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SUPPORTING INFORMATION

Triphenylamine as a Catalytic Donor in Electron Donor-Acceptor Complexes

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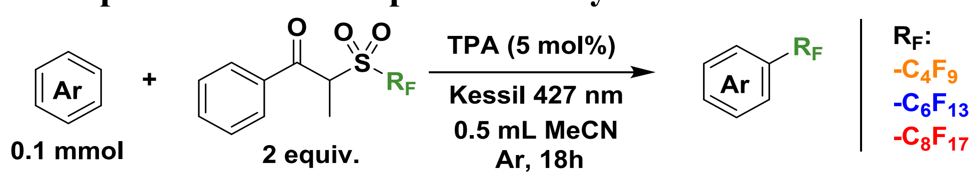
Table of Contents

1. General experimental procedures:

All reactions were carried out under an argon atmosphere using standard Schlenk technique. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (471 MHz) were recorded on an NMR spectrometer with $CDCl_3$ or d^6-acetone as the solvent. Chemical shifts of ^{1}H, ^{13}C and ^{19}F NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale (CDCl3: δ H = 7.26 ppm, δ C = 77.16 ppm). All coupling constants (J values) are reported in Hertz (Hz). High-resolution mass spectrometry was conducted through using atmospheric pressure chemical ionization (APCI) or electro-spraying ionization (ESI), on a Thermo-Scientific Exactive Orbitrap. Protonated molecular ions $[M+H]^+$ or sodium adducts $[M+Na]^+$ were used for empirical formula confirmation. Column chromatography was performed either on silica gel 200−300 mesh, or on C8-reversed phase perfluorinated silica gel. Analytical thin layer chromatography (TLC) was performed using Merck silica gel 60 F254 pre-coated plates (0.25 mm). All reactions were conducted in 10x75 mm Fisher culture-tubes and were irradiated utilizing Kessil PR160L 427nm (45W) LED lamps. All perfluoroalkylating reagents were synthesized, purified and characterized as reported previously in the literature. [1]

2. General procedure for the perfluoroalkylation of aromatics



Scheme S1. The aromatic substrate (0.1 mmol), the corresponding perfluoroalkylating reagent (0.15 – 0.2 mmol, and 0.005 mmol of triphenylamine were added into 0.5 mL acetonitrile inside a glass test tube capped with a rubber septum. Three freeze-pump-thaw cycles under argon were carefully performed before setting the reaction under light irradiation at 20°C using a Kessil PR160L 427nm (45W) LED lamp. Two desk fans were used to keep the temperature below 25°C. After the reaction was finished (14-18 h), the reaction crude was evaporated under reduced pressure, and purified through preparative thin-layer chromatography, using ethyl acetate/hexanes or dichloromethane/hexanes systems as the eluent.

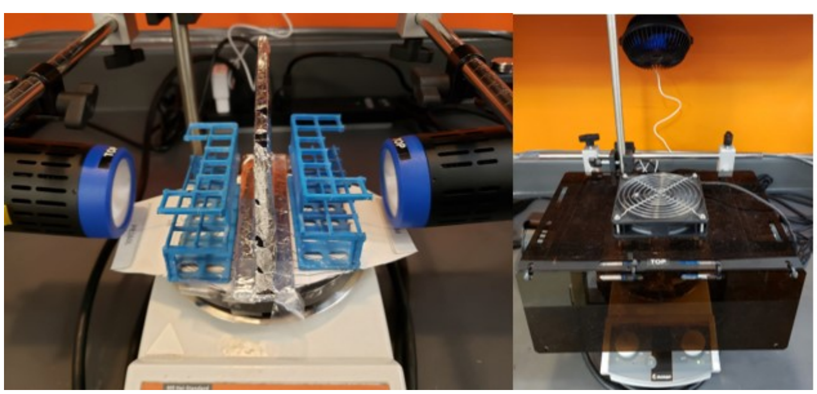


Figure S1. Left: close-up of the Kessil lamp setup, allowing for multiple reactions at the same time, all-absorbing around 200000 mW/cm2. Right: Covered setup and the two auxiliary fans to keep the temperature below 25°C.

3. Mechanistic Studies

3.1 Fluorescence quenching experiments

Solution UV-vis absorption spectra were collected on a JASCO V-670 spectrophotometer in quartz cuvettes from Starna Cells, Inc.

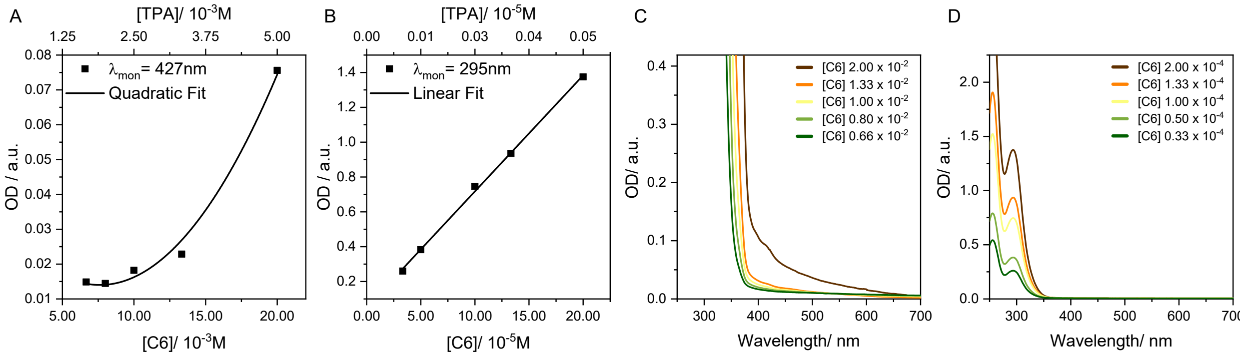


Figure S2. The dependency of absorbance on the concentration of a 1:4 mixture of TPA and C6(0.02 for A,C and 0.0002 for B,D, respectively), following a sequential dilution; whic shows quadratic relationship for l_{CT}=427 nm and a linear relationship for the $l_{p\text{-}p*}$=427 nm.

Steady-state photoluminescence spectra were collected using a Fluorolog 3 fluorometer from Horiba Jobin-Yvon. **The emission lifetimes** of the samples were determined by the Time-Correlated Single Photon Counting (TCSPC) technique using a DeltaDiode 373 nm pulsed laser diode controlled by a DeltaHub controller, both from Horiba Scientific.

A quenching plot for TPA in the presence of C6 was obtained by preparing the solutions of TPA (10^{-5} M) mixed with the corresponding amount of C6 solution (10^{-5} M) in acetonitrile. It is noteworthy that each sample was scanned once (quick scan 0.01s/nm) due to the rapid cyclization of TPA into *N*-phenylcarbazole in the presence of oxygen, as reported previously in the literature.[2]

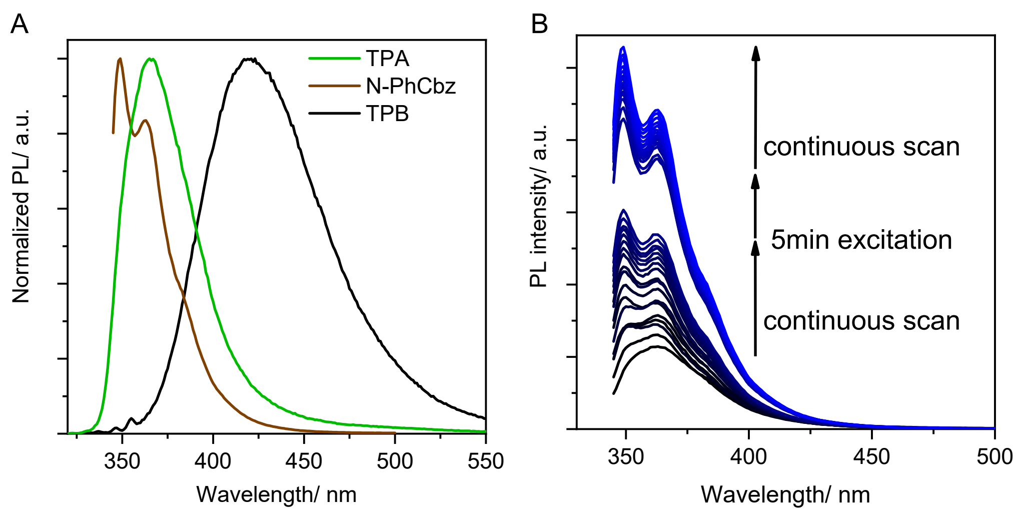


Figure S3. (A) Normalized photoluminescent spectra of TPA, TPB and *N*-phenyl carbazole (*N*-PhCbz) in MeCN. (B)The emergence of a new species(*N*-phenylcarbazole) when a TPA(10^{-5}M)-C6(10^{-4}M) solution is scanned and excited multiple times (scan rate of 0.1s/nm; λ_{ex}=340nm).

The Stern-Volmer plot was obtained from single point emission intensity measurement at 360nm to minimize the amount of photobleaching of TPA. Fluorescence quenching data were analyzed with the Stern–Volmer equation 1:

Equation S1
$$\frac{I}{I_0} = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q]$$

Where I_0 and I are the relative fluorescence intensities in the absence and presence of a quencher, respectively, [Q] is the concentration of the quencher, K_{SV} is the Stern–Volmer quenching constant, k_q is the bimolecular quenching rate constant and τ_0 the average lifetime of the fluorophore in the excited state (1.5ns for TPA).

When small molecules bind independently to a set of equivalent sites on a fluorophore, the equilibrium between free and bound molecules is given by the Hill equation:[3]

Equation S2
$$\log\left(\frac{I_0 - I}{I}\right) = \log K_b + n\, \log[Q]$$

where I_0, I, and [Q] are the same as those in Equation S1. K is the binding constant, and n is the number of binding sites per fluorophore.

Plotting log ((I_o-I)/I)) versus log [Q] (Figure S3B) gives a straight line whose slope equals n (1.2), and the intercept on the Y-axis equals log K (4.02). The complex of TPA with C6 is determined to be a 1:1 ratio with a binding constant of ~1.04×10^4.

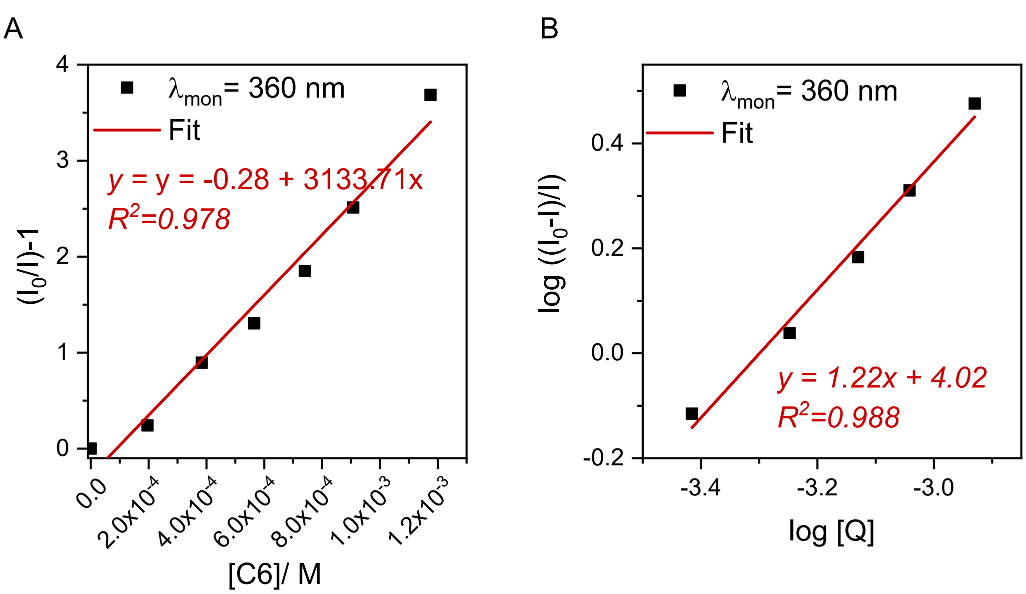


Figure S 4. (A) The Stern-Volmer quenching plot for TPA(10^{-5}M) and various concentrations of C6. (B) Quenching plot, according to the equation S2 and the fitted linear function (red), the calculated error for the y-intercept (i.e., log(K_b)) is 0.24, which corresponds to the binding constant of K_b =1.04±0.44 x 10^4

3.2 Density Functional Theory calculations

Density functional theory (DFT) calculations were performed using B3LYP functional and 6-31G(d) basis set, using geometry optimization and frequency options implemented in Gaussian 16. Rev. B.01.[4] The homolytic bond dissociation energies were calculated by the difference in energy of separated molecular segments (as neutral radicals) with the optimized structure energies.

Table S1

Atom	counts	Theoretical* hfc(G)	Fitted hfc (G)
^{15}N	1	8.8	8.5
^{1}H ortho	6	2.4	1.4
^{1}H para	3	3.6	1.9
^{1}H meta	6	1.5	N.A.

*Obtained from the isotropic fermi contact coupling, in the DFT (B3LYP, 6-31g(d)) optimized $TPA^{\bullet+}$.

3.3 EPR Measurements

Continuous-wave EPR measurements were carried out using a Bruker (Billerica, Elexsys E580) X-band spectrometer fitted with a standard EPR flat cell, from Wilmad-lab glass. The data were obtained at room temperature in air, using MeCN solutions of TPA and C8 (10^{-3} M). An equimolar mix was done in situ and irradiated with a Kessil PR160L 427nm (45W) LED lamp for 5 minutes before introducing the resulting yellow-coloured solution in the flat cell for measurement. The baseline of the obtained EPR signal was corrected using polynomial baseline functions (in the Xepr software from bruker) and the data were fitted with a single radical with hyperfine interactions through N:Ho:HP 1:6:3 matching with the TPA radical cation using a built in software from Bruker.

3.4 Transient absorption setup and sample preparation

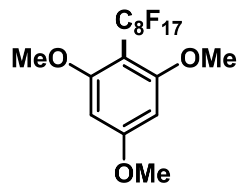
Experiments were conducted using a laser flash photolysis setup (Luzchem). A Nd:YAG (Continuum Surelite CLII-10, 10 Hz, 450 mJ at 1064 nm) laser was used for excitation using its third harmonic with a wavelength centered at 355 nm. 10 mJ laser pulses were used with a pulse width of 6 ns. A 150 W Xe lamp was used as the monitoring light source. The detector consisted of a photomultiplier tube (PMT) connected to a digital oscilloscope (Tektronix TDS2012). All data was collected via the commercially available LFP 7.0 software (Luzchem).

Samples containing TPA alone (~5mM) or in the presence of C6 (~20mM) in acetonitrile were freshly prepared in a 10 x 10 mm quartz cell. O_2 was removed by bubbling argon through the solution and sealed with a septum. Samples were irradiated with at least 10 laser shots to acquire ΔOD temporal evolution traces. The time per division recorded by the detector was varied from

10 μs to 250 μs on a sample-to-sample basis to optimize the time window to fully capture the temporal events. Spectra were acquired at 10 nm intervals in the 400-710 nm range

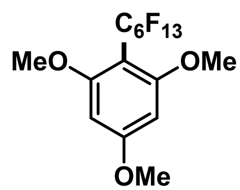
4. Characterization data of reported compounds:

PF1



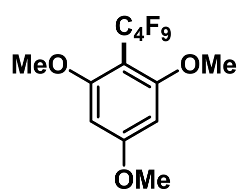
2-(perfluorooctyl)-1,3,5-trimethoxybenzene (1) [5]: White solid. 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.15 (s, 2H), 3.82 (d, J = 18.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.77, 161.70, 161.66, 91.61, 56.18, 55.20. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.86, -102.66, -121.70, -122.07, -122.81, -126.00.

PF2



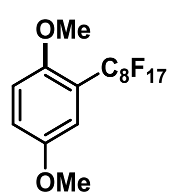
2-(perfluorohexyl)-1,3,5-trimethoxybenzene (2) [5]: White solid. 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.15 (s, 2H), 3.82 (d, J = 18.3 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.26, 162.15, 92.12, 56.71, 55.73. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.69, -102.71, -122.04, -122.16, -122.62, -126.10.

PF3



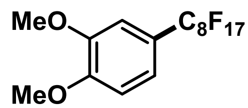
2-(perfluorobutyl)-1,3,5-trimethoxybenzene (3) [5]: White solid. 50% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.14 (d, J = 1.0 Hz, 2H), 3.82 (d, J = 19.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.25, 162.14, 92.11, 56.72, 55.74. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.64, -102.90, -122.97, -126.44.

PF4



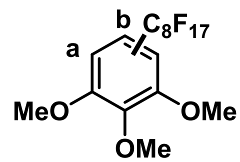
2-(perfluorooctyl)-1,4-dimethoxybenzene (4):[6] White solid. 49% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 – 6.91 (m, 3H), 3.81 (d, J = 10.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.56, 119.14, 114.61, 57.13, 56.30. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.77, -107.66, -121.09, -121.65, -121.91, -122.69, -126.12.

PF5



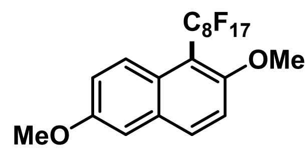
4-(perfluorooctyl)-1,2-dimethoxybenzene (5):[6] White solid. 46% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.02 (d, *J* = 2.1 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 3.93 (d, *J* = 7.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.77, 148.88, 120.05, 110.77, 109.33, 55.90. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.60, -109.60, -121.26, -121.81, -122.71, -126.08.

PF6



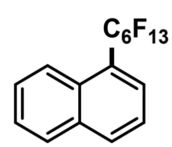
4- and 5-(perfluorooctyl)-1,2,3-trimethoxybenzene (6): White solid. 20% yield (inseparable mixture of isomers 1:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 9.0 Hz, 1H), 6.78 (s, 2H), 6.73 (d, *J* = 9.0 Hz, 1H), 3.96 – 3.85 (m, 16H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.35, 153.74, 143.32, 124.07, 107.08, 104.61, 62.14, 61.32, 61.18, 56.73, 56.48. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.78, -103.27, -104.64, -106.63, -109.98, -120.94, -121.27, -121.61, -121.92, -122.69, -126.05.

PF7



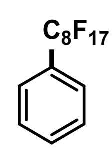
1-(perfluorooctyl)-2,6-dimethoxynaphthalene (8): White solid. 43% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.7 Hz, 1H), 7.90 (d, *J* = 9.1 Hz, 1H), 7.31 (d, *J* = 9.1 Hz, 1H), 7.21 (dd, *J* = 9.6, 2.8 Hz, 1H), 7.10 (d, *J* = 2.8 Hz, 1H), 3.93 (d, *J* = 20.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.86, 149.88, 136.22, 128.69, 126.18, 115.19, 57.55, 55.14. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.76, -99.99, -120.64, -121.66, -122.09, -122.66, -126.07.

PF8

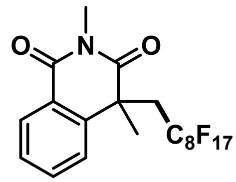


1-perfluorohexylnaphthalene (9)[1]**:** White solid. 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.6 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.95 – 7.90 (m, 1H), 7.83 (d, *J* = 7.3 Hz, 1H), 7.65 – 7.53 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.10, 133.44, 129.01, 126.39, 124.26. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.78, -104.40, -120.21, -121.48, -122.68, -126.12.

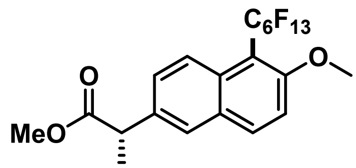
PF9



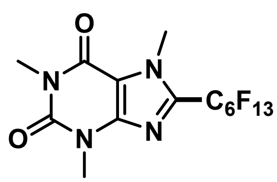
Perfluorooctylbenzene (10)[1]**:** Yellow oil. 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.54 (m, 3H), 7.51 (dd, *J* = 8.3, 6.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.33, 129.39, 129.20, 129.01, 127.28, 127.23, 127.18. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.82, -110.88, -121.30, -121.90, -122.73, -126.12.

PF10 

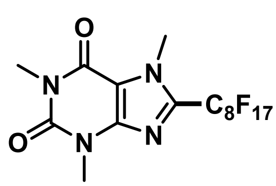
4-(perfluorooctyl)-2,4-dimethylisoquinoline-1,3(2H,4H)-dione (11): Off-white solid. 15% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (dd, J = 7.9, 1.5 Hz, 1H), 7.66 (td, J = 7.6, 1.5 Hz, 1H), 7.56 – 7.39 (m, 2H), 3.42 (s, 4H), 2.84 – 2.65 (m, 1H), 1.68 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.01, 164.16, 141.05, 134.12, 129.74, 128.45, 126.11, 124.49, 43.71, 41.22, 32.36, 30.11, 27.85. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.82, -107.59, -108.18, -112.52, -113.10, -121.53, -121.94, -122.75, -123.77, -126.09.

PF11 

Naproxen methyl ester-C_6F_{13} (13)[1]: White solid. 30% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 9.2 Hz, 1H), 7.98 (d, J = 9.1 Hz, 1H), 7.70 (d, J = 2.1 Hz, 1H), 7.49 (dd, J = 9.2, 2.1 Hz, 1H), 7.34 (d, J = 9.1 Hz, 1H), 3.97 (s, 3H), 3.87 (q, J = 7.1 Hz, 1H), 3.68 (s, 3H), 1.58 (d, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.17, 159.43, 136.57, 135.32, 131.77, 129.85, 128.48, 127.27, 125.41, 115.06, 57.80, 52.56, 45.33, 18.77. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.77, -100.14, -120.66, -121.95, -122.60, -126.03.

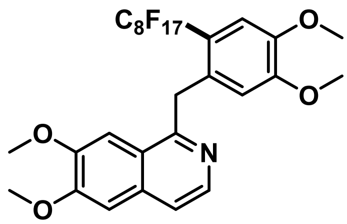
PF12 

Caffeine-C_6F_{13} (14)[1]: White solid. 32% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.19 (s, 3H), 3.59 (s, 3H), 3.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.46, 147.40, 147.01, 33.85, 29.92, 28.24. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.69, -108.96, -120.96, -121.36, -122.67, -126.03.

PF13 

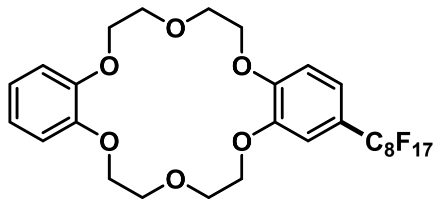
Caffeine-C_8F_{17} (15)[1]: White solid. 30% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.19 (d, J = 1.9 Hz, 3H), 3.60 (s, 3H), 3.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.45, 151.27, 33.84, 29.92, 28.24. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.68, -108.89, -120.91, -121.13, -121.67, -122.65, -126.05.

PF14



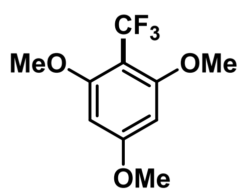
Papaverine-C_8F_{17} (16): White solid. 15% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 5.8 Hz, 1H), 7.53 (d, *J* = 5.8 Hz, 1H), 7.22 (s, 1H), 7.10 (s, 1H), 7.03 (s, 1H), 6.44 (s, 1H), 4.76 (s, 2H), 4.03 (s, 3H), 3.89 (s, 3H), 3.83 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 151.88, 147.67, 123.31, 119.85, 117.99, 113.87, 111.41, 105.66, 104.14, 56.48, 56.41, 56.15, 56.01, 30.00. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.73, -104.30, -120.37, -121.47, -122.65, -126.04.

PF15



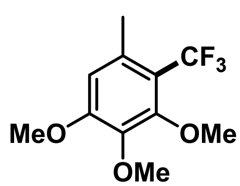
2-(perfluorooctyl)dibenzo[b,k][1,4,7,10,13,16]hexaoxacyclooctadecane(17): White solid. 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (dt, *J* = 8.5, 2.2 Hz, 1H), 7.00 (d, *J* = 2.3 Hz, 1H), 6.88 (dddd, *J* = 17.2, 9.6, 7.1, 3.0 Hz, 5H), 4.31 – 3.89 (m, 16H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.74, 148.70, 129.03, 121.68, 120.85, 113.31, 112.24, 111.35, 70.13, 69.84, 69.00, 68.76, 68.61. ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.99, -109.76, -121.48, -121.95, -122.83, -126.18.

TF1



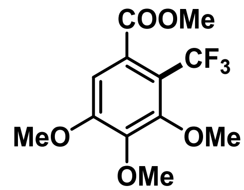
2-(trifluoromethyl)-1,3,5-trimethoxybenzene (TF1)[7]: White solid. 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.13 (s, 2H), 3.83 (d, *J* = 1.3 Hz, 10H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.52, 160.41, 125.44, 123.27, 100.72, 91.24, 56.29, 55.36. ^{19}F NMR (471 MHz, $CDCl_3$) δ -53.96.

TF2



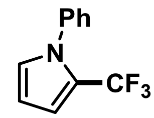
1,2,3-trimethoxy-5-methyl-4-(trifluoromethyl)benzene (TF2)[7]: Colorless oil. 56% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.49 (s, 1H), 3.95 – 3.80 (m, 9H), 2.42 (q, *J* = 3.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.03, 153.28, 140.81, 132.99, 128.67, 125.85, 123.67, 115.24, 110.59, 61.63, 60.70, 55.80, 21.40. ^{19}F NMR (471 MHz, $CDCl_3$) δ -54.30.

TF3



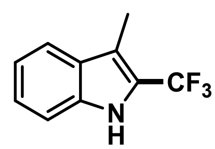
methyl 3,4,5-trimethoxy-2-(trifluoromethyl)benzoate (TF3)[7]: Colorless oil. 45% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (s, 1H), 3.95 (s, 3H), 3.90 (d, J = 8.2 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.86, 156.27, 144.59, 128.81, 124.54, 122.36, 115.13, 107.27, 62.27, 61.31, 56.66, 53.41. ^{19}F NMR (471 MHz, $CDCl_3$) δ -56.86.

TF4



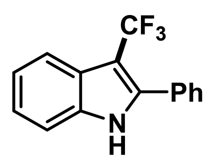
1-phenyl-2-(trifluoromethyl)-1H-pyrrole (TF4)[7]: Yellow oil. 46% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.35 (m, 5H), 6.88 (dd, J = 2.8, 1.7 Hz, 1H), 6.73 (dd, J = 4.0, 1.8 Hz, 1H), 6.32 – 6.22 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.50, 129.38, 128.88, 127.65, 126.91, 122.62, 120.50, 113.12, 108.61. ^{19}F NMR (471 MHz, $CDCl_3$) δ -55.95.

TF5



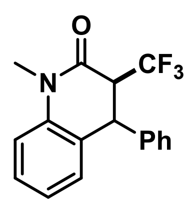
3-methyl-2-(trifluoromethyl)-1H-indole (TF5)[7]: White solid. 50% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.42 – 7.29 (m, 2H), 7.20 (ddd, J = 8.0, 6.8, 1.1 Hz, 1H), 2.45 (d, J = 1.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.58, 128.46, 125.16, 123.58, 120.78, 120.48, 114.45, 111.95, 8.72. ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.64.

TF6



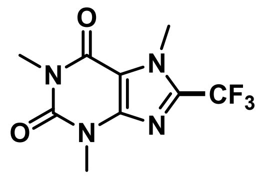
2-phenyl-3-(trifluoromethyl)-1H-indole (TF6)[7]: Yellow solid. 38% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.89 – 7.80 (m, 1H), 7.63 – 7.56 (m, 2H), 7.54 – 7.37 (m, 4H), 7.35 – 7.21 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.92, 135.28, 131.49, 129.77, 129.42, 129.06, 123.85, 122.11, 120.45, 111.47, 103.83. ^{19}F NMR (471 MHz, $CDCl_3$) δ -52.91.

TF7



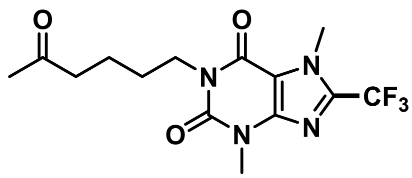
3-(trifluoromethyl)-1-methyl-4-phenyl-3,4-dihydroquinolin-2(1H)-one (TF7):[8] Colorless oil. 42% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (ddd, J = 8.6, 7.3, 1.6 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.24 – 7.19 (m, 2H), 7.14 – 7.09 (m, 2H), 7.01 (dd, J = 7.4, 1.7 Hz, 2H), 4.51 (s, 1H), 3.66 (qd, J = 9.4, 1.4 Hz, 1H), 3.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.63, 140.21, 139.34, 129.33, 128.82, 127.78, 127.06, 124.69, 124.33, 115.39, 53.25, 42.14, 30.39. ^{19}F NMR (471 MHz, $CDCl_3$) δ -67.29.

TF8



Caffeine-CF_3 (TF8)[7]: White solid. 48% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.16 (s, 3H), 3.59 (s, 3H), 3.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.48, 151.36, 146.53, 119.27, 117.12, 109.66, 33.20, 29.91, 28.22. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.39.

TF9



Pentoxifylline-CF_3 (TF9):[9] Off-white solid. 41% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.14 (d, *J* = 1.4 Hz, 3H), 4.01 (t, *J* = 6.9 Hz, 2H), 3.57 (s, 3H), 2.49 (t, *J* = 6.9 Hz, 2H), 2.13 (s, 3H), 1.70 – 1.59 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.96, 155.70, 151.46, 146.95, 139.48, 139.16, 128.83, 119.65, 117.50, 110.06, 43.47, 41.51, 33.57, 33.56, 30.35, 30.22, 29.65, 27.69, 21.27. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.41.

5. References

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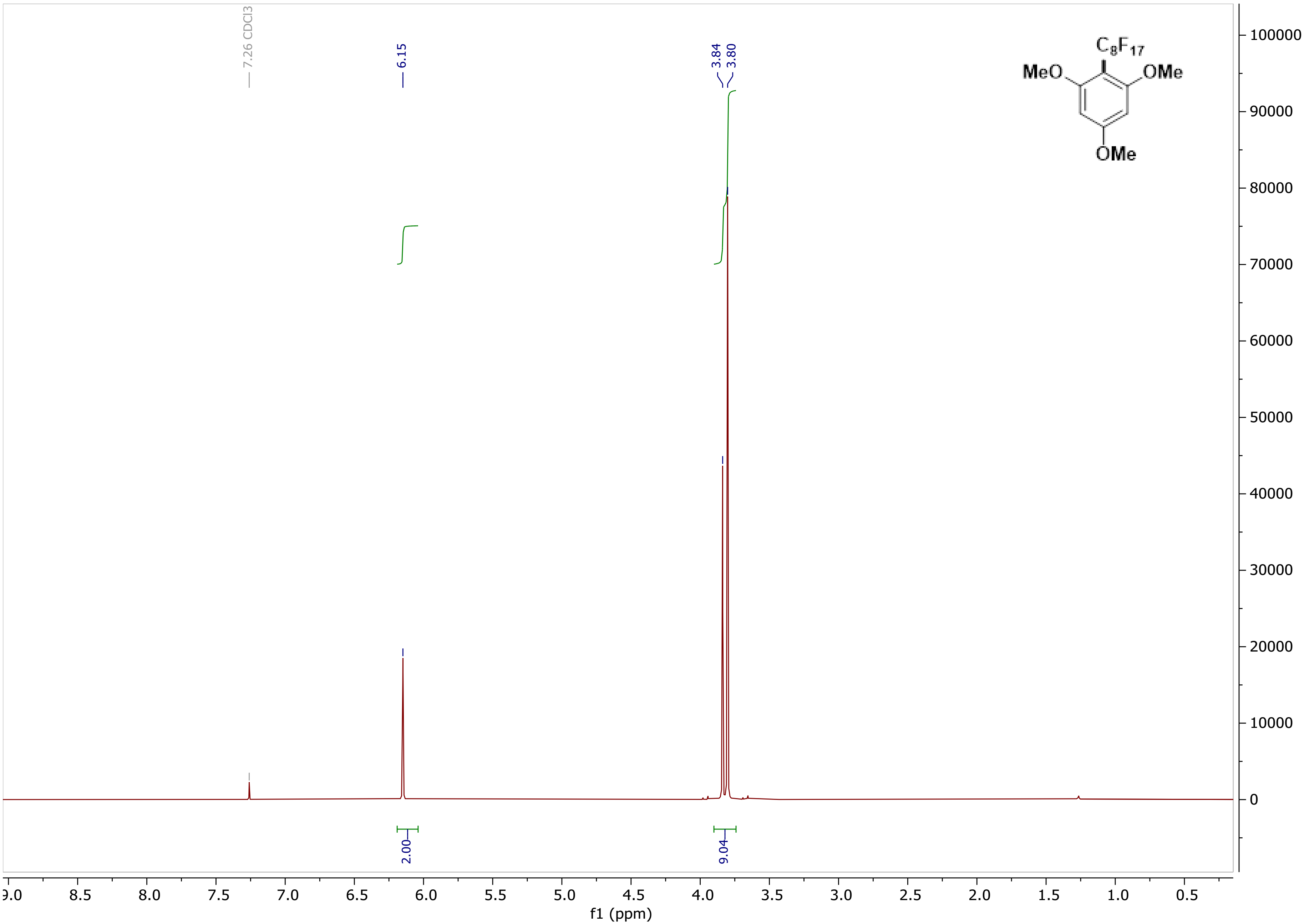
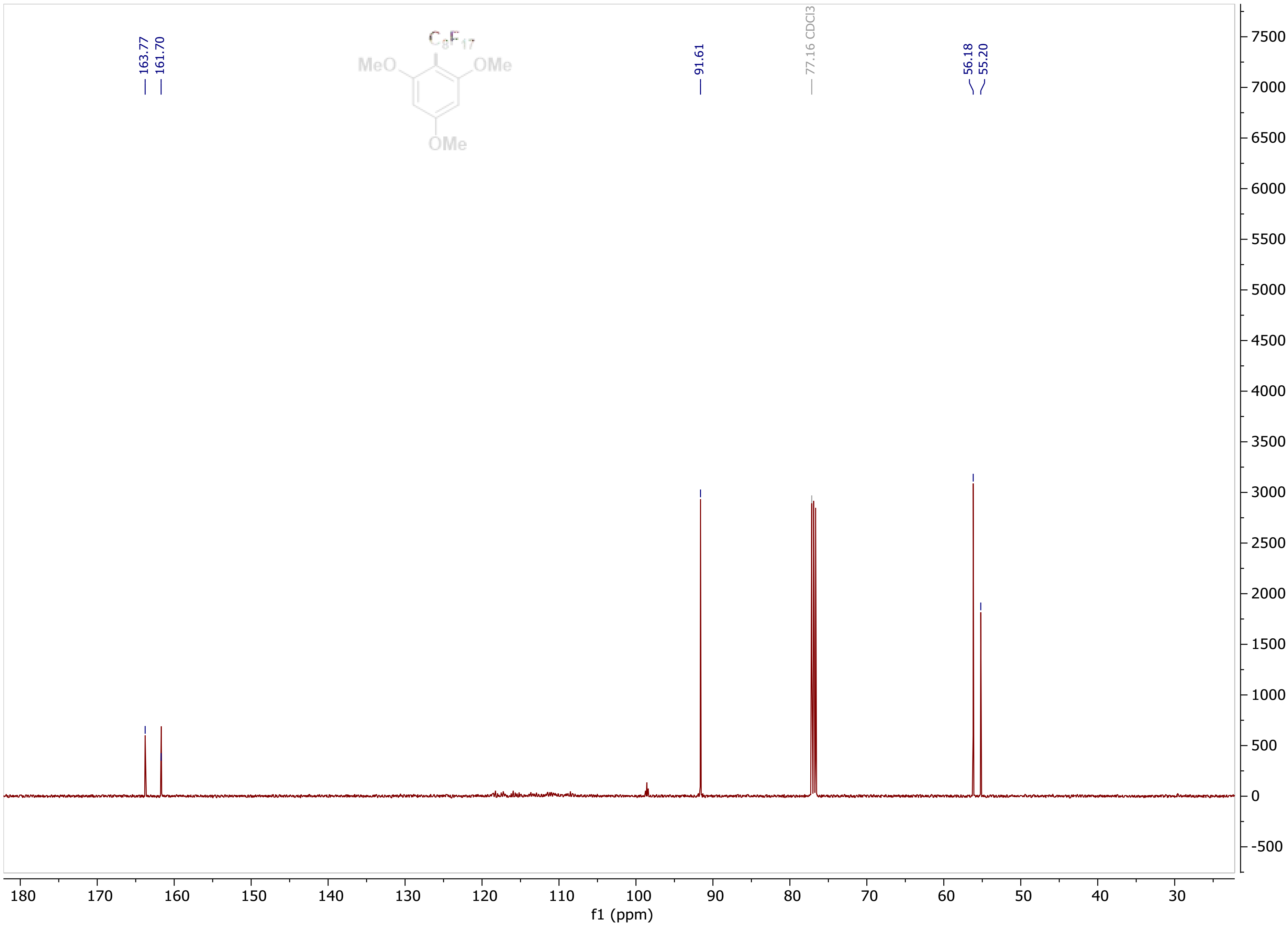
Spectra collection

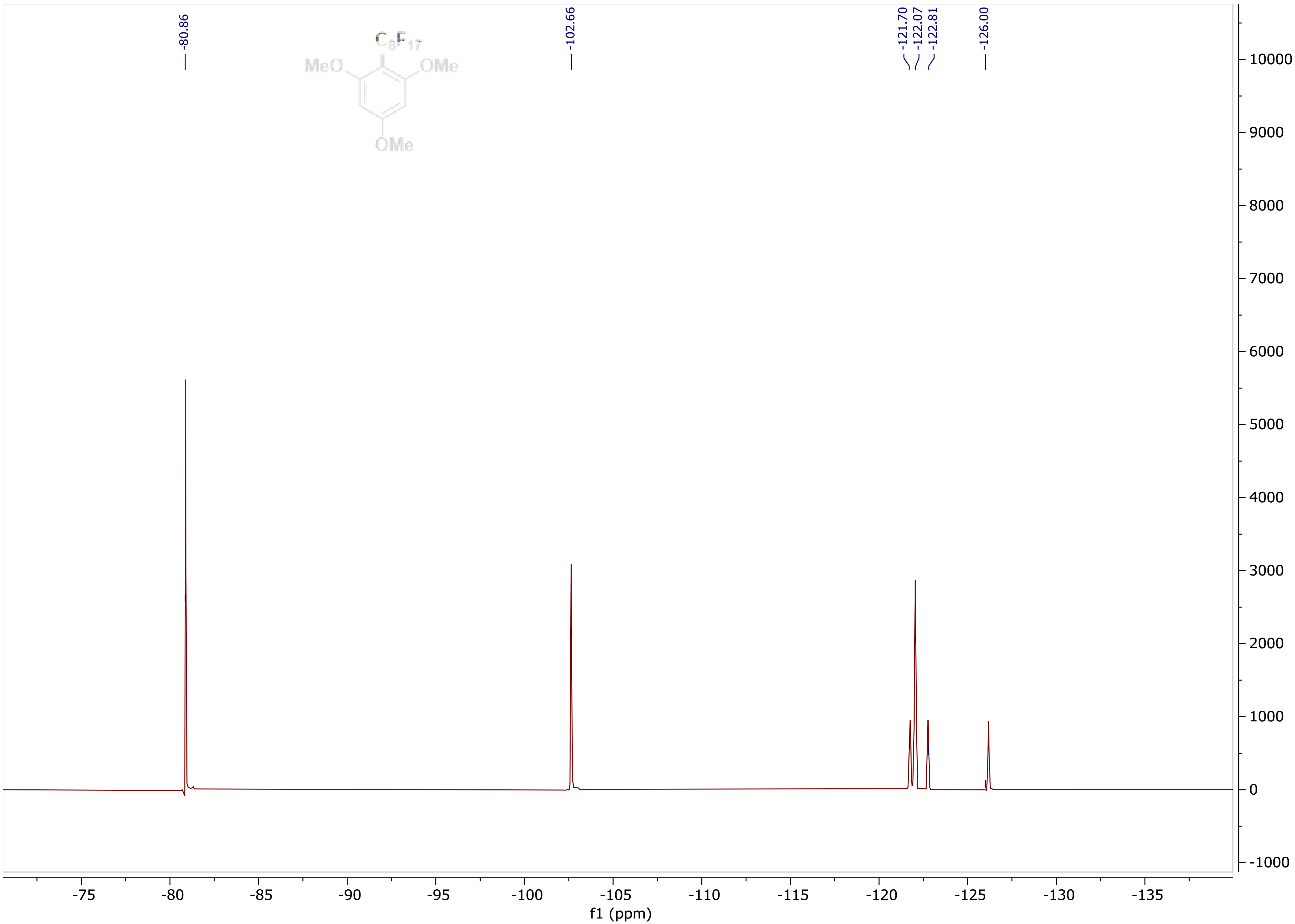
^{1}H NMR of PF1, $CDCl_3$, 500 MHz



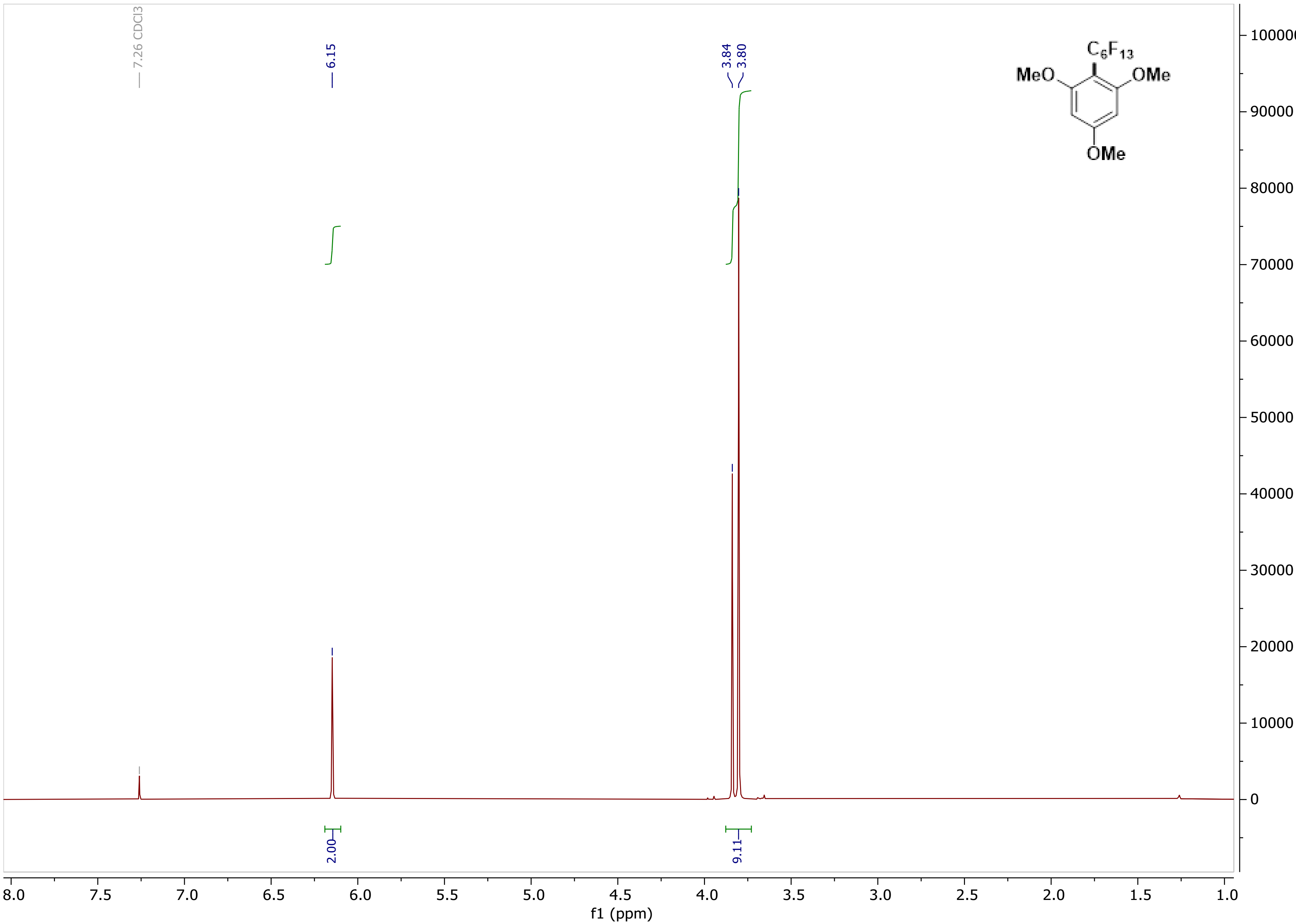
^{13}C NMR of PF1, $CDCl_3$, 126 MHz



^{19}F NMR of PF1, $CDCl_3$, 471 MHz



[1]H NMR of PF2, $CDCl_3$, 500 MHz



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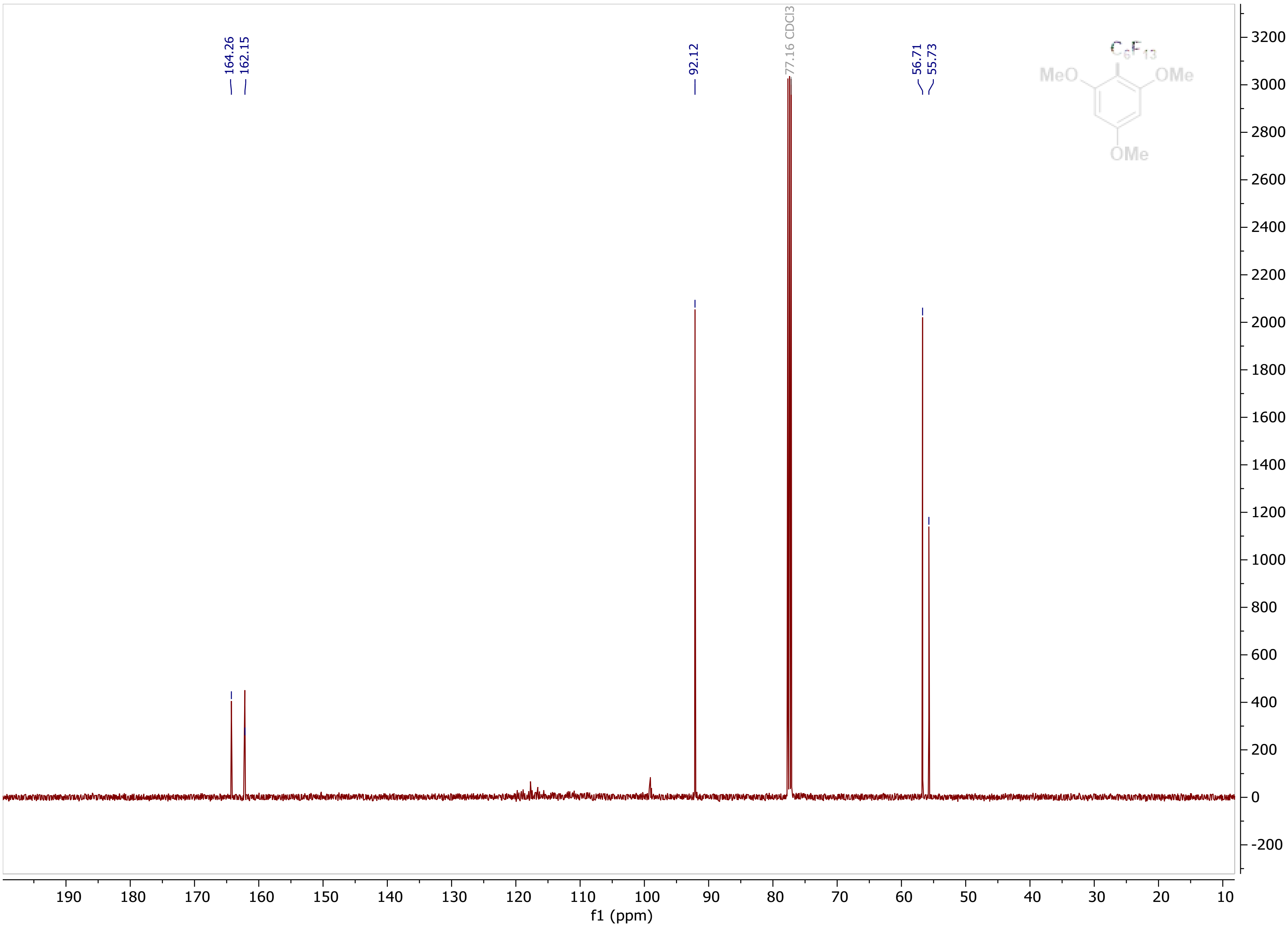

