Supporting Information

Borane promoted aryl transfer reaction for the synthesis of α-aryl functionalised β-hydroxy and β-keto esters

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1. Experimental

1.1 General experimental

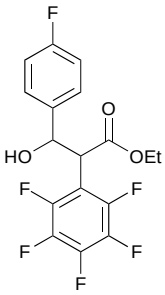
Except for the starting materials, all reactions and manipulations were carried out under an atmosphere of dry, O_2-free nitrogen using standard double-manifold techniques with a rotary oil pump. A nitrogen-filled glove box (MBraun) was used to manipulate solids including the storage of starting materials, ambient temperature reactions, product recovery and sample preparation for analysis. All solvents (toluene, dichloromethane, hexane, dichloroethane) were dried by employing a Grubbs-type column system (Innovative Technology) or a solvent purification system MB SPS-800 and stored under a nitrogen atmosphere. Anhydrous (with Sure/Seal) dichloroethane was purchased from Merck and dried over molecular sieves before use. Deuterated solvents were distilled and/or dried over molecular sieves before use. Chemicals were purchased from commercial suppliers and used as received. All the triarylfluoroboranes and ethyl α-diazomethylacetate **1b** were prepared as per the standard literature report.[1] Thin-layer chromatography (TLC) was performed on pre-coated aluminium sheets of Merck silica gel 60 F254 (0.20 mm). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Avance II 400 or Bruker Avance 500 spectrometers. Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to $CDCl_3$ (7.26/77.16 ppm) as internal standard. NMR spectra were referenced to $CFCl_3$ (^{19}F)[2]. The description of signals includes s = singlet, d = doublet, t = triplet, vt = virtual triplet, q = quartet, and m = multiplet, br. = broad. All coupling constants are absolute values and are expressed in Hertz (Hz). ^{13}C NMR was measured as ^{1}H decoupled. Most ^{13}C signals for the C_6F_5 moity are broadened and not resolved in the ^{13}C NMR spectrum. However, a broad doublet (J_{C-F} = ~250 Hz) is always visible. All spectra were analysed assuming a first order approximation. Yields are given as isolated yields. In case of the β-hydroxy esters, yields combined are the yields for the anti- and the syn-alcohol together, even if collected separately. In case of a mixture of isomers, the integration of the ^{1}H or the ^{19}F NMR is fitted for the racemic *2S*,3S**-alcohol. Only the analytic data for the racemic *2S*,3S**-alcohol is reported since the racemic *2S*,3R**-alcohol is formed in low quantities. IR-Spectra were measured on a Shimadzu IRAffinity-1 photo-spectrometer. Mass spectra were measured on a Waters LCT Premier/XE or a Waters GCT Premier spectrometer. Ions were generated by the Atmospheric Solids, Analysis Probe (ASAP), Electrospray (ES) or Electron Ionisation (EI). The molecular ion peaks values quoted for either molecular ion (M^+), molecular ion plus or minus hydrogen ($M+H^+$, $M-H^-$), molecular ion plus sodium ($M+Na^+$), molecular ion minus hydroxy ($M-OH^+$), and molecular ion minus hydrofluoro ($M-HF^+$).

2. Product Characterisation

2.1 General Procedure: The triaryl borane (1 equiv.) was dissolved in 0.65 mL dry CH_2Cl_2 in a reaction tube which was sealed with a microwave cap in a glovebox under a nitrogen atmosphere. The α-diazo propanoate (1 equiv.), dissolved in 0.65 mL dry CH_2Cl_2, was added dropwise at ambient temperature. Gas evolution was noticed immediately. The reaction mixture was stirred for 10 minutes at room temperature before adding the electrophile (1 equiv.), dissolved in 0.65 mL dry CH_2Cl_2. The reaction was heated to 45 °C for 24 h and quenched by adding 1 mL of a 1M aq. NaOH solution. The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 3 mL). The combined organic layer was dried over $MgSO_4$. All volatiles were removed *in vacuo* and a ^{19}F NMR spectrum was taken to determine the diastereomeric ratio. Afterwards, the crude compound was purified *via* preparative thin layer chromatography using hexane/ethyl acetate as eluent.

2.2 Synthesis and spectral characterisation of α-aryl-β-hydroxy esters

Synthesis of ethyl 3-(4-fluorophenyl)-3-hydroxy-2-(pentafluorophenyl)propanoate (**2a**)



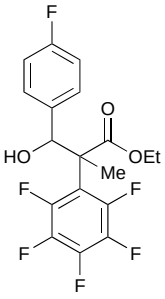
Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (90 mg, 0.18 mmol), ethyl diazoacetate (**1a**, 20 mg, 0.18 mmol, 15% in toluene), and 4-fluorobenzaldehyde (22 mg, 0.18 mmol) in CH_2Cl_2 to afford **2a**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **2a** (*dr*: 1:0.07) was obtained as a mixture of diastereomers as a colourless solid. Yield: 49 mg, 0.13 mmol, 74%.

Note: Some signals of the major (Δ) and the minor (*) isomer are overlapping. The carbon signals of the C_6F_5 substituent of the minor compound are too broad to be observed in the ^{13}C NMR.*

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 7.11–7.19Δ* (m, 2H, Ar-H), 6.88–6.99Δ* (m, 2H, Ar-H), 5.62* (br. s, 1H, OH), 5.28Δ (dd, *J* = 9.2, 2.6 Hz, 1H, CH), 4.36Δ (d, *J* = 2.6 Hz, 1H, CH), 4.17–4.33Δ* (m, 3H, OHΔ, Et-CH_2Δ*, CH*), 3.07* (d, *J* = 2.8 Hz, 1H, CH), 1.20–1.26Δ* (m, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 171.5Δ, 170.5*, 162.7Δ (d, $J_{C–F}$ = 247.5 Hz), 166.3* (d, $J_{C–F}$ = 246.9 Hz), 144.7Δ (br. d, $J_{C–F}$ = 247.5 Hz), 140.7Δ (br. d, $J_{C–F}$ = 253.3 Hz), 274.8Δ (br. d, $J_{C–F}$ = 255.5 Hz), 135.6*, 135.3Δ (d, $J_{C–F}$ = 3.4 Hz), 128.3Δ (d, $J_{C–F}$ = 8.3 Hz), 127.7* (d, $J_{C–F}$ = 8.3 Hz), 115.5Δ (d, $J_{C–F}$ = 21.9 Hz), 115.4* (d, $J_{C–F}$ = 21.7 Hz), 110.6Δ (t, $J_{C–F}$ = 18.5 Hz), 73.0Δ, 71.9*, 62.6Δ, 62.3*, 48.8*, 48.3Δ, 15.4*, 14.1Δ ppm. **^{19}F NMR** (376.5

MHz, $CDCl_3$, 298 K) δ: -113.04[Δ] (s, 1F, Ar-F), -113.86* (s, 1F, Ar-F), -139.61* (br. s, 2F, Ar-F), -140.98[Δ] (ddd, *J* = 20.8, 6.2, 4.0 Hz, 2F, Ar-F), -153.63[Δ] (vt, *J* = 20.8 Hz, 1F, Ar-F), -154.17* (vt, *J* = 20.8 Hz, 1F, Ar-F), -161.38[Δ] (ddd, *J* = 20.8, 6.2, 4.0 Hz, 2F, Ar-F), -162.18* (dt, *J* = 20.8, 6.2 Hz, 1F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3505 (OH), 3046, 2986, 2932, 2855, 1726 (C=O), 1655, 1605, 1522, 1503, 1369, 1300, 1225, 1184, 1157, 1125, 1043, 1015. **HRMS** (ASAP) $[M-H]^+$ $[C_{17}H_{11}O_3F_6]^+$: calculated 377.0612, found 377.0622.

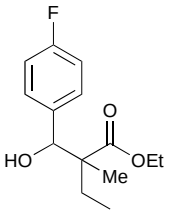
Synthesis of ethyl 3-(4-fluorophenyl)-3-hydroxy-2-methyl-2-(pentafluorophenyl)propanoate (**2b**)



Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-fluorobenzaldehyde (19 mg, 0.16 mmol) in CH_2Cl_2 to afford **2b**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **2b** (*dr*: 1:0.1) was obtained as a colourless oil. Yield combined: 44 mg, 0.11 mmol, 72%.

^{1}H NMR (500.2 MHz, $CDCl_3$, 298 K) δ: 6.87–6.95 (m, 4H, Ar-H), 5.28 (d, *J* = 2.7 Hz, 1H), 4.62 (d, *J* = 2.7 Hz, 1H), 4.22–4.28 (m, 2H, CH_2), 1.74 (t, *J* = 3.0 Hz, 3H, CH_3), 1.23 (t, *J* = 7.1 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 176.5, 162.7 (d, $J_{C–F}$ = 247.4 Hz), 146.0 (br. d, $J_{C–F}$ = 247.7 Hz), 140.4 (br. d, $J_{C–F}$ = 252.8 Hz), 137.7 (br. d, $J_{C–F}$ = 251.8 Hz), 133.7 (d, $J_{C–F}$ = 3.3 Hz), 129.1 (d, $J_{C–F}$ = 8.0 Hz), 114.8 (d, $J_{C–F}$ = 21.6 Hz), 114.8 (br. s), 75.2, 62.5, 53.8, 16.7 (t, $J_{C–F}$ = 6.1 Hz), 14.0 ppm. **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) δ: -113.76–-113.70 (m, 1F, Ar-F), -138.41 (d, *J* = 18.9 Hz, 2F, Ar-F), -154.27 (t, *J* = 20.9 Hz, 1F, Ar-F), -161.88 (ddd, *J* = 20.9, 18.9, 6.7 Hz, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3514 (OH), 3048, 2986, 2961, 2941, 2907, 1719 (C=O), 1655, 1607, 1524, 1489, 1395, 1306, 1263, 1225, 1194, 1159, 1125, 1099, 1076, 1015. **HRMS** (GC-MS) $[M-HF]^+$ $[C_{18}H_{13}O_3F_5]^+$: calculated 372.0779, found 372.0791.

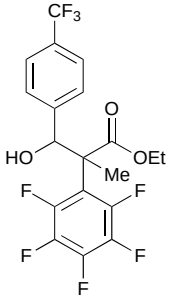
Synthesis of ethyl 2-((4-fluorophenyl)(hydroxy)methyl)-2-methylbutanoate (**2r**)



Synthesised in accordance with the *General Procedure* using BEt_3 (0.16 mL, 0.16 mmol, 1M in hexane), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-fluorobenzaldehyde (19 mg, 0.16 mmol) in CH_2Cl_2 to afford **2r**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired compound **2r** (*dr*: 1:0.58) was obtained as a colourless oil. Yield combined: 30 mg, 0.12 mmol, 76%.

^{1}H NMR (500.2 MHz, $CDCl_3$, 298 K) δ: 7.25–7.28 (m, 2H, Ar-H), 6.99–7.02 (m, 2H, Ar-H), 4.88 (d, J = 4.9 Hz, 1H), 4.13–5.25 (m, 2H, CH_2), 4.17 (d, J = 4.9 Hz, 1H), 1.72–1.79 (m, 1H), 1.23–1.31 (m, 4H, CH_2 and CH_3), 1.02 (s, 3H, CH_3), 0.84 ppm (t, J = 7.5 Hz, 3H, CH_3). **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 177.1, 162.4 (d, $J_{C–F}$ = 245.8 Hz), 136.2 (d, $J_{C–F}$ = 3.2 Hz), 129.3 (d, $J_{C–F}$ = 7.9 Hz), 114.8 (d, $J_{C–F}$ = 20.8 Hz), 77.7, 61.0, 52.1, 30.1, 15.7, 14.4, 9.0 ppm. **^{19}F NMR** (470.6 MHz, $CDCl_3$, 298 K) δ: -114.87–-114.81 ppm. **IR** ν_{max} (cm^{-1}): 3390 (OH), 2974, 2929 2881, 1716 (C=O), 1604, 1508, 1460, 1384, 1367, 1222, 1155, 1130, 1099, 1062, 1033, 1014, 1001. **HRMS** (GC–MS) $[M\text{-}OH]^+$ $[C_{14}H_{18}O_2F]^+$: calculated 237.12853, found 237.1285.

Synthesis of ethyl 3-hydroxy-2-methyl-2-(pentafluorophenyl)-3-(4-(trifluoromethyl) phenylpropanoate (**2c**)

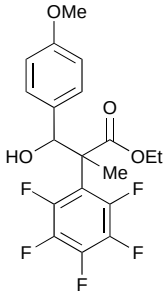


Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-trifluoromethylbenzaldehyde (27 mg, 0.16 mmol) in CH_2Cl_2 to afford **2c**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **2c** (*dr*: 1:0.28) was obtained as a colourless oil. Yield combined: 35 mg, 0.08 mmol, 51%.

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 7.46–7.48 (m, 2H, Ar-CH), 7.07–7.10 (m, 2H, Ar-CH), 5.35 (d, J = 2.8 Hz, 1H), 4.69 (d, J = 2.8 Hz, 1H), 4.23–4.29 (m, 2H, CH_2), 1.75 (t, J = 3.0 Hz, 3H, CH_3), 1.24 (t, J = 7.1 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 176.1, 145.9 (br. d, $J_{C–F}$ = 248.1 Hz), 141.7, 140.6 (br. d, $J_{C–F}$ = 256.1 Hz), 137.7 (br. d, $J_{C–F}$ = 253.5 Hz), 130.5 (q, $J_{C–F}$ = 32.8 Hz), 127.8, 124.6 (q, $J_{C–F}$ = 3.9 Hz), 123.9 (q, $J_{C–F}$ = 271.2 Hz), 114.3 (br. s), 75.3, 62.5, 53.4, 16.6 (t, $J_{C–F}$ = 6.4 Hz), 13.8 ppm. **^{19}F NMR** (376.5 MHz,

$CDCl_3$, 298 K) δ: -62.66 (s, 3F, CF_3), -138.34 (dd, *J* = 21.4, 7.0 Hz, 2F, Ar-F), -153.60 (vt, *J* = 21.4 Hz, 1F, Ar-F), -161.53 (dt, *J* = 21.4, 7.0 Hz, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3509 (OH), 2988, 2941, 2909, 1719 (C=O), 1653, 1622, 1524, 1489, 1416, 1323, 1252, 1165, 1125, 1078, 1067, 1016. **HRMS** (GC–MS) $[M-F]^+$ $[C_{19}H_{14}O_3F_7]^+$: calculated 423.0826, found 423.0819.

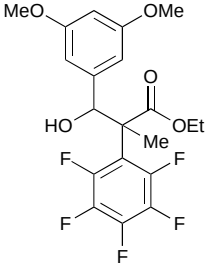
Synthesis of ethyl 3-hydroxy-3-(4-methoxyphenyl)-2-methyl-2-(pentafluorophenyl)-propanoate (**2d**)



Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-methoxybenzaldehyde (21 mg, 0.16 mmol) in CH_2Cl_2 to afford **2d**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired compound **2d** (*one diastereomer*) was obtained as a colourless oil. Yield combined: 23 mg, 0.06 mmol, 36%.

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 6.85–6.89 (m, 2H, Ar-H), 6.70–6.74 (m, 2H, Ar-H), 5.25 (d, *J* = 2.8 Hz, 1H), 4.57 (d, *J* = 2.8 Hz, 1H), 4.21–4.28 (m, 2H, CH_2), 3.76 (s, 3H, OCH_3), 1.75 (t, *J* = 3.1 Hz, 3H, CH_3), 1.23 (t, *J* = 7.4 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 176.6, 159.5, 146.1 (br. d, $J_{C–F}$ = 255.4 Hz), 140.3 (br. d, $J_{C–F}$ = 250.3 Hz), 137.3 (br. d, $J_{C–F}$ = 250.3 Hz), 129.9, 128.5, 115.1 3 (br. t, $J_{C–F}$ = 13.6 Hz), 113.2, 75.4, 62.3, 55.3, 54.0, 16.8 (t, $J_{C–F}$ = 6.1 Hz), 14.0 ppm. **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) δ: -138.44 (dd, *J* = 22.0, 7.0 Hz, 2F, Ar-F), -154.68 (vt, *J* = 22.0 Hz, 1F, Ar-F), -162.20 (dt, *J* = 22.0, 7.0 Hz, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3520 (OH), 3057, 2986, 2961, 2907, 2809 (OCH_3), 1719 (C=O), 1655, 1612, 1524, 1489, 1304, 1248, 1175, 1125, 1103, 1076, 1034. **HRMS** (ES+) $[M-OH]^+$ $[C_{19}H_{16}O_3F_5]^+$: calculated 387.1020, found 387.1040.

Synthesis of ethyl 3-(3,5-dimethoxyphenyl)-3-hydroxy-2-methyl-2-(pentafluorophenyl) propanoate (**2e**)

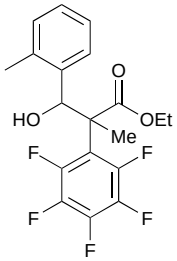


Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 3,5-dimethoxybenzaldehyde (26 mg, 0.16 mmol) in CH_2Cl_2 to afford **2e**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The

desired compound **2e** (*dr:* 1:0.11) was obtained as a colourless solid. Yield combined: 22 mg, 0.05 mmol, 32%.

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 6.34 (vt, *J* = 2.3 Hz, 1H, Ar-H), 6.11 (d, *J* = 2.3 Hz, 2H, Ar-H), 5.22 (d, *J* = 2.9 Hz, 1H), 4.59 (d, *J* = 2.9 Hz, 1H), 4.21–4.29 (m, 2H, CH_2), 3.68 (s, 6H OCH_3), 1.78 (t, *J* = 2.9 Hz, 3H, CH_3), 1.23 (t, *J* = 7.4 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 176.5, 160.2, 146.2 (br. d, $J_{C–F}$ = 248.9 Hz), 140.4 (br. d, $J_{C–F}$ = 243.1 Hz), 140.1, 137.7 (br. d, $J_{C–F}$ = 251.8 Hz), 115.2 (br. s), 105.8, 100.2, 75.9, 62.4, 55.4, 53.9, 17.0, (t, $J_{C–F}$ = 6.0 Hz), 14.0 ppm. **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) δ: -138.28 (dd, *J* = 22.0, 7.0 Hz, 2F, Ar-F), -154.73 (vt, *J* = 22.0 Hz, 1F, Ar-F), -162.22 (dt, *J* = 22.0, 7.0 Hz, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3512 (OH), 2997, 2957, 2938, 2839 (OCH_3), 1719 (C=O), 1653, 1597, 1524, 1489, 1460, 1429, 1246, 1204, 1155, 1123, 1103, 1090, 1065. **HRMS** (ES+) $[M-OH]^+$ $[C_{20}H_{18}O_4F_5]^+$: calculated 417.1125, found 417.1124.

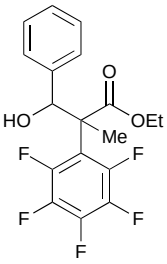
Synthesis of ethyl -3-hydroxy-2-methyl-2-(pentafluorophenyl)-3-(o-tolyl)propanoate (**2f**)



Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 2-methylbenzaldehyde (19 mg, 0.16 mmol) in CH_2Cl_2 to afford **2f**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **2f** (*dr:* 1:0.20) was obtained as a colourless solid. Yield combined: 44 mg, 0.11 mmol, 73%.

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 7.61 (dd, *J* = 7.8, 1.5 Hz, 1H, Ar-H), 7.22 (dt, *J* = 7.6, 1.5 Hz, 1H, Ar-H), 7.15 (dt, *J* = 7.6, 1.5 Hz, 1H, Ar-H), 6.95 (dd, *J* = 7.8, 1.5 Hz, 1H, Ar-H), 5.68 (s, 1H), 4.51 (bs, 1H), 4.27 (q, *J* = 7.2 Hz, 2H, CH_2), 1.85 (t, *J* = 2.5 Hz, 3H, CH_3), 1.80 (s, 3H, *o*-CH_3), 1.25 (t, *J* = 7.2 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 176.6, 146.3 (br. d, $J_{C–F}$ = 250.0 Hz), 140.5 (br. d, $J_{C–F}$ = 254.1 Hz), 137.5 (br. d, $J_{C–F}$ = 251.2 Hz), 136.1, 135.2, 130.3, 128.5, 128.2, 125.8, 114.9, (br. t, $J_{C–F}$ = 13.8 Hz), 70.8, 62.4, 53.7, 18.9, 17.3 (t, $J_{C–F}$ = 5.8 Hz), 13.9 ppm. **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) δ: -137.59 (dd, *J* = 21.4, 5.2 Hz, 2F, Ar-F), -154.53 (vt, *J* = 21.4 Hz, 1F, Ar-F), -162.15 (dt, *J* = 21.4, 5.2 Hz, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3520 (OH), 3057, 2983, 2940, 1719 (C=O), 1653, 1524, 1489, 1381, 1304, 1234, 1119, 1099, 1070, 1043. **HRMS** (ES+) $[M–OH]^+$ $[C_{19}H_{16}O_2F_5]^+$: calculated 371.1070, found 371.1057.

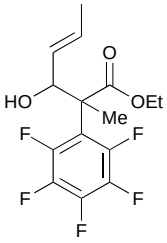
Synthesis of ethyl 3-hydroxy-2-methyl-2-(pentafluorophenyl)-3-phenylpropanoate (**2g**)



Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and benzaldehyde (17 mg, 0.16 mmol) in CH_2Cl_2 to afford **2g**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **2g** (*dr:* 1:0.09) was obtained as a colourless oil. Yield combined: 24 mg, 0.06 mmol, 41%.

^{1}H NMR (500.2 MHz, $CDCl_3$, 298 K) δ: 7.17–7.26 (m, 3H, Ar-H), 6.94 (m, 2H, Ar-H), 5.30 (d, *J* = 2.8 Hz, 1H), 4.58 (d, *J* = 2.8 Hz, 1H), 4.22–4.29 (m, 2H, CH_2), 1.76 (t, *J* = 2.9 Hz, 3H, CH_3), 1.24 (t, *J* = 7.2 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 176.6, 146.1 (br. d, $J_{C–F}$ = 247.8 Hz), 140.4 (br. d, $J_{C–F}$ = 256.6 Hz), 137.6 (br. d, $J_{C–F}$ = 252.2 Hz), 137.7, 128.4, 127.8, 127.4, 115.0 (br. s), 75.8, 62.4, 53.9, 16.8 (t, $J_{C–F}$ = 6.1 Hz), 14.0 ppm. **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) δ: -138.48 (dd, *J* = 21.2, 5.7 Hz, 2F, Ar-F), -154.60 (vt, *J* = 21.2 Hz, 1F, Ar-F), -162.23 (dt, *J* = 21.2, 5.2 Hz, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3522 (OH), 3065, 3032, 2984, 2959, 2907, 1721 (C=O), 1653, 1524, 1489, 1250, 1229, 1125, 1105, 1069. **HRMS** (ASAP+) $[M\text{-}OH]^+$ $[C_{18}H_{14}O_2F_5]^+$: calculated 357.0914, found 257.0920.

Synthesis of ethyl (E)-3-hydroxy-2-methyl-2-(pentafluorophenyl)hex-4-enoate (**2h**)

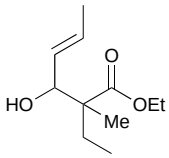


Synthesised in accordance with *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and crotonaldehyde (11 mg, 0.16 mmol) in CH_2Cl_2 to afford **2h**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **2h** (*dr:* 1:0.22) was obtained as a colourless oil. Yield combined: 30 mg, 0.09 mmol, 57%.

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 5.54–5.61 (m, 1H, CH), 5.40–5.46 (m, 1H, CH), 4.57 (vt, *J* = 6.2, 5.3 Hz, 1H), 4.23 (q, *J* = 7.7 Hz, 2H, CH_2), 3.83 (d, *J* = 5.3 Hz, 1H), 1.69 (t, *J* = 3.0, 3H, CH_3), 1.63 (dd, *J* = 6.4, 1.3, 3H, CH_3), 1.24 (t, *J* = 7.7, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 175.4, 145. (br. d, $J_{C–F}$ = 248.7 Hz), 140.2 (br. d, $J_{C–F}$ = 254.3 Hz), 137.8 (br. d, $J_{C–F}$ = 250.2 Hz), 131.0, 127.3, 115.7 (br. s), 75.5, 62.1, 53.1, 18.7 (t, $J_{C–F}$ = 6.4 Hz), 17.9, 14.0 ppm. **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) δ: -138.22 (d, *J* = 17.9 Hz, 2F, Ar-F), -155.23 (t, *J* = 22.5 Hz, 1F, Ar-F), -162.28 (ddd, *J* = 22.5, 17.8, 5.7 Hz, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3522 (OH), 2986, 2941, 2920, 2860, 1721 (C=O), 1655, 1524, 1487, 1383,

1302, 1248, 1231, 1175, 1126, 1098, 1067, 1018. **HRMS** (ES+) $[M–OH]^+$ $[C_{15}H_{14}O_2F_5]^+$: calculated 321.0914, found 321.0916.

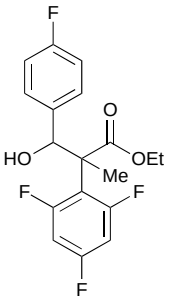
Synthesis of ethyl (E)-2-ethyl-3-hydroxy-2-methylhex-4-enoate (**2s**)



Synthesised in accordance with the *General Procedure* using BEt_3 (0.16 mL, 0.16 mmol, 1M in hexane), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and crotonaldehyde (11 mg, 0.16 mmol) in CH_2Cl_2 to afford **2s**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired compound **2s** (*dr*: 1:0.68) was obtained as a colourless oil. Yield combined: 9 mg, 0.5 mmol, 29%.

^{1}H NMR (500.2 MHz, $CDCl_3$, 298 K) δ: 5.67–5.74 (m, 1H, CH), 5.49–5.54 (m, 1H, CH), 4.11–4.19 (m, 3H), 2.39 (d, J = 4.8 Hz, 1H), 1.80–1.87 (m, 1H, CH_2), 1.71 (dd, J = 6.0, 1.0 Hz, 3H, CH_3), 1.46–1.52 87 (m, 1H, CH_2), 1.26 (t, J = 7.1 Hz, 3H, CH_3), 1.13 (s, 3H, CH_3), 0.87 ppm (t, J = 7.5 Hz, 3H, CH_3). **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ 176.5, 129.7, 129.4, 77.8, 60.6, 51.0, 28.1, 18.0, 17.4, 14.4, 9.1 ppm. **IR** ν_{max} (cm^{-1}): 3500 (OH), 2970, 2935, 2879, 2856, 1718 (C=O), 1458, 1381, 1323, 1300, 1323, 1300, 1232, 1155, 1139, 1112, 1091, 1026. **HRMS** (ASAP) $[M-OH]^+$ $[C_{11}H_{19}O_2]^+$: calculated 183.1385, found 183.1394.

Synthesis of ethyl 3-(4-fluorophenyl)-3-hydroxy-2-methyl-2-(2,4,6-trifluorophenyl)propanoate (**2i**)

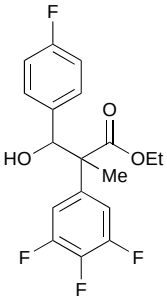


Synthesised in accordance with the *General Procedure* using $B(2,4,6\text{-}F_3C_6H_2)_3$ (63 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-fluorobenzaldehyde (19 mg, 0.16 mmol) in CH_2Cl_2 to afford **2i**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **2i** (*dr:* 1:0.13) was obtained as a colourless oil. Yield combined: 31 mg, 0.09 mmol, 56%.

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 6.81–6.92 (m, 4H, Ar-H), 6.50–6.57 (m, 2H, Ar-H), 5.27 (d, J = 2.4 Hz, 1H), 4.74 (d, J = 2.4 Hz, 1H), 4.17–4.29 (m, 2H, CH_2), 1.70 (t, J = 3.1 Hz, 3H, CH_3), 1.22 (t, J = 7.1 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 177.8, 162.45 (d, $J_{C–F}$ = 249.2 Hz), 160.8–163.0 (m, 2C), 134.1 (d, $J_{C–F}$ = 3.3 Hz), 129.2 (d, $J_{C–F}$ = 8.1 Hz), 114.4 (d, $J_{C–F}$ = 21.4 Hz), 113.4 (dt, $J_{C–F}$ = 15.4, 5.2 Hz), 100.8 (ddd, $J_{C–F}$ = 25.2, 25.2, 3.1 Hz), 75.3, 62.0, 52.8 (t, $J_{C–F}$ = 3.2 Hz), 16.5 (t, $J_{C–F}$ = 6.3 Hz), 14.0 ppm. **^{19}F NMR** (376.5 MHz,

$CDCl_3$, 298 K) δ: -105.60 (d, *J* = 7.4 Hz, 2F, Ar-F), -108,65 (vt, *J* = 7.4 Hz, 1F, Ar-F), -114.61 (s, 1F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3516 (OH), 3103, 3061, 2986, 2905, 1713 (C=O), 1634, 1597, 1510, 1489, 1435, 1254, 1225, 1157, 1121, 1099, 1070, 1043, 1015, 1003. **HRMS** (ES+) $[M\text{-}OH]^+$ $[C_{18}H_{16}O_2F_4]^+$: calculated 339.1008, found 339.1007.

Synthesis of ethyl 3-(4-fluorophenyl)-3-hydroxy-2-methyl-2-(3,4,5-trifluorophenyl)propanoate (**2j**)

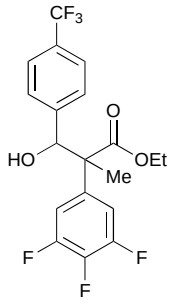


Synthesised in accordance with the *General Procedure* using $B(3,4,5\text{-}F_3C_6H_2)_3$ (63 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-fluorobenzaldehyde (19 mg, 0.16 mmol) in CH_2Cl_2 to afford **2j**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **2j** (*dr:* 1:0.78) was obtained as a mixture of diastereomers as a colourless oil. Yield: 40 mg, 0.11 mmol, 72%.

Note: Some signals of the major (Δ) and the minor (*) isomer are overlapping.

^{1}H NMR (500.2 MHz, $CDCl_3$, 298 K) δ: 6.74–6.91Δ* (m, 6H, Ar-H), 6.31* (s, 1H), 5.24Δ (s, 1H), 4.16–4.29 (m, 2H, CH_2), 3.63* (br. s, 1H), 3.52Δ (br. s, 1H), 1.46* (s, 3H, CH_3), 1.42Δ (s, 3H, CH_3), 1.20–1.24Δ* (m, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 175.9*, 175.7Δ, 162.6Δ (d, $J_{C–F}$ = 246.6 Hz), 162.4* (d, $J_{C–F}$ = 246.6 Hz), 151.1* (ddd, $J_{C–F}$ = 250.8, 9.9, 10.2 Hz), 150.5Δ (ddd, $J_{C–F}$ = 248.6, 9.6, 9.8 Hz), 137.9–140.2Δ* (m, $J_{C–F}$ = 251.8 Hz), 136.5–136.6* (m), 136.5–136.6* (m), 134.4–134.6Δ (m), 134.1Δ (d, $J_{C–F}$ = 3.3 Hz), 133.7* (d, $J_{C–F}$ = 3.3 Hz), 129.8Δ (d, $J_{C–F}$ = 8.2 Hz), 129.1* (d, $J_{C–F}$ = 8.1 Hz), 114.7Δ (d, $J_{C–F}$ = 21.3 Hz), 114.5* (d, $J_{C–F}$ = 21.3 Hz), 112.9Δ (dd, $J_{C–F}$ = 17.2, 5.1 Hz), 111.5* (dd, $J_{C–F}$ = 17.3, 5.1 Hz), 77.8*, 77.7Δ, 62.2*, 62.0Δ, 56.1*, 55.4Δ, 19.9Δ*, 14.8*, 14.0Δ ppm. **^{19}F NMR** (470.6 MHz, $CDCl_3$, 298 K) δ: -113.86–-113.80Δ (m, 1F, Ar-F), -114.47–-114.41* (m, 1F, Ar-F), -133.44* (dd, *J* = 20.7, 8.8 Hz, 2F, Ar-F), -135.05Δ (dd, *J* = 20.6, 9.4 Hz, 2F, Ar-F), -161.08–-160.97* (m, 1F, Ar-F), -161.87–-161.75Δ (m, 1F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3501 (OH), 3086, 3049, 2986, 2938, 2909, 1713 (C=O), 1620, 1605, 1530, 1510, 1466, 1433, 1342, 1225, 1159, 1107, 1076, 1036. **HRMS** (ASAP+) $[M\text{-}OH]^+$ $[C_{18}H_{15}O_2F_4]^+$: calculated 339.1008, found 339.1020.

Synthesis of ethyl 3-hydroxy-2-methyl-3-(4-(trifluoromethyl)phenyl)-2-(3,4,5-trifluorophenyl)propanoate (**2k**)

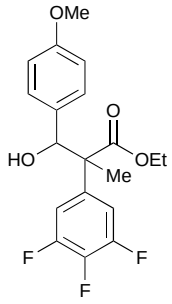


Synthesised in accordance with the *General Procedure* using B(3,4,5-$F_3C_6H_2$)$_3$ (63 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-trifluoromethylbenzaldehyde (27 mg, 0.16 mmol) in CH_2Cl_2 to afford **2k**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **2k** (*dr:* 1:1) was obtained as a mixture of diastereomers as a colourless oil. Yield: 34 mg, 0.08 mmol, 54%.

Note: Some signals of the one ($^{\Delta}$*) and the other (*) isomer are overlapping.*

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 7.56$^{\Delta}$ (d, *J* = 8.3 Hz, 2H, Ar-H), 7.41* (d, *J* = 8.2 Hz, 2H, Ar-H), 7.04* (d, *J* = 8.2 Hz, 2H, Ar-H), 6.94$^{\Delta}$ (d, *J* = 8.3 Hz, 2H, Ar-H), 6.76–6.85$^{\Delta}$* (m, 2H, Ar-H), 5.40$^{\Delta}$ (d, *J* = 3.6 Hz, 1H), 5.32* (d, *J* = 3.2 Hz, 1H), 4.16–4.31$^{\Delta}$* (m, 2H, CH_2), 3.72$^{\Delta}$ (d, *J* = 3.6 Hz, 1H), 3.59* (d, *J* = 3.2 Hz, 1H), 1.46$^{\Delta}$ (s, 3H, CH_3), 1.44* (s, 3H, CH_3), 1.20–1.25$^{\Delta}$* (m, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 175.8$^{\Delta}$, 175.5*, 151.2$^{\Delta}$ (dd, $J_{C–F}$ = 250.3, 9.8 Hz), 150.6* (dd, $J_{C–F}$ = 249.4, 9.7 Hz), 142.3* (d, $J_{C–F}$ = 1.4 Hz), 142.0$^{\Delta}$ (d, $J_{C–F}$ = 1.4 Hz), 139.2$^{\Delta}$ (dd, $J_{C–F}$ = 252.3, 9.7 Hz), 139.2* (dd, $J_{C–F}$ = 252.3, 9.7 Hz), 136.1–136.3* (m), 134.3$^{\Delta}$ (m), 130.5* (q, $J_{C–F}$ = 32.8 Hz), 130.1$^{\Delta}$ (q, $J_{C–F}$ = 32.5 Hz), 128.5*, 127.9$^{\Delta}$, 124.7* (q, $J_{C–F}$ = 3.8 Hz), 124.5$^{\Delta}$ (q, $J_{C–F}$ = 3.8 Hz), 124.1* (q, $J_{C–F}$ = 272.3 Hz), 124.1$^{\Delta}$ (q, $J_{C–F}$ = 272.3 Hz), 112.9$^{\Delta}$ (dd, $J_{C–F}$ = 16.5, 5.4 Hz), 111.5* (dd, $J_{C–F}$ = 16.5, 5.2 Hz), 77.9*, 77.8$^{\Delta}$, 62.3$^{\Delta}$, 62.2*, 56.0$^{\Delta}$, 55.2*, 19.7$^{\Delta}$, 19.7*, 14.7*, 14.0$^{\Delta}$ ppm. **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) δ: -62.60$^{\Delta}$ (s, 3F, CF_3), -62.61* (s, 3F, CF_3), -133.01$^{\Delta}$ (d, *J* = 20.8 Hz, 2F, Ar-F), -134.69* (d, *J* = 20.9 Hz, 2F, Ar-F), -160.52$^{\Delta}$ (vt, *J* = 20.8 Hz, 1F, Ar-F), -161.39* (vt, *J* = 20.9 Hz, 1F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3505 (OH), 3057, 2988, 2941, 2907, 1703 (C=O), 1620, 1531, 1435, 1323, 1244, 1165, 1125, 1067, 1038, 1016. **HRMS** (ASAP+) $[M+Na]^+$ $[C_{19}H_{16}O_3F_6]^+$: calculated 429.0901, found 429.0907.

Synthesis of ethyl 3-hydroxy-3-(4-methoxyphenyl)-2-methyl-2-(3,4,5-trifluorophenyl) propanoate (**2l**)

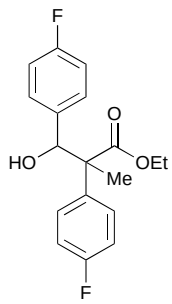


Synthesised in accordance with the *General Procedure* using $B(3,4,5\text{-}F_3C_6H_2)_3$ (63 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-methoxybenzaldehyde (21 mg, 0.16 mmol) in CH_2Cl_2 to afford **2l**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired compound **2l** (*dr:* 1:0.61) was obtained as a colourless oil. Yield: 29 mg, 0.08 mmol, 50%.

Note: Some signals of the one ($^{\Delta}$*) and the other (*) isomer overlap.*

^{1}H NMR (500.2 MHz, $CDCl_3$, 298 K) δ: 6.67–6.87$^{\Delta}$* (m, 6H, Ar-H), 5.28* (d, *J* = 3.6 Hz, 1H), 5.22$^{\Delta}$ (d, *J* = 3.0 Hz, 1H), 4.15–4.28$^{\Delta}$* (m, 2H, CH_2), 3.76$^{\Delta}$ (s, 3H, OCH_3), 3.75* (s, 3H, OCH_3), 3.52* (d, *J* = 3.6 Hz, 1H), 3.38$^{\Delta}$ (d, *J* = 3.0 Hz, 1H), 1.47* (s, 3H, CH_3), 1.42$^{\Delta}$ (s, 3H, CH_3), 1.20–1.24$^{\Delta}$* (m, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 175.9*, 175.7$^{\Delta}$, 159.5$^{\Delta}$, 159.2*, 151.0* (ddd, J_{C-F} = 249.6, 9.8, 4.2 Hz), 150.4$^{\Delta}$ (ddd, J_{C-F} = 248.2, 9.9, 4.1 Hz), 139.0$^{\Delta}$* (br. d. J_{C-F} = 248.2 and 249.6 Hz), 136.8–137.0* (m), 134.9–135.0$^{\Delta}$ (m), 130.5$^{\Delta}$, 130.0*, 129.2$^{\Delta}$, 128.6*, 113.1$^{\Delta}$, 130.0$^{\Delta}$ (dd, J_{C-F} = 17.3, 4.9 Hz), 111.5* (dd, 17.2, 5.4 Hz), 78.0*, 78.0$^{\Delta}$, 62.0*, 61.9$^{\Delta}$, 56.2*, 55.5$^{\Delta}$, 55.3$^{\Delta}$, 55.3*, 20.0$^{\Delta}$*, 15.0*, 14.0$^{\Delta}$ ppm. **^{19}F NMR** (470.6 MHz, $CDCl_3$, 298 K) δ: -133.88* (dd, *J* = 21.4, 10.2 Hz, 2F, Ar-F), -135.45$^{\Delta}$ (dd, *J* = 20.8, 10.0 Hz, 2F, Ar-F), -161.53* (tt, *J* = 21.4, 6.5 Hz, 1F, Ar-F), -162.29$^{\Delta}$ (tt, *J* = 20.8, 6.7 Hz, 1F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3501 (OH), 3080, 3040, 2984, 2957, 2938, 2907, 2839 (OCH_3), 1717 (C=O), 1612, 1530, 1514, 1466, 1433, 1341, 1246, 1175, 1105, 1076, 1034. **HRMS** (ASAP+) $[M\text{-}OH]^+$ $[C_{19}H_{18}O_3F_3]^+$: calculated 351.1208, found 351.1210.

Synthesis of ethyl 2,3-bis(4-fluorophenyl)-3-hydroxy-2-methylpropanoate (**2m**)

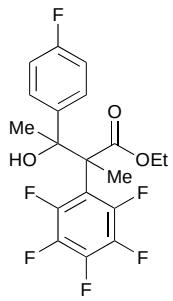


Synthesised in accordance with the *General Procedure* using $B(4\text{-}FC_6H_4)_3$ (46 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-fluorobenzaldehyde (19 mg, 0.16 mmol) in CH_2Cl_2 to afford **2m**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **2m** (*dr:* 1:0.81) was obtained as a colourless oil. Yield: 33 mg, 0.10 mmol, 66%.

Note: Some signals of the major ($^{\Delta}$*) and the minor (*) isomer overlap.*

^{1}H NMR (500.2 MHz, $CDCl_3$, 298 K) δ: 7.07–7.12$^{\Delta}$ (m, 2H, Ar-H), 7.02–7.05* (m, 2H, Ar-H), 6.93–6.99$^{\Delta}$* (m, 2H, Ar-H), 6.76–6.86$^{\Delta}$* (m, 4H$^{\Delta}$ and 2H*, Ar-H), 6.70–6.74$^{\Delta}$* (m, 2H, Ar-H), 5.36* (d, *J* = 3.4 Hz, 1H), 5.24$^{\Delta}$ (d, *J* = 2.9 Hz, 1H), 4.15–4.27$^{\Delta}$* (m, 2H, CH_2), 3.79* (d, *J* = 3.4 Hz, 1H), 3.70$^{\Delta}$ (d, *J* = 2.9 Hz, 1H), 1.49* (s, 3H, CH_3), 1.46$^{\Delta}$ (s, 3H, CH_3), 1.19–1.22$^{\Delta}$* (m, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 177.2*, 176.9$^{\Delta}$, 162.5$^{\Delta}$ (d, $J_{C–F}$ = 246.2 Hz), 162.4$^{\Delta}$ (d, $J_{C–F}$ = 246.6 Hz), 162.2* (d, $J_{C–F}$ = 245.9 Hz), 162.1* (d, $J_{C–F}$ = 245.9 Hz), 135.8$^{\Delta}$ (d, $J_{C–F}$ = 3.4 Hz), 134.5$^{\Delta}$ (d, $J_{C–F}$ = 3.1 Hz), 134.1* (d, $J_{C–F}$ = 3.2 Hz), 133.5* (d, $J_{C–F}$ = 3.3 Hz), 130.0$^{\Delta}$ (d, $J_{C–F}$ = 8.1 Hz), 129.9$^{\Delta}$ (d, $J_{C–F}$ = 8.2 Hz), 129.3* (d, $J_{C–F}$ = 8.2 Hz), 128.6* (d, $J_{C–F}$ = 8.2 Hz), 115.4* (d, $J_{C–F}$ = 21.2 Hz), 114.6$^{\Delta}$ (d, $J_{C–F}$ = 21.2 Hz), 114.3$^{\Delta}$ (d, $J_{C–F}$ = 21.3 Hz), 114.1* (d, $J_{C–F}$ = 21.4 Hz), 78.0*, 78.0$^{\Delta}$, 61.7*, 61.7$^{\Delta}$, 56.0*, 55.1$^{\Delta}$, 20.0$^{\Delta}$*, 14.7*, 14.1$^{\Delta}$ ppm. **^{19}F NMR** (470.6 MHz, $CDCl_3$, 298 K) δ: -114.58–-114.52$^{\Delta}$ (m, 1F, Ar-F), -114.86–-114.80* (m, 1F, Ar-F), -115.33–-115.25$^{\Delta}$* (m, 1F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3510 (OH), 3075, 3049, 2984, 2938, 2907, 1705 (C=O), 1603, 1508, 1466, 1296, 1223, 1157, 1111, 1092, 1042, 1015. **HRMS** (ASAP+) $[M\text{-}OH]^+$ $[C_{18}H_{17}O_2F_2]^+$: calculated 303.1197, found 303.1202.

Synthesis of ethyl 3-(4-flurophenyl)-3-hydroxy-2-methyl-2-(pentafluorophenyl)butanoate (**2n**)

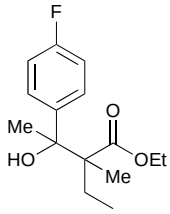


Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-fluoroacetophenone (22 mg, 0.16 mmol) in CH_2Cl_2 to afford **2n**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **2n** (*dr:* 1:0.85) was obtained as a colourless oil. Yield combined: 34 mg, 0.08 mmol, 54%.

^{1}H NMR (500.2 MHz, $CDCl_3$, 298 K) δ: 7.08–7.11 (m, 2H, Ar-H), 6.84–6.88 (m, 2H, Ar-H), 4.51 (s, 1H, OH), 4.18–4.29 (m, 2H, CH_2), 1.92 (s, 3H, CH_3), 1.81 (t, *J* = 3.2 Hz, 3H, CH_3), 1.23 (t, *J* = 7.0 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 175.3, 162.3 (d, $J_{C–F}$ = 248.1 Hz), 146.5 (br. d, $J_{C–F}$ = 246.7 Hz), 140.1 (br. d, $J_{C–F}$ = 253.4 Hz), 138.4 (d, $J_{C–F}$ = 2.9 Hz), 137.4 (br. d, $J_{C–F}$ = 250.1 Hz), 128.7 (d, $J_{C–F}$ = 7.9 Hz), 115.4 (br. s), 114.2 (d, $J_{C–F}$ = 21.2 Hz), 78.7, 62.1, 56.7, 24.7, 22.0 (t, $J_{C–F}$ = 6.1 Hz), 14.0 ppm. **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) δ: -115.24 (s, 1F, Ar-F), -135.48* (br. s, 2F, Ar-F), -154.97 (t, *J* = 22.4 Hz, 1F, Ar-F), -163.16 (dt, *J* = 22.4, 6.9 Hz, 2F, Ar-F) ppm. **Note: signal is very broad and the integration does not fit.* **IR** ν_{max} (cm^{-1}): 3537 (OH), 3051, 2992, 2957, 2930, 2857, 1724 (C=O),

1653, 1605, 1524, 1508, 1485, 1366, 1302, 1229, 1163, 1134, 1094, 1015. **HRMS** (ASAP+) $[M\text{-}OH]^+$ $[C_{19}H_{15}O_2F_6]^+$: calculated 389.0976, found 389.0984.

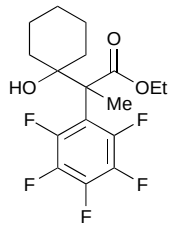
Synthesis of ethyl 2-ethyl-3-(4-fluorophenyl)-3-hydroxy-2-methylbutanoate (**2t**)



Synthesised in accordance with the *General Procedure* using BEt_3 (0.16 mL, 0.16 mmol, 1M in hexane), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-fluoroacetophenone (22 mg, 0.16 mmol) in CH_2Cl_2 to afford **2t**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **2t** (*dr*: 1:0.61) was obtained as a colourless oil. Yield combined: 28 mg, 0.10 mmol, 67%.

^{1}H NMR (500.2 MHz, $CDCl_3$, 298 K) δ: 7.30–7.35 (m, 2H, Ar-H), 6.94–6.99 (m, 2H, Ar-H), 4.58 (s, 1H, OH), 3.97–4.08 (m, 2H, CH_2), 2.21–2.28 (m, 1H, CH_2), 1.56 (s, 3H, CH_3) 1.35–1.43 (m, 2H, CH_2), 1.12 (t, J = 7.1 Hz, 3H, CH_3), 1.09 (s, 3H, CH_3), 0.82 ppm (t, J = 7.5 Hz, 3H, CH_3). **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 177.2, 161.9 (d, $J_{C–F}$ = 245.8 Hz), 141.0 (d, $J_{C–F}$ = 3.3 Hz), 128.6 (d, $J_{C–F}$ = 8.2 Hz), 114.3 (d, $J_{C–F}$ = 21.4 Hz), 77.5, 61.0, 54.9, 27.2, 24.0, 16.9, 14.1, 9.7 ppm. **^{19}F NMR** (470.6 MHz, $CDCl_3$, 298 K) δ: -116.65–-116.59 ppm. **IR** ν_{max} (cm^{-1}): 3300 (OH), 2982, 2943 2883, 1714 (C=O), 1689, 1600, 1508, 1462, 1382, 1367, 1307, 1224, 1188, 1145, 1089, 1047, 1014. **HRMS** (GC–MS) $[M\text{-}OH]^+$ $[C_{15}H_{20}O_2F]^+$: calculated 251.14418, found 251.1442.

Synthesis of ethyl 2-(1-hydroxycyclohexyl)-2-(pentafluorophenyl)propanoate (**2o**)

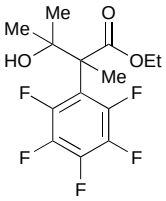


Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and cyclohexanone (15 mg, 0.16 mmol) in CH_2Cl_2 to afford **2o**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **2o** was obtained as a colourless oil. Yield: 23 mg, 0.06 mmol, 40%.

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 4.12–4.24 (m, 2H, CH_2), 3.58 (br. s, 1H, OH), 2.13 (d, J = 13.1 Hz, 1H, Cy-H), 1.79 (t, J = 3.1 Hz, 3H, CH_3), 1.60–1.75 (m, 4H, Cy-H), 1.43–1.54 (m, 2H, Cy-H), 1.19–1.34 (m, 5H, Cy-H, CH_3), 0.95–1.06 (m, 1H, Cy-H) ppm. **^{13}C NMR** (128.5 MHz, $CDCl_3$, 298 K) δ: 175.3, 146.4 (br. d, $J_{C–F}$ = 247.7 Hz), 140.2 (br. d, $J_{C–F}$ = 254.3

Hz), 137.2 (br. d, $J_{C–F}$ = 249.2 Hz), 115.9 (t, $J_{C–F}$ = 13.7 Hz), 76.5, 61.7, 56.5, 32.0, 31.5, 25.8, 21.7, 21.5, 21.1 (t, $J_{C–F}$ = 6.0 Hz), 14.0 ppm. **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) δ: -135.12* (br. s, 2F, Ar-F), -155.25 (t, *J* = 21.0 Hz, 1F, Ar-F), -162.37 (s, 2F, Ar-F) ppm. **Note: signal is very broad and the integration does not fit.* **IR** ν_{max} (cm^{-1}): 3532 (OH), 2938, 2862, 1721 (C=O), 1653, 1524, 1483, 1387, 1300, 1238, 1150, 1119, 1099, 1074, 1032. **HRMS** (ES+) $[M\text{-}OH]^+$ $[C_{17}H_{18}O_2F_5]^+$: calculated 349.1227, found 349.1218.

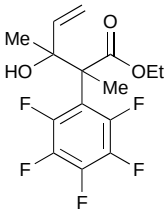
Synthesis of ethyl 3-hydroxy-2,3-dimethyl-2-(pentafluorophenyl)butanoate (**2p**)



Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and acetone (9 mg, 0.16 mmol) in CH_2Cl_2 to afford **2p**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired compound **2p** was obtained as a colourless oil. Yield: 25 mg, 0.08 mmol, 49%.

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 4.14–4.27 (m, 2H, Et-CH_2), 3.90 (br. s, 1H, OH), 1.80 (t, *J* = 3.1 Hz, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.20–1.23 (m, 6H, 2 × CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 175.2, 146.4 (br. d, $J_{C–F}$ = 246.6 Hz), 140.2 (br. d, $J_{C–F}$ = 252.8 Hz), 137.8 (br. d, $J_{C–F}$ = 250.2 Hz), 116.0 (t, $J_{C–F}$ = 17.7 Hz), 75.5, 61.8, 55.7, 25.9, 25.4, 21.8 (t, $J_{C–F}$ = 6.4 Hz), 14.0 ppm. **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) δ: -134.53* (br. s 2F, Ar-F), -155.16 (s, 1F, Ar-F), -162.35 (s, 2F, Ar-F) ppm. **Note: signal is very broad and the integration does not fit.* **IR** ν_{max} (cm^{-1}): 3534 (OH), 2986, 2945, 2911, 1722 (C=O), 1653, 1524, 1485, 1375, 1302, 1236, 1152, 1096, 1059, 1020. **HRMS** (ASAP+) $[M\text{-}OH]^+$ $[C_{14}H_{14}O_2F_5]^+$: calculated 309.0914, found 309.0919.

Synthesis of ethyl 3-hydroxy-2,3-dimethyl-2-(pentafluorophenyl)pent-4-enoate (**2q**)



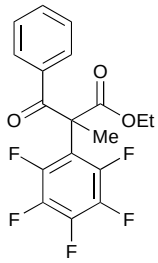
Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 3-buten-2-one (11 mg, 0.16 mmol) in CH_2Cl_2 to afford **2q**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **2q** (*dr:* 1:0.18) was obtained as a mixture of diastereomers as a colourless oil. Yield combined: 21 mg, 0.06 mmol, 40%.

Note: Some signals of the major (Δ) and the minor (*) isomer overlap. The carbon signals of the C_6F_5 substituent of the minor compound are too broad to be observed in the ^{13}C NMR.*

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 6.05* (dd, *J* = 16.3, 10.8 Hz, 1H, CH), 5.95Δ (dd, *J* = 16.5, 10.9 Hz, 1H, CH), 5.32Δ (dd, *J* = 16.5, 1.1 Hz, 1H, CH_2), 5.19Δ (dd, *J* = 10.9, 1.3 Hz, 1H, CH_2), 5.12* (dd, *J* = 16.3, 1.4 Hz, 1H, CH_2), 5.04* (dd, *J* = 10.8, 1.4 Hz, 1H, CH_2), 4.15–4.26Δ* (m, 2H, CH_2), 3.95Δ (br. s, 1H, OH), 3.88* (br. s, 1H, OH), 1.81* (t, *J* = 3.2 Hz, 3H, CH_3), 1.78Δ (t, *J* = 3.2 Hz, 3H, CH_3), 1.43* (s, 3H, CH_3), 1.33Δ (s, 3H, CH_3), 1.22Δ* (t, *J* = 7.2 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 175.1Δ, 174.9*, 146.3Δ (br. d, $J_{C–F}$ = 247.2 Hz), 140.3Δ (br. d, $J_{C–F}$ = 250.6 Hz), 140.0*, 139.8Δ, 137.8Δ (br. d, $J_{C–F}$ = 253.4 Hz), 115.5Δ (br. s), 115.2Δ, 114.6*, 77.4Δ*, 66.0*, 61.9Δ, 55.7*, 55.3Δ, 24.1Δ, 23.2*, 21.9Δ (t, $J_{C–F}$ = 6.4 Hz), 21.6* (t, $J_{C–F}$ = 6.2 Hz), 15.4*, 14.0Δ ppm. **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) δ: -133.82Δ* (br. s, 2F, Ar-F), -154.88Δ (t, *J* = 21.0 Hz, 1F, Ar-F), -155.25* (t, *J* = 21.0 Hz, 1F, Ar-F), -162.30Δ (br. s, 2F, Ar-F), -162.74* (br. s, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3524 (OH), 3092, 2988, 2943, 2911, 1721 (C=O), 1653, 1524, 1485, 1414, 1369, 1302, 1238, 1084. **HRMS** (ES+) $[M\text{-}OH]^+$ $[C_{15}H_{14}O_2F_5]^+$: calculated 321.0914, found 321.0913.

2.3 Synthesis and spectral characterisation of α-aryl β-keto esters

Synthesis of ethyl 2-methyl-3-oxo-2-(pentafluorophenyl)-3-phenylpropanoate (**3b**)



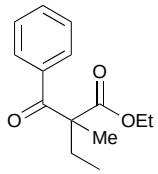
Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and benzoic anhydride (35 mg, 0.16 mmol) in CH_2Cl_2 to afford **3b**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **3b** was obtained as a colourless oil. Yield: 35 mg, 0.09 mmol, 60%.

*Note: **3b** can also be synthesised using benzoyl chloride (22 mg, 0.16 mmol) in 9% yield, or benzonitrile (16 mg, 0.16 mmol) after an additional acidic work up with HCl (1 M) in 36% yield.*

^{1}H NMR (500.2 MHz, $CDCl_3$, 298 K) δ: 7.77–7.79 (m, 2H, Ar-H), 7.50–7.53 (m, 1H, Ar-H), 7.35–7.39 (m, 2H, Ar-H), 4.16–4.26 (m, 2H, CH_2), 1.95 (s, 3H, CH_3), 1.14 (t, *J* = 7.2 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 194.0, 169.4, 144.9 (br. d, $J_{C–F}$ = 251.5 Hz), 140.8 (br. d, $J_{C–F}$ = 256.0 Hz), 136.2 (br. d, $J_{C–F}$ = 253.3 Hz), 153.3, 133.1, 129.0, 128.4, 116.0 (br. s), 63.0, 59.3, 23.1, 13.7 ppm. **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) δ: -134.82 (d, *J* = 17.8 Hz, 2F, Ar-F), -154.11 (t, *J* = 22.5 Hz, 1F, Ar-F), -161.26–-161.14 (m, 2F, Ar-F) ppm.

IR ν_{max} (cm^{-1}): 3061, 2986, 2945, 2907, 1742 (C=O), 1692 (C=O), 1655, 1597, 1524, 1489, 1449, 1381, 1306, 1244, 1215, 1163, 1099, 1076. **HRMS** (ES+) $[M+H]^+$ $[C_{18}H_{14}O_3F_5]^+$: calculated 373.0863, found 373.0865.

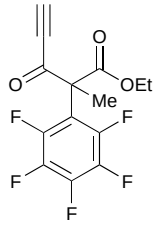
Synthesis of ethyl 2-benzoyl-2-methylbutanoate (**3g**)



Synthesised in accordance with the *General Procedure* using BEt_3 (0.16 mL, 0.16 mmol, 1M in hexane), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and benzoic anhydride (35 mg, 0.16 mmol) in CH_2Cl_2 to afford **3g**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **3g** was obtained as a colourless oil. Yield: 21 mg, 0.9 mmol, 57%.

^{1}H NMR (500.2 MHz, $CDCl_3$, 298 K) δ: 7.81–7.84 (m, 2H, Ar-H), 7.48–7.52 (m, 1H, Ar-H), 7.37–7.42 (m, 2H, Ar-H), 4.11 (q, *J* = 7.1 Hz, 2H, CH_2), 2.07 (dq, *J* = 7.5, 1.8 Hz, 2H, CH_2), 1.50 (s, 3H, CH_3), 1.04 (t, *J* = 7.1 Hz, 3H, CH_3), 0.83 ppm (t, *J* = 7.5 Hz, 3H, CH_3). **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 197.9, 174.5, 135.9, 132.7, 128.6, 128.5, 61.3, 57.4, 29.4, 20.6, 13.9, 8.4.ppm. **IR** ν_{max} (cm^{-1}): 2978, 2939, 2881, 1732 (C=O), 1681 (C=O), 1598, 1581, 1508, 1446, 1386, 1375, 1301, 1244, 1220, 1172, 1149, 1126, 1095, 1053, 1033, 1024, 1010. **HRMS** (GC–MS) $[M+H]^+$ $[C_{14}H_{19}O_3]^+$: calculated 235.13287, found 235.1330.

