Unprecedentedly Simple Method of Synthesis of Aryl Azides and 3-Hydroxytriazenes

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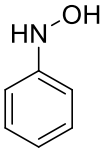
Supporting Information

Contents

General Experimental Procedures

All arylamines, sodium nitrite, hydroxylamine hydrochloride, zinc dust and ammonium chloride were purchased from Sigma-Aldrich. NMR spectra were obtained on a Bruker "Avance 600" (600 MHz ^{1}H, 151 MHz ^{13}C). The chemical shifts are frequency referenced relative to the residual undeuterated solvent peaks. Coupling constants J are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as ''s", ''d", "t" or ''m" for singlet, doublet, triplet or multiplet, respectively. The abbreviation ''br" is given for broadened signals.

N-phenylhydroxylamine[1]



N-phenylhydroxylamine was prepared according to published procedure.[1] Careful recrystallization from benzene yielded 54% of sufficiently pure product as light yellow needles.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.02 – 6.99 (m, 3H), 6.17 (s, 2H).

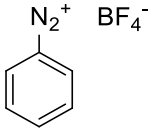
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 149.6 , 129.1 , 122.7 , 115.0.

Aryl diazonium tetrafluoroborates

General procedure for the preparation of aryldiazonium tetrafluoroborates

To a solution of 100 mmol of starting aniline in 40 ml of 48% HBF_4 aq. and 50 ml of deionized water was added a solution of 6.9 g (100 mmol) of $NaNO_2$ in 10 ml of deionized water at 0°C. The reaction mixture was stirred at 700 RPM for 30 min at 0°C. The resulting solid was filtered off, dissolved in 50 ml of acetone and precipitated by addition of 50 ml of diethyl ether. Filtration of the obtained crystals followed by drying in vacuum yields pure product.

Benzenediazonium tetrafluoroborate (1a)[2]

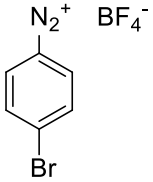


Yield 75%. White solid

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.66 (d, J = 8.4 Hz, 2H), 8.26 (t, J = 7.3 Hz, 1H), 7.98 (t, J = 8.1 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 140.8 , 132.6 , 131.2 , 116.0 .

4-bromobenzenediazonium tetrafluoroborate (1b)[2a, 3]

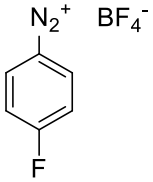


Yield 70%. Pink solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.57 (d, J = 8.5 Hz, 2H), 8.26 (d, J = 8.5 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 136.5 , 134.5 , 133.9 , 115.1 .

4-fluorobenzenediazonium tetrafluoroborate (1c)[2a, 4]

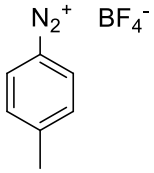


Yield 67%. Gray solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.79 (dd, J = 9.4, 4.5 Hz, 2H), 7.88 (dd, J = 9.4, 8.3 Hz, 2H).

^{13}C{^{1}H} (151 MHz, DMSO-d_6) δ 168.5 (d, J = 267.2 Hz), 137.0 (d, J = 12.4 Hz), 119.44 (d, J = 25.5 Hz), 111.8 .

4-methylbenzenediazonium tetrafluoroborate (1d)[5]

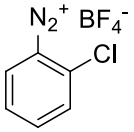


Yield 84%. White solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.47 (d, J = 8.5 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 2.55 – 2.46 (m, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 154.0 , 132.6 , 131.8 , 111.9 , 22.3 .

2-chlorobenzenediazonium tetrafluoroborate (1e)[6]

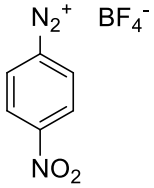


Yield 60%. White solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.85 (dd, J = 8.3, 1.6 Hz, 1H), 8.28 (td, J = 7.9, 1.6 Hz, 1H), 8.20 (dd, J = 8.3, 1.1 Hz, 1H), 7.96 (ddd, J = 8.5, 7.6, 1.2 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 142.3 , 135.4 , 134.7 , 132.2 , 130.1 , 116.6 , 39.5.

4-nitrobenzenediazonium tetrafluoroborate (1f)[2a]

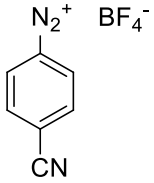


Yield 72%. Yellow solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.93 (d, J = 9.1 Hz, 2H), 8.72 (d, J = 9.1 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 153.2 , 134.5 , 126.0 , 121.8 .

4-cyanobenzenediazonium tetrafluoroborate (1g)[2a]

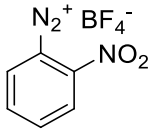


Yield 65%. Pale yellow solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.84 (d, J = 8.8 Hz, 2H), 8.46 (d, J = 8.8 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 134.8 , 133.1 , 121.8 , 121.0 , 116.4 .

2-nitrobenzenediazonium tetrafluoroborate (1h)[4]

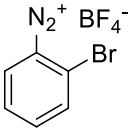


Yield 44%. White solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 9.10 (dd, J = 8.1, 1.4 Hz, 1H), 8.79 (dd, J = 8.3, 1.2 Hz, 1H), 8.53 (td, J = 8.0, 1.4 Hz, 1H), 8.41 (td, J = 7.9, 1.2 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 144.5 , 142.2 , 136.9 , 136.5 , 128.0 , 111.1 .

2-bromobenzenediazonium tetrafluoroborate (1i)[7]

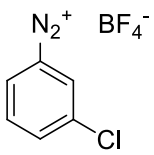


Yield 52%. White solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.84 (dd, J = 8.3, 1.6 Hz, 1H), 8.31 (dd, J = 8.2, 1.1 Hz, 1H), 8.17 (td, J = 7.9, 1.5 Hz, 1H), 7.99 (ddd, J = 8.6, 7.6, 1.2 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 141.8 , 135.2 , 135.0 , 130.3 , 124.3 , 118.6 .

3-chlorobenzenediazonium tetrafluoroborate (1j)[8]

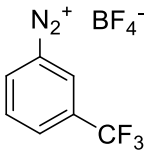


Yield 59%. Pink solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.84 (d, J = 2.5 Hz, 1H), 8.66 (d, J = 8.4 Hz, 1H), 8.36 (dd, J = 8.3, 2.2 Hz, 1H), 8.00 (t, J = 8.3 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 141.1 , 134.7 , 132.8 , 131.7 , 131.5 , 117.7 , 39.5.

3-(trifluoromethyl)benzenediazonium tetrafluoroborate (1k)[9]

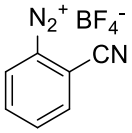


Yield 69%. Pink solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 9.20 (s, 1H), 8.96 (d, J = 8.8 Hz, 1H), 8.66 (d, J = 8.1 Hz, 1H), 8.23 (t, J = 8.2 Hz, 1H).

^{13}C{^{1}H} (151 MHz, DMSO-d_6) δ 137.2 (q, J = 3.0 Hz), 136.5 , 132.78 , 130.8 (q, J = 34.5 Hz), 130.1 (q, J = 3.8 Hz), 124.9 (q, J = 273.7 Hz), 118.3 .

2-cyanobenzenediazonium tetrafluoroborate (1l)[9]

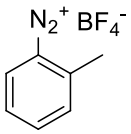


Yield 91%. White solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 9.00 (d, J = 8.0 Hz, 1H), 8.60 (dt, J = 7.4, 1.3 Hz, 1H), 8.46 (ddt, J = 7.8, 5.4, 1.1 Hz, 1H), 8.32 (t, J = 8.1 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 141.0 , 136.41 , 135.5 , 134.6 , 118.6 , 113.7 , 112.4.

2-methylbenzenediazonium tetrafluoroborate (1m)[10]

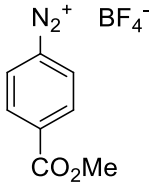


Yield 57%. White solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.64 (dd, J = 8.3, 1.9 Hz, 1H), 8.15 (td, J = 7.7, 1.9 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.80 (t, J = 7.5 Hz, 1H), 2.74 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 143.7 , 140.6 , 132.5 , 132.4 , 128.8 , 127.7 , 18.1.

4-(methoxycarbonyl)benzenediazonium tetrafluoroborate (1n)[4]

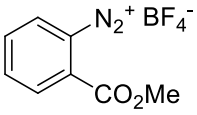


Yield 39%. White solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.79 (d, J = 8.7 Hz, 2H), 8.44 (d, J = 8.7 Hz, 2H), 3.95 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 163.8 , 139.2 , 133.1 , 131.2 , 120.2 , 53.4 .

2-(methoxycarbonyl)benzenediazonium tetrafluoroborate (1o)[4]



Yield 35%. White solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.95 (d, J = 8.3 Hz, 1H), 8.42 (d, J = 8.1 Hz, 1H), 8.38 (t, J = 7.7 Hz, 1H), 8.26 (t, J = 7.8 Hz, 1H), 4.04 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 161.4 , 140.9 , 135.4 , 135.1 , 132.4 , 130.4 , 115.7 , 54.1 .

Aryl azides

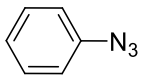
General procedure for the preparation of aryl azides

A screw-cap vial equipped with a magnetic stir bar was charged with 1 mmol (1 eq.) of hydroxylamine hydrochloride, 3 ml of deionized water and 1 mmol of corresponding aryldiazonium tetrafluoroborate. The reaction mixture was stirred at 700 RPM for 24 h at room temperature and extracted with 3x10 ml of dichloromethane. Filtration of the resulting solution through short pad of silica gel (0.5 cm) in almost all cases gave pure product.

Reused water reaction media experiments

A round-bottom 100 ml flask, equipped with magnetic stirrer bar, was charged with 278 mg (4 mmol, 1 eq.) of hydroxylammonium chloride, 10 ml of deionized water, and 868 mg (4 mmol, 1 eq.) of 4-cyanobenzenediazonium tetrafluoroborate (**1g**). Reaction media was stirred at 700 rpm for 24 h at room temperature. The formed precipitate was filtered and washed with water (3.0 ml). The water reaction media after filtration was reused. Yellow solid **2g** was dried under oil pump vacuum. The obtained yields: 541 mg (94%), stage 1; 576 mg (100%), stages 2 and 3; 271 mg (47%), stage 4. After stage 4 the acidity was reduced by addition of 336 mg (4 mmol, 1 eq.) of $NaHCO_3$ prior to reuse. Isolation procedure was the same as above. Yields: 501 mg (87%), stages 5 – 7.

Azidobenzene (2a)[11]

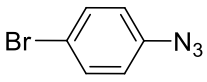


Yield 84%. Yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.1 , 129.8 , 125.0 , 119.1 .

1-azido-4-bromobenzene (2b)[12]

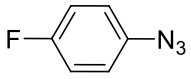


Yield 66%. Yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 139.3, 132.9, 120.8, 117.9.

1-azido-4-fluorobenzene (2c)[13]

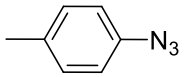


Yield 61%. Brown oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.11 – 7.02 (m, 2H), 7.02 – 6.93 (m, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 160.1 (d, *J* = 244.4 Hz), 135.9 (d, *J* = 3.0 Hz), 120.4 (d, *J* = 8.3 Hz), 116.7 (d, *J* = 23.2 Hz).

1-azido-4-methylbenzene (2d)[11a]

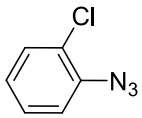


Yield 62%. Brown oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 137.2 , 134.6 , 130.4 , 118.9 , 20.9 .

1-azido-2-chlorobenzene (2e)[14]

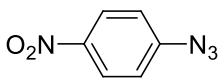


Yield 71%. Yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.10 – 7.04 (m, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 137.1 , 130.7 , 127.8 , 125.6 , 124.9 , 119.6 .

1-azido-4-nitrobenzene (2f)[11a]

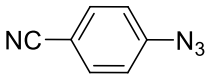


Yield 95%. Red solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 9.1 Hz, 2H), 7.10 (d, *J* = 9.1 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 146.8 , 144.5 , 125.5 , 119.3 .

4-azidobenzonitrile (2g)[11a]

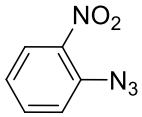


Yield 99%. Yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 8.8, 1.3 Hz, 2H), 7.10 (dd, *J* = 8.8, 1.3 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 145.0 , 133.9 , 119.8 , 118.4 , 108.4 .

1-azido-2-nitrobenzene (2h)[15]

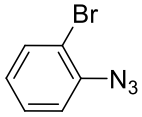


Yield 80%. Brown oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.21 (m, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 151.9, 134.9, 134.1, 126.2, 125.0, 120.9.

1-azido-2-bromobenzene (2i)[12]

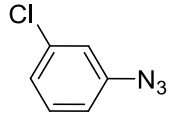


Yield 52%. Brown solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.13 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.01 – 6.96 (m, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 138.6, 133.8, 128.5, 125.9, 119.4, 113.8.

1-azido-3-chlorobenzene (2j)[16]

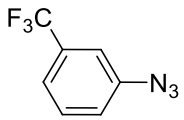


Yield 66%. Yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 (t, *J* = 8.1 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.99 (s, 1H), 6.89 (dd, *J* = 8.1, 1.3 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 141.5 , 135.5 , 130.7 , 125.1 , 119.4 , 117.3 .

1-azido-3-(trifluoromethyl)benzene (2k)[12]

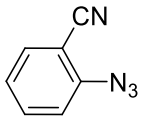


Yield 60%. Brown oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 (t, *J* = 7.9 Hz, 1H), 7.41 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.27 (s, 1H), 7.22 (dd, *J* = 8.1, 2.2 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 141.2 , 132.5 (q, *J* = 33.0 Hz), 130.5 , 123.7 (q, *J* = 272.5 Hz). 122.3 , 121.7 (q, *J* = 3.5 Hz), 116.2 (q, *J* = 3.8 Hz).

2-azidobenzonitrile (2l)[17]

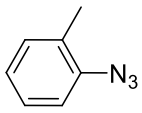


Yield 99%. Yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 – 7.60 (m, 2H), 7.29 – 7.26 (m, 1H), 7.23 (td, *J* = 7.7, 1.0 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 143.5 , 134.1 , 134.0 , 125.1 , 118.9 , 115.7 .

1-azido-2-methylbenzene (2m)[14]

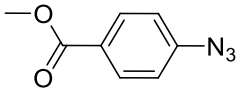


Yield 65%. Yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 2.31 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 138.4, 131.2, 129.6, 127.1, 124.6, 117.9, 17.2.

Methyl 4-azidobenzoate (2n)[18]

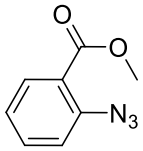


Yield 76%. White oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 (dt, *J* = 8.7, 1.5 Hz, 2H), 7.06 (dt, *J* = 8.7, 1.5 Hz, 2H), 3.90 (t, *J* = 1.5 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 166.4 , 144.9 , 131.5 , 126.8 , 119.0 , 52.3 .

Methyl 2-azidobenzoate (2o)[19]



Yield 99%. Yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 7.11 – 7.07 (m, 1H), 3.82 (s, 3H).

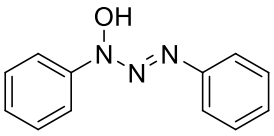
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 165.5 , 139.9 , 133.0 , 131.7 , 124.3 , 122.4 , 119.8 , 52.1 .

1,3-diaryl-3-hydroxy-triazenes

General procedure for the preparation of 1,3-diaryl-3-hydroxy-triazenes

A screw-cap vial equipped with a magnetic stir bar was charged with 109 mg (1 mmol, 1 eq.) of N-phenylhydroxylamine, 3 ml of deionized water and 1 mmol of corresponding aryldiazonium tetrafluoroborate. The reaction mixture was stirred at 700 RPM for 24 h at room temperature, extracted with 3x10 ml of dichloromethane. The resulting solution was concentrated in vacuum. Column chromatography purification in dichloromethane gave pure product.

3-hydroxy-1,3-diphenyltriazene (3a)[20]



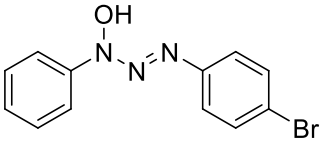
Yield 95%. Gray solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.98 (s, 1H), 8.08 (d, J = 8.3 Hz, 2H), 7.57 (t, J = 7.6 Hz, 2H), 7.54 – 7.49 (m, 3H), 7.37 – 7.32 (m, 2H), 7.02 (t, J = 7.3 Hz, 1H).

^{13}C{^{1}H} (151 MHz, DMSO) δ 143.0, 140.5, 129.7, 129.3, 129.2, 122.5, 119.6, 115.0.

EA calcd. for $C_{12}H_{11}N_3O$: C, 67.59; H, 5.20; N, 19.71. Found: C, 66.97; H, 5.15; N, 19.38.

1-(4-bromophenyl)-3-hydroxy-3-phenyltriazene (3b)[21]



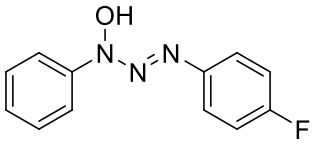
Yield 89%. Gray solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 12.10 (s, 1H), 8.08 (d, J = 7.6 Hz, 2H), 7.60 – 7.49 (m, 5H), 7.46 (d, J = 8.0 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 142.9 , 140.0 , 132.0 , 129.9 , 129.2 , 119.8 , 117.0 .

EA calcd. for $C_{12}H_{10}BrN_3O$: C, 49.34; H, 3.45; N, 14.38. Found: C, 49.03; H, 3.32; N, 14.25.

1-(4-fluorophenyl)-3-hydroxy-3-phenyltriazene (3c)



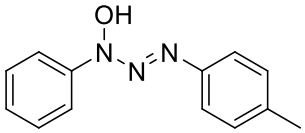
Yield 78%. Brown solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 12.03 (s, 1H), 8.07 (d, J = 7.6 Hz, 2H), 7.65 – 7.42 (m, 5H), 7.20 (t, J = 8.8 Hz, 2H).

^{13}C{^{1}H} (151 MHz, DMSO-d_6) δ 158.01 (d, J = 238.7 Hz), 142.92 , 137.14 , 129.71 , 129.22 , 119.61 , 116.49 (d, J = 7.9 Hz), 115.95 (d, J = 23.1 Hz).

EA calcd. for $C_{12}H_{10}FN_3O$: C, 62.33; H, 4.36; N, 18.17. Found: C, 61.66; H, 4.01; N, 17.78.

3-hydroxy-3-phenyl-1-p-tolyltriazene (3d)[22]



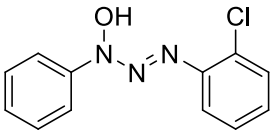
Yield 63%. Gray solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.91 (s, 1H), 8.06 (d, J = 7.9 Hz, 2H), 7.58 – 7.50 (m, 3H), 7.40 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 2.26 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 143.0 , 138.1 , 131.5 , 129.7 , 129.5 , 129.2 , 128.4 , 119.5 , 115.0 , 20.4 .

EA calcd. for $C_{13}H_{13}N_3O$: C, 68.70; H, 5.77; N, 18.49. Found: C, 68.23; H, 5.41; N, 18.21.

1-(2-chlorophenyl)-3-hydroxy-3-phenyltriazene (3e)[23]



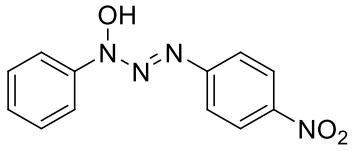
Yield 90%. Brown solid.

^{1}H NMR (600 MHz, Chloroform-d) δ 11.07 (s, 1H), 8.10 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.2 Hz, 1H), 7.53 – 7.46 (m, 3H), 7.39 (d, J = 8.0 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.00 (t, J = 7.7 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 143.2, 136.3, 130.2, 129.9, 129.1, 128.1, 123.5, 120.1, 120.1, 115.7.

EA calcd. for $C_{12}H_{10}ClN_3O$: C, 58.19; H, 4.07; N, 16.97. Found: C, 58.35; H, 4.05; N, 16.89.

3-hydroxy-1-(4-nitrophenyl)-3-phenyltriazene (3f)[24]



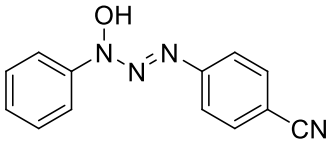
Yield 58%. Yellow solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 12.59 (s, 1H), 8.23 (d, J = 9.2 Hz, 2H), 8.13 (dd, J = 7.9, 2.0 Hz, 2H), 7.66 (d, J = 9.2 Hz, 2H), 7.62 – 7.57 (m, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 146.3 , 142.9 , 141.6 , 130.6 , 129.3 , 125.6 , 120.2 , 114.8 .

EA calcd. for $C_{12}H_{10}N_4O_3$: C, 55.81; H, 3.90; N, 21.70. Found: C, 55.27; H, 3.73; N, 21.82.

4-(3-hydroxy-3-phenyltriazenyl)benzonitrile (3g)



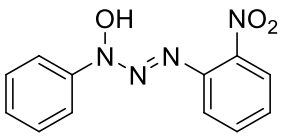
Yield 91%. Orange solid.

^{1}H NMR (600 MHz, Chloroform-d) δ 10.97 (s, 1H), 8.08 (d, J = 7.9 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 7.51 (dd, J = 5.3, 2.0 Hz, 3H), 7.35 (d, J = 8.5 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 143.1, 142.9, 133.9, 130.7, 129.2, 120.2, 119.1, 115.1, 106.0.

EA calcd. for $C_{13}H_{10}N_4O$: C, 65.54; H, 4.23; N, 23.52. Found: C, 64.93; H, 4.21; N, 23.24.

3-hydroxy-1-(2-nitrophenyl)-3-phenyltriazene (3h)



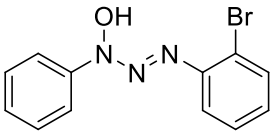
Yield 61%. Yellow solid.

^{1}H NMR (600 MHz, Chloroform-d) δ 12.92 (s, 1H), 8.28 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 6.3 Hz, 2H), 7.92 (d, J = 8.5 Hz, 1H), 7.66 (t, J = 7.8 Hz, 1H), 7.53 – 7.50 (m, 3H), 7.10 (t, J = 7.9 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 143.3, 136.5, 136.1, 133.4, 130.9, 129.2, 126.4, 121.8, 120.6, 116.9.

EA calcd. for $C_{12}H_{10}N_4O_3$: C, 55.81; H, 3.90; N, 21.70. Found: C, 55.25; H, 3.88; N, 21.40.

1-(2-bromophenyl)-3-hydroxy-3-phenyltriazene (3i)



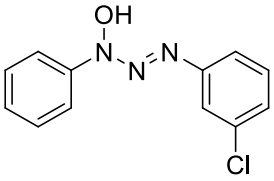
Yield 94%. Pale yellow solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.90 (s, 1H), 8.06 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 8.3 Hz, 1H), 7.60 (d, J = 8.1 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.40 (t, J = 7.8 Hz, 1H), 6.98 (t, J = 6.7 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6) δ 142.3 , 136.5 , 132.7 , 130.4 , 129.2 , 129.0 , 124.2 , 119.7 , 116.0 , 108.9 .

EA calcd. for $C_{12}H_{10}BrN_3O$: C, 49.34; H, 3.45; N, 14.38. Found: C, 49.09; H, 3.36; N, 14.21.

1-(3-chlorophenyl)-3-hydroxy-3-phenyltriazene (3j)[22]



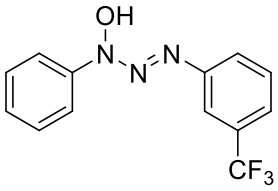
Yield 58%. Brown solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 12.13 (s, 1H), 8.10 (d, J = 7.1 Hz, 2H), 7.59 – 7.53 (m, 4H), 7.47 (d, J = 8.2 Hz, 1H), 7.36 (t, J = 8.1 Hz, 1H), 7.05 (d, J = 7.9 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6) δ 142.9 , 142.1 , 133.9 , 130.9 , 130.0 , 129.2 , 122.0 , 119.8 , 114.5 , 113.6 .

EA calcd. for $C_{12}H_{10}ClN_3O$: C, 58.19; H, 4.07; N, 16.97. Found: C, 57.75; H, 3.91; N, 16.68.

3-hydroxy-3-phenyl-1-(3-(trifluoromethyl)phenyl)triazene (3k)



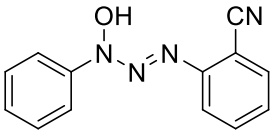
Yield 60%. Brown solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 12.26 (s, 1H), 8.11 (d, J = 7.8 Hz, 2H), 7.79 (d, J = 11.8 Hz, 2H), 7.62 – 7.50 (m, 4H), 7.34 (d, J = 7.7 Hz, 1H).

^{13}C{^{1}H} (151 MHz, DMSO-d_6) δ 142.9 , 141.4 , 130.5 , 130.1 (q, J = 16.1 Hz) , 129.3 , 124.1 (q, J = 273.0 Hz) , 119.9 , 118.6 , 118.5 (q, J = 8.0 Hz).

EA calcd. for $C_{13}H_{10}F_3N_3O$: C, 55.52; H, 3.58; N, 14.94. Found: C, 55.34; H, 3.55; N, 14.74.

2-(3-hydroxy-3-phenyltriazenyl)benzonitrile (3l)



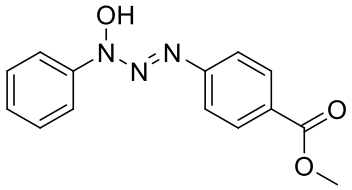
Yield82%. Yellow solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 12.10 (s, 1H), 8.18 – 8.13 (m, 2H), 7.80 (dd, J = 7.9, 1.2 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.62 – 7.56 (m, 3H), 7.21 – 7.17 (m, 1H).

^{13}C{^{1}H} (151 MHz, DMSO) δ 142.8, 142.0, 134.7, 134.3, 130.5, 129.3, 123.1, 119.8, 118.2, 117.9, 97.7.

EA calcd. for $C_{13}H_{10}N_4O$: C, 65.54; H, 4.23; N, 23.52. Found: C, 65.03; H, 4.11; N, 23.18.

Methyl 4-(3-hydroxy-3-phenyltriaz-1-enyl)benzoate (3n)



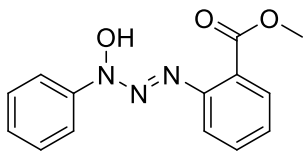
Yield 64%. White solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 12.32 (s, 1H), 8.10 (d, J = 7.7 Hz, 2H), 7.93 (d, J = 8.7 Hz, 2H), 7.61 – 7.54 (m, 5H), 3.82 (s, 3H).

^{13}C{^{1}H} (151 MHz, DMSO) δ 165.9, 144.6, 143.0, 130.8, 130.2, 129.3, 123.04, 120.0, 114.6, 51.8.

EA calcd. for $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.83; N, 15.49. Found: C, 61.68; H, 4.74; N, 15.24.

Methyl 2-(3-hydroxy-3-phenyltriazenyl)benzoate (3o)[25]



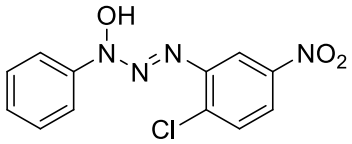
Yield 71%. Brown solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 13.03 (s, 1H), 8.13 (dd, J = 8.3, 1.5 Hz, 2H), 8.00 (dd, J = 8.0, 1.5 Hz, 1H), 7.87 (d, J = 9.3 Hz, 1H), 7.69 (t, J = 7.8 Hz, 1H), 7.65 – 7.52 (m, 3H), 7.14 (t, J = 8.1 Hz, 1H), 3.92 (s, 3H).

^{13}C{^{1}H} (151 MHz, DMSO-d_6) δ 167.0 , 142.7 , 141.2 , 135.1 , 131.0 , 130.5 , 129.4 , 121.9 , 120.0 , 114.9 , 112.3 , 52.5 .

EA calcd. for $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.83; N, 15.49. Found: C, 61.94; H, 4.82; N, 15.47.

1-(2-chloro-5-nitrophenyl)-3-hydroxy-3-phenyltriazene (3p)



Yield 79%. Yellow solid.

^{1}H NMR (600 MHz, Chloroform-d) δ 11.10 (s, 1H), 8.45 (d, J = 2.6 Hz, 1H), 8.14 (dd, J = 7.6, 2.3 Hz, 2H), 7.86 (dd, J = 8.7, 2.6 Hz, 1H), 7.58 – 7.53 (m, 4H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 131.0 , 130.6 , 129.3 , 126.0 , 120.5 , 117.5 , 110.4.

EA calcd. for $C_{12}H_9ClN_4O_3$: C, 49.24; H, 3.10; N, 19.14. Found: C, 48.82; H, 3.01; N, 18.87.

^{1}H and ^{13}C NMR spectra

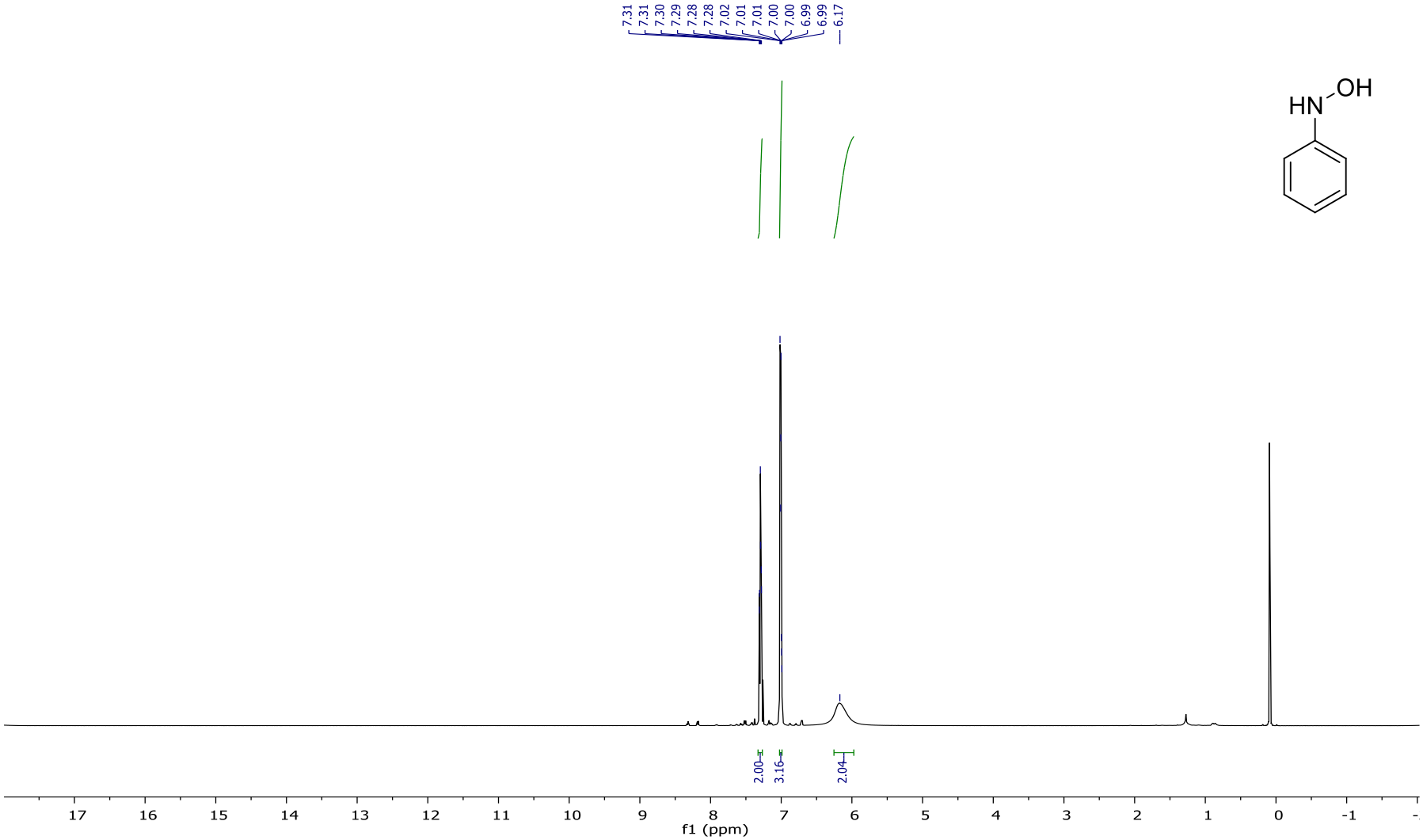


Figure S1. ^{1}H NMR (600 MHz, Chloroform-*d*) of N-phenylhydroxylamine.

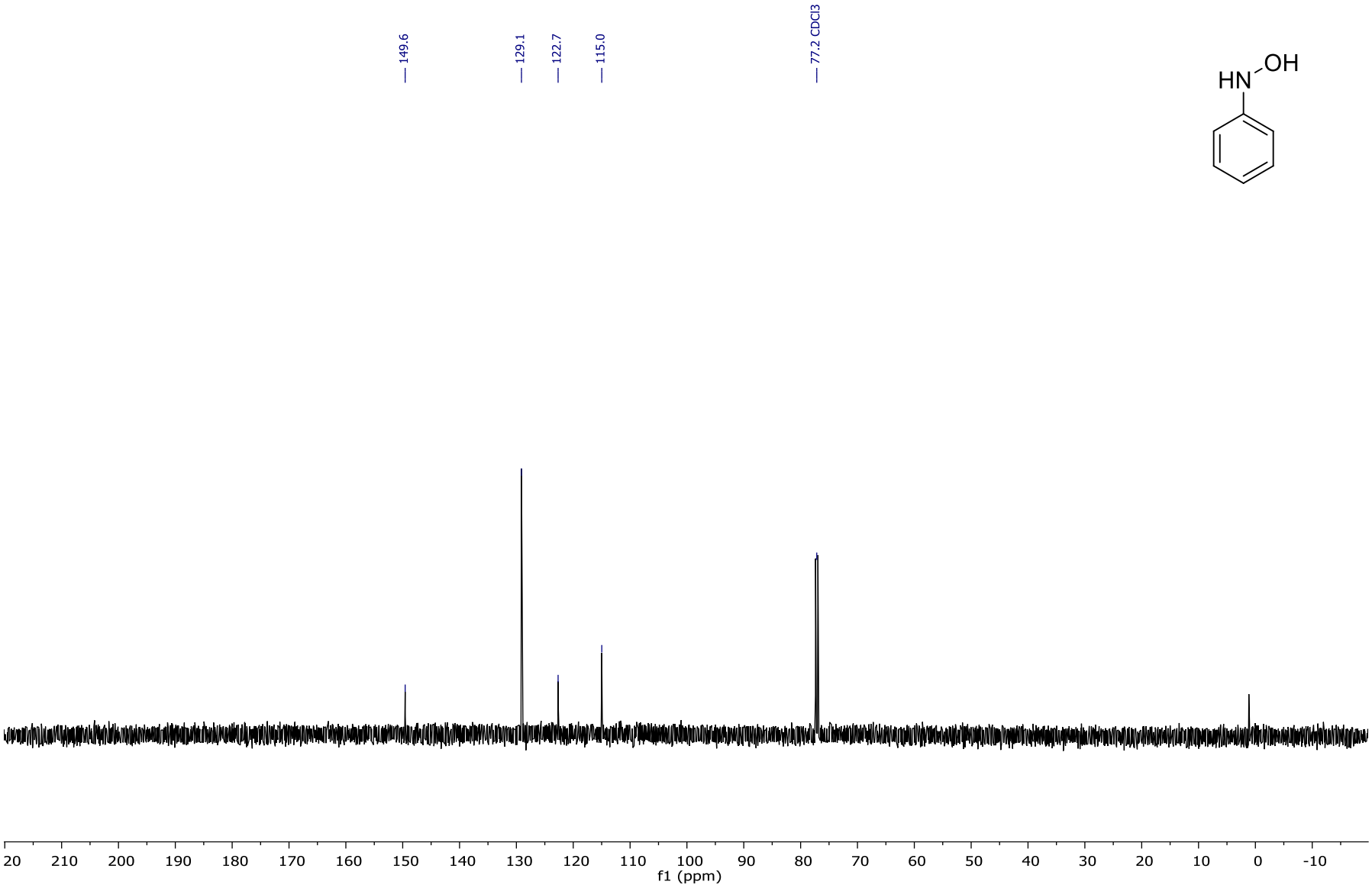


Figure S2. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) of N-phenylhydroxylamine.

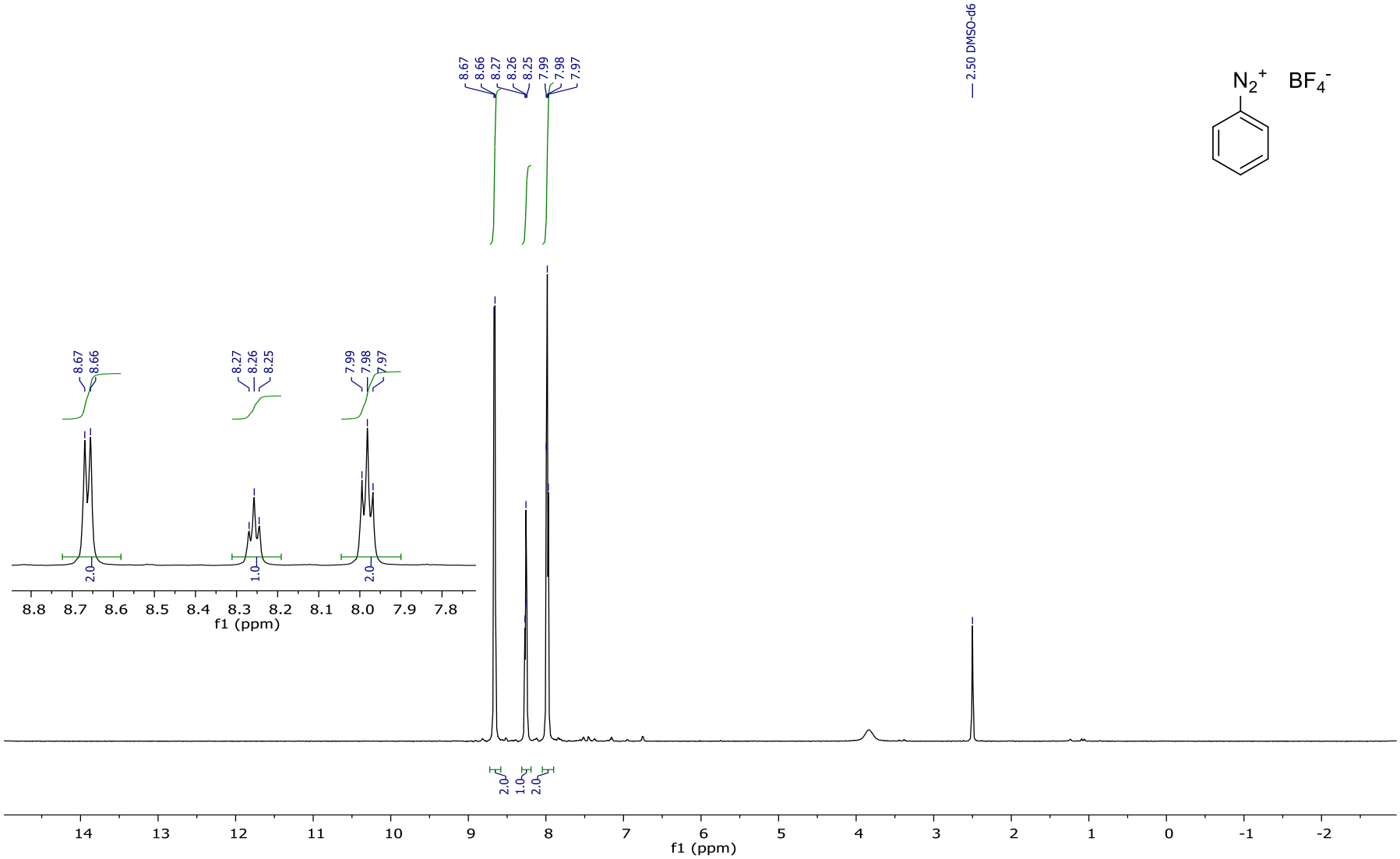


Figure S3. ^{1}H NMR (600 MHz, DMSO-*d*$_6$) of benzenediazonium tetrafluoroborate (1a).

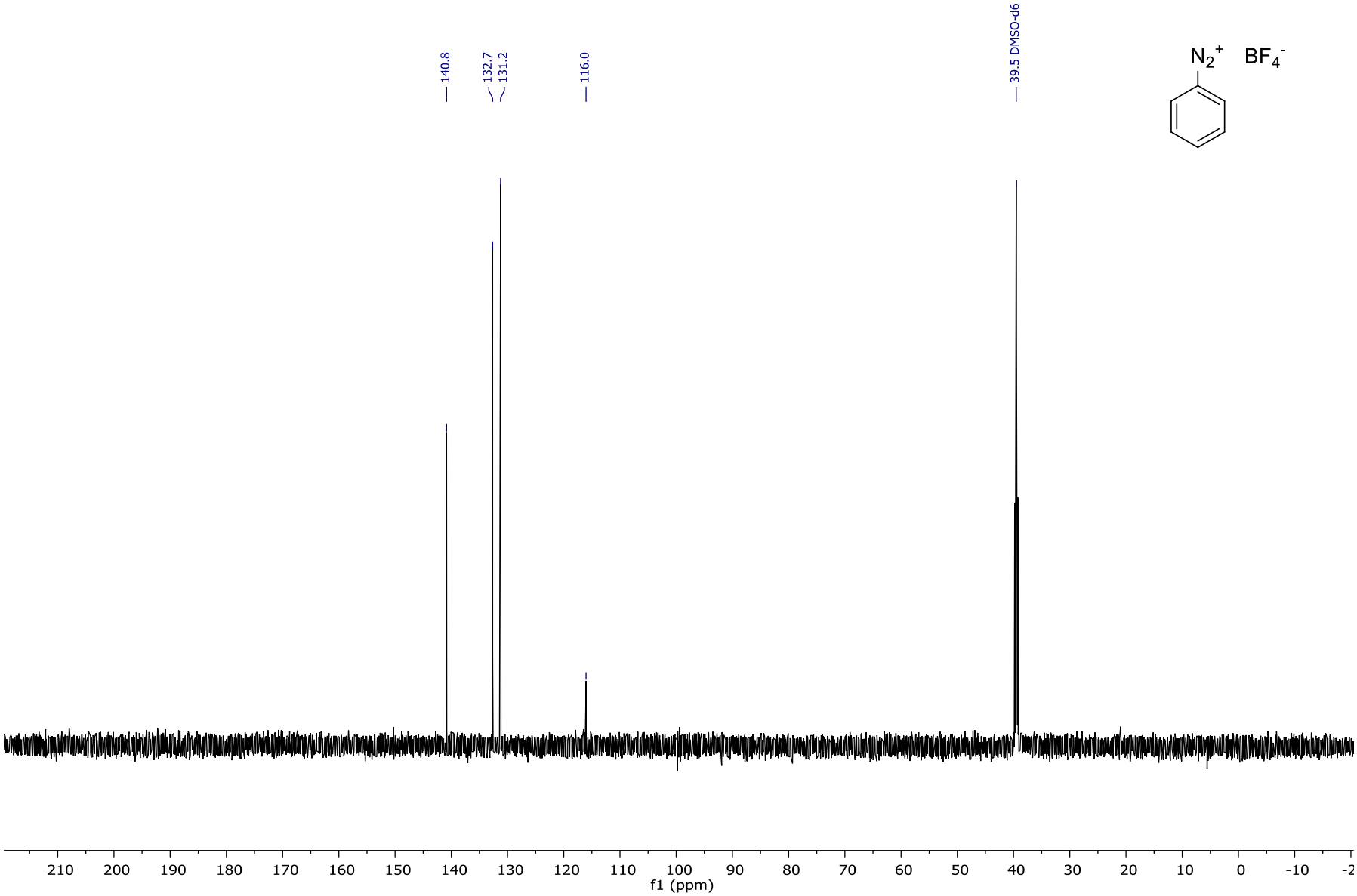


Figure S4. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6) of benzenediazonium tetrafluoroborate (1a).

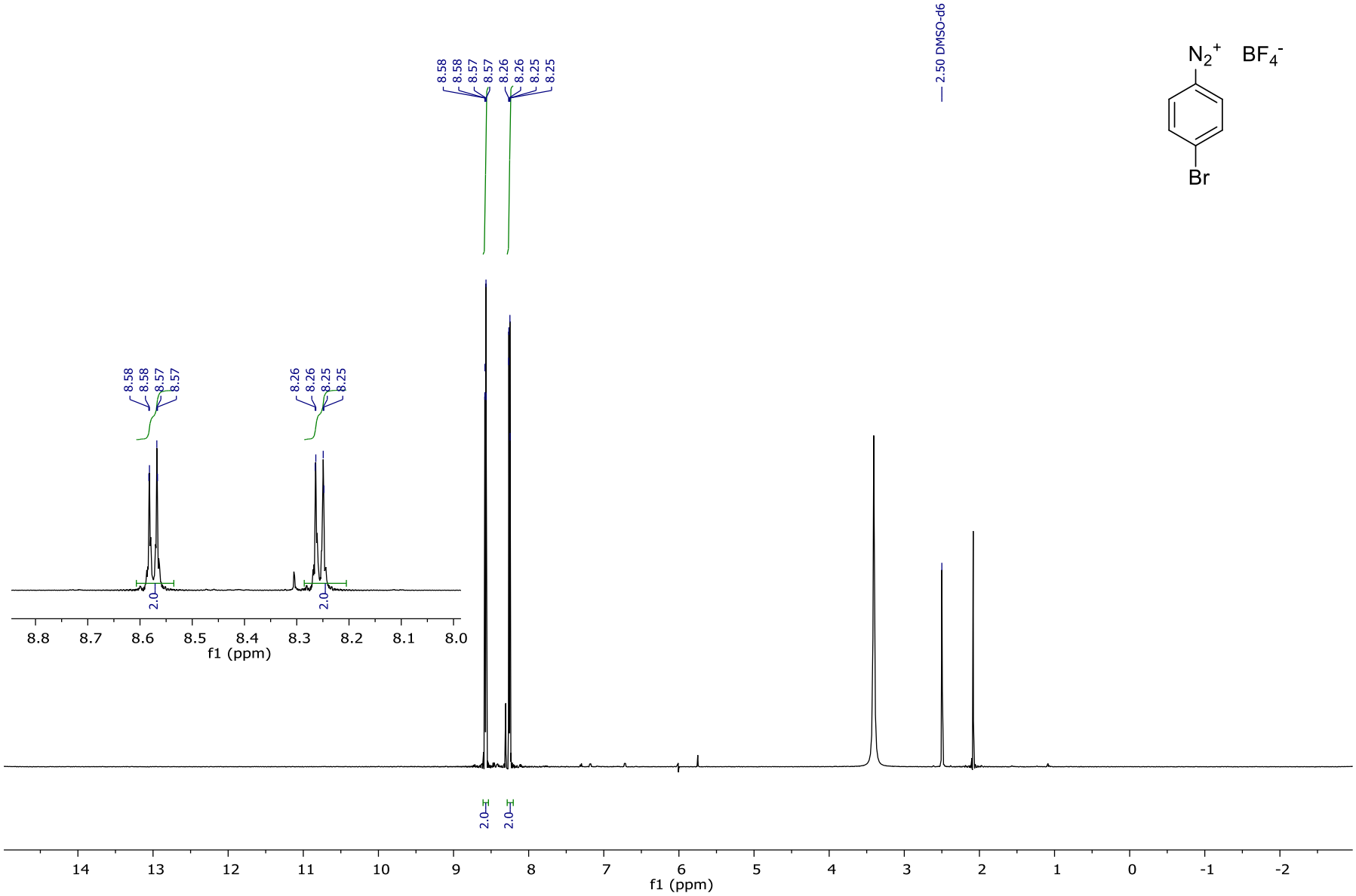


Figure S5. ^{1}H NMR (600 MHz, DMSO-d_6) of 4-bromobenzenediazonium tetrafluoroborate (1b).

