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Making Endo-Cyclizations Favorable Again: Conceptually New Synthetic Approach to Benzotriazoles via Azide Group Directed Lithiation/Cyclization of 2-Azidoaryl Bromides

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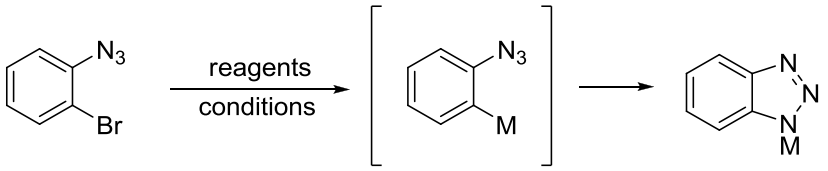
General information

All manipulations with organometallic compounds were carried out using standard Schlenk technique under argon atmosphere. Tetrahydrofuran was distilled over sodium in the presence of benzophenone. Other chemicals and solvents were obtained from commercial sources and used without further purification. 2-Bromoaniline (**1a**), 2,6-dibromo-4-methylaniline (**1h**), 2,6-dibromo-4-methoxyaniline (**1i**), 2-bromo-4,6-difluoroaniline (**1m**), 2,4,6-tribromoaniline (**1q**) were purchased from Sigma-Aldrich and used as received.

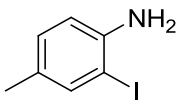
NMR spectra were obtained on a Bruker "Avance 600" (600 MHz ^{1}H, 151 MHz ^{13}C). Chemical shifts (δ) in ppm are reported using the residual undeuterated (^{1}H NMR) or deuterated solvent peaks (^{13}C NMR) as the internal standards.[1] Coupling constants J are given in Hertz as positive values regardless 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.

Table S1. Optimization of the cyclization conditions.



Entry	Reagent, eq., T	Solvent, concentration, time	Yield, %
1	2.5M n-BuLi, 1 eq., -80 °	THF, 0.4M, 2h	66
2	1.7M t-BuLi, 2 eq., -80 °C	THF, 0.4M, 2h	62
3	Mg, 5 eq., reflux	THF, 0.4M, 10h	no reaction
4	1.6M MeLi, 1 eq., -80 °C	THF, 0.4M, 2h	46

*2-iodo-4-methylaniline (**1b-I**)*



The title compound was synthesized with a minor modification of the known procedure.[2] A saturated aqueous solution (40 ml) of sodium bicarbonate was added to a solution of *p*-toluidine (5.00 g, 46.7 mmol) in dichloromethane (40 ml). To the slowly stirred reaction mixture iodine (11.9 g, 46.9 mmol) was added in small portions and the reaction mixture was stirred for 72h. The reaction mixture was washed with a saturated aqueous solution of Na_2SO_3 (3x50 ml), the organic phase was dried over Na_2SO_4. The solvent was evaporated under reduced pressure.

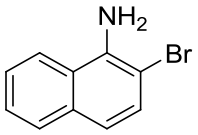
The dark oily residue was purified by flash chromatography (eluent – PE/dichloromethane 2:1) to give 9.00 g (83%) of 2-iodo-4-methylaniline as a yellowish oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 8.1 Hz, 1H), 3.91 (s, 2H), 2.21 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 144.4 , 139.1 , 130.2 , 129.7 , 114.8 , 84.4 , 20.0 .

The NMR data are in agreement with previously reported.[3]

*2-bromonaphthalen-1-amine (**1d**)*



The title compound was synthesized with a minor modification of the known procedure.[4] A solution of N-bromosuccinimide (1.78 g, 10.0 mmol) in dichloromethane (80 ml) was cooled to -80 °C, followed by addition of $ZrCl_4$ (0.117 g, 0.5 mmol) and 1-aminonaphthalene (1.43 g, 10.0 mmol) under argon atmosphere. The reaction mixture was stirred for 4h, and then quenched with saturated $NaHCO_3$ aqueous solution. The reaction mixture was extracted with dichloromethane; combined organic phase was washed with water (2x100 ml) and dried over Na_2SO_4. The solvent was evaporated in vacuum to give crude product (1.64 g, 73%) containing minor byproduct - 4-bromo-1-naphtylamine (product : byproduct = 94 : 6). Pure product was obtained after column chromatography purification (eluent – PE) as a white needles (0.821 g, 37%), m.p. 71-72 °C (lit. data[4]: m.p. 73-76 °C).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (s, 2H), 7.49 (s, 3H), 7.18 (d, *J* = 8.5 Hz, 1H), 4.62 (s, 2H).

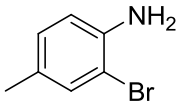
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 139.6 , 133.4 , 129.9 , 128.8 , 126.2 , 125.9 , 123.8 , 121.0 , 119.5 , 104.4 .

The NMR data are in agreement with previously reported.[2a]

General procedure A: aniline bromination

A solution of aniline (20 mmol) in dichloromethane (1M) was cooled to 0 °C followed by dropwise addition of N-bromosuccinimide (20 mmol) solution in dichloromethane (0.15M) while maintaining the temperature below 5 °C. The reaction was monitored by TLC. After the reaction completed, the reaction mixture was washed with a saturated aqueous solution of sodium bicarbonate (2x100 ml) and water (100 ml). The organic phase was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The product was purified by flash chromatography (eluent – PE/dichloromethane in ratio from 5:1 to 1:1).

*2-bromo-4-methylaniline (**1b-Br**)*



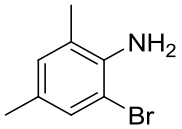
From p-toluidine (7.5 g, 70 mmol), following **General procedure A**, 2-bromo-4-methylaniline (13.02 g, 96%) was obtained as a red oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 (s, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.1 Hz, 1H), 3.92 (s, 2H), 2.23 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 141.7 , 132.8 , 129.2 , 129.1 , 115.9 , 109.4 , 20.2 .

The NMR data are in agreement with previously reported.[5]

*2-bromo-4,6-dimethylaniline (**1c**)*



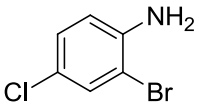
From 2,4-dimethylaniline (9.43 g, 77.8 mmol), following **General procedure A**, 2-bromo-4,6-dimethylaniline (14.87 g, 96%) was obtained as a brown needles, m.p. 45-46 °C (lit. data[6]: m.p. 46-47 °C).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.13 (s, 1H), 6.82 (s, 1H), 3.82 (s, 2H), 2.21 (s, 3H), 2.19 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 139.8 , 130.5 , 130.4 , 128.6 , 123.6 , 109.6 , 20.2 , 18.4 .

The NMR data are in agreement with previously reported.[7]

*2-bromo-4-chloroaniline (**1e**)*



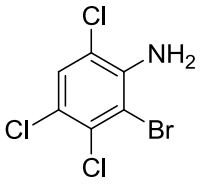
From 4-chloroaniline (2.55 g, 20 mmol), following **General procedure A**, 2-bromo-4-chloroaniline (3.81 g, 92%) was obtained as white needles, m.p. 64-65 °C (lit. data[8]: m.p. 64-66 °C).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40 (s, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 4.07 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 143.0 , 132.0 , 128.5 , 123.1 , 116.3 , 109.3 .

The NMR data are in agreement with previously reported.[8]

*2-bromo-3,4,6-trichloroaniline (**1f**)*



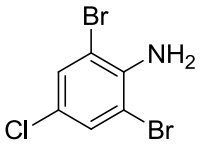
From 2,4,5-trichloroaniline (3.93 g, 20 mmol), following **General procedure A**, 2-bromo-3,4,6-trichloroaniline (5.11 g, 92%) was obtained as white needles, m.p. 93-94 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.37 (s, 1H), 4.67 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 141.6 , 132.2 , 128.8 , 121.0 , 117.2 , 110.1 .

HRMS (ESI) calc. for $C_6H_4BrCl_3N$ $[M+H]^+$: 273.8593, 275.8563, 277.8543; found: 273.8587, 275.8565, 277.8537.

*2,6-dibromo-4-chloroaniline (**1g**)*



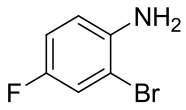
From 4-chloroaniline (1.28 g, 10 mmol) and 2 eq. (3.56 g, 20 mmol) of NBS, following **General procedure A**, 2,6-dibromo-4-chloroaniline (2.63 g, 92%) was obtained as colorless needles, m.p. 94-95 °C (lit. data[9]: m.p. 93-95 °C).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 (s, 2H), 4.49 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 141.1 , 131.4 , 122.7 , 108.5.

The NMR data are in agreement with previously reported.[9]

*2-bromo-4-fluoroaniline (**1j**)*



From 4-fluoroaniline (6.67 g, 60 mmol), following **General procedure A**, 2-bromo-4-fluoroaniline (11.05 g, 97%) was obtained as a red oil.

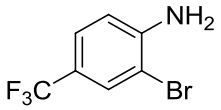
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.17 (dd, *J* = 8.1, 2.8 Hz, 1H), 6.86 (ddd, *J* = 8.8, 8.0, 2.8 Hz, 1H), 6.71 (dd, *J* = 8.8, 5.0 Hz, 1H), 3.90 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 155.5 (d, *J* = 240.0 Hz), 140.7 , 119.3 (d, *J* = 25.3 Hz), 116.0 (d, *J* = 7.8 Hz), 115.4 (d, *J* = 22.2 Hz), 108.8 (d, *J* = 9.8 Hz).

^{19}F NMR (188 MHz, Chloroform-*d*) δ -126.79 .

HRMS (ESI) calc. for C_6H_6BrFN $[M+H]^+$: 189.9668, 191.9647; found: 189.9664, 191.9643.

*2-bromo-4-(trifluoromethyl)aniline (**1k**)*



From 4-(trifluoromethyl)aniline (3.2 g, 20 mmol), following **General procedure A**, 2-bromo-4-(trifluoromethyl)aniline (4.1 g, 86%) was obtained as off-white needles, m.p. 34-35 °C.

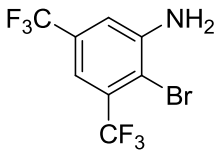
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.66 – 7.61 (m, 1H), 7.37 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.04 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 149.4 , 129.3 (q, *J* = 3.7 Hz), 125.5 (q, *J* = 3.4 Hz), 124.2 (q, *J* = 270.4 Hz), 116.8 (q, *J* = 32.5 Hz), 114.6 , 106.1 .

^{19}F NMR (188 MHz, Chloroform-*d*) δ -62.87 .

The ^{1}H and ^{13}C{^{1}H} NMR data are in agreement with previously reported.[10]

*2-bromo-3,5-bis(trifluoromethyl)aniline (**1l**)*



From 3,5-bis(trifluoromethyl)aniline (4.58 g, 20 mmol), following **General procedure A**, 2-bromo-3,5-bis(trifluoromethyl)aniline (3.6 g, 55%) was obtained as colorless needles, m.p. 36-37 °C.

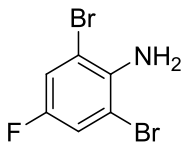
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 1.6 Hz, 1H), 7.14 (d, *J* = 1.8 Hz, 1H), 4.60 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 146.4 , 132.0 (q, *J* = 31.7 Hz), 130.7 (q, *J* = 33.5 Hz), 123.3 (q, *J* = 272.6 Hz), 122.6 (q, *J* = 273.8 Hz), 114.8 – 114.7 (m), 113.6 – 113.3 (m), 109.3 .

^{19}F NMR (188 MHz, Chloroform-*d*) δ -64.62 , -64.89 .

HRMS (ESI) calc. for $C_8H_5BrF_6N$ $[M+H]^+$: 307.9509, 309.9489; found: 307.9509, 309.9489.

*2,6-dibromo-4-fluoroaniline (**1n**)*



From 4-fluoroaniline (0.89 g, 8 mmol) and 2 eq. (2.85 g, 16 mmol) of NBS, following **General procedure A**, 2,6-dibromo-4-fluoroaniline (2.06 g, 95%) was obtained as off-white needles, m.p. 65-66 °C (lit. data[11]: m.p. 63-64 °C).

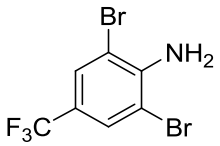
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.20 (s, 1H), 7.18 (s, 1H), 4.02 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 154.3 (d, *J* = 243.2 Hz), 139.1 (d, *J* = 2.3 Hz), 119.1 (d, *J* = 24.9 Hz), 108.1 (d, *J* = 10.4 Hz).

^{19}F NMR (188 MHz, Chloroform-d) δ -126.26 .

HRMS (APCI) calc. for $C_6H_5Br_2FN$ $[M+H]^+$: 267.8773, 269.8777, 271.8732; found: 267.8768, 269.8748, 271.8725.

*2,6-dibromo-4-(trifluoromethyl)aniline (**1o**)*



From 4-(trifluoromethyl)aniline (3.20 g, 20 mmol) and 2 eq. (7.10 g, 40 mmol) of NBS, following **General procedure A**, 2,6-dibromo-4-(trifluoromethyl)aniline (4.66 g, 73%) was obtained as a white microcrystalline solid, m.p. 38-39 °C.

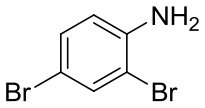
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 (s, 2H), 4.89 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 145.0 , 129.1 (q, *J* = 3.8 Hz), 123.2 (q, *J* = 271.4 Hz), 121.3 (q, *J* = 34.0 Hz), 107.8 .

^{19}F NMR (188 MHz, Chloroform-d) δ -62.96 .

The ^{1}H and ^{13}C{^{1}H} NMR data are in agreement with previously reported.[12]

*2,4-dibromoaniline (**1p**)*



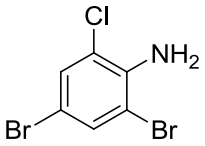
From 4-bromoaniline (5.16 g, 30 mmol), following **General procedure A**, 2,4-dibromoaniline (7.50 g, 99%) was obtained as a gray microcrystalline solid, m.p. 79-80 °C (lit. data[13]: m.p. 79-80 °C).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 2.2 Hz, 1H), 7.19 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 1H), 4.09 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 143.4 , 134.6 , 131.3 , 116.8 , 109.7 ,107.01.

The NMR data are in agreement with previously reported.[14]

*2,4-dibromo-6-chloroaniline (**1r**)*



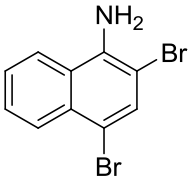
From 2-chloroaniline (2.55 g, 20 mmol) and 2 eq. (7.12 g, 40 mmol) of NBS, following **General procedure A**, 2,4-dibromo-6-chloroaniline (3.17 g, 55%) was obtained as white needles, m.p. 100-101 °C (lit. data[15]: m.p. 95 °C).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 2.0 Hz, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 4.44 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 140.5 , 133.3 , 131.0 , 119.8 , 109.4 , 108.5 .

The NMR data are in agreement with previously reported.[16]

2,4-dibromonaphthalen-1-amine (1s)



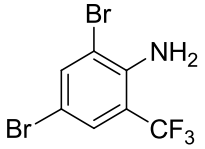
From naphthalen-1-amine (7.16 g, 50 mmol) and 2 eq. (17.8 g, 100 mmol) of NBS, following **General procedure A**, 2,4-dibromonaphthalen-1-amine (11.41 g, 75%) was obtained as off white needles, m.p. 114-115 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.3 Hz, 2H), 7.81 – 7.76 (m, 4H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 2H), 4.61 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 139.8 , 132.8 , 131.5 , 128.2 , 127.5 , 126.6 , 124.6 , 121.5 , 111.0 , 103.5 .

HRMS (ESI) calc. for $C_{10}H_8Br_2N$ $[M+H]^+$: 299.9023, 301.9003, 303.8983; found: 299.9019, 301.8997, 303.8975.

*2,4-dibromo-6-(trifluoromethyl)aniline (**1t**)*



From 2-(trifluoromethyl)aniline (2.42 g, 15 mmol) and 2 eq. (5.34 g, 30 mmol) of NBS, following **General procedure A**, 2,4-dibromo-6-(trifluoromethyl)aniline (4.10 g, 86%) was obtained as white needles, m.p. 40-41 °C.

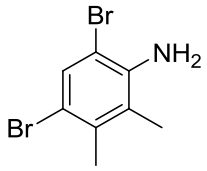
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 (s, 1H), 7.52 (s, 1H), 4.70 (s, 2H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 141.3 , 138.3 , 128.9 (q, *J* = 5.6 Hz), 123.6 (q, *J* = 273.2 Hz), 115.7 (q, *J* = 31.1 Hz), 111.6 , 108.3 .

^{19}F NMR (188 MHz, Chloroform-d) δ -65.21 .

HRMS (ESI) calc. for $C_7H_5Br_2F_3N$ $[M+H]^+$: 317.8741, 319.8720, 321.8700; found: 371.8735, 319.8714, 321.8693.

*4,6-dibromo-2,3-dimethylaniline (**1u**)*



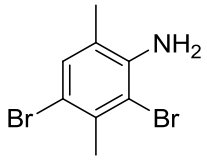
From 2,3-dimethylaniline (1.21 g, 10 mmol) and 2 eq. (3.56 g, 20 mmol) of NBS, following **General procedure A**, 2,4-dibromoaniline (1.96 g, 70%) was obtained as light brown needles, m.p. 62-63 °C (lit. data[6]: m.p. 56-57 °C).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 2.34 (s, 3H), 2.19 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 141.4 , 135.5 , 132.4 , 123.3 , 113.6 , 107.4 , 20.2 , 15.5 .

HRMS (ESI) calc. for $C_8H_{10}Br_2N$ $[M+H]^+$: 277.9180, 279.9160, found: 277.9179, 279.9159.

*2,4-dibromo-3,6-dimethylaniline (**1v**)*



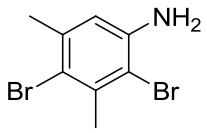
From 2,5-dimethylaniline (1.21 g, 10 mmol) and 2 eq. (3.56 g, 20 mmol) of NBS, following **General procedure A**, 2,4-dibromo-3,6-dimethylaniline (2.54 g, 91%) was obtained as yellowish needles, m.p. 60-61 °C (lit. data[6]: m.p. 64.5-66 °C).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 (s, 1H), 4.31 (s, 2H), 2.53 (s, 3H), 2.18 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 141.7 , 135.0 , 132.4 , 122.3 , 112.6 , 112.2 , 24.2 , 18.1 .

HRMS (ESI) calc. for $C_8H_{10}Br_2N$ $[M+H]^+$: 277.9180, 279.9160, 281.9139; found: 277.9175, 279.9156, 281.9134.

*2,4-dibromo-3,5-dimethylaniline (**1w**)*



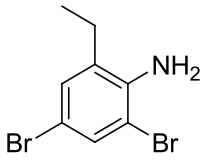
From 3,5-dimethylaniline (1.21 g, 30 mmol) and 2 eq. (3.56 g, 20 mmol) of NBS, following **General procedure A**, 2,4-dibromo-3,5-dimethylaniline (2.69 g, 96%) was obtained as yellowish needles, m.p. 86-87 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.58 (s, 1H), 4.06 (s, 2H), 2.58 (s, 3H), 2.30 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 143.2 , 137.8 , 137.6 , 115.6 , 114.9 , 109.6 , 25.0 , 24.1 .

The NMR data are in agreement with previously reported.[17]

*2,4-dibromo-6-ethylaniline (**1x**)*



From 2-ethylaniline (3.64 g, 30 mmol) and 2 eq. (10.68 g, 60 mmol) of NBS, following **General procedure A**, 2,4-dibromo-6-ethylaniline (8.27 g, 98%) was obtained as a dark red oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 2.2 Hz, 1H), 7.12 (d, *J* = 2.2 Hz, 1H), 4.17 (s, 2H), 2.51 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 140.9 , 132.1 , 130.8 , 130.2 , 110.1 , 109.8 , 24.9 , 12.6 .

The NMR data are in agreement with previously reported.[6]

General procedure B: diazotization-azidation in water[18]

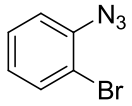
To a solution of concentrated sulfuric acid (60 mmol) in water (11 ml) 15 mmol of corresponding aniline was added. The reaction mixture was heated until complete dissolution of aniline (in some cases additional amount of water was required) and cooled to 0 °C. A solution of sodium nitrite (17.25 mmol) in water (11 ml) was then added dropwise to the reaction mixture while maintaining the temperature below 5 °C. The reaction mixture was stirred for 1h and then 100 ml petroleum ether was added. A solution of sodium azide (16.5 mmol) in water (11 ml) was then added dropwise to the reaction mixture while maintaining the temperature below 10°C. The reaction mixture was warmed to room temperature and stirred for 4h. The organic layer was separated and the aqueous layer was extracted with PE (3x60 ml). The combined organic phase

was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The product was purified by column chromatography (eluent – PE).

General procedure C: diazotization-azidation in trifluoroacetic acid[19]

A solution of aniline (15 mmol) in trifluoroacetic acid (19.5 ml) was cooled to -10 °C followed by addition of solid sodium nitrite (15 mmol) in small portions. The reaction mixture was stirred for 1h while maintaining the temperature below -5 °C. To the solution solid sodium azide (15 mmol) was added in small portions while maintaining the temperature below -5 °C. The reaction mixture was warmed to room temperature, stirred for 1.5h and poured in water (50 ml). The mixture was extracted with dichloromethane (2x50 ml) and the organic layer was washed with 10% aqueous solution of KOH (2x100 ml). The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The product was purified by column chromatography (eluent – PE).

*1-azido-2-bromobenzene (**2a**)*



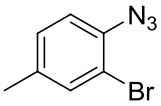
From 2-Bromoaniline (2.58 g, 15 mmol), sodium nitrite (1.19 g, 17.25 mmol) and sodium azide (1.07 g, 16.5 mmol), following **General procedure B,** 1-azido-2-bromobenzene (2.55 g, 86%) was obtained as a yellowish oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.18 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.01 (td, *J* = 7.7, 1.4 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 138.8 , 134.0 , 128.7 , 126.1 , 119.6 , 113.9 .

The NMR data are in agreement with previously reported.[20]

*1-azido-2-bromo-4-methylbenzene (**2b-Br**)*



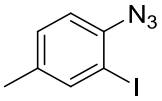
From 2-bromo-4-methylaniline (12.00 g, 64.5 mmol), sodium nitrite (5.10 g, 74.2 mmol) and sodium azide (4.55 g, 70 mmol), following **General procedure B,** 1-azido-2-bromo-4-methylbenzene (11.77 g, 86%) was obtained as a yellowish oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.37 (s, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 2.31 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 136.3 , 135.9 , 134.3 , 129.4 , 119.3 , 113.6 , 20.6 .

The NMR data are in agreement with previously reported.[21]

*1-azido-2-iodo-4-methylbenzene (**2b-I**)*



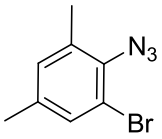
From 2-iodo-4-methylaniline (8.25 g, 35.4 mmol), sodium nitrite (2.80 g, 40.7 mmol) and sodium azide (2.53 g, 38.9 mmol), following **General procedure B,** 1-iodo-2-bromo-4-methylbenzene (8.43 g, 92%) was obtained as a yellowish oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 (s, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 2.29 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 140.4 , 139.0 , 136.5 , 130.4 , 118.2 , 87.7 , 20.5 .

The NMR data are in agreement with previously reported.[22]

*2-azido-1-bromo-3,5-dimethylbenzene (**2c**)*



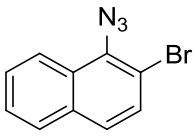
From 2-bromo-4,6-dimethylaniline (12.00 g, 60 mmol), sodium nitrite (4.76 g, 69 mmol) and sodium azide (4.29 g, 66 mmol), following **General procedure B,** 2-azido-1-bromo-3,5-dimethylbenzene (12.59 g, 91%) was obtained as a red-yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.22 (s, 1H), 6.93 (s, 1H), 2.34 (s, 3H), 2.26 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 137.1 , 134.0 , 133.9 , 131.8 , 131.1 , 118.0 , 18.7 .

The NMR data are in agreement with previously reported.[21]

*1-azido-2-bromonaphthalene (**2d**)*



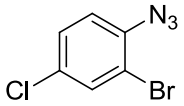
From 2-bromonaphthalen-1-amine (3.79 g, 17 mmol), sodium nitrite (1.17 g, 17 mmol) and sodium azide (1.10 g, 17 mmol), following **General procedure C,** 1-azido-2-bromonaphthalene (0.90 g, 21%) was obtained as a yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.62 – 7.50 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 133.8 , 133.2 , 130.5 , 129.3 , 128.1 , 127.5 , 127.2 , 127.1 , 123.2 , 115.3 .

HRMS (APCI) calc. for $C_{10}H_7BrN$ $[M+H-N_2]^+$: 219.9762, 221.9741; found: 219.9751, 221.9907.

*1-azido-2-bromo-4-chlorobenzene (**2e**)*



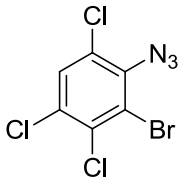
From 2-bromo-4-chloroaniline (1.55 g, 7.5 mmol), sodium nitrite (0.52 g, 7.5 mmol) and sodium azide (0.49 g, 7.5 mmol), following **General procedure C,** 1-azido-2-bromo-4-chlorobenzene (1.2 g, 69%) was obtained as off white needles, m.p. 46-47 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 (s, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 137.6 , 133.6 , 130.7 , 128.8 , 120.2 , 114.4 .

The NMR data are in agreement with previously reported.[23]

*2-azido-3-bromo-1,4,5-trichlorobenzene (**2f**)*



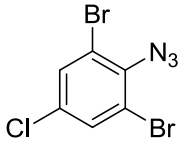
From 2-bromo-3,4,6-trichloroaniline (2.30 g, 8.4 mmol), sodium nitrite (0.57 g, 8.4 mmol) and sodium azide (0.54 g, 8.4 mmol), following **General procedure C,** 2-azido-3-bromo-1,4,5-trichlorobenzene (2.37 g, 94%) was obtained as white needles, m.p. 77-78 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.52 (s, 1H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-*d*) δ 136.0 , 133.7 , 130.7 , 130.1 , 128.1 , 120.6 .

HRMS (APCI) calc. for C_6HBrCl_3N $[M-N_2]^-$: 272.8337, 274.8308, 274.8308, 276.8279; found: 272.8331, 273.8416, 274.8293, 276.8250.

*2-azido-1,3-dibromo-5-chlorobenzene (**2g**)*



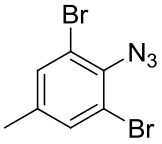
From 2,6-dibromo-4-chloroaniline (2.48 g, 8.7 mmol), sodium nitrite (0.60 g, 8.7 mmol) and sodium azide (0.57 g, 8.7 mmol), following **General procedure C,** 2-azido-1,3-dibromo-5-chlorobenzene (2.47 g, 91%) was obtained as yellowish needles, m.p. 62-63 °C.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.54 (s, 2H).

^{13}C{1H} NMR (151 MHz, Chloroform-*d*) δ 135.8 , 132.7 , 132.3 , 119.0 .

HRMS (APCI) calc. for $C_6H_2Br_2ClN$ $[M-N_2]^-$: 280.8242, 282.8222, 284.8202; found: 280.8253, 282.8229, 284.8195.

*2-azido-1,3-dibromo-5-methylbenzene (**2h**)*



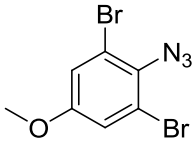
From 2,6-dibromo-4-methylaniline (10.00 g, 37.7 mmol), sodium nitrite (2.99 g, 43.4 mmol) and sodium azide (2.7 g, 41.5 mmol), following **General procedure B,** 2-azido-1,3-dibromo-5-methylbenzene (10.25 g, 93%) was obtained as yellowish needles, m.p. 35-37 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 (s, 2H), 2.29 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 138.6 , 134.1 , 133.5 , 118.5 , 20.4 .

The NMR data are in agreement with previously reported.[24]

*2-azido-1,3-dibromo-5-methoxybenzene (**2i**)*



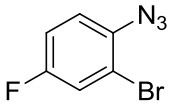
From 2,6-dibromo-4-methoxyaniline (1.69 g, 6 mmol), sodium nitrite (0.48 g, 6.9 mmol) and sodium azide (0.43 g, 6.6 mmol), following **General procedure B**, 2-azido-1,3-dibromo-5-methoxybenzene (1.76 g, 96%) was obtained as yellow needles, m.p. 57-58 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.08 (s, 2H), 3.78 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 158.0 , 130.0 , 119.3 , 118.6 , 56.1 .

HRMS (APCI) calc. for $C_7H_6Br_2ON$ $[M+H]^+$: 277.8816, 279.8796, 281.8775; found: 277.8812, 279.8799, 281.8796.

*1-azido-2-bromo-4-fluorobenzene (**2j**)*



From 2-bromo-4-fluoroaniline (9.50 g, 50 mmol), sodium nitrite (3.96 g, 57.5 mmol) and sodium azide (3.58 g, 55 mmol), following **General procedure B,** 1-azido-2-bromo-4-fluorobenzene (10.56 g, 98%) was obtained as a yellow oil.

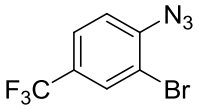
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 (dd, *J* = 7.8, 2.8 Hz, 1H), 7.13 (dd, *J* = 8.8, 4.9 Hz, 1H), 7.08 (ddd, *J* = 8.9, 7.6, 2.8 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 159.4 (d, *J* = 248.9 Hz), 135.1 (d, *J* = 2.9 Hz), 121.2 (d, *J* = 25.5 Hz), 120.2 (d, *J* = 8.7 Hz), 115.8 (d, *J* = 23.1 Hz), 114.3 (d, *J* = 9.8 Hz).

^{19}F NMR (188 MHz, Chloroform-*d*) δ -117.21 .

The ^{1}H and ^{13}C NMR data are in agreement with previously reported.[25]

*1-azido-2-bromo-4-(trifluoromethyl)benzene (**2k**)*



From 2-bromo-4-(trifluoromethyl)aniline (1.00 g, 4.2 mmol), sodium nitrite (0.29 g, 4.2 mmol) and sodium azide (0.27 g, 4.2 mmol), following **General procedure C,** 1-azido-2-bromo-4-(trifluoromethyl)benzene (0.94 g, 85%) was obtained as an orange oil.

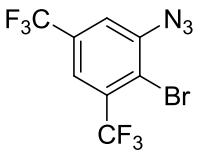
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.27 (s, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 142.6 , 131.2 (q, *J* = 3.5 Hz), 128.2 (q, *J* = 33.5 Hz), 125.8 (q, *J* = 3.1 Hz), 123.1 (q, *J* = 272.6 Hz), 119.5 , 114.1 .

^{19}F NMR (188 MHz, Chloroform-*d*) δ -63.87 .

HRMS (APCI) calc. for $C_7H_3BrF_3N$ $[M\text{-}N_2]^-$: 236.9401, 237.9435, 238.9380; found: 236.9410, 237.9455, 238.9387.

*1-azido-2-bromo-3,5-bis(trifluoromethyl)benzene (**2l**)*



From 2-bromo-3,5-bis(trifluoromethyl)aniline (2.80 g, 9 mmol), sodium nitrite (0.62 g, 9 mmol) and sodium azide (0.59 g, 9 mmol), following **General procedure C,** 1-azido-2-bromo-3,5-bis(trifluoromethyl)benzene (2.69 g, 89%) was obtained as yellowish needles, m.p. 52-53 °C.

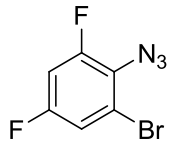
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.70 (s, 1H), 7.55 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-d) δ 142.6 , 133.7 (q, *J* = 31.9 Hz), 131.3 (q, *J* = 34.4 Hz), 122.8 (q, *J* = 273.2 Hz), 122.1 (q, *J* = 274.5 Hz), 120.7 – 120.3 (m), 118.9 (d, *J* = 3.2 Hz), 116.5 .

^{19}F NMR (188 MHz, Chloroform-d) δ -64.67, -64.70.

HRMS (APCI) calc. for $C_8H_2BrF_6N$ $[M\text{-}N_2]^-$: 304.9275, 306.9254, 307.9287; found: 304.9284, 306.9234, 307.9280.

*2-azido-1-bromo-3,5-difluorobenzene (**2m**)*



From 2-bromo-4,6-difluoroaniline (2.08 g, 10 mmol), sodium nitrite (0.69 g, 10 mmol) and sodium azide (0.65 g, 10 mmol), following **General procedure C,** 2-azido-1-bromo-3,5-difluorobenzene (2.08 g, 88%) was obtained as a yellow oil.

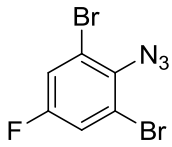
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 6.4 Hz, 1H), 6.89 (t, *J* = 9.4 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 158.9 (dd, *J* = 250.9, 12.7 Hz), 156.8 (dd, *J* = 252.6, 12.7 Hz), 124.3 (dd, *J* = 13.3, 4.5 Hz), 116.7 (dd, *J* = 25.3, 3.7 Hz), 115.9 (dd, *J* = 12.1, 3.2 Hz), 104.6 (dd, *J* = 26.6, 24.0 Hz).

^{19}F NMR (188 MHz, Chloroform-*d*) δ -114.47 , -120.08 .

HRMS (APCI) calc. for $C_6H_2BrF_2N$ $[M-N_2]^-$: 204.9338, 206.9318; found: 204.9346, 206.9260.

*2-azido-1,3-dibromo-5-fluorobenzene (**2n**)*



From 2,6-dibromo-4-fluoroaniline (2.69 g, 10 mmol), sodium nitrite (0.69 g, 10 mmol) and sodium azide (0.65 g, 10 mmol), following **General procedure C,** 2-azido-1,3-dibromo-5-fluorobenzene (2.48 g, 84%) was obtained as white needles, m.p. 39-40 °C.

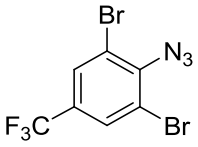
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (s, 1H), 7.31 (s, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 158.6 (d, *J* = 253.7 Hz), 133.7 (d, *J* = 3.9 Hz), 120.4 (d, *J* = 25.2 Hz), 119.2 (d, *J* = 10.5 Hz).

^{19}F NMR (188 MHz, Chloroform-*d*) δ -114.34 .

HRMS (APCI) calc. for $C_6HBr_2FN_3$ $[M-H]^-$: 291.8521, 293.8501, 295.8480; found: 291.8533, 293.8514, 295.8490.

*2-azido-1,3-dibromo-5-(trifluoromethyl)benzene (**2o**)*



From 2,6-dibromo-4-(trifluoromethyl)aniline (4.00 g, 12.5 mmol), sodium nitrite (0.87 g, 12.5 mmol) and sodium azide (0.82 g, 12.5 mmol), following **General procedure C,** 2-azido-1,3-dibromo-5-(trifluoromethyl)benzene (4.20 g, 98%) was obtained as a yellow oil.

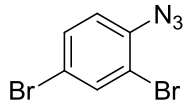
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 140.1 , 130.2 (q, *J* = 3.6 Hz), 129.8 (q, *J* = 34.0 Hz), 122.2 (q, *J* = 273.1 Hz), 118.8 .

^{19}F NMR (188 MHz, Chloroform-*d*) δ -64.15 .

HRMS (APCI) calc. for $C_7H_2Br_2F_3N$ $[M-N_2]^-$: 314.8506, 316.8486, 318.8465; found: 314.8513, 316.8495, 318.8472.

*1-azido-2,4-dibromobenzene (**2p**)*



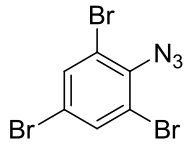
From 2,4-dibromoaniline (7.00 g, 27.9 mmol), sodium nitrite (2.21 g, 32.1 mmol) and sodium azide (2.00 g, 30.7 mmol), following **General procedure B,** 1-azido-2,4-dibromobenzene (7.18 g, 93%) was obtained as yellowish needles, m.p. 61-62°C (lit. data[26]: m.p. 61-62 °C).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 2.0 Hz, 1H), 7.46 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 138.2 , 136.3 , 131.7 , 120.6 , 117.9 , 114.7 .

The NMR data are in agreement with previously reported.[23]

*2-azido-1,3,5-tribromobenzene (**2q**)*



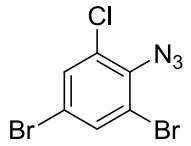
From 2,4,6-tribromoaniline (6.60 g, 20 mmol), sodium nitrite (1.38 g, 20 mmol) and sodium azide (1.3 g, 20 mmol), following **General procedure C,** 2-azido-1,3,5-tribromobenzene (6.14 g, 86%) was obtained as a pink solid, m.p. 70-71 °C (lit. data[27]: m.p. 70.6-71.8 °C).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.67 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 136.2 , 135.4 , 119.4 , 119.3 .

The NMR data are in agreement with previously reported.[27]

*2-azido-1,5-dibromo-3-chlorobenzene (**2r**)*



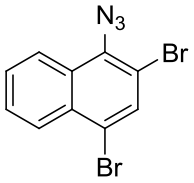
From 2,4-dibromo-6-chloroaniline (3.00 g, 10.5 mmol), sodium nitrite (0.73 g, 10.5 mmol) and sodium azide (0.68 g, 10.5 mmol), following **General procedure C,** 2-azido-1,5-dibromo-3-chlorobenzene (2.92 g, 89%) was obtained as pink needles, m.p. 66-67 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 2.2 Hz, 1H), 7.49 (d, *J* = 2.2 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 134.9 , 134.7 , 132.5 , 130.6 , 118.9 , 118.8 .

HRMS (APCI) calc. for $C_6H_2Br_2ClN$ $[M\text{-}N_2]^-$: 282.8222, 284.8193; found: 282.8229, 284.8197.

*1-azido-2,4-dibromonaphthalene (**2s**)*



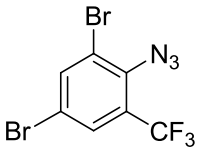
From 2,4-dibromonaphthalen-1-amine (3.50 g, 11.6 mmol), sodium nitrite (0.80 g, 11.6 mmol) and sodium azide (0.76 g, 11.6 mmol), following **General procedure C,** 1-azido-2,4-dibromonaphthalene (2.90 g, 76%) was obtained as off white needles, m.p. 71-72 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 8.3 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.89 (s, 1H), 7.66 – 7.59 (m, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 133.8 , 133.5 , 131.7 , 129.9 , 128.4 , 128.2 , 127.6 , 123.8 , 120.5 , 114.4 .

HRMS (APCI) calc. for $C_{10}H_6Br_2N$ $[M+H\text{-}N_2]^+$: 297.8867, 299.8847, 301.8826; found: 297.8862, 299.8845, 301.8828.

*2-azido-1,5-dibromo-3-(trifluoromethyl)benzene (**2t**)*



From 2,4-dibromo-6-(trifluoromethyl)aniline (3.53 g, 11.1 mmol), sodium nitrite (0.77 g, 11.1 mmol) and sodium azide (0.72 g, 11.1 mmol), following **General procedure C,** 2-azido-1,5-dibromo-3-(trifluoromethyl)benzene (3.26 g, 87%) was obtained as white needles, m.p. 38-39 °C.

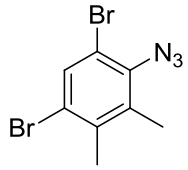
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 1.9 Hz, 1H), 7.74 (d, *J* = 1.8 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 139.7 , 135.7 , 129.6 (q, *J* = 5.1 Hz), 127.1 (q, *J* = 32.2 Hz), 121.8 (q, J = 274.3 Hz), 121.3 , 119.3 .

^{19}F NMR (188 MHz, Chloroform-*d*) δ -63.37 .

HRMS (APCI) calc. for $C_7H_2Br_2F_3N$ $[M-N_2]^-$: 314.7853, 316.7832, 318.7812; found: 314.7859, 316.7837, 318.7809.

*2-azido-1,5-dibromo-3,4-dimethylbenzene (**2u**)*



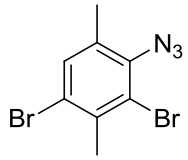
From 4,6-dibromo-2,3-dimethylaniline (1.84 g, 6.6 mmol), sodium nitrite (0.46 g, 6.6 mmol) and sodium azide (0.43 g, 6.6 mmol), following **General procedure C,** 2-azido-1,5-dibromo-3,4-dimethylbenzene (1.73 g, 87%) was obtained as a white solid, m.p. 61-62 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (s, 1H), 2.37 (s, 3H), 2.34 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 137.2 , 136.1 , 134.3 , 133.9 , 122.7 , 116.0 , 20.2 , 16.8 .

HRMS (APCI) calc. for $C_8H_7B_{r2}N$ $[M-N_2]^-$: 274.8945; found: 274.8954.

*2-azido-3,5-dibromo-1,4-dimethylbenzene (**2v**)*



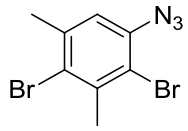
From 2,4-dibromo-3,6-dimethylaniline (2.45 g, 8.8 mmol), sodium nitrite (0.60 g, 8.8 mmol) and sodium azide (0.57 g, 8.8 mmol), following **General procedure C,** 2-azido-3,5-dibromo-1,4-dimethylbenzene (2.22 g, 83%) was obtained as a white solid, m.p. 64-65 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 (s, 1H), 2.56 (s, 3H), 2.35 (s, 3H).

13C{^{1}H} NMR (151 MHz, Chloroform-d) δ 136.7 , 136.7 , 133.5 , 132.7 , 121.8 , 121.7 , 24.2 , 18.4 .

HRMS (APCI) calc. for $C_8H_7Br_2N$ $[M-N_2]^-$: 274.8945, 276.8925, 278.8904; found: 274.8955, 276.8933, 278.8900.

*1-azido-2,4-dibromo-3,5-dimethylbenzene (**2w**)*



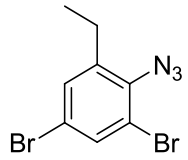
From 2,4-dibromo-3,5-dimethylaniline (2.56 g, 9.2 mmol), sodium nitrite (0.63 g, 9.2 mmol) and sodium azide (0.60 g, 9.2 mmol), following **General procedure C,** 1-azido-2,4-dibromo-3,5-dimethylbenzene (1.97 g, 70%) was obtained as a white solid, m.p. 94-95 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.92 (s, 1H), 2.62 (s, 3H), 2.41 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 139.7 , 138.7 , 137.7 , 123.5 , 118.2 , 113.8 , 25.1 , 24.4 .

HRMS (APCI) calc. for $C_8H_7Br_2N$ [M-N_2]$^-$: 274.8945, 276.8925, 278.8904; found: 274.8950, 276.8928, 278.8898.

*2-azido-1,5-dibromo-3-ethylbenzene (**2x**)*



From 2,4-dibromo-6-ethylaniline (4.00 g, 14.3 mmol), sodium nitrite (1.14 g, 16.5 mmol) and sodium azide (1.03 g, 15.8 mmol), following **General procedure B,** 2-azido-1,5-dibromo-3-ethylbenzene (4.01 g, 91%) was obtained as red oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 (s, 1H), 7.28 (s, 1H), 2.70 (q, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 142.1 , 135.7 , 133.9 , 131.8 , 119.7 , 119.6 , 26.0 , 14.7 .

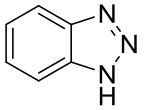
HRMS (APCI) calc. for $C_8H_7Br_2N$ [M-N_2]$^-$: 274.8945, 276.8925, 278.8904; found: 274.8957, 276.8936, 278.8910.

General procedure D: Li-mediated cyclization of 2-azidoaryl bromides

To a cooled (-85 °C) solution of 2-azidoaryl bromide (5 mmol) in anhydrous THF (20 ml) *n*-BuLi (2.5 M in hexanes, 5 mmol) was added dropwise. During the addition the temperature was maintained below -75 °C. Then the reaction mixture was stirred for two hours at -85 – -75 °C and overnight at RT. The reaction was quenched with 1.5 M aqueous HCl (1 ml) and concentrated under reduced pressure. The residue was diluted with water (40 ml) and extracted with EtOAc (4×30 ml). Combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by column

chromatography (elution with DCM to remove byproducts followed by elution with EtOAc to obtain pure product), recrystallization or sublimation.

*1H-benzo[d][1,2,3]triazole (**3a**)*



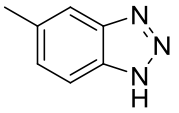
From 1-azido-2-bromobenzene (0.99 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 1H-benzo[d][1,2,3]triazole (0.39 g, 66%) was obtained as a white solid, m.p. 98-99 °C (lit. data[28]: m.p. 99-101 °C).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 13.15 (s, 1H), 7.95 (dd, *J* = 6.3, 3.1 Hz, 2H), 7.42 (dd, *J* = 6.4, 3.0 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 138.9 , 126.3 , 115.1 .

The NMR data are in agreement with previously reported.[29]

*5-methyl-1H-benzo[d][1,2,3]triazole (**3b**)*



From 1-azido-2-bromo-4-methylbenzene (1.06 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 5-methyl-1H-benzo[d][1,2,3]triazole (0.58 g, 87%) was obtained as an off white solid, m.p. 79-80 °C (lit. data[30]: m.p. 80-83 °C).

From 1-azido-2-iodo-4-methylbenzene (1.06 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 5-methyl-1H-benzo[d][1,2,3]triazole (0.55 g, 82%) was obtained as an off white solid, m.p. 79-80 °C (lit. data[30]: m.p. 80-83 °C).

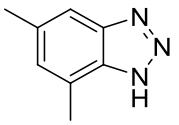
^{1}H NMR (600 MHz, Chloroform-*d*) δ 13.42 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.63 (s, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 2.46 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 138.8 , 138.2 , 137.0 , 128.1 , 115.4 , 113.1 , 21.8 .

The NMR data are in agreement with previously reported.[31]

HRMS (ESI) calc. for $C_7H_8N_3$ $[M+H]^+$: 134.0718; found: 134.0715 .

*5,7-dimethyl-1H-benzo[d][1,2,3]triazole (**3c**)*



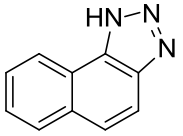
From 2-azido-1-bromo-3,5-dimethylbenzene (1.13 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 5,7-dimethyl-1H-benzo[d][1,2,3]triazole (0.73 g, 99%) was obtained as white needles, m.p. 160 °C (lit. data[4] : m.p. 158 °C).

^{1}H NMR (600 MHz, 151 MHz, DMSO-d_6) δ 15.48 (s, 1H), 7.40 (s, 1H), 7.00 (s, 1H), 2.59 (s, 3H), 2.41 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, 151 MHz, DMSO-d_6 + NaOH/D_2O) δ 145.6 , 144.1 , 131.7 , 126.7 , 124.4 , 113.4 , 22.3 , 18.5 .

HRMS (ESI) calc. for $C_8H_{10}N_3$ $[M+H]^+$: 148.0875; found: 148.0873.

*1H-naphtho[1,2-d][1,2,3]triazole (**3d**)*



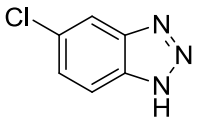
From 1-azido-2-bromonaphthalene (1.24 g, 5 mmol), following **General procedure D** with subsequent sublimation**,** 1H-naphtho[1,2-d][1,2,3]triazole (0.71 g, 84%) was obtained as a white solid.

^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 8.49 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 8.7 Hz, 1H), 7.51 (t, J = 7.3 Hz, 1H), 7.46 – 7.34 (m, 2H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 142.5 , 141.2 , 130.8 , 128.8 , 126.4 , 126.0 , 124.8 , 122.9 , 122.9 , 118.0 .

HRMS (ESI) calc. for $C_{10}H_8N_3$ $[M+H]^+$: 170.0718; found: 170.0715.

*5-chloro-1H-benzo[d][1,2,3]triazole (**3e**)*



From 1-azido-2-bromo-4-chlorobenzene (1.16 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 5-chloro-1H-benzo[d][1,2,3]triazole (0.62 g, 81%) was obtained as an off white solid, m.p. 155-156°C (lit. data[4]: m.p. 157 °C).

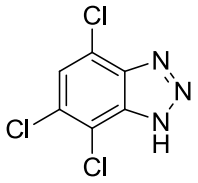
^{1}H NMR (600 MHz, DMSO-d_6+ NaOH/D_2O) δ 7.69 – 7.64 (m, 2H), 6.95 (d, J = 10.2 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6+ NaOH/D_2O) δ 145.9 , 143.9 , 125.3 , 121.1 , 117.9 , 115.4 .

The NMR data are in agreement with previously reported.[31]

HRMS (ESI) calc. for $C_6H_5C_3N_3$ $[M+H]^+$: 154.0172, 156.0142; found: 154.0169, 156.0138.

*4,6,7-trichloro-1H-benzo[d][1,2,3]triazole (**3f**)*



From 2-azido-3-bromo-1,4,5-trichlorobenzene (1.5 g, 5 mmol), following **General procedure D** with subsequent column chromatography, 4,6,7-trichloro-1H-benzo[d][1,2,3]triazole (0.58 g, 53%) was obtained as a white solid.

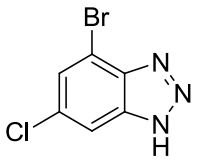
^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 7.23 (s, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 144.3 , 142.6 , 123.2 , 121.3 , 120.4 , 118.1 .

HRMS (ESI) calc. for $C_6H_3Cl_3N_3$ $[M+H]^+$: 221.9393, 223.9363, 225.9333; found: 221.9389, 223.9360, 225.9330.

IR (υ/cm^{-1}): 3105 (m), 3068 (m), 2997 (s), 2947 (s), 2881 (s), 2777 (vs), 2752 (vs), 2682 (vs), 2638 (s), 2569 (s), 2499 (s), 2430 (m), 1705 (w), 1620 (w), 1601 (w), 1577 (w), 1491 (m), 1419 (s), 1375 (s), 1288 (w), 1273 (m), 1255 (m), 1230 (s), 1219 (s), 1201 (s), 1167 (w), 1146 (s), 1082 (s), 1026 (m), 1001 (m), 949 (s), 866 (m), 845 (m), 804 (vs), 669 (w), 644 (m), 606 (w), 577 (s).

*4-bromo-6-chloro-1H-benzo[d][1,2,3]triazole (**3g**)*



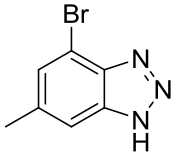
From 2-azido-1,3-dibromo-5-chlorobenzene (1.56 g, 5 mmol), following **General procedure D** with subsequent recrystallization from DCM**,** 4-bromo-6-chloro-1H-benzo[d][1,2,3]triazole (0.9 g, 78%) was obtained as a pink solid.

^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 7.69 (d, J = 1.6 Hz, 1H), 7.19 (d, J = 1.6 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 145.8 , 143.5 , 125.6 , 123.2 , 115.3 , 110.1 .

HRMS (ESI) calc. for $C_6H_4BrClN_3$ $[M+H]^+$: 231.9277, 233.9257, 235.9227; found: 231.9273, 233.9250, 235.9221.

*4-bromo-6-methyl-1H-benzo[d][1,2,3]triazole (**3h**)*



From 2-azido-1,3-dibromo-5-methylbenzene (1.45 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 4-bromo-6-methyl-1H-benzo[d][1,2,3]triazole (0.89 g, 84%) was obtained as a white solid.

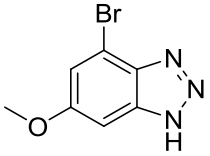
^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 7.41 (s, 1H), 7.03 (s, 1H), 2.35 (s, 3H).

^{13}C{^{1}H} NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 146.3 , 143.0 , 131.8 , 125.7 , 115.2 , 109.2 , 21.5 .

HRMS (ESI) calc. for $C_7H_7BrN_3$ $[M+H]^+$: 211.9823, 213.9803; found: 211.9819, 213.9799.

IR (υ/cm^{-1}): 3062 (m), 3032 (m), 2962 (s), 2920 (s), 2883 (s), 2852 (s), 2738 (s), 2702 (s), 2611 (s), 2517 (s), 2428 (m), 1716 (w), 1620 (m), 1581 (m), 1516 (m), 1450 (m), 1419 (m), 1400 (m), 1363 (m), 1300 (m), 1261 (s), 1244 (m), 1194 (s), 1147 (m), 1095 (s), 1030 (vs), 997 (s), 982 (m), 895 (m), 858 (s), 845 (s), 818 (vs), 804 (s), 762 (w), 623 (w), 590 (m).

4-bromo-6-methoxy-1H-benzo[d][1,2,3]triazole (3i)



From 2-azido-1,3-dibromo-5-methoxybenzene (1.53 g, 5 mmol), following **General procedure D** with subsequent recrystallization from methanol**,** 4-bromo-6-methoxy-1H-benzo[d][1,2,3]triazole (0.82 g, 72%) was obtained as an off white solid.

^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 7.1 (d, J = 2.0 Hz, 1H), 6.8 (d, J = 2.1 Hz, 1H), 3.7 (s, 3H).

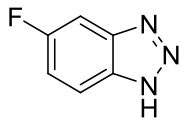
^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 155.6 , 145.6 , 140.4 , 115.5 , 109.6 , 96.1 , 56.2 .

HRMS (ESI) calc. for $C_7H_7BrON_3$ $[M+H]^+$: 227.9773, 229.9752; found: 227.9766, 229.9746.

IR (υ/cm^{-1}): 3064 (m), 3049 (m), 2997 (m), 2956 (s), 2927 (s), 2819 (s), 2765 (s), 1736 (w), 1657 (w), 1624 (s), 1587 (m), 1510 (s), 1464 (w), 1435 (m), 1369 (m), 1311 (s), 1244 (vs),

1190 (s), 1165 (vs), 1070 (w), 1032 (m), 1007 (w), 982 (s), 868 (m), 829 (s), 760 (w), 658 (w), 631 (w), 557 (w).

*5-fluoro-1H-benzo[d][1,2,3]triazole (**3j**)*



From 1-azido-2-bromo-4-fluorobenzene (1.08 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 5-fluoro-1H-benzo[d][1,2,3]triazole (0.63 g, 92%) was obtained as an off white solid, m.p. 147-148 °C (lit. data[31] : m.p. 148-149 °C).

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.99 – 7.91 (m, 1H), 7.64 (d, *J* = 6.9 Hz, 1H), 7.32 – 7.22 (m, 2H).

^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 7.67 (dd, *J* = 8.8, 5.1 Hz, 1H), 7.34 (dd, *J* = 10.2, 2.6 Hz, 1H), 6.85 (ddd, *J* = 9.3, 8.9, 2.4 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 160.4 (d, *J* = 242.0 Hz), 137.5 , 117.7 (d, *J* = 6.3 Hz), 114.8 (d, *J* = 27.8 Hz), 99.1 (d, *J* = 25.0 Hz).

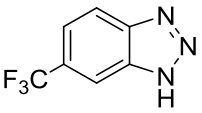
^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 158.6 (d, *J* = 233.4 Hz), 144.8 (d, *J* = 12.7 Hz), 142.4 , 117.6 (d, *J* = 10.9 Hz), 110.4 (d, *J* = 27.4 Hz), 100.2 (d, *J* = 22.8 Hz).

^{19}F NMR (188 MHz, DMSO-d_6 + NaOH/D_2O) δ -119.07 .

HRMS (ESI) calc. for $C_6H_5FN_3$ $[M+H]^+$: 138.0468; found: 138.0465.

IR (υ/cm^{-1}): 3161 (s), 3130 (vs), 3105 (vs), 3074 (vs), 3005 (s), 2910 (s), 2808 (s), 1631 (m), 1599 (m), 1514 (m), 1452 (m), 1300 (m), 1263 (m), 1213 (vs), 1155 (s), 1142 (m), 1072 (m), 1005 (m), 958 (m), 856 (m), 827 (m), 806 (vs), 638 (w), 613 (m).

*6-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (**3k**)*



From 1-azido-2-bromo-4-(trifluoromethyl)benzene (1.33 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 6-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (0.79 g, 84%) was obtained as a white solid, m.p. 114-115 °C (lit. data[30] : m.p. 107-109 °C).

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.36 (s, 1H), 8.08 (d, *J* = 8.6 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 140.2 – 138.9 (m), 139.3 – 138.0 (m), 125.5 (q, *J* = 32.5 Hz), 124.1 (q, J = 272.2 Hz), 121.8 , 116.2 – 114.8 (m), 114.8 – 113.5 (m).

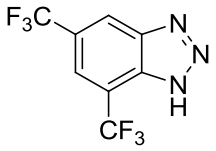
^{19}F NMR (188 MHz, DMSO-d_6 + NaOH/D_2O) δ -55.49 .

The ^{1}H and ^{13}C NMR data are in agreement with previously reported.[30]

HRMS (ESI) calc. for $C_7H_5F_3N_3$ $[M+H]^+$: 188.0436; found: 188.0433.

IR (υ/cm^{-1}): 3089 (m), 3047 (m), 3014 (m), 2966 (m), 2918 (m), 2848 (m), 2804 (m), 2775 (m), 2708 (w), 1635 (w), 1599 (vw), 1508 (vw), 1469 (w), 1415 (w), 1400 (w), 1385 (w), 1331 (vs), 1271 (w), 1236 (s), 1200 (s), 1157 (m), 1136 (s), 1115 (s), 1051 (m), 1012 (m), 995 (m), 933 (m), 889 (m), 822 (m), 806 (m), 756 (w), 687 (w), 675 (w), 646 (w), 575 (w).

*5,7-bis(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (**3l**)*



From 1-azido-2-bromo-3,5-bis(trifluoromethyl)benzene (1.67 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 5,7-bis(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (1.04 g, 82%) was obtained as an off white solid.

^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 8.36 (s, 1H), 7.54 (s, 1H).

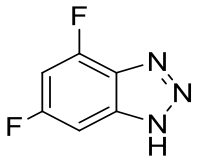
^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 146.0 , 142.3 , 125.4 (q, J = 271.5 Hz), 124.5 (q, J = 272.1 Hz), 120.7 (q, J = 31.9 Hz), 119.2 (q, J = 4.6 Hz), 117.7 (q, J = 33.0 Hz), 115.4 – 114.3 (m).

^{19}F NMR (188 MHz, DMSO-d_6 + NaOH/D_2O) δ -531.17 , -532.71 .

HRMS (ESI) calc. for $C_8H_4F_6N_3$ $[M+H]^+$: 256.0309; found: 256.0306.

IR (υ/cm^{-1}): 3084 (w), 3005 (w), 2912 (w), 2763 (m), 2634 (w), 2540 (w), 1811 (vw), 1614 (vw), 1539 (w), 1419 (w), 1390 (m), 1381 (w), 1286 (s), 1252 (s), 1238 (s), 1200 (s), 1165 (s), 1126 (vs), 1072 (m), 1030 (w), 987 (m), 901 (m), 876 (m), 798 (w), 783 (w), 729 (w), 698 (w), 679 (w), 652 (m).

*4,6-difluoro-1H-benzo[d][1,2,3]triazole (**3m**)*



From 2-azido-1-bromo-3,5-difluorobenzene (1.17 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 4,6-difluoro-1H-benzo[d][1,2,3]triazole (0.73 g, 94%) was obtained as a white solid, m.p. 156-157 °C (lit. data[19] : m.p. 158 °C).

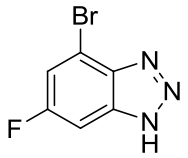
^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 7.23 (d, J = 9.1 Hz, 1H), 6.74 (t, J = 9.7 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 159.3 (d, *J* = 10.4 Hz), 157.7 (d, *J* = 9.7 Hz), 153.0 (d, *J* = 15.5 Hz), 151.3 (d, *J* = 15.9 Hz), 147.5 (dd, *J* = 14.2, 6.2 Hz), 132.7 (d, *J* = 14.9 Hz).

^{19}F NMR (188 MHz, DMSO-d_6 + NaOH/D_2O) δ -116.44 , -118.69 .

HRMS (ESI) calc. for $C_6H_4F_2N_3$ $[M+H]^+$: 156.0373; found: 156.0370.

*4-bromo-6-fluoro-1H-benzo[d][1,2,3]triazole (**3n**)*



From 2-azido-1,3-dibromo-5-fluorobenzene (1.48 g, 5 mmol), following **General procedure D** with subsequent sublimation**,** 4-bromo-6-fluoro-1H-benzo[d][1,2,3]triazole (0.82 g, 76%) was obtained as a white solid.

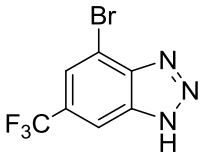
^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 7.40 – 7.37 (m, 1H), 7.16 – 7.13 (m, 1H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 158.4 (d, *J* = 237.9 Hz), 144.5 (d, *J* = 12.8 Hz), 142.0 , 113.9 (d, *J* = 30.6 Hz), 109.7 (d, *J* = 13.7 Hz), 100.4 (d, *J* = 22.9 Hz).

^{19}F NMR (188 MHz, DMSO-d_6 + NaOH/D_2O) δ -118.52 .

HRMS (ESI) calc. for $C_6H_4BrFN_3$ $[M+H]^+$: 215.9573, 217.9552; found: 215.9568, 217.9547.

*4-bromo-6-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (**3o**)*



From 2-azido-1,3-dibromo-5-(trifluoromethyl)benzene (1.7 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 4-bromo-6-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (0.89 g, 67%) was obtained as an off white solid.

^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 8.05 (s, 1H), 7.40 (s, 1H).

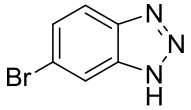
$^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) 145.9 – 145.8 (m), 144.5 (d, *J* = 5.1 Hz), 125.2 (d, *J* = 271.0 Hz), 122.5 (q, *J* = 32.5 Hz), 119.3 – 119.1 (m), 114.2 , 110.4 .

^{19}F NMR (188 MHz, DMSO-d_6 + NaOH/D_2O) δ -55.61.

The NMR data are in agreement with previously reported.[31]

HRMS (ESI) calc. for $C_7H_4BrF_3N_3$ $[M+H]^+$: 265.9541, 267.9520; found: 265.9538, 267.9517.

*6-bromo-1H-benzo[d][1,2,3]triazole (**3p**)*



From 1-azido-2,4-dibromobenzene (1.38 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 6-bromo-1H-benzo[d][1,2,3]triazole (0.79 g, 80%) was obtained as an off white solid, m.p. 143-144 °C (lit. data[18] : m.p. 154 °C).

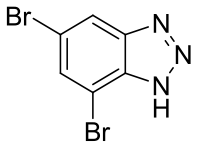
^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 8.00 – 7.99 (m, 2H), 7.75 (dd, *J* = 8.7, 0.5 Hz, 1H), 7.29 (dd, *J* = 8.7, 1.8 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 143.3, 141.2 , 126.7 , 118.3 , 118.0 , 116.7 .

HRMS (ESI) calc. for $C_6H_5BrN_3$ $[M+H]^+$: 197.9667, 199.9646; found: 197.9664, 199.9642.

IR (υ/cm^{-1}): 3130 (m), 3097 (m), 3072 (m), 3024 (s), 2951 (s), 2862 (s), 2752 (vs), 2679 (vs), 2596 (s), 2511 (s), 2411 (m), 1743 (w), 1620 (m), 1587 (w), 1558 (w), 1506 (w), 1462 (w), 1419 (m), 1360 (w), 1309 (vw), 1282 (w), 1271 (m), 1255 (s), 1232 (w), 1207 (vs), 1103 (w), 1047 (s), 1016 (m), 987 (m), 914 (s), 858 (m), 802 (s), 752 (w), 696 (m), 586 (w), 573 (w).

*5,7-dibromo-1H-benzo[d][1,2,3]triazole (**3q**)*



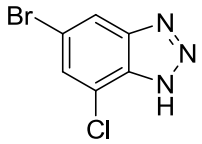
From 2-azido-1,3,5-tribromobenzene (1.78 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 5,7-dibromo-1H-benzo[d][1,2,3]triazole (1.09 g, 79%) was obtained as pink needles.

^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 7.85 – 7.83 (m, 1H), 7.27 (d, *J* = 1.5 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 146.6 , 143.6 , 125.2 , 118.4 , 113.1 , 110.5 .

HRMS (ESI) calc. for $C_6H_4Br_2N_3$ $[M+H]^+$: 275.8772, 277.8752, 279.8731; found: 275.8764, 277.8741, 279.8721.

*5-bromo-7-chloro-1H-benzo[d][1,2,3]triazole (**3r**)*



From 2-azido-1,5-dibromo-3-chlorobenzene (1.56 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 5-bromo-7-chloro-1H-benzo[d][1,2,3]triazole (0.93 g, 80%) was obtained as pink needles.

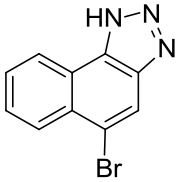
^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 7.82 (s, 1H), 7.15 (s, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 147.3 , 142.3 , 122.7 , 122.2 , 118.1 , 112.9 .

HRMS (ESI) calc. for $C_6H_4BrClN_3$ $[M+H]^+$: 231.9277, 233.9257, 235.9227; found: 231.9271, 233.9248, 235.9221.

IR (υ/cm^{-1}): 3076 (m), 3022 (m), 2945 (m), 2893 (m), 2860 (s), 2748 (s), 2717 (s), 2677 (s), 2592 (s), 2513 (s), 1705 (w), 1614 (m), 1583 (s), 1500 (m), 1417 (s), 1392 (m), 1363 (m), 1296 (vw), 1279 (m), 1269 (m), 1238 (s), 1203 (m), 1188 (vs), 1065 (m), 1034 (m), 1011 (w), 980 (s), 874 (m), 845 (vs), 762 (w), 735 (s), 617 (m), 584 (m).

*5-bromo-1H-naphtho[1,2-d][1,2,3]triazole (**3s**)*



From 1-azido-2,4-dibromonaphthalene (1.63 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 5-bromo-1H-naphtho[1,2-d][1,2,3]triazole (0.68 g, 54%) was obtained as an off white solid.

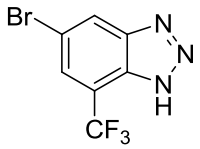
^{1}H NMR (600 MHz, DMSO-d_6) δ 8.58 (d, J = 7.9 Hz, 1H), 8.40 (s, 1H), 8.31 (d, J = 8.2 Hz, 1H), 7.87 – 7.80 (m, 2H), 3.34 (s, 3H).

^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 8.55 (d, J = 7.9 Hz, 1H), 8.16 – 8.11 (m, 2H), 7.59 (t, J = 7.1 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 142.5 , 140.8 , 127.0 , 127.0 , 126.4 , 124.7 , 122.7 , 121.8 , 113.9 .

HRMS (ESI) calc. for $C_{10}H_7BrN_3$ $[M+H]^+$: 247.9823, 249.9803; found: 247.9815, 249.9794.

*5-bromo-7-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (**3t**)*



From 2-azido-1,5-dibromo-3-(trifluoromethyl)benzene (1.73 g, 5 mmol), following **General procedure D** with subsequent recrystallization from DCM**,** 5-bromo-7-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (0.97 g, 73%) was obtained as a pink solid.

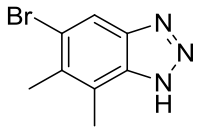
^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 8.15 (dd, J = 1.6, 0.7 Hz, 1H), 7.40 – 7.39 (m, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 148.0 , 139.9 , 126.1 (q, J = 272.5 Hz), 123.4 , 121.0 (q, J = 5.3 Hz), 118.2 (q, J = 32.8 Hz), 111.8 .

^{19}F NMR (188 MHz, DMSO-d_6 + NaOH/D_2O) δ -56.88 .

HRMS (ESI) calc. for $C_7H_4BrF_3N_3$ $[M+H]^+$: 265.9541, 267.9520; found: 265.9539, 267.9518.

*5-bromo-6,7-dimethyl-1H-benzo[d][1,2,3]triazole (**3u**)*



From 2-azido-1,5-dibromo-3,4-dimethylbenzene (1.53 g, 5 mmol), following **General procedure D** using 30 ml THF with subsequent recrystallization from DCM**,** 5-bromo-6,7-dimethyl-1H-benzo[d][1,2,3]triazole (1.00 g, 89%) was obtained as a white solid.

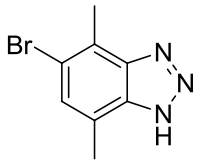
^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 7.74 (s, 1H), 2.57 (s, 3H), 2.33 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 145.5 , 144.0 , 125.6 , 125.2 , 118.6 , 116.8 , 19.2 , 16.0 .

HRMS (ESI) calc. for $C_8H_9BrN_3$ $[M+H]^+$: 225.9980, 227.9959; found: 225.9976, 227.9955.

IR (υ/cm^{-1}): 3128 (w), 3072 (m), 3022 (m), 2952 (m), 2918 (s), 2850 (s), 2760 (vs), 2698 (vs), 2663 (vs), 2602 (vs), 2499 (s), 1616 (m), 1506 (m), 1448 (m), 1383 (s), 1350 (w), 1284 (s), 1219 (vs), 1174 (w), 1082 (m), 1018 (s), 978 (s), 904 (m), 852 (s), 771 (w), 746 (s).

*5-bromo-4,7-dimethyl-1H-benzo[d][1,2,3]triazole (**3v**)*



From 2-azido-3,5-dibromo-1,4-dimethylbenzene (1.53 g, 5 mmol), following **General procedure D** using 30 ml THF with subsequent recrystallization from DCM**,** 5-bromo-4,7-dimethyl-1H-benzo[d][1,2,3]triazole (1.00 g, 89%) was obtained as a white solid.

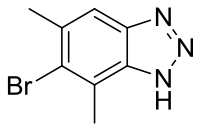
^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 6.87 (s, 1H), 2.54 (s, 3H), 2.48 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 146.0 , 144.0 , 125.7 , 124.0 , 122.9 , 115.5 , 17.9 , 17.5 .

HRMS (ESI) calc. for $C_8H_9BrN_3$ $[M+H]^+$: 225.9980, 227.9959; found: 225.9976, 225.9976.

IR (υ/cm^{-1}): 3140 (w), 3089 (m), 3037 (m), 3005 (s), 2951 (s), 2925 (s), 2802 (vs), 2681 (s), 2602 (s), 2565 (m), 2455 (m), 1716 (w), 1620 (w), 1595 (w), 1523 (w), 1456 (m), 1442 (m), 1385 (m), 1363 (w), 1292 (w), 1279 (w), 1234 (m), 1223 (m), 1217 (m), 1176 (m), 1138 (w), 1093 (w), 1063 (w), 1032 (vw), 1005 (s), 984 (m), 899 (w), 858 (m), 781 (m), 675 (w).

*6-bromo-5,7-dimethyl-1H-benzo[d][1,2,3]triazole (**3w**)*



From 1-azido-2,4-dibromo-3,5-dimethylbenzene (1.53 g, 5 mmol), following **General procedure D** using 30 ml THF with subsequent recrystallization from DCM**,** 6-bromo-5,7-dimethyl-1H-benzo[d][1,2,3]triazole (0.9 g, 79%) was obtained as a red solid.

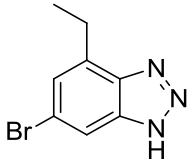
^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) δ 7.50 (s, 1H), 2.61 (s, 3H), 2.37 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) δ 143.3 , 140.6 , 132.1 , 126.4 , 121.3 , 113.7 , 24.8 , 18.8 .

HRMS (ESI) calc. for $C_8H_9BrN_3$ $[M+H]^+$: 225.9980, 227.9959; found: 225.9976, 227.9956.

IR (υ/cm^{-1}): 3141 (m), 3060 (m), 3043 (s), 2978 (s), 2949 (s), 2924 (s), 2879 (s), 2846 (s), 2763 (vs), 2711 (vs), 2686 (vs), 2613 (vs), 2515 (s), 2416 (s), 1711 (m), 1624 (m), 1589 (m), 1516 (m), 1450 (s), 1433 (m), 1417 (s), 1396 (m), 1377 (s), 1360 (m), 1317 (m), 1286 (m), 1265 (m), 1215 (s), 1180 (m), 1105 (m), 1022 (m), 985 (s), 958 (s), 897 (m), 856 (s).

*6-bromo-4-ethyl-1H-benzo[d][1,2,3]triazole (**3x**)*



From 2-azido-1,5-dibromo-3-ethylbenzene (1.53 g, 5 mmol), following **General procedure D** with subsequent column chromatography**,** 6-bromo-4-ethyl-1H-benzo[d][1,2,3]triazole (0.99 g, 83%) was obtained as a white solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.97 (s, 1H), 7.36 (s, 1H), 3.02 (q, *J* = 7.5 Hz, 2H), 1.31 (t, *J* = 7.5 Hz, 3H).

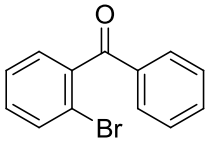
^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 139.9 , 138.1 , 134.0 , 125.8 , 118.2 , 114.7 , 24.1 , 14.1 .

HRMS (ESI) calc. for $C_8H_9BrN_3$ $[M+H]^+$: 225.9980, 227.9959; found: 225.9974, 227.9954.

IR (υ/cm^{-1}): 3138 (m), 3074 (m), 3041 (m), 2970 (s), 2941 (s), 2885 (s), 2744 (vs), 2700 (vs), 2602 (s), 2519 (s), 1738 (w), 1614 (s), 1597 (m), 1516 (m), 1429 (s), 1402 (m), 1379 (m), 1331 (m), 1288 (m), 1250 (s), 1201 (s), 1109 (w), 1080 (s), 1022 (m), 991 (m), 964 (w), 887 (m), 870 (s), 845 (s), 750 (s), 667 (w), 592 (w).

Synthesis of indazole

(2-bromophenyl)(phenyl)methanone



A mixture of 2-bromobenzoic acid (14.07 g, 70 mmol), $SOCl_2$ (6.10 ml, 9.95 g, 84 mmol) and one drop of DMF was refluxed for 4h. After having being cooled to RT the reaction mixture was concentrated in vacuum. The obtained 2-bromobenzoyl chloride (yield 99%) was pure enough for the next step based on NMR spectra.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.40 (m, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-d) δ 166.0 , 135.0 , 135.0 , 134.5 , 133.5 , 127.7 , 121.60.

To a solution of $AlCl_3$ (4.67 g, 73,5 mmol) in dry benzene (100 ml) 2-bromobenzoyl chloride (15.3 g, 70 mmol) was added dropwise at 0 °C. The resulting mixture was stirred overnight at RT. Then the reaction was washed with 1.5 M aqueous HCl (100 ml) and water (100

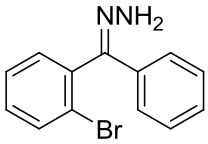
ml), dried over Na_2SO_4 and concentrated under reduced pressure. Passing of the residual oil through a pad of silica with PE afforded pure (2-bromophenyl)(phenyl)methanone (7.2 g, 97%) as a white solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.7 Hz, 2H), 7.67 – 7.58 (m, 2H), 7.44 (dt, *J* = 29.0, 7.3 Hz, 3H), 7.35 (t, *J* = 7.6 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 196.0 , 140.8 , 136.2 , 133.8 , 133.3 , 131.3 , 130.3 , 129.1 , 128.8 , 127.3 , 119.6 .

The NMR data are in agreement with previously reported.[32]

((2-bromophenyl)(phenyl)methylene)hydrazine

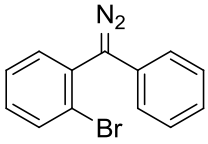


A solution of (2-bromophenyl)(phenyl)methanone (5.22 g, 20 mmol), hydrazine (9.7 ml, 200 mmol) and AcOH (0.4 ml) in ethanol (40 ml) was refluxed for 12h. Concentration of cooled reaction mixture under reduced pressure provided white solid which after washing with hexanes on filter gave pure ((2-bromophenyl)(phenyl)methylene)hydrazine (4.2 g, 76%) as a white crystalline solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 – 7.74 (m, 1H), 7.50 – 7.43 (m, 3H), 7.38 – 7.27 (m, 5H), 7.23 (d, *J* = 4.6 Hz, 1H), 5.35 (s, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 147.6 , 137.0 , 134.5 , 133.6 , 130.6 , 128.5 , 128.3 , 128.3 , 125.9 , 122.6 .

*1-bromo-2-(diazo(phenyl)methyl)benzene (**4**)*

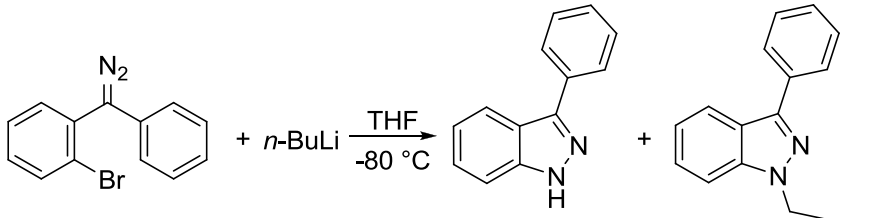


To a vigorously stirred mixture of ((2-bromophenyl)(phenyl)methylene)hydrazine (0.5 g, 1.8 mmol) and $MgSO_4$ (0.16 g, 1.3 mmol) in DCM (4.7 ml) activated MnO_2 (1.57 g, 18 mmol) was added in one portion at 0 °C. The reaction vessel was covered with aluminum foil to prevent access of light. The reaction was slowly warmed up to RT and vigorously stirred overnight. Then the reaction mixture was filtered through a pad of Celite® and the residue on the filter was washed several times (DCM with 1% of Et_3N). The filtrate was concentrated under reduced pressure and submitted to column chromatography (PE/Et_3N, 20:1), which provided 1-bromo-2-(diazo(phenyl)methyl)benzene (0.35 g, 71%) as a red-violet oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.50 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.28 – 7.22 (m, 1H overlapping with $CHCl_3$), 7.09 (t, *J* = 7.4 Hz, 1H), 7.01 – 6.95 (m, 2H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 134.1 , 132.7 , 130.7 , 130.0 , 129.3 , 129.2 , 128.0 , 125.8 , 124.5 , 122.6 .

*Reaction of 1-bromo-2-(diazo(phenyl)methyl)benzene (**4**) with n-BuLi*



4 **5** **5a**

To a cooled (-85 °C) solution of 1-bromo-2-(diazo(phenyl)methyl)benzene (0.38 g, 1.4 mmol) in anhydrous THF (10 ml) *n*-BuLi (2.5 M in hexanes,0.55 ml, 1.4 mmol) was added dropwise. During the addition the temperature was maintained below -75 °C. Then the reaction mixture was stirred for two hours at -85 – -75 °C and overnight at RT. The reaction was quenched with 1.5 M aqueous HCl (1 ml) and concentrated under reduced pressure. The residue was diluted with water (20 ml) and extracted with EtOAc (4×15 ml). Combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography (gradient elution, PE – PE/DCM = 4/1) of residue gave 2 products.

3-Phenyl-1H-indazole 5: 83.4 mg (28% yield), off white solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.83 (br. s, 1H), 8.05 (d, *J* = 7.4 Hz, 3H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.28 – 7.21 (m, 2H overlapping with $CHCl_3$).

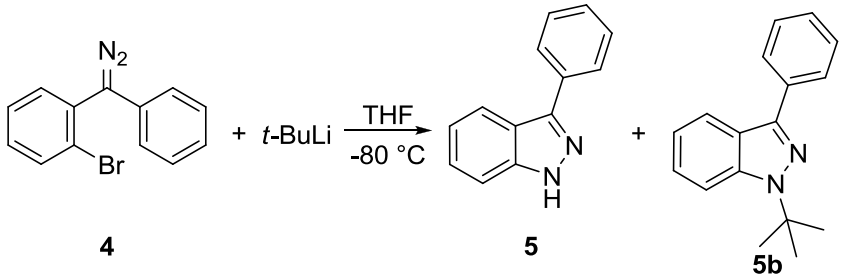
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 145.7 , 141.8 , 133.5 , 129.1 , 128.4 , 127.9 , 127.1 , 121.6 , 121.2 , 121.0 , 110.5.