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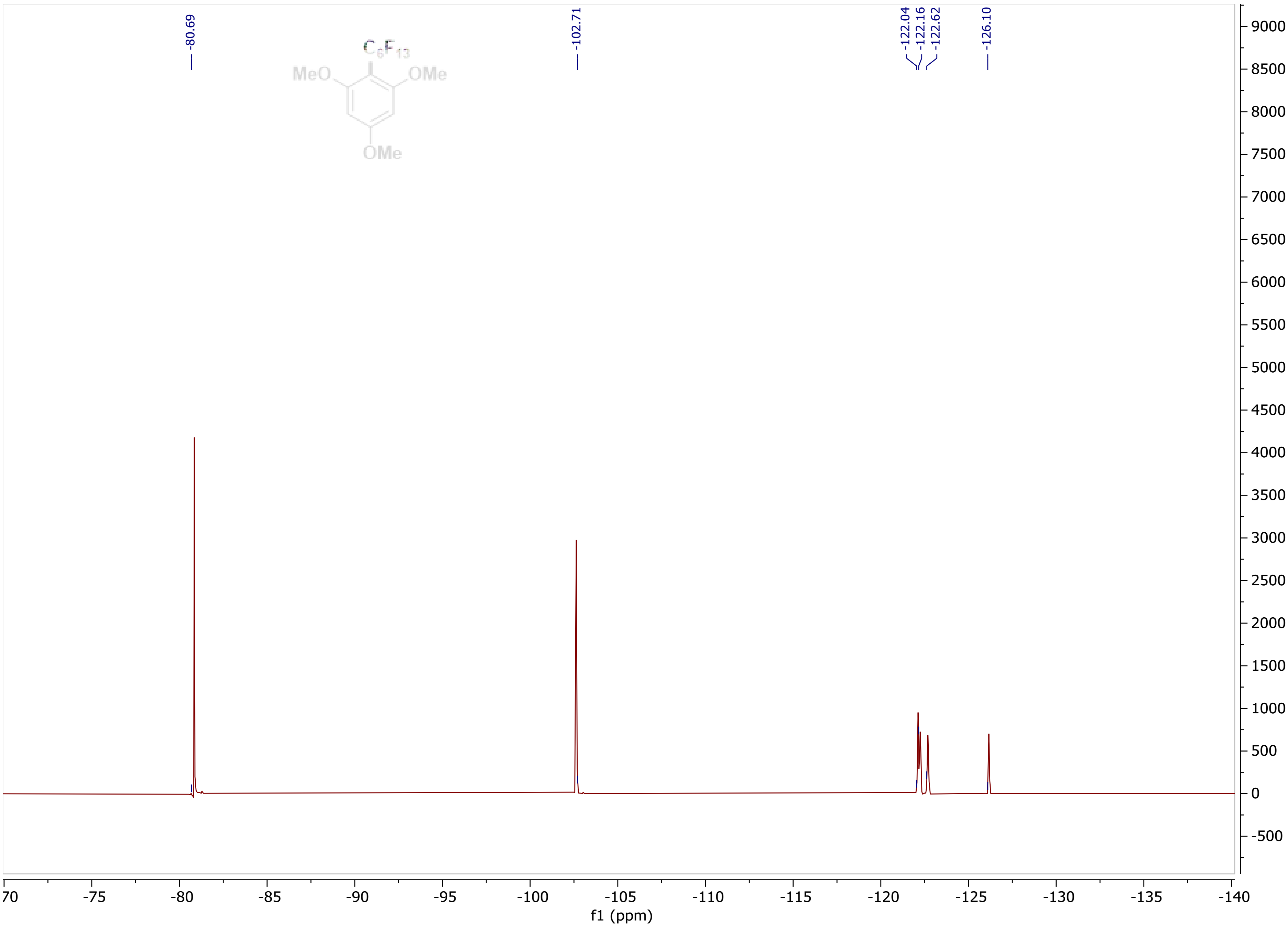

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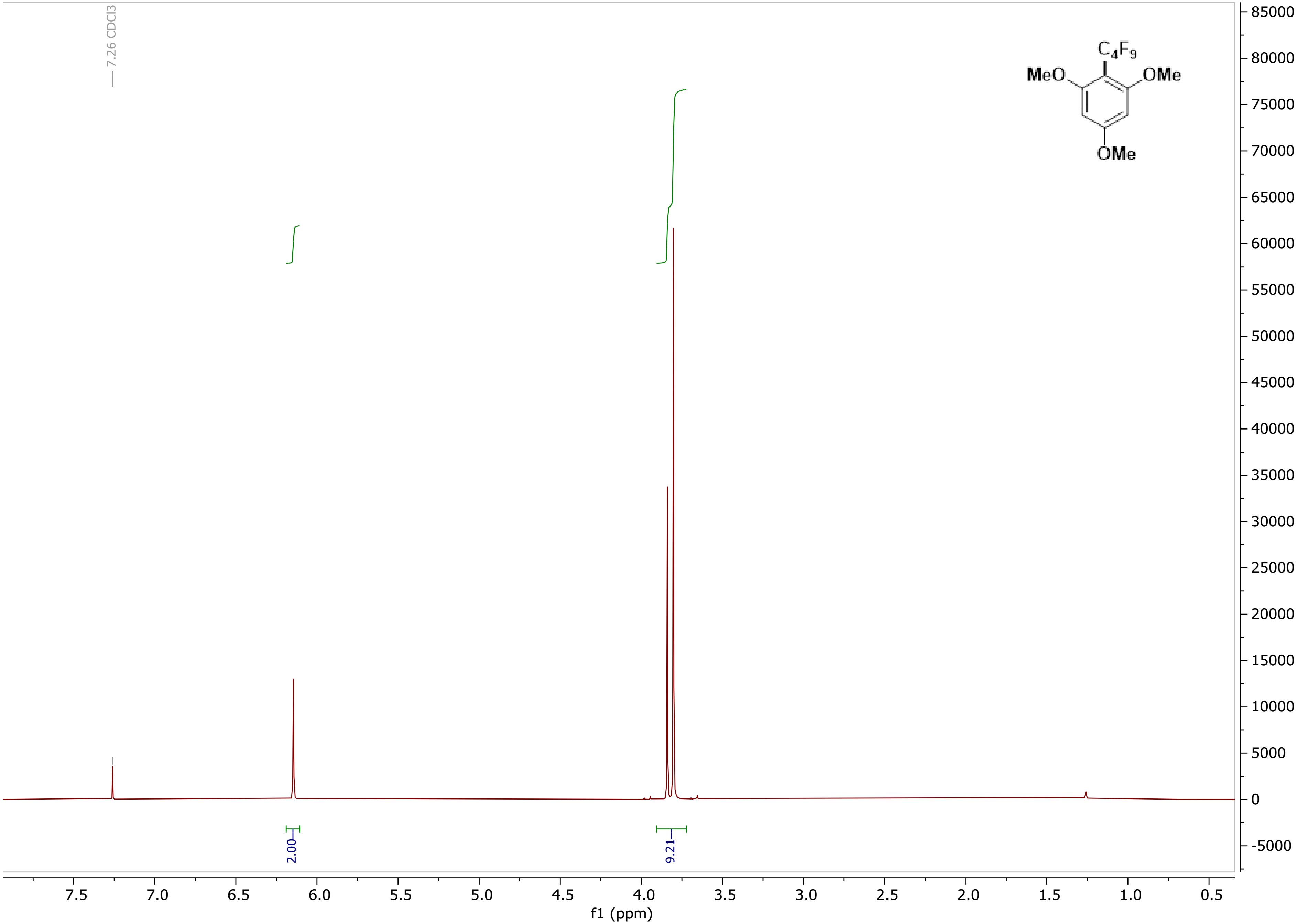

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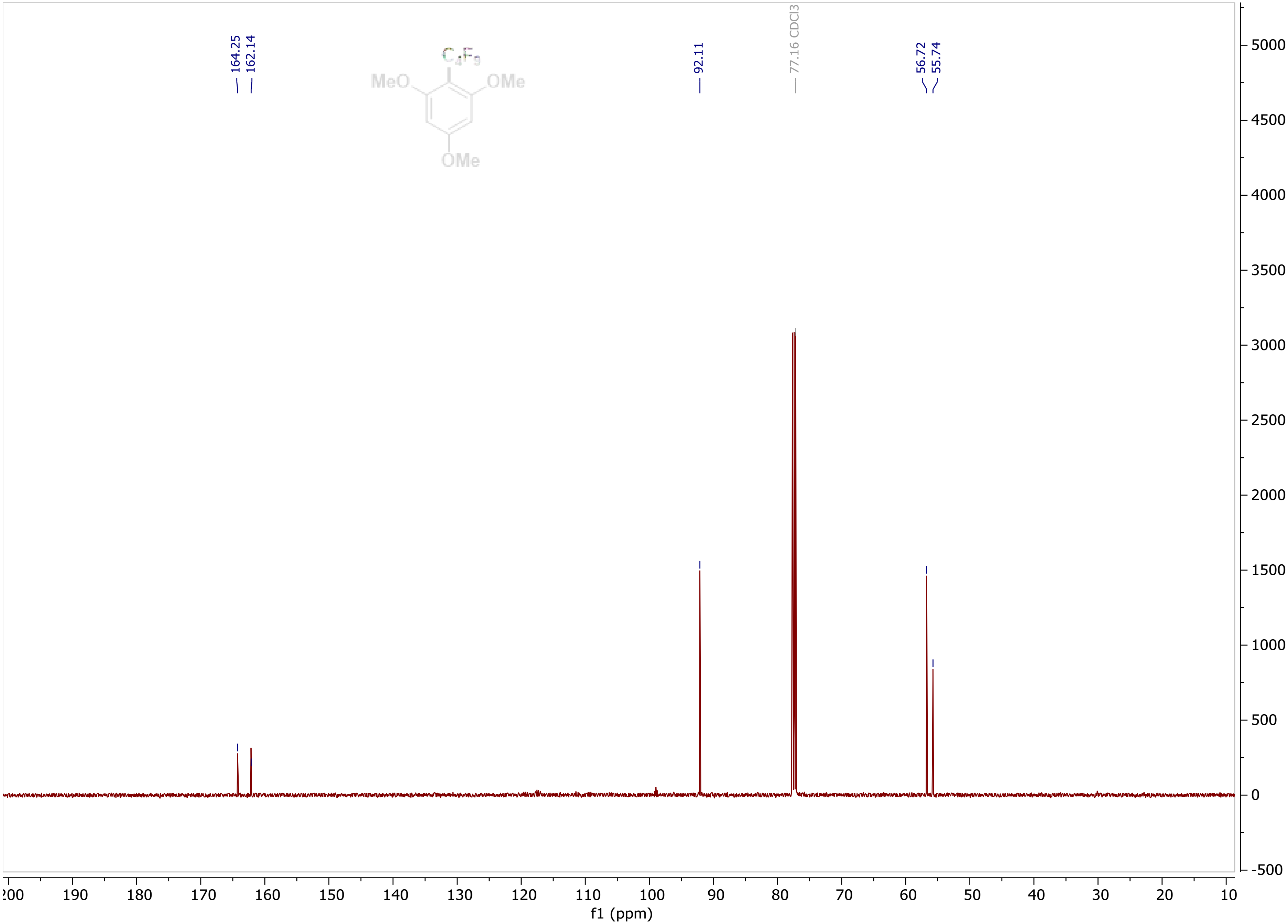

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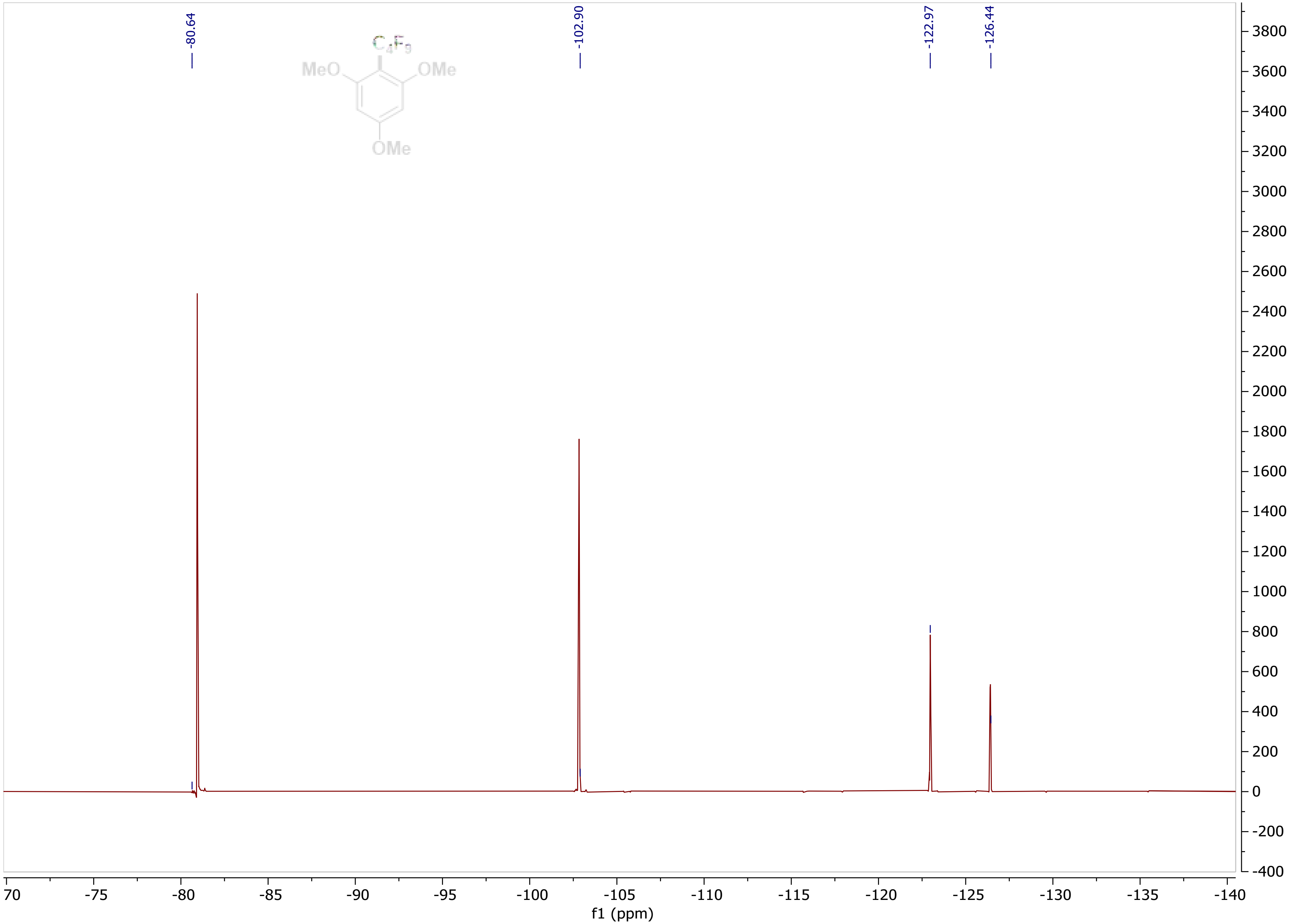
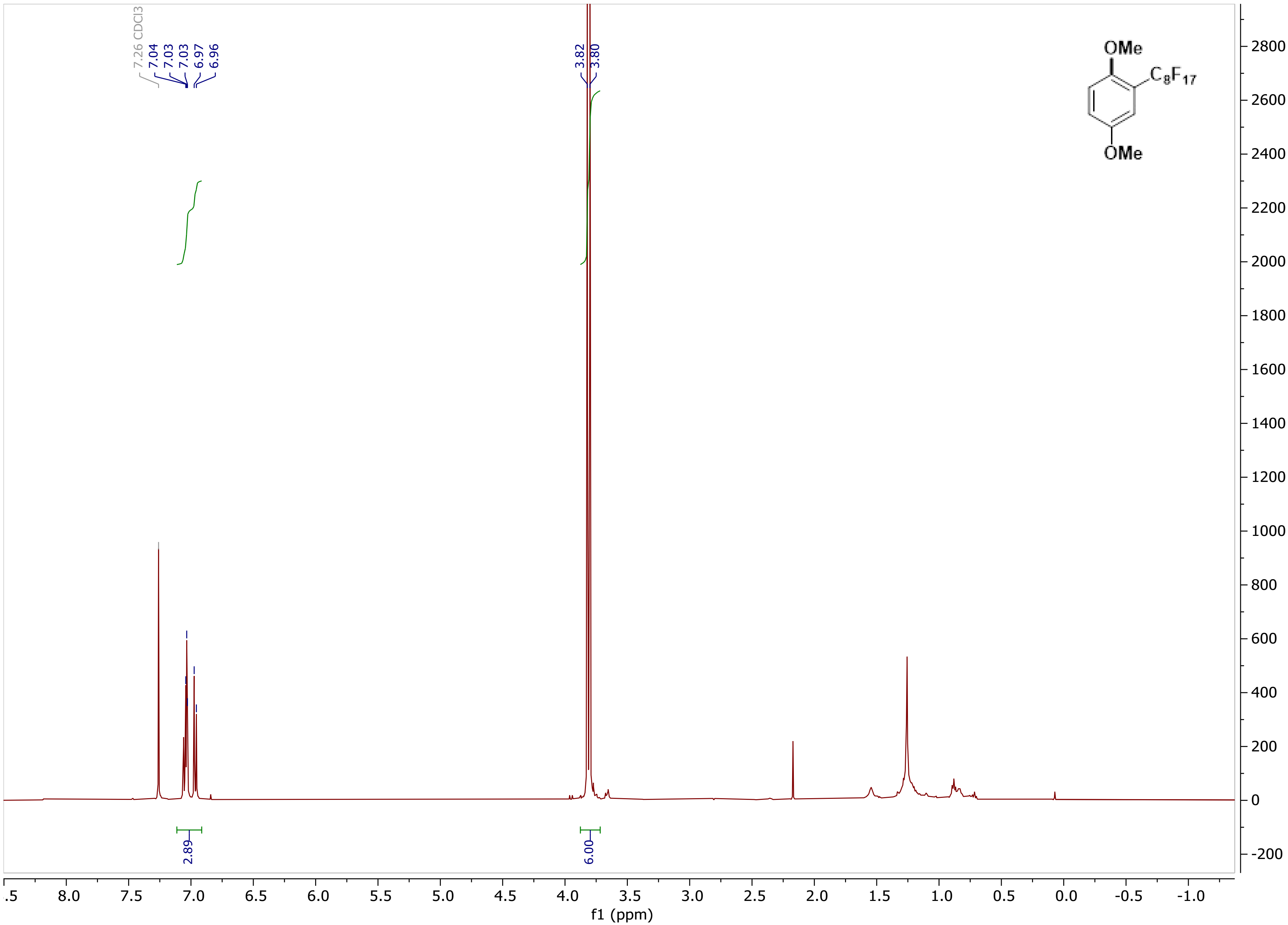
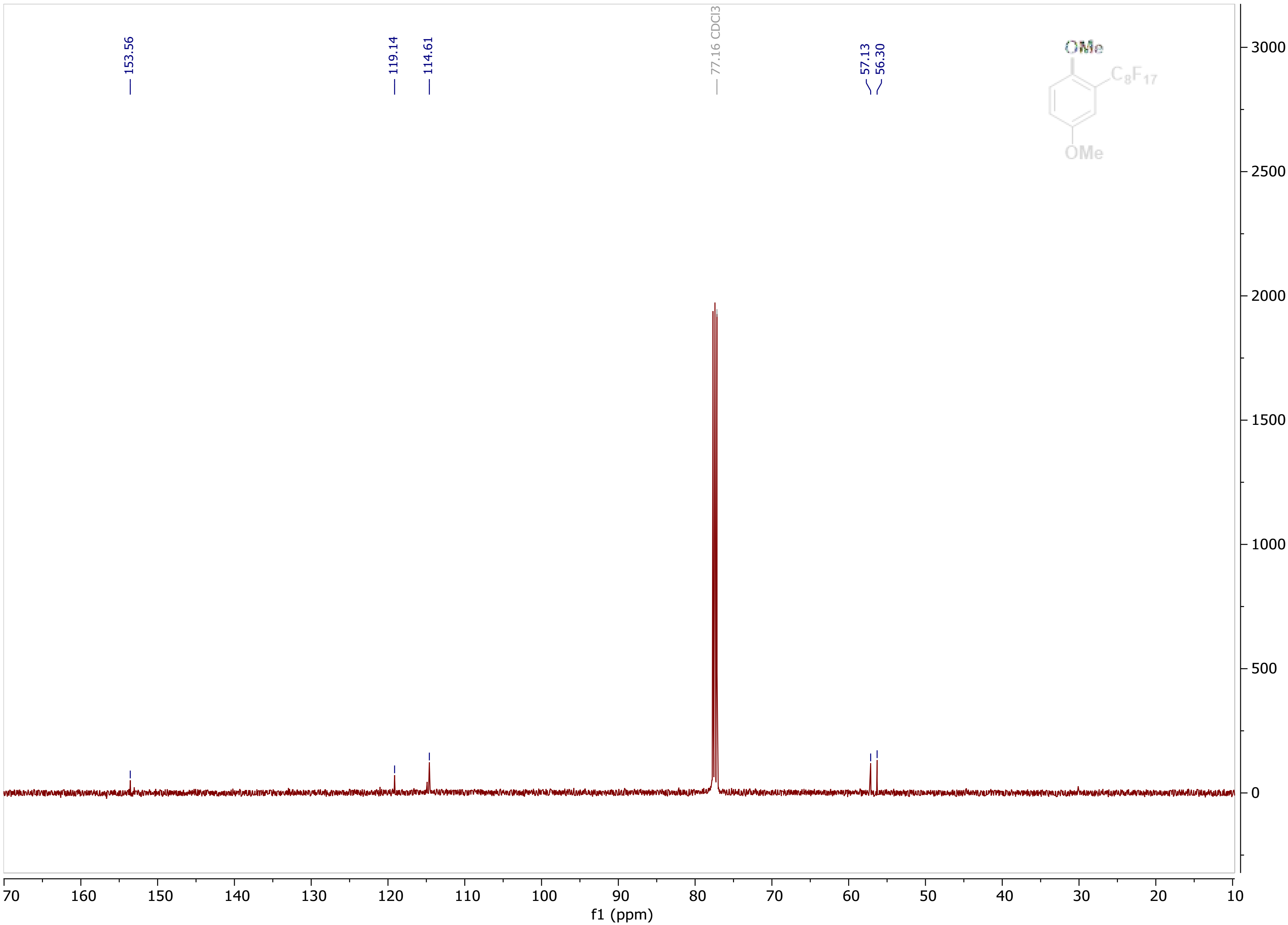


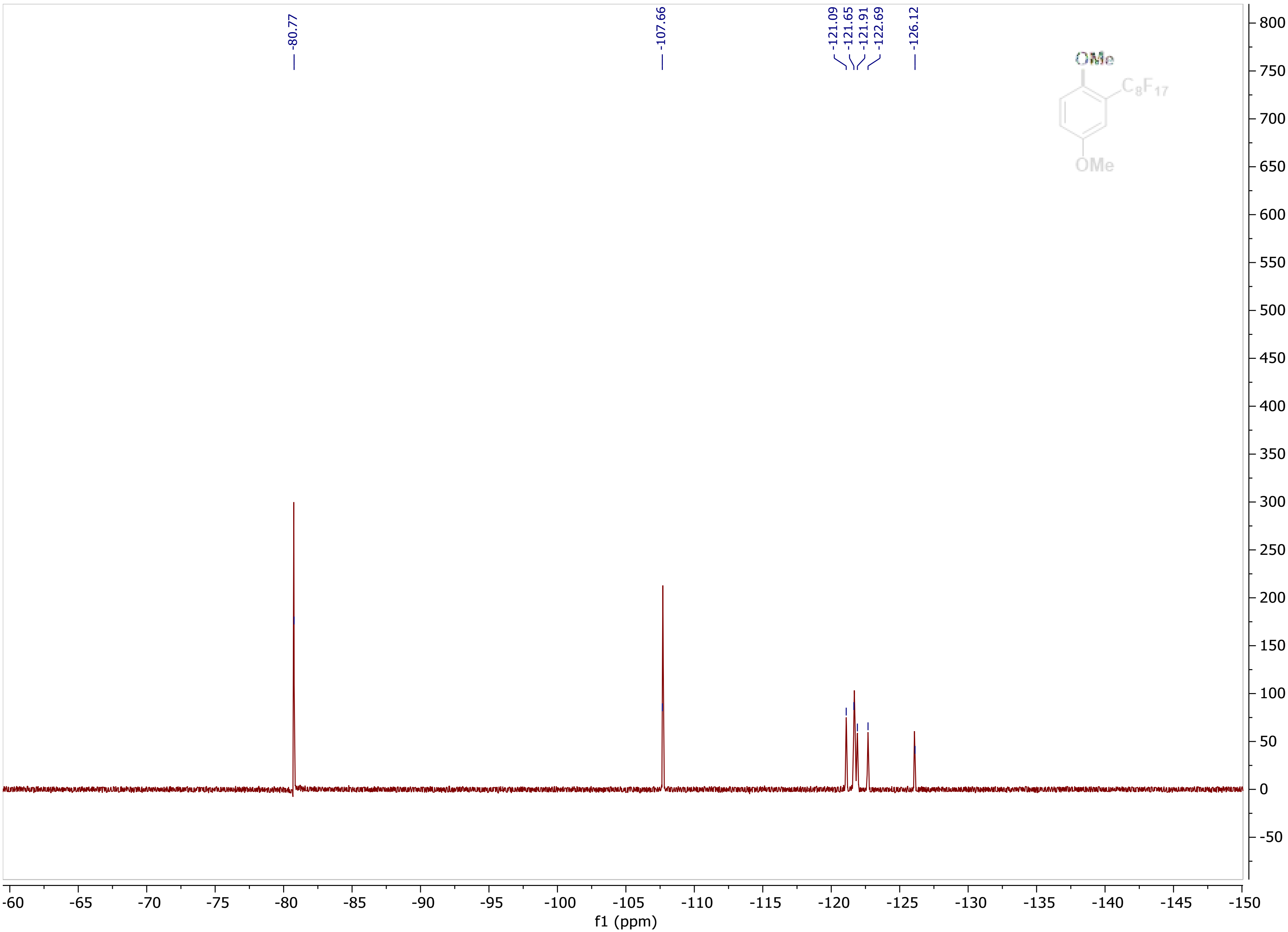
[1]H NMR of PF4, $CDCl_3$, 500 MHz



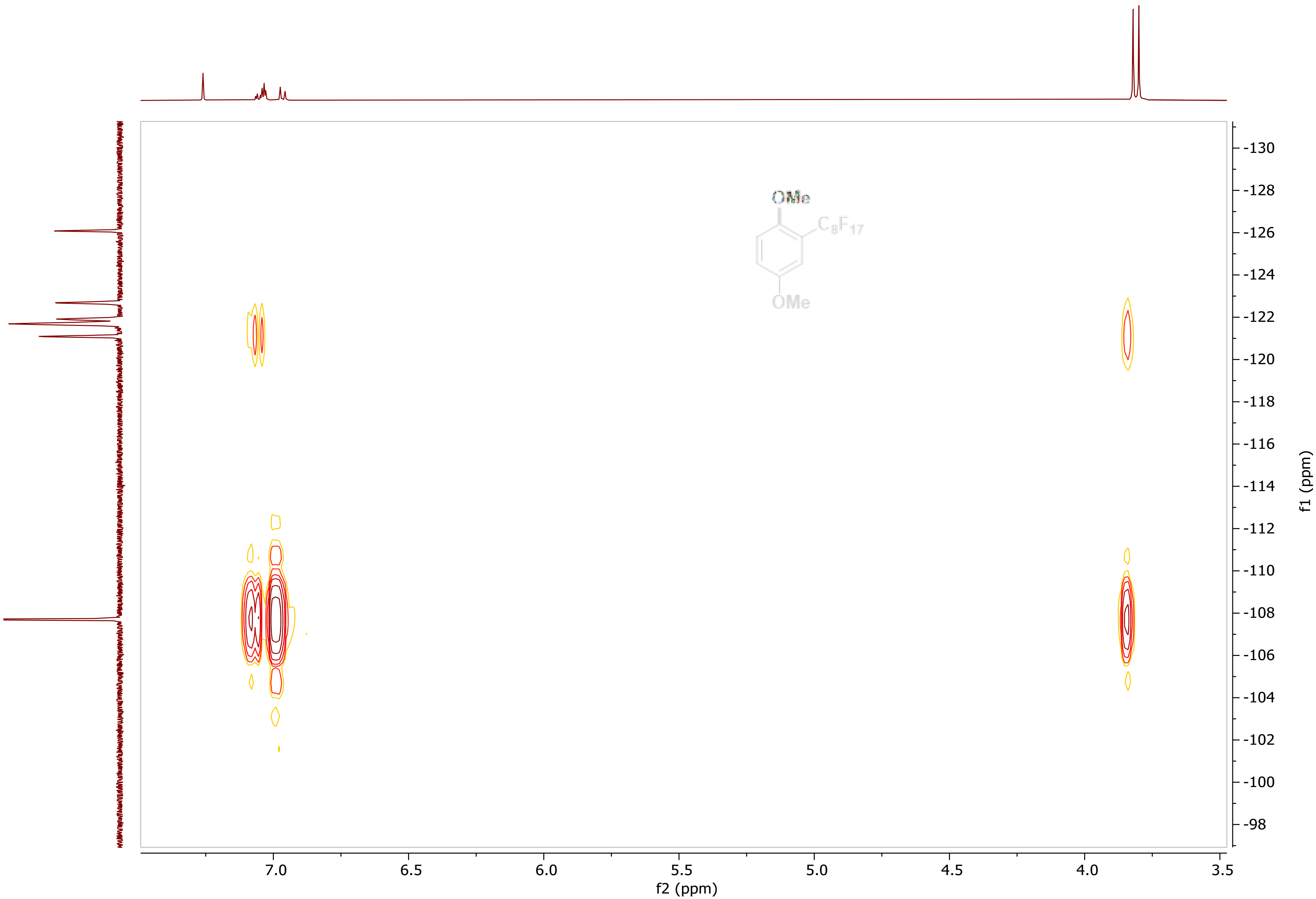
[13]C NMR of PF4, $CDCl_3$, 126 MHz



[19]F NMR of PF4, $CDCl_3$, 471 MHz



^{1}H-^{19}F HMBC of PF4



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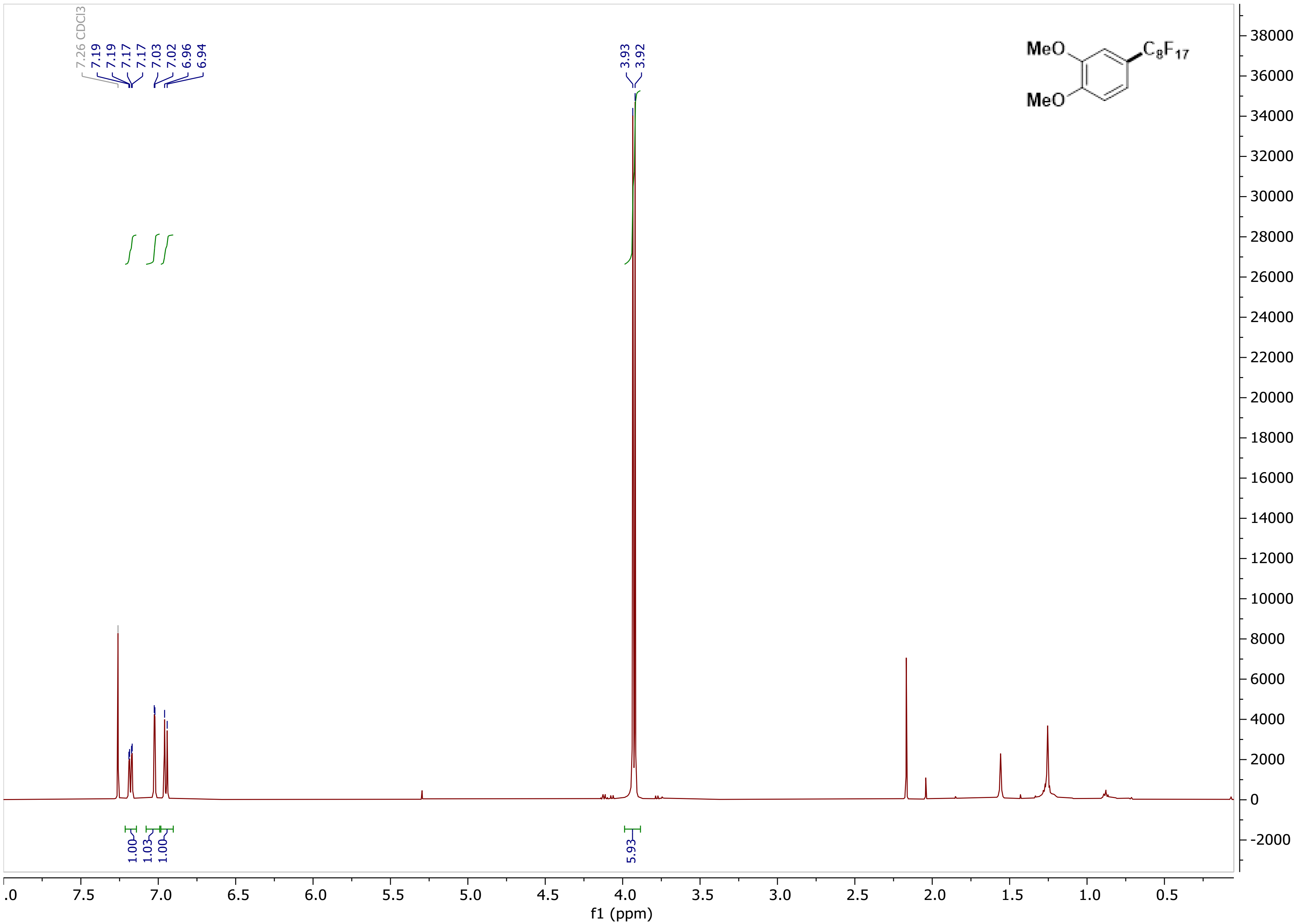
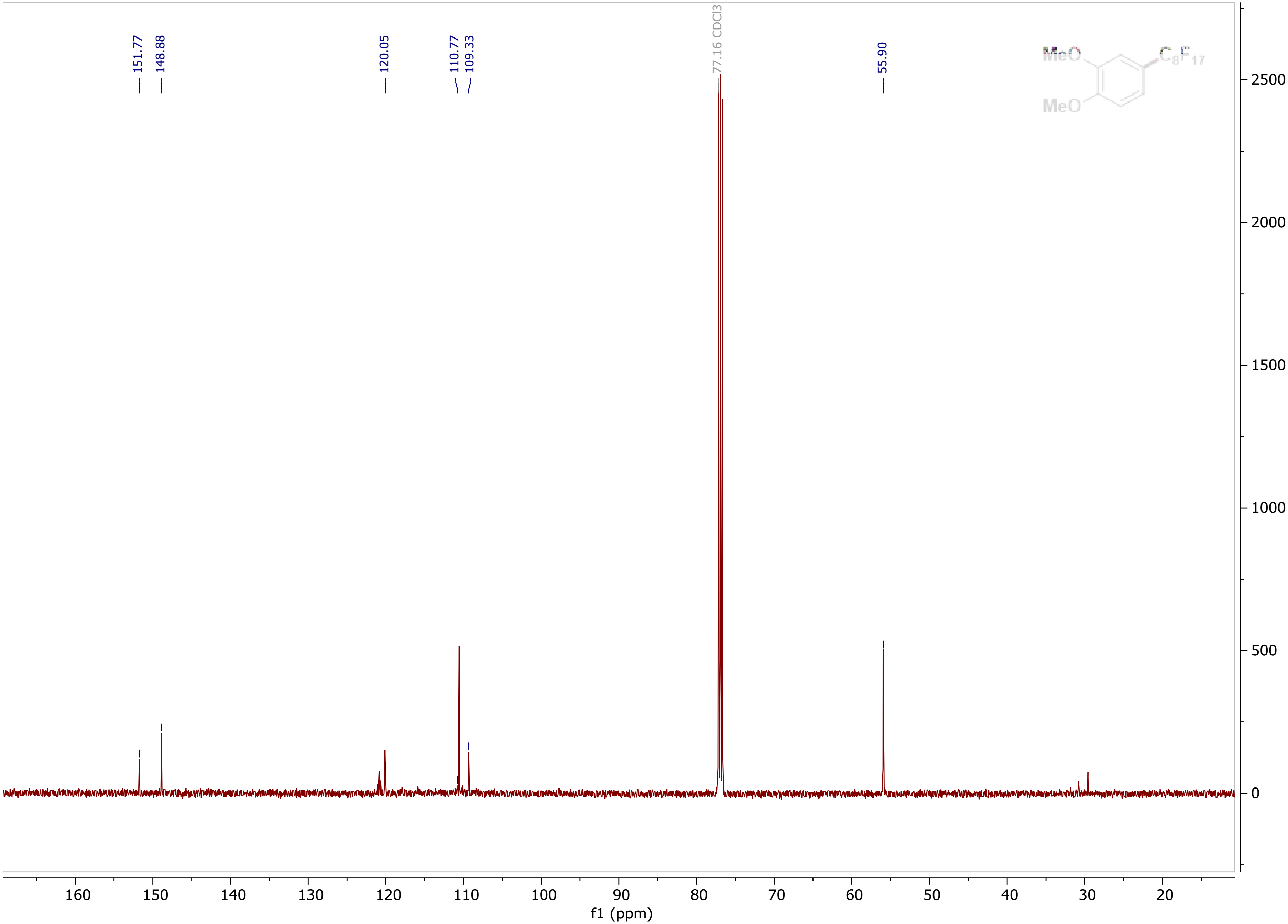


^{13}C NMR of PF5, $CDCl_3$, 126 MHz



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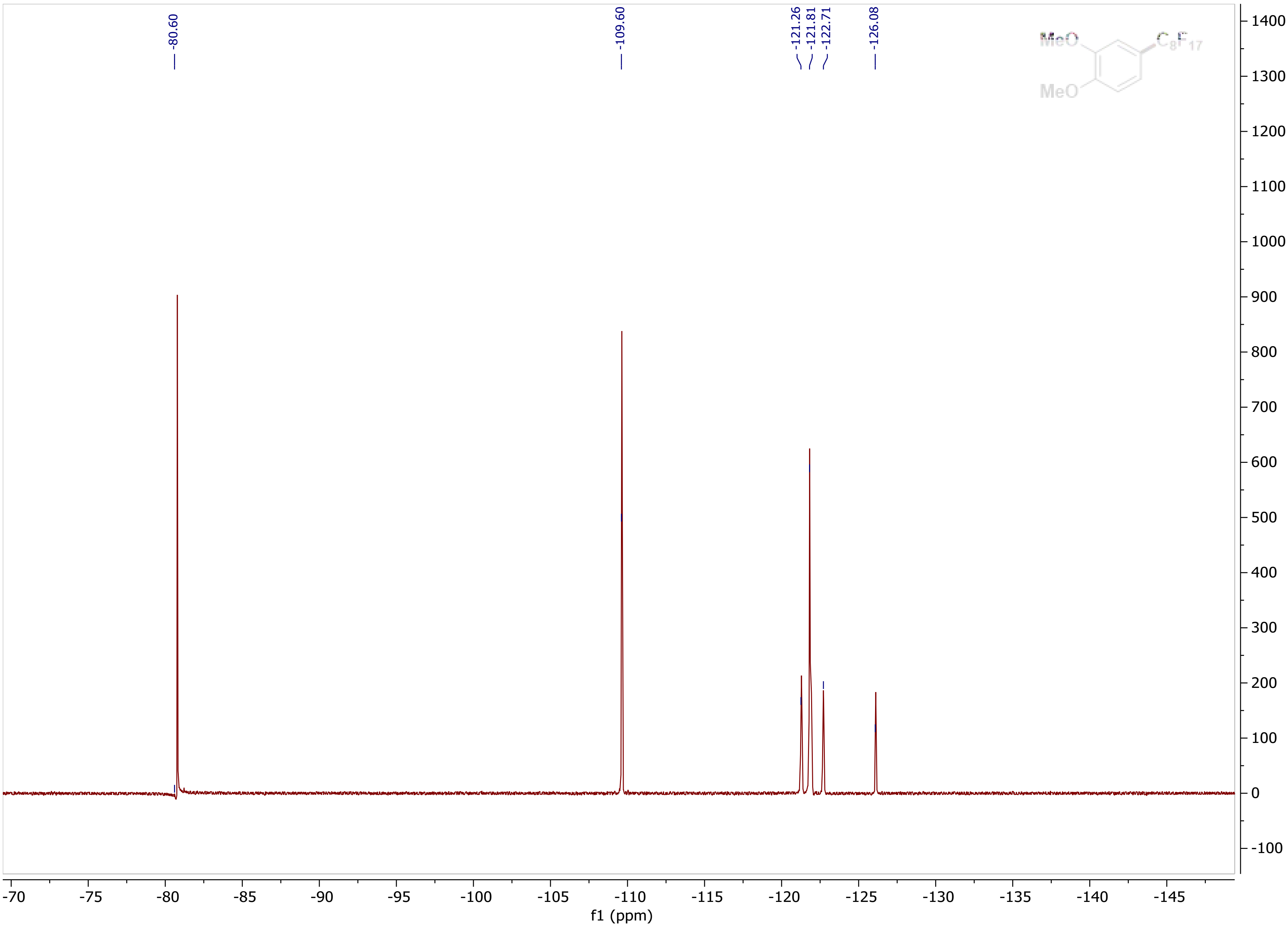

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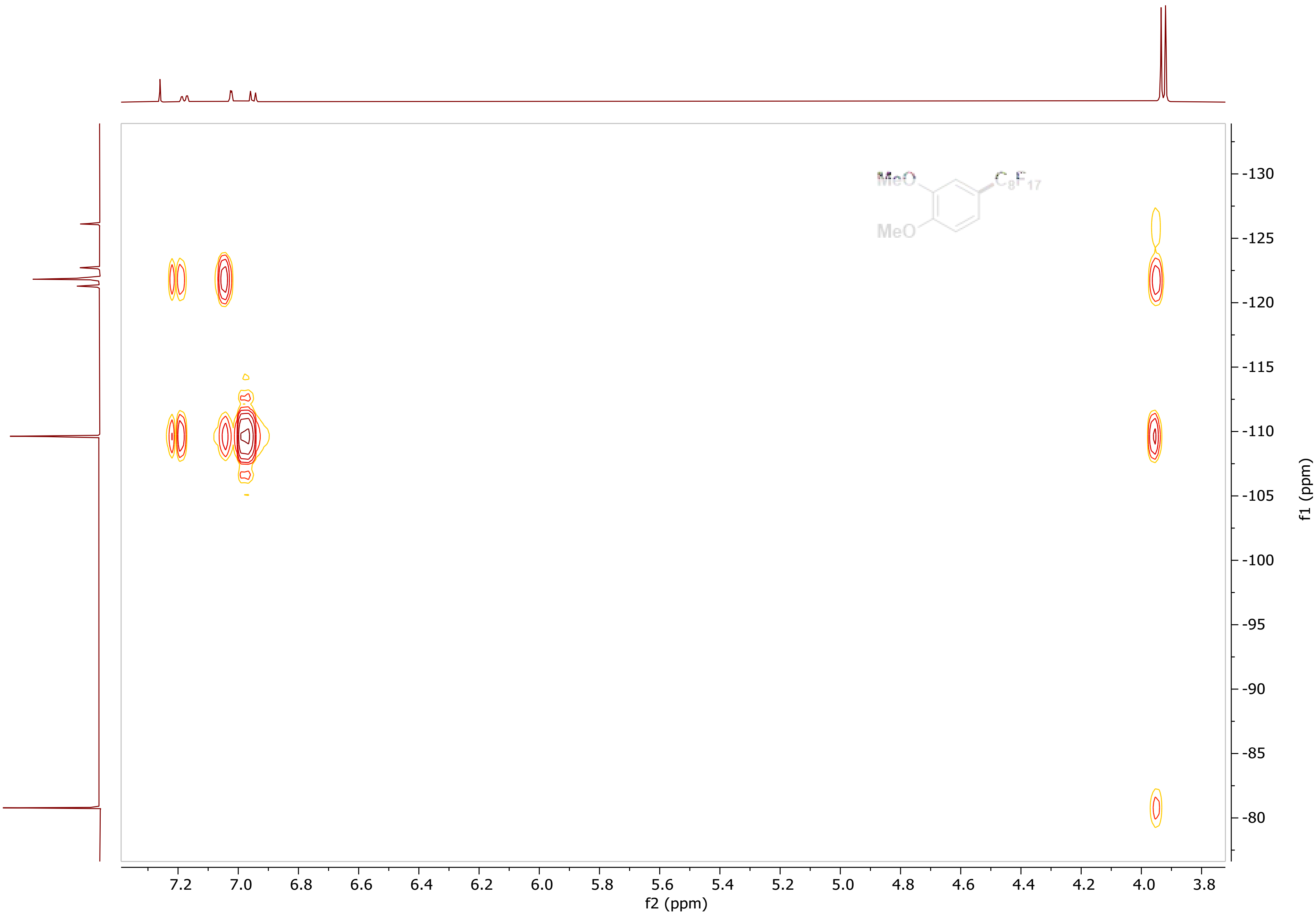

