroborate (**1e**)



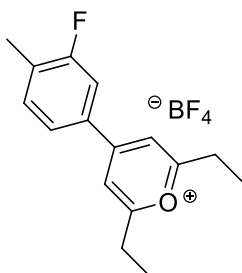
Following **GP-3**, 2-methyl-4,6-diphenylpyrylium tetrafluoroborate (**1e**) was obtained from acetophenone, boron trifluoride diethyl etherate and acetic anhydride as a yellow solid, 48% yield. ^1H NMR (400 MHz, Acetone- d_6) δ 9.11 (d, J = 1.6 Hz, 1H), 8.64 (d, J = 1.4 Hz, 1H), 8.54 (d, J = 7.5 Hz, 2H), 8.43 (d, J = 7.5 Hz, 2H), 7.92 – 7.81 (m, 2H), 7.81 – 7.70 (m, 4H), 3.18 (s, 3H). ^{13}C NMR (101 MHz, Acetone- d_6) δ 178.93, 173.07, 167.34, 136.15, 136.06, 133.51, 131.00, 130.79, 130.60, 130.06, 129.53, 119.72, 115.86, 21.72. ^{11}B NMR (128 MHz, Acetone- d_6) δ -0.87. ^{19}F NMR (376 MHz, Acetone- d_6) δ -151.48, -151.54. The NMR data are in agreement with previously reported.⁶

4-(3-fluoro-4-methylphenyl)-2,6-dimethylpyrylium tetrafluoroborate (**1f**)



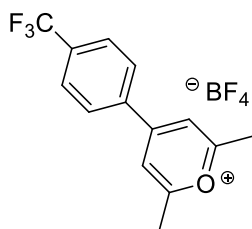
Following **GP-4**, 4-(3-fluoro-4-methylphenyl)-2,6-dimethylpyrylium tetrafluoroborate (**1f**) was obtained from 4-bromo-2-fluoro-1-methylbenzene, butyl lithium and 2,6-dimethyl-4H-pyran-4-one as a brown solid, 31% yield. MP = 190 (dec.) °C. ^1H NMR (400 MHz, Acetone- d_6) δ 8.58 (s, 2H), 8.13 – 7.99 (m, 2H), 7.64 (t, J = 7.9 Hz, 1H), 3.17 – 2.93 (m, 5H of 6H due to fast isotopic exchange), 2.41 (d, J = 2.0 Hz, 3H). ^{13}C NMR (101 MHz, Acetone- d_6) δ 179.80, 165.55 (d, J = 2.4 Hz), 162.69 (d, J = 246.1 Hz), 134.47 (d, J = 17.3 Hz), 134.32 (d, J = 5.2 Hz), 132.50 (d, J = 8.1 Hz), 126.47 (d, J = 3.2 Hz), 119.11, 116.50 (d, J = 24.6 Hz), 21.68, 21.67 – 21.20 (m, due to fast isotopic exchange), 14.91 (d, J = 3.4 Hz). ^{11}B NMR (128 MHz, Acetone- d_6) δ -0.96. ^{19}F NMR (376 MHz, Acetone- d_6) δ -116.03, -151.52, -151.57. HRMS (m/z): calc. for $\text{C}_{14}\text{H}_{14}\text{FO}^+$ [$\text{M}-\text{BF}_4$] $^+$ = 217.1023; found: 217.1026. IR (KBr) cm^{-1} 3101 (VW), 1645 (S), 1615 (S), 1533 (M), 1339 (M), 1240 (M), 1234 (W), 1050 (VS), 1029 (VS), 959 (M), 879 (M), 831 (M), 796 (M).

2,6-diethyl-4-(3-fluoro-4-methylphenyl)pyrylium tetrafluoroborate (**1g**)



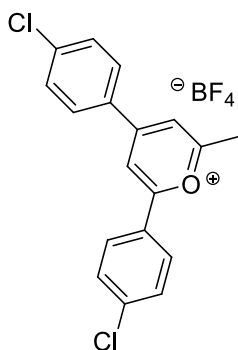
Following **GP-2**, 2,6-diethyl-4-(3-fluoro-4-methylphenyl)pyrylium tetrafluoroborate (**1g**) was obtained from 2-fluoro-1-methyl-4-(prop-1-en-2-yl)benzene, $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ and propionic anhydride as a yellow solid, 17% yield. MP = 151-152 °C. ^1H NMR (400 MHz, Acetone- d_6) δ 8.52 (s, 2H), 8.13 – 8.03 (m, 2H), 7.62 (t, J = 7.8 Hz, 1H), 3.36 (q, J = 7.5 Hz, 4H), 2.41 (d, J = 1.7 Hz, 3H), 1.52 (t, J = 7.5 Hz, 6H). ^{13}C NMR (101 MHz, Acetone- d_6) δ 183.47, 165.84 (d, J = 2.4 Hz), 162.64 (d, J = 245.9 Hz), 134.33, 134.21 (d, J = 5.2 Hz), 134.16, 132.78 (d, J = 8.1 Hz), 126.58 (d, J = 3.2 Hz), 118.14, 116.55 (d, J = 24.6 Hz), 29.16, 14.89 (d, J = 3.4 Hz), 11.03. ^{11}B NMR (128 MHz, Acetone- d_6) δ -0.97. ^{19}F NMR (376 MHz, Acetone- d_6) δ -116.15, -151.45, -151.50. HRMS (m/z): calc. for $\text{C}_{16}\text{H}_{18}\text{FO}^+$ [$\text{M}-\text{BF}_4$] $^+$ = 245.1336; found: 245.1331. IR (KBr) cm^{-1} 3076 (W), 2983 (W), 2944 (W), 2884 (VW), 1643 (M), 1620 (M), 1577 (W), 1532 (S), 1480 (W), 1444 (M), 1407 (W), 1355 (W), 1341 (W), 1272 (W), 1237 (M), 1213 (W), 1095 (M), 1048 (VS), 1038 (VS), 997 (M), 960 (M), 901 (M), 875 (M), 821 (M), 779 (M), 756 (M), 704 (W).

2,6-dimethyl-4-(4-(trifluoromethyl)phenyl)pyrylium tetrafluoroborate (1h)



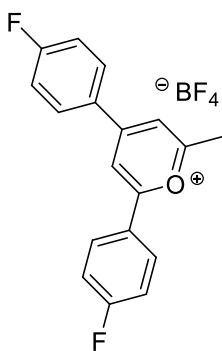
Following **GP-4**, 2,6-dimethyl-4-(4-(trifluoromethyl)phenyl)pyrylium tetrafluoroborate (**1h**) was obtained from 1-bromo-4-(trifluoromethyl)benzene, butyl lithium and 2,6-dimethyl-4H-pyran-4-one as a brown solid, 34% yield. MP = 149-150 °C. ^1H NMR (400 MHz, Acetone- d_6) δ 8.64 (s, 2H), 8.46 (d, J = 8.2 Hz, 2H), 8.05 (d, J = 8.3 Hz, 2H), 3.09 (s, 6H). ^{13}C NMR (101 MHz, Acetone- d_6) δ 180.76 , 165.75 , 137.10 , 135.55 (q, J = 32.8 Hz), 131.12 , 127.67 (q, J = 3.8 Hz), 124.59 (q, J = 272.2 Hz), 120.44 , 21.85 . ^{11}B NMR (128 MHz, Acetone- d_6) δ -0.99 . ^{19}F NMR (376 MHz, Acetone- d_6) δ -63.83 , -151.49 , -151.55 . HRMS (m/z): calc. for $\text{C}_{14}\text{H}_{12}\text{F}_3\text{O}^+ [\text{M}-\text{BF}_4]^+$ = 253.0835; found: 253.0843. IR (KBr) cm^{-1} 3187 (W), 3100 (W), 2943 (VW), 2260 (VW), 1636 (S), 1528 (M), 1476 (M), 1457 (M), 1430 (M), 1398 (M), 1322 (VS), 1172 (M), 1137 (M), 1122 (S), 1096 (M), 1067 (VS), 1051 (VS), 1037 (VS), 1013 (S), 968 (M), 944 (M), 884 (M), 844 (S), 769 (S), 714 (VS), 674 (S).

2,4-bis(4-chlorophenyl)-6-methylpyrylium tetrafluoroborate (1i)



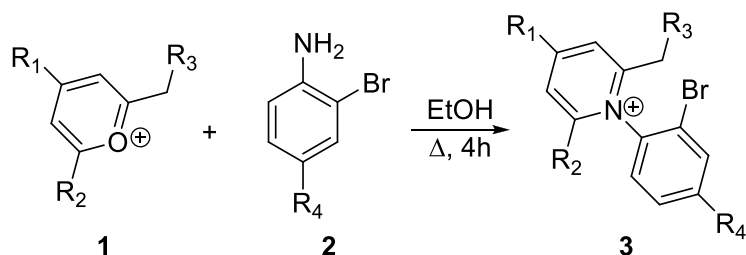
Following **GP-3**, 2,4-bis(4-chlorophenyl)-6-methylpyrylium tetrafluoroborate (**1i**) was obtained from 1-(4-chlorophenyl)ethanone, boron trifluoride diethyl etherate and acetic anhydride as a yellow solid, 44% yield. ^1H NMR (400 MHz, Acetone- d_6) δ 9.19 (d, J = 1.6 Hz, 1H), 8.69 (d, J = 1.6 Hz, 1H), 8.57 (d, J = 8.8 Hz, 2H), 8.46 (d, J = 8.8 Hz, 2H), 7.87 – 7.73 (m, 4H), 3.28 – 3.09 (m, 2H of 3H due to fast isotopic exchange). ^{13}C NMR (101 MHz, Acetone- d_6) δ 179.36 , 172.11 , 166.13 , 142.33 , 142.09 , 132.29 , 132.17 , 131.22 , 131.20 , 131.05 , 128.80 , 119.90 , 116.17 , 22.82 – 19.23 (m, due to fast isotopic exchange). ^{11}B NMR (128 MHz, Acetone- d_6) δ -0.90 . ^{19}F NMR (376 MHz, Acetone- d_6) δ -151.57 , -151.62 . The NMR data are in agreement with previously reported.⁶

2,4-bis(4-fluorophenyl)-6-methylpyrylium tetrafluoroborate (1j)



Following **GP-3**, 2,4-bis(4-fluorophenyl)-6-methylpyrylium tetrafluoroborate (**1j**) was obtained from 1-(4-fluorophenyl)ethanone, boron trifluoride diethyl etherate and acetic anhydride as a yellow solid, 43% yield. ^1H NMR (400 MHz, Acetone- d_6) δ 9.07 (d, J = 1.7 Hz, 1H), 8.66 – 8.60 (m, 2H), 8.60 (d, J = 1.6 Hz, 1H), 8.58 – 8.50 (m, 2H), 7.57 – 7.47 (m, 4H), 3.18 – 3.12 (m, 3H). ^{13}C NMR (101 MHz, Acetone- d_6) δ 178.76 , 171.96 , 167.95 (d, J = 257.4 Hz), 167.68 (d, J = 257.0 Hz), 165.92 , 133.80 (d, J = 9.9 Hz), 132.70 (d, J = 9.9 Hz), 129.90 (d, J = 2.8 Hz), 126.65 (d, J = 3.0 Hz), 119.28 , 118.23 (d, J = 15.5 Hz), 118.00 (d, J = 15.8 Hz), 115.48 , 21.66 . The NMR data are in agreement with previously reported.⁶

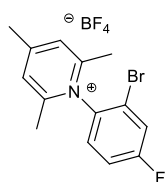
General procedure for pyridinium salts synthesis



A solution of pyrylium salt **1** (10 mmol) and corresponding 2-bromoaniline **2** (12.5 mmol) in ethanol (40 mL) was refluxed for 4h. Then the solvent was evaporated under the reduced pressure and the residue was diluted with a mixture of diethyl ether and ethyl acetate (10:1, 30-40 mL) to form a solid. The solid was filtered, recrystallized from ethanol, filtered once again and dried *in vacuo* to afford corresponding pyridinium salt **3**.

Analytical data of pyridinium salts

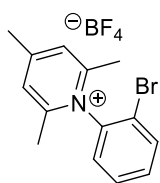
1-(2-bromo-4-fluorophenyl)-2,4,6-trimethylpyridinium tetrafluoroborate (**3a**)



White solid, 74% yield. MP = 160-162 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.15 (dd, J = 8.2, 2.8 Hz, 1H), 8.04 (s, 2H), 7.95 (dd, J = 8.9, 5.4 Hz, 1H), 7.74 (td, J = 8.8, 2.7 Hz, 1H), 2.65 (s, 3H), 2.31 (s, 6H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 162.8 (d, J = 253.9 Hz), 161.0, 154.9, 133.5 (d, J = 3.7 Hz), 129.9 (d, J = 9.6 Hz), 127.7, 122.0 (d, J = 26.7 Hz), 120.1 (d, J = 10.9 Hz), 117.9 (d, J = 23.1 Hz), 21.5, 20.9. ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$) δ = -106.36, -148.23, -148.29. ^{11}B NMR (128 MHz, $\text{DMSO}-d_6$) δ -1.29.

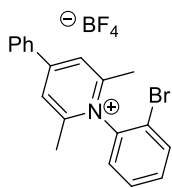
HRMS (m/z): calc. for $\text{C}_{14}\text{H}_{14}\text{BrFN}^+ [\text{M}-\text{BF}_4]^+$ = 294.0288; found: 294.0286. IR (KBr) cm^{-1} 3110 (VW), 3078 (VW), 3049 (VW), 1642 (M), 1593 (W), 1566 (W), 1478 (M), 1442 (W), 1323 (VW), 1265 (W), 1206 (M), 1089 (W), 1048 (VS), 1036 (VS), 961 (W), 877 (M), 835 (M), 668 (W).

1-(2-bromophenyl)-2,4,6-trimethylpyridinium tetrafluoroborate (**3b**)



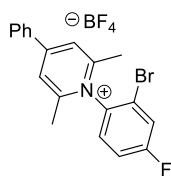
White solid, 75% yield. MP = 162-164 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.08 (dd, 1H), 8.05 (s, 2H), 7.86 (dd, J = 7.9, 1.7 Hz, 1H), 7.85 – 7.77 (m, 1H), 7.70 (td, J = 7.8, 1.7 Hz, 1H), 2.65 (s, 3H), 2.30 (s, 6H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 160.8, 154.5, 136.8, 134.6, 133.4, 130.6, 128.1, 127.7, 118.7, 21.5, 20.9. ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$) δ -148.23, -148.28. ^{11}B NMR (128 MHz, $\text{DMSO}-d_6$) δ -1.29. HRMS (m/z): calc. for $\text{C}_{14}\text{H}_{15}\text{BrN}^+ [\text{M}-\text{BF}_4]^+$ = 276.0382; found: 276.0385. IR (KBr) cm^{-1} 3086 (VW), 3080 (VW), 2927 (VW), 1642 (M), 1566 (W), 1470 (W), 1437 (W), 1379 (VW), 1322 (VW), 1279 (VW), 1249 (VW), 1089 (M), 1050 (VS), 1036 (VS), 1005 (M), 876 (W), 778 (S), 728 (W), 651 (W).

1-(2-bromophenyl)-2,6-dimethyl-4-phenylpyridinium tetrafluoroborate (3c)



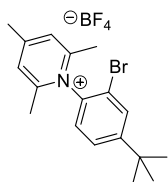
White solid, 94% yield. MP = 187-189 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.85 (d, J = 2.2 Hz, 1H), 8.61 (d, J = 2.1 Hz, 1H), 8.30 (dd, J = 8.0, 1.4 Hz, 2H), 8.03 (dd, J = 8.0, 1.5 Hz, 1H), 7.79 (dd, J = 8.1, 1.3 Hz, 1H), 7.77 – 7.65 (m, 3H), 7.62 (td, J = 7.7, 1.4 Hz, 1H), 7.54 – 7.34 (m, 6H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 156.4, 156.2, 156.0, 137.2, 133.8, 133.1, 133.0, 132.9, 131.8, 130.6, 130.1, 129.8, 129.5, 129.3, 128.7, 128.1, 125.0, 124.4, 119.3, 21.7. ^{11}B NMR (128 MHz, $\text{DMSO-}d_6$) δ -1.26. ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$) δ -148.25, -148.30. ^{15}N NMR ($^1\text{H-}^{15}\text{N}$ ge-HMBC) (41 MHz, $\text{Chloroform-}d$) δ 209.51. HRMS (m/z): calc. for $\text{C}_{24}\text{H}_{19}\text{BrN}^+ [\text{M-BF}_4]^+$ = 400.0695; found: 400.0696. IR (KBr) cm^{-1} 3080 (VW), 2927 (VW), 2854 (VW), 1626 (M), 1598 (W), 1554 (W), 1471 (W), 1444 (W), 1419 (W), 1348 (W), 1283 (VW), 1228 (W), 1048 (VS), 1033 (VS), 888 (W), 765 (S), 724 (W), 697 (S), 654 (W).

1-(2-bromo-4-fluorophenyl)-2,6-dimethyl-4-phenylpyridinium tetrafluoroborate (3d)



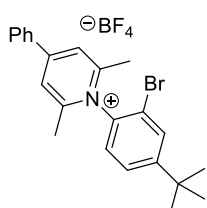
White solid, 86% yield. MP = 217-219 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.64 (s, 2H), 8.22 – 8.14 (m, 3H), 8.01 (dd, J = 8.9, 5.3 Hz, 1H), 7.82 – 7.65 (m, 4H), 2.43 (s, 6H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 162.8 (d, J = 253.9 Hz), 156.1, 156.1, 133.6 (d, J = 3.6 Hz), 133.2, 132.7, 129.9 (d, J = 11.4 Hz), 129.8, 128.3, 123.7, 122.0 (d, J = 26.6 Hz), 120.2 (d, J = 10.8 Hz), 117.9 (d, J = 23.2 Hz), 21.3. ^{11}B NMR (128 MHz, $\text{DMSO-}d_6$) δ -1.28. ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$) δ = -106.25 -148.23, -148.29. HRMS (m/z): calc. for $\text{C}_{19}\text{H}_{16}\text{BrFN}^+ [\text{M-BF}_4]^+$ 356.0446; found: 356.0444. IR (KBr) cm^{-1} 3089 (VW), 2930 (VW), 2853 (VW), 1637 (M), 1597 (W), 1558 (W), 1488 (S), 1440 (W), 1338 (M), 1262 (W), 1203 (M), 1099 (W), 1047 (VS), 1028 (VS), 1009 (S), 888 (M), 858 (S), 829 (M), 780 (S), 697 (M), 670 (M).

1-(2-bromo-4-tert-butylphenyl)-2,4,6-trimethylpyridinium tetrafluoroborate (3e)



White solid, 72% yield. MP = 170-172 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.04 (s, 2H), 8.02 (d, J = 2.0 Hz, 1H), 7.83 (dd, J = 8.4, 2.0 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 2.65 (s, 3H), 2.30 (s, 6H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 160.62, 156.49, 154.69, 134.43, 131.14, 127.62, 127.58, 127.53, 118.35, 35.15, 30.70, 21.48, 20.92. ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$) δ -148.23 -148.28. ^{11}B NMR (128 MHz, $\text{DMSO-}d_6$) δ -1.28. HRMS (m/z): calc. for $\text{C}_{18}\text{H}_{23}\text{BrN}^+ [\text{M-BF}_4]^+$ 332.1008; found: 332.1008. IR (KBr) cm^{-1} 3078 (VW), 2957 (VW), 2870 (VW), 1643 (M), 1560 (W), 1494 (W), 1440 (W), 1414 (W), 1389 (W), 1323 (W), 1271 (W), 1095 (M), 1059 (VS), 1028 (VS), 1003 (M), 876 (W), 869 (W), 841 (M), 634 (M).

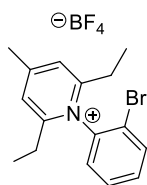
1-(2-bromo-4-tert-butylphenyl)-2,6-dimethyl-4-phenylpyridinium tetrafluoroborate (3f)



White solid, 73% yield. MP = 308°C (dec.) ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.63 (s, 2H), 8.17 (dd, J = 7.3, 2.2 Hz, 2H), 8.05 (d, J = 1.5 Hz, 1H), 7.90 – 7.81 (m, 2H), 7.75 – 7.66 (m, 3H), 2.41 (s, 6H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 156.56, 155.92, 155.89, 134.50, 133.30, 132.61, 131.17, 129.82, 128.26, 127.63, 127.51, 123.62, 118.38, 35.18,

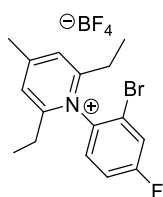
30.72, 21.28. ^{11}B NMR (128 MHz, DMSO- d_6) δ -1.27. ^{19}F NMR (376 MHz, DMSO- d_6) δ -148.22, -148.27. HRMS (m/z): calc. for $\text{C}_{23}\text{H}_{25}\text{BrN}^+ [\text{M-BF}_4]^+ = 394.1165$; found: 394.1165. IR (KBr) cm^{-1} 3082 (W), 2961 (M), 2868 (W), 1639 (VS), 1563 (S), 1494 (S), 1477 (M), 1444 (M), 1339 (S), 1103 (S), 1061 (VS), 1037 (VS), 998 (M), 899 (W), 841 (W), 777 (S), 695 (S), 530 (VW), 520 (W).

1-(2-bromophenyl)-2,6-diethyl-4-methylpyridinium tetrafluoroborate (3g)



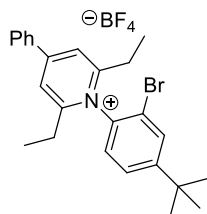
White solid, 64% yield. MP = 151-153 °C. ^1H NMR (400 MHz, Chloroform- d) δ 7.85 (dd, J = 12.5, 8.0 Hz, 2H), 7.70 (t, J = 7.7 Hz, 1H), 7.66 (s, 2H), 7.57 (t, J = 7.7 Hz, 1H), 2.73 (s, 3H), 2.65 – 2.52 (m, 1H), 2.50 – 2.33 (m, 2H), 1.29 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 161.4, 159.2, 136.6, 134.4, 133.2, 130.7, 129.2, 125.7, 119.5, 27.3, 22.7, 11.9. ^{19}F NMR (376 MHz, Chloroform- d) δ -153.70, -153.75. ^{11}B NMR (128 MHz, Chloroform- d) δ -1.28. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform- d) δ 206.67. HRMS (m/z): calc. for $\text{C}_{16}\text{H}_{19}\text{BrN}^+ [\text{M-BF}_4]^+ = 304.0695$; found: 304.0695. IR (KBr) cm^{-1} 3092 (VW), 2989 (VW), 2904 (VW), 1638 (M), 1567 (W), 1472 (W), 1282 (VW), 1046 (VS), 1033 (VS), 1007 (S), 871 (M), 775 (M), 730 (W), 655 (W).

1-(2-bromo-4-fluorophenyl)-2,6-diethyl-4-methylpyridinium tetrafluoroborate (3h)



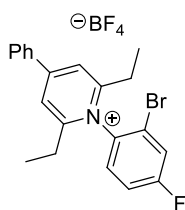
White solid, 77% yield. MP = 135-137 °C. ^1H NMR (400 MHz, Chloroform- d) δ 8.02 (dd, J = 8.9, 5.2 Hz, 1H), 7.64 (s, 2H), 7.57 (dd, J = 7.4, 2.7 Hz, 1H), 7.46 – 7.38 (m, 1H), 2.73 (s, 3H), 2.67 – 2.54 (m, 2H), 2.48 – 2.35 (m, 2H), 1.31 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 163.4 (d, J = 258.7 Hz), 161.5, 159.5, 132.9 (d, J = 3.8 Hz), 131.2 (d, J = 9.3 Hz), 125.7, 121.8 (d, J = 26.0 Hz), 120.4 (d, J = 10.0 Hz), 118.2 (d, J = 22.5 Hz), 27.4, 22.8, 11.8. ^{19}F NMR (376 MHz, DMSO- d_6) δ -106.36, -148.23, -148.29. ^{11}B NMR (128 MHz, DMSO- d_6) δ -1.28. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform- d) δ 204.33. HRMS (m/z): calc. for $\text{C}_{16}\text{H}_{18}\text{BrFN}^+ [\text{M-BF}_4]^+ = 322.0601$; found: 322.0602. IR (KBr) cm^{-1} 3098 (VW), 2995 (VW), 1635 (M), 1592 (W), 1563 (W), 1486 (M), 1389 (VW), 1206 (M), 1047 (VS), 1034 (VS), 1007 (M), 874 (M), 842 (W).

1-(2-bromo-4-tert-butylphenyl)-2,6-diethyl-4-phenylpyridinium tetrafluoroborate (3i)



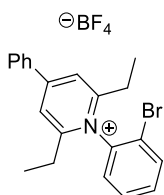
White solid, 84% yield. MP = 274-278 °C (dec.). ^1H NMR (400 MHz, DMSO- d_6) δ 8.47 (s, 1H), 8.24 (d, J = 6.9 Hz, 2H), 8.04 (d, J = 1.9 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.76 – 7.66 (m, 3H), 2.64 (m, 2H), 2.57 – 2.46 (m, 2H), 1.39 (s, 9H), 1.28 (t, J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 194.4, 194.0, 171.3, 171.2, 170.2, 168.7, 167.4, 166.2, 165.9, 164.8, 159.7, 156.8, 72.8, 68.4, 64.7, 50.0. ^{11}B NMR (128 MHz, DMSO- d_6) δ -1.25. ^{19}F NMR (376 MHz, DMSO- d_6) δ -148.27, -148.33. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform- d) δ 207.46. HRMS (m/z): calc. for $\text{C}_{25}\text{H}_{29}\text{BrN}^+ [\text{M-BF}_4]^+ = 422.1478$; found: 422.1478. IR (KBr) cm^{-1} 3098 (VW), 2995 (VW), 1635 (M), 1592 (W), 1563 (W), 1486 (M), 1389 (VW), 1206 (M), 1047 (VS), 1034 (VS), 1007 (M), 874 (M), 842 (W).

1-(2-bromo-4-fluorophenyl)-2,6-diethyl-4-phenylpyridinium tetrafluoroborate (3j)



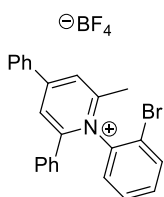
White solid, 86% yield. MP = 148-150 °C. ^1H NMR (400 MHz, Chloroform- d) δ 8.09 (dd, J = 8.7, 5.1 Hz, 1H), 7.94 (s, 2H), 7.92 – 7.84 (m, 2H), 7.64 – 7.55 (m, 4H), 7.48 – 7.37 (m, 1H), 2.69 (m, 2H), 2.49 (m, 2H), 1.35 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform- d) δ 163.5 (d, J = 258.9 Hz), 160.4, 158.7, 134.8, 132.9 (d, J = 4.1 Hz), 132.3, 131.2 (d, J = 9.4 Hz), 129.9, 128.4, 122.3, 121.8 (d, J = 26.1 Hz), 120.4 (d, J = 10.1 Hz), 118.2 (d, J = 22.5 Hz), 27.7, 11.9. ^{11}B NMR (128 MHz, DMSO- d_6) δ -1.28. ^{19}F NMR (376 MHz, Chloroform- d) δ -104.16, -153.46, -153.51. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform- d) δ 204.70. HRMS (m/z): calc. for $\text{C}_{21}\text{H}_{20}\text{BrFN}^+ [\text{M}-\text{BF}_4]^+$ = 384.0758; found: 384.0758. IR (KBr) cm^{-1} 3103 (VW), 2981 (VW), 2947 (VW), 1627 (M), 1595 (W), 1549 (W), 1483 (M), 1198 (M), 1048 (VS), 1034 (VS), 998 (M), 895 (W), 882 (M), 856 (M), 830 (W), 786 (M), 697 (M), 671 (W).

1-(2-bromophenyl)-2,6-diethyl-4-phenylpyridinium tetrafluoroborate (3k)



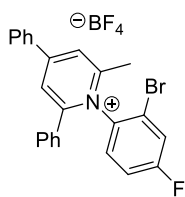
White solid, 68% yield. MP = 188-190 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 8.49 (s, 2H), 8.25 (d, J = 6.0 Hz, 2H), 8.11 (d, J = 7.9 Hz, 1H), 8.03 (d, J = 7.3 Hz, 1H), 7.84 (t, J = 7.5 Hz, 1H), 7.79 – 7.66 (m, 4H), 2.65 (m, 2H), 2.58 – 2.46 (m, 2H), 1.35 – 1.21 (m, 6H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 160.1, 156.5, 136.0, 134.5, 133.6, 133.5, 132.6, 130.2, 129.7, 128.8, 128.6, 122.2, 119.5, 27.1, 12.4. ^{11}B NMR (128 MHz, DMSO- d_6) δ -1.28. ^{19}F NMR (376 MHz, DMSO- d_6) δ -148.27, -148.32. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform- d) δ 207.47. HRMS (m/z): calc. for $\text{C}_{21}\text{H}_{21}\text{BrN}^+ [\text{M}-\text{BF}_4]^+$ 366.0852; found: 366.0852. IR (KBr) cm^{-1} 3066 (VW), 2990 (VW), 2946 (VW), 1629 (M), 1549 (W), 1468 (W), 1437 (W), 1094 (W), 1050 (VS), 1027 (VS), 1008 (M), 883 (M), 771 (S), 700 (M), 656 (W).

1-(2-bromophenyl)-2-methyl-4,6-diphenylpyridinium tetrafluoroborate (3l)



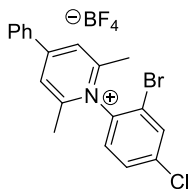
White solid, 61% yield. MP = 110-114 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 8.85 (d, J = 2.2 Hz, 1H), 8.61 (d, J = 2.1 Hz, 1H), 8.30 (dd, J = 8.0, 1.4 Hz, 2H), 8.03 (dd, J = 8.0, 1.5 Hz, 1H), 7.79 (dd, J = 8.1, 1.3 Hz, 1H), 7.77 – 7.65 (m, 3H), 7.62 (td, J = 7.7, 1.4 Hz, 1H), 7.54 – 7.34 (m, 6H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 156.4, 156.2, 156.0, 137.2, 133.8, 133.1, 133.0, 132.9, 131.8, 130.6, 130.1, 129.8, 129.5, 129.3, 128.7, 128.1, 125.0, 124.4, 119.3, 21.7. ^{11}B NMR (128 MHz, DMSO- d_6) δ -1.26. ^{19}F NMR (376 MHz, DMSO- d_6) δ -148.25, -148.30. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform- d) δ 207.07. HRMS (m/z): calc. for $\text{C}_{24}\text{H}_{19}\text{BrN}^+ [\text{M}-\text{BF}_4]^+$ = 400.0695; found: 400.0696. IR (KBr) cm^{-1} 3072 (VW), 2927 (VW), 2857 (VW), 1626 (M), 1554 (W), 1471 (W), 1348 (W), 1048 (VS), 1033 (VS), 999 (M), 888 (W), 765 (S), 697 (S).

1-(2-bromo-4-fluorophenyl)-2-methyl-4,6-diphenylpyridinium tetrafluoroborate (3m)



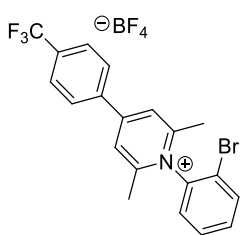
White solid, 85% yield. MP = 116-120 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.85 (d, J = 1.7 Hz, 1H), 8.62 (d, J = 1.8 Hz, 1H), 8.30 (d, J = 6.8 Hz, 2H), 8.12 (dd, J = 8.9, 5.3 Hz, 1H), 7.87 (dd, J = 8.2, 2.7 Hz, 1H), 7.71 (q, J = 7.8, 6.5 Hz, 3H), 7.56 (td, J = 8.6, 2.7 Hz, 1H), 7.52 – 7.39 (m, 5H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 162.3 (d, J = 254.2 Hz), 156.5, 156.2, 134.0 (d, J = 3.6 Hz), 133.1, 132.9, 131.9 (d, J = 9.8 Hz), 131.7, 130.7, 129.8, 129.5, 128.7, 128.2, 125.0, 124.4, 121.2 (d, J = 26.5 Hz), 120.7 (d, J = 10.6 Hz), 116.6 (d, J = 23.2 Hz), 21.7. ^{11}B NMR (128 MHz, $\text{DMSO}-d_6$) δ -1.26. ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$) δ -106.45, -148.23, -148.29. ^{15}N NMR ($^1\text{H}-^{15}\text{N}$ ge-HMBC) (41 MHz, Chloroform- d) δ 205.05. HRMS (m/z): calc. for $\text{C}_{24}\text{H}_{18}\text{BrFN}^+ [\text{M}-\text{BF}_4]^+ = 418.0601$; found: 418.0603. IR (KBr) cm^{-1} 3100 (W), 3067 (W), 1627 (VS), 1597 (M), 1556 (M), 1487 (S), 1349 (M), 1263 (M), 1204 (S), 1080 (S), 1058 (VS), 1036 (VS), 880 (M), 769 (S), 701 (M), 519 (M).

1-(2-bromo-4-chlorophenyl)-2,6-dimethyl-4-phenylpyridinium tetrafluoroborate (3n)



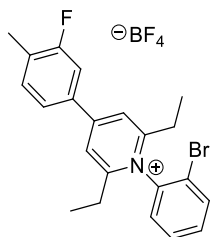
White solid, 82% yield. MP = 202-205 °C. ^1H NMR (400 MHz, Chloroform- d) δ 8.00 (s, 2H), 7.93 – 7.85 (m, 3H), 7.84 (d, J = 2.2 Hz, 1H), 7.66 (dd, J = 8.6, 2.2 Hz, 1H), 7.57 – 7.49 (m, 3H), 2.38 (s, 6H). ^{13}C NMR (101 MHz, Chloroform- d) δ 157.9, 155.3, 138.3, 135.7, 133.7, 133.6, 132.0, 130.9, 129.4, 128.1, 124.2, 119.2, 21.5. ^{19}F NMR (376 MHz, Chloroform- d) δ -152.59, -152.64. ^{11}B NMR (128 MHz, Chloroform- d) δ -1.28. ^{15}N NMR ($^1\text{H}-^{15}\text{N}$ ge-HMBC) (41 MHz, Chloroform- d) δ 205.87. HRMS (m/z): calc. for $\text{C}_{19}\text{H}_{16}\text{BrClN}^+ [\text{M}-\text{BF}_4]^+ = 372.0149$; found: 372.0148. IR (KBr) cm^{-1} 3094 (VW), 1634 (M), 1559 (W), 1475 (W), 1445 (W), 1336 (W), 1217 (W), 1101 (M), 1051 (S), 1030 (VS), 999 (M), 864 (W), 823 (M), 777 (S), 729 (M), 687 (M).

1-(2-bromophenyl)-2,6-dimethyl-4-(4-(trifluoromethyl)phenyl)pyridinium tetrafluoroborate (3o)



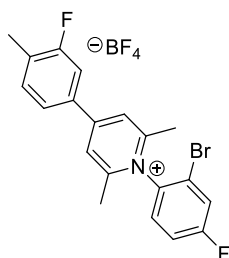
White solid, 79% yield. MP = 218-220°C (dec.). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.73 (s, 2H), 8.37 (d, J = 8.2, 2H), 8.16 – 8.08 (m, 3H), 7.93 (dd, J = 7.9, 1.5, 1H), 7.85 (td, J = 7.8, 1.1, 1H), 7.74 (td, J = 7.8, 1.6, 1H), 2.44 (s, 6H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 156.2, 154.4, 137.4, 136.9, 134.6, 133.5, 131.9 (d, J = 32.3 Hz), 130.7, 129.2, 128.0, 126.6 (q, J = 3.6 Hz), 124.5, 123.8 (q, J = 272.6 Hz), 118.5, 21.3. ^{11}B NMR (128 MHz, $\text{DMSO}-d_6$) δ -1.30. ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$) δ -61.44, -148.24, -148.29. ^{15}N NMR ($^1\text{H}-^{15}\text{N}$ ge-HMBC) (41 MHz, Chloroform- d) δ 211.82. HRMS (m/z): calc. for $\text{C}_{20}\text{H}_{16}\text{BrF}_3\text{N}^+ 406.0413$ [$\text{M}-\text{BF}_4$] $^+ = 406.0413$; found: 406.0412. IR (KBr) cm^{-1} 3091 (VW), 2930 (VW), 2856 (VW), 1638 (M), 1559 (W), 1473 (W), 1441 (W), 1323 (M), 1137 (M), 1067 (VS), 1050 (VS), 1036 (VS), 853 (M), 835 (M), 780 (S), 727 (M), 674 (W).

1-(2-bromophenyl)-2,6-diethyl-4-(3-fluoro-4-methylphenyl)pyridinium tetrafluoroborate (3p)



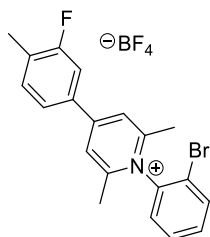
White solid, 94% yield. MP = 205-207 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.51 (s, 2H), 8.17 (d, *J* = 11.0 Hz, 1H), 8.11 (d, *J* = 7.9 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 2.64 (m, 2H), 2.58 – 2.44 (m, 2H), 2.39 (s, 3H), 1.27 (t, *J* = 7.4 Hz, 6H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 161.3 (d, *J* = 243.9 Hz), 160.1, 154.9 (d, *J* = 2.2 Hz), 136.0, 134.4, 133.5, 133.0, 132.9 (d, *J* = 5.1 Hz), 130.2, 129.8 (d, *J* = 17.3 Hz), 128.8, 124.5 (d, *J* = 3.1 Hz), 122.0, 119.5, 114.9 (d, *J* = 24.1 Hz), 27.1, 14.3 (d, *J* = 3.1 Hz), 12.4. ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -115.68, -148.25, -148.31. ¹¹B NMR (128 MHz, DMSO-*d*₆) δ -1.30. ¹⁵N NMR (¹H-¹⁵N ge-HMBC) (41 MHz, Chloroform-*d*) δ 207.85. HRMS (*m/z*): calc. for C₂₂H₂₂BrFN⁺ [M-BF₄]⁺ = 398.0914; found: 398.0914. IR (KBr) cm⁻¹ 3073 (VW), 2992 (VW), 1631 (M), 1552 (W), 1468 (W), 1404 (W), 1091 (W), 1028 (S), 1008 (M), 879 (W), 817 (W), 773 (M).

1-(2-bromo-4-fluorophenyl)-4-(3-fluoro-4-methylphenyl)-2,6-dimethylpyridinium tetrafluoroborate (3q)



White solid, 73% yield. MP = 187-190 °C (dec.). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.67 (s, 2H), 8.17 (dd, *J* = 8.2, 2.8 Hz, 1H), 8.06 (dd, *J* = 11.0, 1.9 Hz, 1H), 8.04 – 7.94 (m, 2H), 7.77 (td, *J* = 8.5, 2.8 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 2.41 (s, 6H), 2.38 (d, *J* = 1.9 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.0 (d, *J* = 254.4 Hz), 166.5 (d, *J* = 244.4 Hz), 161.4, 159.8 (d, *J* = 2.0 Hz), 138.8 (d, *J* = 3.7 Hz), 138.3 (d, *J* = 5.2 Hz), 137.9 (d, *J* = 8.0 Hz), 135.2 (d, *J* = 4.4 Hz), 135.1 (d, *J* = 3.3 Hz), 129.5 (d, *J* = 3.3 Hz), 128.7, 127.3 (d, *J* = 26.8 Hz), 125.4 (d, *J* = 10.9 Hz), 123.2 (d, *J* = 23.2 Hz), 119.9 (d, *J* = 24.1 Hz), 26.5, 19.6 (d, *J* = 3.1 Hz). ¹¹B NMR (128 MHz, DMSO-*d*₆) δ -1.30. ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -106.21, -115.46, -148.22, -148.28. HRMS (*m/z*): calc. for C₂₀H₁₇BrF₂N⁺ [M-BF₄]⁺ = 388.0507; found: 388.0506. IR (KBr) cm⁻¹ 3096 (VW), 1636 (S), 1555 (W), 1485 (M), 1442 (W), 1341 (W), 1265 (M), 1242 (W), 1206 (M), 1056 (VS), 1033 (VS), 874 (M), 826 (M), 811 (M), 727 (VS), 3r cm⁻¹ 1636(VS), 1074(VS), 1044 (S), 1120 (S), 1339 (S), 1473 (S), 1558 (S), 724 (S), 776 (S), 1241 (S), 815 (S), 522 (M), 2992 (M), 454 (M).

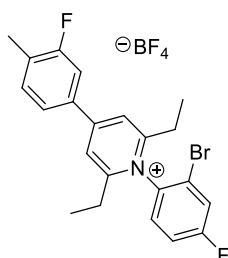
1-(2-bromophenyl)-4-(3-fluoro-4-methylphenyl)-2,6-dimethylpyridinium tetrafluoroborate (3r)



White solid, 89% yield. MP = 195-197 °C (dec.). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.68 (s, 2H), 8.11 (d, *J* = 9.1 Hz, 1H), 8.06 (dd, *J* = 11.1, 1.5 Hz, 1H), 7.99 (d, *J* = 1.6 Hz, 1H), 7.92 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.84 (t, *J* = 7.1 Hz, 1H), 7.73 (td, *J* = 7.9, 1.6 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 2.40 (s, 6H), 2.38 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 161.3 (d, *J* = 244.3 Hz), 155.7, 154.4 (d, *J* = 2.2 Hz), 136.8, 134.6, 133.4, 133.1 (d, *J* = 5.4 Hz), 132.7 (d, *J* = 8.1 Hz), 130.7, 129.8 (d, *J* = 17.2 Hz), 124.2 (d, *J* = 3.2 Hz), 123.4, 118.7, 114.6 (d, *J* = 24.1 Hz), 21.2, 14.3 (d, *J* = 2.9 Hz). ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -115.48, -148.23, -148.28. ¹¹B NMR (128 MHz, DMSO-*d*₆) δ

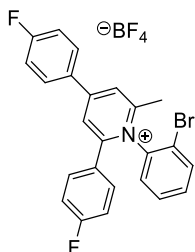
-1.30. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 207.94. HRMS (*m/z*): calc. for $\text{C}_{20}\text{H}_{18}\text{BrFN}^+ [\text{M-BF}_4]^+ = 370.0601$; found: 370.0601. IR (KBr) cm^{-1} 3067 (M), 3030 (M), 3002 (M), 2921 (W), 1636 (VS), 1626 (S), 1558 (S), 1473 (S), 1436 (S), 1397 (S), 1339 (S), 1241 (S), 1120 (S), 1074 (VS), 1027 (VS), 876 (M), 815 (S), 776 (S), 724 (S), 533 (M), 477 (M), 454 (M).

1-(2-bromo-4-fluorophenyl)-2,6-diethyl-4-(3-fluoro-4-methylphenyl)pyridinium tetrafluoroborate (3s)



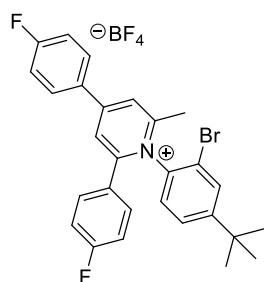
White solid, 85% yield. MP = 199-200°C. ^1H NMR (400 MHz, DMSO-*d*₆) δ 8.50 (s, 2H), 8.20 – 8.14 (m, 2H), 8.10 (dd, $J=8.9$, 5.3 Hz, 1H), 8.05 (d, $J=8.0$ Hz, 1H), 7.76 (td, $J=8.5$, 2.8 Hz, 1H), 7.64 (t, $J=8.0$ Hz, 1H), 2.66 (m, 2H), 2.60 – 2.45 (m, 2H), 2.39 (s, 3H), 1.27 (t, $J=7.4$ Hz, 6H). ^{13}C NMR (101 MHz, DMSO-*d*₆) δ 162.8 (d, $J = 254.4$ Hz), 161.3 (d, $J = 244.3$ Hz), 160.5, 155.0 (d, $J = 2.1$ Hz), 133.0, 132.9 (d, $J = 5.1$), 132.6 (d, $J = 3.5$ Hz), 130.5 (d, $J = 9.8$ Hz), 129.7 (d, $J = 17.3$ Hz), 124.5 (d, $J = 2.8$ Hz), 122.0, 121.9 (d, $J = 26.8$ Hz), 120.9 (d, $J = 10.8$ Hz), 117.5 (d, $J = 23.1$ Hz), 115.0 (d, $J = 24.3$ Hz), 27.2, 14.3 (d, $J = 2.9$ Hz), 12.4. ^{19}F NMR (376 MHz, DMSO-*d*₆) δ -106.0, -115.7, -148.2, -148.3. ^{11}B NMR (128 MHz, DMSO-*d*₆) δ -1.30. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 206.05. HRMS (*m/z*): calc. for $\text{C}_{22}\text{H}_{21}\text{BrF}_2\text{N}^+ [\text{M-BF}_4]^+ = 398.0914$; found: 398.0914. IR (KBr) cm^{-1} 3090 (VW), 2981 (VW), 2949 (VW), 1631 (M), 1595 (W), 1550 (W), 1491 (M), 1463 (W), 1401 (W), 1273 (W), 1205 (M), 1046 (VS), 1034 (VS), 1005 (M), 878 (M), 834 (M), 807 (M).

1-(2-bromophenyl)-2,4-bis(4-fluorophenyl)-6-methylpyridinium tetrafluoroborate (3t)



White solid, 83% yield. MP = 209-212°C. ^1H NMR (400 MHz, DMSO-*d*₆) δ 8.84 (d, $J = 2.2$ Hz, 1H), 8.63 (d, $J = 2.2$ Hz, 1H), 8.40 (dd, $J = 8.8$ Hz, 5.3, 2H), 8.03 (dd, $J = 8.1$ Hz, 1.6, 1H), 7.81 (dd, $J = 8.1$ Hz, 1.3, 1H), 7.64 (td, $J = 7.8$, 1.3 Hz, 1H), 7.60 – 7.53 (m, 4H), 7.50 (td, $J = 7.8$, 1.6 Hz, 1H), 7.27 (t, $J = 8.8$ Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, DMSO-*d*₆) δ 165.0 (d, $J = 252.7$ Hz), 163.0 (d, $J = 249.5$ Hz), 156.2, 155.2, 155.0, 137.1, 133.9, 133.1, 132.2 (d, $J = 9.1$ Hz), 131.6 (d, $J = 9.3$ Hz), 130.1, 129.6 (d, $J = 2.9$ Hz), 129.4, 128.2 (d, $J = 3.3$ Hz), 124.9, 124.5, 119.2, 116.9 (d, $J = 22.0$ Hz), 115.3 (d, $J = 22.3$ Hz), 21.7. ^{11}B NMR (128 MHz, DMSO-*d*₆) δ -1.26. ^{19}F NMR (376 MHz, DMSO-*d*₆) δ -106.59, -109.36, -148.24, -148.29. HRMS (*m/z*): calc. for $\text{C}_{24}\text{H}_{17}\text{BrF}_2\text{N}^+ [\text{M-BF}_4]^+ = 436.0507$; found 436.0509. IR (KBr) cm^{-1} 3089 (VW), 1625 (M), 1594 (M), 1553 (W), 1510 (M), 1469 (M), 1442 (W), 1348 (W), 1223 (M), 1163 (M), 1059 (VS), 1033 (S), 838 (VS), 777 (S), 735 (W).

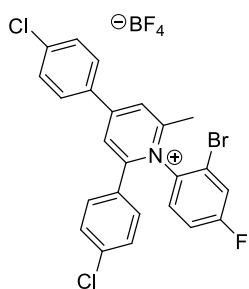
1-(2-bromo-4-tert-butylphenyl)-2,4-bis(4-fluorophenyl)-6-methylpyridinium tetrafluoroborate (3u)



White solid, 71% yield. MP = 214-218°C. ^1H NMR (400 MHz, DMSO-*d*₆) δ 8.82 (d, $J = 2.2$ Hz, 1H), 8.61 (d, $J = 2.2$ Hz, 1H), 8.39 (dd, $J = 8.9$, 5.3 Hz, 2H), 7.93 (d, $J = 8.4$ Hz, 1H), 7.73 (d, $J = 2.1$ Hz, 1H), 7.65 (dd, $J = 8.4$, 2.1 Hz, 1H), 7.61 – 7.49 (m, 4H), 7.26 (t, $J =$

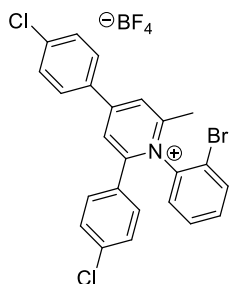
8.8 Hz, 2H), 2.50 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 165.0 (d, J = 252.8 Hz), 163.0 (d, J = 249.5 Hz), 156.4, 156.3, 155.1, 155.1, 134.6, 132.2 (d, J = 9.0 Hz), 131.5 (d, J = 9.4 Hz), 130.3, 129.6 (d, J = 2.9 Hz), 129.6, 128.2 (d, J = 3.1 Hz), 126.3, 124.8, 124.4, 119.0, 116.9 (d, J = 22.0 Hz), 115.2 (d, J = 22.2 Hz), 35.0, 30.6, 21.7. ^{11}B NMR (128 MHz, DMSO- d_6) δ -1.26. ^{19}F NMR (376 MHz, DMSO- d_6) δ -106.66, -109.55, -148.23, -148.28. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform- d) δ 206.67. HRMS (m/z): calc. for $\text{C}_{28}\text{H}_{25}\text{BrF}_2\text{N}^+ [\text{M}-\text{BF}_4]^+ = 492.1133$; found 492.1130. IR (KBr) cm^{-1} 3100 (VW), 2967 (VW), 1628 (M), 1596 (M), 1562 (W), 1510 (M), 1493 (M), 1470 (M), 1388 (W), 1352 (W), 1228 (S), 1163 (M), 1113 (M), 1051 (VS), 1042 (VS), 1003 (M), 845 (VS), 819 (M).

1-(2-bromo-4-fluorophenyl)-2,4-bis(4-chlorophenyl)-6-methylpyridinium tetrafluoroborate (3v)



White solid, 88% yield. MP = 218-219°C. ^1H NMR (400 MHz, DMSO- d_6) δ 8.88 (d, J = 2.3 Hz, 1H), 8.66 (d, J = 2.3 Hz, 1H), 8.33 (d, J = 8.3 Hz, 2H), 8.12 (dd, J = 8.9 Hz, 5.2 Hz, 1H), 7.90 (dd, J = 8.2, 2.8 Hz, 1H), 7.80 (d, J = 8.3 Hz, 2H), 7.59 (td, J = 8.5, 2.7 Hz, 1H), 7.52 (q, J = 8.5 Hz, 4H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 162.4 (d, J = 254.5 Hz), 156.8, 155.2, 155.0, 138.2, 135.7, 133.7 (d, J = 3.8 Hz), 131.8, 131.8 (d, J = 11.0 Hz), 131.5, 130.6, 130.4, 129.9, 128.4, 125.2, 124.6, 121.4 (d, J = 26.7 Hz), 120.5 (d, J = 10.4 Hz), 116.8 (d, J = 23.2 Hz), 21.7. ^{11}B NMR (128 MHz, DMSO- d_6) δ -1.26. ^{19}F NMR (376 MHz, DMSO- d_6) δ -106.01, -148.23, -148.28. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform- d) δ 205.50. HRMS (m/z): calc. for $\text{C}_{24}\text{H}_{16}\text{BrCl}_2\text{FN}^+ [\text{M}-\text{BF}_4]^+ = 485.9822$; found 485.9822. IR (KBr) cm^{-1} 3104 (W), 1632 (VS), 1581 (M), 1552 (M), 1488 (VS), 1469 (S), 1392 (M), 1350 (M), 1267 (M), 1207 (S), 1090 (VS), 1059 (VS), 1012 (S), 882 (M), 829 (S), 608 (W), 522 (M).

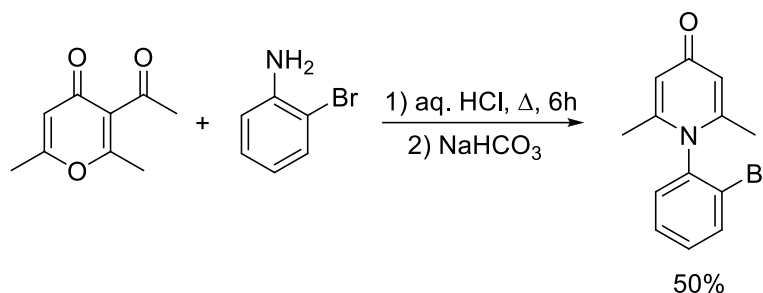
1-(2-bromophenyl)-2,4-bis(4-chlorophenyl)-6-methylpyridinium tetrafluoroborate (3w)



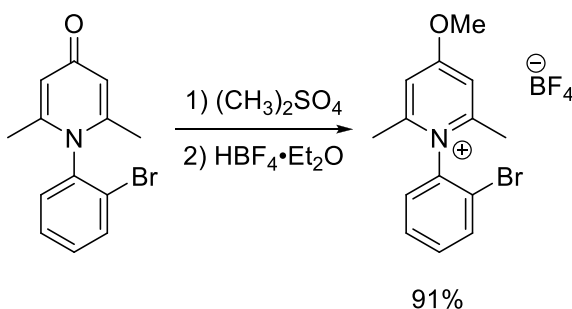
White solid, 73% yield. MP = 210-212°C. ^1H NMR (400 MHz, DMSO- d_6) δ 8.87 (d, J = 2.2 Hz, 1H), 8.66 (d, J = 2.2 Hz, 1H), 8.35 – 8.28 (m, 2H), 8.02 (dd, J = 8.0, 1.6 Hz, 1H), 7.86 – 7.72 (m, 3H), 7.64 (td, J = 7.8 Hz, 1.4, 1H), 7.54 – 7.45 (m, 5H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 156.5, 155.0, 154.8, 138.1, 137.0, 135.6, 134.0, 133.2, 131.9, 131.4, 130.5, 130.4, 130.0, 129.9, 129.4, 128.2, 125.2, 124.6, 119.2, 21.7. ^{11}B NMR (128 MHz, DMSO- d_6) δ -1.26. ^{19}F NMR (376 MHz, DMSO- d_6) δ -148.23, -148.28. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform- d) δ 207.49. HRMS (m/z): calc. for $\text{C}_{24}\text{H}_{17}\text{BrCl}_2\text{N}^+ [\text{M}-\text{BF}_4]^+ = 467.9916$; found 467.9914. IR (KBr) cm^{-1} 3101 (W), 3075 (W), 1629 (S), 1594 (S), 1556 (M), 1495 (M), 1470 (M), 1445 (W), 1389 (W), 1349 (M), 1080 (S), 1056 (VS), 1012 (S), 832 (S), 768 (M), 726 (W), 513 (M).

1-(2-bromophenyl)-4-methoxy-2,6-dimethylpyridinium tetrafluoroborate (3x)

Synthesis of 1-(2-bromophenyl)-4-methoxy-2,6-dimethylpyridinium tetrafluoroborate (**3x**) was performed using commercially available dehydroacetic acid and 2-bromoaniline via modified literature procedure⁷:



A mixture of 3.36 g (20 mmol) of dehydroacetic acid and 3.44 g (20 mmol) of 2-bromoaniline in 10 ml of concentrated HCl was refluxed for 6h. The reaction mixture was cooled to the room temperature and filtered. The precipitate was discarded (2-bromoanilinium hydrochloride), the filtrate was neutralized with saturated aqueous NaHCO₃ and extracted with ethyl acetate. Organic extracts were evaporated to dryness and the residue was purified by chromatography (ethyl acetate – methanol = 95:5) to give 2.8 g (50%) of 1-(2-bromophenyl)-2,6-dimethylpyridin-4(1H)-one as white solid and was further used without additional purification. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.51 (td, *J* = 7.6, 1.4 Hz, 1H), 7.41 (td, *J* = 7.8, 1.6 Hz, 1H), 7.31 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.30 (s, 2H), 1.87 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 179.84 , 148.33 , 138.85 , 134.31 , 131.47 , 129.87 , 129.30 , 123.48 , 117.74 , 20.94 .

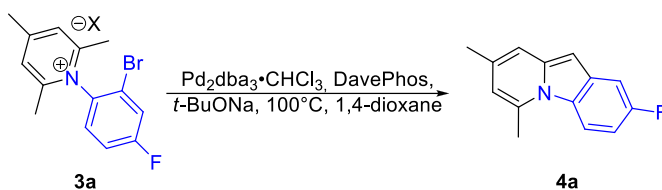


Methylation of 1-(2-bromophenyl)-2,6-dimethylpyridin-4(1H)-one was performed by modified literature procedure.⁸ A neat mixture of 1.39 g (50 mmol) of 1-(2-bromophenyl)-2,6-dimethylpyridin-4(1H)-one and 2.02 g (160 mmol, 3.2 eq.) of dimethyl sulfate was stirred for 5h at 60 °C. The reaction mixture was cooled to 0 °C and HBF₄•Et₂O (2 ml, 150 mmol, 3 eq.) was added. The reaction mixture was stirred for 30 minutes, diluted with 10 ml of diethyl ether and filtered. The precipitate was washed with Et₂O-MeOH mixture (6 ml, Et₂O-MeOH = 5:1), dried in vacuum to give 1.74 g (91%) of 1-(2-bromophenyl)-4-methoxy-2,6-dimethylpyridinium tetrafluoroborate (**3x**) as a white solid. MP = 192-193 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.06 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.84 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.82 – 7.75 (m, 3H), 7.68 (td, *J* = 7.8, 1.7 Hz, 1H), 4.16 (s, 3H), 2.26 (s, 6H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 171.31 , 156.68 , 136.53 , 134.44 , 133.23 , 130.50 , 128.75 , 119.50 , 112.51 , 58.25 , 21.03 . ¹¹B NMR (128 MHz, DMSO-*d*₆) δ -1.28 . ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -148.25 , -148.30 . ¹⁵N NMR (¹H-¹⁵N ge-HMBC) (41 MHz, Chloroform-*d*) δ 196.37. HRMS (*m/z*): calc. for C₁₄H₁₅BrNO⁺ [M-BF₄]⁺ = 292.0332; found 292.0346. IR (KBr) cm⁻¹ 3093 (W), 1634 (S), 1562 (M), 1491 (M), 1473 (M), 1458 (W), 1438 (W), 1396 (W), 1383 (W), 1357 (W), 1339 (S), 1283 (W), 1244 (W),

1200 (M), 1170 (M), 1094 (M), 1047 (VS), 1034 (VS), 993 (S), 968 (M), 964 (M), 925 (M), 881 (M), 776 (S), 767 (M), 733 (M), 730 (M), 725 (M), 652 (M), 618 (M).

Optimization of cyclization conditions

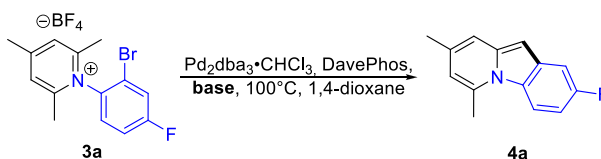
Table S1. Optimization of the anion^a



Entry	Anion	Yield, %
1^a	BF_4^-	78
2	ClO_4^-	65
3	PF_6^-	75

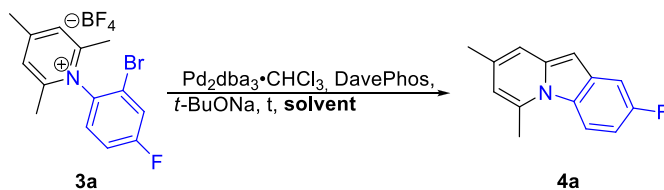
^aReaction conditions: **3a** (0.5 mmol), $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (0.5 mol%), DavePhos (2 mol%), $t\text{-BuONa}$ (1.5 mmol), 1,4-dioxane (4 ml), 100°C , 14h

Table S2. Optimization of base^a



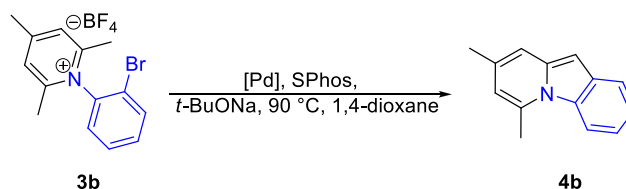
Entry	Base	Equivalent	Yield, %
1	$t\text{-BuOK}$	3	72
2	Cs_2CO_3	3	41
3	K_2CO_3	3	38
4^a	$t\text{-BuONa}$	3	78
5	$t\text{-BuONa}$	4	53
6	$t\text{-BuONa}$	2	55

^aReaction conditions: **3a** (0.5 mmol), $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (0.5 mol%), DavePhos (2 mol%), **base**, 1,4-dioxane (4 ml), 100°C , 14h

Table S3. Optimization of the solvent^a

Entry	Solvent	Temperature, °C	Yield ^b , %
1	1,2-Dimethoxyethane	80	72
2	Toluene	100	41
3	<i>n</i> -Butanol	100	38
4^a	1,4-Dioxane	100	78

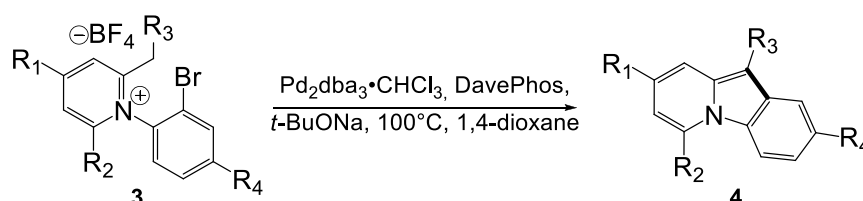
^aReaction conditions: **3a** (0.5 mmol), Pd₂dba₃·CHCl₃ (0.5 mol%), DavePhos (2 mol%), *t*-BuONa (1.5 mmol), 1,4-dioxane (4 ml), 100°C, 14h

Table S4. Optimization of the palladium salt^a

Entry	Palladium catalyst	Yield ^b , %
1	1 mol% Pd(OAc) ₂	58
2	0.5 mol% [Pd(cinn)Cl] ₂	55
3	0.5 mol% Pd ₂ dba ₃ ·CHCl ₃	64

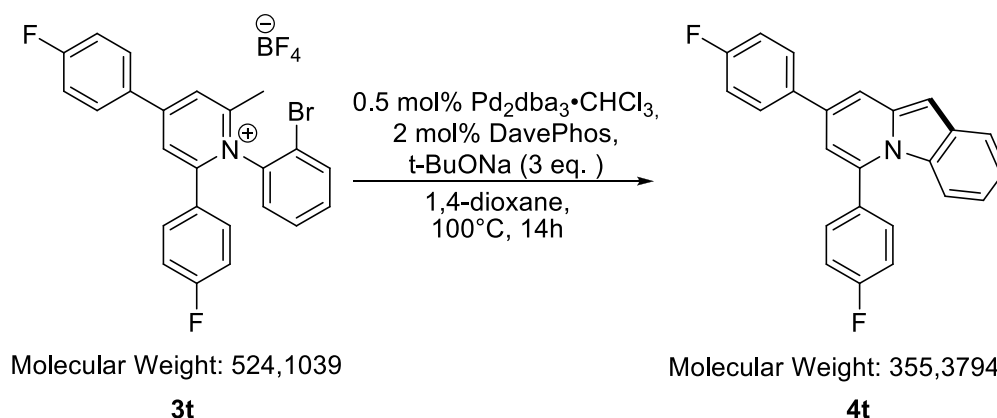
^aReaction conditions: **3a** (0.5 mmol), palladium catalyst (x mol%), DavePhos (2 mol%), *t*-BuONa (1.5 mmol), 1,4-dioxane (4 ml), 100°C, 14h

General procedure for pyrido[1,2-*a*]indoles synthesis



A screw-cap vial equipped with a magnetic stir bar was charged with 0.5 mmol of pyridinium tetrafluoroborate **3** (1 eq), Pd₂dba₃·CHCl₃ (2.6 mg, 0.5 mol%), DavePhos (3.9 mg, 2 mol%) and anhydrous 1,4-dioxane (4 mL). The reaction mixture was bubbled with argon and finally powdered *t*-BuONa (144 mg, 1.5 mmol, 3 eq) was added. The vial was transferred to a preheated oil bath (100 °C) and heated for 14h. The reaction mixture was cooled, diluted with water and extracted with ethyl acetate (3 × 7 mL). The extract was dried over Na₂SO₄, filtered and evaporated. The residue was purified by flash chromatography (eluent CH₂Cl₂/hexane = 1/2) to give pyrido[1,2-*a*]indole **4**.

Large-scale synthesis of 4t



A 250 ml round-bottom flask equipped with a magnetic stir bar and reflux condenser was charged with 5.24 g (10 mmol, 1 eq) of 1-(2-bromophenyl)-2,4-bis(4-fluorophenyl)-6-methylpyridinium tetrafluoroborate (**3t**), 51.7 mg (0.05 mmol, 0.05 mol%) of $\text{Pd}_2\text{dba}_3\cdot\text{CHCl}_3$, 80 mg (0.2 mmol, 2 mol%) DavePhos and anhydrous 1,4-dioxane (80 ml). The reaction mixture was bubbled with argon and powdered *t*-BuONa (2.88 g, 30 mmol, 3 eq) was added. The reaction flask was transferred to a preheated oil bath (100 °C) and stirred for 14h. The reaction mixture was cooled, diluted with water (200 ml) and extracted with ethyl acetate (3 × 30 ml). The organic extract was dried over Na_2SO_4 , filtered and evaporated. The residue was purified by flash chromatography (eluent $\text{CH}_2\text{Cl}_2/\text{hexane} = 1/2$) to give 3.29 g (92%) of 6,8-bis(4-fluorophenyl)pyrido[1,2-*a*]indole **4t** as a yellow solid.

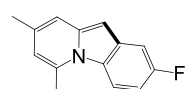
General procedure for one-pot synthesis of pyrido[1,2-*a*]indoles from pyrylium salts

A mixture of pyrylium salt (0.5 mmol) and 2-bromoaniline (0.5 mmol) in ethanol (10 ml) was refluxed for 5h. The reaction mixture was evaporated to dryness, the residue was suspended in 1,4-dioxane (10 ml) and evaporated again. The residue was dried in vacuum, followed by addition of anhydrous 1,4-dioxane (4 ml), $\text{Pd}_2\text{dba}_3\cdot\text{CHCl}_3$ (2.6 mg, 0.5 mol%), DavePhos (3.9 mg, 2 mol%). The suspension was bubbled with argon and powdered *t*BuONa (144 mg, 3 eq) was added. The reaction flask was transferred to a preheated oil bath (100 °C) and heated for 14h. The reaction mixture was cooled, diluted with water and extracted with ethyl acetate (3 × 7 mL). The extract was dried over Na_2SO_4 , filtered and evaporated. The residue was purified by flash chromatography (eluent $\text{CH}_2\text{Cl}_2/\text{hexane} = 1/2$) to give pyrido[1,2-*a*]indole **4**.

This procedure allowed to obtain pyrido[1,2-*a*]indoles **4c** and **4m** in 60 and 70% yields, respectively. If 1,4-dioxane was used instead of ethanol for the reaction of pyrylium salt with 2-bromoaniline, pyrido[1,2-*a*]indoles **4c** and **4m** were isolated in 43 and 34% yields, respectively.

Analytical data of pyrido[1,2-*a*]indoles

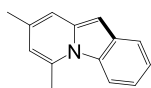
2-fluoro-6,8-dimethylpyrido[1,2-*a*]indole (**4a**)



Green solid, 78% yield. MP = 103-105°C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.07 (dd, $J = 9.3, 4.4$ Hz, 1H), 7.38 – 7.33 (m, 1H), 7.10 (s, 1H), 6.90 (td, $J = 9.1, 2.6$ Hz, 1H), 6.54 (s, 1H), 6.13 (s, 1H), 2.91 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.2 (d, $J = 238.1$ Hz), 140.4, 137.2, 133.0, 131.5 (d, $J = 10.6$ Hz), 127.9, 116.0 (d, $J = 10.1$ Hz), 114.7, 112.2, 107.1 (d, $J = 26.4$ Hz), 103.9 (d, $J = 22.9$ Hz).

Hz), 22.5, 21.2. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 169.68. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -121.1. HRMS (*m/z*): calc. for $\text{C}_{14}\text{H}_{13}\text{FN}^+$ [$\text{M}+\text{H}$] $^+$ = 214.1027; found 214.1032. IR (KBr) cm^{-1} 2947 (VW), 2914 (VW), 2852 (VW), 1654 (W), 1608 (M), 1542 (M), 1472 (M), 1435 (M), 1376 (W), 1335 (M), 1300 (W), 1254 (W), 1210 (M), 1176 (M), 1163 (M), 1108 (M), 1069 (W), 1034 (W), 950 (M), 859 (M), 817 (S), 781 (VS), 741 (M), 695 (S), 642 (W), 612 (W).

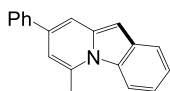
6,8-dimethylpyrido[1,2-*a*]indole (**4b**)



Green solid, 74% yield. MP = 104-106°C. ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, J = 8.6 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 7.13 (s, 1H), 6.61 (s, 1H), 6.11 (s, 1H), 2.97 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.0, 137.4, 132.2, 131.1, 130.8, 122.2, 120.0, 118.6, 115.1, 114.9, 111.9, 91.2, 22.7, 21.2. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 169.63. HRMS (*m/z*): calc. for $\text{C}_{14}\text{H}_{14}\text{N}^+$ [$\text{M}+\text{H}$] $^+$ = 196.1121; found 196.1130. IR (KBr) cm^{-1} 3046 (VW), 2962 (VW), 2904 (VW), 2848 (VW), 1738 (VW), 1650 (W), 1601 (W), 1534 (M), 1475 (W), 1432 (M), 1410 (M), 1375 (W), 1329 (W), 1312 (M), 1287 (M), 1218 (M), 1166 (W), 1121 (W), 1033 (W), 970 (W), 861 (M), 815 (S), 759 (S), 746 (VS), 726 (S), 701 (S).

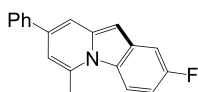
6-methyl-8-phenylpyrido[1,2-*a*]indole (**4c**)



Yellow solid, 90% yield. MP = 117-119°C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.2 (d, J = 8.6 Hz, 1H), 7.8 (d, J = 8.0 Hz, 1H), 7.7 (d, J = 7.4 Hz, 2H), 7.6 (d, J = 1.9 Hz, 1H), 7.5 (t, J = 7.6 Hz, 2H), 7.4 (t, J = 7.4 Hz, 2H), 7.3 – 7.2 (m, 1H), 6.8 (s, 1H), 6.6 (s, 1H), 3.1 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.3, 138.7, 138.2, 134.1, 131.2, 130.9, 129.0, 127.8, 126.6, 122.5, 120.3, 119.5, 115.2, 113.9, 108.8, 93.7, 23.0. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 169.36. HRMS (*m/z*): calc. for $\text{C}_{19}\text{H}_{16}\text{N}^+$ [$\text{M}+\text{H}$] $^+$ = 258.1277; found 258.1284. IR (KBr) cm^{-1} 3110 (W), 3050 (W), 2990 (W), 1634 (W), 1597 (W), 1534 (S), 1437 (M), 1329 (M), 1316 (S), 1294 (M), 1210 (M), 1054 (M), 1024 (W), 867 (S), 765 (VS), 756 (VS), 725 (S), 701 (S), 685 (S).

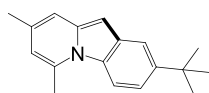
2-fluoro-6-methyl-8-phenylpyrido[1,2-*a*]indole (**4d**)



Yellow solid, 81% yield. MP = 144-146 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.13 (dd, J = 9.3, 4.4 Hz, 1H), 7.69 (d, J = 7.4 Hz, 2H), 7.59 (s, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.43 – 7.36 (m, 2H), 6.96 (td, J = 9.1, 2.6 Hz, 1H), 6.75 (s, 1H), 6.61 (s, 1H), 3.02 (s, 3H).

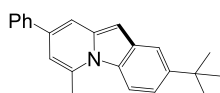
^{13}C NMR (101 MHz, CDCl_3) δ 159.3 (d, J = 238.8 Hz), 140.1, 139.1, 138.0, 134.8, 131.7 (d, J = 10.6 Hz), 129.0, 128.0, 126.6, 116.2 (d, J = 10.0 Hz), 113.5, 109.1, 108.0 (d, J = 26.6 Hz), 104.2 (d, J = 23.0 Hz), 93.6 (d, J = 4.9 Hz), 22.9. ^{19}F NMR (376 MHz, CDCl_3) δ -120.5. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 168.92. HRMS (*m/z*): calc. for $\text{C}_{19}\text{H}_{15}\text{FN}^+$ [$\text{M}+\text{H}$] $^+$ = 276.1183; found 276.1201. IR (KBr) cm^{-1} 3040 (VW), 3002 (VW), 2965 (VW), 2928 (VW), 1636 (W), 1609 (S), 1537 (S), 1496 (M), 1442 (M), 1337 (M), 1205 (M), 1176 (S), 1113 (S), 949 (M), 851 (S), 781 (M), 764 (VS), 701 (M), 693 (M), 452 (W), 432 (W).

2-tert-butyl-6,8-dimethylpyrido[1,2-a]indole (4e)



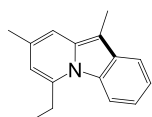
Green solid, 81% yield. MP = 103-105 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 1.8 Hz, 1H), 7.29 (d, J = 1.9 Hz, 1H), 7.11 (s, 1H), 6.58 (s, 1H), 6.08 (s, 1H), 2.96 (s, 3H), 2.30 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.1, 139.1, 137.2, 131.8, 129.3, 117.2, 115.7, 114.8, 114.6, 111.5, 91.1, 34.8, 31.9, 22.5, 21.2. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 169.28. HRMS (m/z): calc. for $\text{C}_{18}\text{H}_{22}\text{N}^+$ $[\text{M}+\text{H}]^+ = 252.1747$; found 252.1756. IR (KBr) cm^{-1} 2957 (W), 2900 (VW), 2860 (VW), 1648 (W), 1610 (M), 1536 (M), 1476 (M), 1440 (M), 1413 (W), 1363 (W), 1333 (W), 1294 (M), 1225 (M), 1172 (W), 1031 (W), 923 (W), 868 (s), 810 (s), 791 (s), 738 (s), 694 VS 644 (M).

2-tert-butyl-6-methyl-8-phenylpyrido[1,2-a]indole (4f)



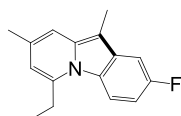
Green solid, 84% yield. MP = 123-125 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, J = 9.0 Hz, 1H), 7.81 (d, J = 2.0 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.61 (d, J = 2.1 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.41 – 7.31 (m, 2H), 6.79 (s, 1H), 6.57 (s, 1H), 3.06 (s, 3H), 1.47 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.4, 139.4, 138.8, 138.0, 133.8, 130.9, 129.4, 129.0, 127.7, 126.6, 118.1, 115.9, 114.8, 113.8, 108.4, 93.6, 34.9, 31.9, 22.9. HRMS (m/z): calc. for $\text{C}_{23}\text{H}_{24}\text{N}^+$ $[\text{M}+\text{H}]^+ = 314.1903$; found 314.1913. IR (KBr) cm^{-1} 2961 (W), 2951 (W), 2860 (VW), 1610 (W), 1597 (W), 1539 (M), 1494 (W), 1438 (W), 1411 (W), 1358 (W), 1301 (W), 1237 (VW), 1211 (W), 1154 (VW), 1093 (W), 1055 (W), 964 (VW), 871 (W), 864 (M), 819 (M), 789 (S), 764 (VS), 745 (W), 727 (W), 695 (VS), 645 (W).

6-ethyl-8,10-dimethylpyrido[1,2-a]indole (4g)



Yellow solid, 55% yield. MP = 70-72 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, J = 8.6 Hz, 1H), 7.77 (dd, J = 8.0 Hz, 2.6, 1H), 7.49 – 7.33 (m, 1H), 7.25 – 7.15 (m, 1H), 7.09 (s, 1H), 6.08 (s, 1H), 3.32 (q, J = 7.3 Hz, 2H), 2.52 (s, 3H), 2.34 (s, 3H), 1.49 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.8, 135.8, 130.8, 130.6, 129.7, 121.5, 118.7, 118.0, 115.3, 113.0, 108.9, 98.2, 27.6, 21.5, 12.1, 8.3. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 165.37. HRMS (m/z): calc. for $\text{C}_{16}\text{H}_{18}\text{N}^+$ $[\text{M}+\text{H}]^+ = 224.1434$; found 224.1427. IR (KBr) cm^{-1} 2975 (VW), 2910 (W), 2856 (VW), 1649 (W), 1603 (W), 1551 (M), 1480 (W), 1453 (W), 1434 (W), 1420 (W), 1379 (W), 1336 (W), 1305 (M), 1286 (W), 1208 (W), 1188 (W), 1025 (W), 978 (W), 841 (M), 801 (M), 748 (M), 739 (VS), 705 (S).

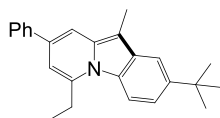
6-ethyl-2-fluoro-8,10-dimethylpyrido[1,2-a]indole (4h)



Yellow solid, 45% yield. MP = 78-80 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.99 (dd, J = 9.3, 4.4 Hz, 1H), 7.31 (dd, J = 9.7, 2.7 Hz, 1H), 7.26 (s, 1H), 7.06 (s, 1H), 6.90 (td, J = 9.1, 2.7 Hz, 1H), 6.11 (s, 1H), 3.26 (q, J = 7.4 Hz, 2H), 2.44 (s, 3H), 2.33 (s, 3H), 1.47 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.0 (d, J = 238.1 Hz), 142.7, 137.4, 131.6, 131.5 (d, J = 9.9 Hz), 126.4, 116.2 (d, J = 9.9 Hz), 112.8, 109.0, 107.0 (d, J = 26.4 Hz), 102.0 (d, J = 22.7 Hz), 98.2 (d, J = 4.9 Hz), 27.4, 21.5, 11.9, 8.3. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 165.40.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -121.39. HRMS (*m/z*): calc. for $\text{C}_{16}\text{H}_{17}\text{FN}^+$ $[\text{M}+\text{H}]^+ = 242.1340$; found 242.1334. IR (KBr) cm^{-1} 2979 (W), 2913 (W), 2854 (W), 1654 (W), 1610 (S), 1543 (S), 1456 (S), 1371 (W), 1342 (M), 1299 (W), 1209 (S), 1159 (S), 1049 (W), 982 (M), 946 (M), 928 (M), 882 (M), 845 (S), 829 (S), 800 (S), 777 (VS), 690 (M), 619 (S).

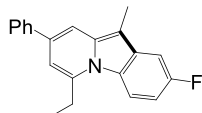
2-*tert*-butyl-6-ethyl-10-methyl-8-phenylpyrido[1,2-*a*]indole (4i)



Orange solid, 69% yield. MP = 145-146°C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, $J = 9.0$ Hz, 1H), 7.79 – 7.72 (m, 3H), 7.58 (s, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.38 (t, $J = 8.3$ Hz, 2H), 6.55 (s, 1H), 3.40 (q, $J = 7.3$ Hz, 2H), 2.62 (s, 3H), 1.56 (t, $J = 7.3$ Hz, 3H), 1.51 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.7, 143.4, 140.0, 135.8, 132.4, 130.6, 129.0, 128.0, 127.5, 126.5, 118.2, 115.0, 113.7, 112.0, 105.4, 100.9, 34.9, 32.0, 27.7. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 164.32. HRMS (*m/z*): calc. for $\text{C}_{25}\text{H}_{28}\text{N}^+$ $[\text{M}+\text{H}]^+ = 342.2216$; found 342.2210.

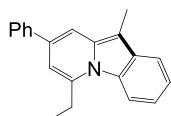
6-ethyl-2-fluoro-10-methyl-8-phenylpyrido[1,2-*a*]indole (4j)



Orange solid, 77% yield. MP = 132-134°C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.03 (dd, $J = 9.2, 4.3$ Hz, 1H), 7.72 (d, $J = 7.3$ Hz, 2H), 7.54 (d, $J = 1.6$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.42 – 7.34 (m, 2H), 6.97 (td, $J = 9.0, 2.6$ Hz, 1H), 6.58 (s, 1H), 3.34 (q, $J = 7.3$ Hz, 2H), 2.53 (s, 3H), 1.54 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.0 (d, $J = 238.8$ Hz), 143.4, 139.7, 137.2, 133.5, 131.6 (d, $J = 9.8$ Hz), 129.0, 127.8, 126.6, 126.5, 116.4 (d, $J = 9.8$ Hz), 111.7, 108.0 (d, $J = 26.5$ Hz), 105.9, 102.2 (d, $J = 22.7$ Hz), 100.8 (d, $J = 5.0$ Hz), 27.7, 11.9, 8.5. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 160.00. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -125.6. HRMS (*m/z*): calc. for $\text{C}_{21}\text{H}_{19}\text{FN}^+$ $[\text{M}+\text{H}]^+ = 304.1496$; found 304.1467. IR (KBr) cm^{-1} 2975 (VW), 2912 (VW), 2883 (VW), 2858 (VW), 1611 (M), 1601 (W), 1551 (W), 1530 (W), 1495 (W), 1459 (M), 1449 (W), 1438 (M), 1346 (W), 1207 (M), 1170 (M), 1132 (W), 985 (W), 938 (W), 887 (W), 846 (M), 764 (S), 757 (VS), 693 (S).

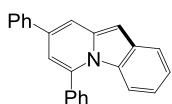
6-ethyl-10-methyl-8-phenylpyrido[1,2-*a*]indole (4k)



Orange solid, 74% yield. MP = 126-128 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, $J = 8.6$ Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.75 (d, $J = 7.7$ Hz, 2H), 7.58 (s, 1H), 7.50 (t, $J = 7.6$ Hz, 2H), 7.40 (dt, $J = 11.8, 7.3$ Hz, 2H), 7.29 (d, $J = 7.9$ Hz, 1H), 6.58 (s, 1H), 3.41 (q, $J = 7.3$ Hz, 2H), 2.61 (s, 3H), 1.56 (t, $J = 7.3$ Hz, 3H).

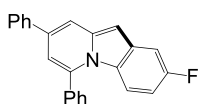
^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 139.9, 135.6, 132.8, 130.7, 129.8, 129.0, 127.6, 126.6, 121.8, 119.5, 118.3, 115.4, 112.1, 105.8, 100.9, 27.9, 12.1, 8.5. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 164.65. HRMS (*m/z*): calc. for $\text{C}_{21}\text{H}_{20}\text{N}^+$ $[\text{M}+\text{H}]^+ = 286.1590$; found 286.1570. IR (KBr) cm^{-1} 3032 (W), 2977 (W), 2927 (W), 2855 (W), 1599 (M), 1553 (W), 1531 (W), 1482 (M), 1452 (M), 1435 (M), 1378 (M), 1326 (W), 1304 (W), 1297 (W), 1201 (M), 843 (M), 760 (S), 734 (VS), 699 (S).

6,8-diphenylpyrido[1,2-*a*]indole (4l)



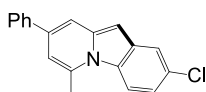
Yellow solid, 82% yield. MP = 141-143 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.76 (m, 1H), 7.73 (d, J = 4.2 Hz, 3H), 7.61 (s, 5H), 7.48 (t, J = 7.3 Hz, 2H), 7.38 (t, J = 7.3 Hz, 1H), 7.27 (t, J = 9.8 Hz, 1H), 6.89 (t, J = 4.4 Hz, 2H), 6.66 (s, 1H), 6.62 – 6.54 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.5, 139.1, 138.6, 136.6, 134.0, 130.7, 130.5, 129.6, 129.3, 129.1, 129.0, 127.9, 126.5, 122.5. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 166.37. HRMS (m/z): calc. for $\text{C}_{24}\text{H}_{18}\text{N}^+$ $[\text{M}+\text{H}]^+ = 320.1434$; found 320.1431 IR (KBr) cm^{-1} 3058 (W), 3032 (W), 1634 (W), 1597 (M), 1537 (M), 1488 (M), 1475 (M), 1443 (S), 1314 (S), 1291 (S), 1227 (M), 1107 (M), 864 (M), 843 (M), 762 (VS), 736 (M), 698 (VS), 596 (M).

2-fluoro-6,8-diphenylpyrido[1,2-*a*]indole (4m)



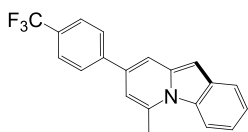
Yellow solid, 98% yield. MP = 123-125 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.72 (s, 1H), 7.71 – 7.68 (m, 3H), 7.63 – 7.57 (m, 5H), 7.47 (t, J = 7.6 Hz, 2H), 7.42 – 7.33 (m, 2H), 6.81 (s, 1H), 6.66 (d, J = 1.7 Hz, 1H), 6.60 (td, J = 9.2, 2.1 Hz, 1H), 6.49 – 6.43 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.3 (d, J = 239.0 Hz), 140.4, 140.0, 138.9, 136.3, 134.7, 131.4 (d, J = 10.6 Hz), 129.8, 129.3, 129.3, 129.1, 128.1, 127.2, 126.6, 116.0 (d, J = 9.7 Hz), 114.8, 110.6, 107.9 (d, J = 26.4 Hz), 104.1 (d, J = 23.1 Hz), 93.8 (d, J = 5.0 Hz). ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 166.77. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.4. HRMS (m/z): calc. for $\text{C}_{24}\text{H}_{17}\text{FN}^+$ $[\text{M}+\text{H}]^+ = 338.1340$; found 338.1339. IR (KBr) cm^{-1} 3061 (VW), 3030 (VW), 1609 (W), 1599 (W), 1577 (VW), 1533 (W), 1488 (W), 1444 (M), 1338 (W), 1294 (W), 1259 (W), 1222 (W), 1179 (W), 1106 (M), 1075 (W), 1028 (W), 991 (W), 954 (W), 860 (W), 847 (M), 835 (M), 787 (M), 758 (VS), 698 (VS), 642 (W).

2-chloro-6-methyl-8-phenylpyrido[1,2-*a*]indole (4n)



Yellow solid, 50% yield. MP = 144-146 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, J = 9.1 Hz, 1H), 7.75 (d, J = 2.2 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.58 (d, J = 1.9 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.3 Hz, 1H), 7.14 (dd, J = 9.1, 2.1 Hz, 1H), 6.72 (s, 1H), 6.61 (s, 1H), 3.00 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.7, 139.1, 138.0, 134.9, 131.8, 129.5, 129.0, 128.3, 128.0, 126.6, 119.6, 119.2, 116.1, 113.7, 109.4, 93.2, 22.9. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 169.30. HRMS (m/z): calc. for $\text{C}_{19}\text{H}_{15}\text{ClN}^+$ $[\text{M}+\text{H}]^+ = 292.0888$; found 292.0880. IR (KBr) cm^{-1} 3053 (VW), 3034 (VW), 1636 (VW), 1593 (W), 1534 (M), 1494 (W), 1435 (M), 1334 (W), 1325 (W), 1296 (W), 1206 (W), 1141 (W), 1068 (W), 1030 (W), 965 (W), 902 (W), 860 (S), 826 (W), 775 (M), 761 (VS), 729 (W), 701 (M), 691 (M).

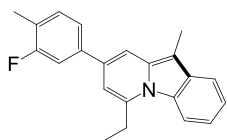
6-methyl-8-(4-(trifluoromethyl)phenyl)pyrido[1,2-*a*]indole (4o)



Yellow solid, 65% yield. MP = 168-170 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.23 (d, J = 8.6 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 8.3 Hz, 2H), 7.63 (s, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.4 Hz, 1H), 6.86 (s, 1H), 6.54 (s, 1H), 3.07 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.8, 138.5, 138.1, 132.4, 131.3, 130.8, 129.6 (q, J = 32.5 Hz), 126.8, 125.9 (q, J = 3.7 Hz), 124.4 (q, J =

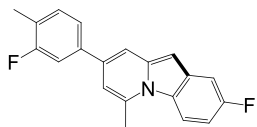
272.0 Hz), 122.7, 120.6, 120.0, 115.3, 114.8, 108.1, 94.6, 23.0. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 168.98. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.4. HRMS (*m/z*): calc. for $\text{C}_{20}\text{H}_{15}\text{F}_3\text{N}^+$ $[\text{M}+\text{H}]^+ = 326.1151$; found 326.1147. IR (KBr) cm^{-1} 3077 (VW), 2916 (VW), 2860 (VW), 1611 (M), 1539 (M), 1468 (W), 1444 (W), 1419 (W), 1327 (S), 1317 (S), 1294 (M), 1261 (W), 1165 (M), 1110 (VS), 1069 (S), 1052 (M), 1011 (M), 839 (S), 828 (M), 812 (S), 781 (M), 765 (M), 746 (S), 701 (S), 658 (M), 627 (M).

6-ethyl-8-(3-fluoro-4-methylphenyl)-10-methylpyrido[1,2-*a*]indole (4p)



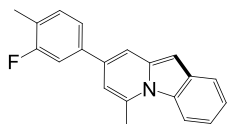
Orange solid, 92% yield. MP = 81-82 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, $J = 8.7$ Hz, 1H), 7.80 (d, $J = 8.1$ Hz, 1H), 7.54 (d, $J = 1.8$ Hz, 1H), 7.47 – 7.34 (m, 3H), 7.32 – 7.22 (m, 2H), 6.50 (s, 1H), 3.40 (q, $J = 7.1$ Hz, 2H), 2.60 (s, 3H), 2.34 (s, 3H), 1.55 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.8 (d, $J = 244.3$ Hz), 143.7, 139.4 (d, $J = 7.7$ Hz), 135.4, 131.9 (d, $J = 5.7$ Hz), 131.5, 130.8, 129.8, 124.1 (d, $J = 17.3$ Hz), 121.8, 121.7 (d, $J = 3.1$ Hz), 119.7, 118.4, 115.4, 112.9 (d, $J = 23.1$ Hz), 112.0, 105.3, 101.2, 27.8, 14.5 (d, $J = 3.4$ Hz), 12.1, 8.5. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 164.84. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.3. HRMS (*m/z*): calc. for $\text{C}_{22}\text{H}_{21}\text{FN}^+$ $[\text{M}+\text{H}]^+ = 318.1653$; found 318.1625. IR (KBr) cm^{-1} 3059 (VW), 2997 (VW), 2973 (VW), 2940 (VW), 2912 (VW), 2883 (VW), 2857 (VW), 1639 (VW), 1621 (VW), 1601 (VW), 1575 (W), 1550 (W), 1531 (W), 1510 (W), 1483 (W), 1452 (W), 1375 (W), 1327 (M), 1310 (M), 1272 (M), 1247 (W), 1199 (W), 1176 (M), 1158 (W), 1127 (M), 1113 (W), 938 (M), 870 (M), 842 (S), 816 (VS), 757 (W), 732 (VS), 700 (S), 656 (W), 645 (W).

2-fluoro-8-(3-fluoro-4-methylphenyl)-6-methylpyrido[1,2-*a*]indole (4q)



Yellow solid, 80% yield. MP = 152-154 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.11 (dd, $J = 9.3, 4.4$ Hz, 1H), 7.54 (d, $J = 1.6$ Hz, 1H), 7.43 – 7.29 (m, 3H), 7.25 (t, $J = 7.9$ Hz, 1H), 6.96 (td, $J = 9.1, 2.6$ Hz, 1H), 6.74 (s, 1H), 6.54 (s, 1H), 3.01 (s, 3H), 2.33 (d, $J = 1.5$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.8 (d, $J = 244.7$ Hz), 159.3 (d, $J = 238.9$ Hz), 139.9, 138.6 (d, $J = 7.7$ Hz), 138.1, 133.5 (d, $J = 2.2$ Hz), 132.0 (d, $J = 5.7$ Hz), 131.6 (d, $J = 10.7$ Hz), 128.0, 124.5 (d, $J = 17.3$ Hz), 121.8 (d, $J = 3.2$ Hz), 116.2 (d, $J = 10.0$ Hz), 113.4, 113.0 (d, $J = 23.2$ Hz), 108.6, 108.2 (d, $J = 26.6$ Hz), 104.2 (d, $J = 22.9$ Hz), 93.9 (d, $J = 4.8$ Hz), 22.9, 14.5. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 169.07. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.0, -120.4. HRMS (*m/z*): calc. for $\text{C}_{20}\text{H}_{16}\text{F}_2\text{N}^+$ $[\text{M}+\text{H}]^+ = 308.1245$; found 308.1251. IR (KBr) cm^{-1} 2986 (VW), 2959 (VW), 2924 (VW), 2862 (VW), 1642 (W), 1609 (M), 1575 (W), 1537 (M), 1502 (W), 1442 (M), 1336 (W), 1262 (M), 1212 (W), 1175 (W), 1163 (W), 1124 (M), 1111 (M), 1003 (W), 949 (M), 857 (M), 839 (S), 819 (VS), 776 (M), 747 (M), 708 (M), 655 (M).

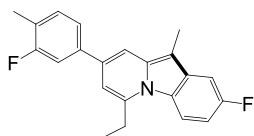
8-(3-fluoro-4-methylphenyl)-6-methylpyrido[1,2-*a*]indole (4r)



Yellow solid, 81% yield. MP = 135-136 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, $J = 8.7$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.58 (s, 1H), 7.42 – 7.31 (m, 3H), 7.30 – 7.20 (m, 2H), 6.81 (s, 1H), 6.52 (s,

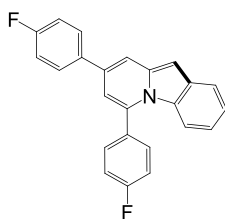
1H), 3.06 (s, 3H), 2.34 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 161.8 (d, *J* = 244.6 Hz), 138.9 (d, *J* = 7.7 Hz), 138.4, 138.2, 132.8, 131.9 (d, *J* = 5.7 Hz), 131.3, 130.9, 124.3 (d, *J* = 17.4 Hz), 122.5, 121.8 (d, *J* = 3.1 Hz), 120.4, 119.6, 115.2, 113.7, 113.0 (d, *J* = 23.2 Hz), 108.3, 93.9, 23.0, 14.5 (d, *J* = 3.4 Hz). ¹⁵N NMR (¹H-¹⁵N ge-HMBC) (41 MHz, Chloroform-*d*) δ 169.02. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -117.2. HRMS (*m/z*): calc. for C₂₀H₁₇FN⁺ [*M*+H]⁺ = 290.1340; found 290.1350. IR (KBr) cm⁻¹ 3107 (VW), 3055 (VW), 2985 (VW), 2917 (VW), 2858 (VW), 1641 (VW), 1623 (W), 1604 (W), 1573 (W), 1539 (W), 1507 (M), 1478 (W), 1435 (W), 1417 (W), 1400 (W), 1314 (M), 1271 (W), 1246 (W), 1213 (W), 1173 (M), 1126 (S), 942 (M), 860 (VS), 813 (VS), 757 (S), 744 (S), 732 (VS), 723 (S), 699 (S).

6-ethyl-2-fluoro-8-(3-fluoro-4-methylphenyl)-10-methylpyrido[1,2-*a*]indole (4s)



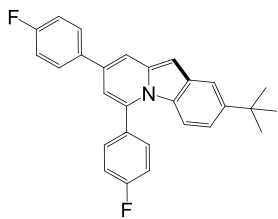
Orange solid, 89% yield. MP = 108-110 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (dd, *J* = 9.3, 4.3 Hz, 1H), 7.48 (s, 1H), 7.41 – 7.35 (m, 2H), 7.34 (s, 1H), 7.730-7.22 (m, 1H), 6.96 (td, *J* = 9.0, 2.6 Hz, 1H), 6.50 (s, 1H), 3.30 (q, *J* = 7.0 Hz, 2H), 2.51 (s, 3H), 2.34 (s, 3H), 1.52 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 161.8 (d, *J* = 244.5 Hz), 159.0 (d, *J* = 239.1 Hz), 143.5, 139.1 (d, *J* = 7.9 Hz), 136.9, 132.2, 131.9 (d, *J* = 5.7 Hz), 131.6 (d, *J* = 9.8 Hz), 126.5, 124.3 (d, *J* = 17.4 Hz), 121.8 (d, *J* = 2.9 Hz), 116.4 (d, *J* = 9.9 Hz), 113.0 (d, *J* = 23.1 Hz), 111.5, 108.1 (d, *J* = 26.6 Hz), 105.4, 102.3 (d, *J* = 22.8 Hz), 101.1 (d, *J* = 5.1 Hz), 27.7, 14.5 (d, *J* = 3.3 Hz), 11.9, 8.4. ¹⁵N NMR (¹H-¹⁵N ge-HMBC) (41 MHz, Chloroform-*d*) δ 164.81. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -117.1, -120.8. HRMS (*m/z*): calc. for C₂₂H₂₀F₂N⁺ [*M*+H]⁺ = 336.1558; found 336.1539. IR (KBr) cm⁻¹ 2980 (VW), 2967 (VW), 2938 (VW), 2915 (VW), 2891 (VW), 2854 (VW), 1608 (M), 1572 (W), 1549 (W), 1534 (M), 1504 (W), 1453 (M), 1431 (W), 1375 (W), 1348 (M), 1307 (W), 1271 (W), 1251 (W), 1207 (M), 1179 (M), 1130 (M), 985 (W), 926 (M), 887 (M), 874 (S), 853 (S), 836 (M), 805 (S), 768 (VS), 707 (W), 693 (M), 607 (S).

6,8-bis(4-fluorophenyl)pyrido[1,2-*a*]indole (4t)



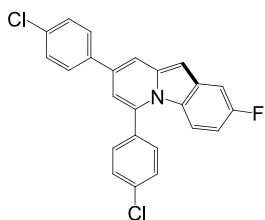
Yellow solid, 87% yield. MP = 137-140 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.63 (m, 3H), 7.60 – 7.55 (m, 2H), 7.32 – 7.24 (m, 3H), 7.15 (t, *J* = 8.7 Hz, 2H), 6.91 (t, *J* = 7.8 Hz, 1H), 6.87 (s, 1H), 6.57 (d, *J* = 8.7 Hz, 1H), 6.55 (d, *J* = 1.9 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.6 (d, *J* = 249.6 Hz), 162.8 (d, *J* = 247.6 Hz), 139.5, 138.4, 135.2 (d, *J* = 3.3 Hz), 133.0, 132.6 (d, *J* = 3.4 Hz), 131.2 (d, *J* = 8.3 Hz), 130.8, 130.4, 128.2 (d, *J* = 8.1 Hz), 122.6, 120.5, 119.4, 116.4 (d, *J* = 21.7 Hz), 116.0 (d, *J* = 21.6 Hz), 115.2, 114.8, 110.5, 94.2. ¹⁵N NMR (¹H-¹⁵N ge-HMBC) (41 MHz, Chloroform-*d*) δ 165.95. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -111.0, -114.4. HRMS (*m/z*): calc. for C₂₄H₁₆F₂N⁺ [*M*+H]⁺ = 356.1245, found 356.1239. IR (KBr) cm⁻¹ 3099 (VW), 3067 (VW), 3041 (VW), 1639 (W), 1599 (M), 1526 (W), 1501 (S), 1313 (M), 1290 (M), 1228 (M), 1220 (S), 1155 (M), 1099 (W), 1014 (W), 989 (W), 847 (M), 829 (VS), 814 (S), 784 (M), 758 (M), 742 (S), 727 (M), 703 (S).

2-tert-butyl-6,8-bis(4-fluorophenyl)pyrido[1,2-a]indole (4u)



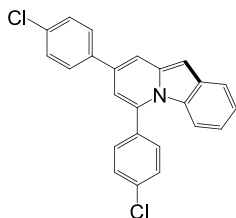
Yellow solid, 68% yield. MP = 187-189 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.70 – 7.63 (m, 3H), 7.58 (dd, J = 8.5, 5.4 Hz, 2H), 7.30 (t, J = 8.6 Hz, 2H), 7.15 (t, J = 8.6 Hz, 2H), 7.02 (dd, J = 9.1, 1.8 Hz, 1H), 6.84 (s, 1H), 6.54 – 6.48 (m, 2H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.5 (d, J = 249.4 Hz), 162.7 (d, J = 247.4 Hz), 145.6, 139.3, 138.6, 135.3 (d, J = 3.2 Hz), 132.6 (d, J = 3.5 Hz), 132.6, 131.3 (d, J = 8.2 Hz), 130.8, 128.6, 128.1 (d, J = 8.0 Hz), 118.2, 116.3 (d, J = 21.6 Hz), 116.0, 115.9 (d, J = 21.6 Hz), 115.1, 114.3, 110.0, 94.2, 34.9, 31.8. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 166.09. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.1, -114.5. HRMS (*m/z*): calc. for $\text{C}_{28}\text{H}_{24}\text{F}_2\text{N}$ [$\text{M}+\text{H}$] $^+$ = 412.1871; found 412.1880. IR (KBr) cm^{-1} 3101 (VW), 3054 (VW), 2952 (VW), 2924 (VW), 2854 (VW), 1612 (M), 1596 (W), 1538 (W), 1486 (S), 1445 (M), 1336 (M), 1318 (W), 1298 (W), 1173 (M), 1105 (M), 1089 (S), 1013 (M), 991 (W), 949 (W), 818 (VS), 784 (M), 753 (W), 707 (M).

6,8-bis(4-chlorophenyl)-2-fluoropyrido[1,2-a]indole (4v)



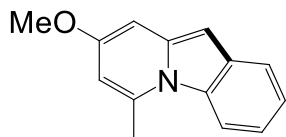
Yellow solid, 88% yield. MP = 160-162 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, J = 1.9 Hz, 1H), 7.62 (t, J = 2.0 Hz, 1H), 7.60 (dd, J = 2.0 Hz, 2H), 7.57 (t, J = 2.0 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.45 – 7.40 (m, 2H), 7.36 (dd, J = 9.4, 2.5 Hz, 1H), 6.82 (s, 1H), 6.66 (td, J = 9.1, 2.6 Hz, 1H), 6.57 – 6.52 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.3 (d, J = 239.6 Hz), 139.7, 139.3, 137.2, 136.0, 134.5, 134.2, 133.3, 131.4 (d, J = 10.4 Hz), 130.6, 129.7, 129.3, 127.8, 127.1, 115.8 (d, J = 9.7 Hz), 115.2, 110.5, 108.4 (d, J = 26.5 Hz), 104.4 (d, J = 23.2 Hz), 94.5 (d, J = 4.8 Hz). ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 165.41. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -119.9. HRMS (*m/z*): calc. for $\text{C}_{24}\text{H}_{14}\text{Cl}_2\text{FN}^+$ [$\text{M}+\text{H}$] $^+$ = 406.0560; found 406.0546. IR (KBr) cm^{-1} 3087 (VW), 3045 (VW), 2955 (VW), 2922 (VW), 2864 (VW), 1612 (M), 1538 (W), 1486 (S), 1445 (M), 1336 (M), 1318 (W), 1298 (W), 1173 (M), 1105 (M), 1089 (S), 1013 (M), 990 (W), 949 (W), 827 (VS), 819 (VS), 784 (M), 753 (M), 718 (W), 707 (M), 604 (W).

6,8-bis(4-chlorophenyl)pyrido[1,2-a]indole (4w)



Yellow solid, 79% yield. MP = 172-174 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 1.9 Hz, 1H), 7.44 (dt, 2H), 7.40 (dt, J = 8.5 Hz, 2H), 7.35 (dt, 2H), 7.25 (dt, 2H), 7.09 (t, 1H), 6.76 (t, J = 7.8 Hz, 1H), 6.71 (s, 1H), 6.47 (d, J = 8.7 Hz, 1H), 6.36 (d, J = 1.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.4, 138.3, 137.4, 135.8, 134.9, 134.0, 132.6, 130.7, 130.6, 130.4, 129.5, 129.2, 127.7, 122.7, 120.6, 119.7, 115.6, 114.8, 110.3. ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform-*d*) δ 165.42. HRMS (*m/z*): calc. for $\text{C}_{24}\text{H}_{16}\text{Cl}_2\text{N}^+$ [$\text{M}+\text{H}$] $^+$ = 388.0654 found 388.0600. IR (KBr) cm^{-1} 3098 (VW), 3048 (VW), 1638 (VW), 1593 (W), 1525 (W), 1486 (M), 1475 (W), 1445 (W), 1313 (W), 1288 (W), 1106 (W), 1086 (M), 1013 (M), 833 (M), 819 (VS), 764 (M), 745 (S), 729 (M), 704 (M).

8-methoxy-6-methylpyrido[1,2-a]indole (4x)

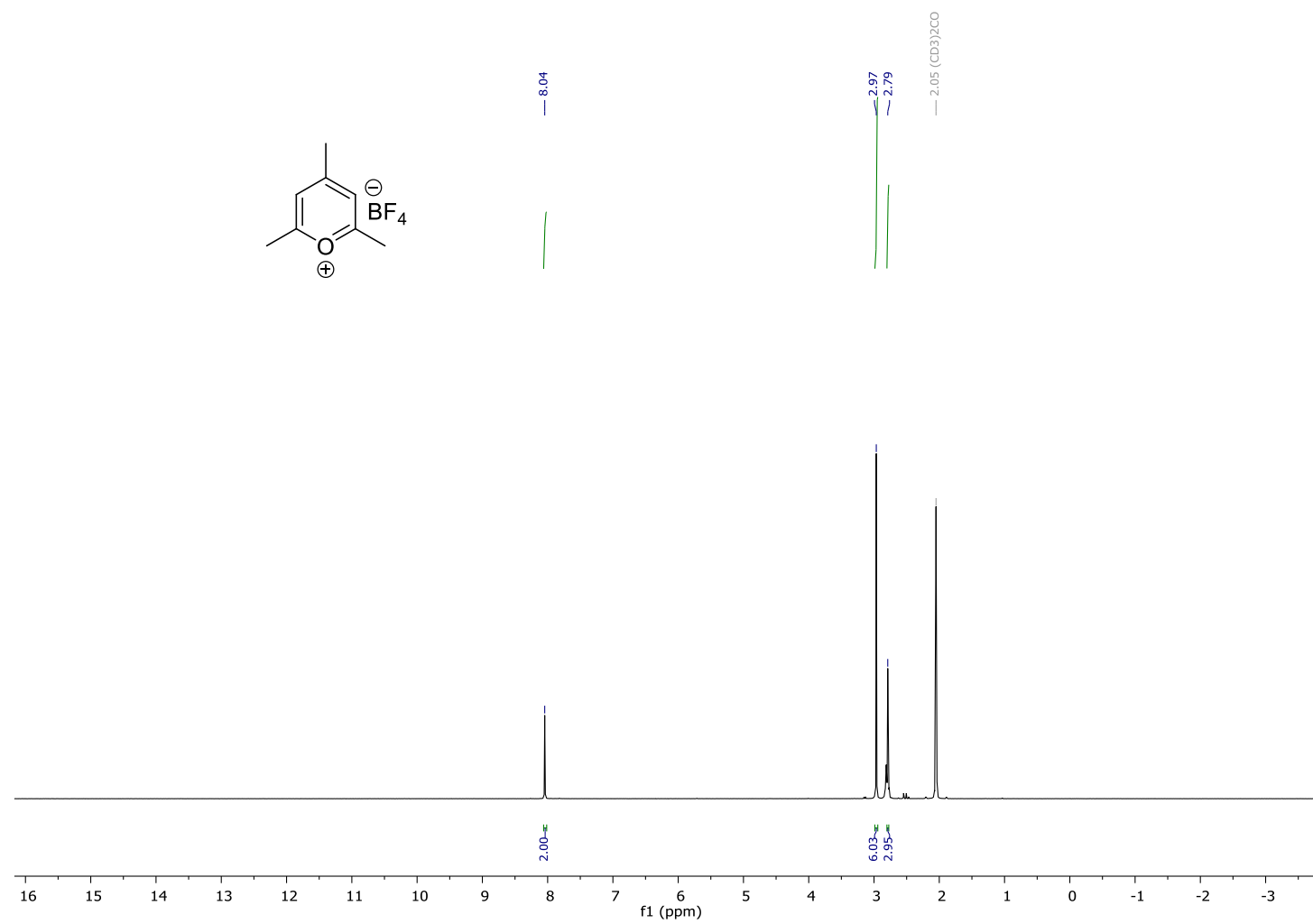


Green solid, 90% yield. MP = 104-105 °C. ^1H NMR (400 MHz, Benzene- d_6) δ 7.87 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.6 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 7.16 – 7.11 (m, 1H), 6.66 (s, 1H), 6.30 (d, J = 2.5 Hz, 1H), 5.89 – 5.81 (m, 1H), 3.26 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, Benzene- d_6) δ 155.38 , 139.95 , 139.74 , 132.16 , 131.58 , 122.60 , 119.72 , 118.59 , 115.10 , 104.60 , 92.33 , 91.63 , 54.54 , 21.87 . ^{15}N NMR (^1H - ^{15}N ge-HMBC) (41 MHz, Chloroform- d) δ 166.04. HRMS (m/z): calc. for $\text{C}_{14}\text{H}_{14}\text{NO}^+$ $[\text{M}+\text{H}]^+ = 212.1070$ found 212.1078. IR (KBr) cm^{-1} 3047 (W), 3002 (W), 2962 (W), 2926 (W), 2853 (W), 2830 (W), 1651 (S), 1603 (M), 1553 (S), 1523 (M), 1495 (W), 1478 (M), 1469 (M), 1448 (S), 1431 (S), 1411 (M), 1383 (M), 1360 (W), 1341 (M), 1328 (M), 1315 (S), 1281 (S), 1242 (S), 1224 (S), 1202 (S), 1166 (S), 1159 (S), 1137 (S), 1065 (M), 1054 (S), 1036 (M), 1025 (M), 992 (M), 965 (M), 940 (M), 927 (M), 864 (M), 846 (M), 815 (VS), 802 (S), 760 (S), 745 (VS), 726 (VS), 697 (VS).

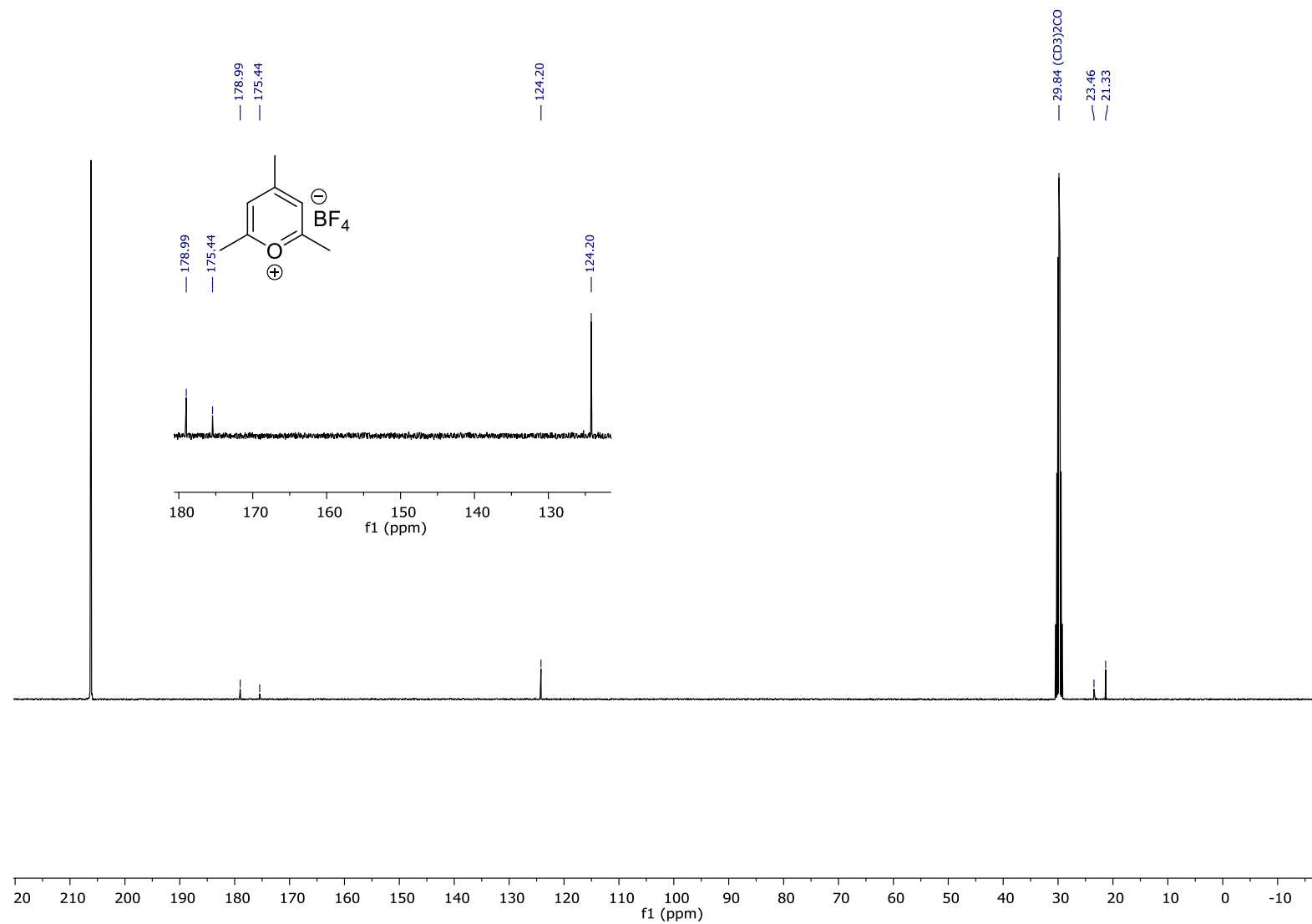
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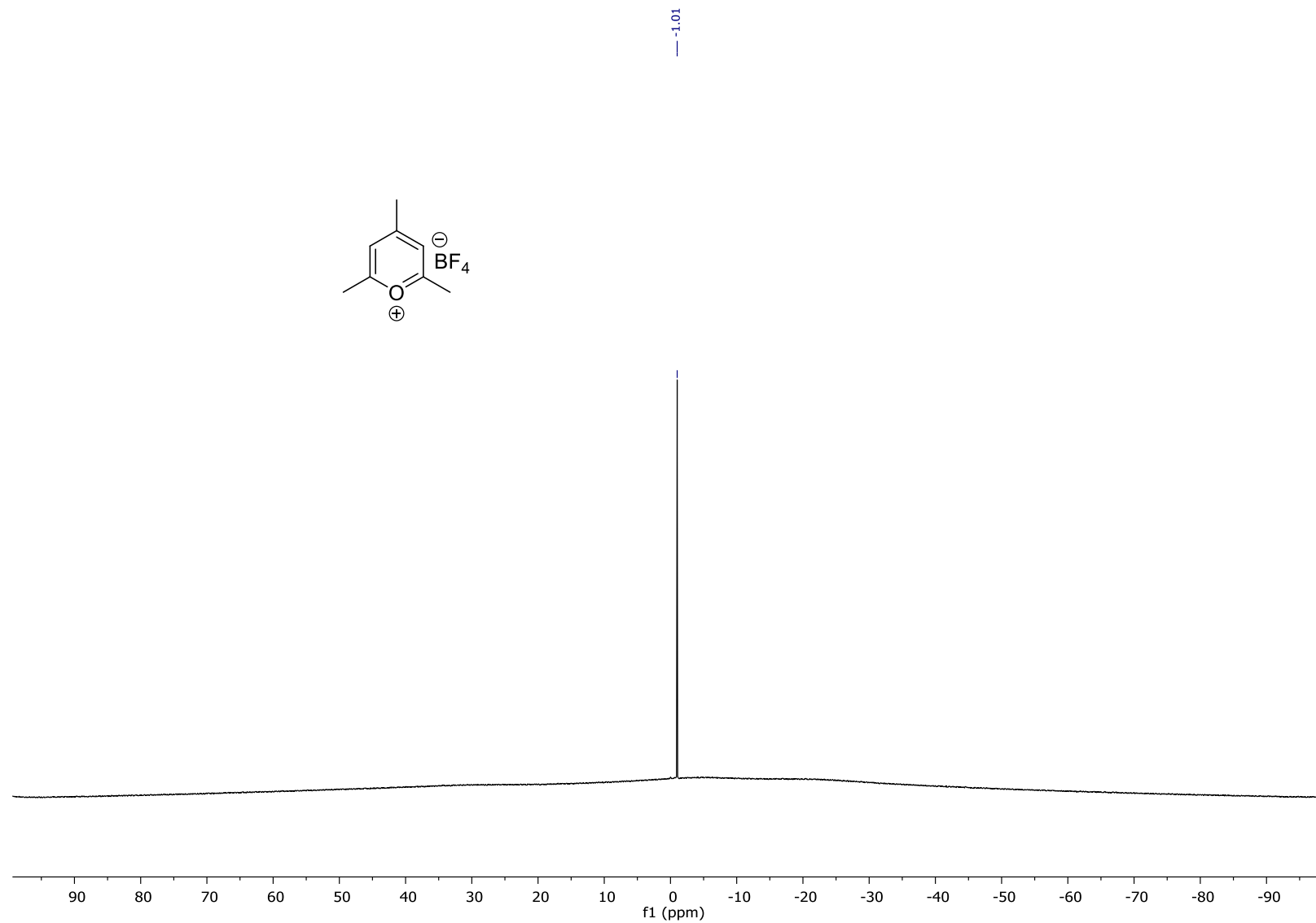
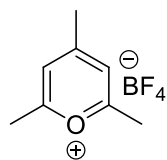
NMR spectra



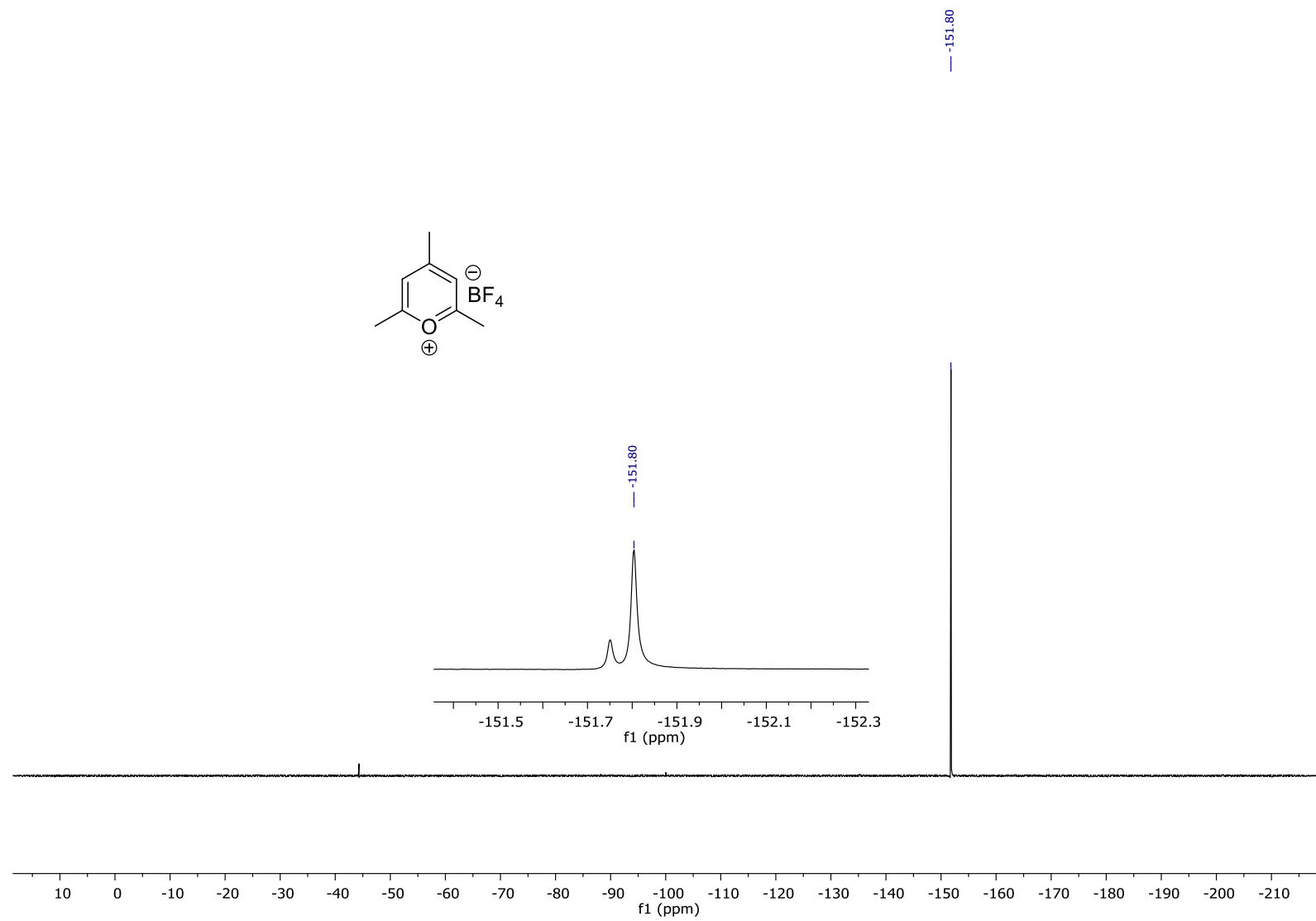
¹H NMR for 1a



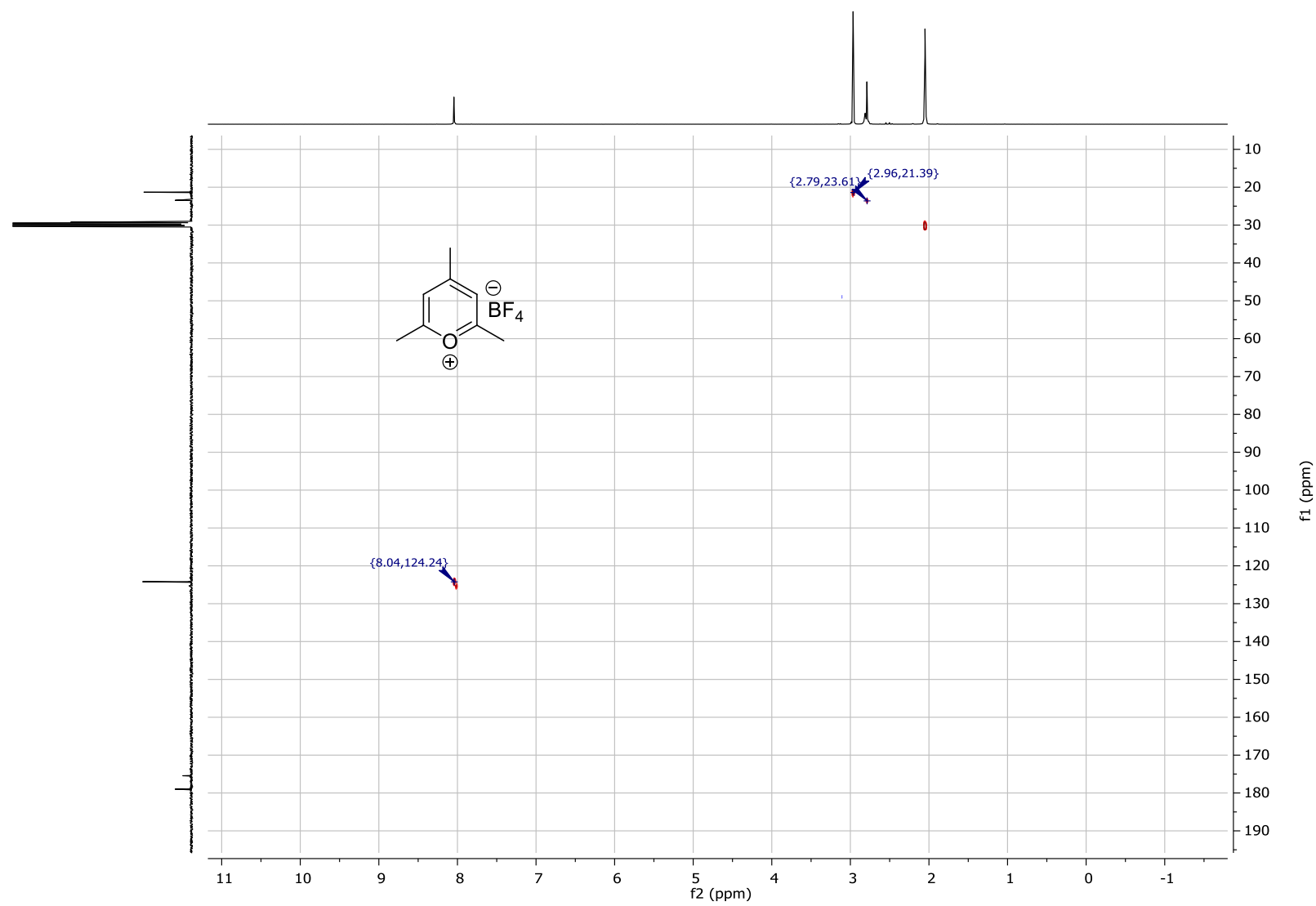
¹³C NMR for 1a



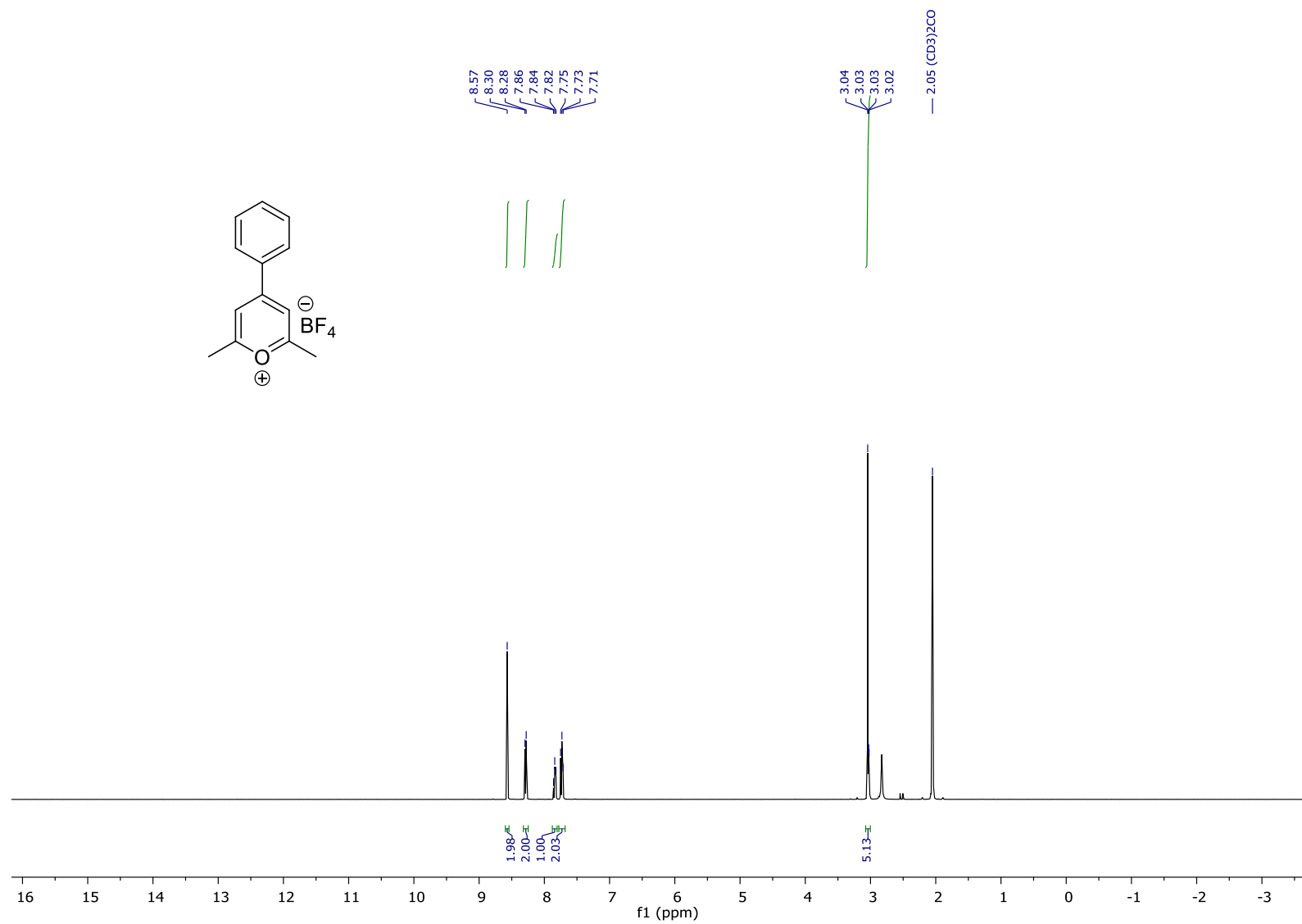
^{11}B NMR for 1a



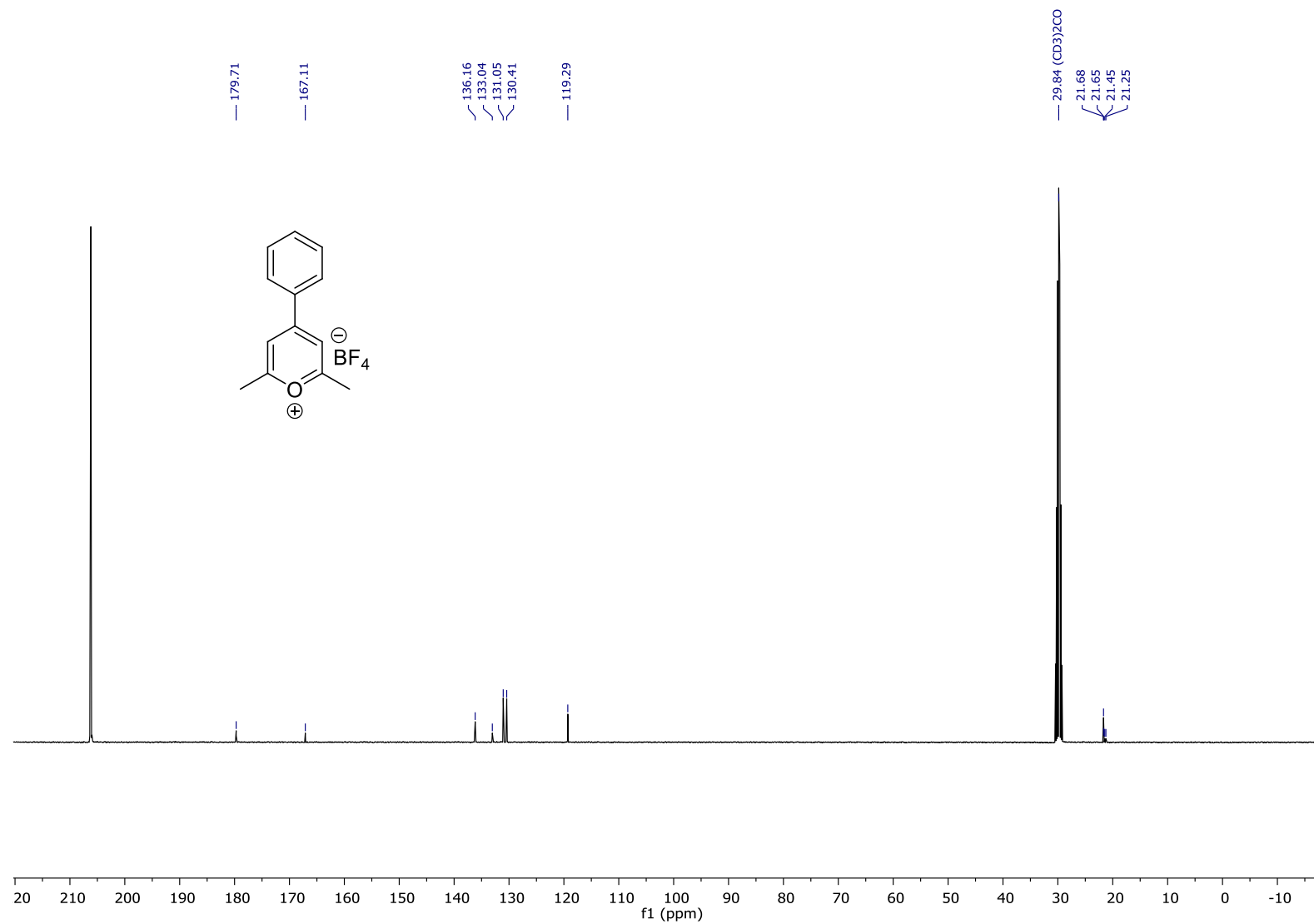
^{19}F NMR for 1a



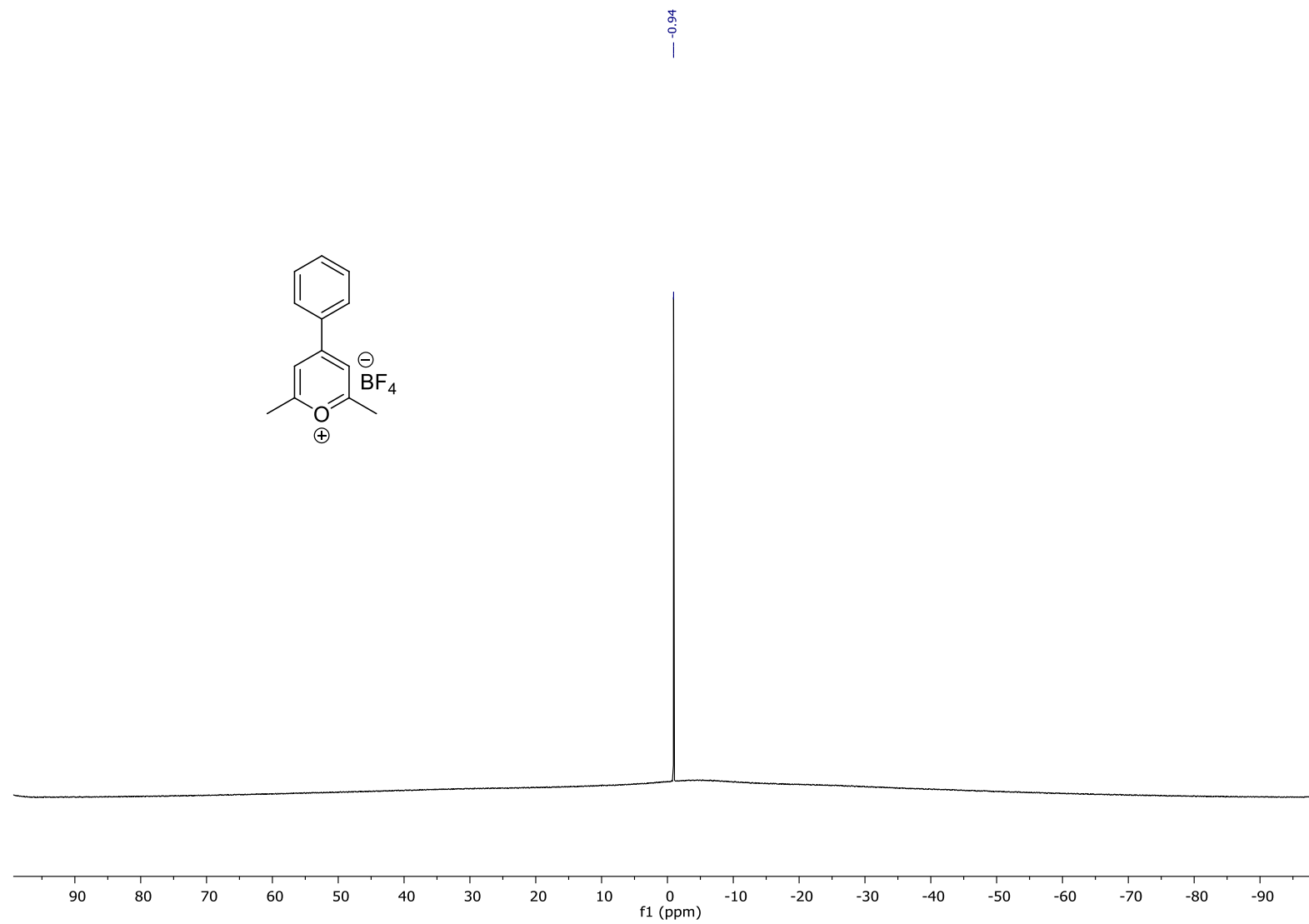
^1H - ^{13}C HSQC for 1a



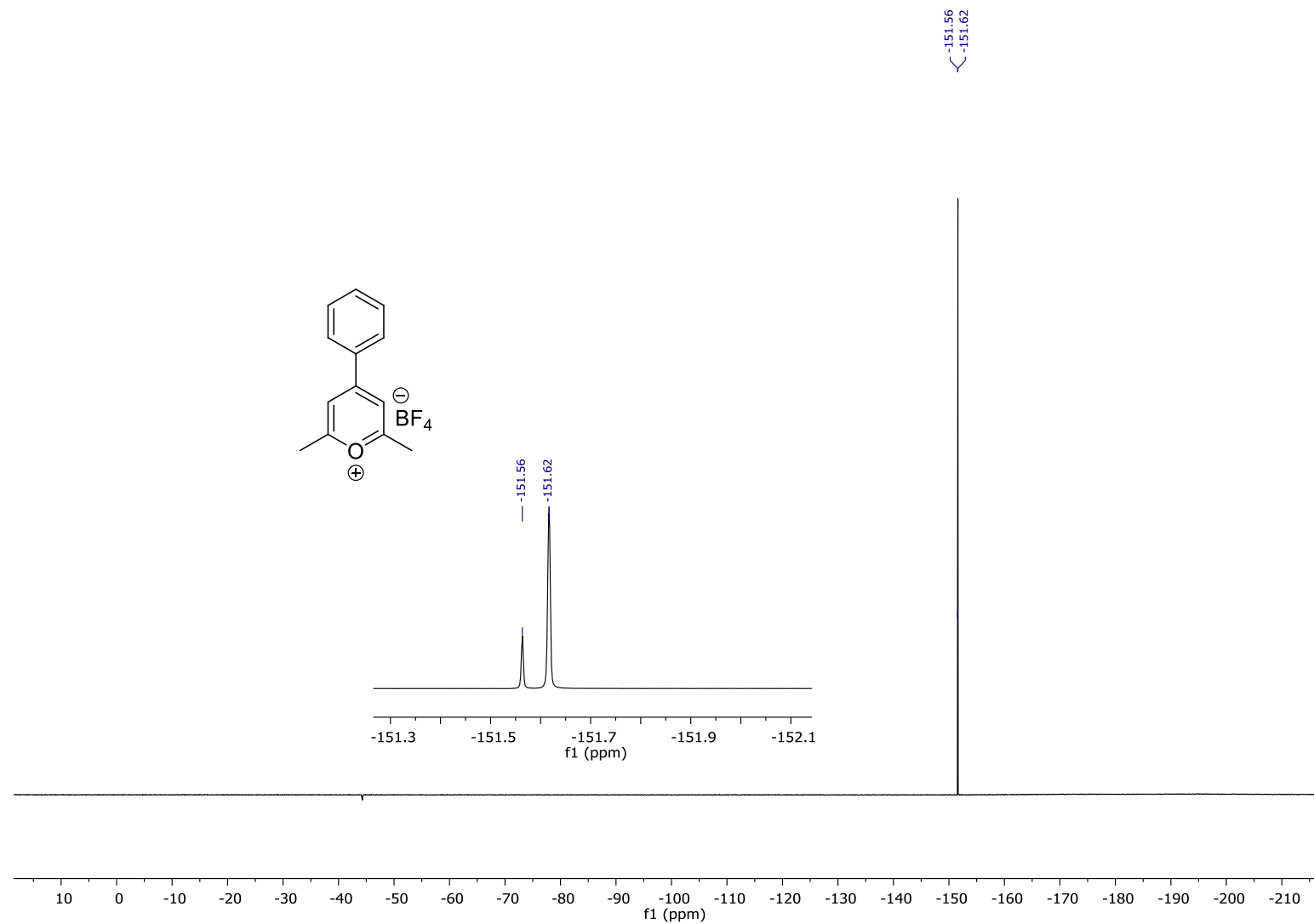
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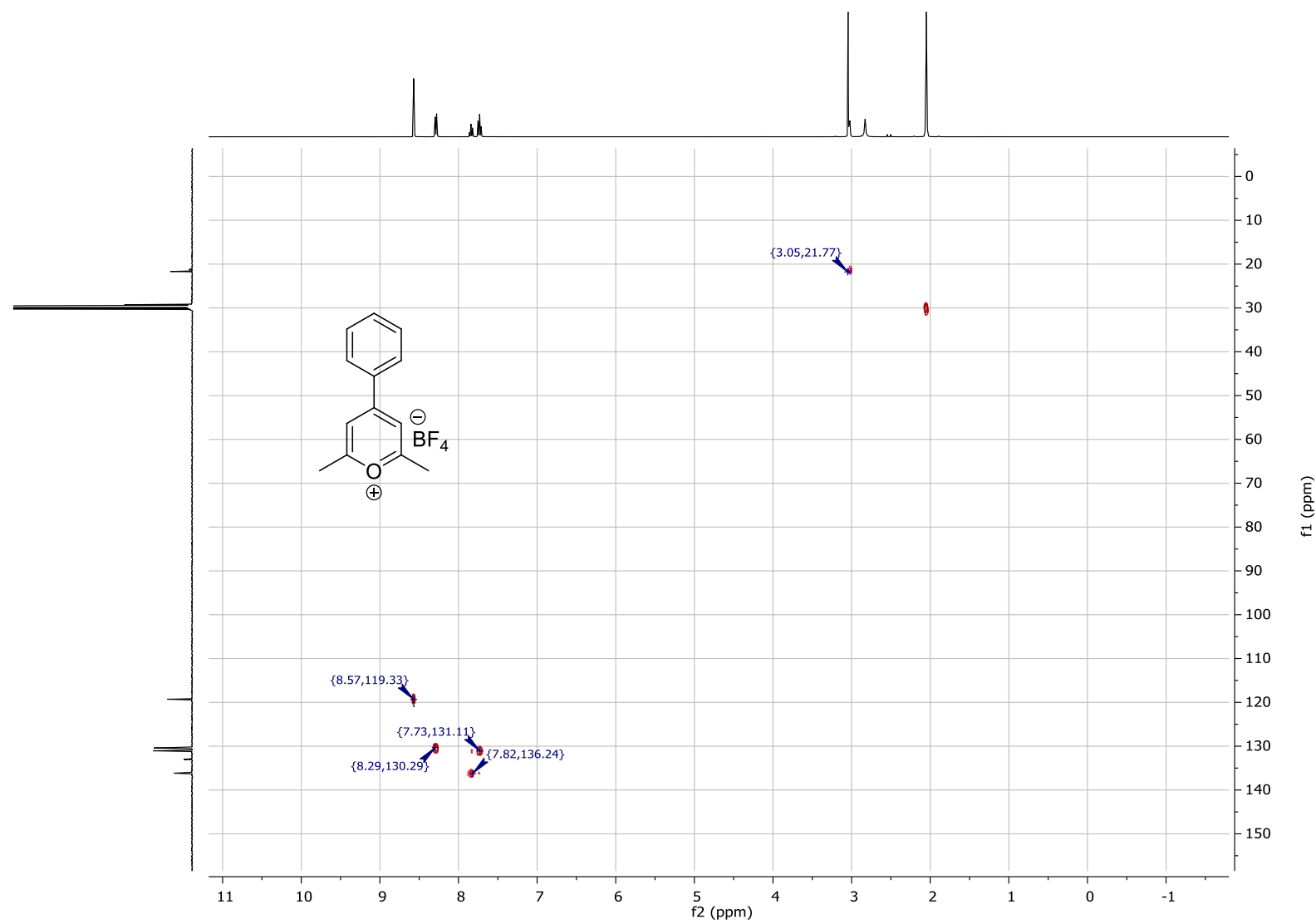
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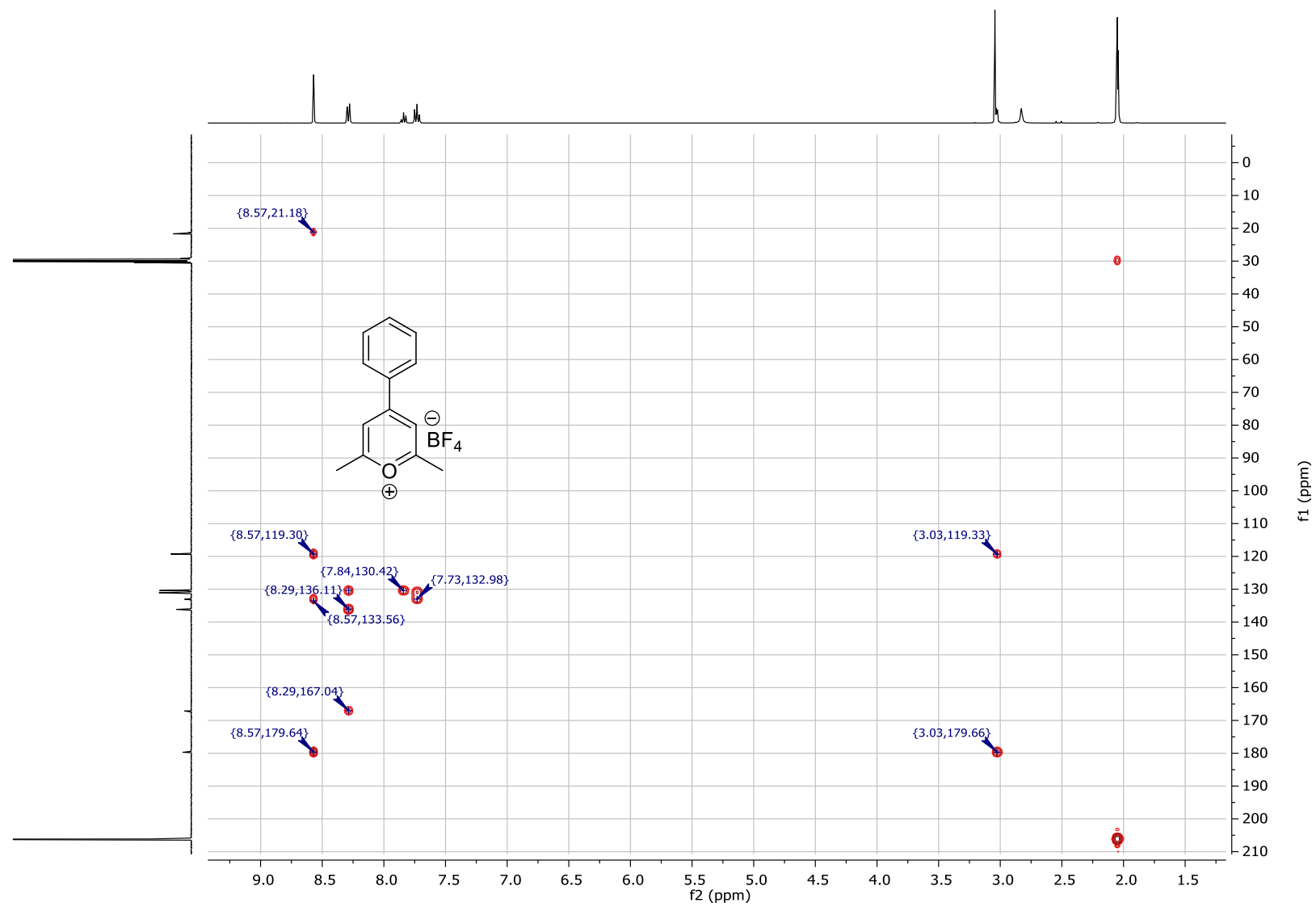
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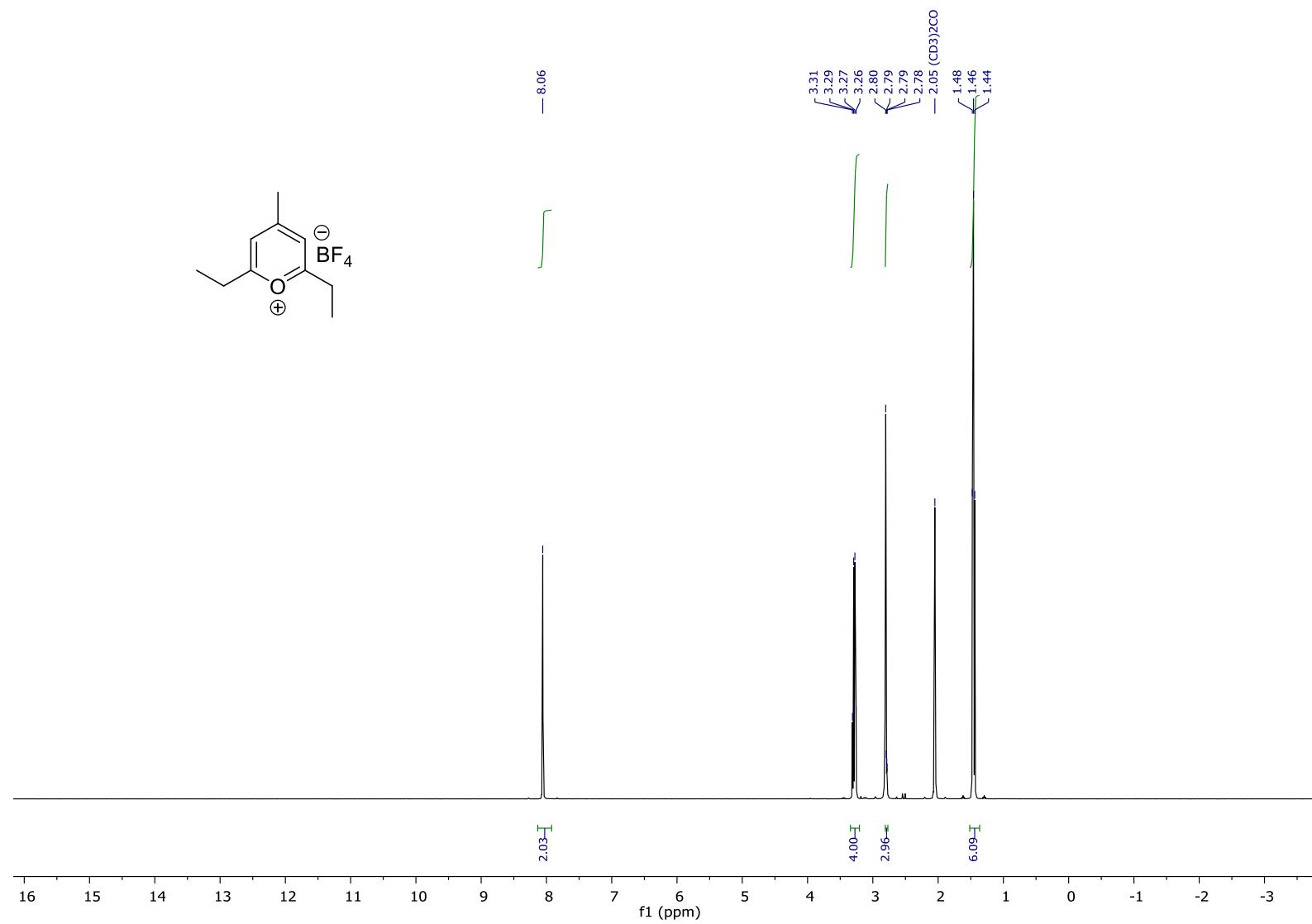
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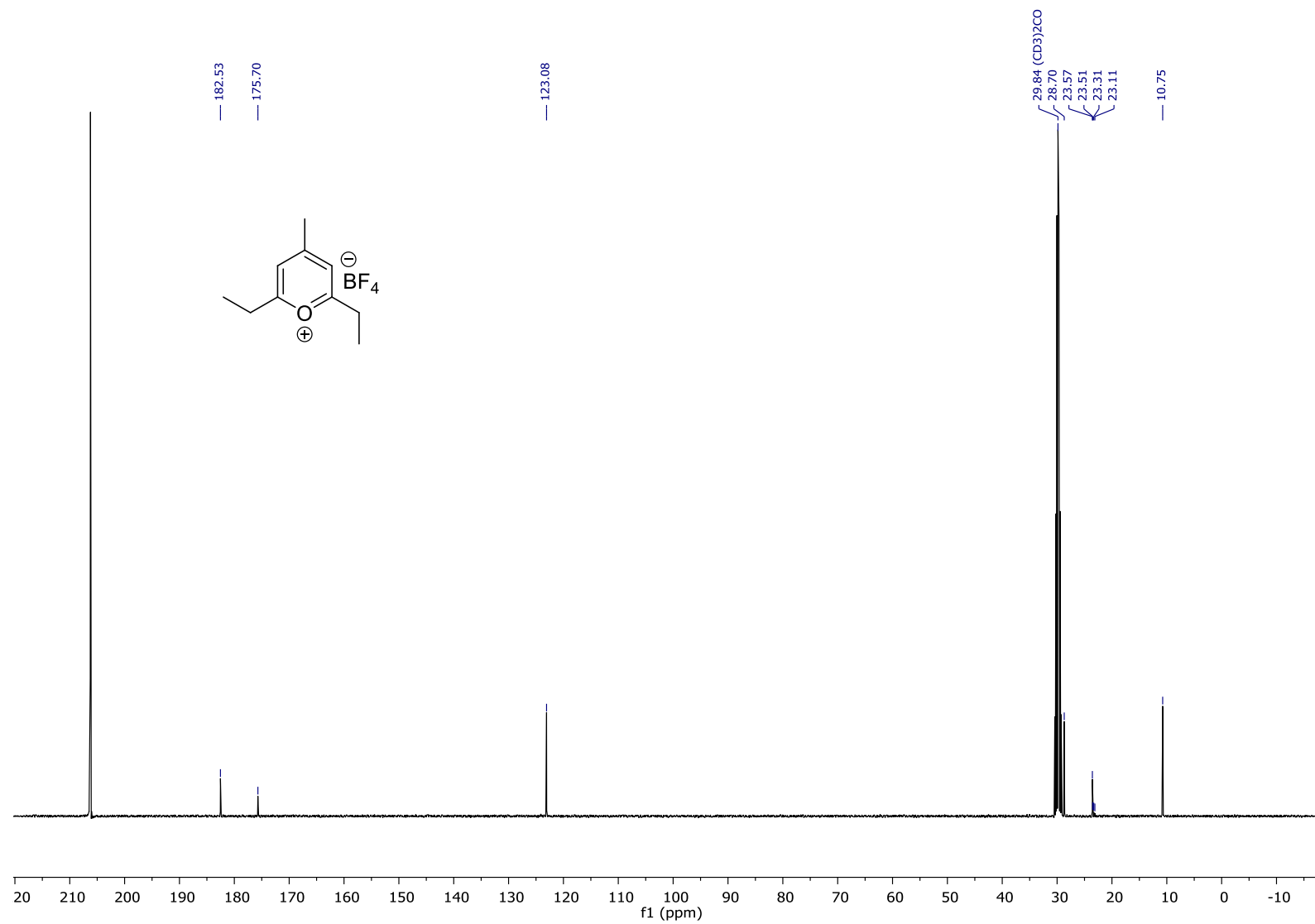
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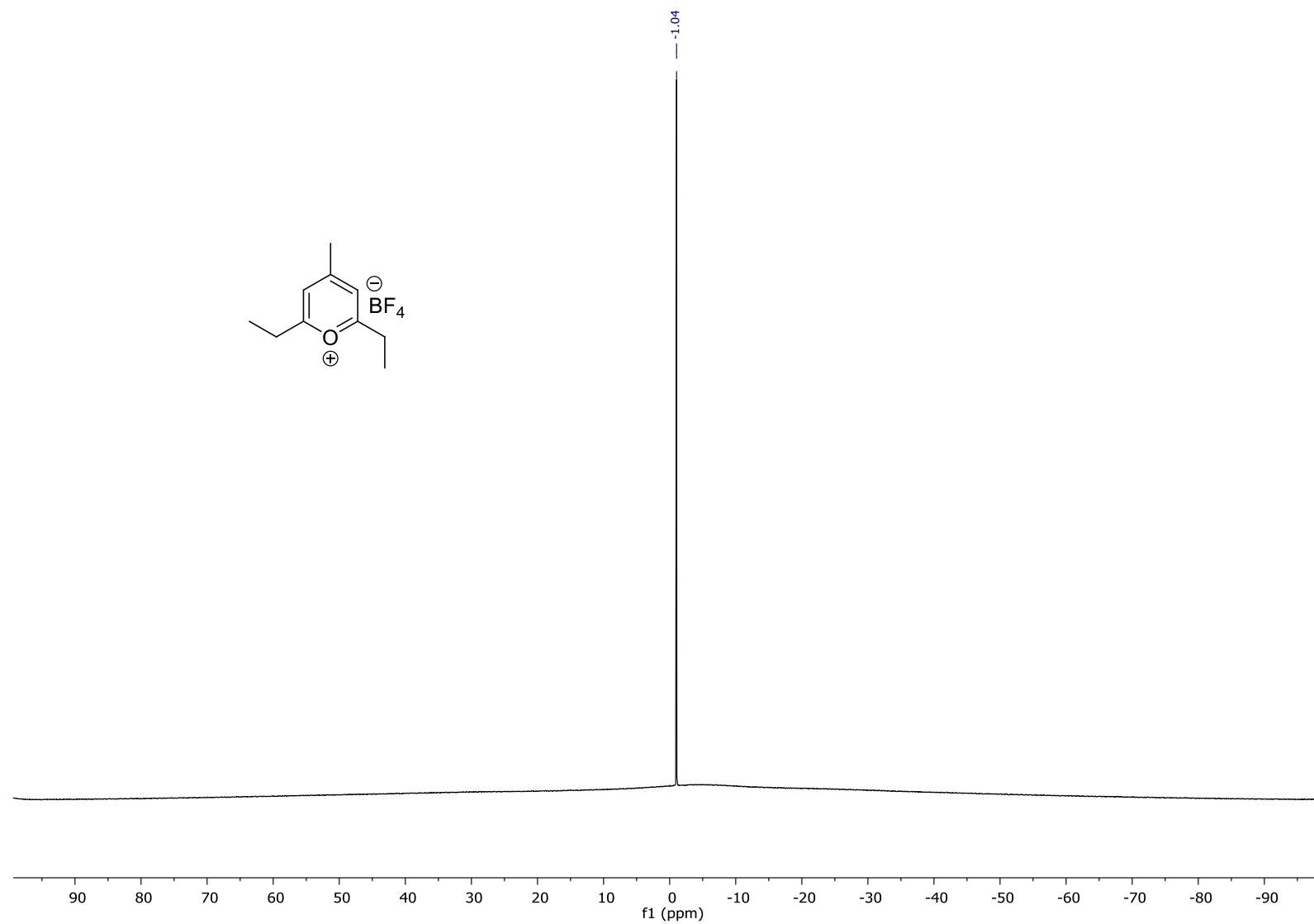
¹H-¹³C HMBC for 1b