The NMR data are in agreement with previously reported.[33]

1-*n*-Butyl-3-phenyl-1H-indazole 5a: 68.2 mg (19% yield), off white solid.

^{1}H NMR (600 MHz, Chloroform-d) δ 8.00 (dd, J = 29.0, 7.7 Hz, 3H), 7.51 (t, J = 7.0 Hz, 2H), 7.47 – 7.37 (m, 4H), 7.21 (d, J = 6.8 Hz, 1H), 4.44 (t, J = 6.7 Hz, 2H), 2.02 – 1.91 (m, 2H), 1.41 (q, J = 6.9 Hz, 2H), 0.97 (t, J = 5.8 Hz, 3H).

Reaction of 1-bromo-2-(diazo(phenyl)methyl)benzene (4) with t-BuLi



4 **5** **5b**

Following the same procedure as above, but with *t*-BuLi (1.7 M, 2.59 ml, 4.4 mmol) instead of *n*-BuLi, mixture of the products was obtained from 1-bromo-2-(diazo(phenyl)methyl)benzene (0.60 g, 2.2 mmol): 3-phenyl-1H-indazole **5** (137.1 mg, 29%) and 1-*tert*-butyl-3-phenyl-1H-indazole **5b** (46.8 mg, 6%).

3-Phenyl-1H-indazole 5:

^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.83 (br. s, 1H), 8.05 (d, *J* = 7.4 Hz, 3H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.28 – 7.21 (m, 2H overlapping with $CHCl_3$).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 145.7 , 141.8 , 133.5 , 129.1 , 128.4 , 127.9 , 127.1 , 121.6 , 121.2 , 121.0 , 110.5 .

The NMR data are in agreement with previously reported.[33]

1-*tert*-Butyl-3-phenyl-1H-indazole 5b:

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 7.3 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.34 (m, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 1.84 (s, 9H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 142.0 , 139.7 , 134.3 , 128.9 , 127.7 , 127.7 , 125.3 , 123.3 , 121.6 , 120.5 , 112.5 , 29.8 .

The NMR data are in agreement with previously reported.[1]

HRMS (ESI) calc. for $C_{17}H_{19}N_2$ $[M+H]^+$: 251.1548, 252.1582; found: 251.1546, 252.1578.

^{1}H, ^{13}C and ^{19}F NMR spectra

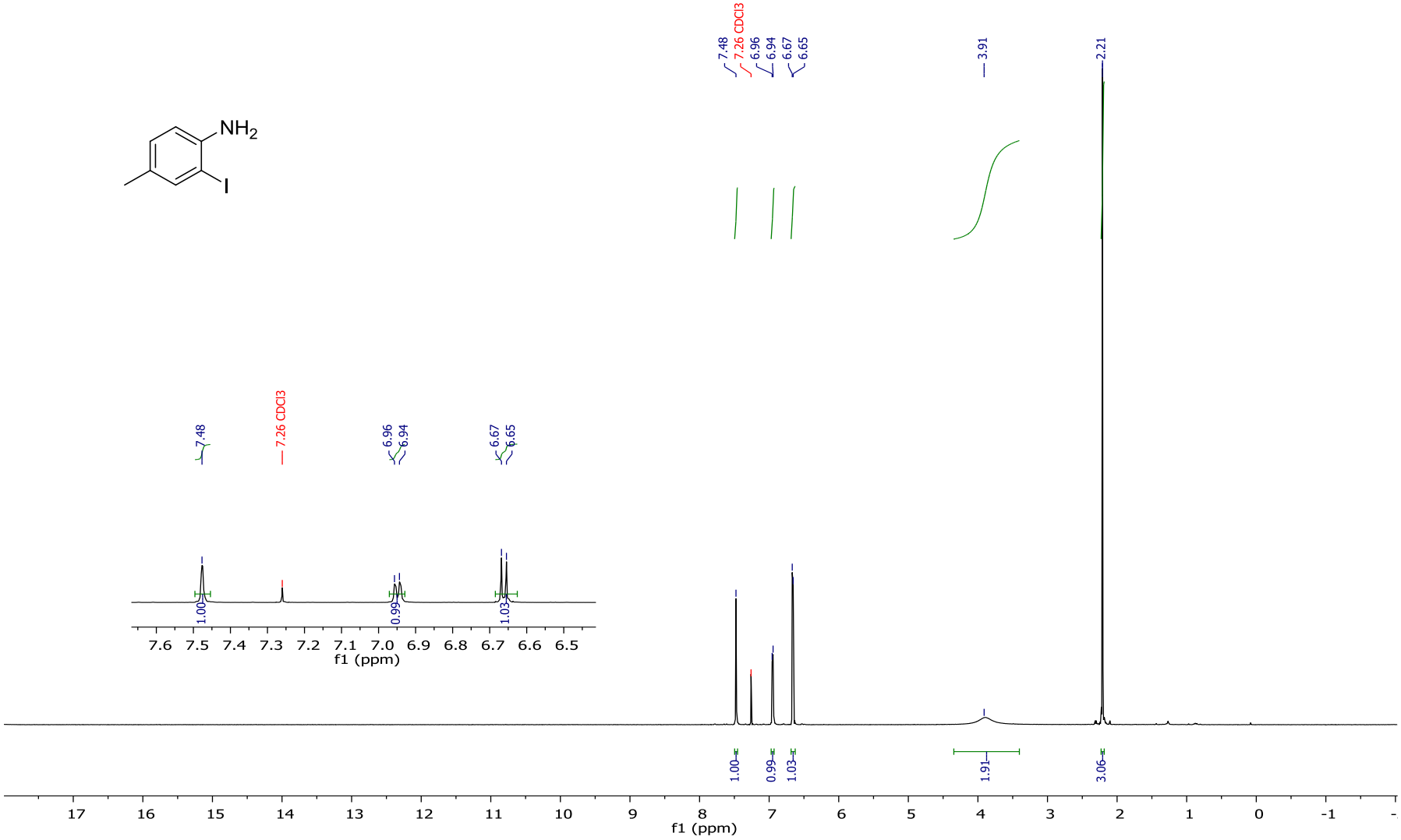


Figure S1. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2-iodo-4-methylaniline (1b-I).

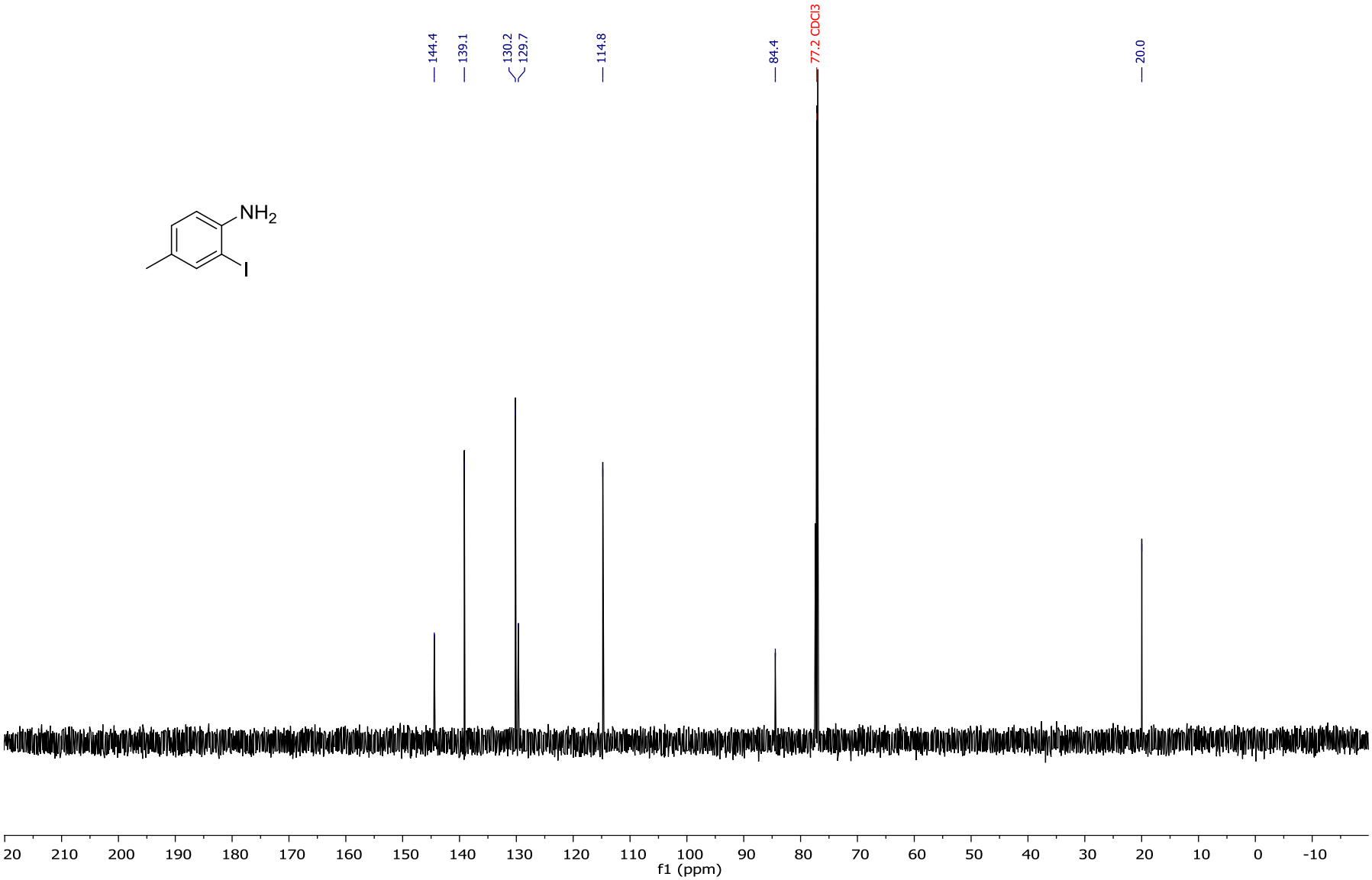


Figure S2. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-iodo-4-methylaniline (1b-I).

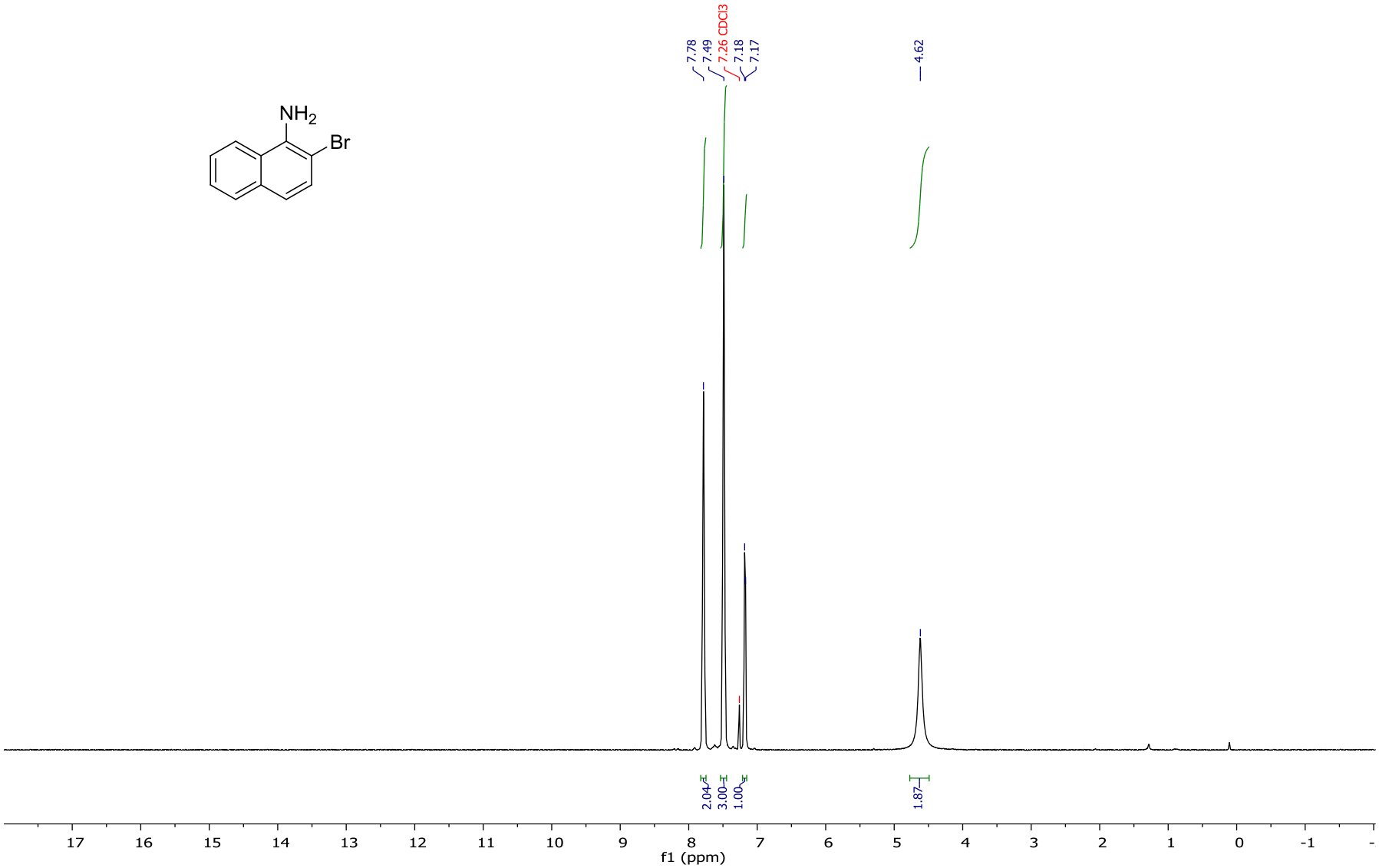


Figure S3. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2-bromonaphthalen-1-amine (1d).

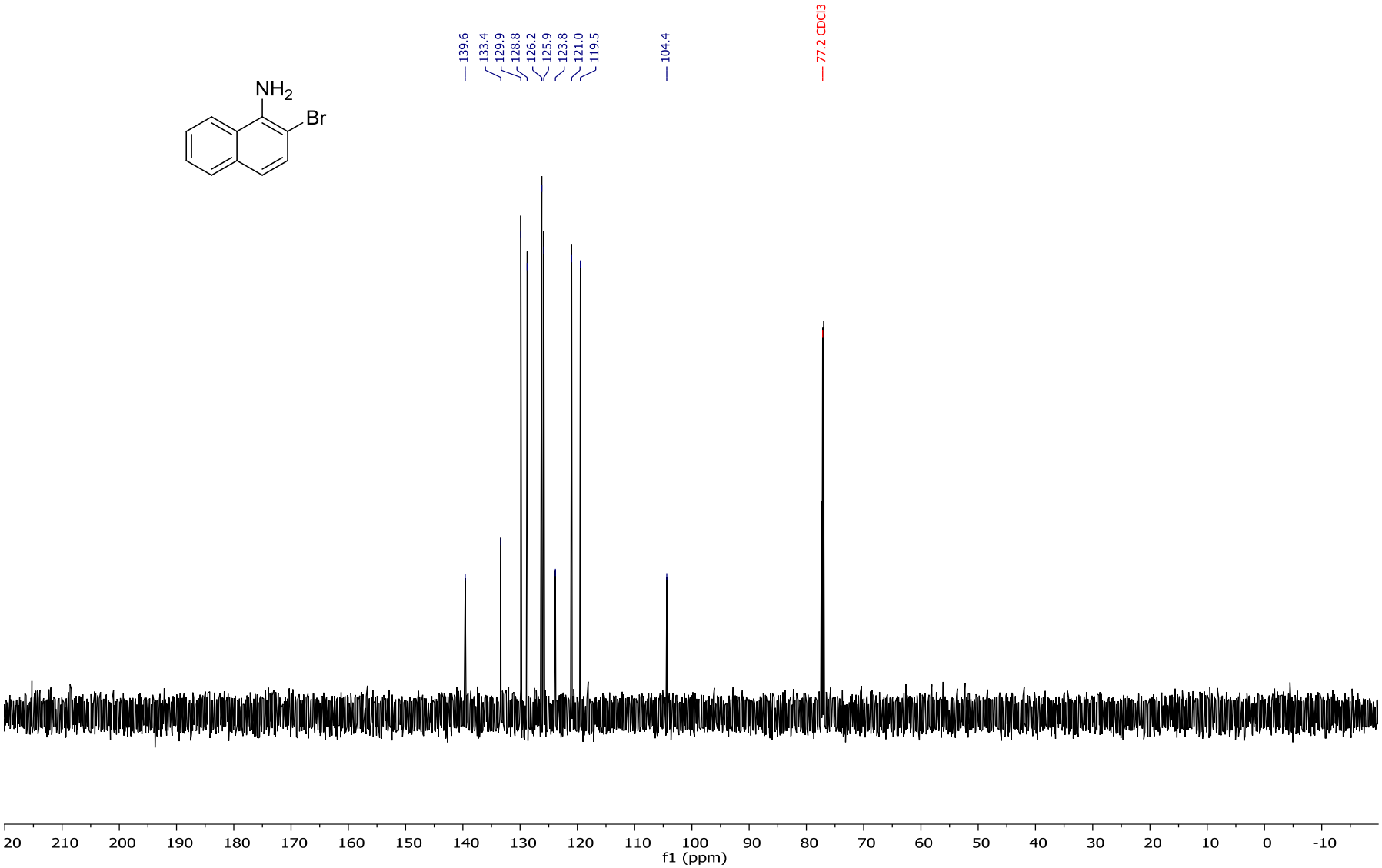


Figure S4. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-bromonaphthalen-1-amine (1d).

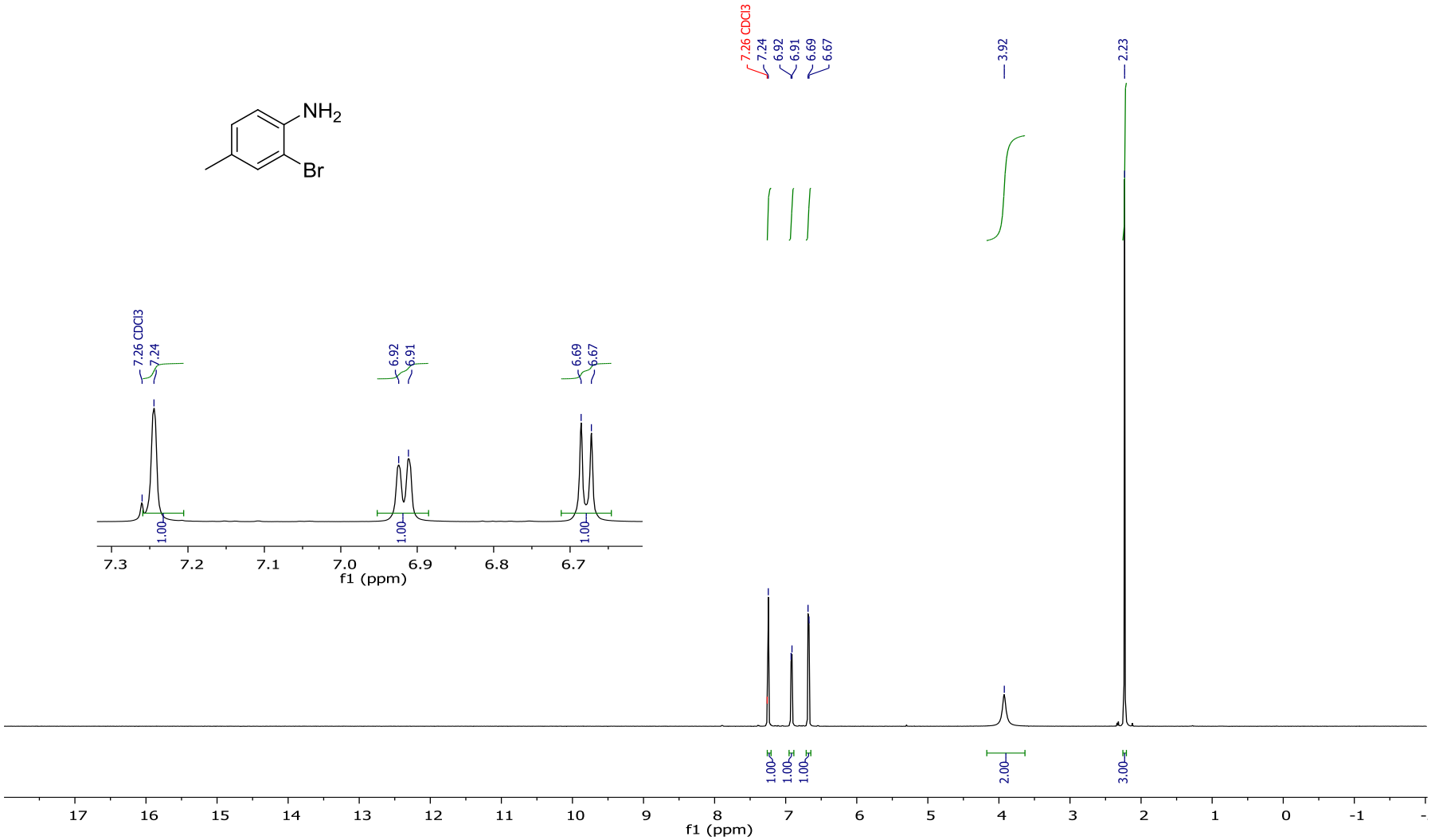


Figure S5. ^{1}H NMR (600 MHz, Chloroform-d) of 2-bromo-4-methylaniline (1b-Br).

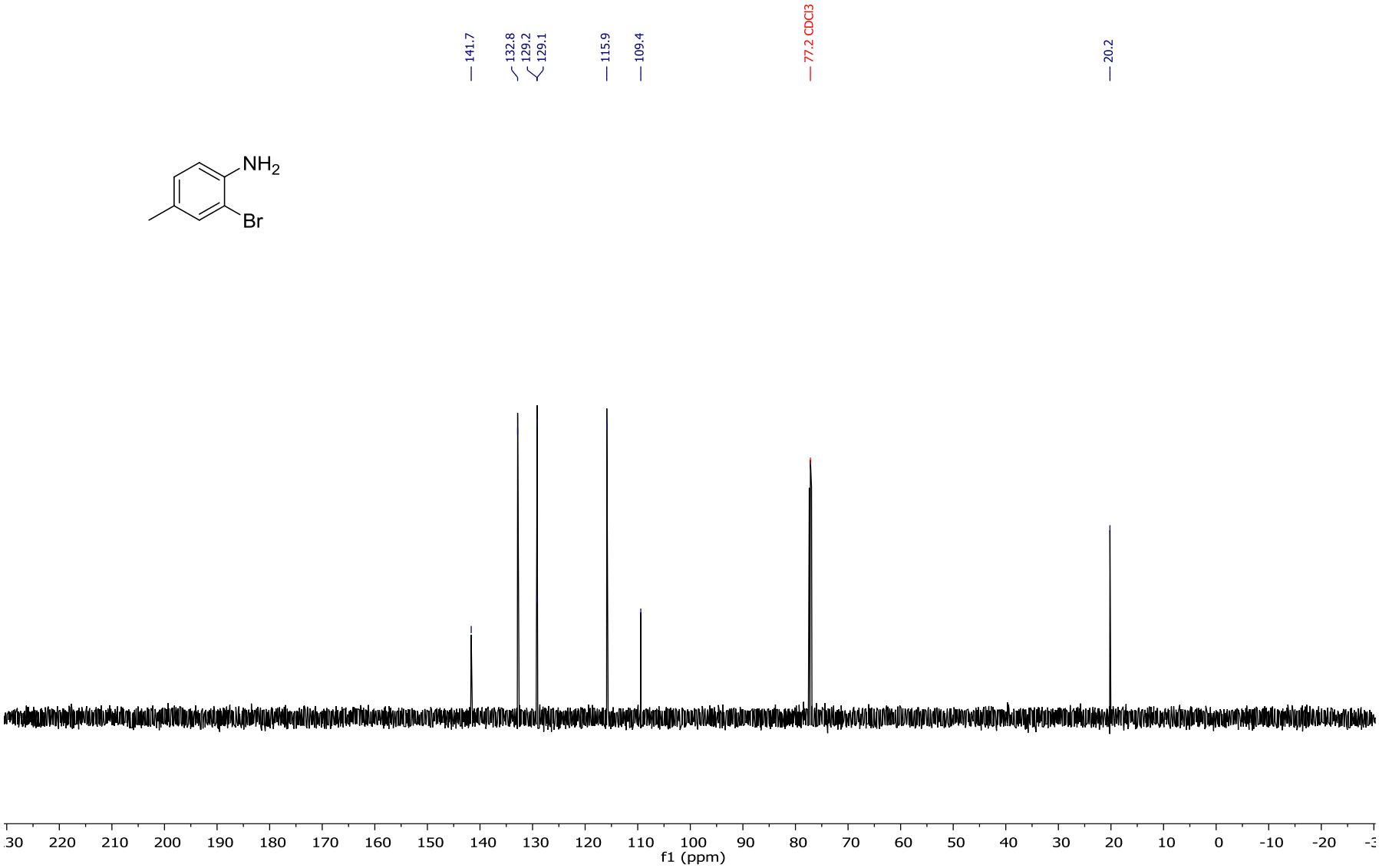


Figure S6. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-bromo-4-methylaniline (1b-Br).

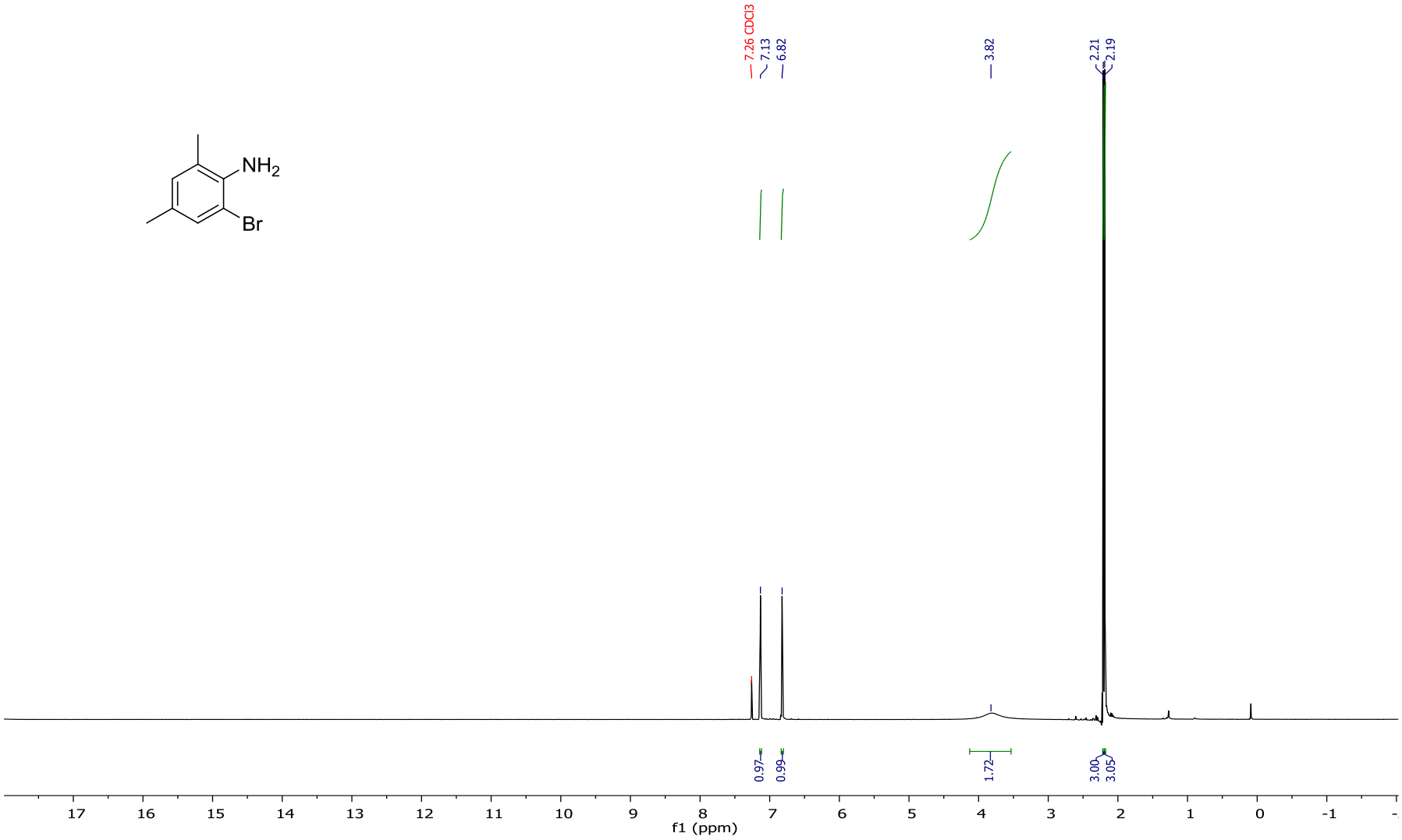


Figure S7. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2-bromo-4,6-dimethylaniline (1c).

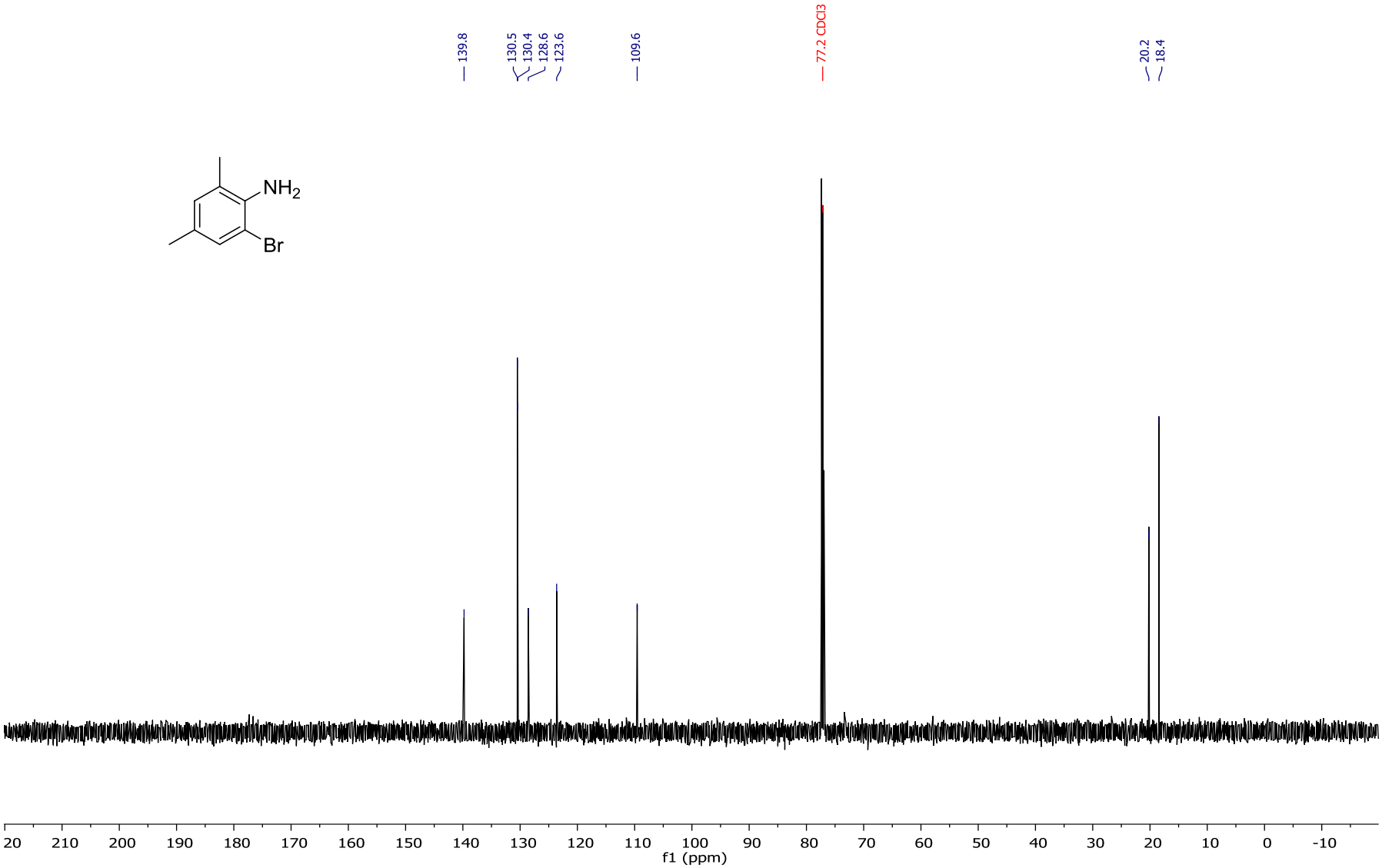


Figure S8. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-bromo-4,6-dimethylaniline (1c).

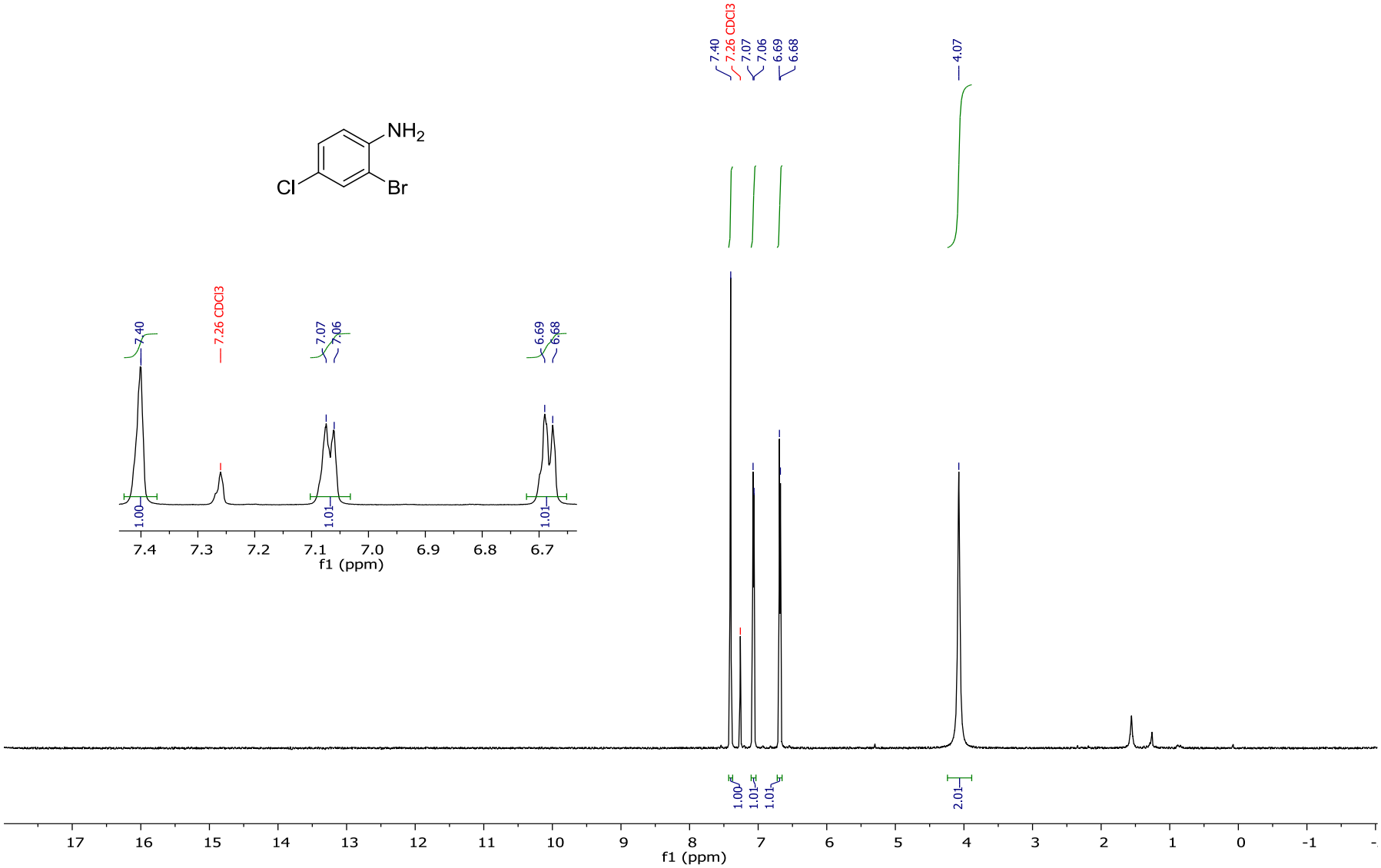


Figure S9. ^{1}H NMR (600 MHz, Chloroform-d) of 2-bromo-4-chloroaniline (1e).

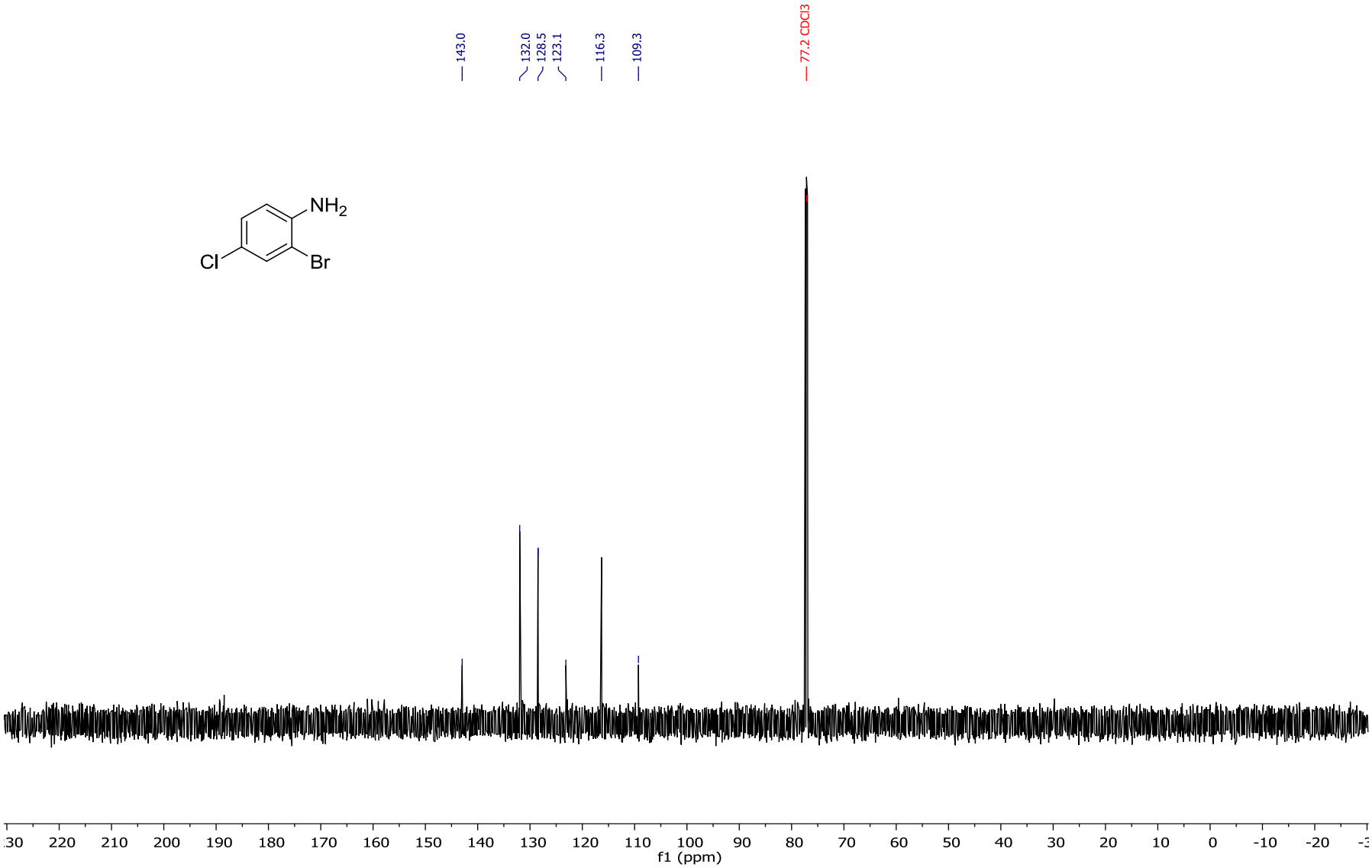


Figure S10. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-bromo-4-chloroaniline (1e).

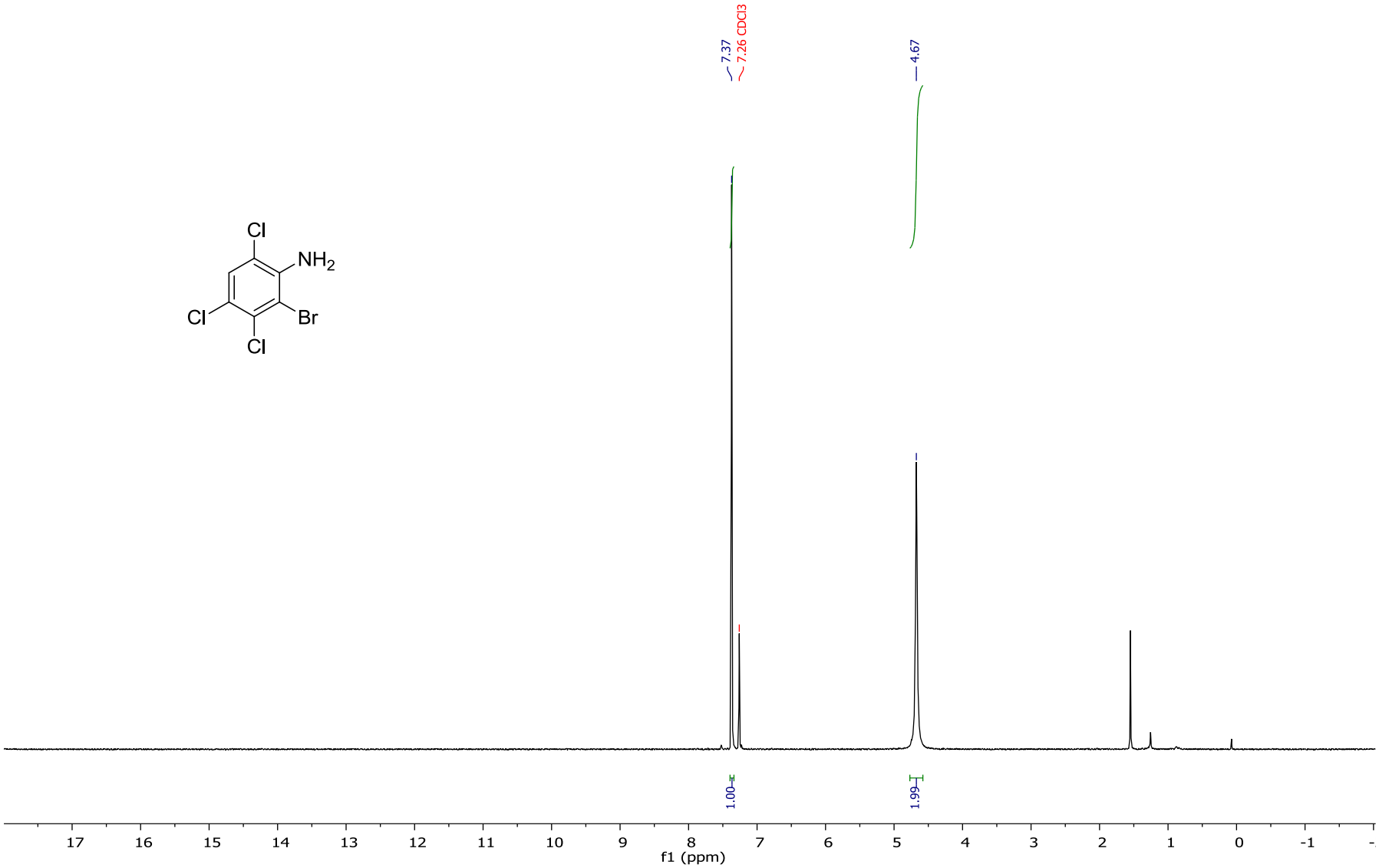


Figure S11. ^{1}H NMR (600 MHz, Chloroform-d) of 2-bromo-3,4,6-trichloroaniline (1f).

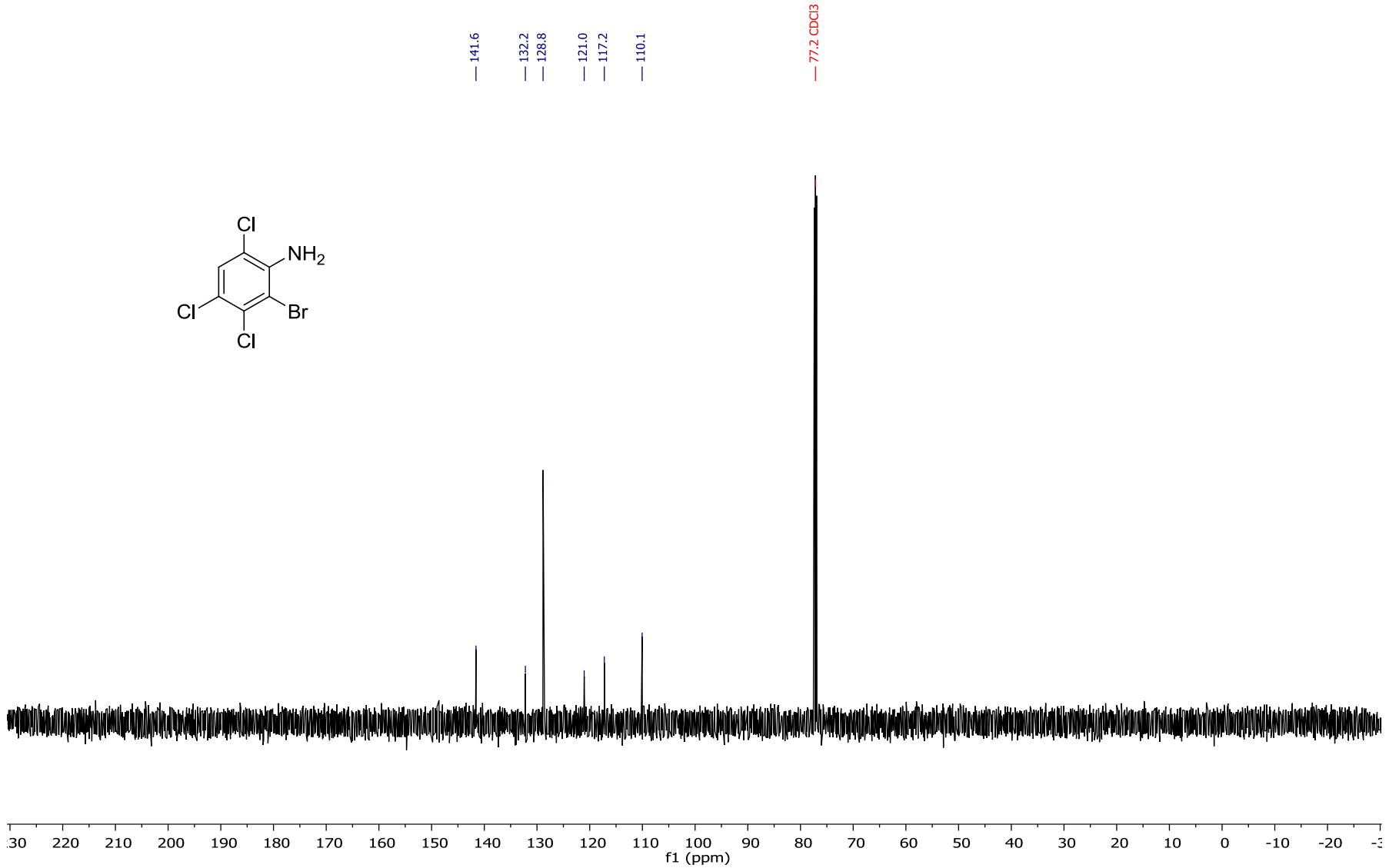


Figure S12. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-bromo-3,4,6-trichloroaniline (1f).

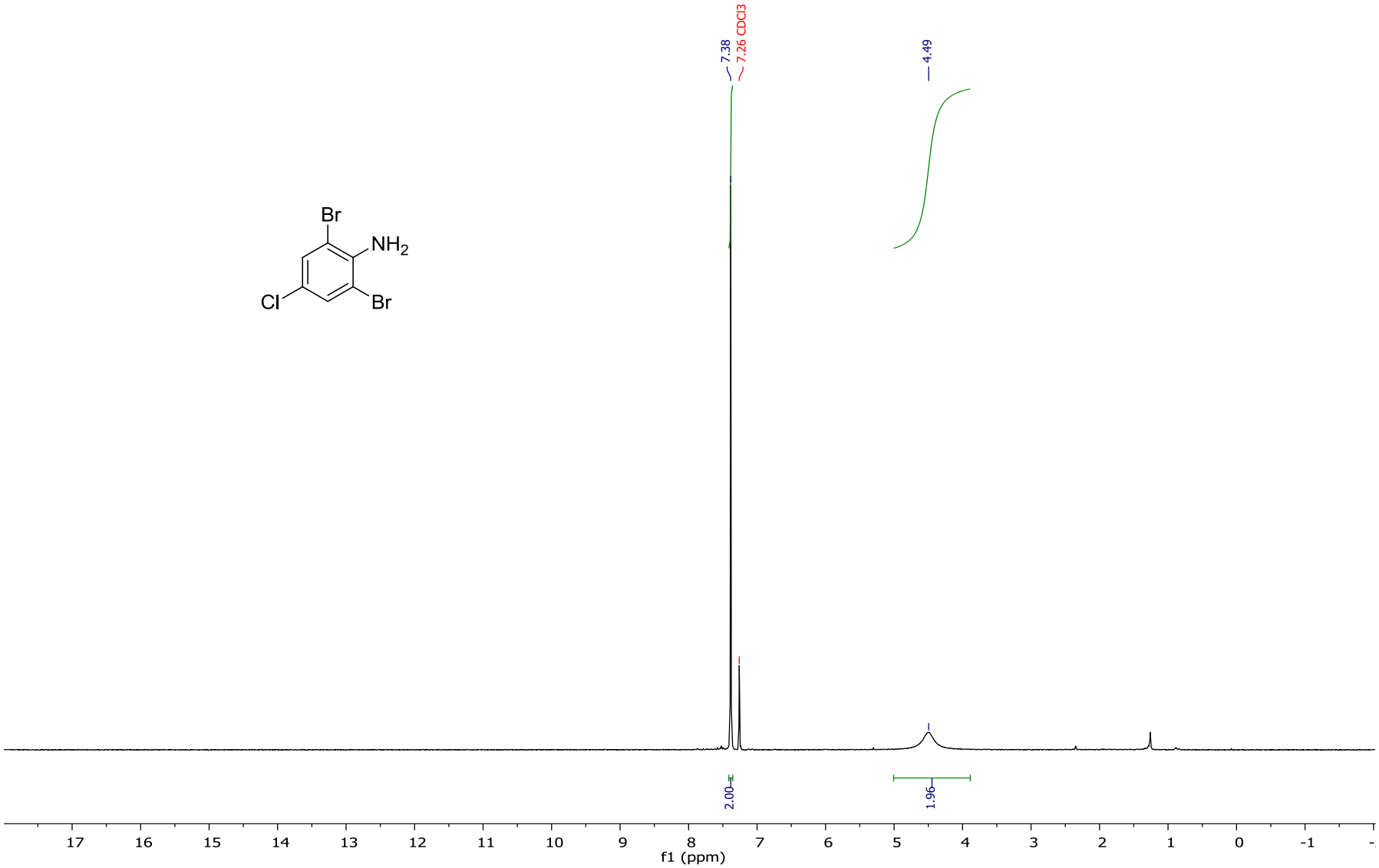


Figure S13. ^{1}H NMR (600 MHz, Chloroform-d) of 2,6-dibromo-4-chloroaniline (1g).

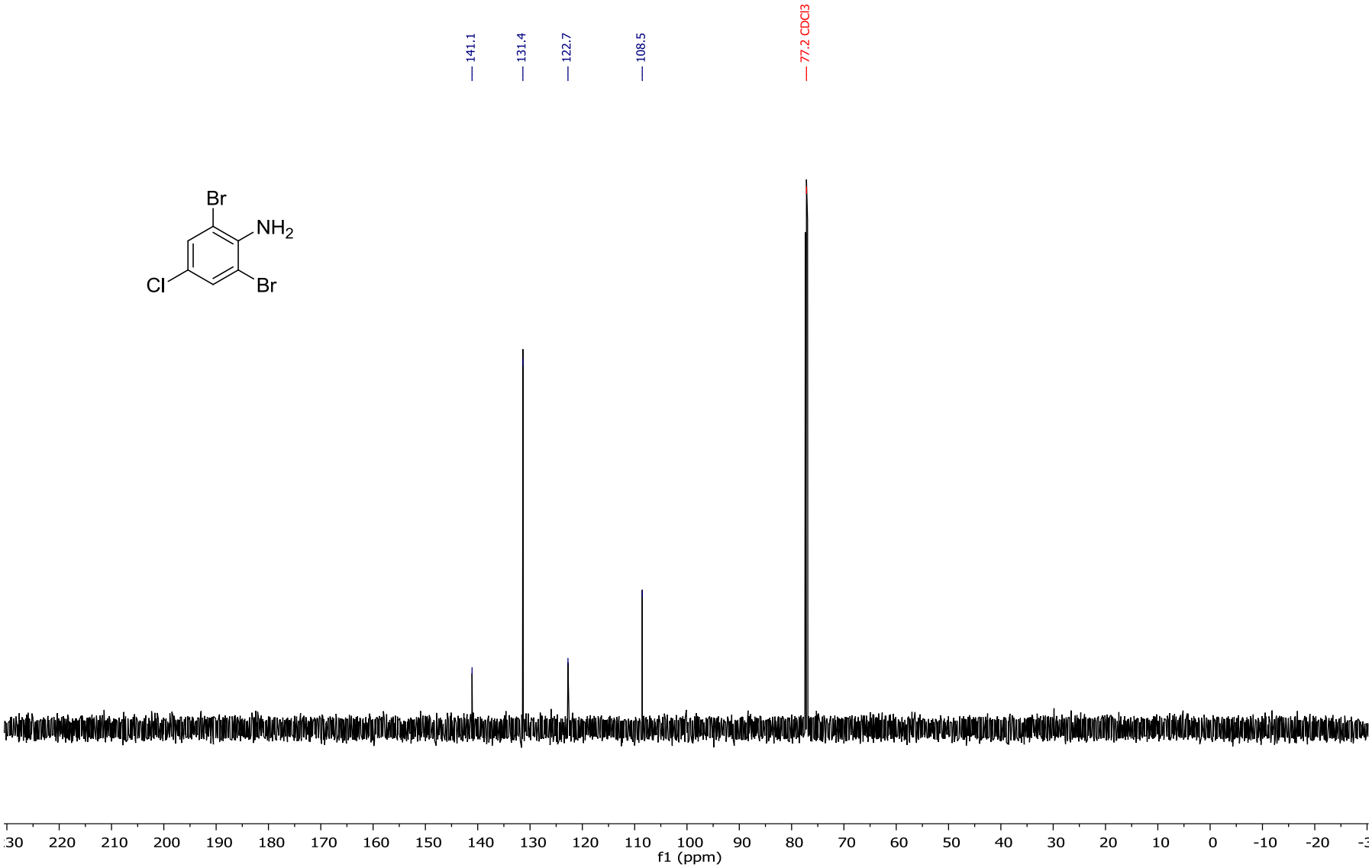


Figure S14. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2,6-dibromo-4-chloroaniline (1g).

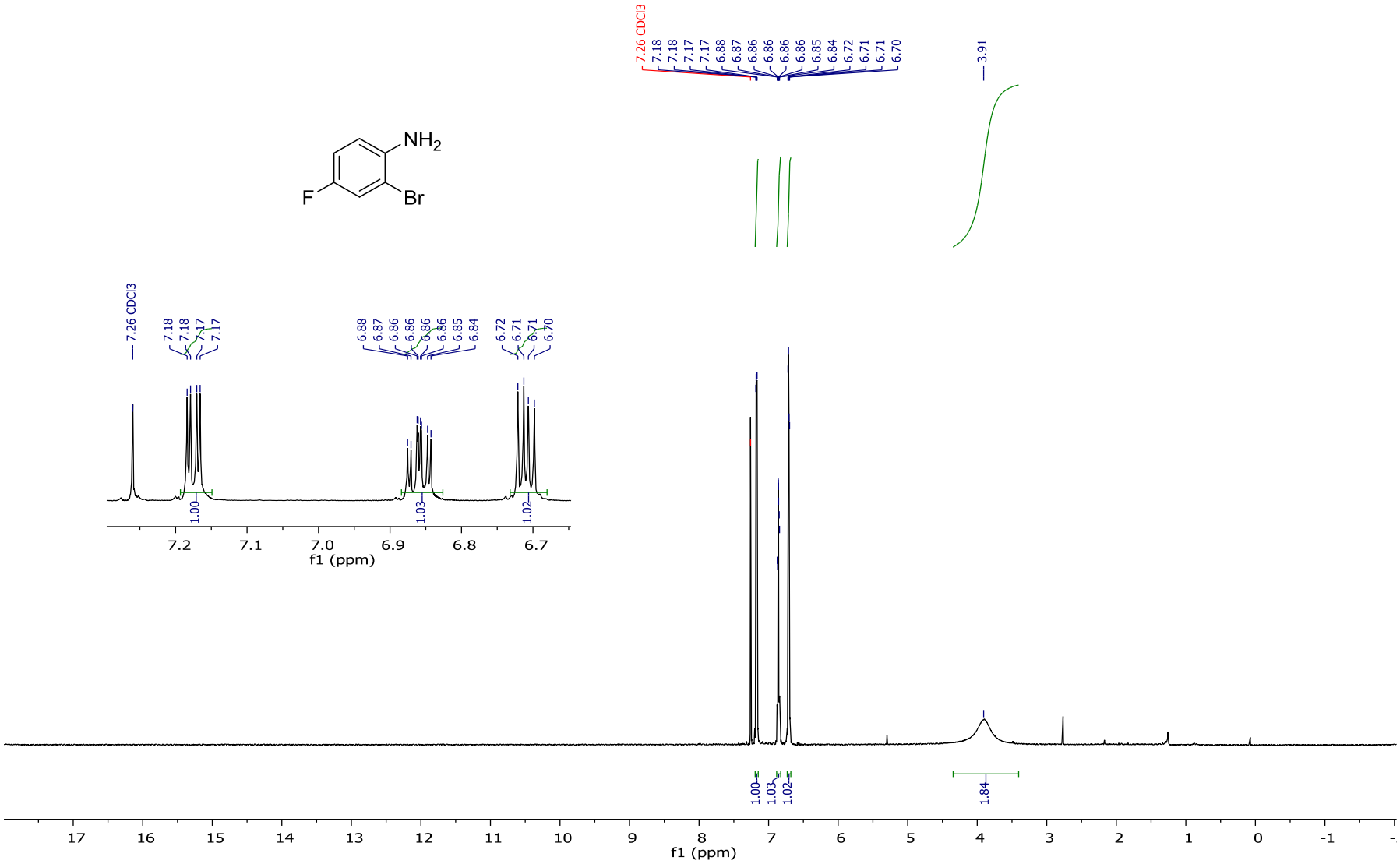


Figure S15. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2-bromo-4-fluoroaniline (1j).

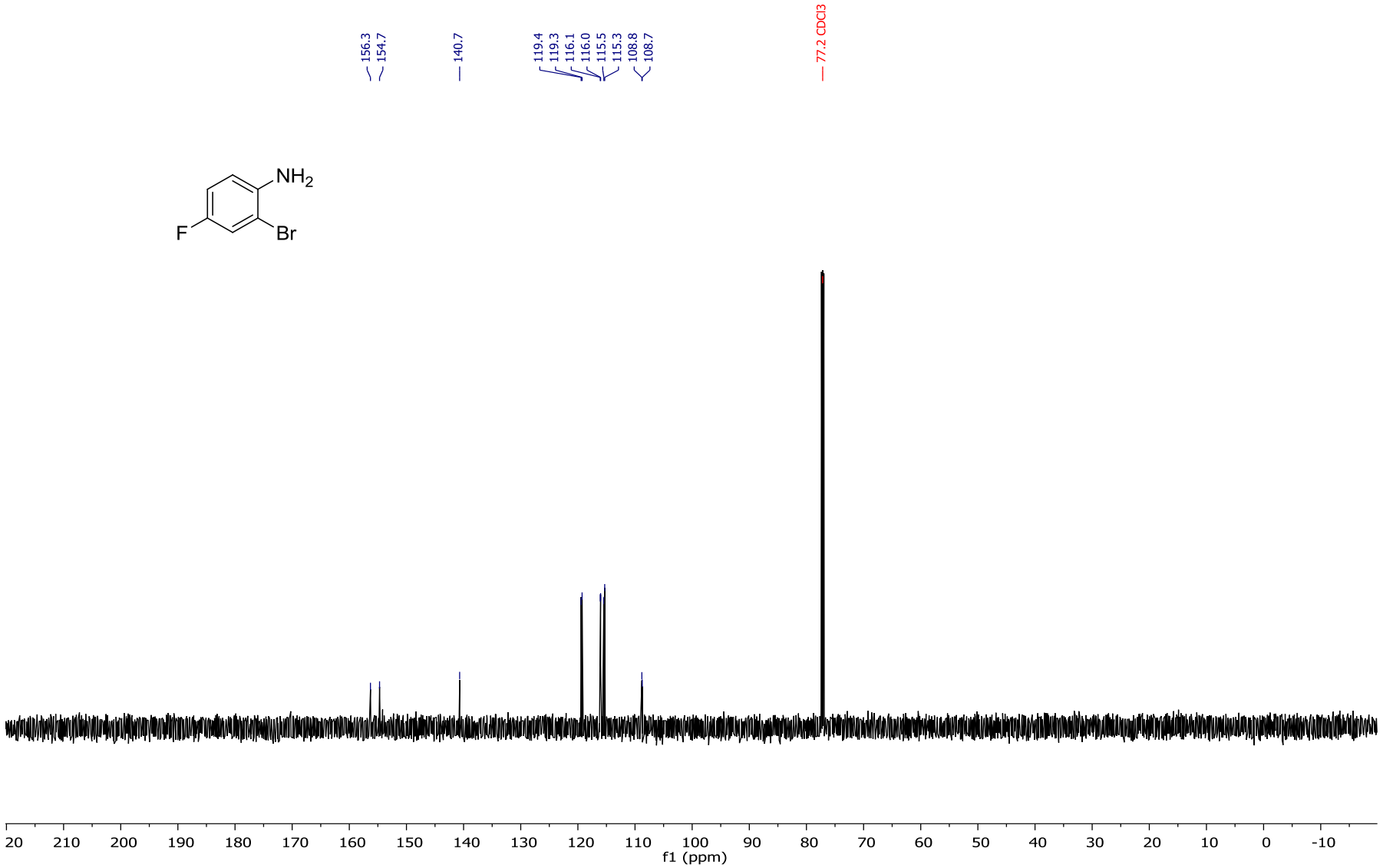


Figure S16. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-bromo-4-fluoroaniline (1j).

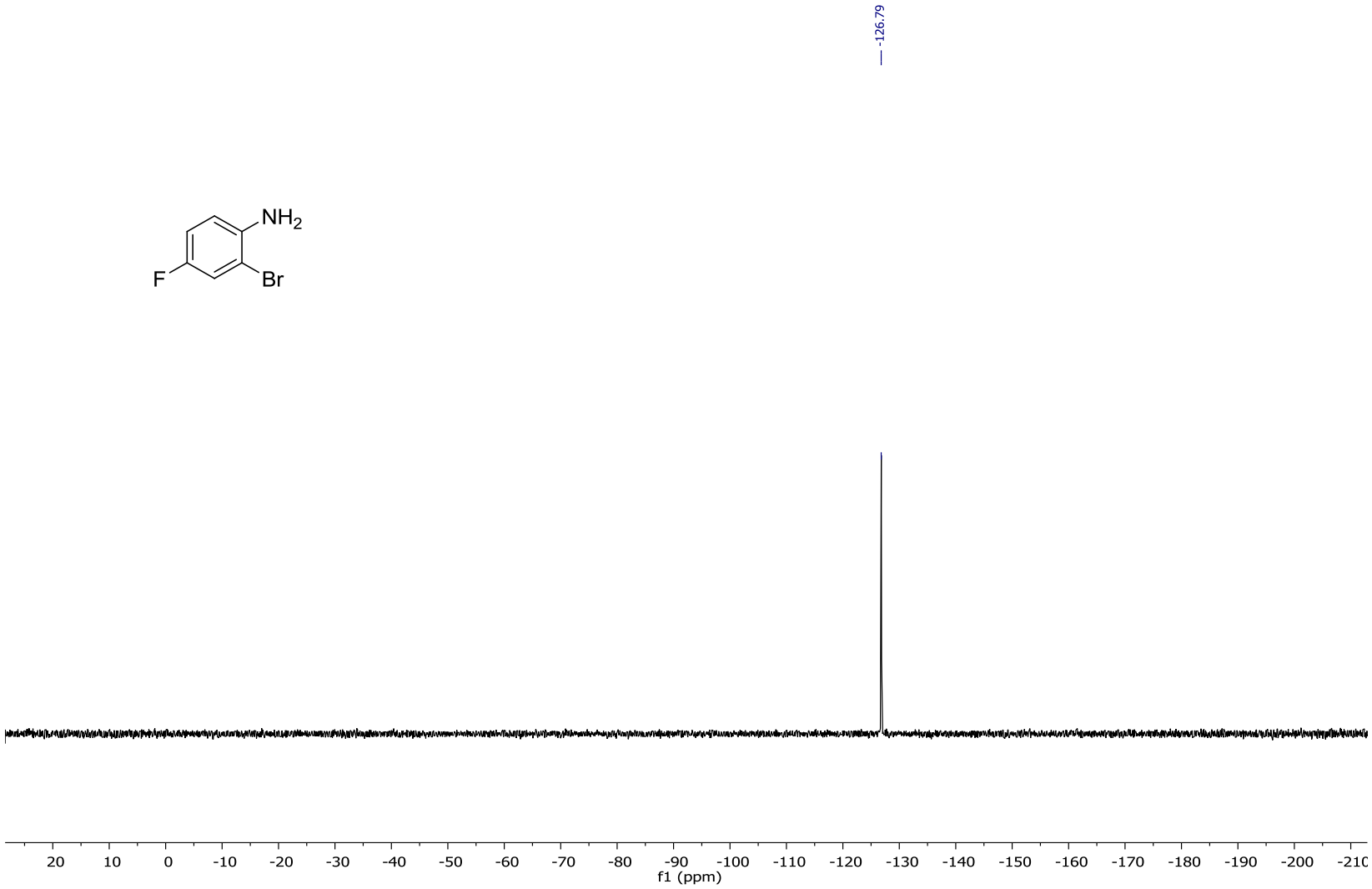


Figure S17. ^{19}F NMR (188 MHz, Chloroform-d) of 2-bromo-4-fluoroaniline (1j).

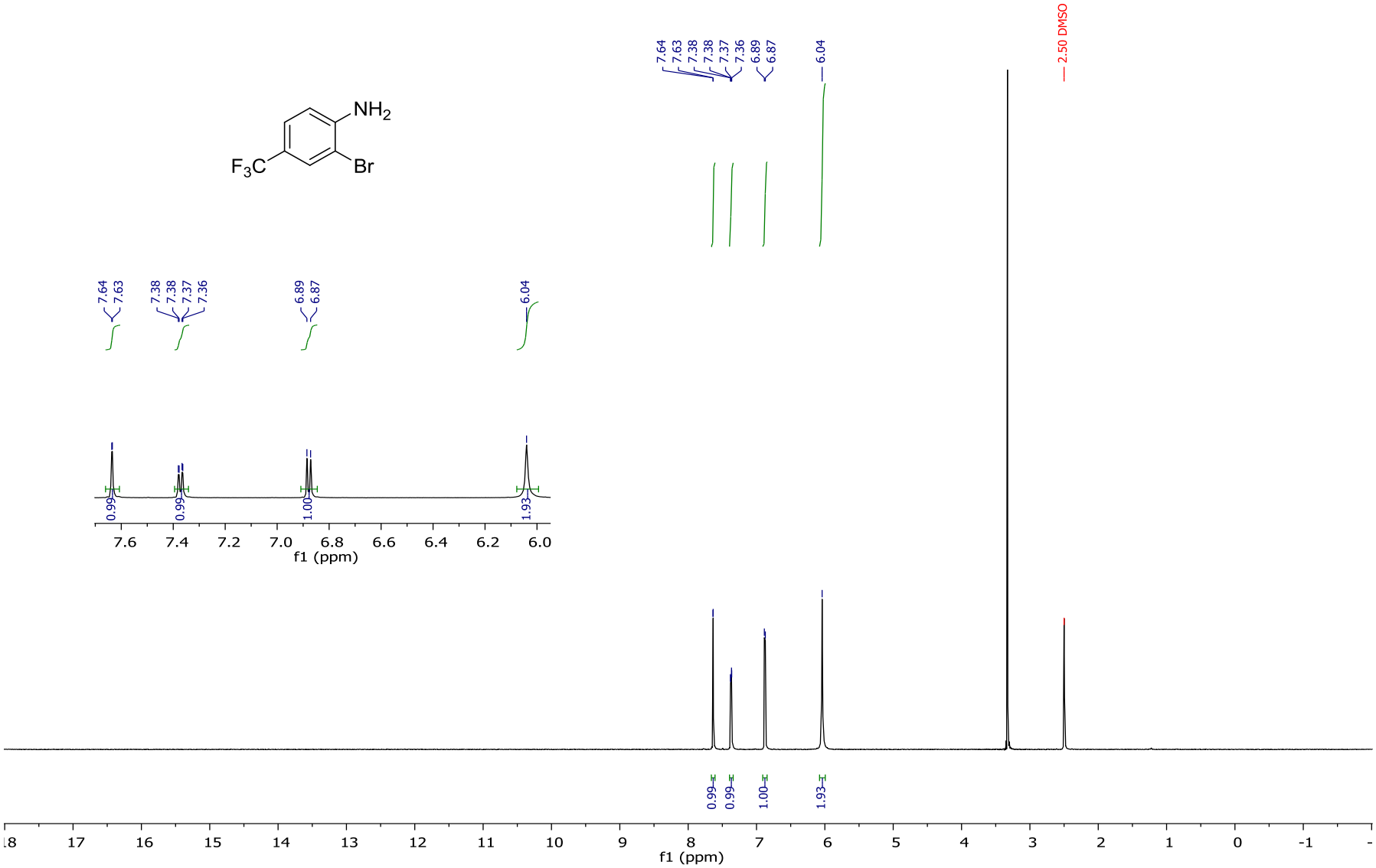


Figure S18. ^{1}H NMR (600 MHz, DMSO-d6) of 2-bromo-4-(trifluoromethyl)aniline (1k).

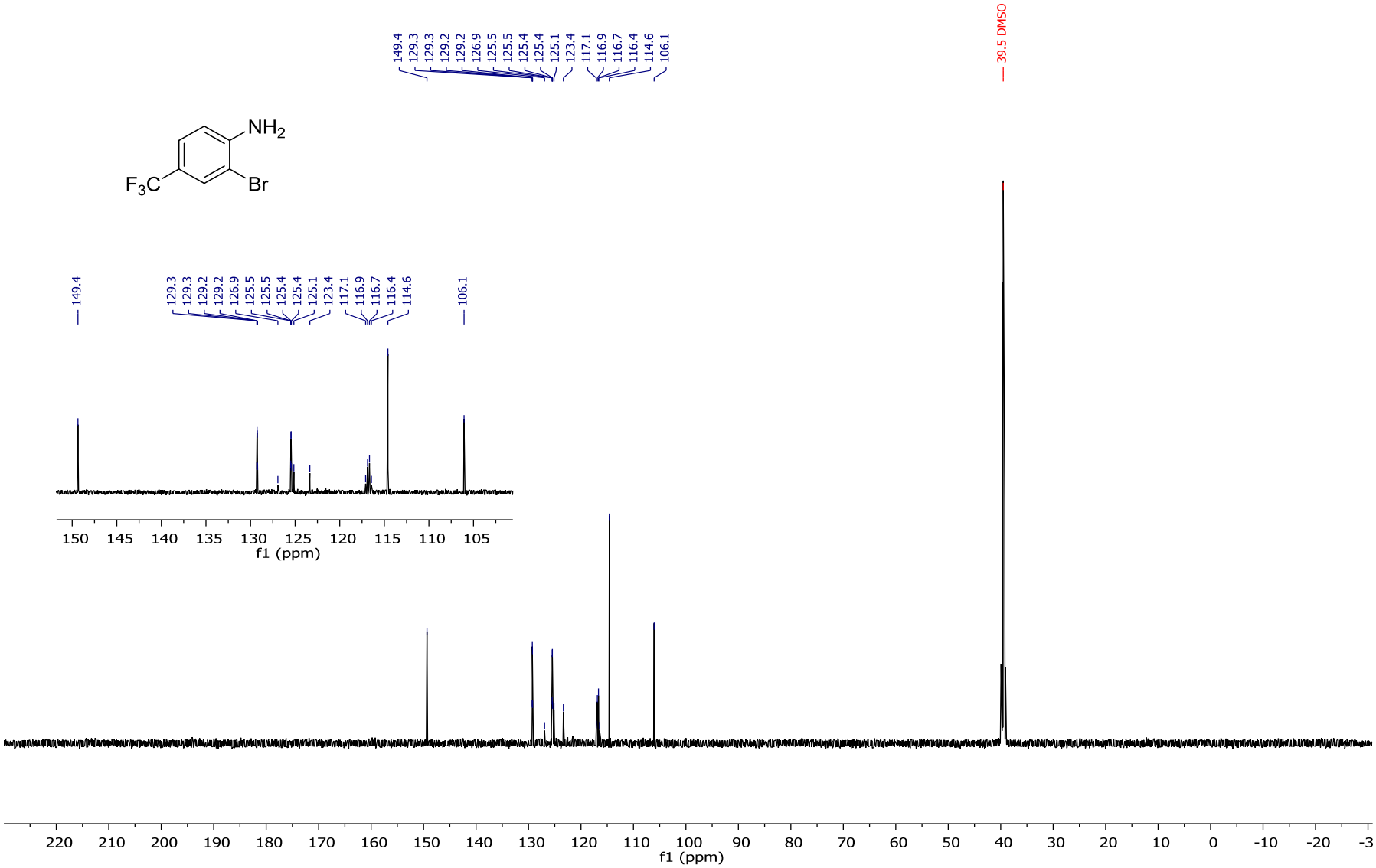


Figure S19. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d6) of 2-bromo-4-(trifluoromethyl)aniline (1k).

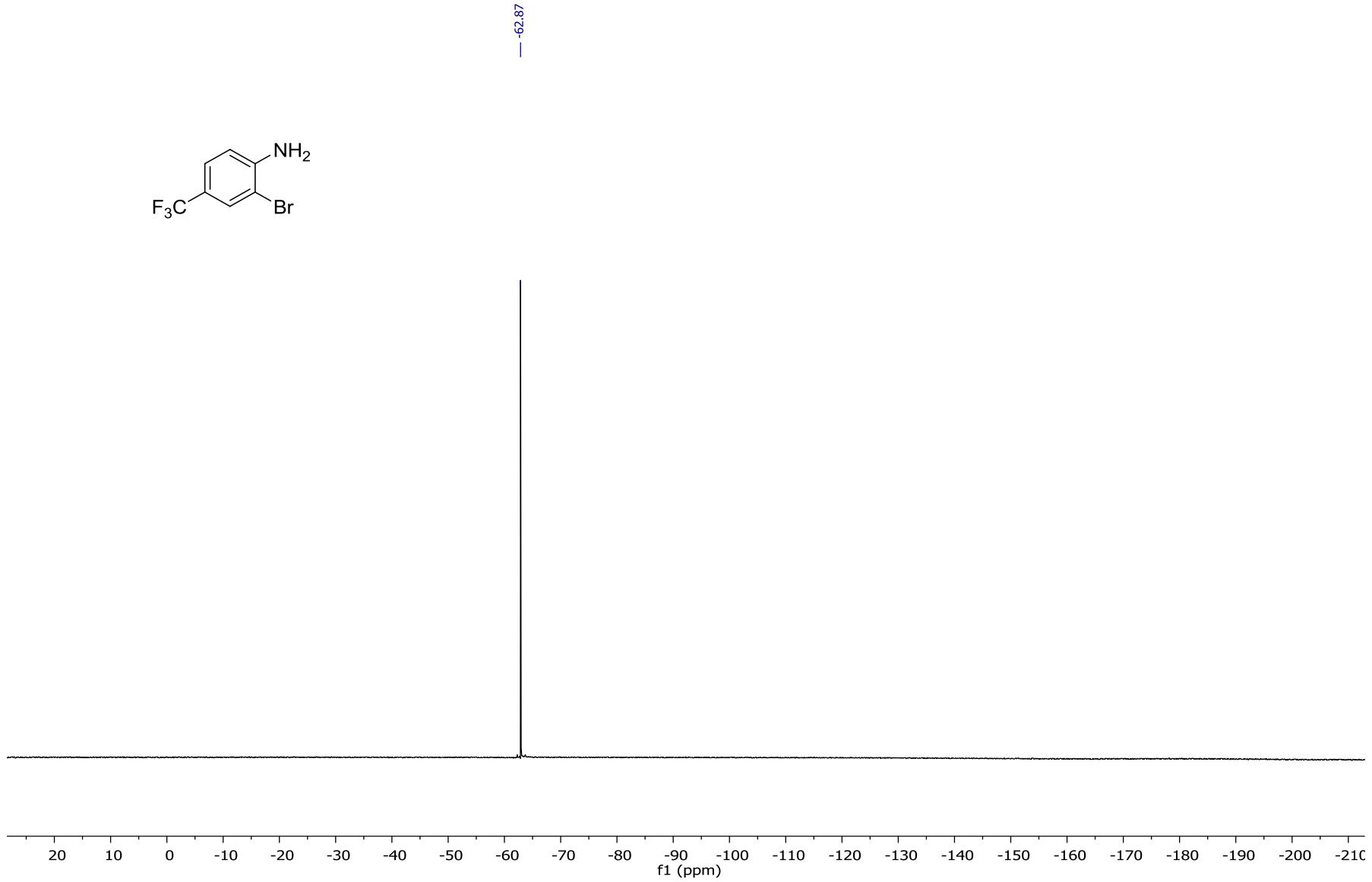


Figure S20. ^{19}F NMR (188 MHz, Chloroform-*d*) of 2-bromo-4-(trifluoromethyl)aniline (1k).

