

Supporting Information

Thionyl fluoride as a Sulfur(IV) SuFEx Hub for the Efficient Syntheses of Sulfinamides and Sulfinates Esters

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Experimental Protocols and Data

Reactions: All reactions were performed in disposable scintillation 20 mL (28 x 61 mm) glass vials, or round-bottom flasks. Screw caps and PTFE/Silicone septa (22 mm x 0.060") were from Chemglass Life Sciences. Polyethylene tubing (I.D. 1.67 mm) was from Becton Dickinson. Disposable 1 mL syringes (I.D. 4.69 mm), 3 mL Syringes (I.D. 9.65 mm), 5 mL Syringes (I.D. 12.45 mm), 10 mL Syringes (I.D. 15.90 mm), and 30 mL Syringes (I.D. 22.90 mm) were from Norm-Ject and Henk-Ject. Disposable needles 16 G x 1 ½ (1.6 mm x 40 mm) and 21 G x 2 (0.8 mm x 5 mm) were from BD PrecisionGlide™. Hypodermic Needles (22 G x 4") were from Air-Tite™. White sleeve stoppers (24 x 40 mm) were from VWR®, white sleeve stoppers (OD 14 mm) were from Kimble®, and red Suba-Seal® septa were from Chemglass.

Reagents: Unless otherwise stated, all reagents were obtained from commercial sources. THF was obtained from a solvent purification system and stored over molecular sieves. The methanol used to synthesise compound **6i** was distilled over Mg turnings with I₂ and stored over molecular sieves. Dipropylamine was distilled over CaSO₄ and stored over KOH.

Chromatography: Flash chromatography was performed using Silicycle F60 silica gel (230-400 mesh) with pressure provided by compressed air. Automated chromatography was performed using a Biotage system with C18 RediSep®Rf Gold columns. Thin-layer chromatography (TLC) was performed on Merck Silica gel 60 F254 TLC aluminium sheets and visualized with 254 nm light and/or using a KMnO₄ stain followed by heating with a heat gun.

Infrared spectra (IR) were obtained using a PerkinElmer Frontier FT-IR spectrometer. The spectra are reported in cm⁻¹.

Melting points (mp) were determined by the open capillary method using a Mel-Temp II apparatus.

Mass spectrometry: Data was obtained on a Kratos Concept I1HQ or on a 1260 HPLC mass spectrometer coupled to an Agilent 6120B single quadrupole mass detector.

NMR spectra All ^{19}F and ^1H NMR data collected on a Bruker AV300 NMR spectrometer, equipped with an autosampler. All spectra were collected at room temperature. ^1H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to the residual solvent peak (CDCl_3 : ^1H : $\delta = 7.26$ ppm, ^{13}C : $\delta = 77.16$ ppm). ^{19}F NMR chemical shifts are reported in parts per million (ppm) and are referenced to CFCl_3 . NMR spectroscopic yields were determined by ^{19}F NMR using a α,α,α -trifluorotoluene (PhCF_3) as an internal standard. The relaxation time was set to 40 seconds to complete relaxation of all fluorine nuclei. Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), multiplet (m), doublet of doublets (dd), doublet of triplets (dt) and triplet of doublets (td). Assignment of peaks was done based on the chemical shifts, multiplicities, and integrals of the peaks. Coupling constants (J) are reported in Hz.

General procedure for the determination of NMR spectroscopy yields

To the reaction mixture containing substrate (0.5 mmol) was added PhCF_3 (33 μL , 0.267 mmol). An aliquot was removed by pipette and diluted in CDCl_3 for NMR analysis.

All ^{19}F NMR spectroscopy yields were calculated using PhCF_3 as an internal standard (^{19}F NMR: 282 MHz, Chloroform- d , $\delta -63.72$ ppm). Four scans and a relaxation delay of 40 seconds were used with the spectrum centre set between the substrate and PhCF_3 shifts. A sample calculation for the determination of ^{19}F yield is as follows:

$$\left(\frac{\left(\frac{\text{integration value of product}}{\text{number of nuclei in product}} \right)}{\left(\frac{\text{integration value of internal standard}}{\text{number of nuclei in internal standard}} \right)} \right) \left(\frac{\left(\frac{\text{mass internal standard (g)}}{\text{MW internal standard} \left(\frac{\text{g}}{\text{mol}} \right)} \right)}{\left(\frac{\text{mass substrate (g)}}{\text{MW substrate} \left(\frac{\text{g}}{\text{mol}} \right)} \right)} \right) \times 100\%$$

= Yield (%)

Notes on Optimization

Issues with the use of MISF in THF

As discussed in the paper, we initially attempted to use *N*-methylimidazolium sulfinylfluoride (MISF) as a SuFEx hub to access sulfinamides and sulfinate esters.

MISF was synthesised from a solution of SOF₂. The residual SOF₂ was removed by sparging the solution with nitrogen for 10 min. It was difficult to determine at what point the SOF₂ was completely removed, as the chemical shifts for SOF₂ and MISF as observed by ¹⁹F NMR spectroscopy are identical. MISF, additionally, is not very stable in THF. This results in being hard to quantify exactly how much MISF is being used in a reaction, and whether the solution still contains residual SOF₂, resulting in inconsistent yields and data.

Challenges with the quantification of the aminosulfinyl fluoride intermediate

The yield of dibenzylamino sulfinyl fluoride intermediate as determined by ¹⁹F NMR spectroscopy varies, with a maximum of 88% observed. This is likely because it is both hydrolytically unstable and also appears to decompose rapidly even in the absence of water. This resulted in unreliable quantification by NMR spectroscopy, and sometimes higher yields of final products are obtained than that was observed of the intermediate.

Sulfoxide formation during optimization

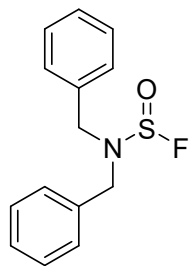
Our optimized conditions afforded the desired sulfinamide **4a** in 88% crude ¹⁹F NMR spectroscopic yield along with the formation of sulfoxide by-product in 26% yield. This adds up to 114% compared to SOF₂. A possible explanation for this inconsistency is that there was additional SOF₂ present in the reaction mixture after forming the aminosulfinyl fluoride intermediate. Although this excess SOF₂ was not seen by NMR spectroscopy, the SOF₂ may be

being quenched by water in the NMR tube/solvent. Therefore, we may be adding >1 equiv. of SOF₂ to the amine, leading to additional sulfoxide formation by reaction of this excess SOF₂ with diaryl zinc.

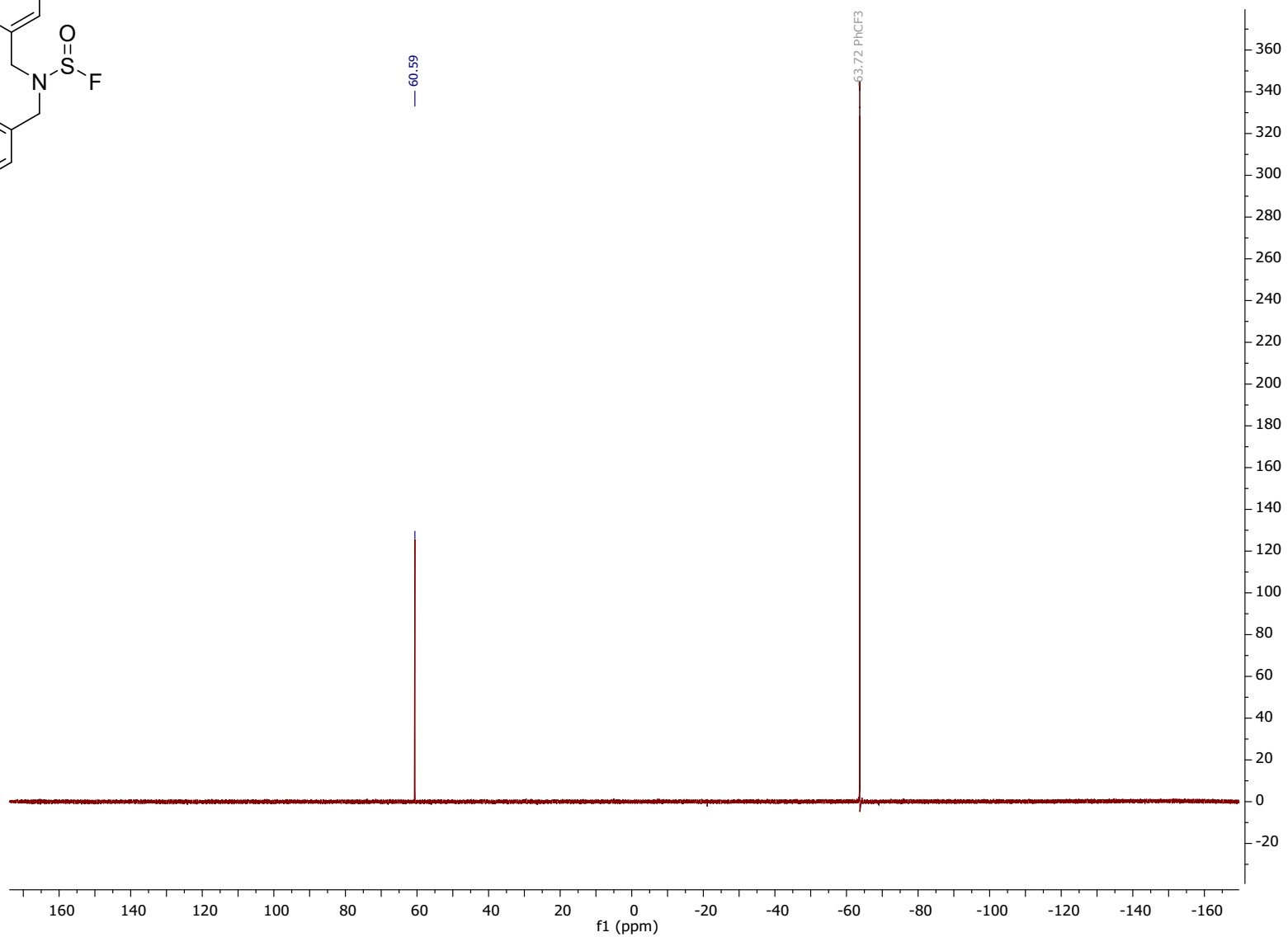
We wanted to rule out that further reaction of the sulfinamide with diaryl zinc was forming the sulfoxide, so we treated purified sulfinamide with diaryl zinc. No reaction was observed, confirming this was not an issue.

Previous literature with aryl boronic acids

Prof. Shi and co-workers had previously theorised that an aminosulfinyl fluoride was acting as their reactive intermediate in their coupling of aryl boronic acids and DAST to generate sulfinamides.¹ While we did not observe the desired product, our reaction was carried out in a different solvent than what was previously reported.



7a $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, Chloroform-*d*). *Not isolated*. Contains PhCF_3 as an internal standard.



Concentrations and solvents of the organometallic reagents used during optimization

4-Fluorophenylmagnesium bromide: 1 M in THF.

Bis(4-fluorophenyl)zinc: 0.25 M in THF.

4-Fluorophenylzinc chloride: 0.33 M in THF.

Phenylithium: 1.9 M in dibutyl ether.

Synthesis of Organozinc Compounds

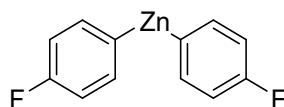
Titration of Grignard reagents for organozinc synthesis

An oven-dried 3.70 mL vial with a stir bar was filled with argon and cooled to room temperature. To the vial was added 100 mg of diphenylacetic acid. Under argon, THF (2 mL) was added to the vial and stirred until the diphenylacetic acid was dissolved. A 1 mL syringe was flushed with argon gas three times. The Grignard reagent solution was taken up into the syringe followed by a cushion of inert gas and inserted into the vial. The solution of the Grignard reagent was added dropwise until a pale-yellow colour appeared and the total volume of solution used was recorded.

$$\text{Molarity (M)} = \frac{\text{Mass}_{\text{diphenylacetic acid}}}{(\text{MW}_{\text{diphenylacetic acid}} \times \text{Volume}_{\text{Grignard reagent}})}$$

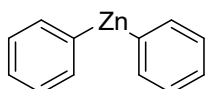
$$\text{MW}_{\text{diphenylacetic acid}} = 212.24 \text{ g/mol}$$

Bis(4-fluorophenyl) zinc



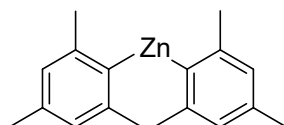
To a solution of ZnCl_2 in THF (0.5 M, 2 mL, 1.0 mmol) under argon at rt was added a solution of 4-fluorophenylmagnesium bromide in THF (1 M, 2 mL, 2.0 mmol). The solution was stirred for 1 h. and used directly.

Diphenylzinc



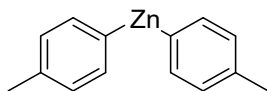
To a solution of ZnCl_2 in THF (0.5 M, 2 mL, 1.0 mmol) under argon at rt was added a solution of phenylmagnesium bromide in Et_2O (3 M, 0.67 mL, 2.0 mmol). The solution was stirred for 1 h. and used directly.

Dimesitylzinc



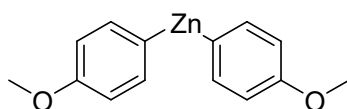
To a solution of ZnCl_2 in THF (0.5 M, 2 mL, 1.0 mmol) under argon at rt was added a solution of 2-mesitylmagnesium bromide in Et_2O (0.87 M, 2.30 mL, 2.0 mmol). The solution was stirred for 1 h. and used directly.

Di-p-tolyl zinc



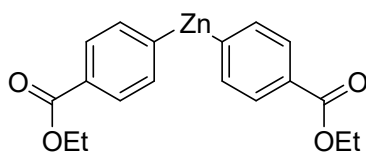
To a solution of ZnCl_2 in THF (0.5 M, 2 mL, 1.0 mmol) under argon at rt was added a solution of p-tolylmagnesium bromide in THF (1 M, 2 mL, 2.0 mmol). The solution was stirred for 1 h. and used directly.

Bis(4-methoxyphenyl) zinc



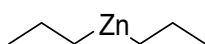
To a solution of ZnCl_2 in THF (0.5 M, 8 mL, 4.0 mmol) under argon at rt was added a solution of 4-methoxyphenylmagnesium bromide in THF (0.5 M, 16 mL, 8.0 mmol). The solution was stirred for 1 h. and used directly.

Bis(4-ethoxycarbonyl)phenyl)zinc



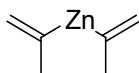
Following adapted literature procedures,^{2,3} to a solution of ethyl-4-iodobenzoate (552 mg, 2.0 mmol) in THF (2 mL) under argon at $-42\text{ }^{\circ}\text{C}$ was slowly added a solution of isopropylmagnesium chloride in THF (1.62 M, 1.23 mL, 2.0 mmol). The solution was stirred at $-42\text{ }^{\circ}\text{C}$ for 3 h. A solution of ZnCl_2 in THF (0.5 M, 2 mL, 1.0 mmol) was then added slowly at $-42\text{ }^{\circ}\text{C}$. The mixture was stirred with warming to rt for 1 h. and used directly.

Dipropyl zinc



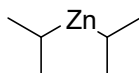
To a solution of ZnCl_2 in THF (0.5 M, 2 mL, 1.0 mmol) under argon at $-10\text{ }^{\circ}\text{C}$ was dropwise added a solution of propylmagnesium chloride in THF (2 M, 1 mL, 2.0 mmol). The solution was stirred for 10 minutes at $-10\text{ }^{\circ}\text{C}$, then rt for 1 h. and used directly.

Diisopropenyl zinc



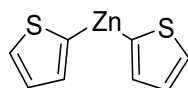
To a solution of ZnCl_2 in THF (0.5 M, 2 mL, 1.0 mmol) under argon at $-10\text{ }^{\circ}\text{C}$ was dropwise added a solution of isopropenylmagnesium bromide in THF (0.469 M, 4.26 mL, 2.0 mmol). The solution was stirred for 10 minutes at $-10\text{ }^{\circ}\text{C}$, then rt for 1 h. and used directly.

Diisopropylzinc



To a solution of ZnCl₂ in THF (0.5 M, 2 mL, 1.0 mmol) under argon at –10 °C was dropwise added a solution of isopropylmagnesium chloride in THF (1.62 M, 1.23 mL, 2.0 mmol). The solution was stirred for 10 minutes at –10 °C, then rt for 1 h. and used directly.

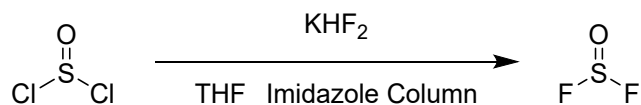
Di-2-thienylzinc



Under argon, to an oven-dried 20 mL vial was added 2-bromothiophene (2.00 mmol) and anhydrous THF (9 mL). The vial was cooled to –78 °C. To this was then slowly added a solution of *n*-butyllithium in hexane (1.25 mL, 1.6 molar, 2.00 mmol) at –78 °C and then stirred for 3 h at –78 °C.

Then a solution of zinc(II) chloride in THF (2.00 mL, 0.5 molar, 1.00 mmol) was slowly added at –78 °C. The solution was then stirred overnight at rt. The solution was used directly.

Procedure for the Generation of Thionyl Fluoride (SOF₂)



Note: gaseous thionyl fluoride is hazardous. Gas generation/reagent manipulation should only be conducted in a fully operational fume hood. In addition to standard PPE, face and/or reaction shields are recommended.

To a 20 mL vial was added KHF₂ (7.0 g, 90 mmol, 3.0 equiv). To a 100 mL round-bottom flask equipped with a stir bar was added THF (60 mL). Both the vial and the flask were sealed with rubber septa, and the two vessels were connected via needle, tubing, and a column of imidazole (27 g), as shown in Figure SI-1. Note that the imidazole was packed tightly into the syringe body to form the column. To the 20 mL vial was added thionyl chloride (2.2 mL, 30 mmol, 1.0 equiv) via a 5 mL syringe in a single portion. The syringe was not removed from the 20 mL vial. The generated gaseous thionyl fluoride passed through the imidazole column in order to quench any gaseous HCl, before dissolving in the solvent in the round-bottom flask. The gas generation was allowed to proceed for 30 – 60 min until either (1) the solvent began to flow backwards up the polyethylene tubing inserted into the round-bottom flask, or (2) the syringe plunger began to be pushed out. At this point, an empty balloon was quickly inserted through the septum of the round-bottom flask to release the pressure in the system and increase the concentration of dissolved thionyl fluoride. After either a cessation of bubbling, or near-consumption of the imidazole column (visualized by a front of green-black liquified imidazole), the polyethylene tubing was removed from the round-bottom flask. To a 1.0 mL aliquot of the resulting solution was added PhCF₃ (10 μL) as an internal standard. The concentration of thionyl fluoride in solution was quantified using quantitative ¹⁹F NMR spectroscopy. SOF₂ concentrations: 0.10 – 0.25 M.

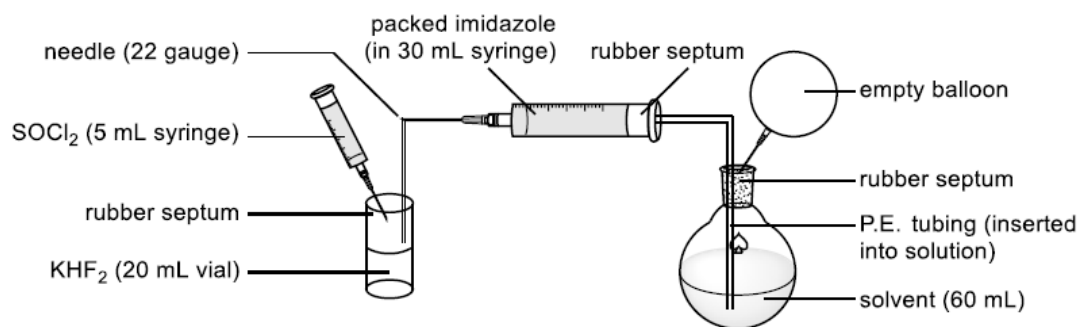
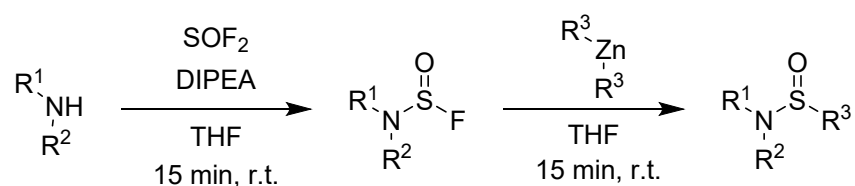


Figure SI-1. Schematic of SOF_2 generation apparatus

Synthesis of Sulfinamides

General procedure for the SOF₂-mediated synthesis of sulfinamides 4a-q

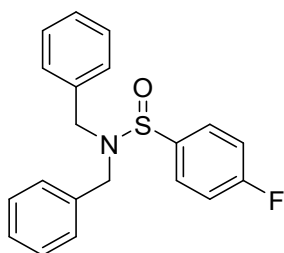


To a 20 mL vial equipped with a stir bar was added amine (0.5 mmol, 1 equiv) and DIPEA (0.5 mmol, 1 equiv). To this vial was added SOF₂ in THF (0.5 mmol, 1 equiv). The mixture was stirred at rt for 15 minutes.

This mixture was then added dropwise to a stirring solution of organozinc in THF (1 mmol, 2 equiv) at rt under argon. The mixture was stirred for 15 minutes. PhCF₃ (30 μL) was added as an internal standard. An aliquot of the mixture was sampled to quantify formation of the sulfinamide product by ¹⁹F NMR spectroscopy.

The mixture was quenched with saturated NH₄Cl_(aq) (10 mL) and diluted with water (5 mL). The solution was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL). The organic layer was dried over sodium sulfate and the solvent was removed *in vacuo* to afford crude product. The crude was then purified by column chromatography to afford to pure sulfinamide.

Compound 4a



Compound **4a** was prepared on 0.5 mmol scale following the general procedure using dibenzylamine (98.6 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in THF, 4 mL, 1.0 mmol). The crude product was purification by flash column chromatography (40–60% Et₂O in hexanes) to afford **4a** as a colourless oil (130 mg, 77% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.78 – 7.67 (m, 2H), 7.37 – 7.12 (m, 12H), 4.18 – 4.02 (m, 4H).

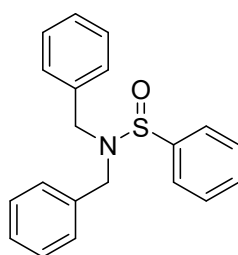
¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -109.0 (tt, *J* = 8.4, 5.2 Hz)

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 164.5 (d, *J* = 251.5 Hz), 139.9 (d, *J* = 3.0 Hz), 136.4, 129.1, 128.7, 128.7 (d, *J* = 9.1 Hz), 127.8, 116.3 (d, *J* = 22.4 Hz), 51.4.

IR (cm⁻¹): 3064, 3030, 2916, 1587, 1487, 1455, 1365, 1223, 1152.

HRMS (FD) *m/z*: [M]⁺ Calcd for C₂₀H₁₈FNOS 339.1093, found 339.1085.

Compound **4b**



Compound **4b** was prepared on a 0.5 mmol scale following the general procedure using dibenzylamine (98.6 mg, 0.5 mmol) and diphenyl zinc (0.374 M in THF/Et₂O, 2.67 mL, 1.0 mmol). The crude product was purified by flash column chromatography (20–30% Et₂O in hexanes) to afford **4b** as a pale-yellow oil (131 mg, 81% yield).

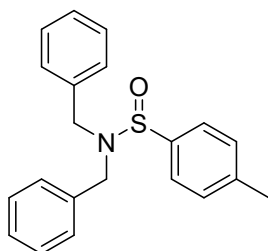
Data obtained matched the literature.⁴

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.80 – 7.70 (m, 2H), 7.57 – 7.43 (m, 3H), 7.34 – 7.14 (m, 10H), 4.16 – 4.04 (m, 4H).

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 144.3, 136.5, 131.1, 129.2, 129.1, 128.6, 127.7, 126.4, 51.5.

LRMS (FD) *m/z*: [M]⁺ Calcd for 321.1, found 321.2.

Compound 4c



Compound **4c** was prepared on a 0.5 mmol scale following the general procedure using dibenzylamine (98.6 mg, 0.5 mmol) and di-*p*-tolyl zinc (0.25 M in THF, 4 mL, 1.0 mmol). The crude product was purified by flash column chromatography (30-45% Et₂O in hexanes) to afford **4c** as a pale-yellow oil (99 mg, 59% yield).

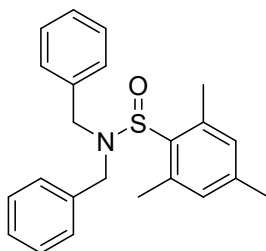
Data obtained matched the literature.⁵

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.23 (m, 12H), 4.18 (s, 4H), 2.49 (s, 3H).

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 141.5, 141.2, 136.6, 129.8, 129.2, 128.6, 127.7, 126.3, 51.3, 21.5.

HRMS (FD) *m/z*: [M]⁺ Calcd for 335.1344, found 335.1355.

Compound 4d



Compound **4d** was prepared on a 0.5 mmol scale following the general procedure using dibenzylamine (98.6 mg, 0.5 mmol) and dimesityl zinc (0.232 M in THF/Et₂O, 4.30 mL, 1.0 mmol). The crude product was purified by flash column chromatography (20-30% Et₂O in hexanes), and by drying at 65 °C under high vacuum overnight to afford **4d** as a white solid (133 mg, 73% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.33 – 7.18 (m, 6H), 7.12 – 7.03 (m, 4H), 6.86 (s, 2H), 4.39 – 4.00 (m, 4H), 2.52 (s, 6H), 2.29 (s, 3H).

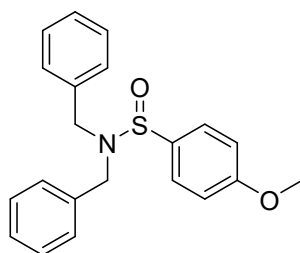
¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 140.7, 138.5, 136.5, 135.5, 131.4, 129.3, 128.5, 127.6, 52.1, 21.1, 20.1.

IR (cm⁻¹): 2913, 2860, 1598, 1493, 1455, 1435, 1356, 1235, 1203, 1110.

MP: 122–125 °C.

HRMS (FD) m/z: [M]⁺ Calcd for 363.1657, found 363.1671.

Compound 4e



Compound **4e** was prepared on a 0.5 mmol scale following the general procedure using dibenzylamine (98.6 mg, 0.5 mmol) and bis(4-methoxyphenyl) zinc (0.167 M in THF, 5.99 mL, 1.0 mmol). To the crude was added dimethyl sulfone to quantify the yield by ^1H NMR spectroscopy, 67% yield was observed. The crude product was purified by flash column chromatography (2-10% Et₂O in DCM) to afford **4e** as a colourless oil (86 mg, 49% yield).

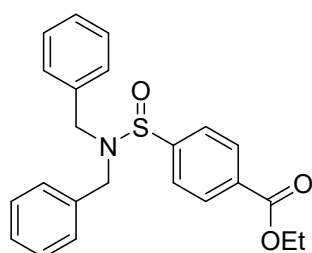
^1H NMR: (300 MHz, Chloroform-*d*) δ 7.70 – 7.62 (m, 2H), 7.36 – 7.13 (m, 10H), 7.06 – 6.98 (m, 2H), 4.16 – 4.03 (m, 4H), 3.85 (s, 3H).

^{13}C NMR: (75 MHz, Chloroform-*d*) δ 161.9, 136.7, 135.5, 129.2, 128.6, 128.0, 127.7, 114.5, 55.6, 51.2.

IR (cm⁻¹): 3063, 3029, 2912, 2838, 1592, 1578, 1493, 1455, 1441, 1407, 1365, 1306, 1249, 1205, 1181, 1170, 1133, 1088, 1065, 1026.

HRMS (FD) *m/z*: [M]⁺ Calcd for 351.1293, found 351.1286.

Compound 4f



Compound **4f** was prepared on a 0.5 mmol scale following the general procedure using dibenzylamine (98.6 mg, 0.5 mmol) and bis(4-(ethoxycarbonyl)phenyl) zinc (0.191 M in THF, 5.23 mL, 1.0 mmol). The crude product was purified by flash column chromatography (20-40% Et₂O in hexanes) to afford **4f** as a colourless oil (179 mg, 91% yield).

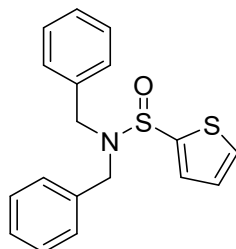
¹H NMR: (300 MHz, Chloroform-*d*) δ 8.24 – 8.12 (m, 2H), 7.86 – 7.76 (m, 2H), 7.37 – 7.11 (m, 10H), 4.40 (qd, *J* = 7.1, 1.5 Hz, 2H), 4.10 (s, 4H), 1.41 (td, *J* = 7.1, 1.5 Hz, 3H).

¹³C NMR: (75 MHz, Chloroform-*d*) δ 165.81, 149.05, 136.21, 133.07, 130.19, 129.14, 128.71, 127.91, 126.47, 61.58, 51.66, 14.42.

IR (cm⁻¹): 3061, 3030, 2982, 2909, 2859, 1717, 1596, 1575, 1496, 1455, 1397, 1367, 1269, 1205, 1170, 1106, 1083, 1066, 1027, 1015.

HRMS (FD) *m/z*: [M]⁺ Calcd for 393.1399, found 393.1411.

Compound **4g**



Compound **4g** was prepared on a 0.5 mmol scale following the general procedure using dibenzylamine (98.6 mg, 0.5 mmol) and di-(thiophen-2-yl) zinc (0.0816 M in THF/hexanes, 12.25 mL, 1.0 mmol). The crude product was purified by flash column chromatography (20-35% Et₂O in hexanes) to afford **4g** as a pale-yellow oil (111 mg, 68% yield).

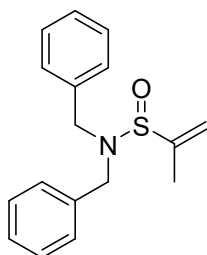
¹H NMR: (300 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.46 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.35 – 7.21 (m, 10H), 7.14 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.27 – 4.11 (m, 4H).

^{13}C NMR: (75 MHz, Chloroform-*d*) δ 147.6, 136.2, 131.5, 130.3, 129.2, 128.7, 128.1, 127.8, 51.1.

IR (cm^{-1}): 3063, 3029, 2913, 2856, 1603, 1495, 1455, 1404, 1365, 1339, 1217, 1129, 1073.

HRMS (FD) m/z : $[\text{M}]^+$ Calcd for 327.0752, found 327.0756.

Compound 4h



Compound **4h** was prepared on a 0.5 mmol scale following the general procedure using dibenzylamine (98.6 mg, 0.5 mmol) and diisopropenyl zinc (0.16 M in THF, 6.26 mL, 1.0 mmol). The crude product was purified by flash column chromatography (50% Et₂O in hexanes) to afford **4h** as a pale-yellow oil (98 mg, 69% yield).

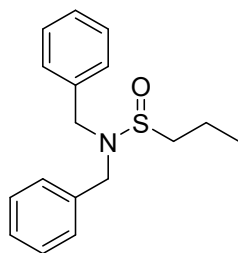
^1H NMR: (300 MHz, Chloroform-*d*) δ 7.38 – 7.22 (m, 10H), 6.03 (d, J = 1.0 Hz, 1H), 5.73 (q, J = 1.5 Hz, 1H), 4.13 (s, 4H), 1.98 (t, J = 1.2 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR: (75 MHz, Chloroform-*d*) δ 148.4, 136.6, 129.3, 128.6, 127.7, 120.5, 51.2, 16.9.

IR (cm^{-1}): 3030, 2916, 2856, 1495, 1455, 1367, 1266, 1241, 1204, 1132.

HRMS (FD) m/z : $[\text{M}+\text{H}]^+$ Calcd for 286.1266, found 286.1275.

Compound 4i



Compound **4i** was prepared on a 0.5 mmol scale following the general procedure using dibenzylamine (98.6 mg, 0.5 mmol) and dipropyl zinc (0.33 M in THF/Et₂O, 3 mL, 1.0 mmol). The crude product was purified by flash column chromatography (10-20% Et₂O in DCM) to afford **4i** as a colourless oil (100 mg, 69% yield).

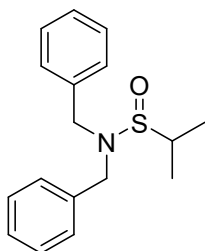
¹H NMR: (300 MHz, Chloroform-*d*) δ 7.36 – 7.21 (m, 10H), 4.31 (d, *J* = 15.1 Hz, 2H), 4.12 (d, *J* = 15.1 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 1.78 – 1.58 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

¹³C NMR: (75 MHz, Chloroform-*d*) δ 137.0, 128.8, 128.7, 127.7, 56.6, 51.3, 17.4, 13.5.

IR (cm⁻¹): 3029, 2964, 2931, 2874, 1603, 1495, 1454, 1365, 1241, 1204, 1136.

HRMS (FD) m/z: [M+H]⁺ Calcd for 288.1409, found 288.1422.

Compound **4j**



Compound **4j** was prepared on a 0.5 mmol scale following the general procedure using dibenzylamine (98.6 mg, 0.5 mmol) and diisopropyl zinc (0.31 M in THF, 3.23 mL, 1.0 mmol). The crude product was purified by flash column chromatography (10-20% Et₂O in DCM), and

by drying at 65 °C under high vacuum overnight to afford **4j** as a colourless oil (110 mg, 77% yield).

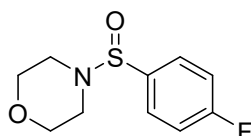
¹H NMR: (300 MHz, Chloroform-*d*) δ 7.38 – 7.20 (m, 10H), 4.34 – 4.05 (m, 4H), 2.93 (hept, *J* = 6.9 Hz, 1H), 1.31 (d, *J* = 7.0 Hz, 3H), 1.16 (d, *J* = 6.9 Hz, 3H).

¹³C NMR: (75 MHz, Chloroform-*d*) δ 136.9, 129.1, 128.6, 127.7, 52.9, 51.7, 17.3, 16.9.

IR (cm⁻¹): 3030, 2962, 2925, 2867, 1603, 1495, 1454, 1365, 1235, 1205, 1135, 1066.

HRMS (FD) m/z: [M+H]⁺ Calcd for 288.1417, found 288.1414.

Compound **4k**



Compound **4k** was prepared on a 0.5 mmol scale following the general procedure using morpholine (43.6 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in THF, 4 mL, 1.0 mmol). The crude product was purified by automated column chromatography (0-50% MeCN in water) to afford **4k** as a white solid (82 mg, 72% yield).

Data obtained matched the literature.¹

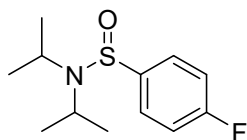
¹H NMR: (300 MHz, Chloroform-*d*) δ 7.70 – 7.62 (m, 2H), 7.20 (t, *J* = 8.6 Hz, 2H), 3.80 – 3.63 (m, 4H), 3.22 – 2.88 (m, 4H).

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -108.9 (tt, *J* = 8.4, 5.2 Hz)

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 164.6 (d, *J* = 251.7 Hz), 138.0 (d, *J* = 3.0 Hz), 128.6 (d, *J* = 8.9 Hz), 116.3 (d, *J* = 22.3 Hz), 67.0, 45.9.

LRMS (FD) m/z: [M]⁺ Calcd for C₁₀H₁₂FNO₂S 229.1, found 229.1.

Compound 4l



Compound **4l** was prepared on a 0.5 mmol scale following the general procedure using diisopropylamine (50.6 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in THF, 4 mL, 1.0 mmol). The crude product was purified by automated column chromatography (5-60% MeCN in water) to afford **4l** as a pale-yellow oil (55 mg, 45% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.67 – 7.57 (m, 2H), 7.21 – 7.11 (m, 2H), 3.53 (hept, *J* = 6.8 Hz, 2H), 1.40 (d, *J* = 6.7 Hz, 6H), 1.11 (d, *J* = 6.8 Hz, 6H).

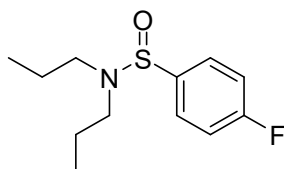
¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -110.8 (tt, *J* = 8.5, 5.2 Hz)

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 164.0 (d, *J* = 250.2 Hz), 140.2 (d, *J* = 3.1 Hz), 128.7 (d, *J* = 8.8 Hz), 115.8 (d, *J* = 22.3 Hz), 46.5, 23.8 (d, *J* = 12.8 Hz).

IR (cm⁻¹): 2967, 2934, 2873, 1588, 1488, 1461, 1391, 1367, 1222, 1178, 1151, 1123.

HRMS (FD) m/z: [M]⁺ Calcd for 243.1093, found 243.1087.

Compound 4m



Compound **4m** was prepared on a 0.5 mmol scale following the general procedure using dipropylamine (50.6 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in THF, 4 mL, 1.0 mmol). The crude product was purified by flash column chromatography (20-30% Et₂O in hexanes) to afford **4m** as a colourless oil (110 mg, 90% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.72 – 7.58 (m, 2H), 7.24 – 7.11 (m, 2H), 3.12 – 2.87 (m, 4H), 1.73 – 1.34 (m, 4H), 0.81 (t, *J* = 7.3 Hz, 6H).

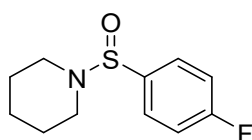
¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -109.9 (tt, *J* = 8.3, 5.2 Hz).

¹³C NMR: (75 MHz, Chloroform-*d*) δ 164.3 (d, *J* = 250.7 Hz), 140.2 (d, *J* = 3.0 Hz), 128.6 (d, *J* = 8.8 Hz), 116.0 (d, *J* = 22.4 Hz), 49.9, 22.1, 11.6.

IR (cm⁻¹): 2964, 2935, 2875, 1588, 1489, 1467, 1382, 1287, 1221, 1152.

HRMS (FD) *m/z*: [M]⁺ Calcd for 243.1093, found 243.1001.

Compound **4n**



Compound **4n** was prepared on a 0.5 mmol scale following the general procedure using piperidine (42.6 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in THF, 4 mL, 1.0 mmol). The crude product was purified by flash column chromatography (1-6% acetone in toluene) to afford **4n** as a white solid (82 mg, 72% yield).

Data obtained matched the literature.⁶

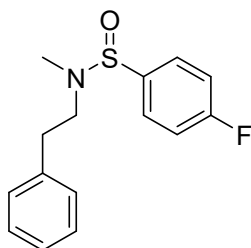
¹H NMR: (300 MHz, Chloroform-*d*) δ 7.70 – 7.58 (m, 2H), 7.24 – 7.12 (m, 2H), 3.18 – 3.04 (m, 2H), 3.01 – 2.86 (m, 2H), 1.67 – 1.46 (m, 6H).

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -109.9 (tt, *J* = 8.5, 5.2 Hz)

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 164.4 (d, *J* = 250.8 Hz), 139.2 (d, *J* = 3.0 Hz), 128.6 (d, *J* = 8.8 Hz), 116.1 (d, *J* = 22.3 Hz), 47.0, 26.3, 24.0.

LRMS (FD) m/z: [M]⁺ Calcd for 227.1, found 227.1.

Compound 4o



Compound **4o** was prepared on a 0.5 mmol scale following the general procedure using N-methyl-2-phenylethan-1-amine (67.6 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in THF, 4 mL, 1.0 mmol). The crude product was purified by flash column chromatography (60-70% Et₂O in hexanes) to afford **4o** as a colourless oil (108 mg, 78% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.39 – 7.21 (m, 5H), 7.17 – 7.03 (m, 4H), 3.54 – 3.28 (m, 2H), 2.89 (t, *J* = 7.2 Hz, 2H), 2.56 (s, 3H).

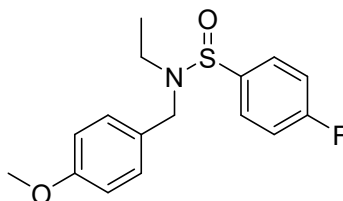
¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -109.8 (tt, *J* = 8.4, 5.2 Hz)

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 164.3 (d, *J* = 250.9 Hz), 139.5 (d, *J* = 2.9 Hz), 138.9, 128.9, 128.7, 128.5 (d, *J* = 8.8 Hz), 126.6, 116.0 (d, *J* = 22.4 Hz), 54.0, 34.8, 32.4.

IR (cm⁻¹): 3064, 3029, 2927, 2862, 1587, 1487, 1454, 1418, 1399, 1364, 1287, 1221, 1185, 1152.

HRMS (FD) m/z: [M]⁺ Calcd for 277.0937, found 277.0948.

Compound 4p



Compound **4p** was prepared on a 0.5 mmol scale following the general procedure using N-(4-methoxybenzyl)ethanamine (82.6 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in THF, 4 mL, 1.0 mmol). The crude product was purified by flash column chromatography (1-5% acetone in toluene) to afford **4p** as a colourless oil (130 mg, 85% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.75 – 7.66 (m, 2H), 7.24 – 7.10 (m, 4H), 6.88 – 6.80 (m, 2H), 4.09 (s, 2H), 3.79 (s, 3H), 3.05 (q, *J* = 7.3 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H).

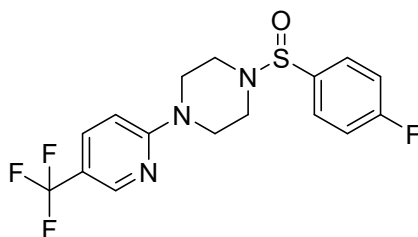
¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -110.0 (tt, *J* = 8.3, 5.3 Hz).

¹³C NMR: (75 MHz, Chloroform-*d*) δ 164.4 (d, *J* = 251.1 Hz), 159.3, 140.1 (d, *J* = 2.8 Hz), 129.9, 128.8, 128.7 (d, *J* = 8.9 Hz), 116.1 (d, *J* = 22.4 Hz), 114.1, 55.4, 50.2, 42.5, 14.2.

HRMS (FD) m/z: [M]⁺ Calcd for 307.1042, found 307.1066.

IR (cm⁻¹): 3066, 2973, 2934, 2870, 2837, 1612, 1586, 1512, 1488, 1464, 1443, 1380, 1364, 1302, 1244, 1222, 1173, 1152, 1083.

Compound 4q



Compound **4q** was prepared on a 0.5 mmol scale following the general procedure using 1-(5-(trifluoromethyl)pyridin-2-yl)piperazine (116 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in THF, 4 mL, 1.0 mmol). The crude product was purified by flash column chromatography (100% Et₂O) to afford **4q** as a white solid (106 mg, 57% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.75 – 7.59 (m, 3H), 7.30 – 7.17 (m, 2H), 6.62 (d, *J* = 9.0 Hz, 1H), 3.80 – 3.62 (m, 4H), 3.34 – 3.03 (m, 4H).

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -61.2, -108.7 (td, *J* = 8.4, 4.2 Hz).

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 164.7 (d, *J* = 252.0 Hz), 160.2 (d, *J* = 1.1 Hz), 145.9 (q, *J* = 4.4 Hz), 138.3 (d, *J* = 3.0 Hz), 134.8 (q, *J* = 3.3 Hz), 128.6 (d, *J* = 8.9 Hz), 124.6 (d, *J* = 270.4 Hz), 116.4 (d, *J* = 22.4 Hz), 116.8 – 115.3 (m), 105.9, 45.6, 45.2.

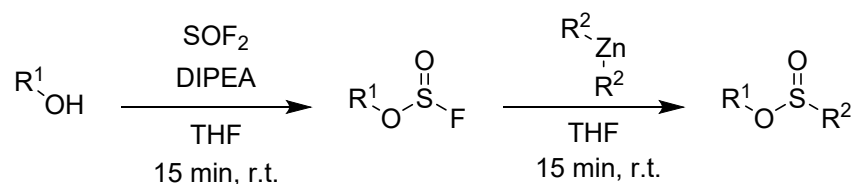
IR (cm⁻¹): 2900, 2854, 1614, 1589, 1563, 1504, 1493, 1448, 1412, 1383, 1339, 1325, 1317, 1281, 1259, 1243, 1226, 1175, 1114.

MP: 123–125 °C.

HRMS (FD) m/z: [M]⁺ Calcd for 373.0872, found 373.0873.

Synthesis of Sulfinates Esters

General procedure for the SOF₂-mediated synthesis of sulfinates esters 6a-k

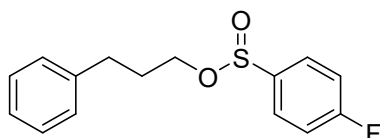


To a 20 mL vial equipped with a stir bar was added alcohol (0.5 mmol, 1 equiv) and DIPEA (0.5 mmol, 1 equiv). To this was added SOF₂ in THF (0.5 mmol, 1 equiv). The mixture was stirred at rt for 15 minutes.

This mixture was then added dropwise to a stirring solution of organozinc in THF (1 mmol, 2 equiv) at rt under argon. The reaction was stirred for 15 minutes. PhCF₃ (30 μL) was added as an internal standard. An aliquot of the mixture was sampled to quantify formation of the sulfinates ester product.

The reaction was quenched with water (10 mL) and brine (10 mL). The solution was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL). The organic layer was dried over sodium sulfate and the solvent was removed *in vacuo* to afford crude product. This crude was then purified by column chromatography to afford pure sulfinates ester.

Compound 6a



Compound **6a** was prepared on a 0.5 mmol scale following the general procedure slightly modified* using 3-phenyl-1-propanol (68.1 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in THF, 4 mL, 1.0 mmol). The crude product was purified by flash column chromatography (10-20% Et₂O in hexanes) to afford **6a** as a pale-yellow oil (86 mg, 62% yield).

*After the aliquot for ¹⁹F NMR was taken, acetic acid (1 mmol, 2 equiv) was added. Solvent was removed *in vacuo* and the crude was purified by flash column chromatography.

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.76 – 7.66 (m, 2H), 7.33 – 7.09 (m, 7H), 4.06 (dt, *J* = 10.0, 6.4 Hz, 1H), 3.64 (dt, *J* = 10.0, 6.3 Hz, 1H), 2.67 (dd, *J* = 8.5, 6.8 Hz, 2H), 2.03 – 1.89 (m, 2H).

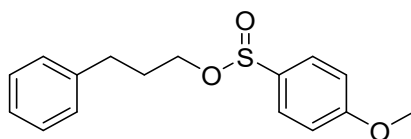
¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -107.15 (tt, *J* = 8.3, 5.2 Hz)

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 165.1 (d, *J* = 252.9 Hz), 141.0, 140.7 (d, *J* = 3.1 Hz), 128.6, 128.5, 127.8 (d, *J* = 9.1 Hz), 126.2, 116.5 (d, *J* = 22.4 Hz), 64.1, 32.0, 31.4.

IR (cm⁻¹): 3065, 3028, 2951, 1588, 1490, 1454, 1402, 1381, 1291, 1227, 1154, 1130, 1092.

HRMS (FD) *m/z*: [M]⁺ Calcd for 278.0777, found 278.0789.

Compound **6b**



Compound **6b** was prepared on a 2.0 mmol scale following the general procedure using 3-phenyl-1-propanol (272 mg, 2.0 mmol) and bis(4-methoxyphenyl)zinc (0.167 M in THF, 24 mL, 4.0 mmol). The crude product was purified by flash column chromatography (20-35% Et₂O in hexanes) to afford **6b** as a colourless oil (474 mg, 82% yield).

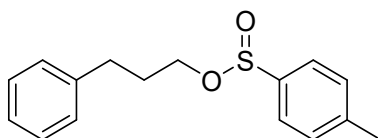
¹H NMR: (300 MHz, Chloroform-*d*) δ 7.69 – 7.58 (m, 2H), 7.31 – 7.09 (m, 5H), 7.07 – 6.99 (m, 2H), 4.03 (dt, *J* = 10.0, 6.4 Hz, 1H), 3.87 (s, 3H), 3.63 (dt, *J* = 10.0, 6.3 Hz, 1H), 2.71 – 2.61 (m, 2H), 2.01 – 1.88 (m, 2H).

¹³C NMR: (75 MHz, Chloroform-*d*) δ 162.8, 141.2, 136.5, 128.6, 128.5, 127.2, 126.1, 114.5, 63.5, 55.7, 32.1, 31.5.

IR (cm⁻¹): 3062, 3027, 2945, 2840, 1593, 1578, 1494, 1454, 1442, 1409, 1379, 1306, 1252, 1172, 1125, 1105, 1082.

HRMS (FD) m/z: [M]⁺ Calcd for 290.0977, found 290.0971.

Compound 6c



Compound **6c** was prepared on a 0.5 mmol scale following the general procedure using 3-phenyl-1-propanol (68.1 mg, 0.5 mmol) and di-*p*-tolyl zinc (0.25 M in THF, 4 mL, 1.0 mmol). The crude product was purified by flash column chromatography (10-20% Et₂O in hexanes) to afford **6c** as a colourless oil (101 mg, 74% yield).