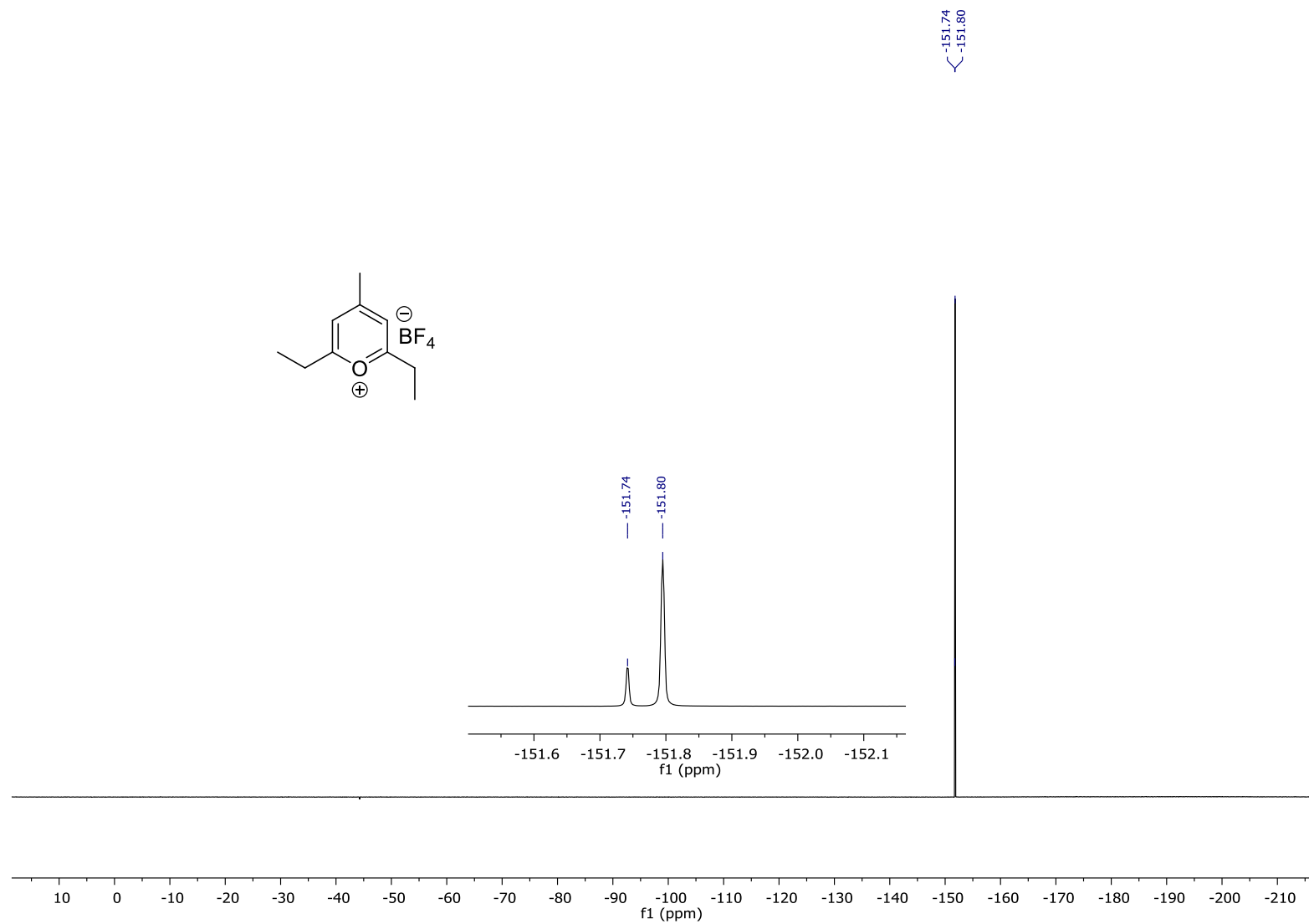
¹H NMR for 1c



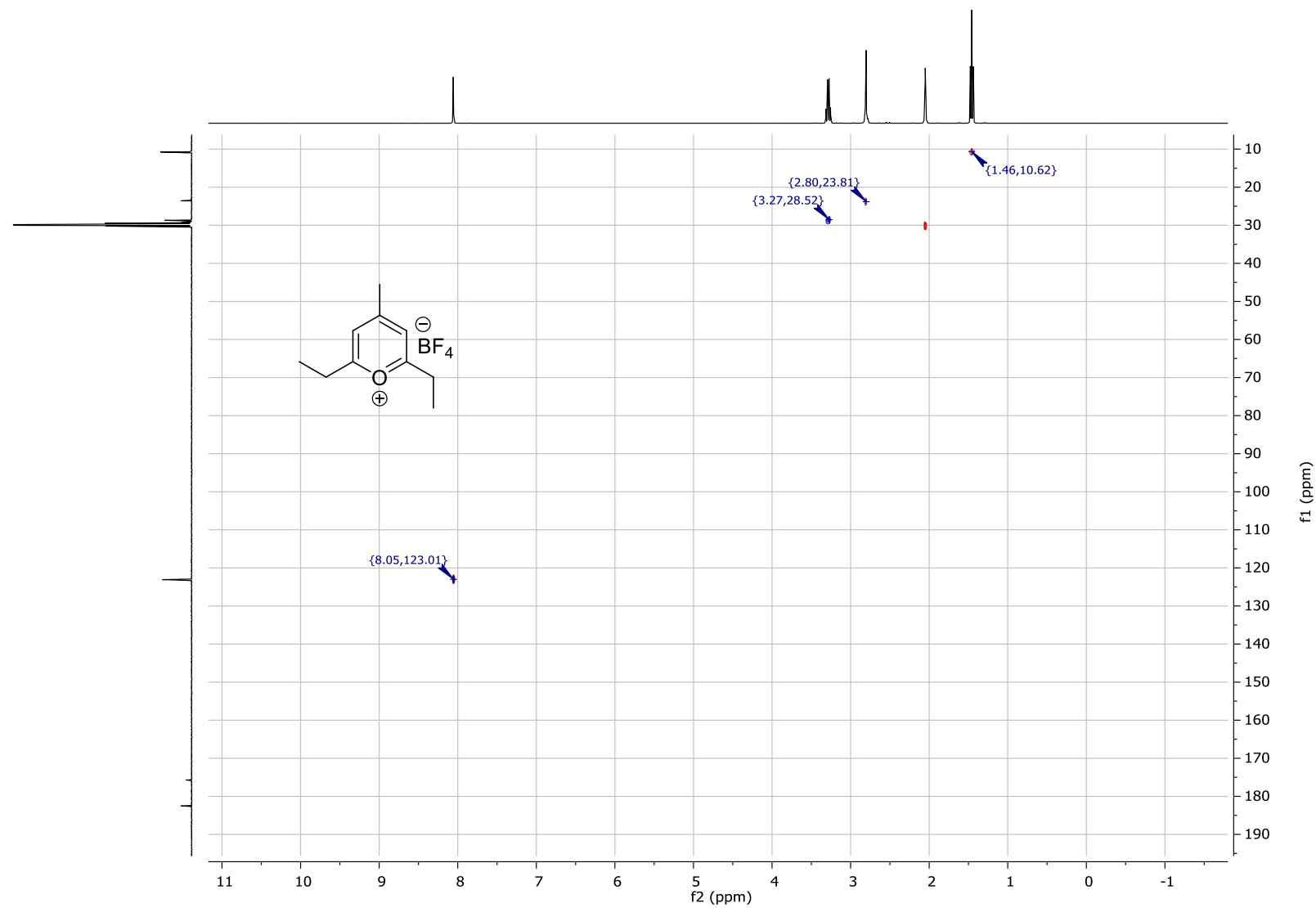
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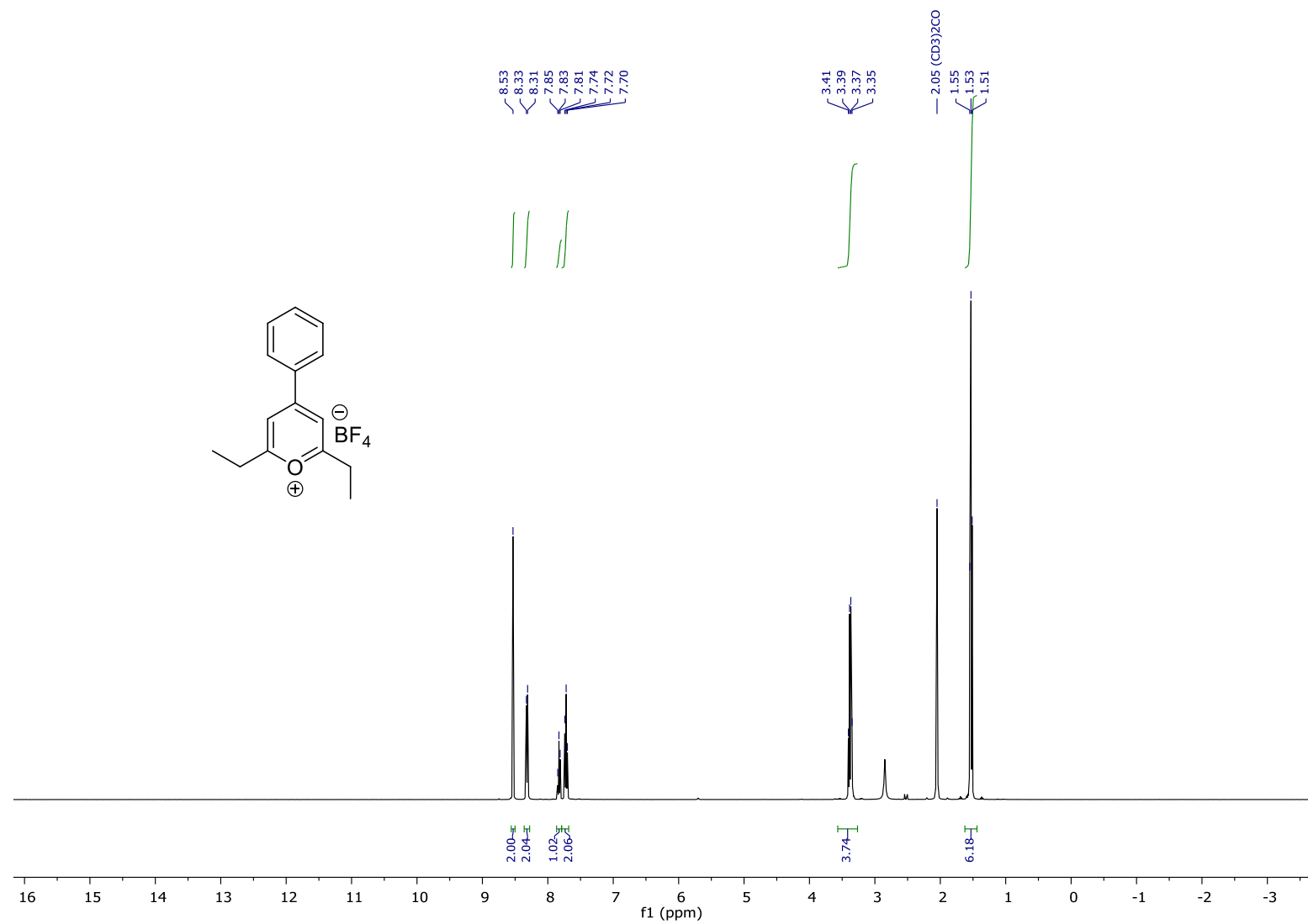


^{11}B NMR for 1c

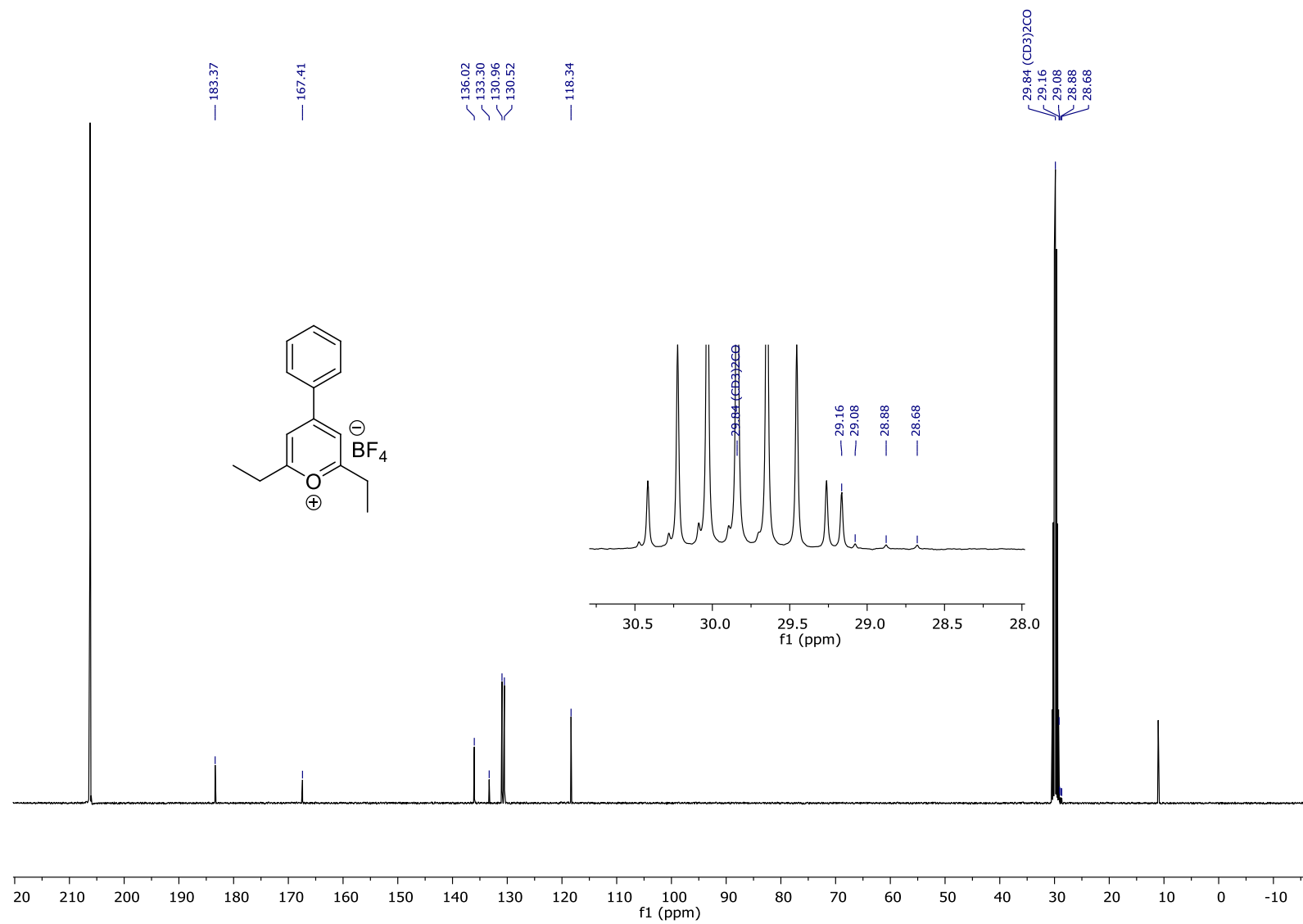


^{19}F NMR for **1c**

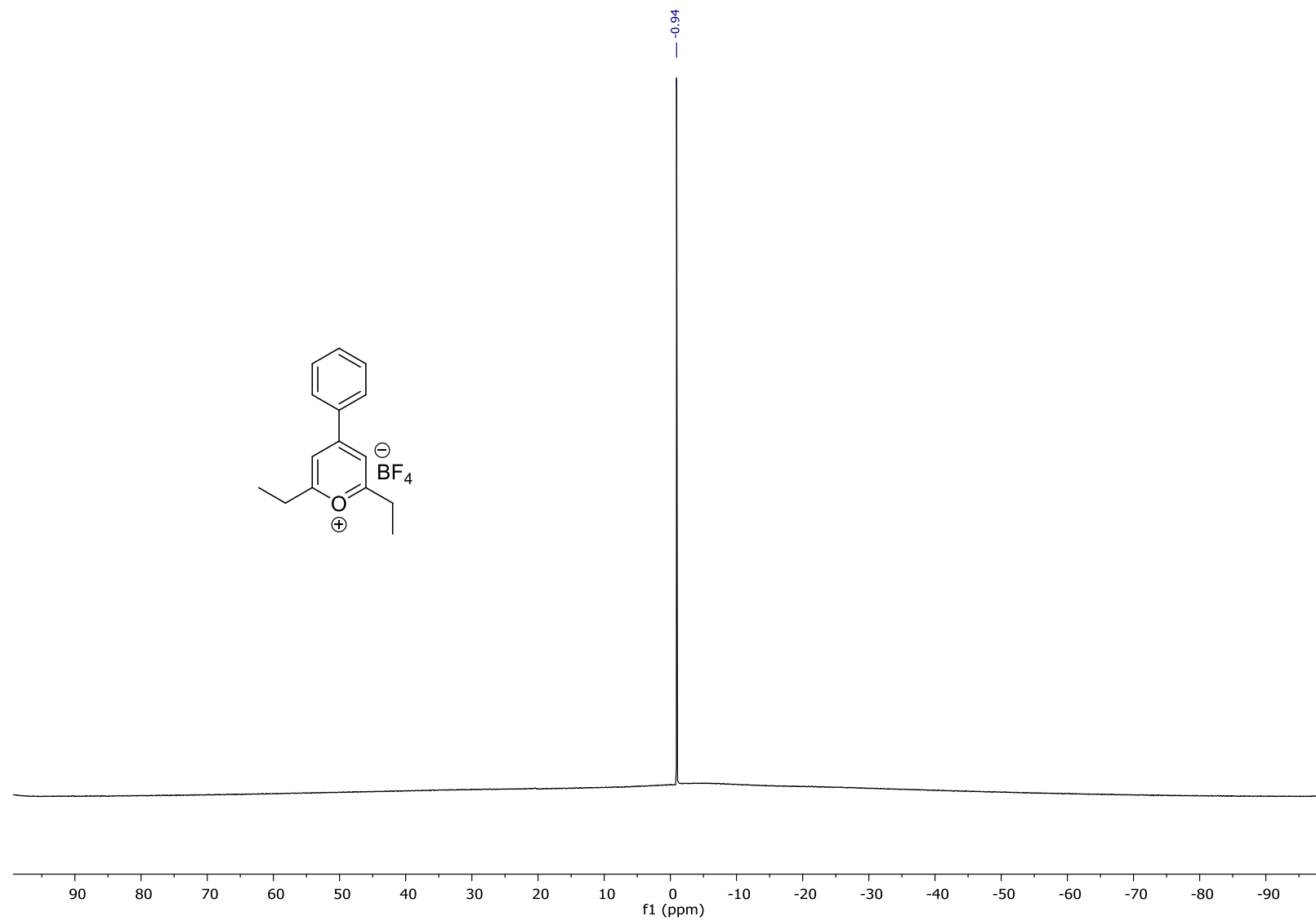




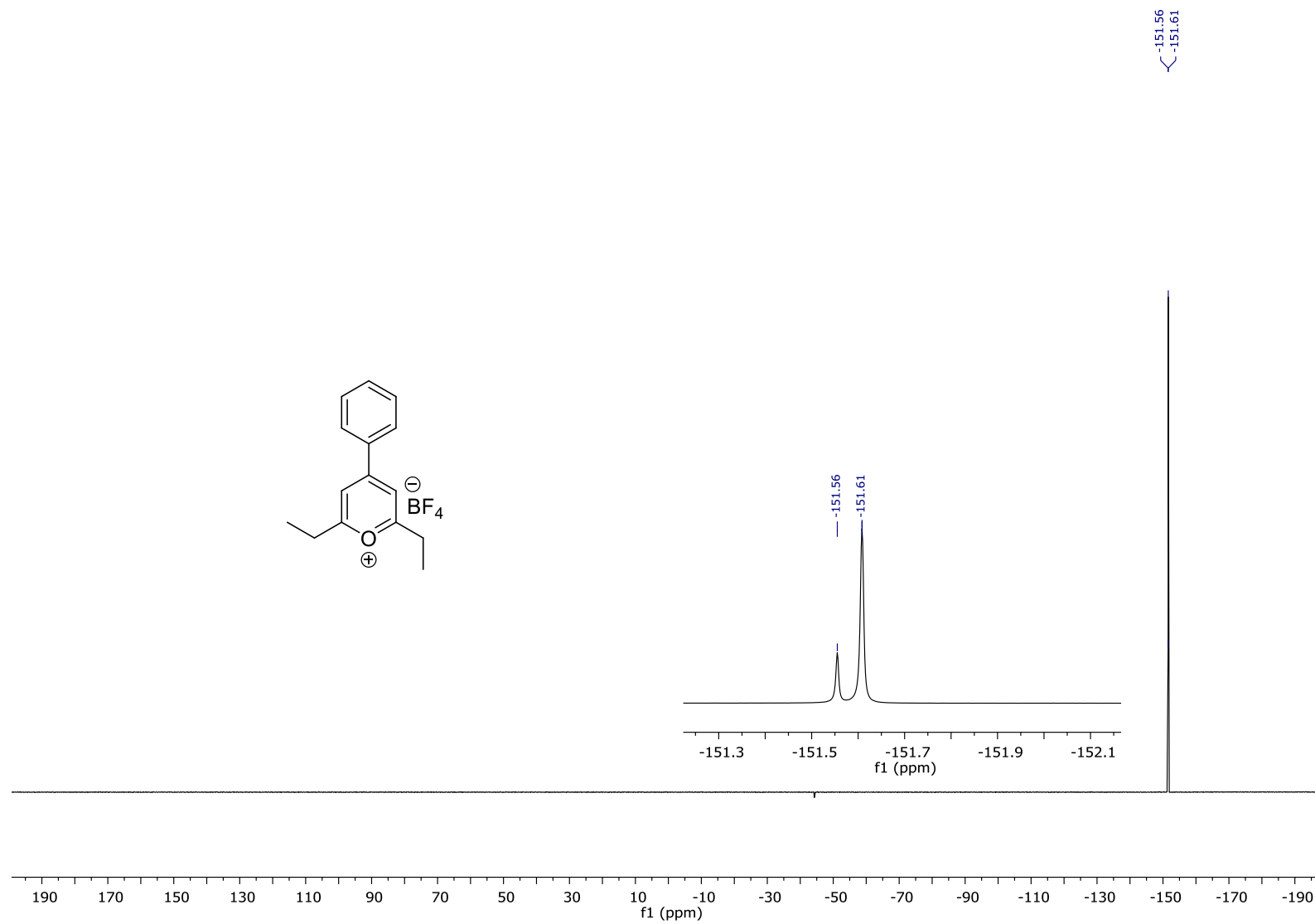
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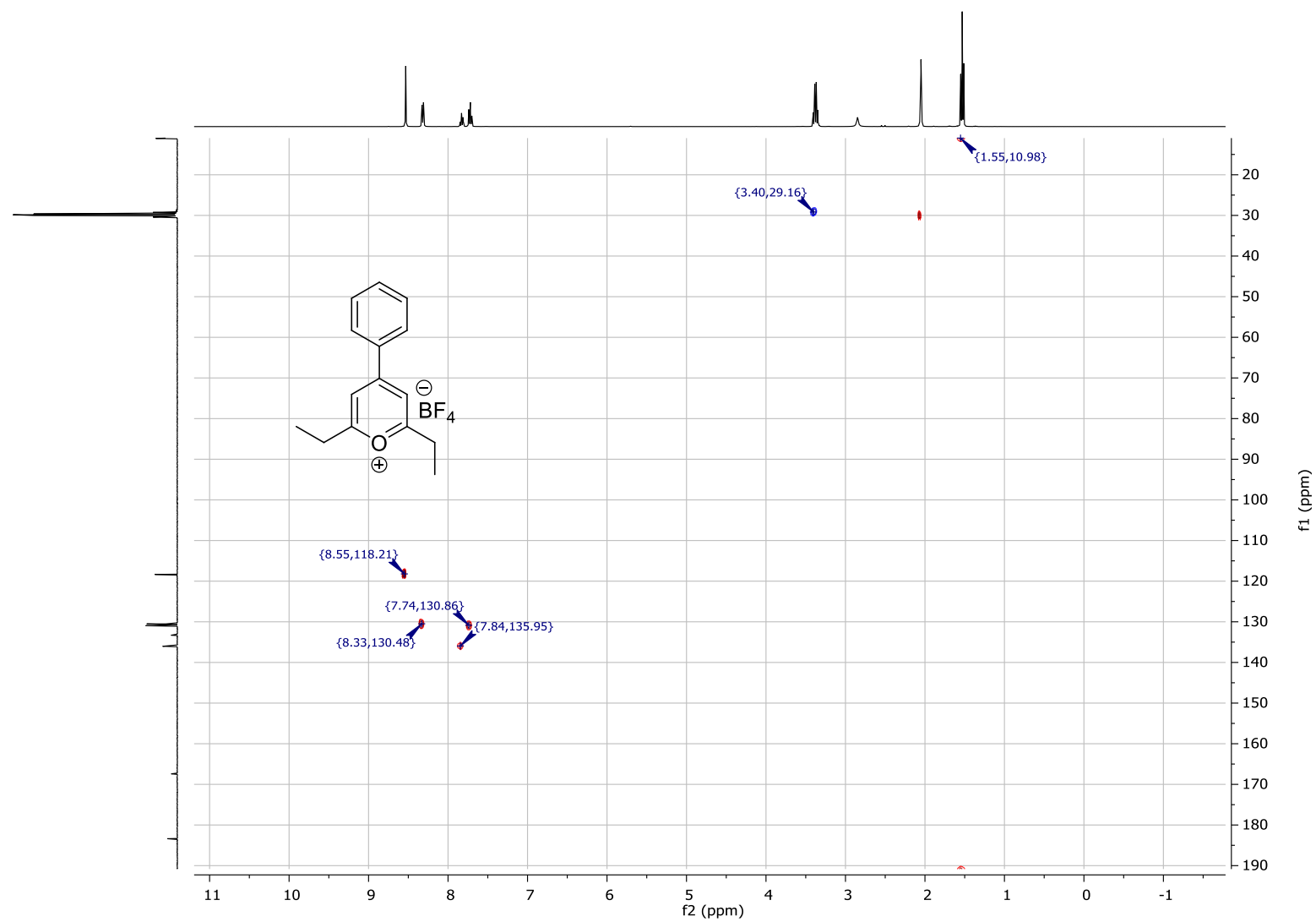
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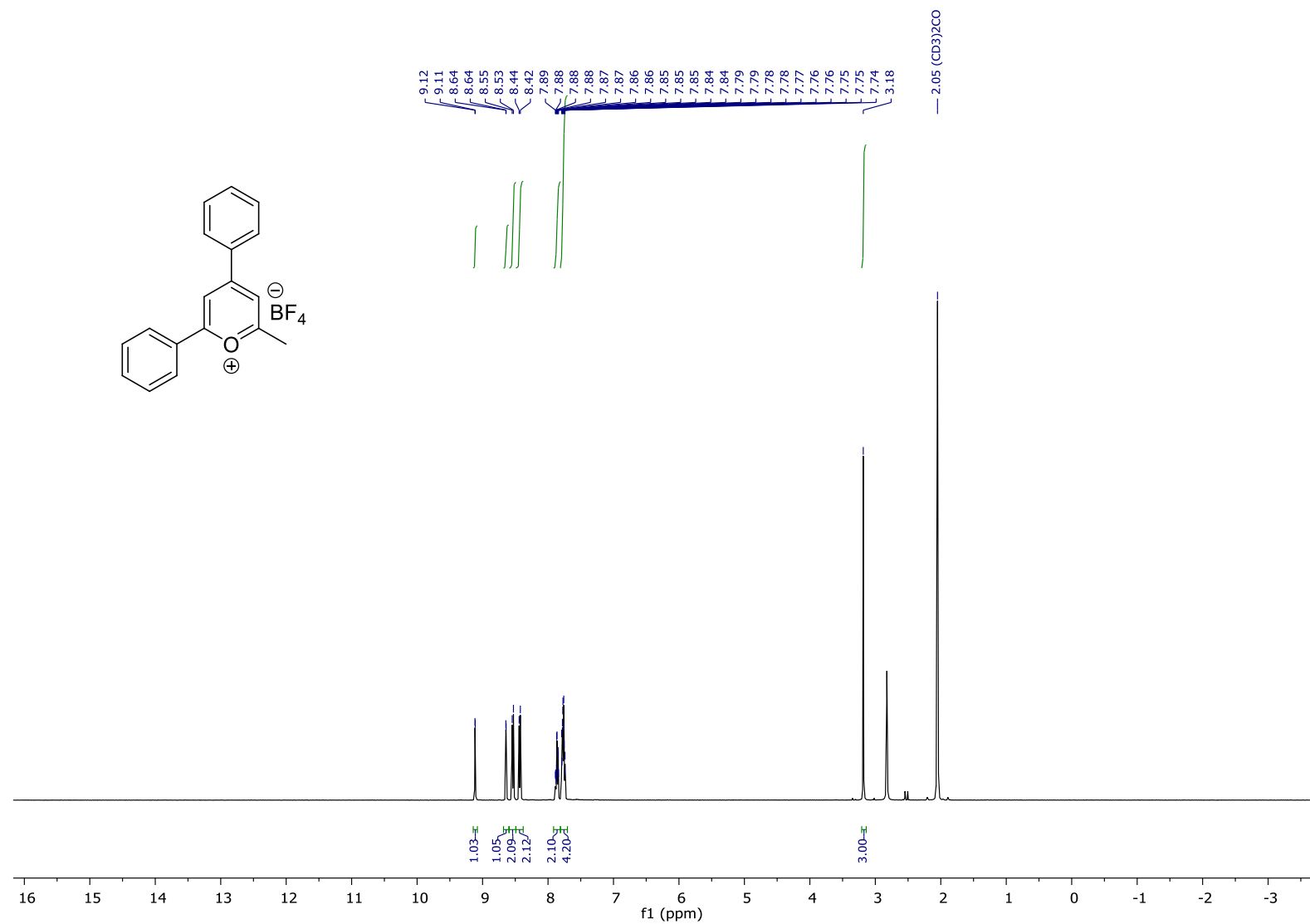
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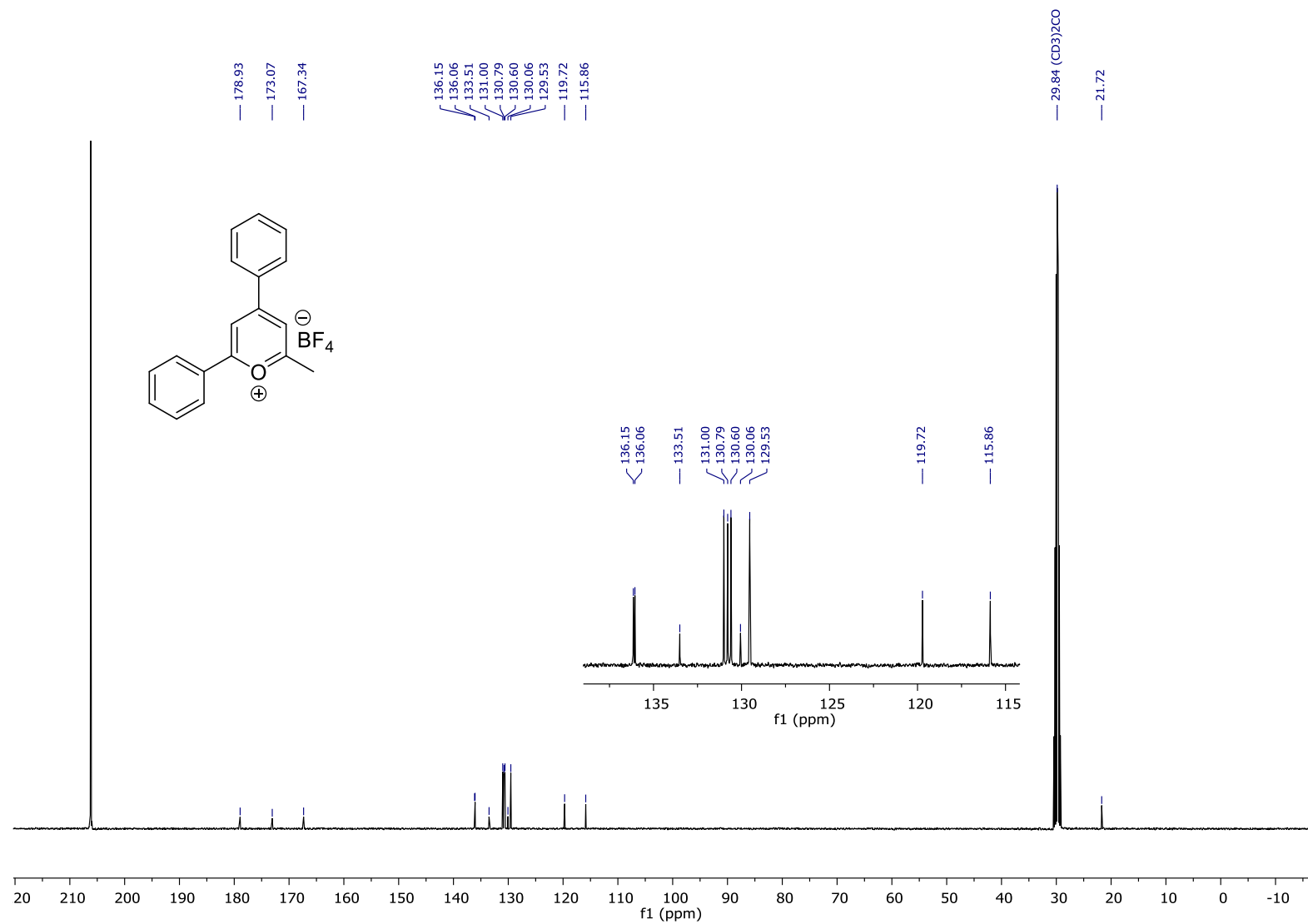
^{19}F NMR for 1d



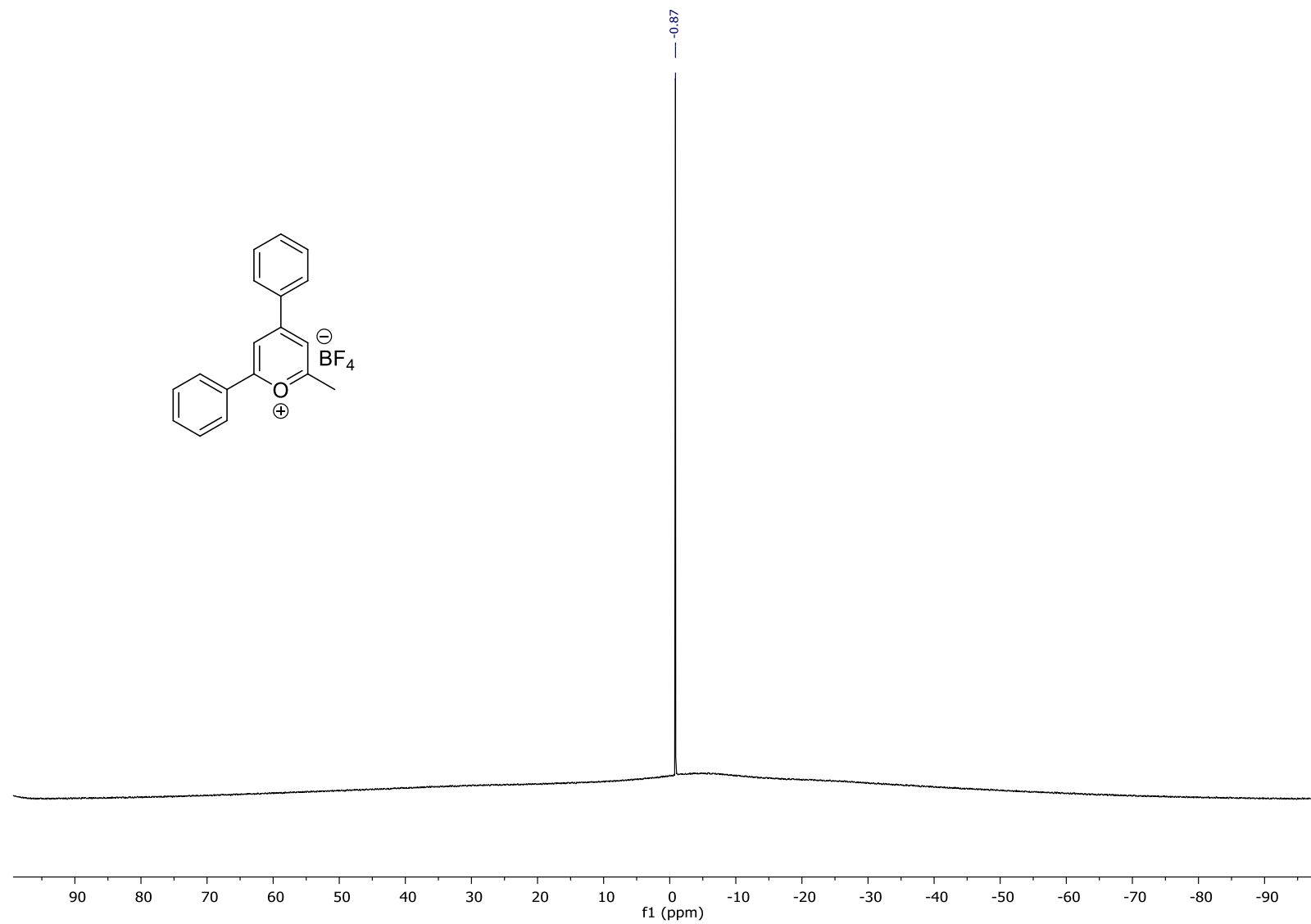
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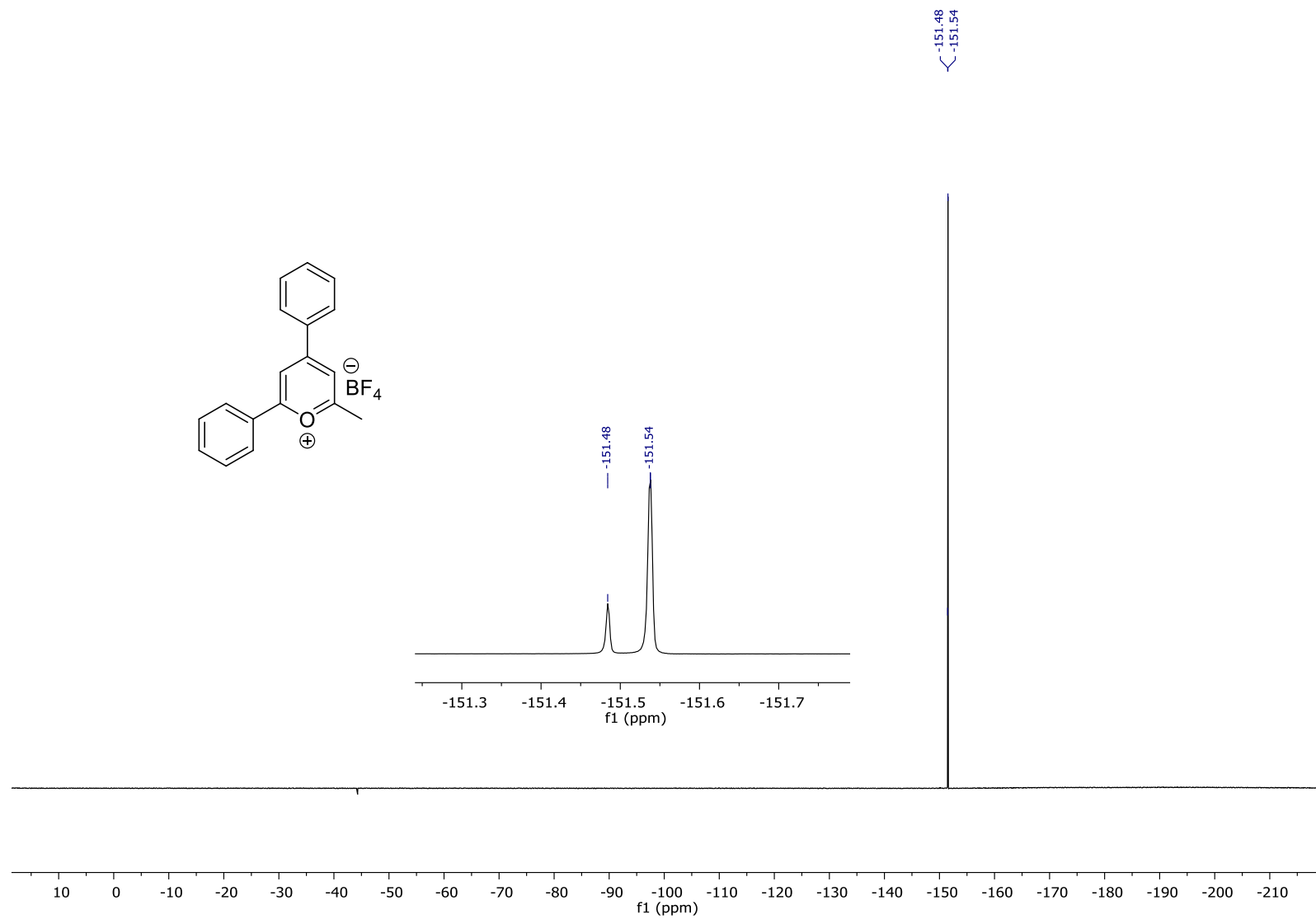
^1H NMR for 1e



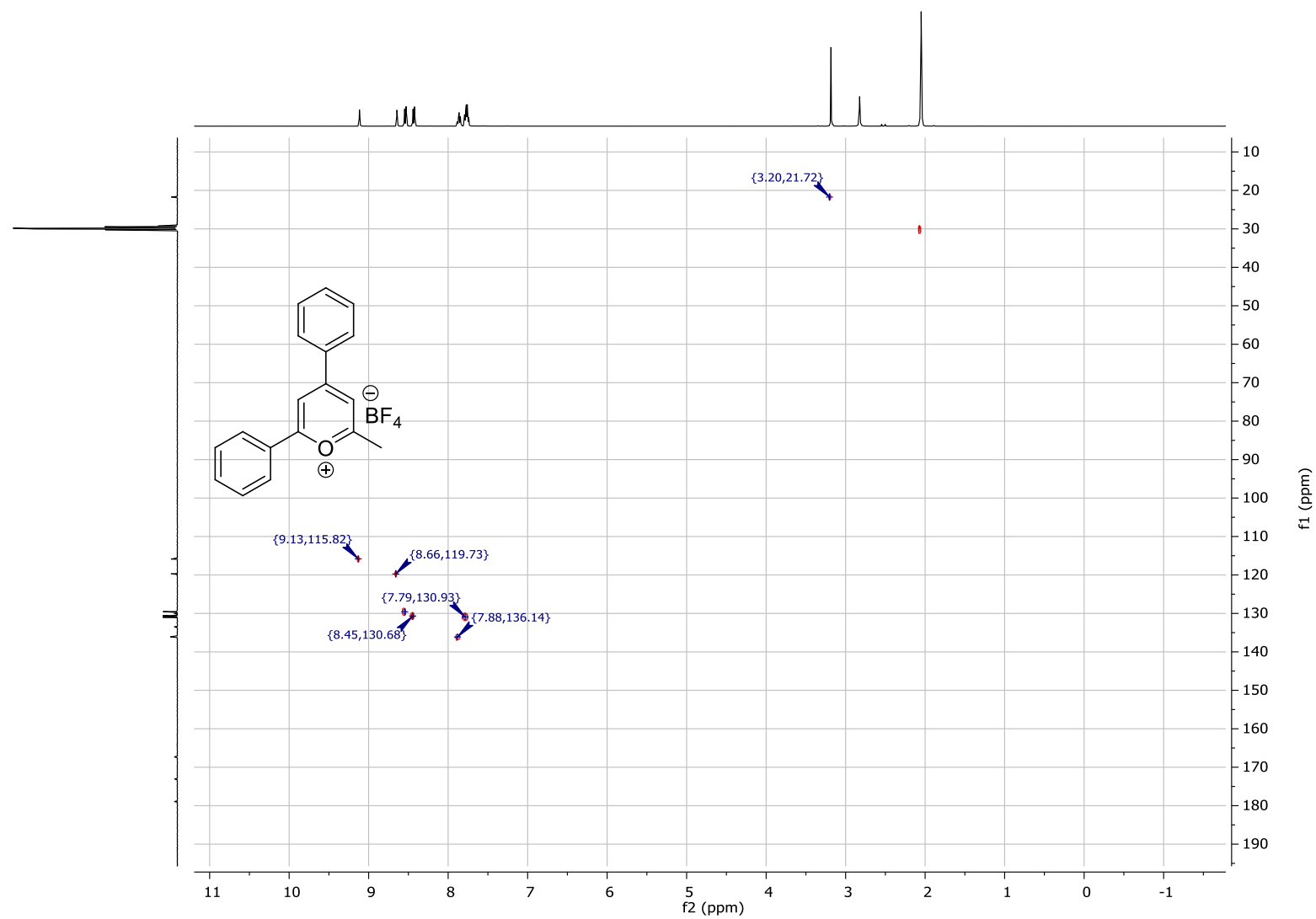
¹³C NMR for 1e

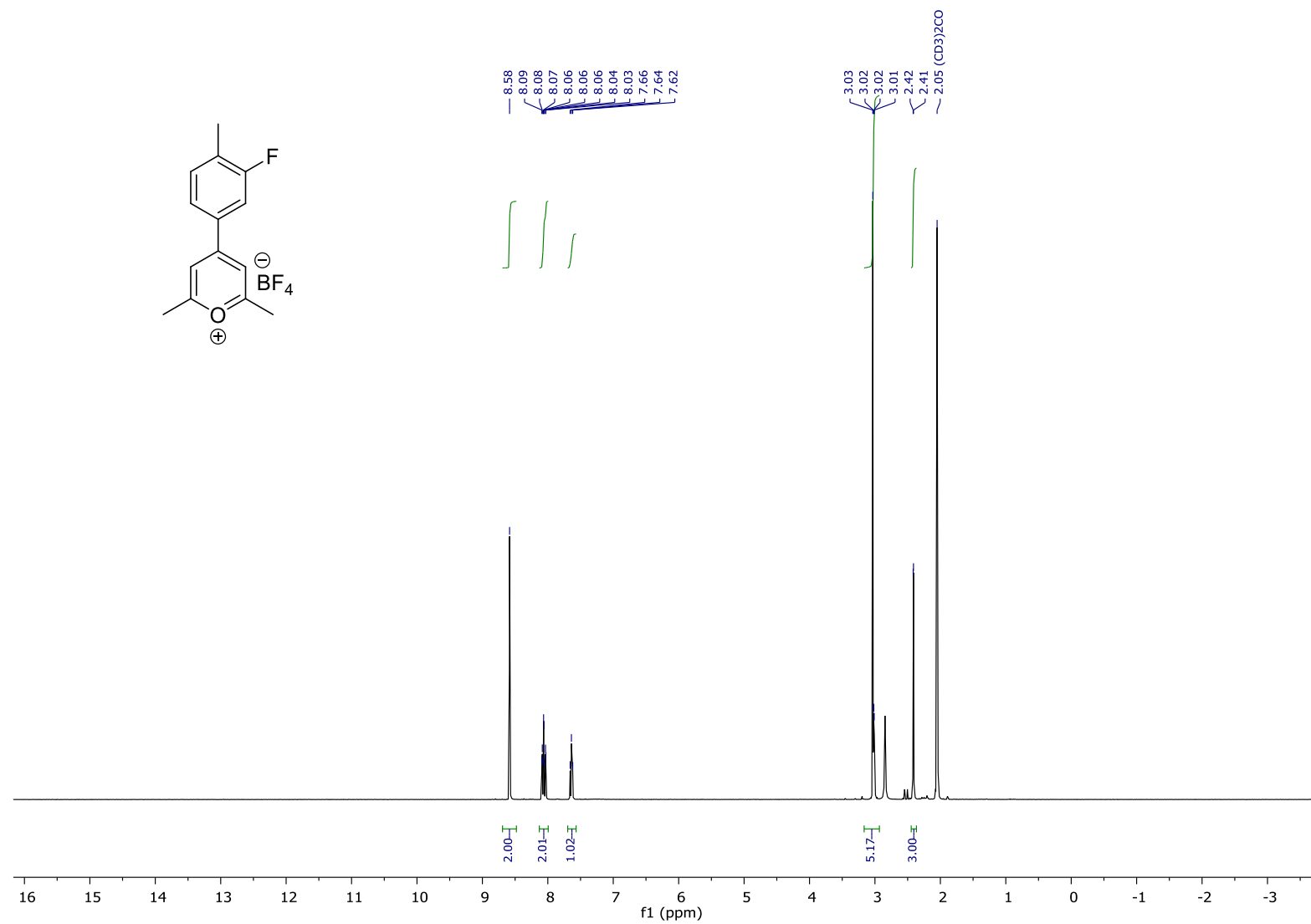


^{11}B NMR for 1e

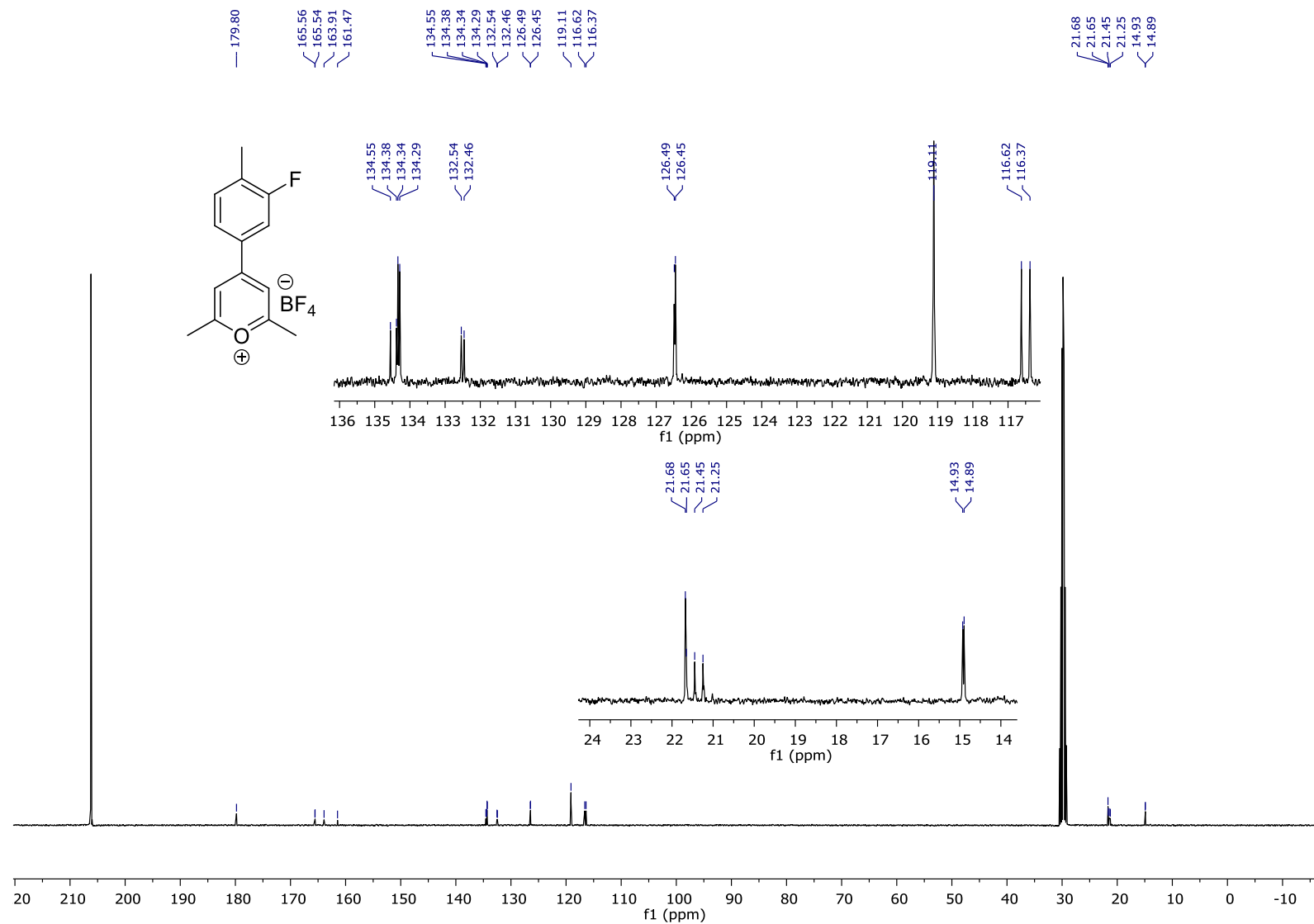


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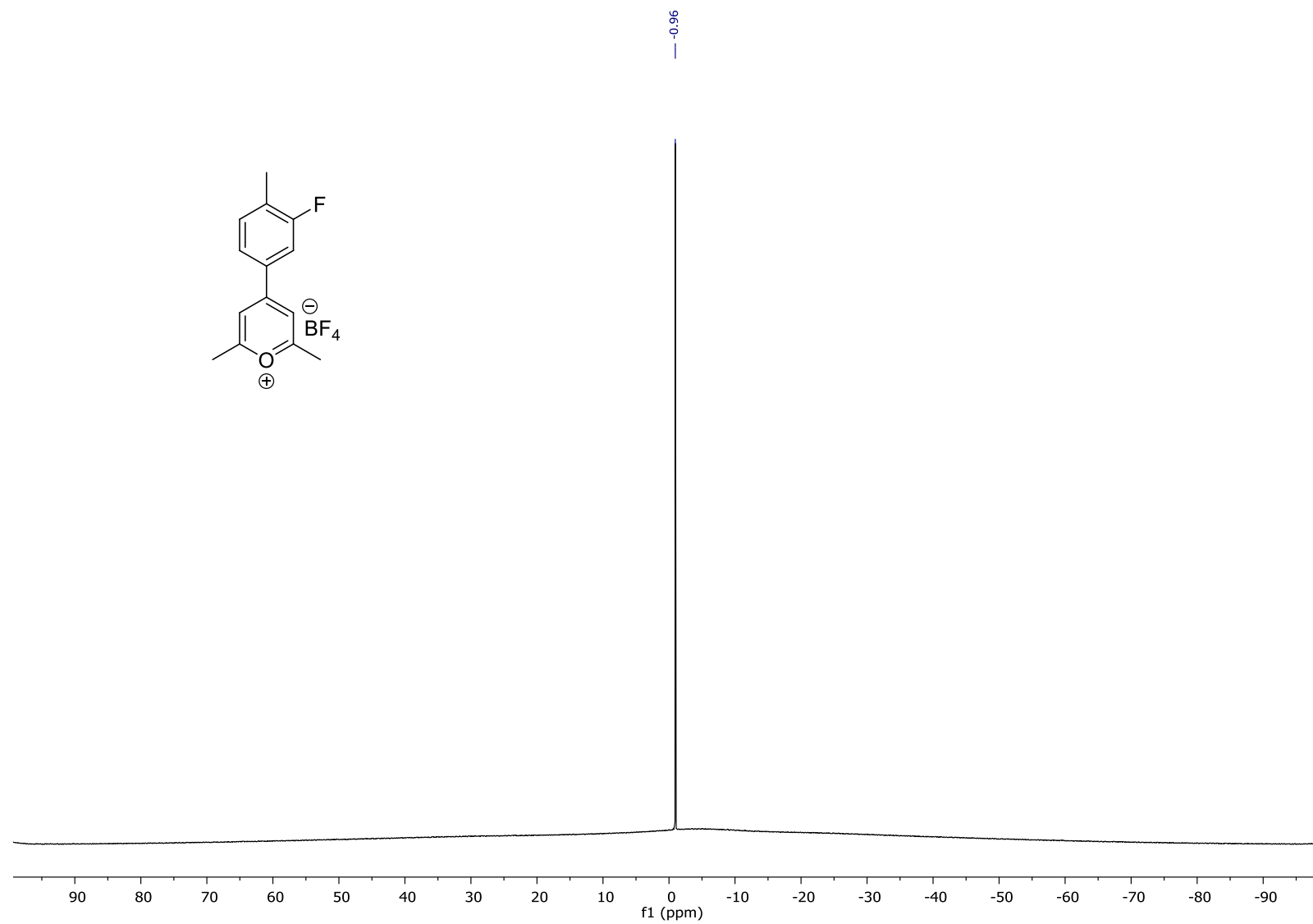




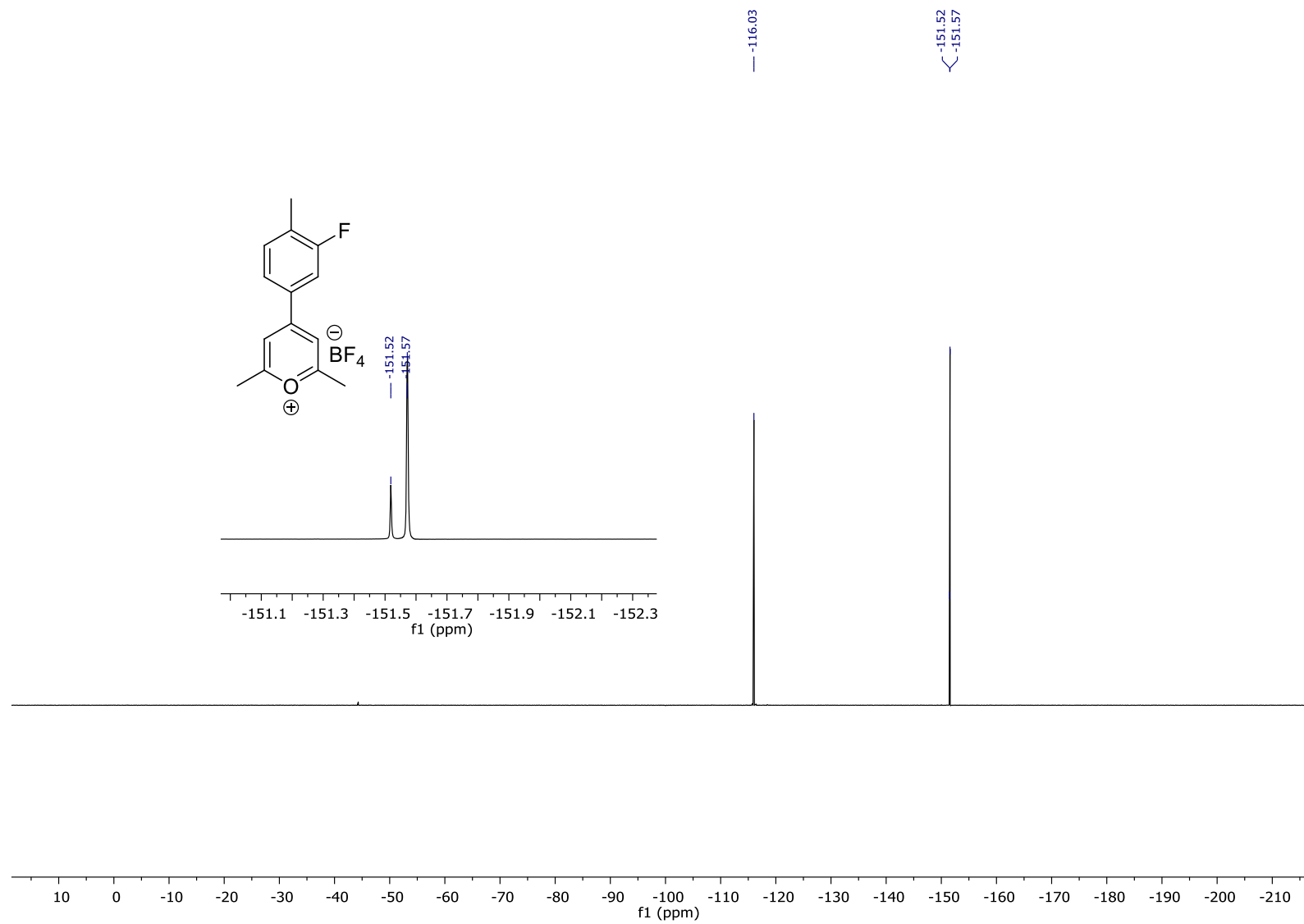
¹H NMR for 1f



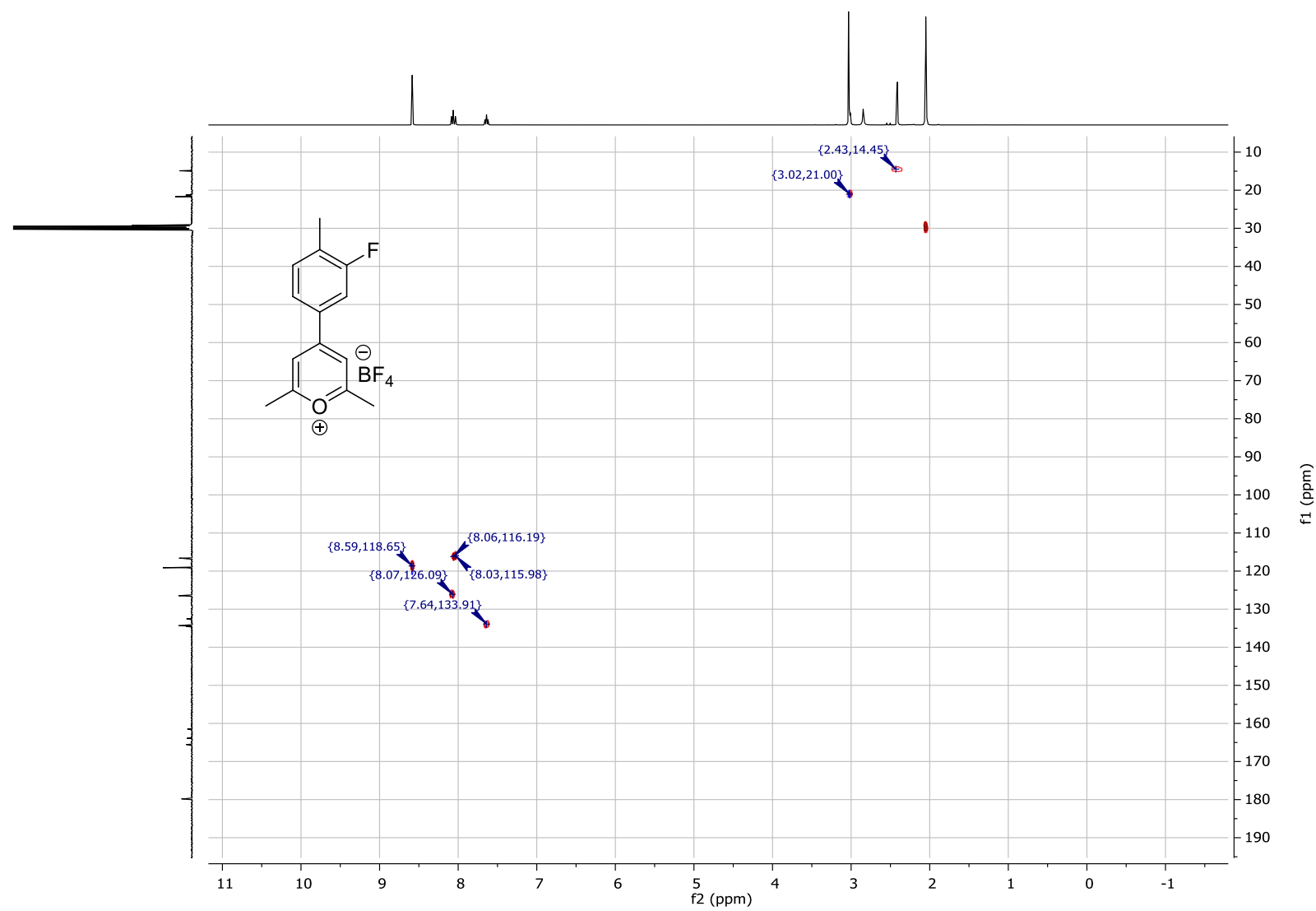
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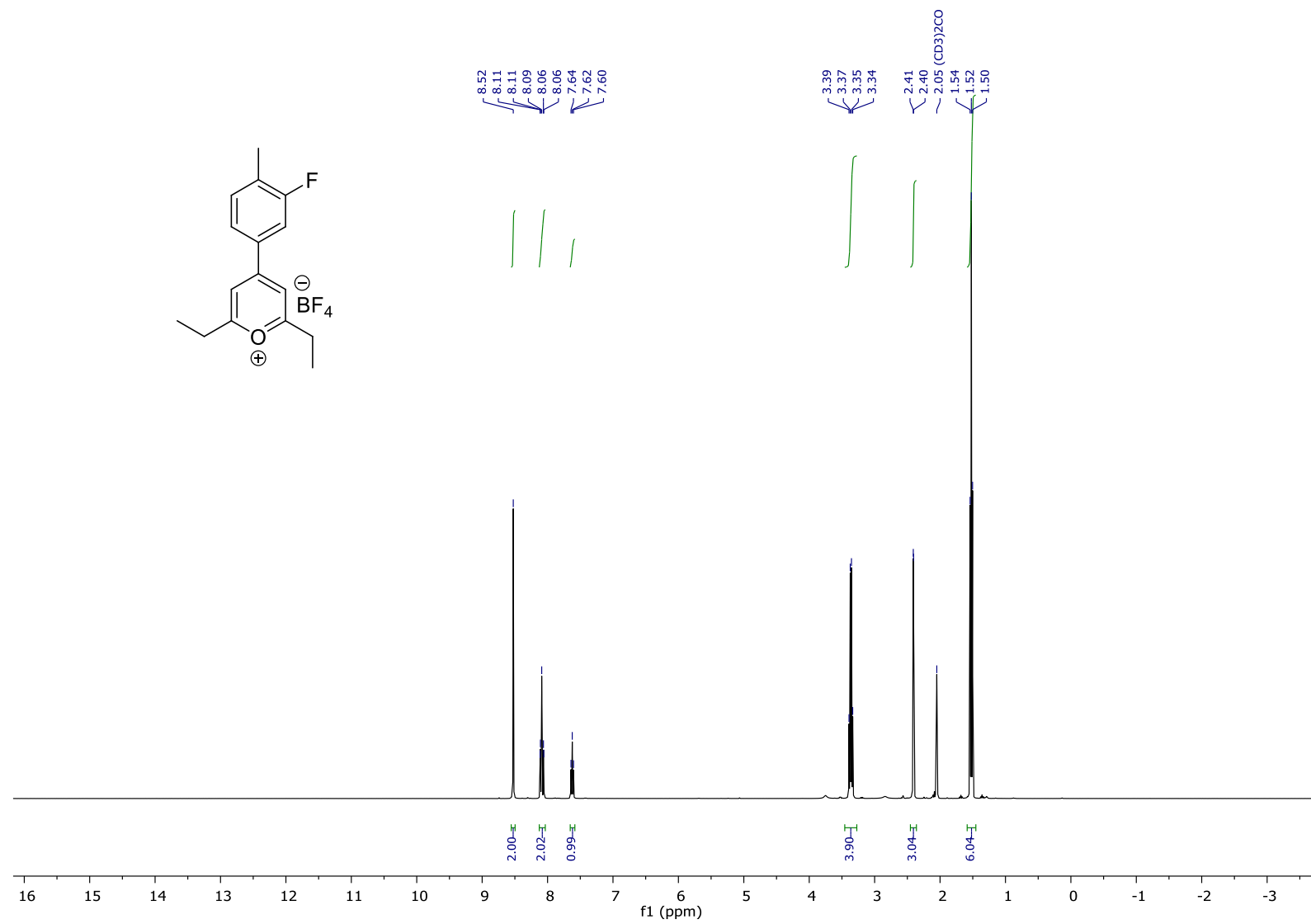
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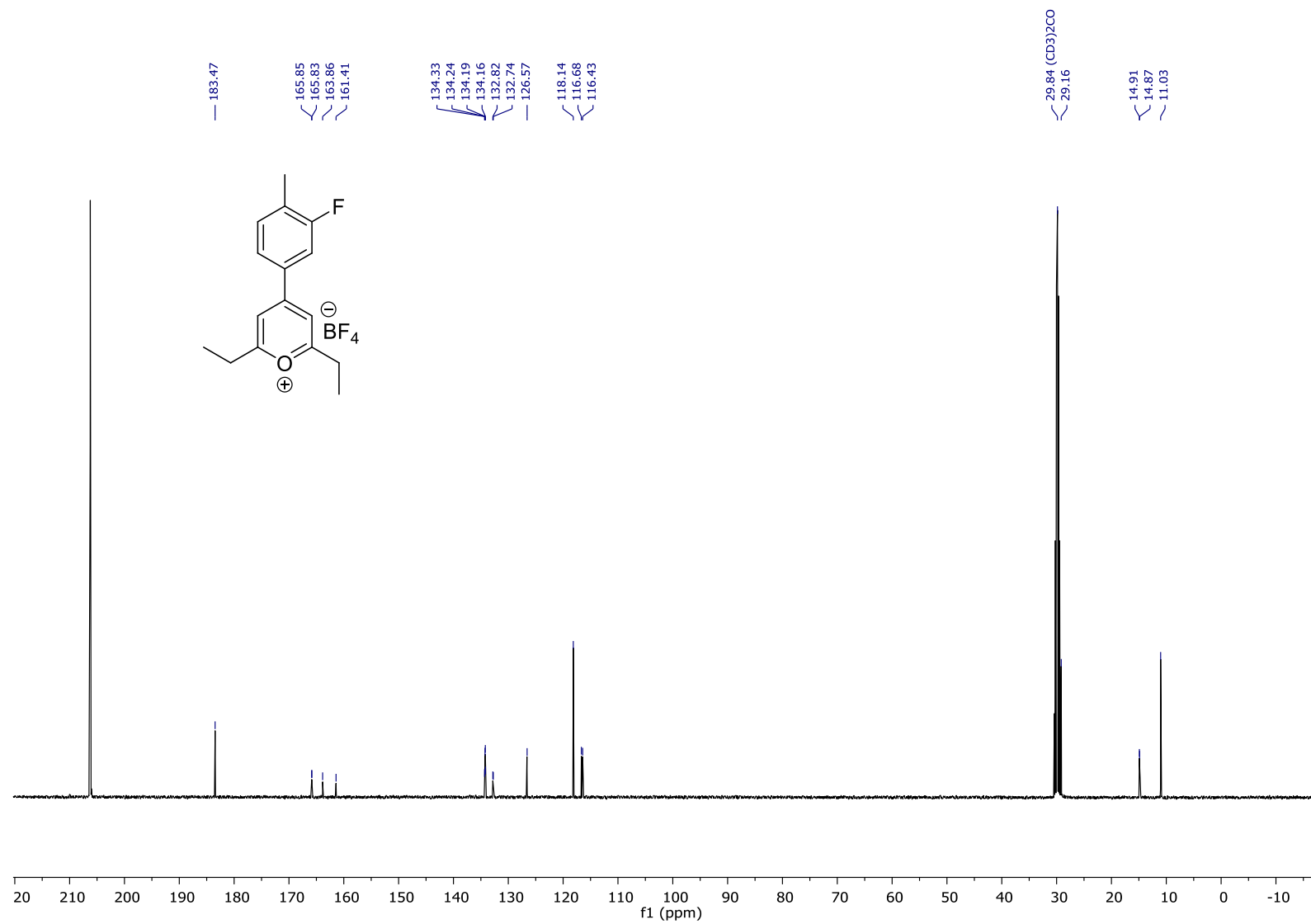
¹⁹F NMR for 1f



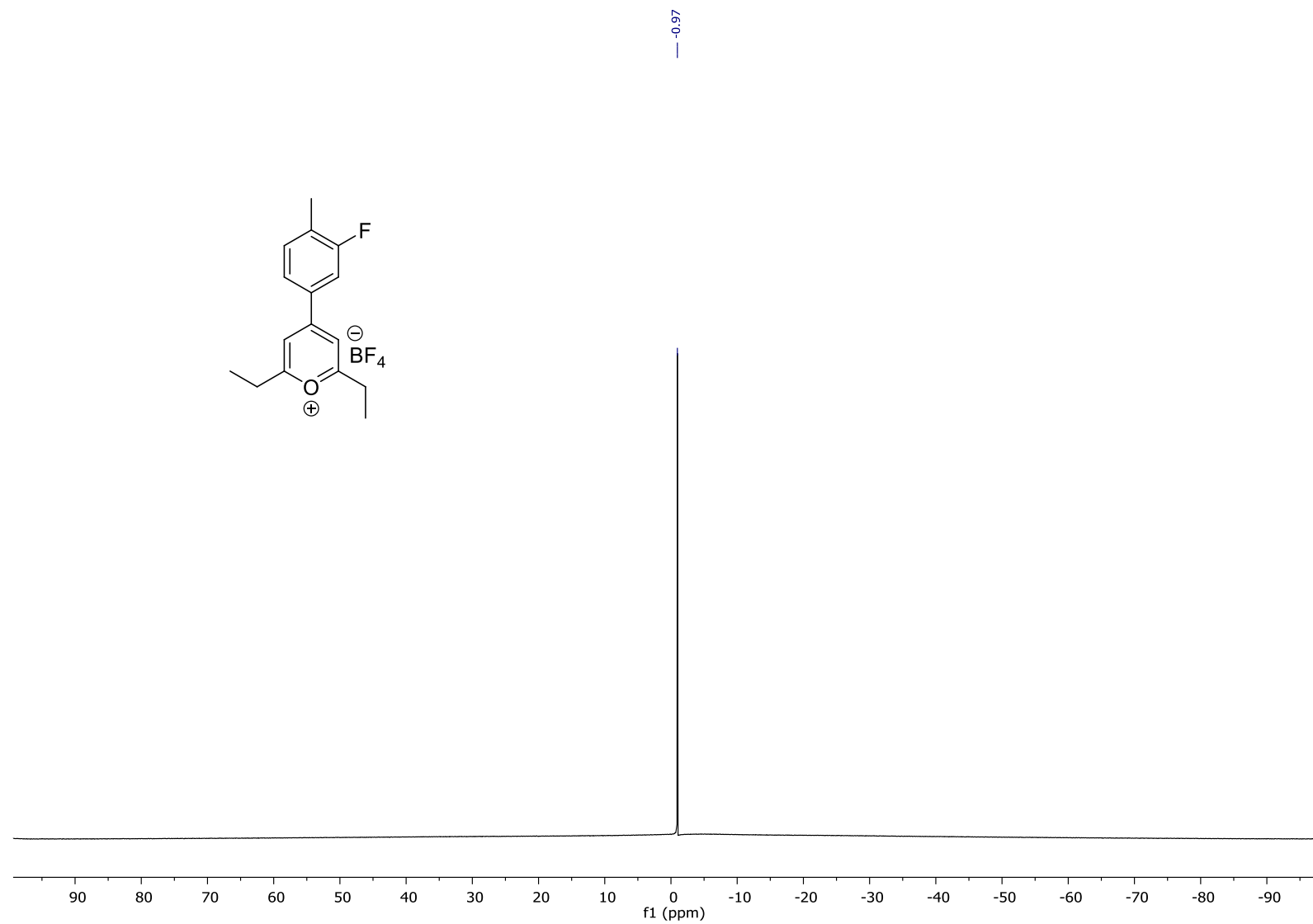
¹H-¹³C HSQC for 1f



¹H NMR for 1g



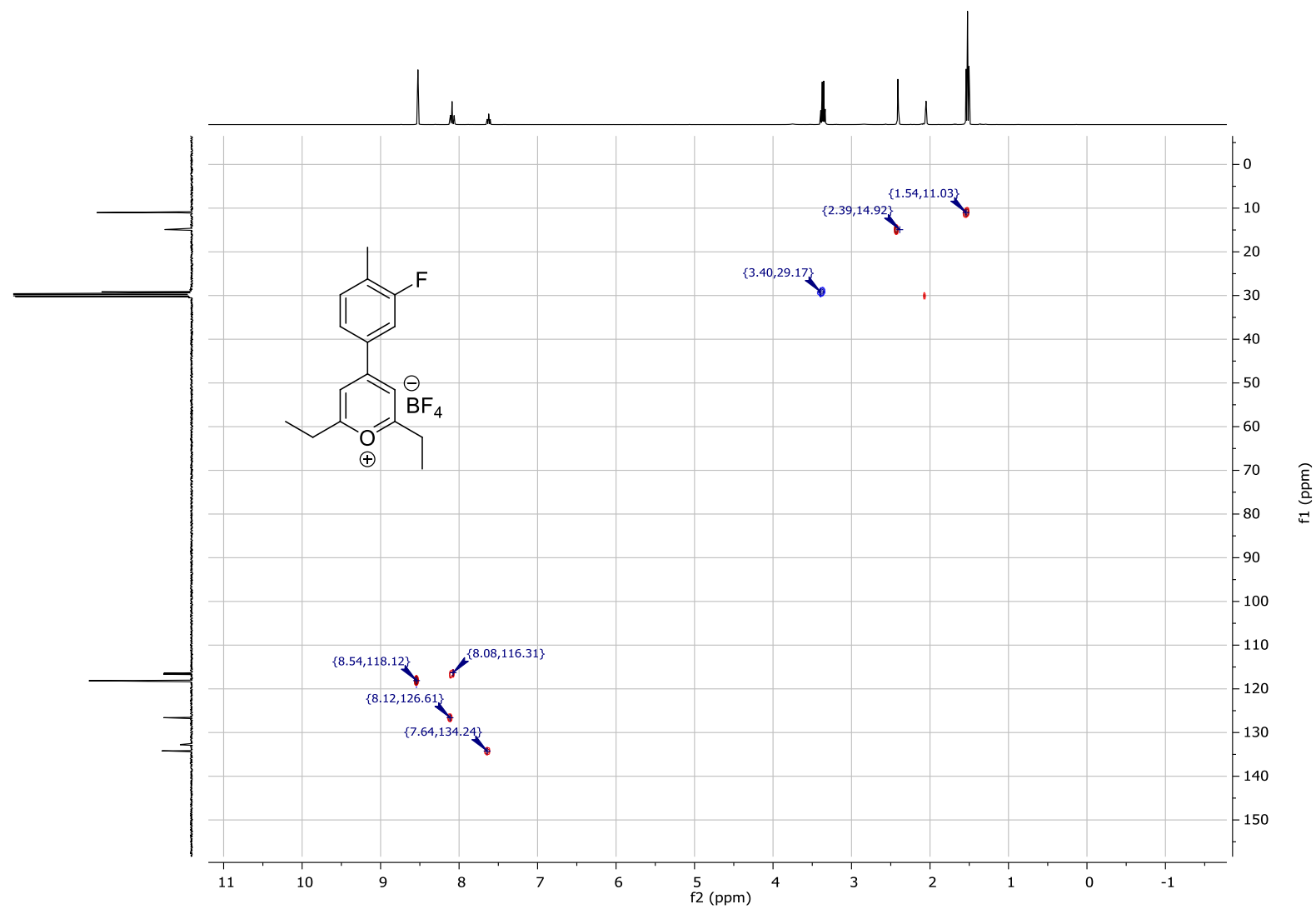
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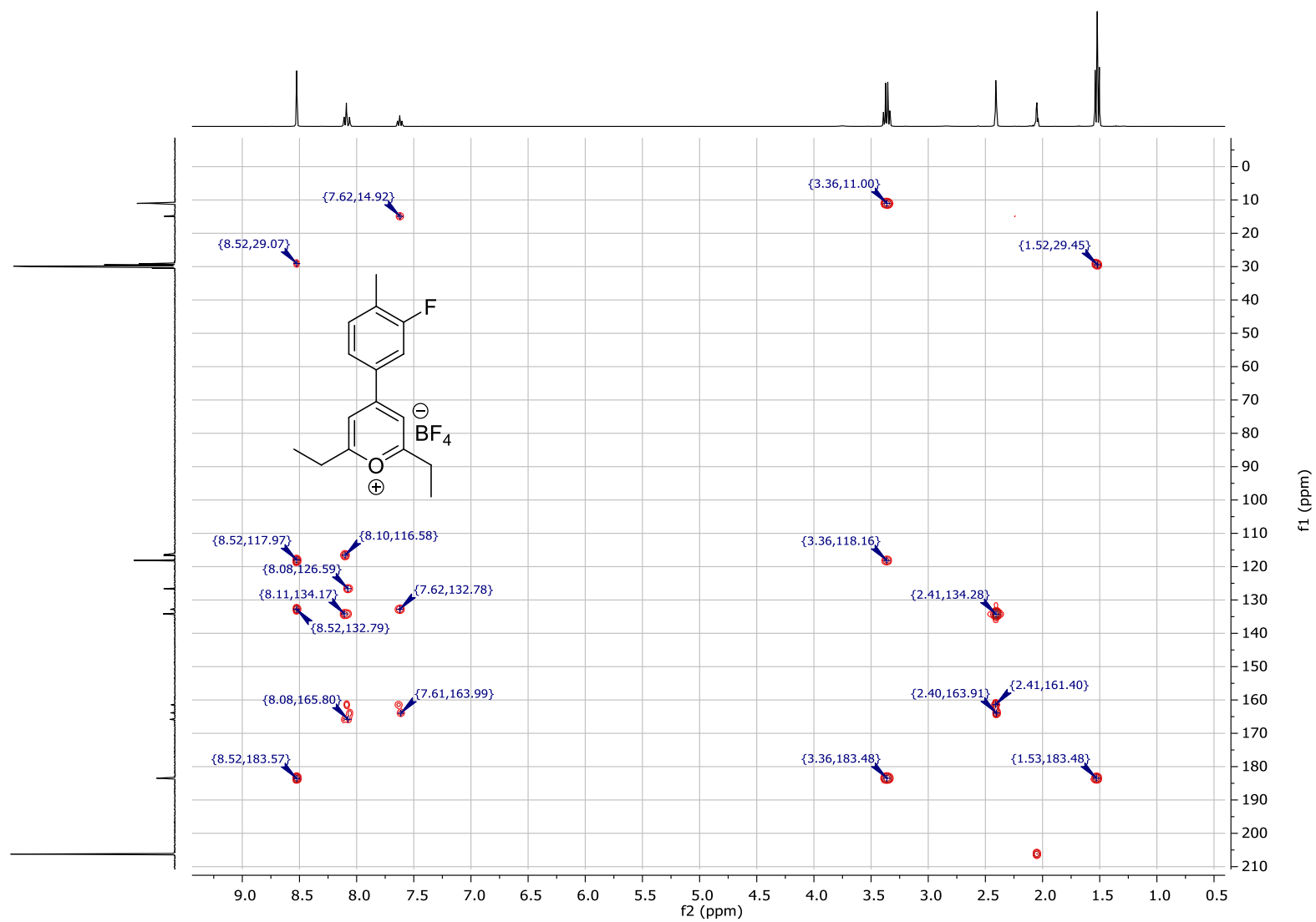
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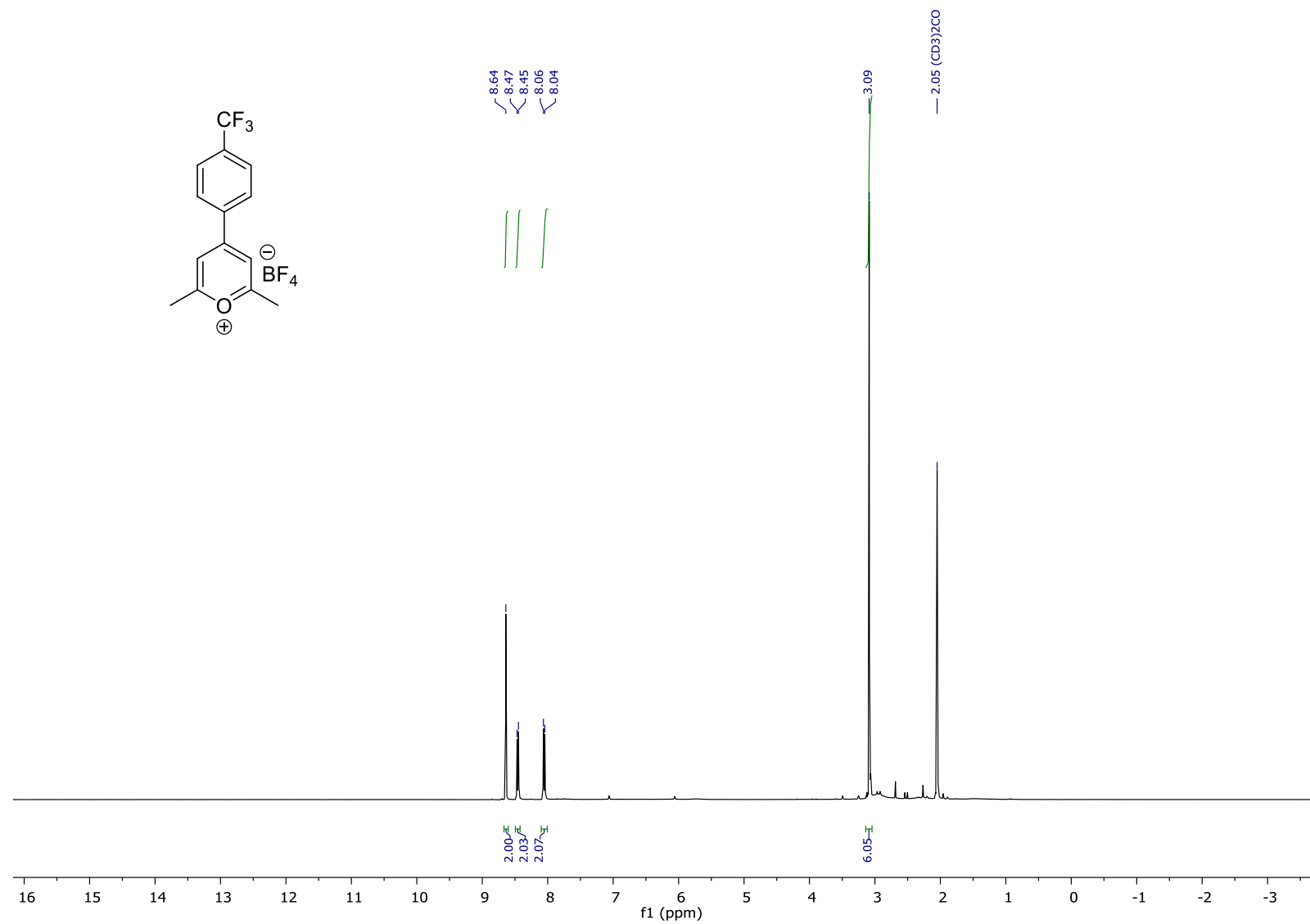
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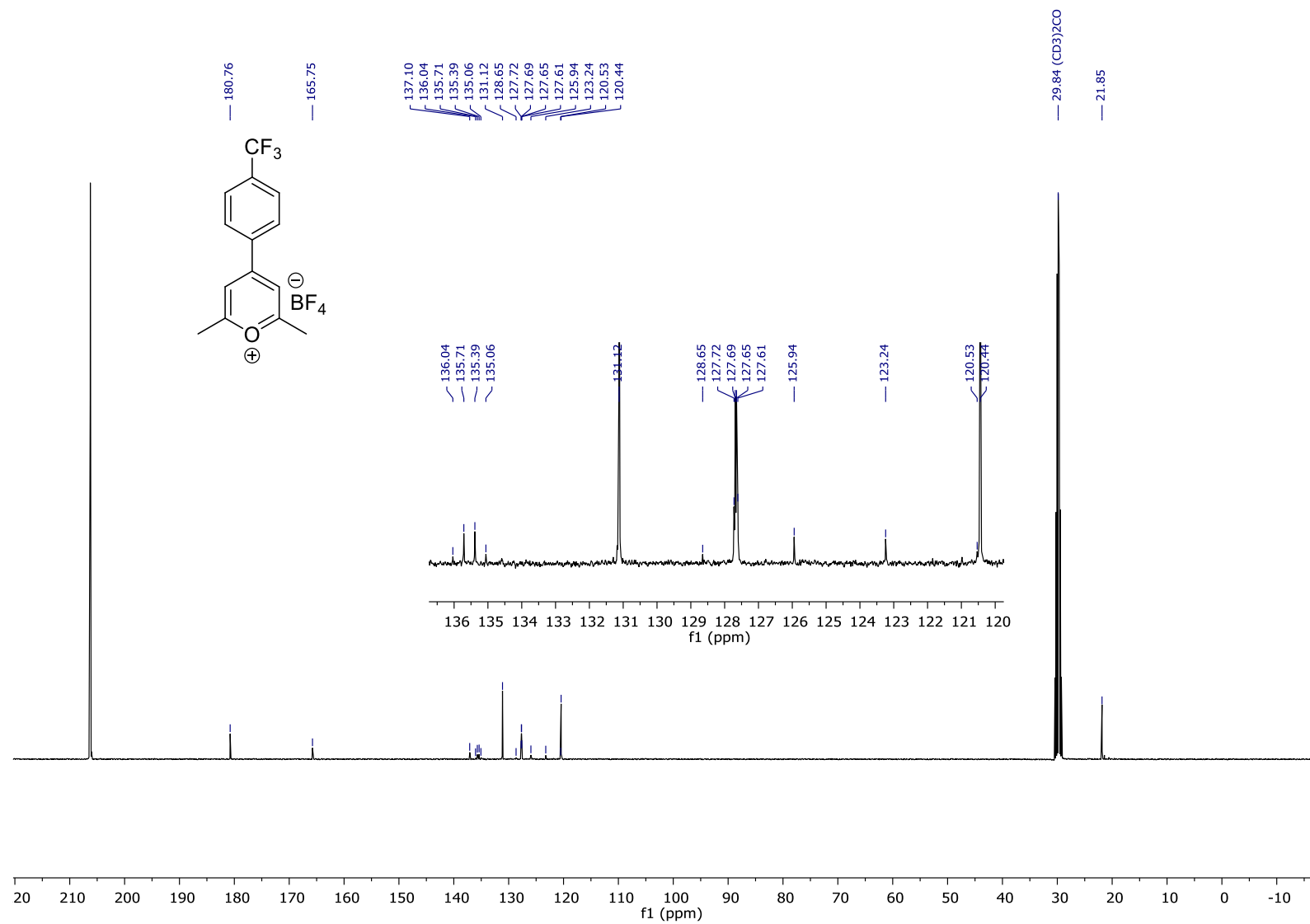
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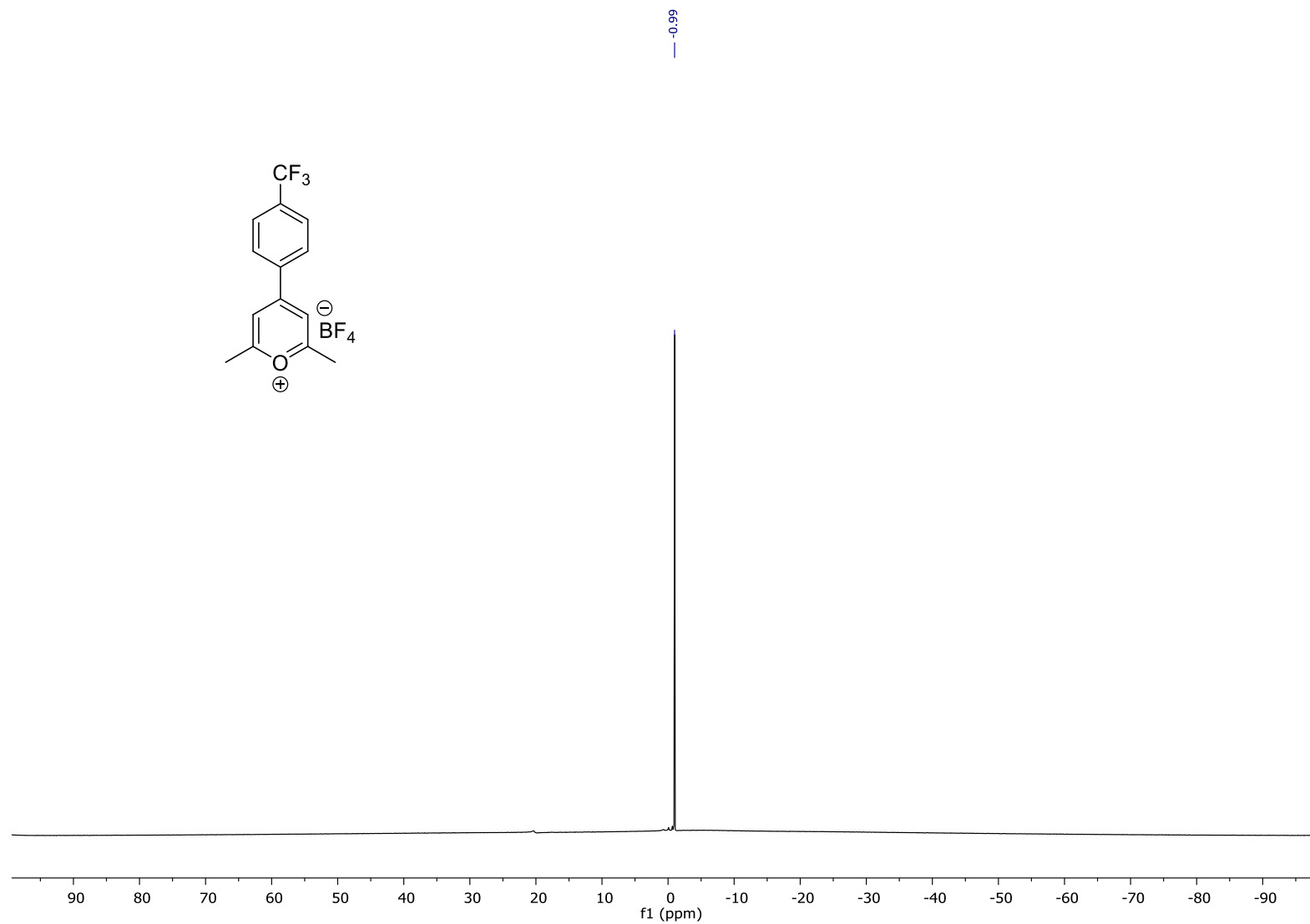
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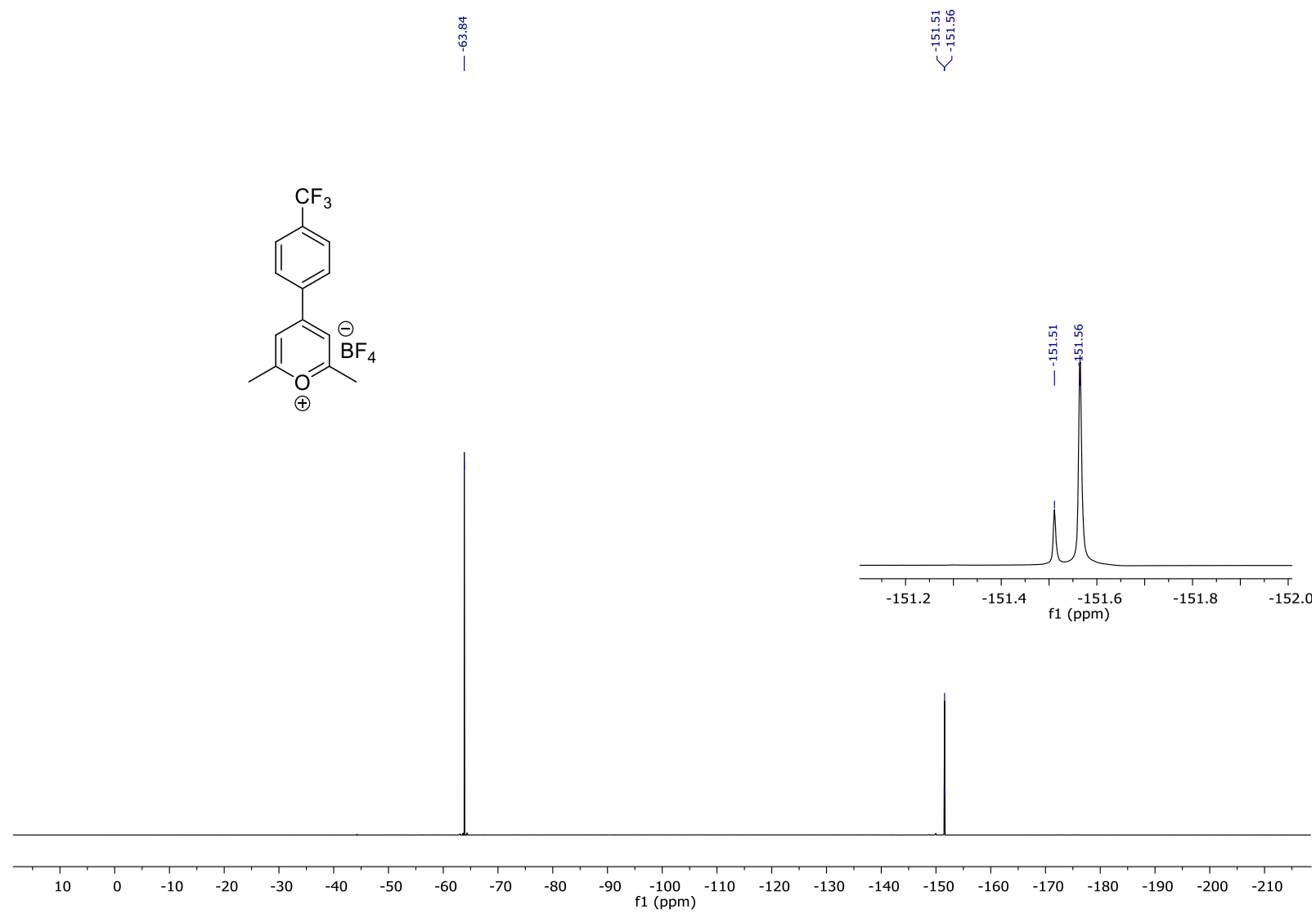
¹H NMR for 1h



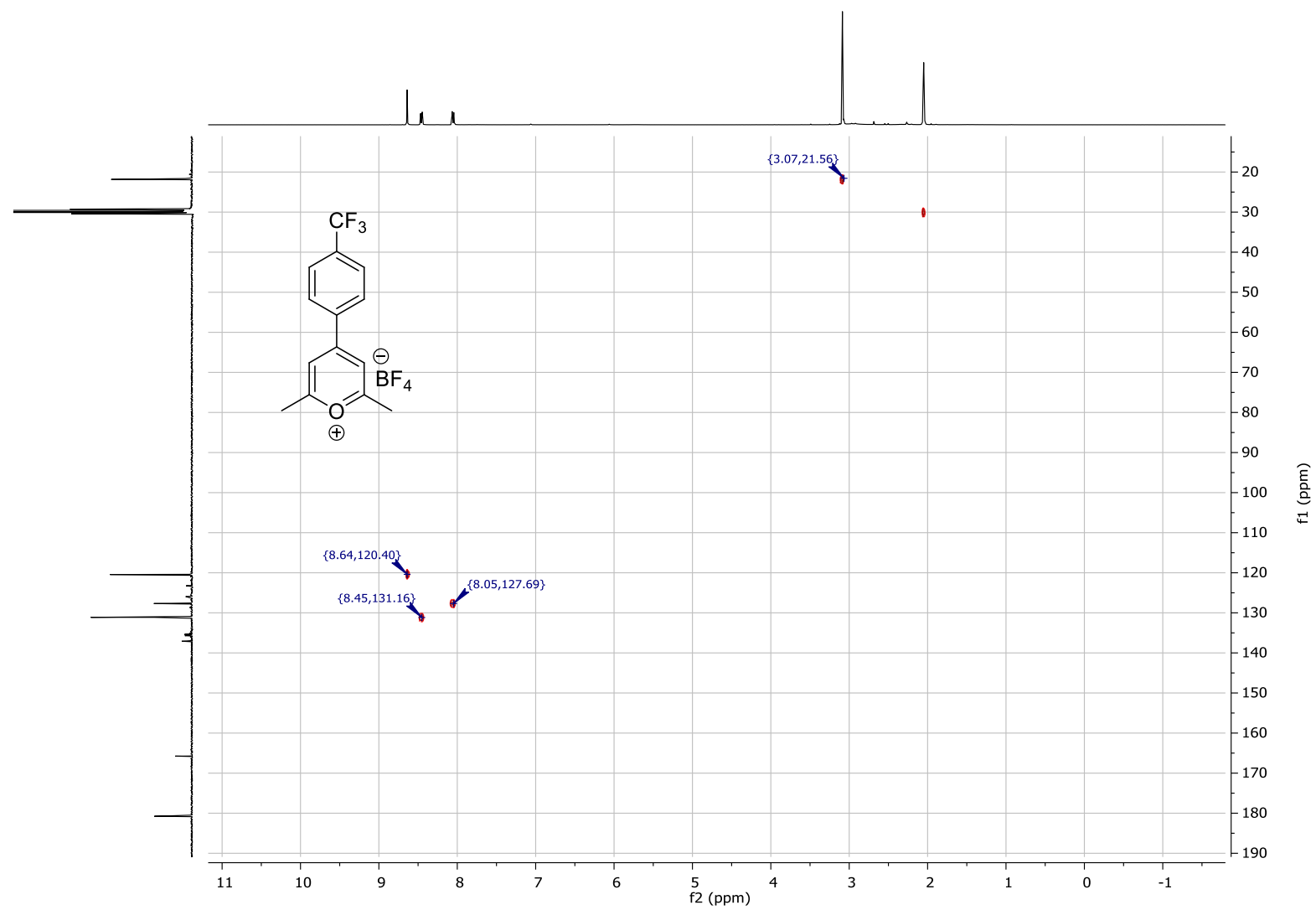
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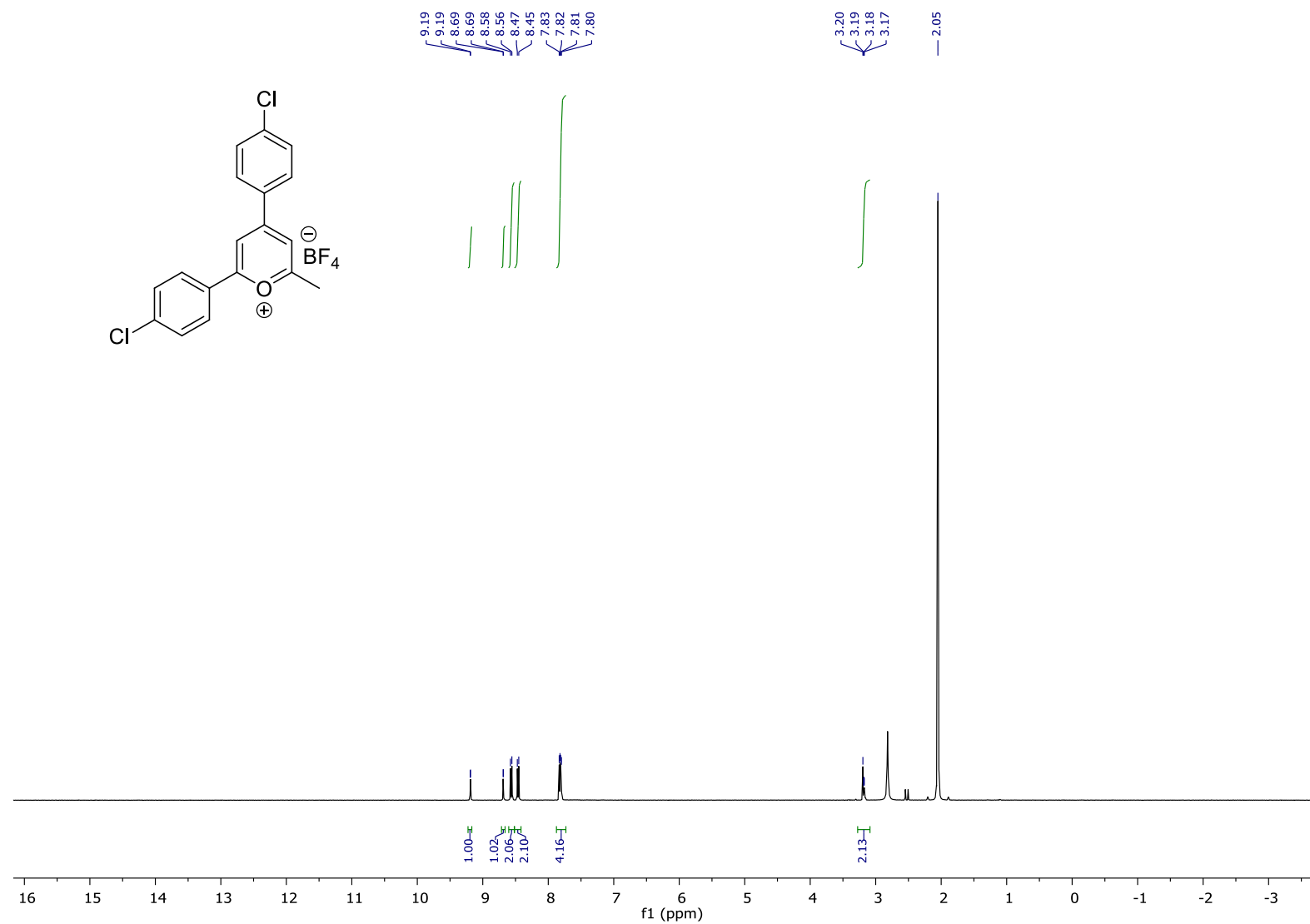
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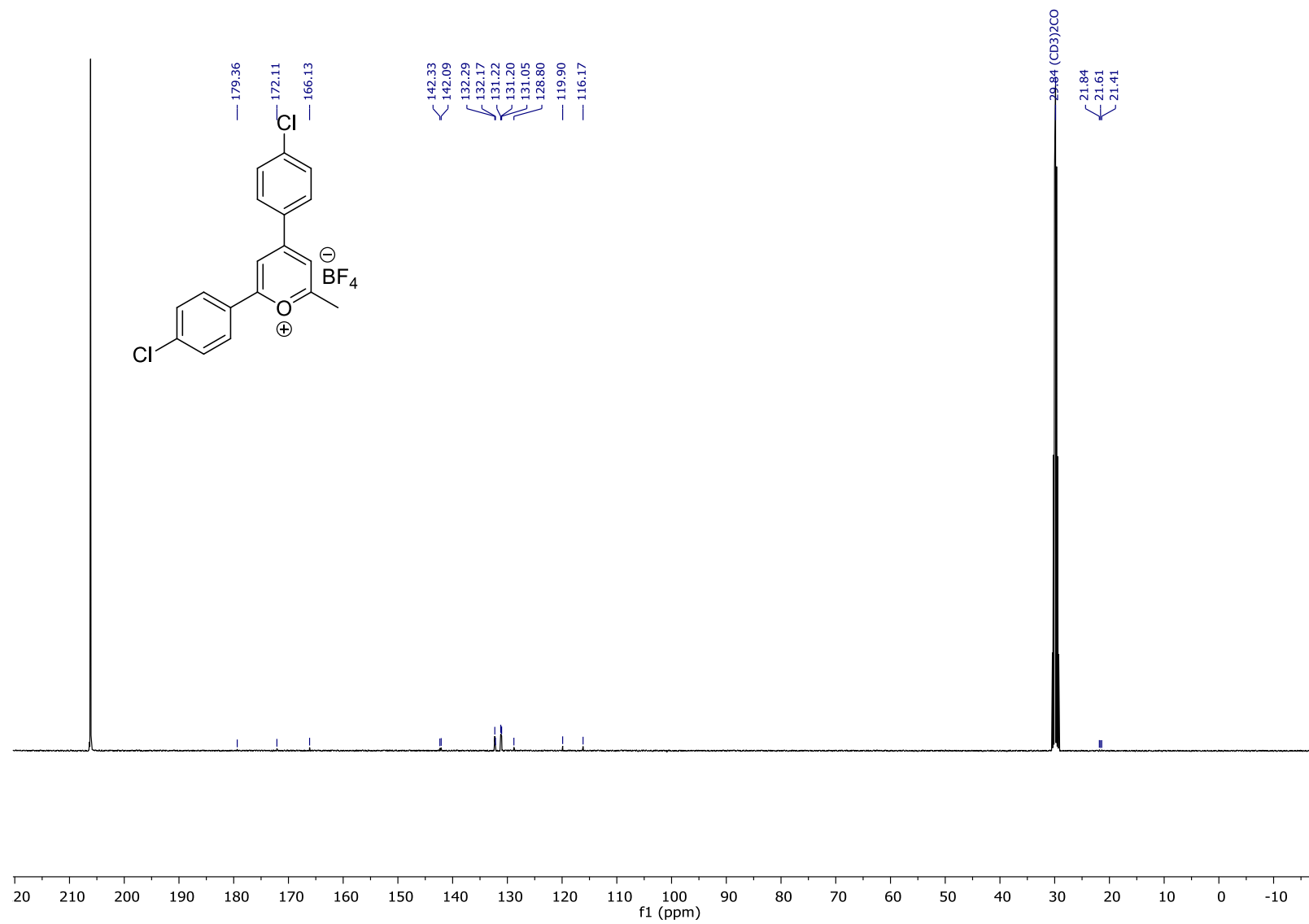
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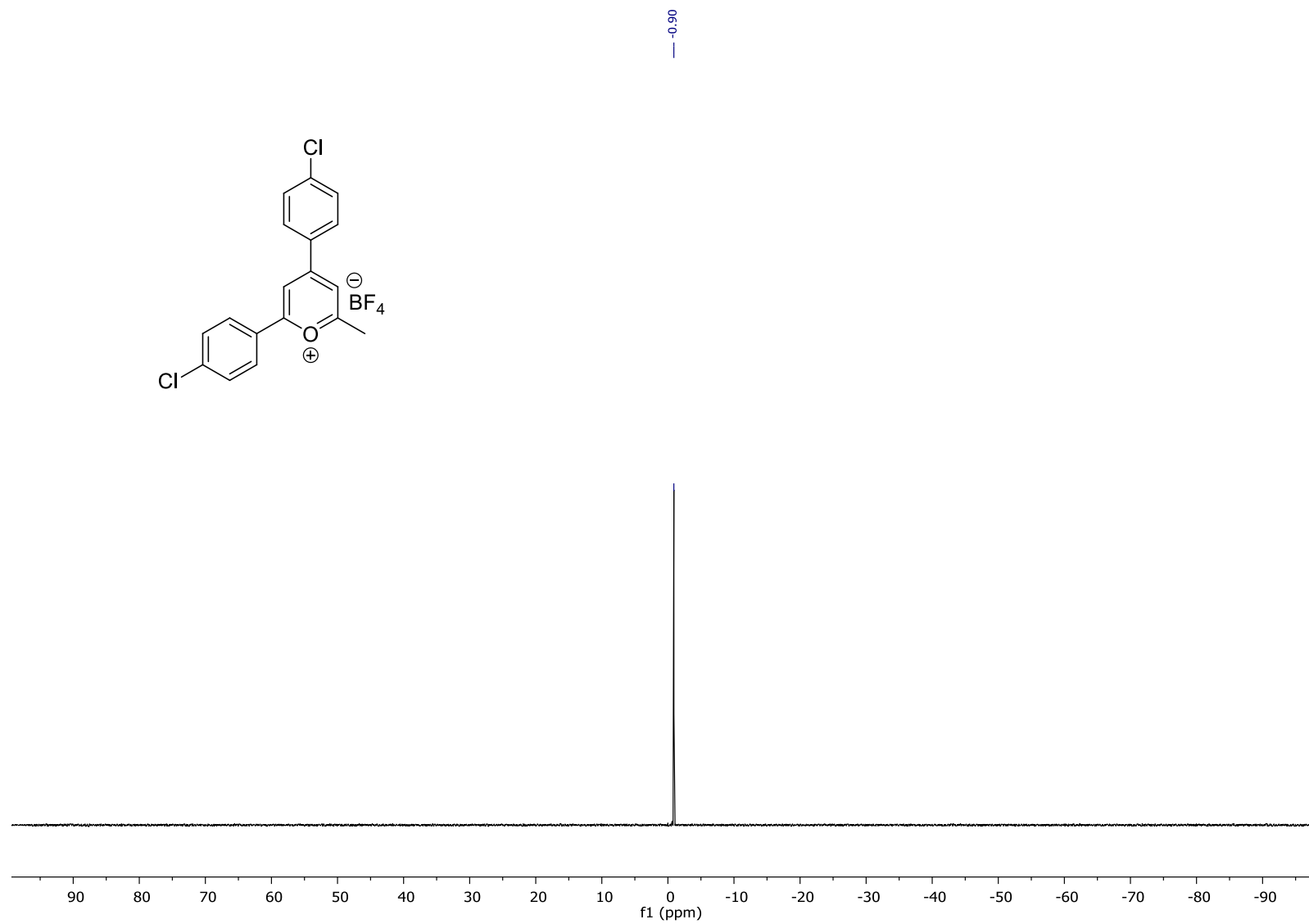
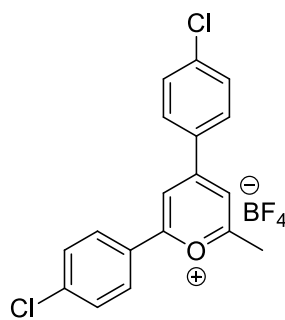
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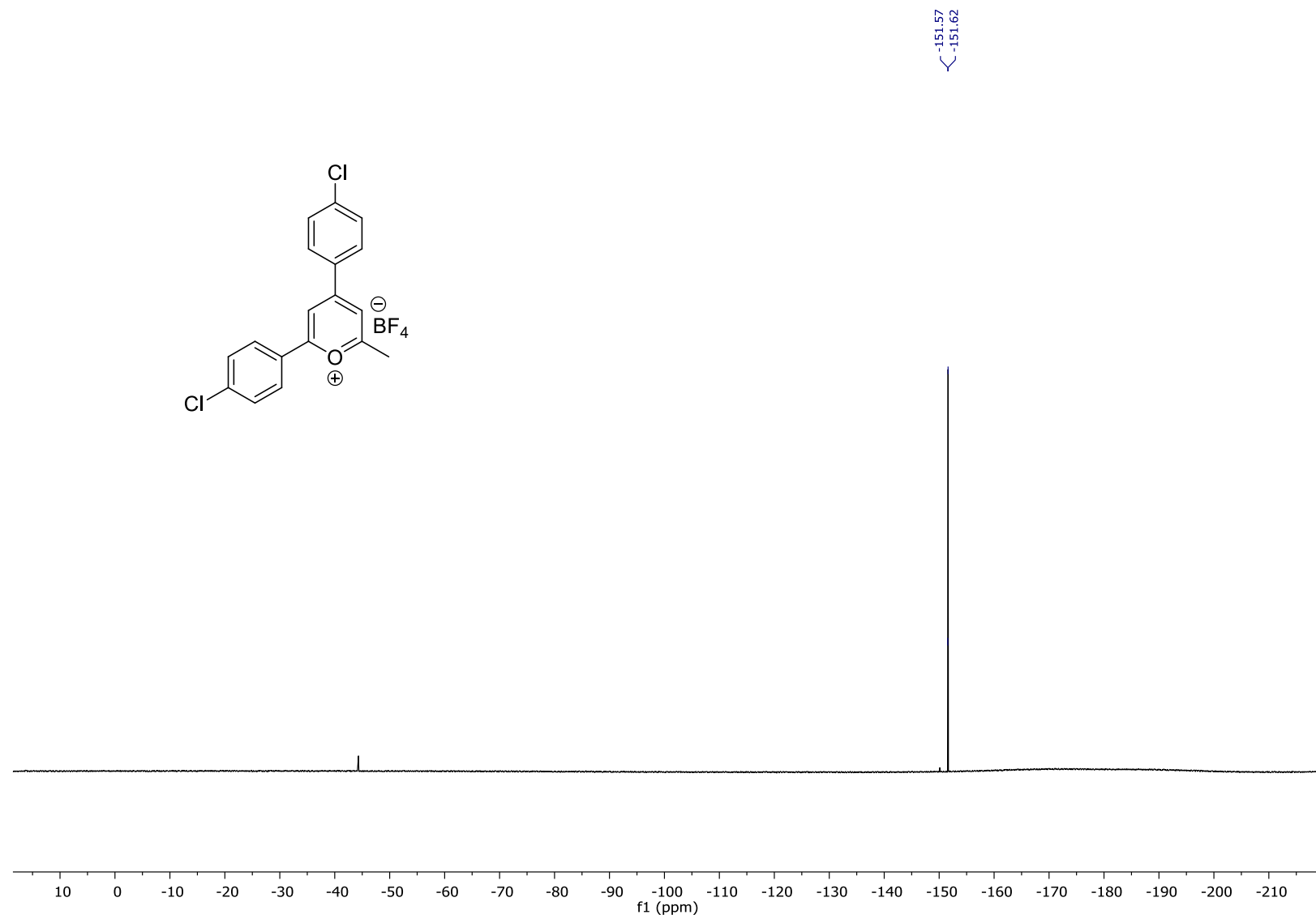
¹H NMR for 1i



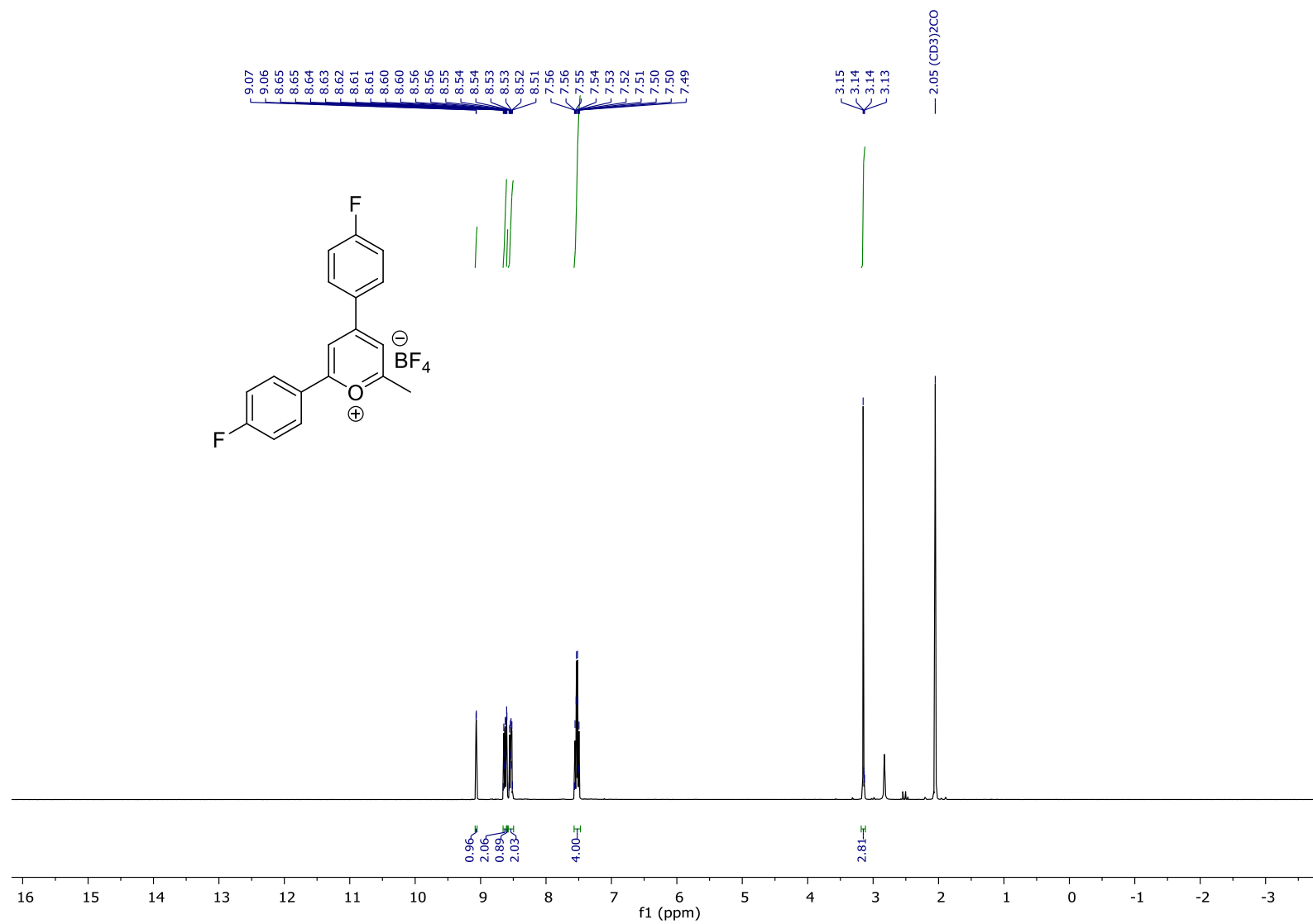
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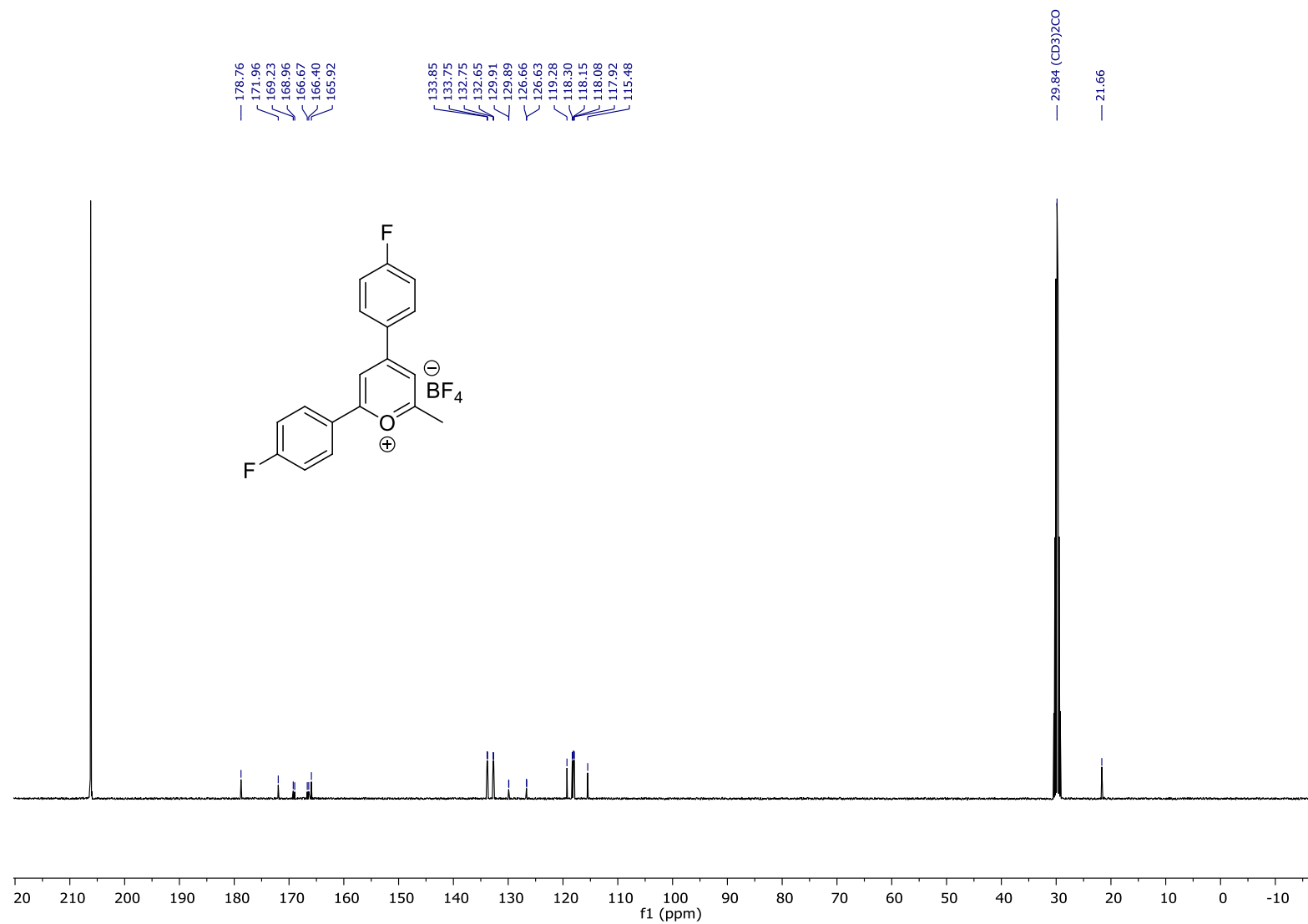
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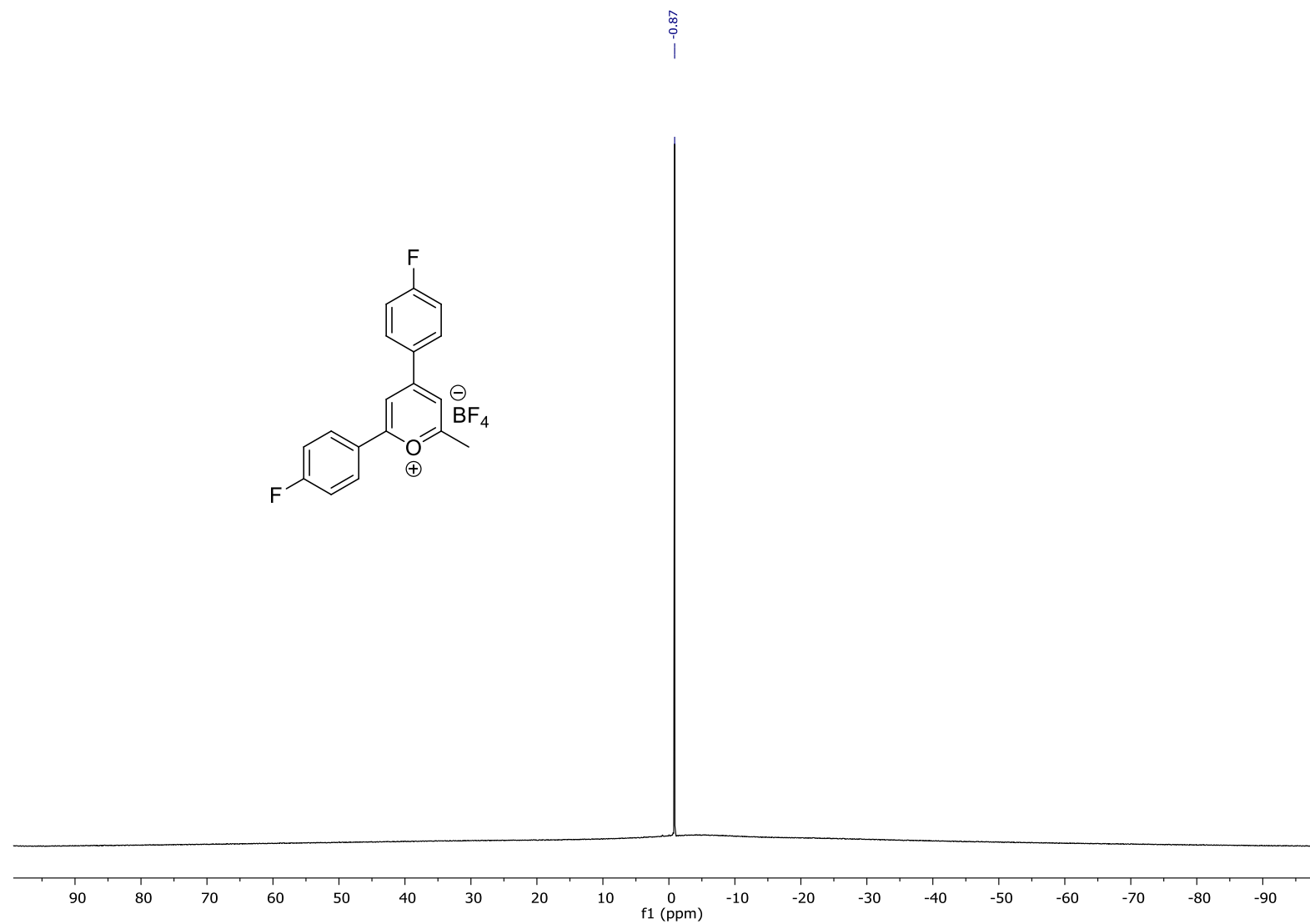
^{19}F NMR for **1i**