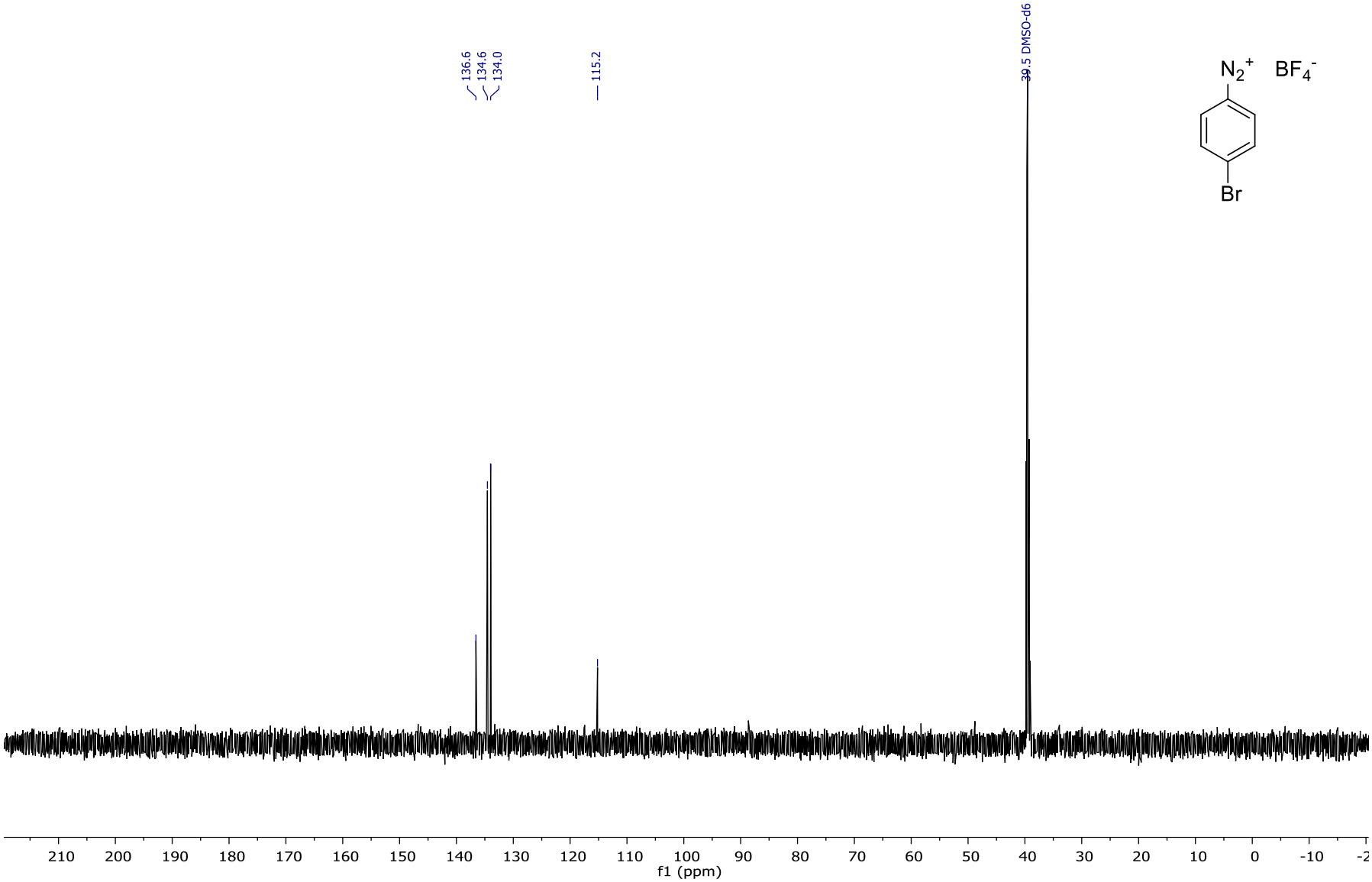


Figure S6. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6) of 4-bromobenzenediazonium tetrafluoroborate (1b).

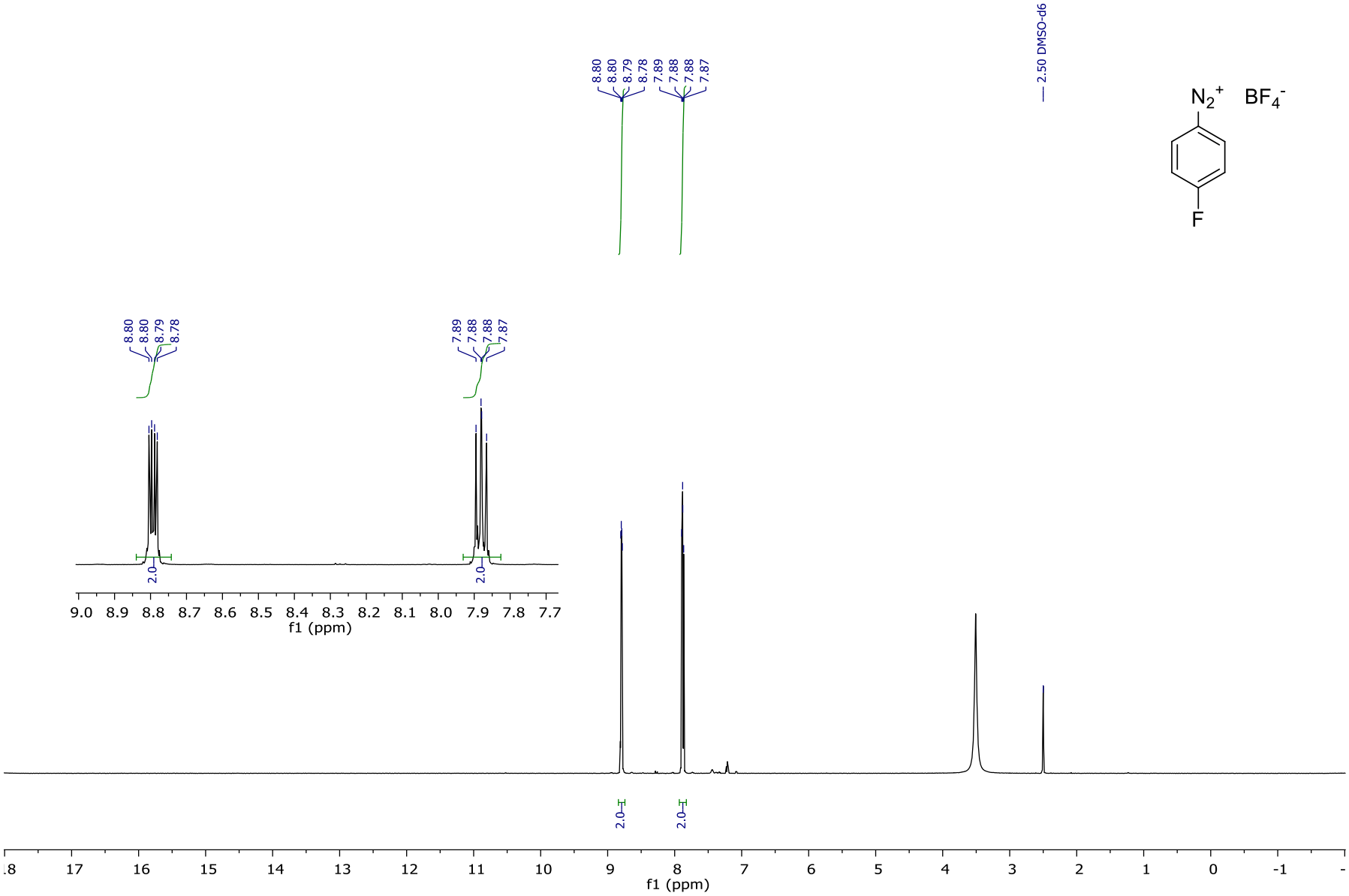


Figure S7. ^{1}H NMR (600 MHz, DMSO-d_6) of 4-fluorobenzenediazonium tetrafluoroborate (1c).

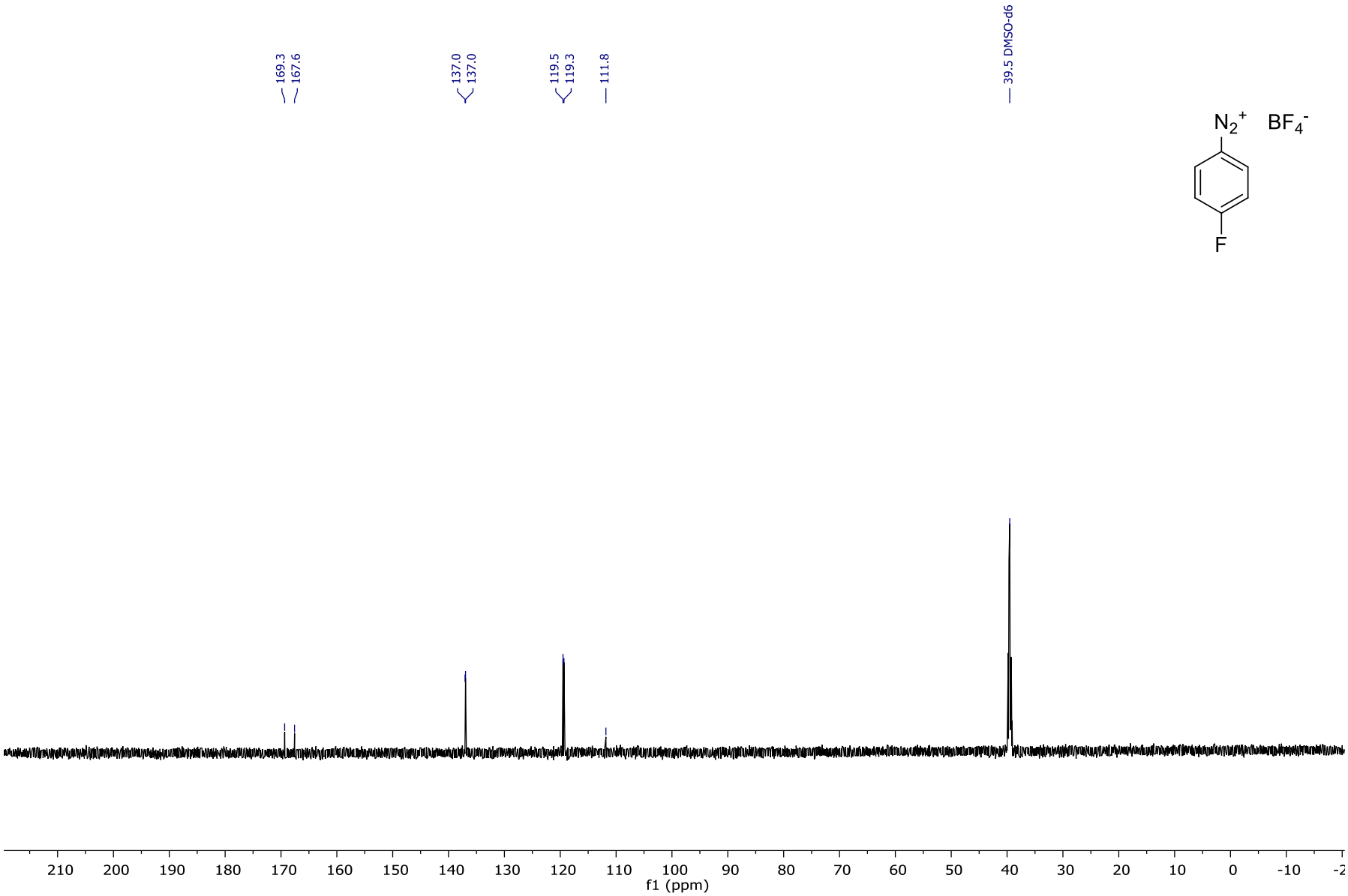


Figure S8. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6) of 4-fluorobenzenediazonium tetrafluoroborate (1c).

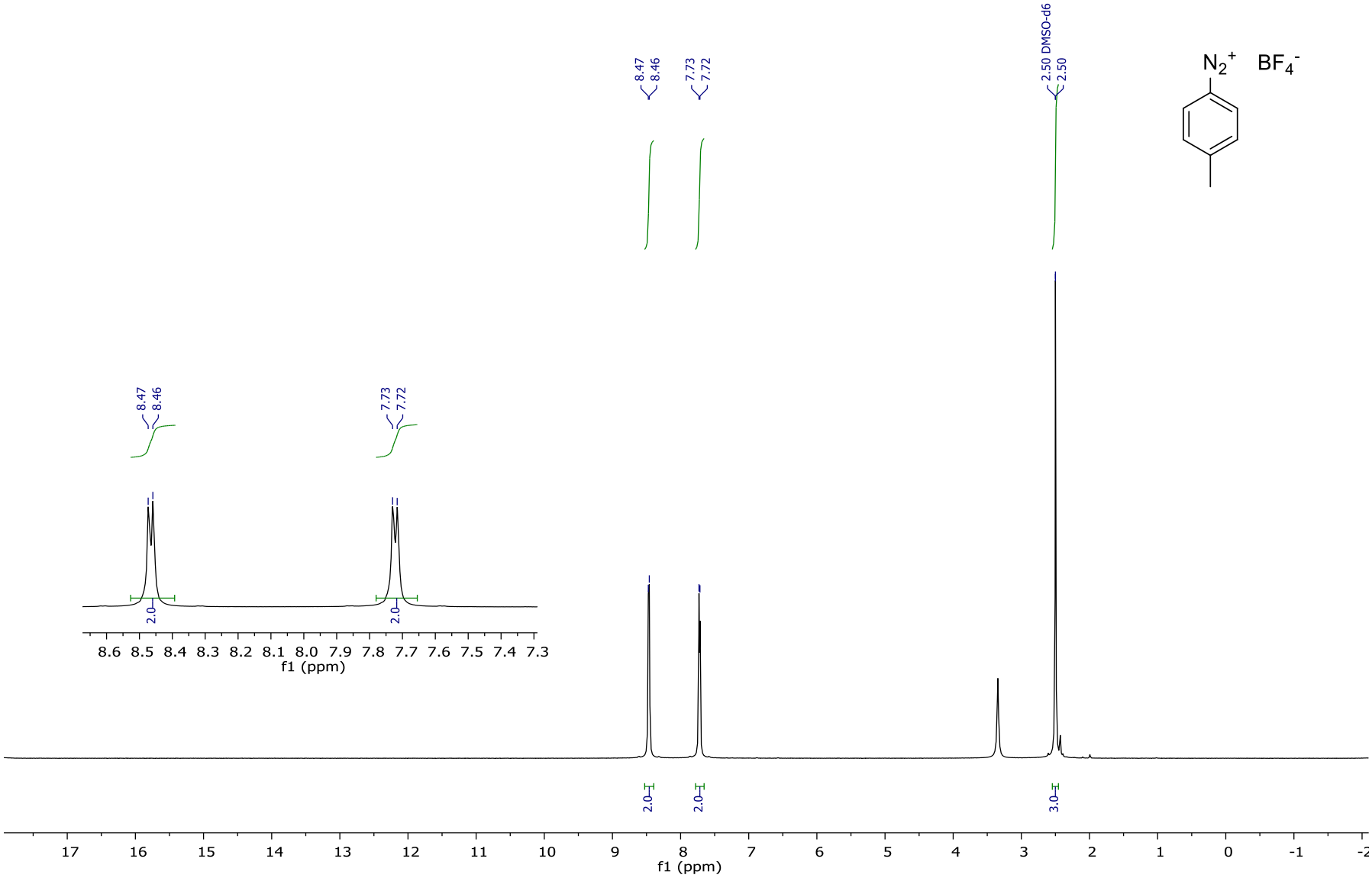


Figure S9. ^{1}H NMR (600 MHz, DMSO-d_6) of 4-methylbenzenediazonium tetrafluoroborate (1d).

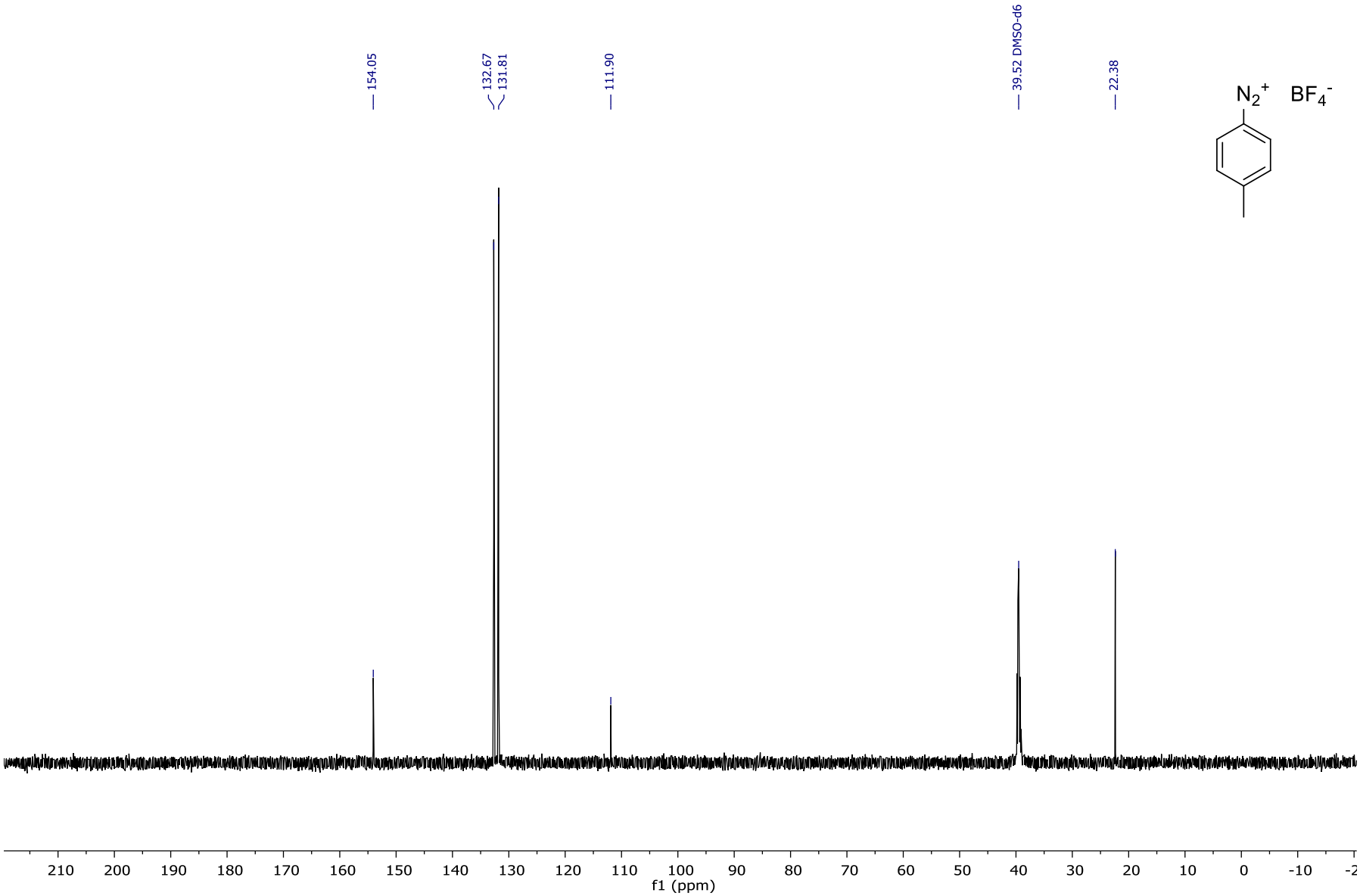


Figure S10. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6) of 4-methylbenzenediazonium tetrafluoroborate (1d).

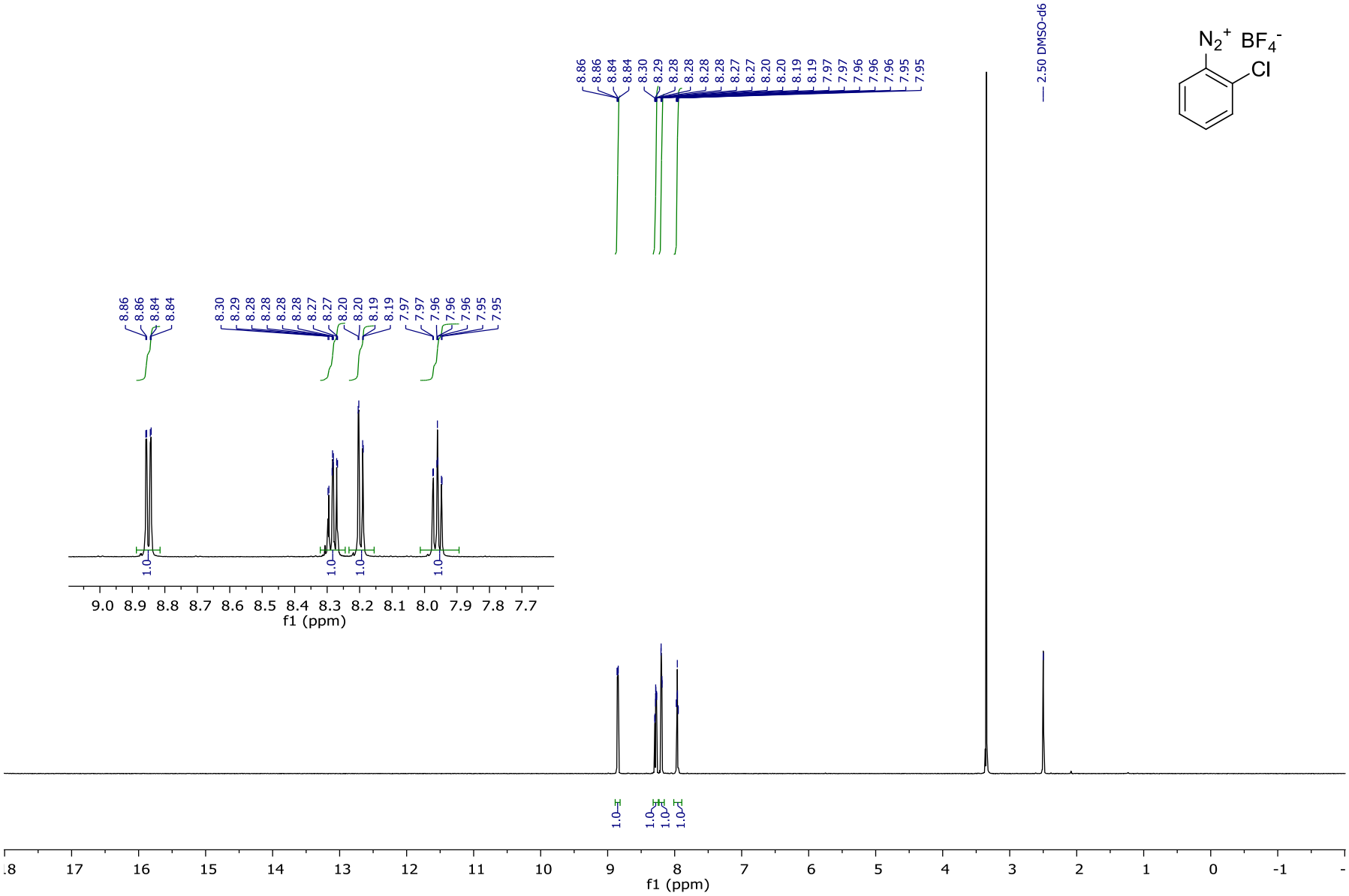


Figure S11. ^{1}H NMR (600 MHz, DMSO-*d*$_6$) of 2-chlorobenzenediazonium tetrafluoroborate (1e).

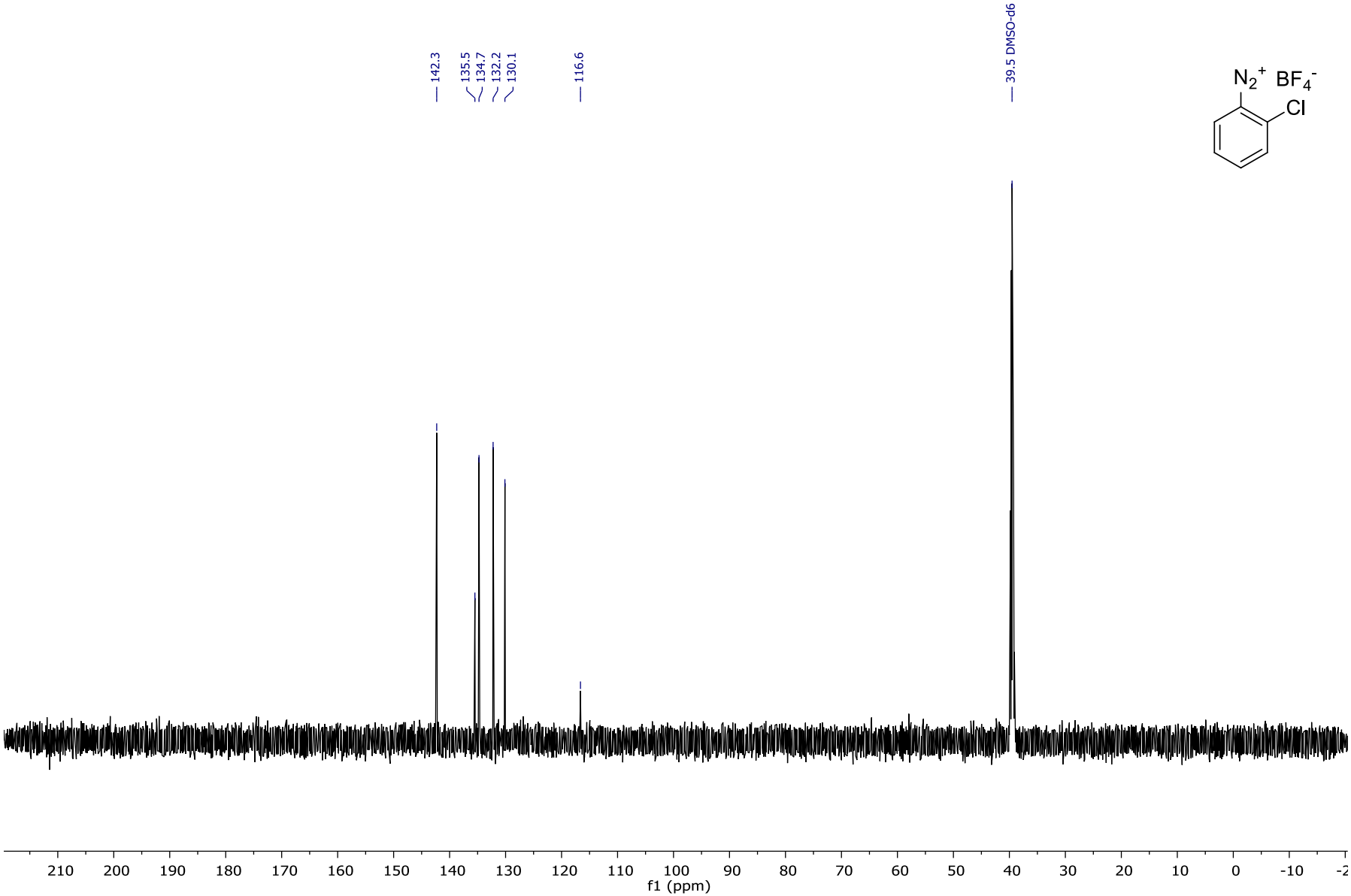


Figure S12. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6) of 2-chlorobenzenediazonium tetrafluoroborate (1e).

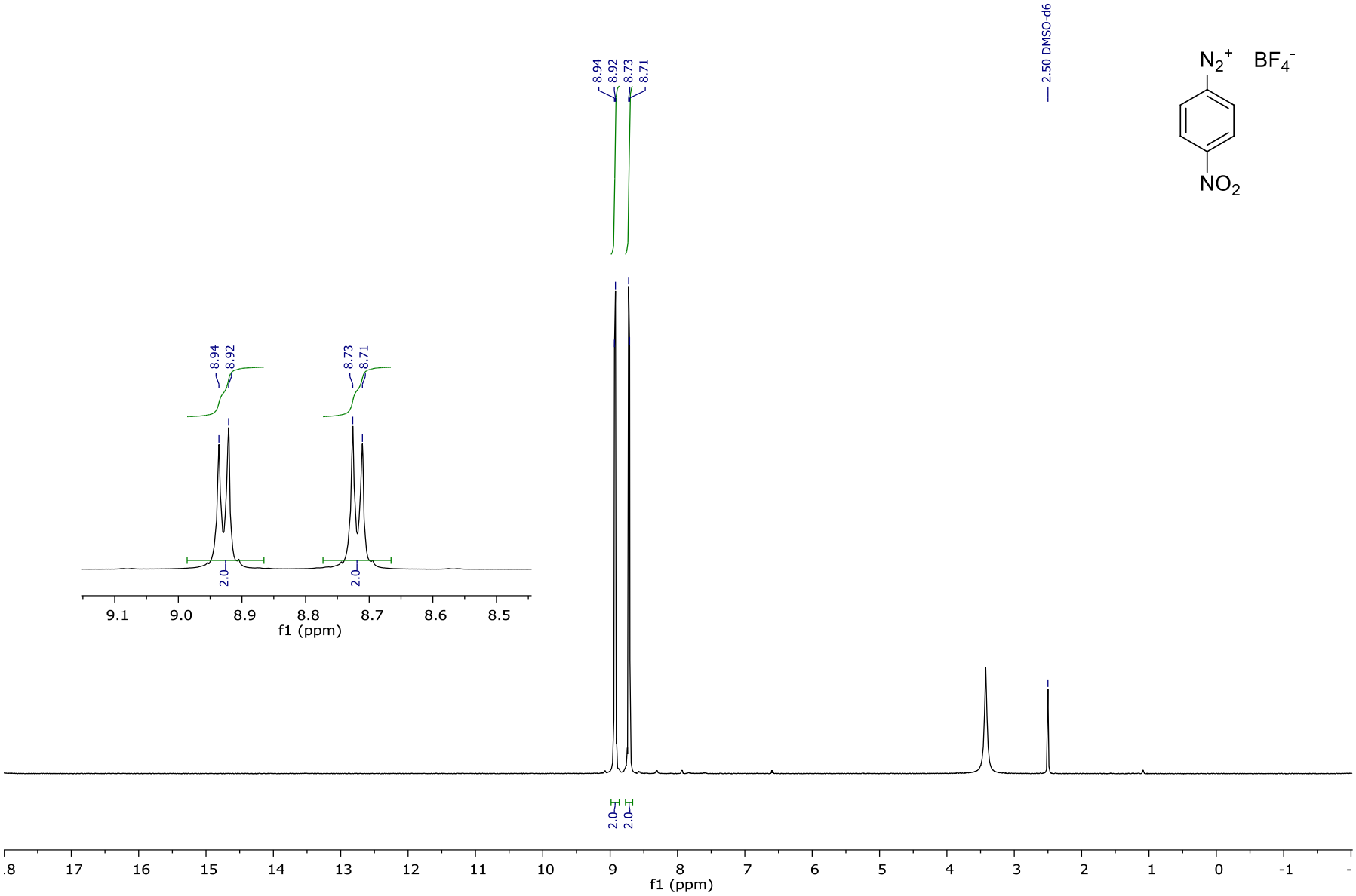


Figure S13. ^{1}H NMR (600 MHz, DMSO-d_6) of 4-nitrobenzenediazonium tetrafluoroborate (1f).

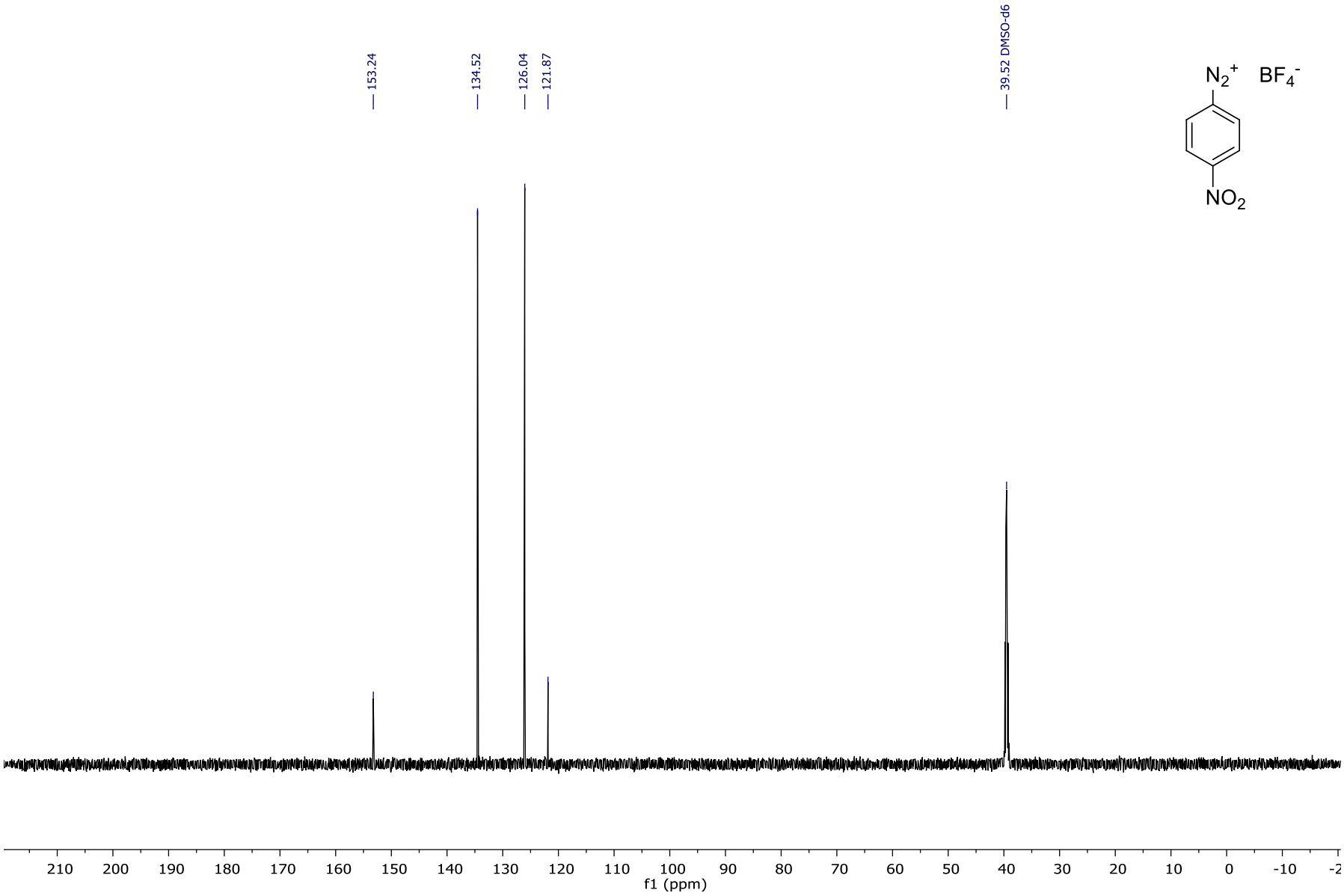


Figure S14. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6) of 4-nitrobenzenediazonium tetrafluoroborate (1f).

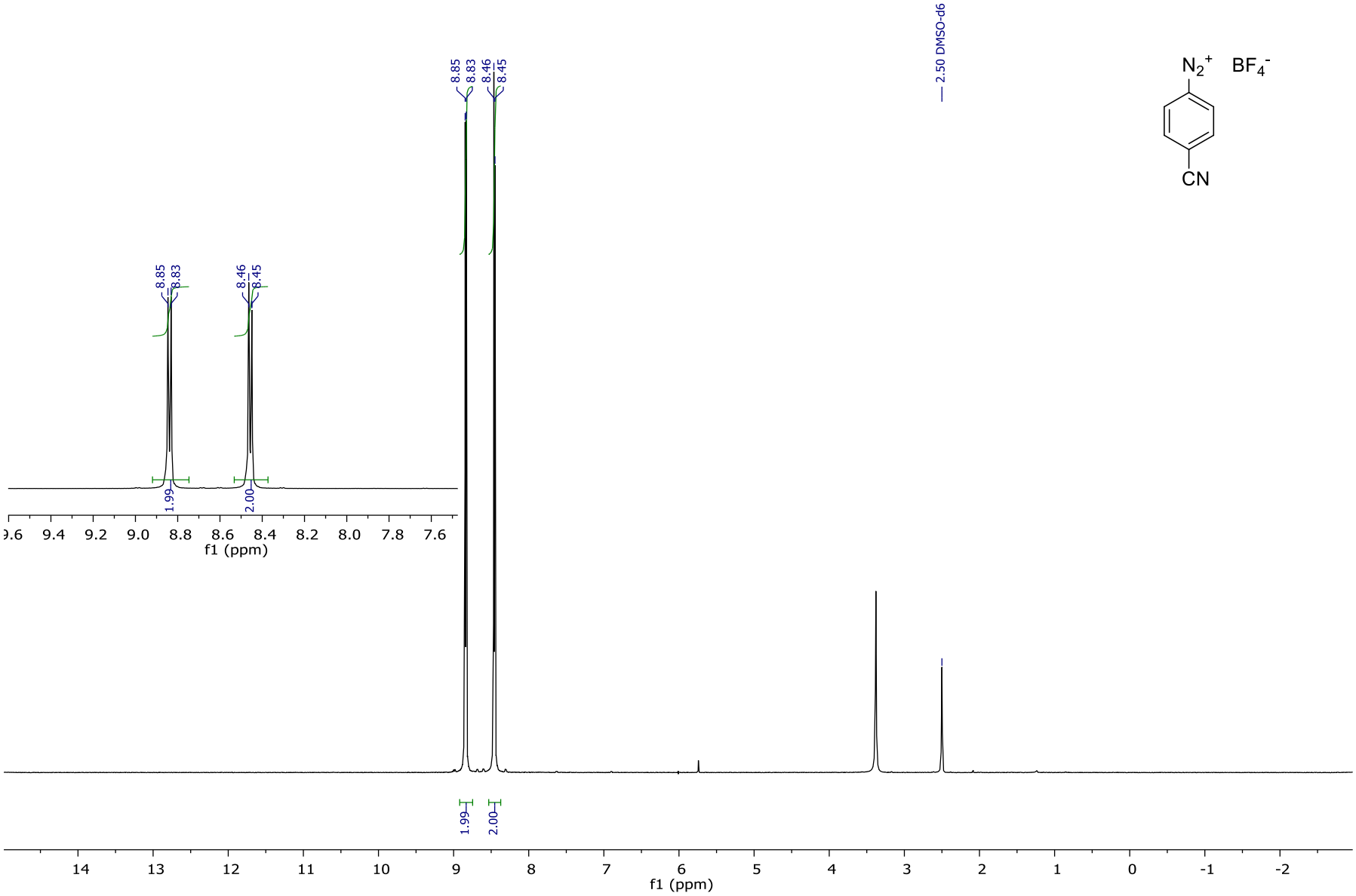


Figure S15. ^{1}H NMR (600 MHz, DMSO-d_6) of 4-cyanobenzenediazonium tetrafluoroborate (1g).

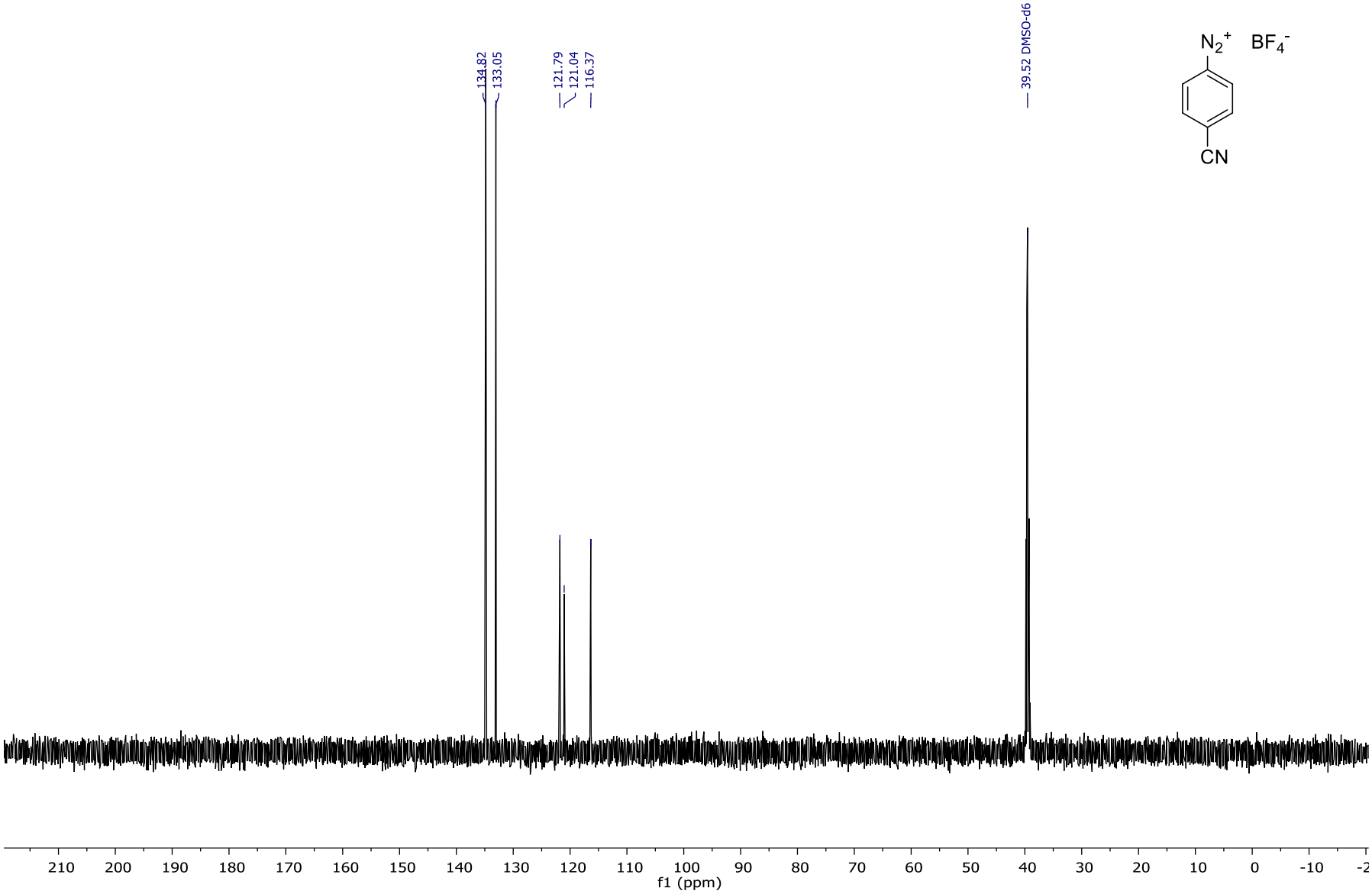


Figure S16. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6) of 4-cyanobenzenediazonium tetrafluoroborate (1g).

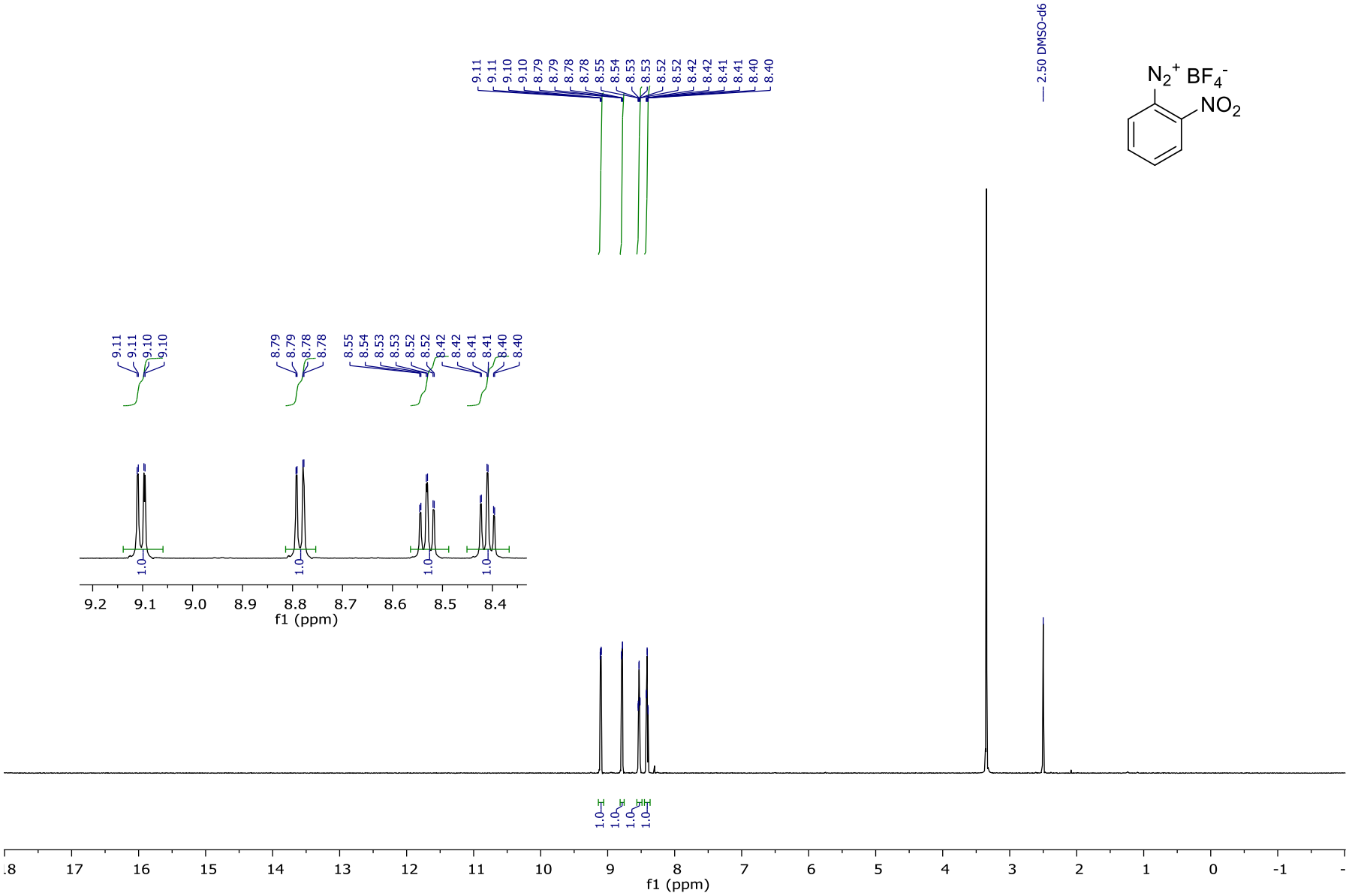


Figure S17. ^{1}H NMR (600 MHz, DMSO-d_6) of 2-nitrobenzenediazonium tetrafluoroborate (1h).

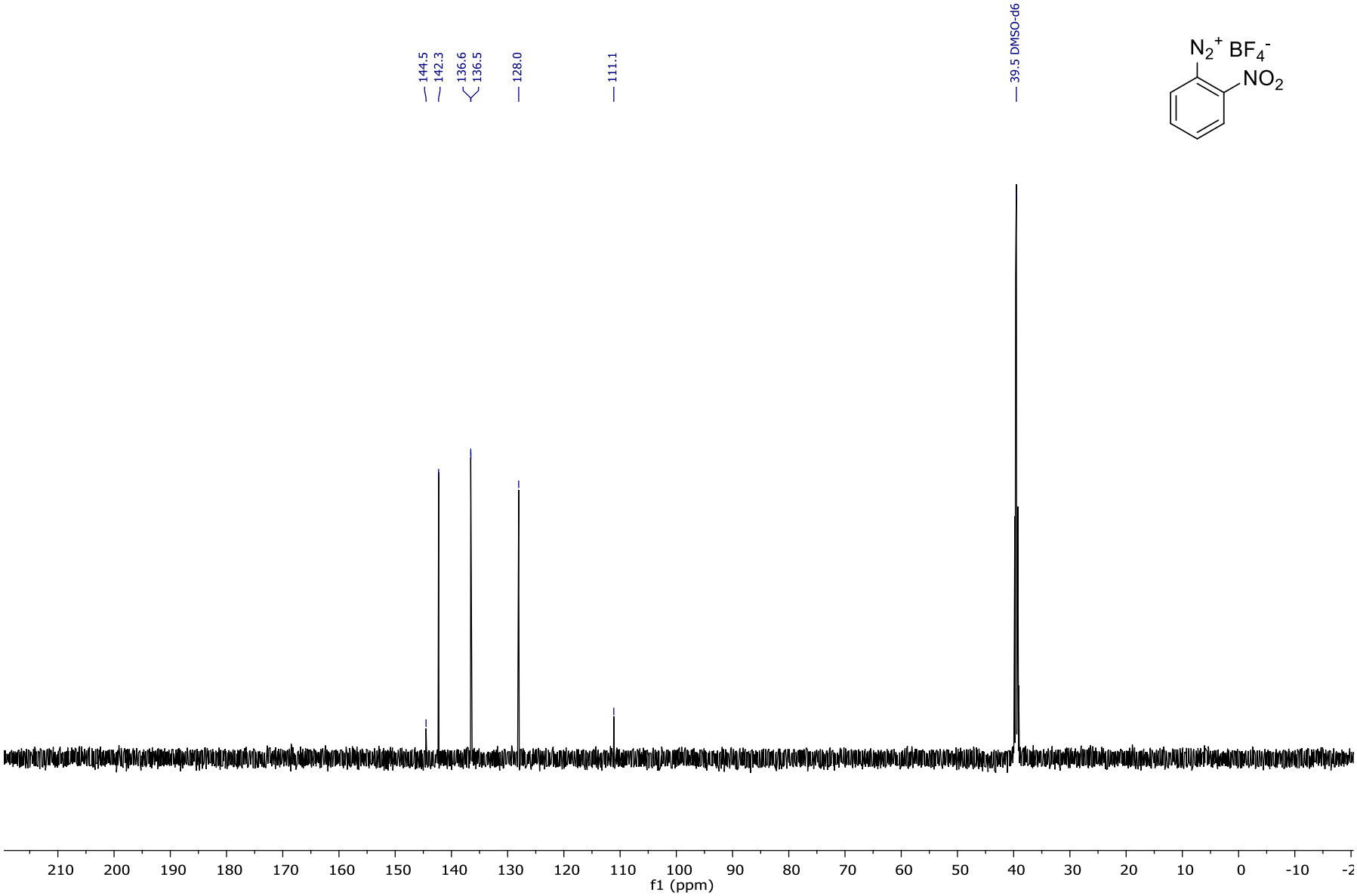


Figure S18. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6) of 2-nitrobenzenediazonium tetrafluoroborate (1h).

