Electronic Supplementary Material (ESI) for Chemical Communications.


Supporting Information

# Facile Synthesis of Sulfonyl Fluorides from Sulfonic acids

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# Contents

# Experimental Protocols and Data

**Materials:** All chemicals were from commercial sources Sigma-Aldrich, TCI, AK Scientific, Enamine, Oakwood Chemical and Alfa Aesar. Reactions were performed in disposable scintillation 20 mL glass vials equipped with PTFE/Silicone septa purchased from ChemGlass Life Sciences LLC, 3.7 mL glass scintillation vials with PTFE lined screw caps, or 20 mL Biotage® microwave reaction vials equipped with Biotage® microwave vial caps. Polyethylene tubing (I.D. 1.67 mm) was purchased 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 16G x 1 ½ (1.6 mm x 40 mm) and 21G x 2 (0.8 mm x 5 mm) were from BD PrecisionGlide™. Hypodermic Needles (22G x 4") were from Air-Tite™. White sleeve stoppers (24 x 40 mm) were from VWR®, white sleeve stoppers (OD 14mm) were from Kimble®, and red Suba-Seal® septa were from Chemglass. Aluminium heating blocks were used for reactions performed at elevated temperatures.

Column chromatography was performed using SiliaFlash F60 (40-64 μm) silica from Silicycle. Thin layer chromatography (TLC) was run on TLC Silica gel 60 $F_{254}$ aluminum sheets from Merck. Flash column chromatography was performed on a Teledyne ISCO CombiFlash NextGen 300 system using a pre-packed 12 g 60 Å silica column.

**Mass Spectrometry:** Low-resolution gas chromatography/mass spectroscopy (GCMS) was performed using an Agilent 5977A MSD coupled to 7890B GC, or Agilent 6890/5972. Low-resolution liquid chromatography/mass spectroscopy (LCMS) was performed on Agilent 1200/6120. High-resolution mass spectra (HRMS) were acquired on a Waters Xevo G2-XS QTOF.

**NMR Spectroscopy:** Proton nuclear magnetic resonance ($^{1}$H NMR) spectra, carbon nuclear magnetic resonance ($^{13}$C NMR) spectra, and fluorine nuclear magnetic resonance ($^{19}$F NMR) spectra were obtained on a Bruker AV-300 or Bruker 400 spectrometer. $^{1}$H, $^{13}$C, and $^{19}$F NMR chemical shifts are reported in parts per million (ppm) relative to the residual solvent peak ($CDCl_3$: $^{1}$H: δ = 7.26 ppm, $^{13}$C: δ = 77.16 ppm), $(CD_3)_2SO$: $^{1}$H: δ = 2.50 ppm, $^{13}$C: δ = 39.52 ppm). $^{19}$F NMR chemical shifts were referenced to $CFCl_3$. All $^{19}$FNMR yields were determined using $PhCF_3$ as an internal standard. Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (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.

**Example Procedure for $^{19}$F NMR Spectroscopy Yield Determination**

To the reaction mixture containing substrate (0.5 mmol) was added $PhCF_3$ (29.2 mg, 0.2 mmol). The mixture was stirred for 20 seconds before an aliquot was removed by syringe and diluted in $CDCl_3$. Four scans and a relaxation delay of 40 seconds were used with the spectrum center set between the substrate and $PhCF_3$ shifts. Example calculation:

$$\left(\frac{\left(\frac{integration\ of\ product}{number\ of\ product\ F\ nuclei}\right)}{\left(\frac{integration\ of\ internal\ standard}{number\ of\ internal\ standard\ F\ nucleo}\right)}\right)\left(\frac{\frac{mass\ of\ internal\ standard\ (g)}{internal\ standard\ MW\ (g\ mol^{-1})}}{\frac{mass\ of\ subtrate\ (g)}{substrate\ MW(g\ mol^{-1})}}\right)\times 100 = Yield\ (\%)$$

# General Methods and Protocols

### Method for $SOF_2$ generation in DMF (7 mL Scale)

2 × 20 mL vials capped with PTFE/Silicone septa were connected by an imidazole-filled 10 mL syringe. To vial A was added $KHF_2$ (1.8g, 23 mmol, 3 equiv) and to vial B was added DMF (7 mL) and a magnetic stir-bar. Vial A was charged with thionyl chloride (0.6 mL, 8.2 mmol, 1 equiv), leaving the syringe (3 mL) in the septum. The gas generation slowly increased in rate over the space of 30 minutes until the system pressure started to push the 3 mL syringe plunger, at which point an empty balloon was added to vial B. Vial B was stirred until the gas generation subsided. This method of generation was previously reported by our group.[1]

$SOF_2$ reacts with DMF at room temperature: decreasing the concentration of $SOF_2$ dissolved in DMF over time and varying the concentration between each generation. Immediate quantification of $SOF_2$ in DMF by $^{19}F$ NMR spectroscopy led to an average concentration of 0.2M.

Note: $SOF_2$ is a toxic gas and can act as a HF releaser. All work should be performed in a fume hood and precautions should be made to avoid any contact with skin.

### General Method A: Sulfonyl fluoride synthesis from sulfonic acid pyridinium derivatives using DMF-dissolved thionyl fluoride solution

To a 20 mL microwave vial equipped with a magnetic stir-bar was added pyridinium sulfonic acid (0.5 mmol, 1 equiv) and $SOF_2$ dissolved in DMF (7 mL, 0.2 M, 1.4 mmol). The microwave vial was capped with a Biotage® septum and heated to 130 °C for 1 hour before the solution was cooled, vented, and the crude yield determined by $^{19}F$ NMR spectroscopy using trifluorotoluene as an internal standard. The solution was diluted in DCM (20 mL), washed with $H_2O$ (25 mL) and brine (25 mL), dried over magnesium sulfate, and concentrated under reduced pressure to afford brown oils. Products were subsequently isolated by flash column chromatography.

### General Method B: Sulfonyl fluoride synthesis from sulfonic acid sodium salt derivatives using DMF-dissolved Thionyl fluoride solution

To a 20 mL microwave vial equipped with a magnetic stir-bar was added sulfonic acid sodium salt (0.5 mmol, 1 equiv) and $SOF_2$ dissolved in DMF (7 mL, 0.2 M, 1.4 mmol). The microwave vial was capped with a Biotage® septum and purged with argon. $BF_3{\bullet}OEt_2$ (123 µL, 1 mmol, 2 equiv) was charged and the vial was immediately heated to 130 °C for 1 hour before the solution was cooled, vented, and the crude yield determined by $^{19}F$ NMR spectroscopy using trifluorotoluene as an internal standard. The solution was diluted in DCM (20 mL), washed with $H_2O$ (25 mL) and brine (25 mL), dried over magnesium sulfate, and concentrated under reduced pressure to afford brown oils. Products were subsequently isolated by flash column chromatography.

**General Method C: Sulfonyl fluoride synthesis from sulfonic acid pyridinium salt or free acid derivatives using Xtalfluor-E and Xtalfluor-M**

To a 4 mL vial equipped with a magnetic stir-bar was added sulfonic acid (0.25 mmol, 1 equiv), NaF (10 mg, 0.25 mmol, 1 equiv), pyridine (20 µl, 0.25 mmol, 1 equiv) and anhydrous MeCN (0.3 mL) before being purged with nitrogen and sealed. Xtalfluor salt (0.5 mmol, 2 equiv) dissolved in anhydrous MeCN (0.7 mL) was charged to the vial and stirred at 50 °C for 1 hour. The reaction mixture was diluted with DCM (20 mL), washed with $H_2O$ (20 mL) and brine (2 × 20 mL), dried over $Na_2SO_4$ or $MgSO_4$, and concentrated under reduced pressure. Products were subsequently isolated by flash chromatography or by pipette column.

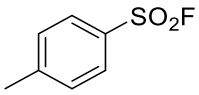
Note: Pyridinium derivatives of sulfonic acids were also successful at room temperature with no additional source of fluoride, see: main text, Table 3, Entry 2. However, heating reactions to 50 °C in the presence of NaF was used for all substrates to encompass all acid derivatives into a single method.

**General Method D: Sulfonyl fluoride synthesis from sulfonic acid sodium salt derivatives using Xtalfluor-E**

To a 4 mL vial equipped with a magnetic stir-bar was added sulfonic acid sodium salt (0.25 mmol, 1 equiv), NaF (10 mg, 0.25 mmol, 1 equiv) and anhydrous MeCN (0.3 mL) before and purged with nitrogen and sealed. Xtalfluor-E (114 mg, 0.5 mmol, 2 equiv) dissolved in anhydrous MeCN (0.7 mL) was charged to the vial and stirred at 50 °C for 1 hour. The reaction mixture was diluted with DCM (20 mL), washed with $H_2O$ (20 mL) and brine (2 × 20 mL), dried over $Na_2SO_4$ or $MgSO_4$, and concentrated under reduced pressure. Products were subsequently isolated by either flash chromatography or by pipette column.

# Experimental Data

**4-Methylbenzenesulfonyl fluoride (3a)**



Following general procedure **A** using pyridinium *p*-toluenesulfonate, compound **3a** was prepared on a 0.5 mmol scale affording 98% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The spectroscopic data were consistent with those previously reported.[1]

Following general procedure **B** using sodium *p*-toluenesulfonate, compound **3a** was prepared on a 0.5 mmol scale affording 99% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography on silica (5% diethyl ether in pentane) to afford a white solid (82 mg, 94%). The spectroscopic data were consistent with those previously reported.[2]

Following general procedure **D** using sodium *p*-toluenesulfonic acid, compound **3a** was prepared on a 0.25 mmol scale affording 95% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The product was purified by manual pipette silica gel chromatography (100% EtOAc) to afford a white solid (27 mg, 63%). The spectroscopic data were consistent with those previously reported.[2]

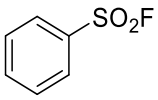
**$^{19}$F{1H} NMR** (282 MHz, Chloroform-*d*) δ +65.1.

**$^{1}$H NMR** (300 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 2.49 (s, 3H).

**$^{13}$C NMR** (75 MHz, Chloroform-*d*) δ 147.2, 130.4, 130.1, 128.6, 22.0.

**LMRS-EI** (m/z) 174.1

**Benzenesulfonyl fluoride (3b)**



Following general procedure **B** using sodium benzenesulfonate, compound **3b** was prepared on a 0.5 mmol scale affording 98% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography on silica (5% diethyl ether in pentane) to afford a pale-yellow oil (75 mg, 94%). The spectroscopic data were consistent with those previously reported.[2]

Following general procedure **D** using benznesulfonic acid, compound **3b** was prepared on a 0.25 mmol scale affording 86% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The product was purified pipette column chromatography on silica (100% EtOAc) to afford a yellow oil (29 mg, 73%). The spectroscopic data were consistent with those previously reported.[1]

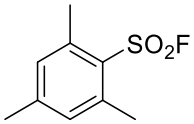
**$^{19}$F{1H} NMR** (282 MHz, Chloroform-*d*) δ +64.8.

**$^{1}$H NMR** (300 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.2 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.9 Hz, 2H).

**$^{13}$C NMR** (75 MHz, Chloroform-*d*) δ 135.7, 133.3 (d, *J* = 24.3 Hz), 129.8, 128.5.

**LMRS-EI** (m/z) 160.1

**2,4,6-Trimethylbenzenesulfonyl fluoride (3c)**




Following general procedure **B** using sodium mesitylenesulfonate, compound **3c** was prepared on a 0.5 mmol scale affording 99% yield determined by $^{19}$F{H} NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography on silica (5% diethyl ether in hexane) to afford a white solid (99 mg, 98%). The spectroscopic data were consistent with those previously reported.[3]

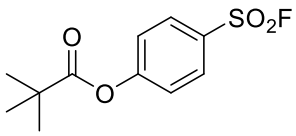
**$^{19}$F{1H} NMR** (282 MHz, Chloroform-*d*) δ +67.1.

**$^{1}$H NMR** (300 MHz, Chloroform-*d*) δ 7.03 (s, 3H), 2.64 (d, *J* = 1.9 Hz, 6H), 2.35 (s, 3H).

**$^{13}$C NMR** (75 MHz, Chloroform-*d*) δ 145.2, 140.2, 132.0, 129.4, 22.5, 21.3.

**LMRS-EI** (m/z) 202.1

**4-(Pivaloyloxy)benzenesulfonyl fluoride (3d)**




Following general procedure **B** using sodium 4-(pivaloyloxy)benzenesulfonate, compound **3d** was prepared on a 0.5 mmol scale affording 98% yield determined by $^{19}$F{H} NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography on silica (10% diethyl ether in hexane) to afford a white solid (129 mg, 99%).

Following general procedure **D** using sodium 4-(pivaloyloxy)benzenesulfonate, compound **3d** was prepared on a 0.25 mmol scale affording 100% yield determined by $^{19}$F{H} NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography on silica (100% EtOAc) to afford a brown solid (50.8 mg, 78%).

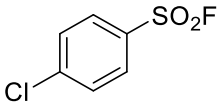
**$^{19}$F{1H} NMR** (282 MHz, Chloroform-*d*) δ +65.4.

**$^{1}$H NMR** (300 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 1.38 (s, 9H).

**$^{13}$C NMR** (75 MHz, Chloroform-*d*) δ 176.1, 156.9, 130.4, 130.0 (d, *J* = 25.3 Hz), 123.2, 39.5, 27.1.

**HRMS-FD+** calculated for [M] 260.05186, found 260.05225.

**4-Chlorobenzenesulfonyl fluoride (3e)**




Following general procedure **B** using sodium 4-chlorobenzenesulfonate, compound **3e** was prepared on a 0.5 mmol scale affording 91% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography on silica (10% diethyl ether in hexane) to afford a white solid (88 mg, 90%). The spectroscopic data were consistent with those previously reported.[2]

Following general procedure **C** using sodium 4-chlorobenzenesulfonate, compound **3e** was prepared on a 0.25 mmol scale affording 89% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography on silica (7% diethyl ether in petroleum ether) to afford a white solid (40 mg, 82%). The spectroscopic data were consistent with those previously reported.[2]

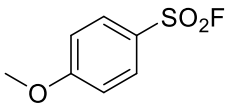
**$^{19}$F{1H} NMR** (282 MHz, Chloroform-*d*) δ +65.3.

**$^{1}$H NMR** (300 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H).

**$^{13}$C NMR** (75 MHz, Chloroform-*d*) δ 142.8, 131.6 (d, *J* = 25.9 Hz), 130.3, 130.0.

**LMRS-EI** (m/z) 194.0

**4-Methoxybenzenesulfonyl fluoride (3f)**




Following general procedure **B** using sodium 4-methoxybenzenesulfonate, compound **3f** was prepared on a 0.5 mmol scale affording 91% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography on silica (20% diethyl ether in hexane) to afford pale yellow oil (84 mg, 88%). The spectroscopic data were consistent with those previously reported.[4]

Following general procedure **C** using sodium 4-methoxybenzenesulfonic acid, compound **3f** was prepared on a 0.25 mmol scale affording 100% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography on silica (100 % EtOAc) to afford pale yellow liquid (31 mg, 66%). The spectroscopic data were consistent with those previously reported.[4]

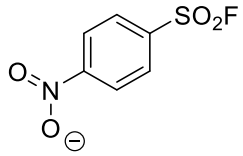
**$^{19}$F{1H} NMR** (282 MHz, Chloroform-*d*) δ +66.2.

**$^{1}$H NMR** (300 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 9 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 3.92 (s, 3H).

**$^{13}$C NMR** (75 MHz, Chloroform-*d*) δ 165.4, 131.0, 124.2 (d, *J* = 24.6 Hz,), 115.0, 56.0.

**LMRS-EI** (m/z) 190.1

**4-Nitrobenzenesulfonyl fluoride (3g)**



Following general procedure **B** using pyridinium 4-nitrobenzenesulfonic acid, compound **3g** was prepared on a 0.5 mmol scale affording 80% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography on silica (13% diethyl ether in hexane) to afford a white solid (86 mg, 80%). The spectroscopic data were consistent with those previously reported.[2]

Following general procedure **C** using 4-nitrobenzenesulfonic acid, compound **3g** was prepared on a 0.25 mmol after stirring at 50 °C for 16 hours. The product was purified by Combiflash silica gel column chromatography (0-100% EtOAc in hexane) to afford an off-white solid (21 mg, 41%). The spectroscopic data were consistent with those previously reported.[2]

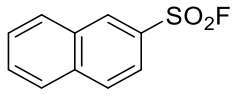
**$^{19}$F{1H} NMR** (282 MHz, Chloroform-*d*) δ +64.9.

**$^{1}$H NMR** (300 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 8.2 Hz, 2H), 8.25 (d, *J* = 8.9 Hz, 2H).

**$^{13}$C NMR** (75 MHz, Chloroform-*d*) δ 151.9, 138.5 (d, *J* = 27.1 Hz), 130.1, 125.0.

**LMRS-EI** (m/z) 205.1

**Naphthalene-2-sulfonyl fluoride (3h)**



Following general procedure **B** using sodium naphthalene-2-sulfonate, compound **3h** was prepared on a 0.5 mmol scale affording 100% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography on silica (20% diethyl ether in hexane) to afford a white solid (104 mg, 99%). The spectroscopic data were consistent with those previously reported.[5]

Following general procedure **D** using sodium benzenesulfonate, compound **3h** was prepared on a 0.25 mmol scale affording 87% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography by Combiflash silica gel chromatography (0-100% in EtOAc in hexane) to afford a white solid (42 mg, 80%). The spectroscopic data were consistent with those previously reported.[5]

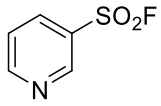
**$^{19}$F{1H} NMR** (282 MHz, Chloroform-*d*) δ +65.2.

**$^{1}$H NMR** (300 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 8.11–7.89 (m, 4H), 7.81–7.64 (m, 2H).

**$^{13}$C NMR** (75 MHz, Chloroform-*d*) δ 136.2, 132.0, 131.1, 130.5, 130.2, 130.1, 129.8, 129.7, 128.5, 125.3, 122.3.

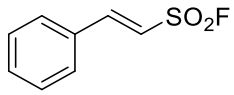
**LMRS-EI** (m/z) 210.0

**3-Pyridinesulfonyl fluoride (3i)**



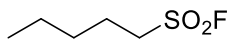
Following general procedure **B** using pyridinium (*E*)-2-phenylethene-1-sulfonic acid, compound **3i** was prepared on a 0.5 mmol scale affording 14% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The spectroscopic data were consistent with those previously reported.[6]

**(*E*)-2-phenylethene-1-sulfonyl fluoride (3j)**



Following general procedure **B** using sodium (*E*)-2-phenylethene-1-sulfonic acid, compound **3j** was prepared on a 0.5 mmol scale affording 0% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture.

**1-Pentanesulfonyl fluoride (3k)**



Following general procedure **B** using sodium 1-pentanesulfonate, compound **3k** was prepared on a 0.5 mmol scale affording 92% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography on silica (10% diethyl ether in pentane) to afford a colourless oil (70 mg). Residual diethyl ethyl was unable to be removed without significant product loss due to the volatility of **3k**. Adjusted for diethyl ether content, the yield was calculated as 90%. The spectroscopic data were consistent with those previously reported.[7]

Following general procedure **D** using sodium benzenesulfonate, compound **3k** was prepared on a 0.5 mmol scale affording 40% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The spectroscopic data were consistent with those previously reported.[7]

Note: Mass analysis of the crude reaction by GC-MS identified the major product as 1-pentene. Olefin side products observed with aliphatic substrates result from the *N*-sulfinyl fluoride by-products released when Xtalfluor salts are used in deoxygenation reactions.[8] *N*-Sulfinyl fluorides have been previously reported to decompose at temperatures exceeding 0°C,[9] releasing either diethylamine or morpholine depending on the Xtalfluor salt used. The released amines are primed to deprotonate the acidic proton alpha to the sulfonyl fluoride group. Similar olefin-containing side products were reported when using Xtalfluor salts in the deoxyfluorination of ketones because of the acidic protons alpha to the alkyl difluoride.[10]

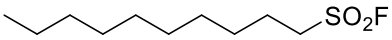
**$^{19}$F{1H} NMR** (282 MHz, Chloroform-*d*) δ +52.1.

**$^{1}$H NMR** (300 MHz, Chloroform-*d*) δ 3.39–3.31 (m, 2H), 2.01–1.88 (m, 2H), 1.53–1.33 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, Chloroform-*d*) δ 51.0 (d, *J* = 16.1 Hz), 30.0, 23.2, 22.0, 13.7.