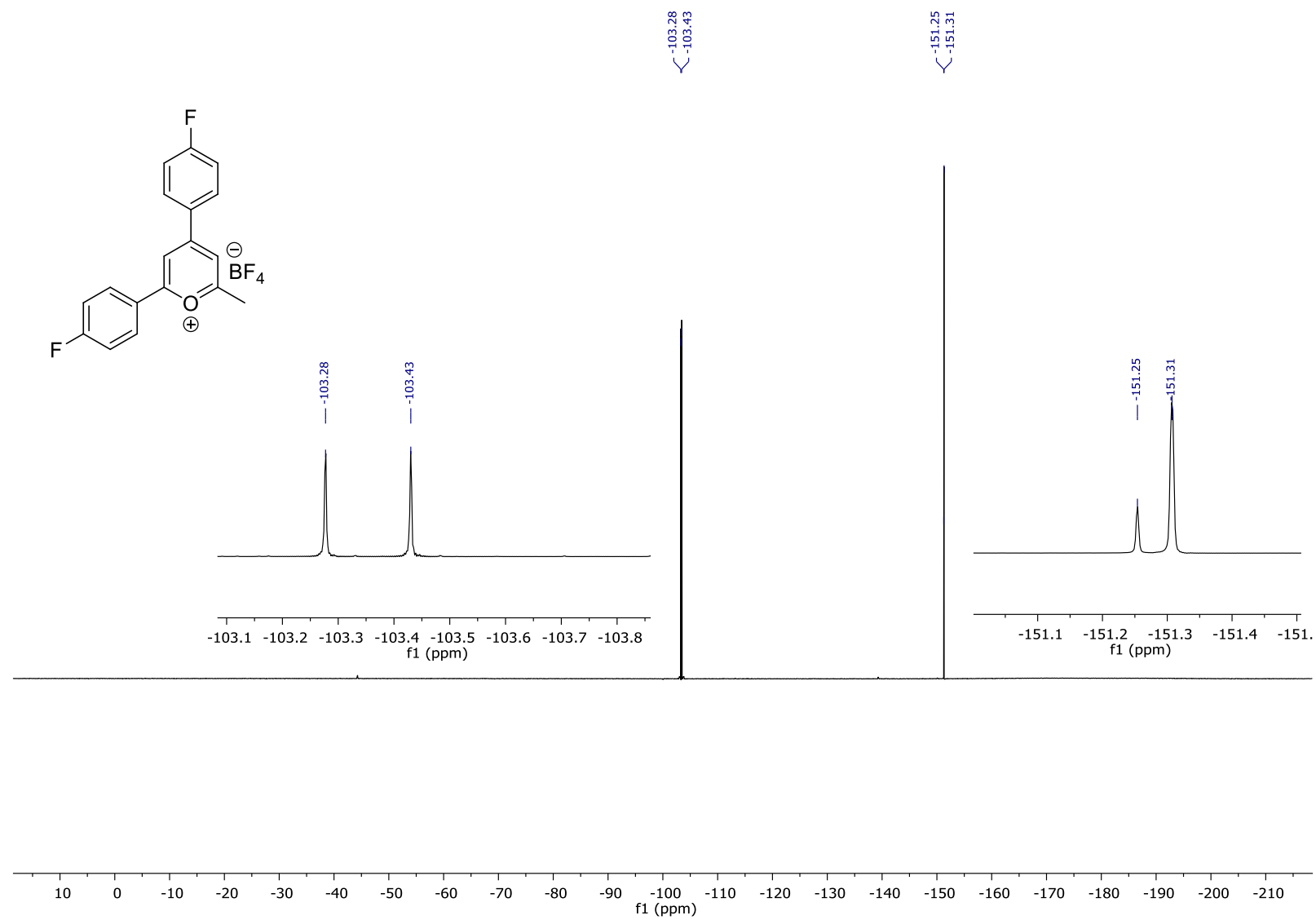
¹H NMR for 1j



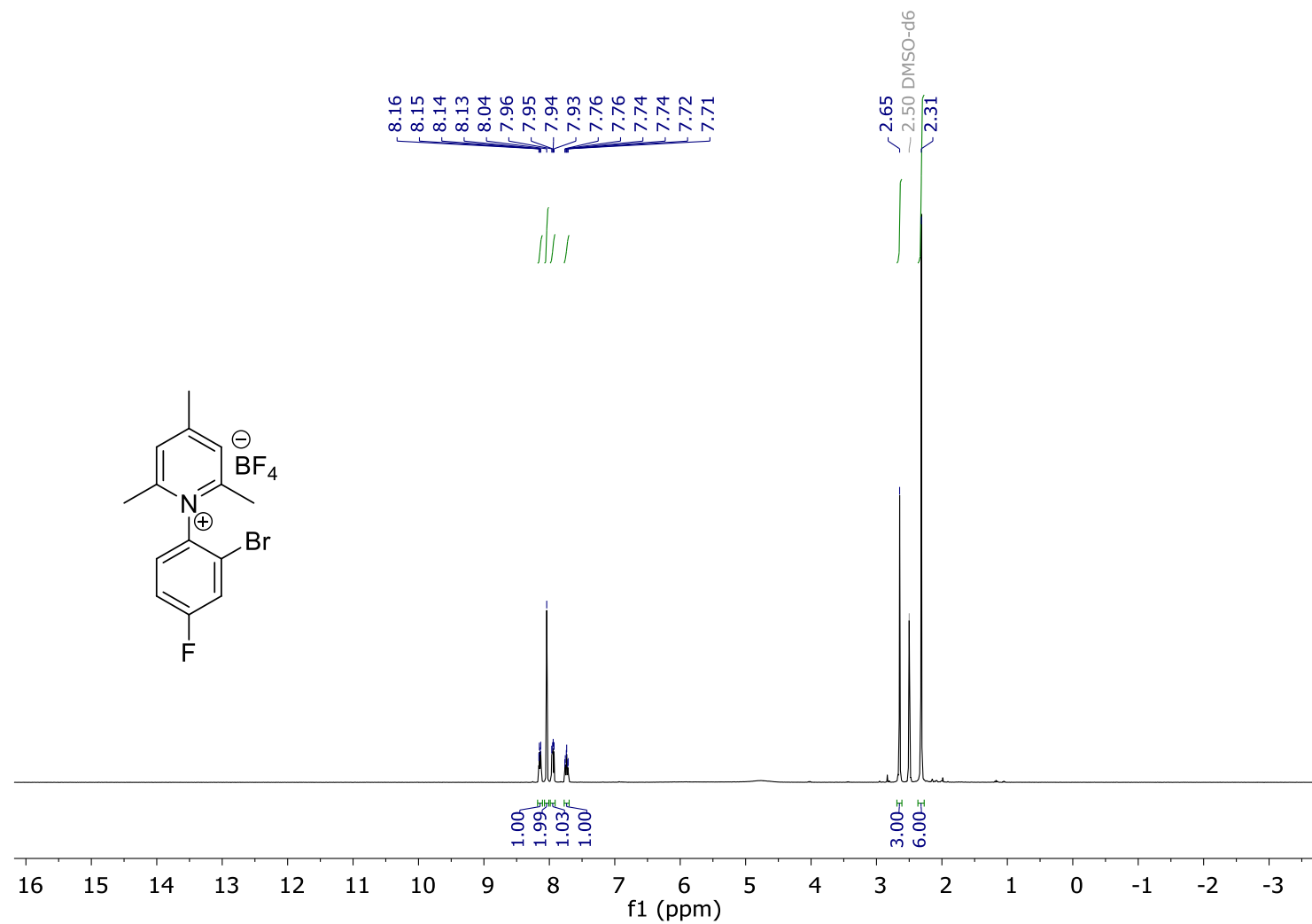
¹³C NMR for 1j



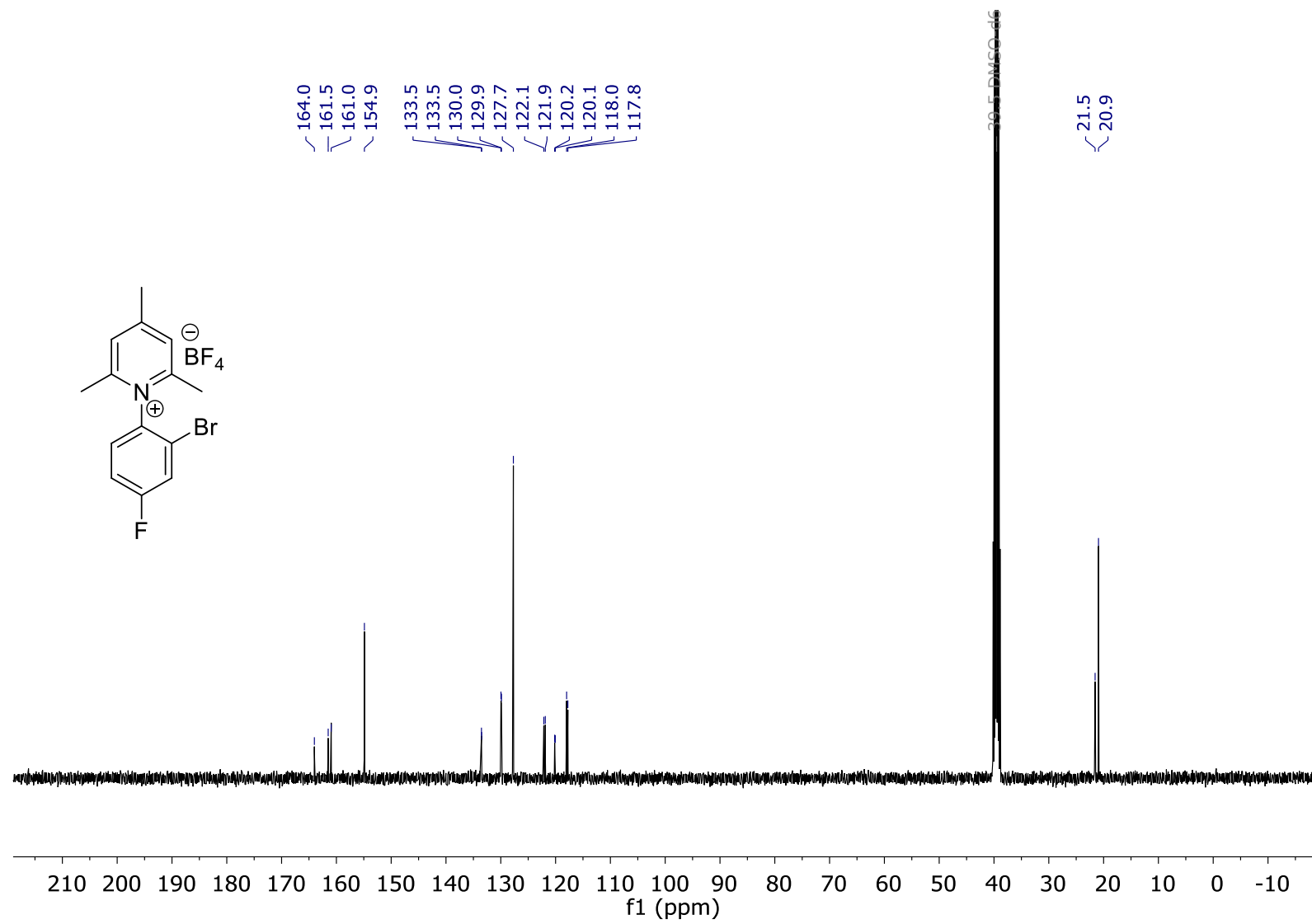
^{11}B NMR for 1j



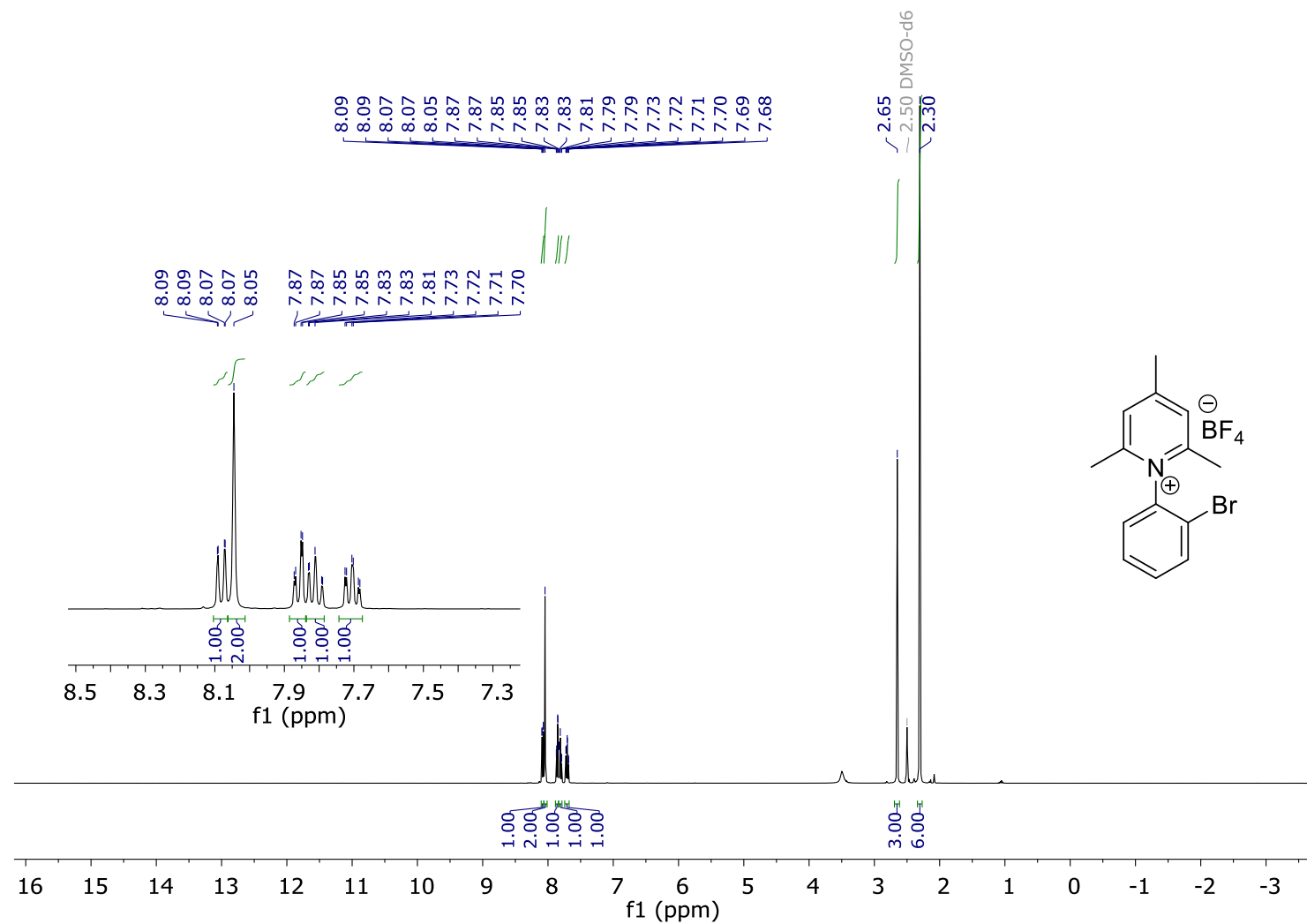
^{19}F NMR for **1j**



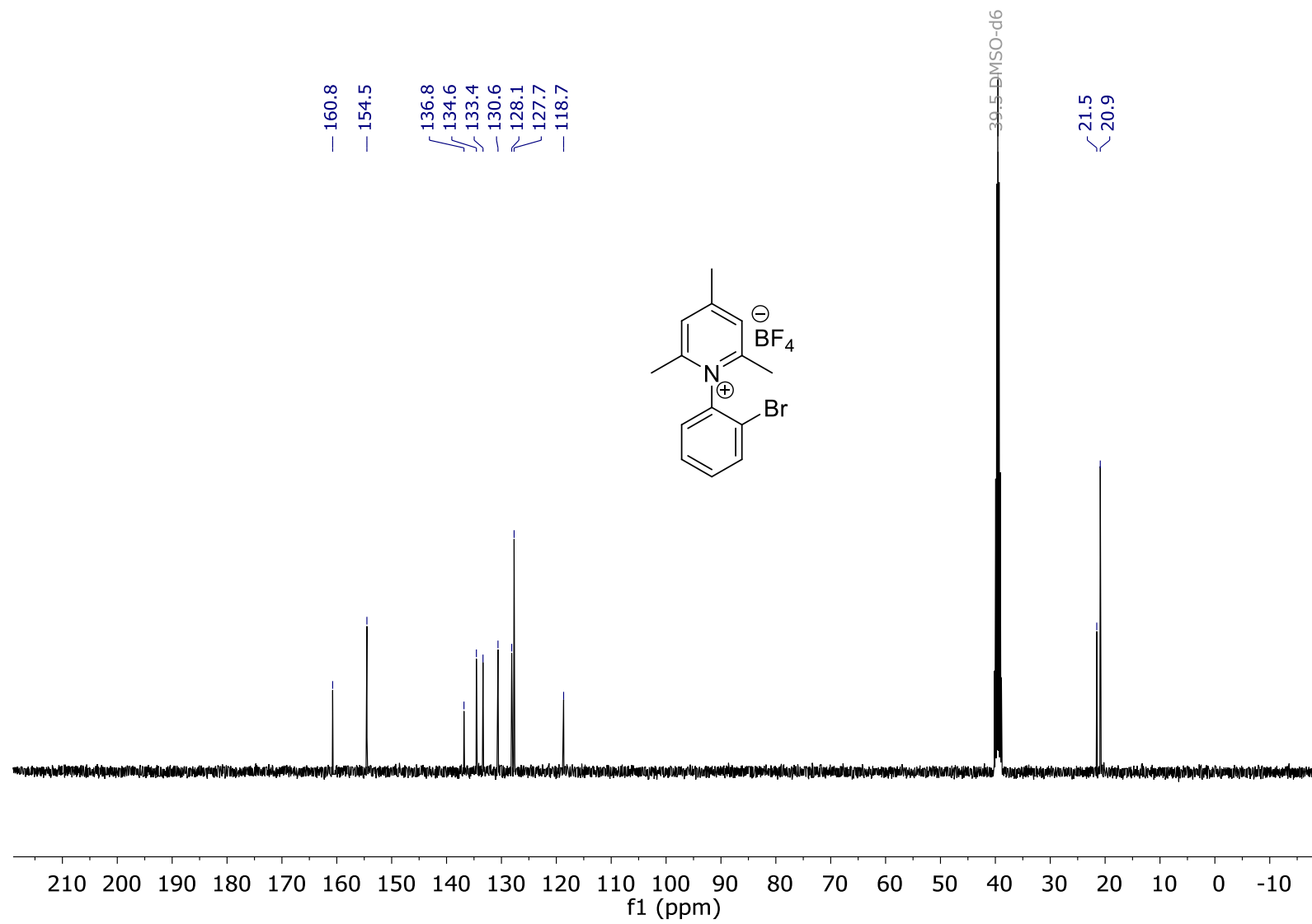
¹H NMR for 3a



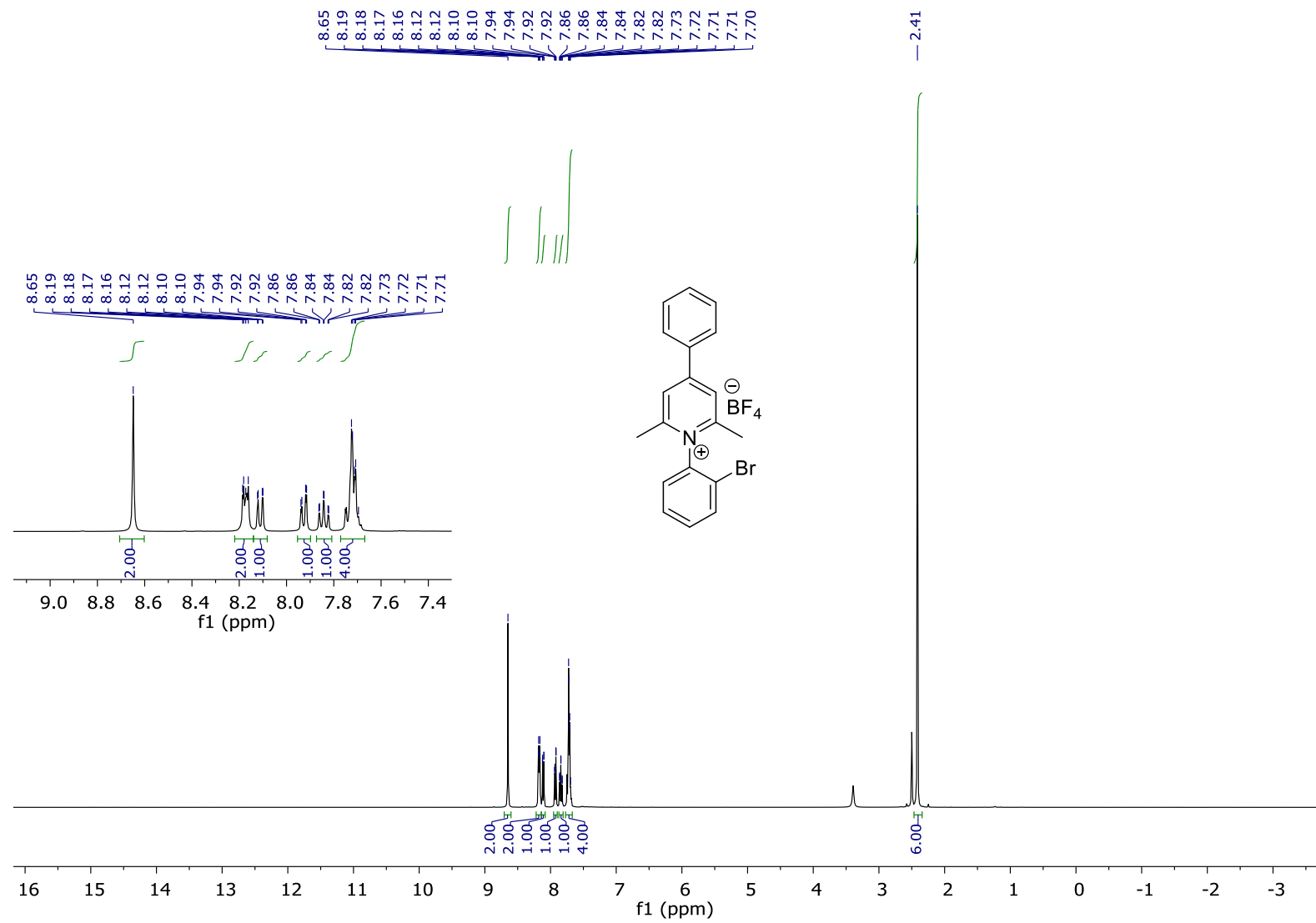
¹³C NMR for 3a



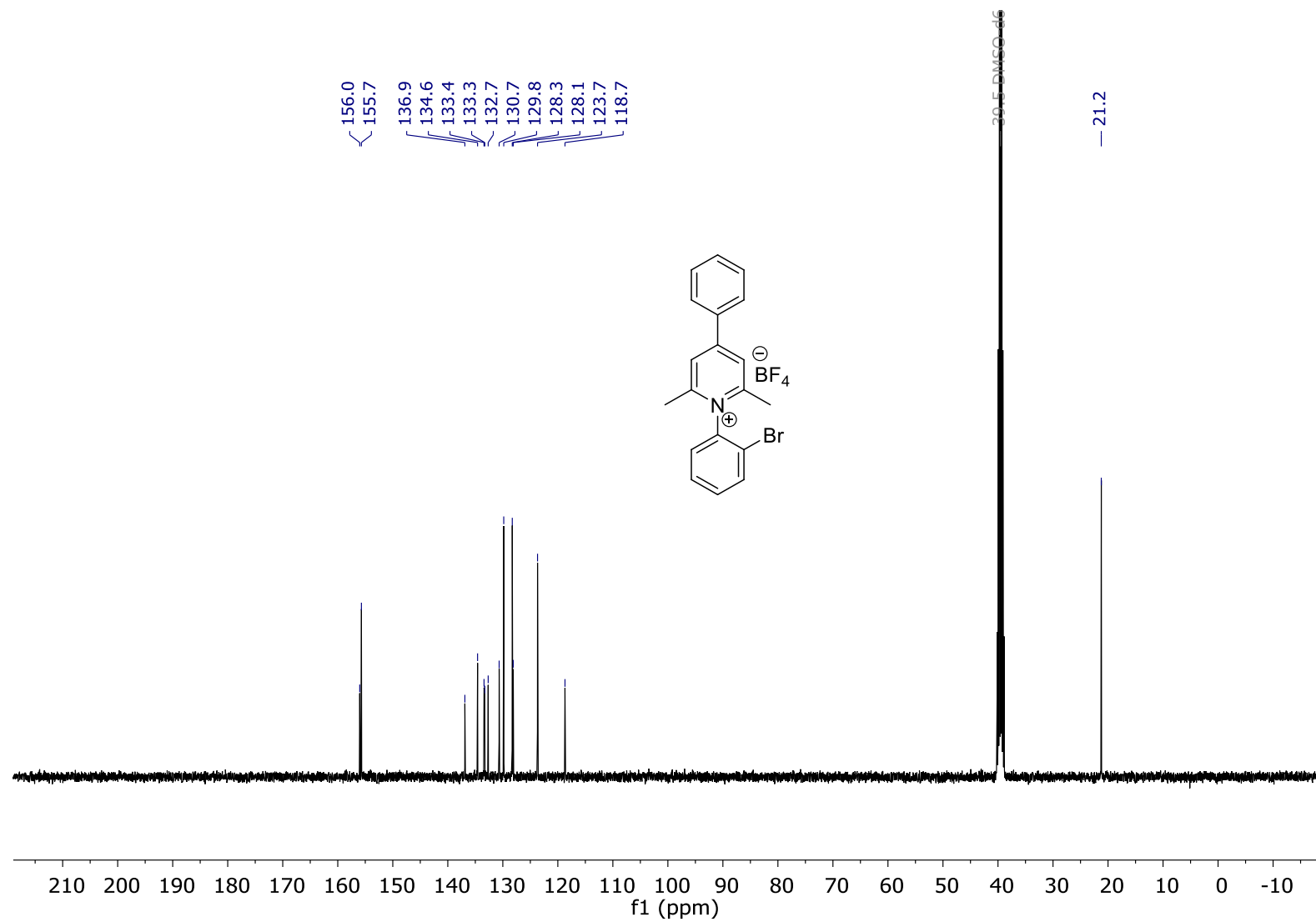
¹H NMR for 3b



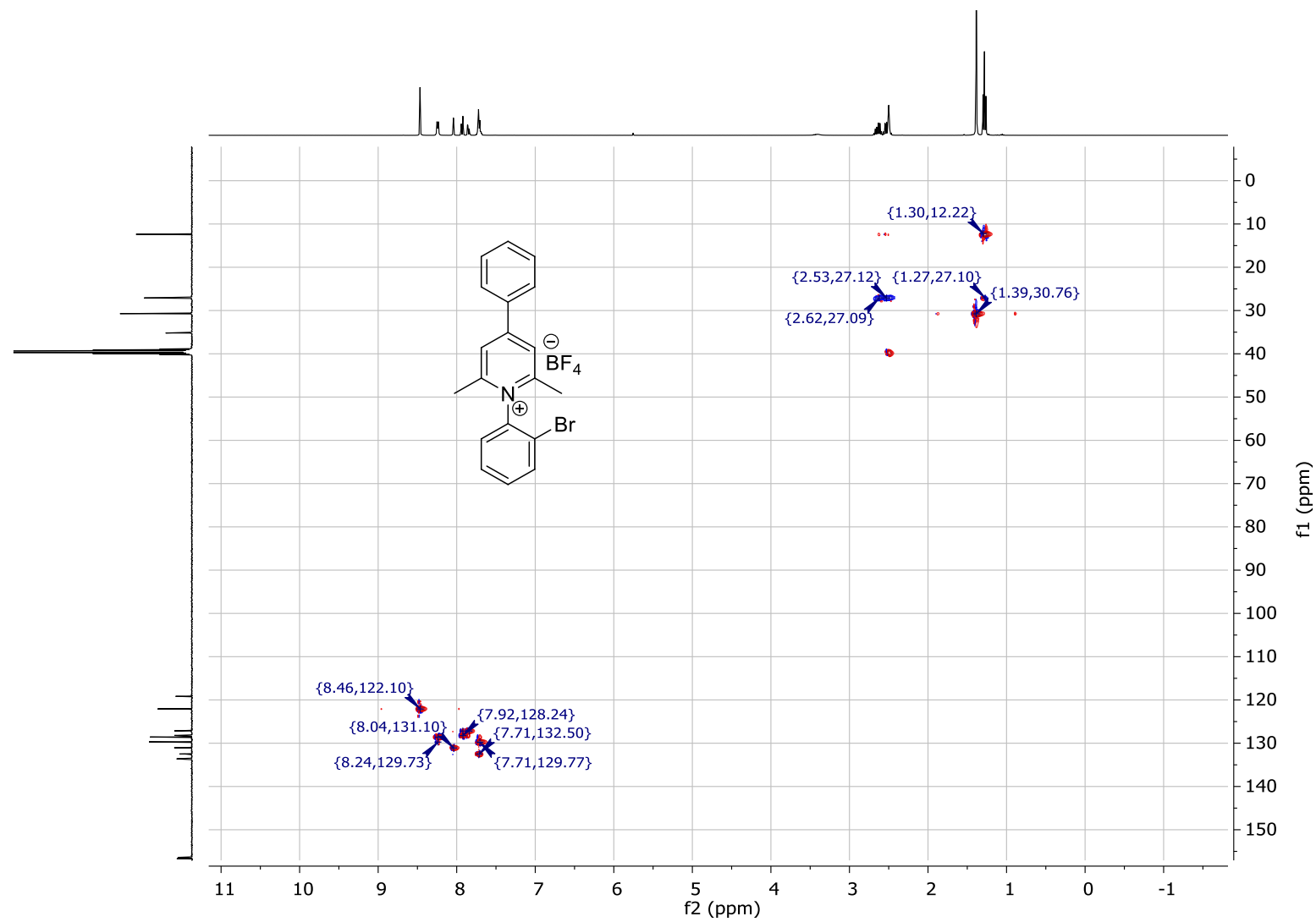
¹³C NMR for 3b



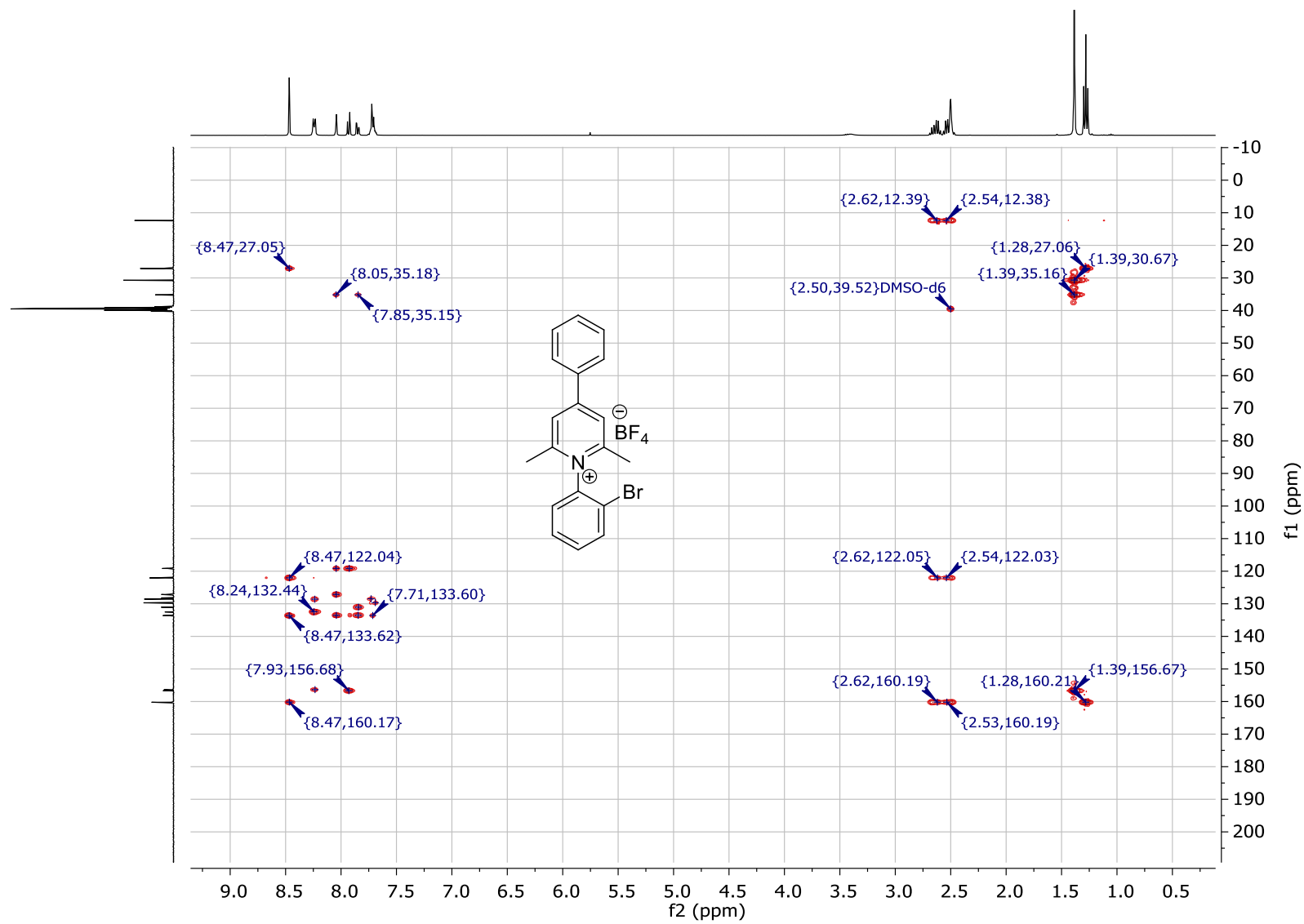
¹H NMR for 3c



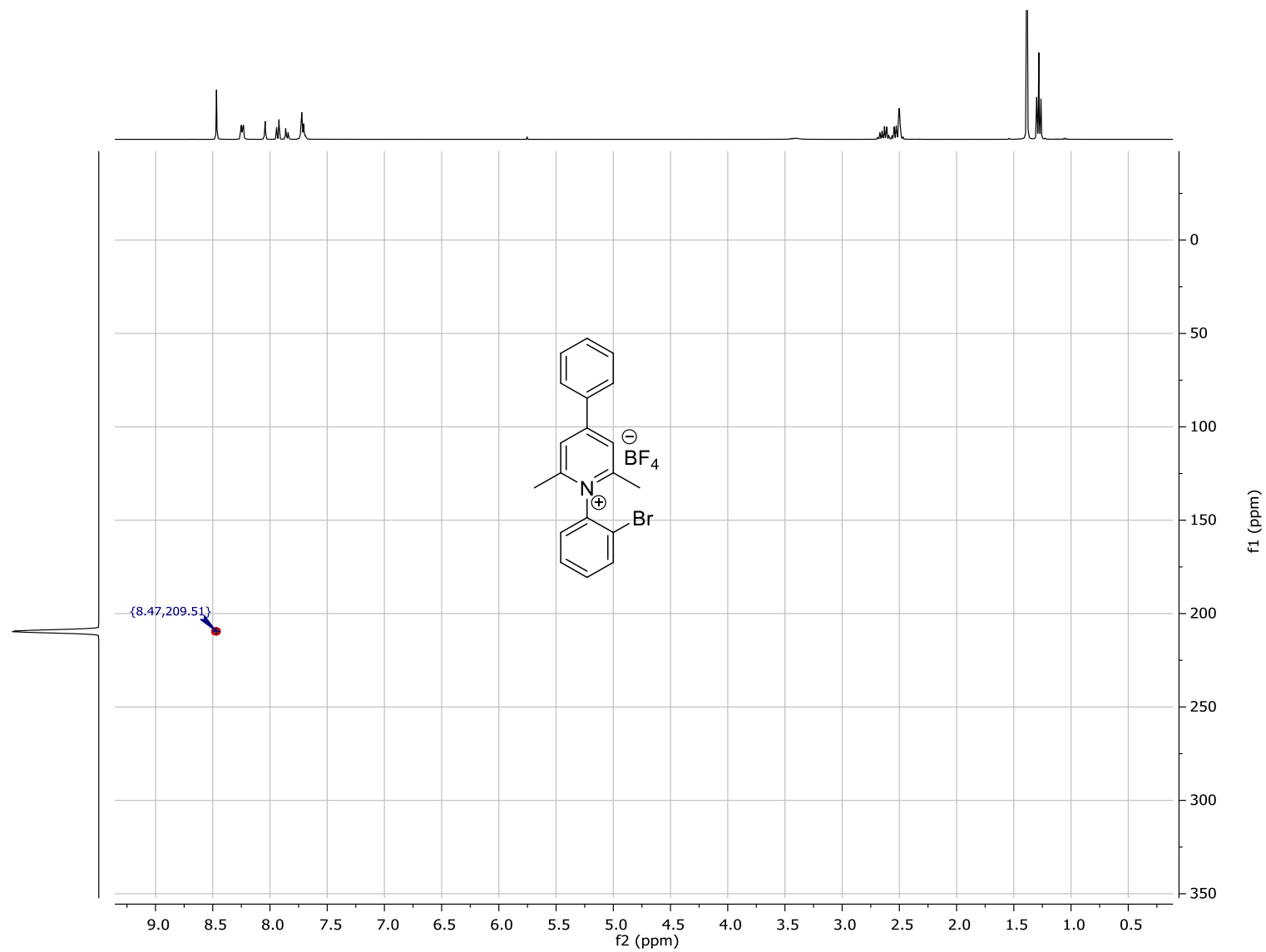
¹³C NMR for 3c



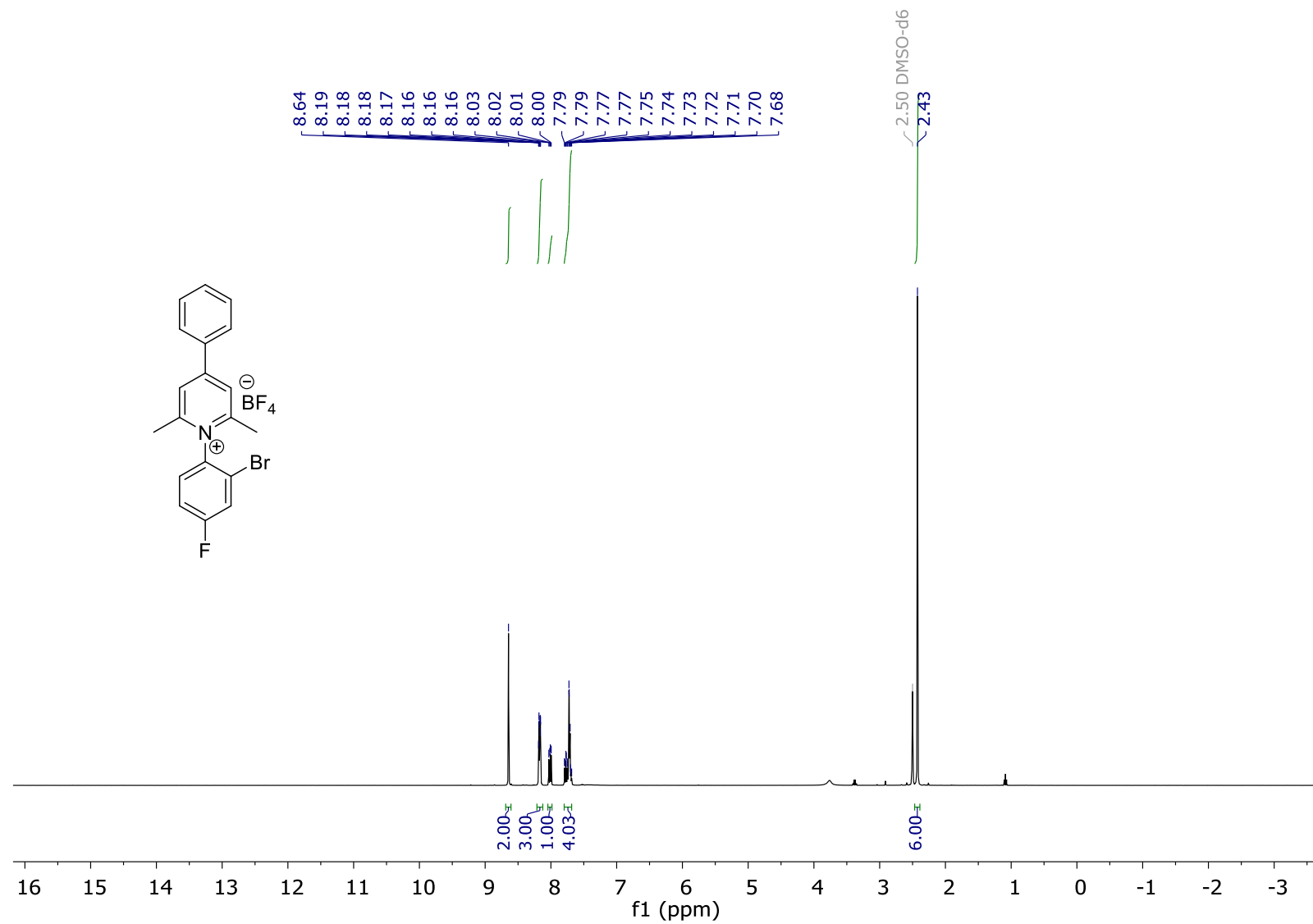
^1H - ^{13}C HSQC for 3c



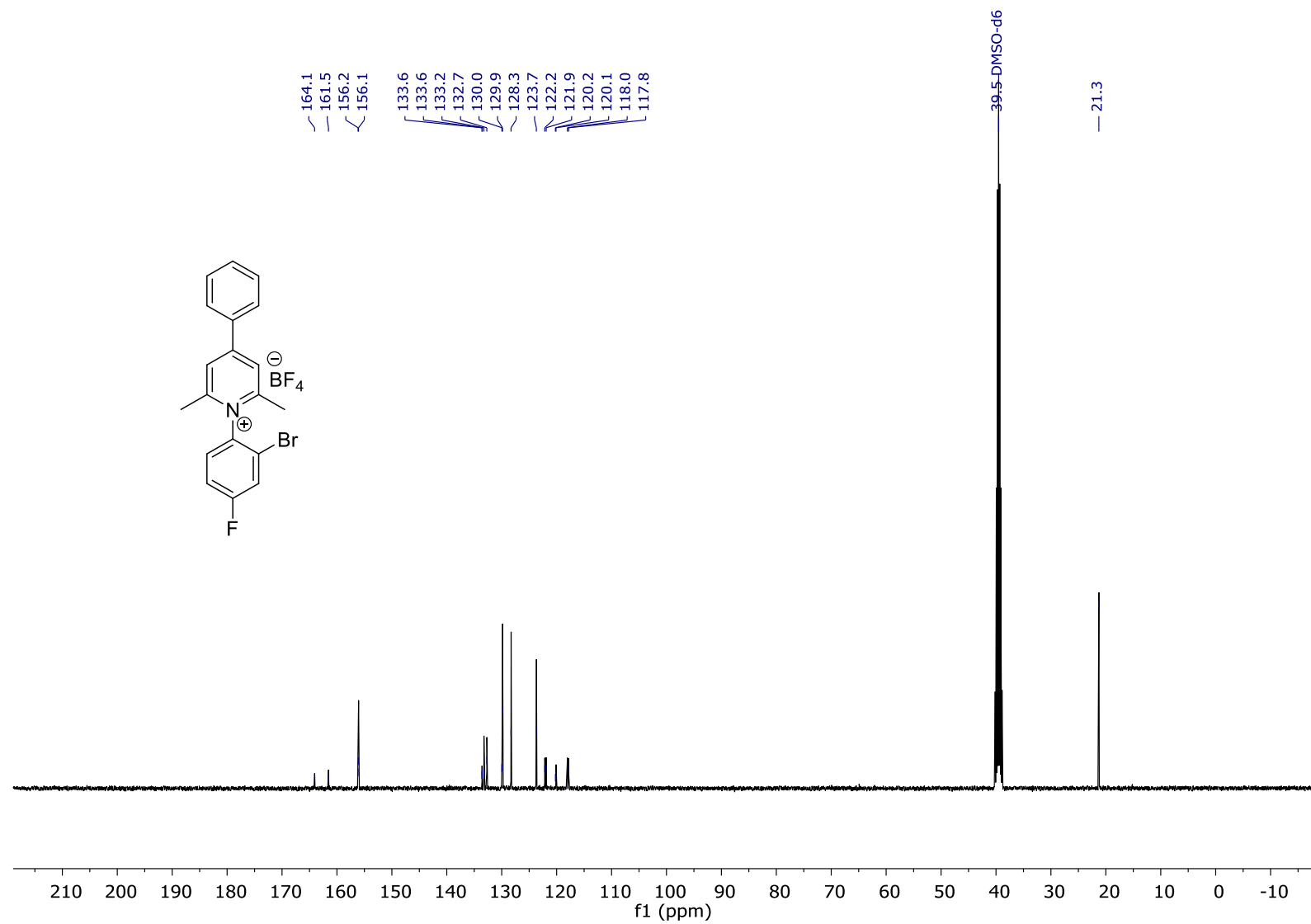
^1H - ^{13}C HMBC for 3c



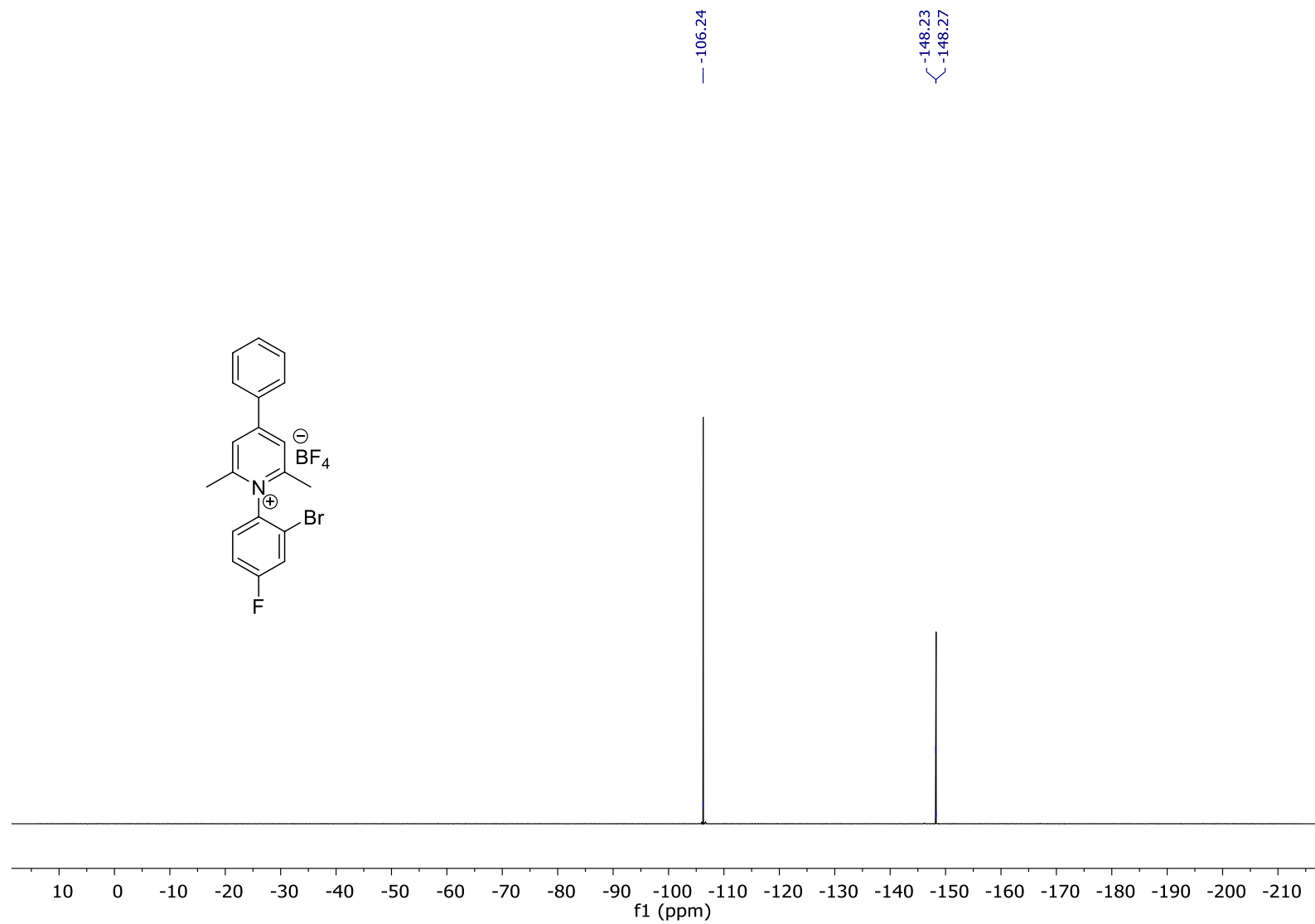
^1H - ^{15}N HMBC for 3c



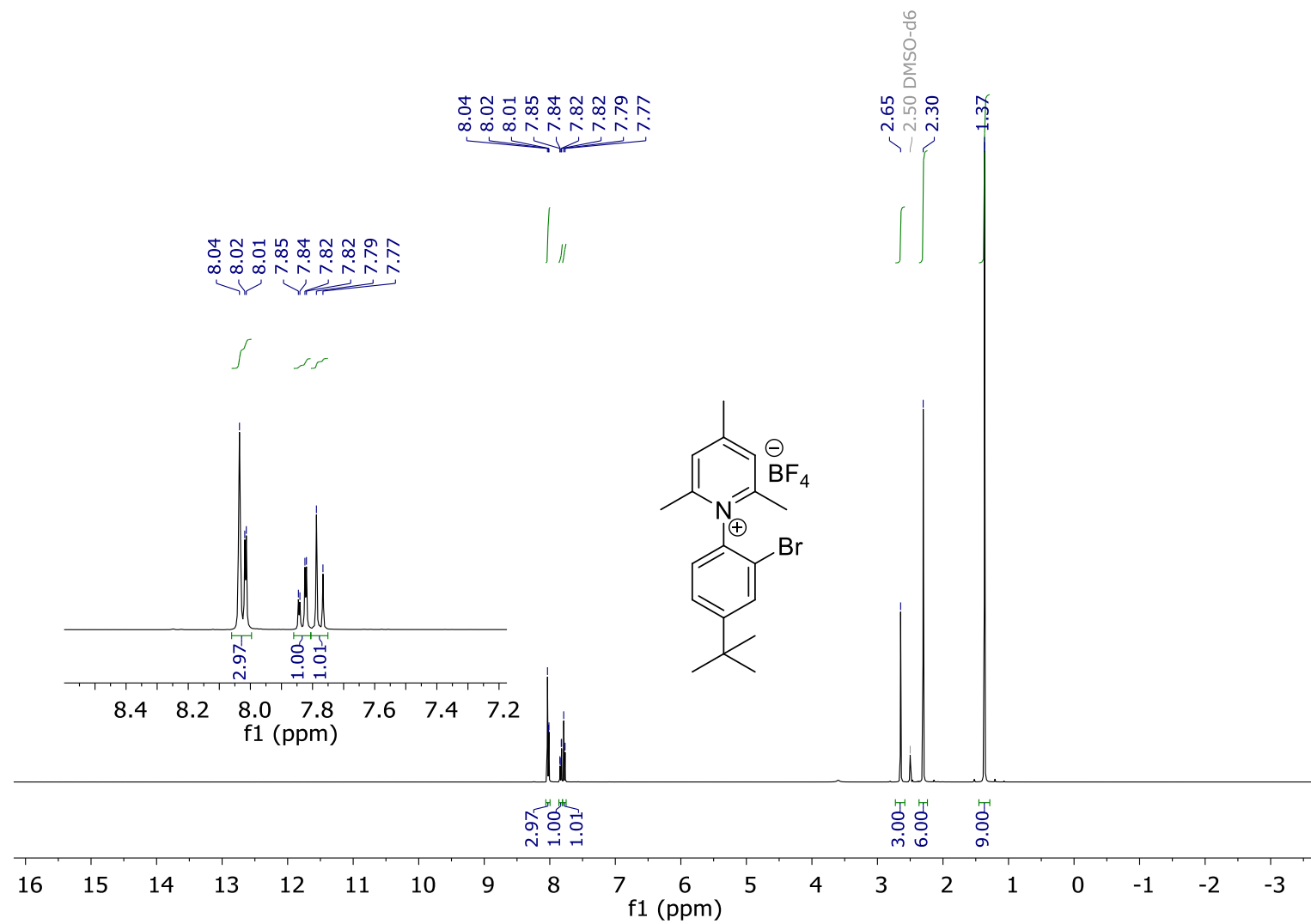
¹H NMR for 3d



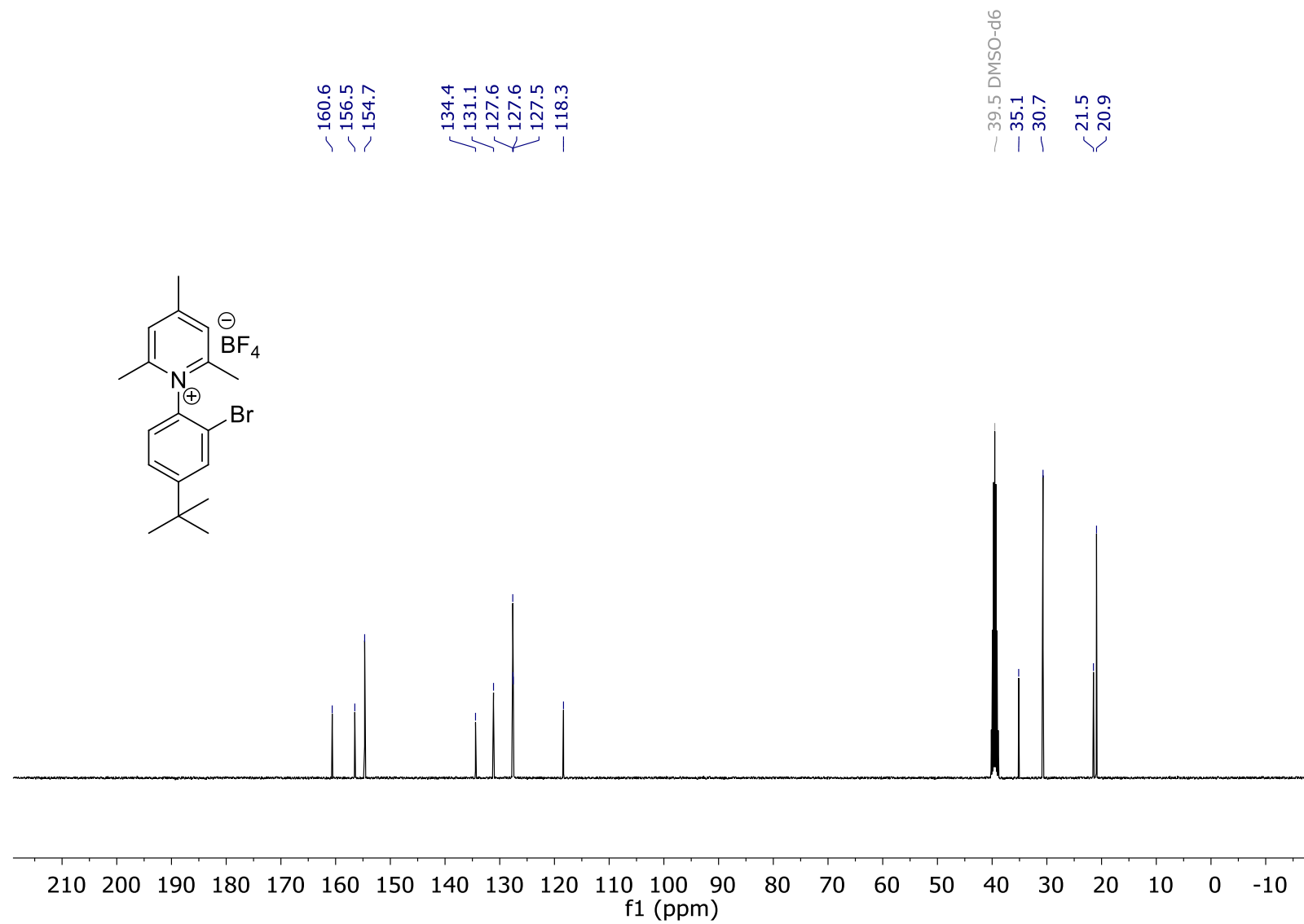
¹³C NMR for 3d



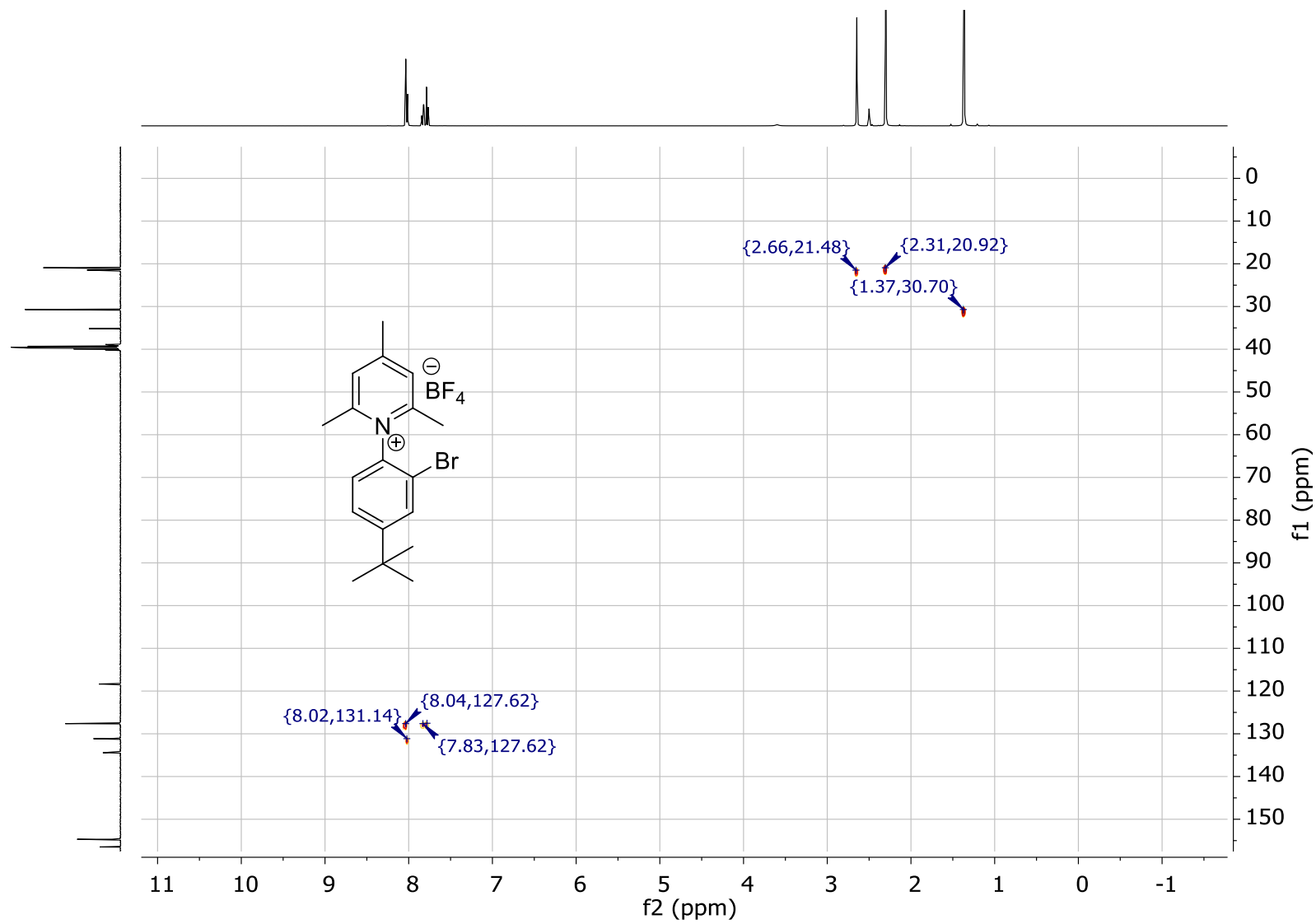
^{19}F NMR for 3d



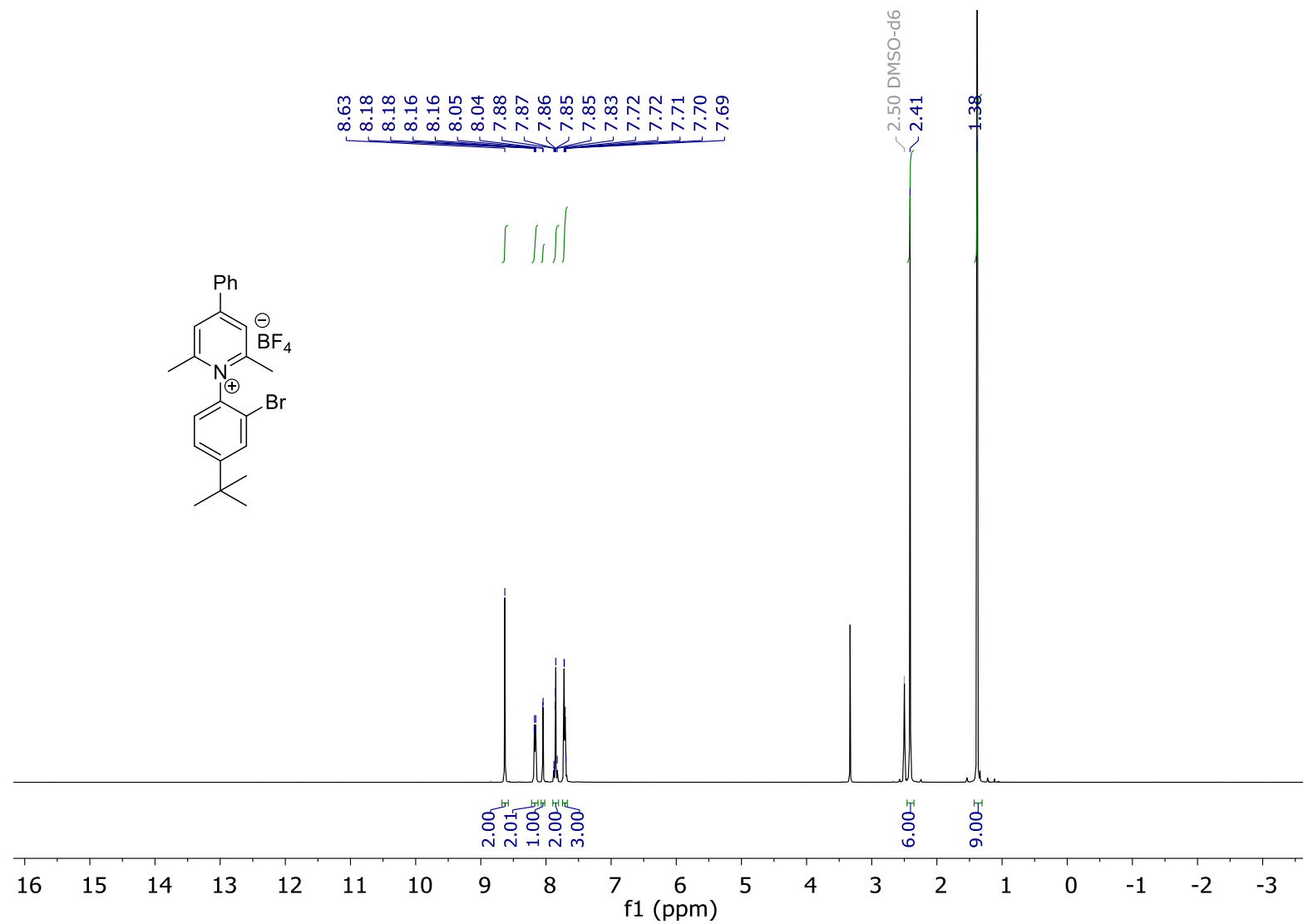
¹H NMR for 3e



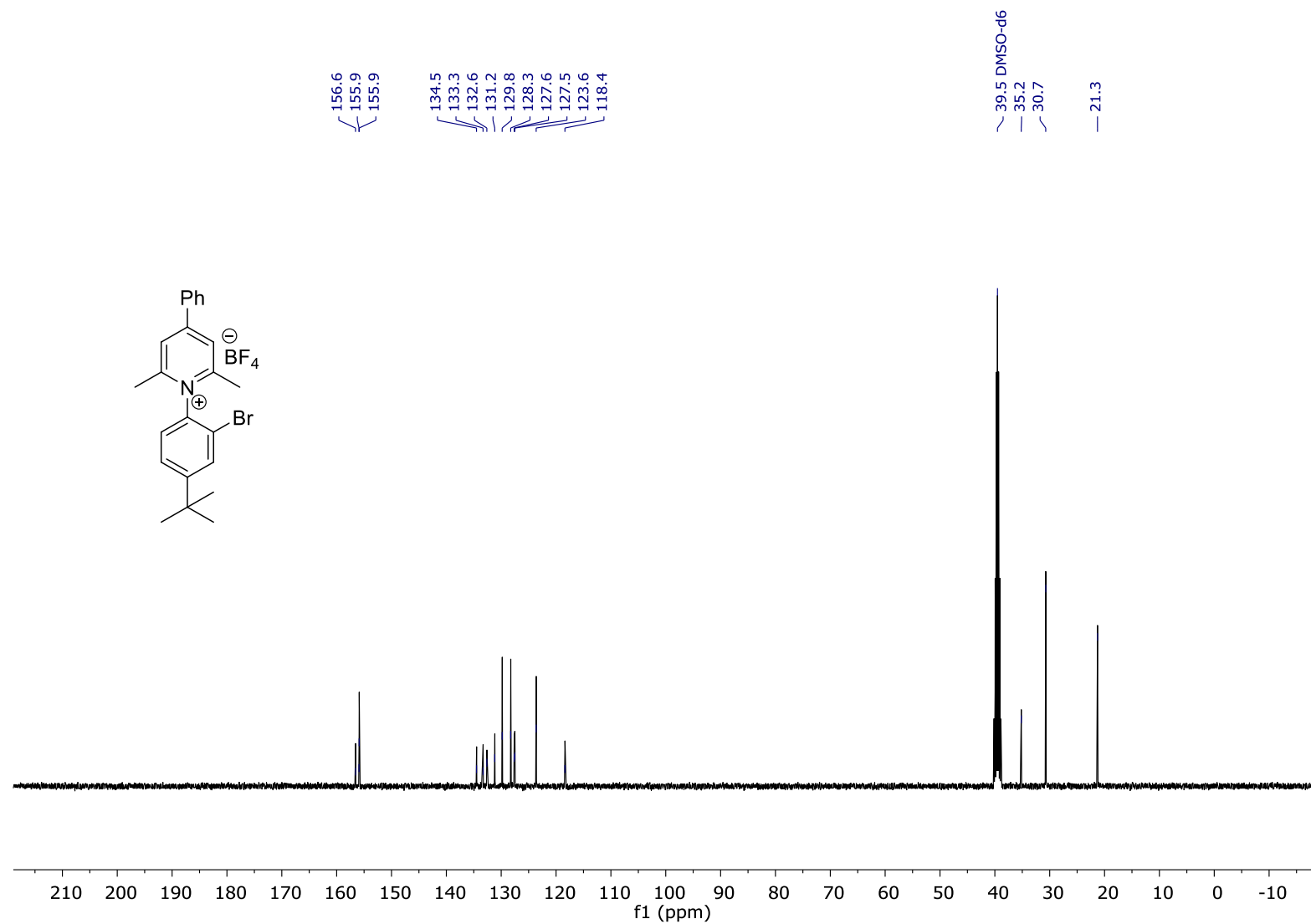
¹³C NMR for 3e



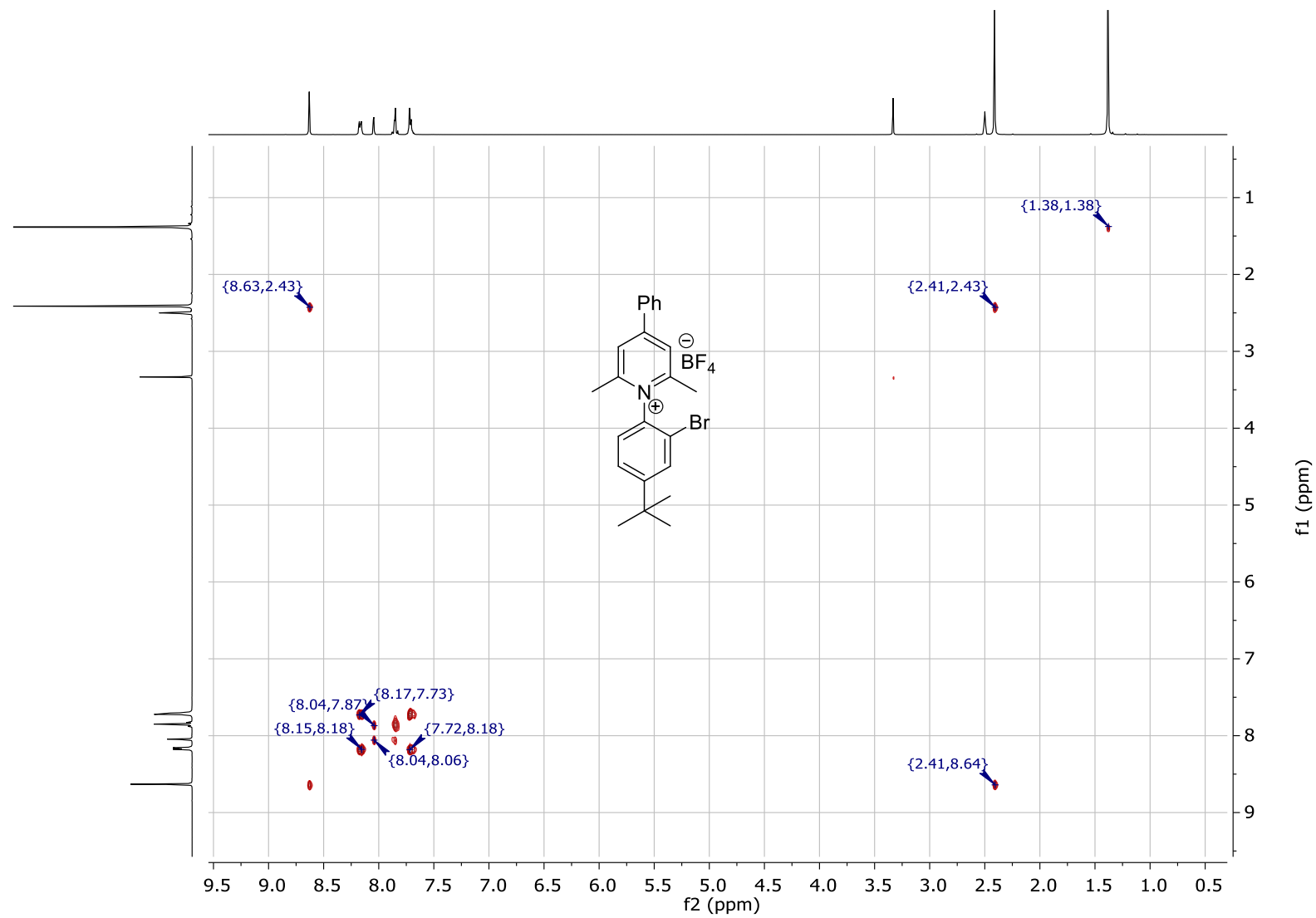
^1H - ^{13}C HSQC for 3e



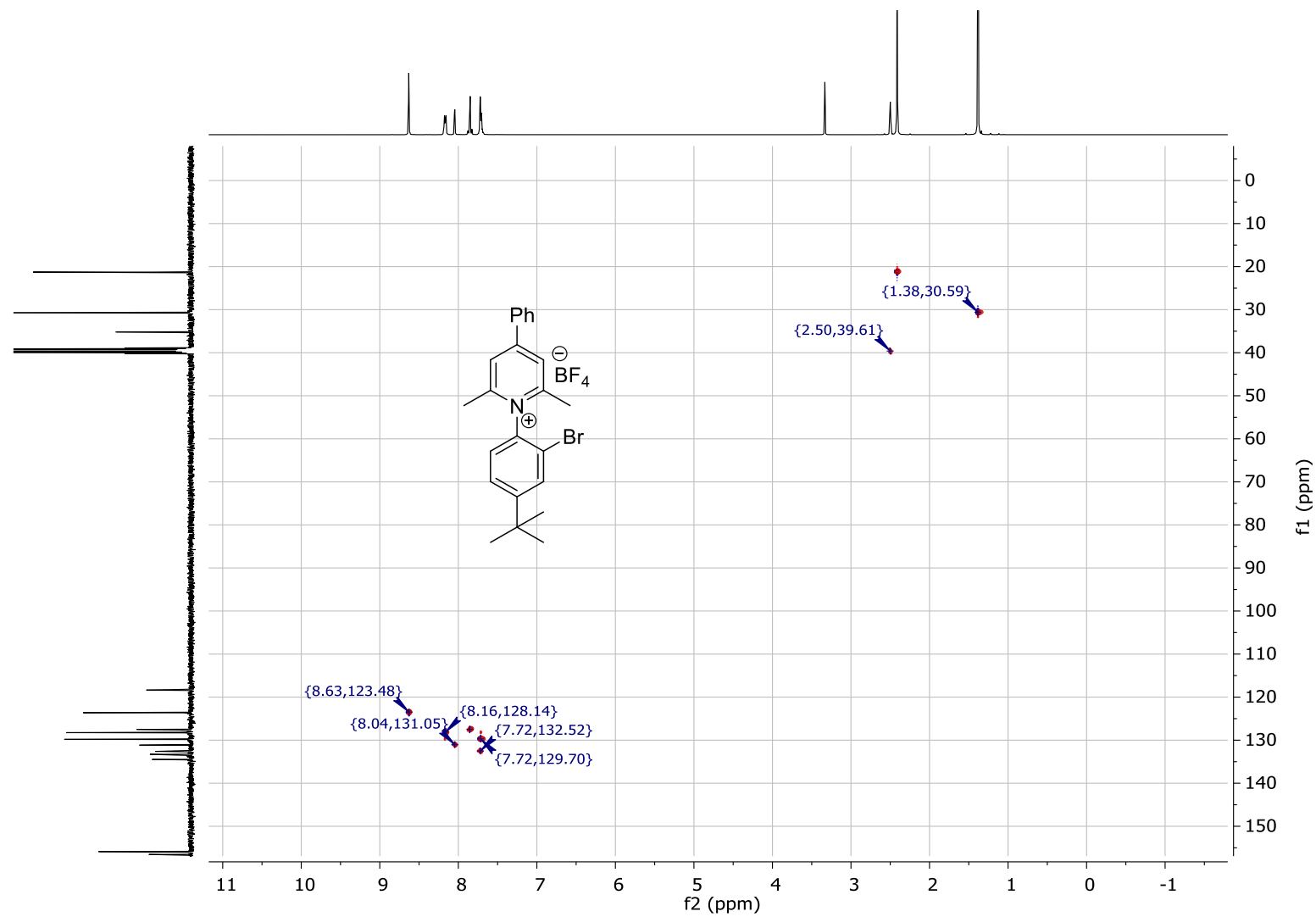
¹H NMR for 3f



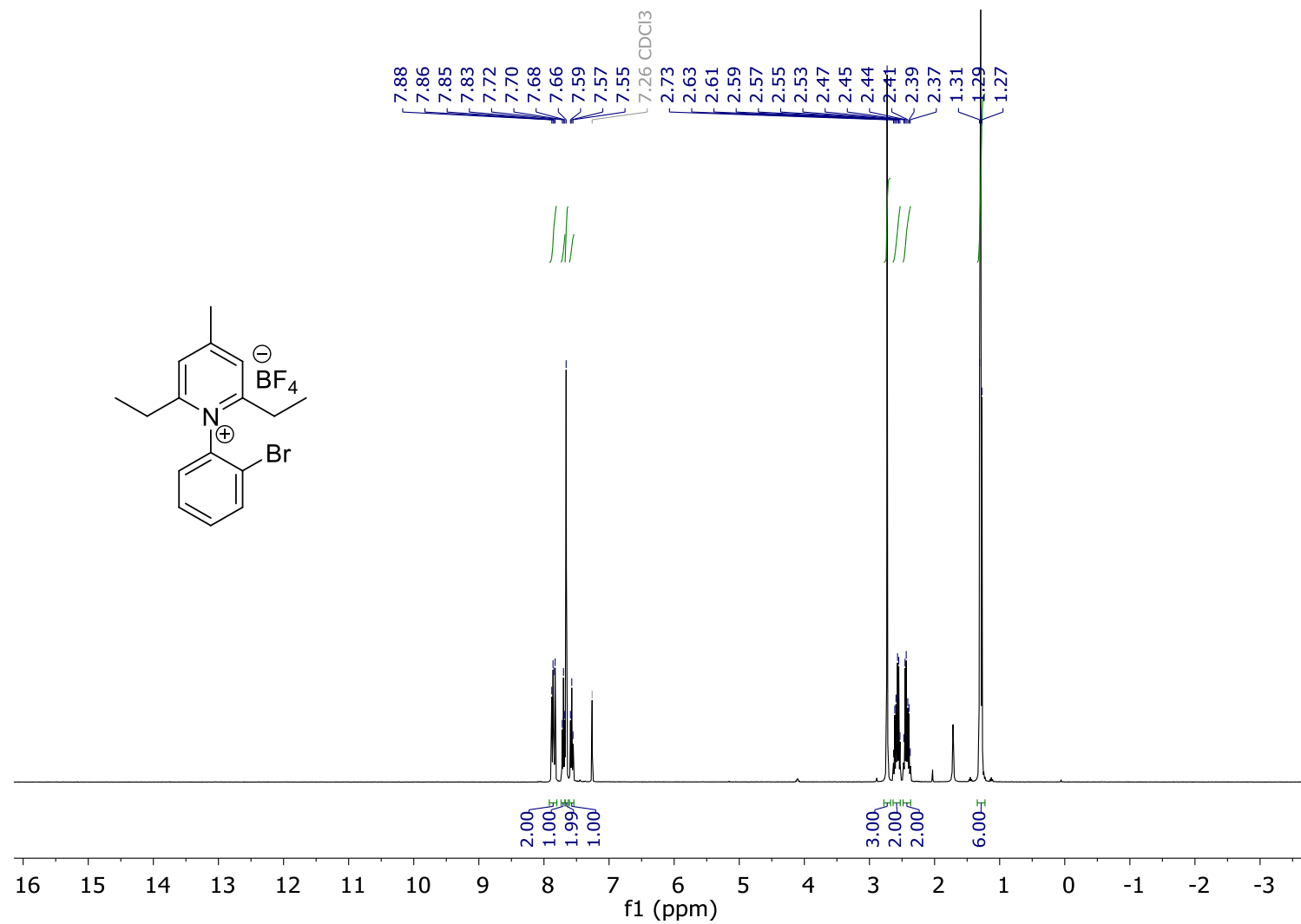
¹³C NMR for 3f



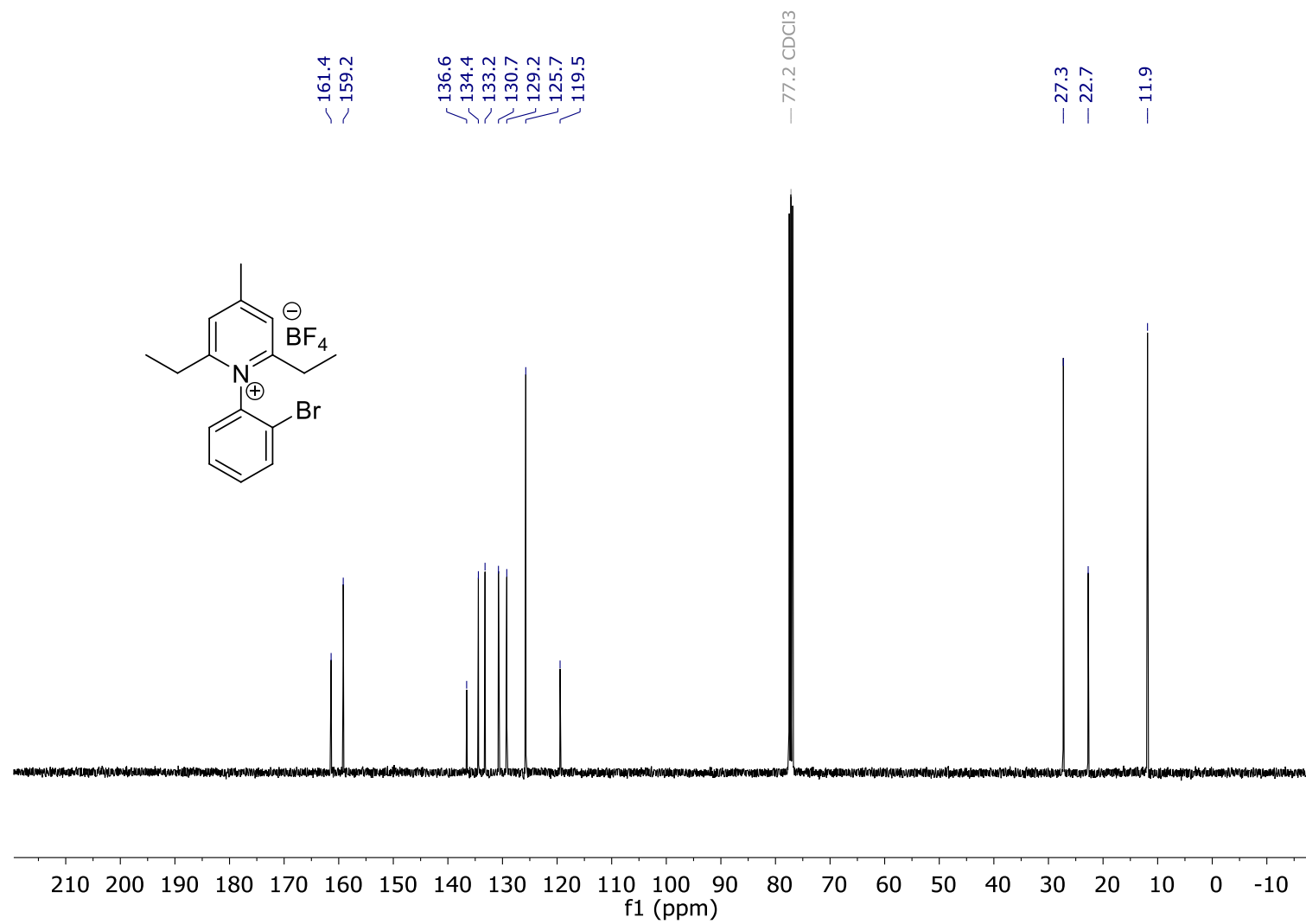
¹H-¹H COSY for 3f



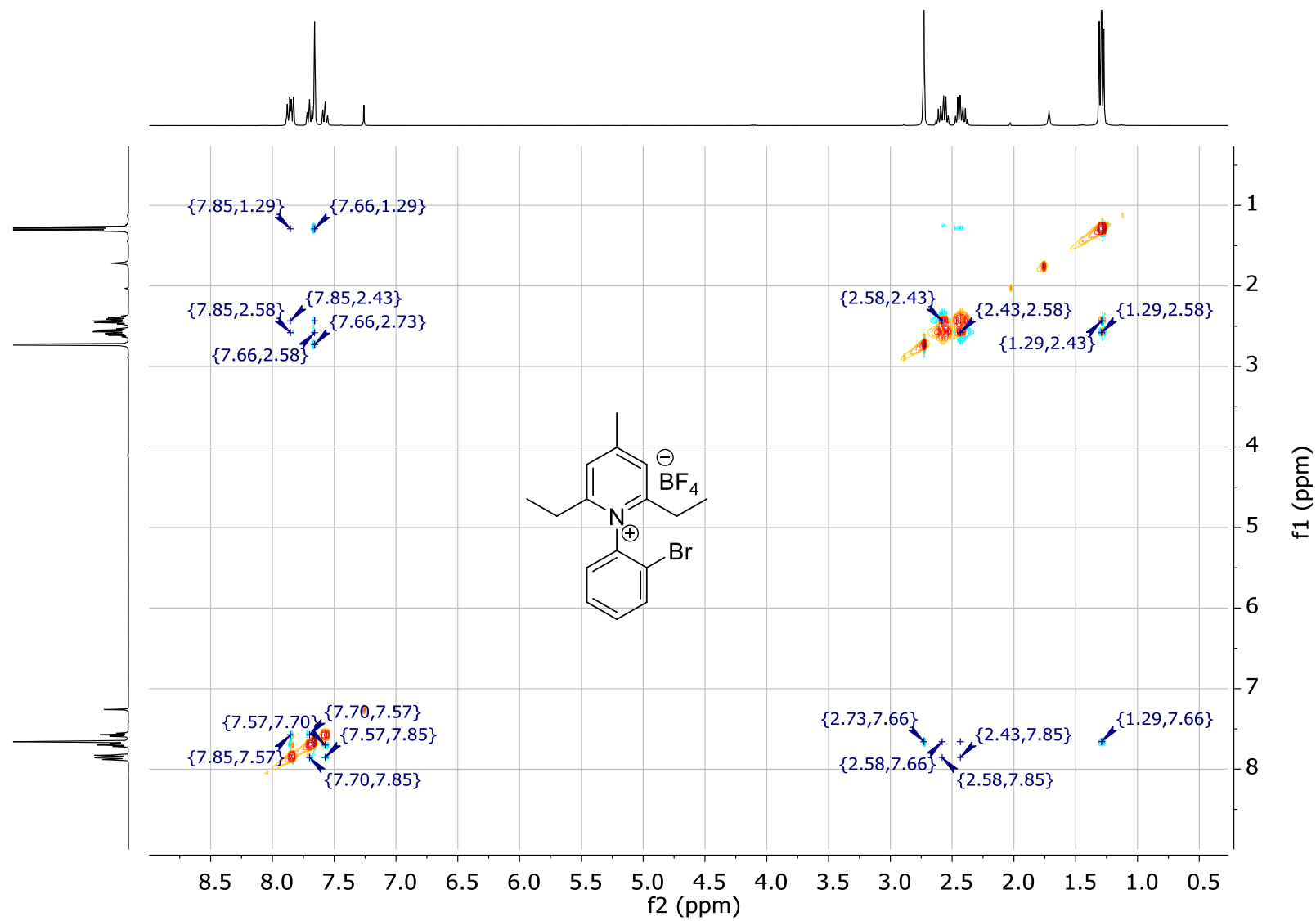
^1H - ^{13}C HSQC for 3f



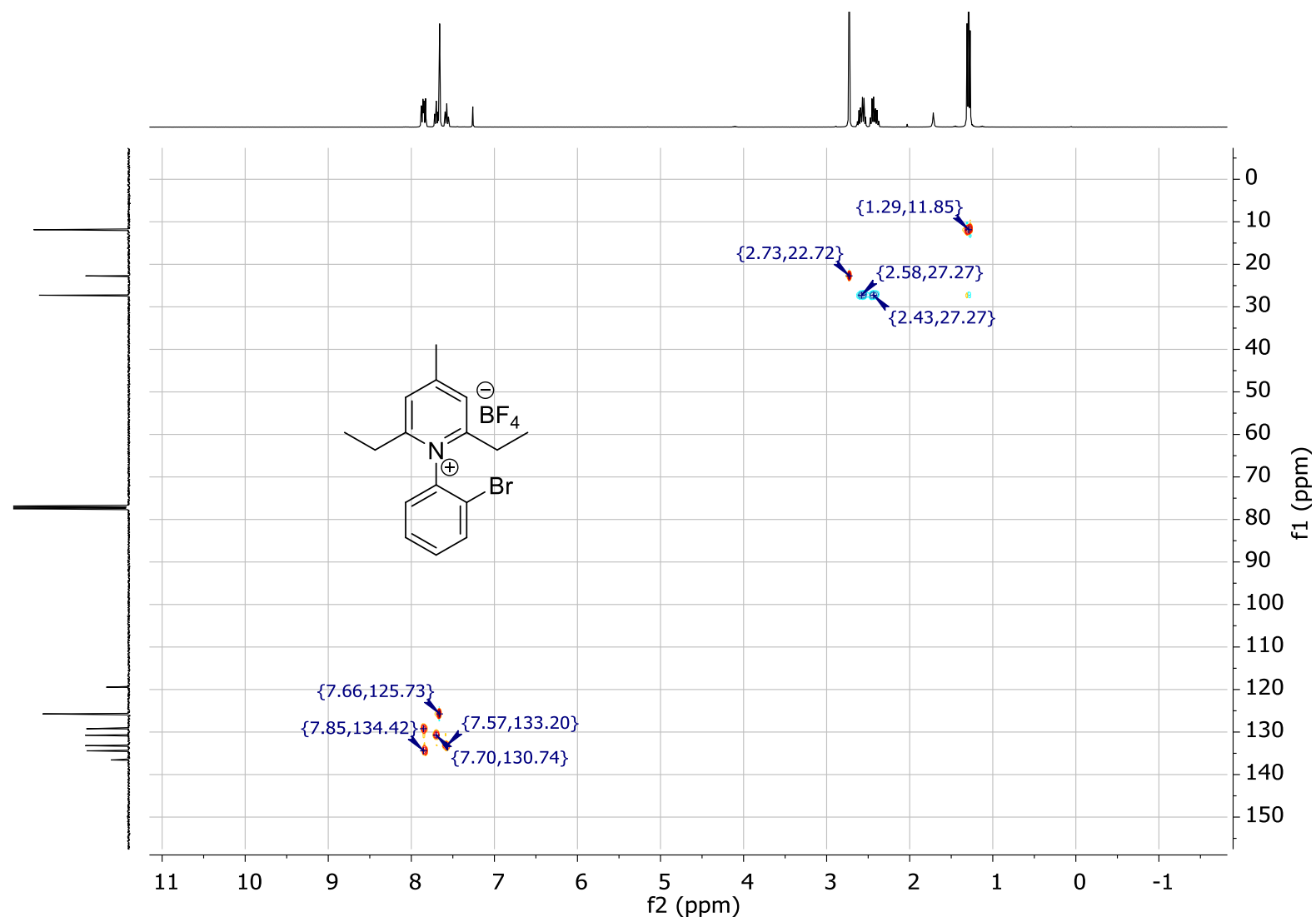
¹H NMR for 3g



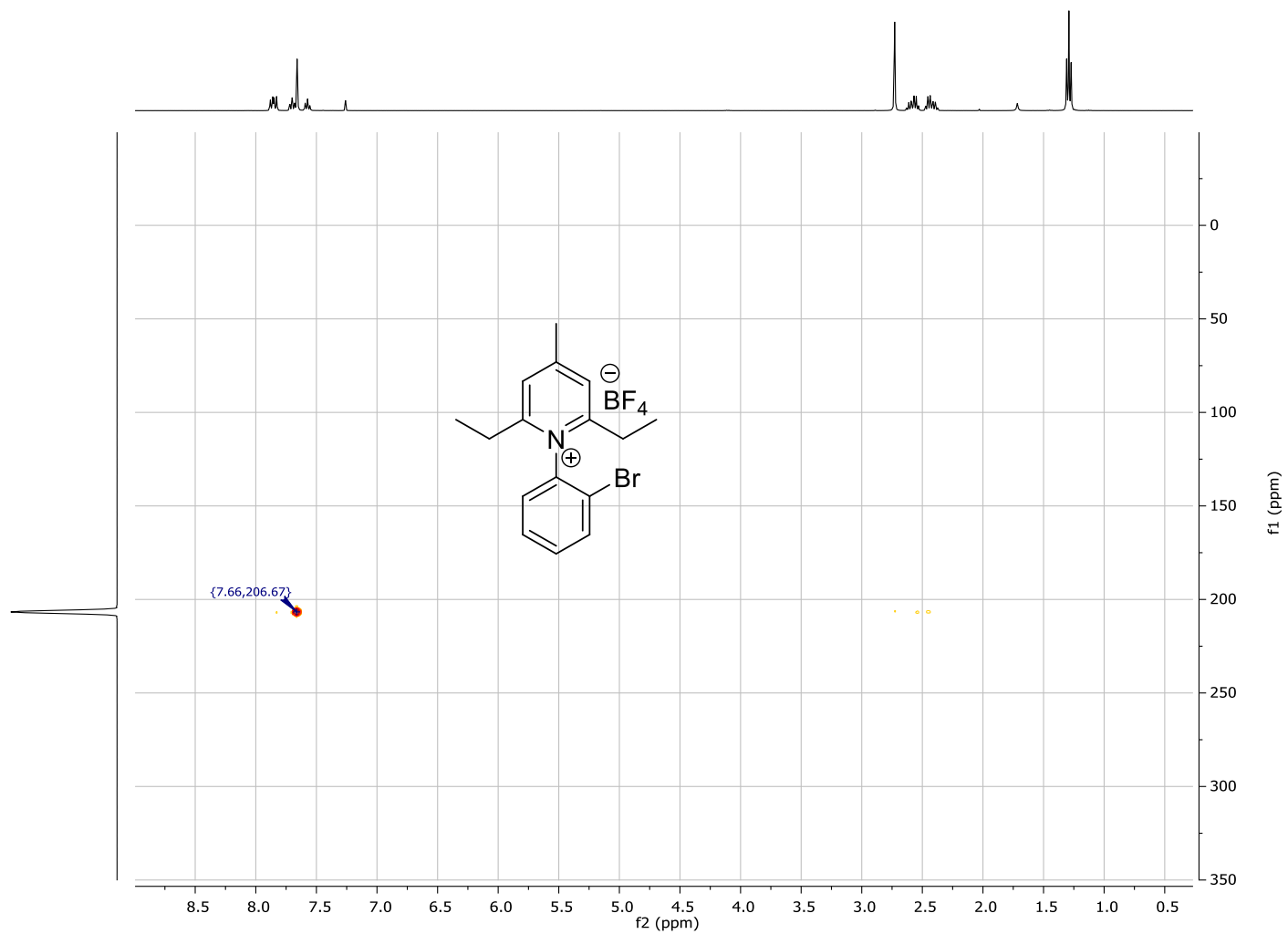
¹³C NMR for 3g



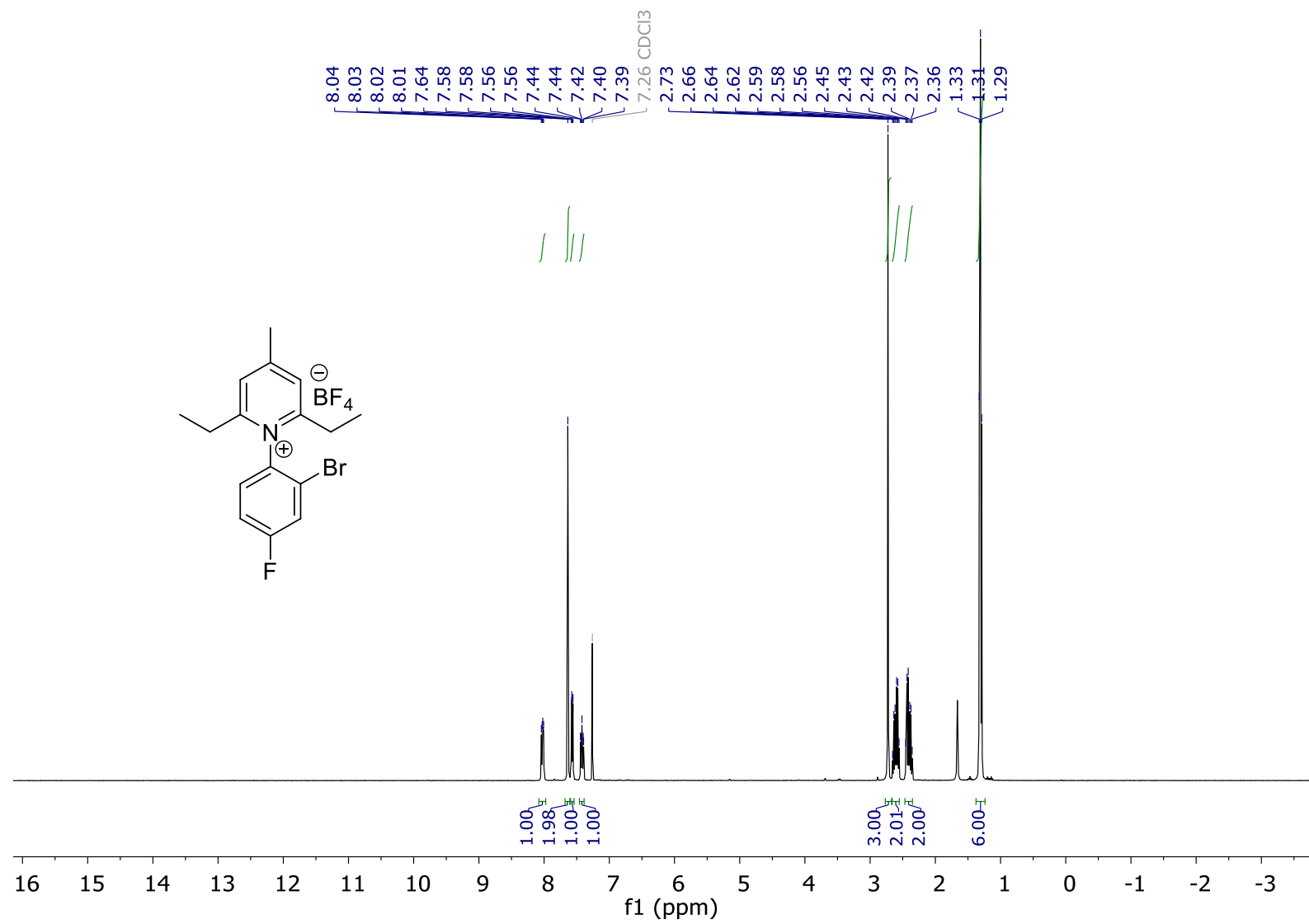
^1H - ^1H NOESY for 3g



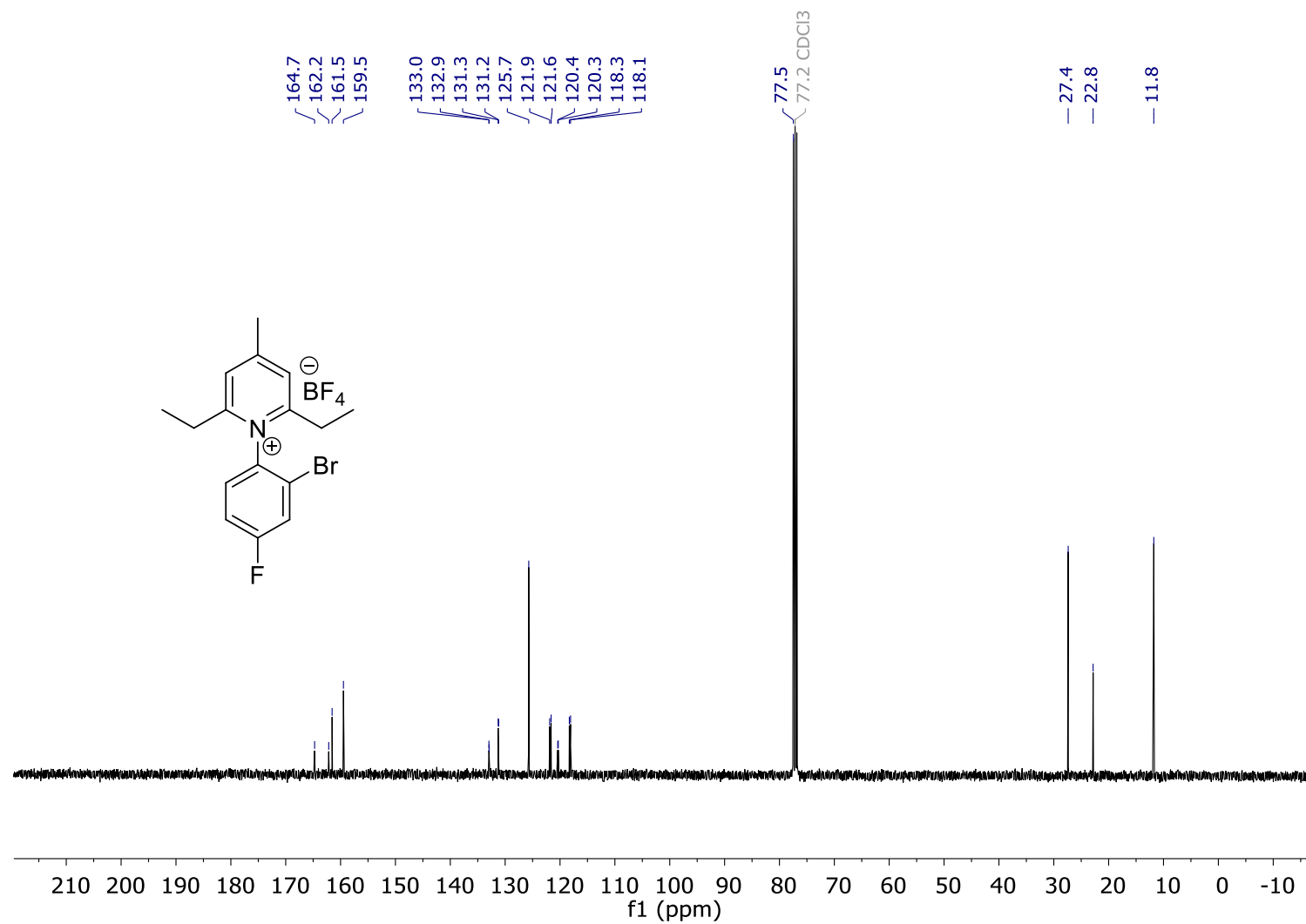
¹H-¹³C HSQC for 3g



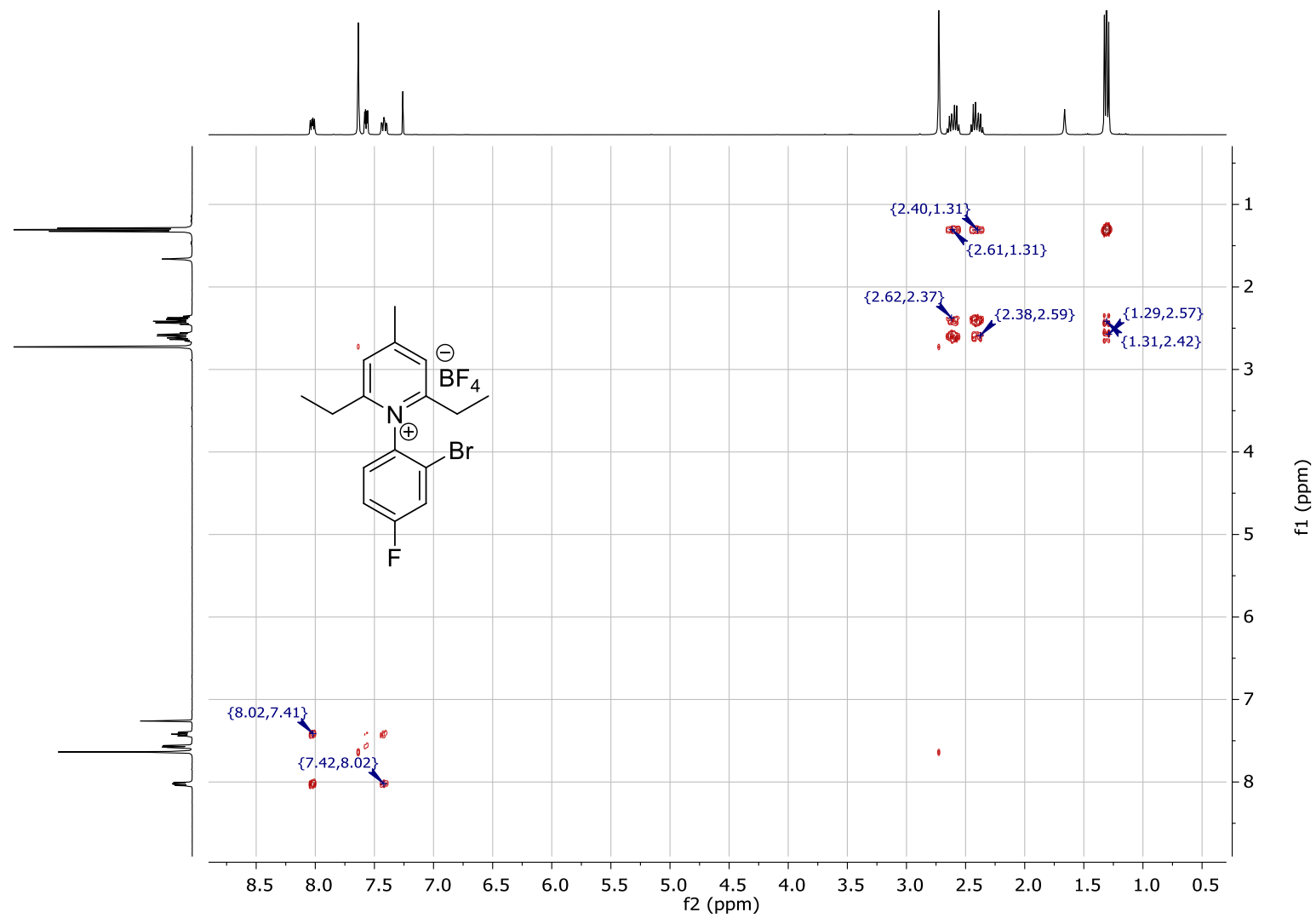
^1H - ^{15}N HMBC for 3g



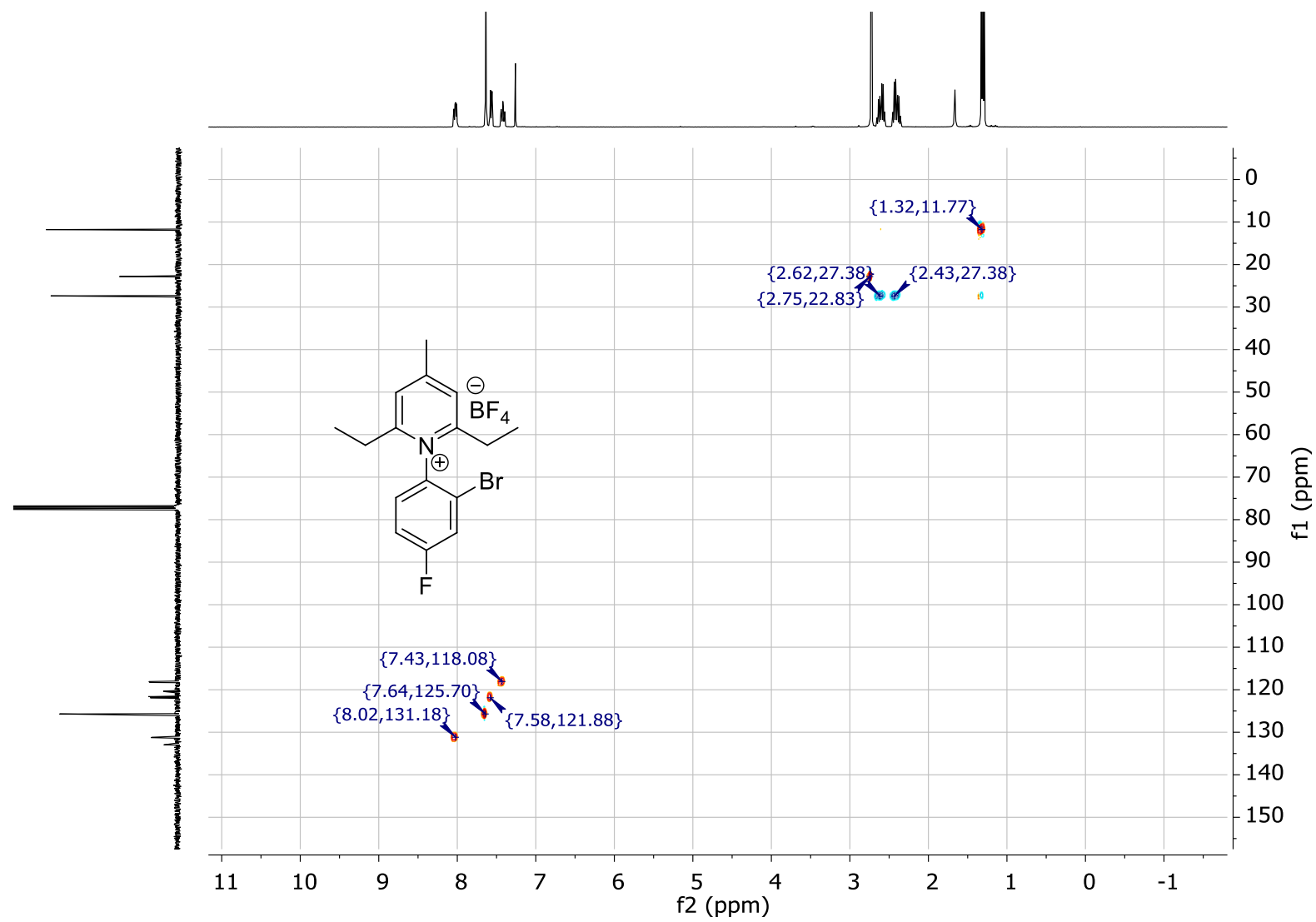
¹H NMR for 3h



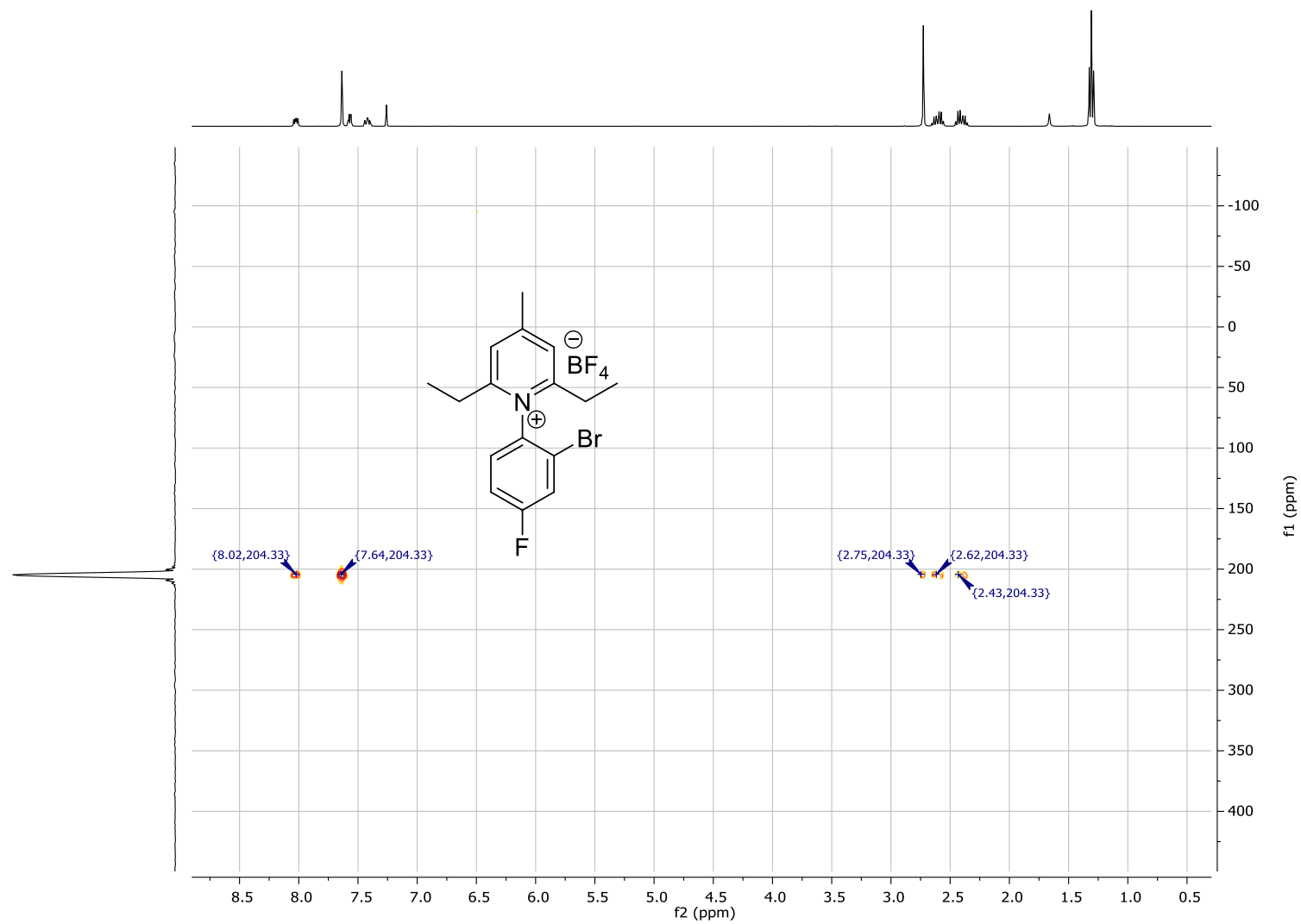
¹³C NMR for 3h



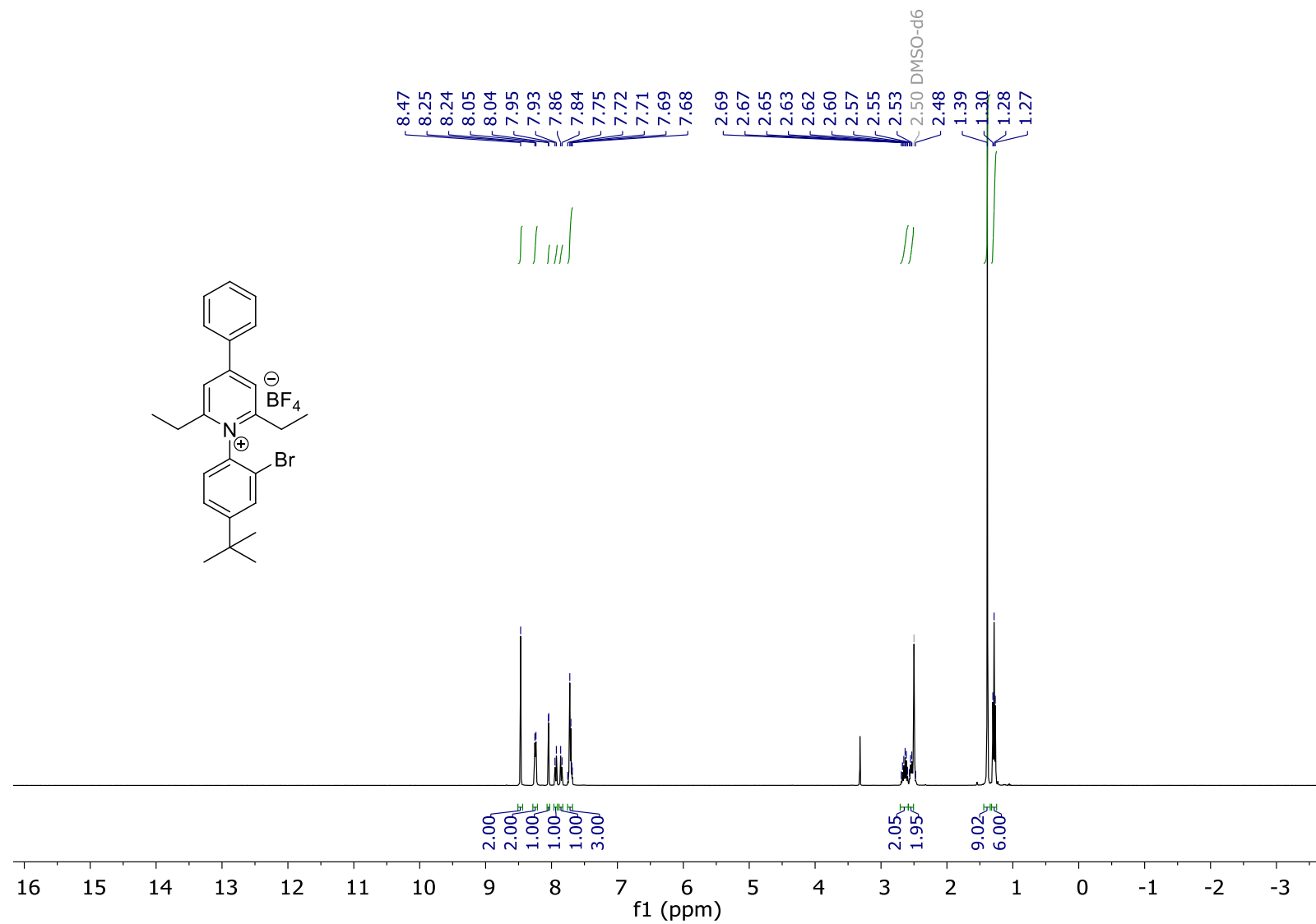
^1H - ^1H COSY for 3h



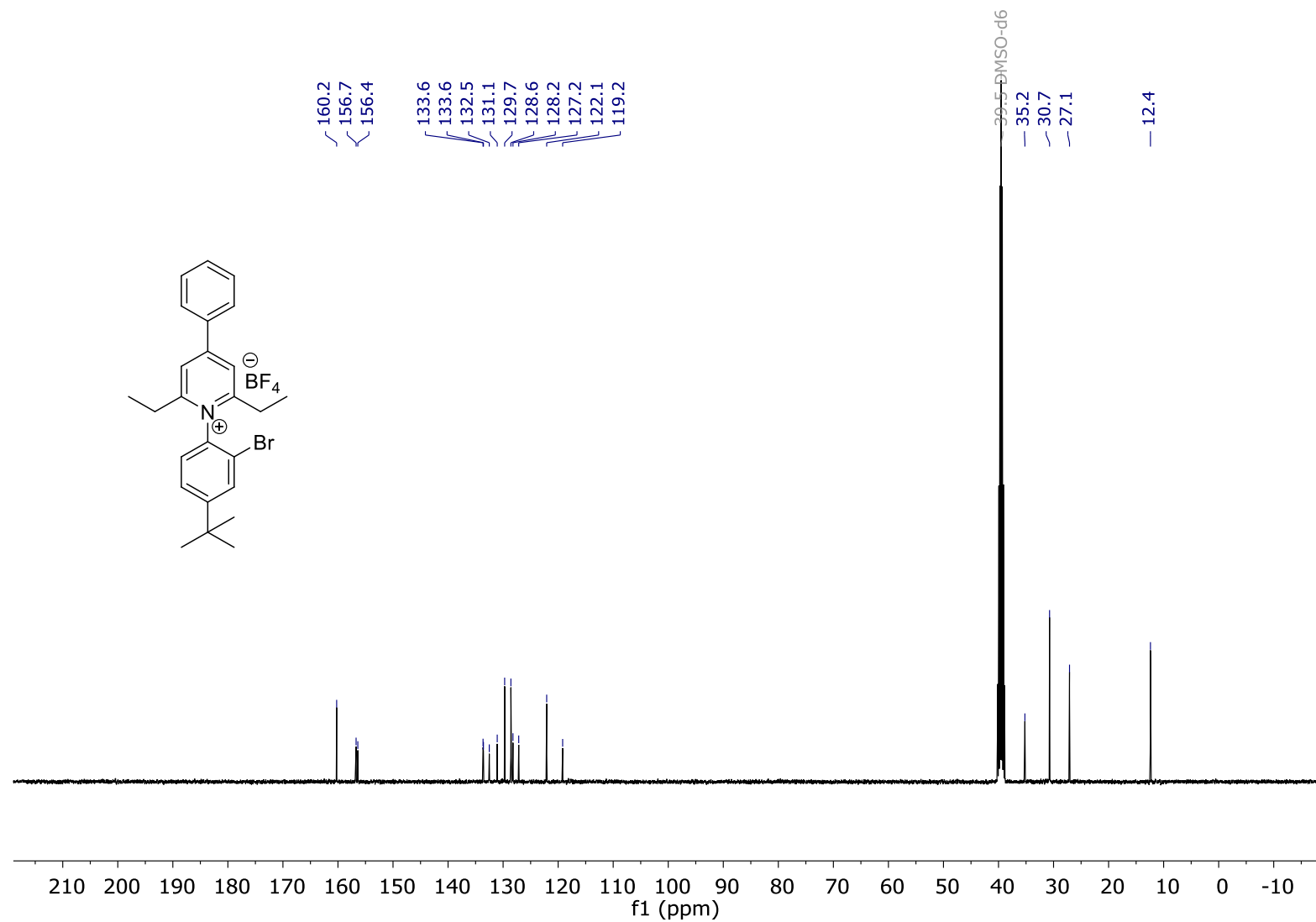
¹H-¹³C HSQC for 3h



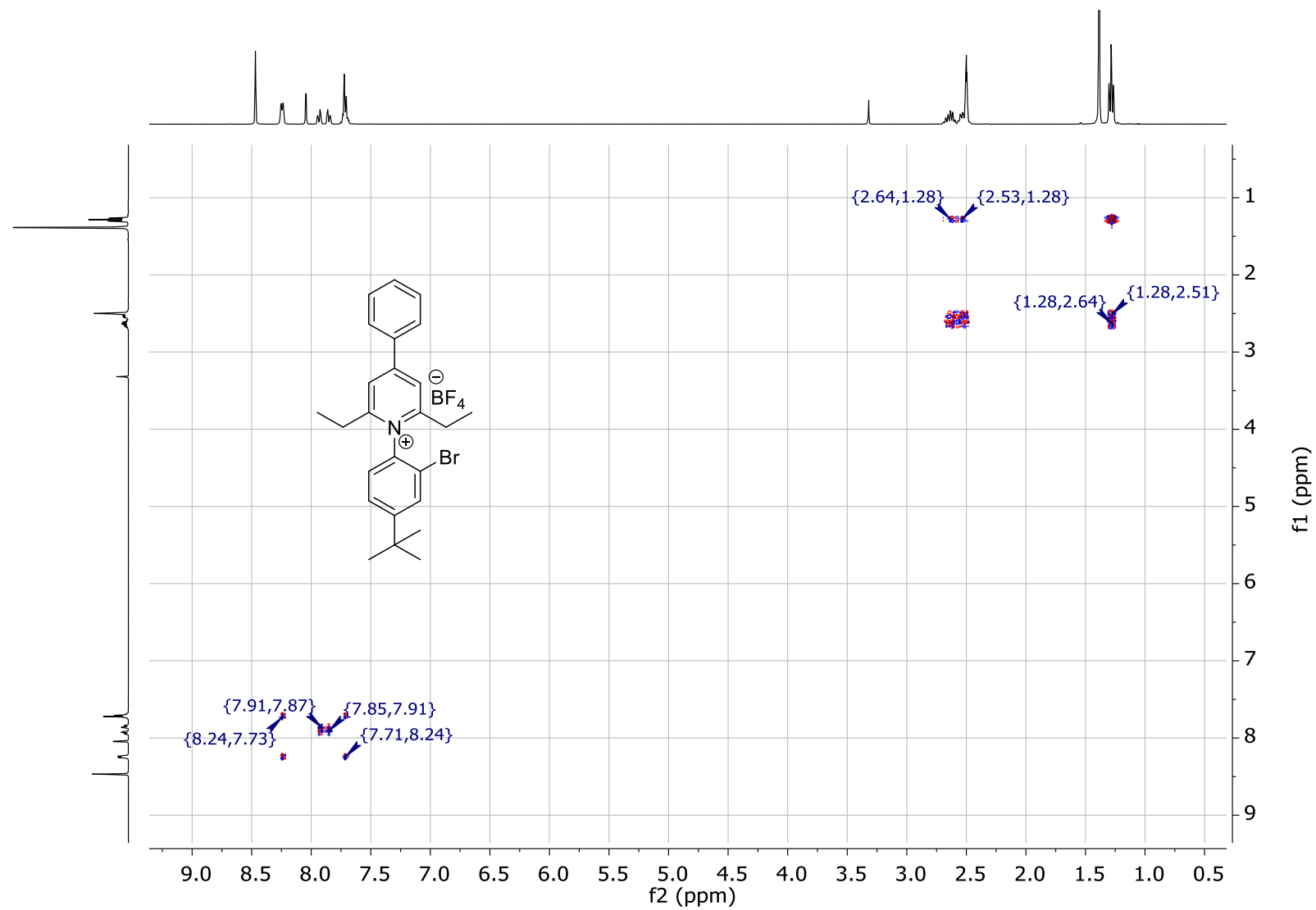
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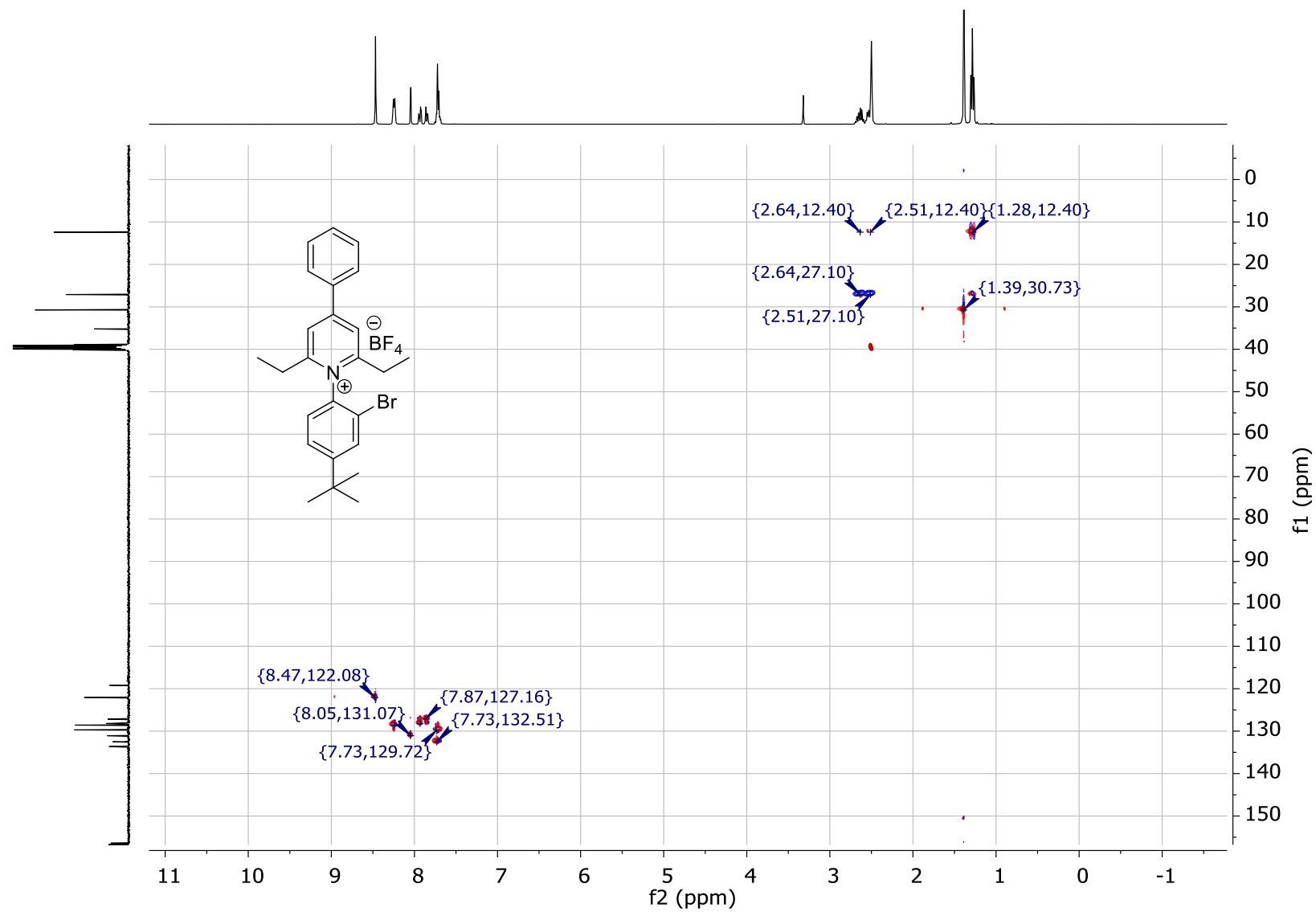
¹H NMR for 3i