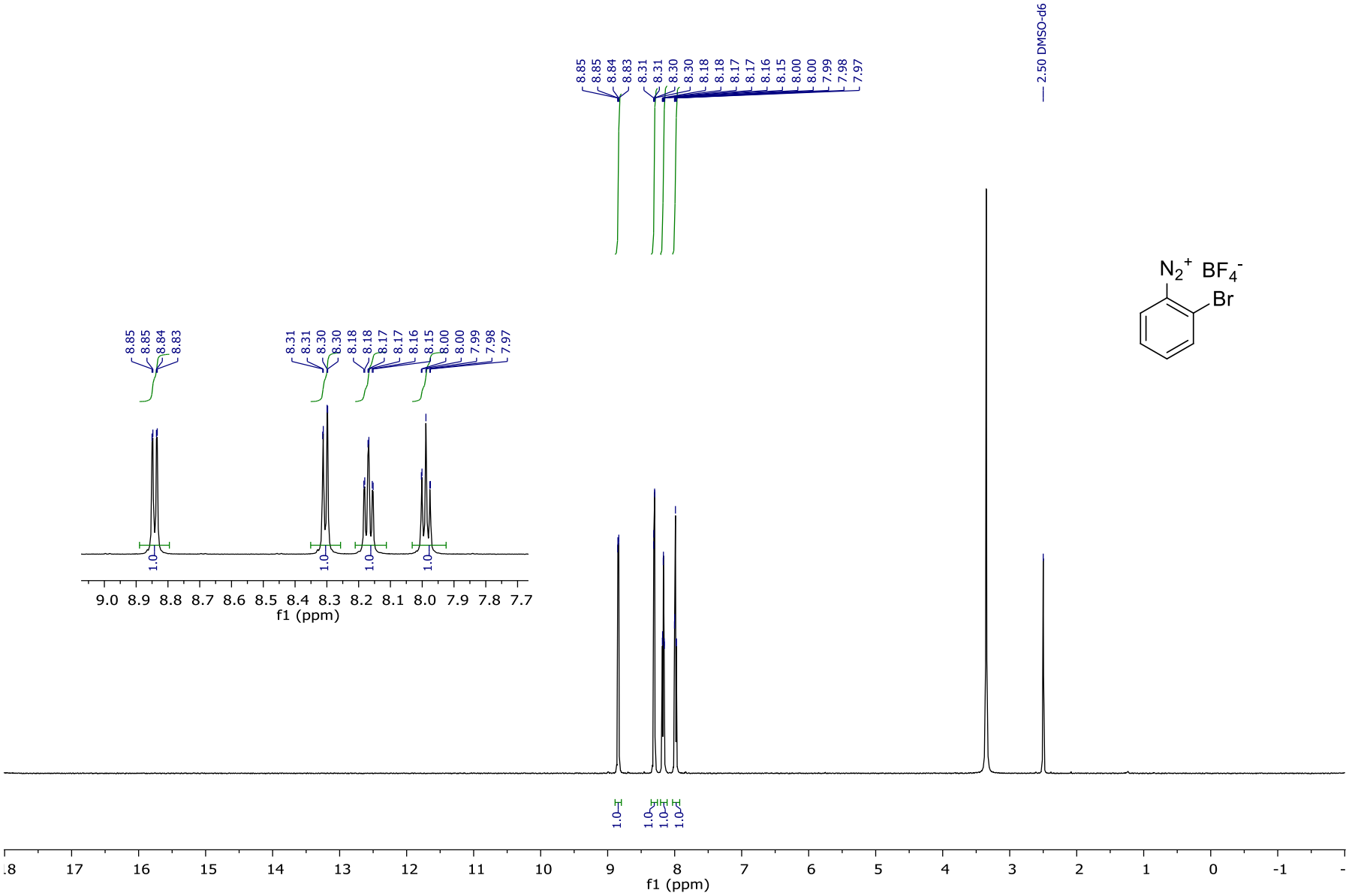


Figure S19. ^{1}H NMR (600 MHz, DMSO-d_6) of 2-bromobenzenediazonium tetrafluoroborate (1i).

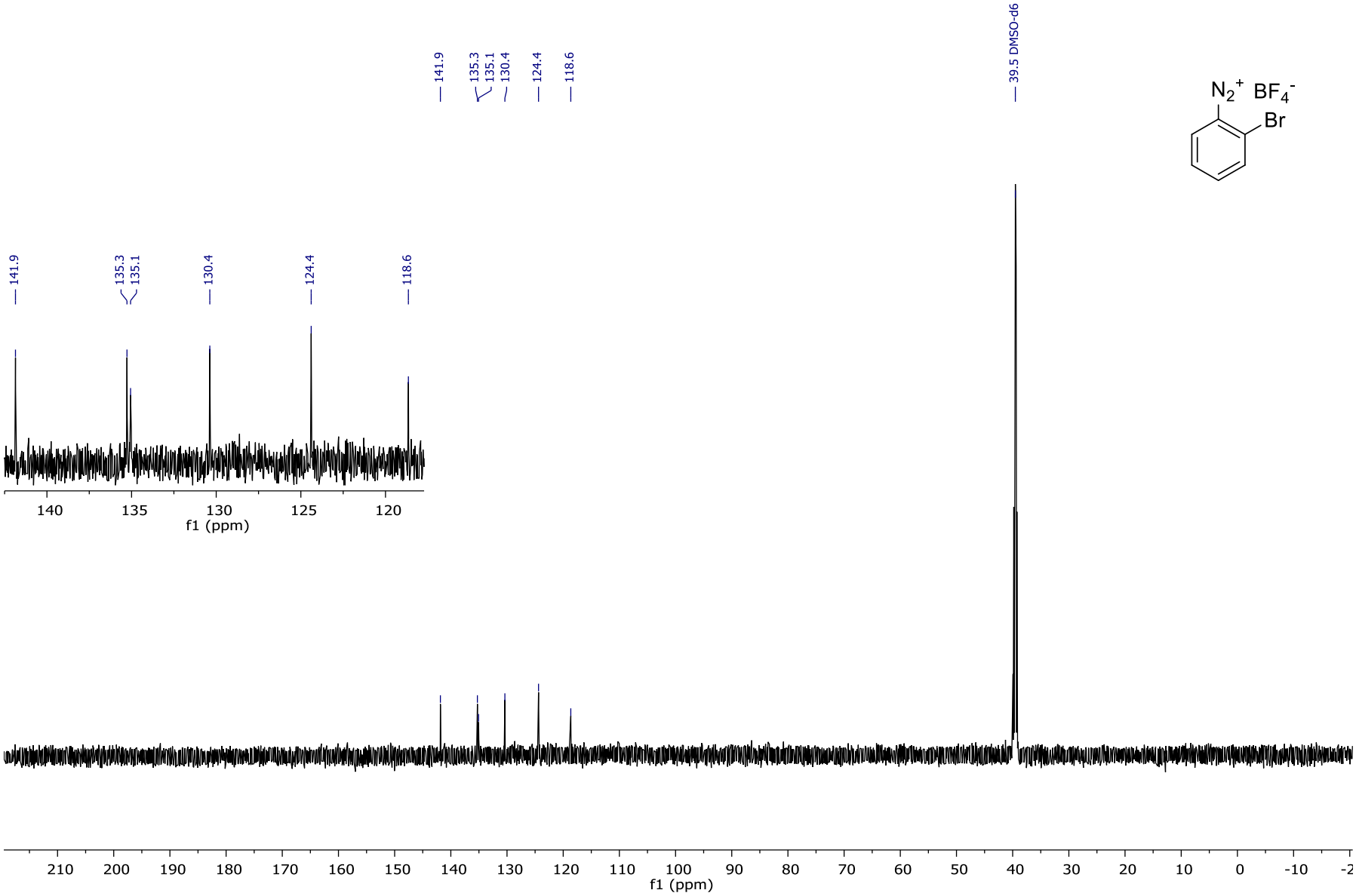


Figure S20. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6) of 2-bromobenzenediazonium tetrafluoroborate (1i).

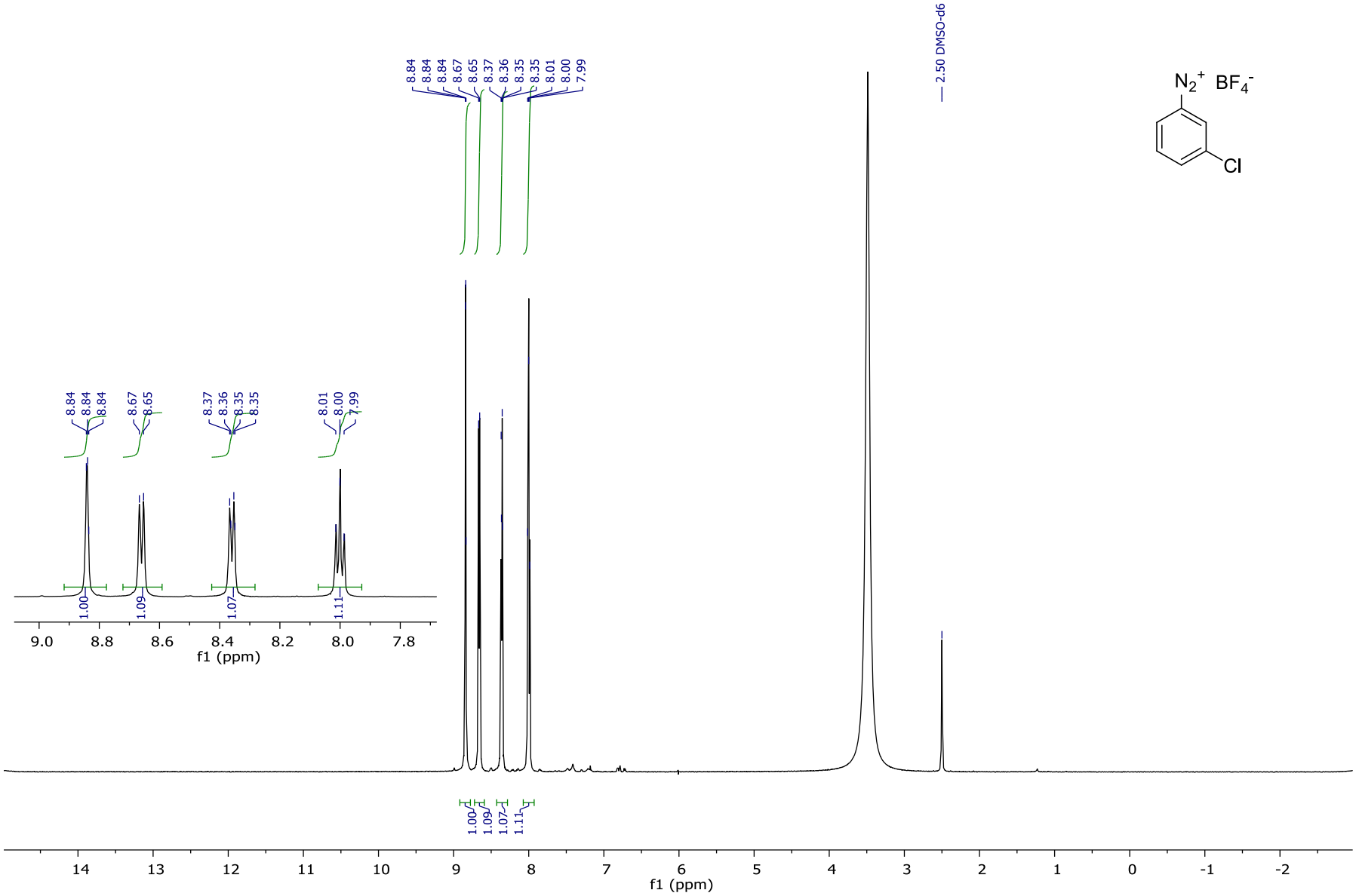


Figure S21. ^{1}H NMR (600 MHz, DMSO-*d*$_6$) of 3-chlorobenzenediazonium tetrafluoroborate (1j).

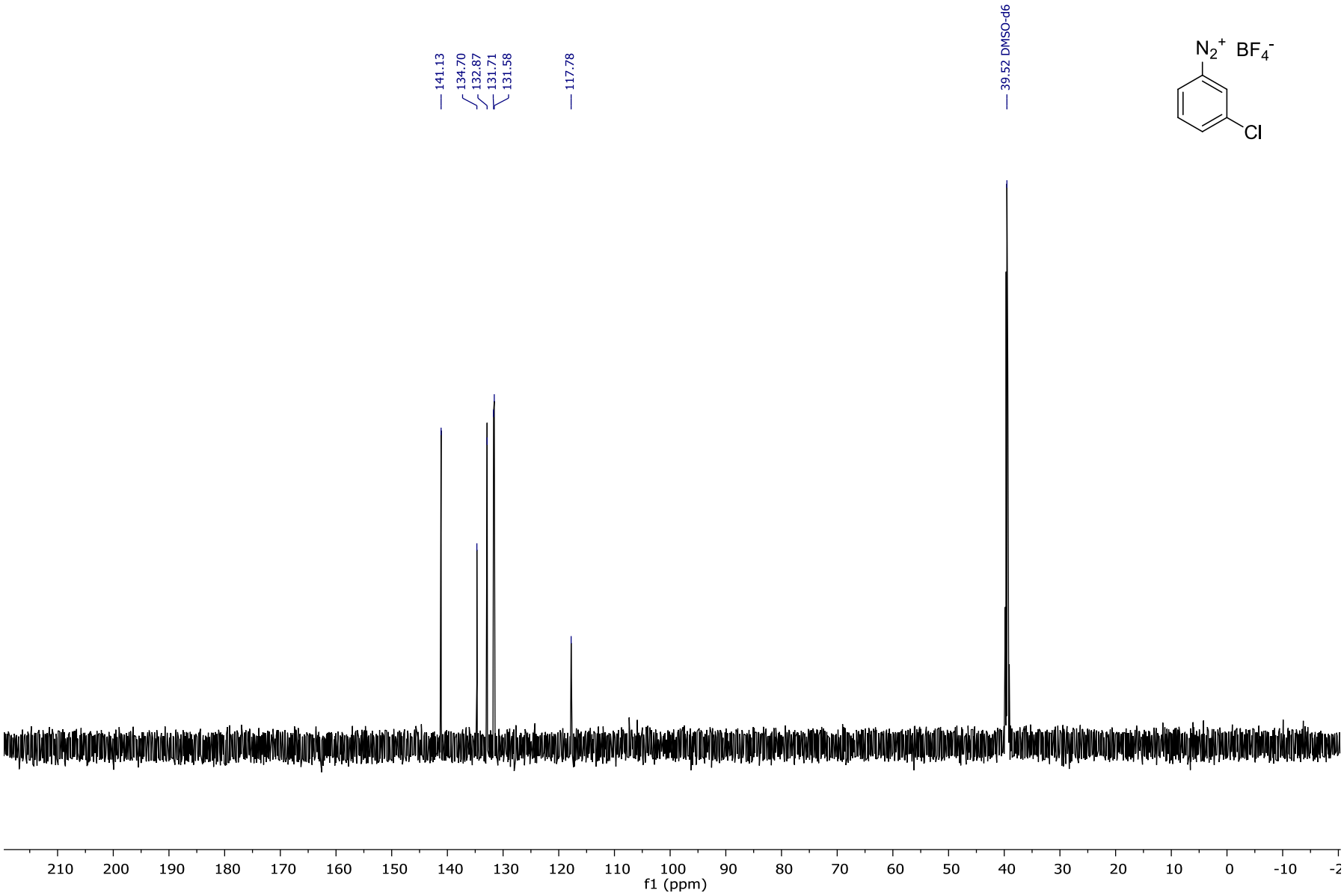


Figure S22. $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6) of 3-chlorobenzenediazonium tetrafluoroborate (1j).

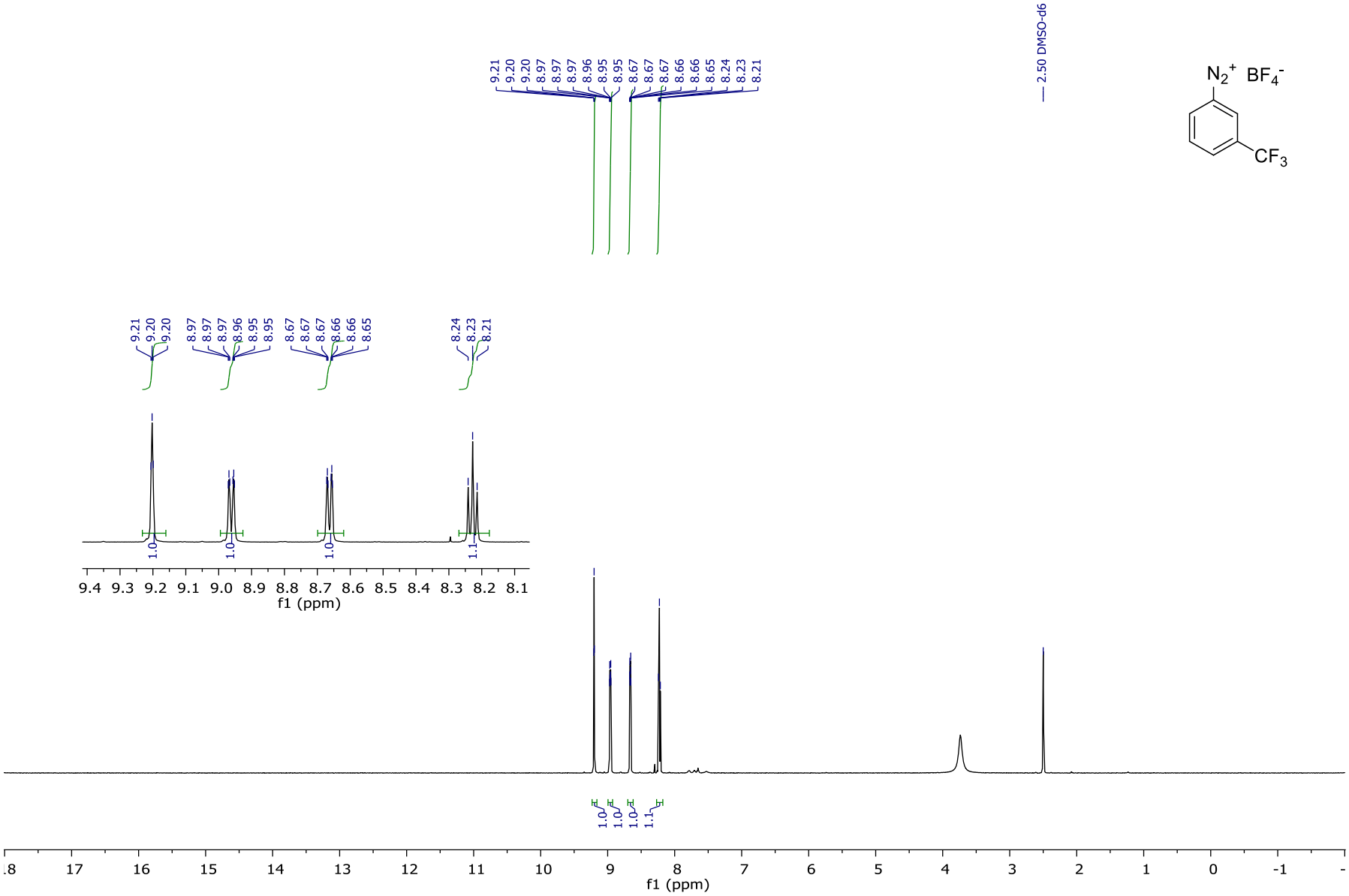


Figure S23. ^{1}H NMR (600 MHz, DMSO-d_6) of 3-(trifluoromethyl)benzenediazonium tetrafluoroborate (1k).

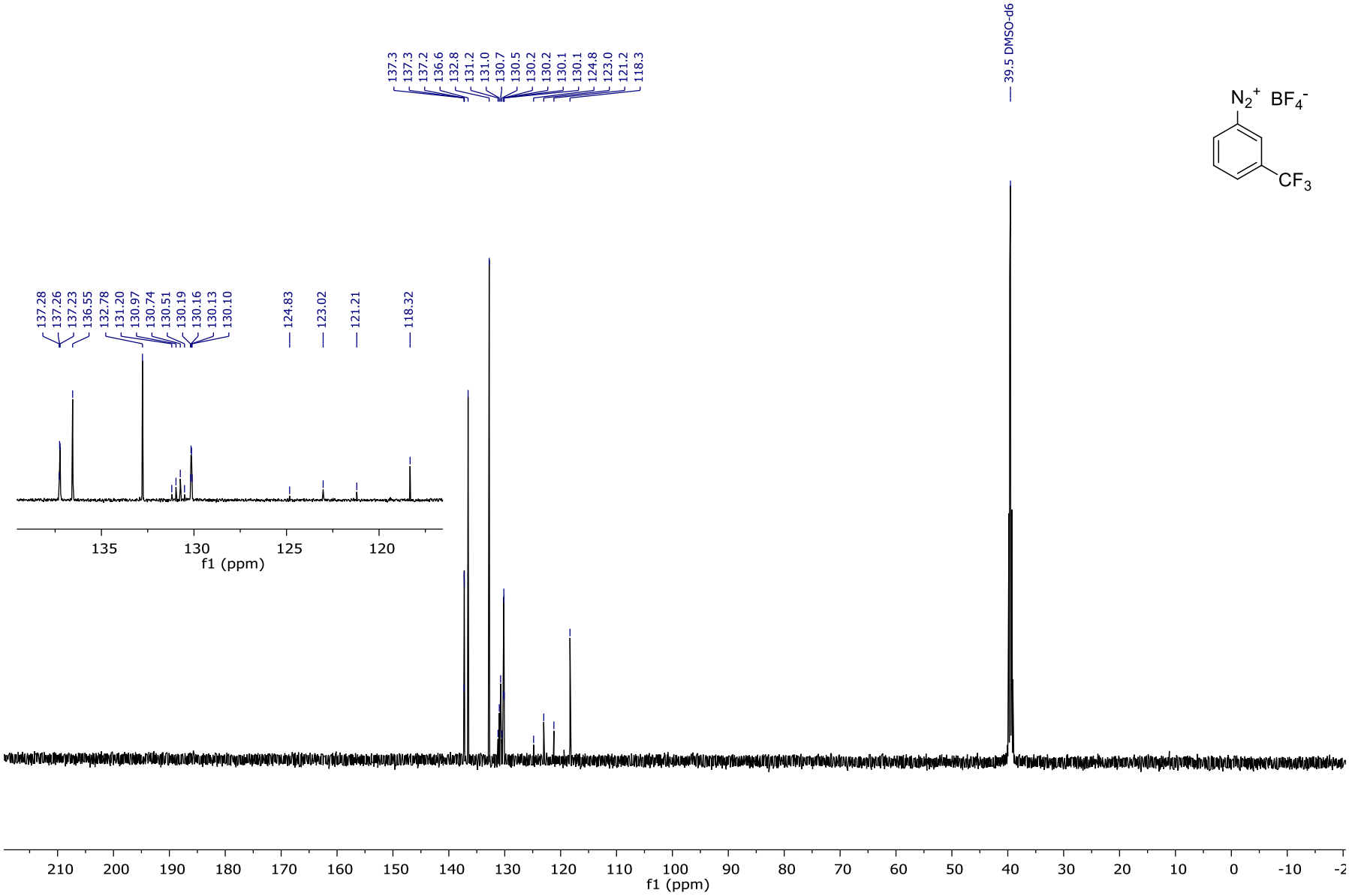


Figure S24. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6) of 3-(trifluoromethyl)benzenediazonium tetrafluoroborate (1k).

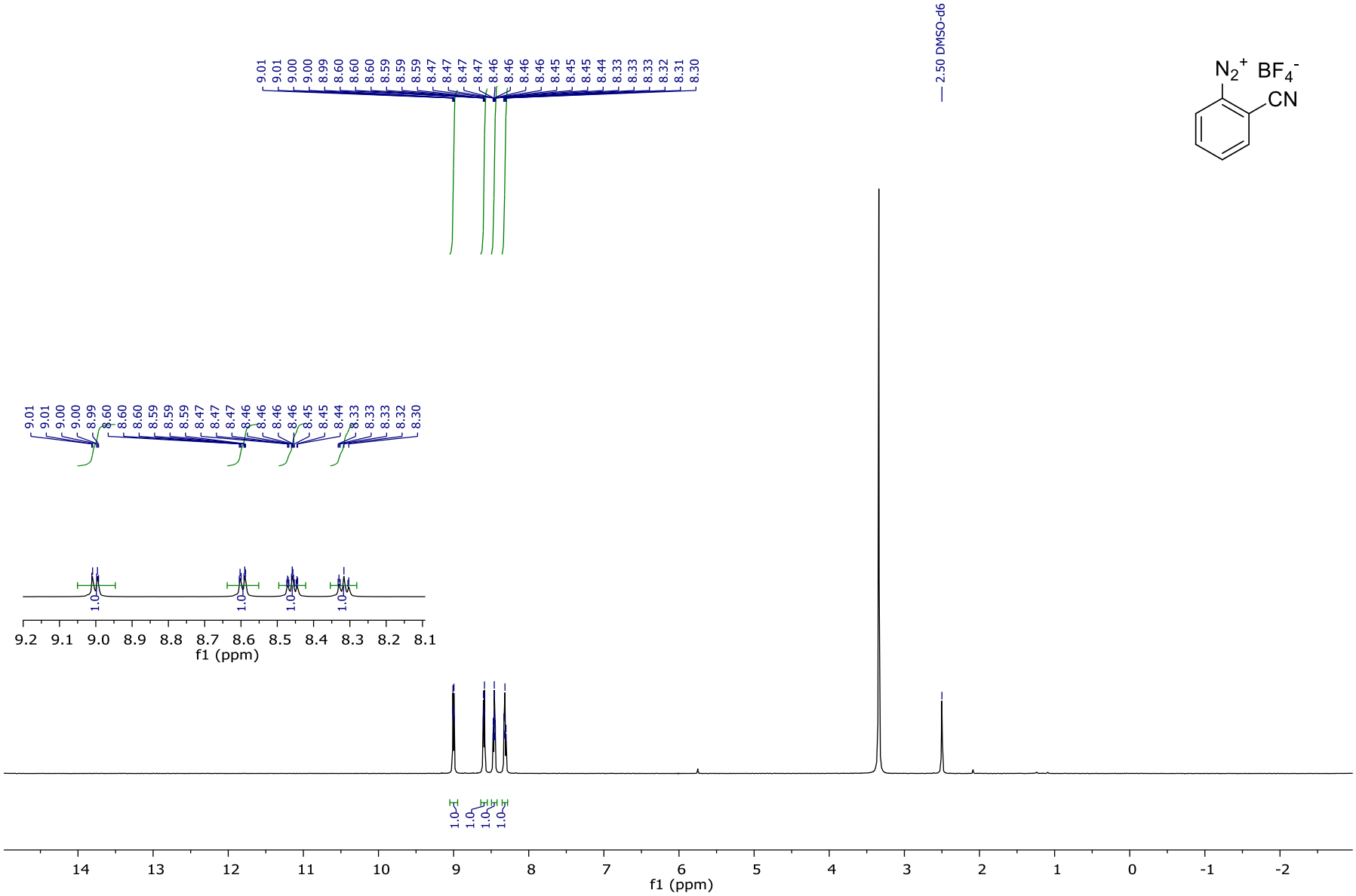


Figure S25. ^{1}H NMR (600 MHz, DMSO-*d*$_6$) of 2-cyanobenzenediazonium tetrafluoroborate (1l).

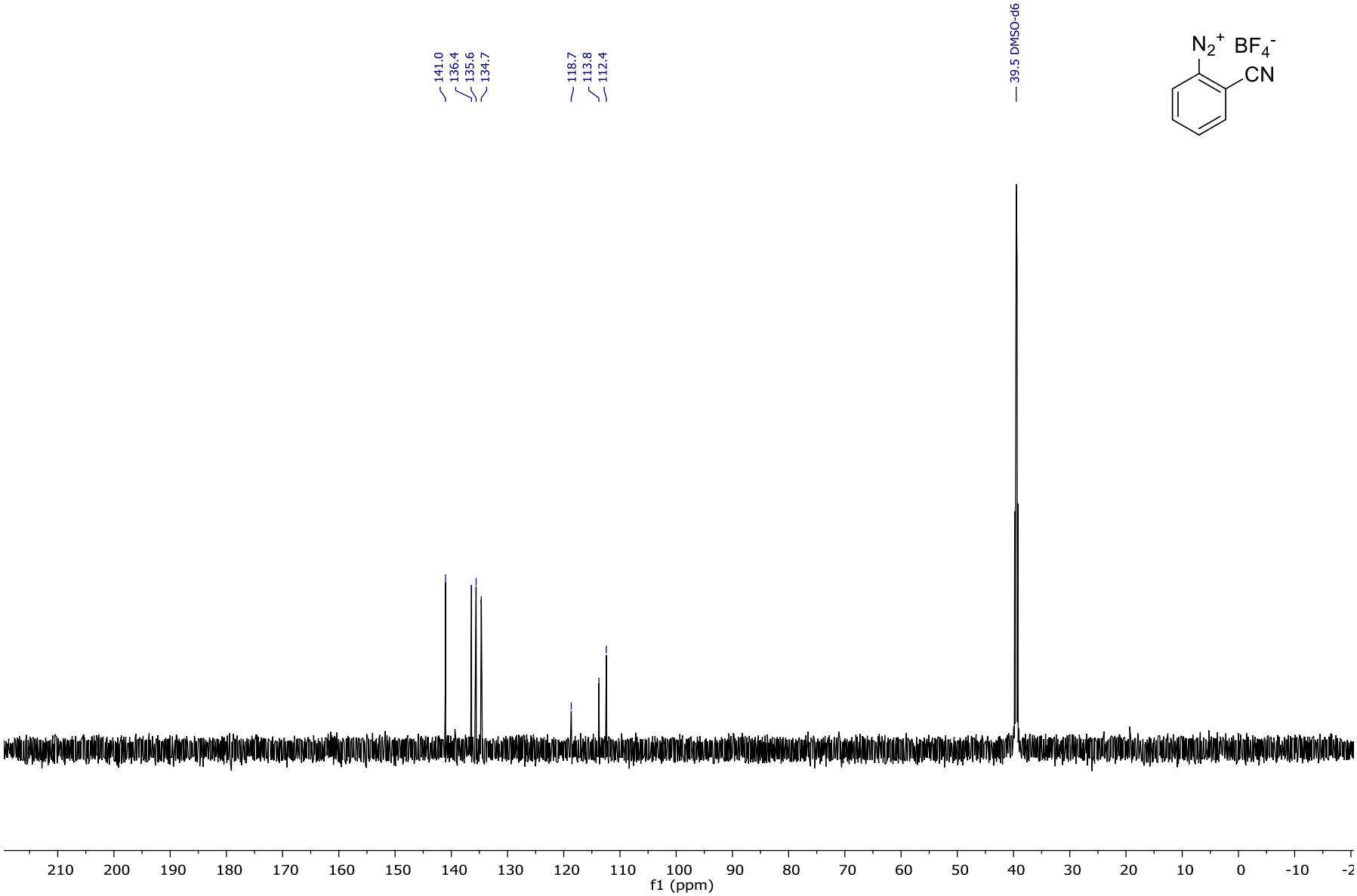


Figure S26. $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6) of 2-cyanobenzenediazonium tetrafluoroborate (1l).

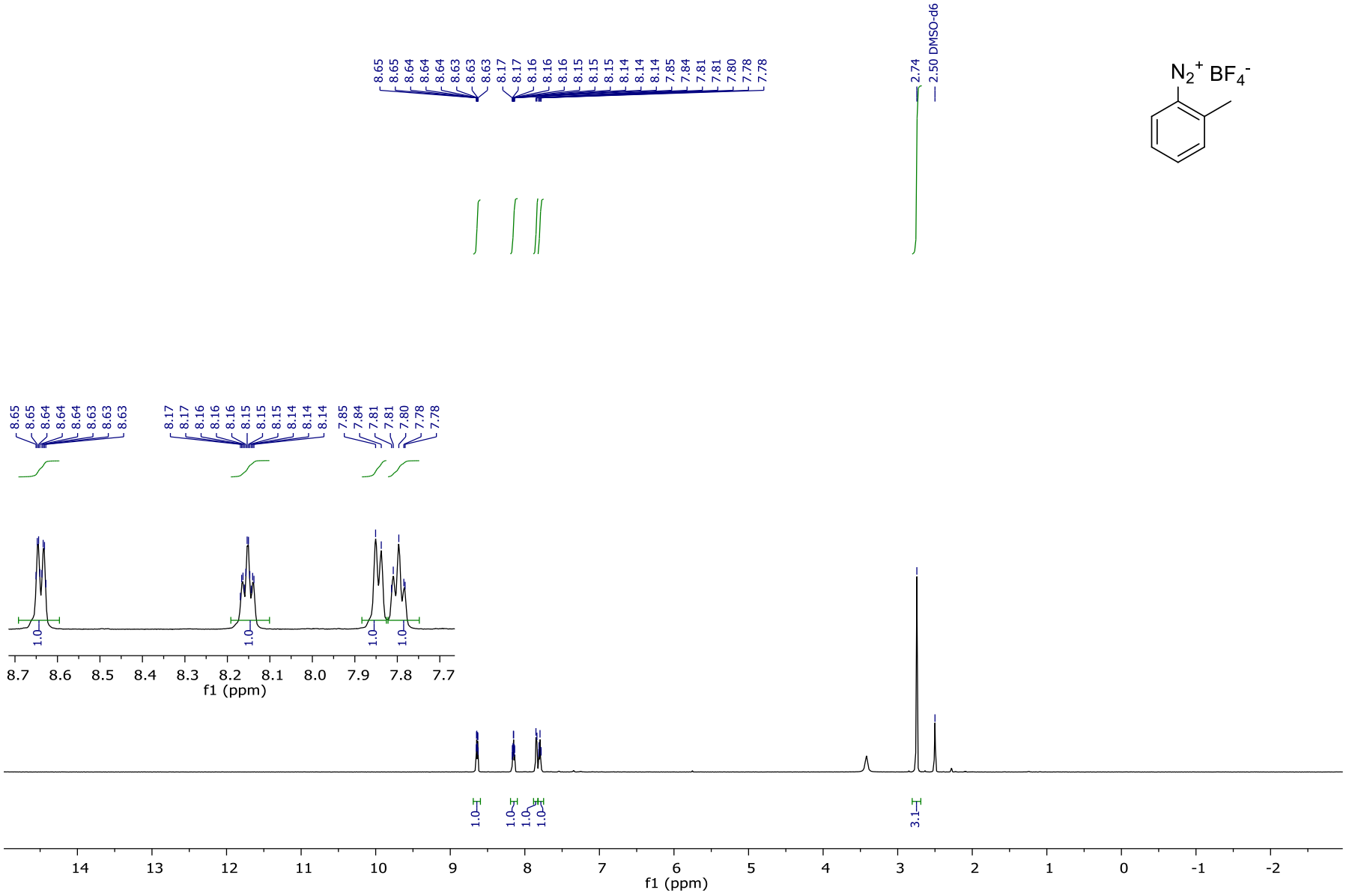


Figure S27. ^{1}H NMR (600 MHz, DMSO-d_6) of 2-methylbenzenediazonium tetrafluoroborate (1m).

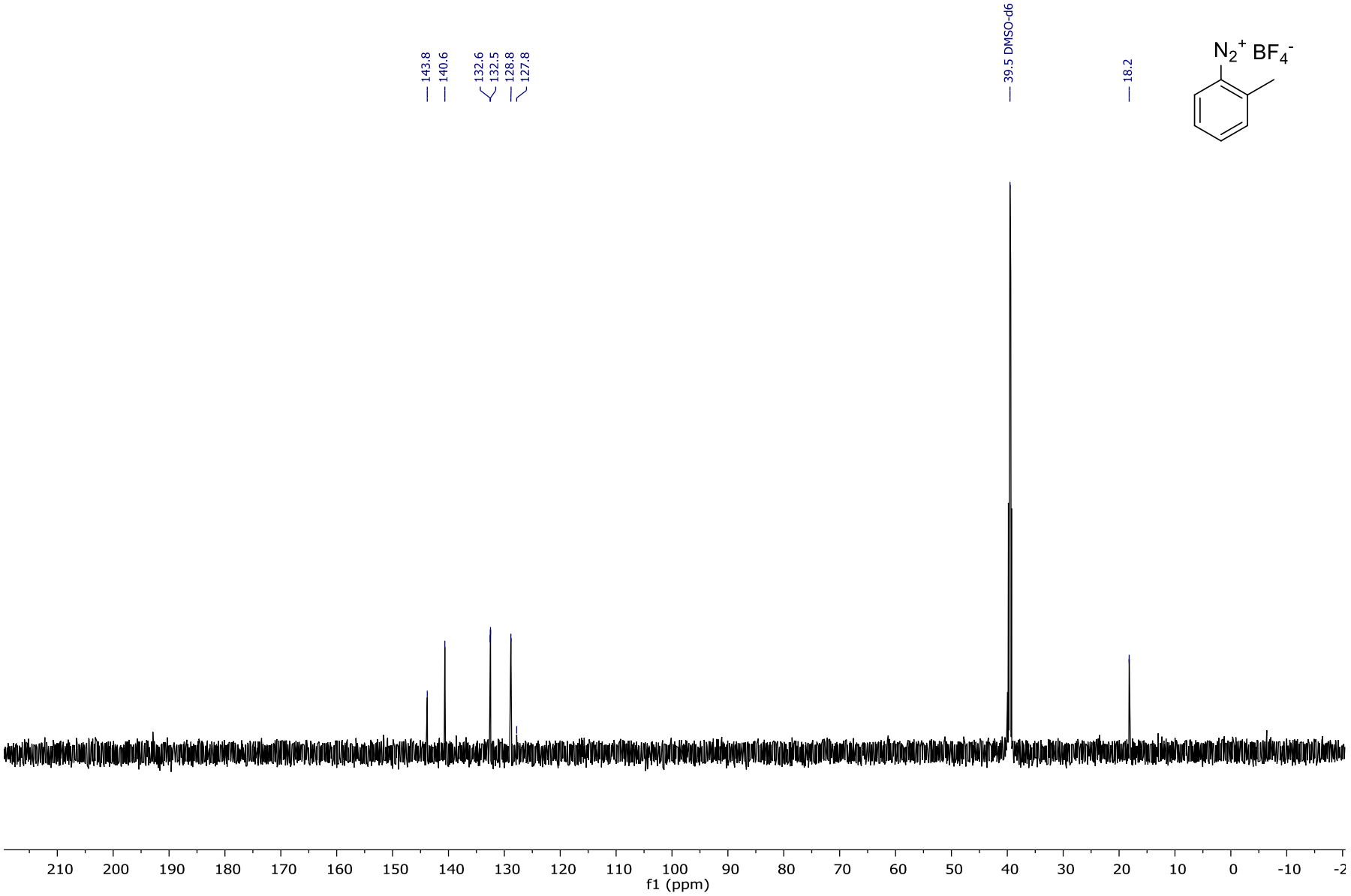


Figure S28. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6) of 2-methylbenzenediazonium tetrafluoroborate (1m).

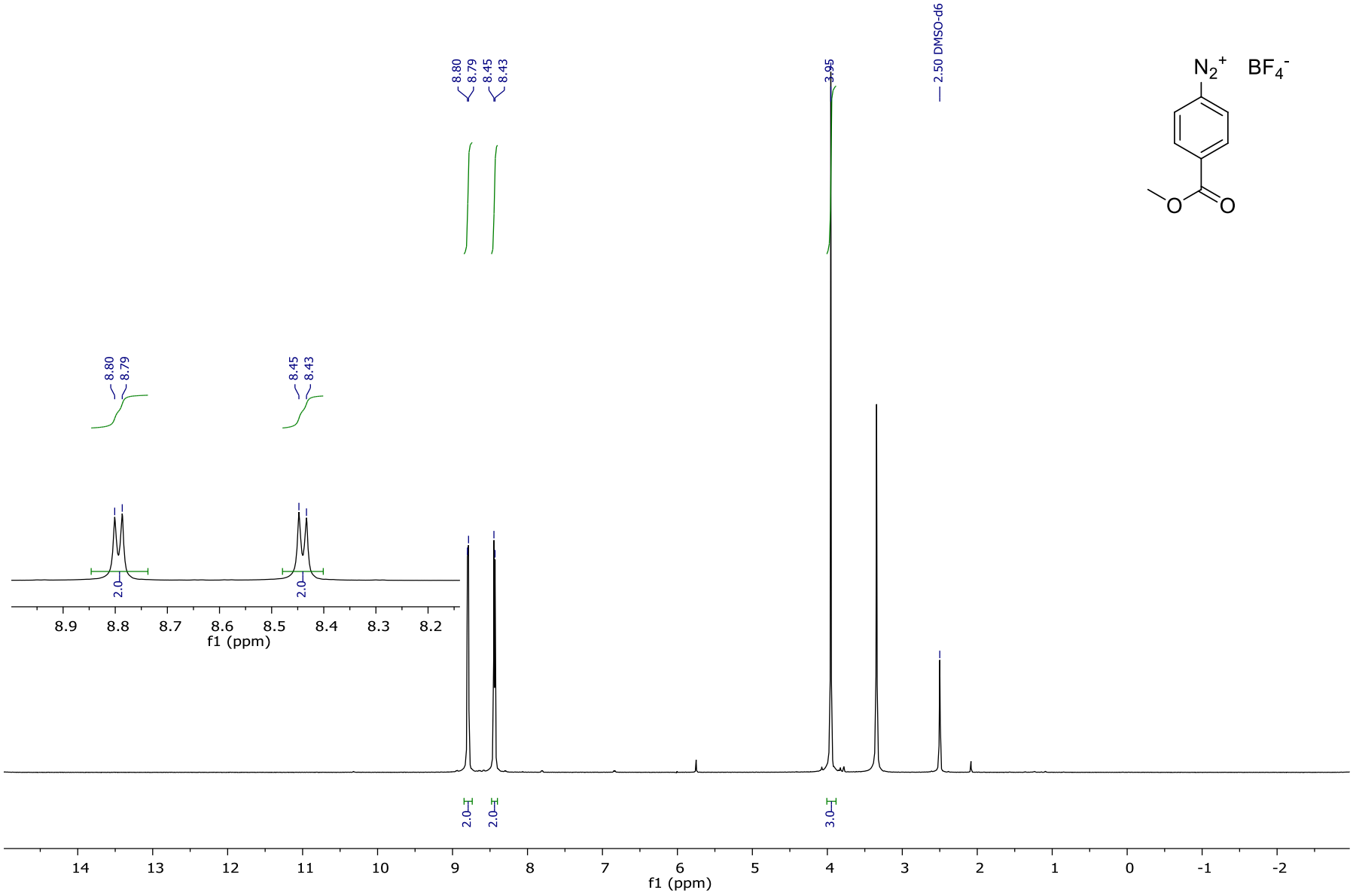


Figure S29. ^{1}H NMR (600 MHz, DMSO-d_6) of 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate (1n).

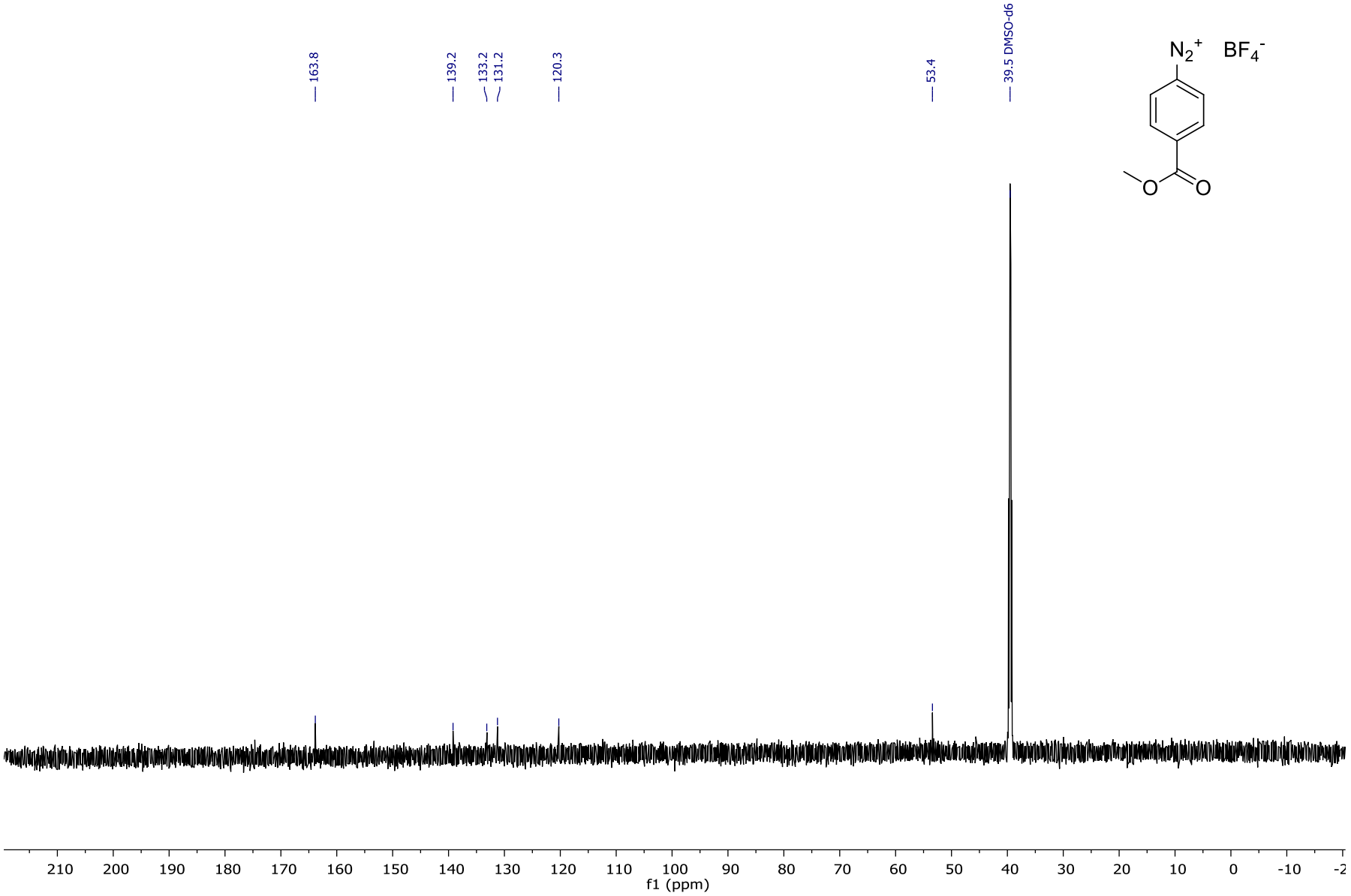


Figure S30. $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6) of 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate (1n).