**LMRS-EI** (m/z) 154.2

**1-Decanesulfonyl fluoride (3l)**



Following general procedure **B** using sodium 1-pentanesulfonate, compound **3l** was prepared on a 0.5 mmol scale affording 99% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography on silica (5% diethyl ether in hexane) to afford a colourless oil (221 mg, 99%). The spectroscopic data were consistent with those previously reported.[8]

Following general procedure **D** using sodium benzenesulfonate, compound **3l** was prepared on a 0.25 mmol scale by stirring at 50 °C for 16 hours. The product was purified by Combiflash silica gel column chromatography (0-100% EtOAc in hexane) to afford an amber oil (52 mg, 94%). The spectroscopic data were consistent with those previously reported.[8]

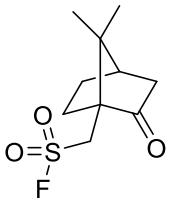
**$^{19}$F{1H} NMR** (282 MHz, Chloroform-*d*) δ +52.1.

**$^{1}$H NMR** (300 MHz, Chloroform-*d*) δ 3.42–3.29 (m, 2H), 2.02–1.88 (m, 2H), 1.50–1.41 (m, 2H), 1.37–1.18 (m, 12H), 0.87 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, Chloroform-*d*) δ 51.0 (d, *J* = 15.9 Hz), 32.0, 29.5, 29.3, 29.3, 28.9, 28.0, 23.5, 22.8, 14.2.

**LMRS-EI** (m/z) 224.2

**((1S)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonyl fluoride (3m)**



Following general procedure **B** using a solution of camphorsulfonic acid (116 mg, 0.5 mmol) and pyridine (40 µL, 0.5 mmol) in DMF (1 mL), compound **3m** was prepared affording 95% yield determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. The product was purified by column chromatography on silica (10-25% diethyl ether in hexane) to afford white crystals (111 mg, 95%). The spectroscopic data were consistent with those previously reported.[9]

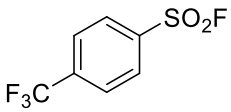
**$^{19}$F{1H} NMR** (282 MHz, Chloroform-*d*) δ +63.2.

**$^{1}$H NMR** (300 MHz, Chloroform-*d*) δ 3.86 (dd, *J* = 15.2, 2.6 Hz, 1H), 3.29 (dd, *J* = 15.2, 2.9 Hz, 1H), 2.50–2.31 (m, 2H), 2.15–2.03 (m, 1H), 1.99 (d, *J* = 18.6 Hz, 1H), 1.80–1.69 (m, 1H), 1.54–1.44 (m, 1H), 1.13 (s, 3H), 0.92 (s, 3H).

**$^{13}$C NMR** (75 MHz, Chloroform-*d*) δ 213.2, 58.0, 48.5 (d, *J* = 18.3 Hz), 48.1, 43.1, 42.5, 26.9, 25.3, 19.8, 19.7.

**LMRS-EI** (m/z) 234.2

**4-(Trifluoromethyl)benzenesulfonyl fluoride (3n)**



Following general procedure **C** with a 3 hour reaction time using benzo[d]thiazole-6-sulfonic acid, compound **3n** was prepared on a 0.25 mmol scale. The product was purified by column chromatography (5% $Et_2O$ in hexane) to afford a white solid (51 mg, 89% yield). The spectroscopic data were consistent with those previously reported.[3]

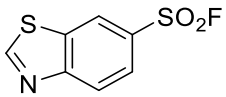
**$^{19}$F{1H} NMR** (377 MHz, Chloroform-*d*) δ +65.9, -63.5.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 8.72 (d, *J* = 1.9 Hz, 1H), 8.37 (d, *J* = 8.6 Hz, 1H), 8.14 (dd, *J* = 8.7, 1.9 Hz, 1H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 137.3 (q, *J* = 33.6 Hz), 136.7 (d, *J* = 27.4 Hz), 129.2, 127.0 (q, 3.7 Hz), 122.85 (q, 273.9 Hz).

**LRMS** Not found. Consistent with previous literature,[11] we were unable to establish the mass.

**Benzo[d]thiazole-6-sulfonyl fluoride (3o)**



Following general procedure **C** using benzo[d]thiazole-6-sulfonic acid, compound **3n** was prepared on a 0.25 mmol scale. The product was purified by column chromatography (100% EtOAc) to afford a tan solid (37 mg, 70% yield).

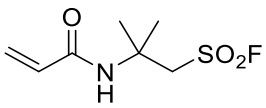
**$^{19}$F{1H} NMR** (377 MHz, Chloroform-*d*) δ +68.5.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 8.72 (d, *J* = 1.9 Hz, 1H), 8.37 (d, *J* = 8.6 Hz, 1H), 8.14 (dd, *J* = 8.7, 1.9 Hz, 1H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 159.8, 157.4, 134.7, 130.0, 125.7, 124.1 (d, *J* = 101.0 Hz).

**HRMS-ESI** (m/z) calculated for $[M+H]^+$ 217.9740, found 217.9747.

**2-Acrylamido-2-methylpropane-1-sulfonyl fluoride (3p)**



Following the general procedure **C** with a 16 hour reaction time using 2-acrylamido-2-methylpropane-1-sulfonic acid, compound **3o** was prepared on a 0.25 mmol scale affording 58% yield determined by $^{19}$F{H} NMR spectroscopy of the crude reaction mixture. The product was purified Combiflash silica gel column chromatography (0-100% EtOAc in hexane) to afford a yellow solid (22 mg, 0.105 mmol, 42% yield).

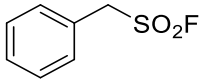
**$^{19}$F{1H} NMR** (377 MHz, DMSO- $d_6$) δ 64.3.

**$^{1}$H NMR** (400 MHz, DMSO- $d_6$) δ 8.22 (s, 1H), 6.32-6.21 (m, 1H), 6.12-6.03 (m, 1H), 5.60-5.54 (m, 1H), 4.51-4.45 (m, 2H), 1.45 (s, 6H).

**$^{13}$C NMR** (101 MHz, DMSO- $d_6$) δ 165.0, 131.7, 125.6, 56.1 (d, $J$ = 9.5 Hz), 50.8, 26.6.

**HRMS-ESI** calculated for $[M+H]^+$ 210.0595, found 210.059

**Phenylmethanesulfonyl fluoride (3q)**



Following the general procedure **D** with a 4 hour reaction time using sodium phenylmethanesulfonate, compound **3p** was prepared on a 0.25 mmol scale affording 59% yield after 1 hour determined by $^{19}$F{H} NMR spectroscopy of the crude reaction mixture. The product was purified by manual pipette silica gel column chromatography (100% EtOAc) to afford a light yellow solid (36 mg, 0.207 mmol, 82% yield). The spectroscopic data were consistent with those previously reported.[7]

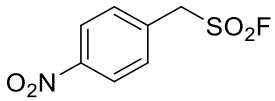
**$^{19}$F{1H} NMR** (377 MHz, DMSO- $d_6$) δ +51.3.

**$^{1}$H NMR** (400 MHz, DMSO- $d_6$) δ 7.51–7.44 (m, 5H), 5.35 (d, $J$ = 5.2 Hz).

**$^{13}$C NMR** (101 MHz, DMSO- $d_6$) δ 131.0, 129.4, 129.0, 126.9, 55.2 (d, $J$ = 14.6 Hz).

**LRMS-EI** calculated for [M] 174.02, found 173.95.

**(4-Nitrophenyl)methanesulfonyl fluoride (3r)**



Following general procedure **D** using hydridosodium(II) (4-nitrophenyl)methanesulfonate hydride, compound **3q** was prepared on a 0.25 mmol scale affording 82% yield after 1 hour determined by $^{19}$F{H} NMR spectroscopy of the crude reaction mixture. The product was purified by manual silica gel column chromatography (100% EtOAc) to afford a brown solid (35.0 mg, 0.160 mmol, 64% yield). The spectroscopic data were consistent with those previously reported.[10]

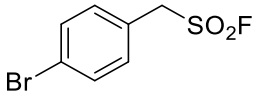
**$^{19}$F{1H} NMR** (377 MHz, DMSO- $d_6$) δ 52.6.

**$^{1}$H NMR** (400 MHz, DMSO- $d_6$) δ 8.33–8.31 (m, 2H), 8.02–7.76 (m, 2H), 5.60 (d, $J$ = 5.6 Hz, 2H).

**$^{13}$C NMR** (101 MHz, DMSO- $d_6$) δ 148.1, 134.2, 132.4, 124.1, 54.3 (d, $J$ = 15.2 Hz).

**LRMS-ESI** calculated for [M-] 217.99, found 218.00.

**(4-Bromophenyl)methanesulfonyl fluoride (3s)**




Following general procedure **D**, with a 16 hour reaction time using sodium (4-bromophenyl)methanesulfonate, compound 3r was prepared on a 0.250 mmol scale affording 36% yield after 1 hour determined by $^{19}F\{H\}$ NMR spectroscopy of the crude reaction mixture. After washing the diluted reaction mixture with DI $H_2O$, the aqueous layer was washed twice with additional DCM. The product was purified by Combiflash silica gel column chromatography (0-100% ethyl acetate in hexanes) to afford a yellow solid (45 mg, 71% yield).

**$^{19}$F{1H} NMR** (377 MHz, DMSO- $d_6$) δ 51.4.

**$^{1}$H NMR** (400 MHz, DMSO- $d_6$) δ 7.68 (d, *J* = 7.4 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 5.37 (d, *J* = 5.4 Hz, 2H).

**$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 133.1, 132.0, 126.4, 123.1, 54.4 (d, *J* = 14.9 Hz).

**HRMS-FD+** calculated for [M] 251.92559, found 251.92516.

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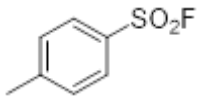
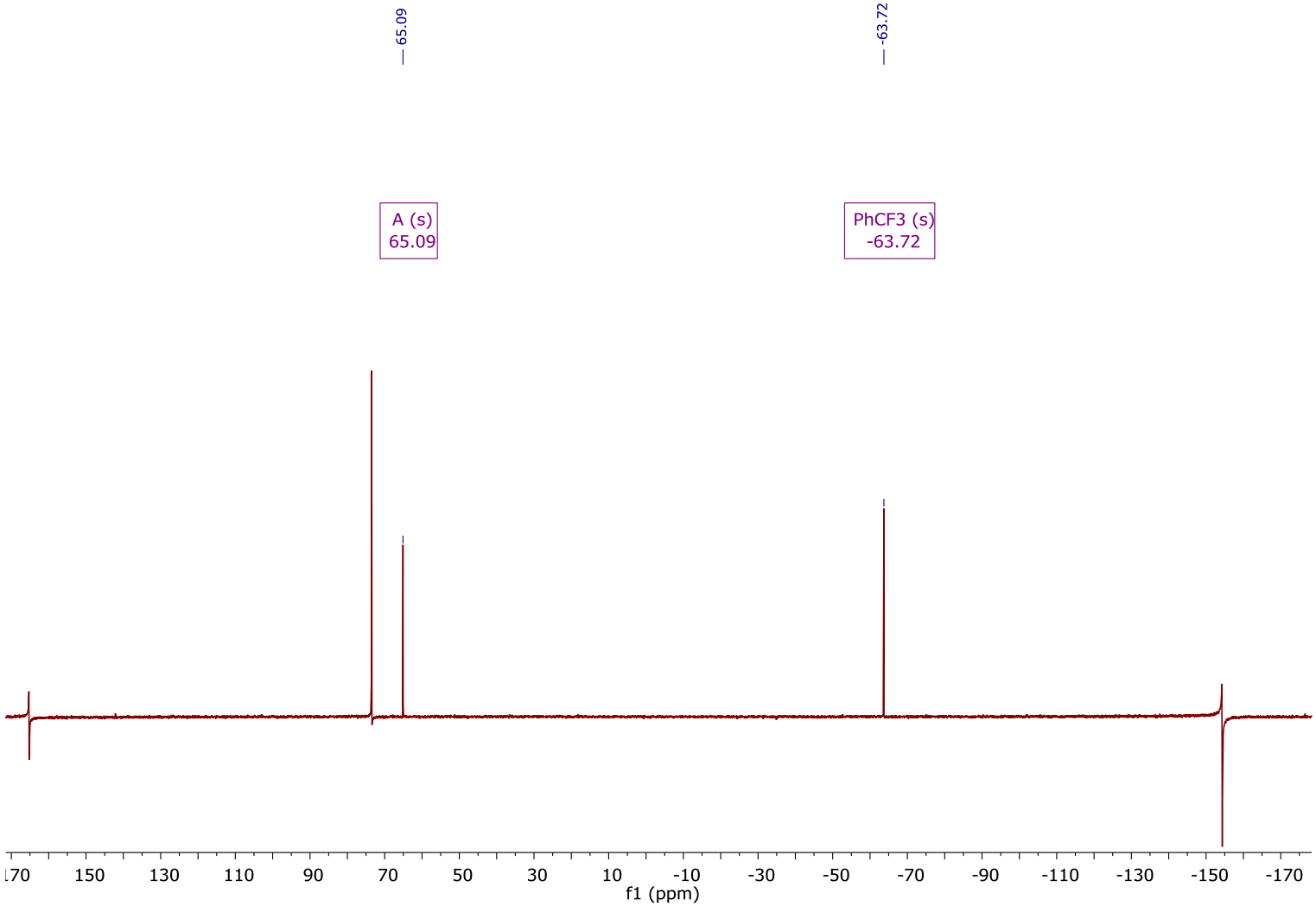
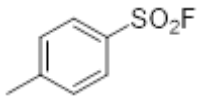


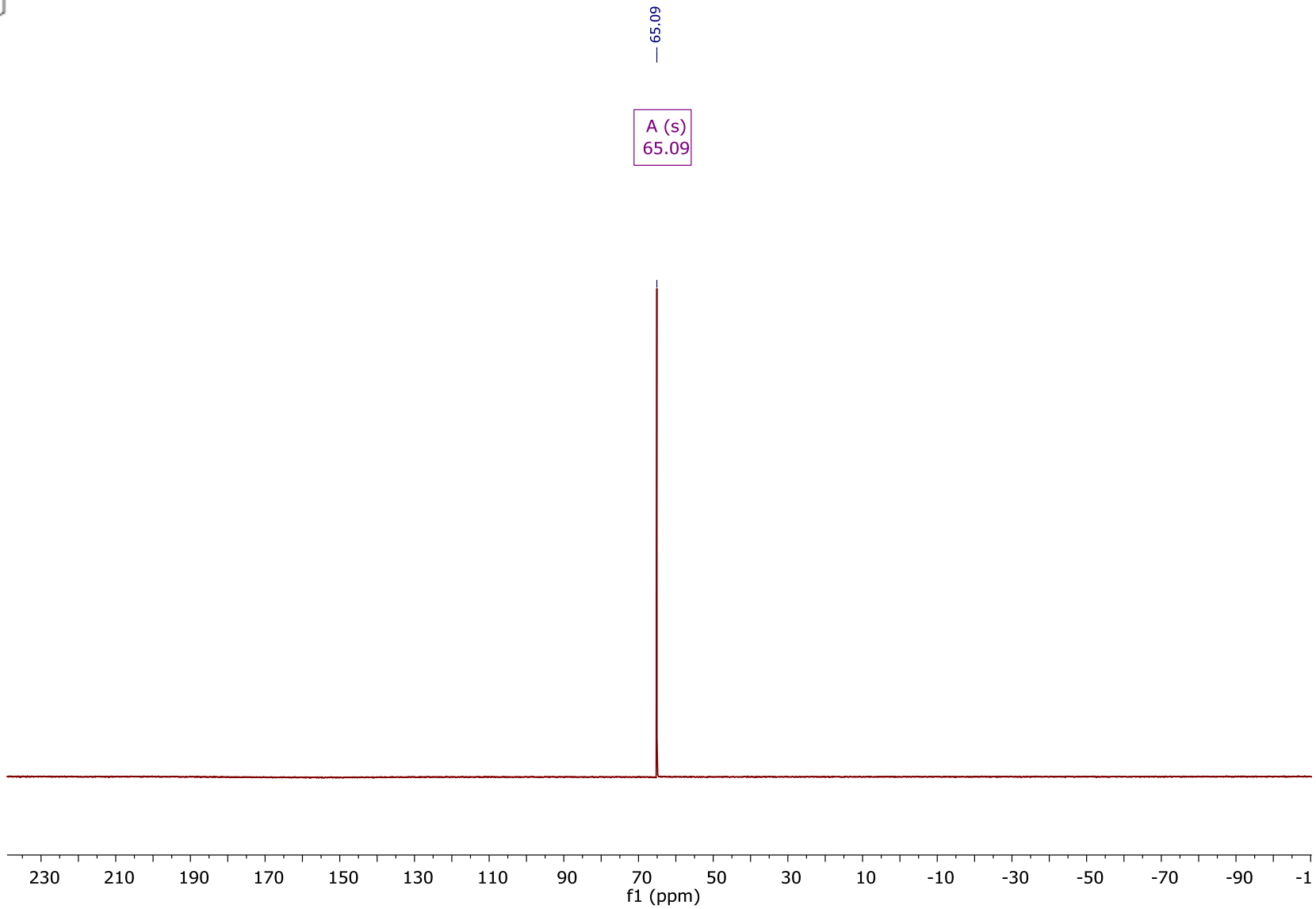

# NMR Spectra

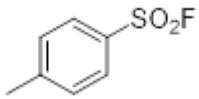
**3a Crude Reaction $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**