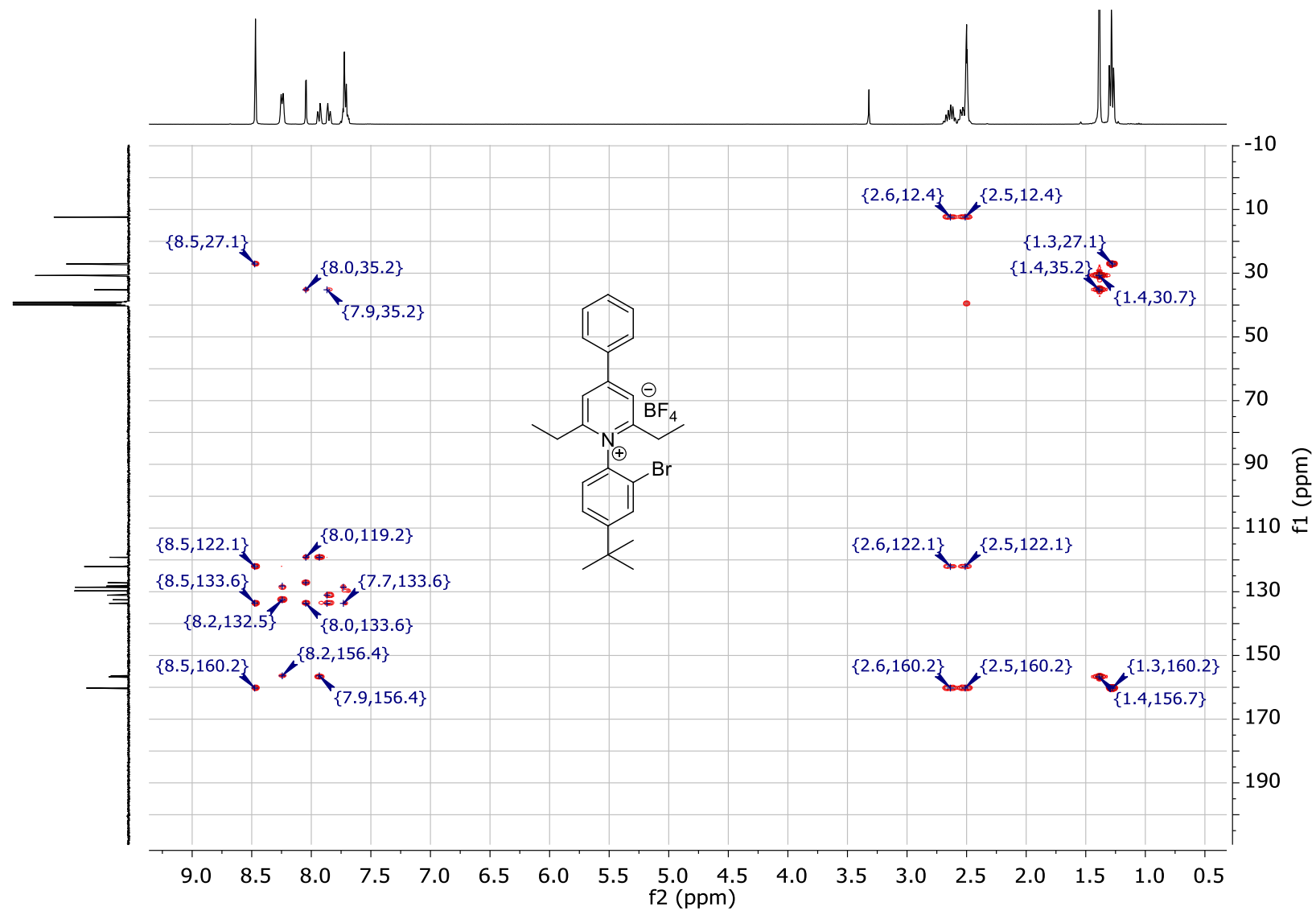
¹³C NMR for 3i



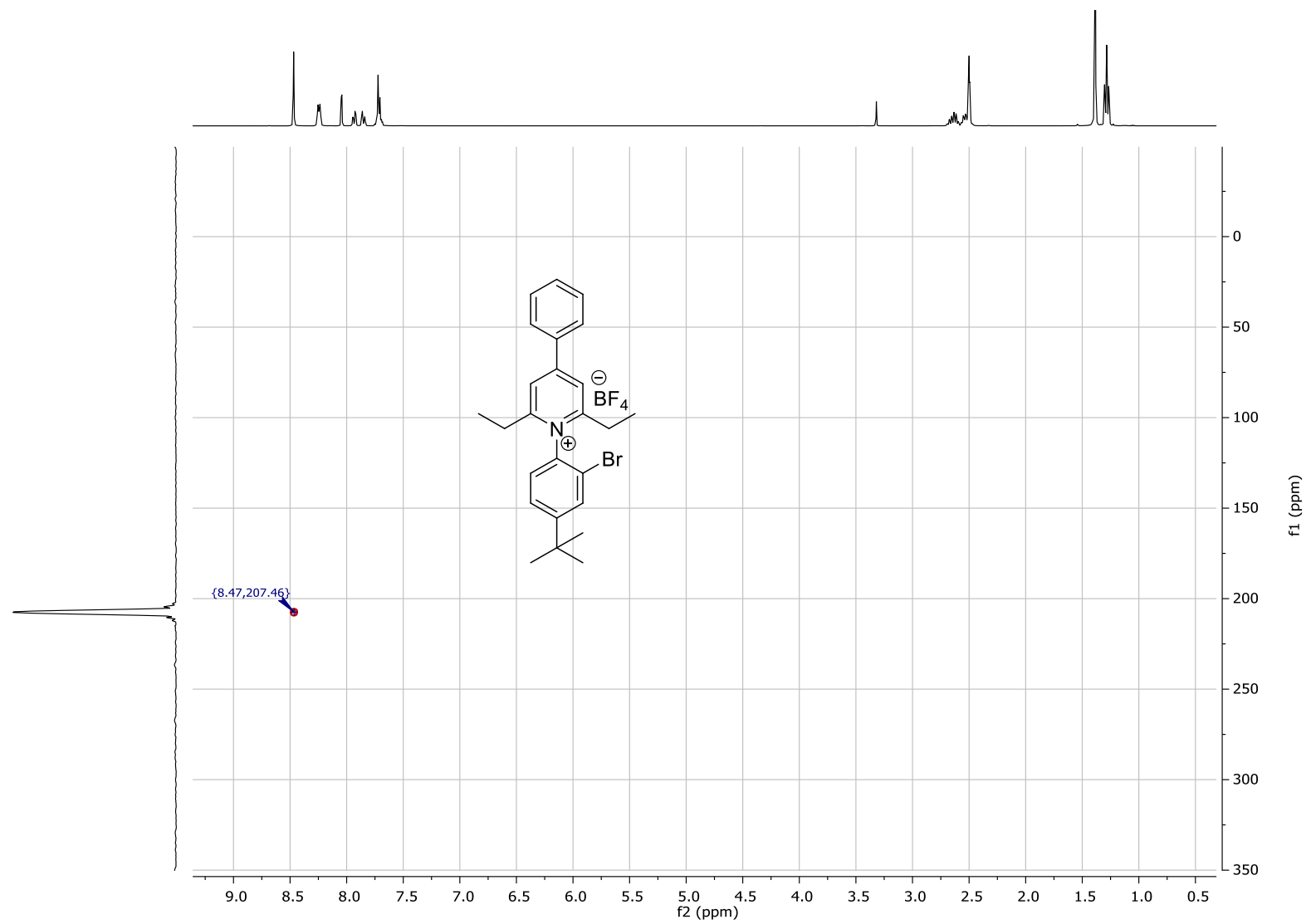
^1H - ^1H COSY for 3i



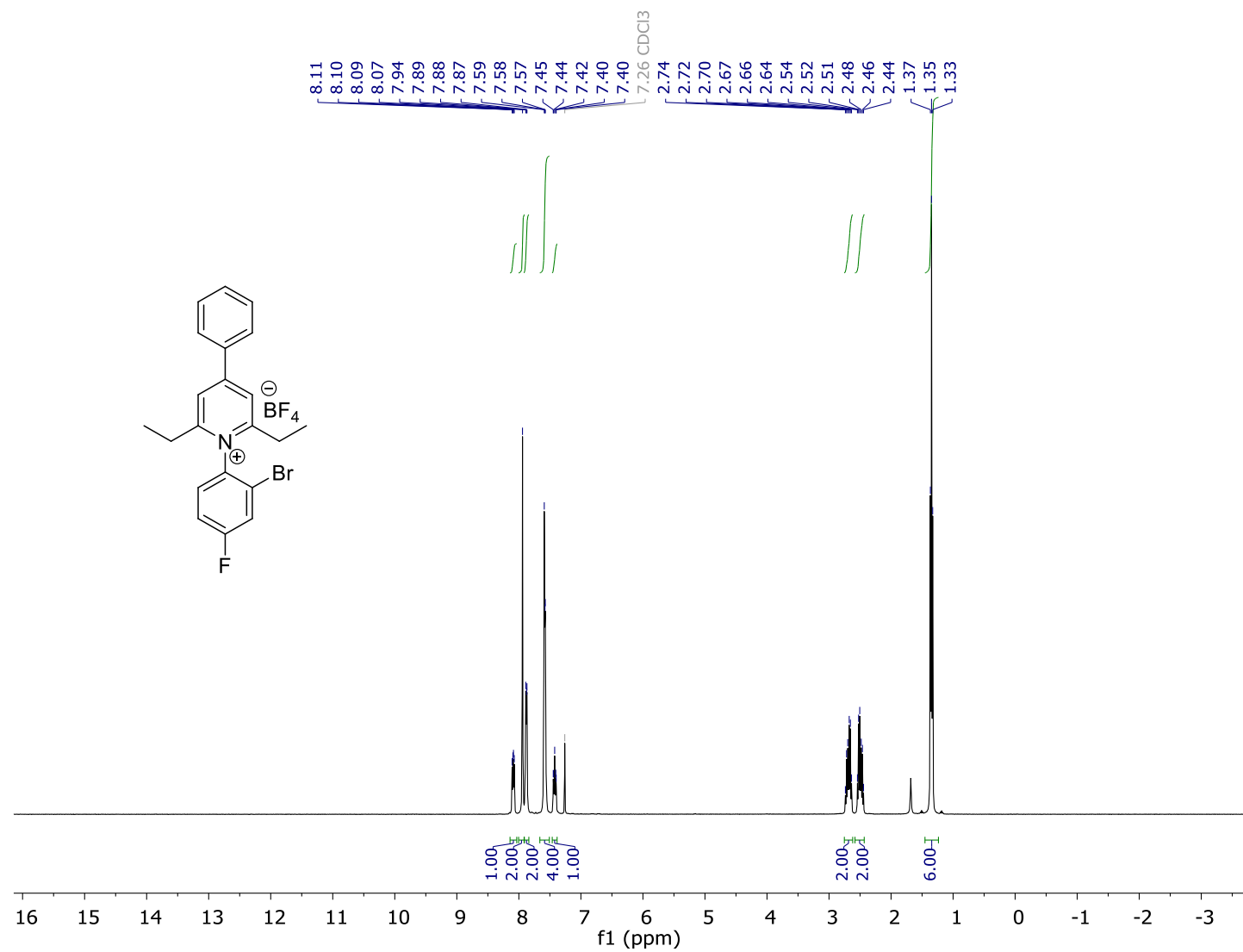
^1H - ^{13}C HSQC for 3i



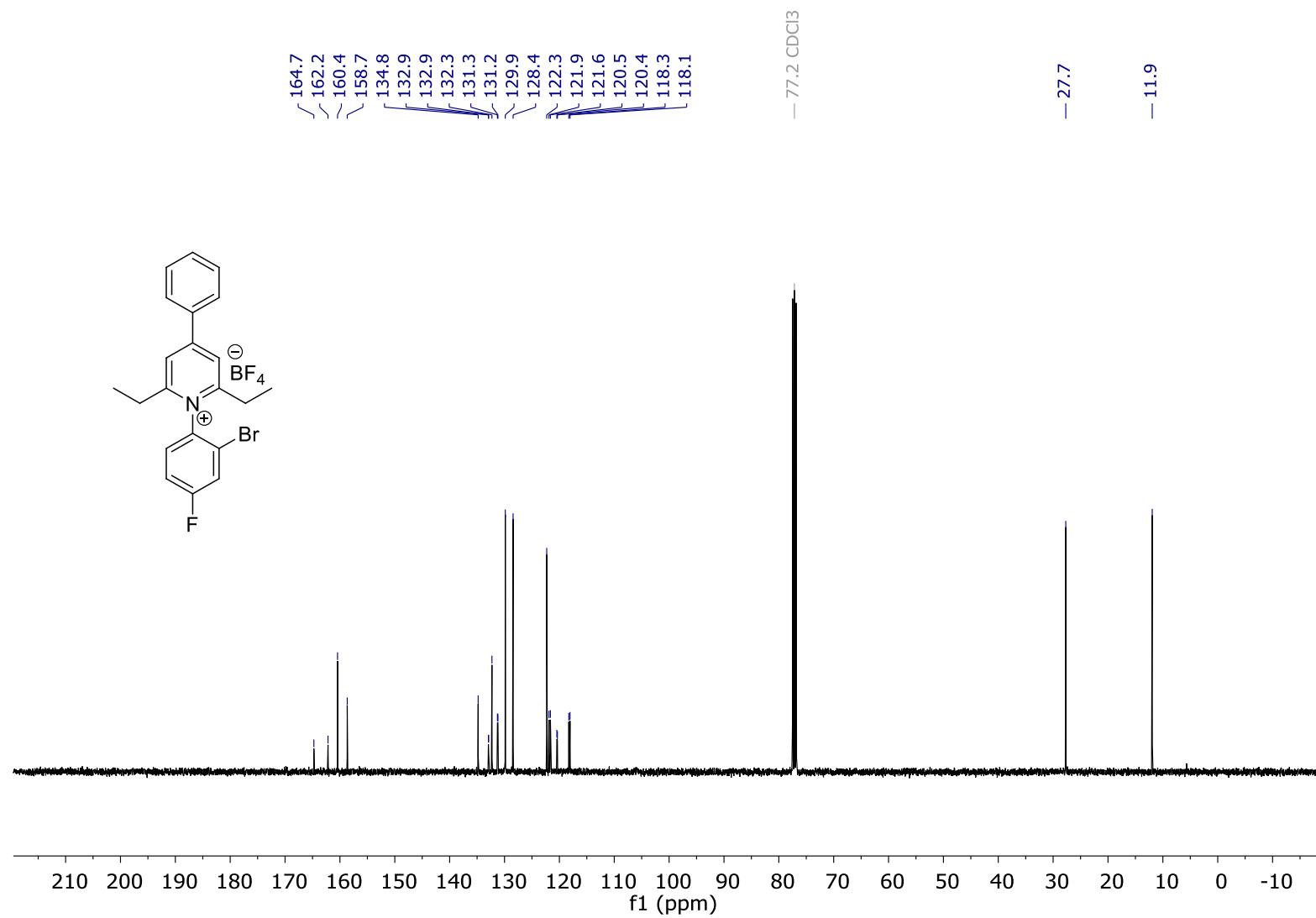
¹H-¹³C HMBC for 3i



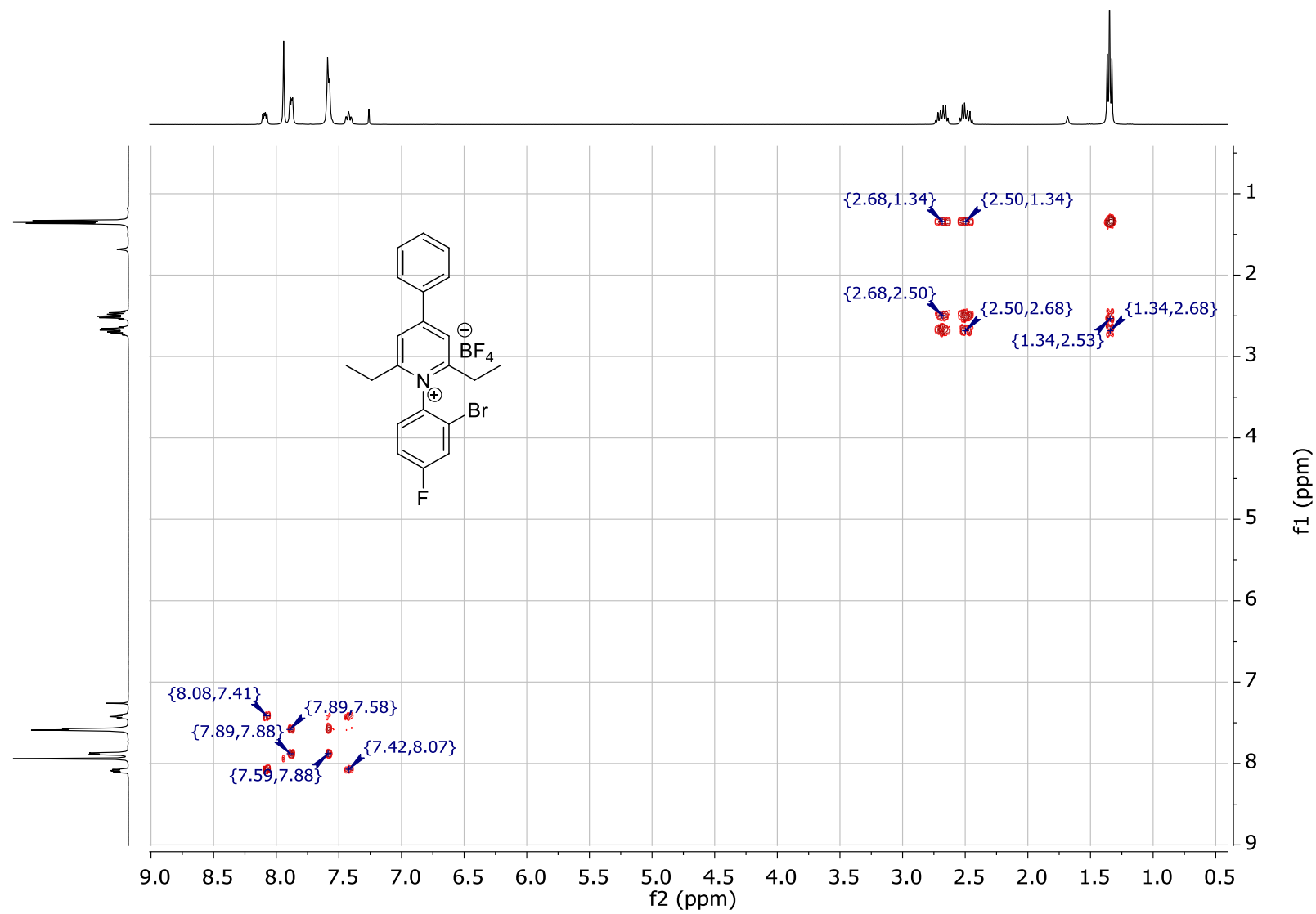
^1H - ^{15}N HMBC for **3i**



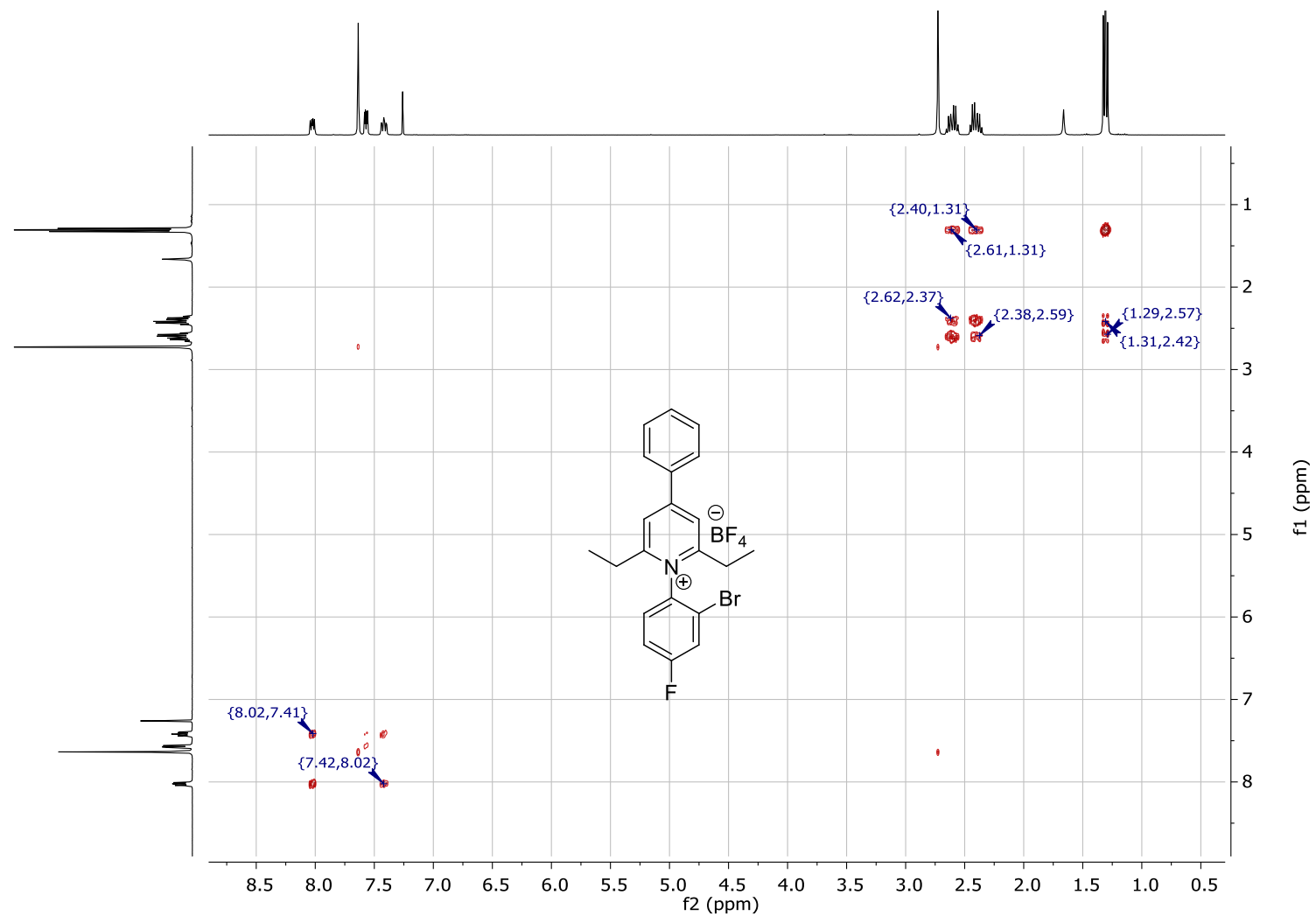
¹H NMR for 3j



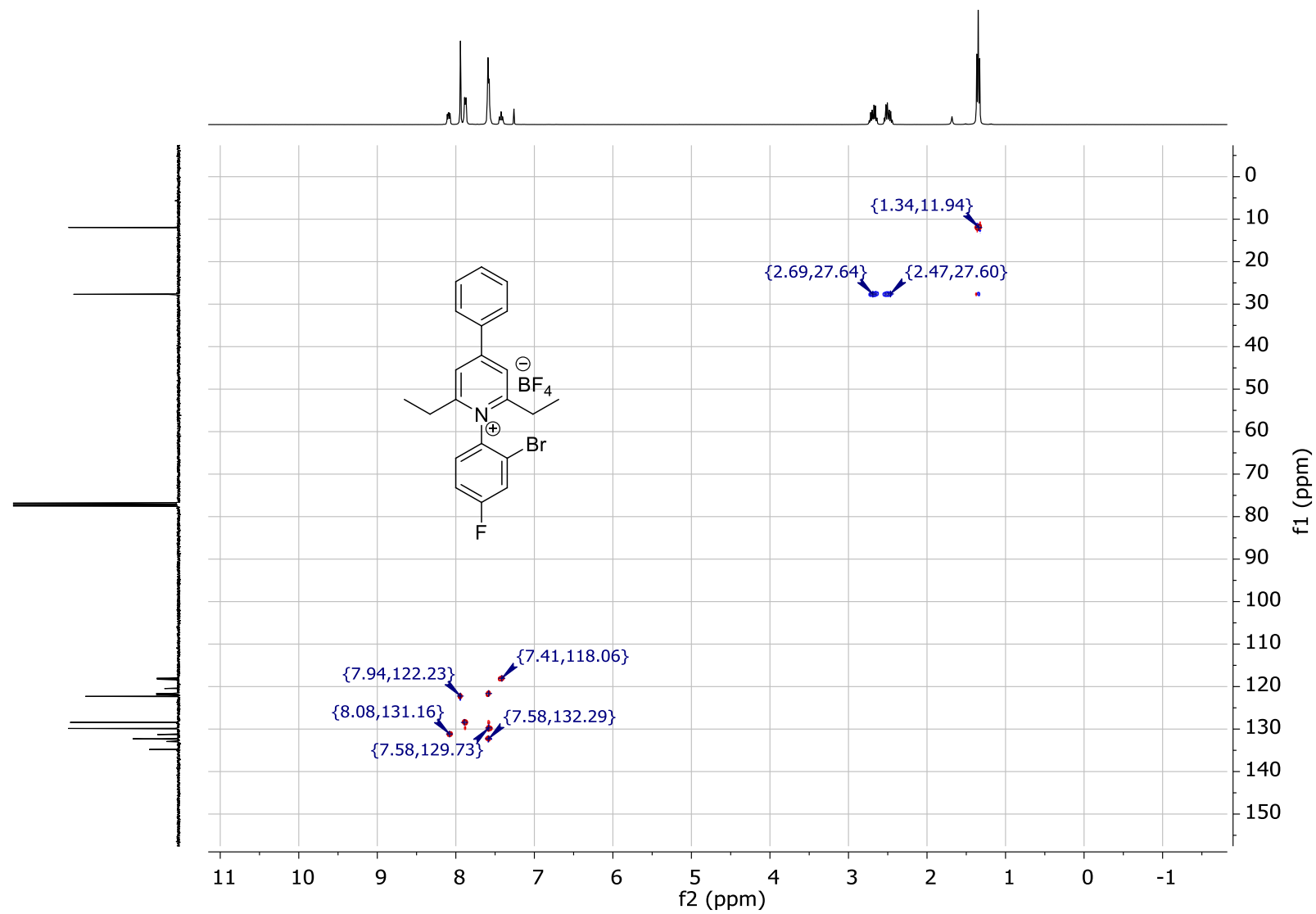
¹³C NMR for 3j



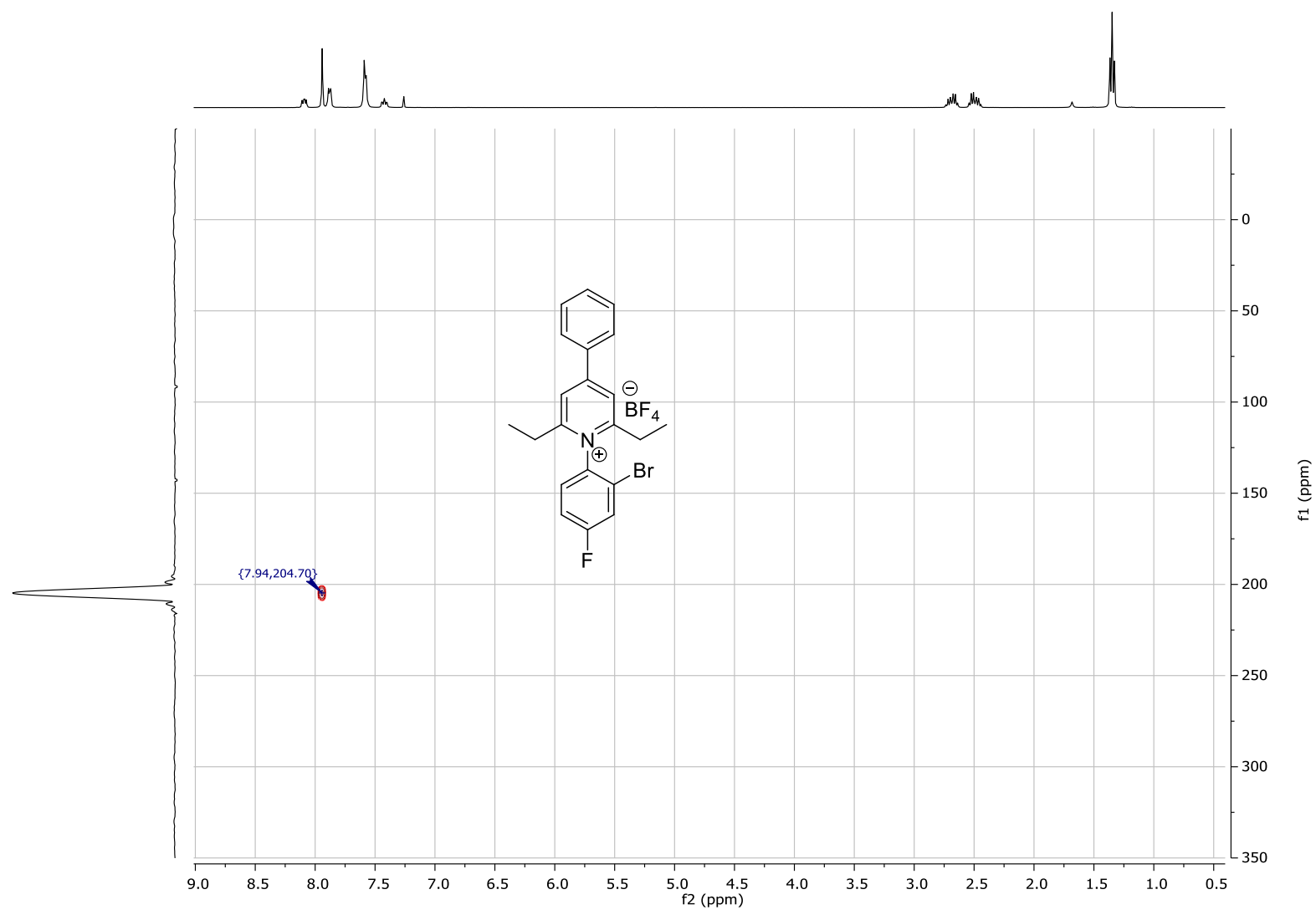
^1H - ^{13}C HMBC for 3j



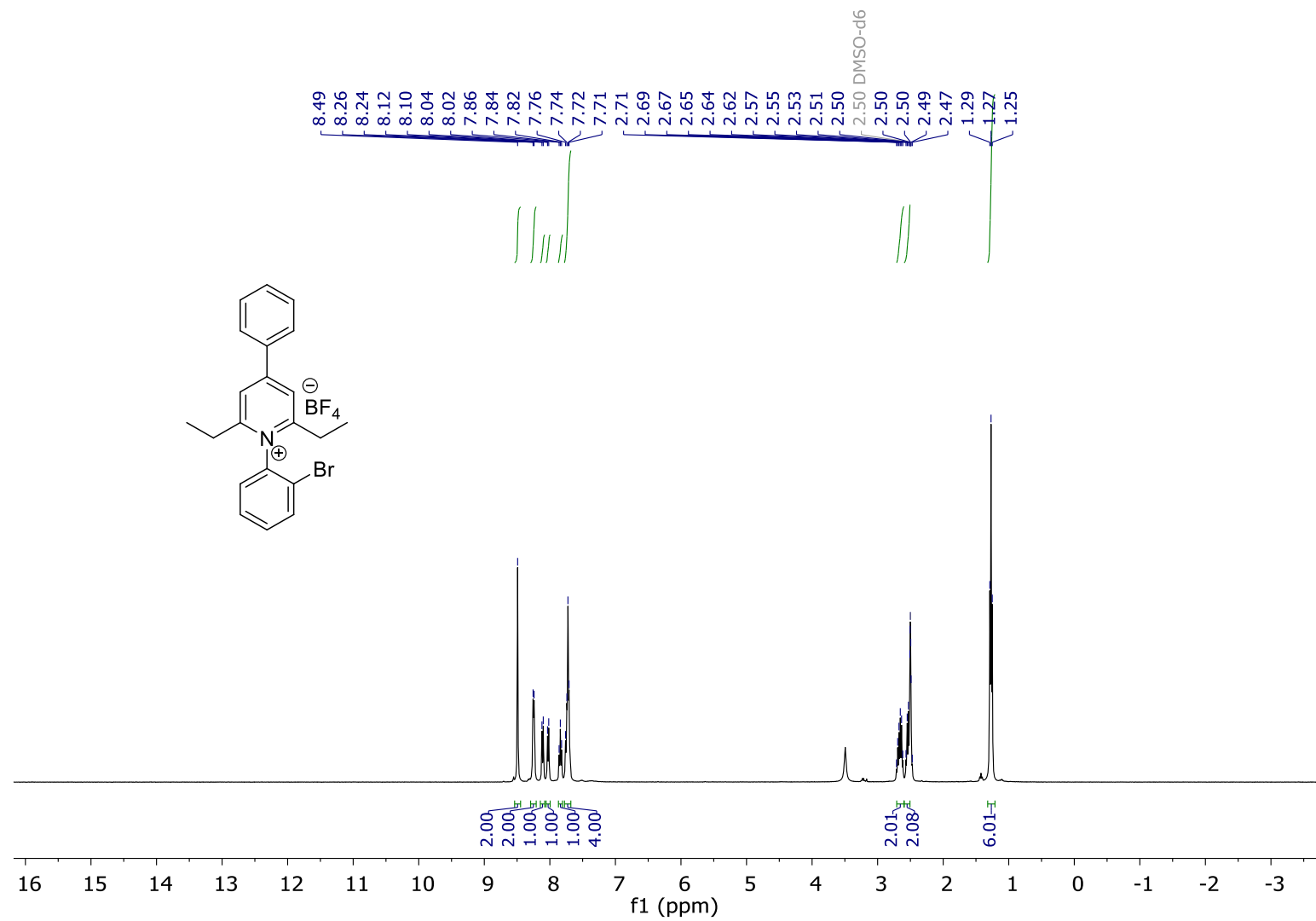
^1H - ^1H NOESY for 3j



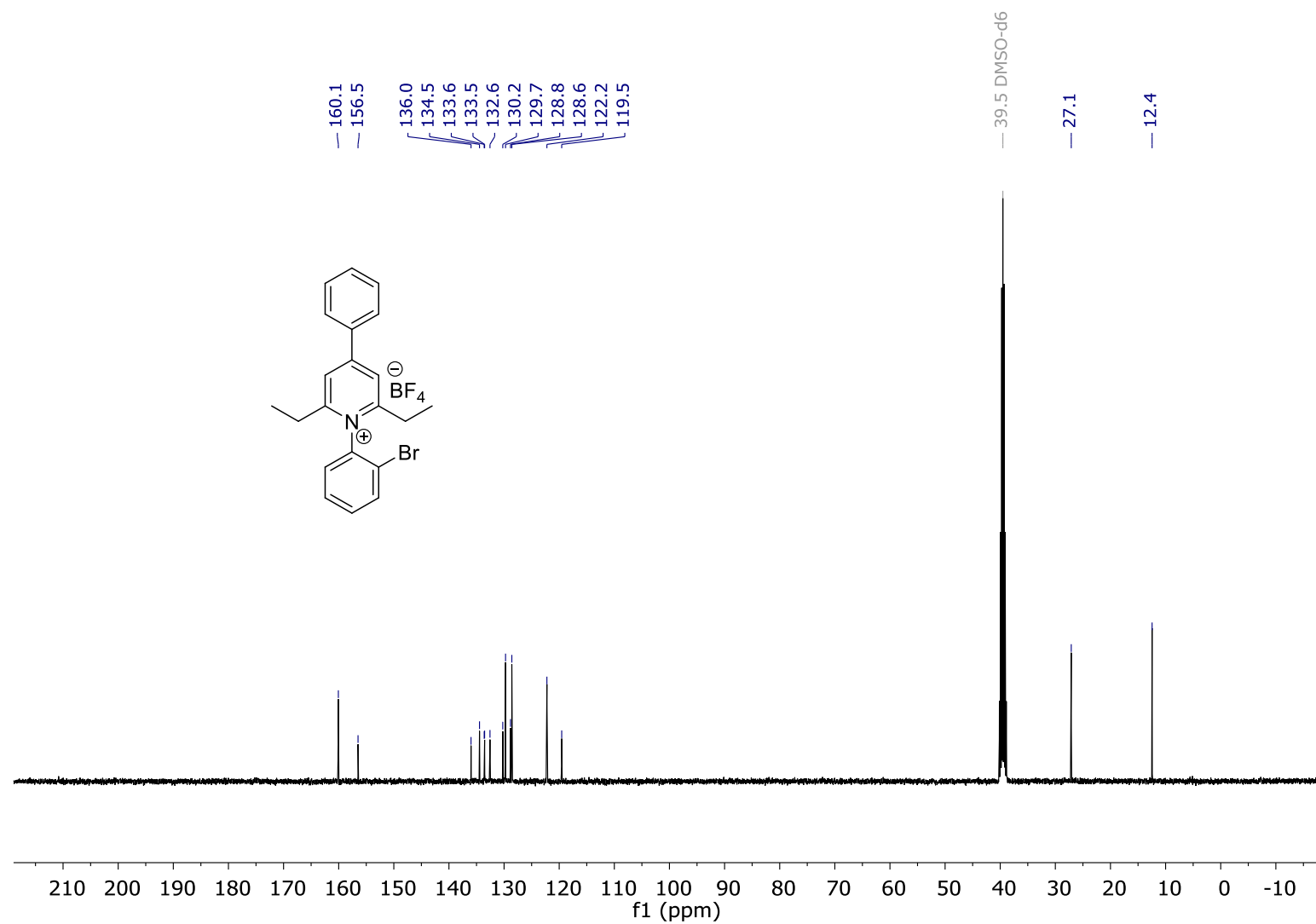
^1H - ^{13}C HSQC for 3j



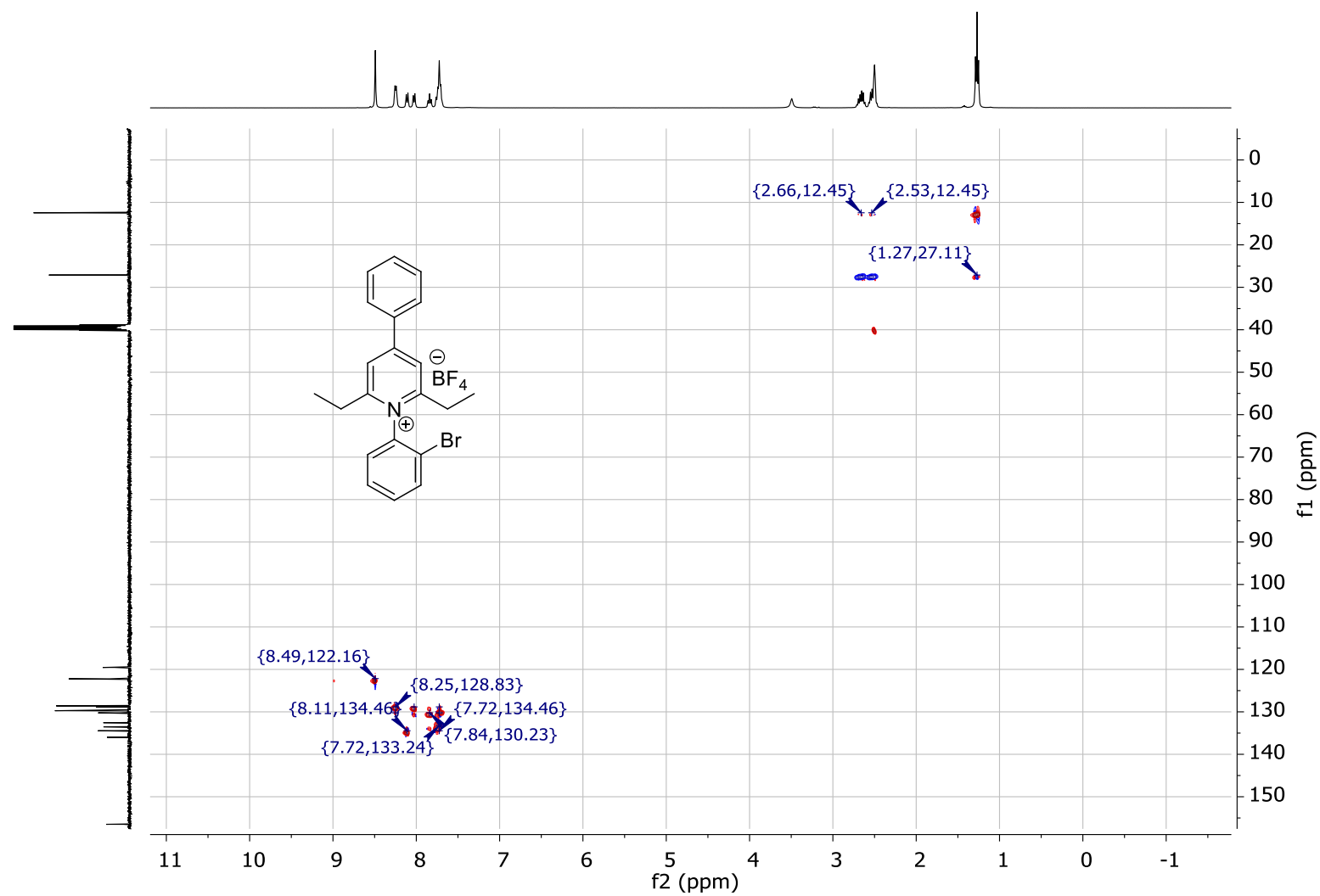
^1H - ^{15}N HMBC 3j



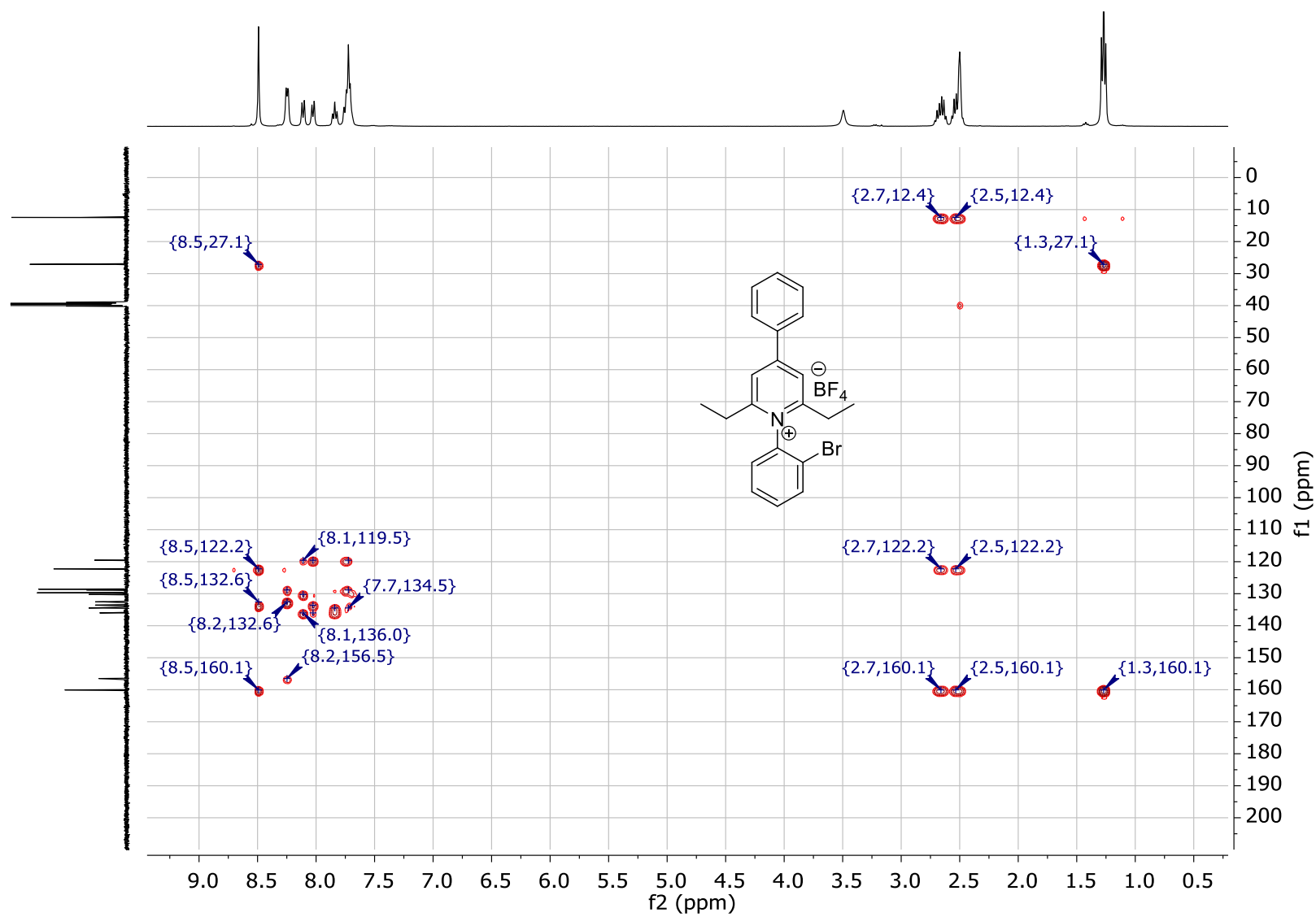
¹H NMR for 3k



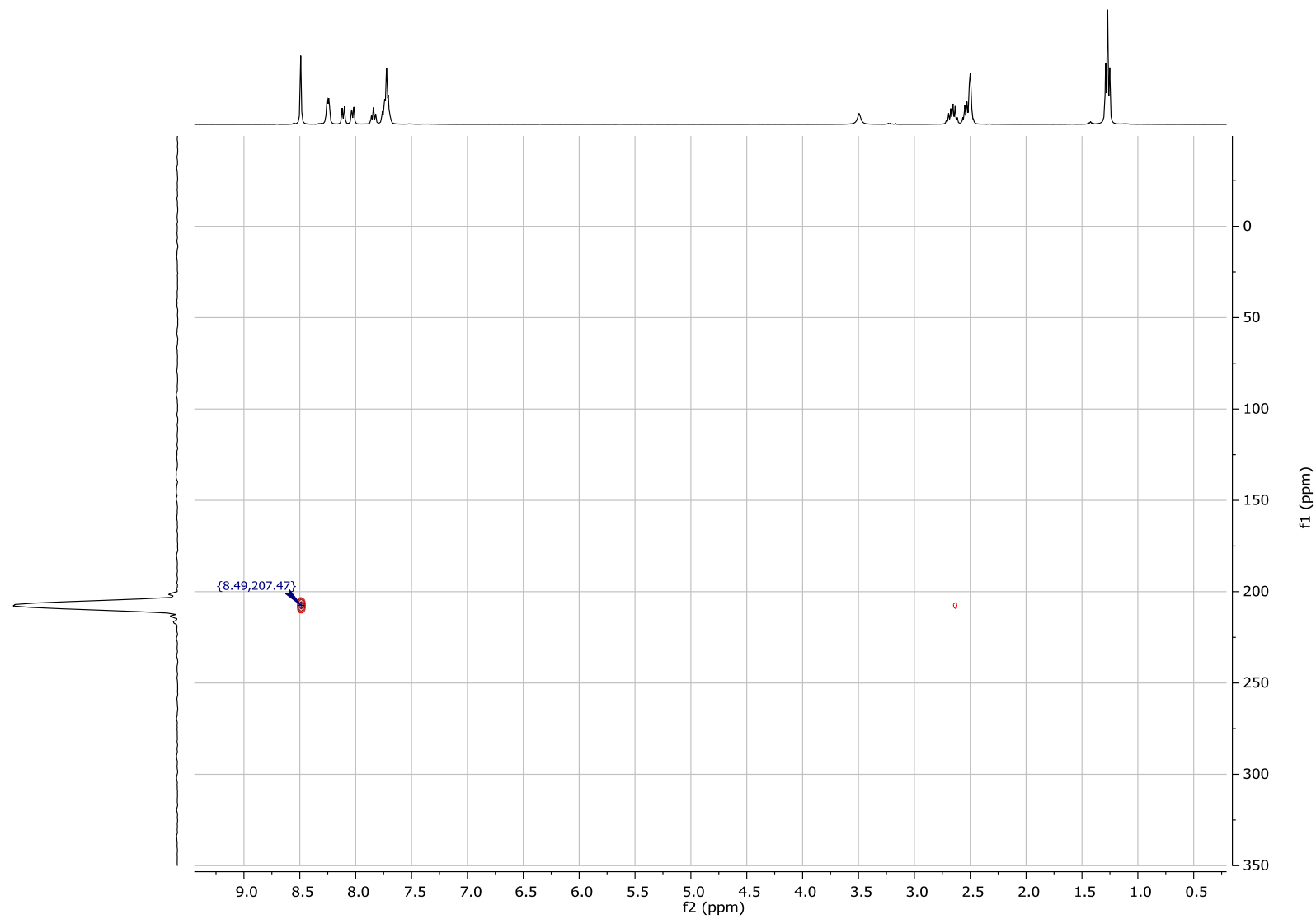
¹³C NMR for 3k



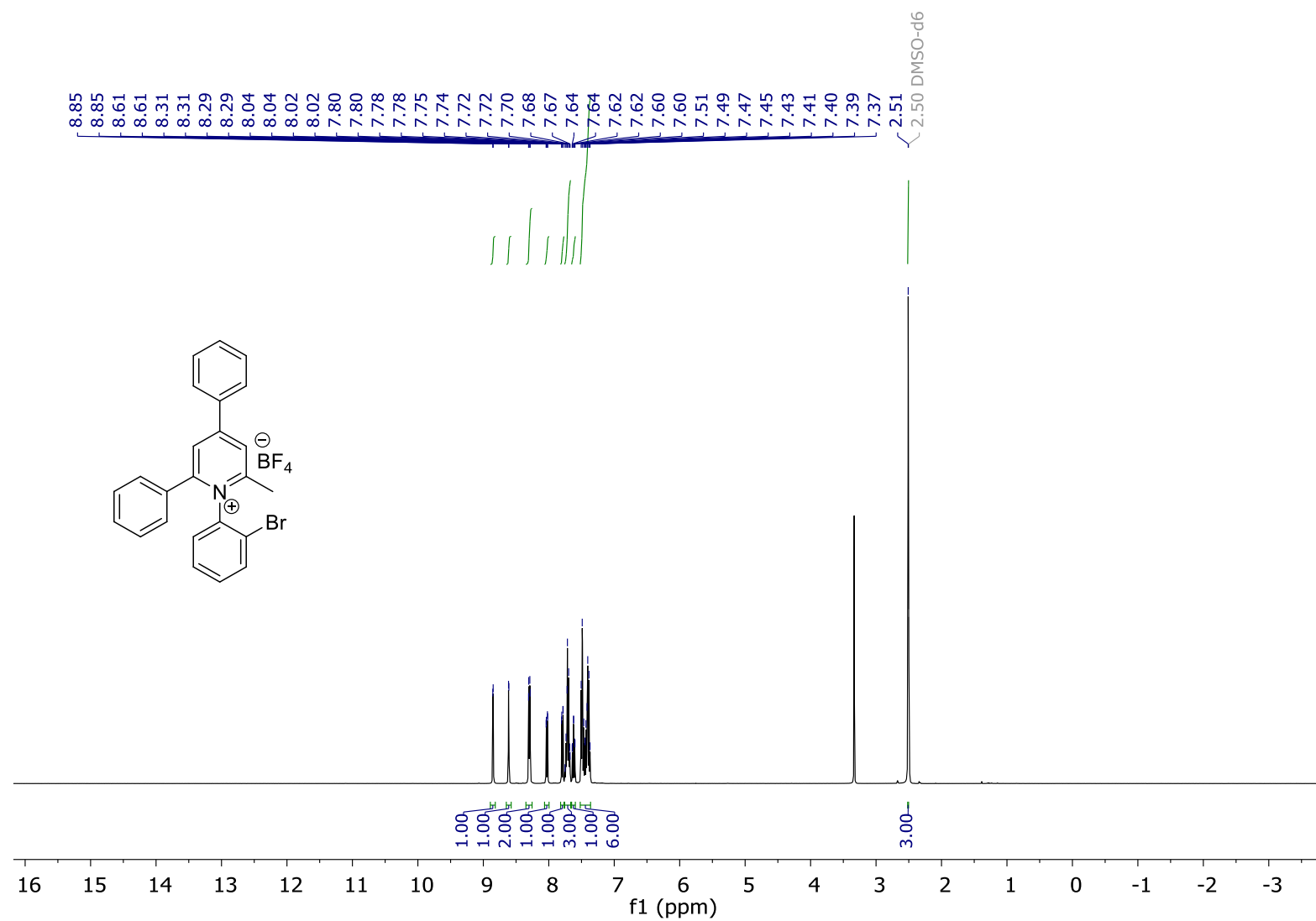
¹H-¹³C HSQC for 3k



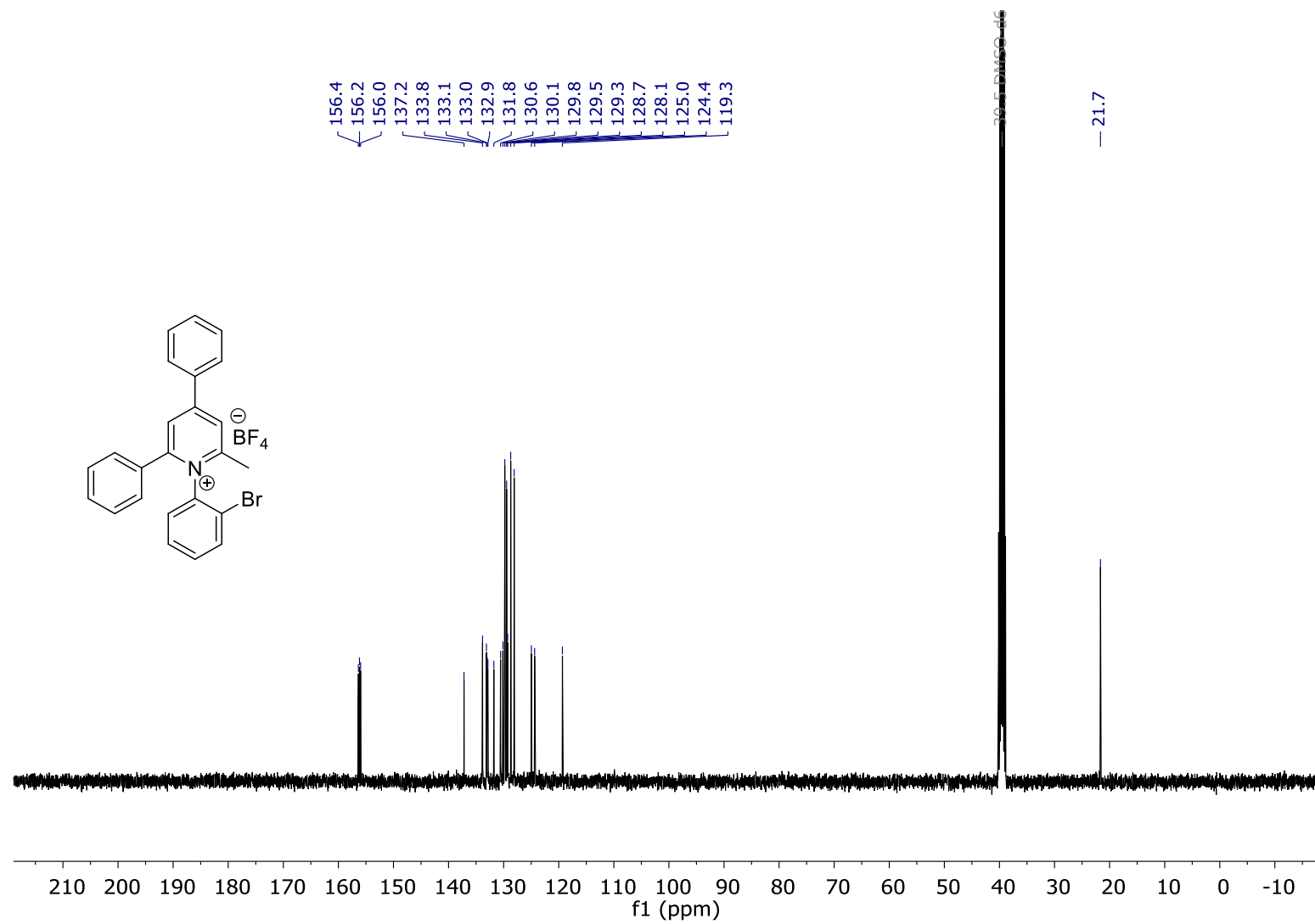
^1H - ^{13}C HMBC for 3k



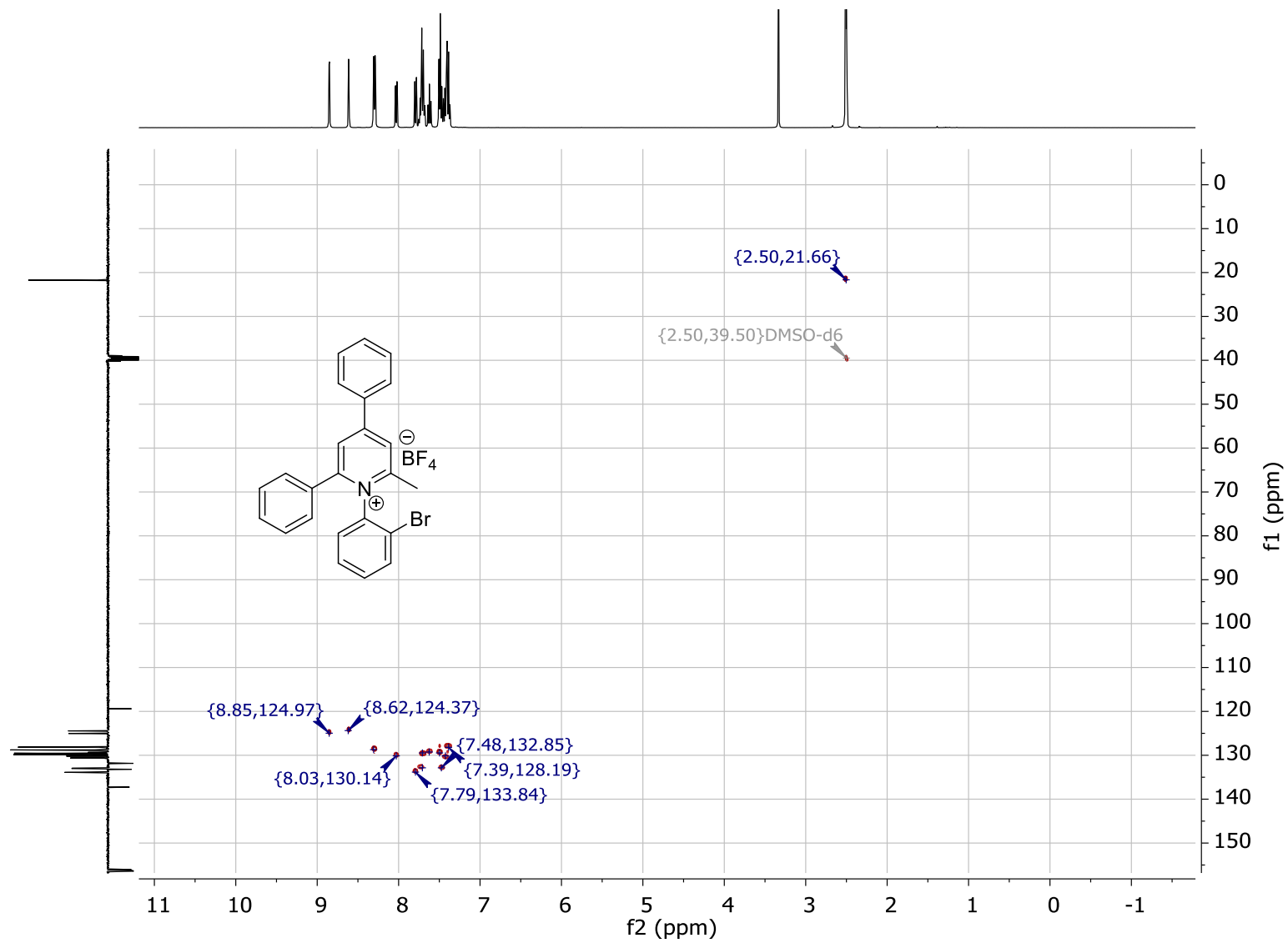
^1H - ^{15}N HMBC 3k



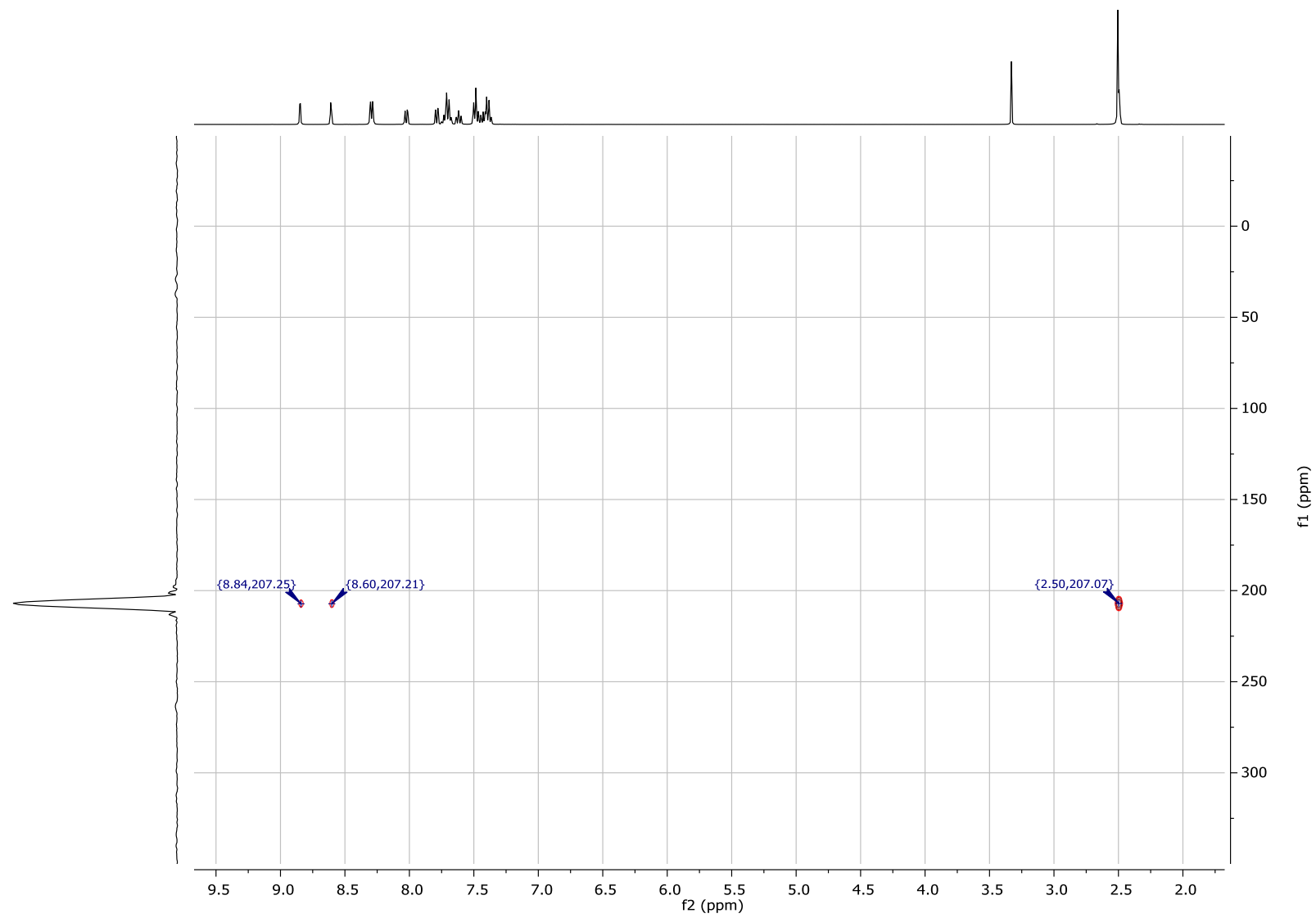
¹H NMR for 3l



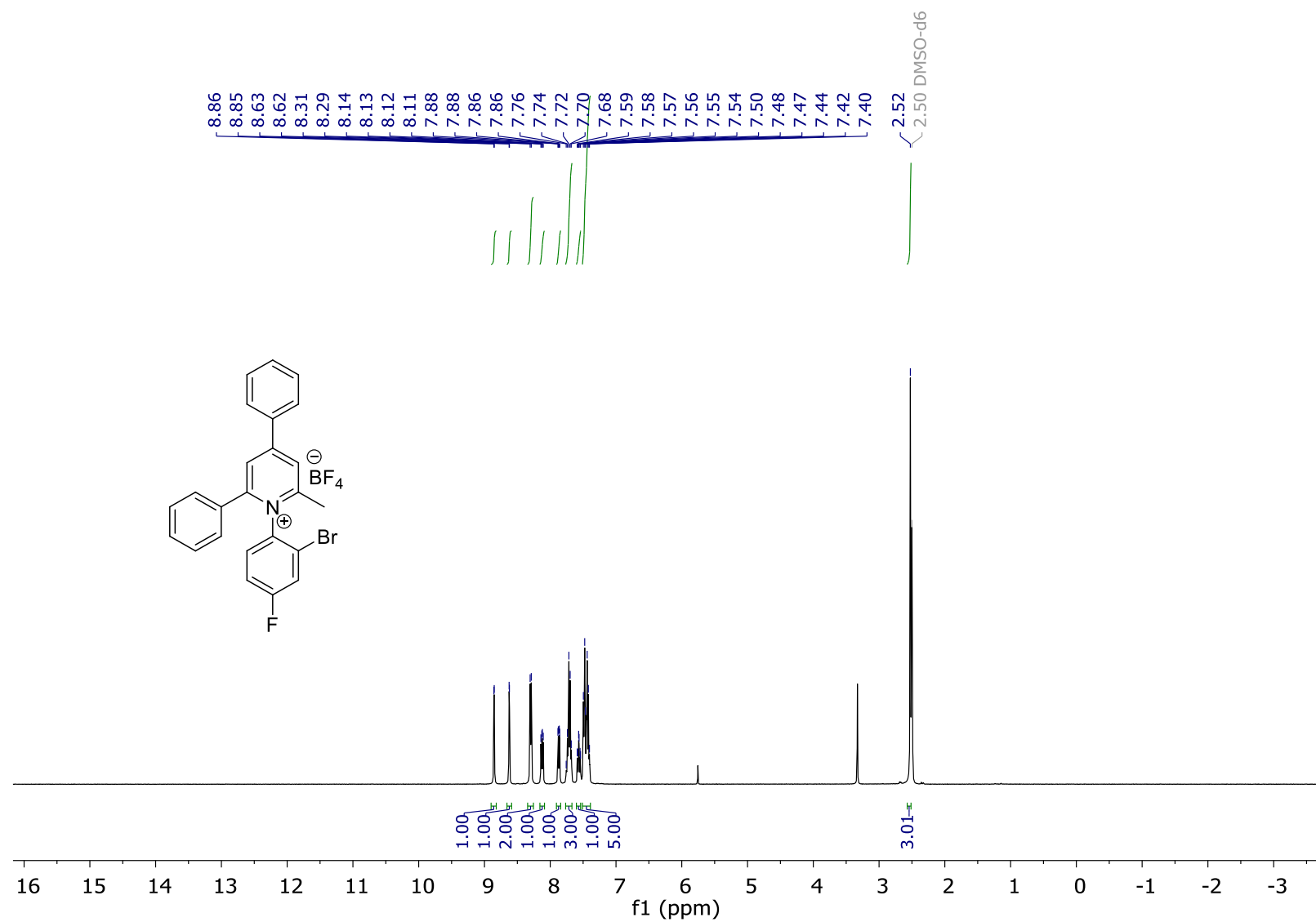
¹³C NMR for 3l



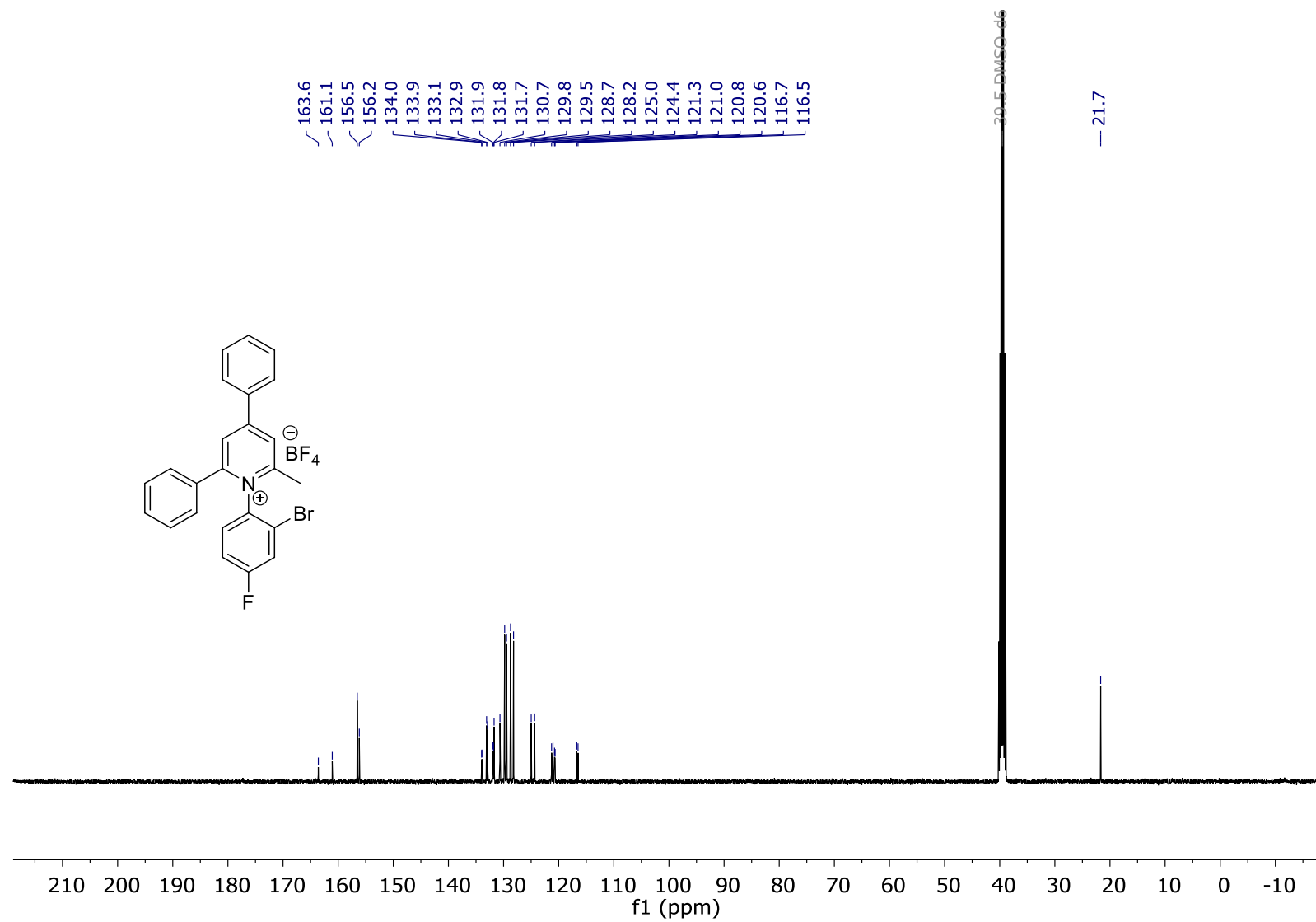
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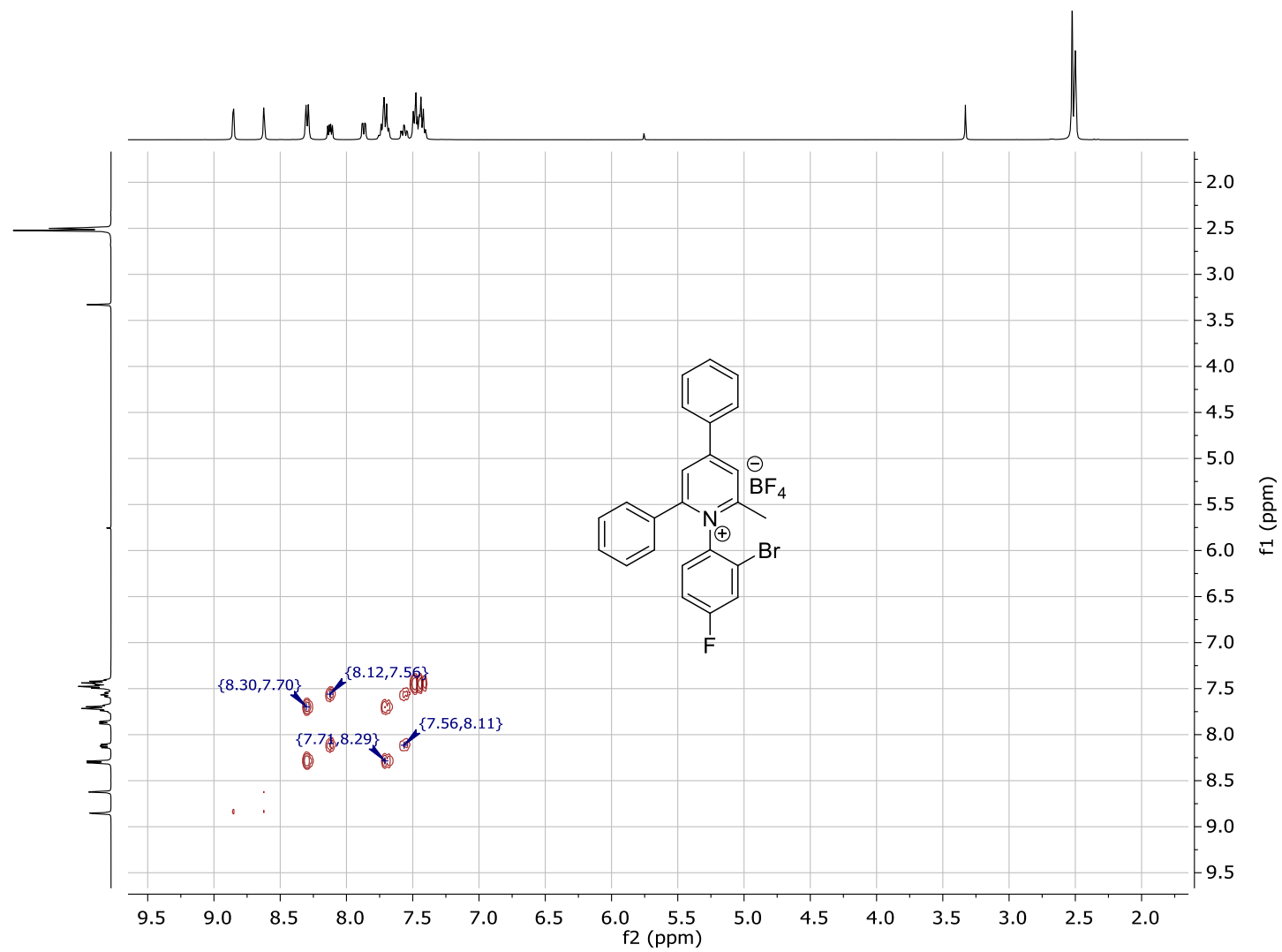
^1H - ^{15}N HMBC for 3l



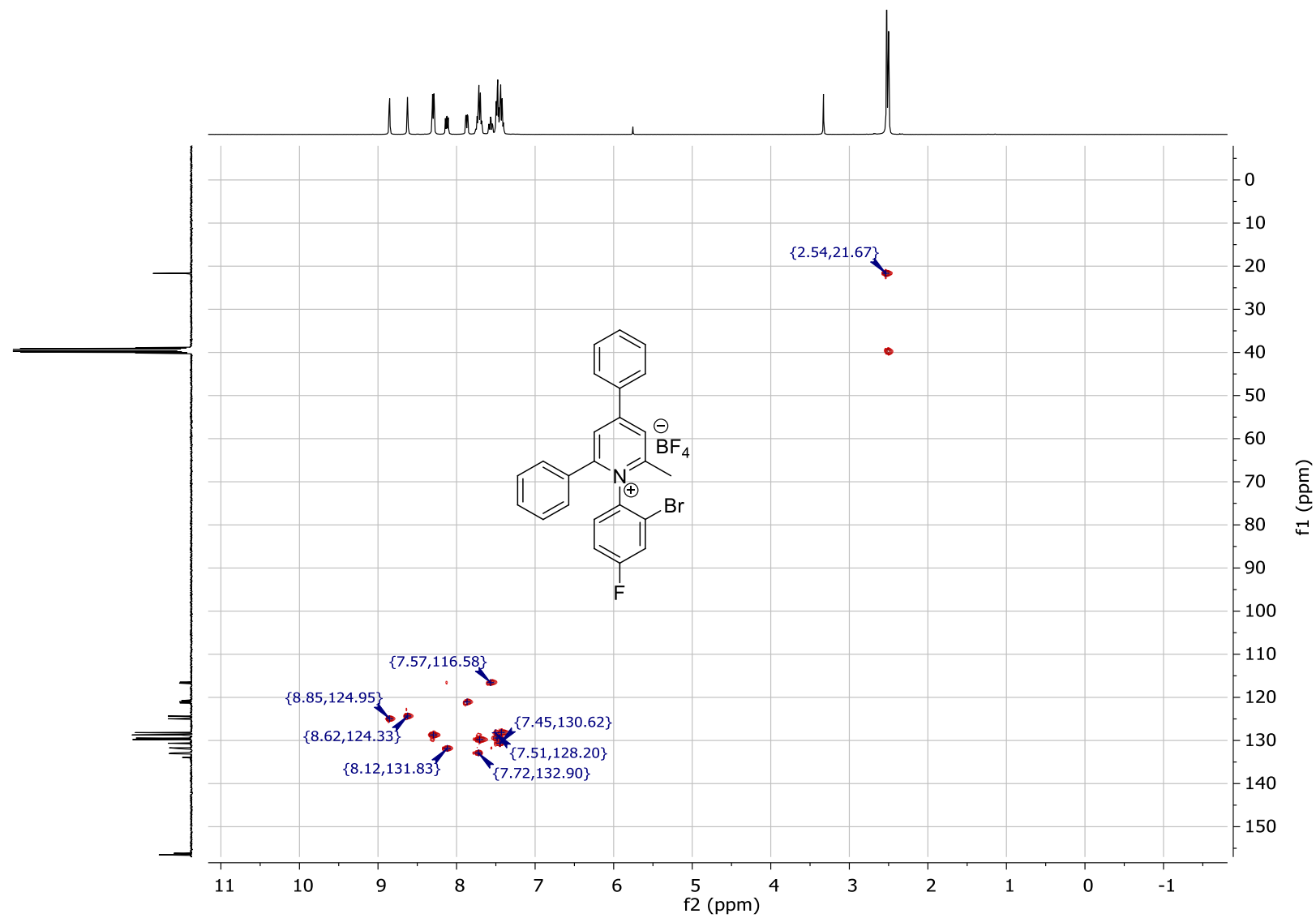
¹H NMR for 3m



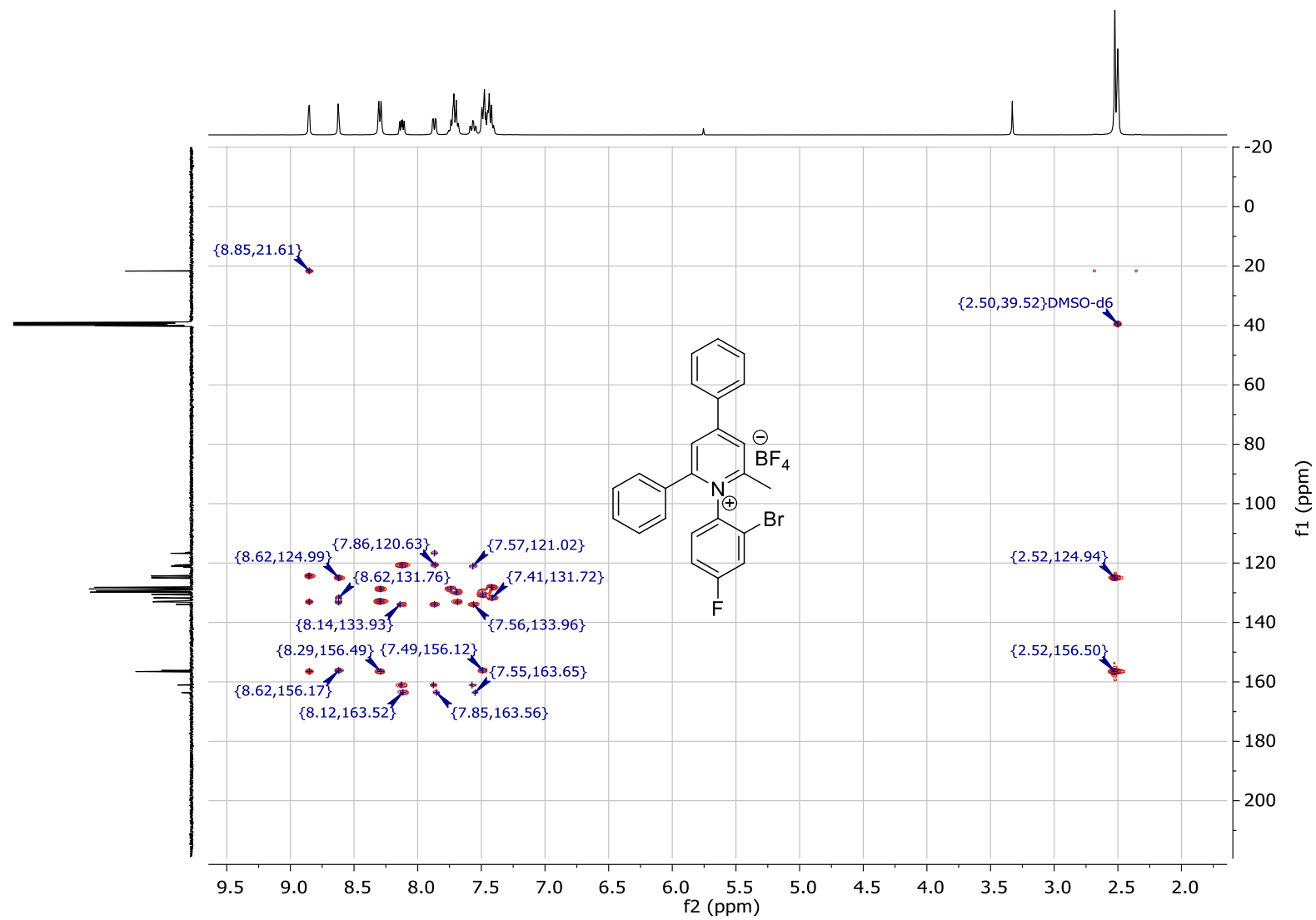
¹³C NMR for 3m



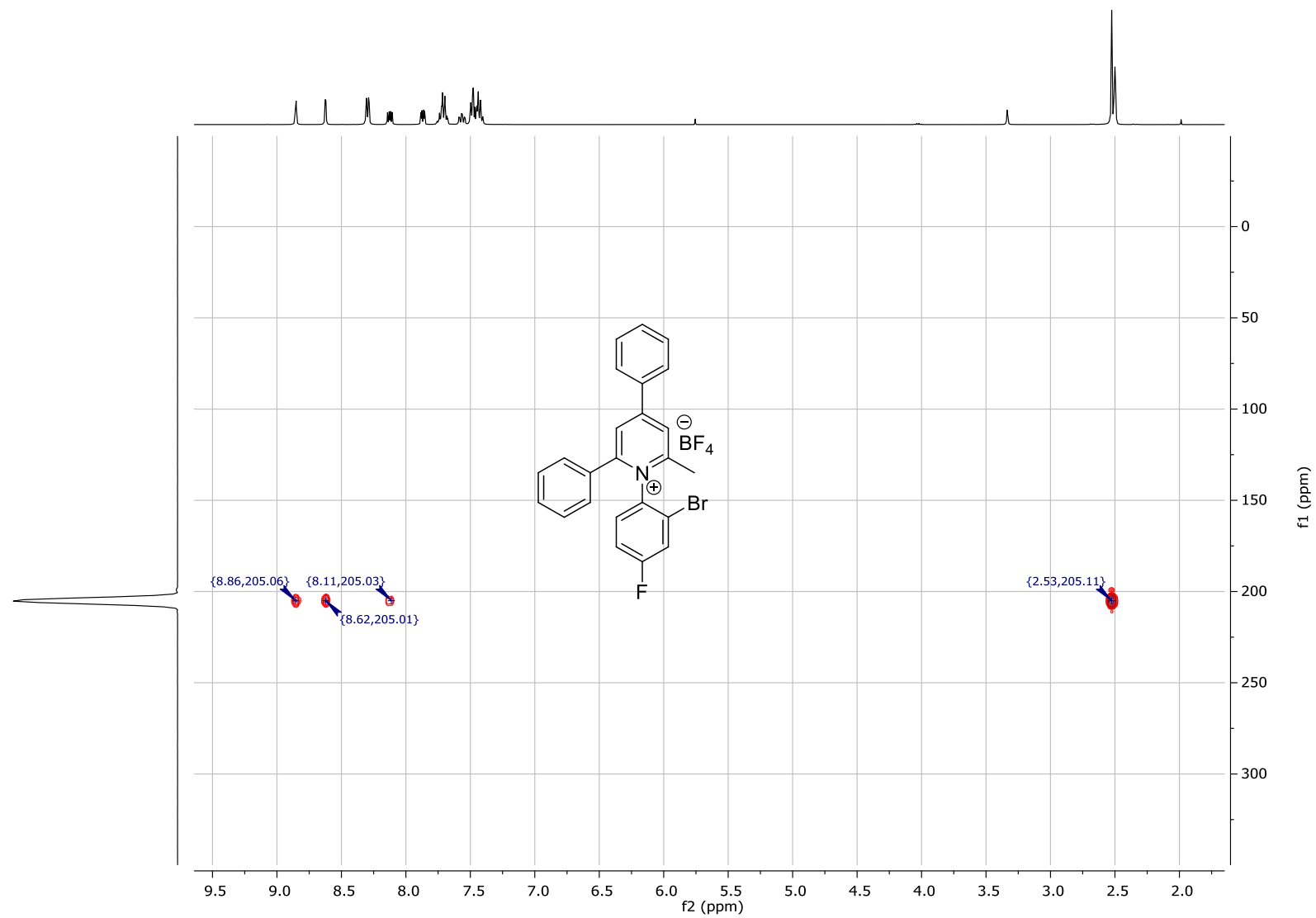
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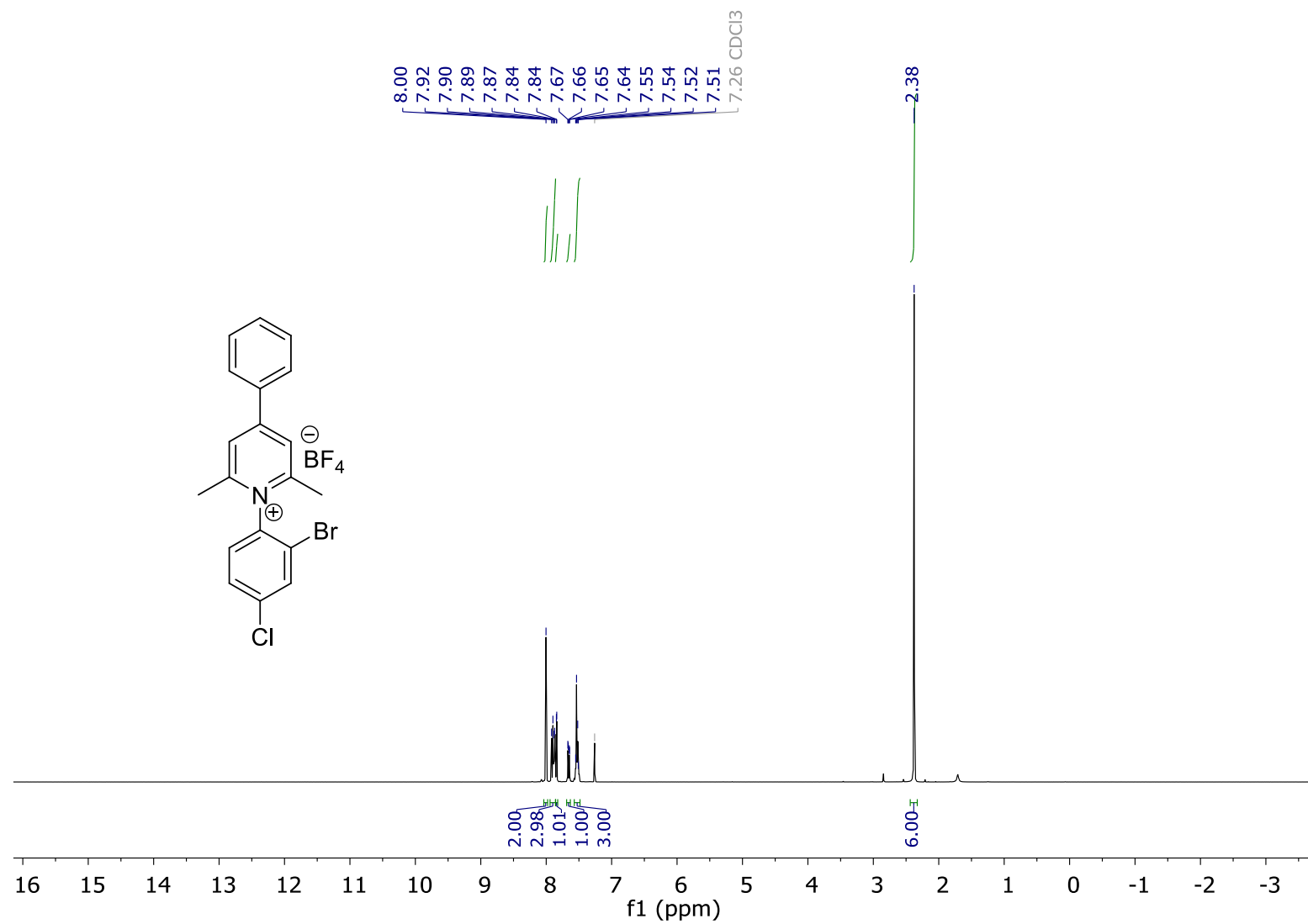
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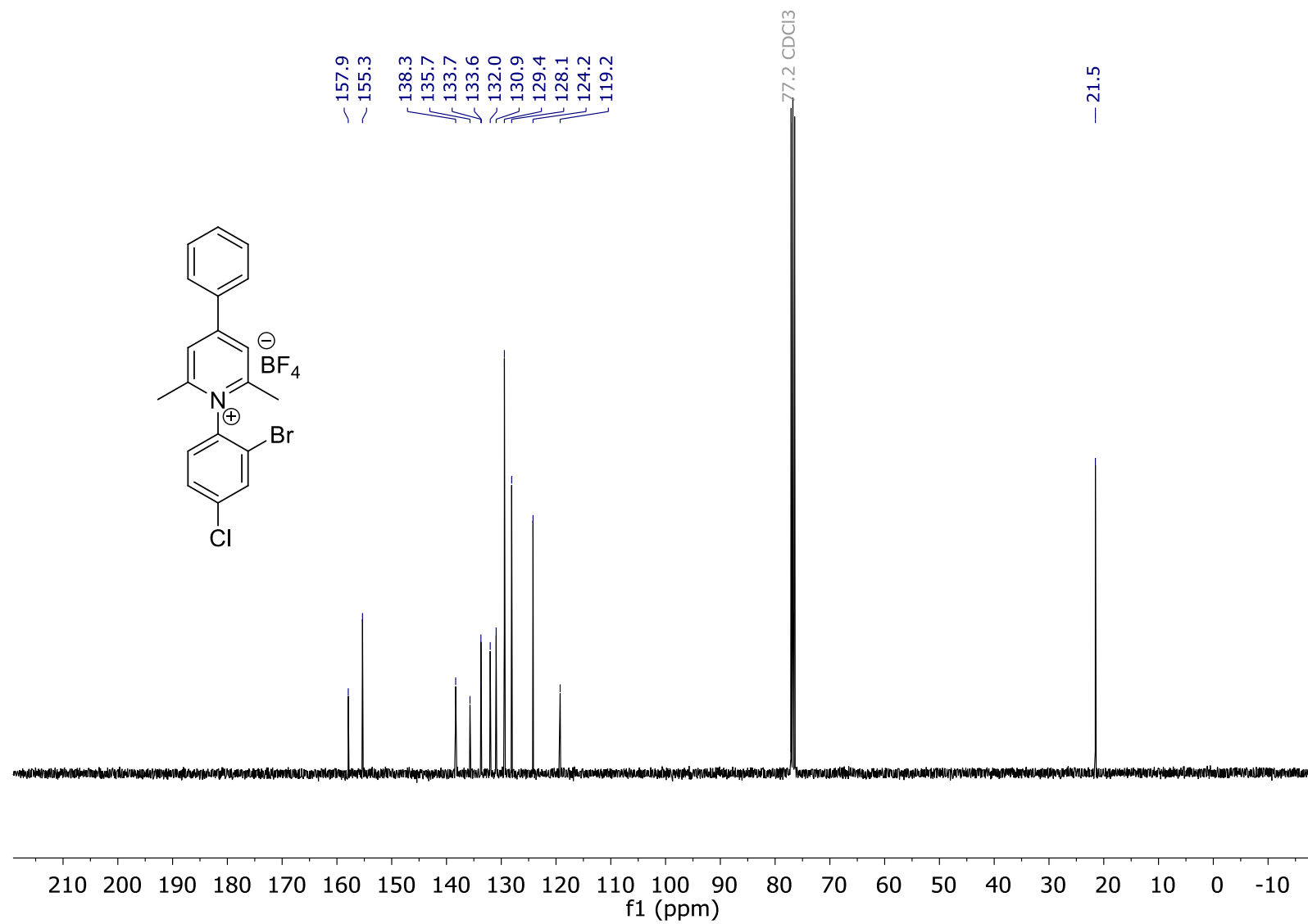
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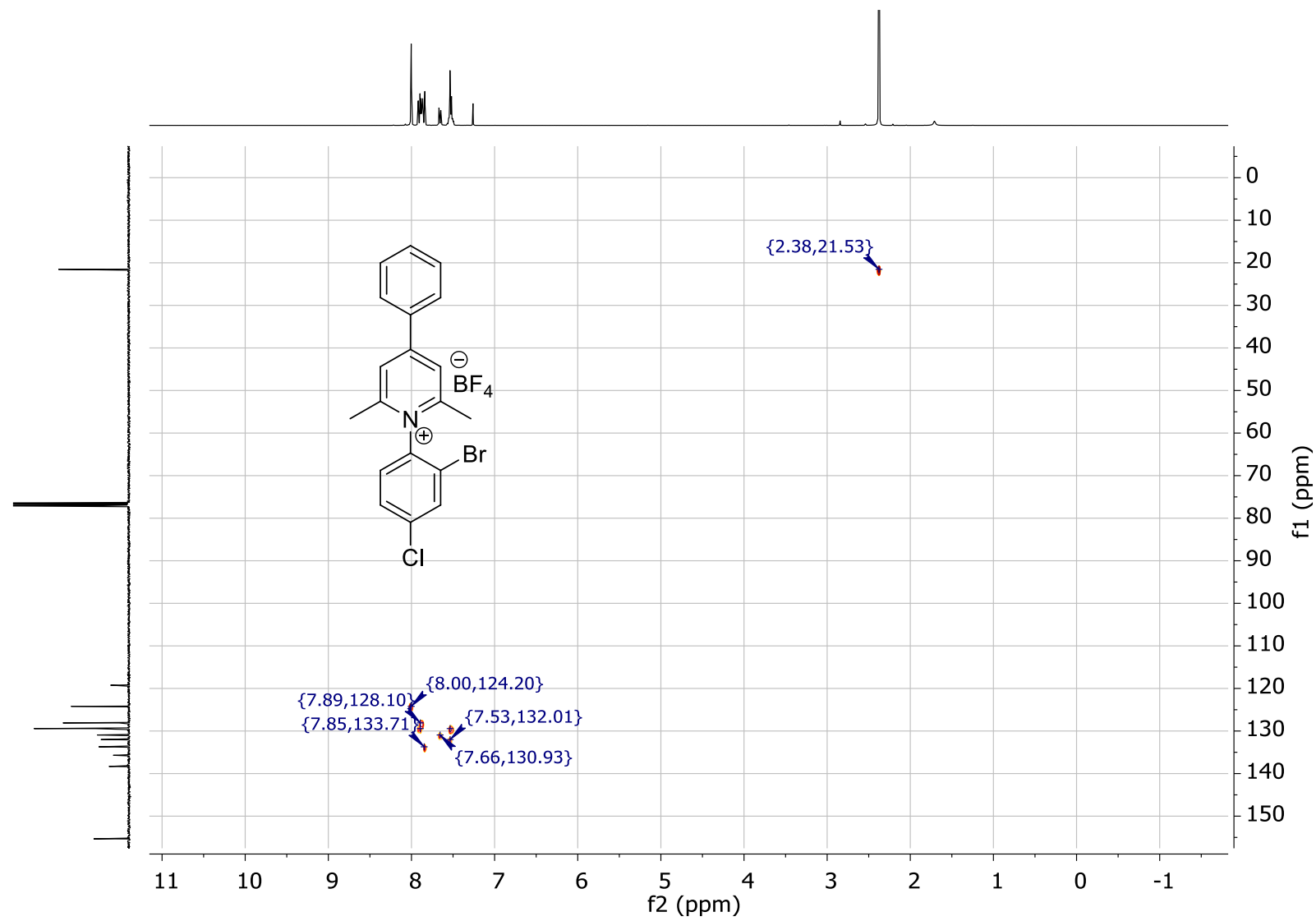
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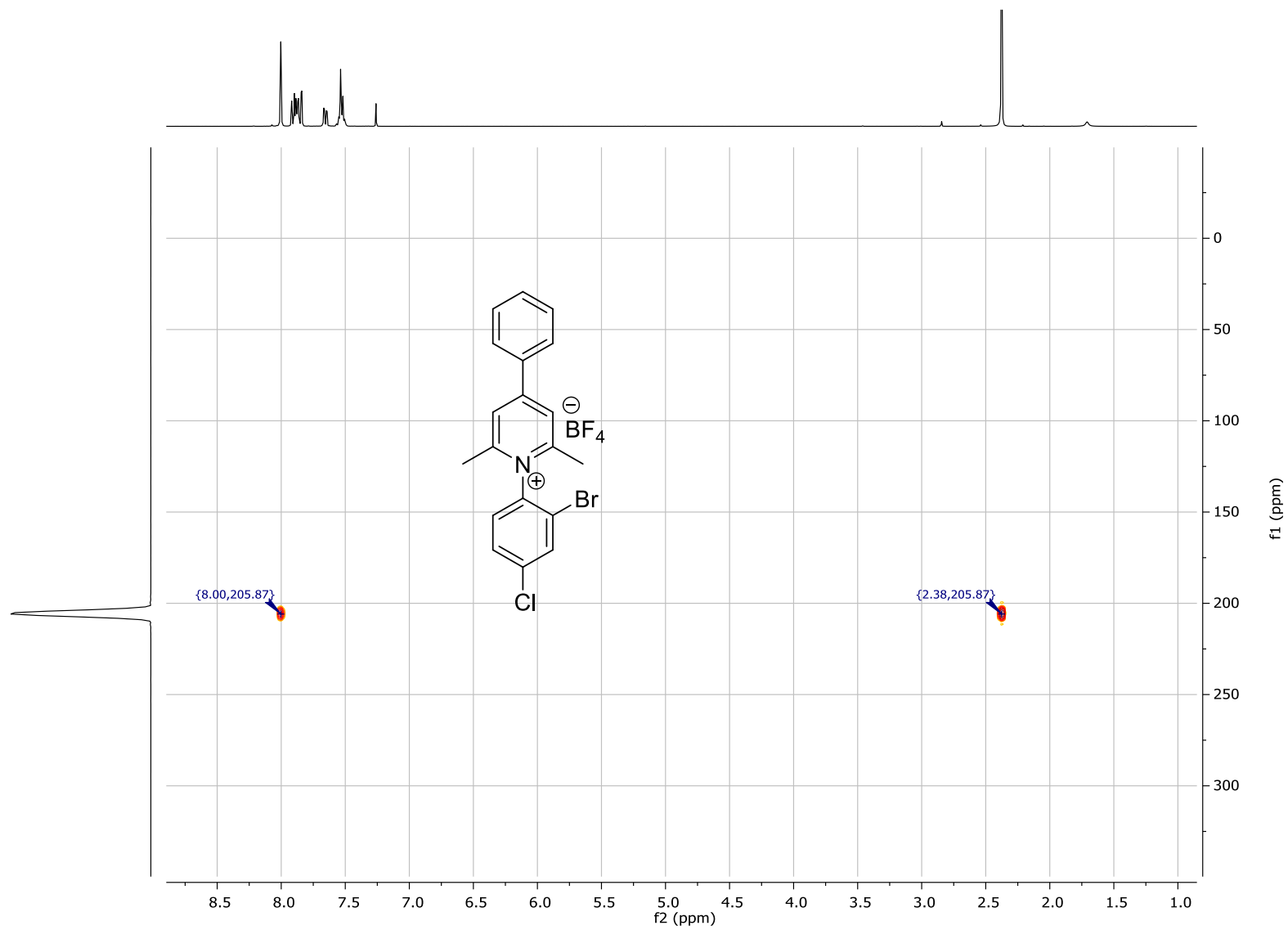
¹H NMR for 3n



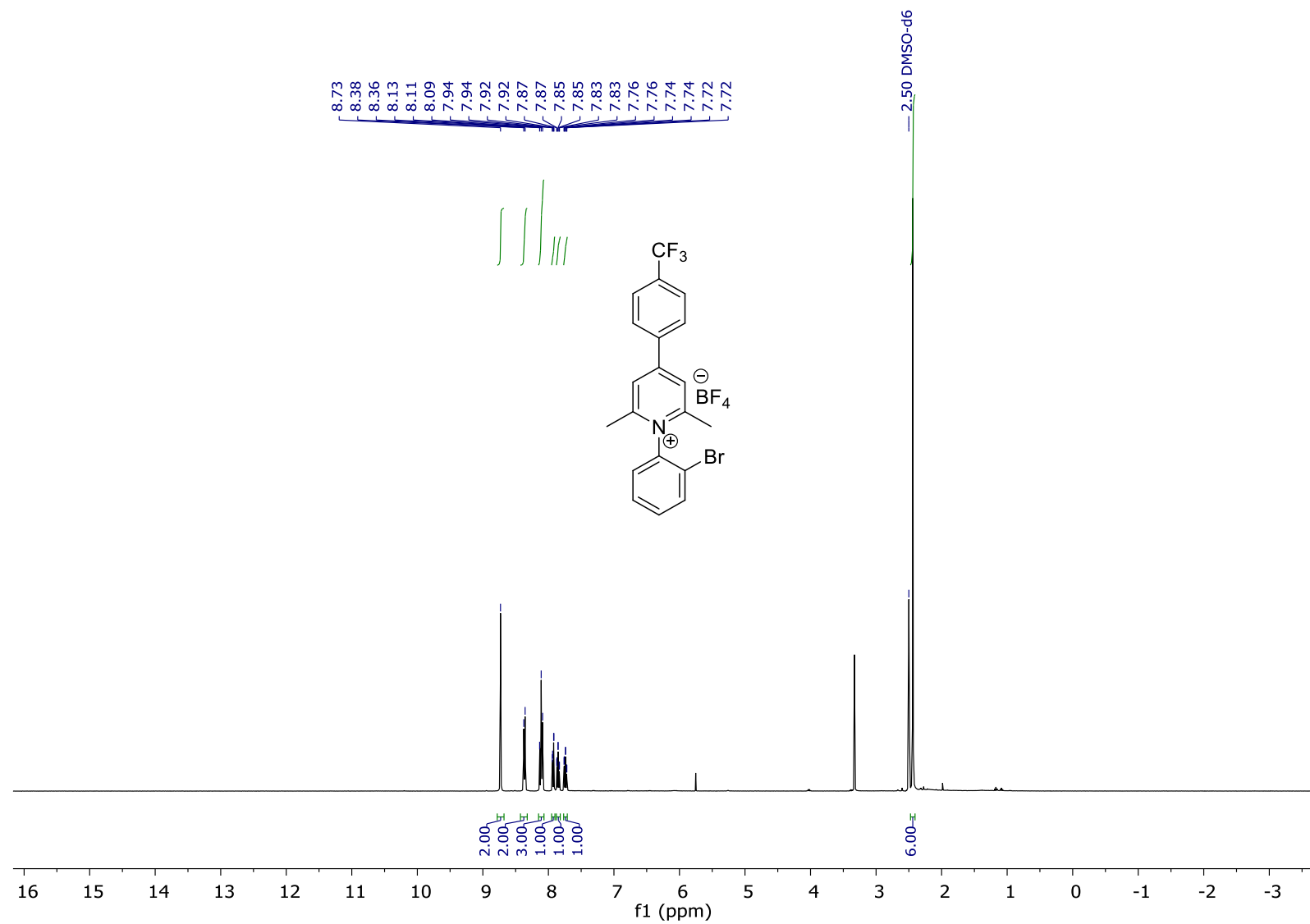
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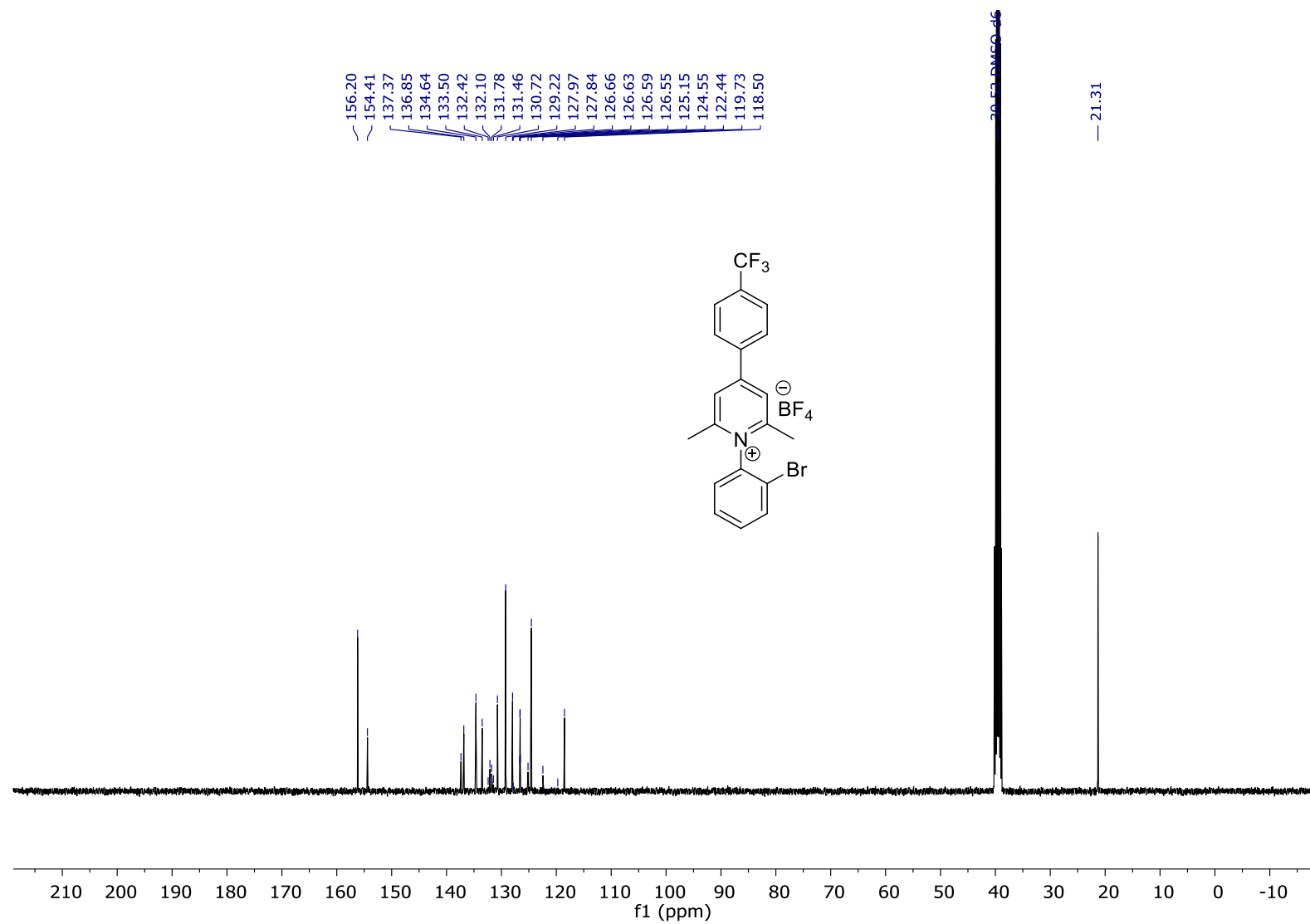
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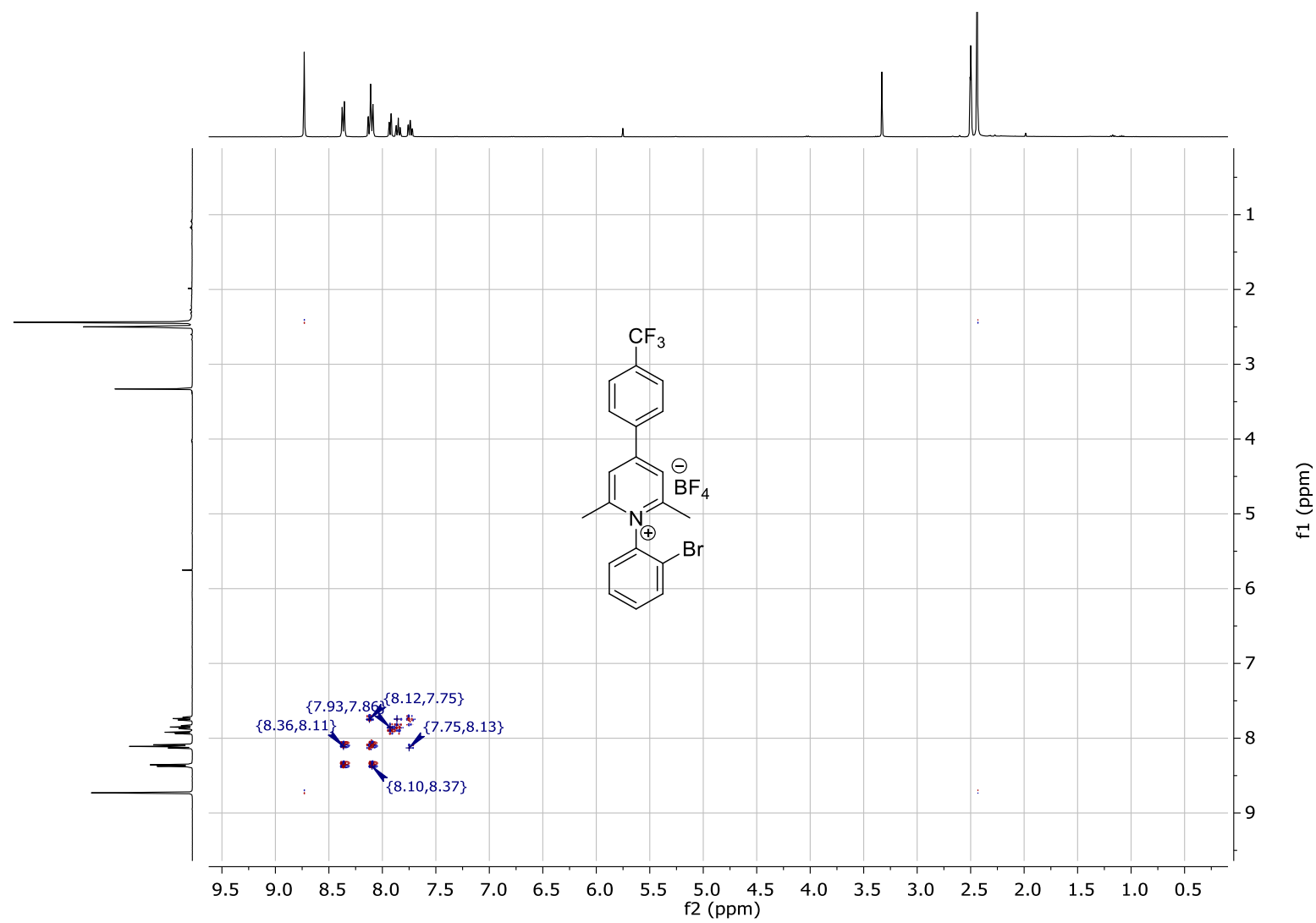
^1H - ^{15}N HMBC for **3n**



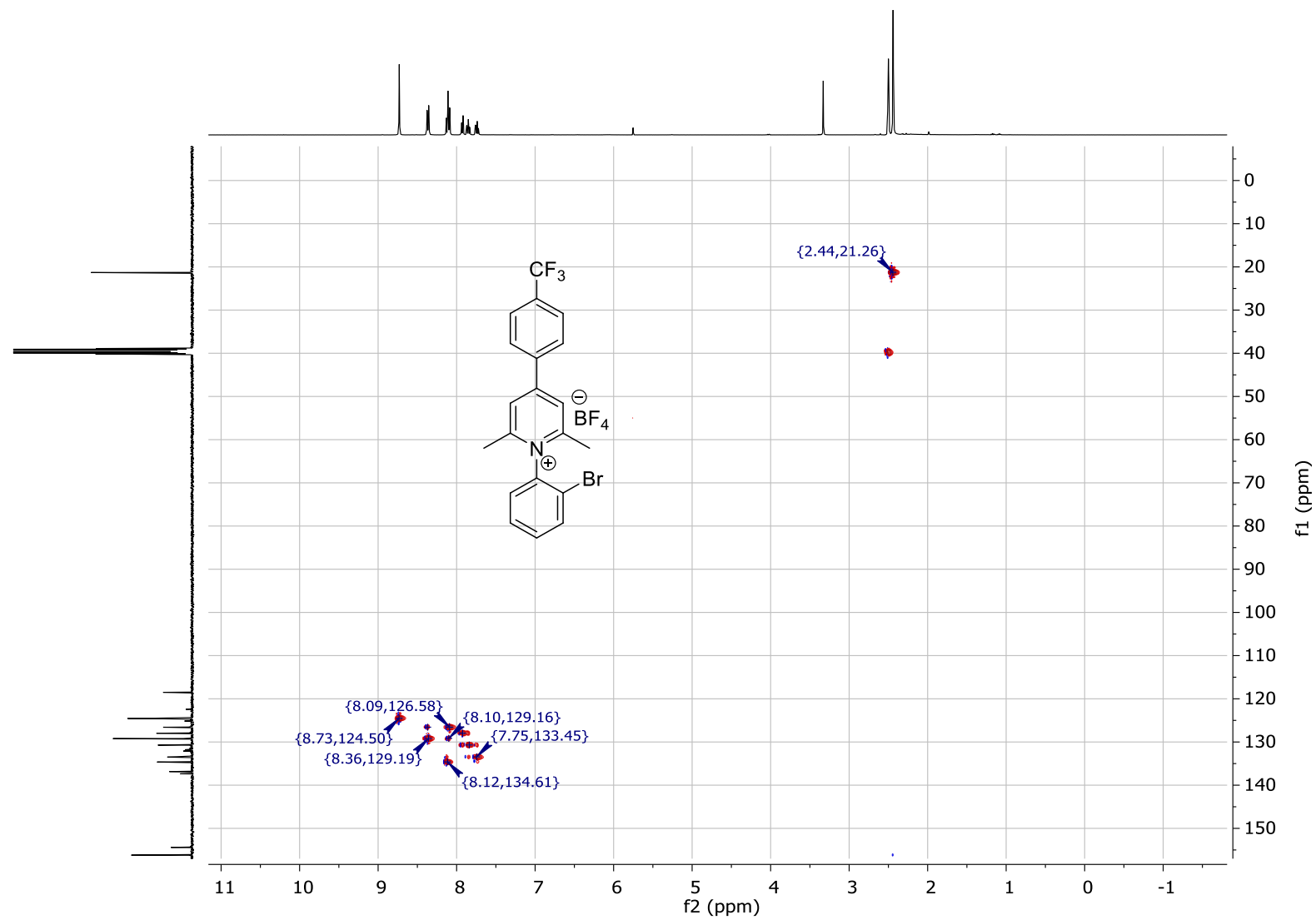
¹H NMR for 3o



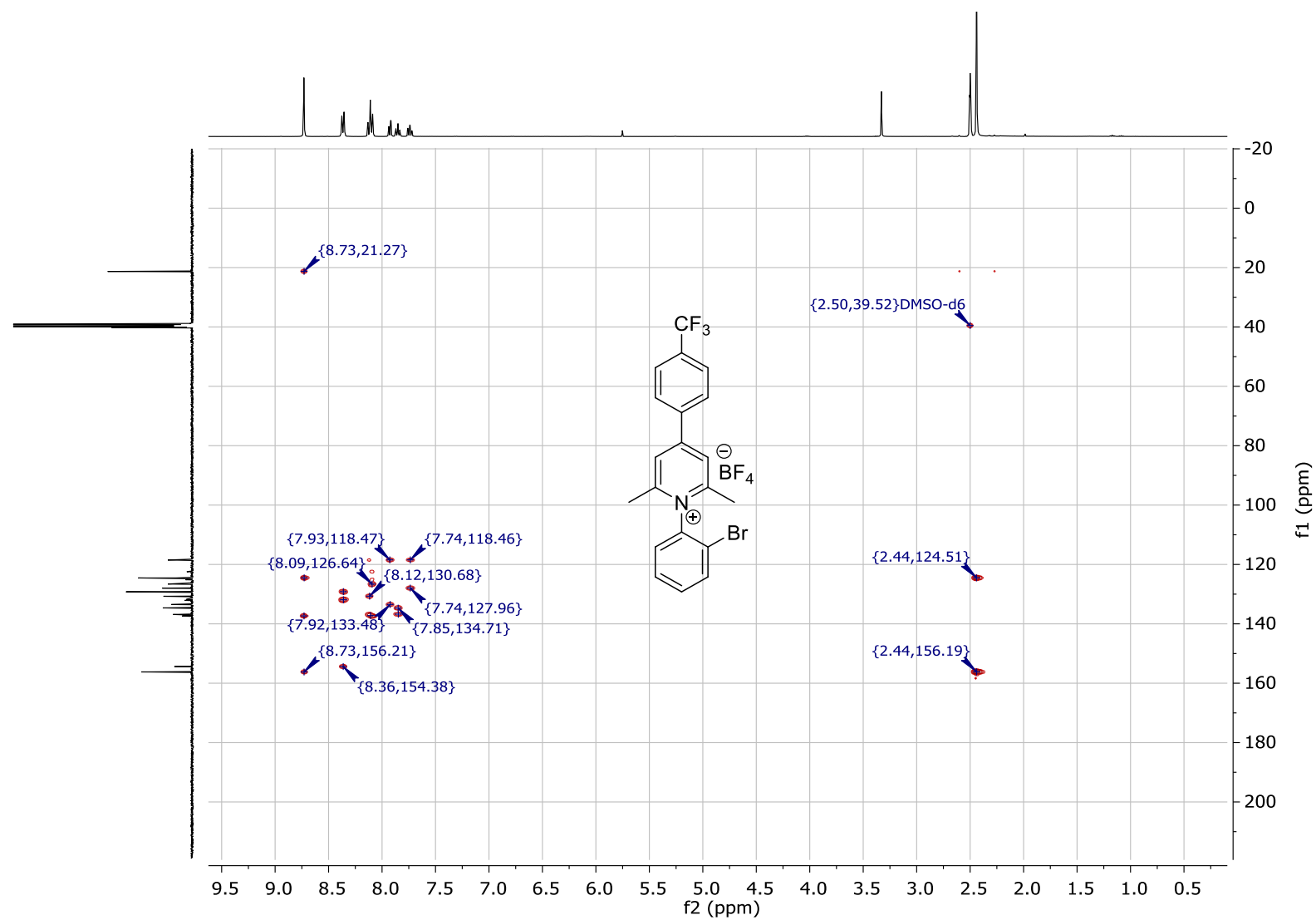
¹³C NMR for 3o



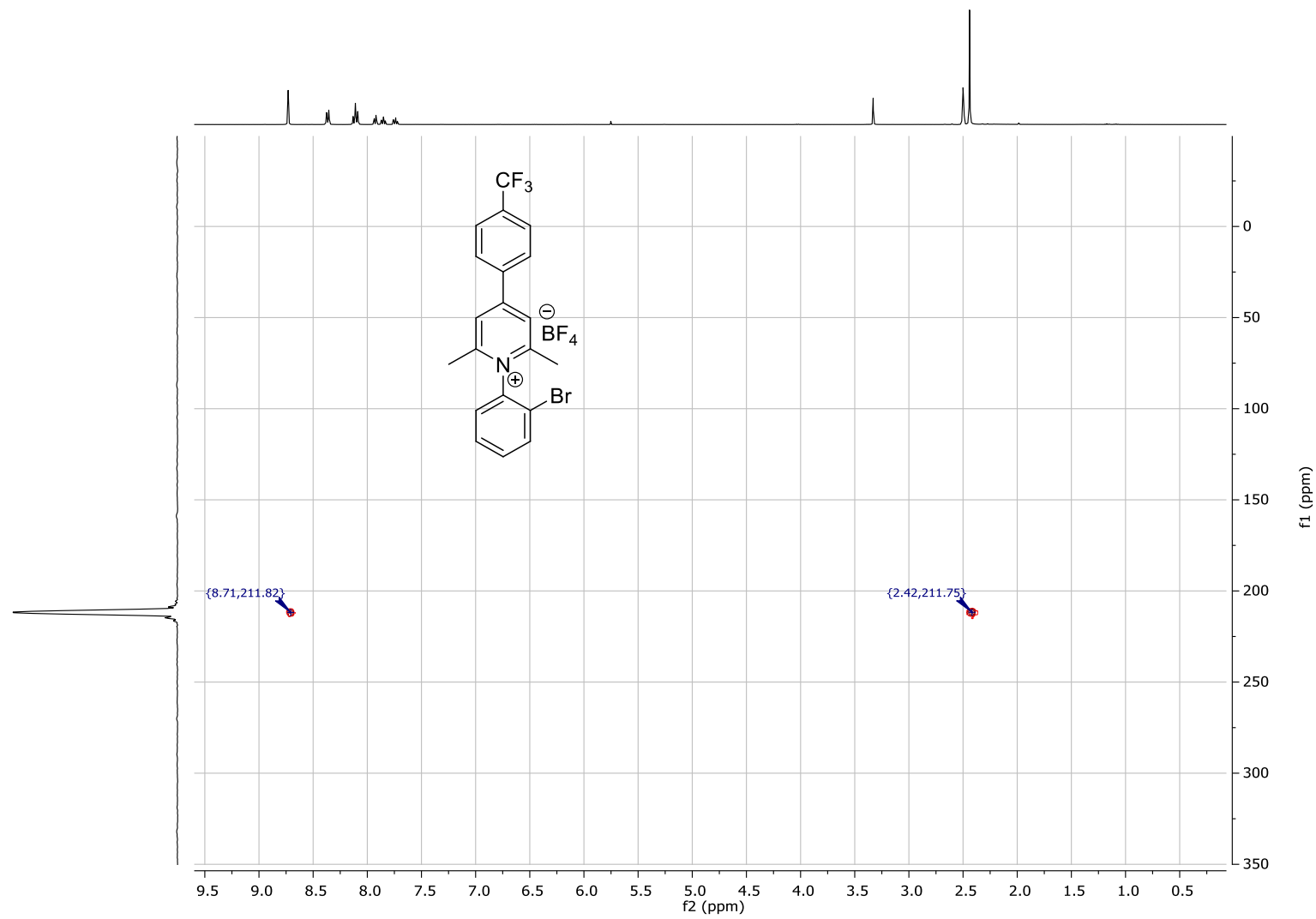
^1H - ^1H COSY for **3o**



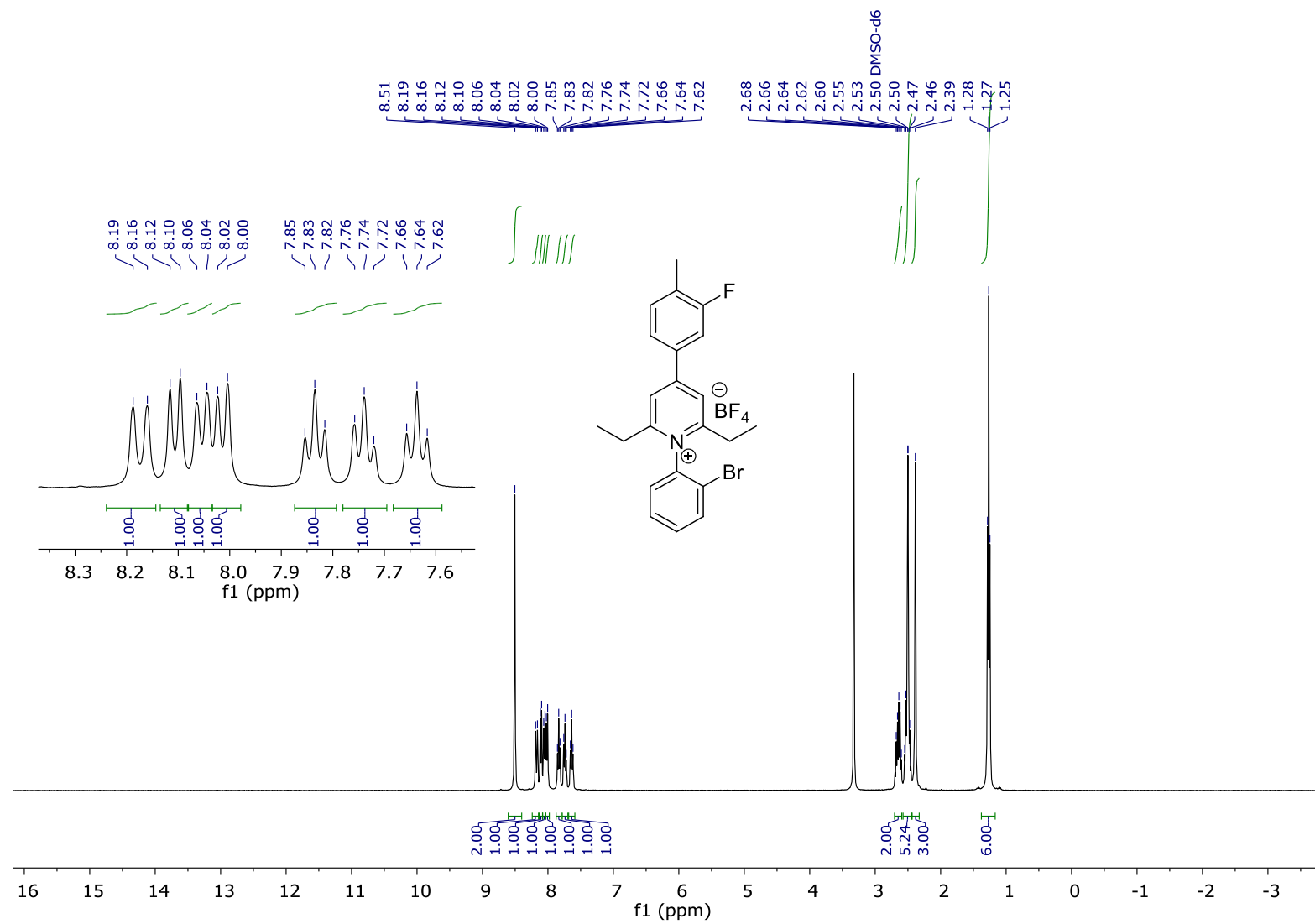
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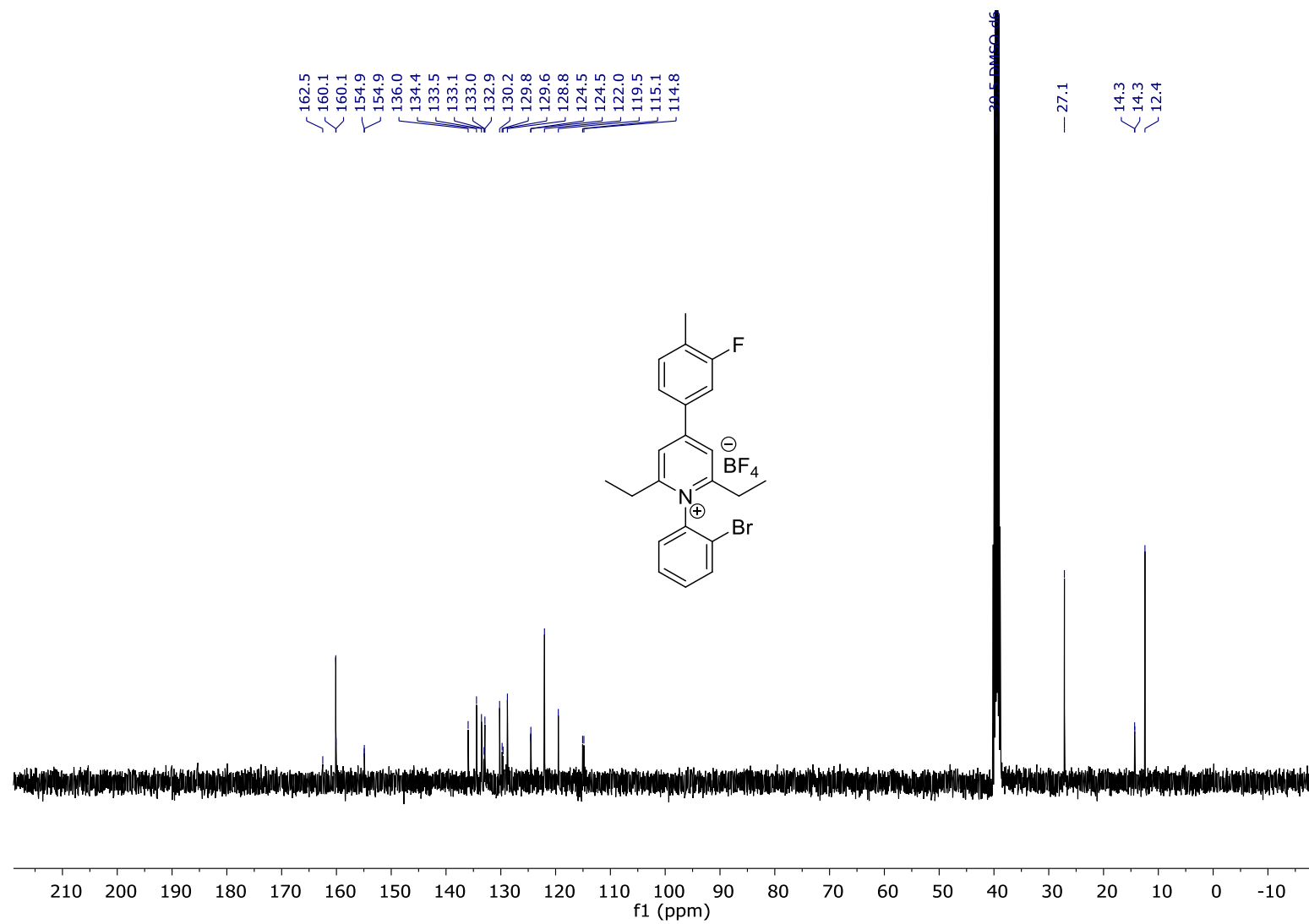
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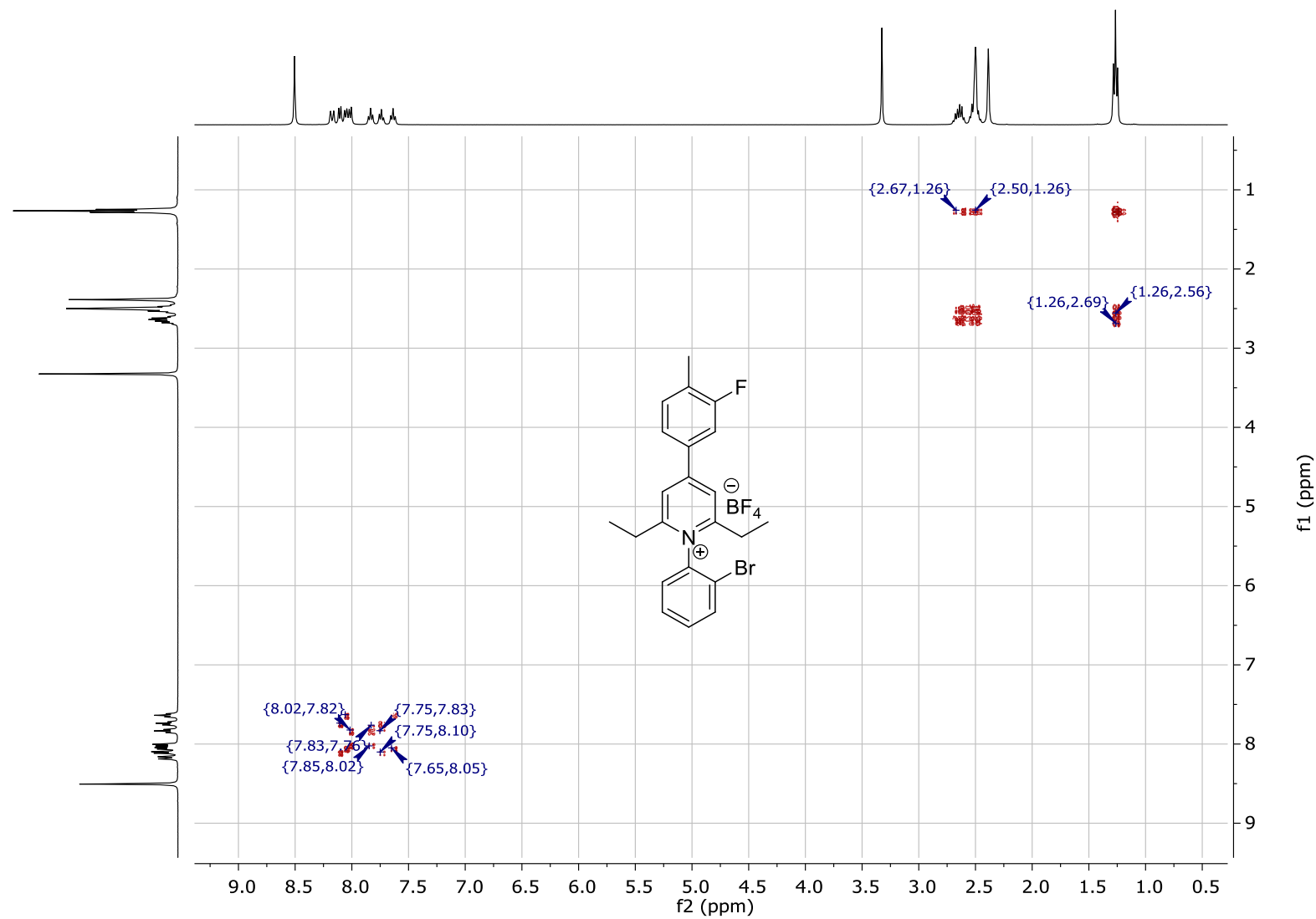
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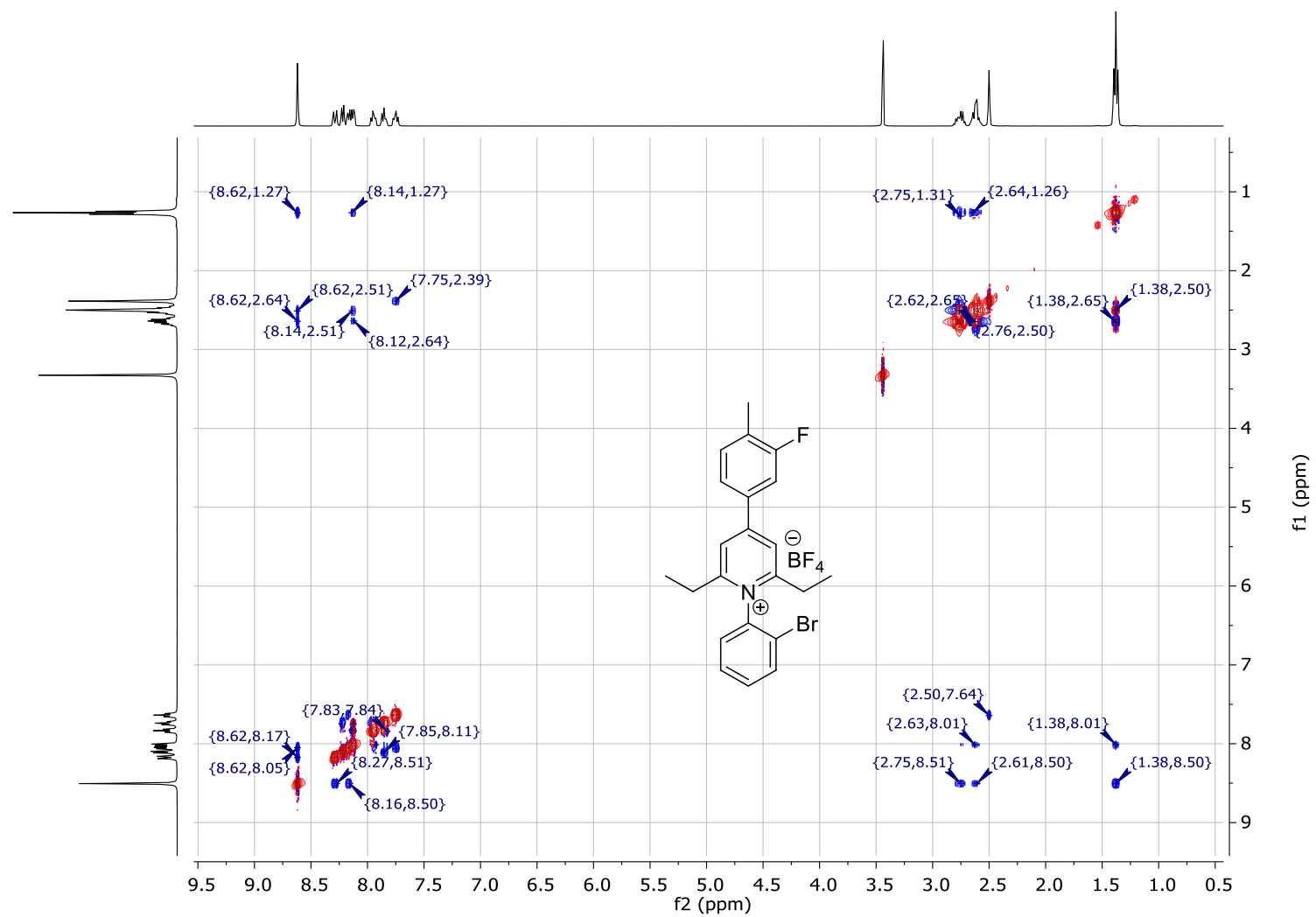
¹H NMR for 3p



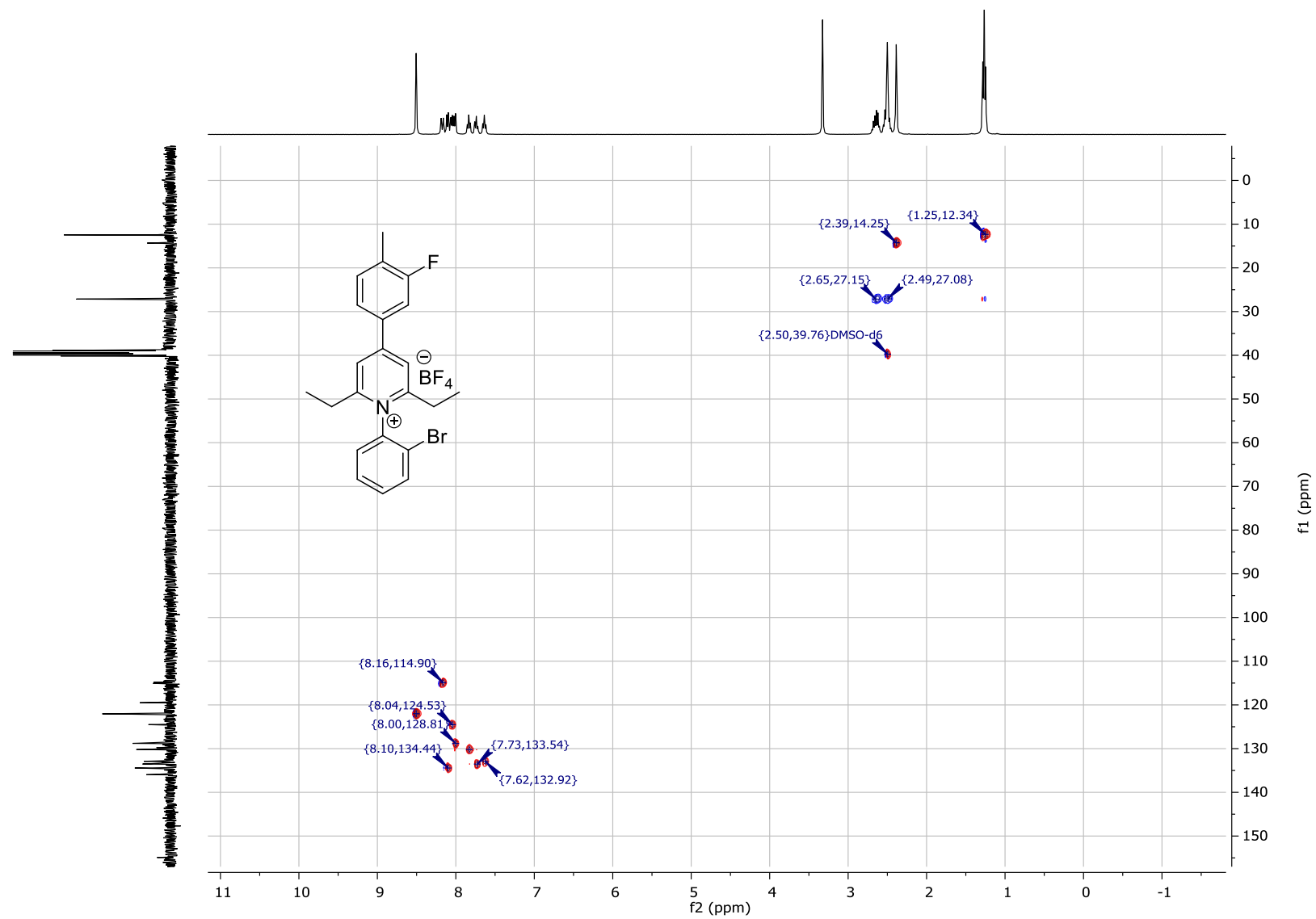
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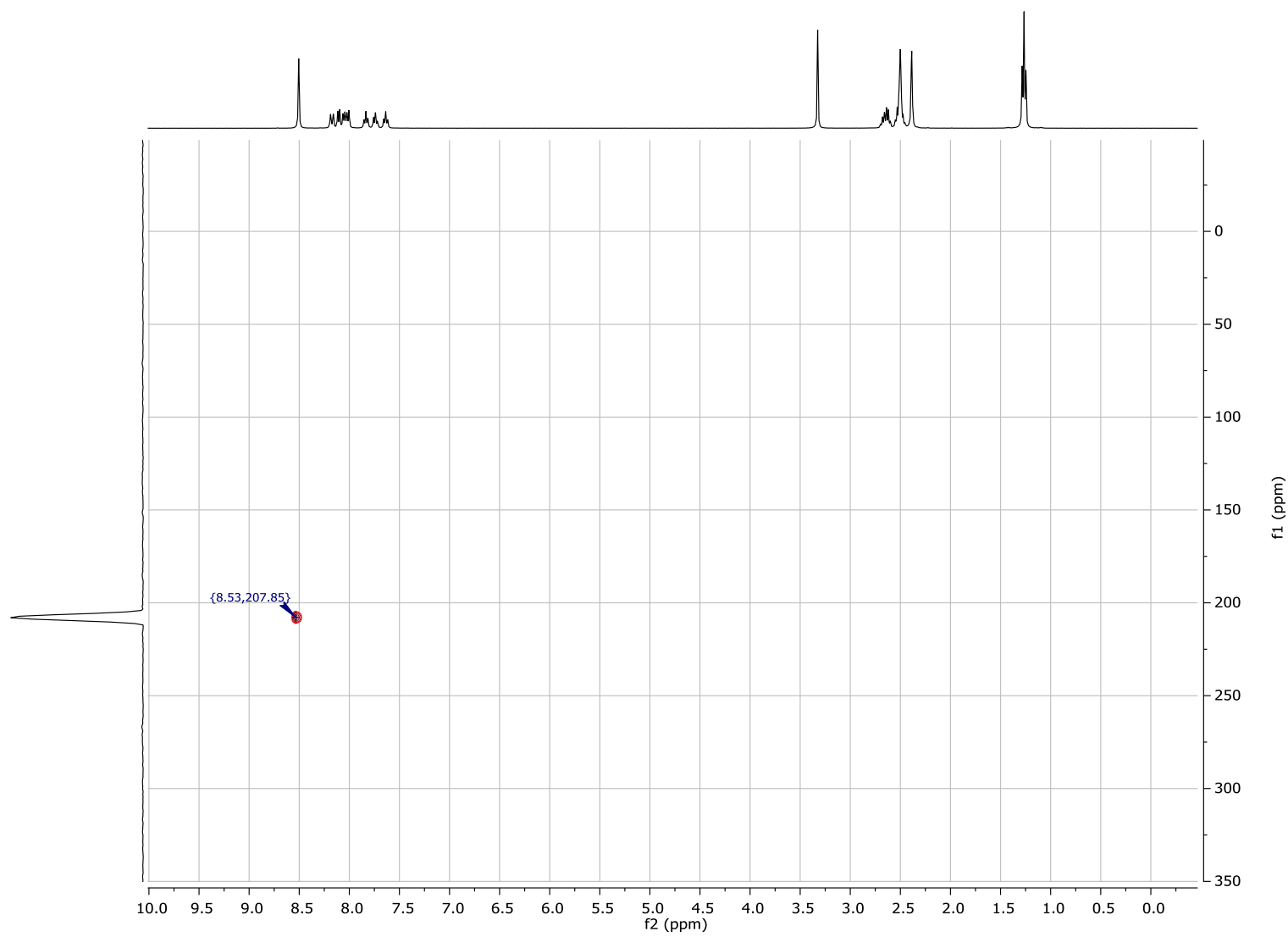
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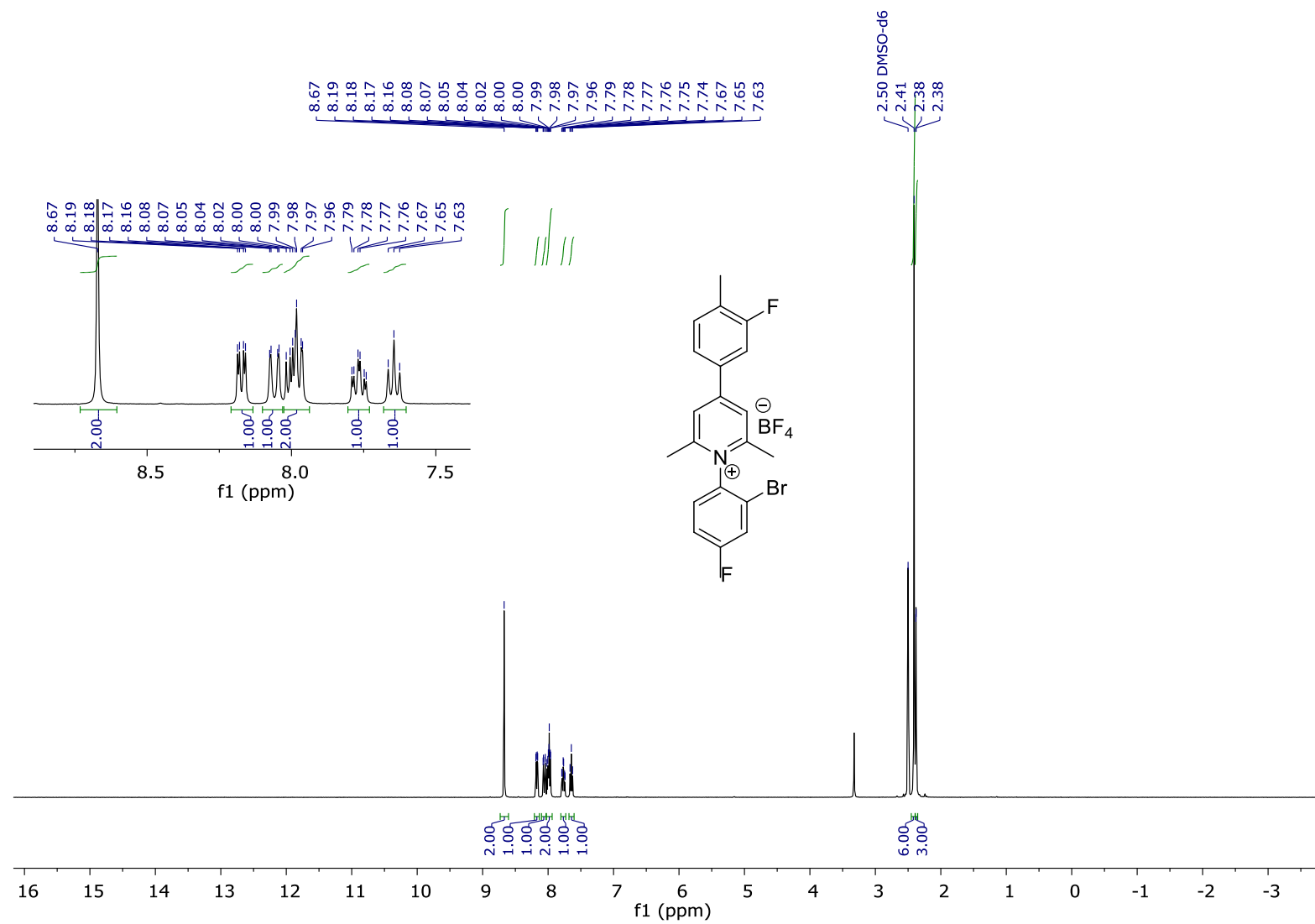
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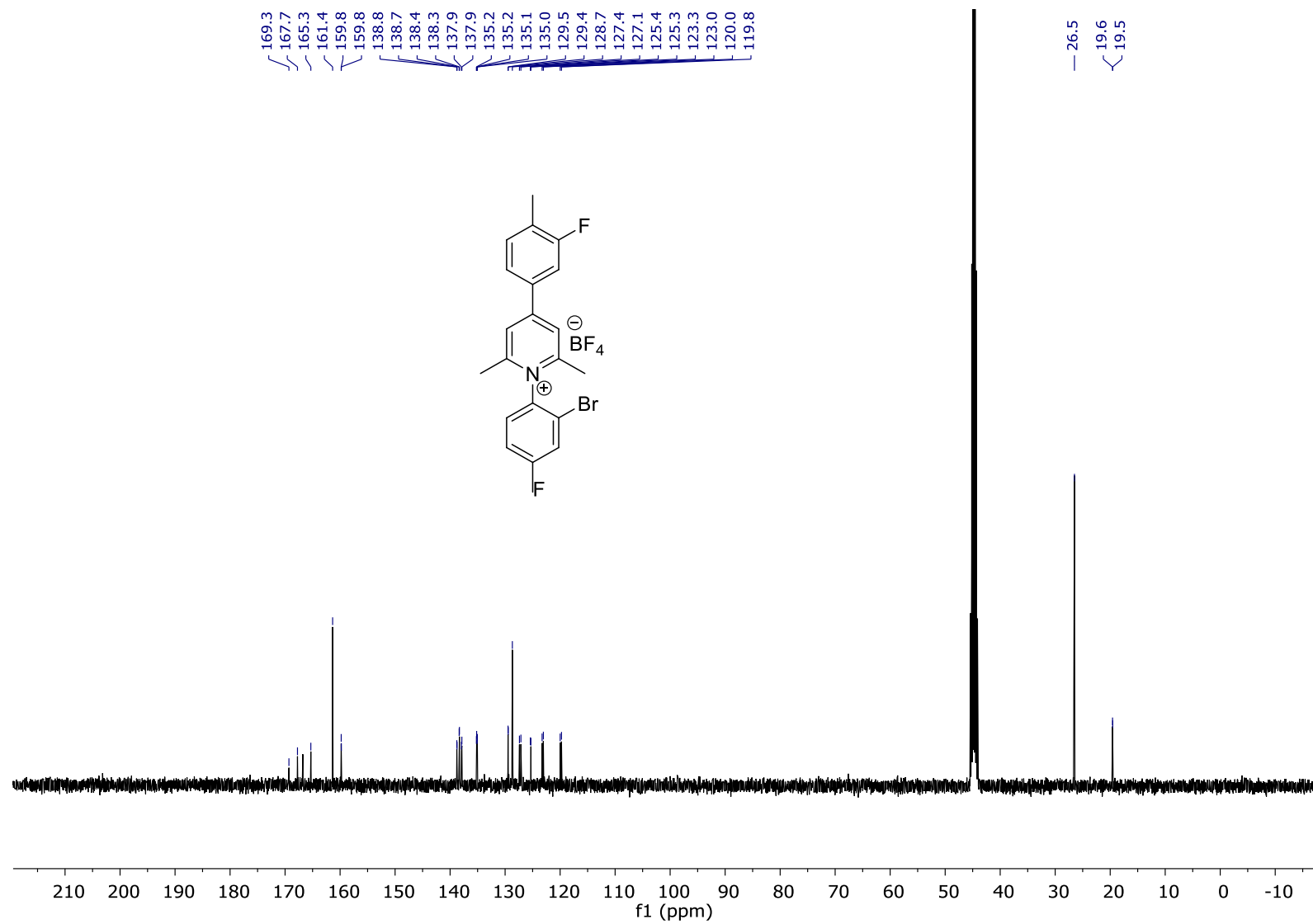
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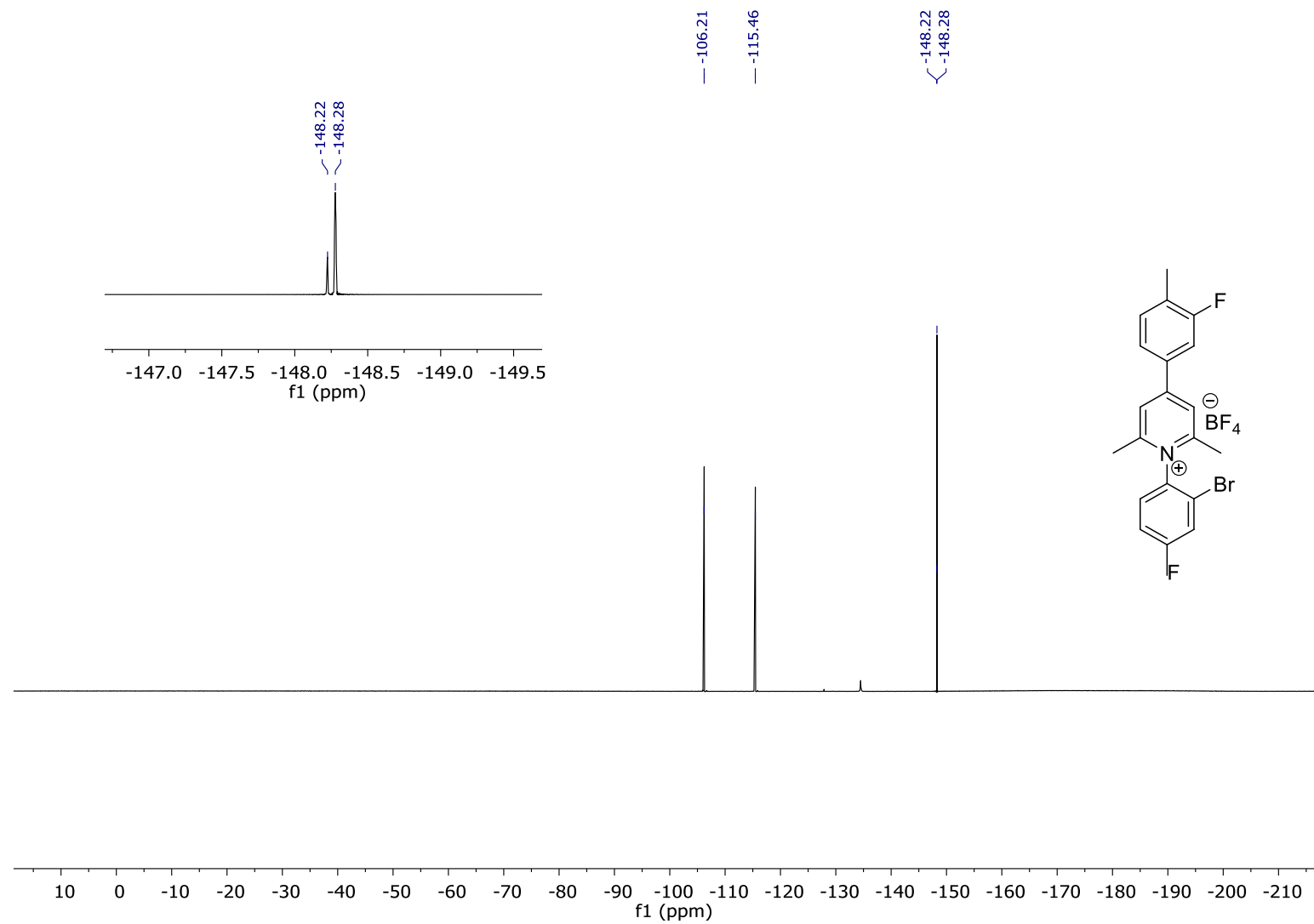
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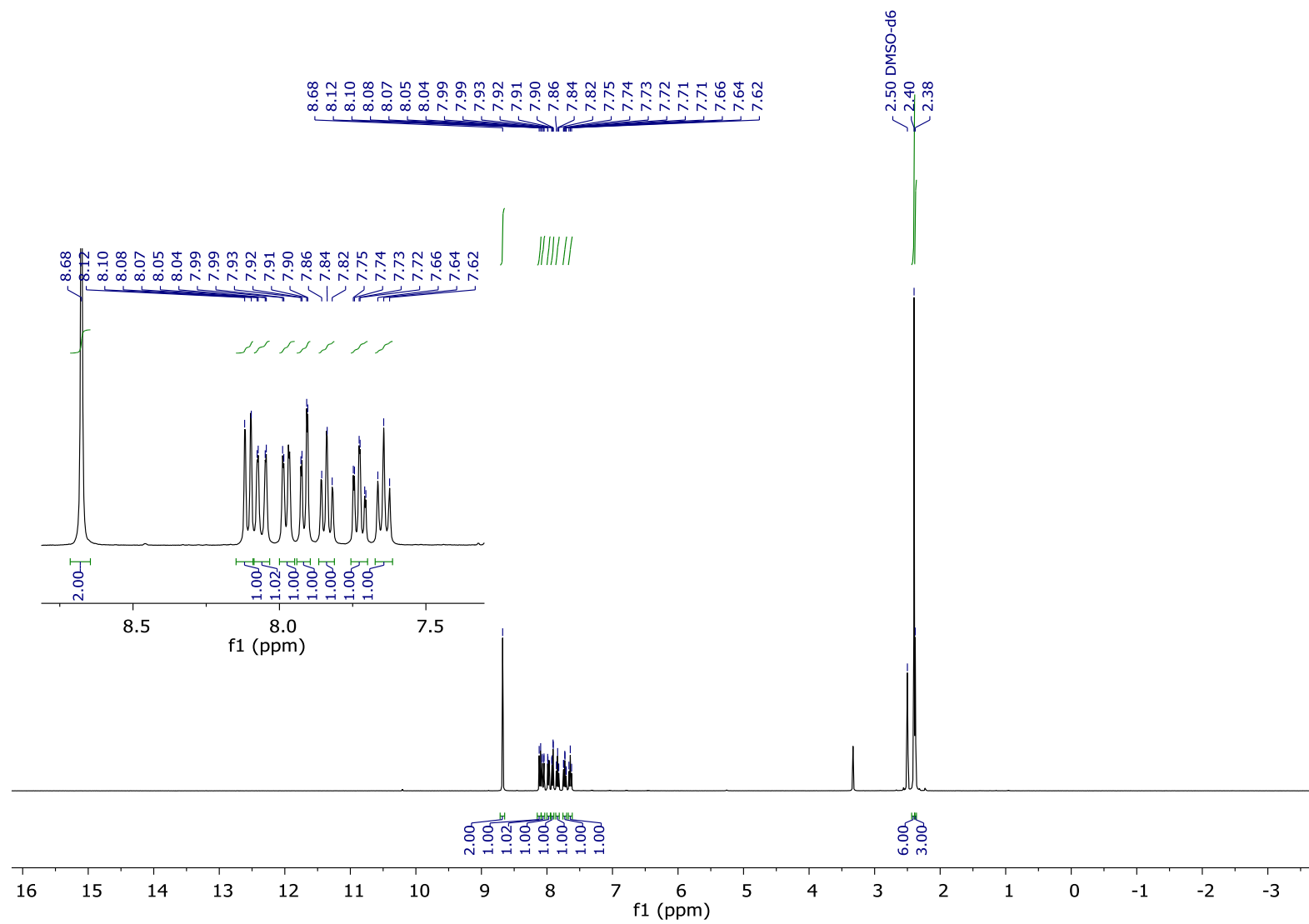
¹H NMR for 3q



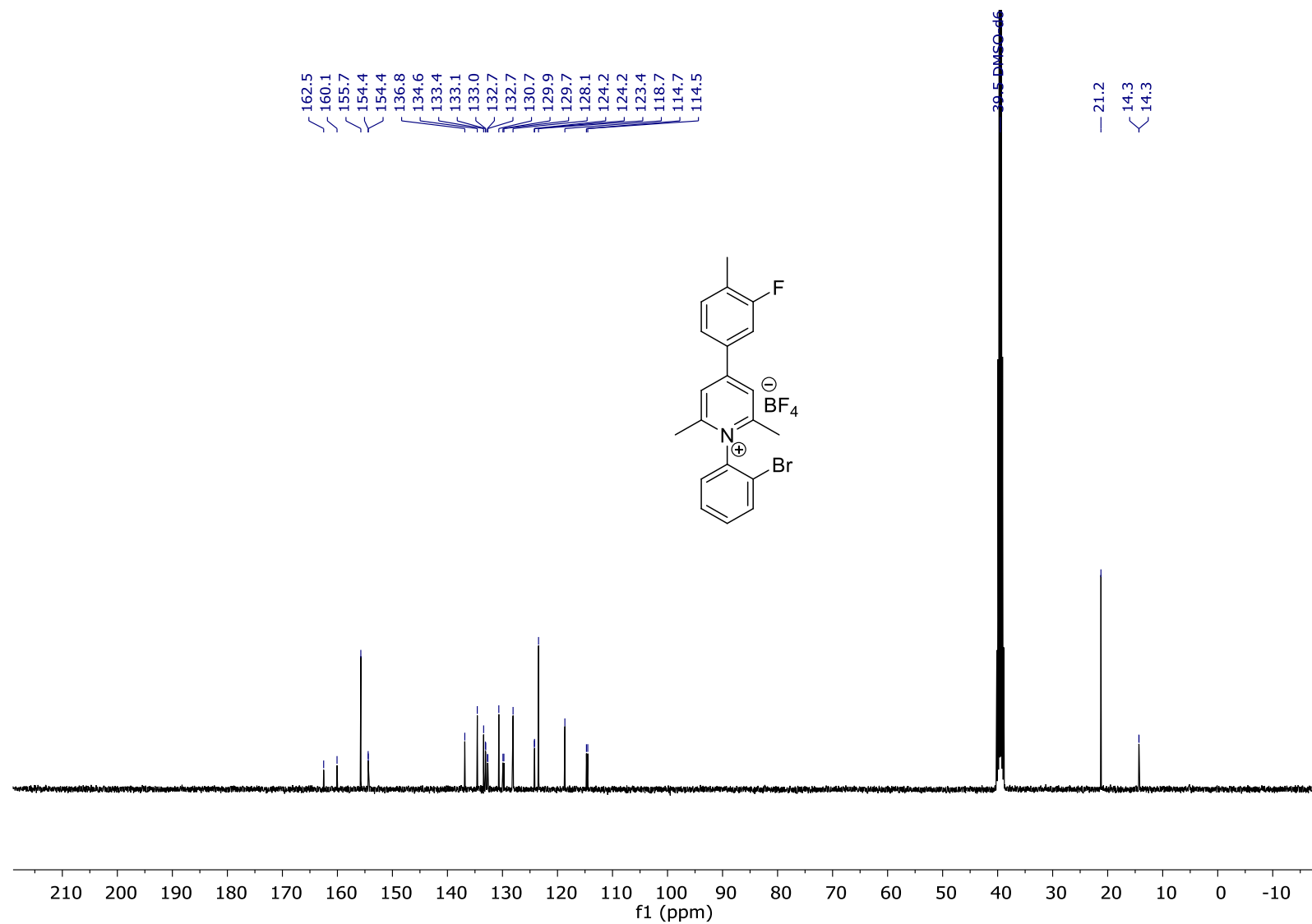
¹³C NMR for 3q



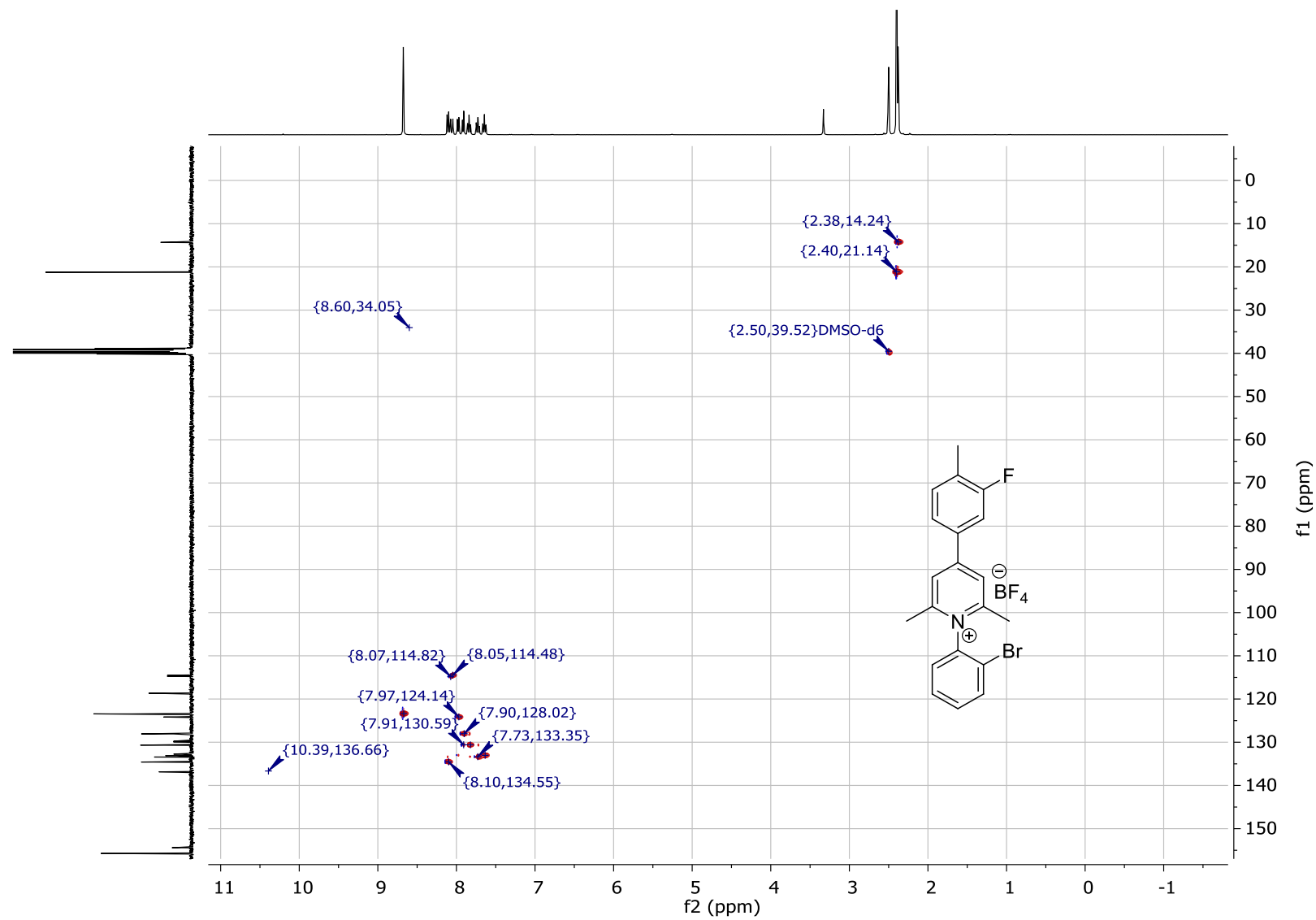
¹⁹F NMR for 3q



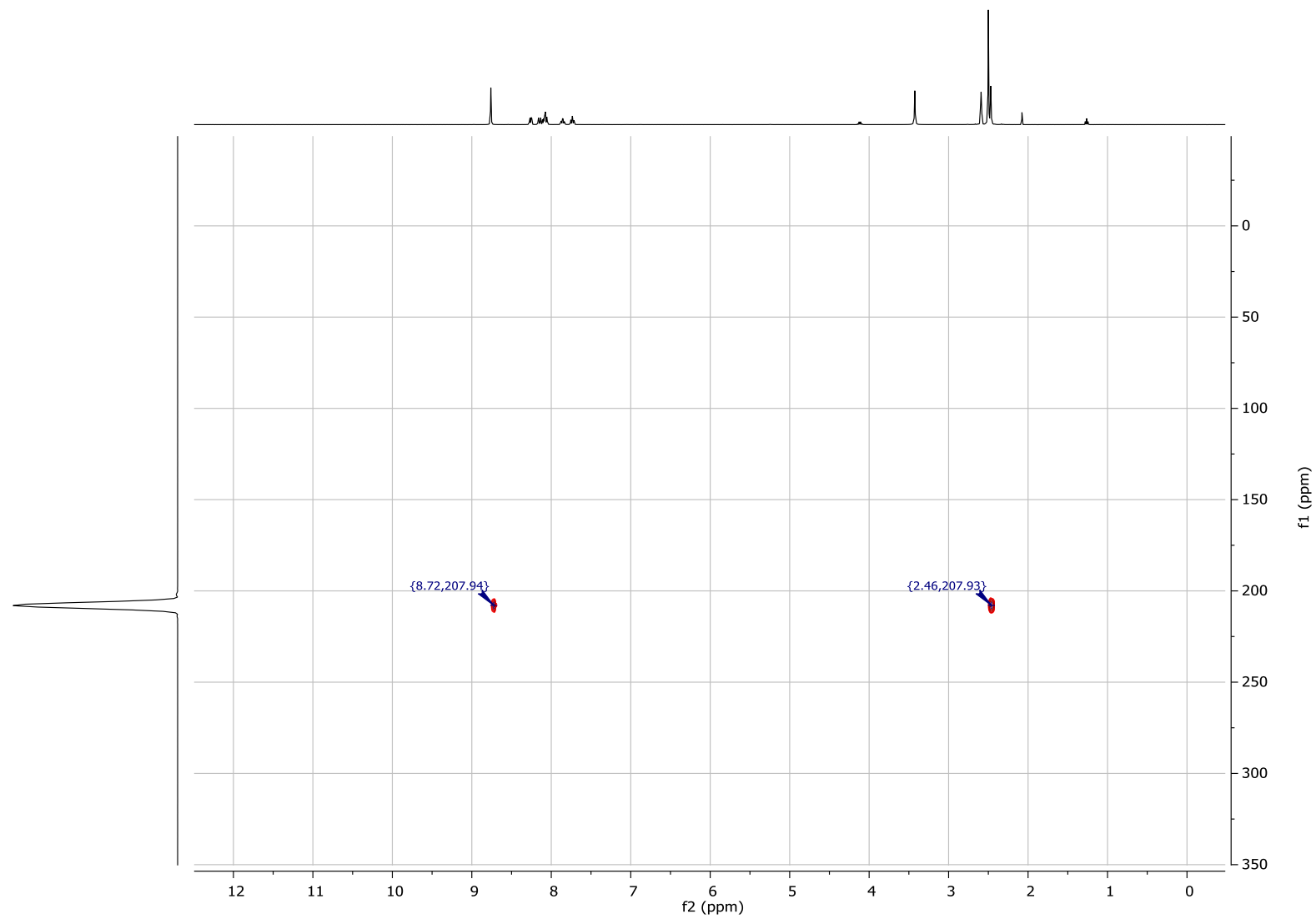
¹H NMR for 3r



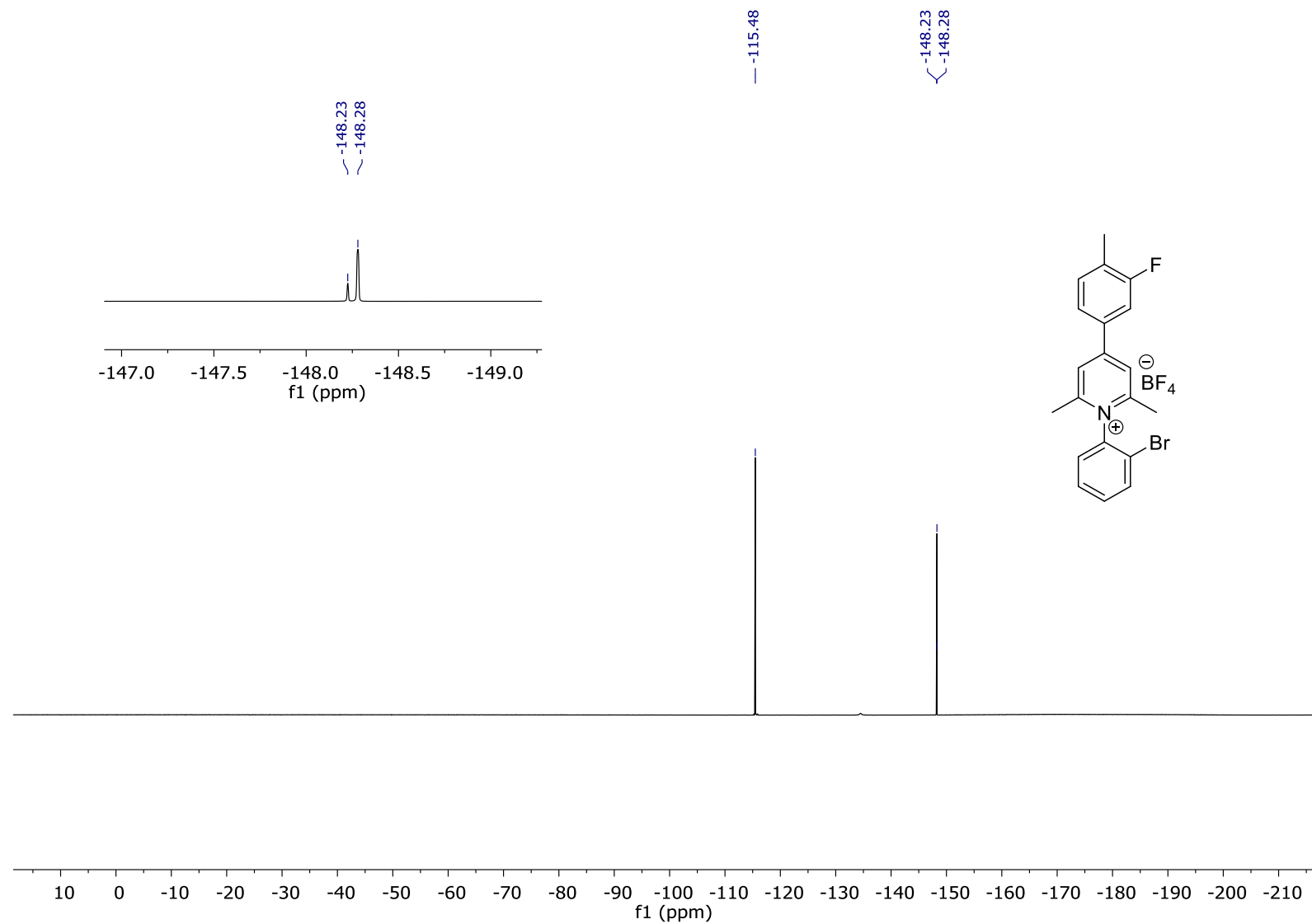
¹³C NMR for 3r



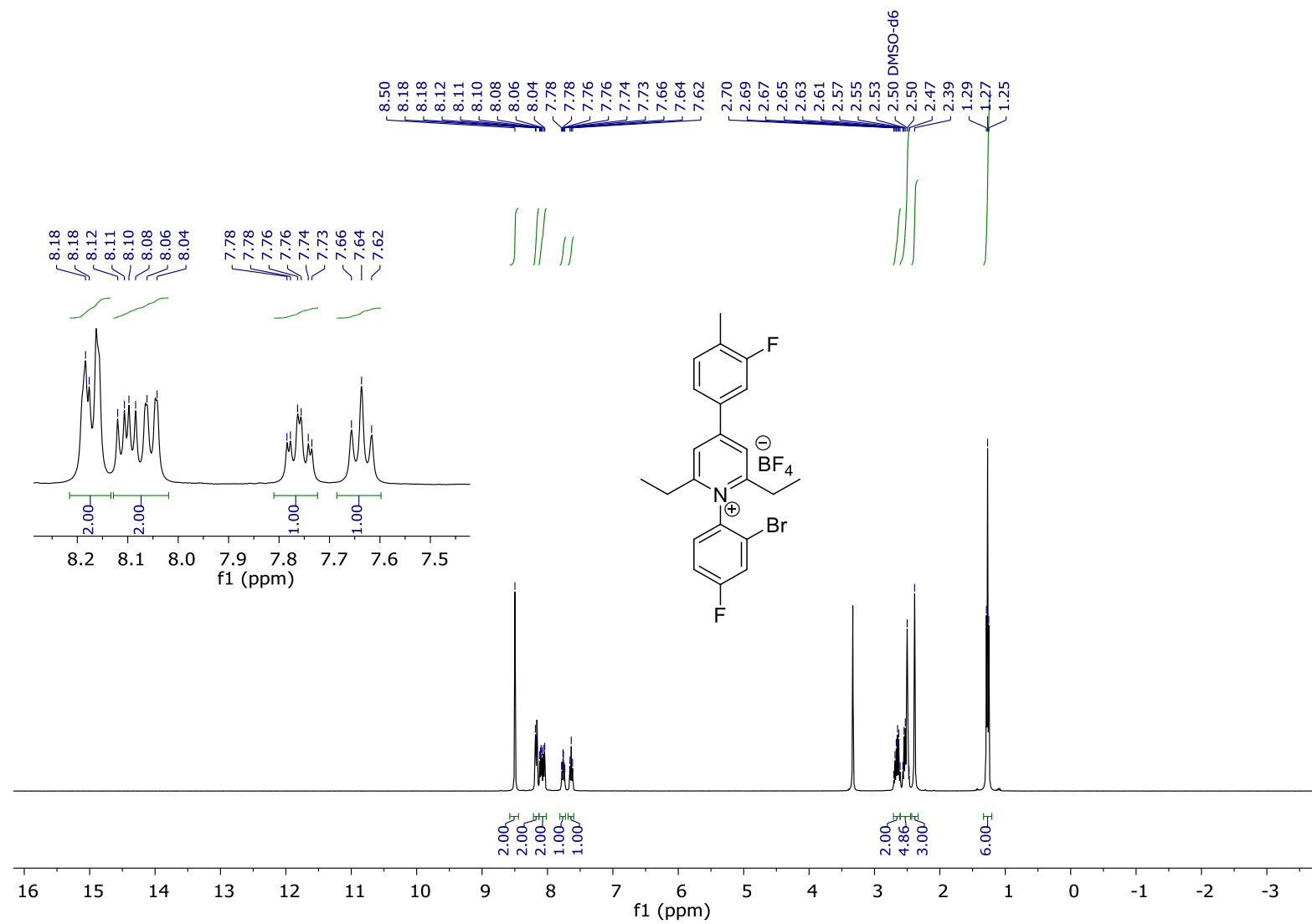
¹H-¹³C HSQC for 3r



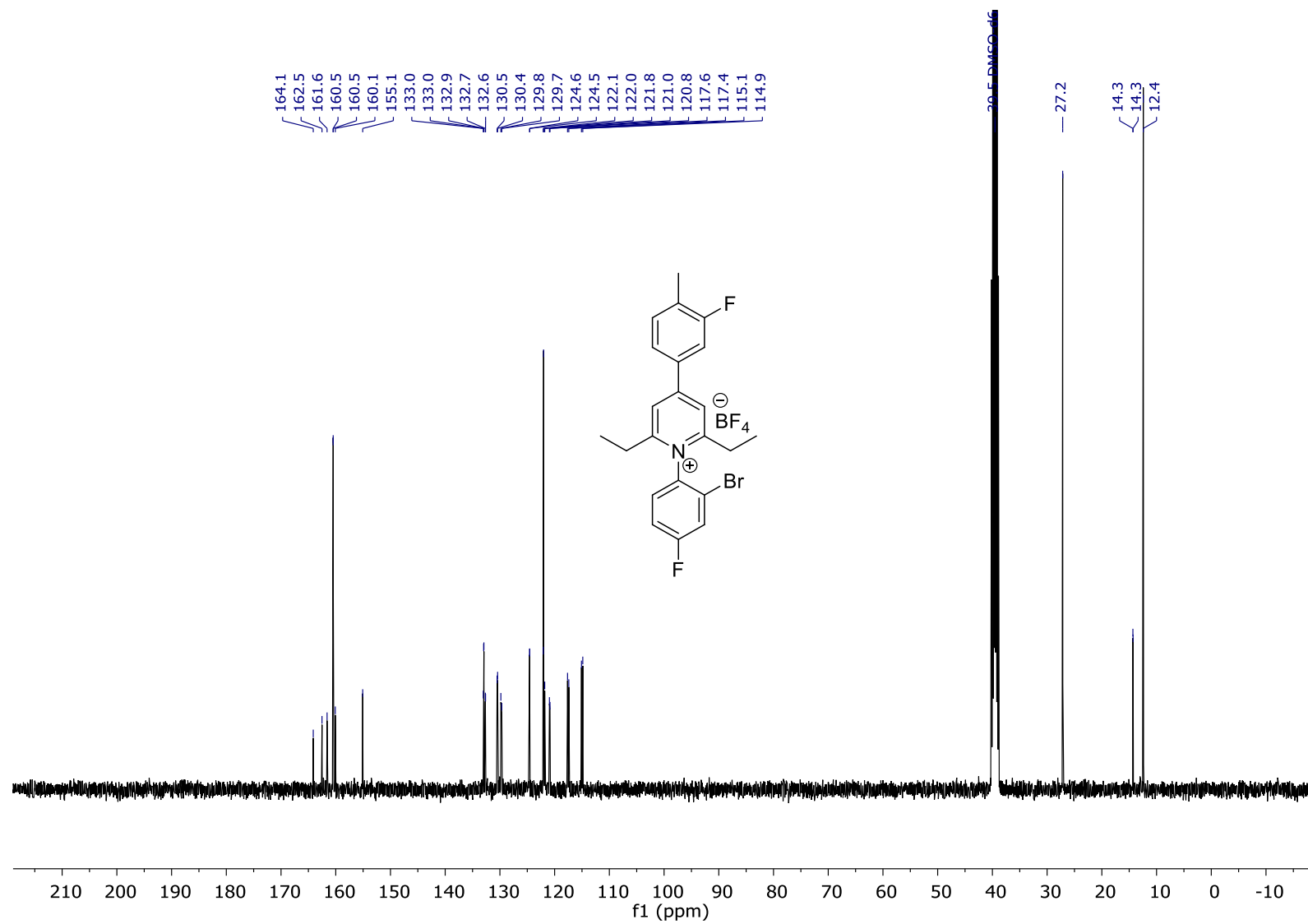
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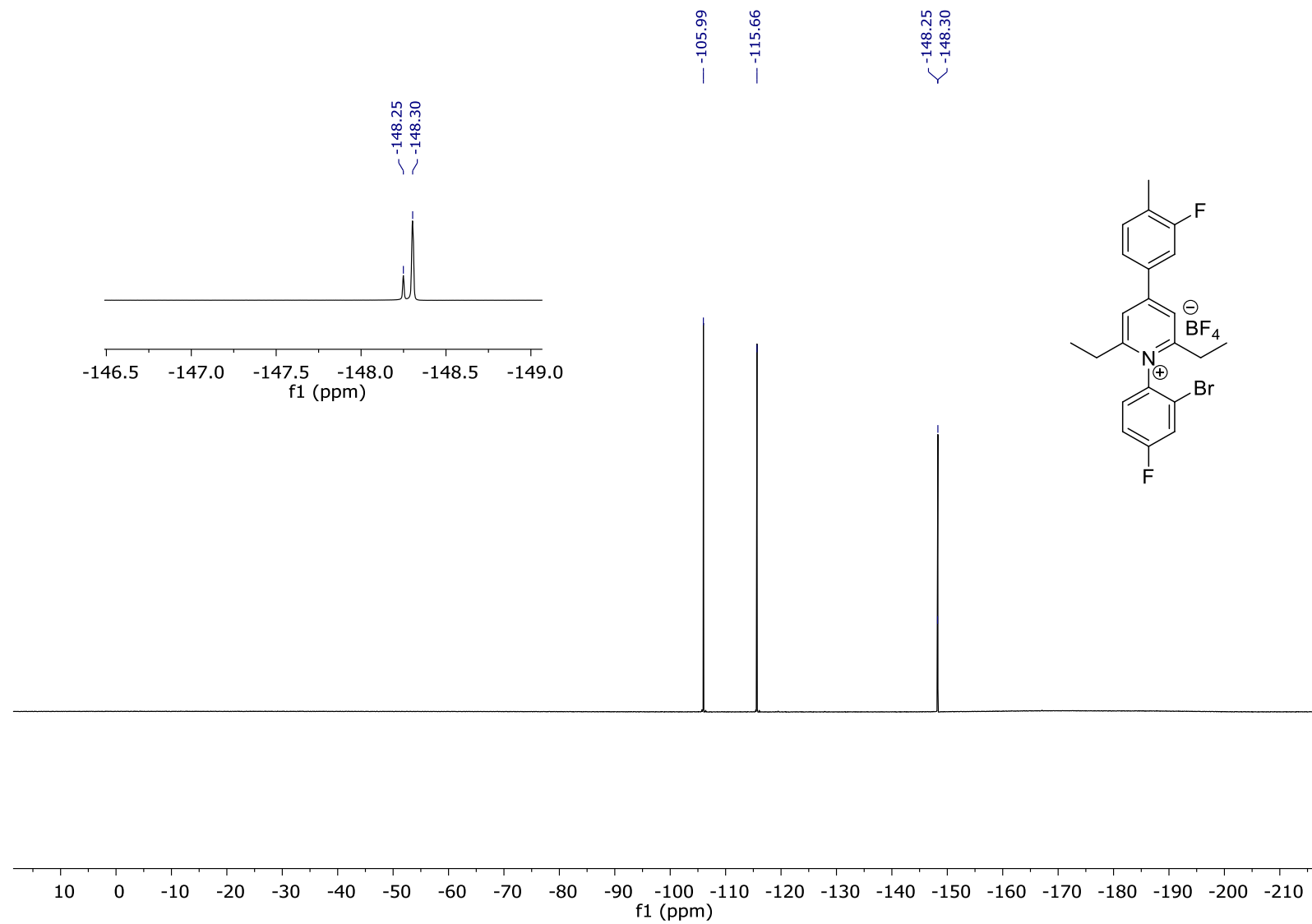
¹⁹F NMR for 3r