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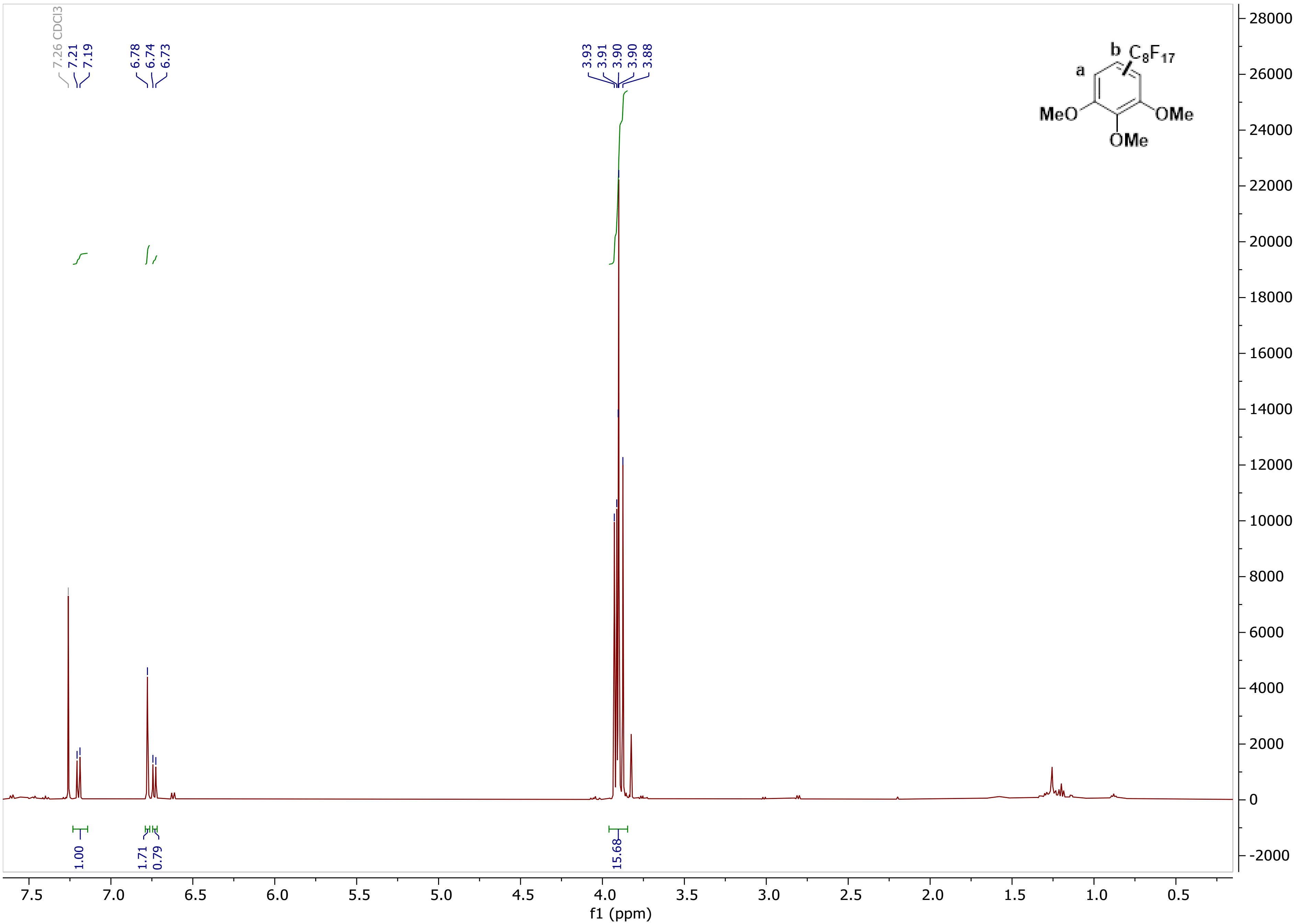
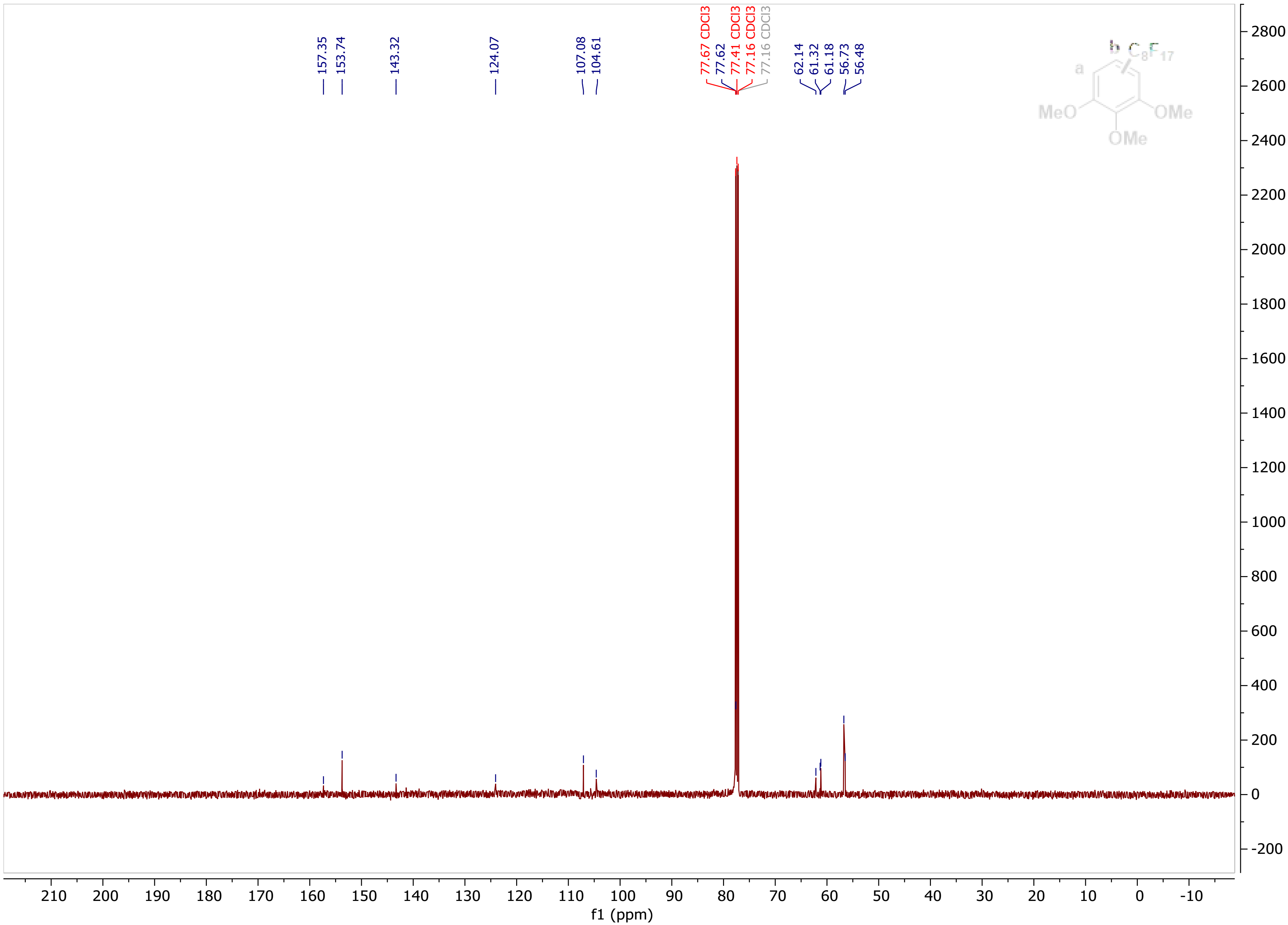
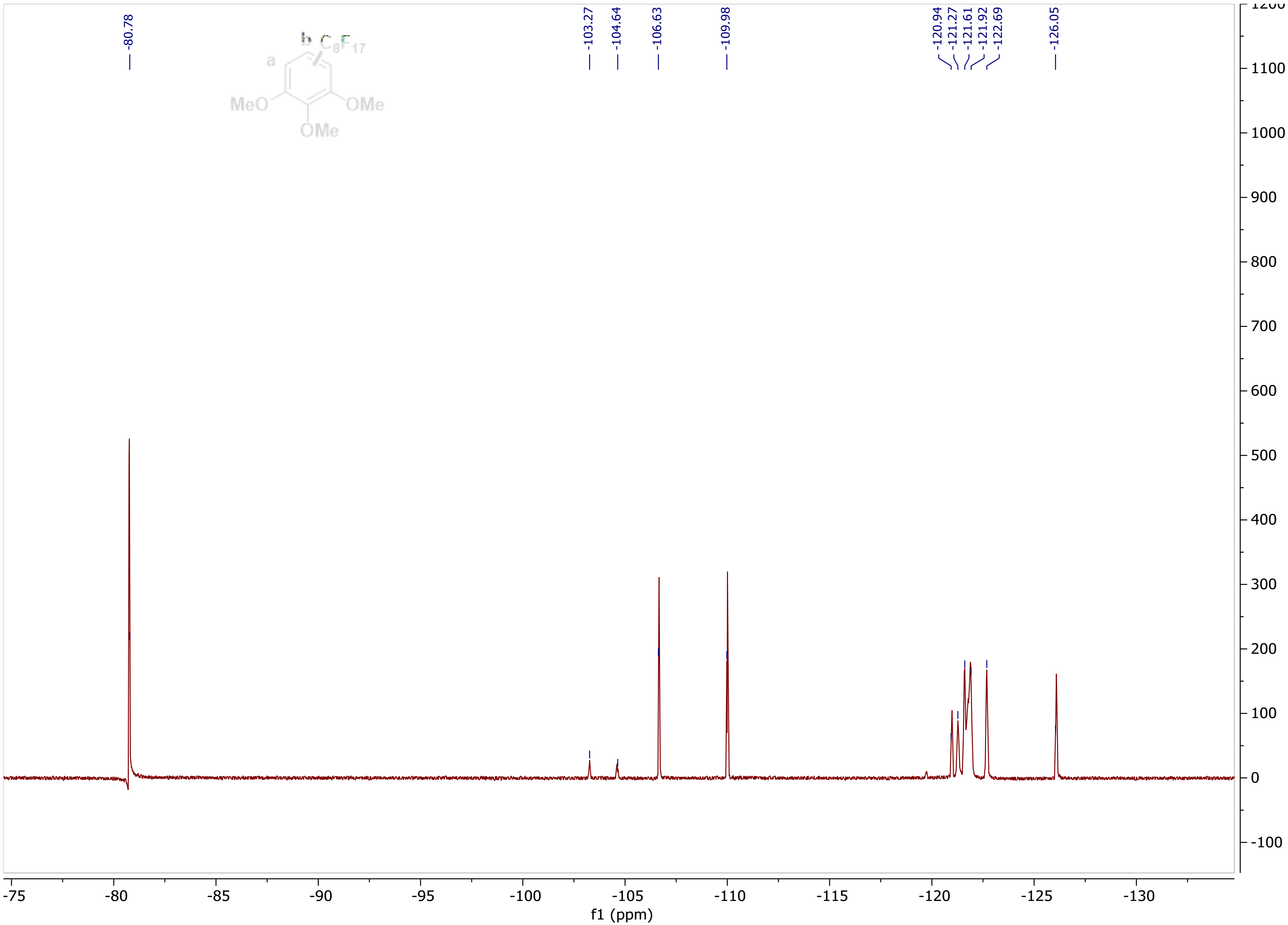


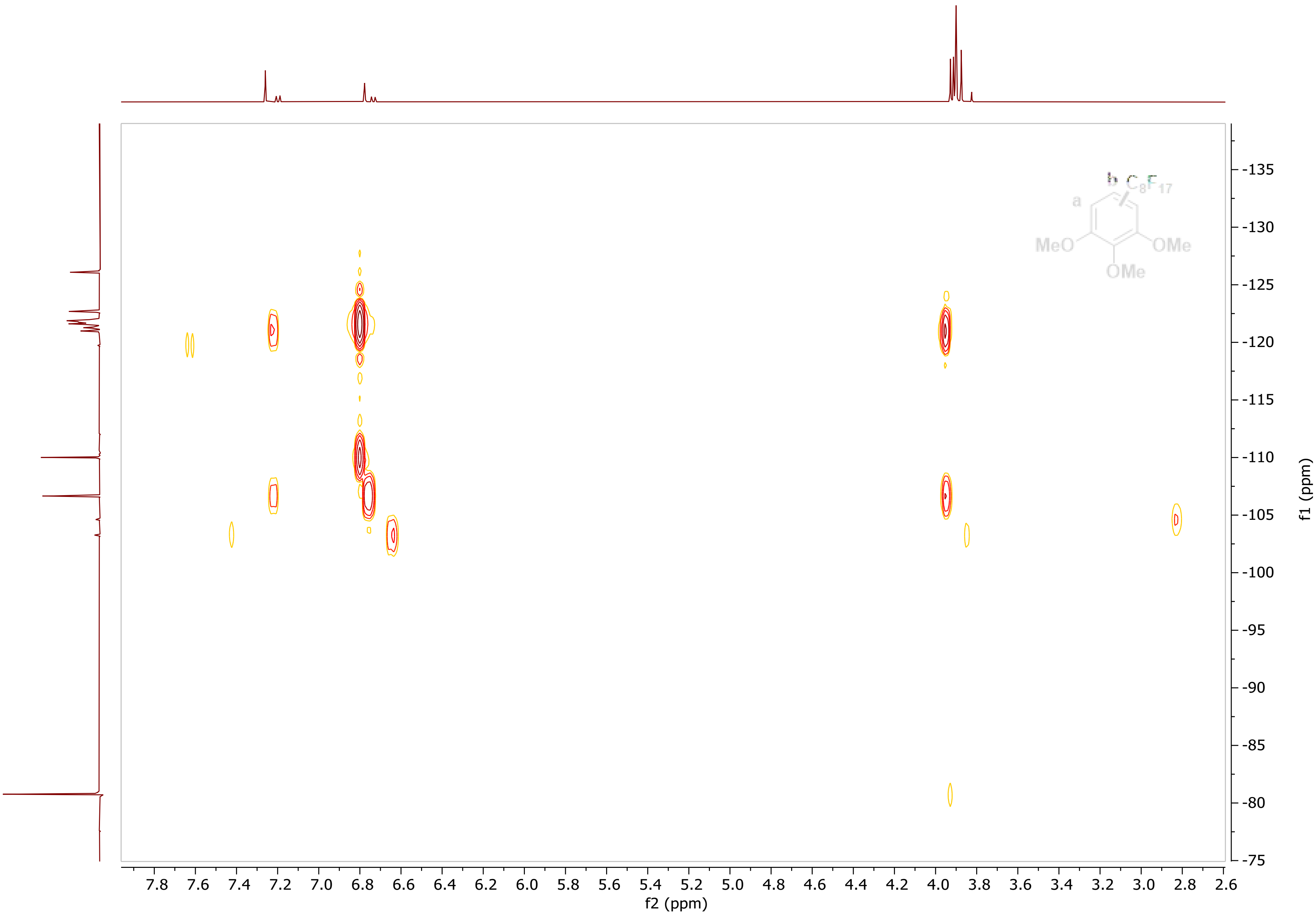
^{13}C NMR of PF6, $CDCl_3$, 126 MHz



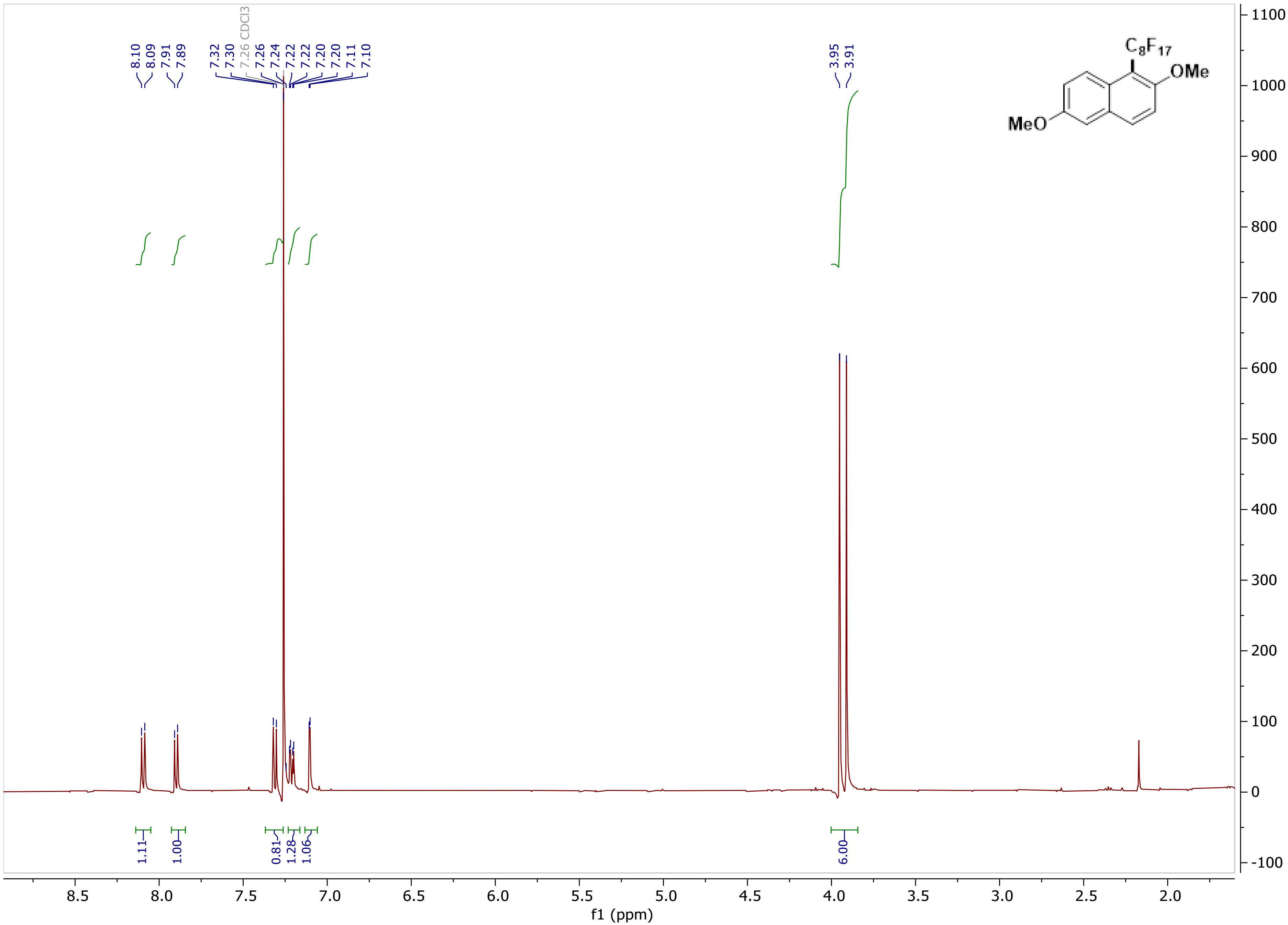
^{19}F NMR of PF6, $CDCl_3$, 471 MHz



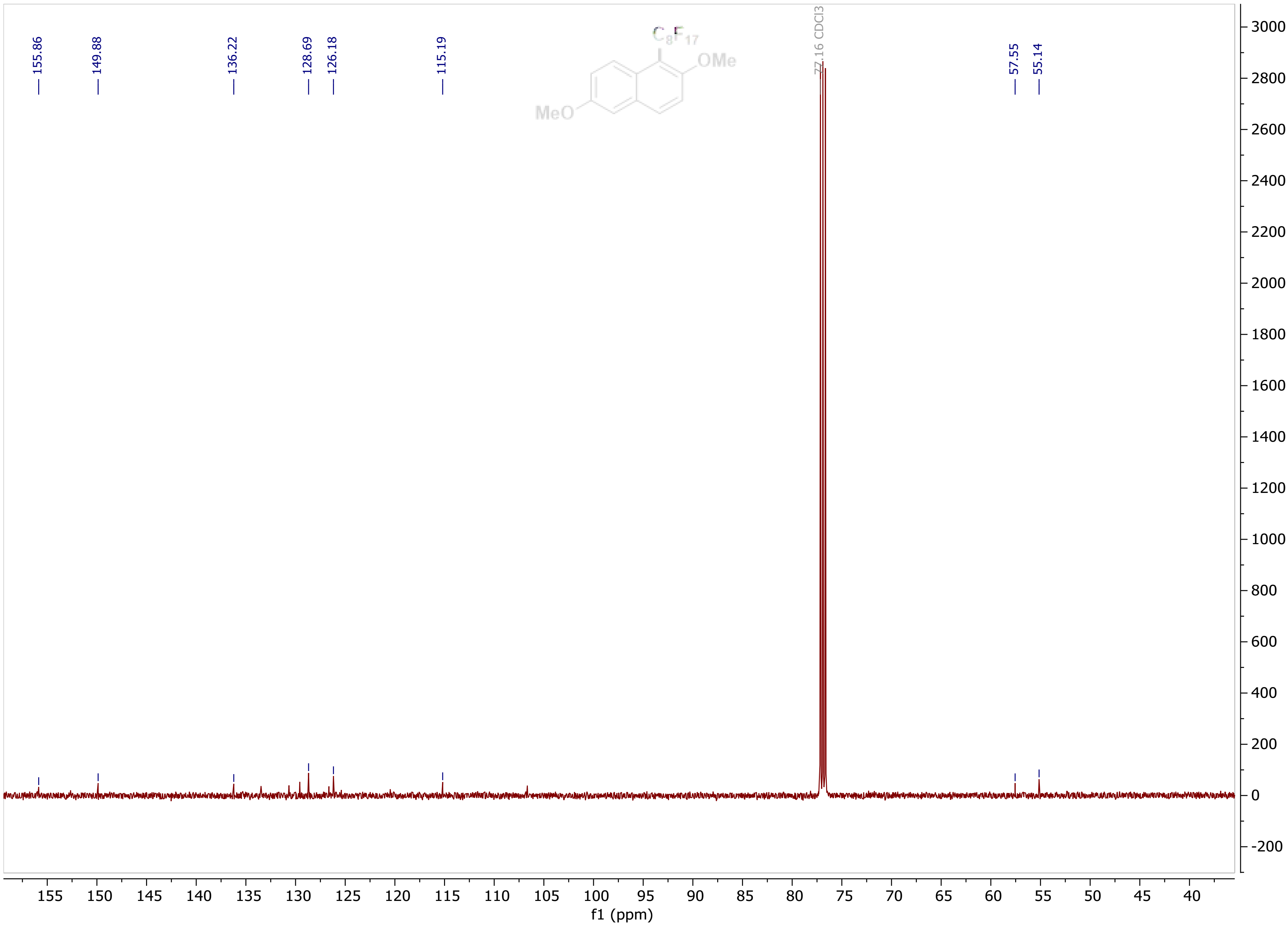
[1]H-[19]F HMBC of PF6



^{1}H NMR of PF7, $CDCl_3$, 500 MHz



^{13}C NMR of PF7, $CDCl_3$, 126 MHz



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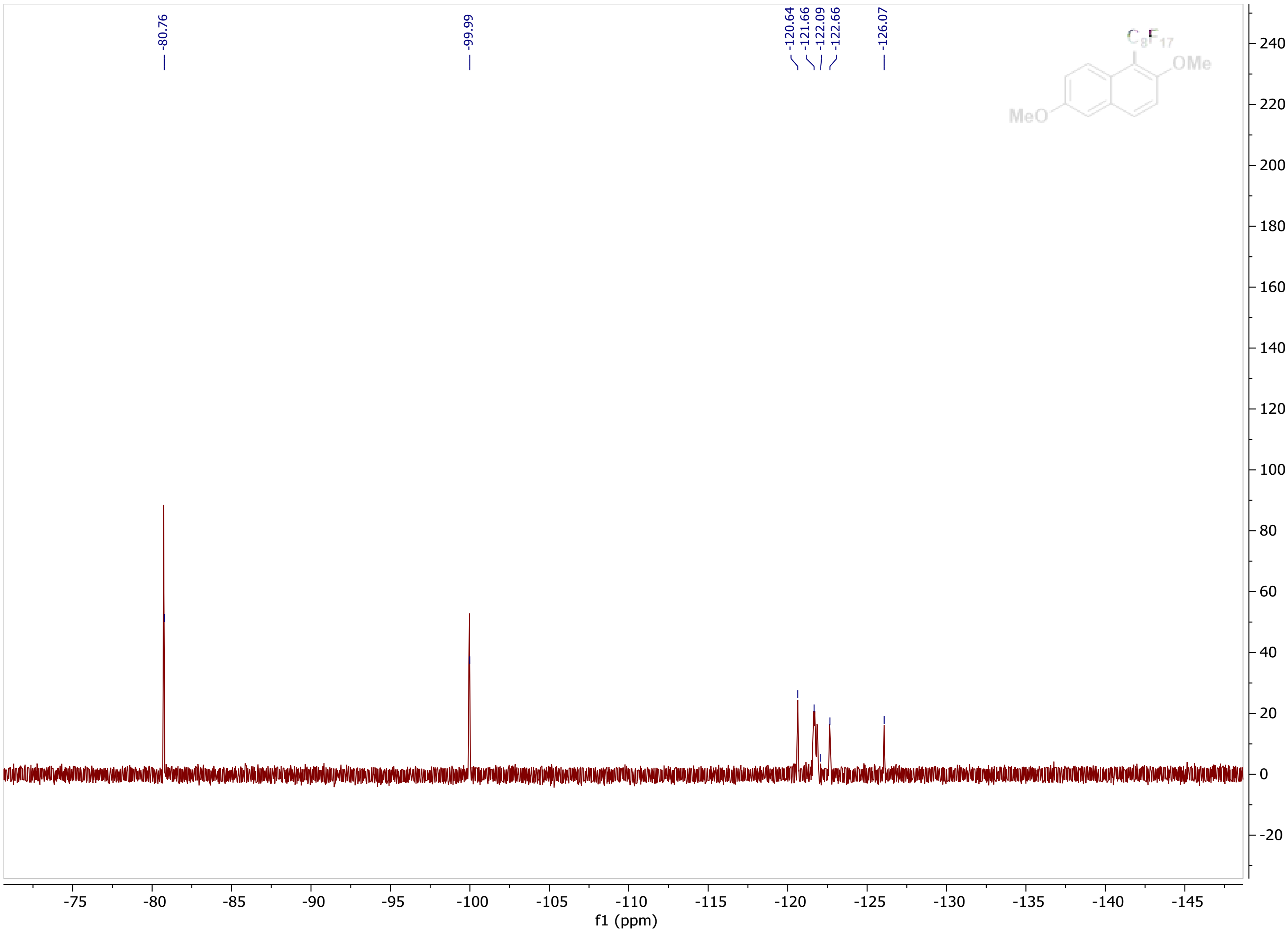
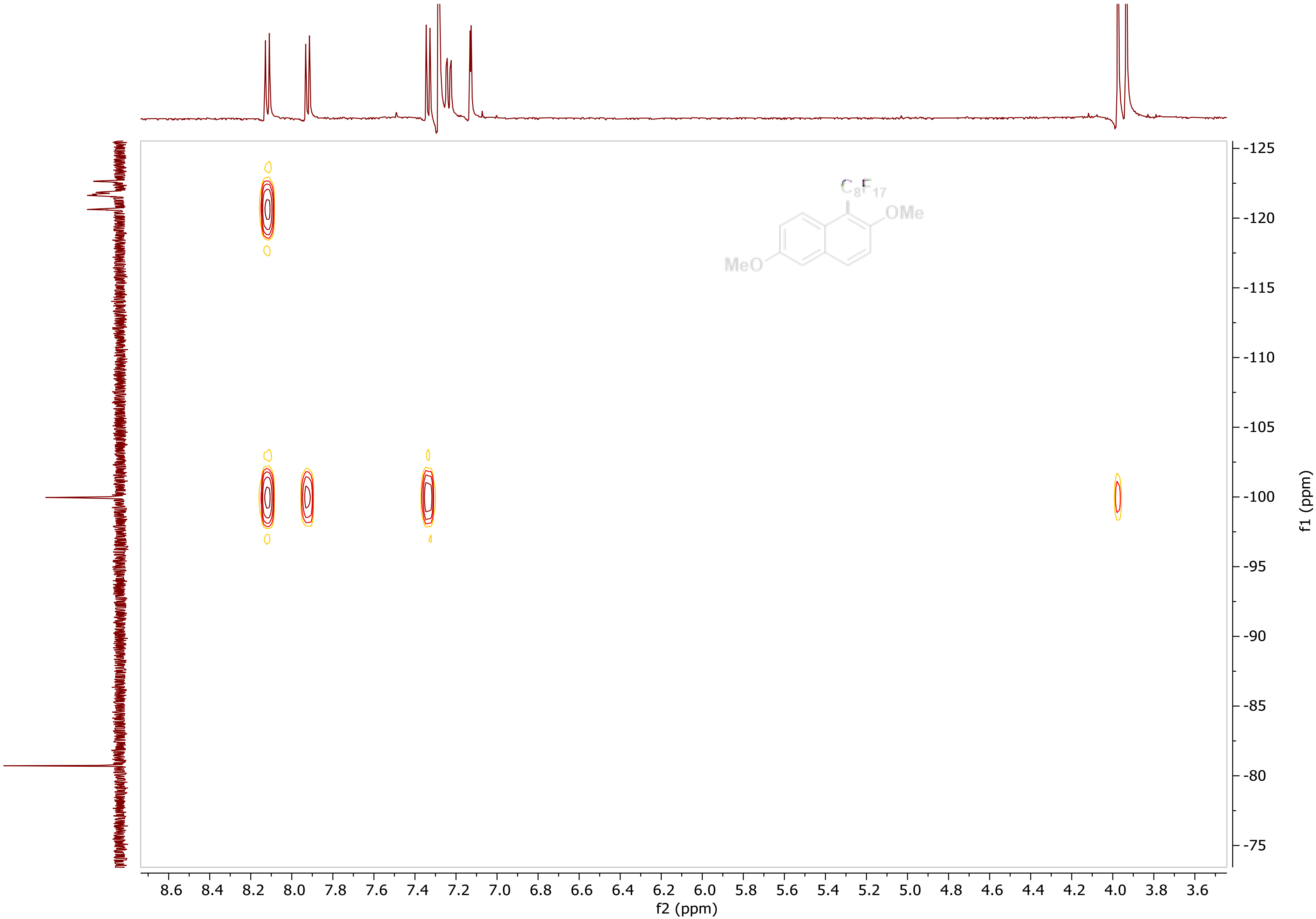


^1H-^{19}F HMBC of PF7



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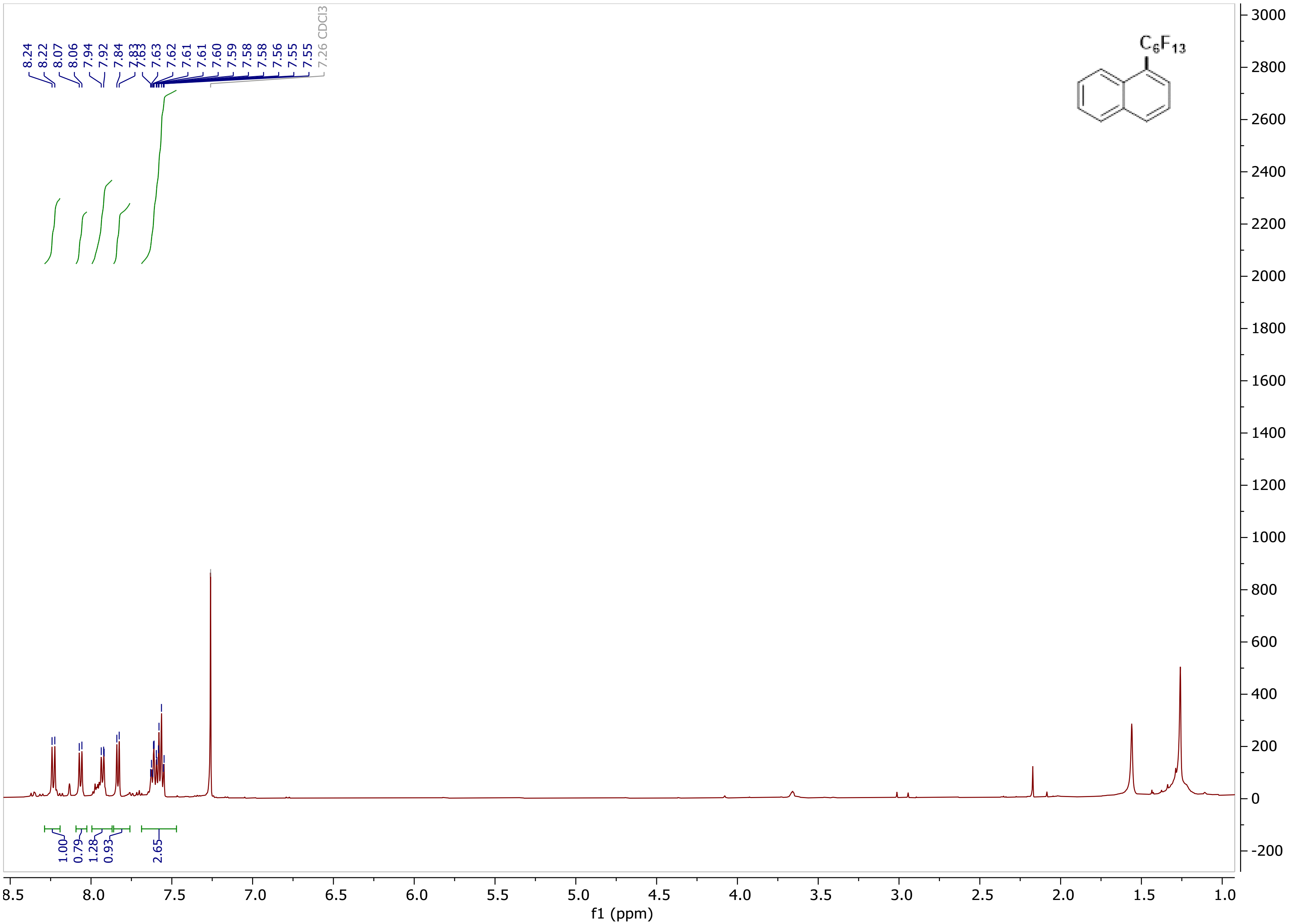

8.24
8.22
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7.26 CDCl3
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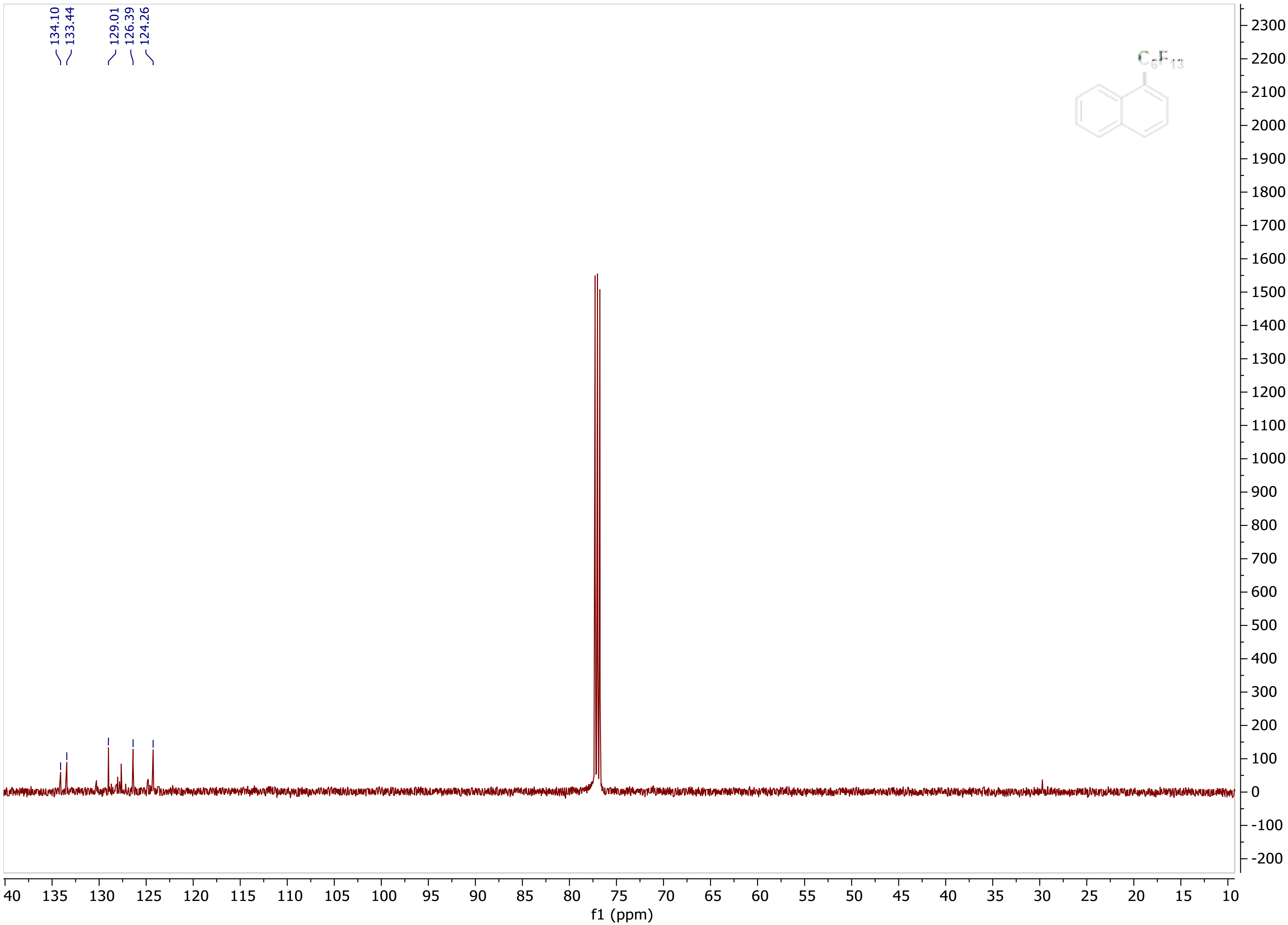
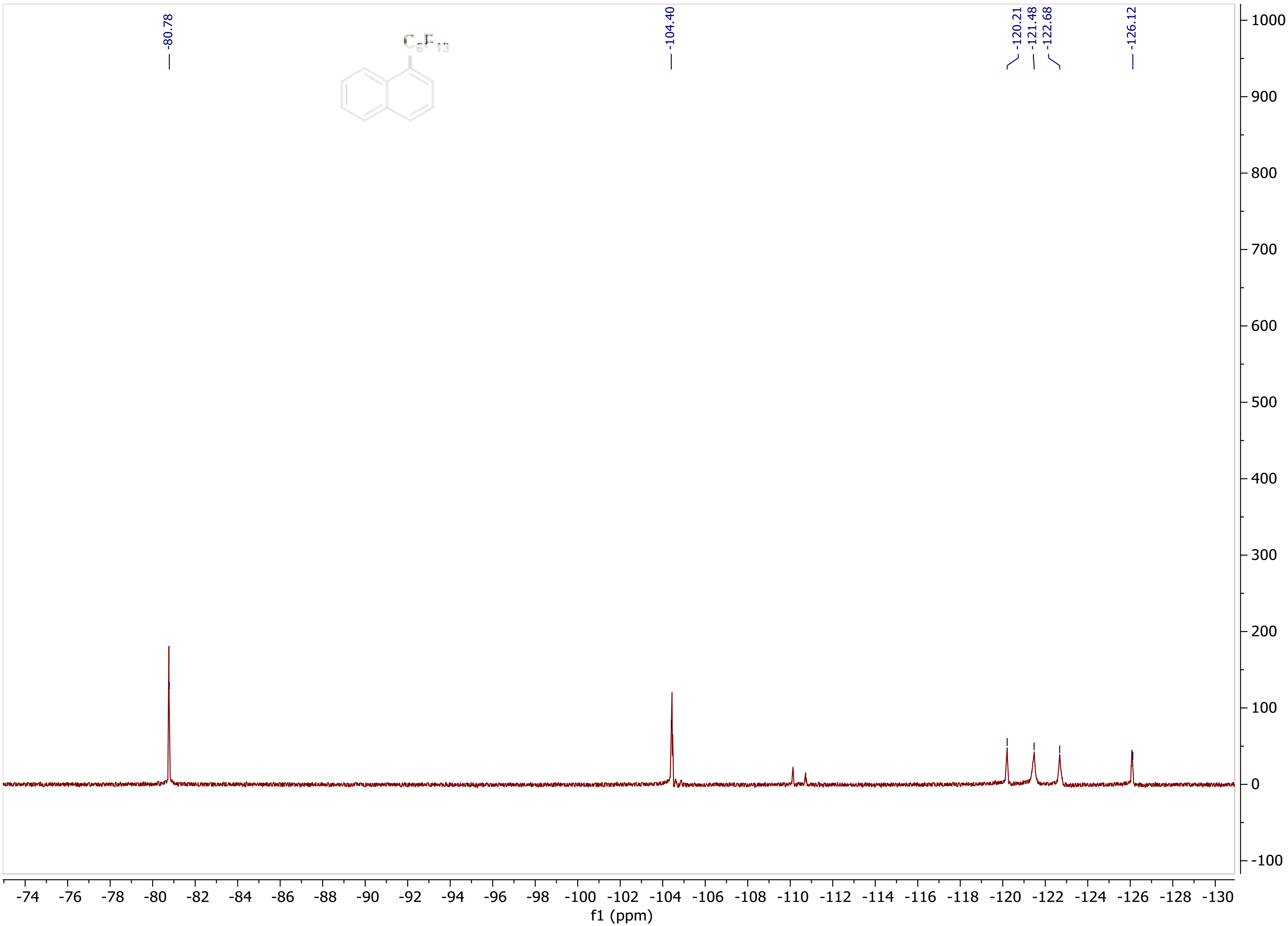
1.28
0.93
2.65
f1 (ppm)

^{13}C NMR of PF8, $CDCl_3$, 126 MHz



^{19}F NMR of PF8, $CDCl_3$, 471 MHz



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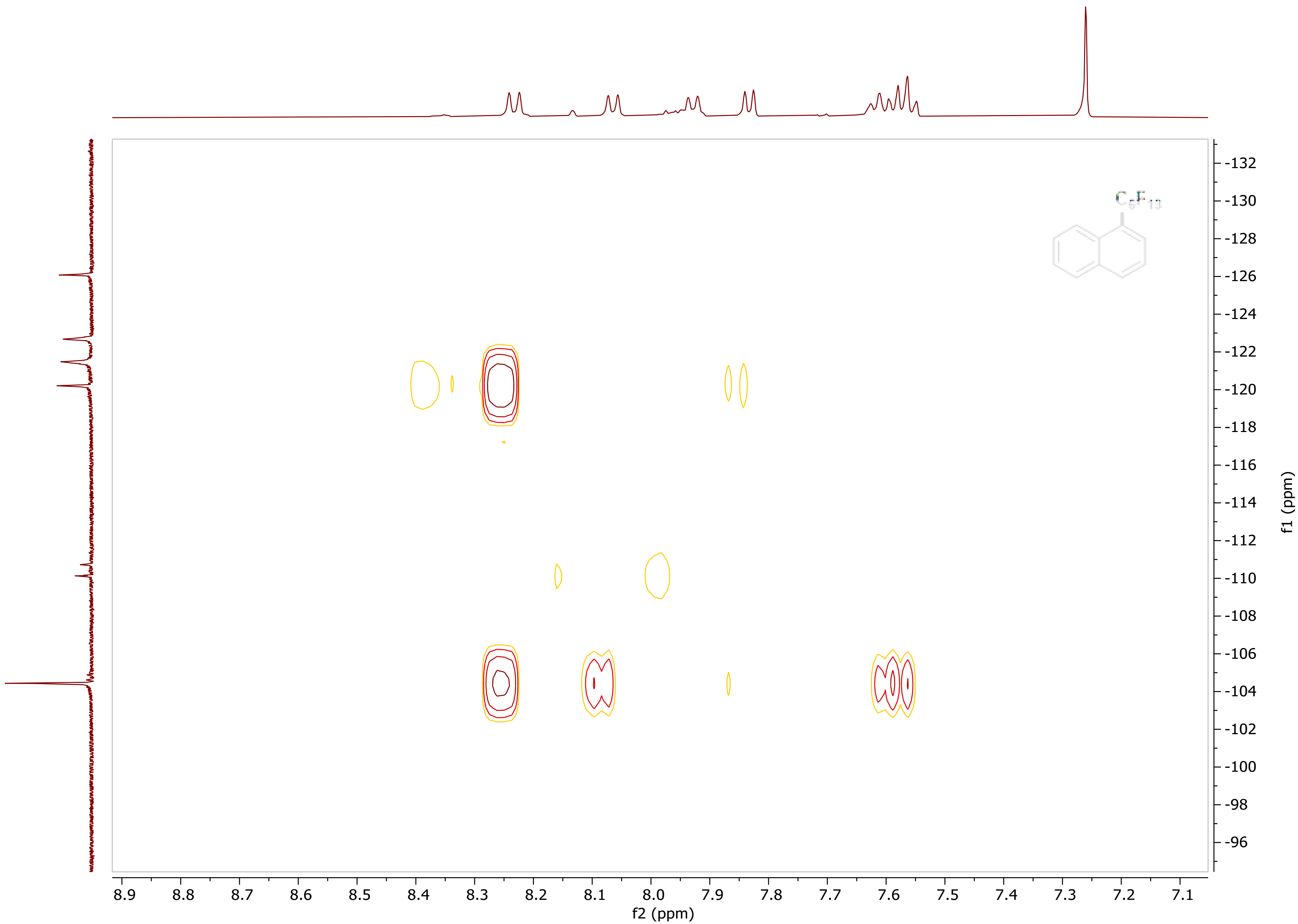
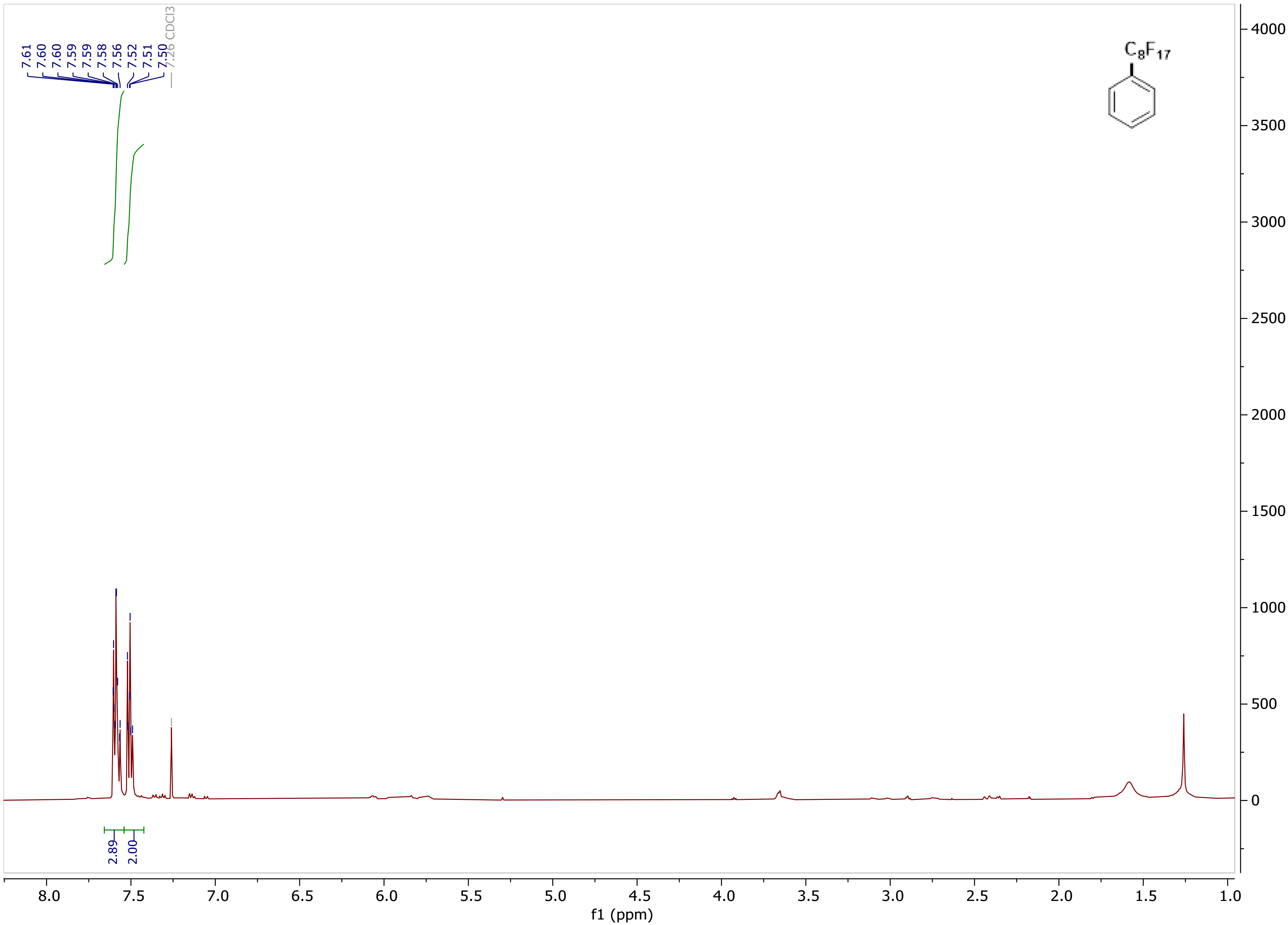
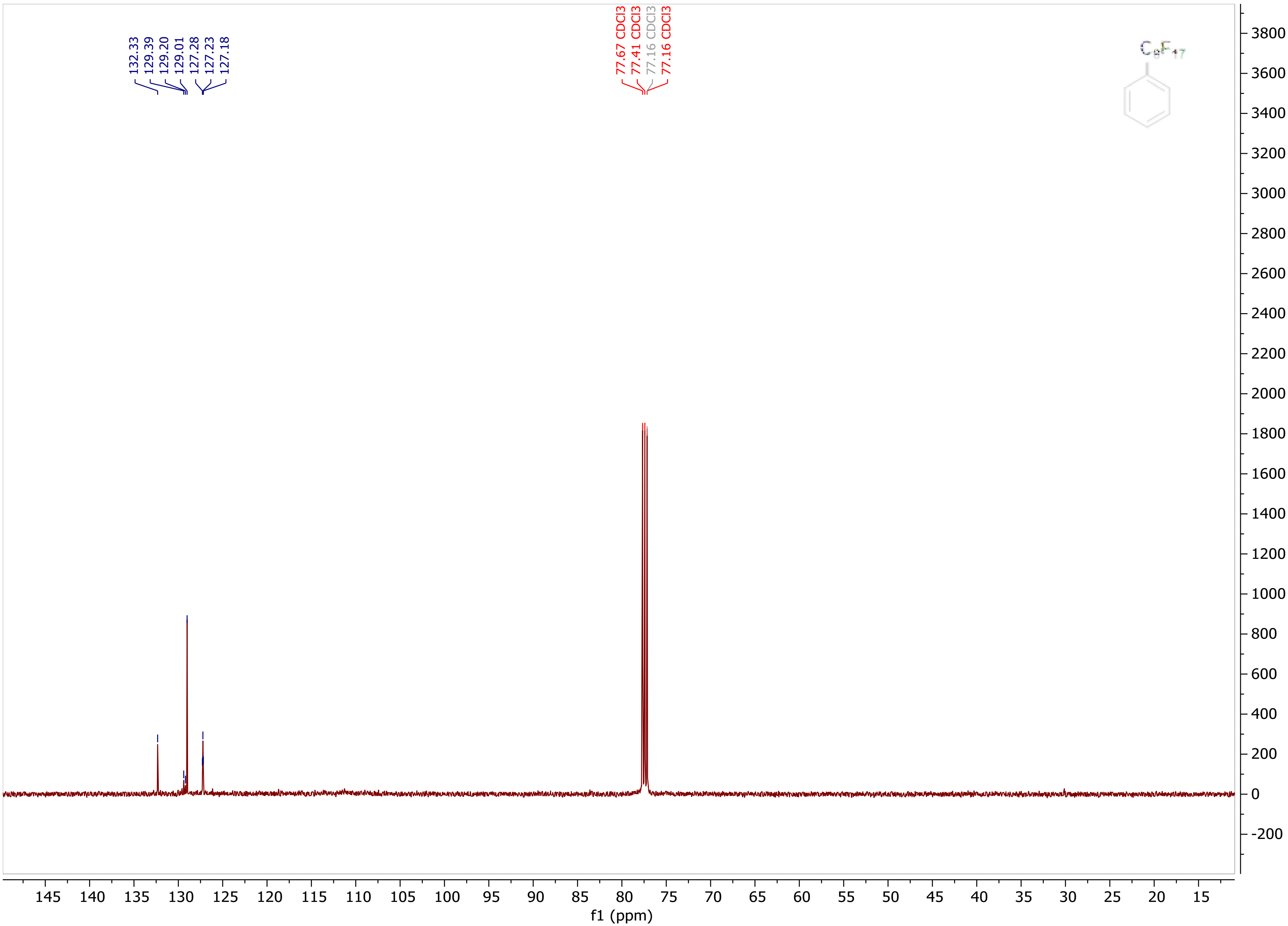