Synthesis of ethyl 2-methyl-3-oxo-2-(pentafluorophenyl)pent-4-ynoate (**3c**)

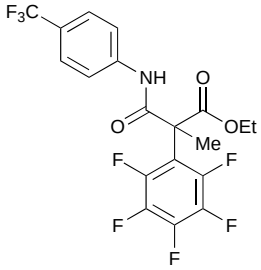


Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and methyl propiolate (13 mg, 0.16 mmol) in CH_2Cl_2 to afford **3c**. The crude reaction mixture was purified by filtering over a short plug of silica gel with $CHCl_3$ as eluent. Afterwards the crude compound was washed with pentane (1 × 1 mL). The desired compound **3c** was obtained as a colourless solid. Yield: 18 mg, 0.09 mmol, 36%. *Note: Compound **3c** decomposes on silica gel and in $CDCl_3$ solution.*

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 4.24–4.36 (m, 2H, Et-CH_2), 3.34 (s, 1H, CH), 1.91 (t, *J* = 1.3 Hz, 3H, CH_3), 1.29 (t, *J* = 7.2 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 179.8, 167.9, 145.4 (br. d, $J_{C–F}$ = 251.3 Hz), 141.1 (br. d, $J_{C–F}$ = 253.9 Hz), 138.0 (br. d, $J_{C–F}$ = 255.8 Hz), 113.4 (br. s), 82.3, 78.8, 63.3, 60.9, 20.9, 13.8 ppm. **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) δ: -135.83 (d, *J* = 20.0 Hz, 2F, Ar-F), -153.35 (t, *J* = 20.8 Hz, 1F, Ar-F), -

161.27–-161.15 (m, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3005, 2989, 2100 (C≡C), 1745 (C=O), 1523, 1492, 1450, 1274, 1261, 1143. **HRMS** (GC–MS) $[M+H]^+$ $[C_{14}H_{10}O_3F_5]^+$: calculated 321.05446, found 321.0544.

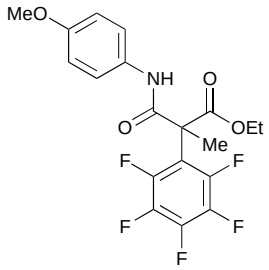
Synthesis of ethyl 2-methyl-3-oxo-2-(pentafluorophenyl)-3-((4-(trifluoromethyl)phenyl) amino) propanoate (**3d**)



Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-trifluoromethylphenyl isocyanate (29 mg, 0.16 mmol) in CH_2Cl_2 to afford **3d**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired compound **3d** was obtained as a colourless solid. Yield: 12 mg, 0.03 mmol, 17%.

^{1}H NMR (500.2 MHz, $CDCl_3$, 298 K) δ: 9.73 (s, 1H, NH), 7.66 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.60 (d, *J* = 8.6 Hz, 2H, Ar-H), 4.26–4.39 (m, 2H, CH_2), 2.04 (t, *J* = 1.9 Hz, 3H, CH_3), 1.29 (t, *J* = 7.2 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 173.2, 166.7, 145.9 (br. d, $J_{C–F}$ = 252.3 Hz), 141.0 (br. d, $J_{C–F}$ = 255.3 Hz), 140.5, 137.9 (br. d, $J_{C–F}$ = 253.7 Hz), 126.8 (q, $J_{C–F}$ = 32.2 Hz), 126.5 (q, $J_{C–F}$ = 3.8 Hz), 124.2 (q, $J_{C–F}$ = 270.6 Hz), 199.9, 114.8 (br. s), 63.8, 55.5, 23.5 (t, $J_{C–F}$ = 4.4 Hz), 13.9 ppm. **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) δ: -62.20 (s, 3F, CF_3), -139.35–-139.27 (m, 2F, Ar-F), -153.78 (t, *J* = 21.6 Hz, 1F, Ar-F), -161.43–-161.28 (m, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3323 (NH), 3047, 2988, 2943, 2880, 1738 (C=O), 1676 (C=O), 1603, 1524, 1491, 1452, 1408, 1317, 1248, 1184, 1169, 1155, 1119, 1105, 1067, 1016. **HRMS** (ES+) $[M+H]^+$ $[C_{19}H_{14}O_3F_8]^+$: calculated 456.0846, found 456.0846.

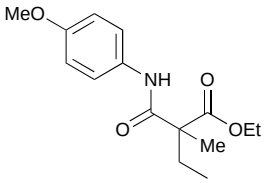
Synthesis of ethyl 3-((4-methoxyphenyl)amino)-2-methyl-3-oxo-2-(pentafluorophenyl) propanoate (**3e**)



Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-methoxyphenyl isocyanate (23 mg, 0.16 mmol) in CH_2Cl_2 to afford **3e**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired compound **3e** was obtained as a colourless solid. Yield: 35 mg, 0.08 mmol, 54%.

^{1}H NMR (500.2 MHz, $CDCl_3$, 298 K) δ: 9.27 (s, 1H, NH), 7.41–7.44 (m, 2H, Ar-H), 6.85–6.88 (m, 2H, Ar-H), 4.24–4.38 (m, 2H, CH_2), 3.79 (s, 3H, OCH_3), 2.01 (t, J = 2.0 Hz, 3H, CH_3), 1.29 (t, J = 7.2 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 173.0, 166.0, 156.9, 146.0 (br. d, $J_{C–F}$ = 249.6 Hz), 140.8 (br. d, $J_{C–F}$ = 256.7 Hz), 137.9 (br. d, $J_{C–F}$ = 252.3 Hz), 130.6, 122.0, 115.3 (br. s), 114.3, 63.4, 55.6, 55.3, 23.4 (t, $J_{C–F}$ = 4.2 Hz), 13.9 ppm. **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) δ: -139.14 (d, J = 16.5 Hz, 2F, Ar-F), -154.49 (t, J = 16.5 Hz, 1F, Ar-F), –161.83–-161.73 (m, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3335 (NH), 3310 (NH), 3057, 2988, 2940, 2911, 2839 (OCH_3), 1719 (C=O), 1684 (C=O), 1655, 1599, 1522, 1512, 1493, 1414, 1383, 1300, 1246, 1167, 1126, 1111, 1080, 1061, 1034, 1015. **HRMS** (ES+) $[M+H]^+$ $[C_{19}H_{17}NO_4F_5]^+$: calculated 418.1078, found 418.1077.

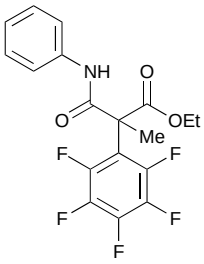
Synthesis of ethyl 2-((4-methoxyphenyl)carbamoyl)-2-methylbutanoate (**3h**)



Synthesised in accordance with the *General Procedure* using BEt_3 (0.16 mL, 0.16 mmol, 1M in hexane), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-methoxyphenyl isocyanate (23 mg, 0.16 mmol) in CH_2Cl_2 to afford **3h**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired compound **3h** was obtained as a colourless oil. Yield: 6 mg, 0.2 mmol, 14%.

^{1}H NMR (500.2 MHz, $CDCl_3$, 298 K) δ: 9.09 (s, 1H, NH), 7.44–7.47 (m, 2H, Ar-H), 6.84–6.87 (m, 2H, Ar-H), 4.20–4.30 (m, 2H, CH_2), 3.79 (s, 3H, OCH_3), 2.06–2.13 (m, 1H, CH_2), 1.89–1.96 (m, 1H, CH_2), 1.50 (s, 3H, CH_3), 1.32 (t, J = 7.1 Hz, 3H, CH_3), 0.91 ppm (t, J = 7.8 Hz, 3H, CH_3). **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 175.9, 169.3, 156.5, 131.2, 121.9, 114.2, 61.9, 55.7, 54.7, 32.2, 20.8, 14.2, 9.7 ppm. **IR** ν_{max} (cm^{-1}): 3330 (NH), 2976, 2937, 2881, 2837, 1734 (C=O), 1712, 1681, 1598, 1512, 1462, 1444, 1411, 1377, 1300, 1246, 1174, 1151, 1128, 1112, 1055, 1033. **HRMS** (ASAP) $[M+H]^+$ $[C_{15}H_{22}O_4N]^+$: calculated 280.1549, found 280.1557.

Synthesis of ethyl 2-methyl-3-oxo-2-(pentafluorophenyl)-3-(phenylamino)propanoate (**3f**)

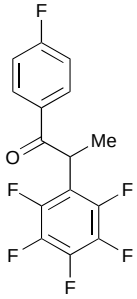


Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and phenyl isocyanate (19 mg, 0.16 mmol) in CH_2Cl_2 to afford **3f**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired compound **3f** was obtained as a colourless solid. Yield: 17 mg, 0.04 mmol, 28%.

^{1}H NMR (500.2 MHz, $CDCl_3$, 298 K) δ: 9.41 (s, 1H, NH), 7.51–7.54 (m, 2H, Ar-H), 7.32–7.36 (m, 2H, Ar-H), 7.12–7.16 (m, 1H, Ar-H), 4.25–4.38 (m, 2H, CH_2), 2.02 (t, J = 2.0 Hz, 3H, CH_3), 1.29 (t, J = 7.2 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 173.0, 166.1, 145.9 (br. d, $J_{C–F}$ = 247.4 Hz), 140.9 (br. d, $J_{C–F}$ = 254.2 Hz), 137.9 (br. d, $J_{C–F}$ = 256.1 Hz), 137.5, 129.2, 125.0, 120.3, 115.2 (br. s), 63.5, 55.5, 23.4 (t, $J_{C–F}$ = 3.9 Hz), 14.0 ppm. **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) δ: -139.09 (d, J = 16.9 Hz, 2F, Ar-F), -154.32 (t, J = 20.5 Hz, 1F, Ar-F), -161.66 (dt, J = 20.5, 16.9 Hz, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3335 (NH), 3310 (NH), 3063, 2986, 2941, 2853, 1721 (C=O), 1684 (C=O), 1655, 1599, 1524, 1491, 1443, 1383, 1308, 1246, 1165, 1125, 1098, 1078, 1061, 1015. **HRMS** (ES+) $[M+H]^+$ $[C_{18}H_{15}NO_3F_5]^+$: calculated 388.0972, found 388.0970.

2.4 Synthesis and spectral characterisation of α-aryl ketones

Synthesis of 1-(4-fluorophenyl)-2-(pentafluorophenyl)propan-1-one (**7a**)

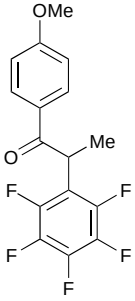


Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-fluorobenzoyl chloride (25 mg, 0.16 mmol) in CH_2Cl_2 to afford **7a**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired compound **7a** was obtained as a colourless oil. Yield: 16 mg, 0.05 mmol, 32%. *Note: **7a** is contaminated with a small amount of the β-keto ester.*

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 7.84–7.87 (m, 2H, Ar-H), 7.08–7.11 (m, 2H, Ar-H), 4.80 (q, J = 7.4 Hz, 1H, CH), 1.60 (d, J = 7.4 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 195.3, 165.9 (d, $J_{C–F}$ = 255.5 Hz), 144.8 (br. d, $J_{C–F}$ = 247.9 Hz), 140.6 (br. d, $J_{C–F}$ = 259.3 Hz), 137.9 (br. d, $J_{C–F}$ = 252.9 Hz), 132.0 (d, $J_{C–F}$ = 2.9 Hz), 131.0 (d, $J_{C–F}$ = 9.4 Hz), 116.2 (d, $J_{C–F}$ = 22.7 Hz), 115.2 (br. s), 38.2, 16.1 ppm. **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) δ: -104.42–-104.36 (m, 1F, Ar-F), -142.14 (dd, J = 21.2, 6.7 Hz, 2F, Ar-F), -154.89 (t,

J = 20.9 Hz, 1F, Ar-F), -161.08 (dd, *J* = 20.9, 21.2 Hz, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3076, 2988, 2941, 2884, 1746, 1694 (C=O), 1655, 1599, 1522, 1499, 1456, 1408, 1381, 1306, 1296, 1225, 1157, 1148, 1128, 1070, 1030. **HRMS** (ES+) $[M+H]^+$ $[C_{15}H_9OF_6]^+$: calculated 319.0558, found 319.0565.

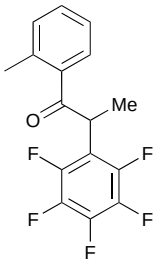
Synthesis of 1-(4-methoxyphenyl)-2-(pentafluorophenyl)propan-1-one (**7b**)



Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-methoxybenzoyl chloride (27 mg, 0.16 mmol) in CH_2Cl_2 to afford **7b**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired compound **7b** was obtained as a colourless oil. Yield: 22 mg, 0.07 mmol, 43%.

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 7.82 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.89 (d, *J* = 8.7 Hz, 2H, Ar-H), 4.81 (q, *J* = 7.9 Hz, 1H, CH), 3.84 (s, 3H, OCH_3), 1.59 (d, *J* = 7.9 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 195.2, 163.7, 144.9 (br. d, $J_{C–F}$ = 247.9 Hz), 140.4 (br. d, $J_{C–F}$ = 253.7 Hz), 137.8 (br. d, $J_{C–F}$ = 253.7 Hz), 130.6, 128.4, 115.7 (br. s), 114.1, 55.6, 37.9, 16.2 ppm. **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) δ: -142.10 (dd, *J* = 21.1, 6.7 Hz, 2F, Ar-F), -155.56 (t, *J* = 21.2 Hz, 1F, Ar-F), -161.46 (ddd, *J* = 21.2, 21.1, 6.7 Hz, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3057, 2986, 2940, 2843 (OCH_3), 1686 (C=O), 1655, 1599, 1574, 1520, 1499, 1458, 1420, 1379, 1312, 1258, 1219, 1171, 1148, 1128, 1069, 1030. **HRMS** (ES+) $[M+H]^+$ $[C_{16}H_{12}O_2F_5]^+$: calculated 331.0757, found 331.0764.

Synthesis of 2-(pentafluorophenyl)-1-(o-tolyl)propan-1-one (**7c**)

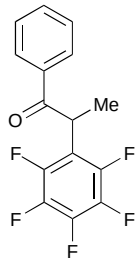


Synthesised in accordance with *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 2-methylbenzoyl chloride (24 mg, 0.16 mmol) in CH_2Cl_2 to afford **7c**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (90:10 v/v) as eluent. The desired compound **7c** was obtained as a colourless solid. Yield: 9 mg, 0.03 mmol, 18%.

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 7.44 (dd, *J* = 7.8, 1.2 Hz, 1H, Ar-H), 7.32 (dt, *J* = 7.8, 1.3 Hz, 1H, Ar-H), 7.22–7.25 (m, 1H, Ar-H), 7.15–7.19 (m, 1H, Ar-H), 4.76 (q, *J* = 7.2 Hz, 1H, CH), 2.46 (s, 3H, *o*-CH_3), 1.56 (d, *J* = 7.2 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz,

$CDCl_3$, 298 K) δ: 200.5, 144.9 (br. d, $J_{C–F}$ = 246.1 Hz), 140.9 9 (br. d, $J_{C–F}$ = 254.3 Hz), 138.8, 137.7 9 (br. d, $J_{C–F}$ = 250.4 Hz), 136.4, 132.3, 131.5, 127.3, 125.7, 115.2, 40.3, 25.5, 20.6, 15.6 ppm. **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) δ: -142.45 (dd, *J* = 22.1, 7.2 Hz, 2F, Ar-F), -155.37 (t, *J* = 22.1 Hz, 1F, Ar-F), -161.53 (ddd, *J* = 22.1, 22.1 7.2 Hz, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3067, 3019, 2994, 2959, 2926, 2853, 1701 (C=O), 1655, 1599, 1520, 1501, 1456, 1383, 1354, 1298, 1273, 1217, 1198, 1153, 1125, 1082, 1059, 1016. **HRMS** (AP+) $[M+H]^+$ $[C_{16}H_{12}OF_5]^+$: calculated 315.0808, found 315.0808.

Synthesis of 2-(pentafluorophenyl)-1-phenylpropan-1-one (**7d**)



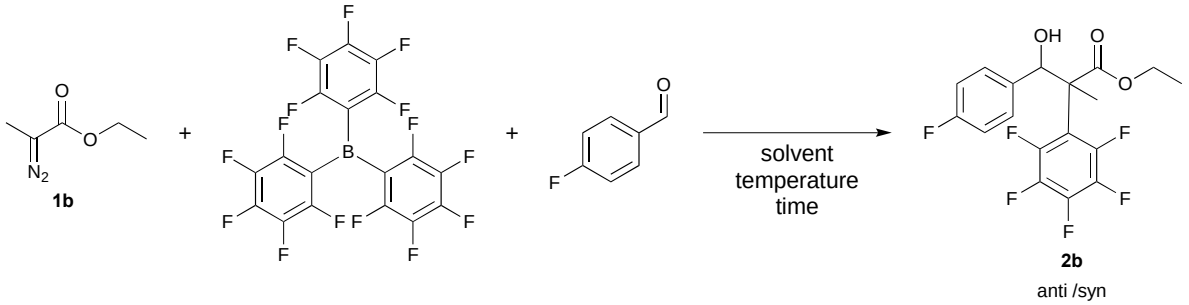
Synthesised in accordance with the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and benzoyl chloride (22 mg, 0.16 mmol) in CH_2Cl_2 to afford **7d**. The crude reaction mixture was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. The desired compound **7d** was obtained as a colourless solid. Yield: 20 mg, 0.07 mmol, 43%.

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 7.81–7.83 (m, 2H, Ar-H), 7.51–7.55 (m, 1H, Ar-H), 7.40–7.44 (m, 2H, Ar-H), 4.85 (q, *J* = 7.2 Hz, 1H, CH), 1.61 (d, *J* = 7.2 Hz, 3H, CH_3) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) δ: 196.9, 144.9 (br. d, $J_{C–F}$ = 246.9 Hz), 140.5 (br. d, $J_{C–F}$ = 252.6 Hz), 137.8 (br. d, $J_{C–F}$ = 250.2 Hz), 135.7, 133.4, 128.9, 128.3, 155.4 (br. s), 38.3, 16.1 ppm. **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) δ: -142.13 (dd, *J* = 22.1, 7.2 Hz, 2F, Ar-F), -155.26 (t, *J* = 22.1 Hz, 1F, Ar-F), -161.36 (ddd, *J* = 22.1, 22.1 7.2 Hz, 2F, Ar-F) ppm. **IR** ν_{max} (cm^{-1}): 3055, 2941, 2916, 2855, 1697(C=O), 1657, 1597, 1522, 1499, 1454, 1447, 1379, 1225, 1128, 1069, 1026. **HRMS** (ES+) $[M+H]^+$ $[C_{15}H_{10}OF_5]^+$: calculated 301.0652, found 301.0657.

3. Optimisation of reaction conditions and determination of diastereomeric ratio

3.1 Variation of solvent, temperature, and time

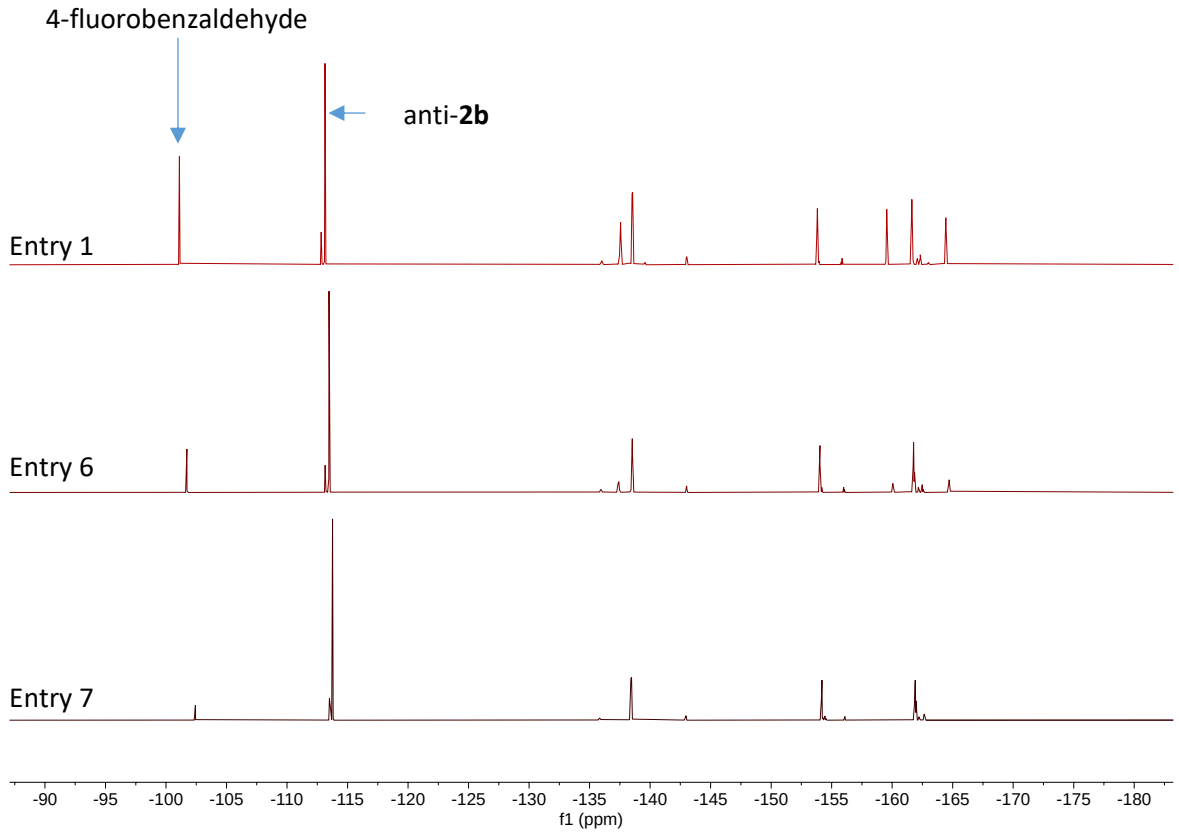
Following the *General Procedure* using $B(C_6F_5)_3$ (80 mg, 0.16 mmol), ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-fluorobenzaldehyde (19 mg, 0.16 mmol) in CH_2Cl_2 to afford **2b**. A ^{19}F NMR spectrum was recorded of the crude reaction mixture to determine the diastereomeric ratio (see below) before it was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. Yields reported are isolated yields.



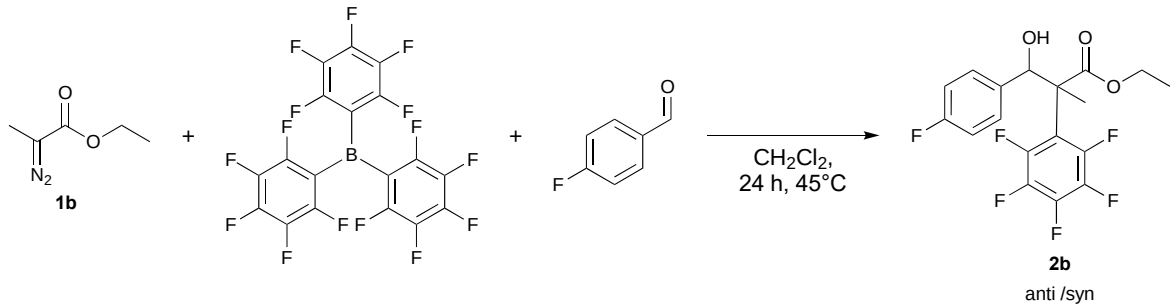
Entry	Solvent	Temperature	Time	Yield anti	Yield syn	*dr*	Yield combined
1	CH_2Cl_2	45 °C	20 h	53%	9%	1:0.10	62%
2	Toluene	45 °C	20 h	35%	6%	1:0.14	41%
3	Hexane	45 °C	20 h	37%	3%	1:0.12	40%
4	CH_2Cl_2	20 °C	20 h	35%	8%	1:0.10	43%
5	$C_2H_4Cl_2$	60 °C	20 h	23%	8%	1:0.26	31%
6	CH_2Cl_2	45 °C	24 h	60%	12%	1:0.10	72%
7	CH_2Cl_2	45 °C	30 h	60%	10%	1:0.10	70%

Upon longer reaction times, the consumption of the 4-fluorobenzaldehyde starting material increases (see Figure S1). However, the isolated yields of entry 6 and 7 are almost identical.

Figure S1: Comparison of the **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) spectra of the crude reaction mixture from the reactions of entry 1, 6, and 7.



3.2 Variation of amount of $B(C_6F_5)_3$



Entry	Eq. BCF	Yield anti	Yield syn	*dr*	Yield combiend
8	0.8	45%	11%	1:0.15	56%
9	0.6	37%	8%	1:0.15	45%
10	1.2	46%	6%	1:0.15	52%

Following the *General Procedure* using $B(C_6F_5)_3$, ethyl α-diazomethylacetate (**1b**, 20 mg, 0.16 mmol), and 4-fluorobenzaldehyde (19 mg, 0.16 mmol) in CH_2Cl_2 to afford **2b**. A ^{19}F NMR spectrum was recorded of the crude reaction mixture to determine the diastereomeric ratio (see below) before it was purified *via* preparative thin layer chromatography using hexane/ethyl acetate (95:05 v/v) as eluent. Yields reported are isolated yields.

3.3 Example of determination of the diastereomeric ratio

For the determination of the diastereomeric ratio of **2b**, the ^{19}F signals belonging to syn- and anti-**2b** in the ^{19}F NMR spectrum of the crude reaction mixture from the reaction of **1b**, $B(C_6F_5)_3$, and 4-fluorobenzaldehyde (entry 7) were integrated after identification from the crude reaction mixture (see Figure S2 and S3).

Figure S2: Comparison of the **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) spectra of pure syn-**2b**, anti-**2b** and the crude reaction mixture from the reaction of entry 7.

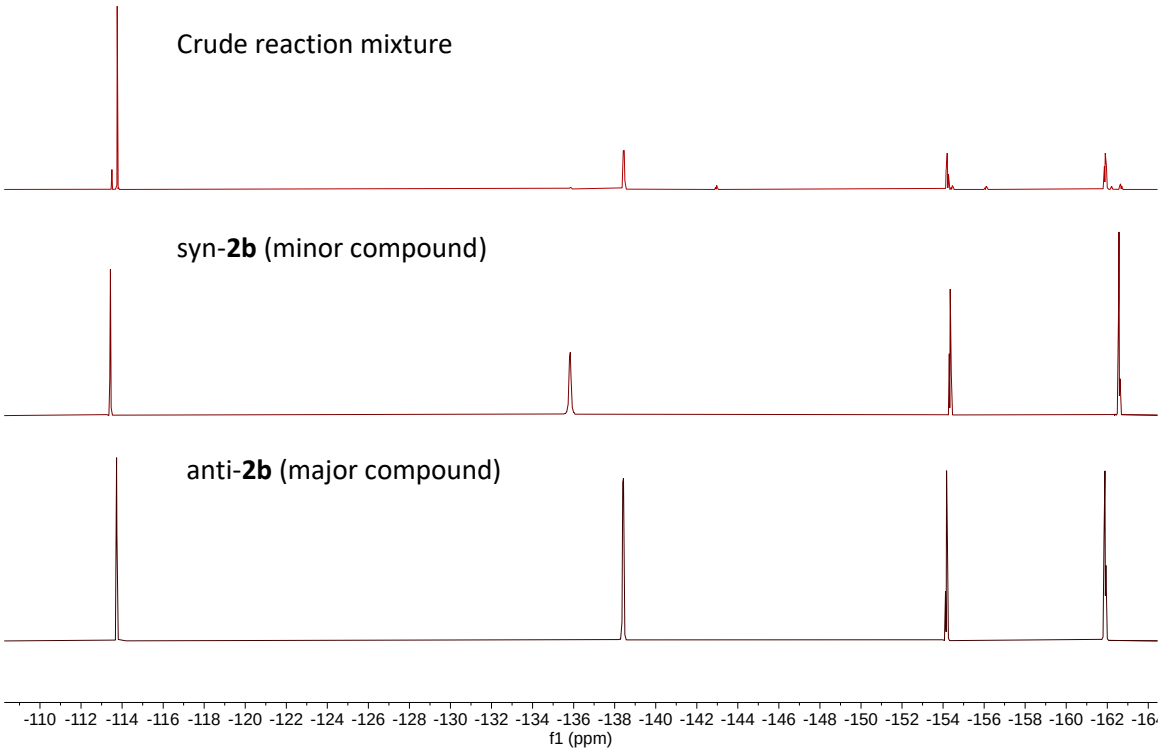
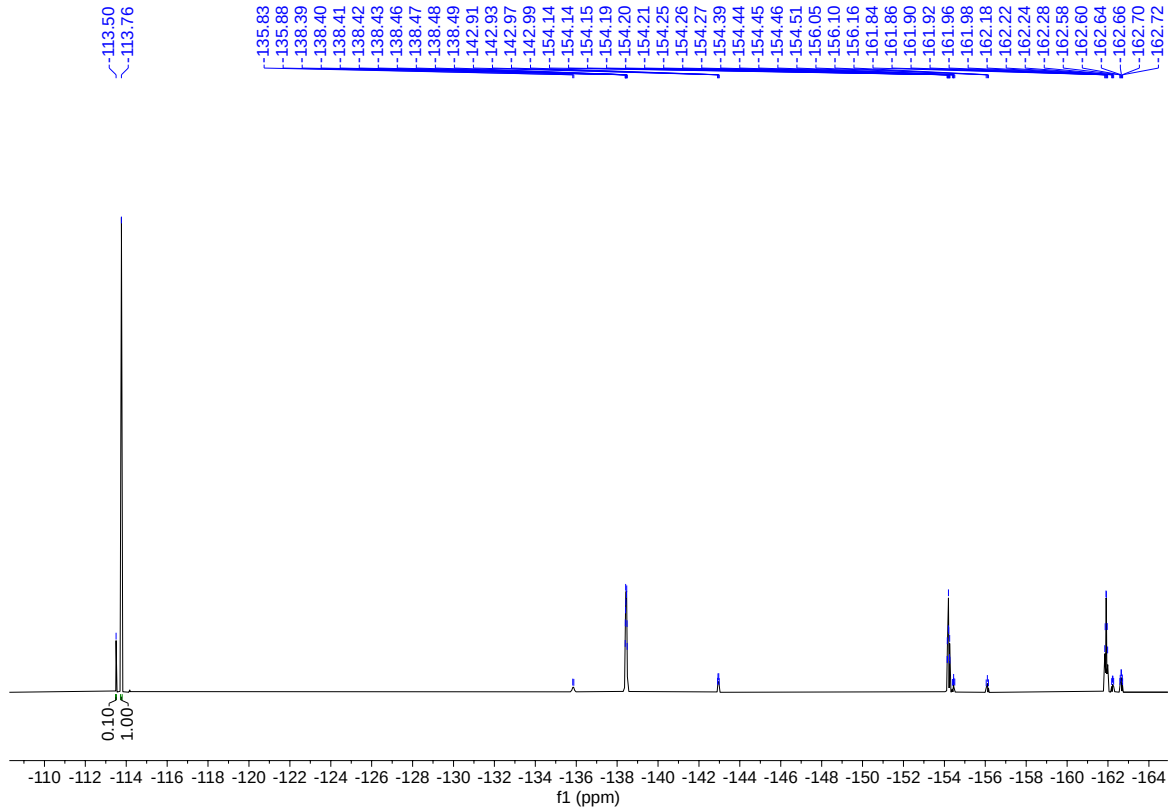
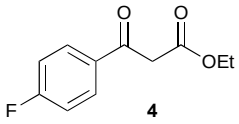


Figure S3: **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) spectrum of the crude reaction mixture from the reaction of entry 7.



4. Side products of reaction of 1a, $B(C_6F_5)_3$, and 4-fluorobenzaldehyde

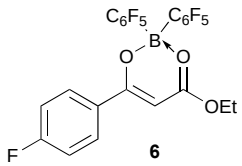
Following the *General Procedure* using $B(C_6F_5)_3$ (90 mg, 0.18 mmol), ethyl diazoacetate (**1a**, 20 mg, 0.18 mmol, 15% in toluene), and 4-fluorobenzaldehyde (22 mg, 0.18 mmol) in CH_2Cl_2, a mixture of compounds **4** and **6** (in addition to **2a**) could be isolated *via* preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. Total amount of the mixture of **4** and **6**: 8 mg, ratio **4**:**6** = 0.2:1. *Note: In this reaction, **2a** was formed in 30 mg (45%, 0.08 mmol).*



4

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 7.96–8.01 (m, 2H, Ar-H), 7.16–7.20 (m, 2H, Ar-H), 4.22 (q, *J* = 7.4 Hz, 2H, CH_2), 3.96 (s, 2H, CH_2), 1.26 (t, *J* = 7.4 Hz, 3H, CH_3) ppm. The values are in agreement with the literature.[3]

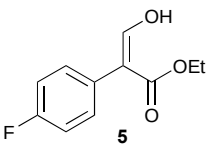
A clean sample of **6** could be generated by repeated preparative thin layer chromatography using hexane/ethyl acetate (95:5 v/v) as eluent. Single crystals of **6** could be obtained by slow evaporation of a concentrated solution of **6** in $CHCl_3$. *Note: The quantities of **6** obtained were too small for measuring the **^{13}C NMR** spectrum.*



6

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 7.97–8.01 (m, 2H, Ar-H), 7.16–7.20 (m, 2H, Ar-H), 5.90 (s, 1H, CH), 4.61 (q, *J* = 7.2 Hz, CH_2), 1.46 (t, *J* = 7.2 Hz, CH_3) ppm. **^{11}B NMR** (157.4 MHz, $CDCl_3$, 298 K) δ: 6.2 ppm. **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) δ: -103.14–-103-08 (m, 1F, Ar–F), -136.31 (dd, *J* = 23.8, 8.5 Hz, 4F, Ar-F), -156.12 (t, *J* = 23.8, Hz, 2F, Ar-F), -163.36 (dt, *J* = 23.8, 8.5 Hz, 4F, Ar-F) ppm.

Following the *General Procedure* using catalytic amounts of $B(C_6F_5)_3$ (9 mg, 0.02 mmol), ethyl diazoacetate (**1a**, 20 mg, 0.18 mmol, 15% in toluene), and 4-fluorobenzaldehyde (22 mg, 0.18 mmol) in CH_2Cl_2, additional to compounds **4** and **6**, **5** could be identified in the crude reaction mixture.



5

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ: 12.08 (d, *J* = 12.6 Hz, 1H, OH), 7.18–7.25 (m, 3H, CH and Ar-H), 6.99–7.04 (m, 2H, Ar-H), 4.28 (q, *J* = 7.2 Hz, CH_2), 1.28 (t, *J* = 7.2 Hz, H_3) ppm. The values are in agreement with the literature.[4]

5. NMR Spectra

Figure S4: **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K) spectrum of **2a**.

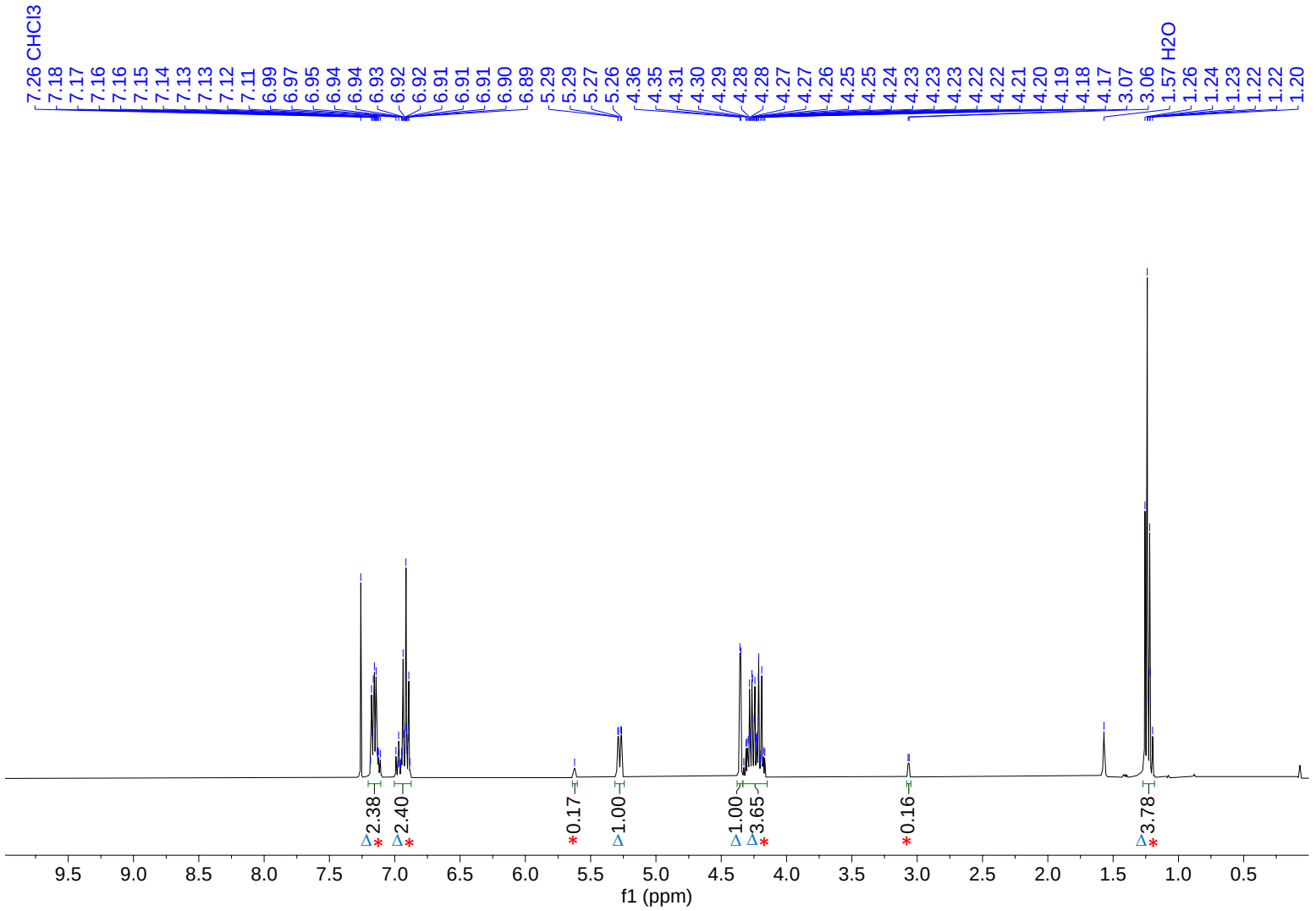


Figure S5: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2a**.

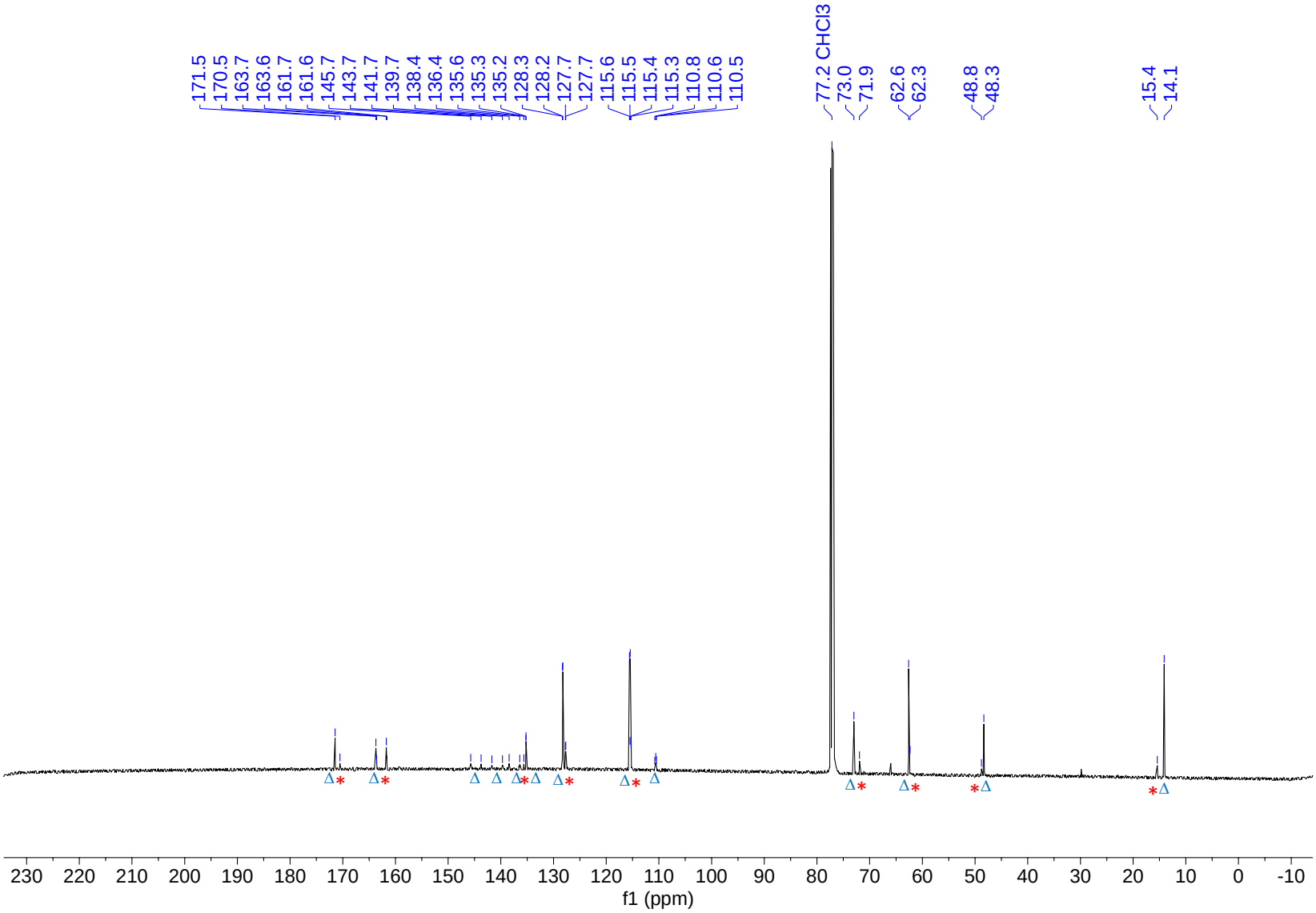


Figure S6: **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) spectrum of the diasteriomeric mixture of **2a**. Signals of the minor compound are marked with *.

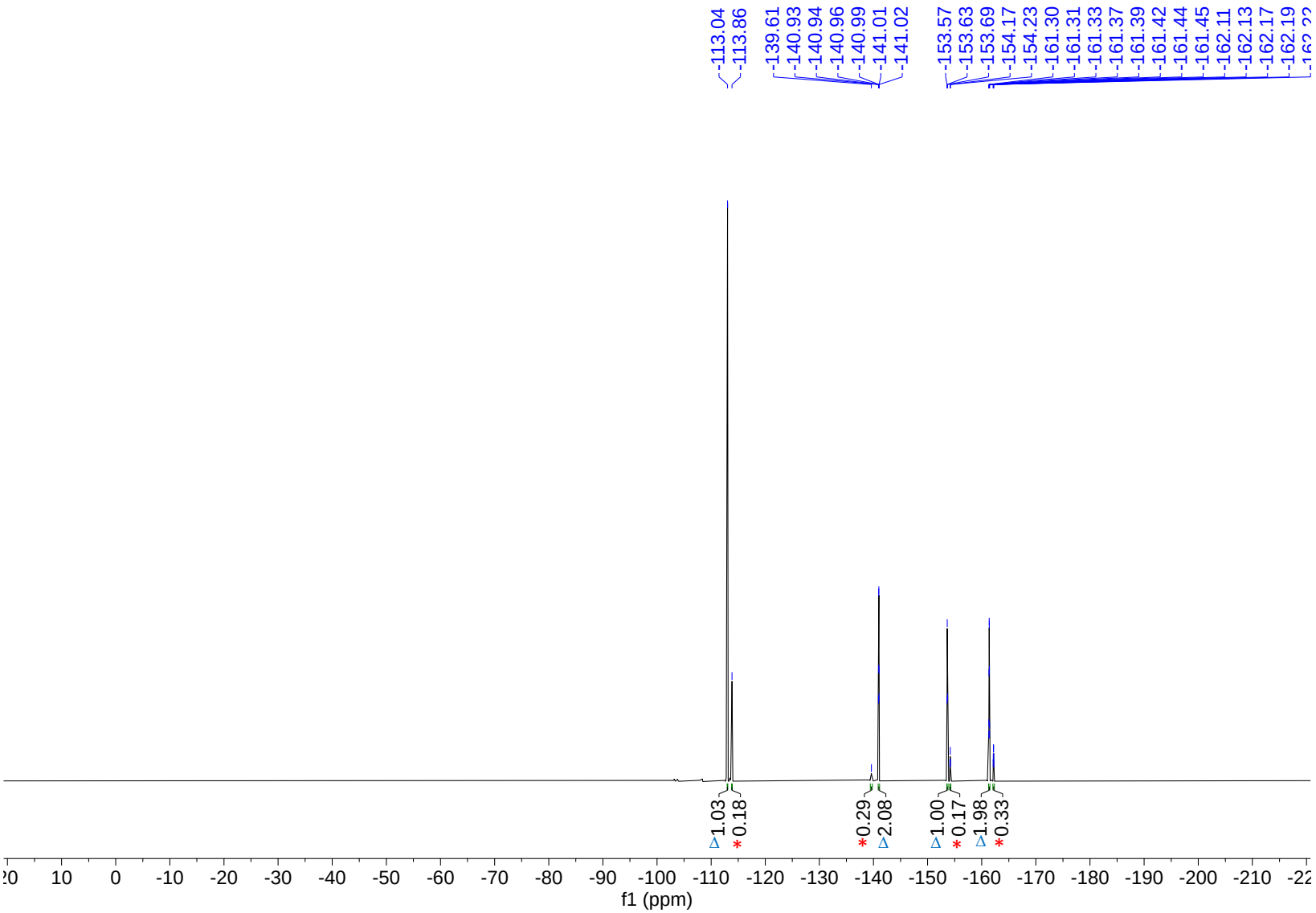


Figure S7: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **2b**.

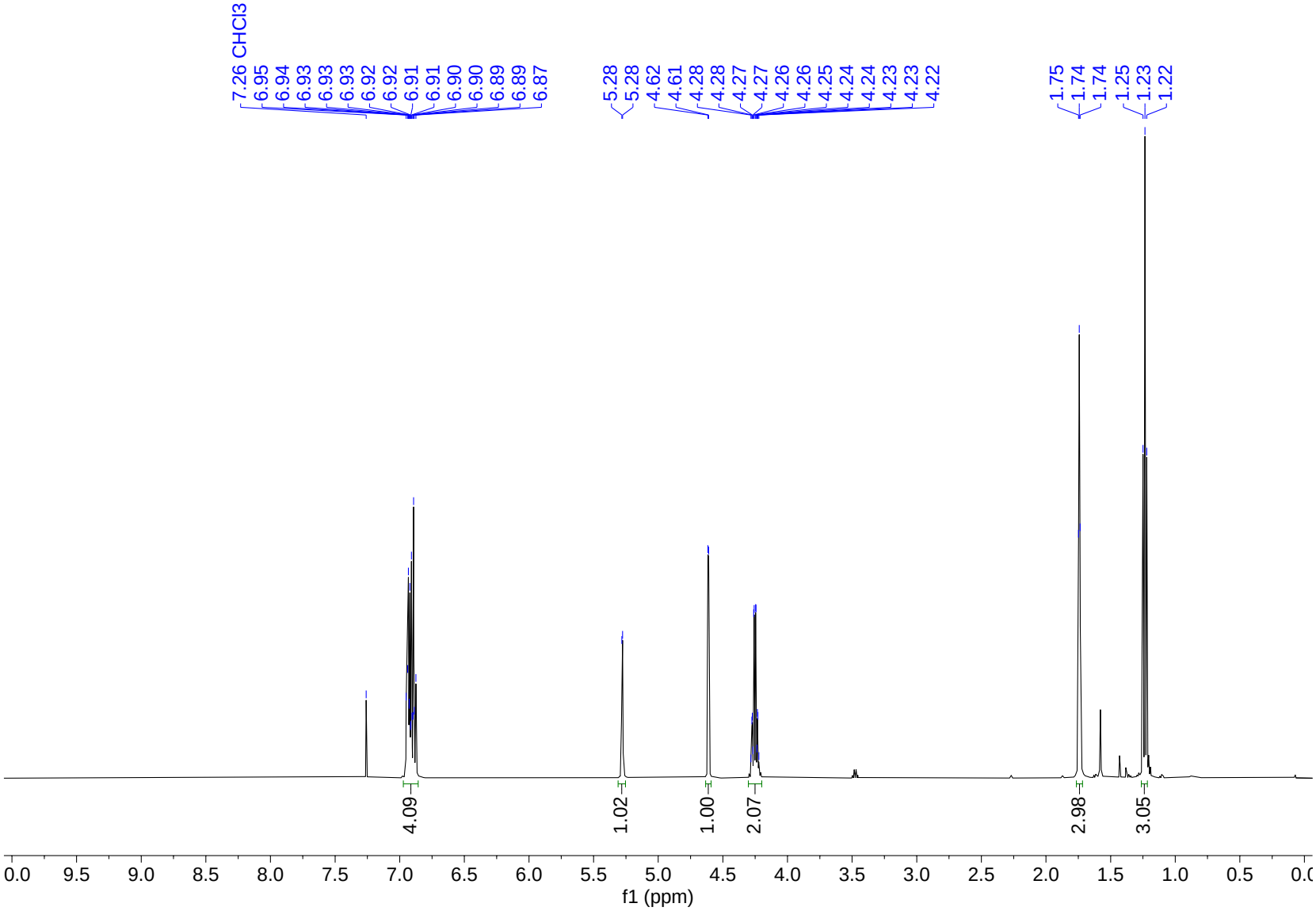


Figure S8: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2b**.

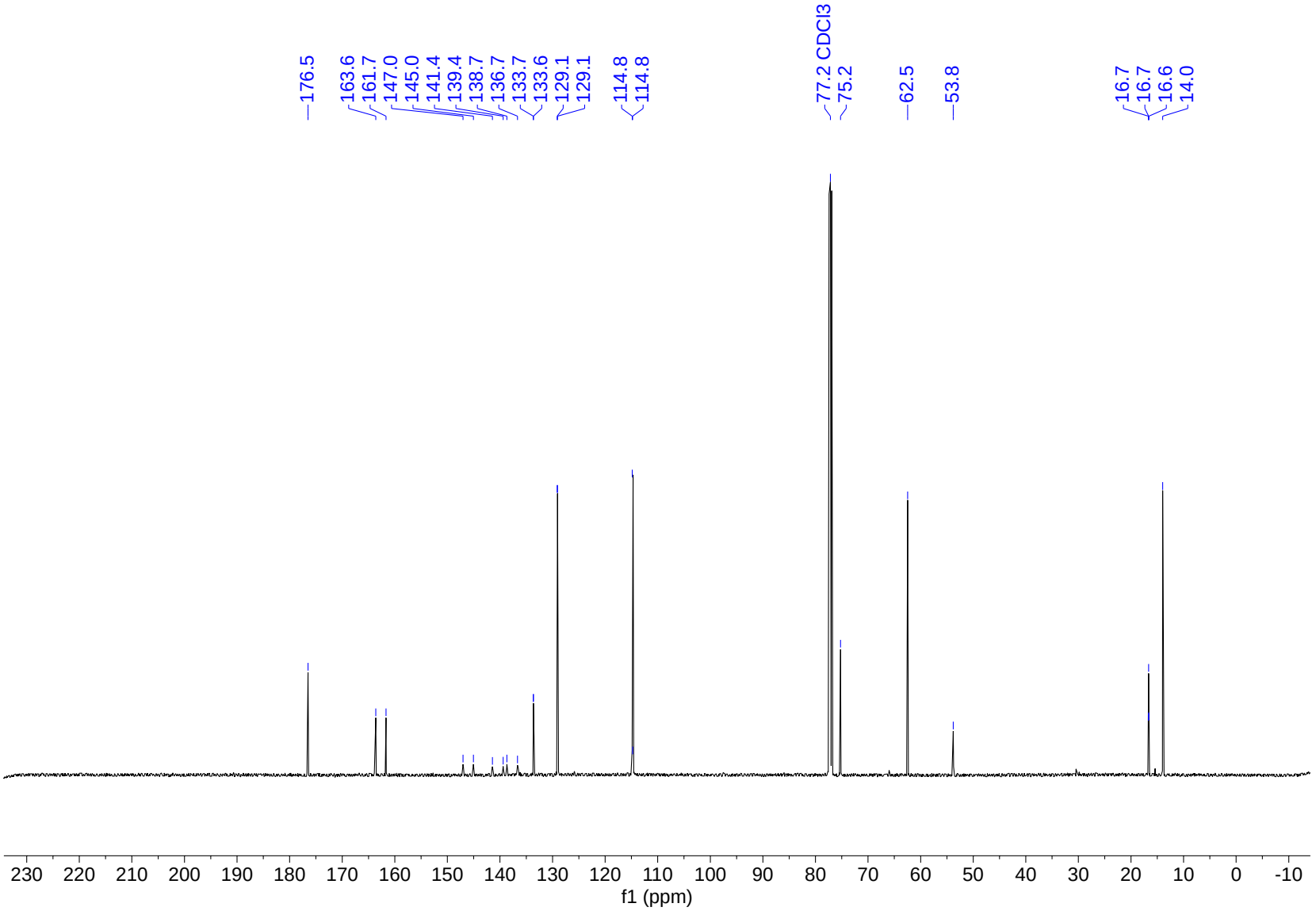


Figure S9: **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) spectrum of **2b**.

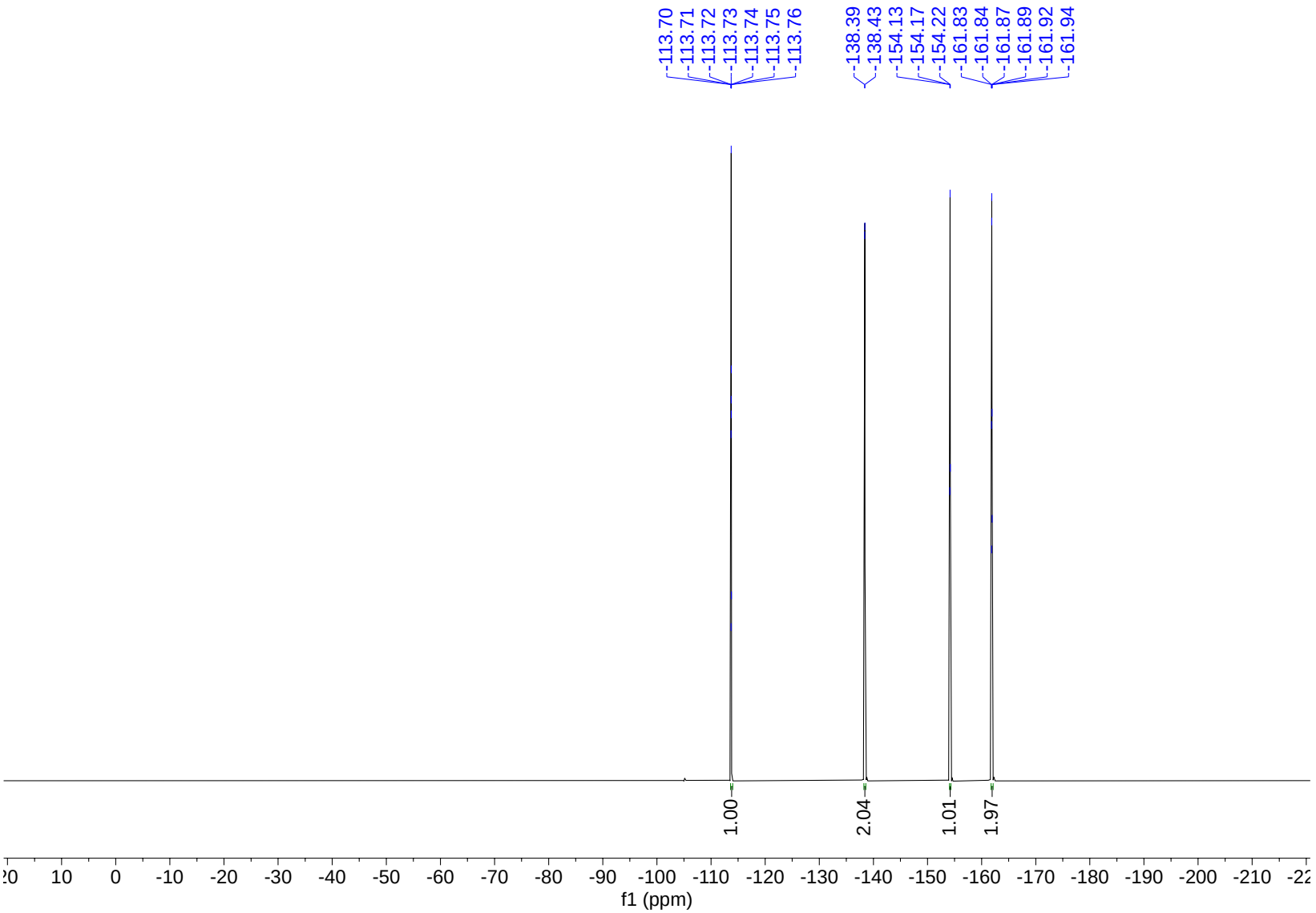


Figure S10: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **2r**.

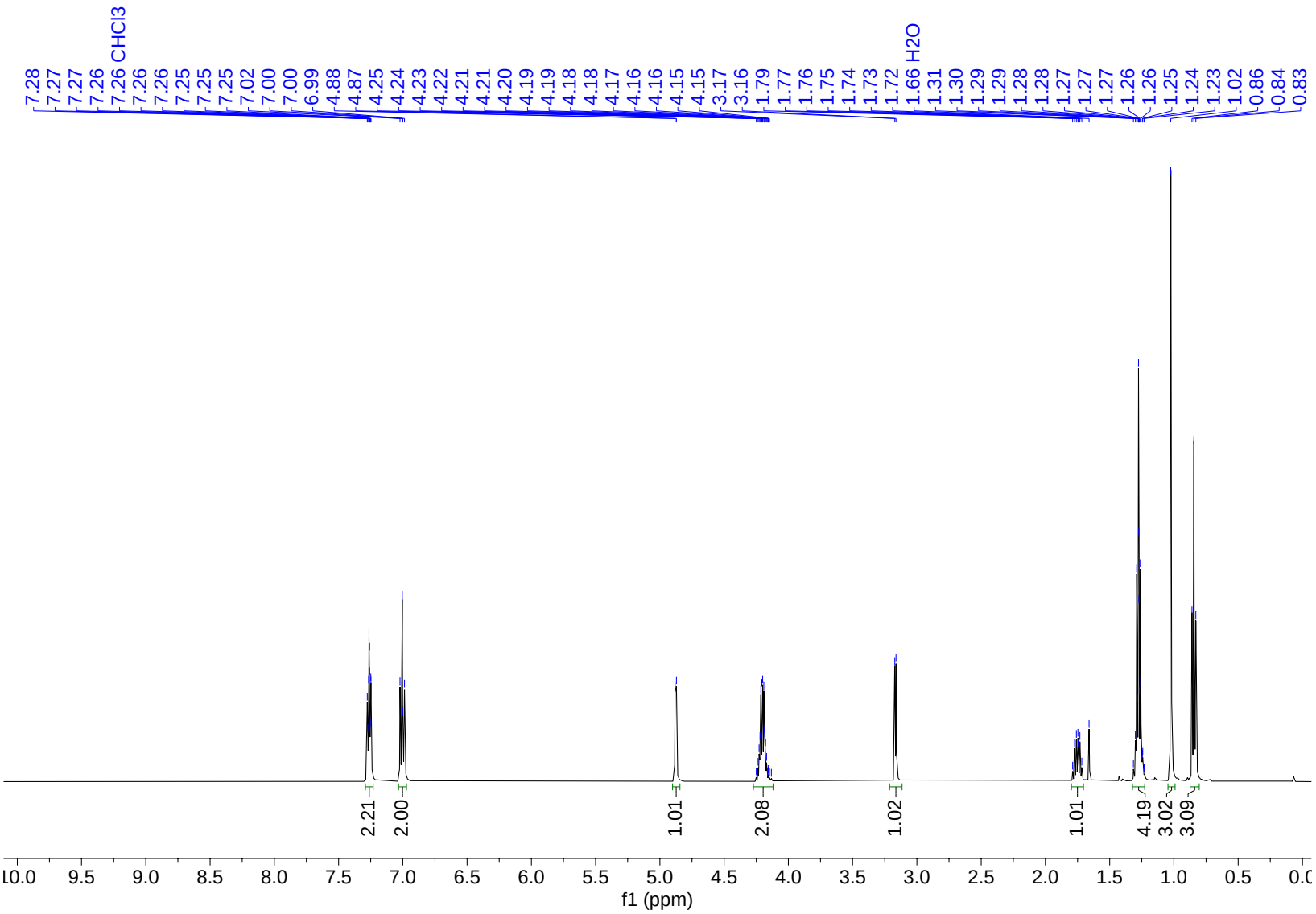


Figure S11: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2r**.