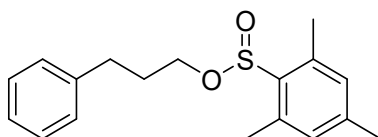
¹H NMR: (300 MHz, Chloroform-*d*) δ 7.63 – 7.56 (m, 2H), 7.37 – 7.31 (m, 2H), 7.30 – 7.11 (m, 5H), 4.05 (dt, *J* = 10.0, 6.4 Hz, 1H), 3.63 (dt, *J* = 10.0, 6.3 Hz, 1H), 2.71 – 2.61 (m, 2H), 2.43 (s, 3H), 2.01 – 1.88 (m, 2H).

¹³C NMR: (75 MHz, Chloroform-*d*) δ 142.8, 141.9, 141.2, 129.8, 128.6, 128.5, 126.1, 125.3, 63.8, 32.1, 31.5, 21.7.

IR (cm⁻¹): 3027, 2950, 1597, 1496, 1454, 1380, 1130, 1080.

HRMS (FD) m/z: [M]⁺ Calcd for 274.1028, found 274.1037.

Compound 6d



Compound **6d** was prepared on a 0.5 mmol scale following the general procedure using 3-phenyl-1-propanol (68.1 mg, 0.5 mmol) and dimesityl zinc (0.232 M in THF/Et₂O, 4.30 mL, 1.0 mmol). The crude product was purified by flash column chromatography (5-20% Et₂O in hexanes), and by heating to 90 °C under high vacuum for 1 h to afford **6d** as a bright yellow oil (114 mg, 75% yield).

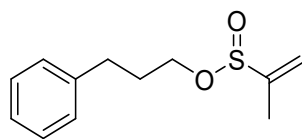
¹H NMR: (300 MHz, Chloroform-*d*) δ 7.33 – 7.21 (m, 2H), 7.22 – 7.11 (m, 3H), 6.89 – 6.84 (m, 2H), 4.16 – 4.01 (m, 2H), 2.76 – 2.66 (m, 2H), 2.61 (s, 6H), 2.29 (s, 3H), 2.10 – 1.98 (m, 2H).

¹³C NMR: (75 MHz, Chloroform-*d*) δ 142.0, 141.1, 138.5, 137.8, 130.8, 126.2, 68.0, 32.1, 31.9, 21.3, 19.2.

IR (cm⁻¹): 3027, 2932, 2978, 1602, 1570, 1496, 1454, 1380, 1294, 1246, 1204, 1178, 1125.

HRMS (FD) m/z: [M]⁺ Calcd for 302.1341, found 302.1336.

Compound 6e



Compound **6e** was prepared on a 0.5 mmol scale following the general procedure using 3-phenyl-1-propanol (68.1 mg, 0.5 mmol) and diisopropenyl zinc (0.16 M in THF, 6.26 mL, 1.0 mmol). The crude product was purified by flash column chromatography (10-20% Et₂O in hexanes) to afford **6e** as a colourless oil (77 mg, 68% yield).

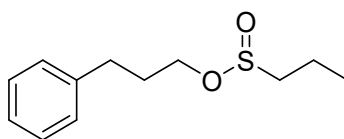
¹H NMR: (300 MHz, Chloroform-*d*) δ 7.35 – 7.26 (m, 2H), 7.25 – 7.16 (m, 3H), 5.84 (s, 1H), 5.64 (s, 1H), 4.09 – 3.85 (m, 2H), 2.74 (t, *J* = 7.7 Hz, 2H), 2.10 – 1.97 (m, 5H).

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 151.1, 141.1, 128.6, 126.2, 119.7, 65.7, 32.0, 31.7, 13.7.

IR (cm⁻¹): 3027, 2950, 2882, 1637, 1604, 1497, 1454, 1379, 1128, 1090.

HRMS (FD) *m/z*: [M]⁺ Calcd for 224.0871, found 224.0882.

Compound 6f



Compound **6f** was prepared on a 0.5 mmol scale following the general procedure using 3-phenyl-1-propanol (68.1 mg, 0.5 mmol) and dipropyl zinc (0.33 M in THF, 3 mL, 1.0 mmol). The crude product was purified by flash column chromatography (20-30% Et₂O in hexanes) to afford **6f** as a colourless oil (80 mg, 70% yield).

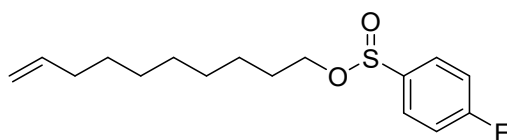
¹H NMR: (300 MHz, Chloroform-*d*) δ 7.33 – 7.25 (m, 2H), 7.20 (td, J = 6.4, 1.6 Hz, 3H), 4.13 – 3.95 (m, 2H), 2.82 – 2.61 (m, 4H), 2.09 – 1.96 (m, 2H), 1.76 (h, J = 7.5 Hz, 2H), 1.07 (t, J = 7.4 Hz, 3H).

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 141.1, 128.6, 128.6, 126.2, 68.0, 59.2, 32.0, 31.8, 15.3, 13.6.

IR (cm⁻¹): 3027, 2964, 2877, 1603, 1496, 1454, 1406, 1382, 1126, 1089.

LRMS (FD) m/z: [M]⁺ Calcd for 226.1028, found 226.1022.

Compound 6g



Compound **6g** was prepared on a 0.5 mmol scale following the general procedure using dec-9-en-1-ol (78.1 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in THF, 4 mL, 1.0 mmol). The crude product was purified by flash column chromatography (5-10% Et₂O in hexanes) to afford **6g** as a colourless oil (86 mg, 58% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.77 – 7.66 (m, 2H), 7.25 – 7.17 (m, 2H), 5.80 (ddt, J = 16.9, 10.1, 6.7 Hz, 1H), 5.04 – 4.88 (m, 2H), 4.03 (dt, J = 9.8, 6.6 Hz, 1H), 3.62 (dt, J = 9.9, 6.6 Hz, 1H), 2.10 – 1.96 (m, 2H), 1.70 – 1.54 (m, 2H), 1.41 – 1.20 (m, 10H).

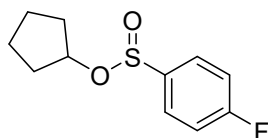
¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -107.3 (ddd, J = 13.2, 8.5, 4.9 Hz).

¹³C NMR: (75 MHz, Chloroform-*d*) δ 165.1 (d, J = 252.7 Hz), 140.9 (d, J = 3.1 Hz), 139.3, 127.8 (d, J = 9.1 Hz), 116.4 (d, J = 22.5 Hz), 114.3, 65.1, 33.9, 29.8, 29.4, 29.2, 29.1, 29.0, 25.8.

IR (cm⁻¹): 3073, 2927, 2855, 1641, 1589, 1491, 1229, 1133, 1092, 1078.

HRMS (FD) m/z: [M]⁺ Calcd for 298.1403, found 298.1405.

Compound 6h



Compound **6h** was prepared on a 0.5 mmol scale following the general procedure using cyclopentanol (43.1 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in THF, 4 mL, 1.0 mmol). The crude product was purified by flash column chromatography (10-25% Et₂O in hexanes) to afford **6h** as a colourless oil (68 mg, 59% yield).

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.75 – 7.64 (m, 2H), 7.25 – 7.16 (m, 2H), 4.83 (p, *J* = 4.4 Hz, 1H), 1.89 (dt, *J* = 6.2, 4.1 Hz, 2H), 1.83 – 1.49 (m, 6H).

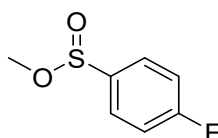
¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -107.7 (tt, *J* = 8.6, 5.0 Hz).

¹³C NMR: (75 MHz, Chloroform-*d*) δ 165.0 (d, *J* = 252.4 Hz), 141.8 (d, *J* = 3.1 Hz), 127.7 (d, *J* = 9.1 Hz), 116.4 (d, *J* = 22.4 Hz), 81.3, 34.3, 33.9, 23.5, 23.4.

IR (cm⁻¹): 2962, 2875, 1588, 1491, 1451, 1435, 1401, 1355, 1291, 1225, 1154, 1128, 1092.

HRMS (FD) m/z: [M]⁺ Calcd for 228.0620, found 228.0625.

Compound 6i



Compound **6i** was prepared on a 0.5 mmol scale following the general procedure freshly distilled methanol (16.0 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in THF, 4 mL, 1.0

mmol). The crude product was purified by flash column chromatography (20-25% Et₂O in hexanes) to afford **6i** as a colourless oil (38 mg, 44% yield).

Data obtained matched the literature.⁷

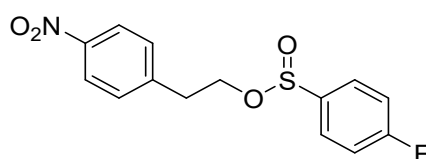
¹H NMR: (300 MHz, Chloroform-*d*) δ 7.76 – 7.65 (m, 2H), 7.28 – 7.18 (m, 2H), 3.48 (s, 3H).

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -106.7 (tt, *J* = 8.3, 5.2 Hz).

¹³C NMR: (75 MHz, Chloroform-*d*) δ 165.2 (d, *J* = 253.1 Hz), 140.0 (d, *J* = 3.1 Hz), 128.0 (d, *J* = 9.2 Hz), 116.5 (d, *J* = 22.5 Hz), 49.8.

LRMS (GC) *m/z*: [M]⁺ Calcd for 174.0, found 174.0.

Compound **6j**



Compound **6j** was prepared on a 0.5 mmol scale following the general procedure using 2-(4-nitrophenyl)ethan-1-ol (83.6 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in THF, 4 mL, 1.0 mmol). The crude product was purified by flash column chromatography (50-100% DCM in hexanes and then 30-50% Et₂O in hexanes) to afford **6j** as a pale-yellow oil (86 mg, 98% purity, 55% yield) contaminated with 2% residual 2-(4-nitrophenyl)ethan-1-ol, which we were not able to remove completely by column chromatography.

¹H NMR: (300 MHz, Chloroform-*d*) δ 8.20 – 8.08 (m, 2H), 7.67 – 7.55 (m, 2H), 7.37 – 7.27 (m, 2H), 7.26 – 7.12 (m, 2H), 4.28 (dt, *J* = 10.1, 6.5 Hz, 1H), 3.80 (dt, *J* = 10.1, 6.5 Hz, 1H), 3.04 (t, *J* = 6.5 Hz, 2H).

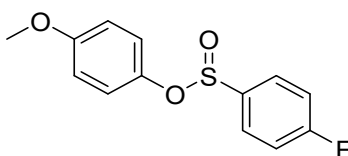
¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -106.34 – -106.56 (m)

¹³C{¹H} NMR: (75 MHz, Chloroform-*d*) δ 165.2 (d, J = 253.7 Hz), 147.1, 145.2, 140.1 (d, J = 3.1 Hz), 130.0, 127.8 (d, J = 9.1 Hz), 123.9, 116.6 (d, J = 22.5 Hz), 63.6, 36.1.

IR (cm⁻¹): 3075, 2953, 1599, 1588, 1516, 1490, 1343, 1319, 1226, 1154, 1129, 1093.

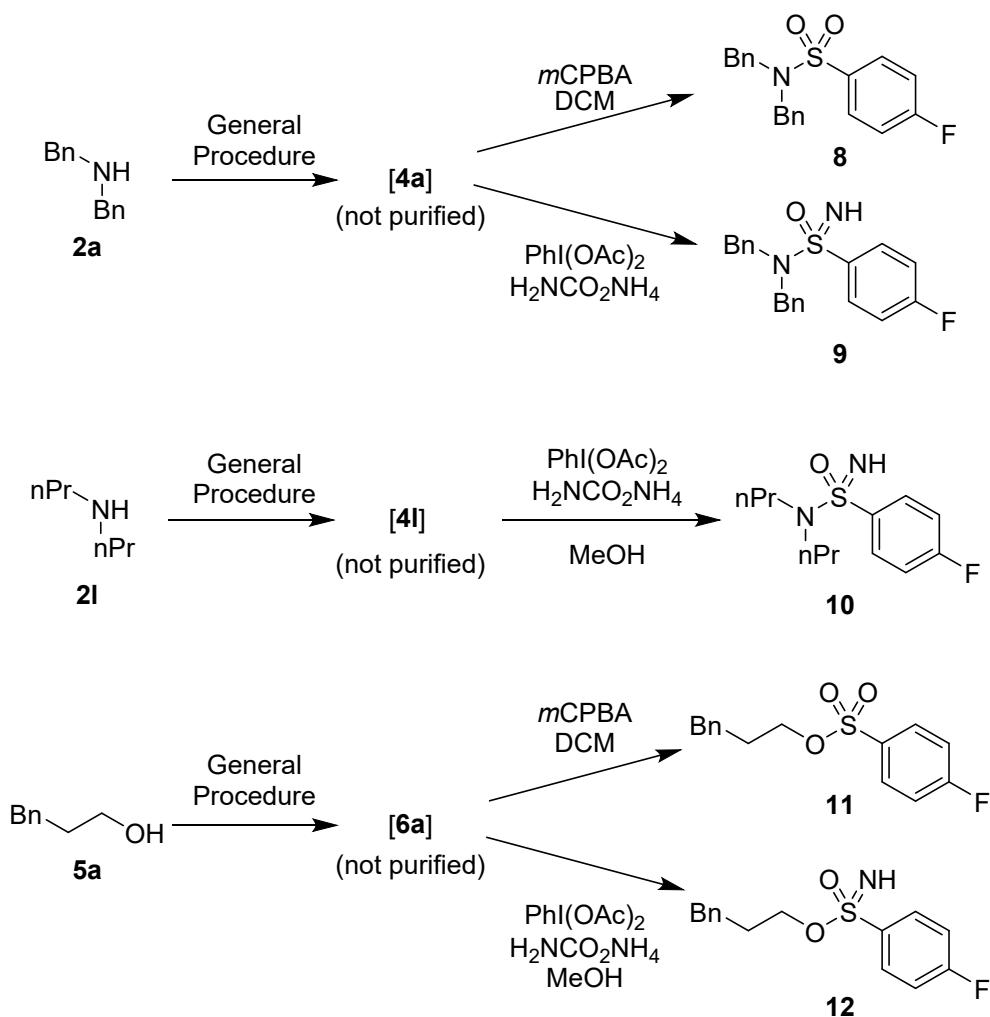
HRMS (FD) m/z: [M]⁺ Calcd for 309.0471, found 309.0486.

Compound 6k

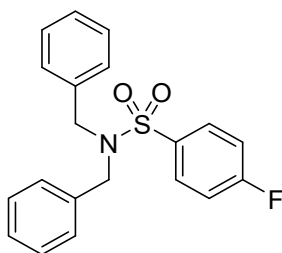


Compound **6k** was prepared on a 0.5 mmol scale following the general procedure using 4-methoxyphenol and bis(4-fluorophenyl) zinc (0.25 M in THF, 4 mL, 1.0 mmol). The yield of the product in the reaction mixture was observed to be 66% by ¹⁹F NMR spectroscopy. The product was not isolated due to hydrolytic instability.

Synthesis of S(VI) Compounds



Compound 8



Compound **8** was prepared on a 0.5 mmol scale first following the general sulfonamide procedure using dibenzylamine (98.6 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in THF). Without further purification, this crude **4a** was dissolved in DCM (6 mL), and *m*CPBA (70% wt, 247 mg, 2 equiv) was added. The solution was stirred for 50 minutes, upon which

^{19}F NMR spectroscopy showed complete consumption of the sulfinamide. The solution was quenched with addition of saturated aqueous sodium bisulfate solution (10 mL). The mixture was extracted with DCM (3 x 10 mL), the combined organic layers were then washed with saturated aqueous sodium bicarbonate solution (2 x 10 mL) and brine (10 mL). The organic layer was then dried over sodium sulfate and solvent removed *in vacuo*. The crude product was then purified by flash column chromatography (10-20% Et₂O in hexanes) to afford **8** as a white solid (116 mg, 65% yield over two steps).

Data obtained matched the literature.⁸

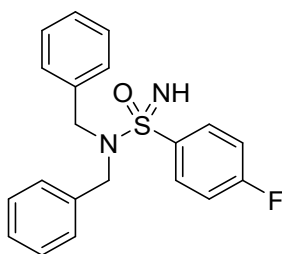
^1H NMR: (300 MHz, Chloroform-*d*) δ 7.87 – 7.78 (m, 2H), 7.28 – 7.19 (m, 6H), 7.20 – 7.12 (m, 2H), 7.10 – 7.01 (m, 4H), 4.34 (s, 4H).

^{19}F NMR: (282 MHz, Chloroform-*d*) δ -105.5 – -105.7 (m).

^{13}C NMR: (75 MHz, Chloroform-*d*) δ 165.1 (d, J = 254.6 Hz), 137.1 (d, J = 3.3 Hz), 135.5, 129.9 (d, J = 9.2 Hz), 128.7, 128.7, 127.9, 116.4 (d, J = 22.4 Hz), 50.6.

LRMS (FD) m/z : [M]⁺ Calcd for 355.1, found 355.2.

Compound 9



Compound **9** was prepared on a 0.5 mmol scale first following the general sulfinamide procedure using dibenzylamine (98.6 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in

THF). Without further purification, to this crude **4a** was added (diacetyoxyiodo)benzene (1.058 g, 6.57 equiv.), ammonium carbamate (342 mg, 8.78 equiv.) and methanol (10 mL). The mixture was stirred for 90 minutes. The reaction was then quenched with the addition of aqueous saturated sodium bicarbonate solution (15 mL), extracted with EtOAc (3 x 15 mL), the combined organic layers were washed with brine (20 mL), then dried over sodium sulfate and solvent removed *in vacuo*. The crude product was then purified by flash column chromatography (10-20% EtOAc in hexanes) to afford **9** as a pale-yellow oil (81 mg, 46% yield over 2 steps).

Data obtained matched the literature.⁹

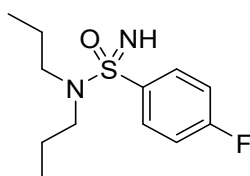
¹H NMR: (300 MHz, Chloroform-*d*) δ 8.01 – 7.92 (m, 2H), 7.25 – 7.10 (m, 8H), 7.09 – 6.99 (m, 4H), 4.37 (s, 4H), 2.65 (s, 1H).

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -106.6 (tt, $J = 8.3, 5.1$ Hz).

¹³C NMR: (75 MHz, Chloroform-*d*) δ 165.0 (d, $J = 254.0$ Hz), 137.2 (d, $J = 3.1$ Hz), 136.5, 130.1 (d, $J = 9.2$ Hz), 128.6, 128.5, 127.7, 116.1 (d, $J = 22.3$ Hz), 51.9.

LRMS (ESI-API) m/z: [M+H]⁺ Calcd for 355.1, found 355.1.

Compound 10



Compound **10** was prepared on a 0.5 mmol scale first following the general sulfinamide procedure using dipropylamine (50.6 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in

THF). Without further purification, to this crude **4I** was added (diacetyoxyiodo)benzene (644 mg, 4 equiv.), ammonium carbamate (208 mg, 5.33 equiv.) and methanol (10 mL). The mixture was stirred for 1 hour. To the mixture was then added (diacetyoxyiodo)benzene (644 mg, 4 equiv.), ammonium carbamate (208 mg, 5.33 equiv.). The mixture was then stirred for a further 1 hour. The reaction was then quenched with the addition of aqueous saturated sodium bicarbonate solution (20 mL), extracted with EtOAc (3 x 20 mL), the combined organic layers were washed with brine (20 mL), then dried over sodium sulfate and solvent removed *in vacuo*. The crude product was then purified by flash column chromatography (20-30% EtOAc in hexanes) to afford **10** as a pale-yellow oil (66 mg, 51% yield over 2 steps).

¹H NMR: (300 MHz, Chloroform-*d*) δ 7.99 – 7.89 (m, 2H), 7.19 – 7.10 (m, 2H), 3.20 – 2.95 (m, 4H), 2.43 (s, 1H), 1.63 – 1.44 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H).

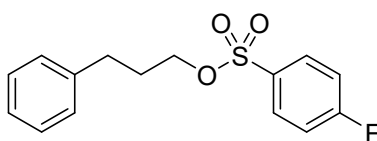
¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -107.5 – -107.7 (m).

¹³C NMR: (75 MHz, Chloroform-*d*) δ 164.8 (d, *J* = 253.2 Hz), 136.6 (d, *J* = 3.1 Hz), 130.0 (d, *J* = 9.1 Hz), 116.0 (d, *J* = 22.4 Hz), 51.1, 22.5, 11.4.

IR (cm⁻¹): 3346, 3282, 2966, 2935, 2876, 1590, 1490, 1467, 1403, 1382, 1346, 1294, 1249, 1226, 1183, 1170, 1156, 1130, 1094, 1074.

HRMS (FD) m/z: [M]⁺Calcd for 258.1202, found 258.1196.

Compound 11



Compound **11** was prepared on a 0.5 mmol scale first following general sulfinate ester procedure using 3-phenyl-propan-1-ol (68.1 mg, 0.5 mmol) and bis(4-fluorophenyl) zinc (0.25 M in THF). Without further purification, this crude **6a** was dissolved in DCM (6 mL), and mCPBA (70% wt, 247 mg, 2 equiv.) was added. The solution was stirred for 50 minutes, upon which ^{19}F NMR spectroscopy showed complete consumption of the sulfinate ester. The solution was quenched with addition of saturated aqueous sodium bisulfate solution (10 mL). The mixture was extracted with DCM (3 x 10 mL), the combined organic layers were then washed with saturated aqueous sodium bicarbonate solution (2 x 10 mL) and brine (10 mL). The organic layer was then dried over sodium sulfate and solvent removed *in vacuo*. The crude product was then purified by flash column chromatography (10-20% Et₂O in hexanes) to afford **11** as a colourless oil (97 mg, 66% yield over two steps).

^1H NMR: (300 MHz, Chloroform-*d*) δ 8.01 – 7.84 (m, 2H), 7.29 – 7.15 (m, 5H), 7.11 – 7.05 (m, 2H), 4.06 (t, J = 6.2 Hz, 2H), 2.66 (t, J = 7.5 Hz, 2H), 2.07 – 1.91 (m, 2H).

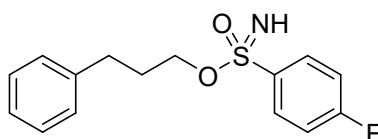
^{19}F NMR: (282 MHz, Chloroform-*d*) δ -103.5 (tt, J = 8.2, 4.9 Hz).

^{13}C NMR: (75 MHz, Chloroform-*d*) δ 165.9 (d, J = 256.5 Hz), 140.3, 132.3 (d, J = 3.4 Hz), 130.8 (d, J = 9.5 Hz), 128.7, 128.5, 126.4, 116.7 (d, J = 22.7 Hz), 70.0, 31.5, 30.5.

IR (cm⁻¹): 3029, 2958, 1593, 1495, 1408, 1361, 1294, 1239, 1182, 1156, 1096.

HRMS (FD) m/z : [M]⁺ Calcd for 294.0726, found 294.0715

Compound 12



Compound **12** was prepared on a 0.5 mmol scale first following the general sulfinic acid ester procedure using 3-phenyl-propanol and bis(4-fluorophenyl) zinc (0.25 M in THF). Without further purification, to this crude **6a** was added (diacetyoxyiodo)benzene (644 mg, 4 equiv.), ammonium carbamate (208 mg, 5.33 equiv.) and methanol (10 mL). The mixture was stirred for 1 hour in an open flask. To the mixture was then added (diacetyoxyiodo)benzene (644 mg, 4 equiv.), ammonium carbamate (208 mg, 5.33 equiv.). The mixture was then stirred for a further 1.5 hours. The reaction was then quenched with the addition of aqueous saturated sodium bicarbonate solution (20 mL), extracted with EtOAc (3 x 20 mL), the combined organic layers were washed with brine (20 mL), then dried over sodium sulfate and solvent removed *in vacuo*. The crude product was purified by flash column chromatography (20-30% EtOAc in hexanes) to afford **12** as a pale-yellow oil (88 mg, 60% yield over 2 steps).

¹H NMR: (300 MHz, Chloroform-*d*) δ 8.08 – 7.95 (m, 2H), 7.30 – 7.13 (m, 5H), 7.13 – 7.04 (m, 2H), 4.01 – 3.85 (m, 2H), 3.23 (s, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.01 – 1.84 (m, 2H).

¹⁹F NMR: (282 MHz, Chloroform-*d*) δ -104.8 (tt, *J* = 8.3, 5.0 Hz).

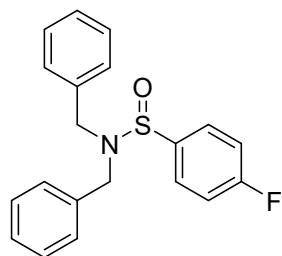
¹³C NMR: (75 MHz, Chloroform-*d*) δ 165.5 (d, *J* = 255.4 Hz), 140.6, 134.1 (d, *J* = 3.3 Hz), 130.6 (d, *J* = 9.4 Hz), 128.6, 128.5, 126.3, 116.3 (d, *J* = 22.7 Hz), 68.9, 31.8, 30.6.

IR (cm⁻¹): 3297, 3066, 3028, 2954, 1590, 1492, 1455, 1406, 1302, 1273, 1232, 1145, 1082.

HRMS (FD) m/z: [M+H]⁺ Calcd for 294.0964, found 294.0975.

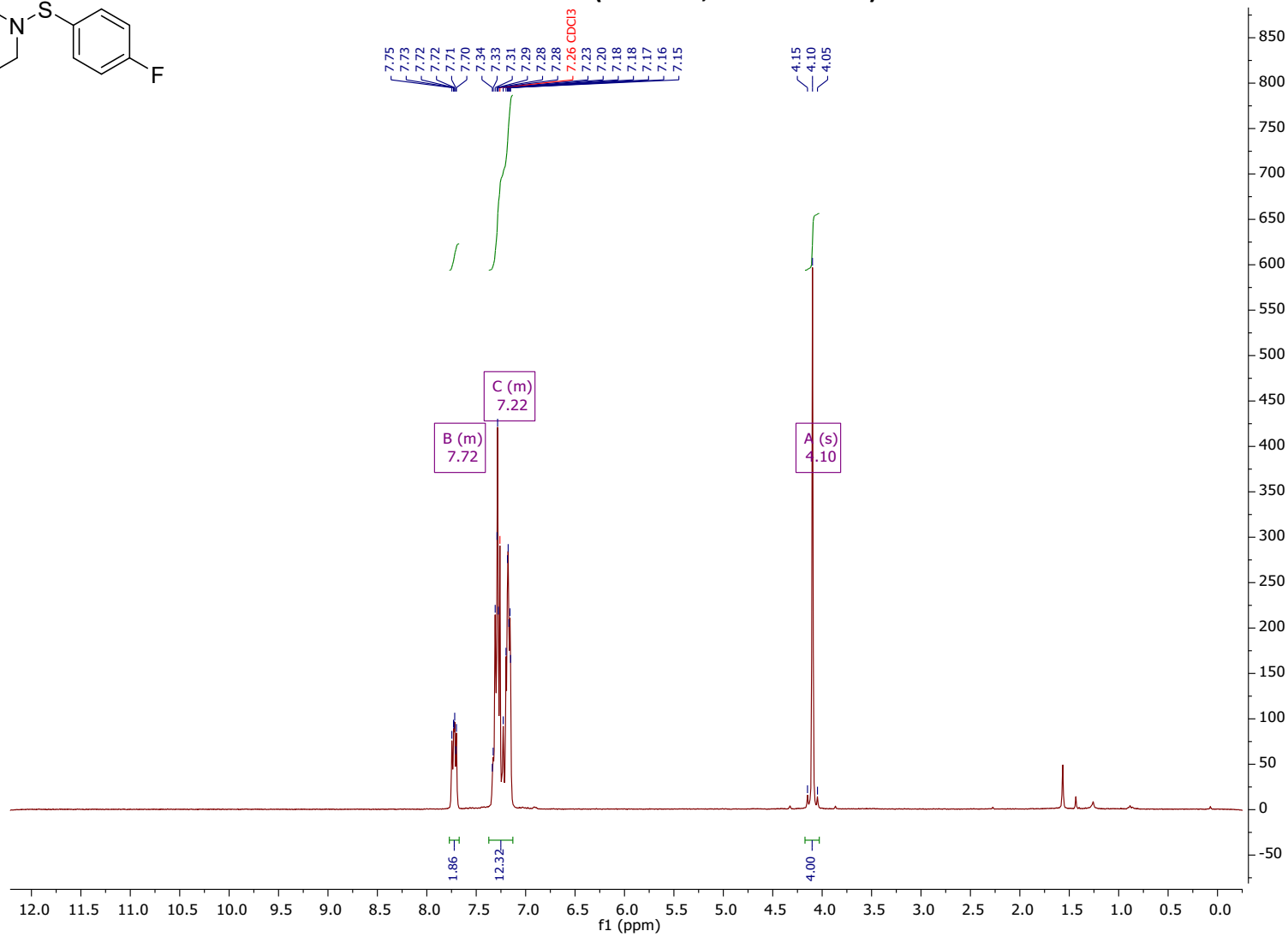
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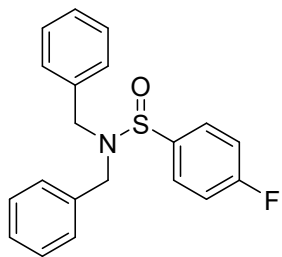
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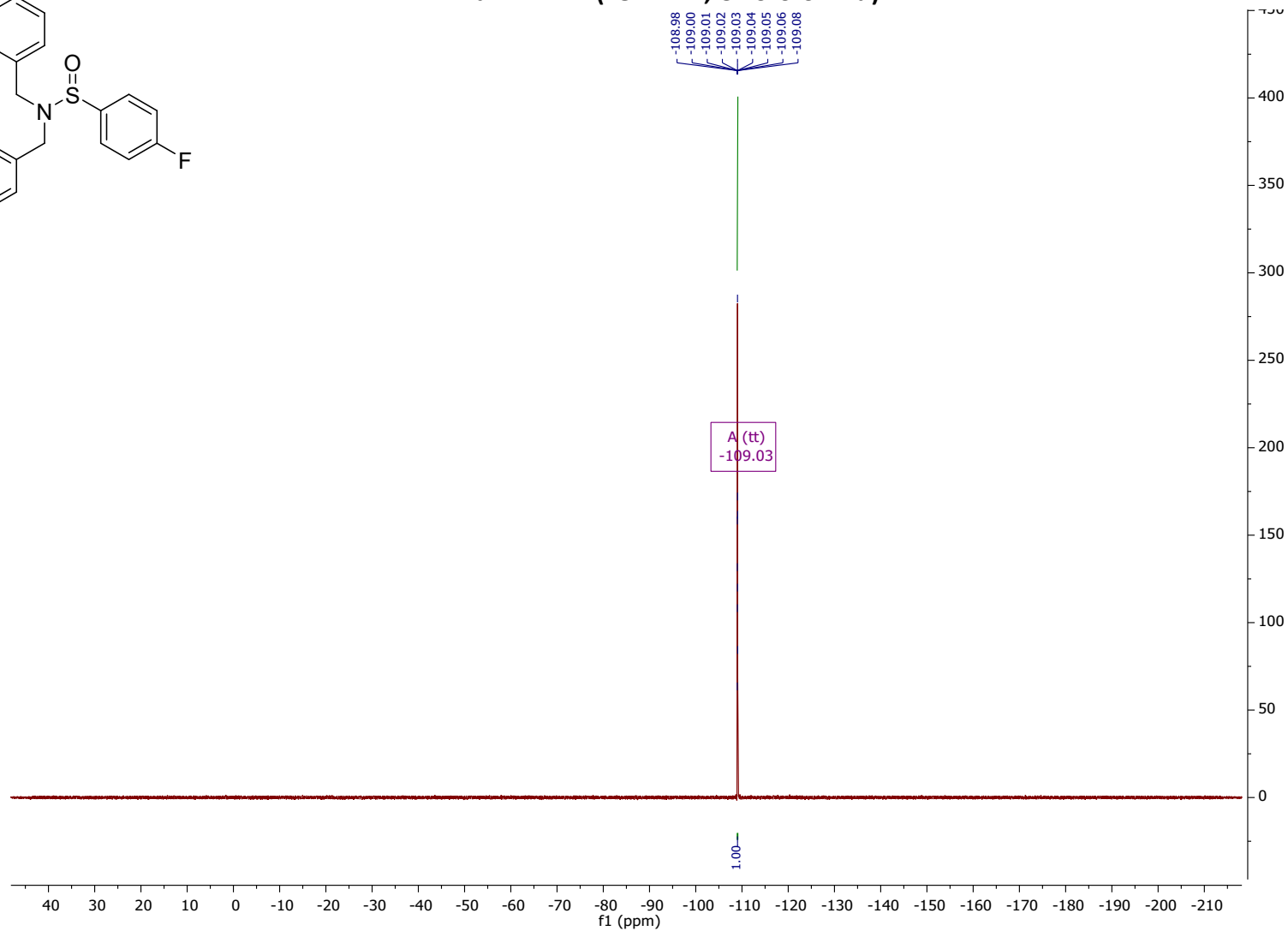
NMR Spectra

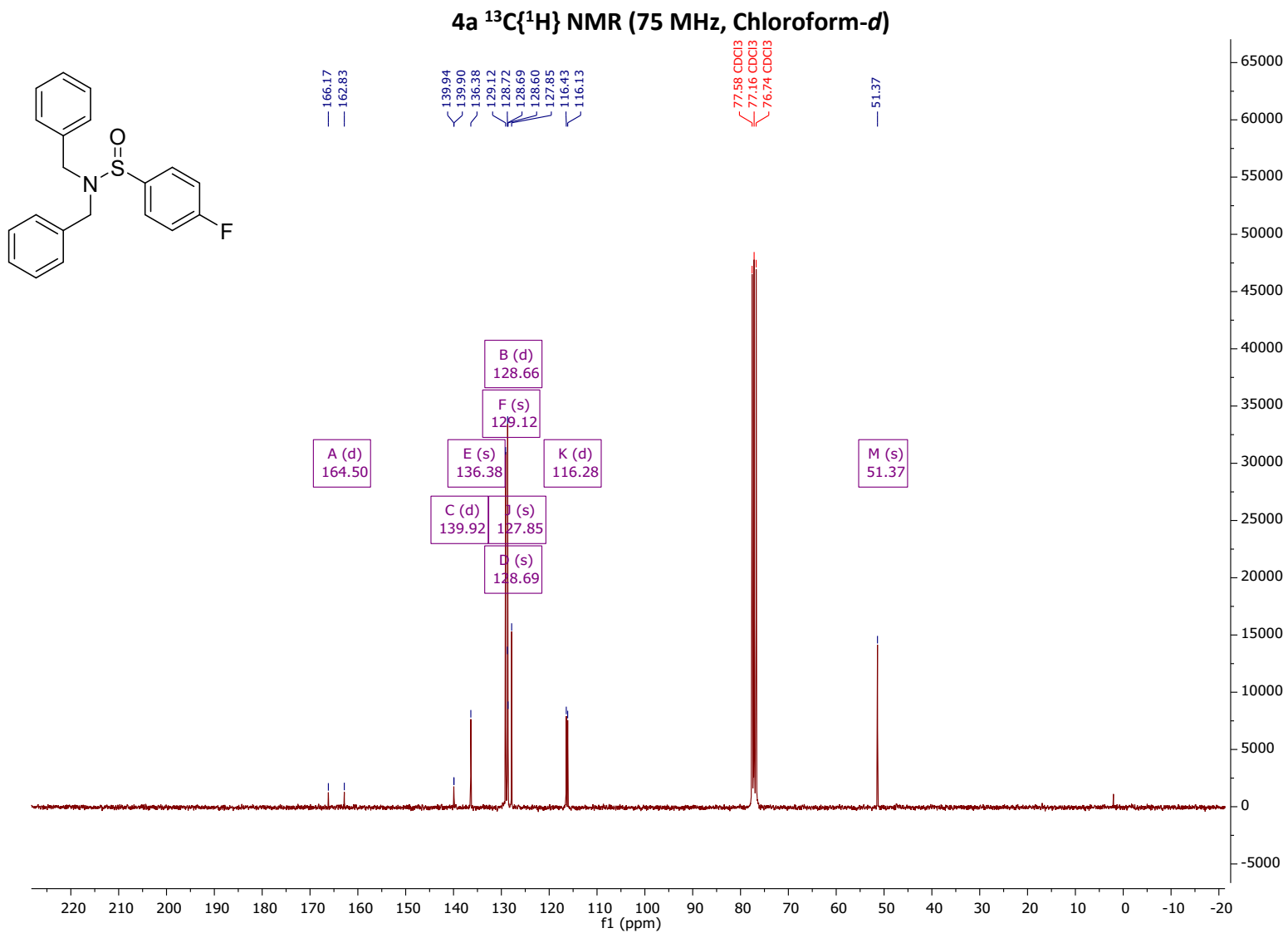
4a ¹H NMR (300 MHz, Chloroform-d)

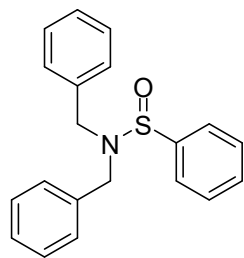




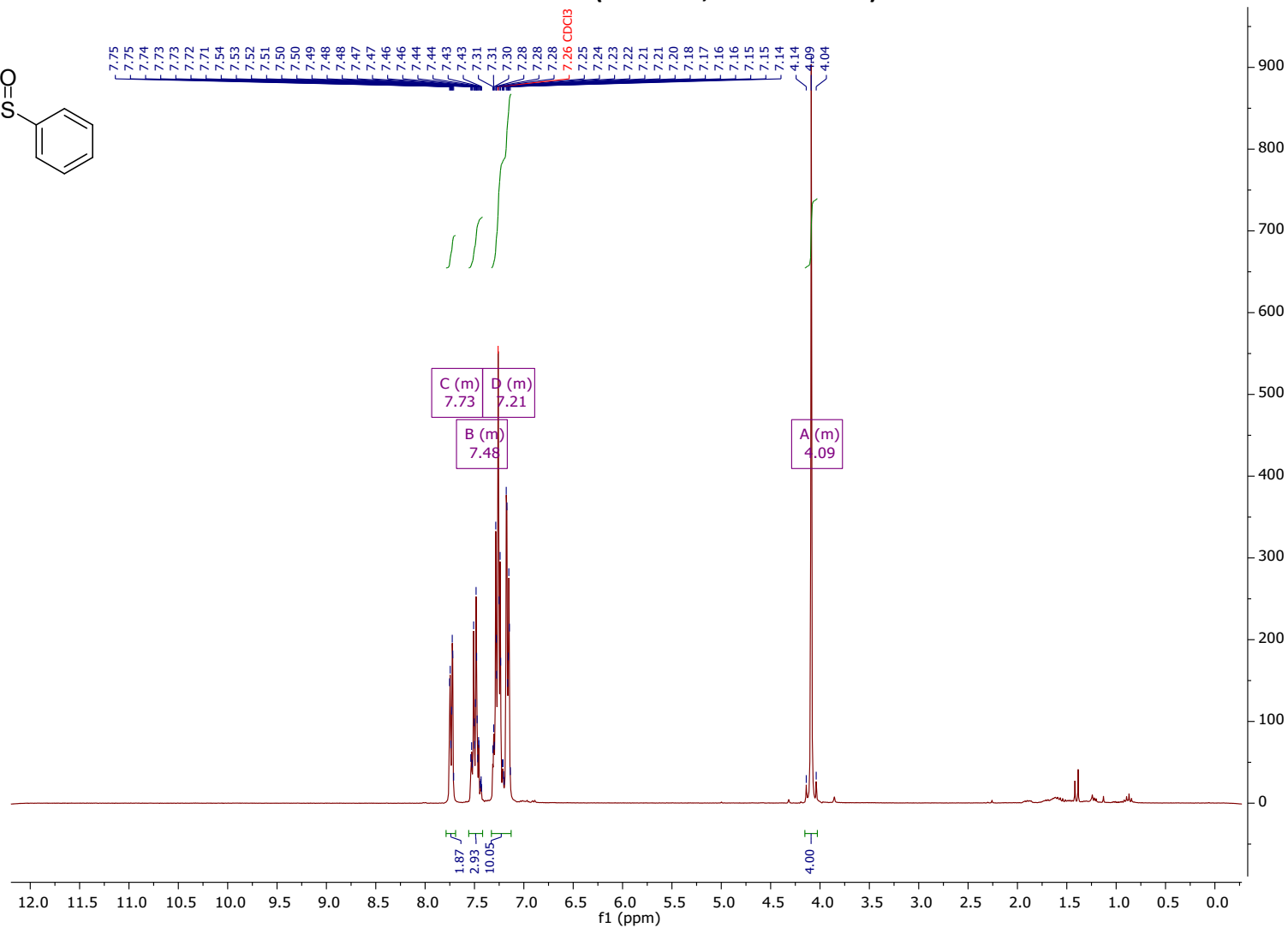
4a ¹⁹F NMR (282 MHz, Chloroform-d)



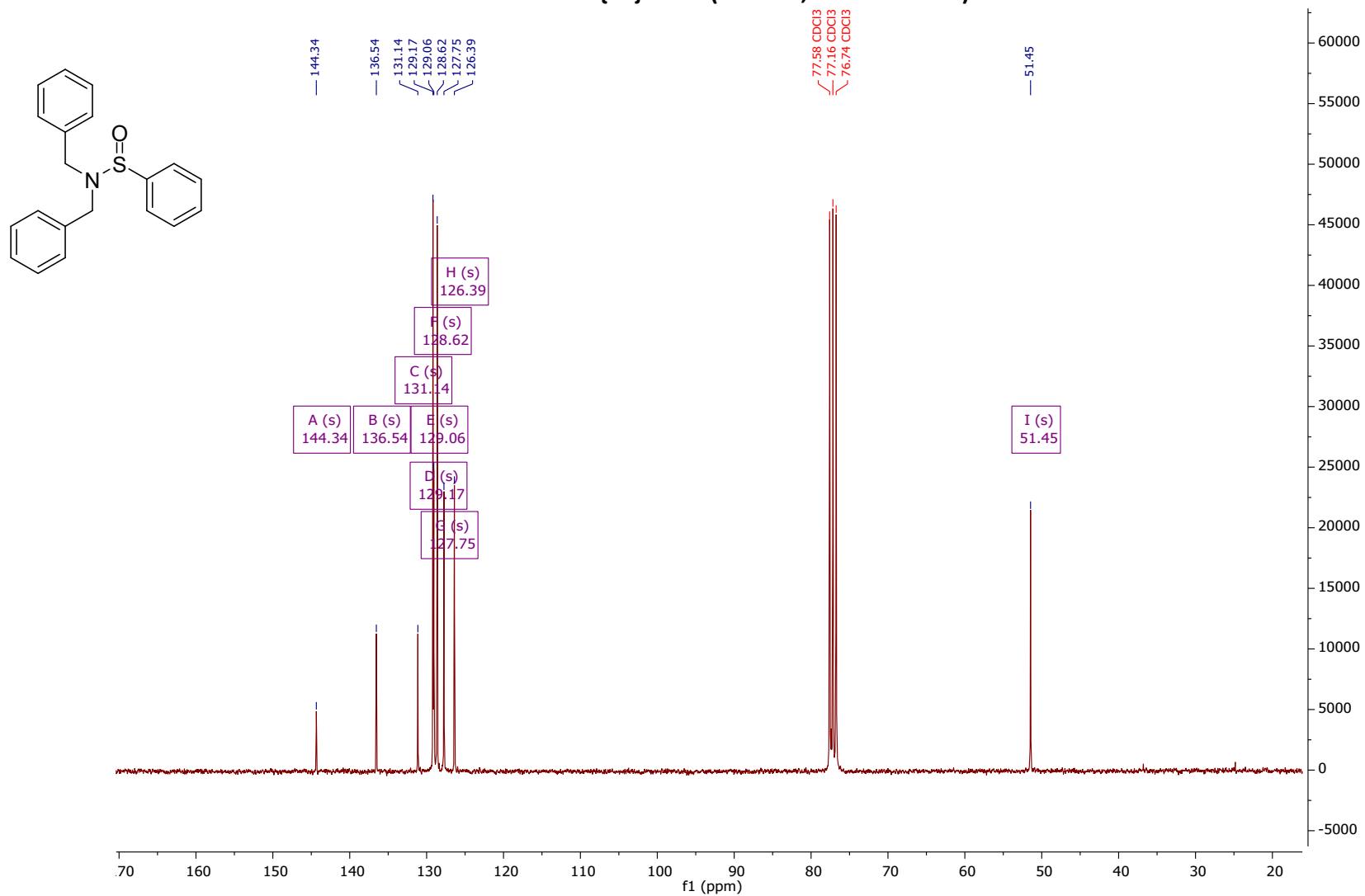




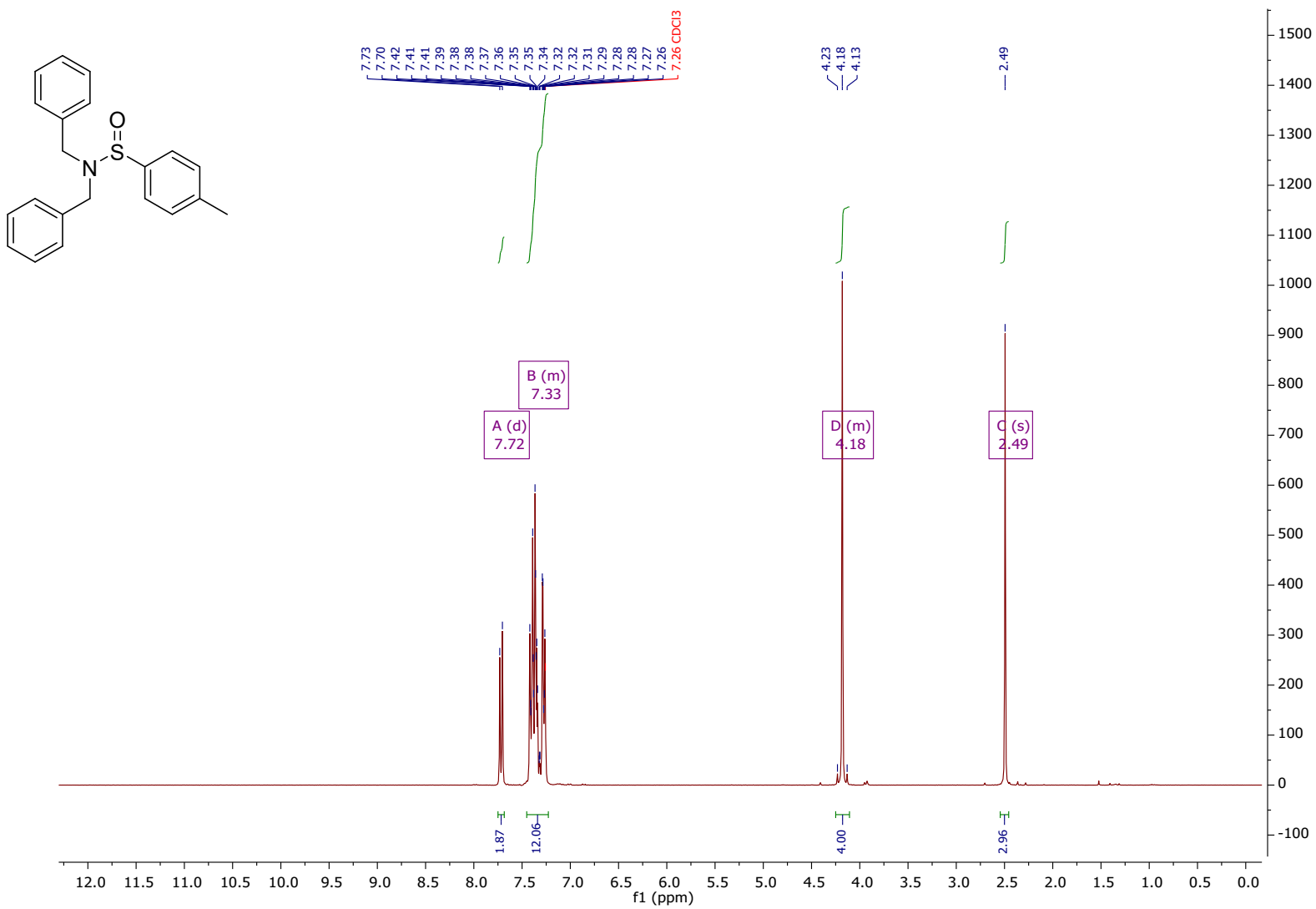
4b ¹H NMR (300 MHz, Chloroform-d)

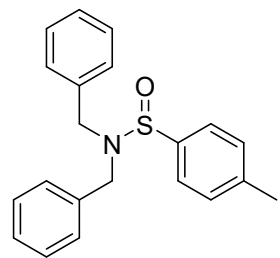


4b $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)