^{1}H NMR of PF9, $CDCl_3$, 500 MHz



^{13}C NMR of PF9, $CDCl_3$, 126 MHz



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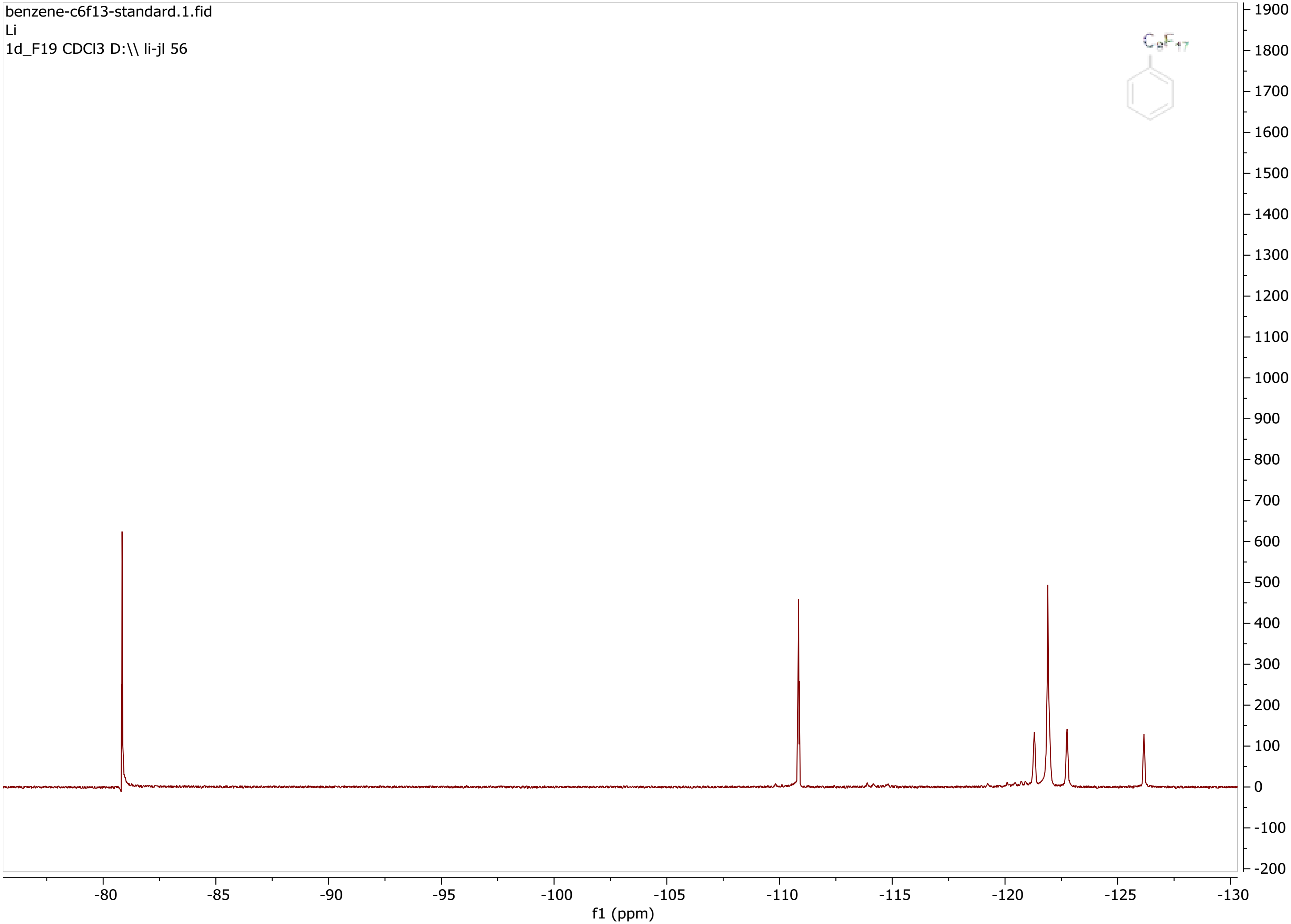
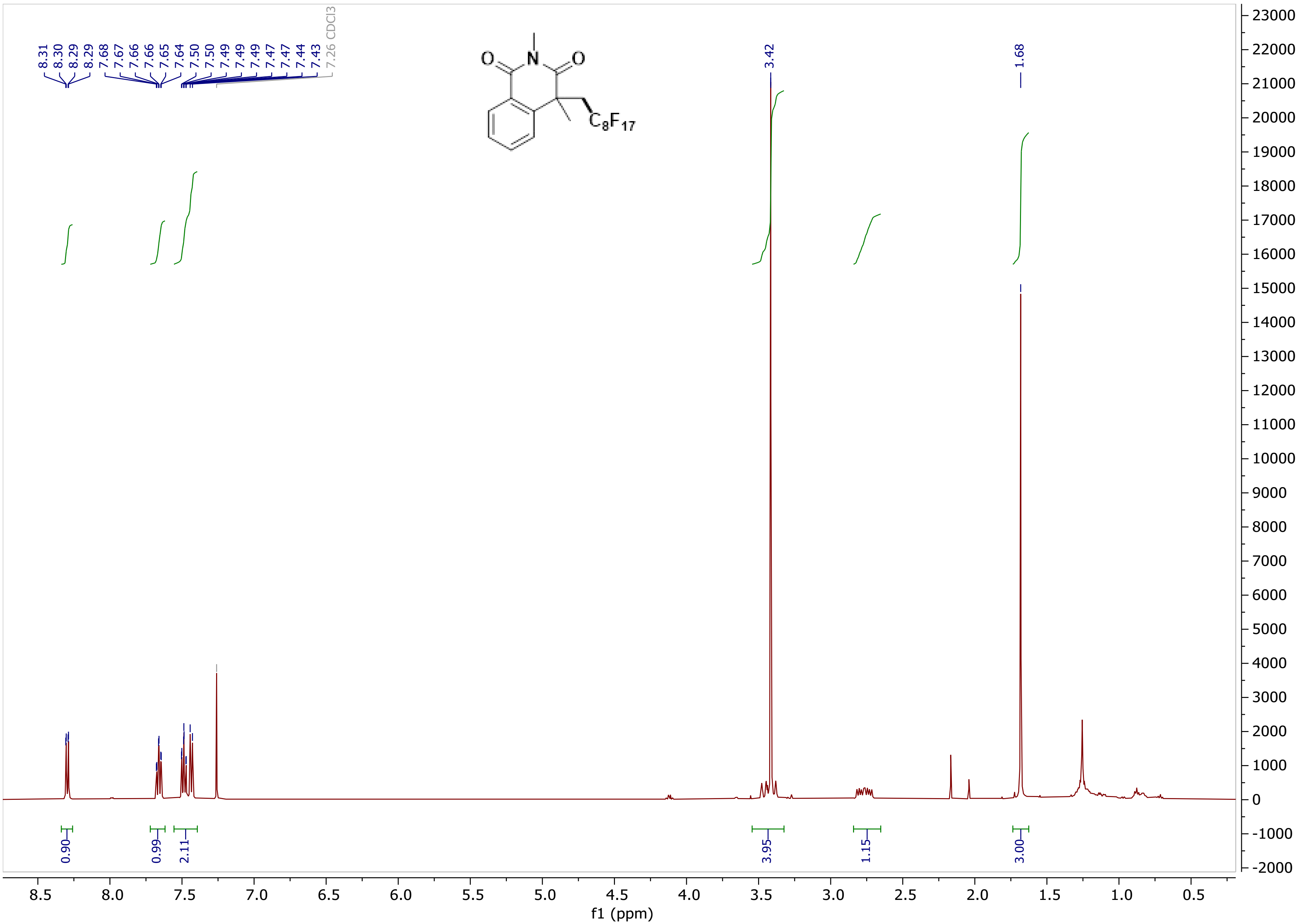


^{1}H NMR of PF10, $CDCl_3$, 500 MHz



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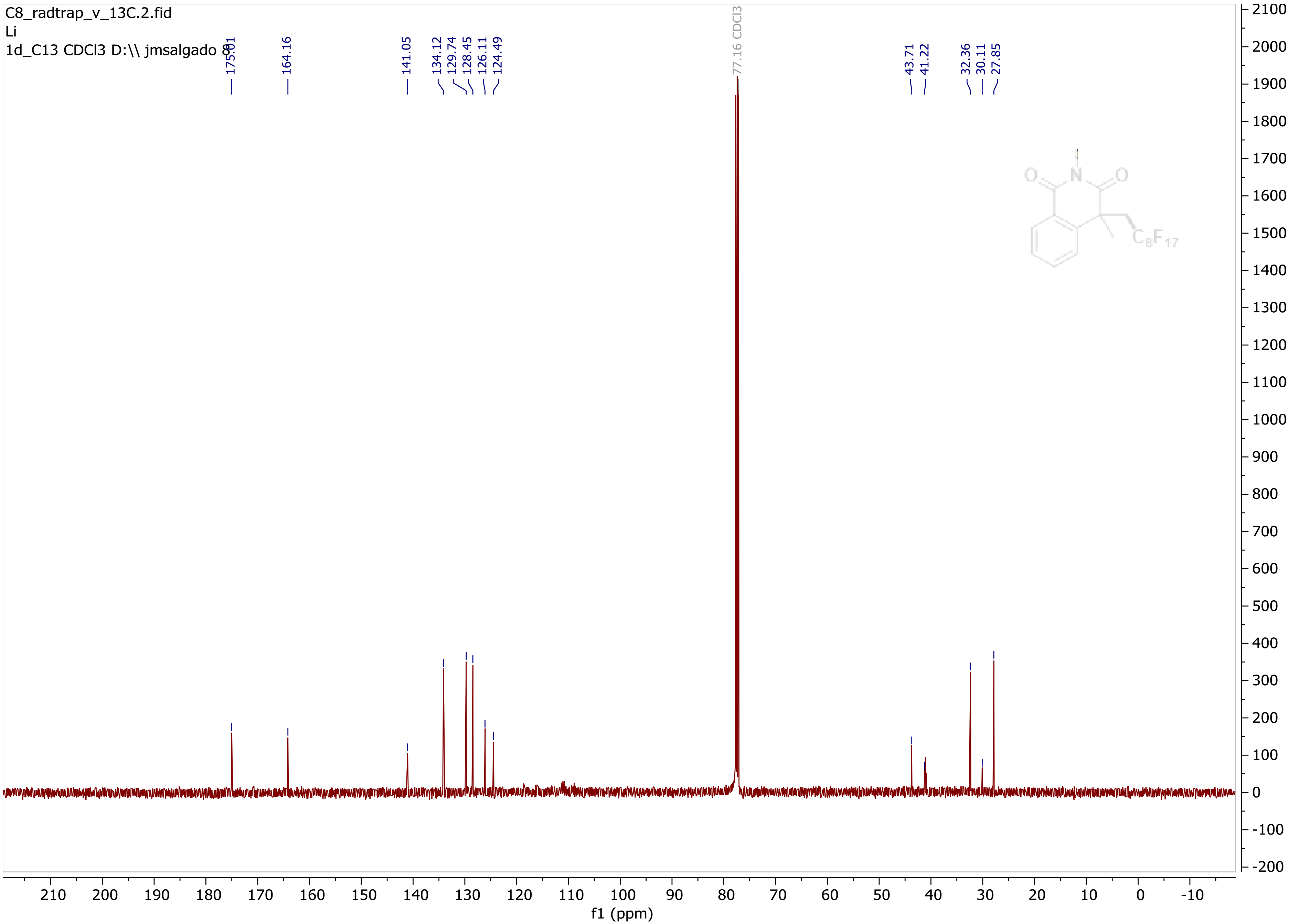

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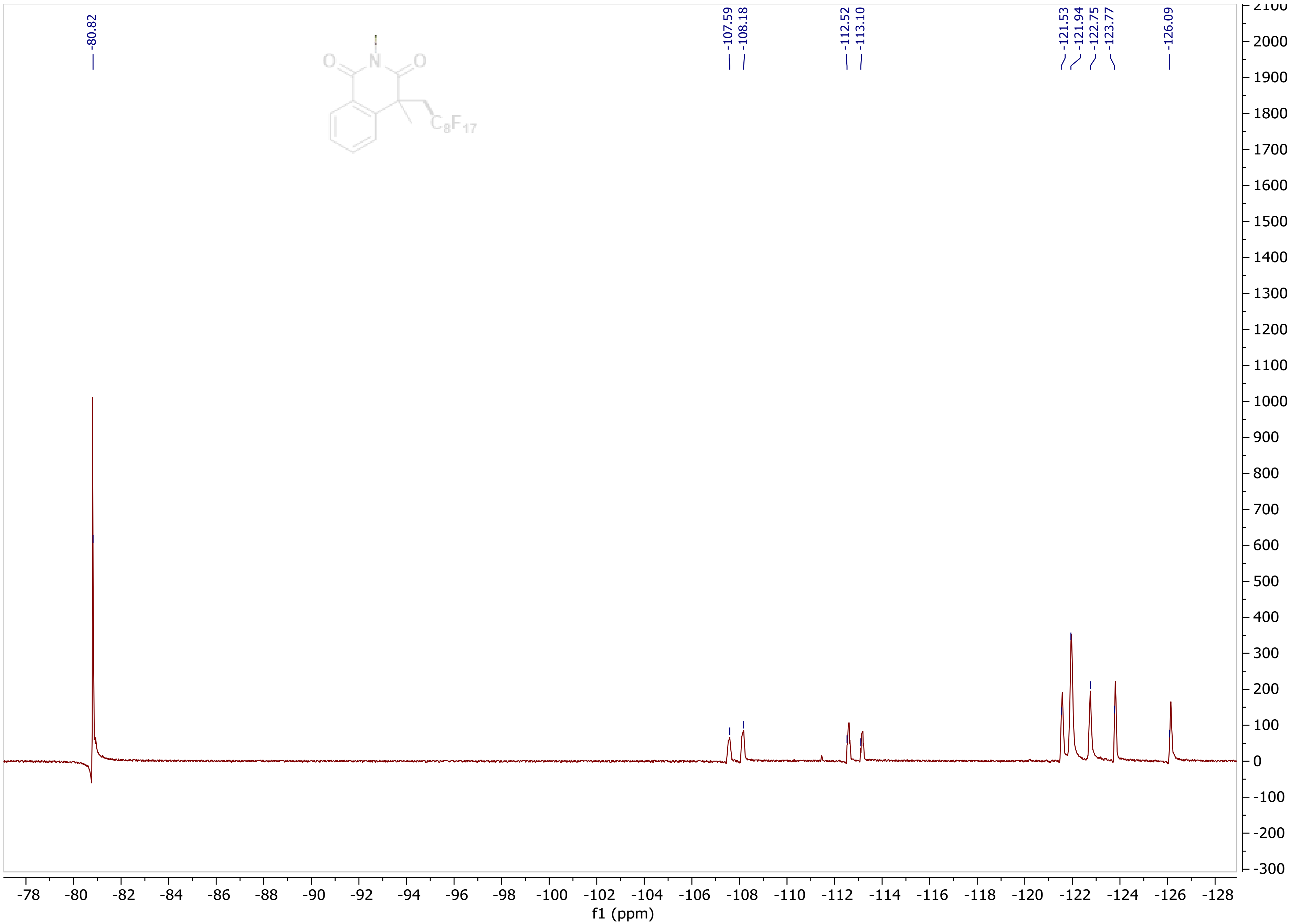
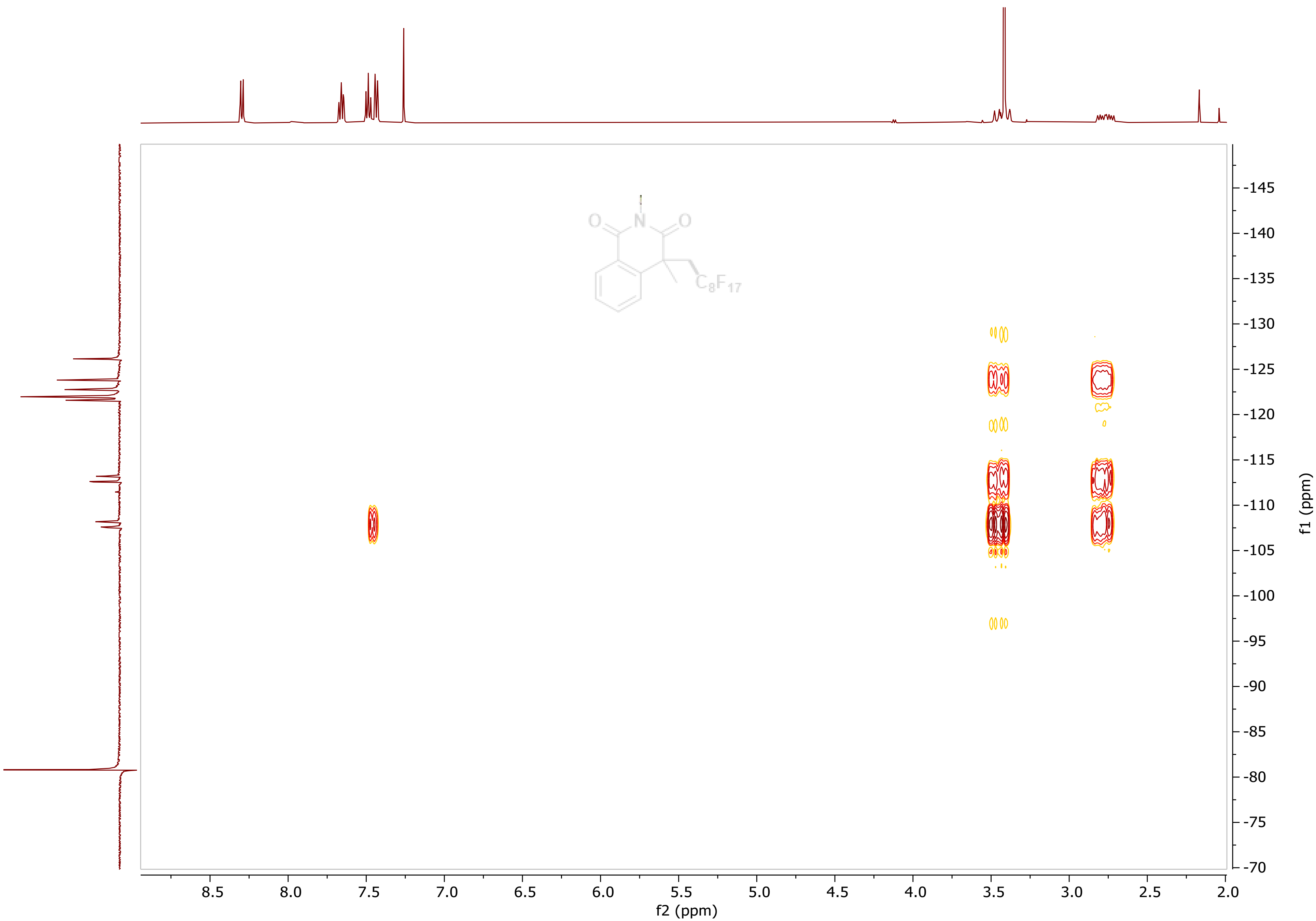
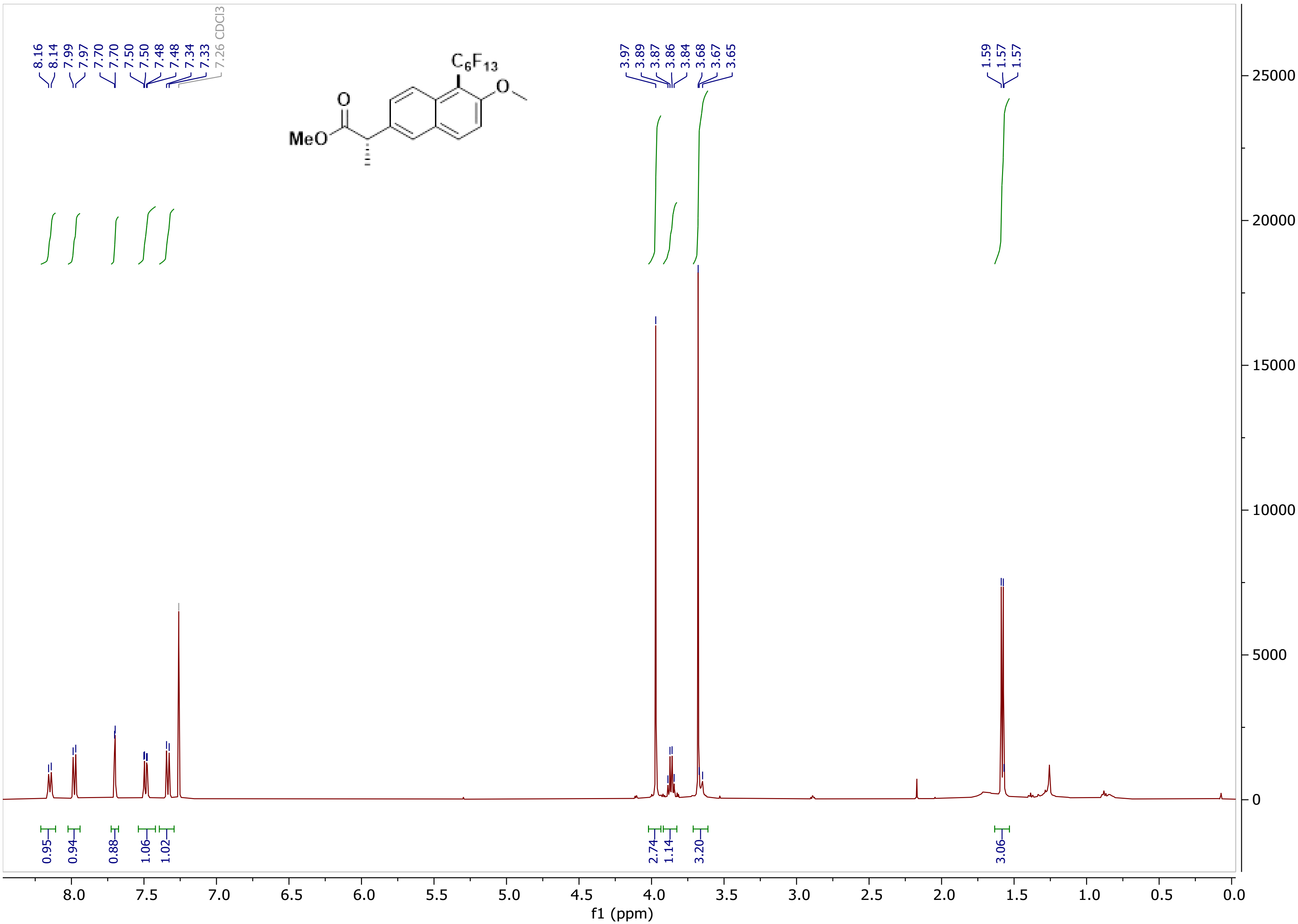