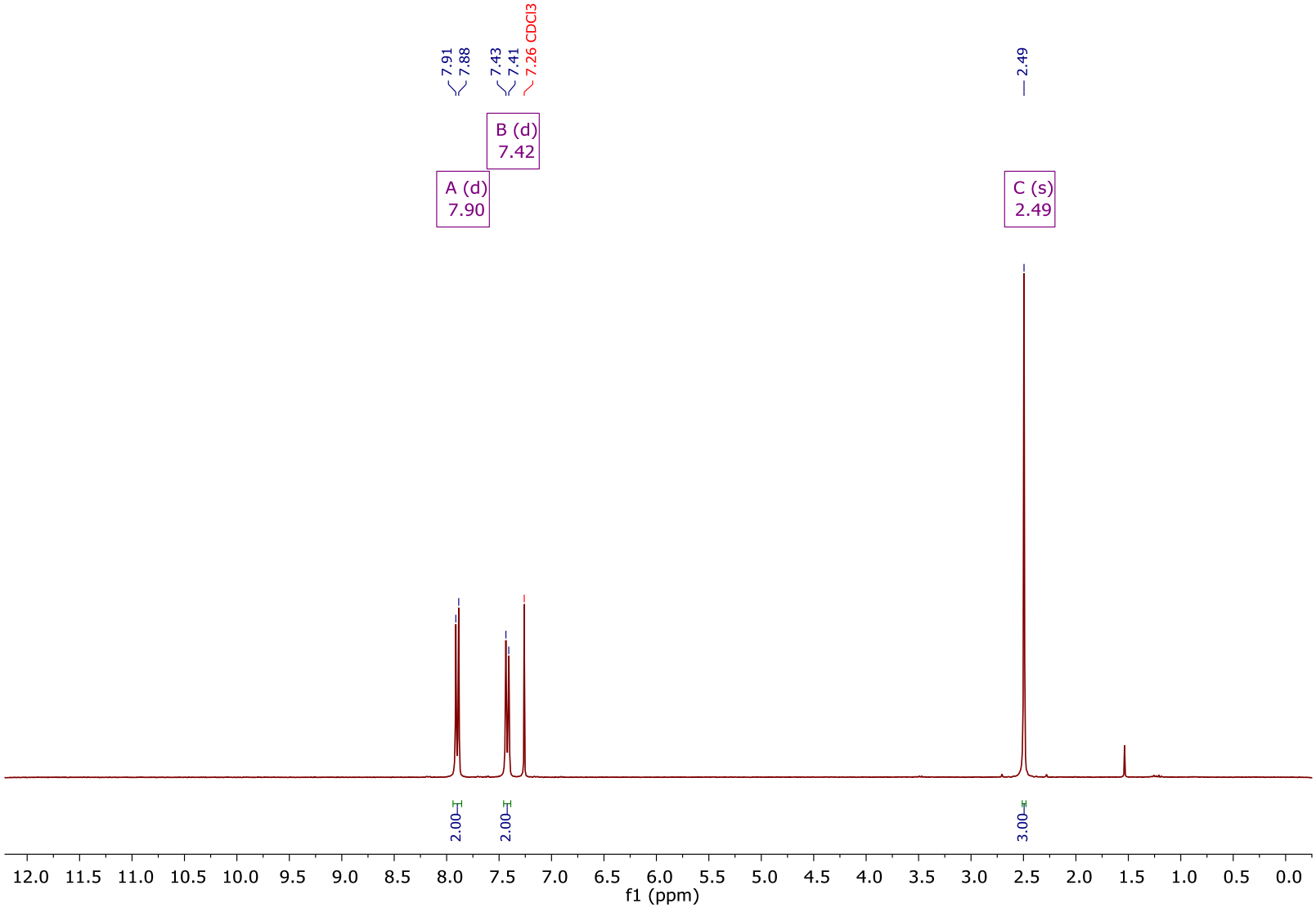


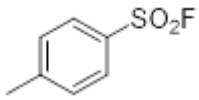

**3a $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**



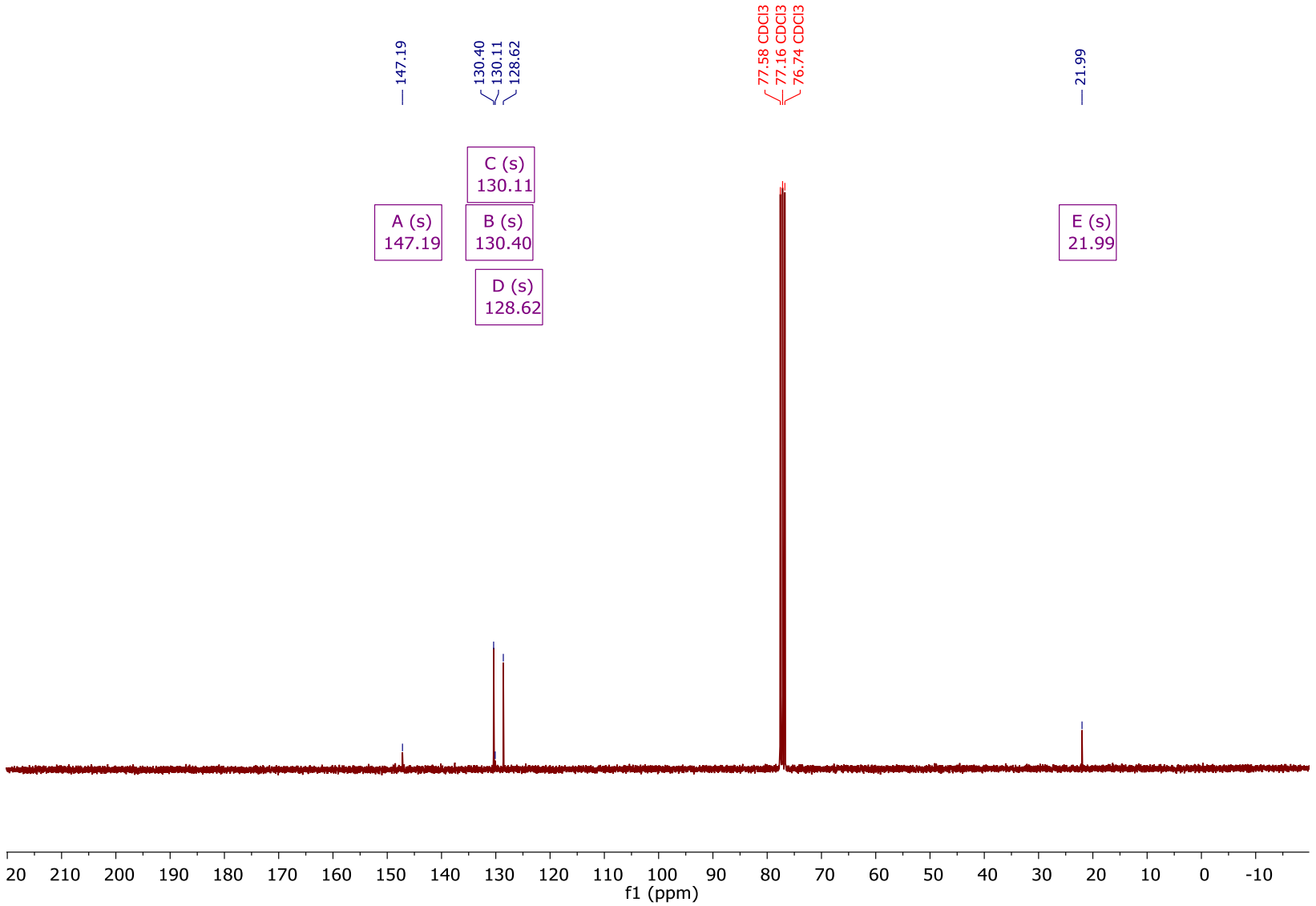


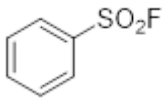

**3a $^{1}$H NMR (300 MHz, chloroform-*d*)**



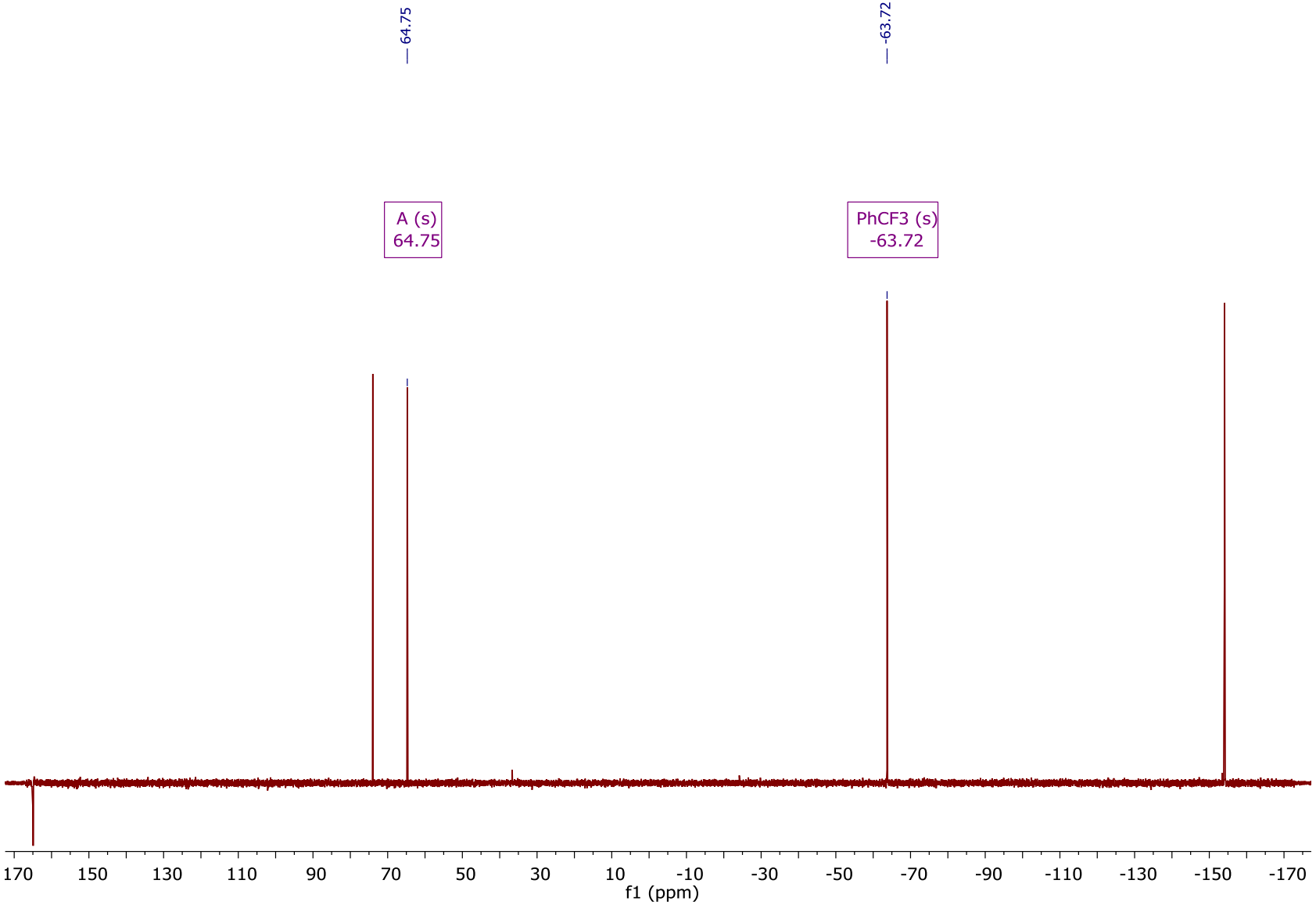


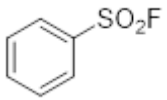

**3a $^{13}$C NMR (75 MHz, chloroform-*d*)**



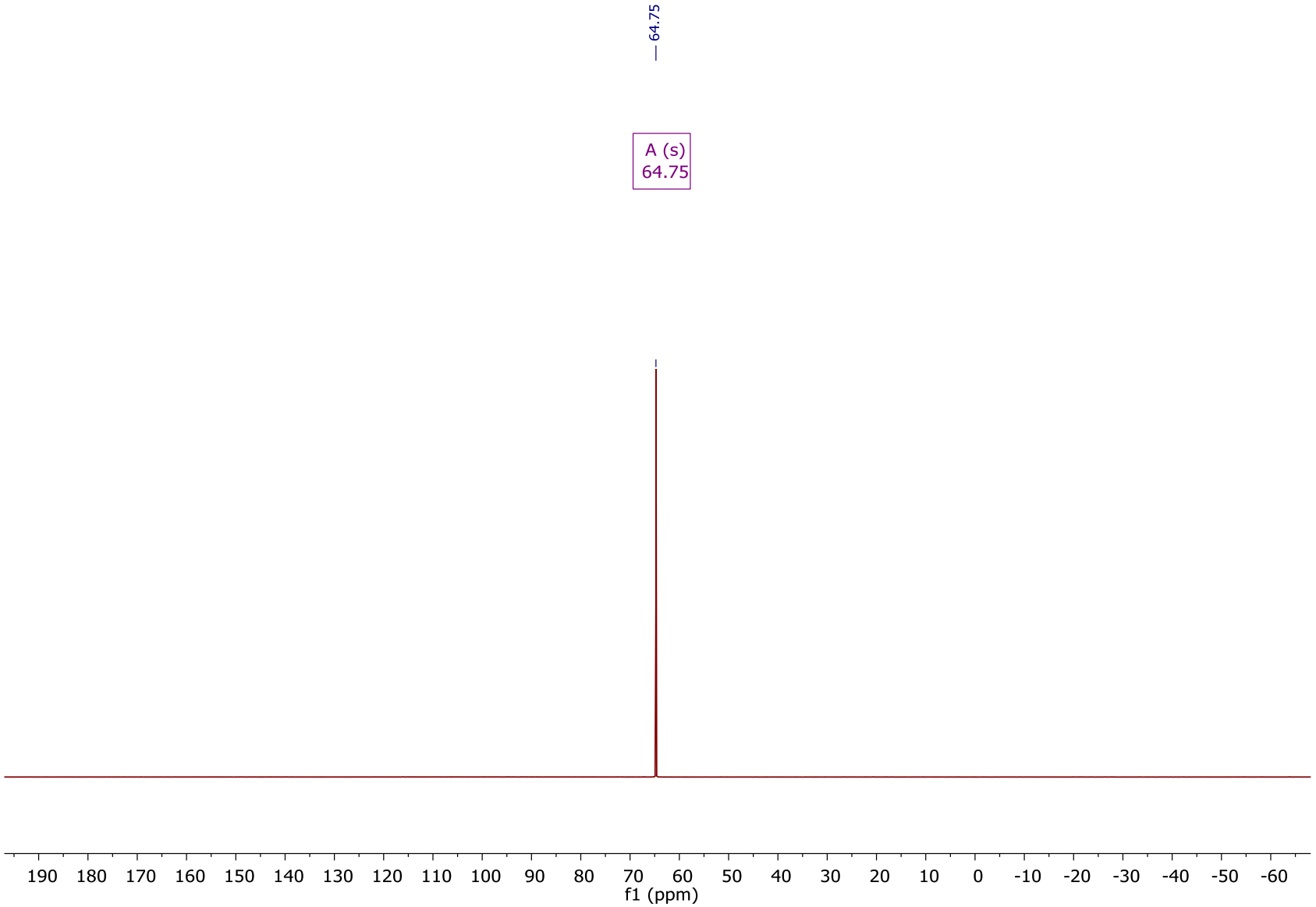


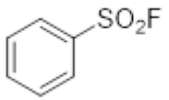

**3b Crude Reaction $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**



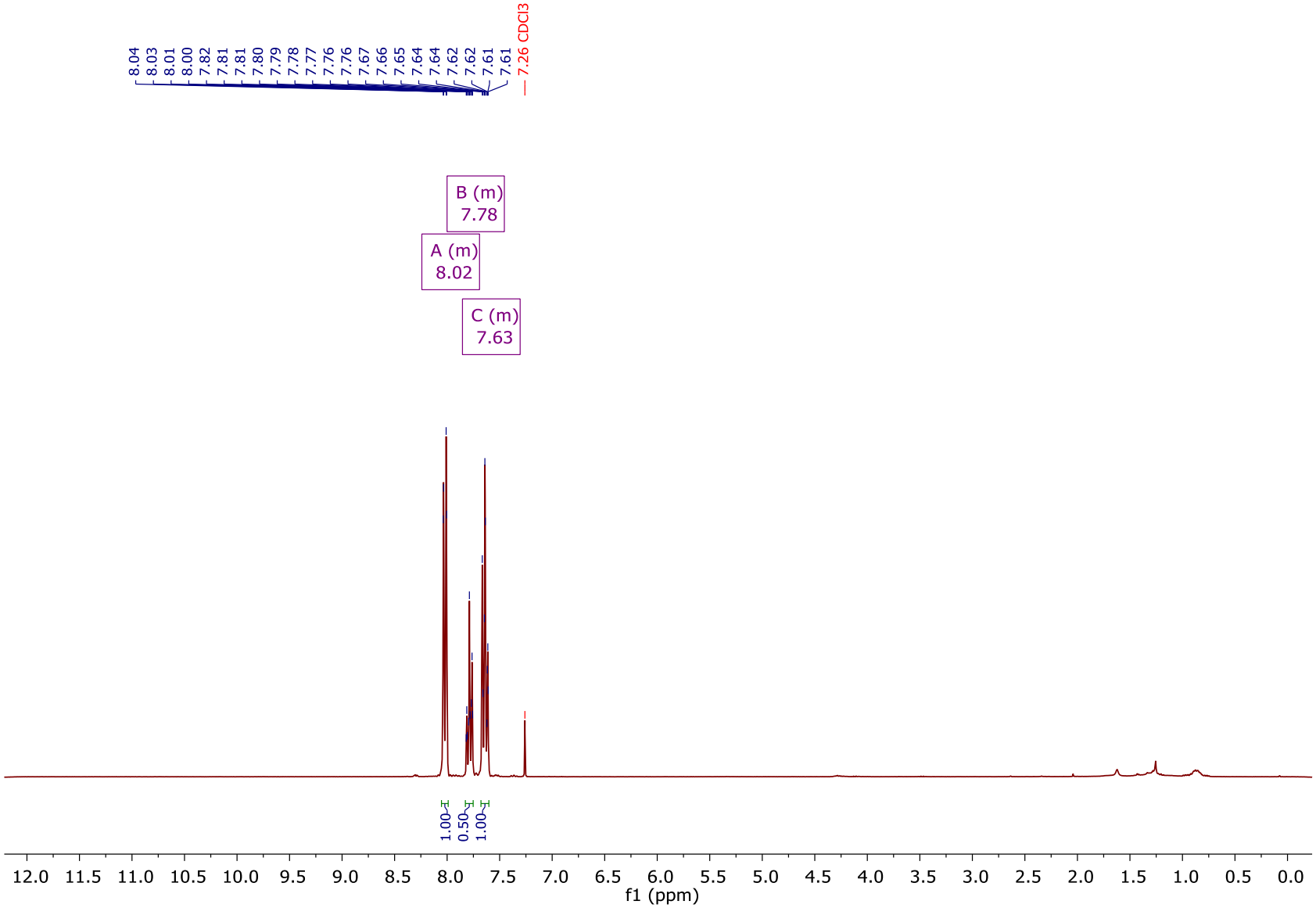


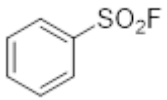

**3b $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**



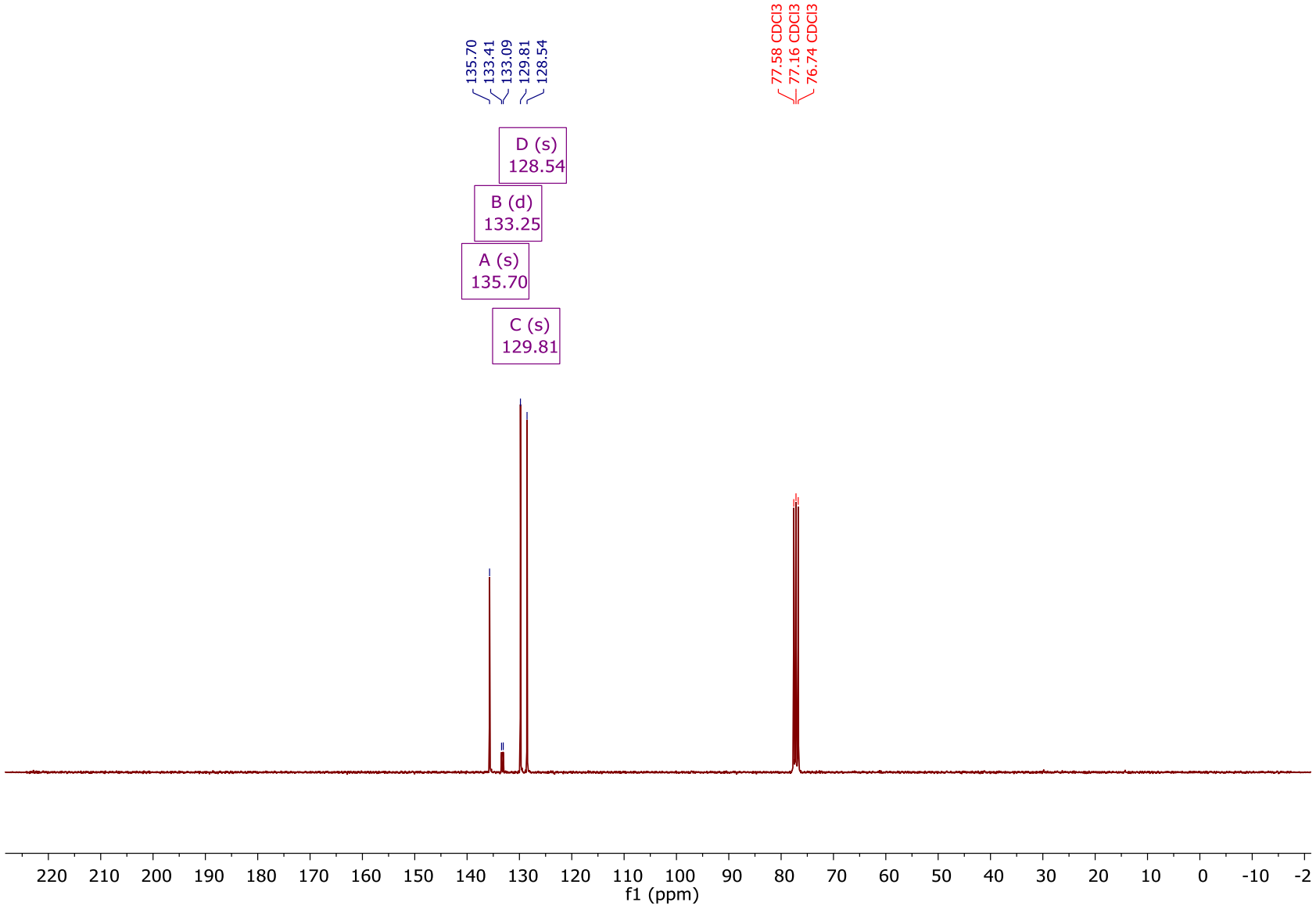



**3b $^{1}$H NMR (300 MHz, chloroform-*d*)**

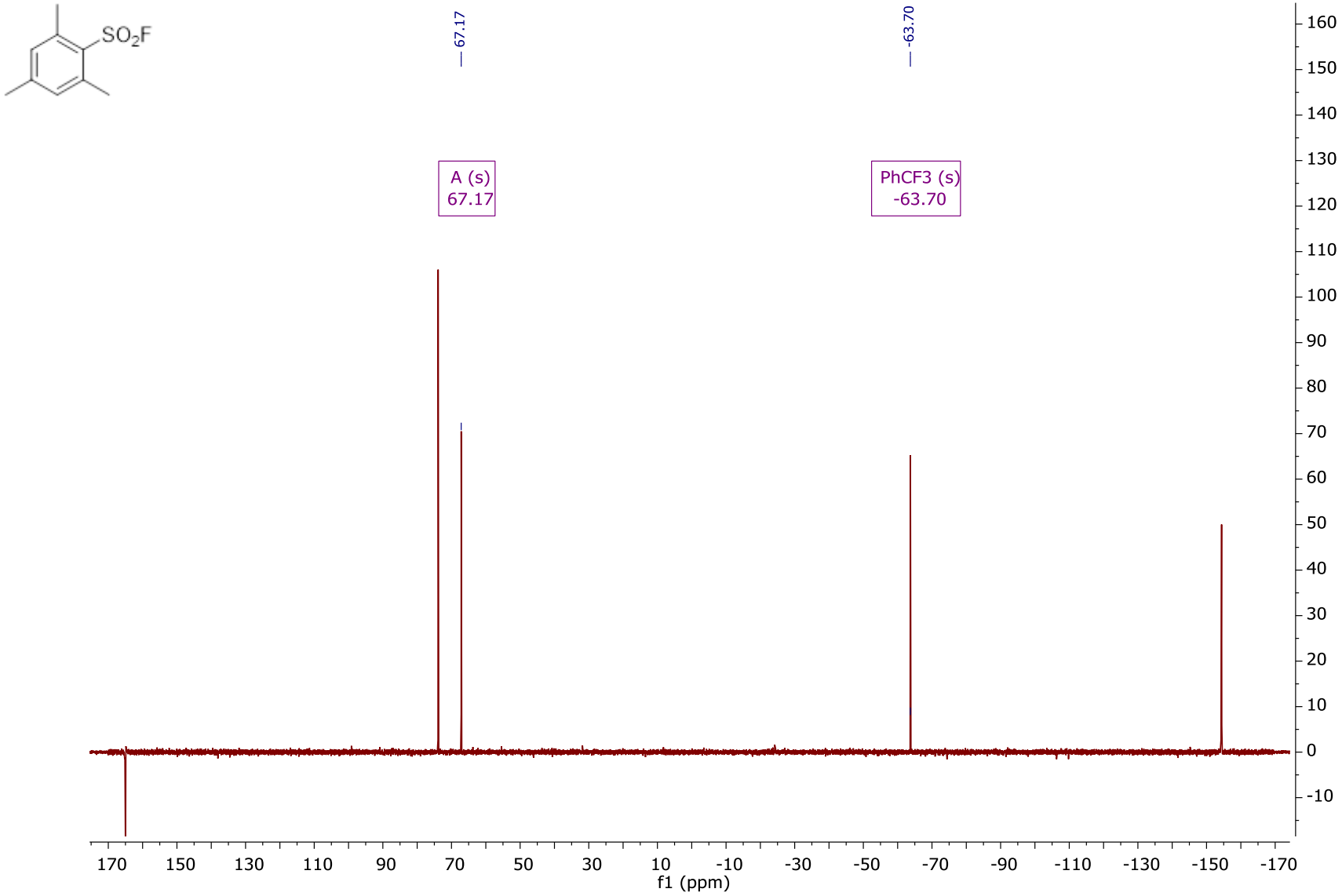




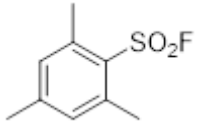

**3b $^{13}$C NMR (75 MHz, chloroform-*d*)**

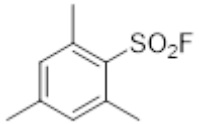


**3c Crude Reaction $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**

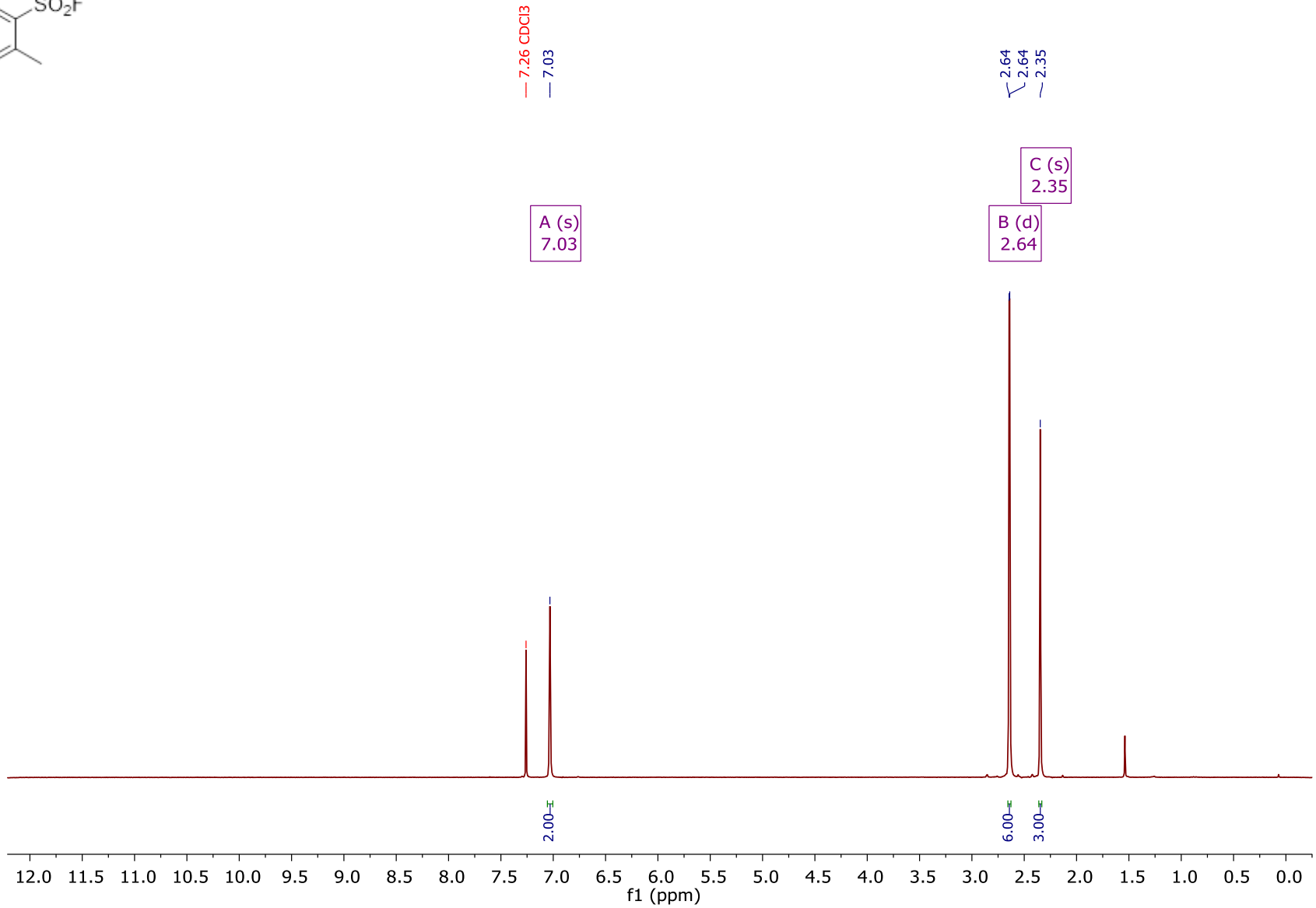


**3c $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**

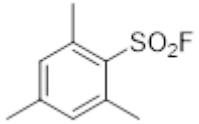