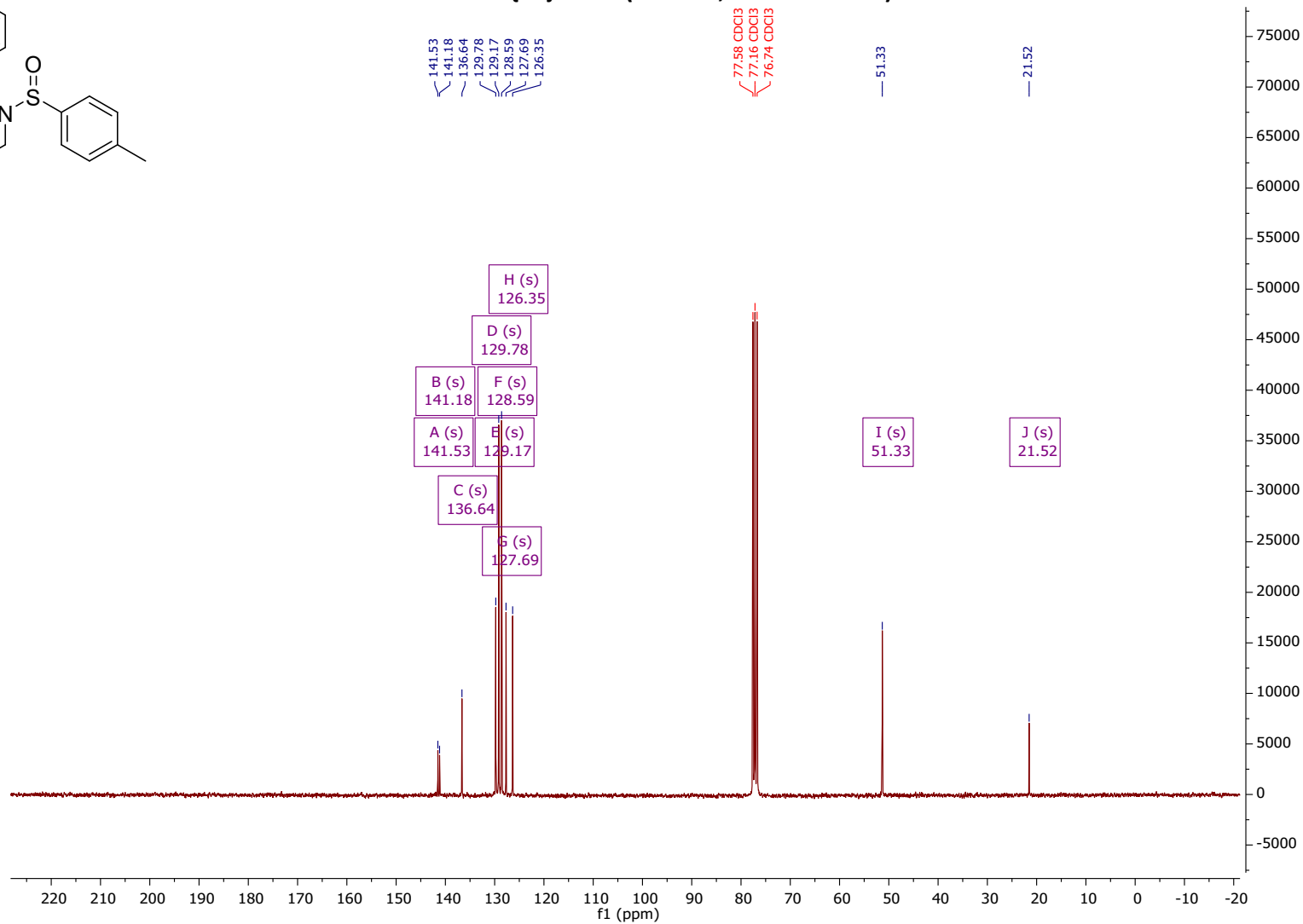


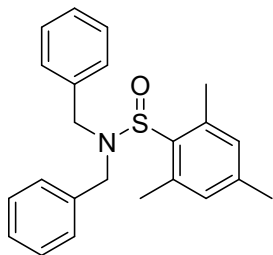
4c ¹H NMR (300 MHz, Chloroform-d)



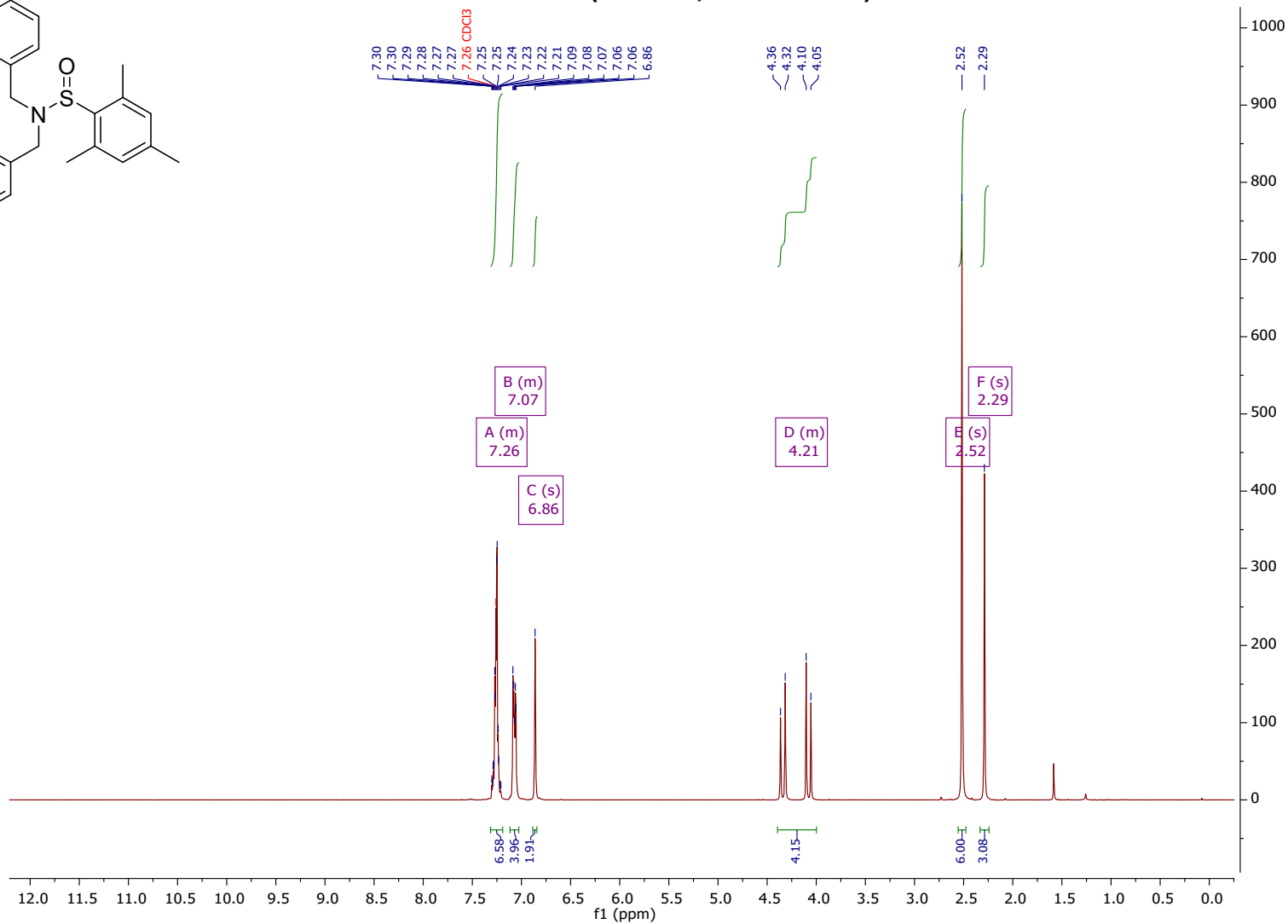


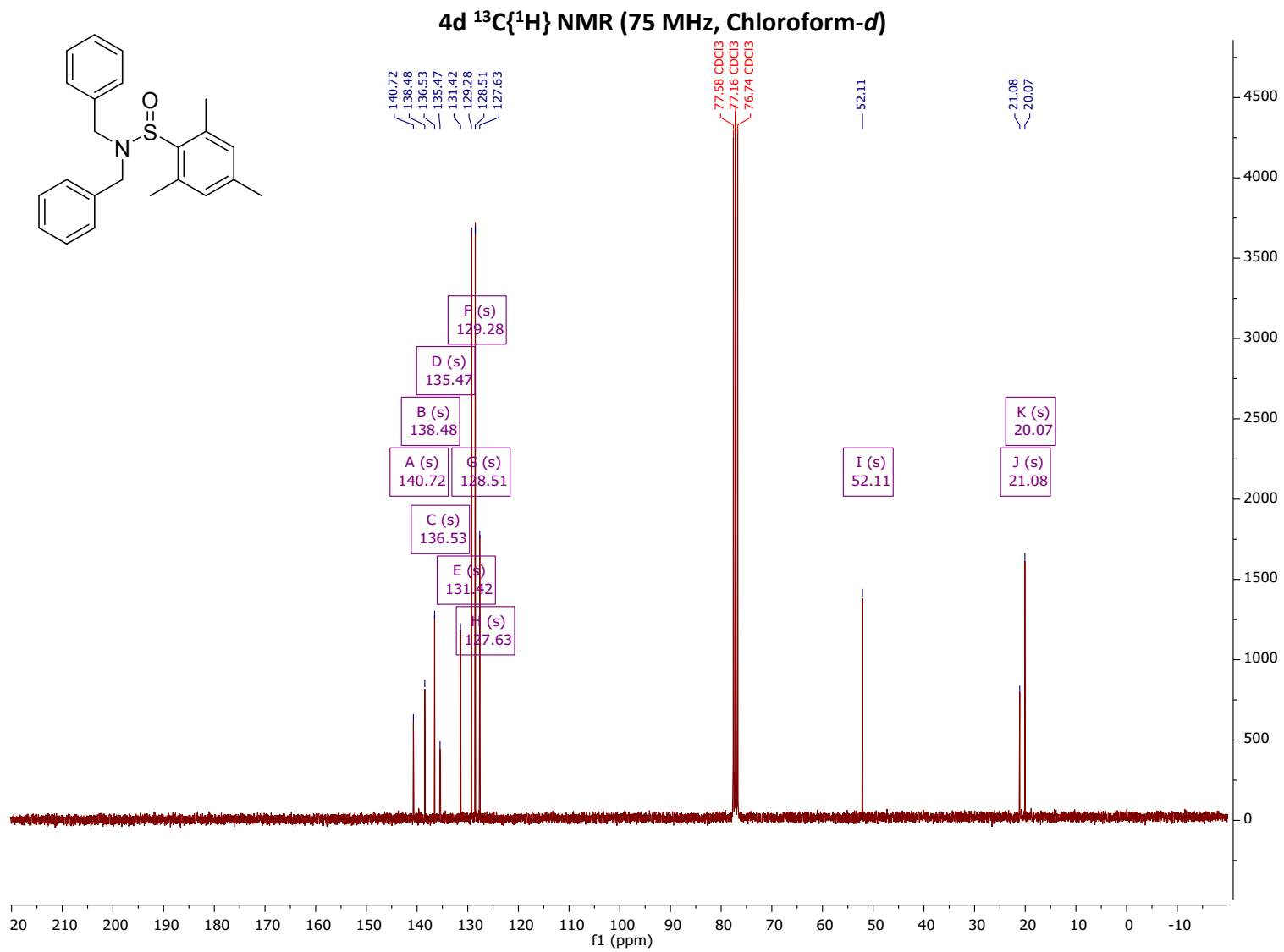
4c $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform- d)

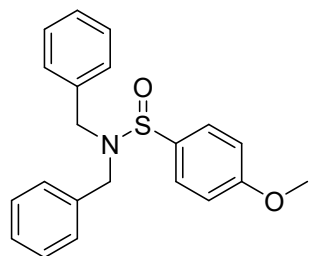




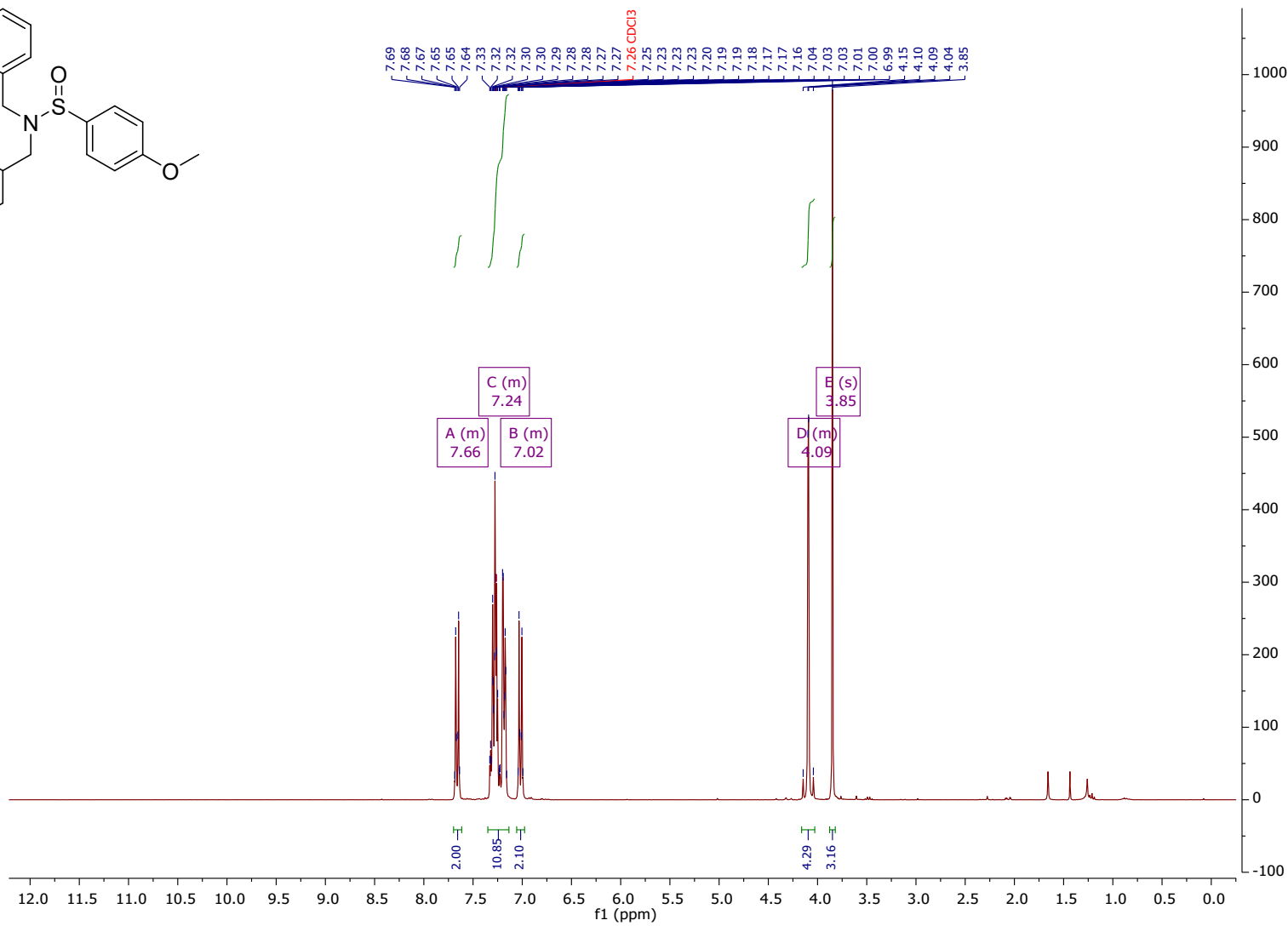
4d ¹H NMR (300 MHz, Chloroform-d)



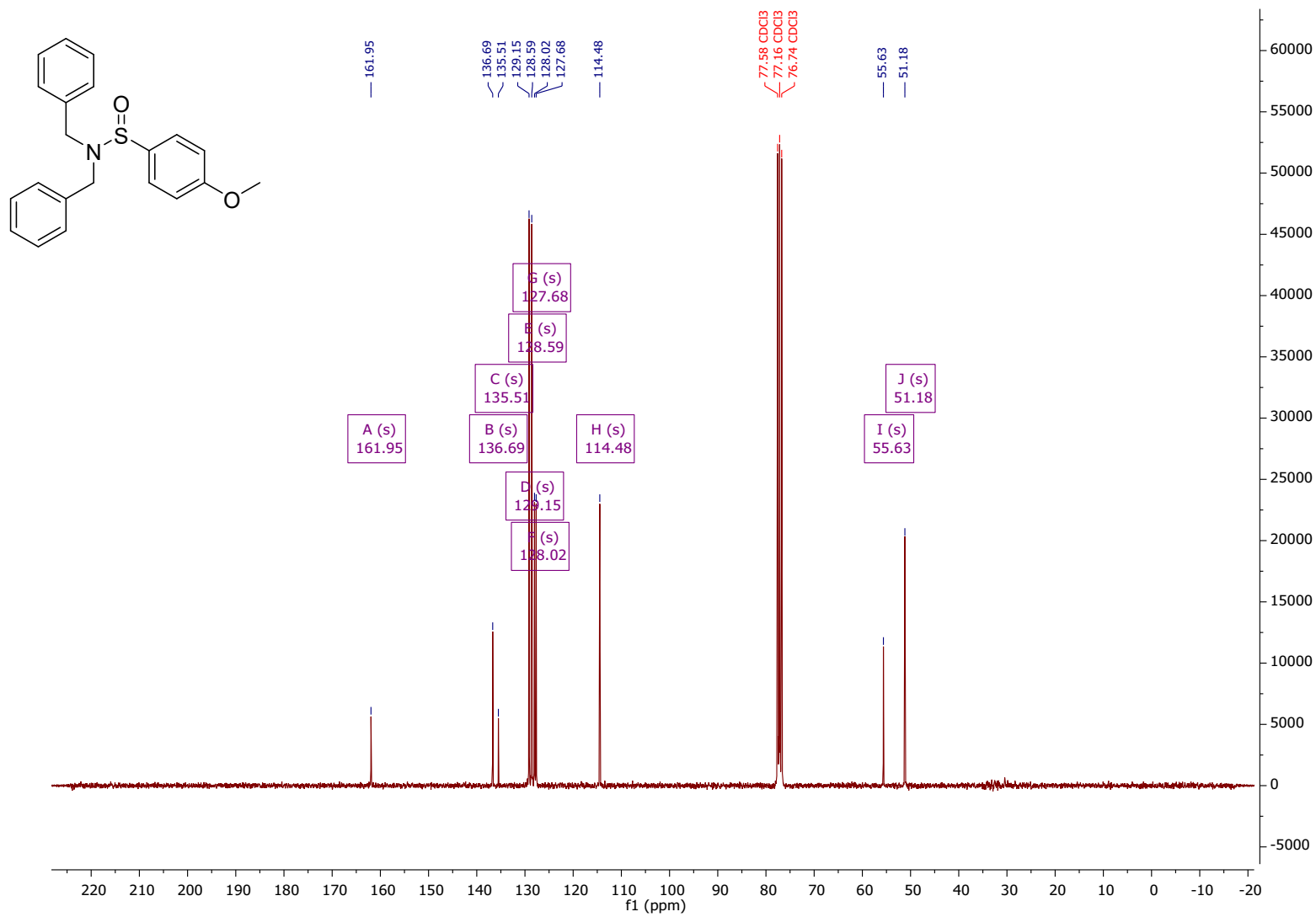


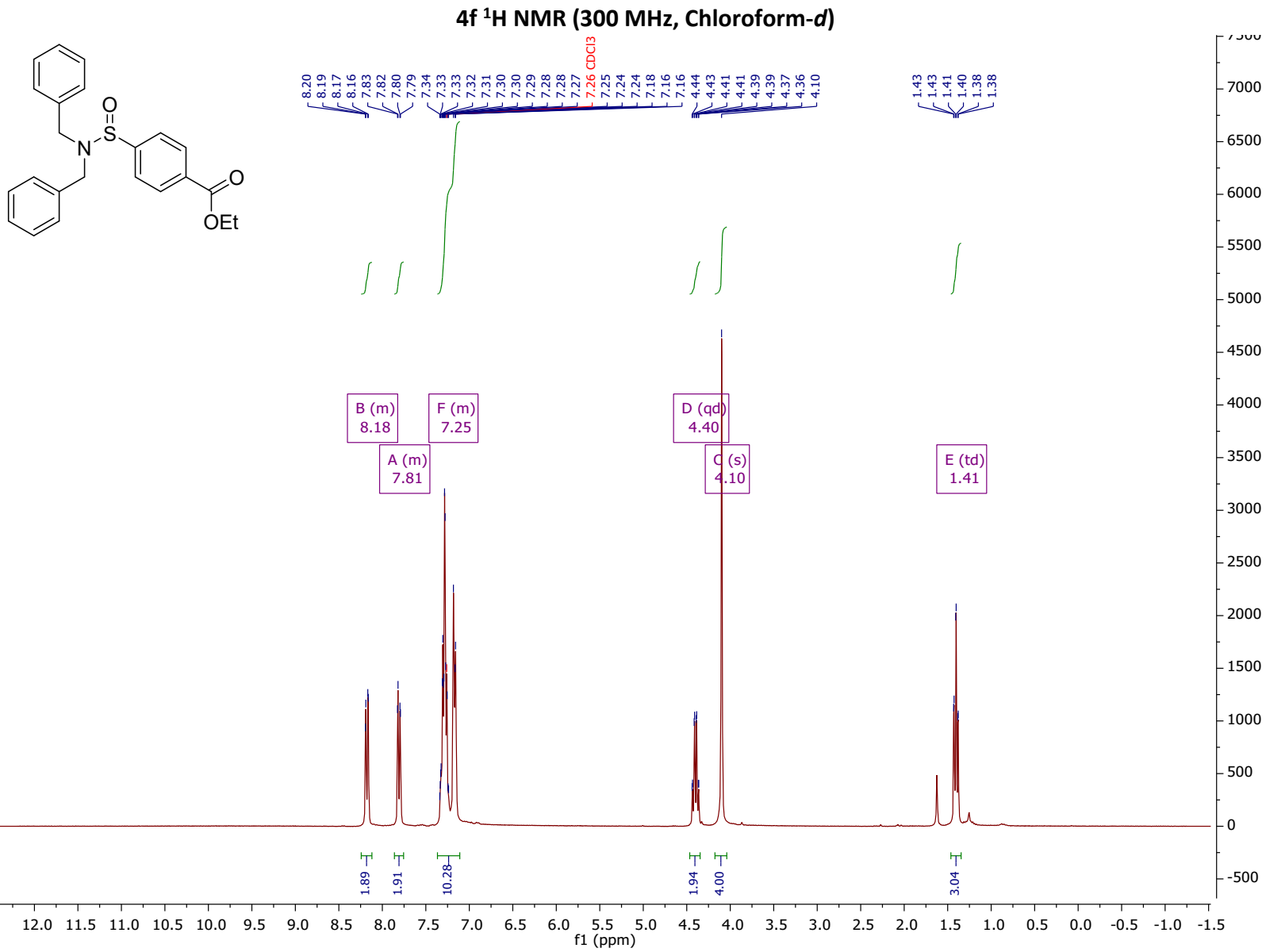


4e ¹H NMR (300 MHz, Chloroform-d)

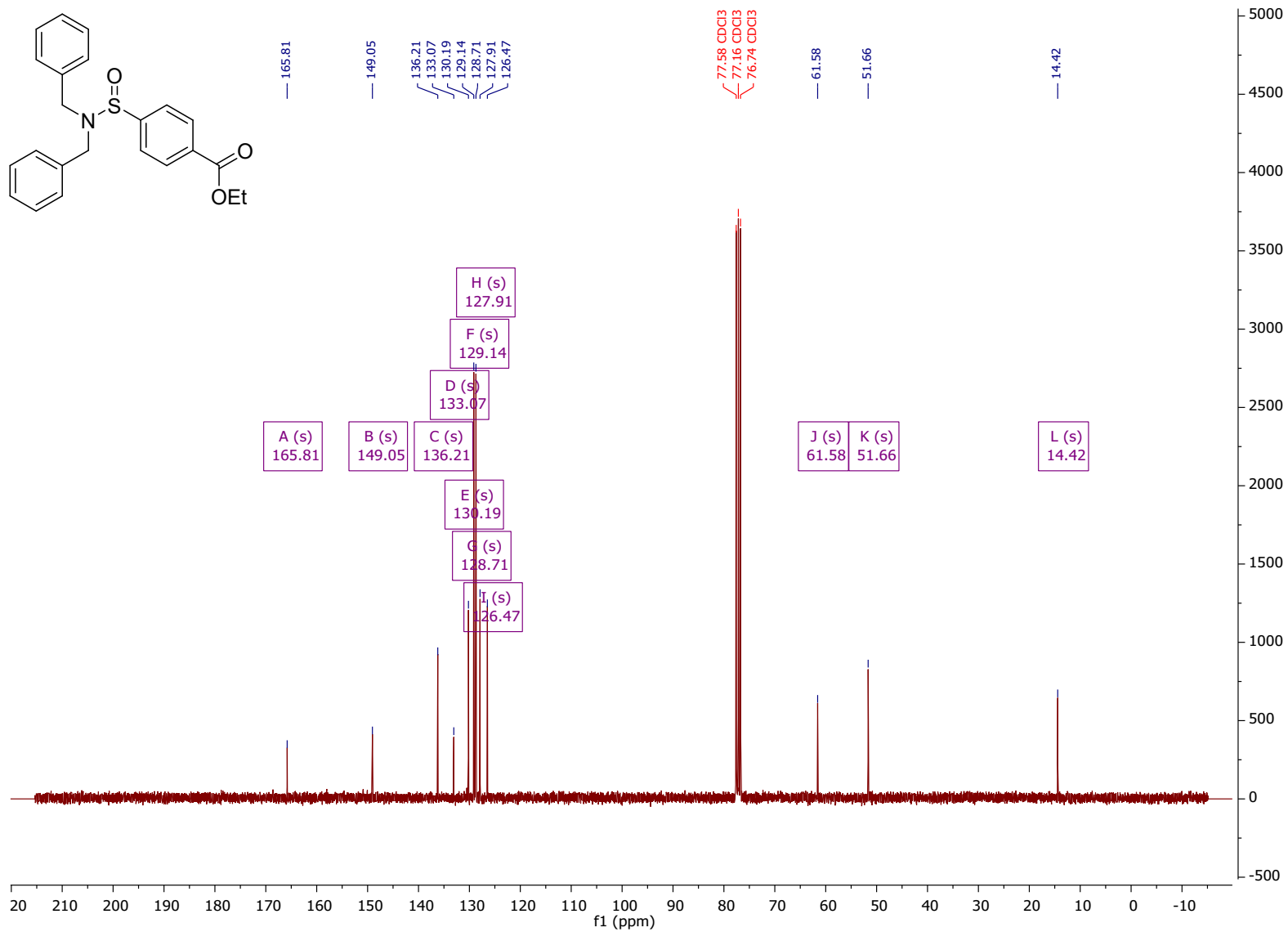


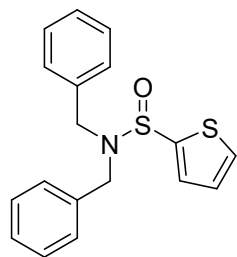
4e $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)



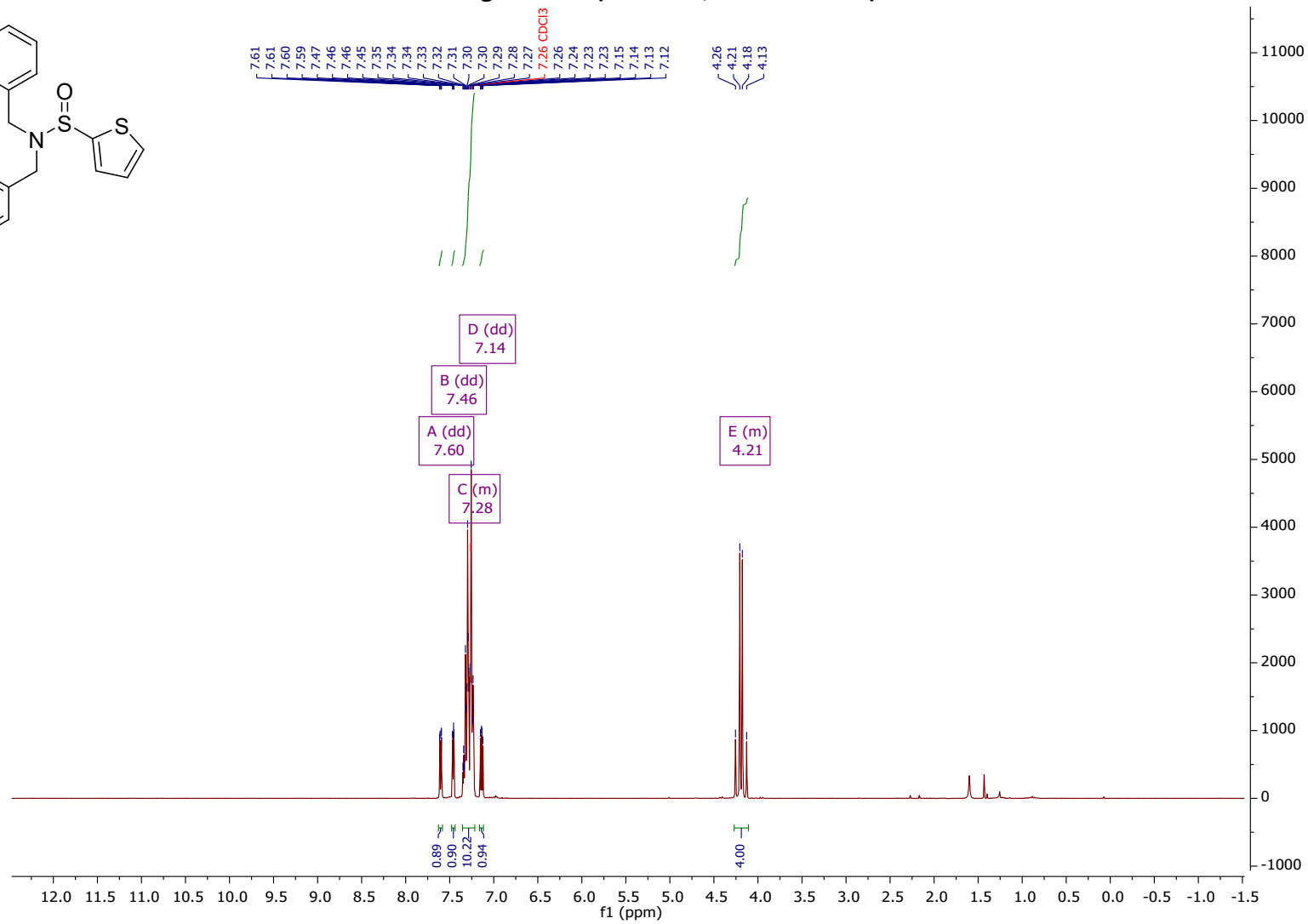


4f ¹³C{¹H} NMR (75 MHz, Chloroform-d)

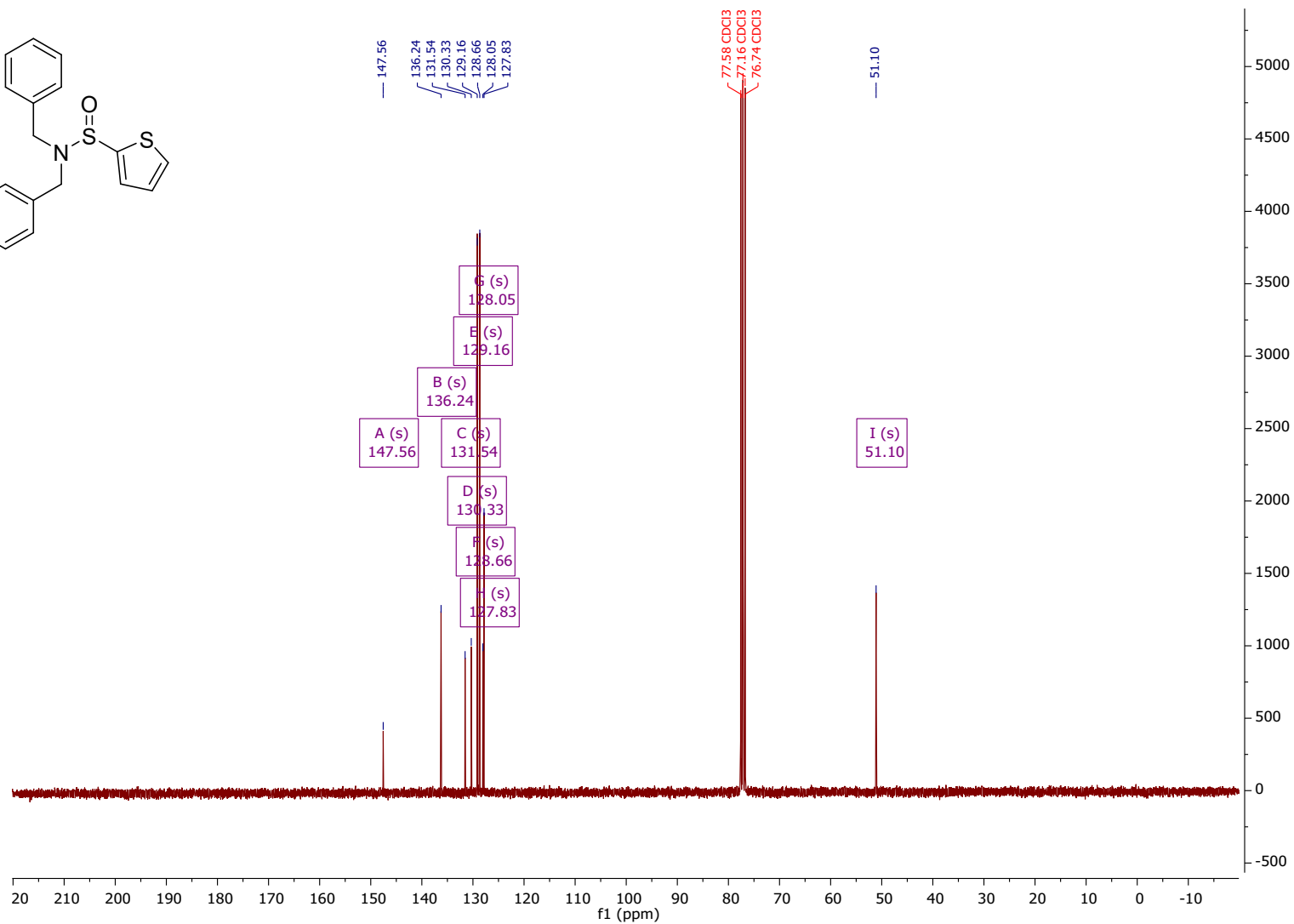
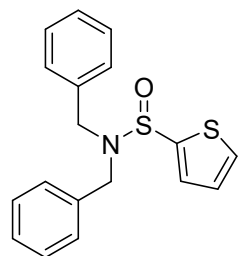


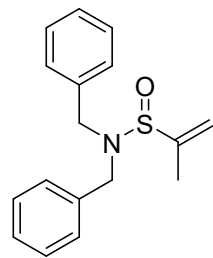


4g ¹H NMR (300 MHz, Chloroform-*d*)

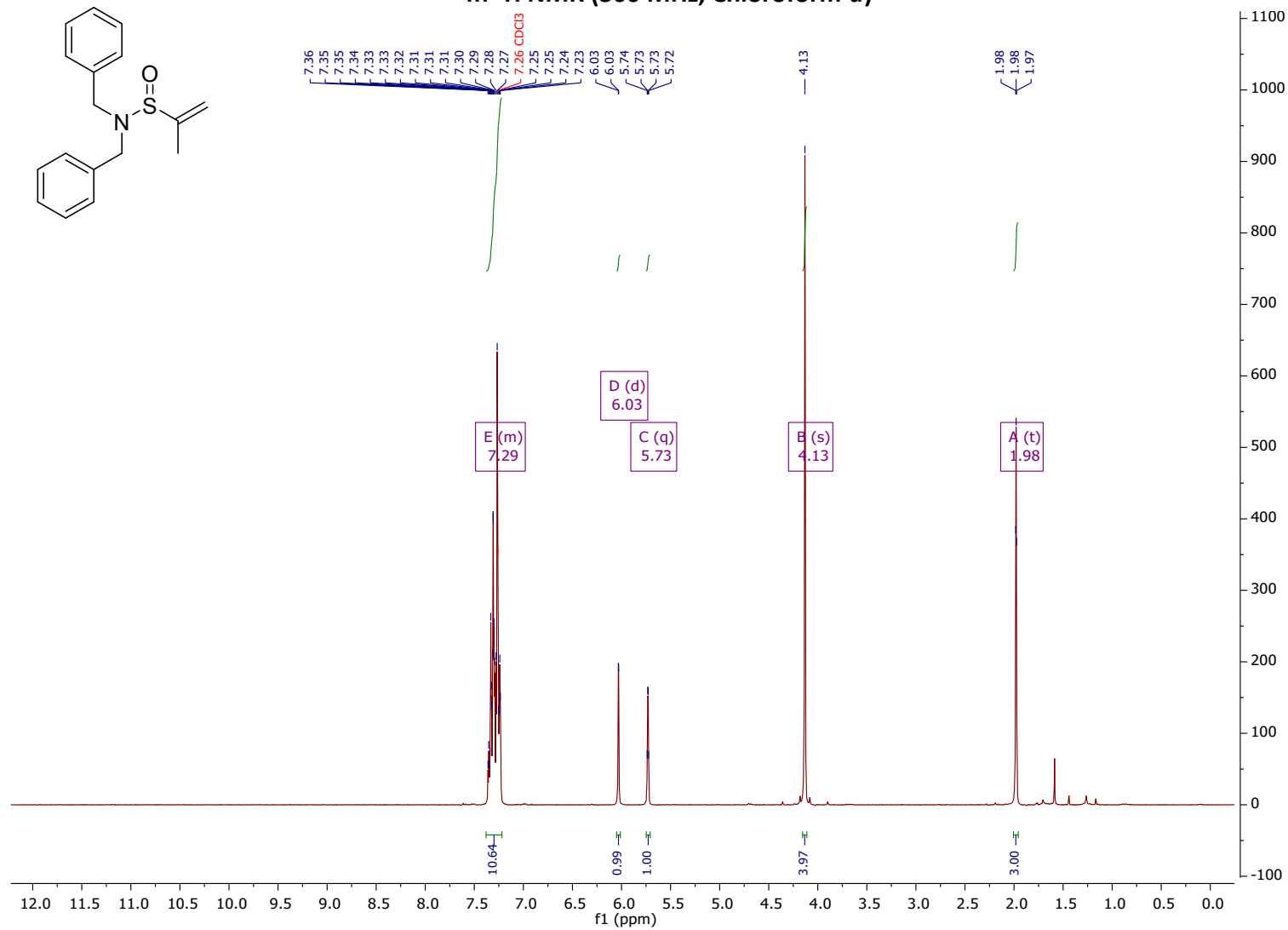


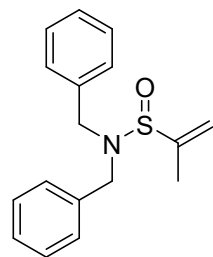
4g $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)



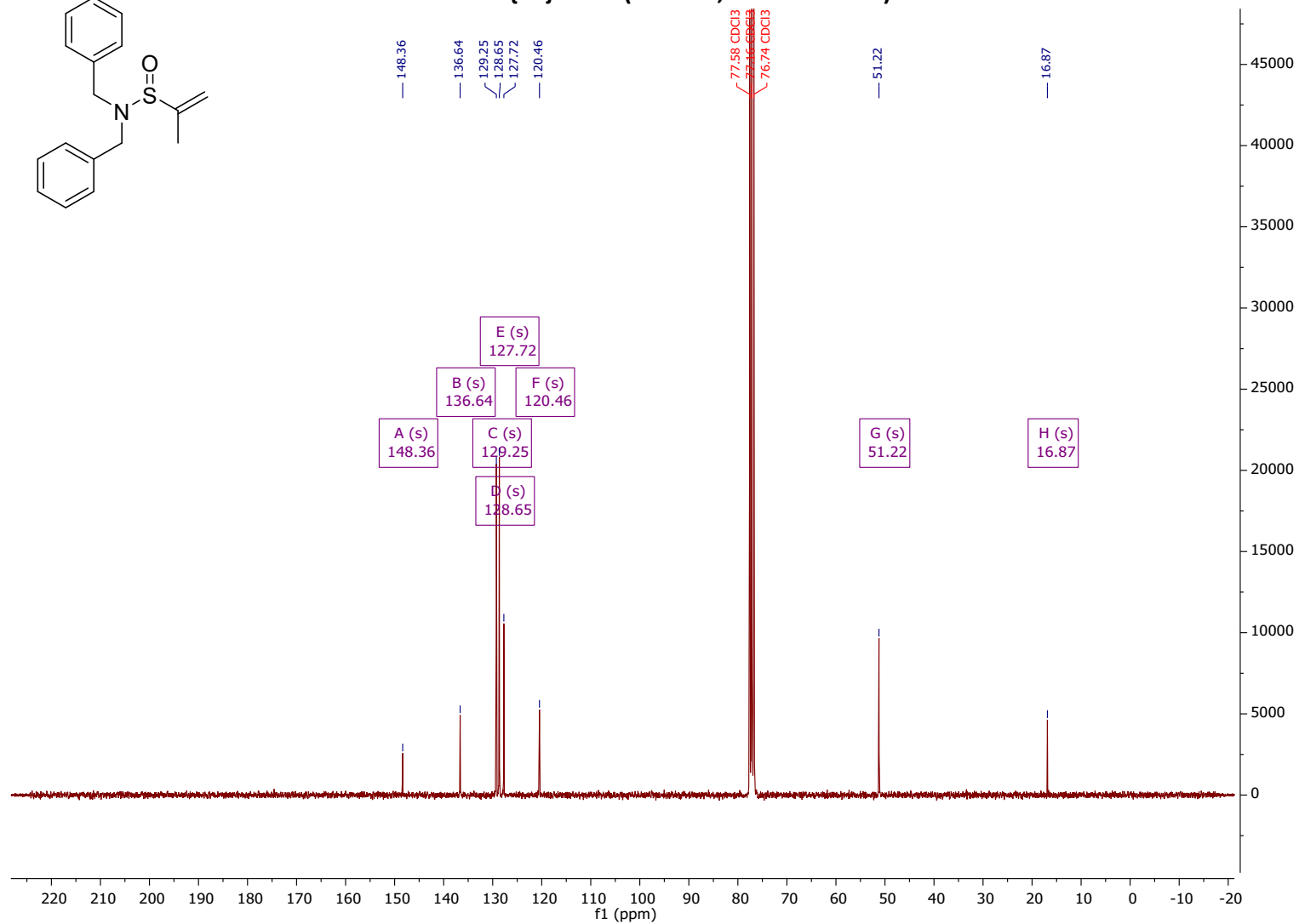


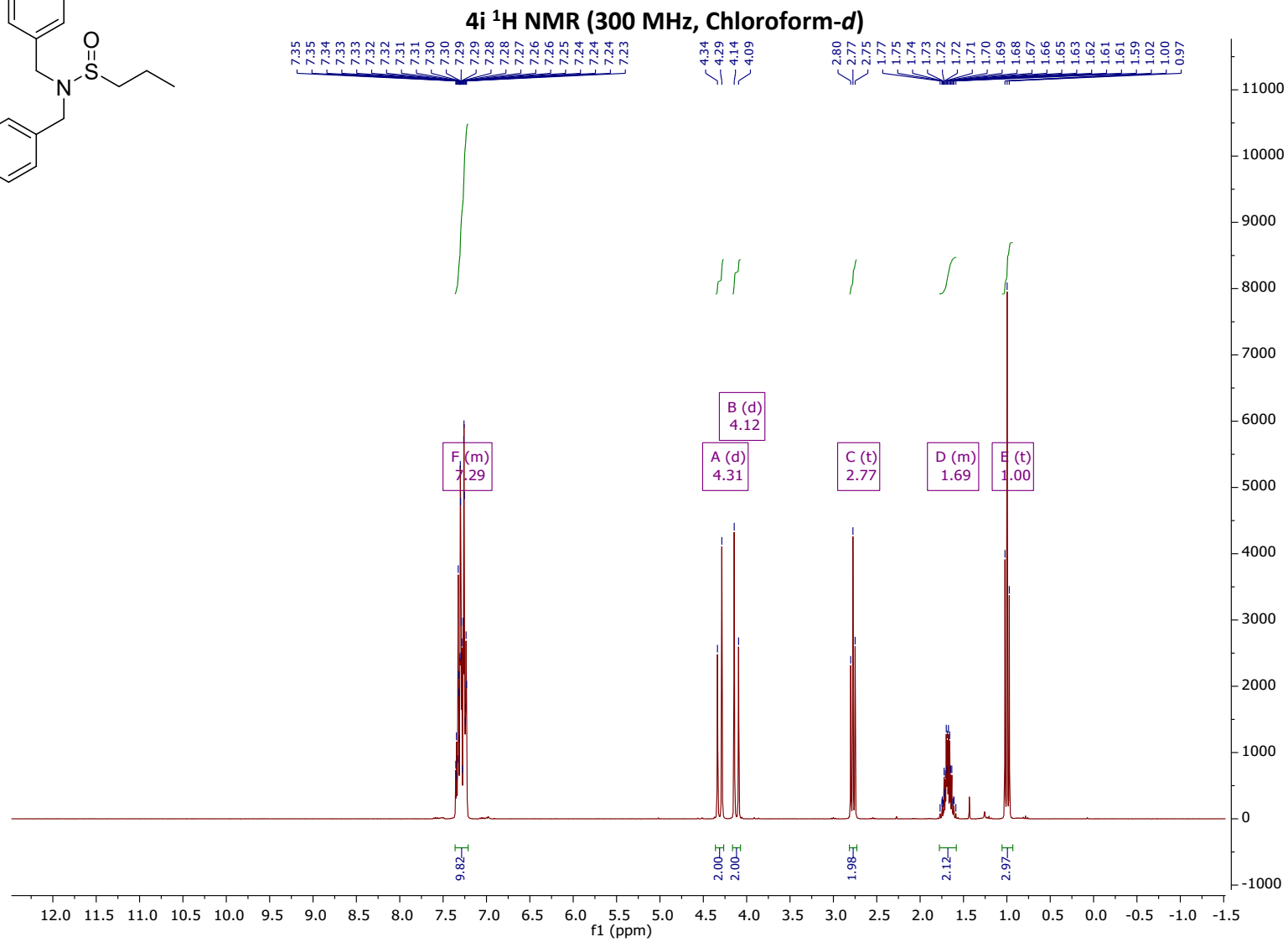
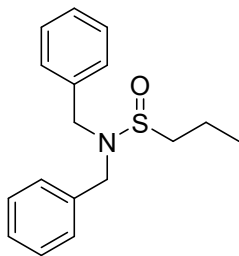
4h ¹H NMR (300 MHz, Chloroform-d)