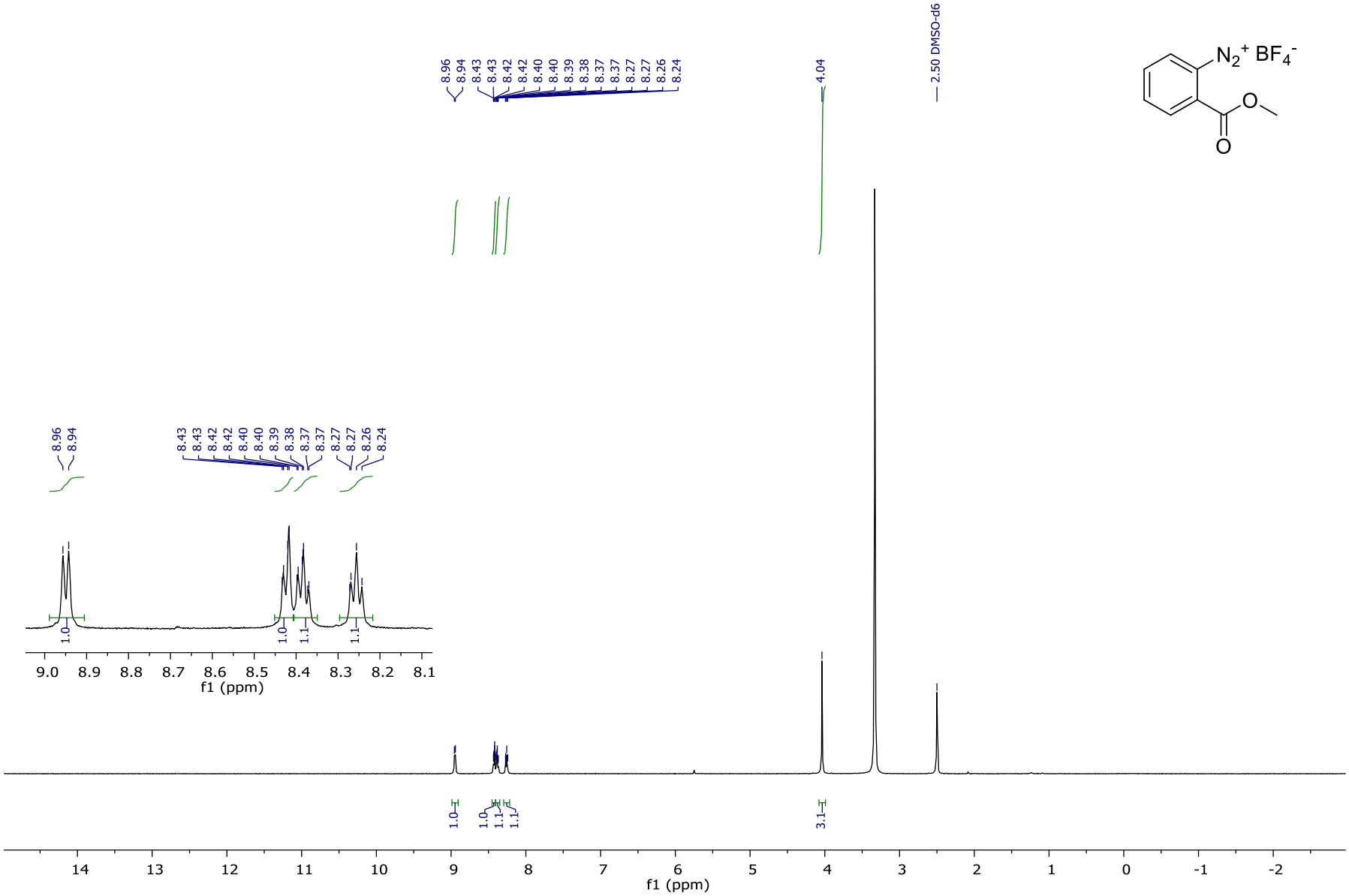


Figure S31. ^{1}H NMR (600 MHz, DMSO-*d*$_6$) of 2-(methoxycarbonyl)benzenediazonium tetrafluoroborate (1o).

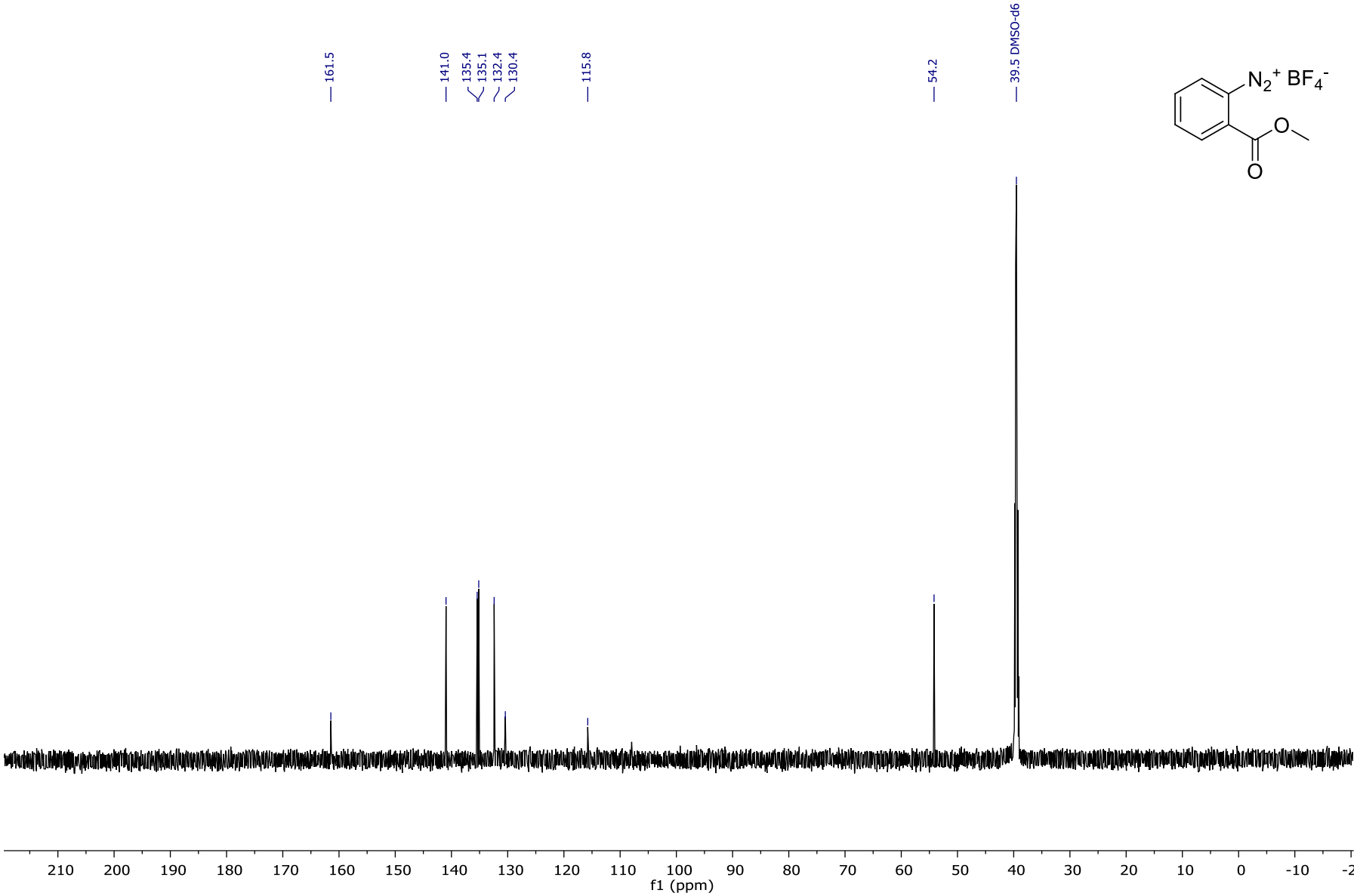


Figure S32. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6) of 2-(methoxycarbonyl)benzenediazonium tetrafluoroborate (1o).

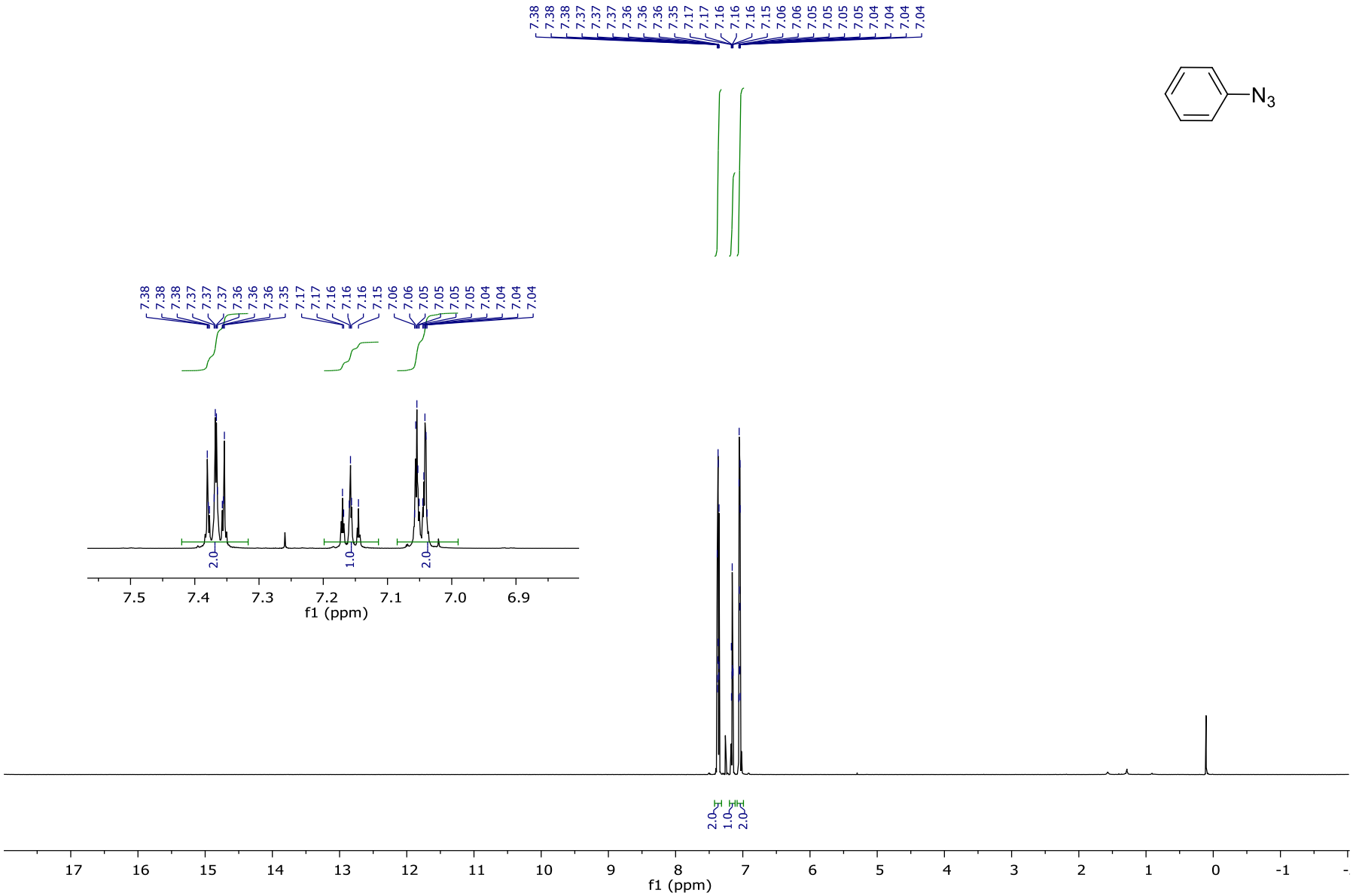


Figure S33. ^{1}H NMR (600 MHz, Chloroform-*d*) of azidobenzene (2a).

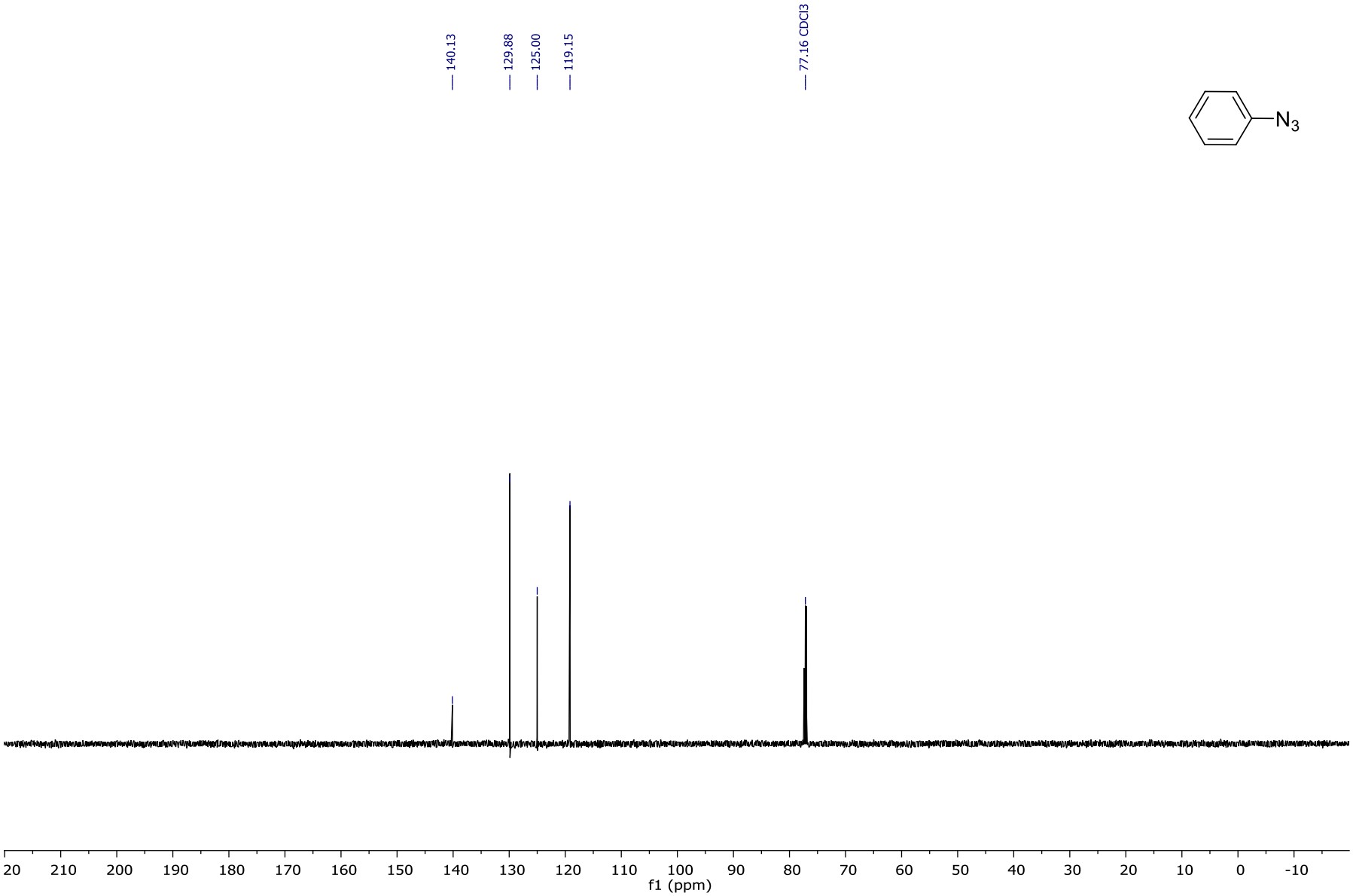


Figure S34. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) of azidobenzene (2a).

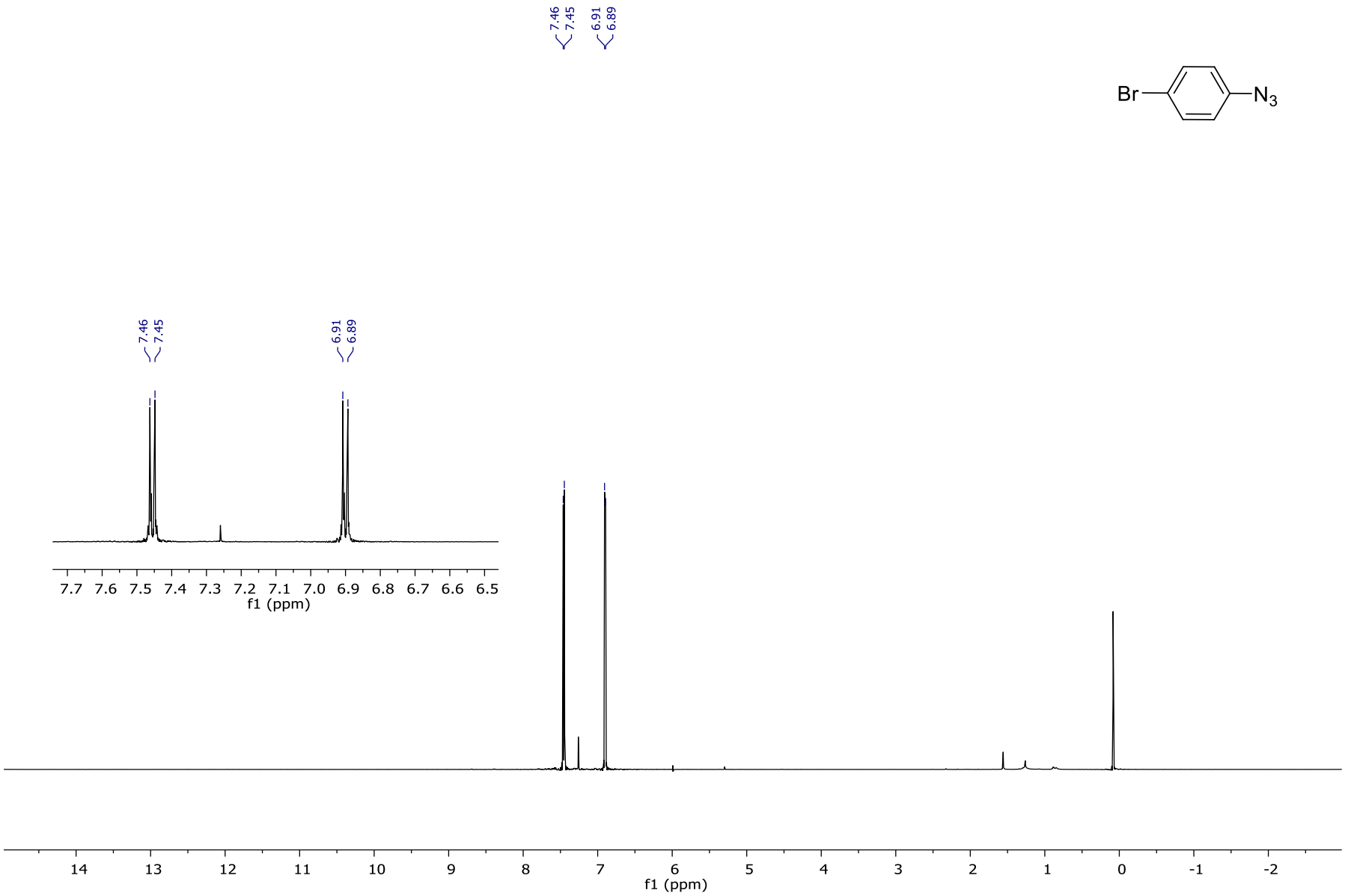


Figure S35. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-azido-4-bromobenzene (2b).

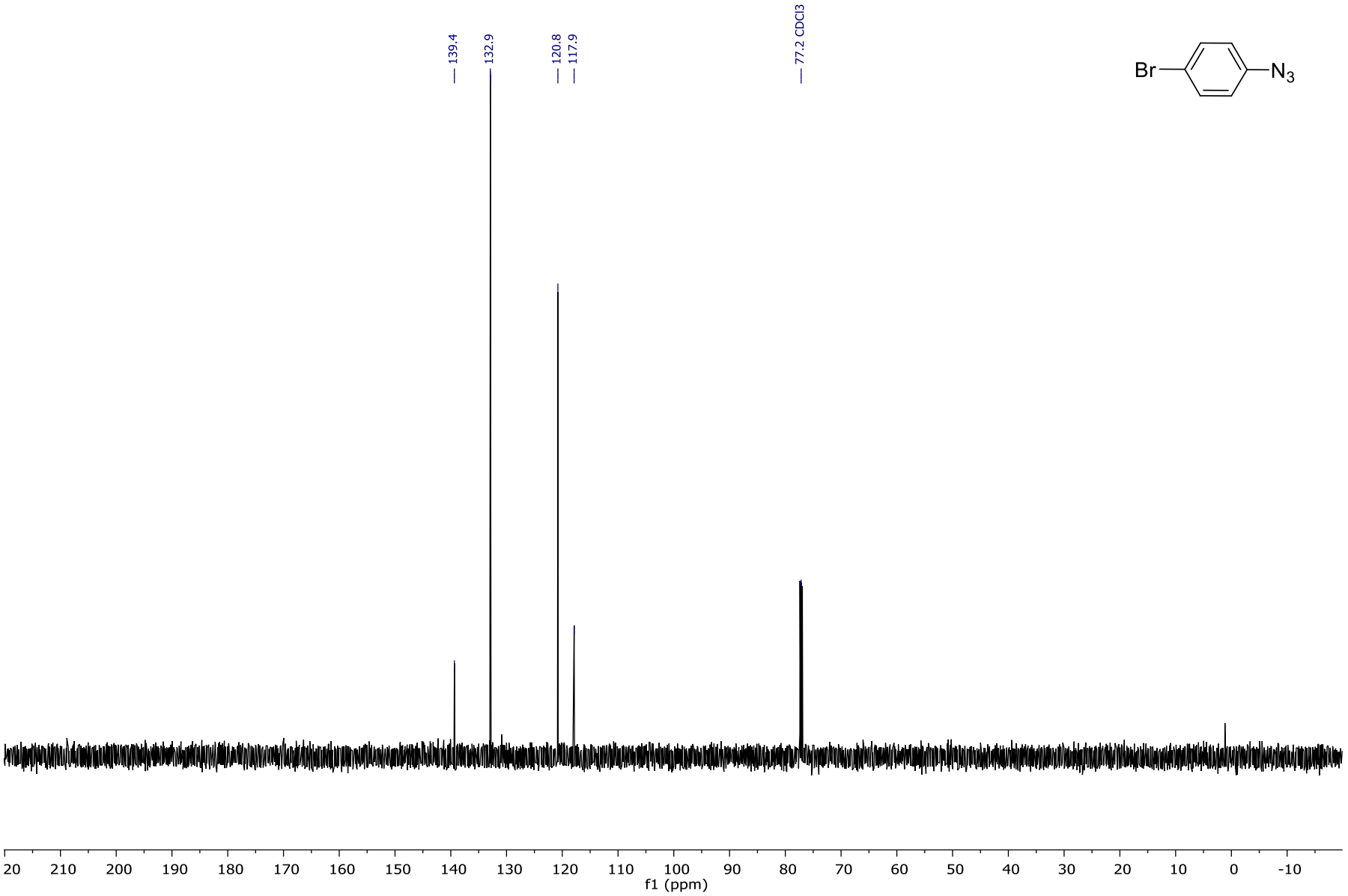


Figure S36. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) of 1-azido-4-bromobenzene (2b).

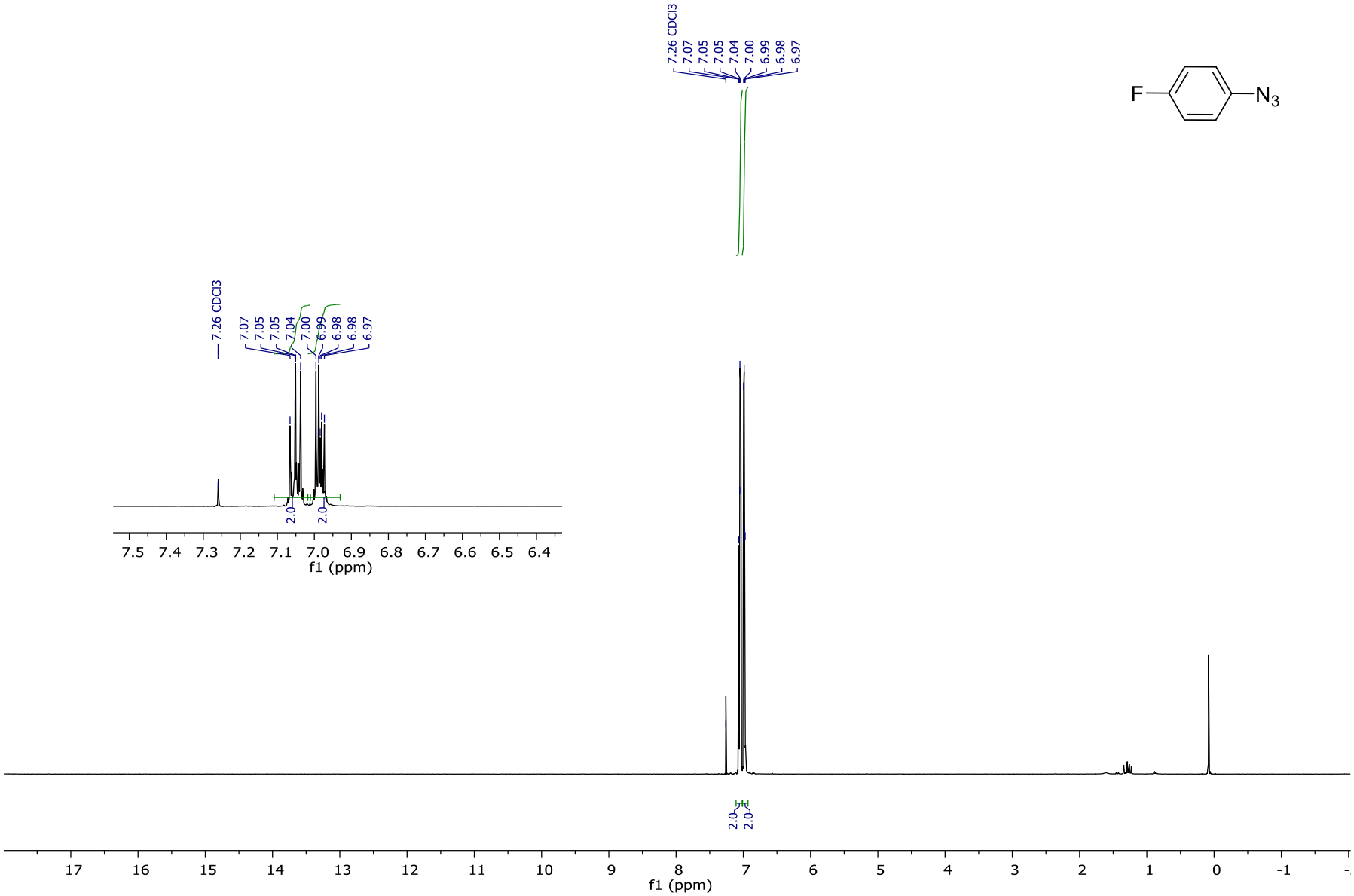


Figure S37. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-azido-4-fluorobenzene (2c).

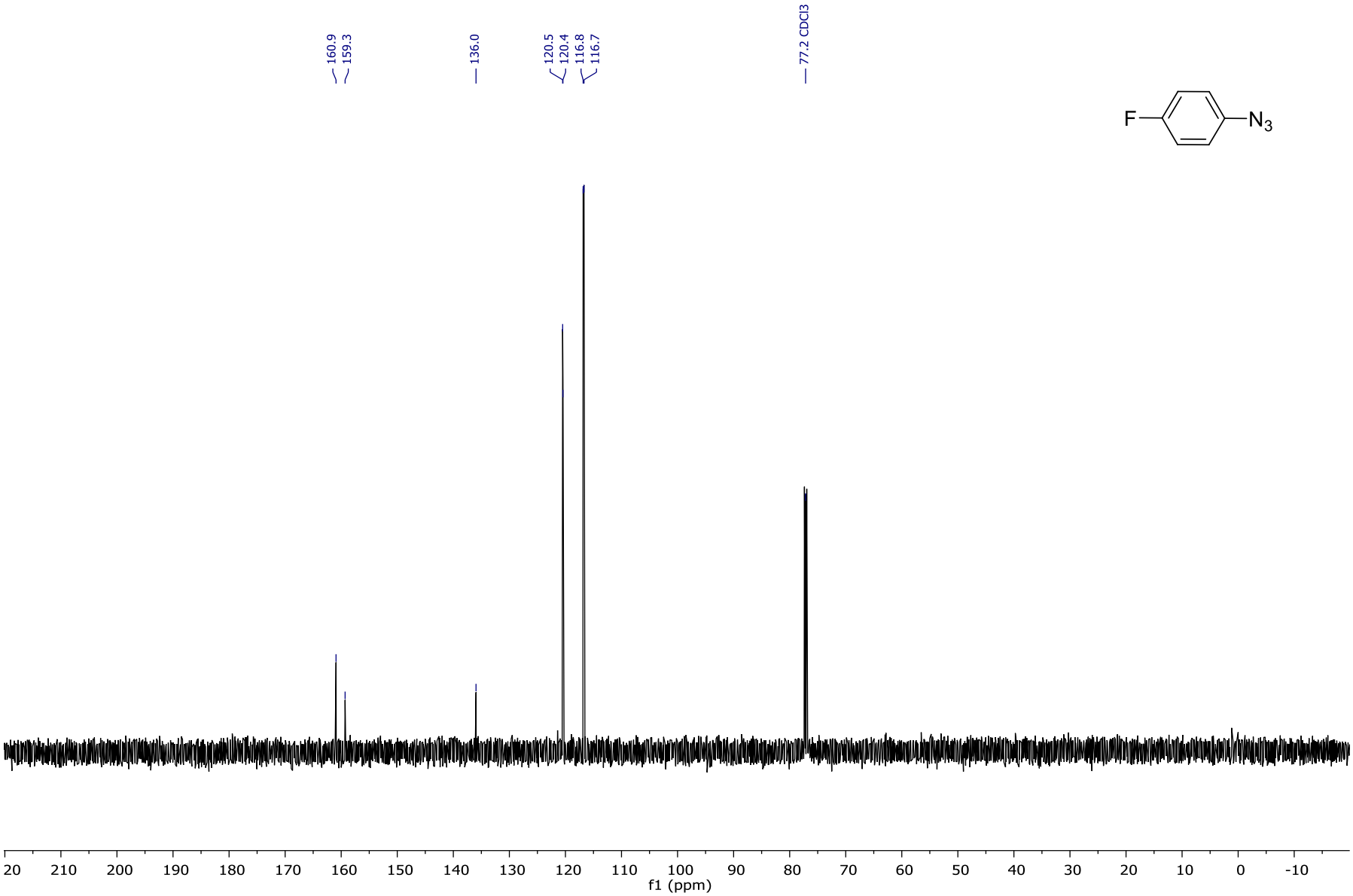


Figure S38. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) of 1-azido-4-fluorobenzene (2c).

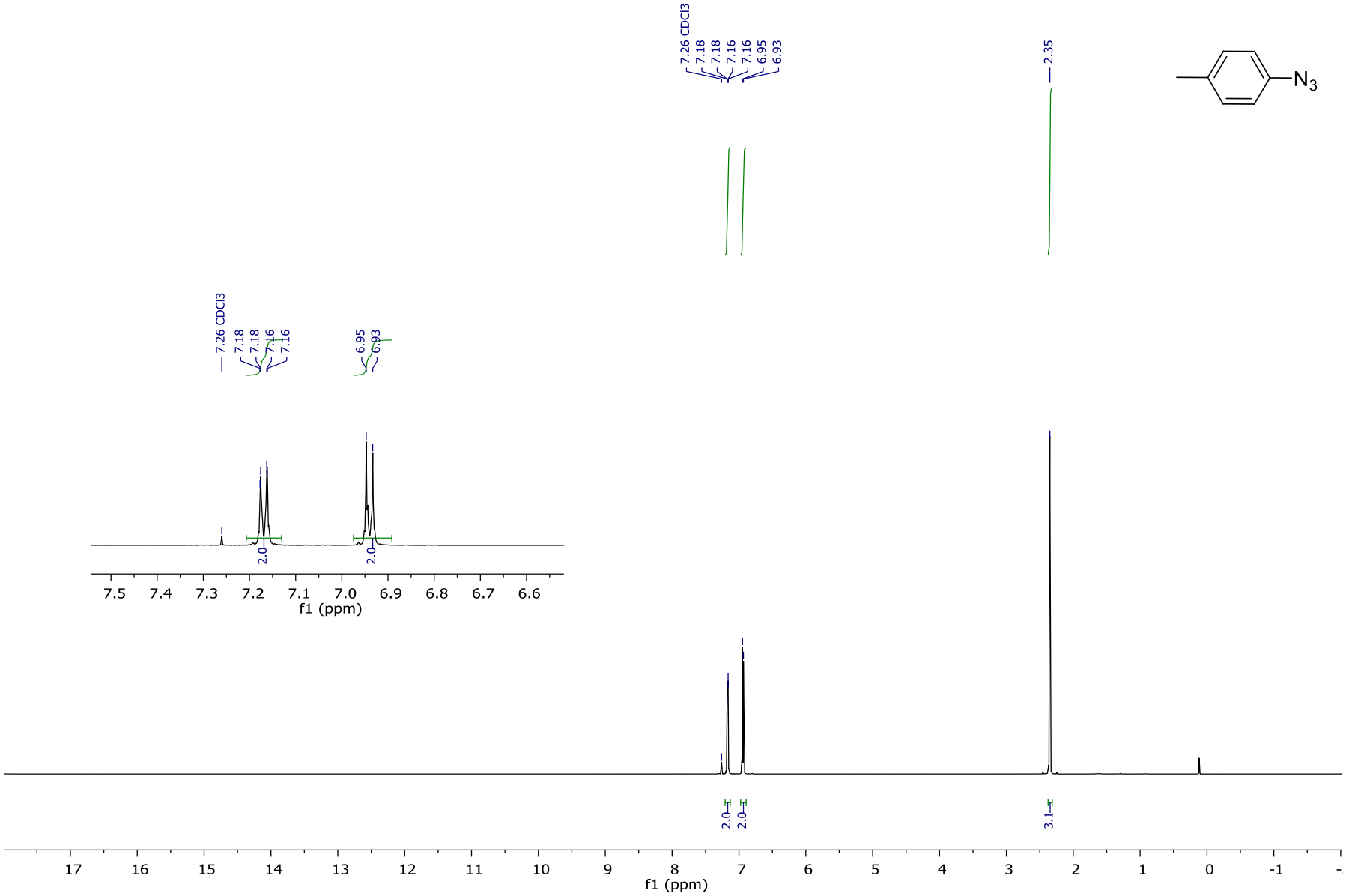


Figure S39. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-azido-4-methylbenzene (2d).

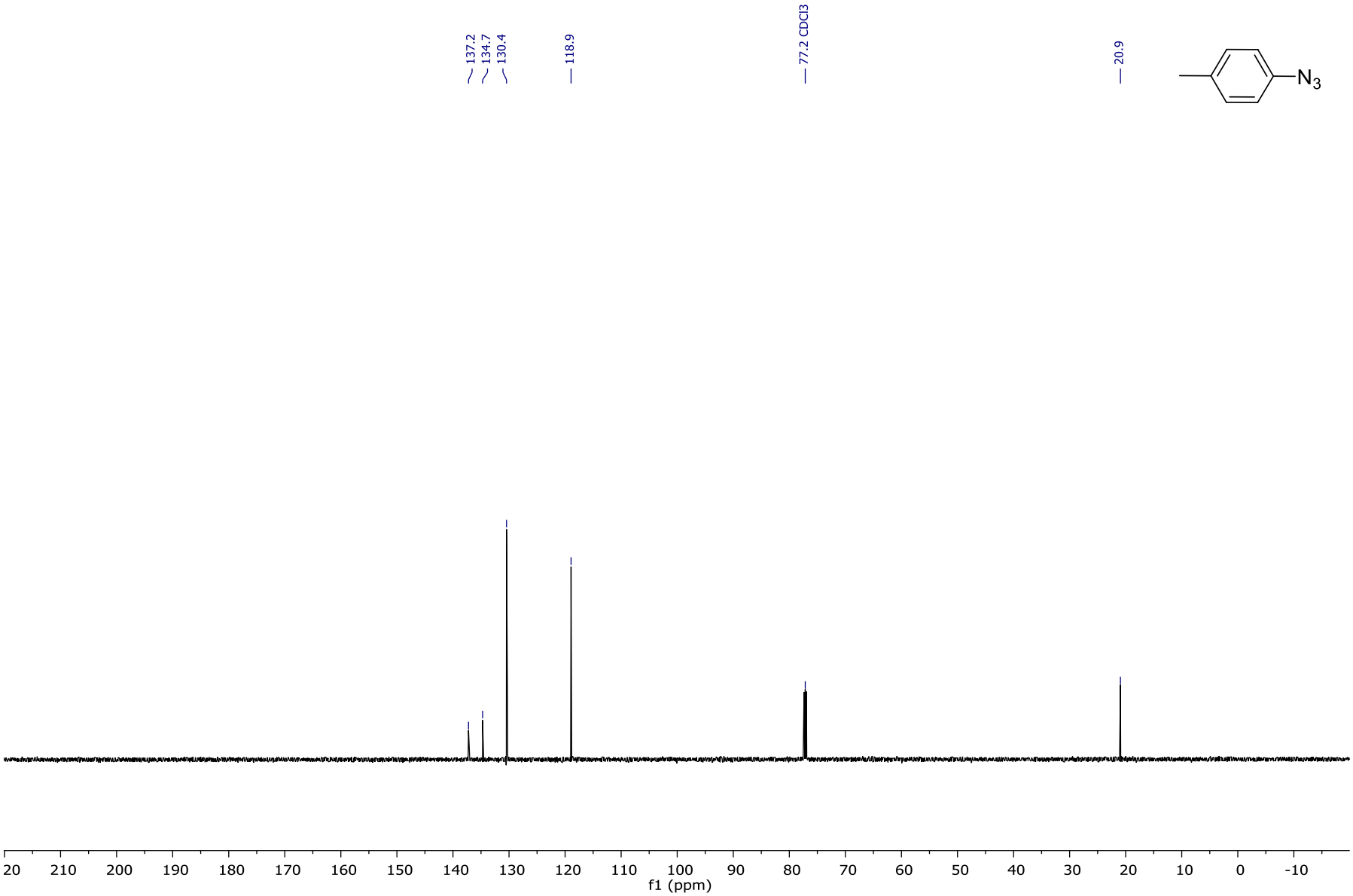


Figure S40. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) of 1-azido-4-methylbenzene (2d).

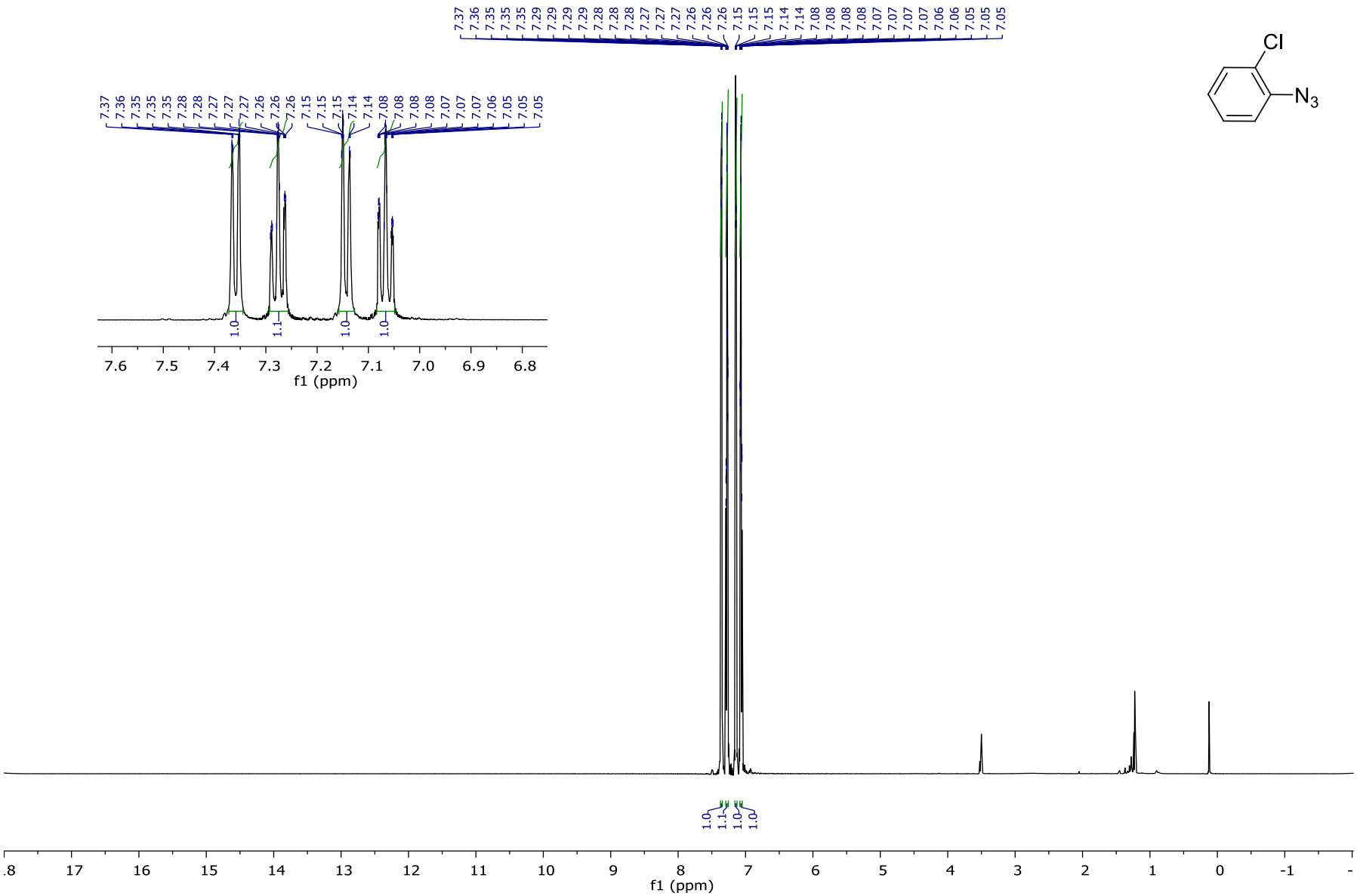


Figure S41. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-azido-2-chlorobenzene (2e).

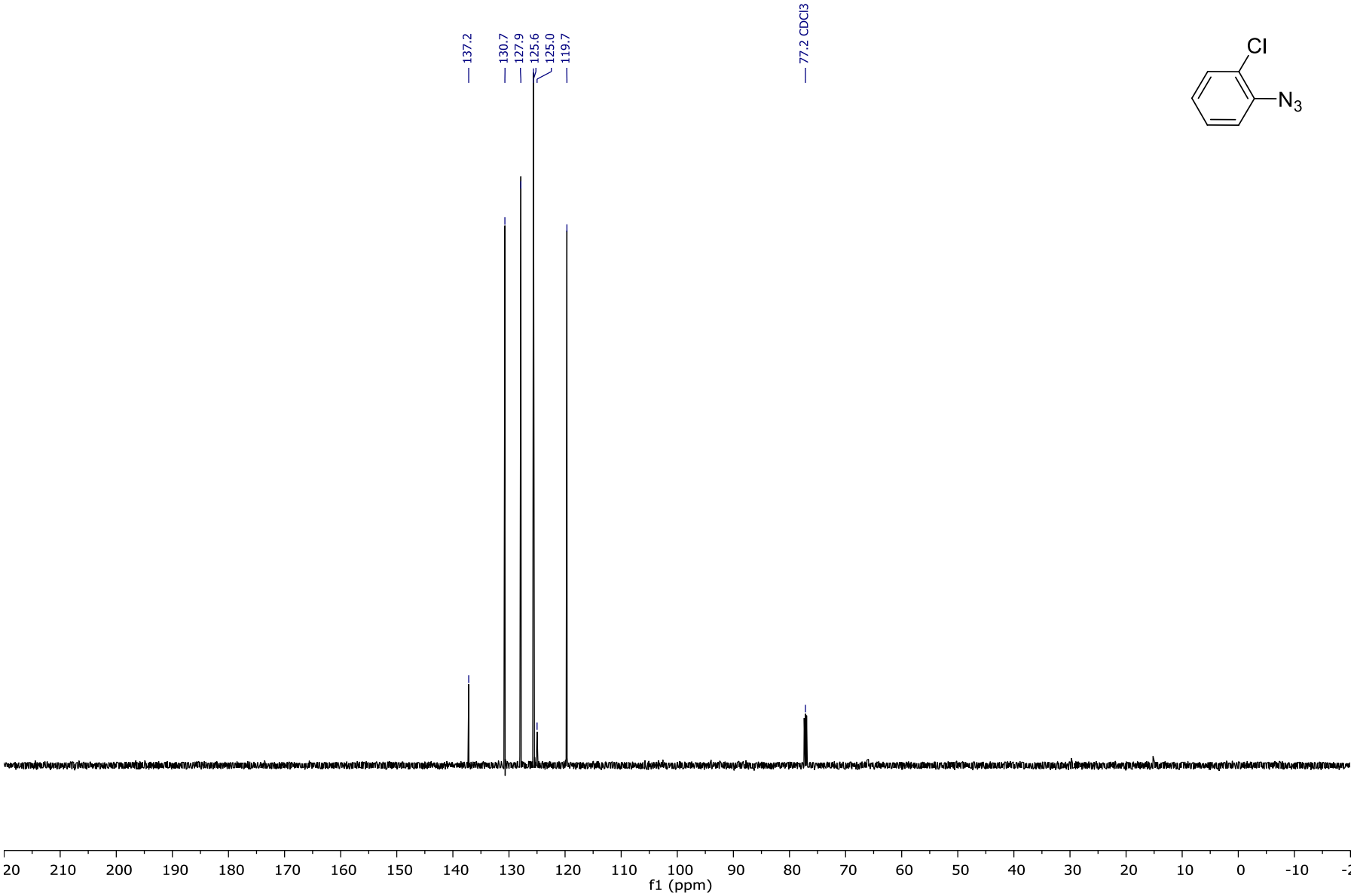


Figure S42. $^{13}C\{^{1}H\}$ NMR (600 MHz, Chloroform-*d*) of 1-azido-2-chlorobenzene (2e).

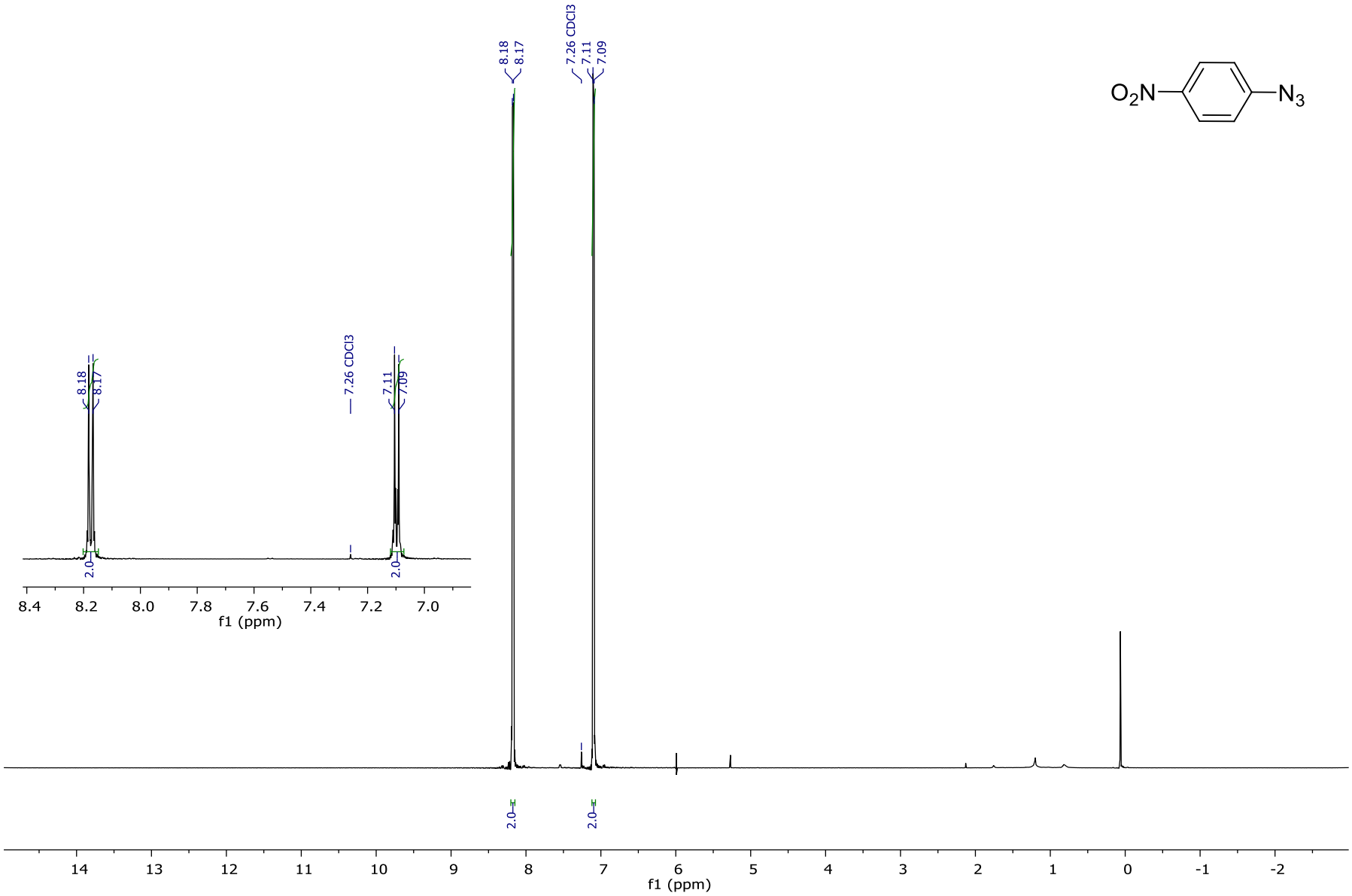


Figure S43. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-azido-4-nitrobenzene (2f).