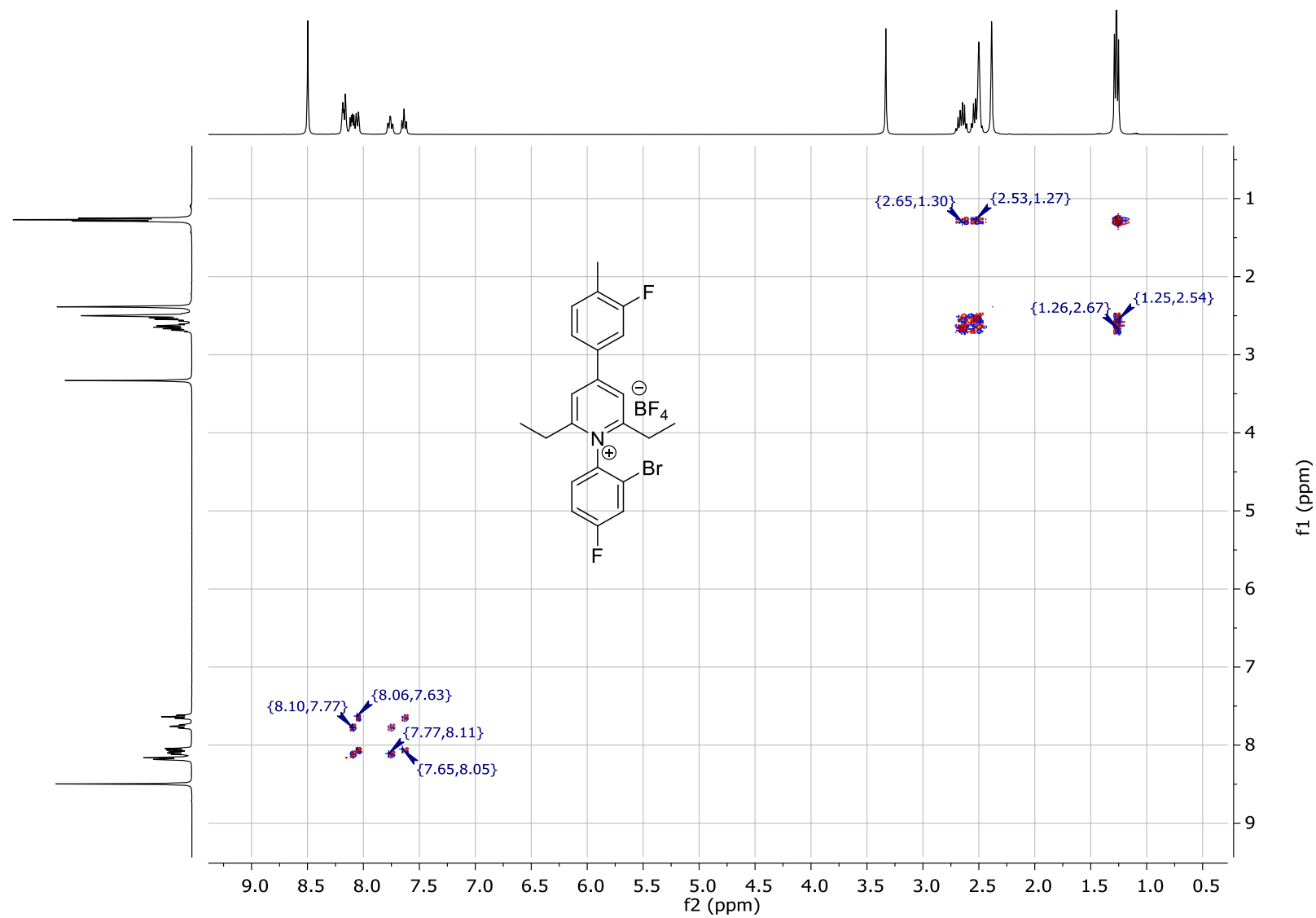
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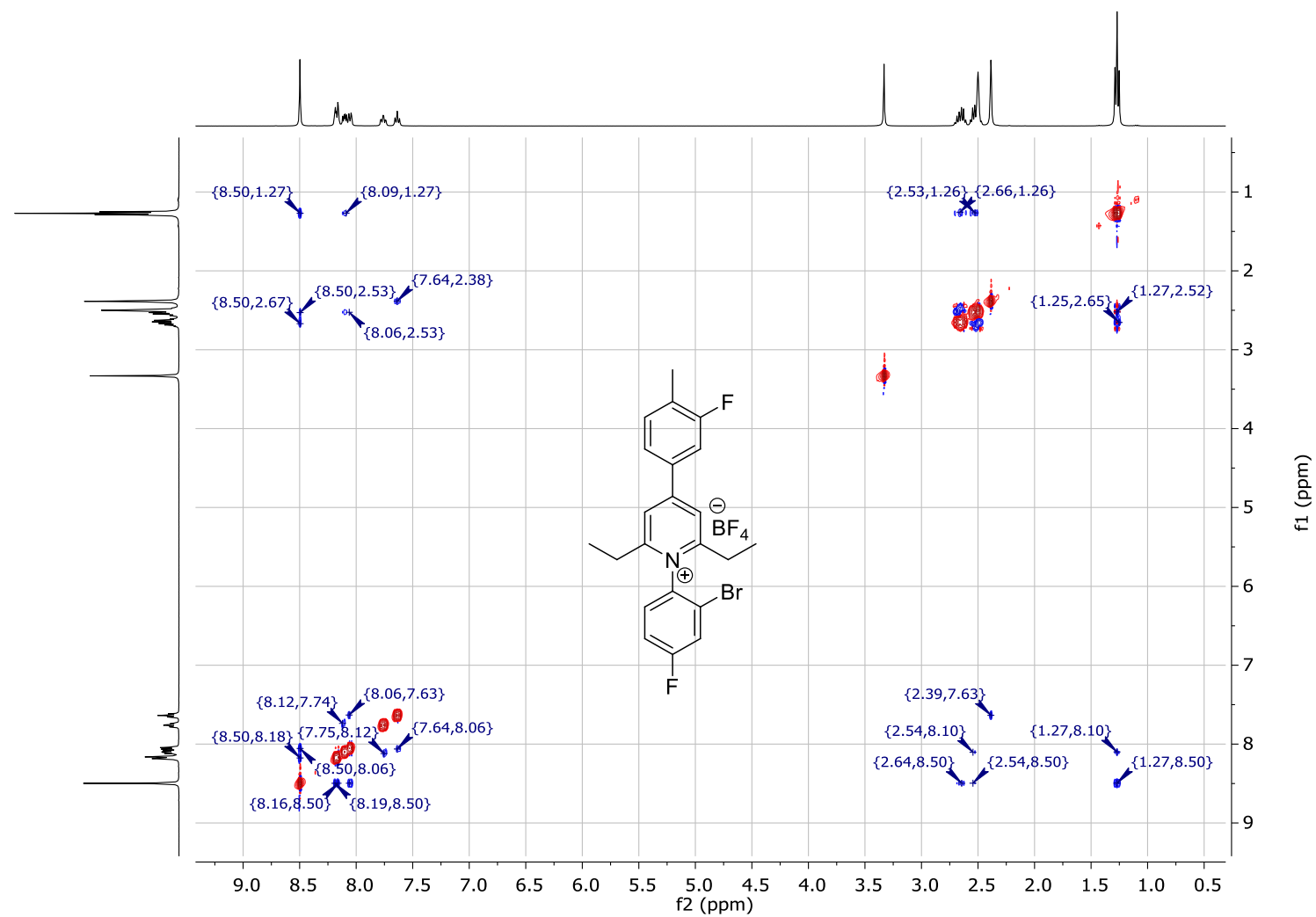
¹³C NMR for 3s



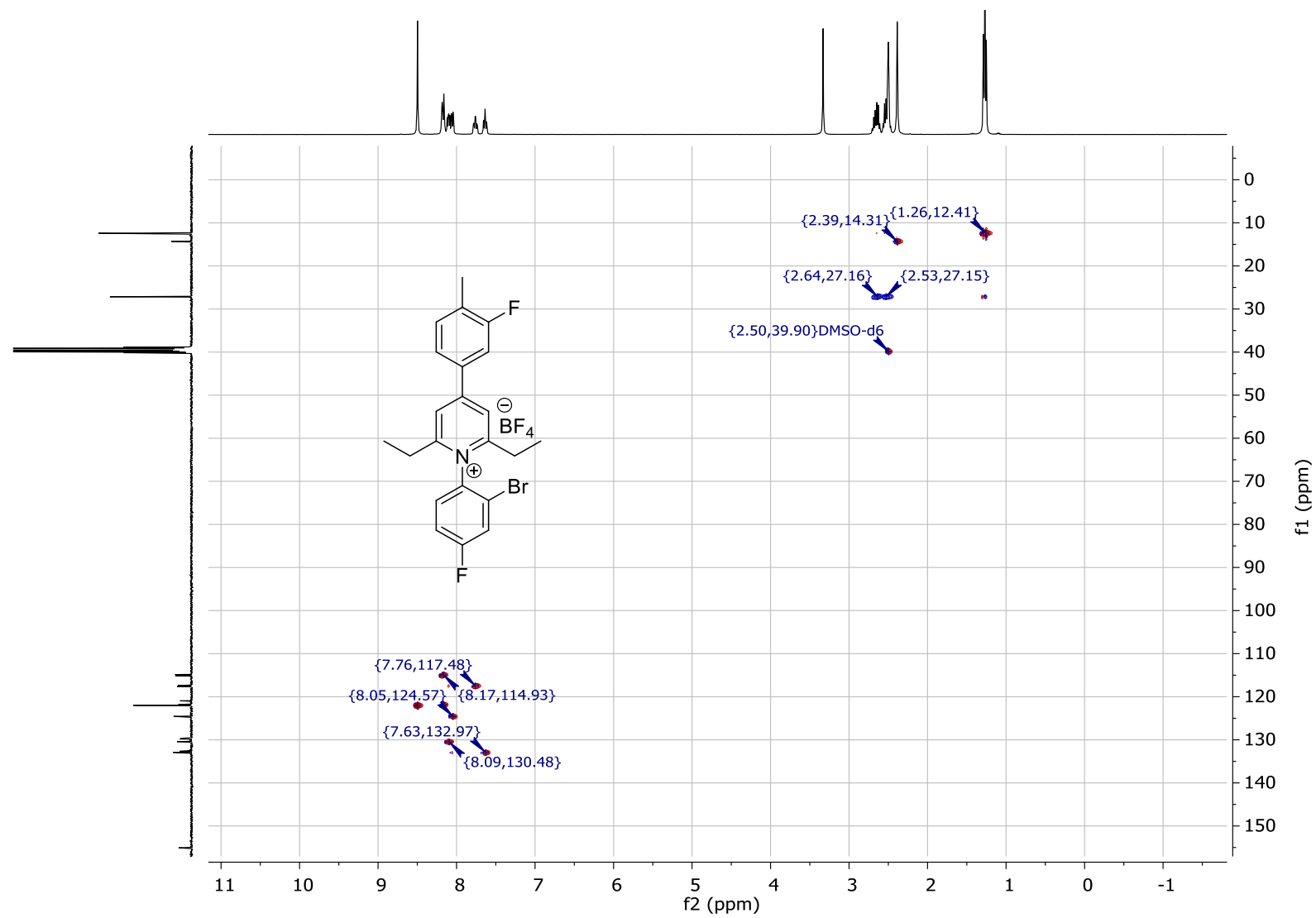
¹⁹F NMR for 3s



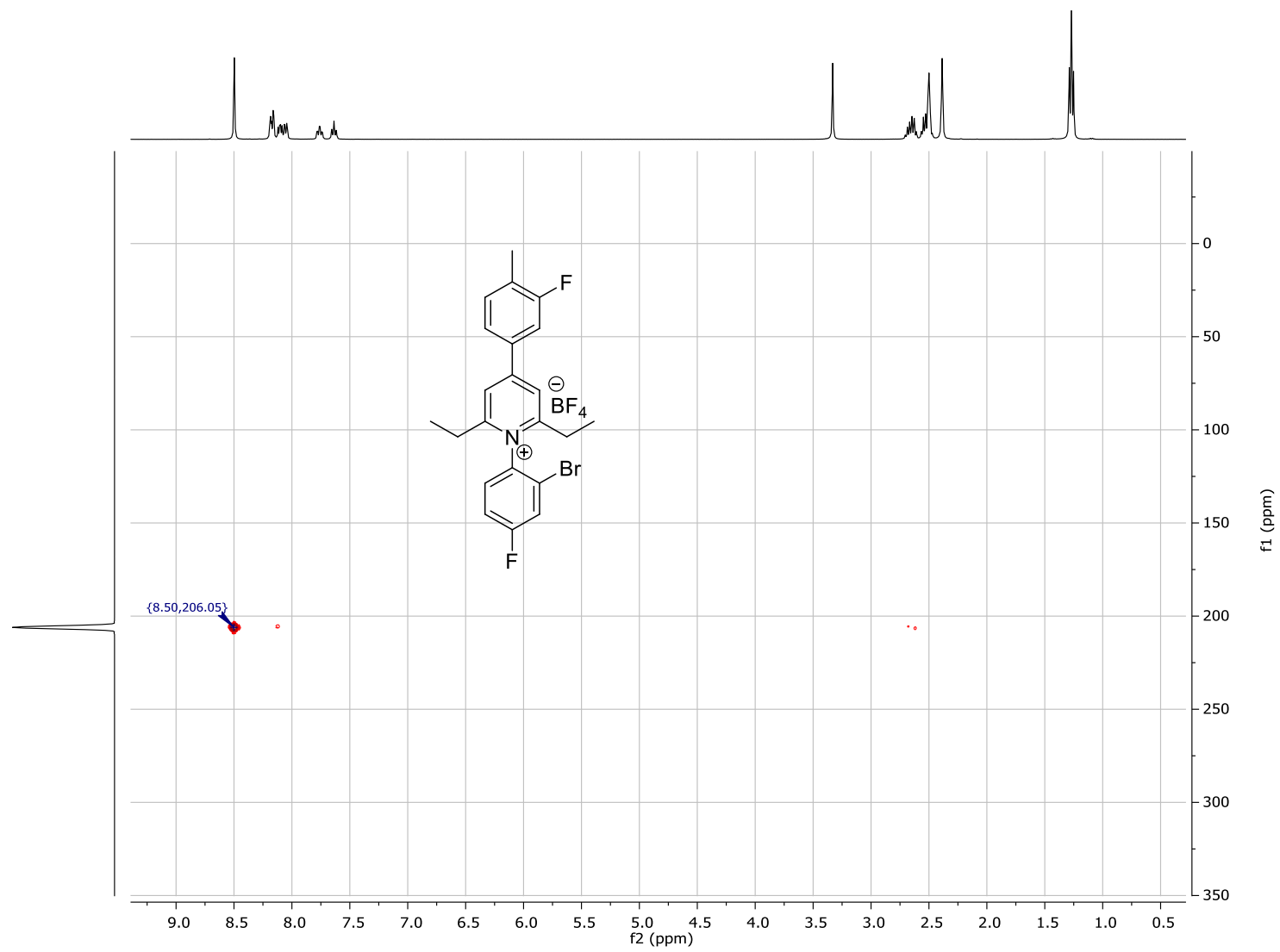
¹H-¹H COSY for 3s



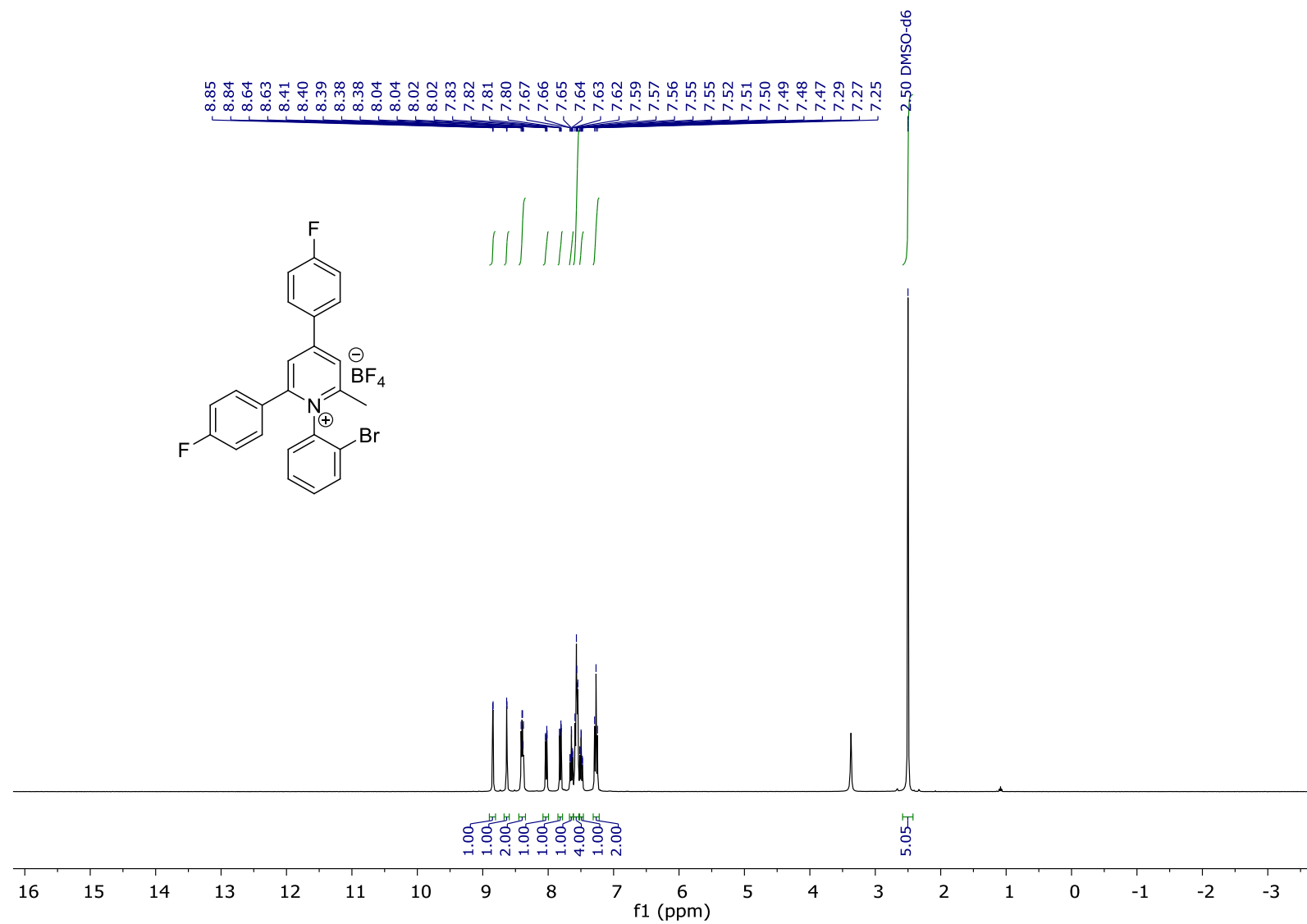
^1H - ^1H NOESY for 3s



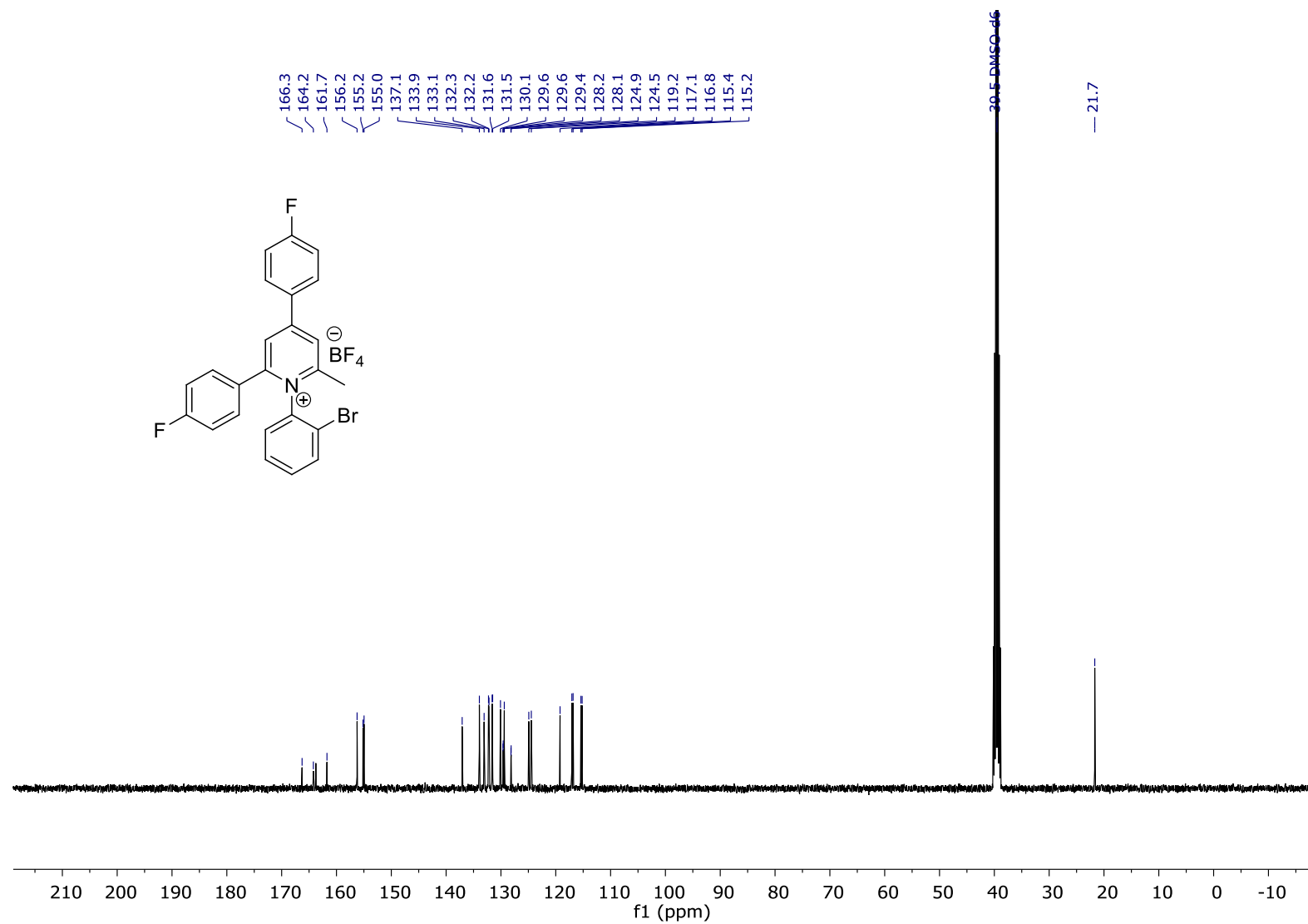
¹H-¹³C HSQC for 3s



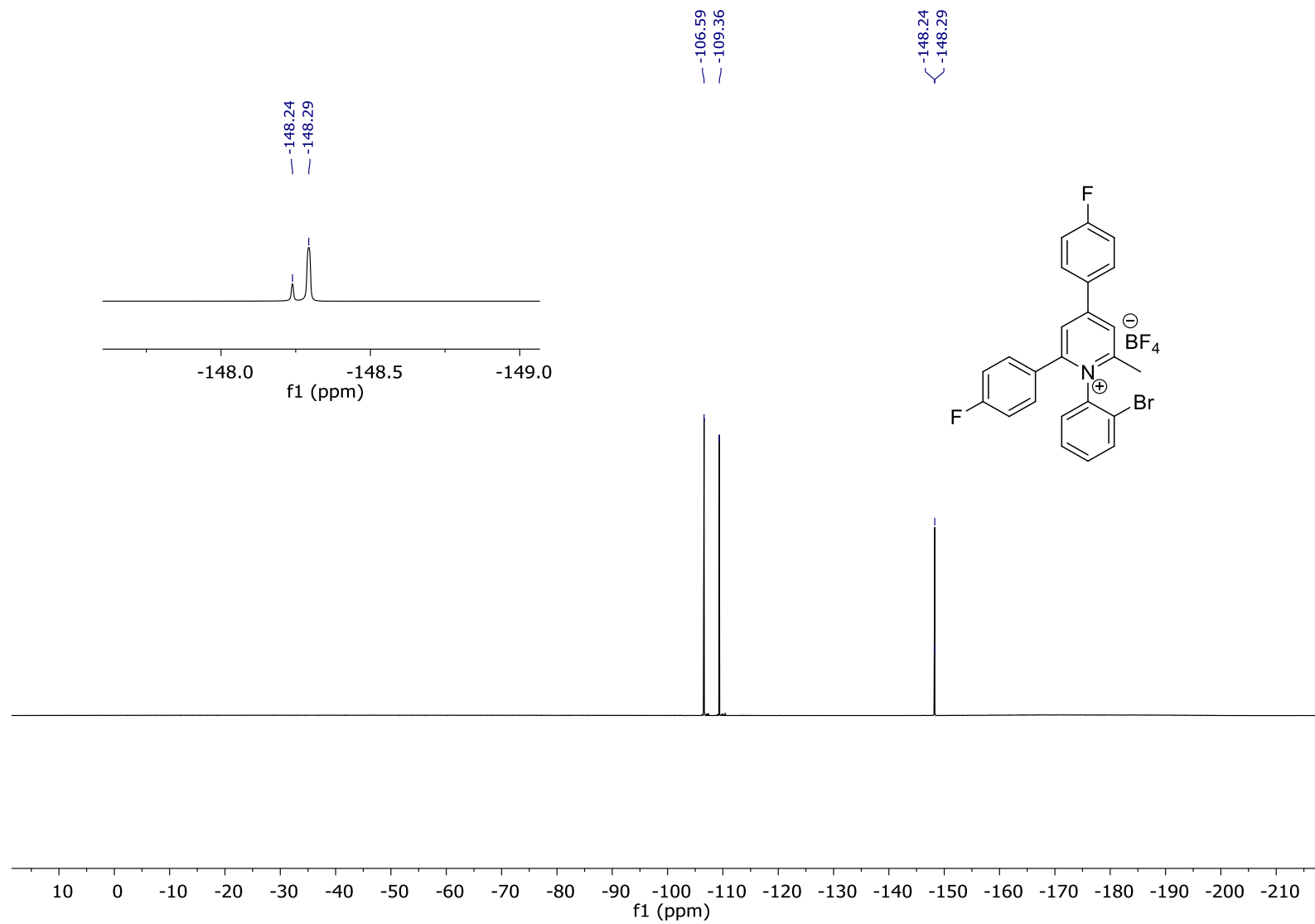
^1H - ^{15}N HMBC for 3s



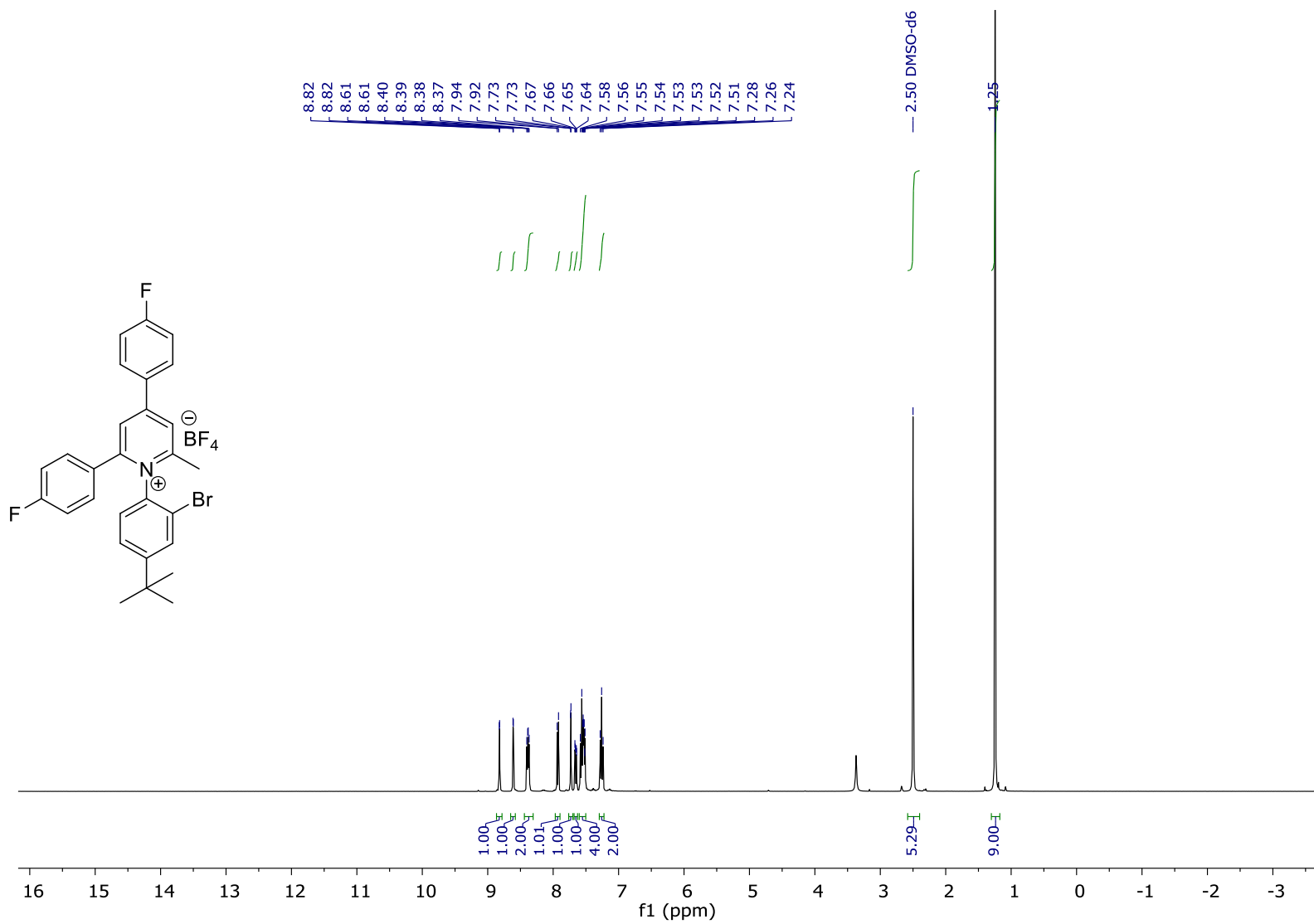
¹H NMR for 3t



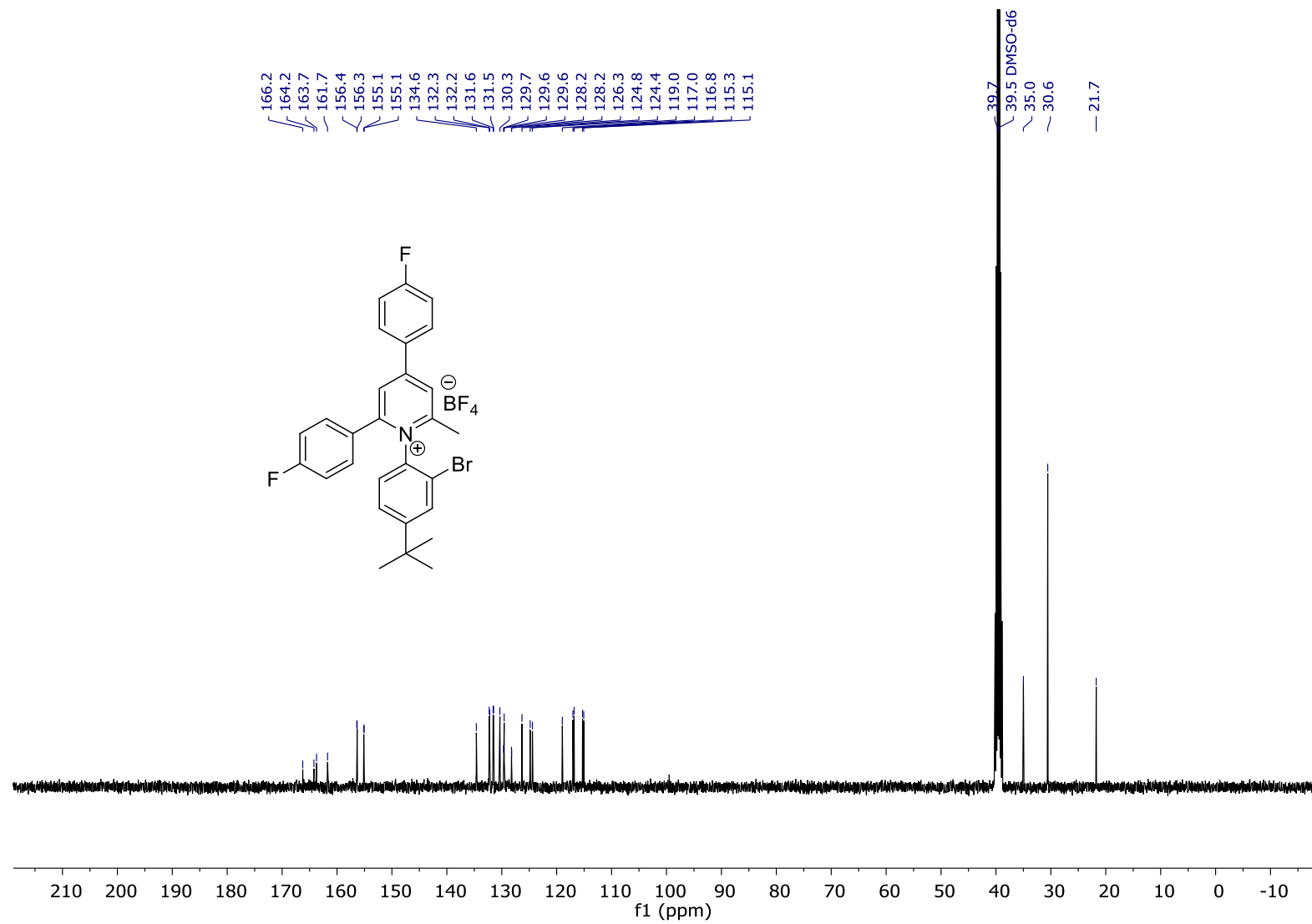
¹³C NMR for 3t



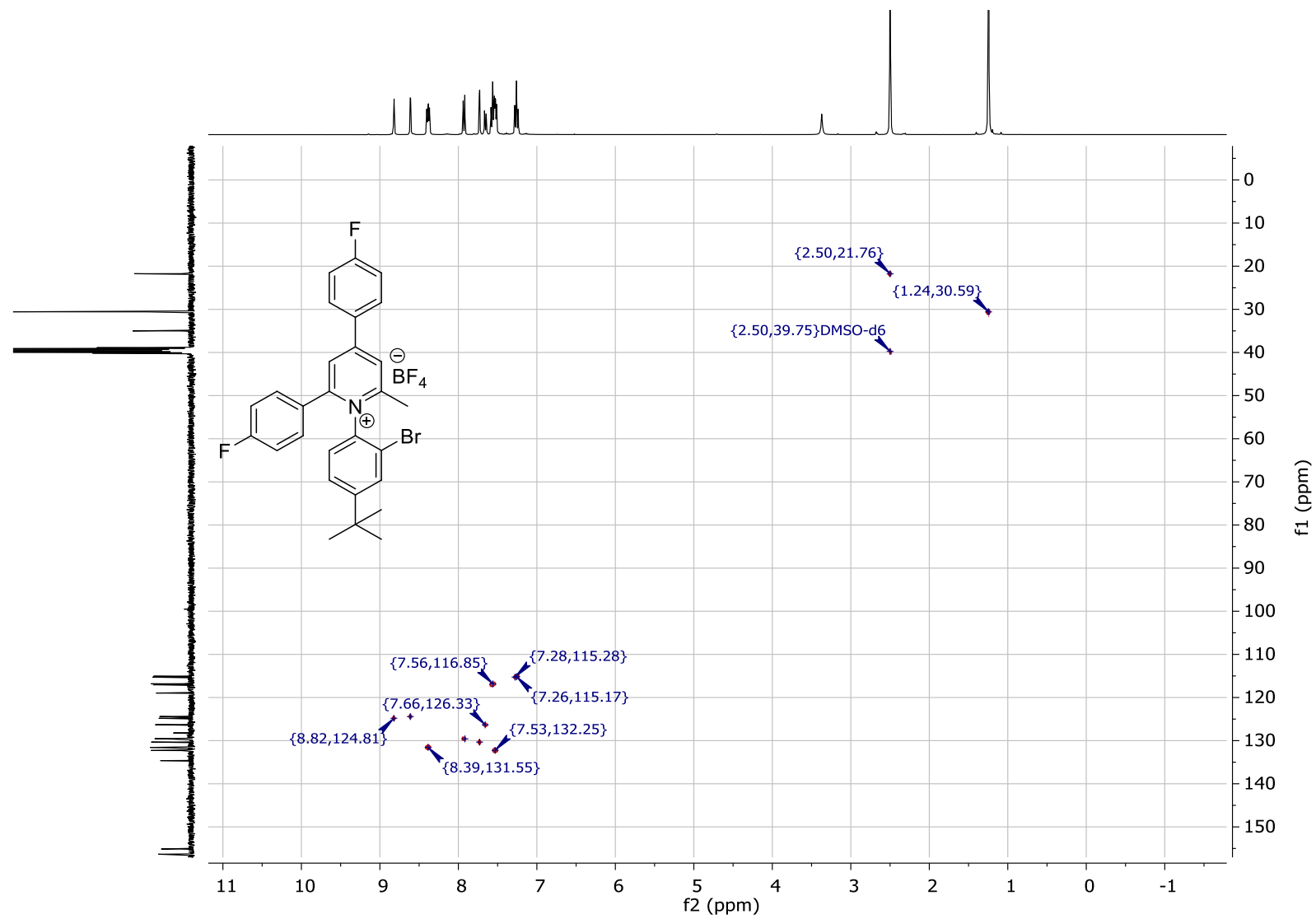
¹⁹F NMR for 3t



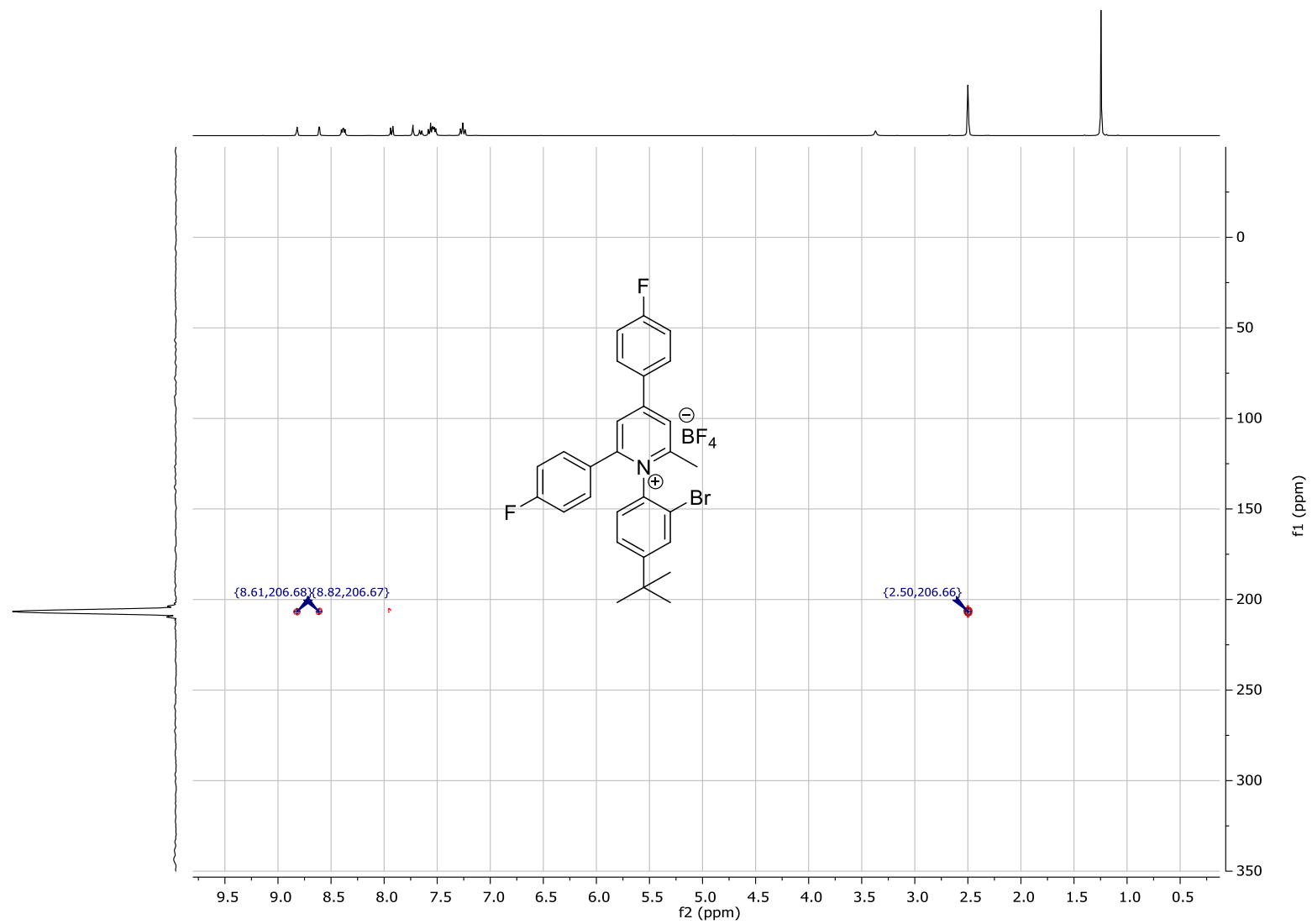
¹H NMR for 3u



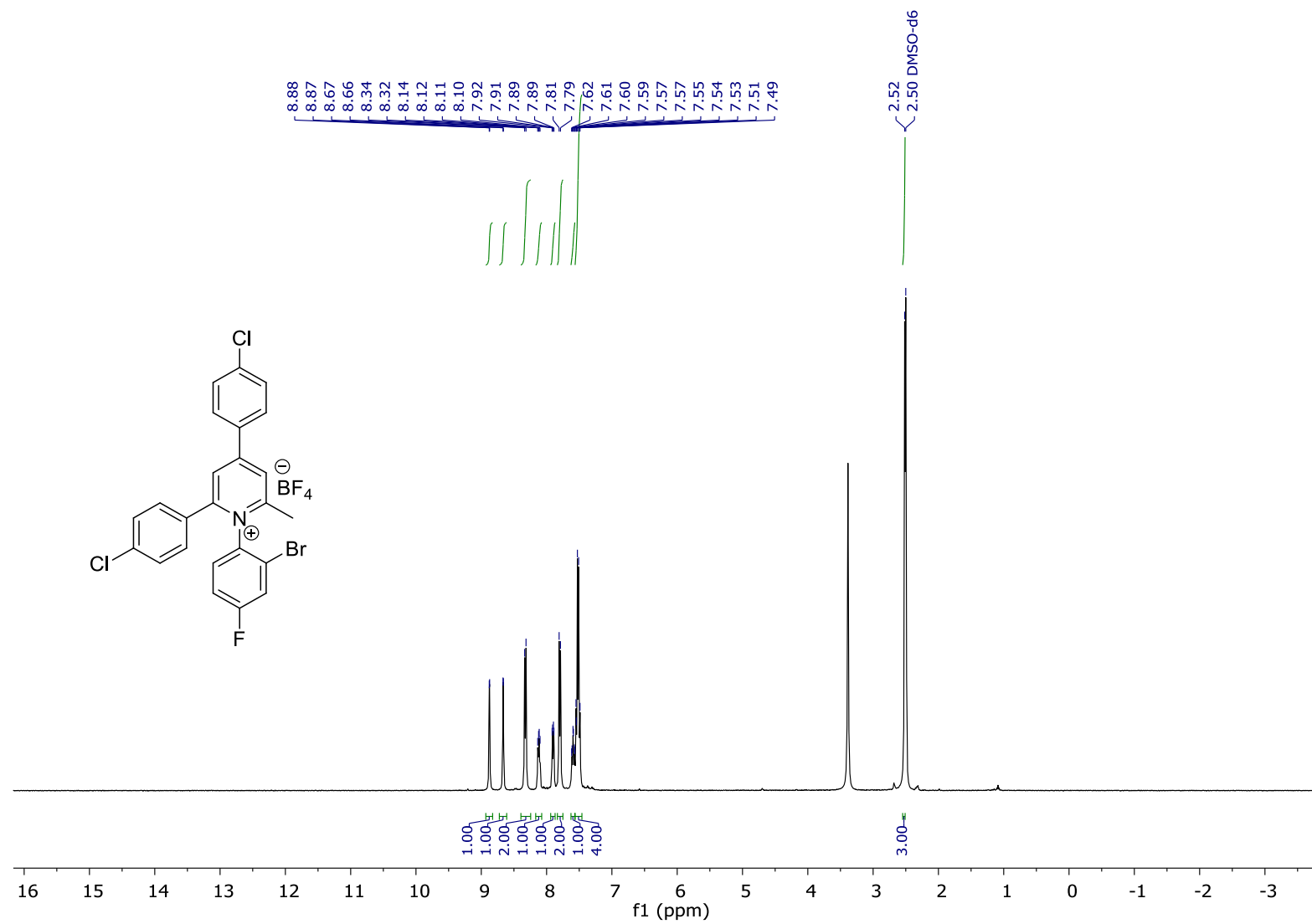
¹³C NMR for 3u



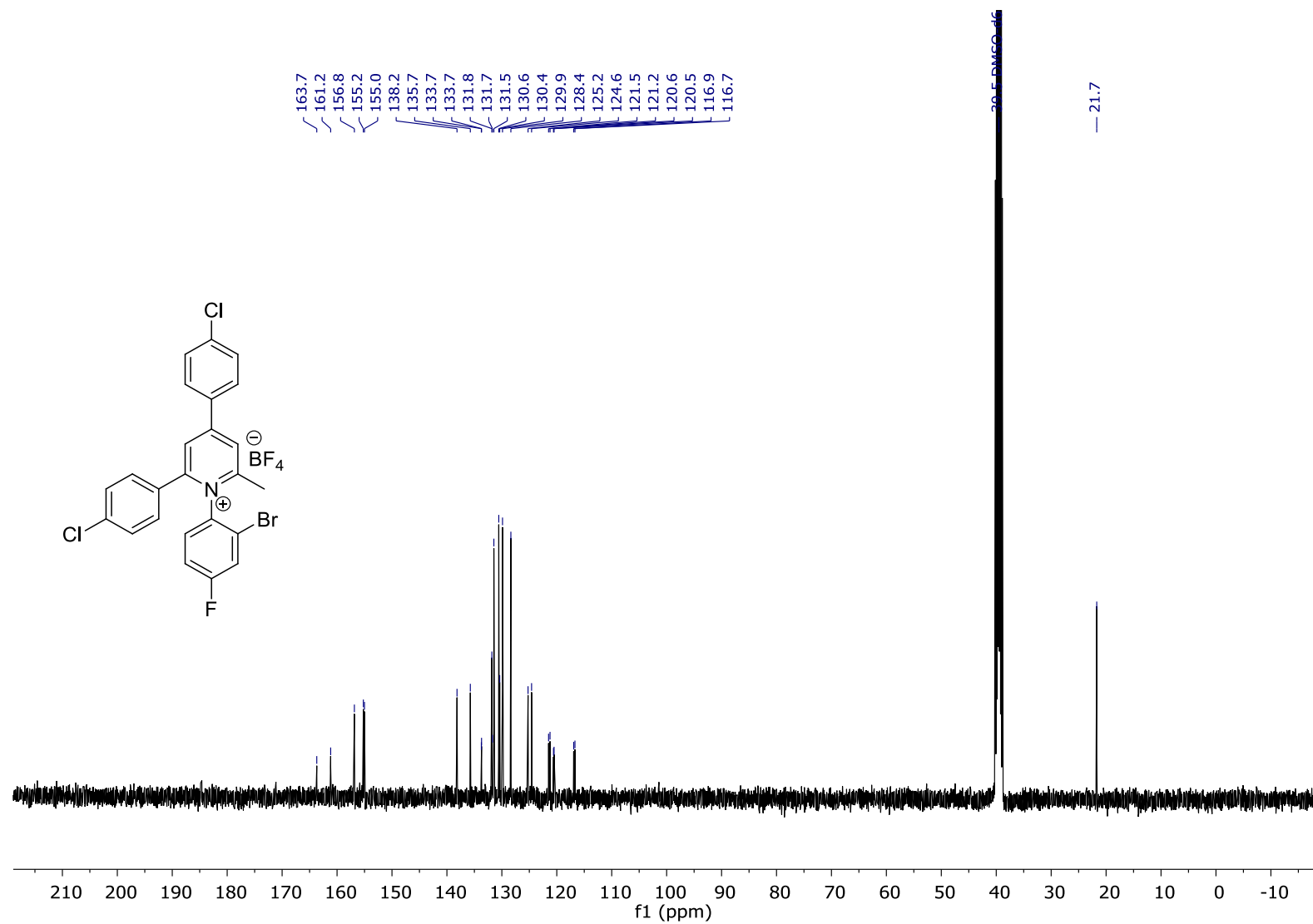
¹H-¹³C HSQC for 3u



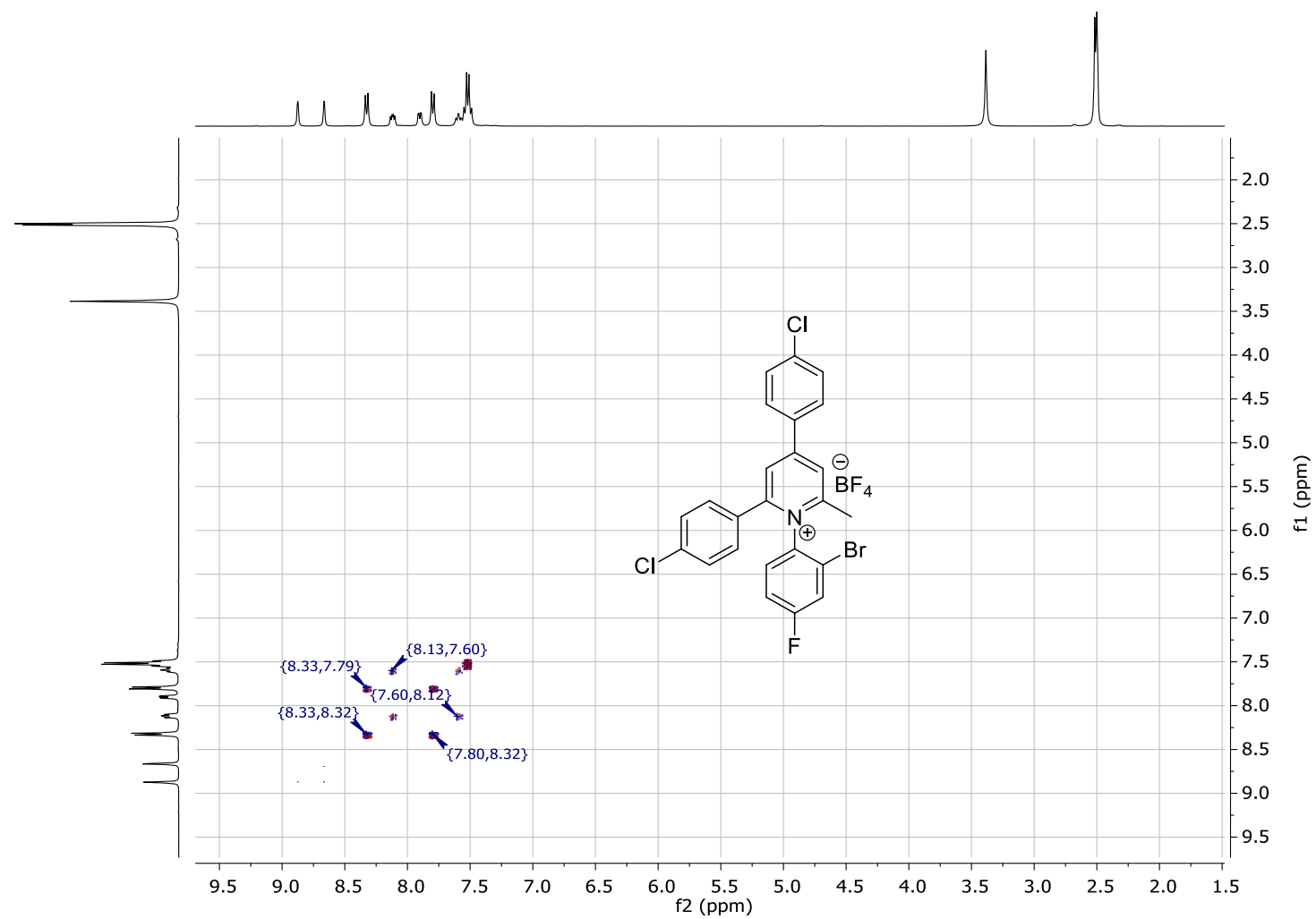
^1H - ^{15}N HMBC for 3u

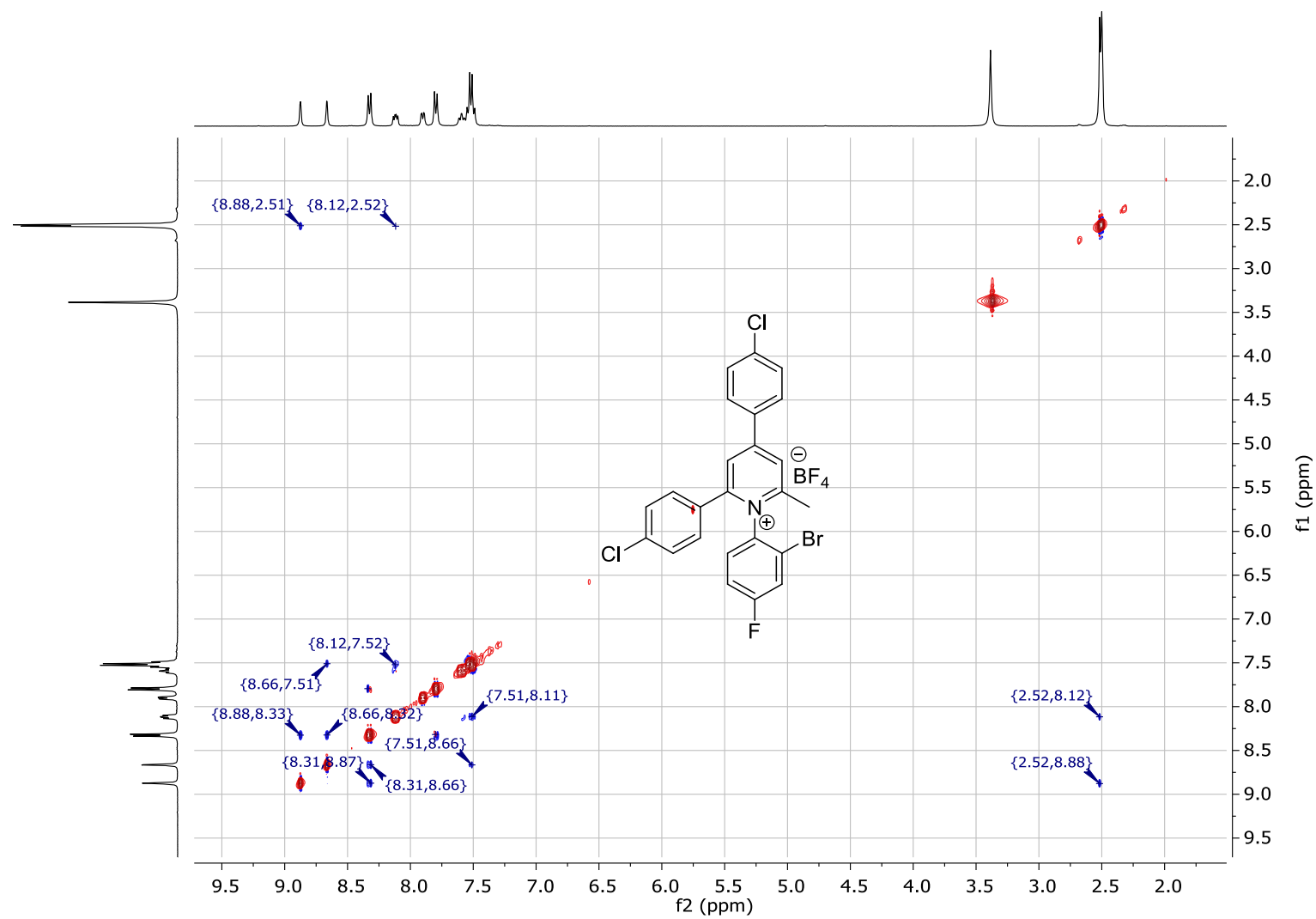


¹H NMR for 3v

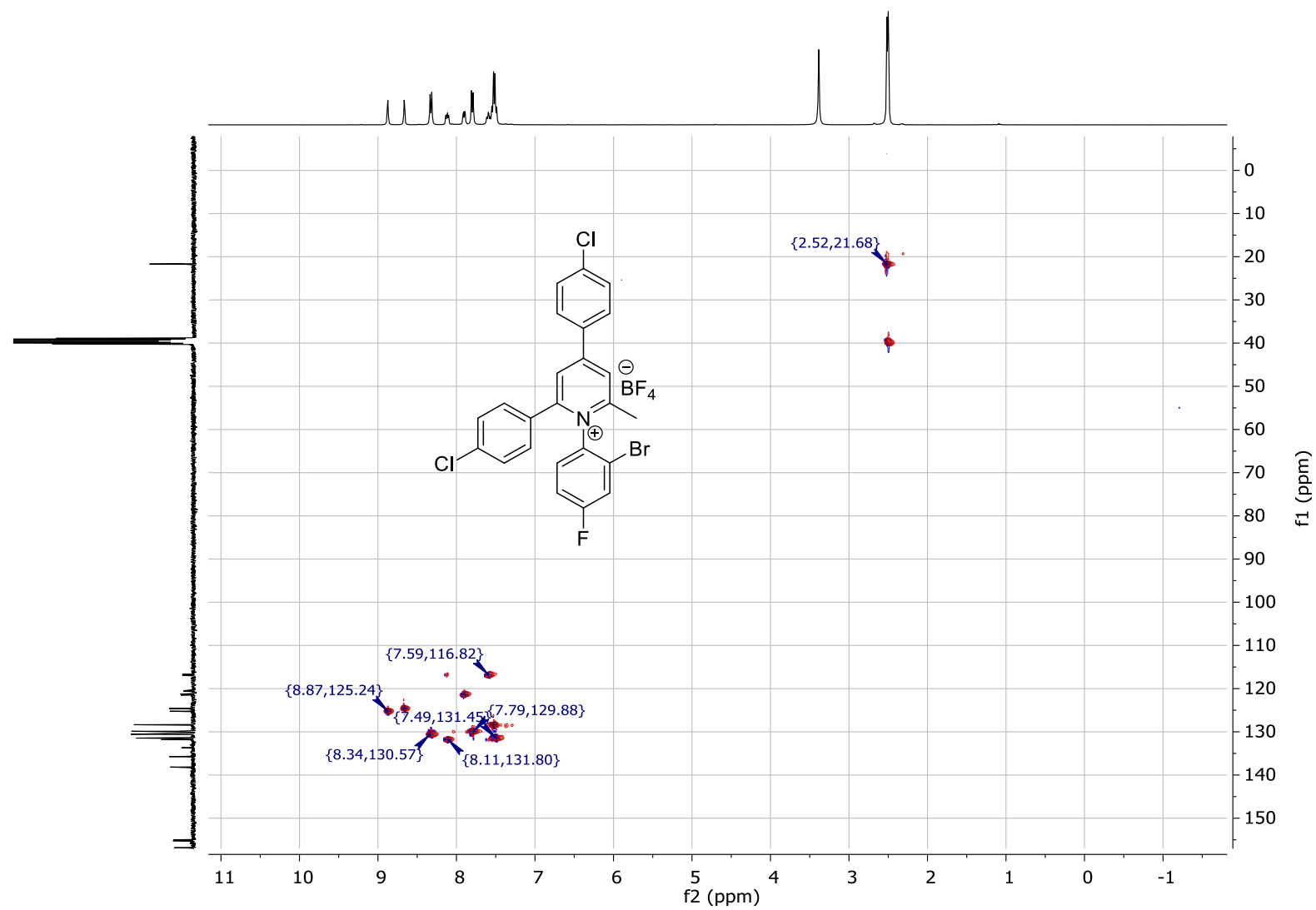


¹³C NMR for 3v

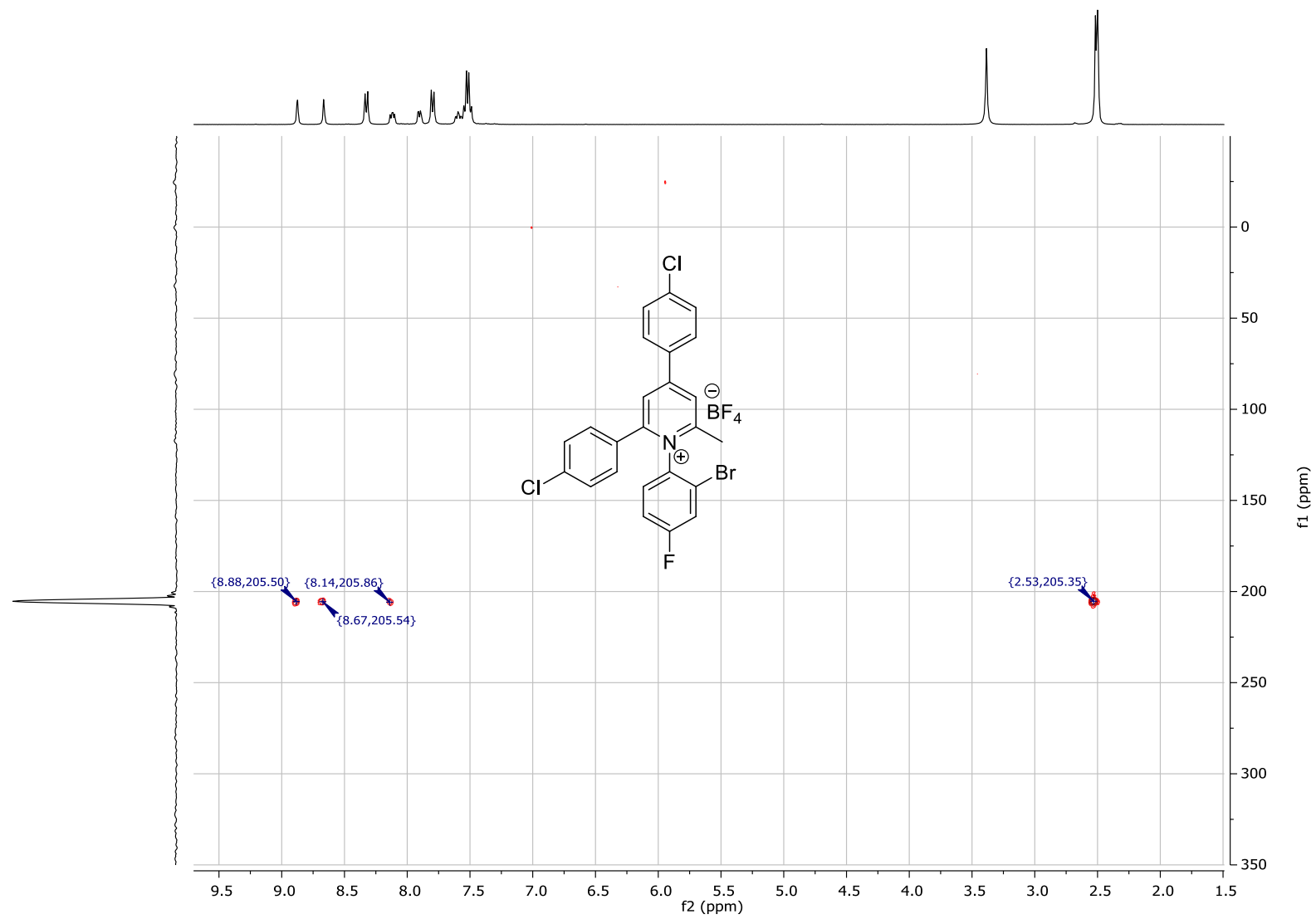




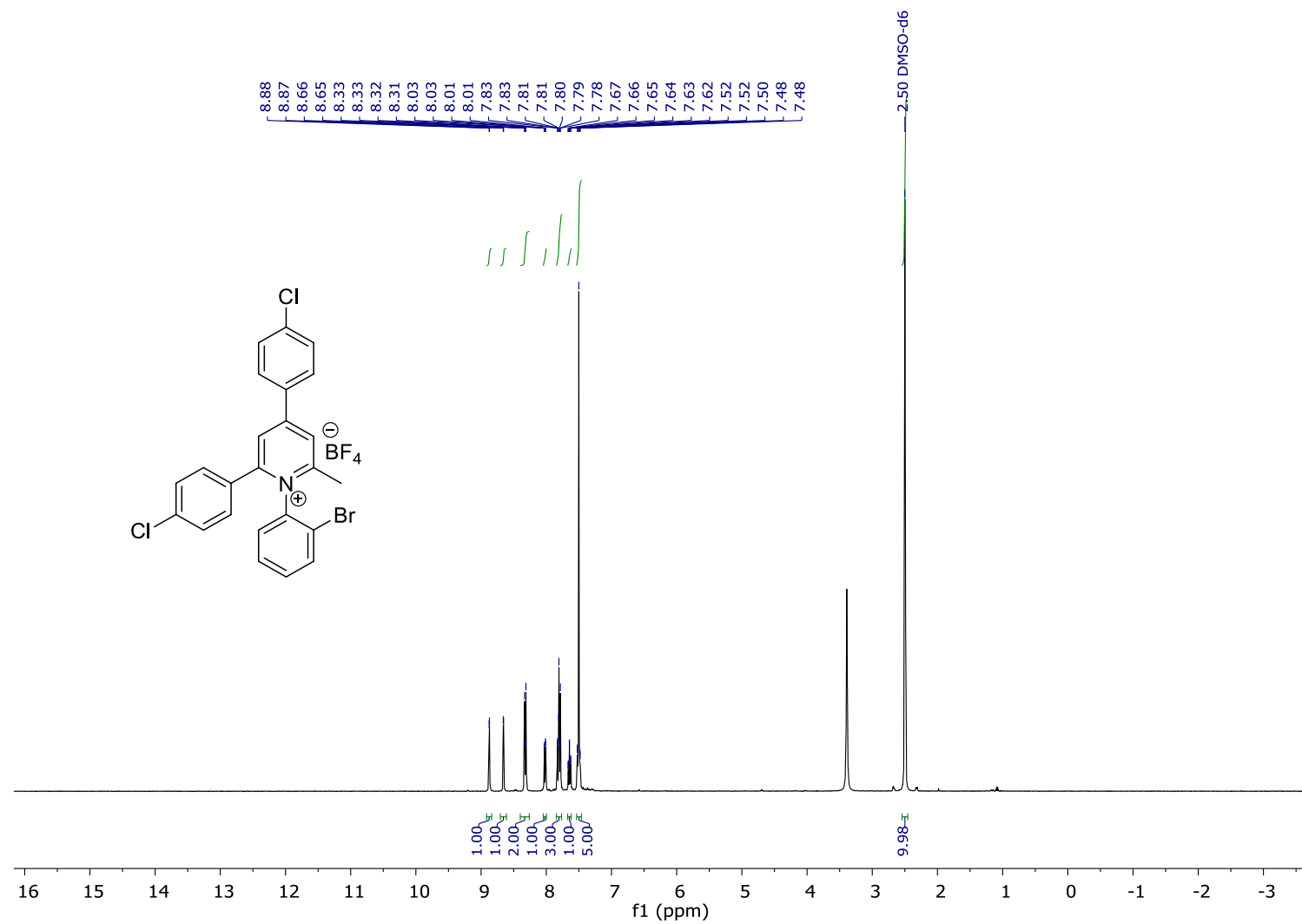
^1H - ^1H NOESY for 3v



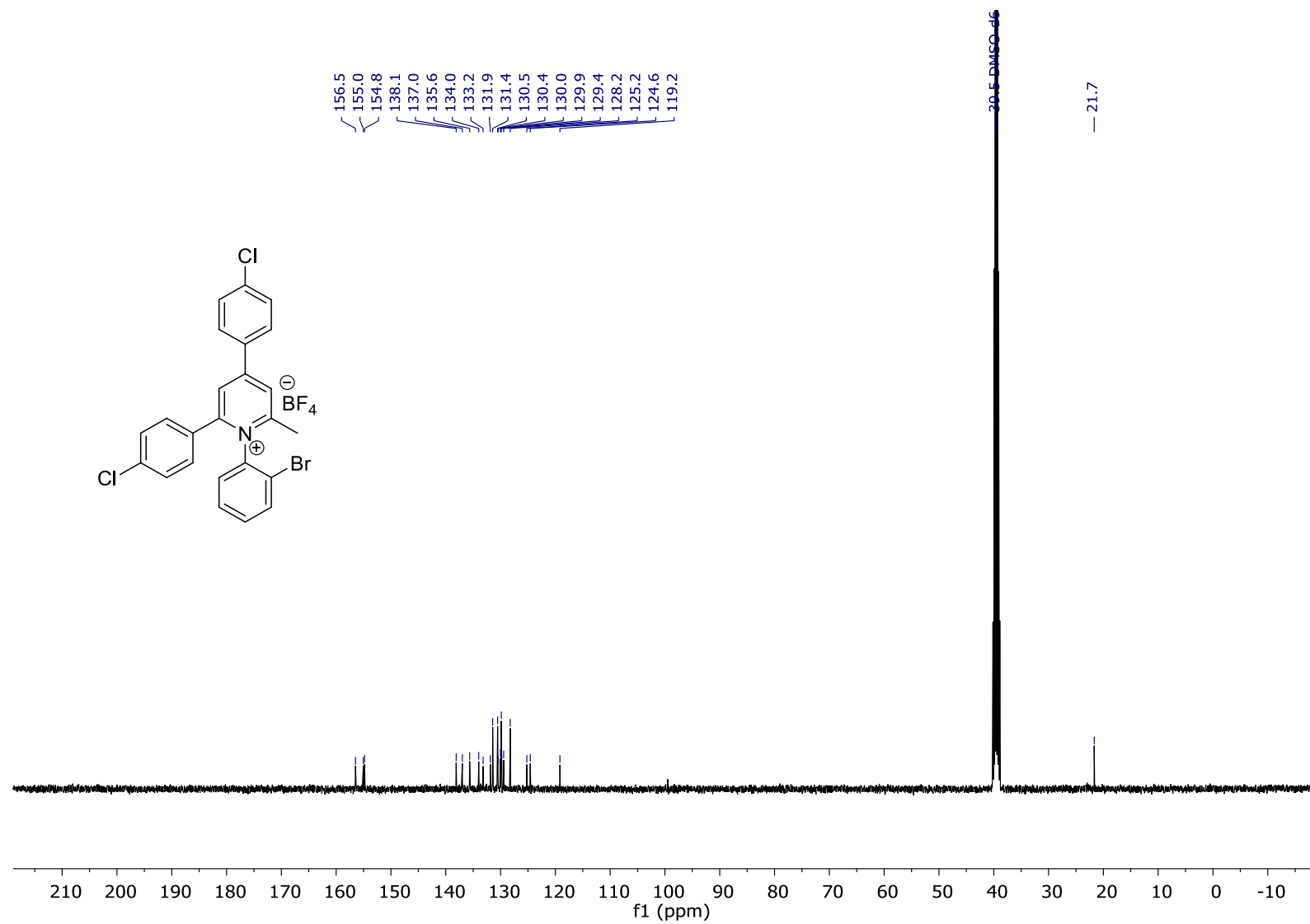
^1H - ^{13}C HSQC for 3v



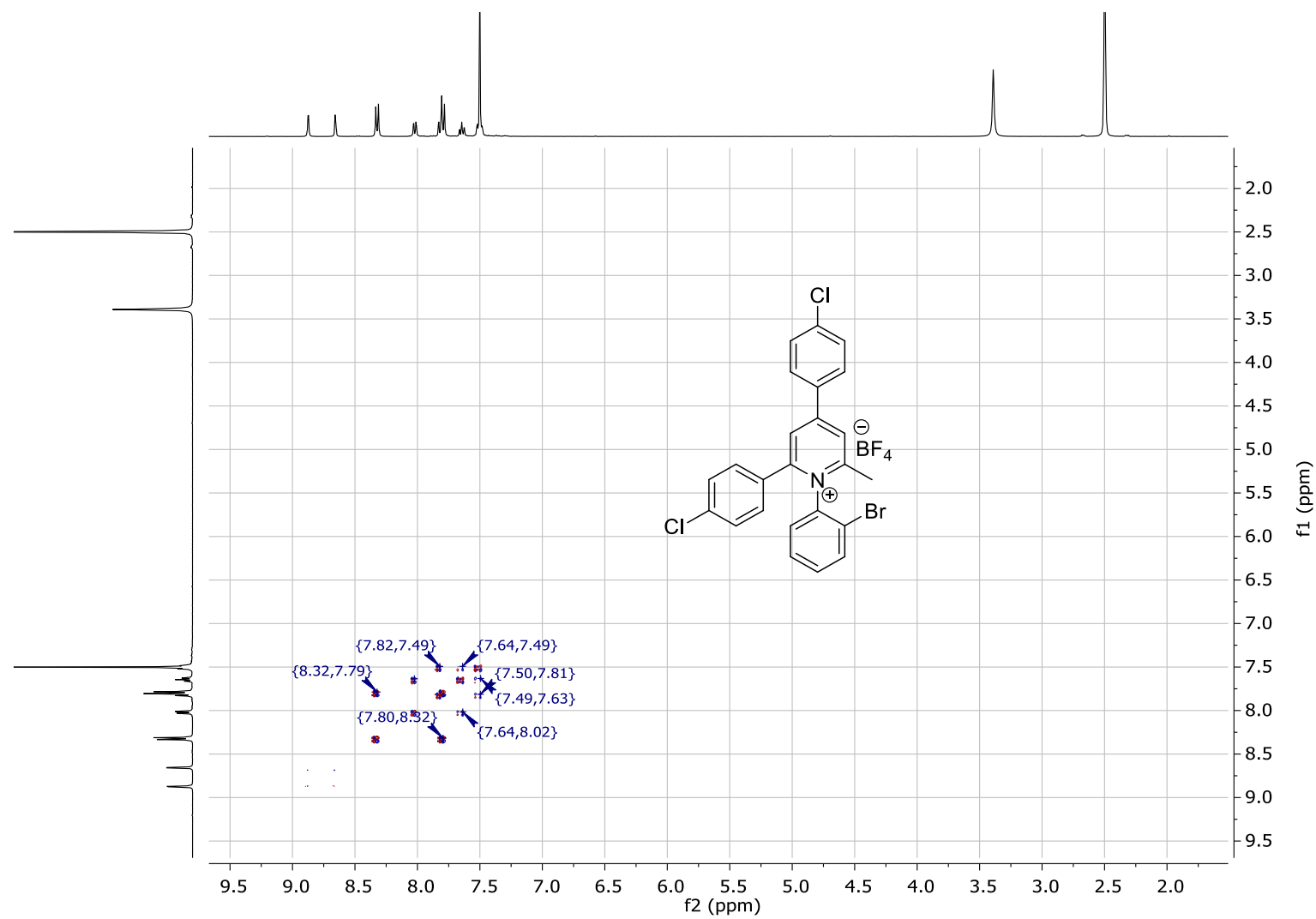
¹H-¹⁵N HMBC for 3v



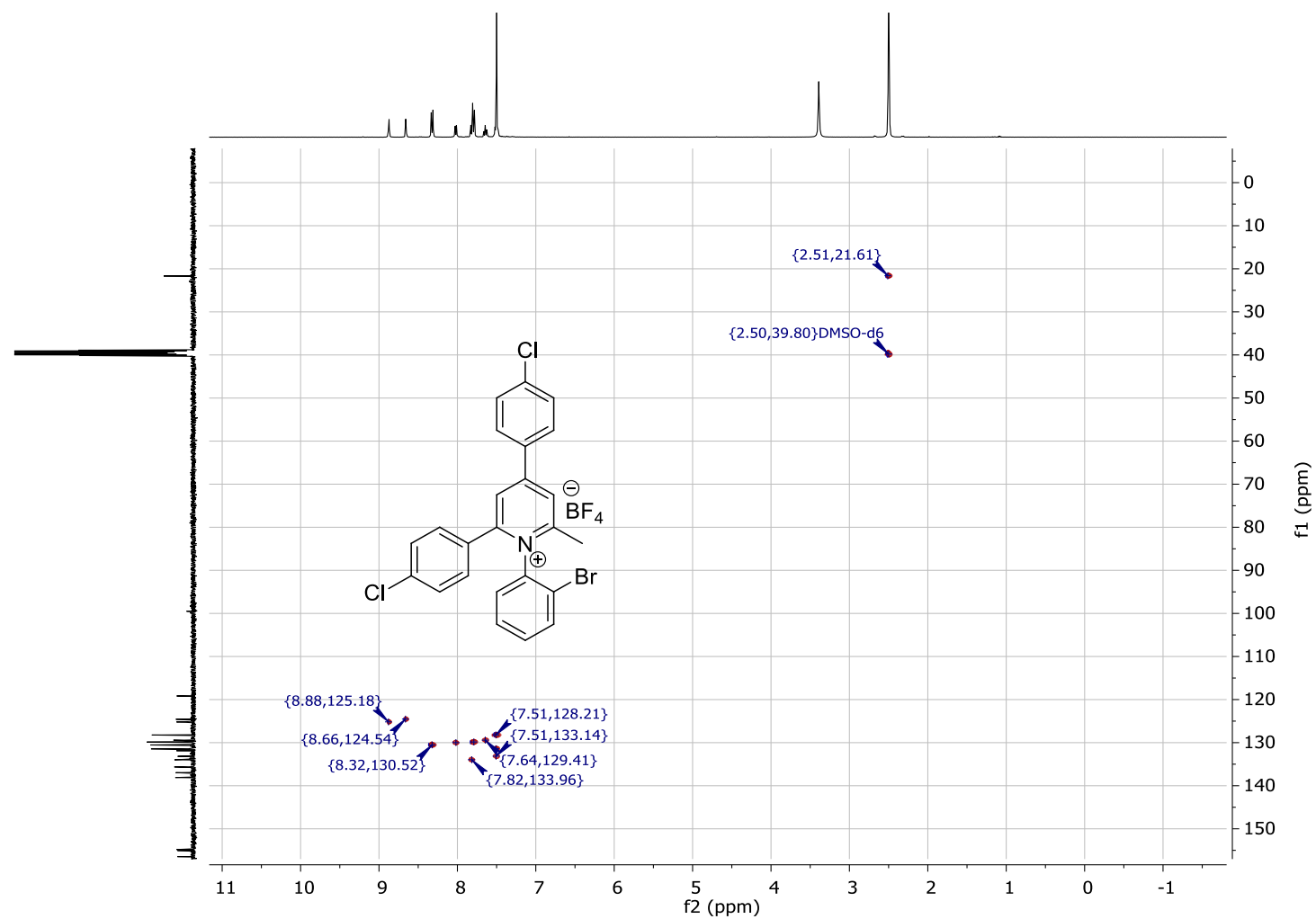
¹H NMR for 3w



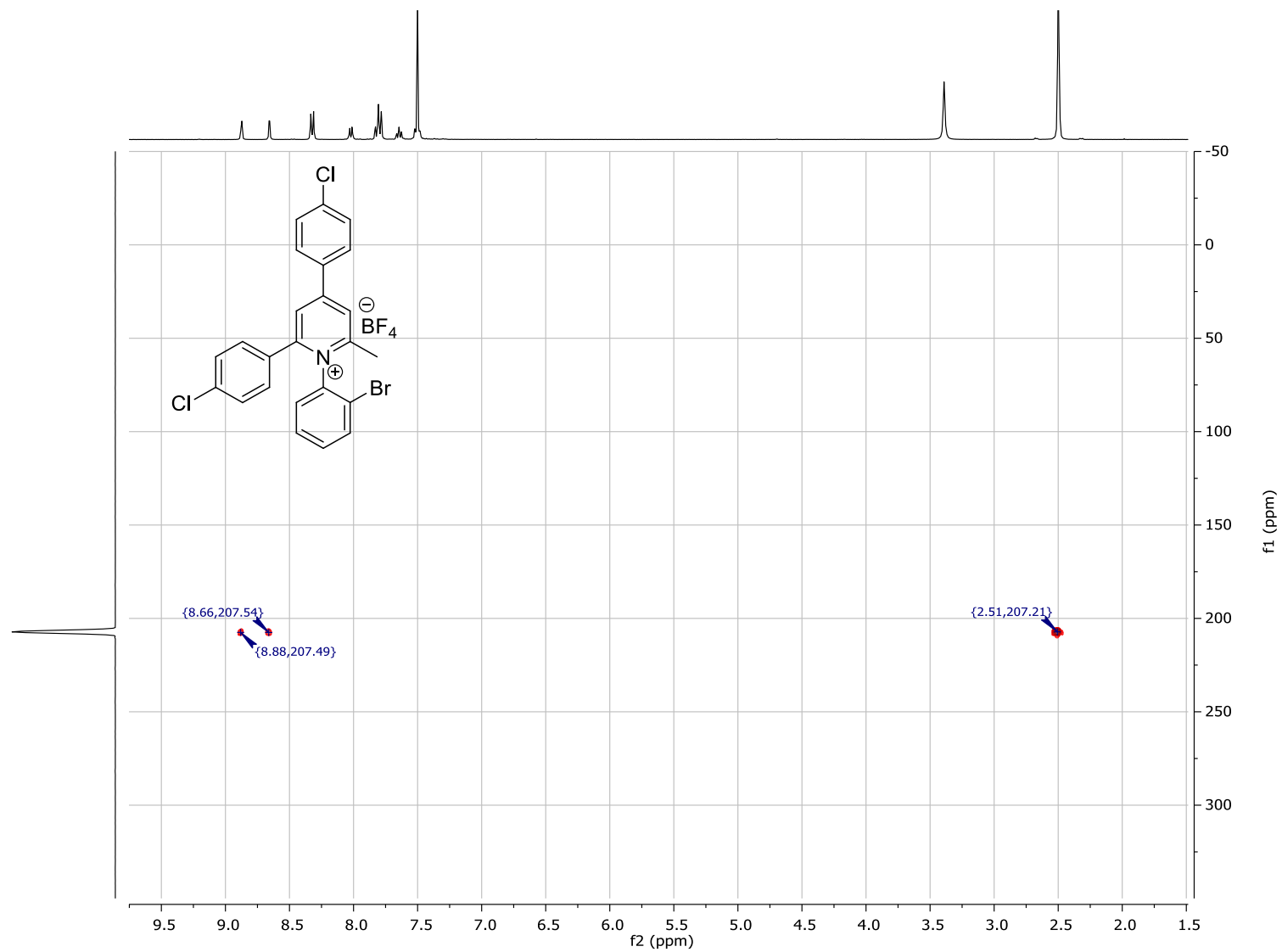
¹³C NMR for 3w



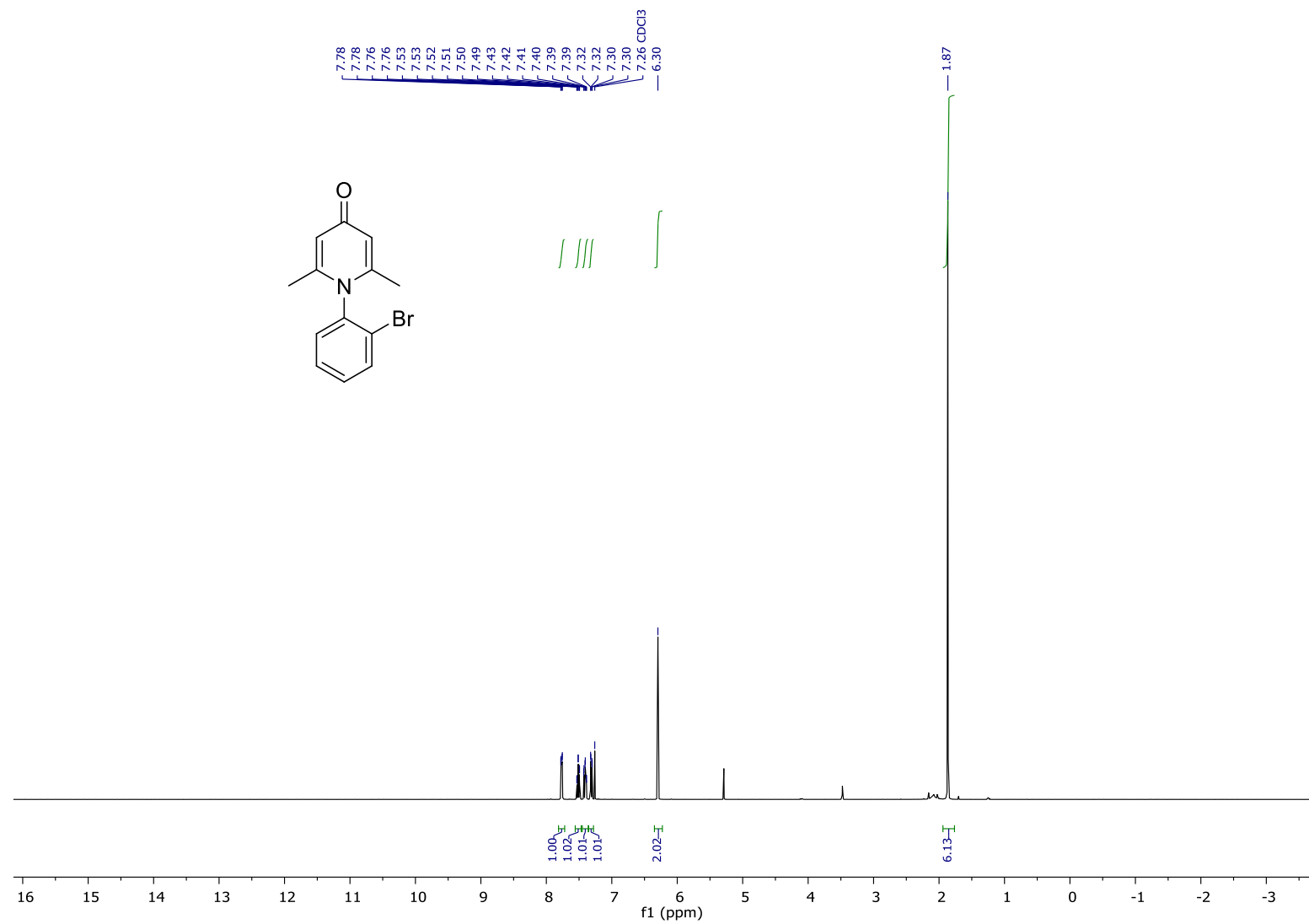
^1H - ^1H COSY for 3w



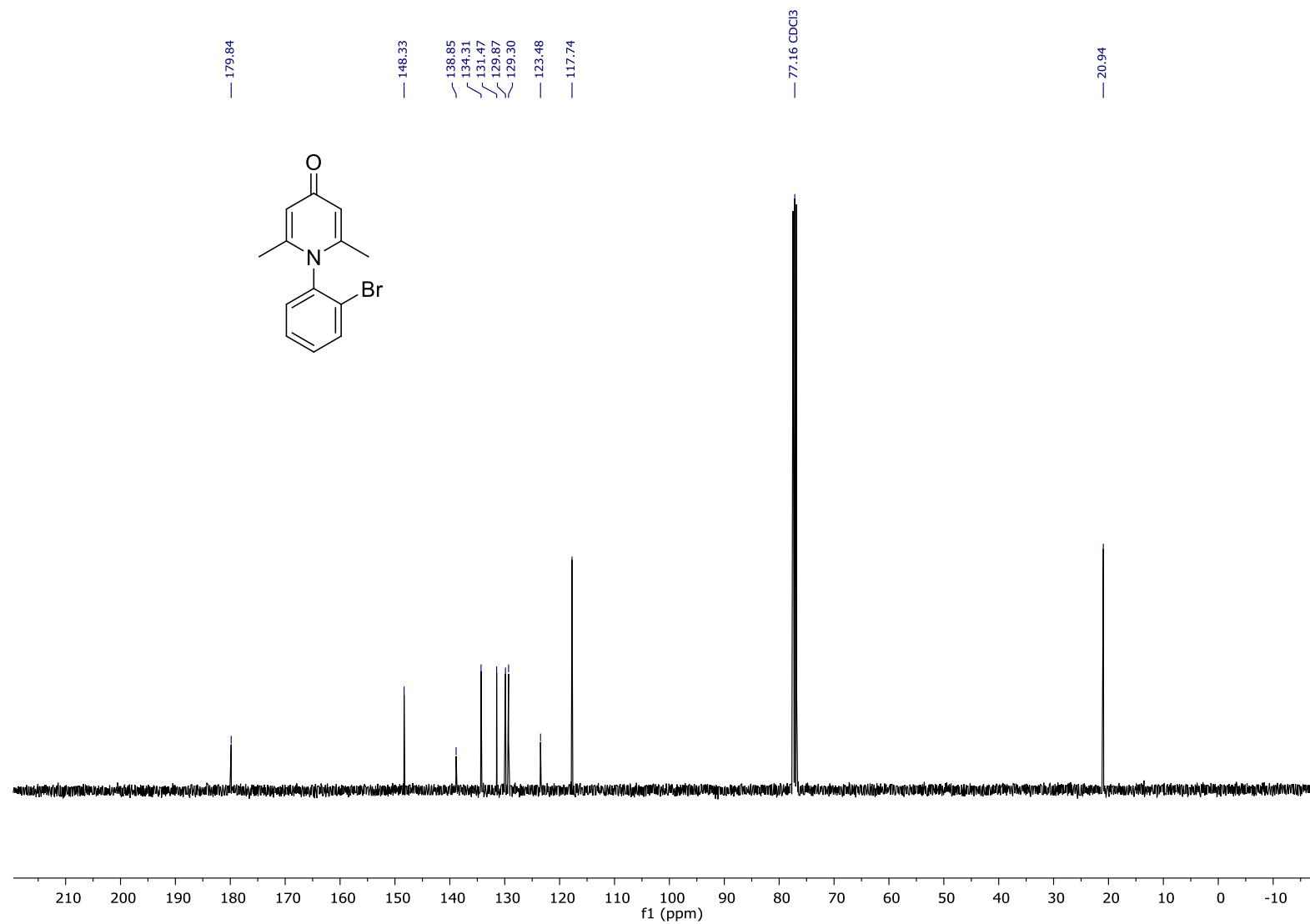
^1H - ^{13}C HSQC for 3w



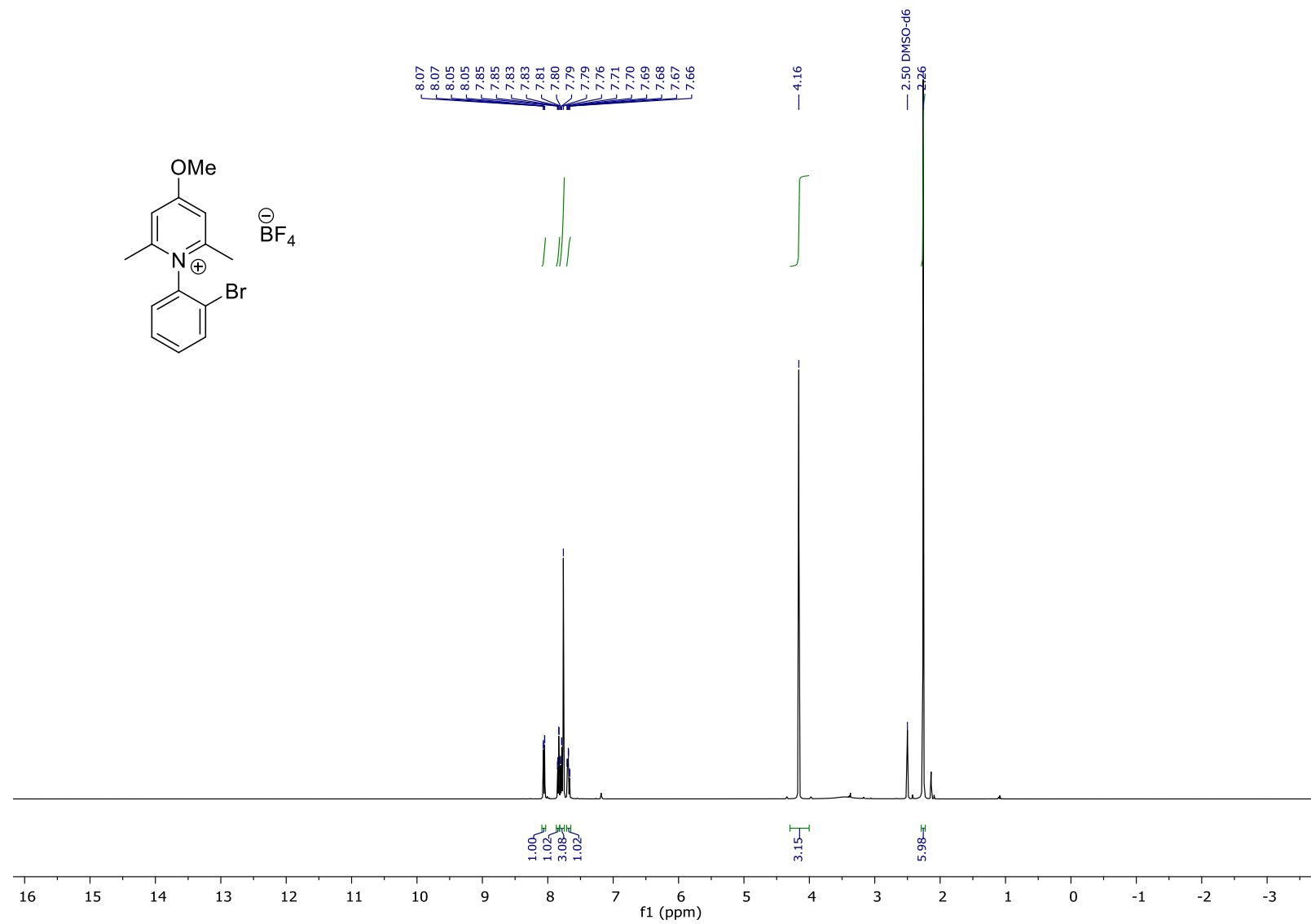
^1H - ^{15}N HMBC for 3w



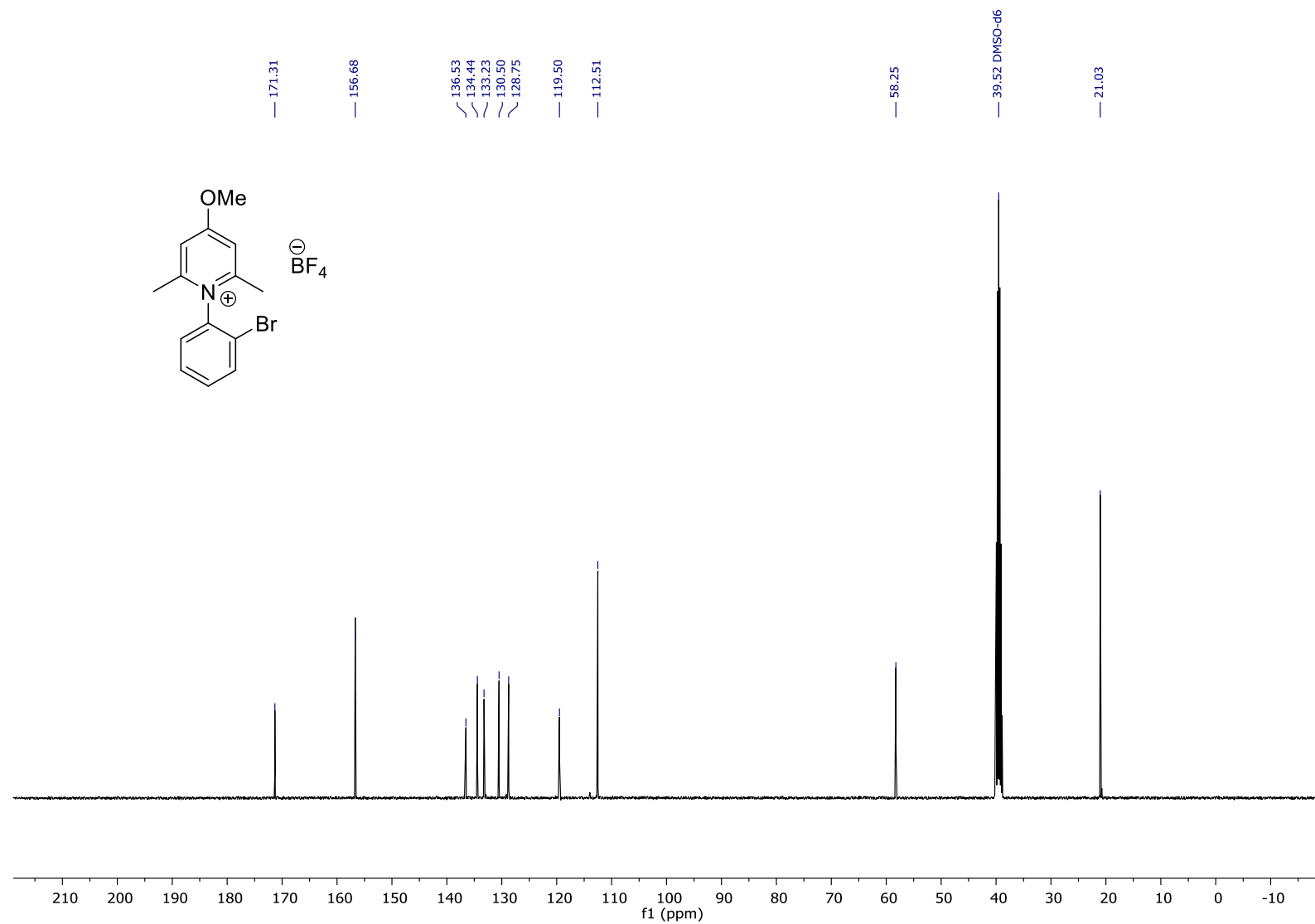
¹H NMR of 1-(2-bromophenyl)-2,6-dimethylpyridin-4(1H)-one



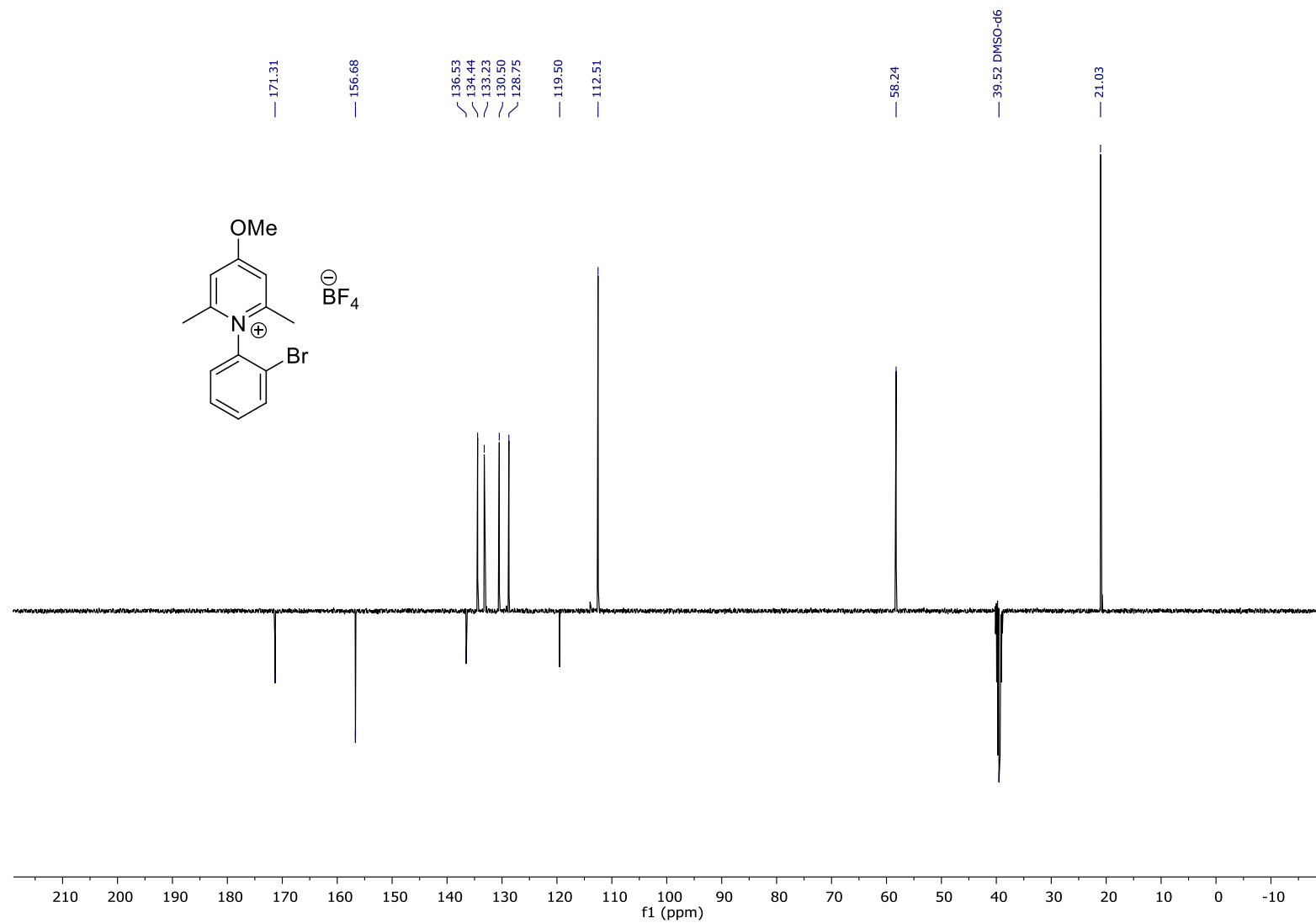
¹³C NMR of 1-(2-bromophenyl)-2,6-dimethylpyridin-4(1H)-one