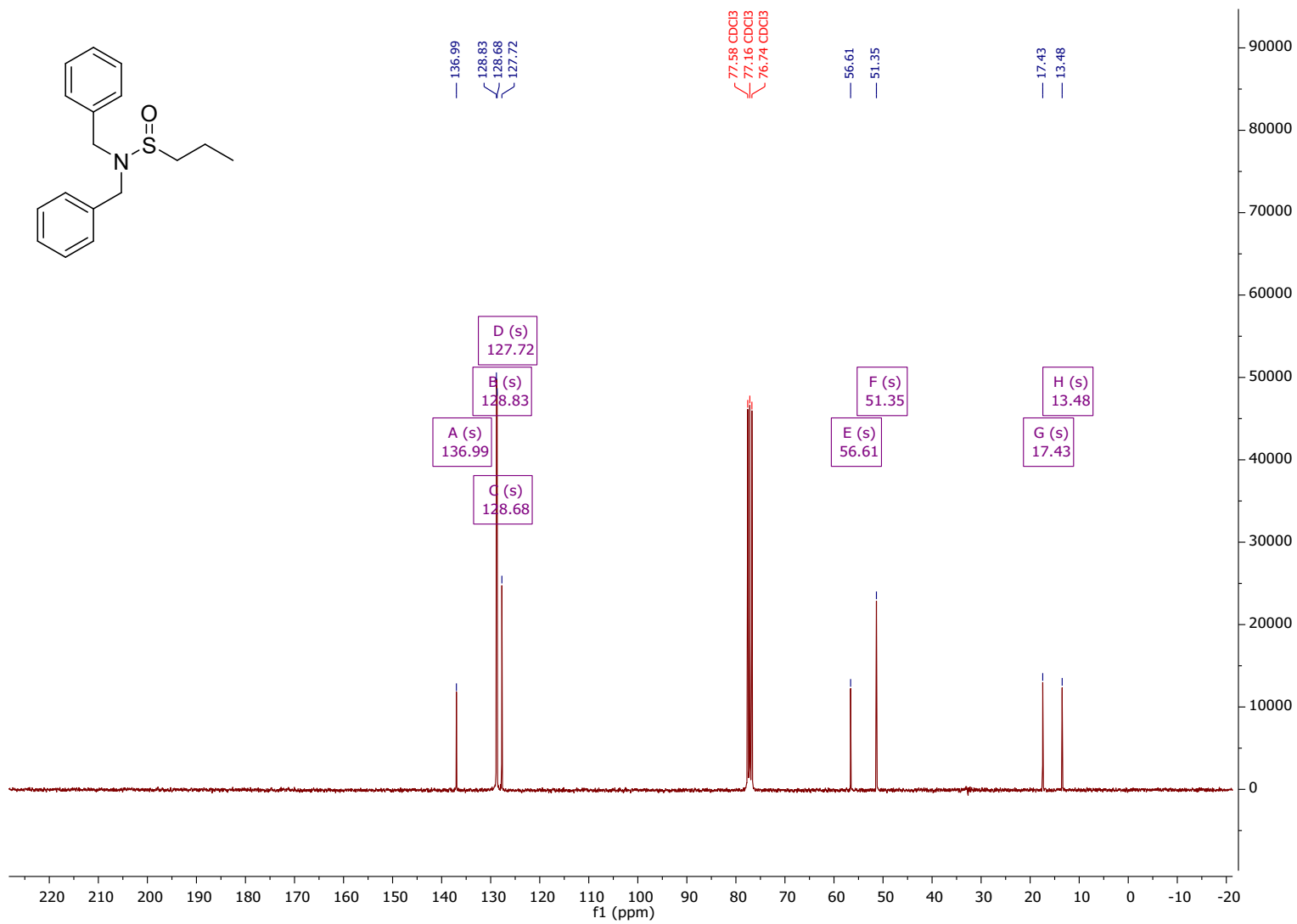


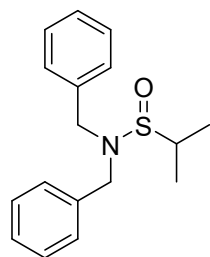
4h $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)



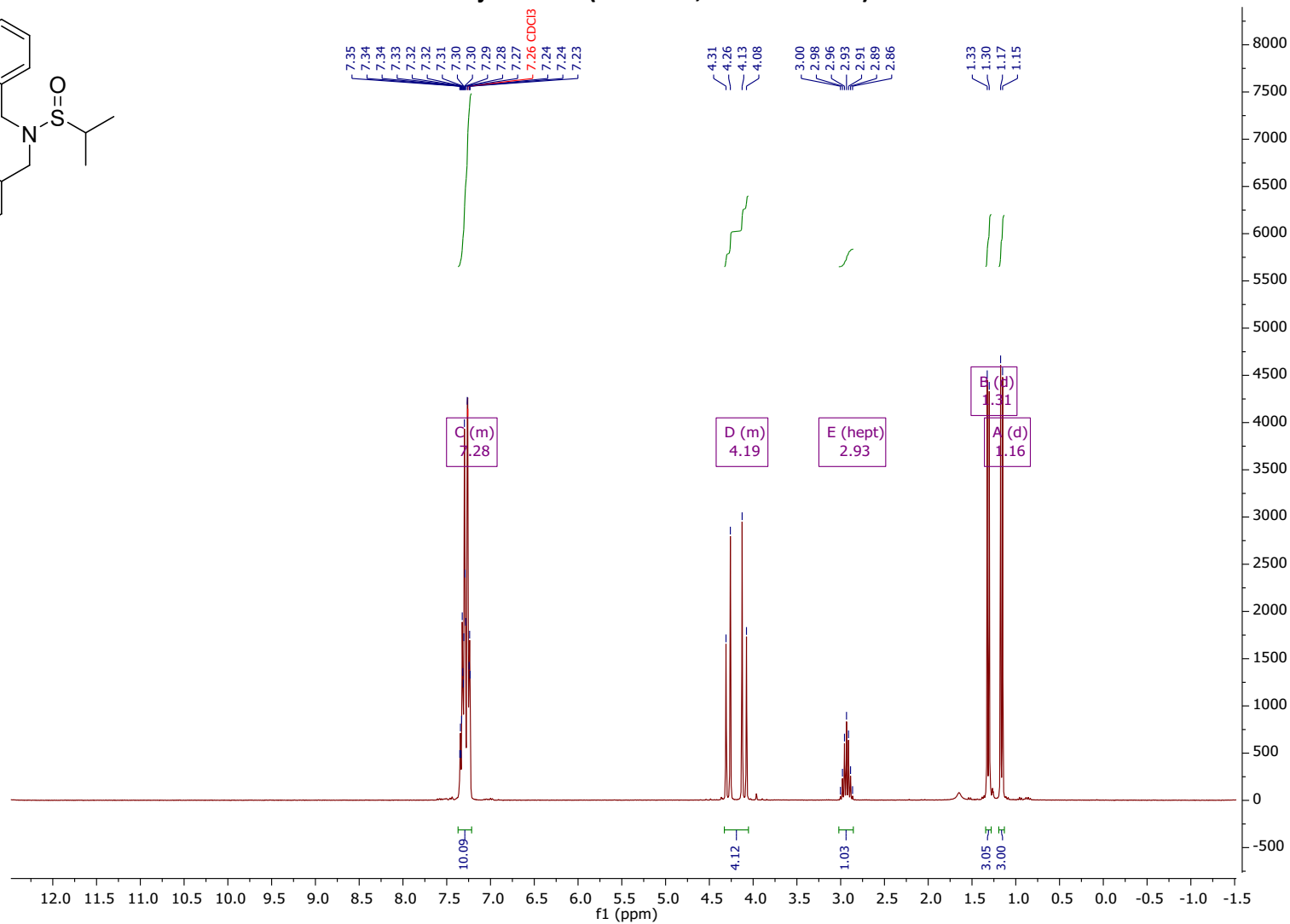


4i ¹³C{¹H} NMR (75 MHz, Chloroform-*d*)

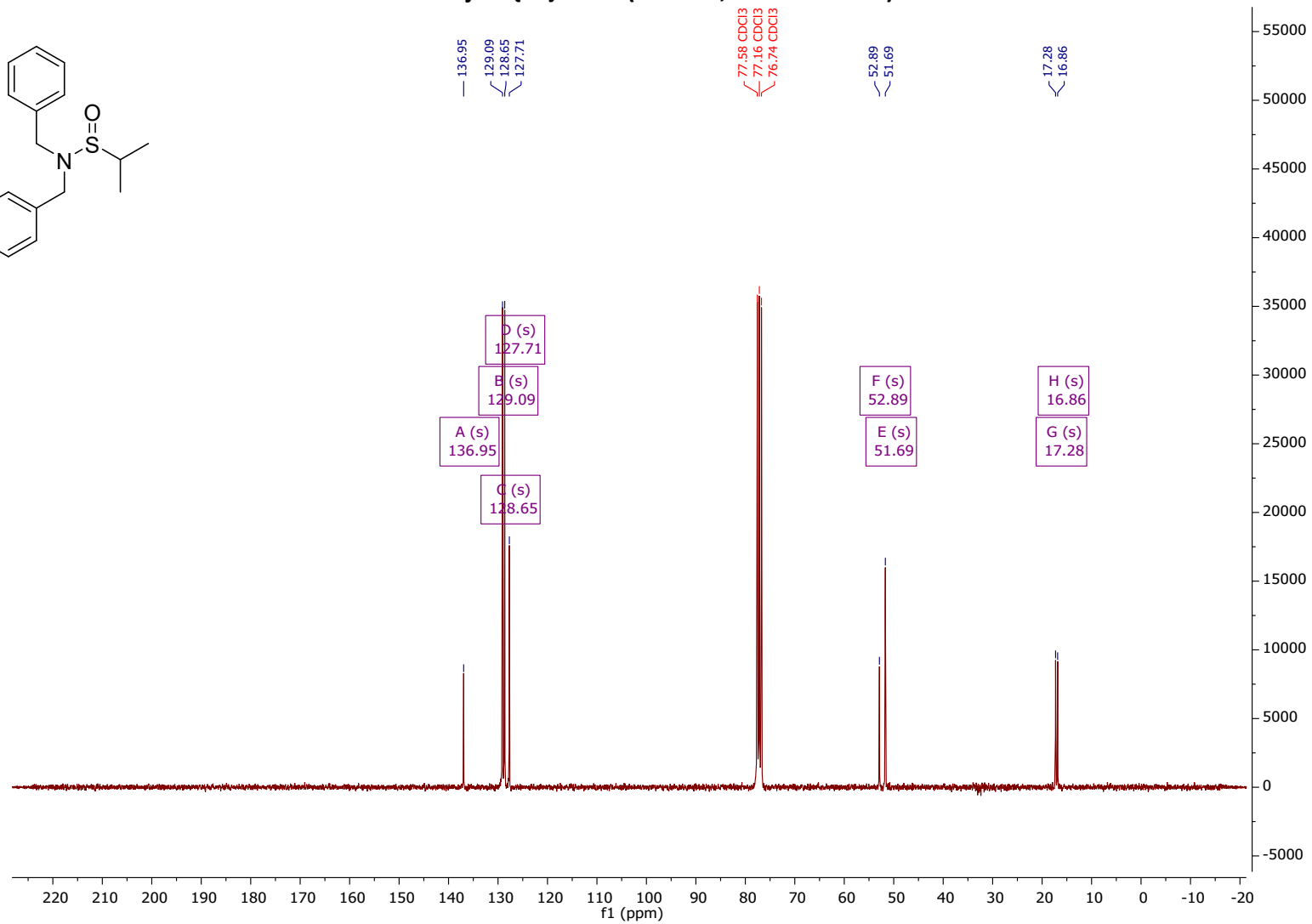
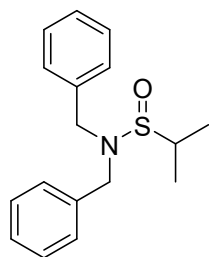


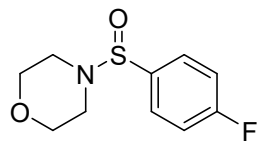


4j ¹H NMR (300 MHz, Chloroform-d)

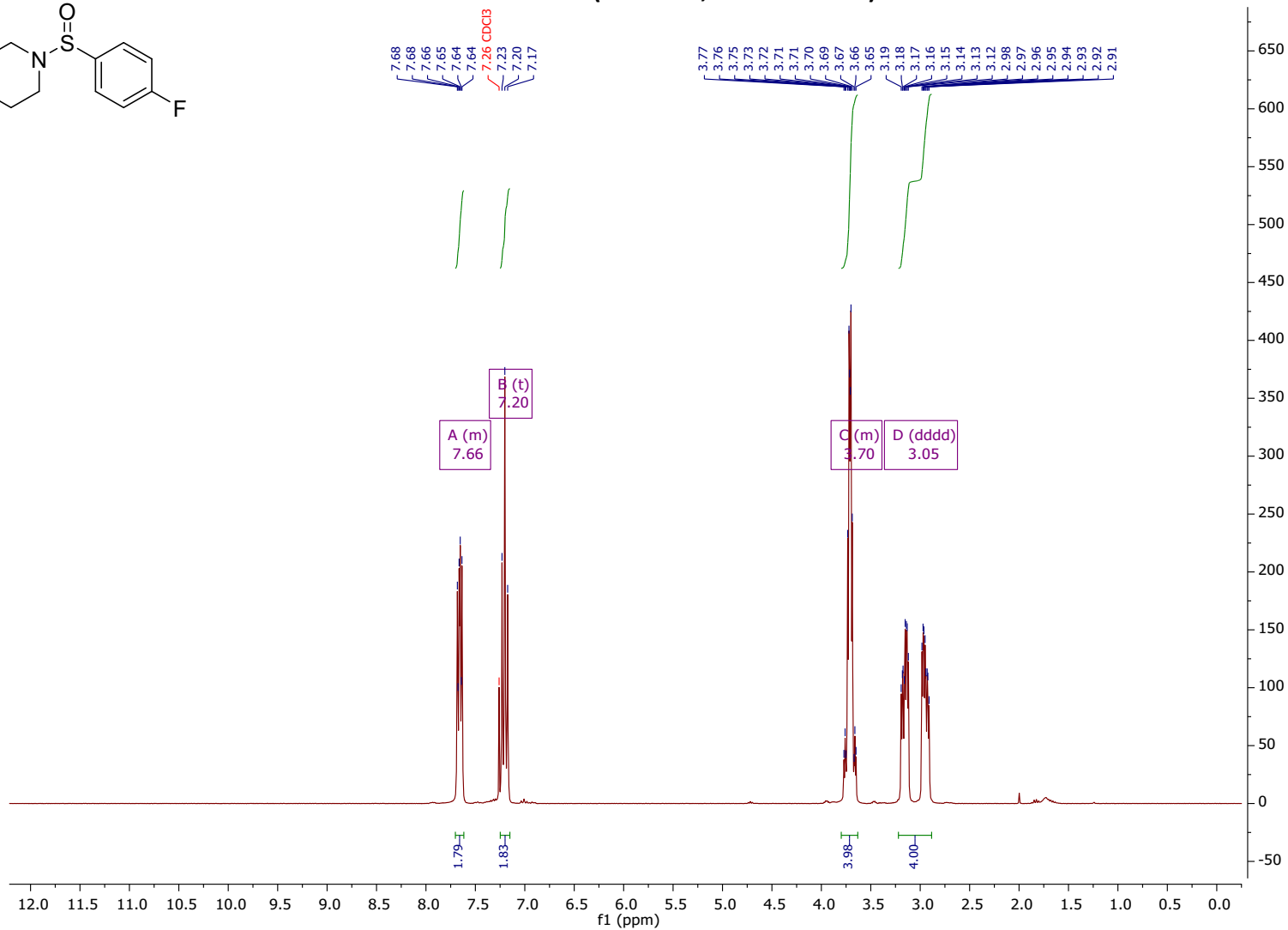


4j ¹³C{¹H} NMR (75 MHz, Chloroform-d)

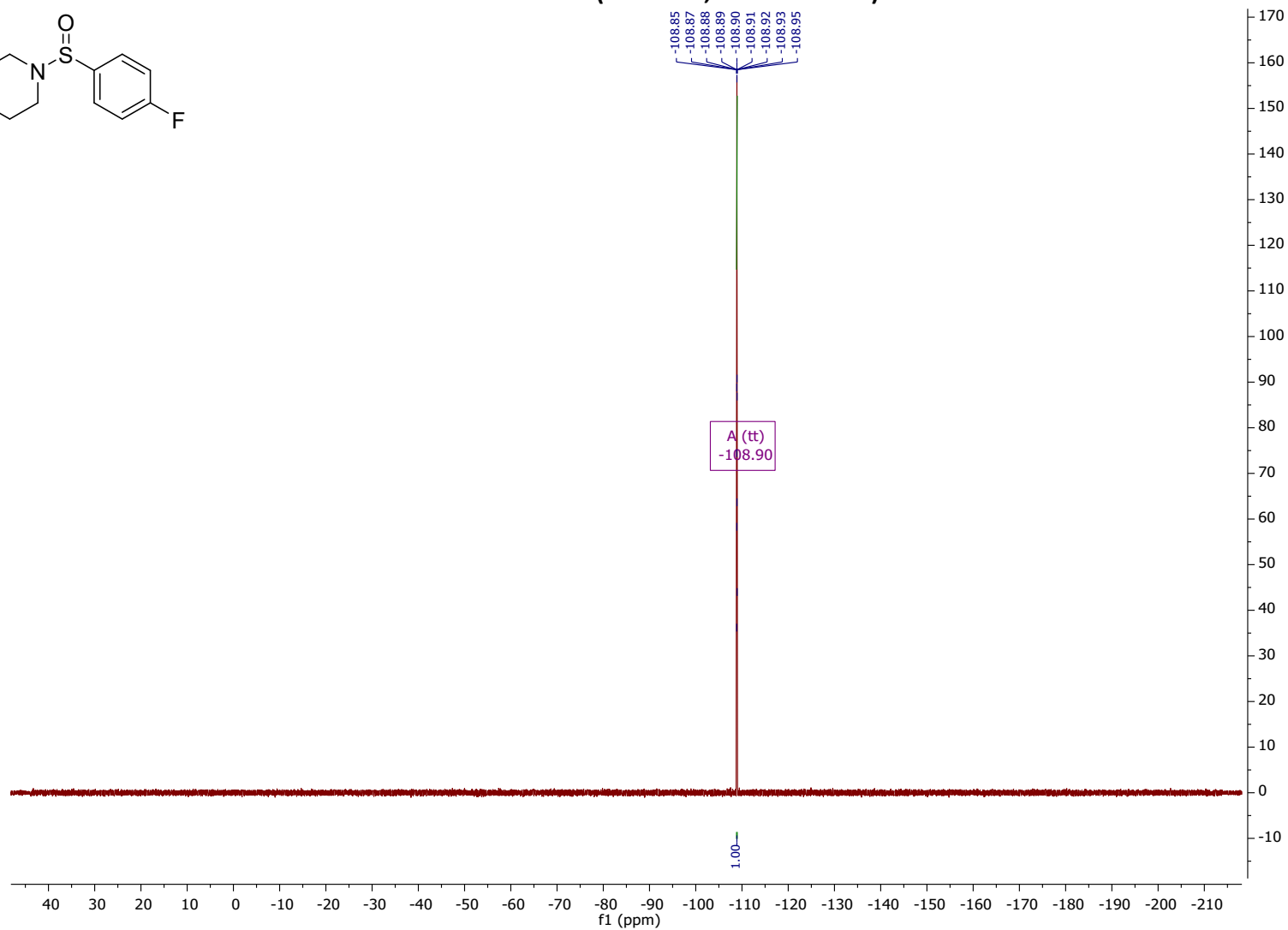
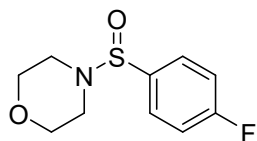




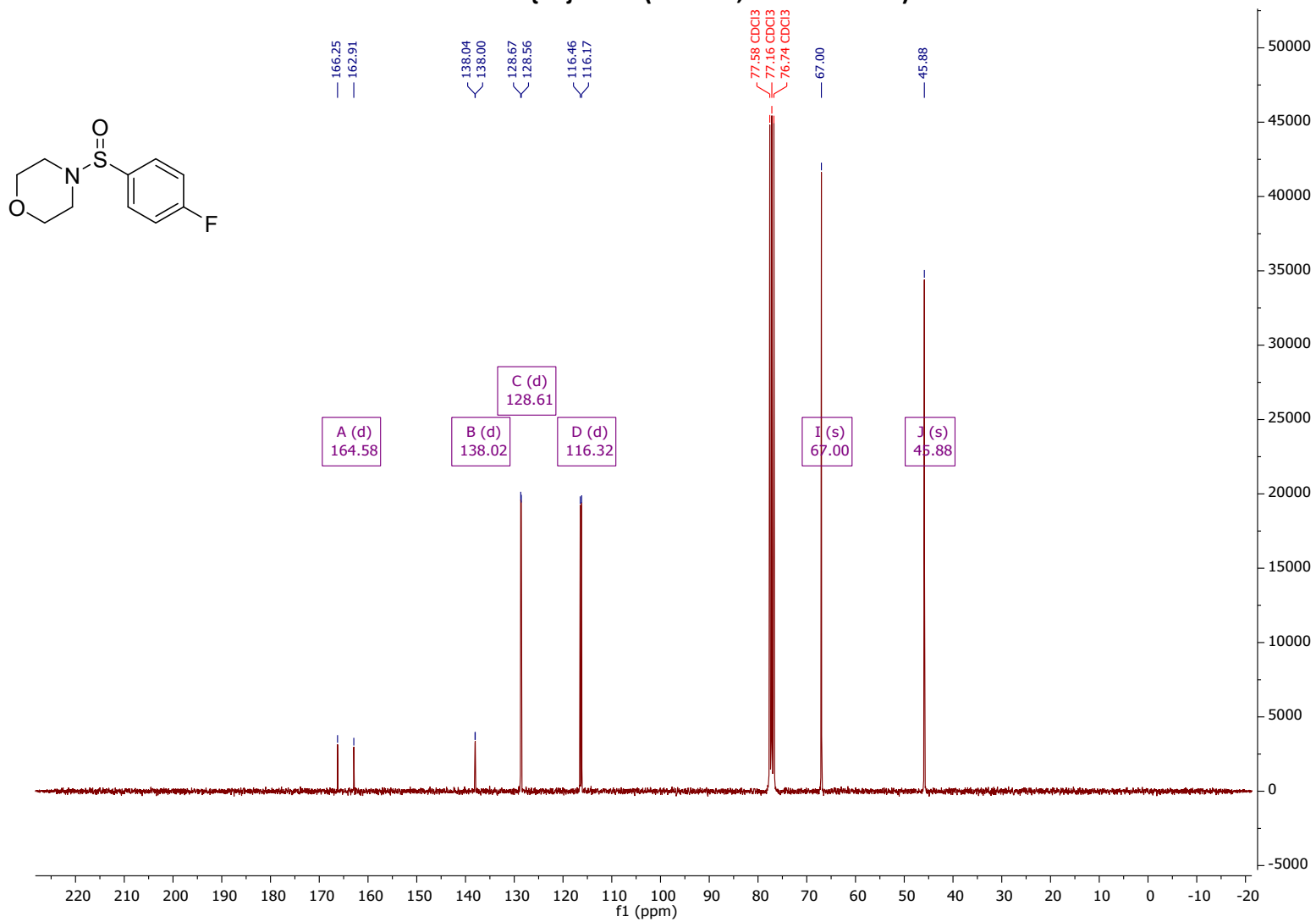
4k ¹H NMR (300 MHz, Chloroform-d)

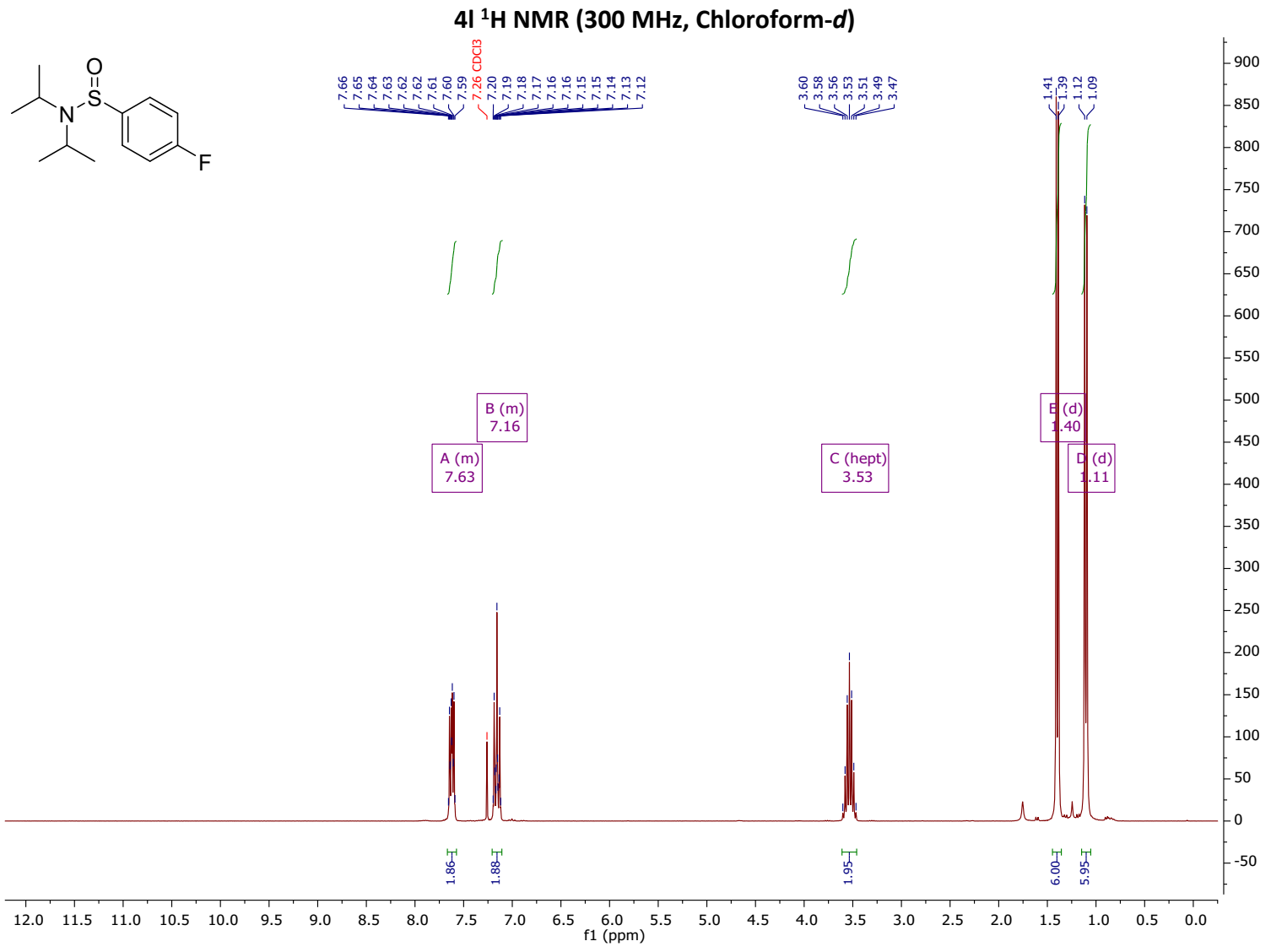


4k ¹⁹F NMR (282 MHz, Chloroform-d)

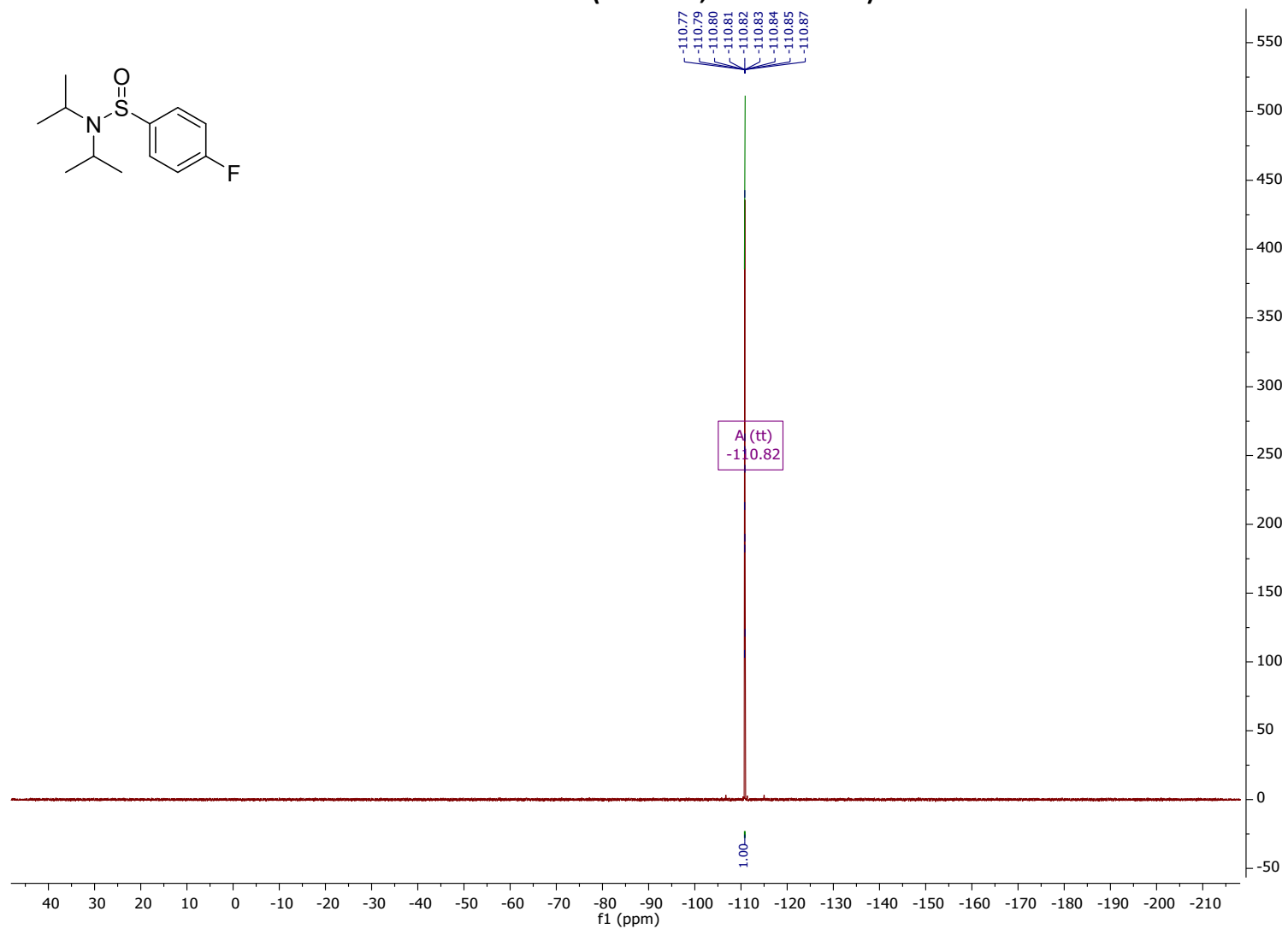


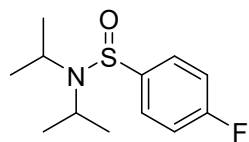
4k $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)



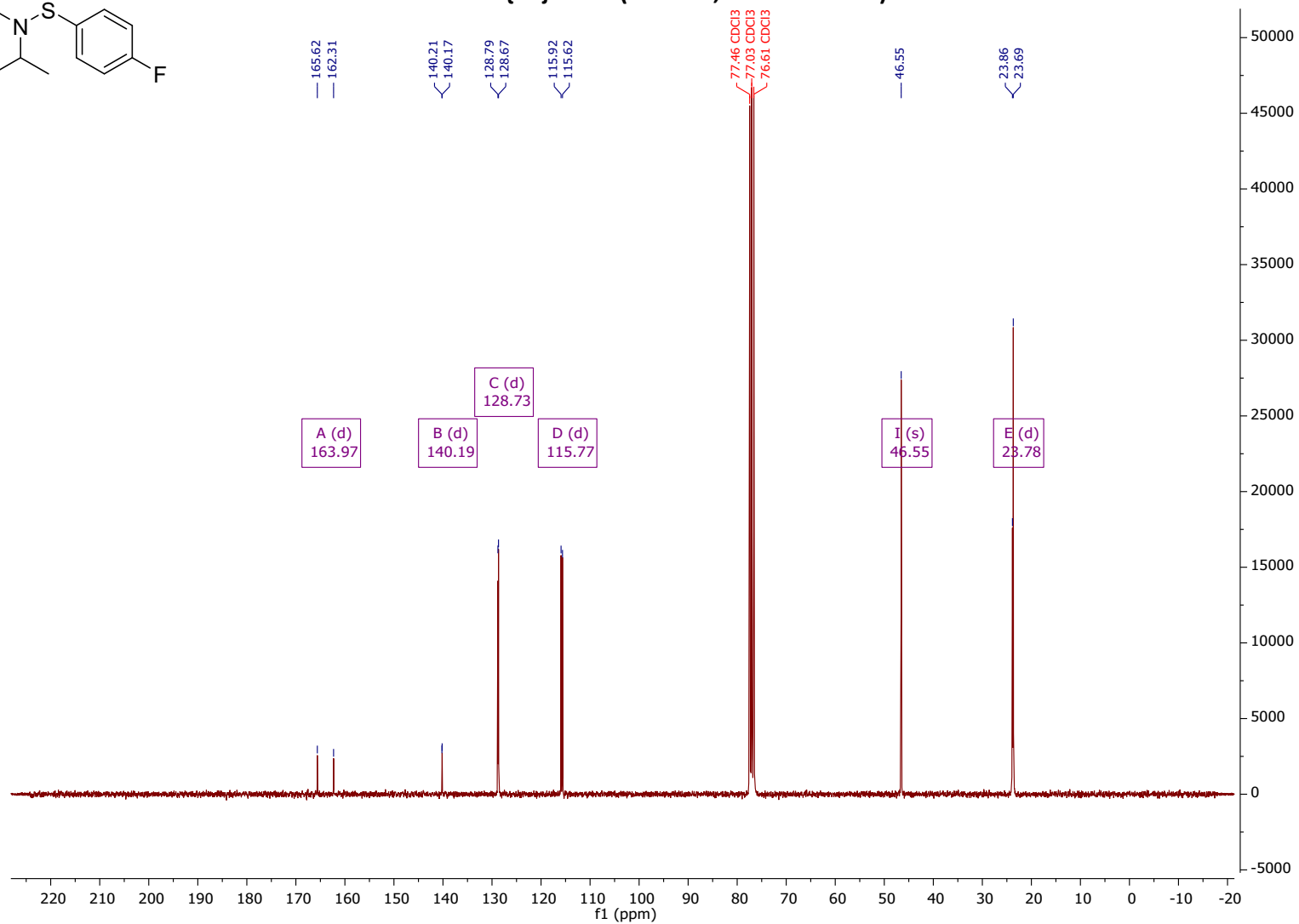


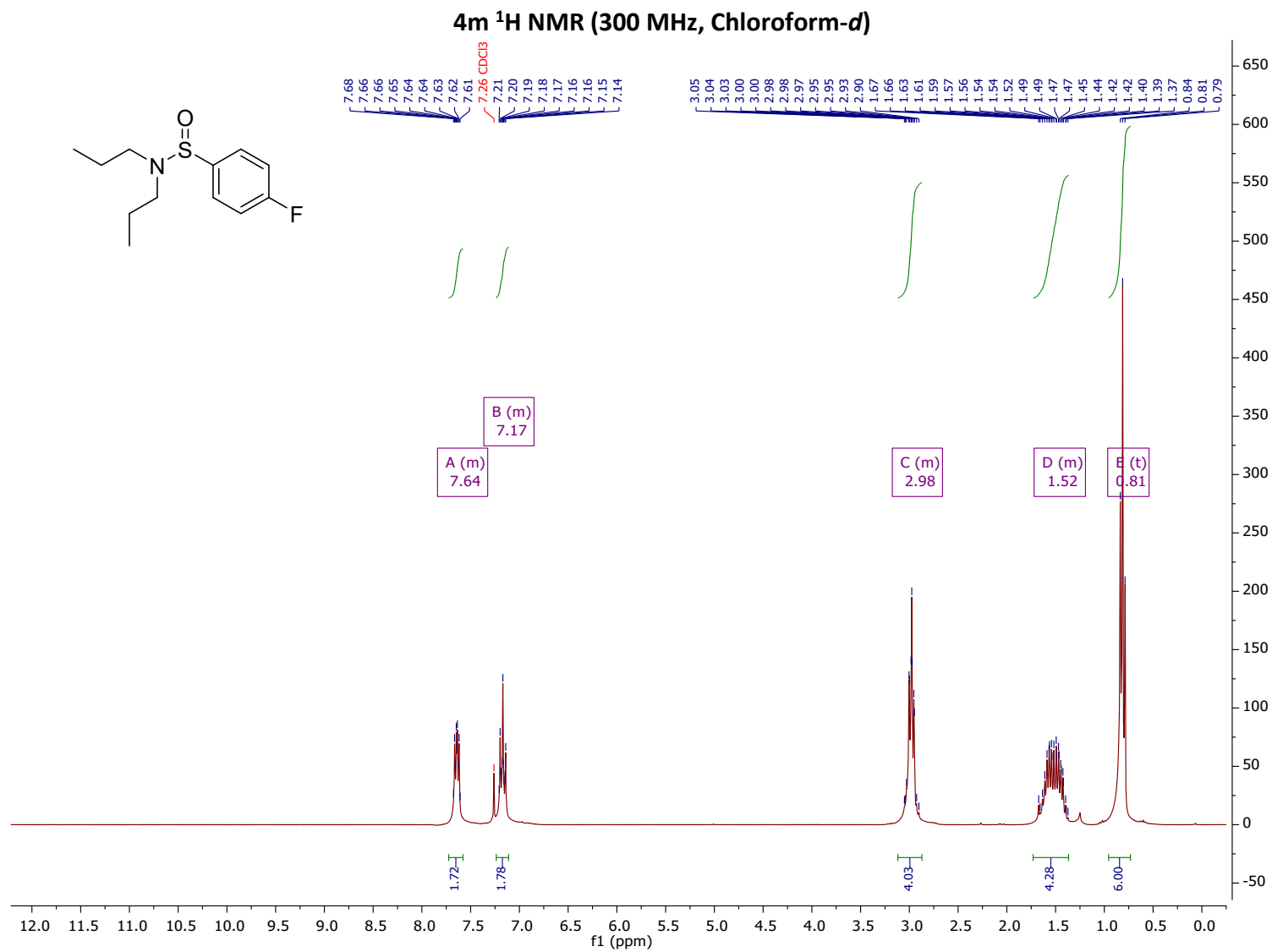
4I ¹⁹F NMR (282 MHz, Chloroform-*d*)



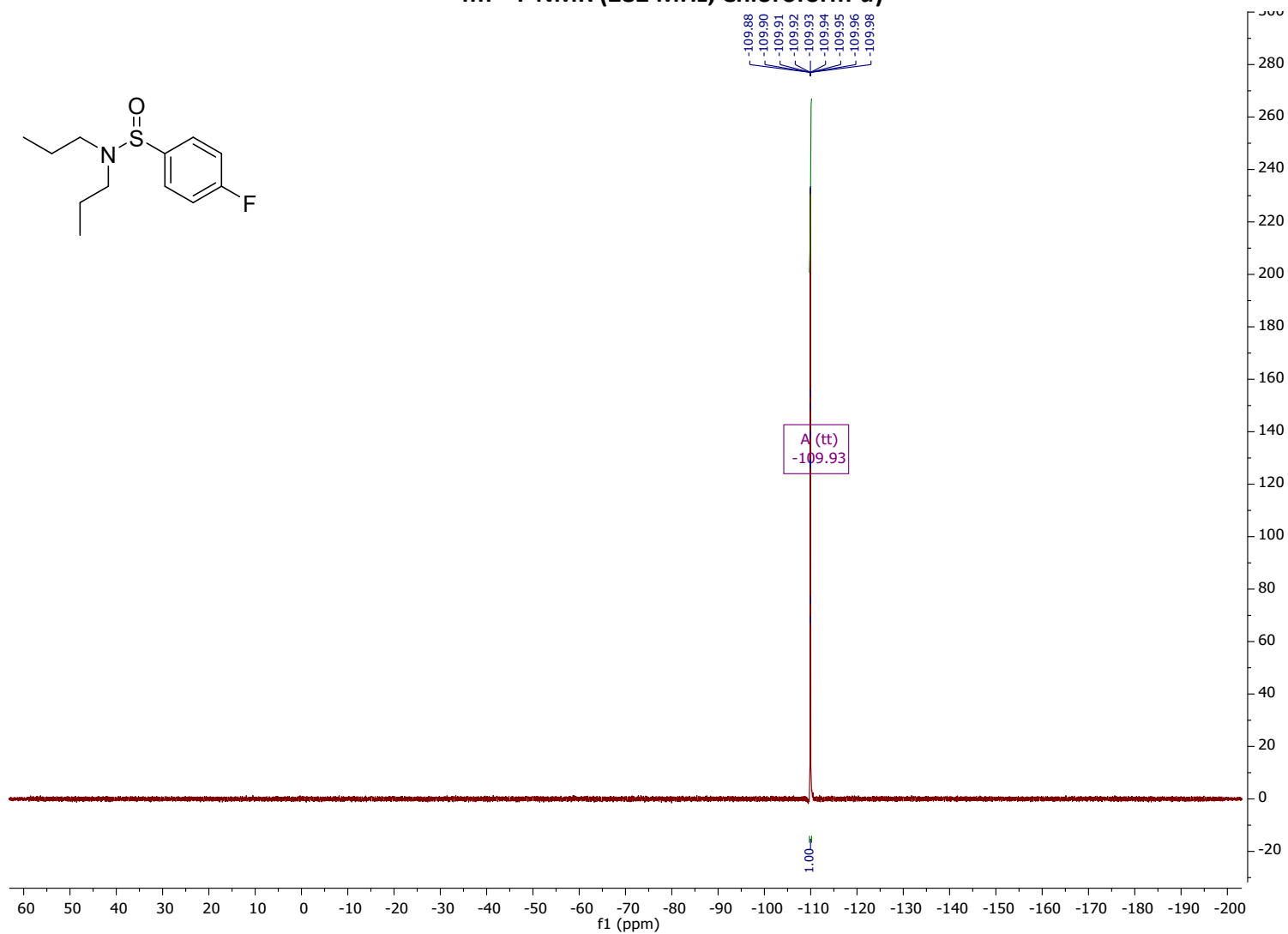


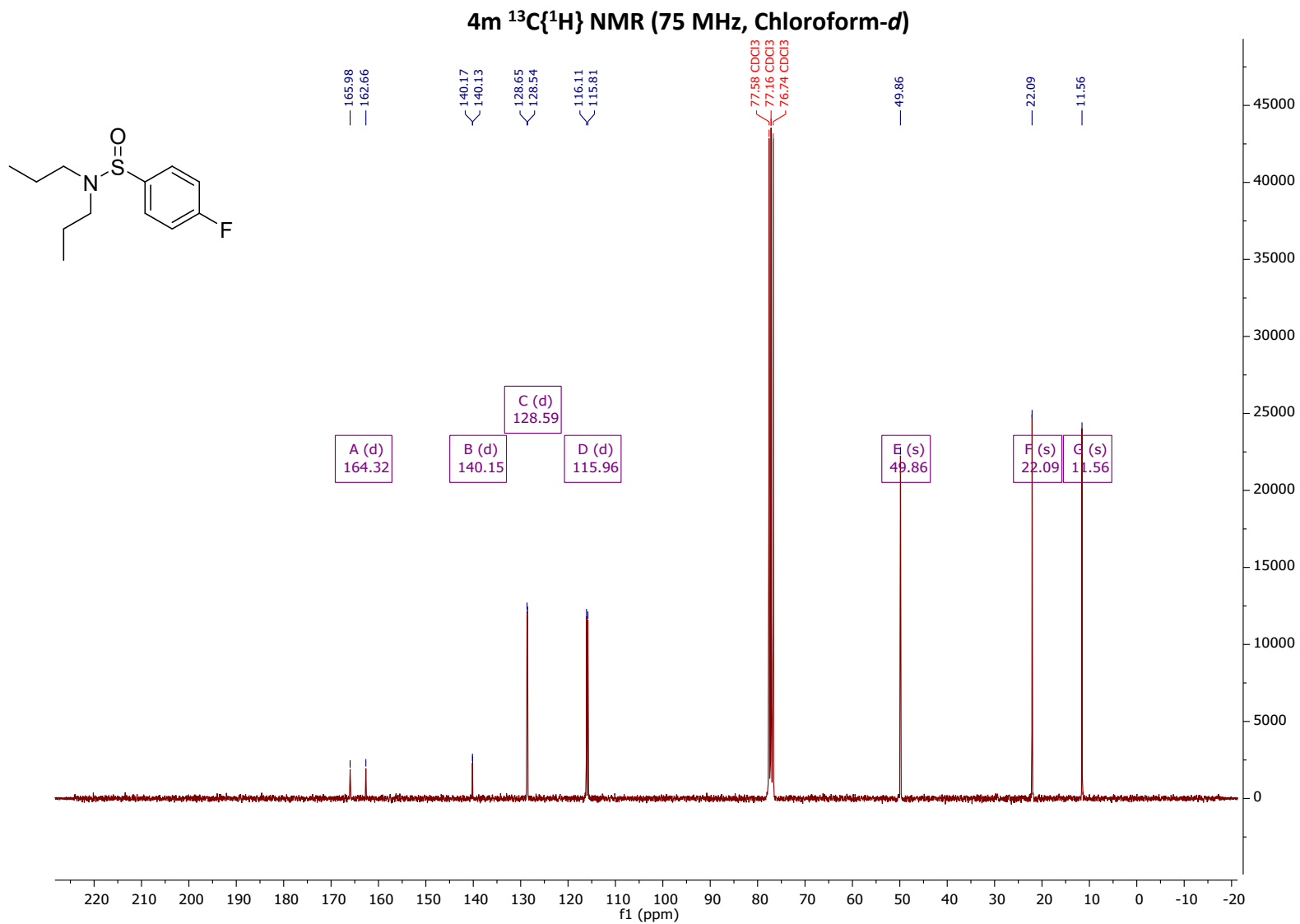
4f ¹³C{¹H} NMR (75 MHz, Chloroform-*d*)

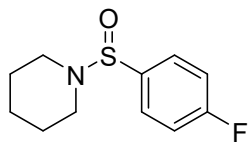




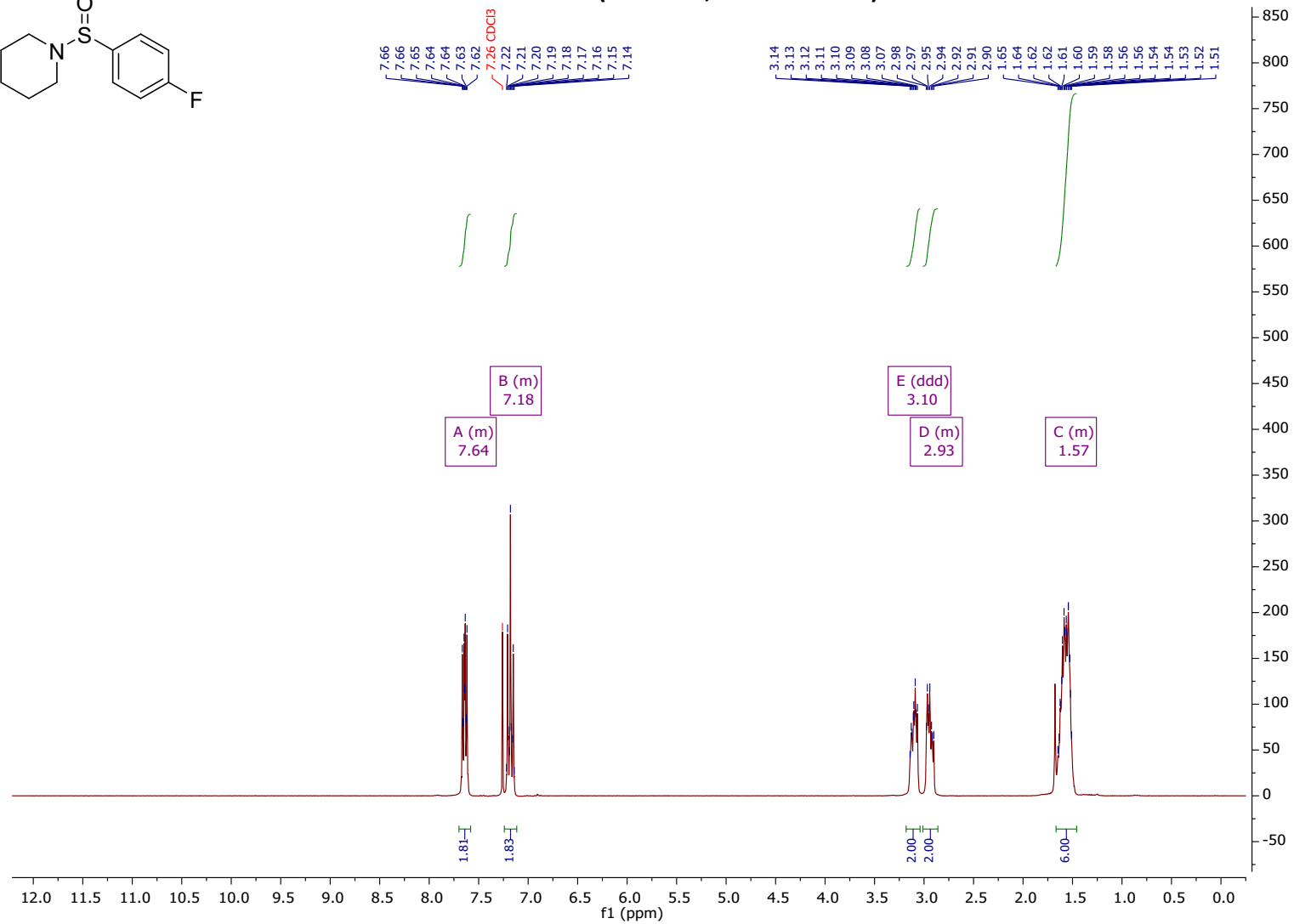
4m ¹⁹F NMR (282 MHz, Chloroform-d)