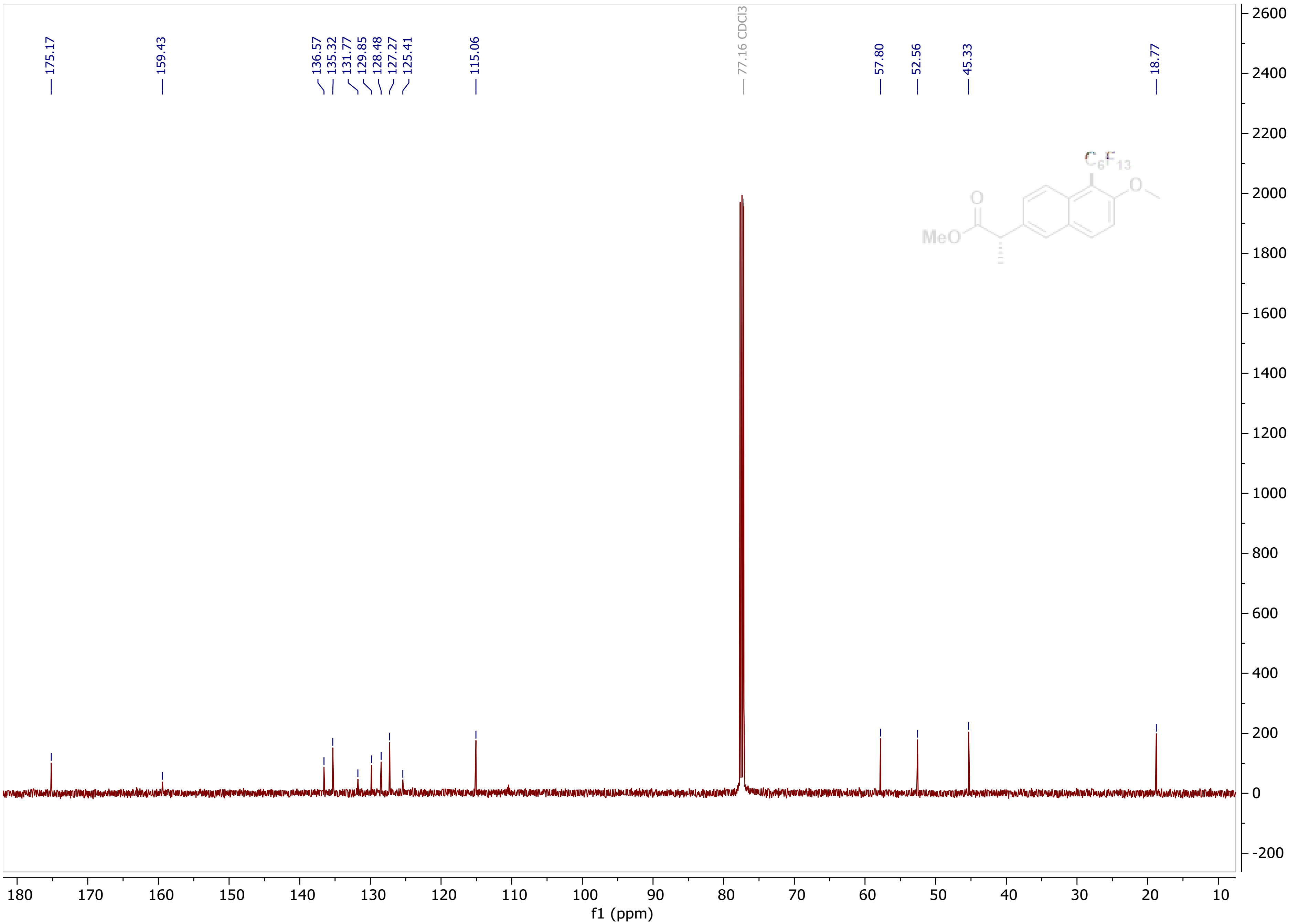
^1H-^{19}F HMBC of PF10



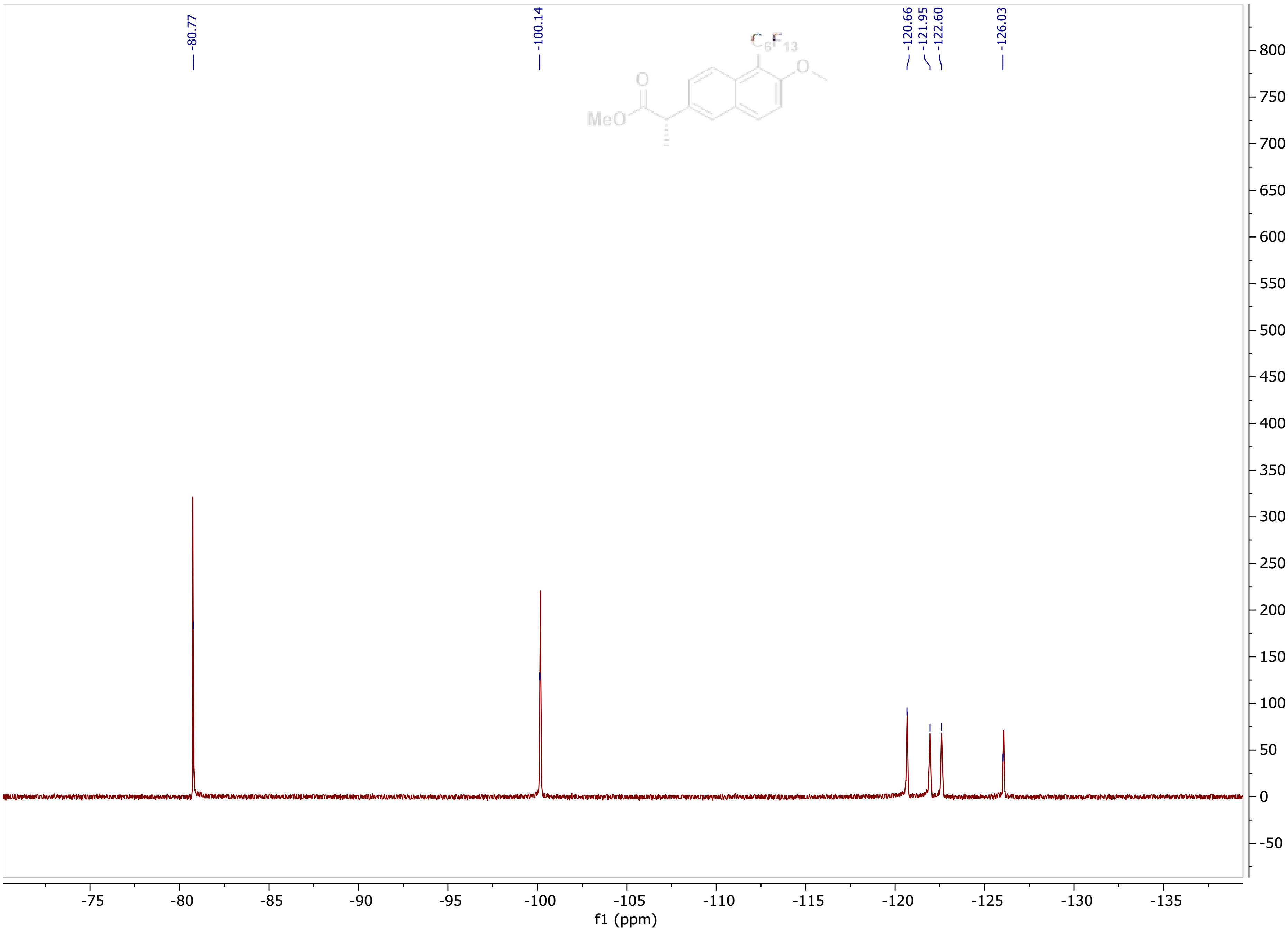
^{1}H NMR of PF11, $CDCl_3$, 500 MHz



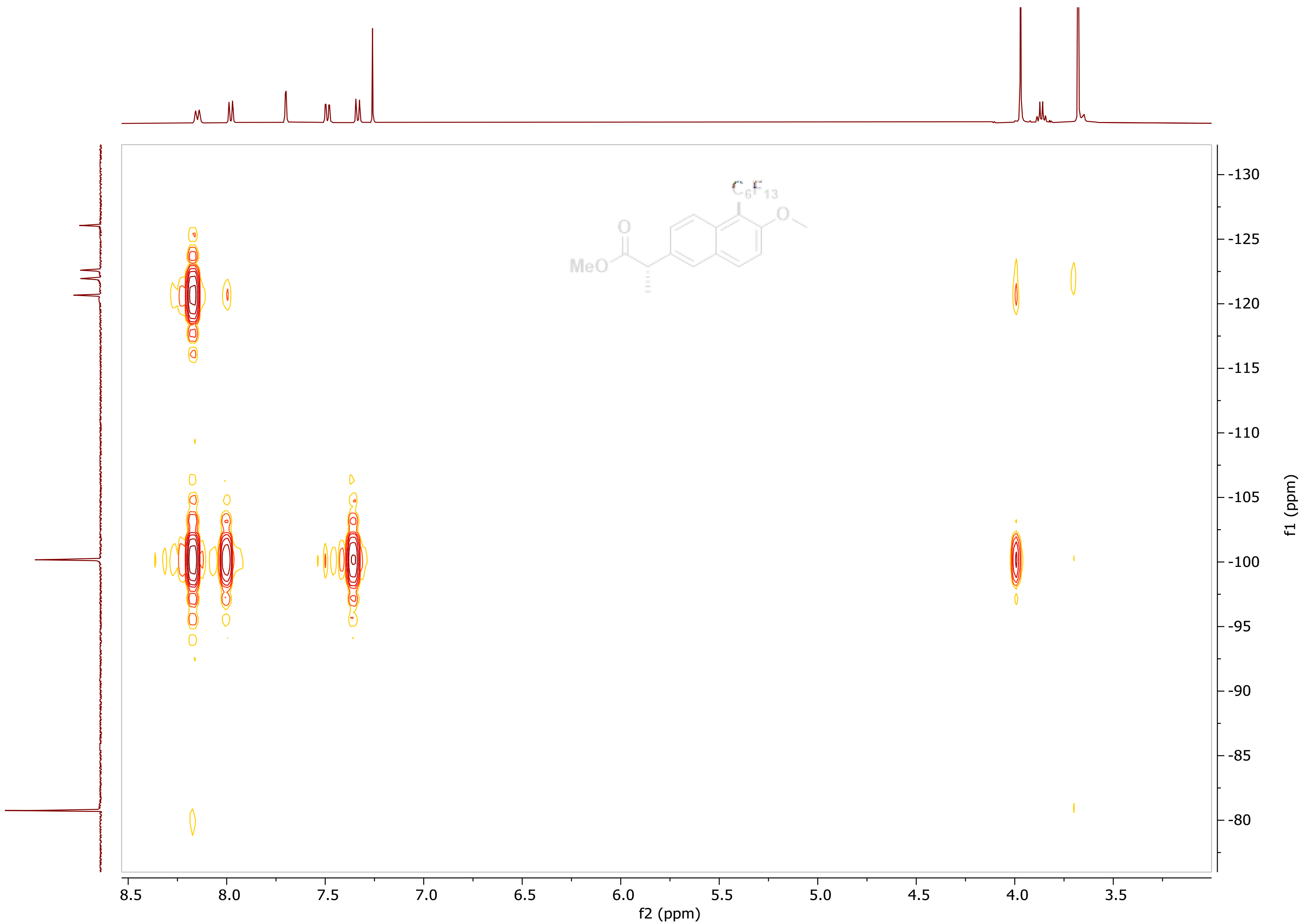
^{13}C NMR of PF11, $CDCl_3$, 126 MHz



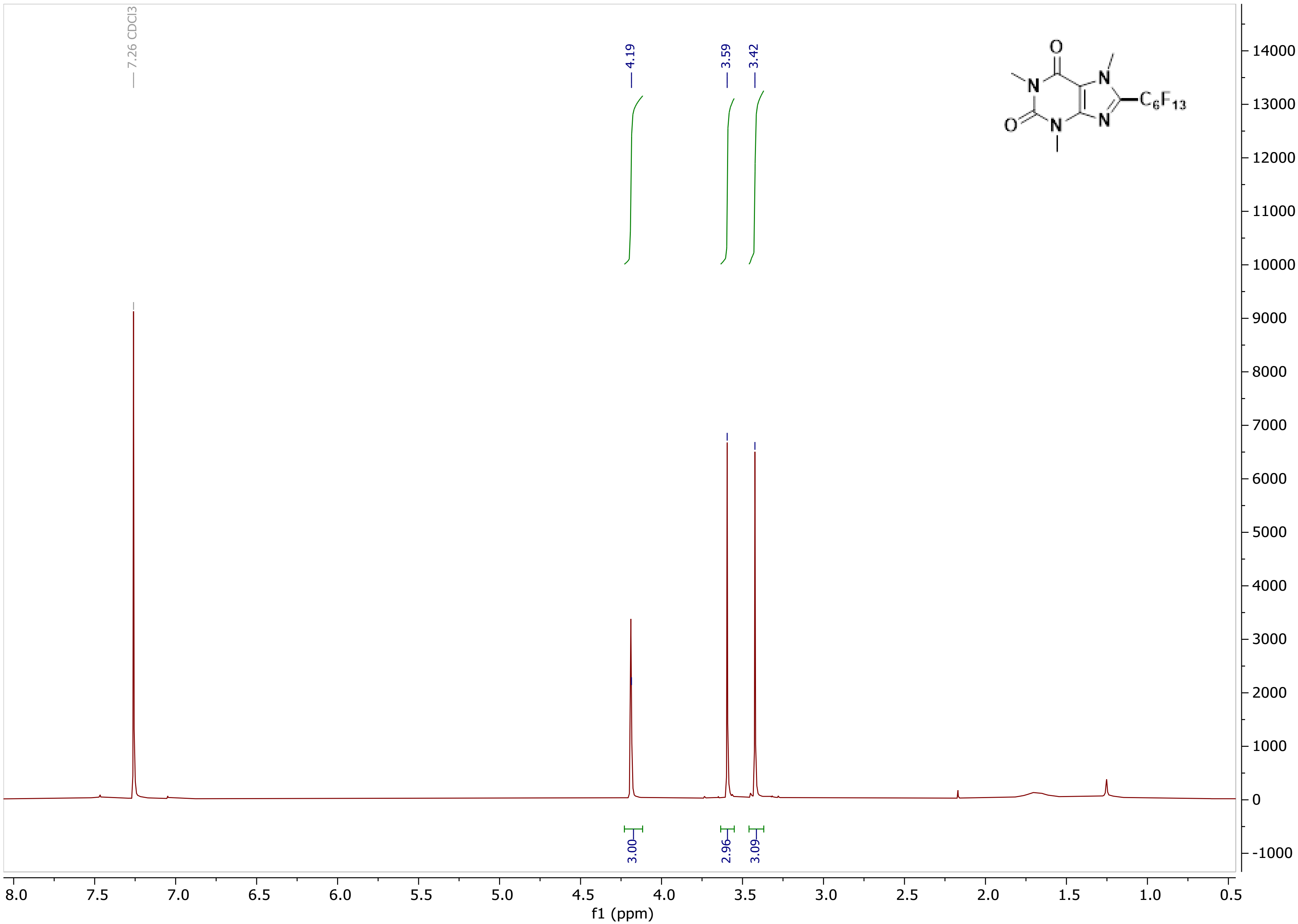
^{19}F NMR of PF11, $CDCl_3$, 471 MHz



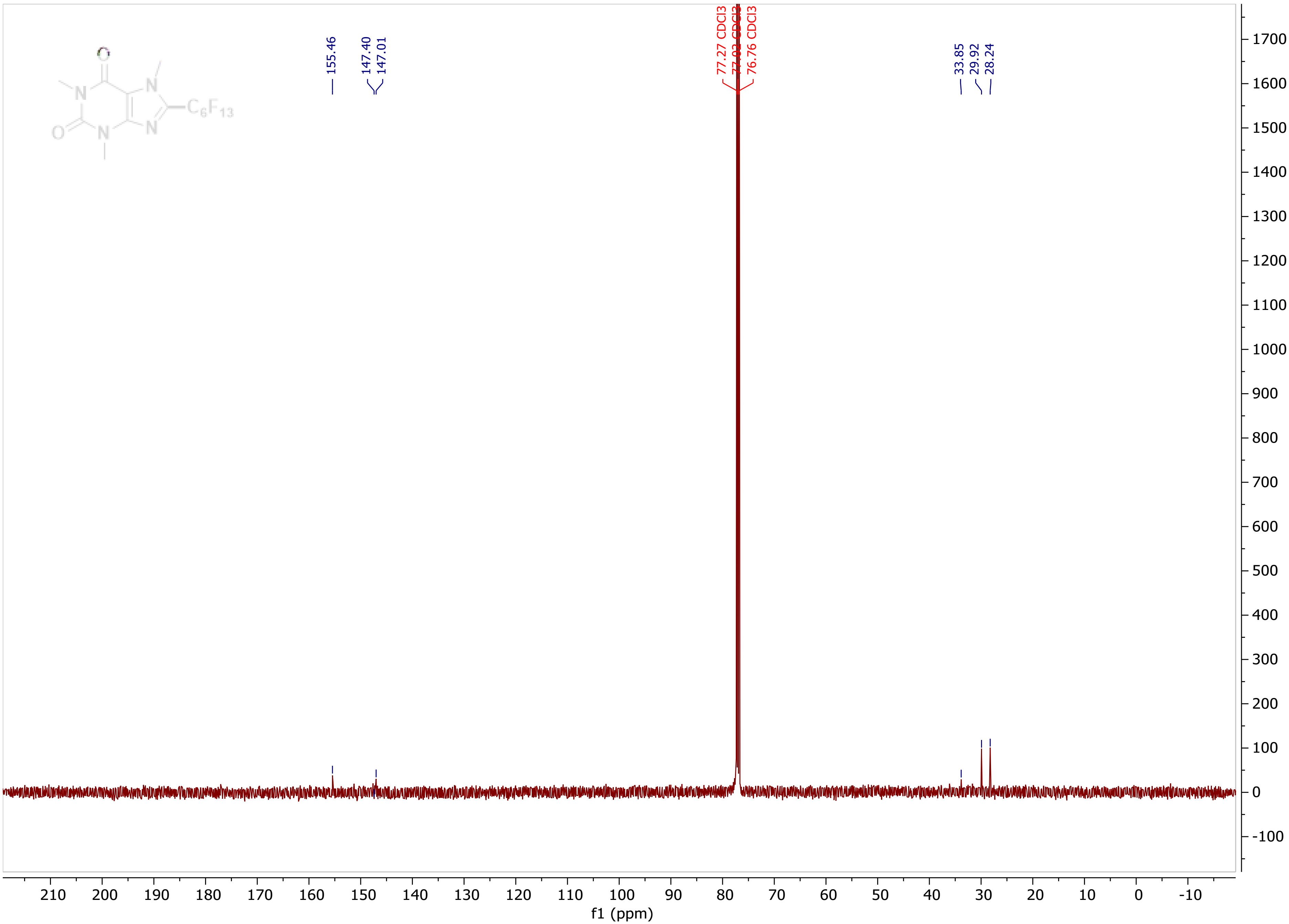
^{1}H-^{19}F HMBC of PF11



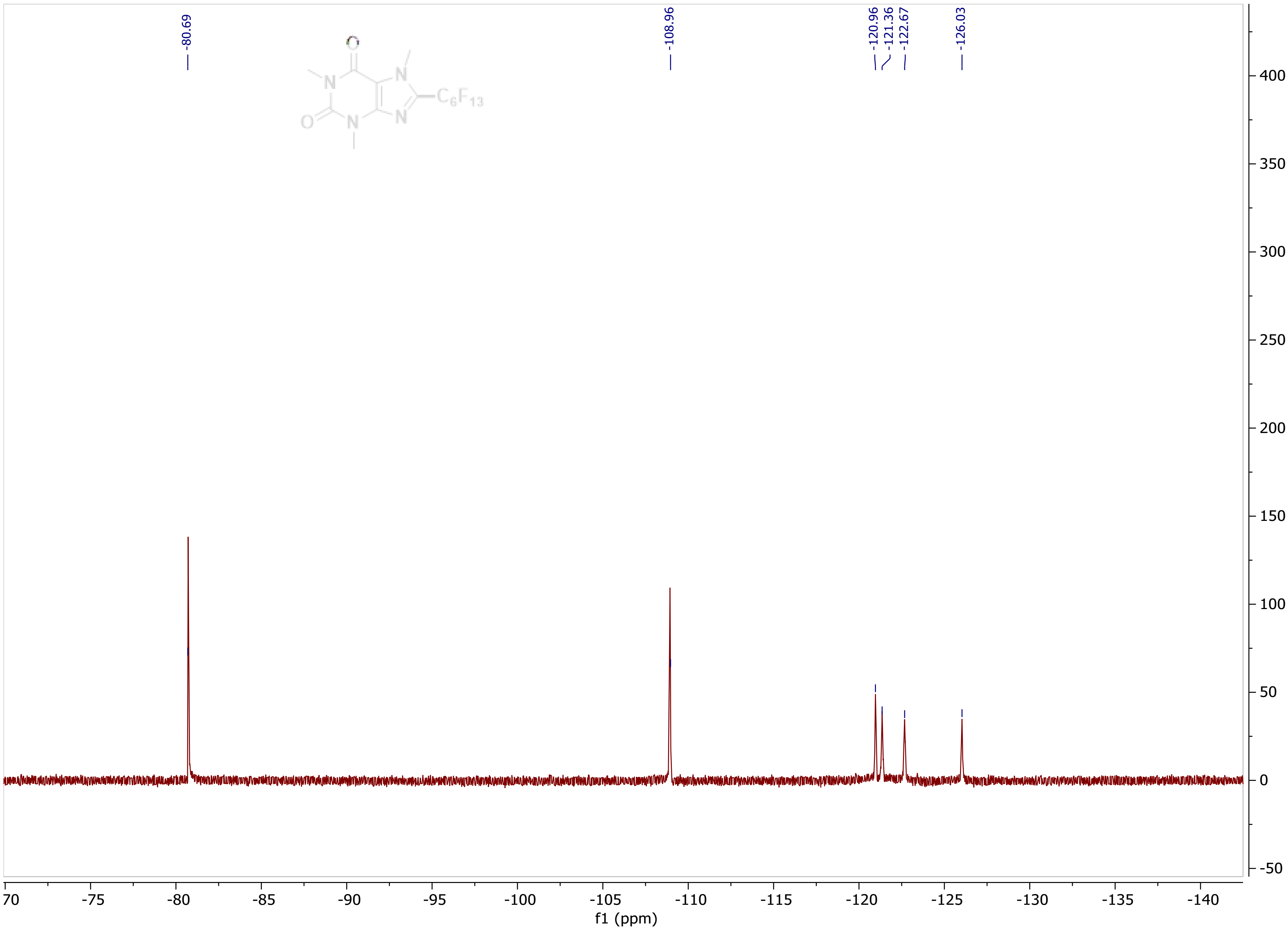
[1]H NMR of PF12 $CDCl_3$, 500 MHz



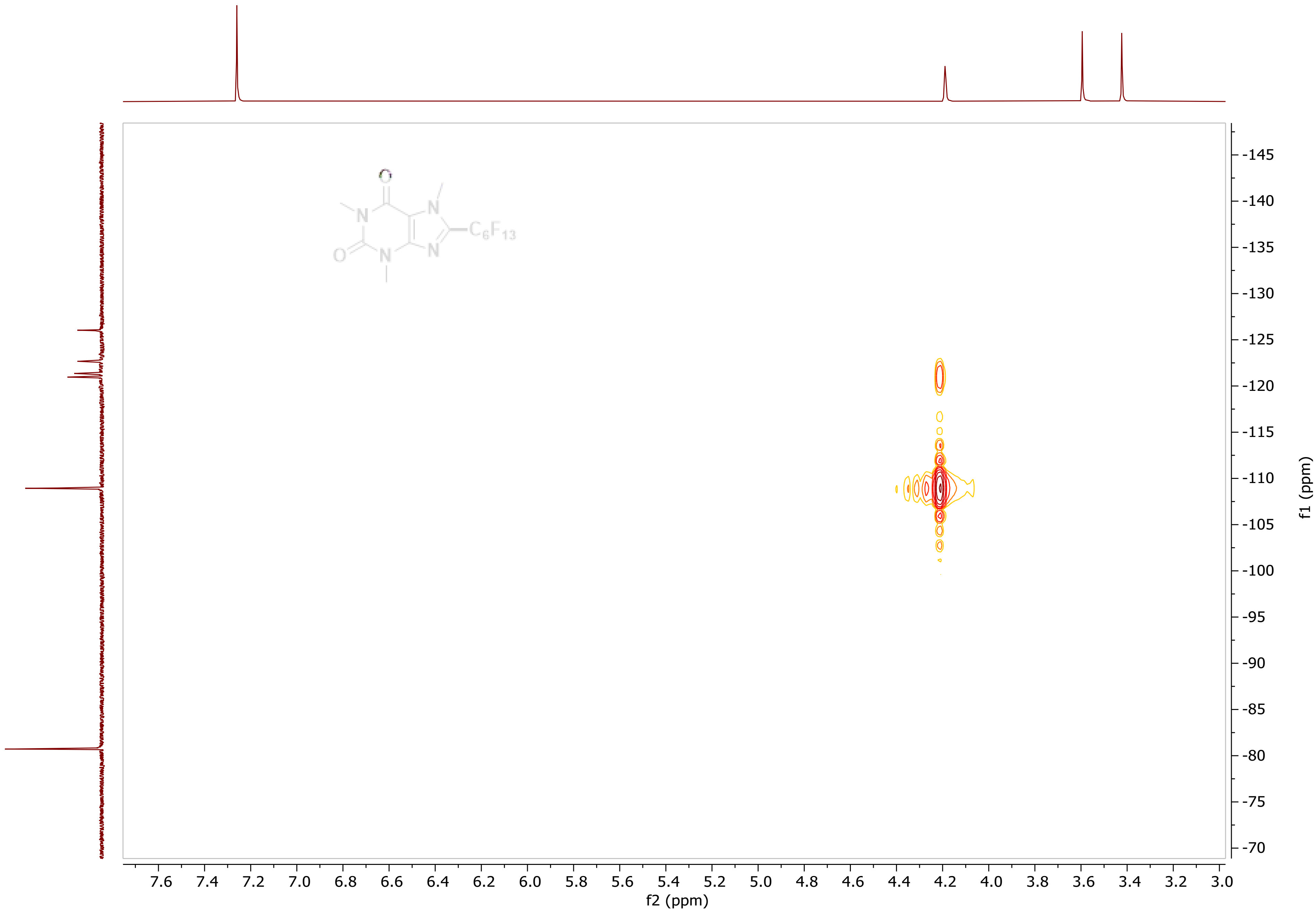
^{13}C NMR of PF12, $CDCl_3$, 126 MHz



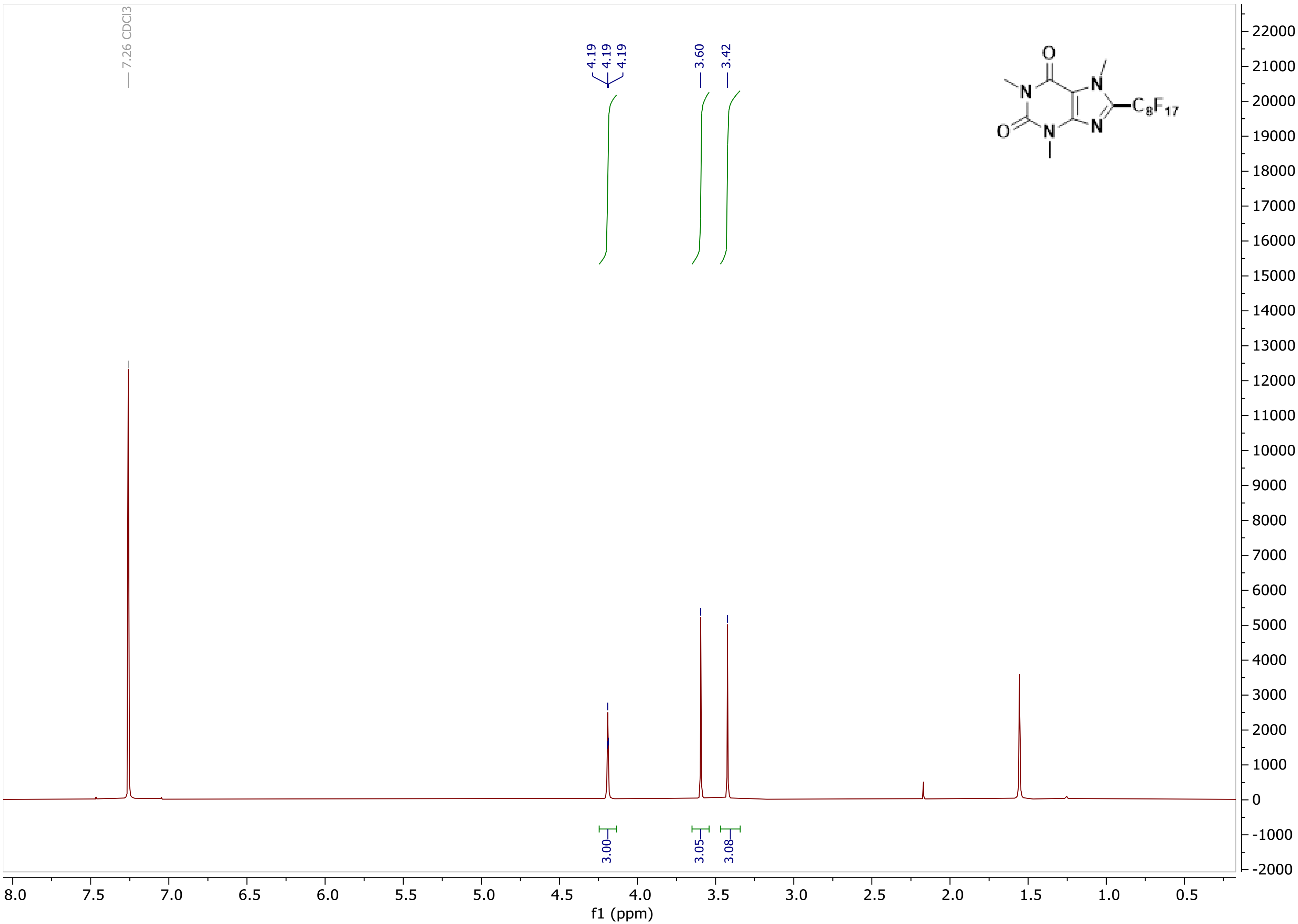
[19]F NMR of PF12, $CDCl_3$, 471 MHz



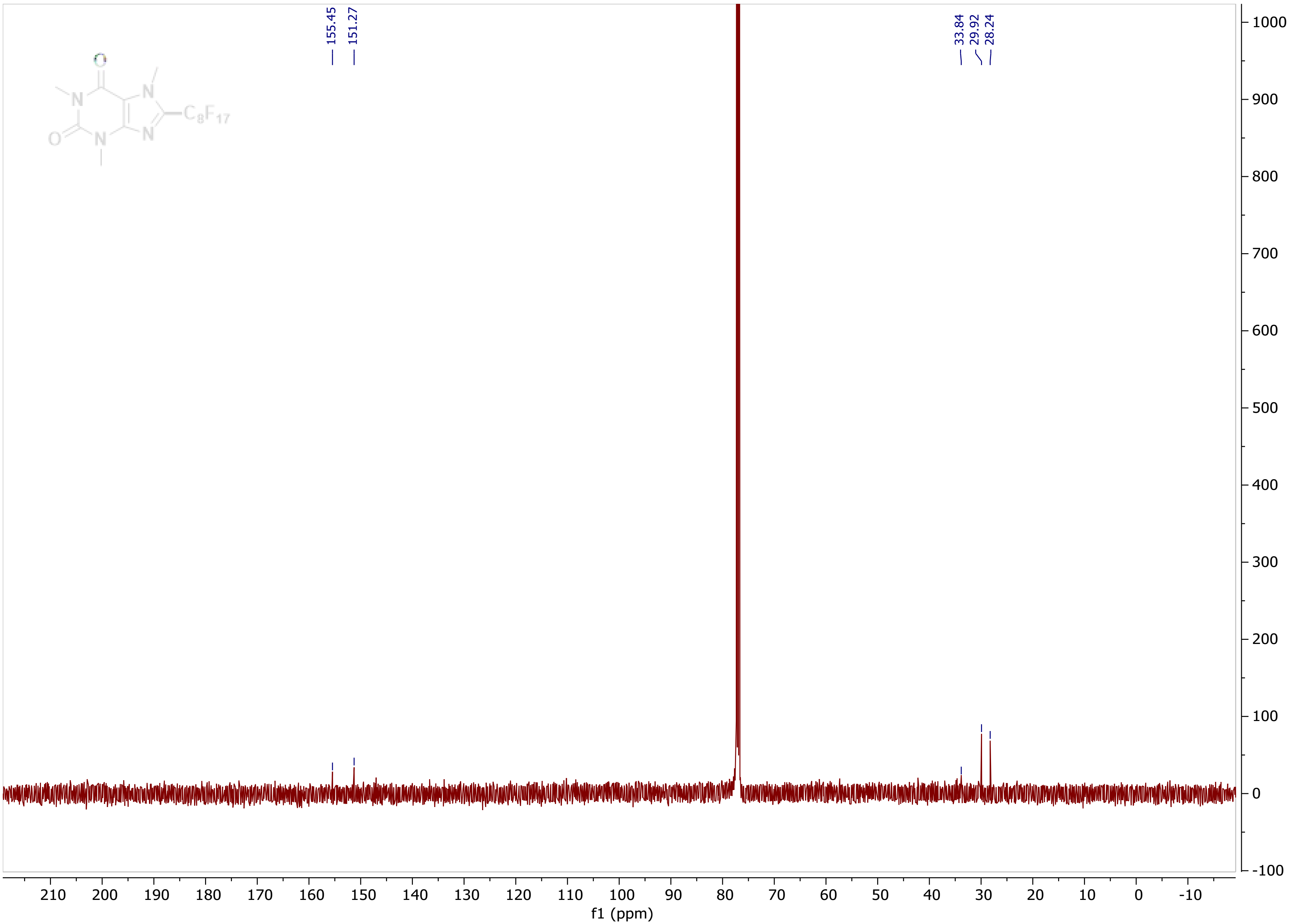
^{1}H-^{19}F HMBC of PF12



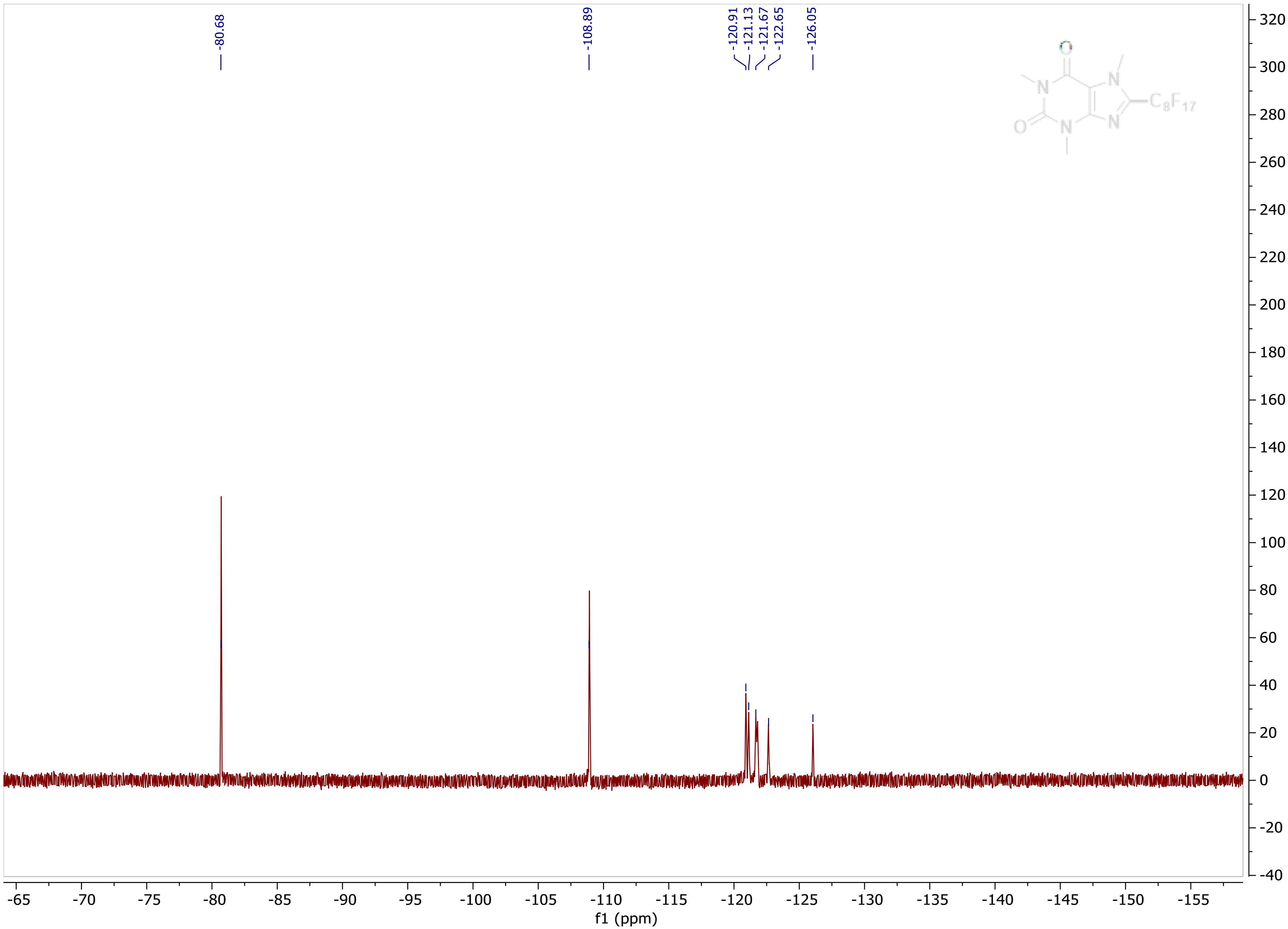
[1]H NMR of PF13, $CDCl_3$, 500 MHz



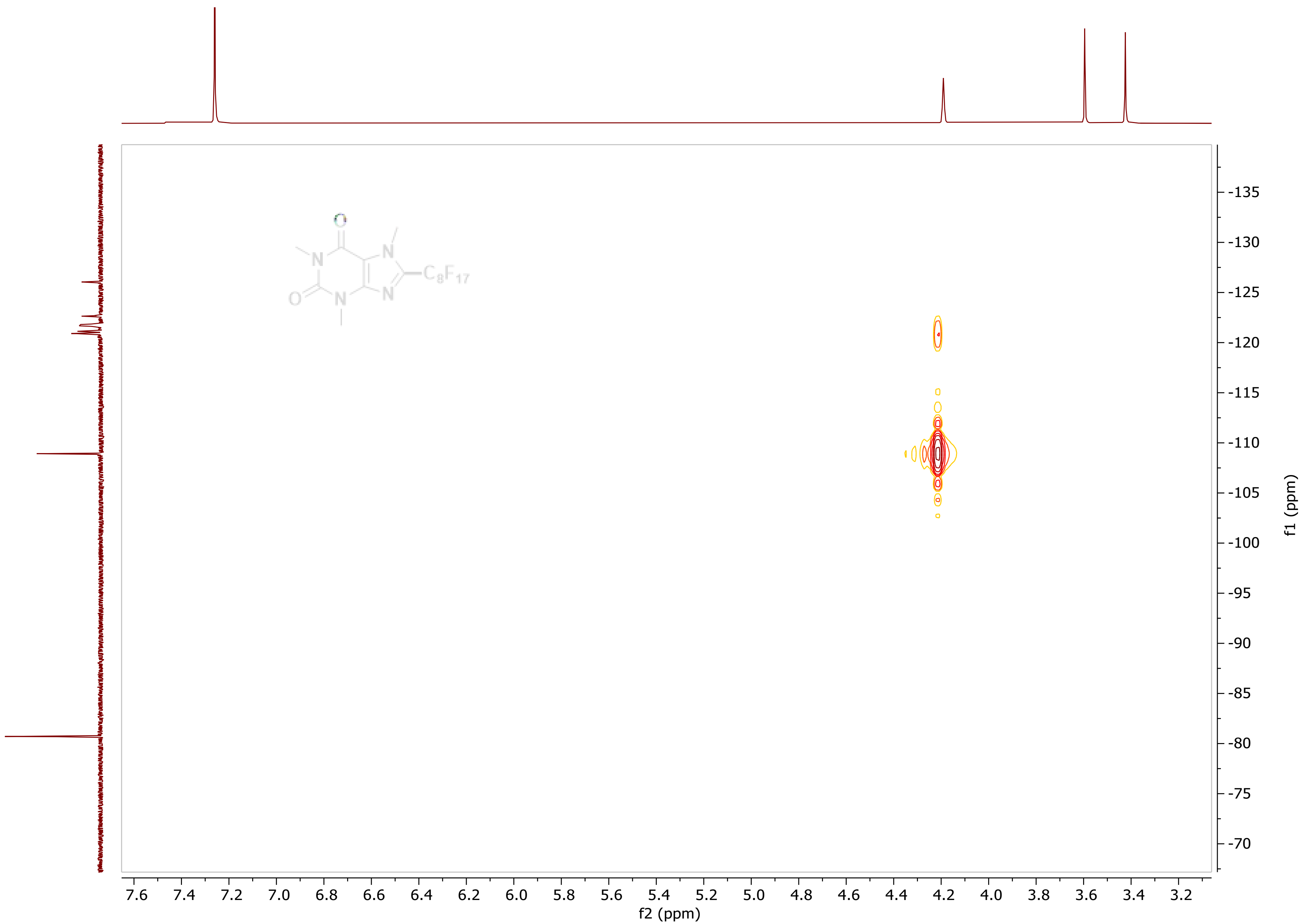
^{13}C NMR of PF13, $CDCl_3$, 126 MHz



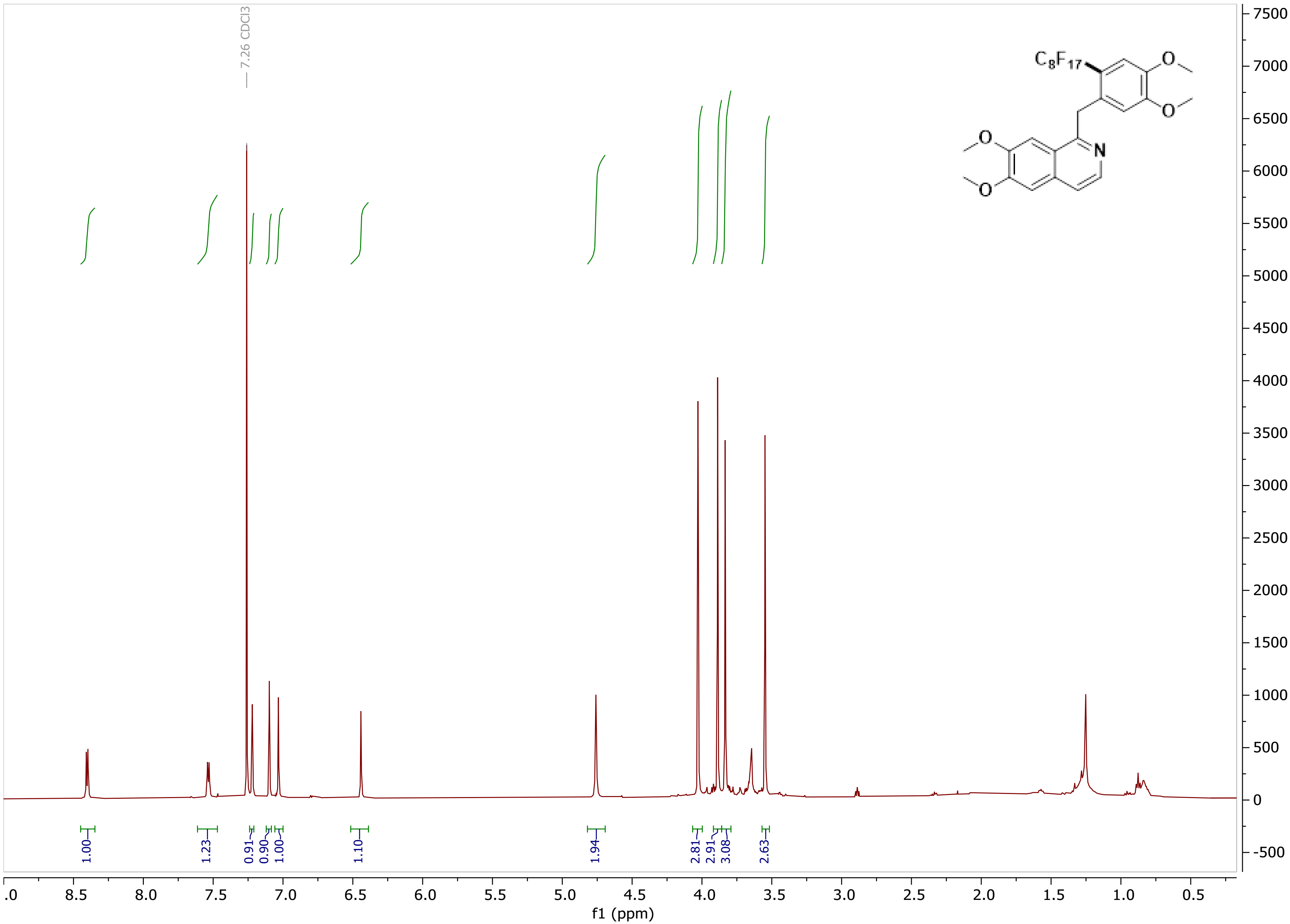
^{19}F NMR of PF13, $CDCl_3$, 471 MHz



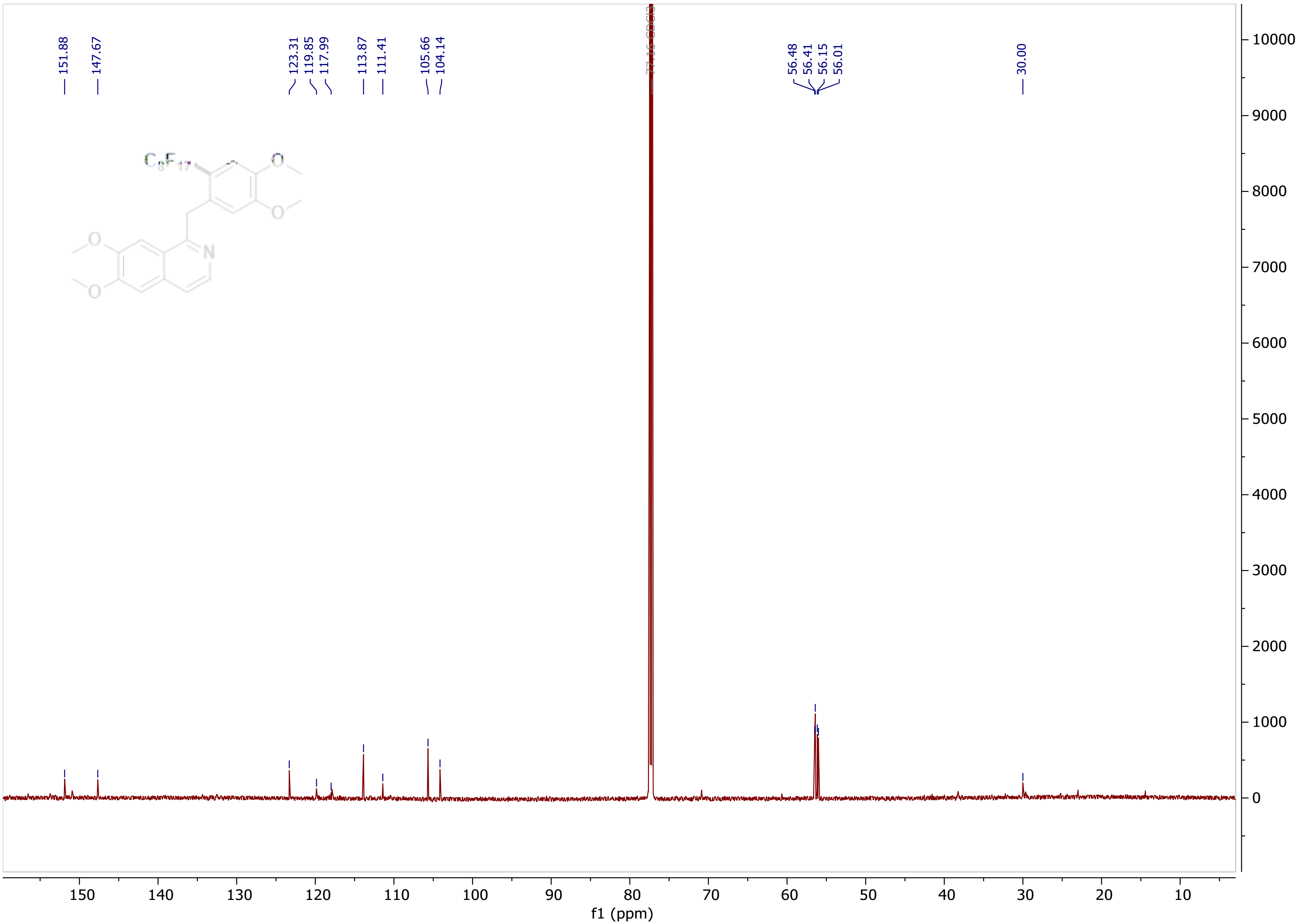
^{1}H-^{19}F HMBC of PF13



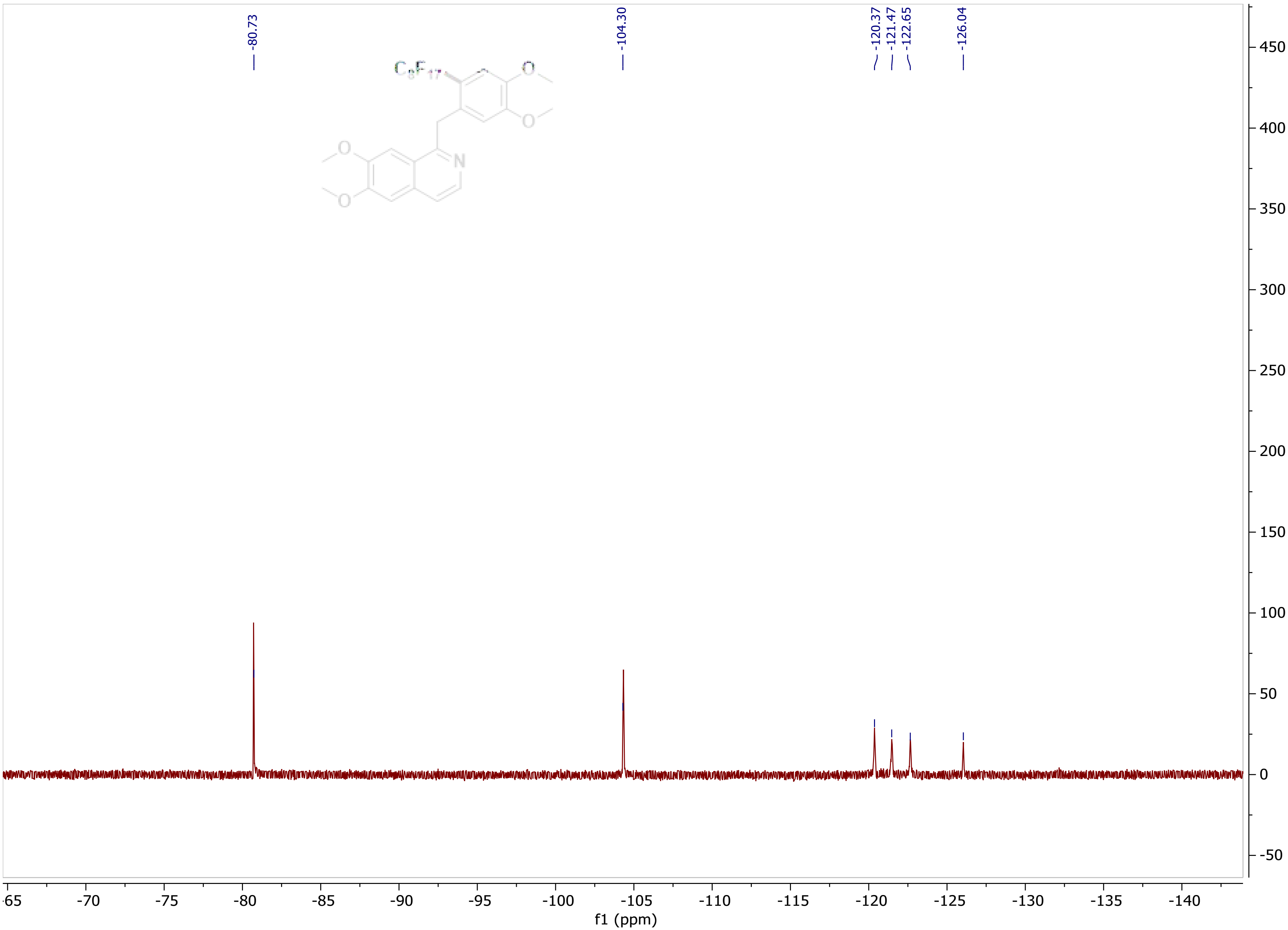
^1H NMR of PF14, $CDCl_3$, 500 MHz