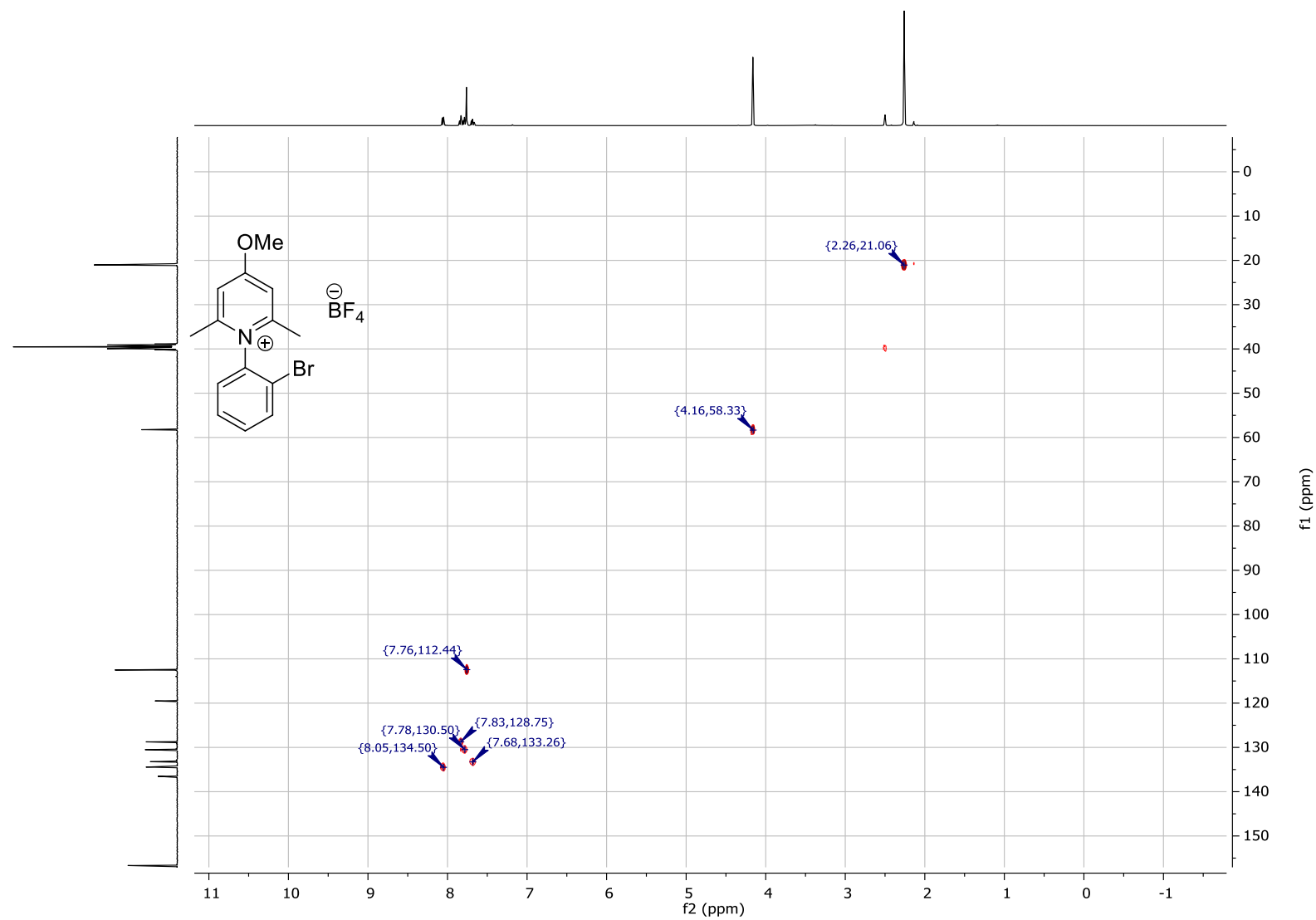
¹H NMR for 3x



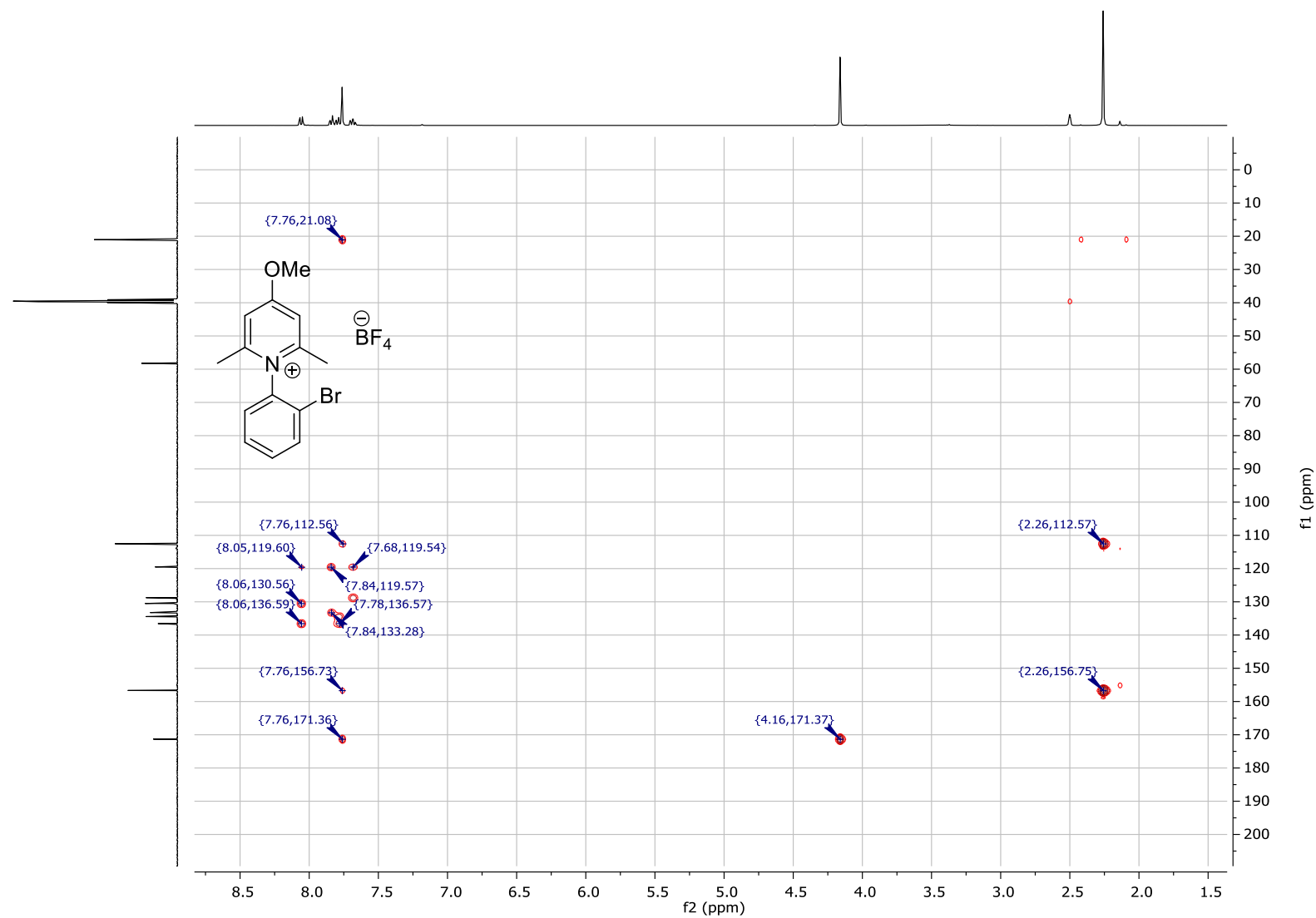
¹³C NMR for 3x



¹³C DEPTQ-135 NMR for 3x



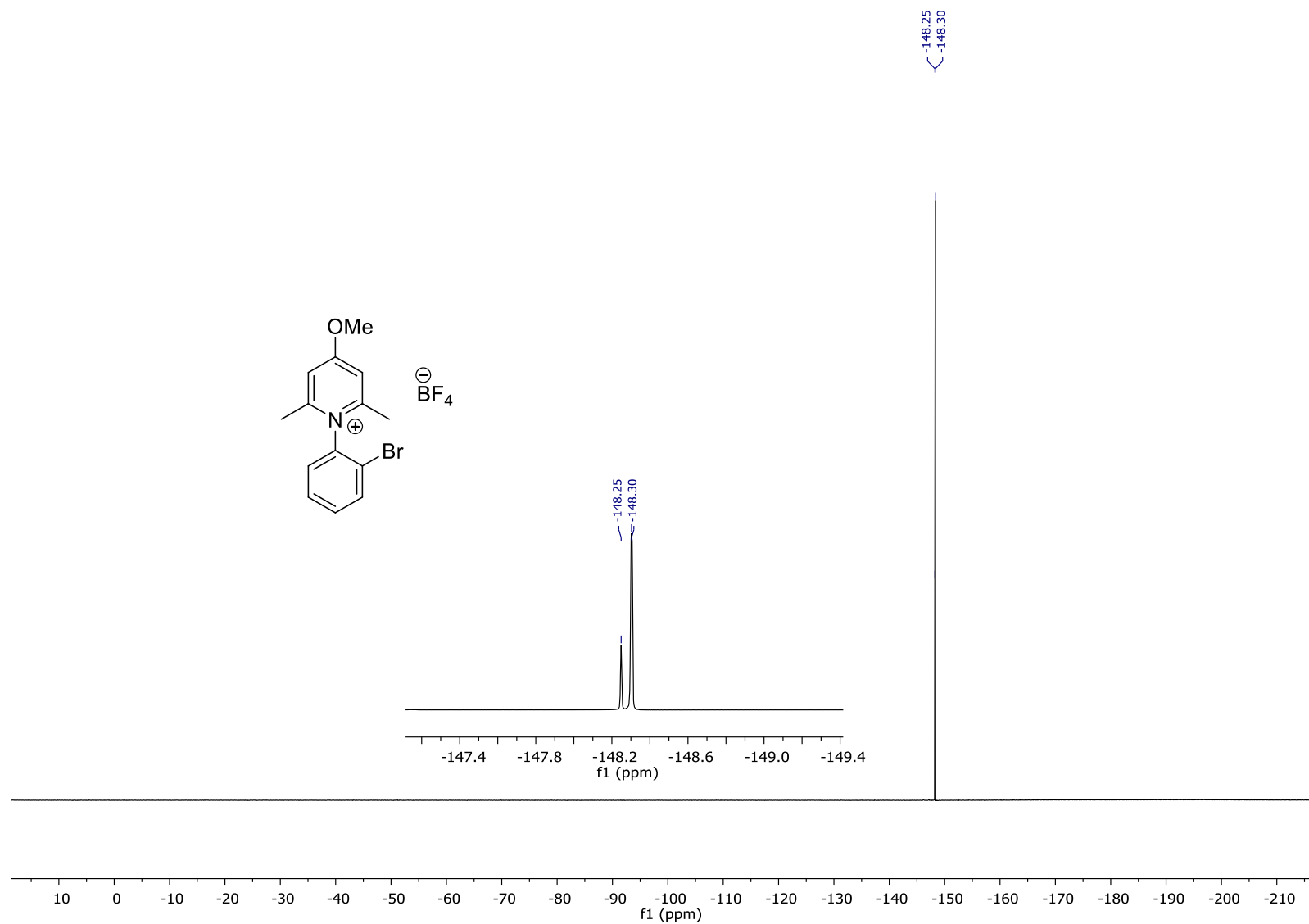
^1H - ^{13}C HSQC for 3x



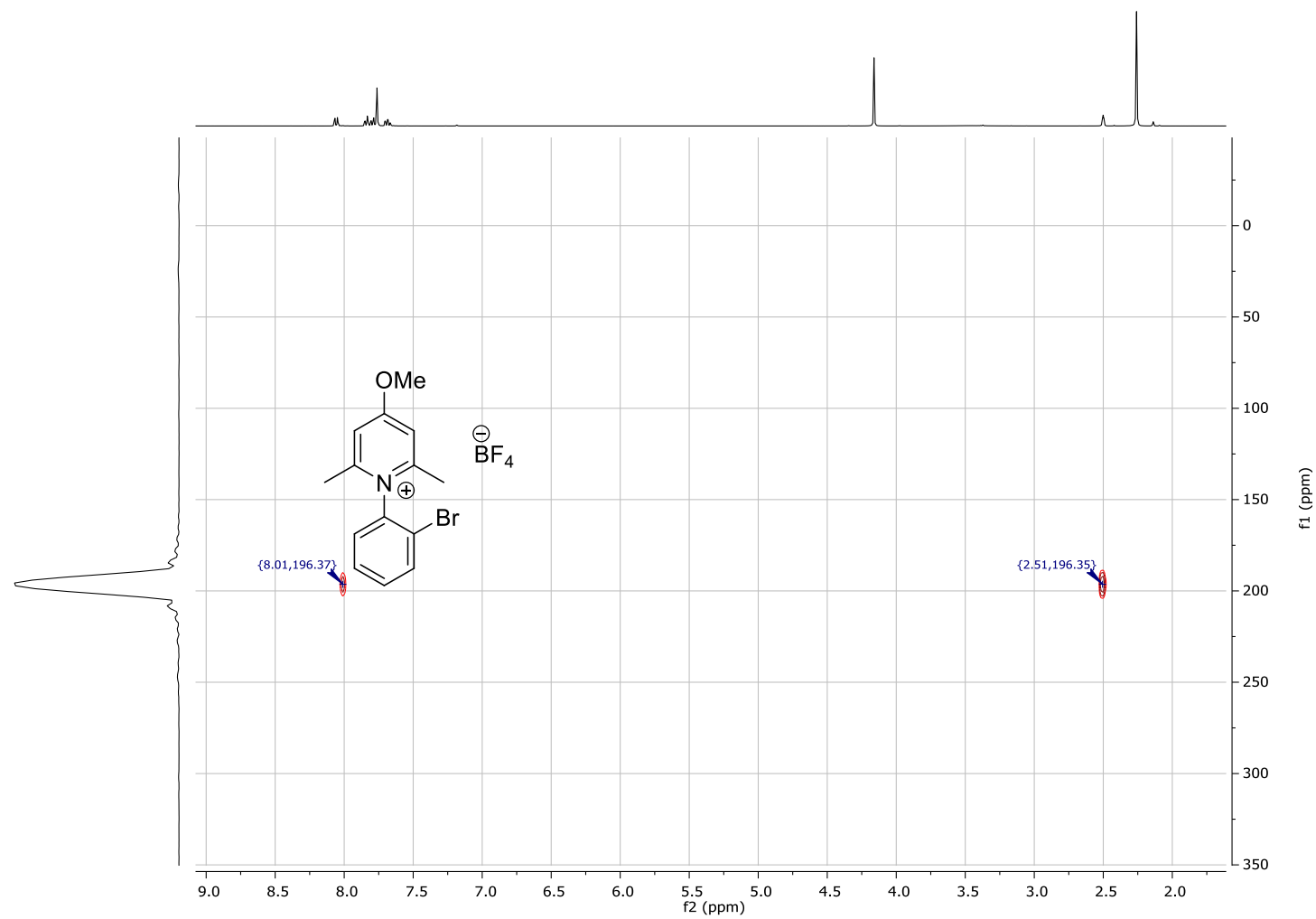
^1H - ^{13}C HMBC for 3x



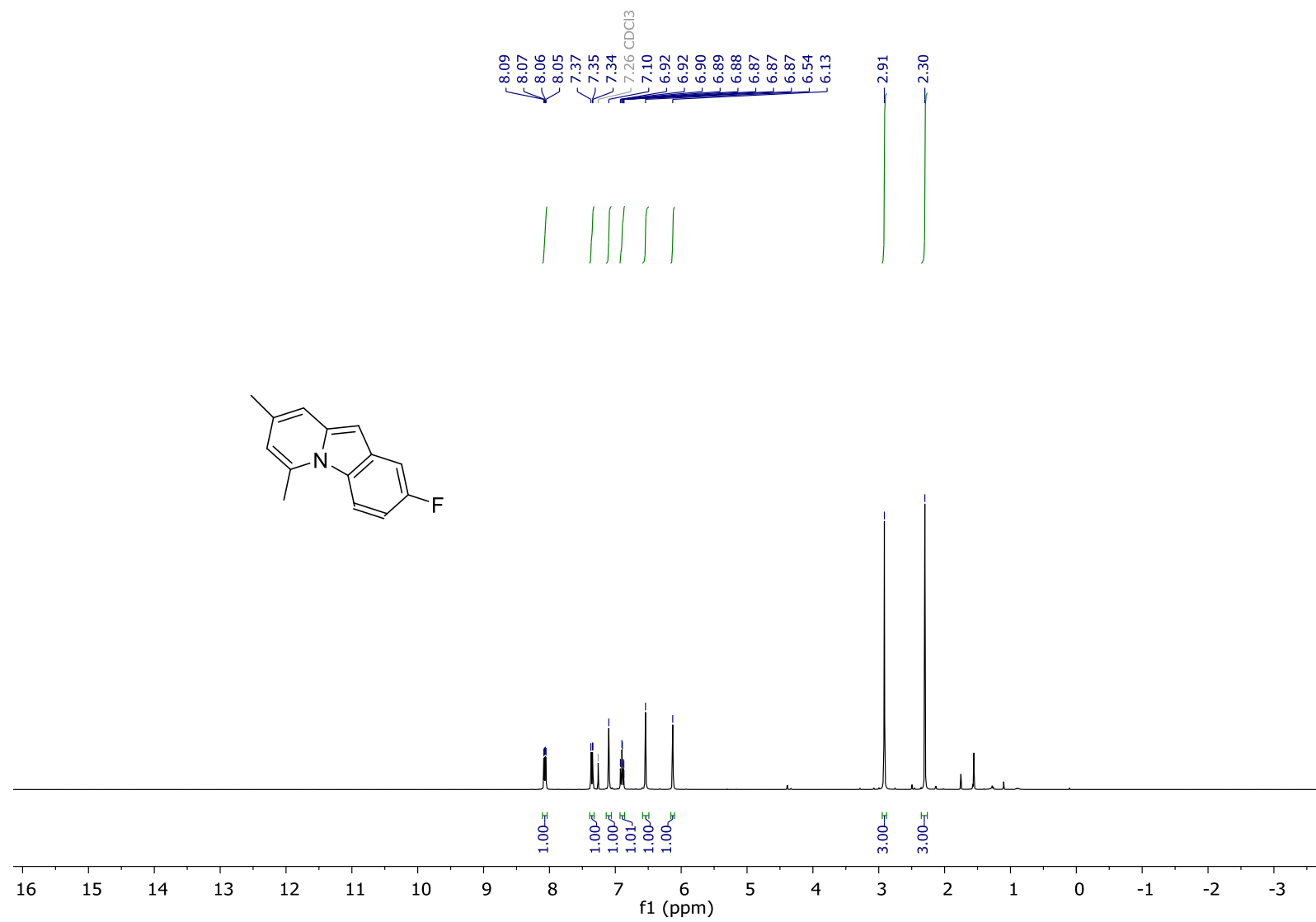
¹¹B NMR for 3x



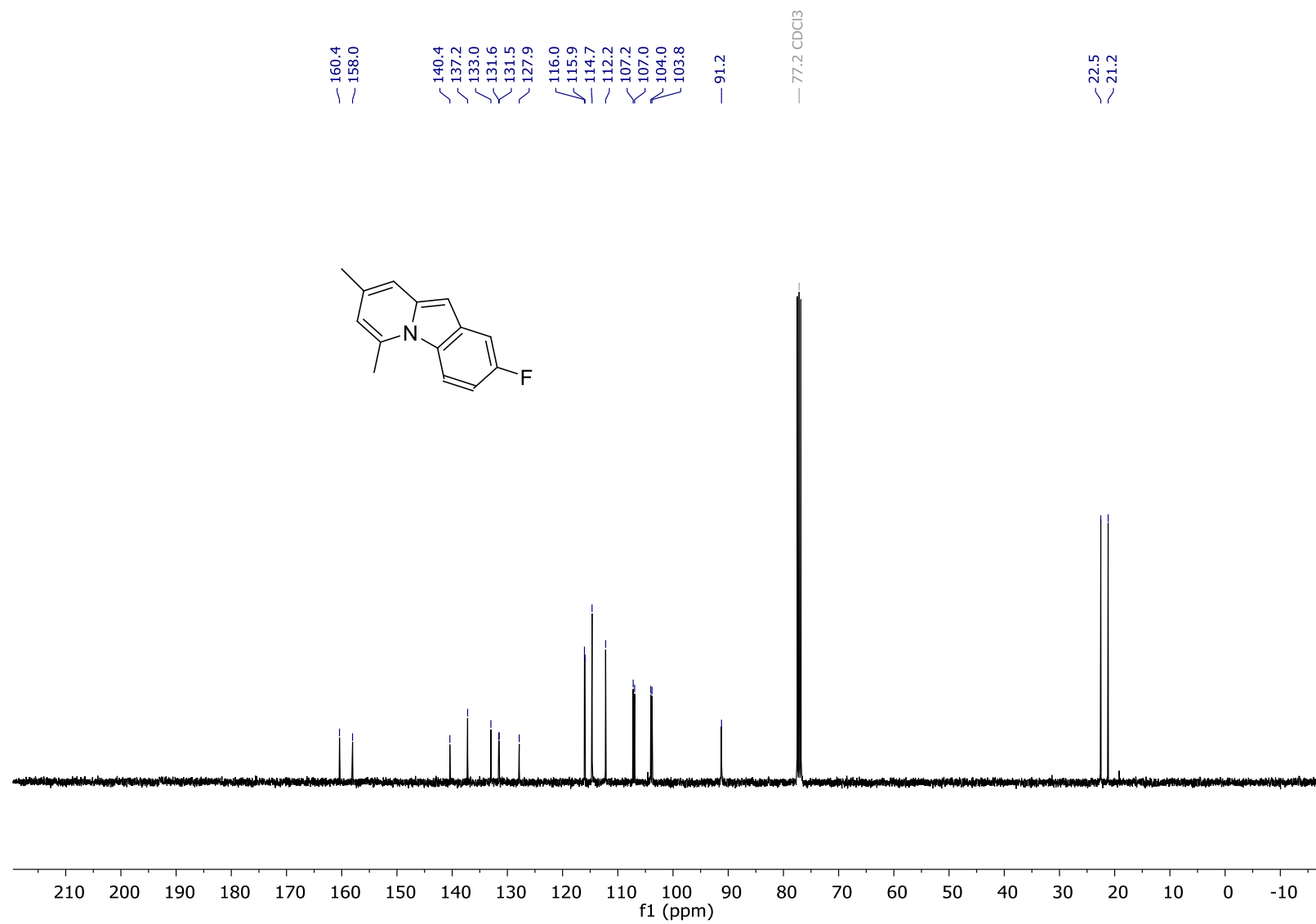
¹⁹F NMR for 3x



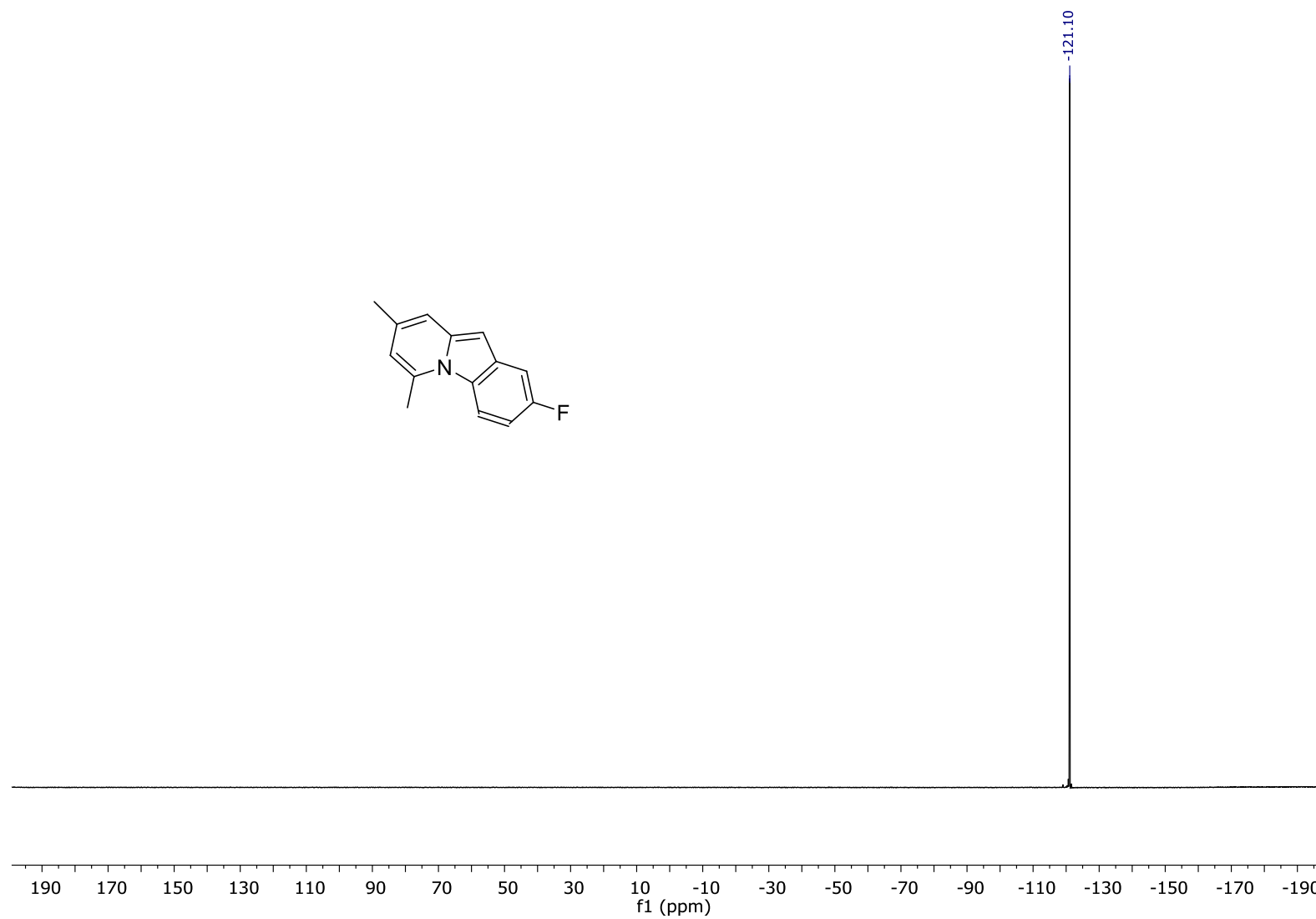
¹H-¹⁵N HMBC for 3x



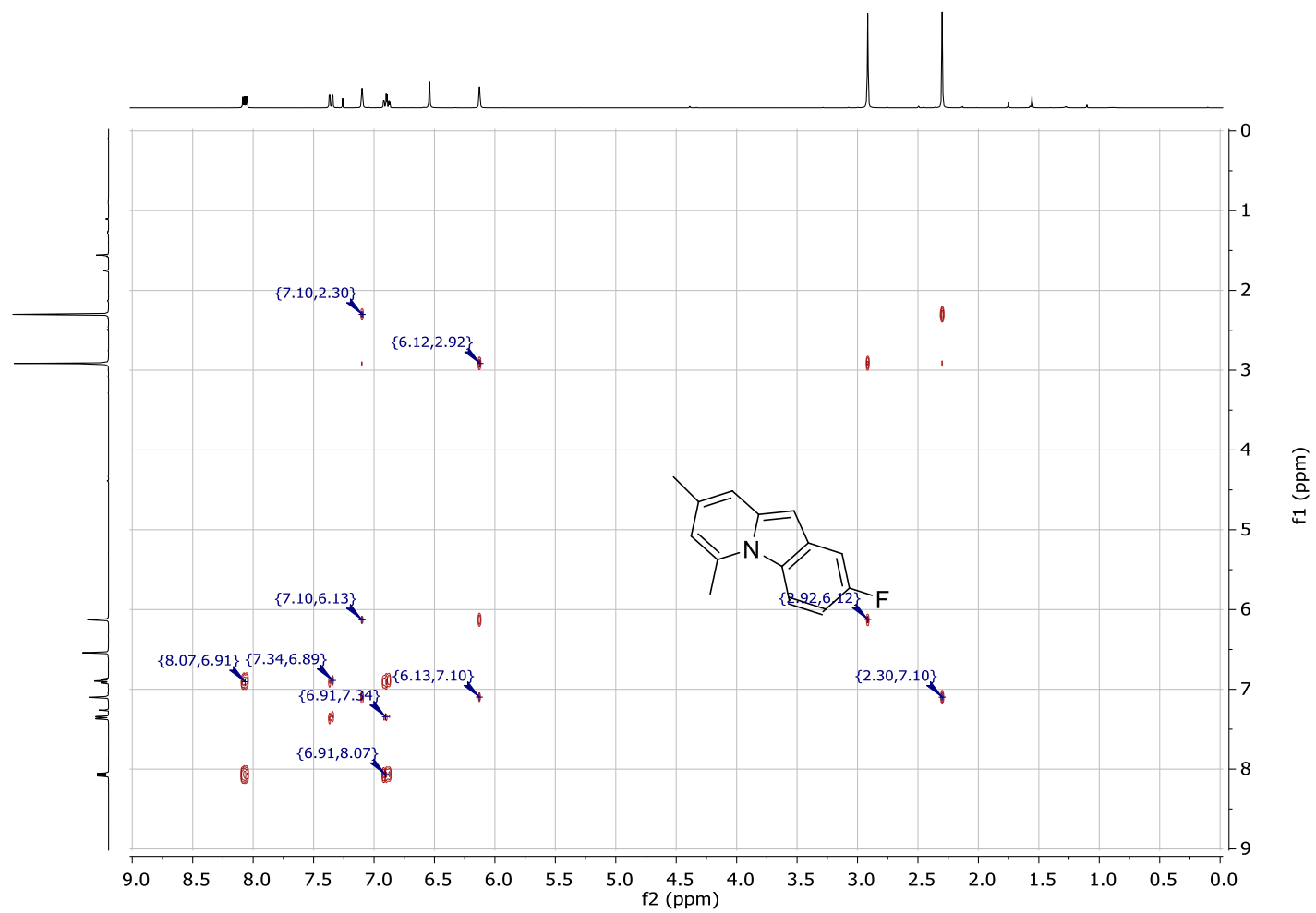
¹H NMR for 4a

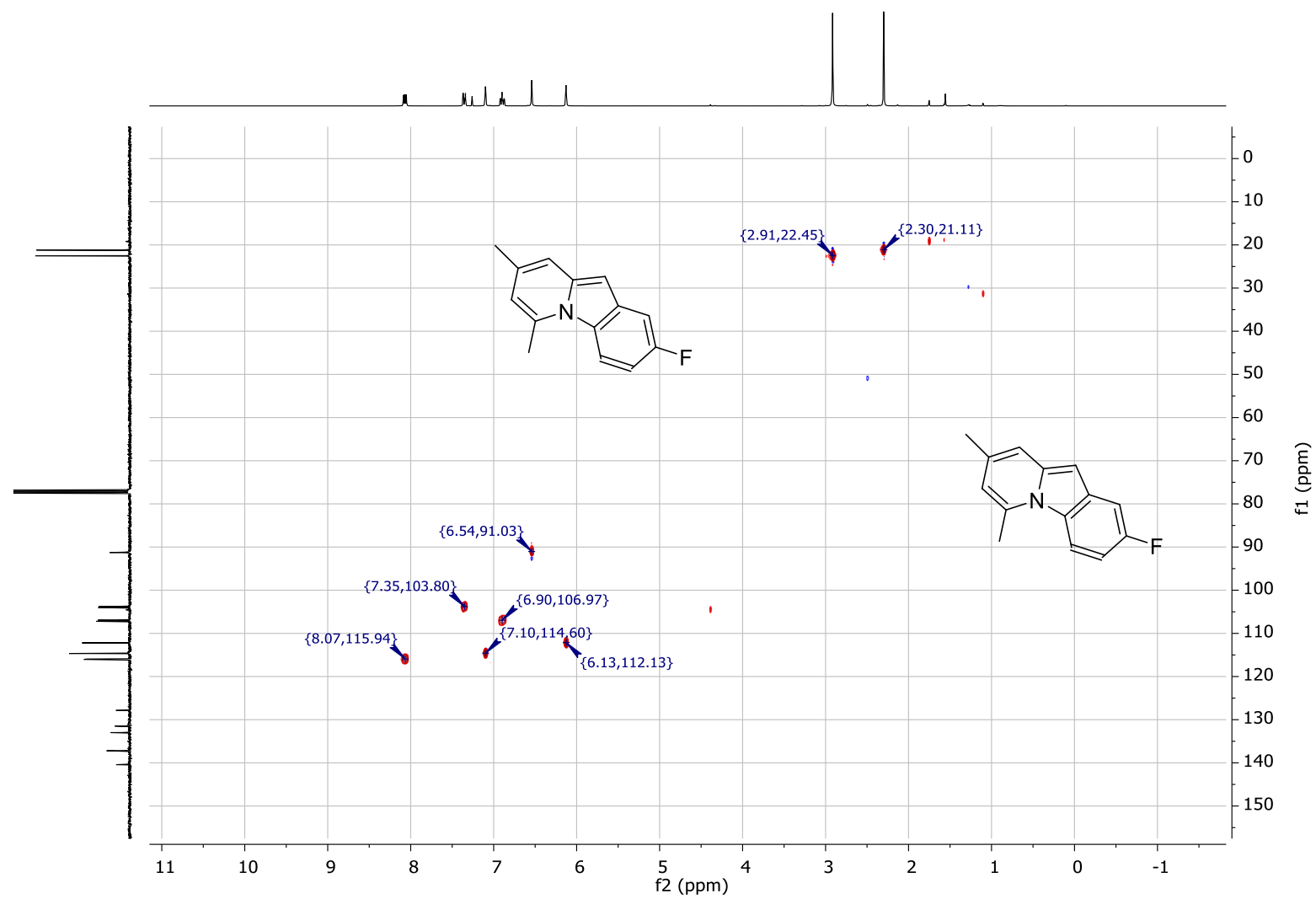


¹³C NMR for 4a

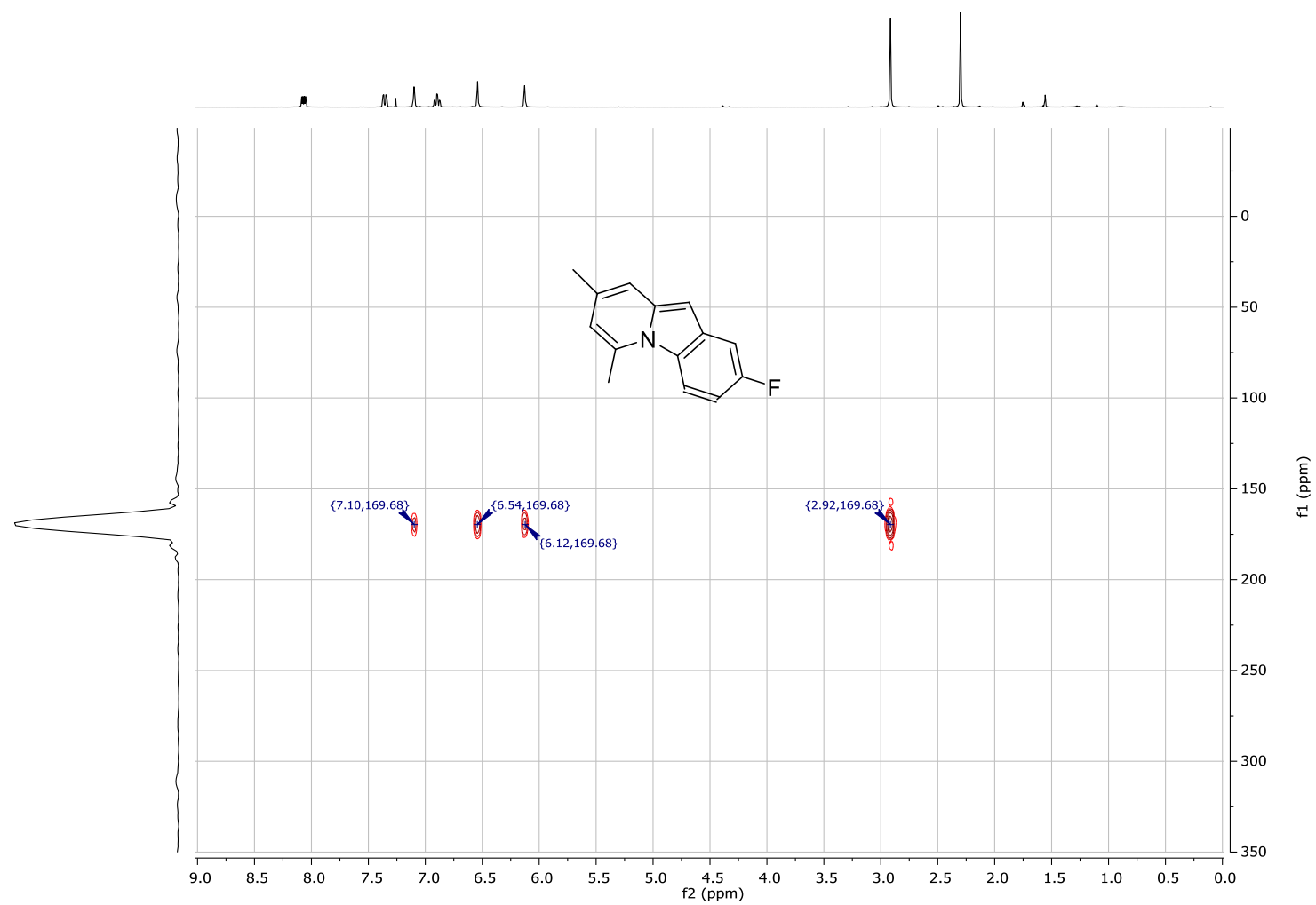


^{19}F NMR for 4a

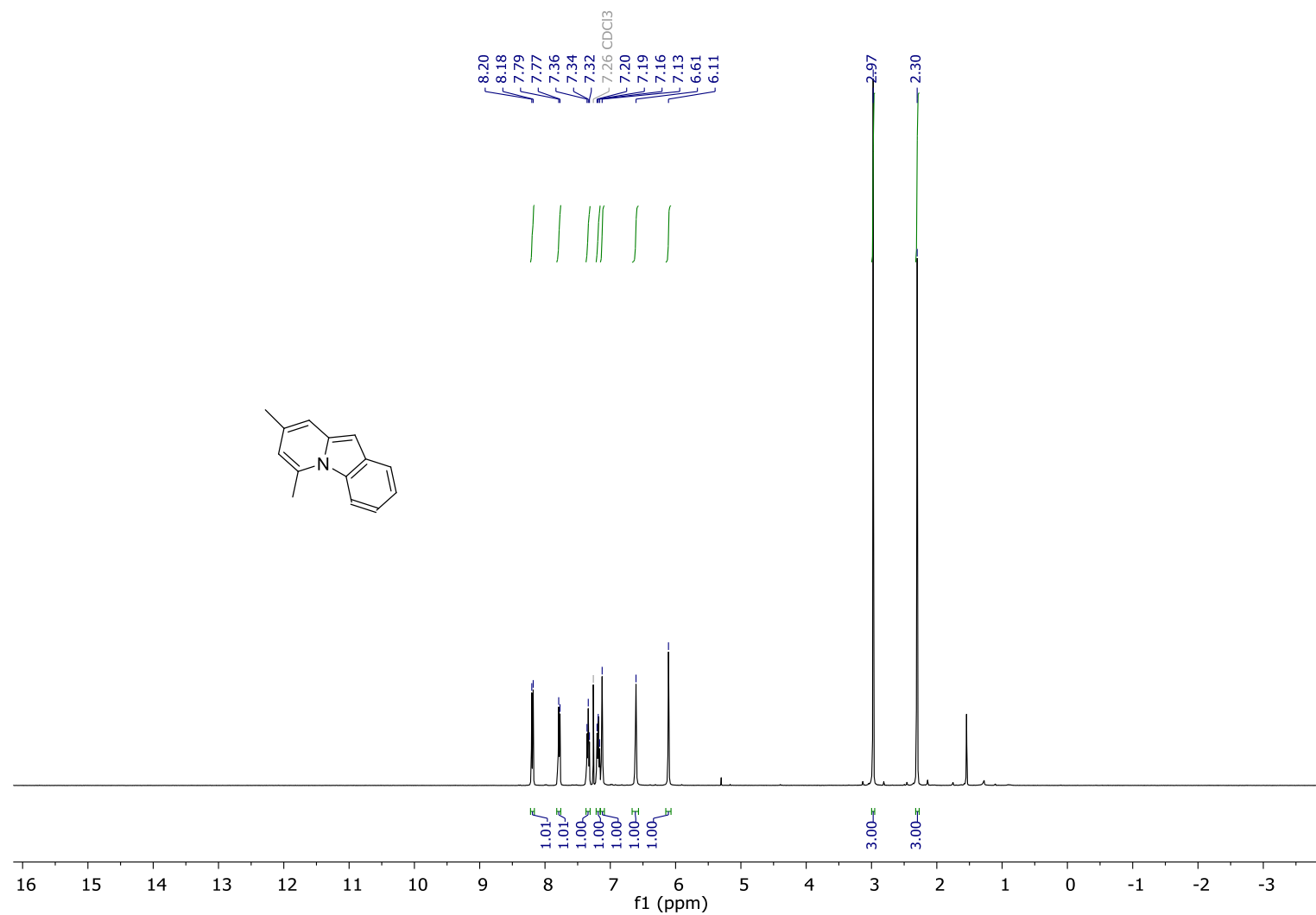




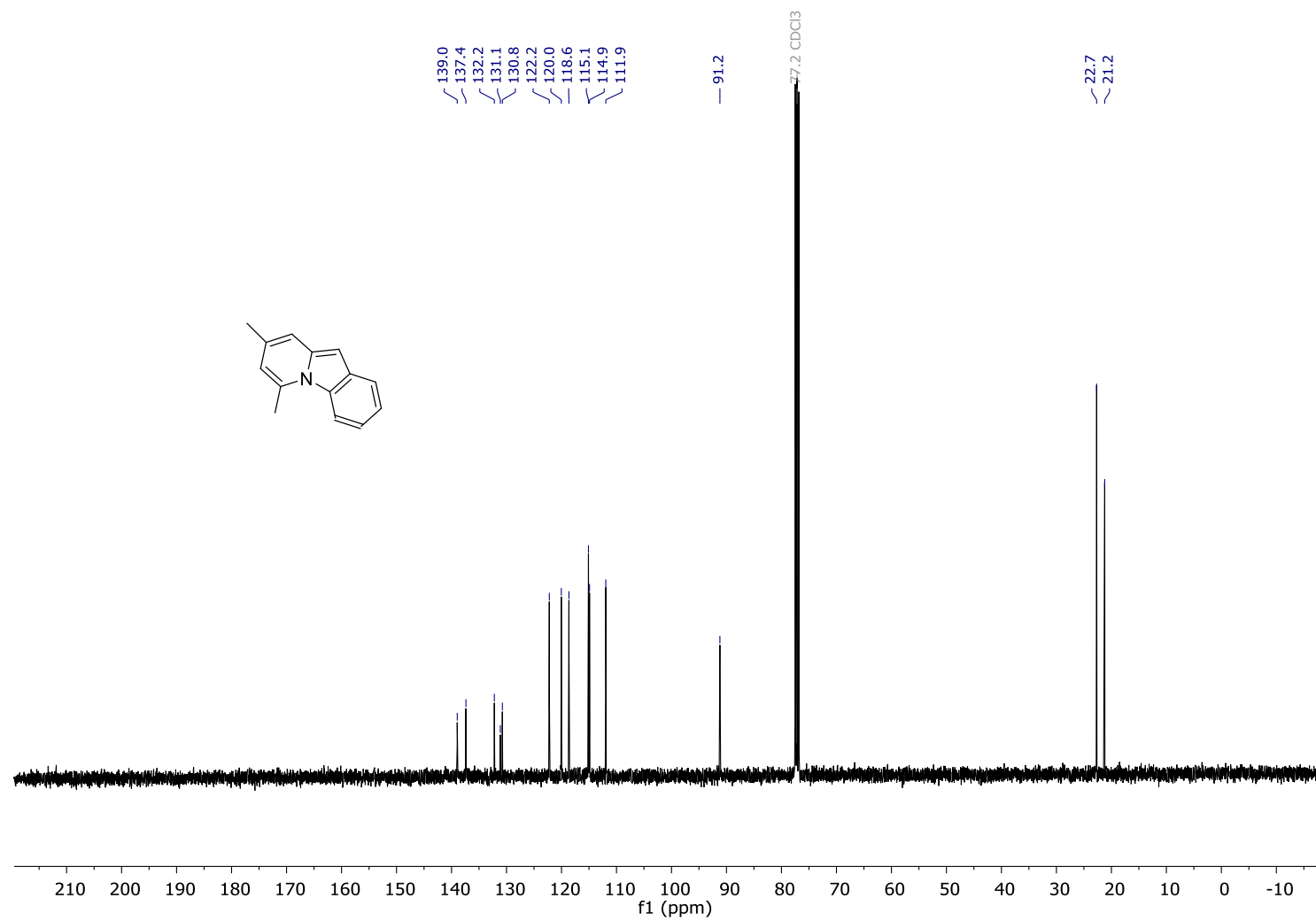
¹H-¹³C HSQC for 4a



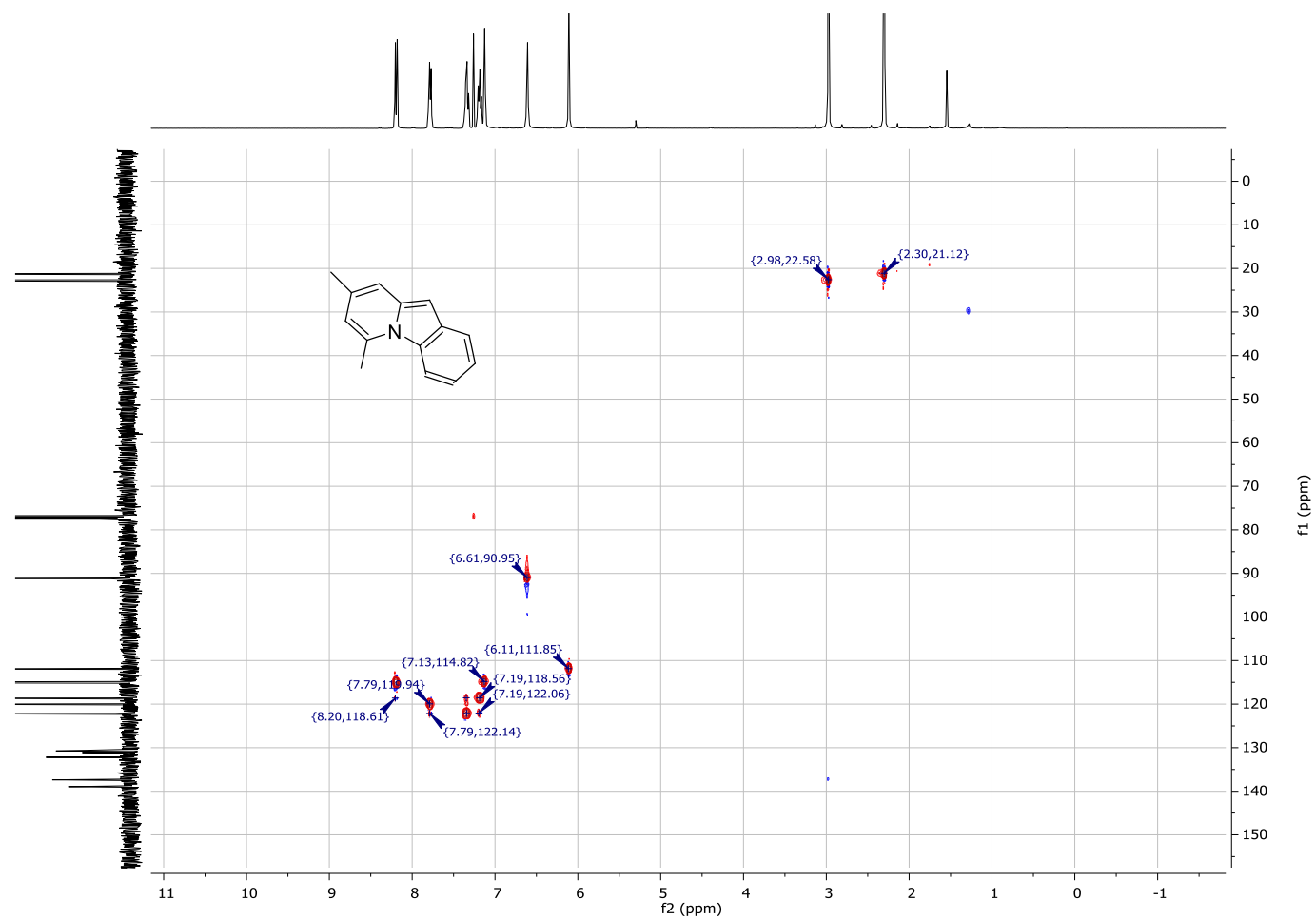
^1H - ^{15}N HMBC for 4a



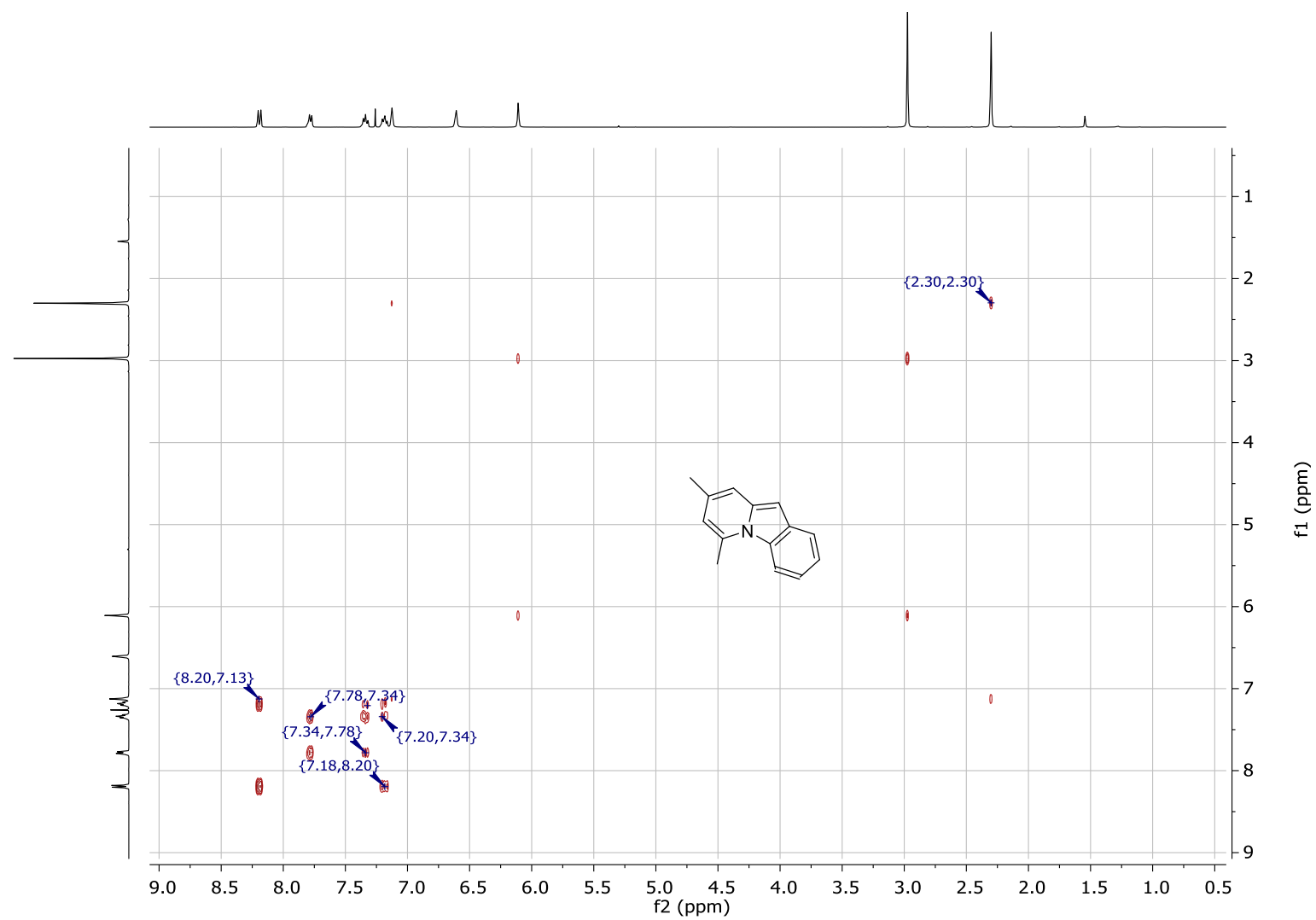
¹H NMR for 4b



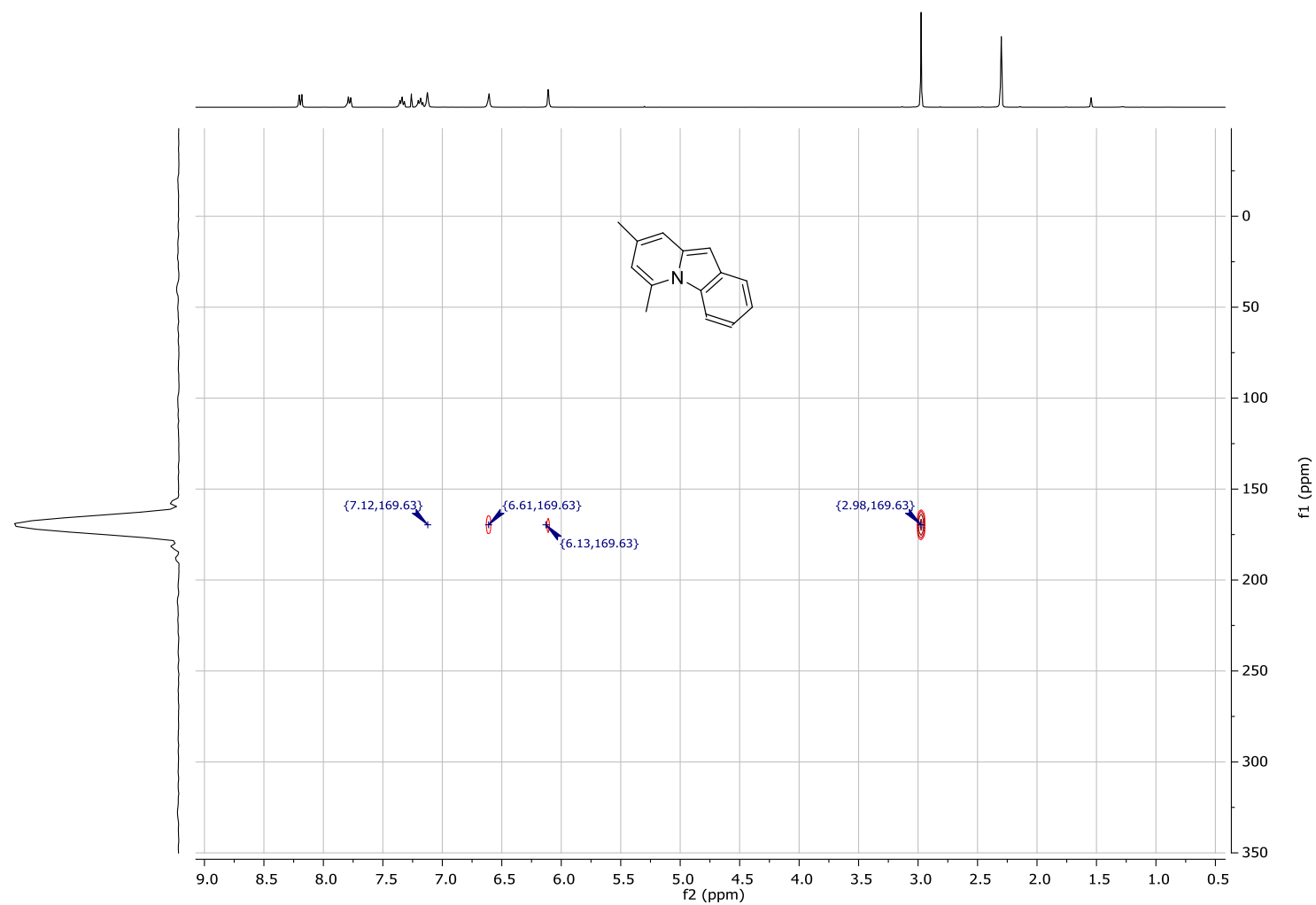
¹³C NMR for 4b



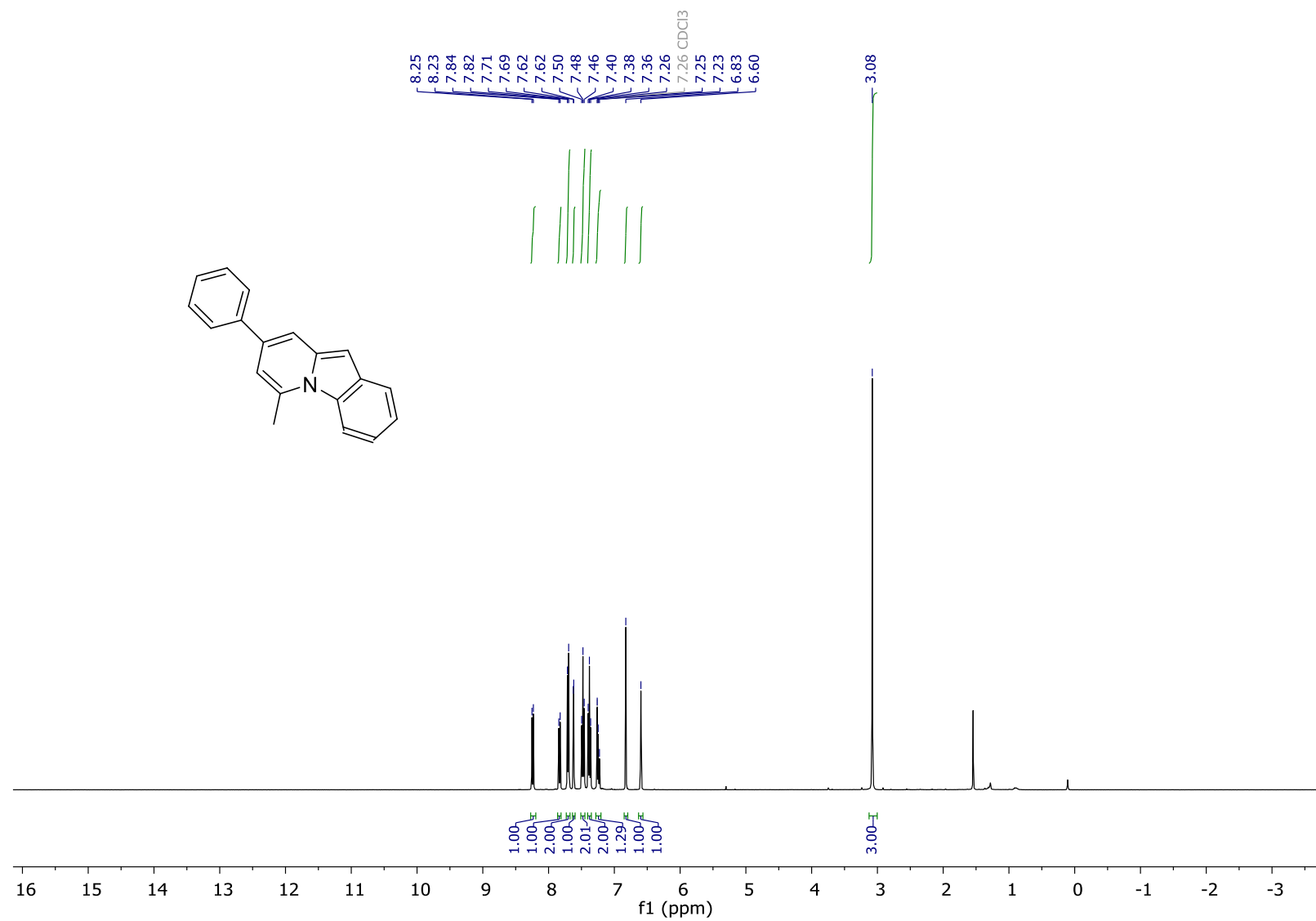
^1H - ^{13}C HSQC for 4b



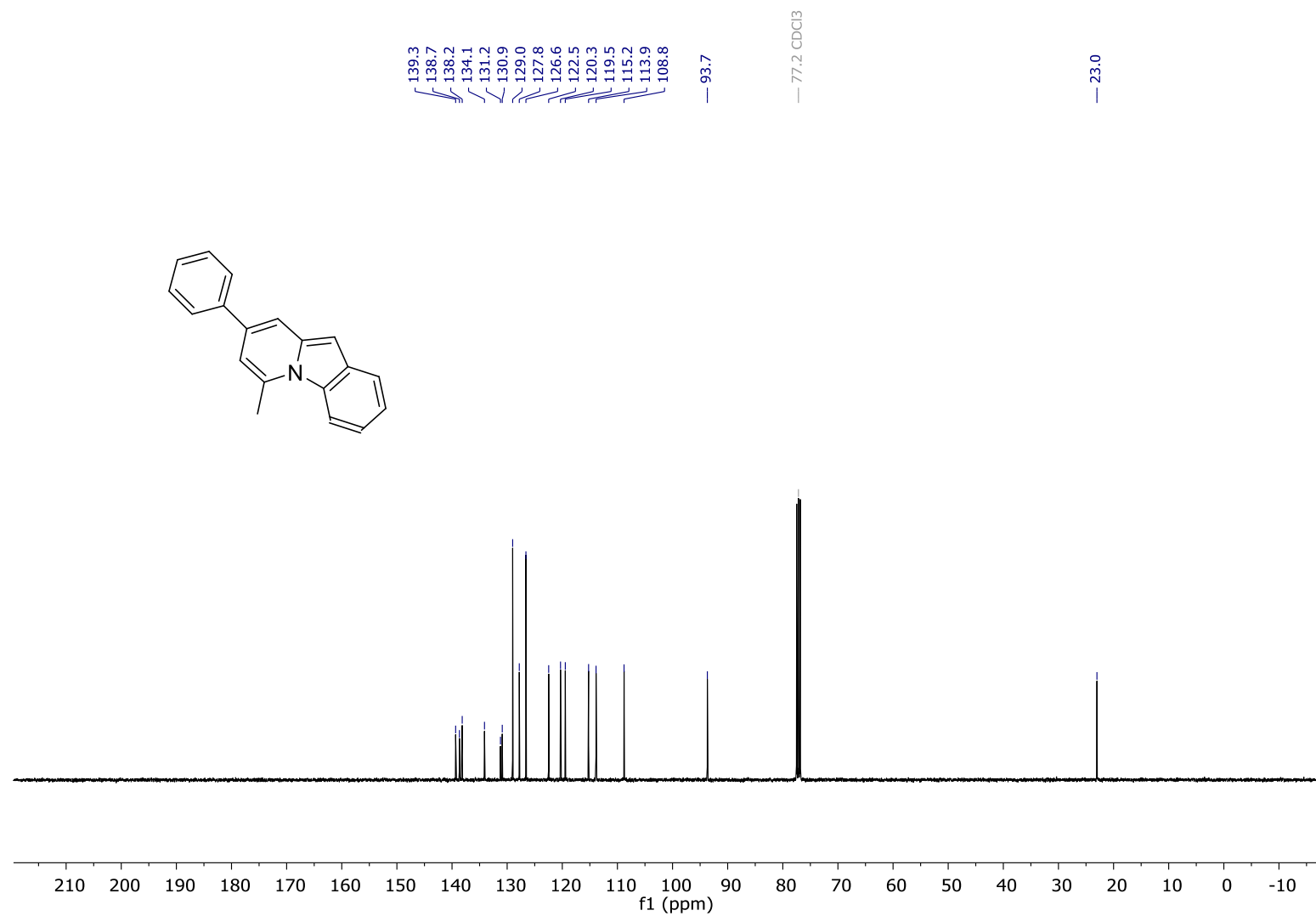
^1H - ^1H COSY for 4b



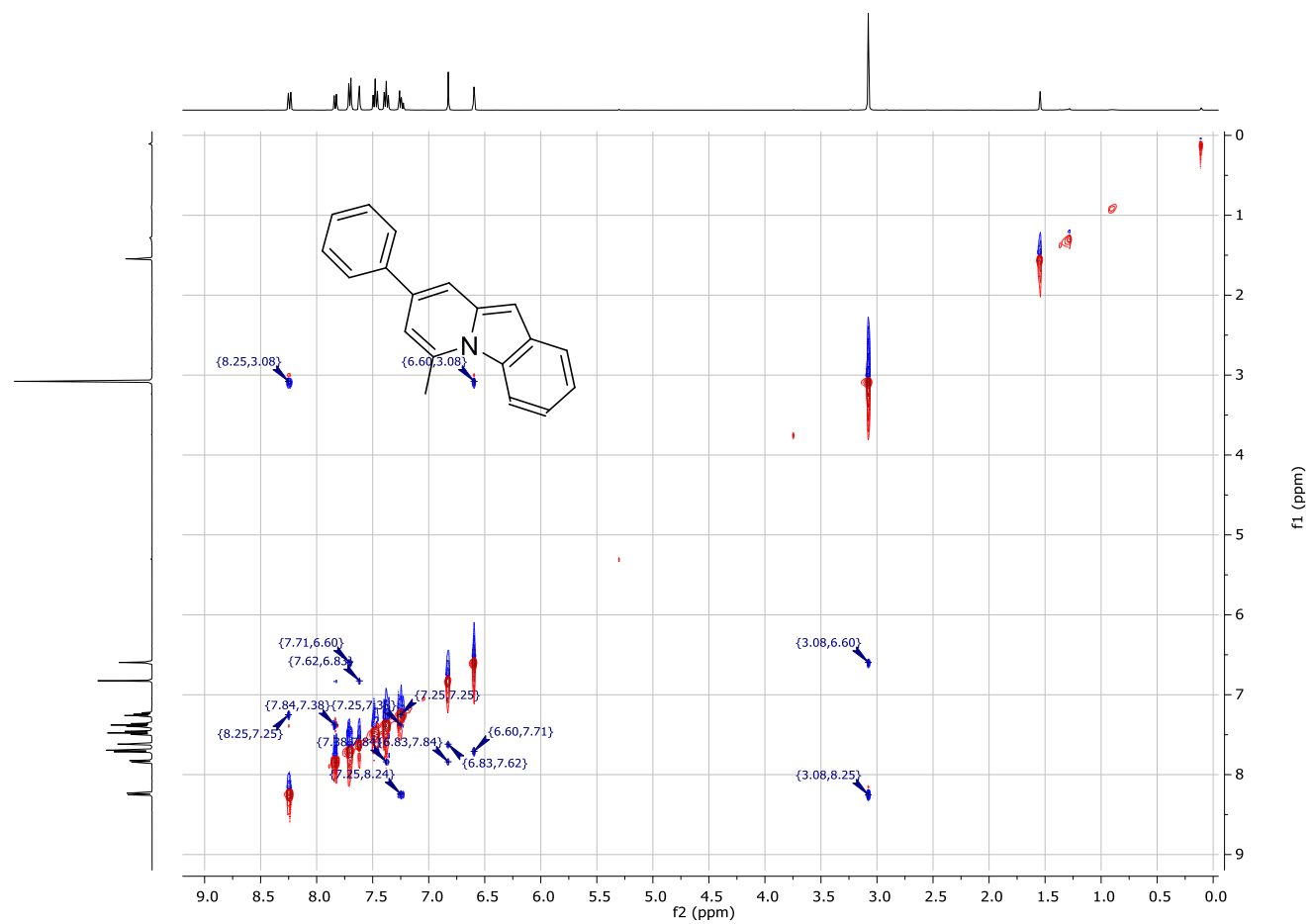
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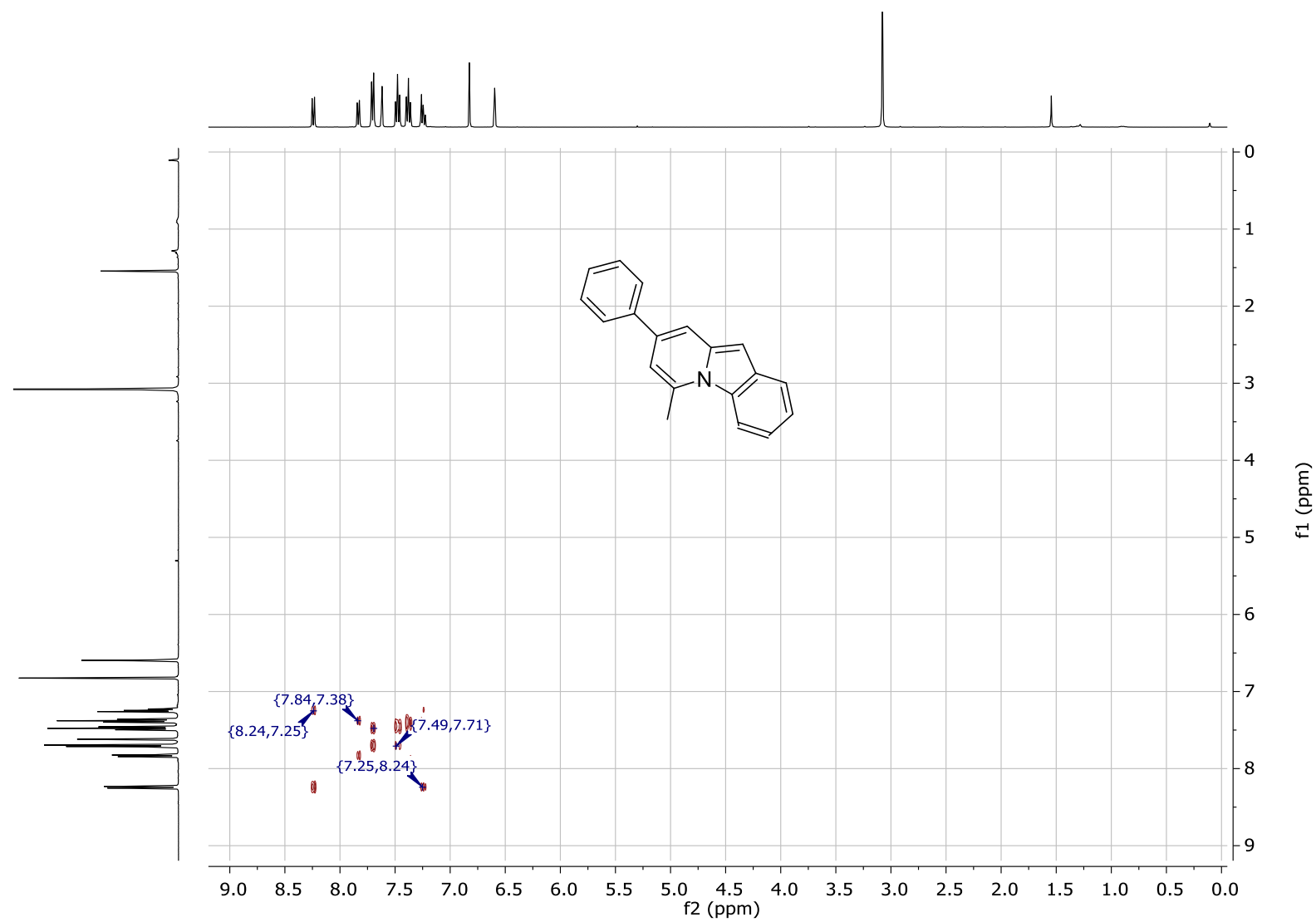
¹H NMR for 4c



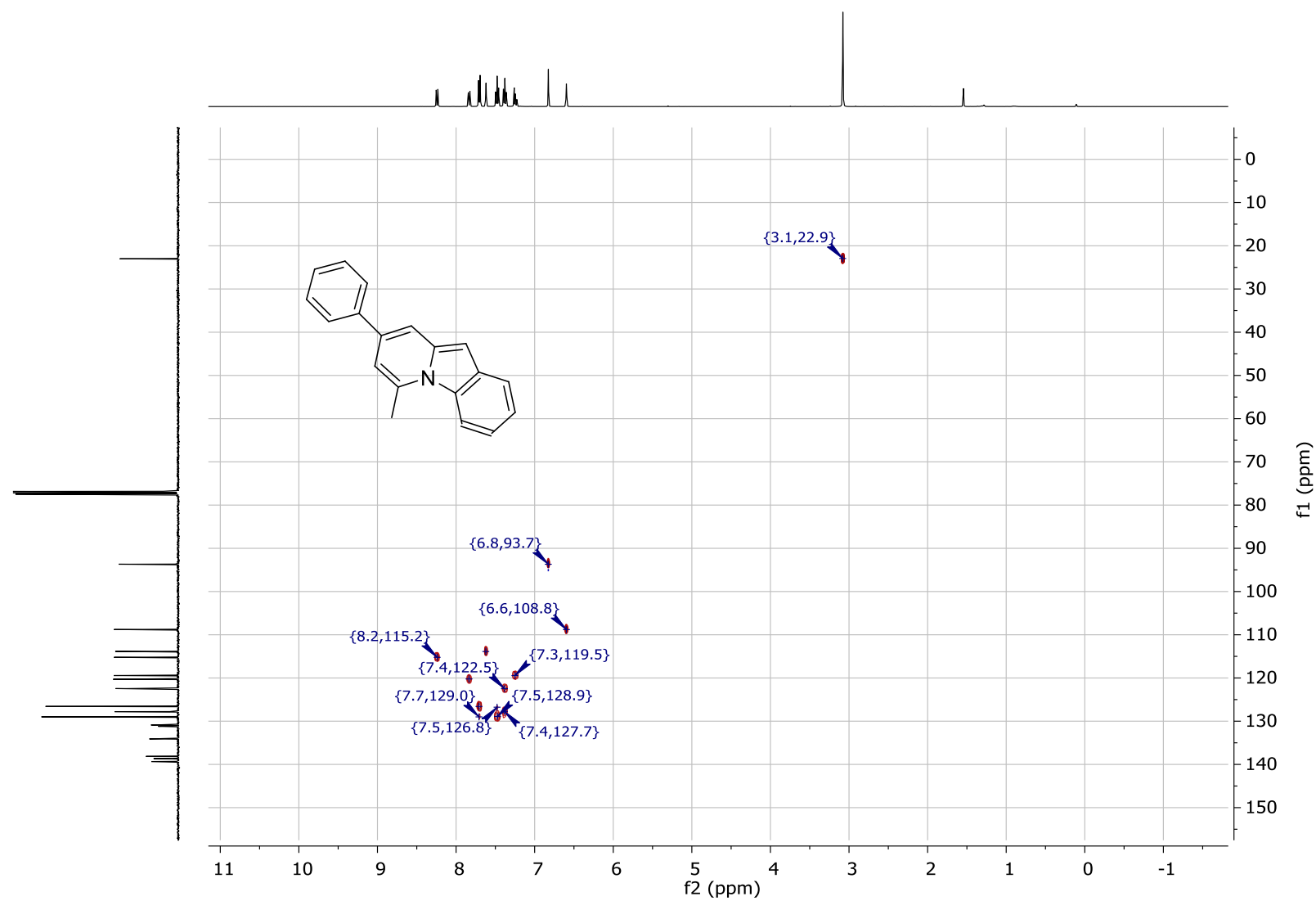
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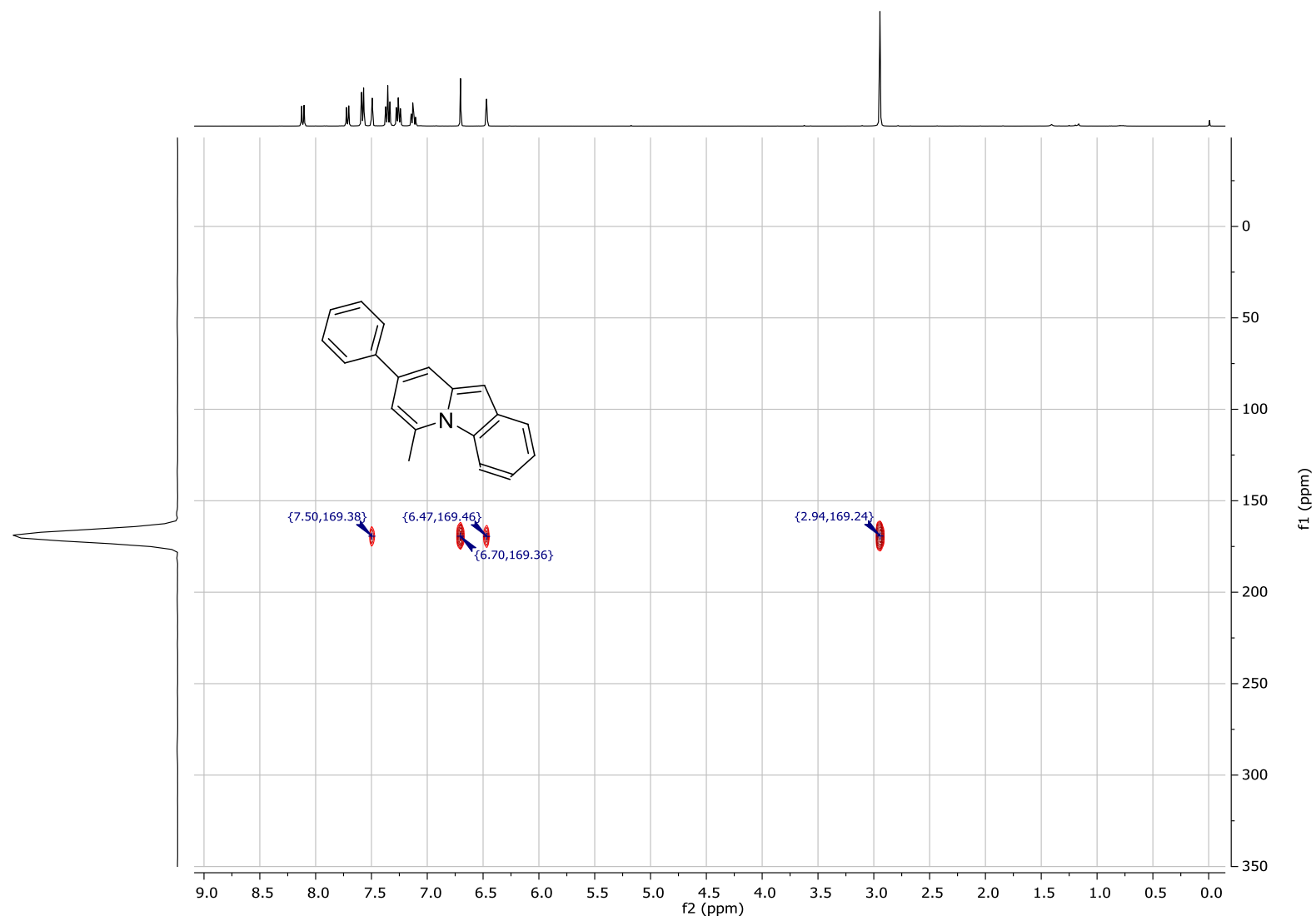
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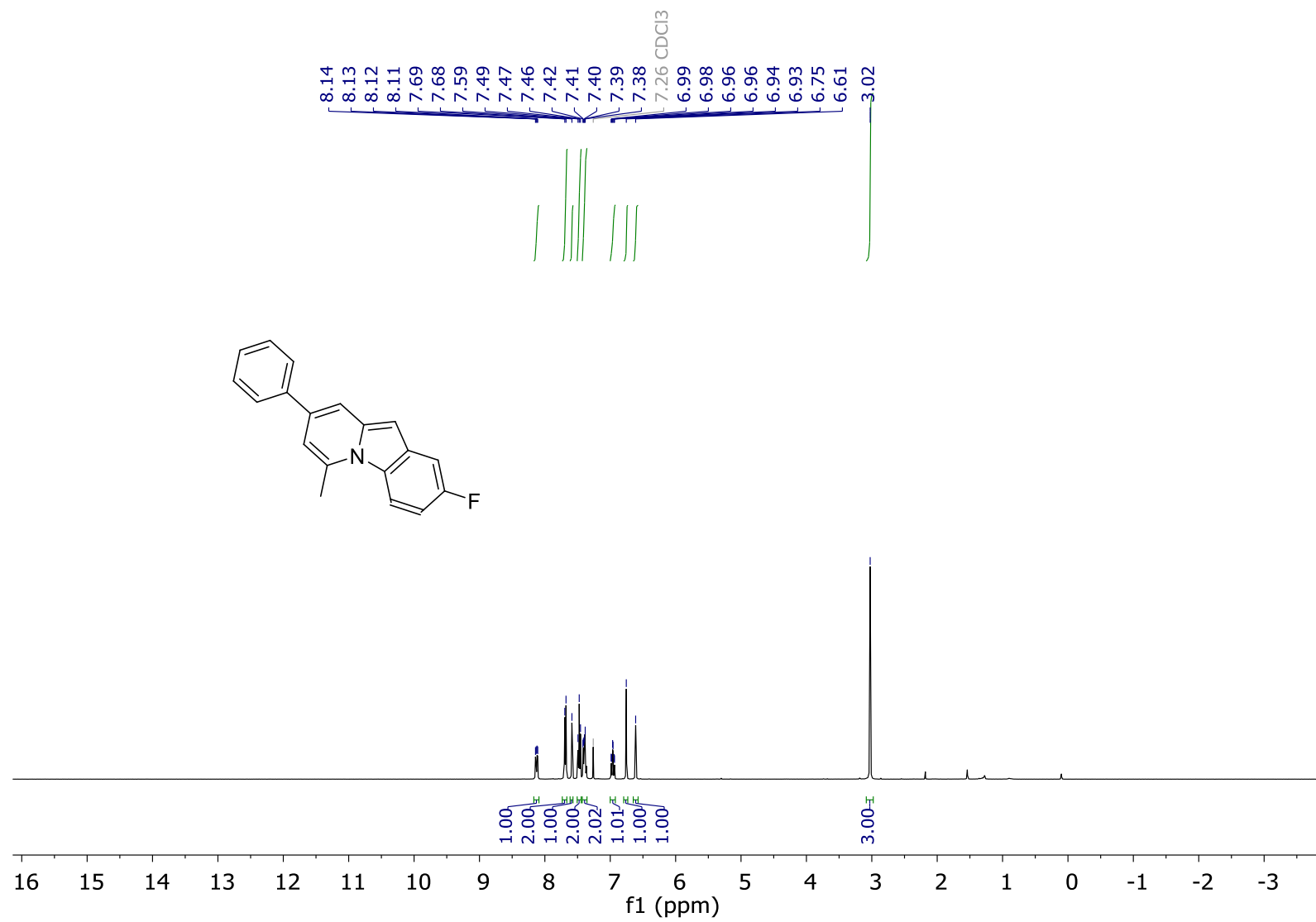
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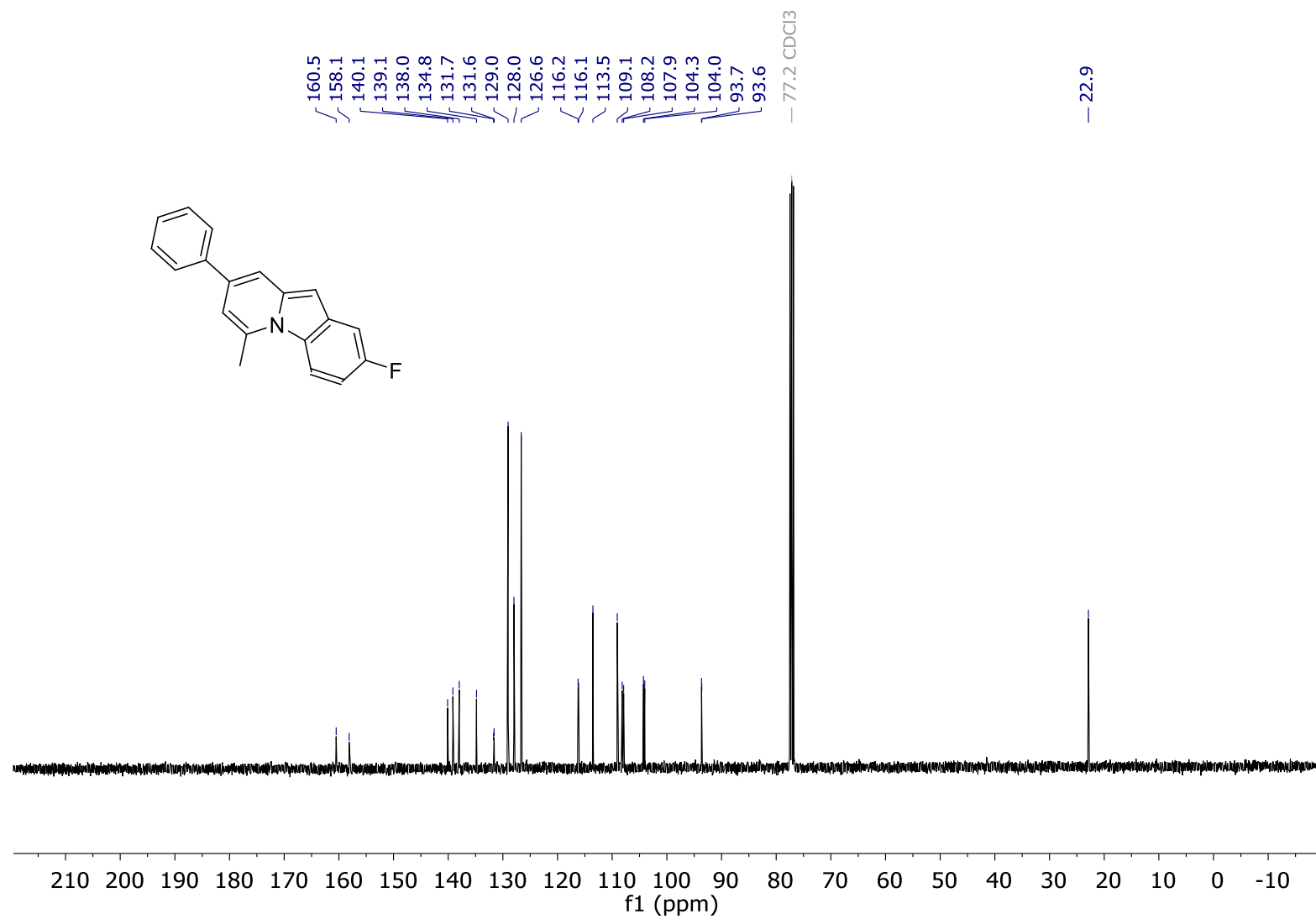
¹H-¹³C HSQC for 4c



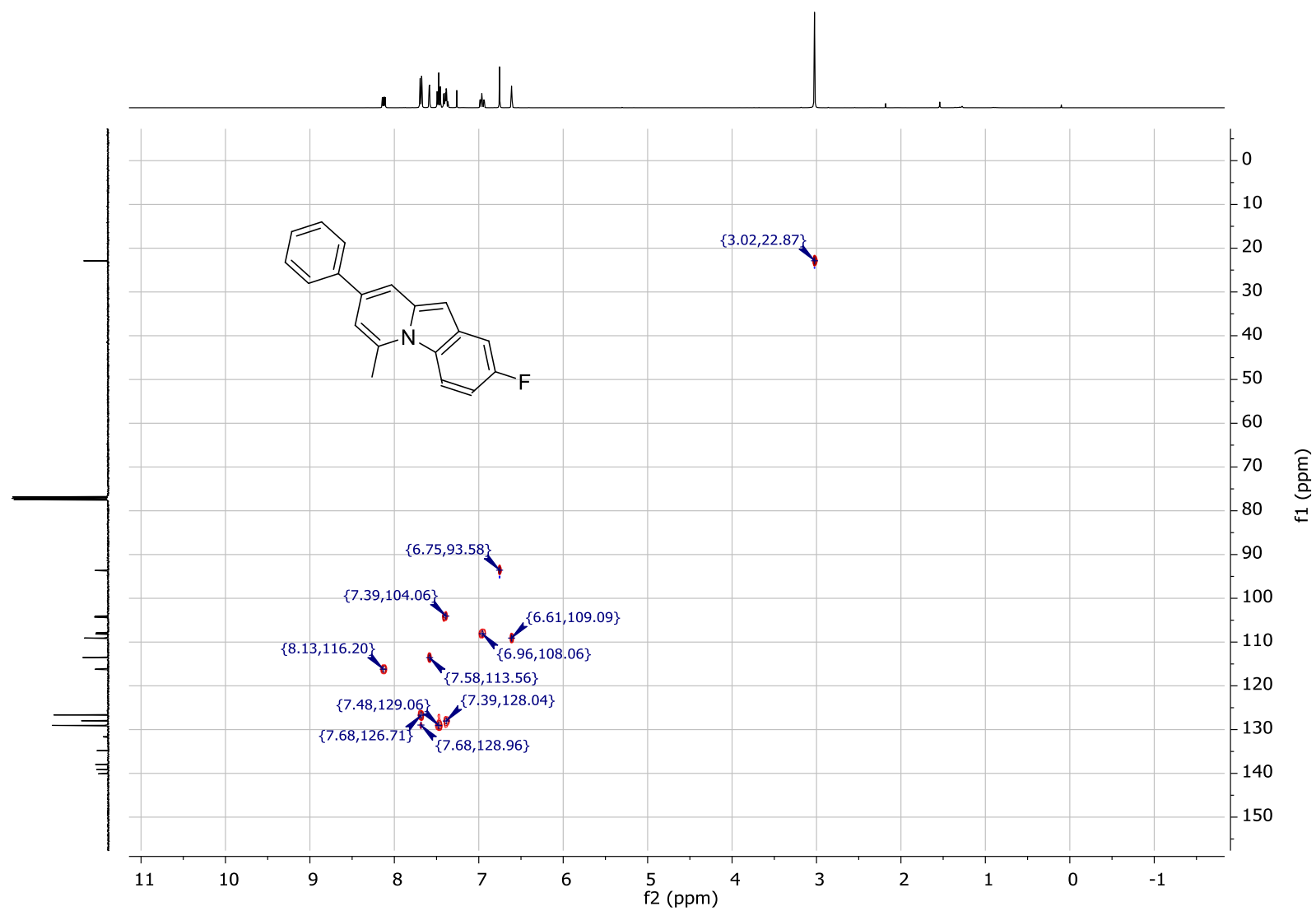
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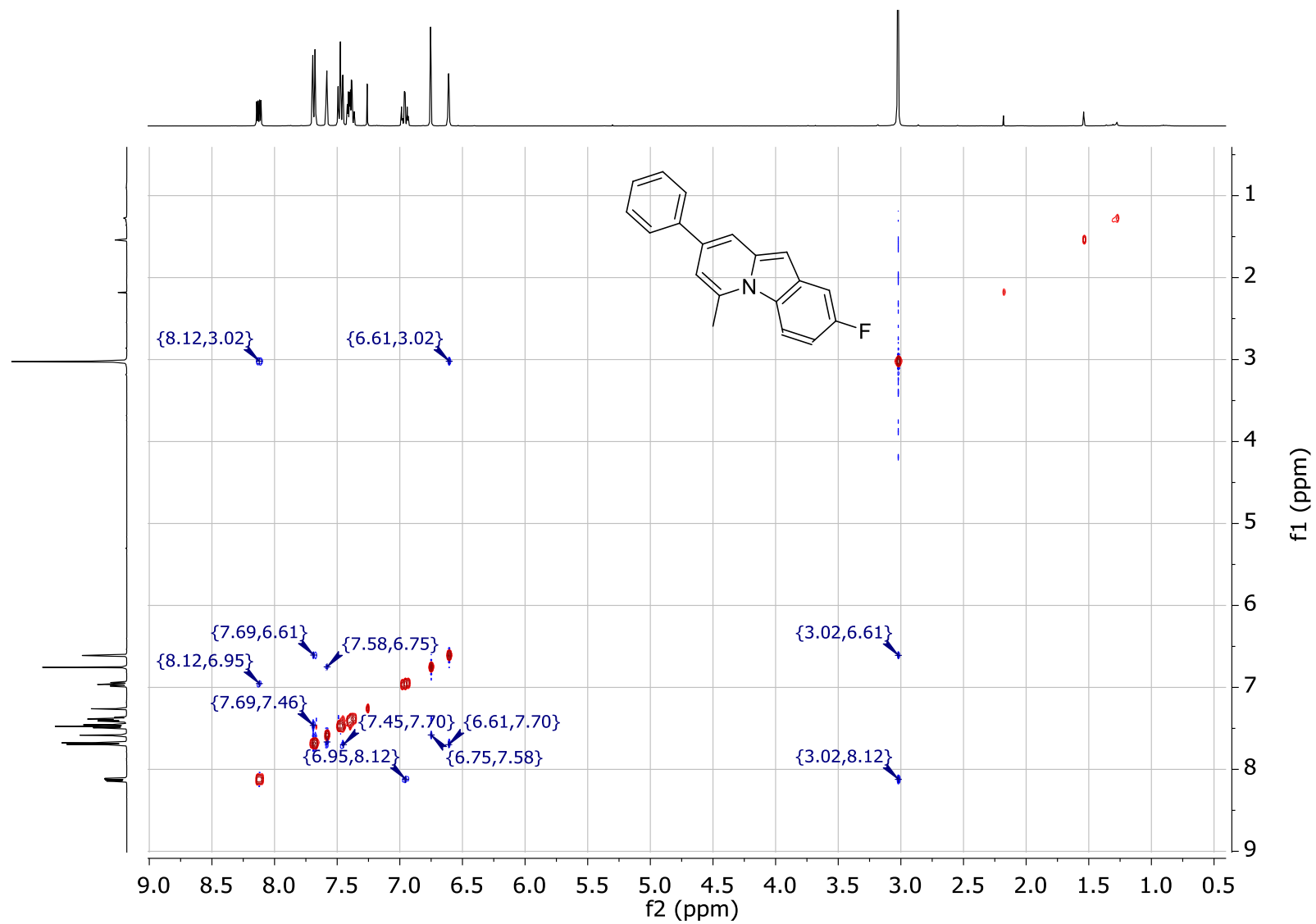
¹H NMR for 4d



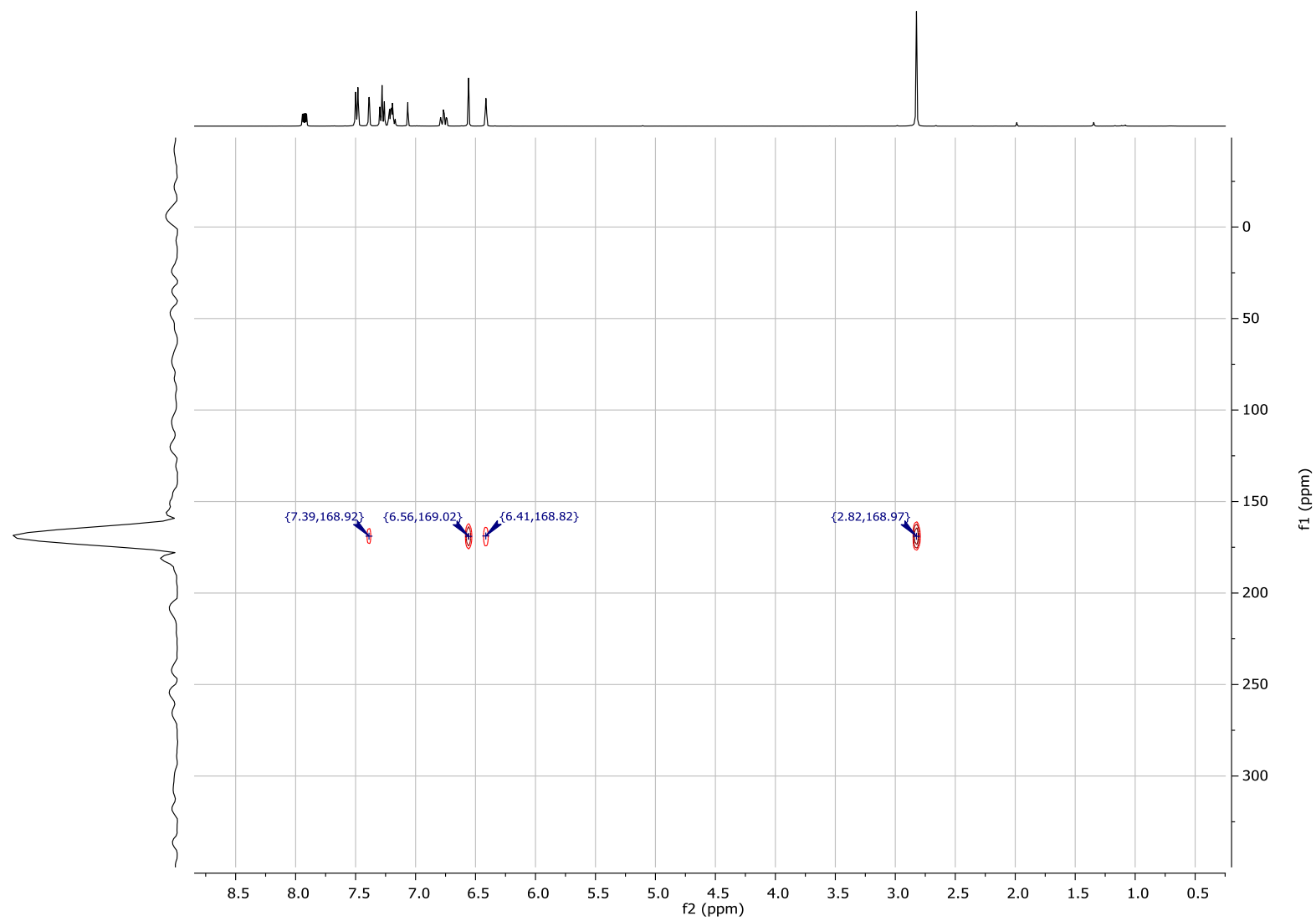
¹³C NMR for 4d



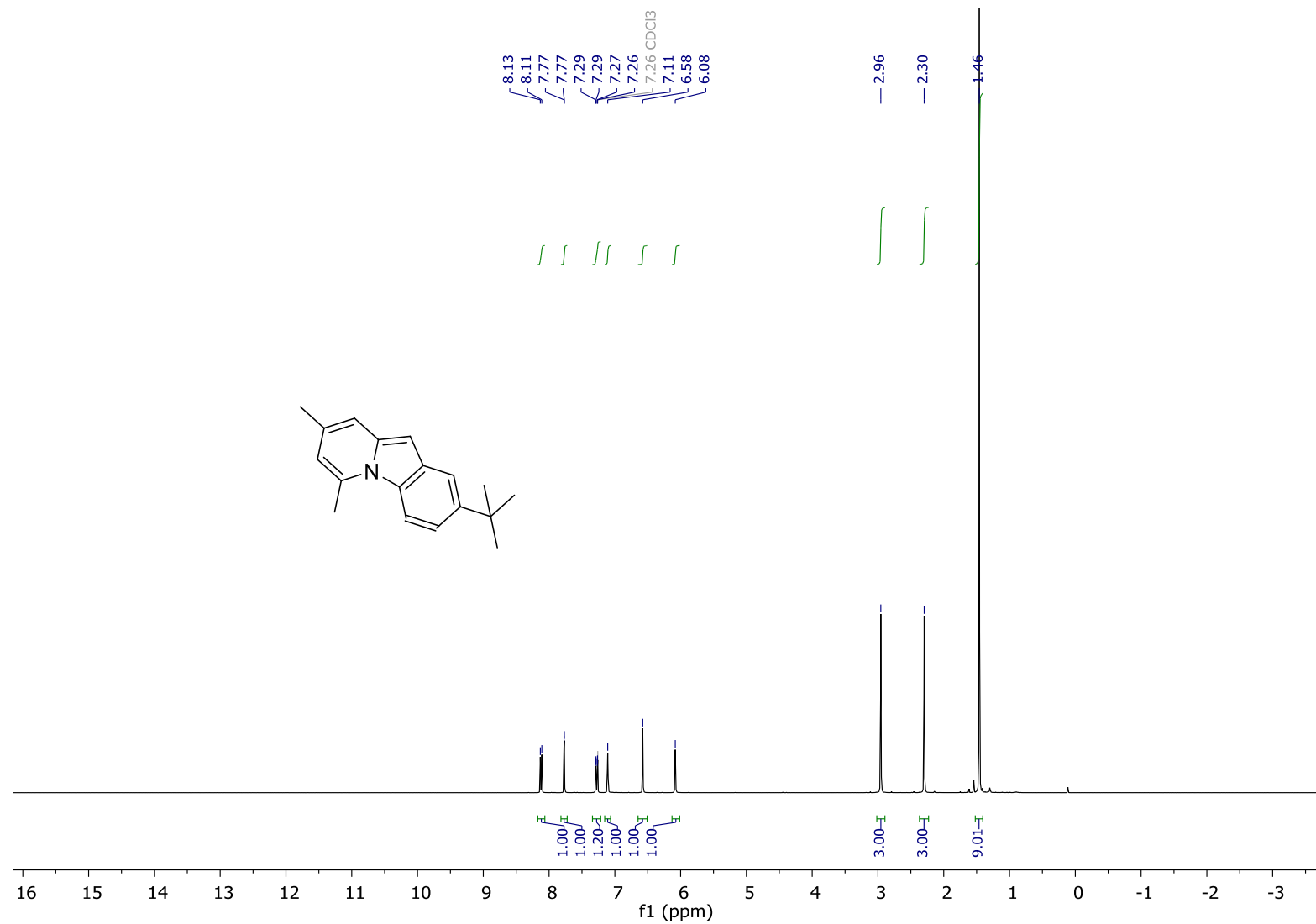
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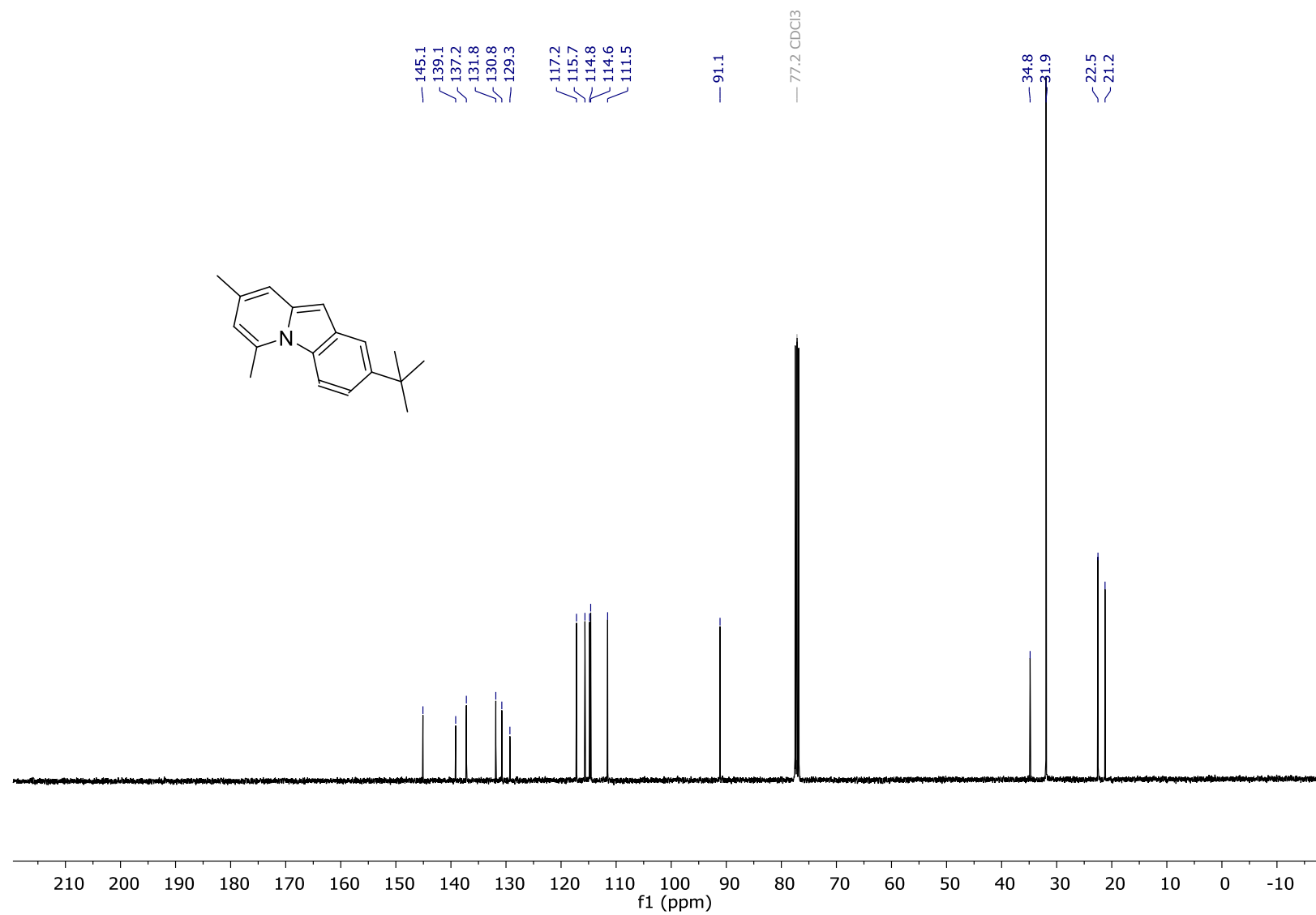
^1H - ^1H NOESY for 4d



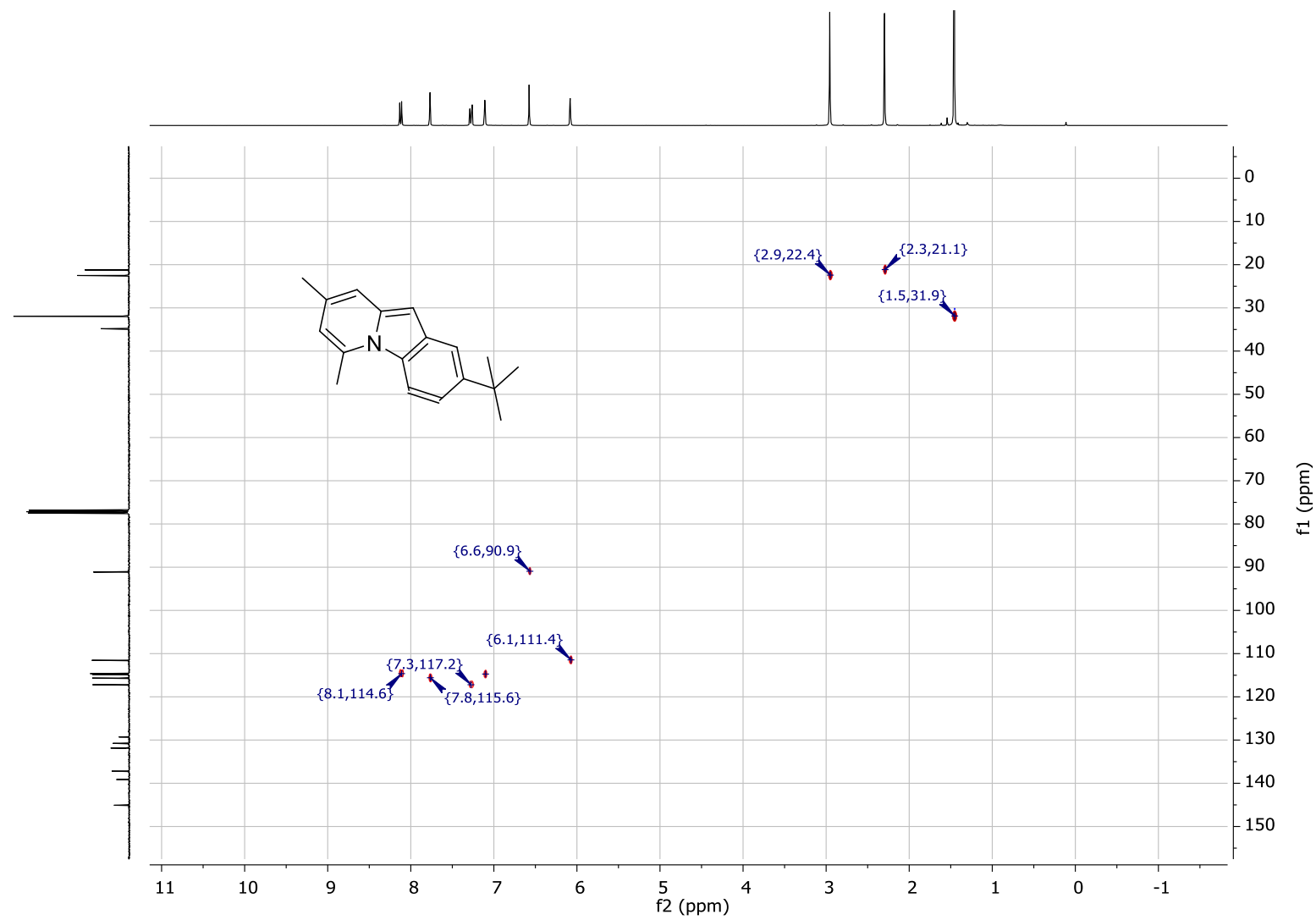
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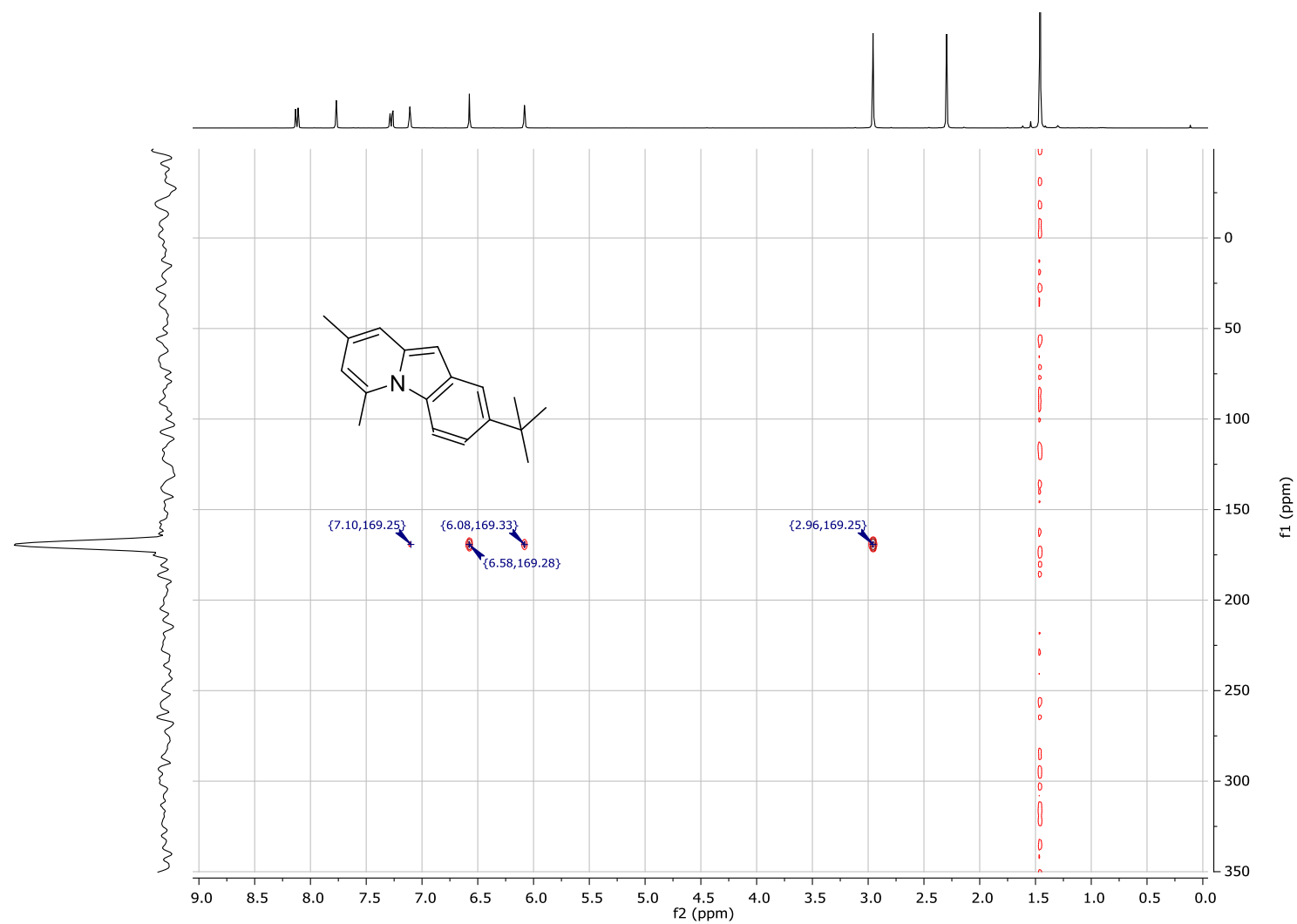
¹H NMR for 4e



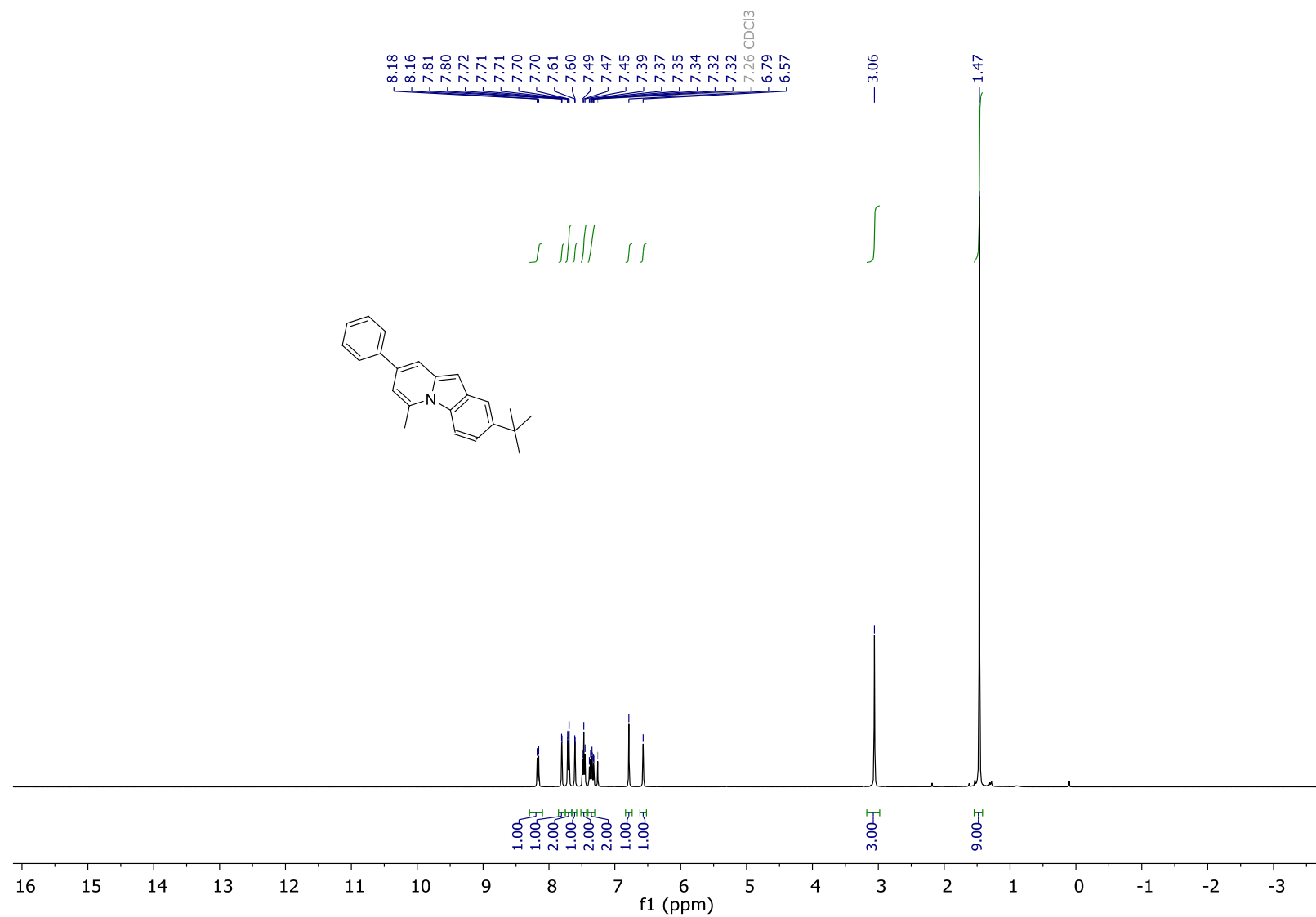
¹³C NMR for 4e



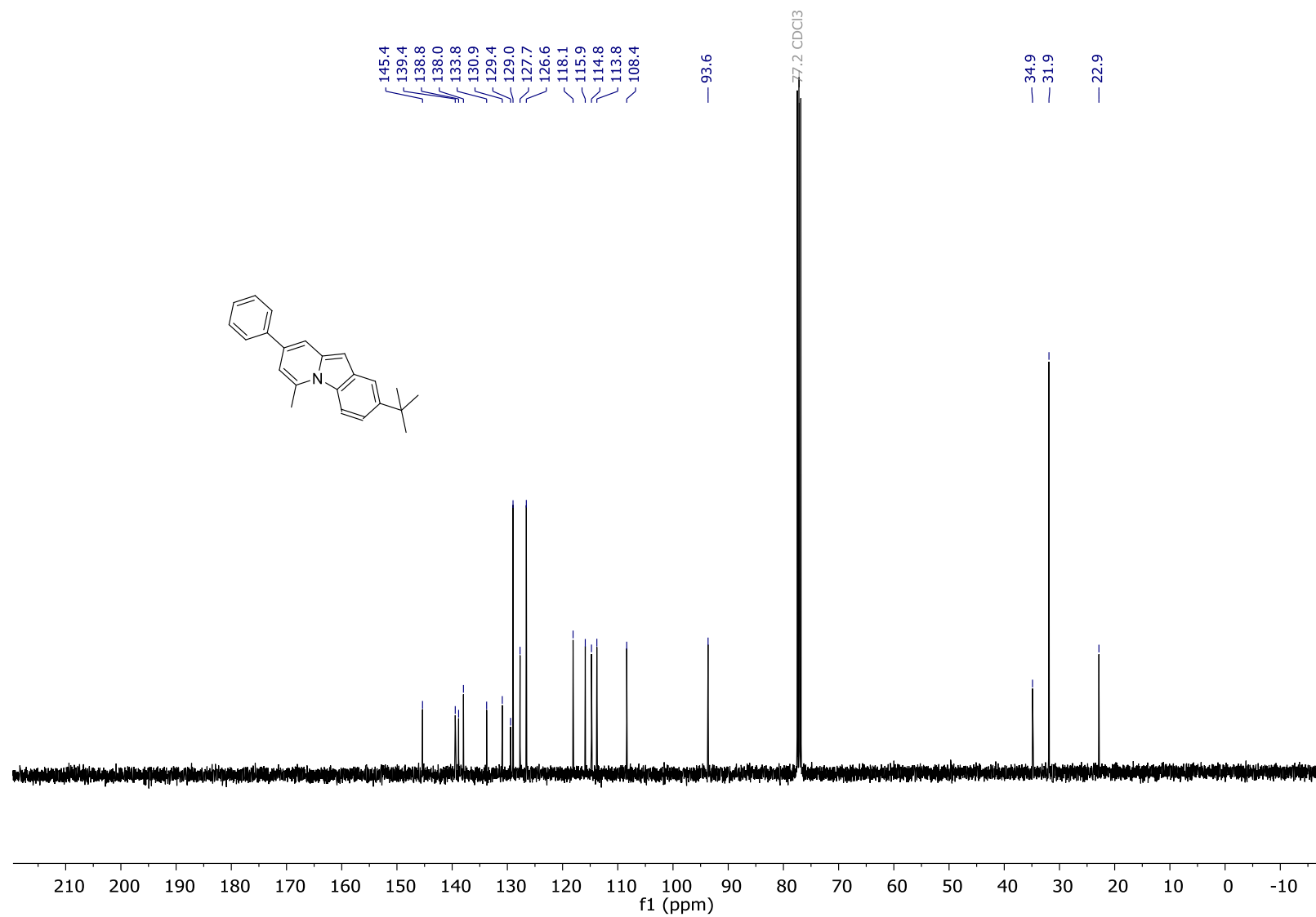
^1H - ^{13}C HSQC for 4e



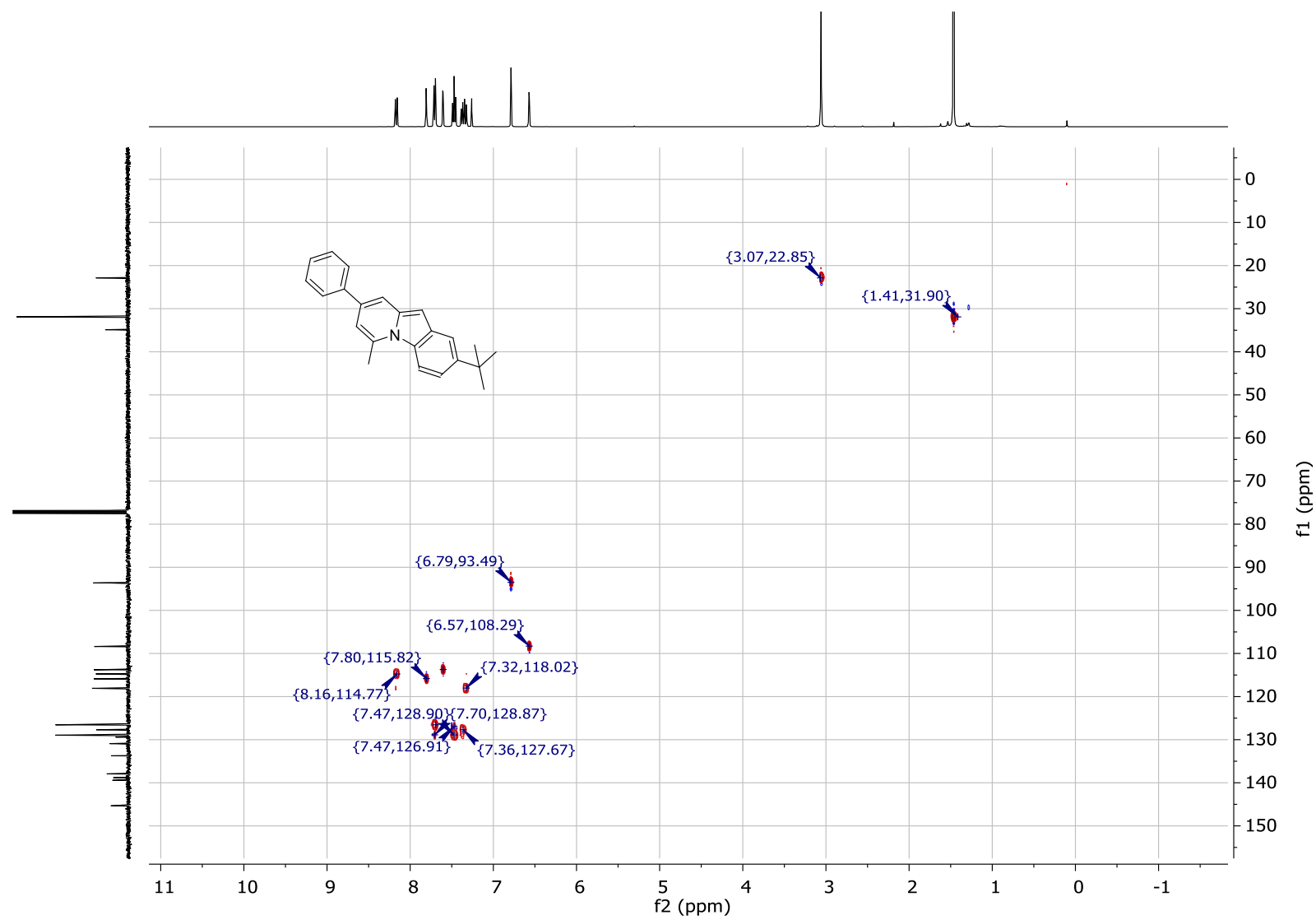
^{15}N - ^1H HMBC for 4e



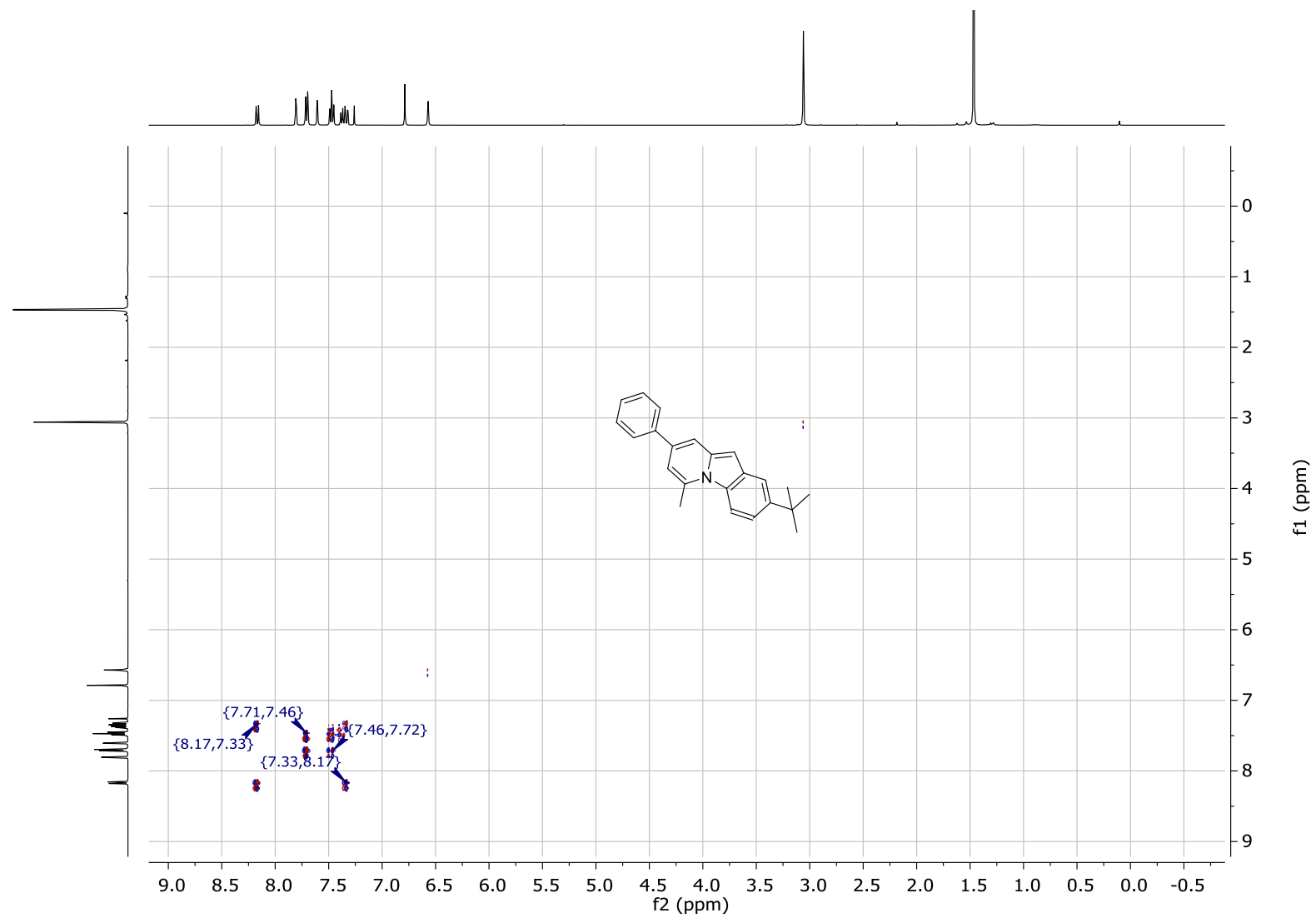
¹H NMR for 4f

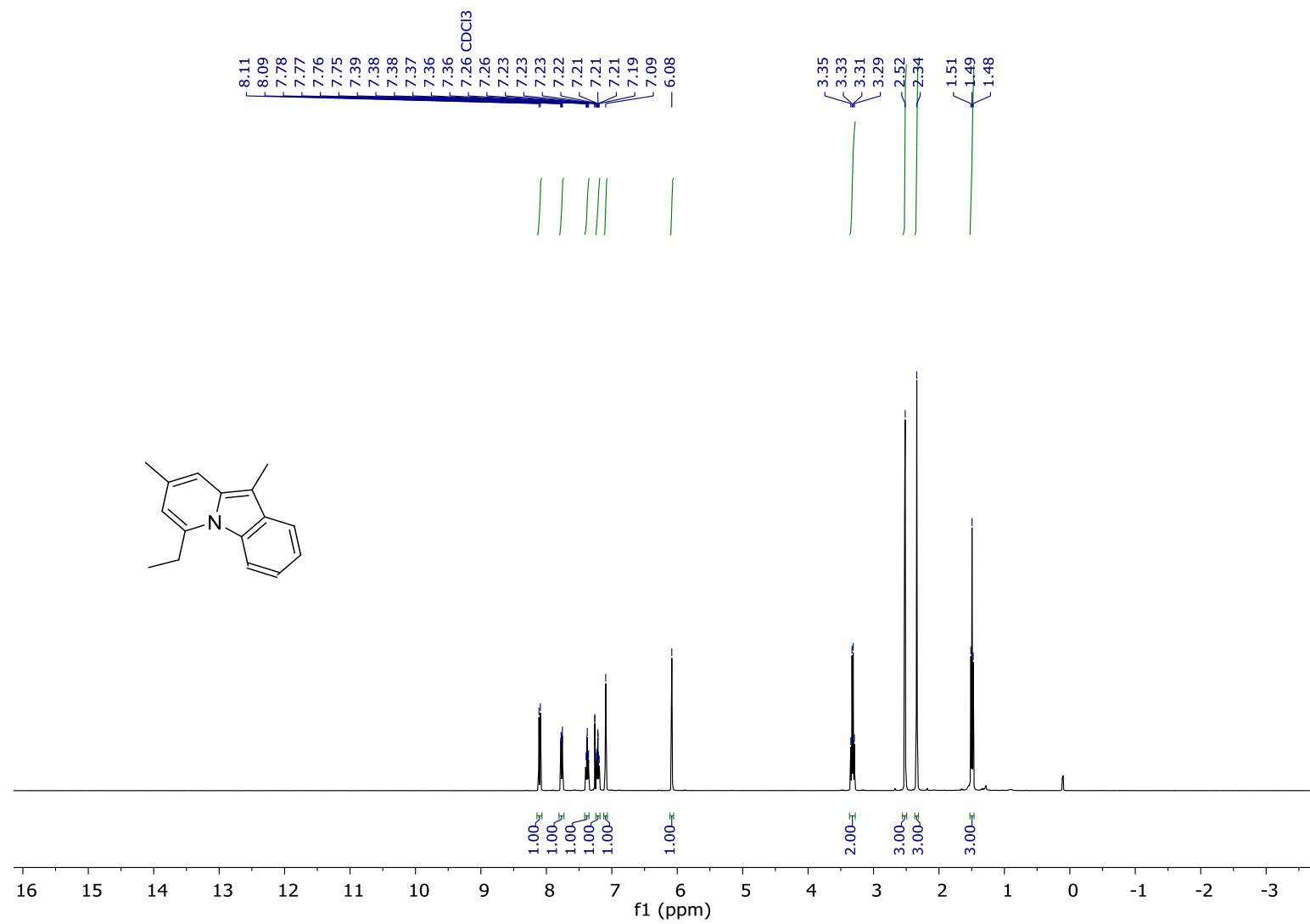


¹³C NMR of 4f

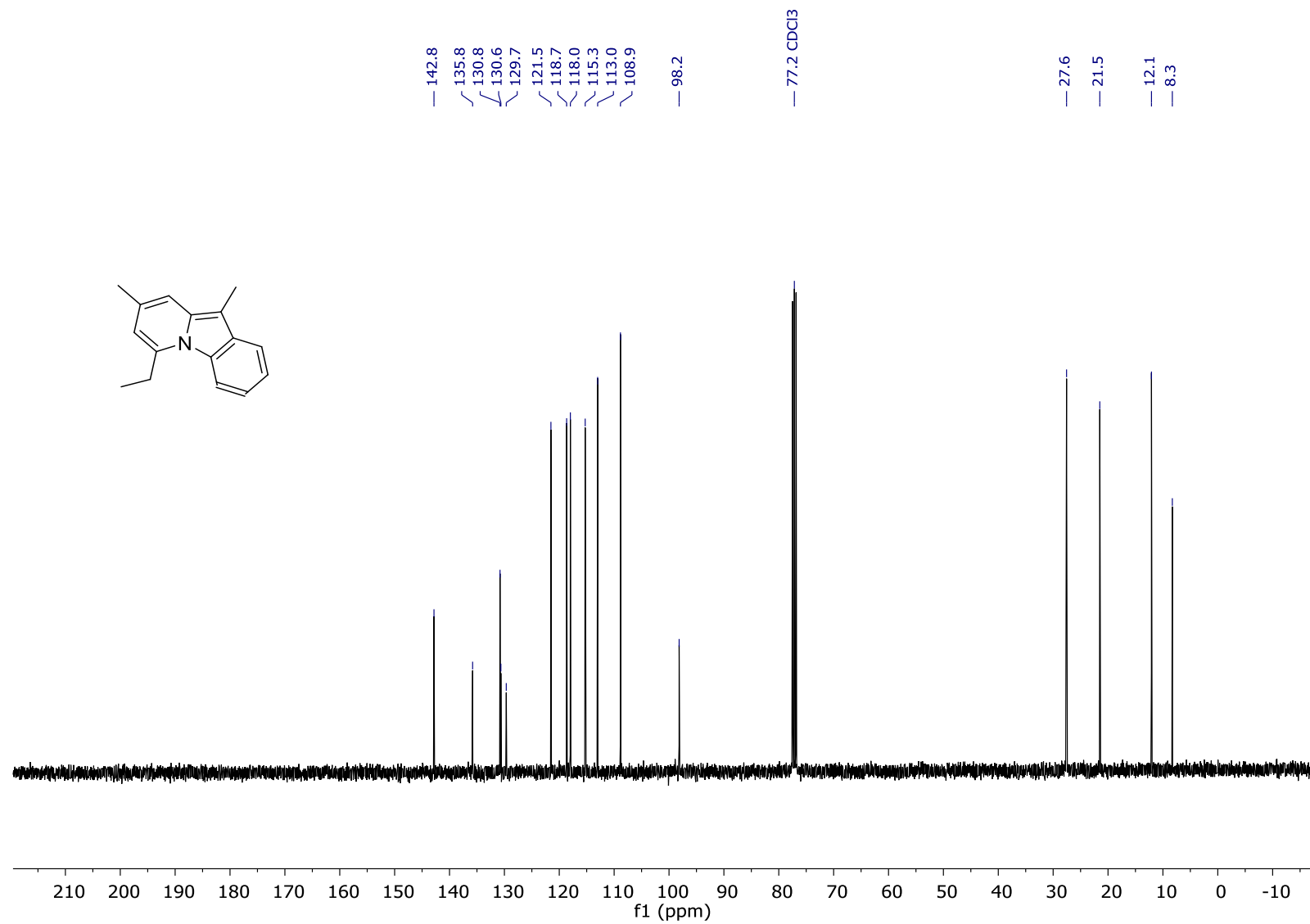


^1H - ^{13}C HSQC for 4f

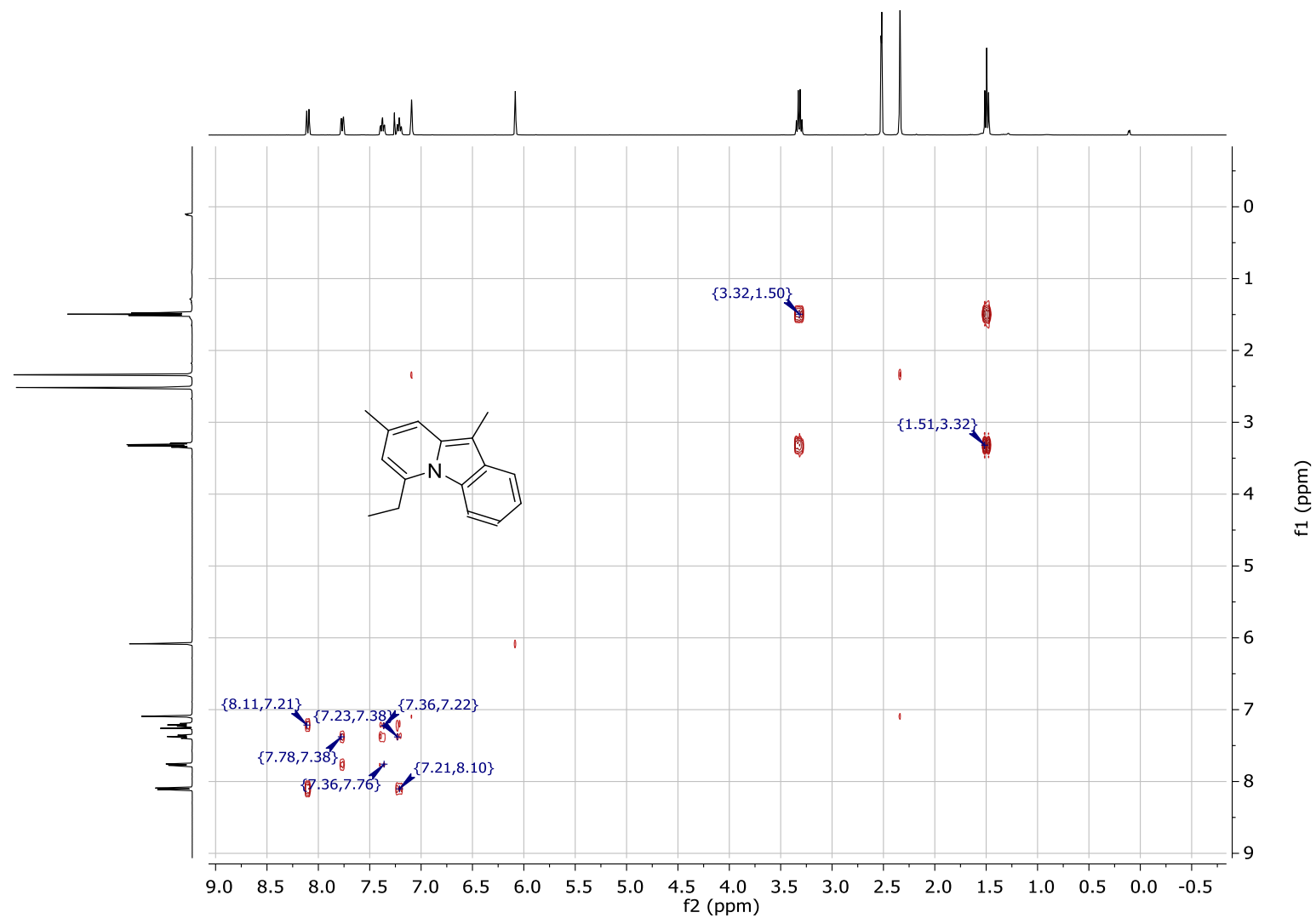




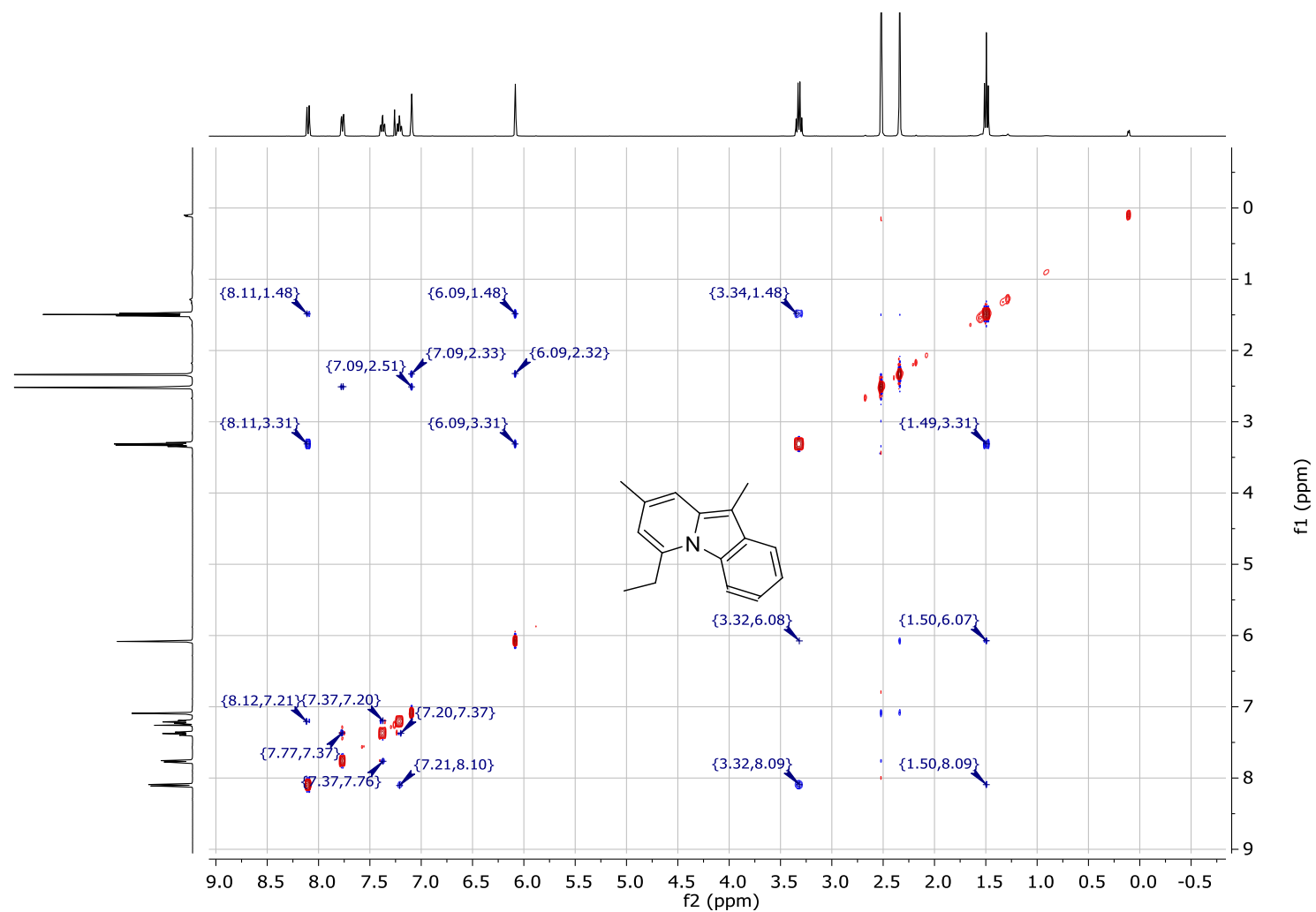
¹H NMR for 4g



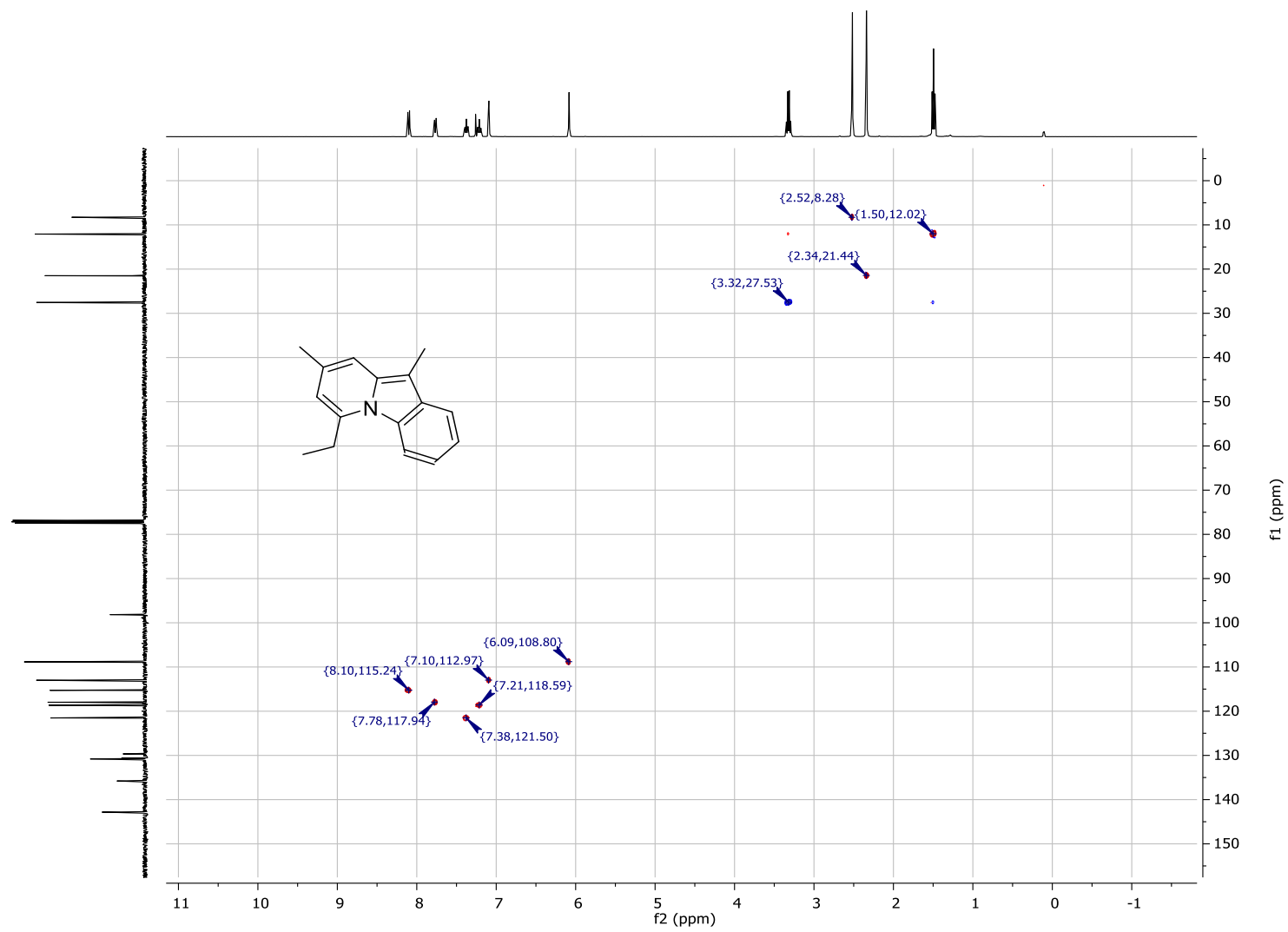
^{13}C NMR for 4g



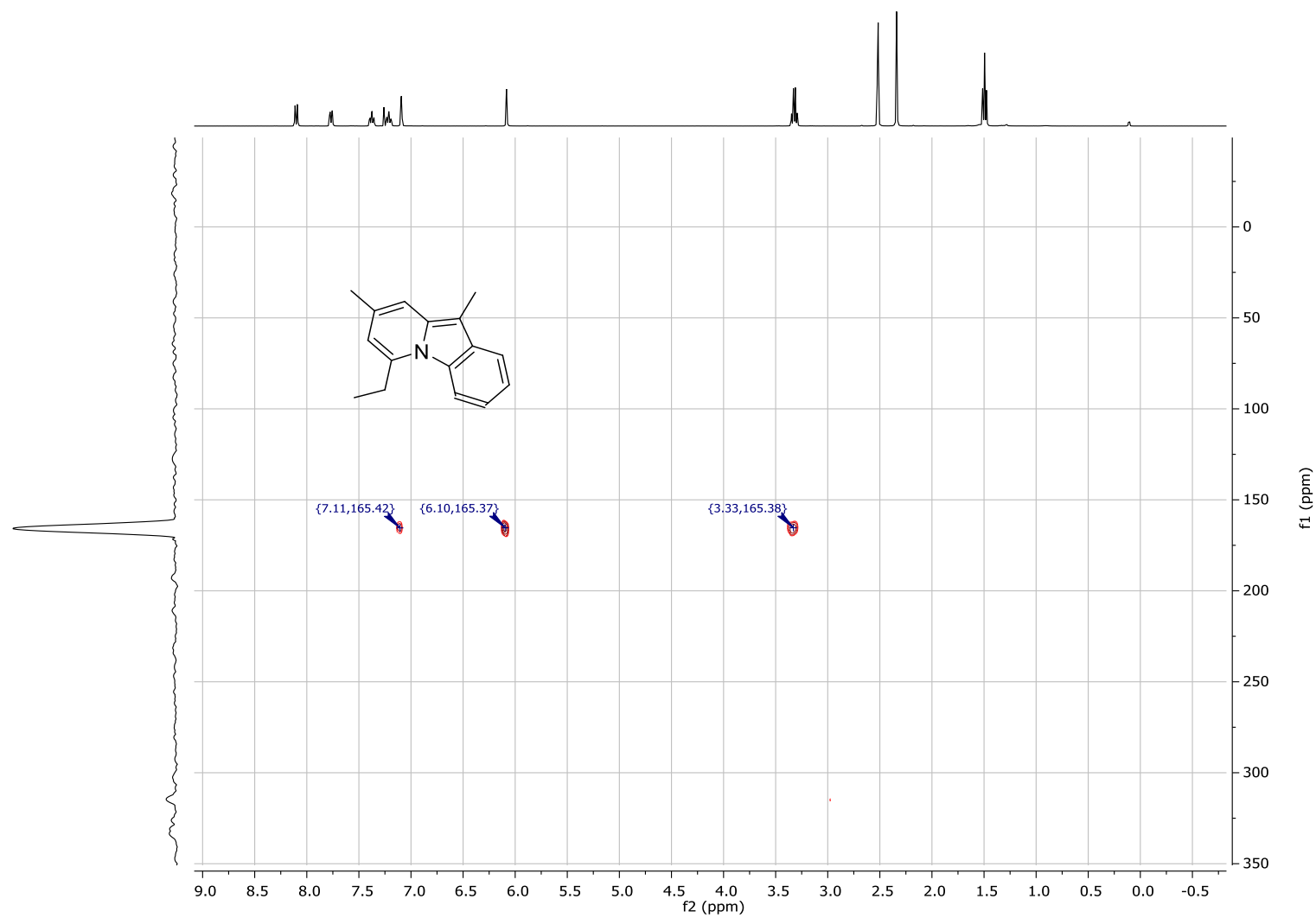
¹H-¹H COSY for 4g



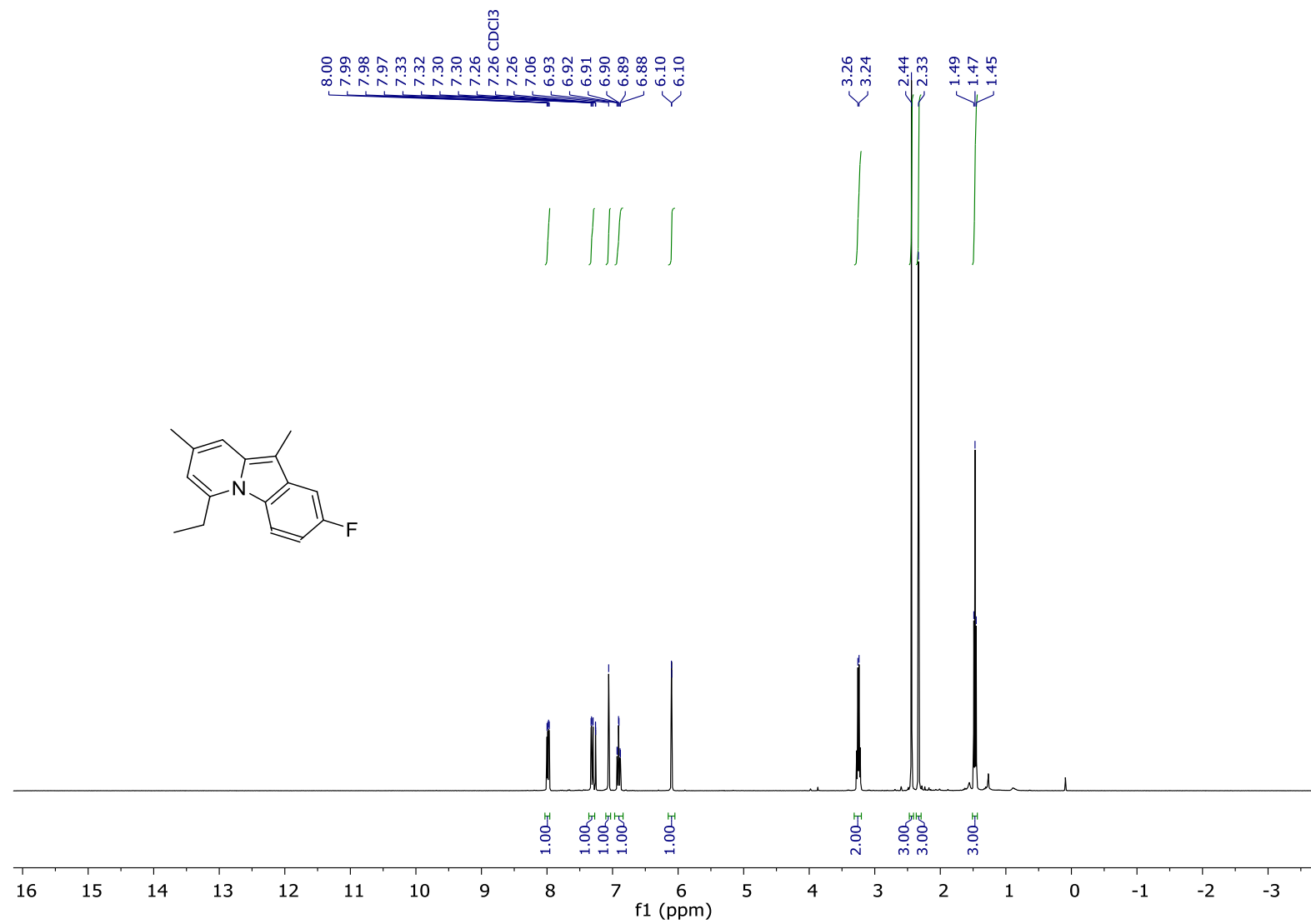
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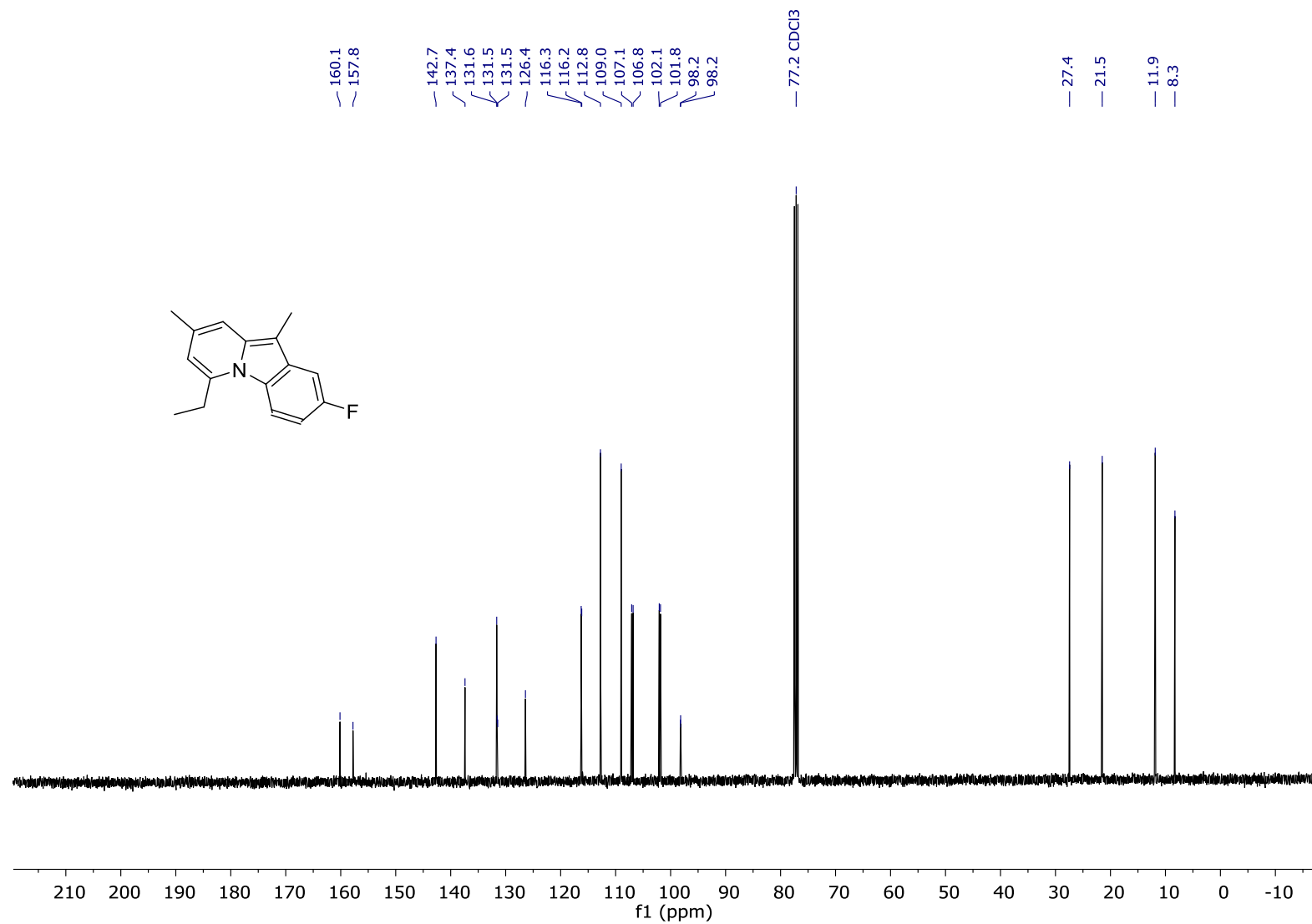
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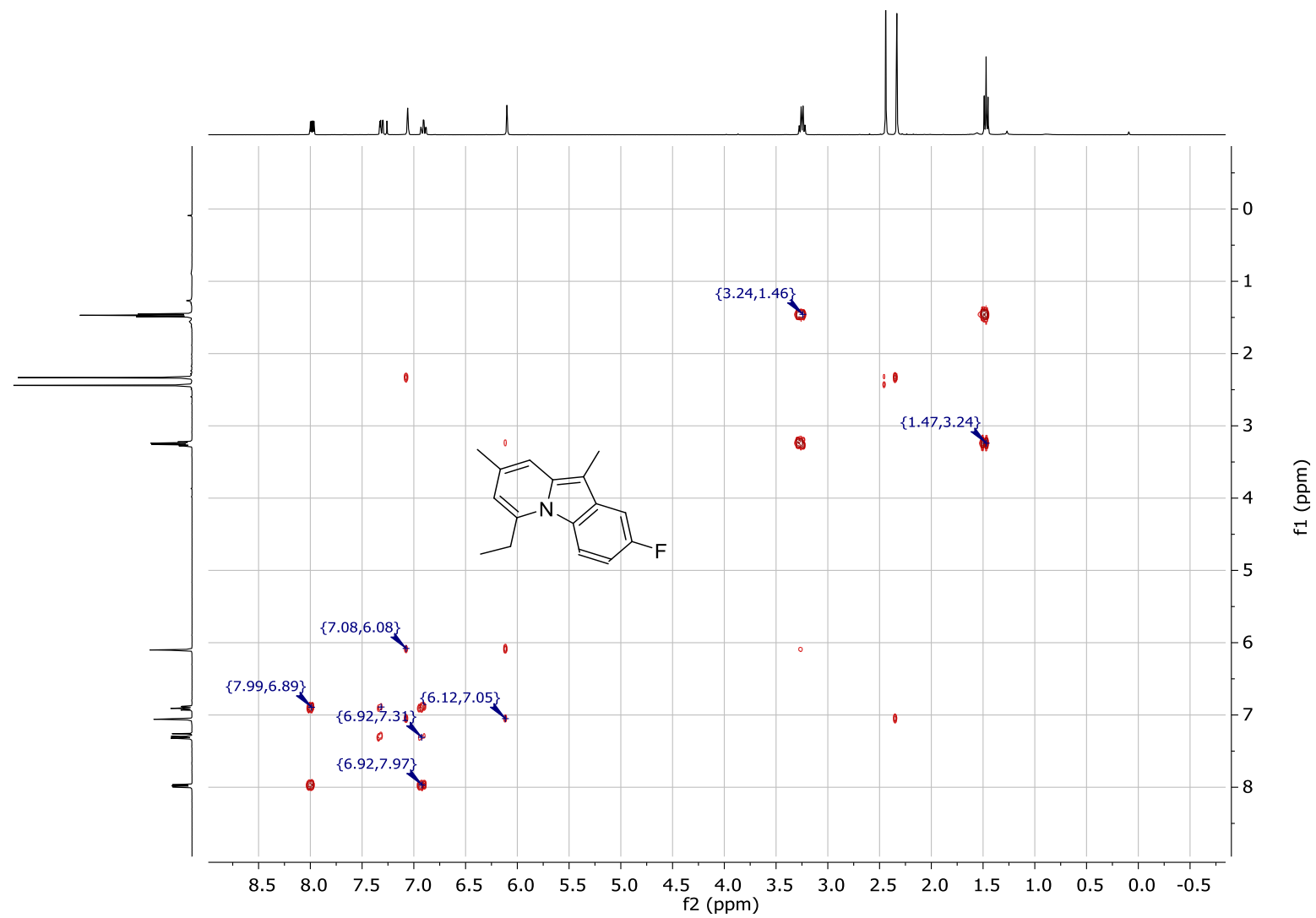
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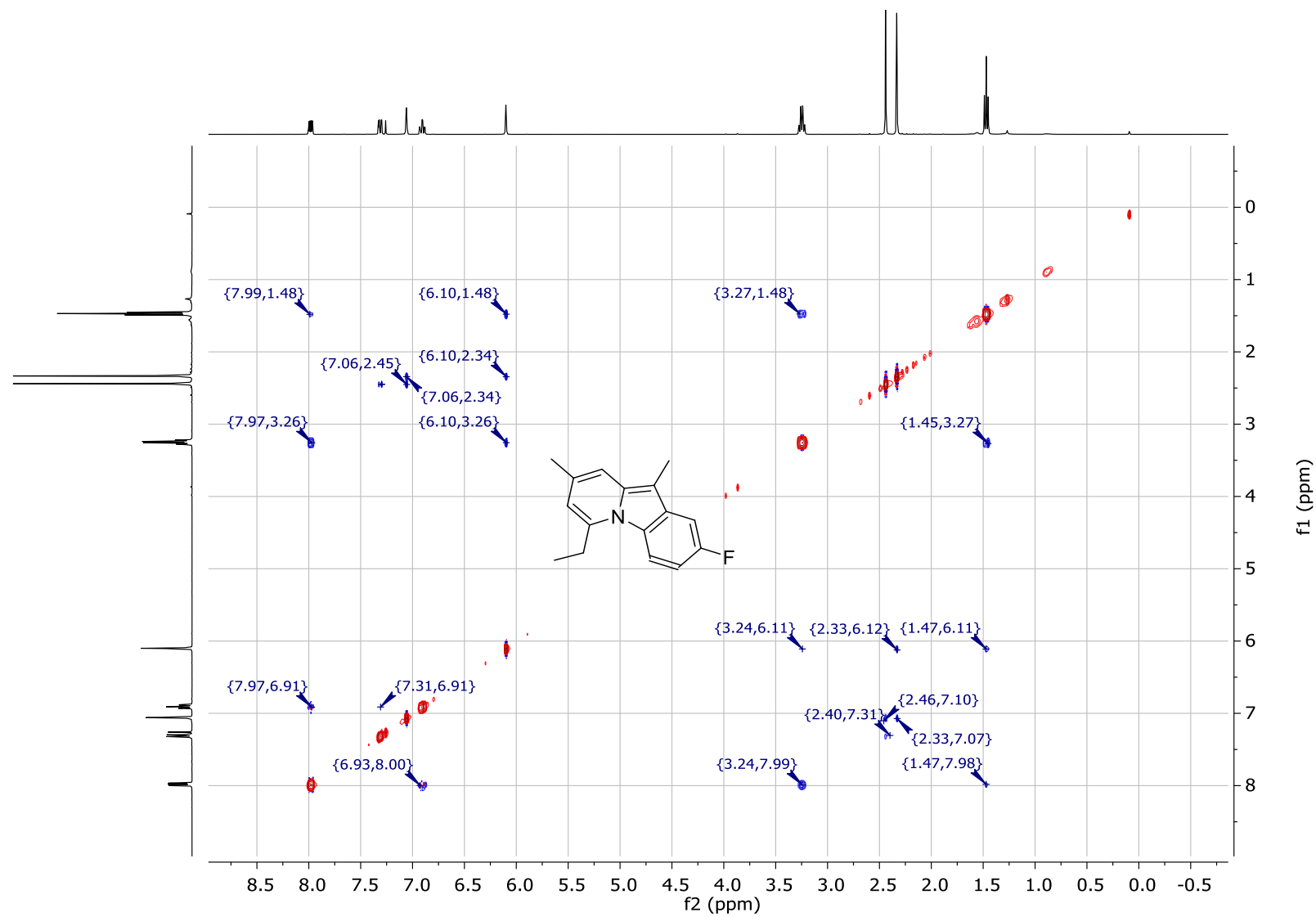


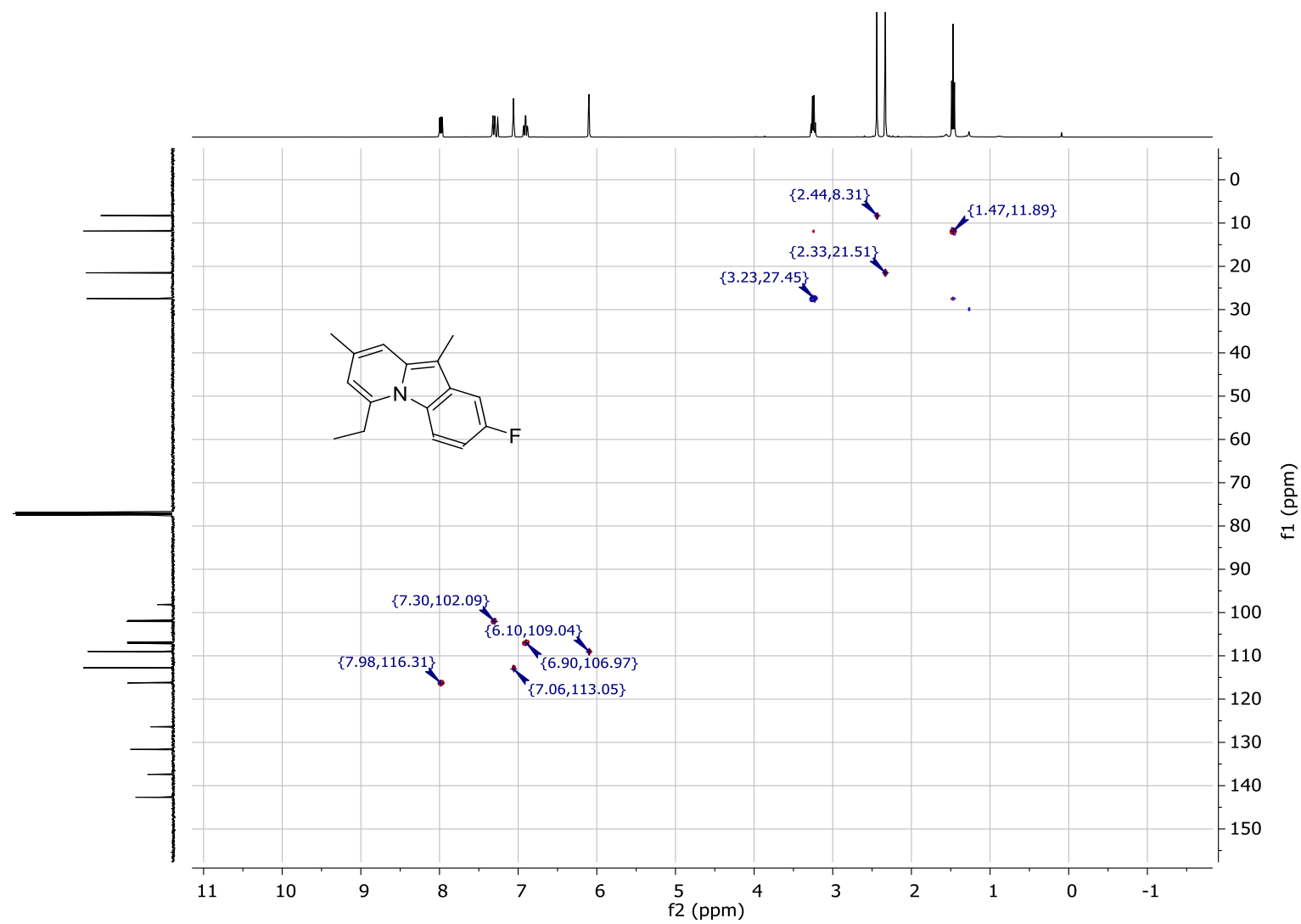
¹H NMR for 4h



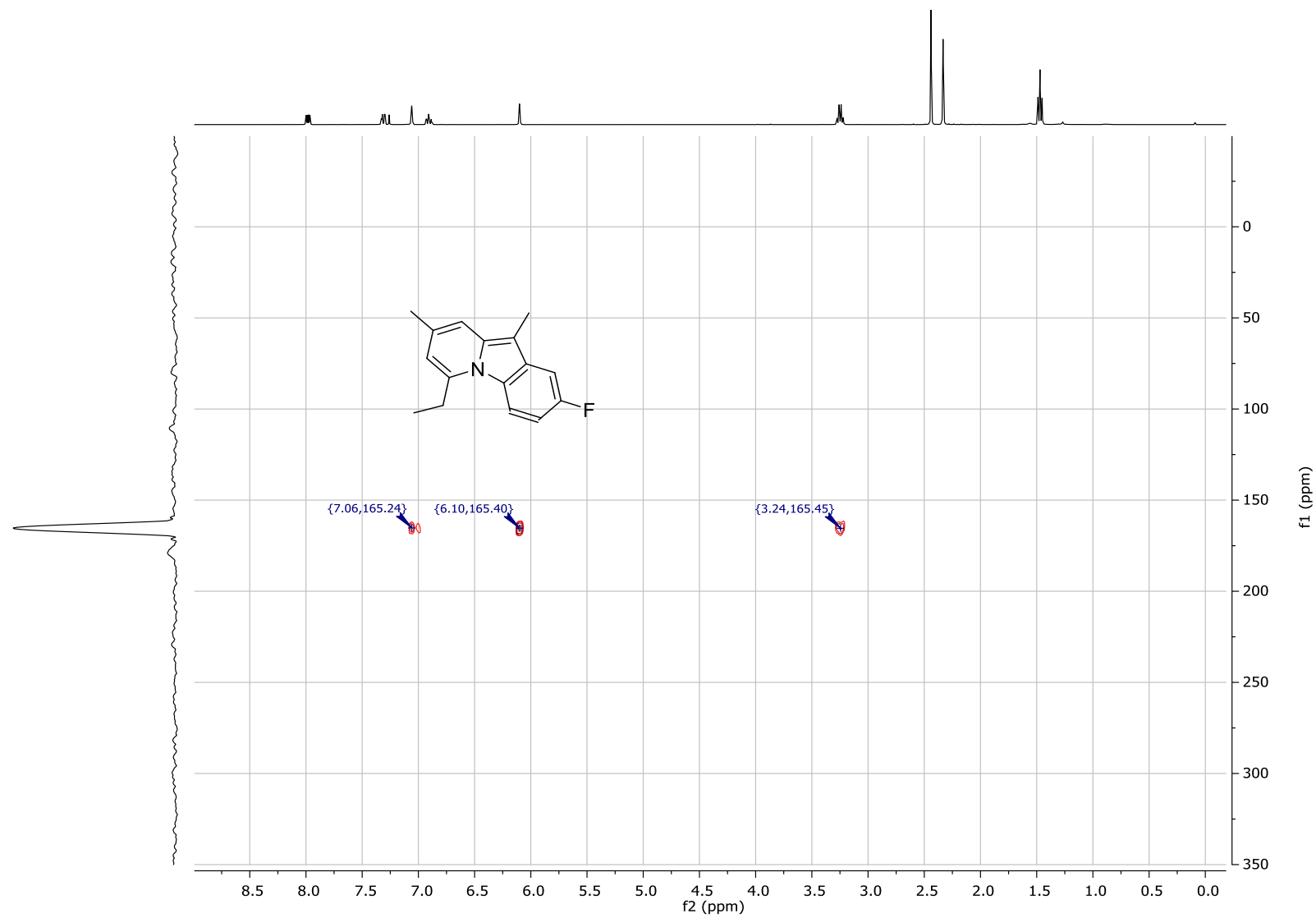
¹³C NMR for 4h



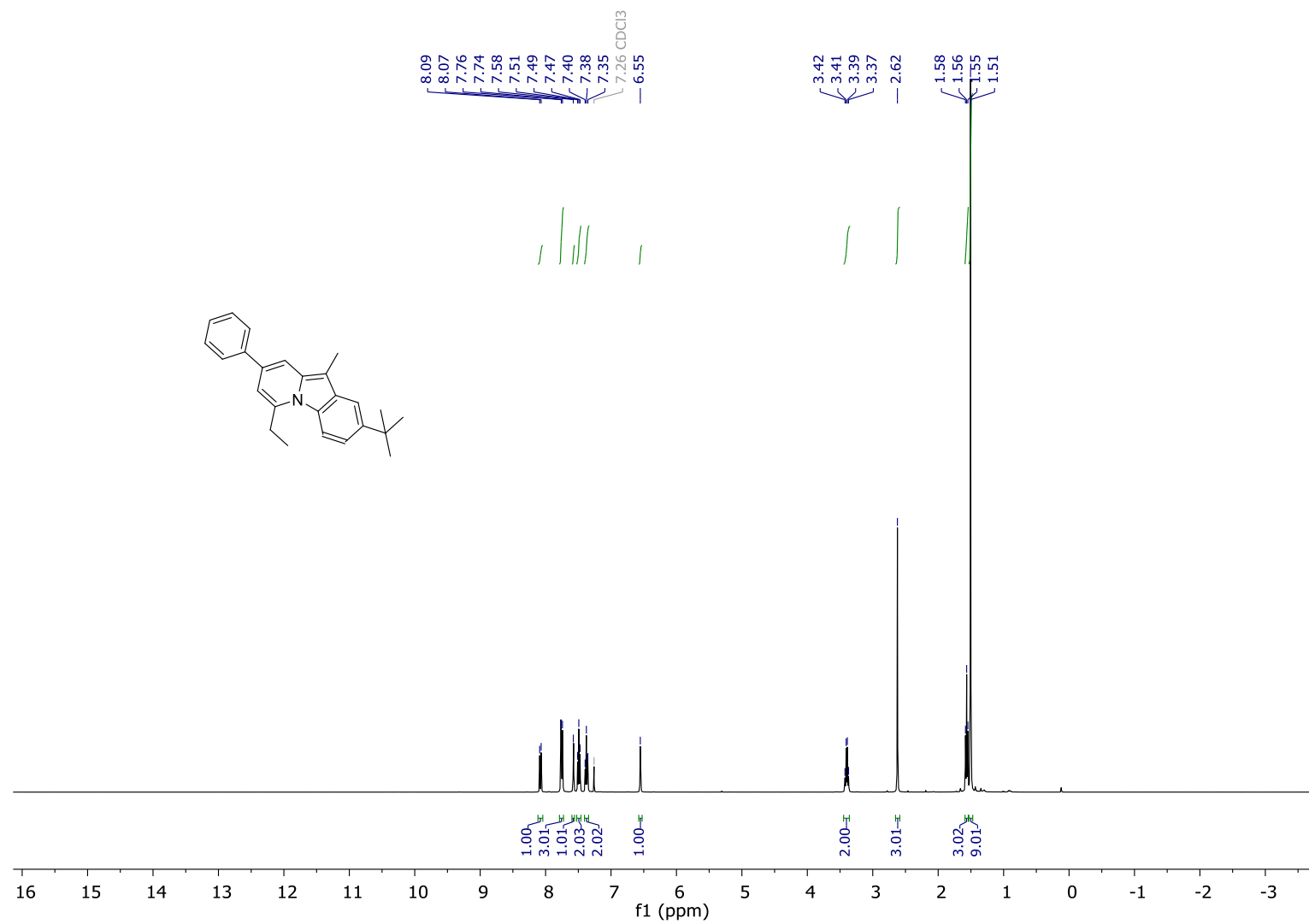




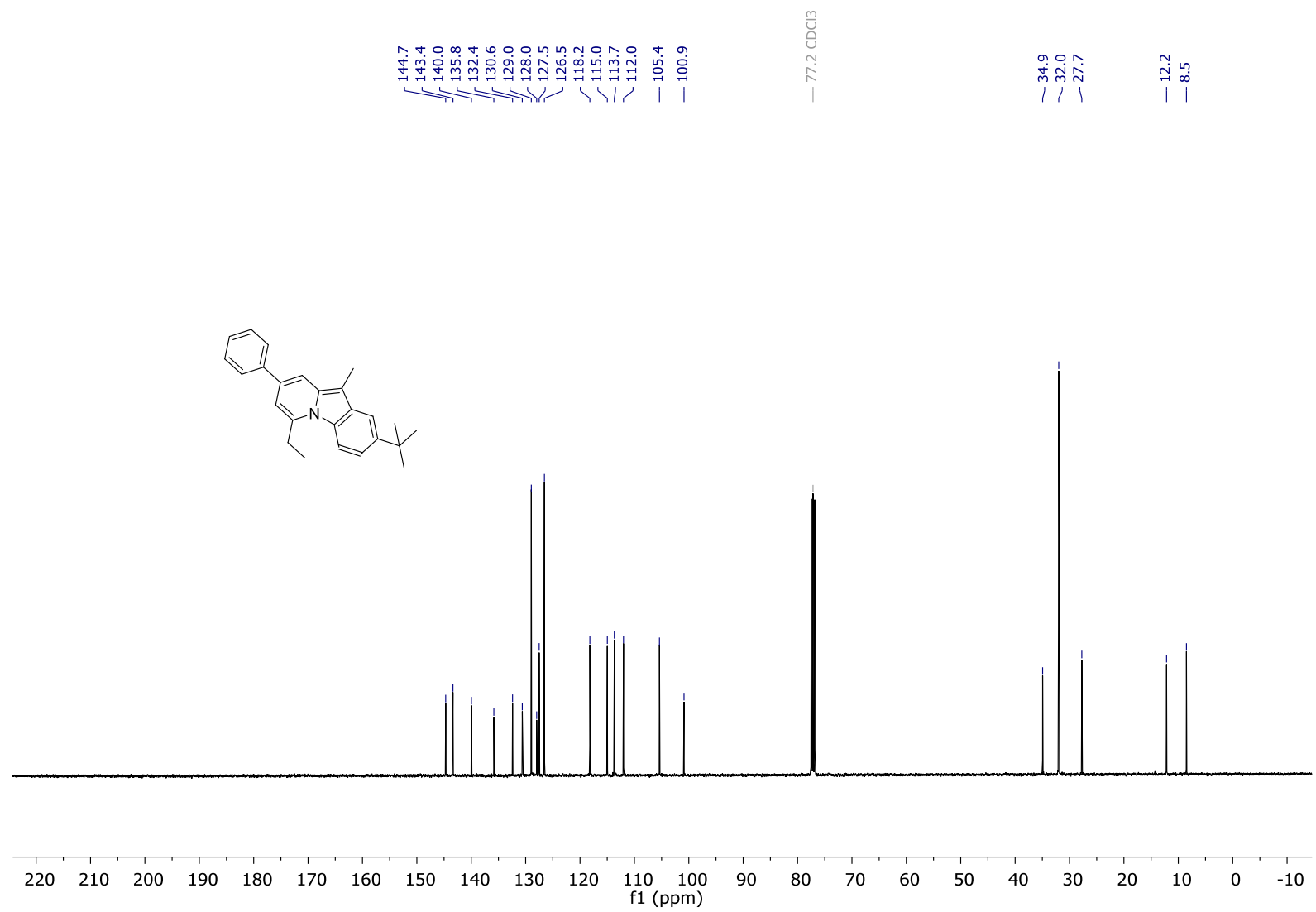
^1H - ^{13}C HSQC for 4h



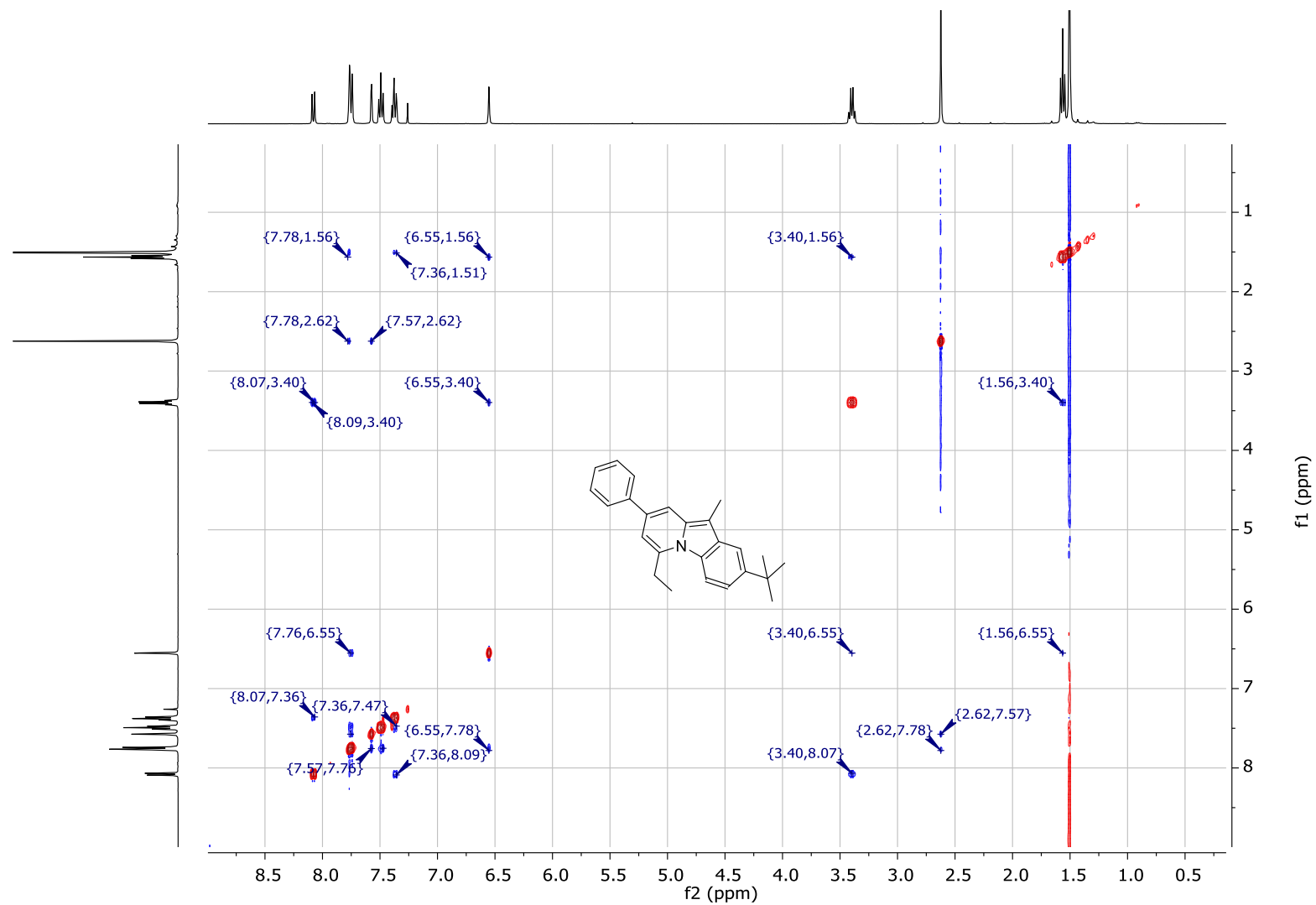
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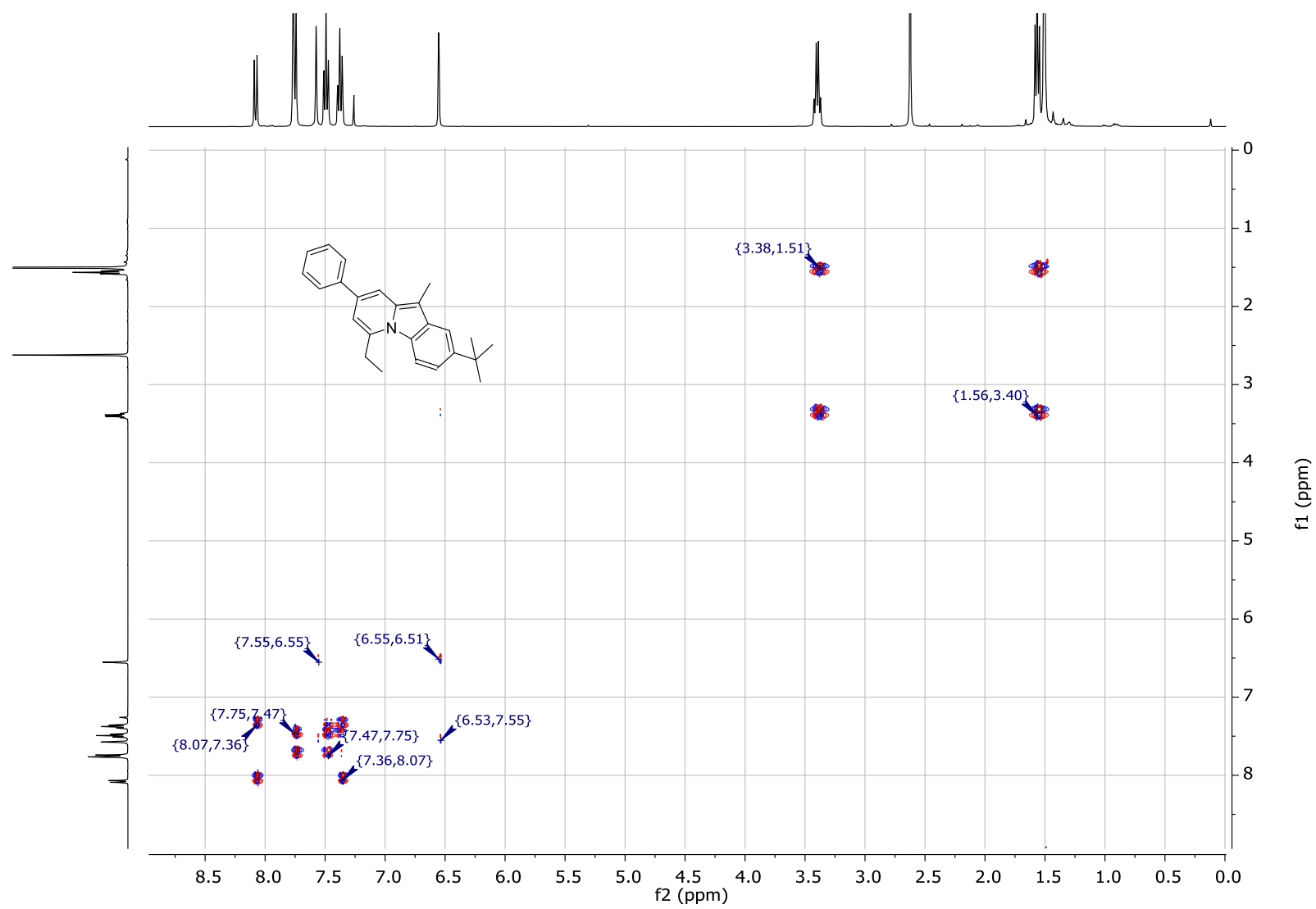
¹H NMR for 4i