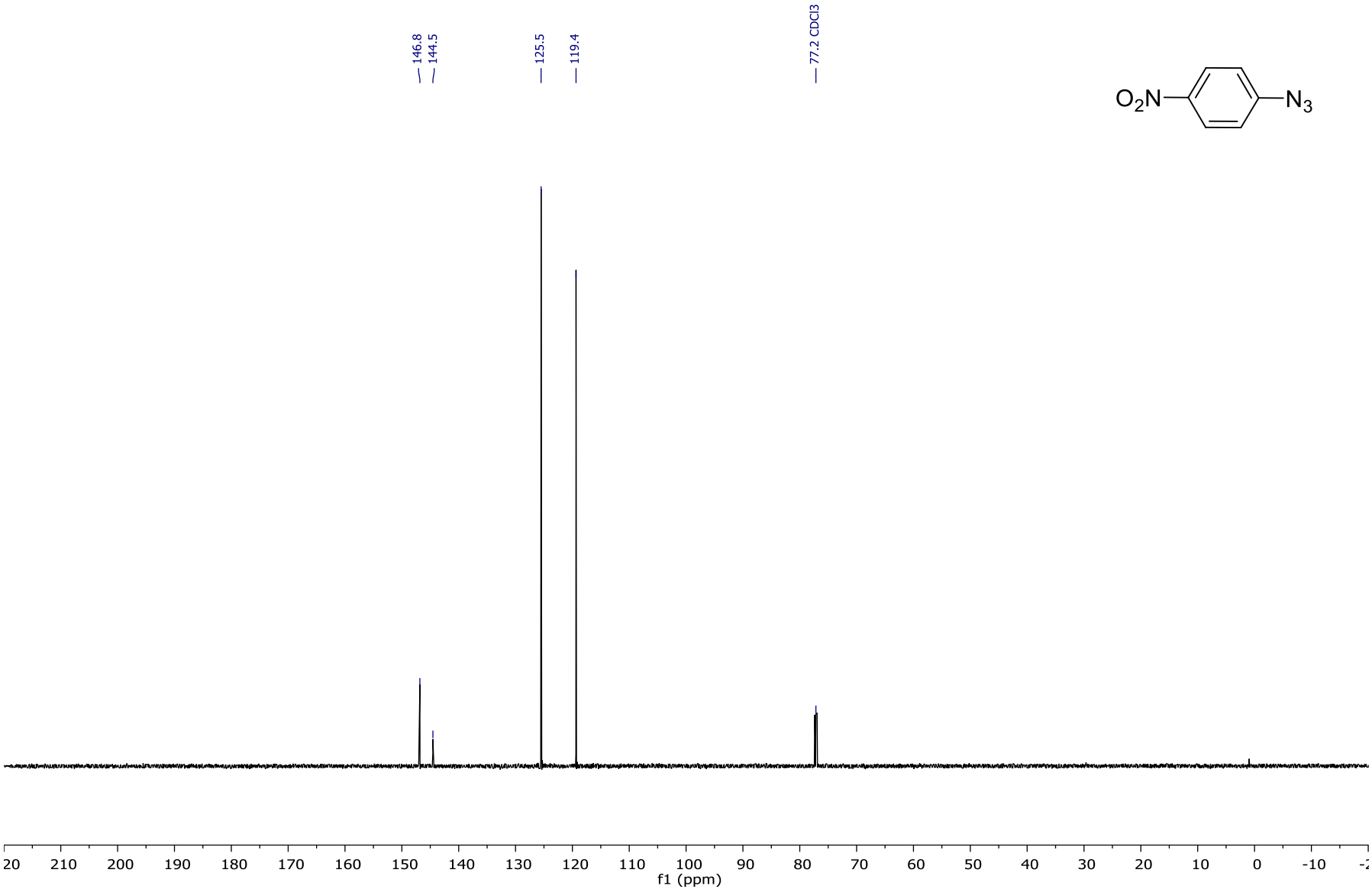


Figure S44. $^{13}C\{^{1}H\}$ NMR (600 MHz, Chloroform-*d*) of 1-azido-4-nitrobenzene (2f).

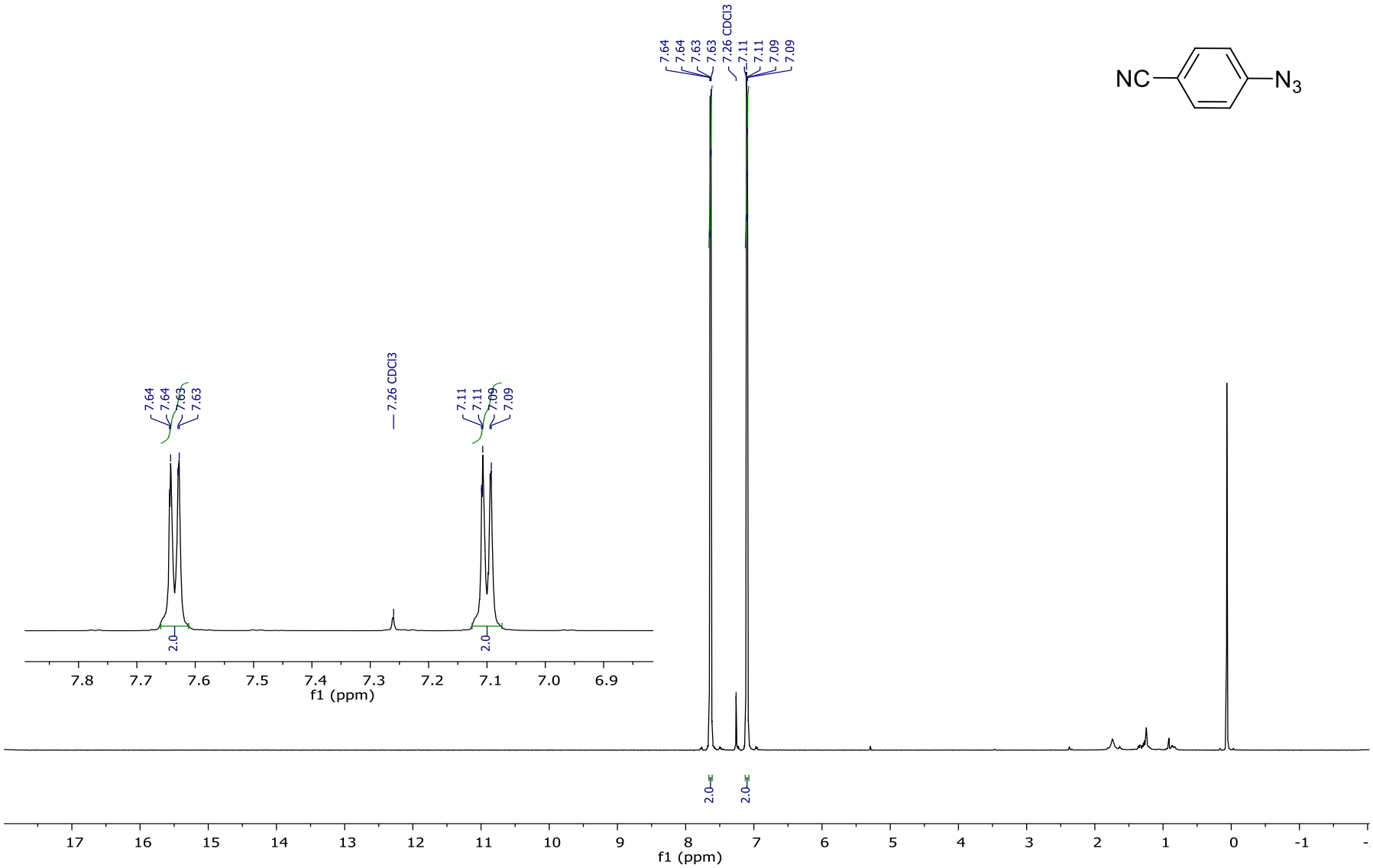


Figure S45. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-azidobenzonitrile (2g).

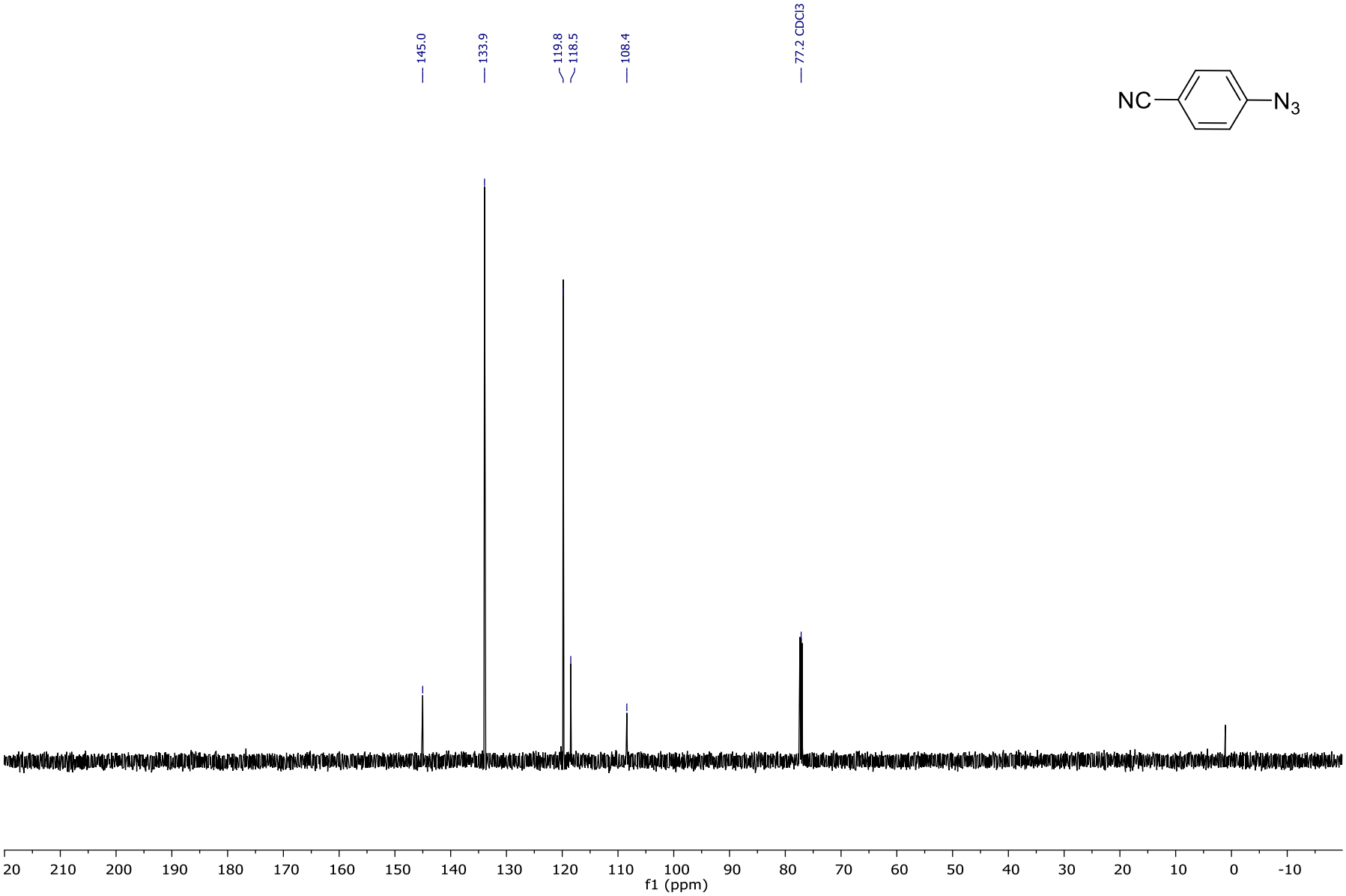


Figure S46. $^{13}C\{^{1}H\}$ NMR (600 MHz, Chloroform-*d*) of 4-azidobenzonitrile (2g).

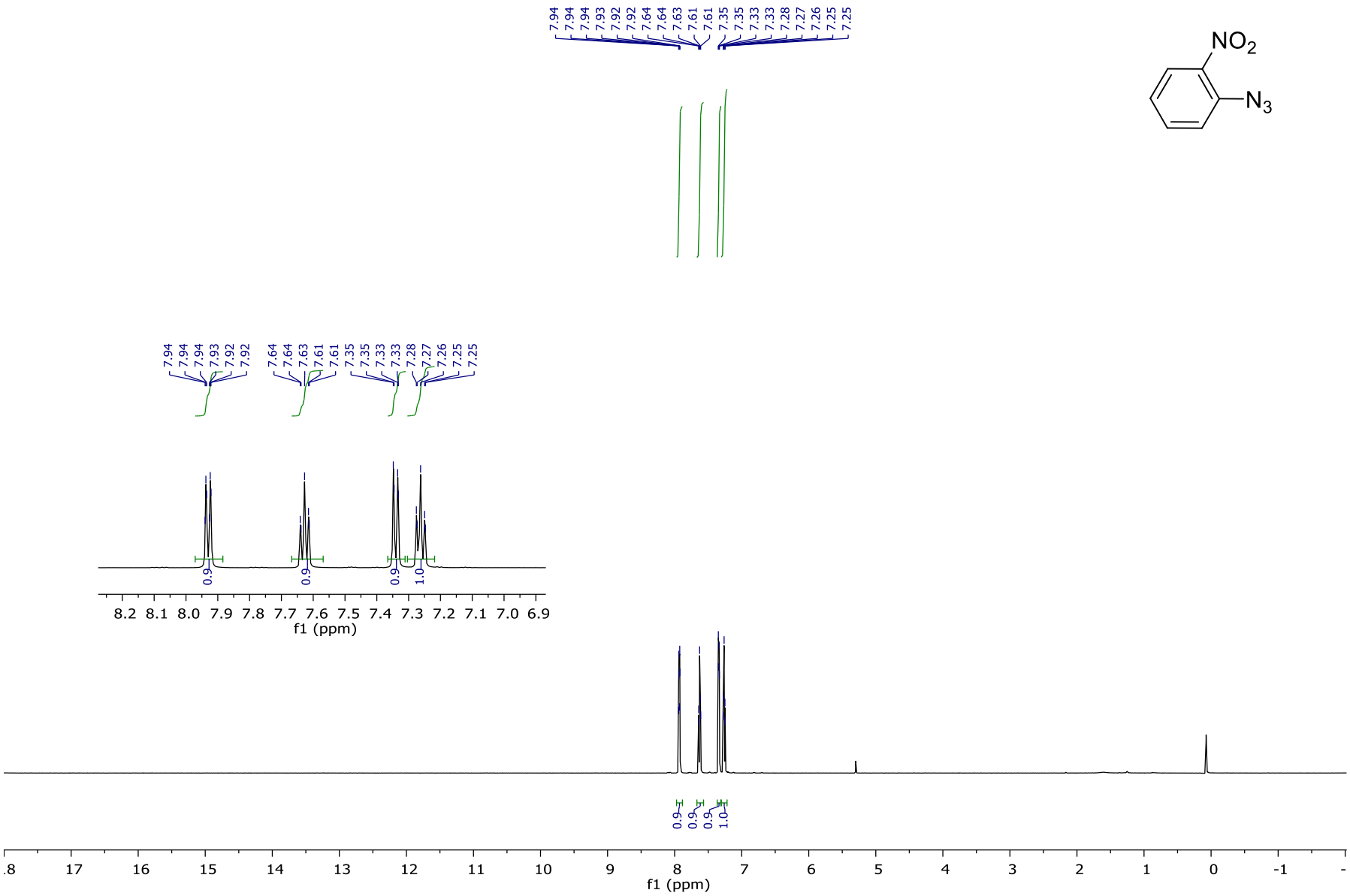


Figure S47. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-azido-2-nitrobenzene (2h).

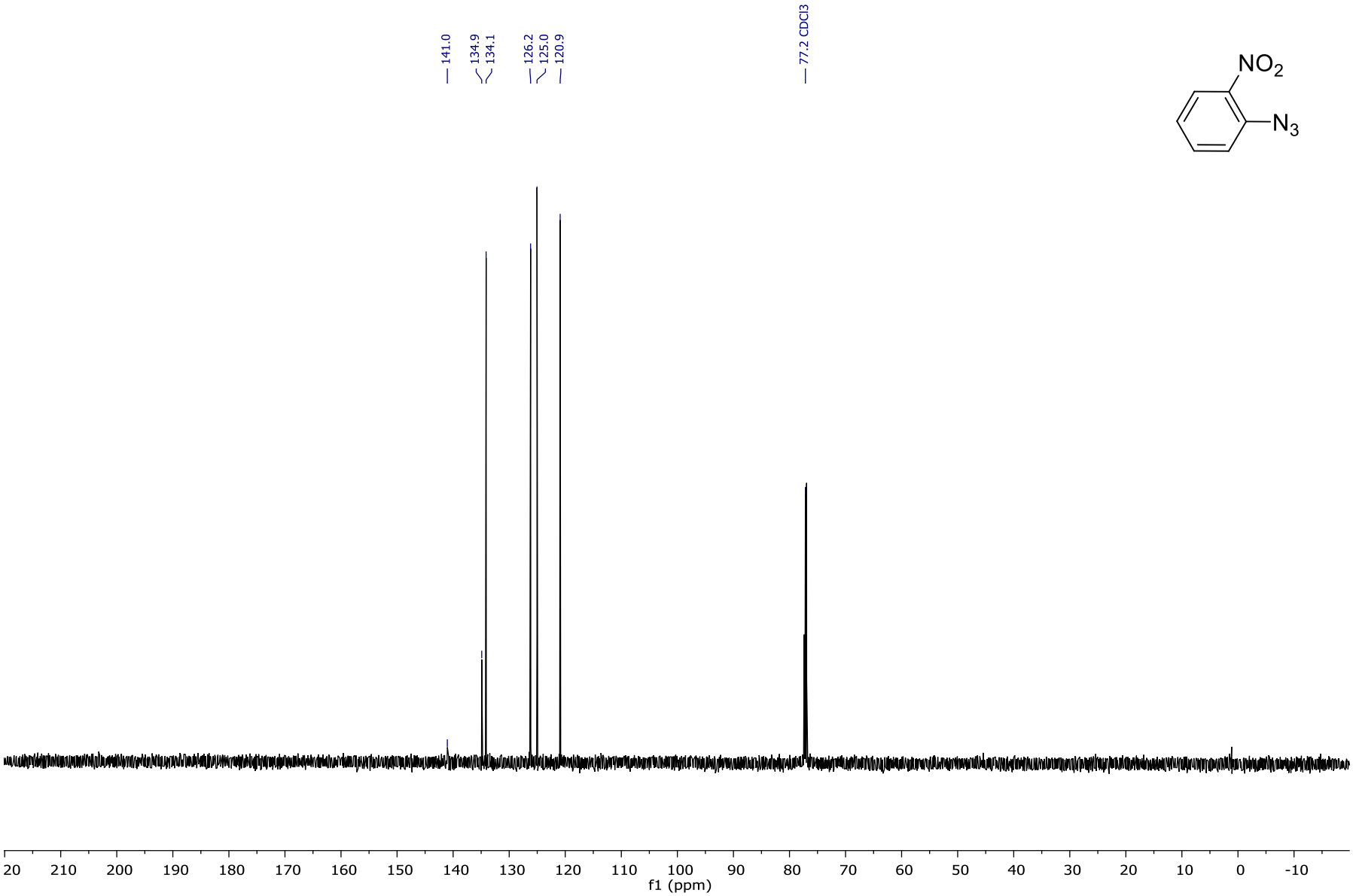


Figure S48. $^{13}C\{^{1}H\}$ NMR (600 MHz, Chloroform-*d*) of 1-azido-2-nitrobenzene (2h).

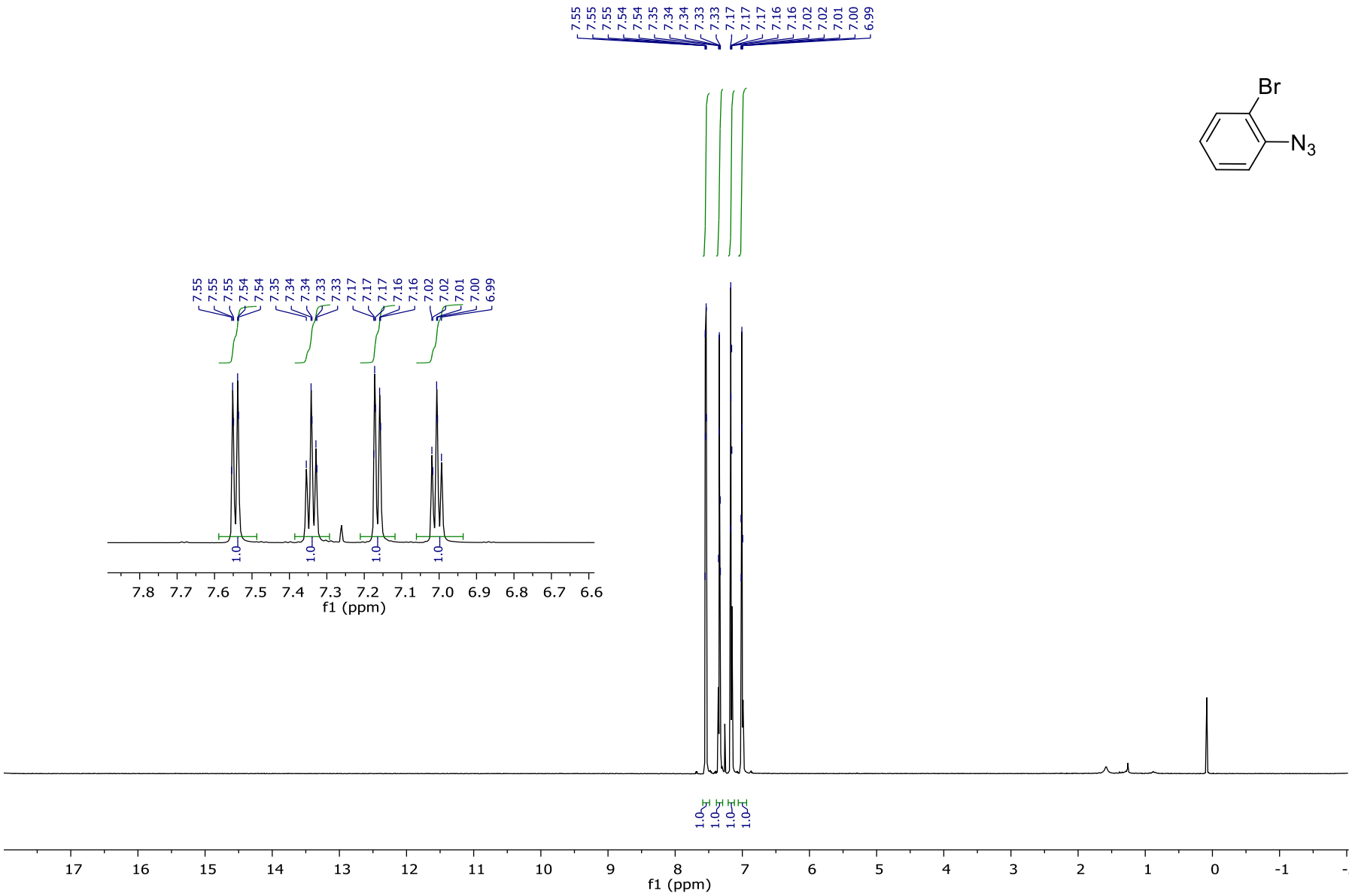


Figure S49. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-azido-2-bromobenzene (2i).

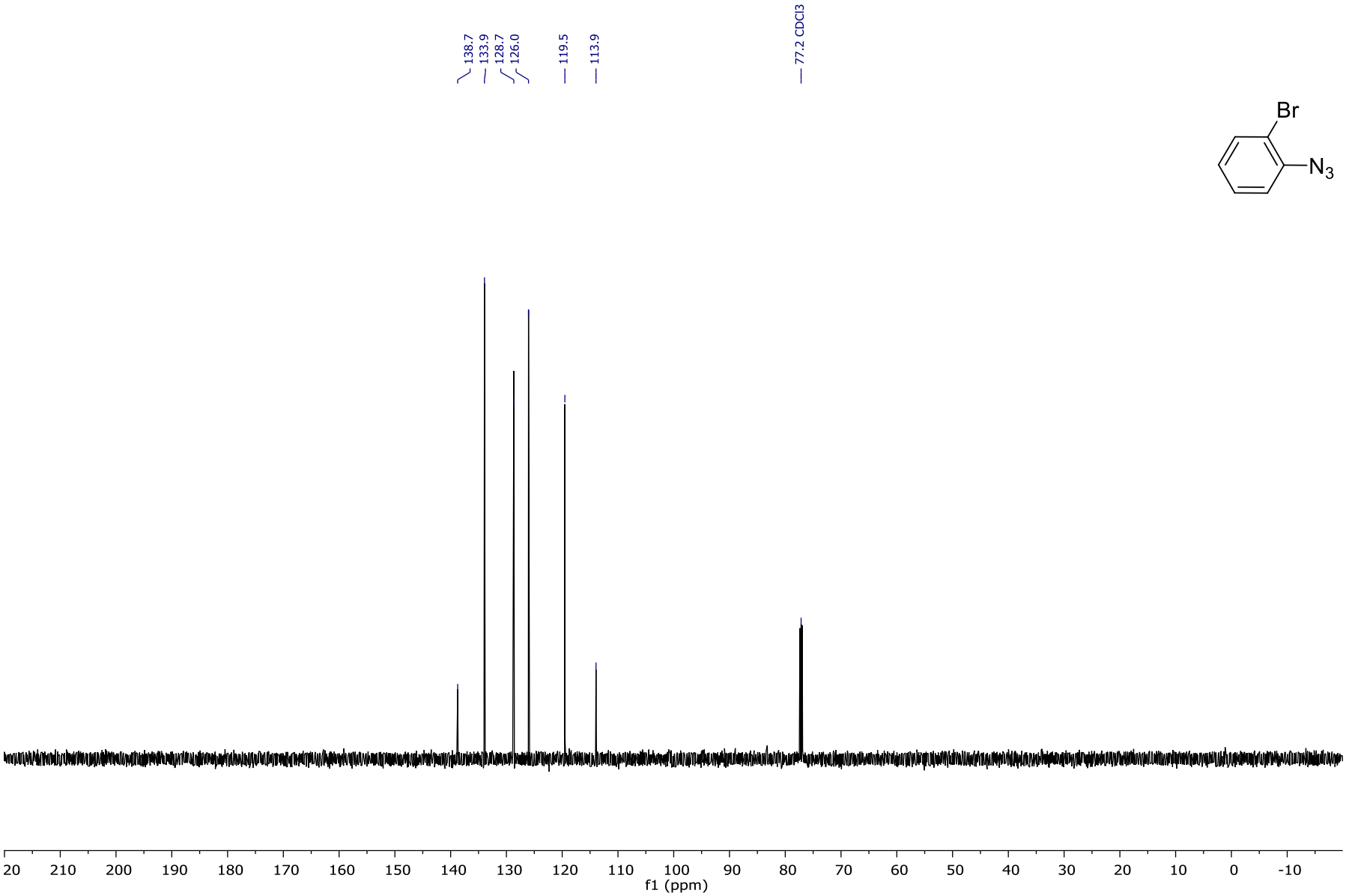


Figure S50. $^{13}C\{^{1}H\}$ NMR (600 MHz, Chloroform-*d*) of 1-azido-2-bromobenzene (2i).

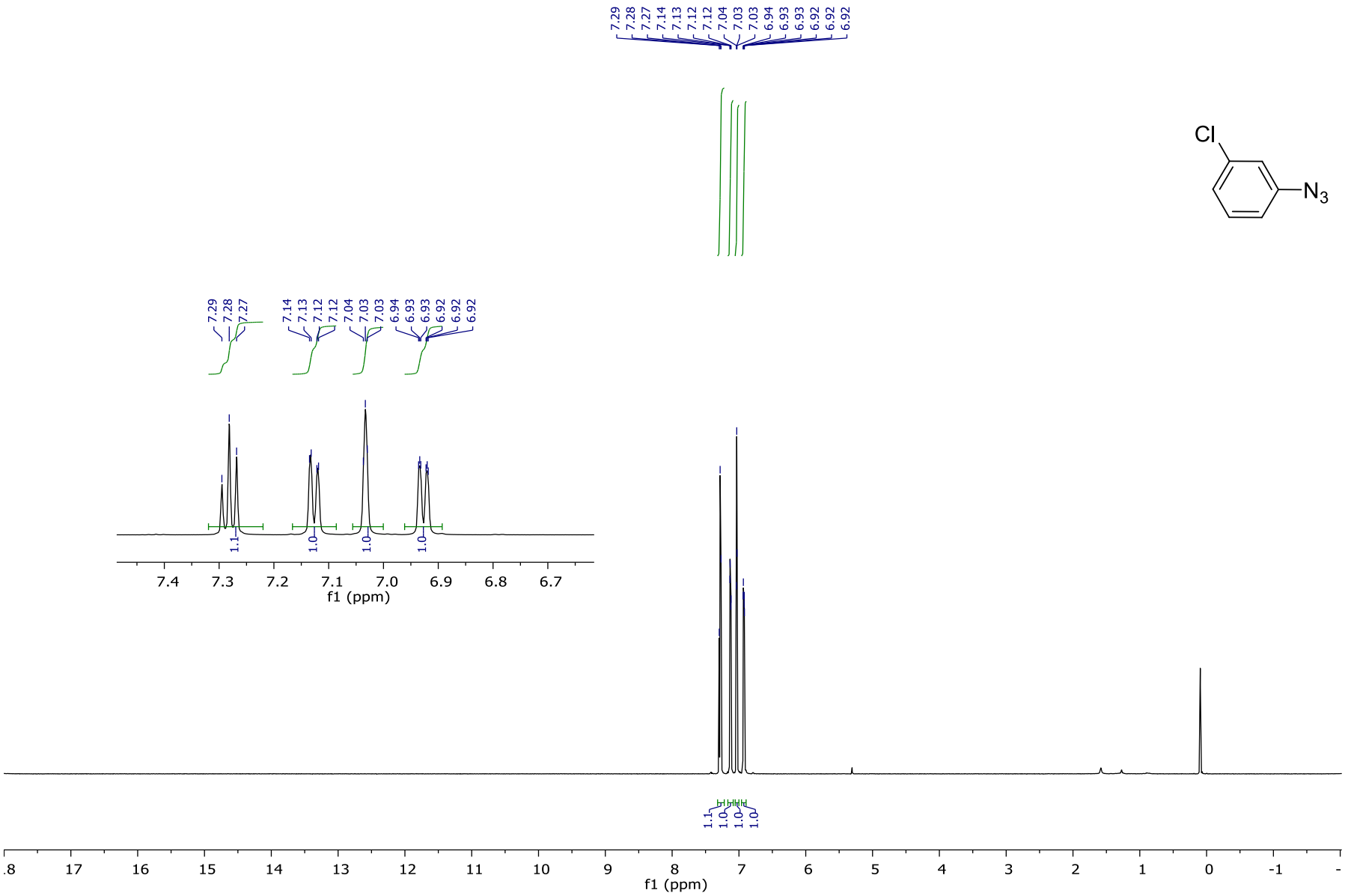


Figure S51. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-azido-3-chlorobenzene (2j).

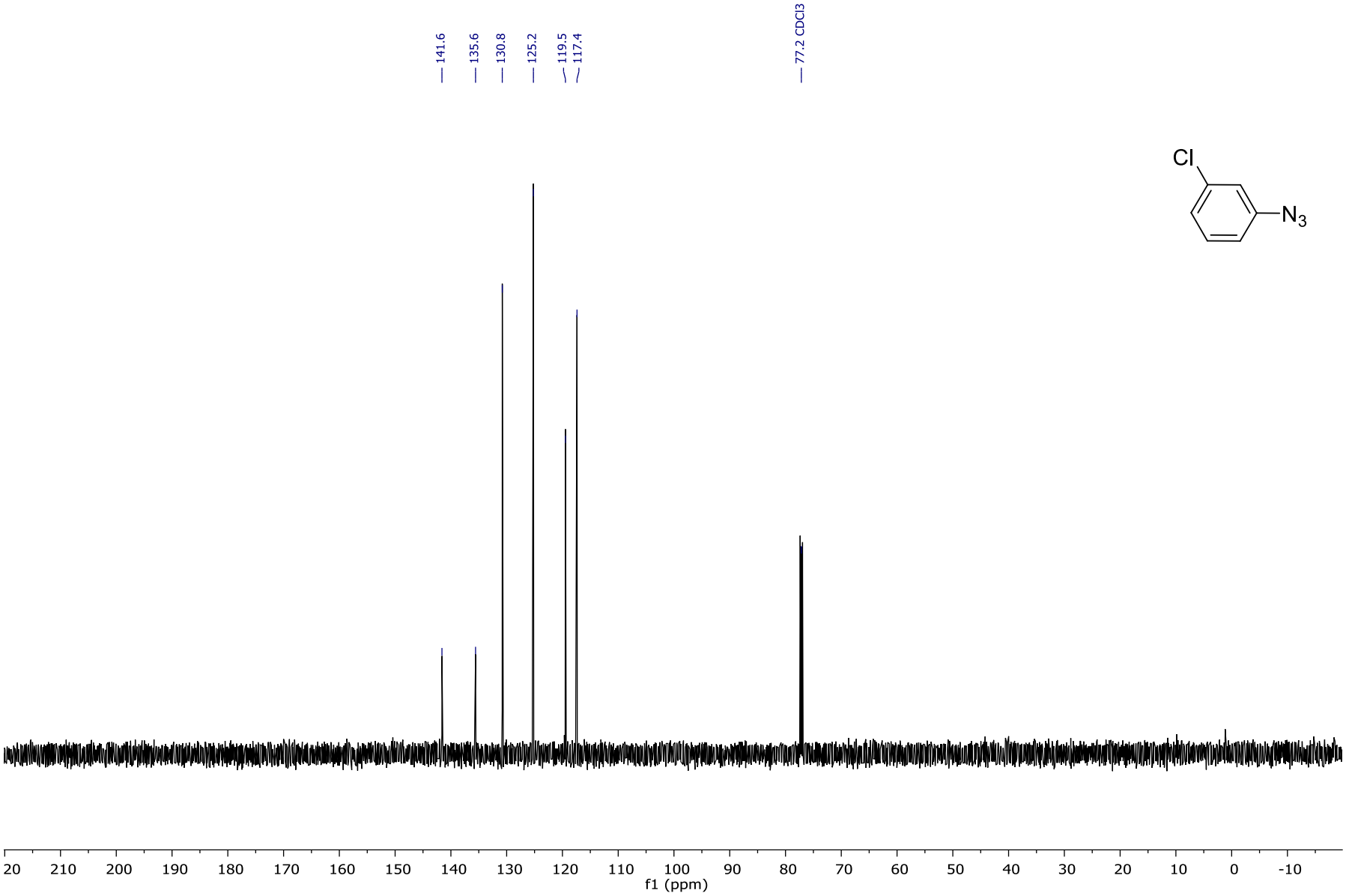


Figure S52. $^{13}C\{^{1}H\}$ NMR (600 MHz, Chloroform-*d*) of 1-azido-3-chlorobenzene (2j).

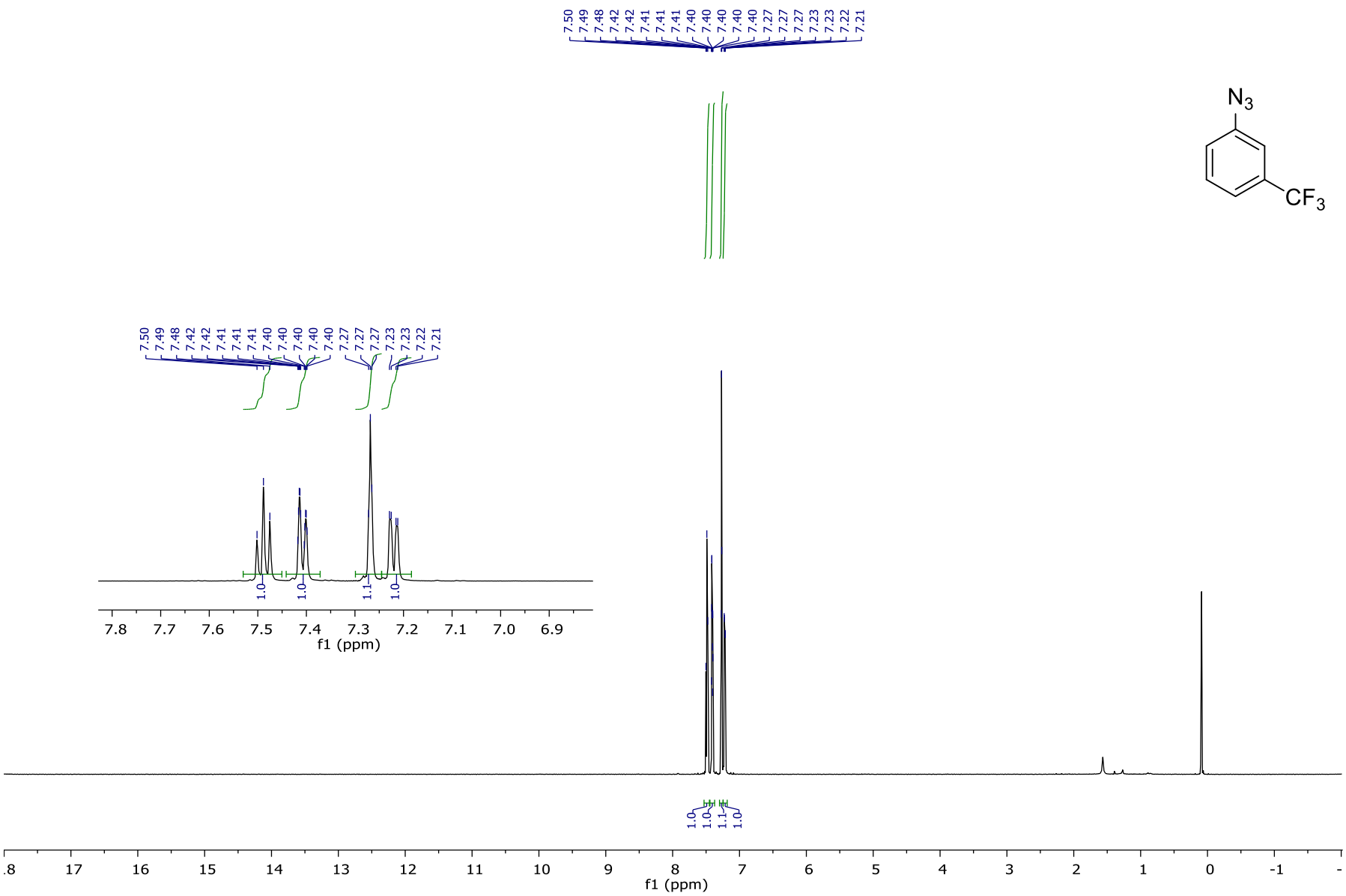


Figure S53. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-azido-3-(trifluoromethyl)benzene (2k).

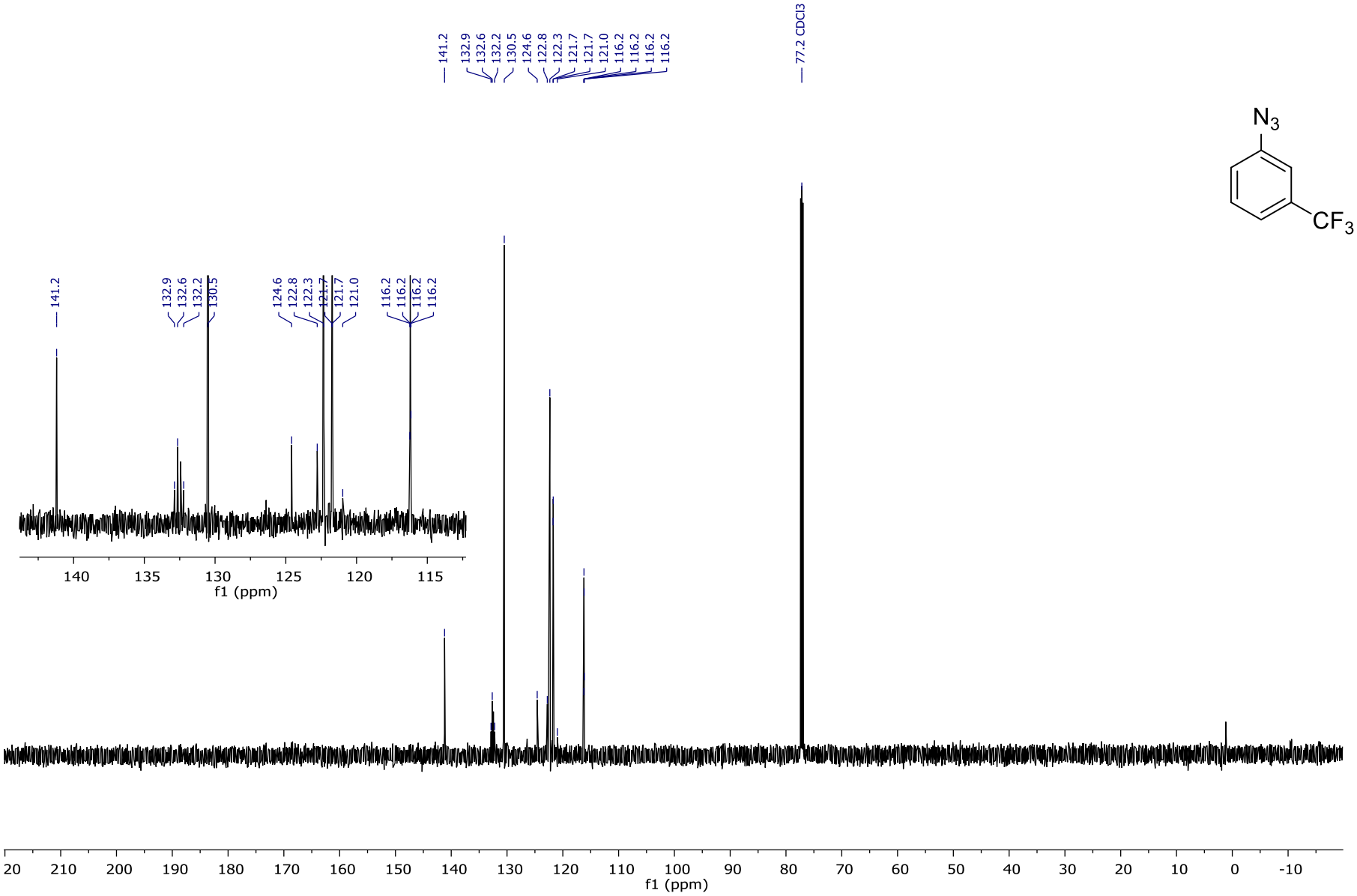


Figure S54. $^{13}C\{^{1}H\}$ NMR (600 MHz, Chloroform-*d*) of 1-azido-3-(trifluoromethyl)benzene (2k).

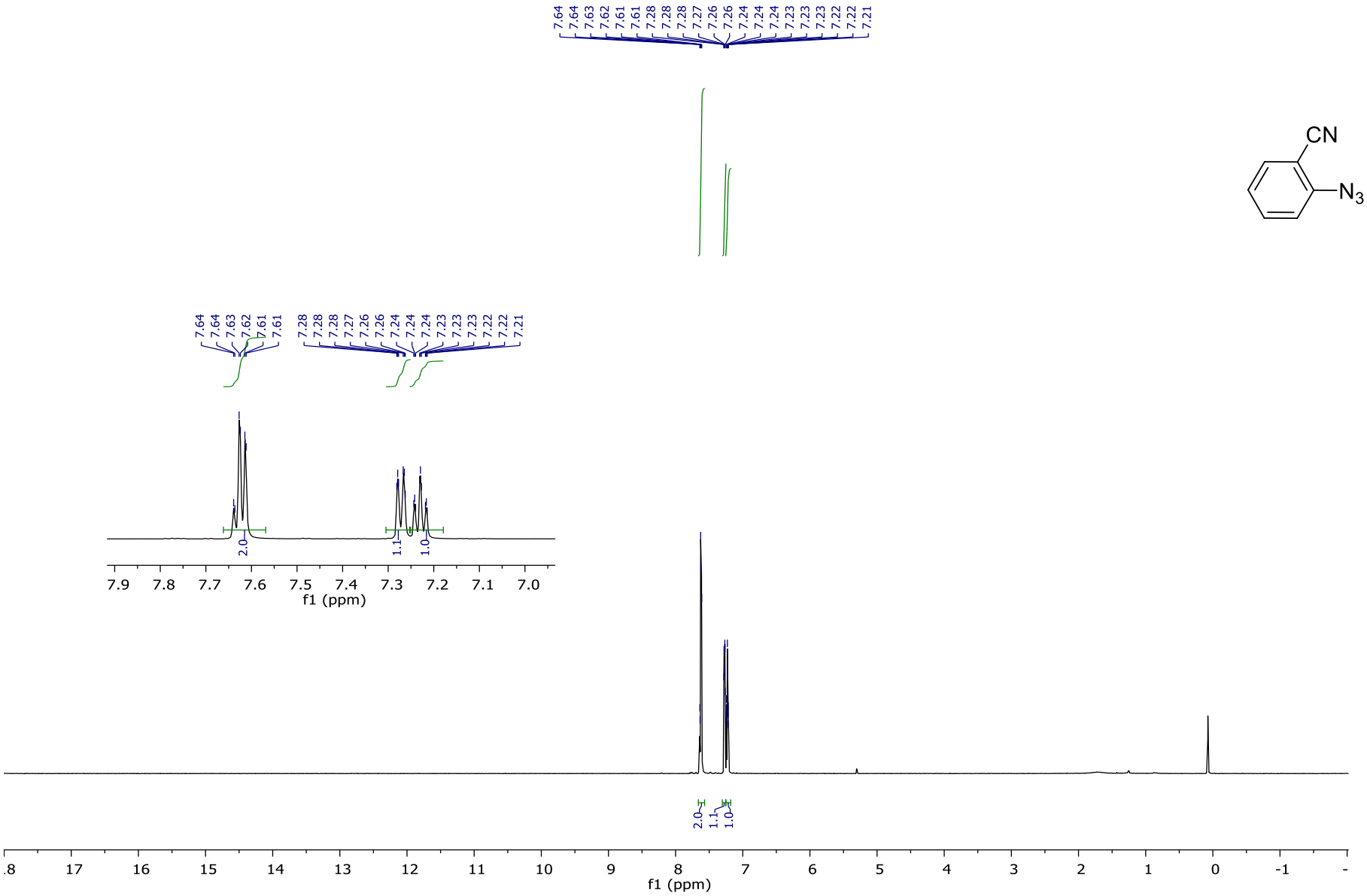


Figure S55. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2-azidobenzonitrile (2l).