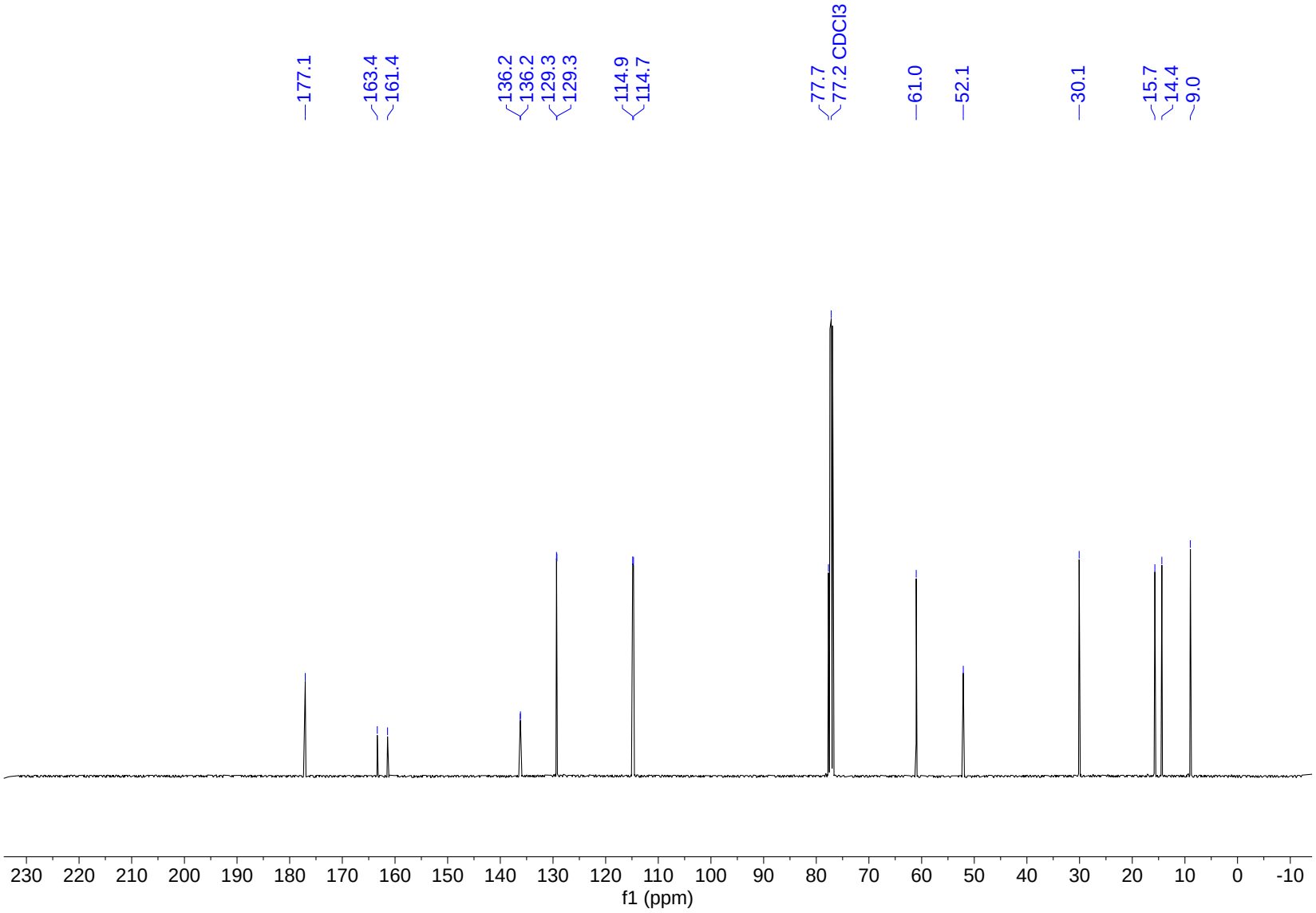


Figure S12: **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) spectrum of **2r**.

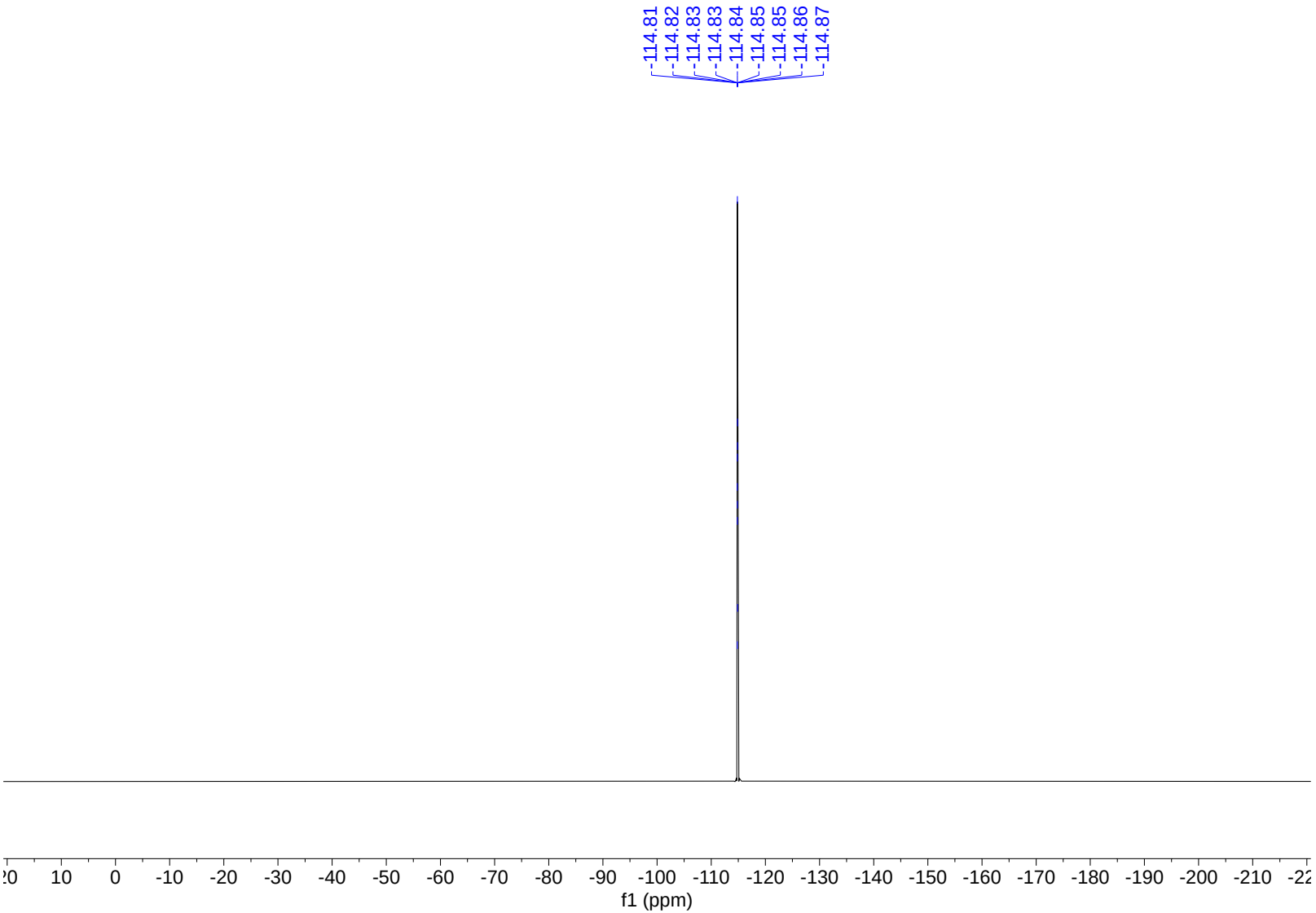


Figure S13: **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K) spectrum of **2c**.

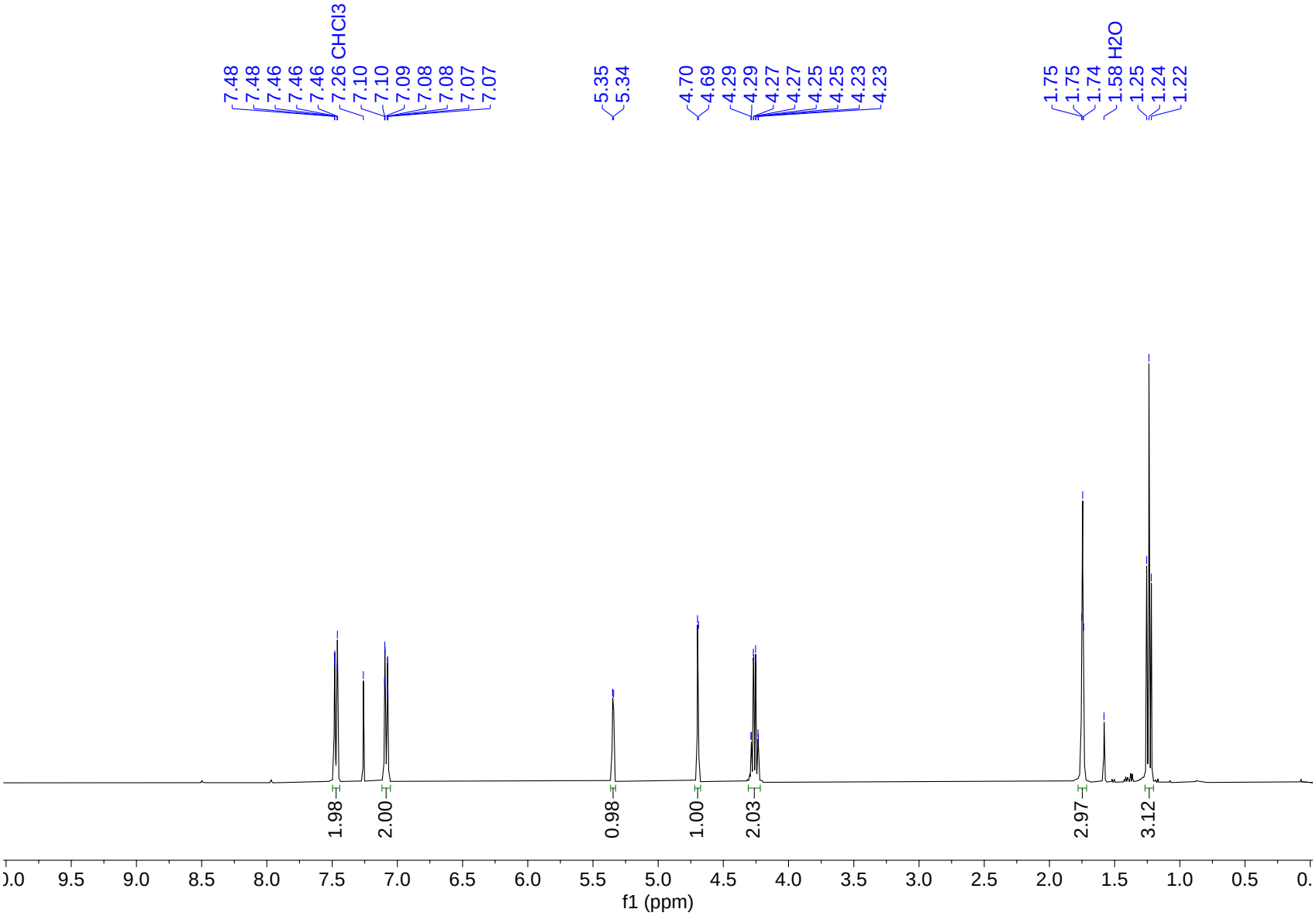


Figure S14: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2c**.

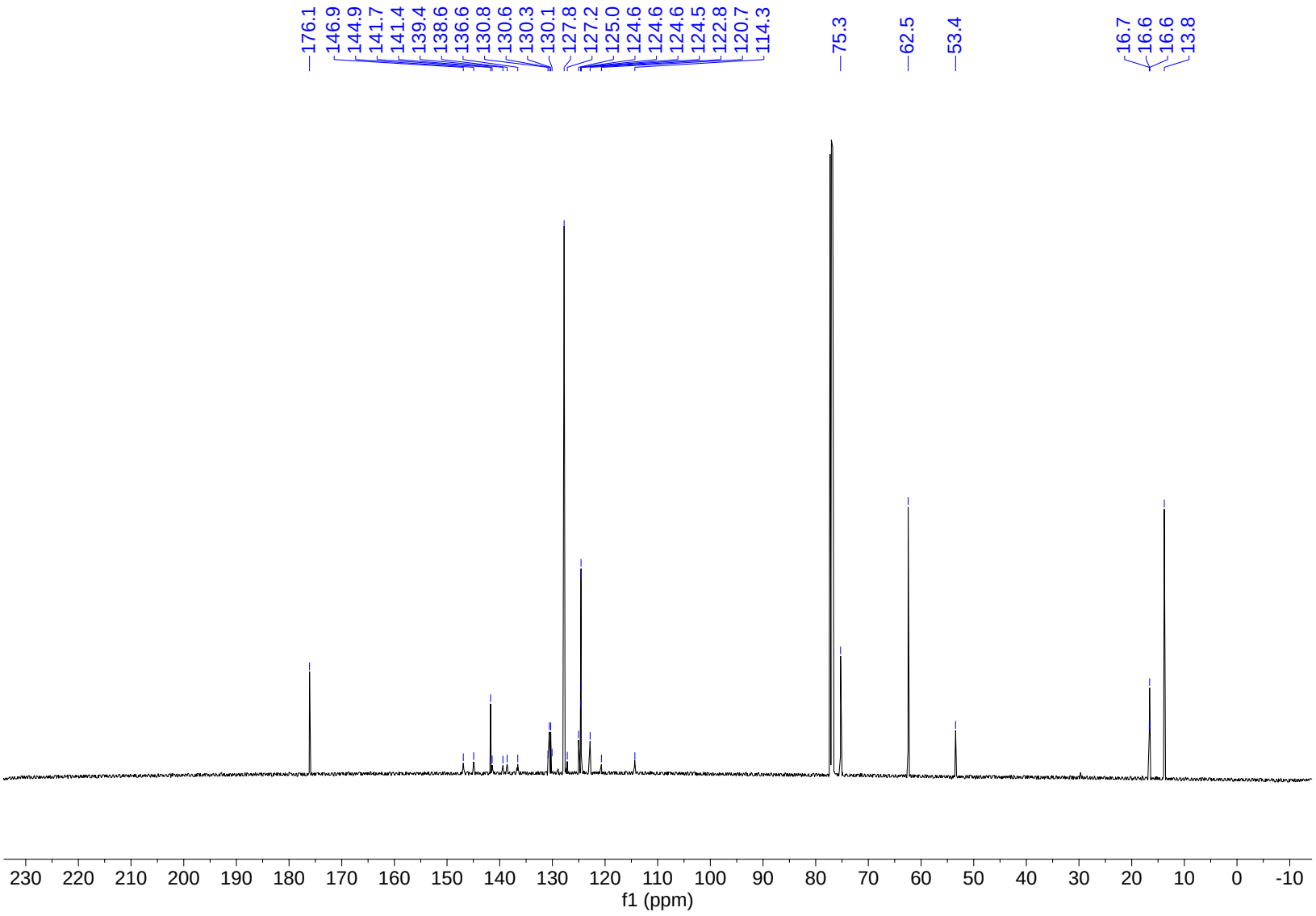


Figure S15: **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) spectrum of **2c**.

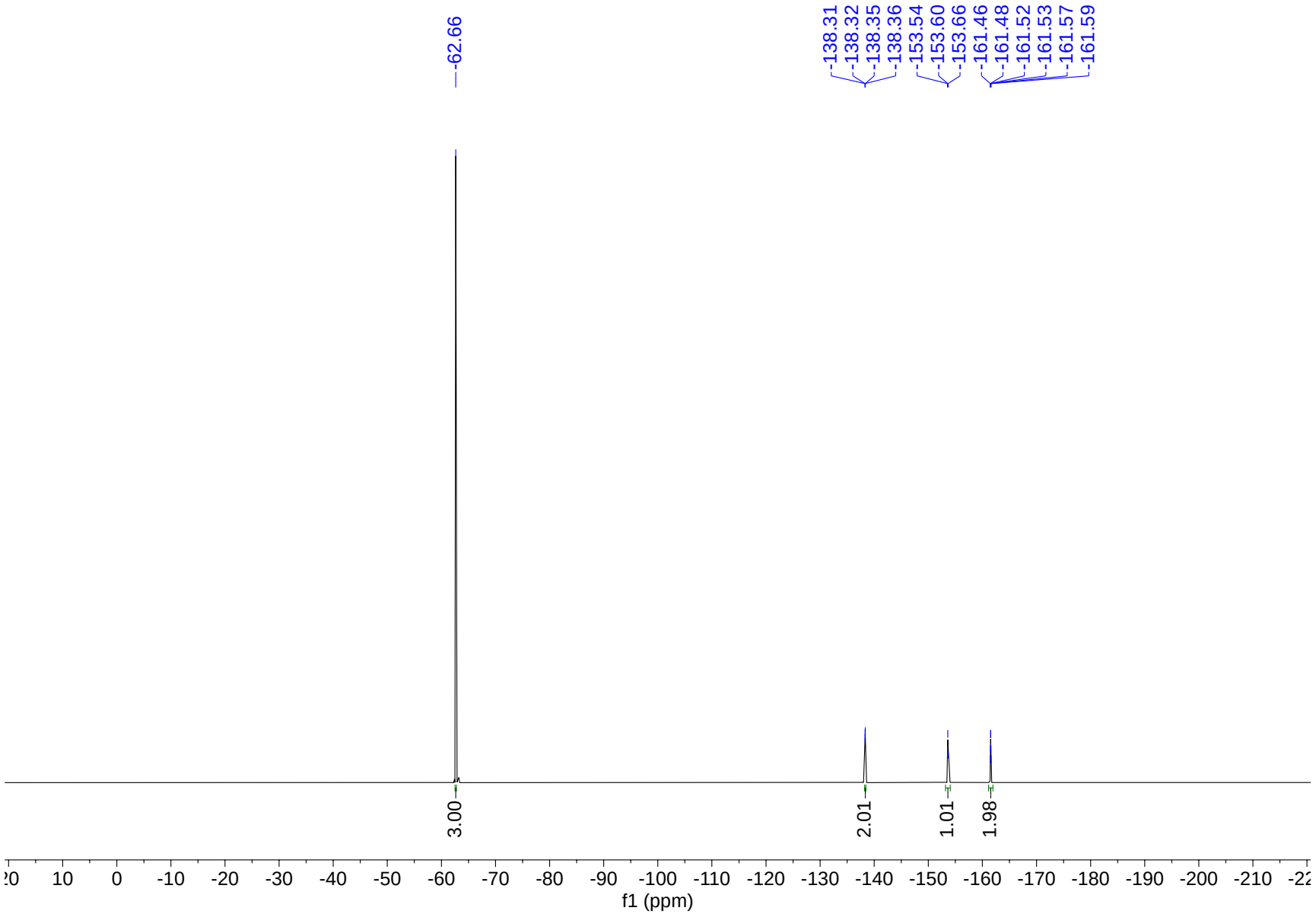


Figure S16: **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K) spectrum of **2d**.

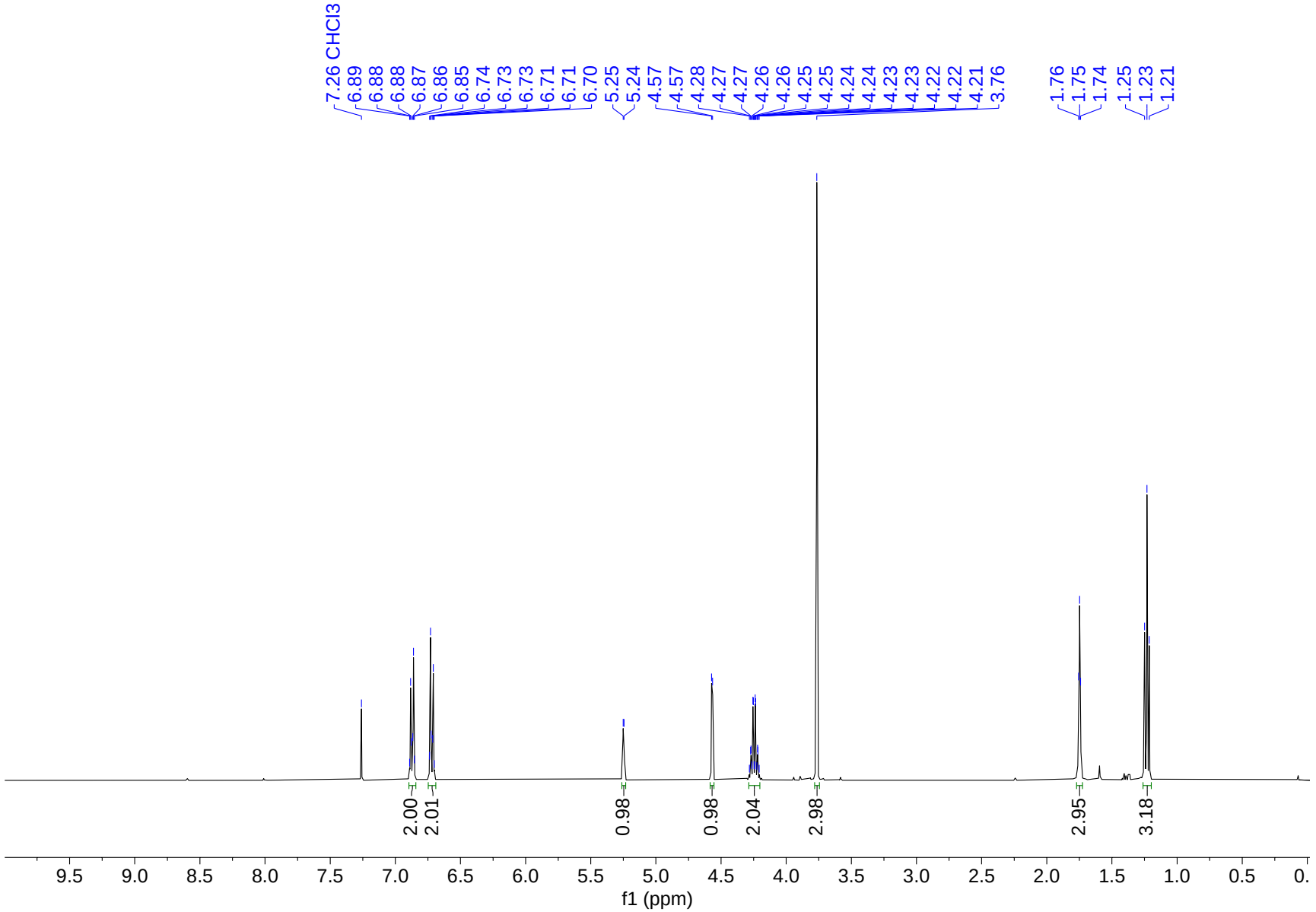


Figure S17: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2d**.

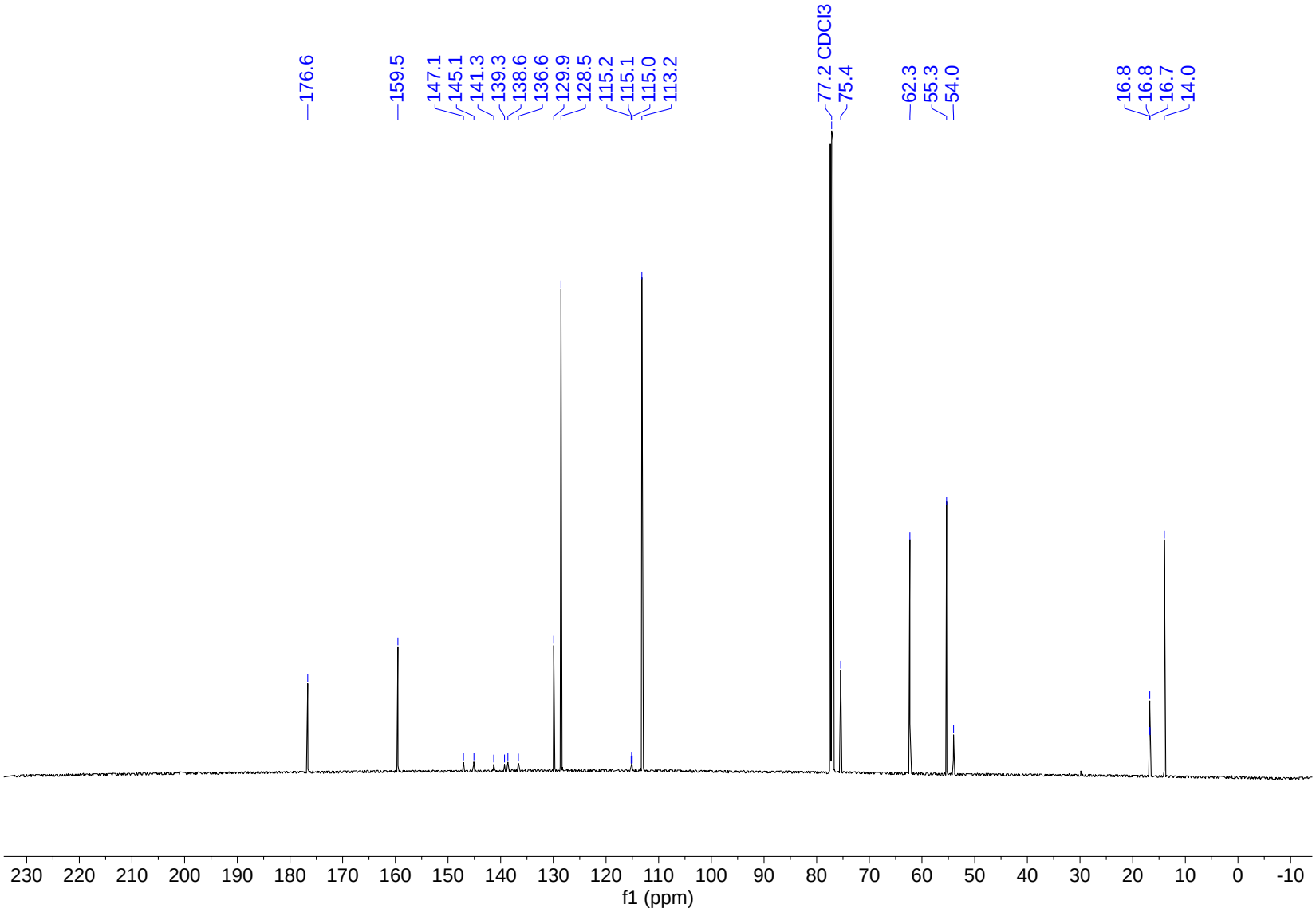


Figure S18: **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) spectrum of **2d**.

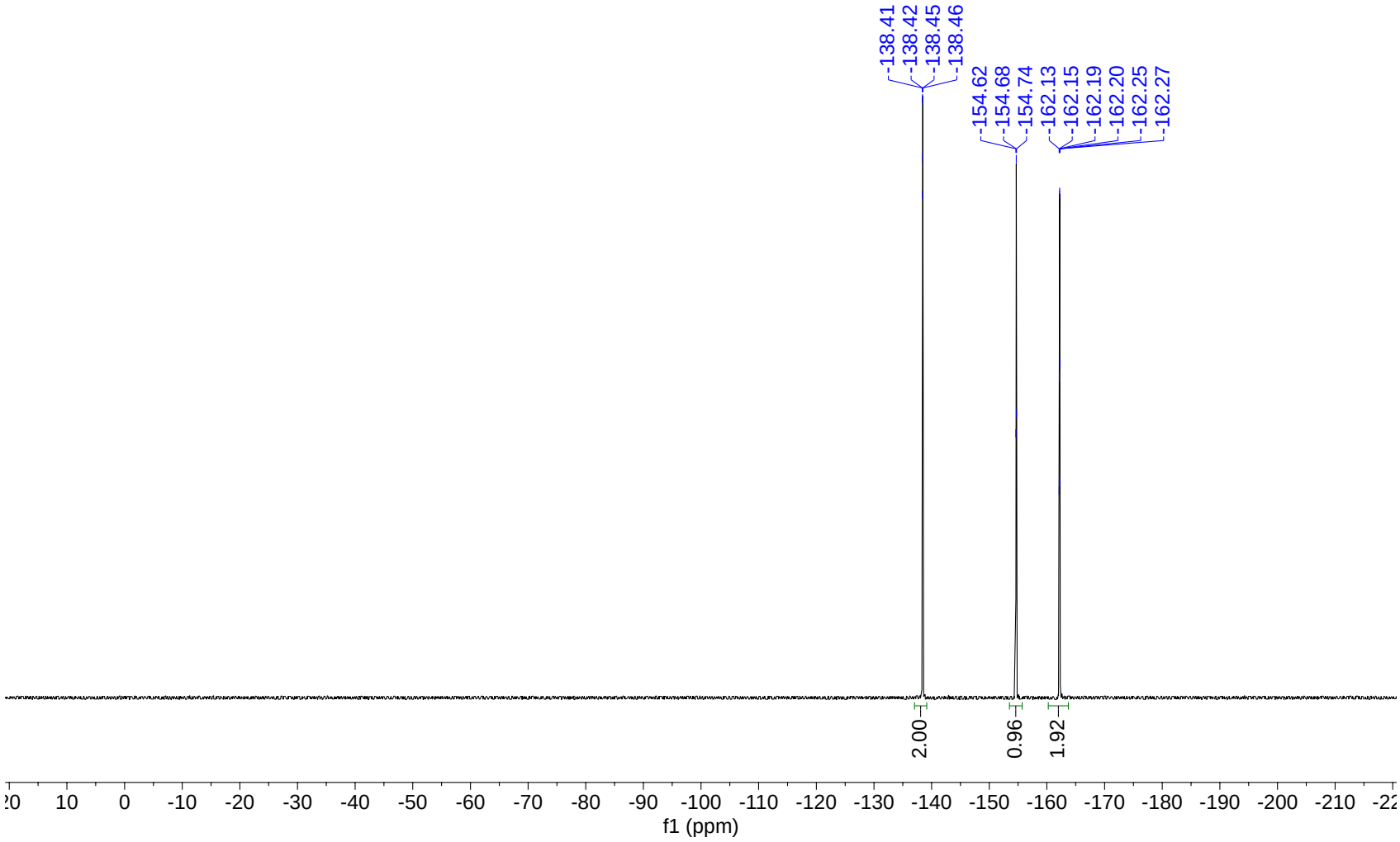


Figure S19: **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K) spectrum of **2e**.

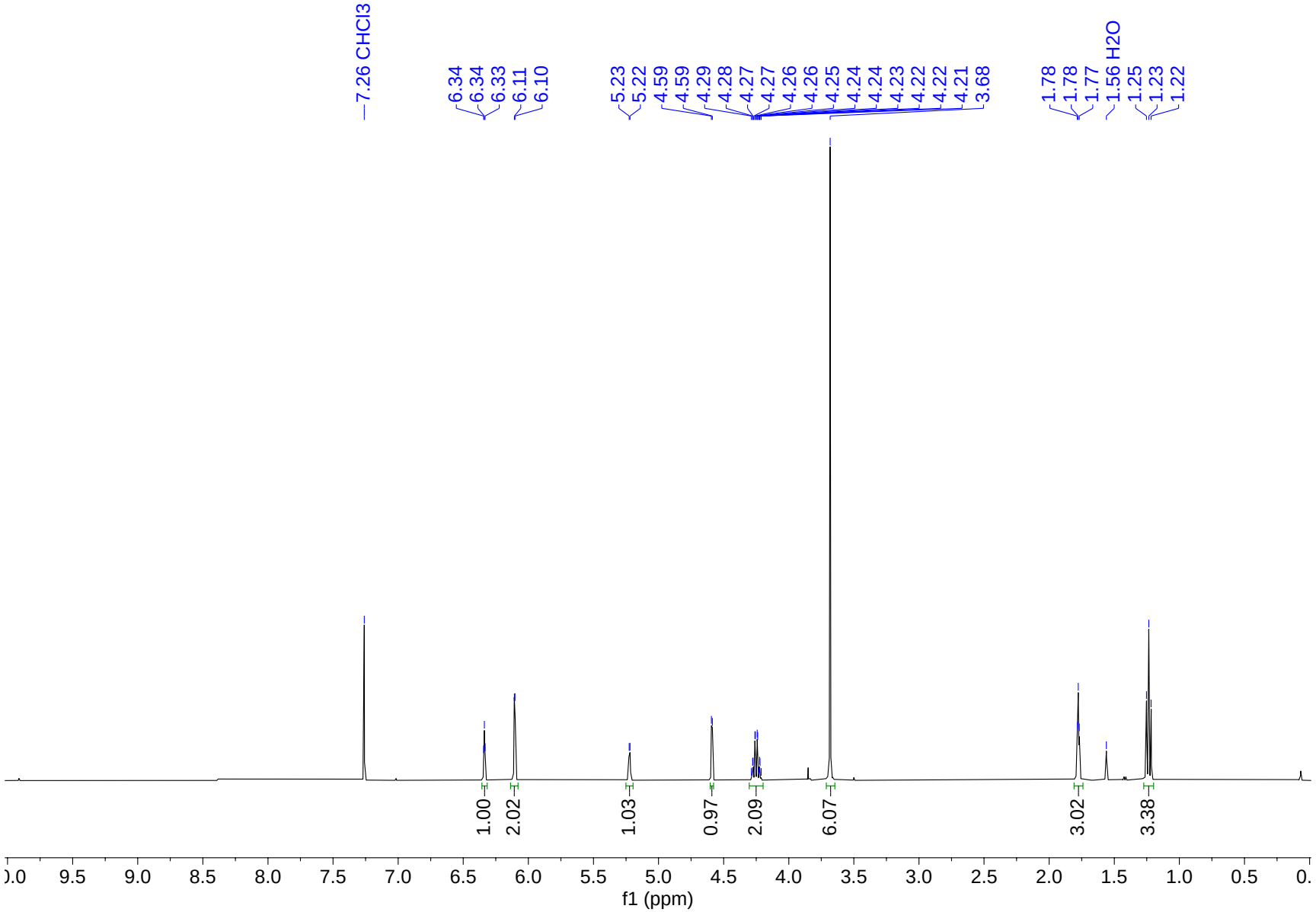


Figure S20: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2e**.

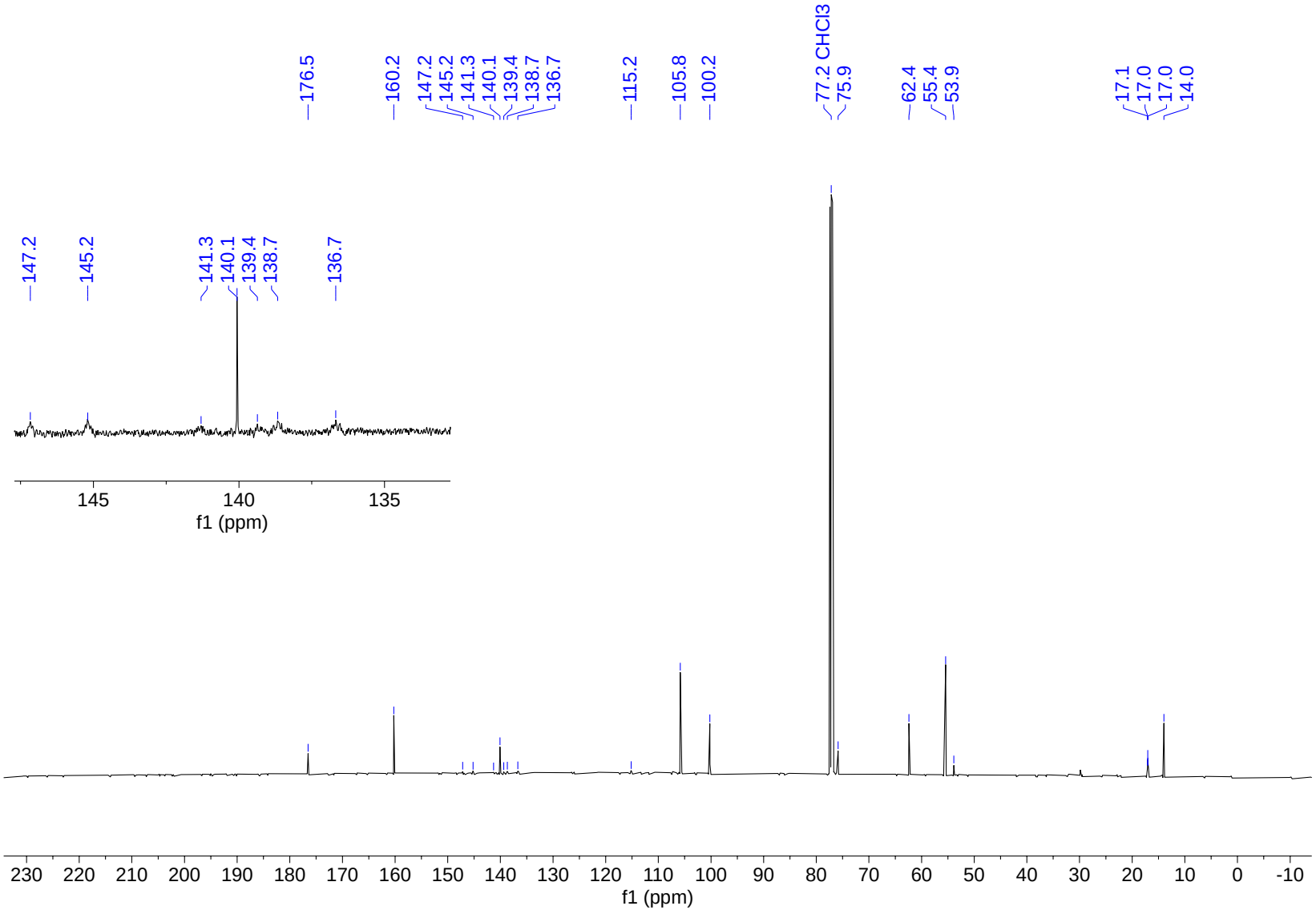


Figure S21: **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) spectrum of **2e**.

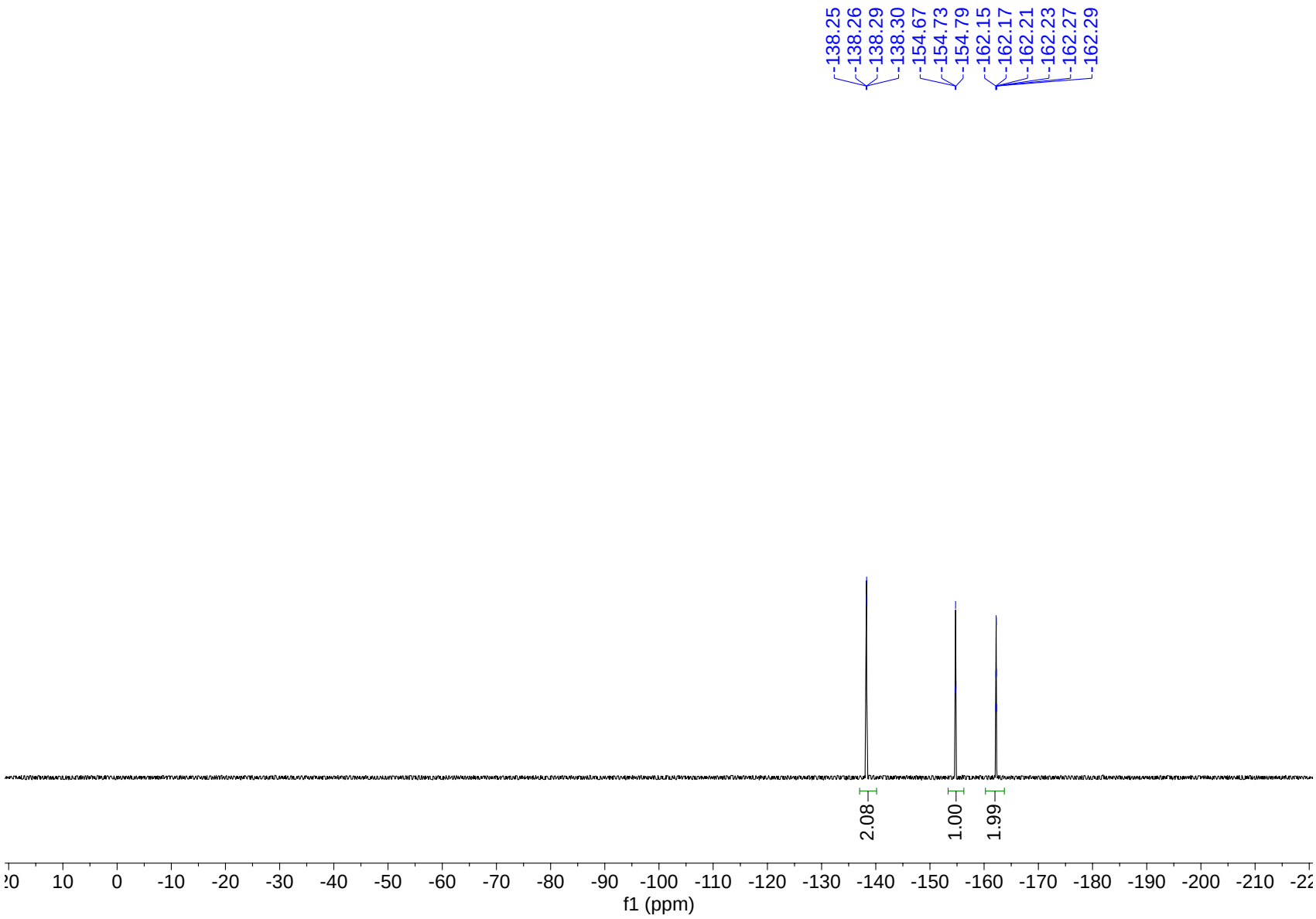


Figure S22: **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K) spectrum of **2f**.

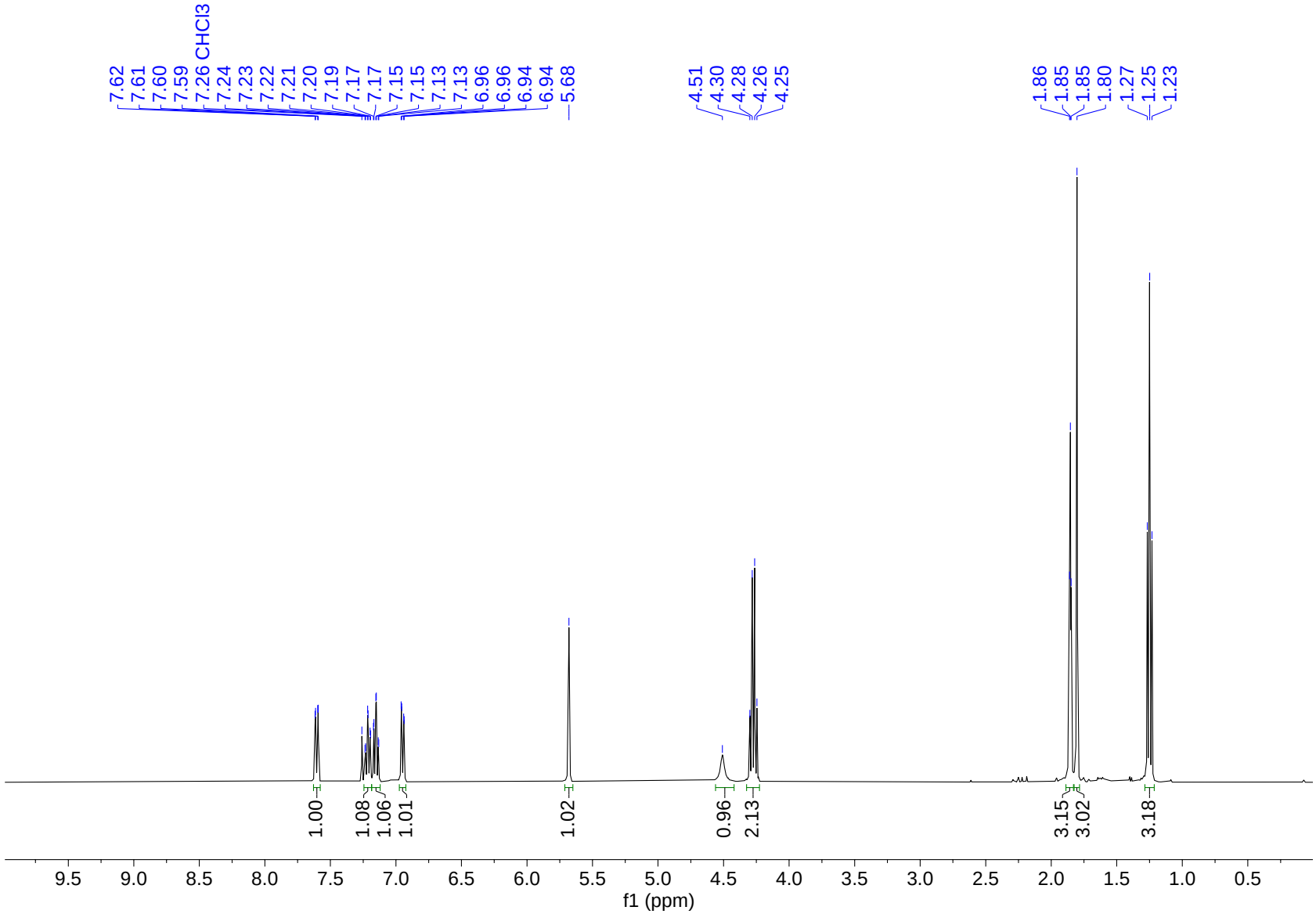


Figure S23: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2f**.

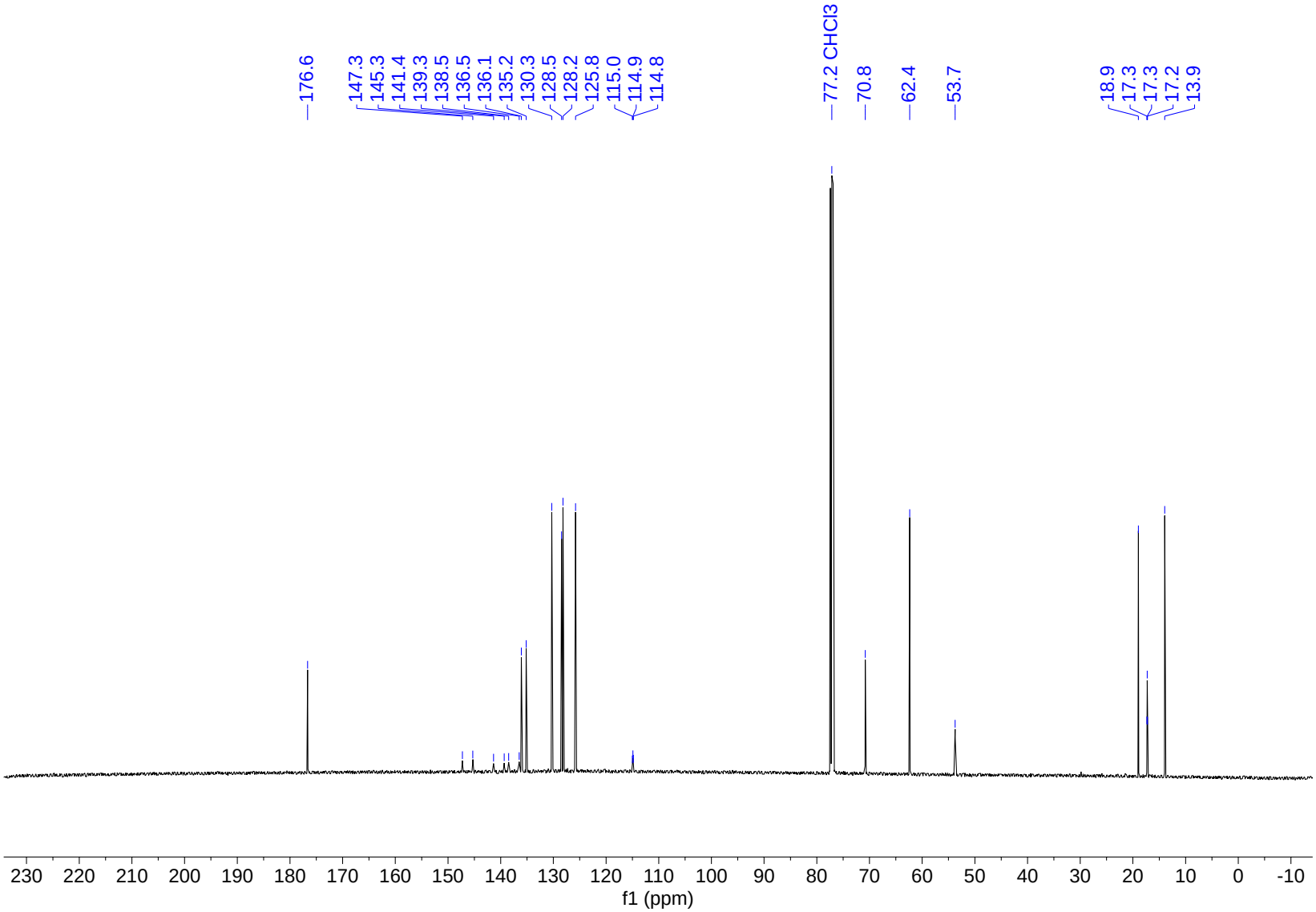


Figure S24: **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) spectrum of **2f**.

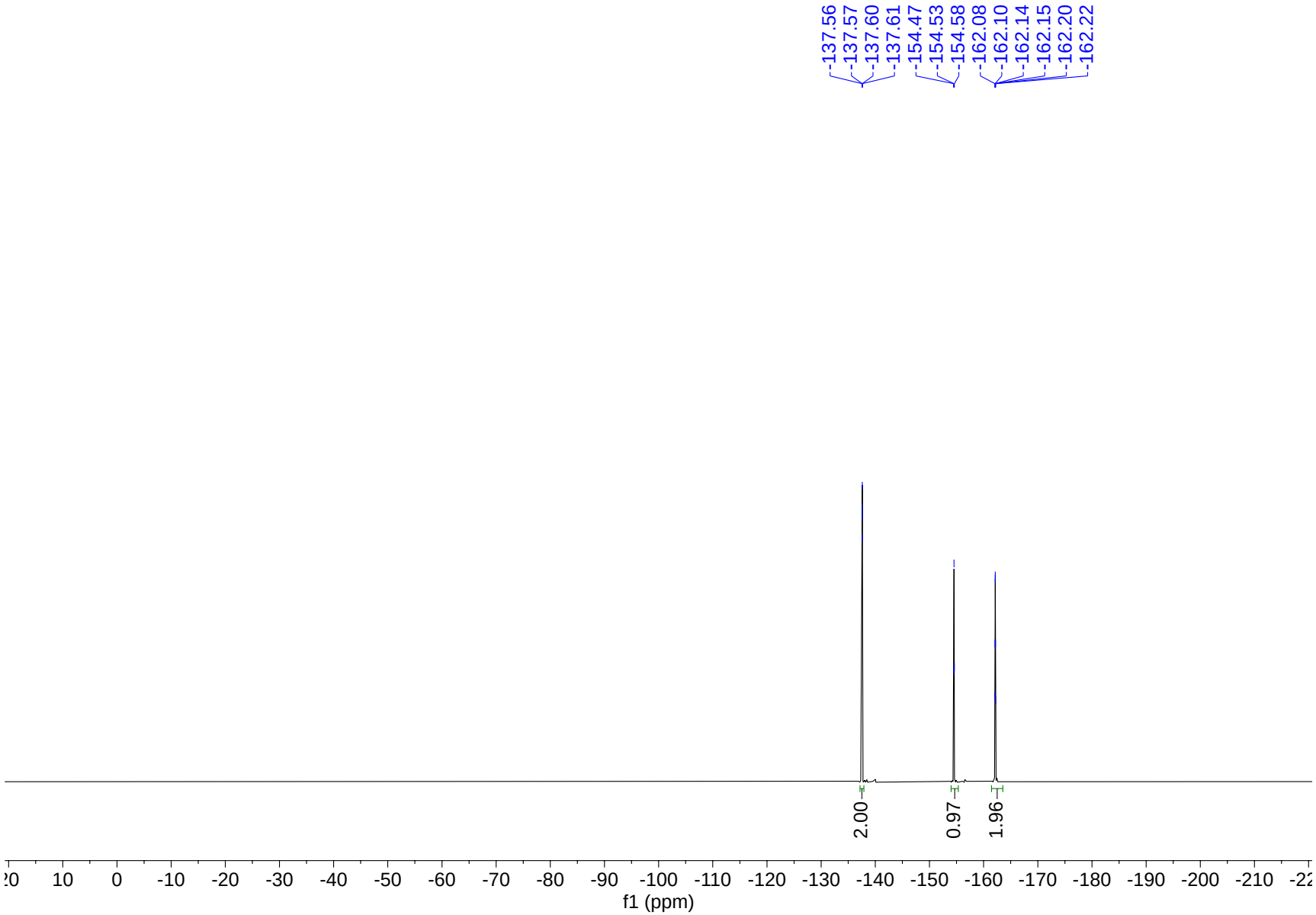


Figure S25: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **2g**.

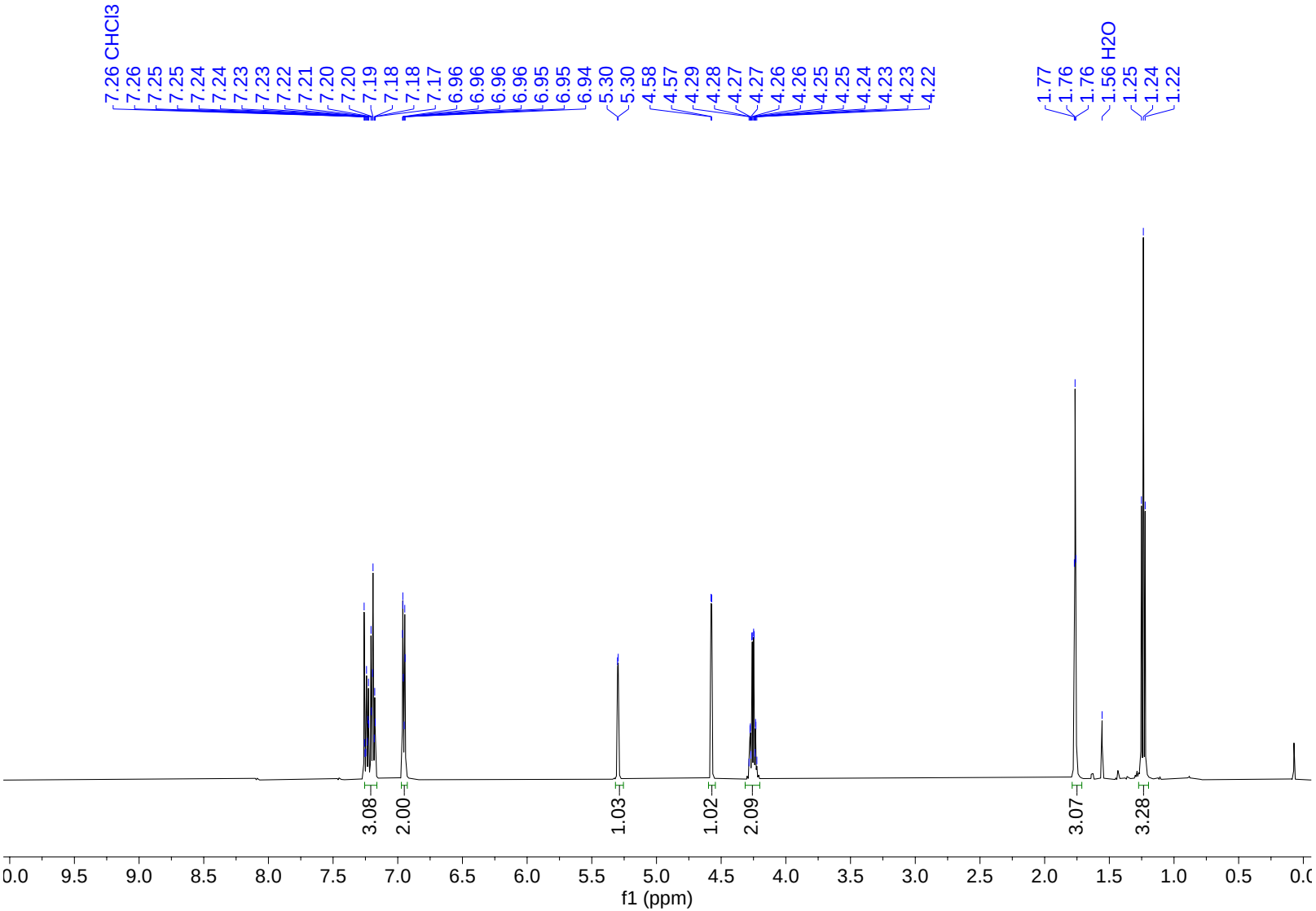


Figure S26: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2g**.