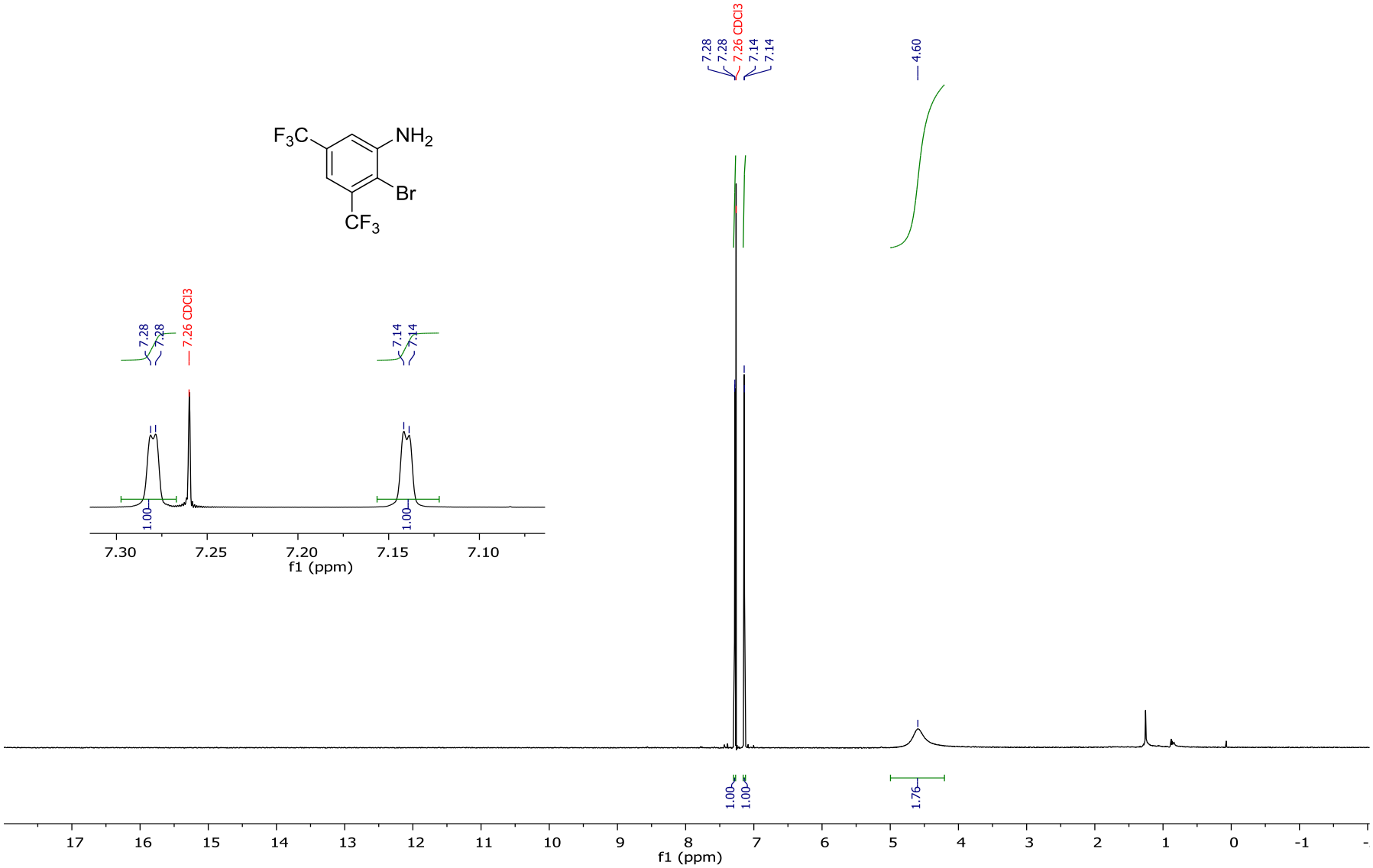


Figure S21. ^{1}H NMR (600 MHz, Chloroform-d) of 2-bromo-3,5-bis(trifluoromethyl)aniline (1l).

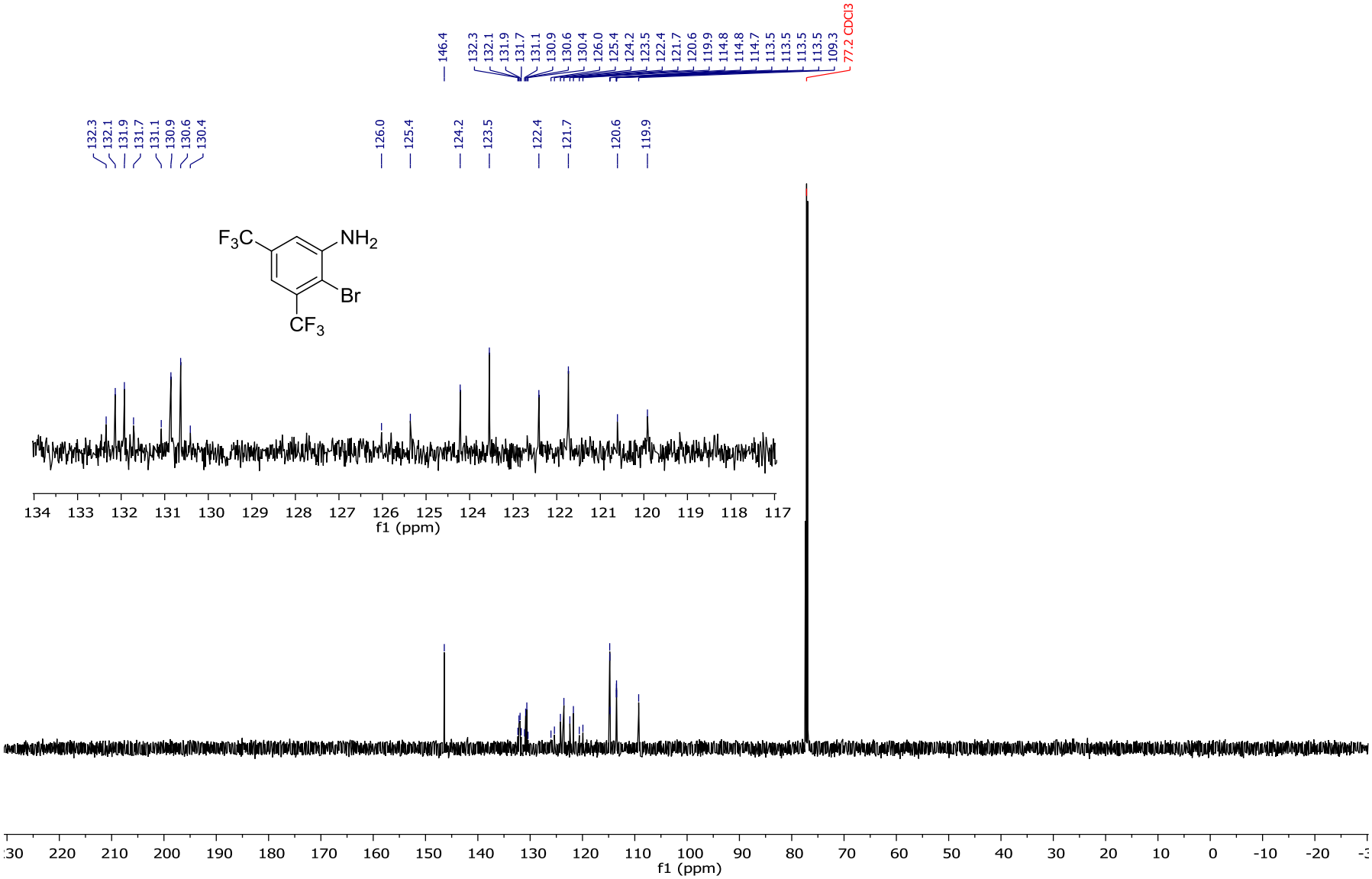


Figure S22. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-bromo-3,5-bis(trifluoromethyl)aniline (1l).

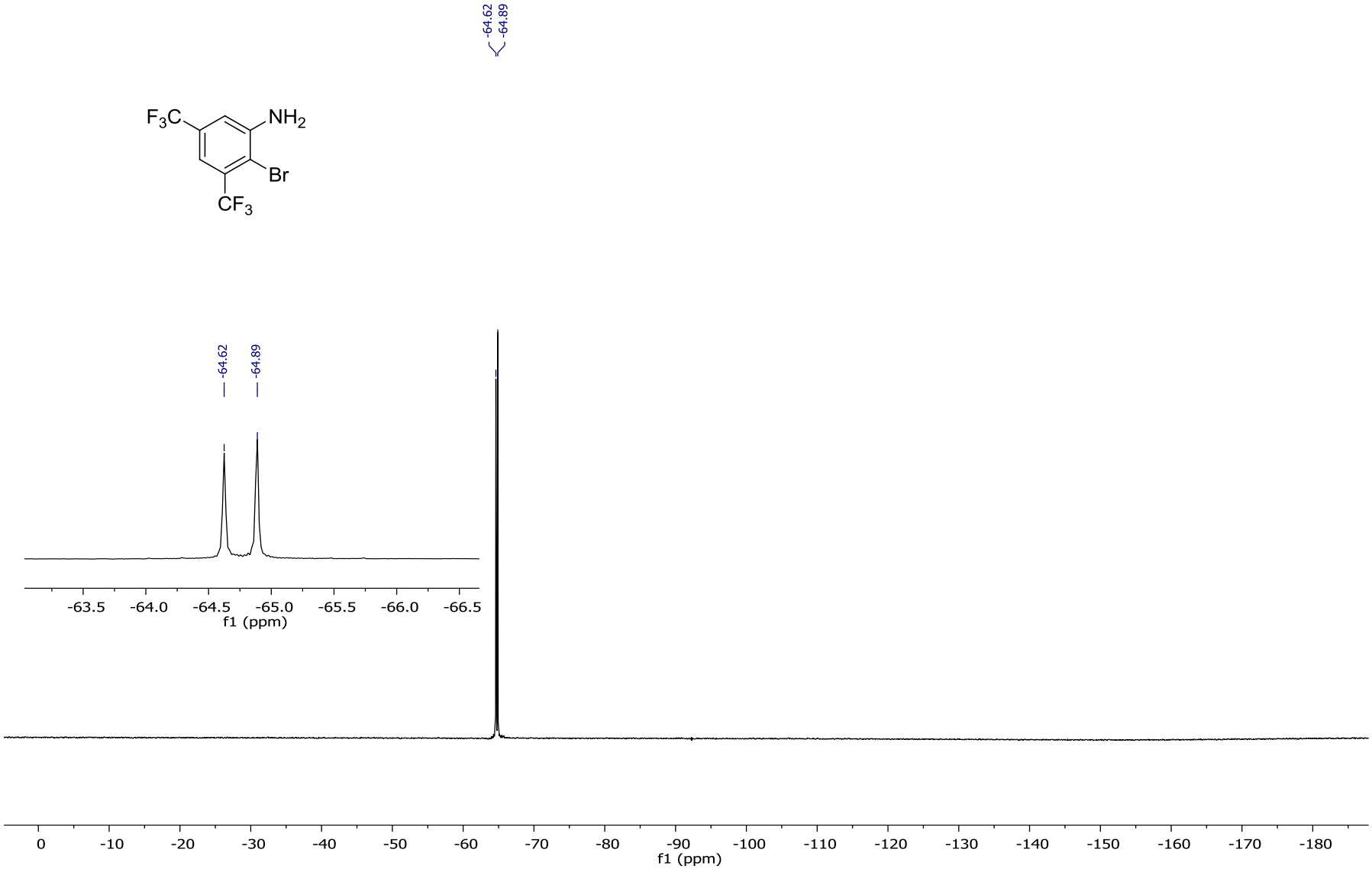


Figure S23. ^{19}F NMR (188 MHz, Chloroform-*d*) of 2-bromo-3,5-bis(trifluoromethyl)aniline (1l).

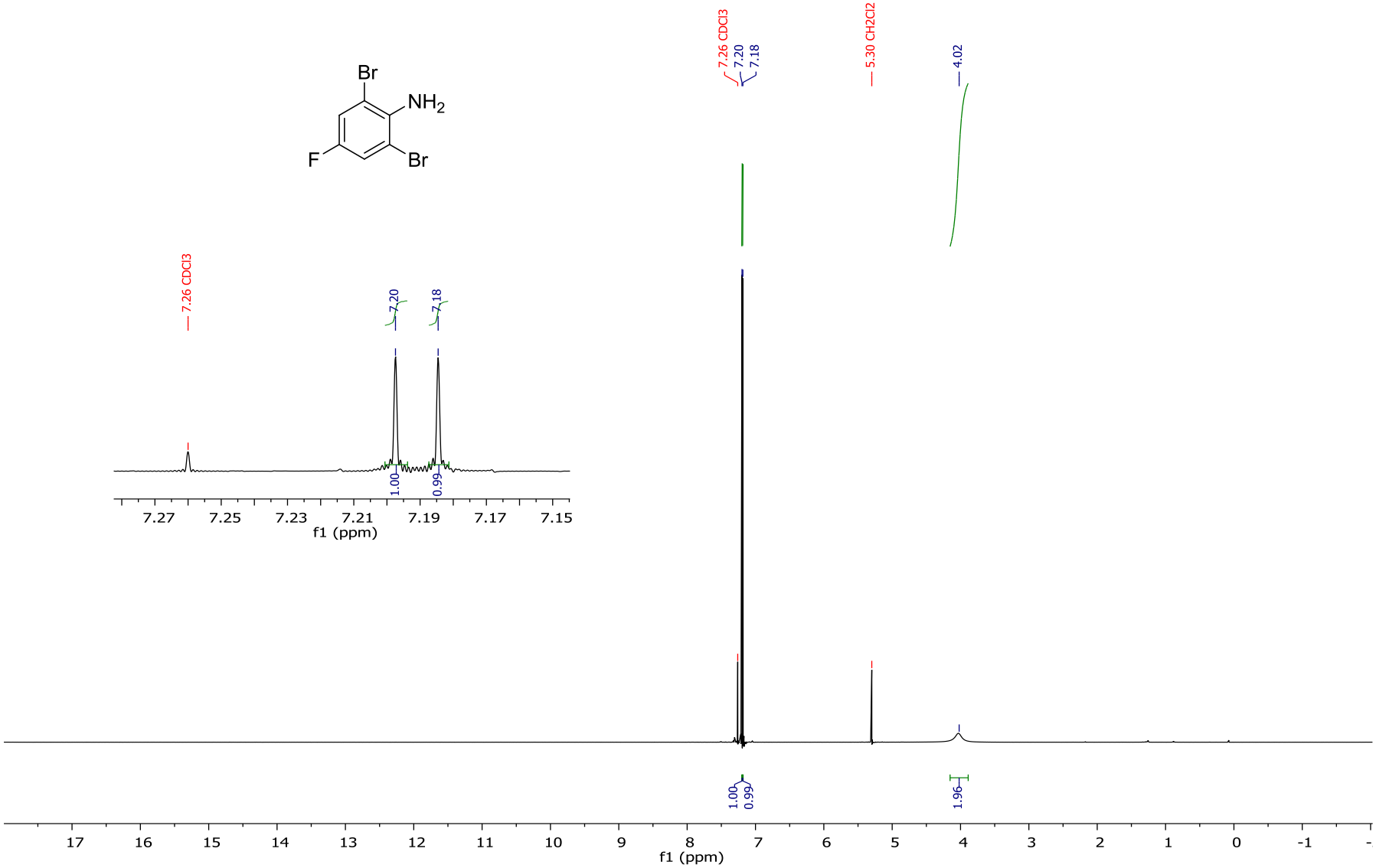


Figure S24. ^{1}H NMR (600 MHz, Chloroform-d) of 2,6-dibromo-4-fluoroaniline (1n).

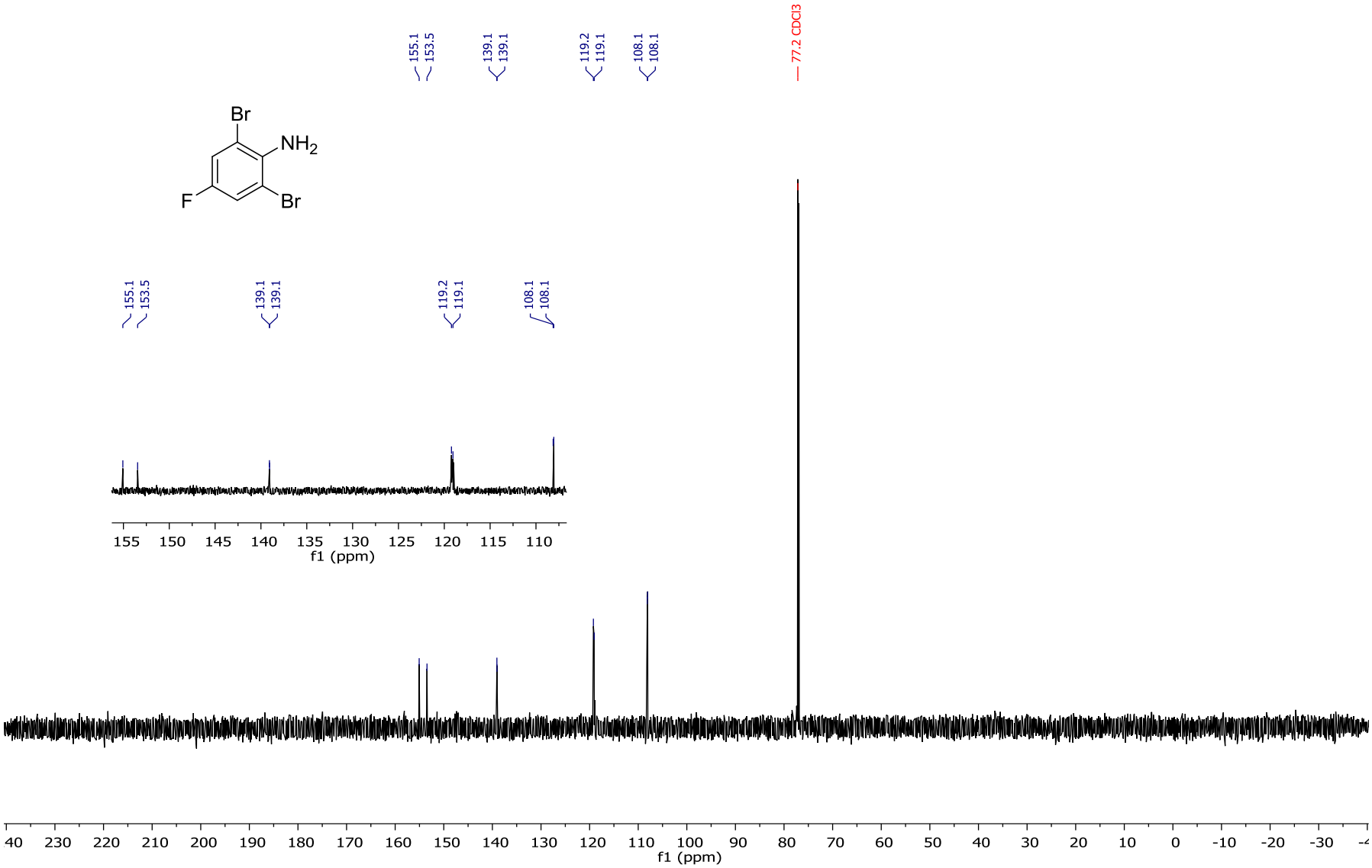


Figure S25. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2,6-dibromo-4-fluoroaniline (1n).

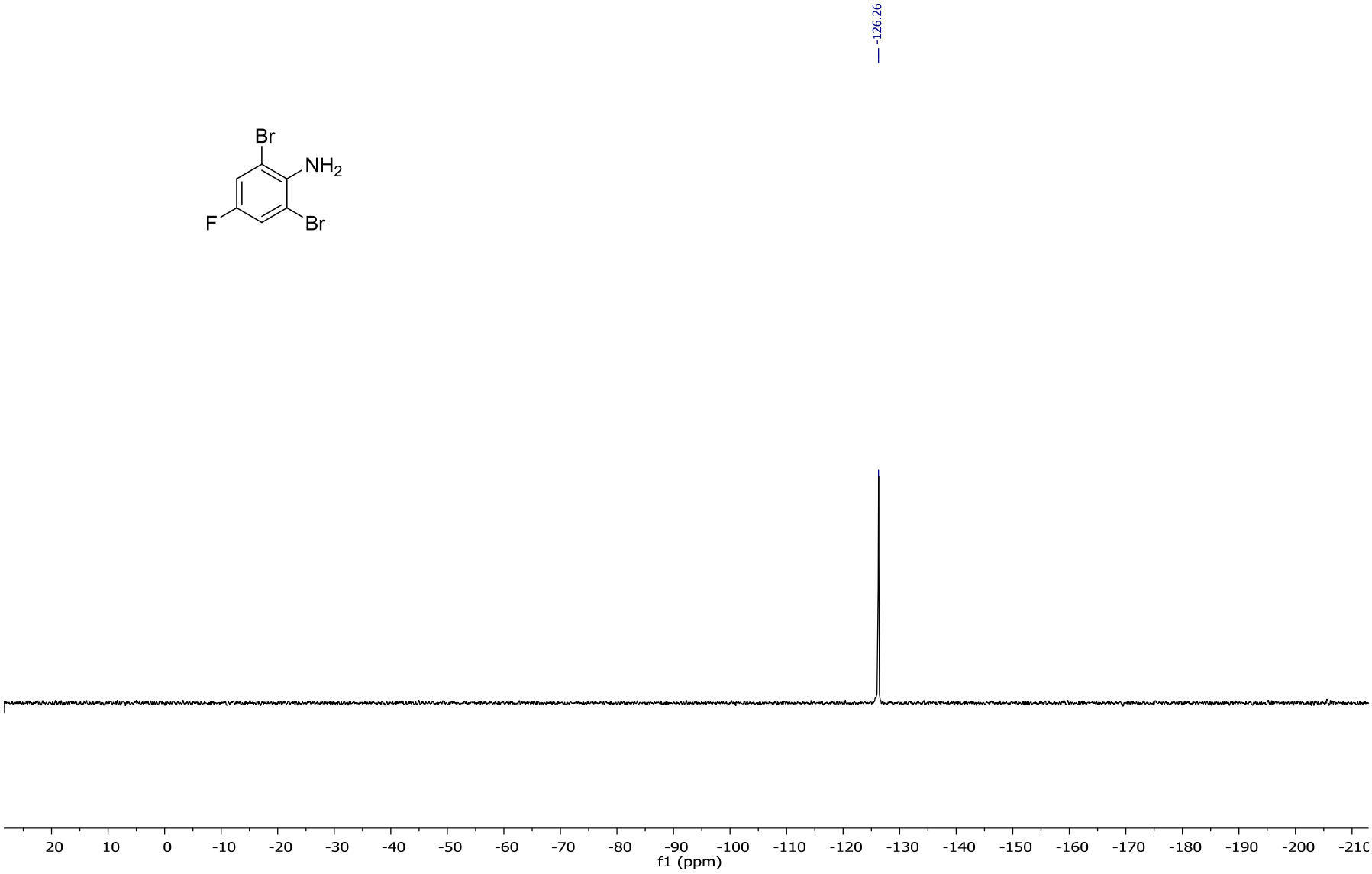


Figure S26. ^{19}F NMR (188 MHz, Chloroform-*d*) of 2,6-dibromo-4-fluoroaniline (1n).

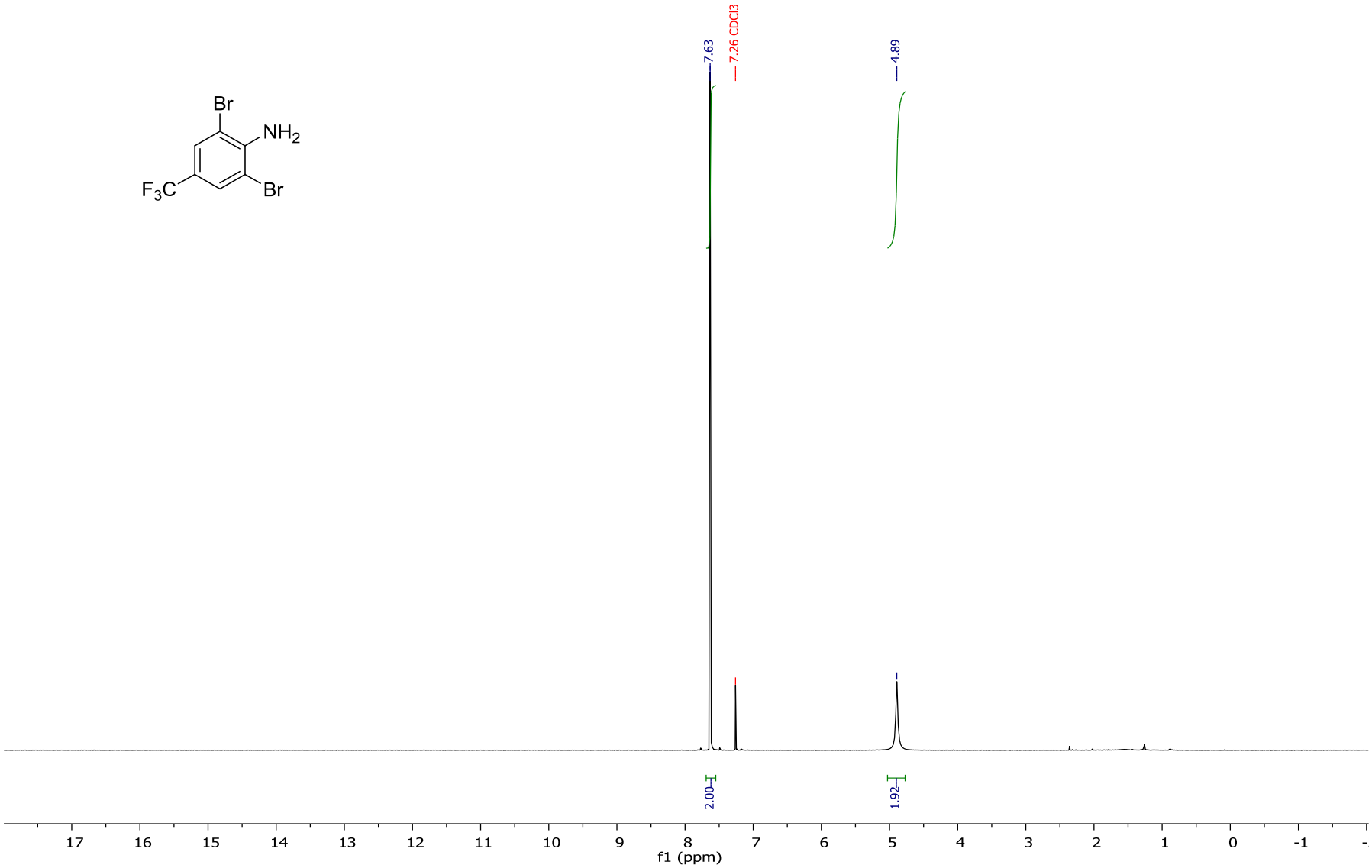


Figure S27. ^{1}H NMR (600 MHz, Chloroform-d) of 2,6-dibromo-4-(trifluoromethyl)aniline (1o).

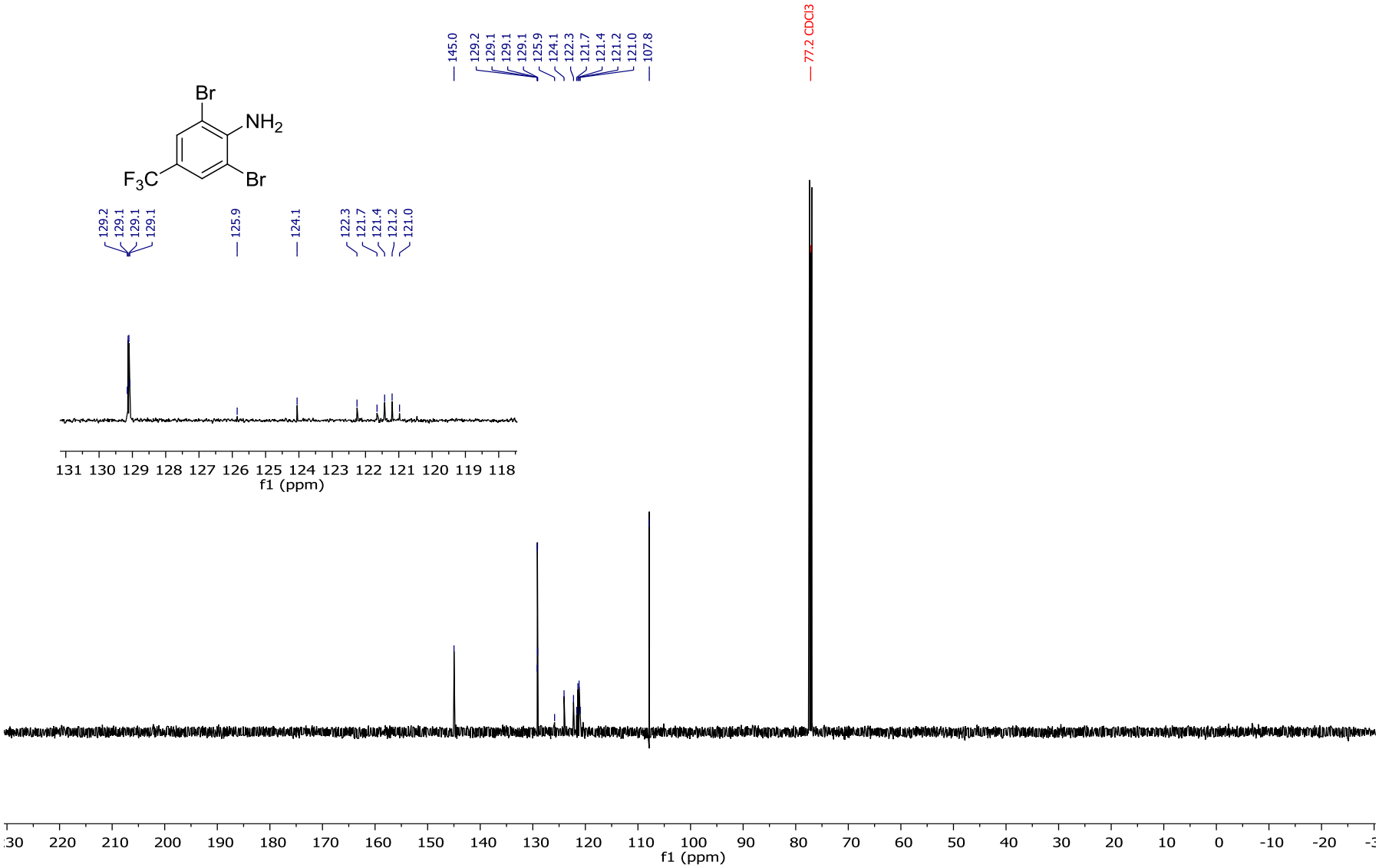


Figure S28. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2,6-dibromo-4-(trifluoromethyl)aniline (1o).

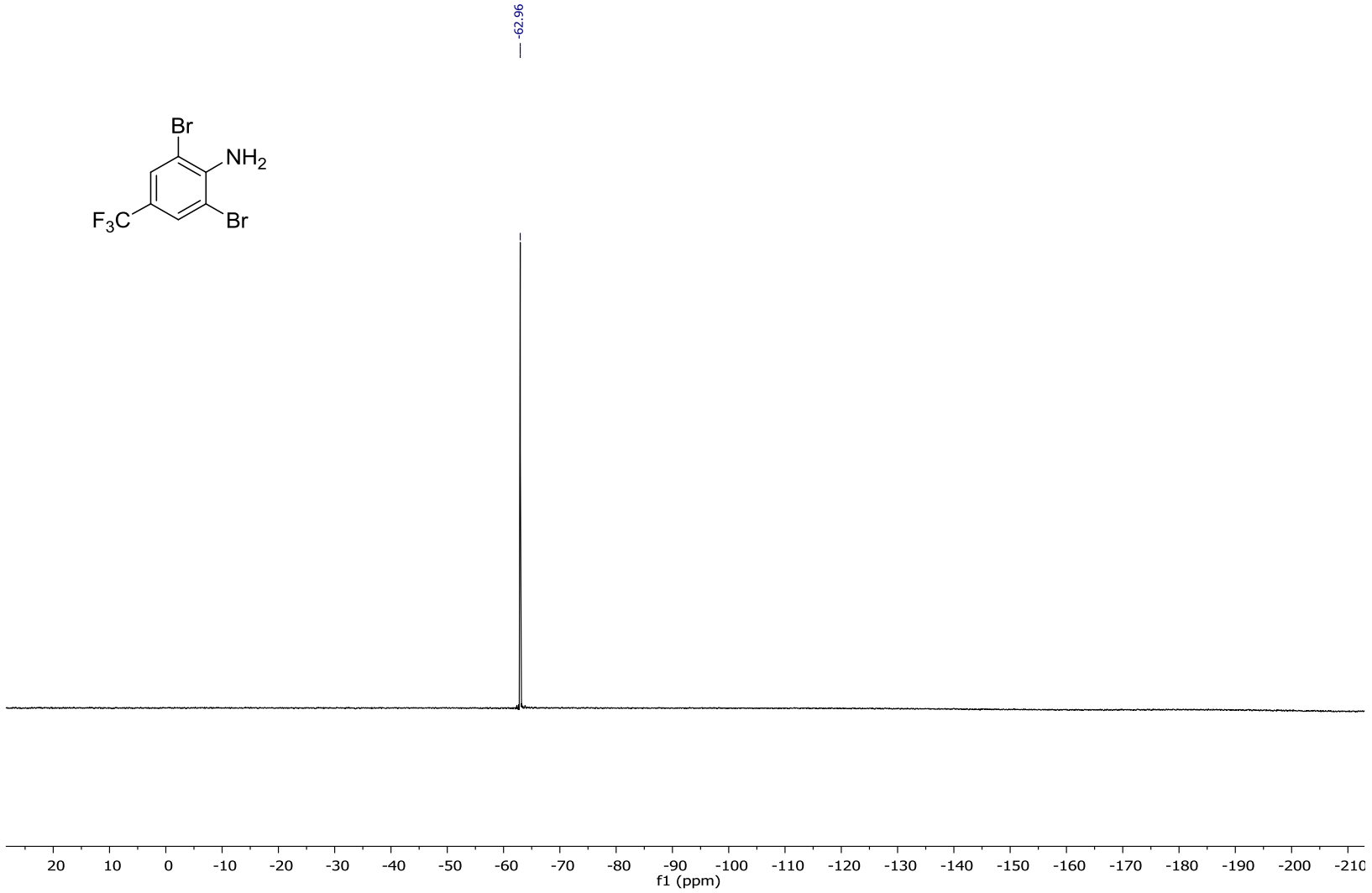


Figure S29. ^{19}F NMR (188 MHz, Chloroform-*d*) of 2,6-dibromo-4-(trifluoromethyl)aniline (1o).

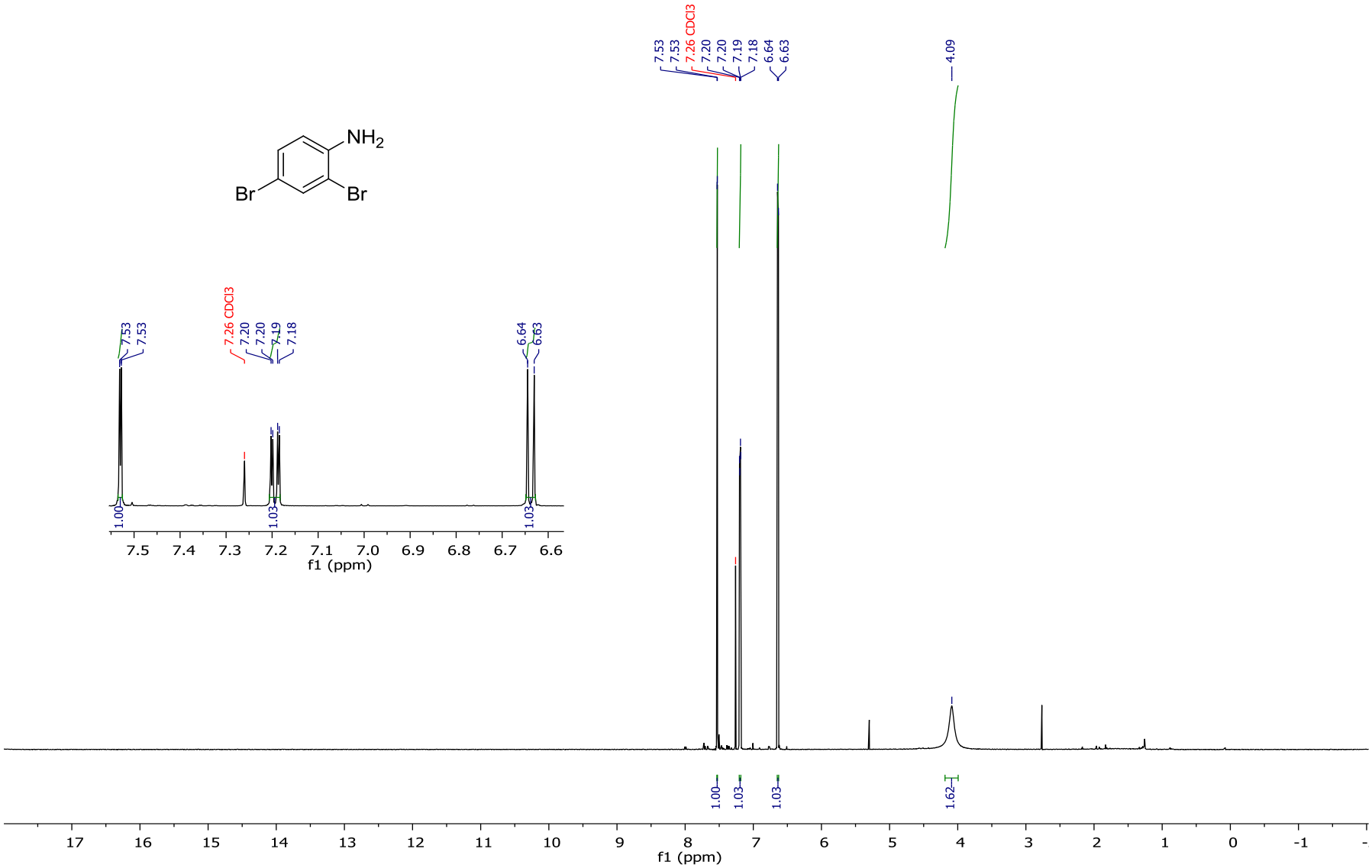


Figure S30. ^{1}H NMR (600 MHz, Chloroform-*d*) of 2,4-dibromoaniline (1p).

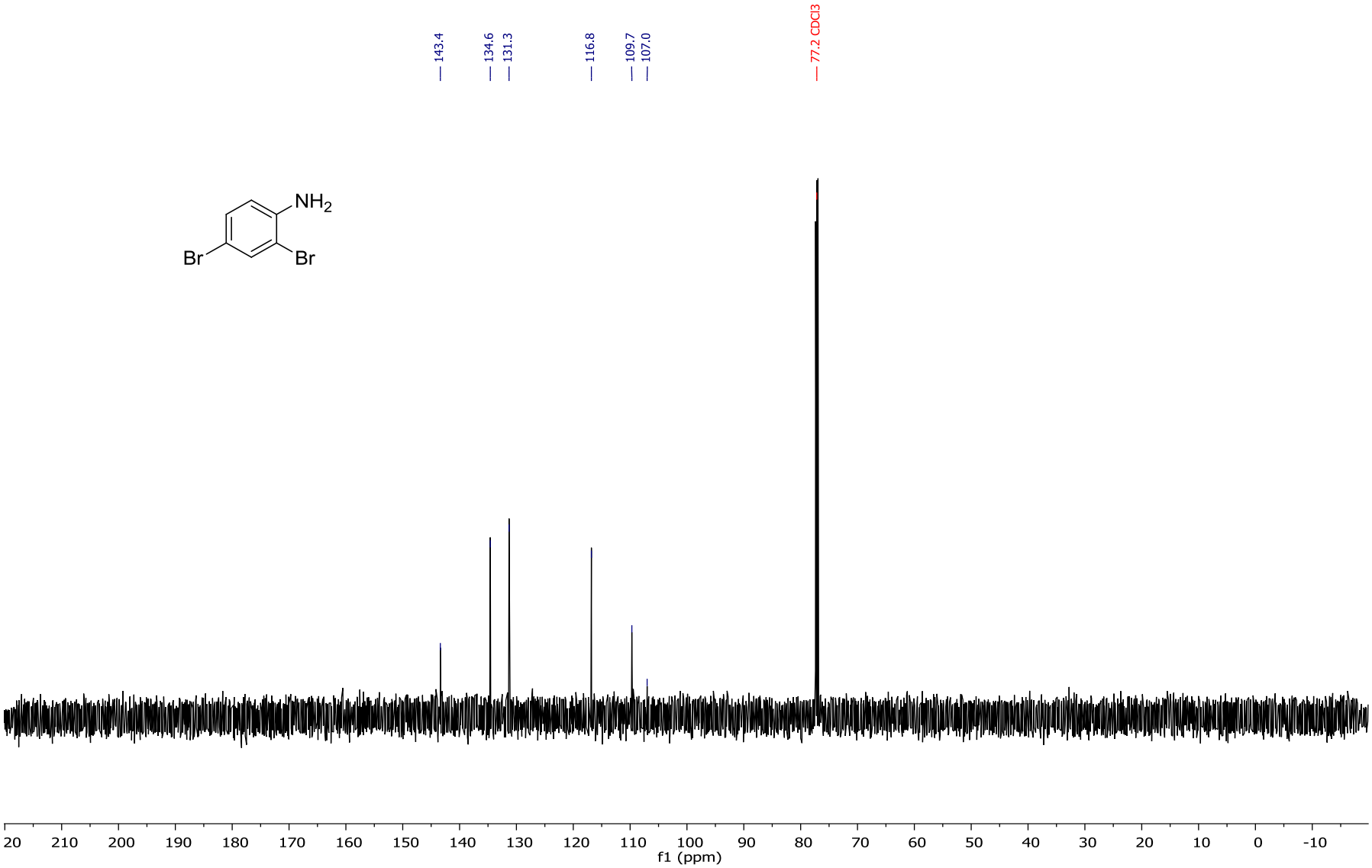


Figure S31. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2,4-dibromoaniline (1p).

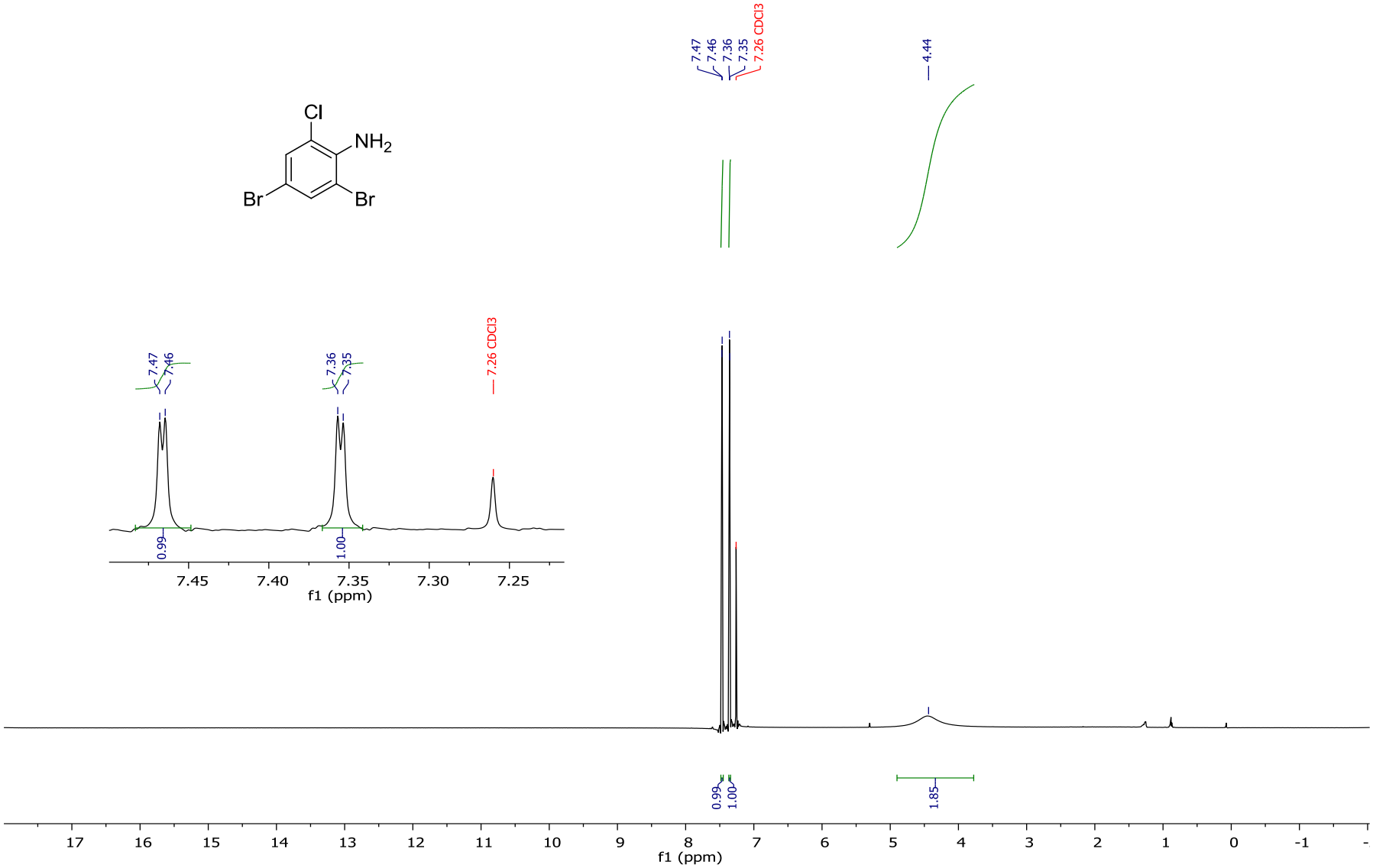


Figure S32. ^{1}H NMR (600 MHz, Chloroform-d) of 2,4-dibromo-6-chloroaniline (1r).

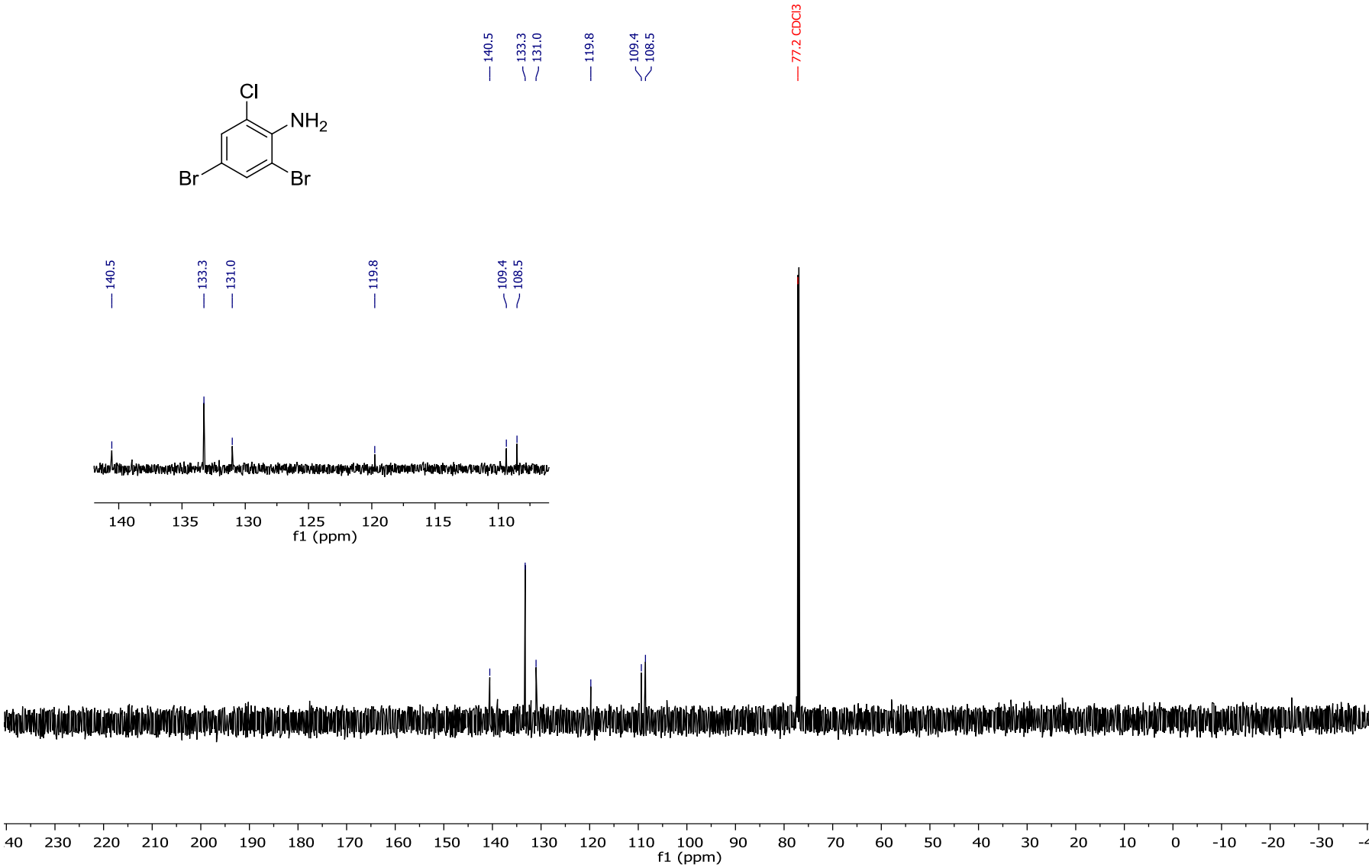


Figure S33. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2,4-dibromo-6-chloroaniline (1r).

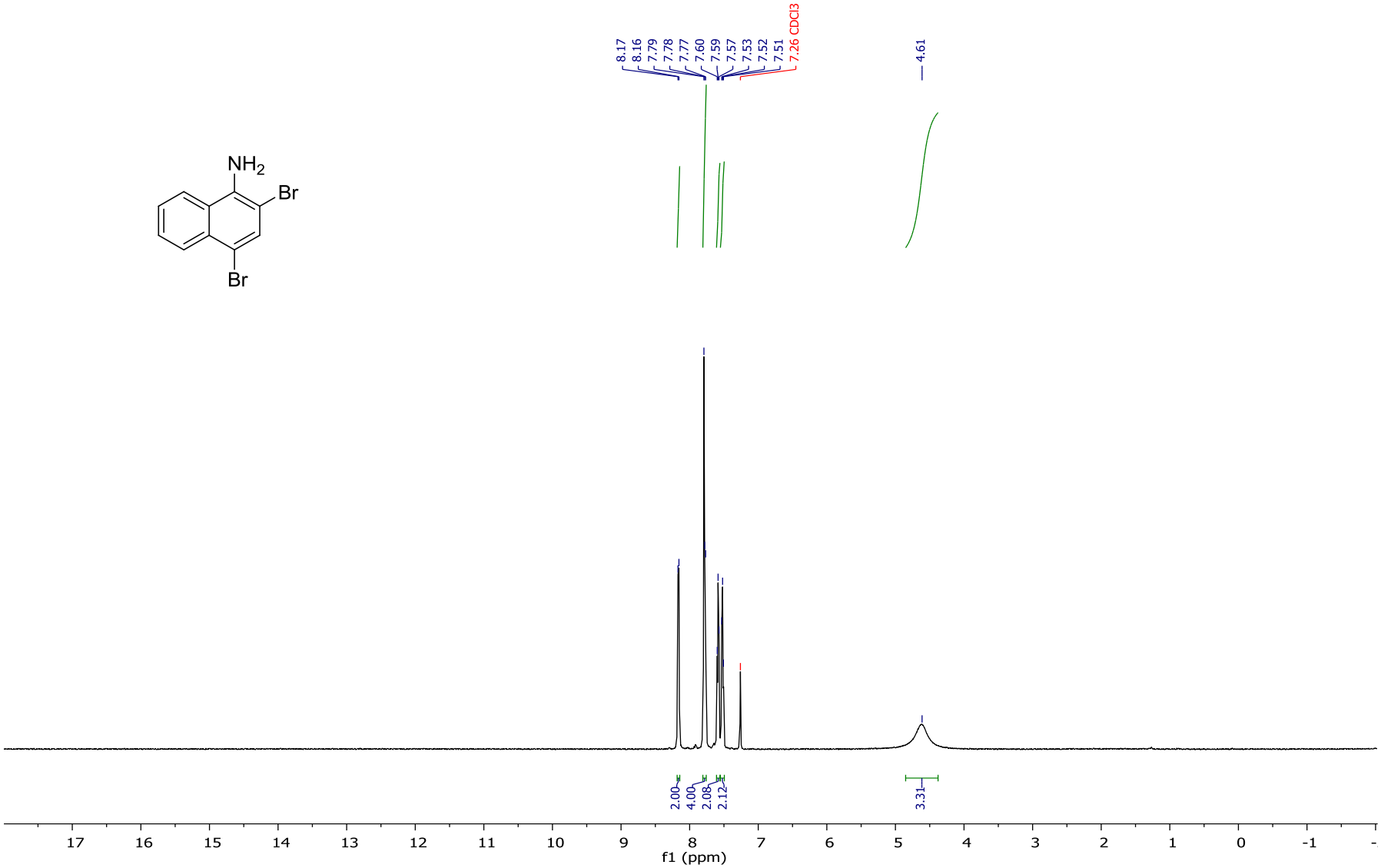


Figure S34. ^{1}H NMR (600 MHz, Chloroform-d) of 2,4-dibromonaphthalen-1-amine (1s).

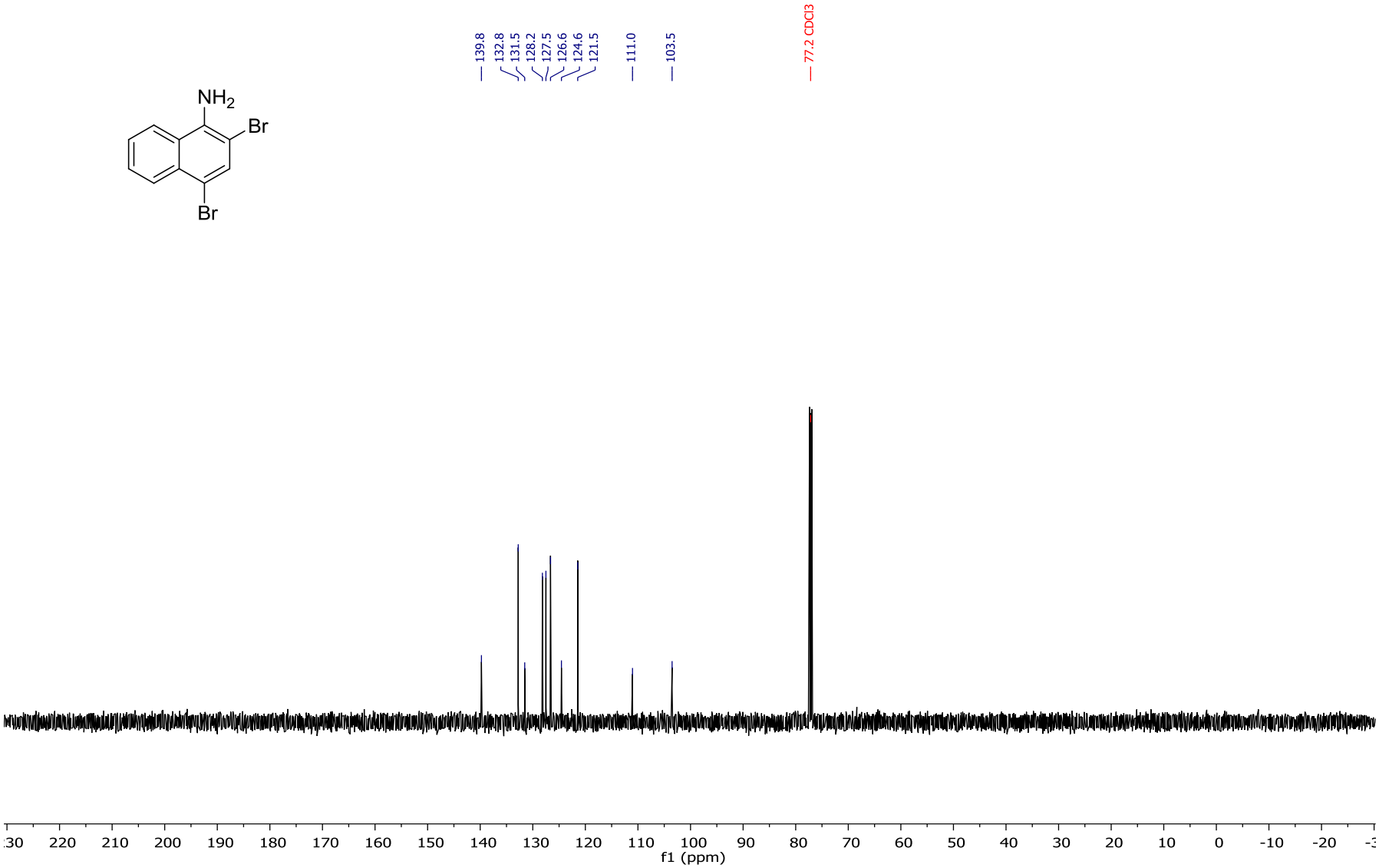


Figure S35. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2,4-dibromonaphthalen-1-amine (1s).

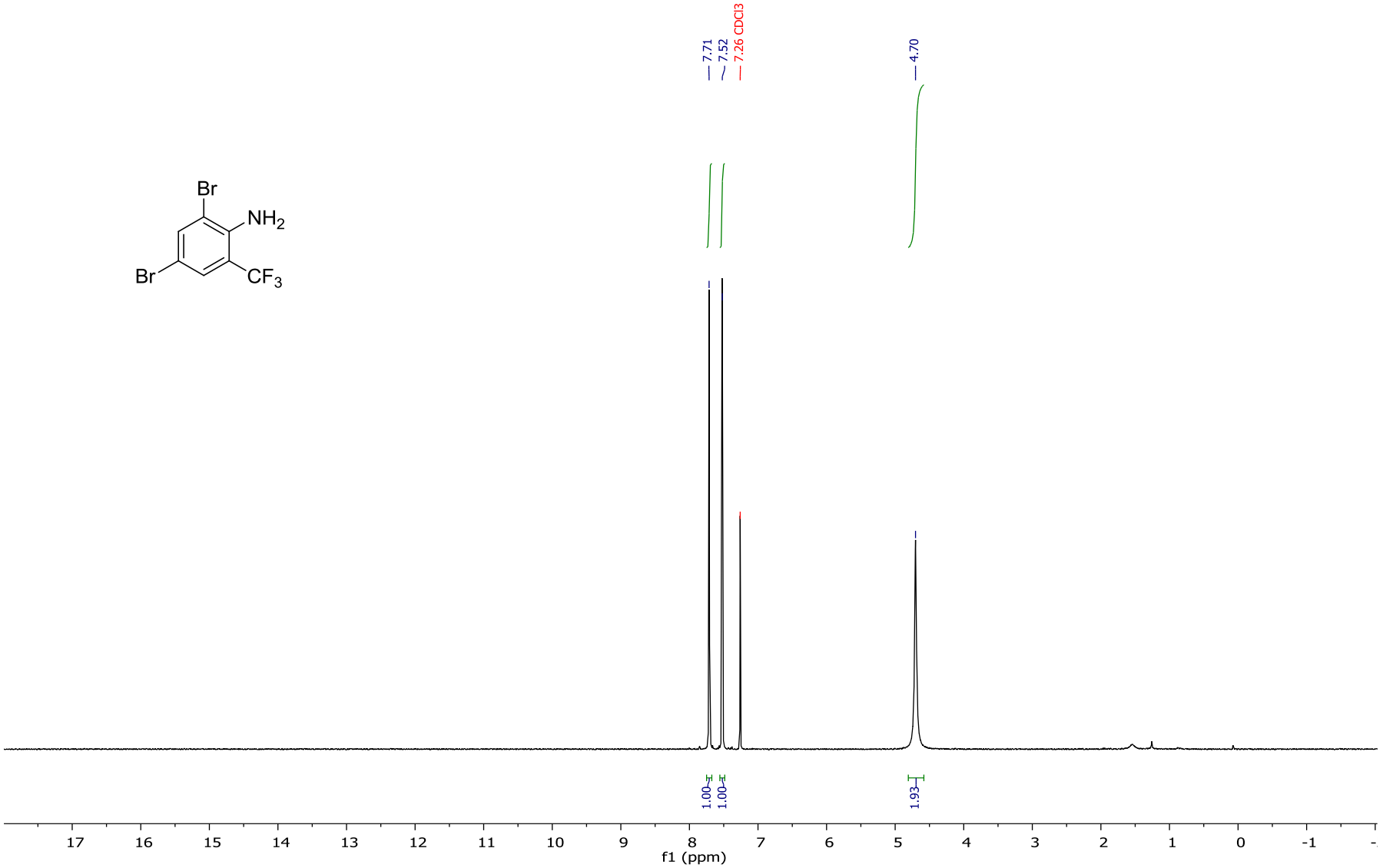


Figure S36. ^{1}H NMR (600 MHz, Chloroform-d) of 2,4-dibromo-6-(trifluoromethyl)aniline (1t).

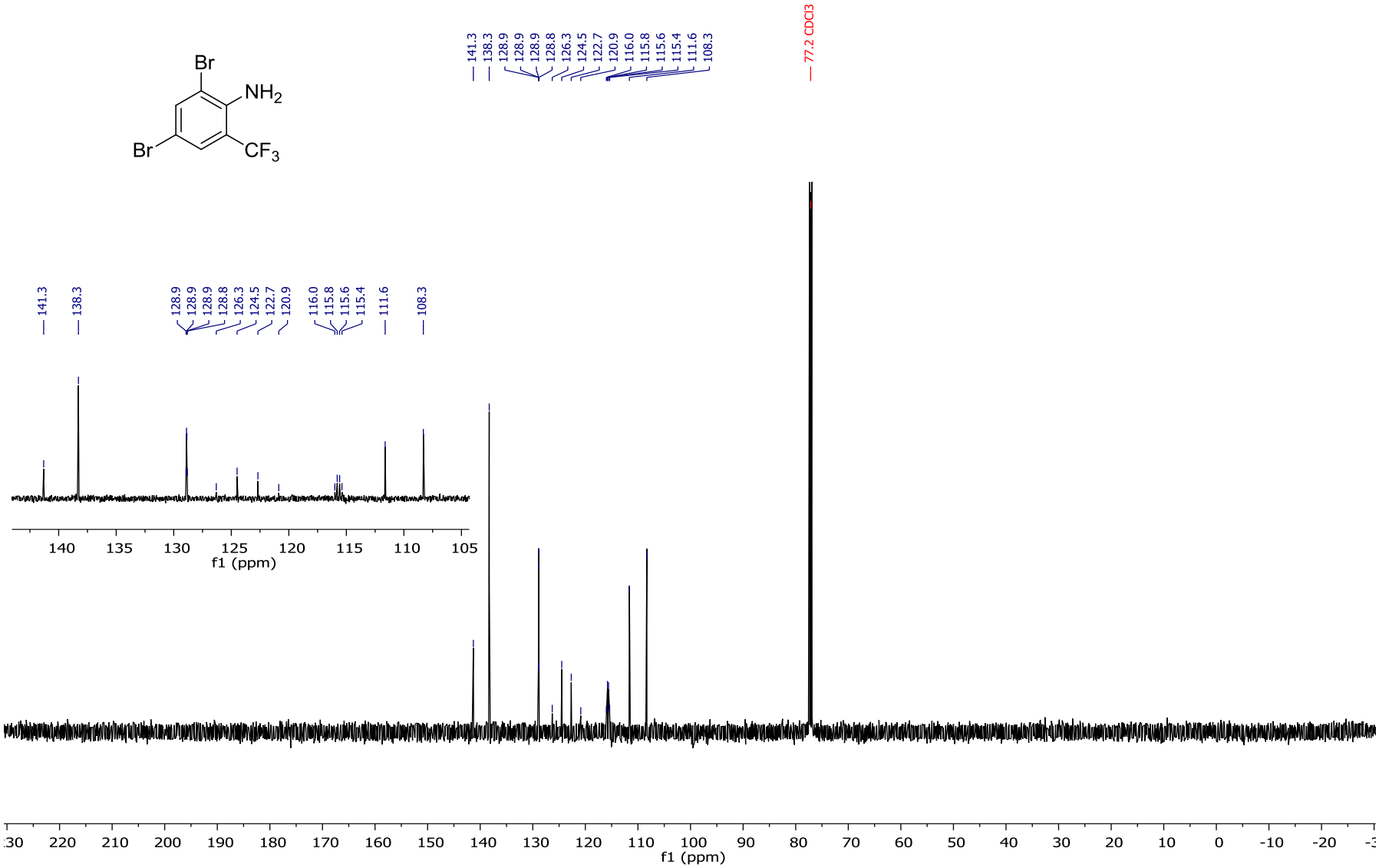


Figure S37. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2,4-dibromo-6-(trifluoromethyl)aniline (1t).

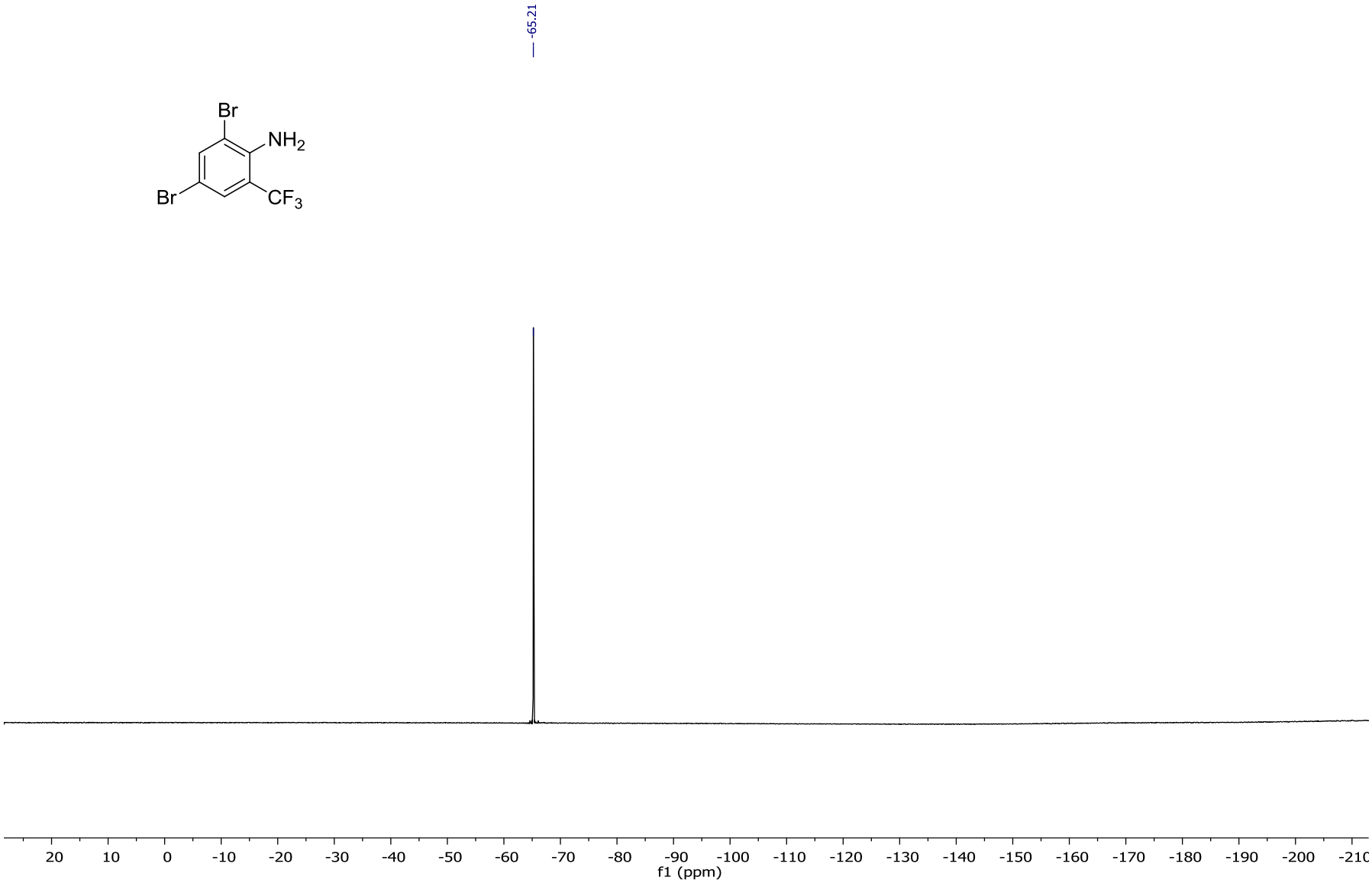


Figure S38. ^{19}F NMR (188 MHz, Chloroform-*d*) of 2,4-dibromo-6-(trifluoromethyl)aniline (1t).

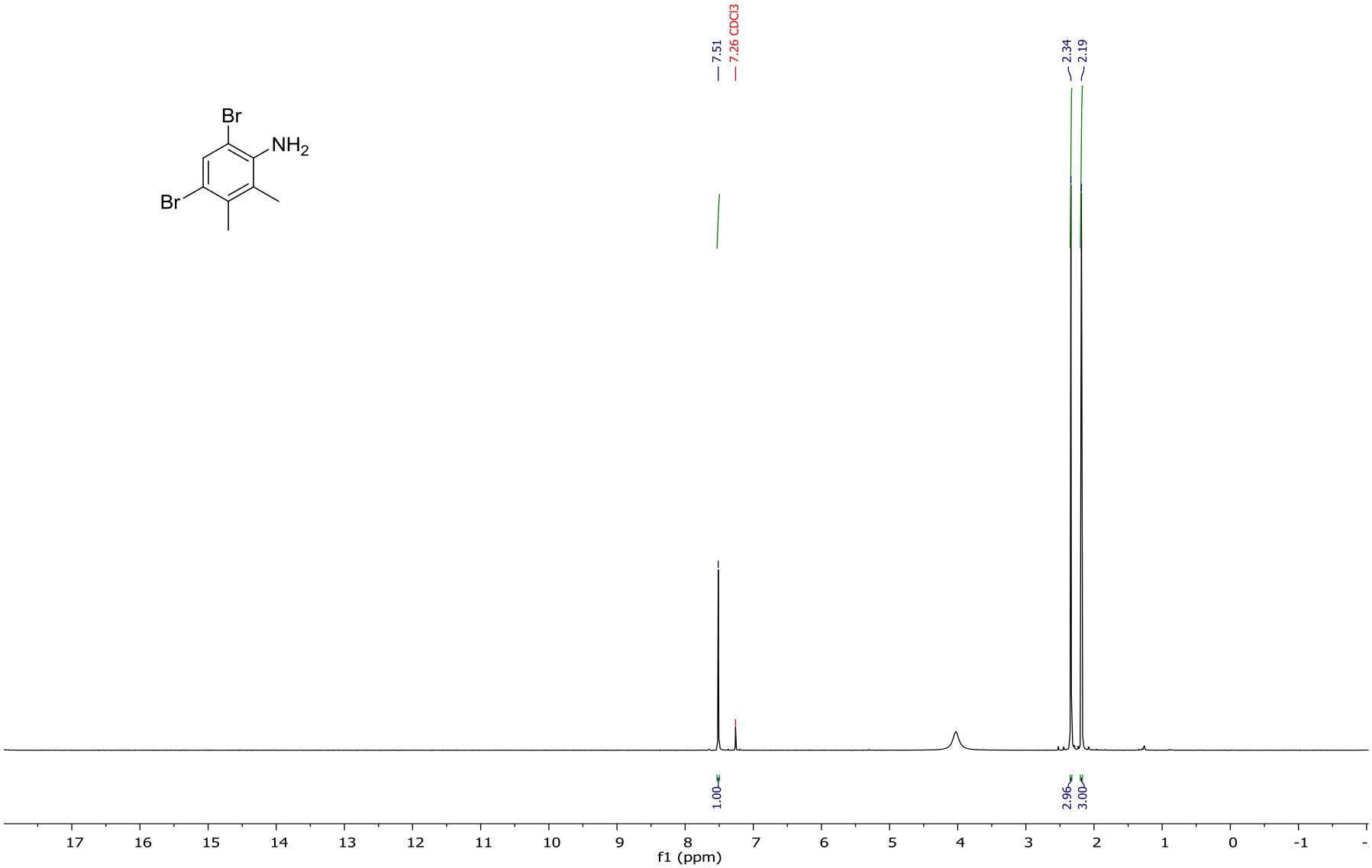


Figure S39. ^{1}H NMR (600 MHz, Chloroform-d) of 4,6-dibromo-2,3-dimethylaniline (1u).

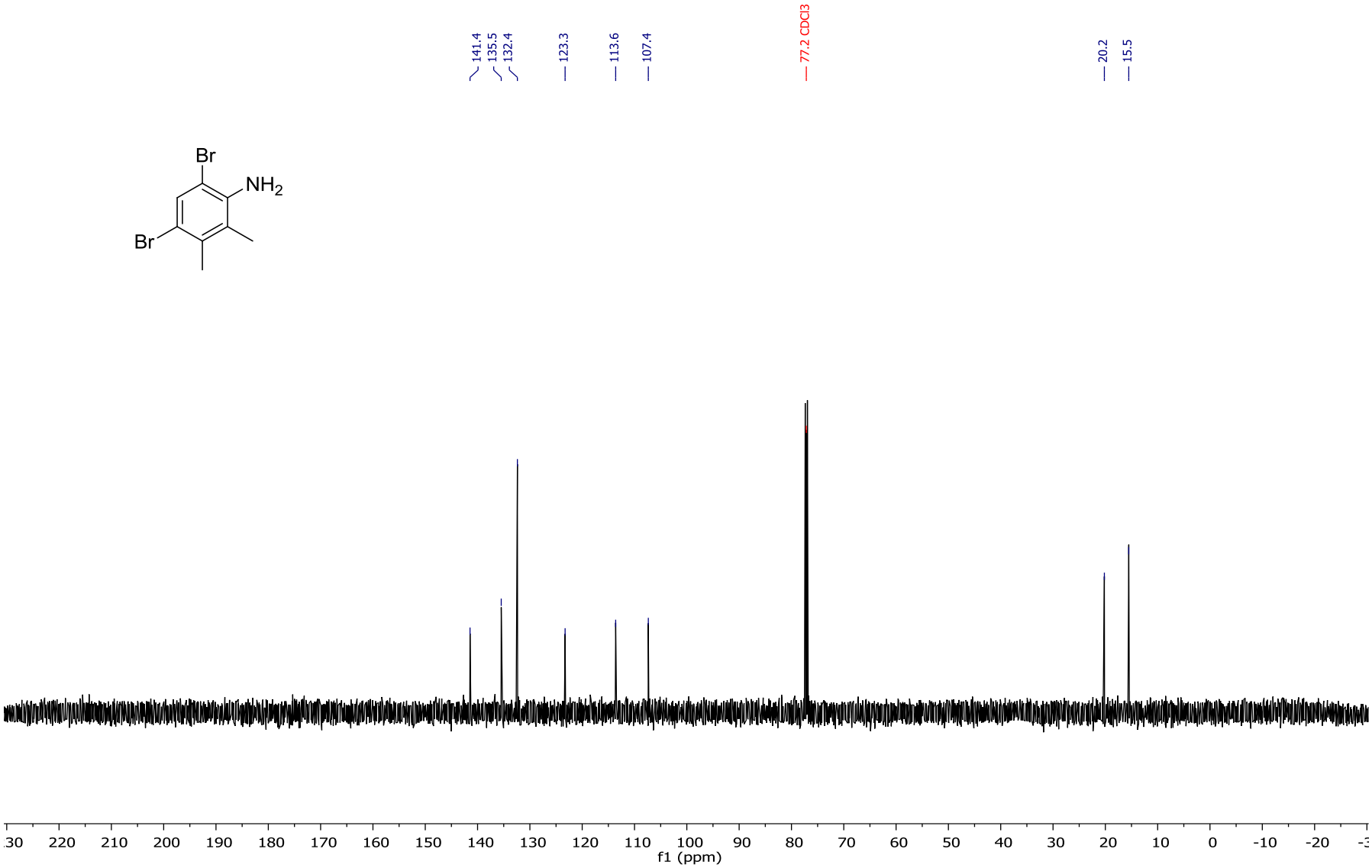


Figure S40. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 4,6-dibromo-2,3-dimethylaniline (1u).

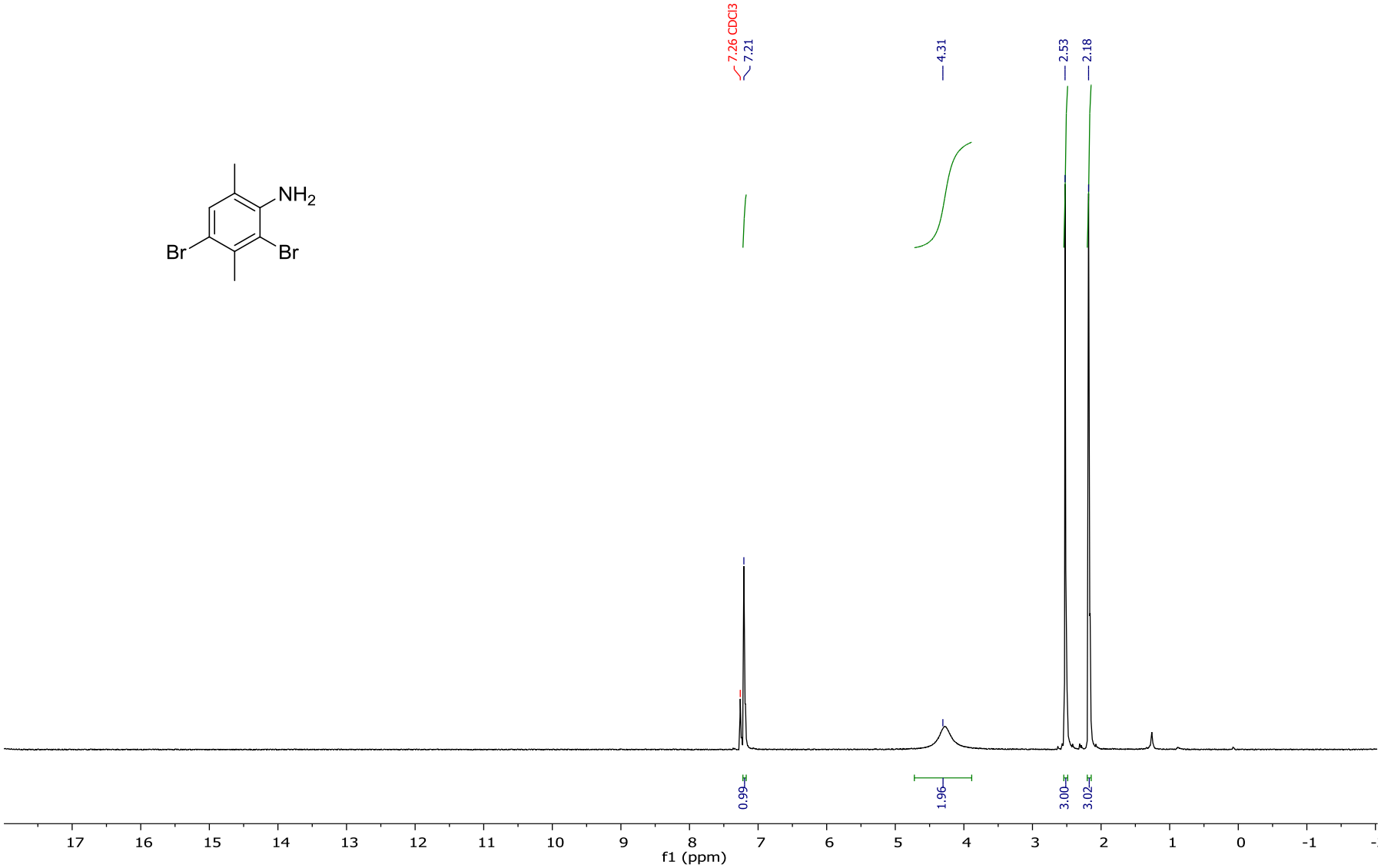


Figure S41. ^{1}H NMR (600 MHz, Chloroform-d) of 2,4-dibromo-3,6-dimethylaniline (1v).