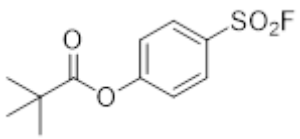



**3c $^{1}$H NMR (300 MHz, chloroform-*d*)**

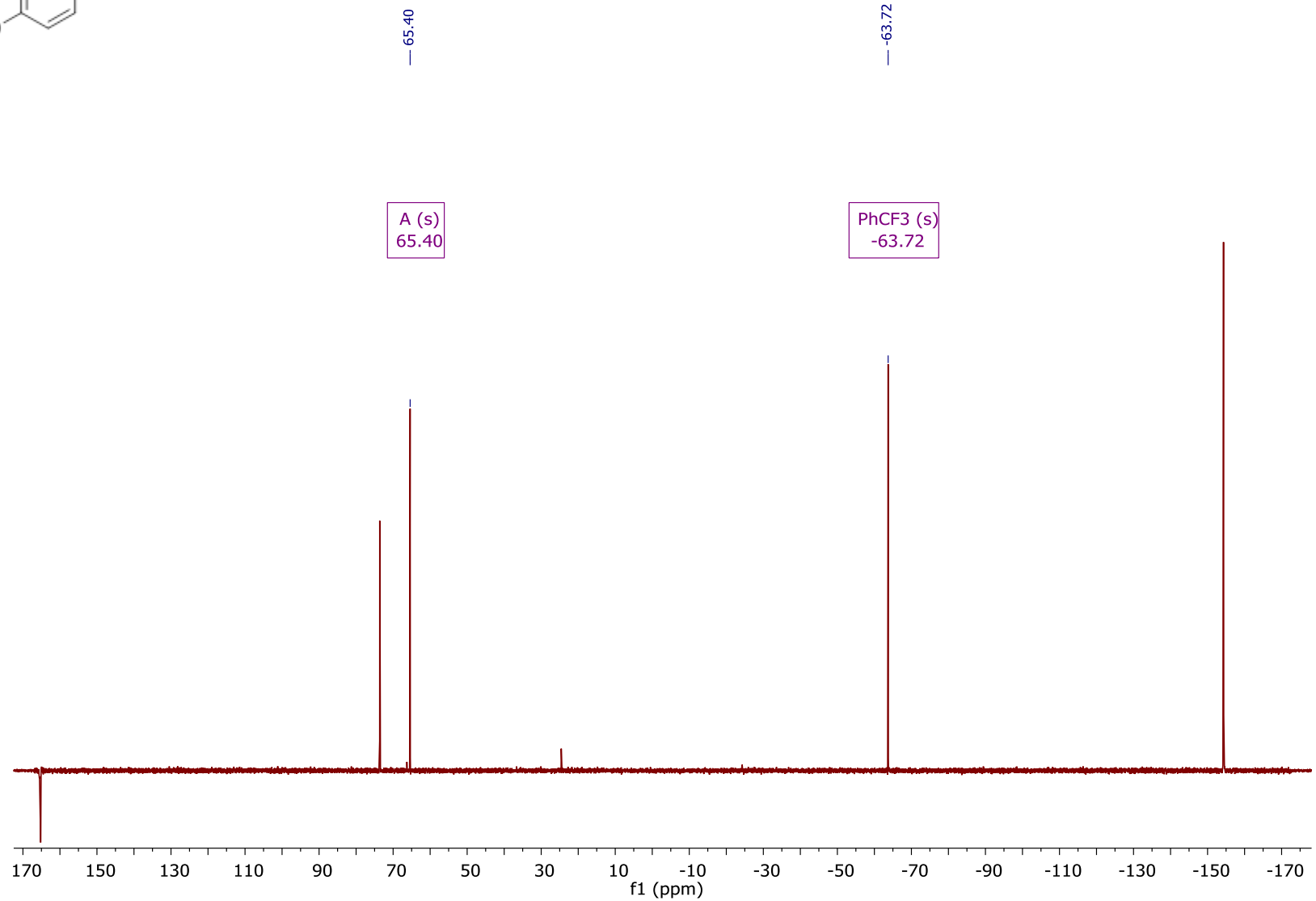


**3c $^{13}$C NMR (75 MHz, chloroform-*d*)**

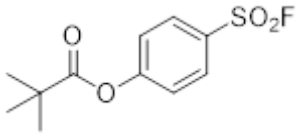


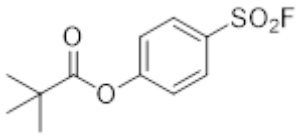



**3d Crude Reaction $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**



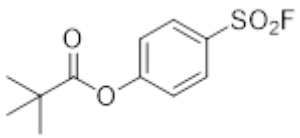
**3d $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**

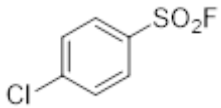





**3d $^{1}$H NMR (300 MHz, chloroform-*d*)**

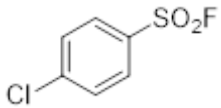
**3d $^{13}$C NMR (75 MHz, chloroform-*d*)**



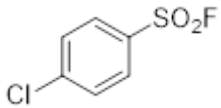



**3e Crude Reaction $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**

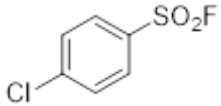
**3e $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**

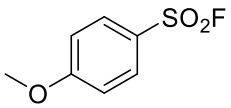


**3e $^{1}$H NMR (300 MHz, chloroform-*d*)**



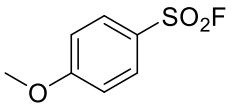
**3e $^{13}$C NMR (75 MHz, chloroform-*d*)**



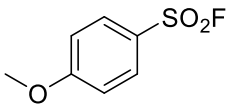



**3f Crude Reaction $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**

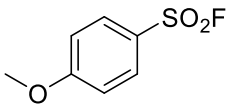
**3f $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**