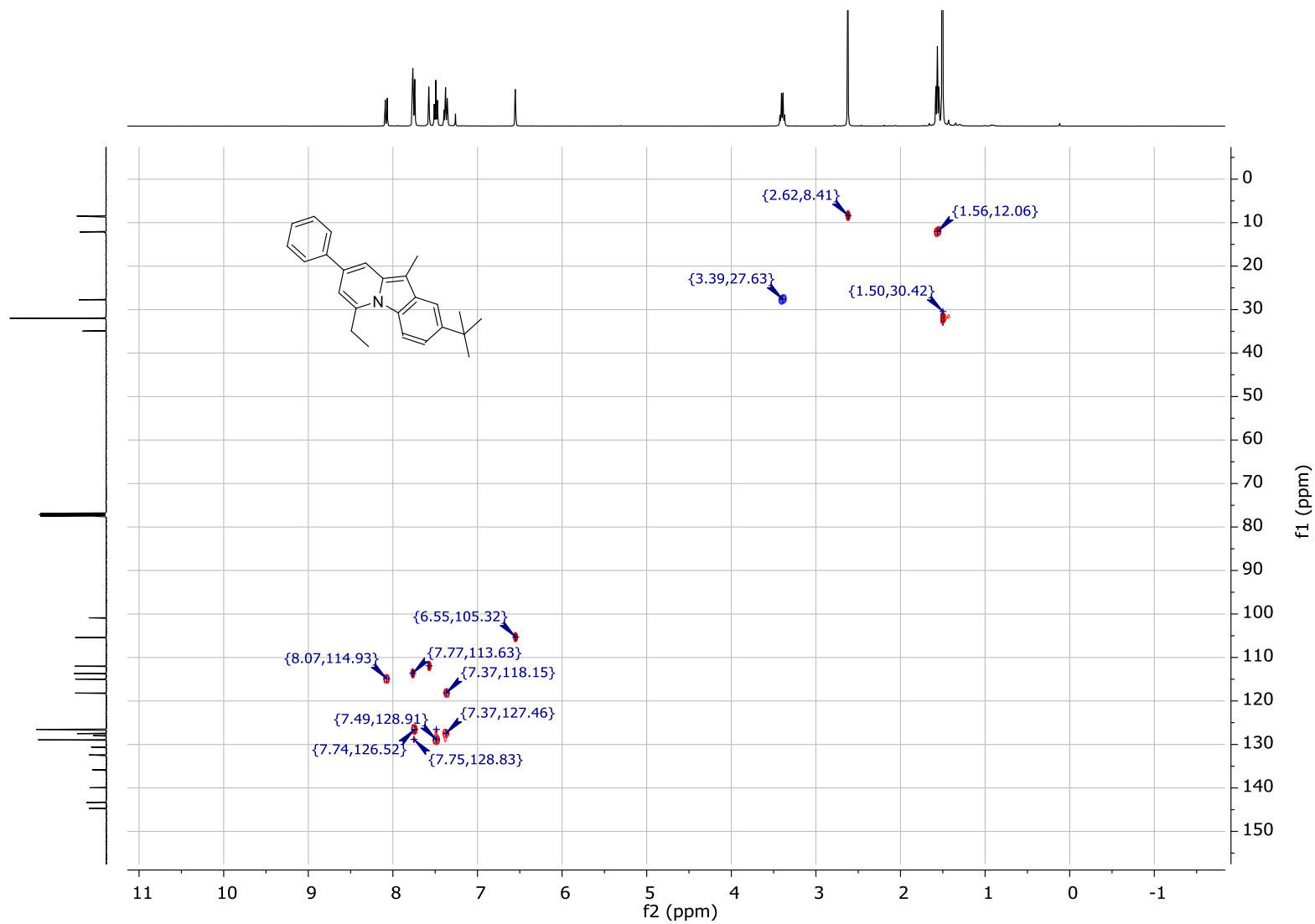
¹³C NMR for 4i



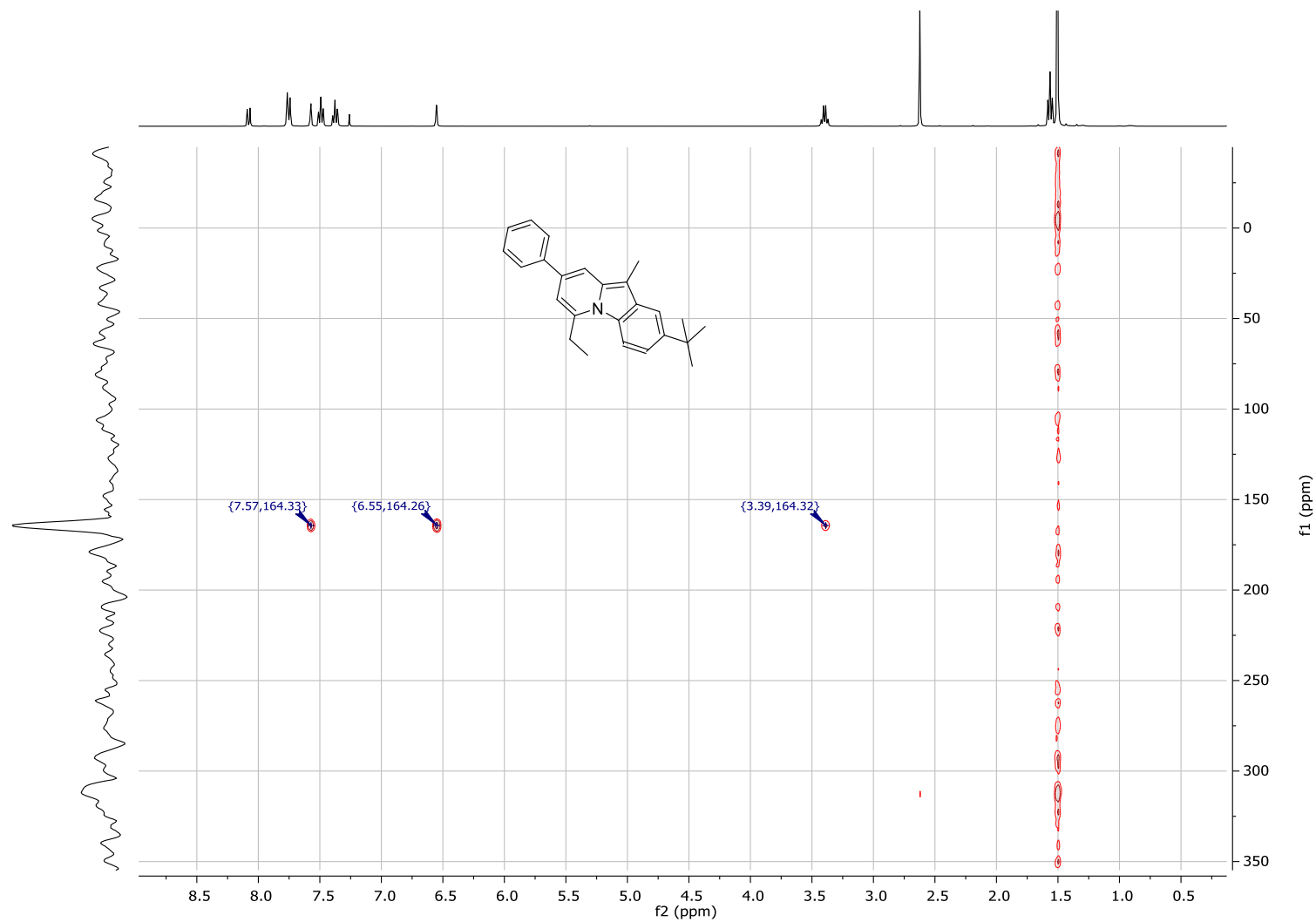
^1H - ^1H NOESY for 4i



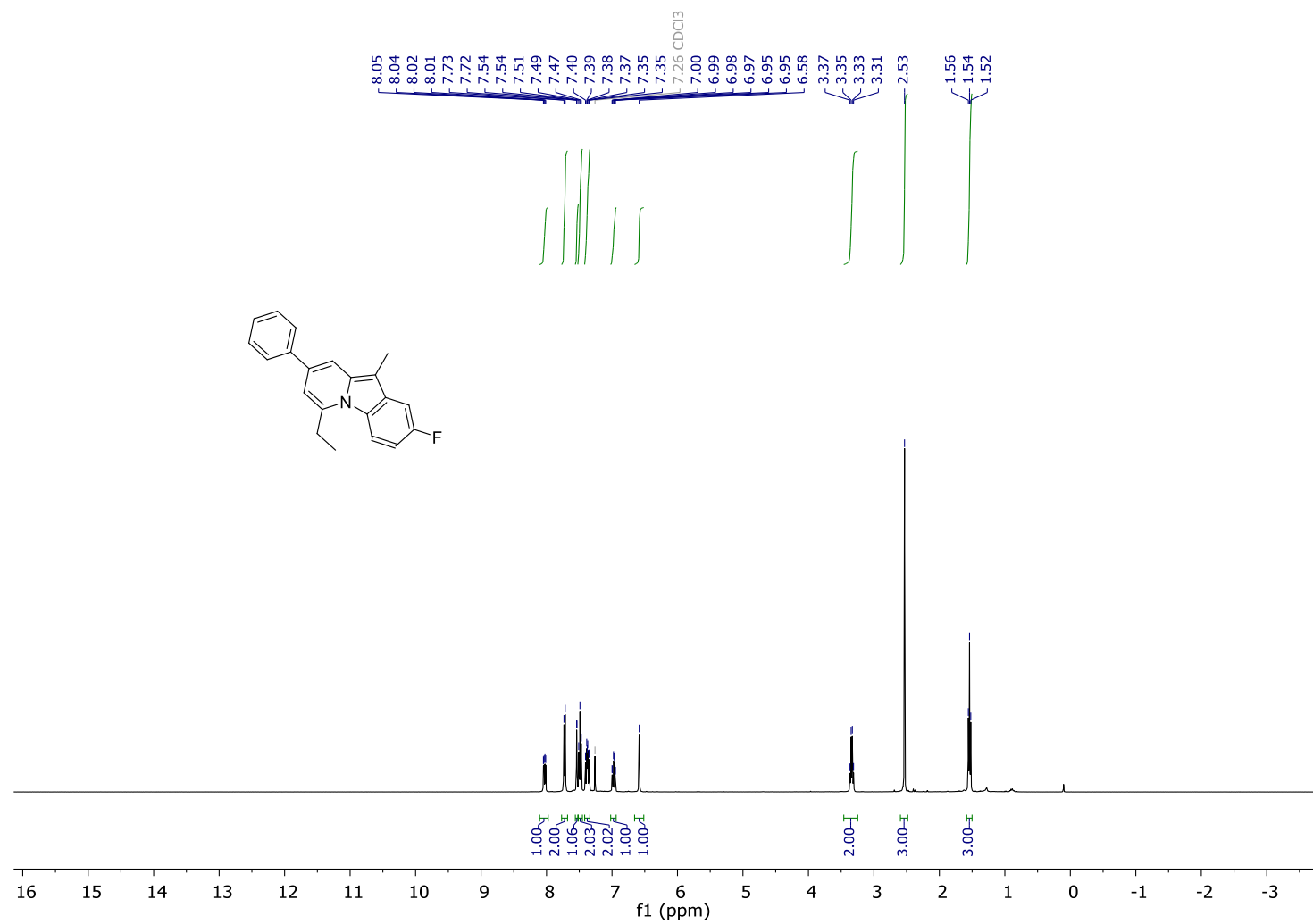
^1H - ^1H COSY for 4i



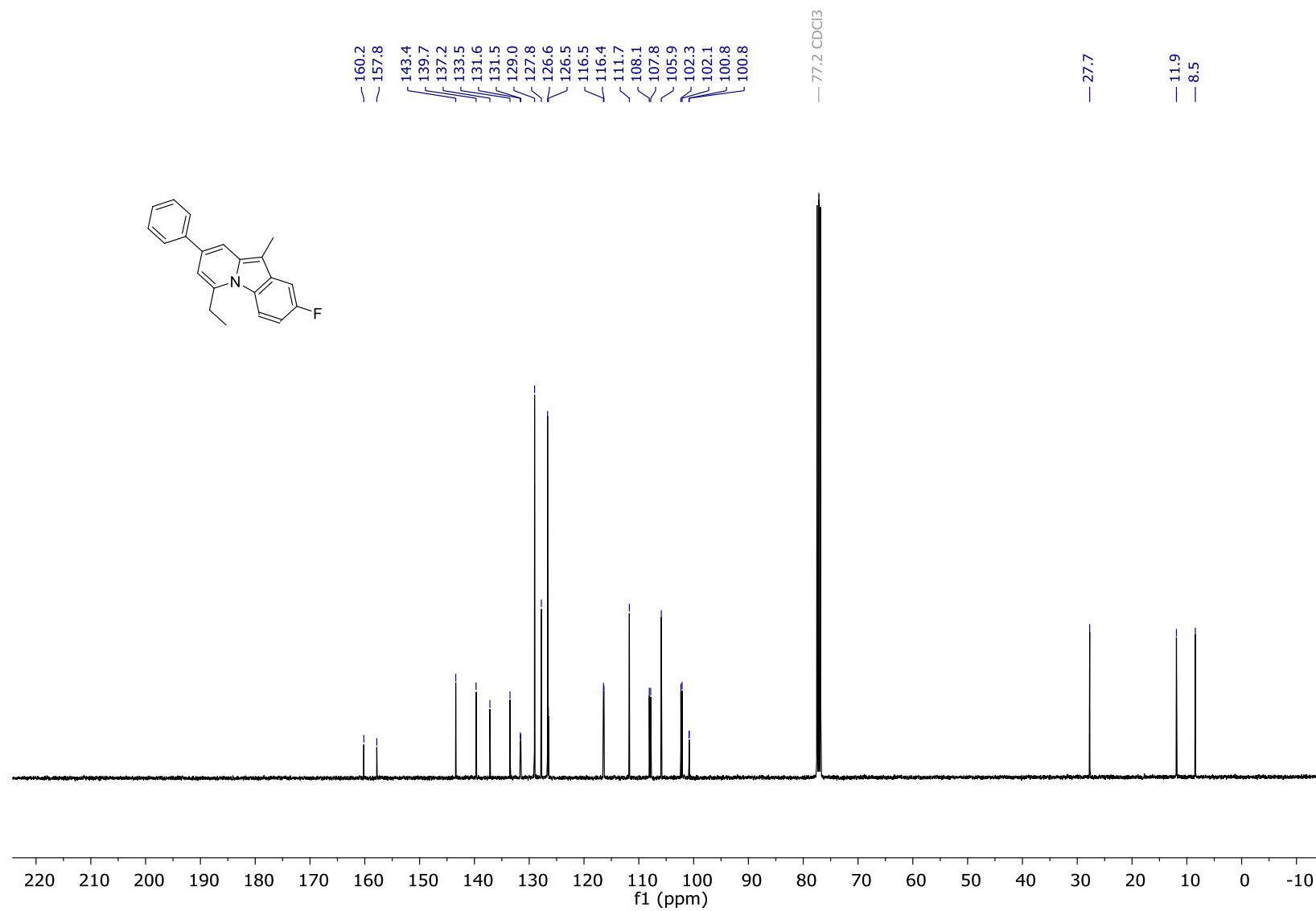
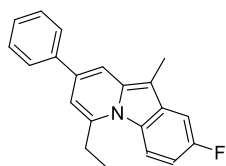
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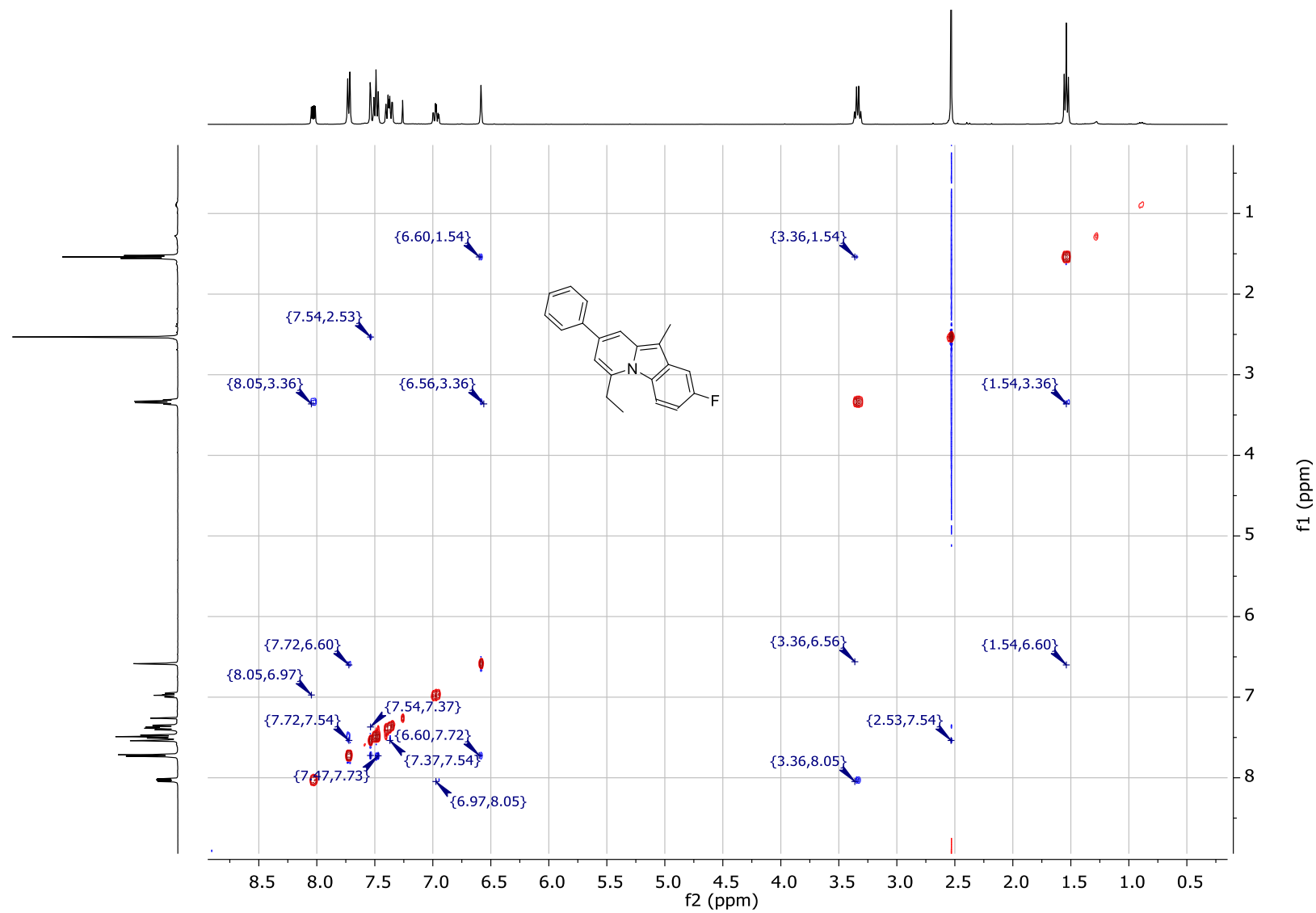
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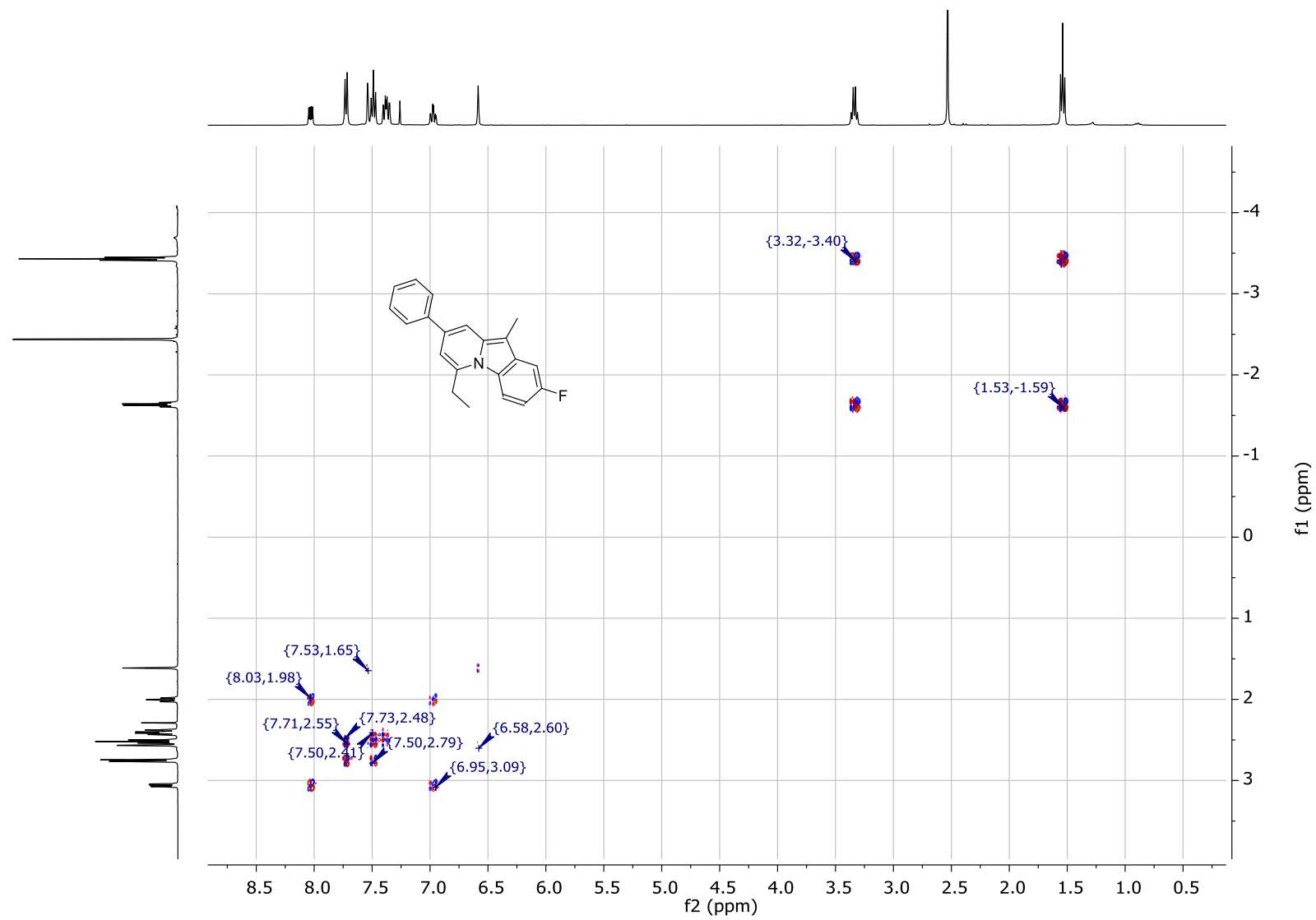
¹H NMR for 4j



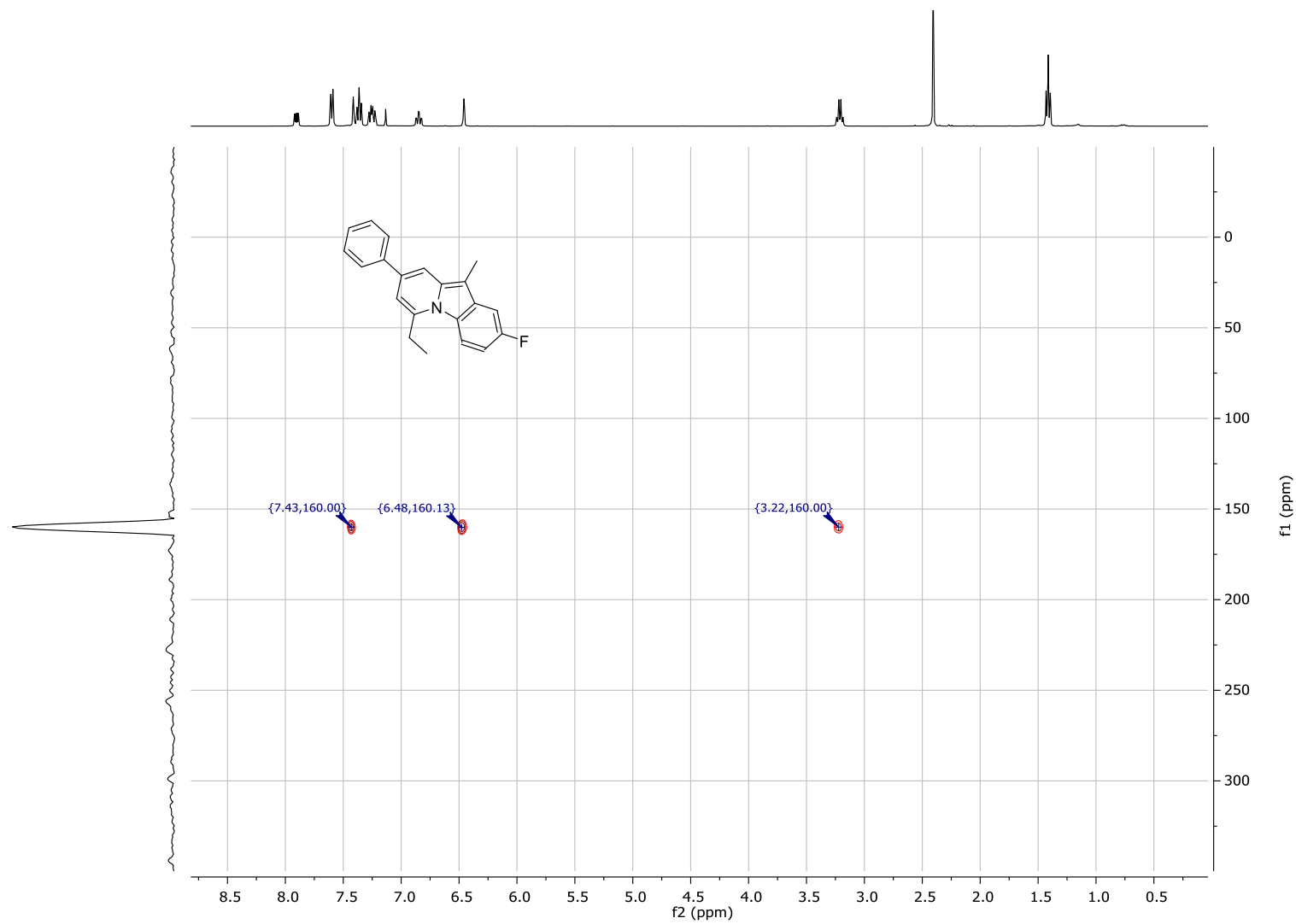
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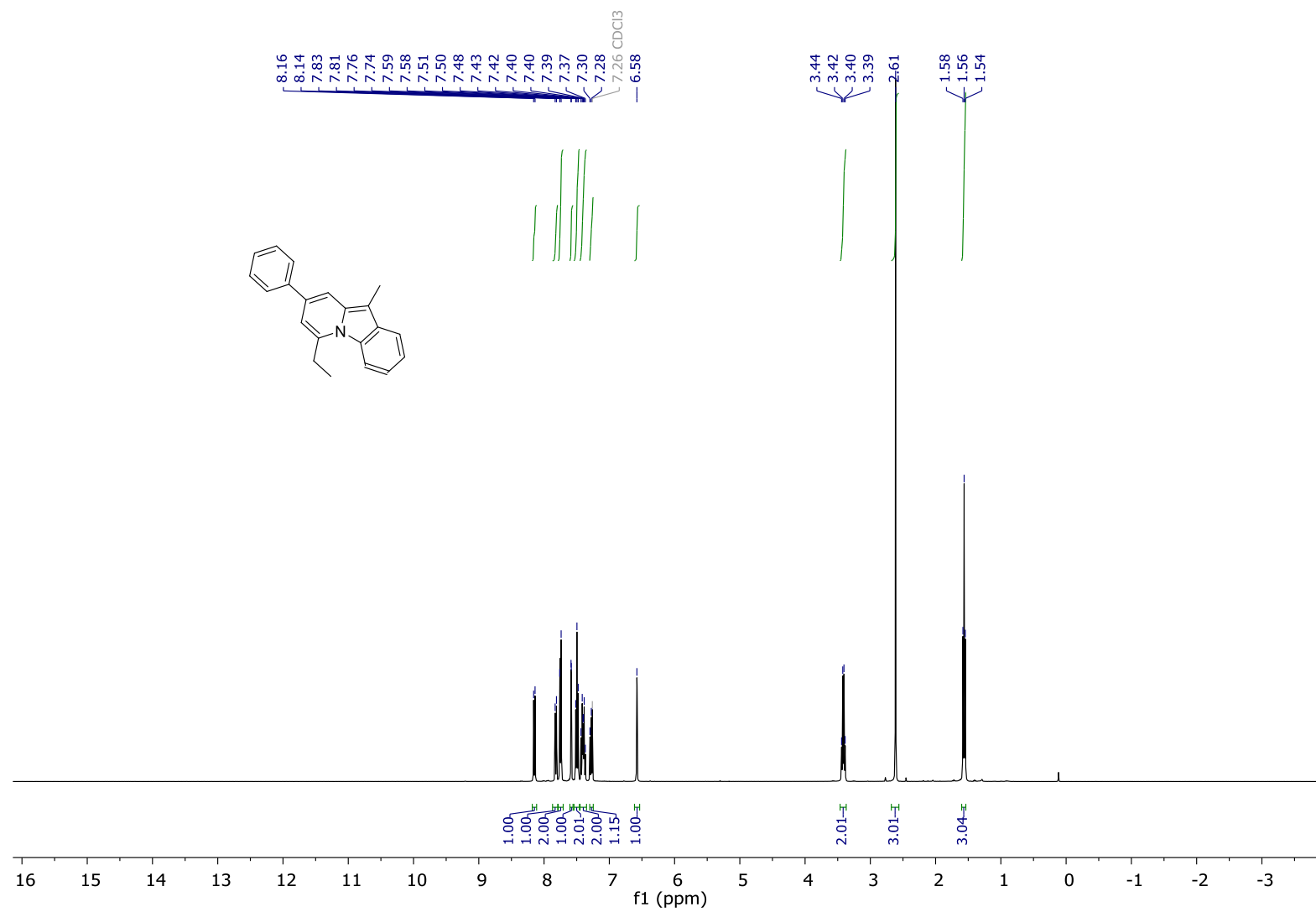
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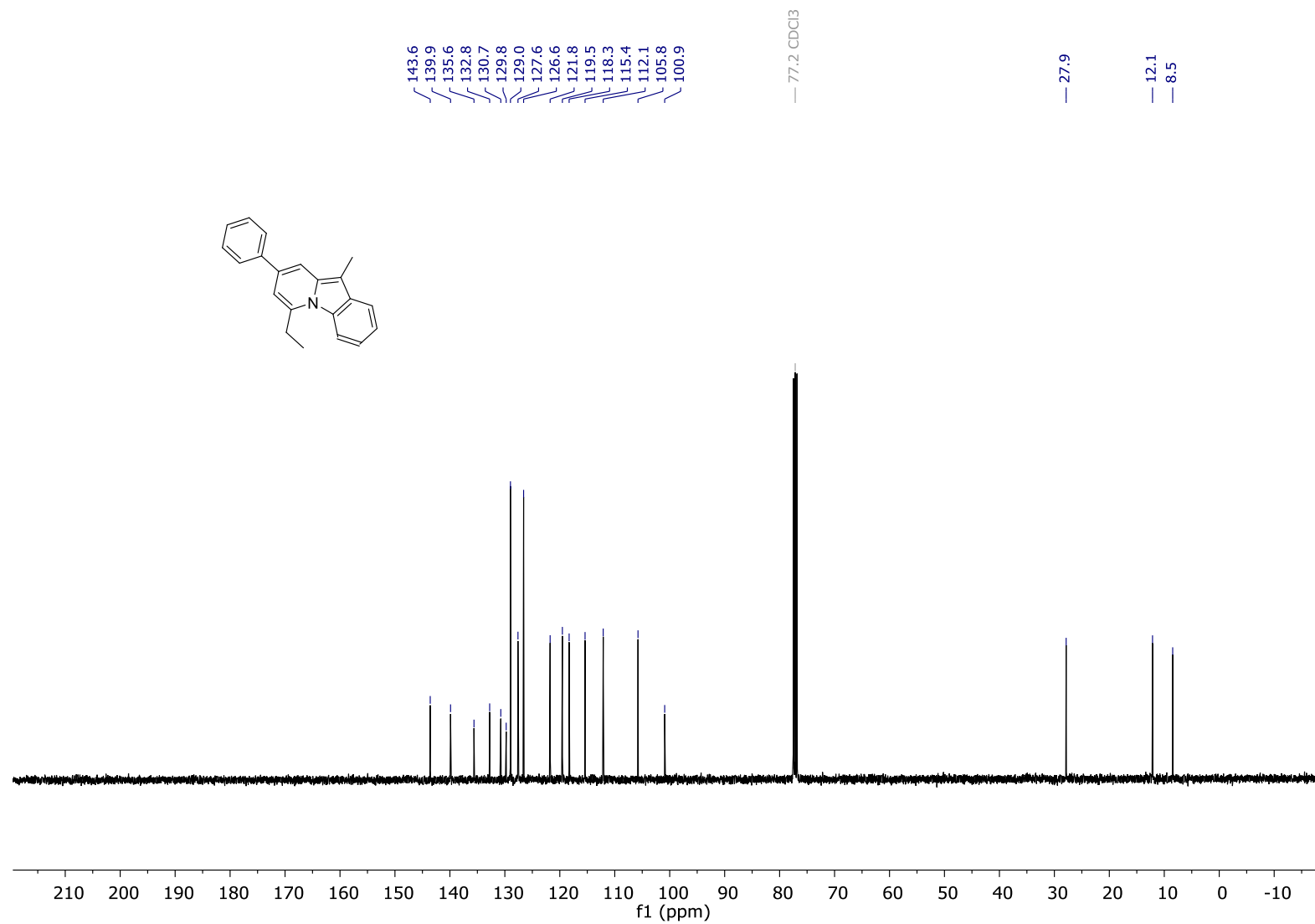
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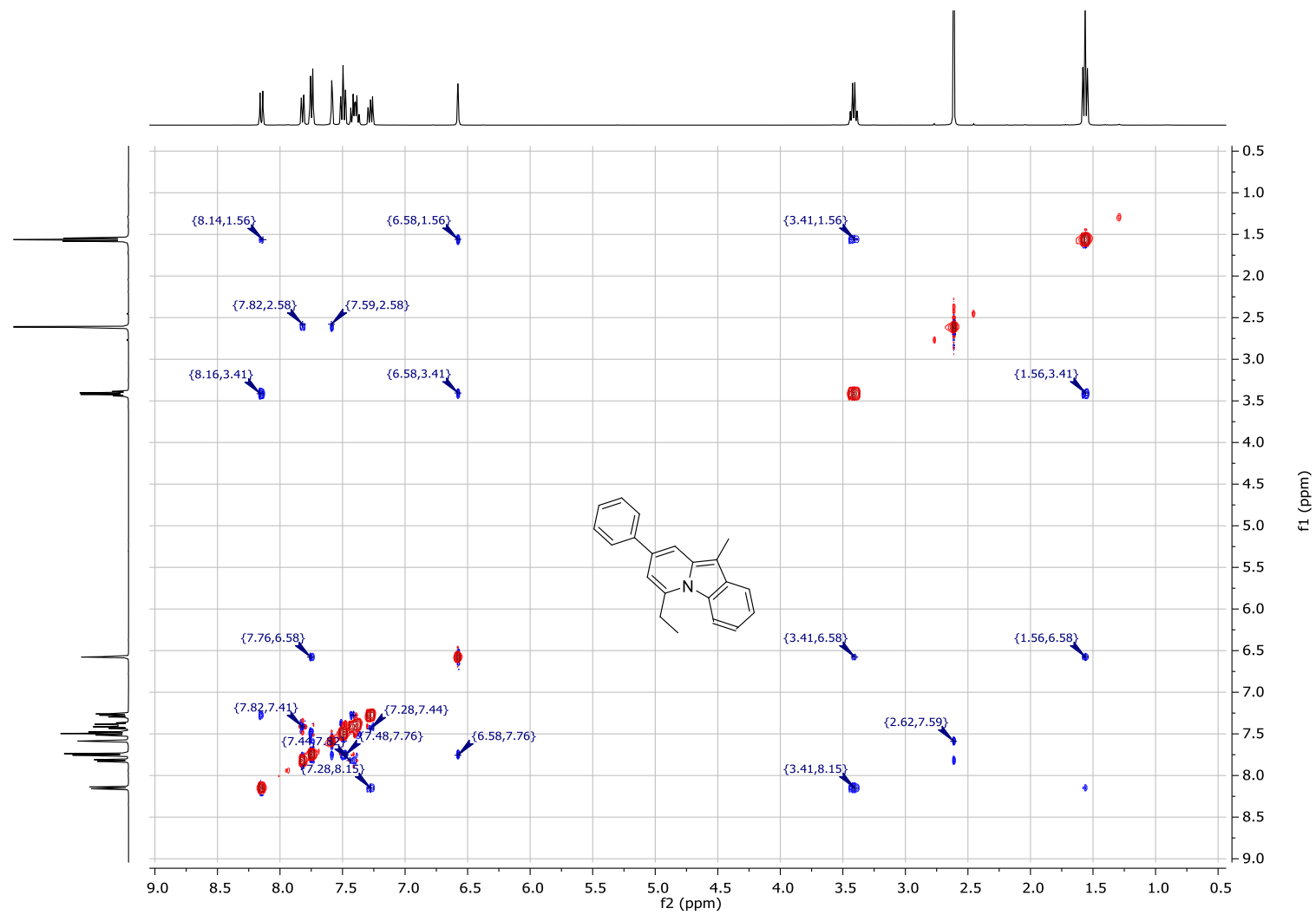
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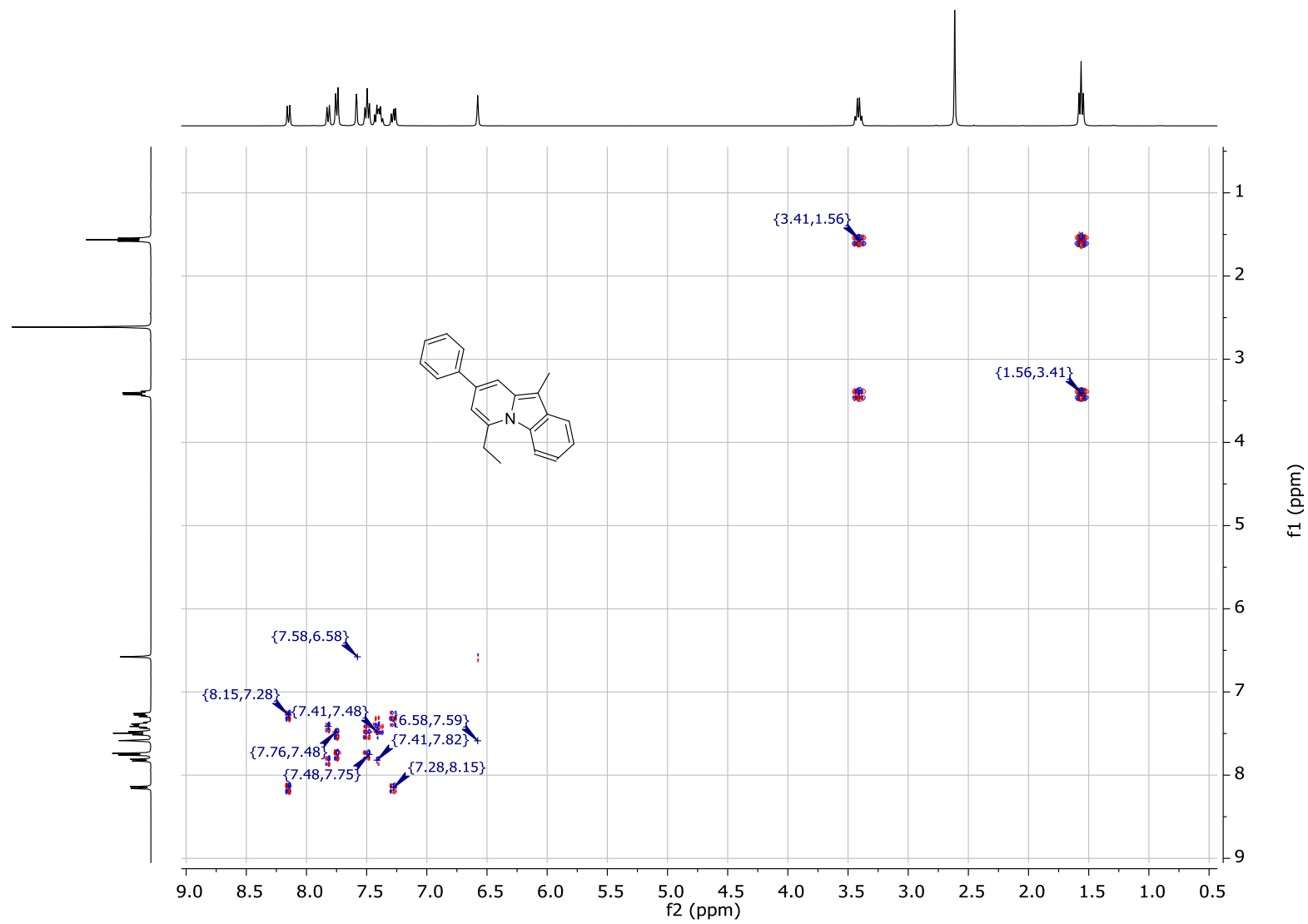
¹H NMR for 4k



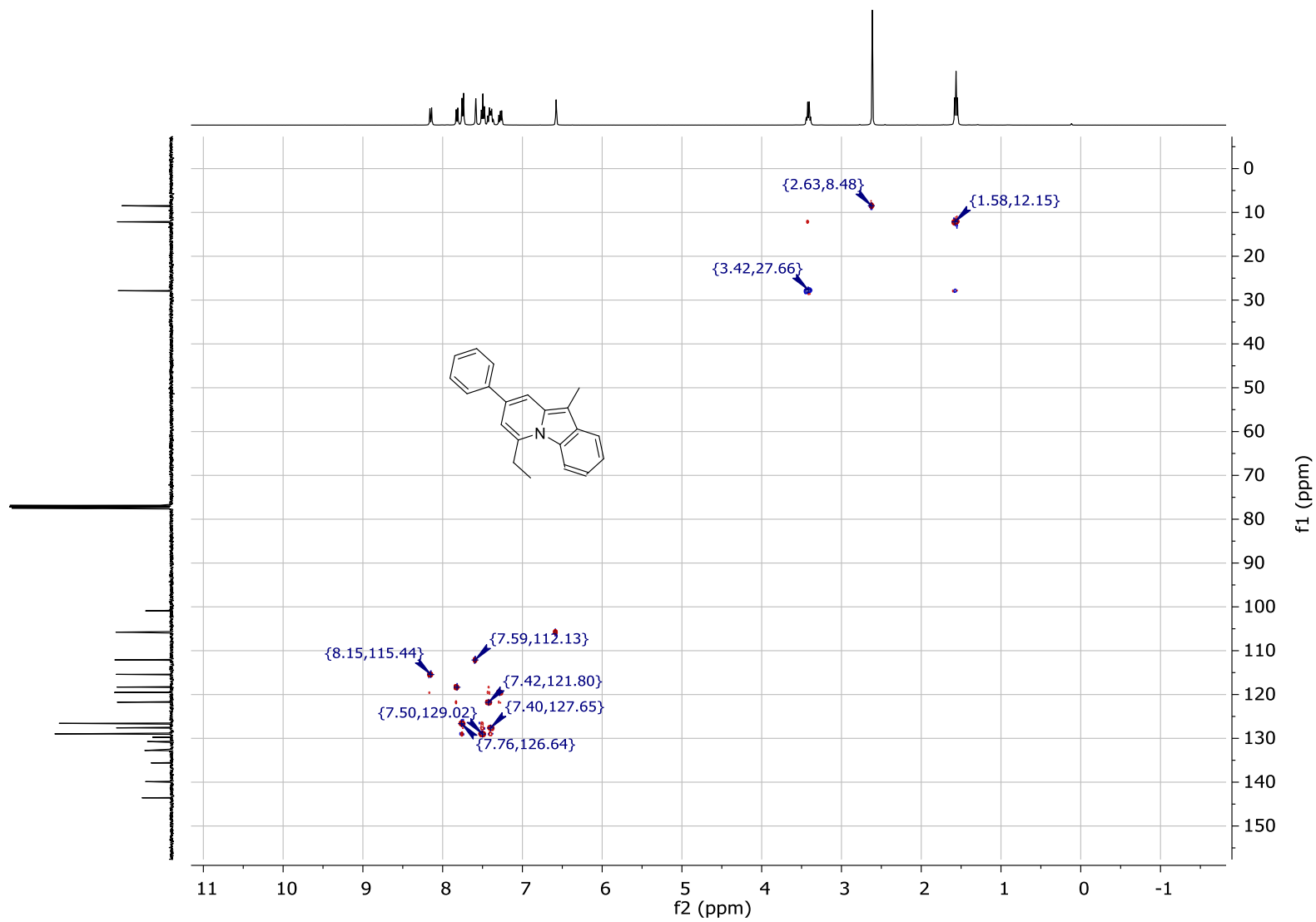
¹³C NMR for 4k



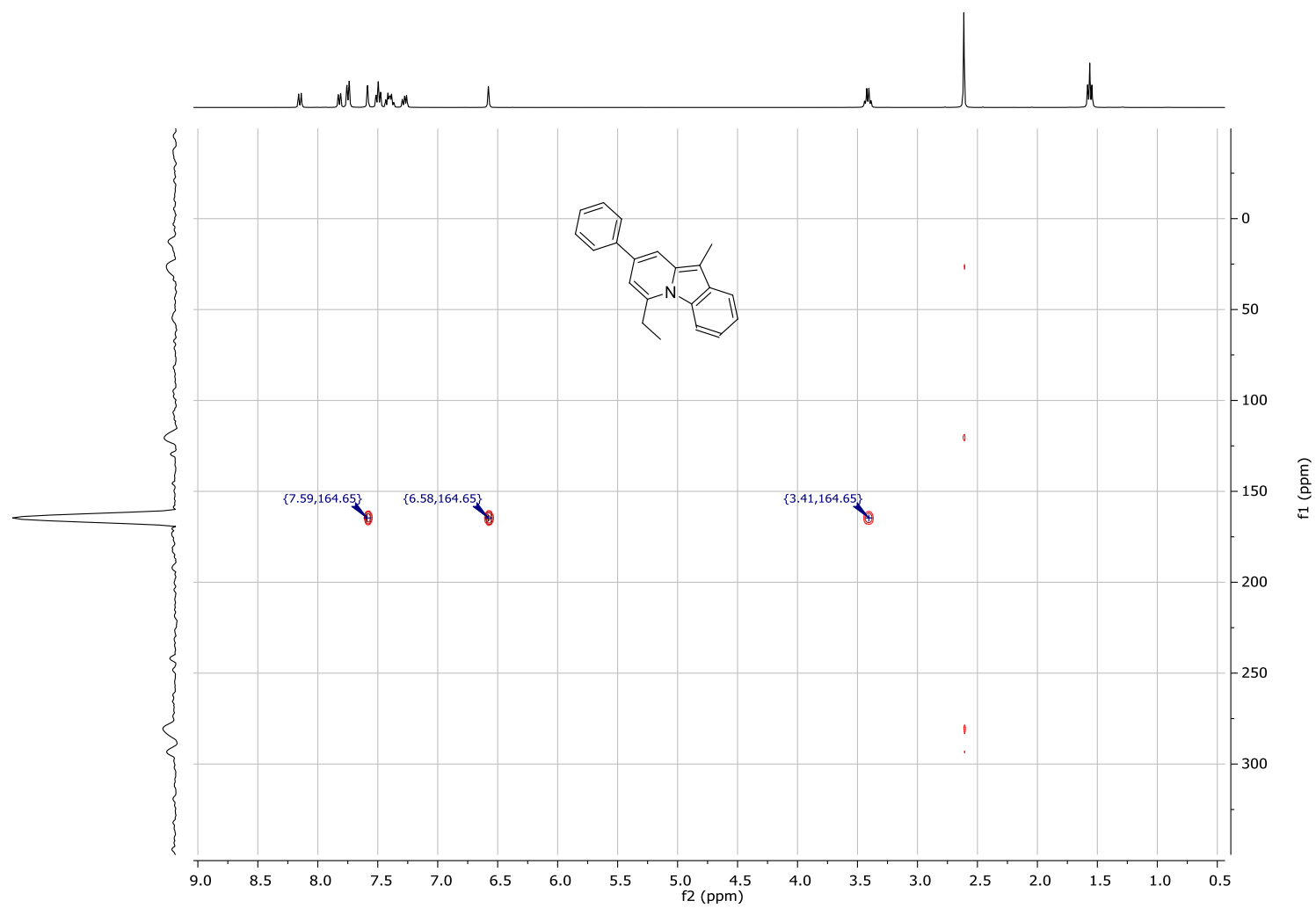
^1H - ^1H NOESY for 4k



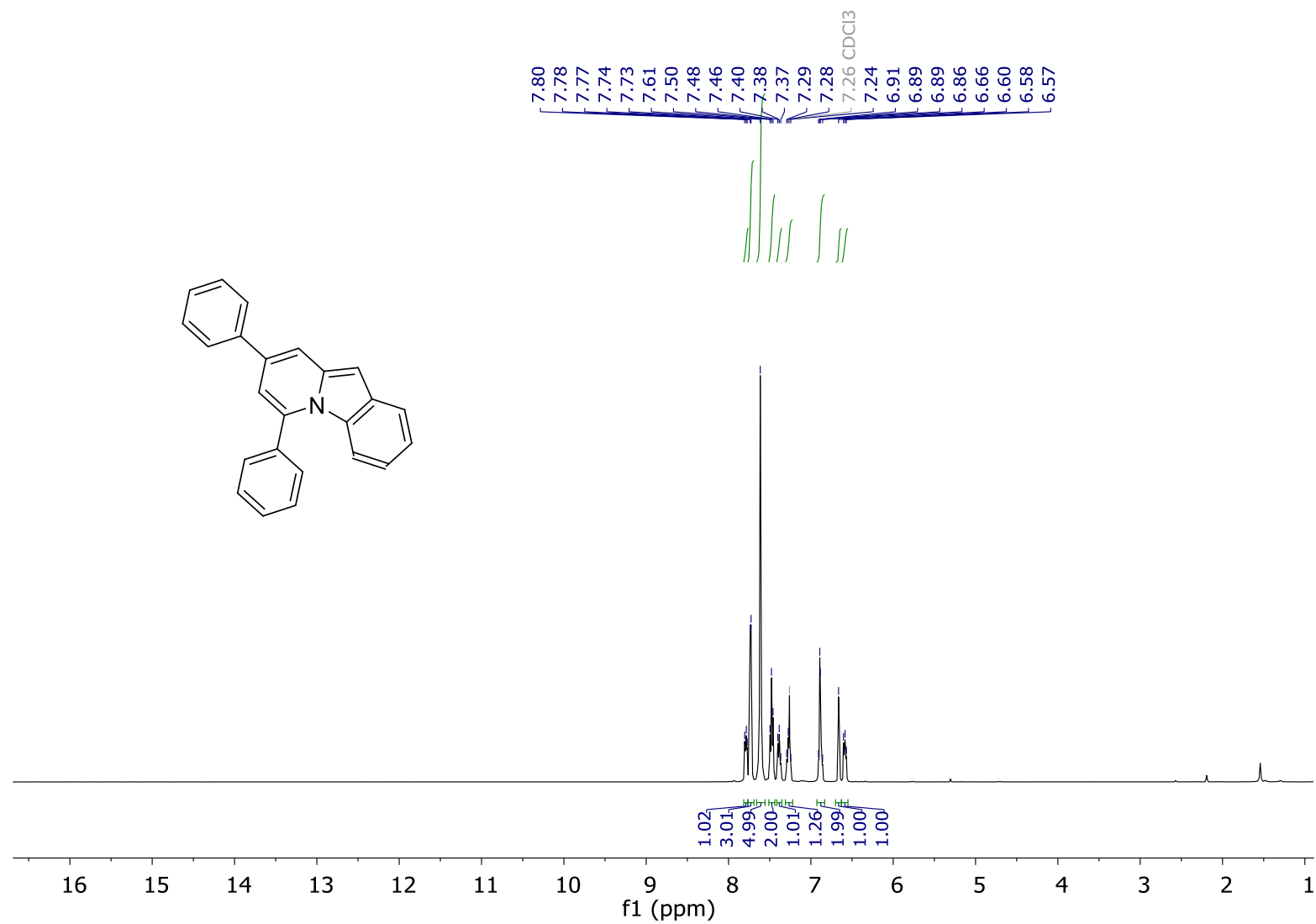
^1H - ^1H COSY for 4k



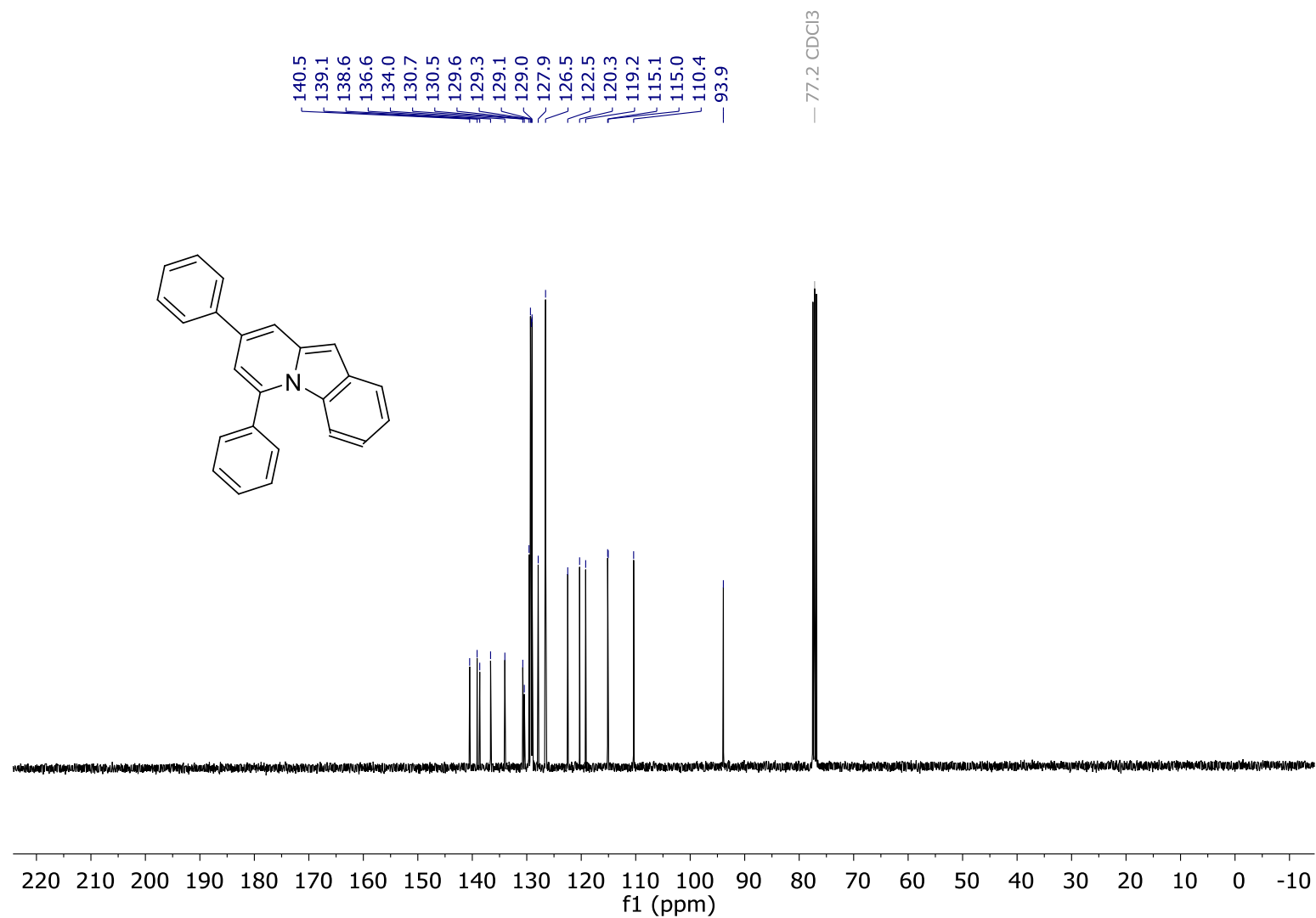
^1H - ^{13}C HSQC for 4k



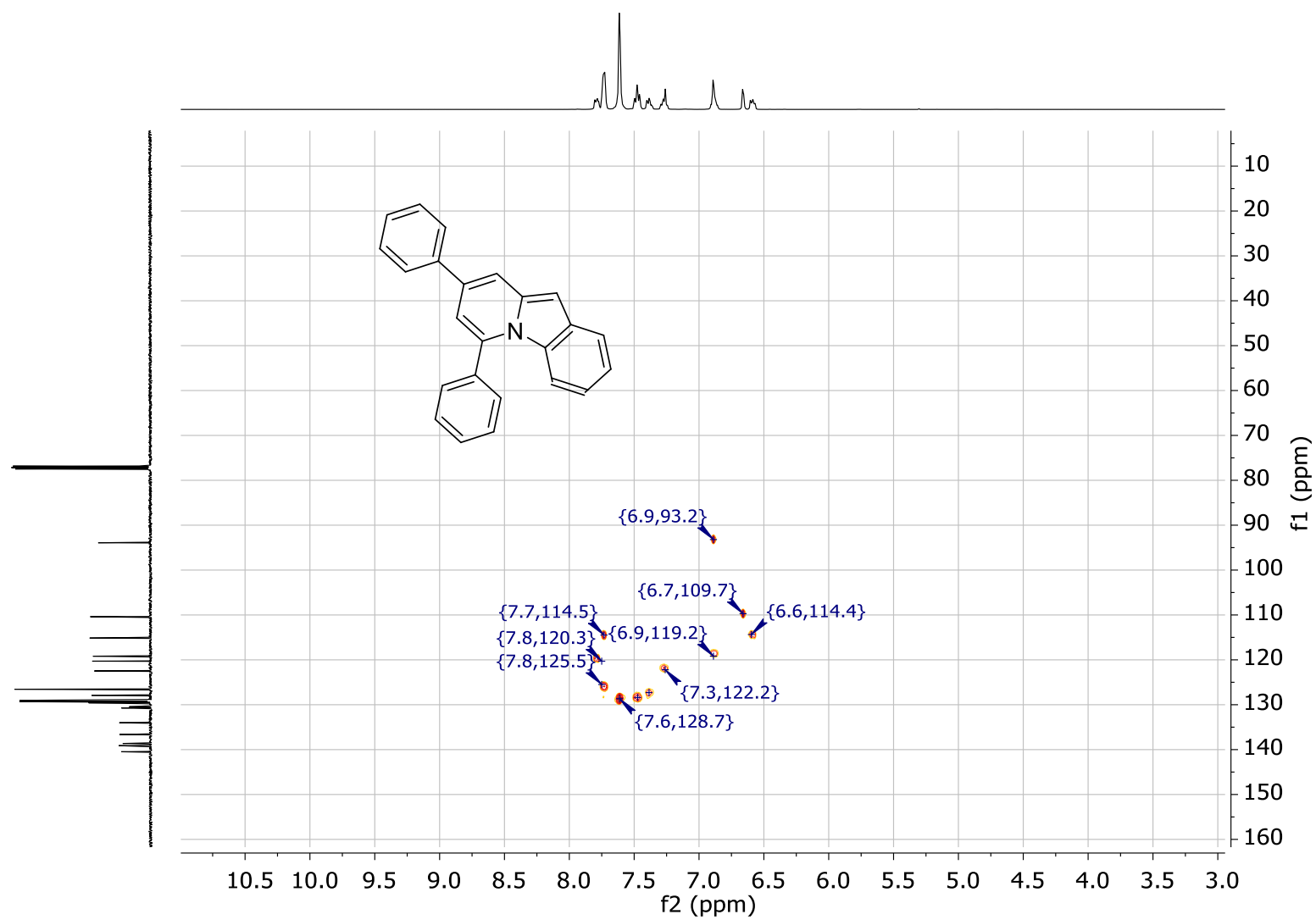
^1H - ^{15}N HMBC for 4k



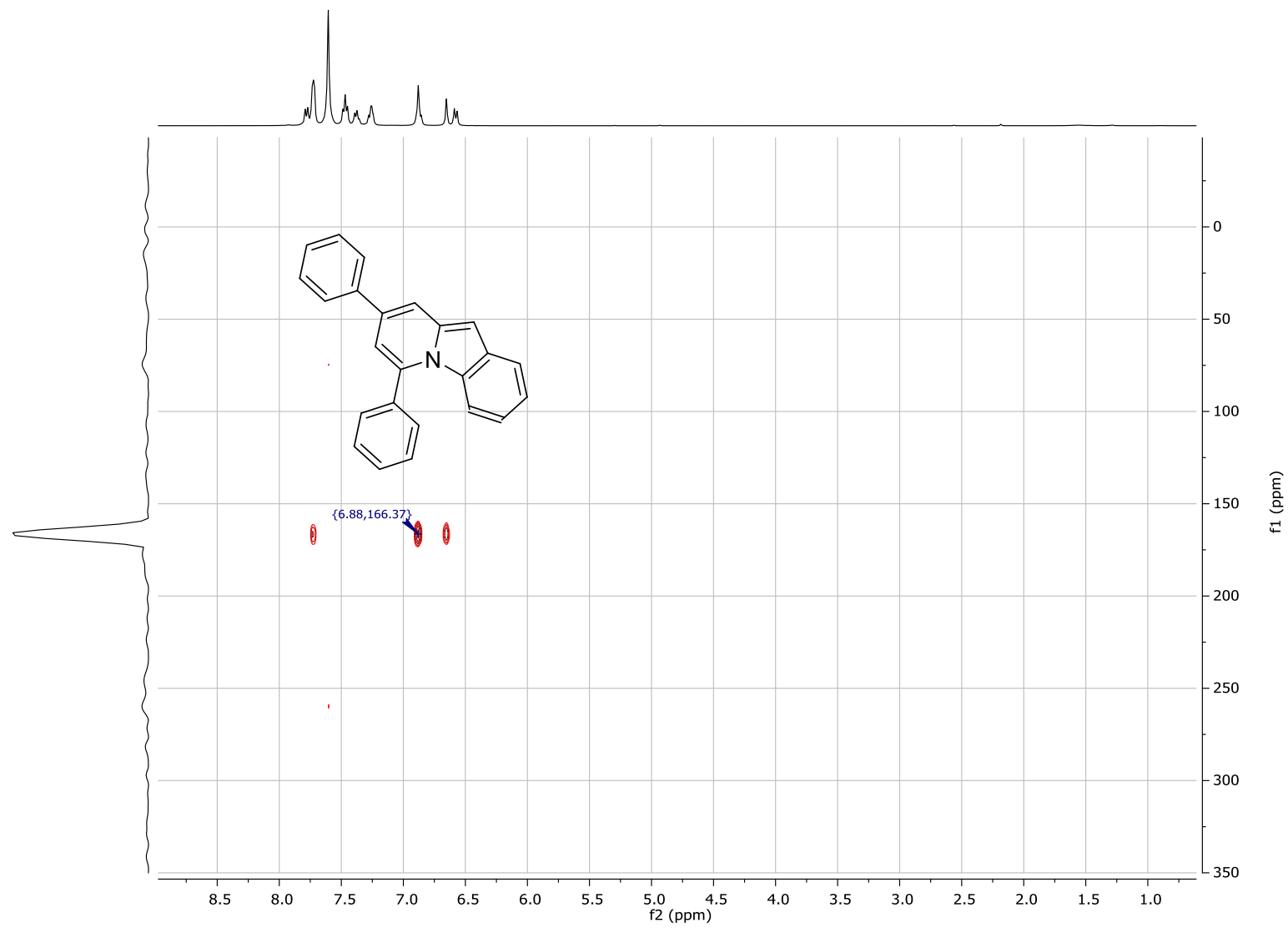
¹H NMR for 4l



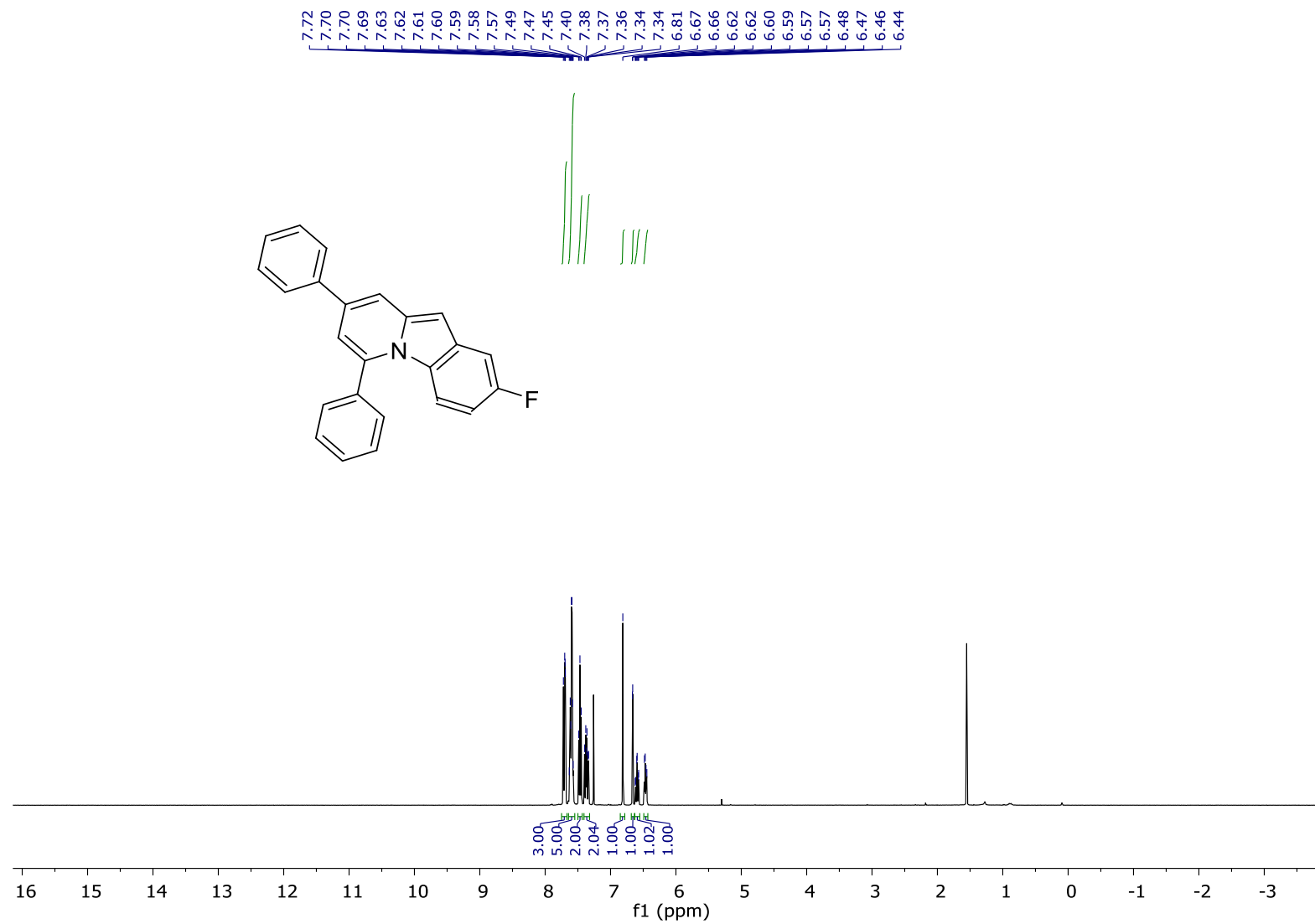
¹³C NMR for 4l



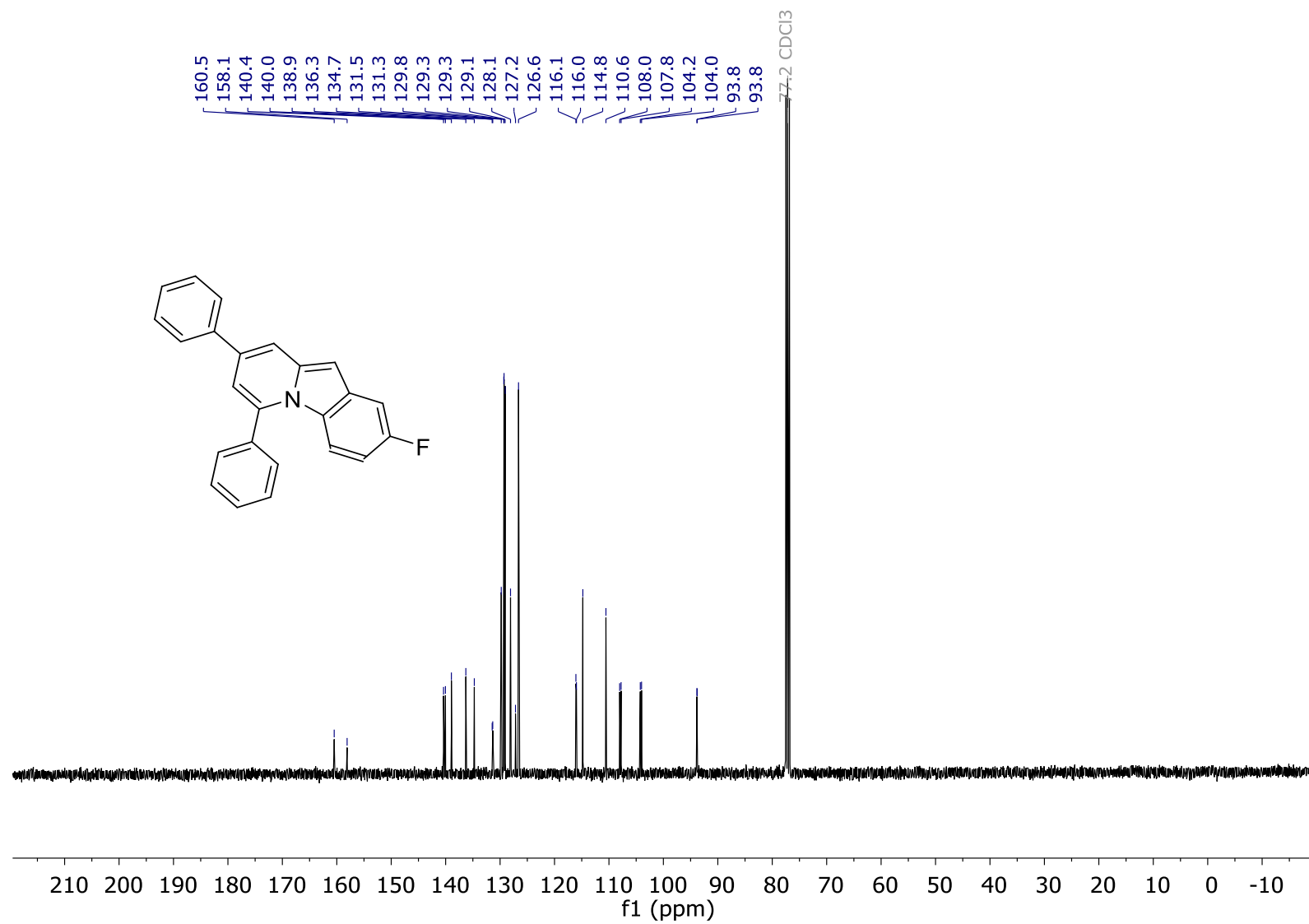
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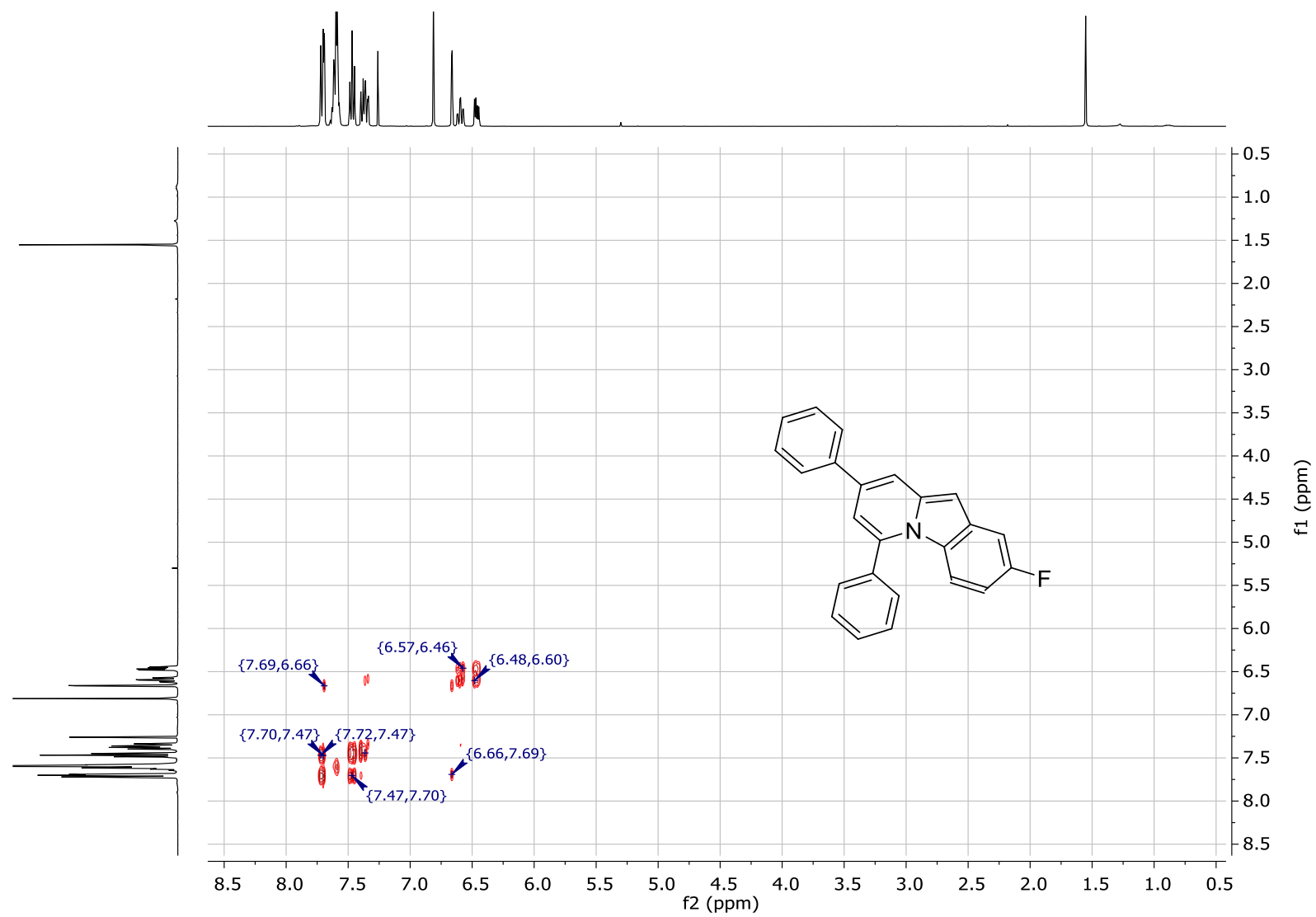
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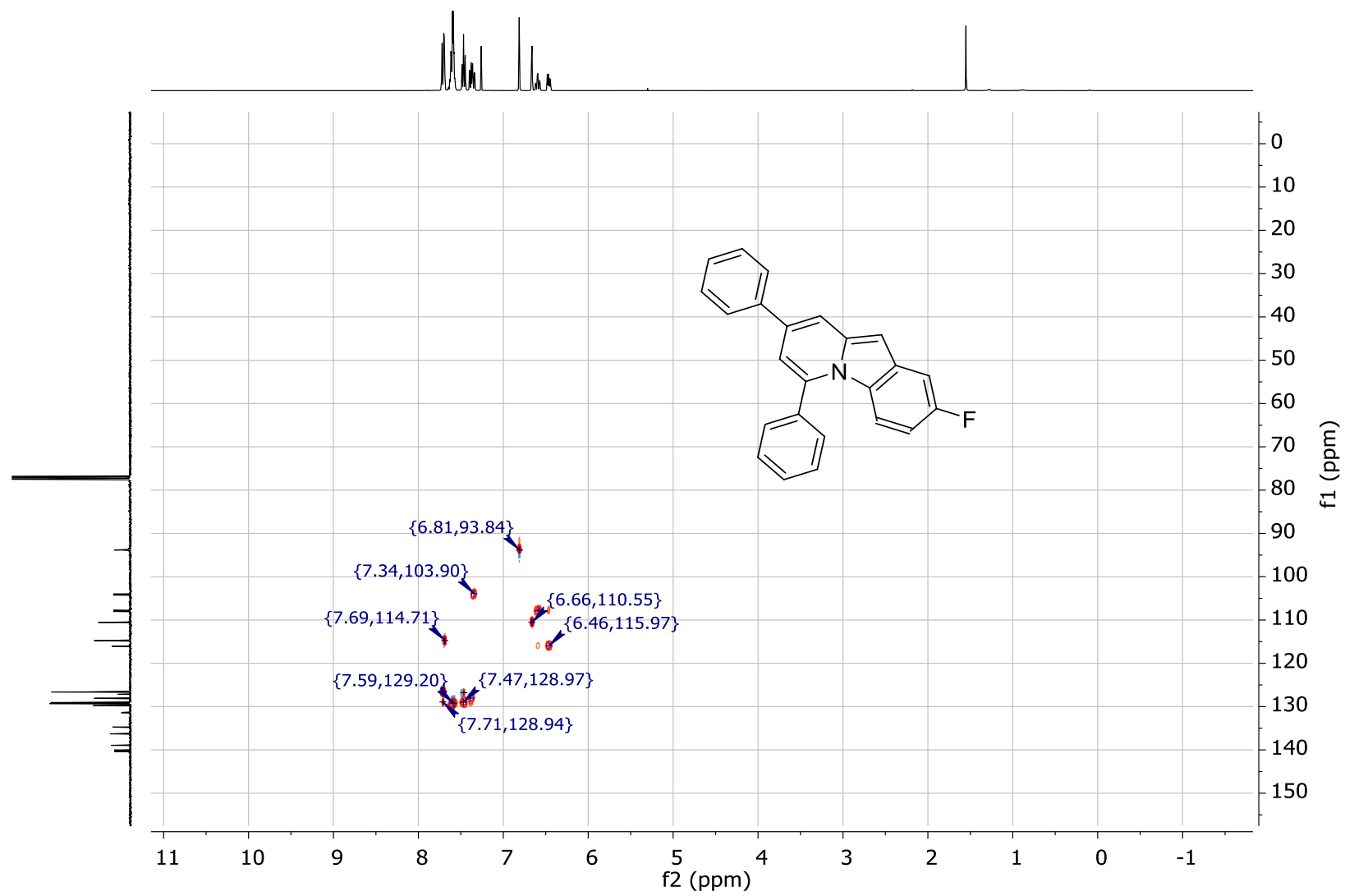


¹H NMR for 4m

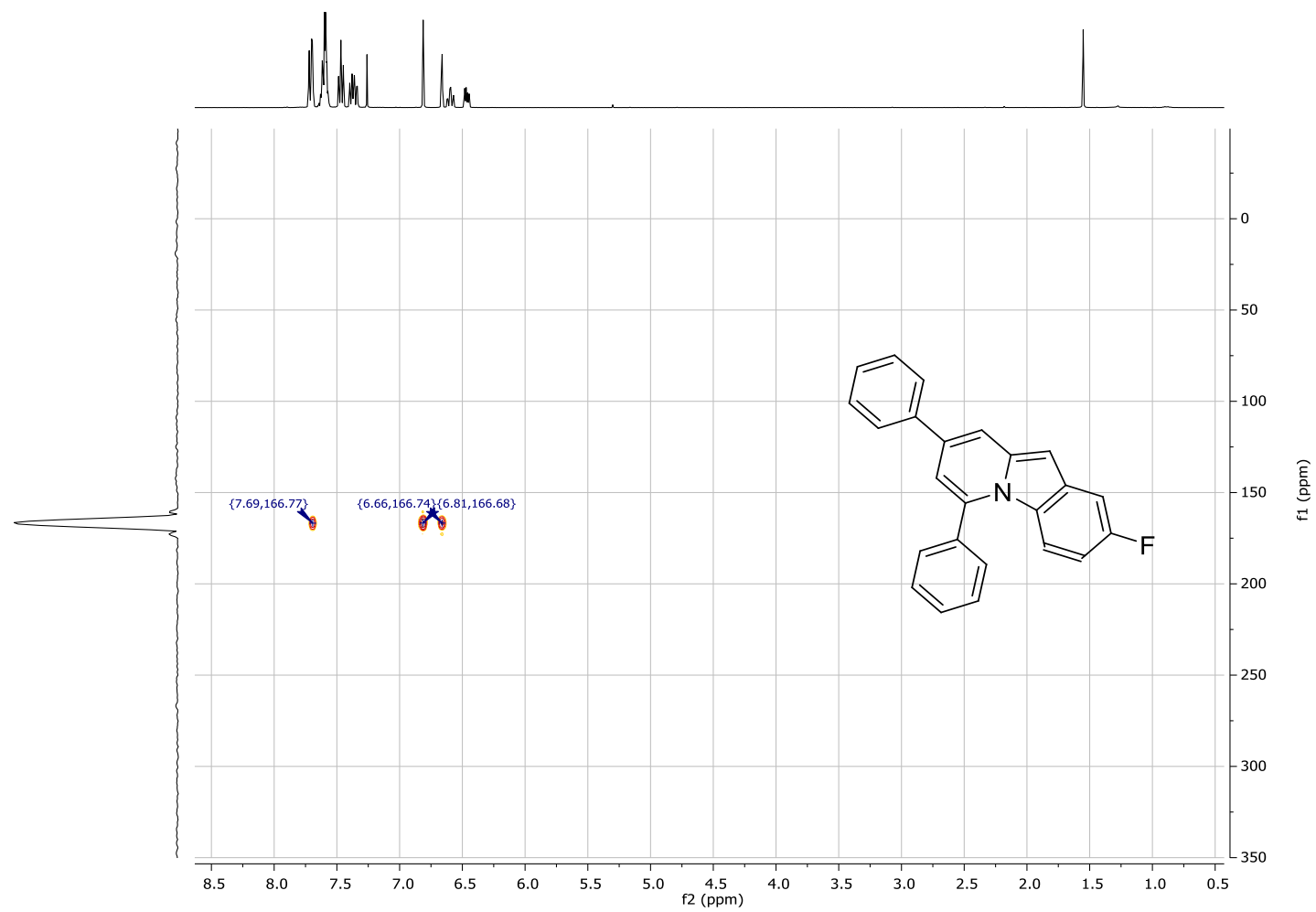


¹³C NMR for 4m

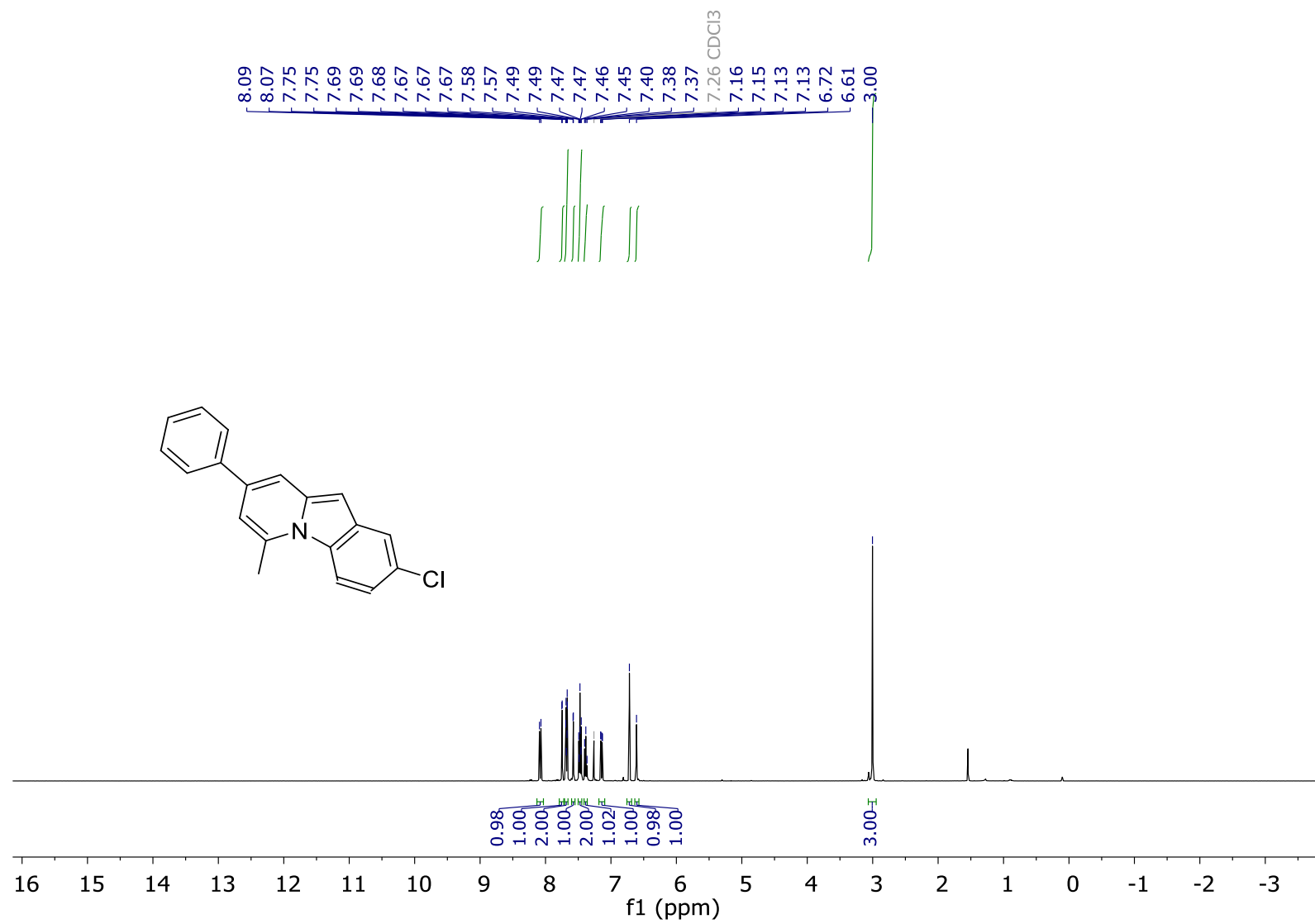




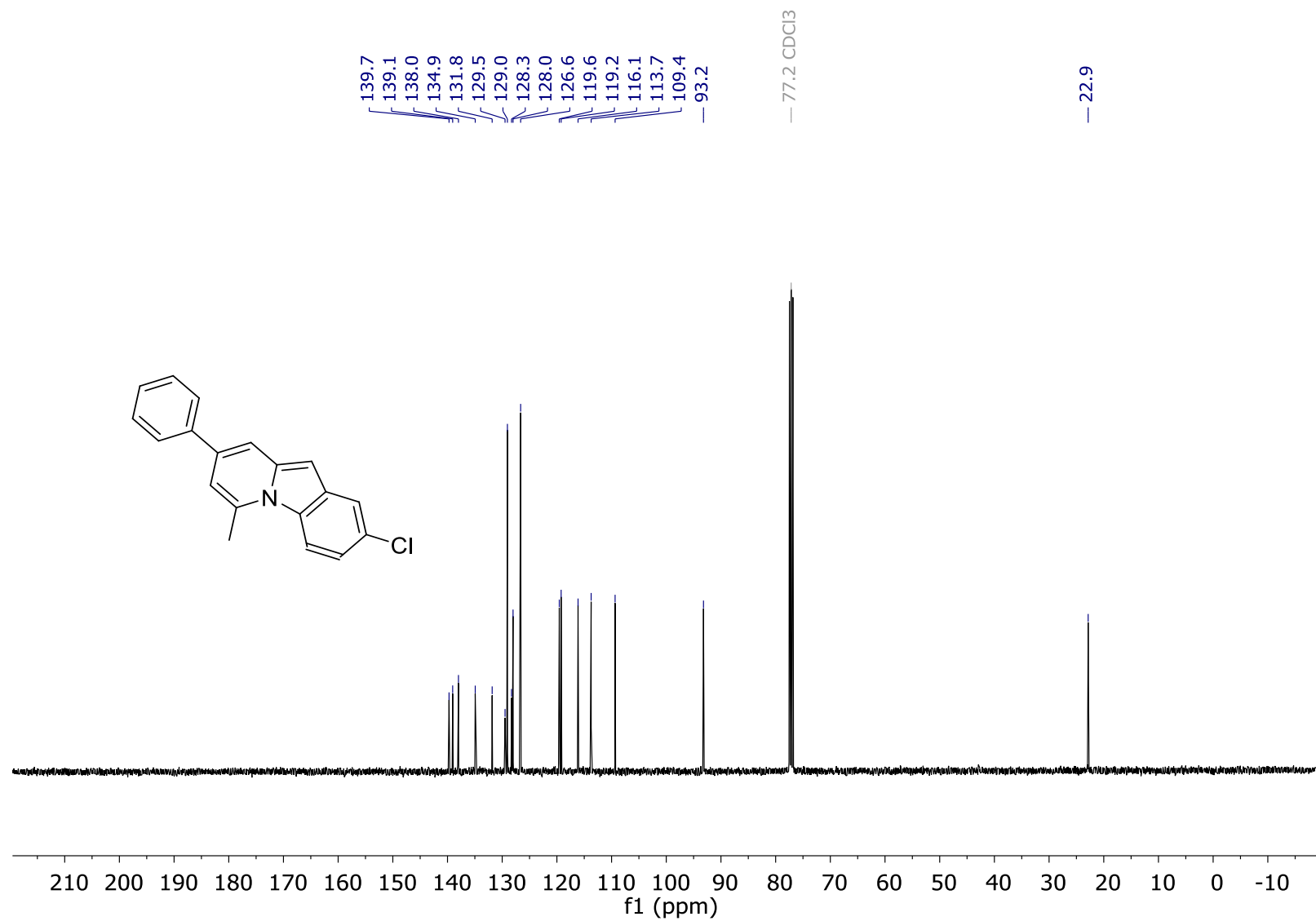
^1H - ^{13}C HSQC for 4m



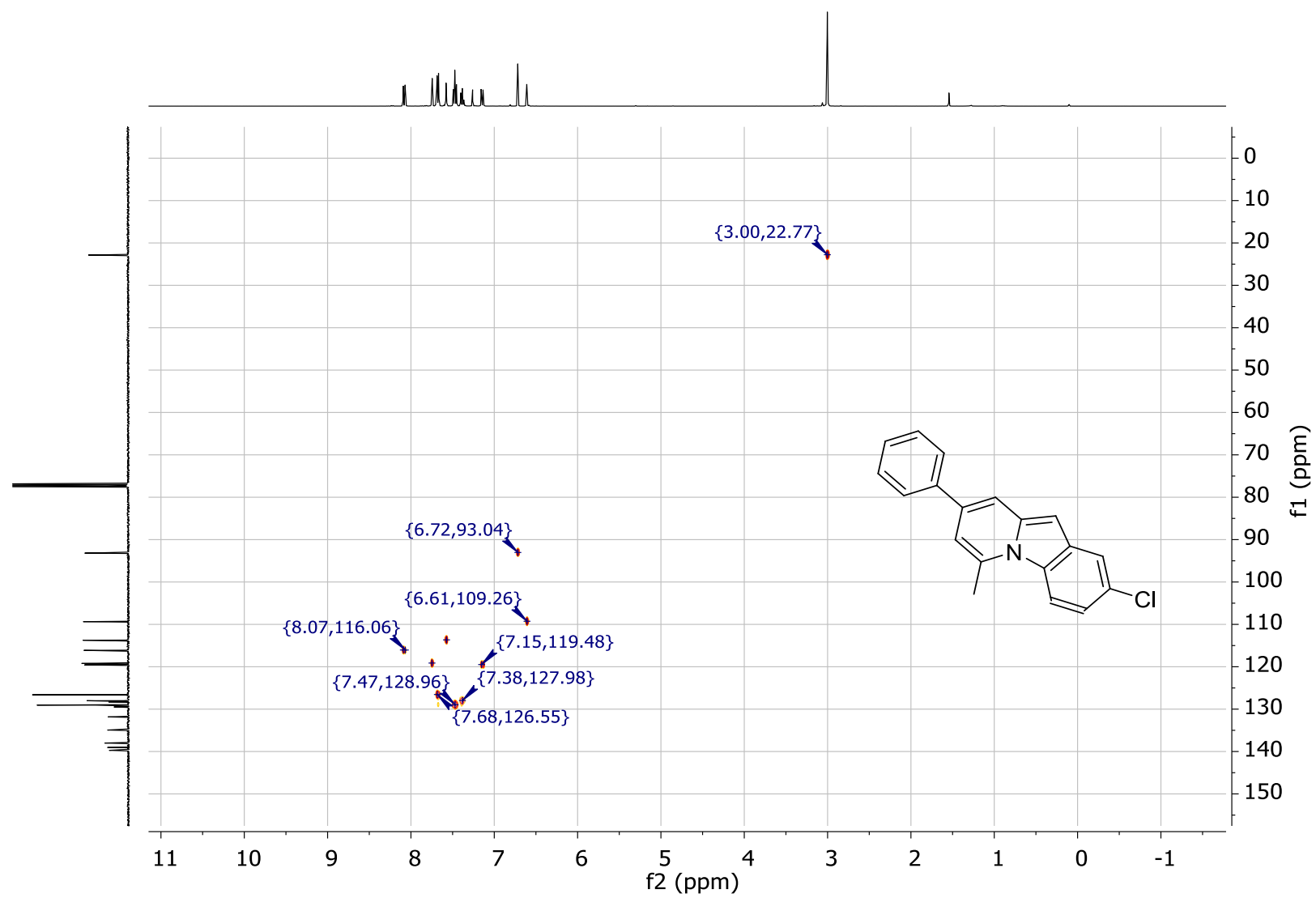
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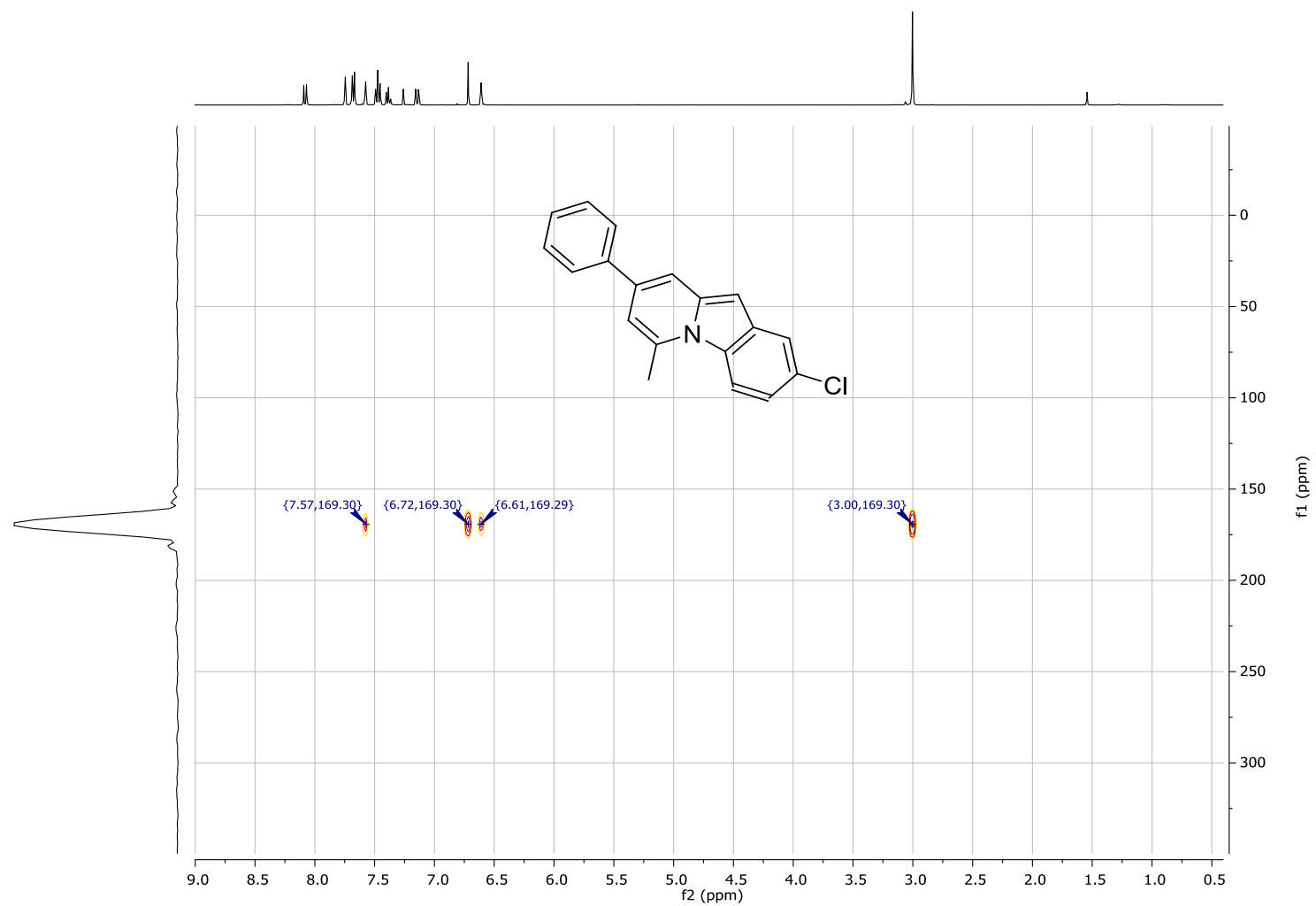
¹H NMR for 4n



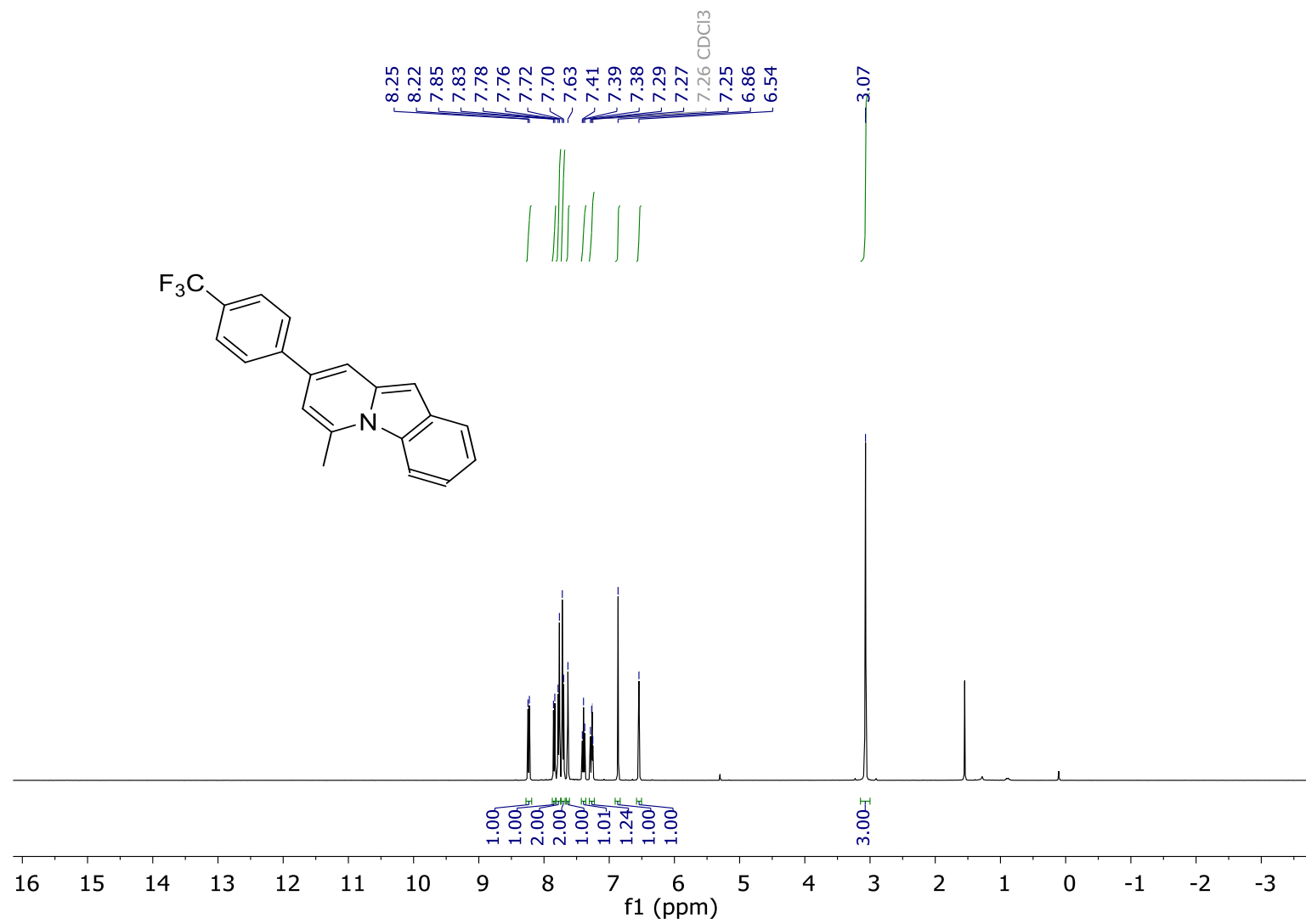
¹³C NMR for 4n



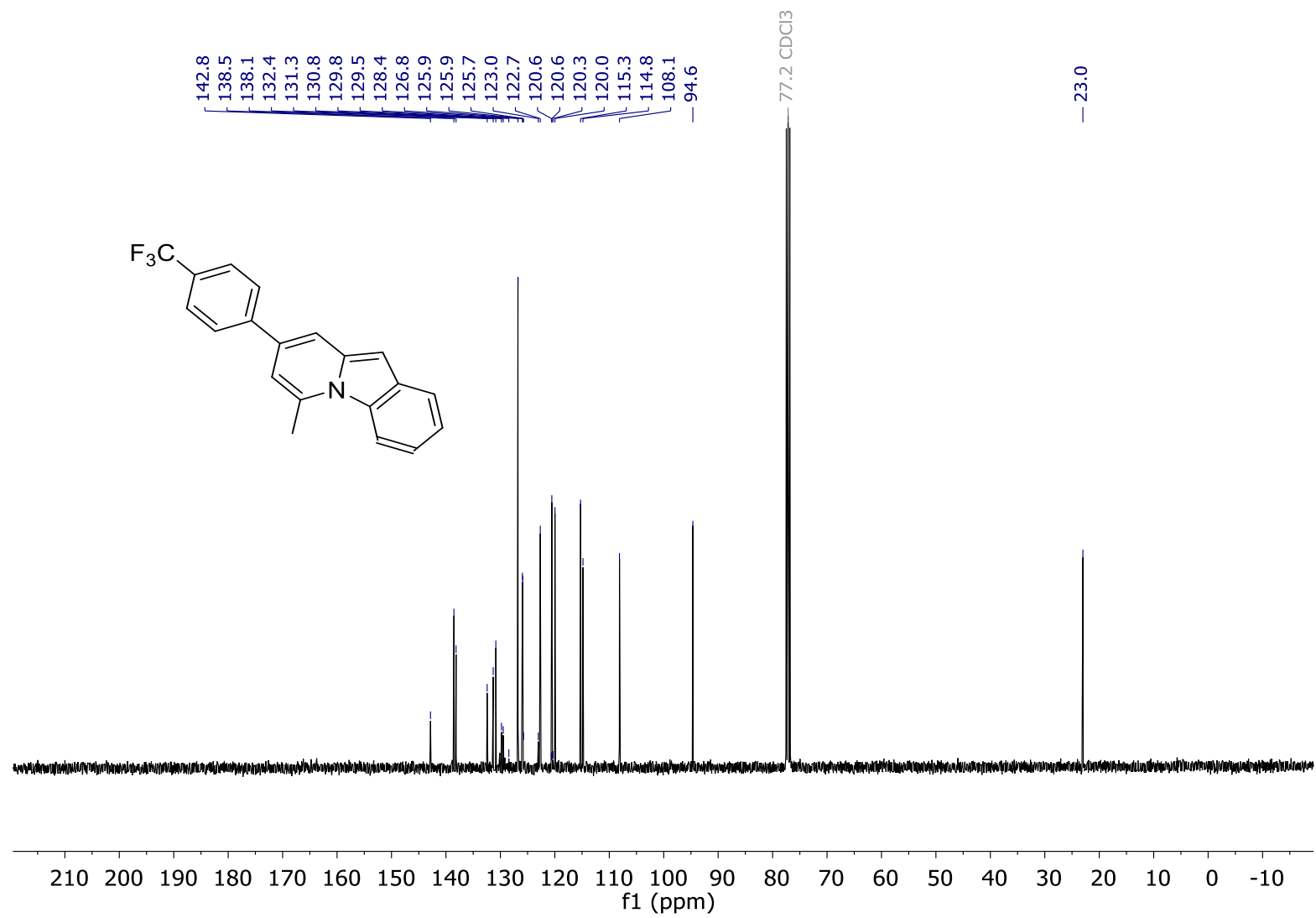
¹H-¹³C HSQC for 4n



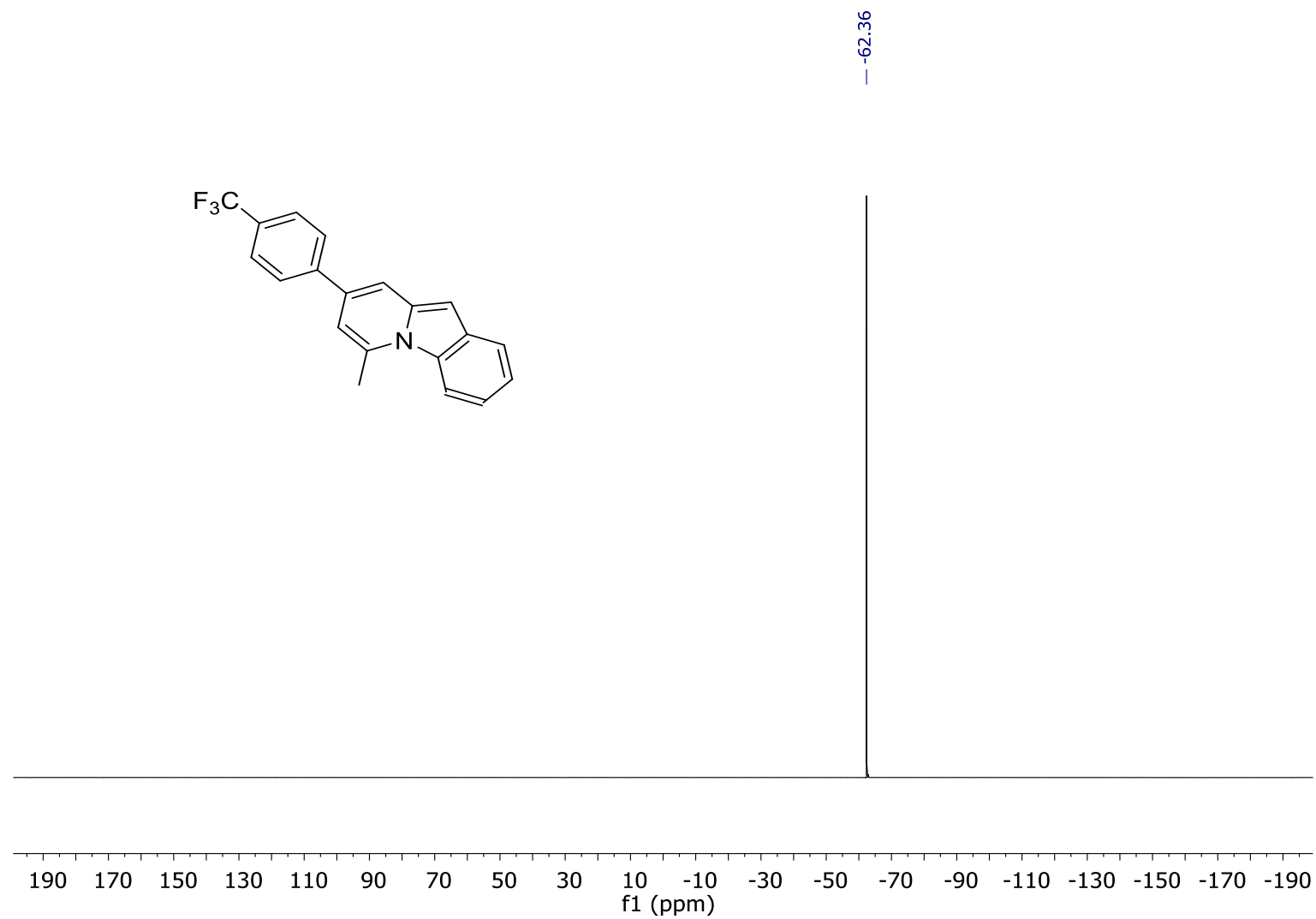
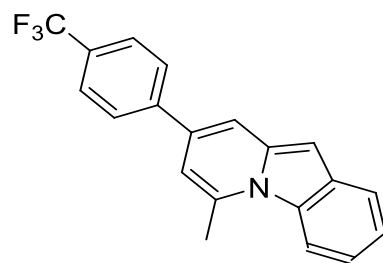
^1H - ^{15}N HMBC for 4n



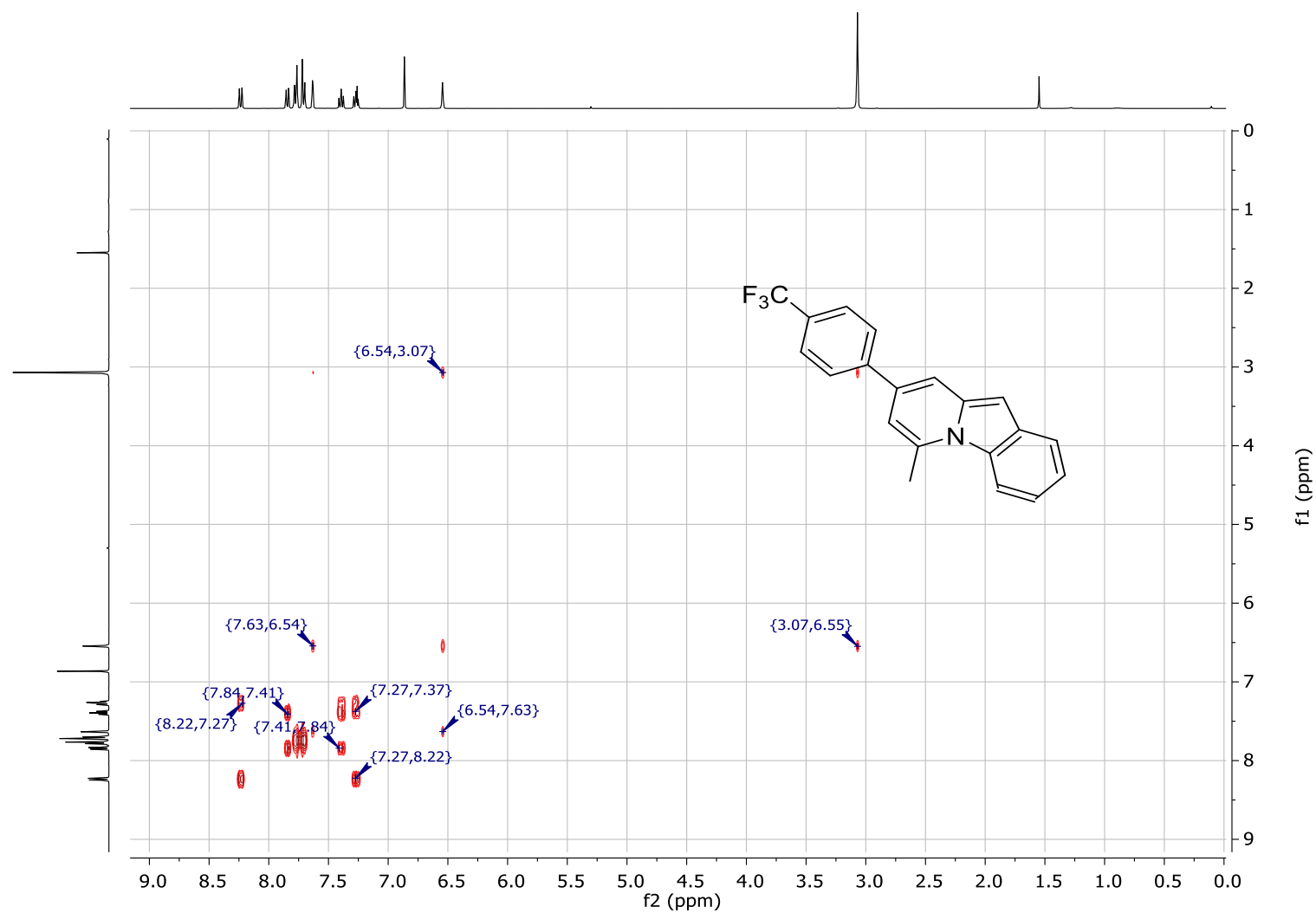
¹H NMR for 4o



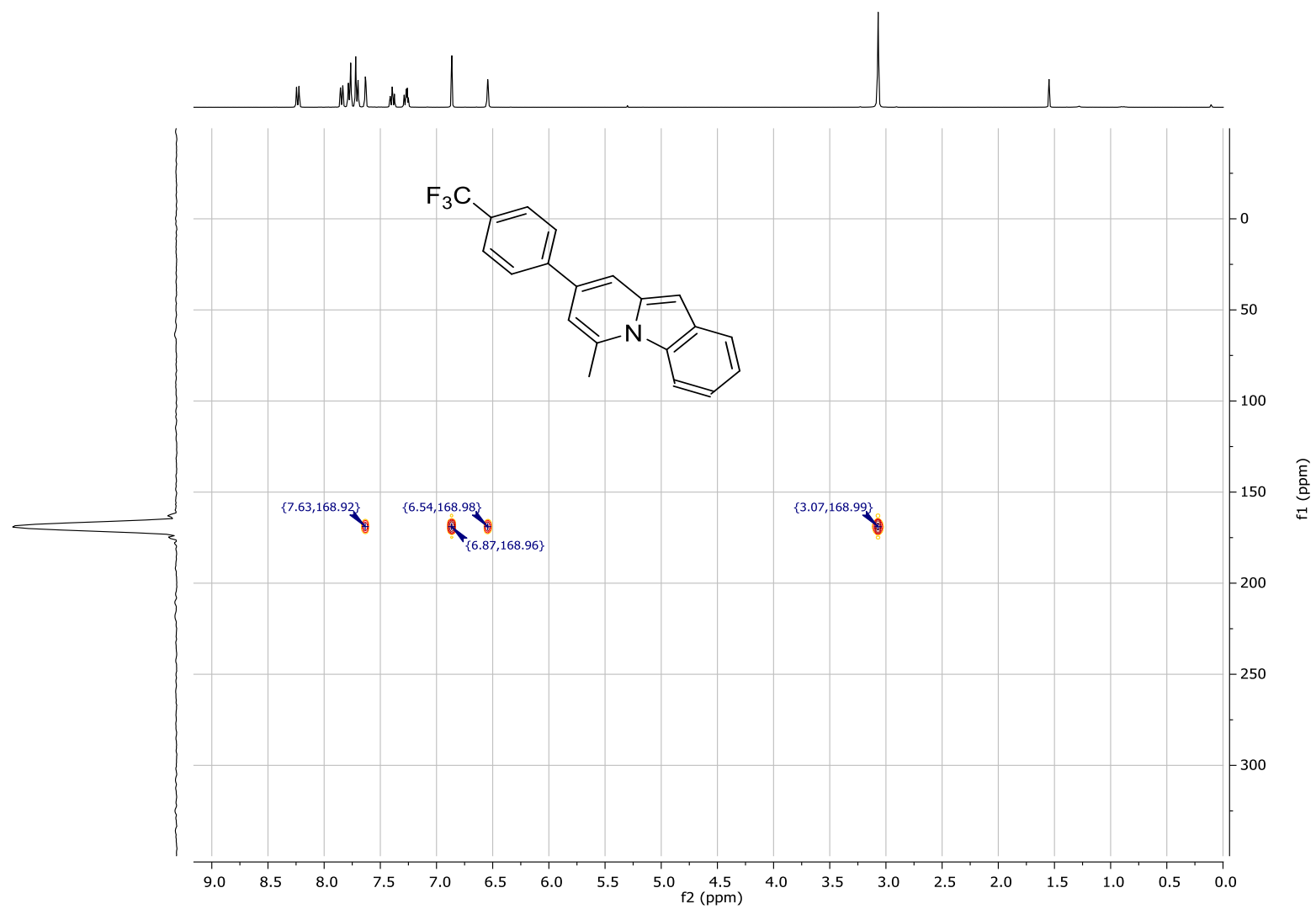
¹³C NMR for 4o



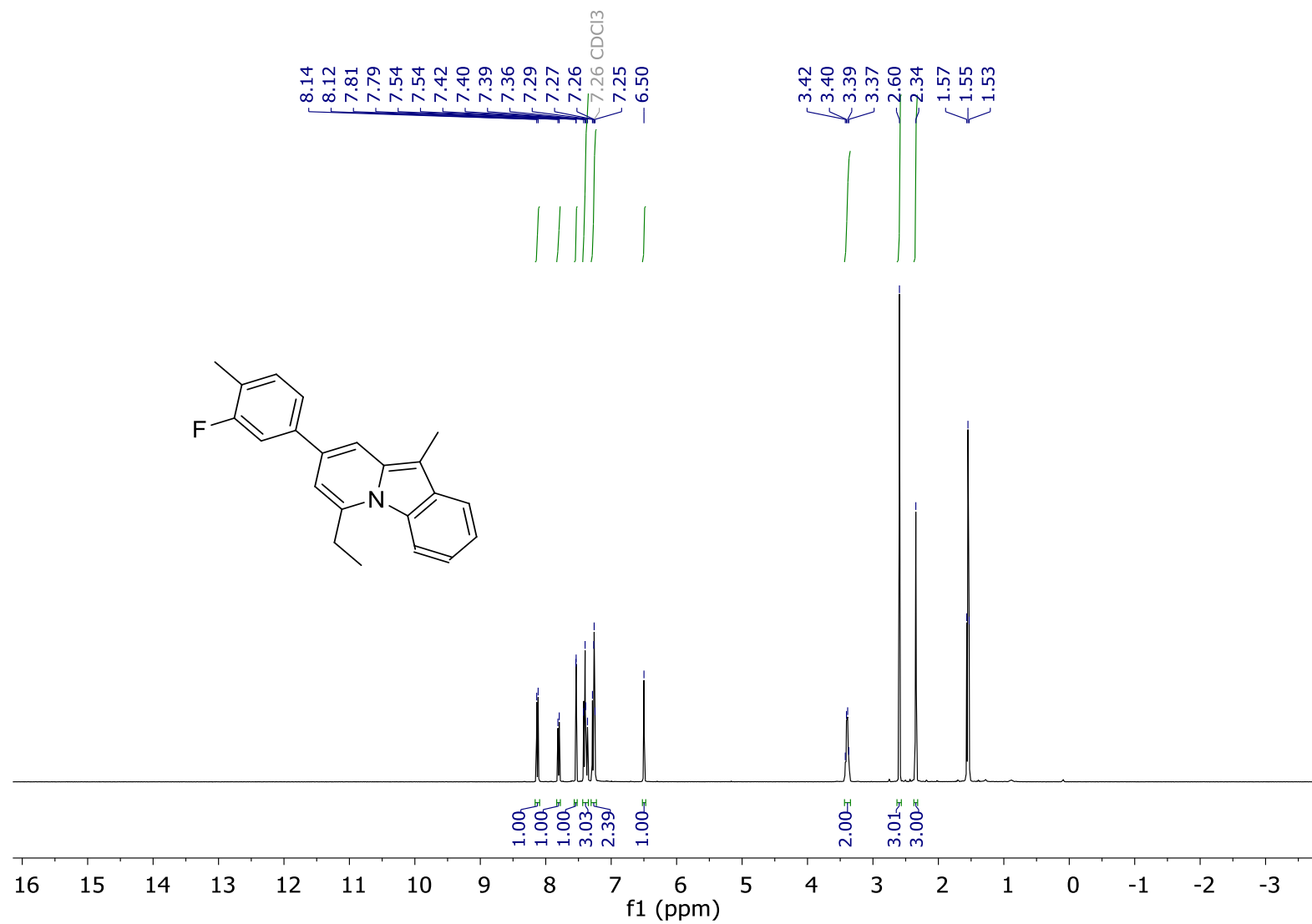
¹⁹F NMR for 4o



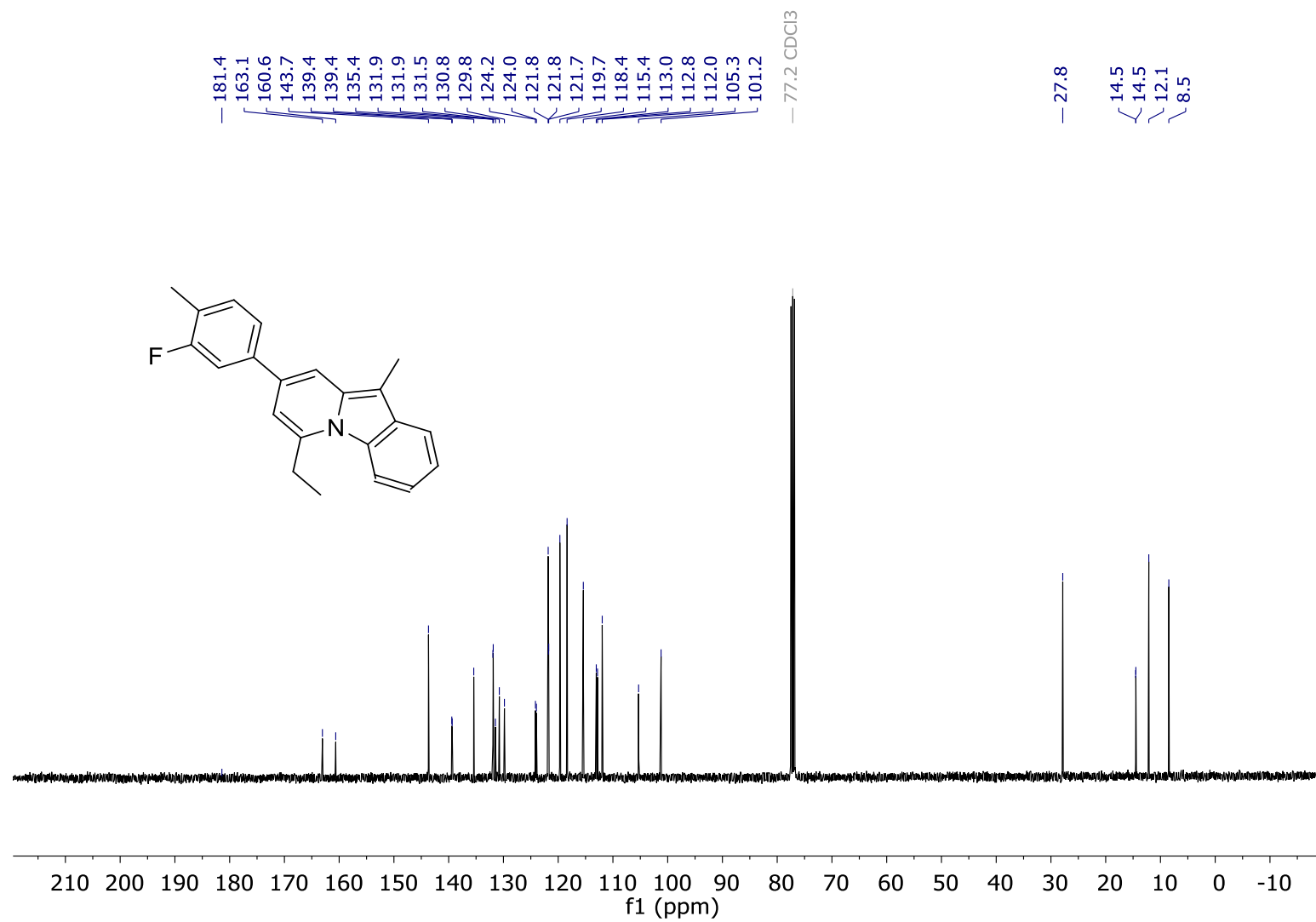
^1H - ^1H COSY for 4o



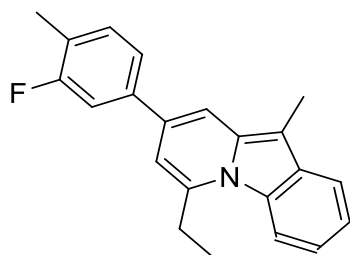
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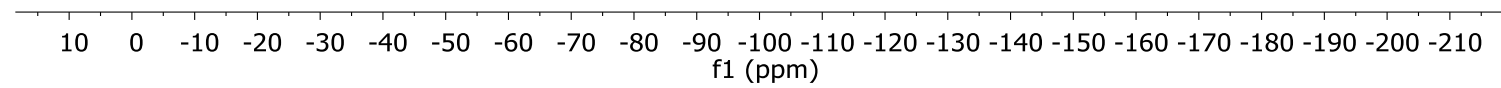
¹H NMR for 4p



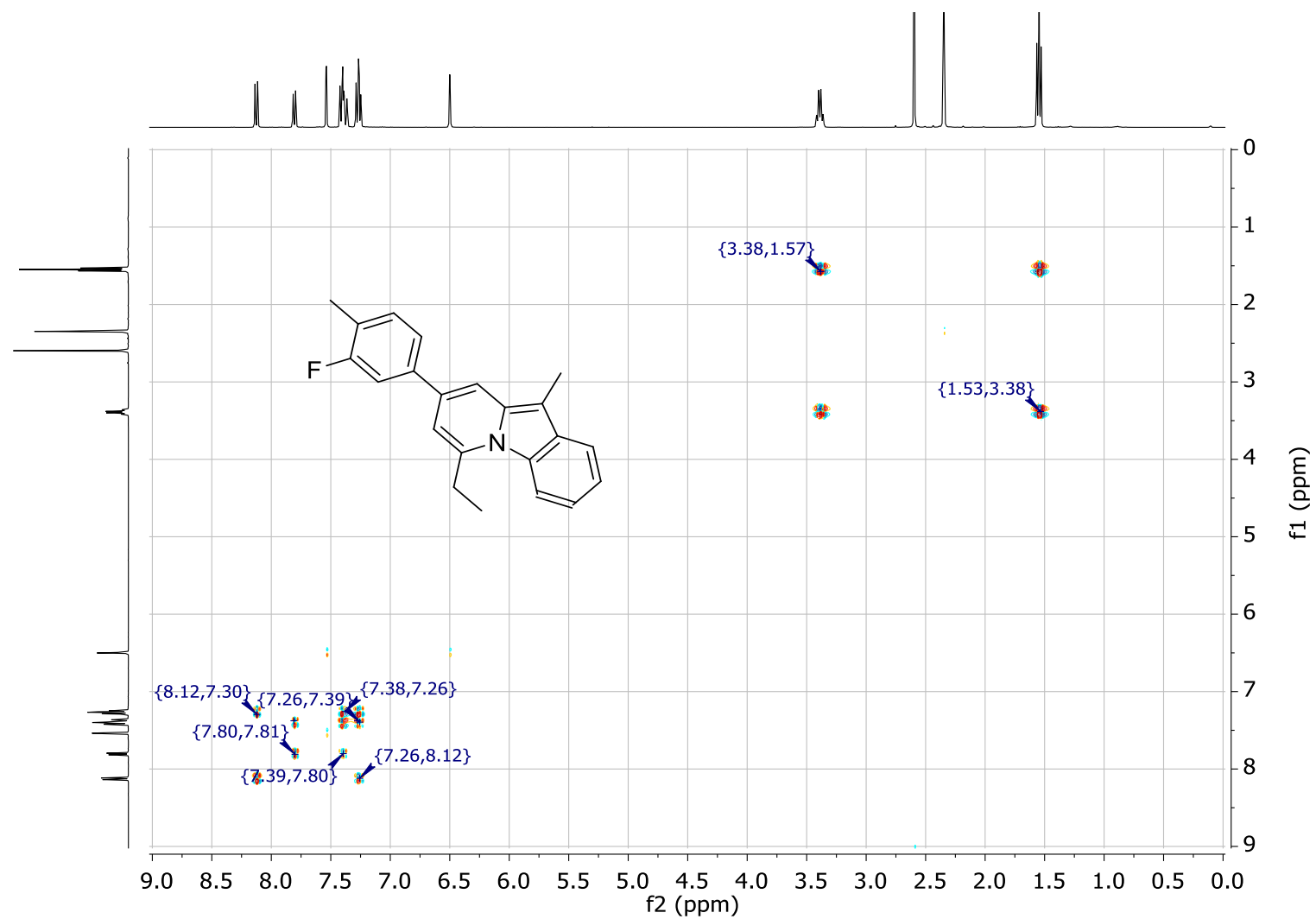
¹³C NMR for 4p



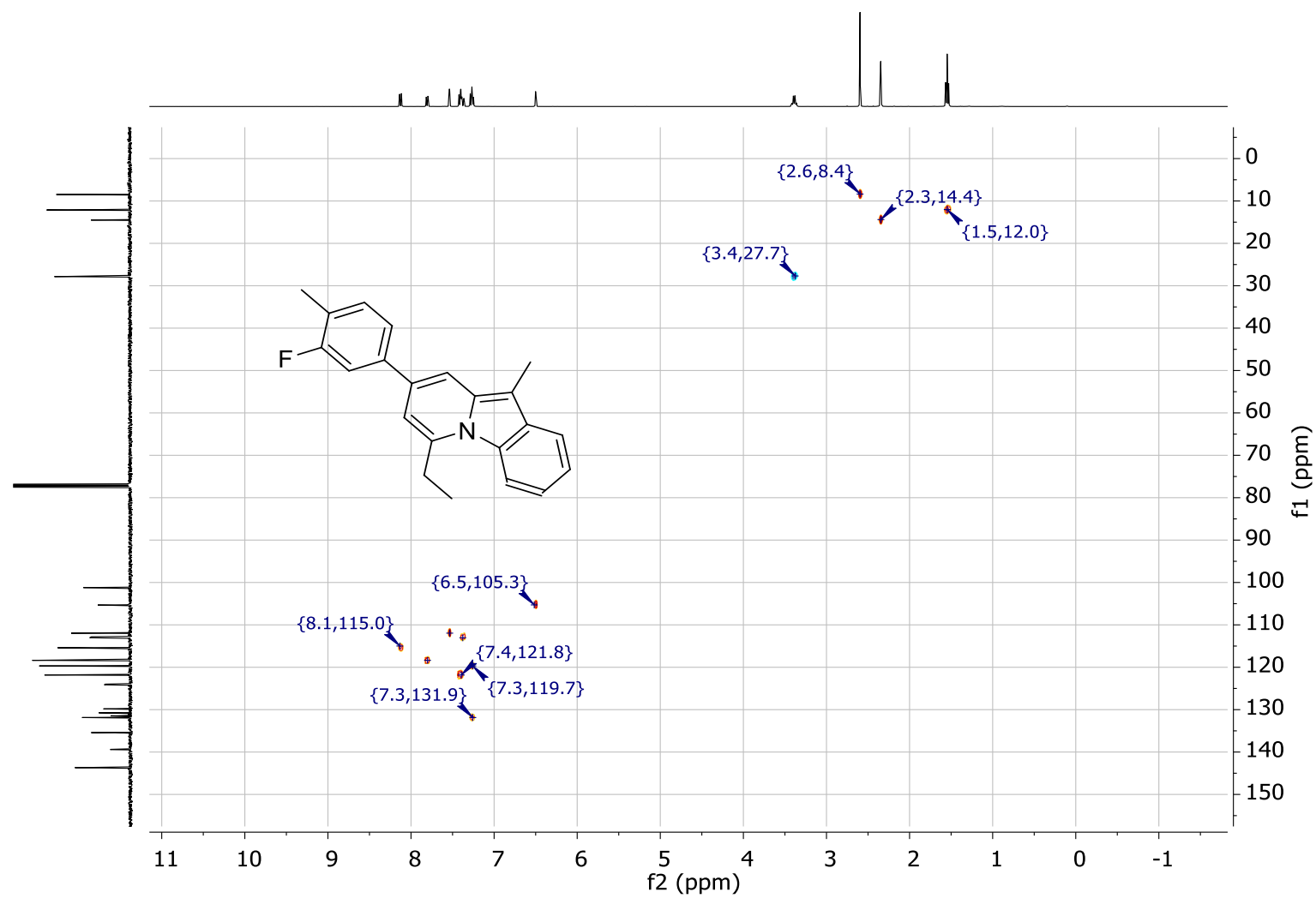
-117.25



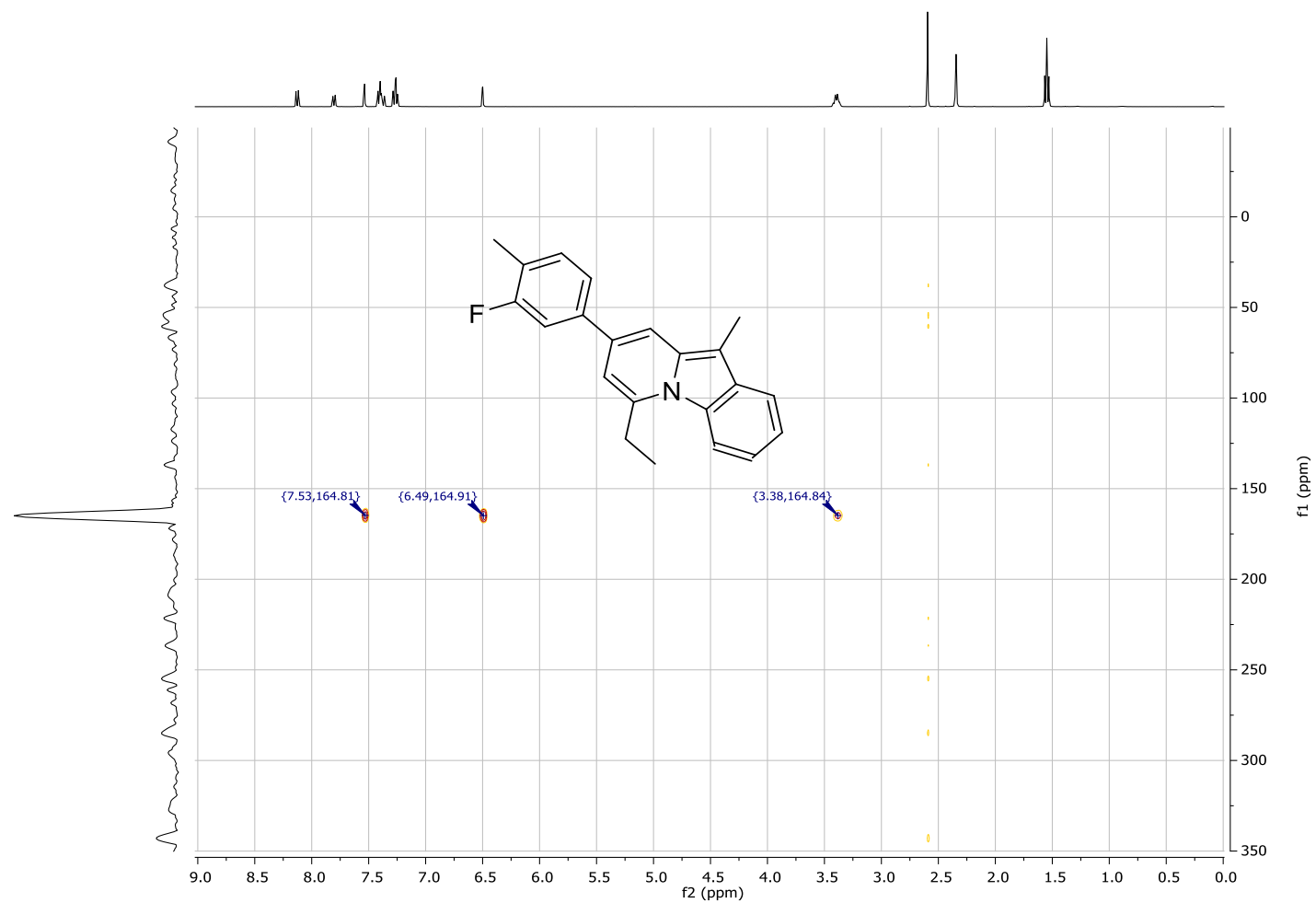
^{19}F NMR for 4p



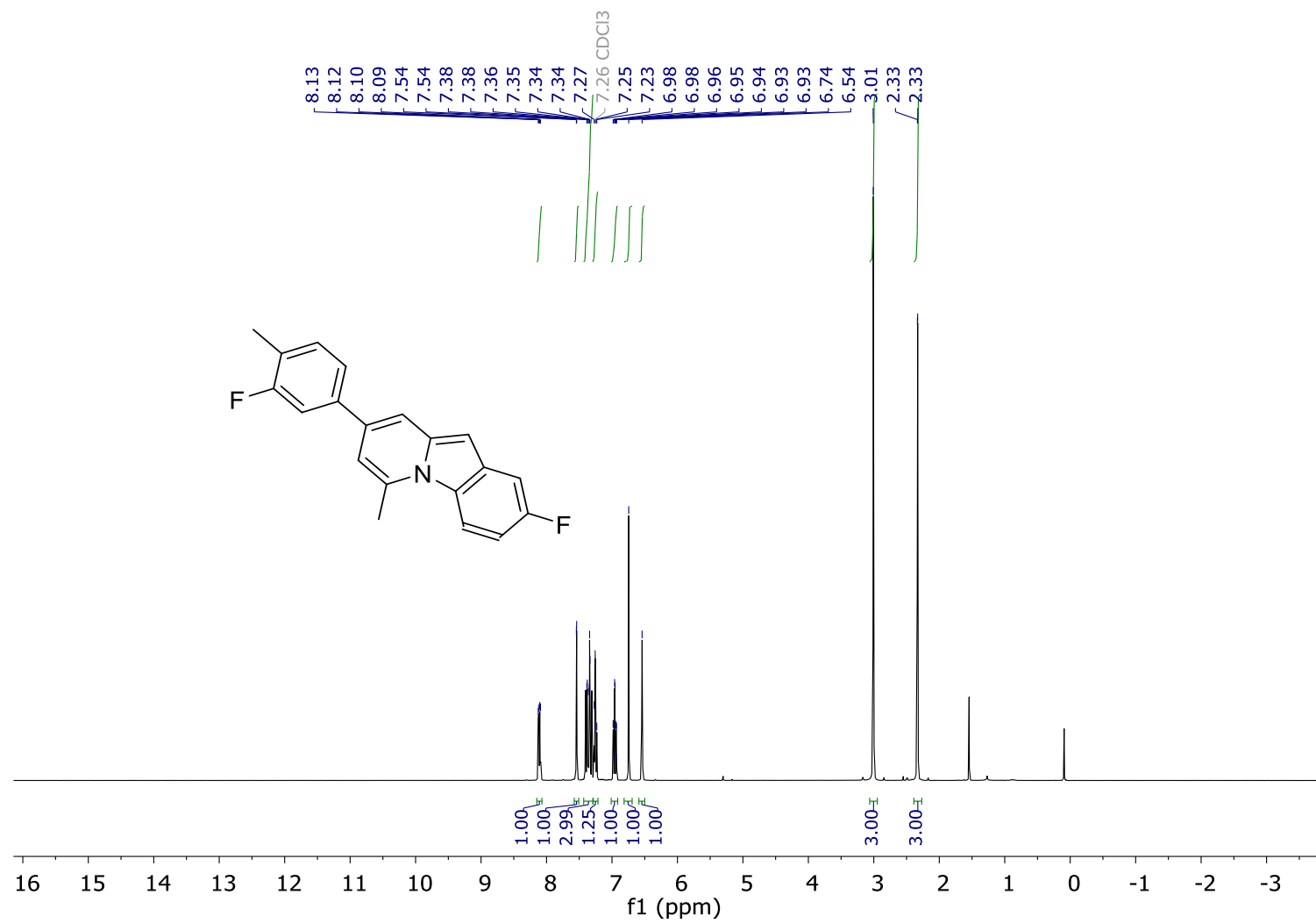
^1H - ^1H COSY for 4p



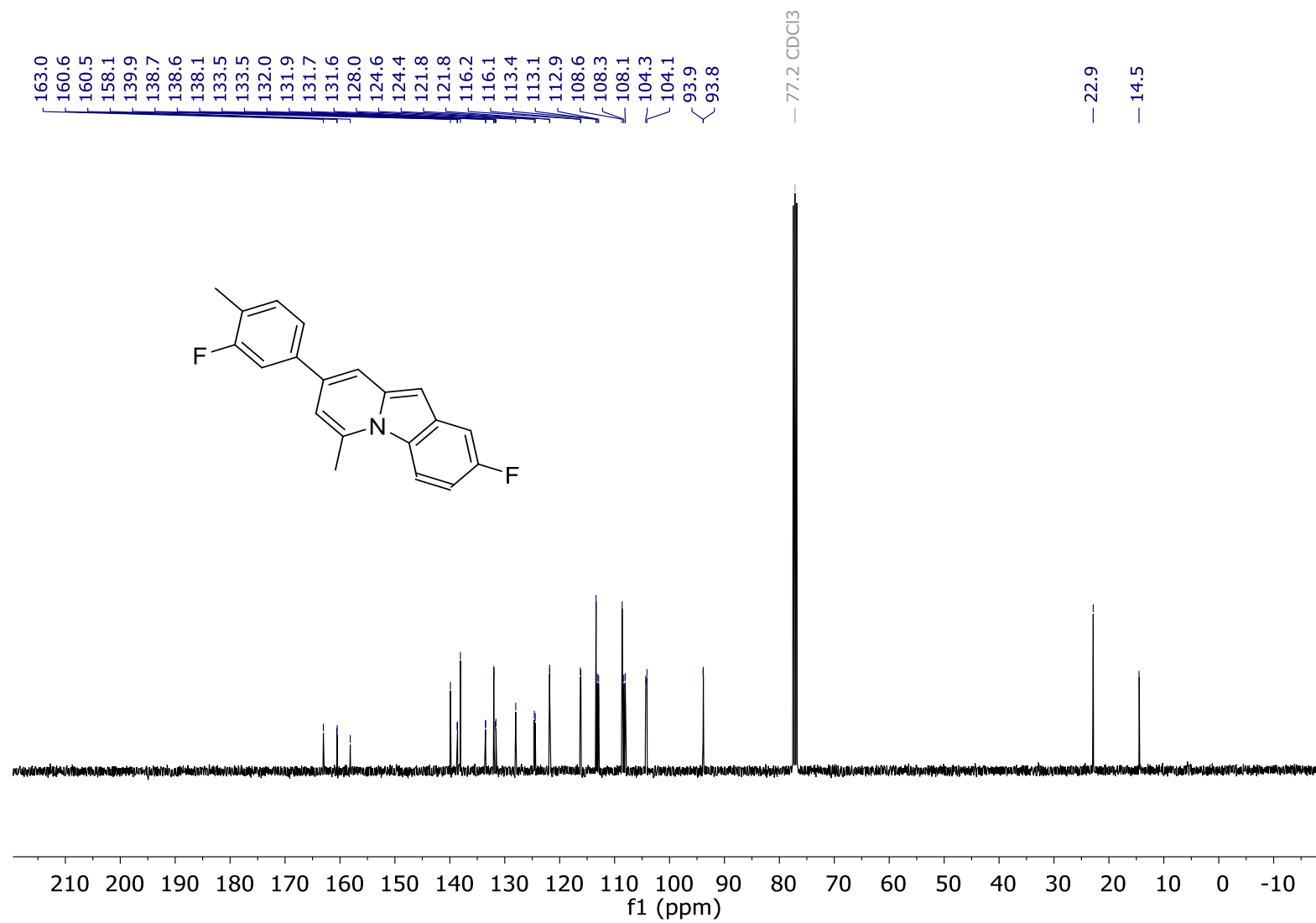
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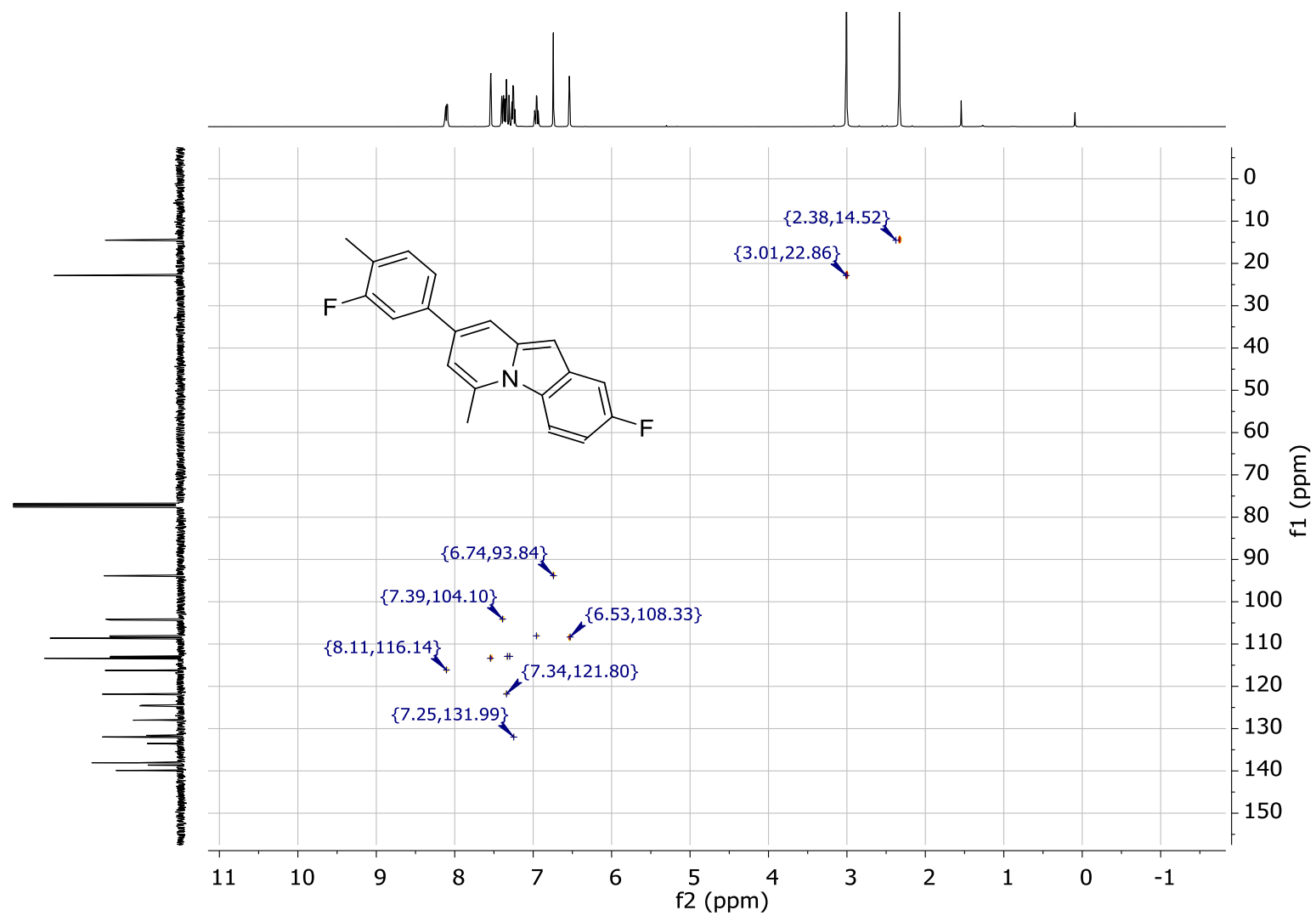
^1H - ^{15}N HMBC for 4p