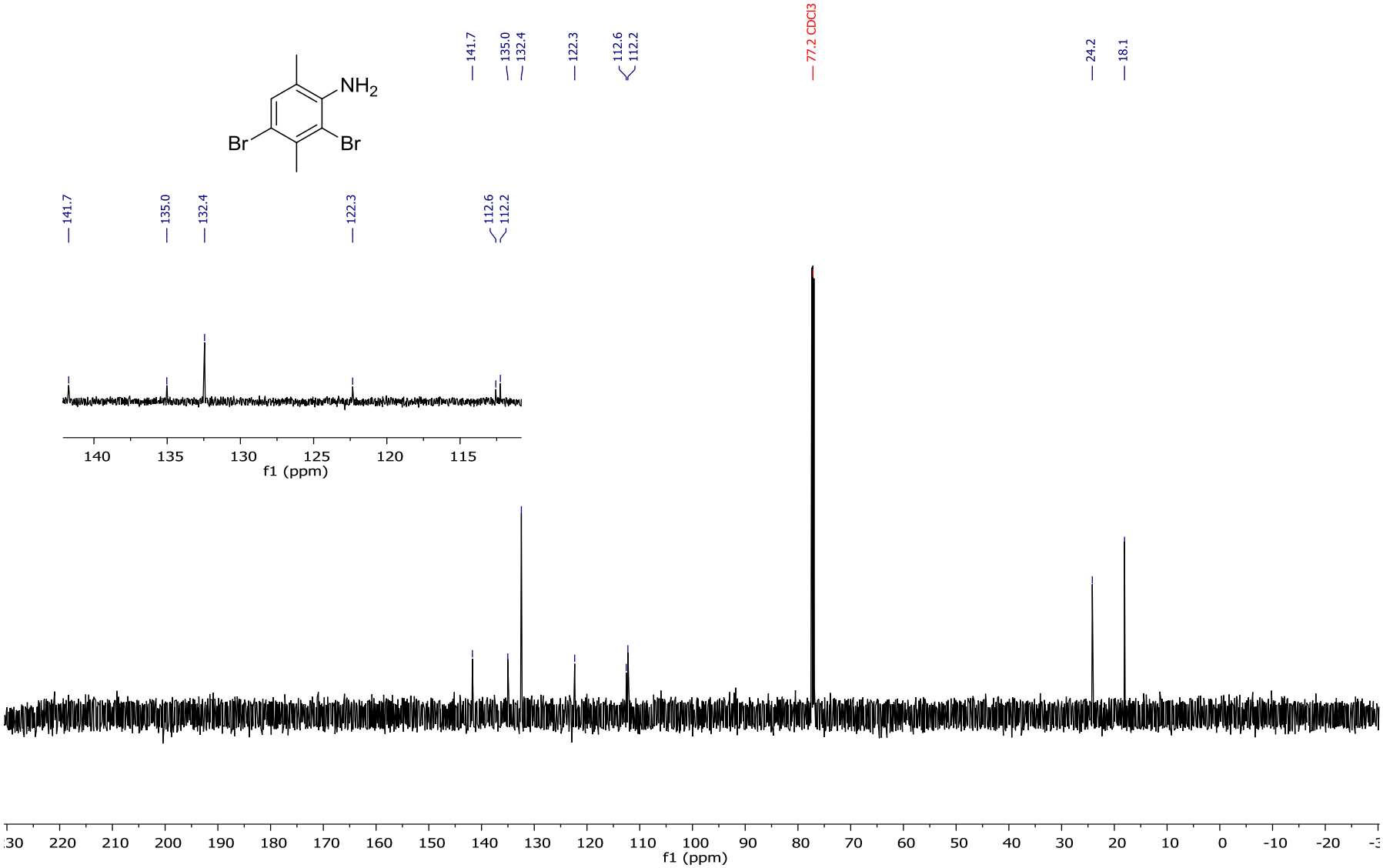


Figure S42. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2,4-dibromo-3,6-dimethylaniline (1v).

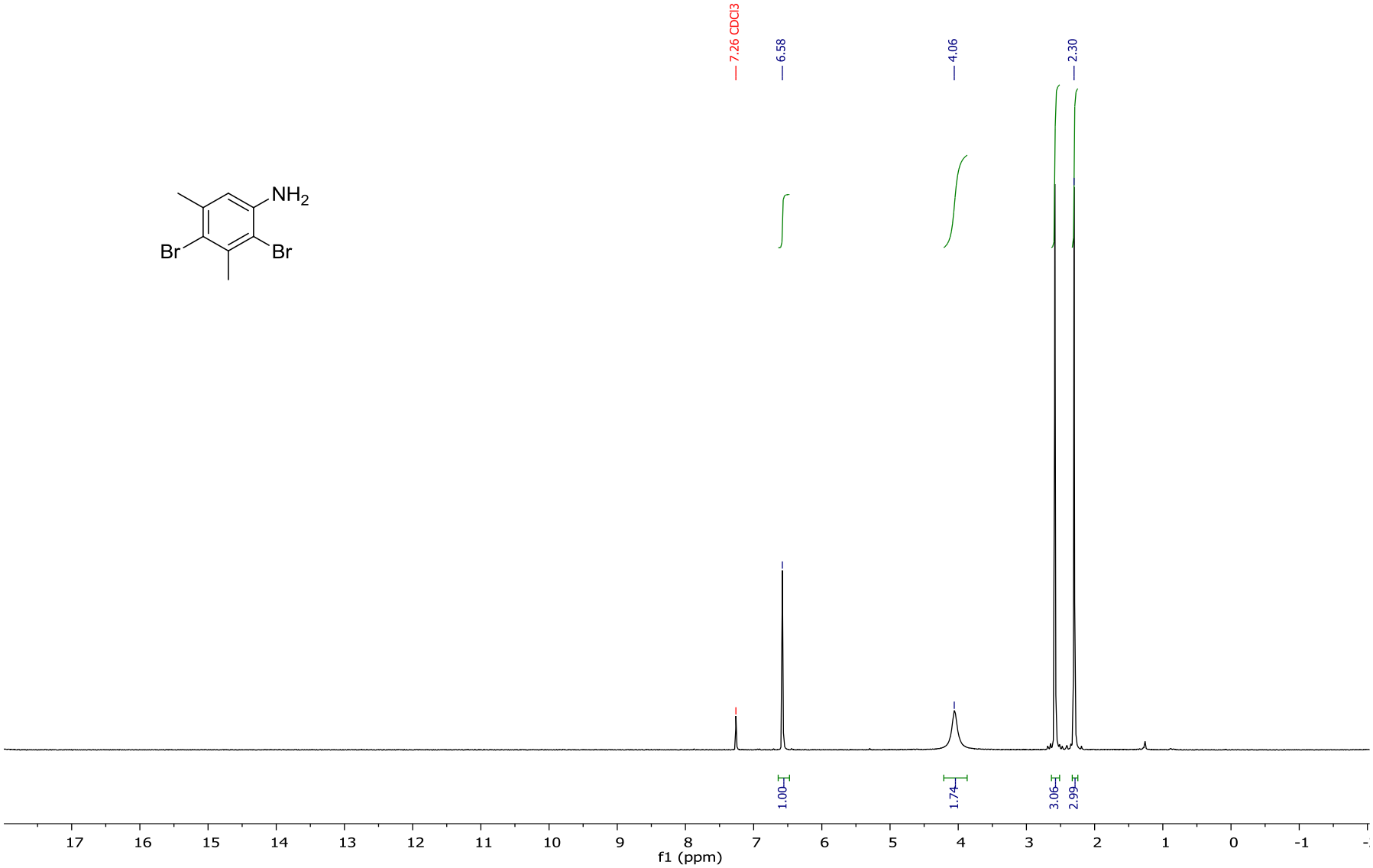


Figure S43. ^{1}H NMR (600 MHz, Chloroform-d) of 2,4-dibromo-3,5-dimethylaniline (1w).

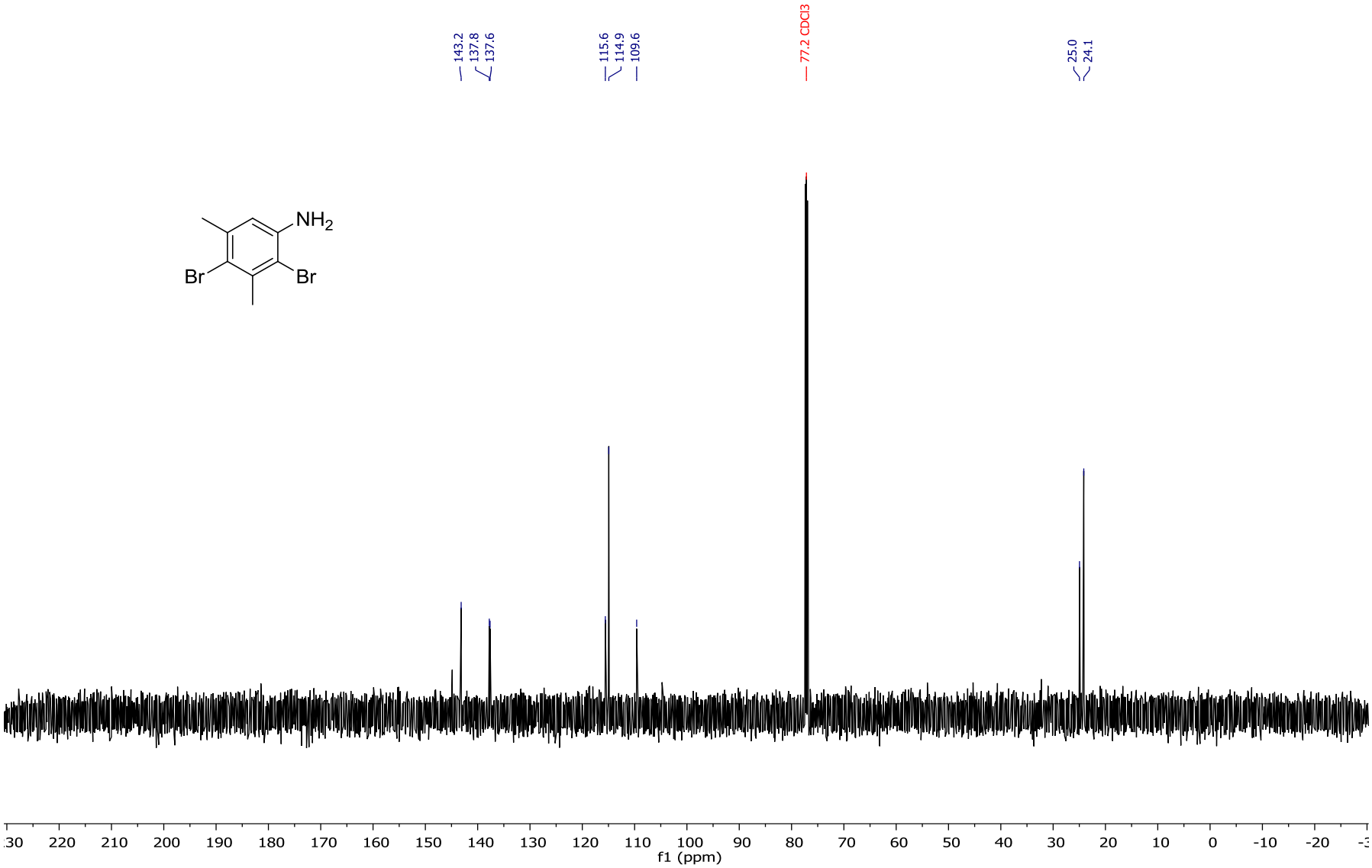


Figure S44. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2,4-dibromo-3,5-dimethylaniline (1w).

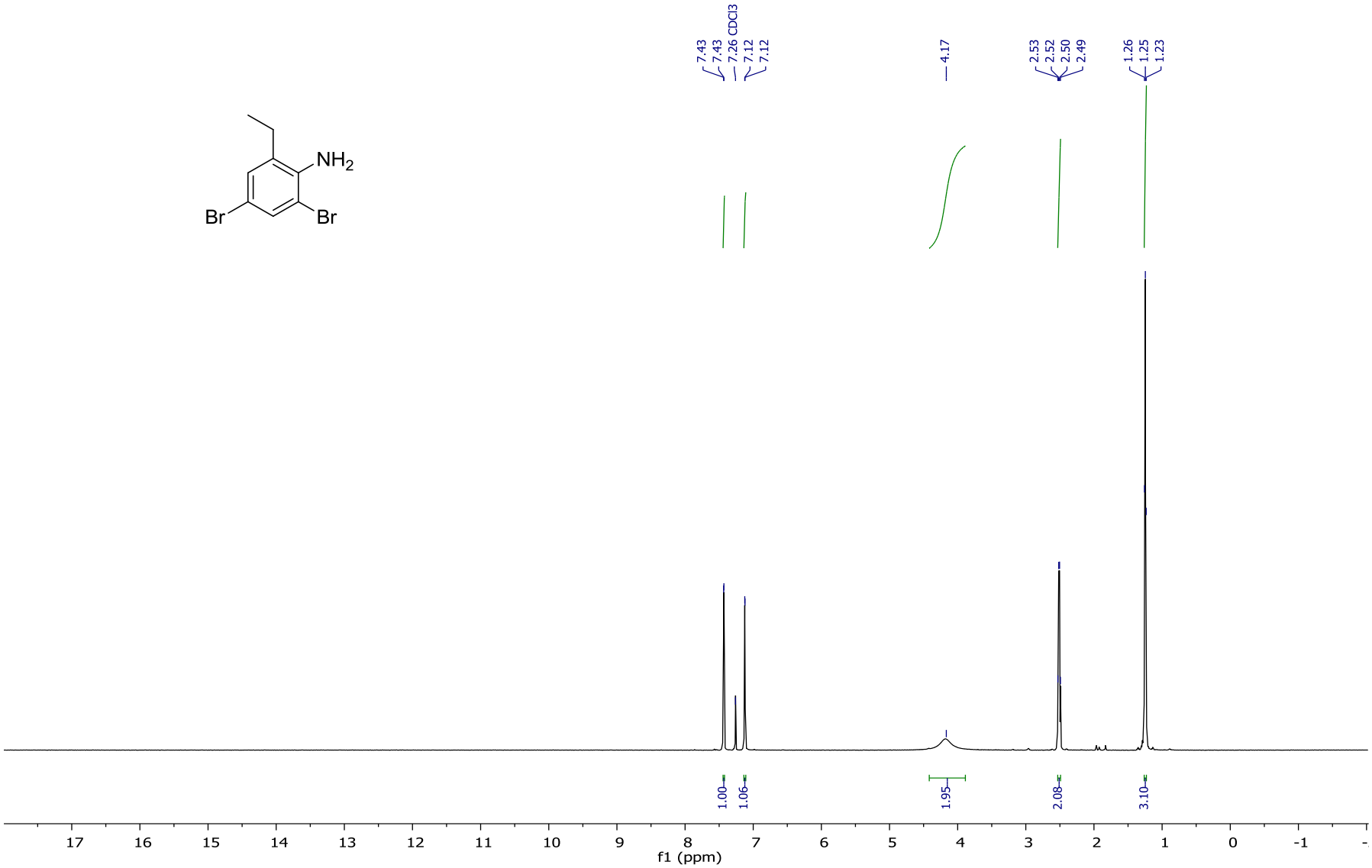


Figure S45. ^{1}H NMR (600 MHz, Chloroform-d) of 2,4-dibromo-6-ethylaniline (1x).

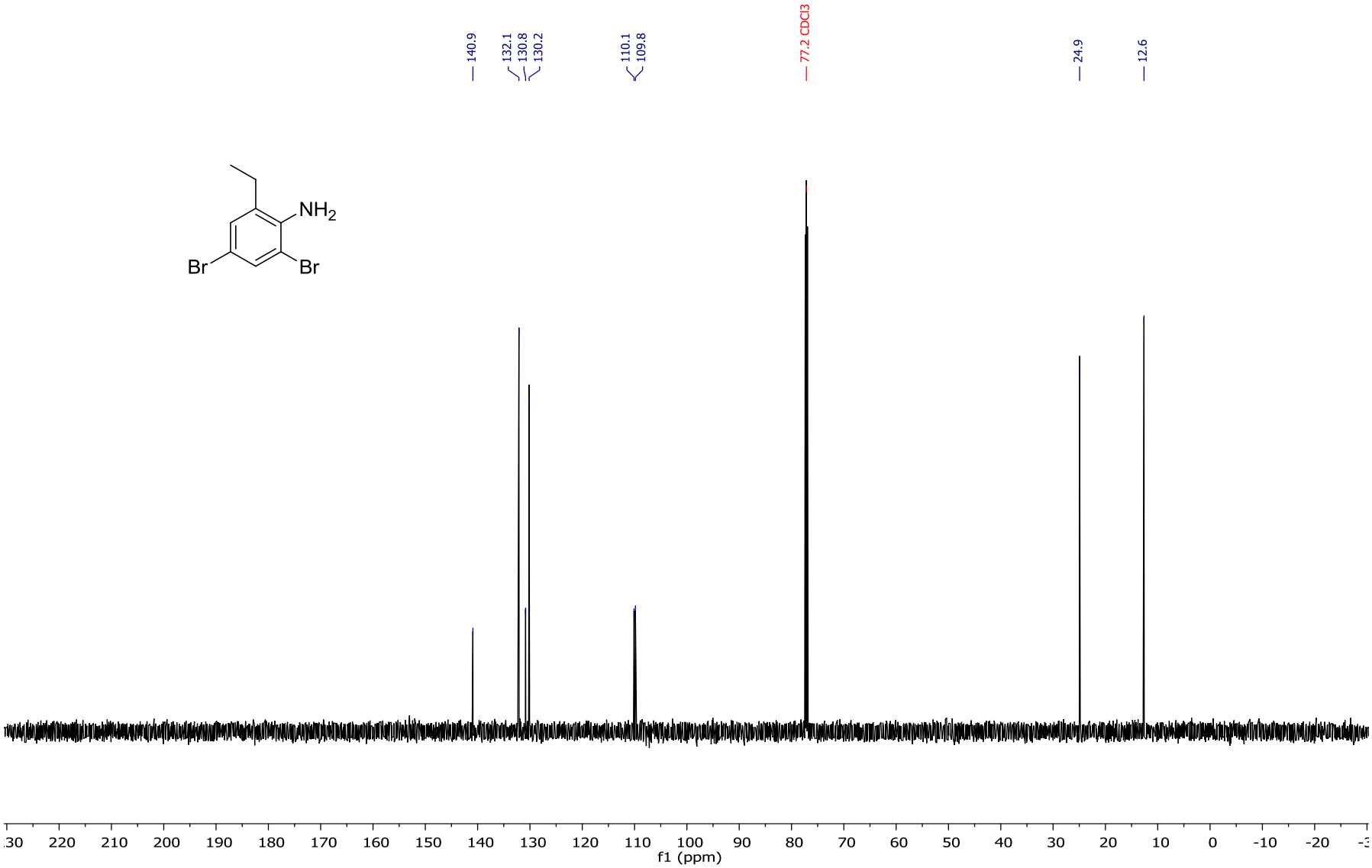


Figure S46. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2,4-dibromo-6-ethylaniline (1x).

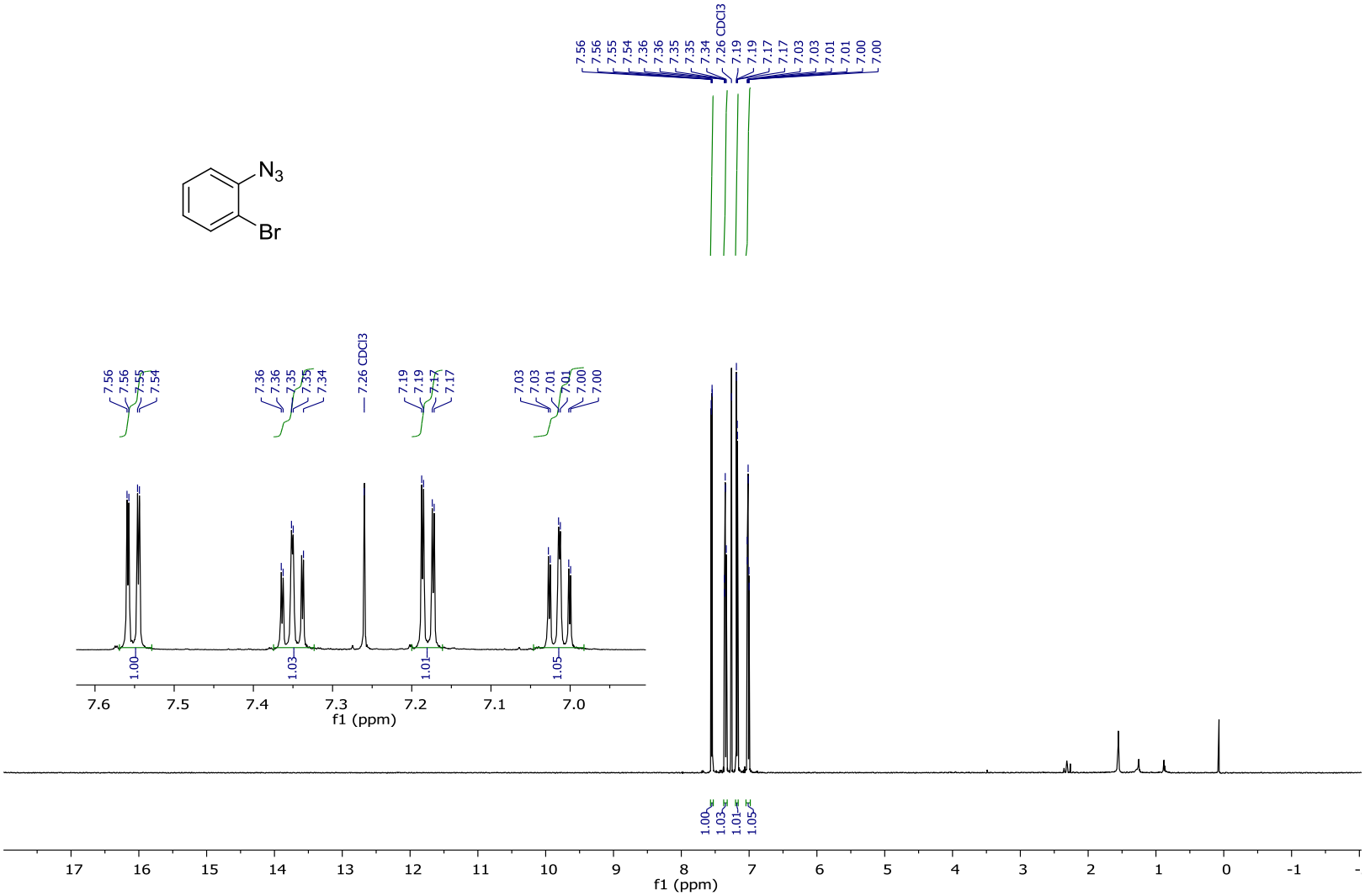


Figure S47. ^{1}H NMR (600 MHz, Chloroform-d) of 1-azido-2-bromobenzene (2a)

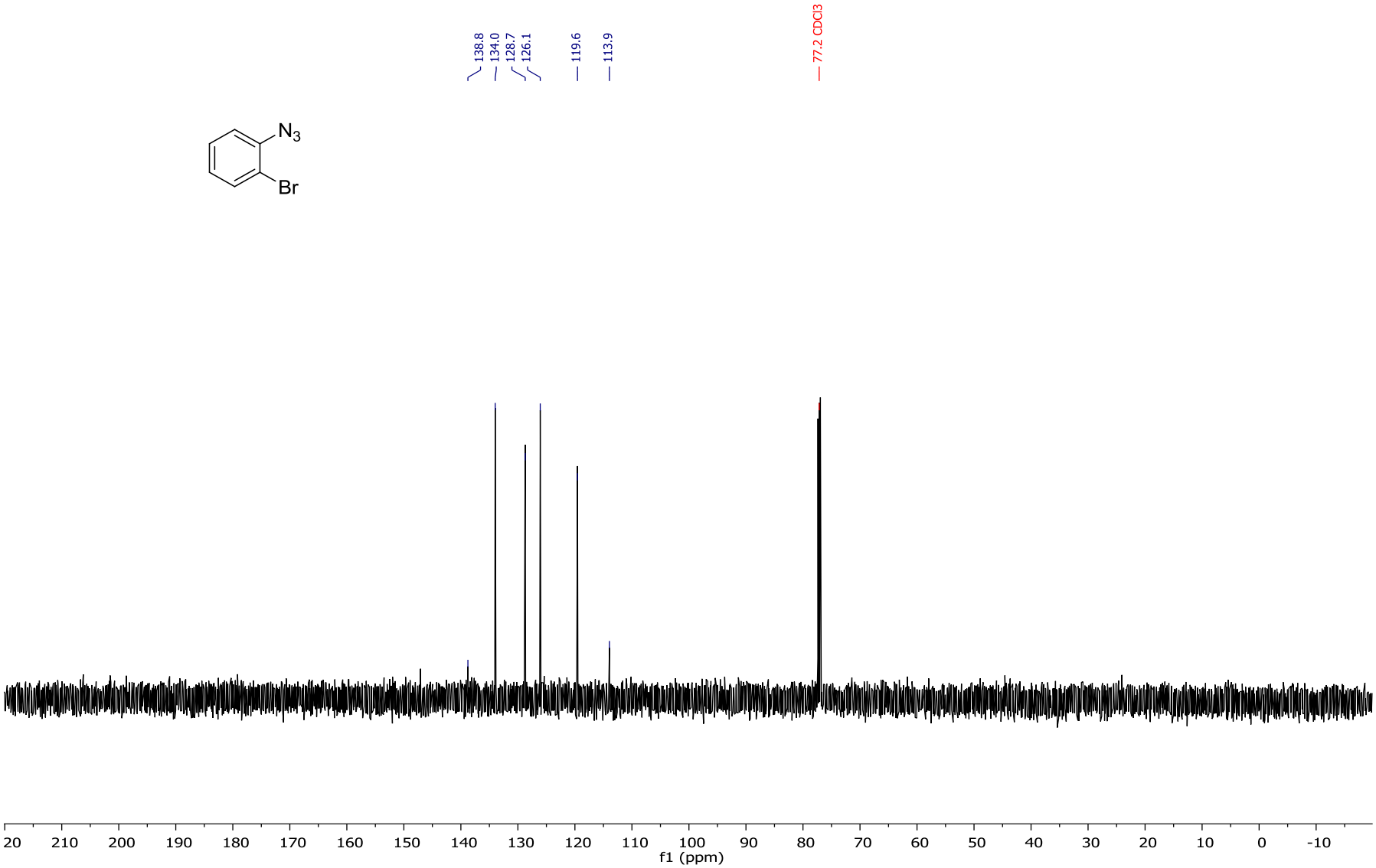


Figure S48. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-azido-2-bromobenzene (2a).

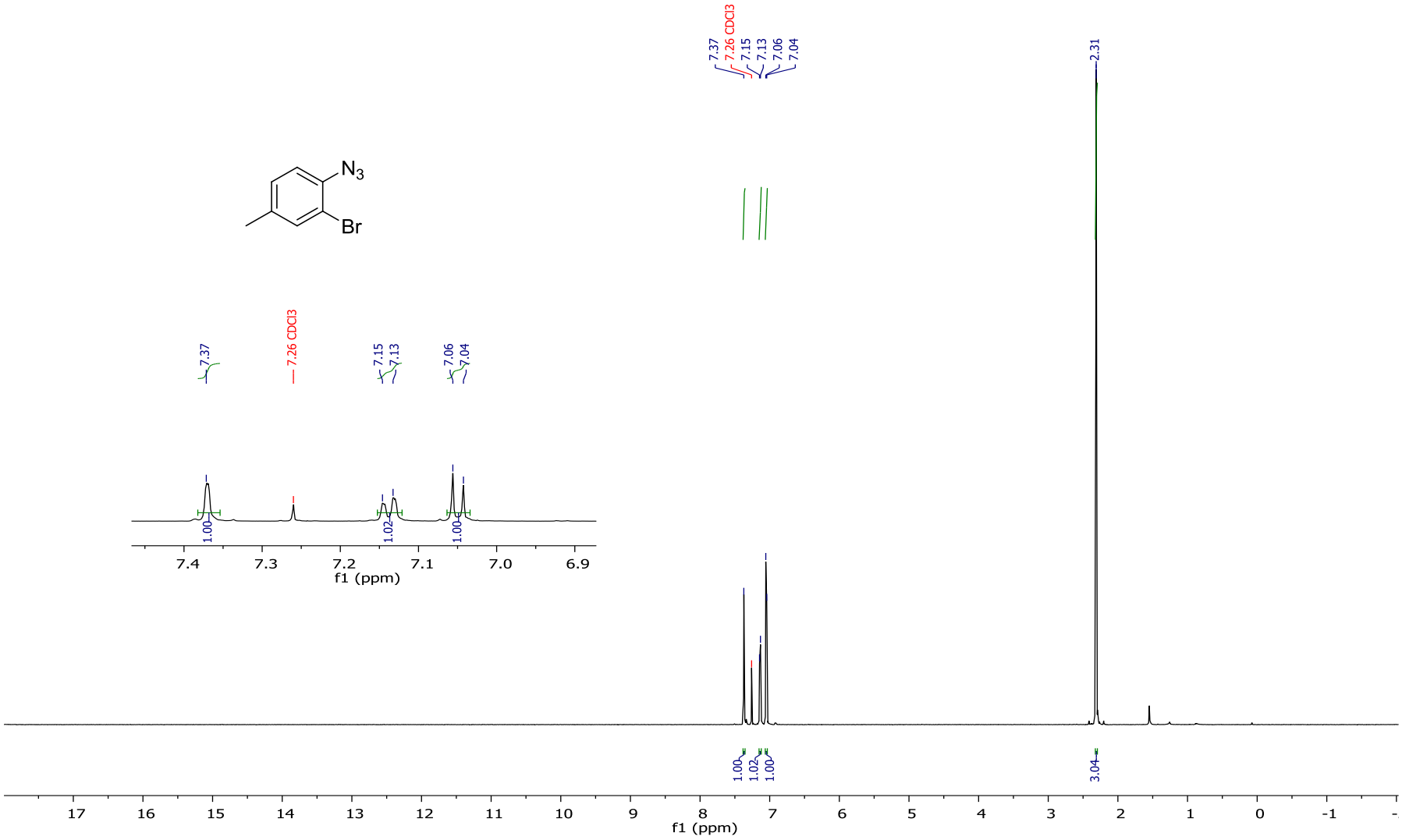


Figure S49. ^{1}H NMR (600 MHz, Chloroform-d) of 1-azido-2-bromo-4-methylbenzene (2b-Br).

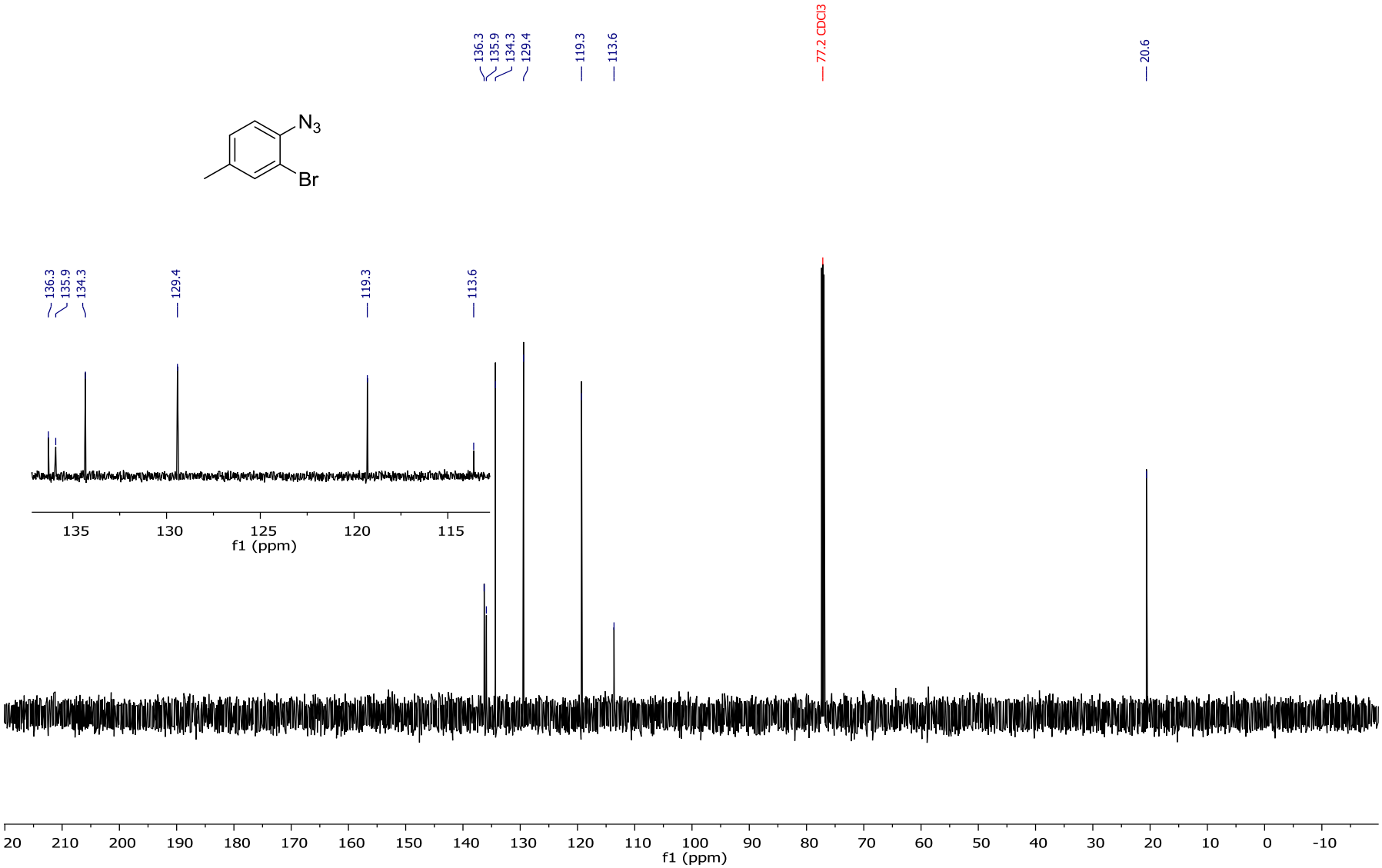


Figure S50. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-azido-2-bromo-4-methylbenzene (2b-Br).

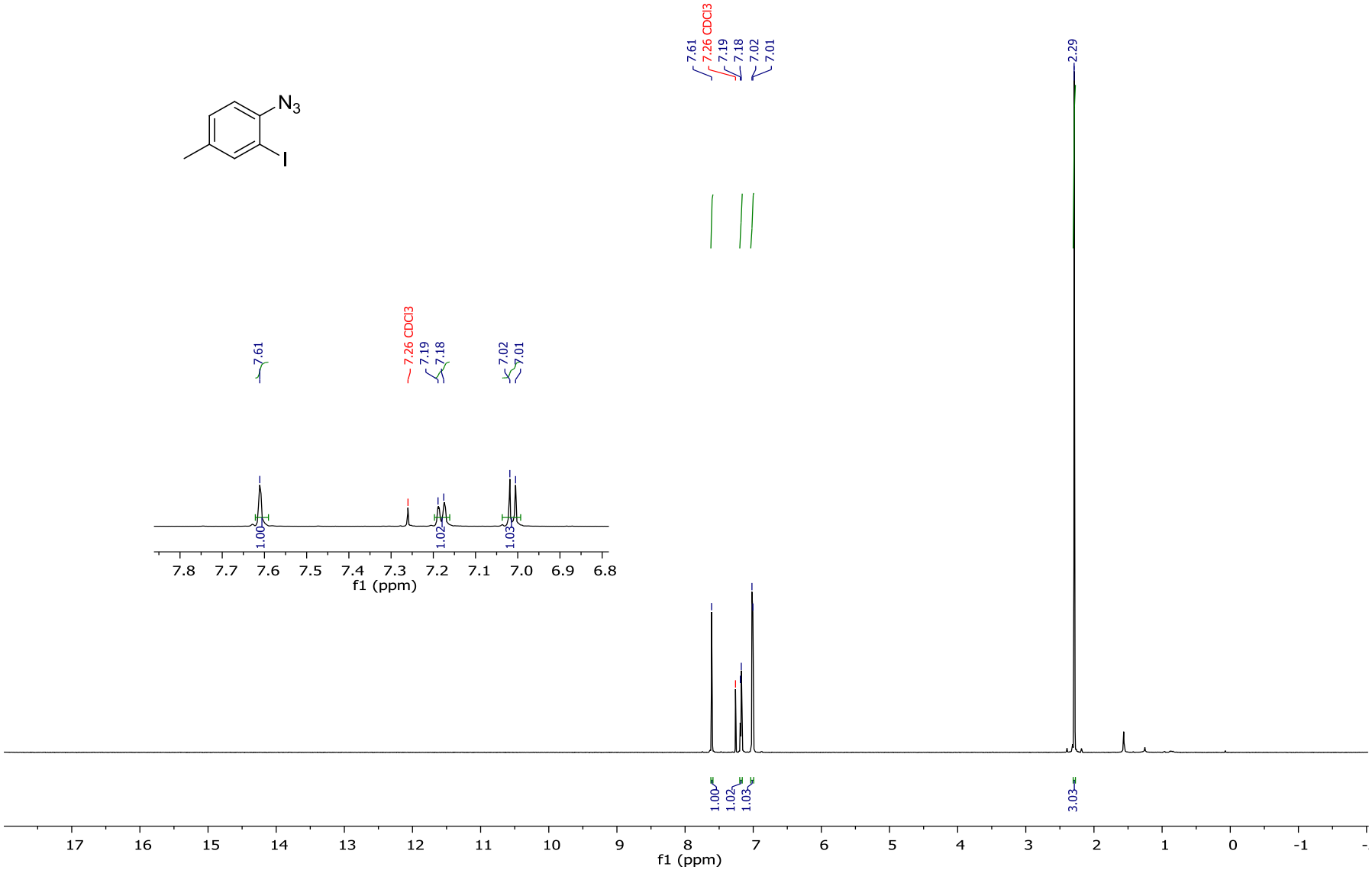


Figure S51. ^{1}H NMR (600 MHz, Chloroform-d) of 1-azido-2-iodo-4-methylbenzene (2b-I).

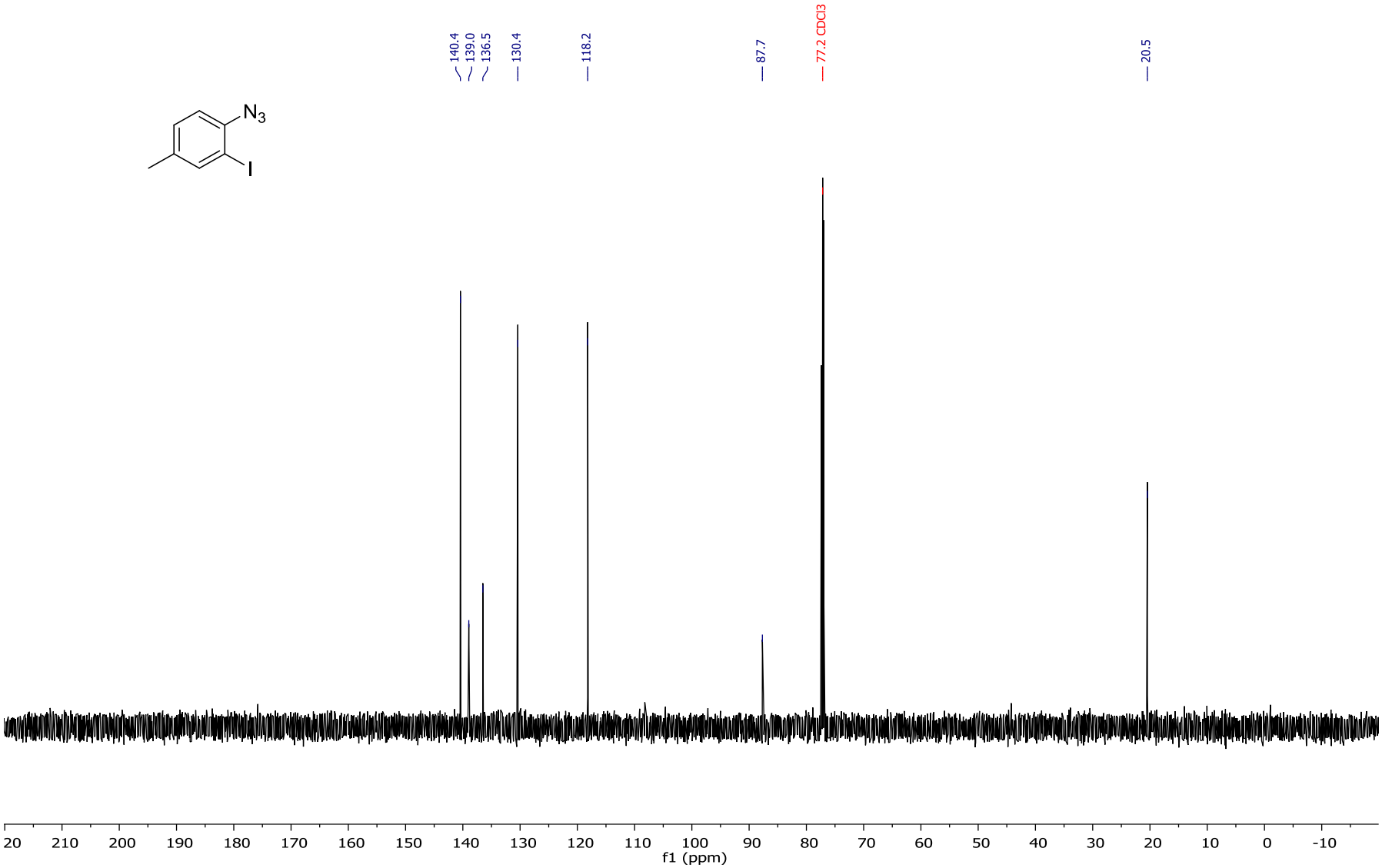


Figure S52. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-azido-2-iodo-4-methylbenzene (2b-I).

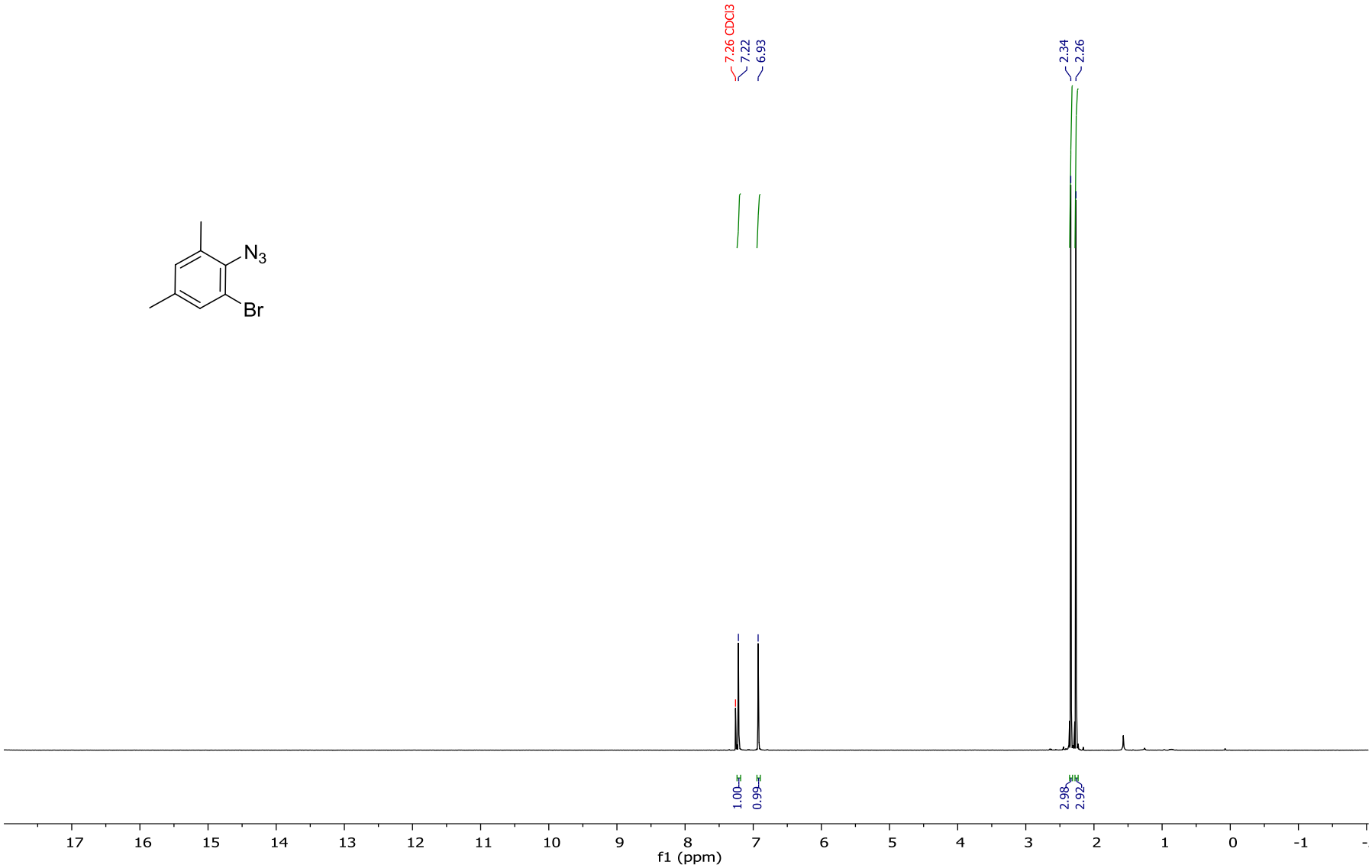


Figure S53. ^{1}H NMR (600 MHz, Chloroform-d) of 2-azido-1-bromo-3,5-dimethylbenzene (2c).

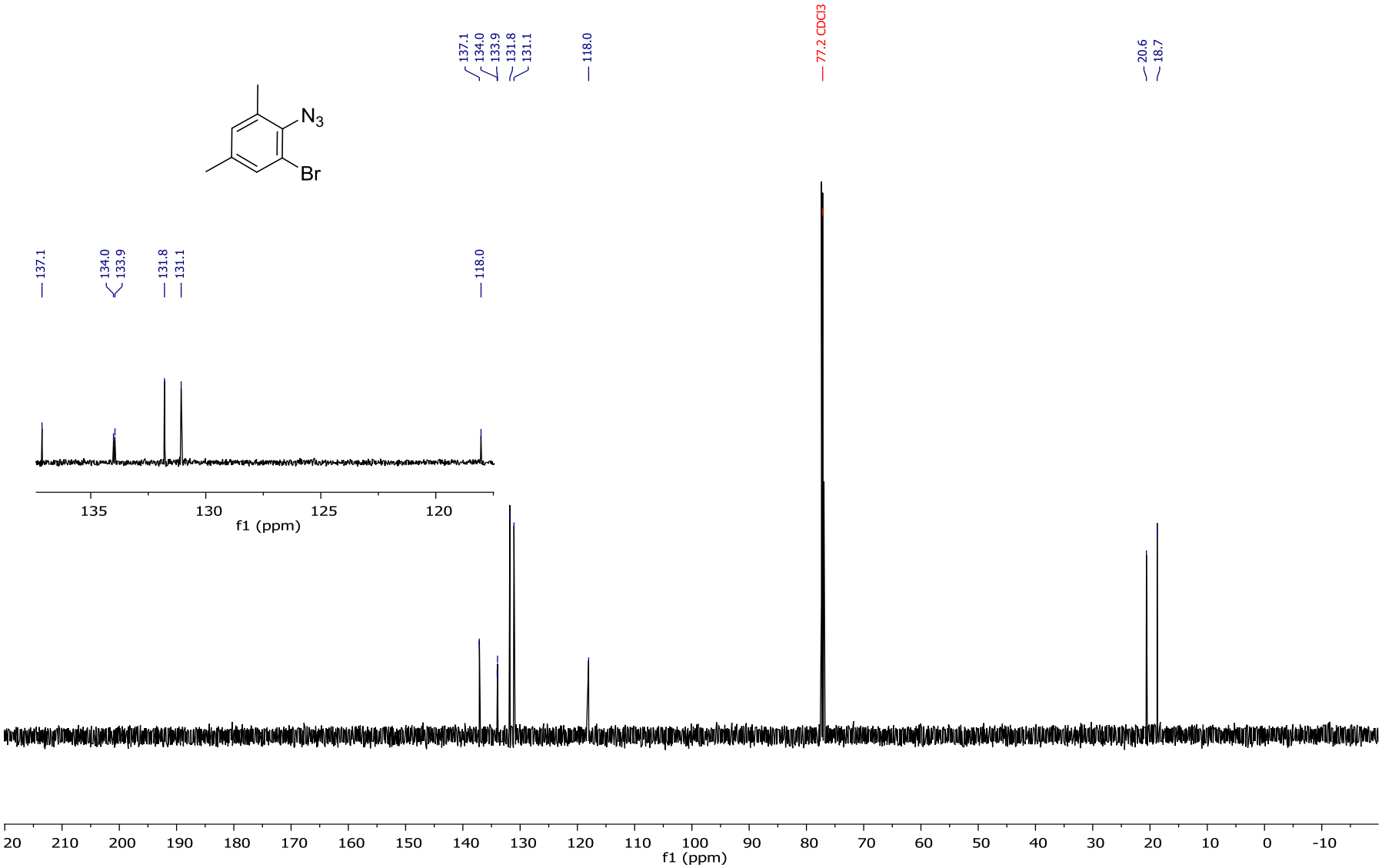


Figure S54. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-azido-1-bromo-3,5-dimethylbenzene (2c).

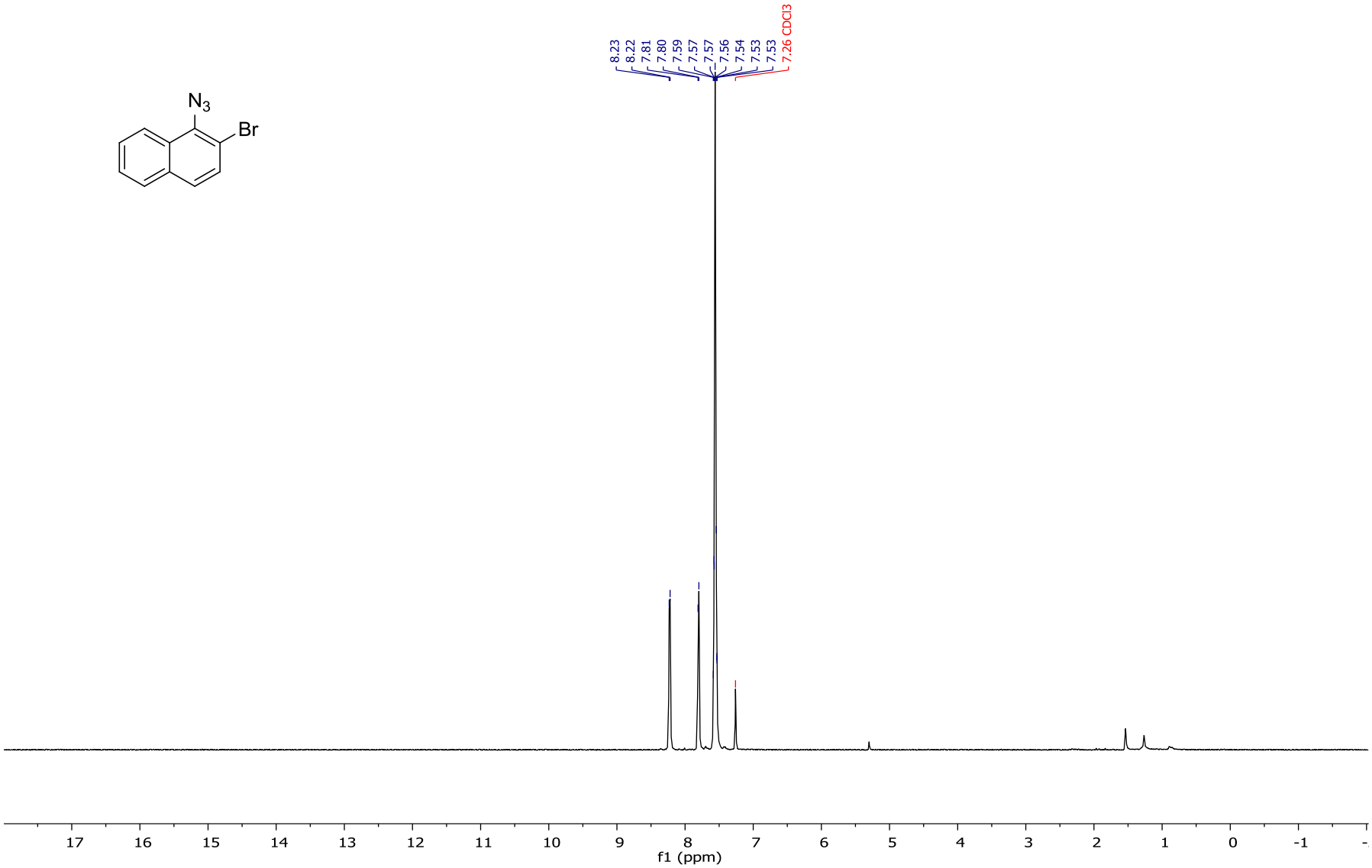


Figure S55. ^{1}H NMR (600 MHz, Chloroform-d) of 1-azido-2-bromonaphthalene (2d).

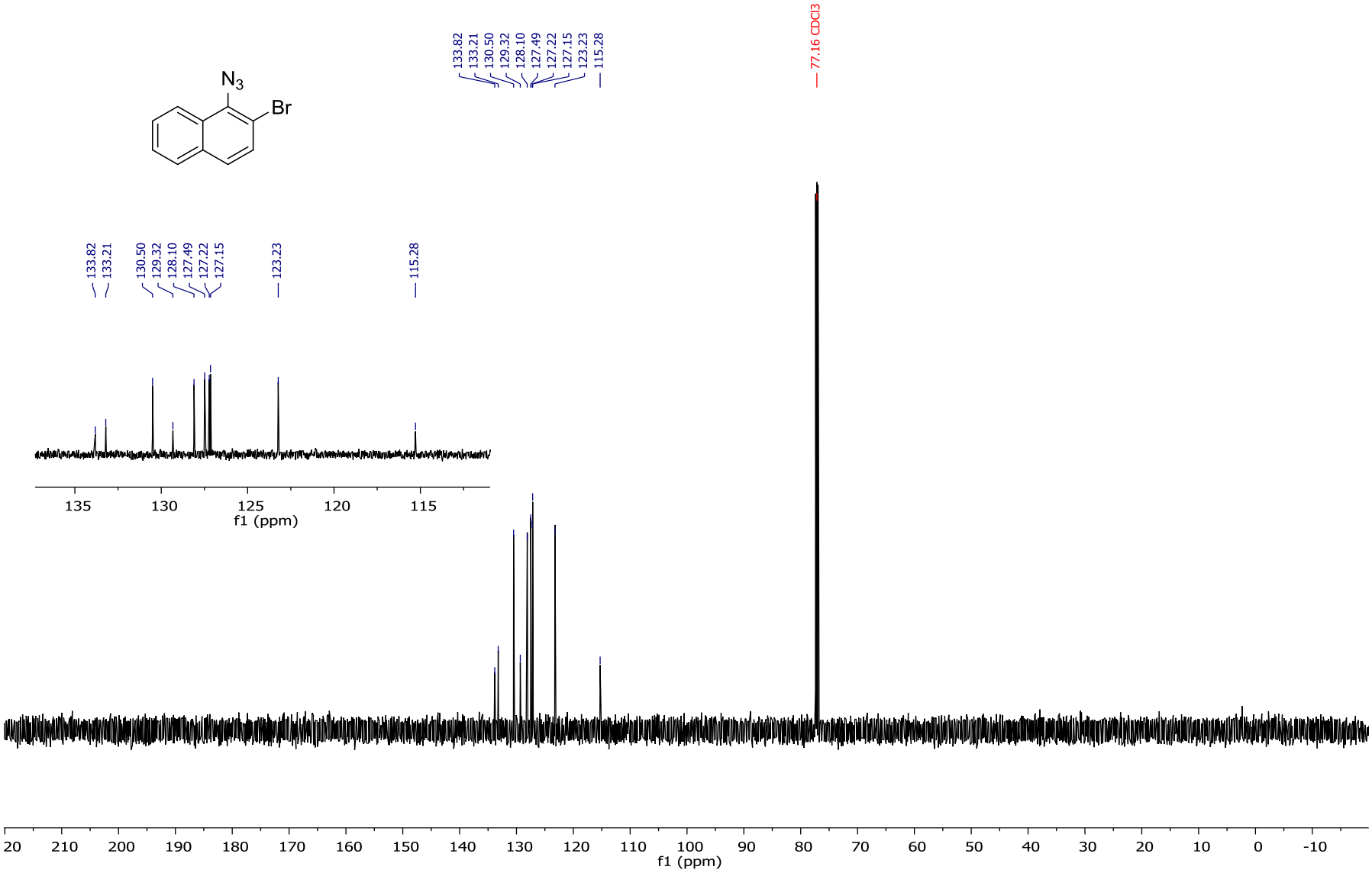


Figure S56. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-azido-2-bromonaphthalene (2d).

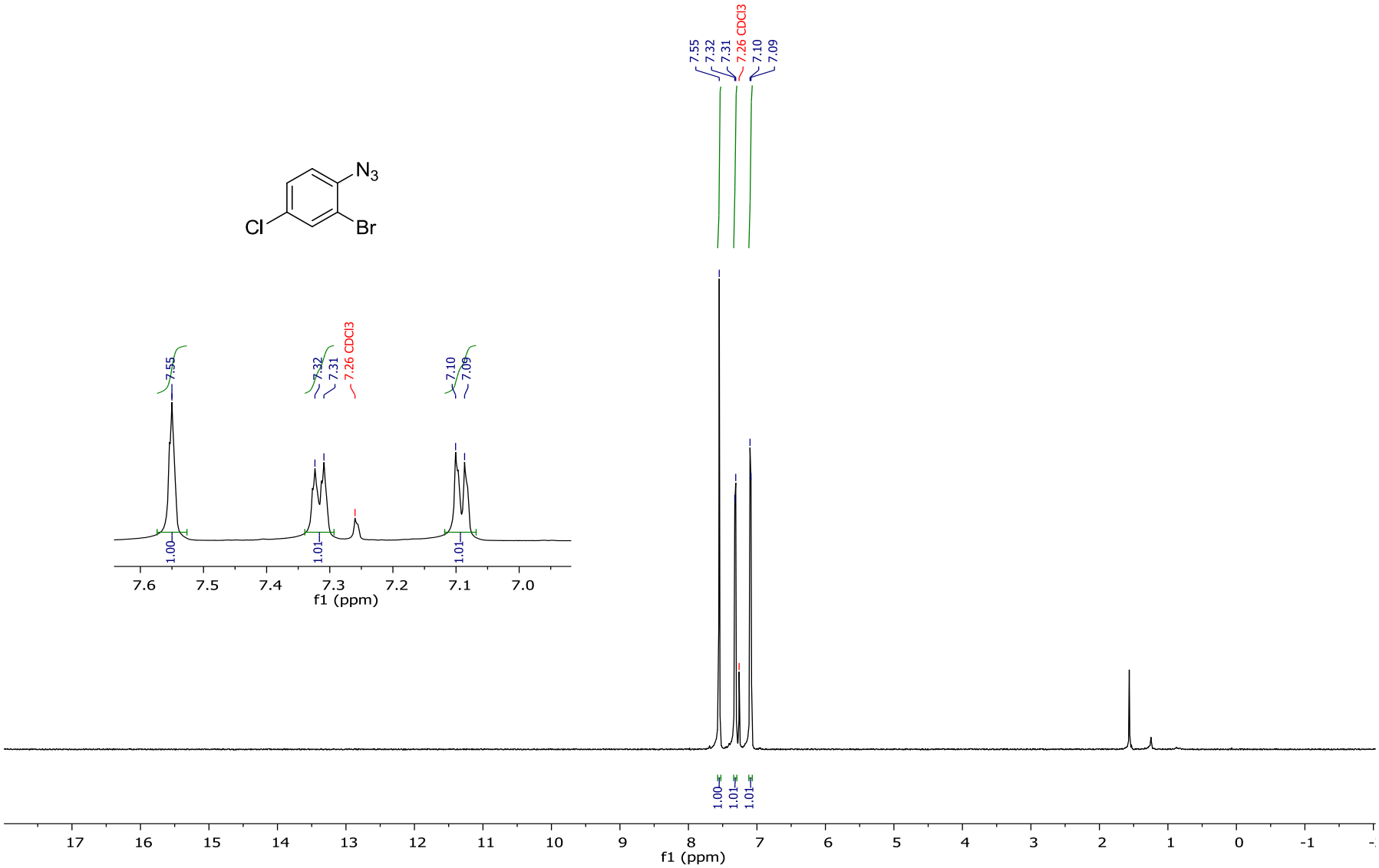


Figure S57. ^{1}H NMR (600 MHz, Chloroform-d) of 1-azido-2-bromo-4-chlorobenzene (2e).

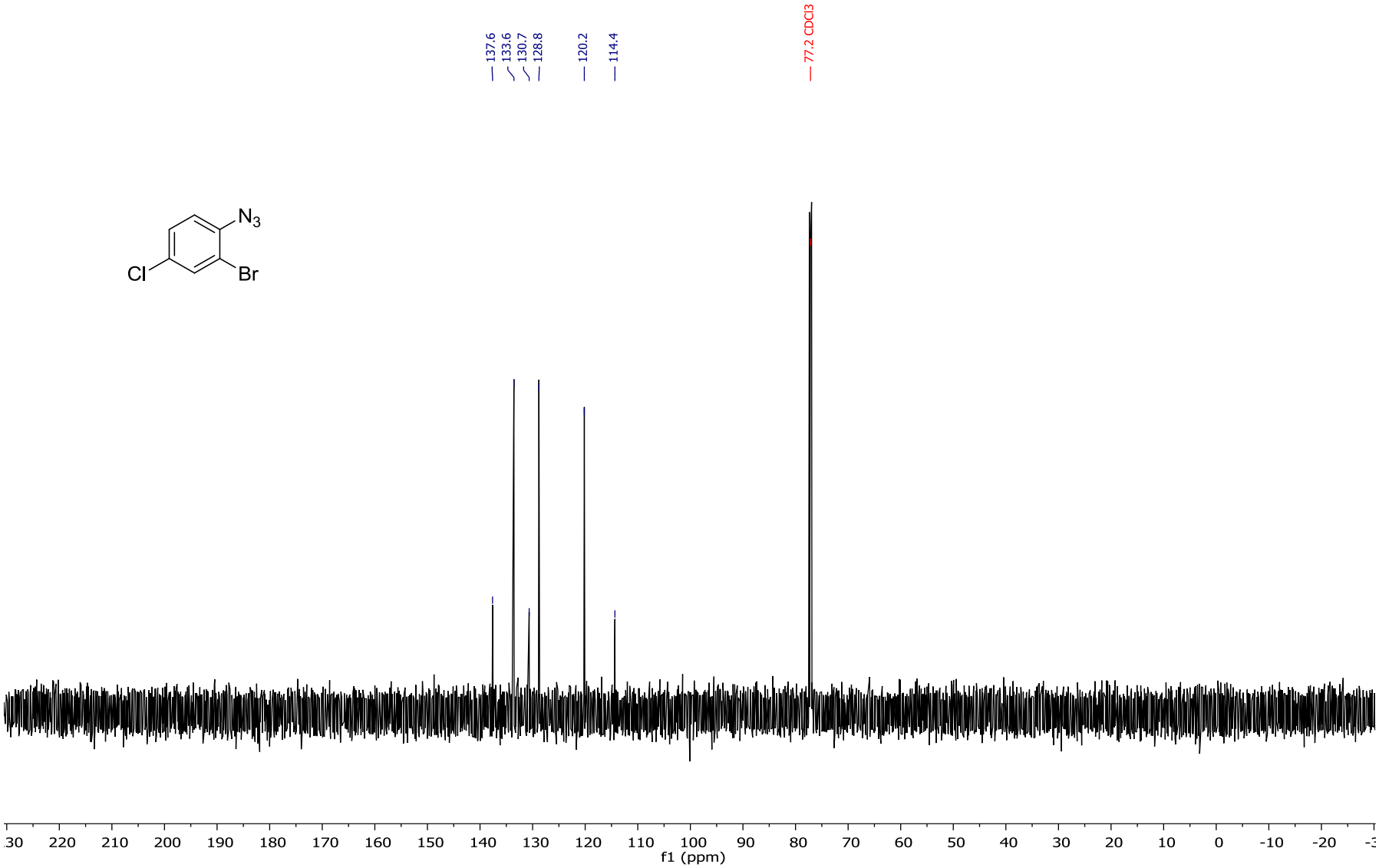


Figure S58. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-azido-2-bromo-4-chlorobenzene (2e).

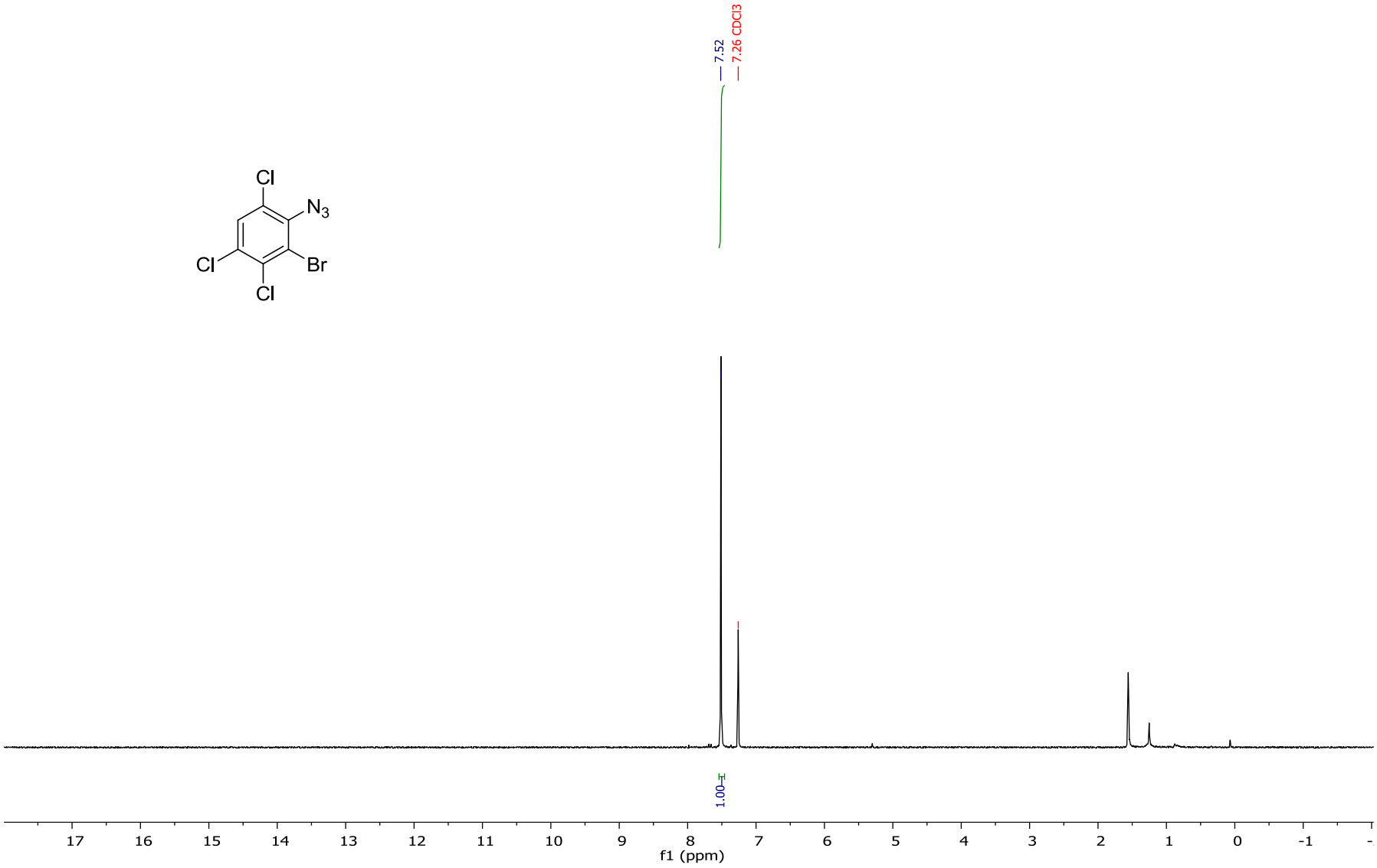


Figure S59. ^{1}H NMR (600 MHz, Chloroform-d) of 2-azido-3-bromo-1,4,5-trichlorobenzene (2f).

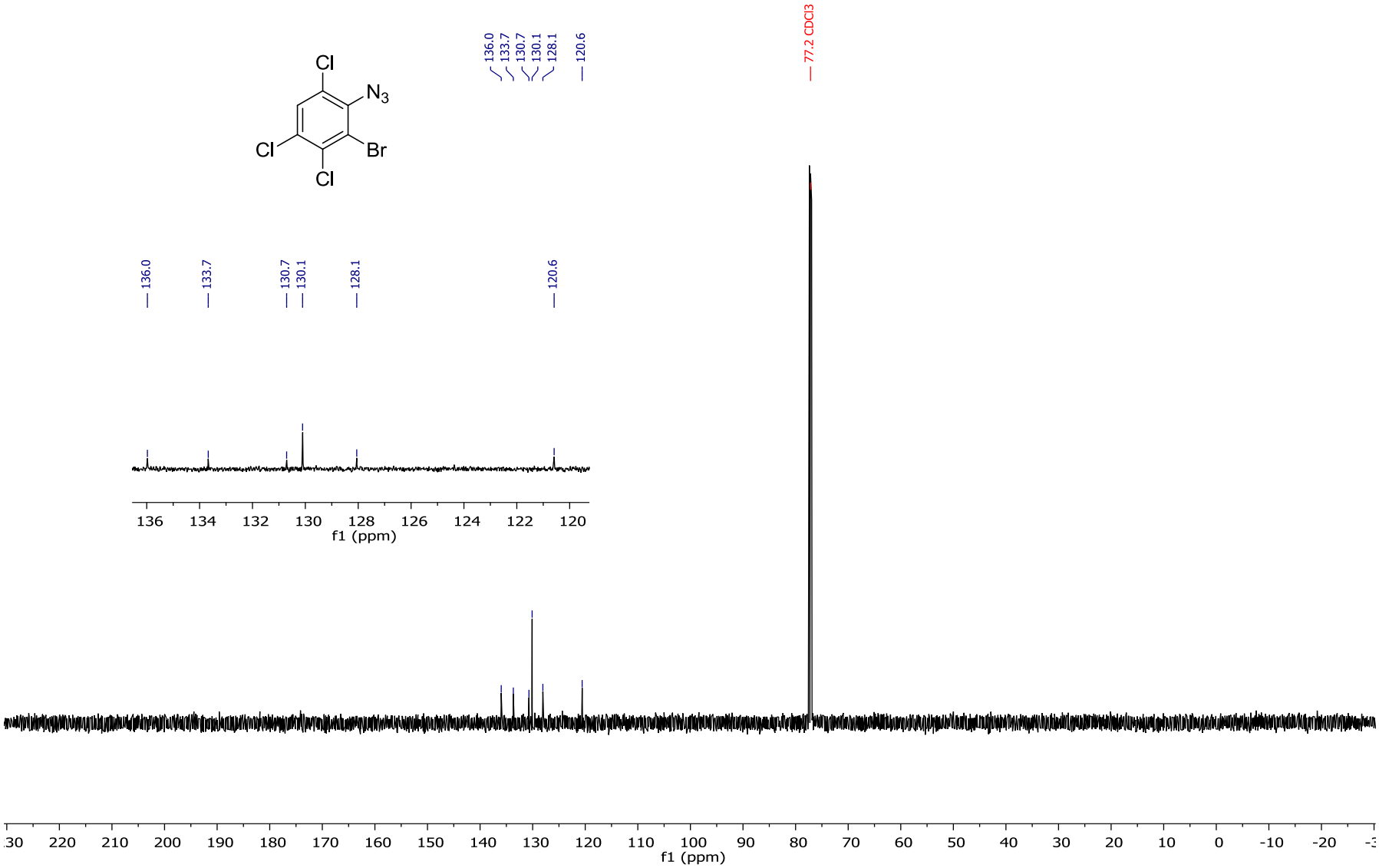


Figure S60. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-azido-3-bromo-1,4,5-trichlorobenzene (2f).

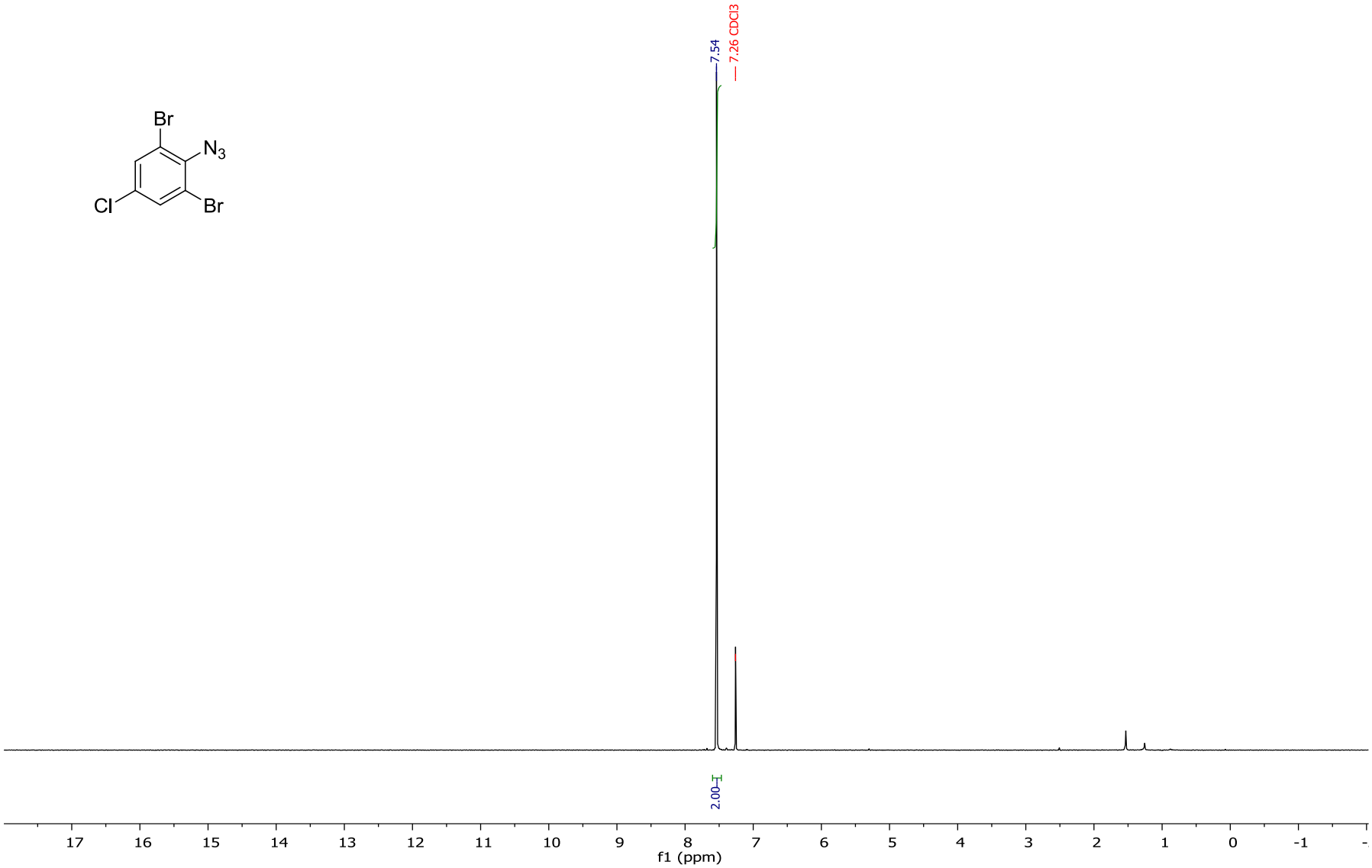


Figure S61. ^{1}H NMR (600 MHz, Chloroform-d) of 2-azido-1,3-dibromo-5-chlorobenzene (2g).

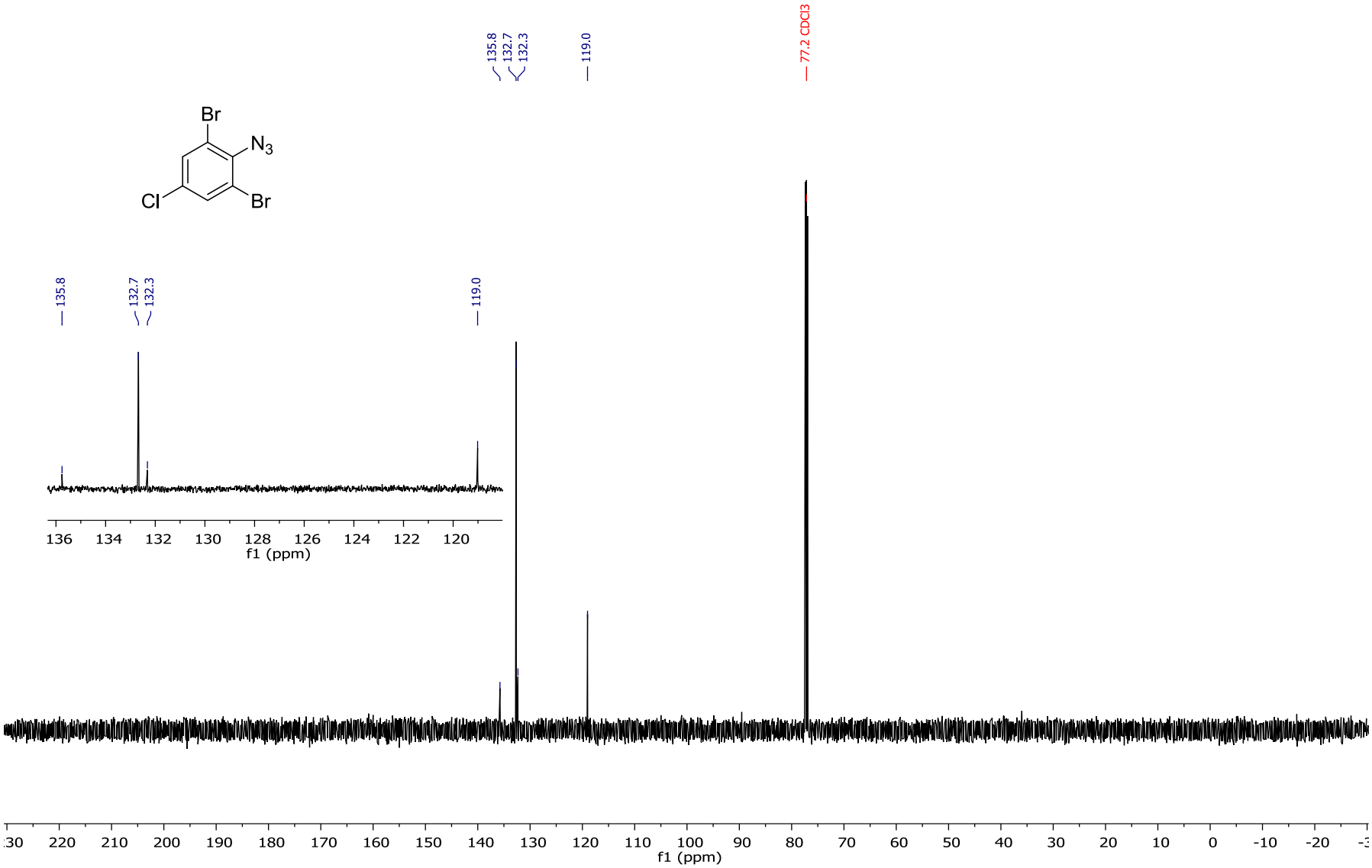


Figure S62. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-azido-1,3-dibromo-5-chlorobenzene (2g).