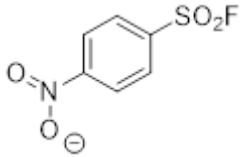


**3f $^{1}$H NMR (300 MHz, chloroform-*d*)**

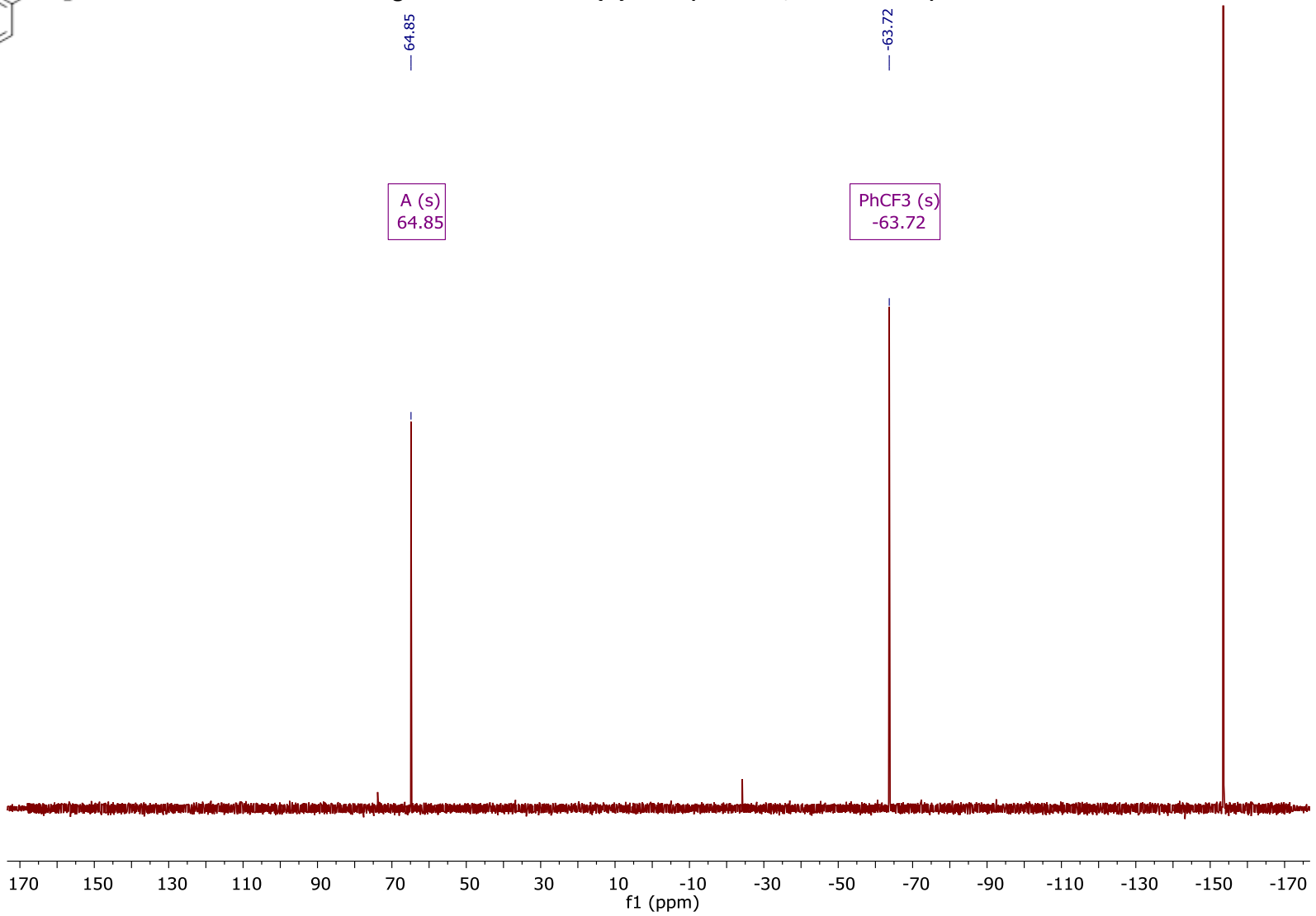


**3f $^{13}$C NMR (75 MHz, chloroform-*d*)**

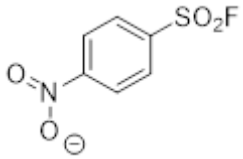


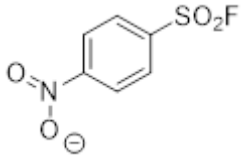



**3g Crude Reaction $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**

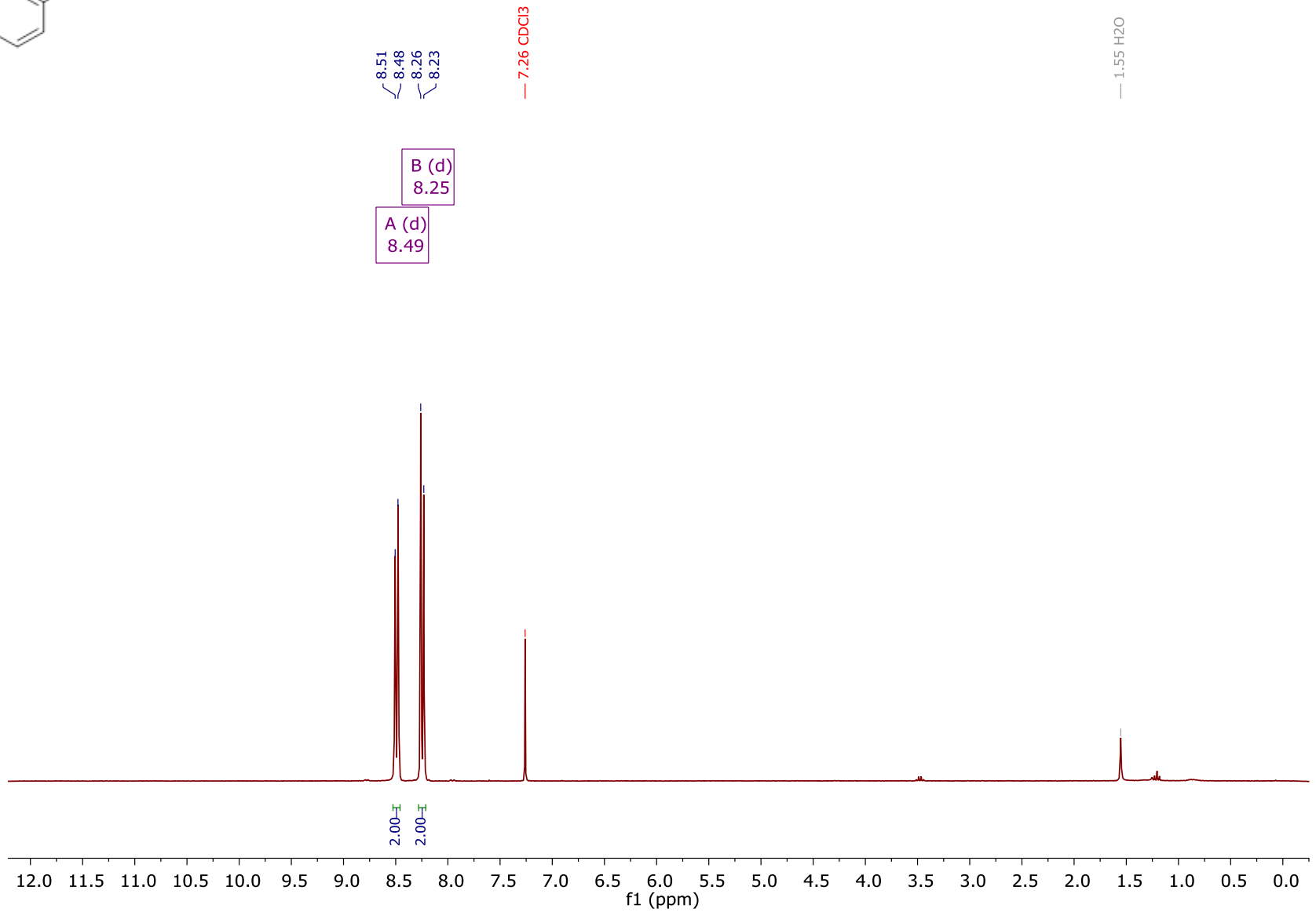


**3g $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**

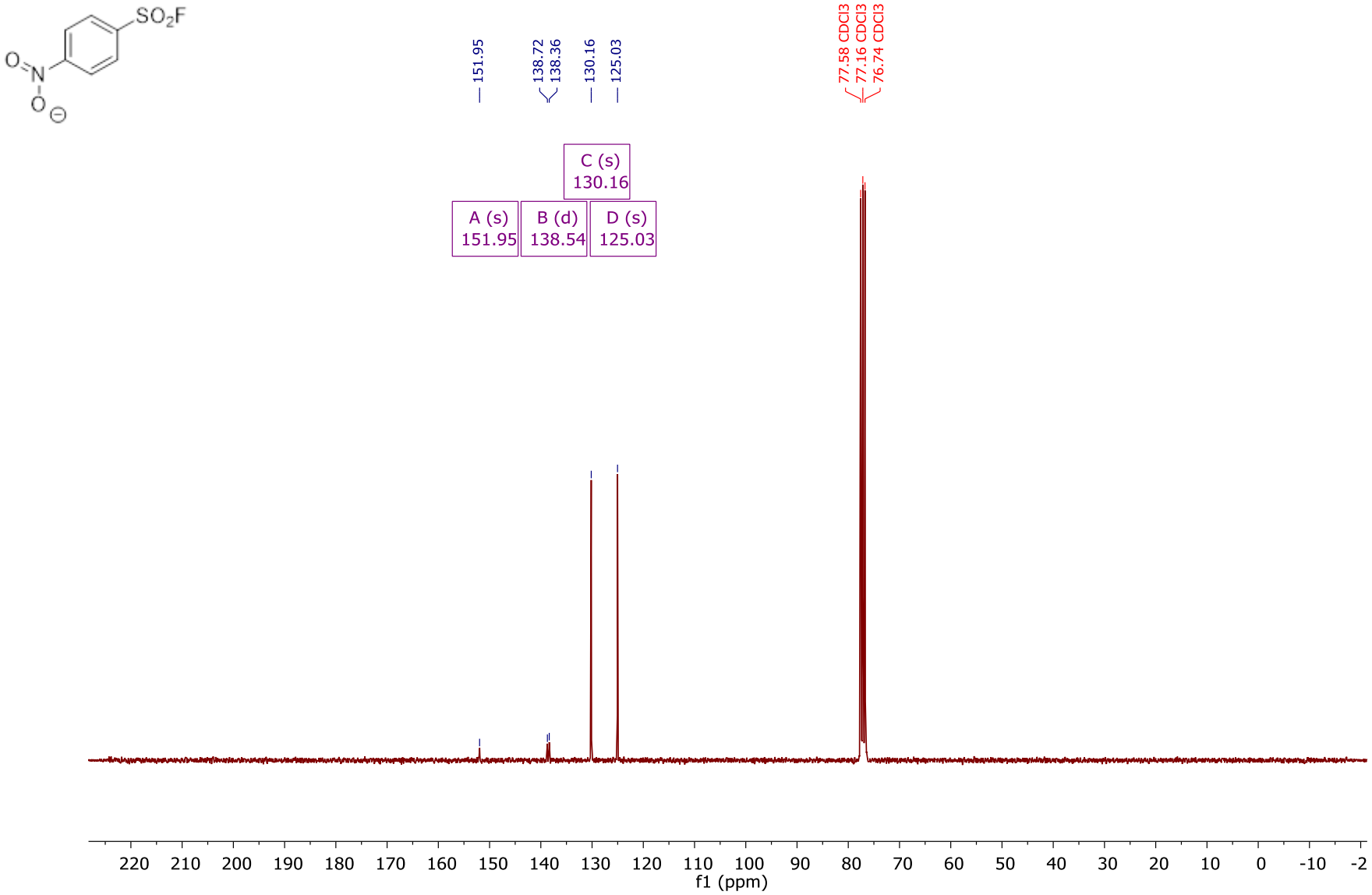


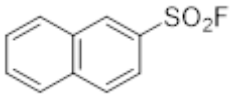



**3g $^{1}$H NMR (300 MHz, chloroform-*d*)**

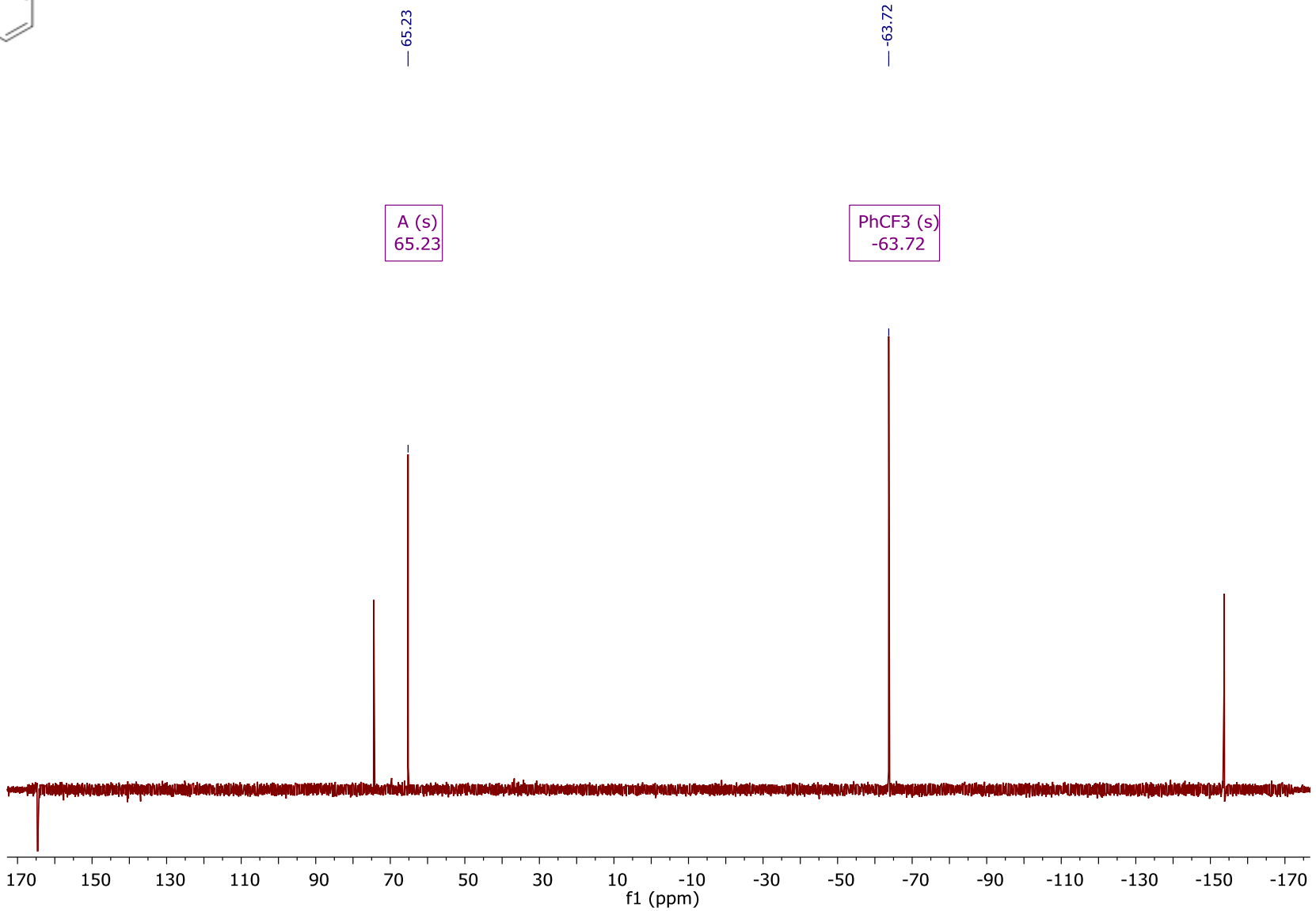


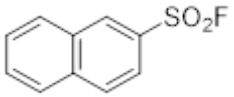
**3g $^{13}$C NMR (75 MHz, chloroform-*d*)**