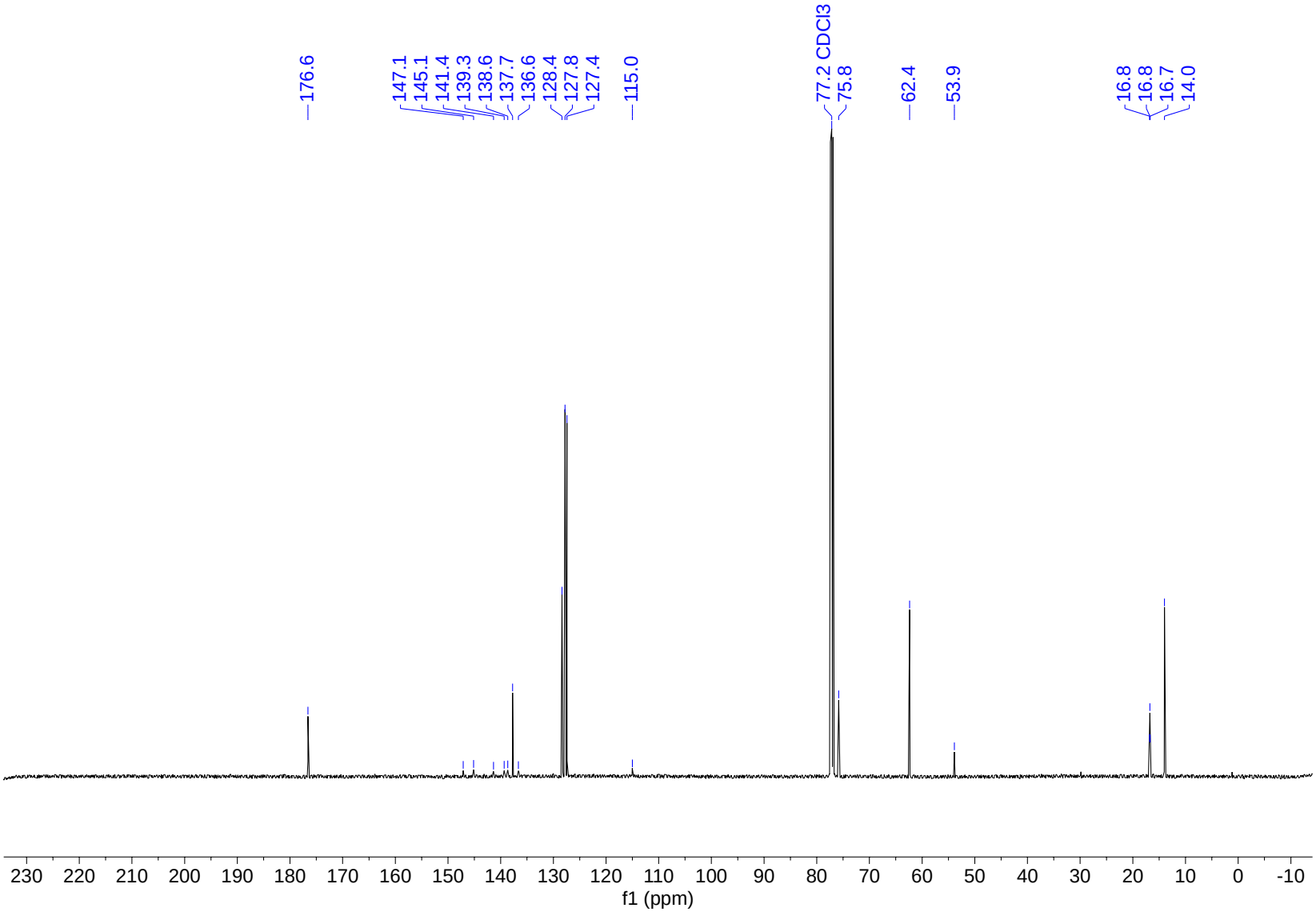


Figure S27: **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) spectrum of **2g**.

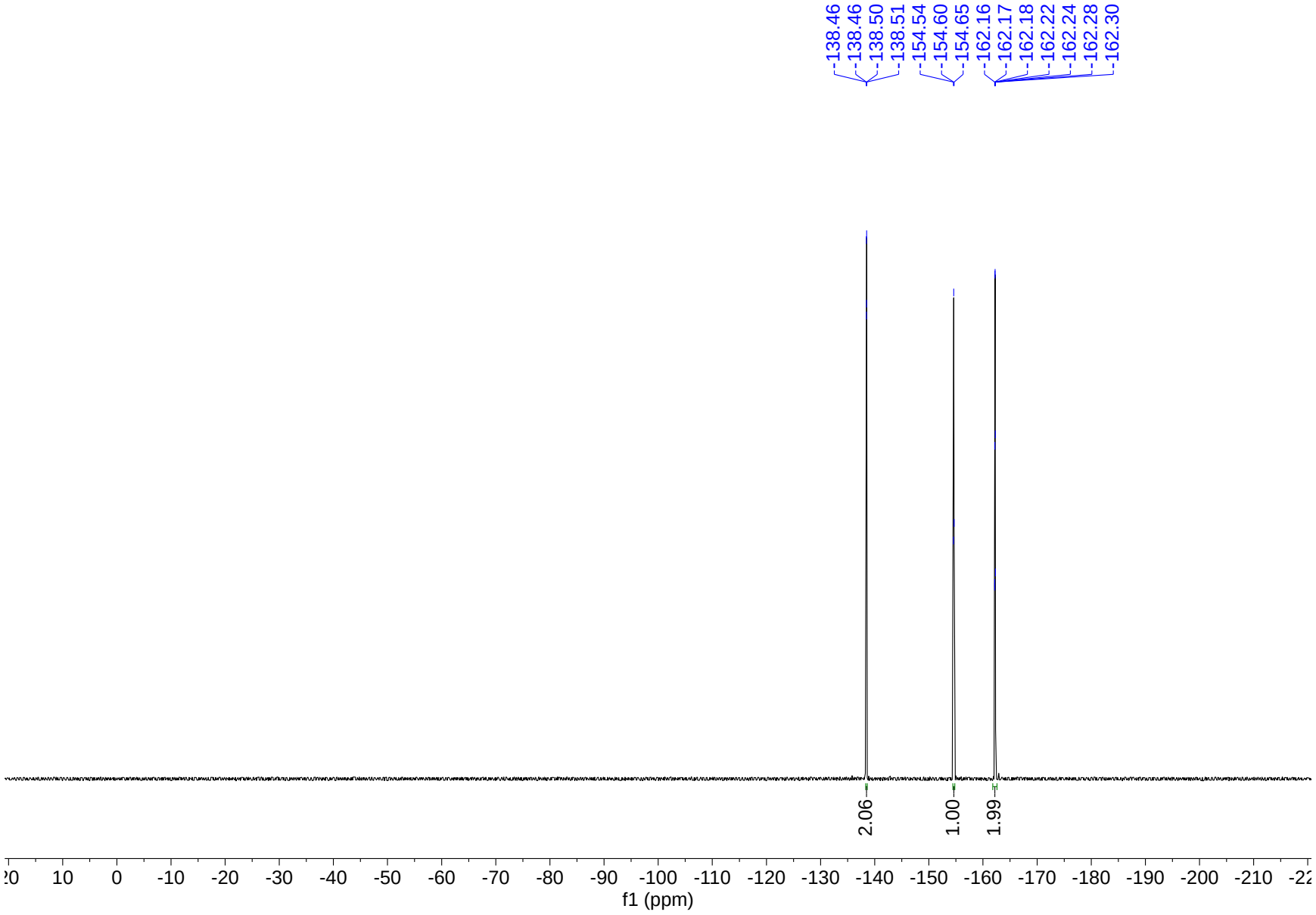


Figure S28: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **2h**.

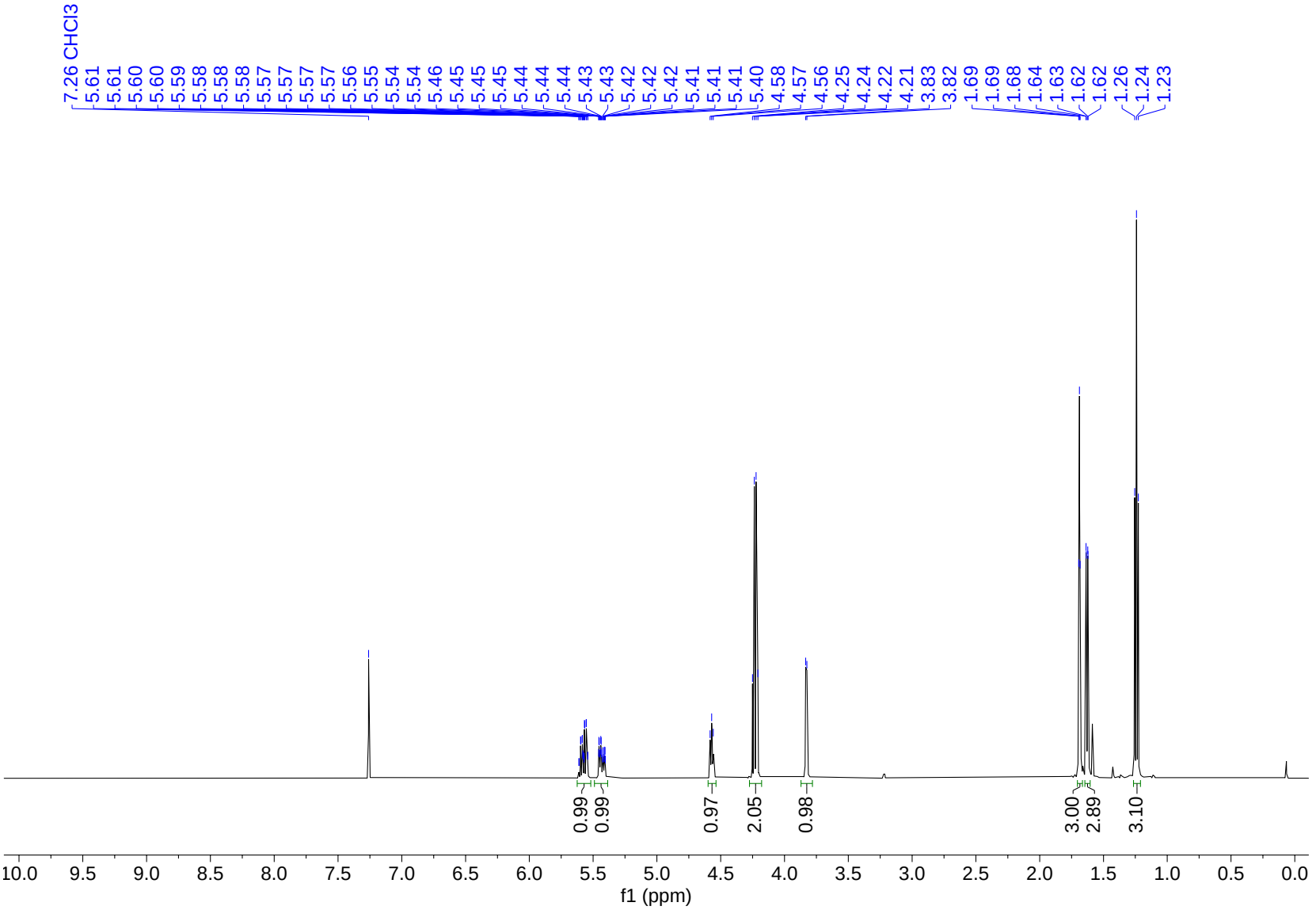


Figure S29: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2h**.

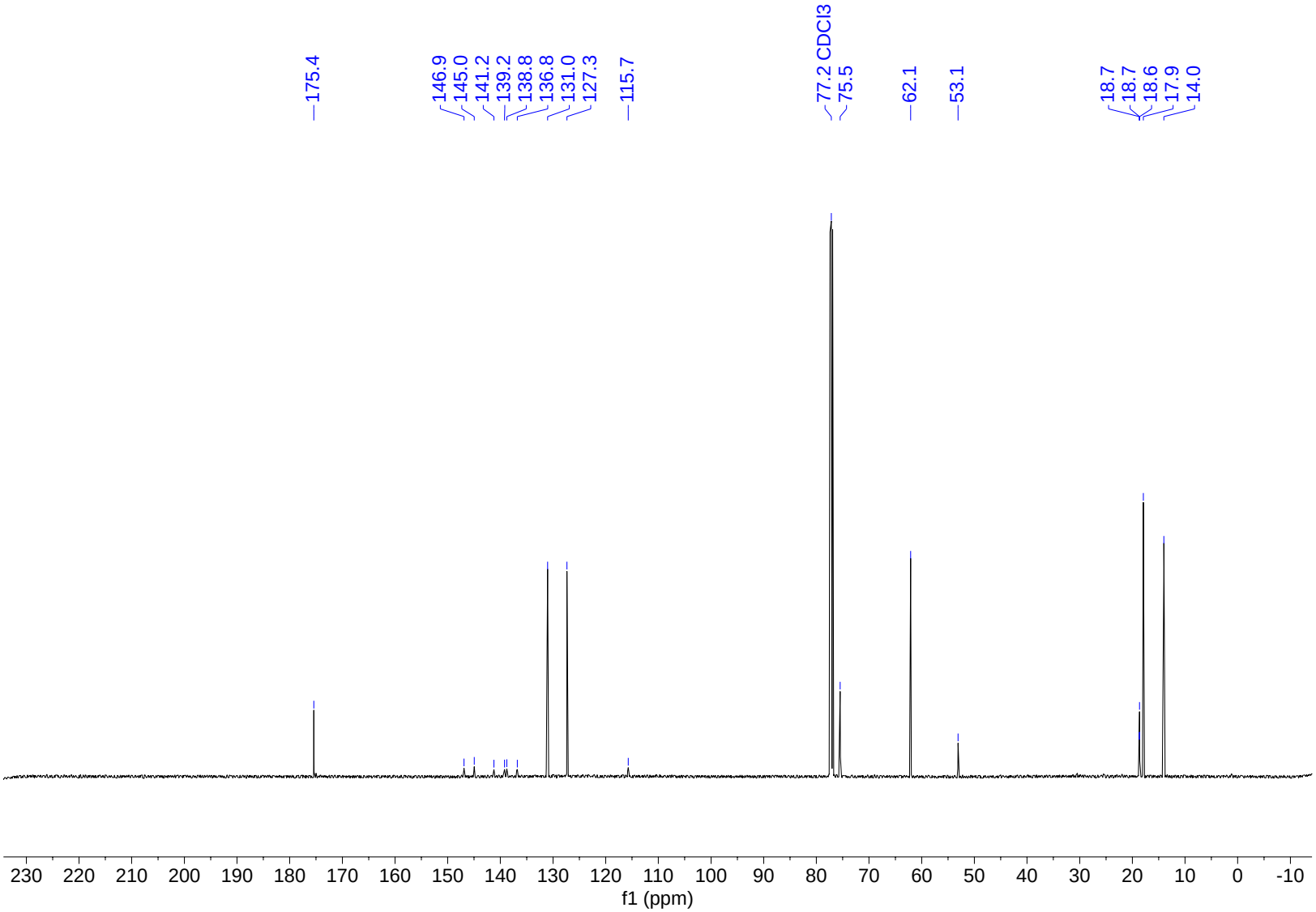


Figure S30: **^{19}F NMR** (470.6 MHz, $CDCl_3$, 298 K) spectrum of **2h**.

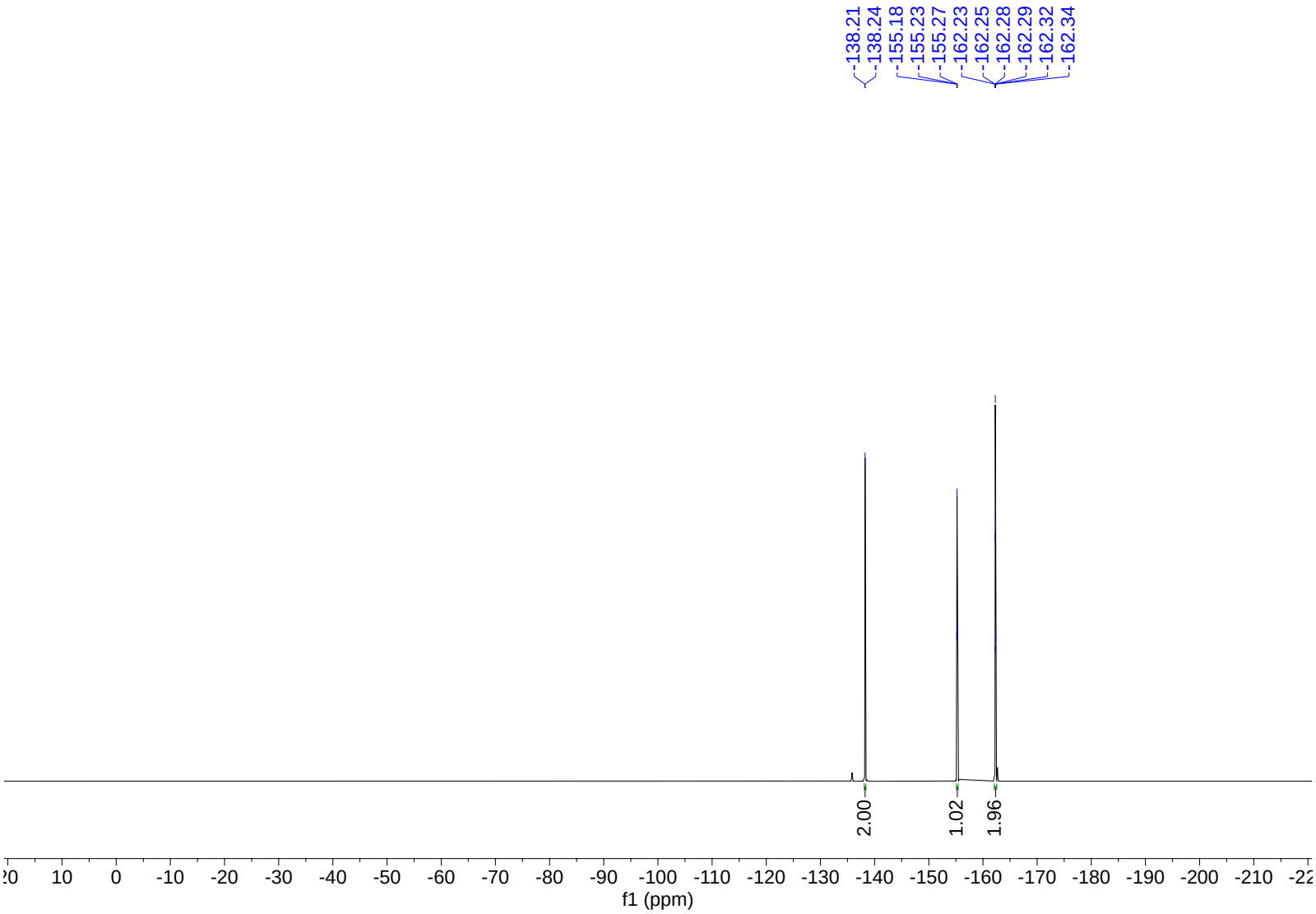


Figure S31: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **2s**.

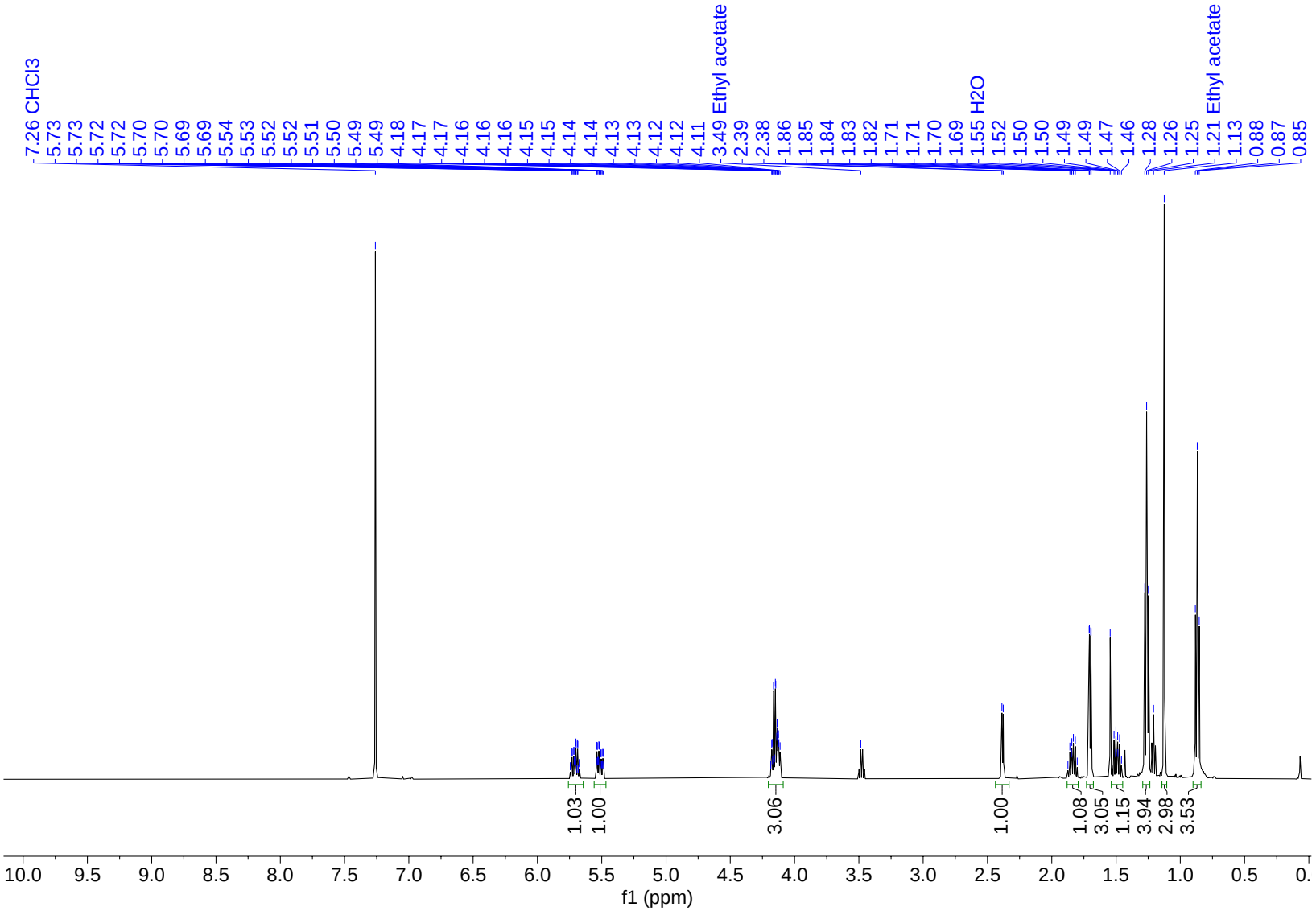


Figure S32: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2s**.

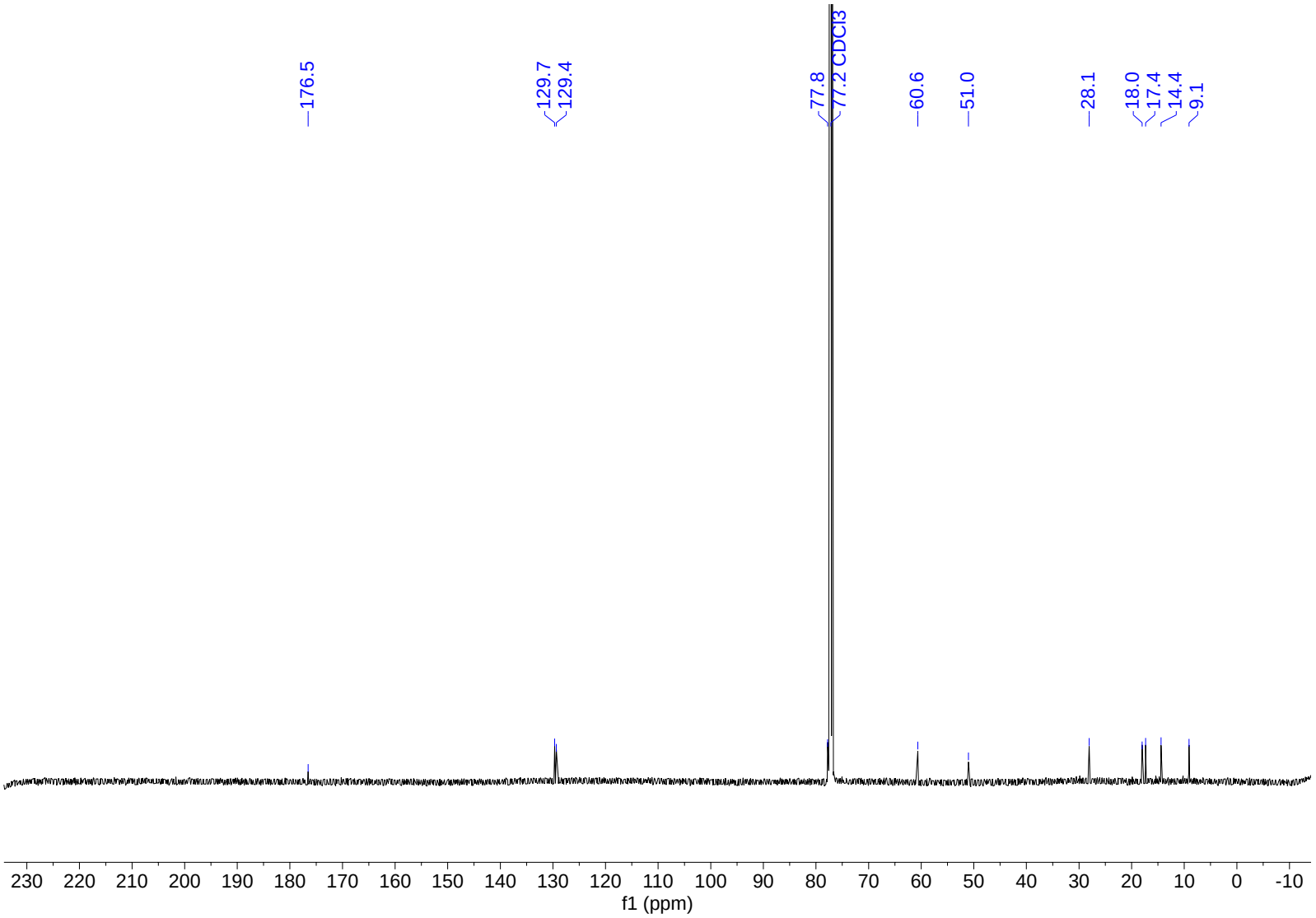


Figure S33: **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K) spectrum of **2i**.

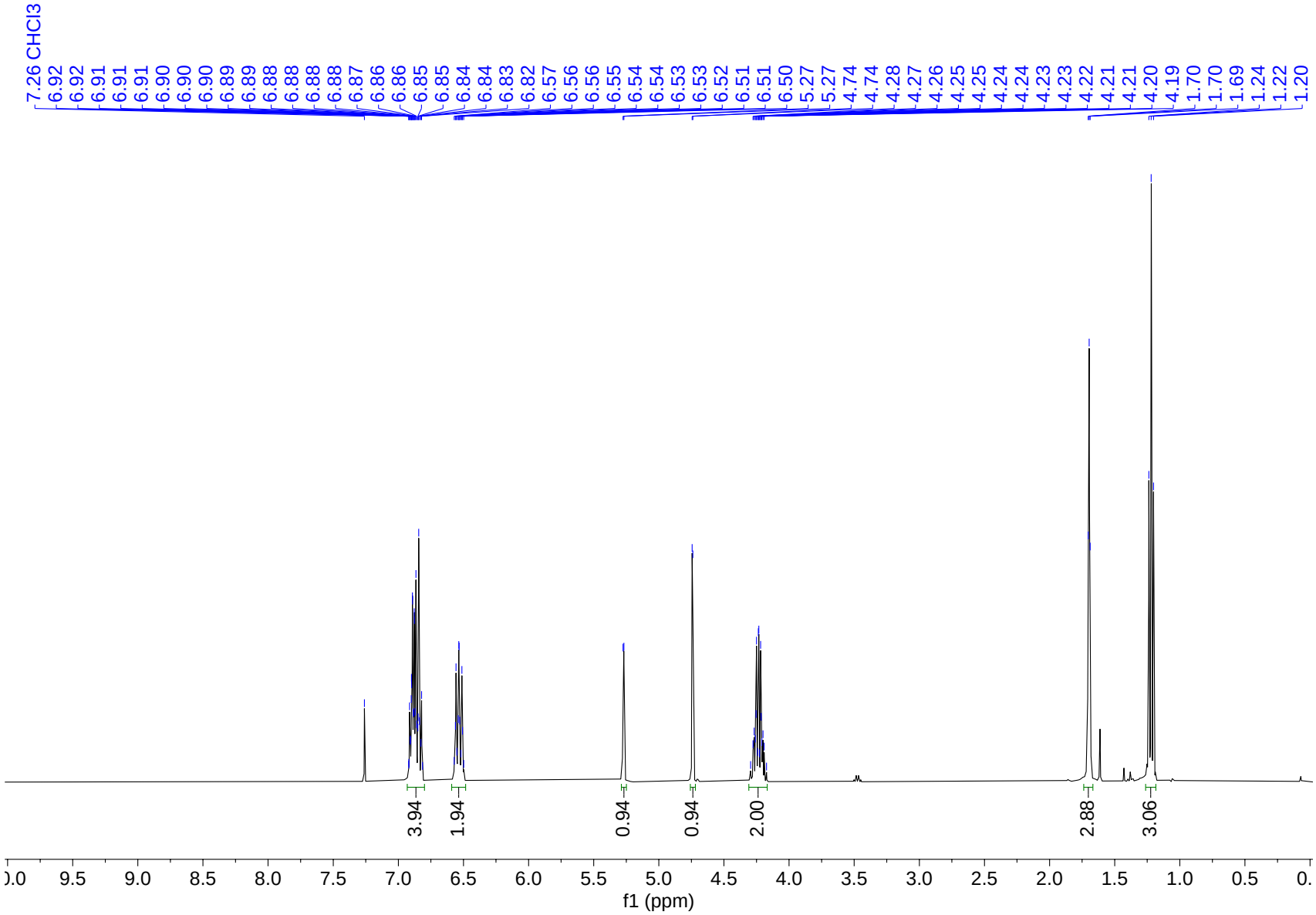


Figure S34: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2i**.

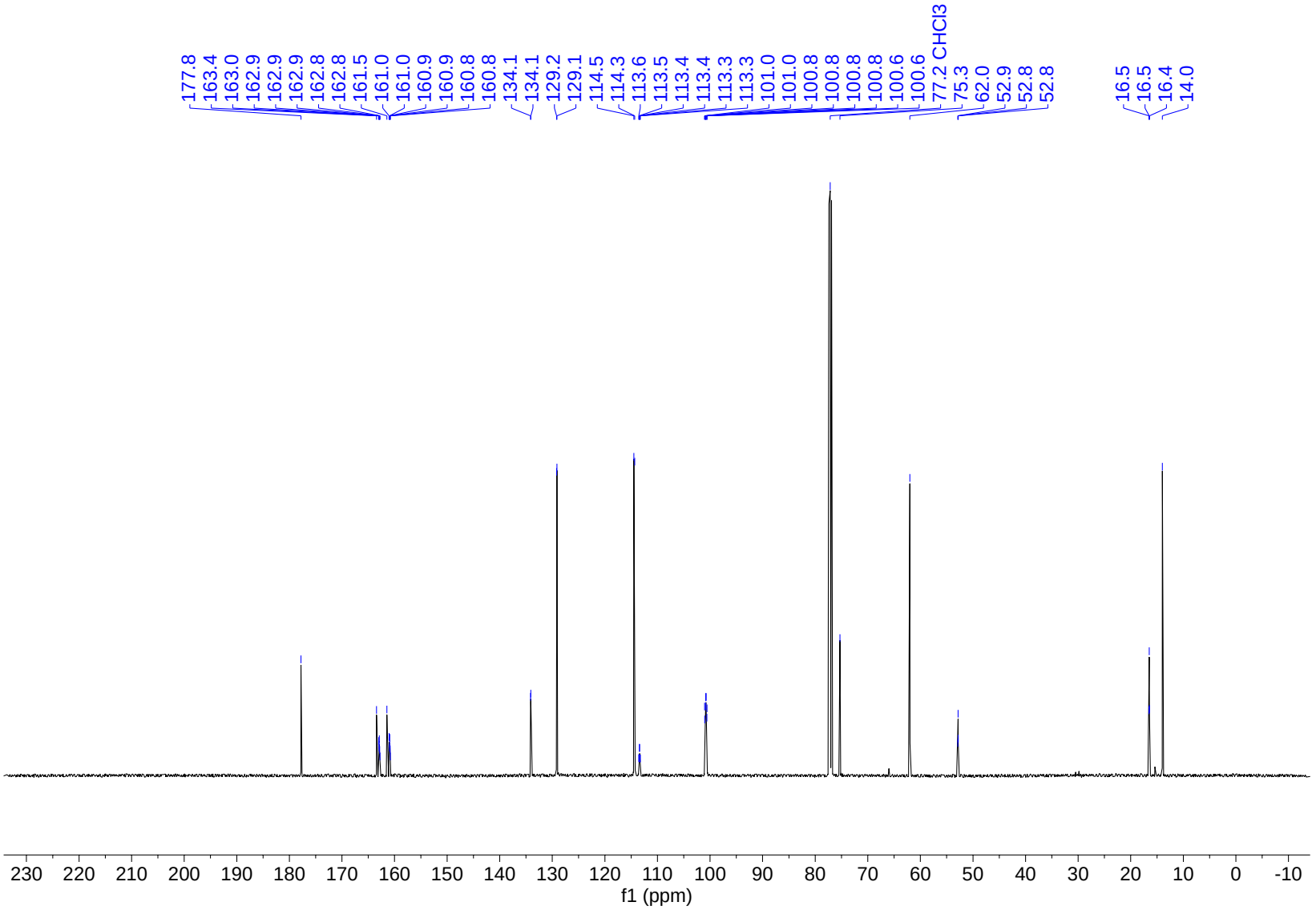


Figure S35: **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) spectrum of **2i**.

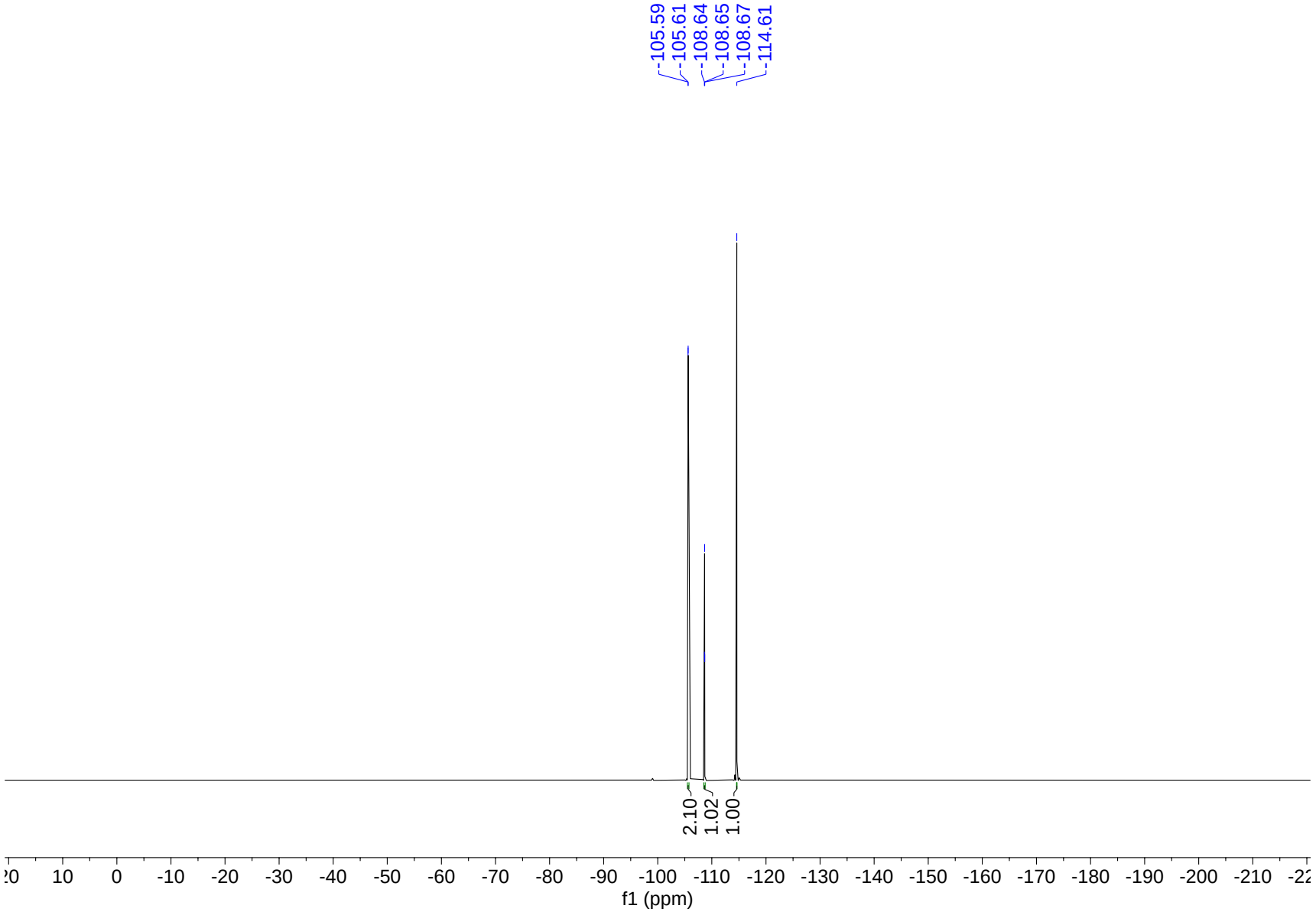


Figure S36: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **2j**.

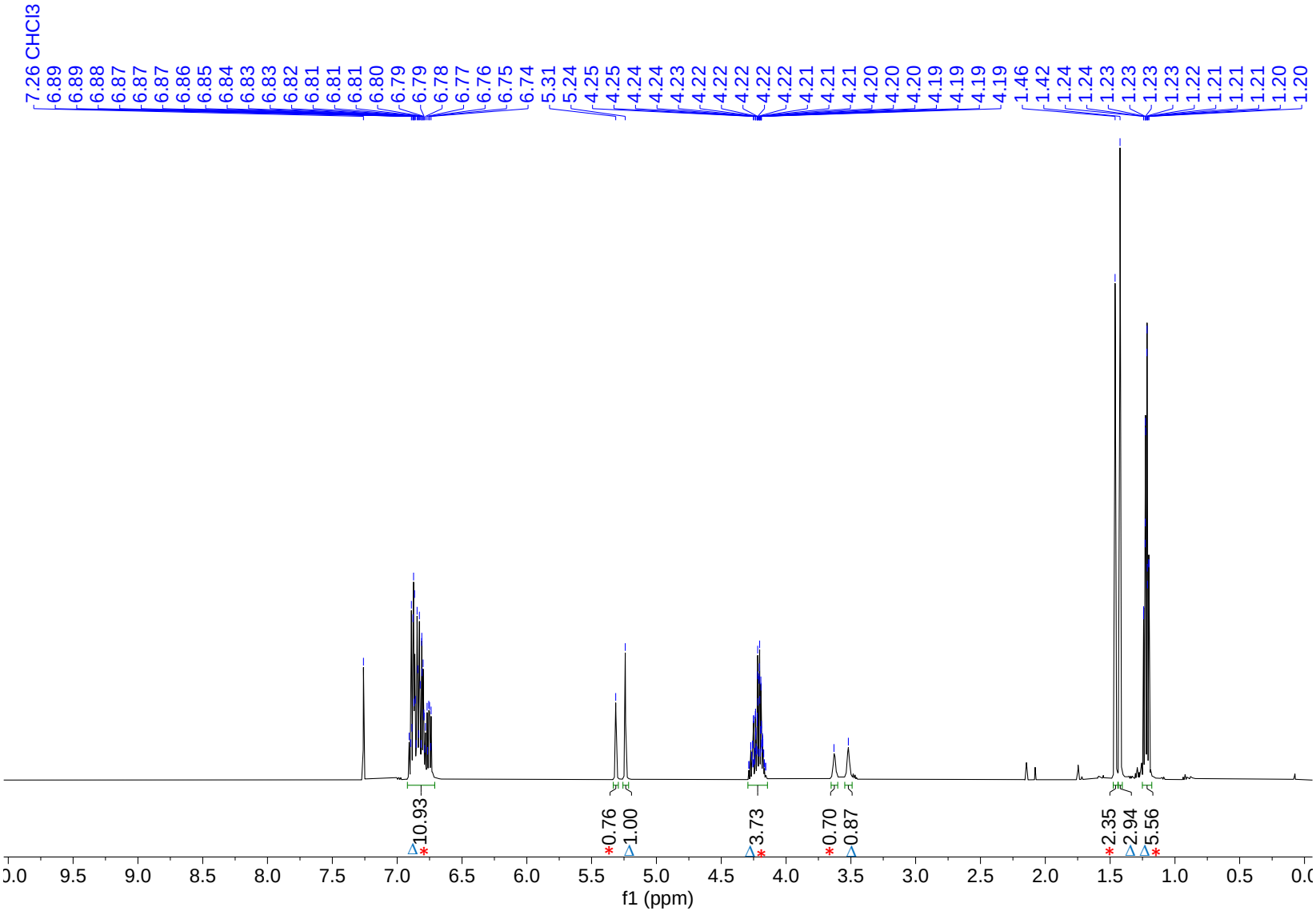


Figure S37: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2j**.

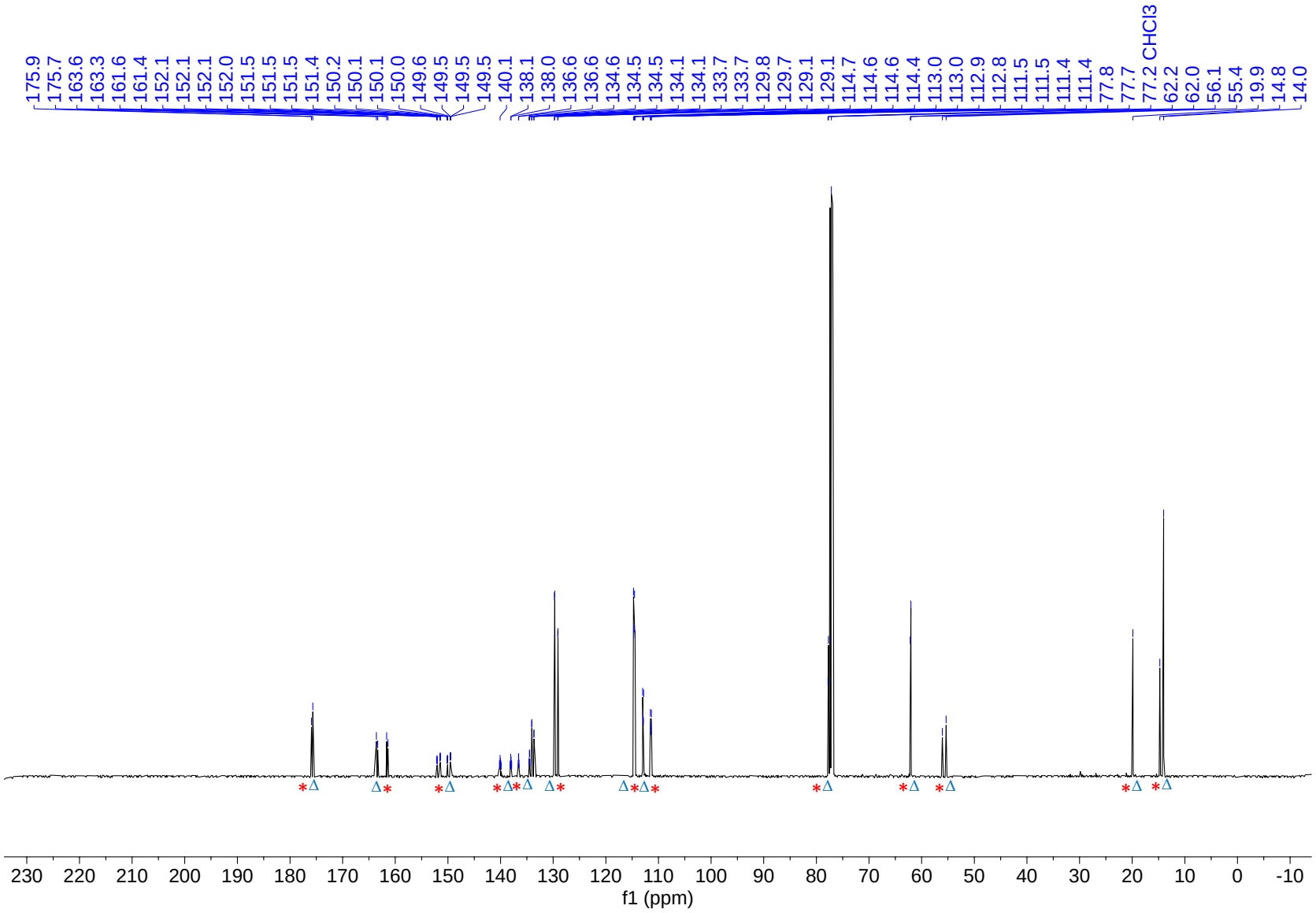


Figure S38: **^{19}F NMR** (470.6 MHz, $CDCl_3$, 298 K) spectrum of **2j**.

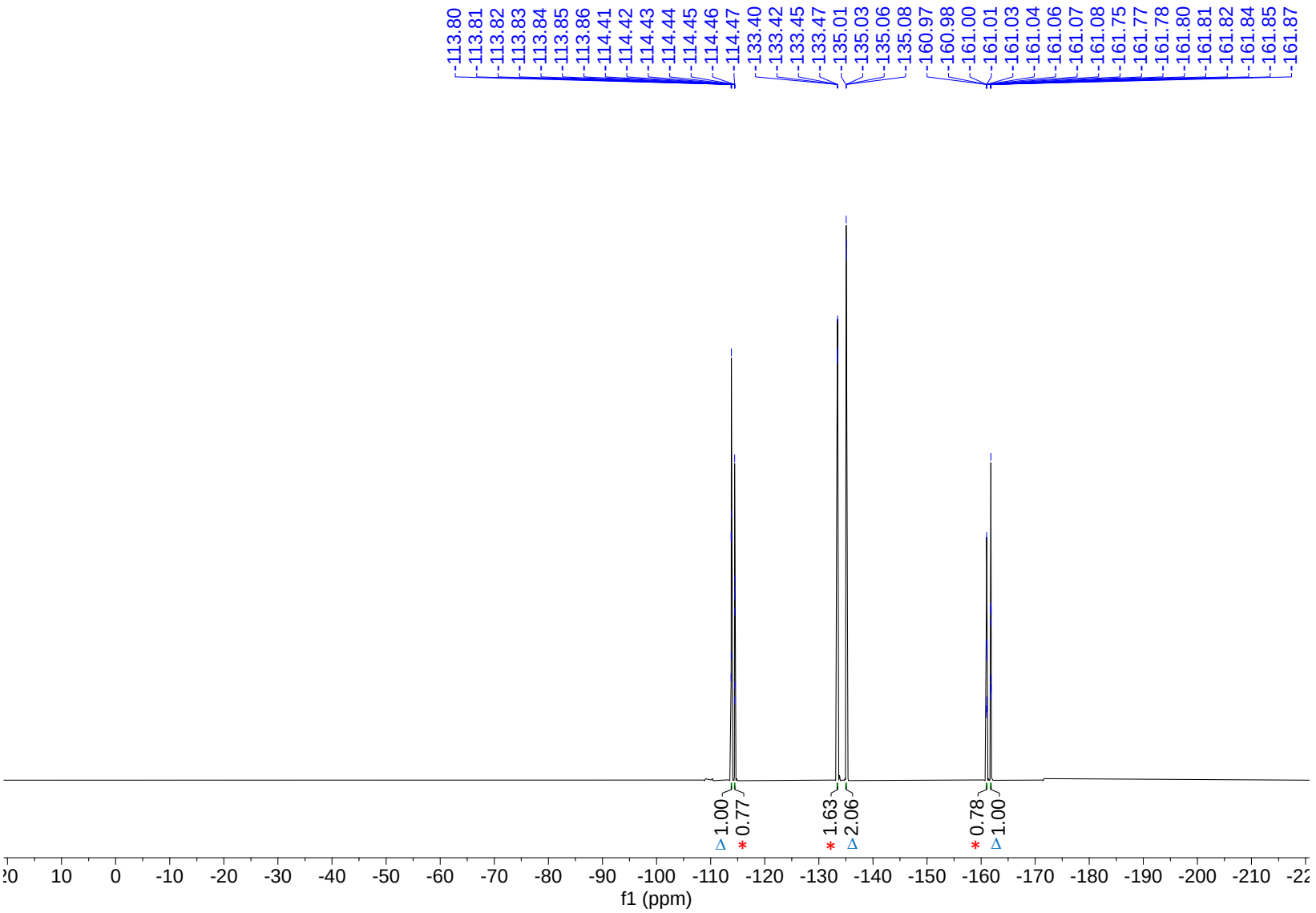


Figure S39: **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K) spectrum of **2k**.

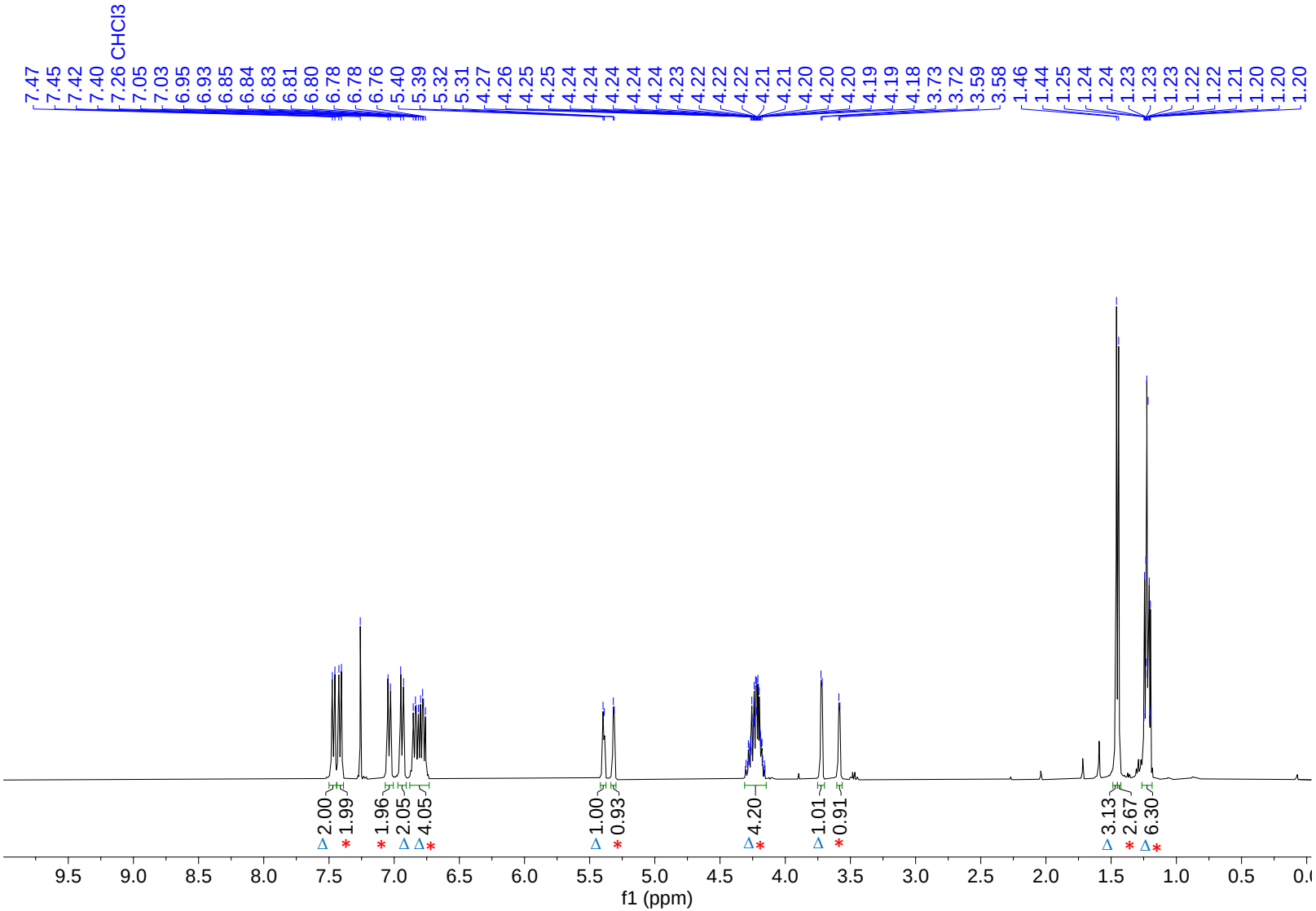


Figure S40: **^{13}C NMR** ($CDCl_3$, 298 K) spectrum of **2k**.

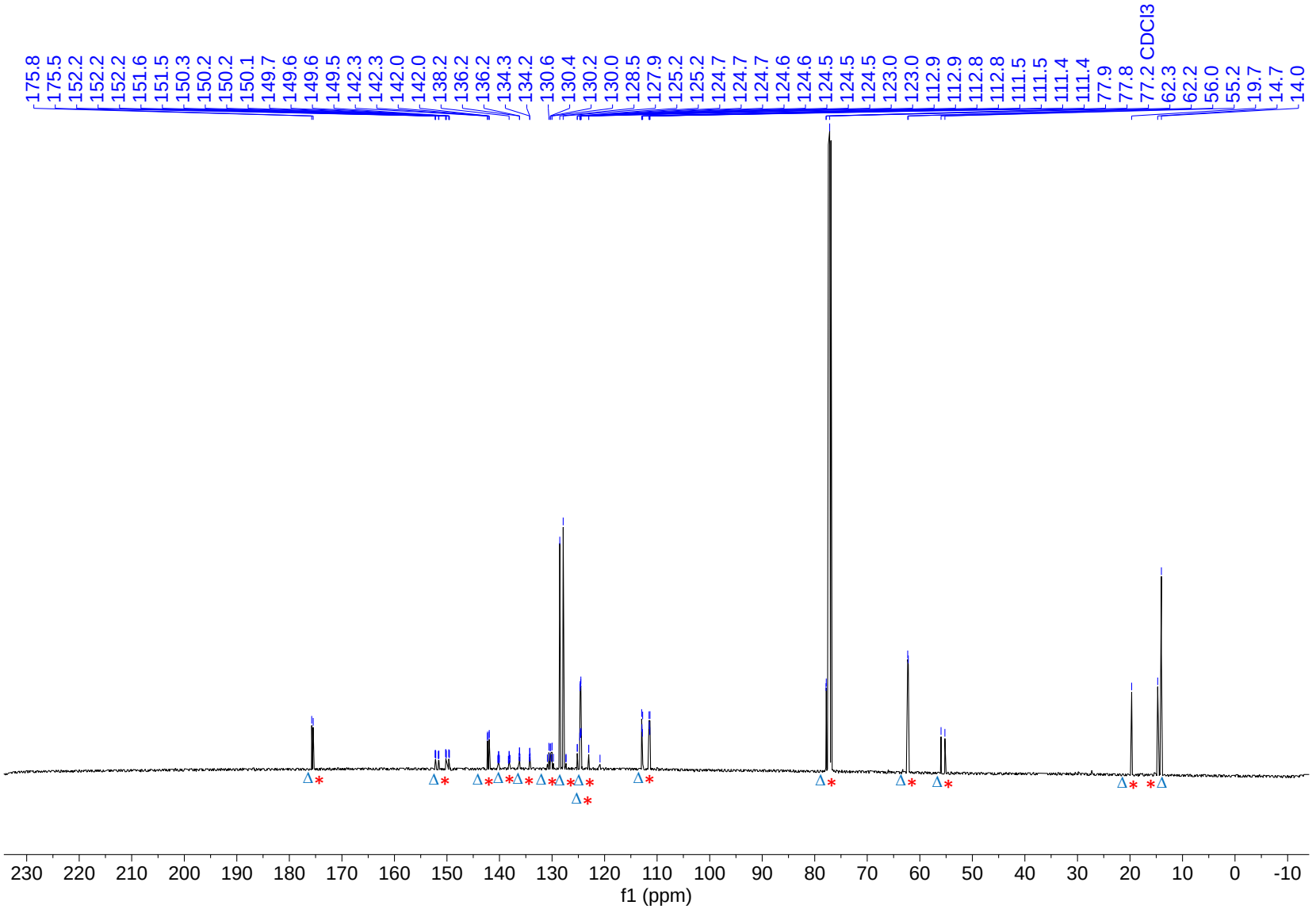


Figure S41: **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) spectrum of **2k**.

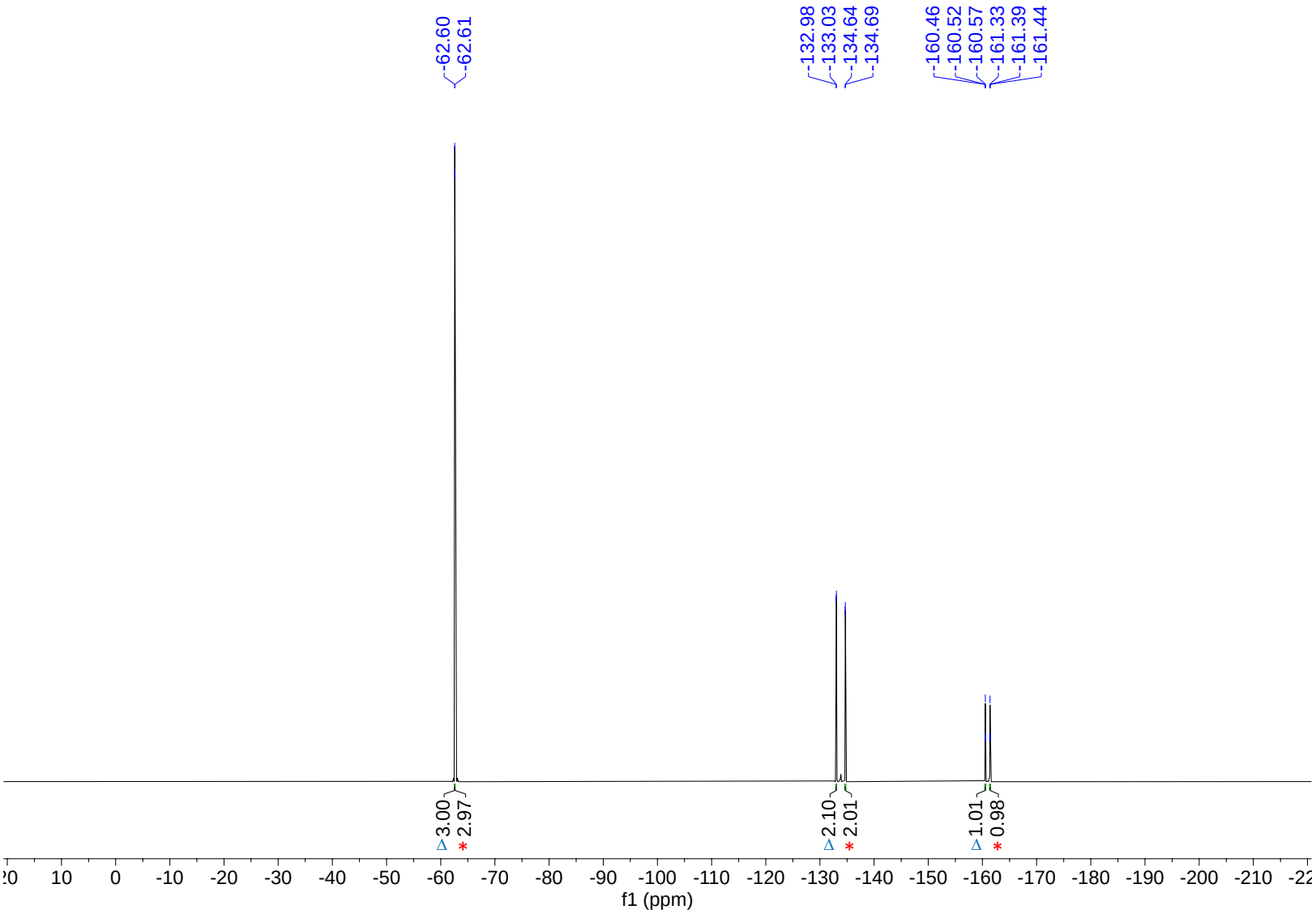


Figure S42: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **2l**.