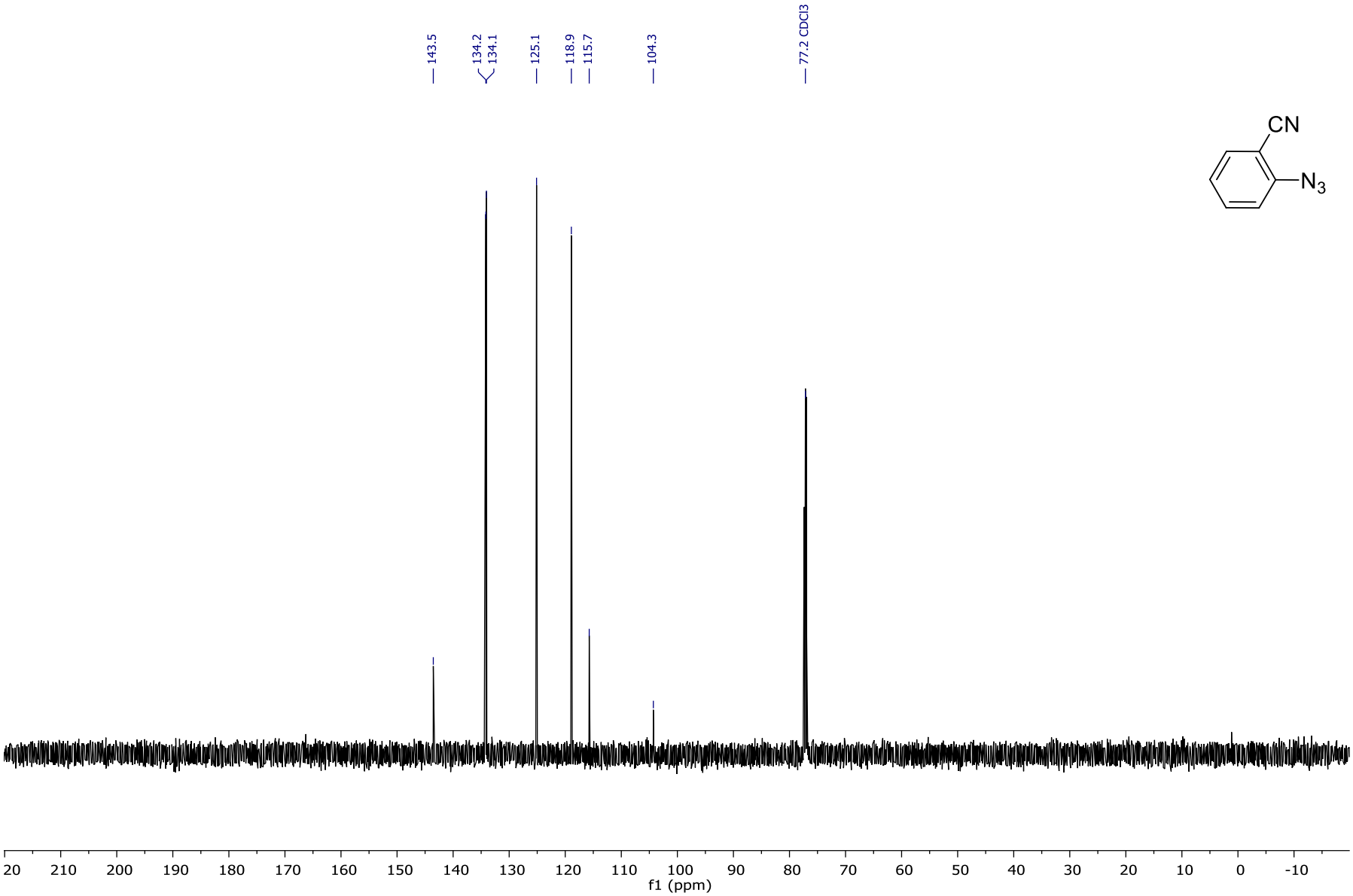


Figure S56. $^{13}C\{^{1}H\}$ NMR (600 MHz, Chloroform-*d*) of 2-azidobenzonitrile (2l).

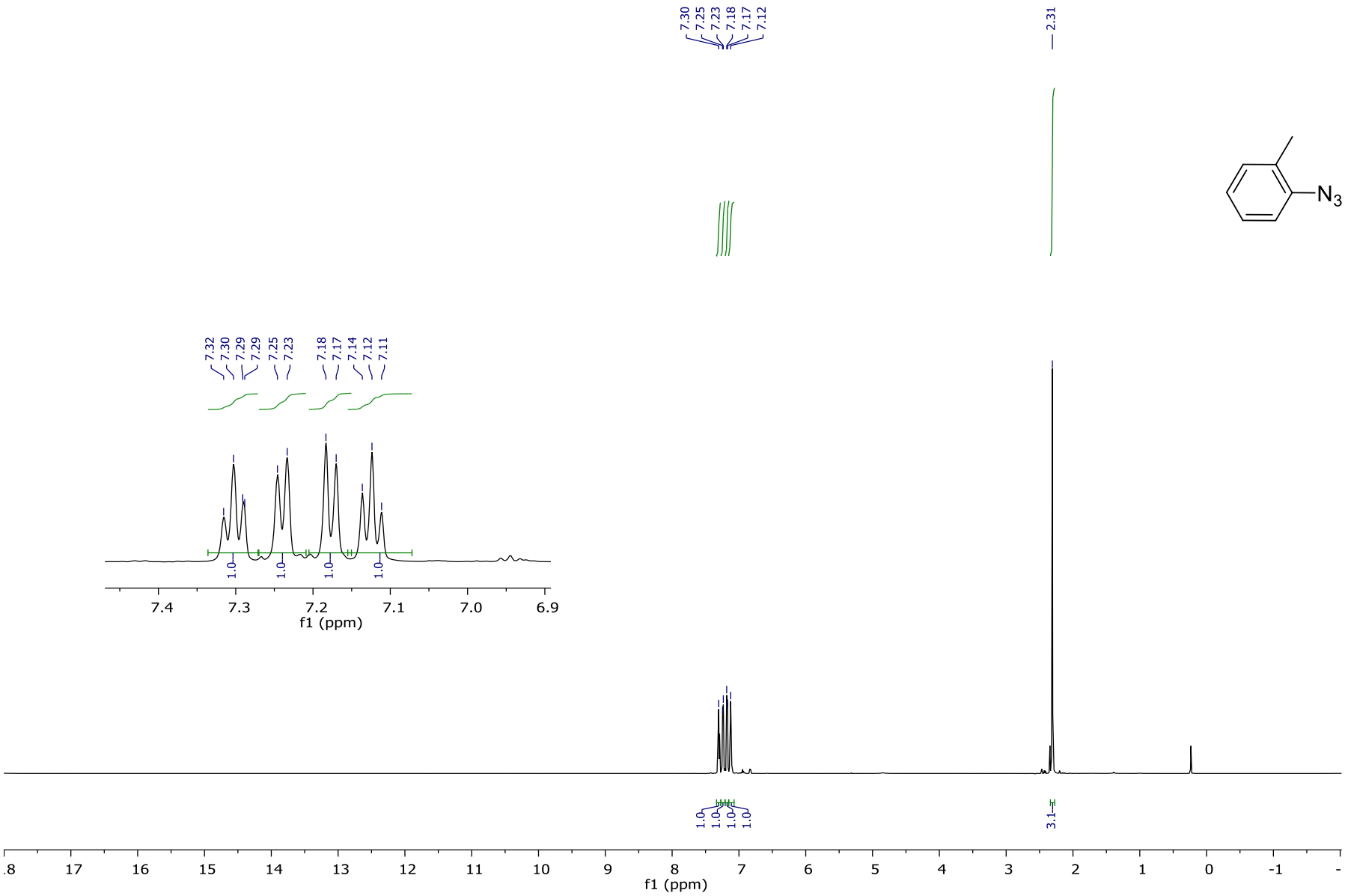


Figure S57. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-azido-2-methylbenzene (2m).

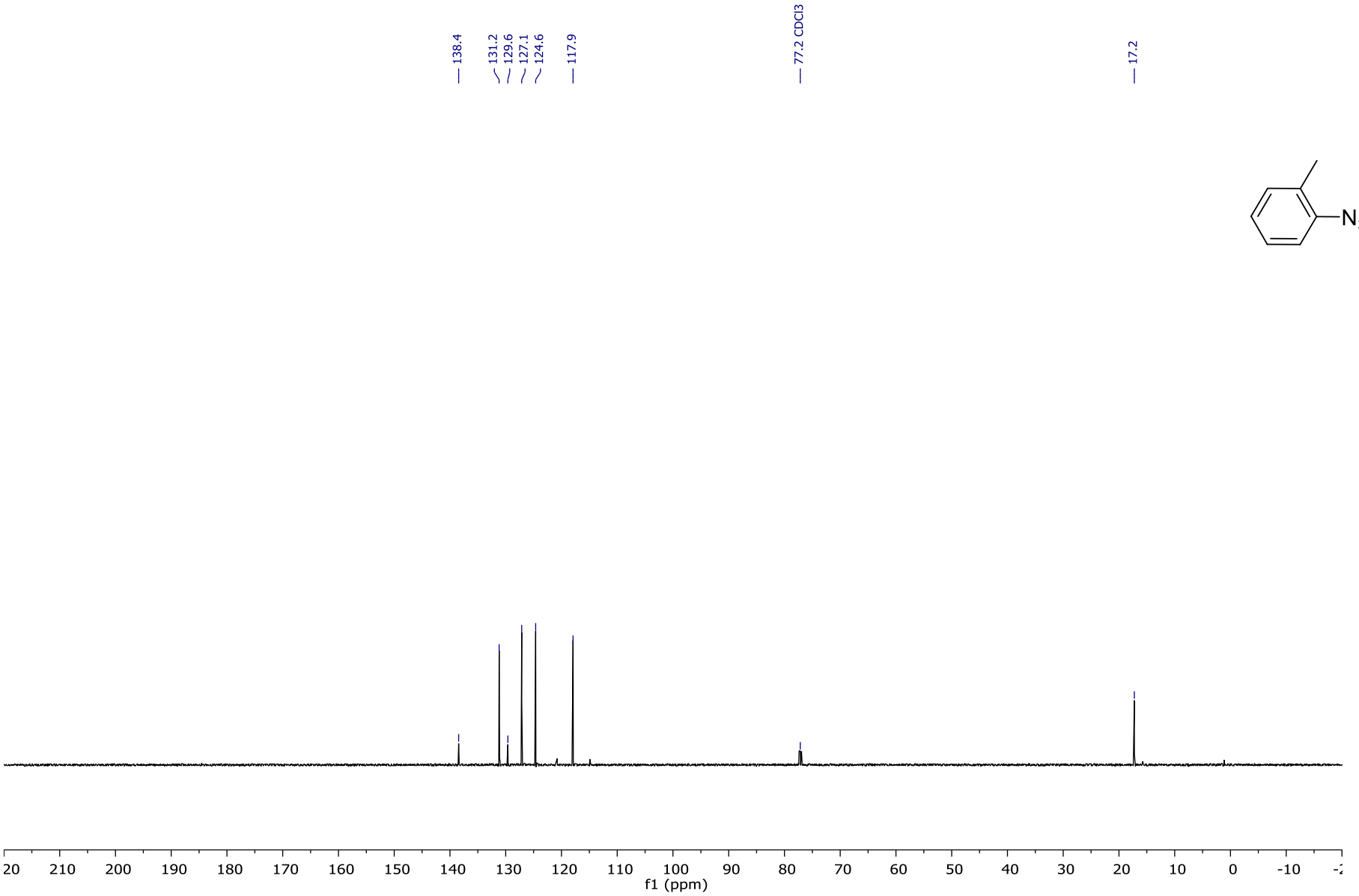


Figure S58. $^{13}C\{^{1}H\}$ NMR (600 MHz, Chloroform-*d*) of 1-azido-2-methylbenzene (2m).

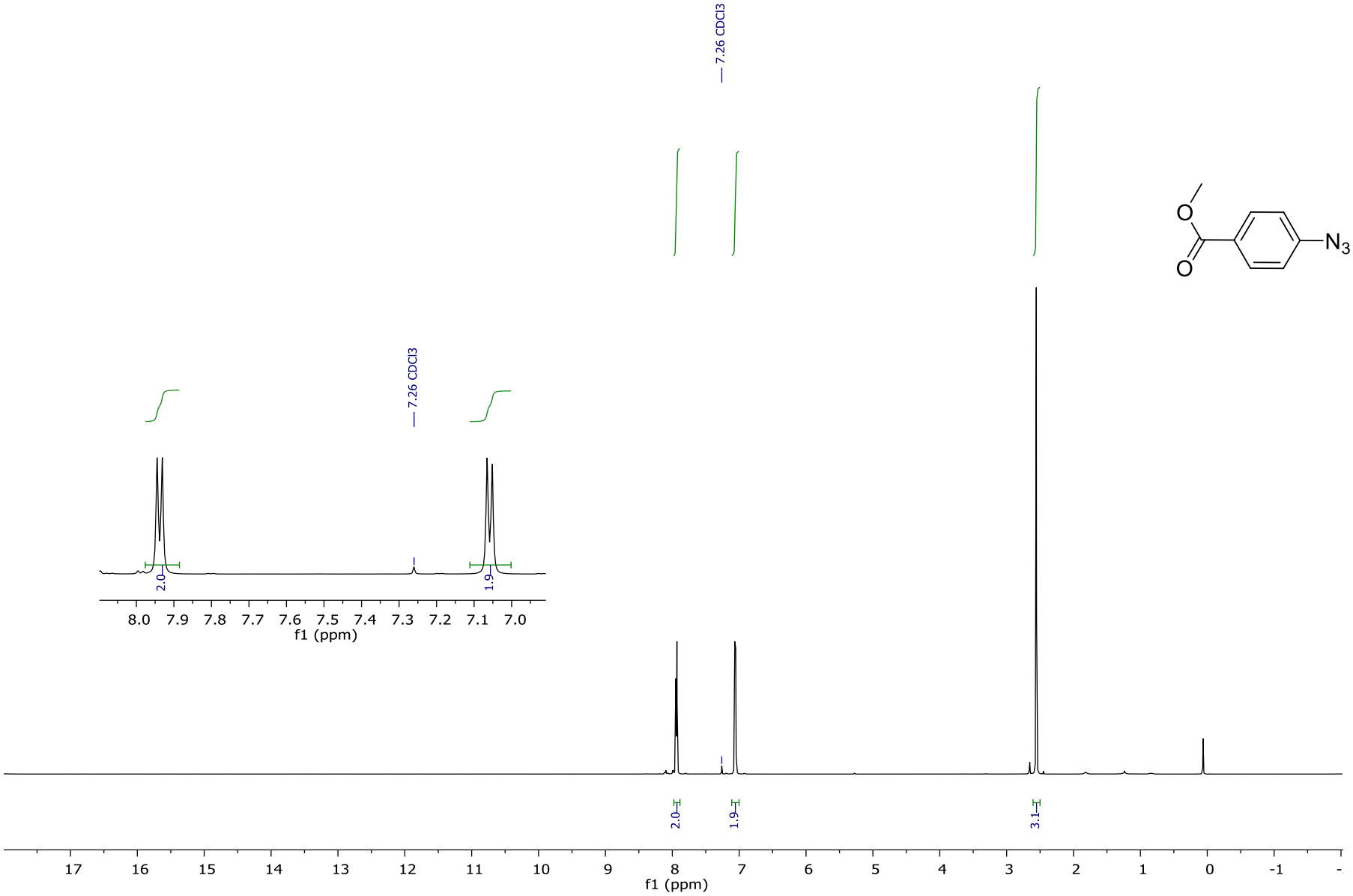


Figure S59. ^{1}H NMR (600 MHz, Chloroform-*d*) of methyl 4-azidobenzoate (2n).

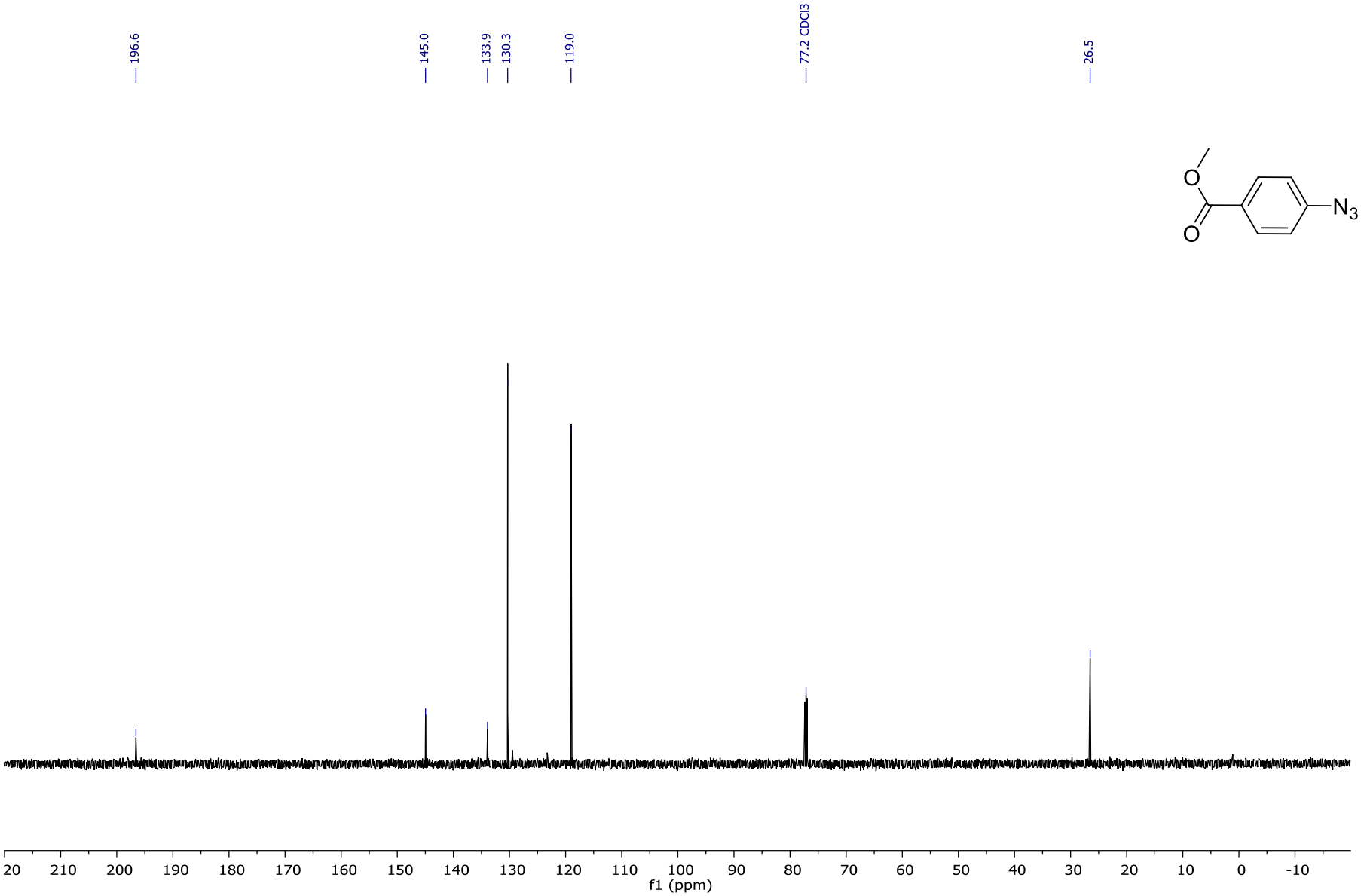


Figure S60. $^{13}C\{^{1}H\}$ NMR (600 MHz, Chloroform-*d*) of methyl 4-azidobenzoate (2n).

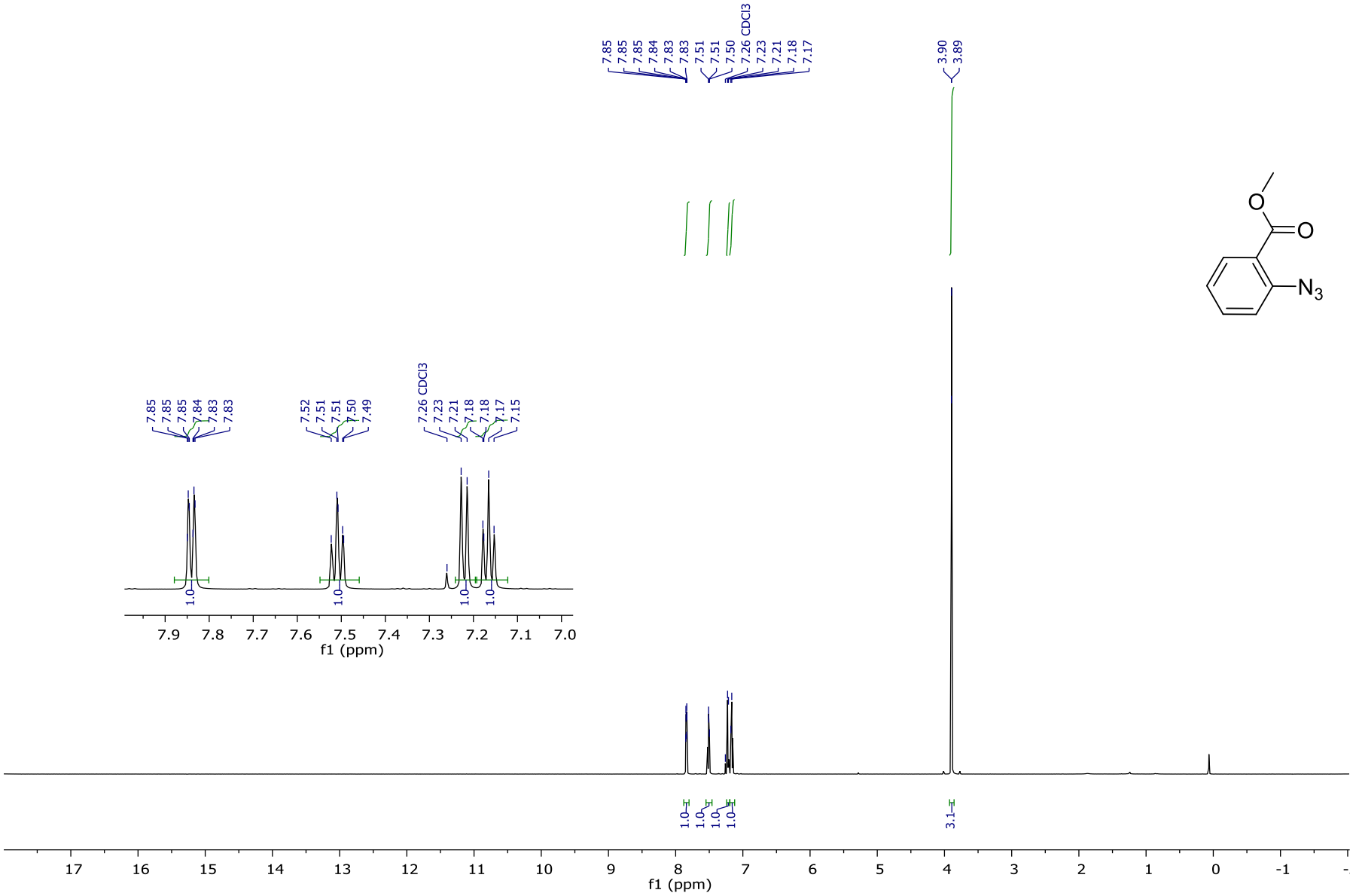


Figure S61. ^{1}H NMR (600 MHz, Chloroform-*d*) of methyl 2-azidobenzoate (2o).

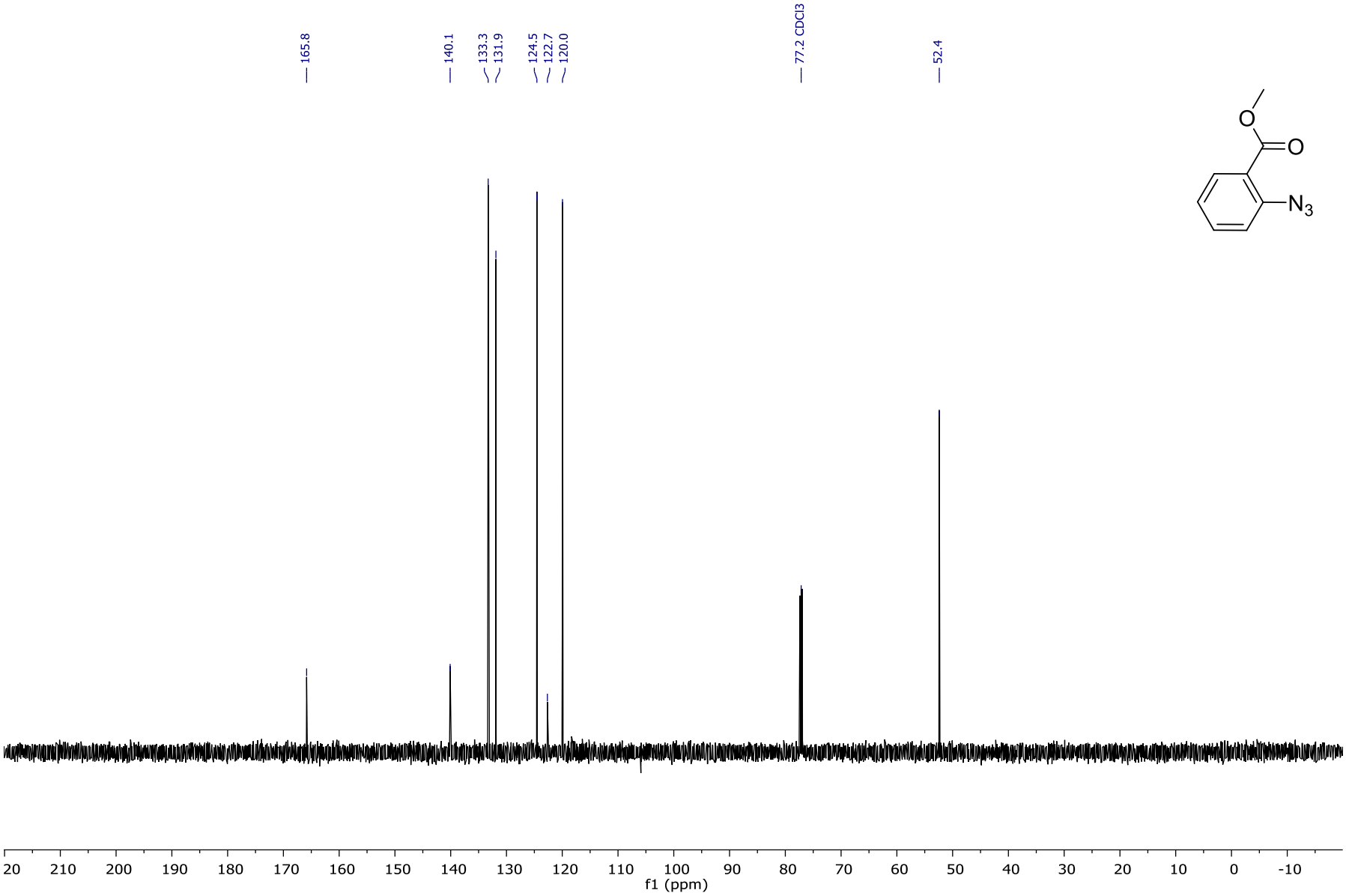


Figure S62. $^{13}C\{^{1}H\}$ NMR (600 MHz, Chloroform-*d*) of methyl 2-azidobenzoate (2o).

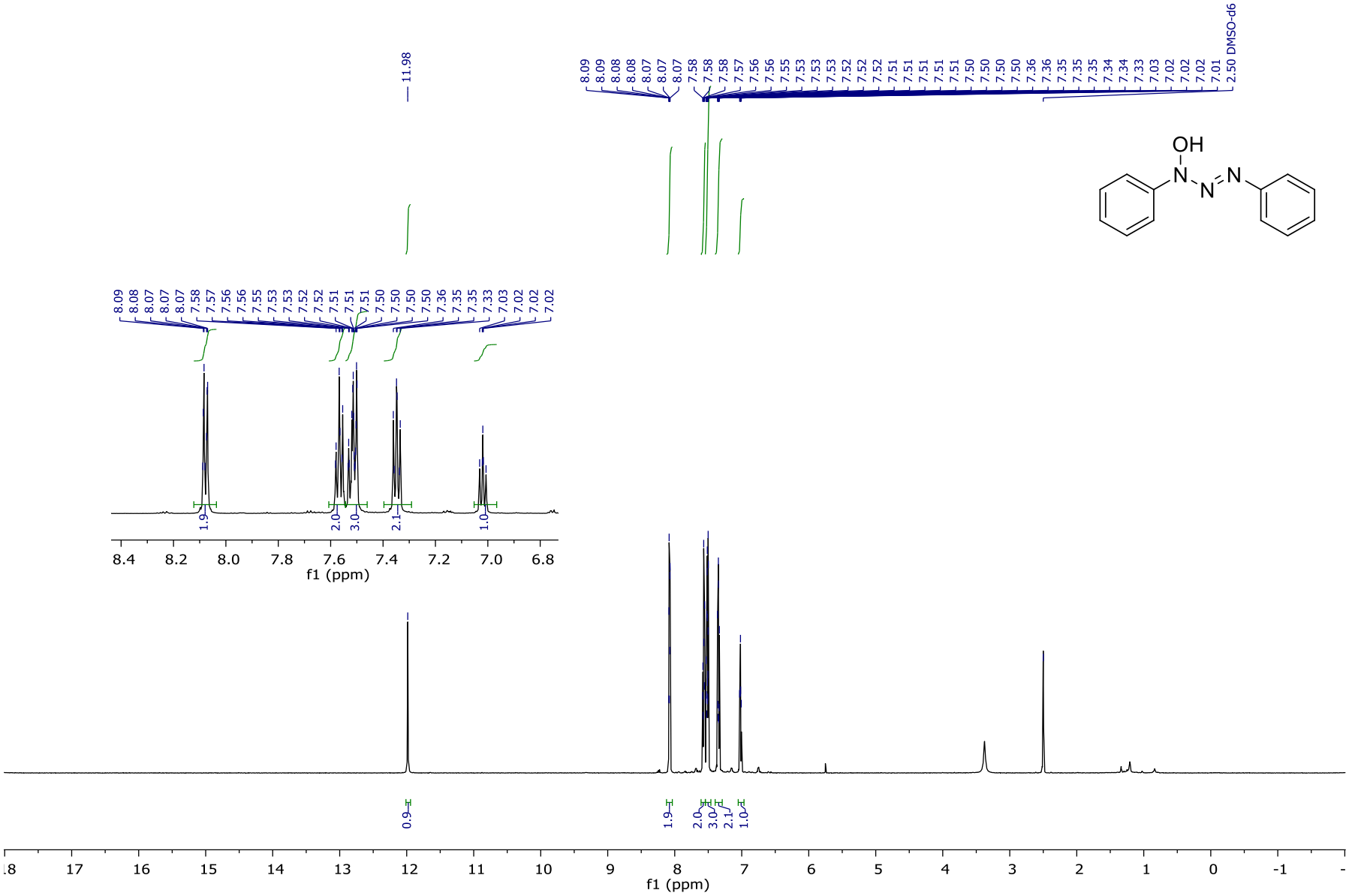


Figure S63. ^{1}H NMR (600 MHz, DMSO-*d*$_6$) of 3-hydroxy-1,3-diphenyltriazene (3a).

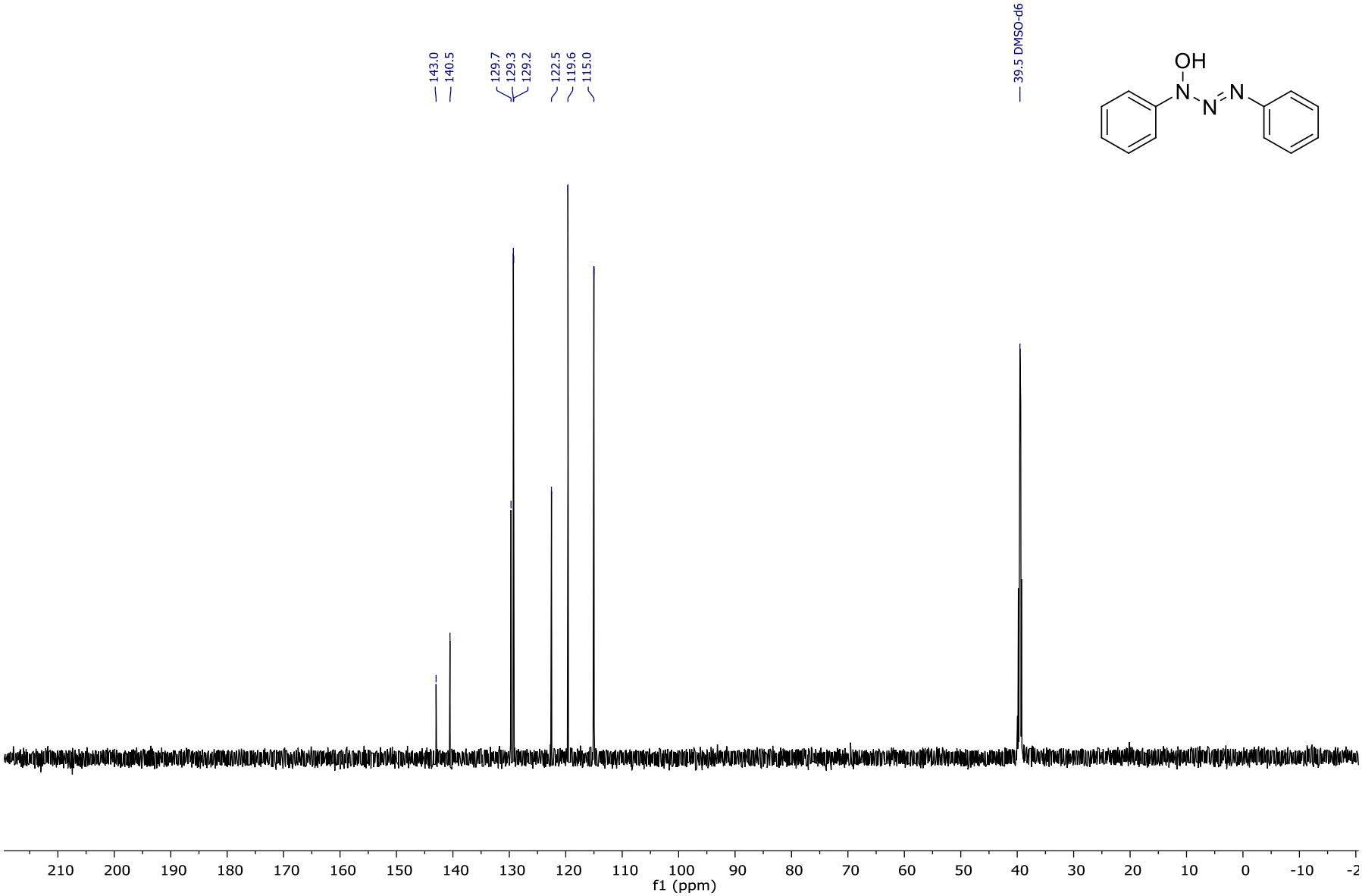


Figure S64. $^{13}C\{^{1}H\}$ NMR (600 MHz, DMSO-d_6) of 3-hydroxy-1,3-diphenyltriazene (3a).

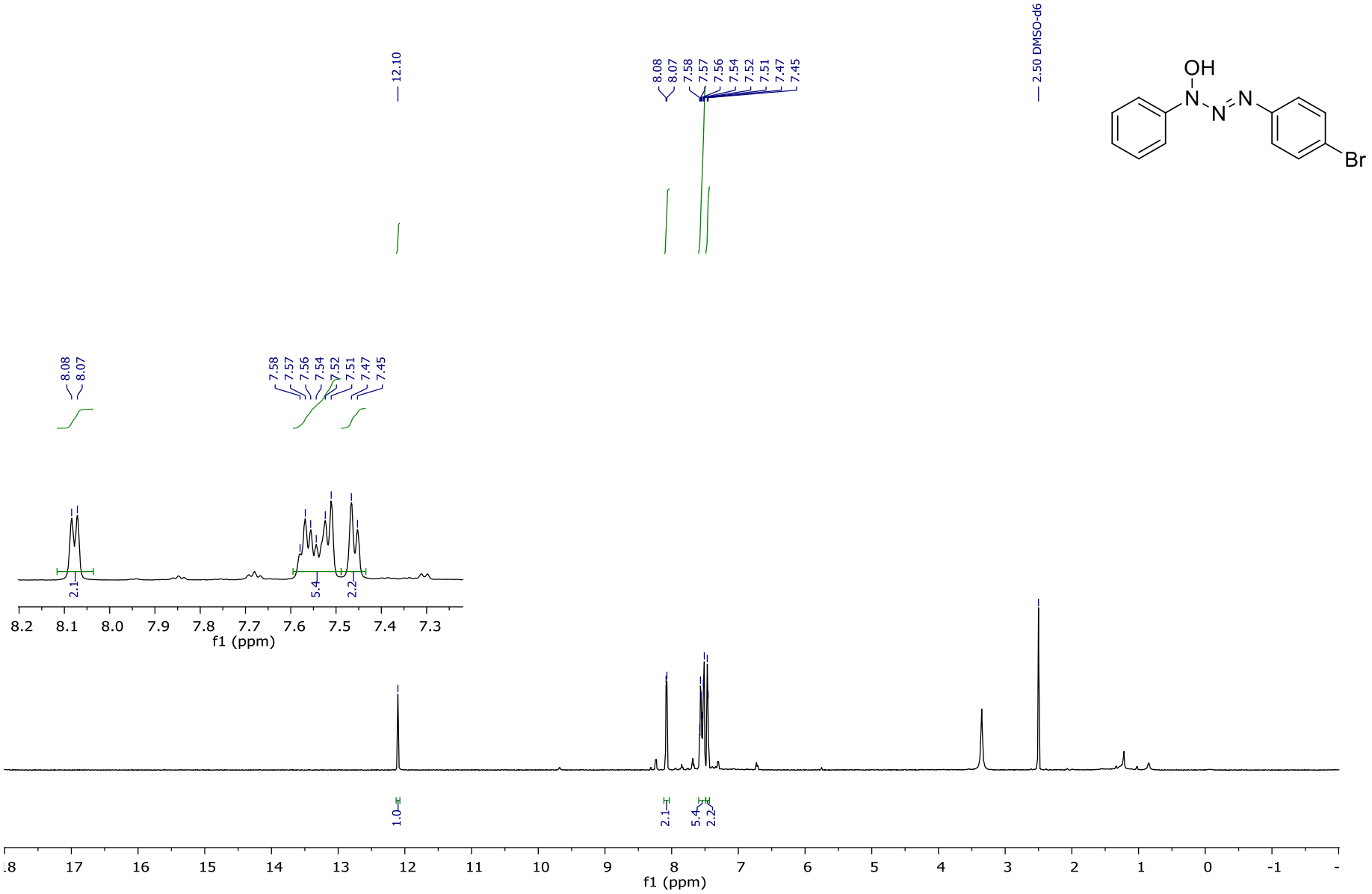


Figure S65. ^{1}H NMR (600 MHz, DMSO-d_6) of 1-(4-bromophenyl)-3-hydroxy-3-phenyltriazene (3b).

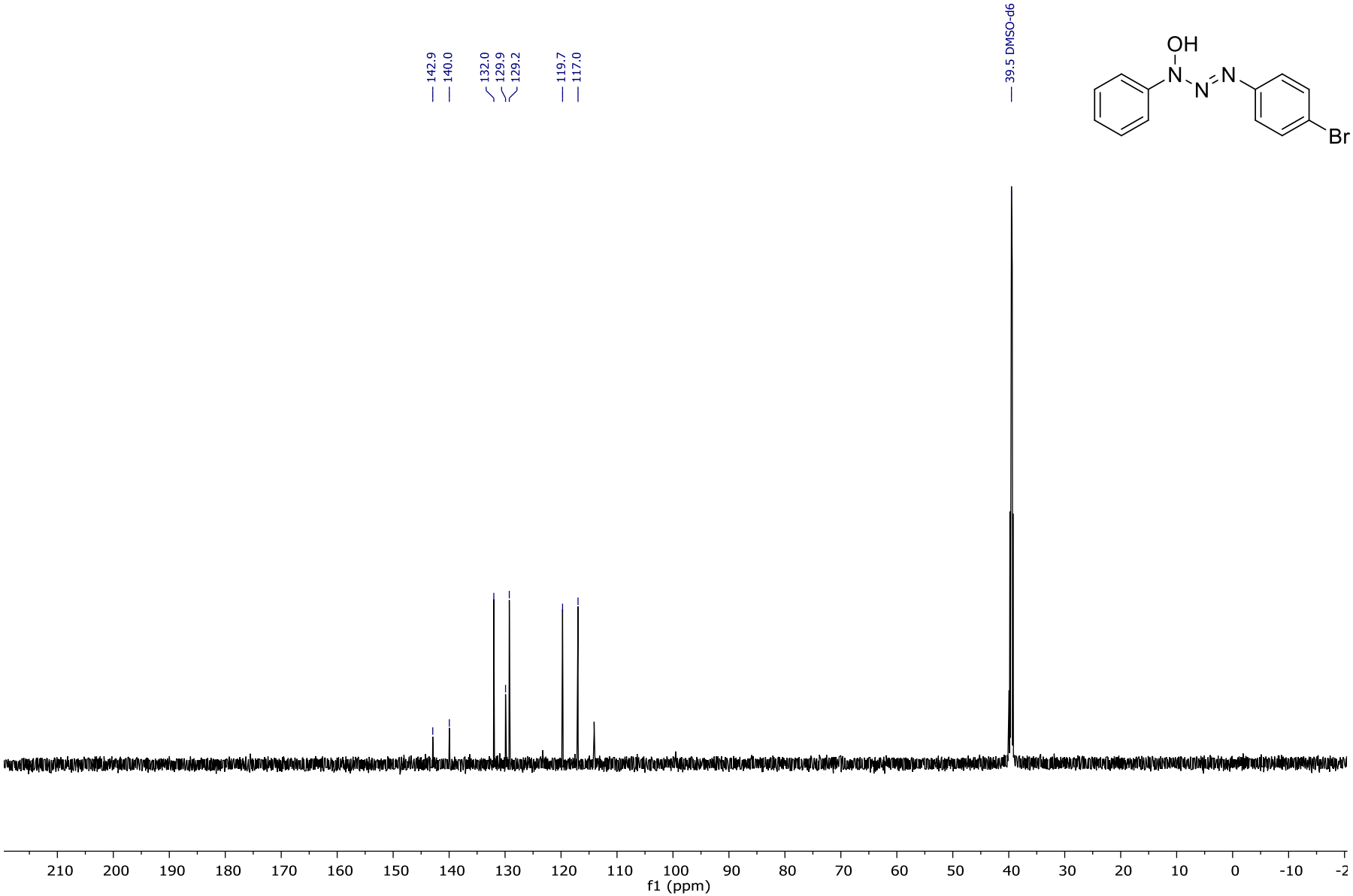


Figure S66. $^{13}C\{^{1}H\}$ NMR (600 MHz, DMSO-d_6) of 1-(4-bromophenyl)-3-hydroxy-3-phenyltriazene (3b).

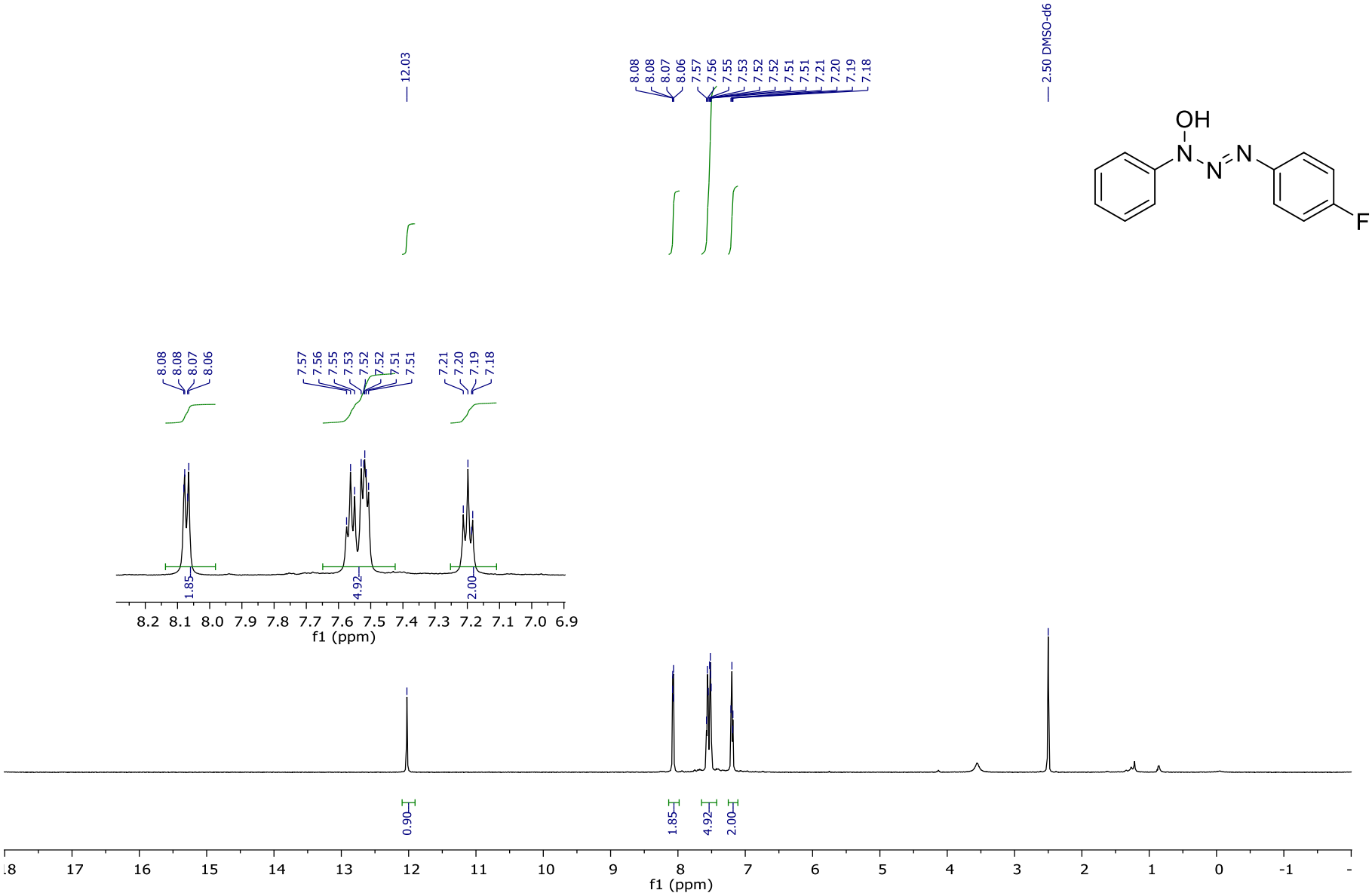


Figure S67. ^{1}H NMR (600 MHz, DMSO-d_6) of 1-(4-fluorophenyl)-3-hydroxy-3-phenyltriazene (3c).