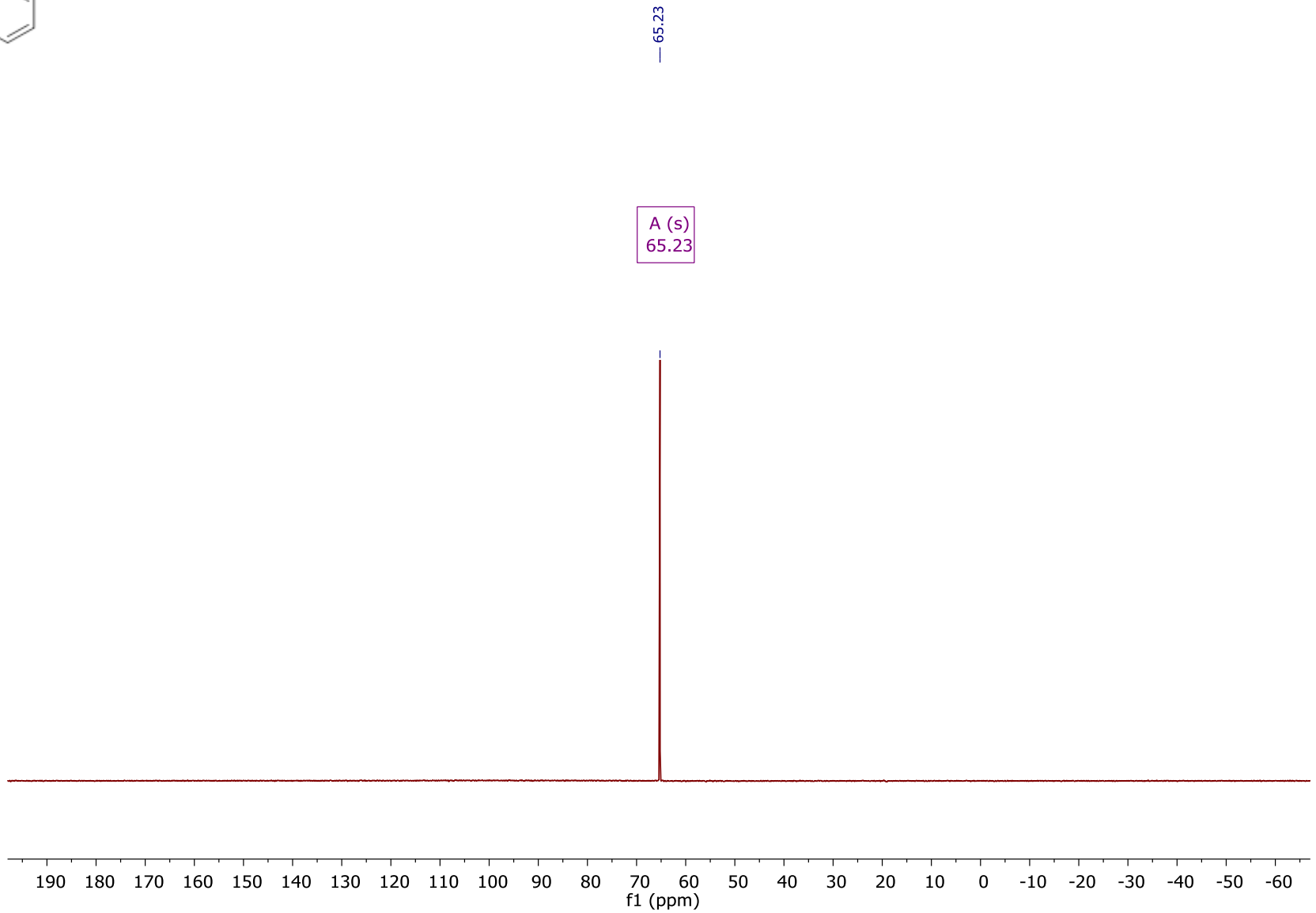



**3h Crude Reaction $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**

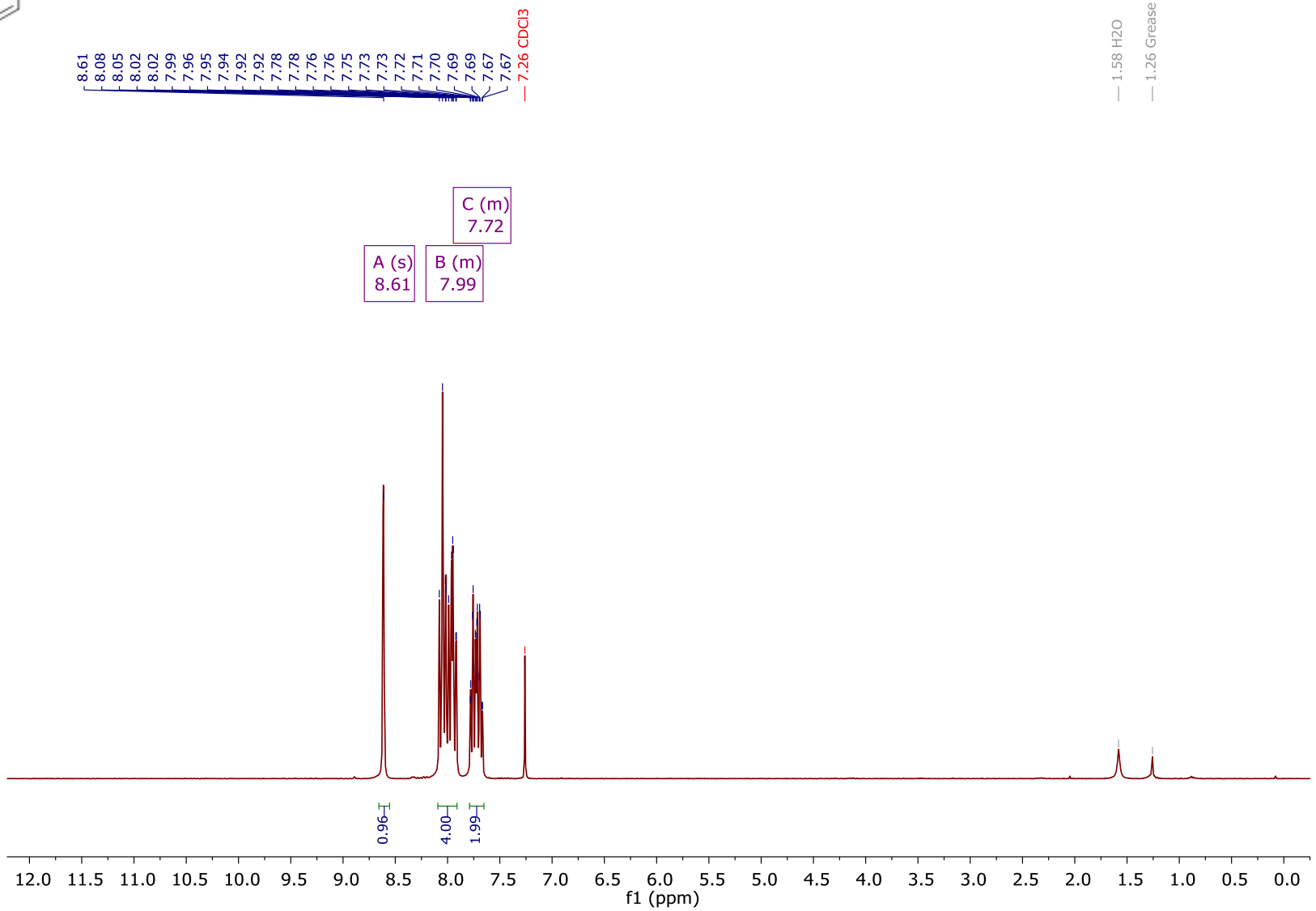


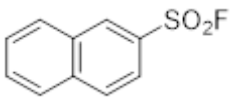



**3h $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**

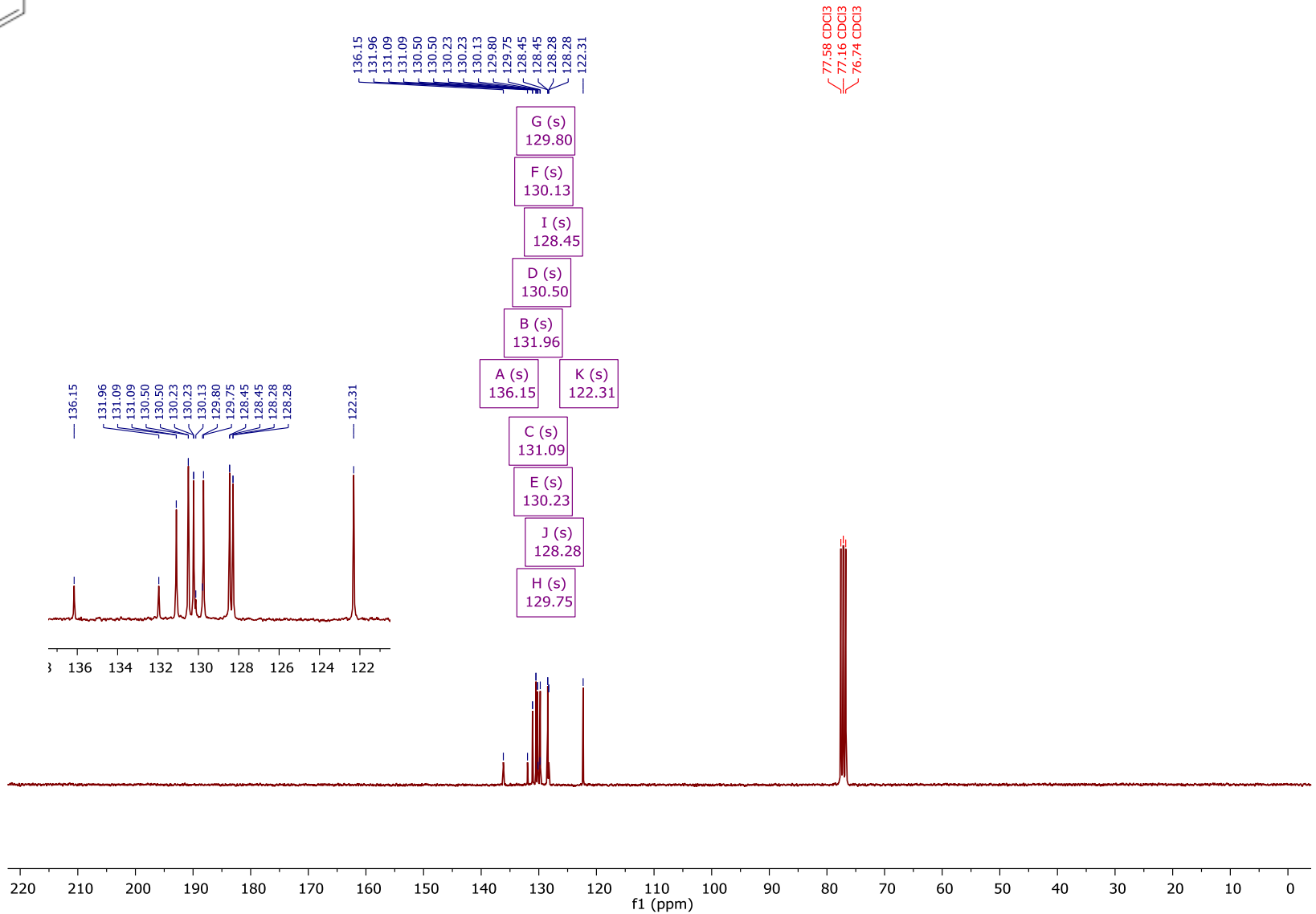


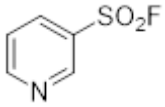

**3h $^1$H NMR (300 MHz, chloroform-*d*)**



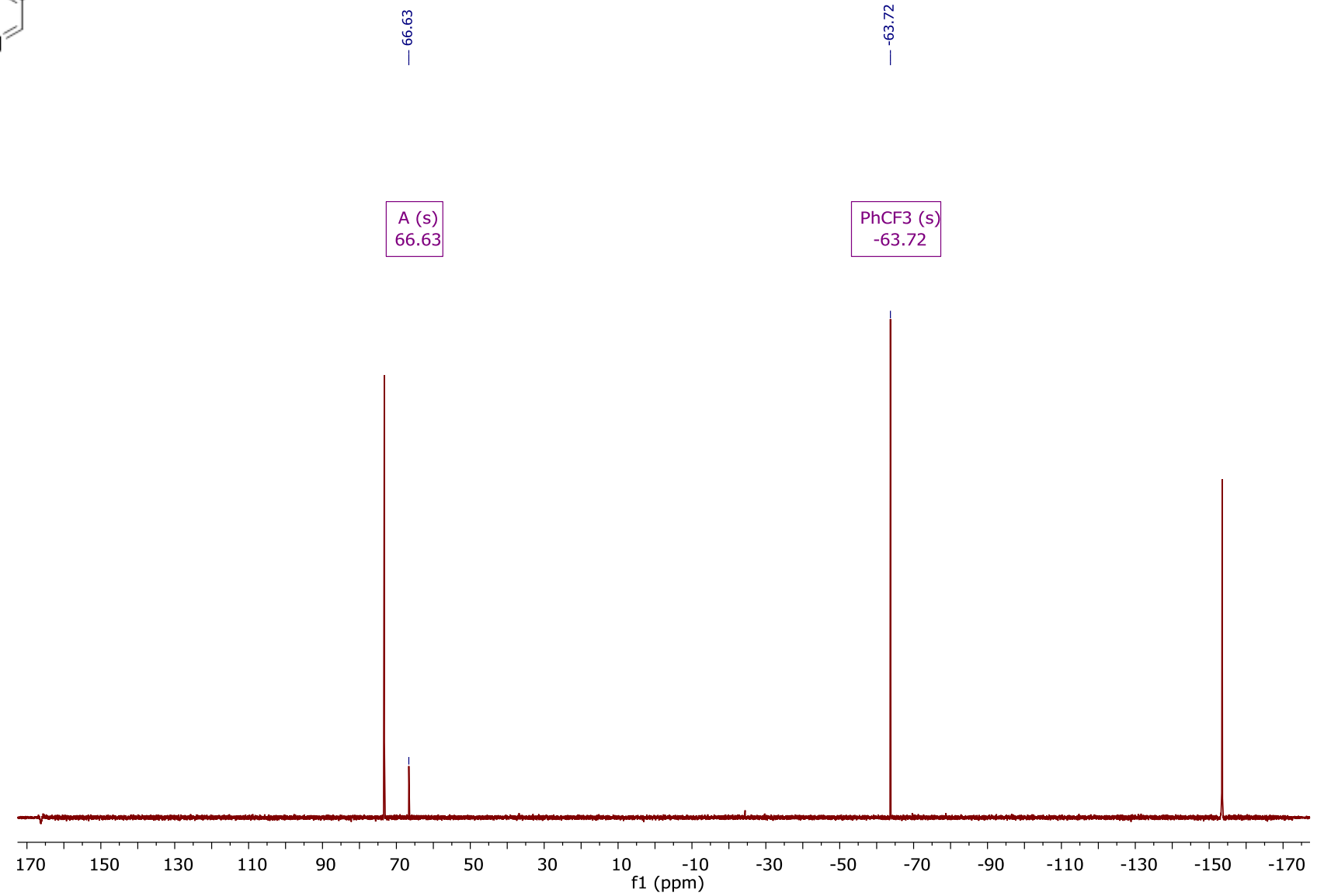



**3h $^{13}$C NMR (75 MHz, chloroform-*d*)**

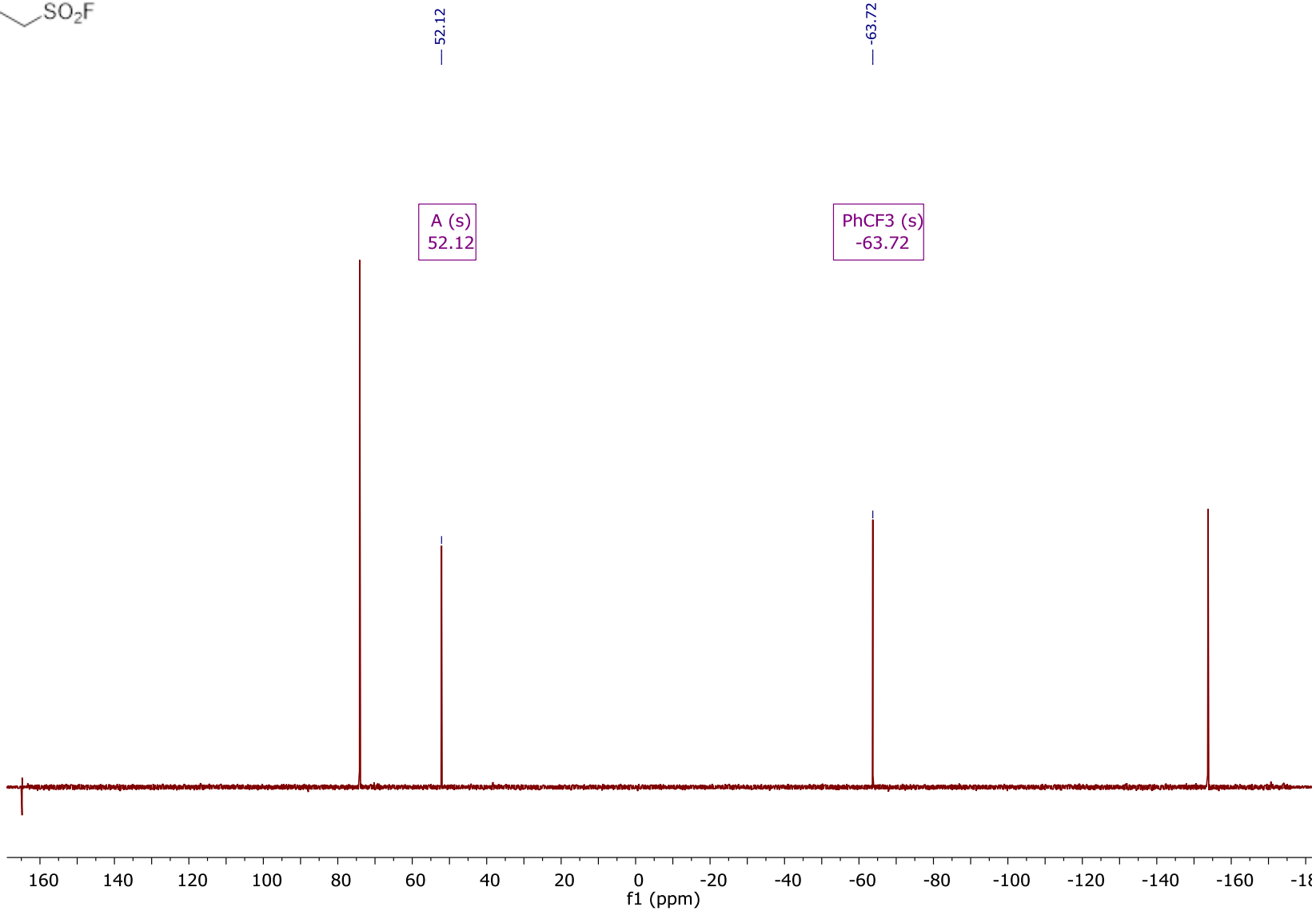





**3i Crude Reaction $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**



**3k Crude Reaction $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**

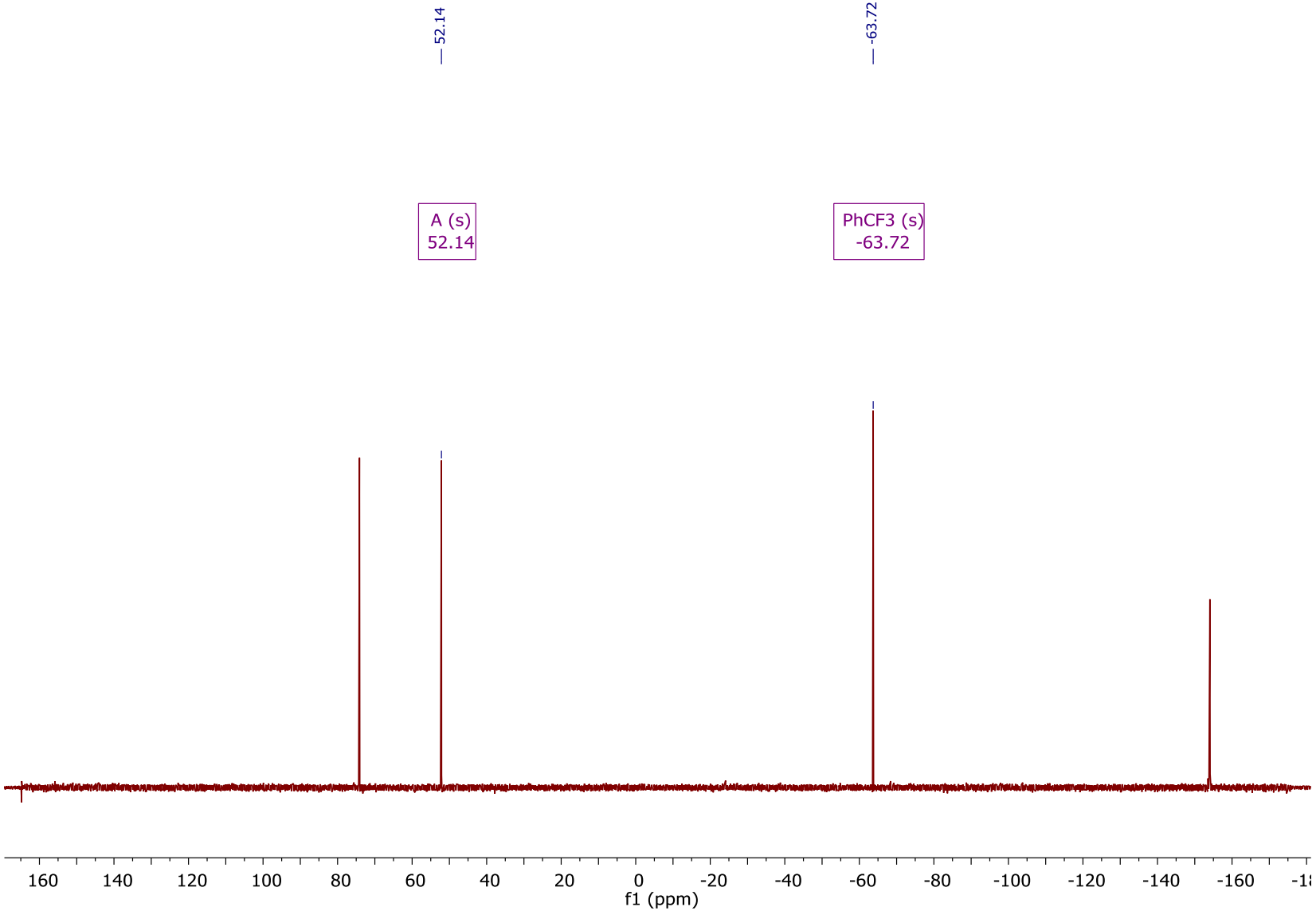



**3k $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**


**3k $^{1}$H NMR (300 MHz, chloroform-*d*)**

**3k $^{19}F\{H\}$ NMR (75 MHz, chloroform-*d*)**

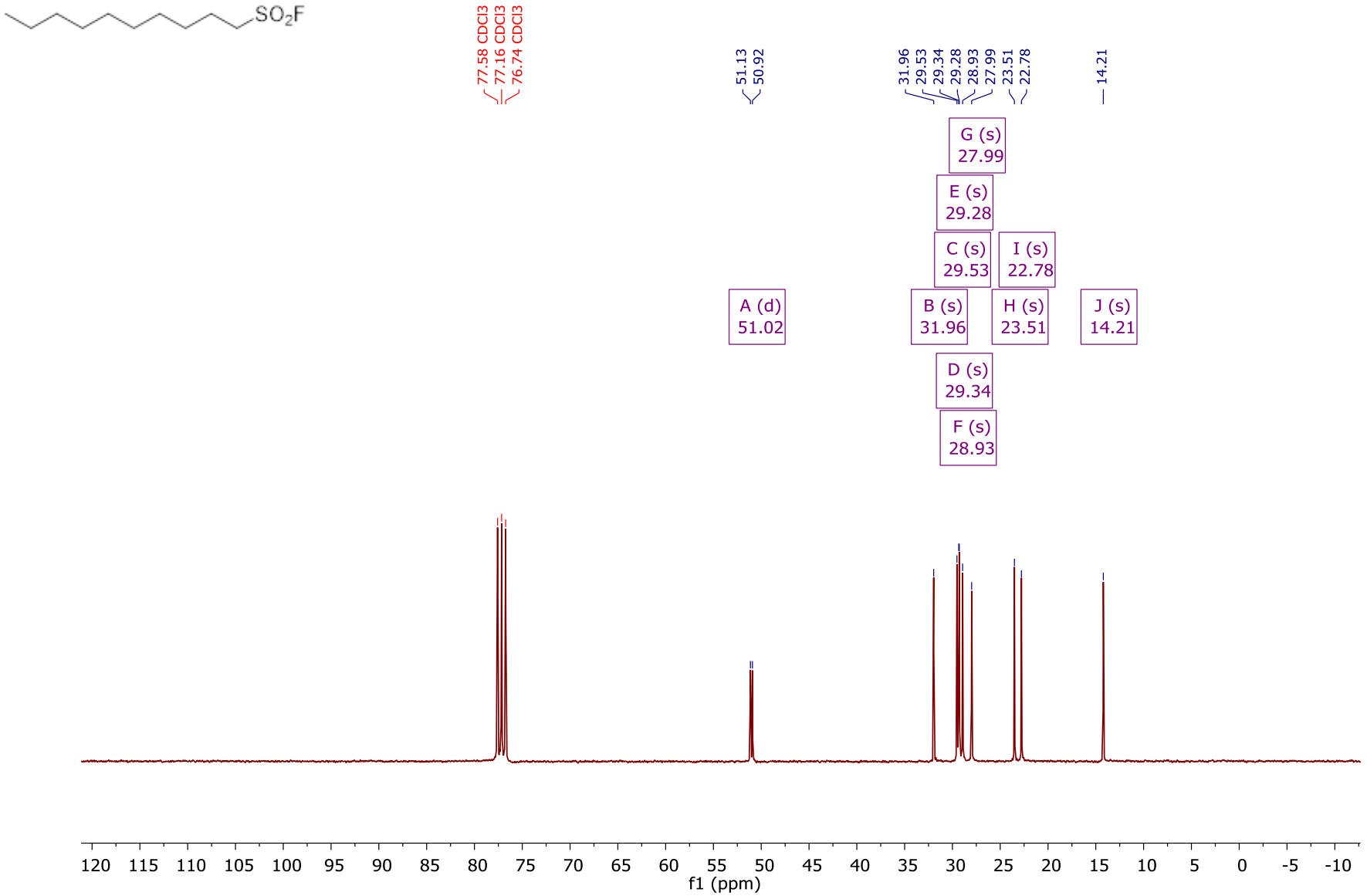

**3l Crude Reaction $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**



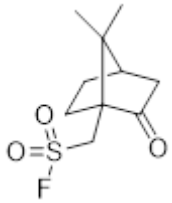
**3l $^{19}F\{H\}$ NMR (282 MHz, chloroform-*d*)**

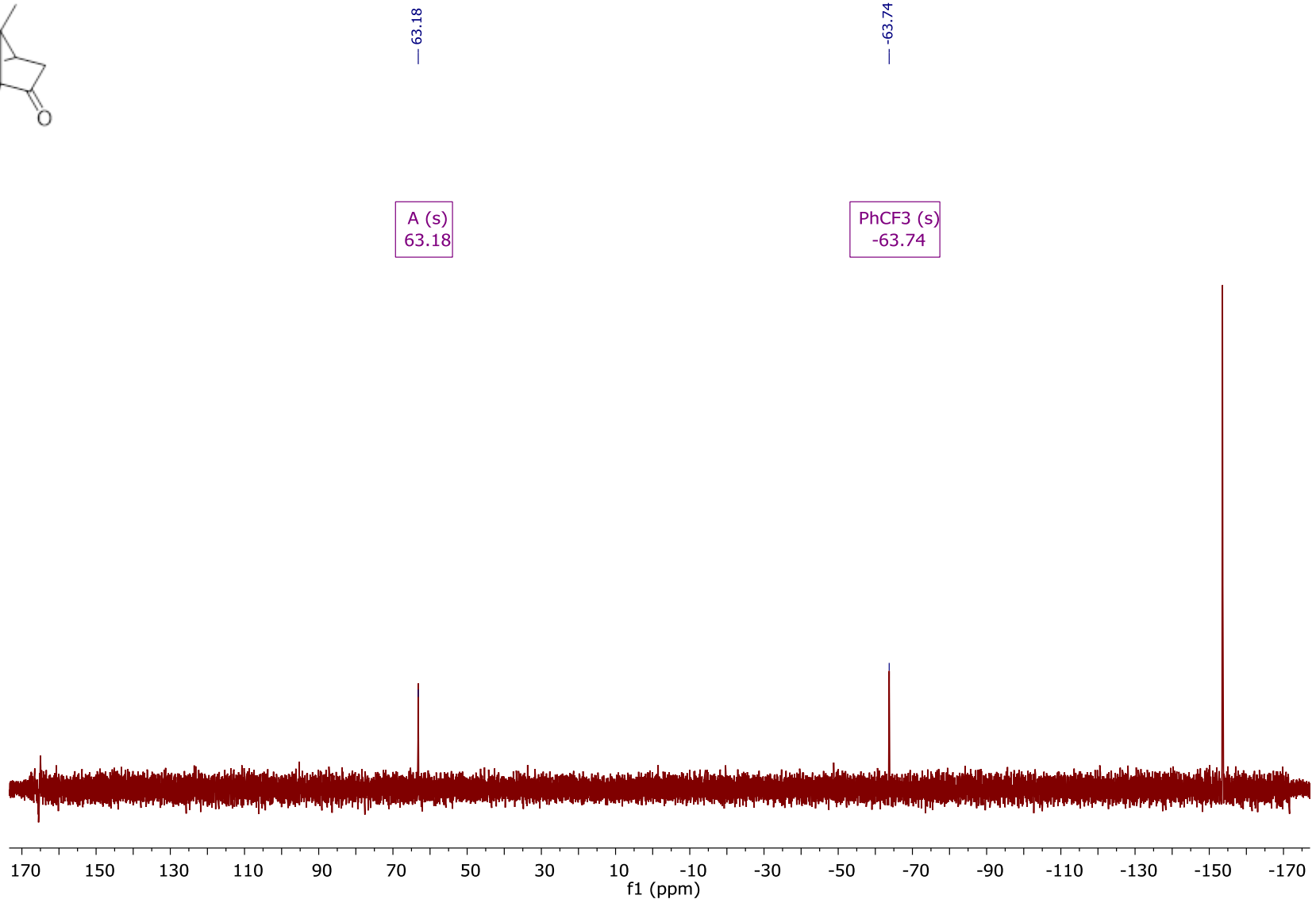
**3l $^{1}$H NMR (300 MHz, chloroform-*d*)**