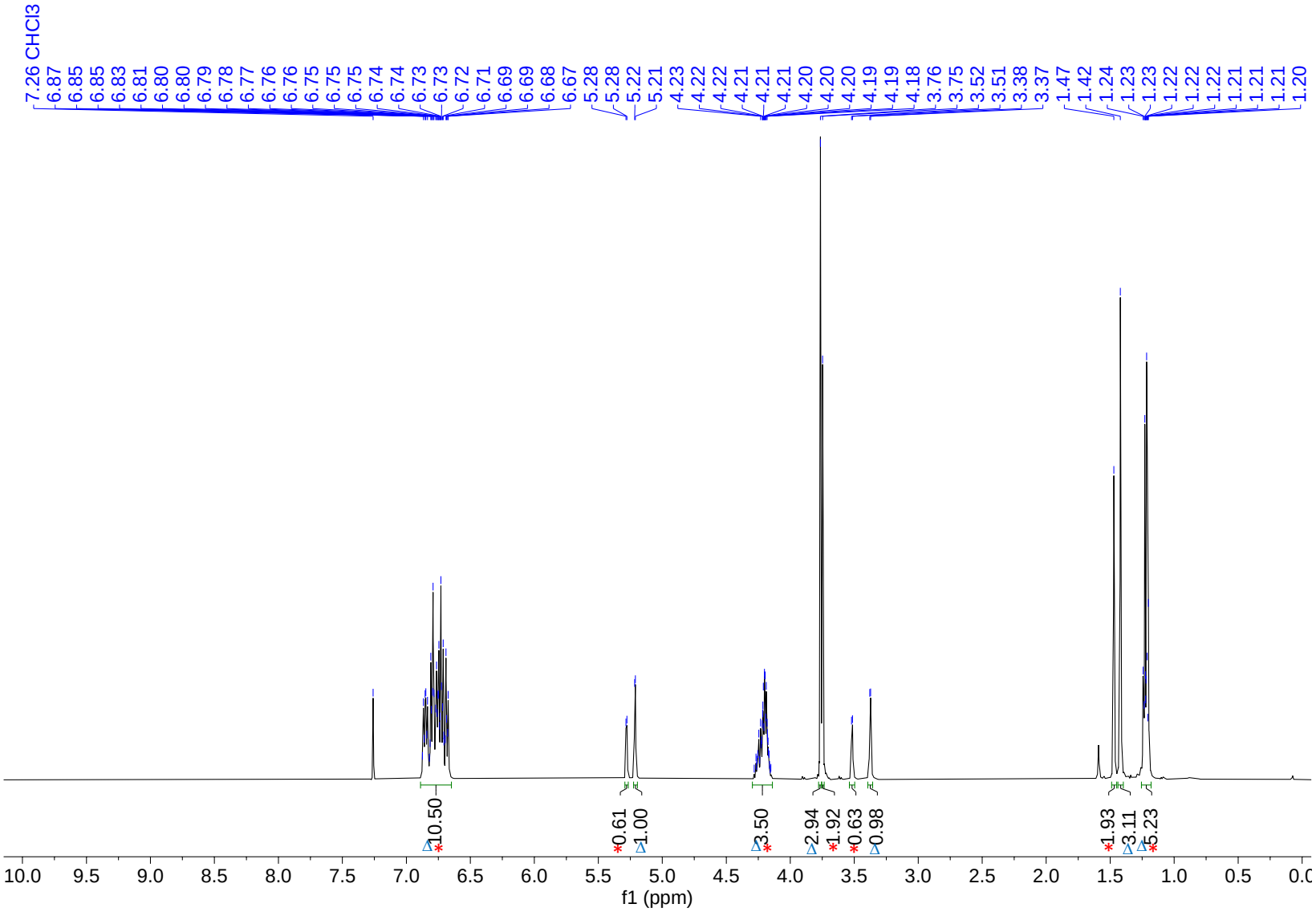


Figure S43: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2l**.

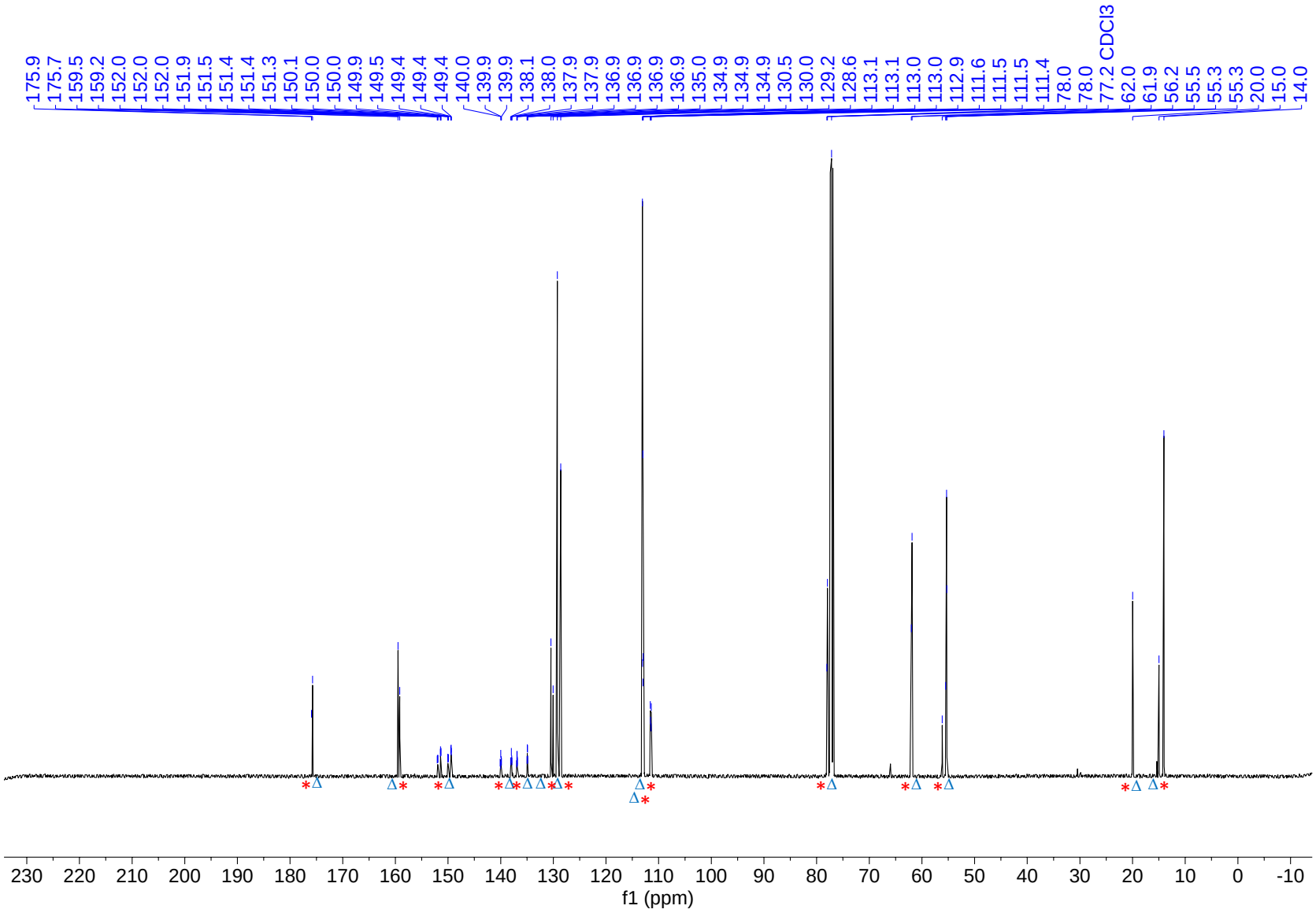


Figure S44: **^{19}F NMR** (470.6 MHz, $CDCl_3$, 298 K) spectrum of **2l**.

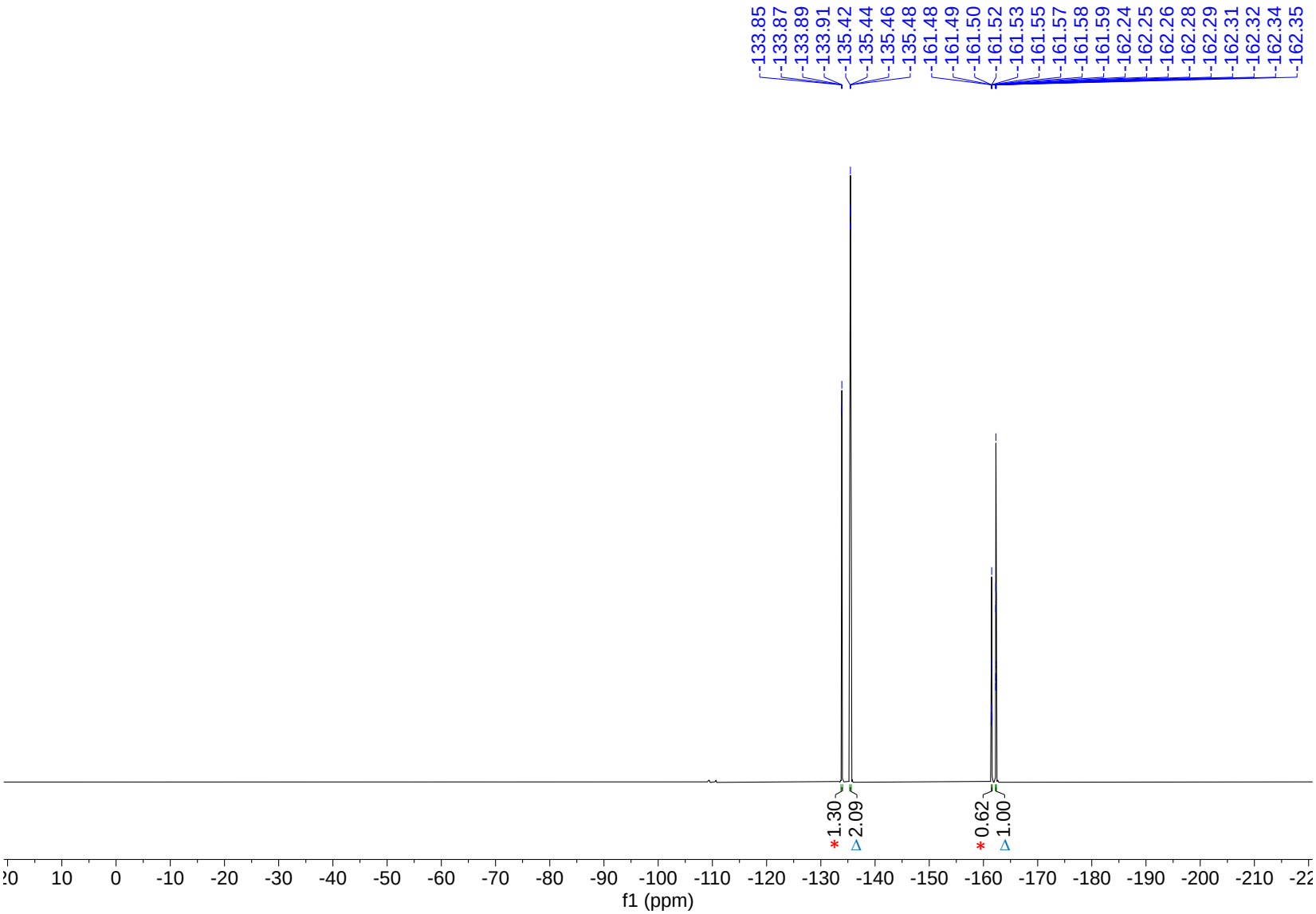


Figure S45: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **2m**.

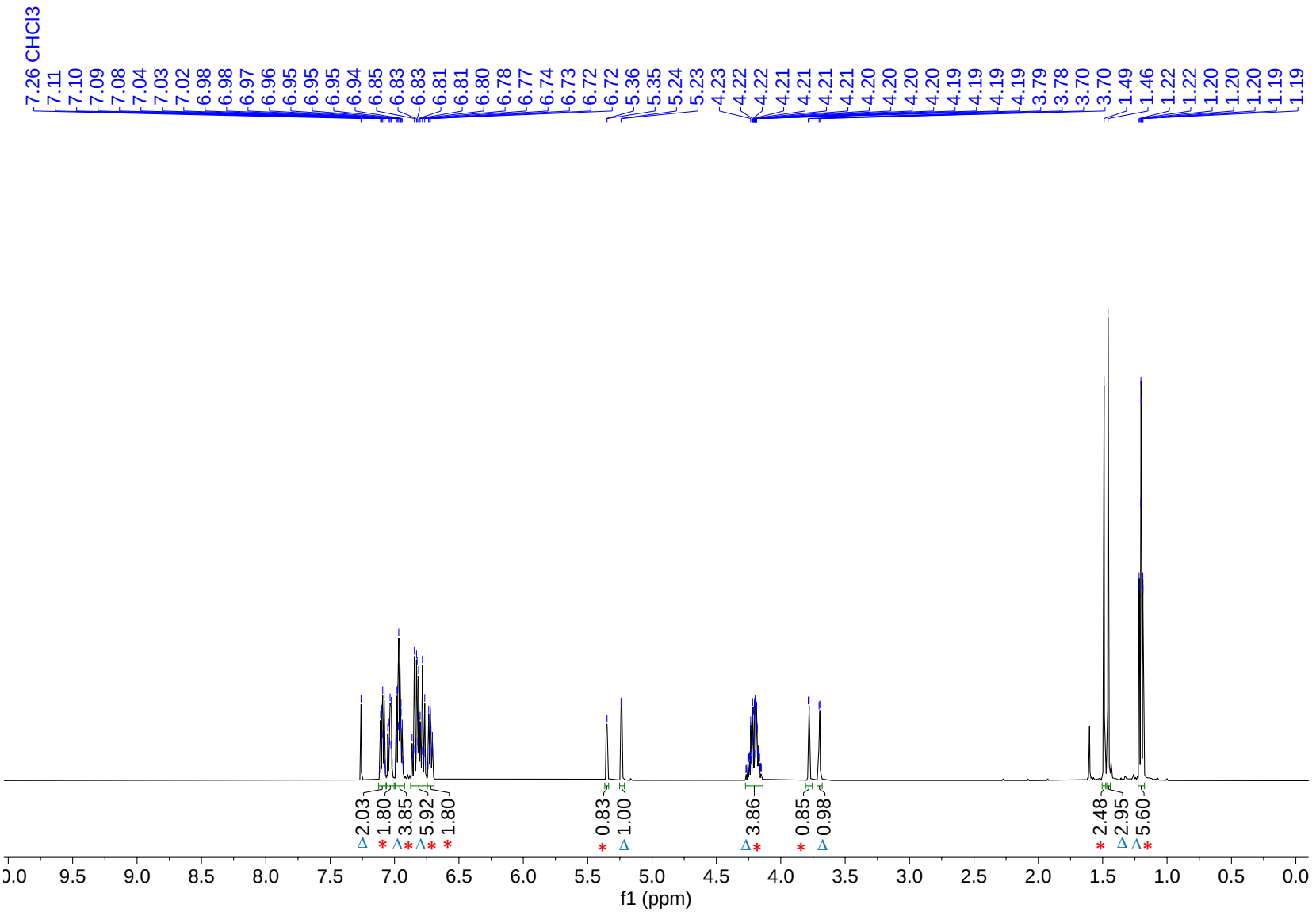


Figure S46: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2m**.

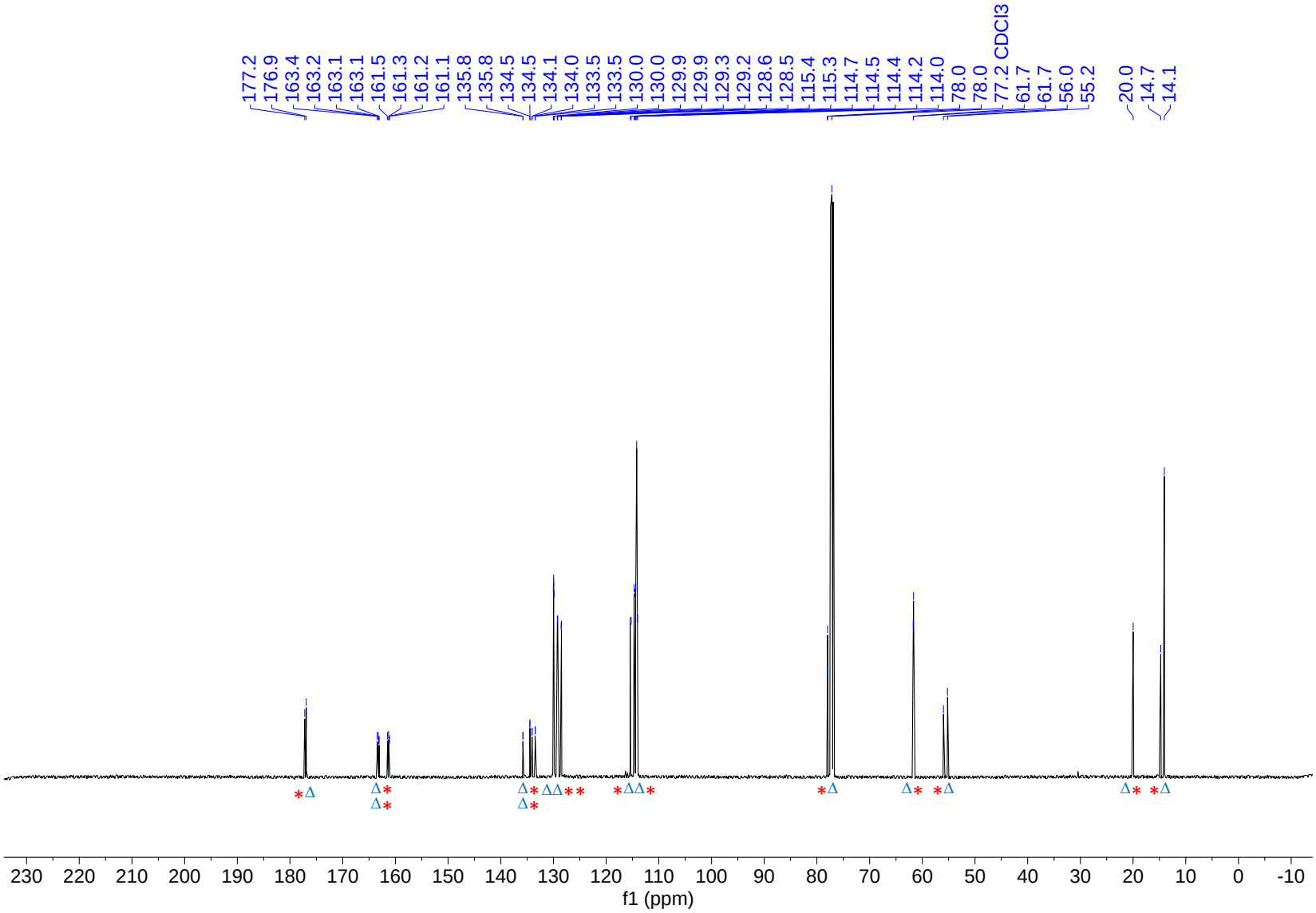


Figure S47: **^{19}F NMR** (470.6 MHz, $CDCl_3$, 298 K) spectrum of **2m**.

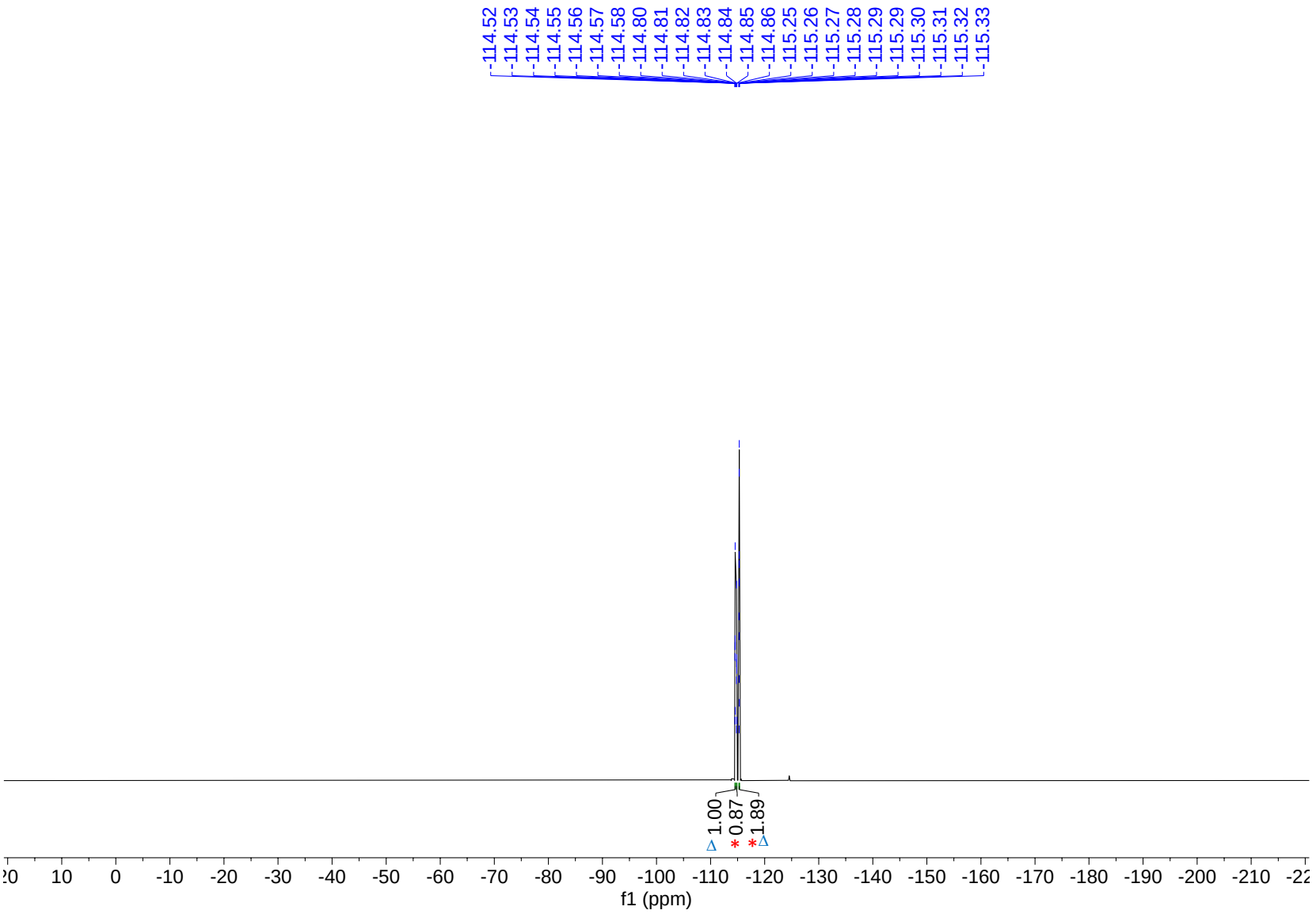


Figure S48: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **2n**.

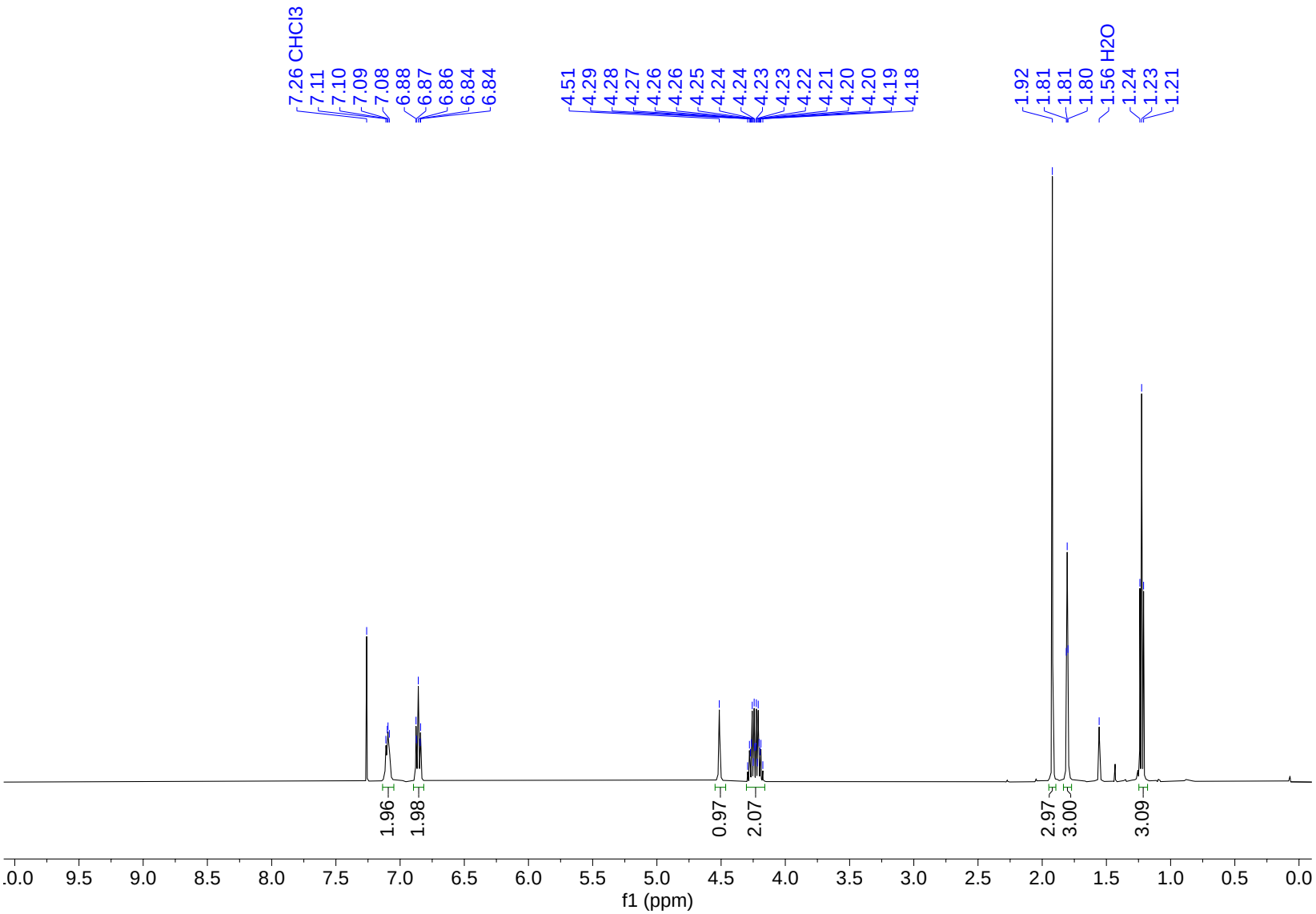


Figure S49: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2n**.

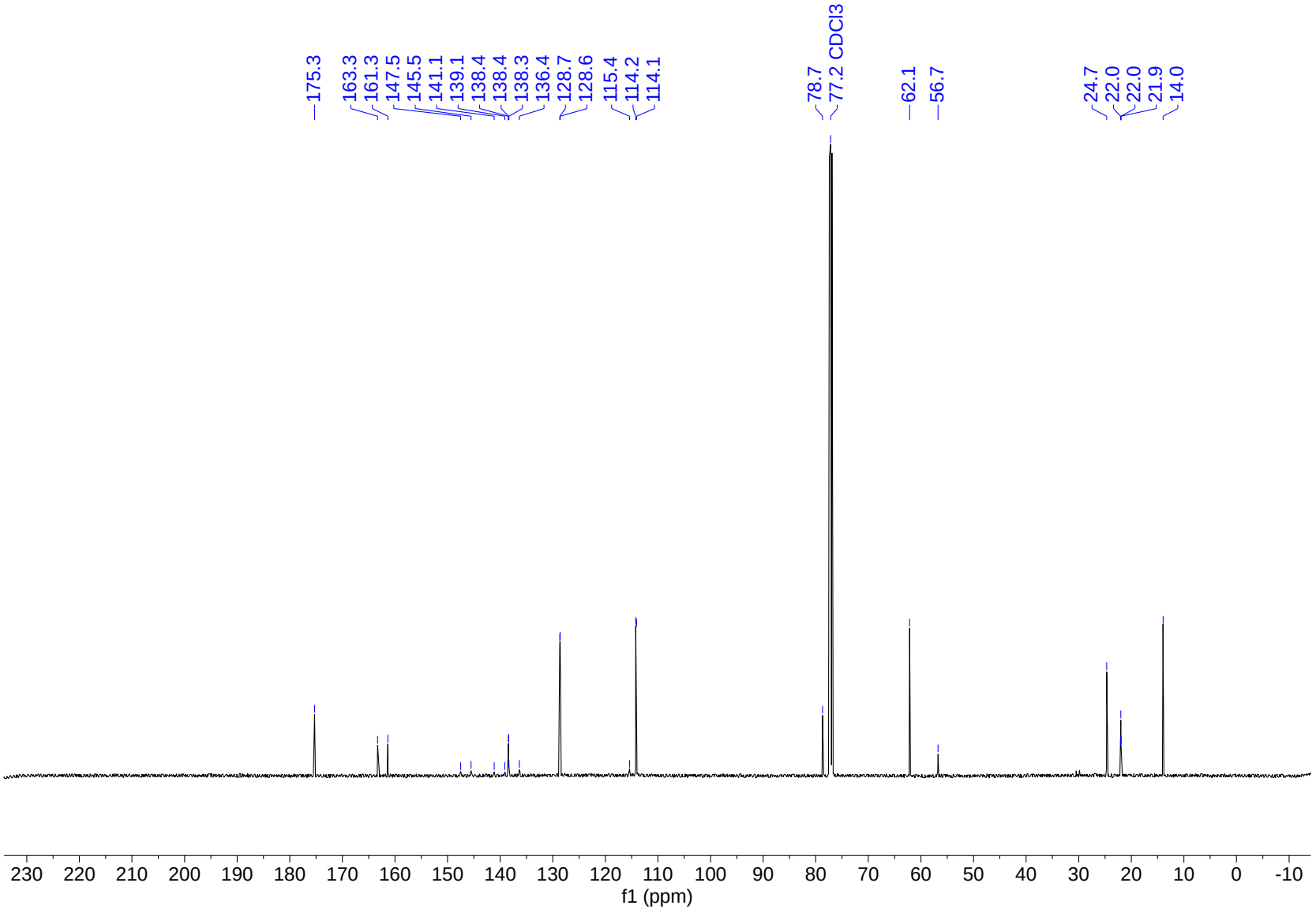


Figure S50: **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) spectrum of **2n**.

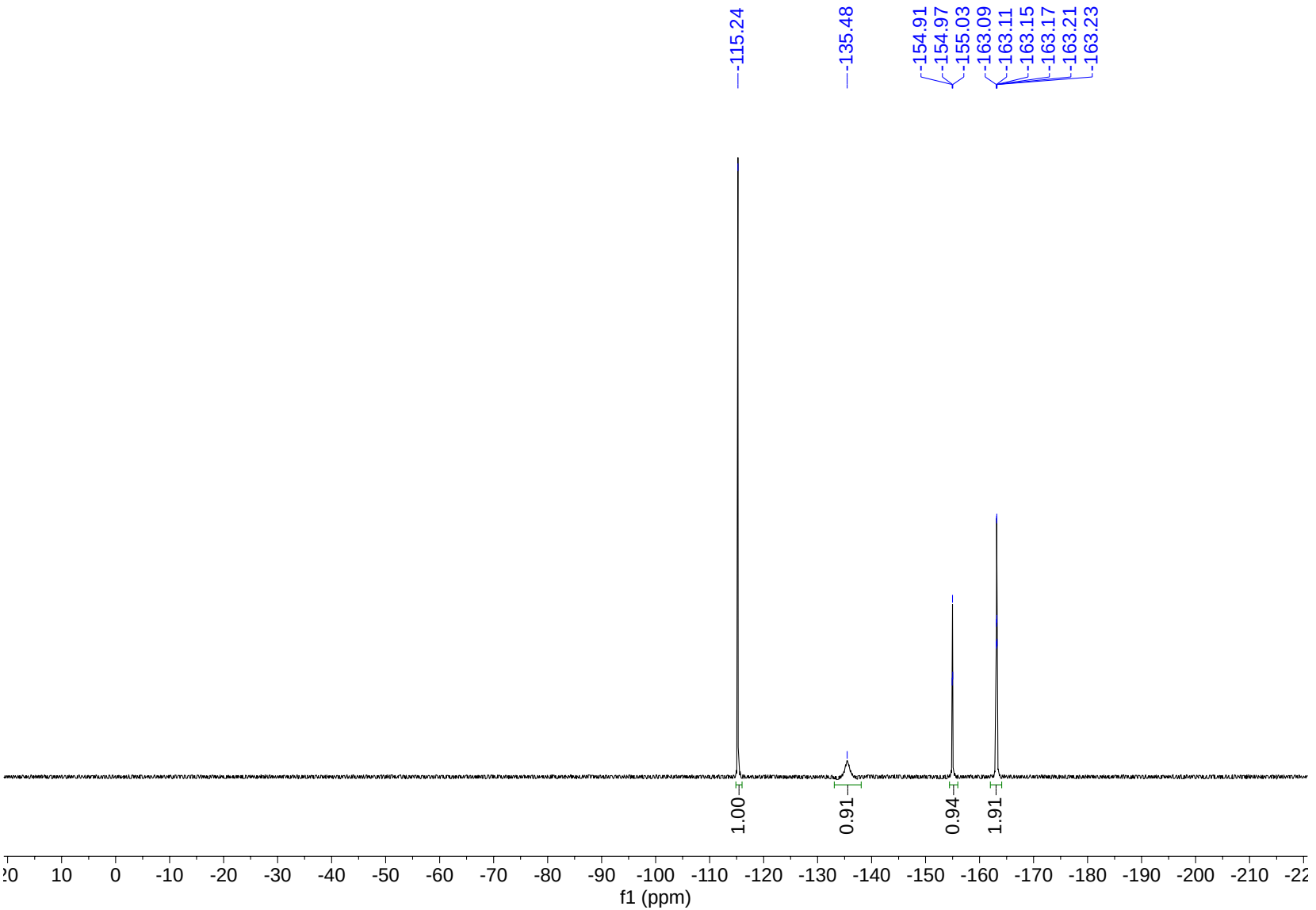


Figure S51: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **2t**.

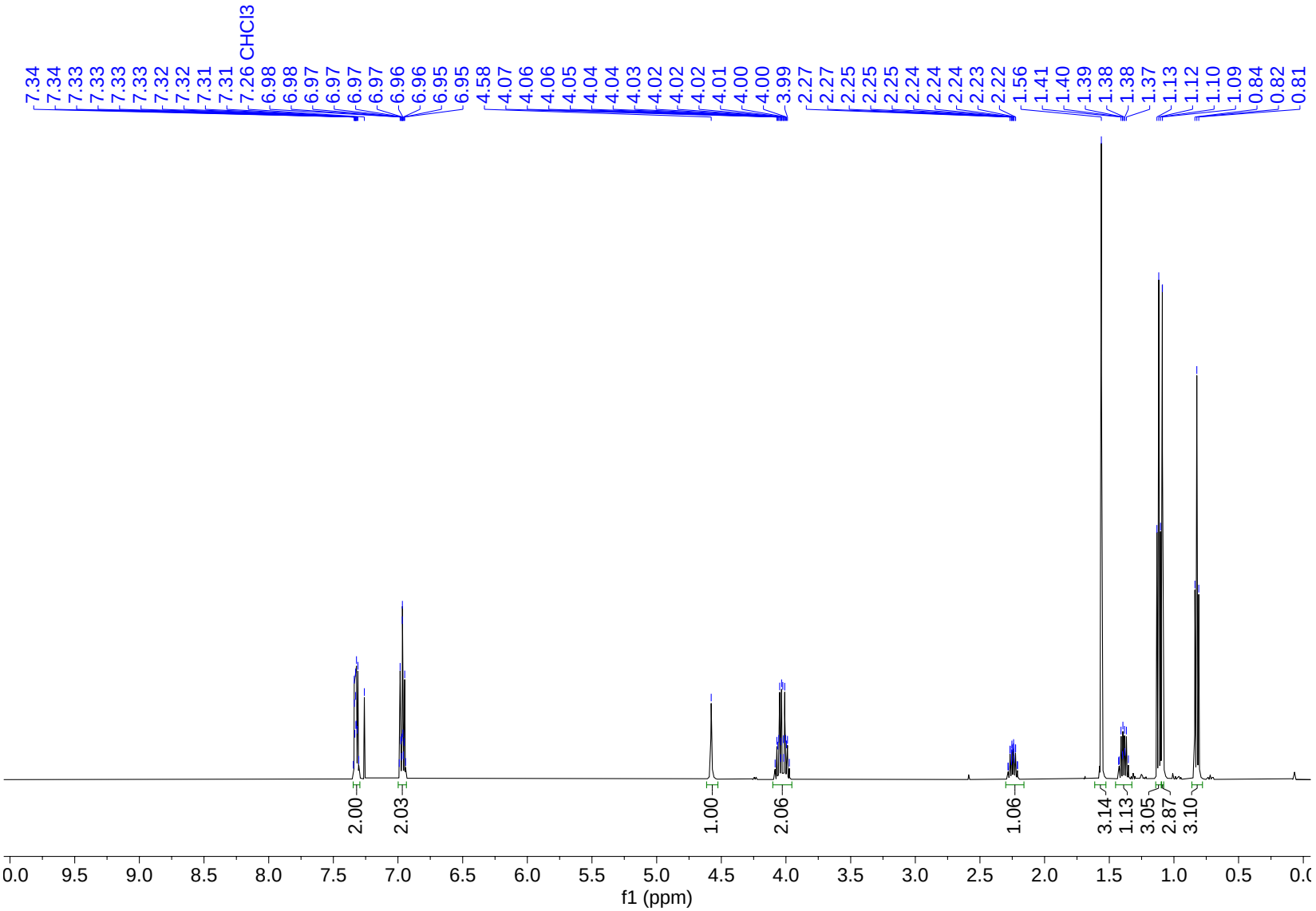


Figure S52: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2t**.

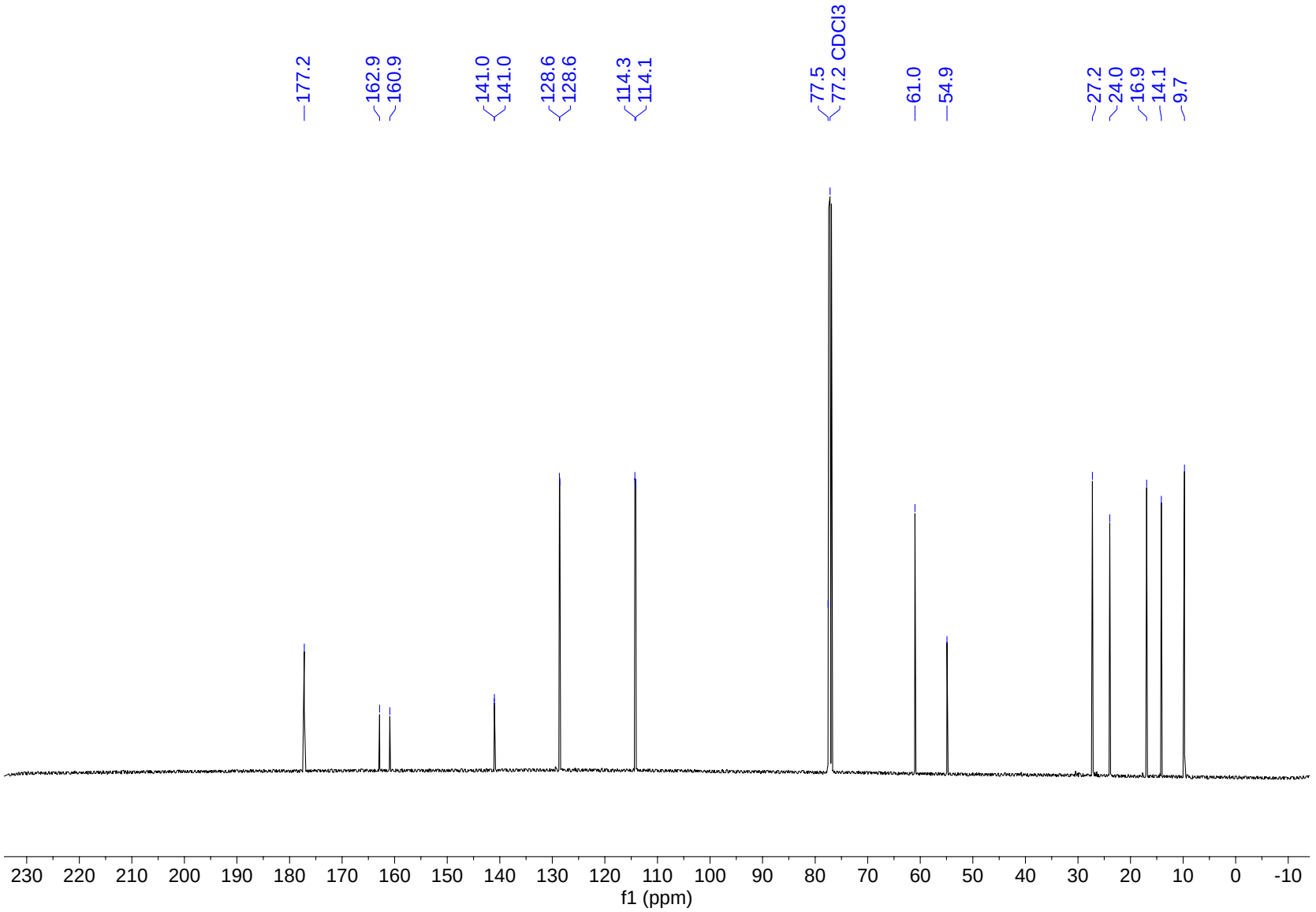


Figure S53: **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) spectrum of **2t**.

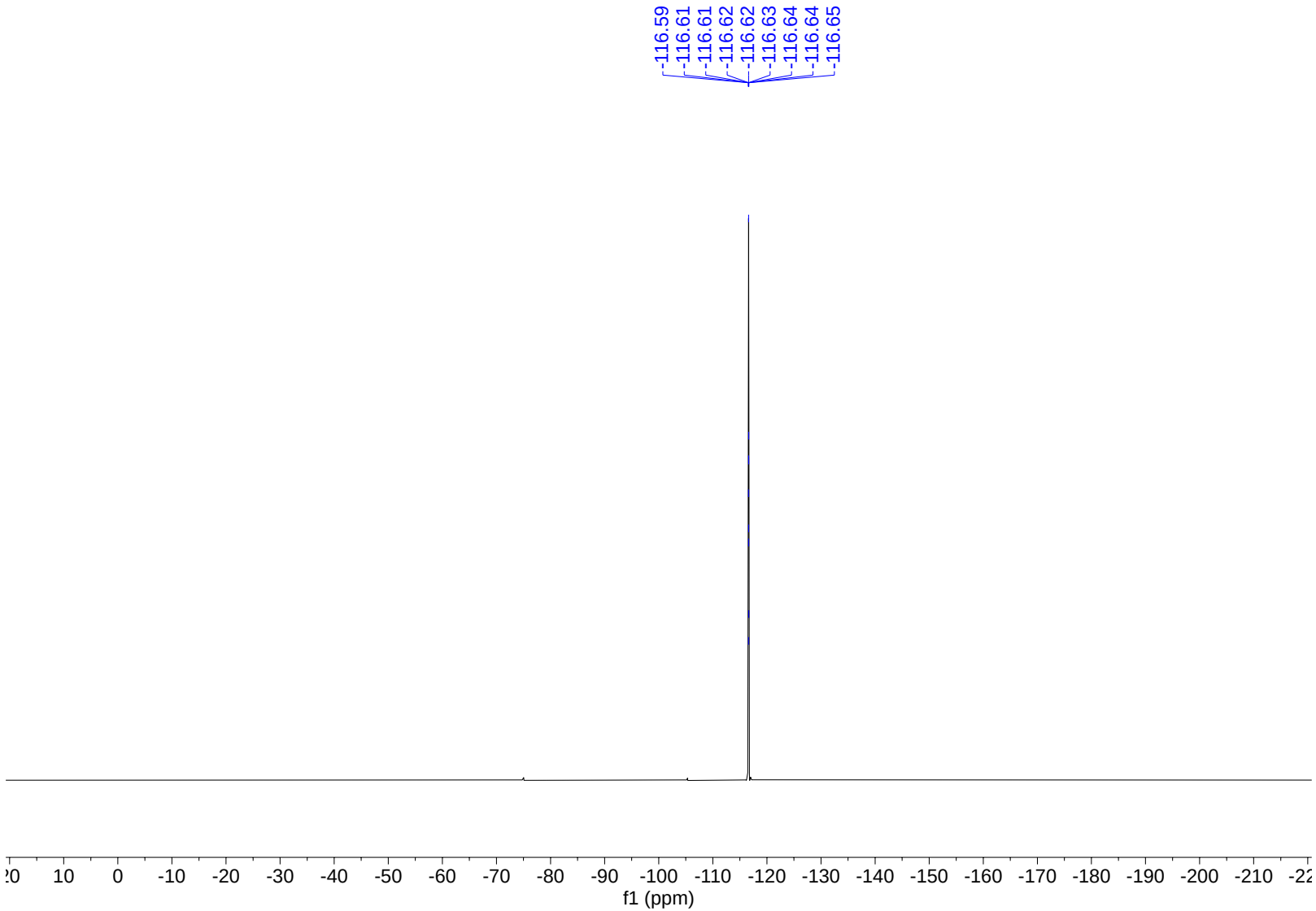


Figure S54: **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K) spectrum of **2o**.

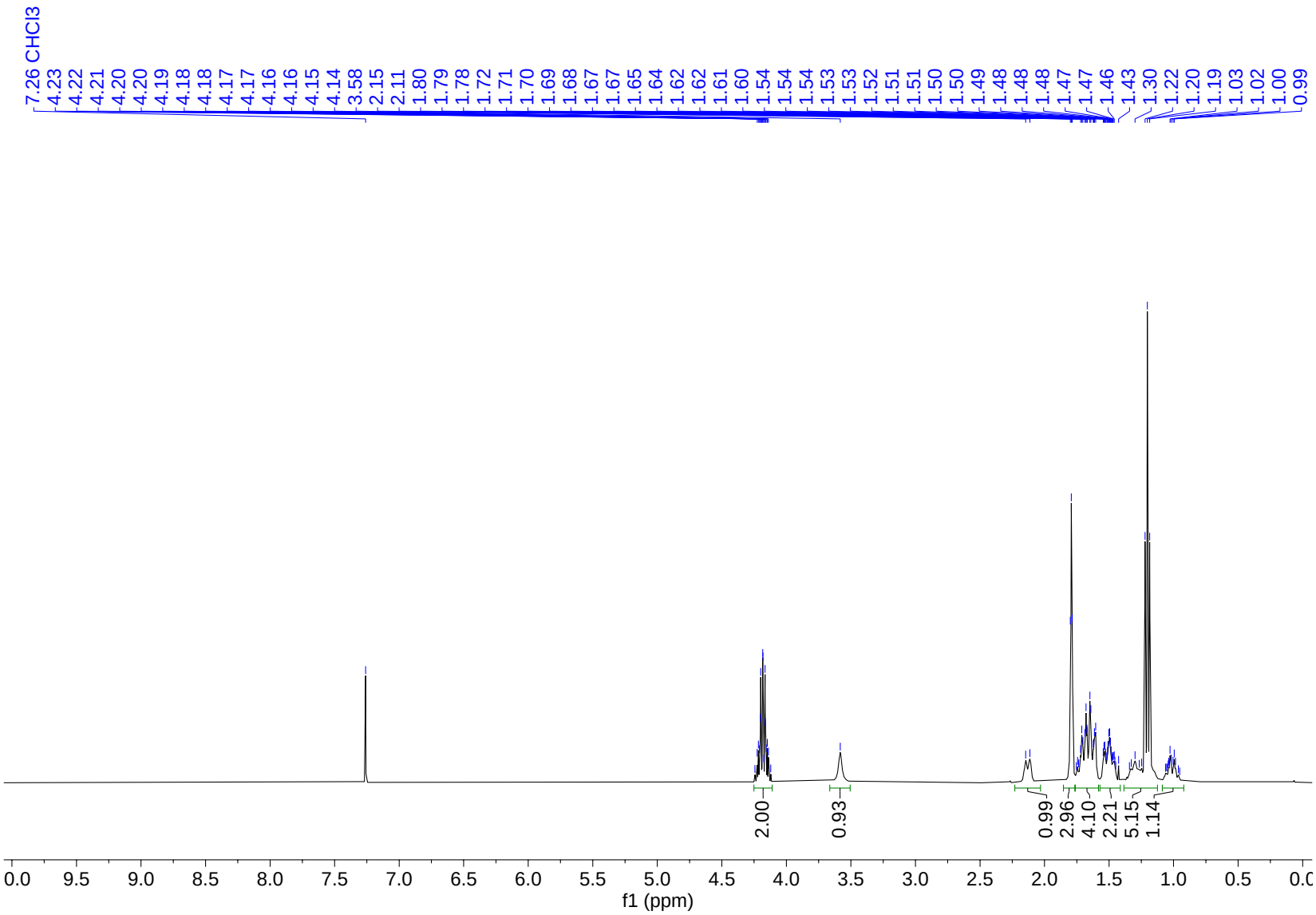


Figure S55: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2o**.

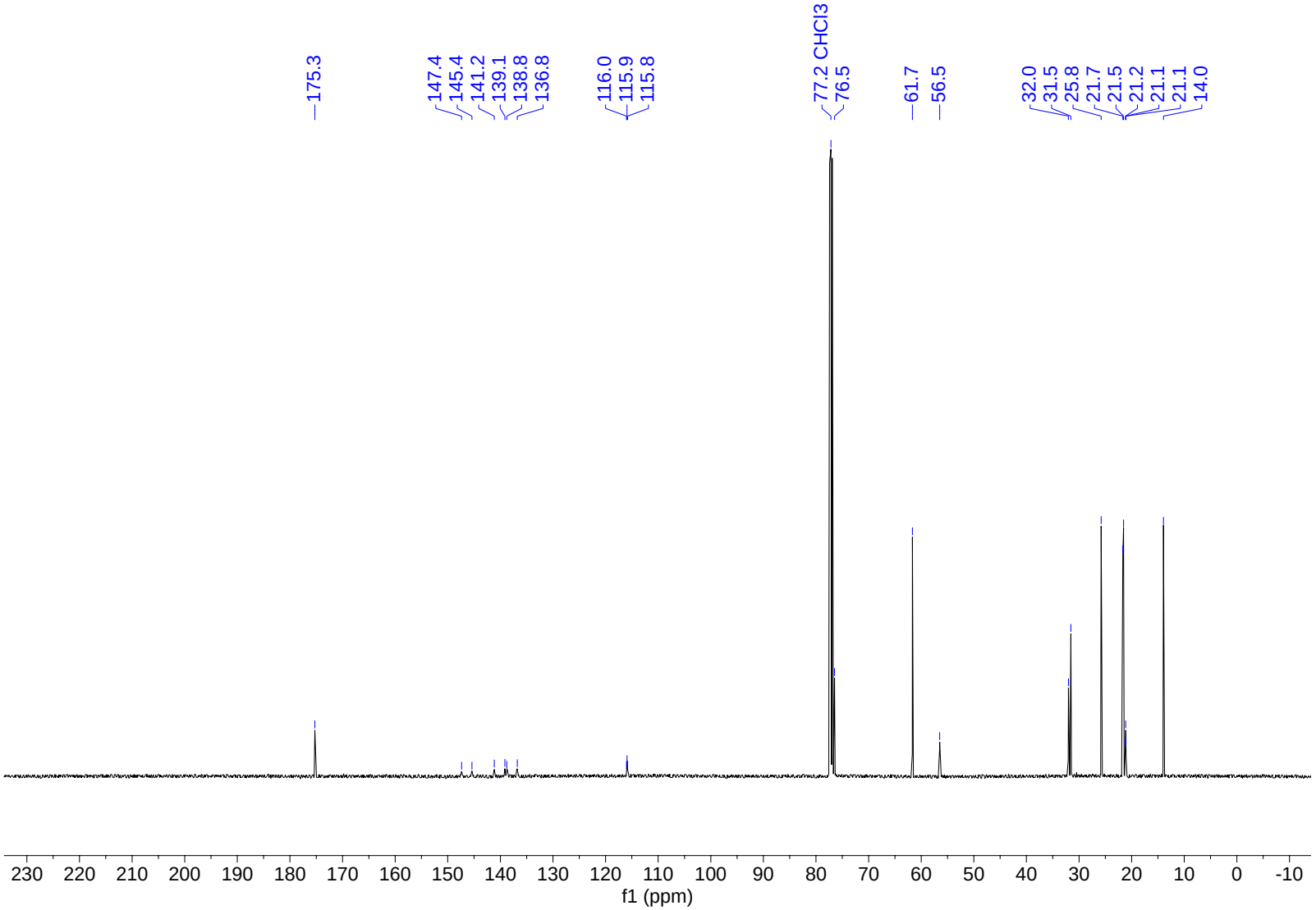


Figure S56: **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) spectrum of **2o**.

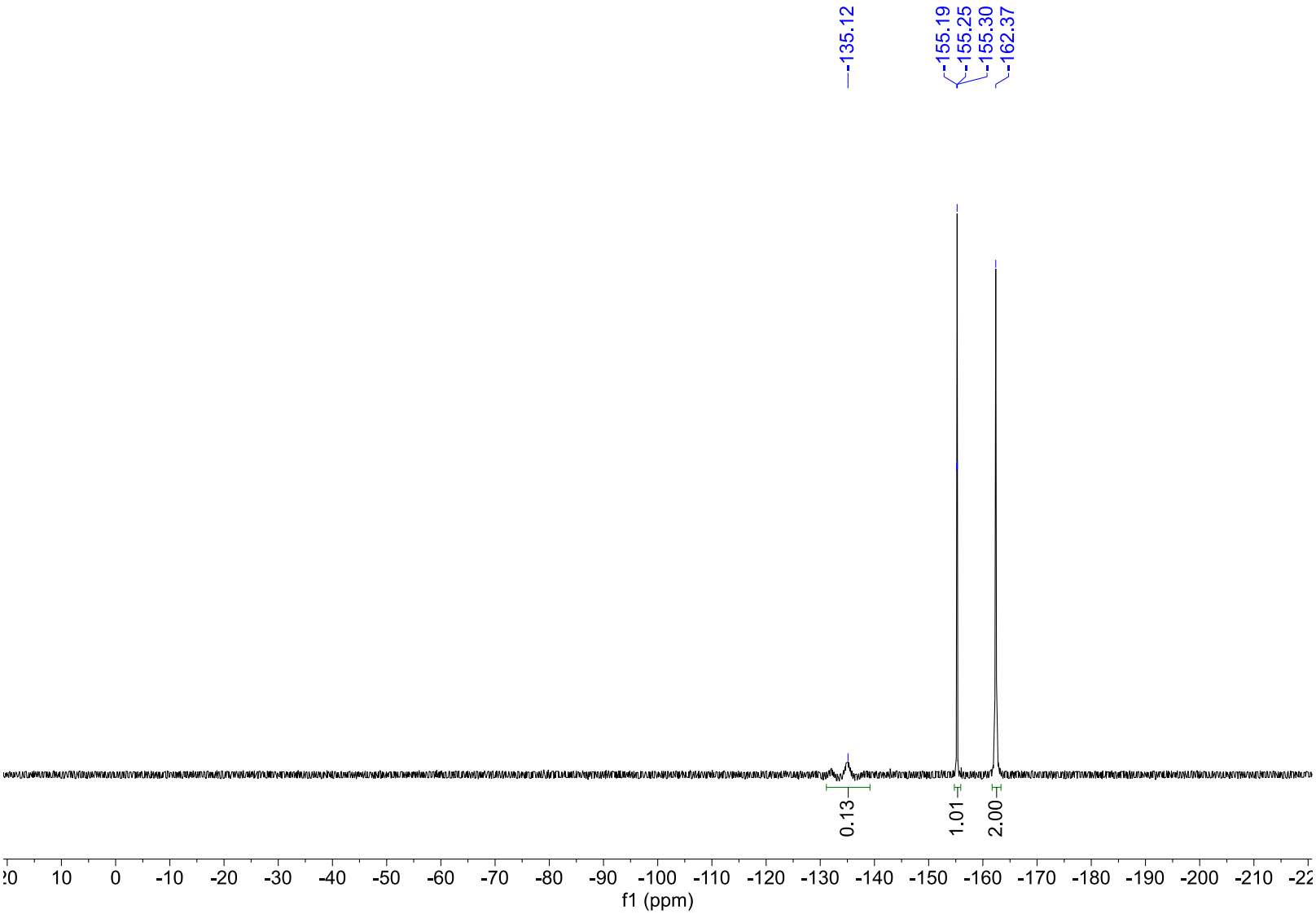


Figure S57: **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K) spectrum of **2p**.