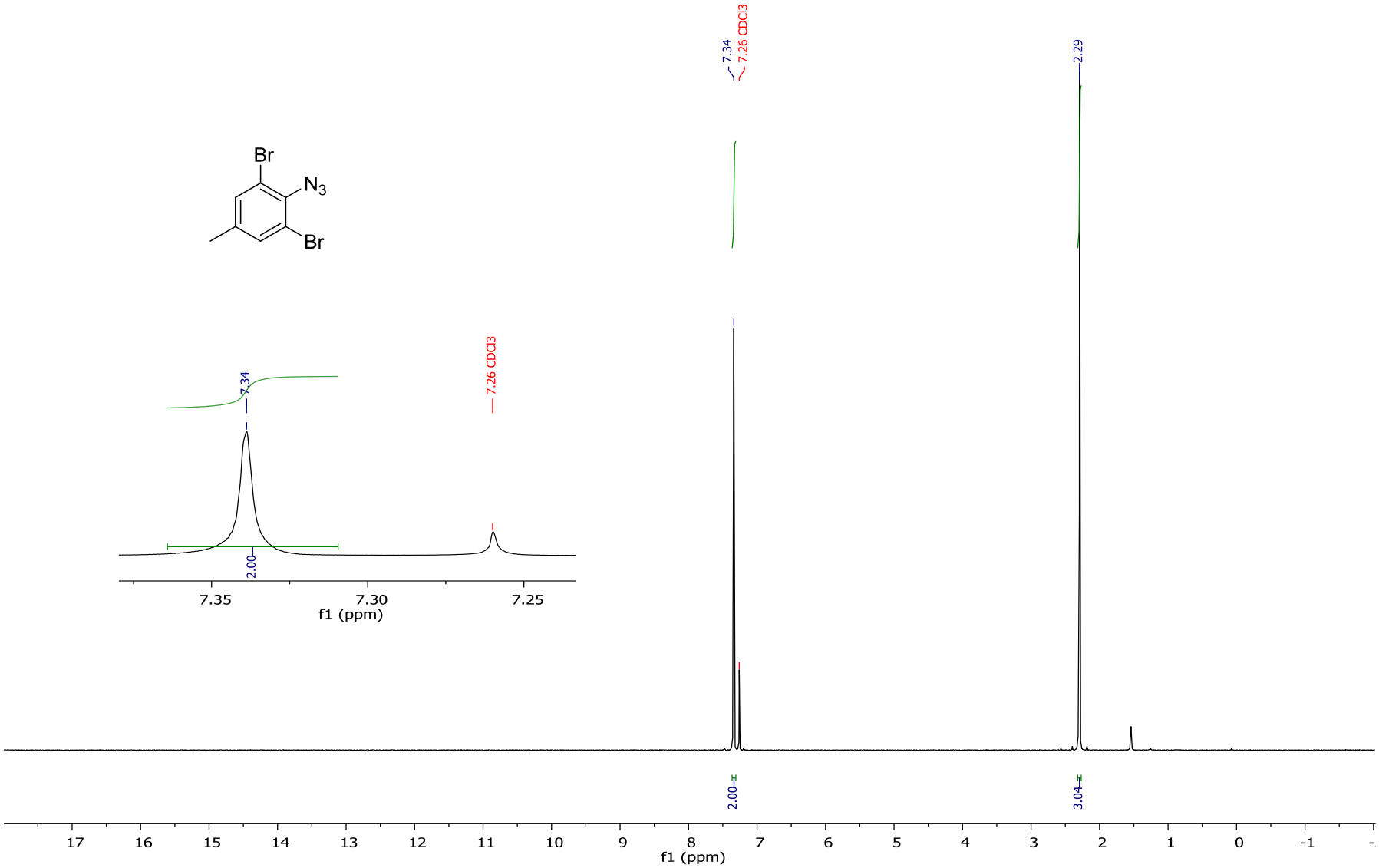


Figure S63. ^{1}H NMR (600 MHz, Chloroform-d) of 2-azido-1,3-dibromo-5-methylbenzene (2h).

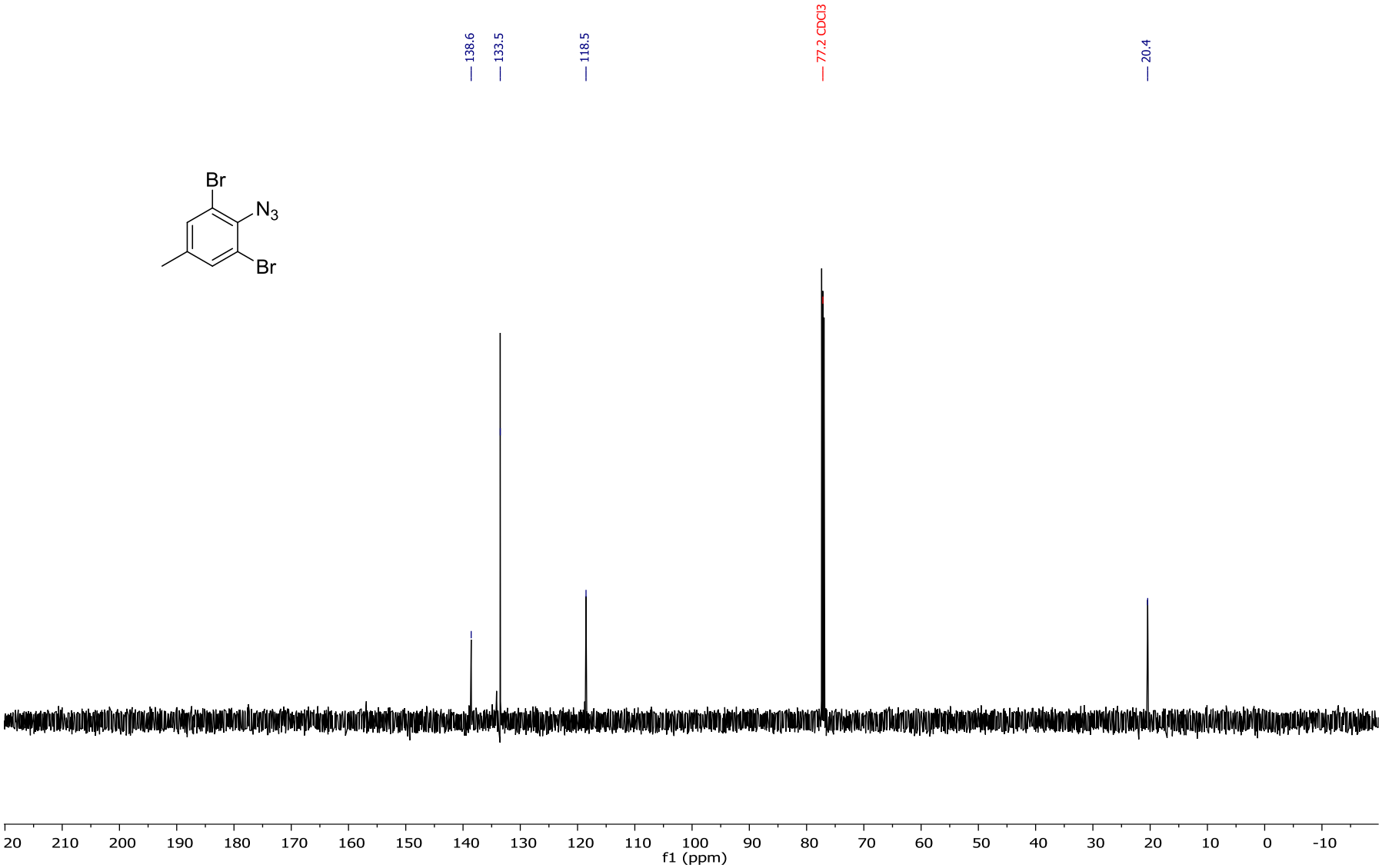


Figure S64. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-azido-1,3-dibromo-5-methylbenzene (2h).

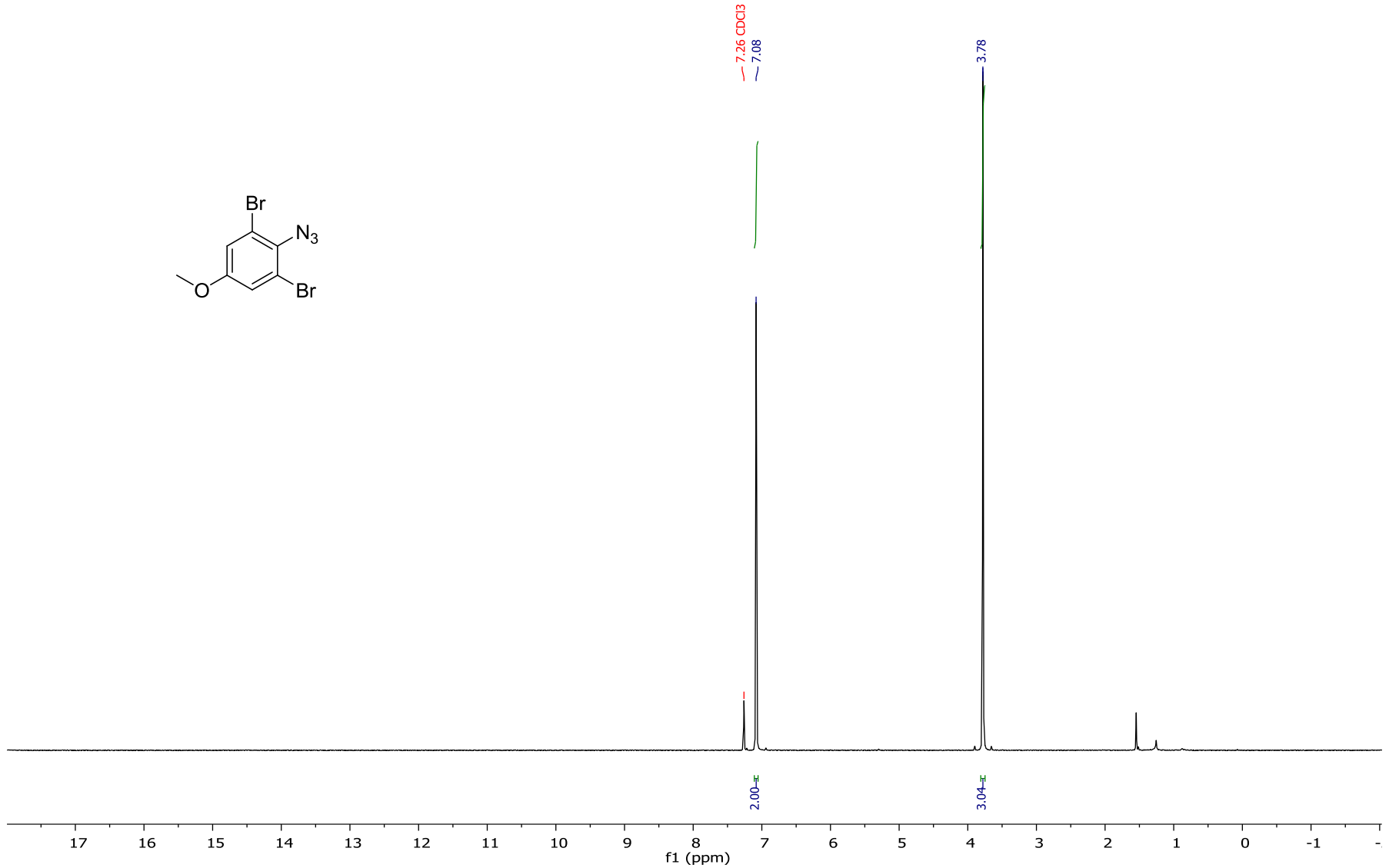


Figure S65. ^{1}H NMR (600 MHz, Chloroform-d) of 2-azido-1,3-dibromo-5-methoxybenzene (2i).

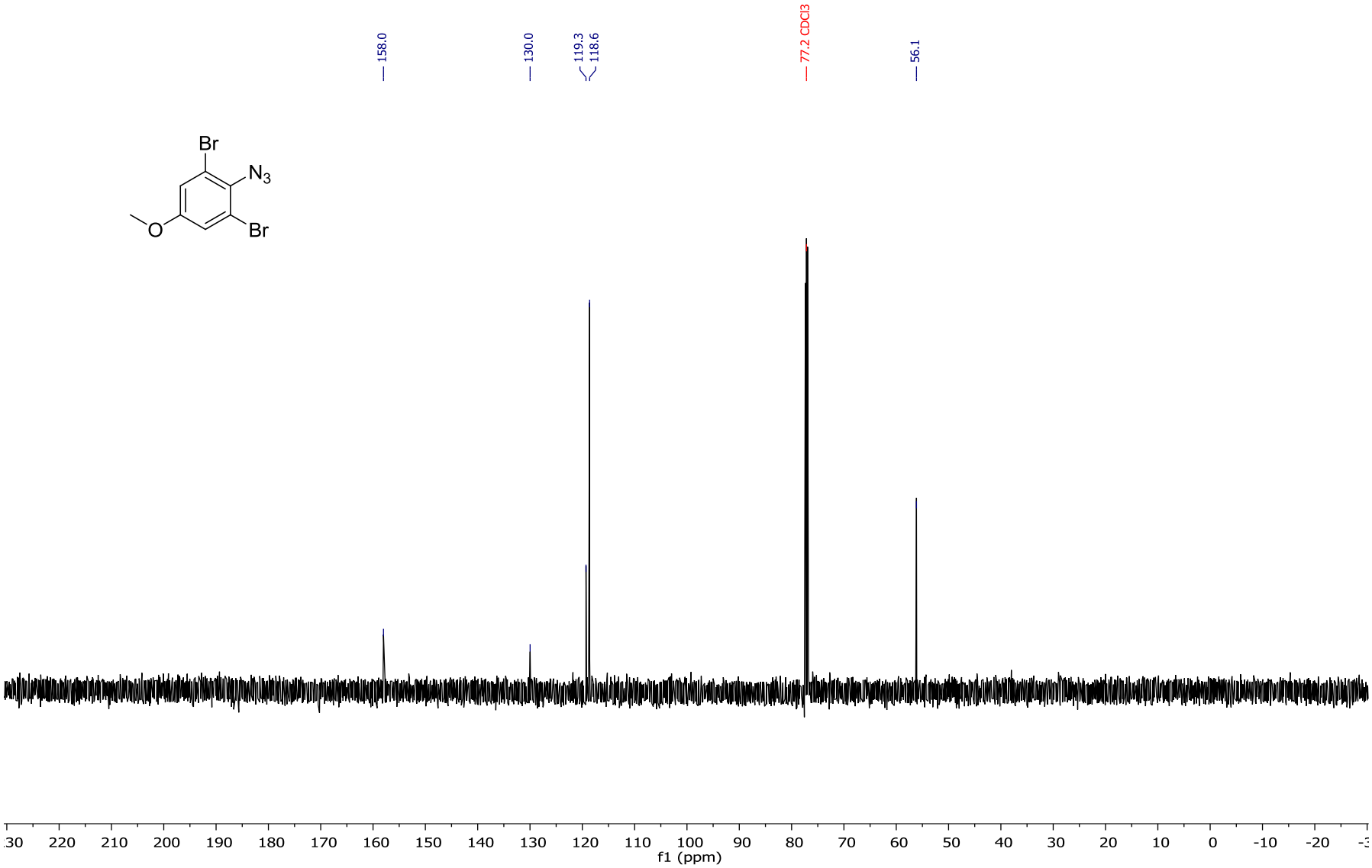


Figure S66. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-azido-1,3-dibromo-5-methoxybenzene (2i).

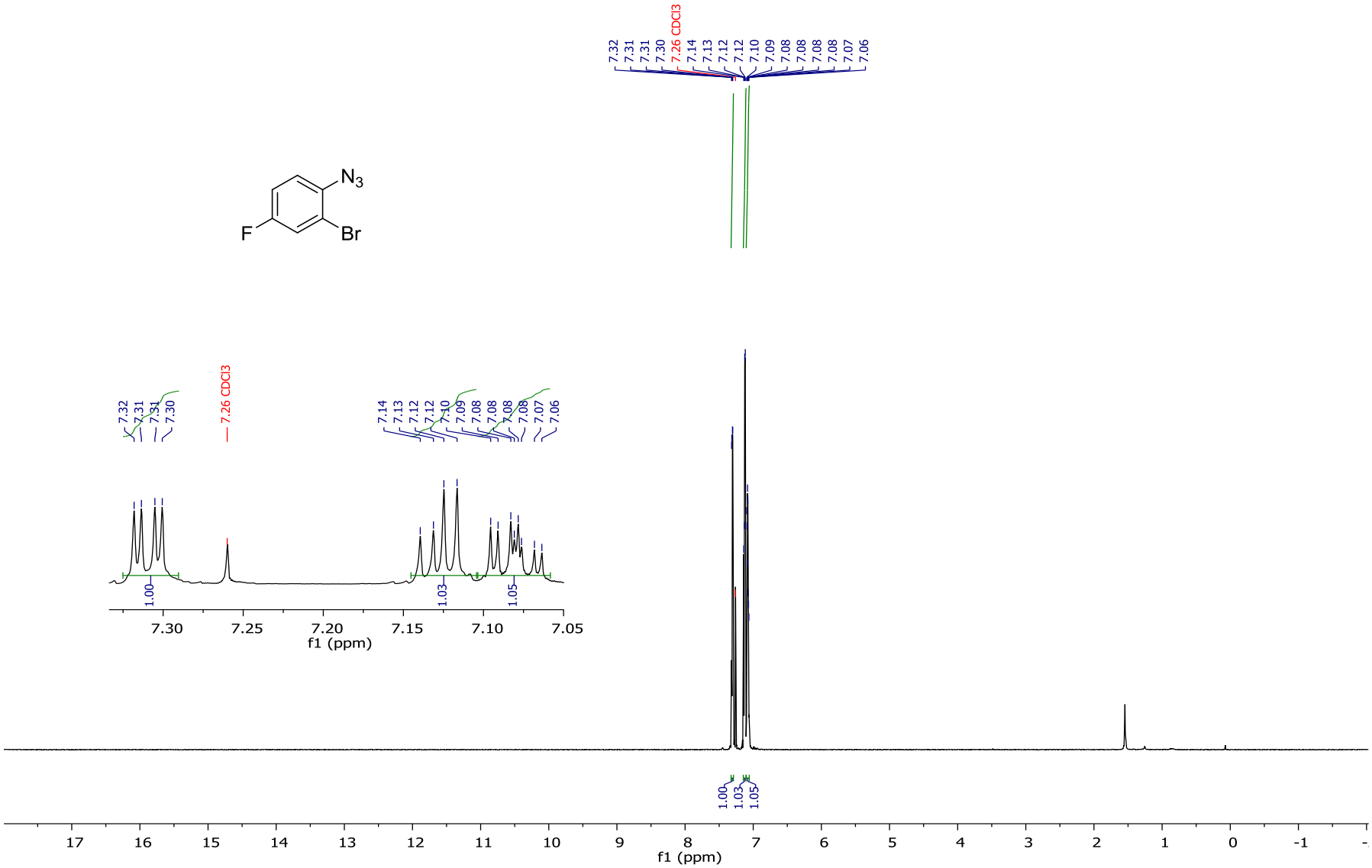


Figure S67. ^{1}H NMR (600 MHz, Chloroform-d) of 1-azido-2-bromo-4-fluorobenzene (2j).

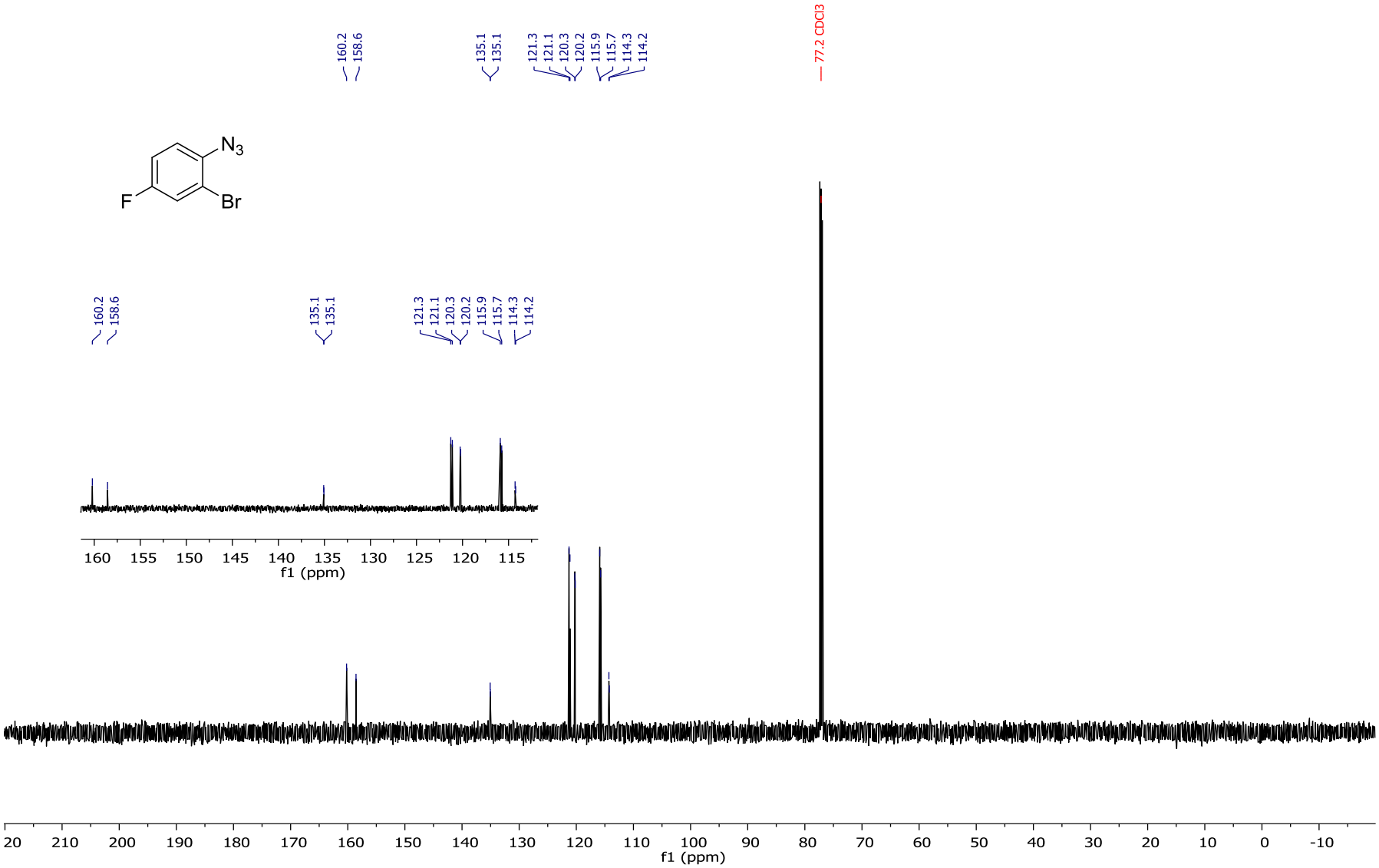


Figure S68. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-azido-2-bromo-4-fluorobenzene (2j).

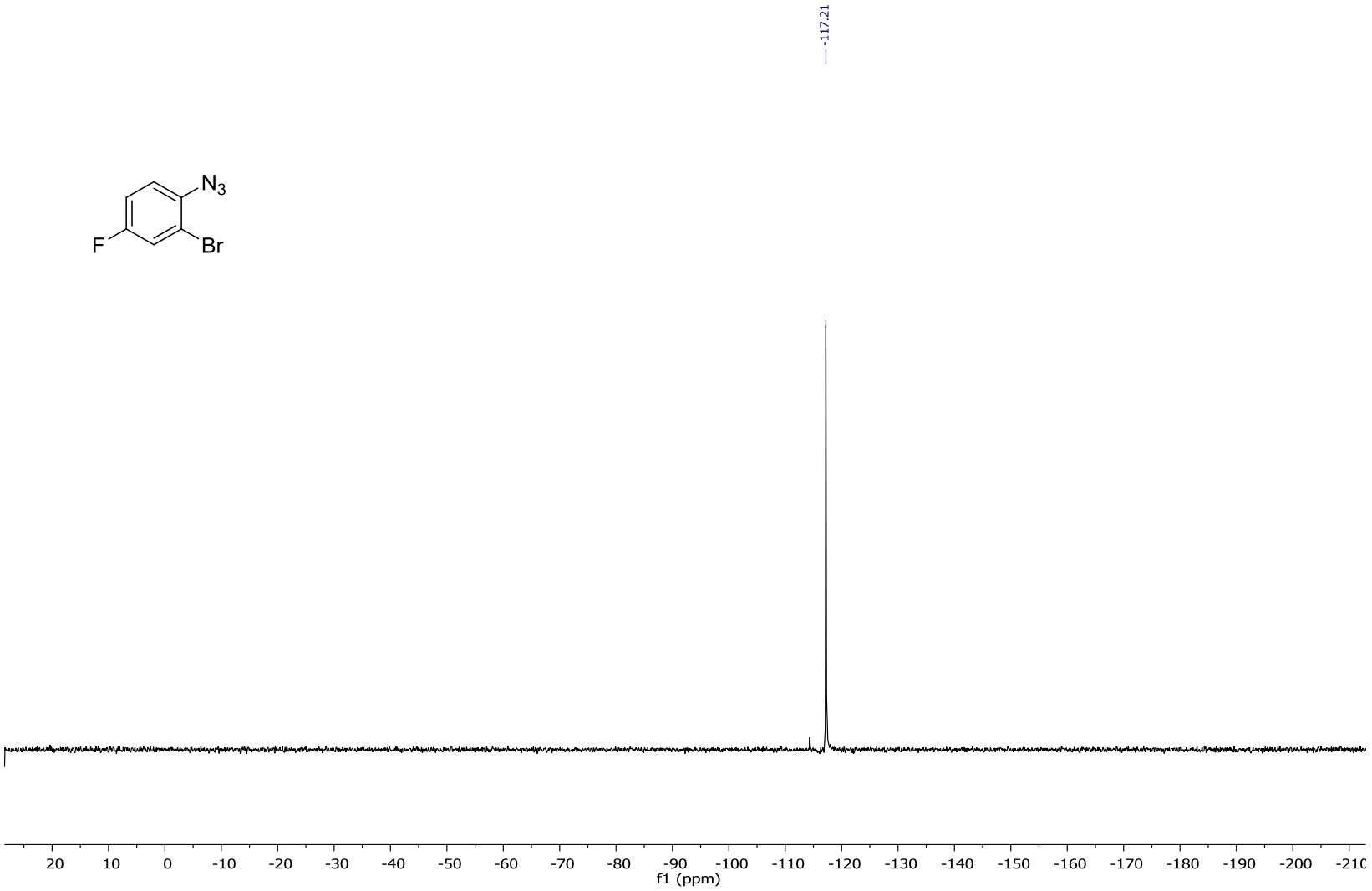


Figure S69. ^{19}F NMR (188 MHz, Chloroform-*d*) of 1-azido-2-bromo-4-fluorobenzene (2j).

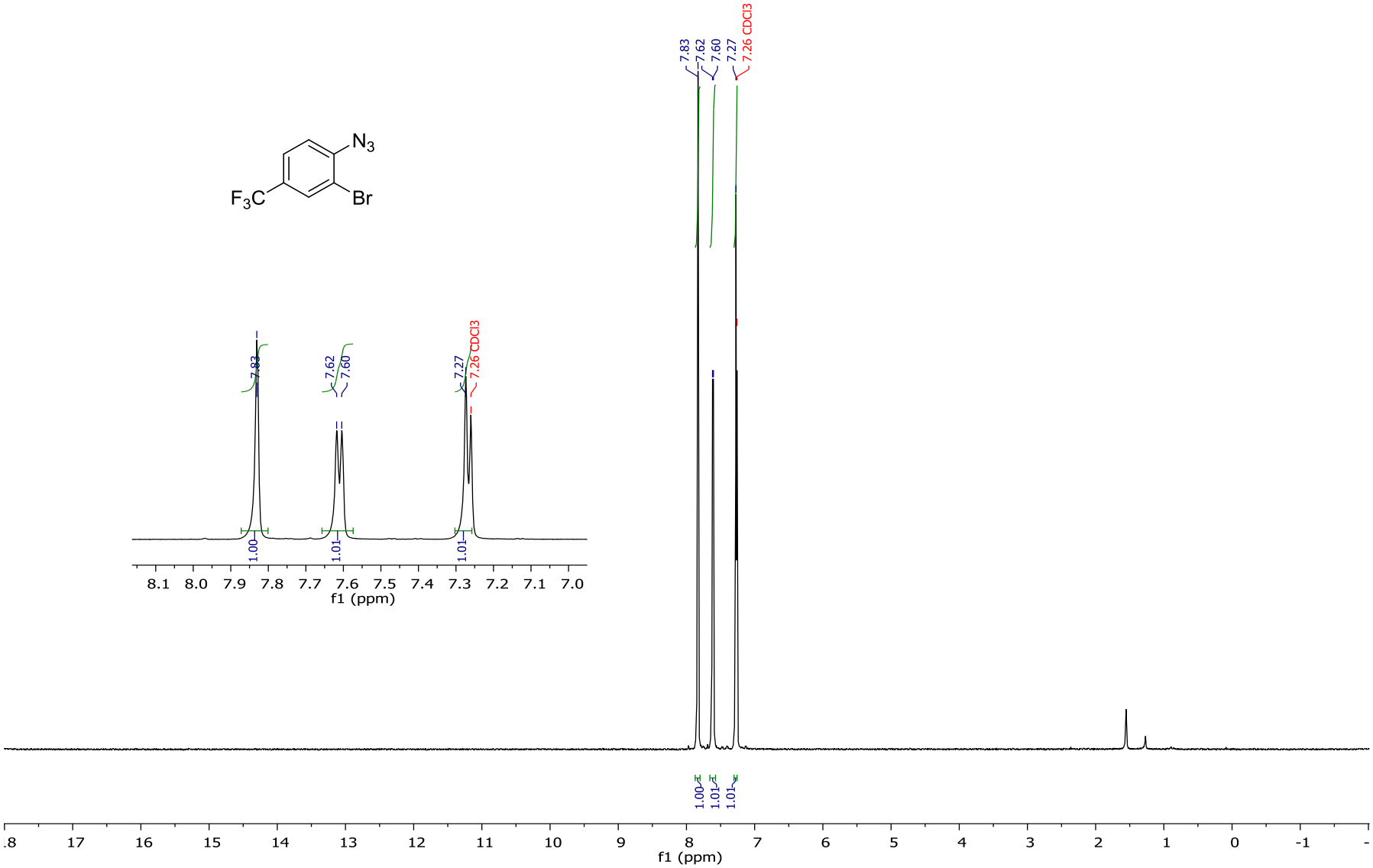


Figure S70. ^{1}H NMR (600 MHz, Chloroform-d) of 1-azido-2-bromo-4-(trifluoromethyl)benzene (2k).

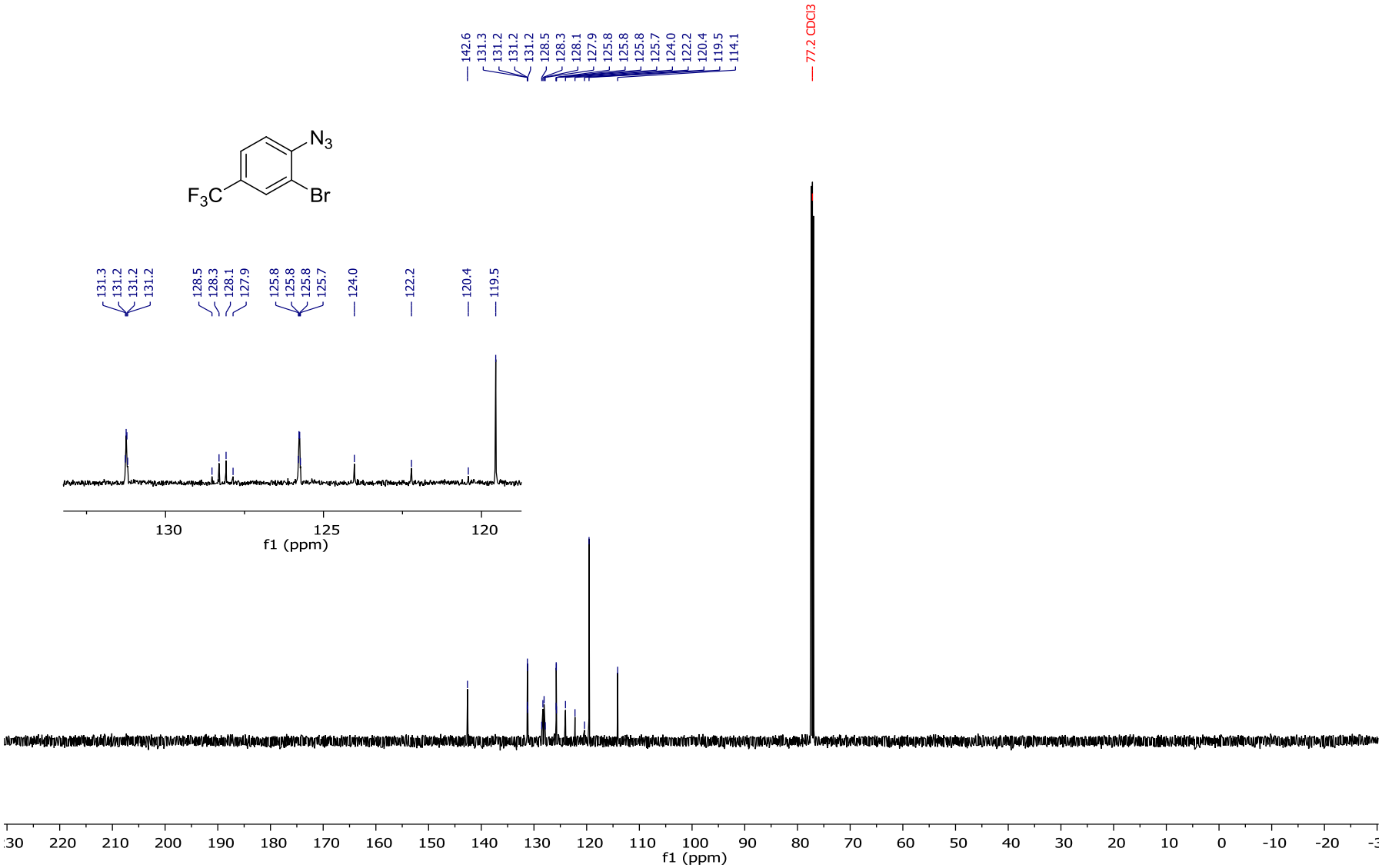


Figure S71. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-azido-2-bromo-4-(trifluoromethyl)benzene (2k).

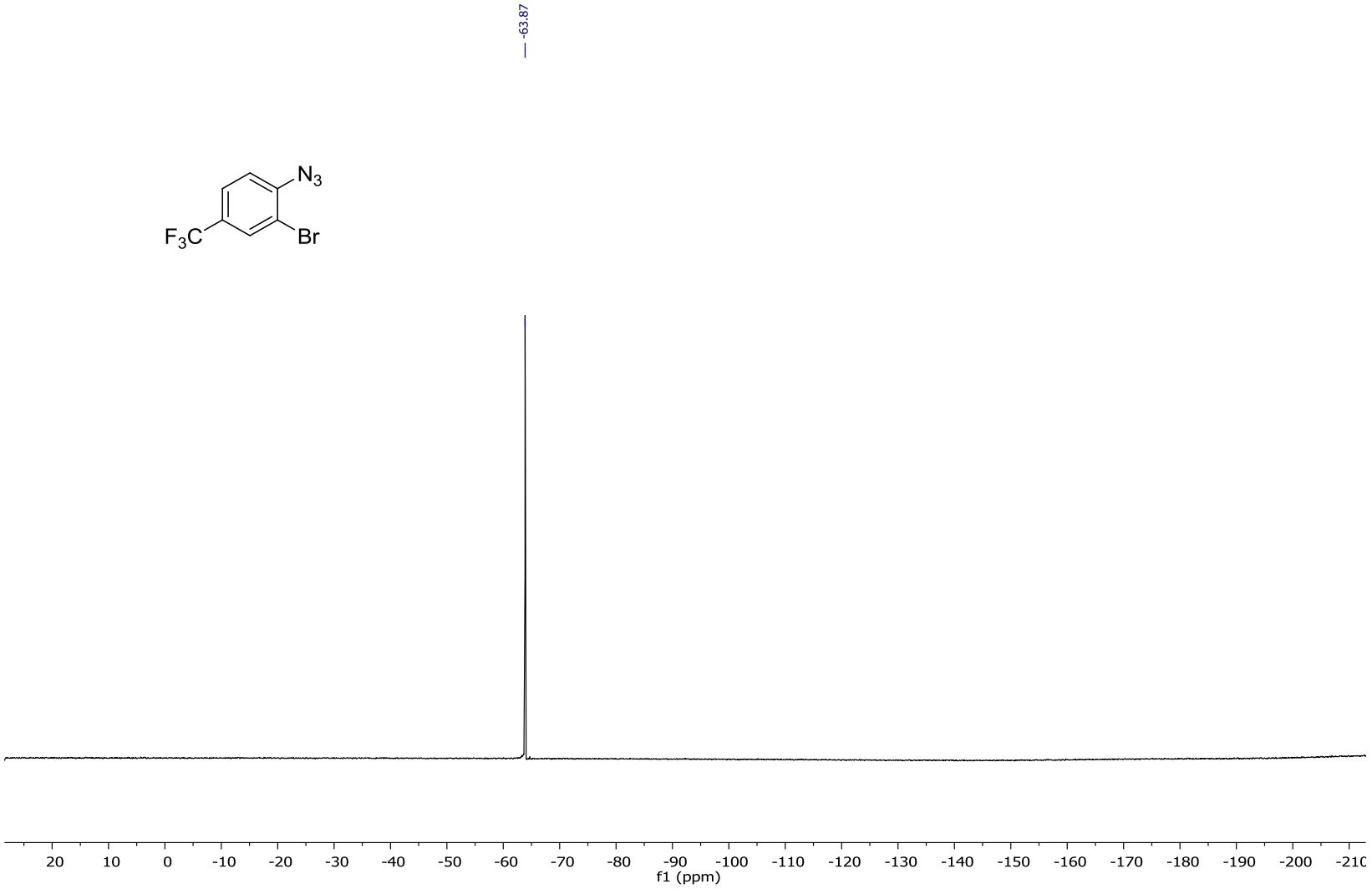


Figure S72. ^{19}F NMR (188 MHz, Chloroform-*d*) of 1-azido-2-bromo-4-(trifluoromethyl)benzene (2k).

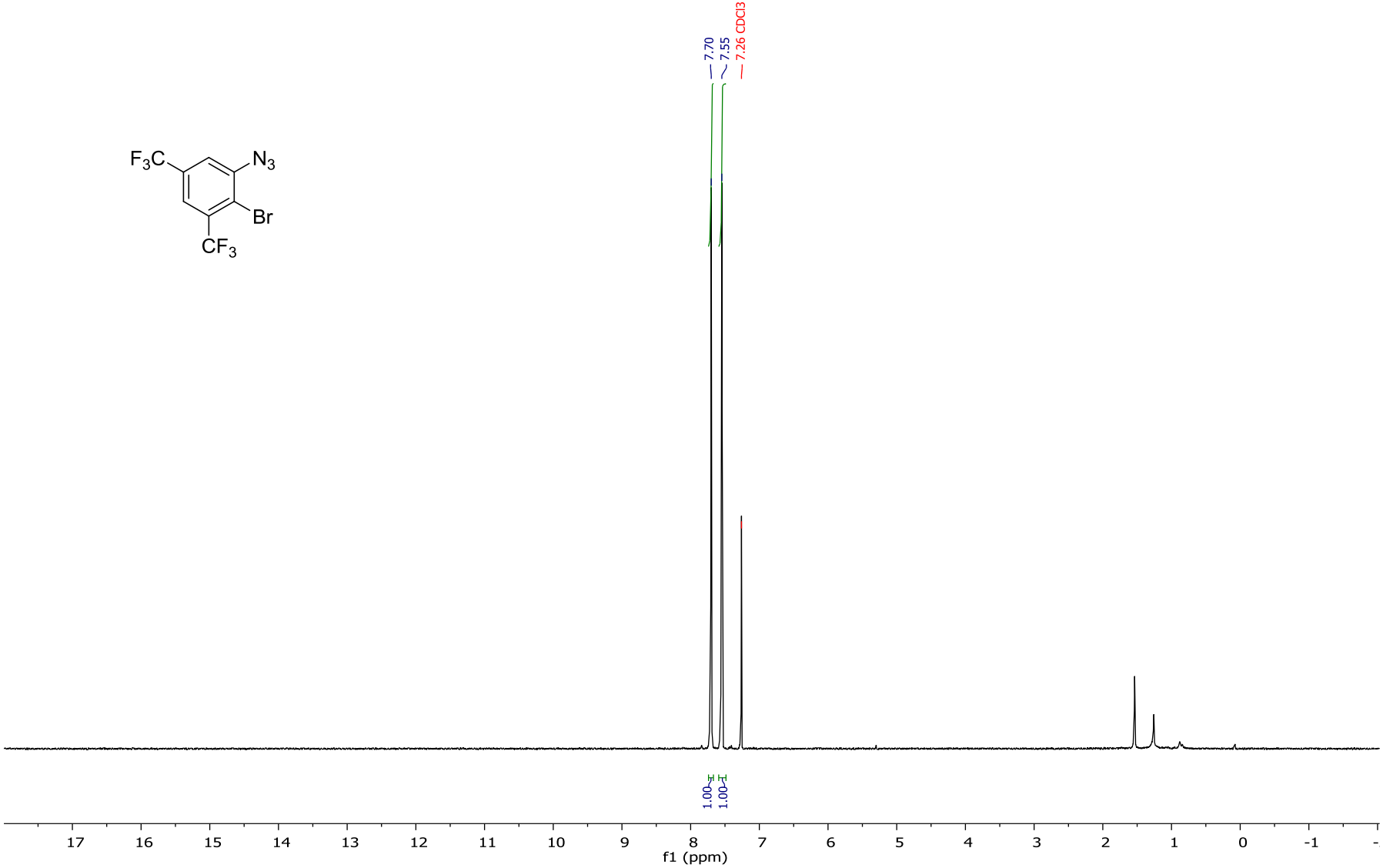


Figure S73. ^{1}H NMR (600 MHz, Chloroform-d) of 1-azido-2-bromo-3,5-bis(trifluoromethyl)benzene (2l).

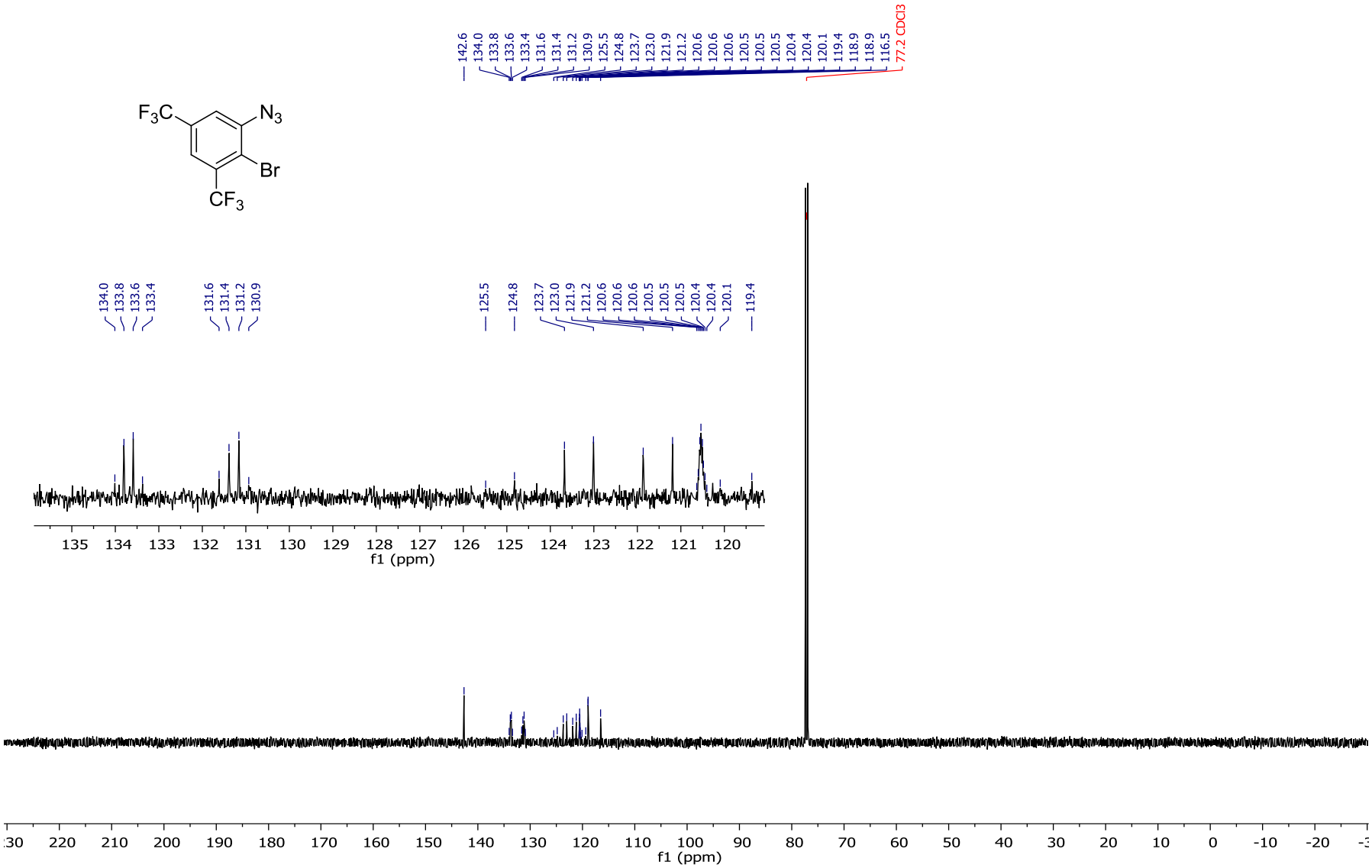


Figure S74. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-azido-2-bromo-3,5-bis(trifluoromethyl)benzene (2l).

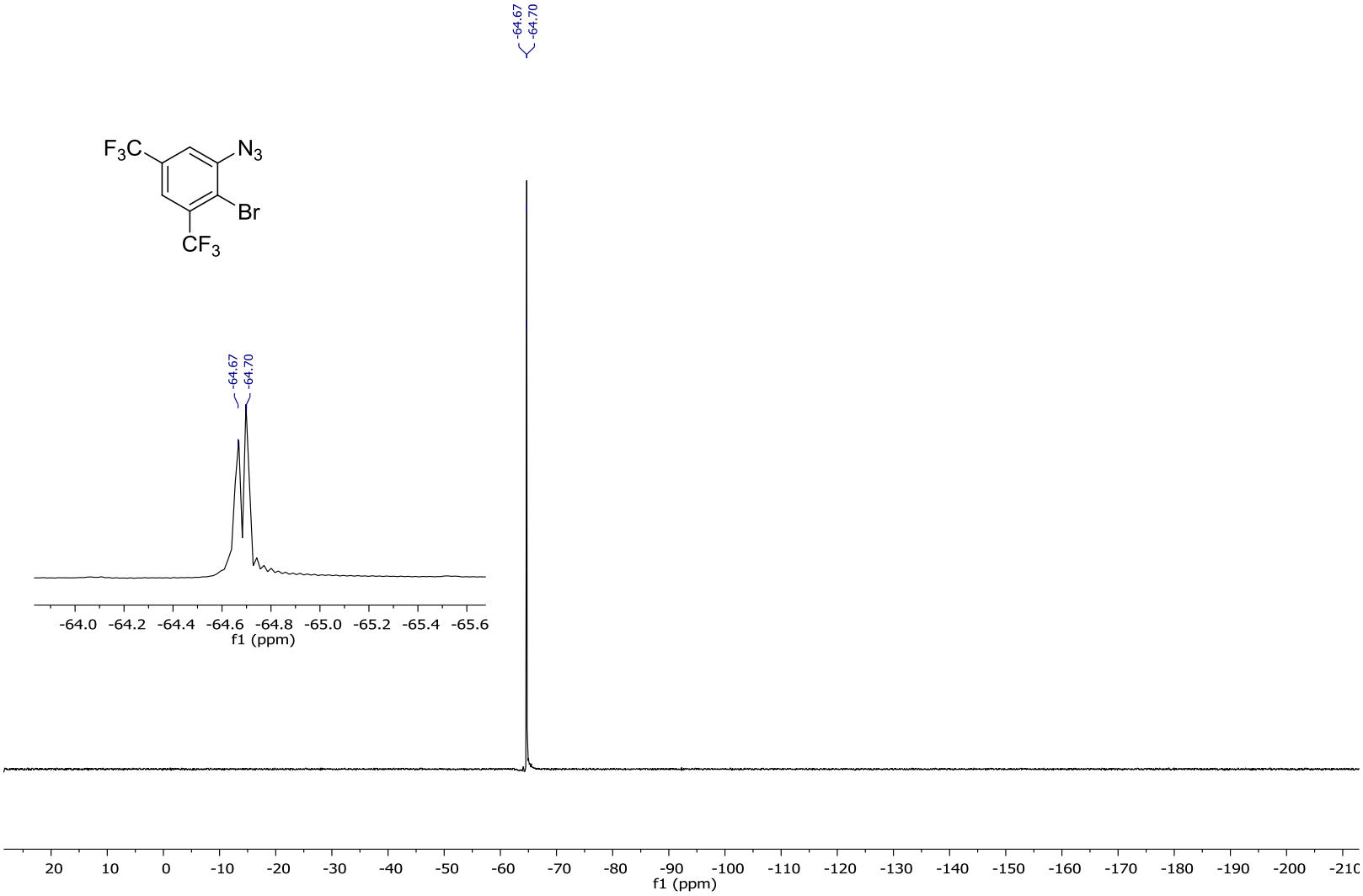


Figure S75. ^{19}F NMR (188 MHz, Chloroform-*d*) of 1-azido-2-bromo-3,5-bis(trifluoromethyl)benzene (2l).

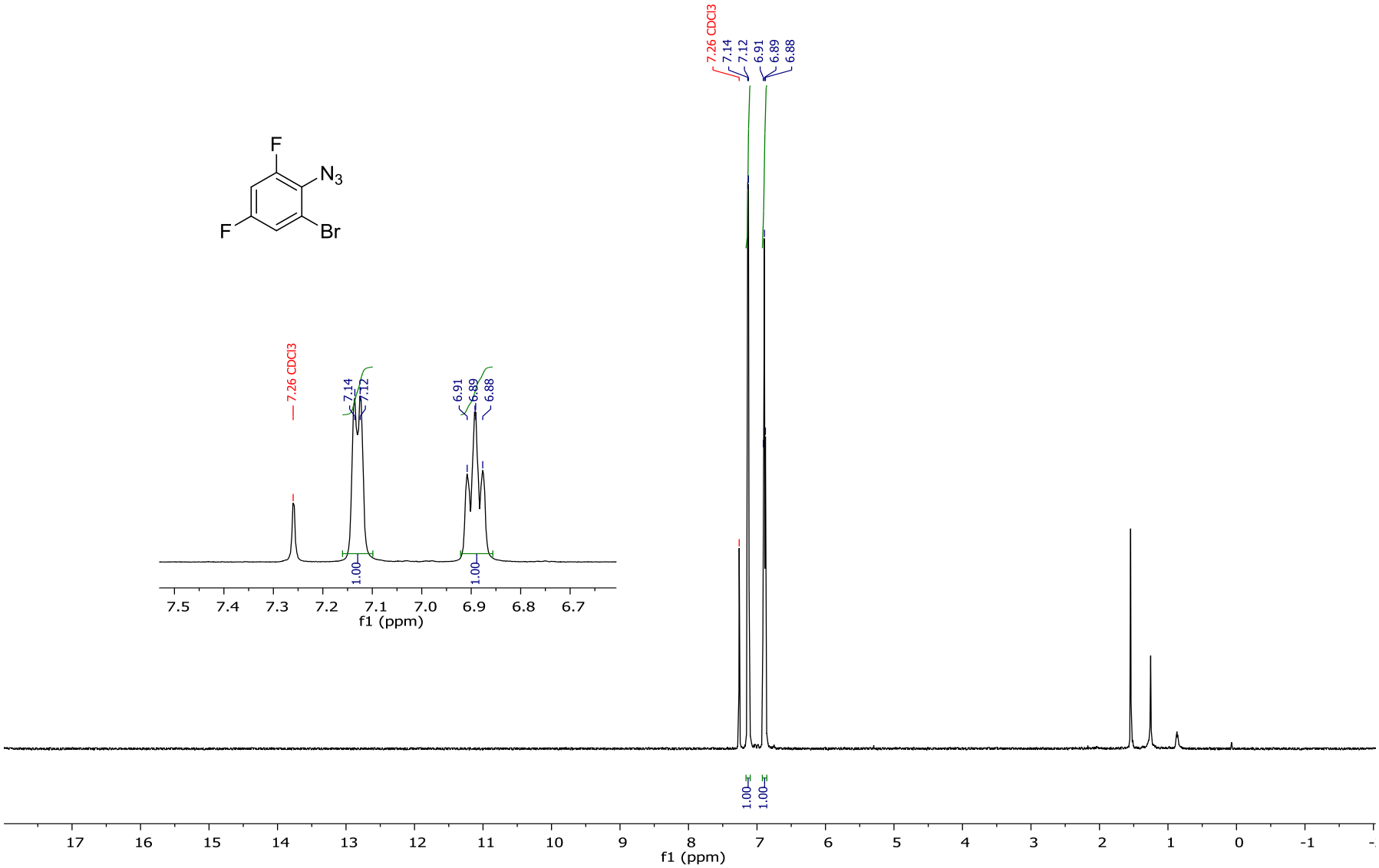


Figure S76. ^{1}H NMR (600 MHz, Chloroform-d) of 2-azido-1-bromo-3,5-difluorobenzene (2m).

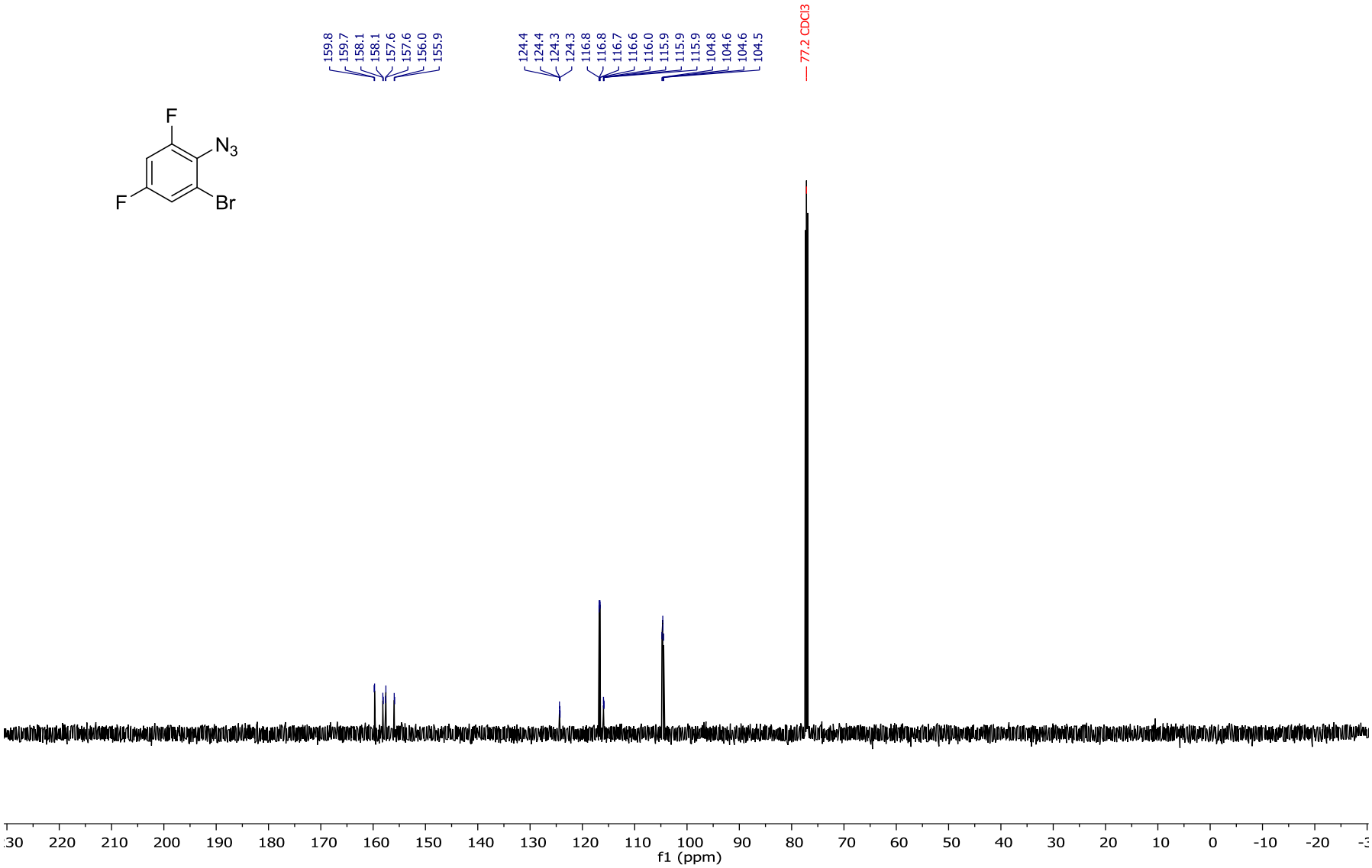


Figure S77. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-azido-1-bromo-3,5-difluorobenzene (2m).

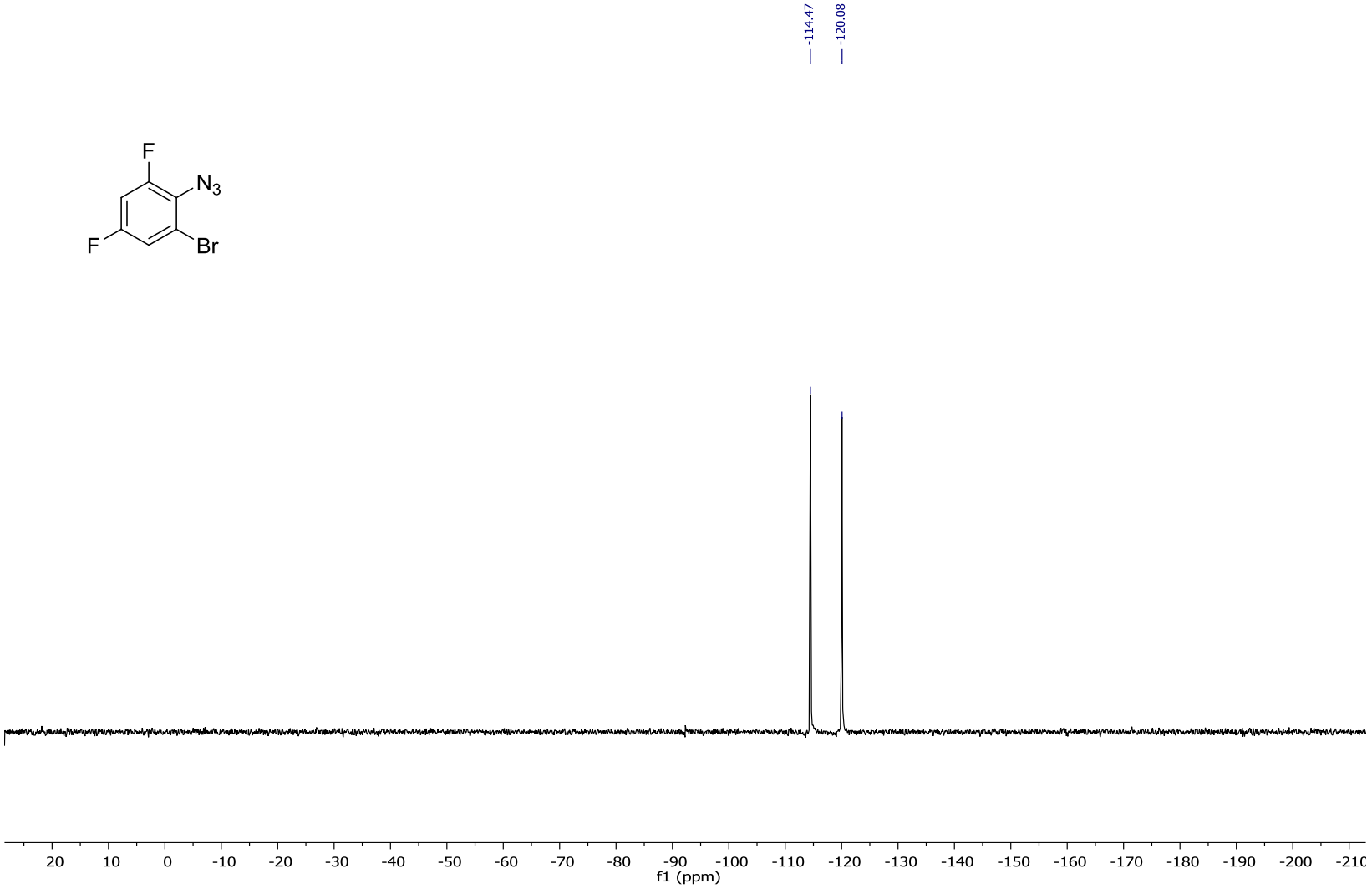


Figure S78. ^{19}F NMR (188 MHz, Chloroform-*d*) of 2-azido-1-bromo-3,5-difluorobenzene (2m).

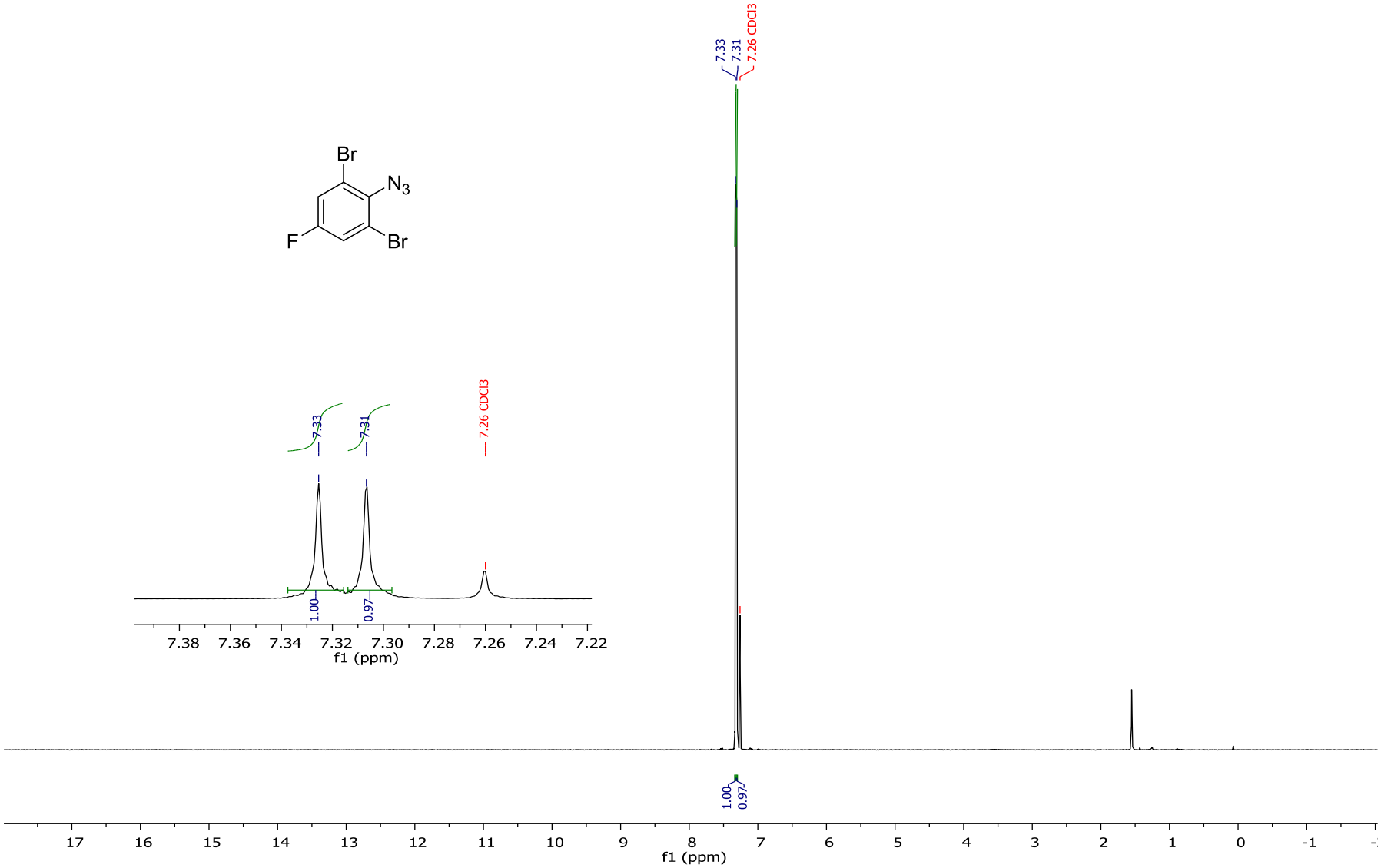


Figure S79. ^{1}H NMR (600 MHz, Chloroform-d) of 2-azido-1,3-dibromo-5-fluorobenzene (2n).

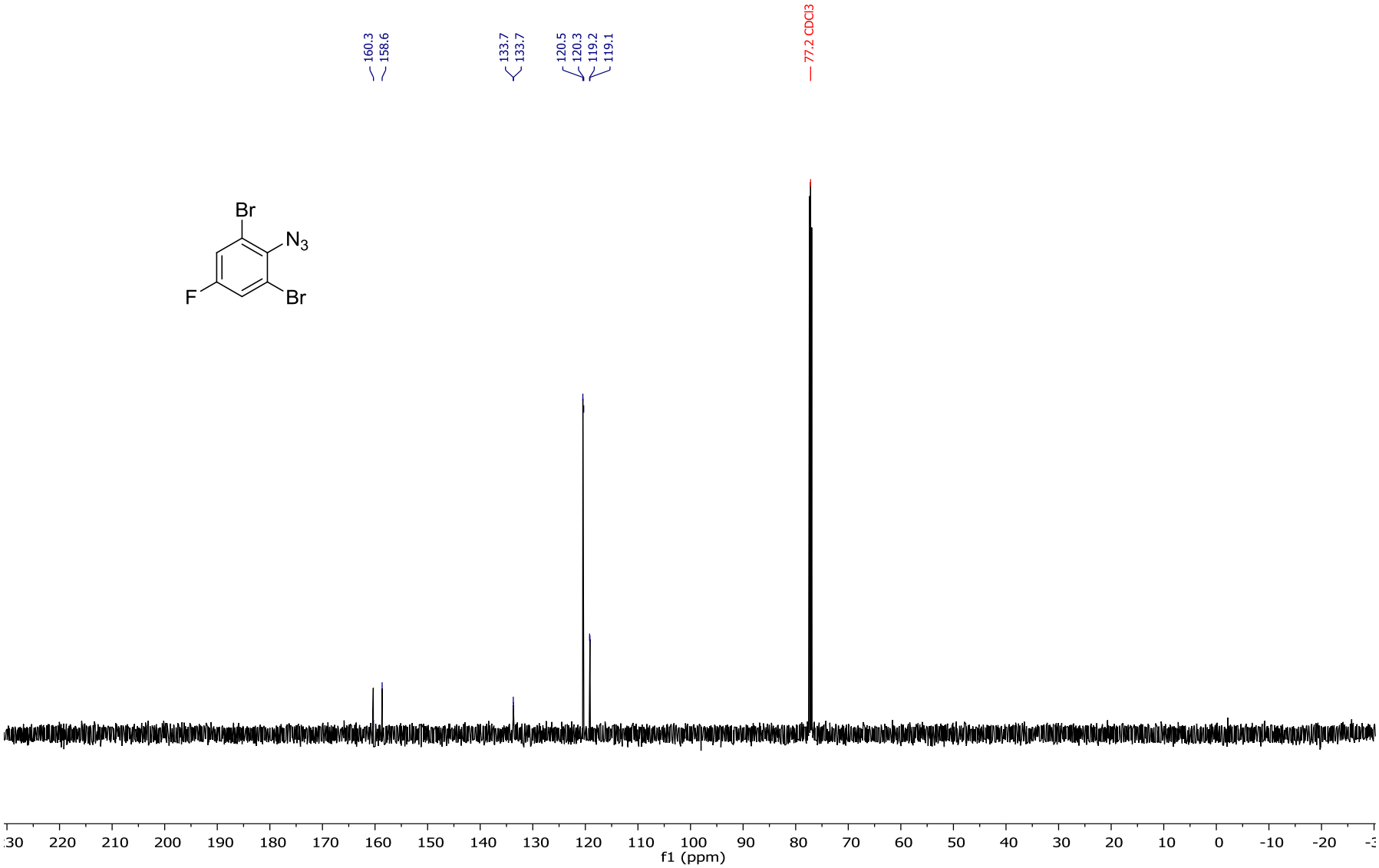


Figure S80. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-azido-1,3-dibromo-5-fluorobenzene (2n).

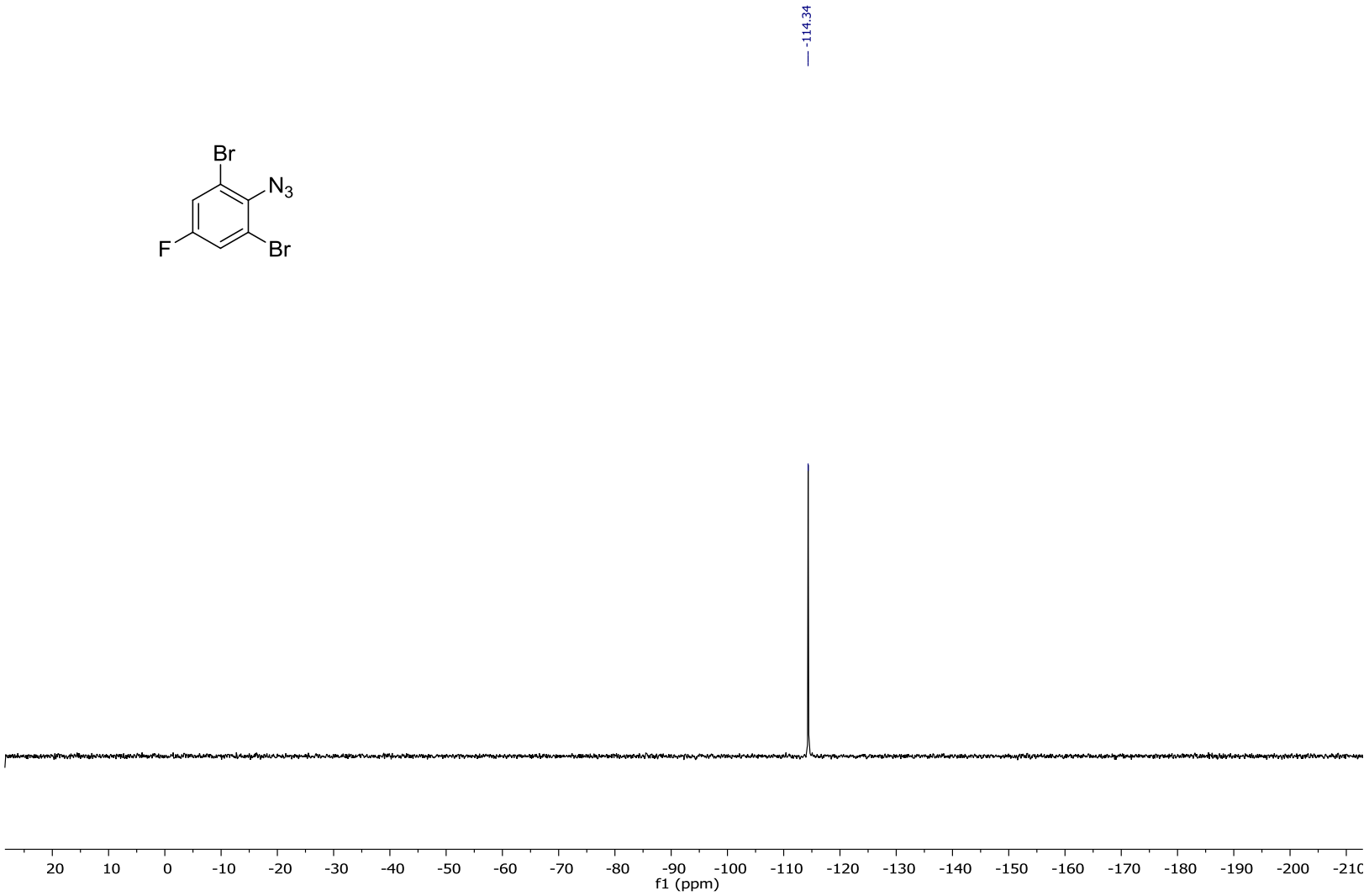


Figure S81. ^{19}F NMR (188 MHz, Chloroform-*d*) of 2-azido-1,3-dibromo-5-fluorobenzene (2n).

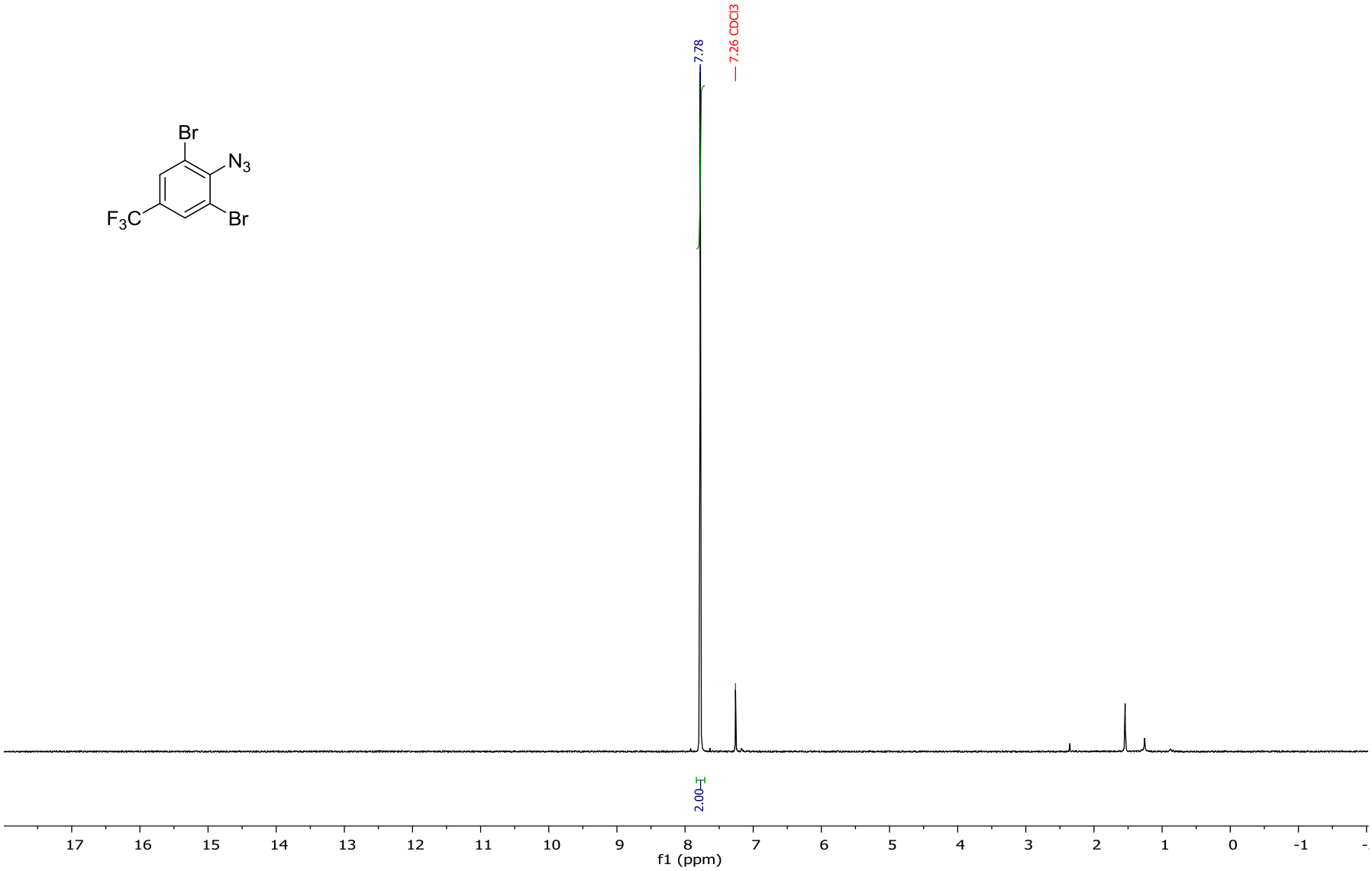


Figure S82. ^{1}H NMR (600 MHz, Chloroform-d) of 2-azido-1,3-dibromo-5-(trifluoromethyl)benzene (2o).