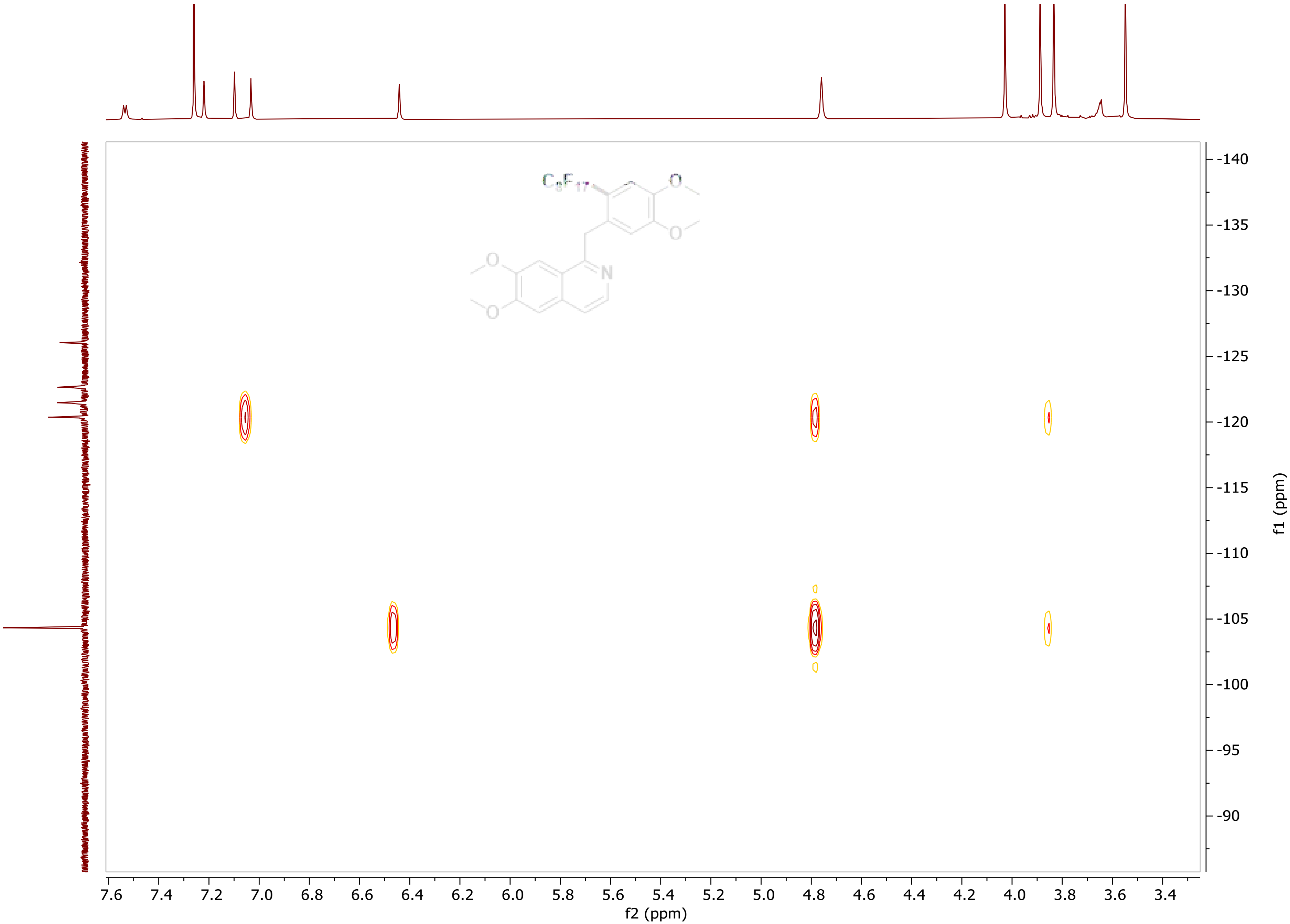
^{13}C NMR of PF14, $CDCl_3$, 126 MHz



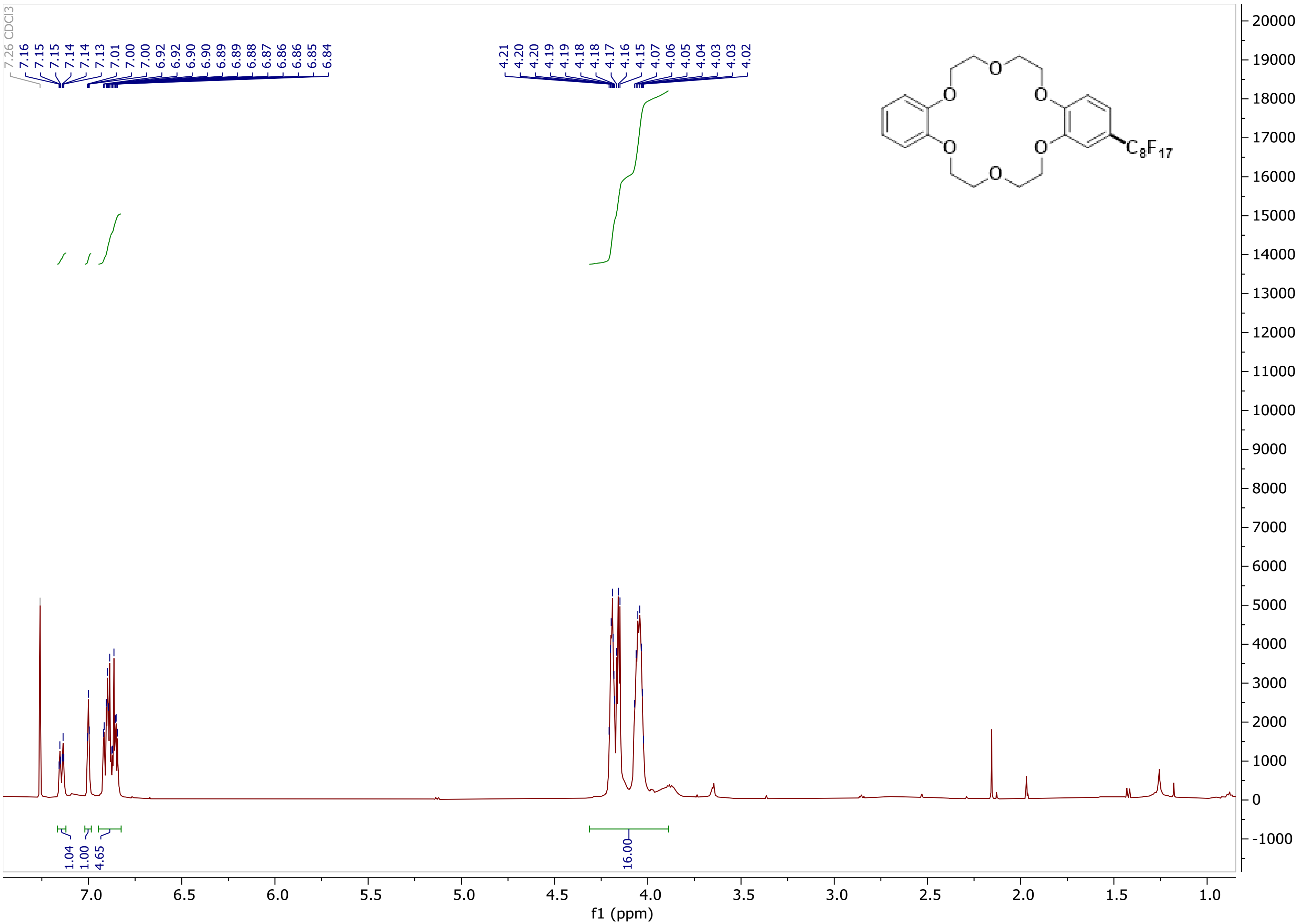
^{19}F NMR of PF14, $CDCl_3$, 471 MHz



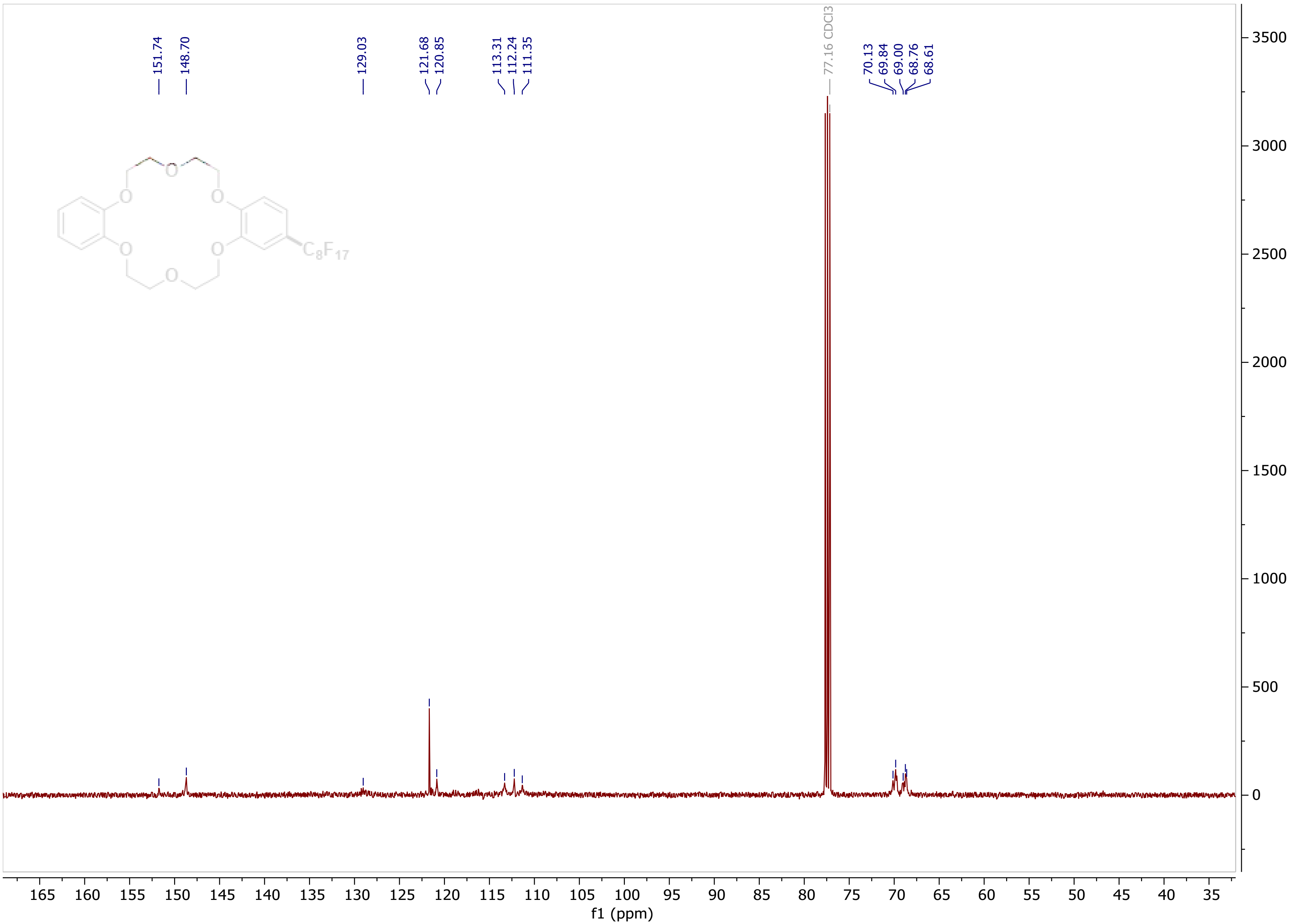
^{1}H-^{19}F HMBC of PF14



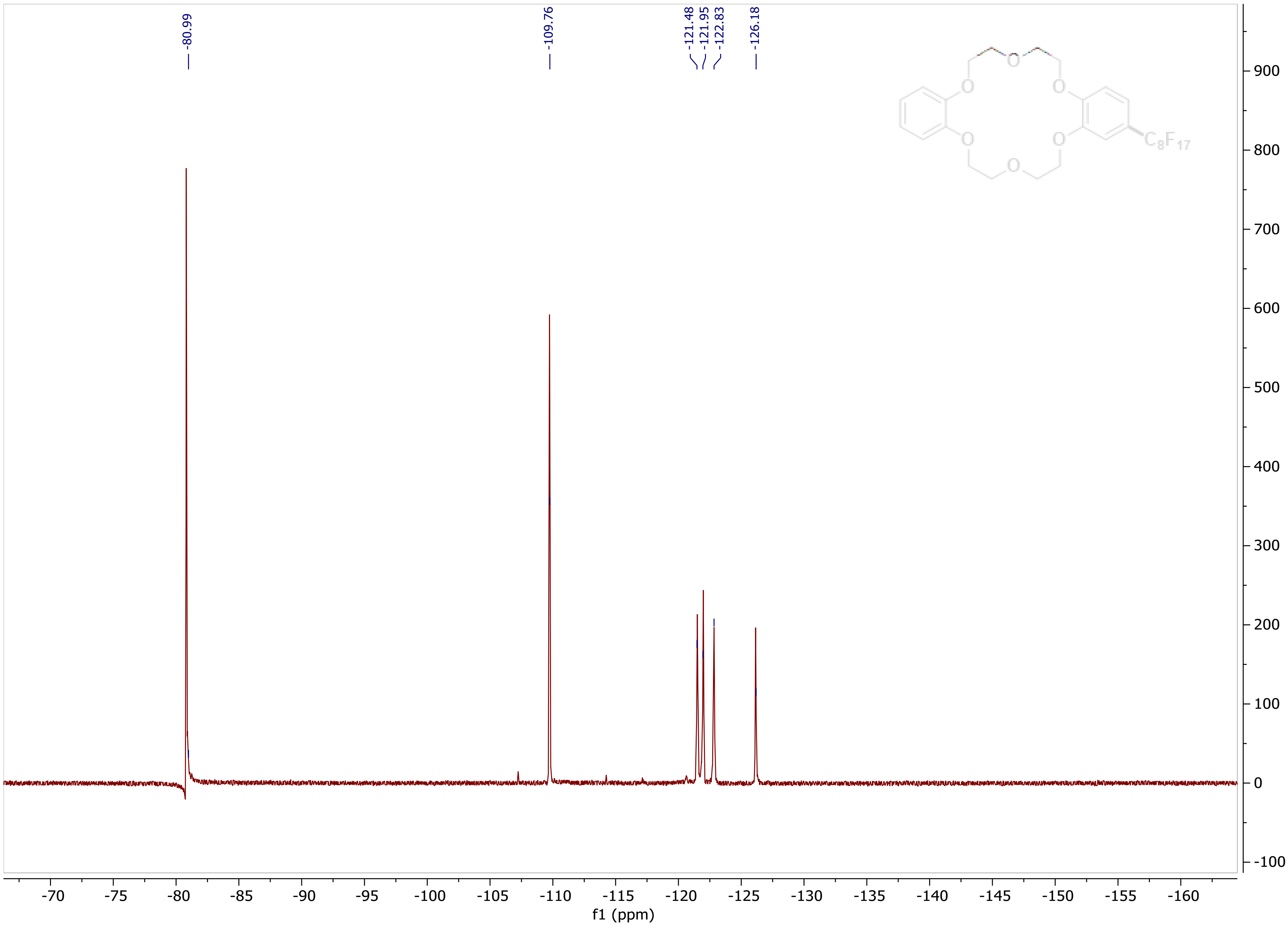
^1H NMR of PF15, $CDCl_3$, 500 MHz



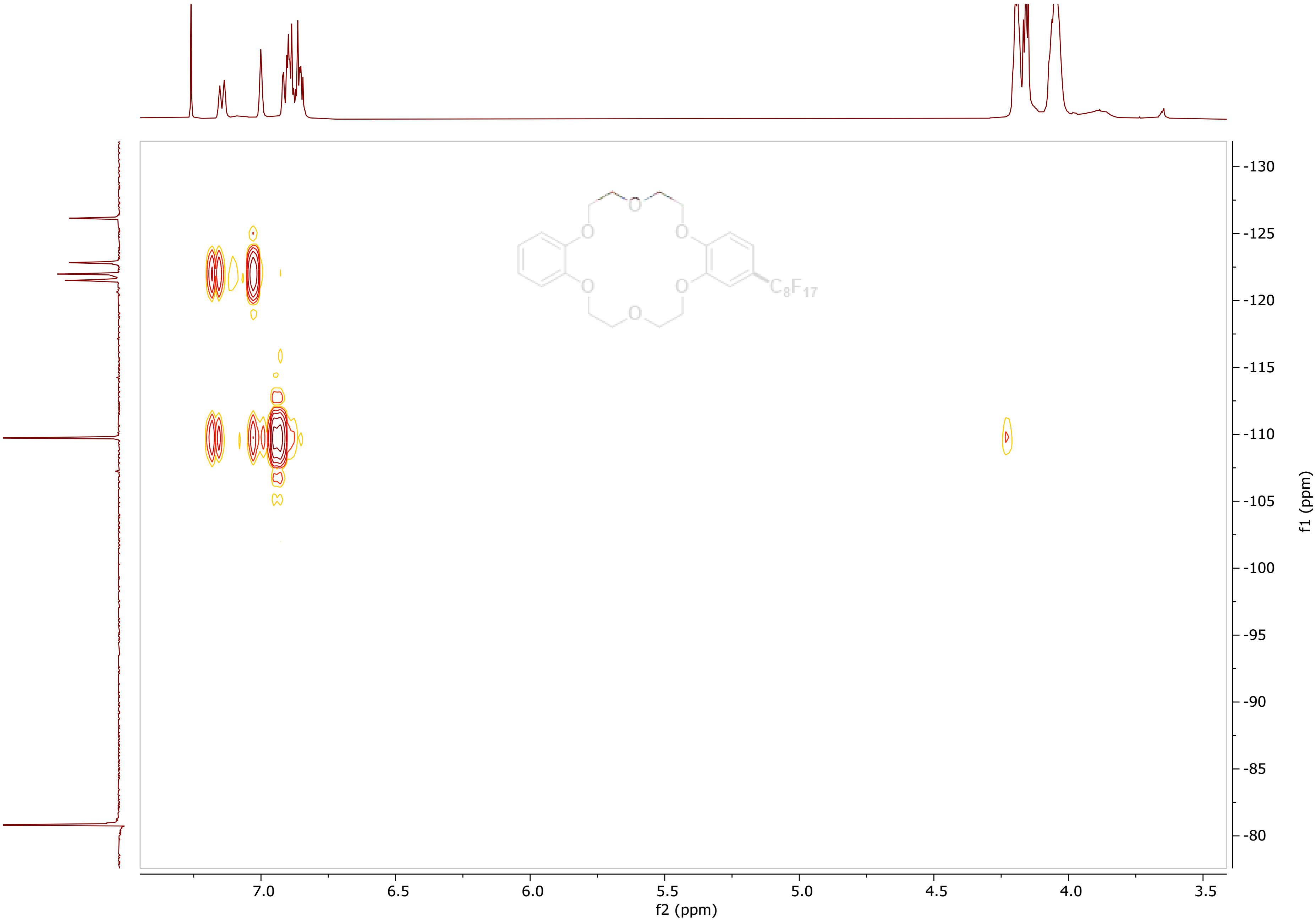
^{13}C NMR of PF15, $CDCl_3$, 126 MHz



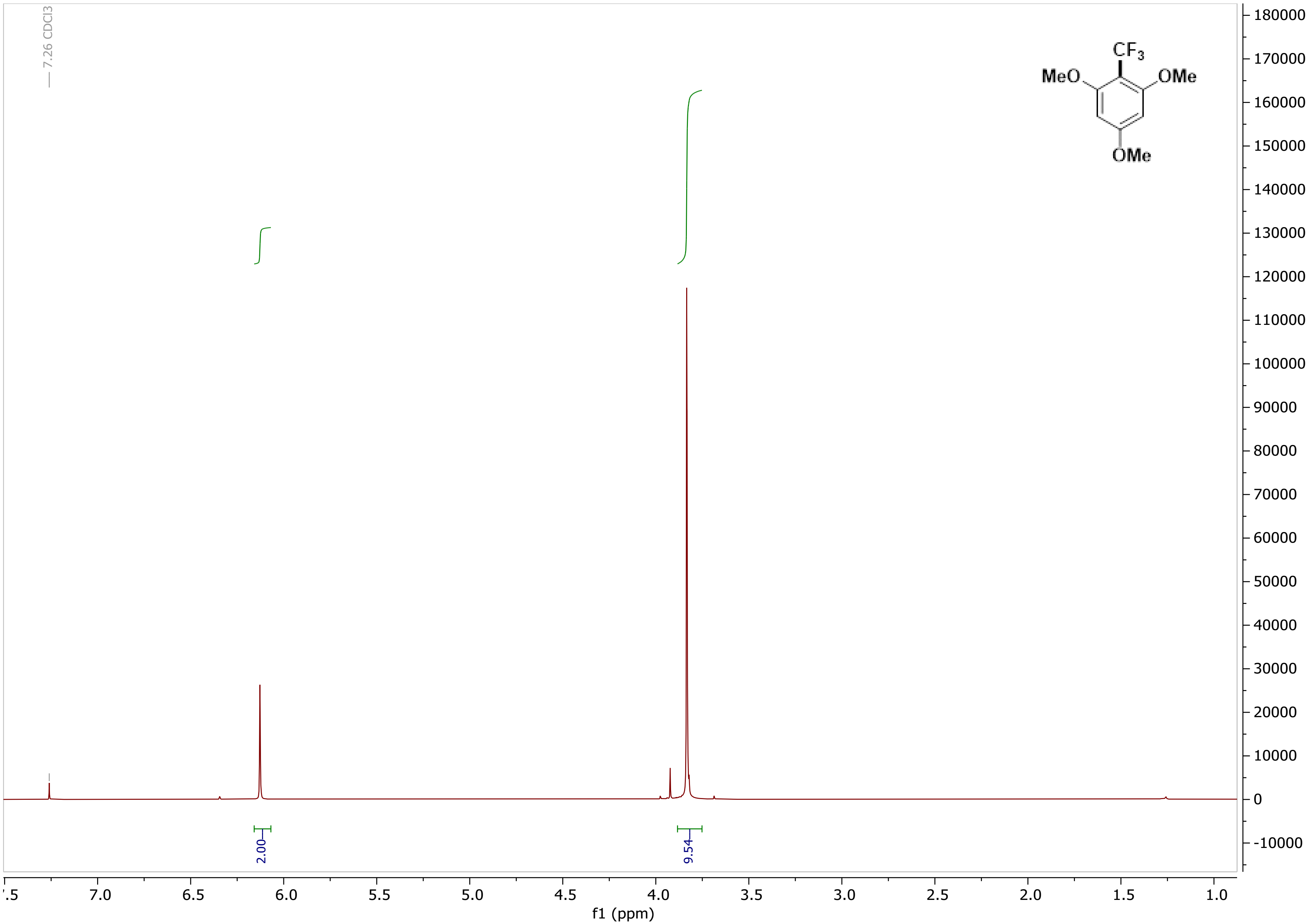
^{19}F NMR of PF15, $CDCl_3$, 471 MHz



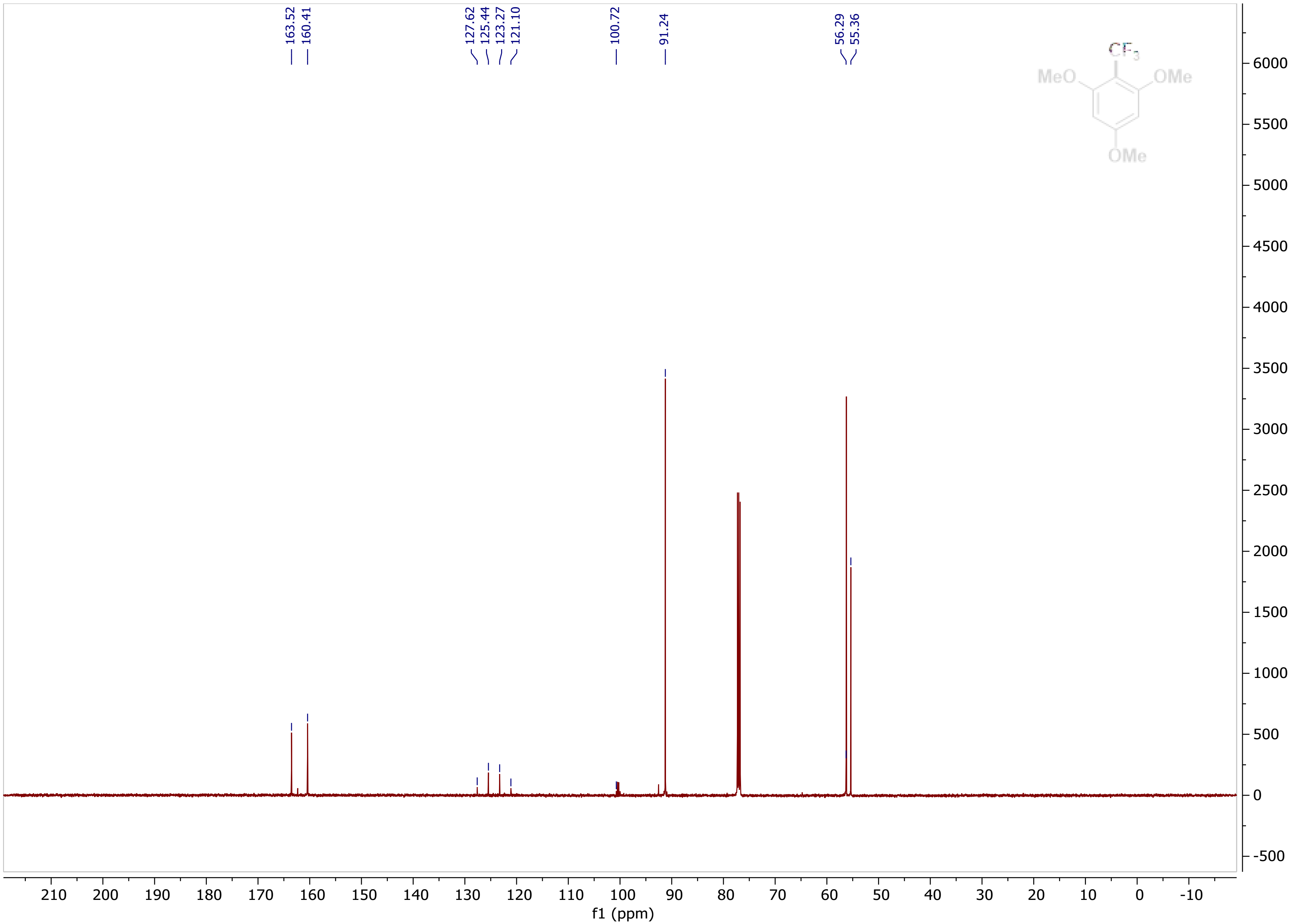
^{1}H-^{19}F HMBC of PF15



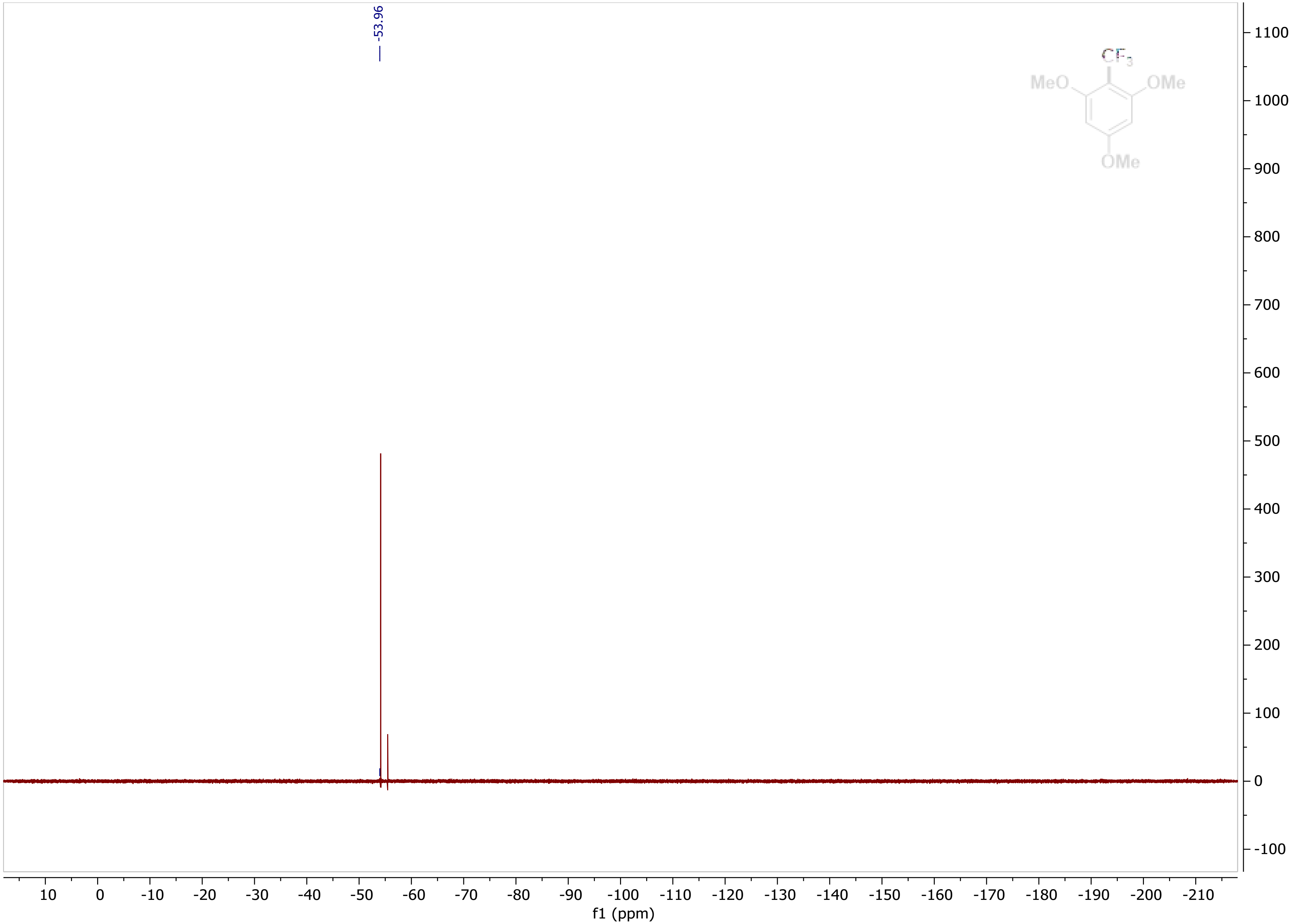
^{1}H NMR of TF1, $CDCl_3$, 500 MHz



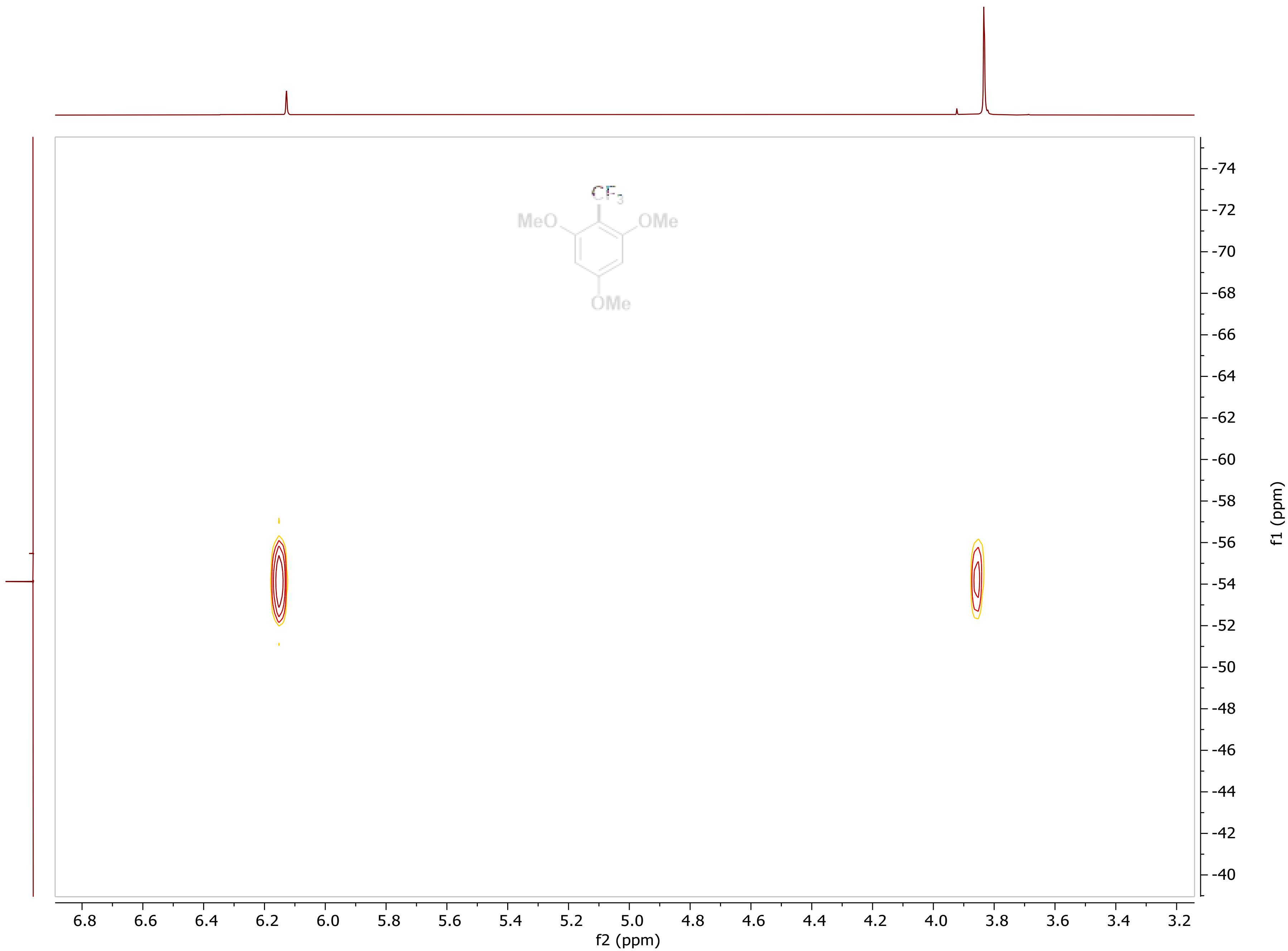
^{13}C NMR of TF1, $CDCl_3$, 126 MHz



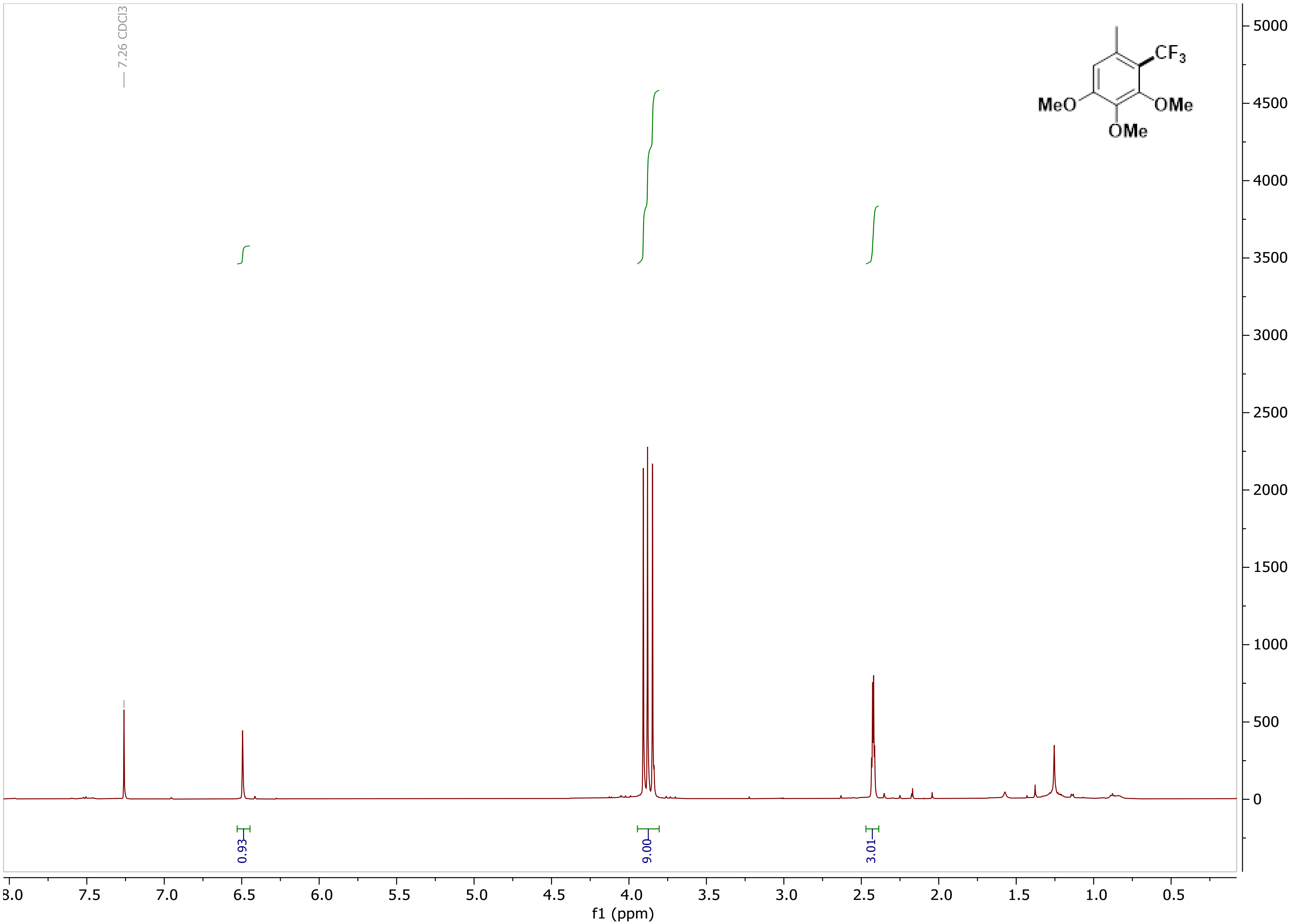
^{19}F NMR of TF1, $CDCl_3$, 471 MHz



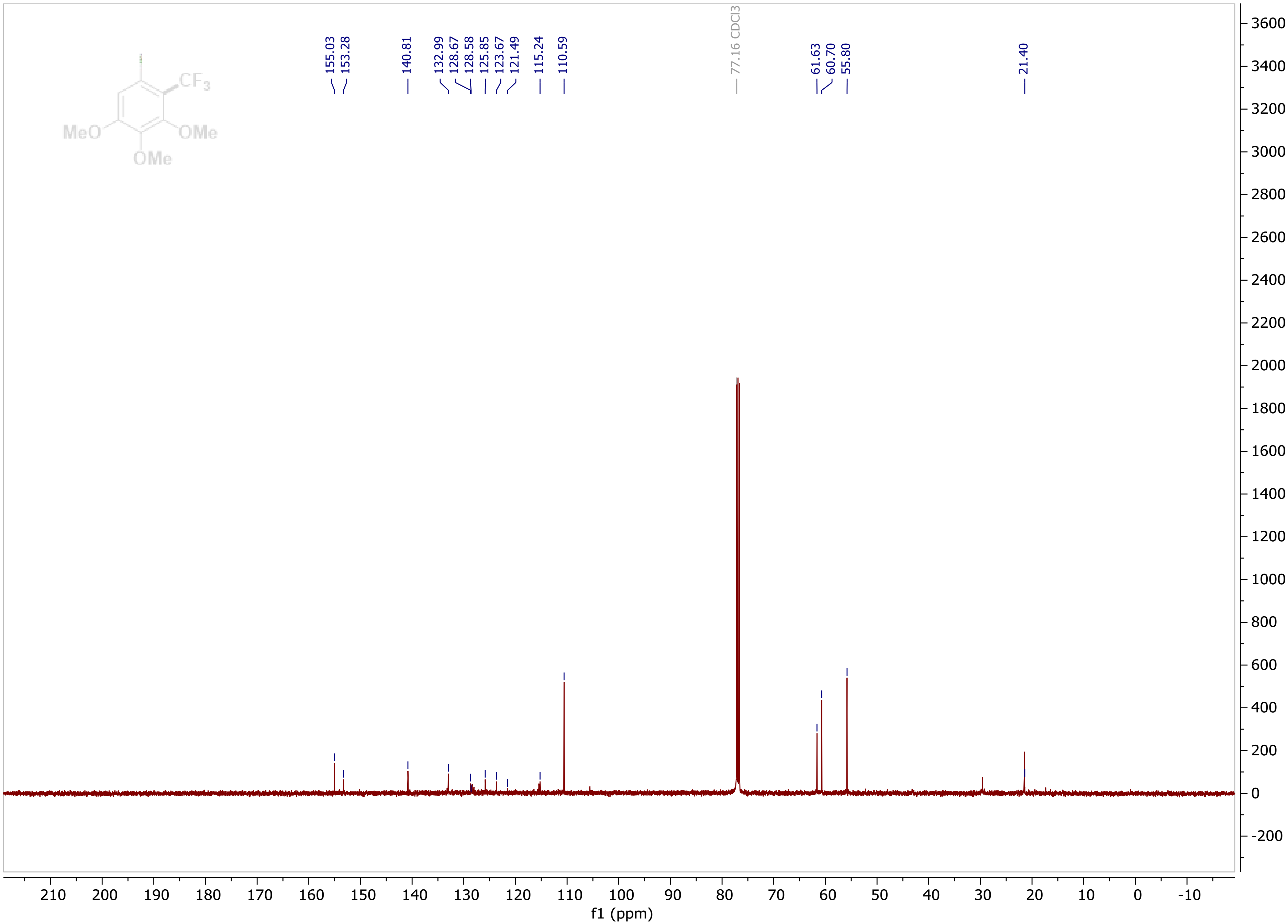
^{1}H-^{19}F HMBC of TF1



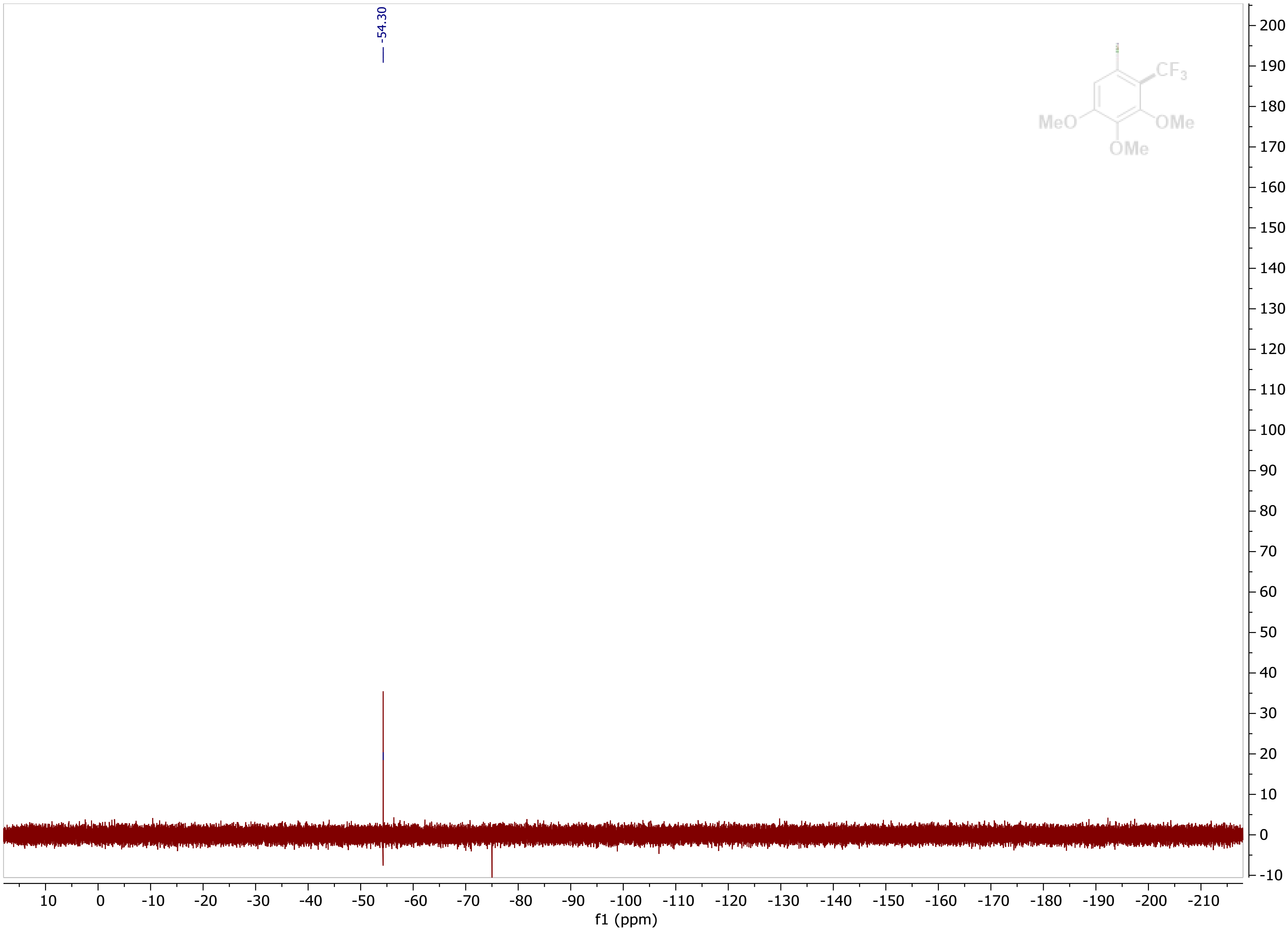
[1]H NMR of TF2, $CDCl_3$, 500 MHz



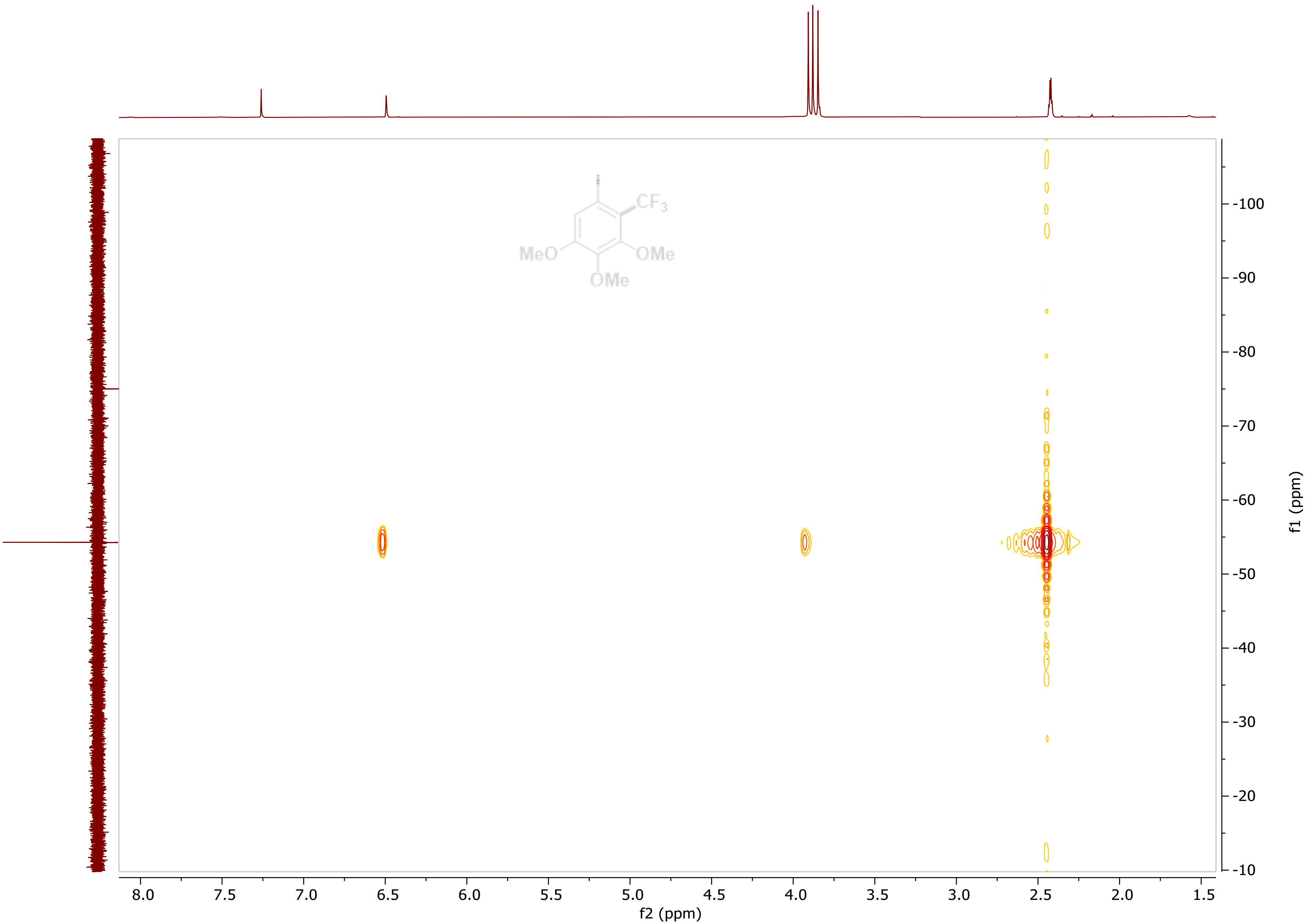
^{13}C NMR of TF2, $CDCl_3$, 126 MHz



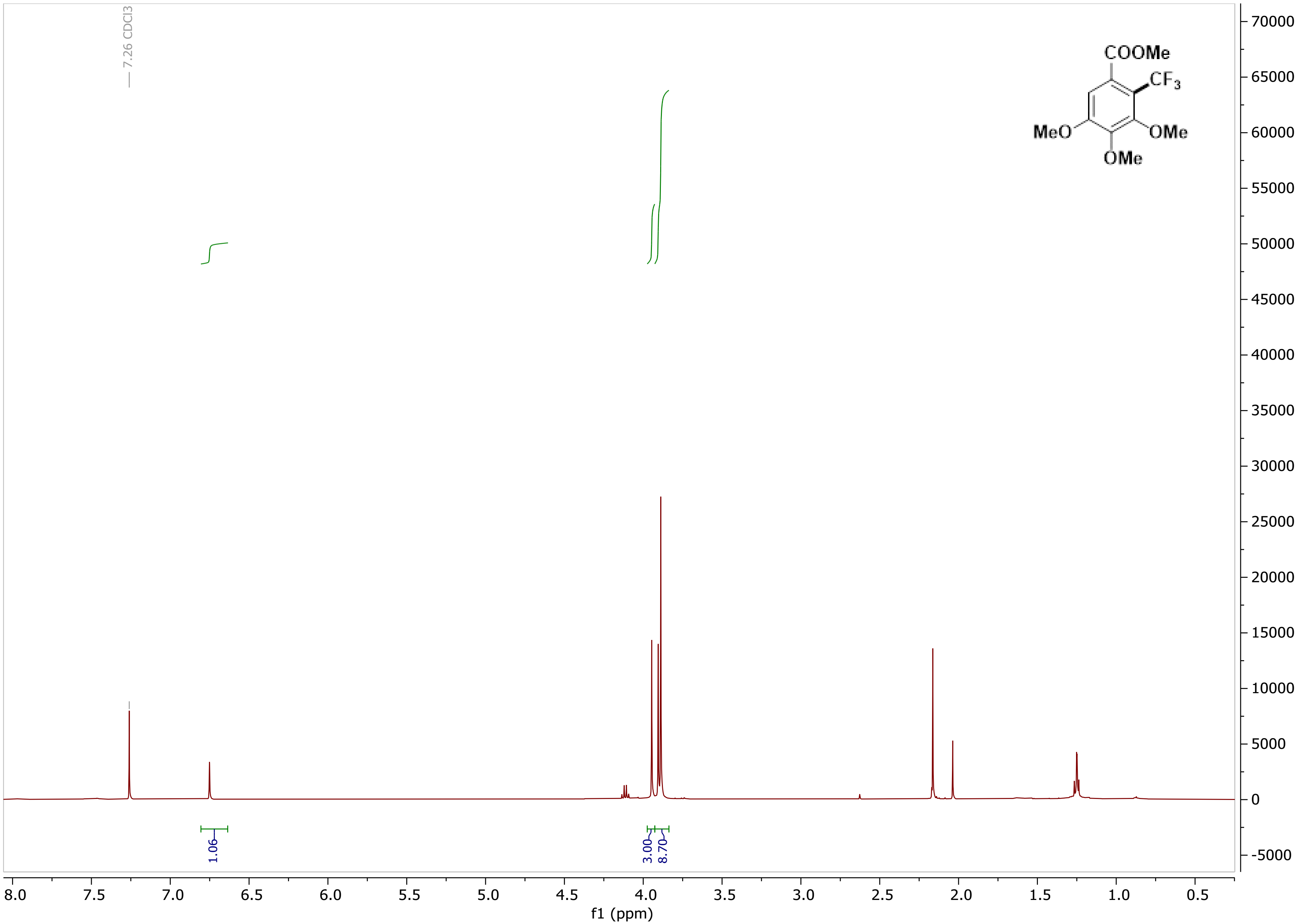
^{19}F NMR of TF2, $CDCl_3$, 471 MHz