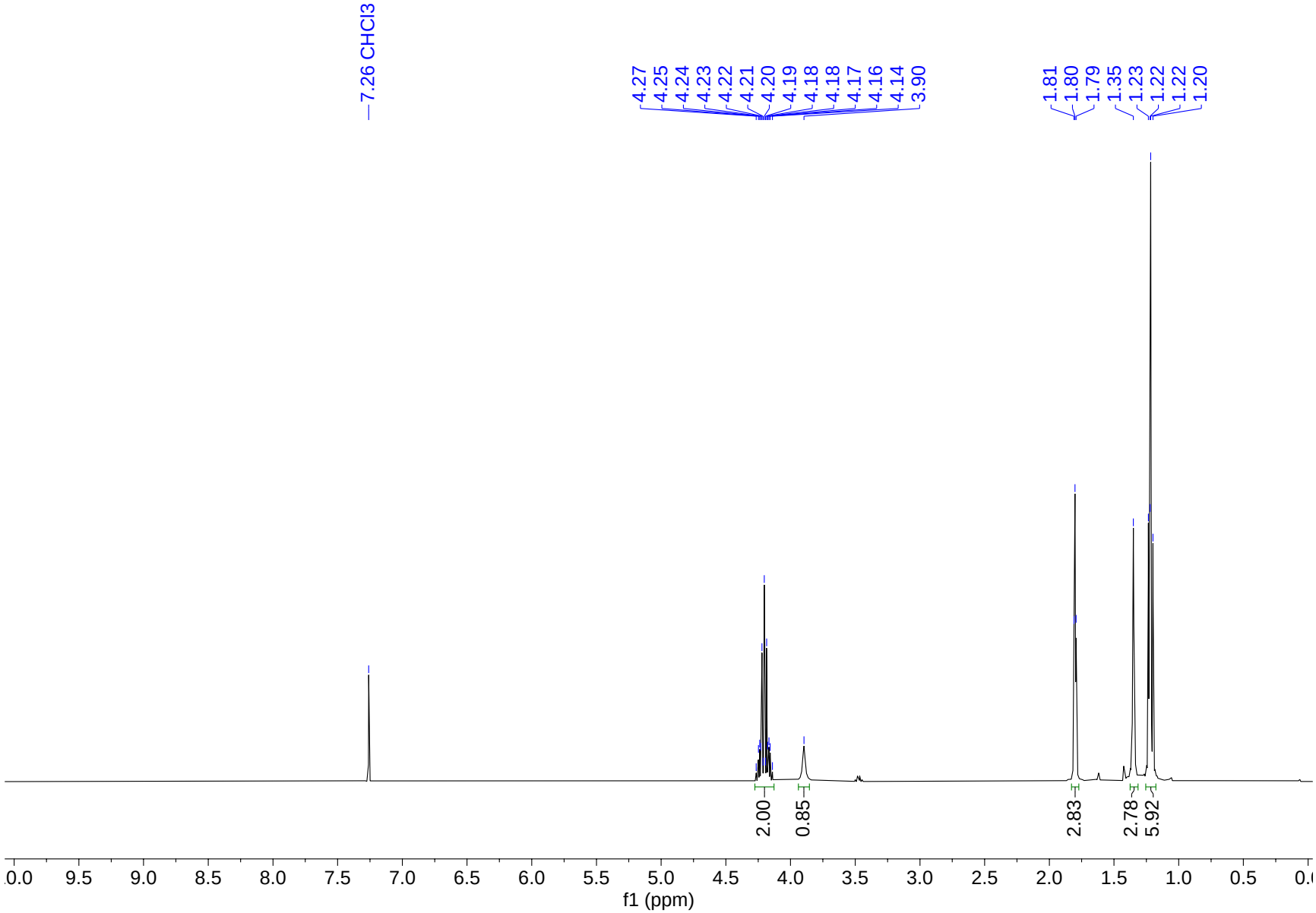


Figure S58: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2p**.

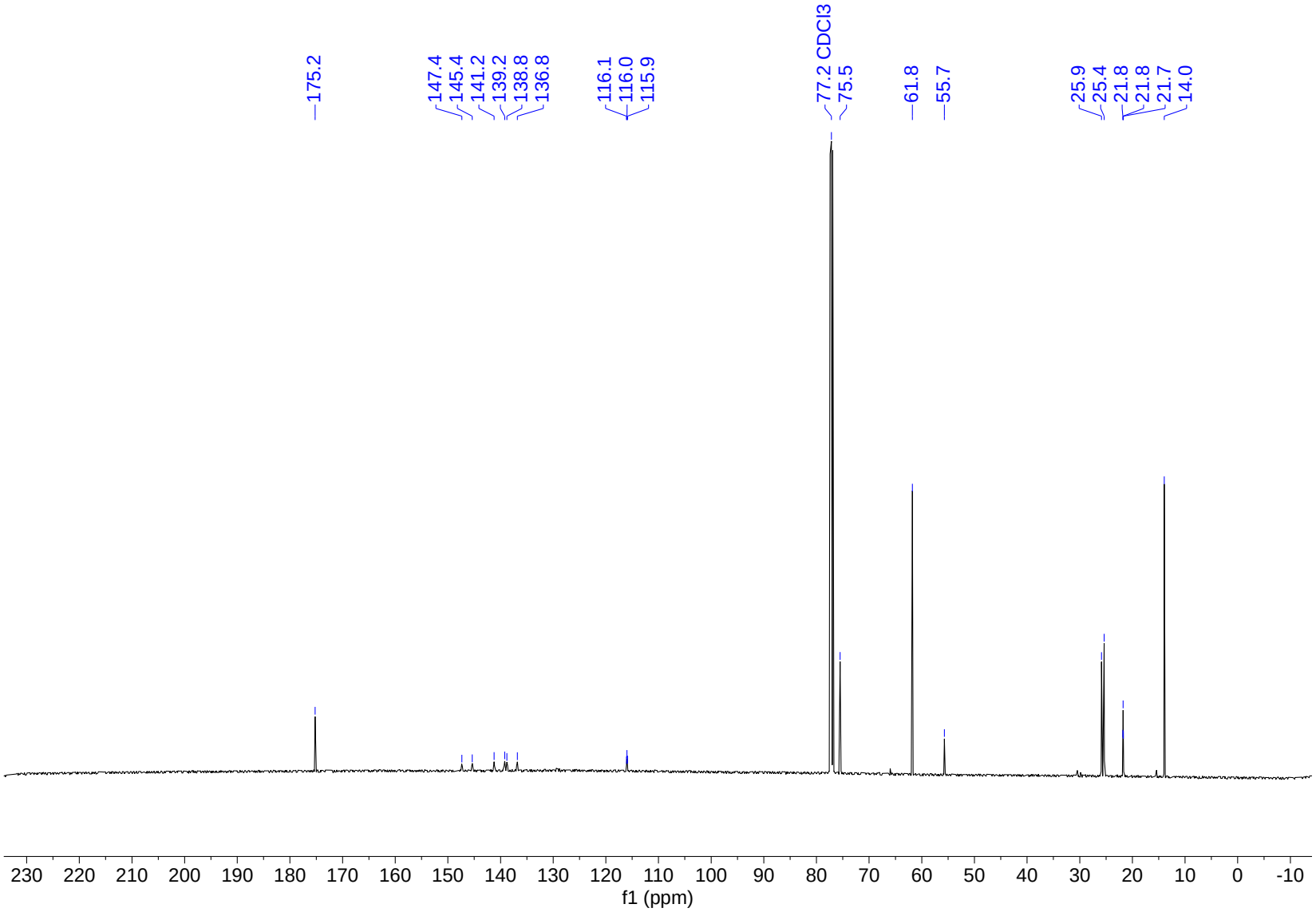


Figure S59: **^{19}F NMR** (376.5 MHz, $CDCl_3$, 298 K) spectrum of **2p**.

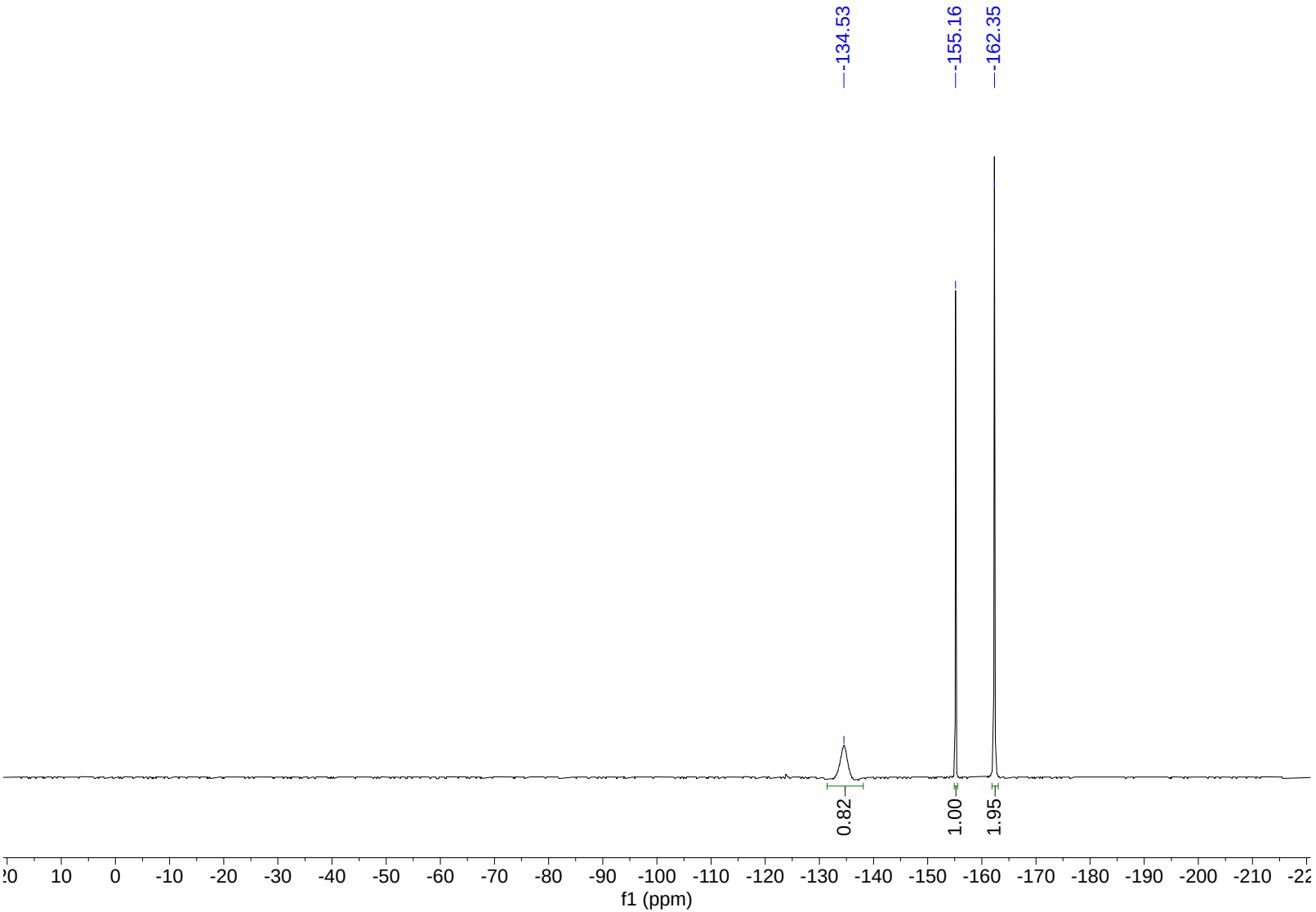


Figure S60: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **2q**.

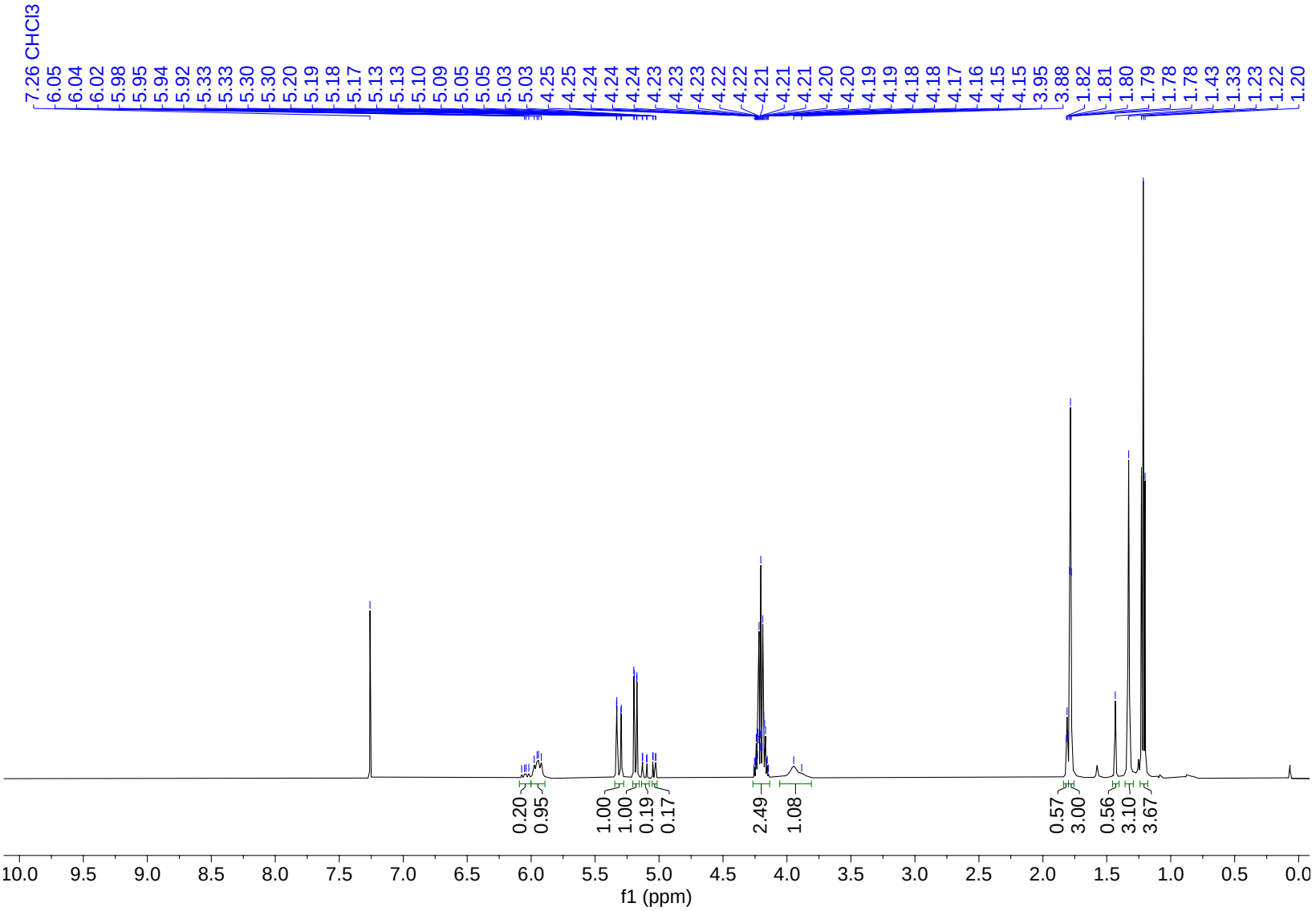


Figure S61: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **2q**.

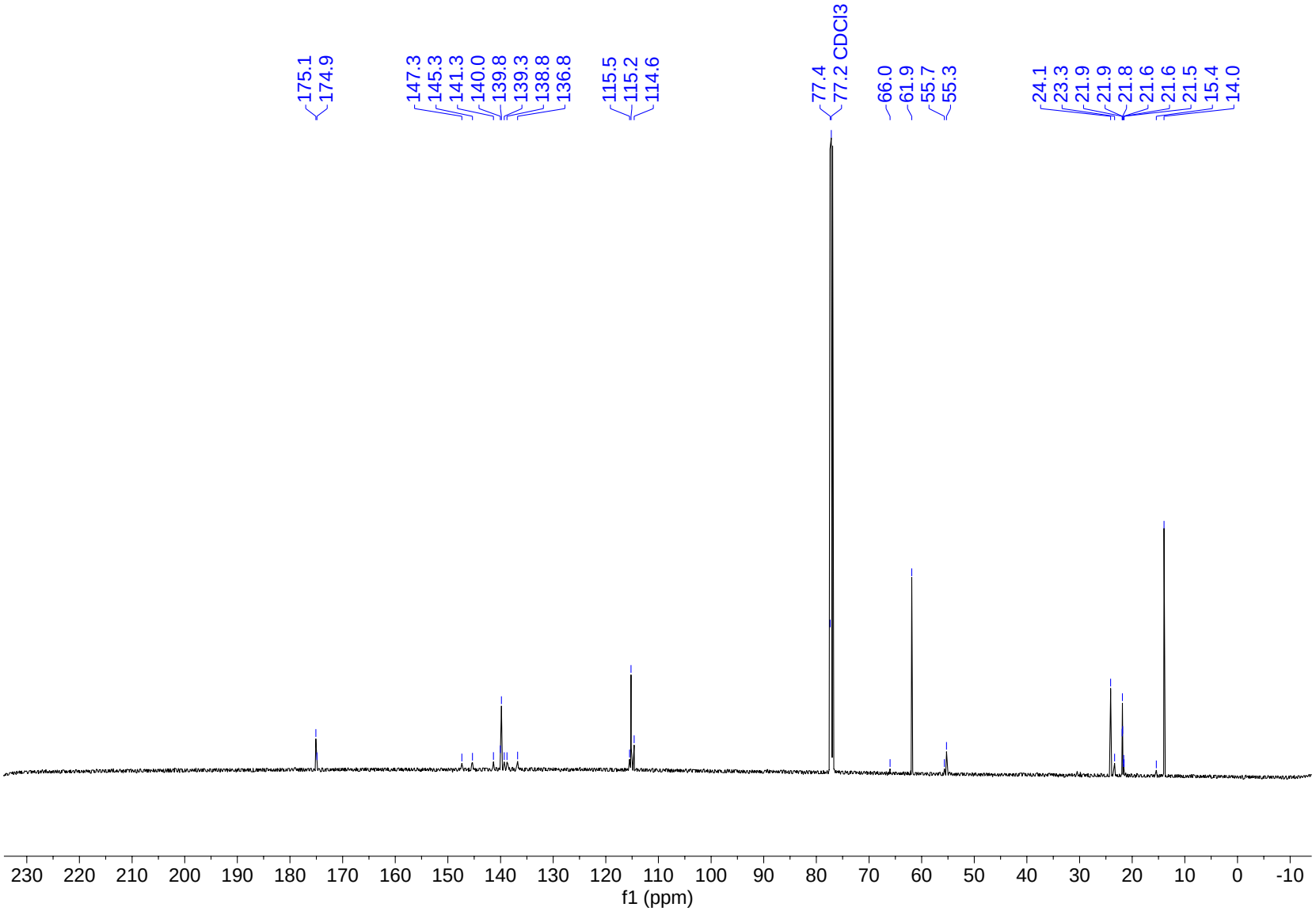


Figure S62: **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) spectrum of **2q**.

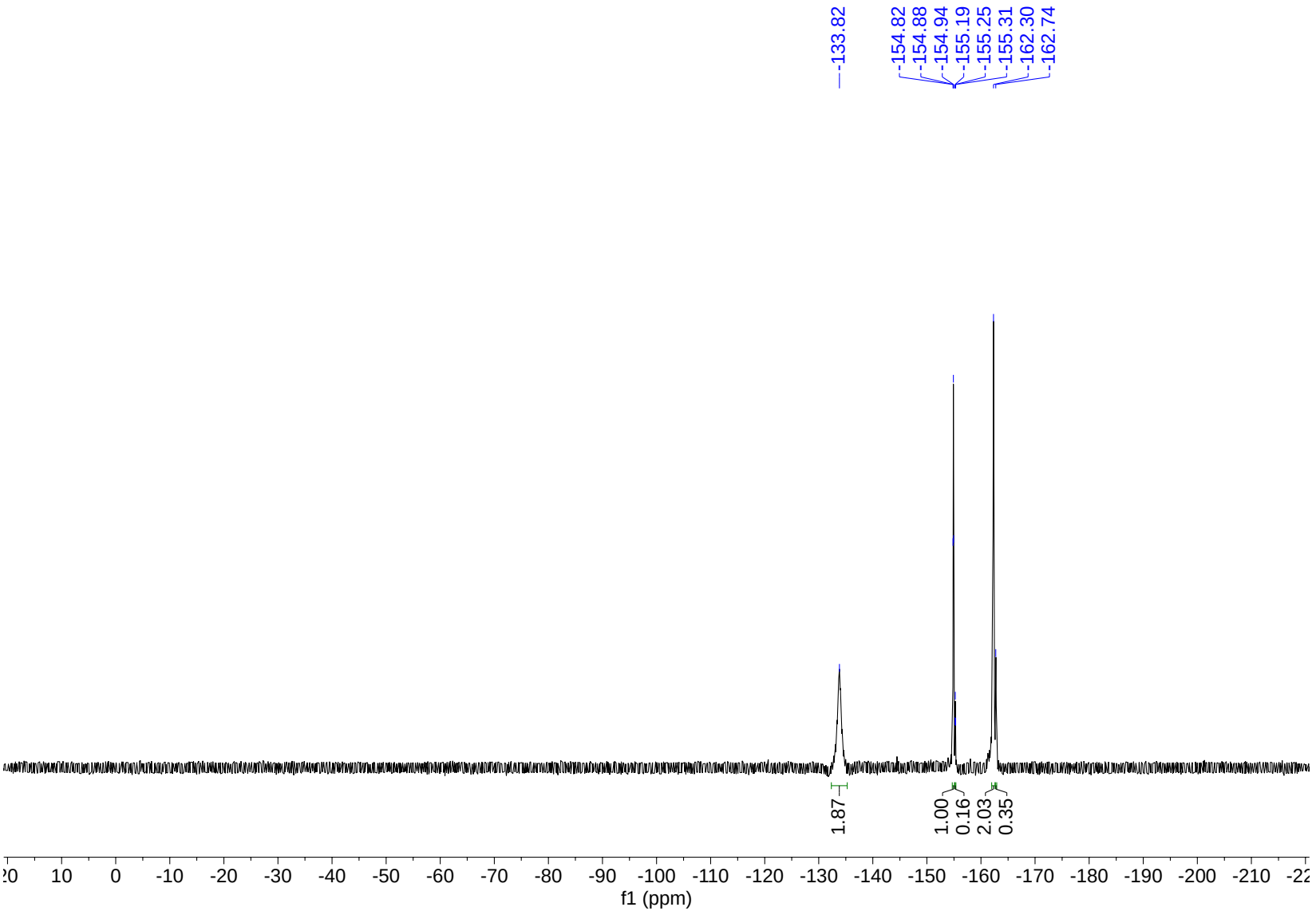


Figure S63: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **3b**.

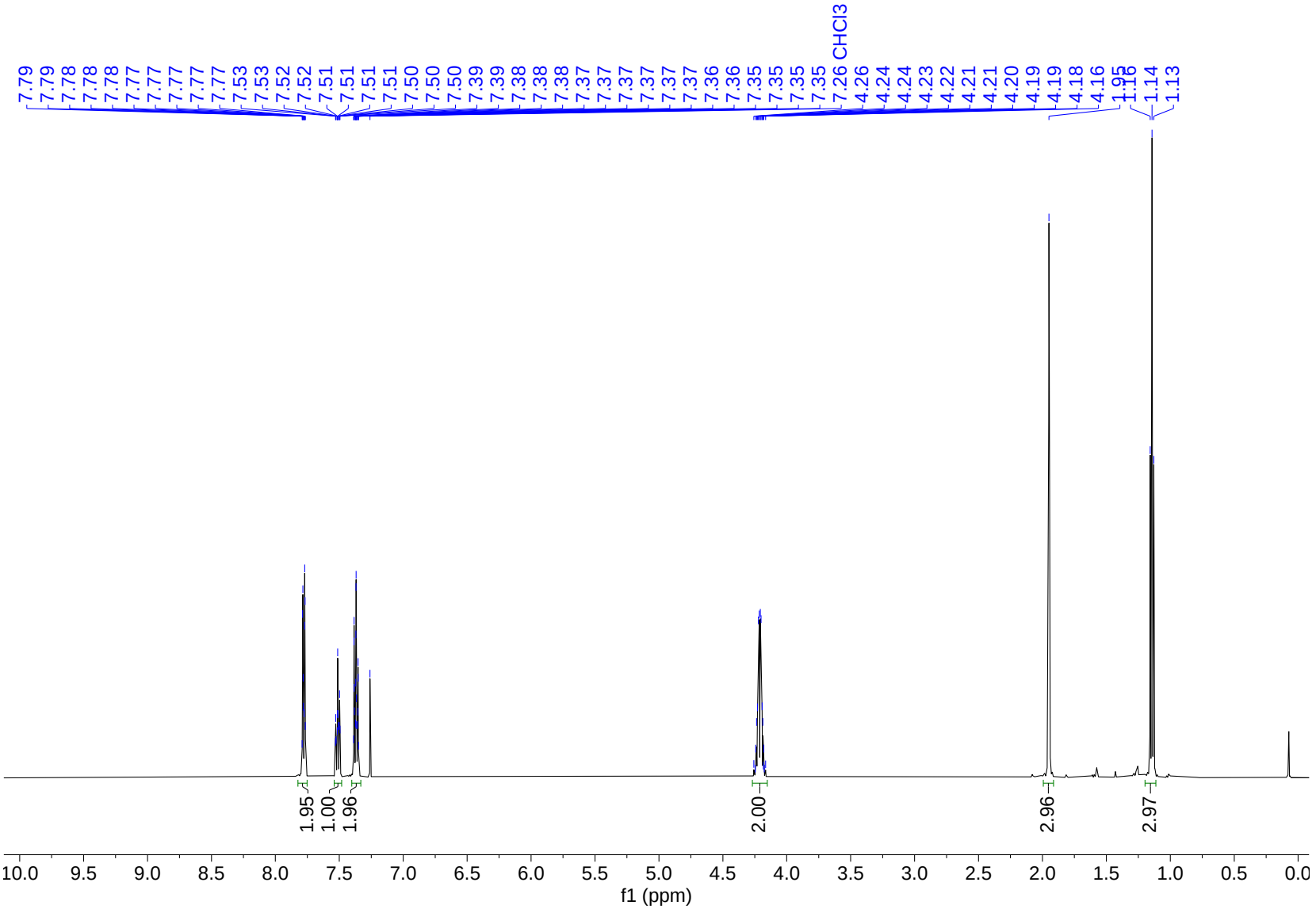


Figure S64: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **3b**.

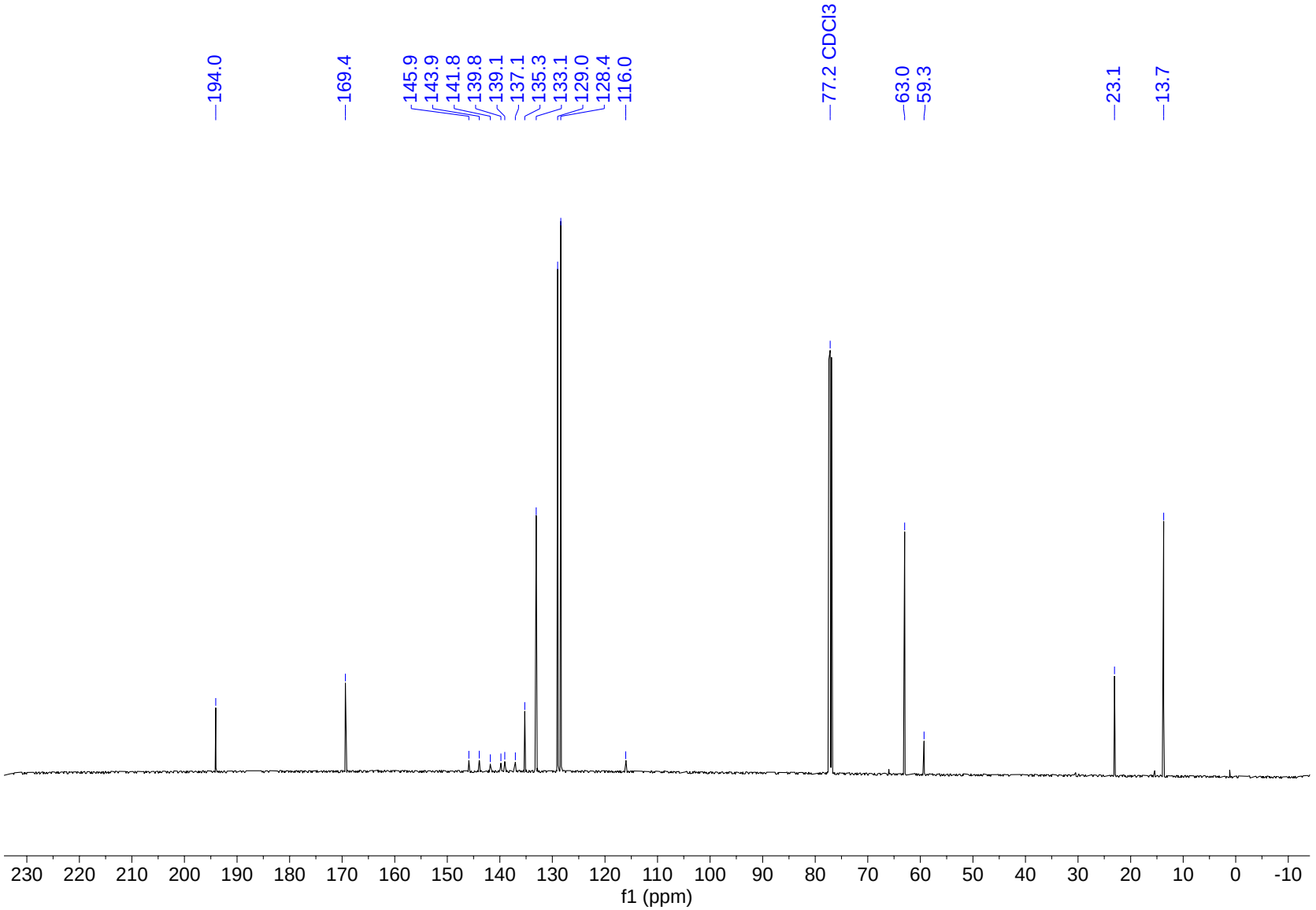


Figure S65: **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) spectrum of **3b**.

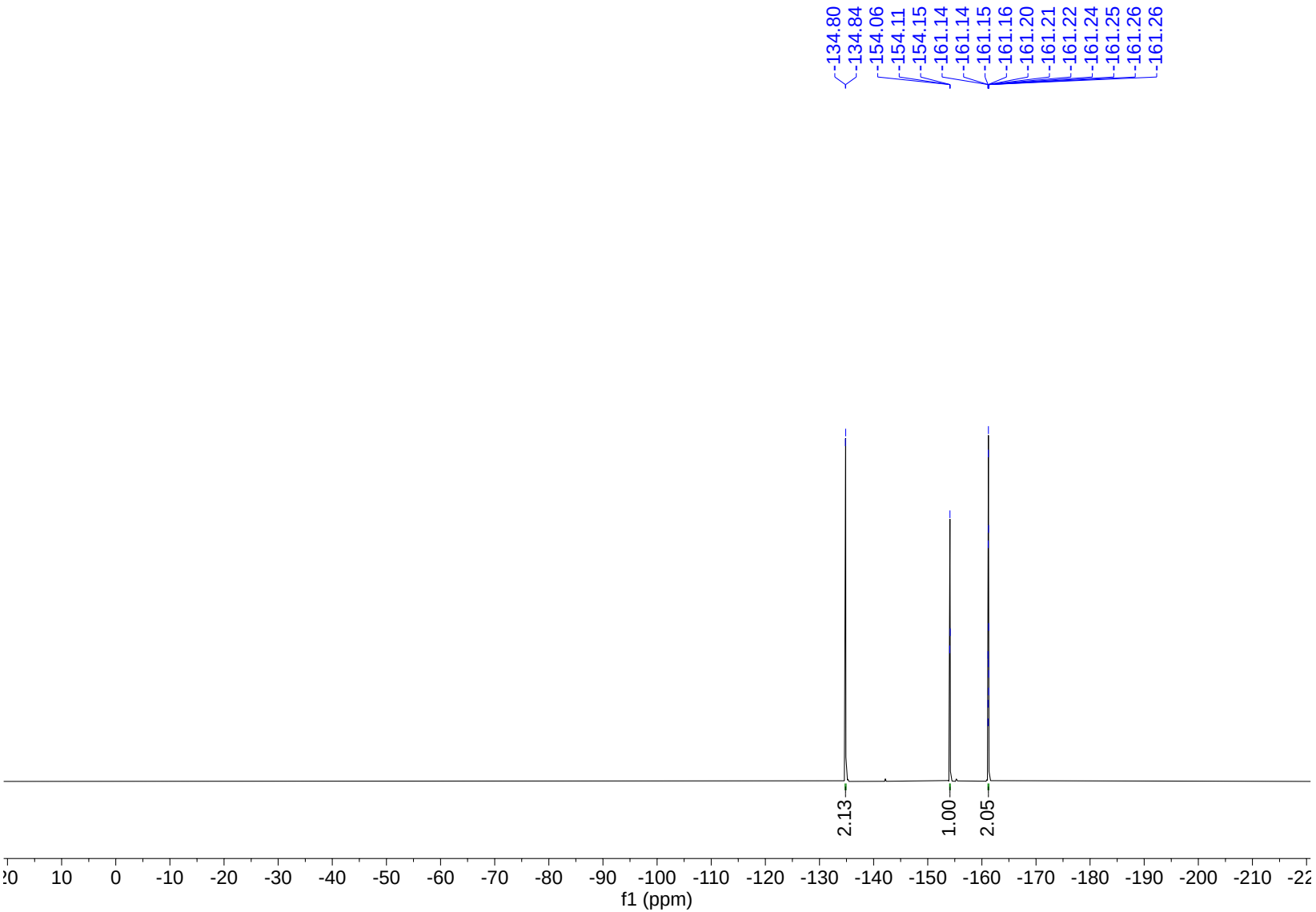


Figure S66: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **3g**.

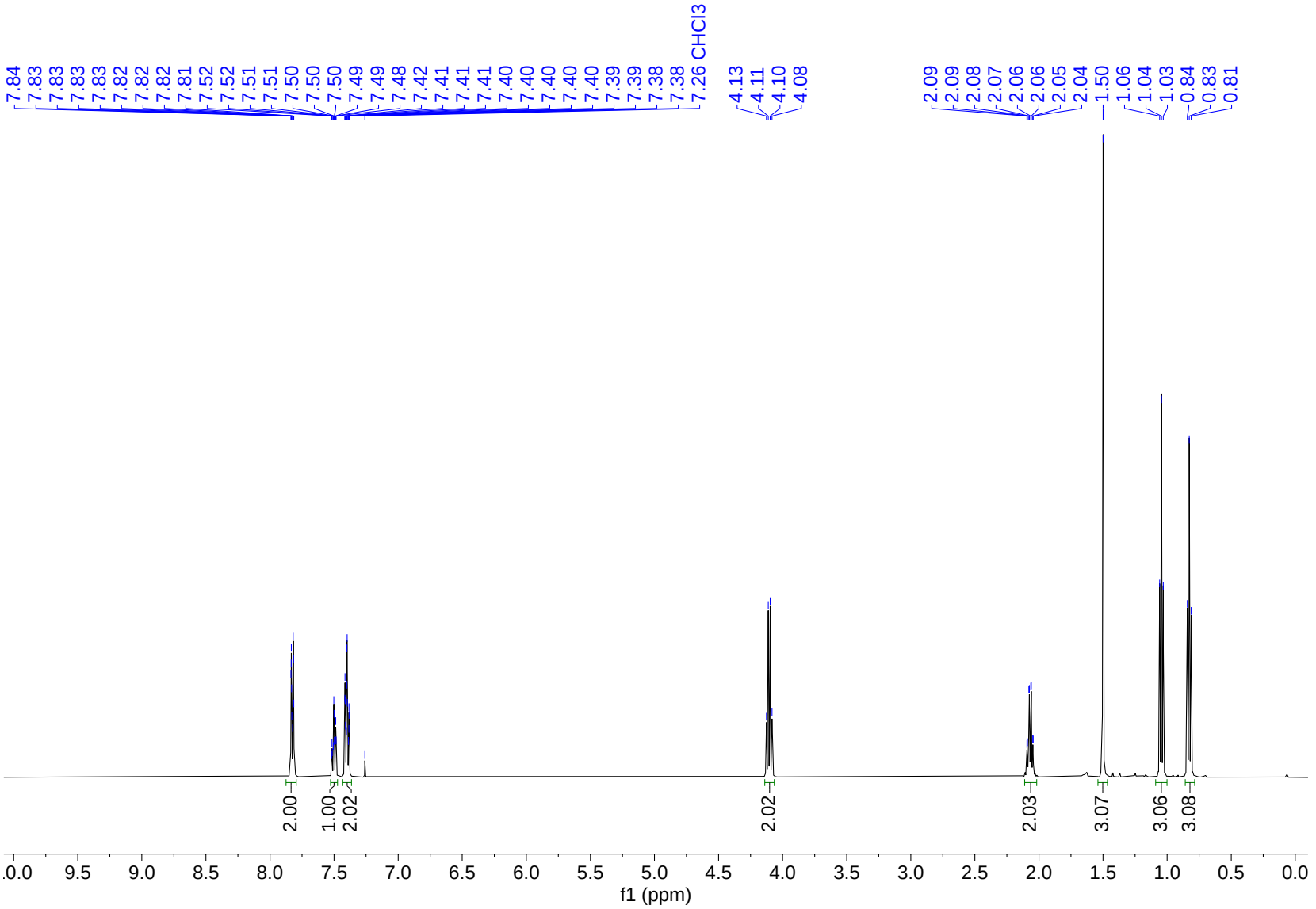


Figure S67: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **3g**.

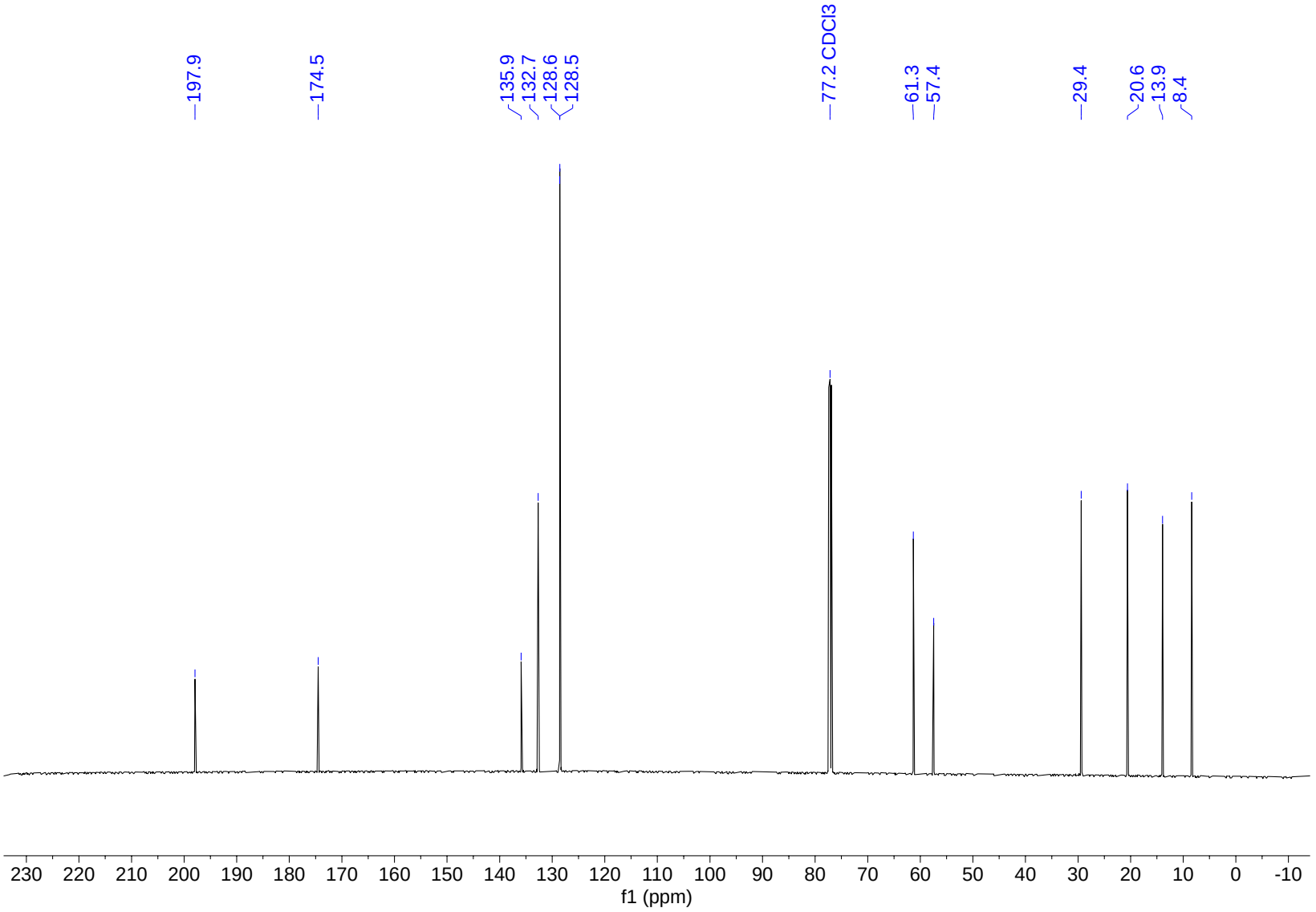


Figure S68: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **3c**. *Note: **3c** is decomposing quickly in solution. Additional signals are those of decomposition products.*

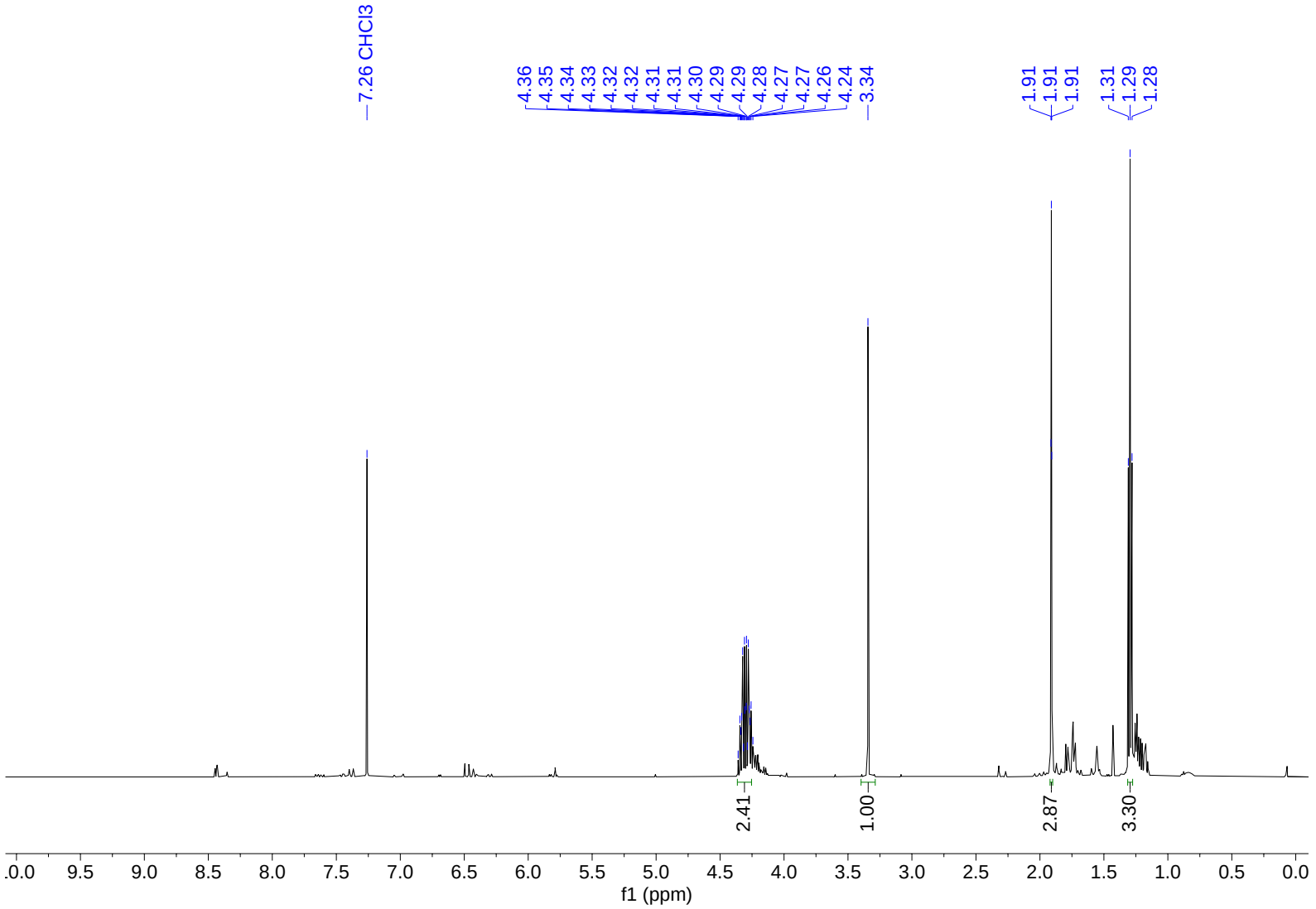


Figure S69: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **3c**. *Note: **3c** is decomposing quickly in solution. Additional signals are those of decomposition products.*

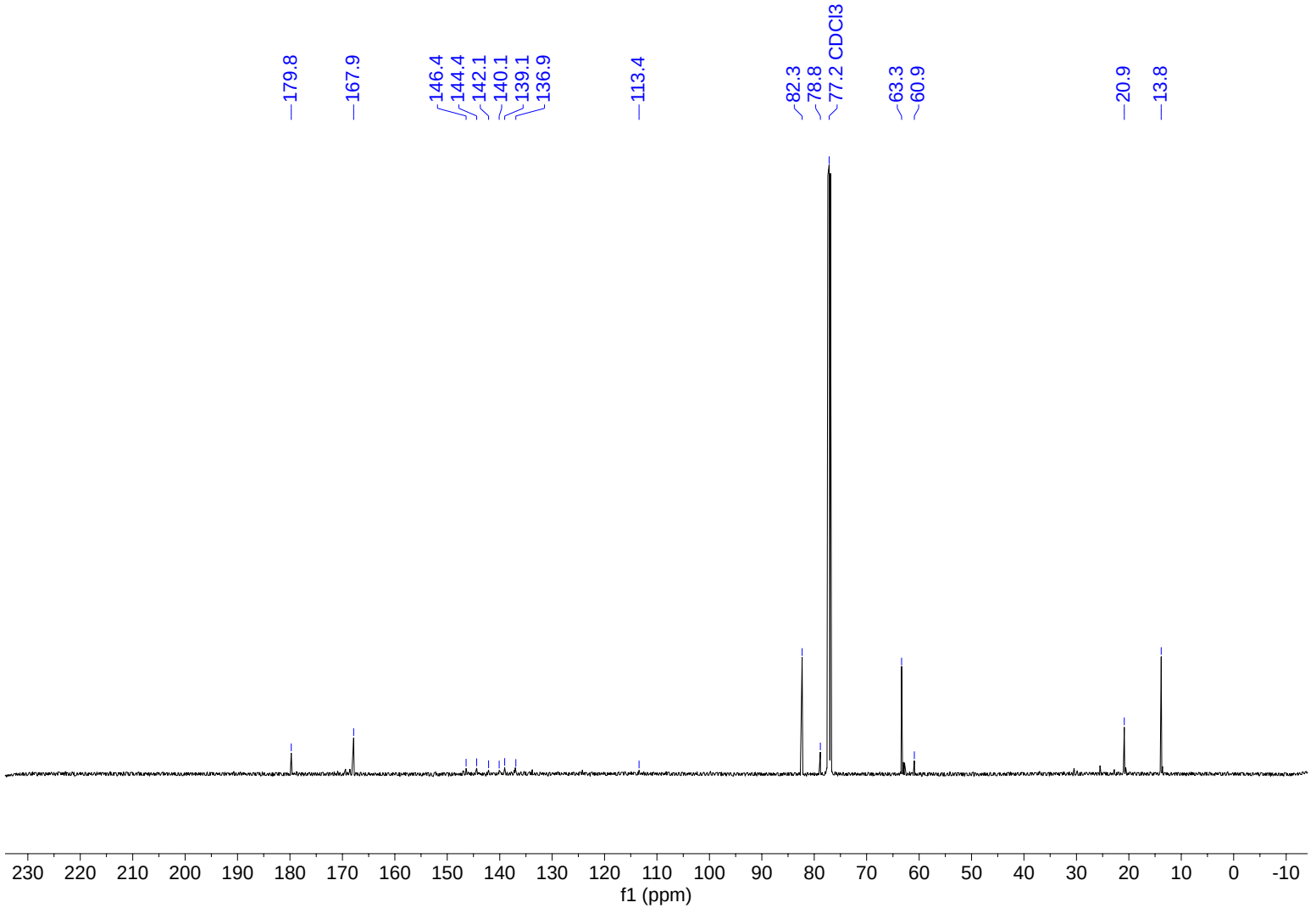


Figure S70: **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) spectrum of **3c**. *Note: **3c** is decomposing quickly in solution. Additional signals are those of decomposition products.*

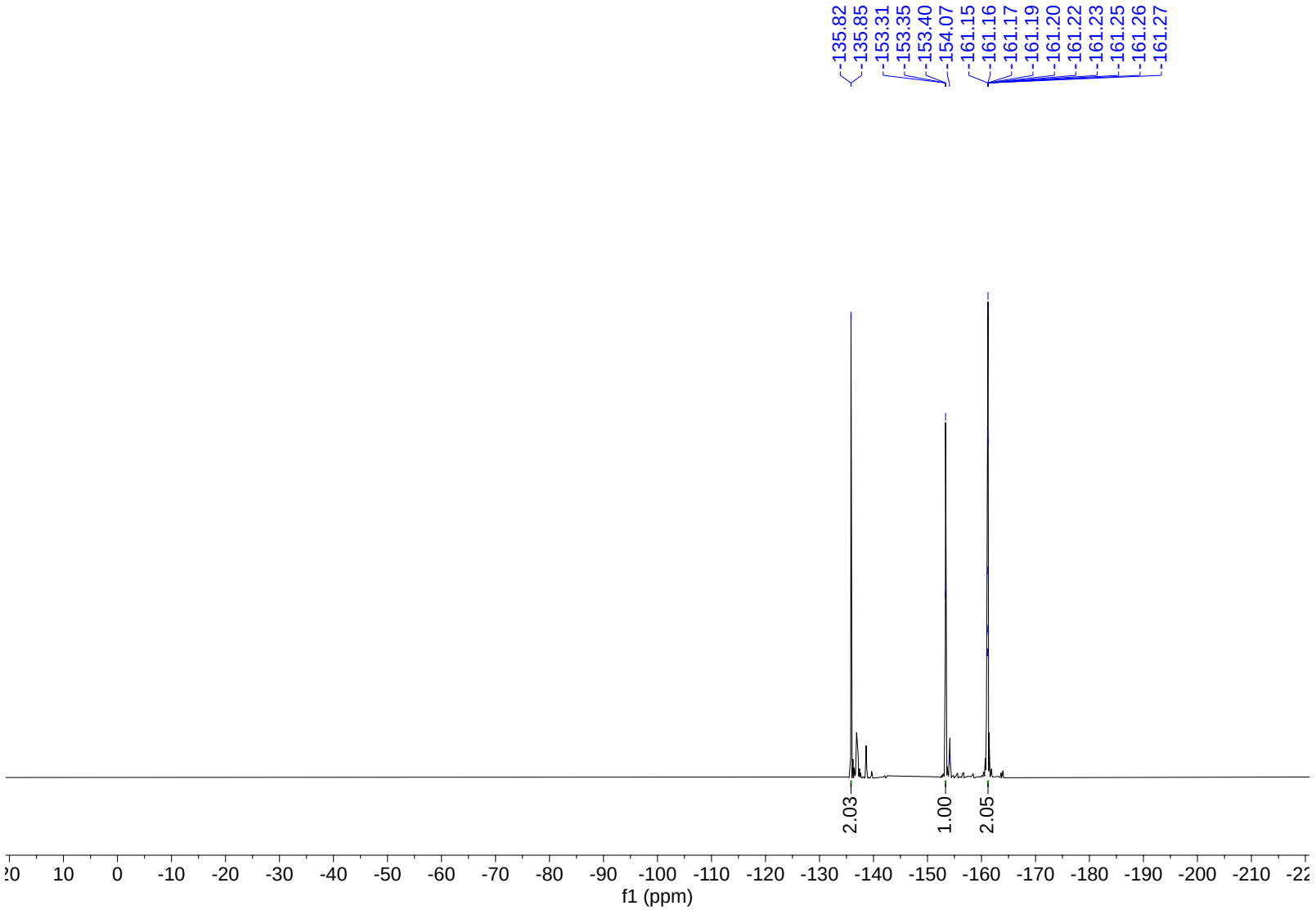


Figure S71: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **3d**.

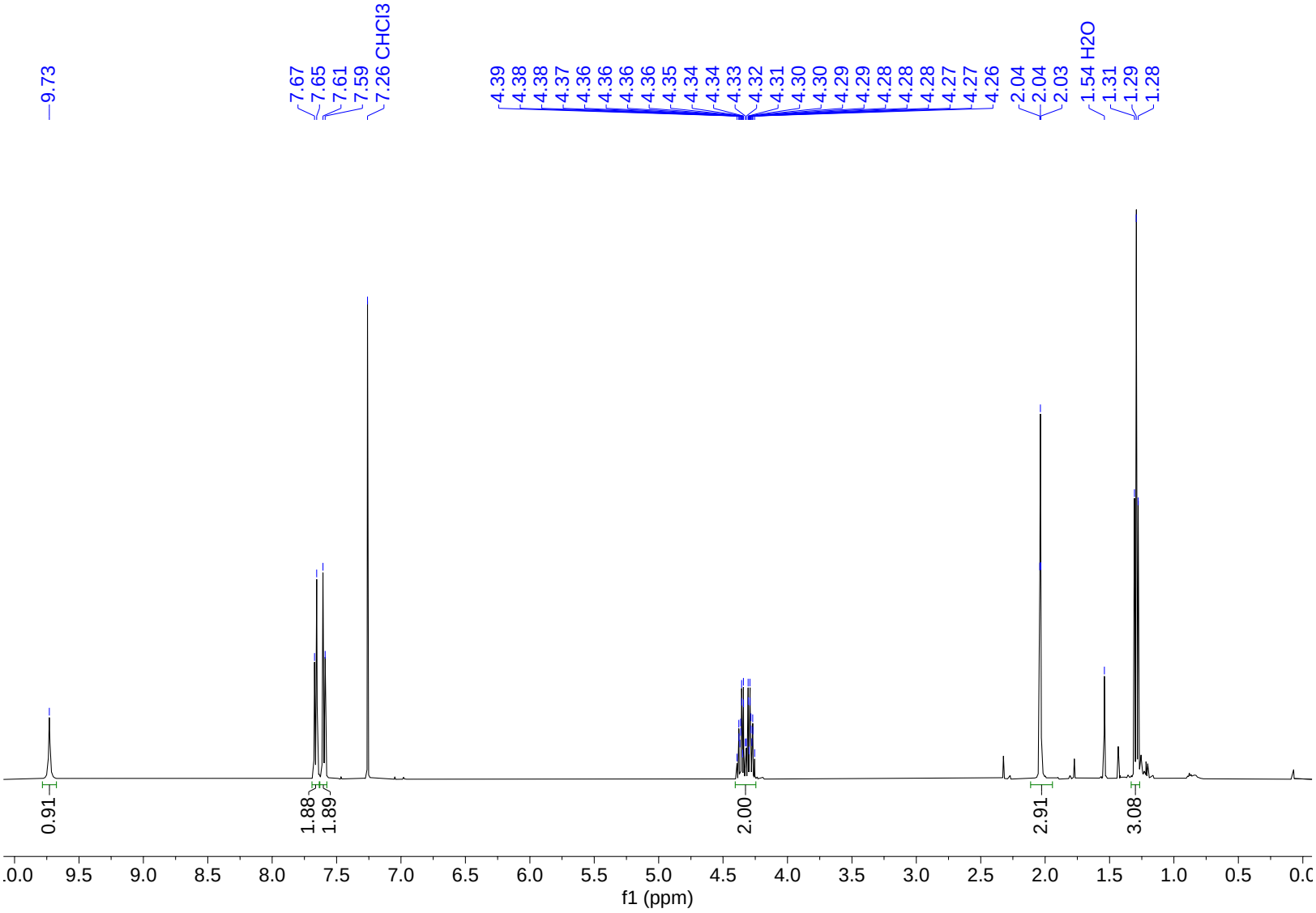


Figure S72: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **3d**.

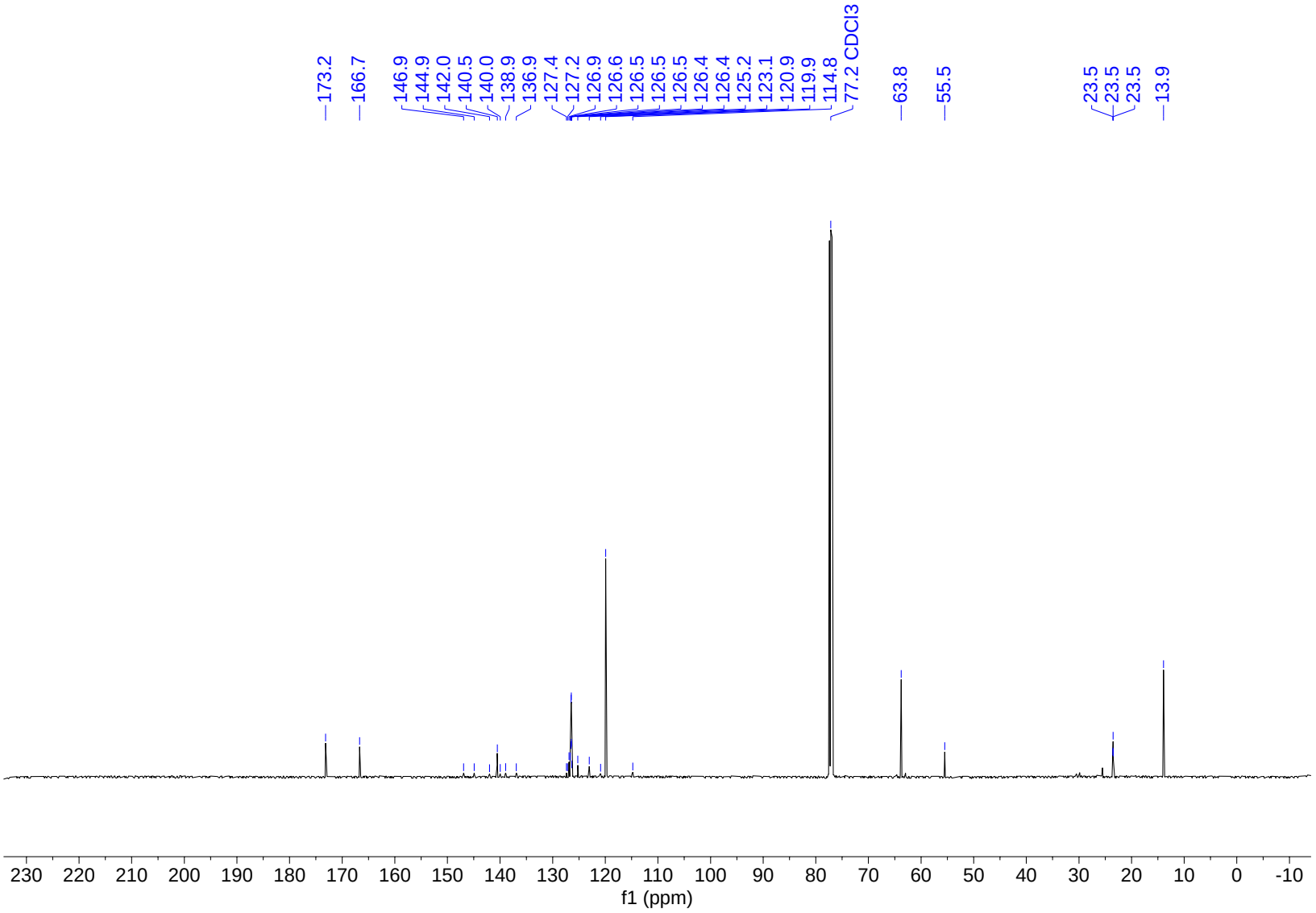


Figure S73: **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) spectrum of **3d**.