**3l $^{13}$C NMR (75 MHz, chloroform-*d*)**

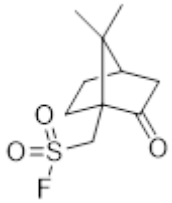


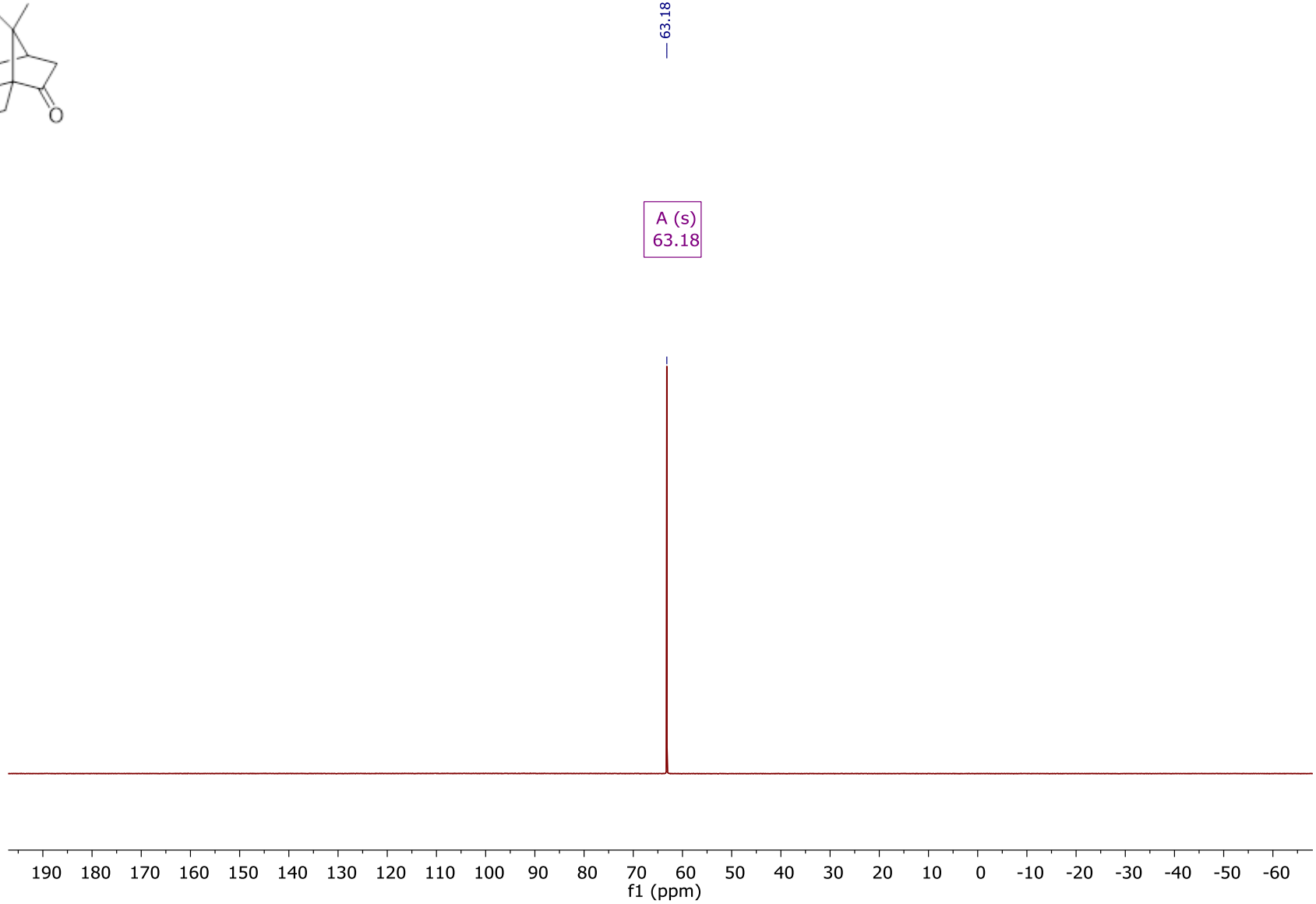
**3m Crude Reaction $^{19}$F NMR (282 MHz, chloroform-*d*)**



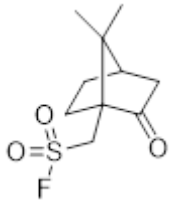



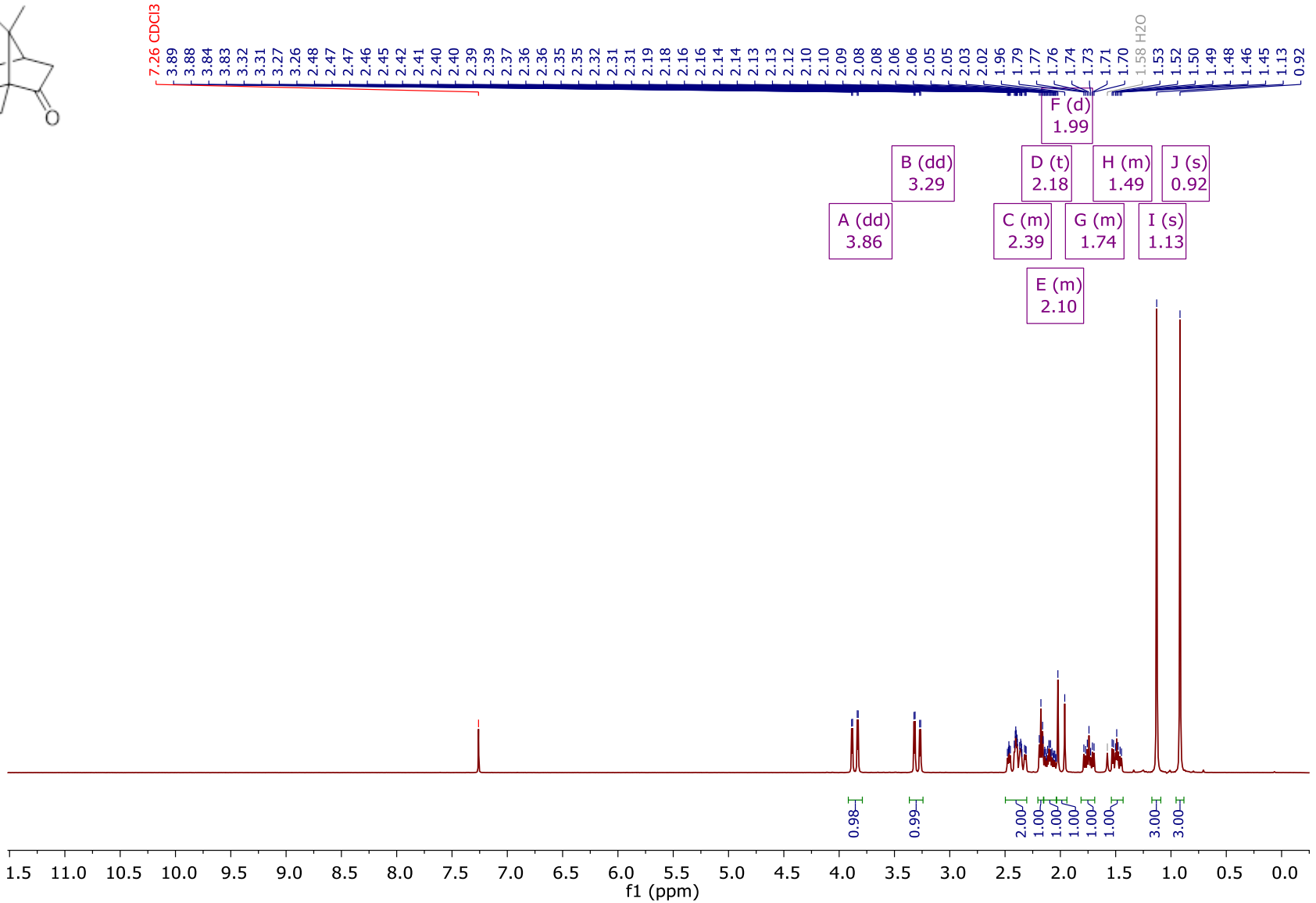
**3m $^{19}$F NMR (282 MHz, chloroform-*d*)**



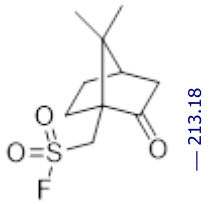



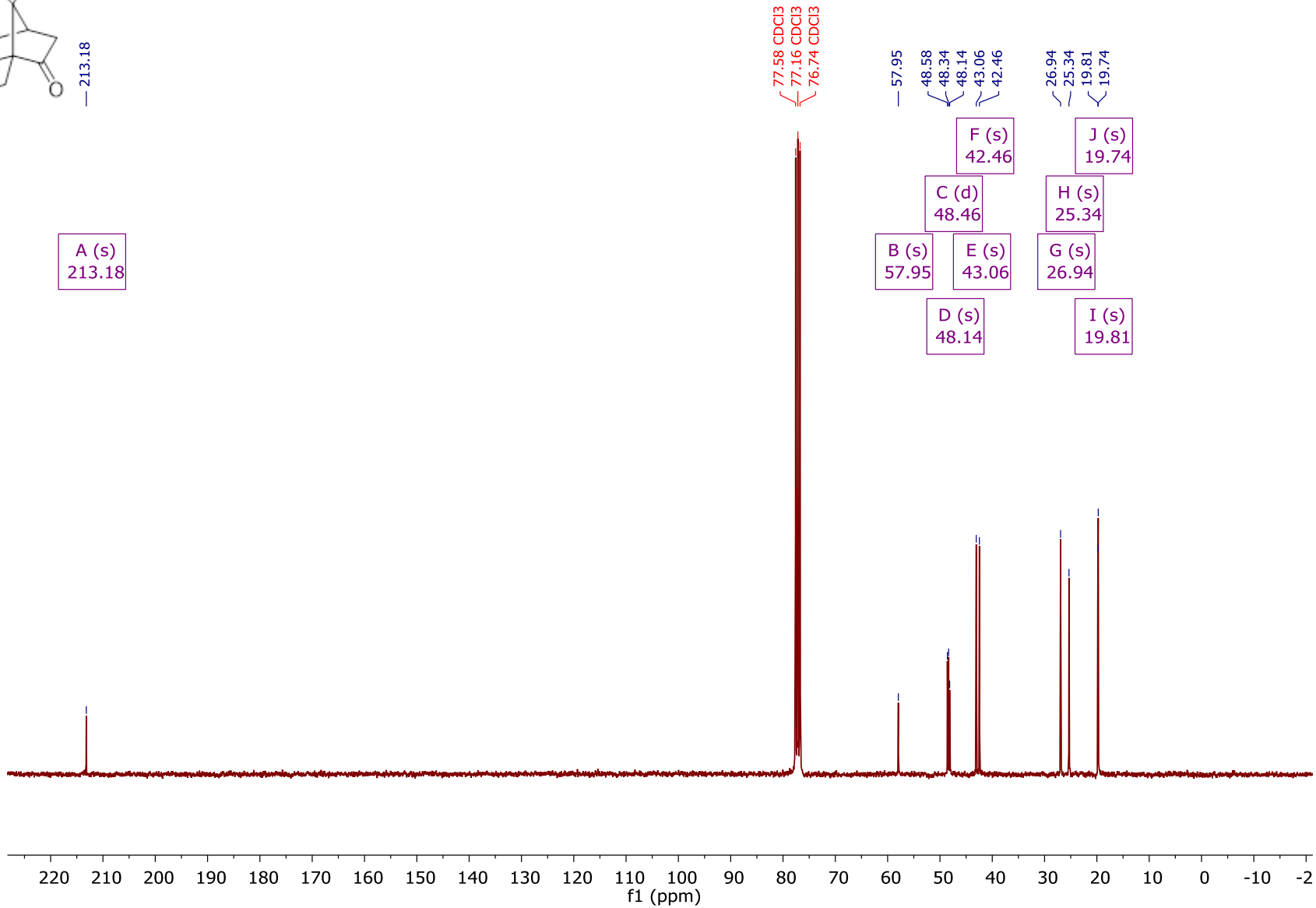
**3m $^{1}$H NMR (300 MHz, chloroform-*d*)**



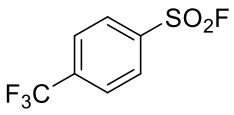



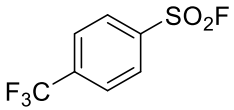
**3m $^{13}$C NMR (75 MHz, chloroform-*d*)**



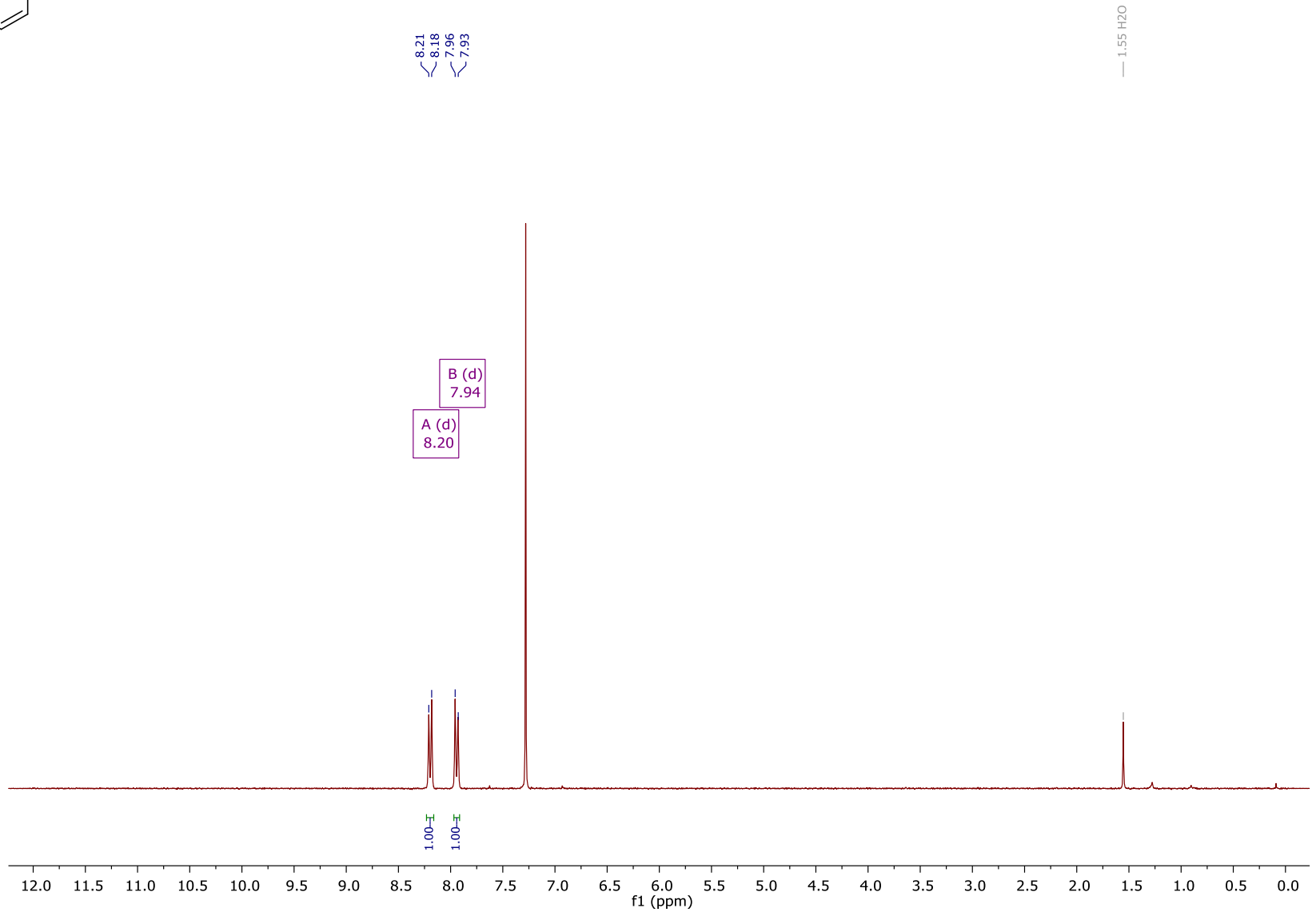



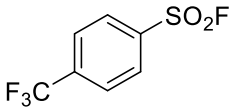
**3n $^{19}$F NMR (300 MHz, chloroform-*d*)**



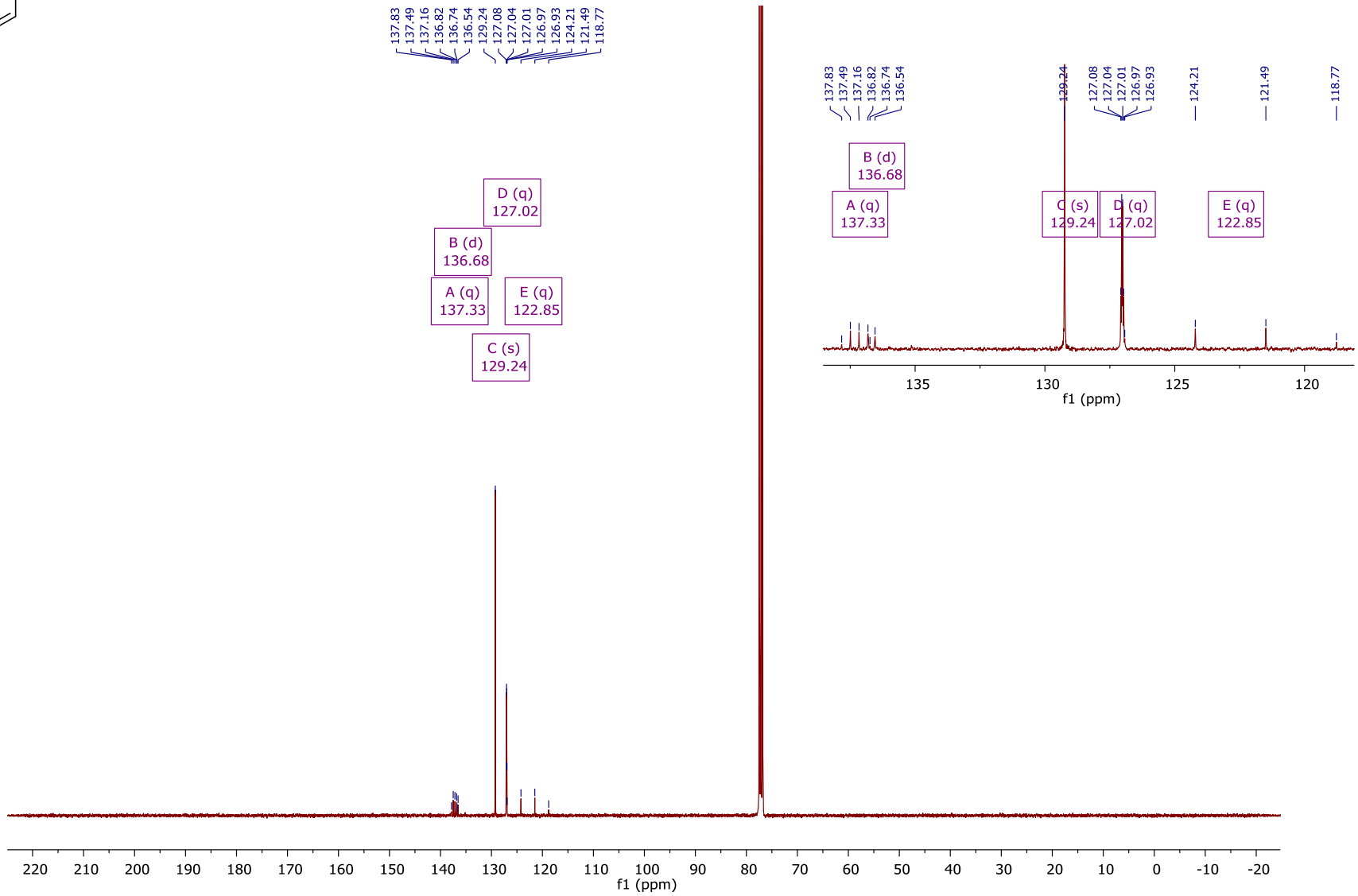



**3n $^{1}$H NMR (377 MHz, chloroform-*d*)**

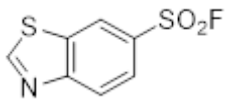




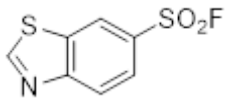

**3n $^{13}$C NMR (101 MHz, chloroform-*d*)**



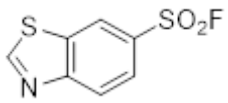
**3o $^{19}$F NMR (377 MHz, chloroform-*d*)**