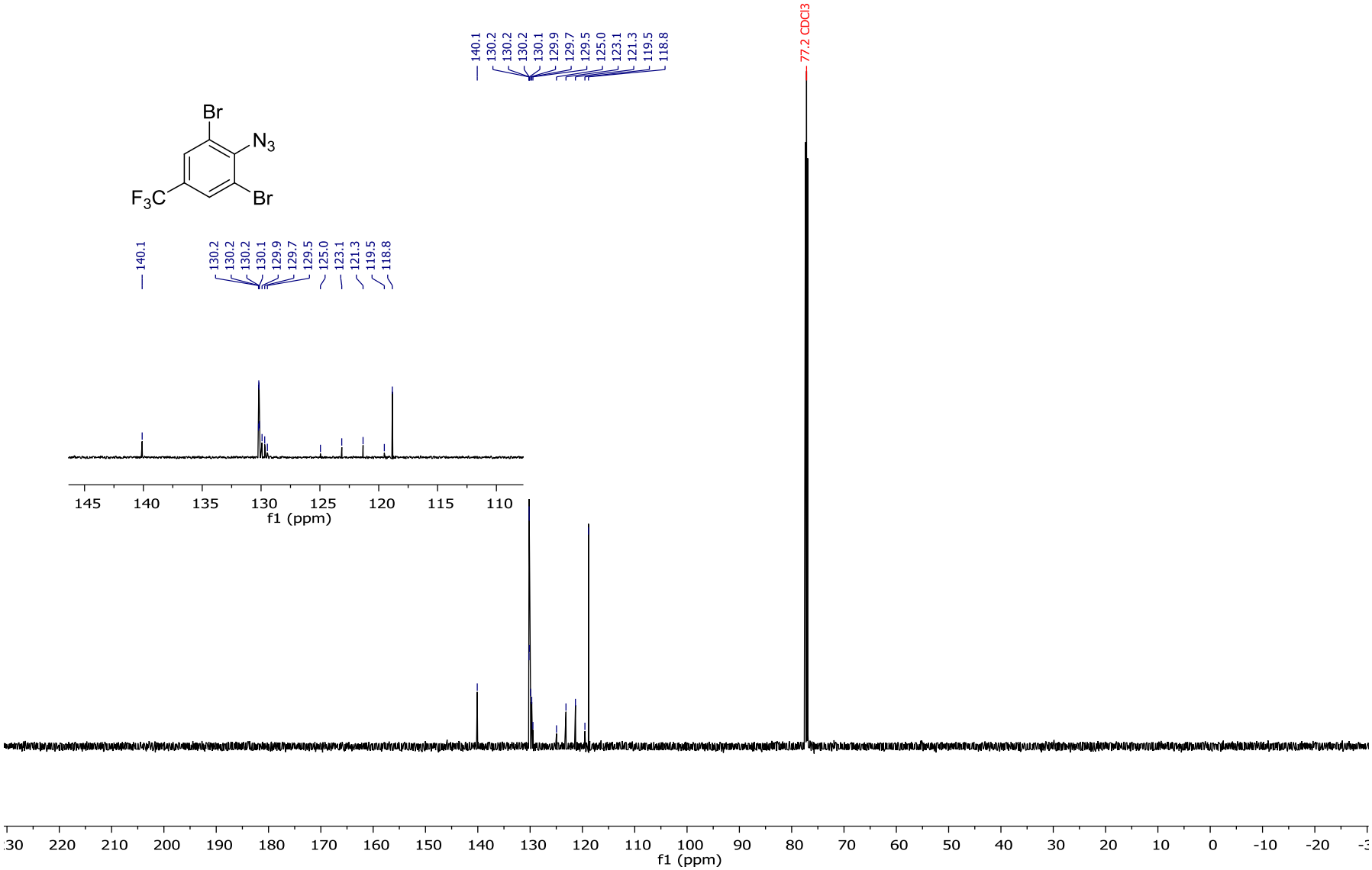


Figure S83. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-azido-1,3-dibromo-5-(trifluoromethyl)benzene (2o).

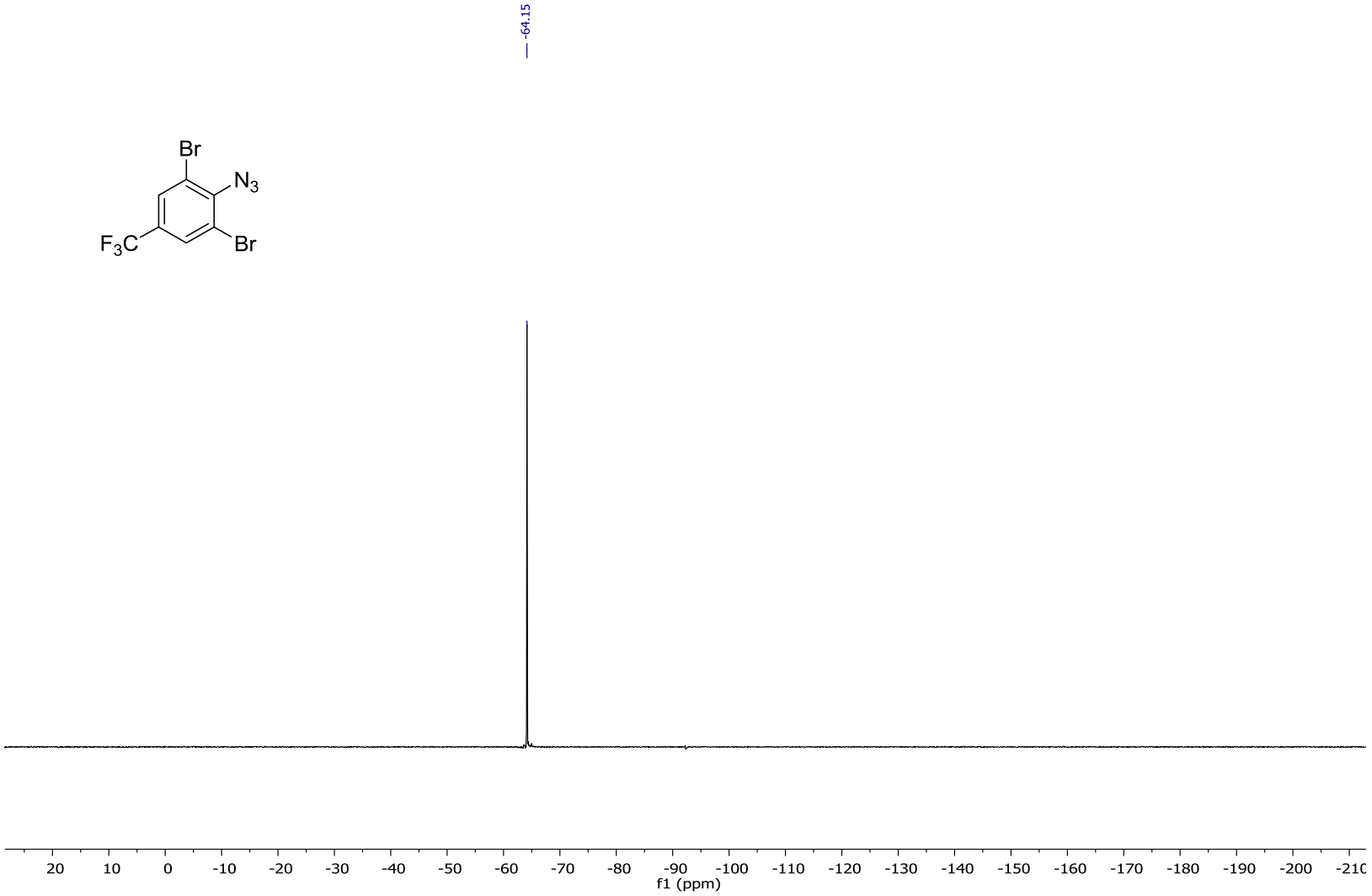


Figure S84. ^{19}F NMR (188 MHz, Chloroform-*d*) of 2-azido-1,3-dibromo-5-(trifluoromethyl)benzene (2o).

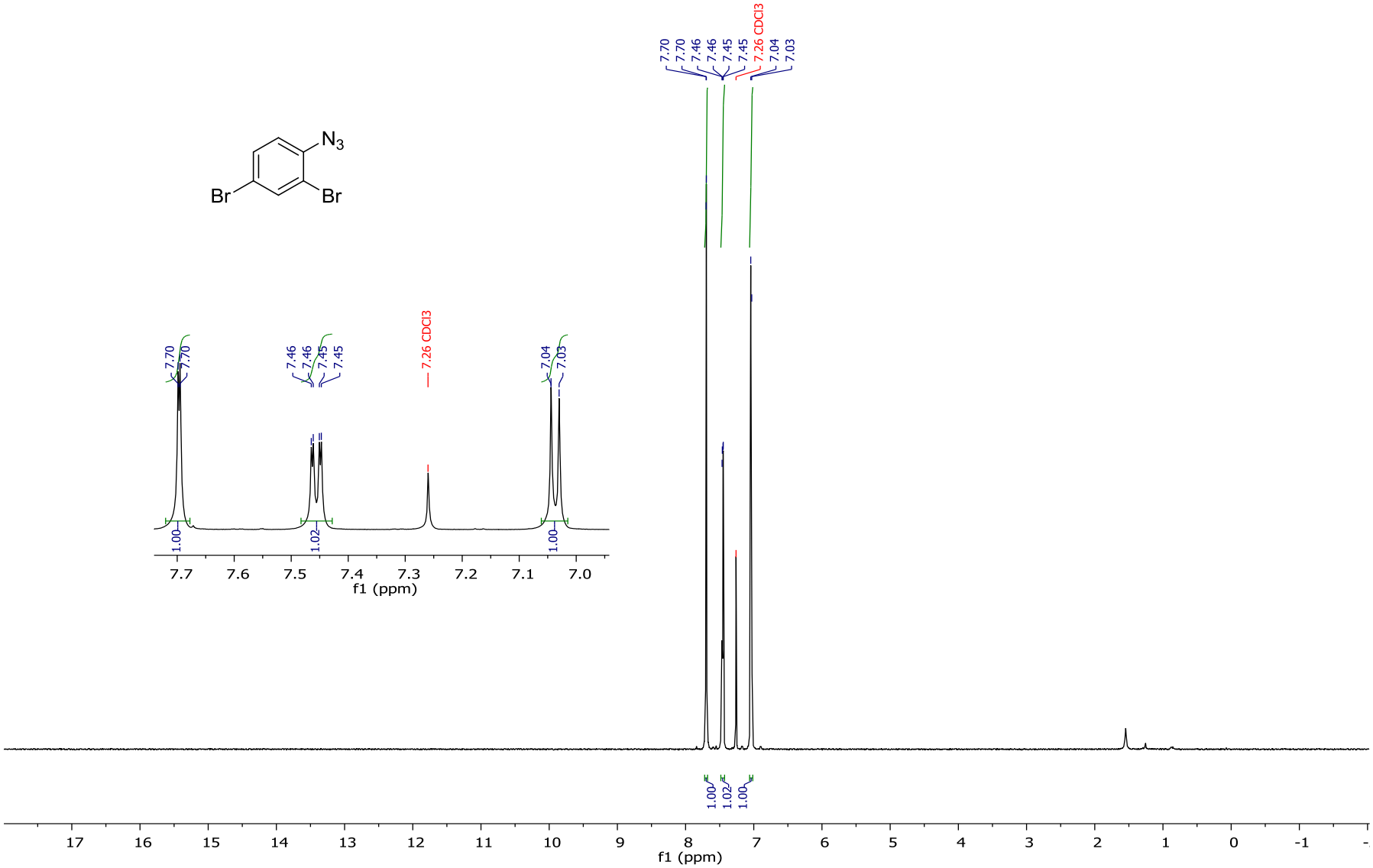


Figure S85. ^{1}H NMR (600 MHz, Chloroform-d) of 1-azido-2,4-dibromobenzene (2p).

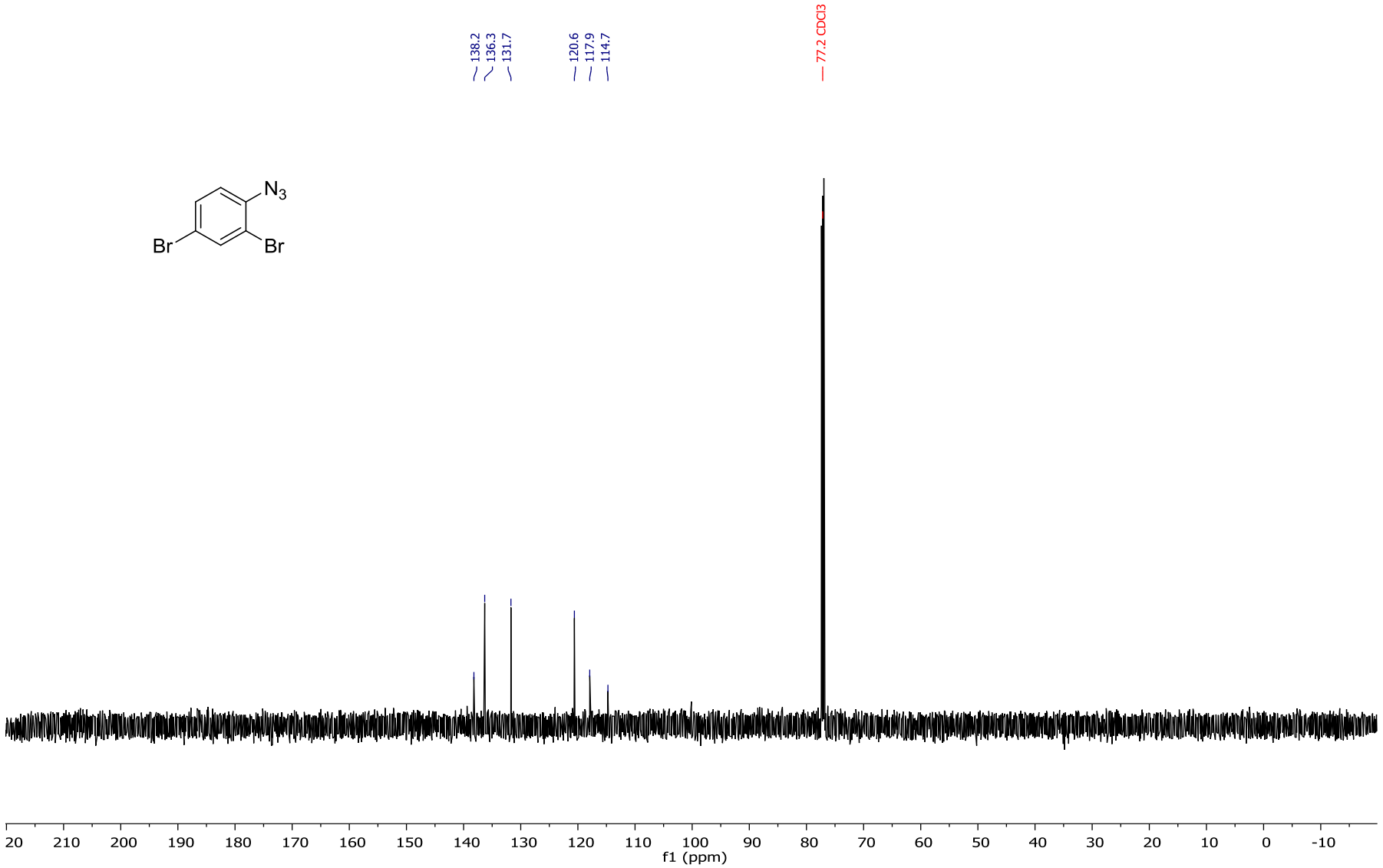


Figure S86. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-azido-2,4-dibromobenzene (2p).

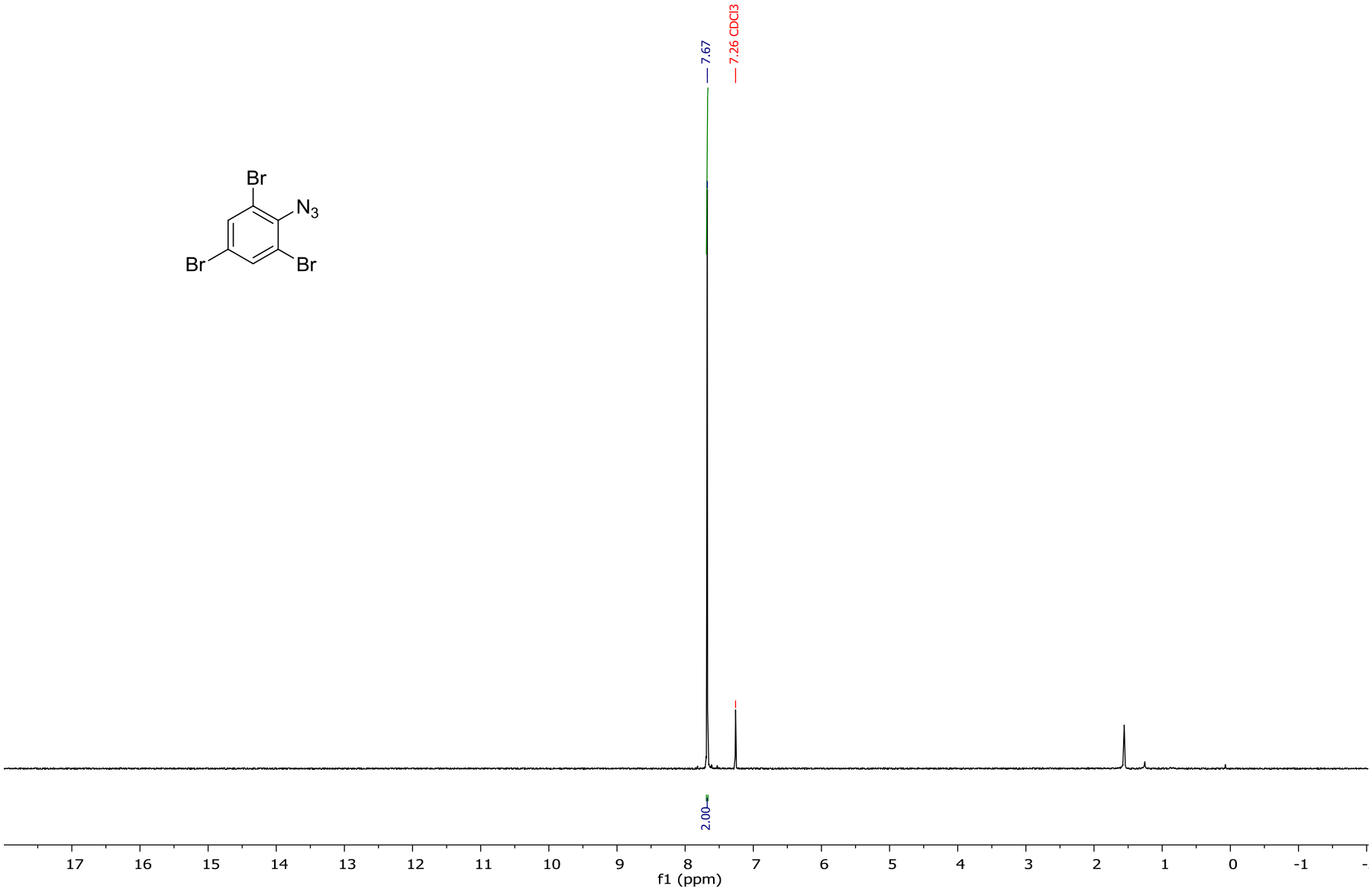


Figure S87. ^{1}H NMR (600 MHz, Chloroform-d) of 2-azido-1,3,5-tribromobenzene (2q).

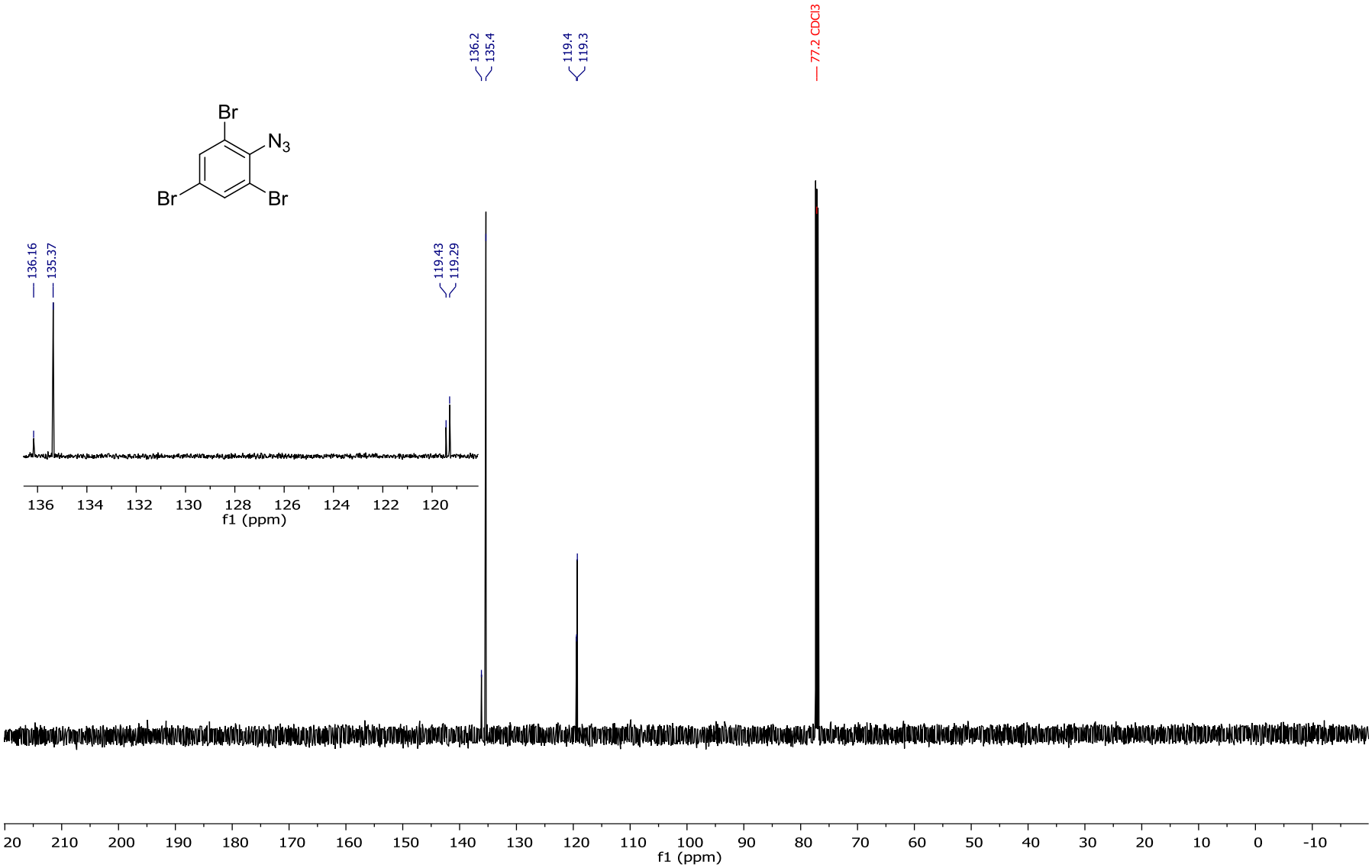


Figure S88. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-azido-1,3,5-tribromobenzene (2q).

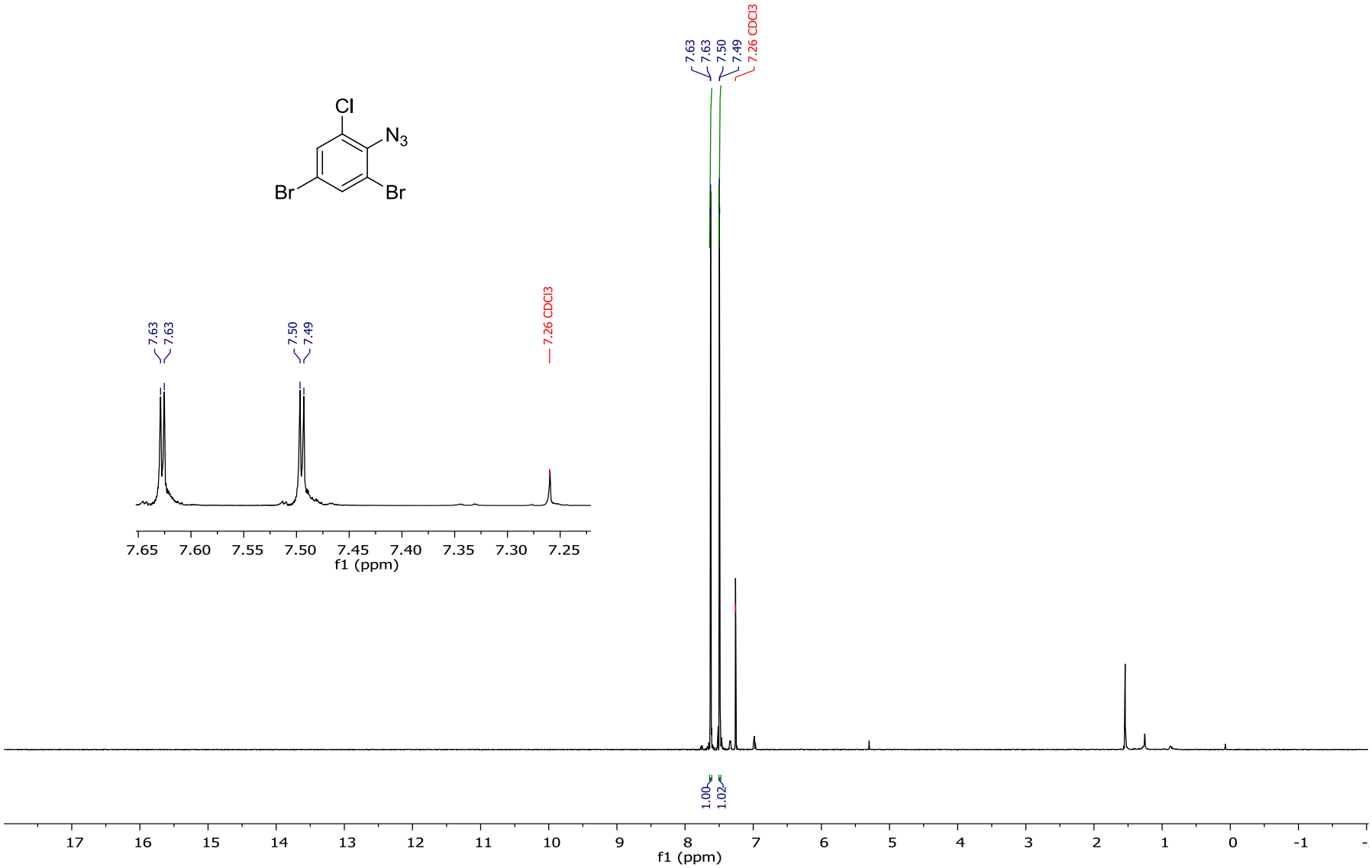


Figure S89. ^{1}H NMR (600 MHz, Chloroform-d) of 2-azido-1,5-dibromo-3-chlorobenzene (2r).

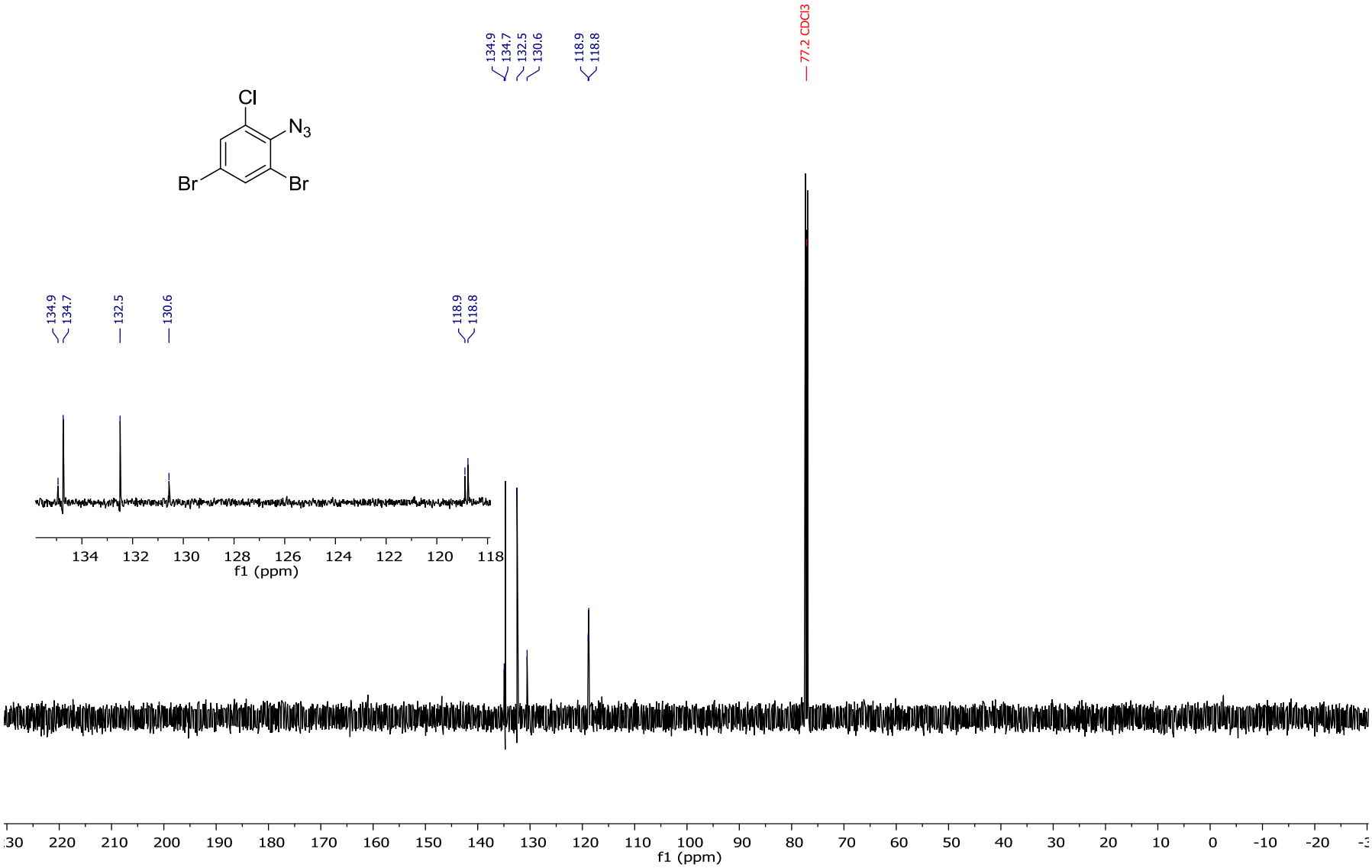


Figure S90. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-azido-1,5-dibromo-3-chlorobenzene(2r).

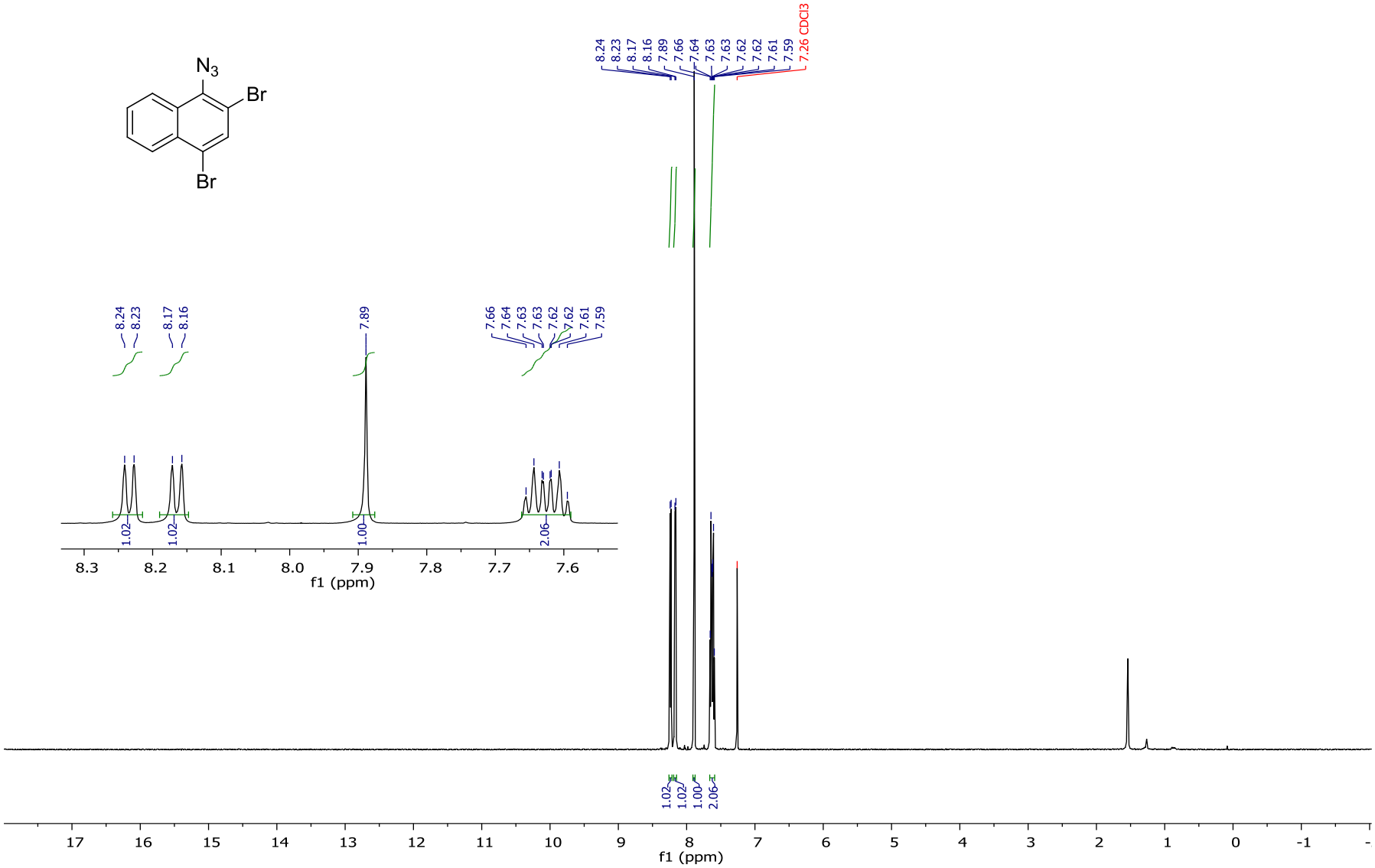


Figure S91. ^{1}H NMR (600 MHz, Chloroform-d) of 1-azido-2,4-dibromonaphthalene (2s).

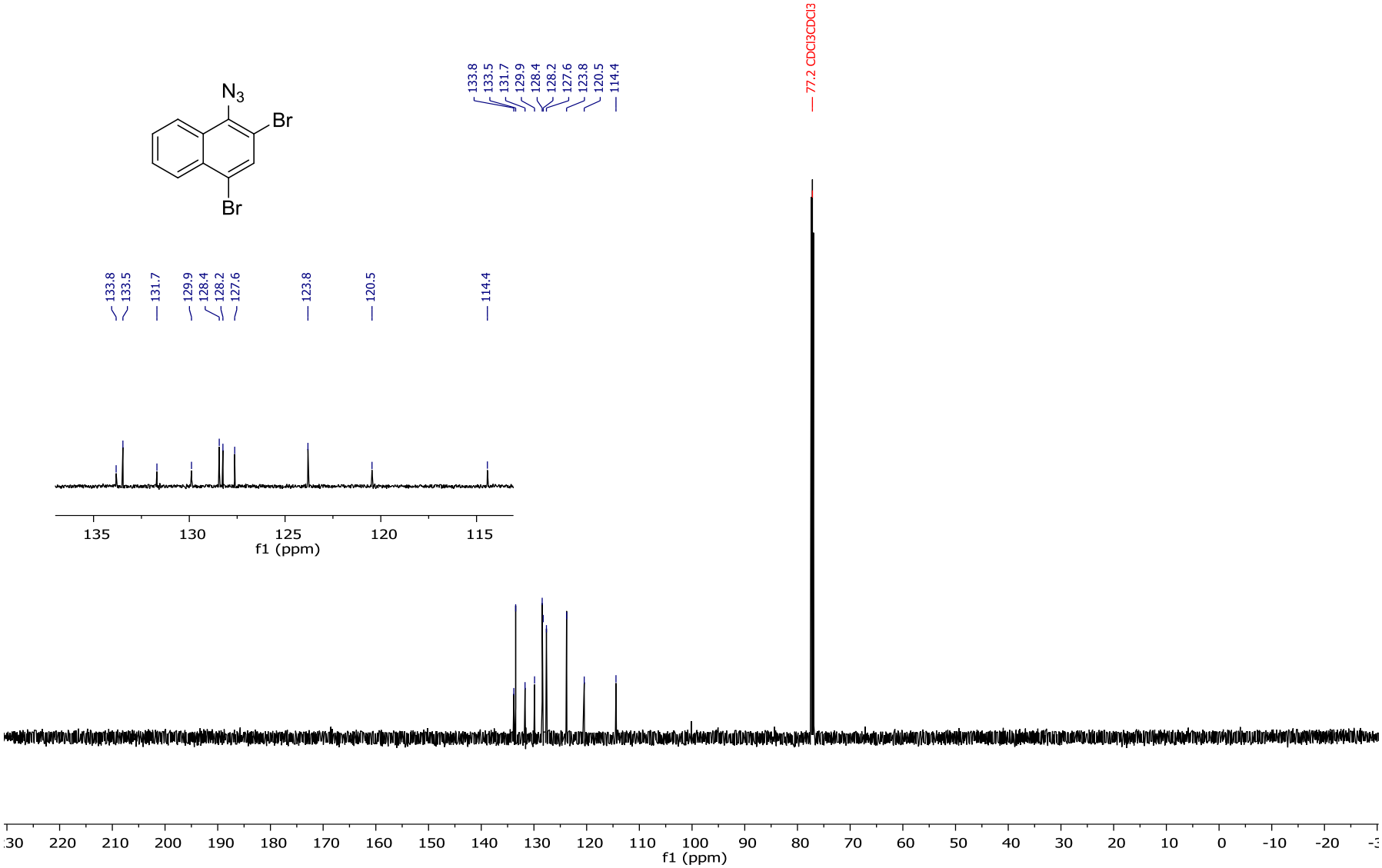


Figure S92. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-azido-2,4-dibromonaphthalene (2s).

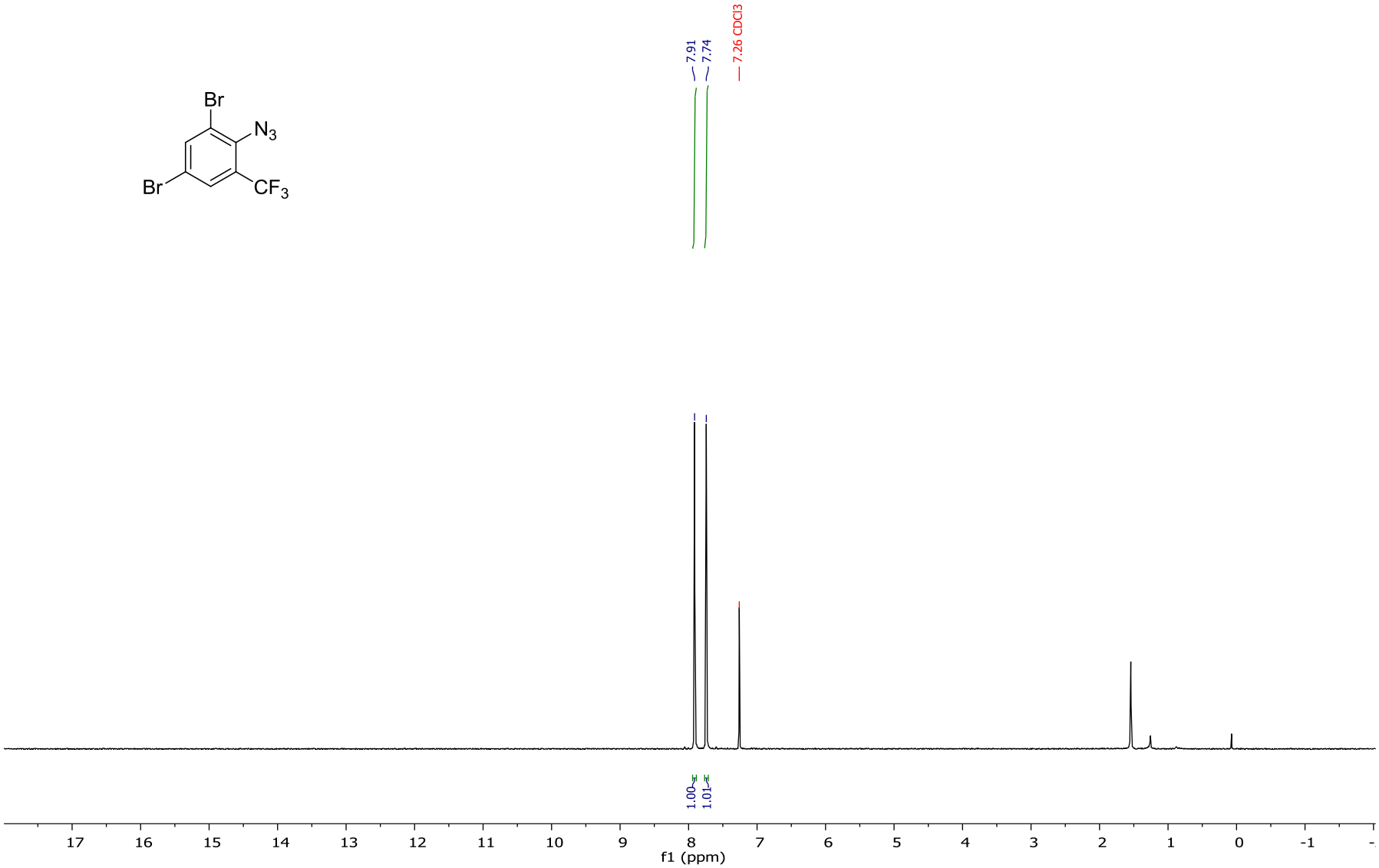


Figure S93. ^{1}H NMR (600 MHz, Chloroform-d) of 2-azido-1,5-dibromo-3-(trifluoromethyl)benzene (2t).

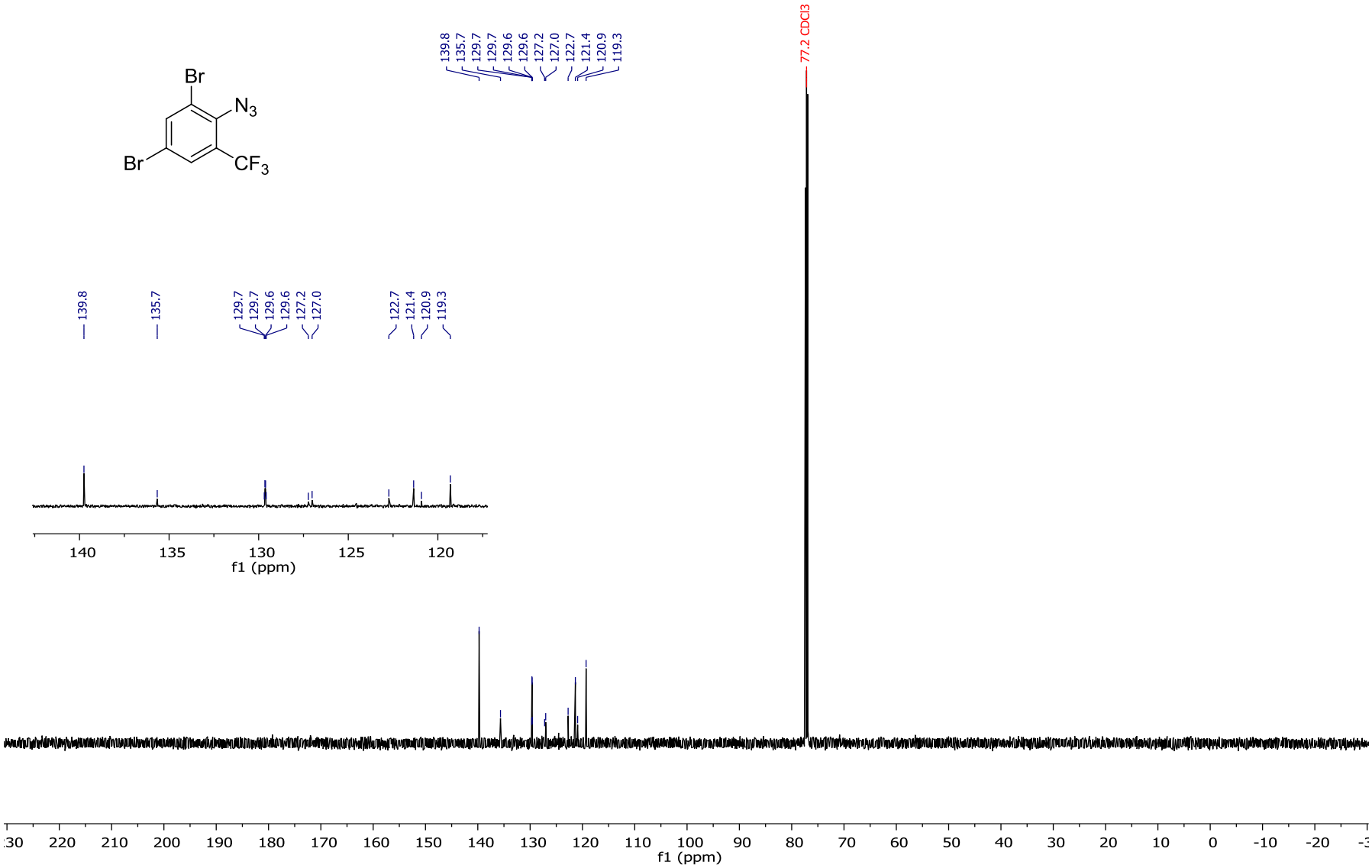


Figure S94. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-azido-1,5-dibromo-3-(trifluoromethyl)benzene (2t).

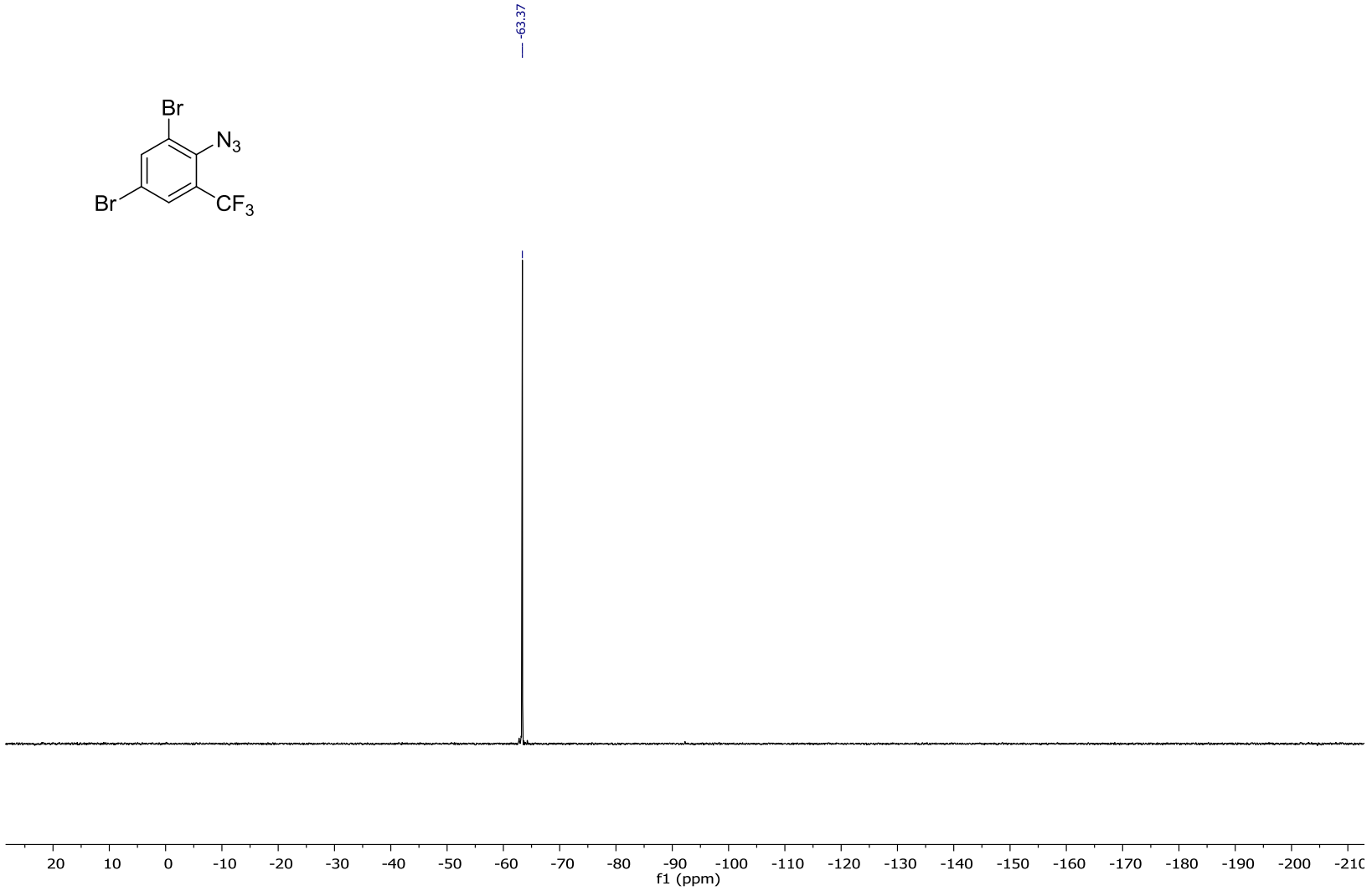


Figure S95. ^{19}F NMR (188 MHz, Chloroform-*d*) of 2-azido-1,5-dibromo-3-(trifluoromethyl)benzene (2t).

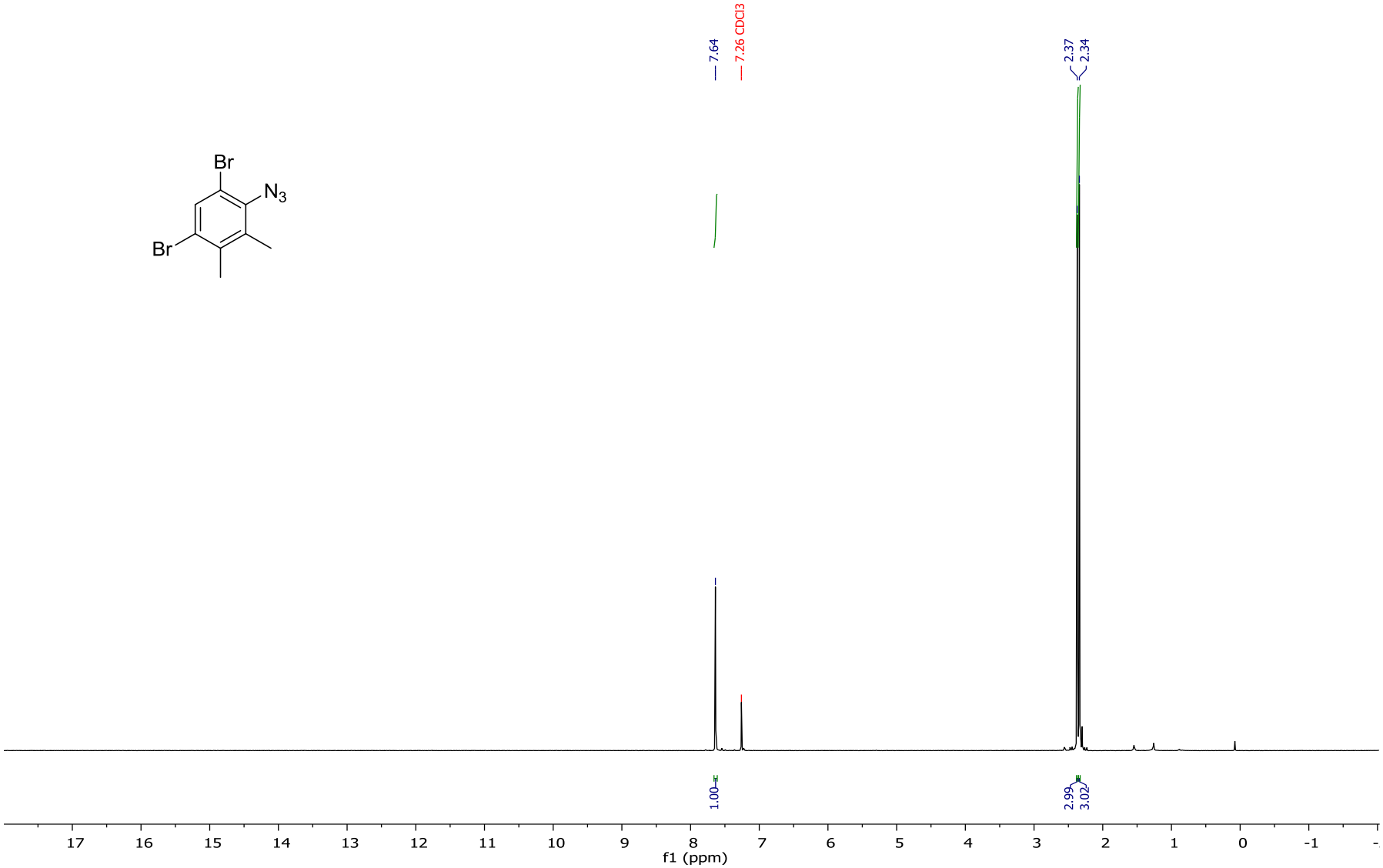


Figure S96. ^{1}H NMR (600 MHz, Chloroform-d) of 2-azido-1,5-dibromo-3,4-dimethylbenzene (2u).

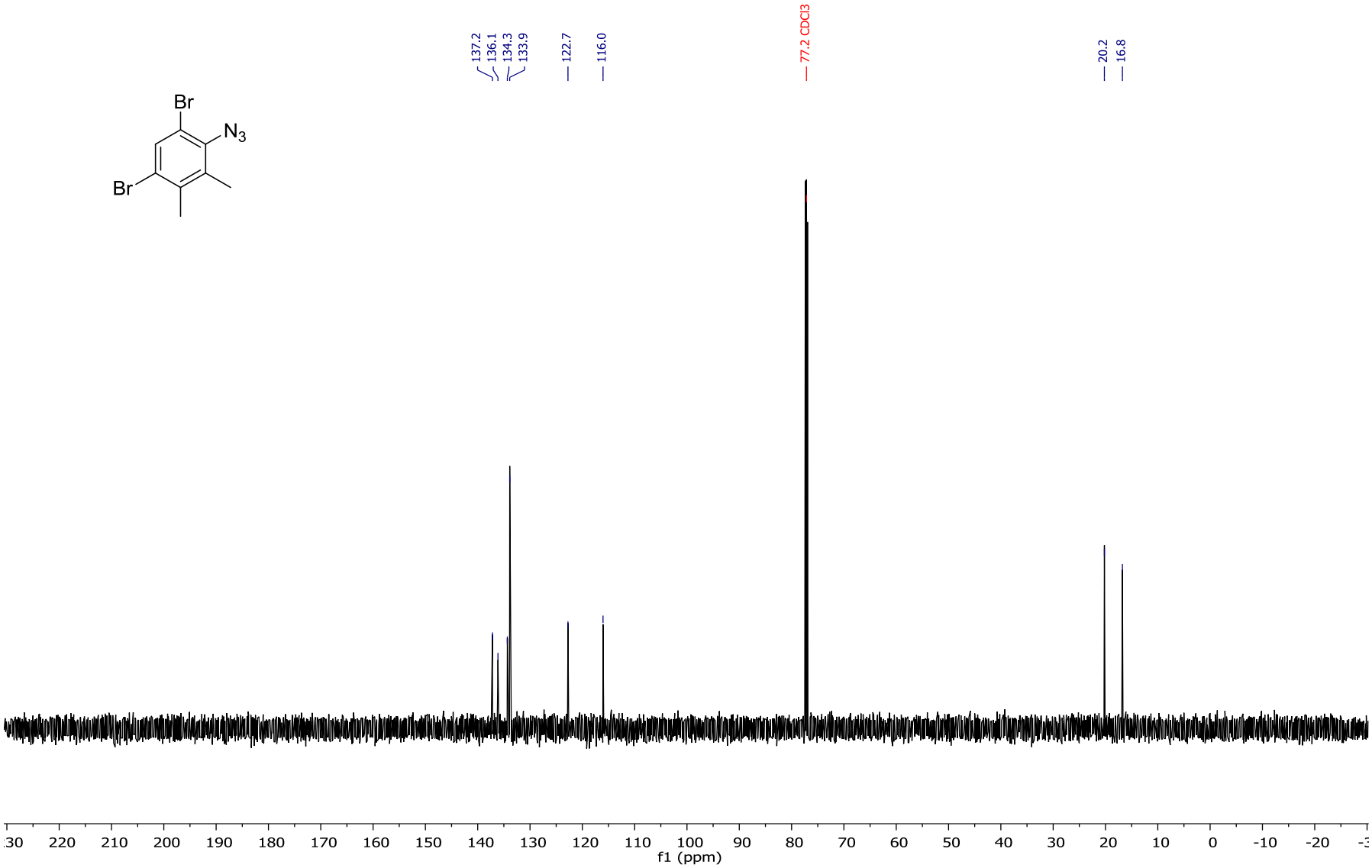


Figure S97. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-azido-1,5-dibromo-3,4-dimethylbenzene (2u).

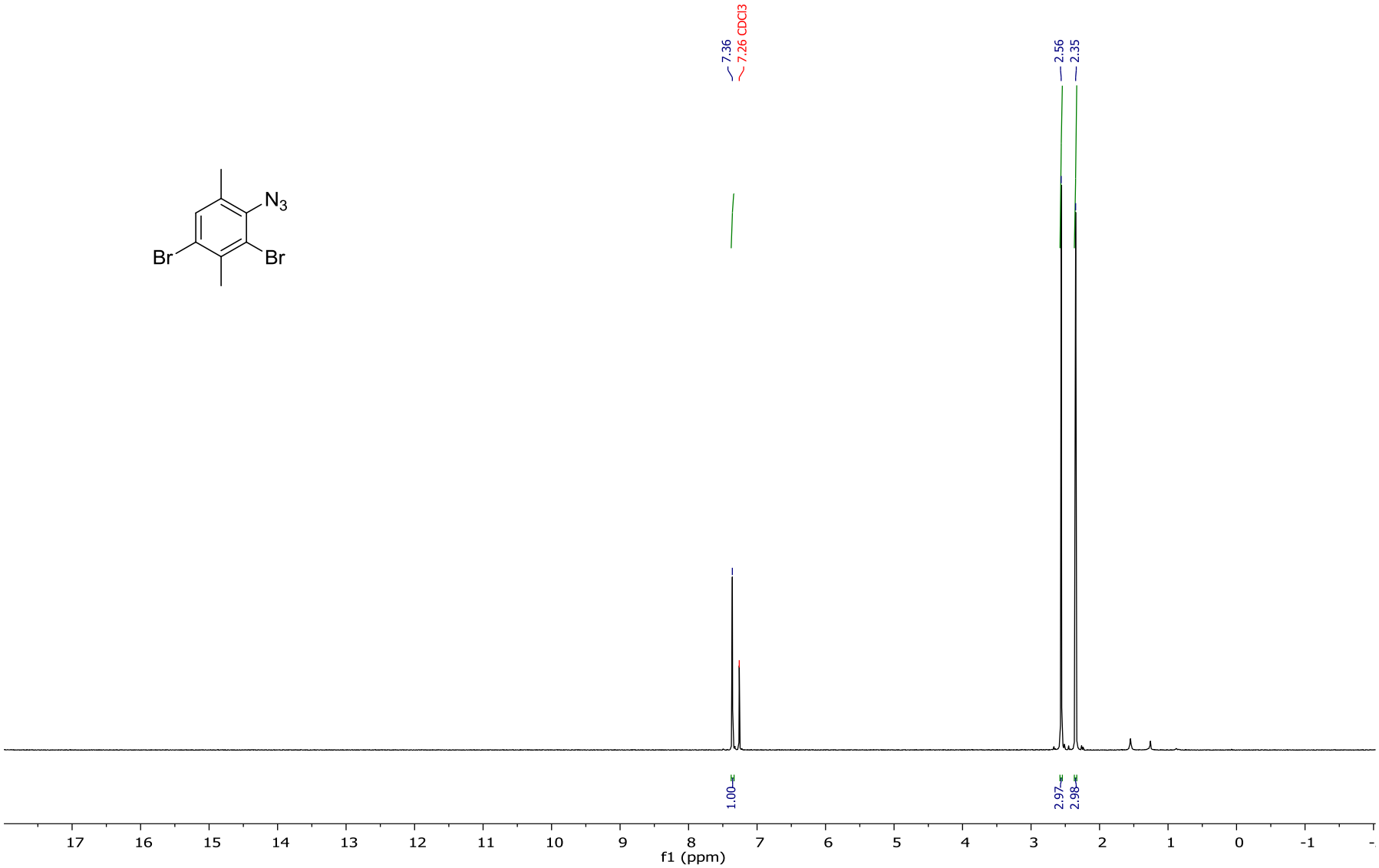


Figure S98. ^{1}H NMR (600 MHz, Chloroform-d) of 2-azido-3,5-dibromo-1,4-dimethylbenzene (2v).

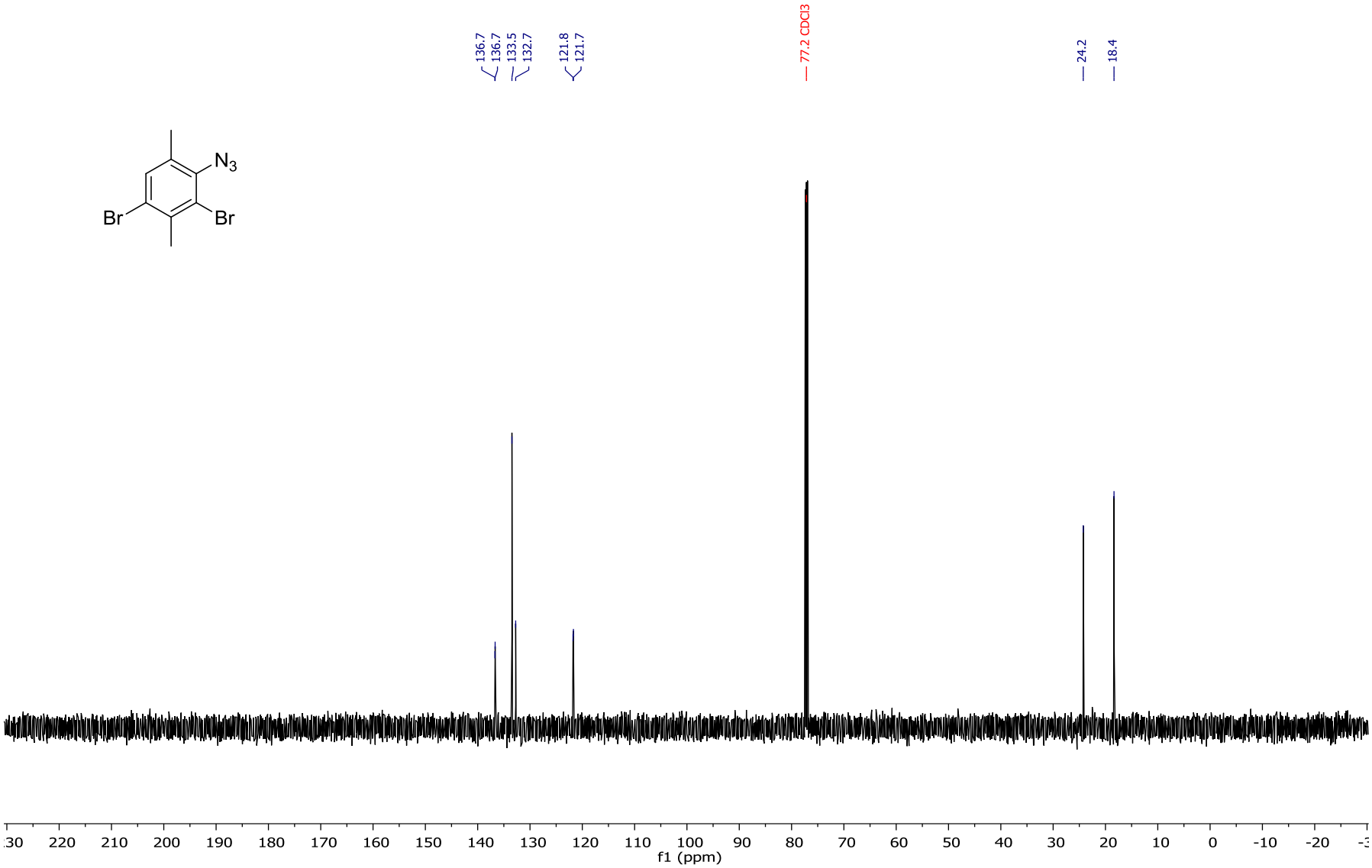


Figure S99. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-azido-3,5-dibromo-1,4-dimethylbenzene (2v).

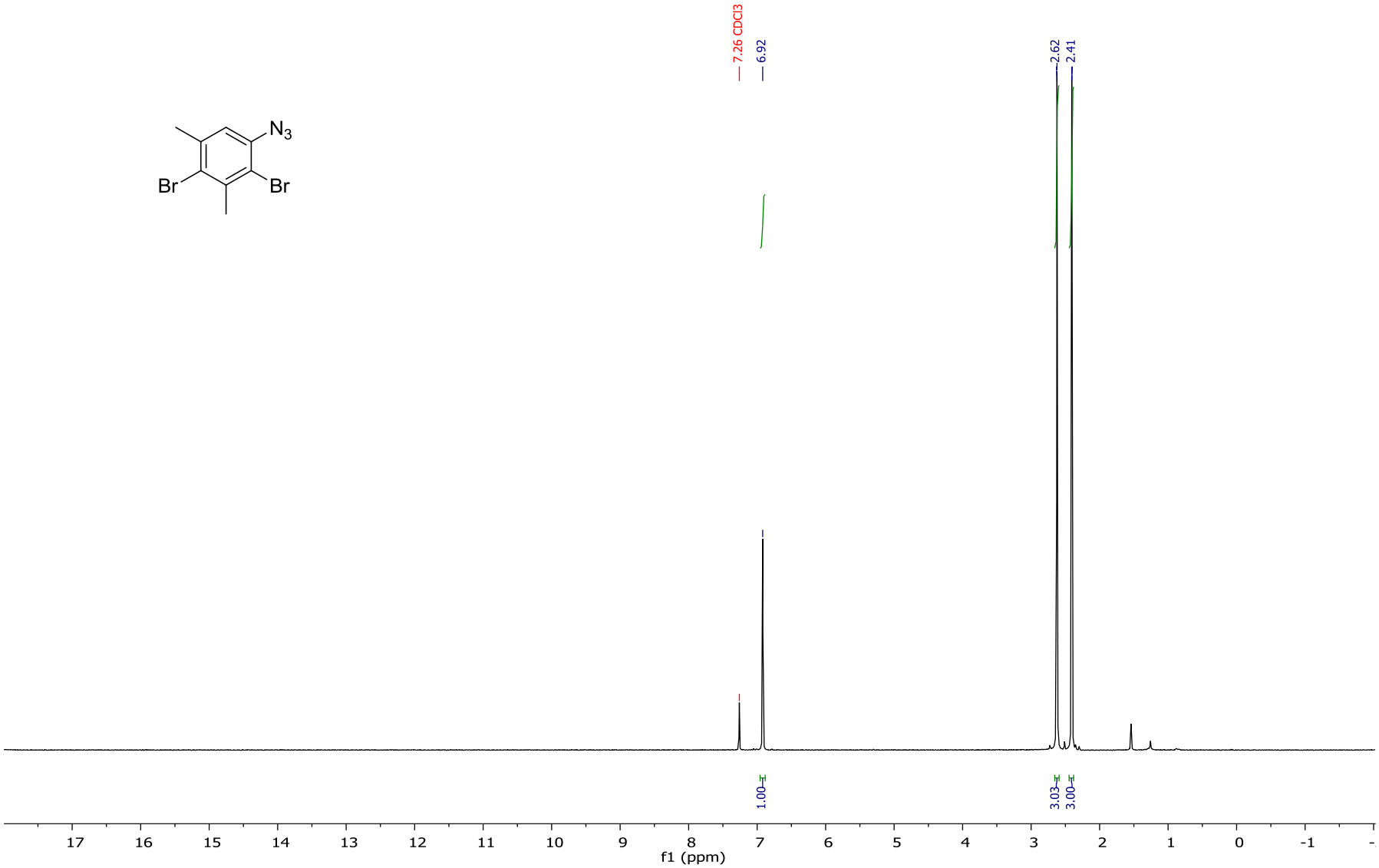


Figure S100. ^{1}H NMR (600 MHz, Chloroform-d) of 1-azido-2,4-dibromo-3,5-dimethylbenzene (2w).

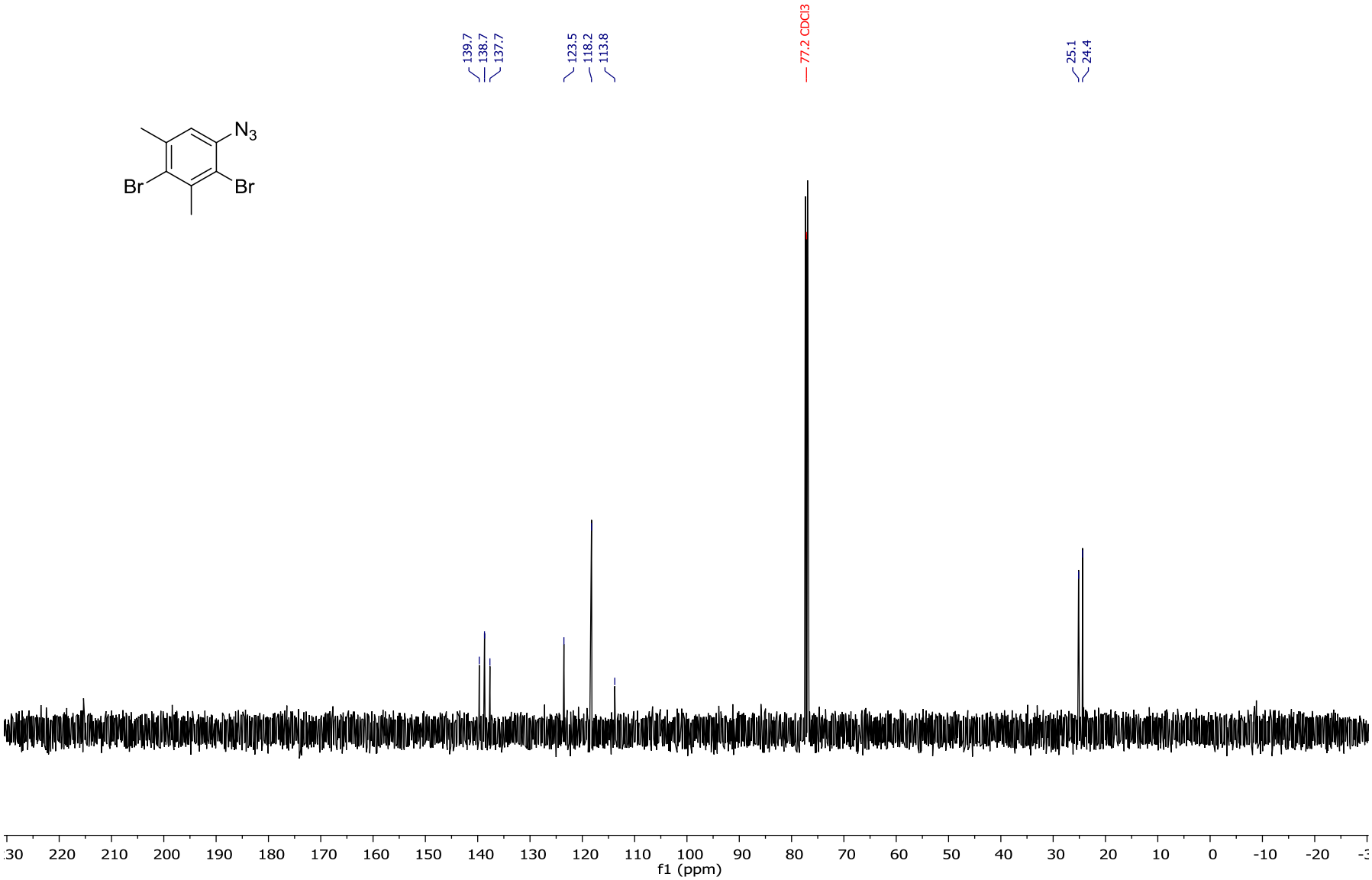


Figure S101. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-azido-2,4-dibromo-3,5-dimethylbenzene (2w).

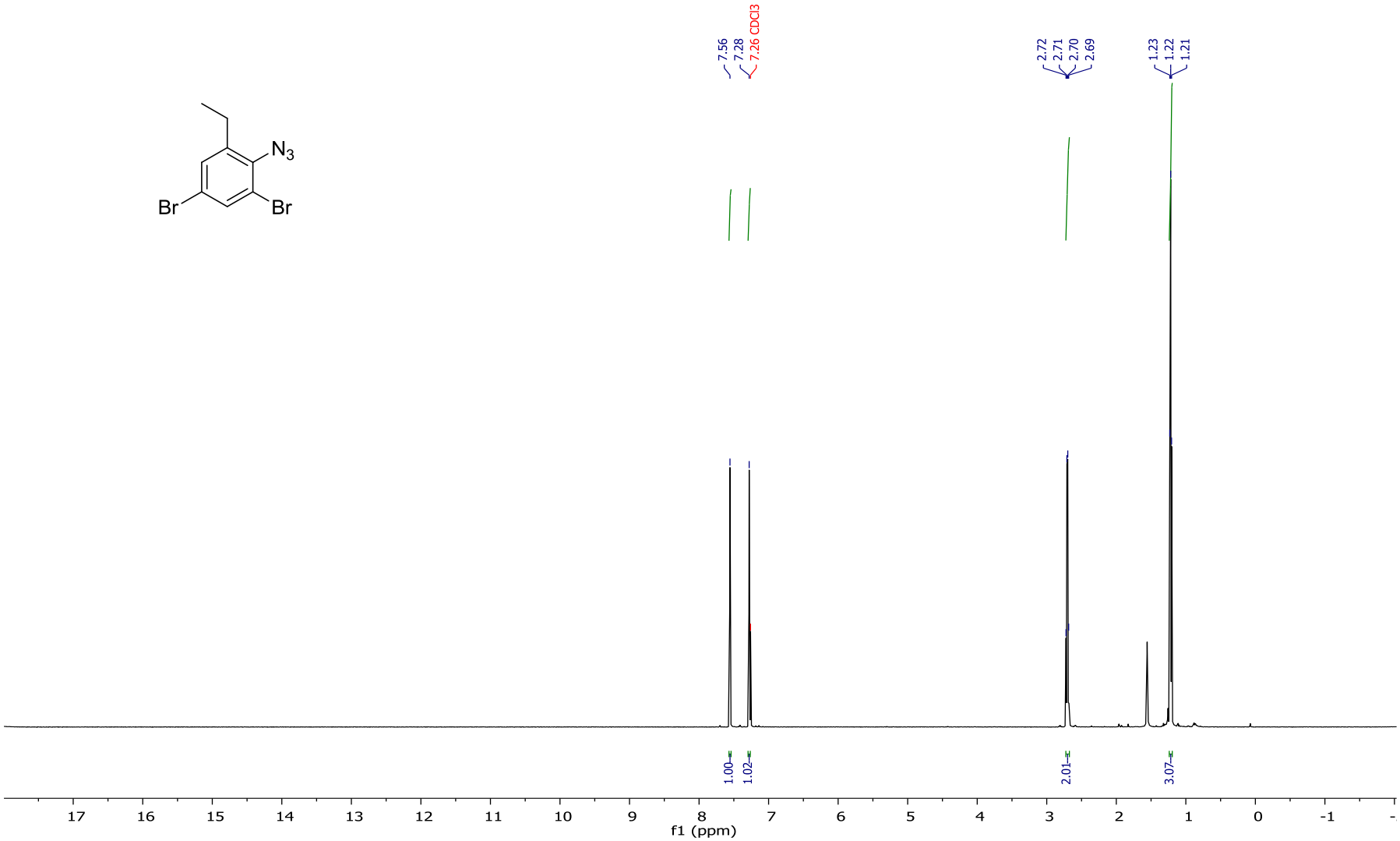


Figure S102. ^{1}H NMR (600 MHz, Chloroform-d) of 2-azido-1,5-dibromo-3-ethylbenzene (2x).

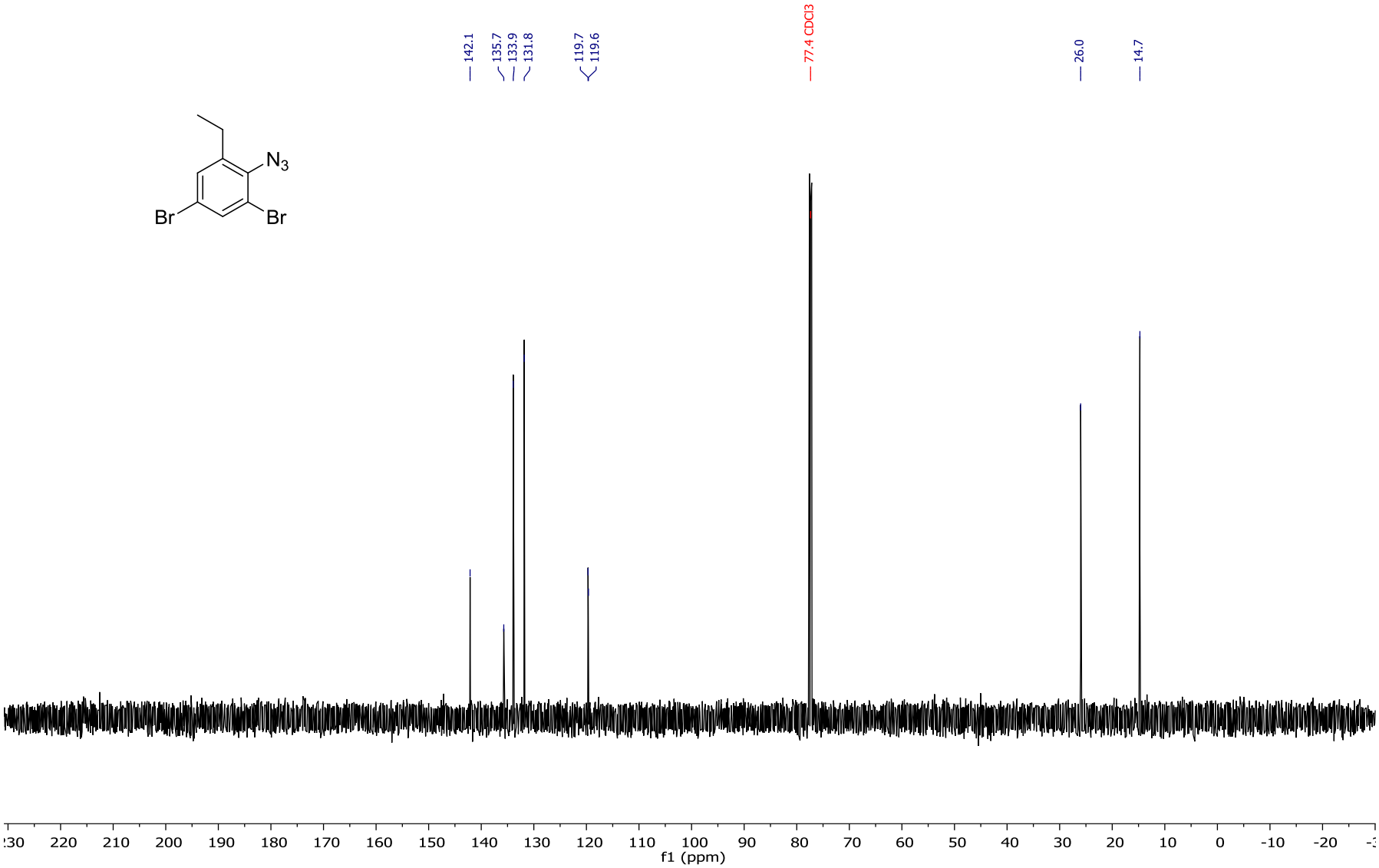


Figure S103. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 2-azido-1,5-dibromo-3-ethylbenzene (2x).