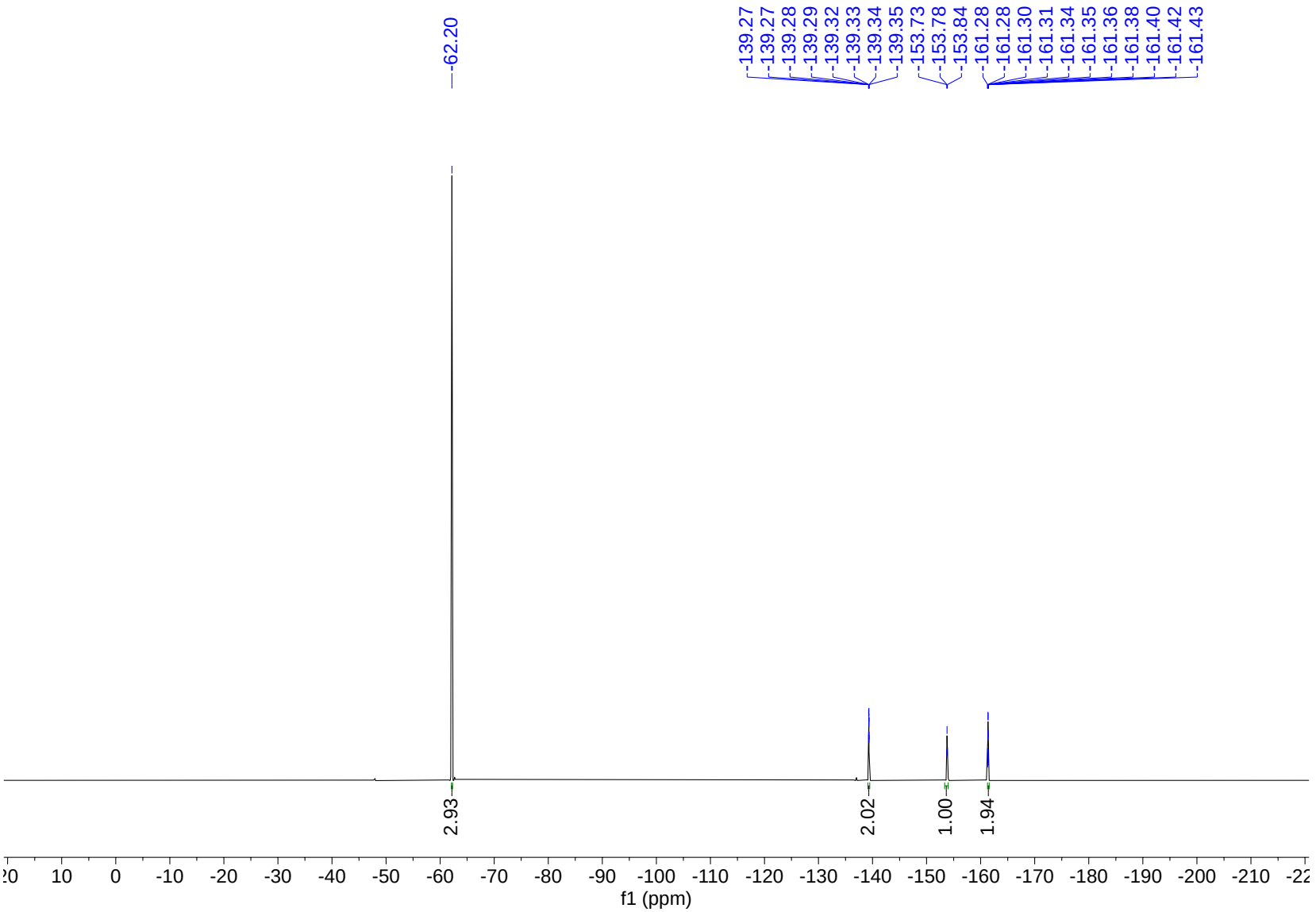


Figure S74: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **3e**.

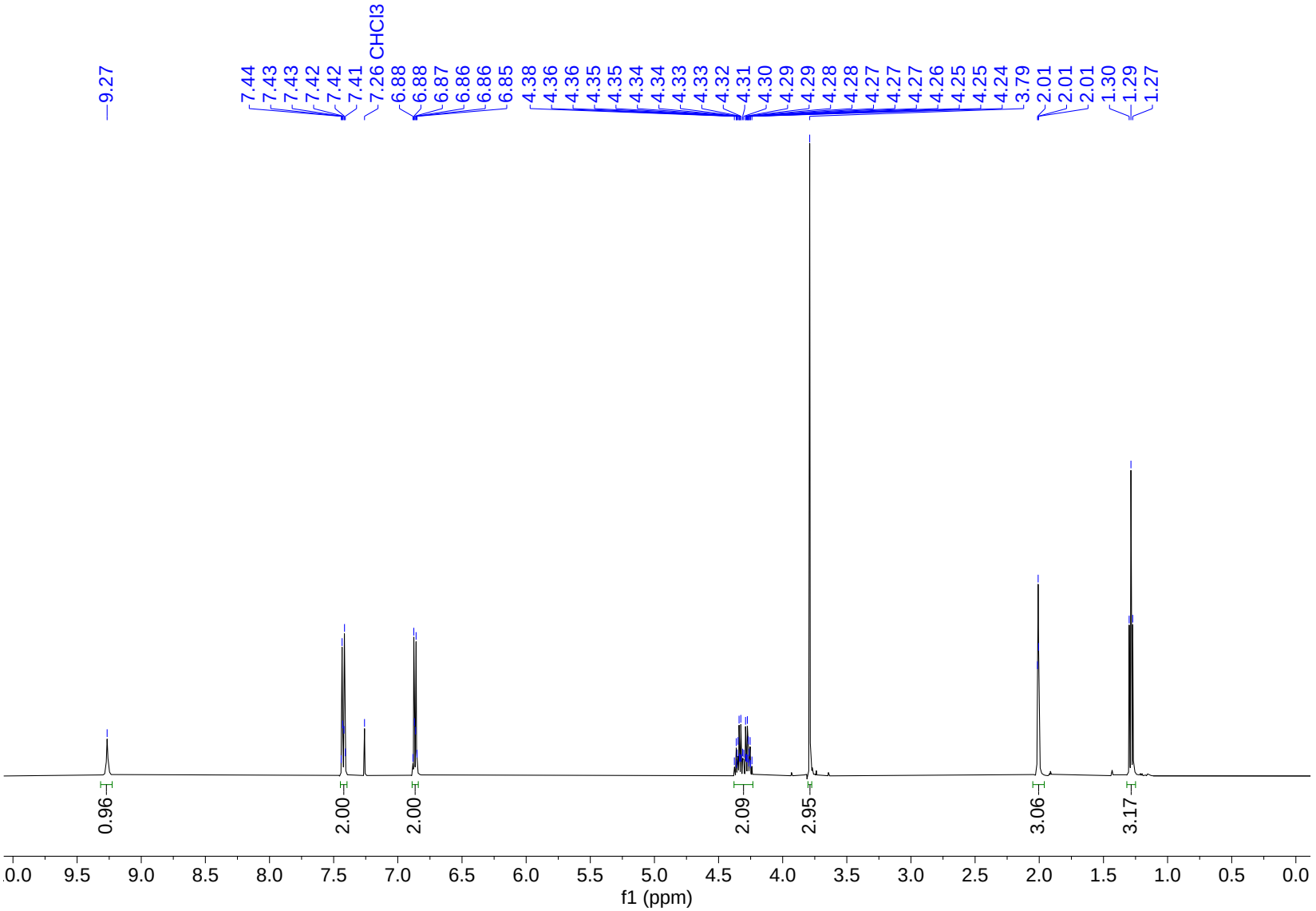


Figure S75: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **3e**.

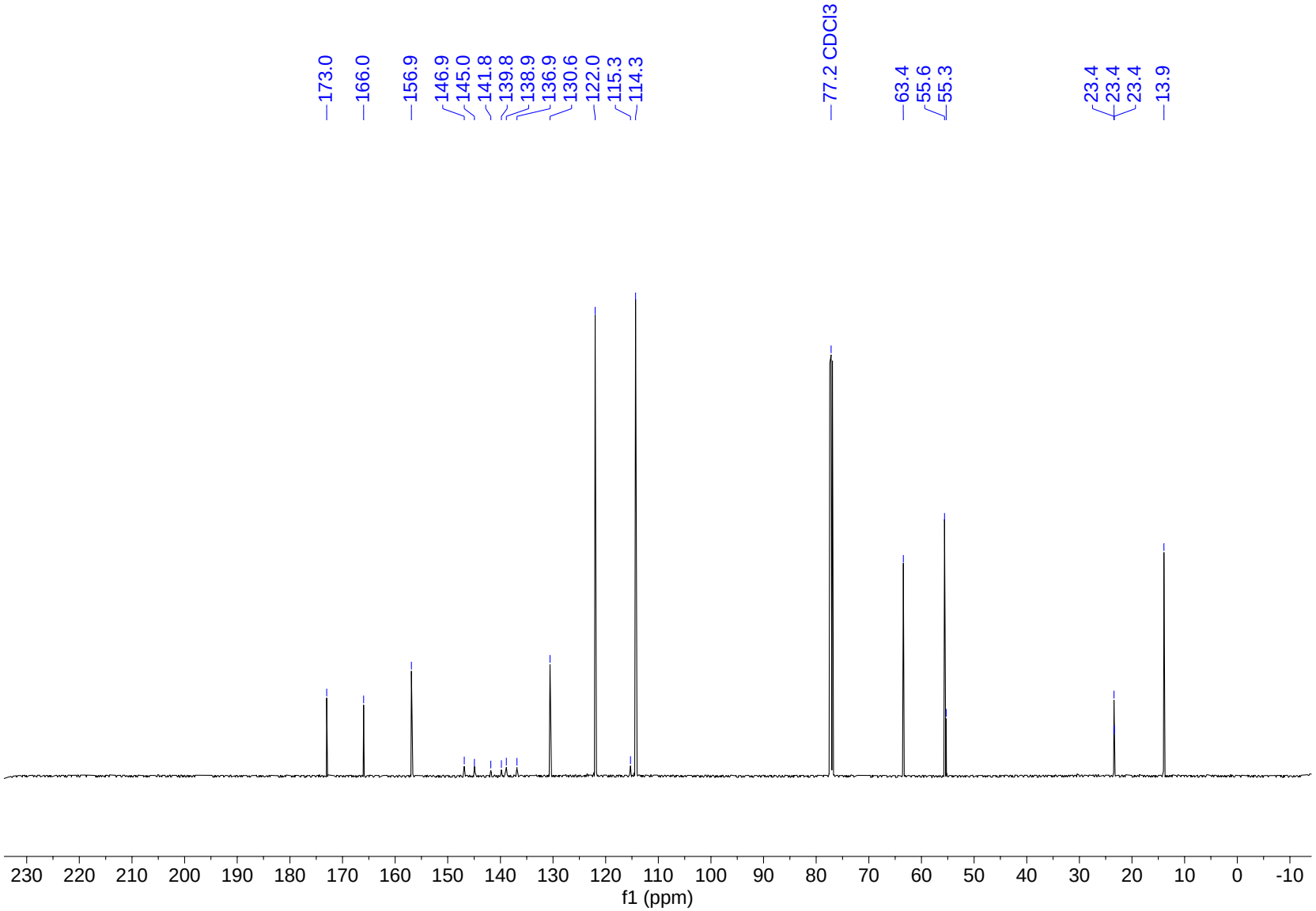


Figure S76: **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) spectrum of **3e**.

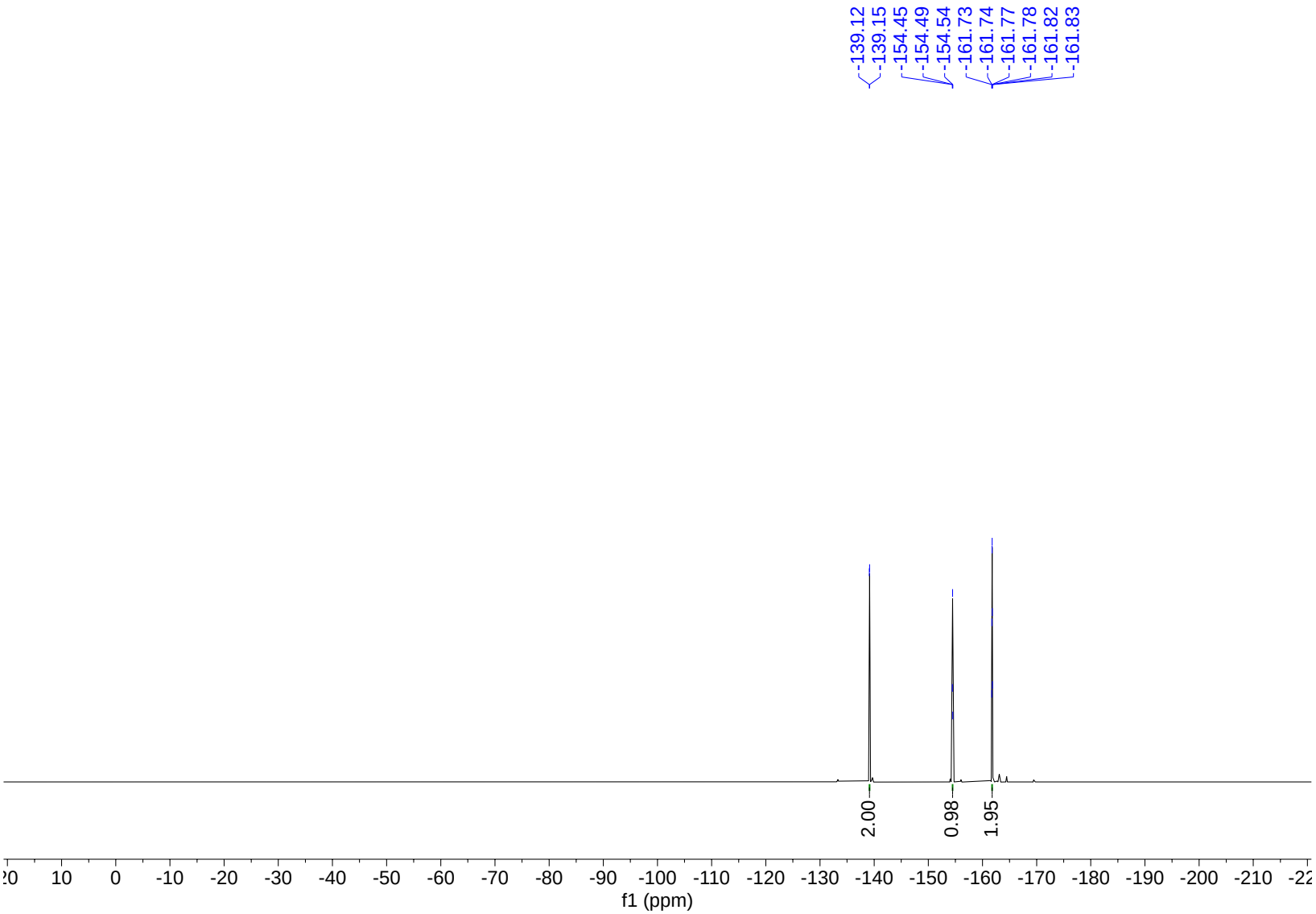


Figure S77: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **3h**.

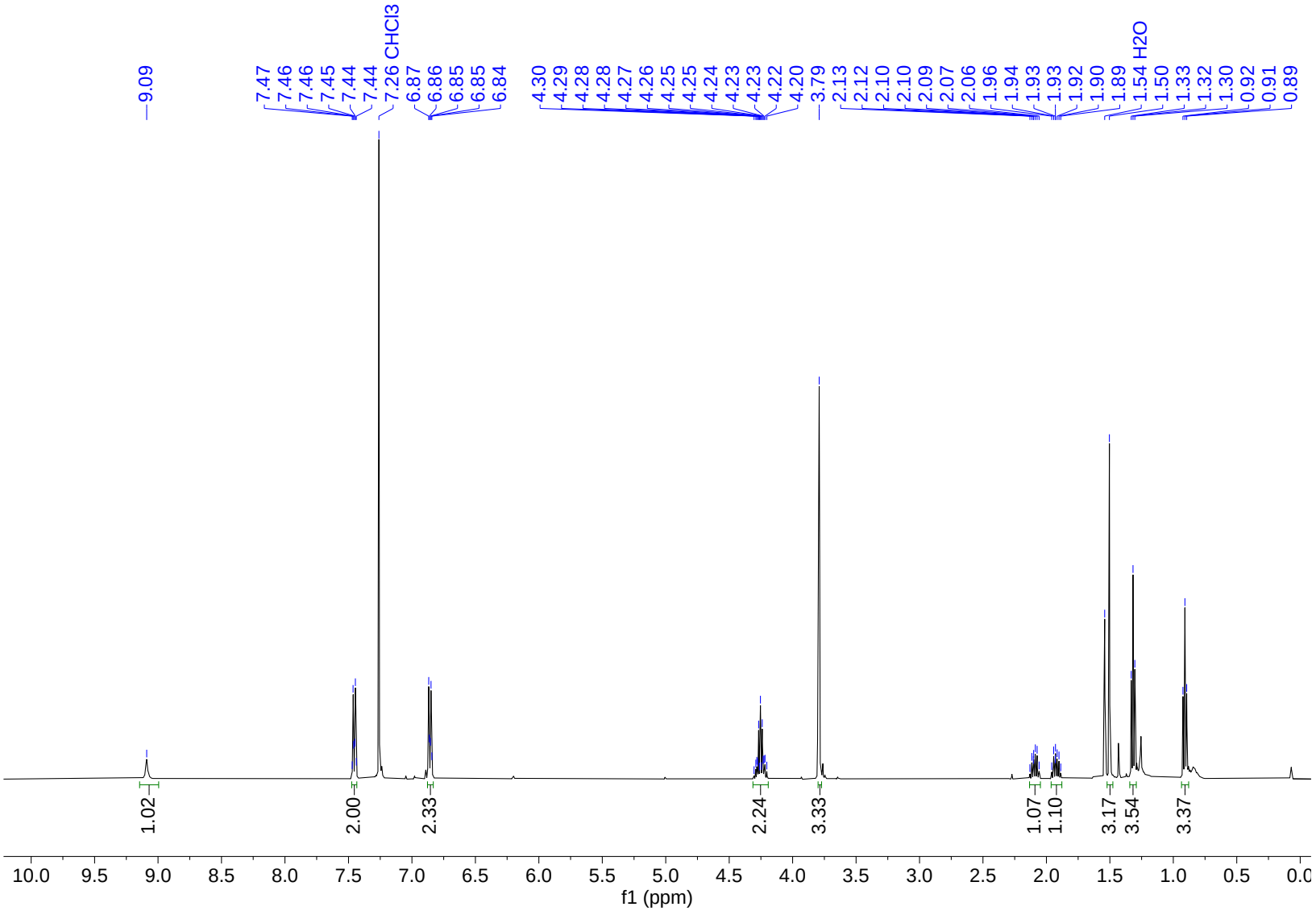


Figure S78: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **3h**.

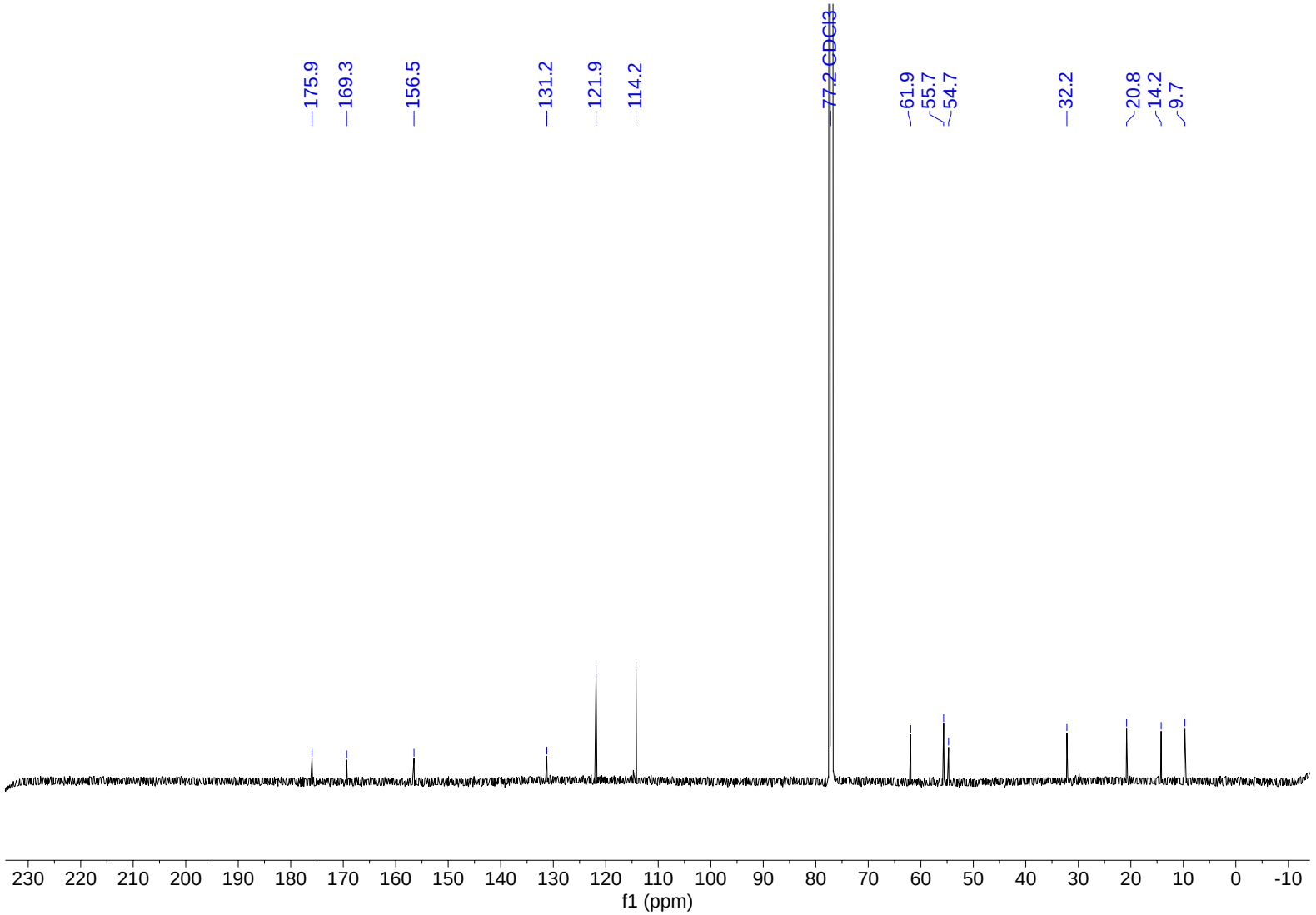


Figure S79: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **3f**.

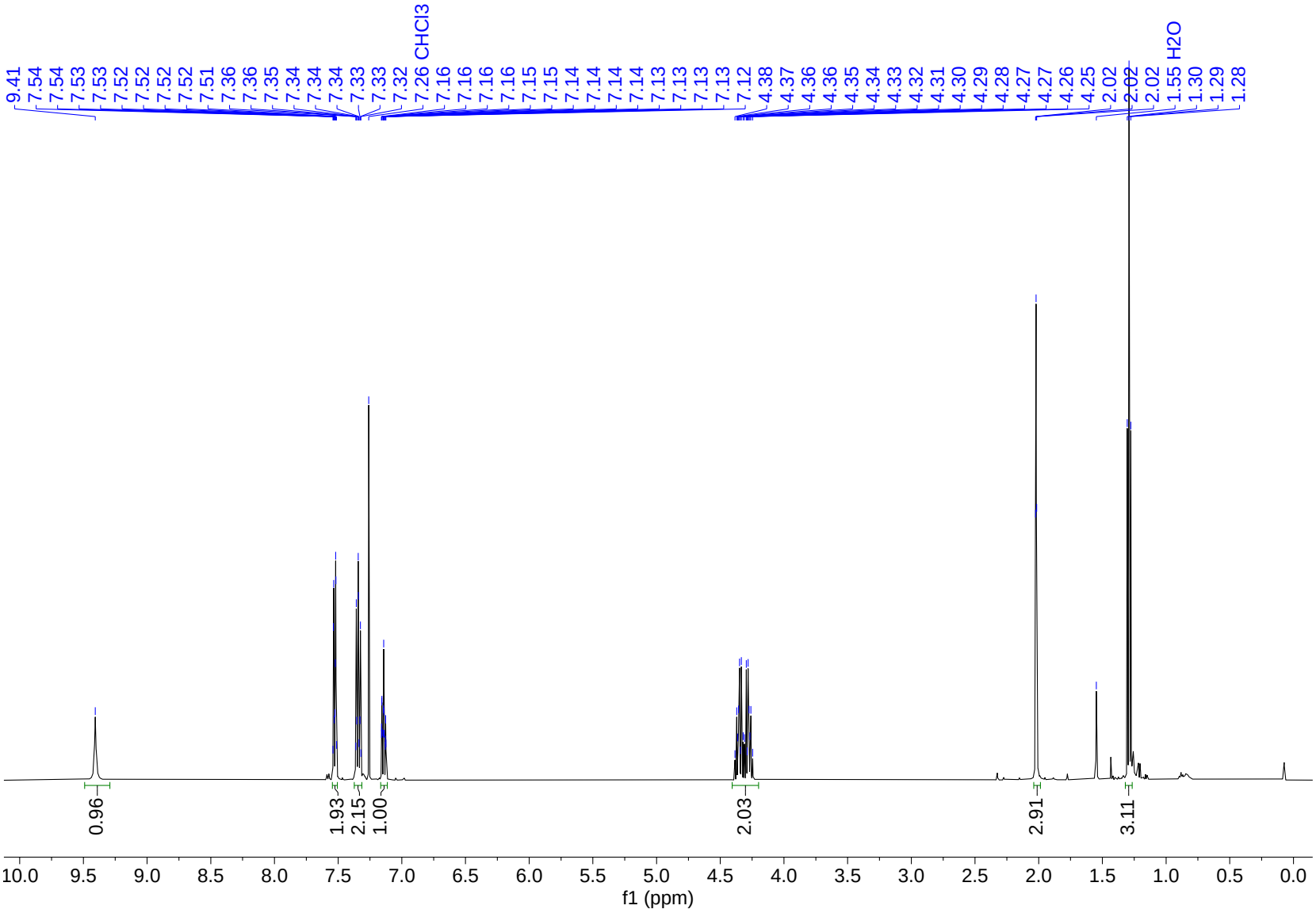


Figure S80: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **3f**.

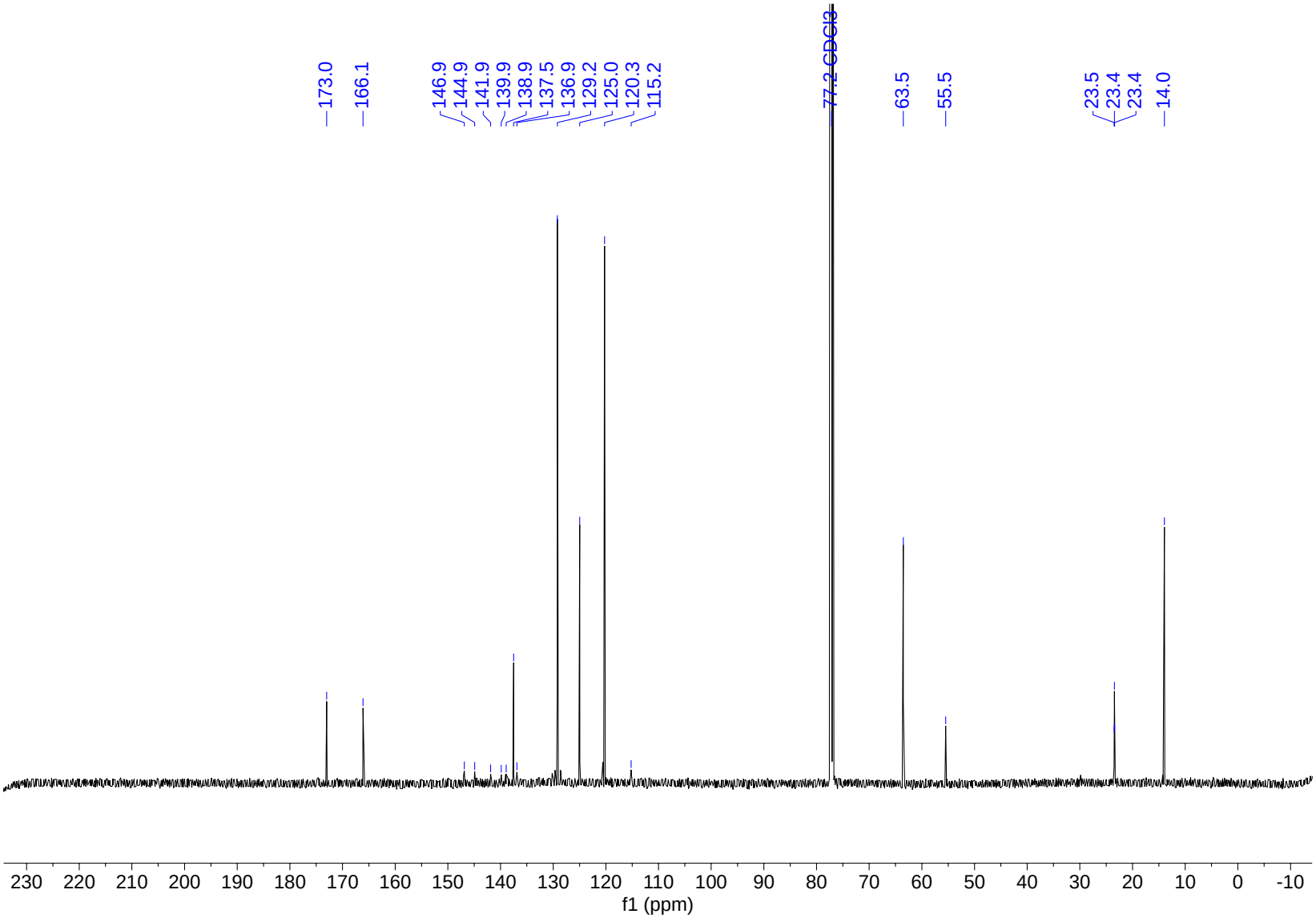


Figure S81: **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) spectrum of **3f**.

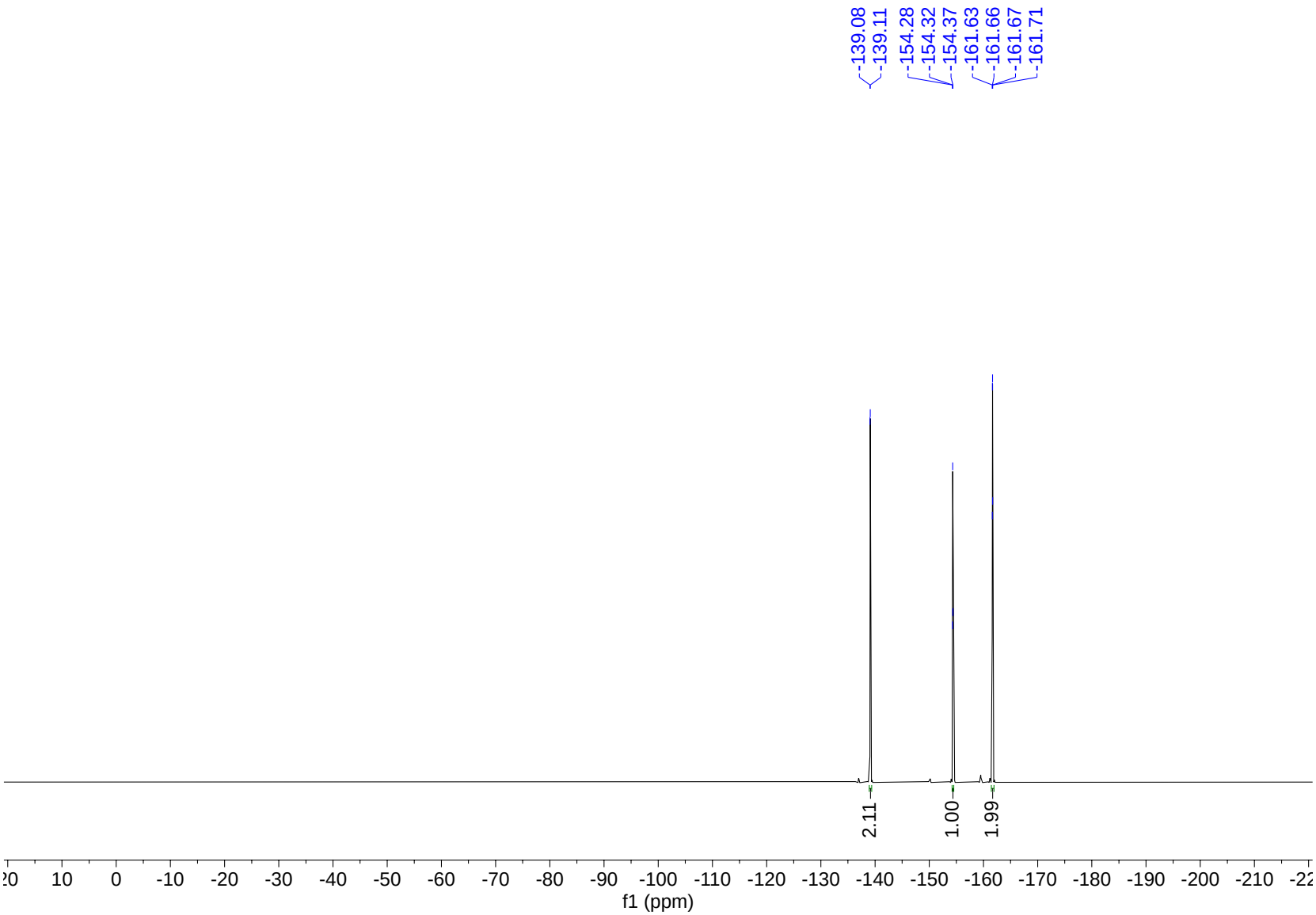


Figure S82: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **7a** contaminated with the β-keto ester.

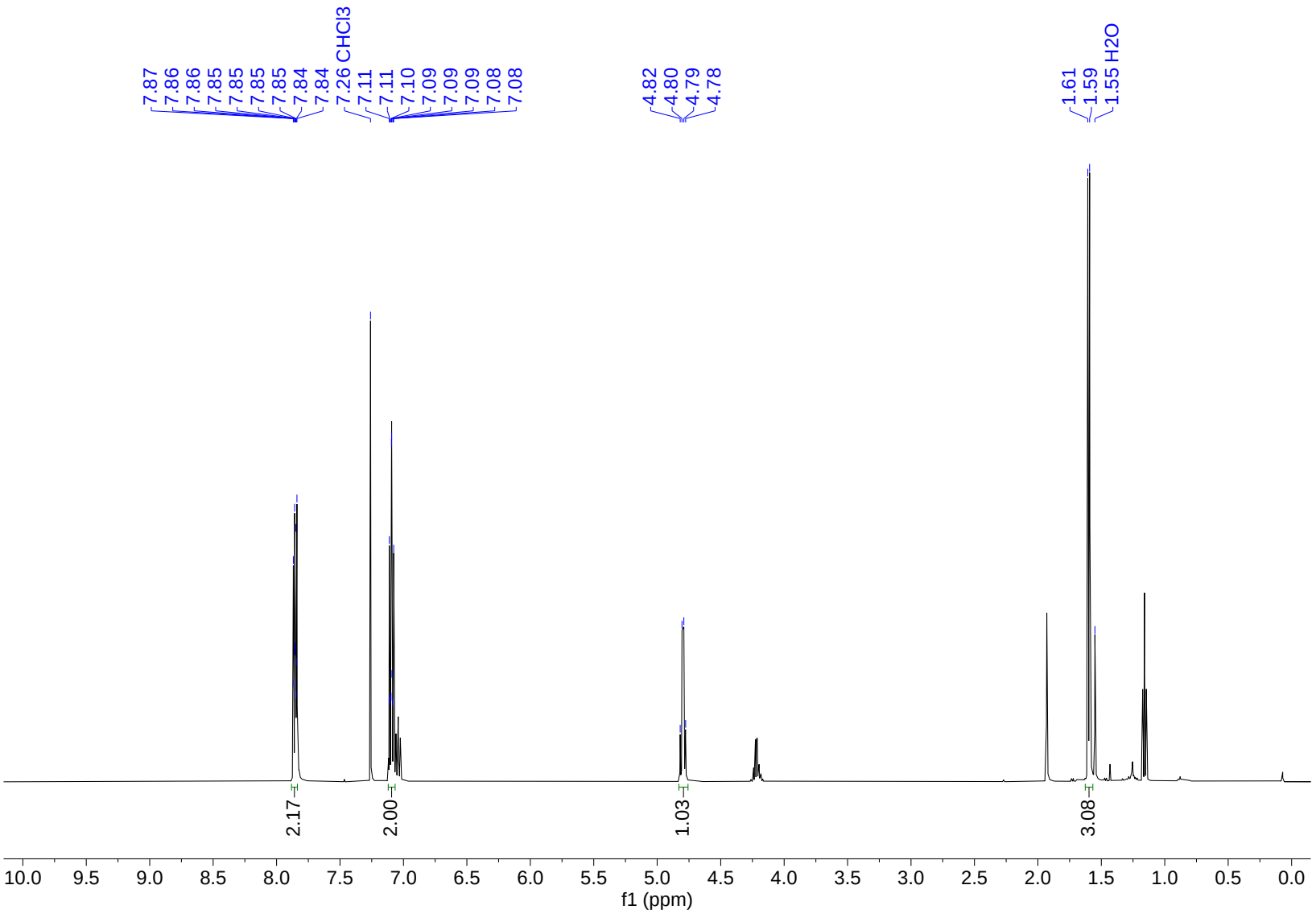


Figure S83: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **7a** contaminated with the β-keto ester.

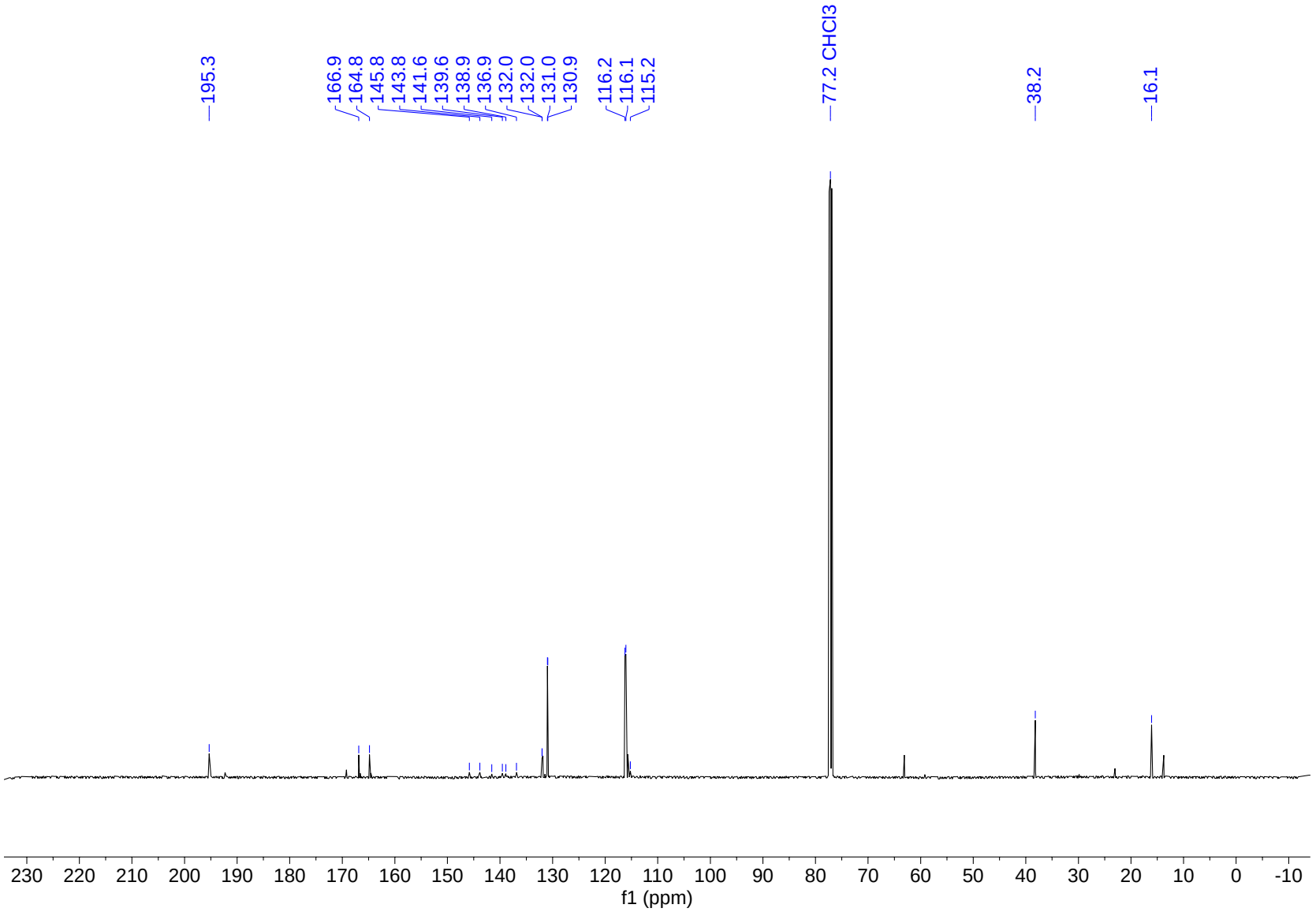


Figure S84: **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) spectrum of **7a** contaminated with the β-keto ester.

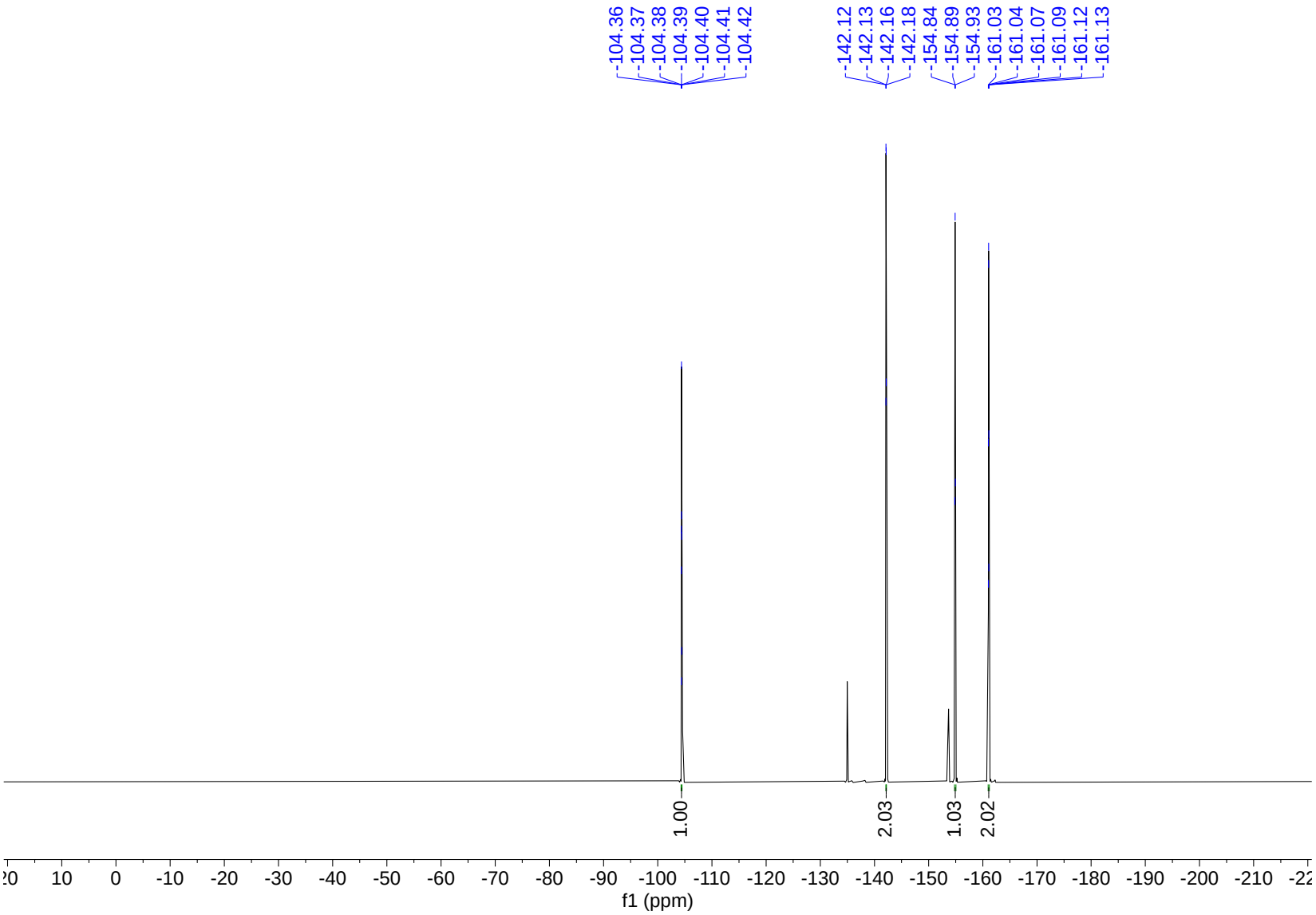


Figure S85: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **7b**.

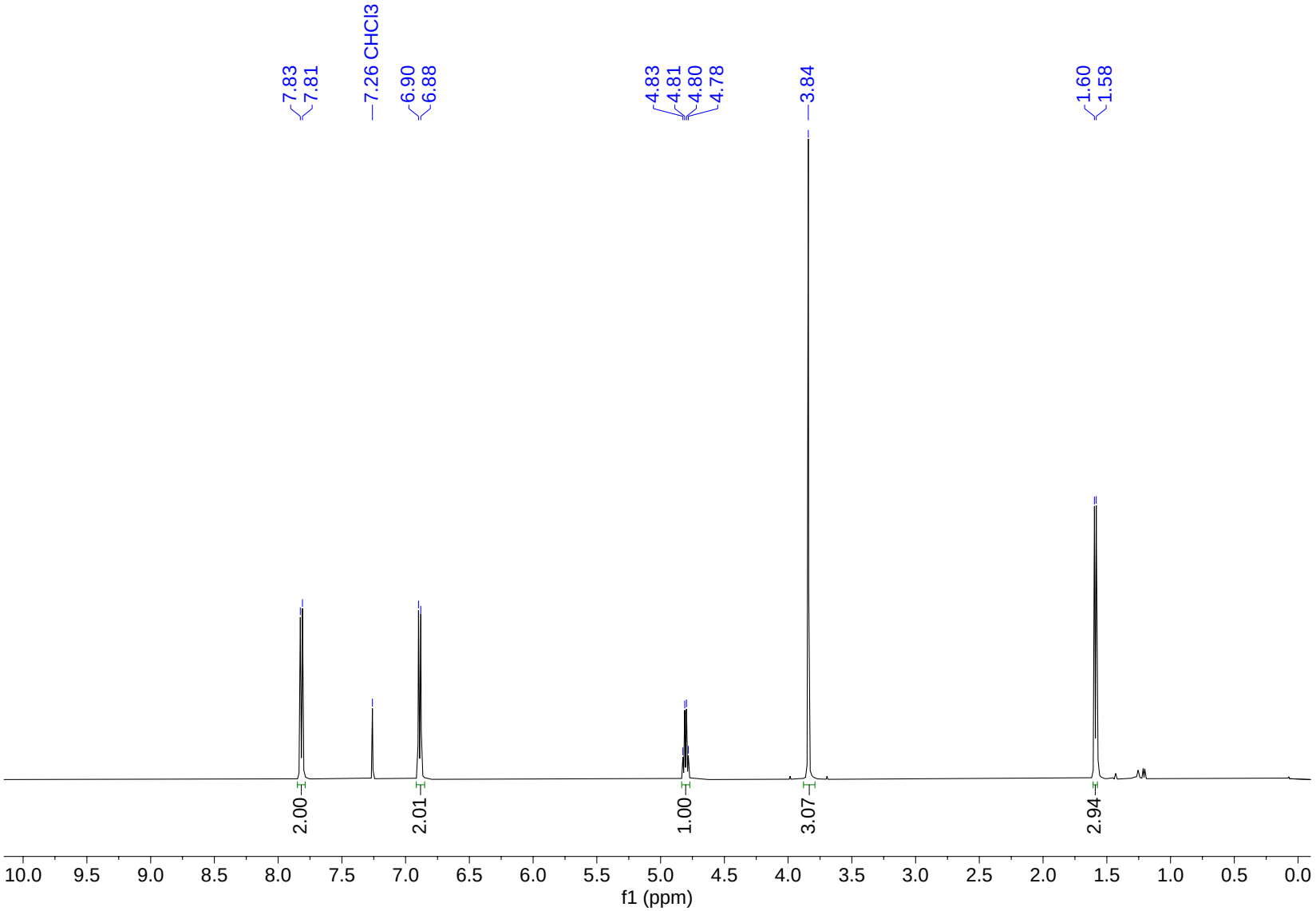


Figure S86: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **7b**.

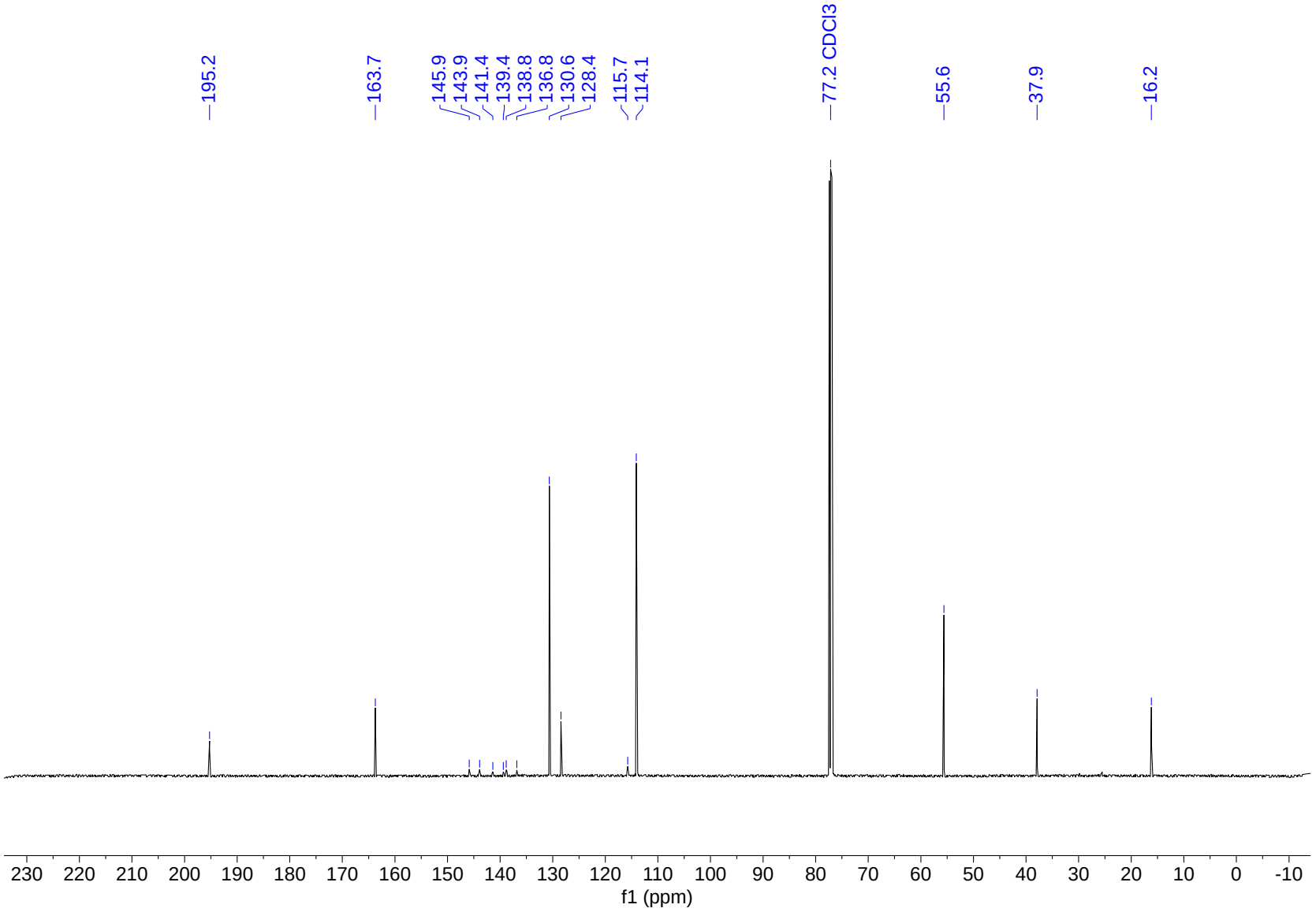


Figure S87: **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) spectrum of **7b**.

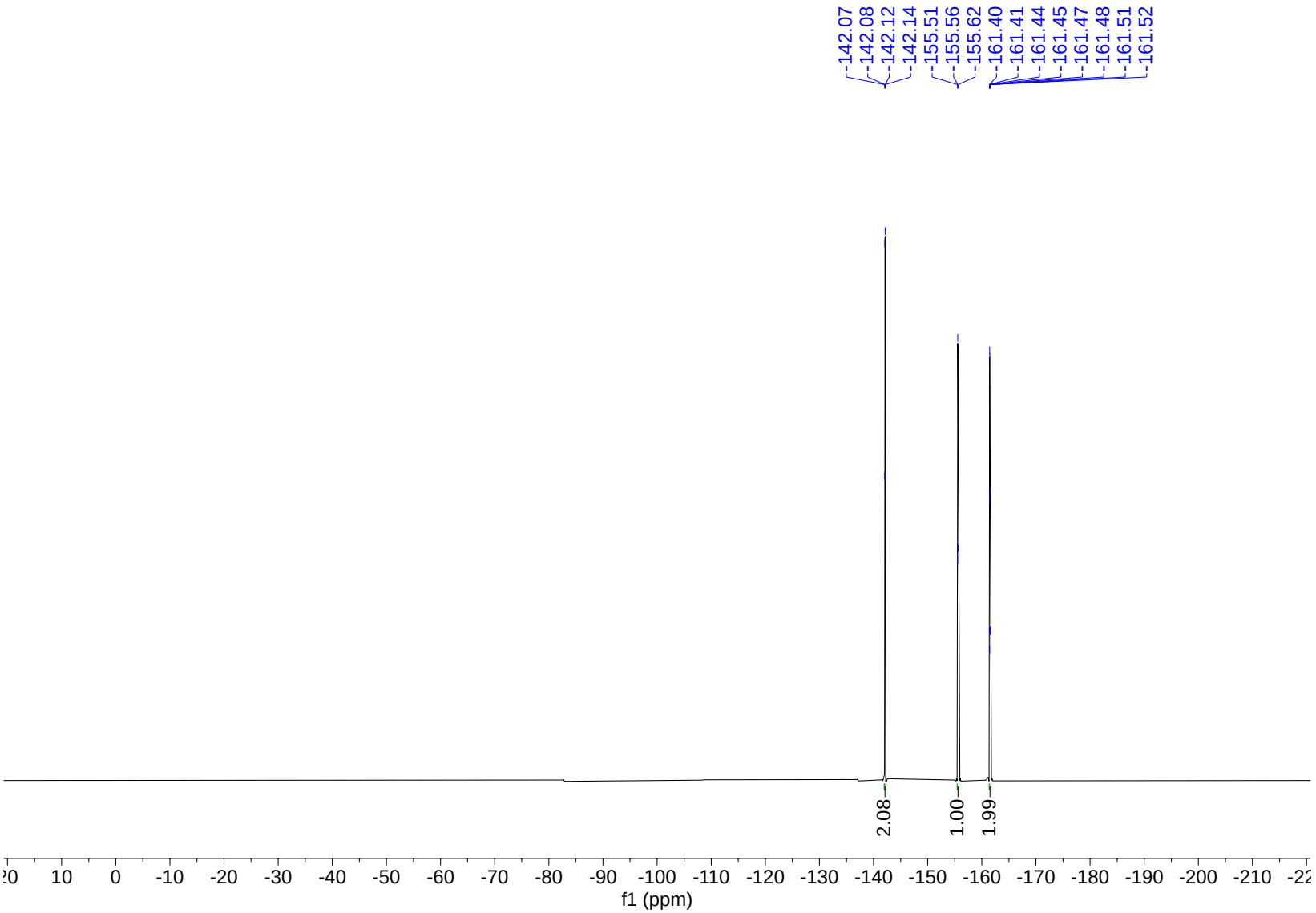


Figure S88: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **7c**.

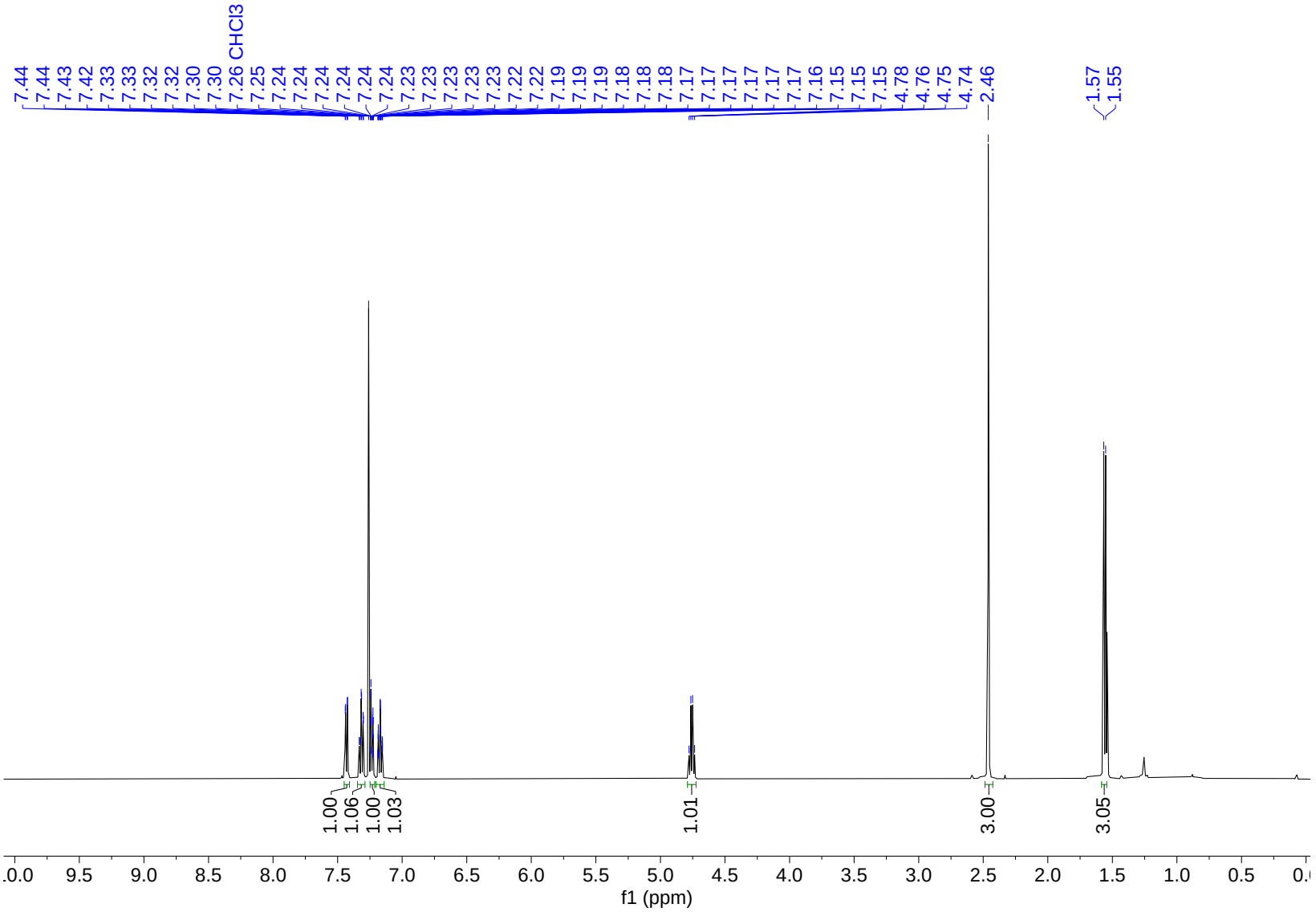


Figure S89: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **7c**.