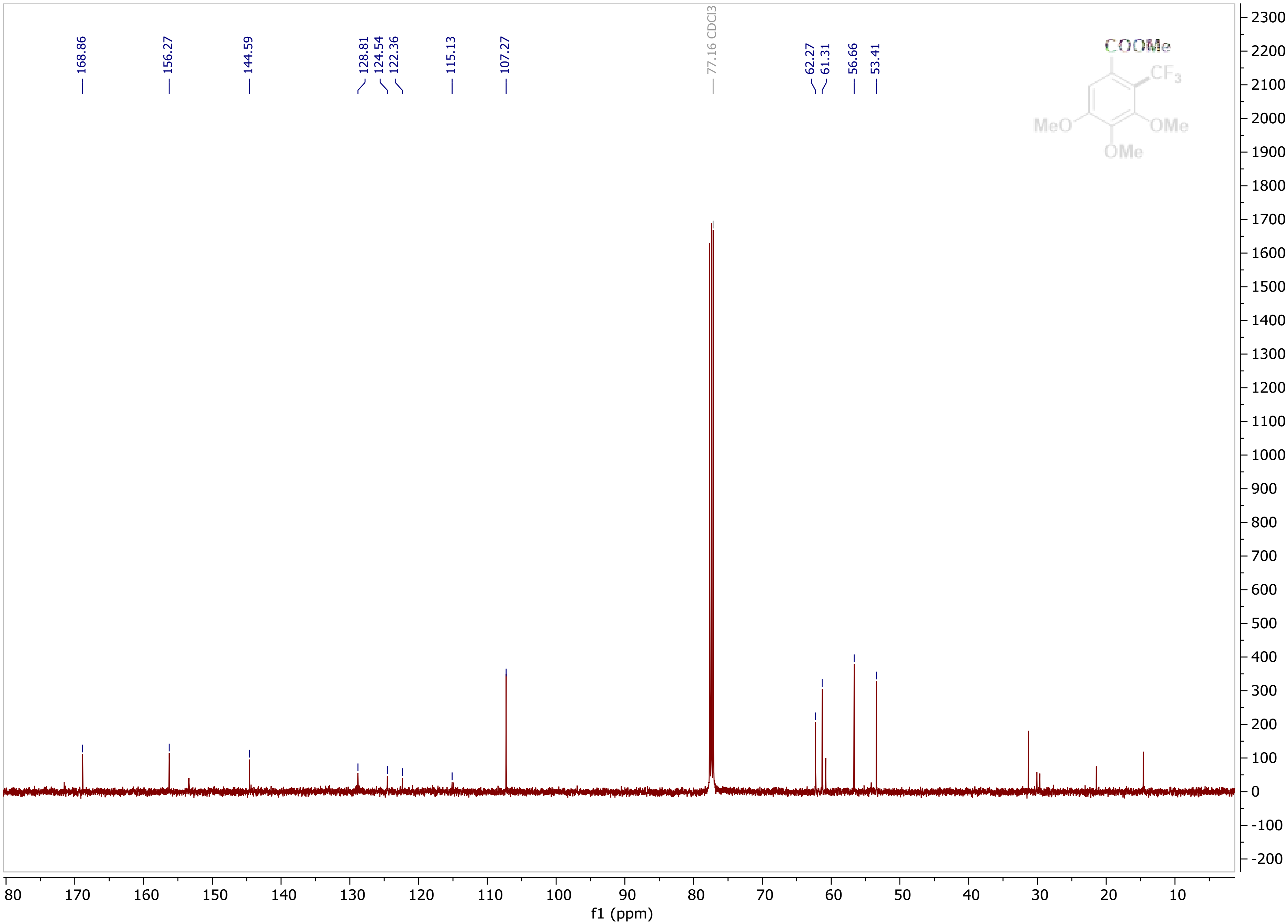
^1H-^{19}F HMBC of TF2



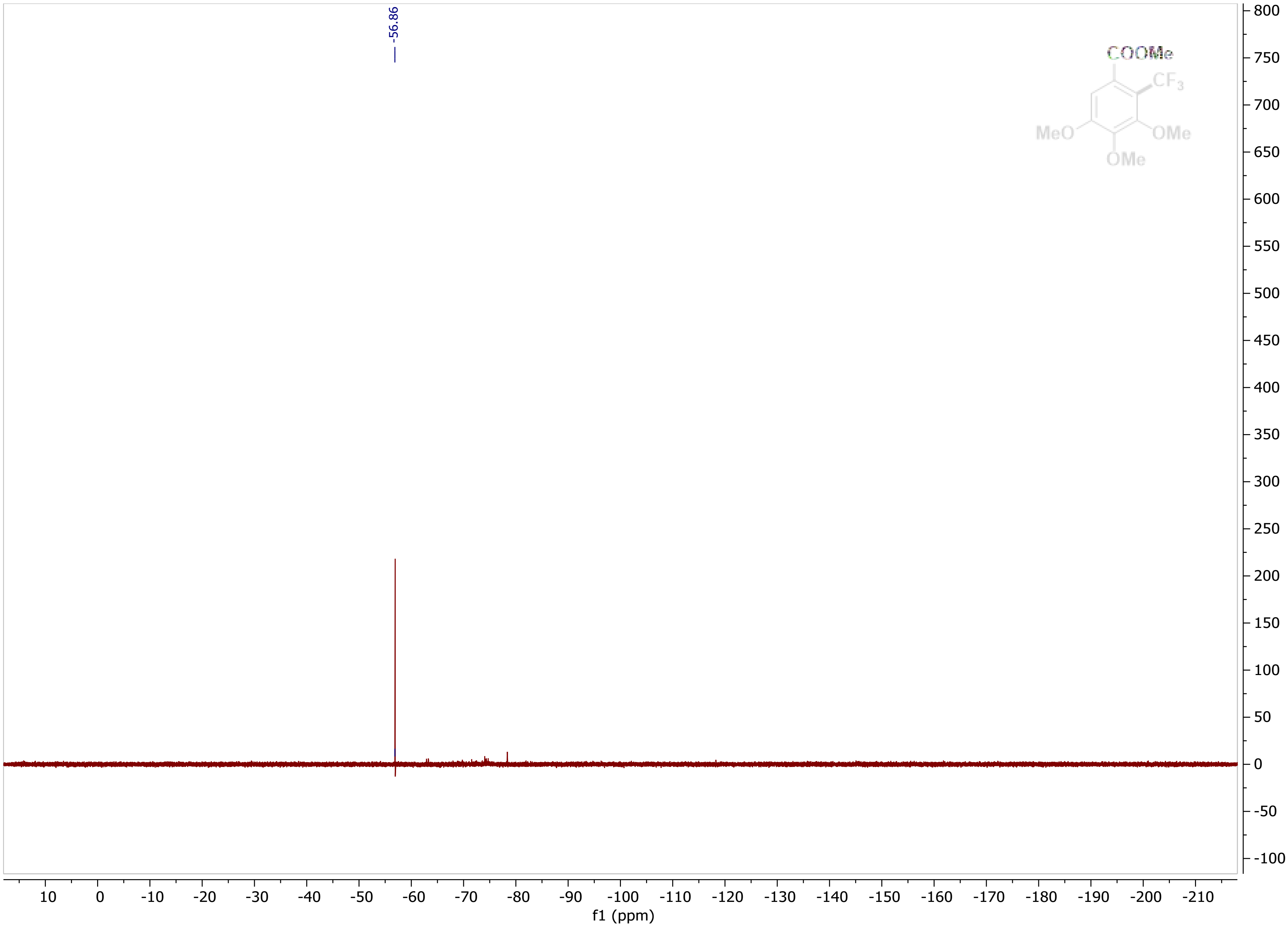
^{1}H NMR of TF3, $CDCl_3$, 500 MHz



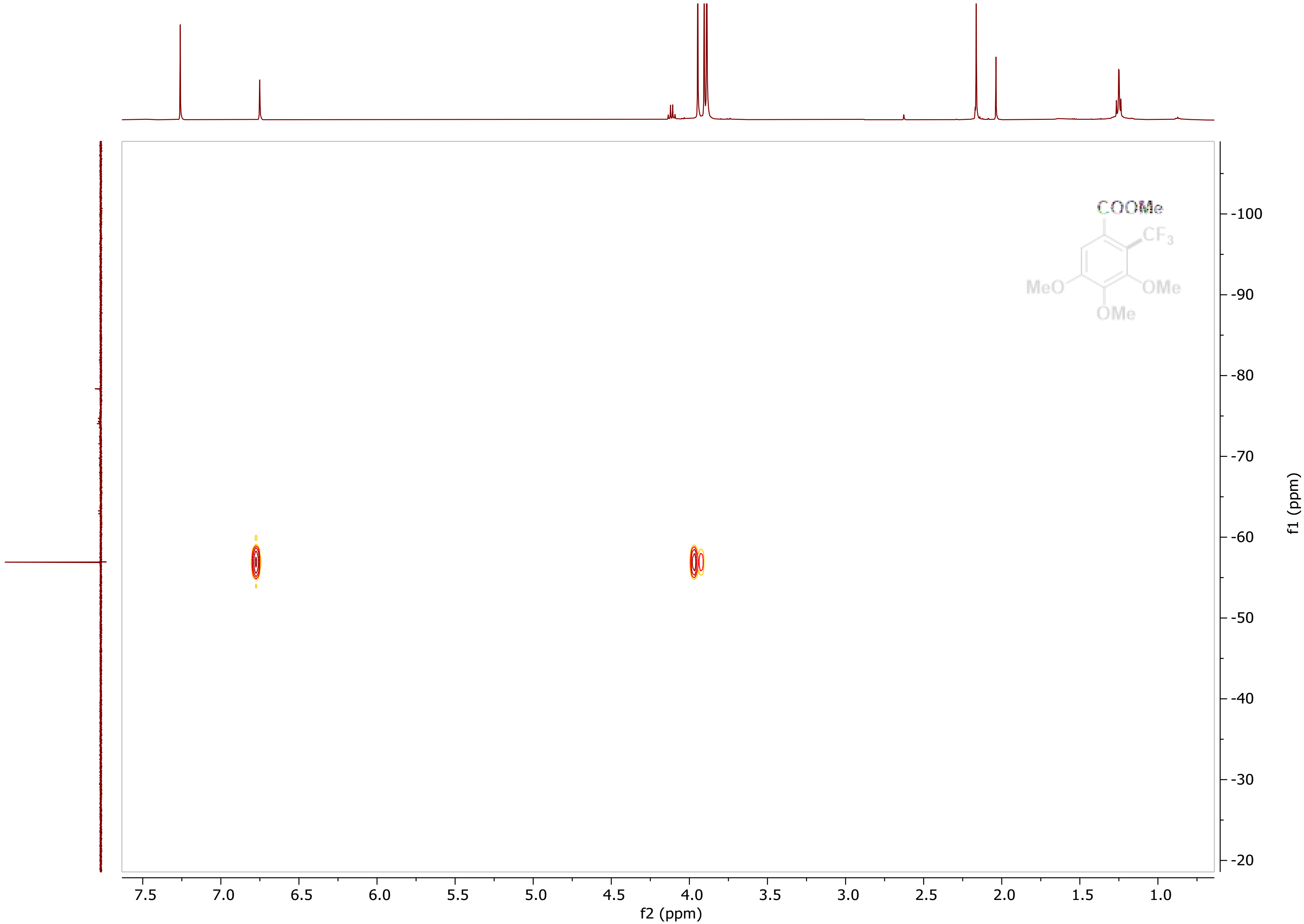
^{13}C NMR of TF3, $CDCl_3$, 126 MHz



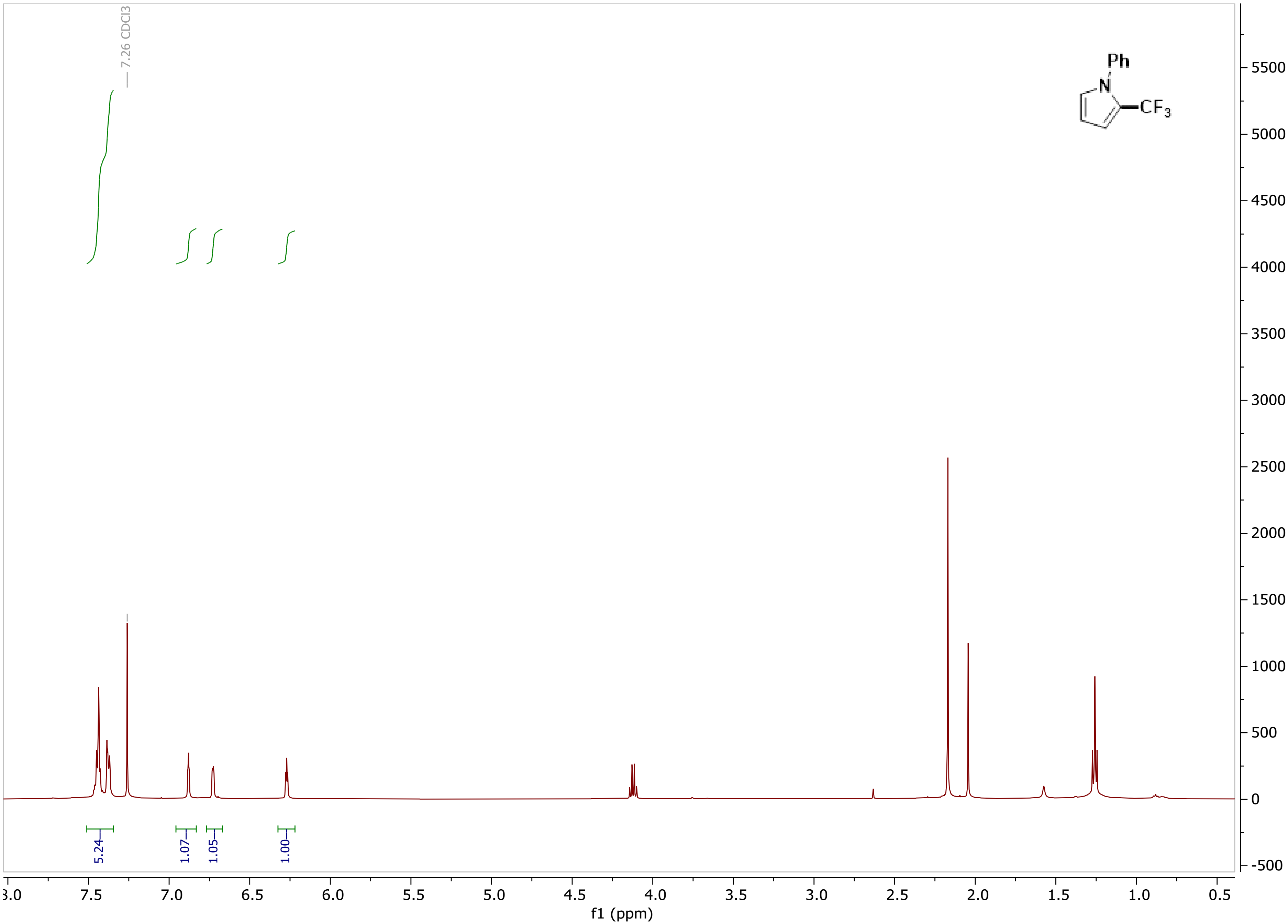
^{19}F NMR of TF3, $CDCl_3$, 471 MHz



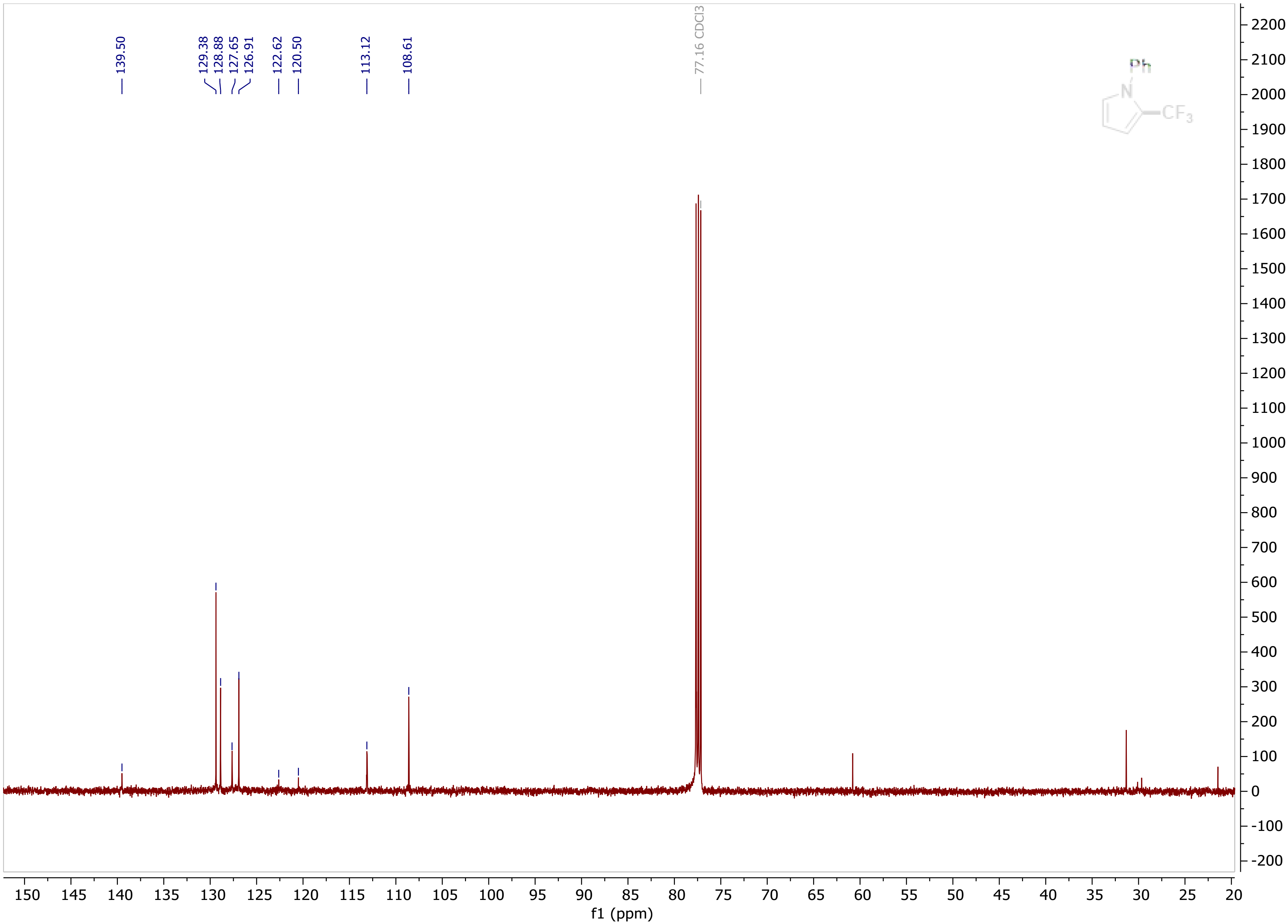
^{1}H-^{19}F HMBC of TF3



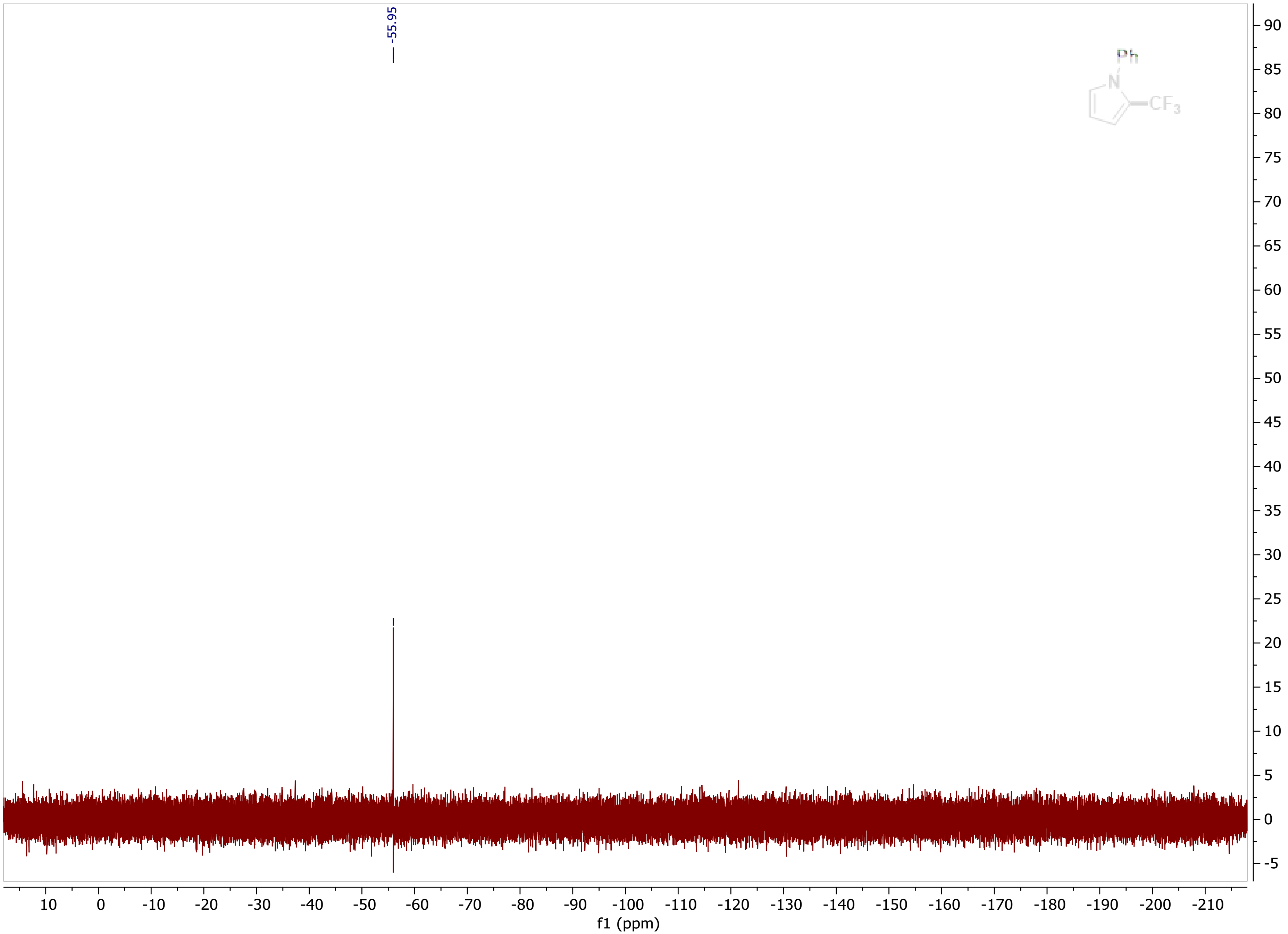
[1]H NMR of TF4, $CDCl_3$, 500 MHz



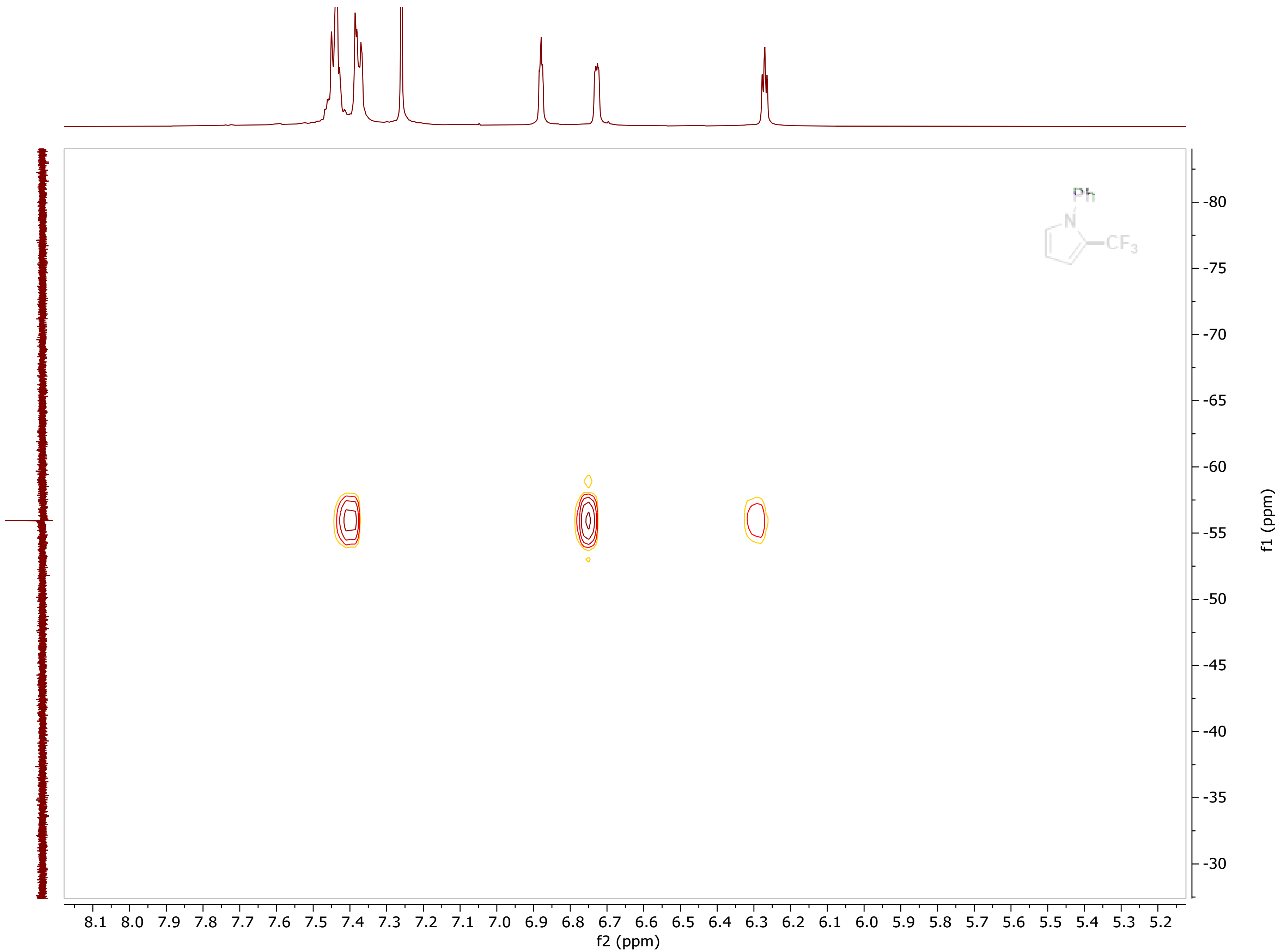
^{13}C NMR of TF4, $CDCl_3$, 126 MHz



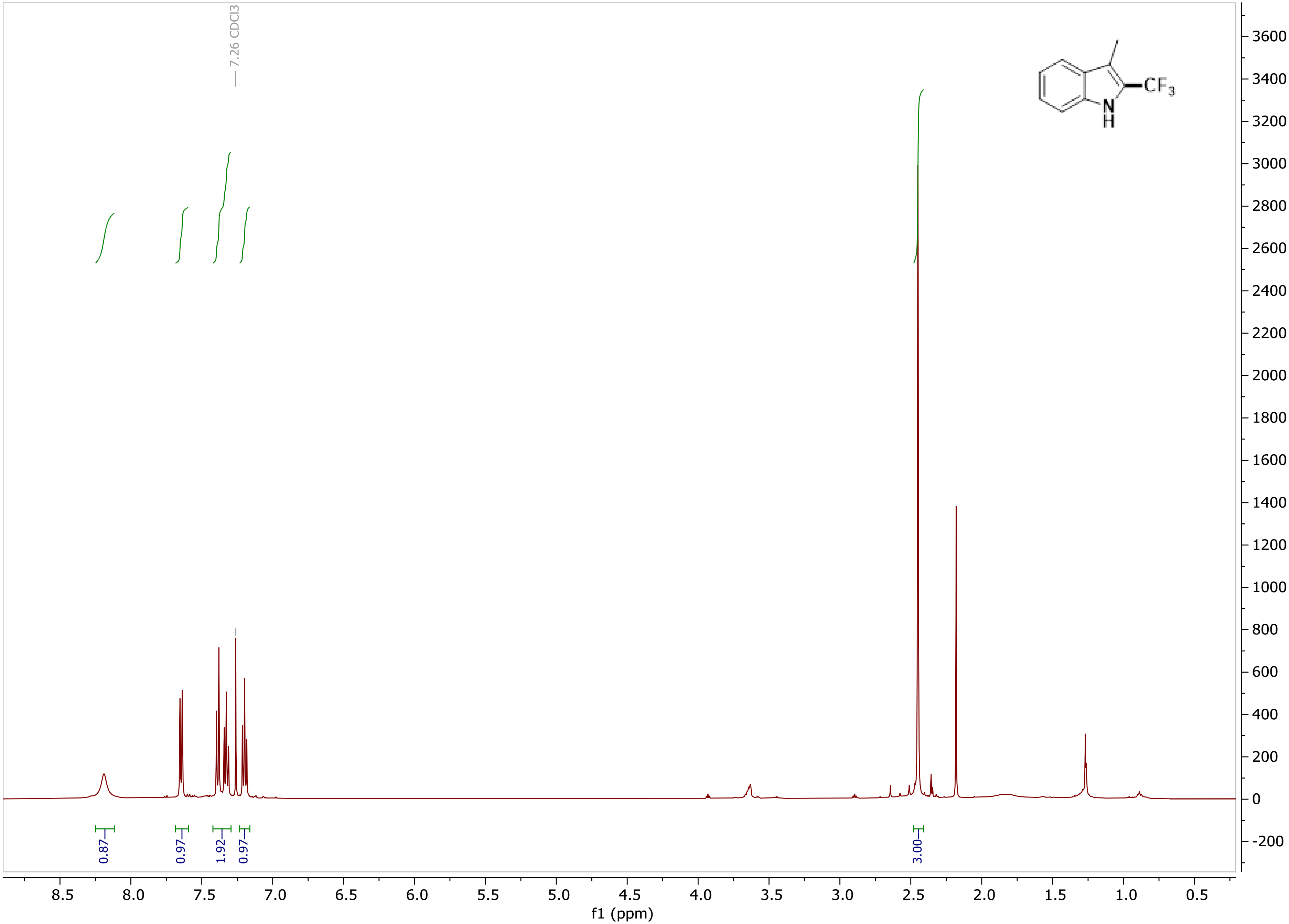
^{19}F NMR of TF4, $CDCl_3$, 471 MHz



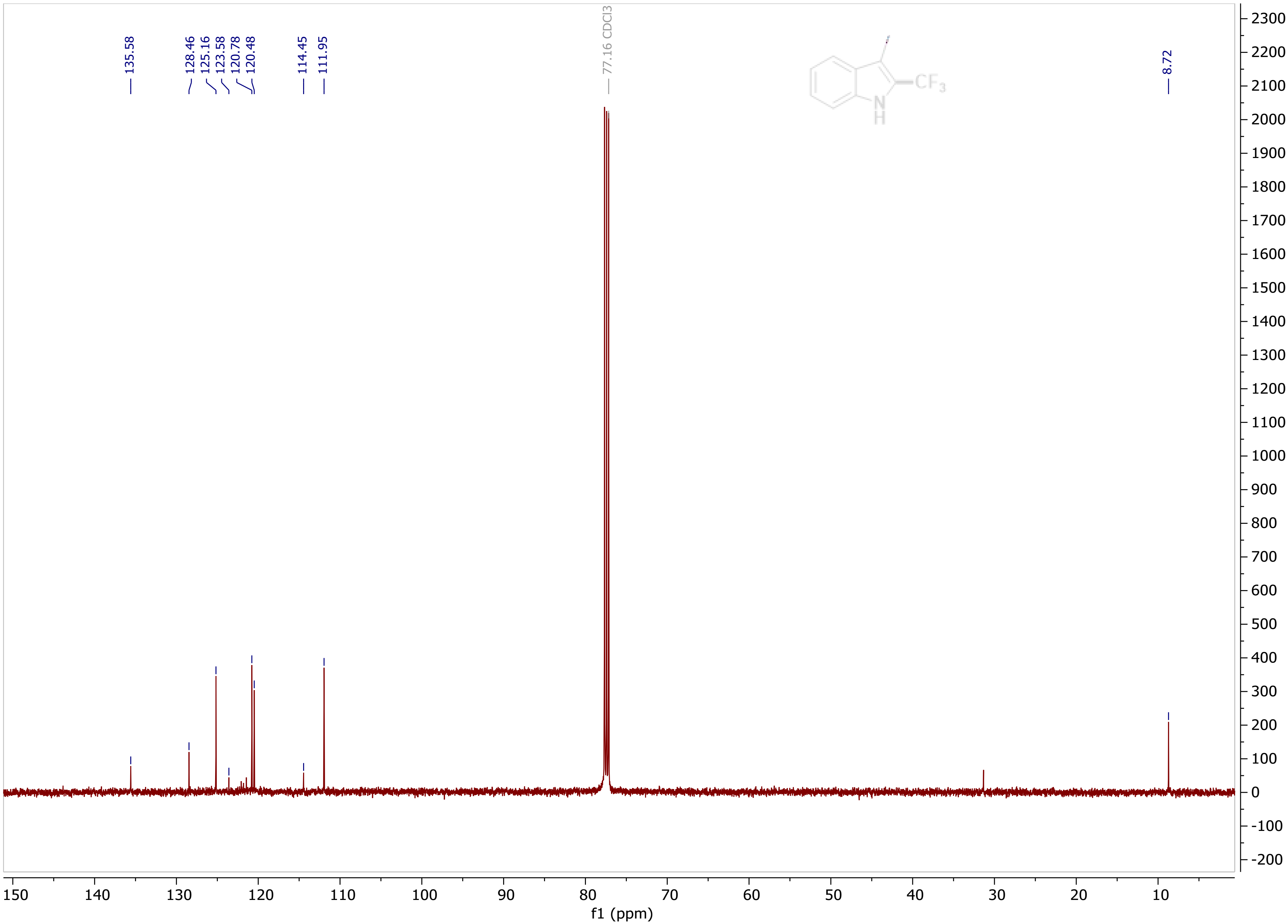
^{1}H-^{19}F HMBC of TF4



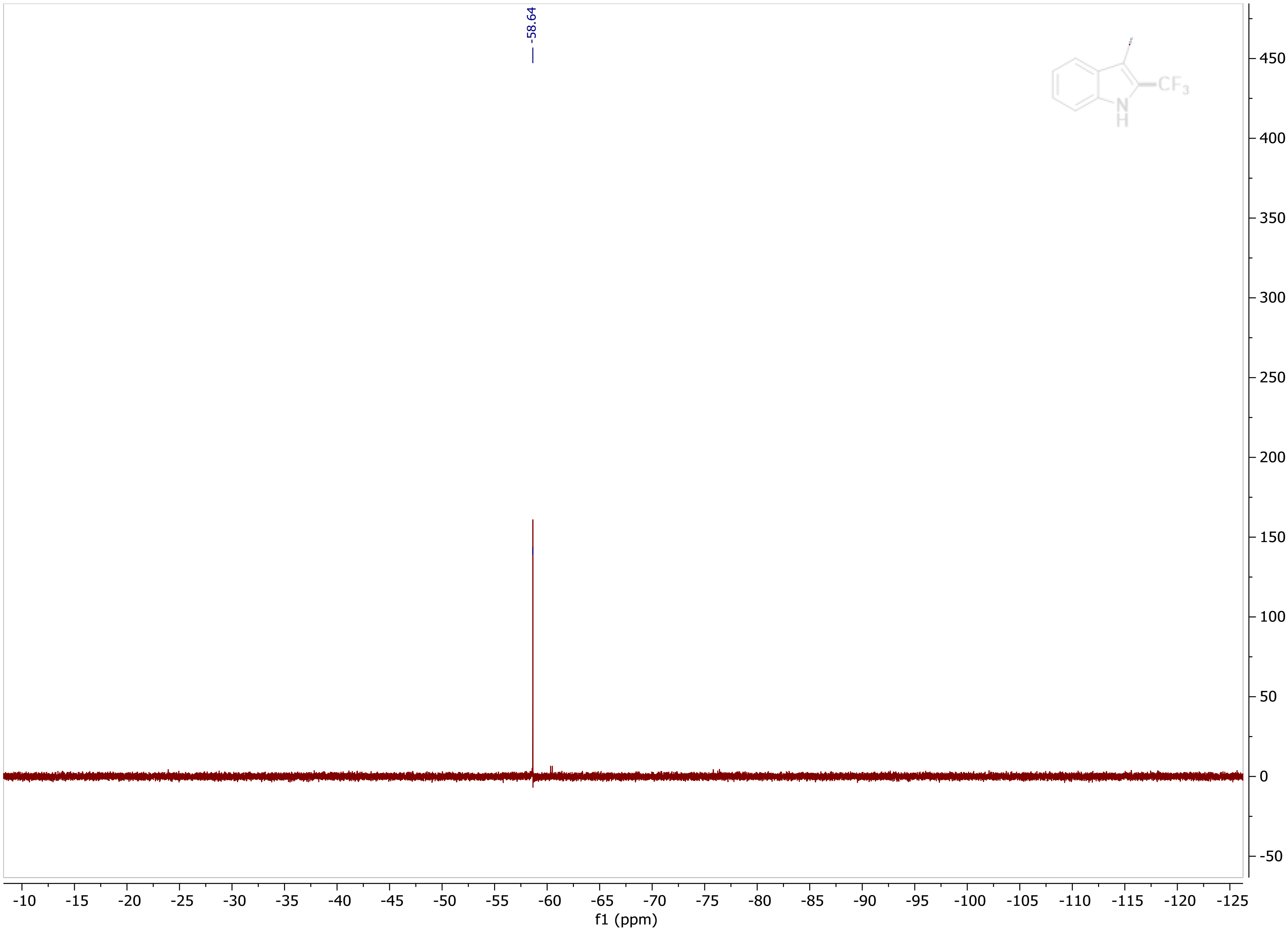
[1]H NMR of TF5, $CDCl_3$, 500 MHz



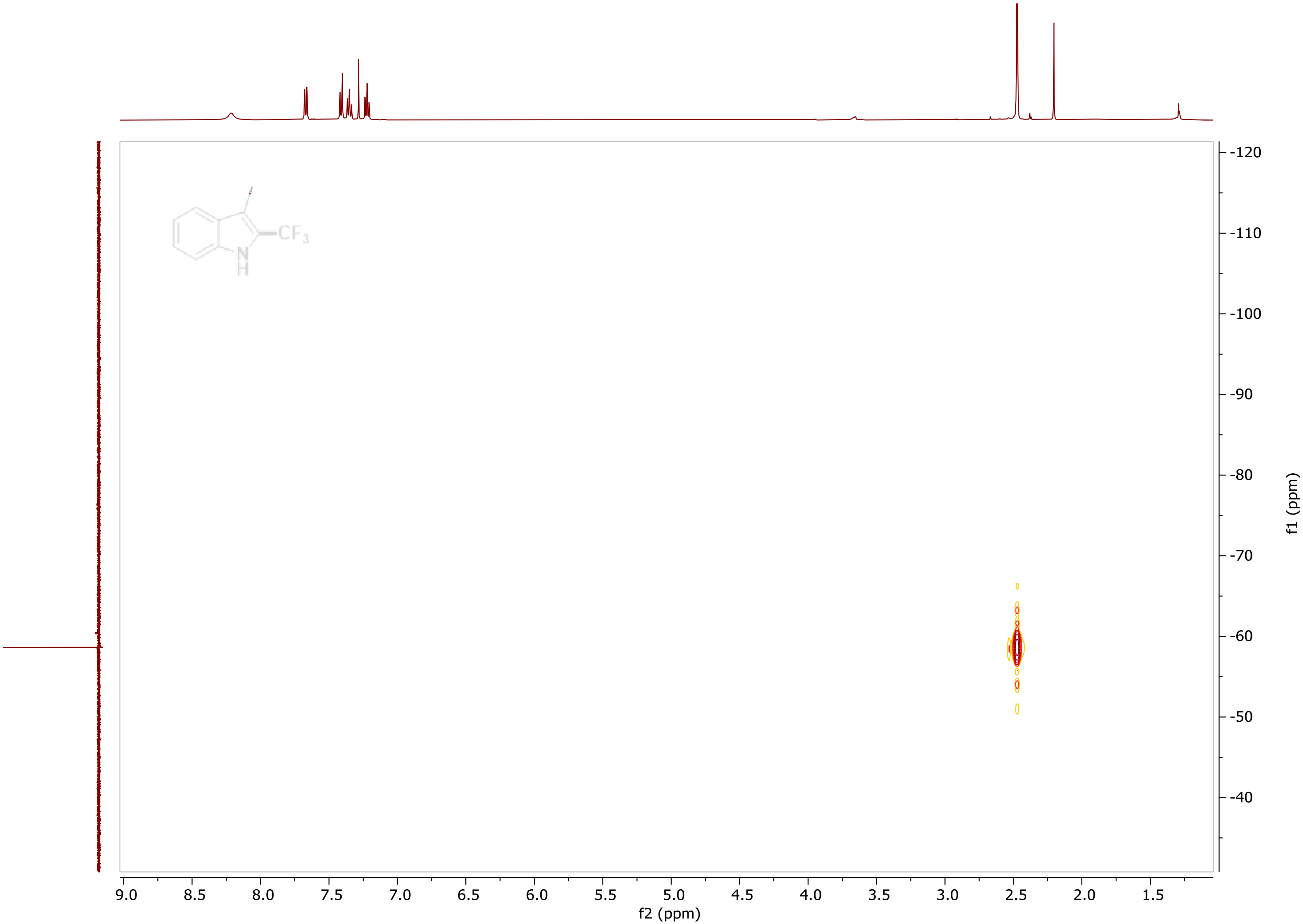
^{13}C NMR of TF5, $CDCl_3$, 126 MHz



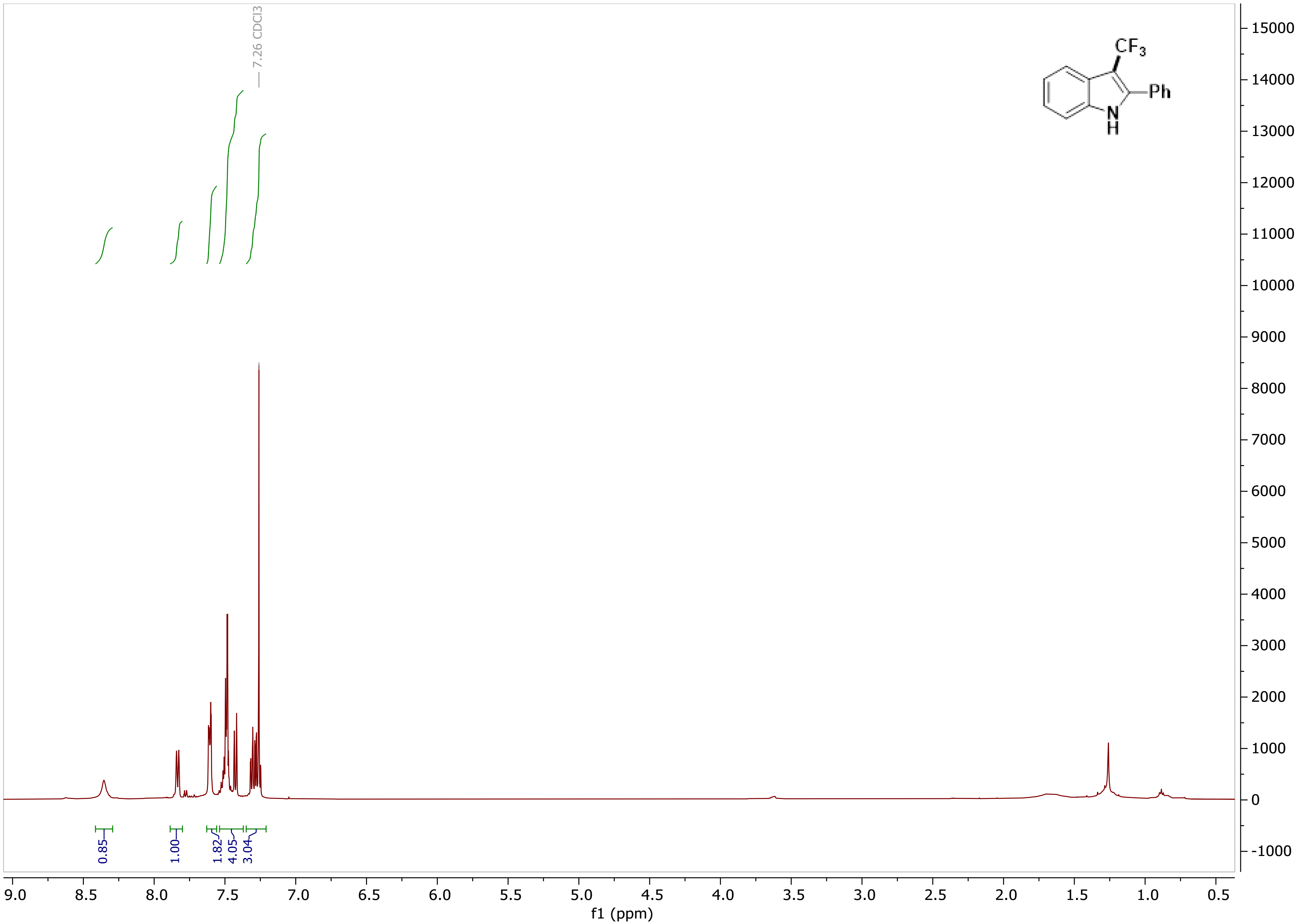
^{19}F NMR of TF5, $CDCl_3$, 471 MHz



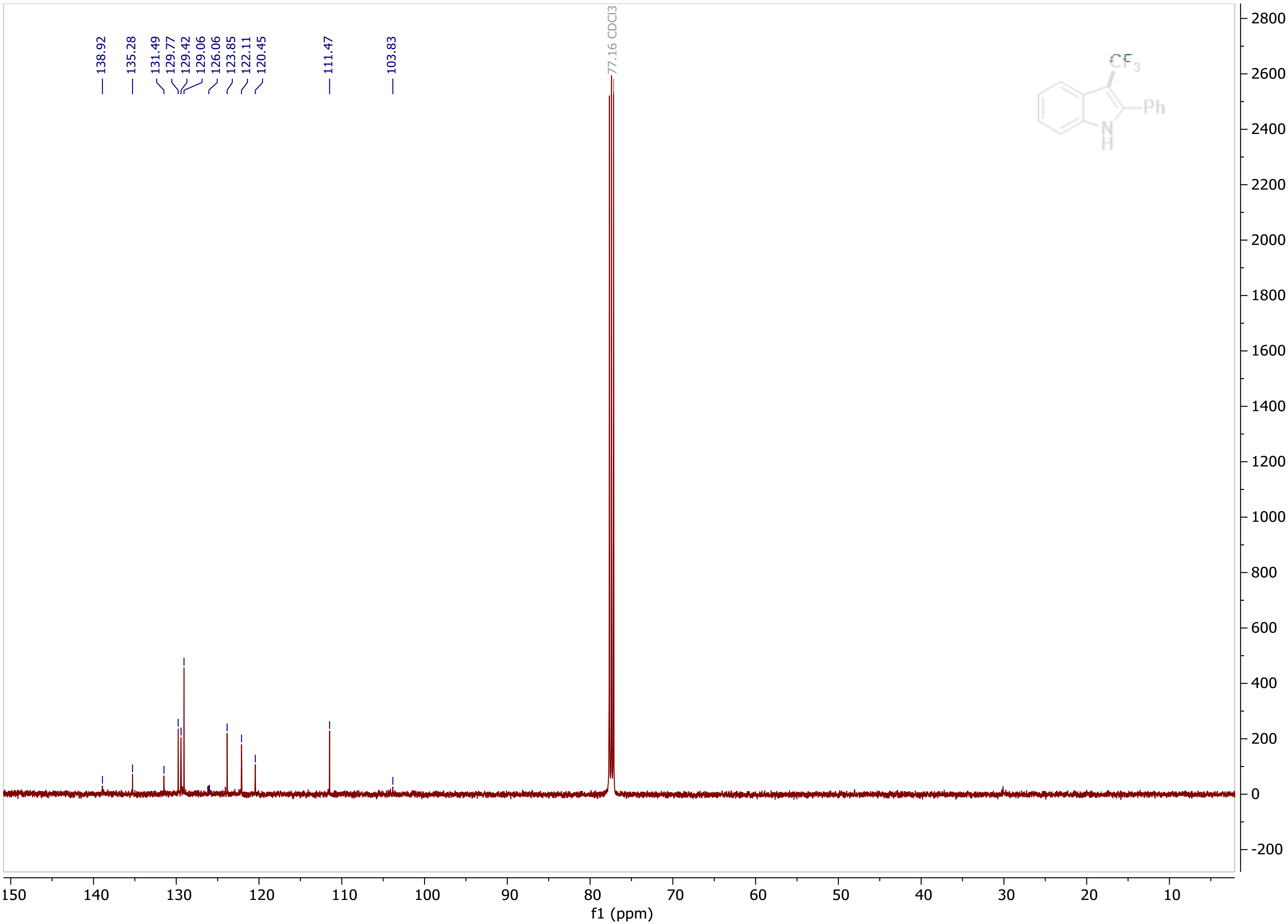
^{1}H-^{19}F HMBC of TF5



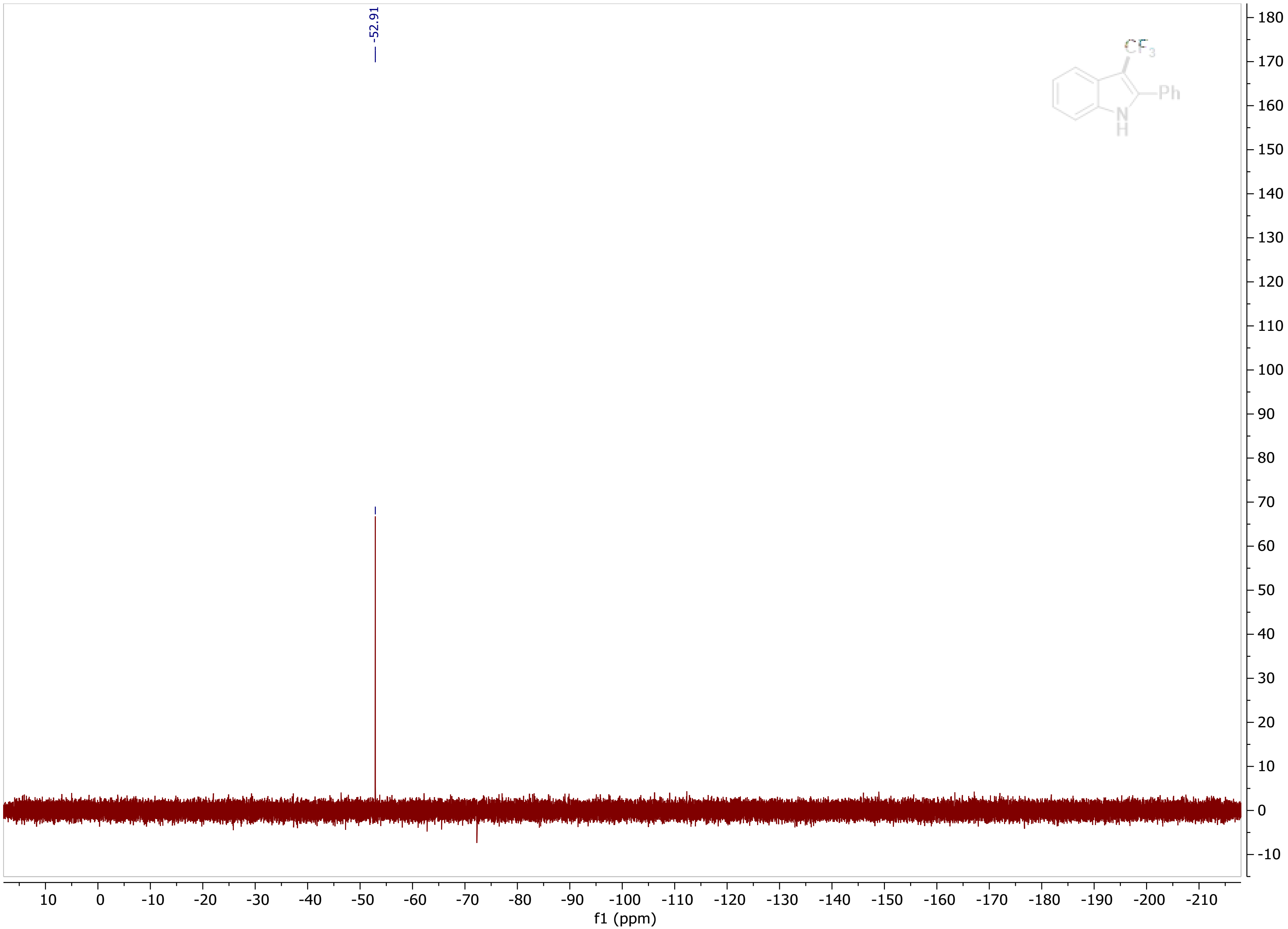
^{1}H NMR of TF6, $CDCl_3$, 500 MHz