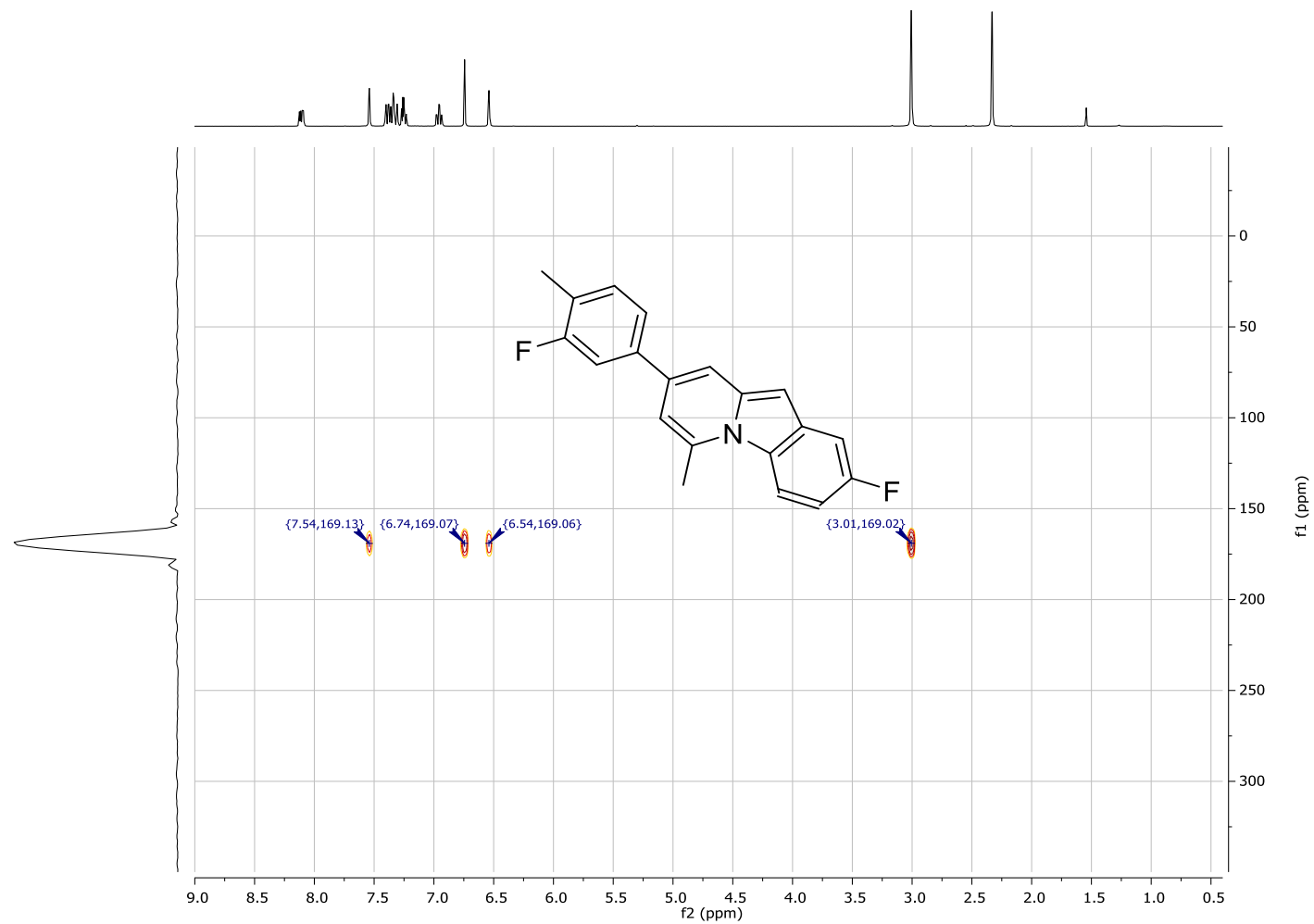


¹H NMR for 4q

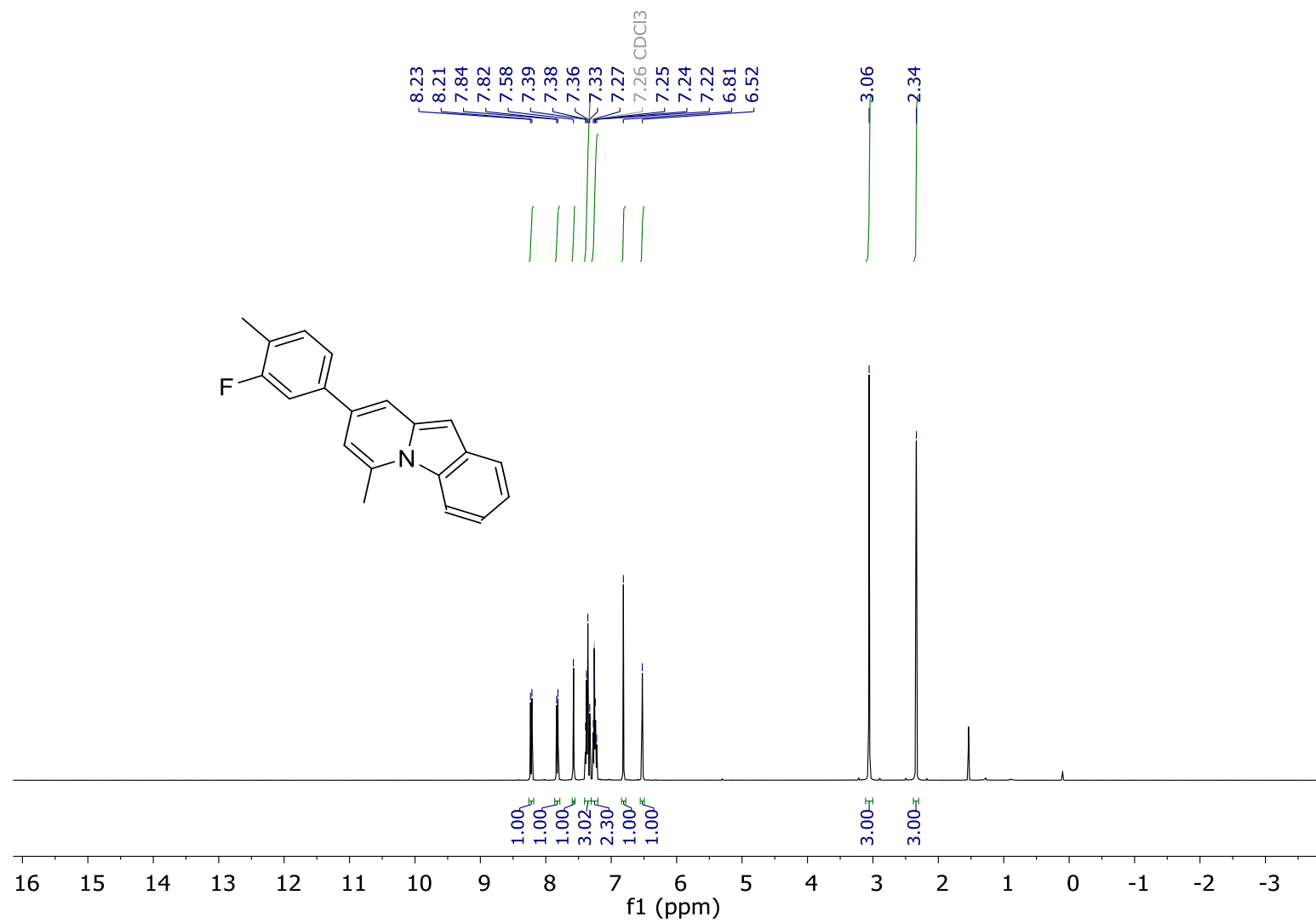


¹³C NMR for 4q

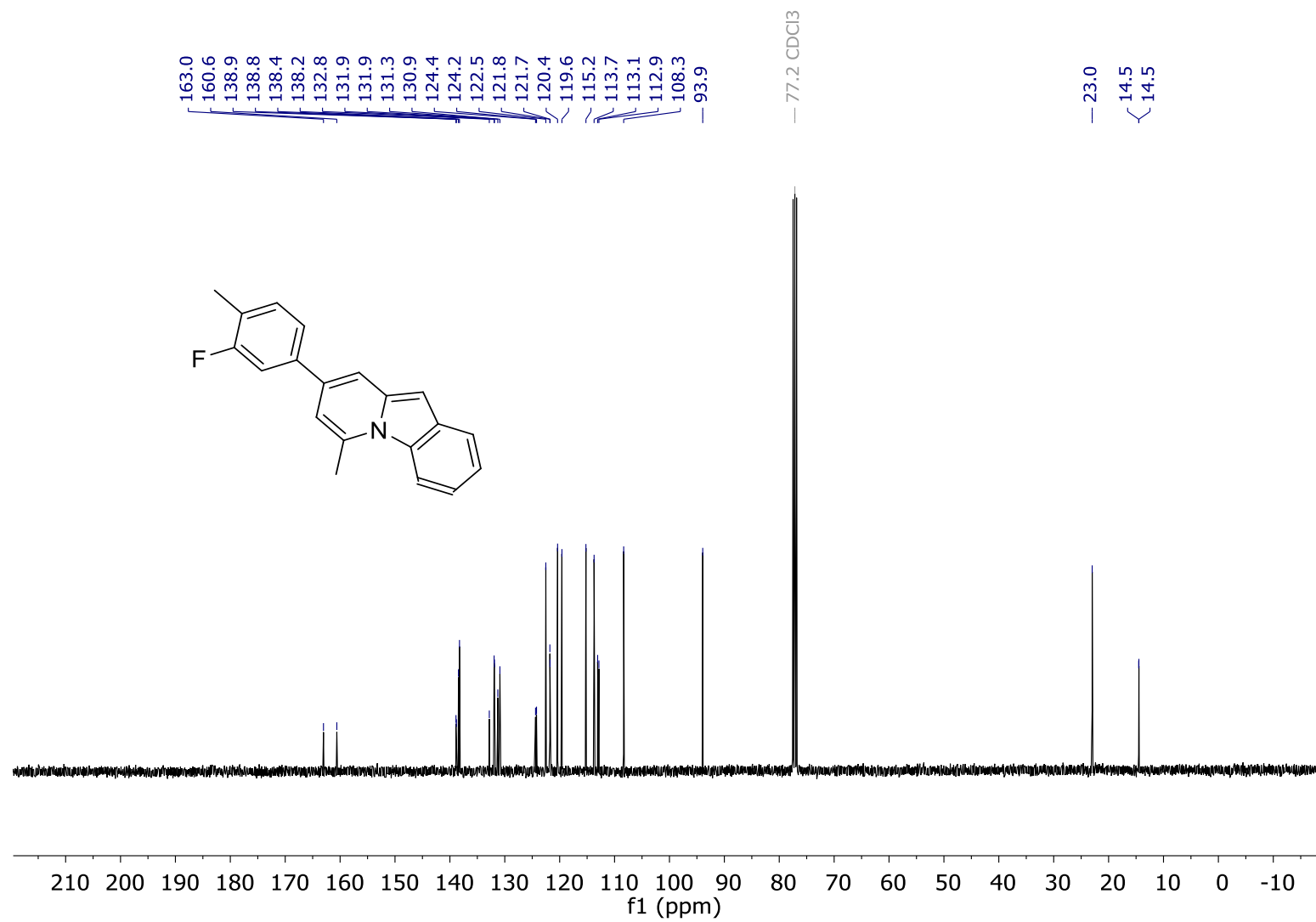




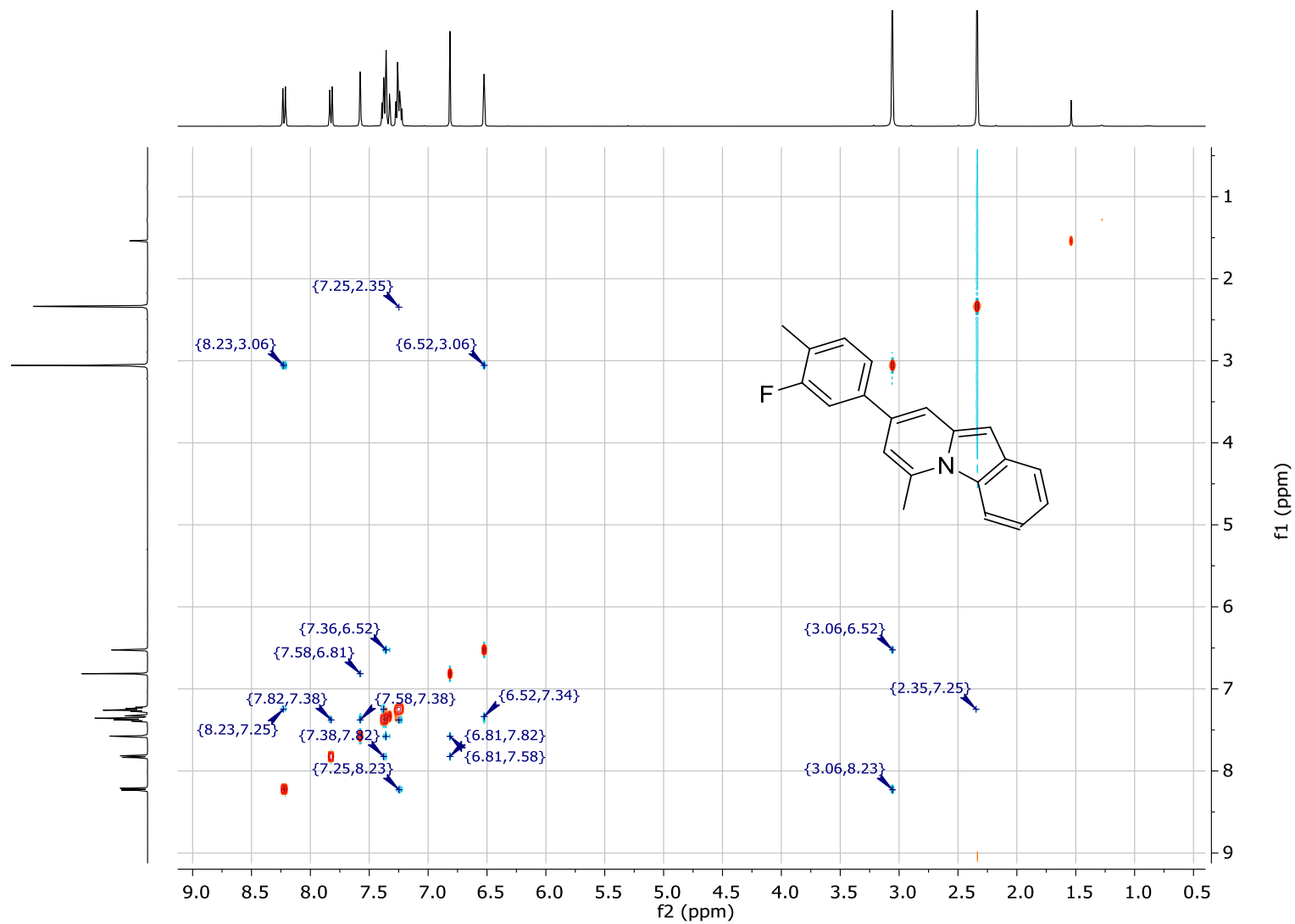
^1H - ^{15}N HMBC for 4q



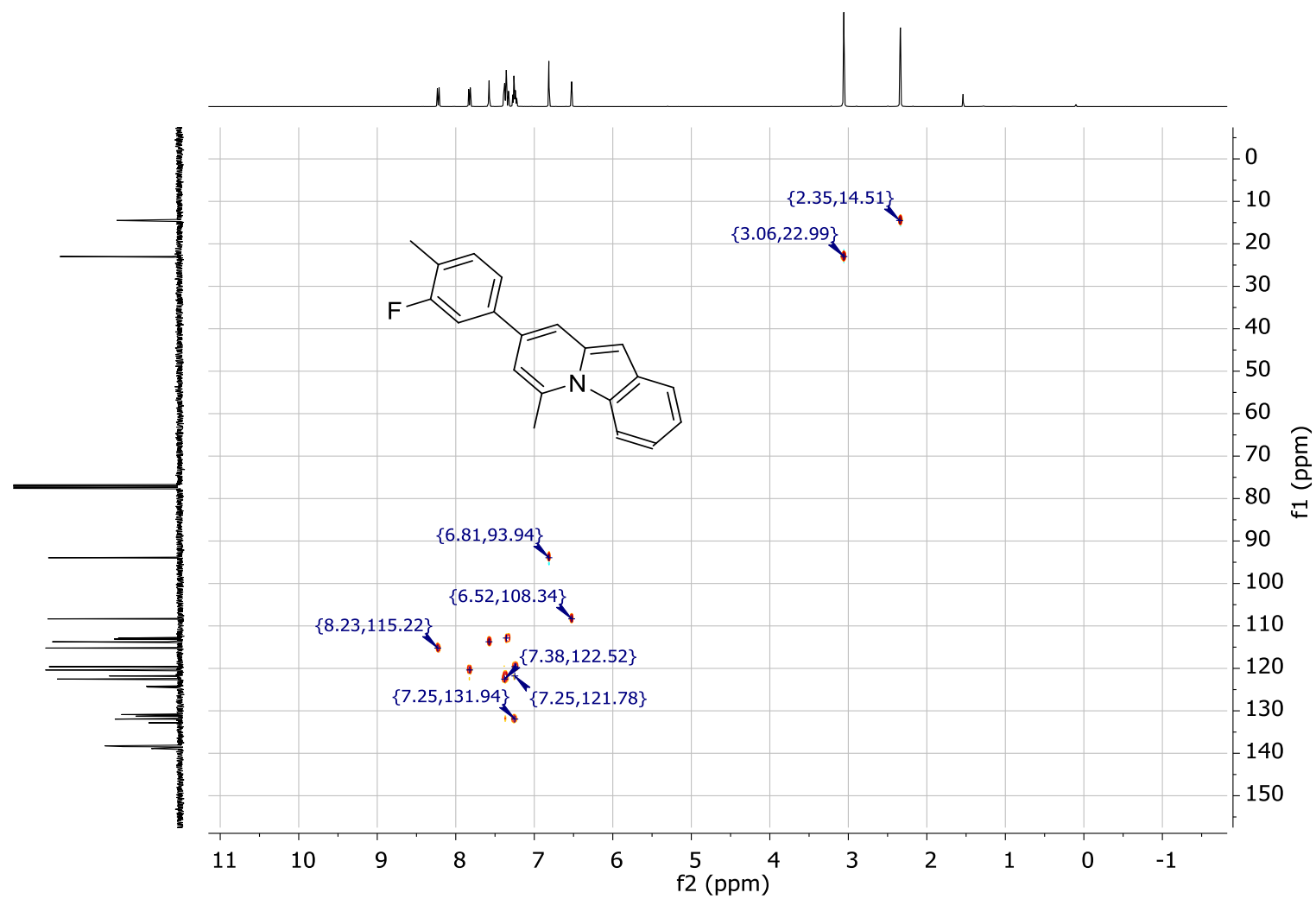
¹H NMR for 4r



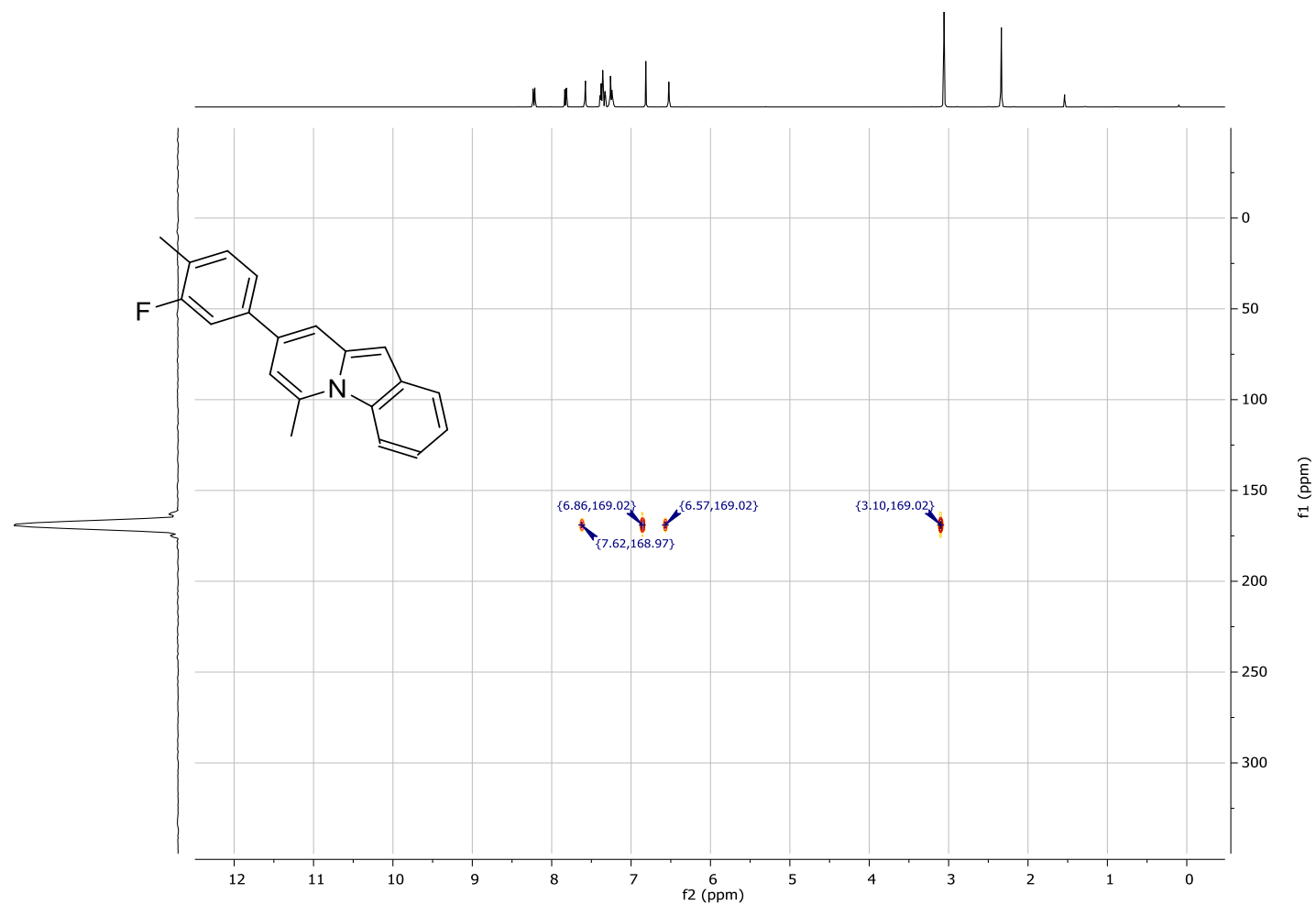
¹³C NMR for 4r



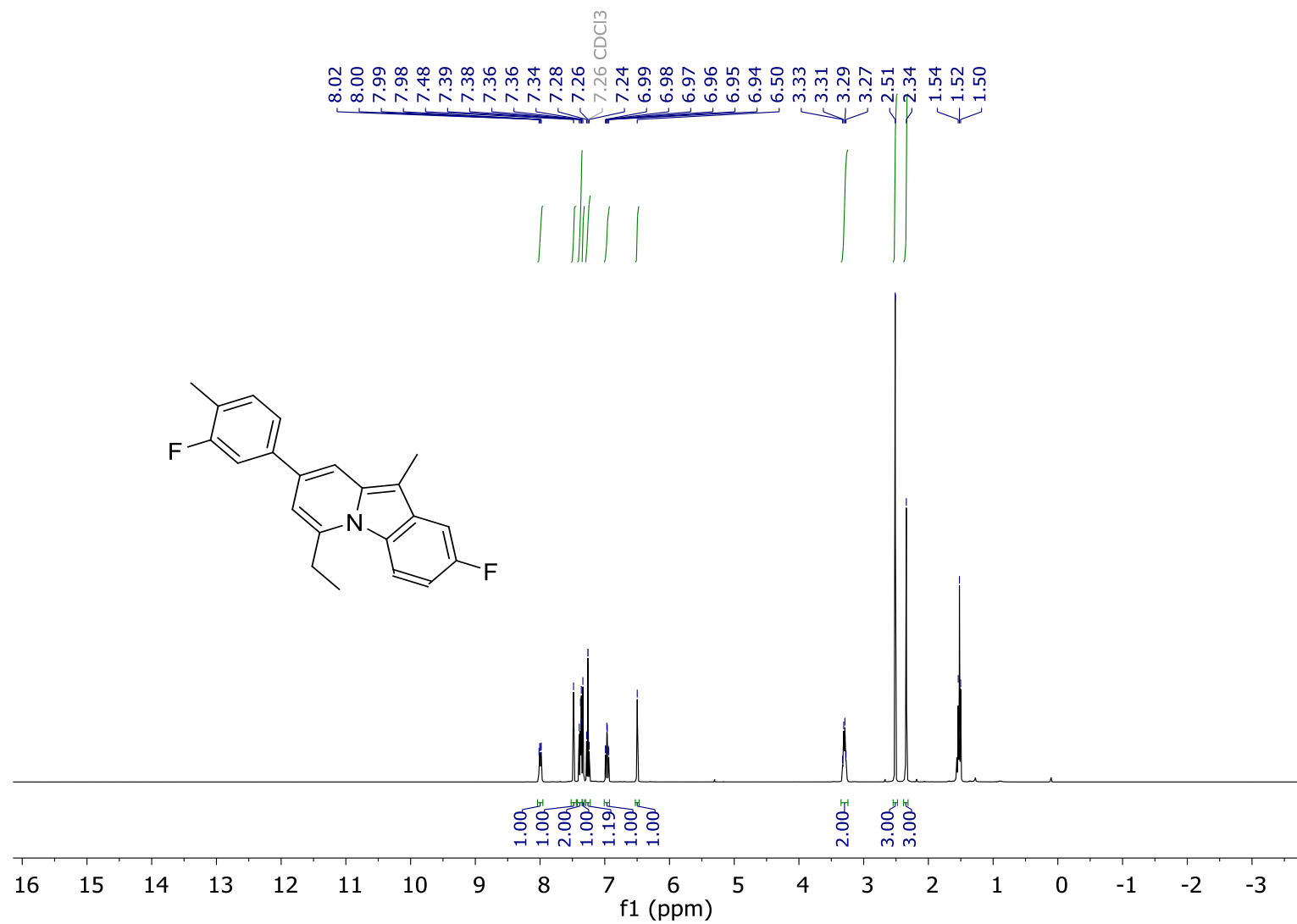
¹H-¹H COSY for 4r



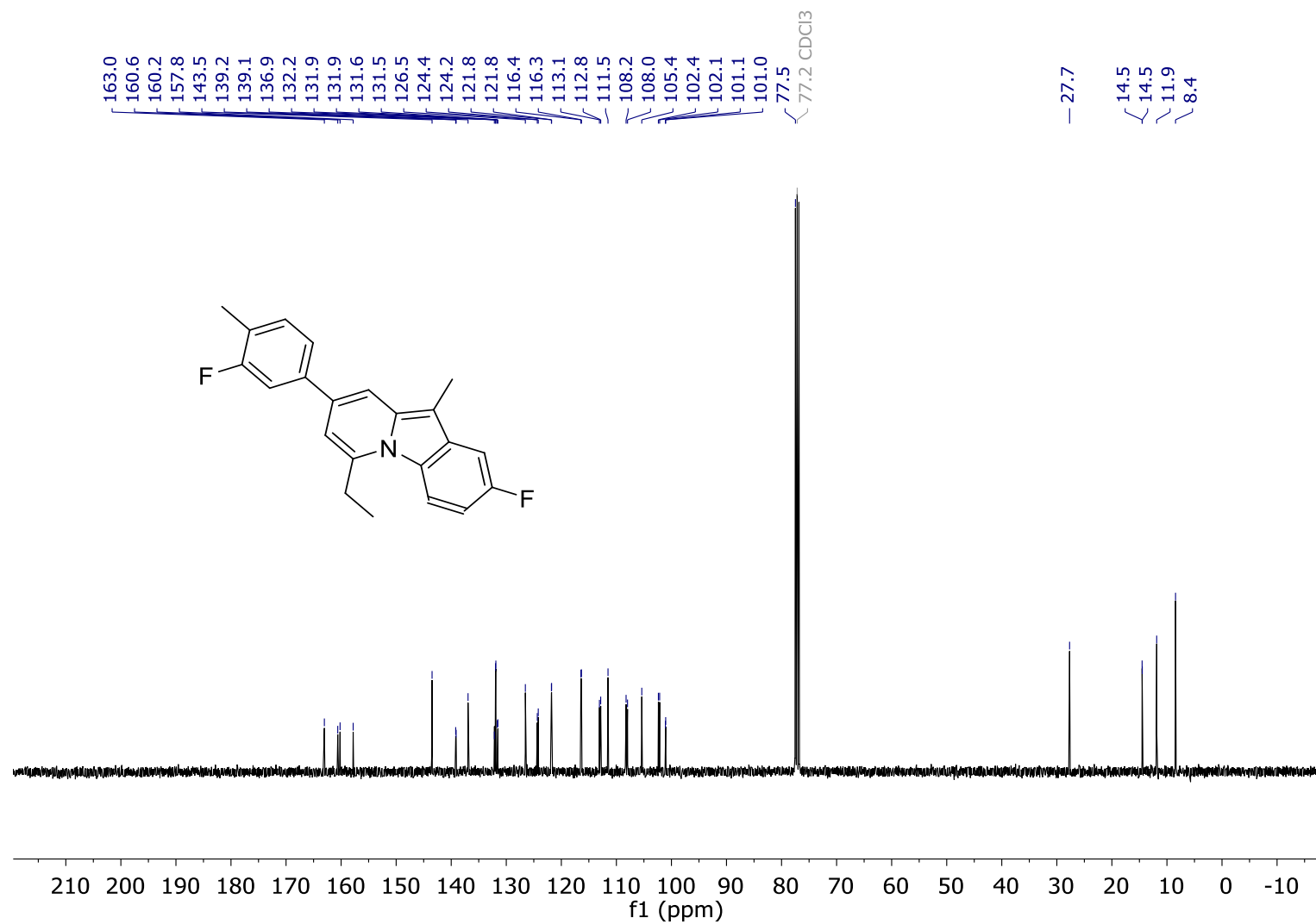
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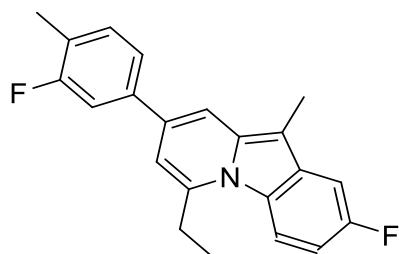
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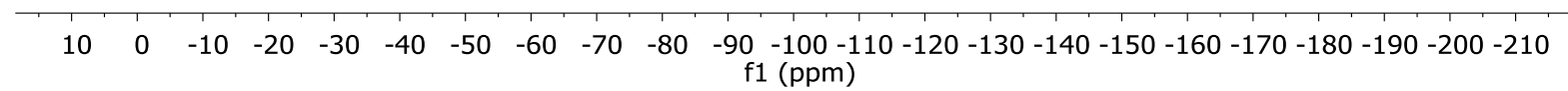
¹H NMR for 4s



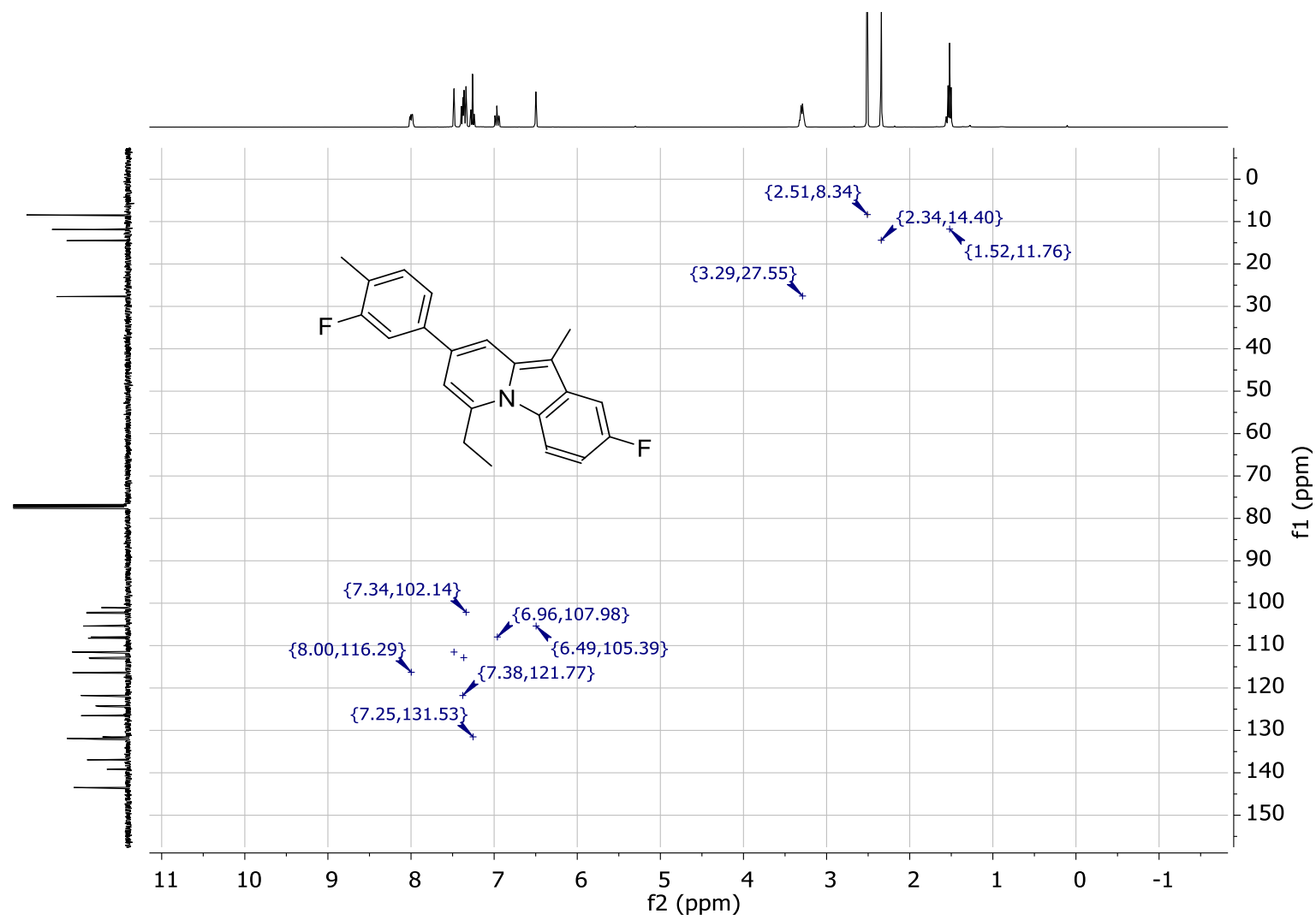
¹³C NMR for 4s



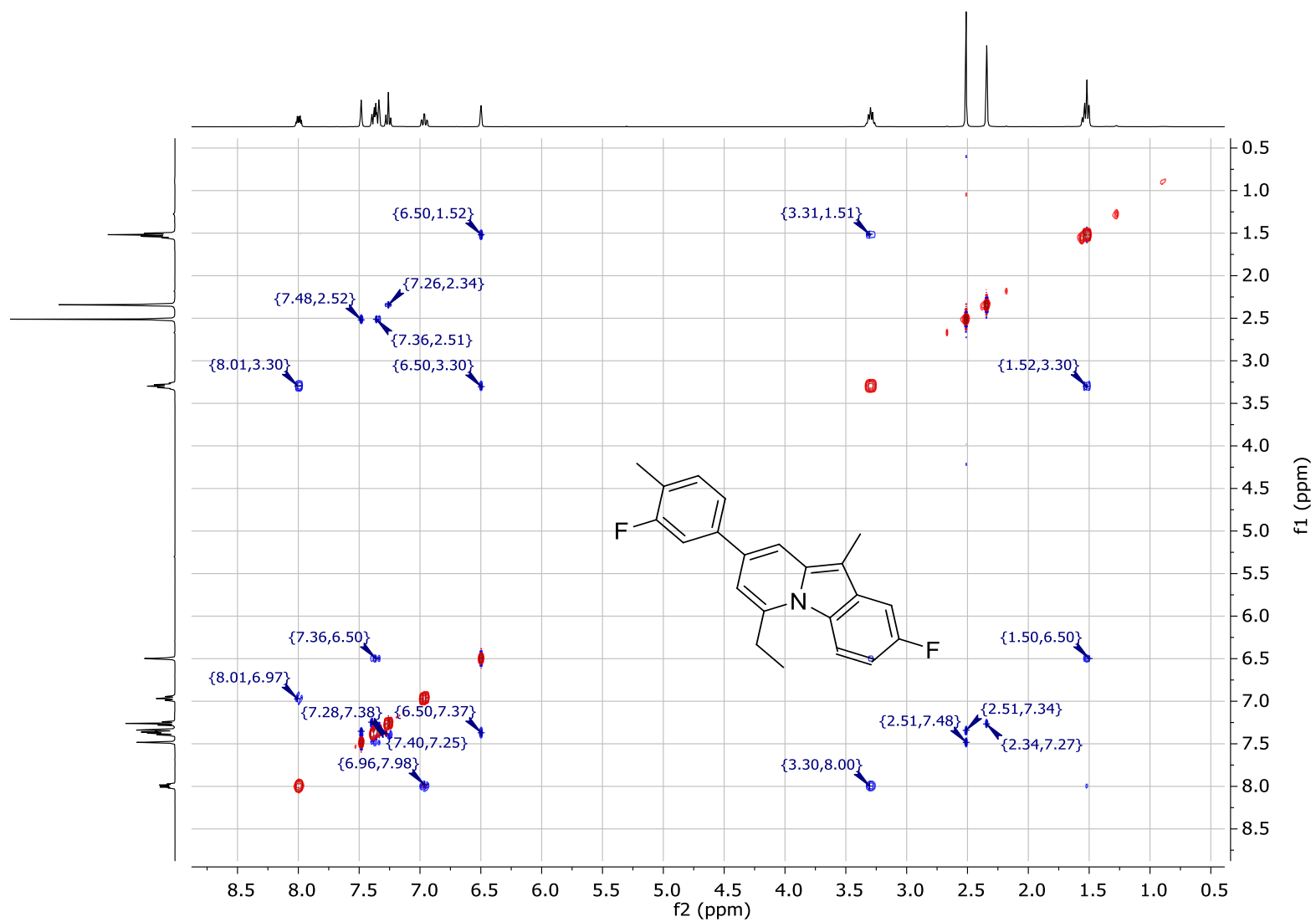
-117.11
-120.76



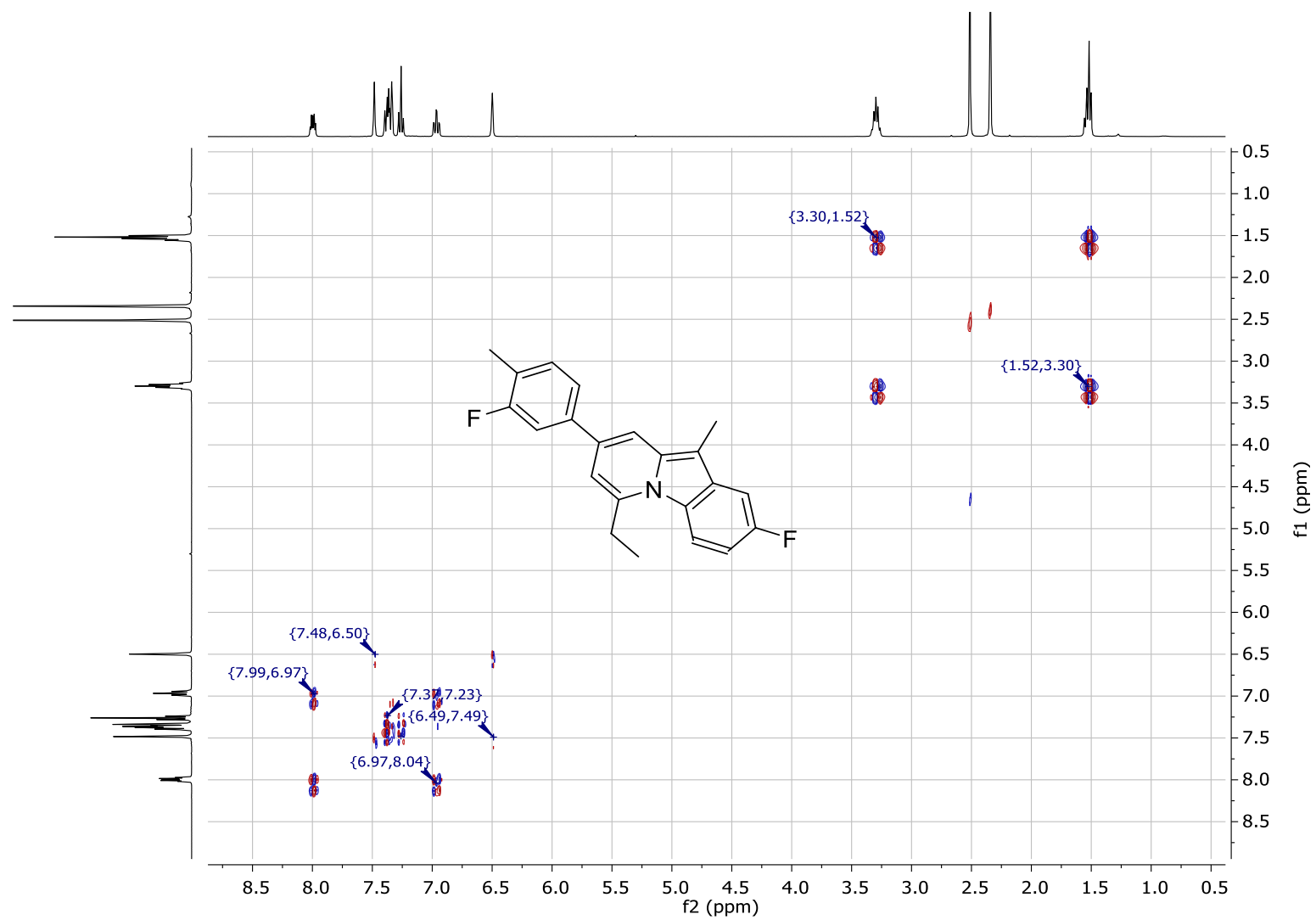
^{19}F NMR for 4s



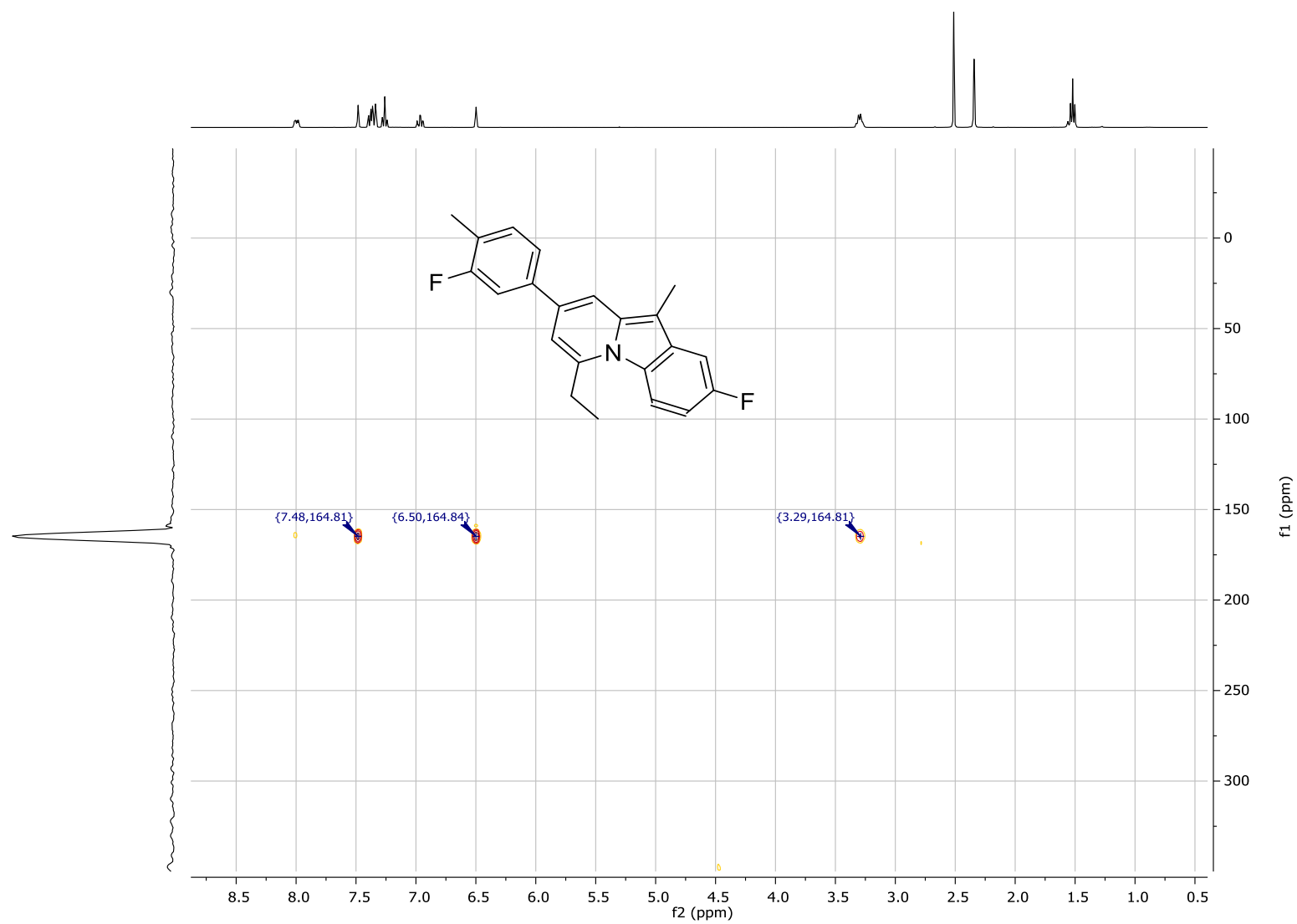
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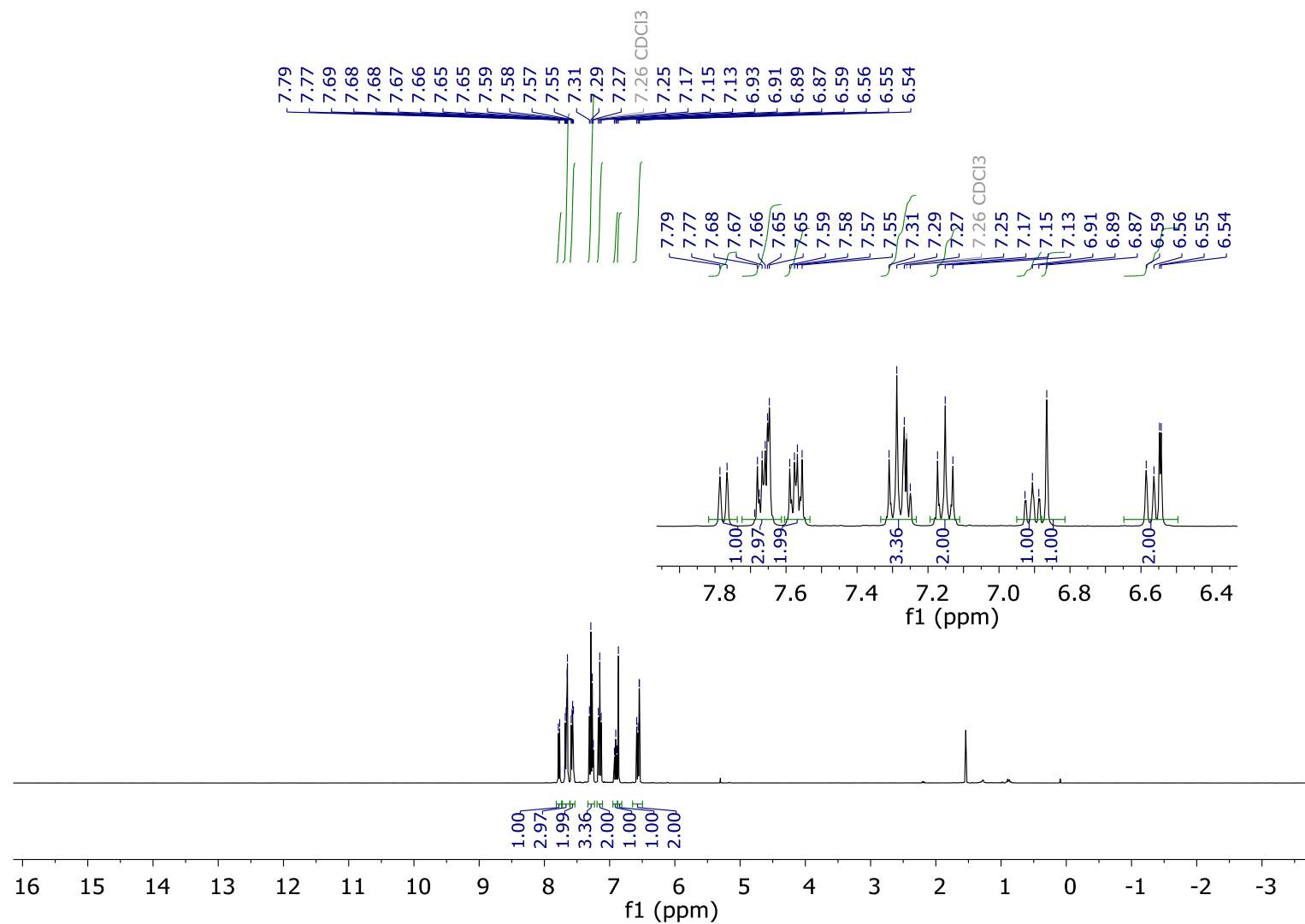
^1H - ^1H NOESY for 4s



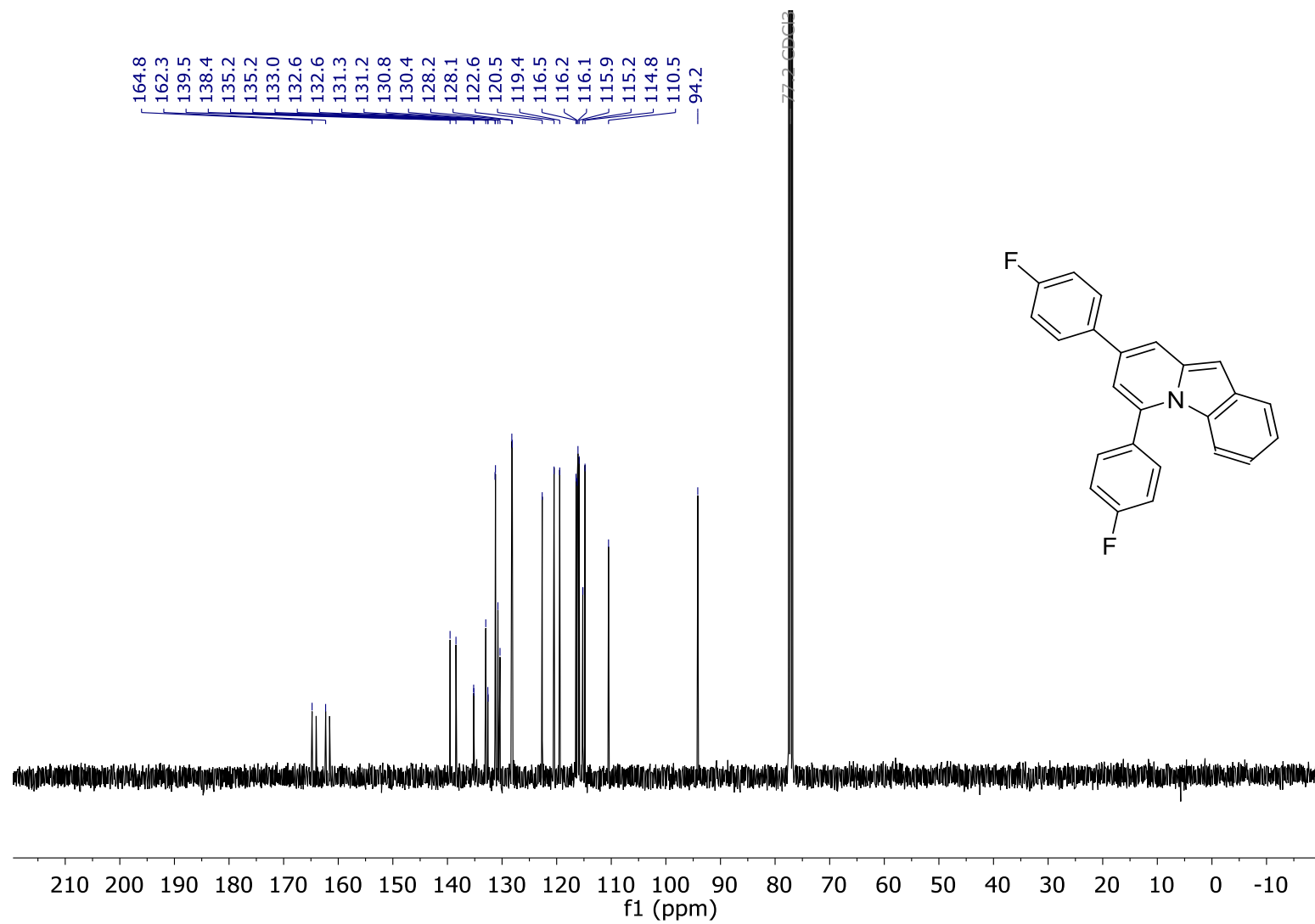
^1H - ^1H COSY for **4s**



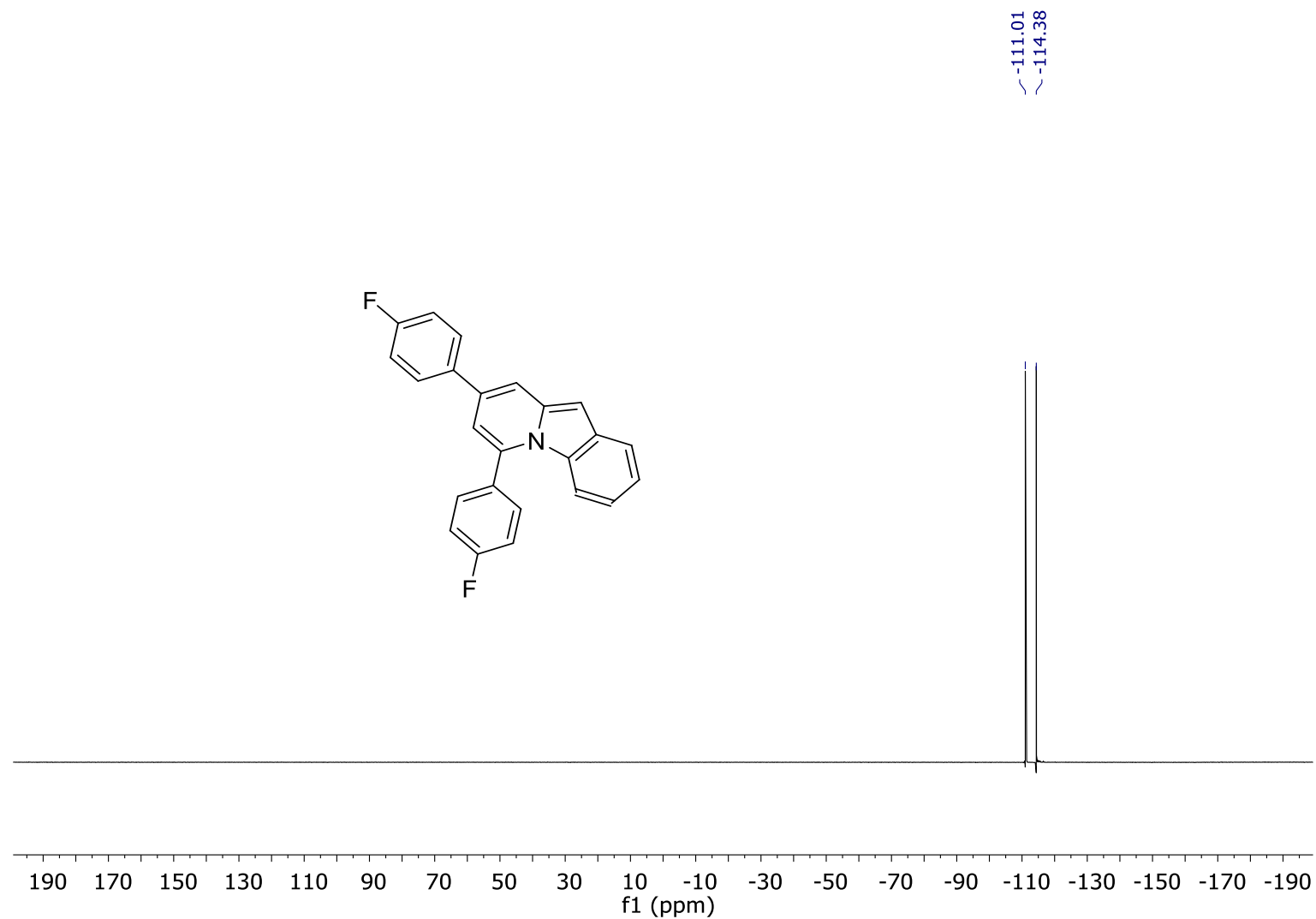
^1H - ^{15}N HMBC for 4s



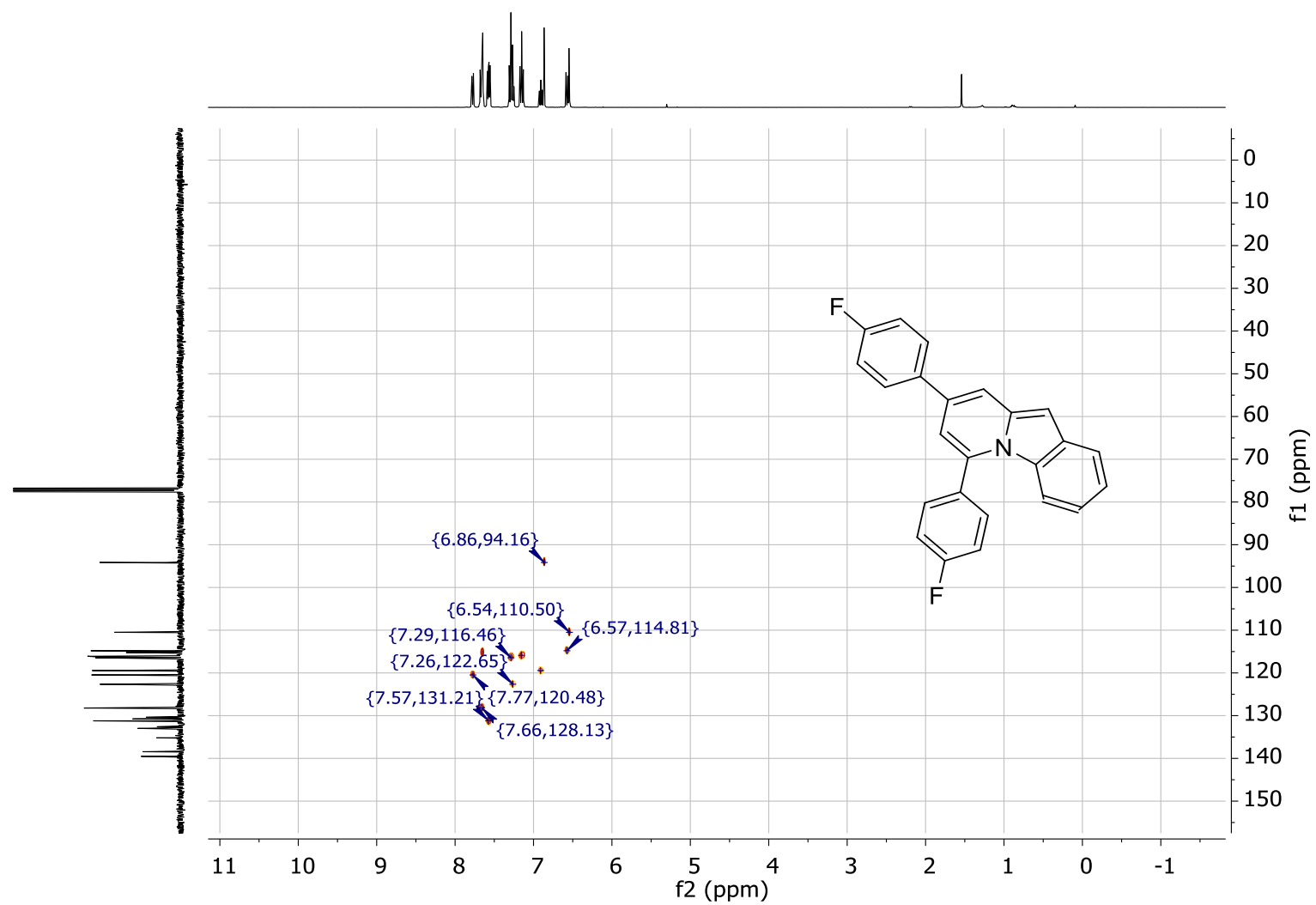
¹H NMR for 4t

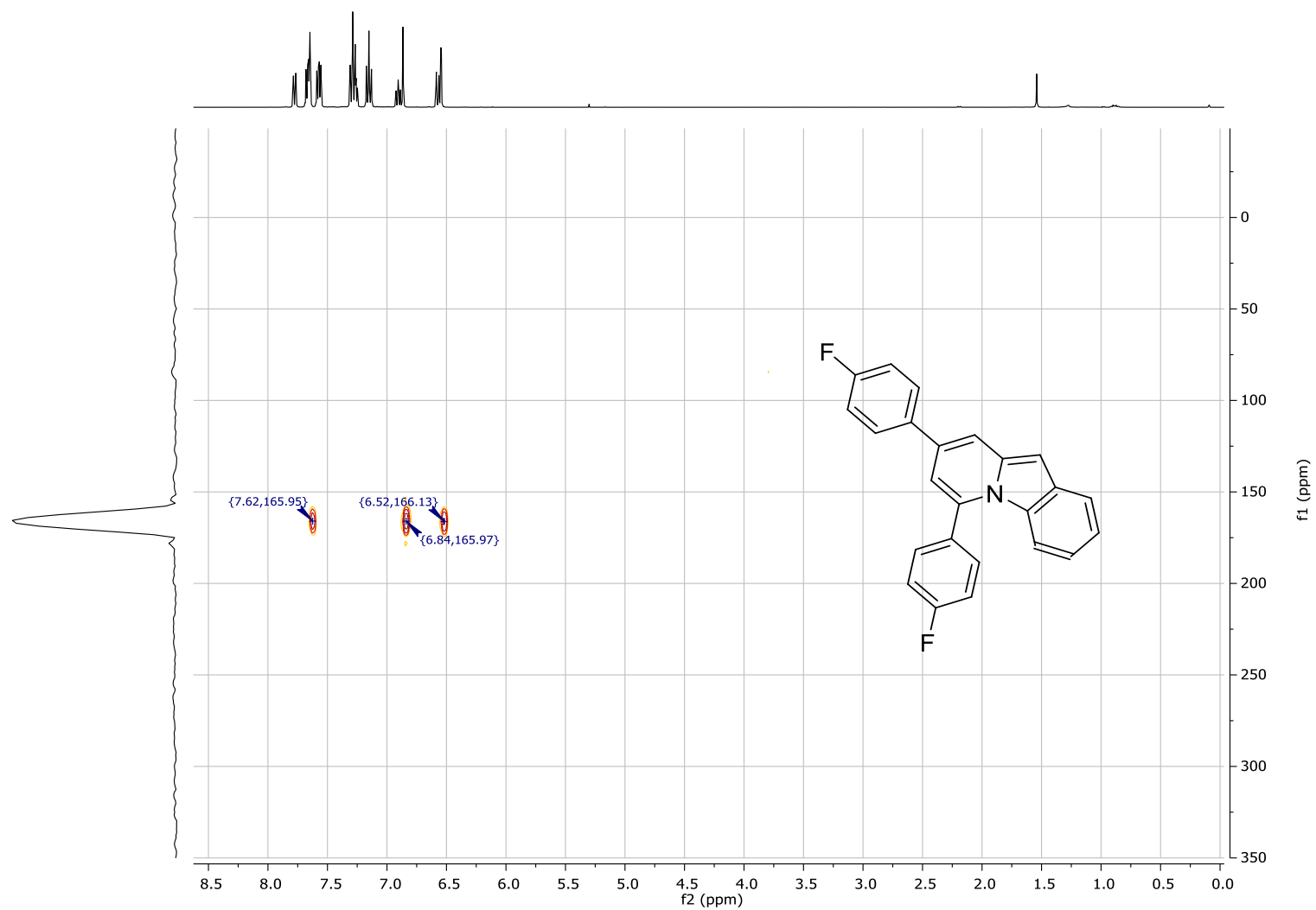


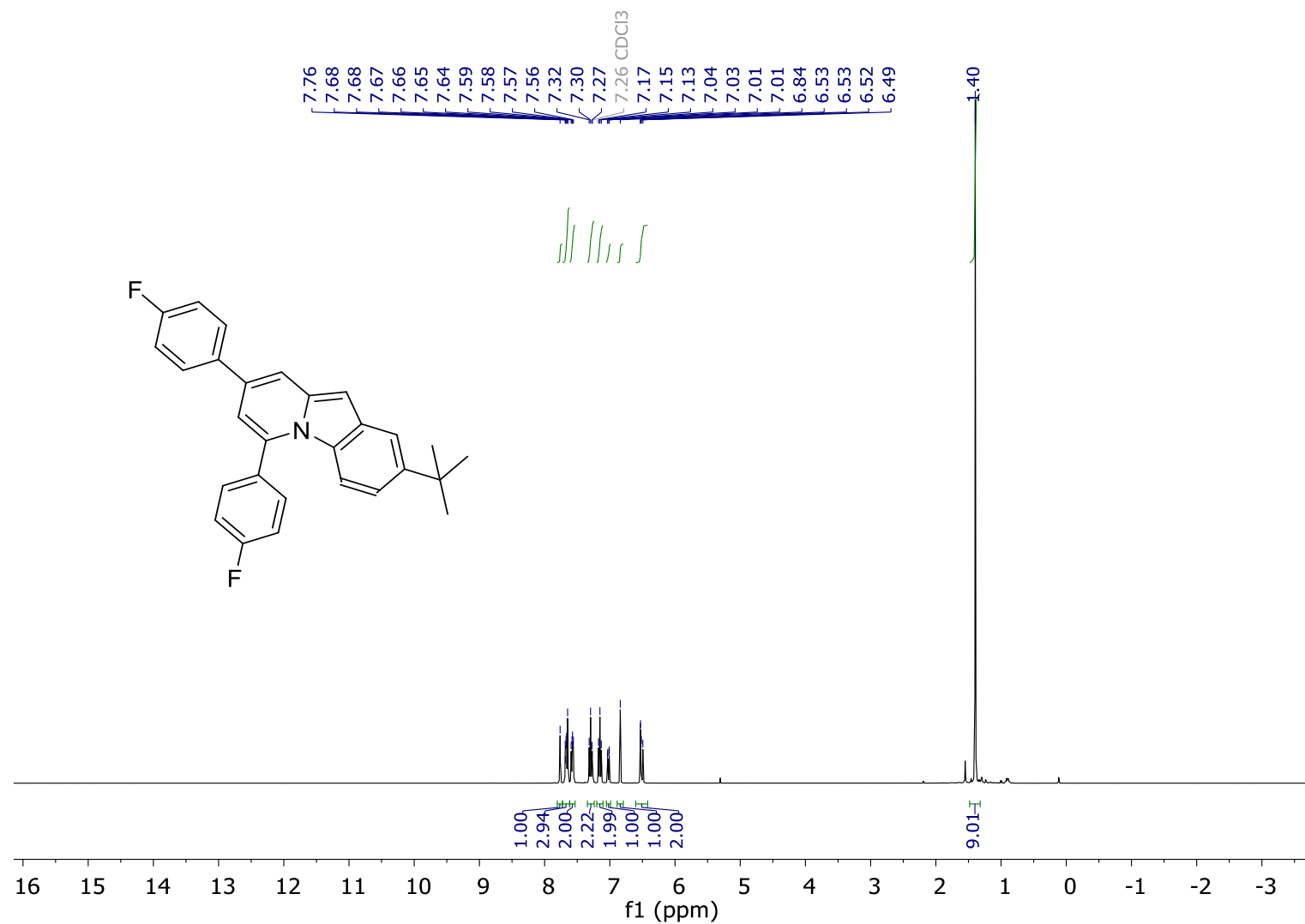
¹³C NMR for 4t



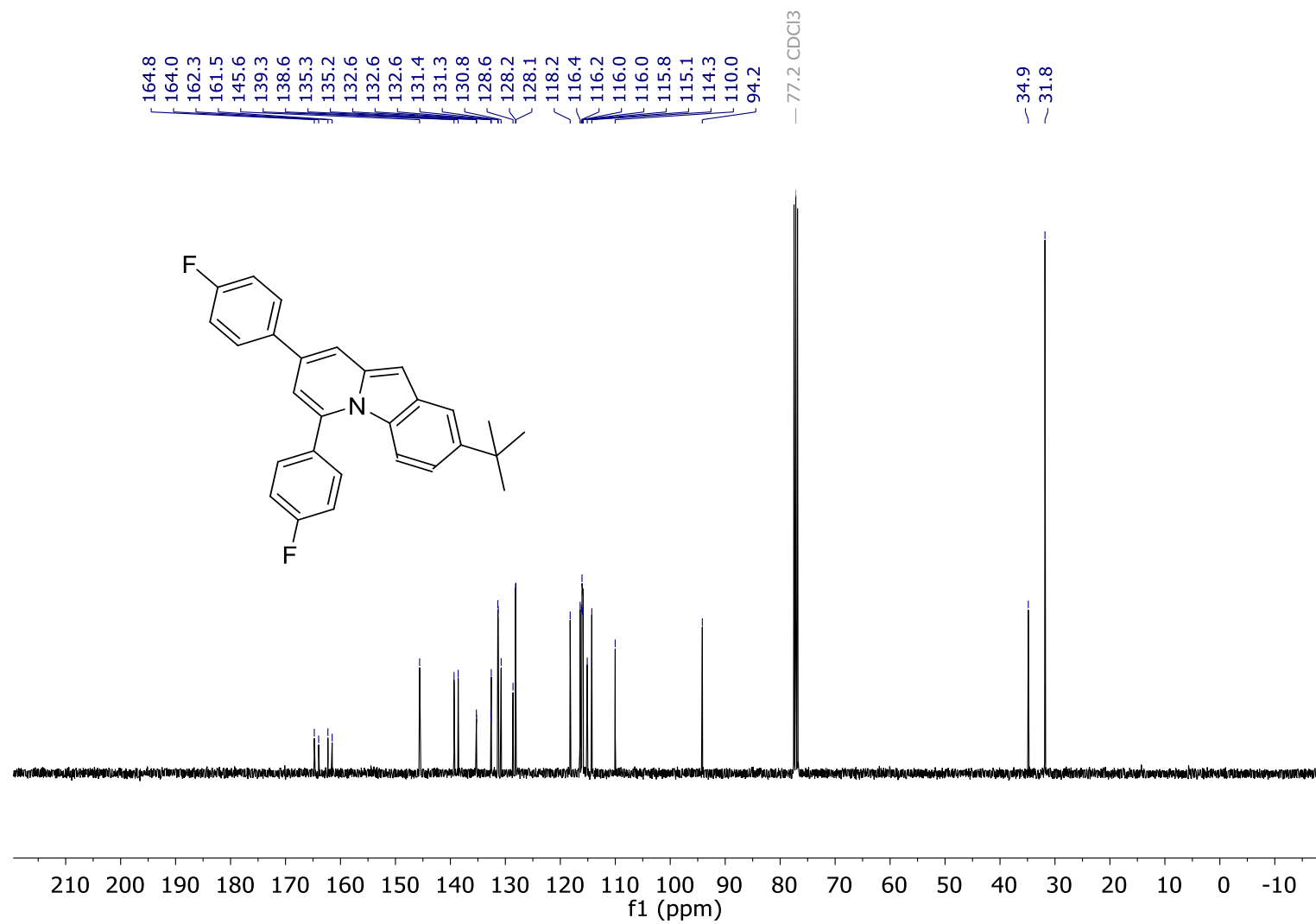
^{19}F NMR for 4t



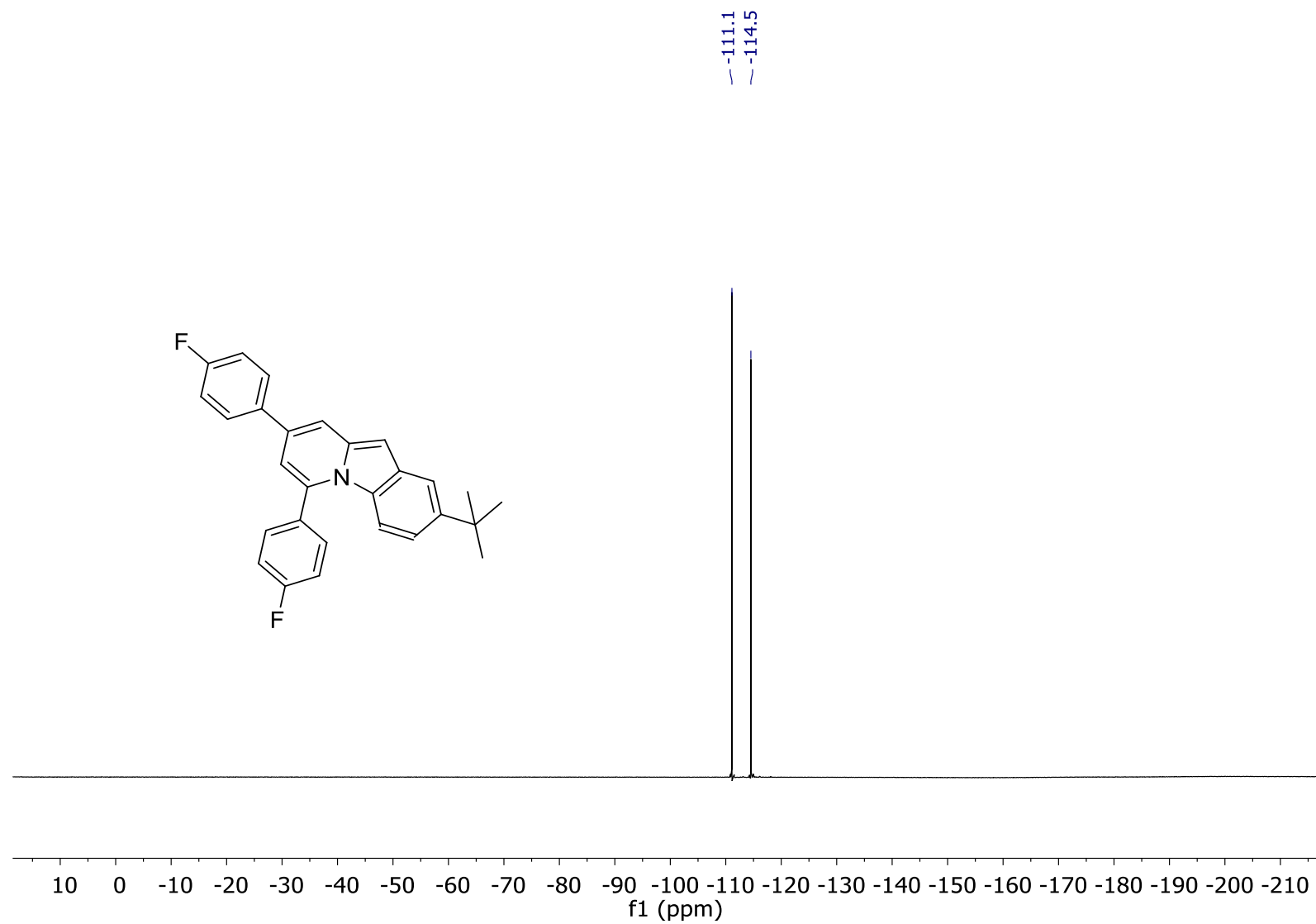




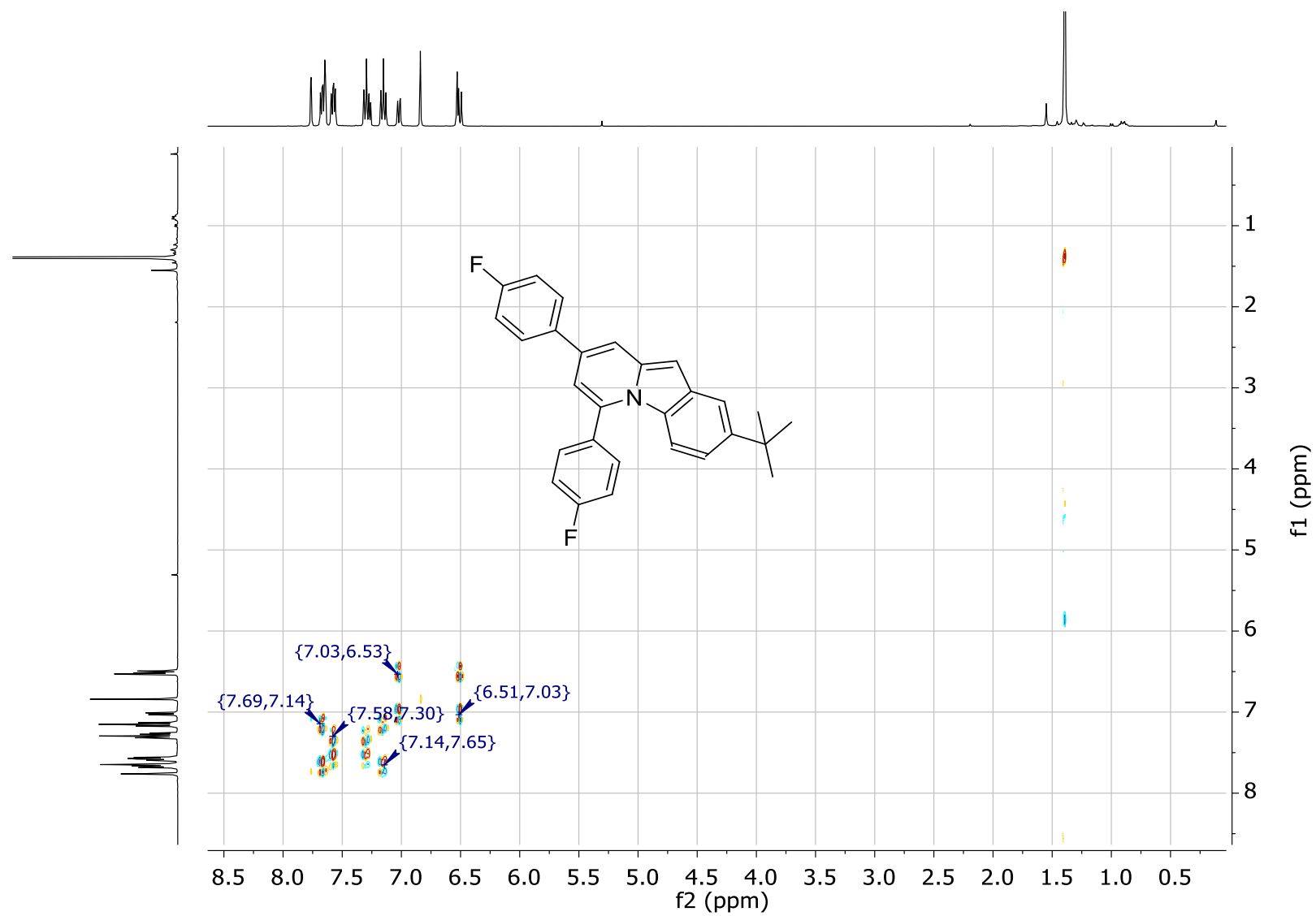
¹H NMR for 4u



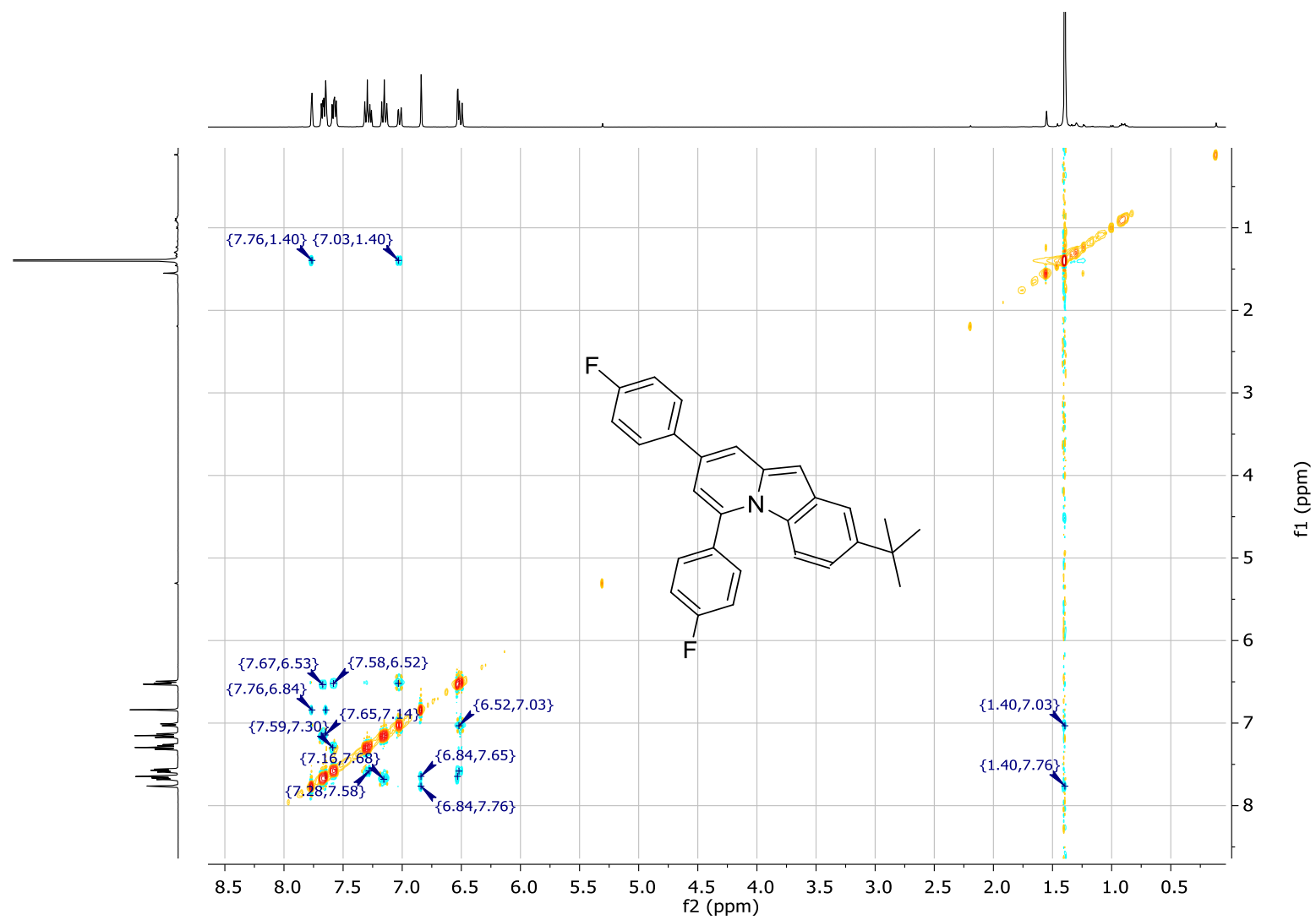
¹³C NMR for 4u



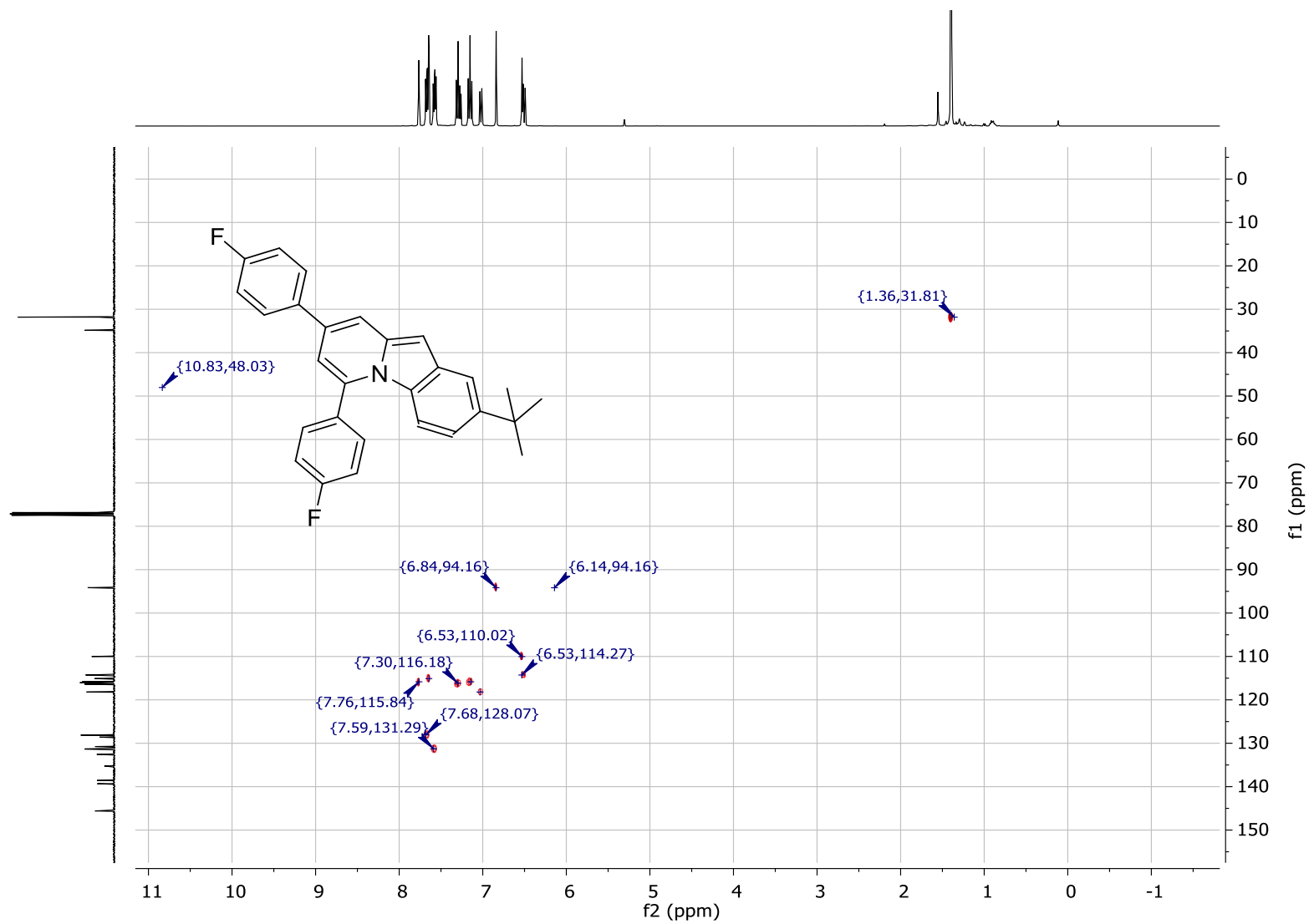
^{19}F NMR for 4u



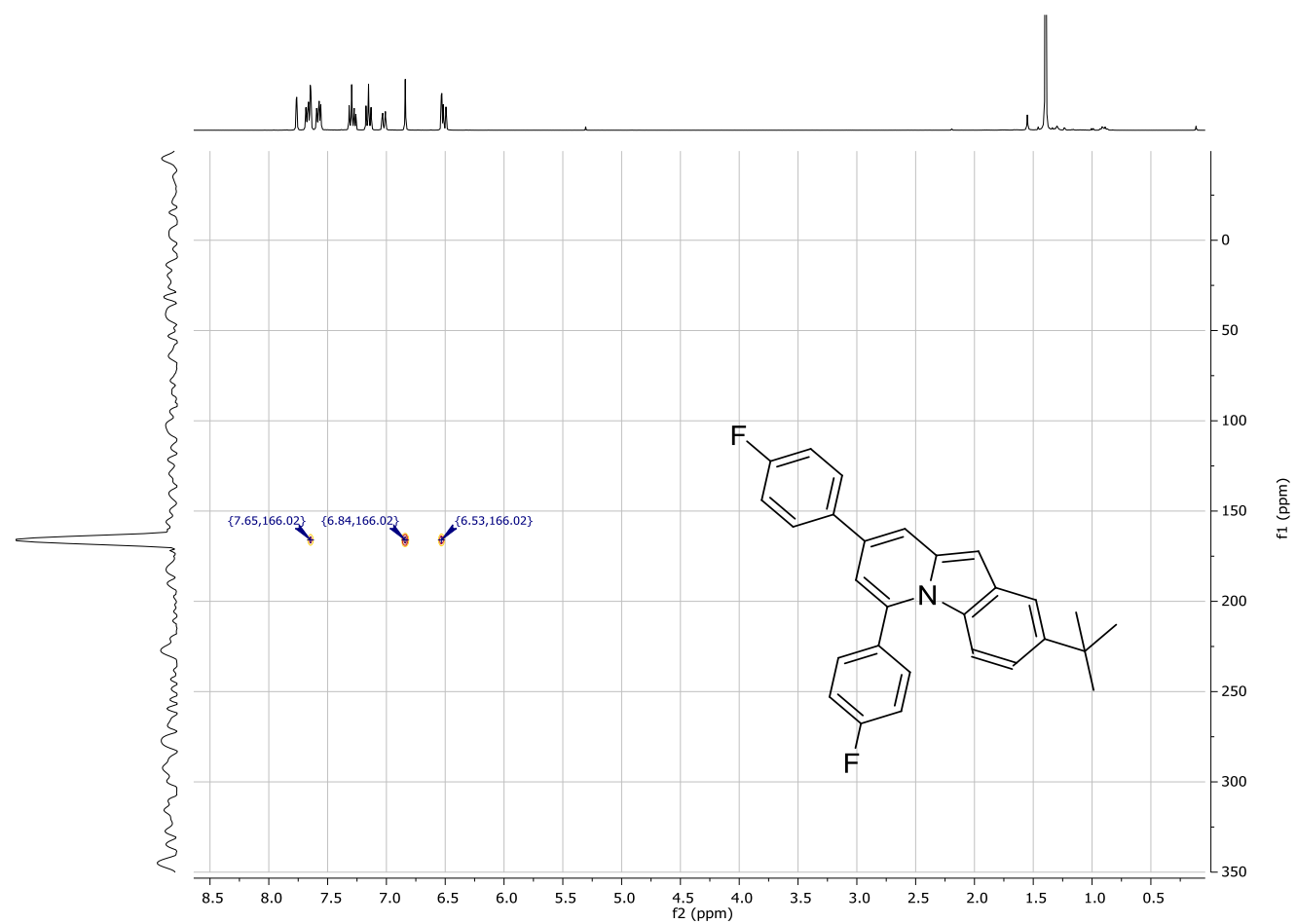
^1H - ^1H COSY for 4u



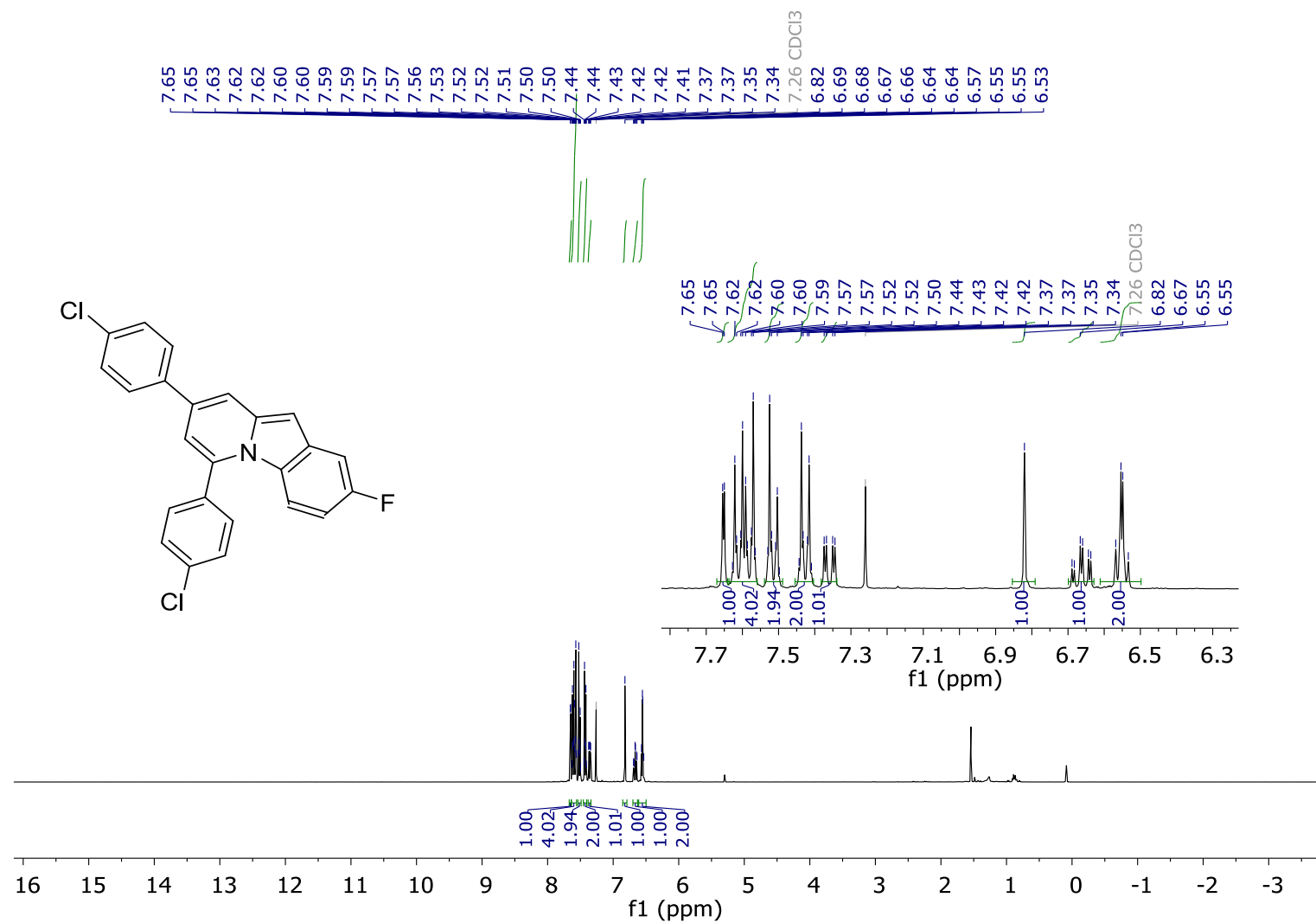
¹H-¹H NOESY for 4u



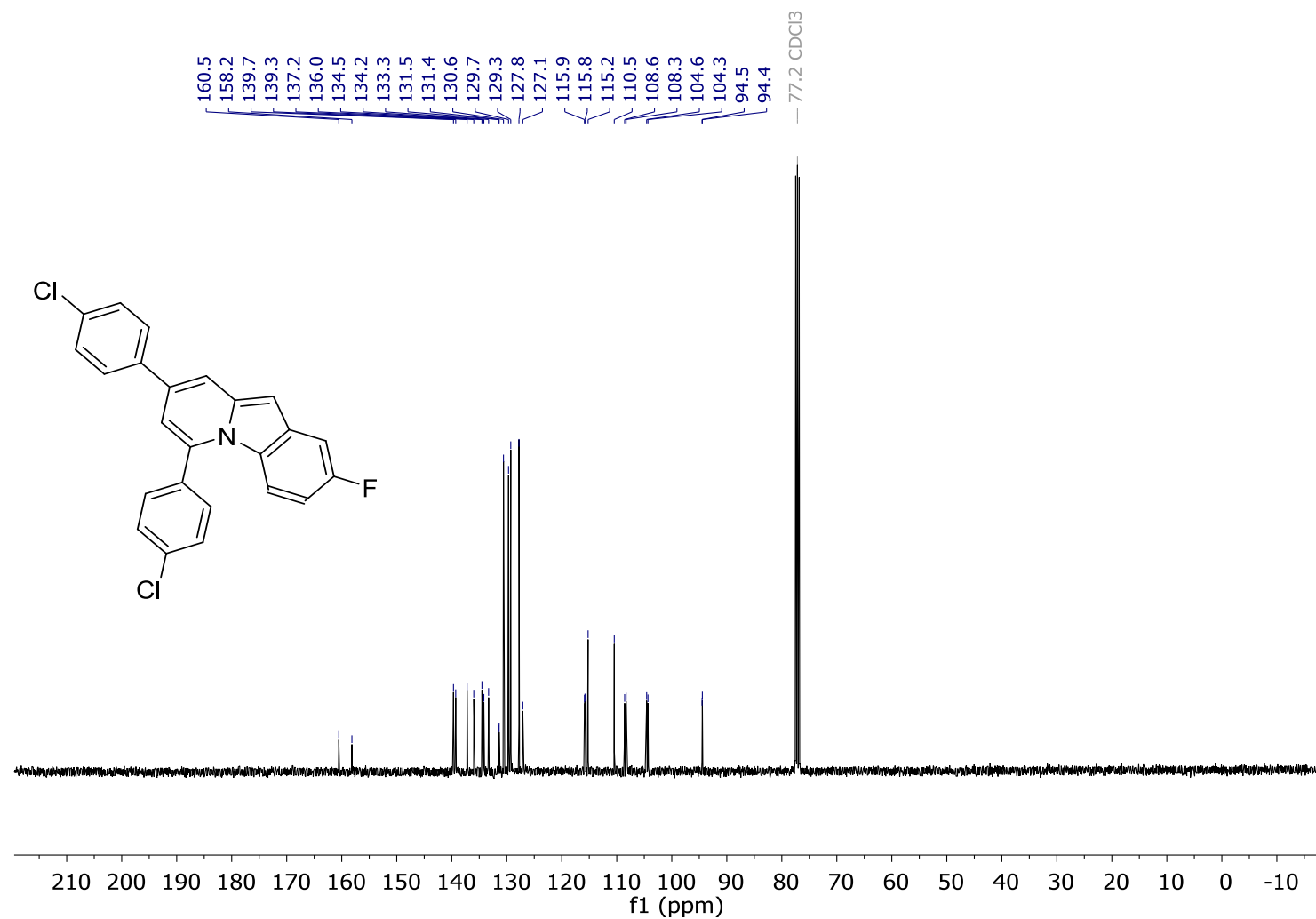
^1H - ^{13}C HSQC for 4u



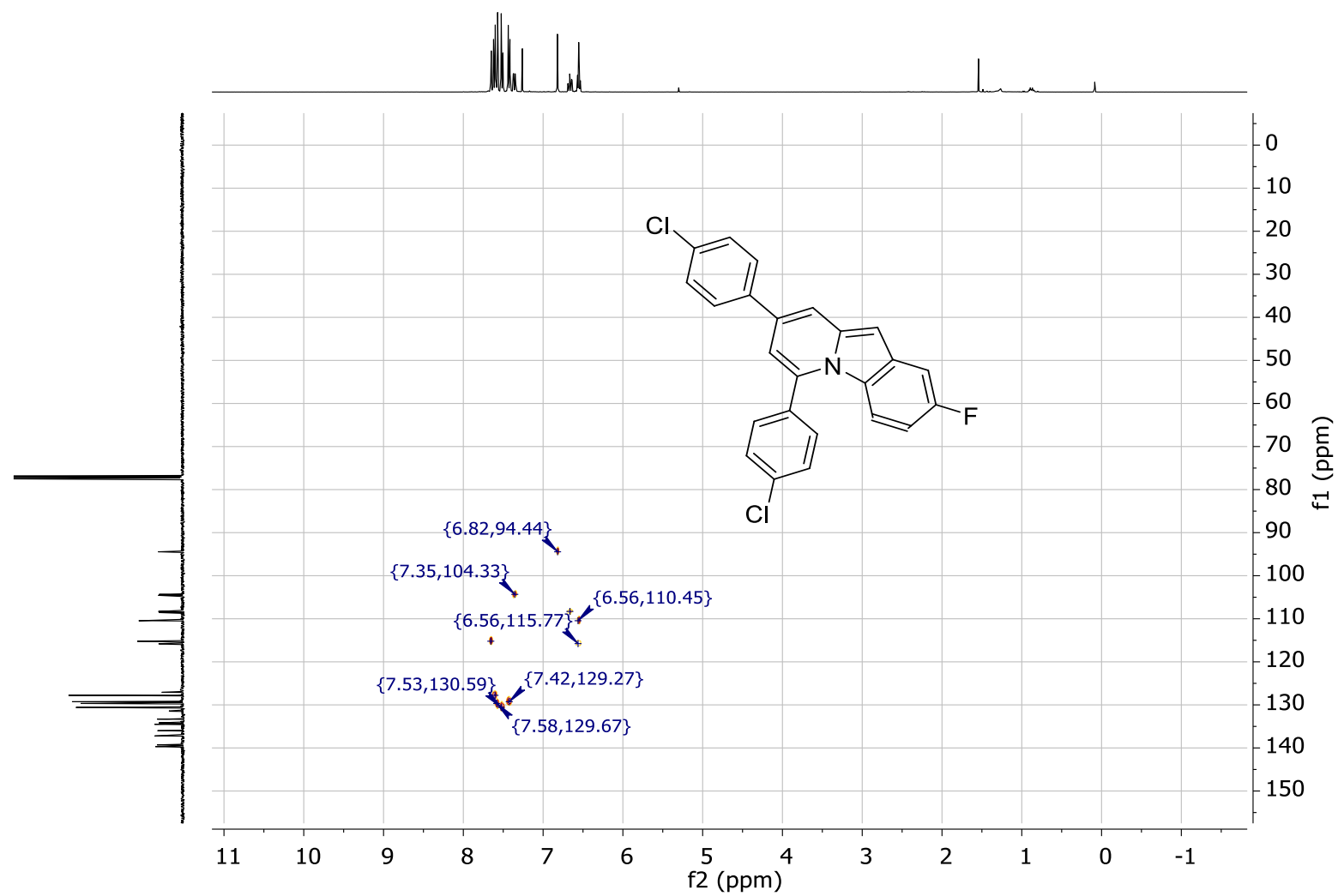
^1H - ^{15}N HMBC for 4u



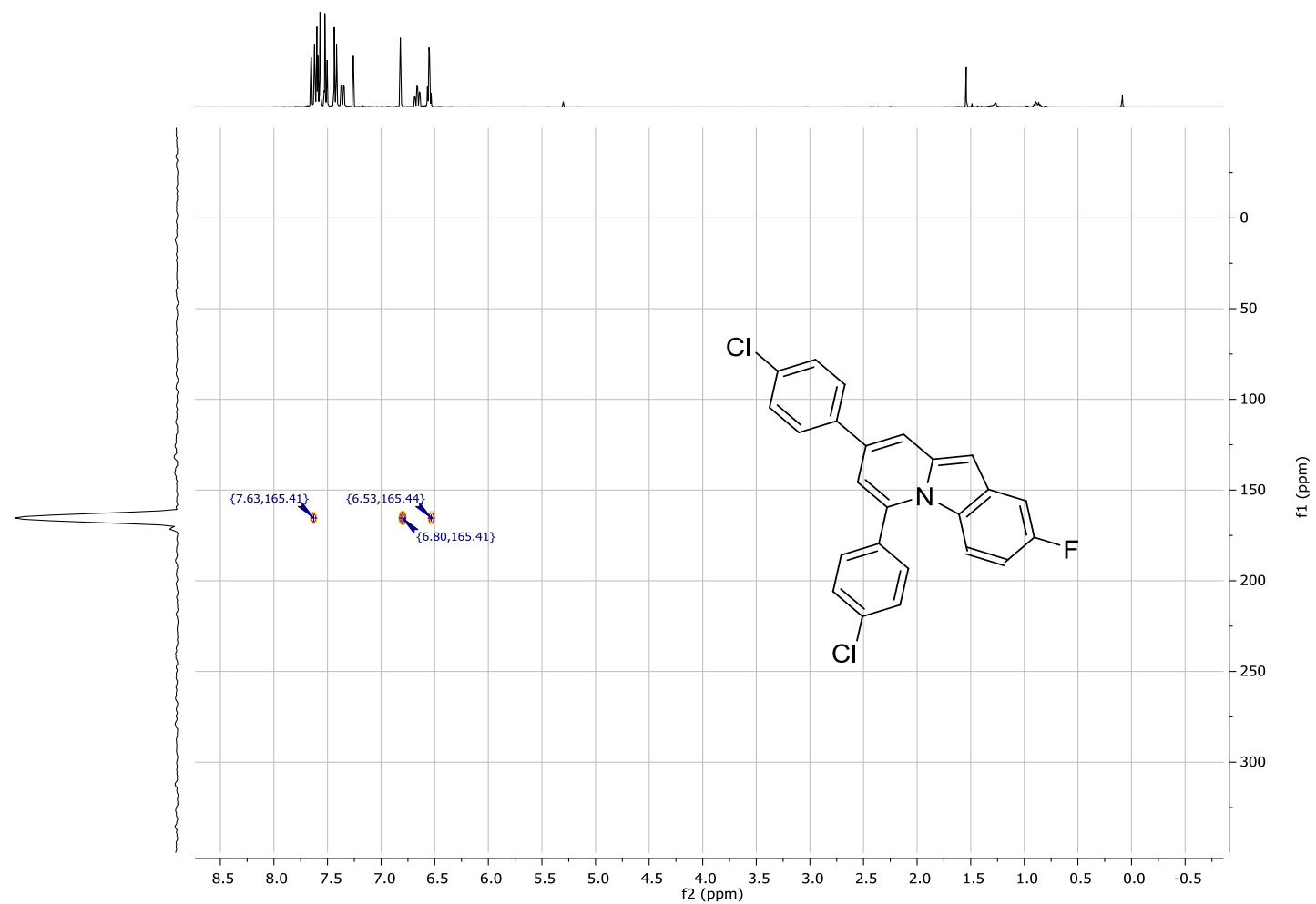
¹H NMR for 4v

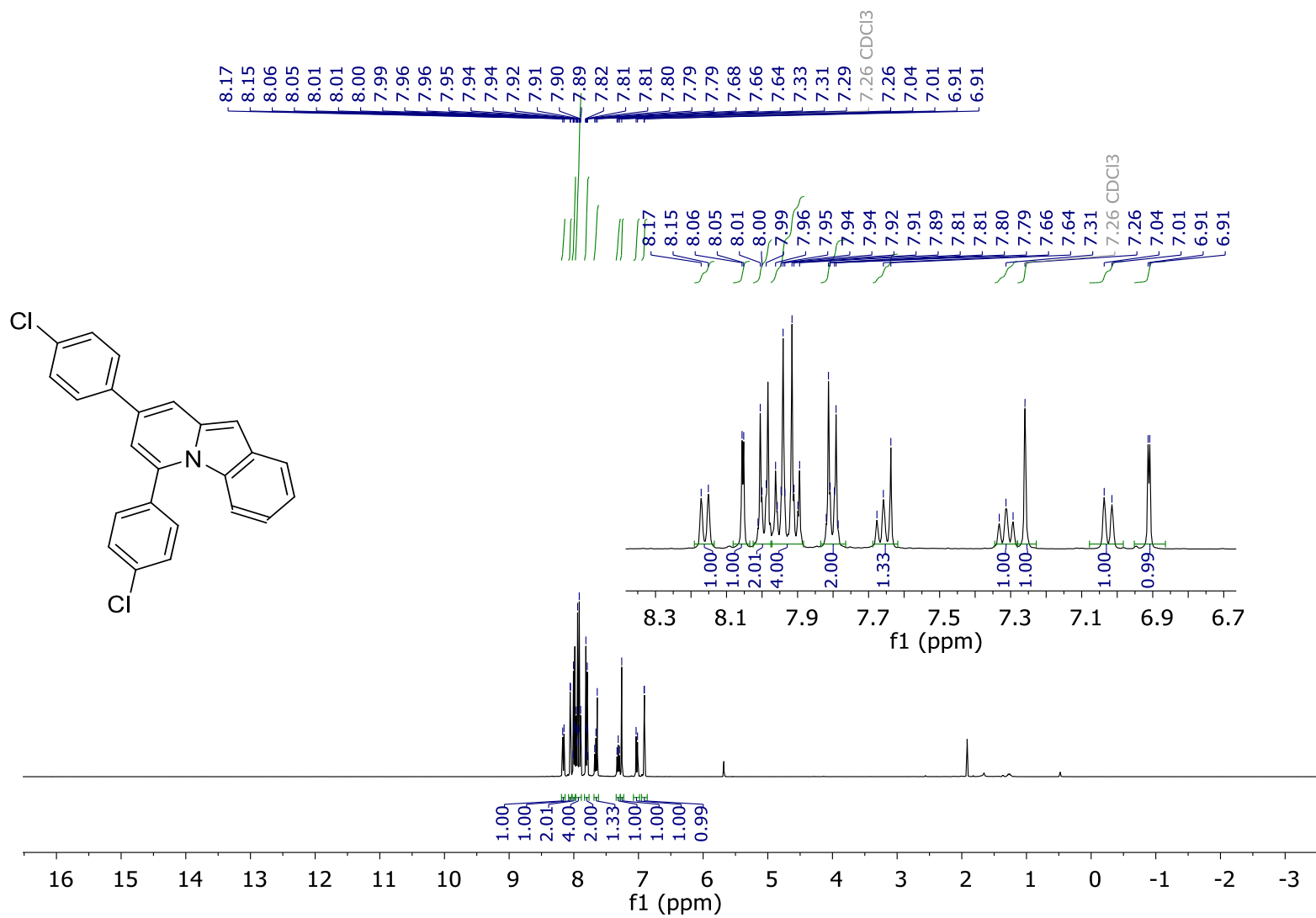


¹³C NMR for 4v

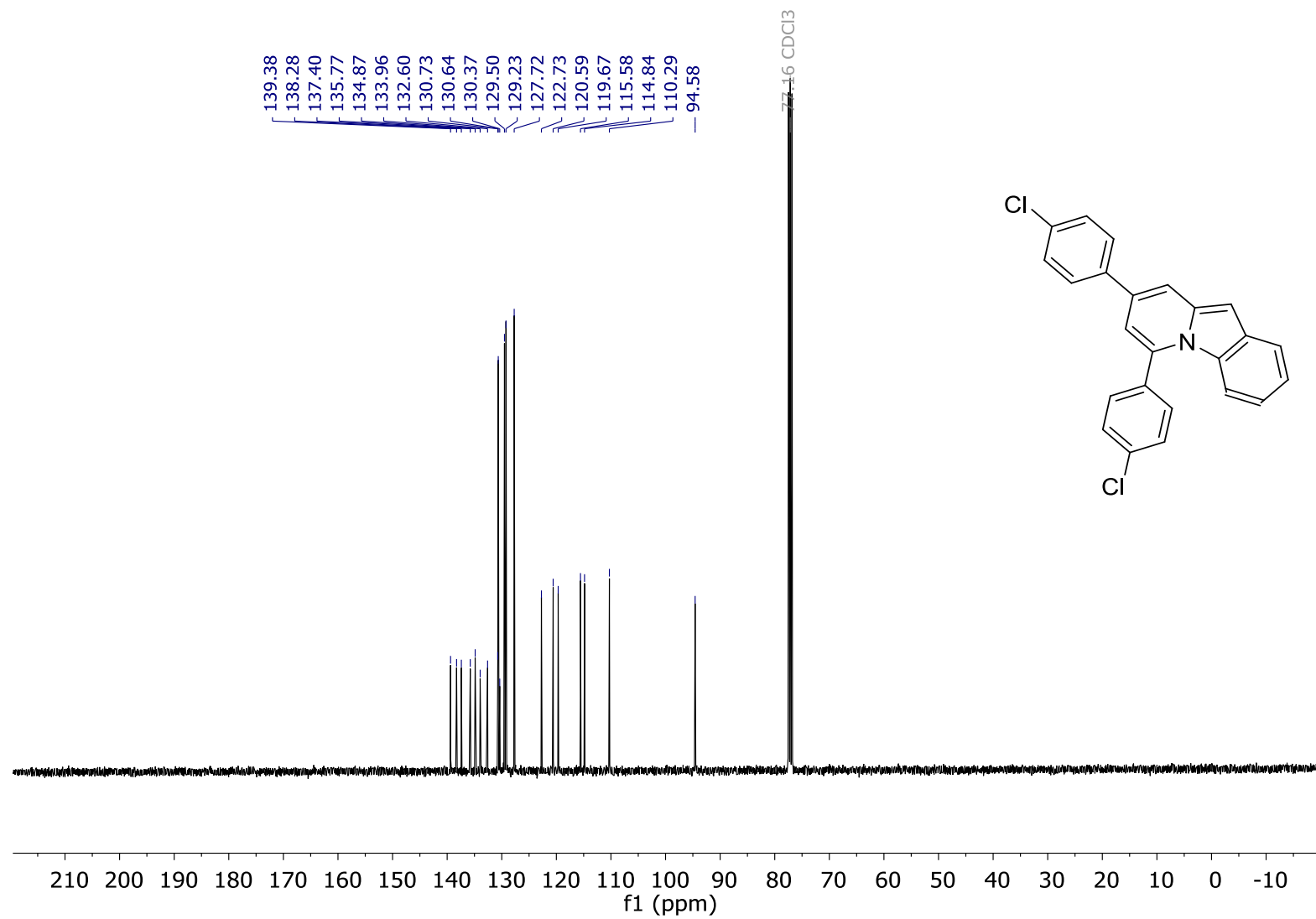


^1H - ^{13}C HSQC for 4v

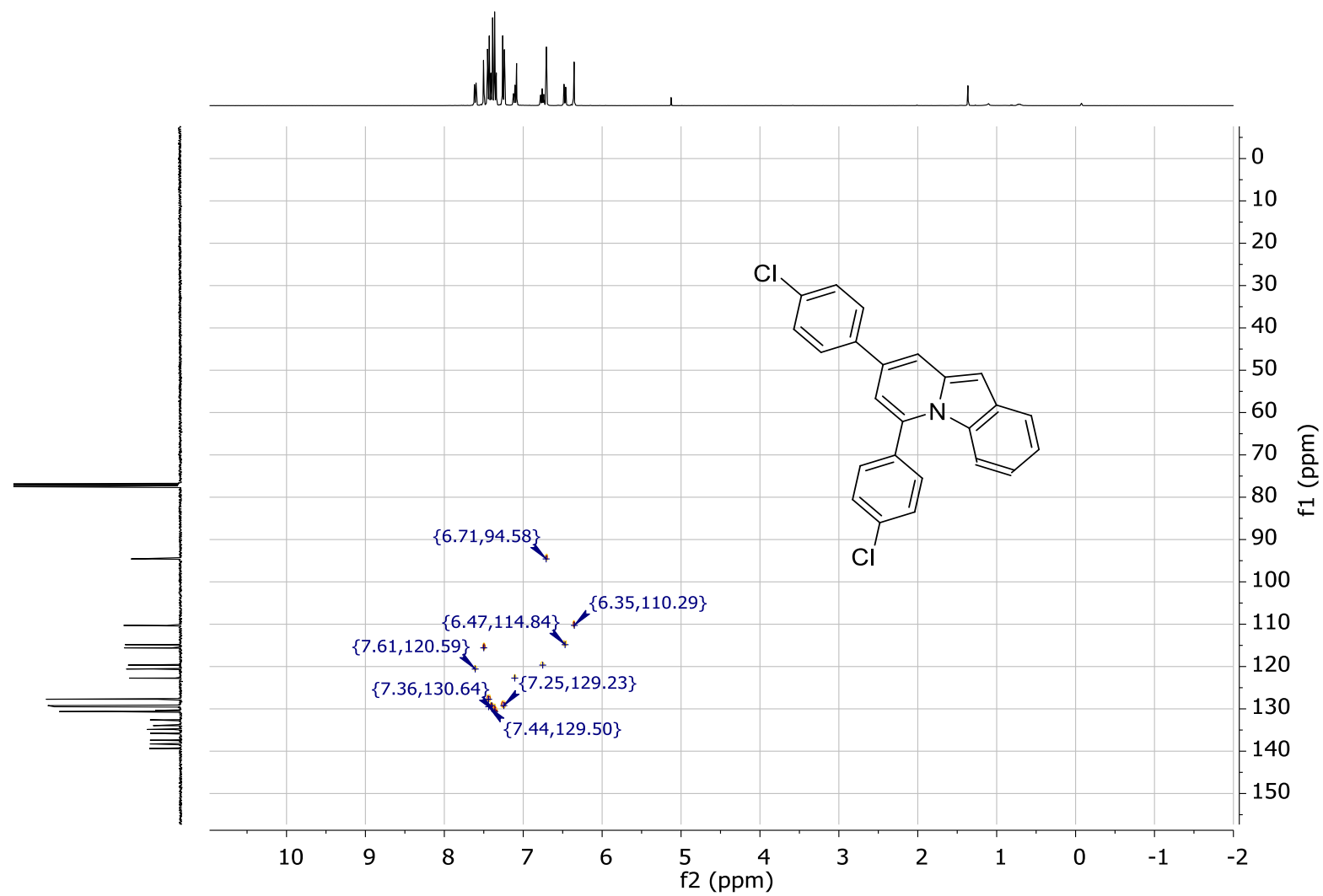




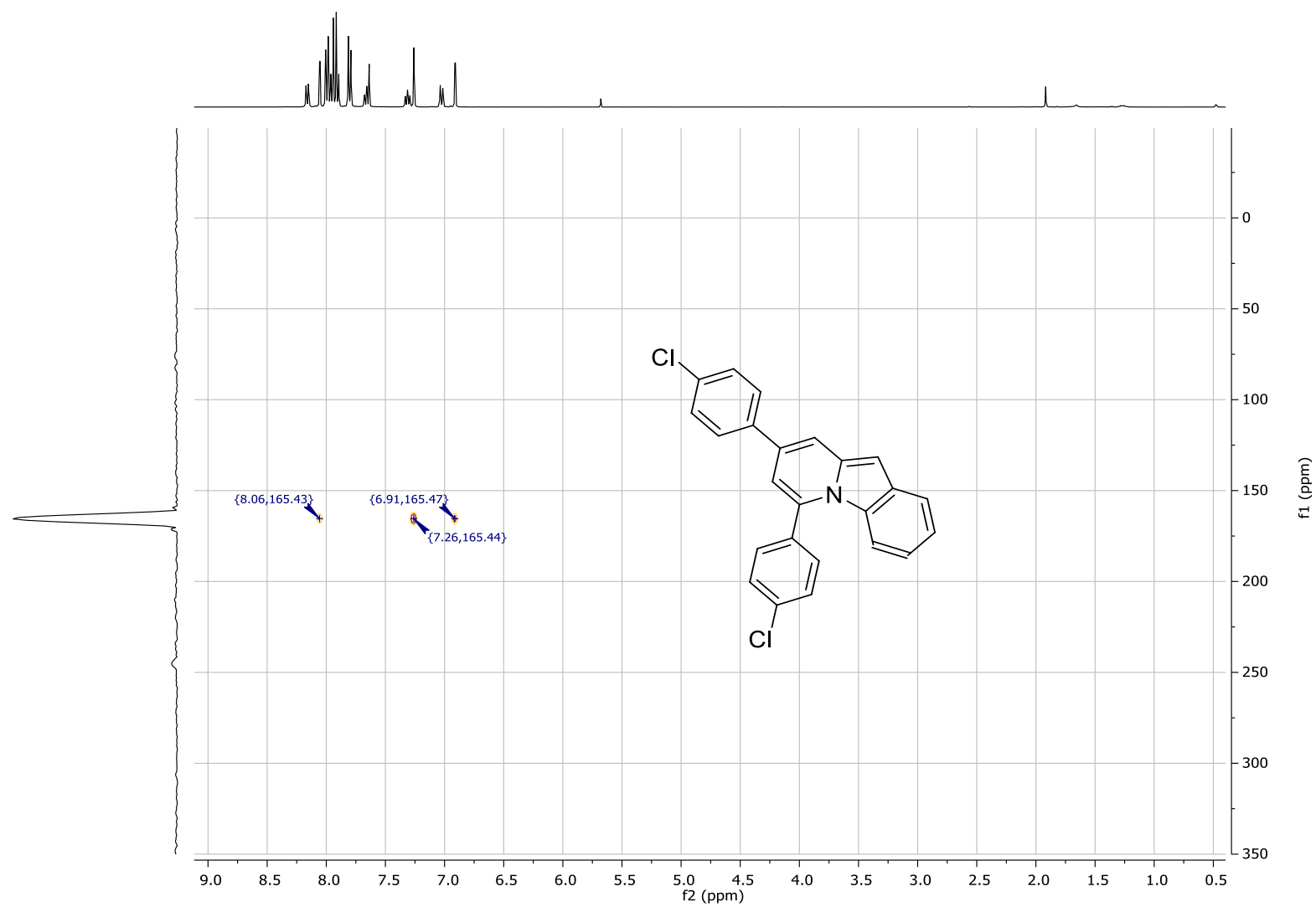
¹H NMR for 4w



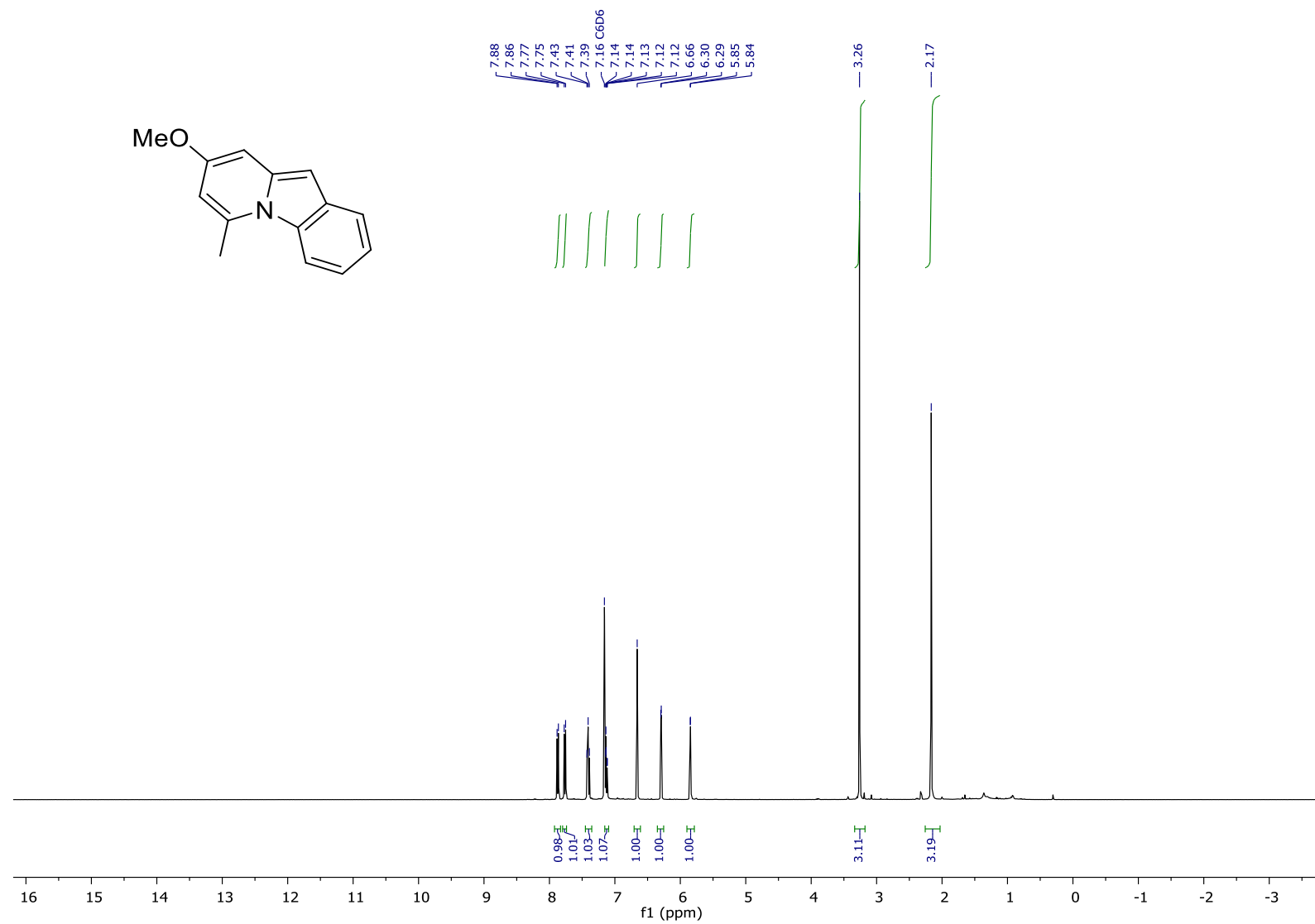
¹³C NMR for 4w



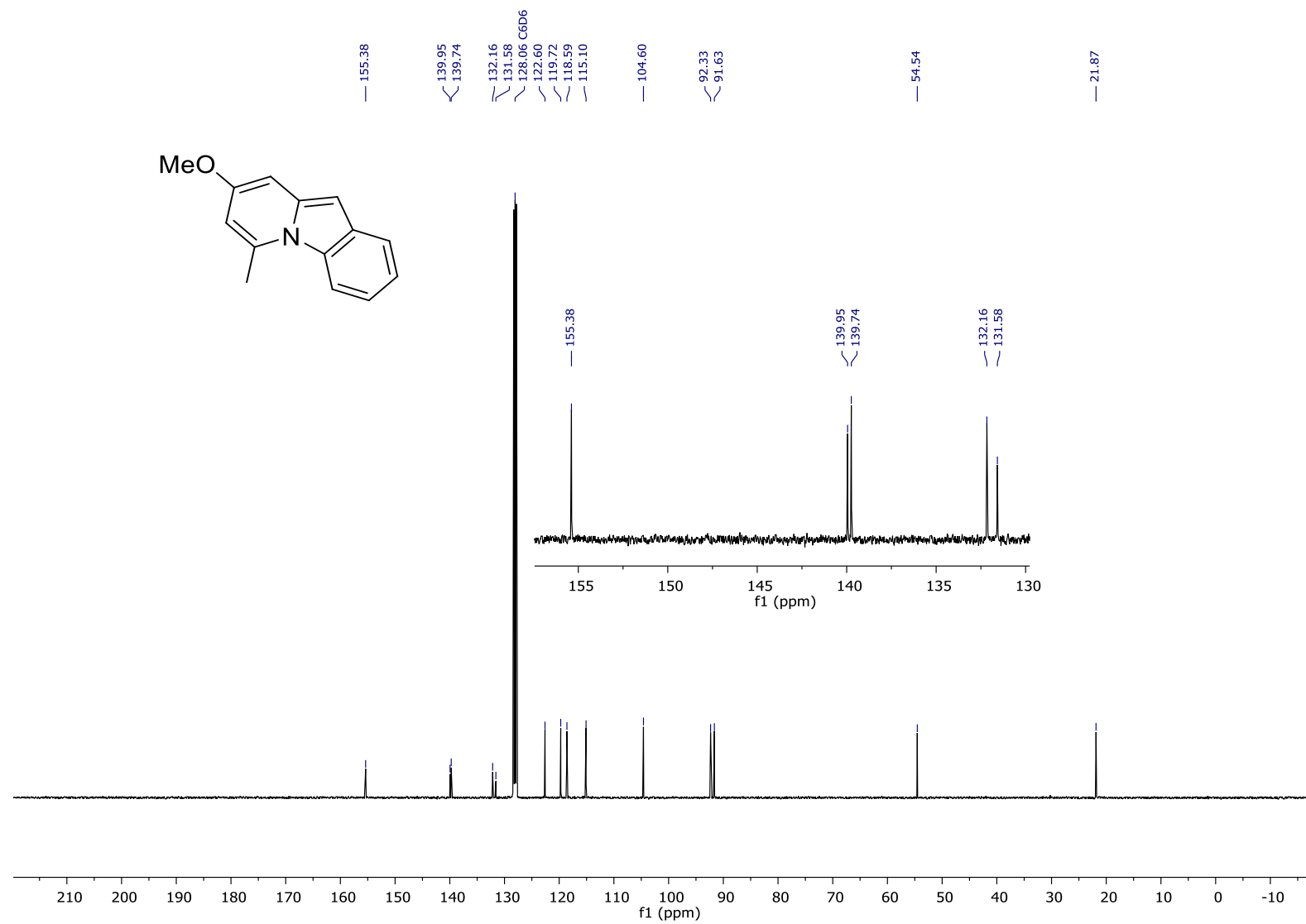
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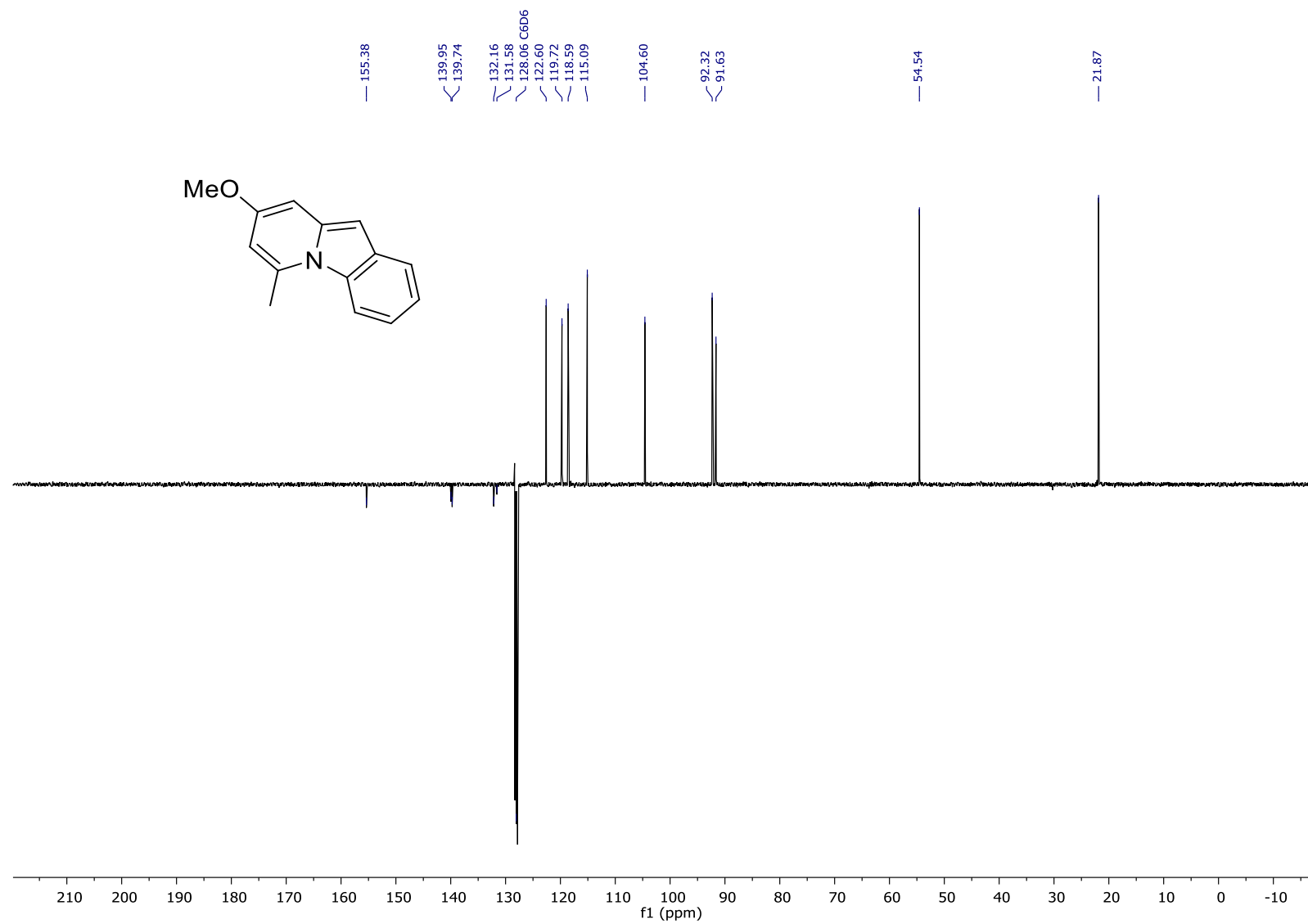
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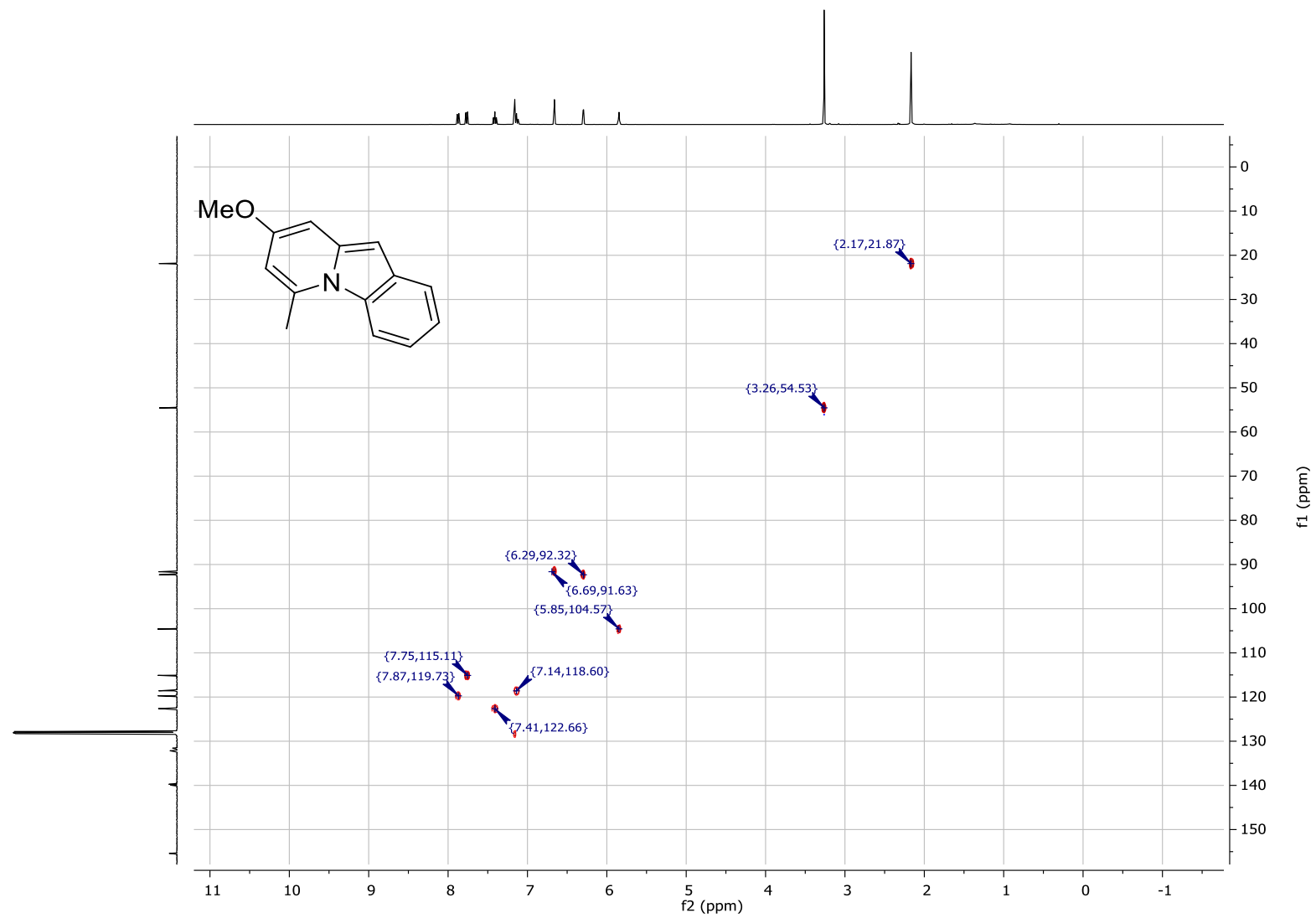
¹H NMR for 4x



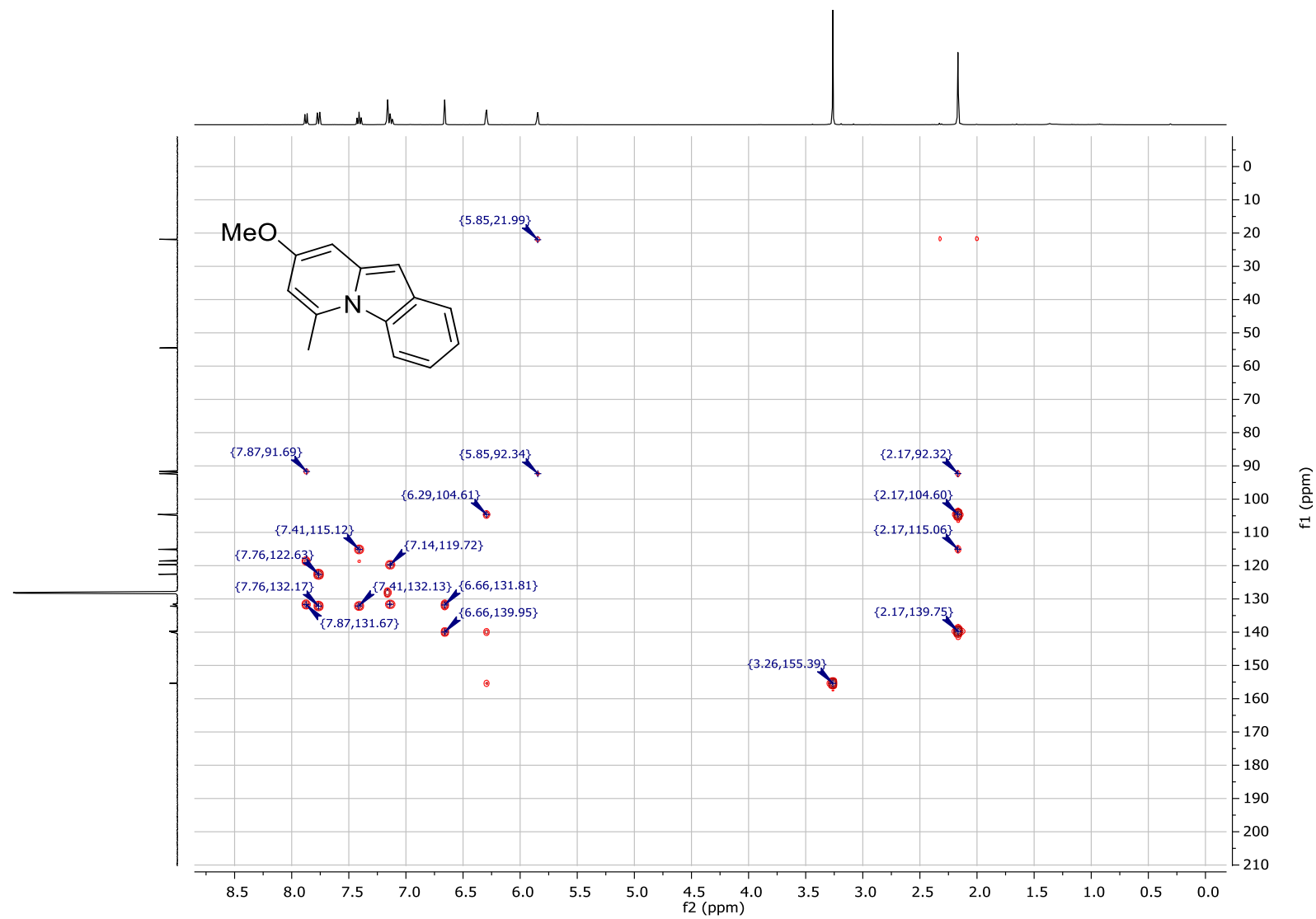
¹³C NMR for 4x



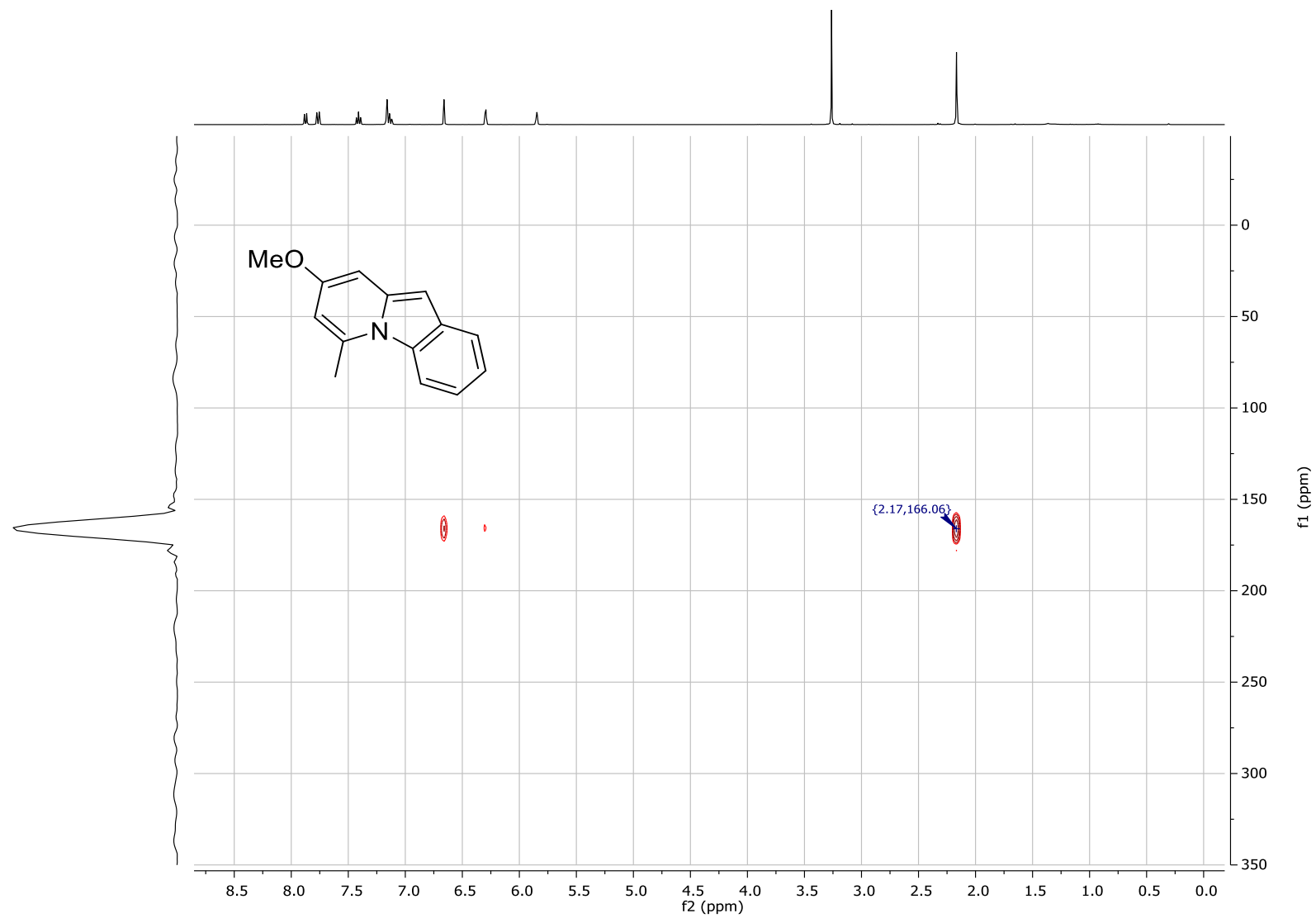
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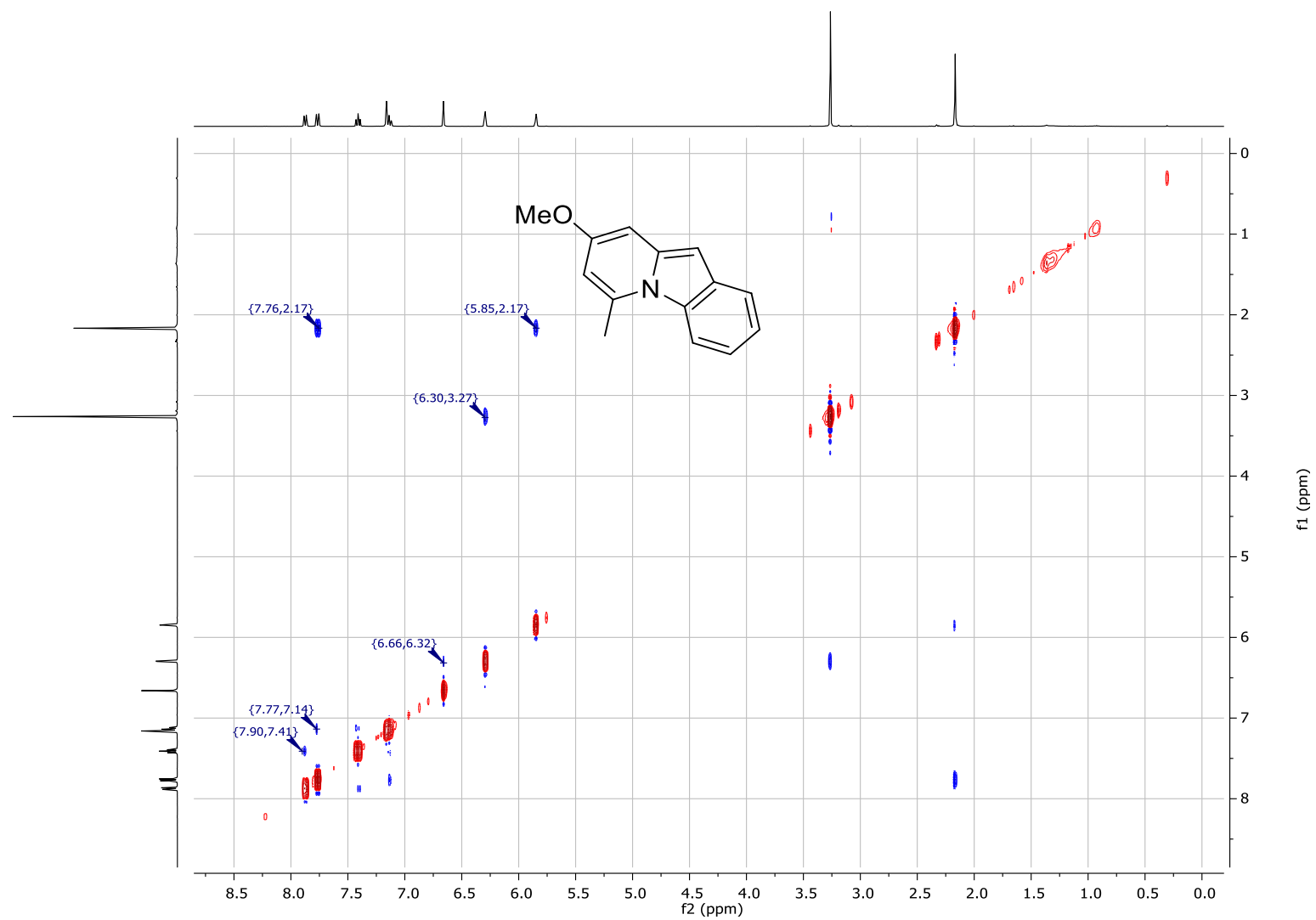
^1H - ^{13}C HSQC for 4x



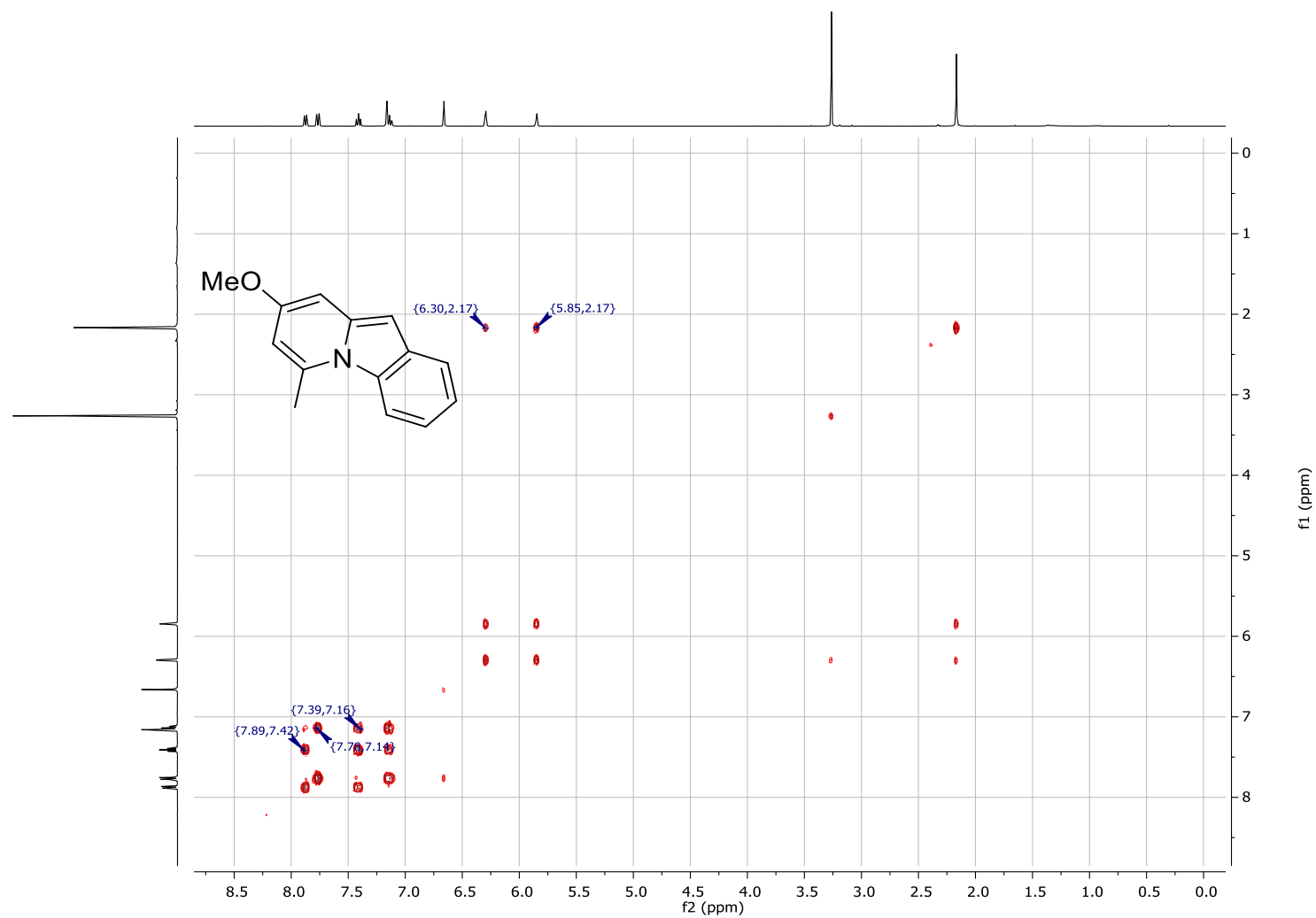
^1H - ^{13}C HMBC for 4x



^1H - ^{15}N HMBC for 4x



^1H - ^1H NOESY for 4x



^1H - ^1H COSY for 4x