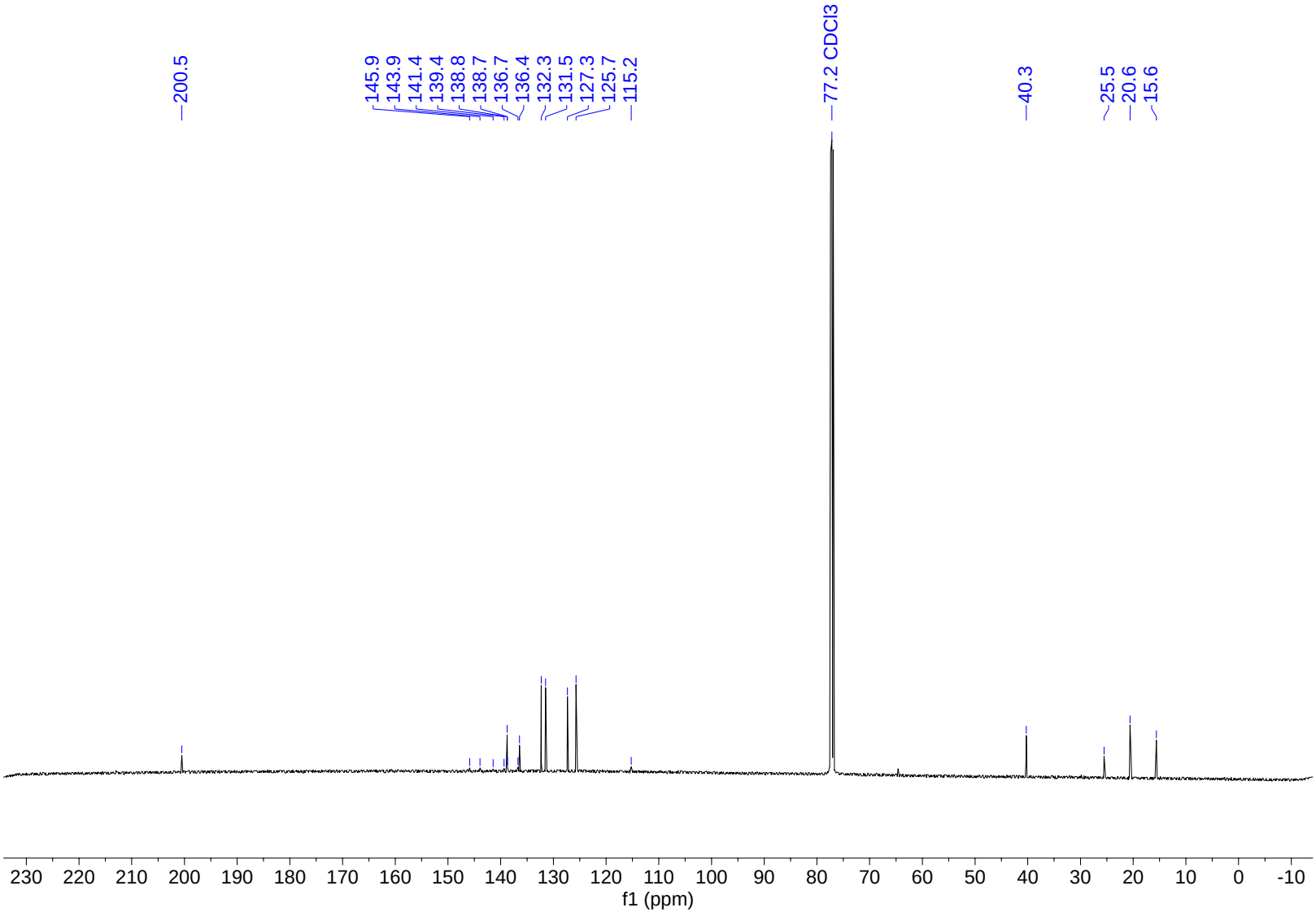


Figure S90: **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) spectrum of **7c**.

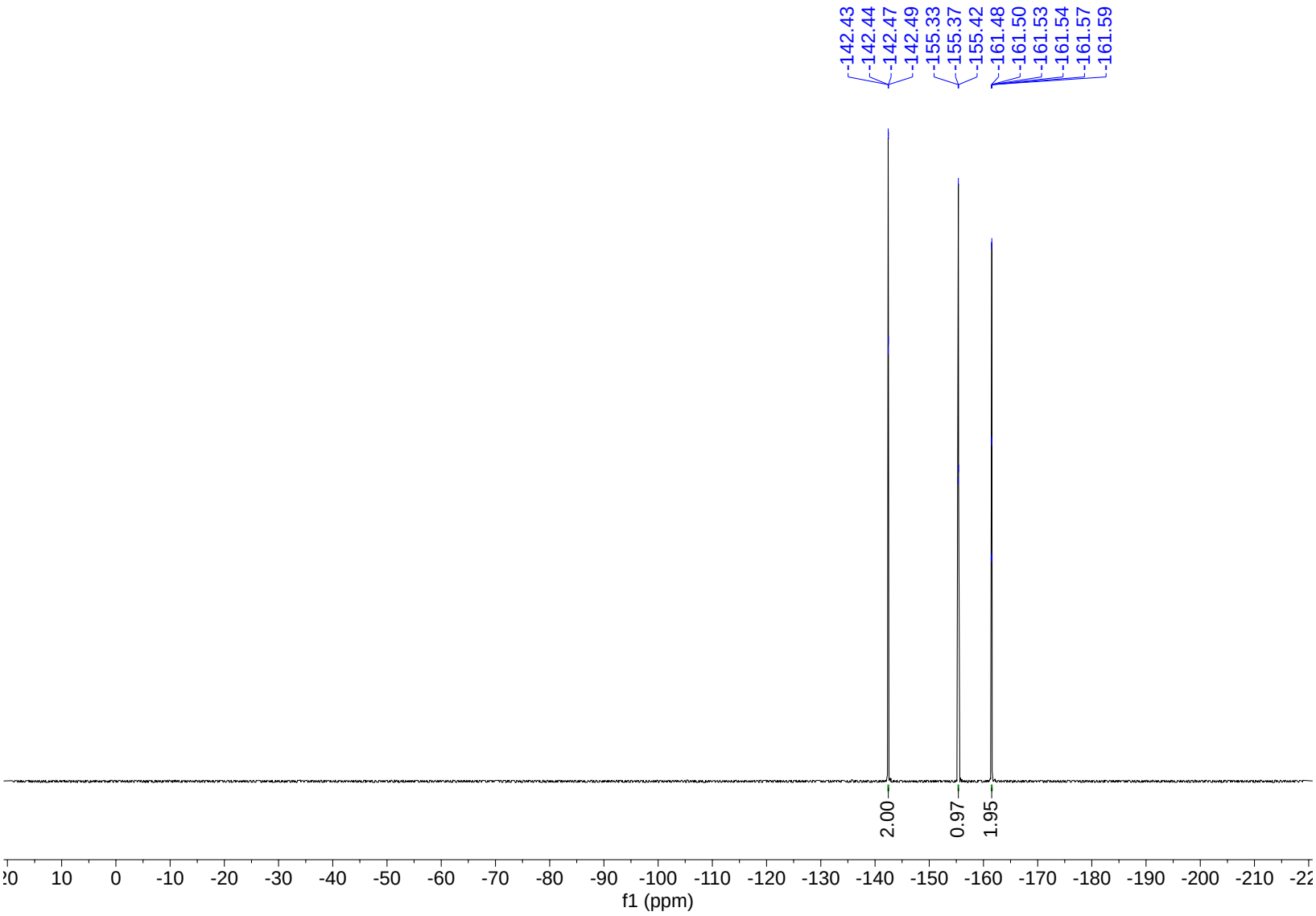


Figure S91: **^{1}H NMR** (500.2 MHz, $CDCl_3$, 298 K) spectrum of **7d**.

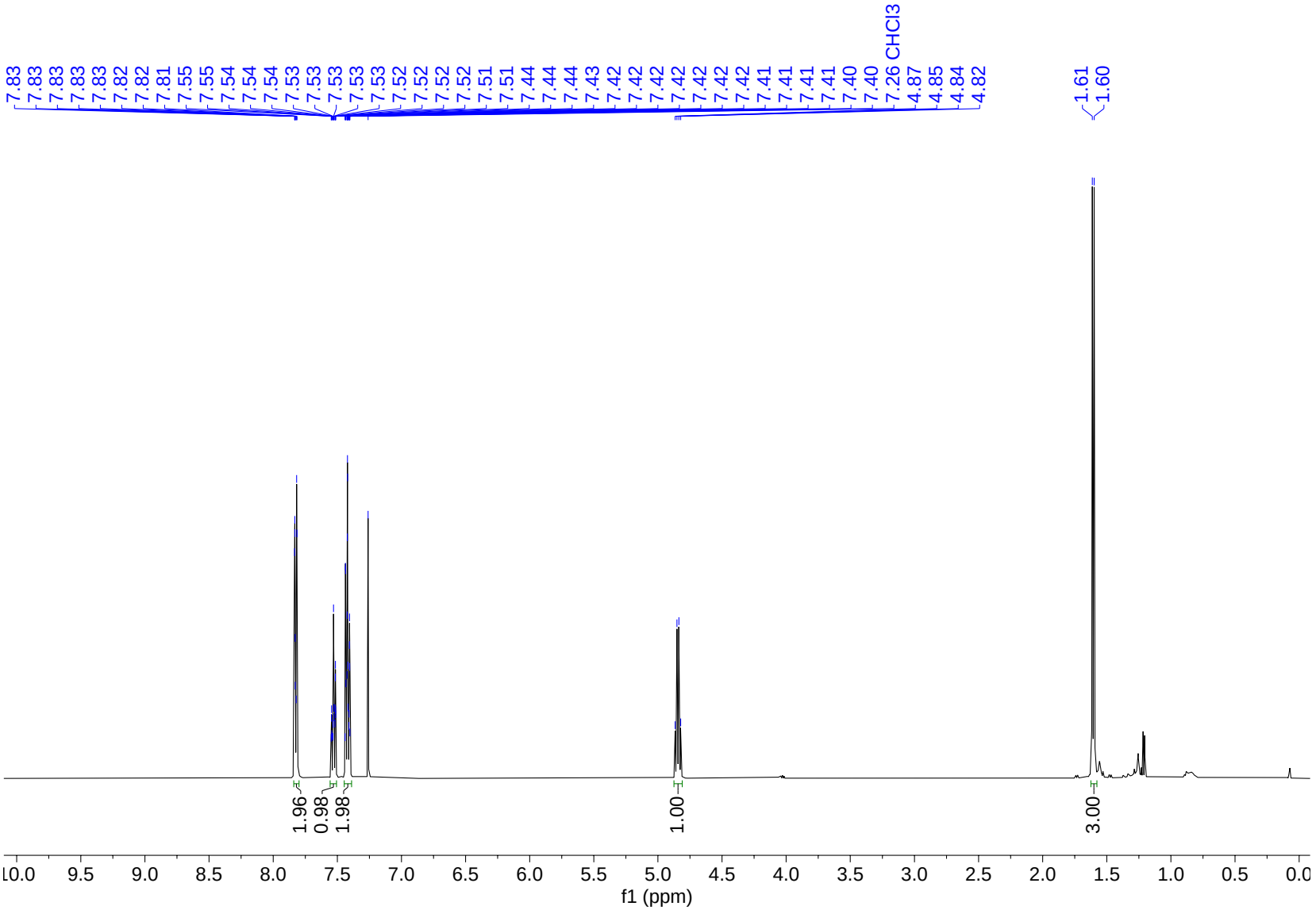


Figure S92: **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K) spectrum of **7d**.

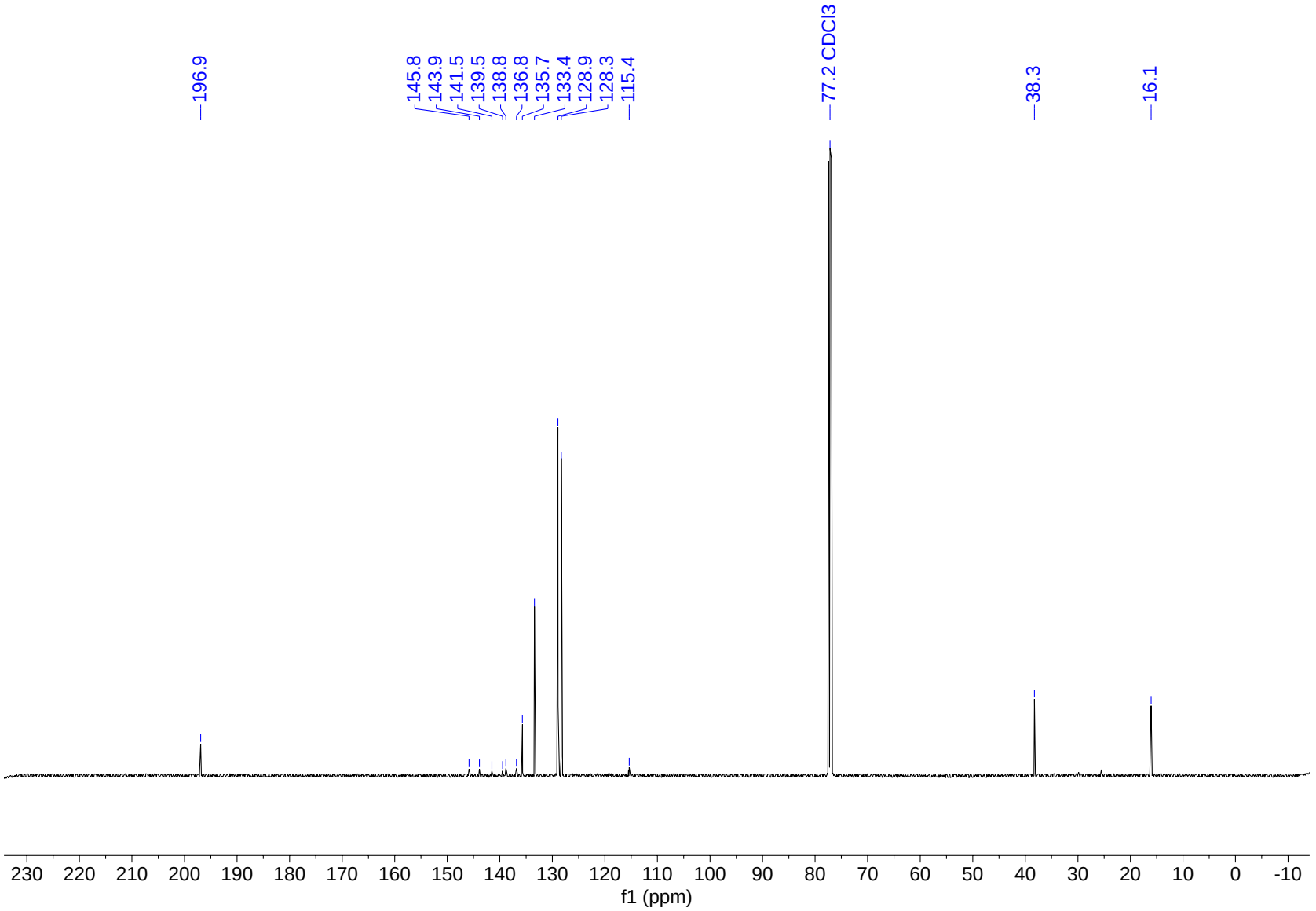


Figure S93: **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) spectrum of **7d**.

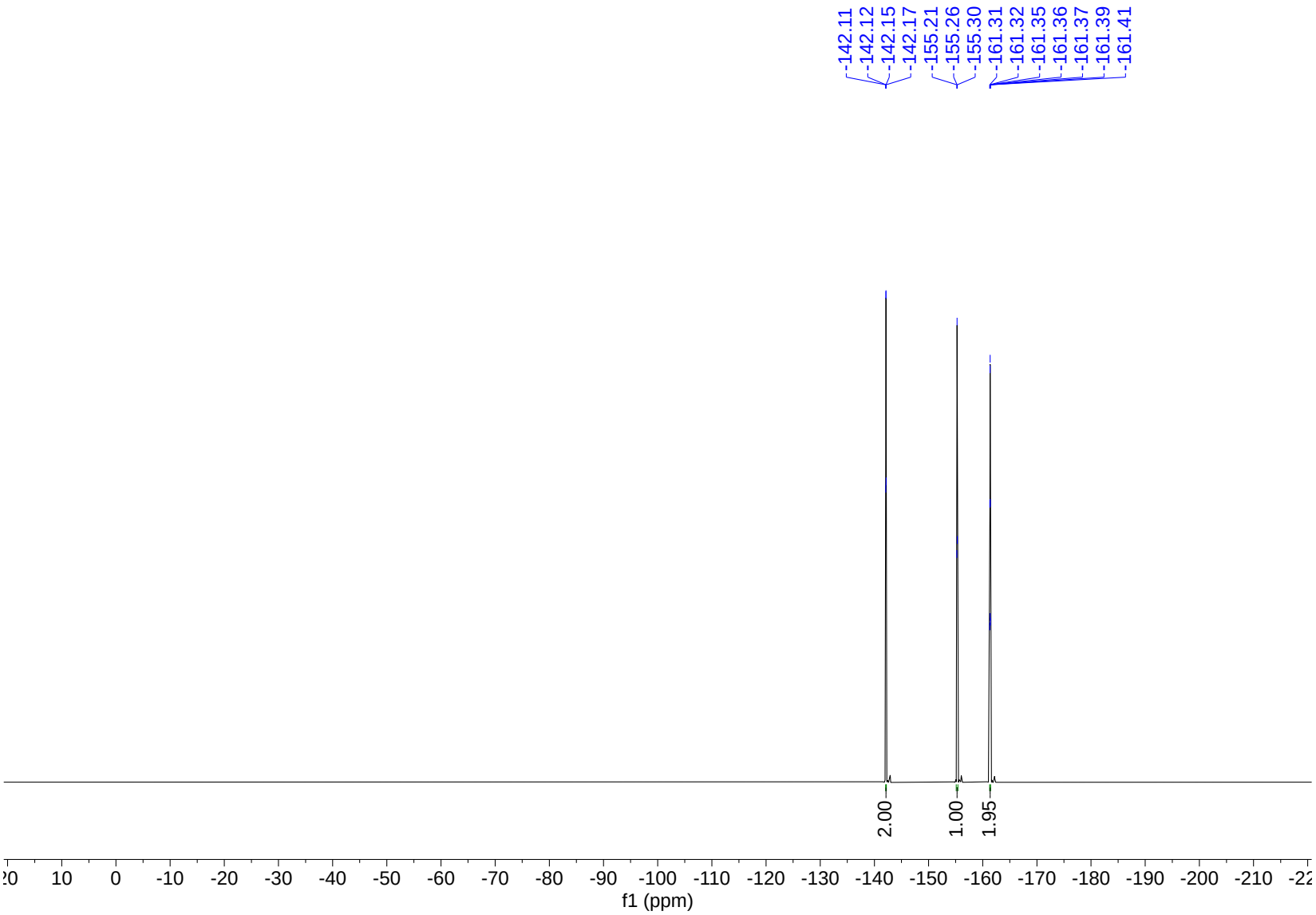


Figure S94: **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K) spectrum of the mixture of **4** and **6**.

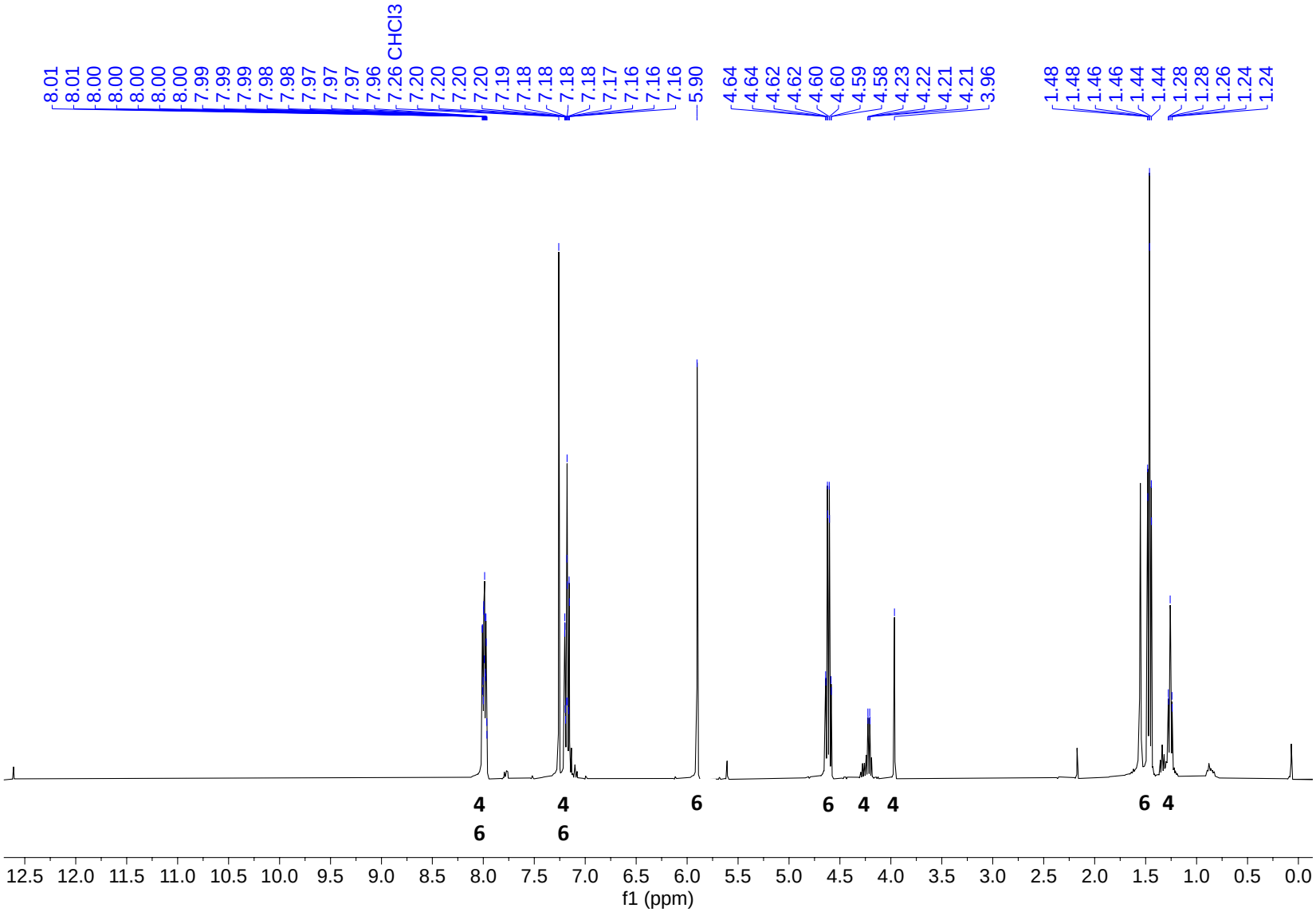


Figure S95: **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K) spectrum of **6**.

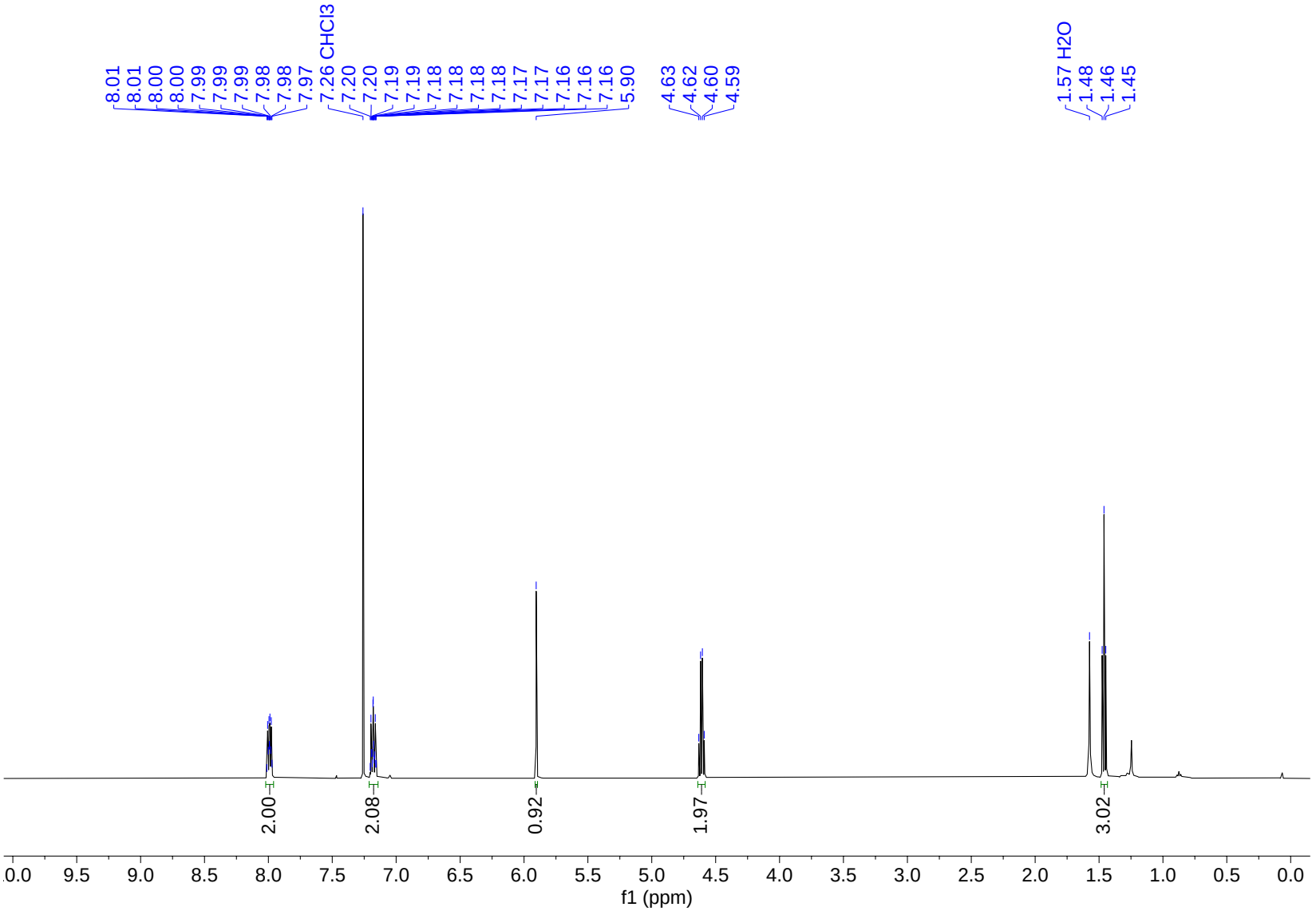


Figure S96: **^{11}B NMR** (157.4 MHz, $CDCl_3$, 298 K) spectrum of **6**.

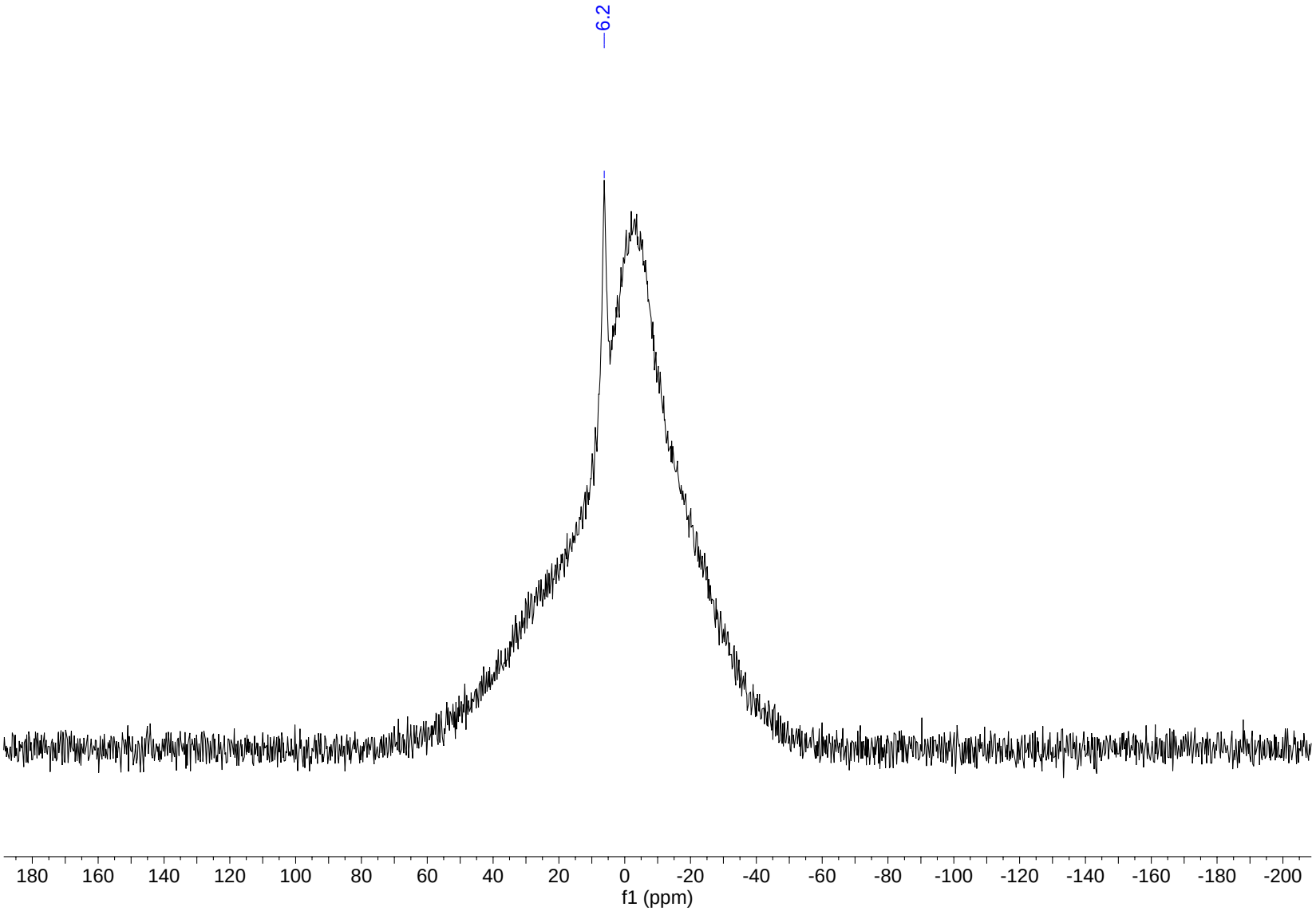


Figure S97: **^{19}F NMR** (470.2 MHz, $CDCl_3$, 298 K) spectrum of **6**.

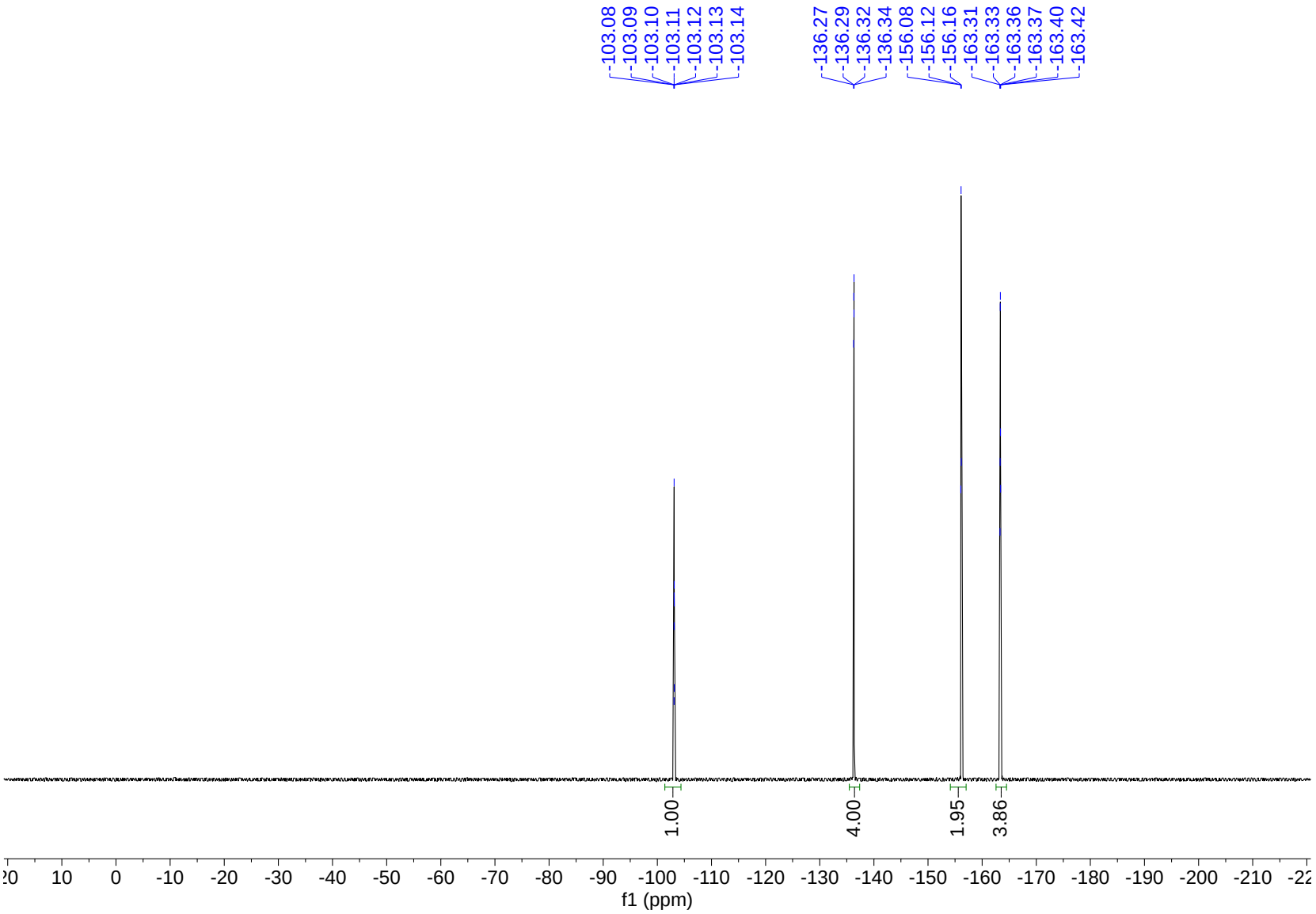
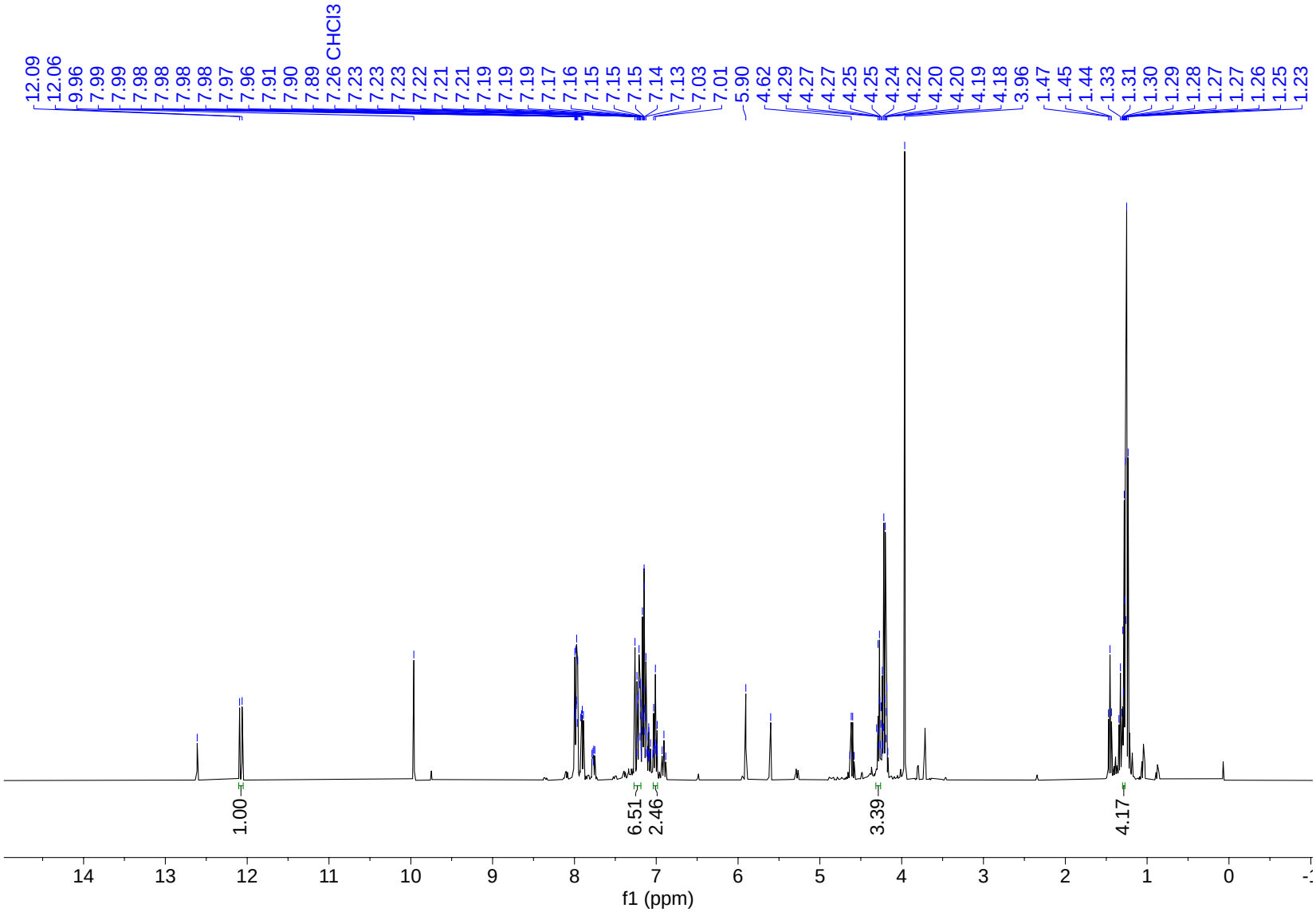


Figure S98: **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K) spectrum of the crude reaction mixture including **5**.



6. Crystallographic Data

6.1 Single crystal X-ray diffraction experimental

Single crystals of **6**, **2a**, **2k**, **2c**, and **2i** were grown by slow evaporation of a concentrated $CHCl_3$ solution. **8** was grown by vapour diffusion using CH_2Cl_2/pentane. Crystallographic studies were undertaken on single crystal mounted in paratone and studied on an Agilent SuperNova Dual Atlas three-circle diffractometer using Cu- Kα radiation and a CCD detector. Measurements were taken at 150(2) K with temperatures maintained using an Oxford cryostream. Data were collected and integrated and data corrected for absorption using a numerical absorption correction based on Gaussian integration over a multifaceted crystal model within CrysAlisPro.[5] The structures were solved by direct methods and refined against F2 within SHELXL-2013.[6] The structures have been deposited with the Cambridge Structural Database (CCDC deposition numbers **2154538**–**2154540**, **2154542**, **2154543**, and **2154565**). These can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

6.2 Solid-state structures

Figure S99: Solid-state structure of compound **6**, thermal ellipsoids drawn at 50% probability. Carbon: black; oxygen: red; boron: pink; fluorine: green. H atoms omitted for clarity.

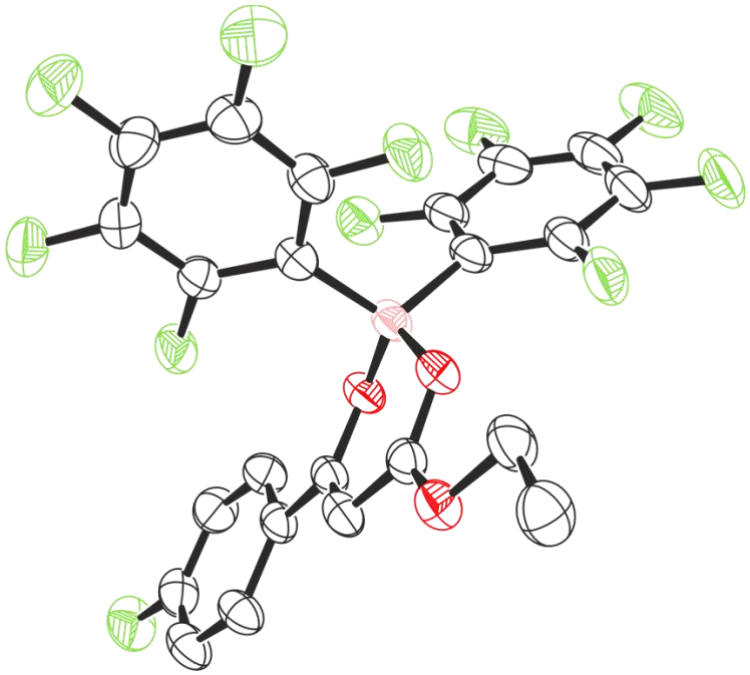


Figure S100: Solid-state structure of compound **2a**, thermal ellipsoids drawn at 50% probability. Carbon: black; oxygen: red; fluorine: green. H atoms omitted for clarity.

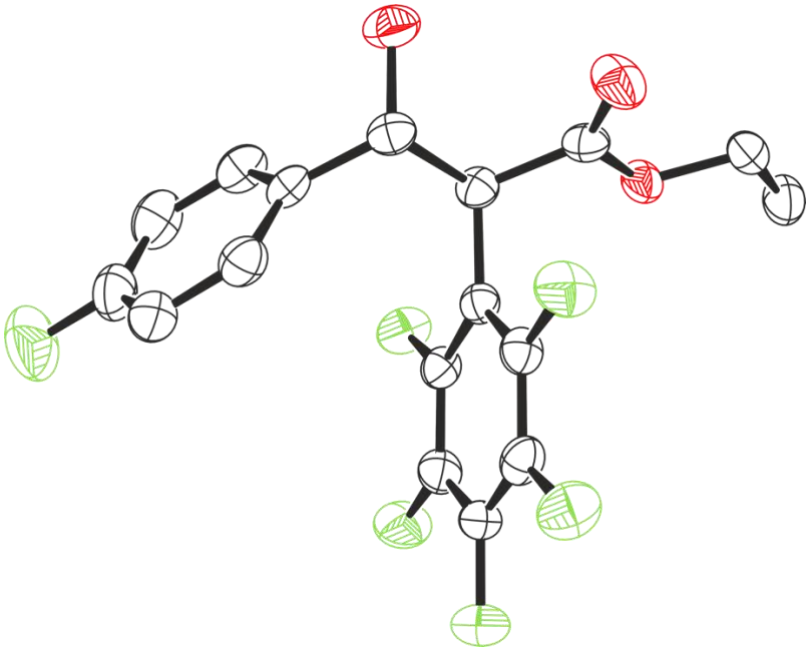


Figure S101: Solid-state structure of compound **2k**, thermal ellipsoids drawn at 50% probability. Carbon: black; oxygen: red; fluorine: green. H atoms omitted for clarity.

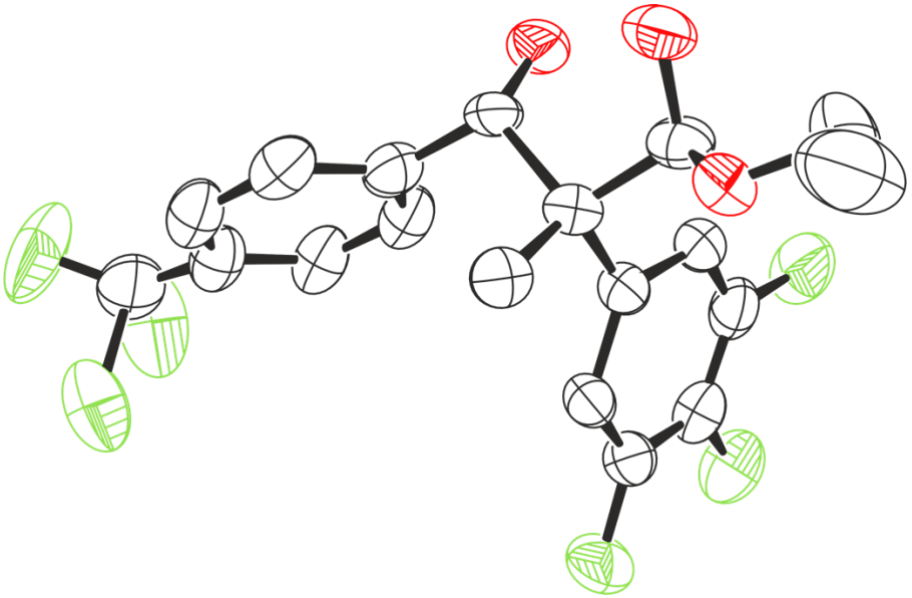


Figure S102: Solid-state structure of compound **2c**, thermal ellipsoids drawn at 50% probability. Carbon: black; oxygen: red; fluorine: green. H atoms omitted for clarity.

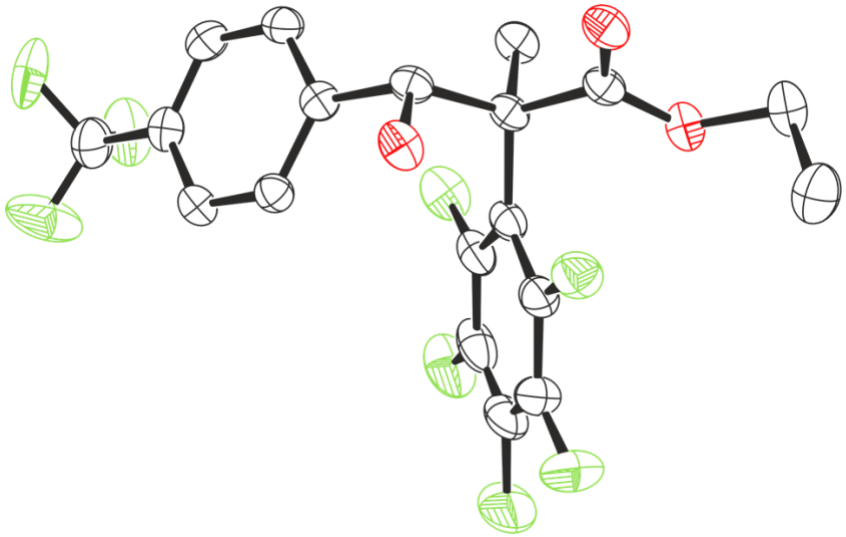


Figure S103: Solid-state structure of compound **2i**, thermal ellipsoids drawn at 50% probability. Carbon: black; oxygen: red; fluorine: green. H atoms omitted for clarity.

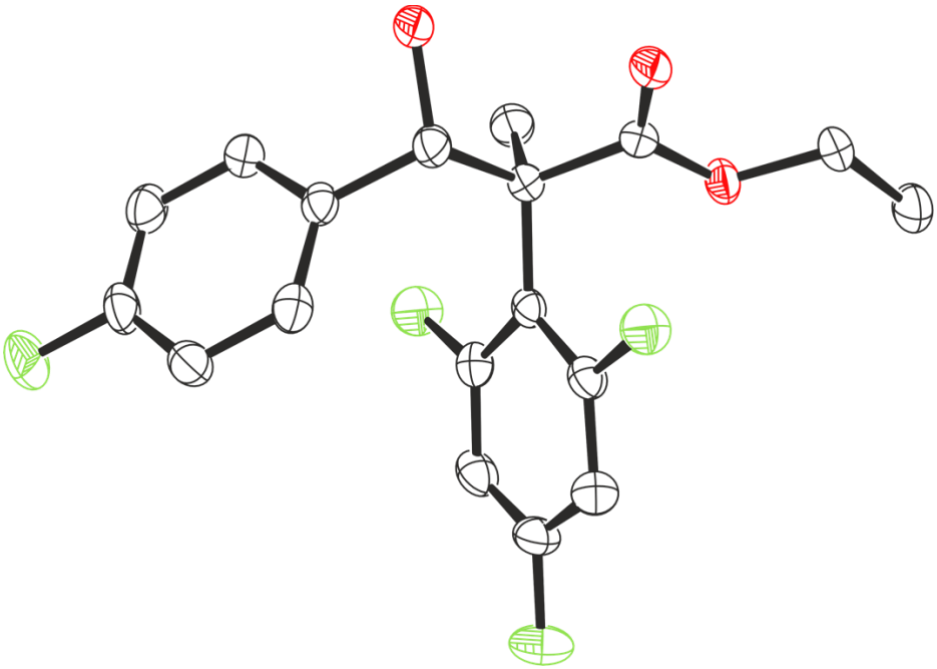
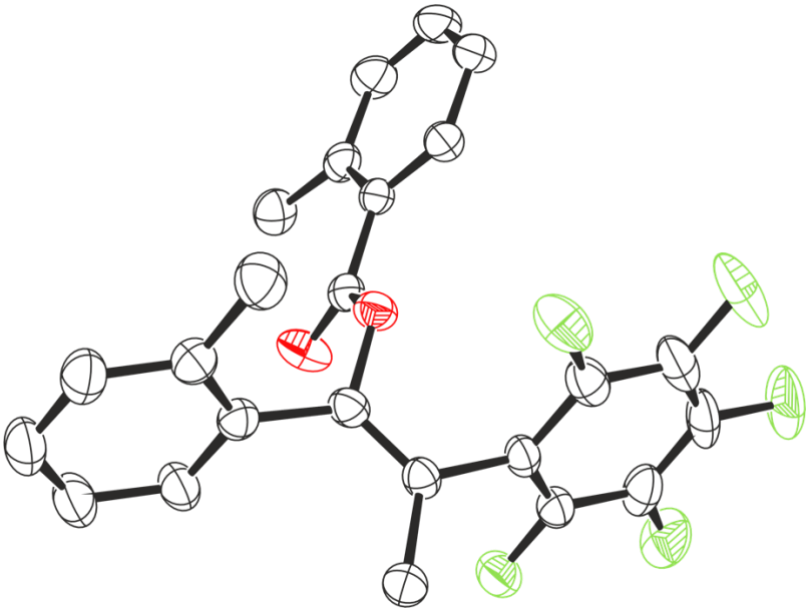


Figure S104: Solid-state structure of compound **8**, thermal ellipsoids drawn at 50% probability. Carbon: black; oxygen: red; fluorine: green. H atoms omitted for clarity.



6.3 X-ray refinement data

Table S1. Crystal data and structure refinement for compound **6**. [RM2146b] CCDC 2154540

Empirical formula	$C_{23}H_{10}BF_{11}O_3$
Formula weight	554.12
Temperature/K	180(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	9.1068(3)
b/Å	13.2125(4)
c/Å	18.2143(7)
α/°	90
β/°	93.148(3)
γ/°	90
Volume/Å^3	2188.32(13)
Z	4
Density (ρ_{calc}g/cm^3)	1.682
Absorption coefficient (μ/mm^{-1})	1.555
F(000)	1104.0
Crystal size/mm^3	0.492 × 0.115 × 0.073
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	4.136 to 72.900
Index ranges	$-11 \leq h \leq 8$, $-15 \leq k \leq 16$, $-20 \leq l \leq 22$
Reflections collected	8687
Independent reflections	4222 [R_{int} = 0.0256, R_{sigma} = 0.0334]
Data/restraints/parameters	4222/0/344
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.041, wR_2 = 0.106
Final R indexes [all data]	R_1 = 0.057, wR_2 = 0.120
Largest diff. peak/hole / e Å^{-3}	0.233/-0.230

Table S2. Crystal data and structure refinement for compound **2a** (RM2140) CCDC 2154539

Empirical formula	$C_{17}H_{12}F_6O_3$
Formula weight	378.27
Temperature/K	200(2)
Crystal system	triclinic
Space group	*P-1*
a/Å	5.8206 (3)
b/Å	17.0082 (9)
c/Å	18.1536 (10)
α/°	63.134 (5)
β/°	87.435 (4)
γ/°	88.496 (4)
Volume/Å^3	1601.54 (16)
Z	4
Density (ρ_{calc}g/cm^3)	1.569
Absorption coefficient (μ/mm^{-1})	0.152
F(000)	768
Crystal size/mm^3	0.30 × 0.15 × 0.10
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.008 to 28.242
Index ranges	$-7 \leq h \leq 7$, $-23 \leq k \leq 22$, $-20 \leq l \leq 24$
Reflections collected	14036
Independent reflections	7680 [R_{int} = 0.0337, R_{sigma} = 0.0597]
Data/restraints/parameters	7680/0/475
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.059, wR_2 = 0.141
Final R indexes [all data]	R_1 = 0.105, wR_2 = 0.170
Largest diff. peak/hole / e Å^{-3}	0.63/-0.27

Table S3. Crystal data and structure refinement for compound **2k** (RM1831h) CCDC 2154538

Empirical formula	$C_{19}H_{16}F_6O_3$
Formula weight	406.32
Temperature/K	200(2)
Crystal system	triclinic
Space group	*P-1*
a/Å	7.1188 (2)
b/Å	10.3636 (3)
c/Å	12.8288 (4)
α/°	101.608 (3)
β/°	91.454 (2)
γ/°	100.640 (3)
Volume/Å^3	909.24 (5)
Z	2
Density (ρ_{calc}g/cm^3)	1.484
Absorption coefficient (μ/mm^{-1})	1.236
F(000)	416.0
Crystal size/mm^3	0.548 × 0.425 × 0.188
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	4.401 to 73.332
Index ranges	$-8 \leq h \leq 8$, $-12 \leq k \leq 12$, $-15 \leq l \leq 15$
Reflections collected	31816
Independent reflections	3644 [R_{int} = 0.0433, R_{sigma} = 0.0175]
Data/restraints/parameters	3644/0/344
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.055, wR_2 = 0.139
Final R indexes [all data]	R_1 = 0.067, wR_2 = 0.147
Largest diff. peak/hole / e Å^{-3}	0.23/-0.23

Table S4. Crystal data and structure refinement for compound **2c** (RM2204) CCDC 2154542

Empirical formula	$C_{19}H_{14}F_8O_3$
Formula weight	442.30
Temperature/K	180(2)
Crystal system	triclinic
Space group	*P-1*
a/Å	9.4520 (5)
b/Å	10.4243 (9)
c/Å	10.9360 (7)
α/°	71.015 (7)
β/°	74.269 (5)
γ/°	66.462 (7)
Volume/$Å^3$	921.67 (13)
Z	2
Density ($\rho_{calc}g/cm^3$)	1.594
Absorption coefficient (μ/mm^{-1})	0.160
F(000)	448.0
Crystal size/mm^3	0.442 × 0.227 × 0.137
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.924 to 28.971
Index ranges	$-11 \leq h \leq 11$, $-12 \leq k \leq 10$, $-12 \leq l \leq 12$
Reflections collected	6540
Independent reflections	3144 [R_{int} = 0.0217, R_{sigma} = 0.0338]
Data/restraints/parameters	3144/1/304
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.038, wR_2 = 0.088
Final R indexes [all data]	R_1 = 0.050, wR_2 = 0.097
Largest diff. peak/hole / e $Å^{-3}$	0.18/-0.21

Table S5. Crystal data and structure refinement for compound **2i** (RM2205) CCDC 2154543

Empirical formula	$C_{18}H_{16}F_4O_3$
Formula weight	356.31
Temperature/K	180 (2)
Crystal system	triclinic
Space group	*P-1*
a/Å	8.0494 (7)
b/Å	9.9716 (7)
c/Å	11.4118 (7)
α/°	113.593 (6)
β/°	103.792 (7)
γ/°	90.918 (7)
Volume/Å^3	808.80 (11)
Z	2
Density (ρ_{calc}g/cm^3)	1.463
Absorption coefficient (μ/mm^{-1})	0.129
F(000)	368.0
Crystal size/mm^3	0.367 × 0.312 × 0.264
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.087 to 28.697
Index ranges	$-9 \leq h \leq 6$, $-12 \leq k \leq 10$, $-13 \leq l \leq 13$
Reflections collected	6366
Independent reflections	2948 [R_{int} = 0.0233, R_{sigma} = 0.0384]
Data/restraints/parameters	2948/1/231
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.038, wR_2 = 0.081
Final R indexes [all data]	R_1 = 0.057, wR_2 = 0.092
Largest diff. peak/hole / e Å^{-3}	0.22/-0.21

Table S6. Crystal data and structure refinement for compound **8** (RM2221) CCDC 2154565

Empirical formula	$C_{24}H_{17}F_5O_2$
Formula weight	432.37
Temperature/K	180 (2)
Crystal system	triclinic
Space group	*P-1*
a/Å	7.8551 (4)
b/Å	7.9171 (4)
c/Å	17.1195 (13)
α/°	101.373 (6)
β/°	99.385 (5)
γ/°	101.484 (5)
Volume/$Å^3$	999.91 (11)
Z	2
Density ($\rho_{calc}g/cm^3$)	1.436
Absorption coefficient (μ/mm^{-1})	0.122
F(000)	444.0
Crystal size/mm^3	0.234 × 0.202 × 0.041
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.266 to 29.399
Index ranges	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-16 \leq l \leq 23$
Reflections collected	8968
Independent reflections	4669 [R_{int} = 0.0040, R_{sigma} = 0.0602]
Data/restraints/parameters	4669/0/283
Goodness-of-fit on F^2	1.094
Final R indexes [I>=2σ (I)]	R_1 = 0.088, wR_2 = 0.233
Final R indexes [all data]	R_1 = 0.118, wR_2 = 0.256
Largest diff. peak/hole / e $Å^{-3}$	0.40/-0.31

7. References

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