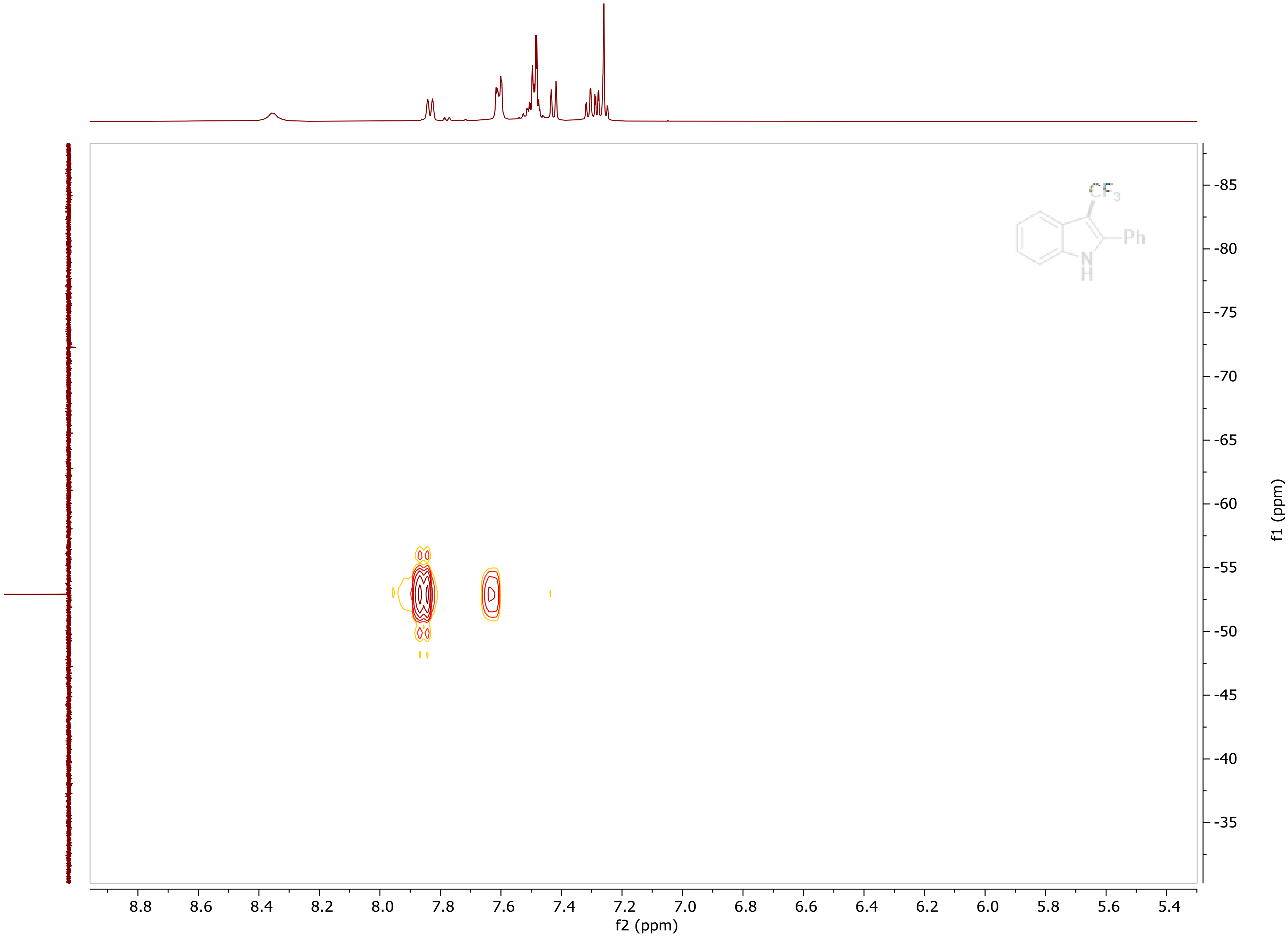
^{13}C NMR of TF6, $CDCl_3$, 126 MHz



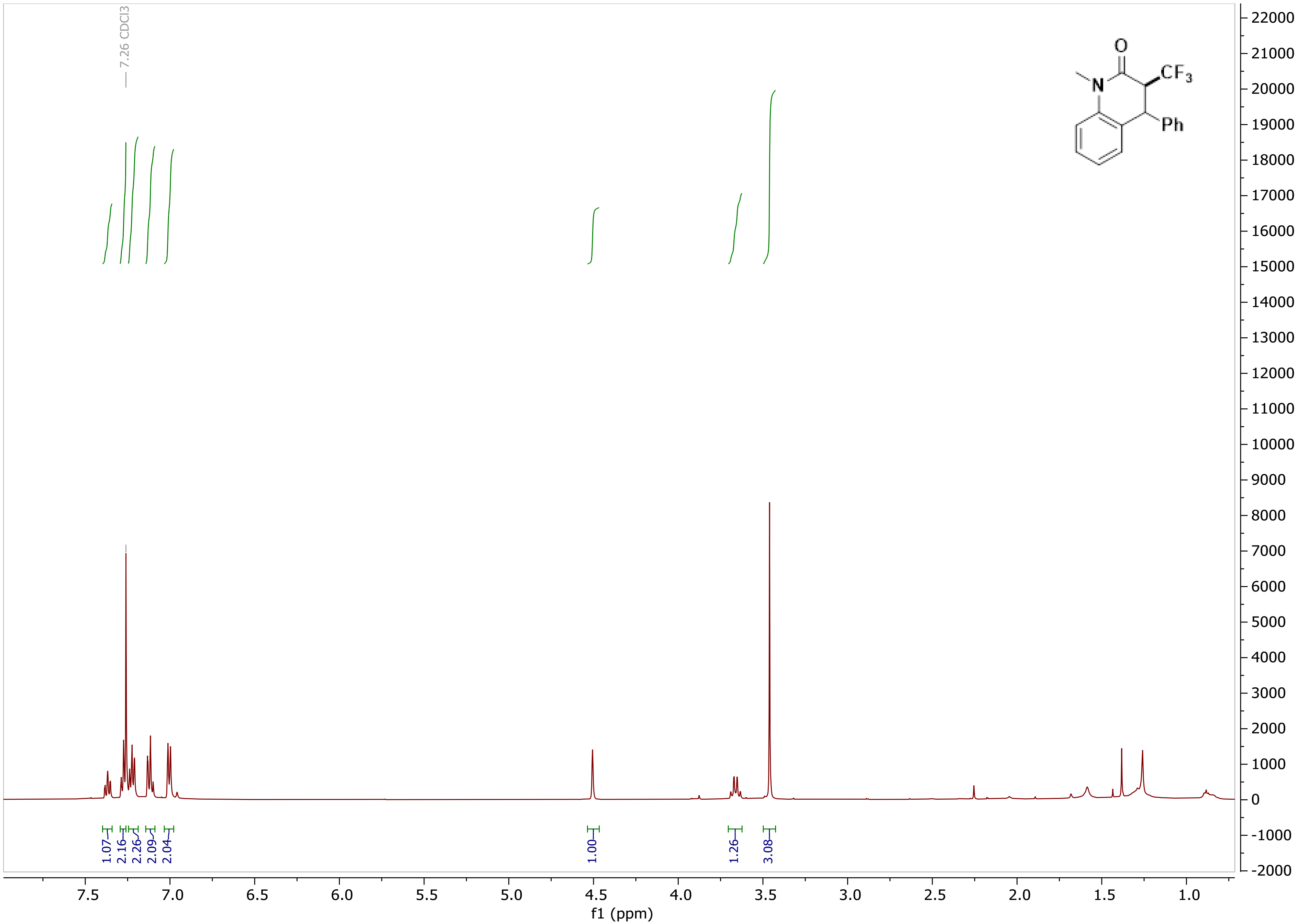
^{19}F NMR of TF6, $CDCl_3$, 471 MHz



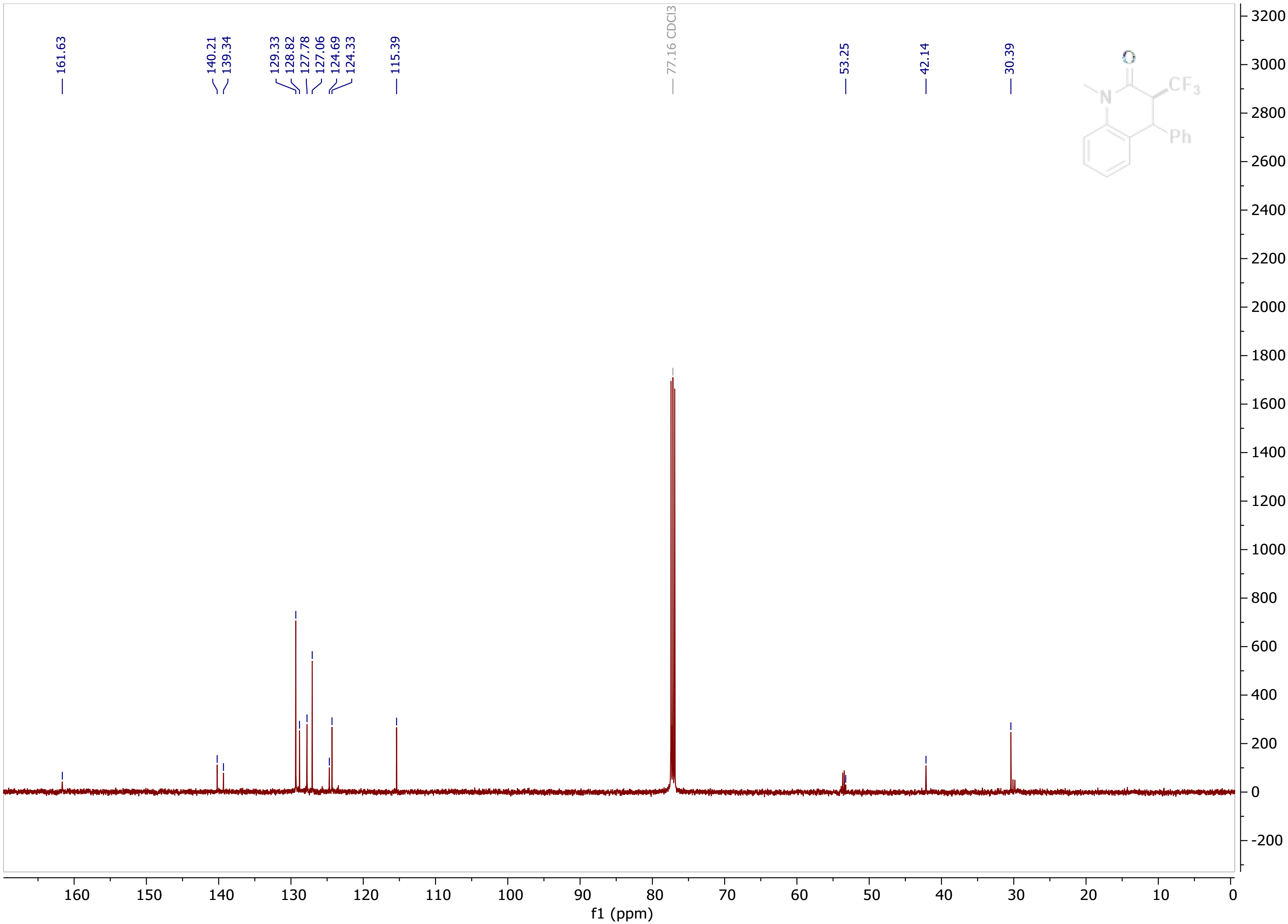
^{1}H-^{19}F HMBC of TF6



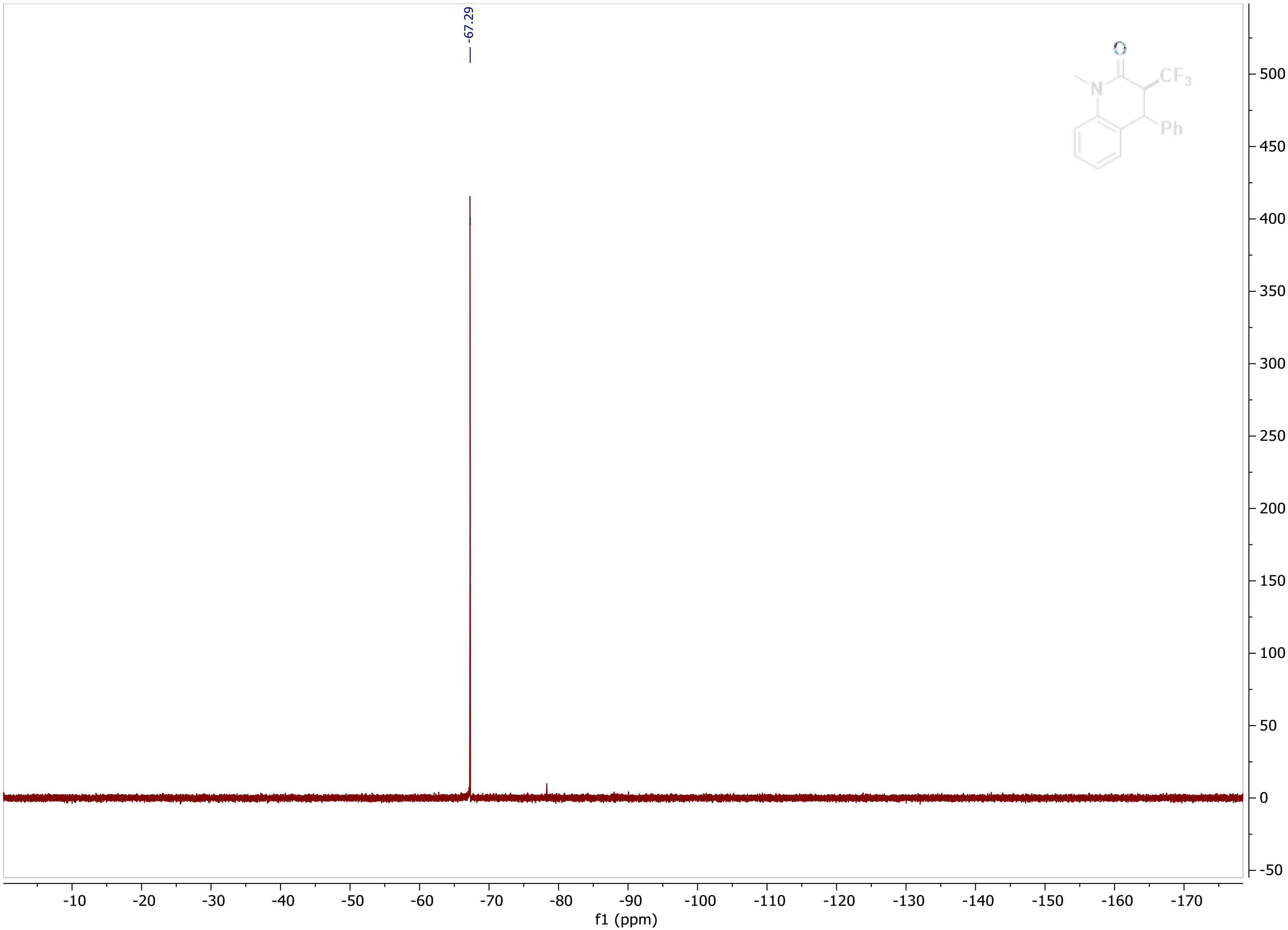
[1]H NMR of TF7, $CDCl_3$, 500 MHz



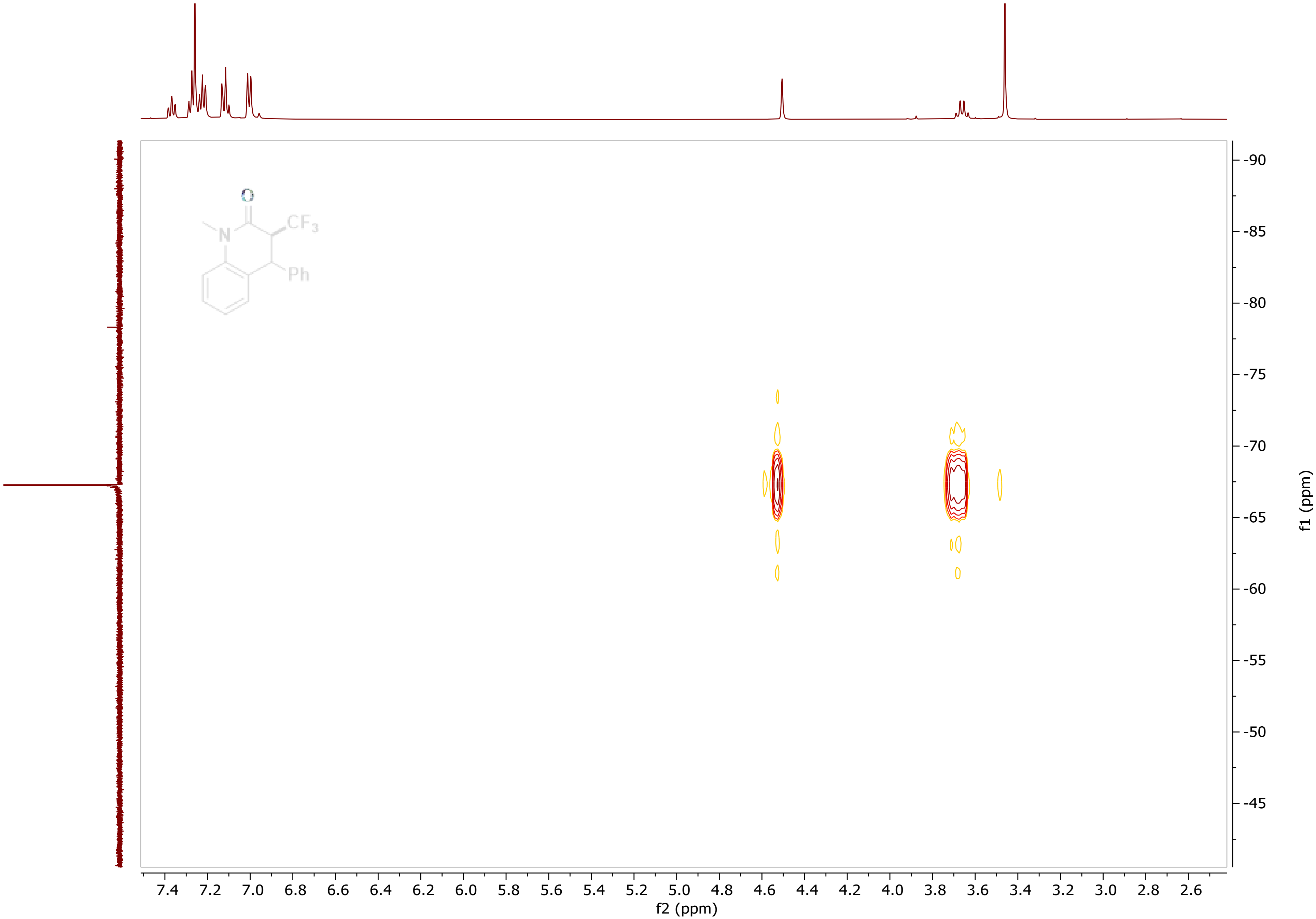
^{13}C NMR of TF7, $CDCl_3$, 126 MHz



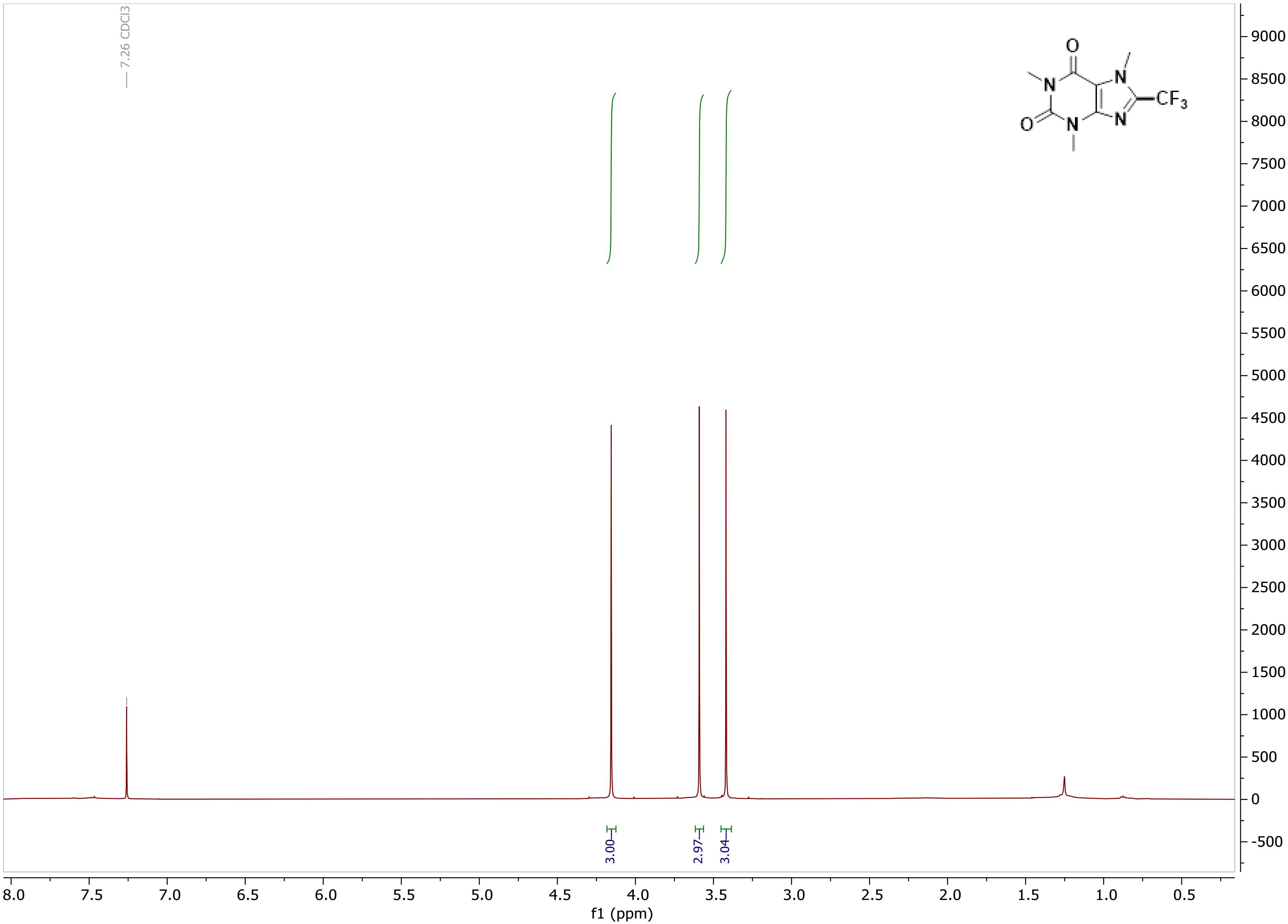
^{19}F NMR of TF7, $CDCl_3$, 471 MHz



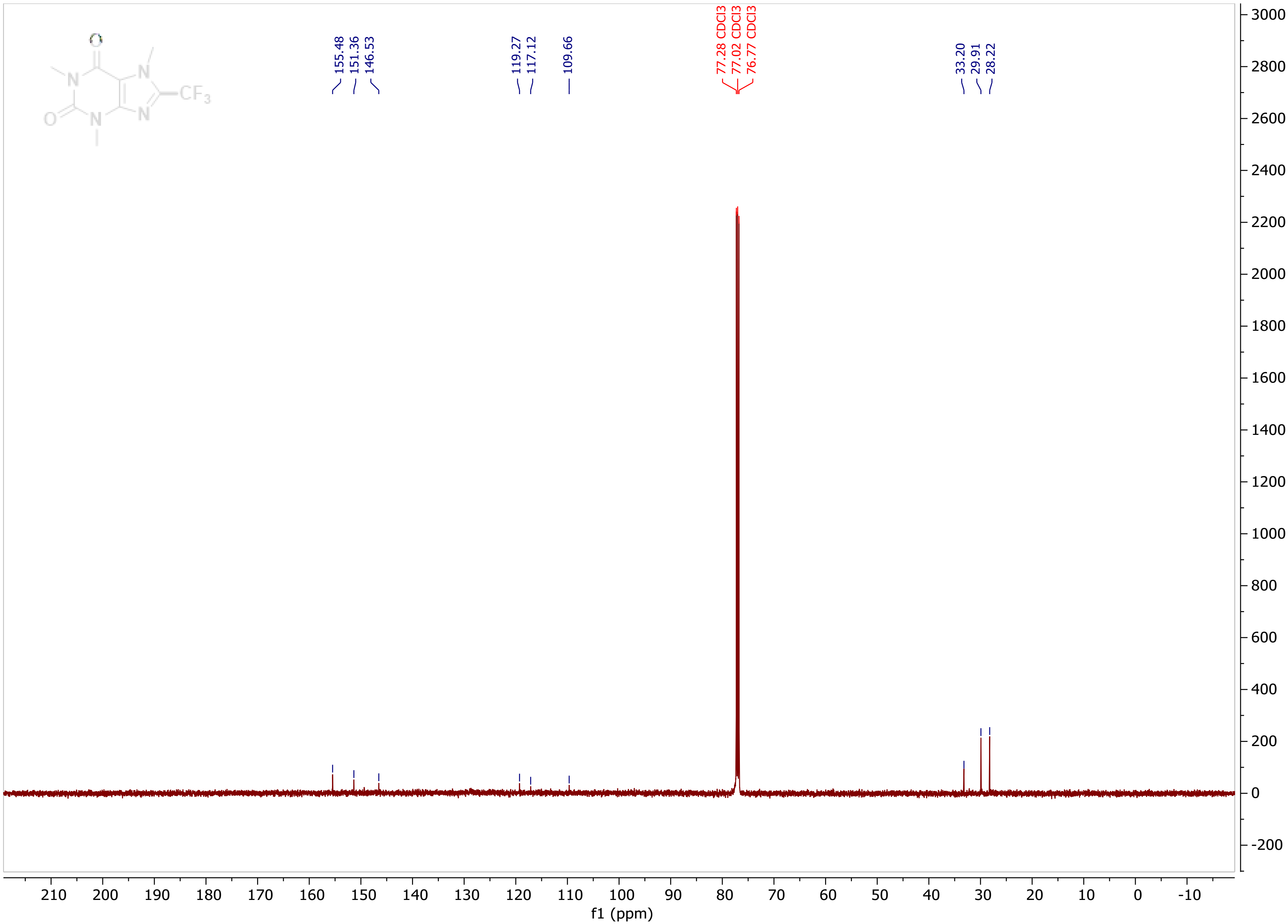
^{1}H-^{19}F HMBC of TF7



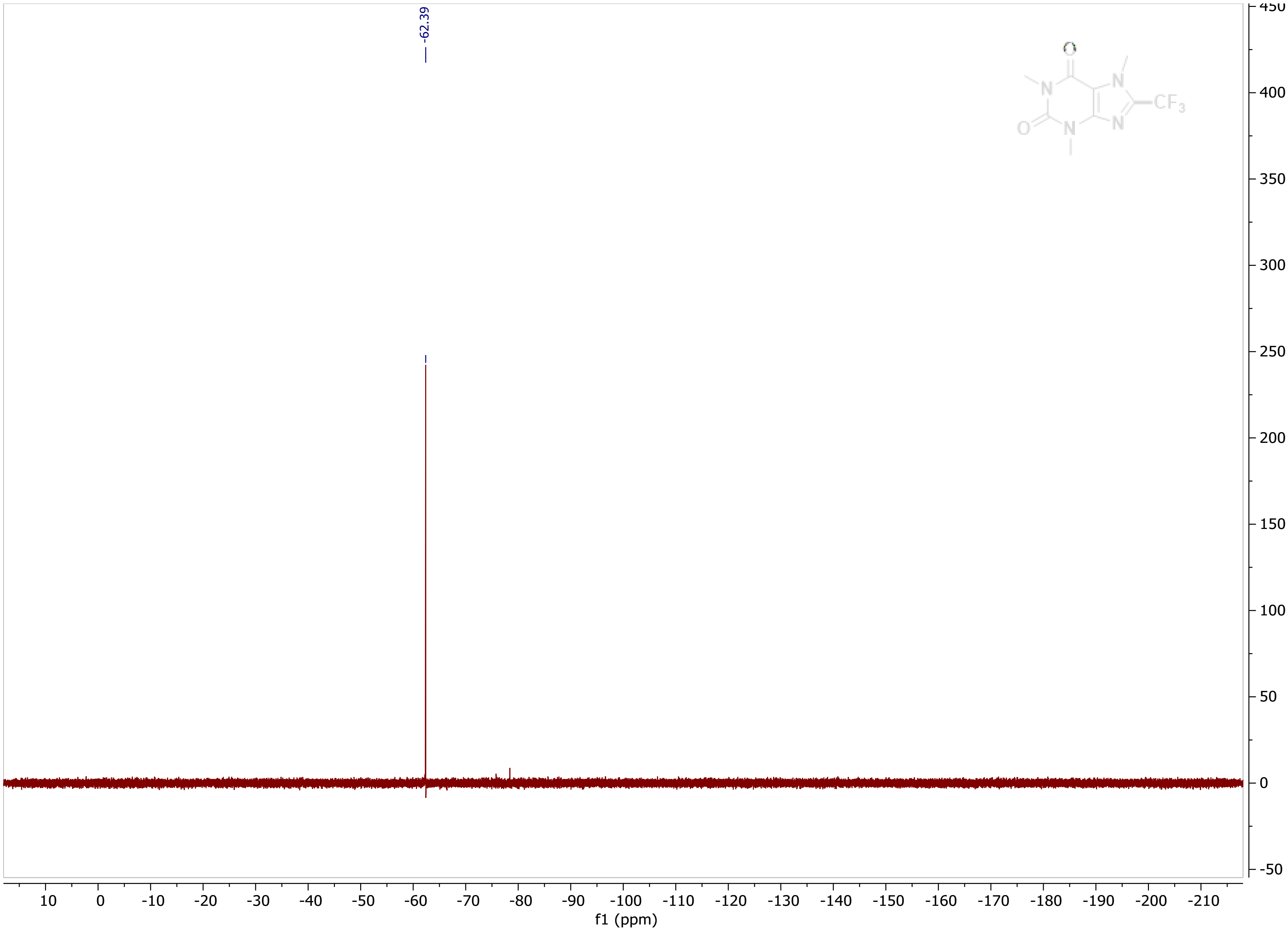
[1]H NMR of TF8, $CDCl_3$, 500 MHz



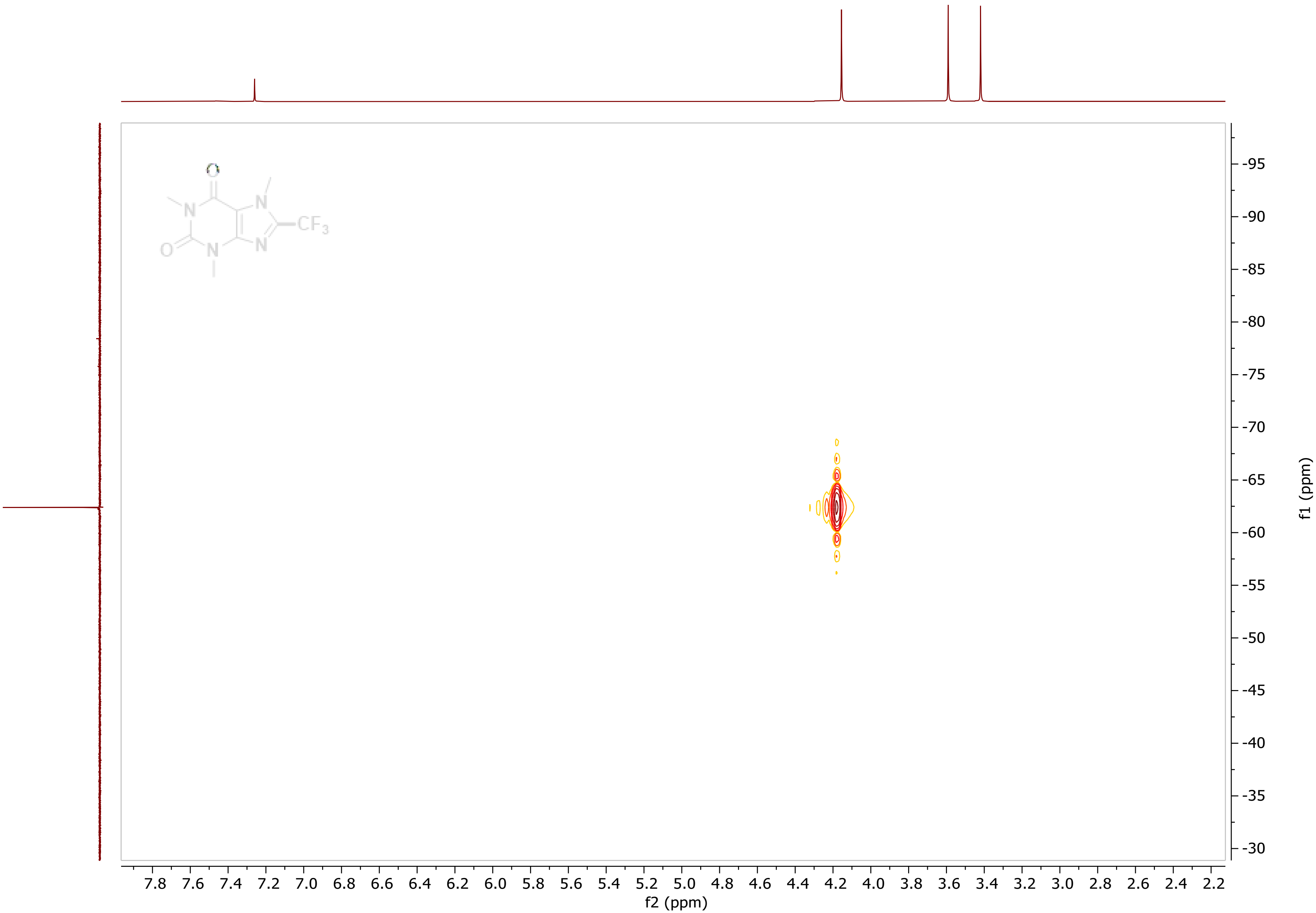
^{13}C NMR of TF8, $CDCl_3$, 126 MHz



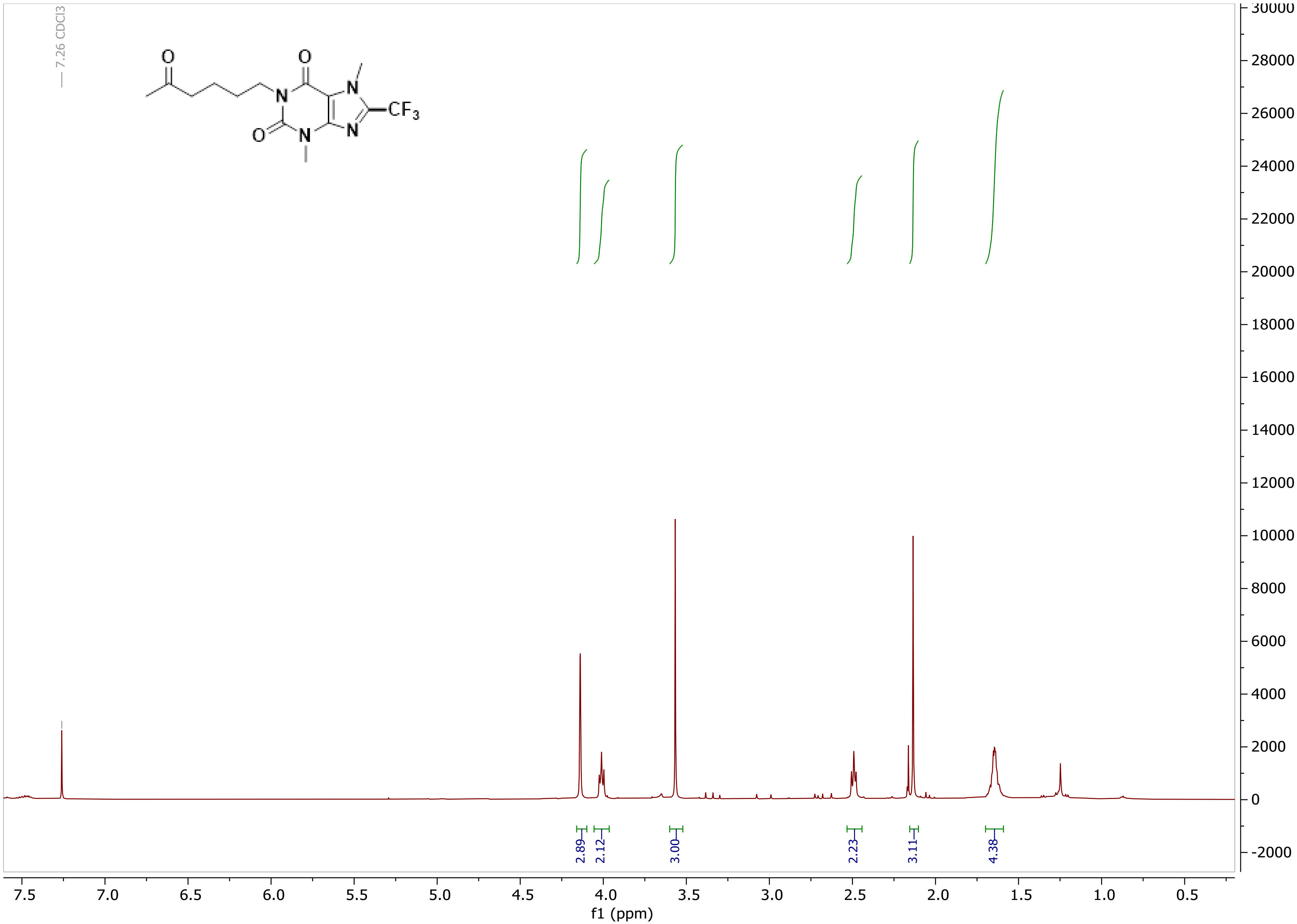
^{19}F NMR of TF8, $CDCl_3$, 471 MHz



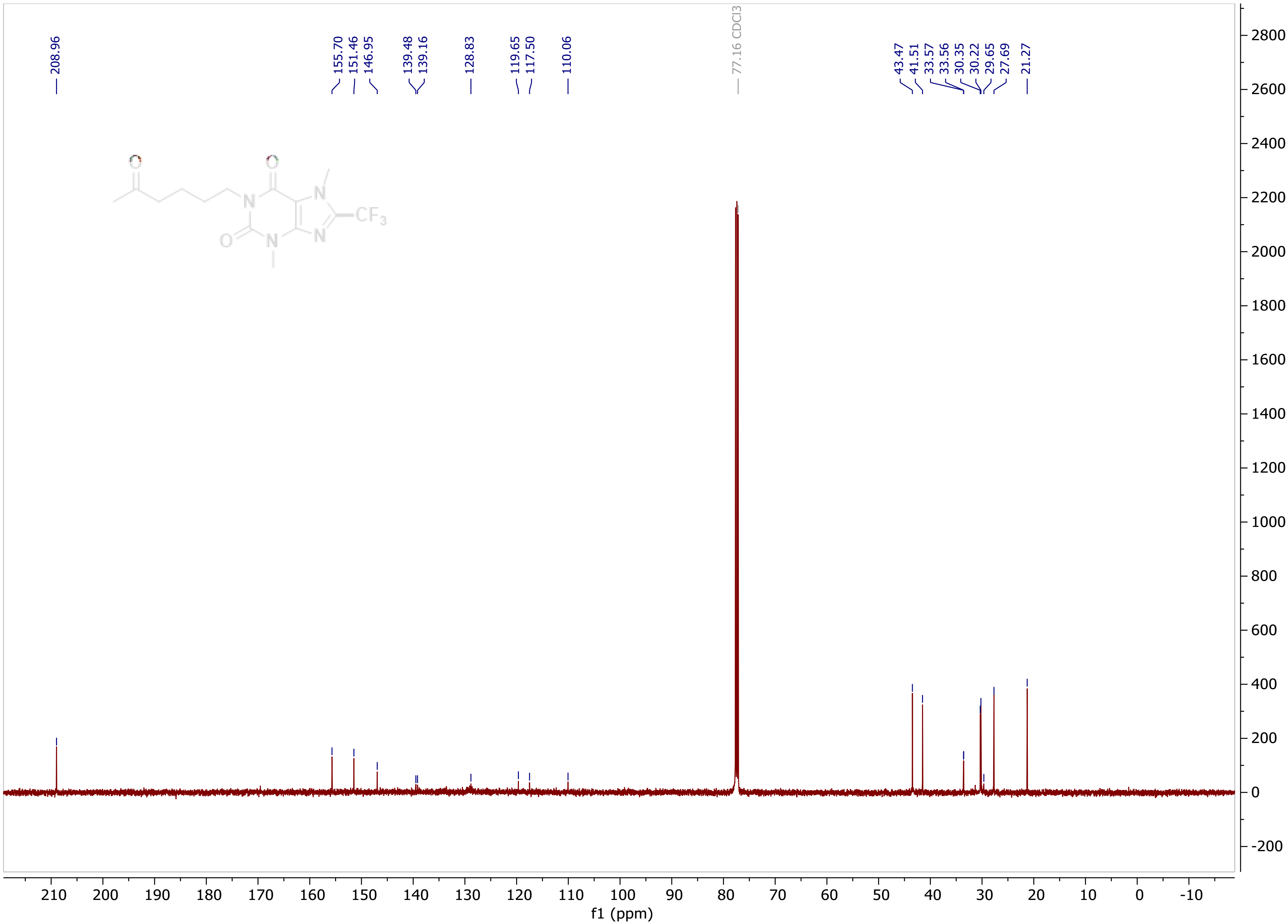
^1H-^{19}F HMBC of TF8



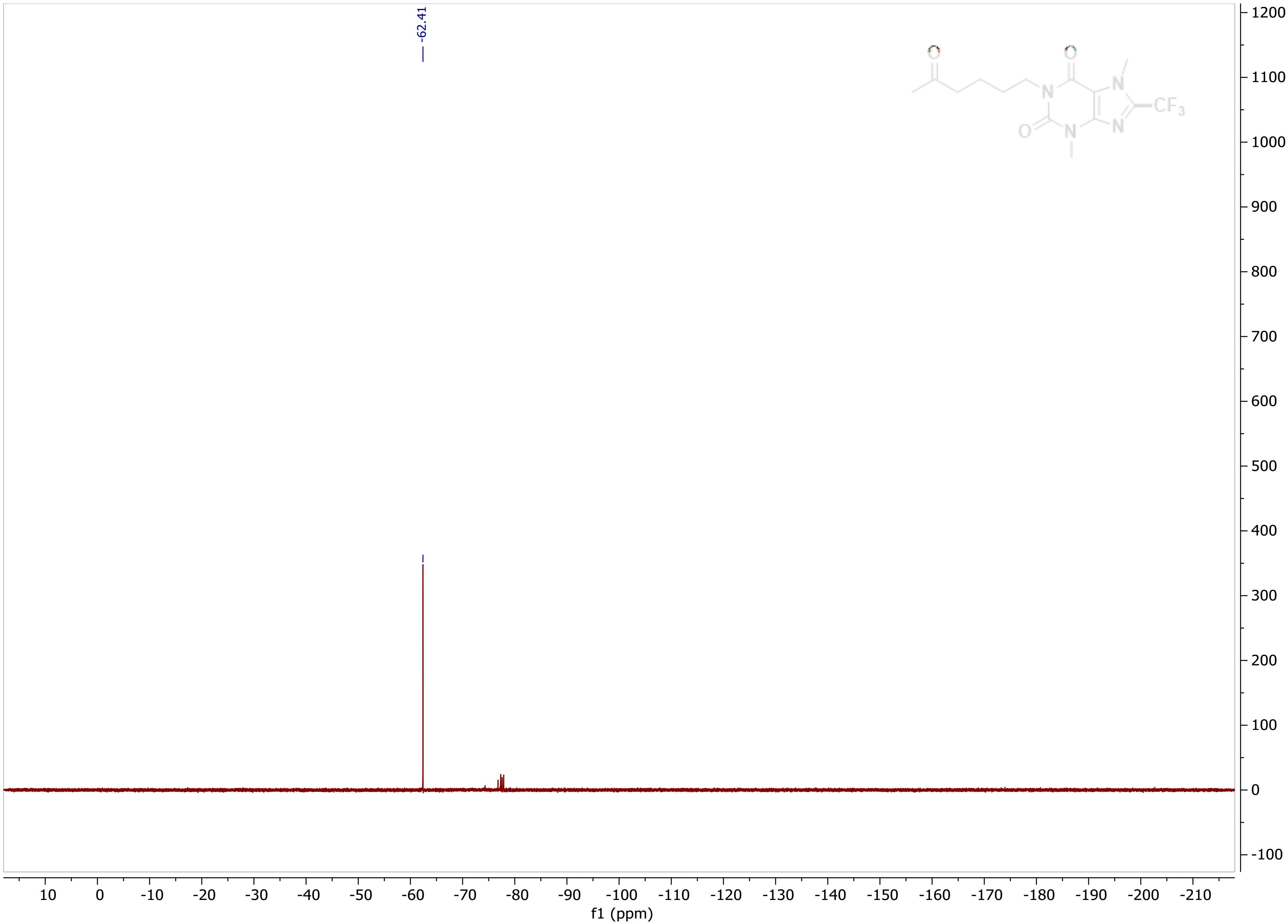
[1]H NMR of TF9, $CDCl_3$, 500 MHz



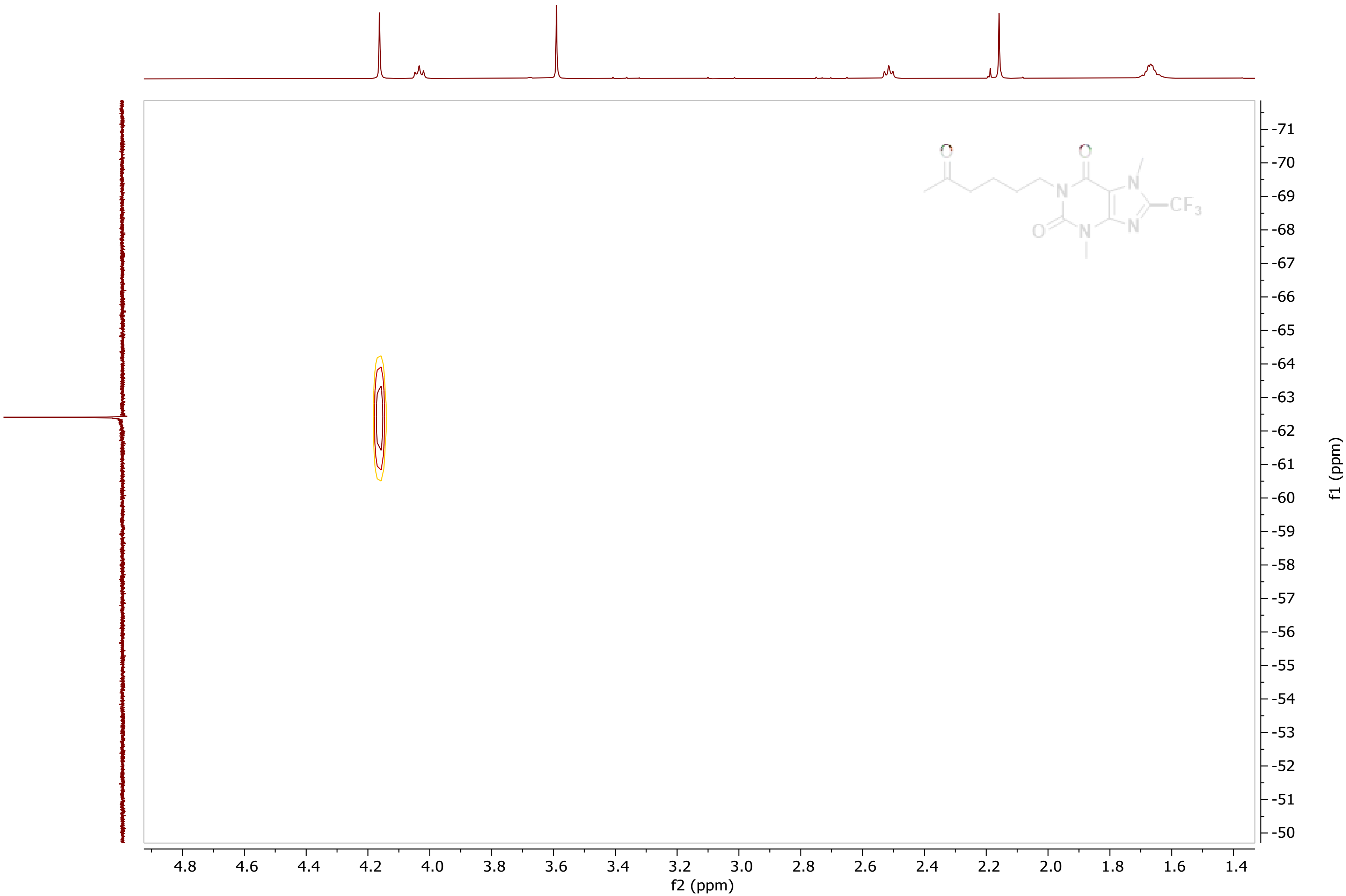
^{13}C NMR of TF9, $CDCl_3$, 126 MHz



^{19}F NMR of TF9, $CDCl_3$, 471 MHz



^{1}H-^{19}F HMBC of TF9



f2 (ppm)
f1 (ppm)
CF3