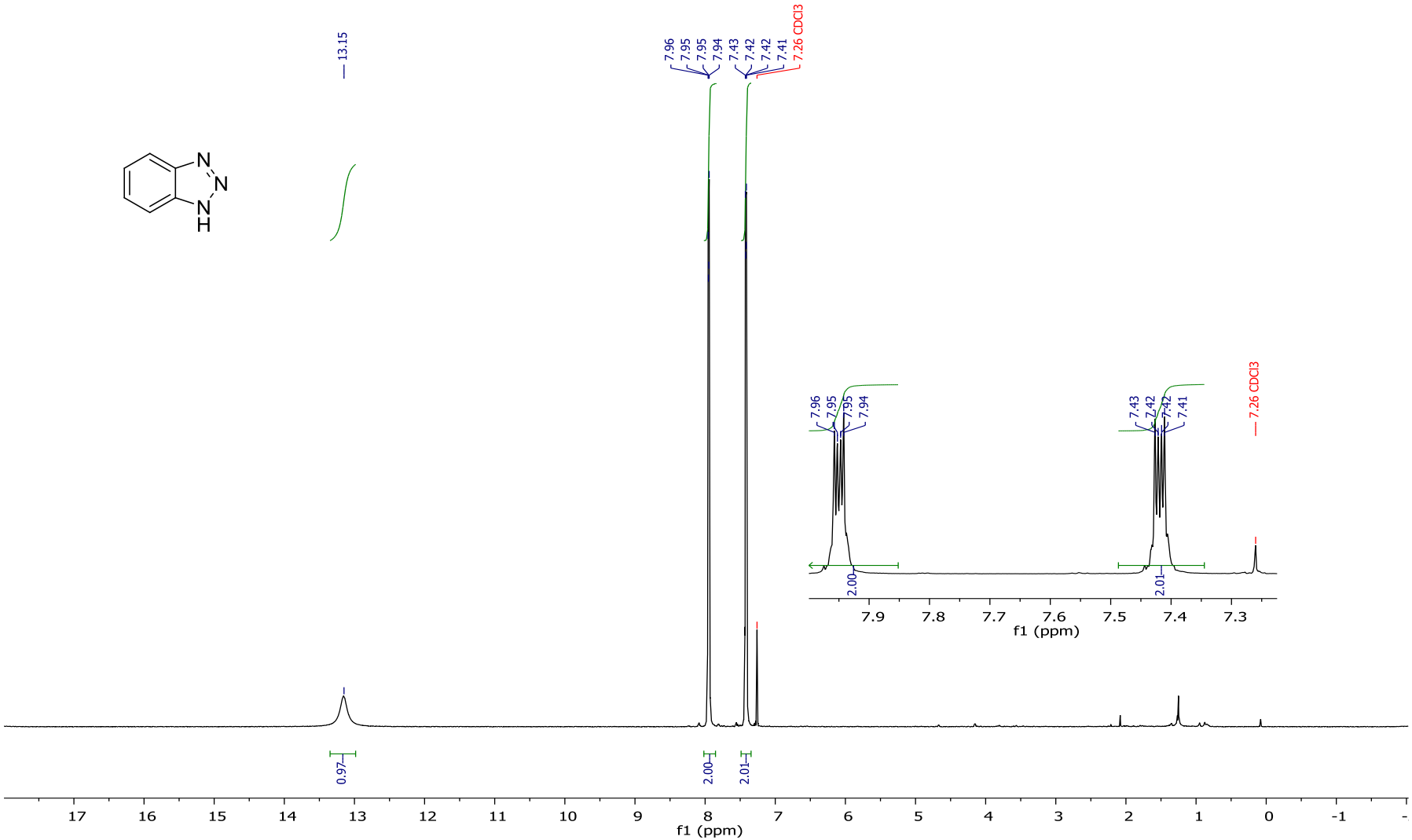


Figure S104. ^{1}H NMR (600 MHz, Chloroform-d) of 1H-benzo[d][1,2,3]triazole (3a).

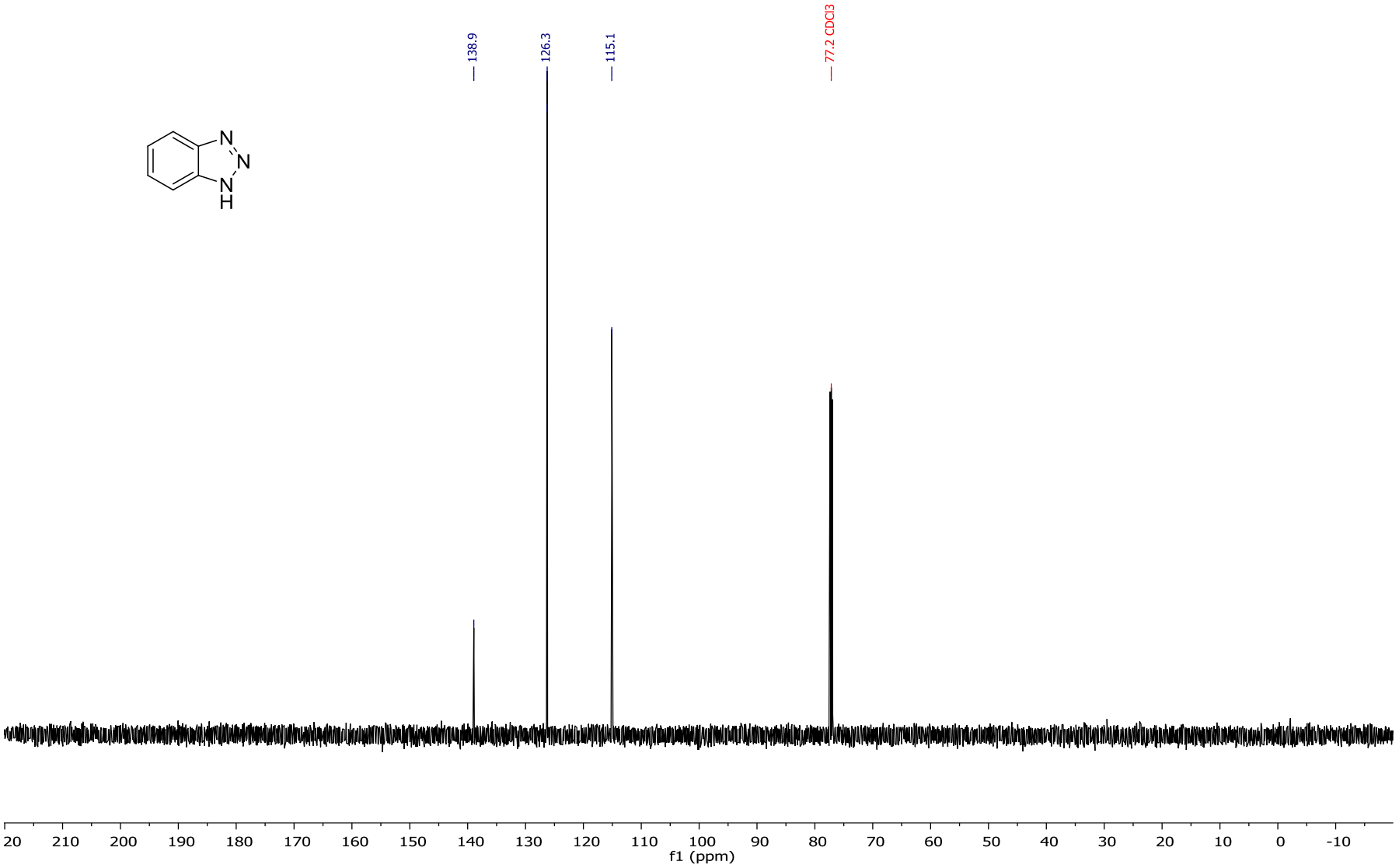


Figure S105. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1H-benzo[d][1,2,3]triazole (3a).

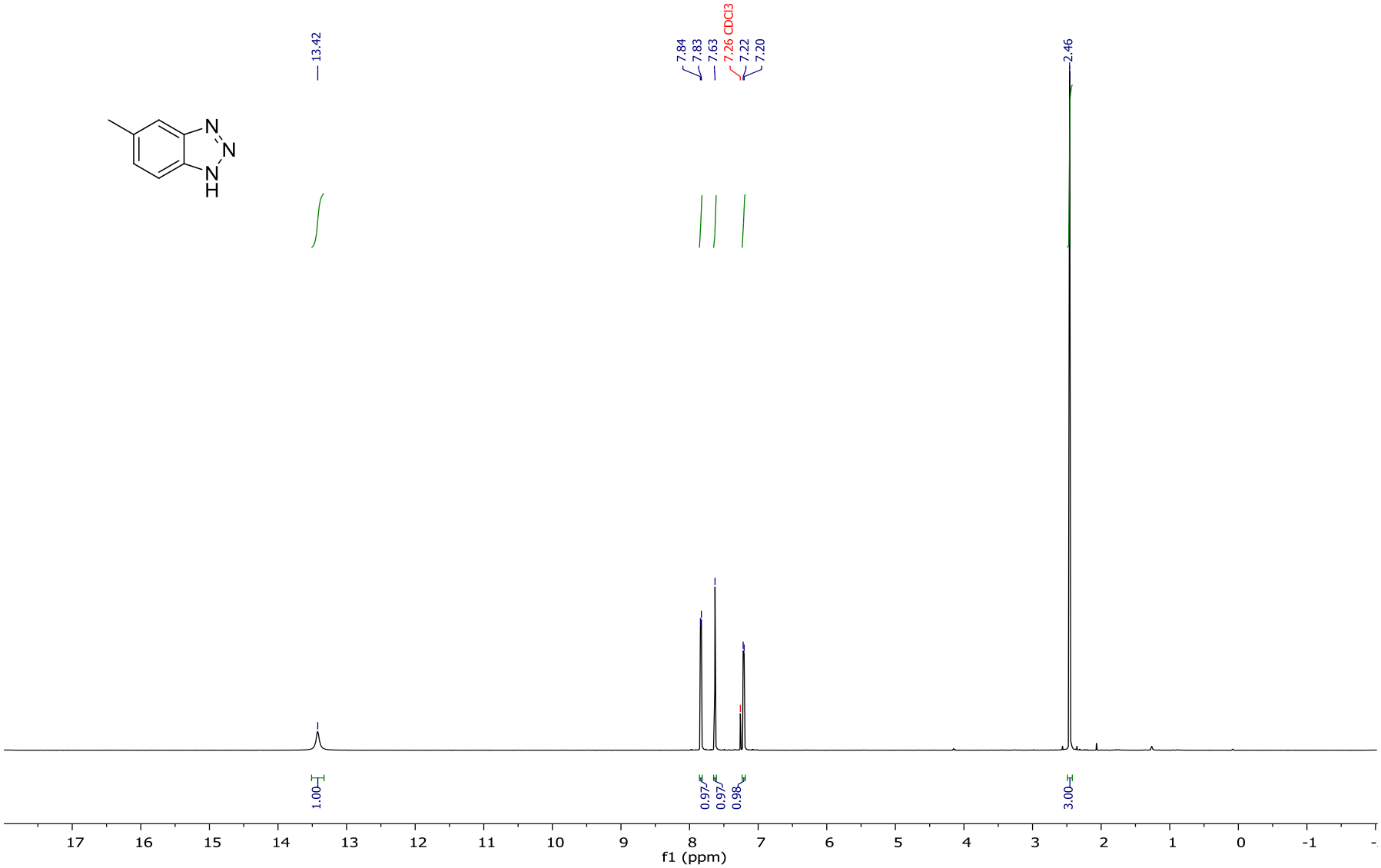


Figure S106. ^{1}H NMR (600 MHz, Chloroform-d) of 5-methyl-1H-benzo[d][1,2,3]triazole (3b).

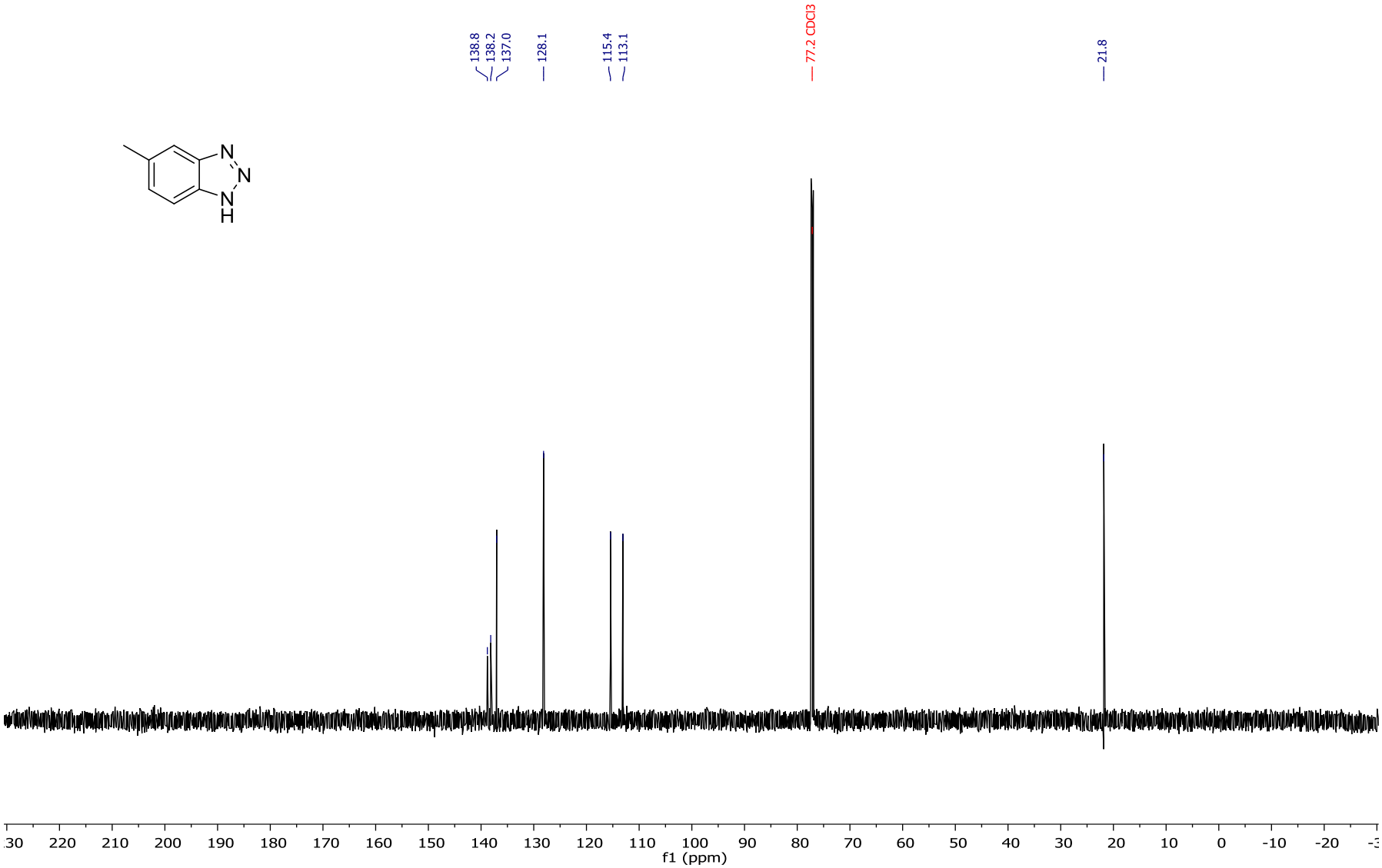


Figure S107. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 5-methyl-1H-benzo[d][1,2,3]triazole (3b).

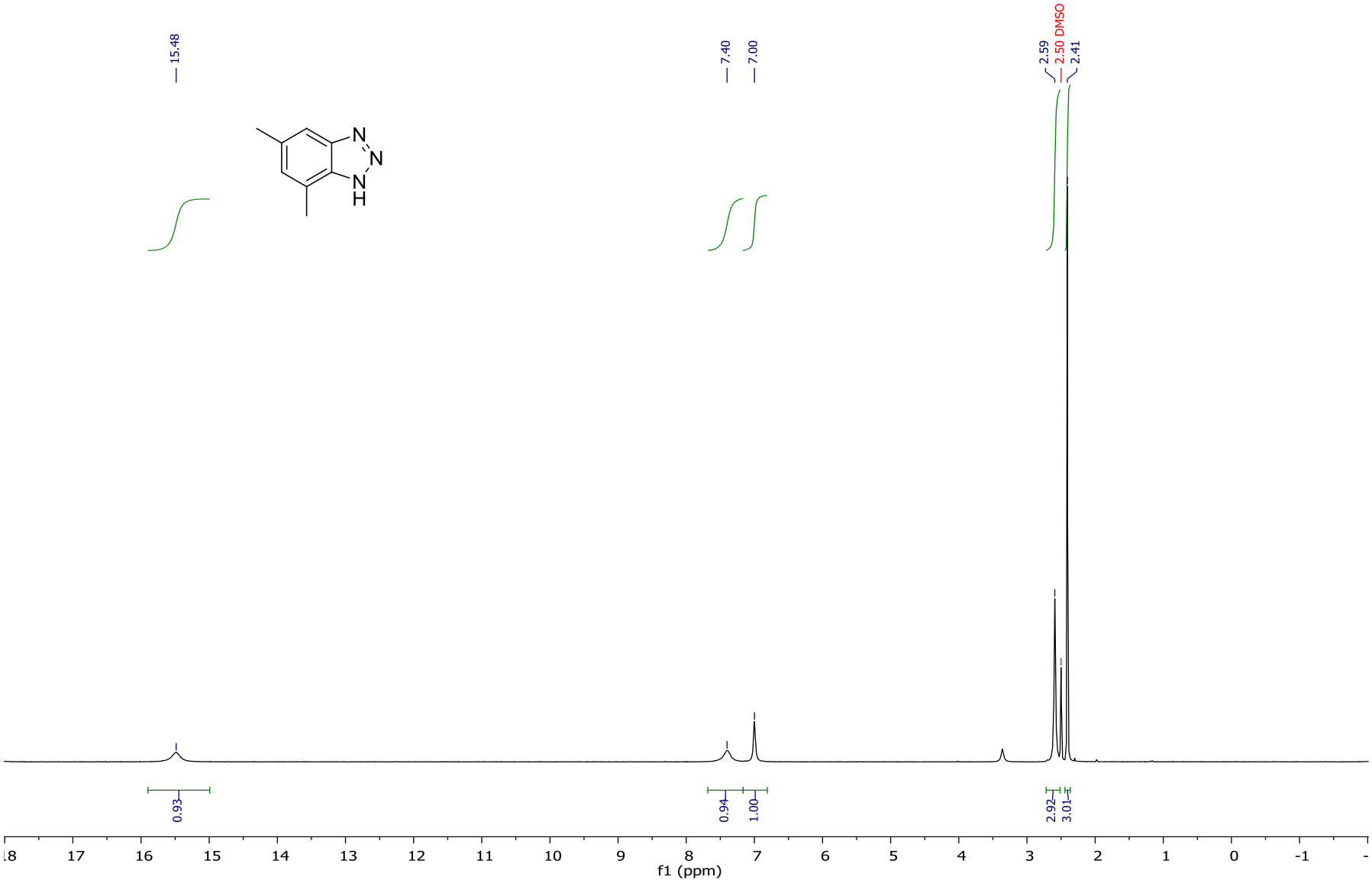


Figure S108. ^{1}H NMR (600 MHz, DMSO-d_6) of 5,7-dimethyl-1H-benzo[d][1,2,3]triazole (3c).

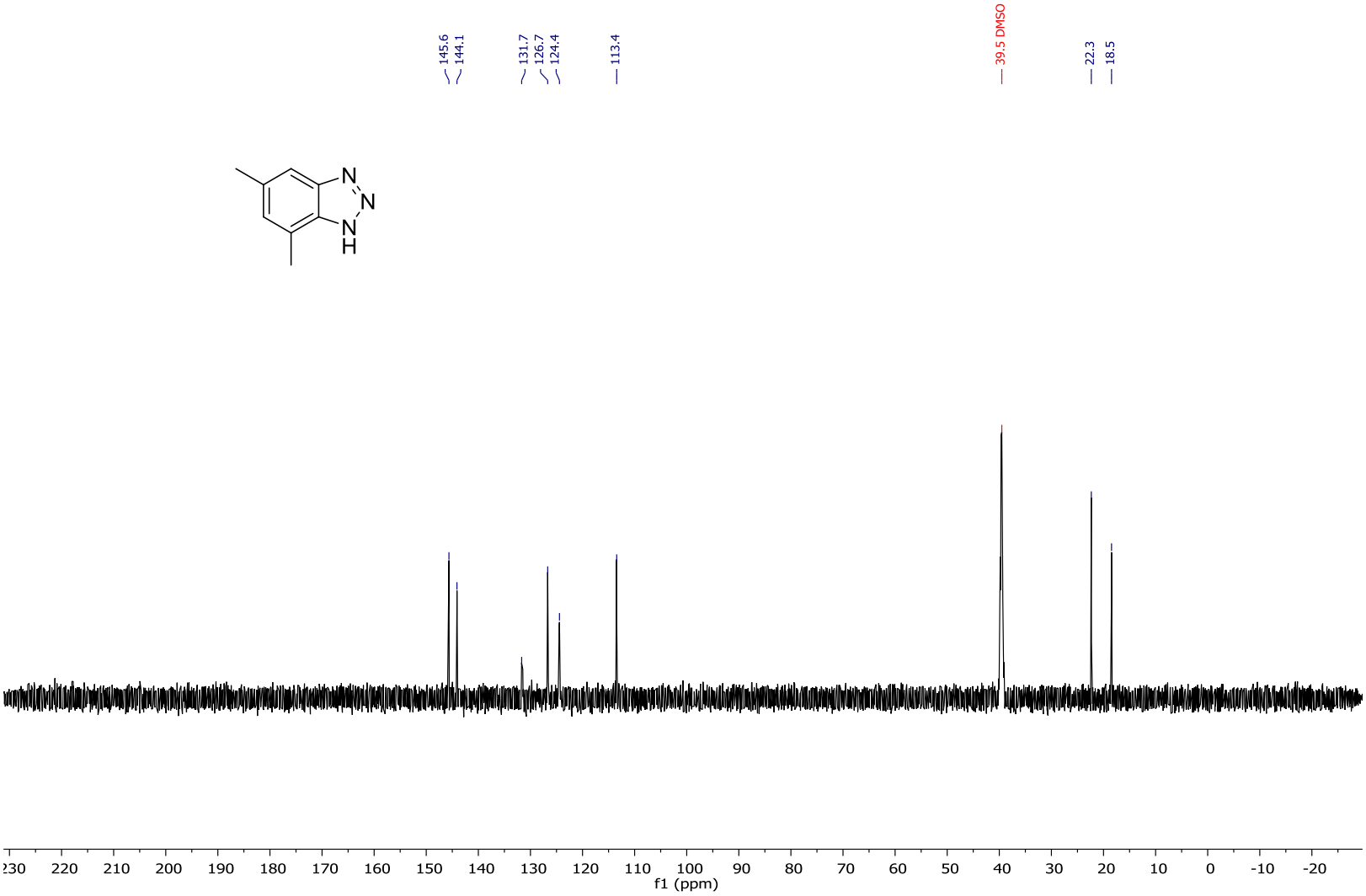


Figure S109. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 5,7-dimethyl-1H-benzo[d][1,2,3]triazole (3c).

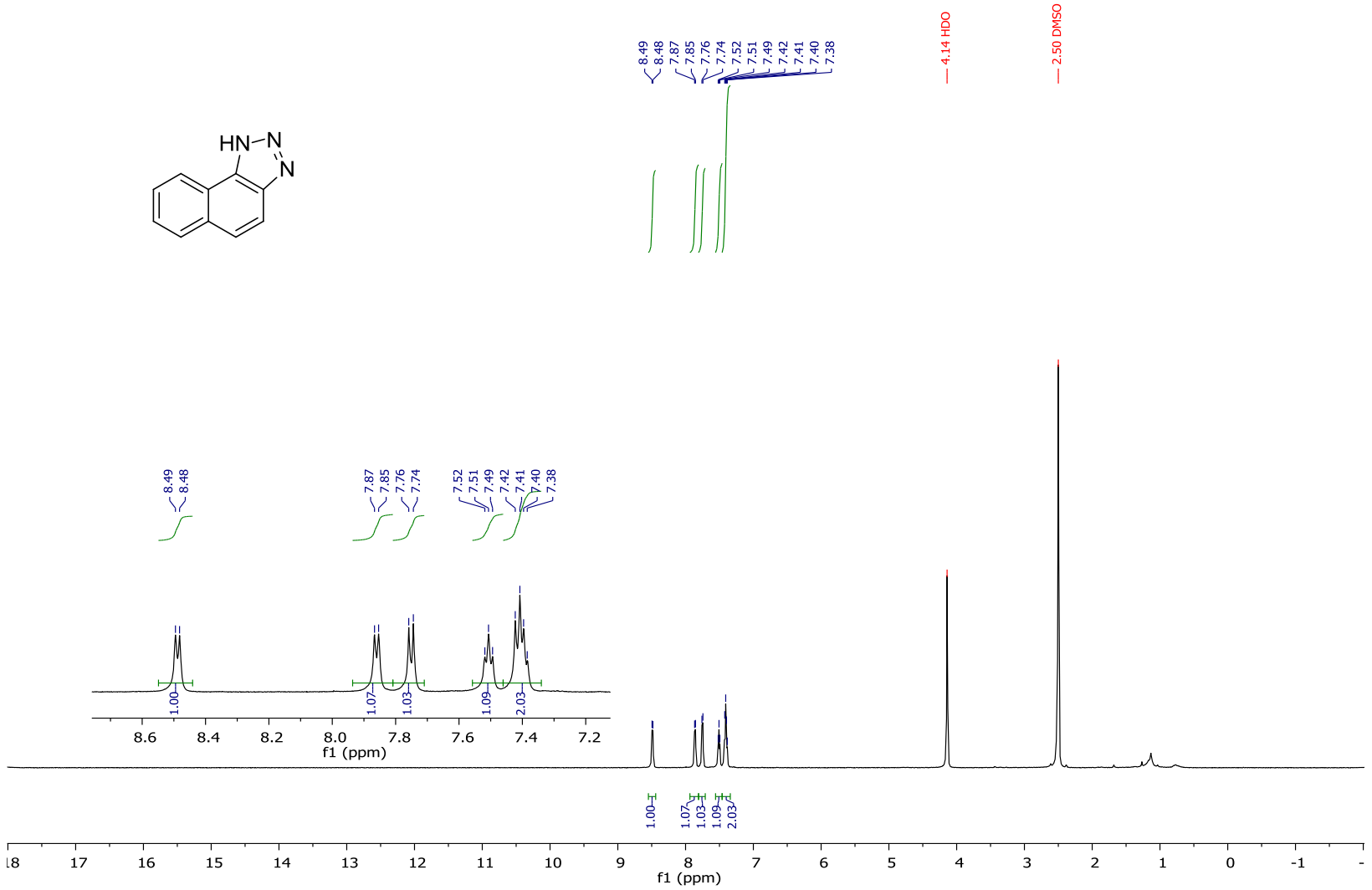


Figure S110. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 1H-naphtho[1,2-d][1,2,3]triazole (3d).

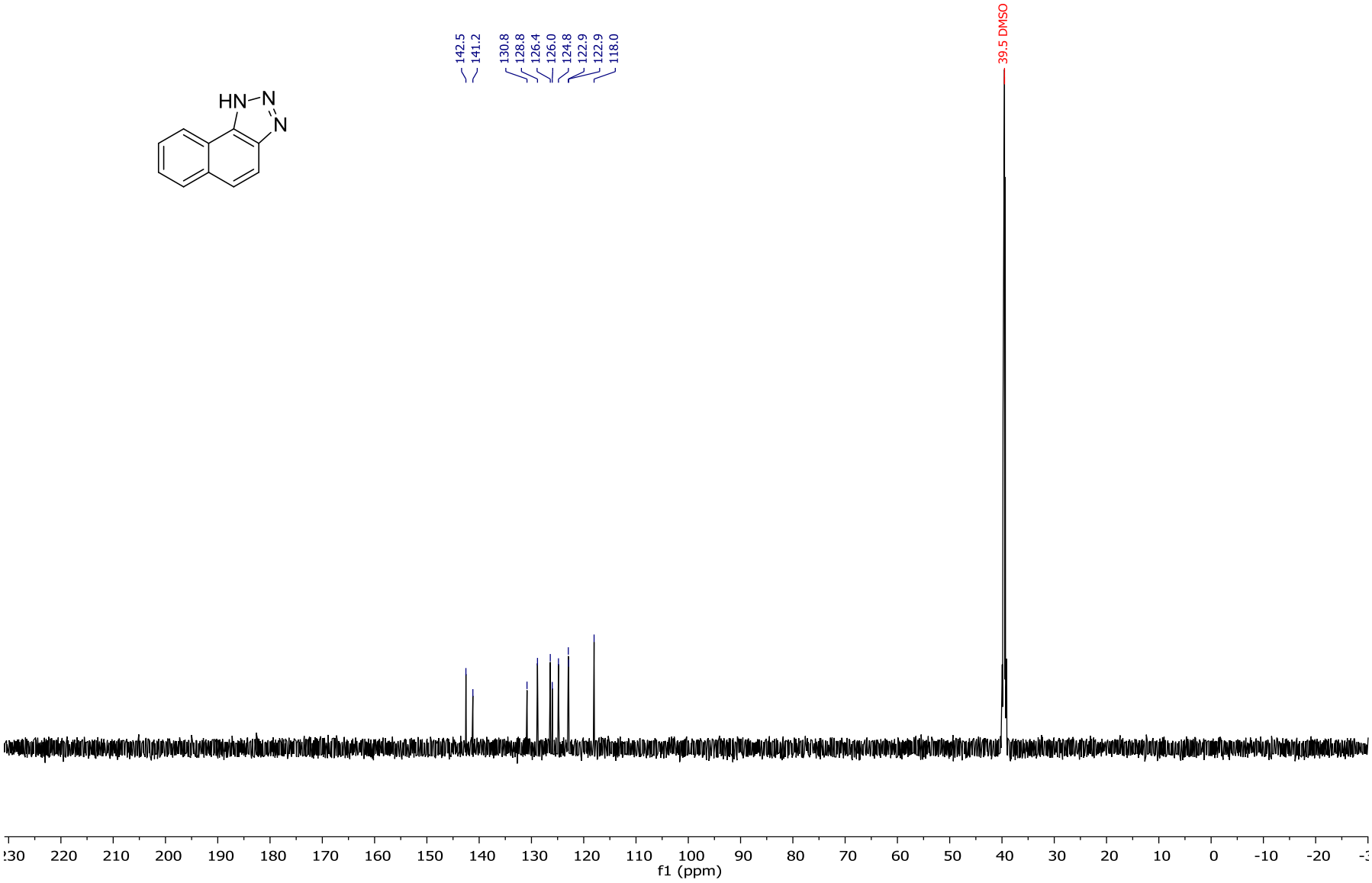


Figure S111. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 1H-naphtho[1,2-d][1,2,3]triazole (3d).

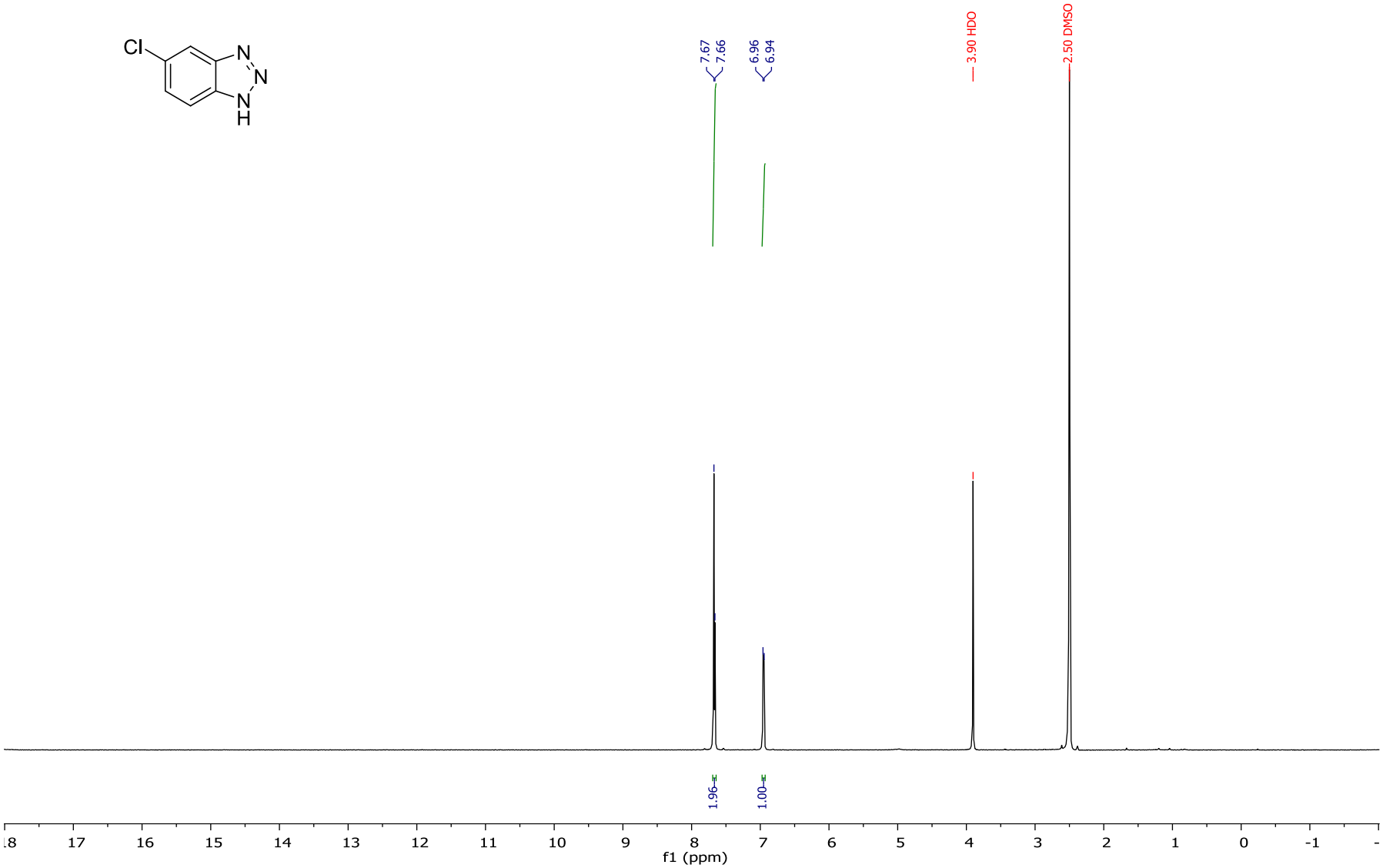


Figure S112. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 5-chloro-1H-benzo[d][1,2,3]triazole (3e).

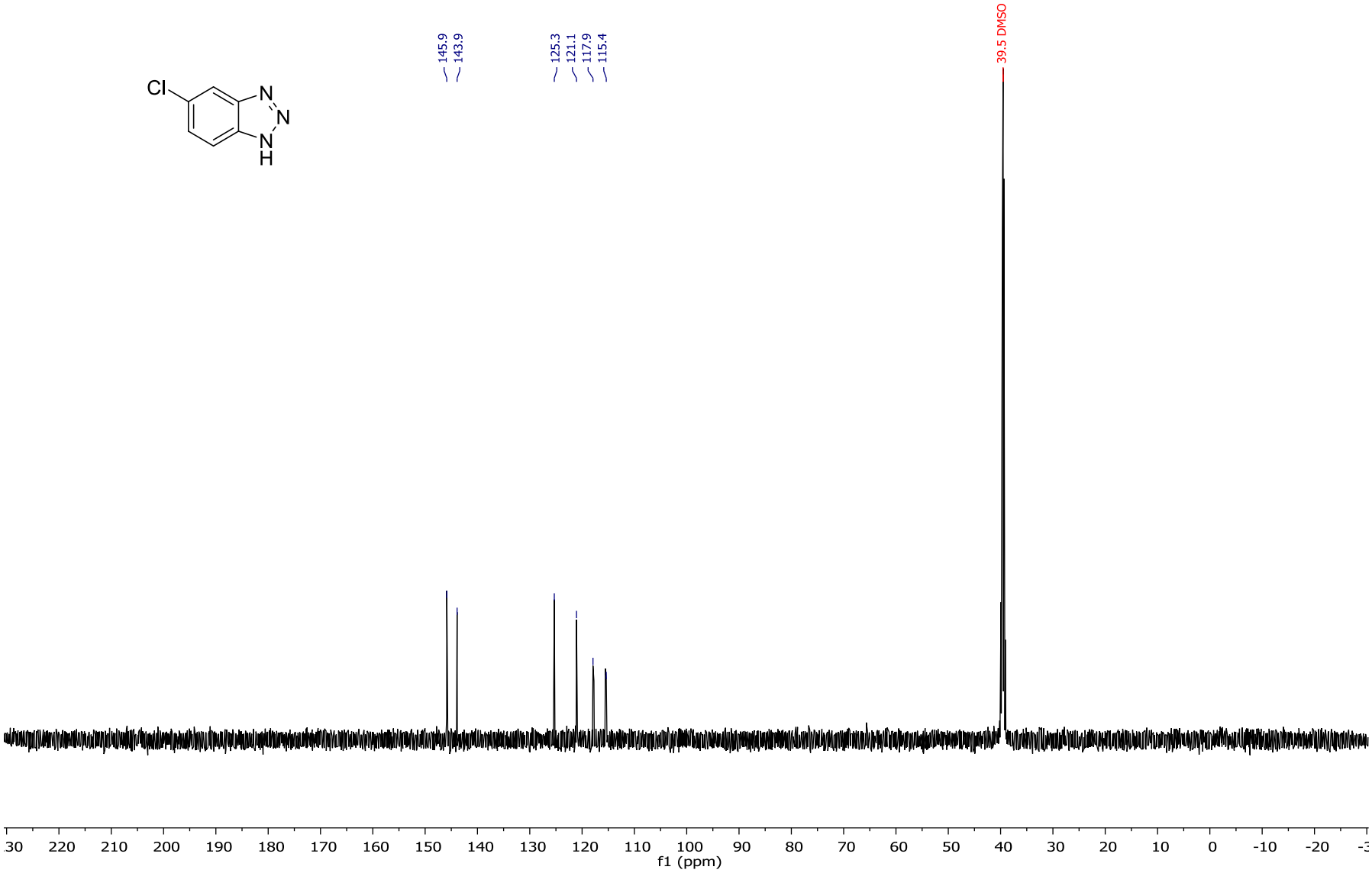


Figure S113. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 5-chloro-1H-benzo[d][1,2,3]triazole (3e).

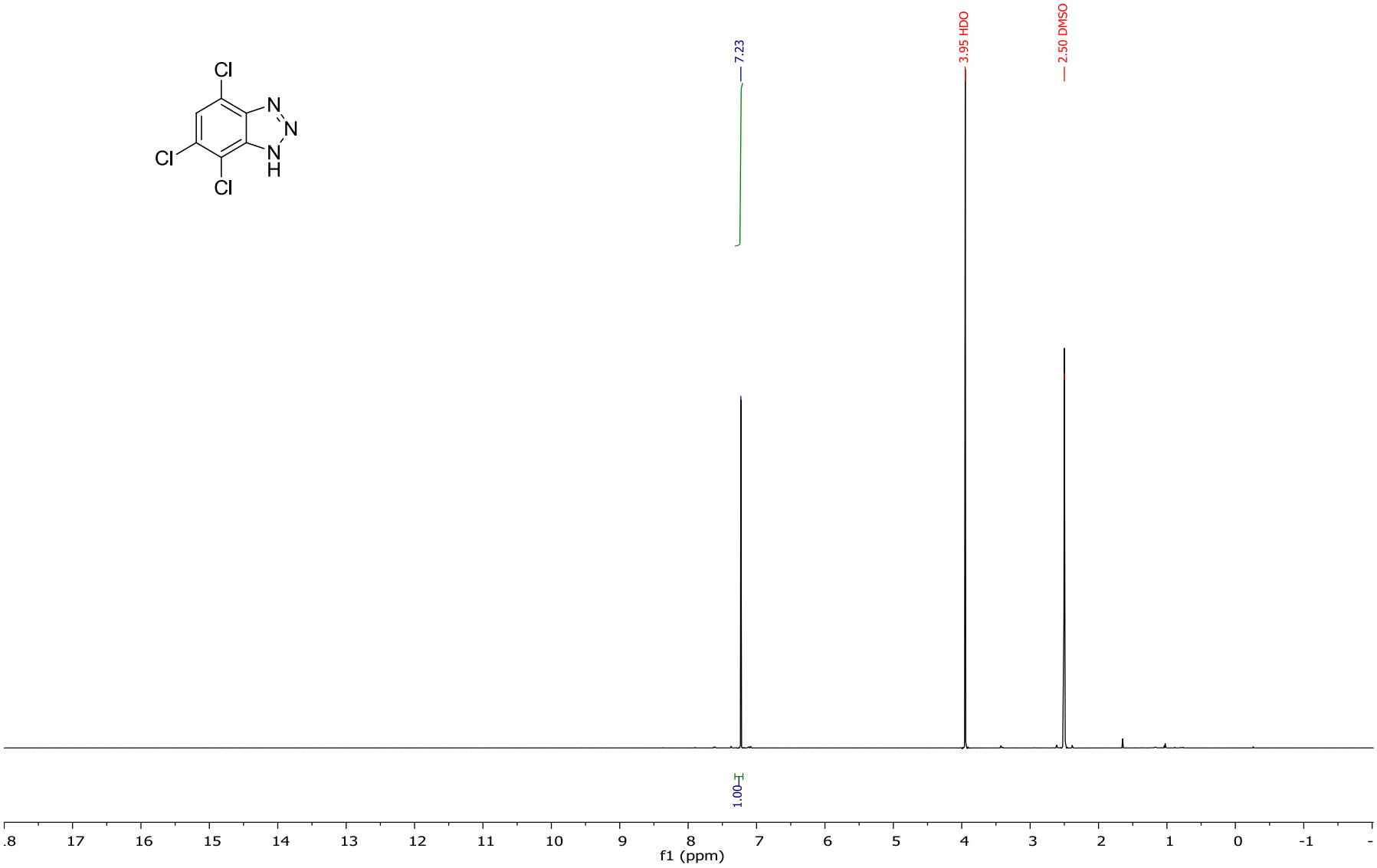


Figure S114. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 4,6,7-trichloro-1H-benzo[d][1,2,3]triazole (3f).

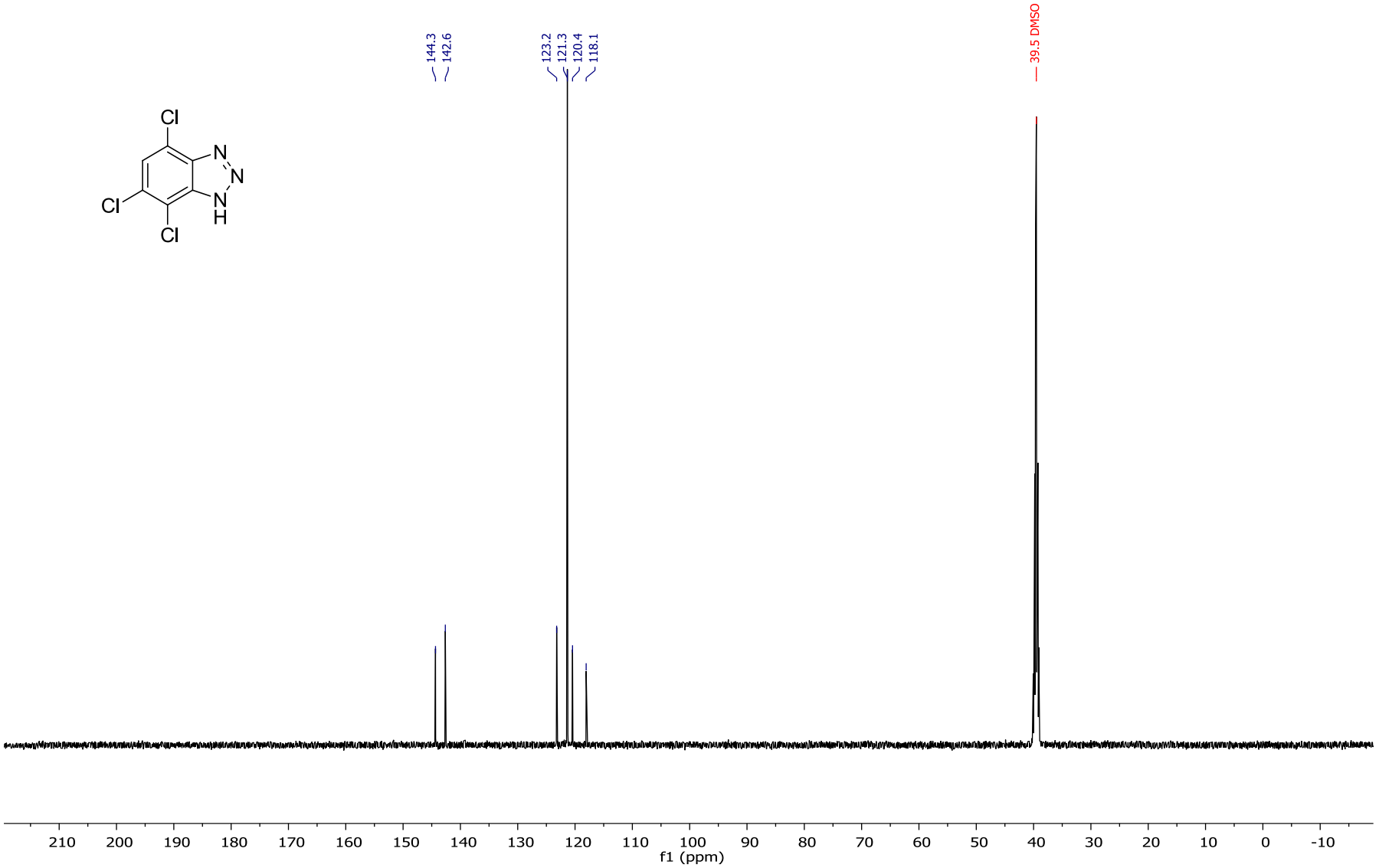


Figure S115. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 4,6,7-trichloro-1H-benzo[d][1,2,3]triazole (3f).

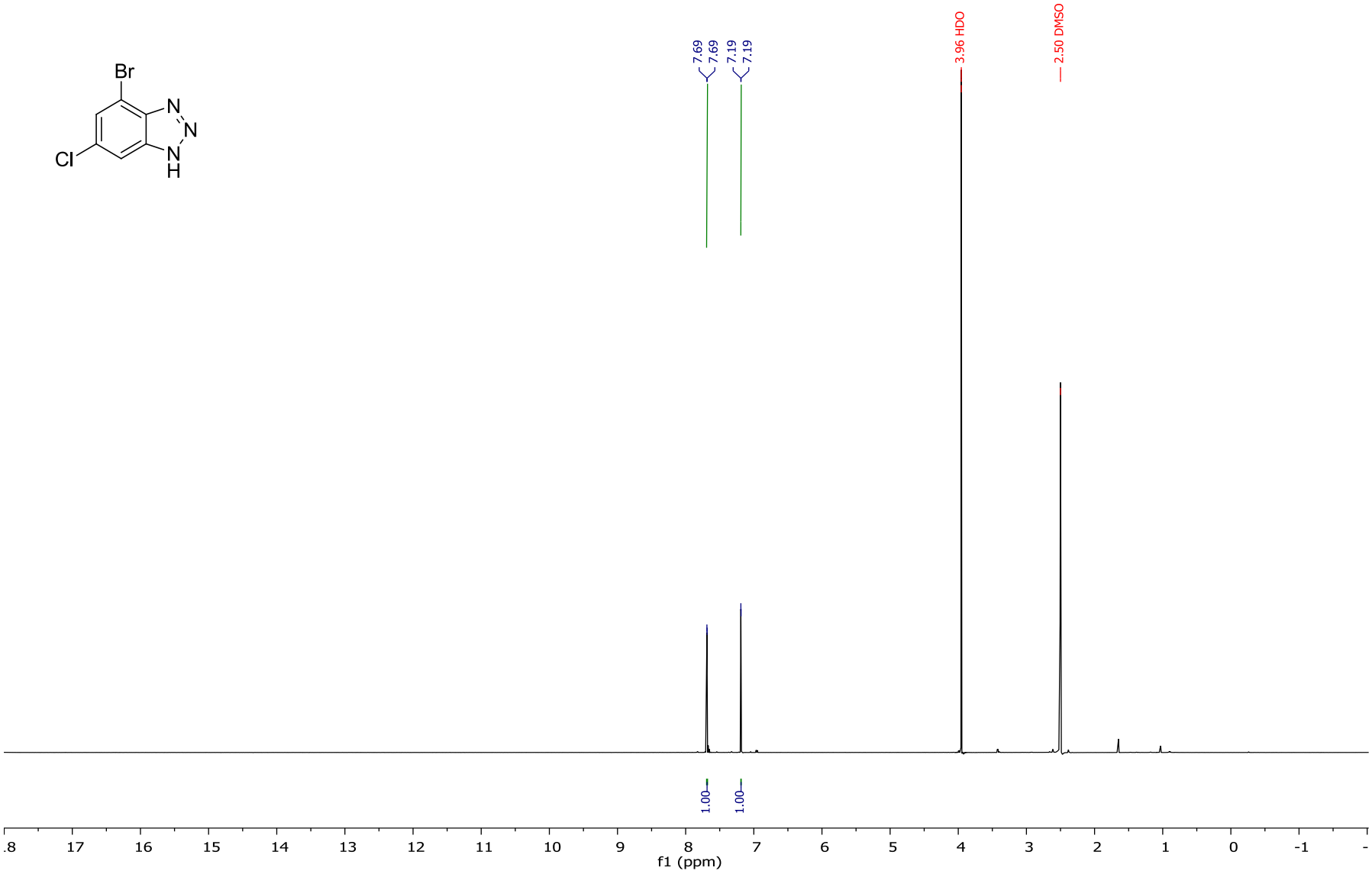


Figure S116. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 4-bromo-6-chloro-1H-benzo[d][1,2,3]triazole (3g).

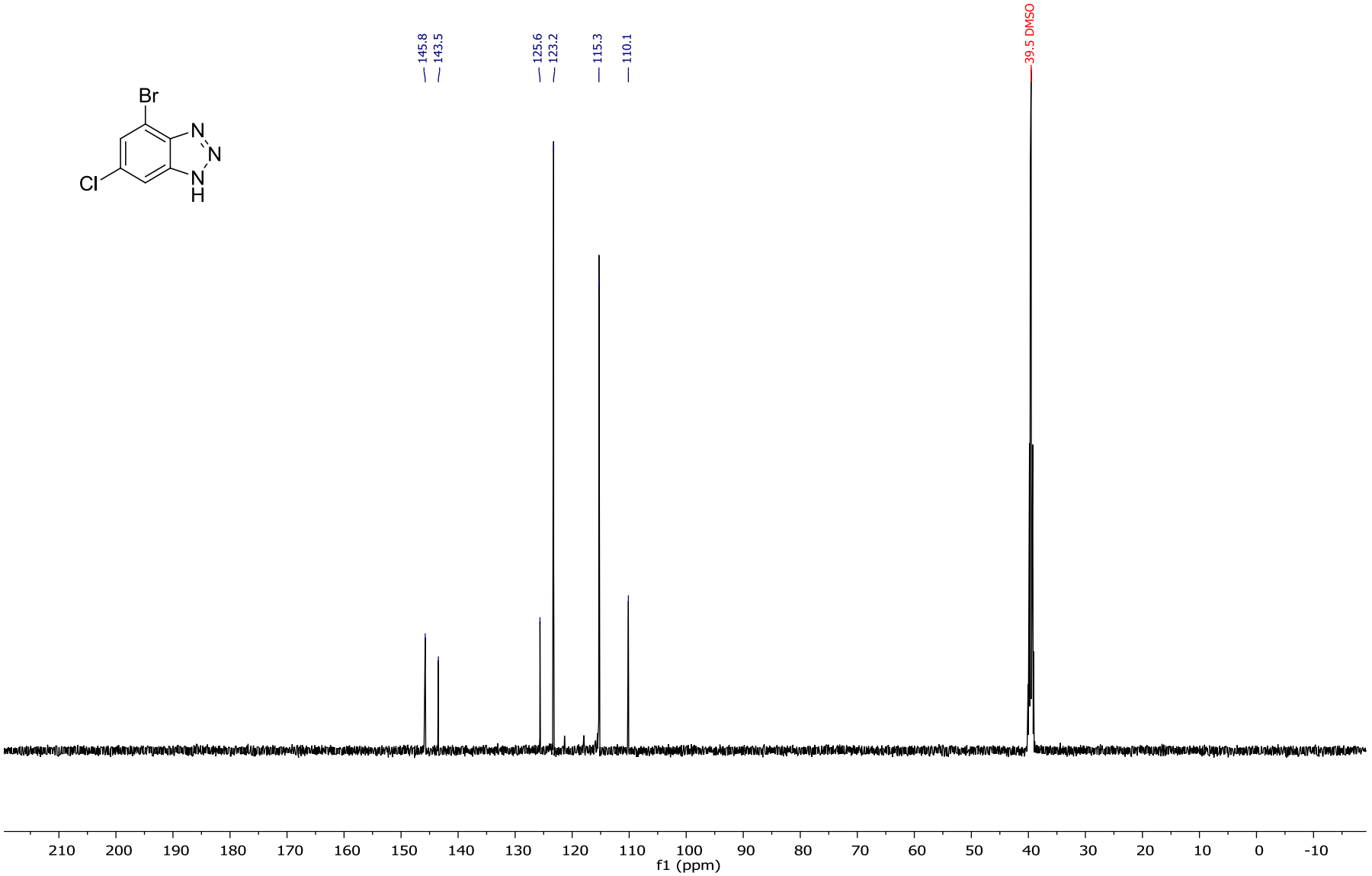


Figure S117. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 4-bromo-6-chloro-1H-benzo[d][1,2,3]triazole (3g).

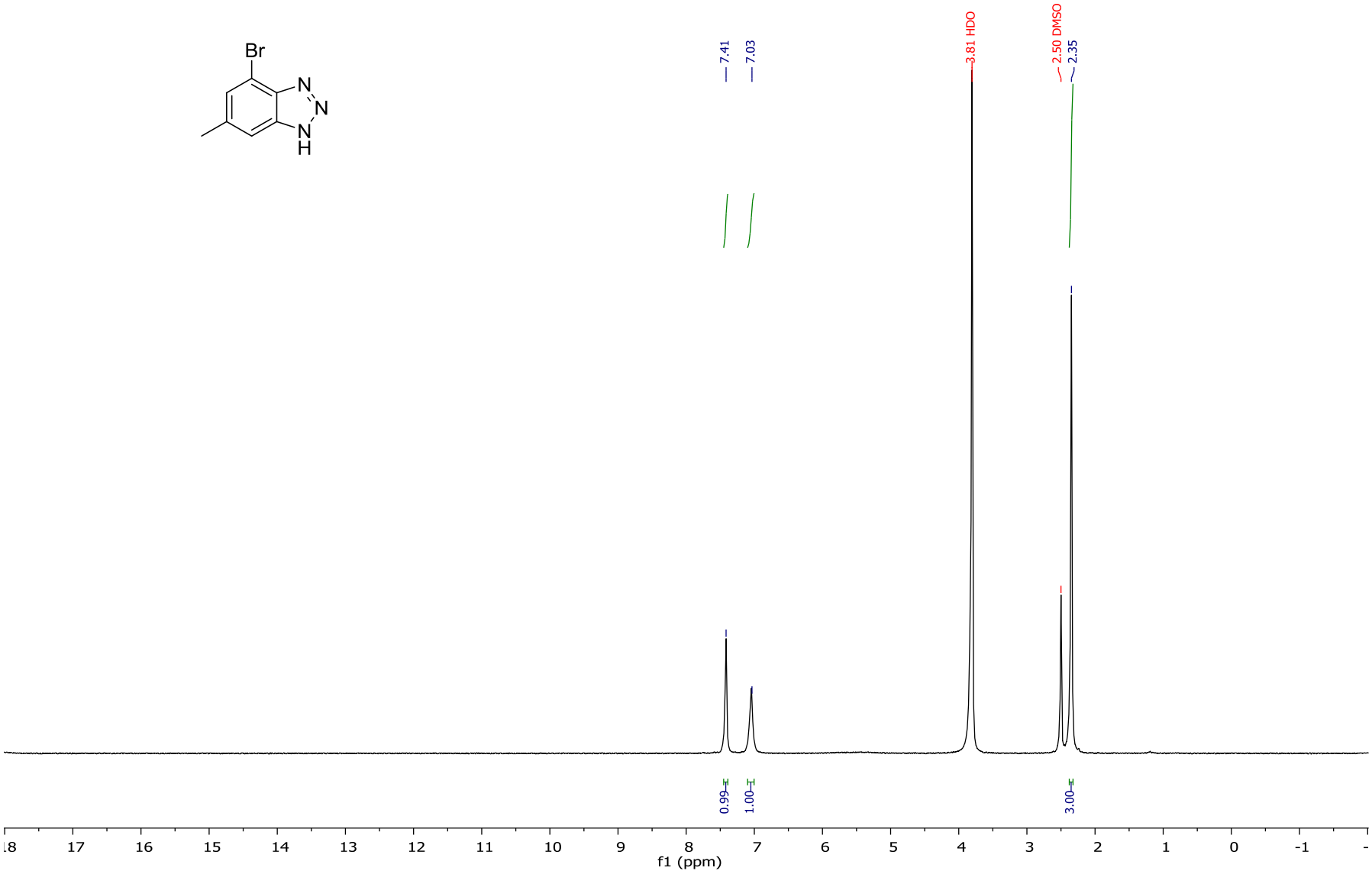


Figure S118. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 4-bromo-6-methyl-1H-benzo[d][1,2,3]triazole (3h).

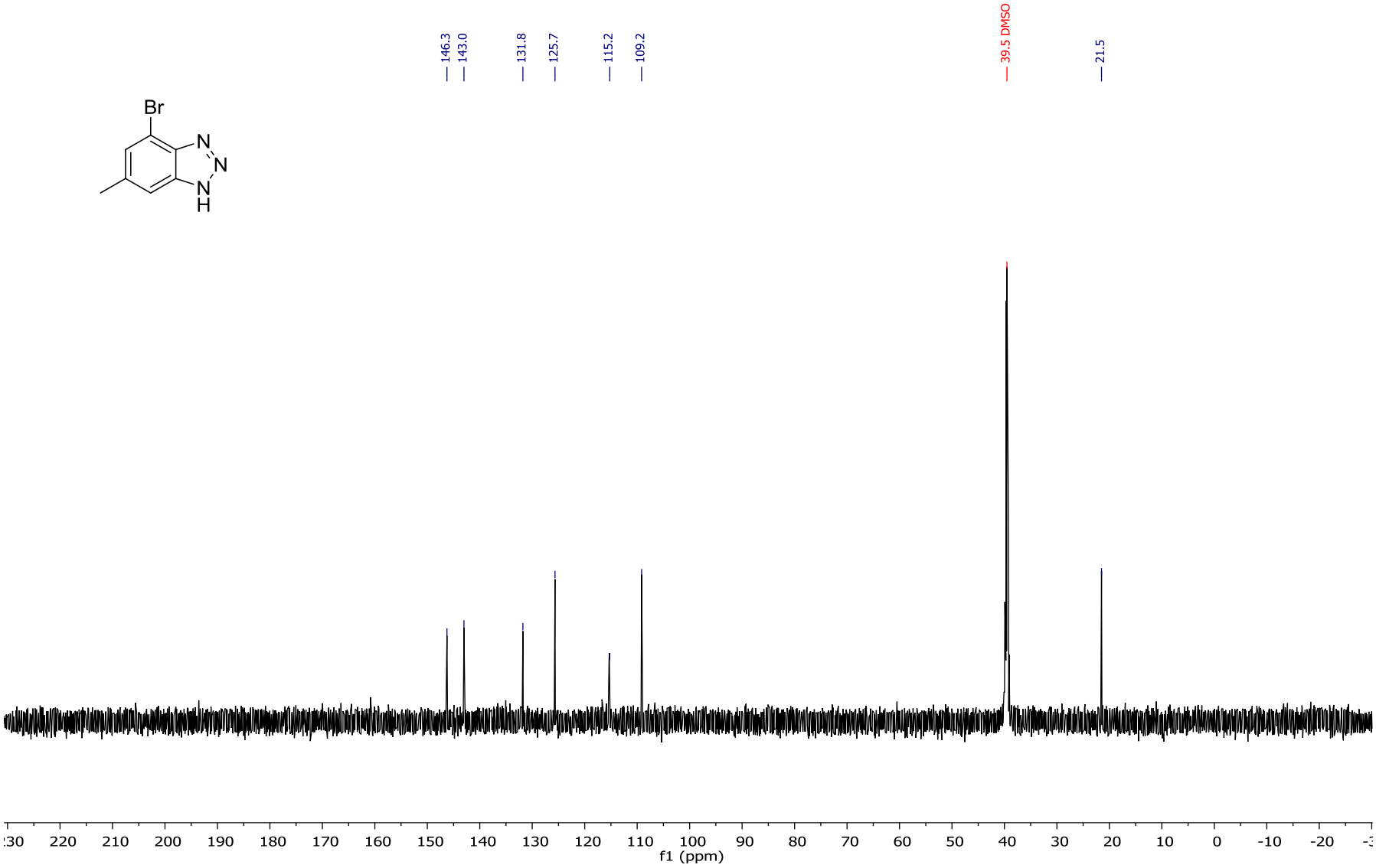


Figure S119. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 4-bromo-6-methyl-1H-benzo[d][1,2,3]triazole (3h).

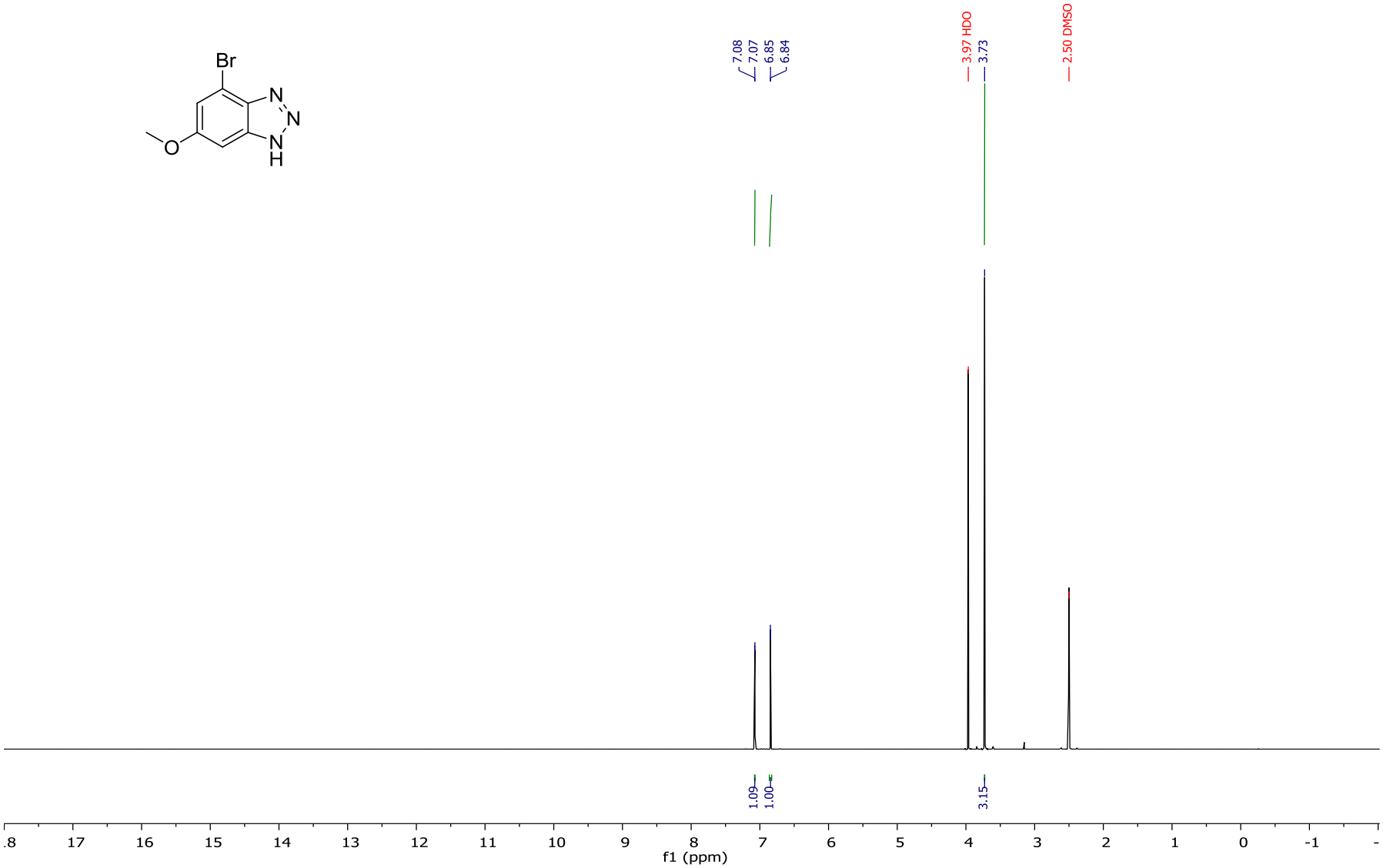


Figure S120. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 4-bromo-6-methoxy-1H-benzo[d][1,2,3]triazole (3i).

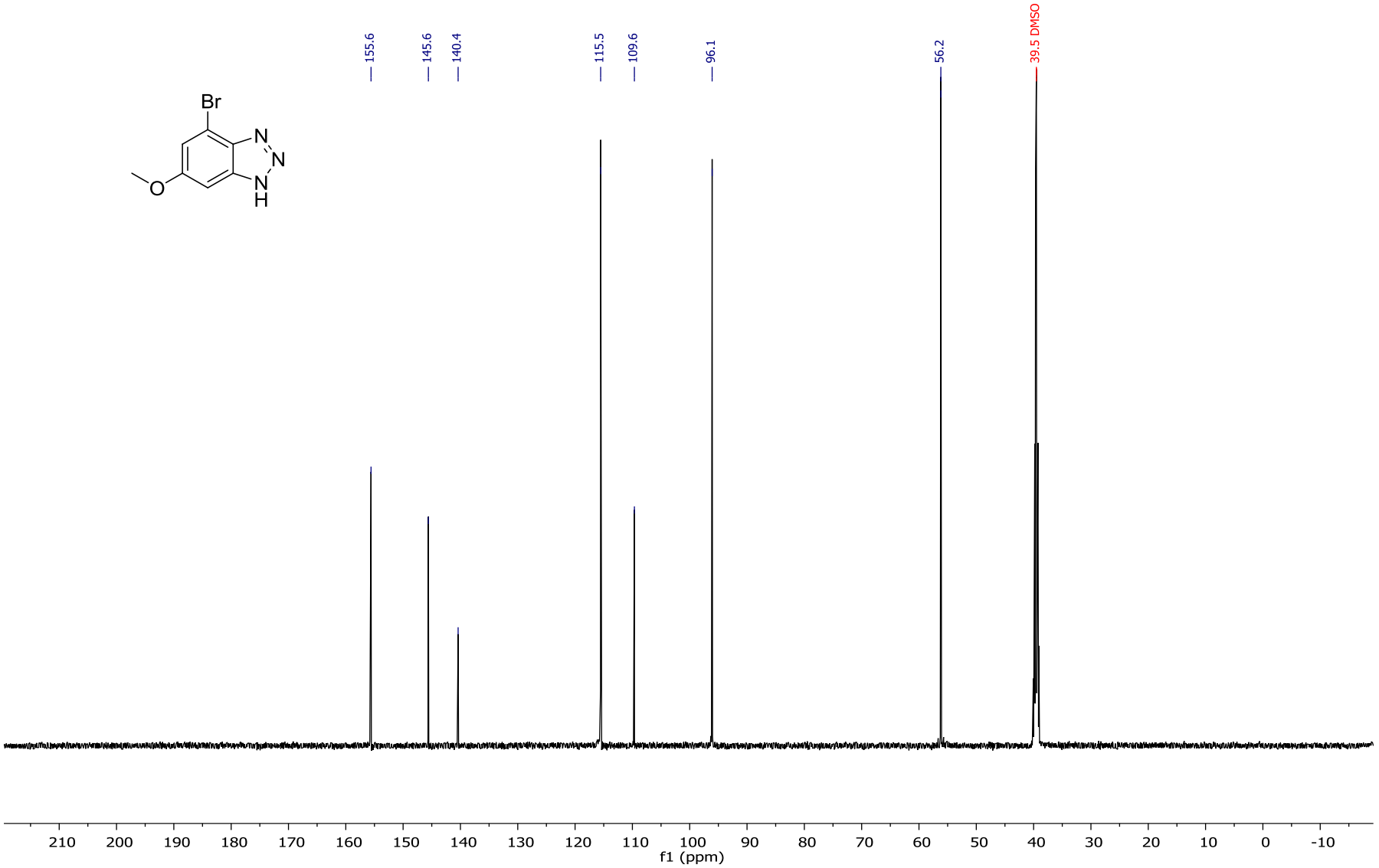


Figure S121. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 4-bromo-6-methoxy-1H-benzo[d][1,2,3]triazole (3i).

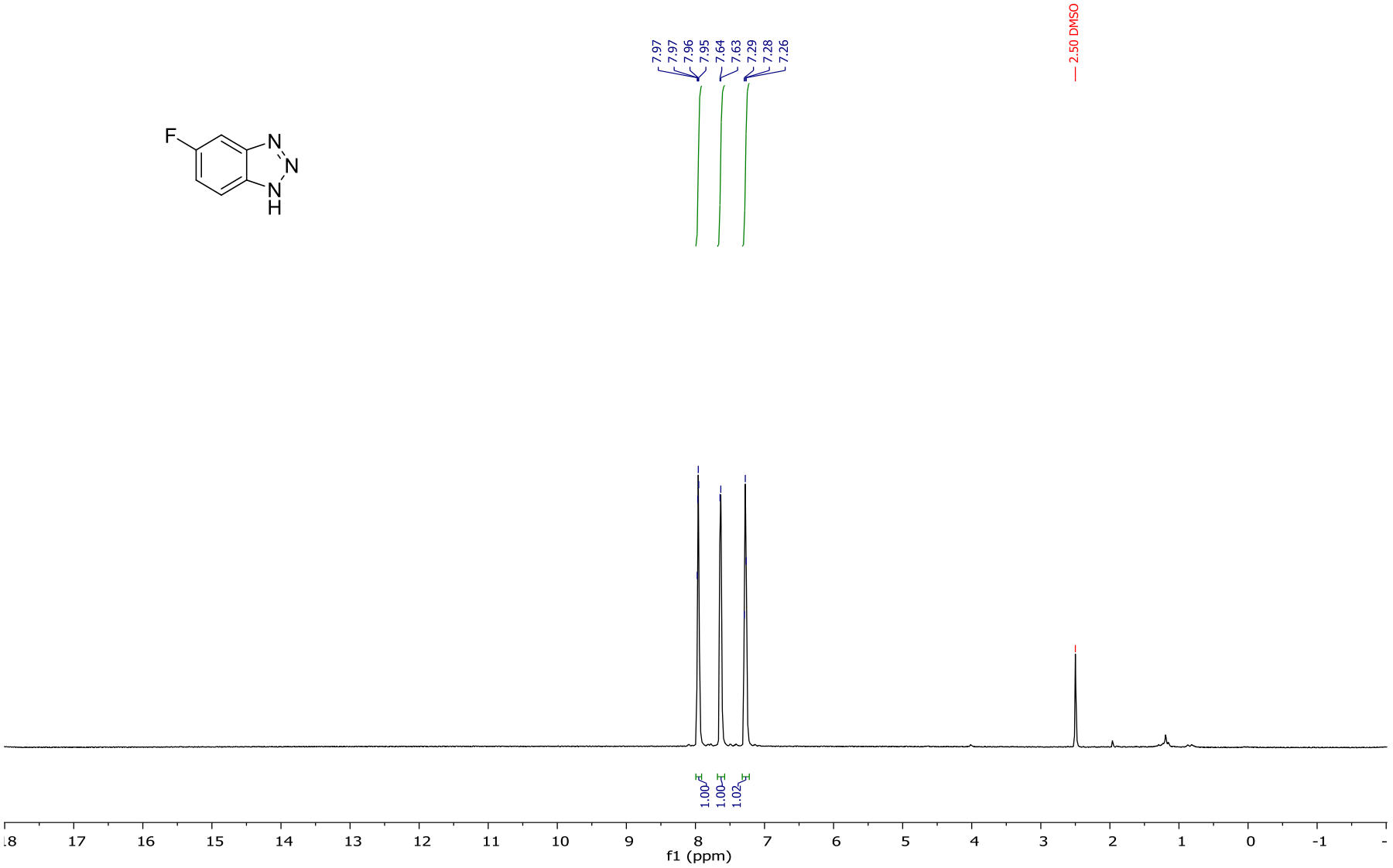


Figure S122. ^{1}H NMR (600 MHz, DMSO-d6) of 5-fluoro-1H-benzo[d][1,2,3]triazole (3j).

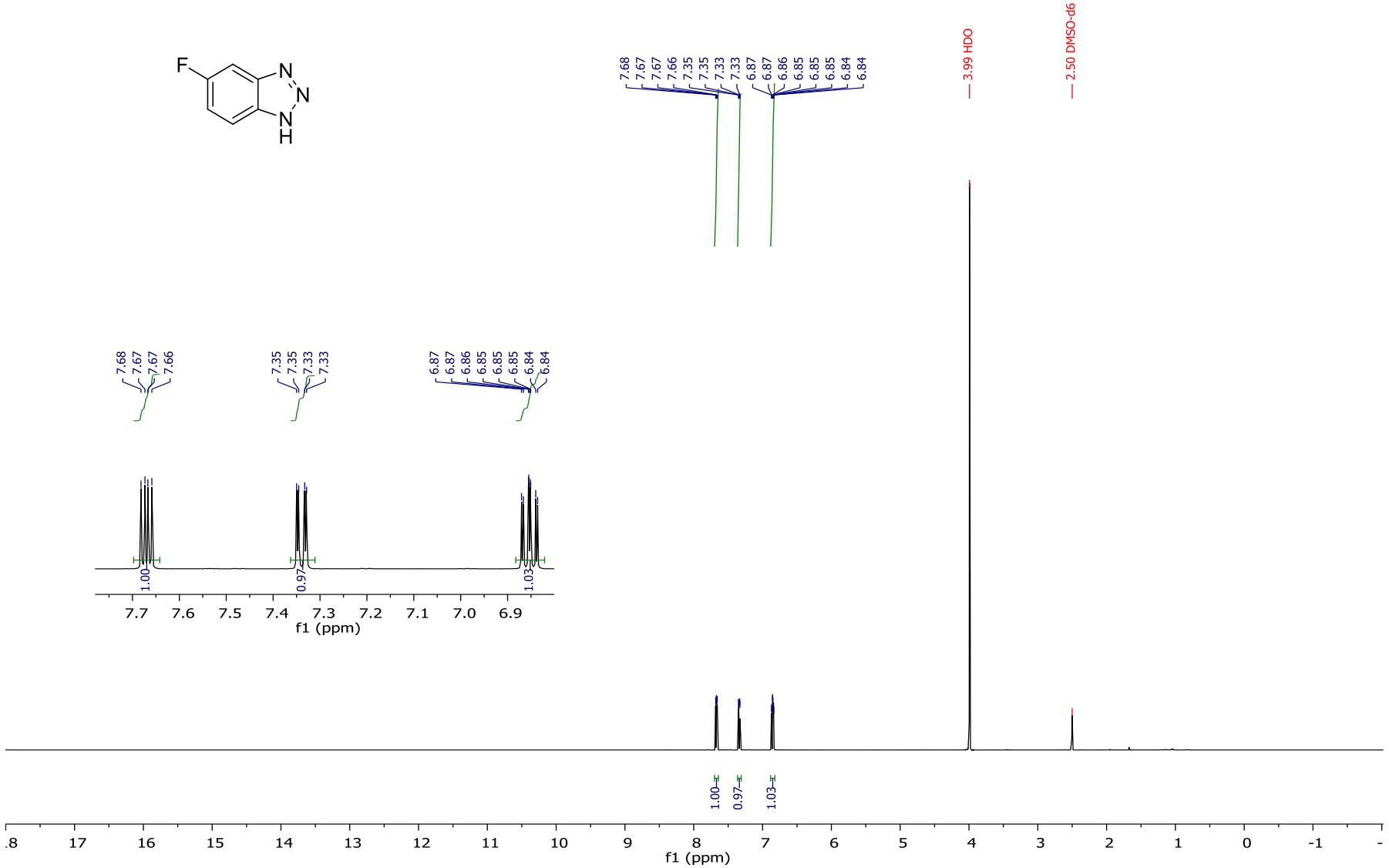


Figure S123. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 5-fluoro-1H-benzo[d][1,2,3]triazole (3j).