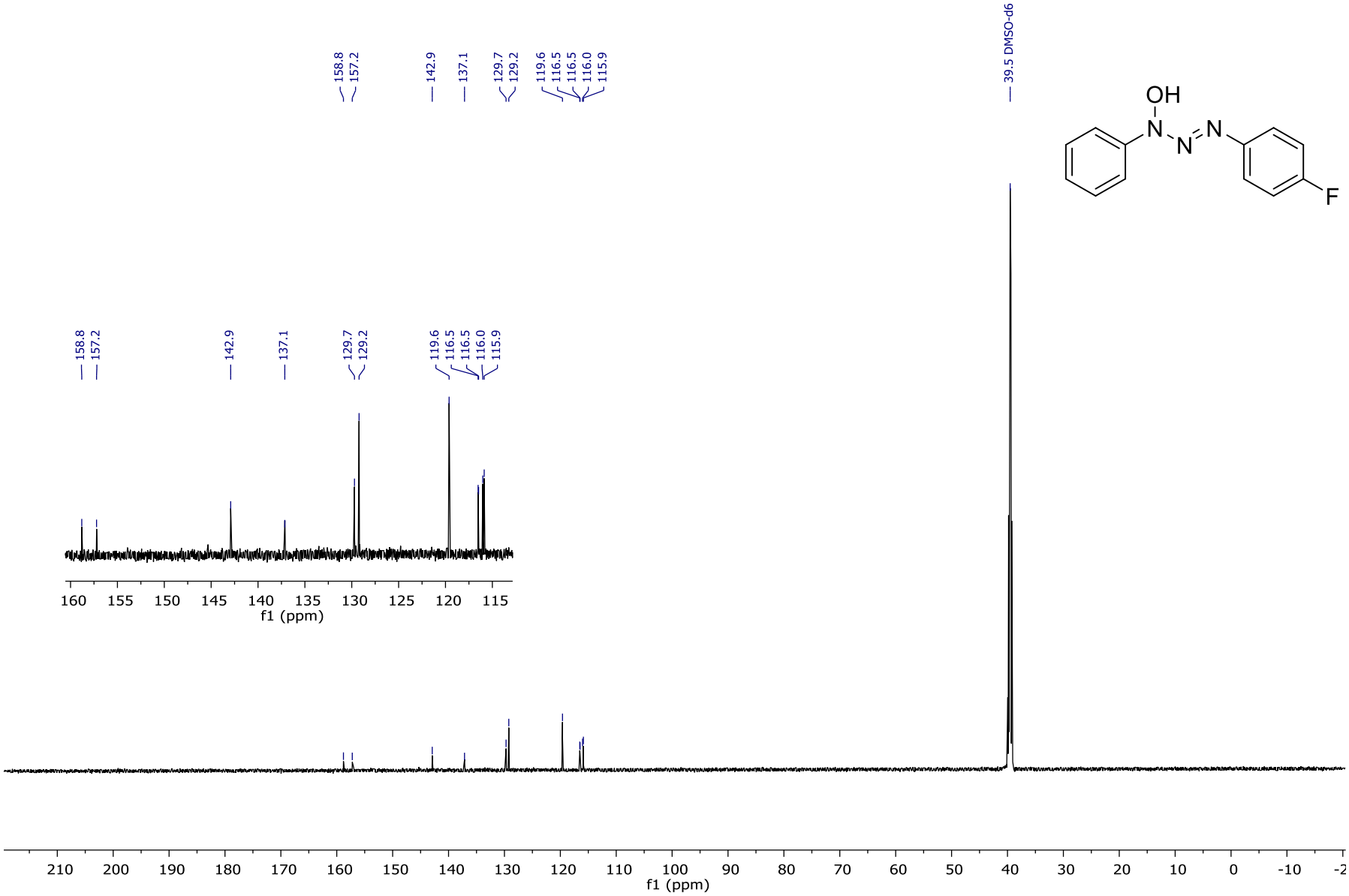


Figure S68. $^{13}C\{^{1}H\}$ NMR (600 MHz, DMSO-d_6) of 1-(4-fluorophenyl)-3-hydroxy-3-phenyltriazene (3c).

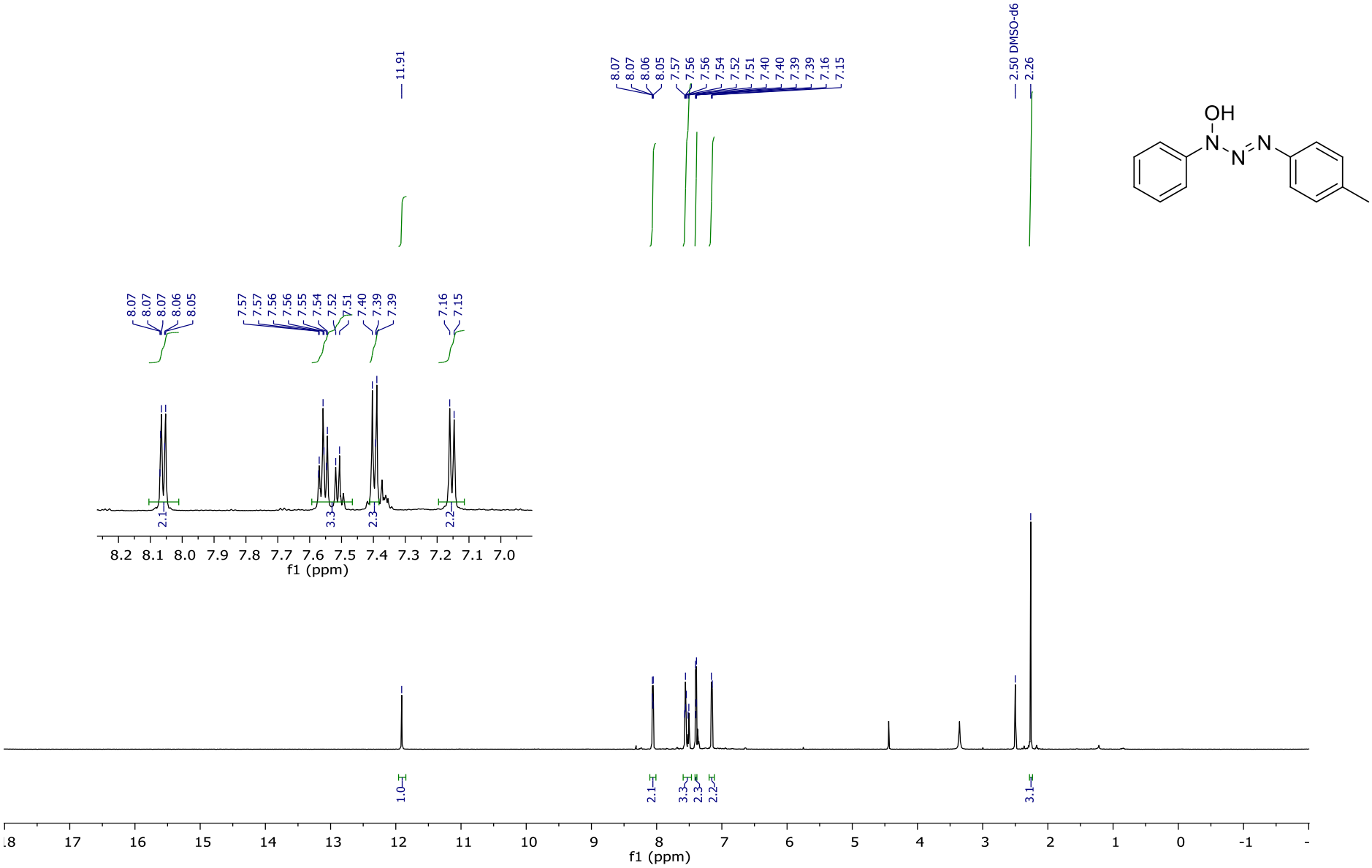


Figure S69. ^{1}H NMR (600 MHz, DMSO-d_6) of 3-hydroxy-3-phenyl-1-p-tolyltriazene (3d).

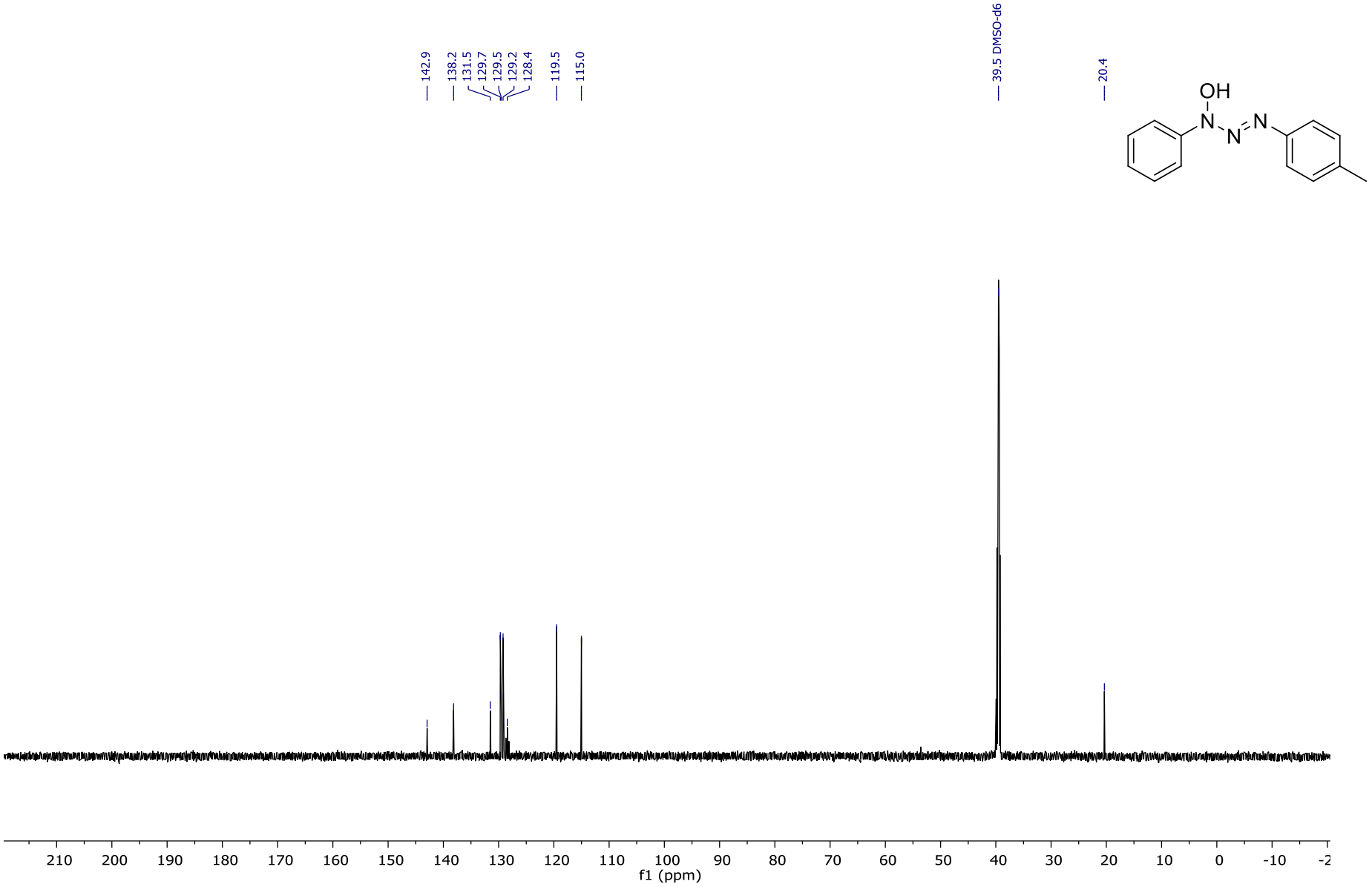


Figure S70. $^{13}C\{^{1}H\}$ NMR (600 MHz, DMSO-d_6) of 3-hydroxy-3-phenyl-1-p-tolyltriazene (3d).

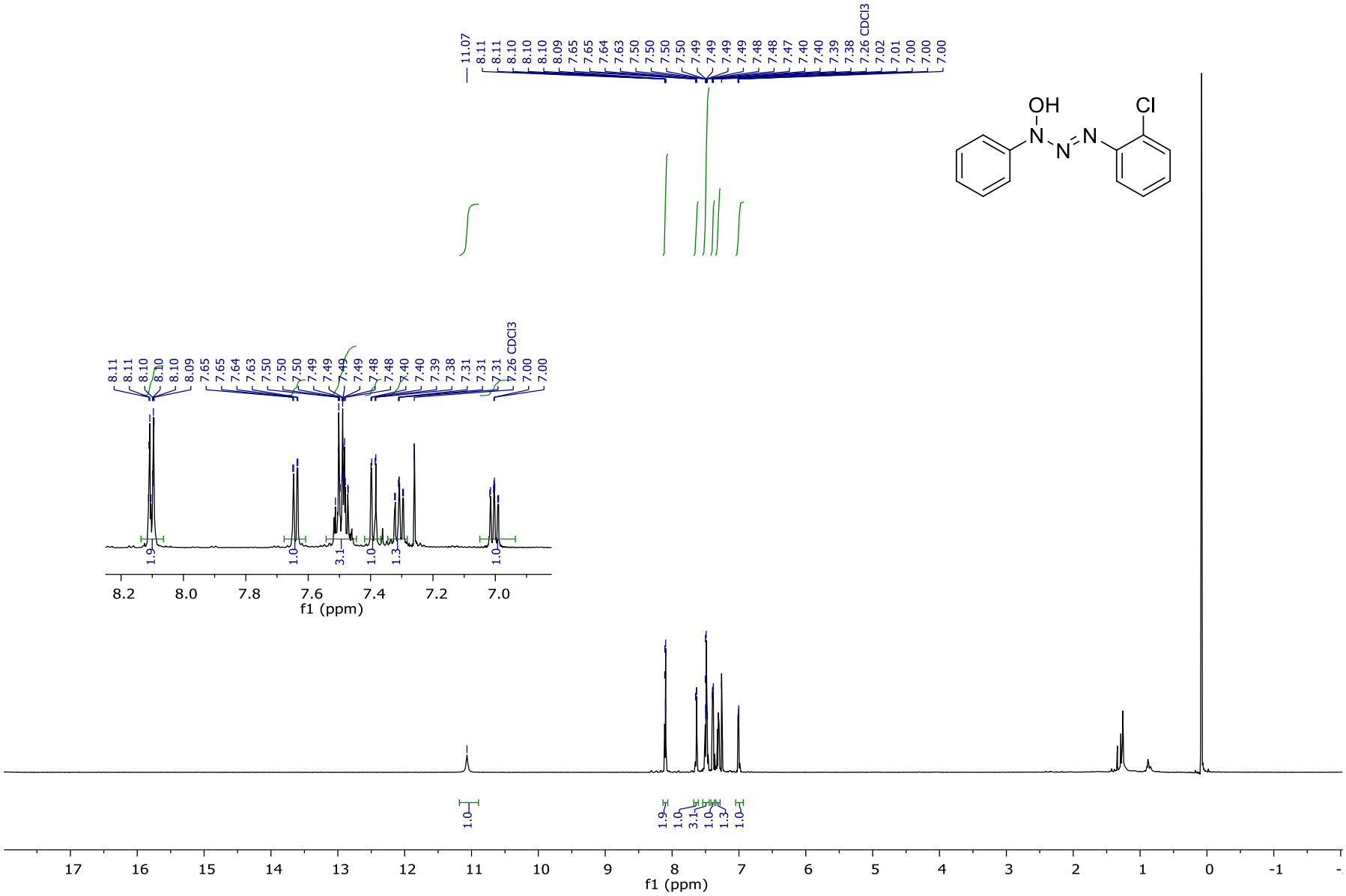


Figure S71. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-(2-chlorophenyl)-3-hydroxy-3-phenyltriazene (3e).

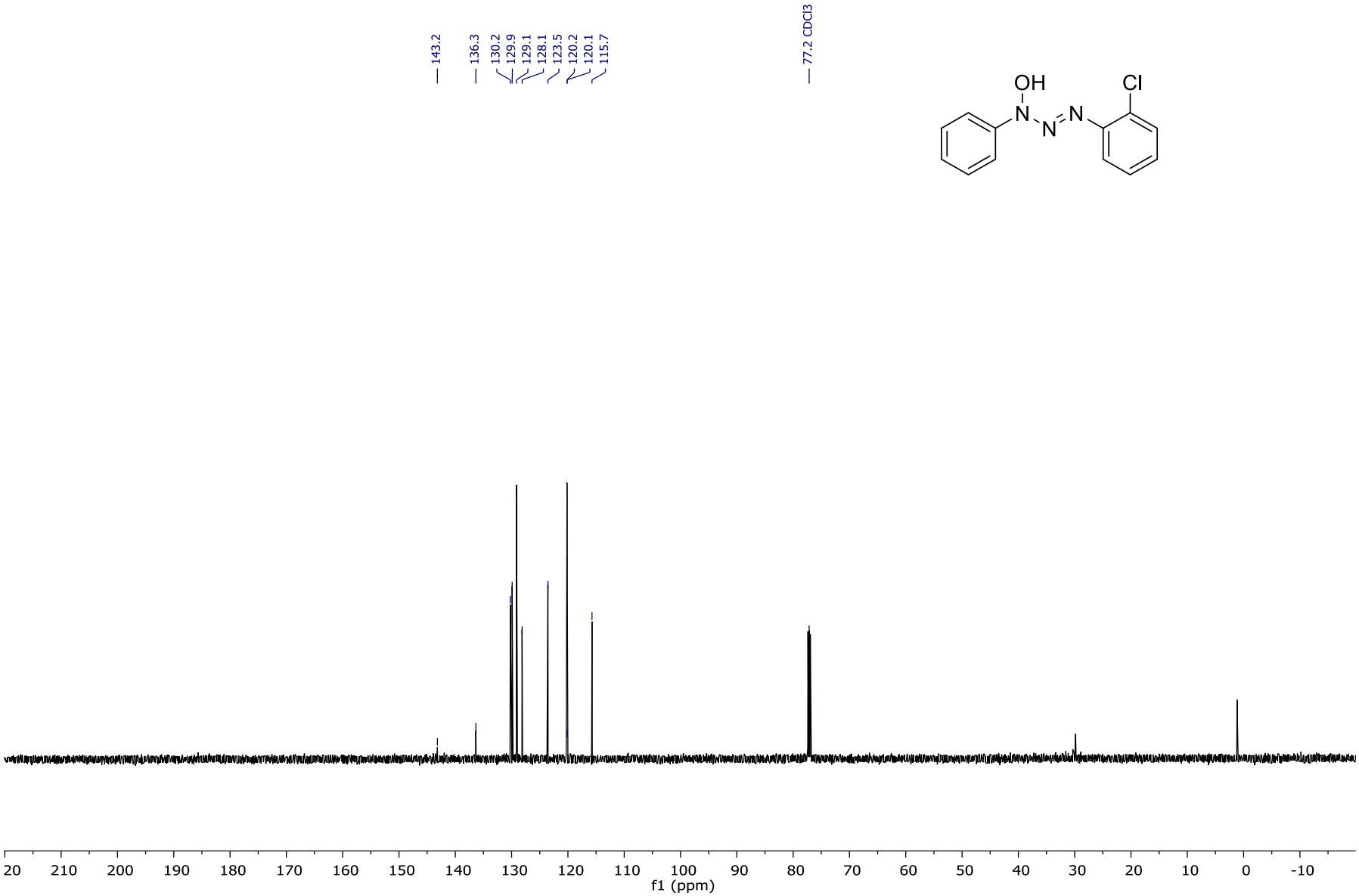


Figure S72. $^{13}C\{^{1}H\}$ NMR (600 MHz, Chloroform-*d*) of 1-(2-chlorophenyl)-3-hydroxy-3-phenyltriazene (3e).

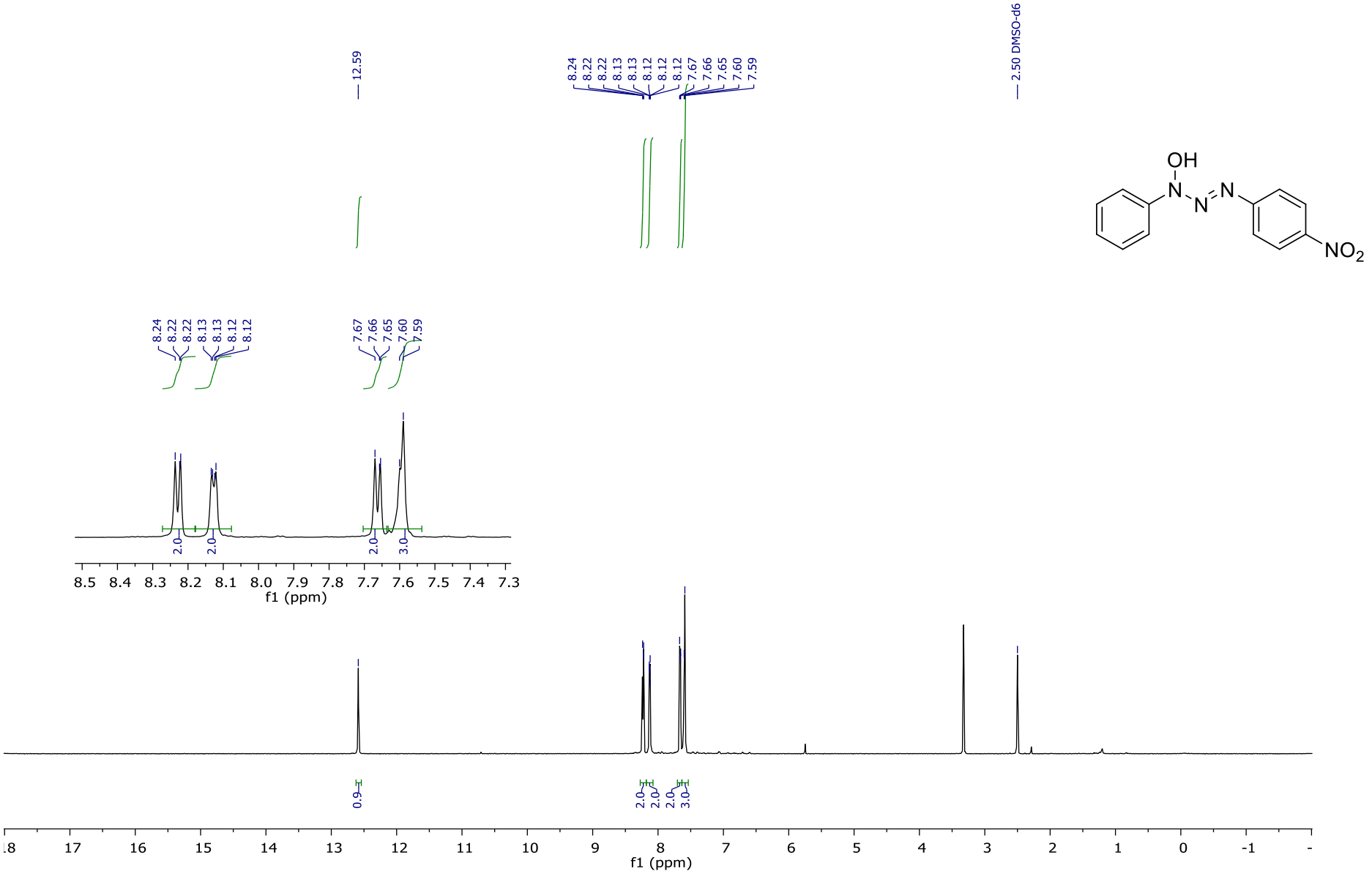


Figure S73. ^{1}H NMR (600 MHz, DMSO-d_6) of 3-hydroxy-1-(4-nitrophenyl)-3-phenyltriazene (3f).

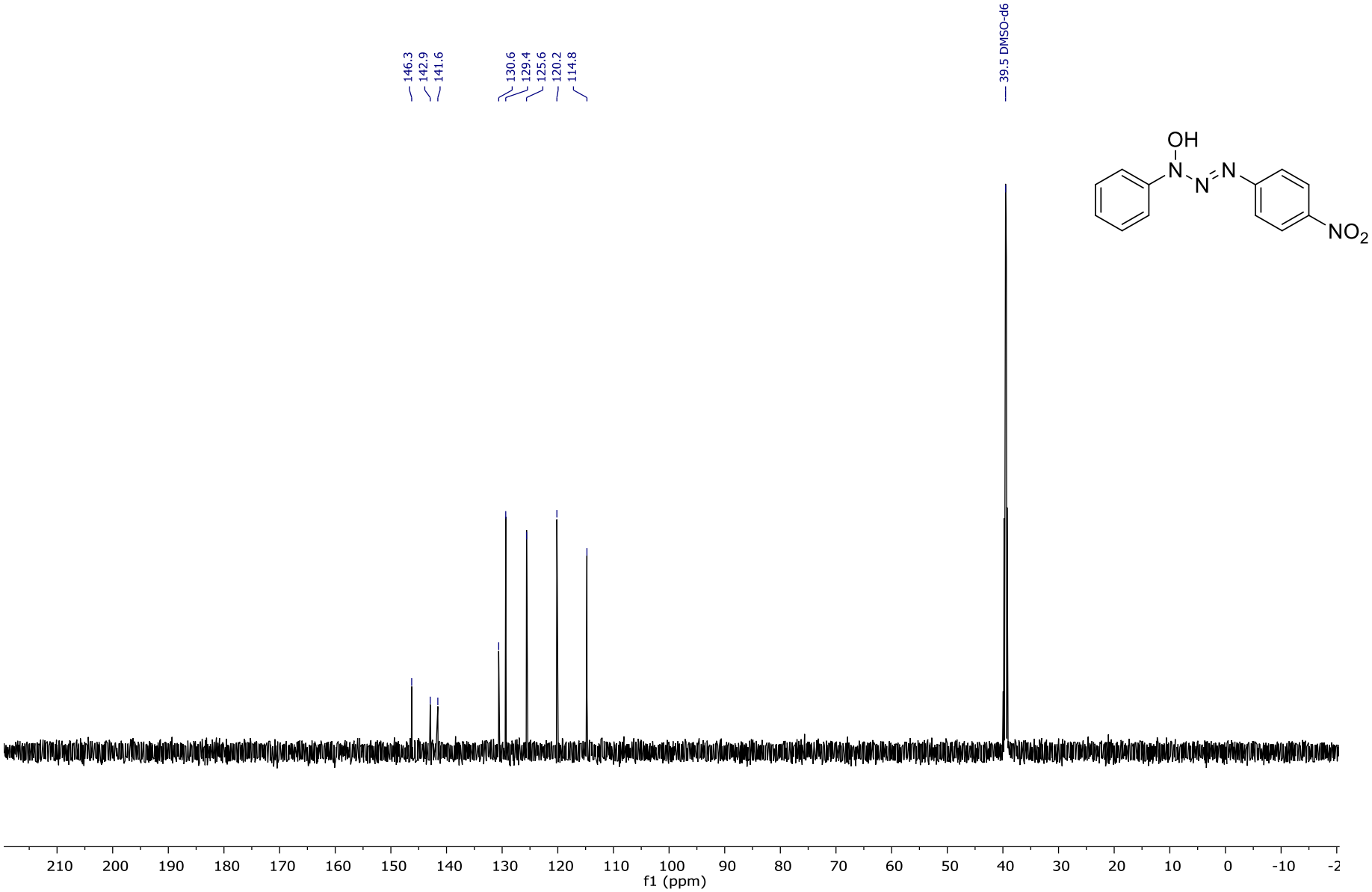


Figure S74. $^{13}C\{^{1}H\}$ NMR (600 MHz, DMSO-d_6) of 3-hydroxy-1-(4-nitrophenyl)-3-phenyltriazene (3f).

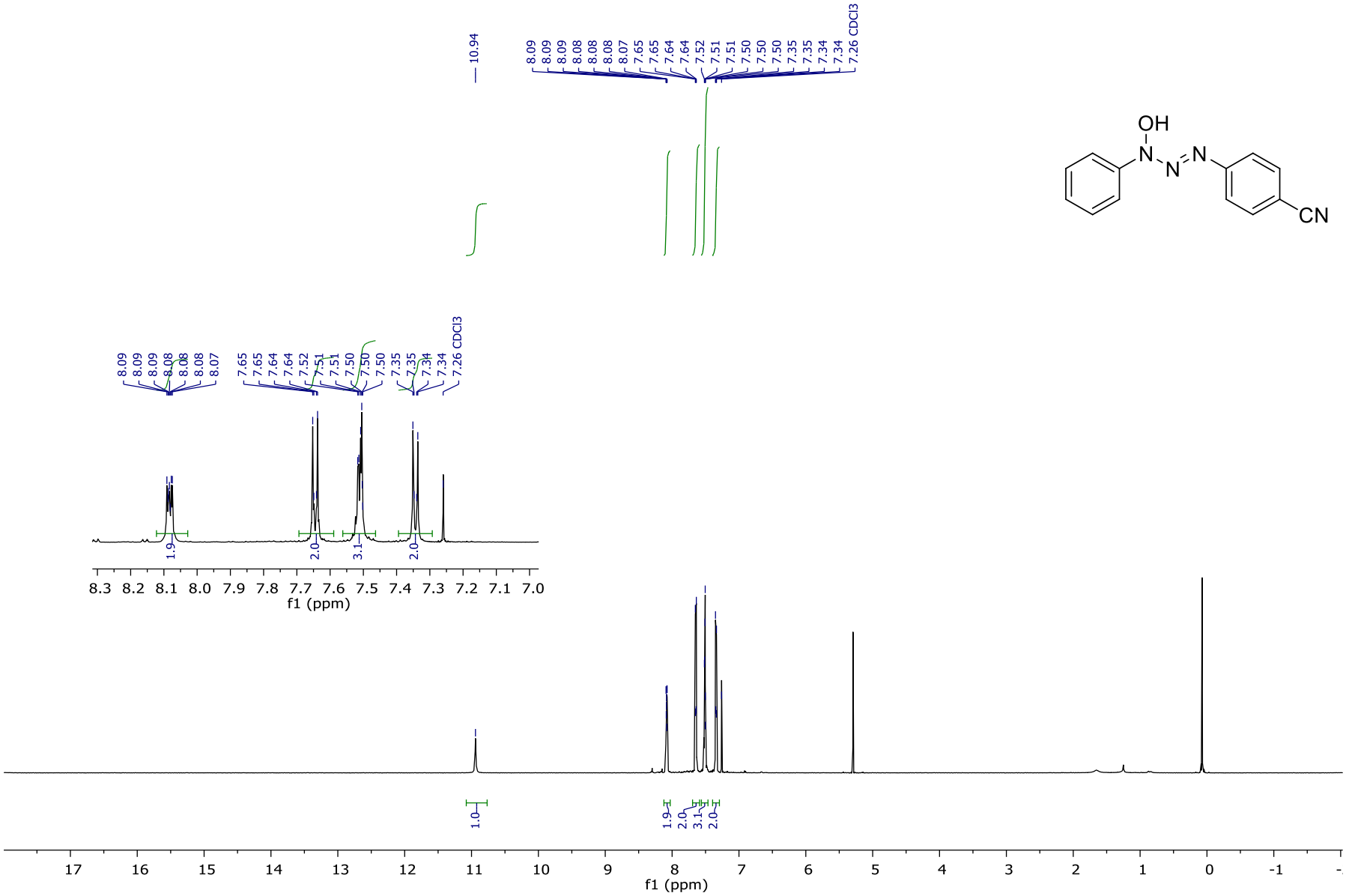


Figure S75. ^{1}H NMR (600 MHz, Chloroform-*d*) of 4-(3-hydroxy-3-phenyltriazenyl)benzonitrile (3g).

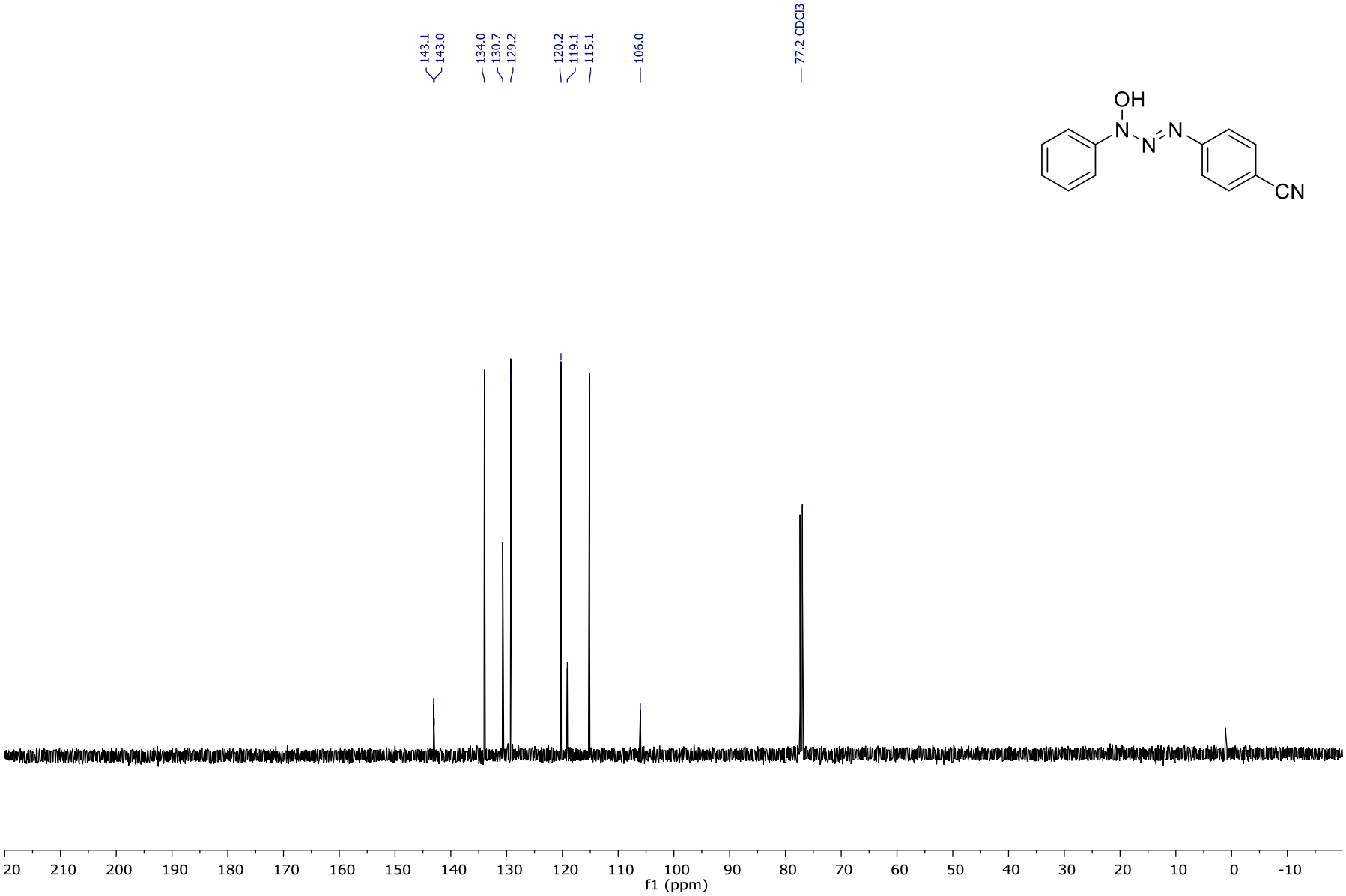


Figure S76. $^{13}C\{^{1}H\}$ NMR (600 MHz, Chloroform-*d*) of 4-(3-hydroxy-3-phenyltriazenyl)benzonitrile (3g).

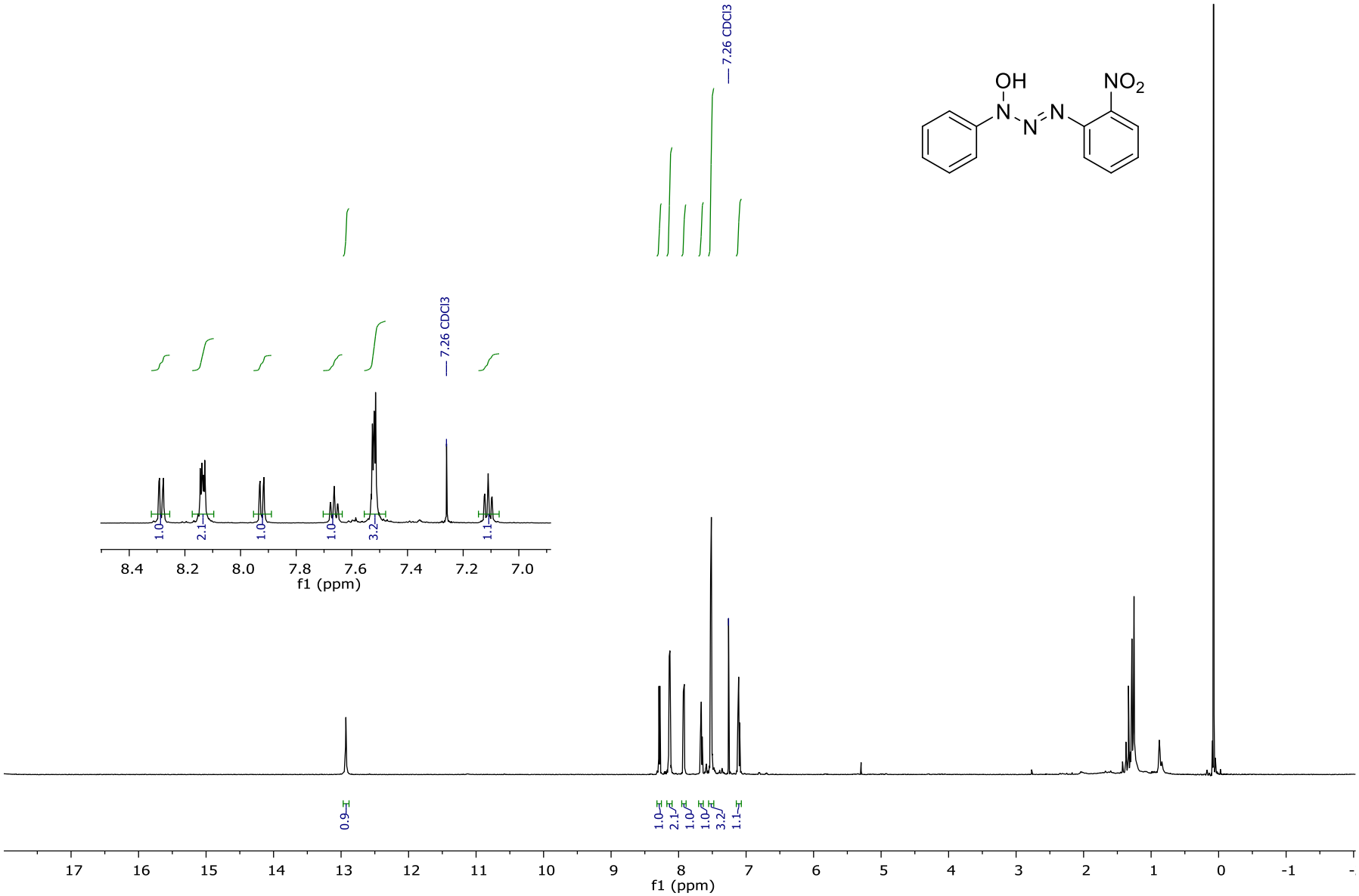


Figure S77. ^{1}H NMR (600 MHz, Chloroform-*d*) of 3-hydroxy-1-(2-nitrophenyl)-3-phenyltriazene (3h).

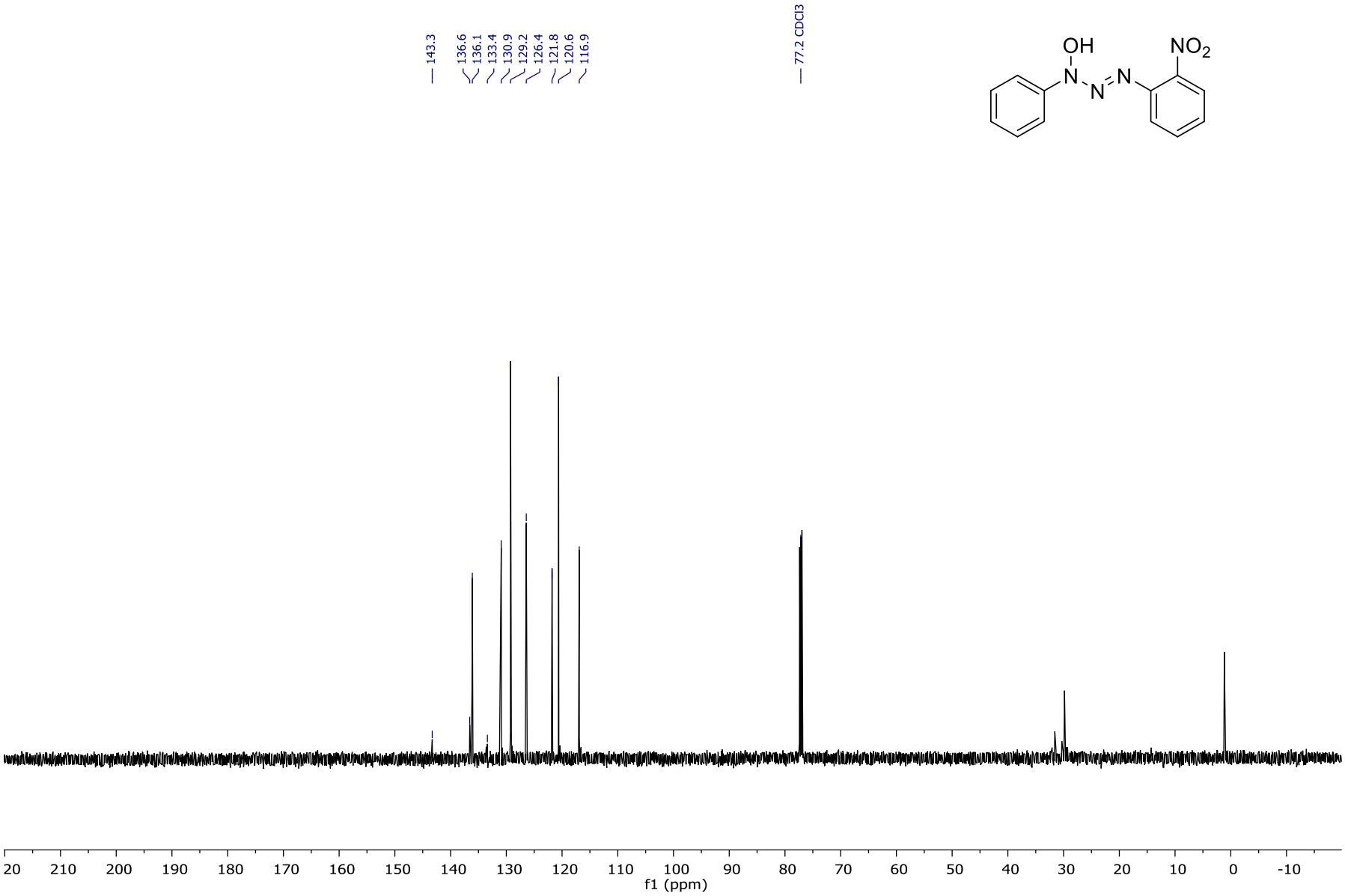


Figure S78. $^{13}C\{^{1}H\}$ NMR (600 MHz, Chloroform-*d*) of 3-hydroxy-1-(2-nitrophenyl)-3-phenyltriazene (3h).

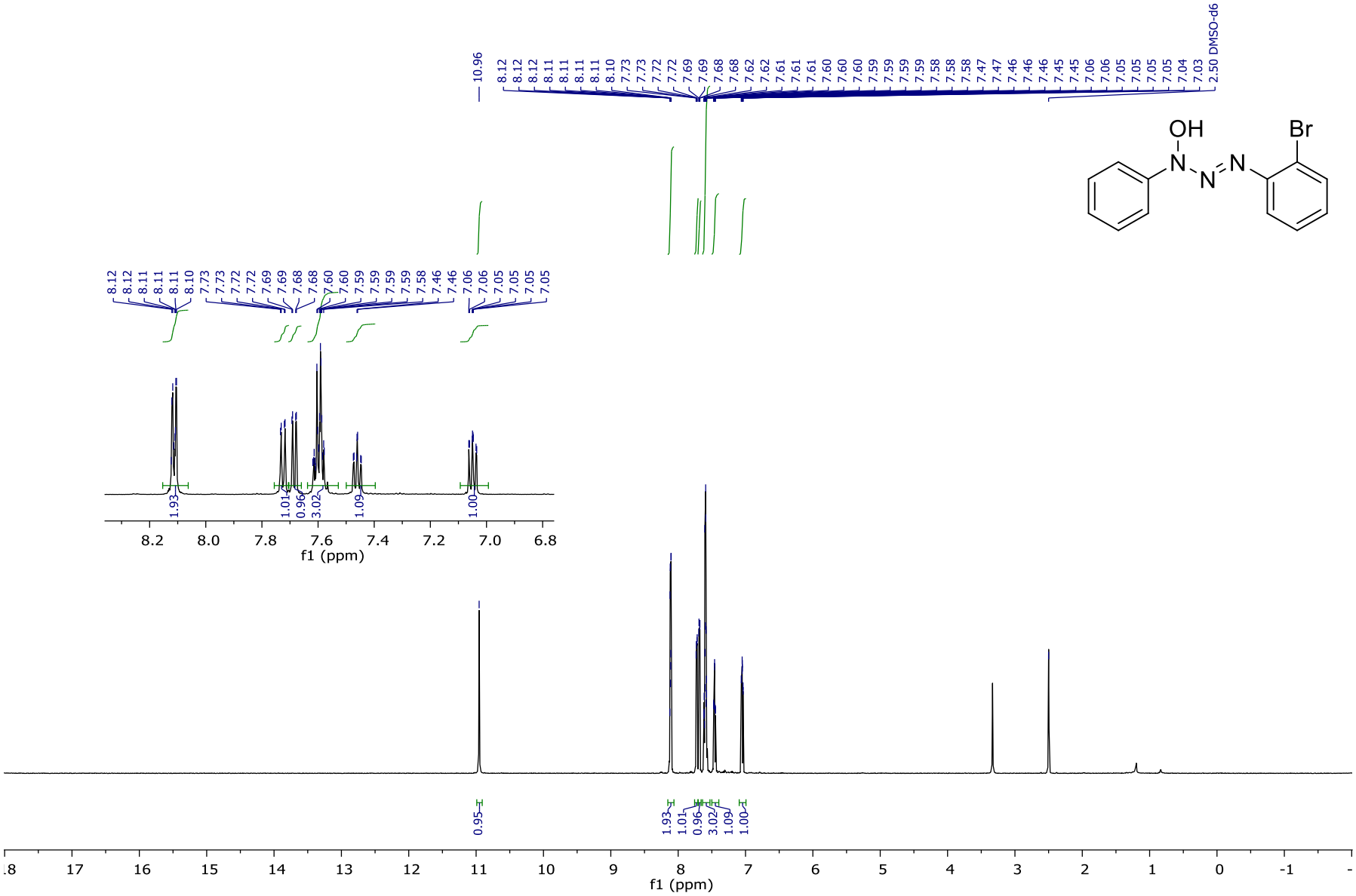


Figure S79. ^{1}H NMR (600 MHz, DMSO-*d*$_6$) of 1-(2-bromophenyl)-3-hydroxy-3-phenyltriazene (3i).

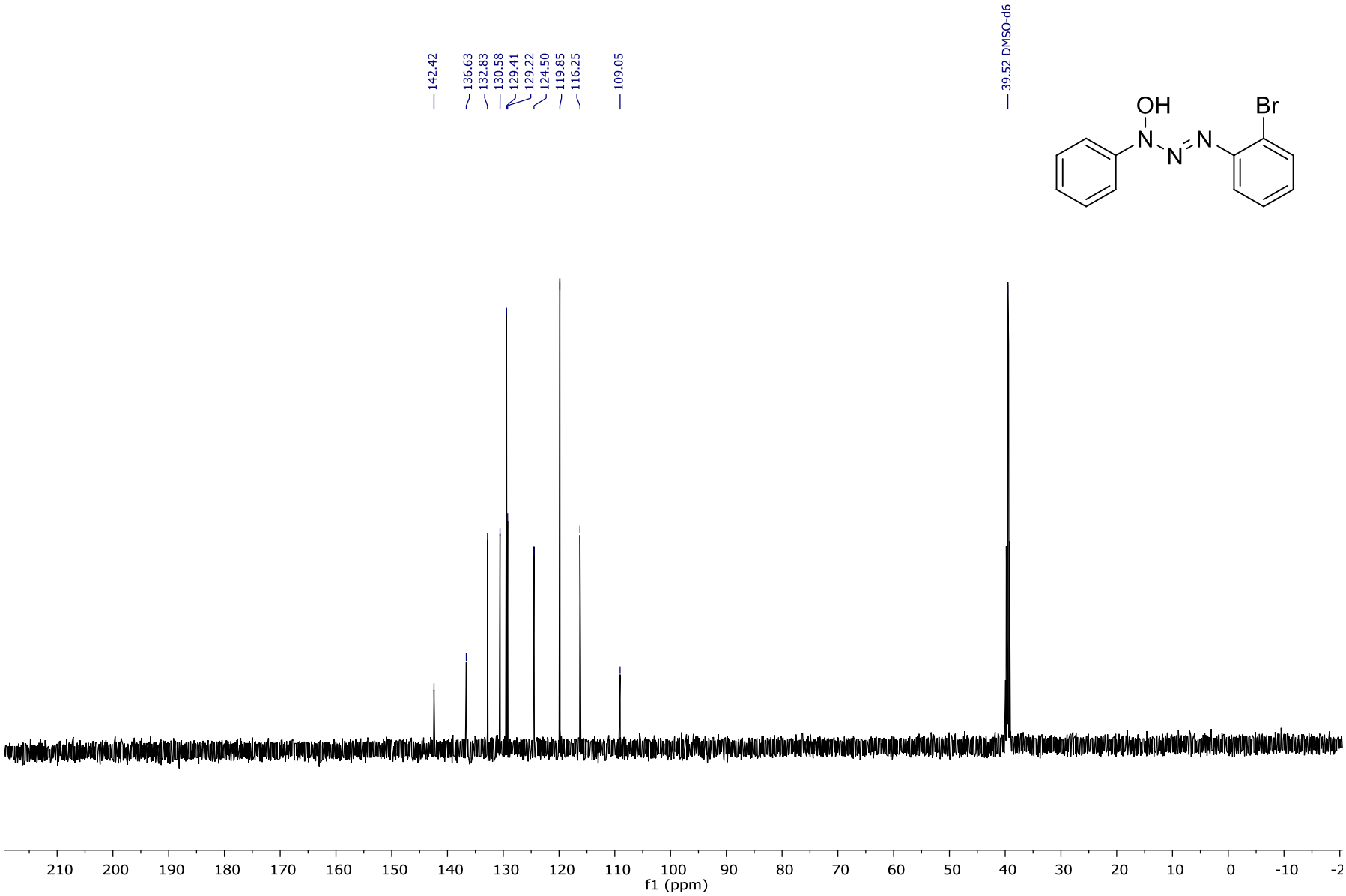


Figure S80. $^{13}C\{^{1}H\}$ NMR (600 MHz, DMSO-d_6) of 1-(2-bromophenyl)-3-hydroxy-3-phenyltriazene (3i).