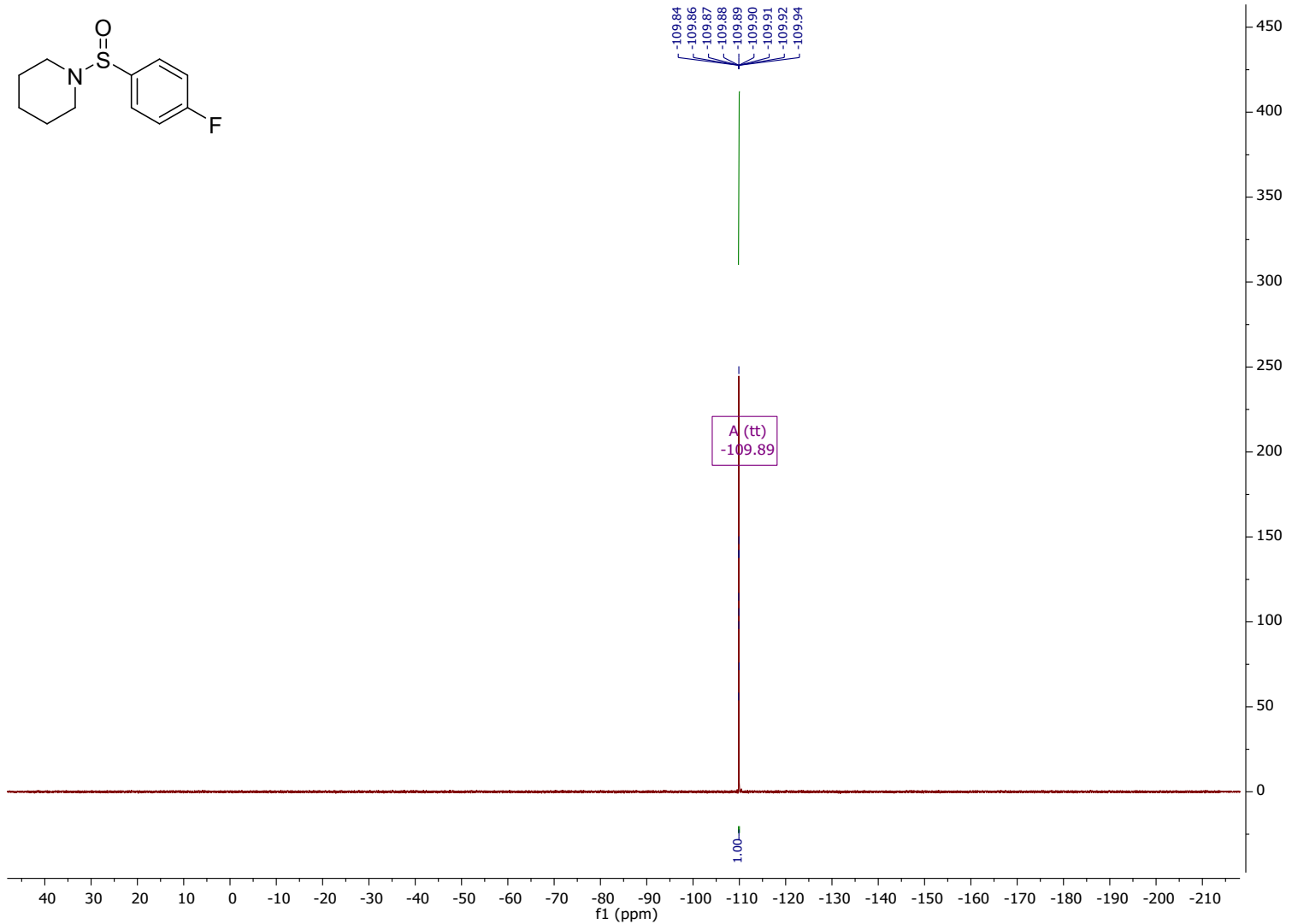




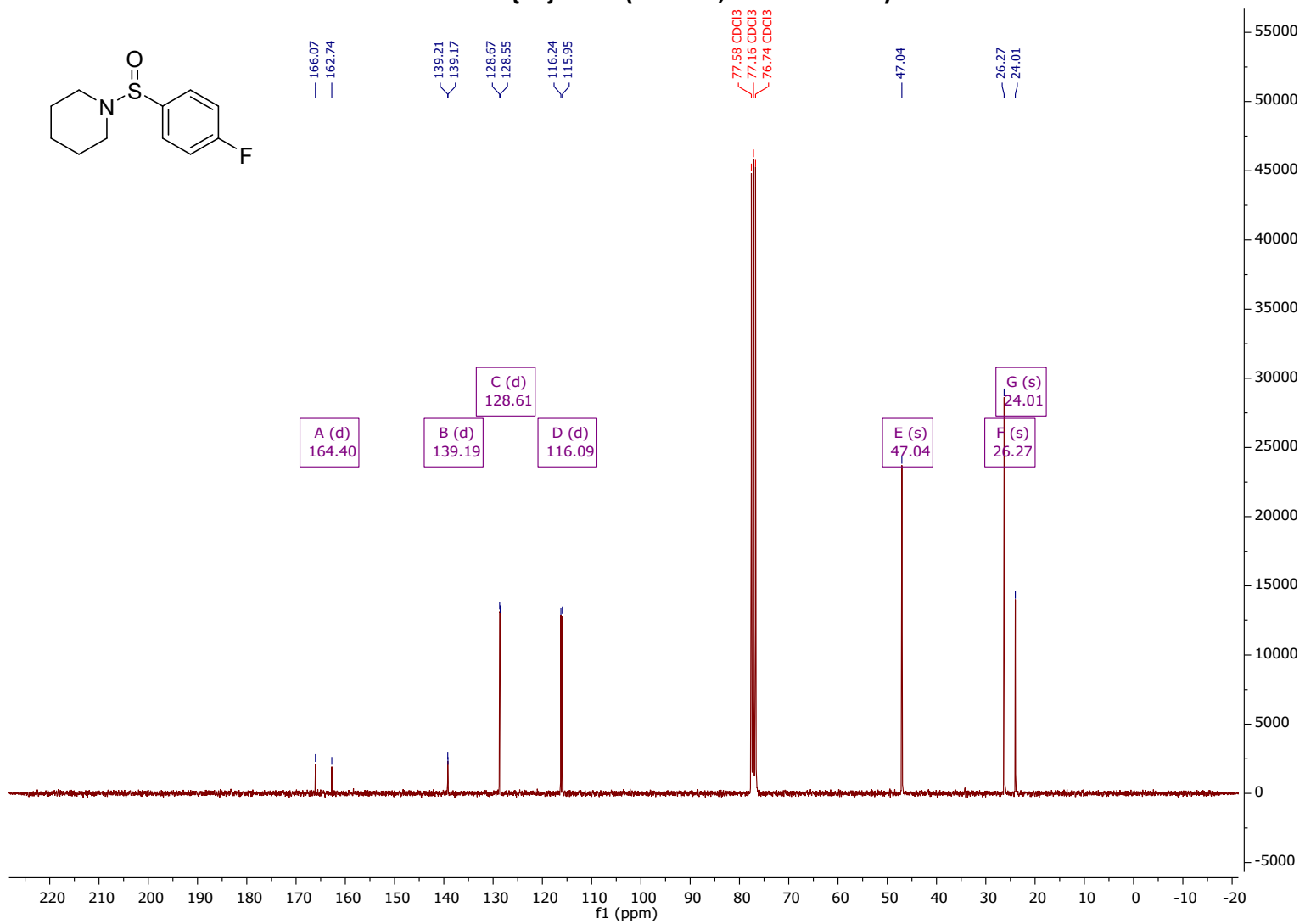
4n ¹H NMR (300 MHz, Chloroform-d)



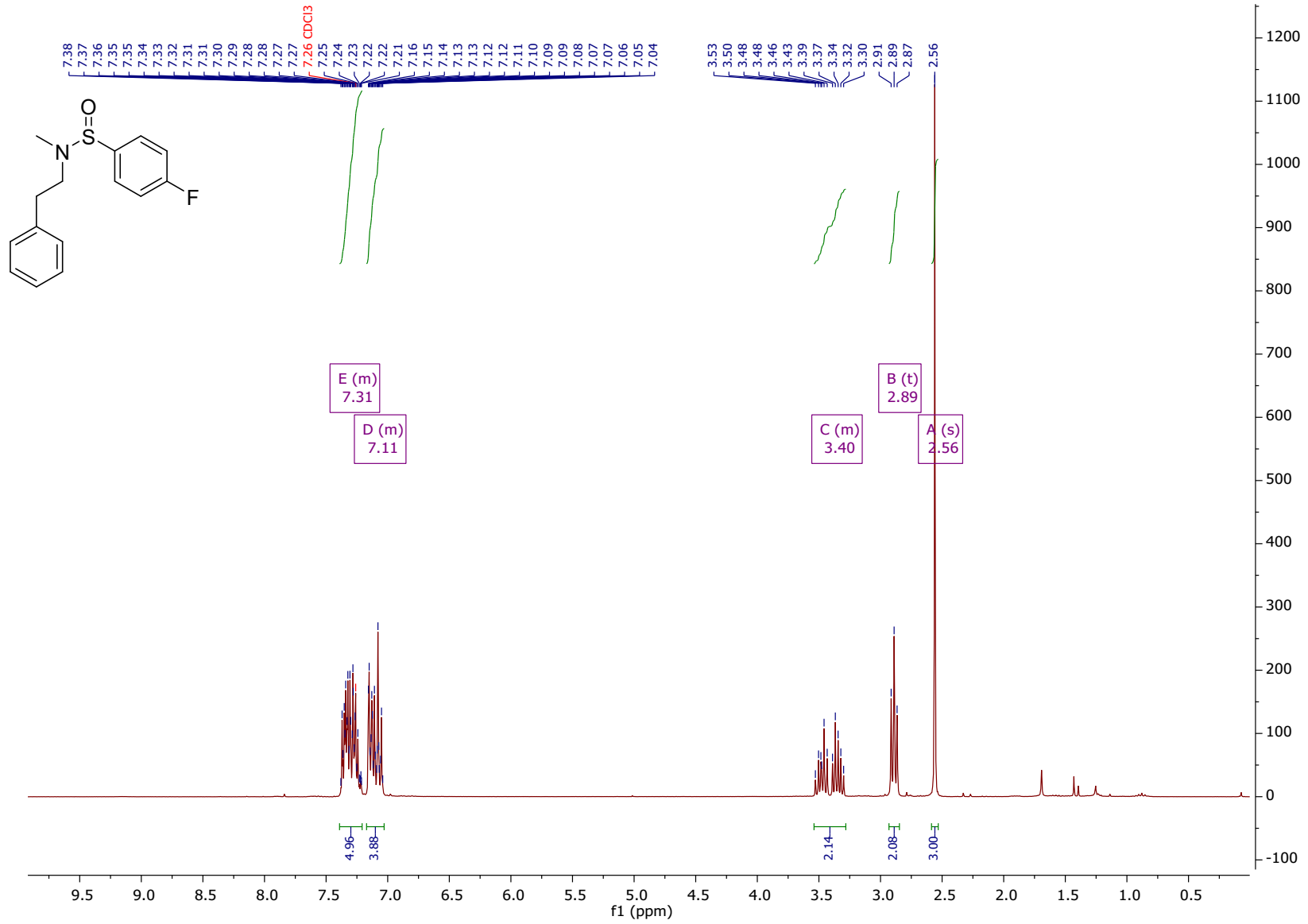
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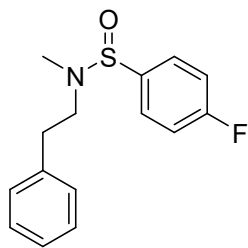


4n $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)

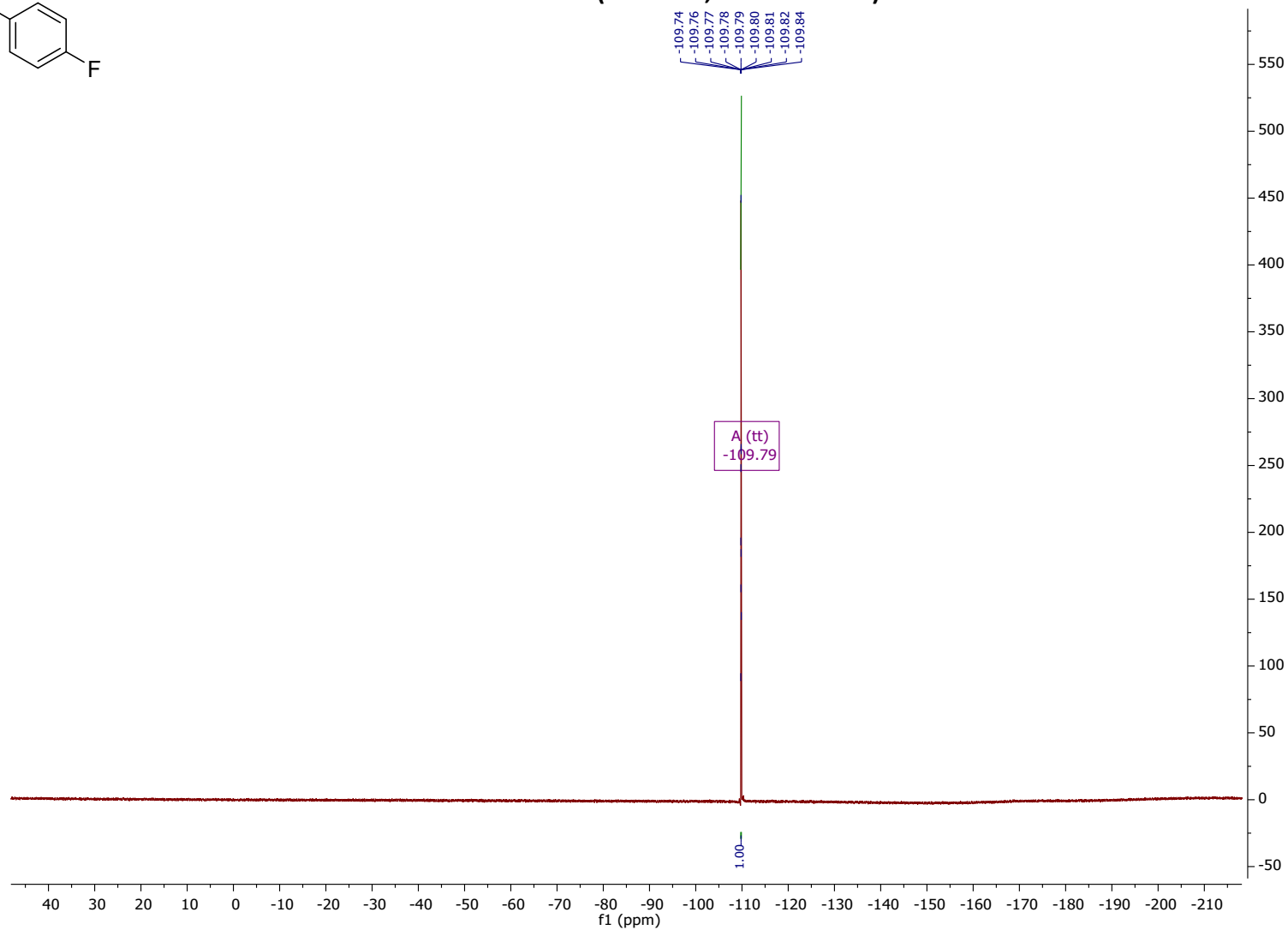


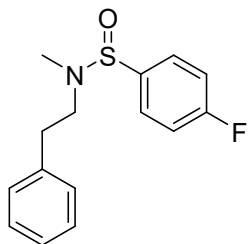
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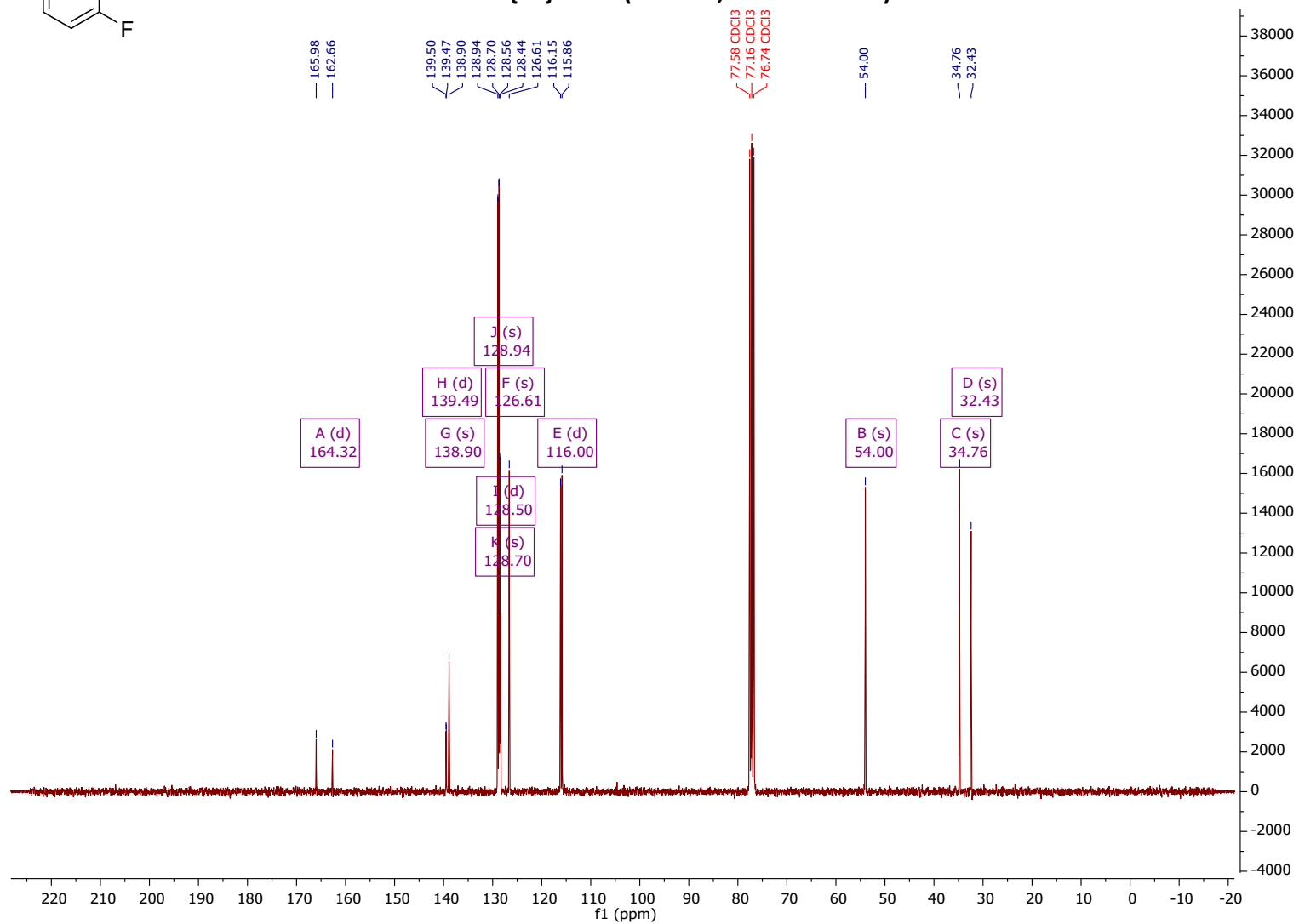


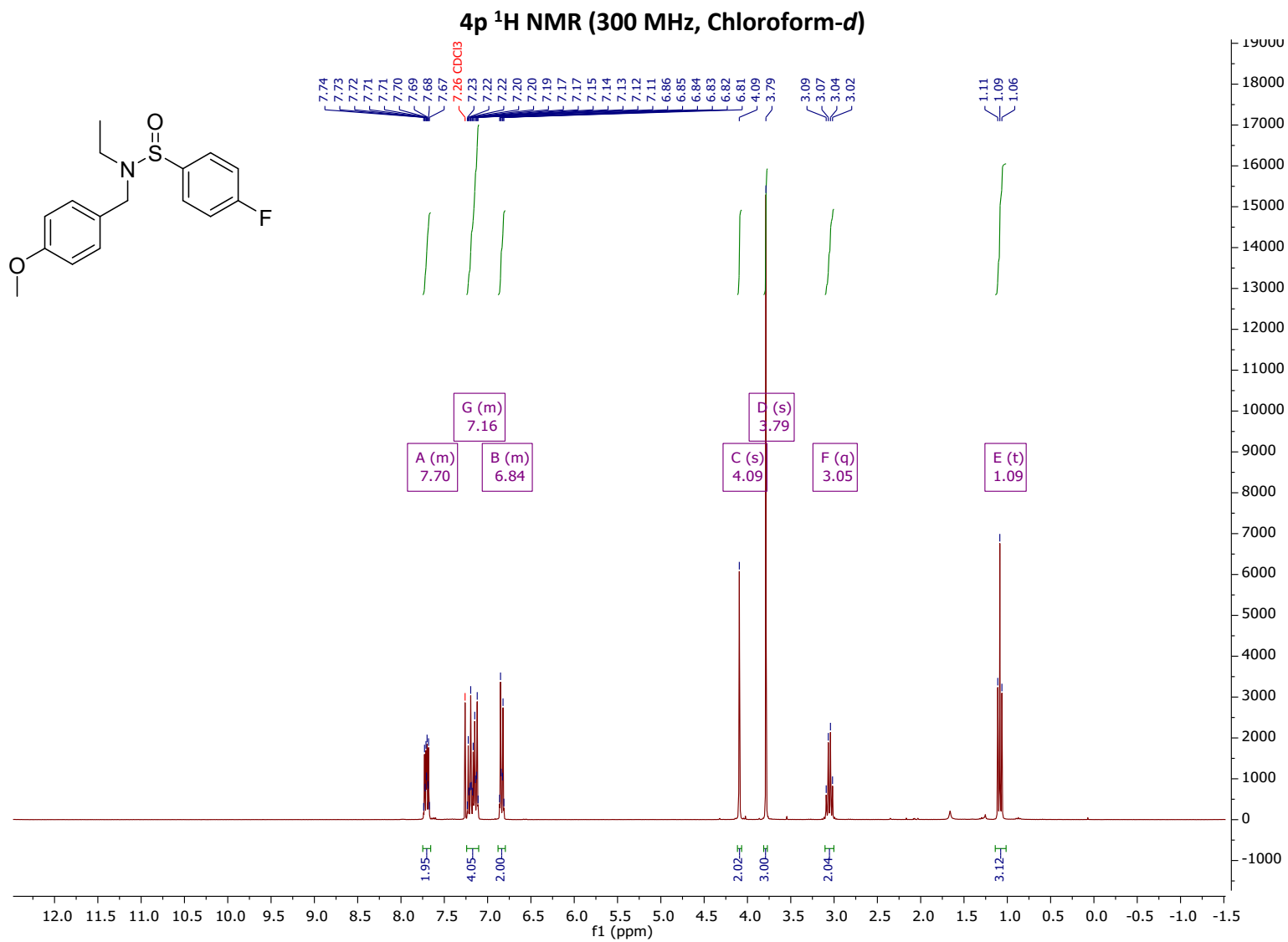
4o ¹⁹F NMR (282 MHz, Chloroform-d)



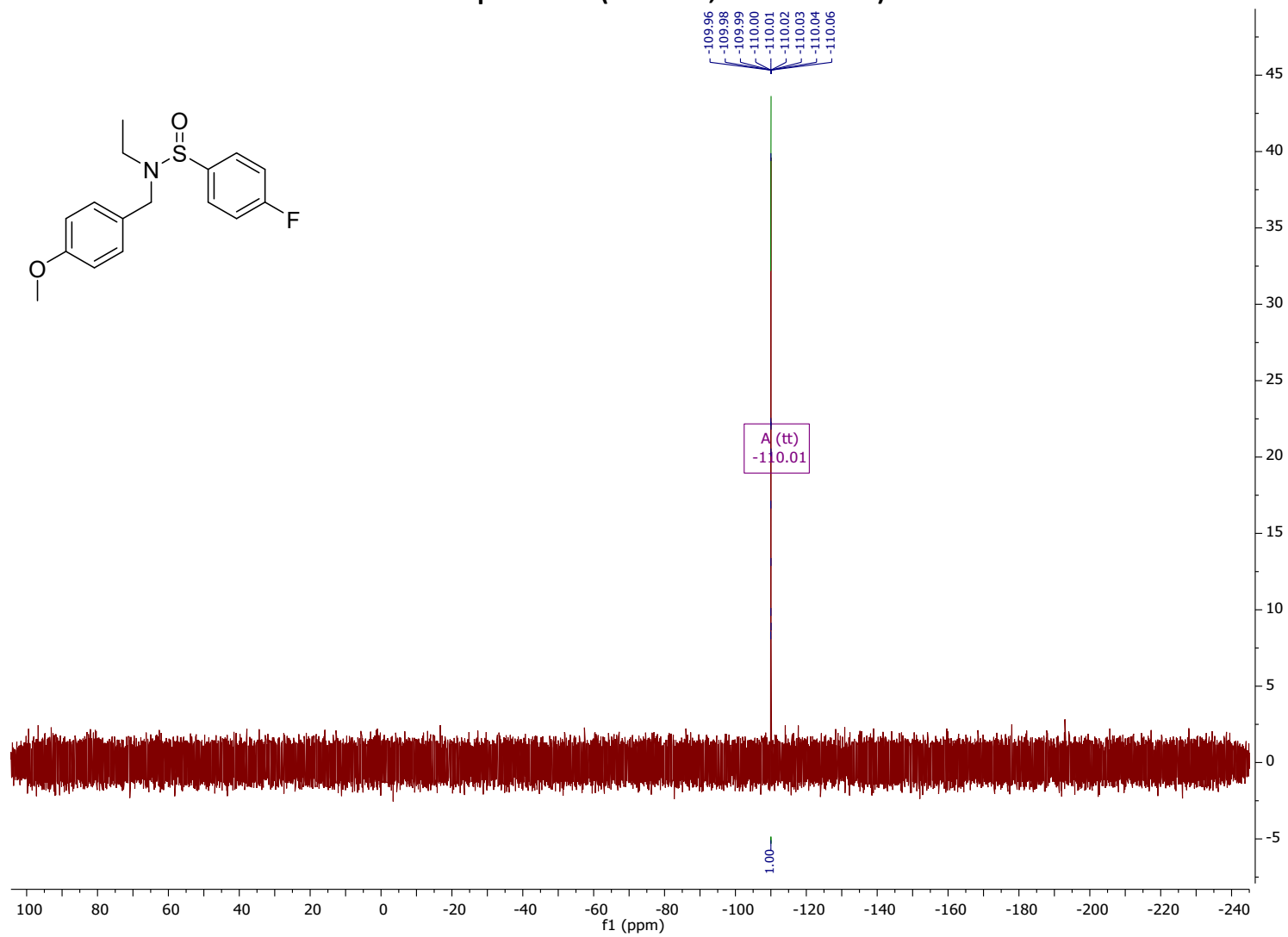


4o $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)

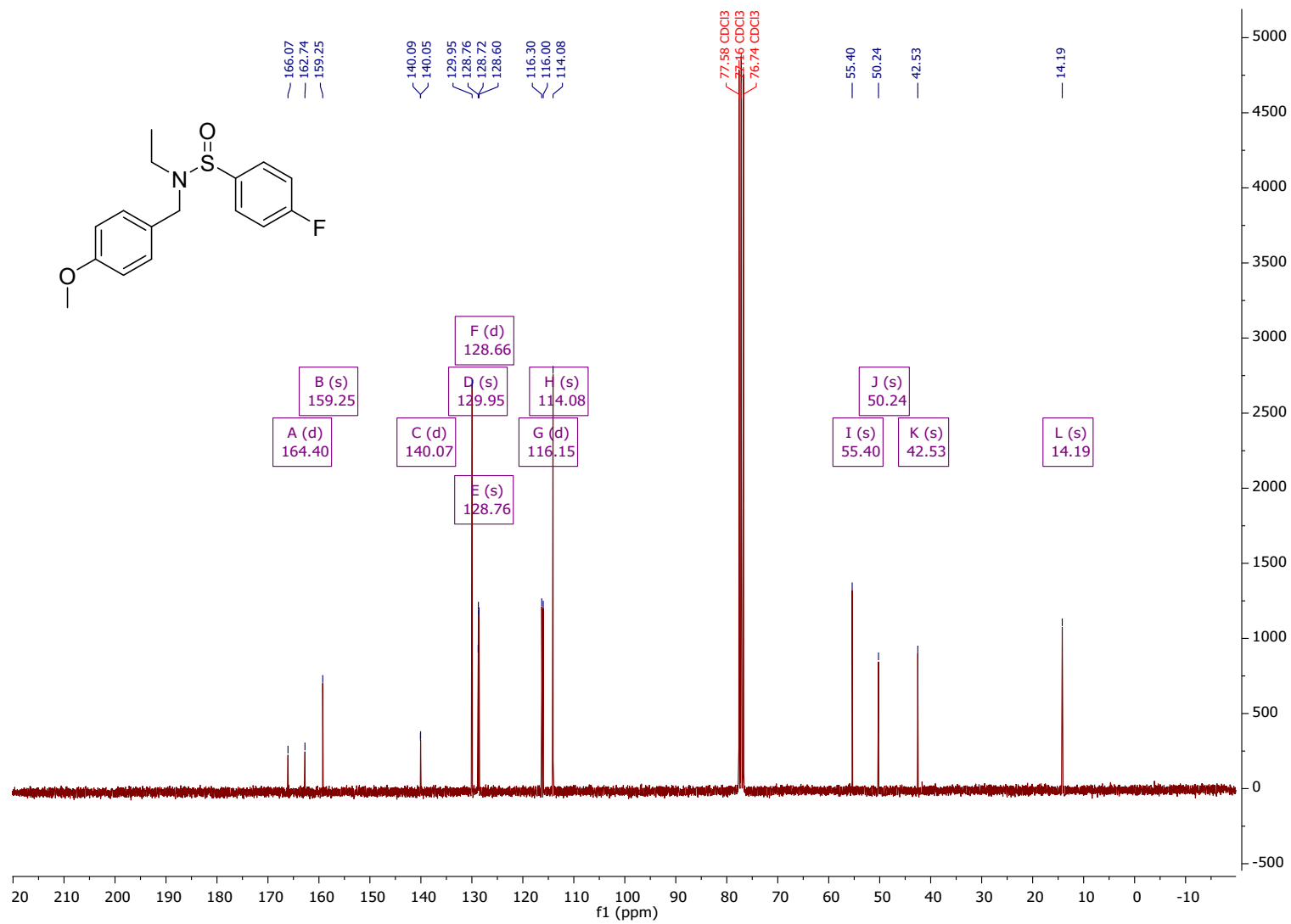


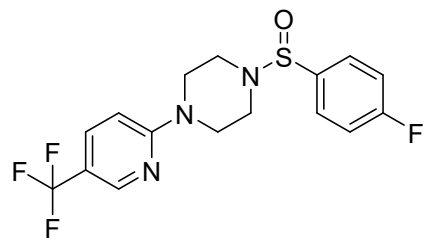


4p ^{19}F NMR (282 MHz, Chloroform-*d*)

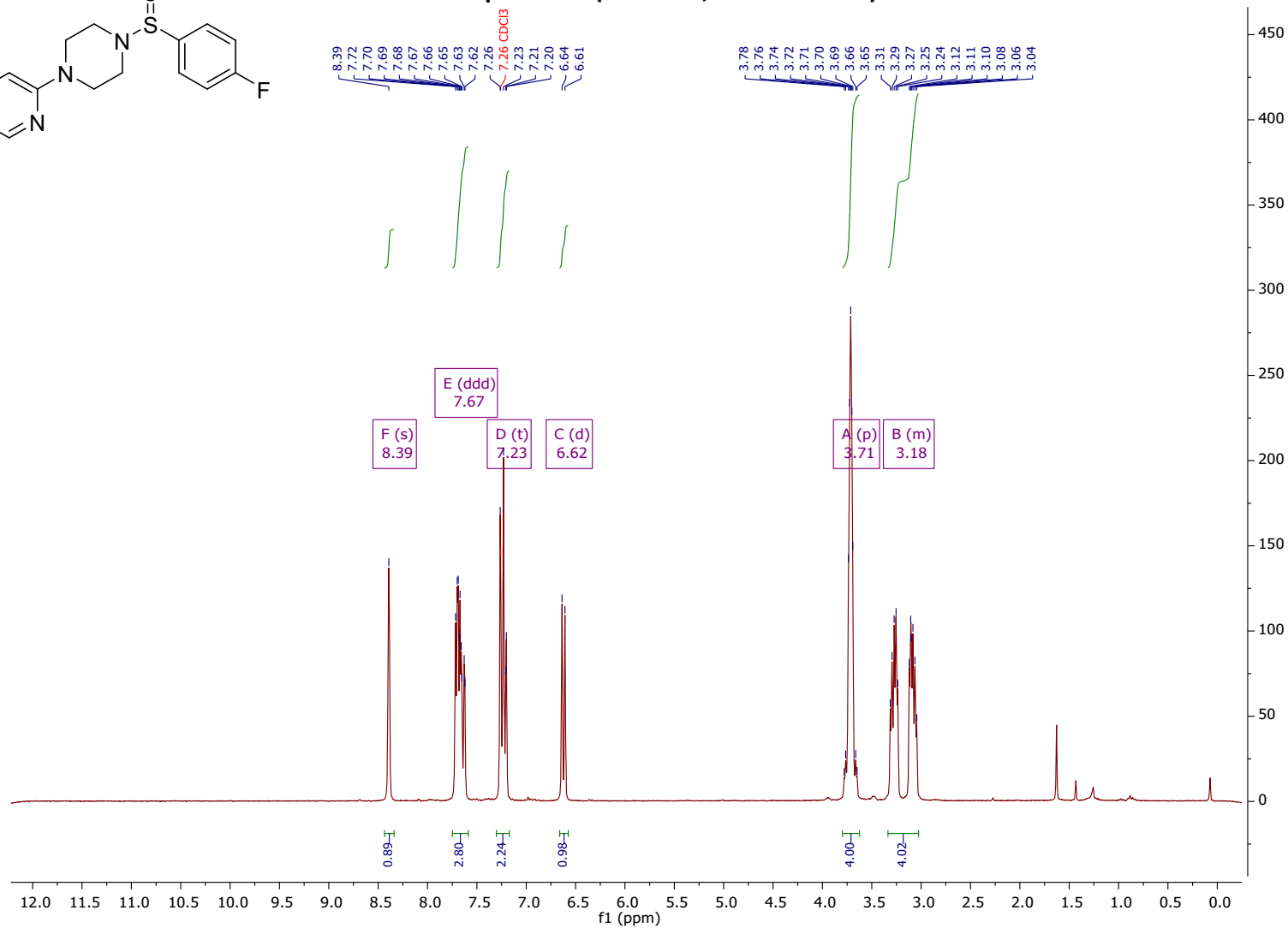


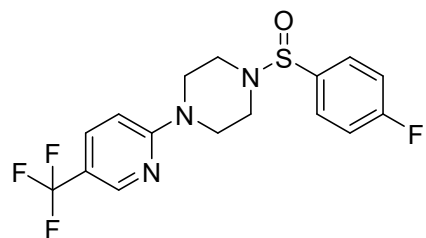
4p $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)



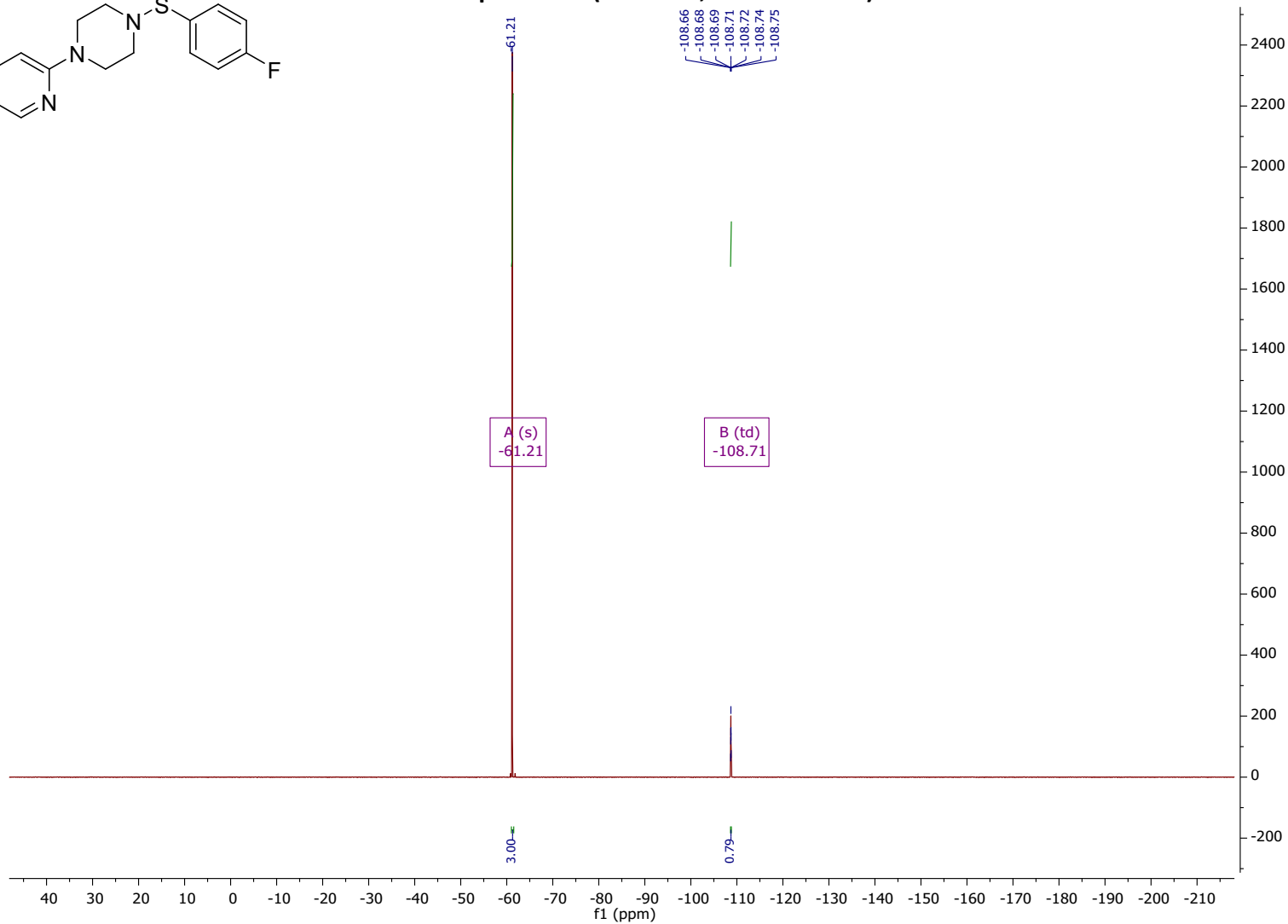


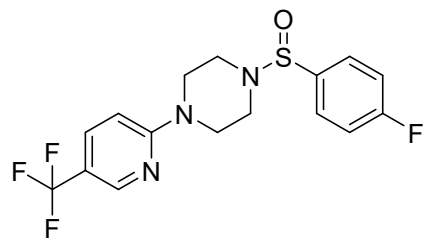
4q ¹H NMR (300 MHz, Chloroform-d)



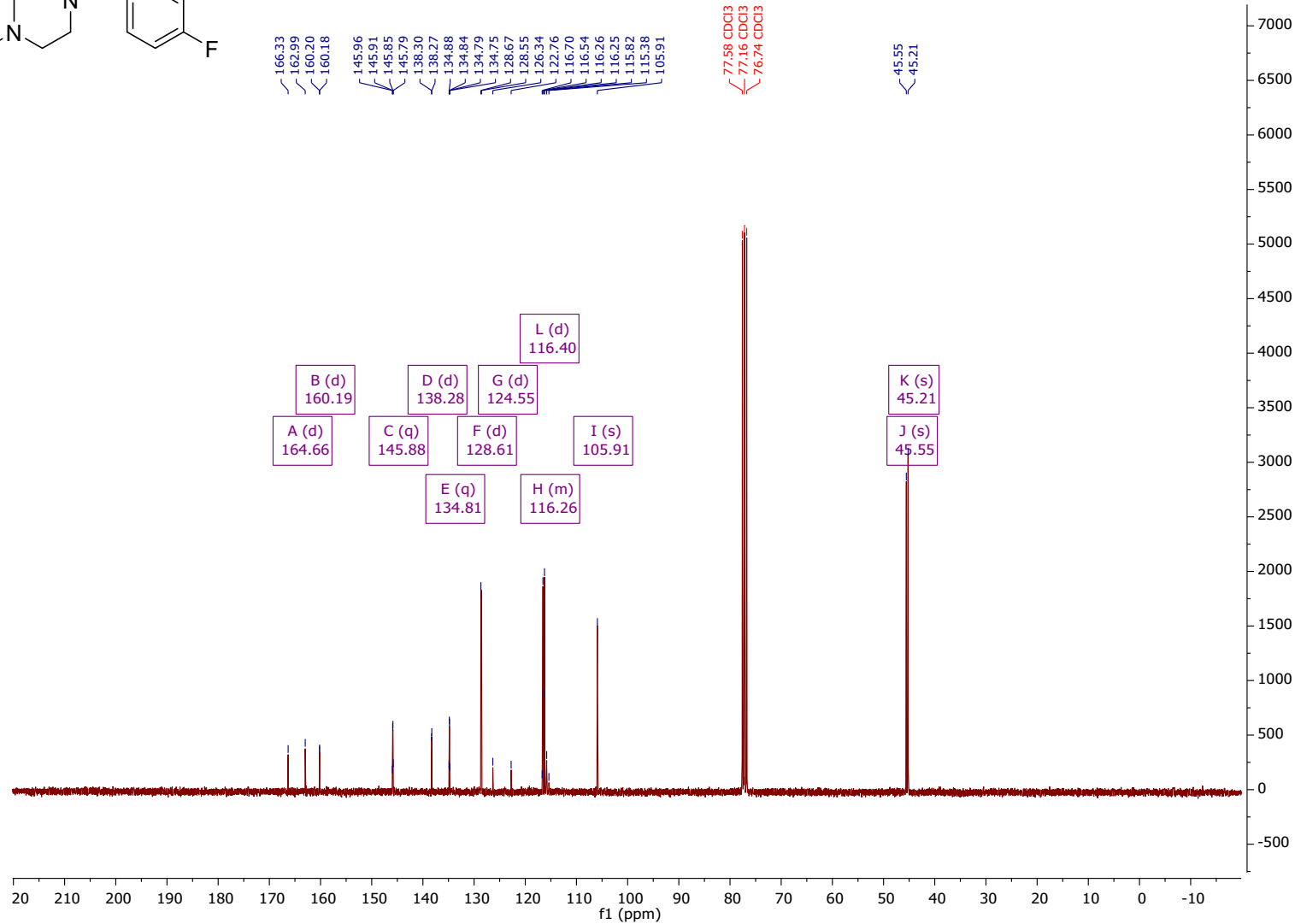


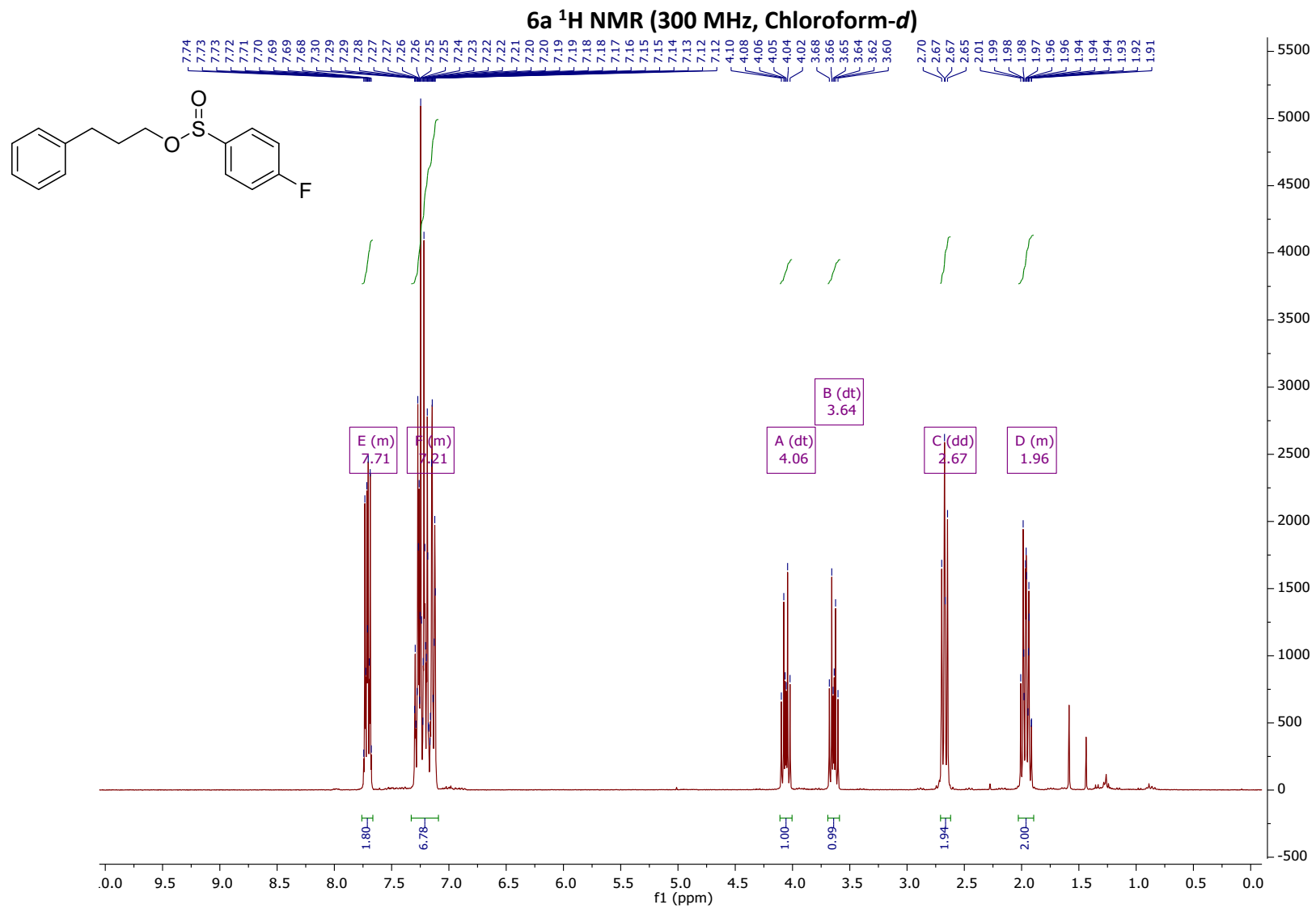
4q ¹⁹F NMR (282 MHz, Chloroform-d)

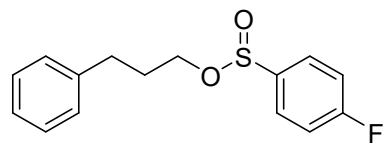




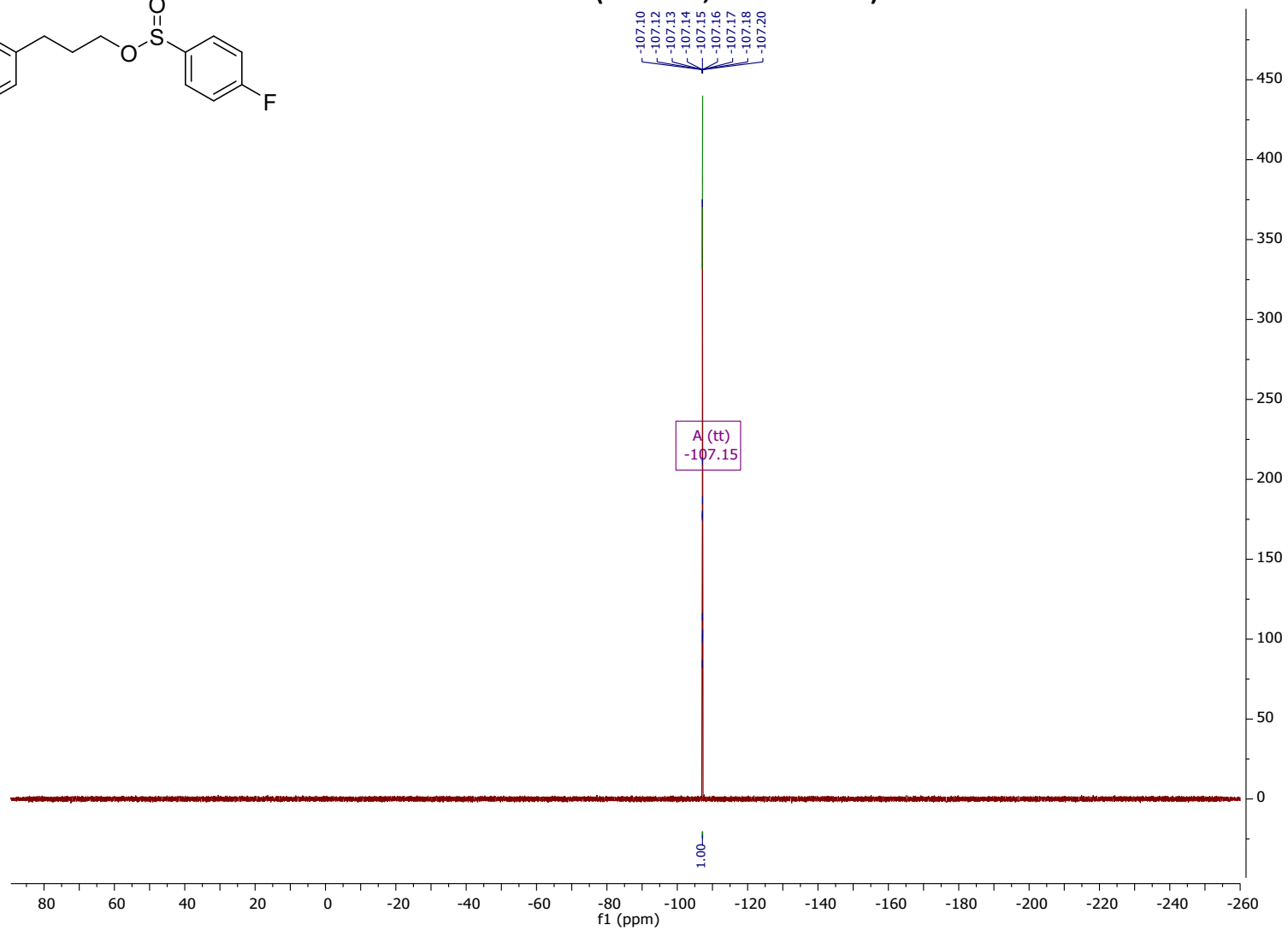
4q $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)