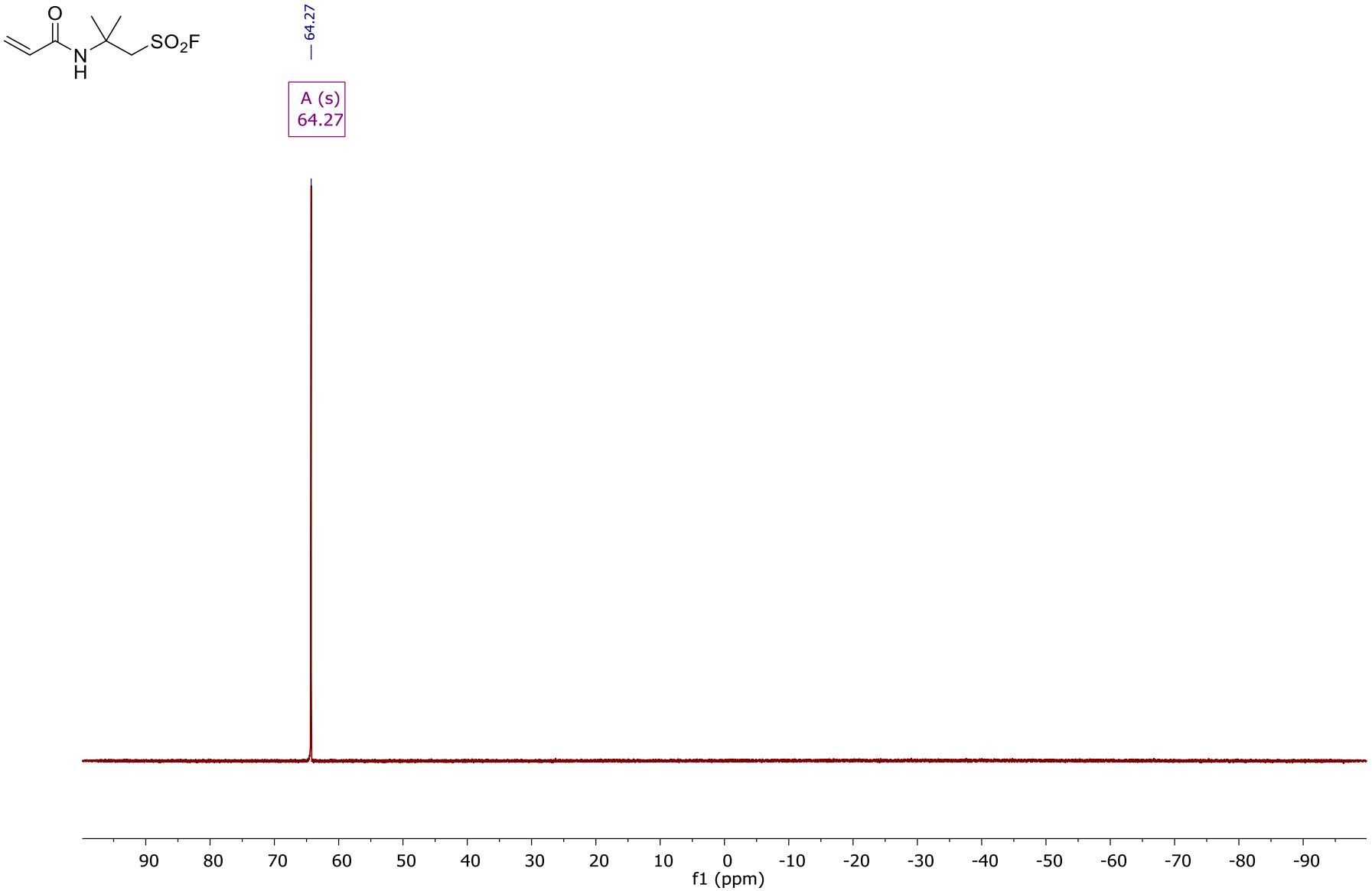
**3o $^{1}$H NMR (400 MHz, chloroform-*d*)**



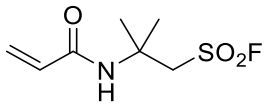
**3o $^{13}$C NMR (101 MHz, chloroform-*d*)**



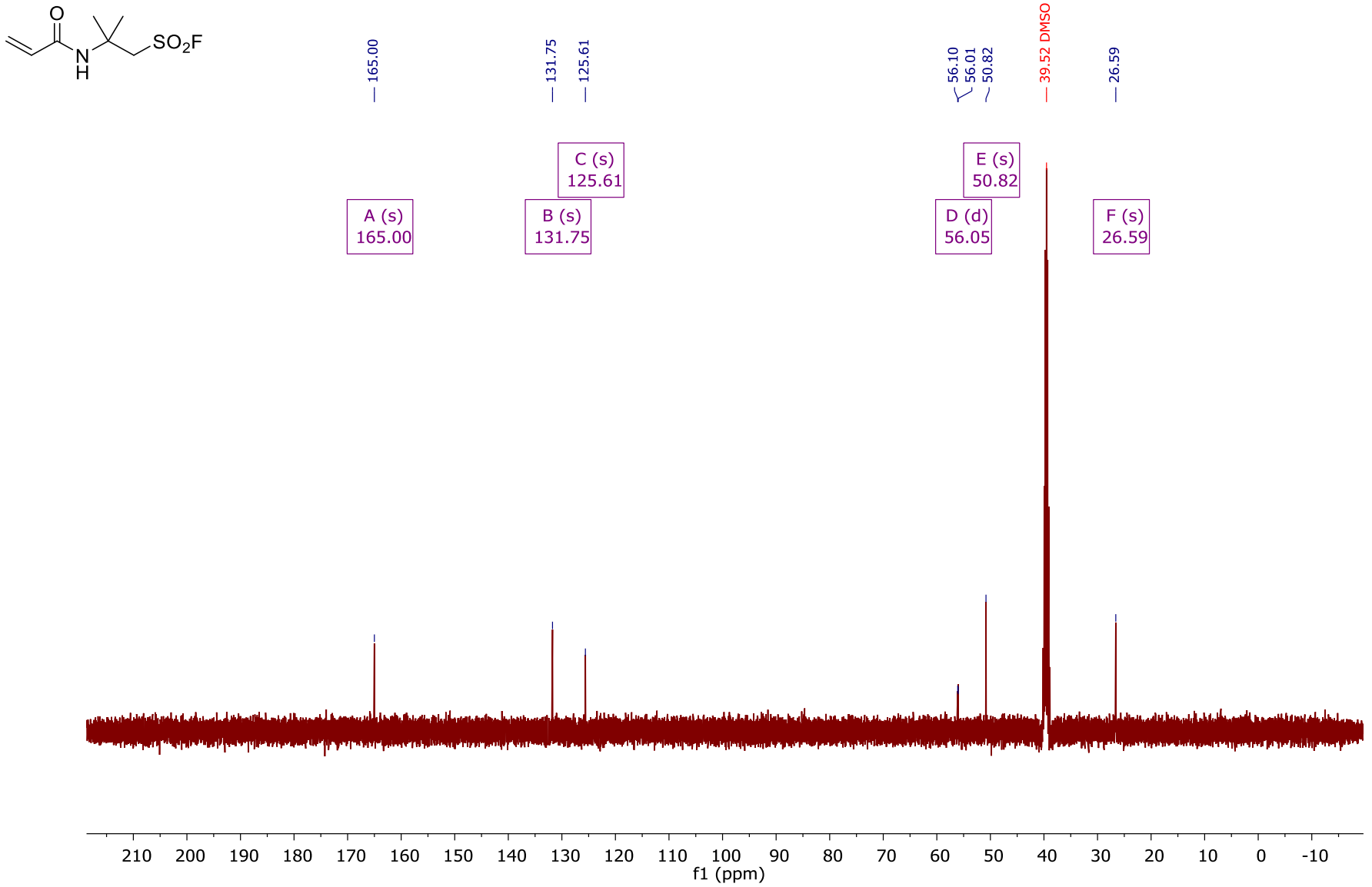
**3p $^{19}$F NMR (377 MHz, DMSO-$d_6$)**

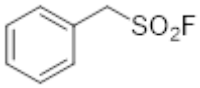


**3p $^{1}$H NMR (400 MHz, DMSO-$d_6$)**

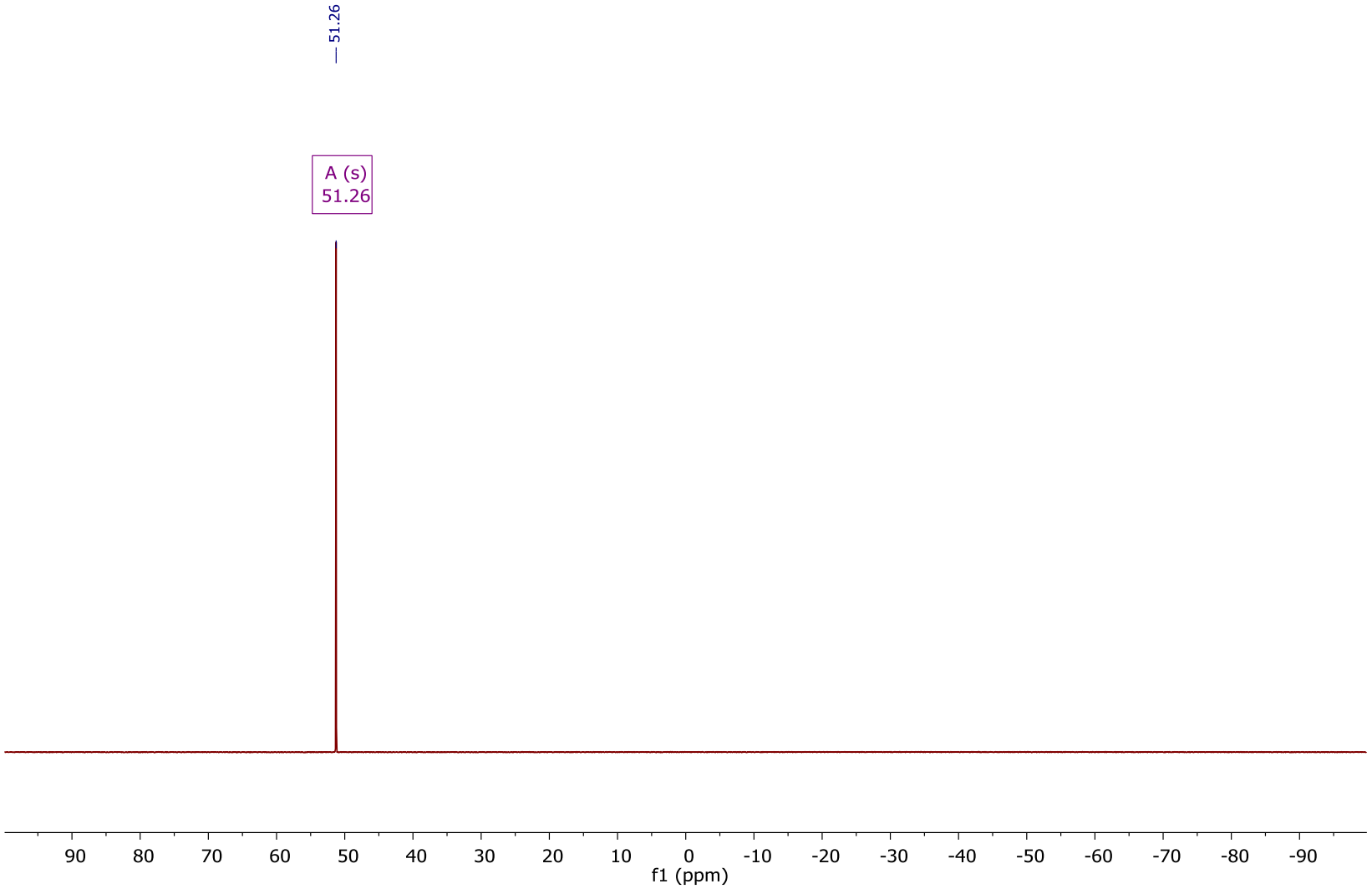


**3p $^{13}$C NMR (101 MHz, DMSO-$d_6$)**

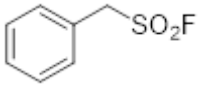


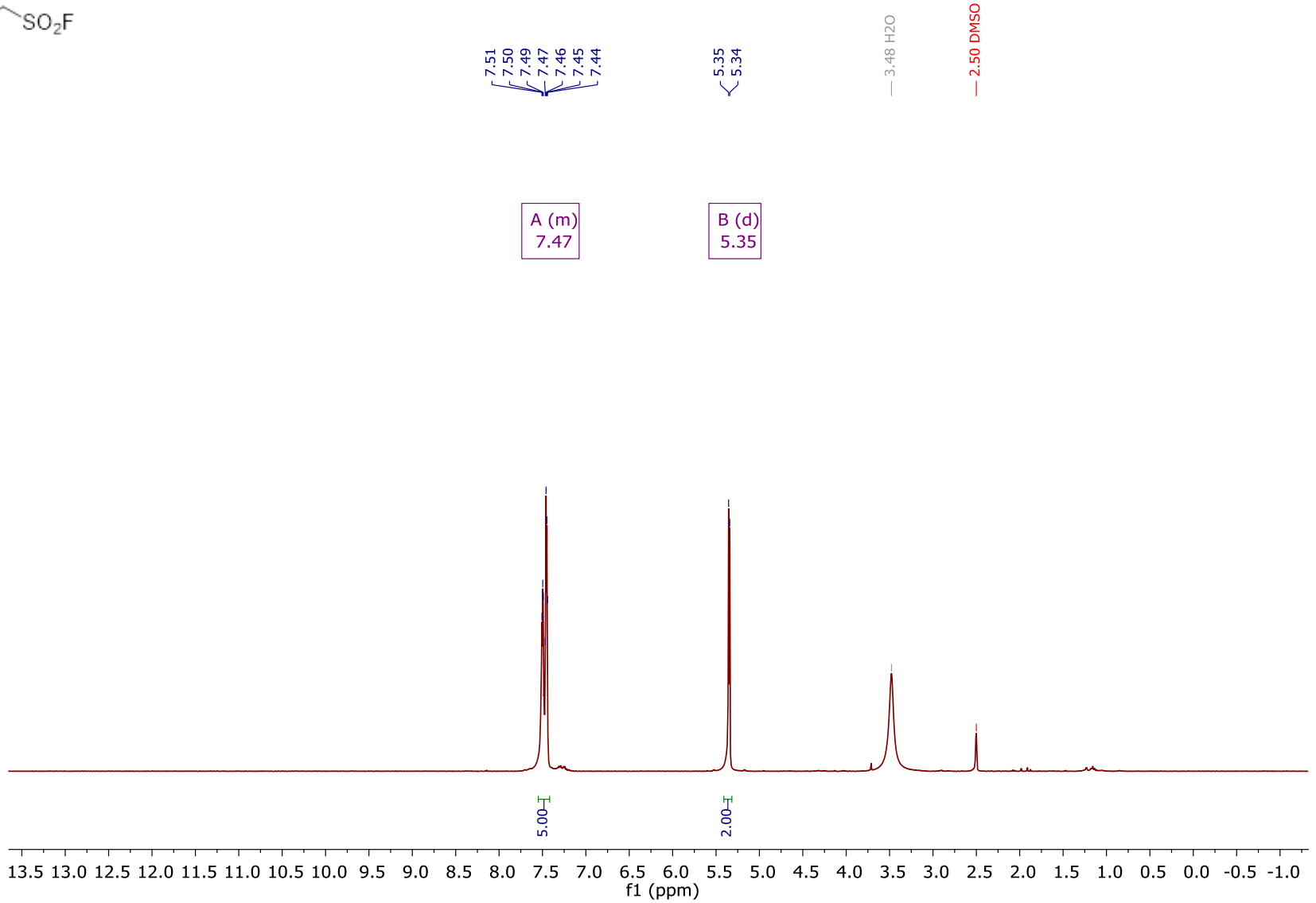



**3q $^{13}$C NMR (377 MHz, DMSO-$d_6$)**

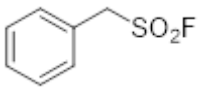


**3q $^1$H NMR (400 MHz, DMSO-$d_6$)**

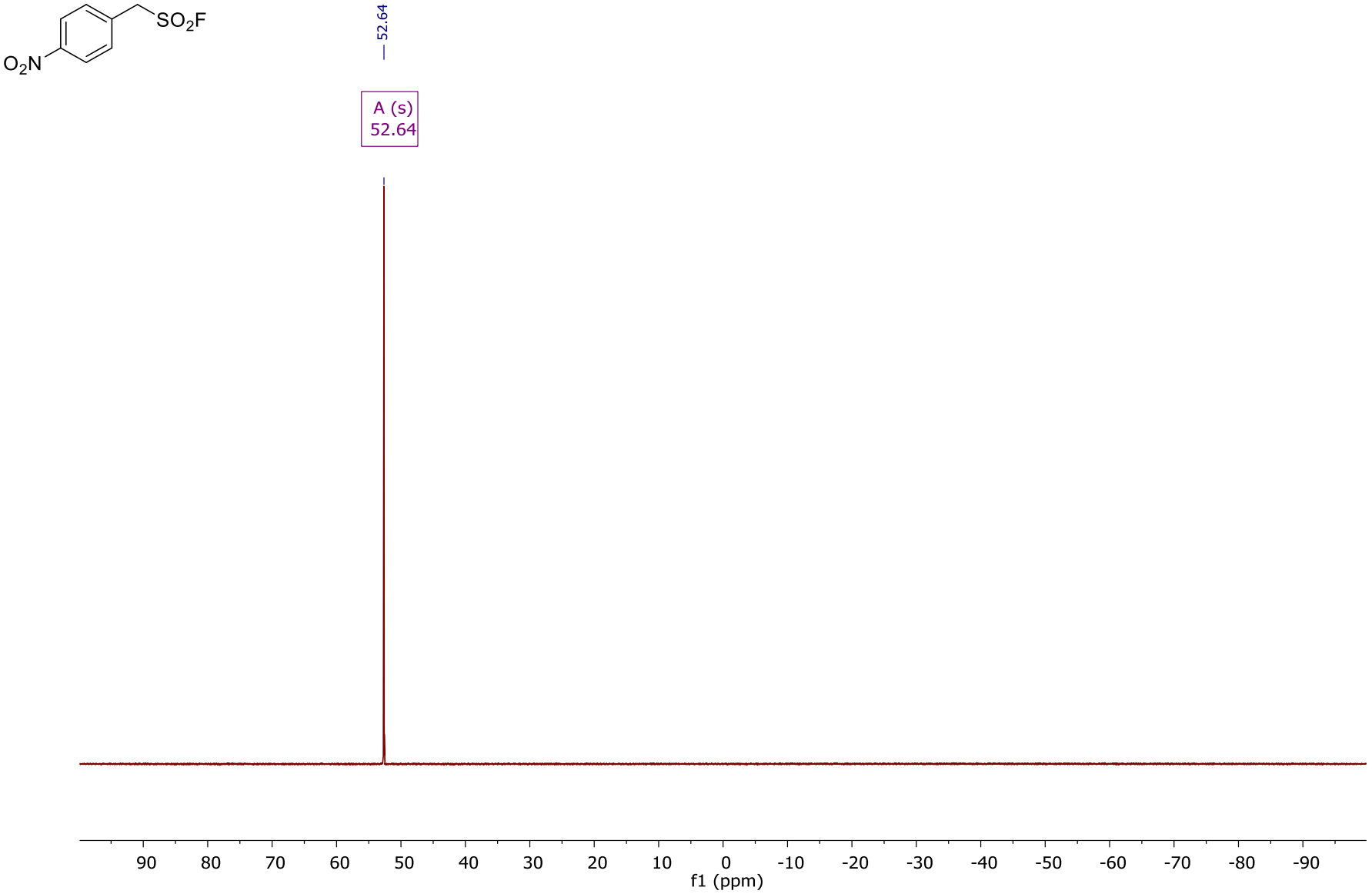


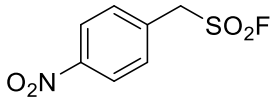
**3q $^{13}$C NMR (101 MHz, DMSO-$d_6$)**



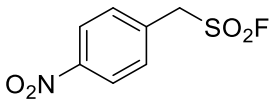
**3r $^{19}$F NMR (377 MHz, DMSO-$d_6$)**



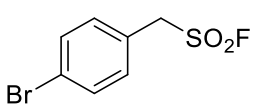
**3r $^{1}$H NMR (400 MHz, DMSO-$d_6$)**



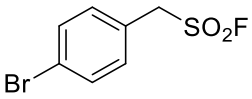
**3r $^{13}$C NMR (101 MHz, DMSO-$d_6$)**



**3s $^{19}$F NMR (377 MHz, DMSO-$d_6$)**



**3s $^{1}$H NMR (400 MHz, DMSO-$d_6$)**



**3s $^{13}$C NMR (101 MHz, DMSO-$d_6$)**