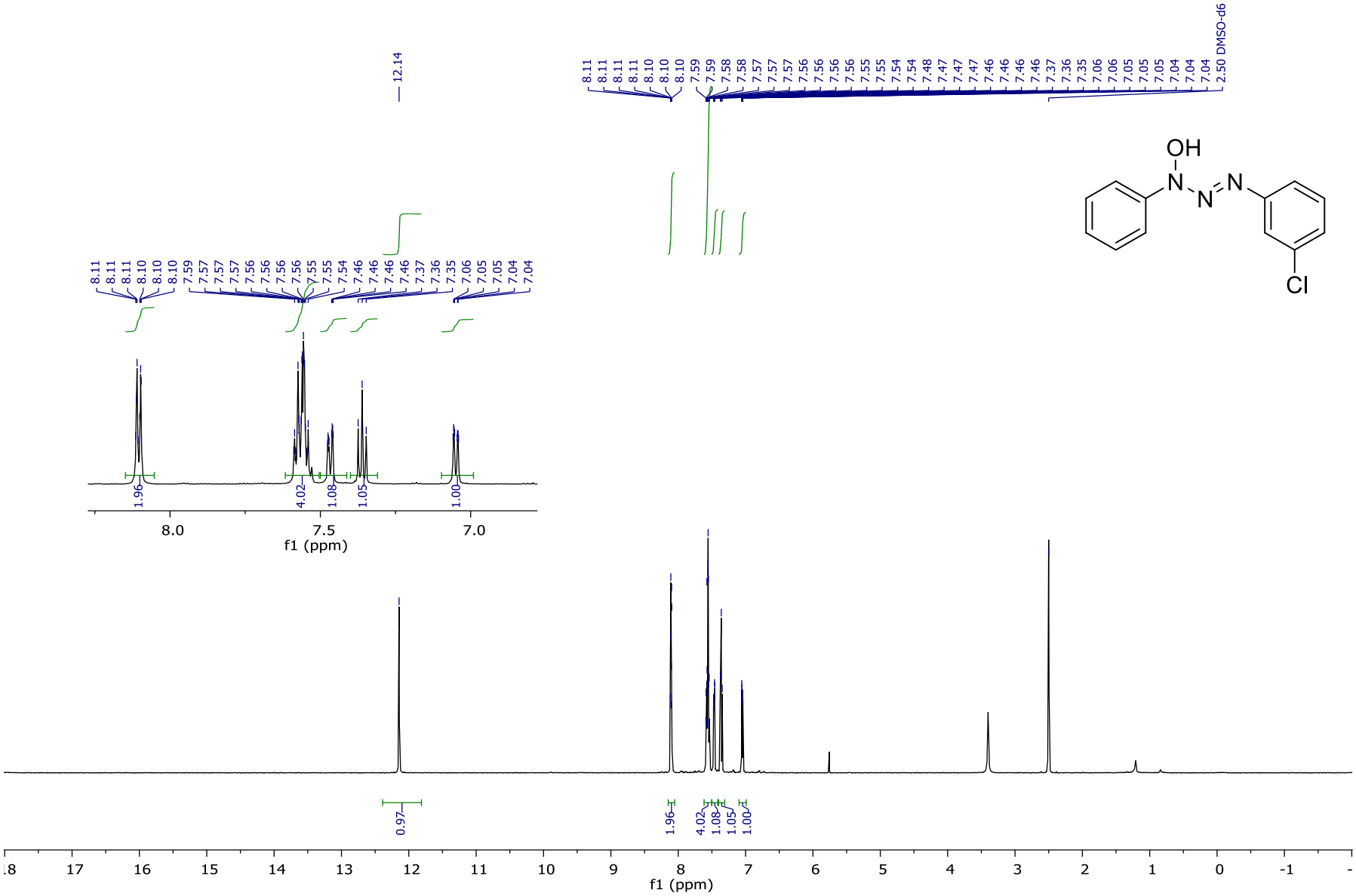


Figure S81. ^{1}H NMR (600 MHz, DMSO-*d*$_6$) of 1-(3-chlorophenyl)-3-hydroxy-3-phenyltriazene (3j).

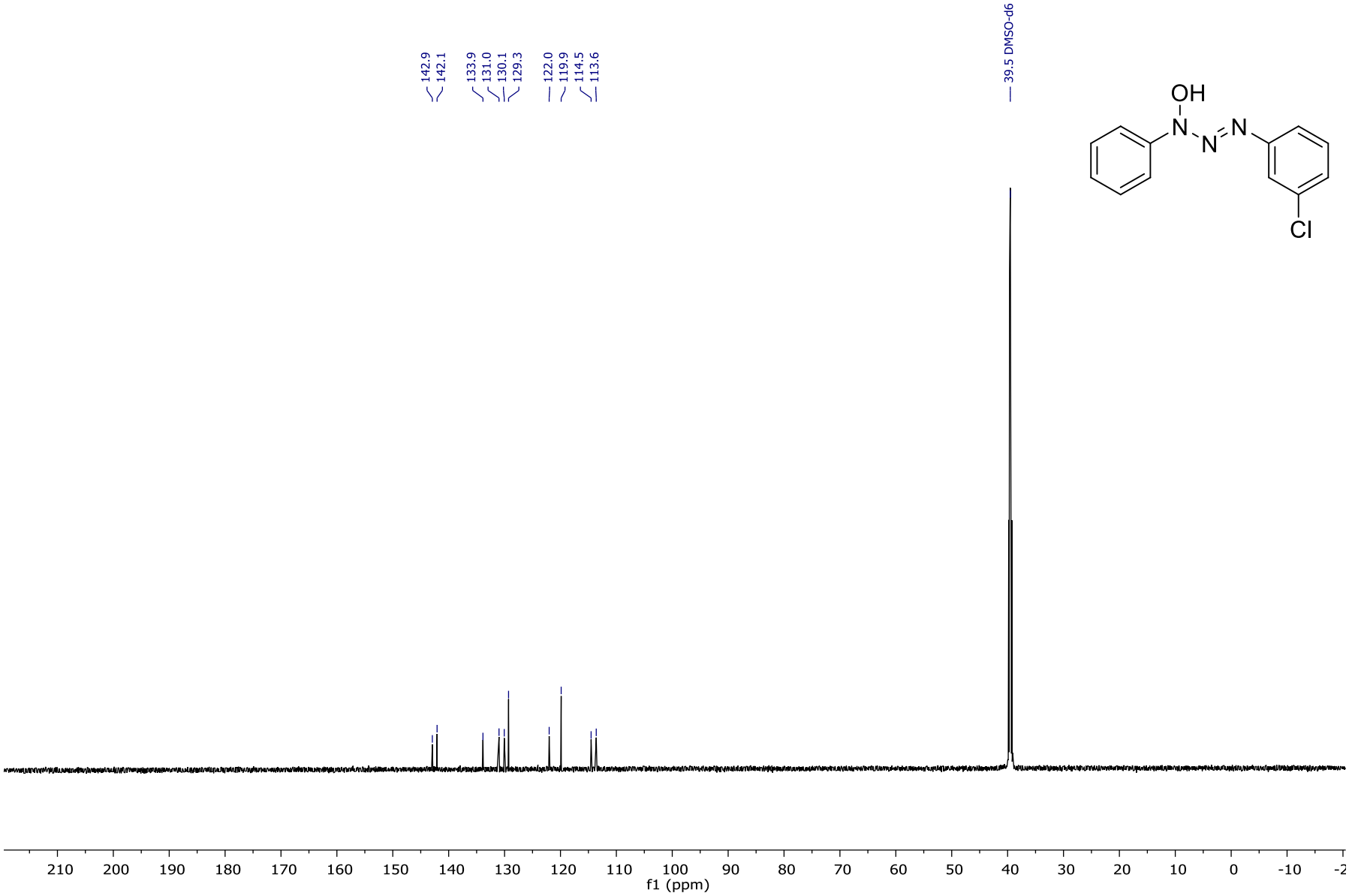


Figure S82. $^{13}C\{^{1}H\}$ NMR (600 MHz, DMSO-d_6) of 1-(3-chlorophenyl)-3-hydroxy-3-phenyltriazene (3j).

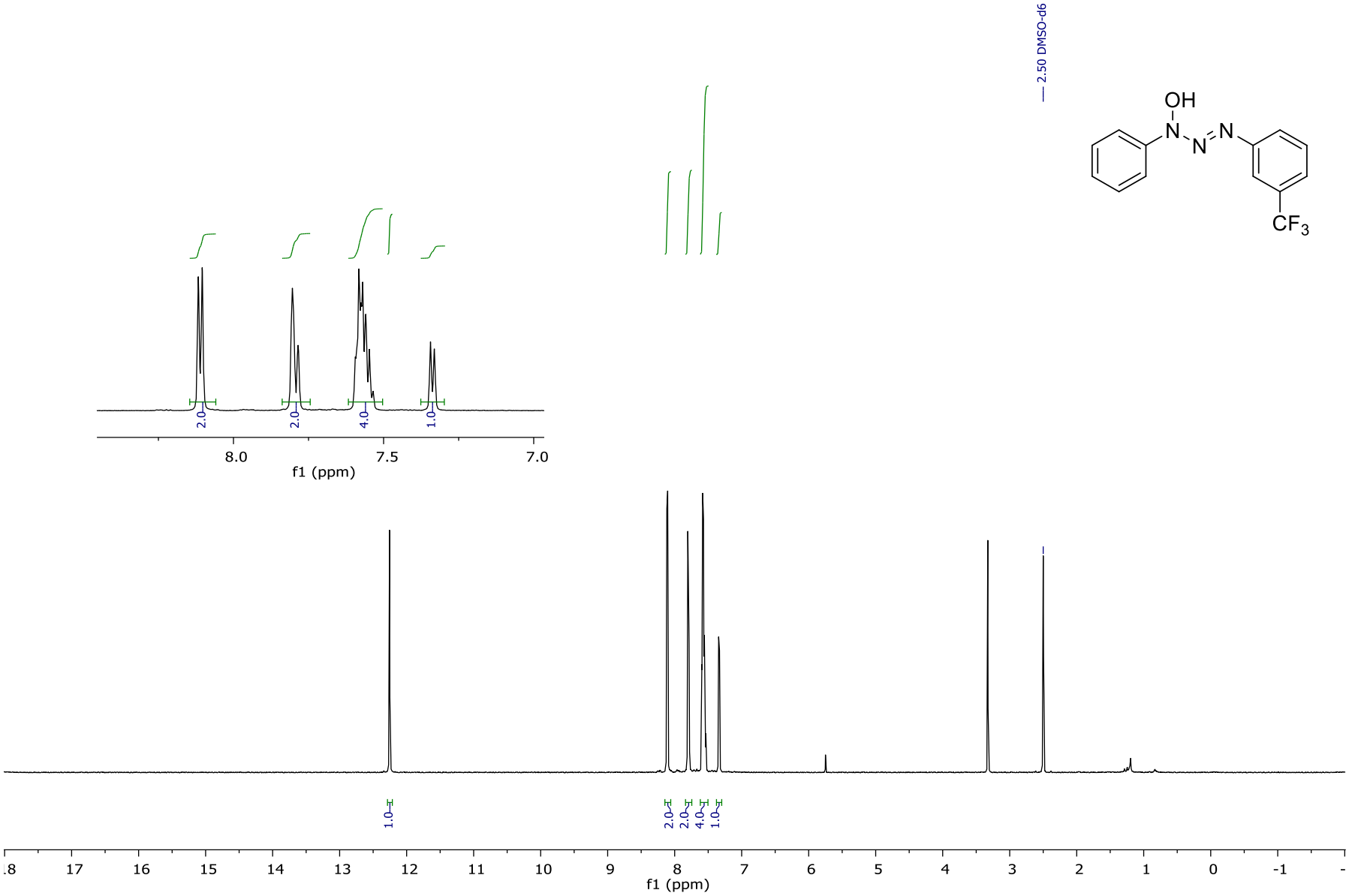


Figure S83. ^{1}H NMR (600 MHz, DMSO-d_6) of 3-hydroxy-3-phenyl-1-(3-(trifluoromethyl)phenyl)triazene (3k).

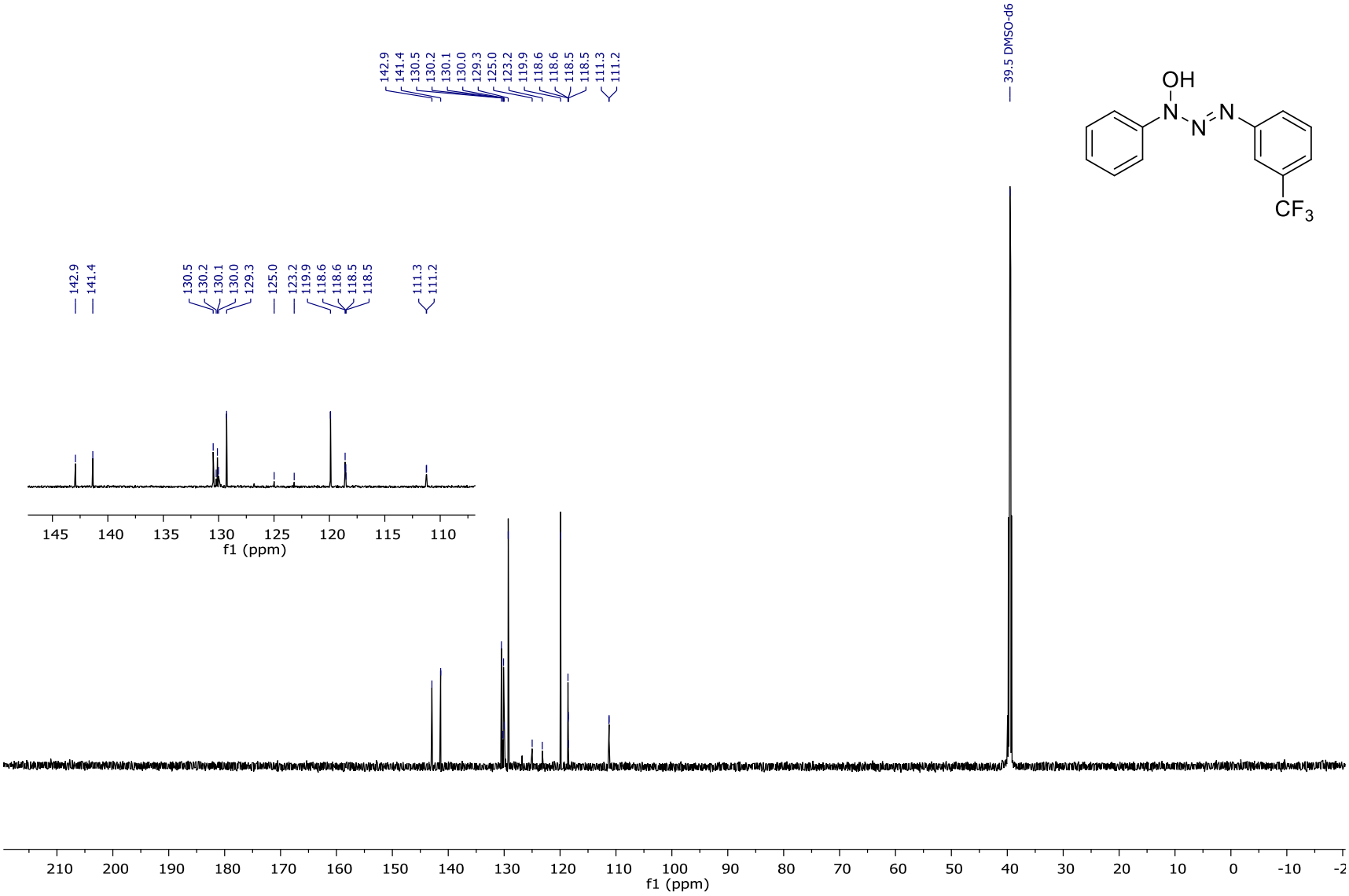


Figure S84. $^{13}C\{^{1}H\}$ NMR (600 MHz, DMSO-d_6) of 3-hydroxy-3-phenyl-1-(3-(trifluoromethyl)phenyl)triazene (3k).

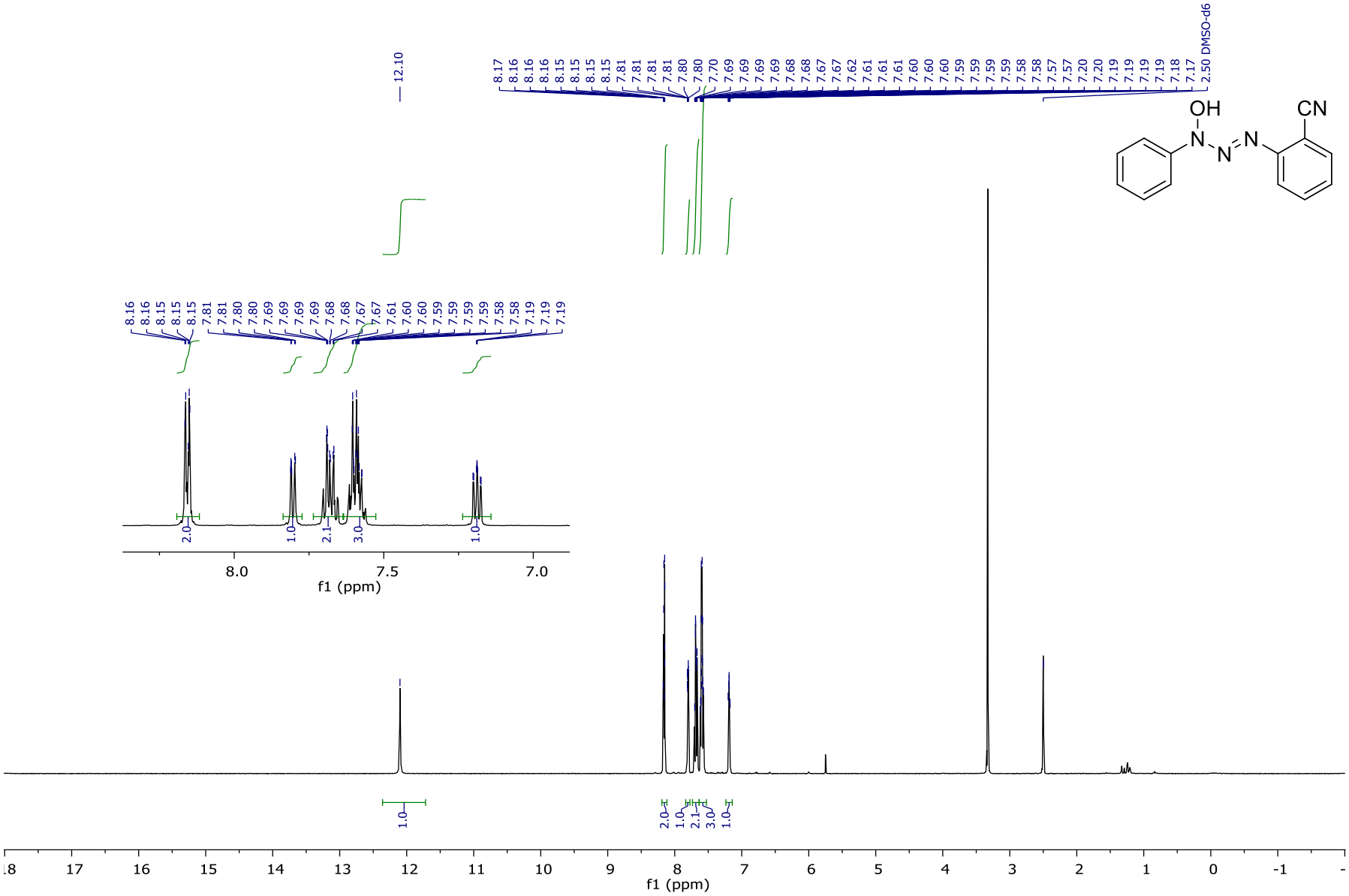


Figure S85. ^{1}H NMR (600 MHz, DMSO-d_6) of 2-(3-hydroxy-3-phenyltriazenyl)benzonitrile (3l).

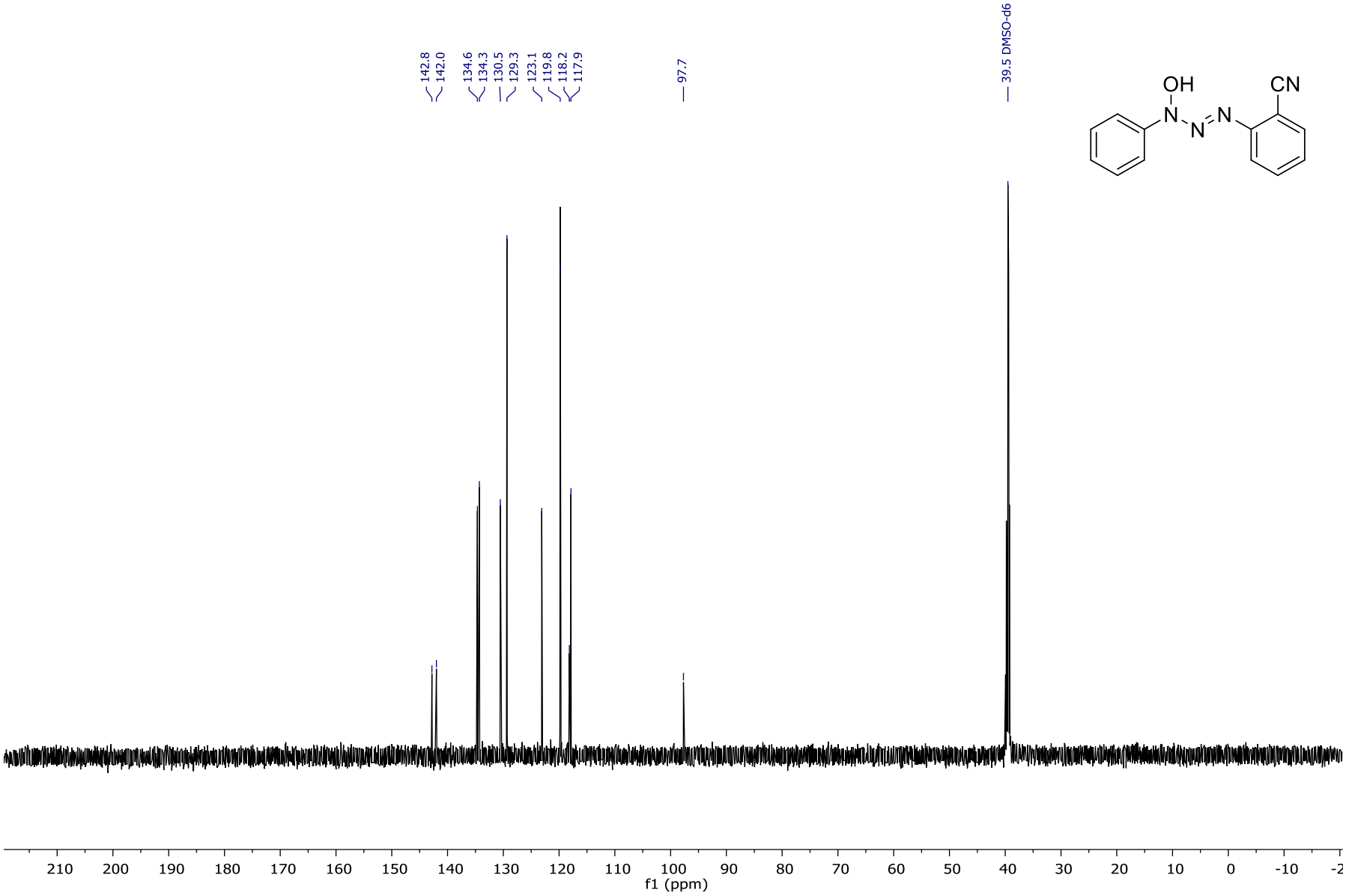


Figure S86. $^{13}C\{^{1}H\}$ NMR (600 MHz, DMSO-d_6) of 2-(3-hydroxy-3-phenyltriazenyl)benzonitrile (3l).

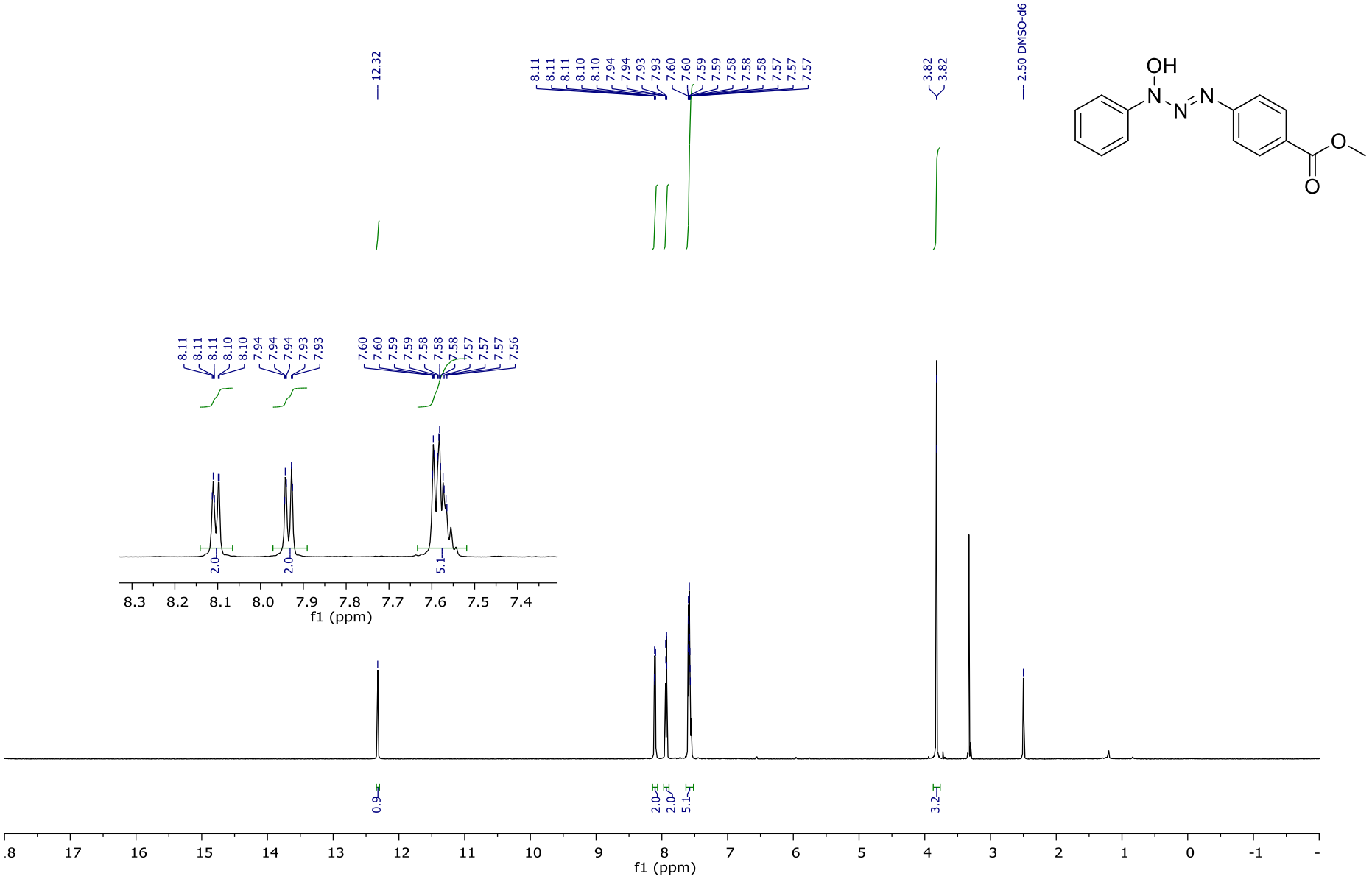


Figure S87. ^{1}H NMR (600 MHz, DMSO-d_6) of methyl 4-(3-hydroxy-3-phenyltriaz-1-enyl)benzoate (3n).

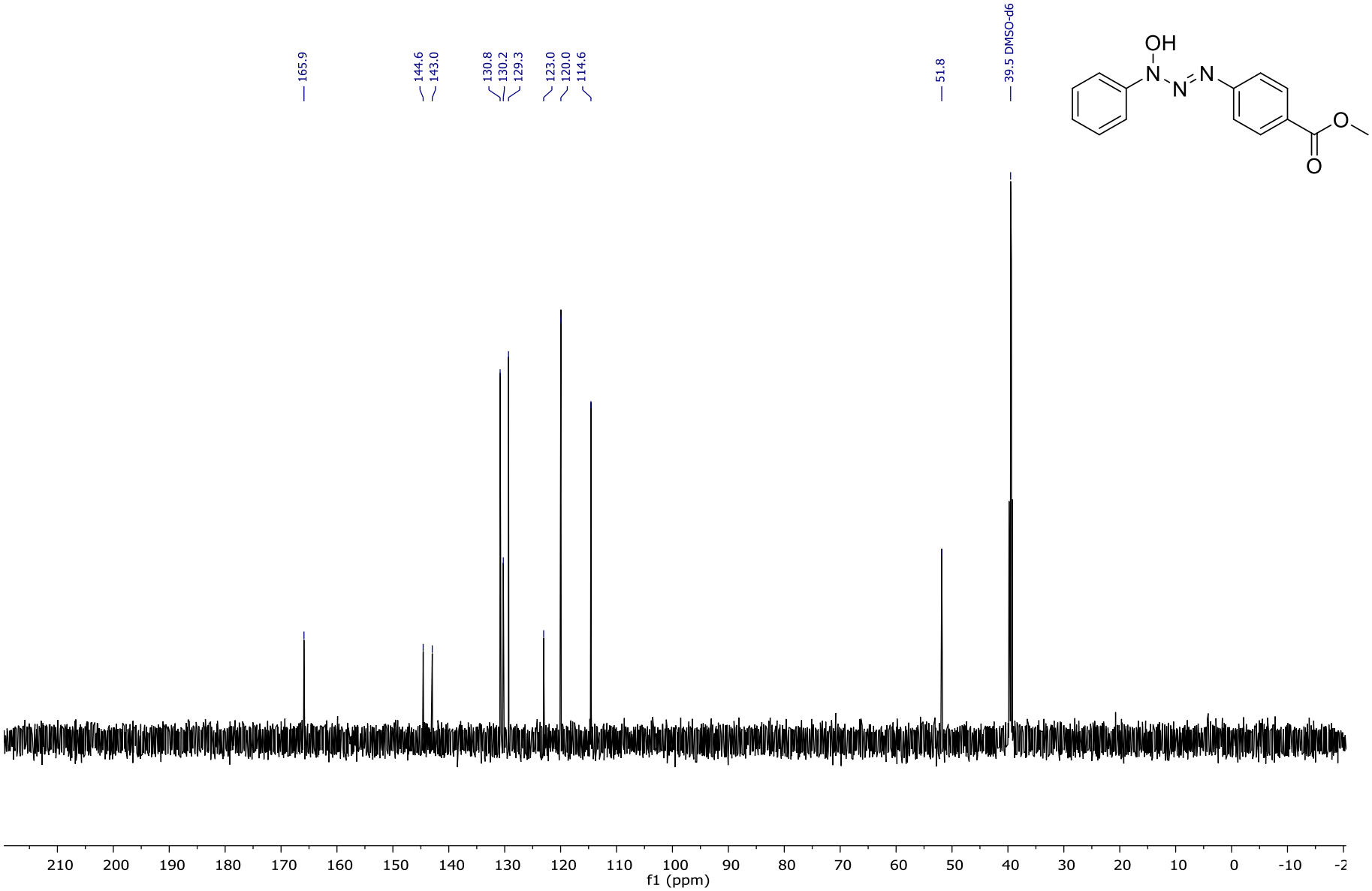


Figure S88. $^{13}C\{^{1}H\}$ NMR (600 MHz, DMSO-d_6) of methyl 4-(3-hydroxy-3-phenyltriaz-1-enyl)benzoate (3n).

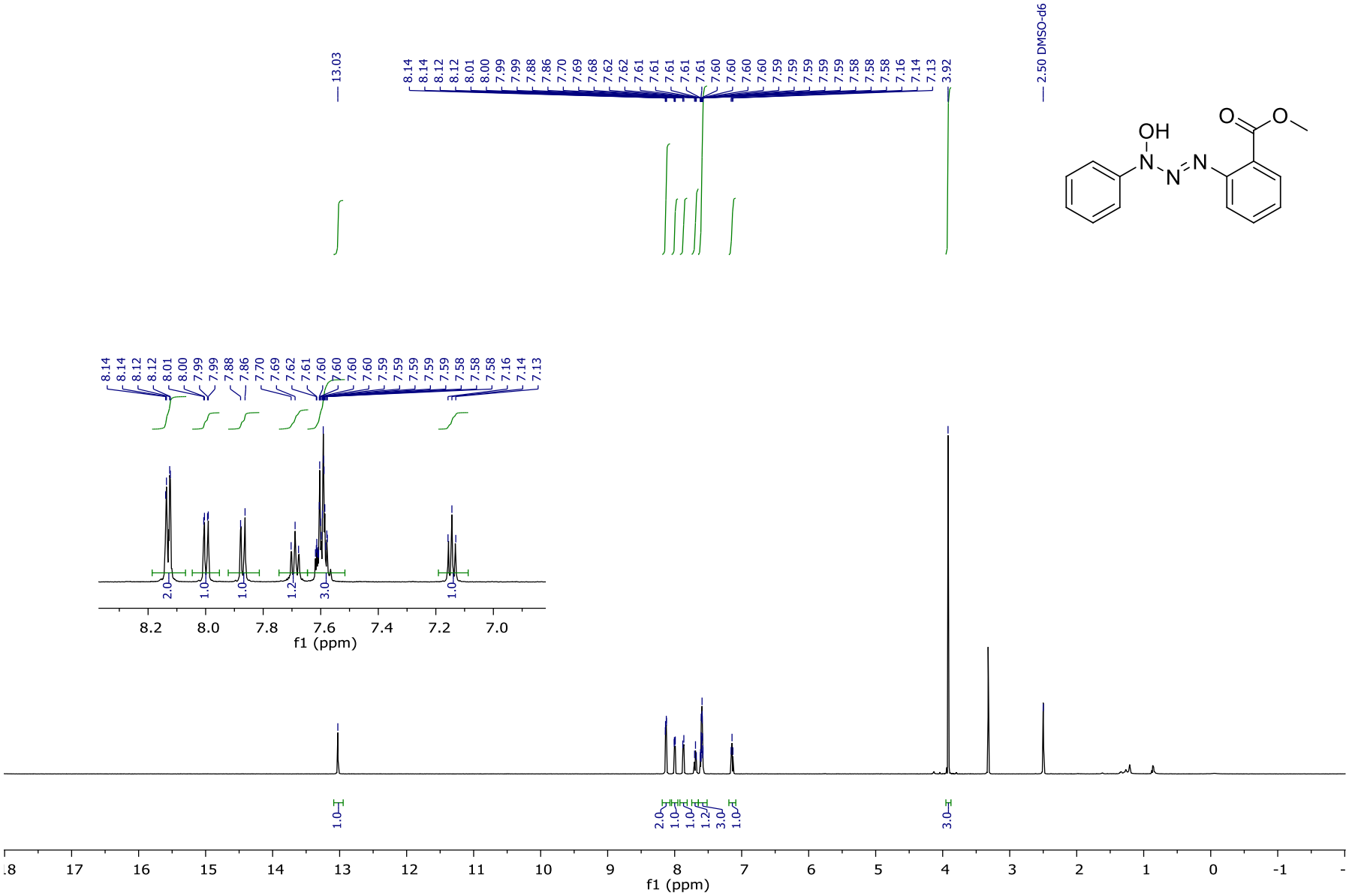


Figure S89. ^{1}H NMR (600 MHz, DMSO-d_6) of methyl 2-(3-hydroxy-3-phenyltriazenyl)benzoate (3o).

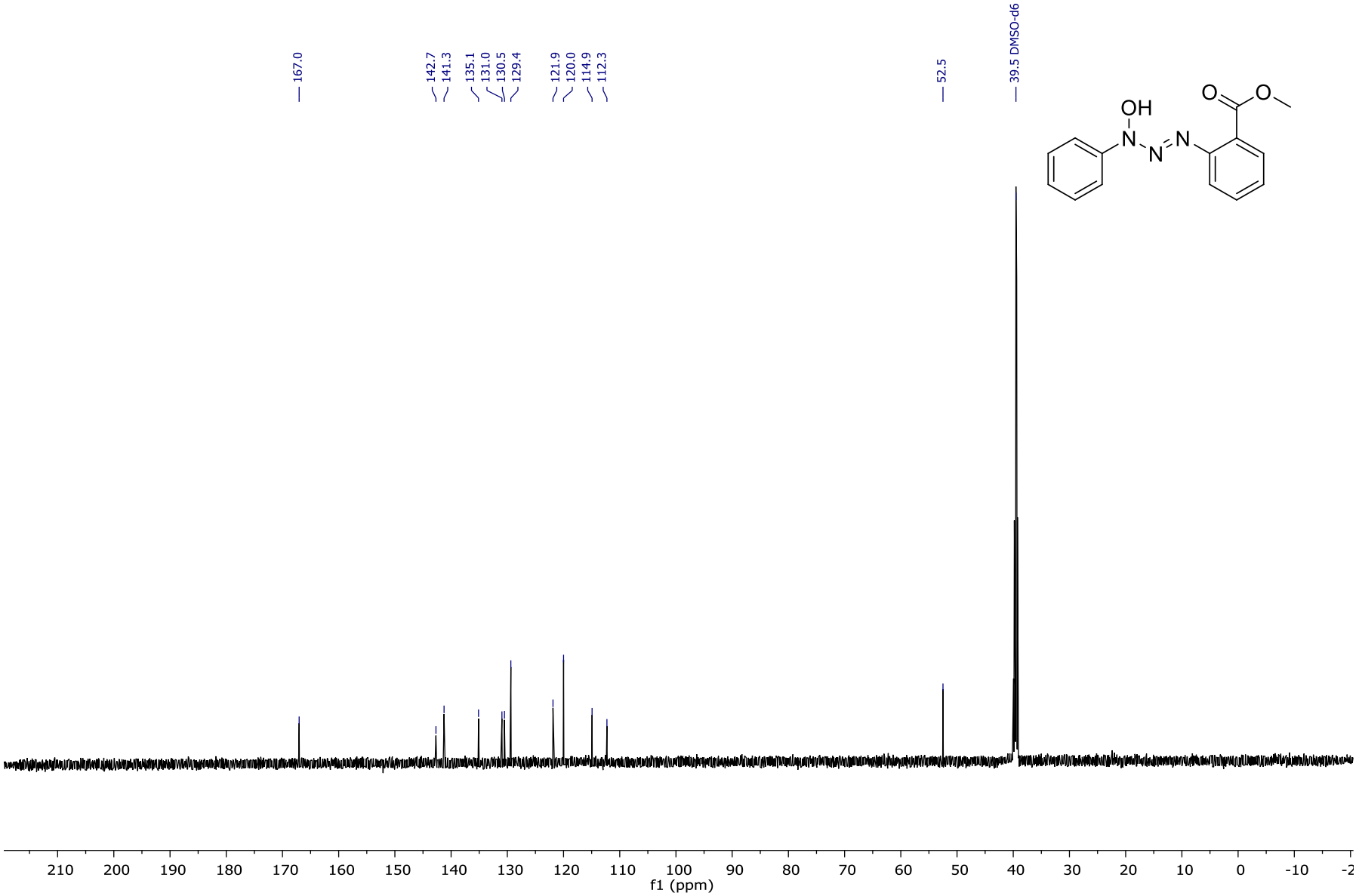


Figure S90. $^{13}C\{^{1}H\}$ NMR (600 MHz, DMSO-d_6) of methyl 2-(3-hydroxy-3-phenyltriazenyl)benzoate (3o).

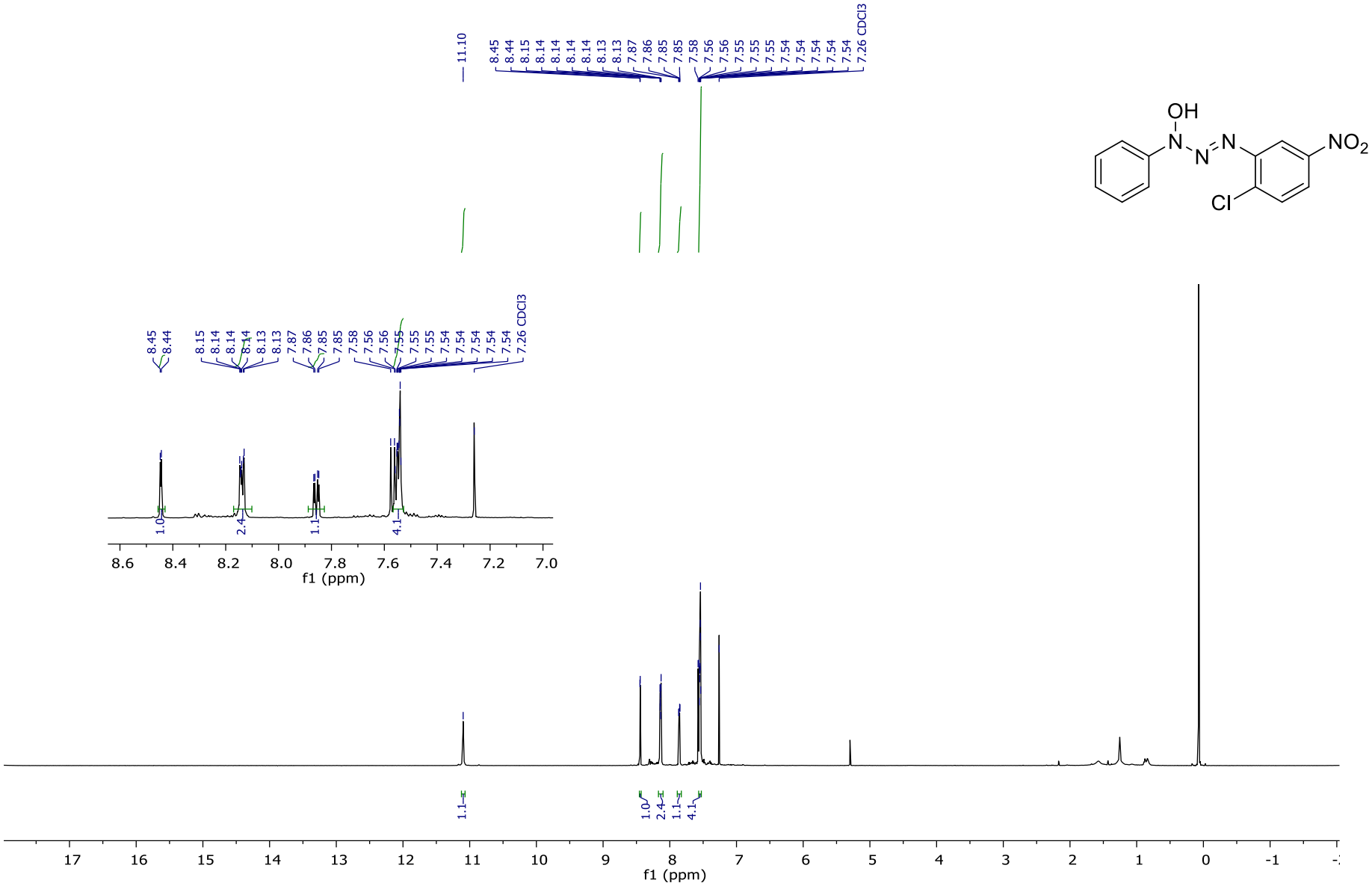


Figure S91. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-(2-chloro-5-nitrophenyl)-3-hydroxy-3-phenyltriazene (3p).

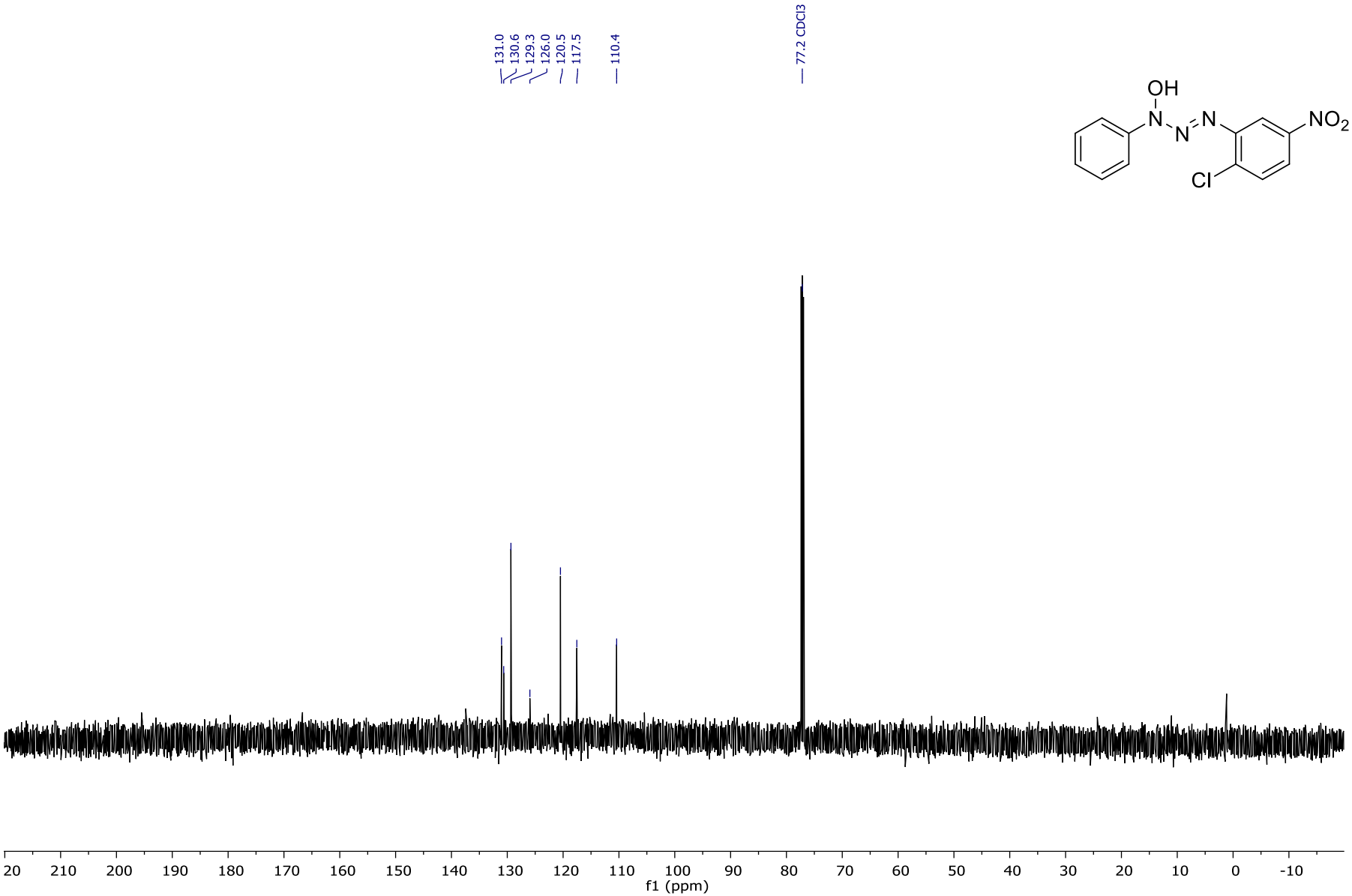


Figure S92. $^{13}C\{^{1}H\}$ NMR (600 MHz, Chloroform-*d*) of 1-(2-chloro-5-nitrophenyl)-3-hydroxy-3-phenyltriazene (3p).

References

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