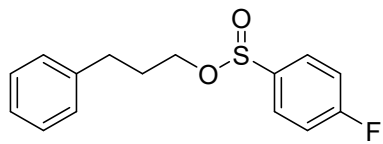




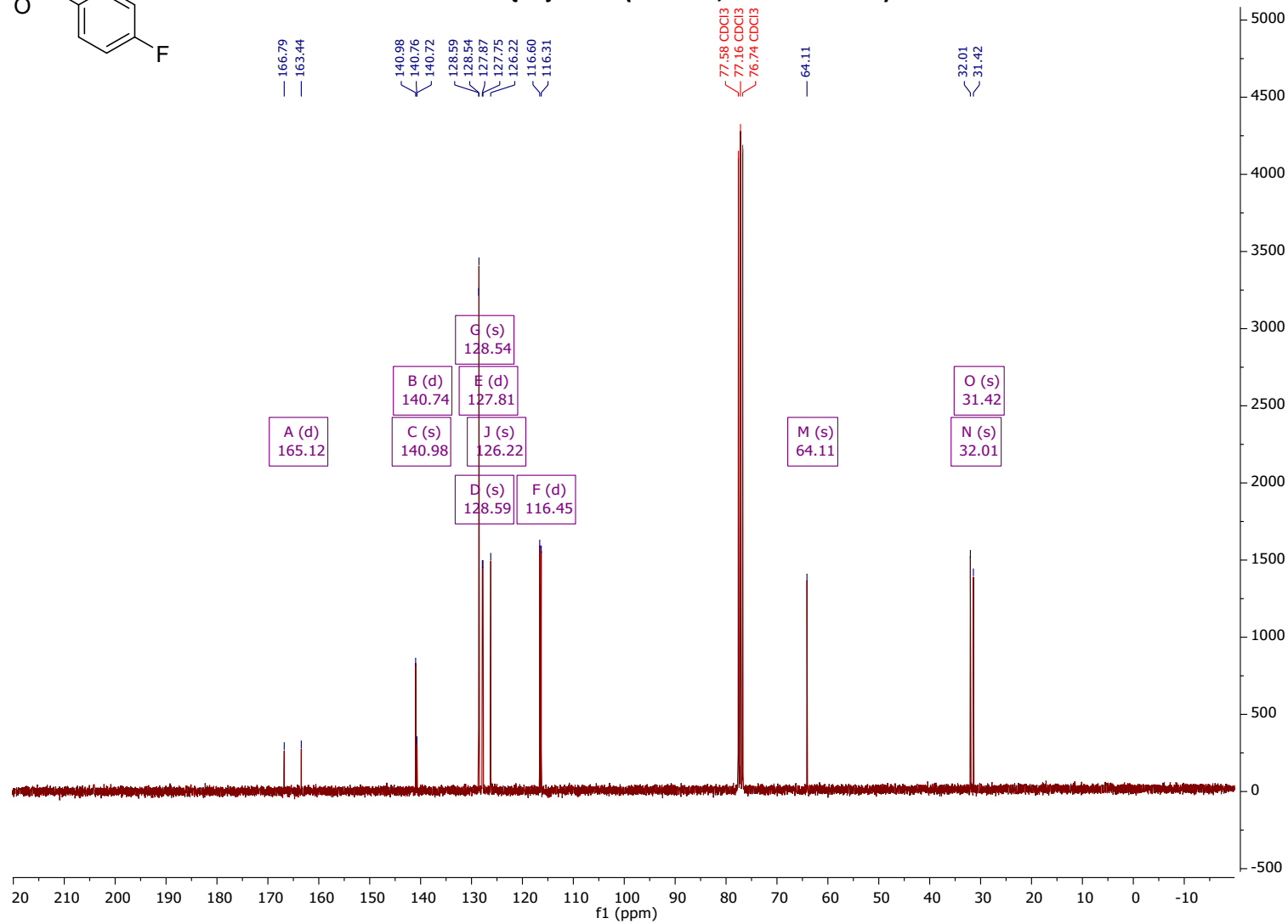


6a ¹⁹F NMR (282 MHz, Chloroform-*d*)

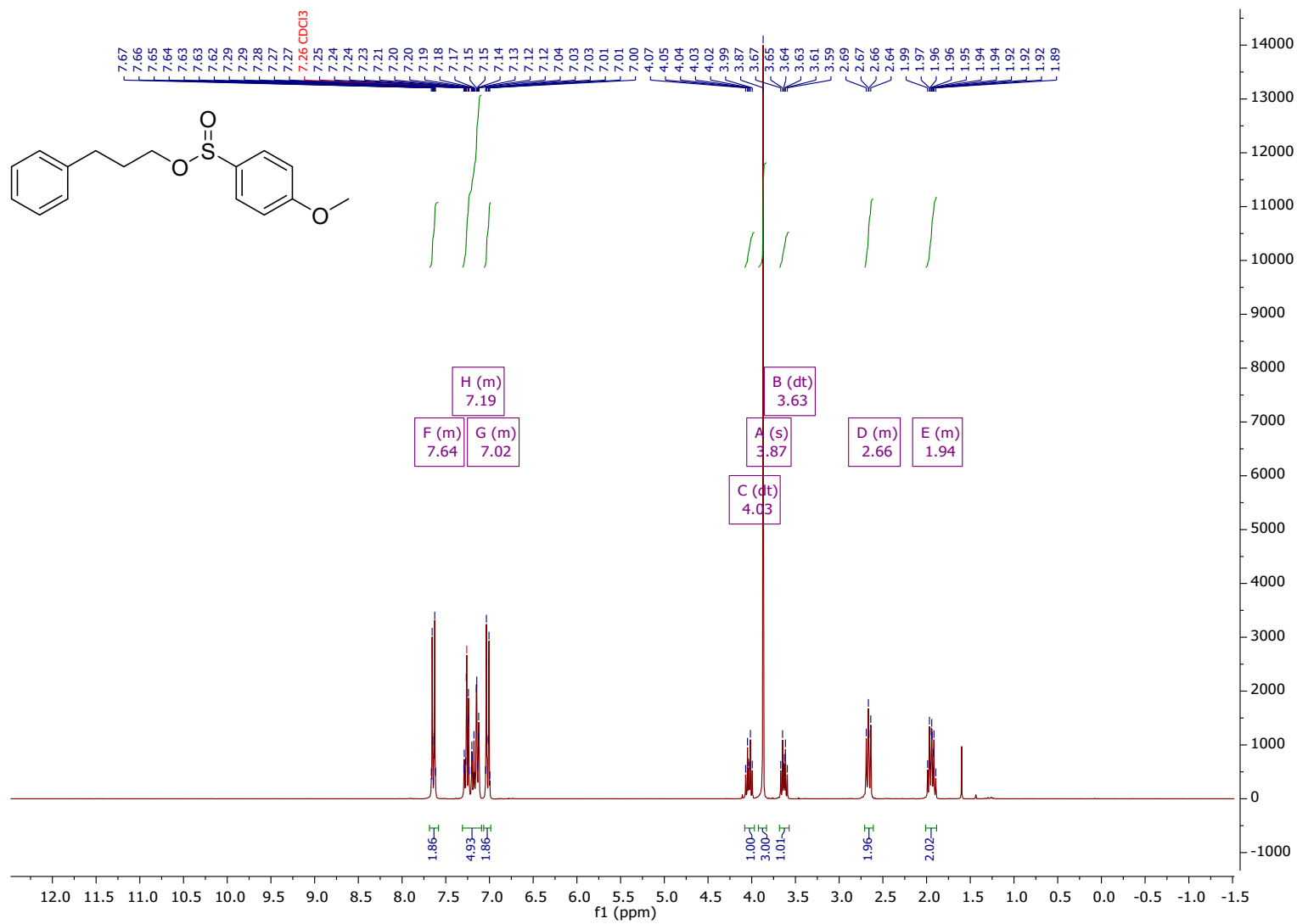




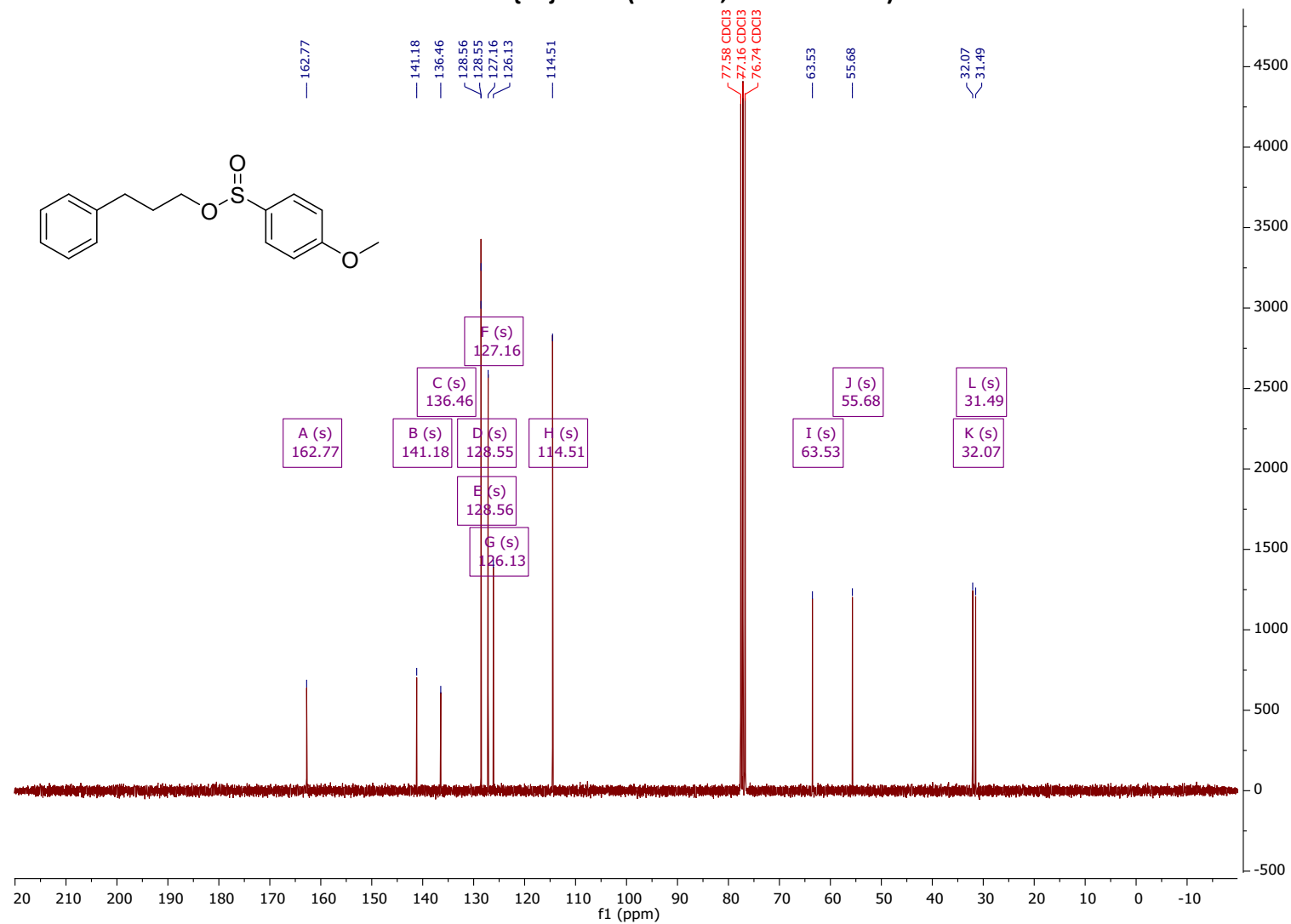
6a $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)



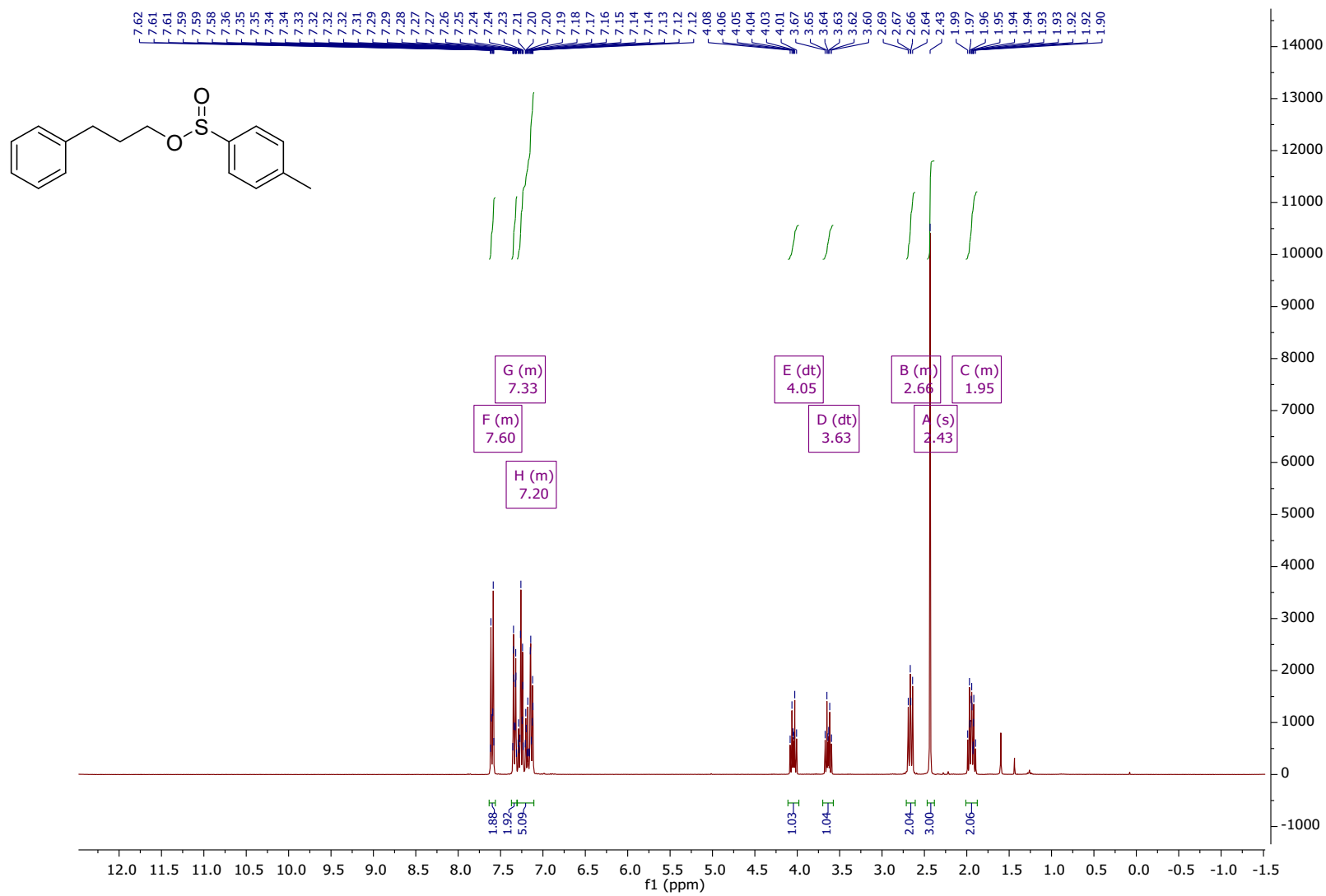
6b ¹H NMR (300 MHz, Chloroform-d)



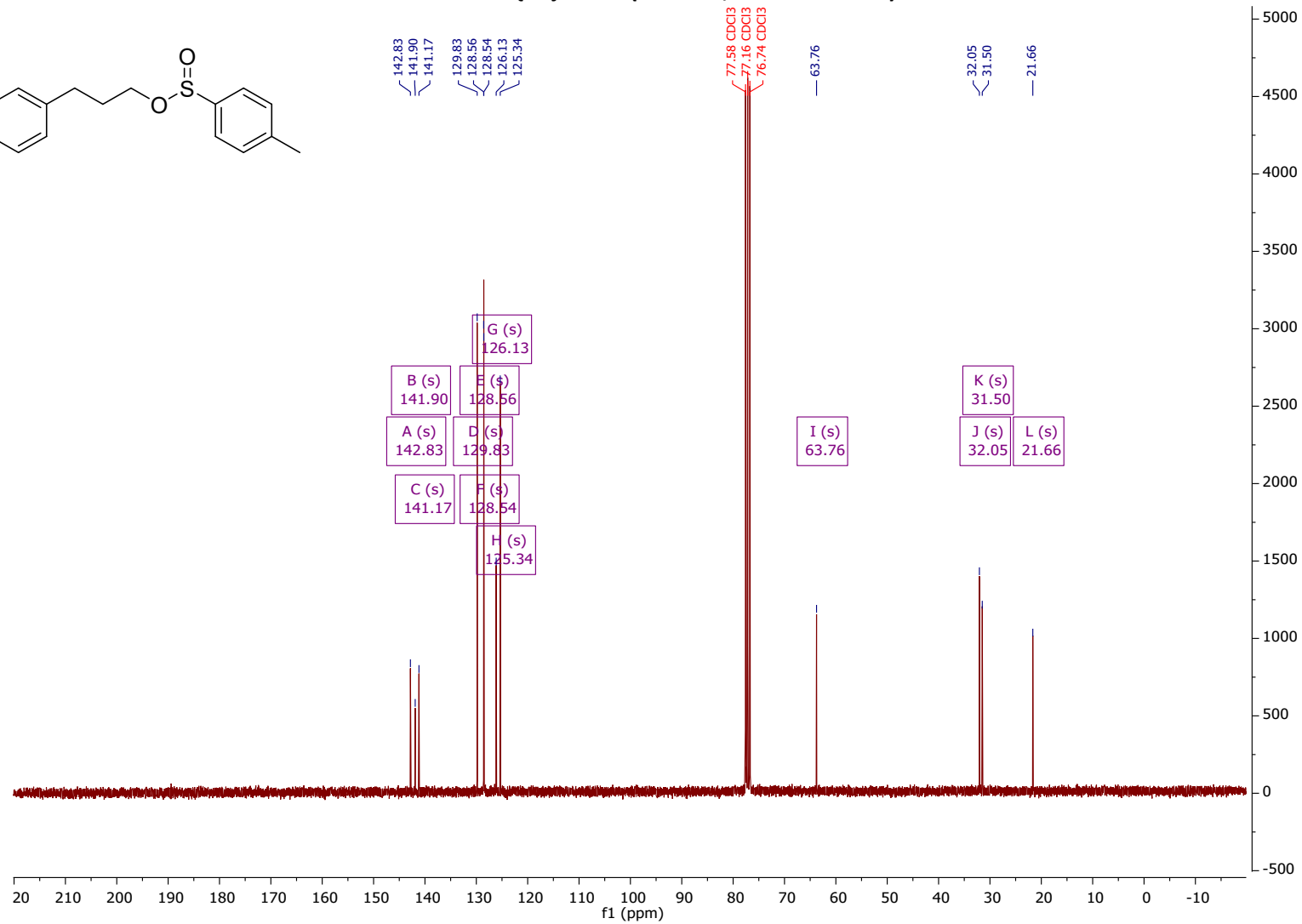
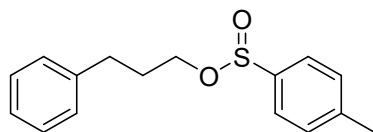
6b ¹³C{¹H} NMR (75 MHz, Chloroform-d)



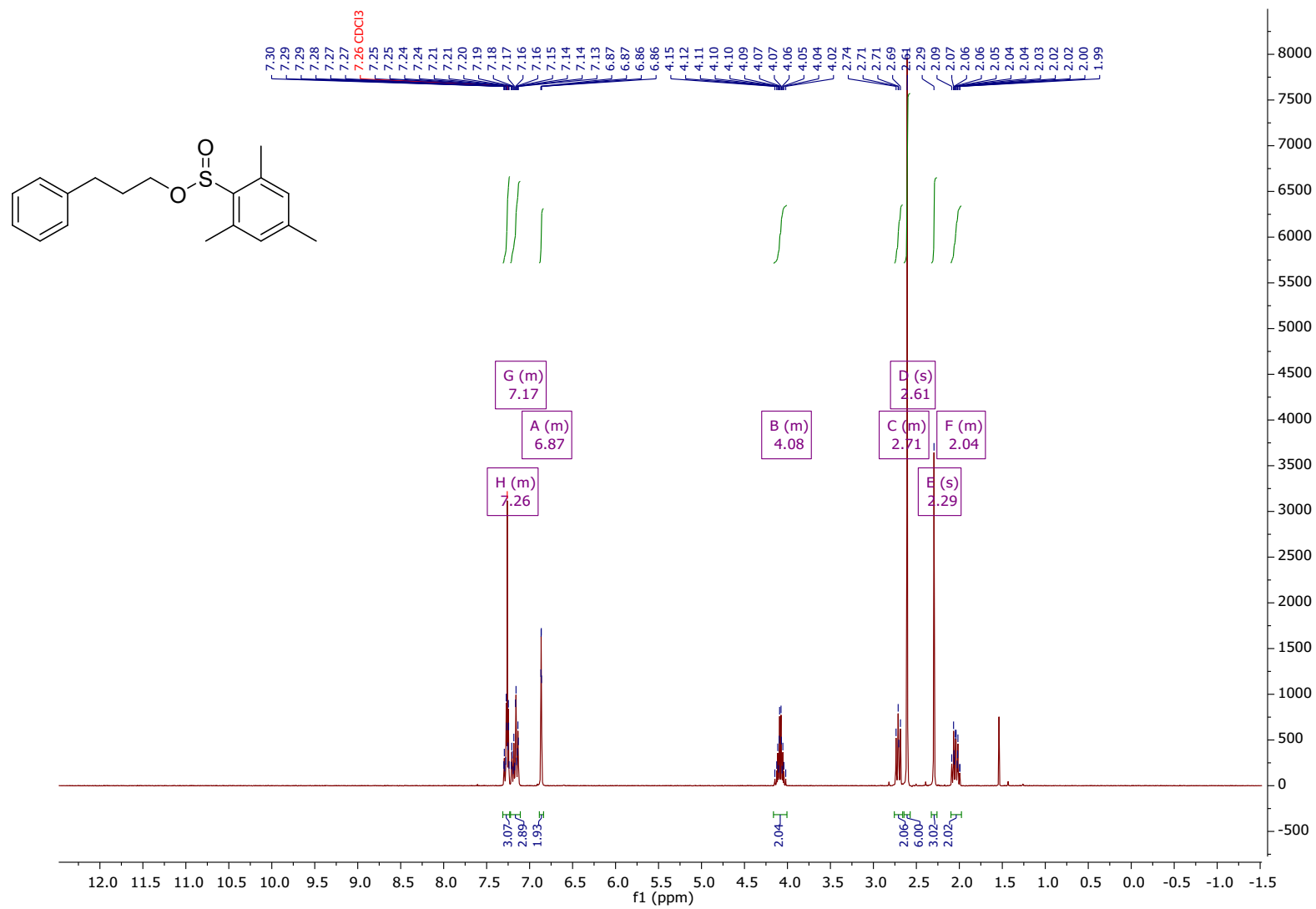
6c ¹H NMR (300 MHz, Chloroform-d)



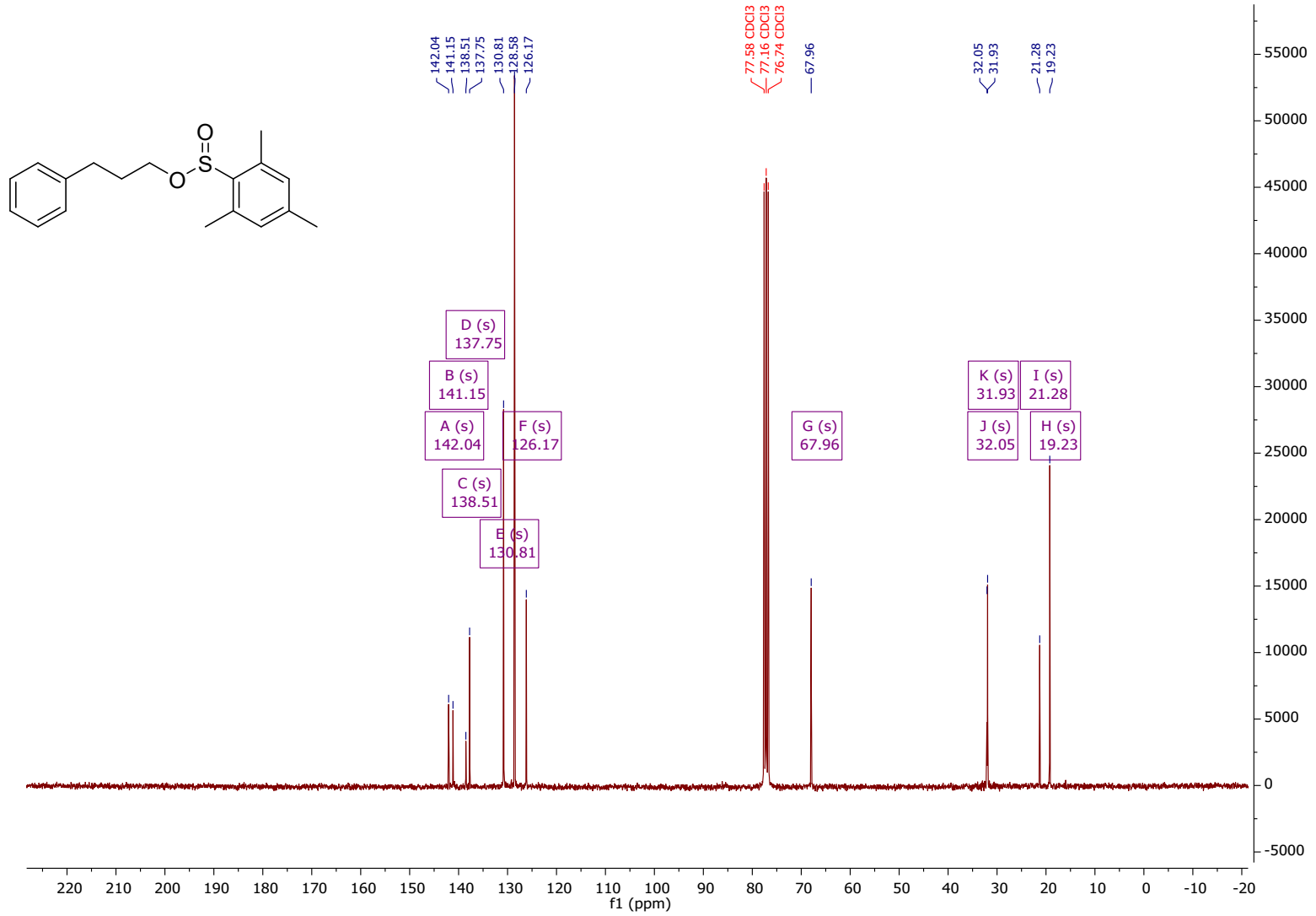
6c ¹³C{¹H} NMR (75 MHz, Chloroform-d)

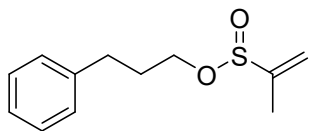


6d ¹H NMR (300 MHz, Chloroform-d)

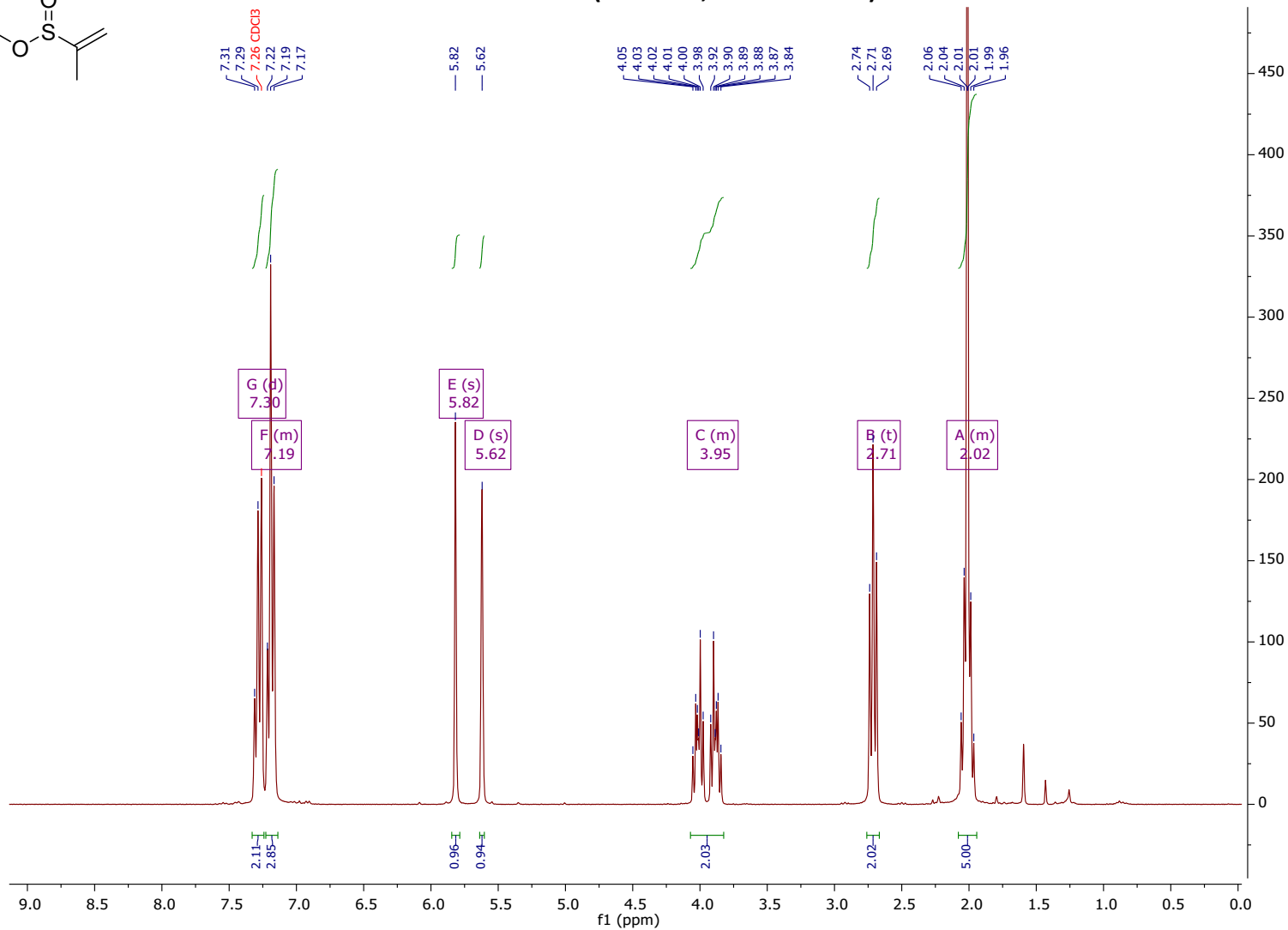


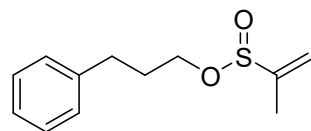
6d $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)



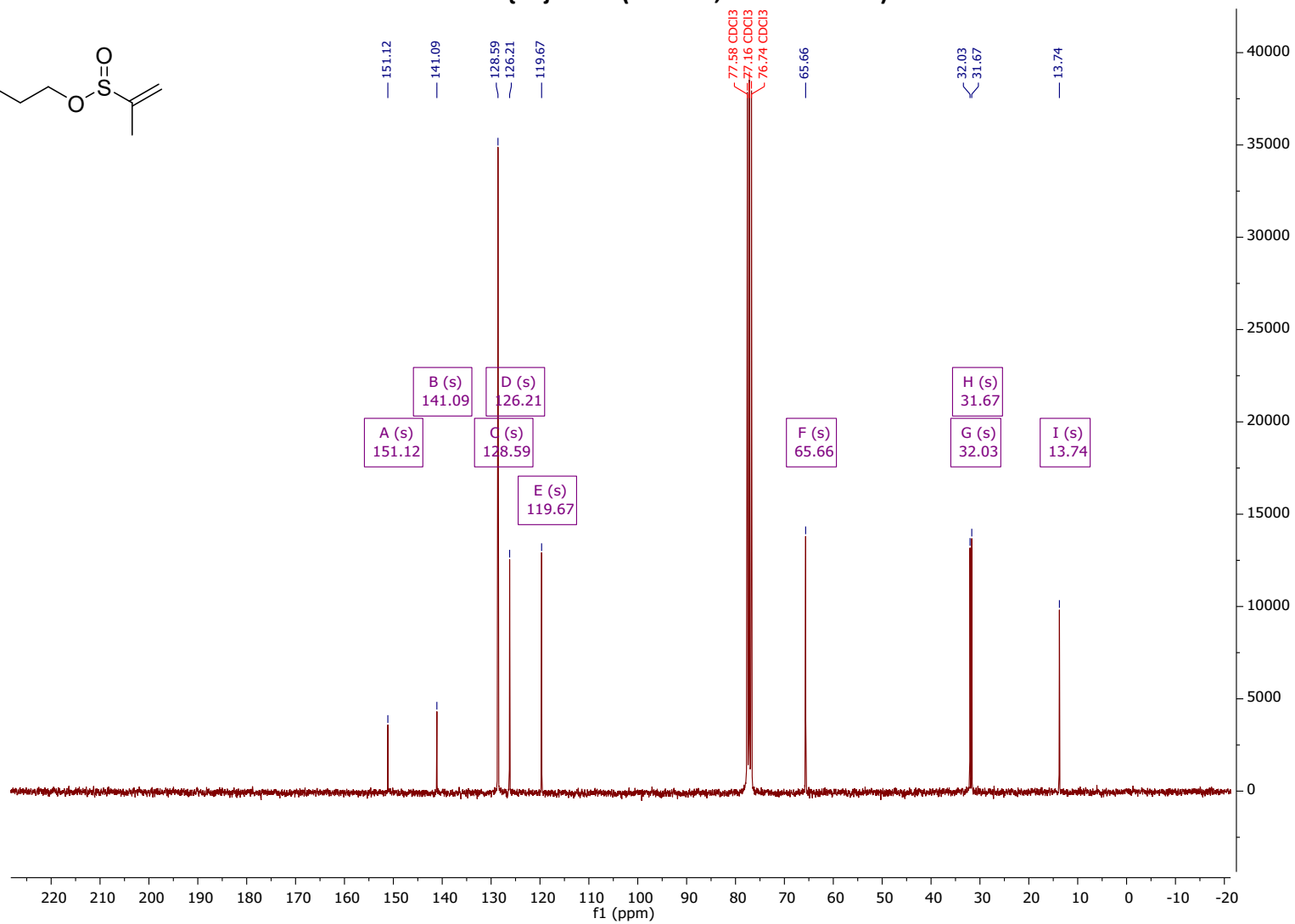


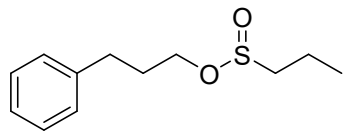
6e ¹H NMR (300 MHz, Chloroform-d)



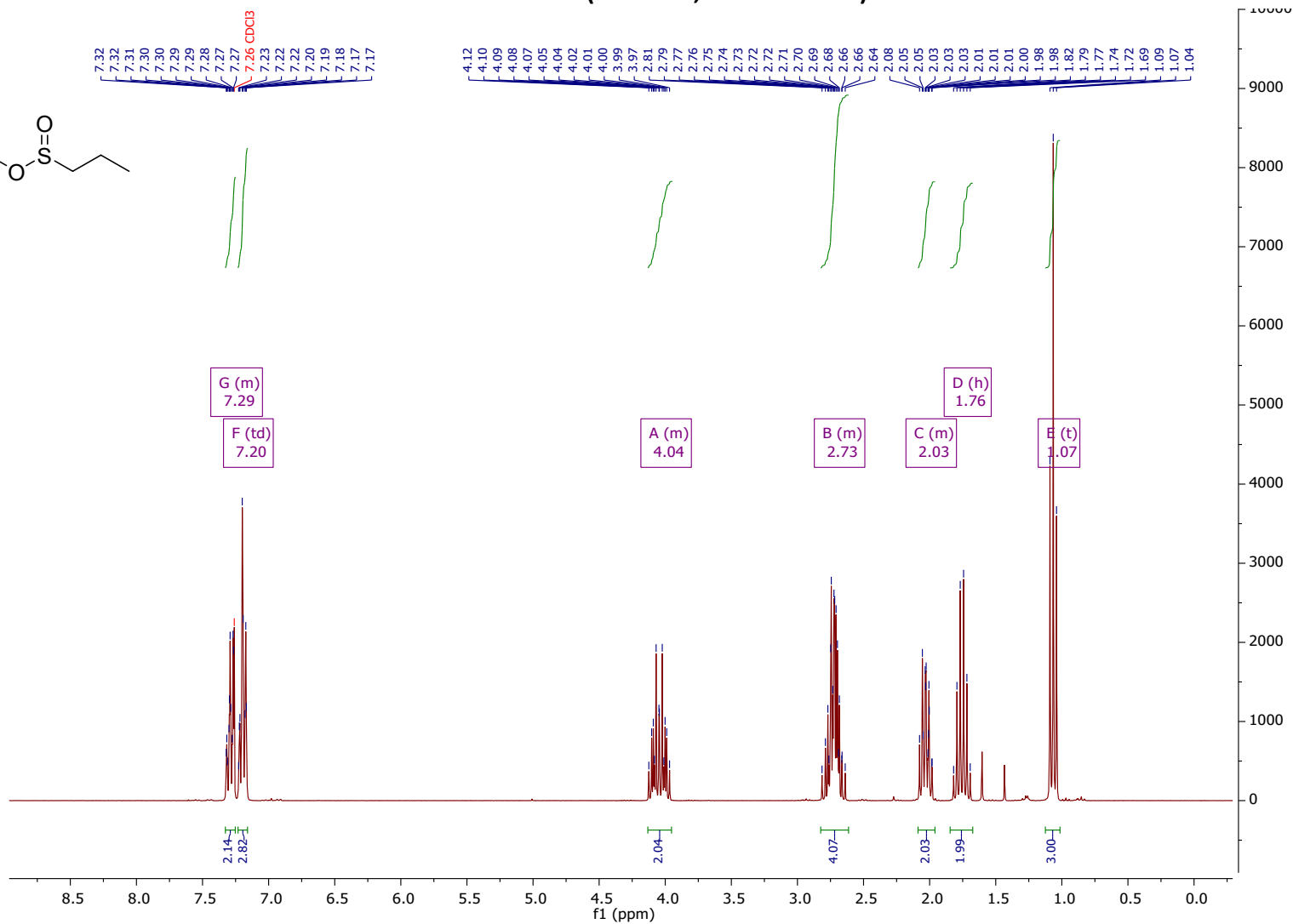


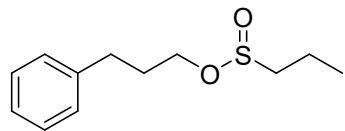
6e $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)



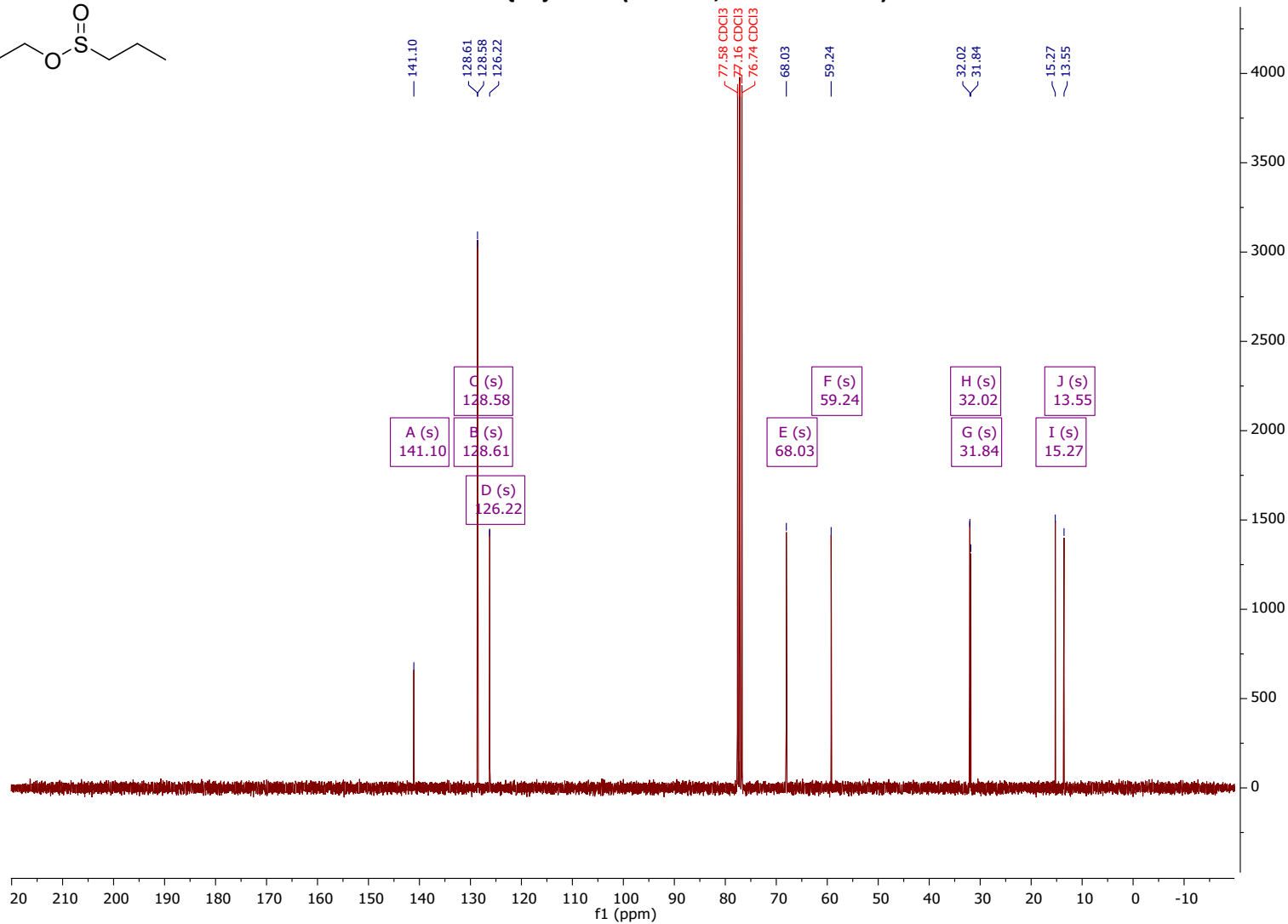


6f ¹H NMR (300 MHz, Chloroform-d)

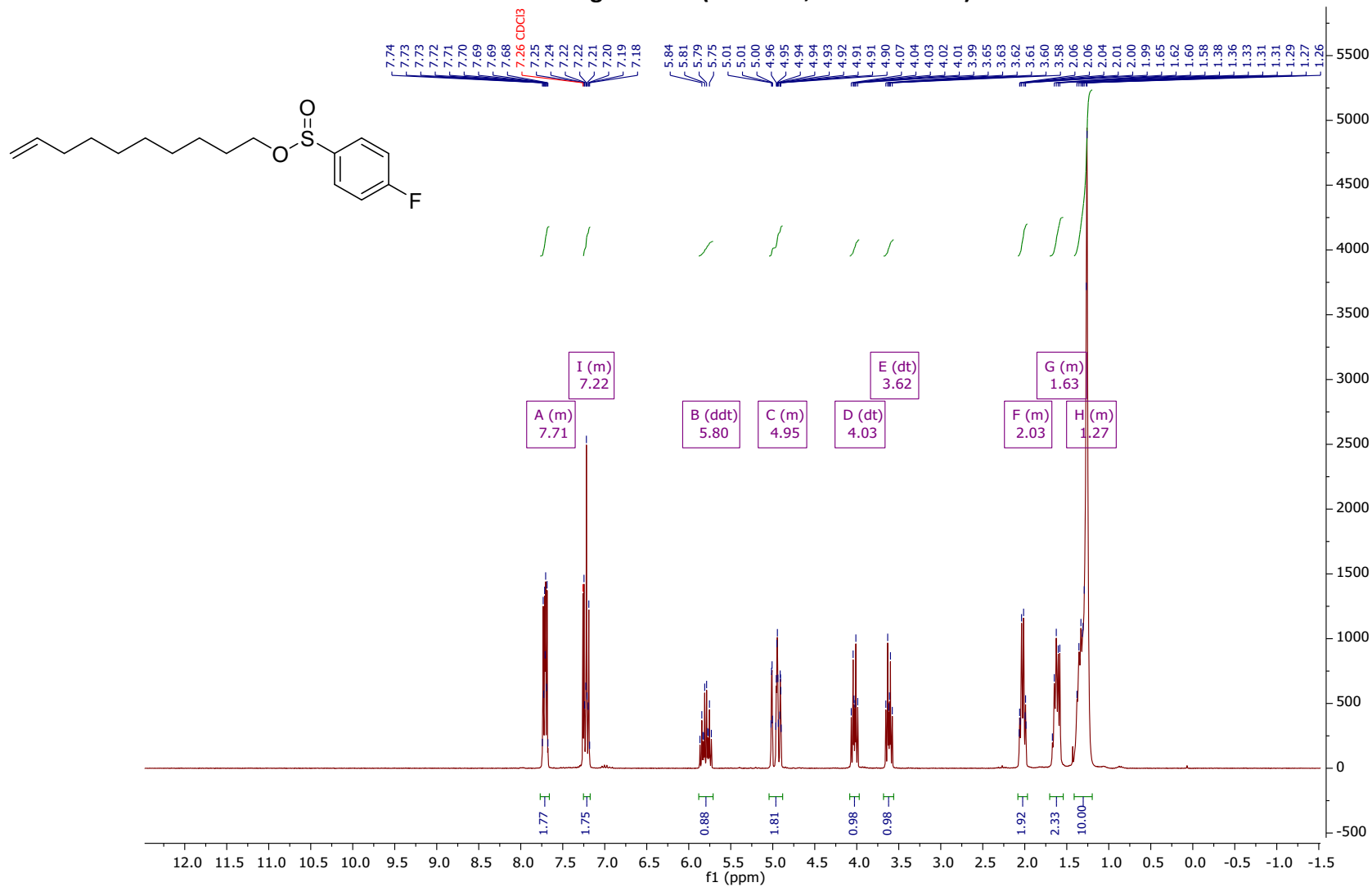




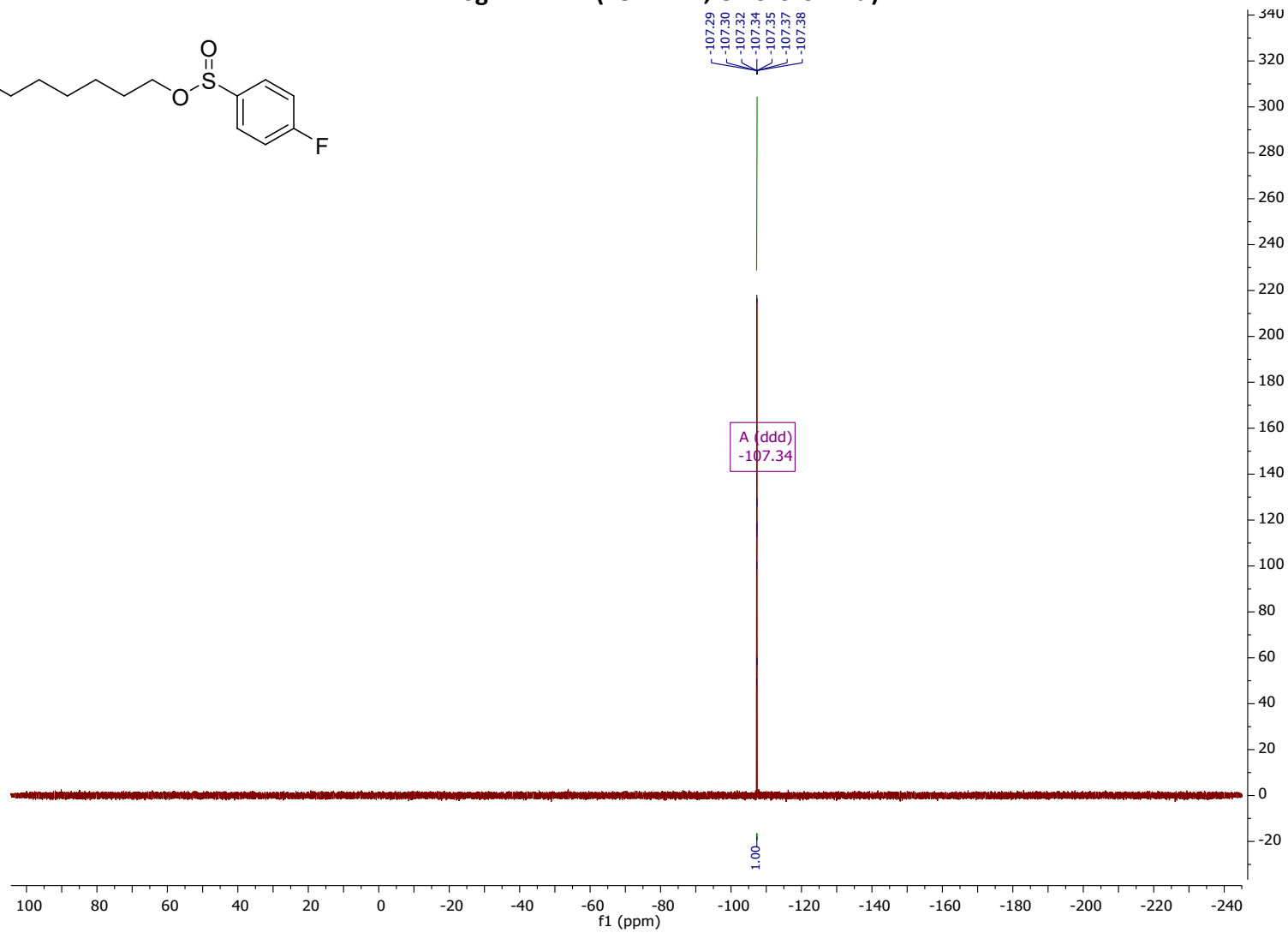
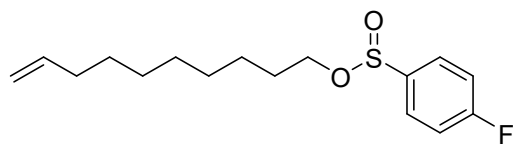
6f $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)



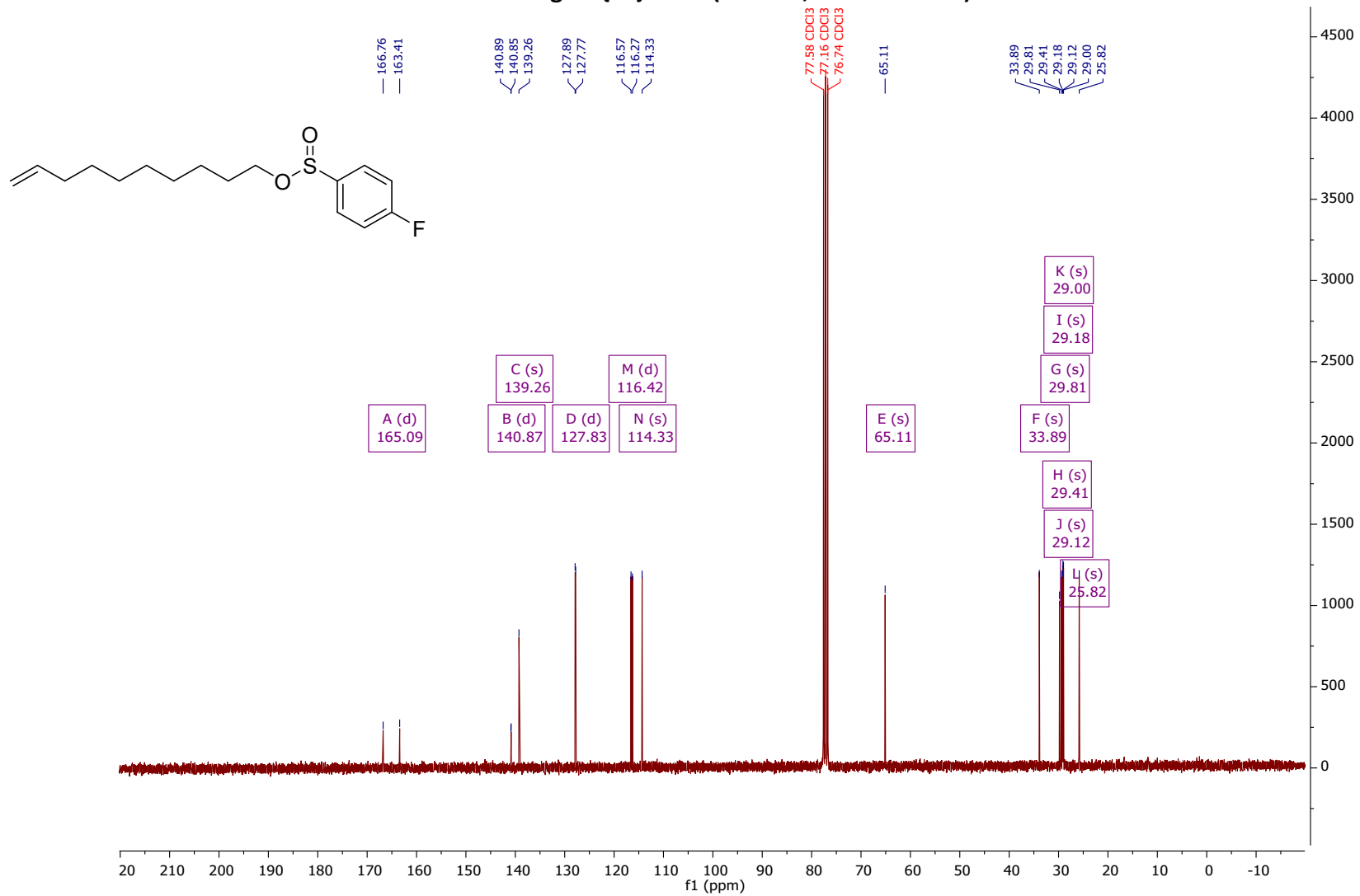
6g ¹H NMR (300 MHz, Chloroform-d)

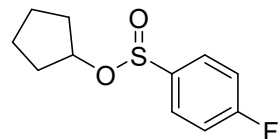


6g ¹⁹F NMR (282 MHz, Chloroform-*d*)

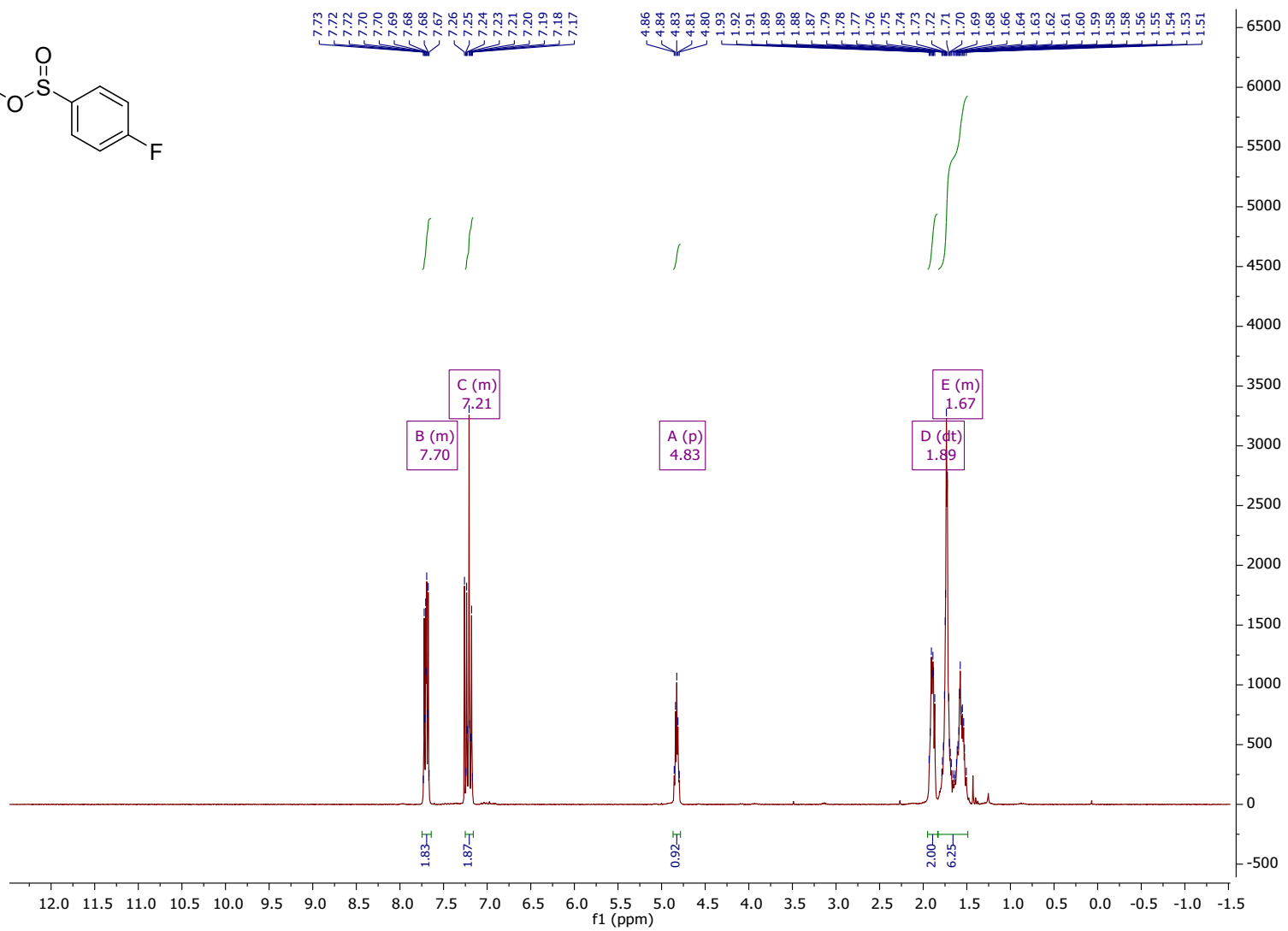


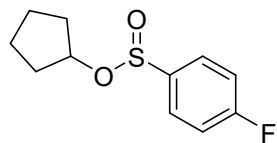
6g $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)



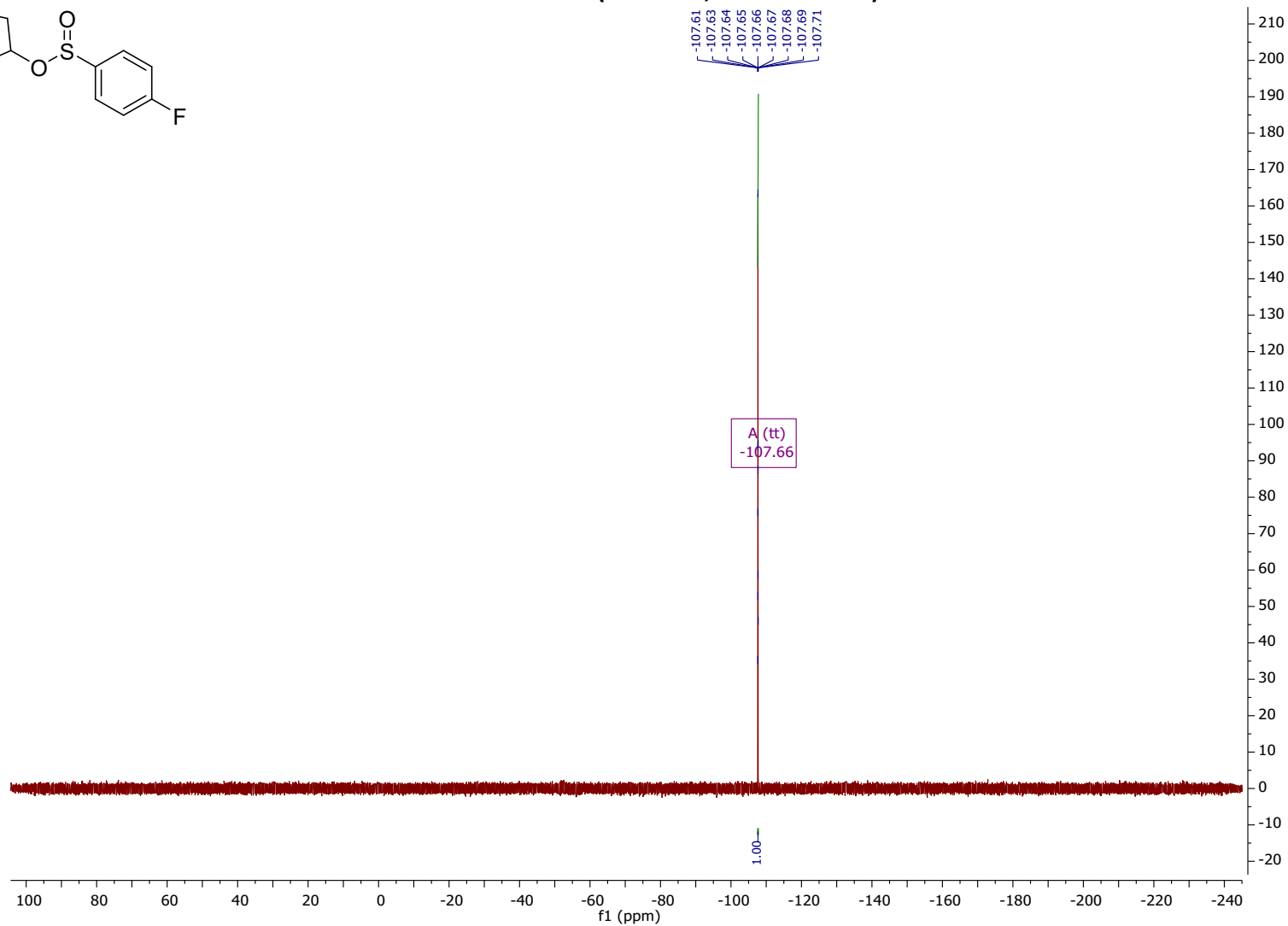


6h ¹H NMR (300 MHz, Chloroform-d)

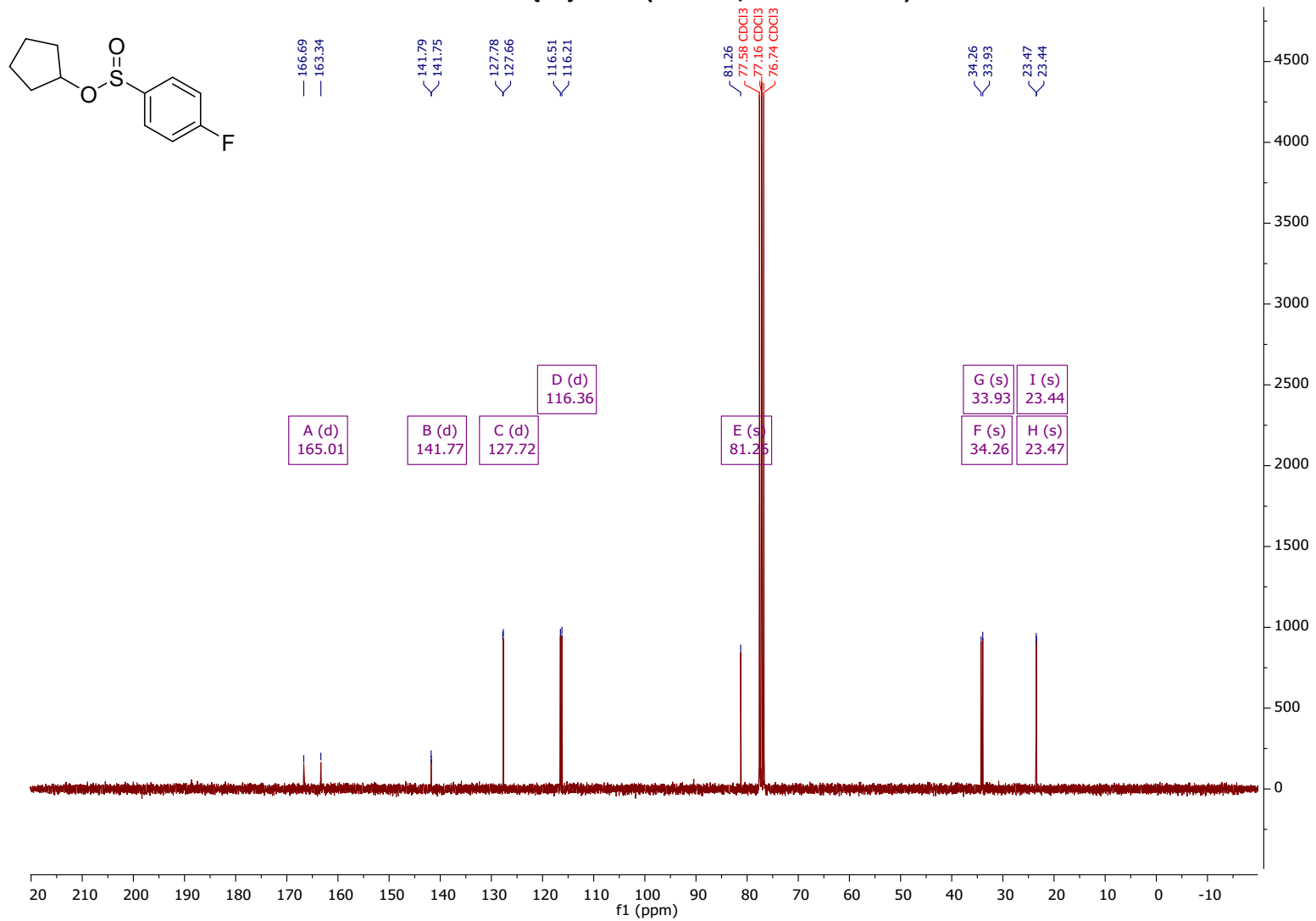




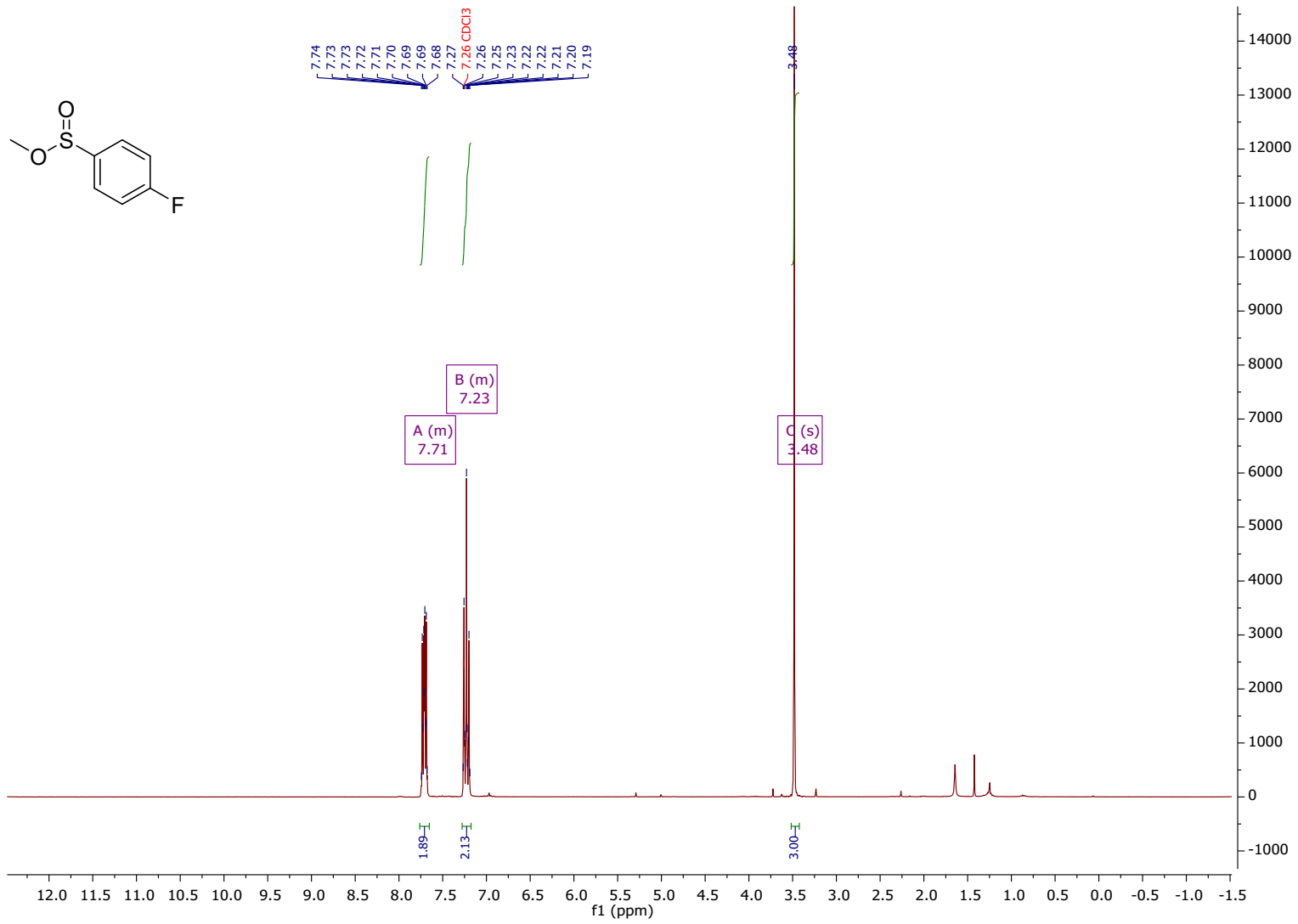
6h ^{19}F NMR (282 MHz, Chloroform-*d*)



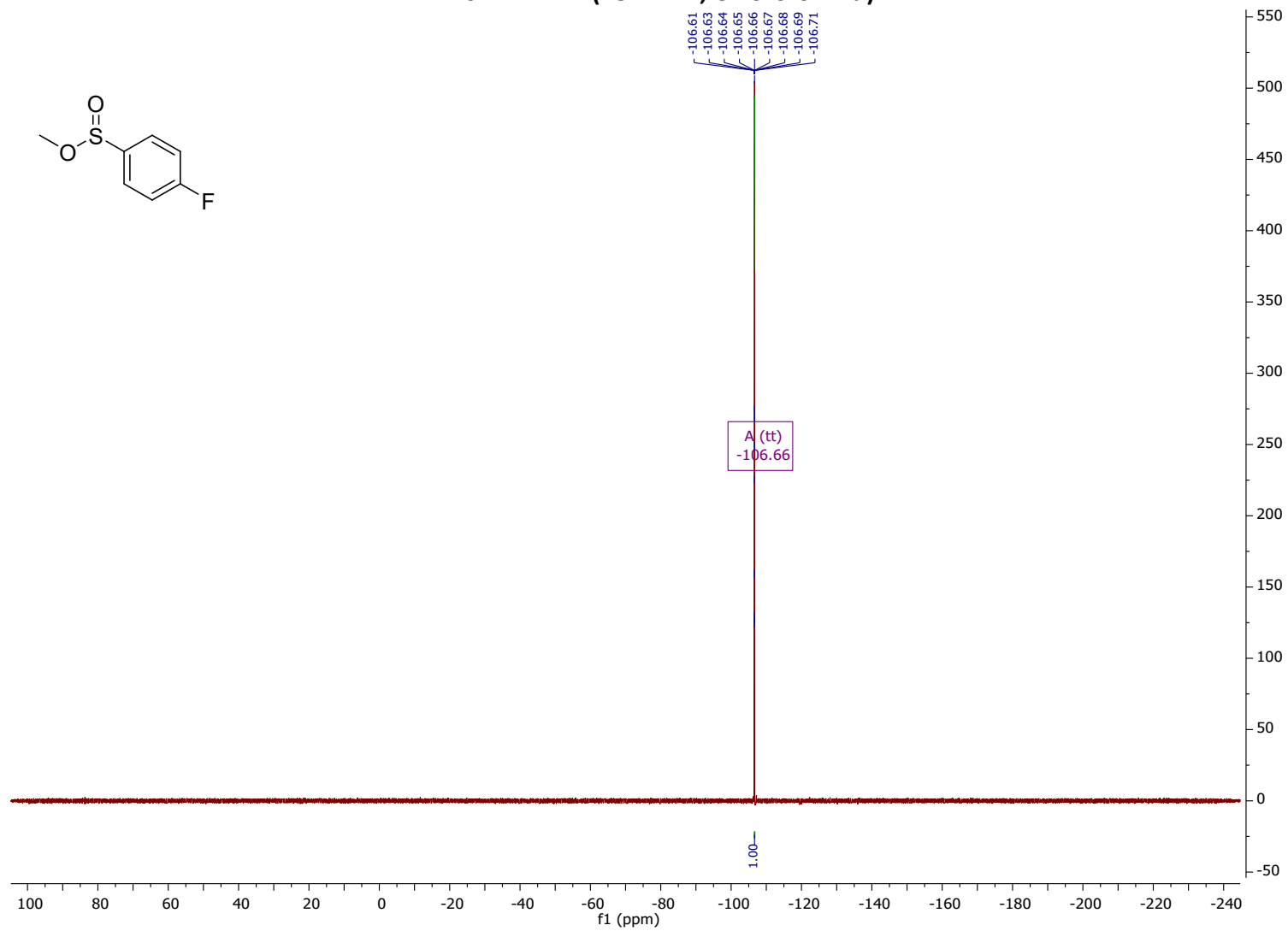
6h $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)



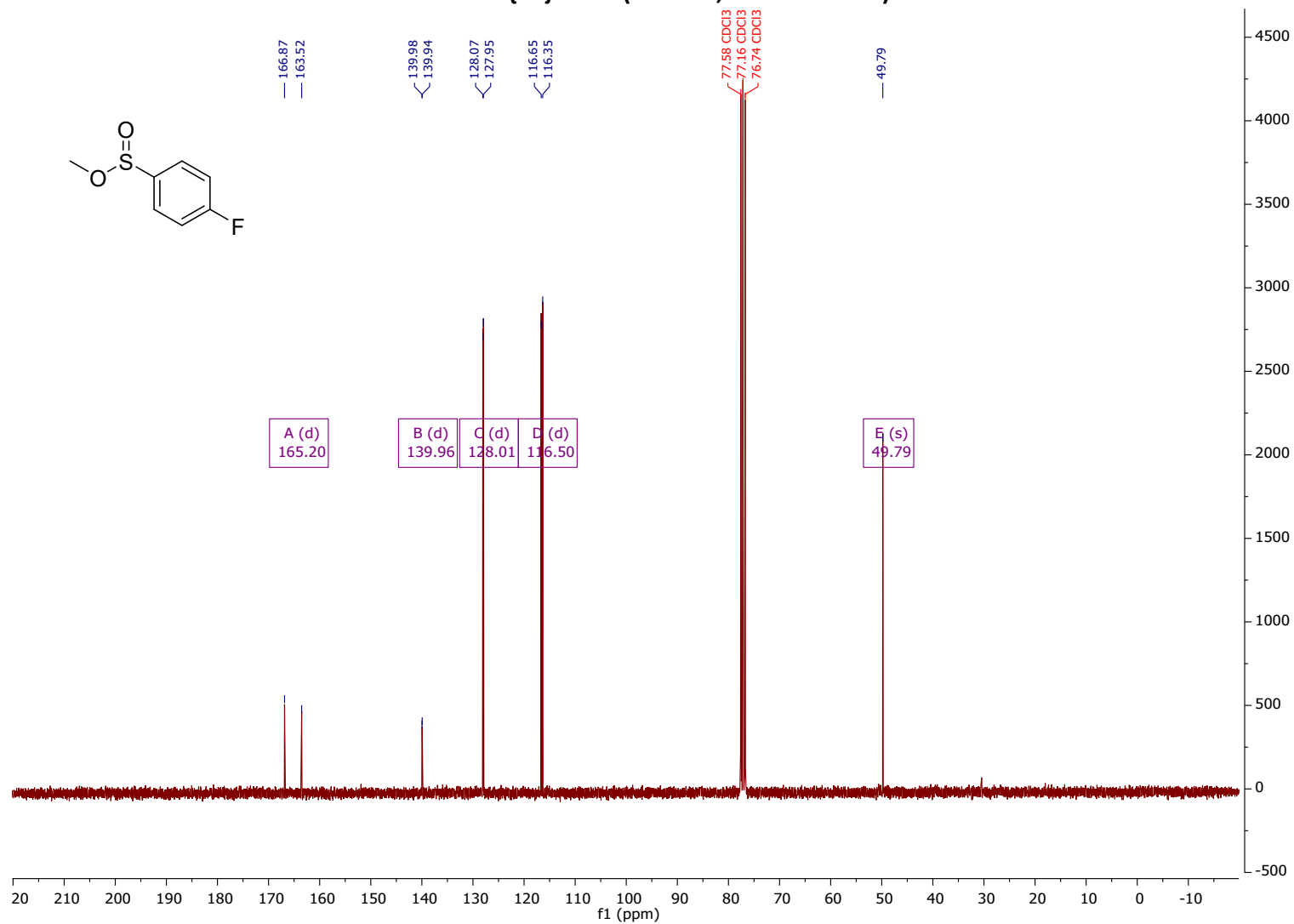
6i ¹H NMR (300 MHz, Chloroform-*d*)



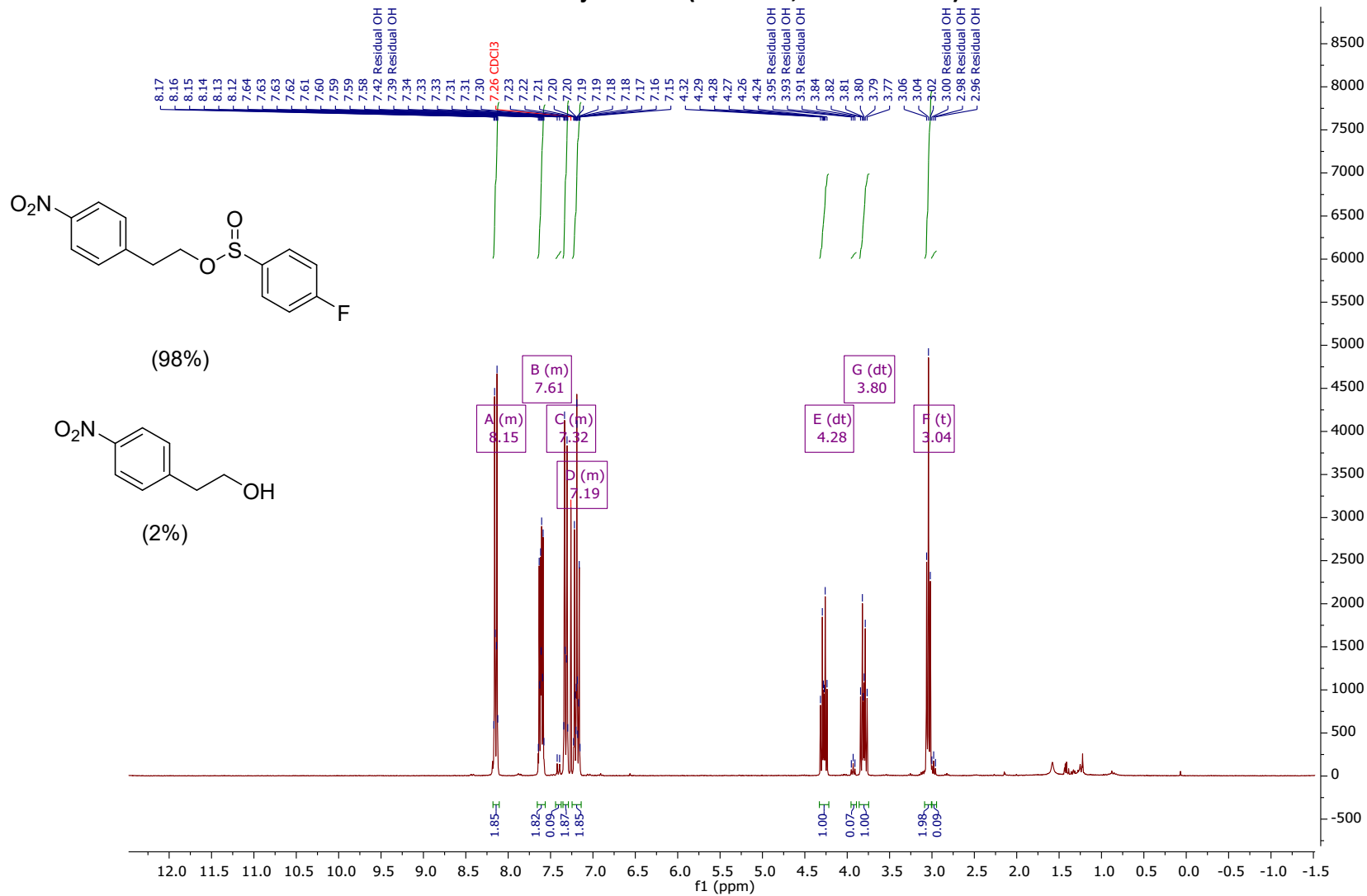
6i ¹⁹F NMR (282 MHz, Chloroform-*d*)

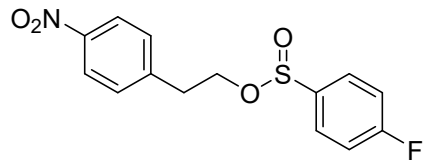


6i ¹³C{¹H} NMR (75 MHz, Chloroform-*d*)

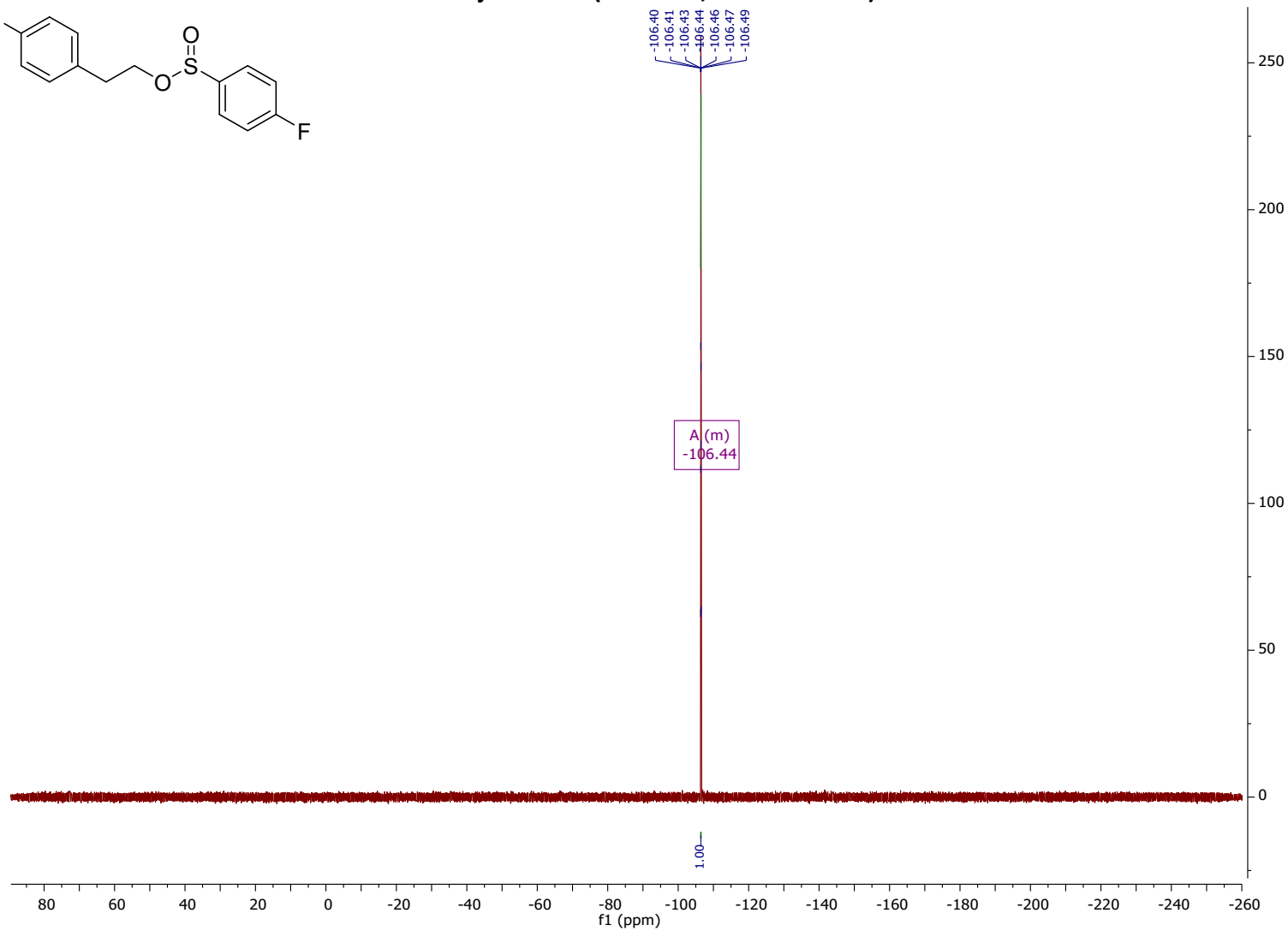


6j ¹H NMR (300 MHz, Chloroform-d)

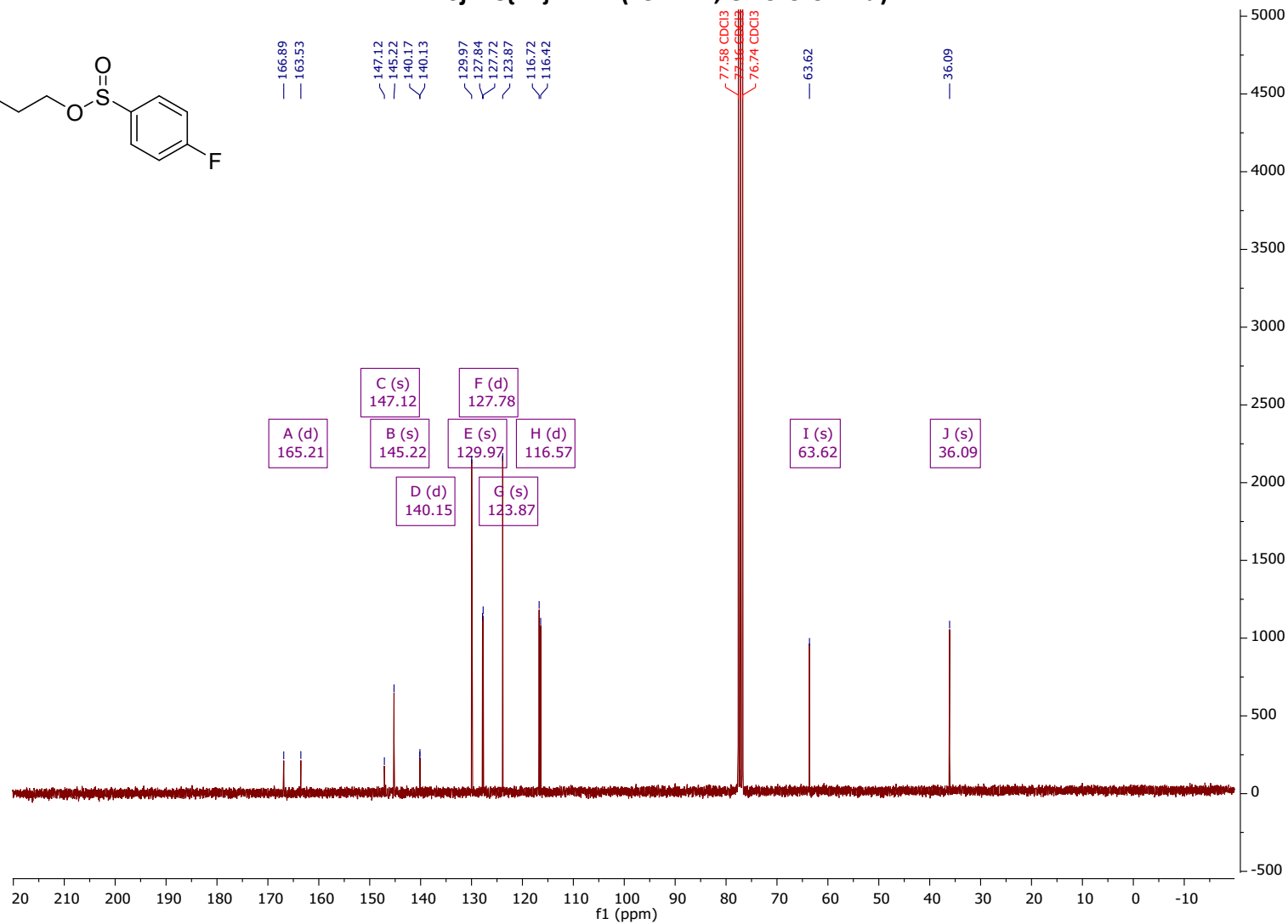
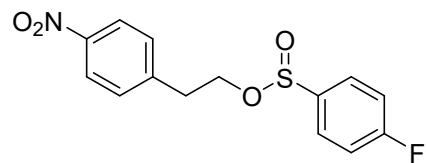


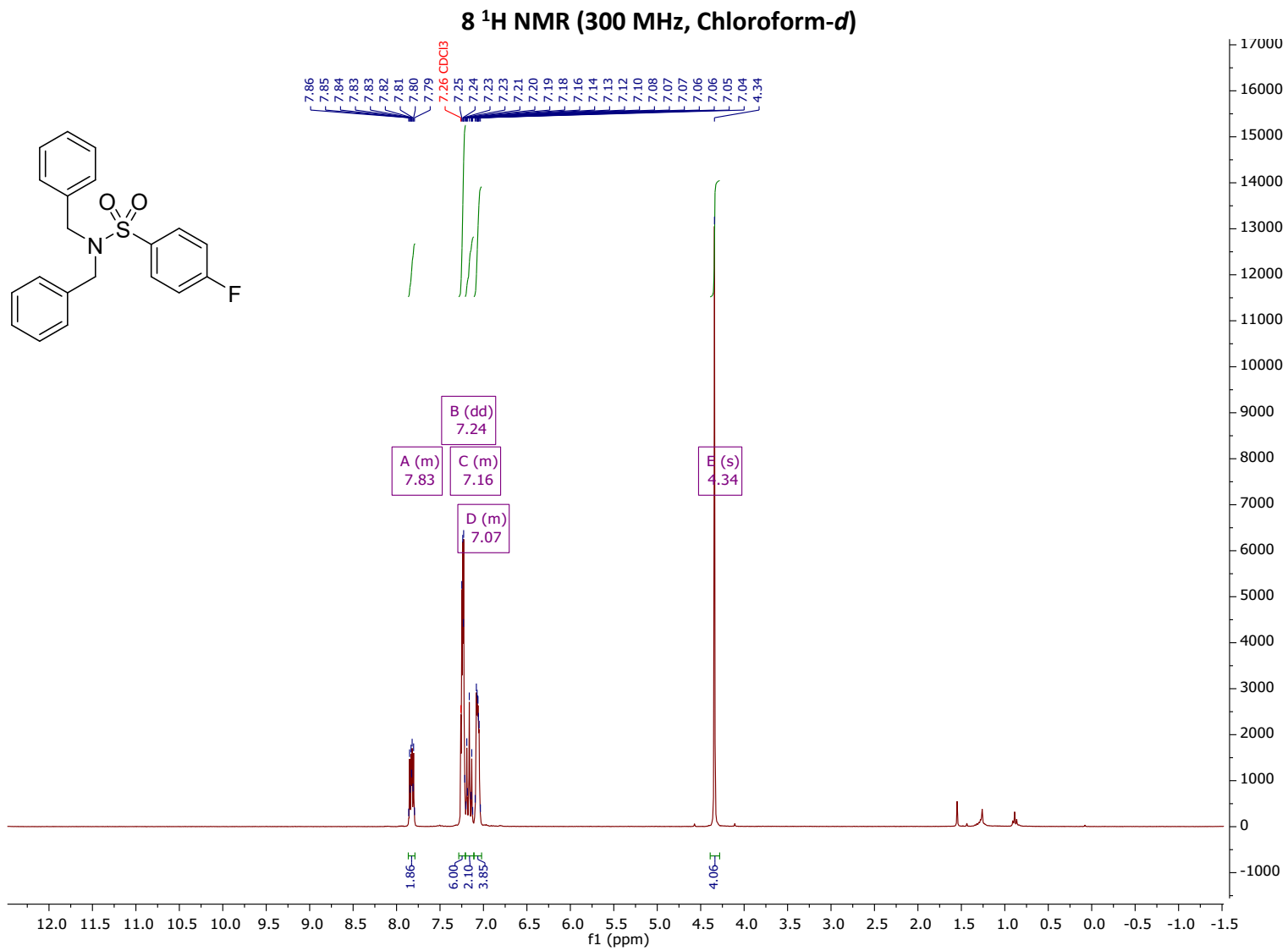


6j ¹⁹F NMR (282 MHz, Chloroform-*d*)

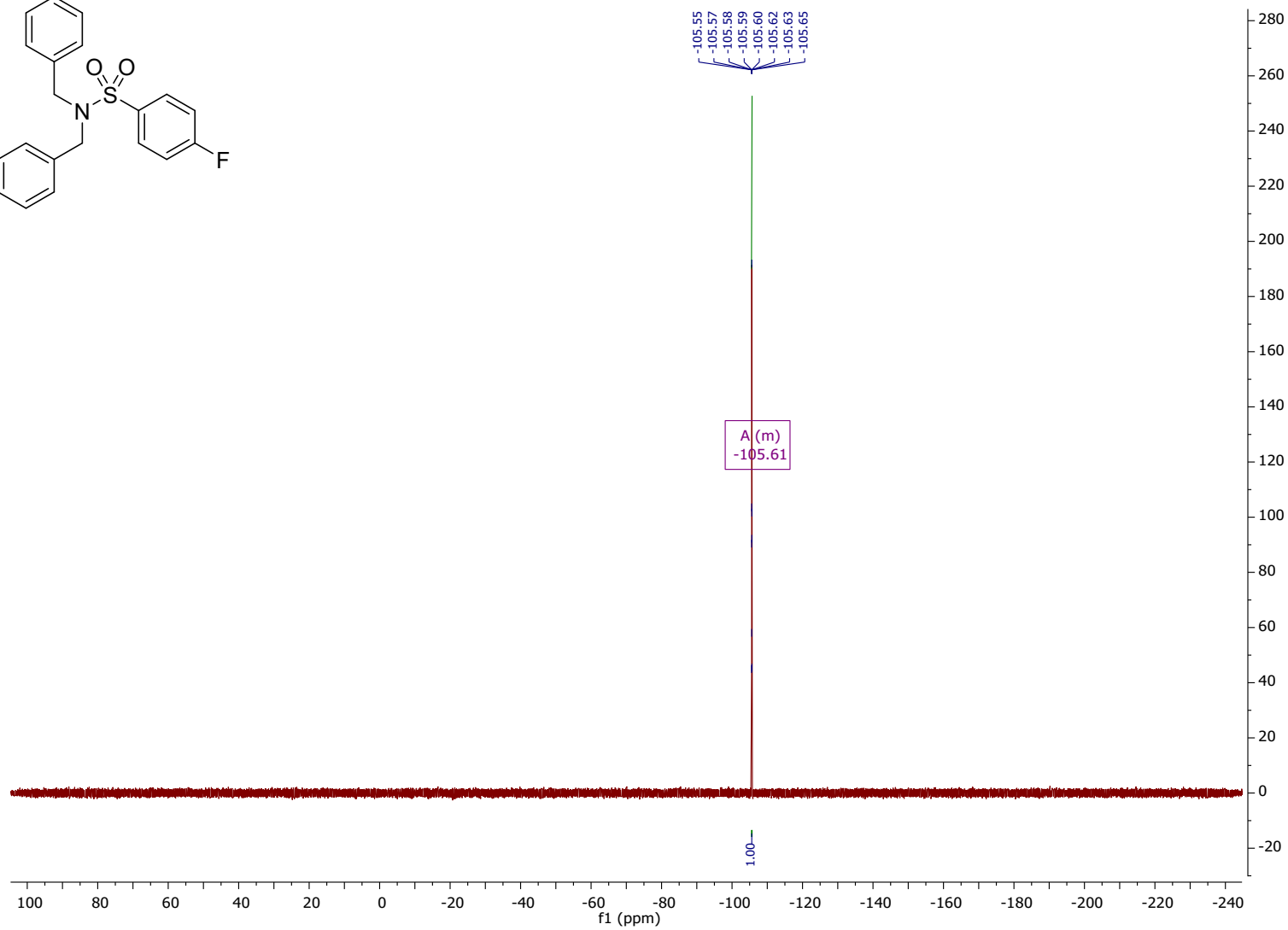
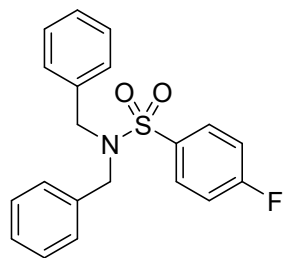


6j ¹³C{¹H} NMR (75 MHz, Chloroform-d)

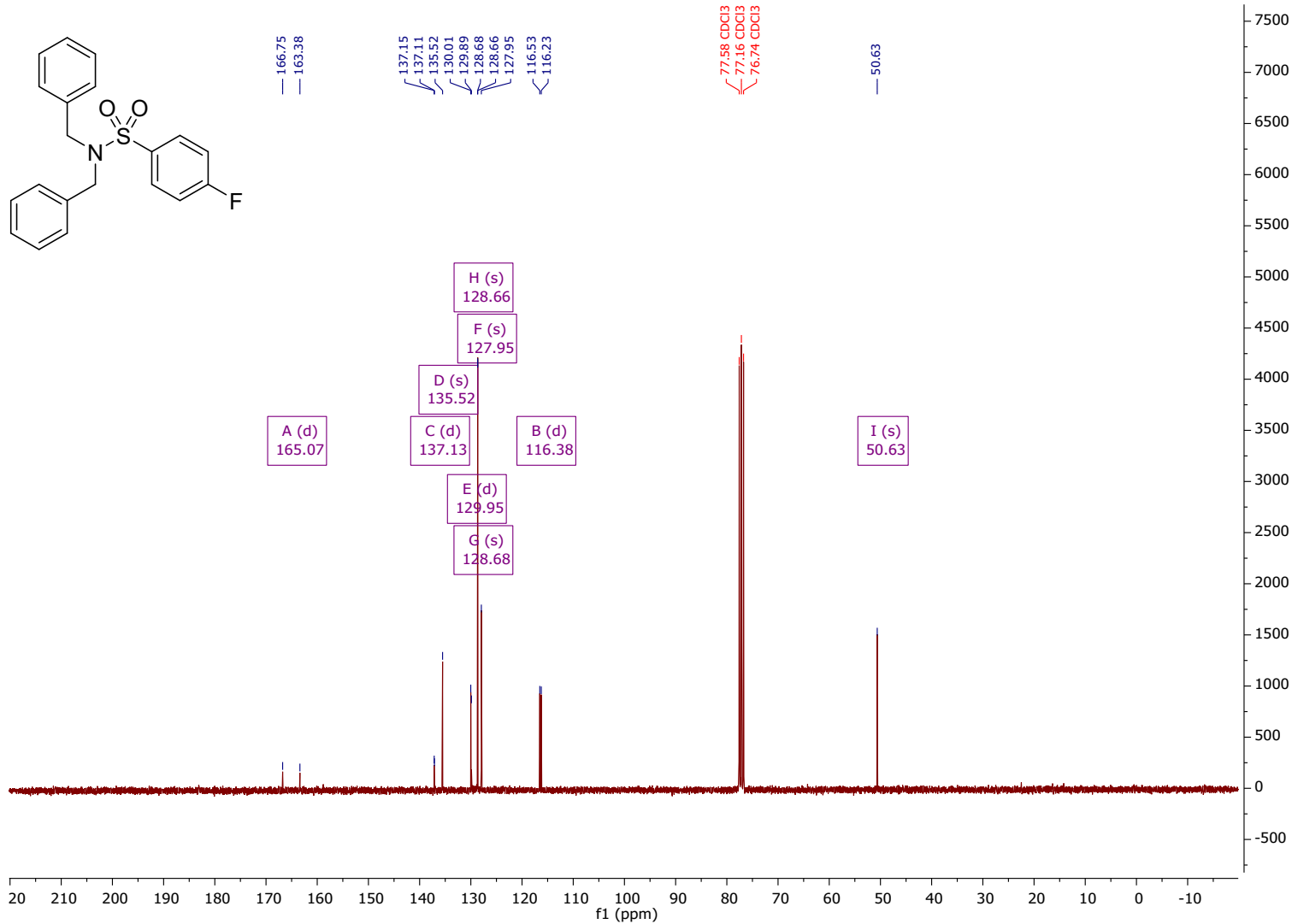


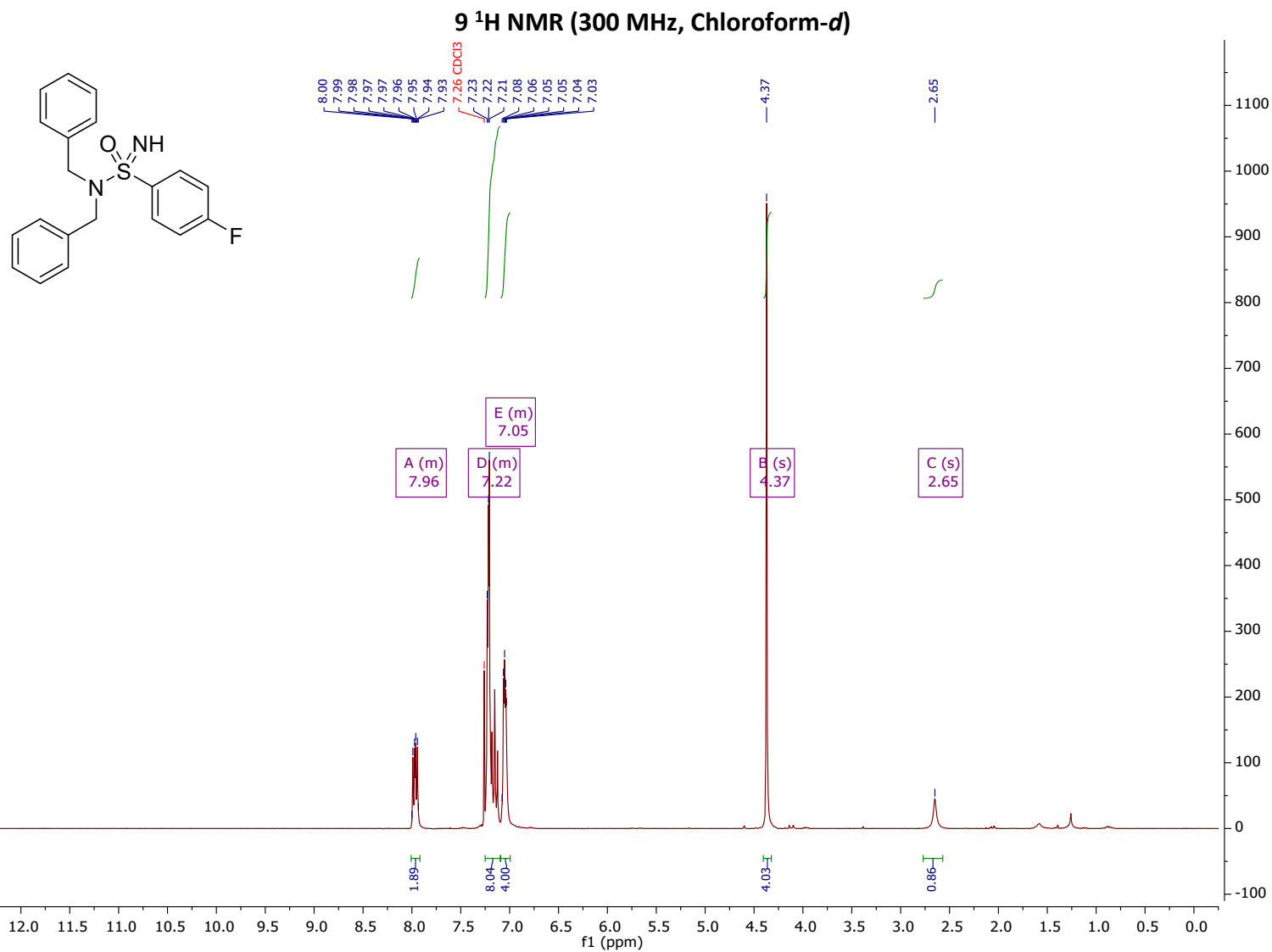


8 ¹⁹F NMR (282 MHz, Chloroform-*d*)

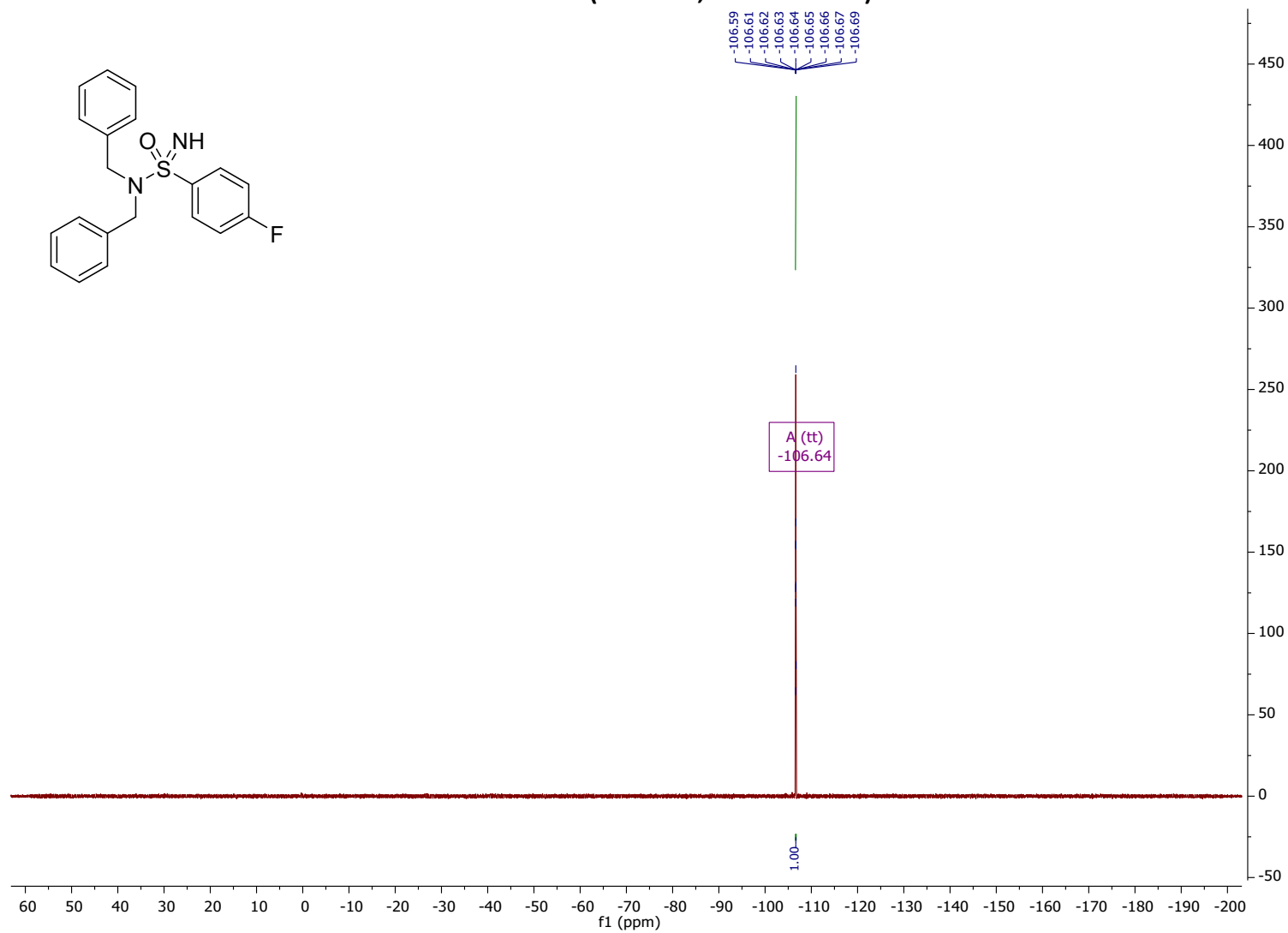


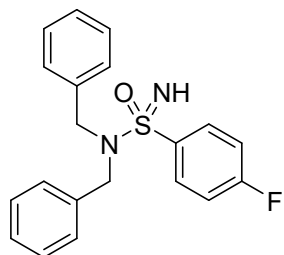
8 $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)



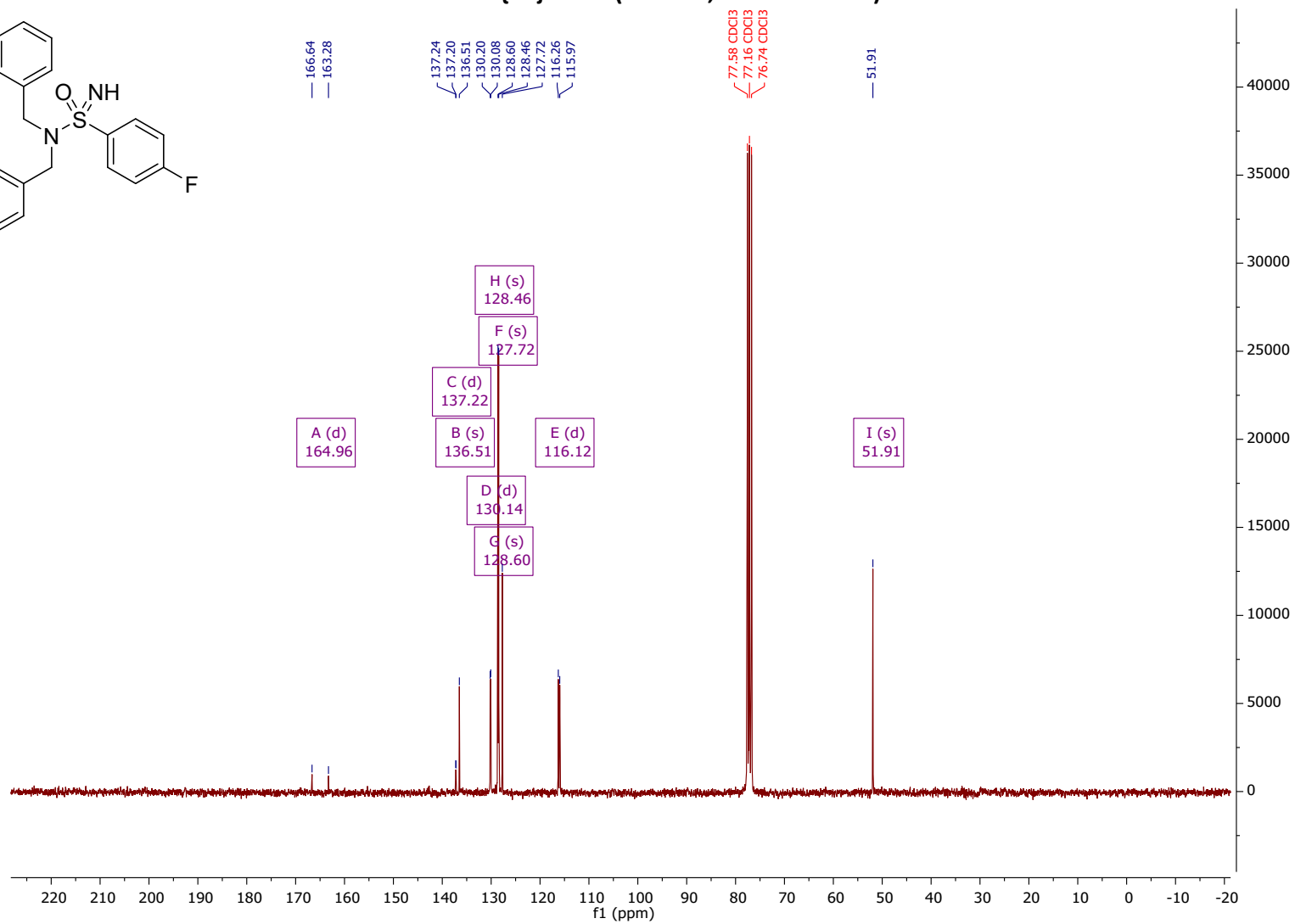


9 ¹⁹F NMR (282 MHz, Chloroform-d)

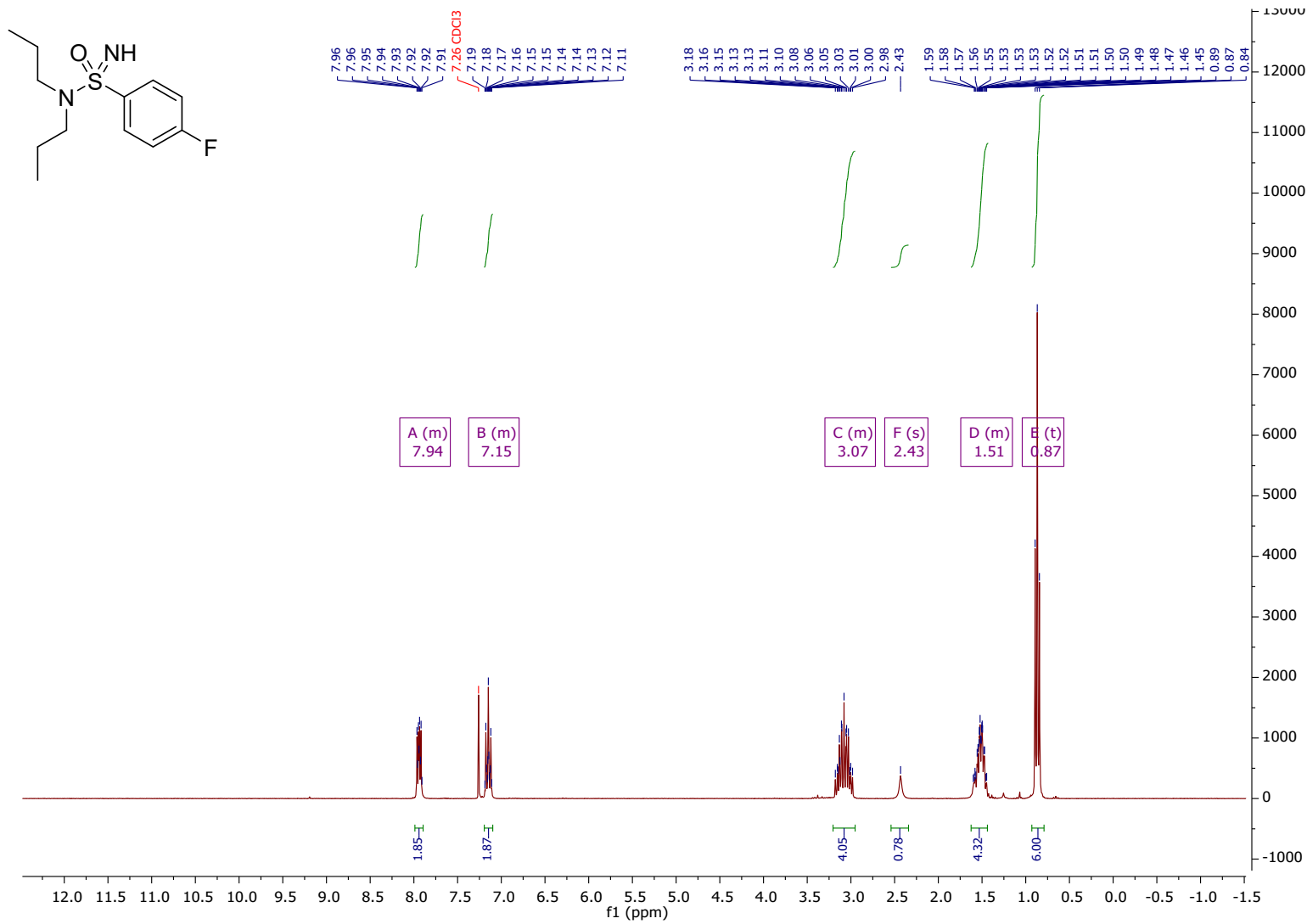


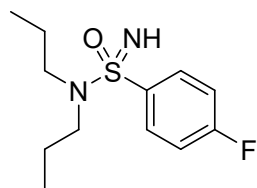


9 $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)

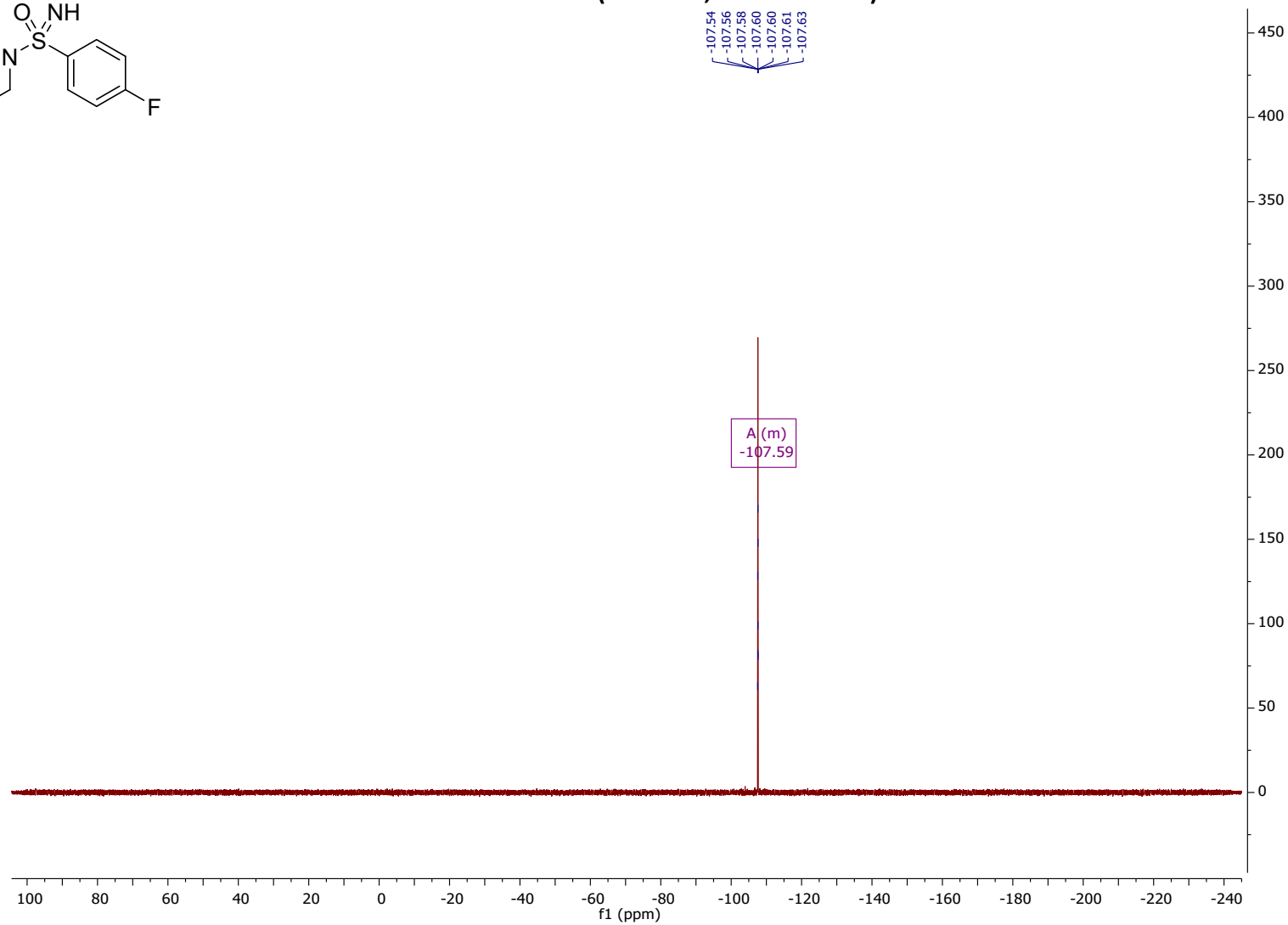


10 ¹H NMR (300 MHz, Chloroform-d)

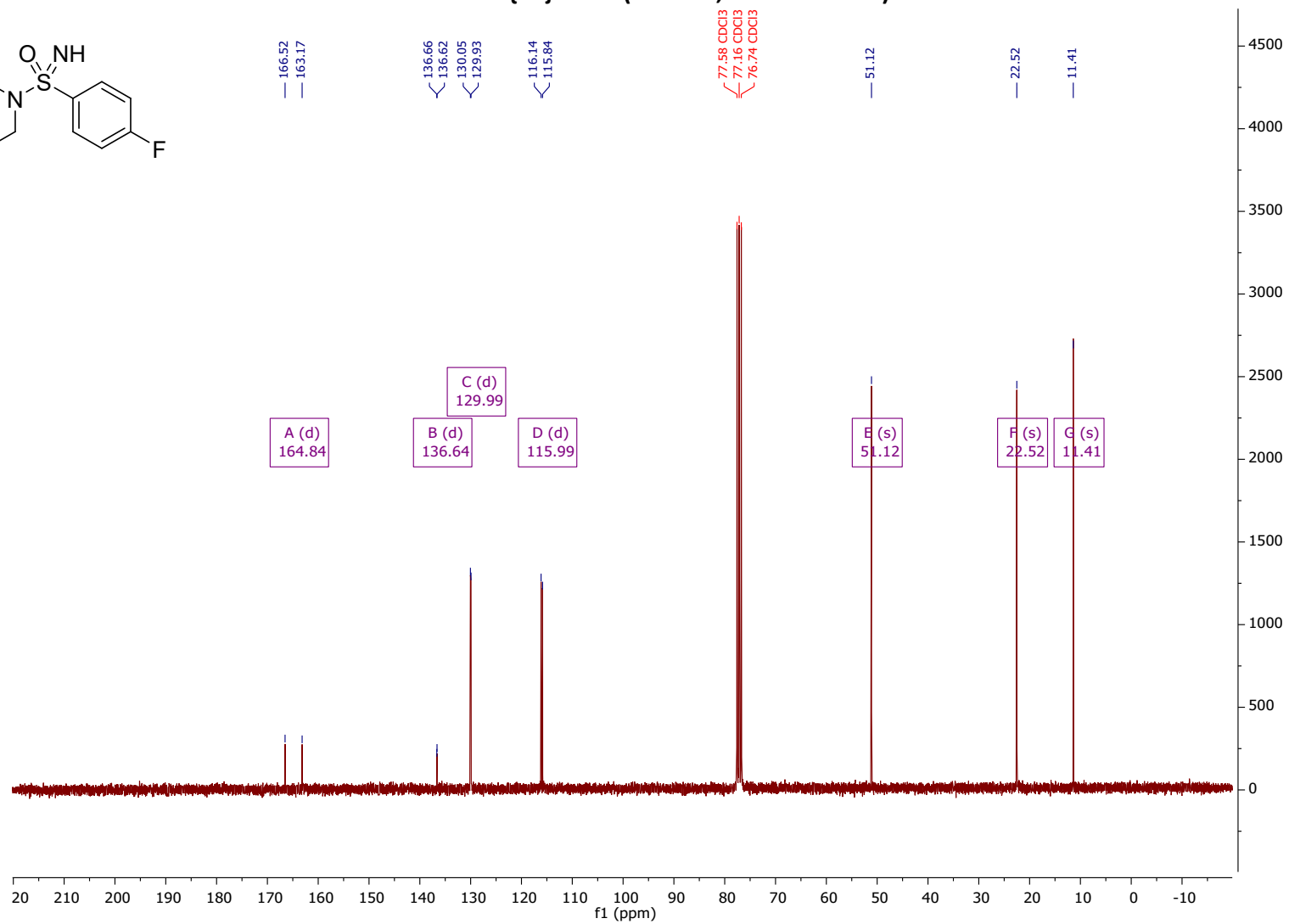
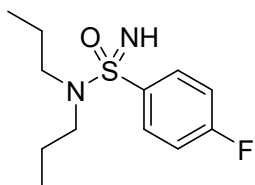


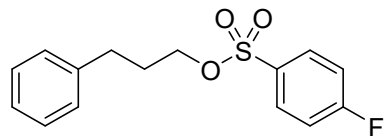


^{19}F NMR (282 MHz, Chloroform-*d*)

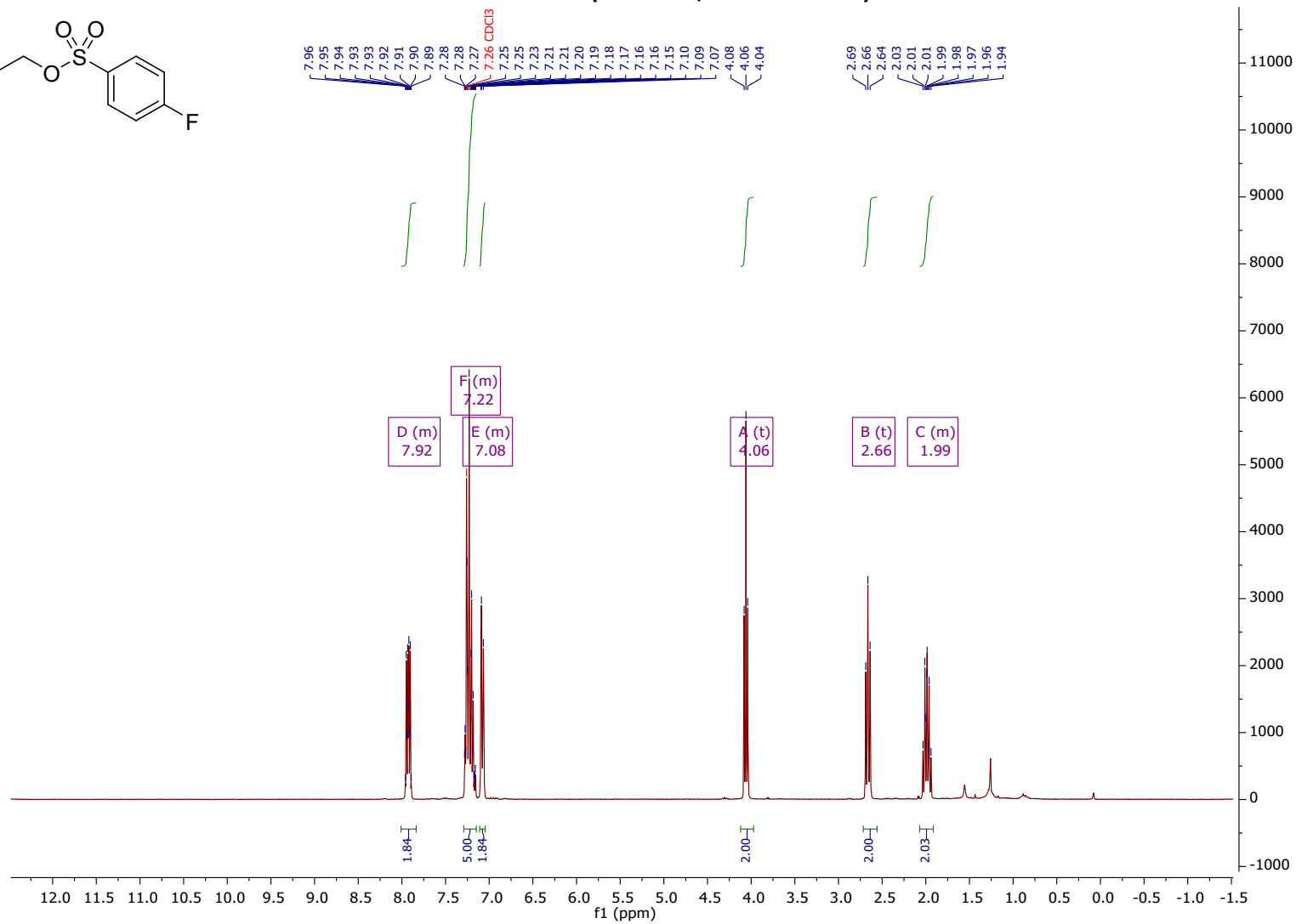


10 ¹³C{¹H} NMR (75 MHz, Chloroform-*d*)

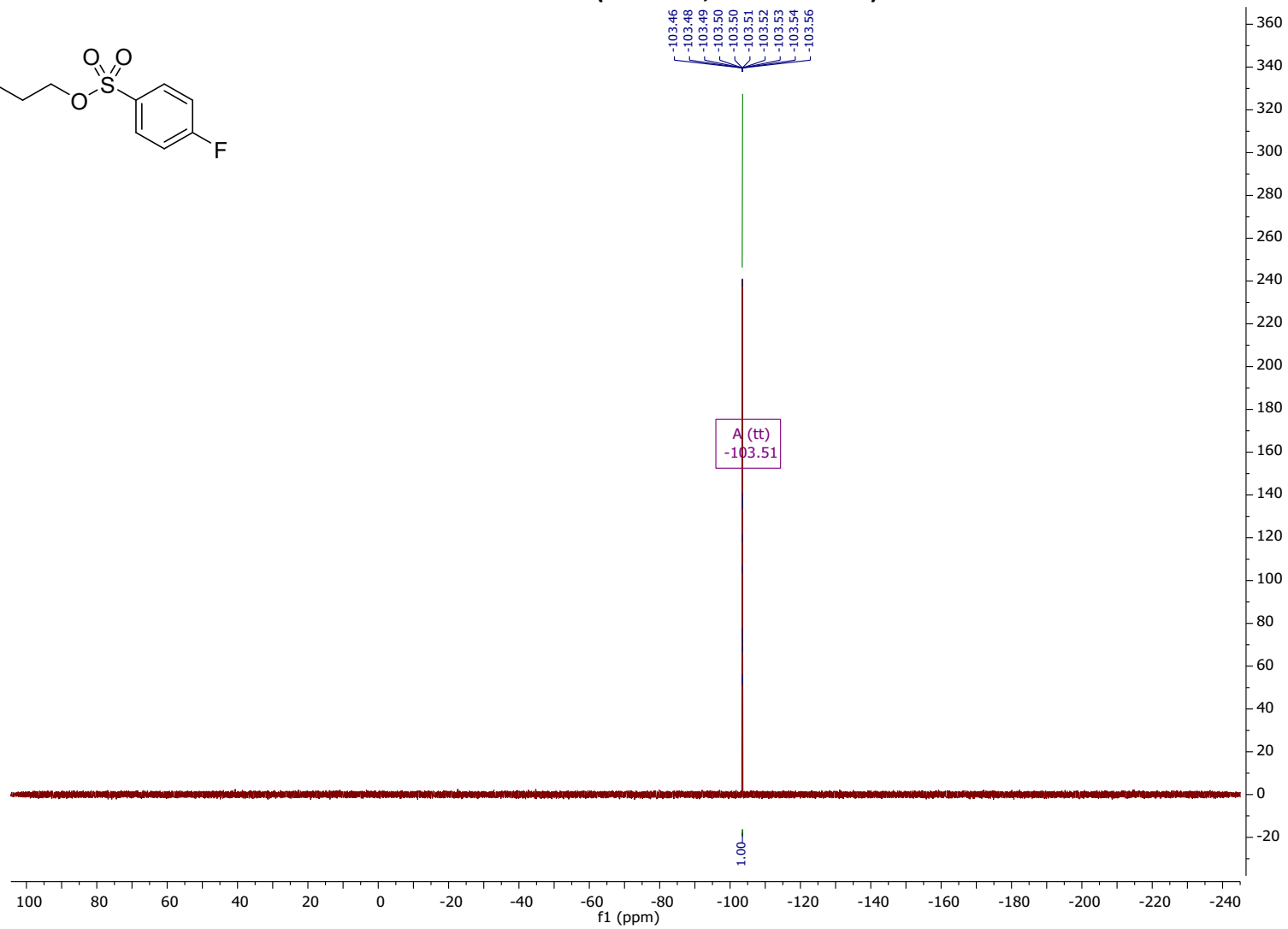
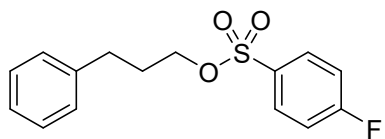




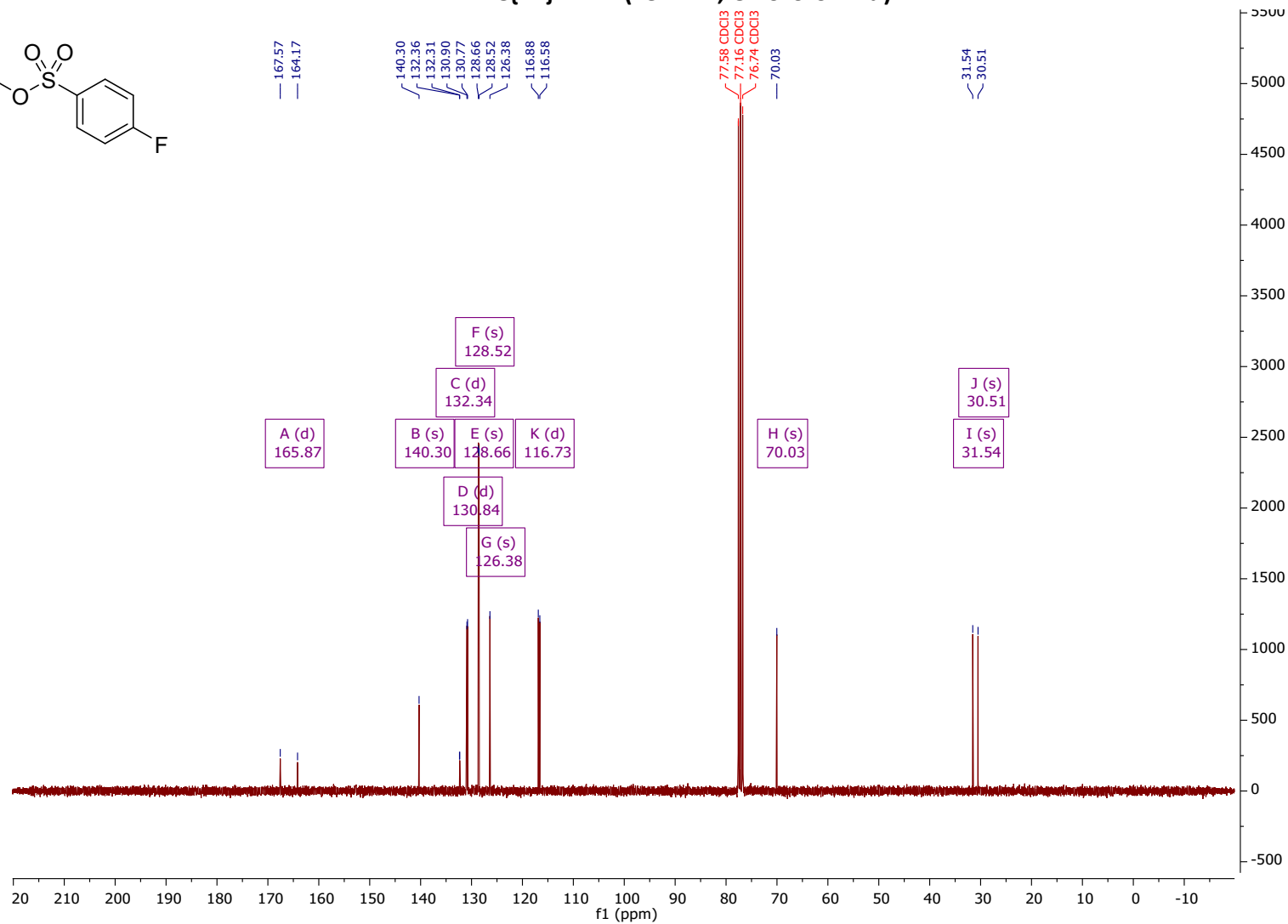
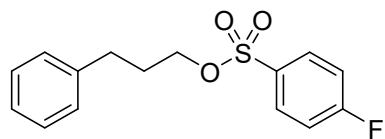
11 ¹H NMR (300 MHz, Chloroform-d)

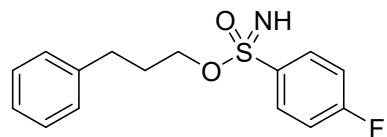


11 ¹⁹F NMR (282 MHz, Chloroform-*d*)

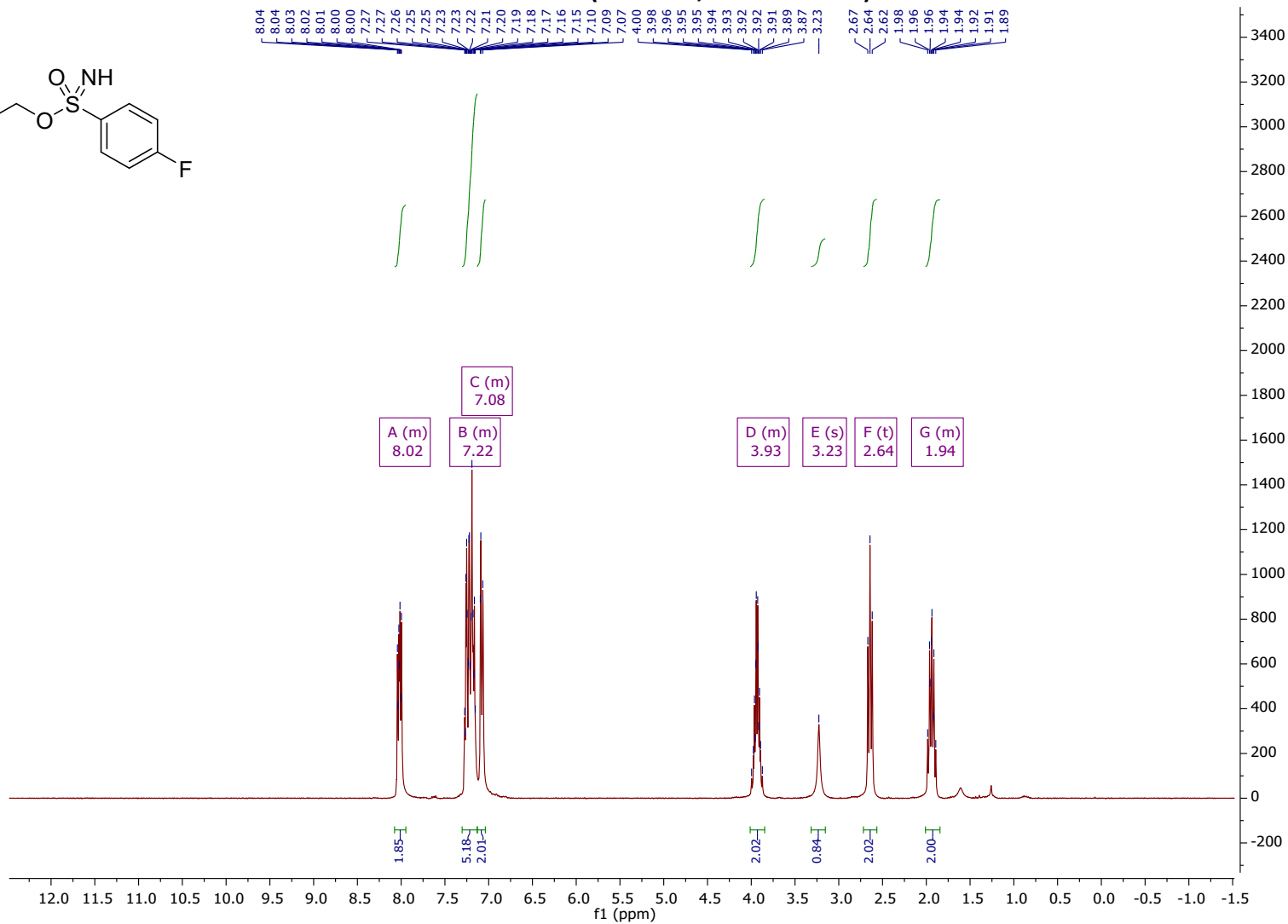


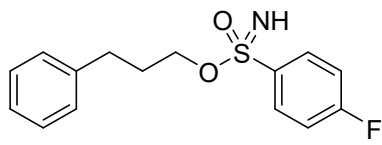
11 $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)



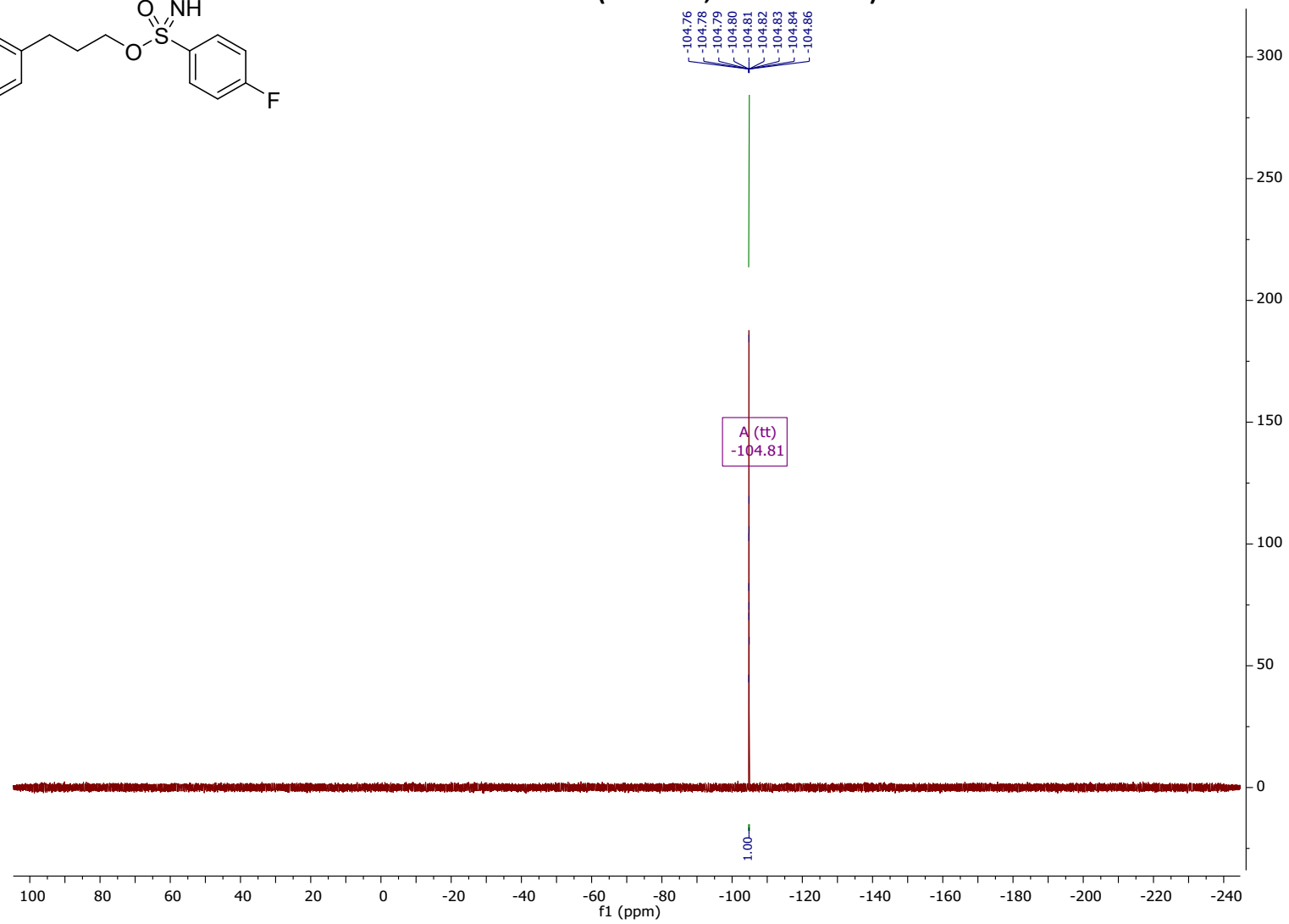


12 ¹H NMR (300 MHz, Chloroform-d)





12 ¹⁹F NMR (282 MHz, Chloroform-*d*)



12 $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, Chloroform-*d*)