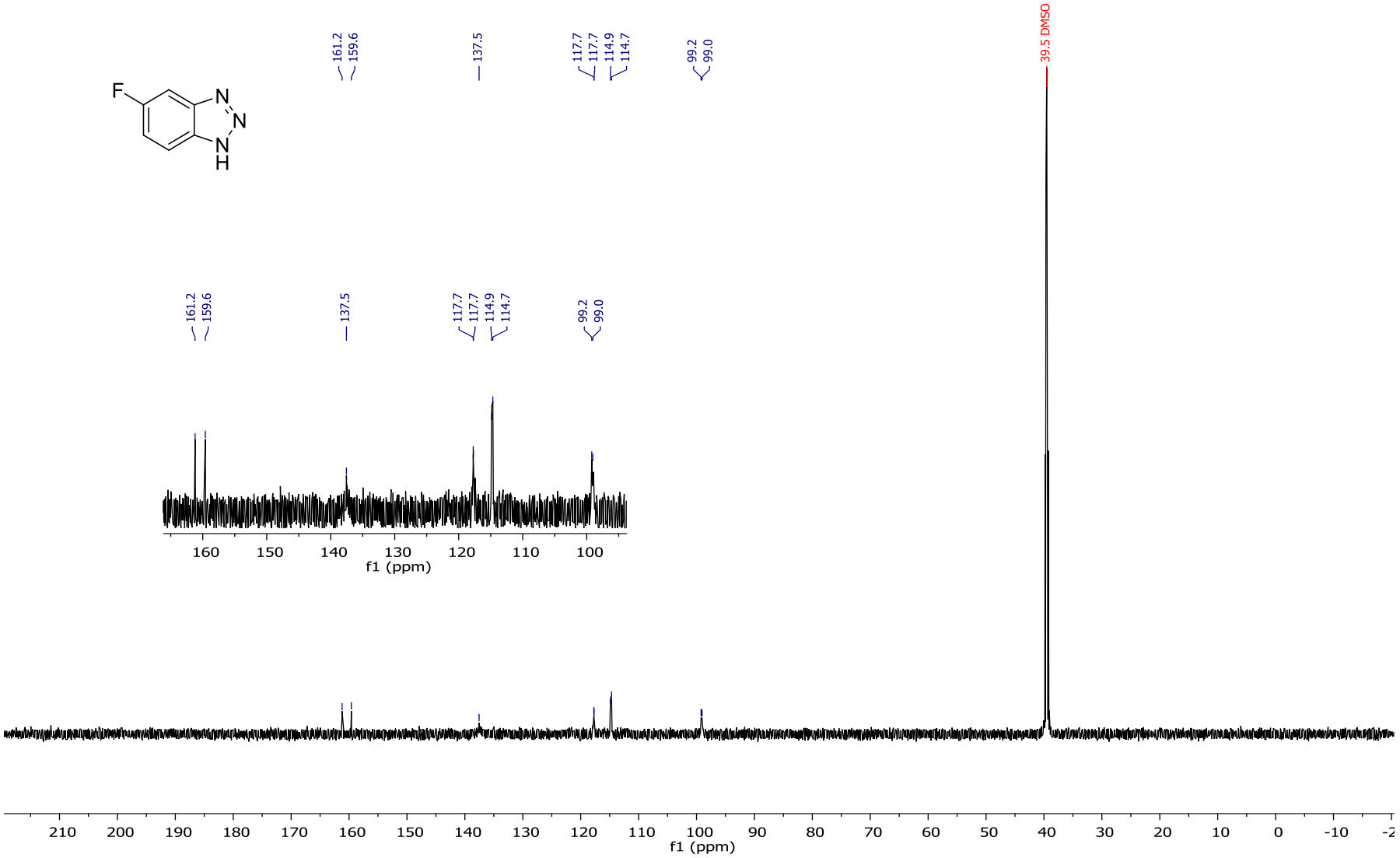


Figure S124. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d6) of 5-fluoro-1H-benzo[d][1,2,3]triazole (3j).

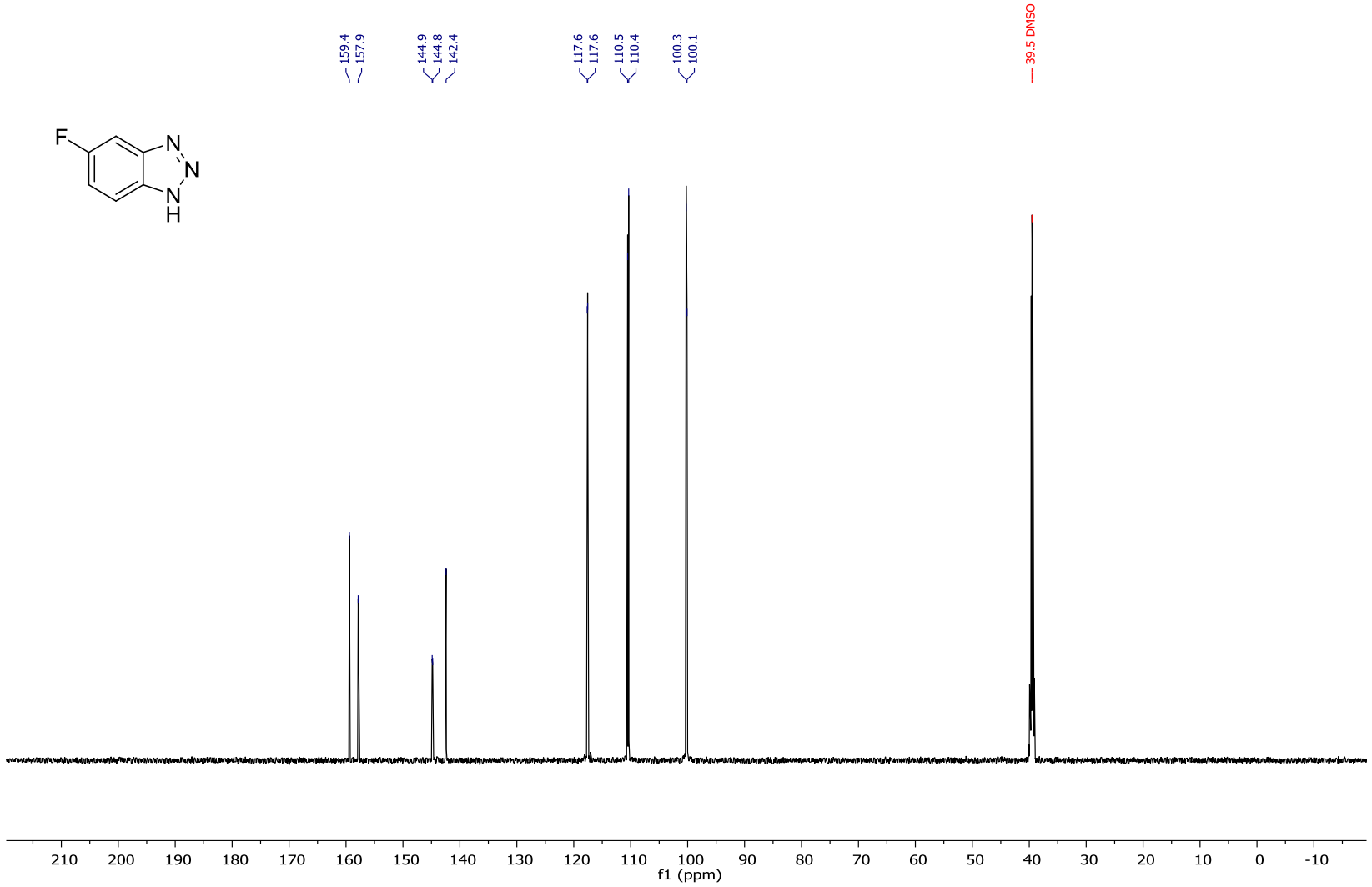


Figure S125. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 5-fluoro-1H-benzo[d][1,2,3]triazole (3j).

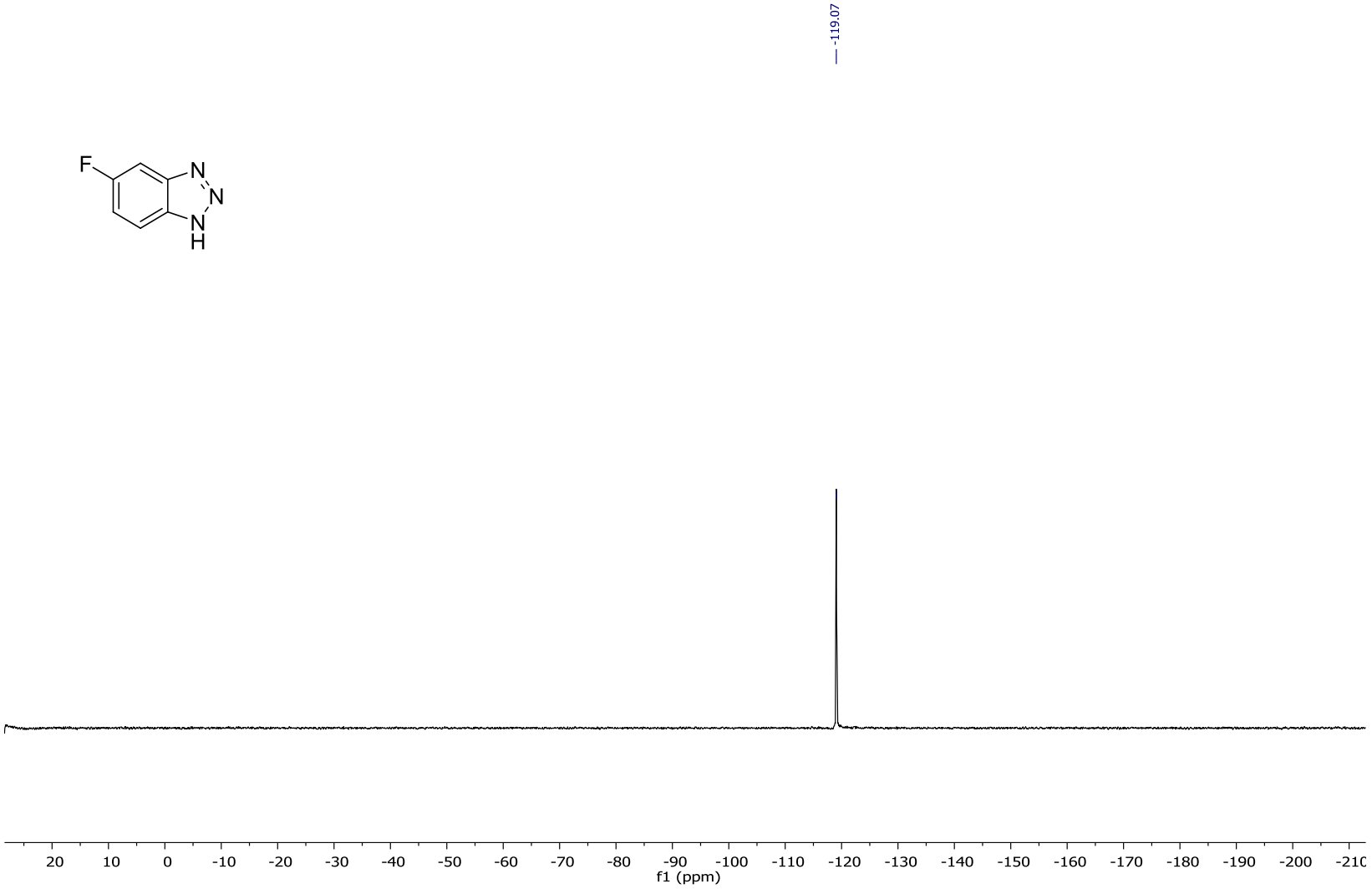


Figure S126. ^{19}F NMR (188 MHz, DMSO-d_6 + NaOH/D_2O) of 5-fluoro-1H-benzo[d][1,2,3]triazole (3j).

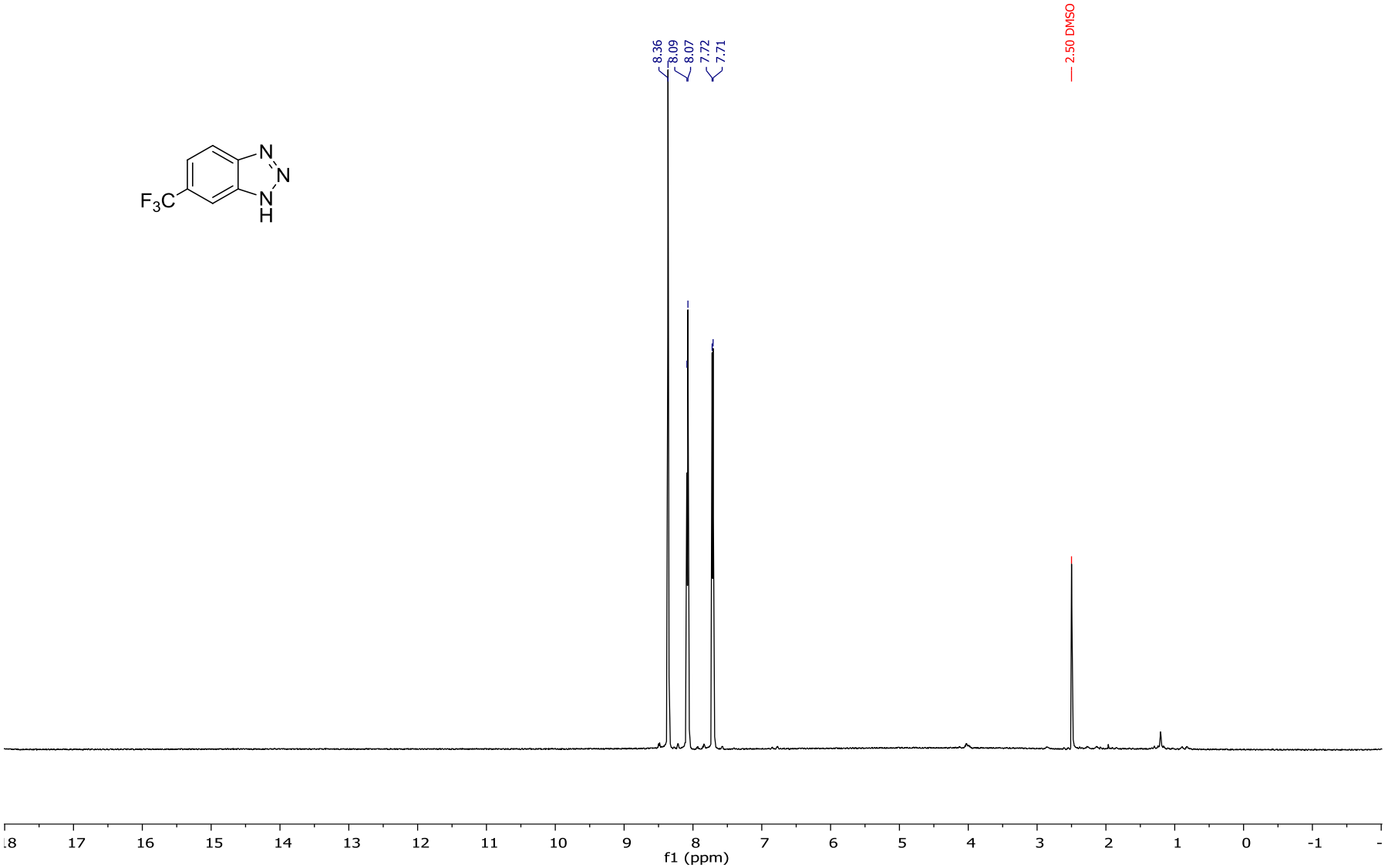


Figure S127. ^{1}H NMR (600 MHz, DMSO-d6) of 6-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (3k).

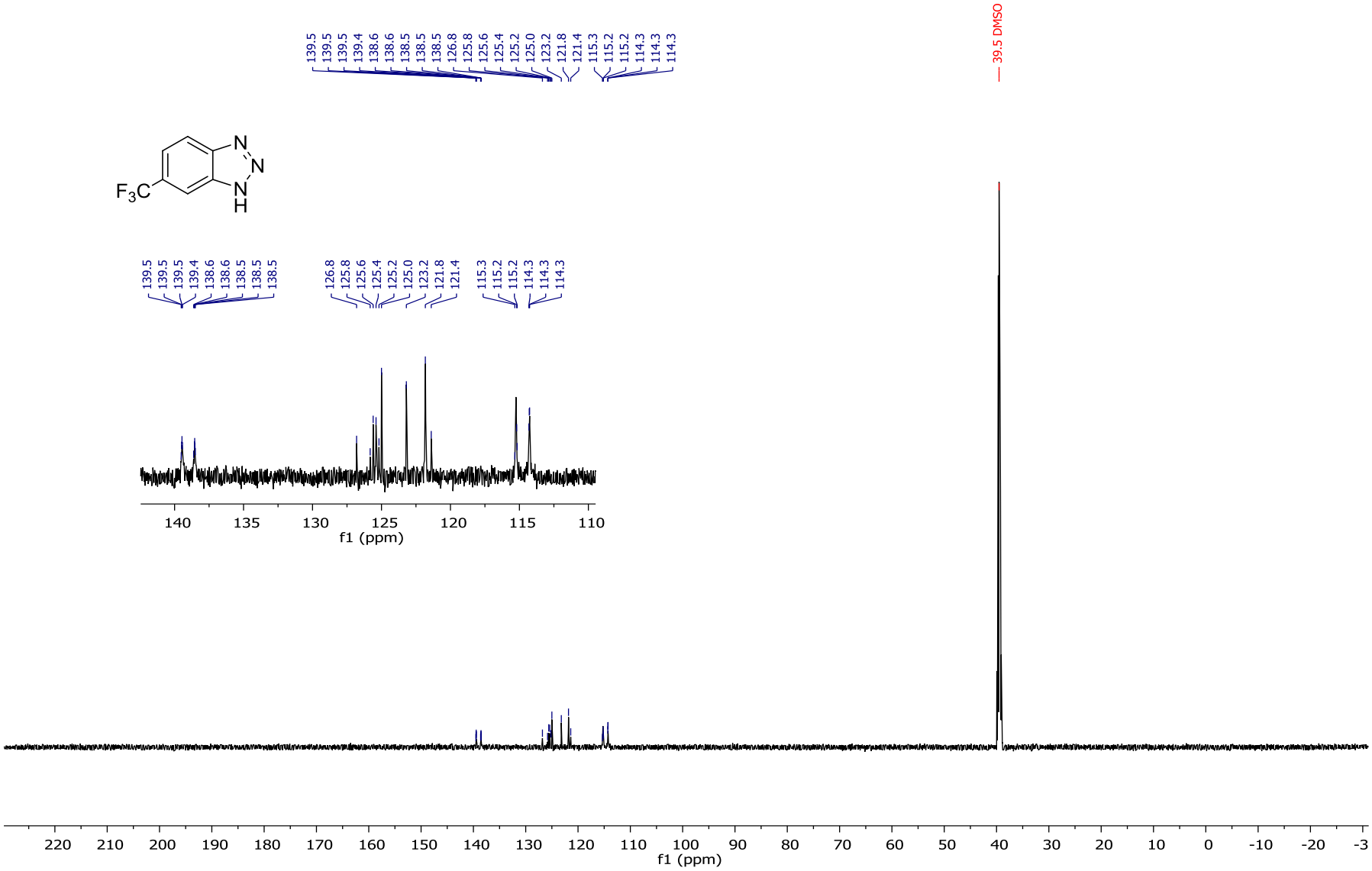


Figure S128. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d6) of 6-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (3k).

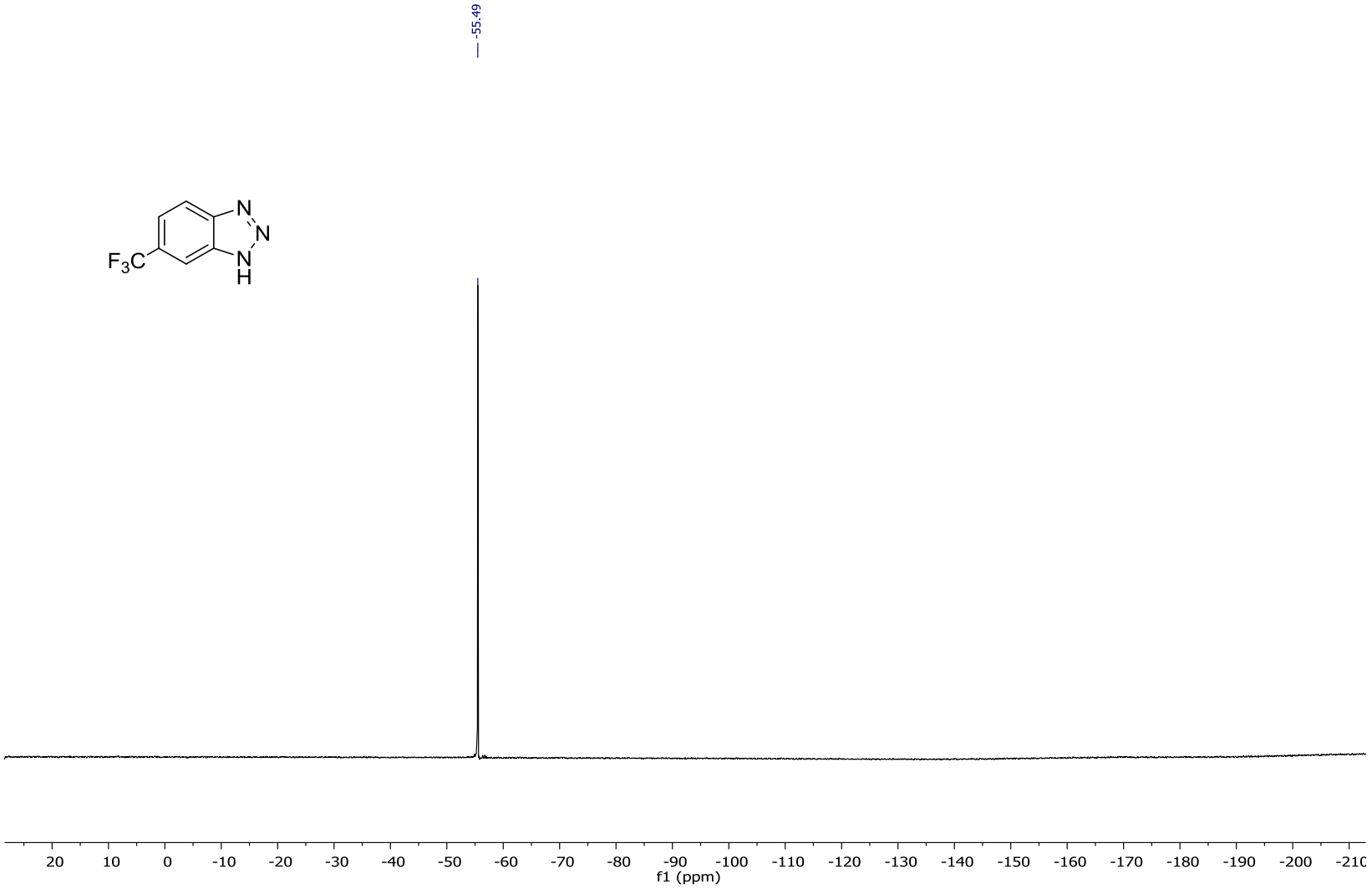


Figure S129. ^{19}F NMR (188 MHz, DMSO-d_6 + NaOH/D_2O) of 6-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (3k).

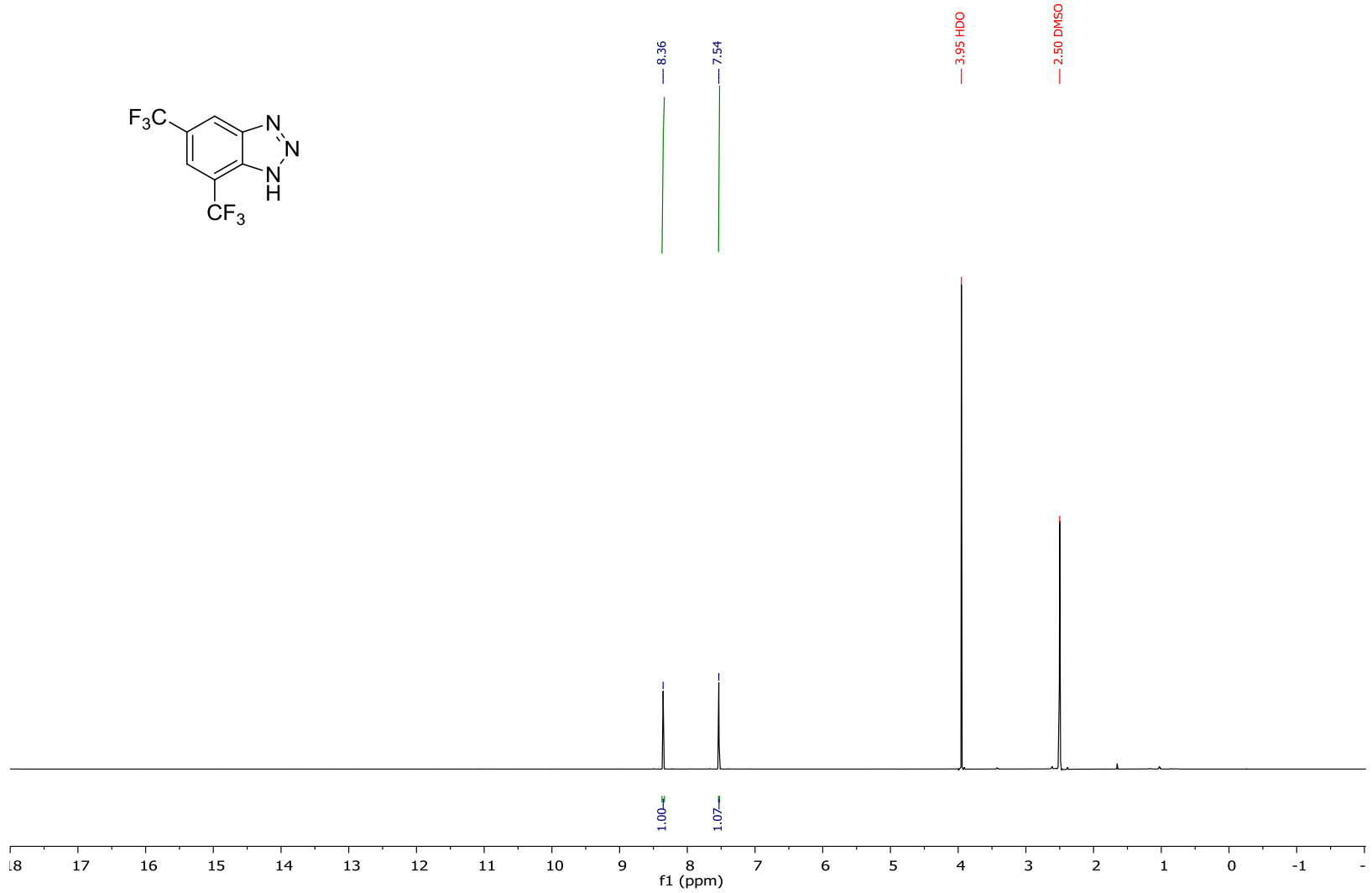


Figure S130. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 5,7-bis(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (3l).

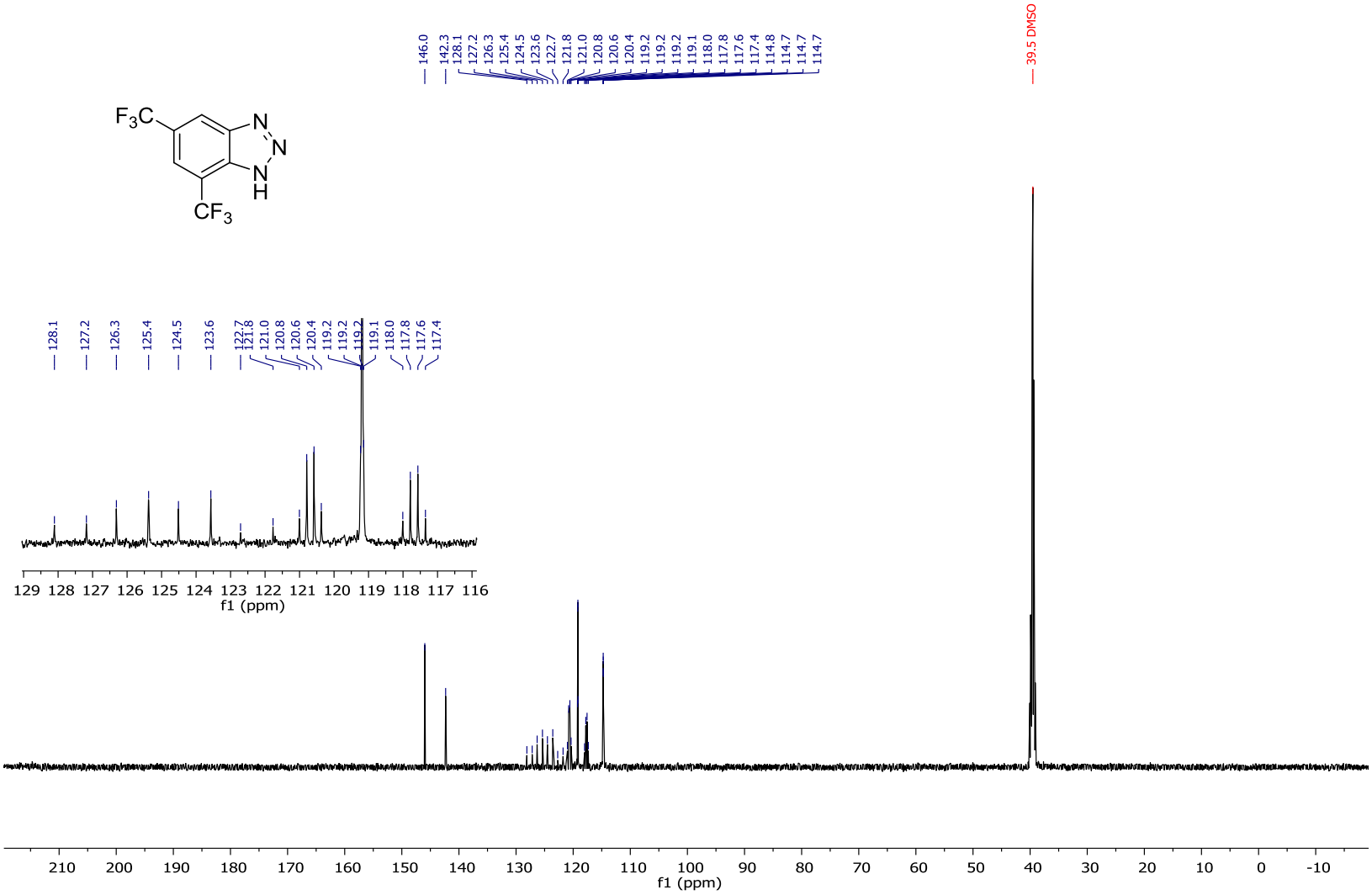


Figure S131. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 5,7-bis(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (3l).

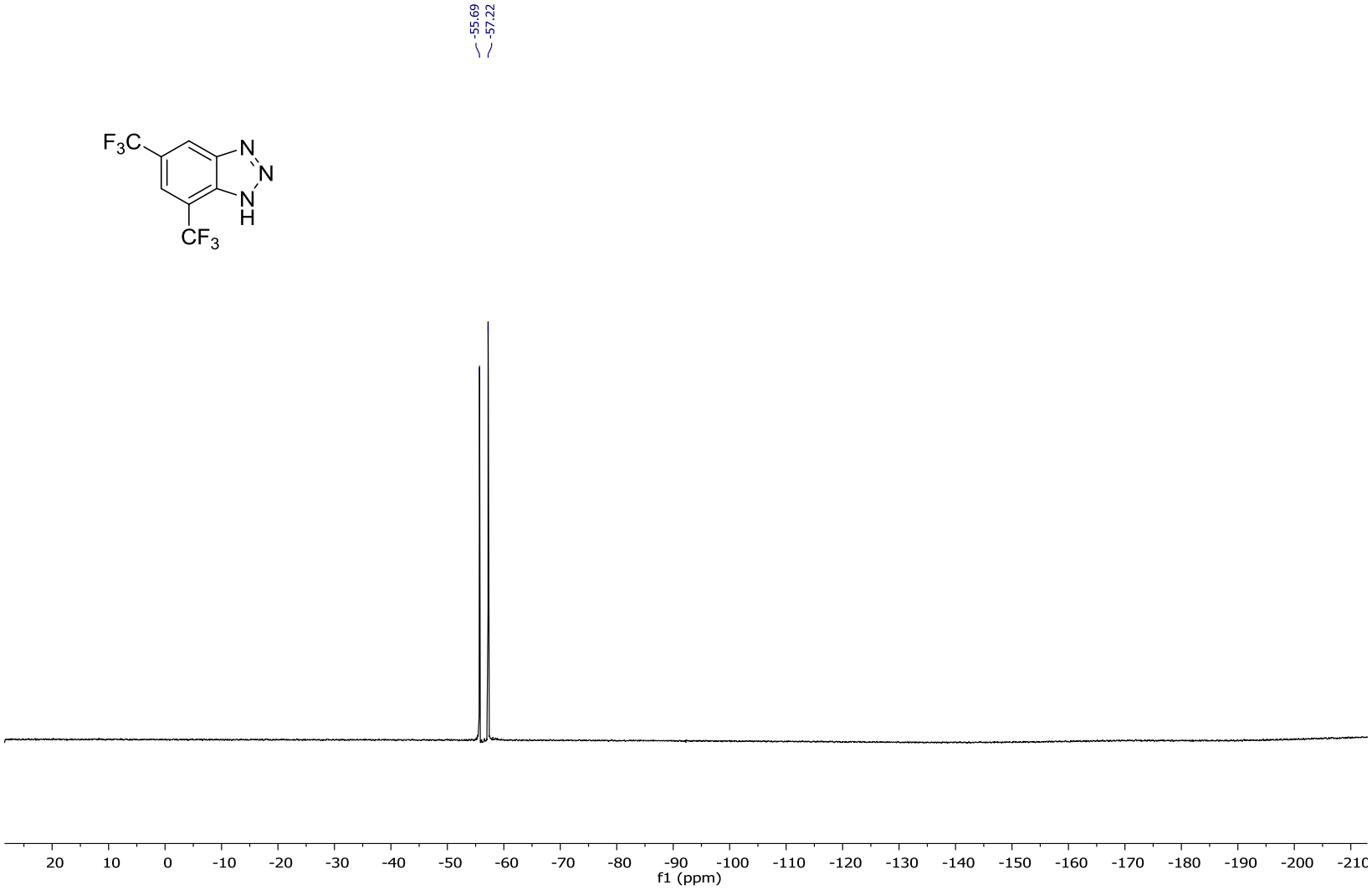


Figure S132. ^{19}F NMR (188 MHz, DMSO-d_6 + NaOH/D_2O) of 5,7-bis(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (3l).

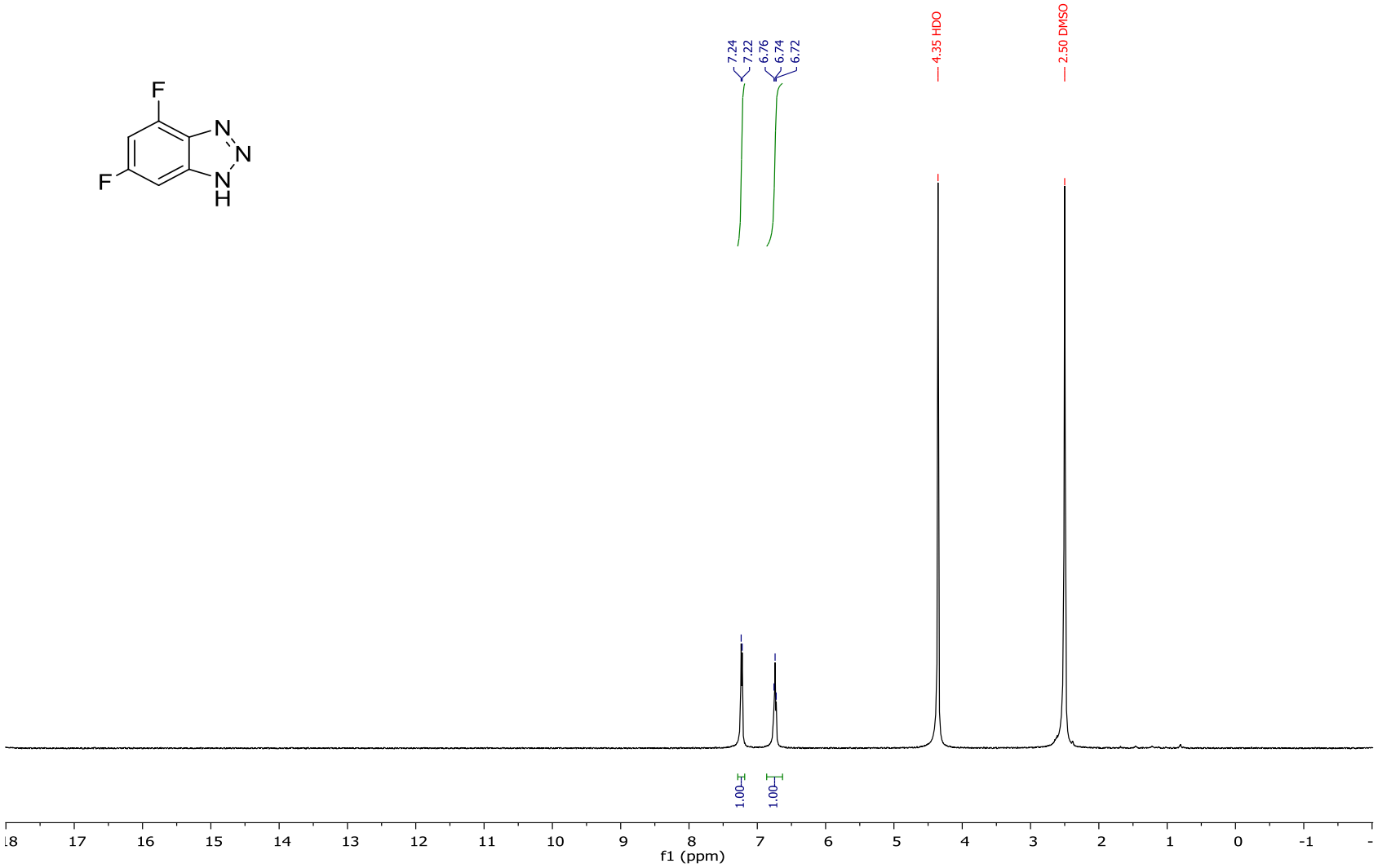


Figure S133. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 4,6-difluoro-1H-benzo[d][1,2,3]triazole (3m).

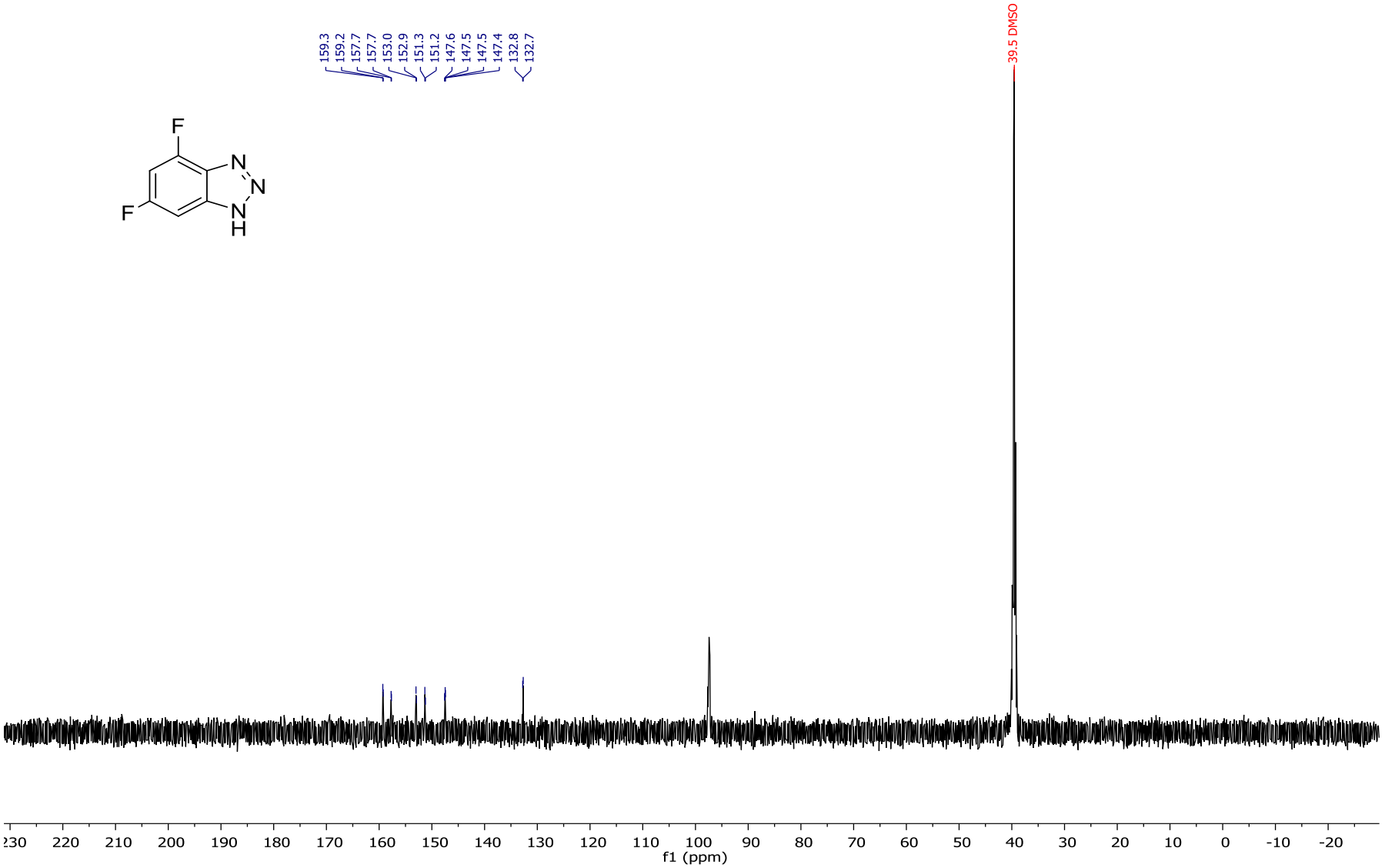


Figure S134. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 4,6-difluoro-1H-benzo[d][1,2,3]triazole (3m).

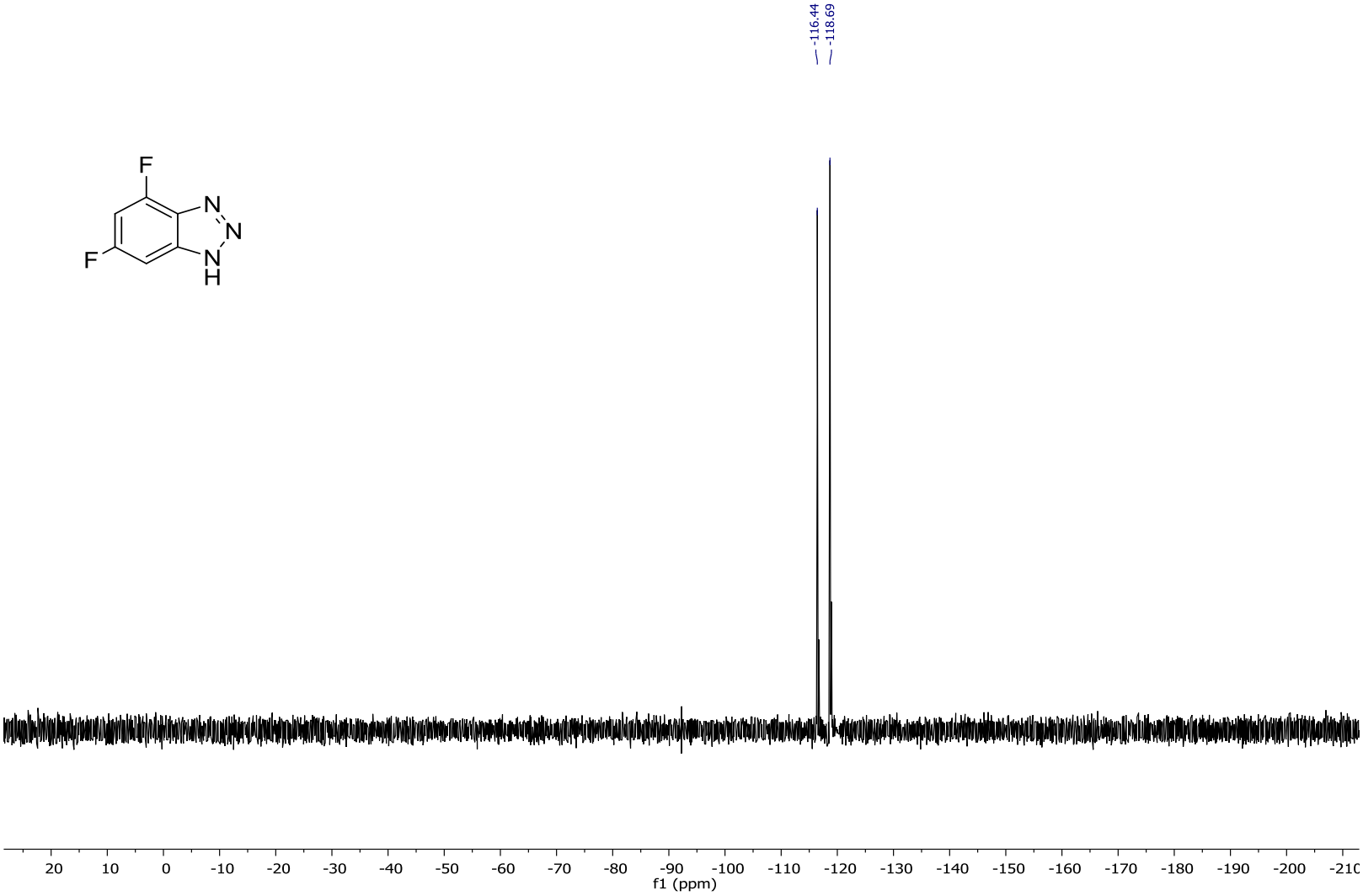


Figure S135. ^{19}F NMR (188 MHz, DMSO-d_6 + NaOH/D_2O) of 4,6-difluoro-1H-benzo[d][1,2,3]triazole (3m).

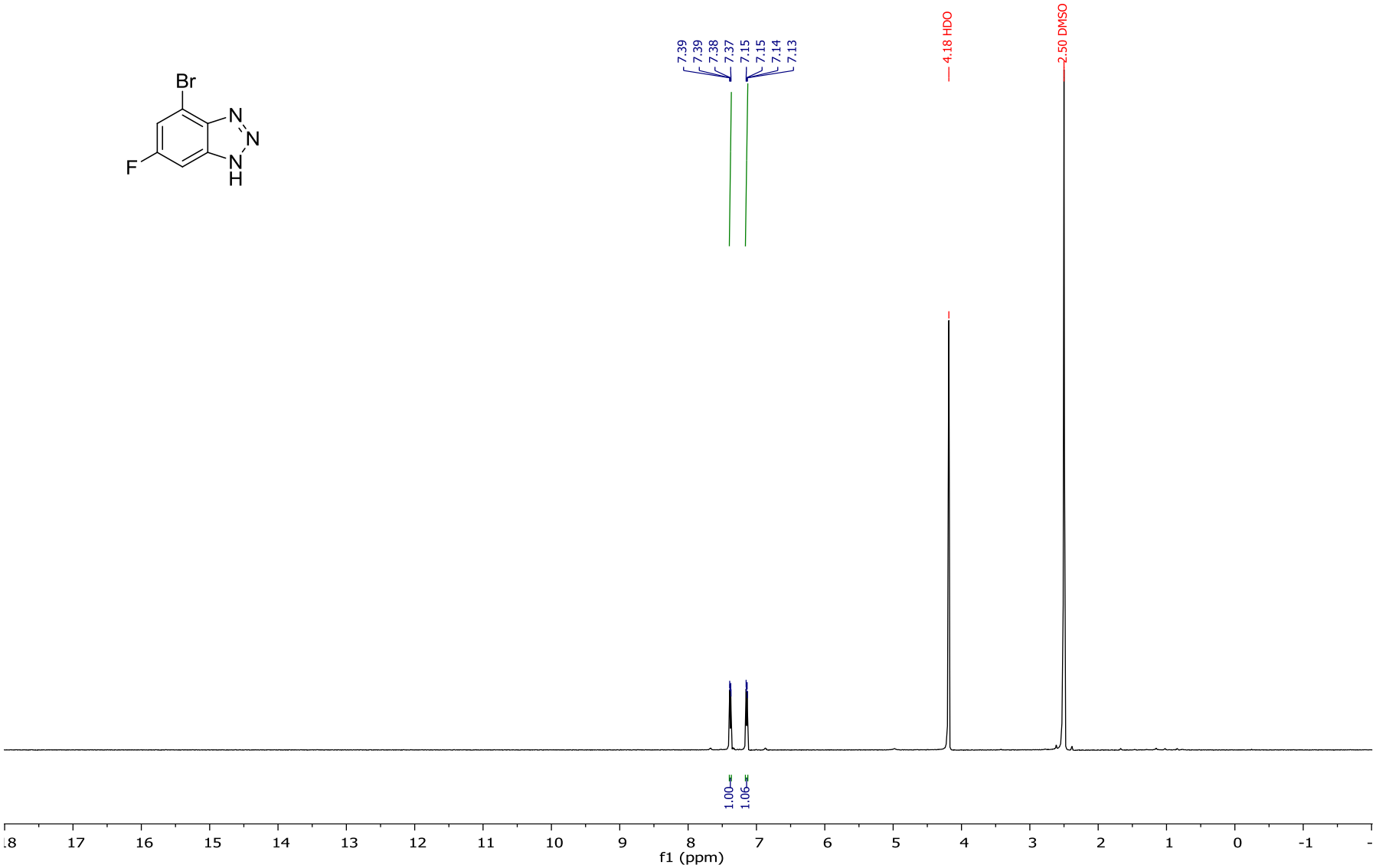


Figure S136. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 4-bromo-6-fluoro-1H-benzo[d][1,2,3]triazole (3n).

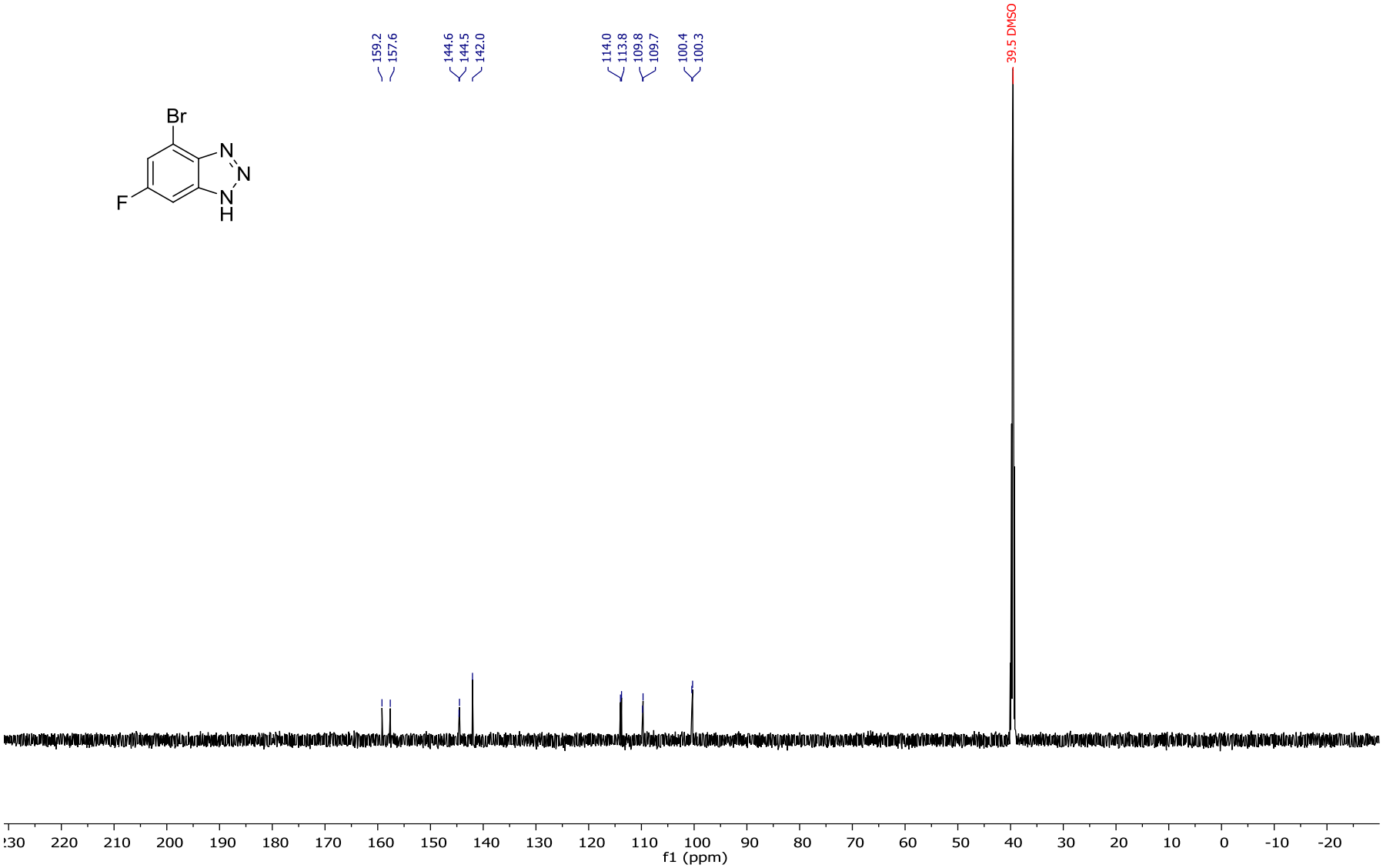


Figure S137. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 4-bromo-6-fluoro-1H-benzo[d][1,2,3]triazole (3n).

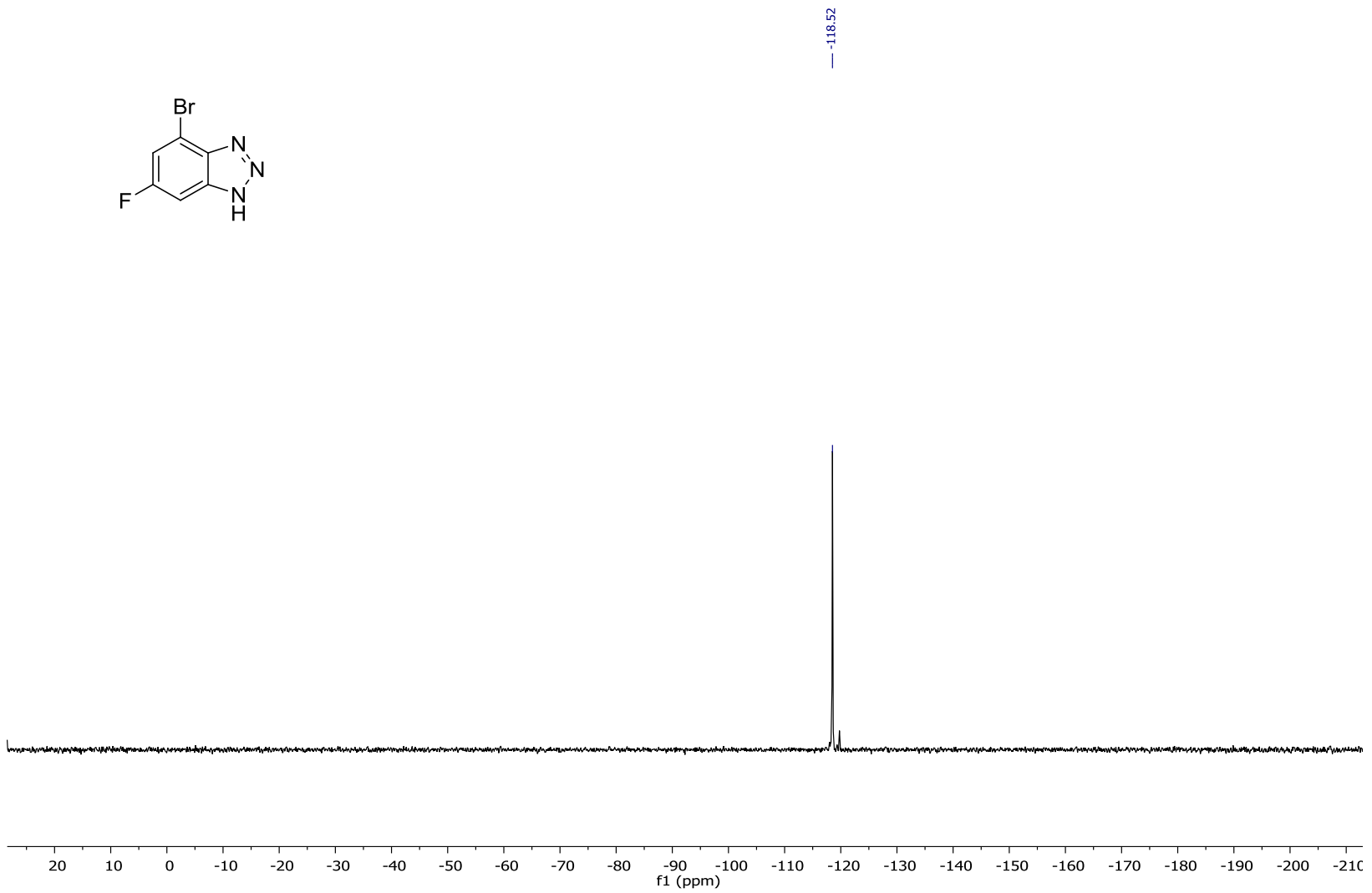


Figure S138. ^{19}F NMR (188 MHz, DMSO-d_6 + NaOH/D_2O) of 4-bromo-6-fluoro-1H-benzo[d][1,2,3]triazole (3n).

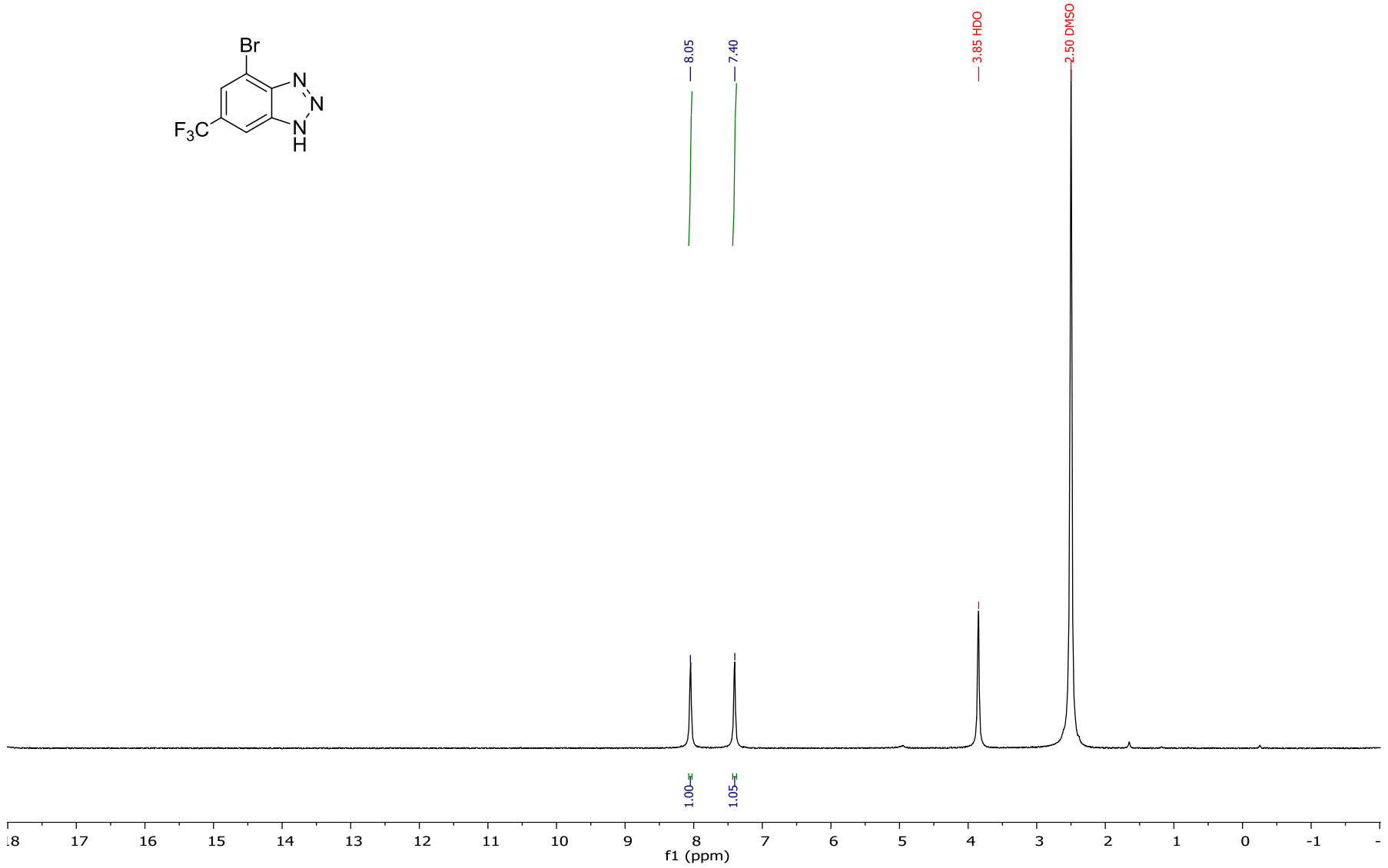


Figure S139. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 4-bromo-6-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (3o).

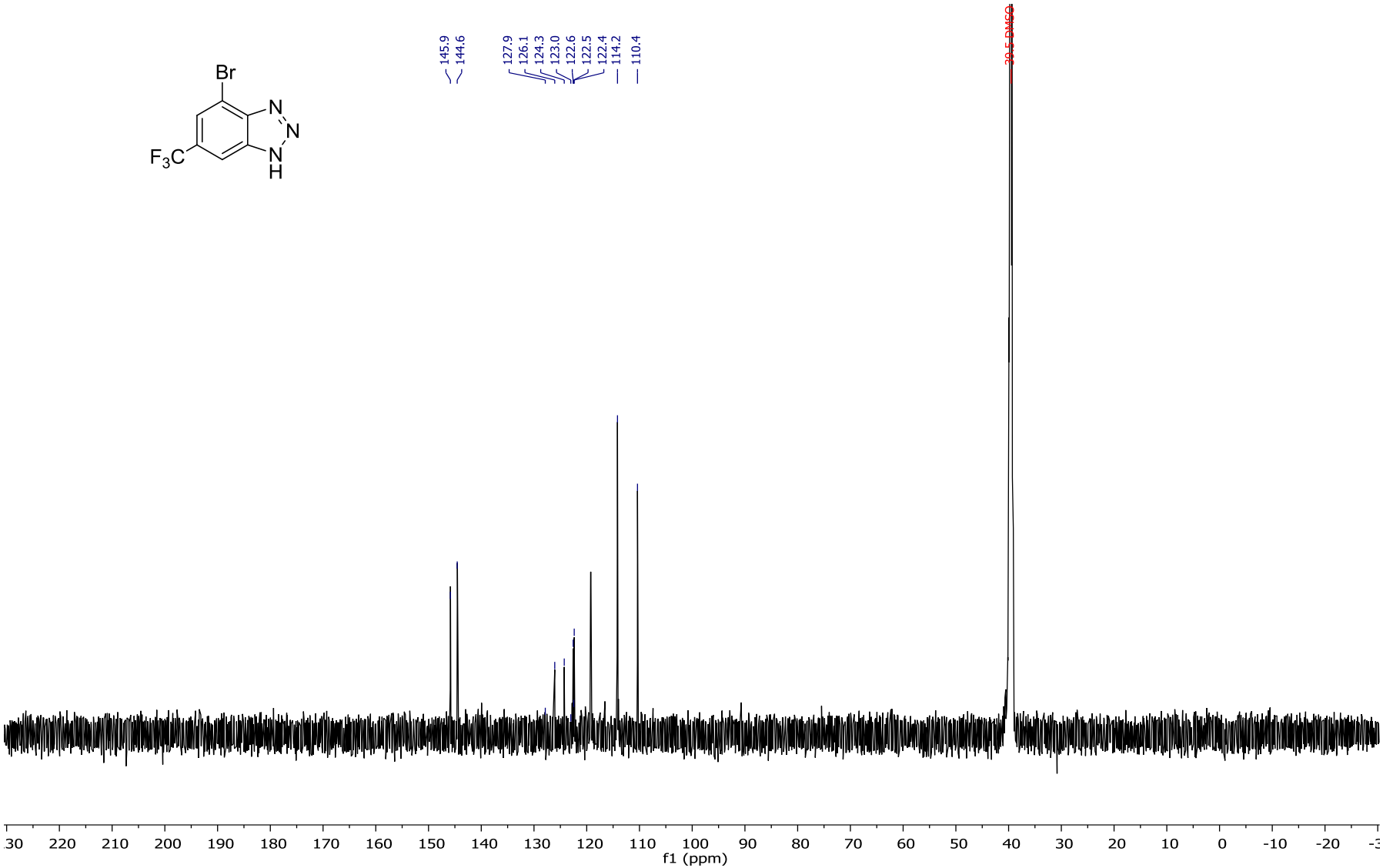


Figure S140. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 4-bromo-6-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (3o).

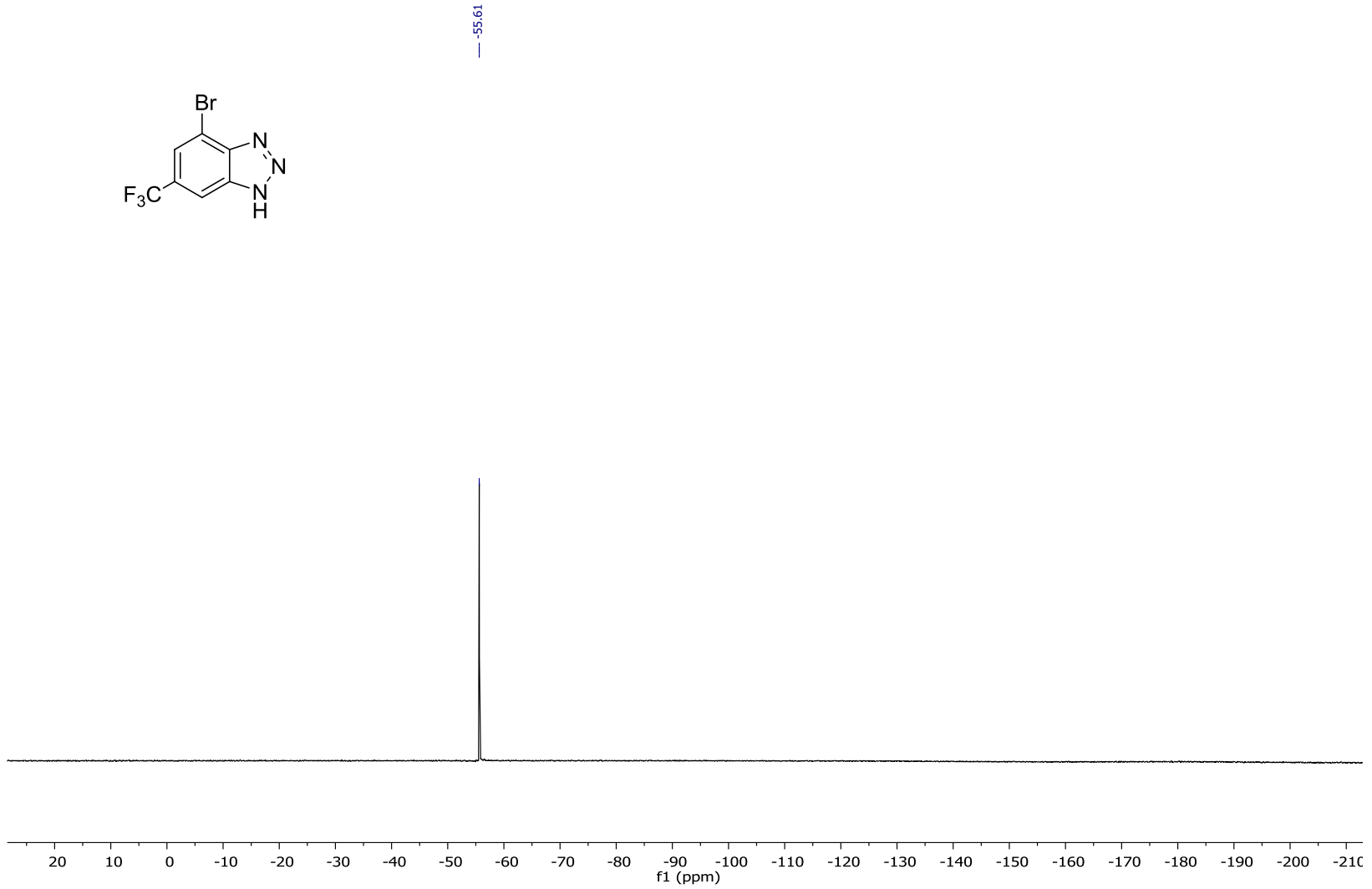


Figure S141. ^{19}F NMR (188 MHz, DMSO-d_6 + NaOH/D_2O) of 4-bromo-6-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (3o).

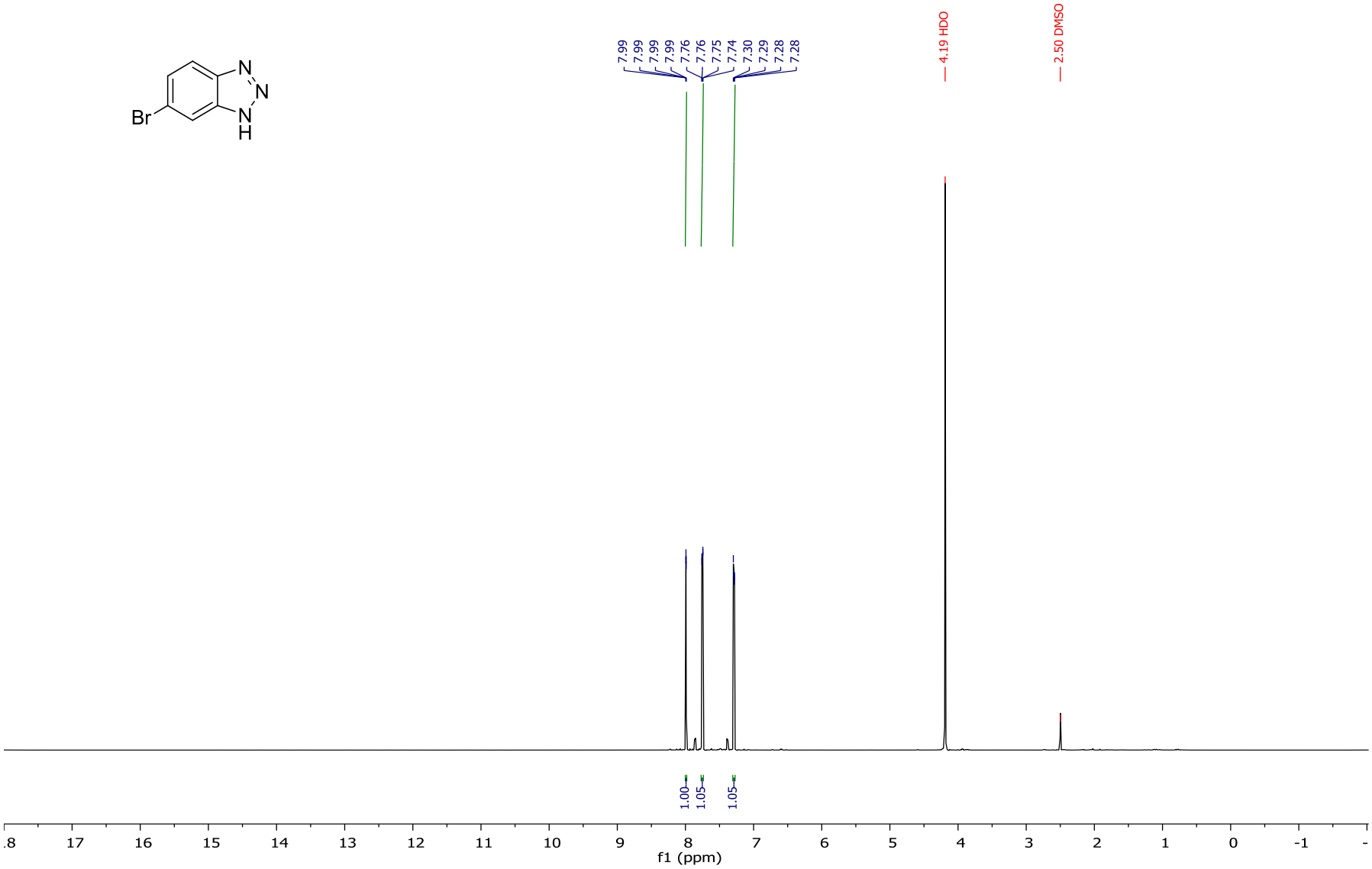


Figure S142. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 6-bromo-1H-benzo[d][1,2,3]triazole (3p).

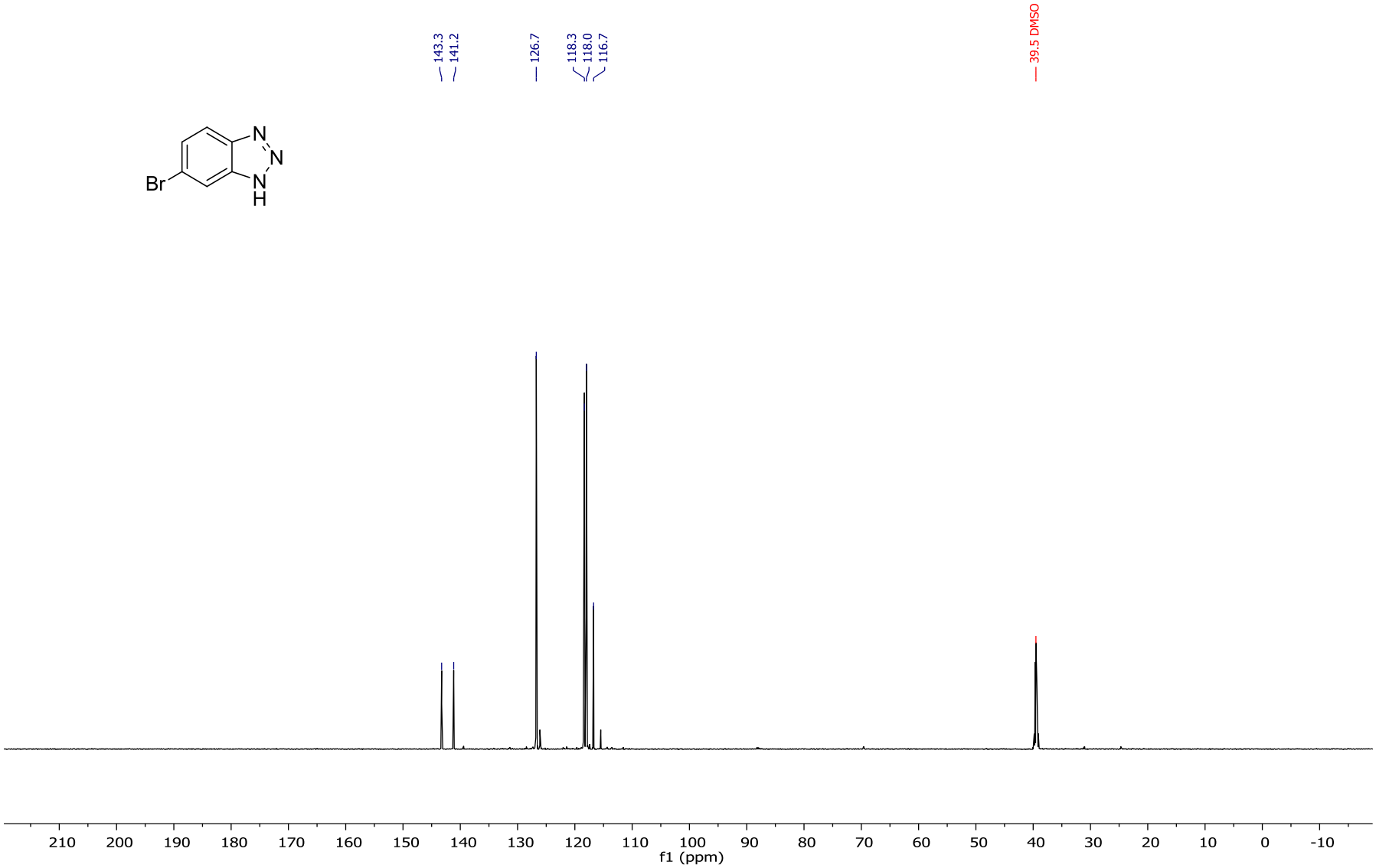


Figure S143. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 6-bromo-1H-benzo[d][1,2,3]triazole (3p).

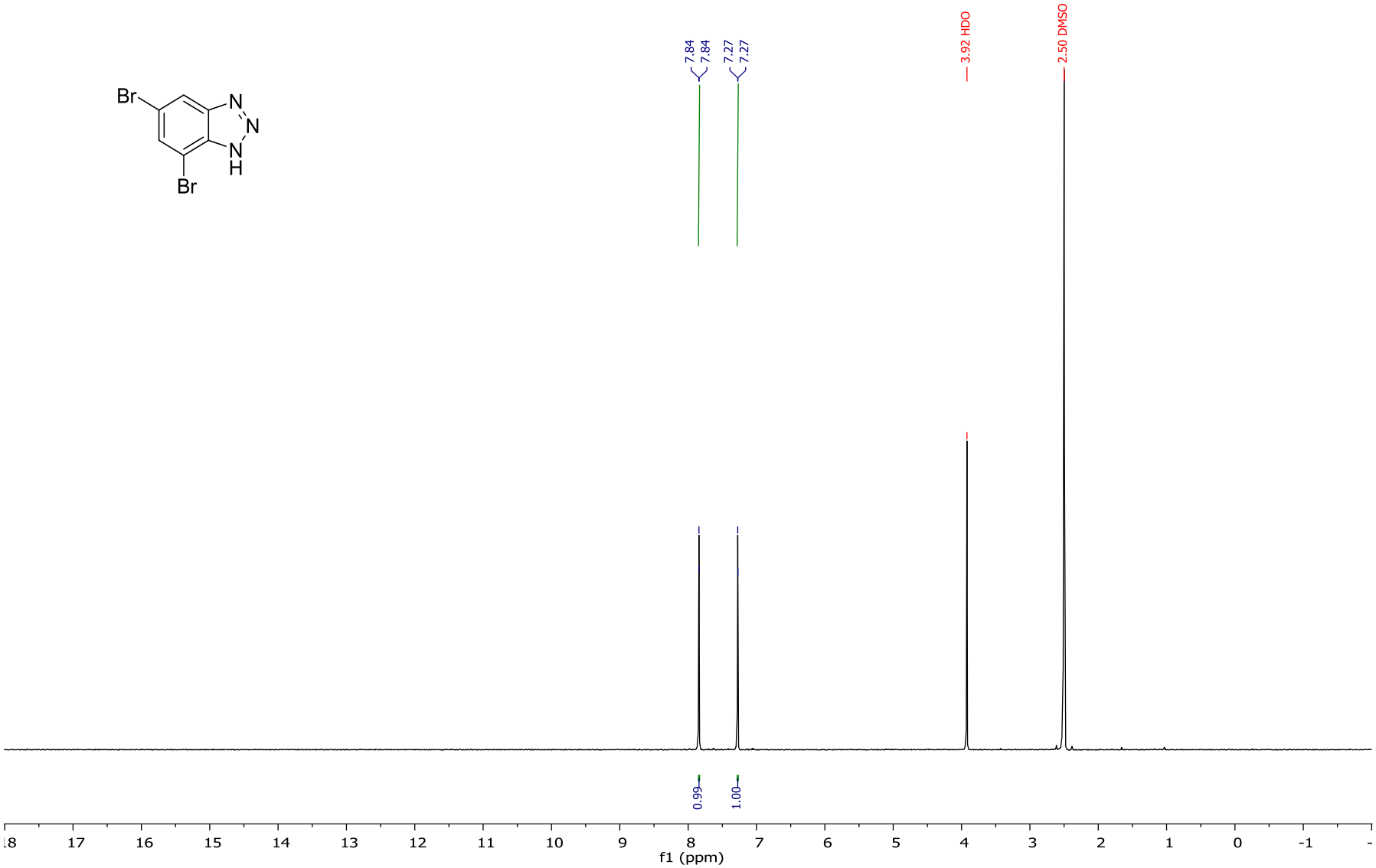


Figure S144. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 5,7-dibromo-1H-benzo[d][1,2,3]triazole (3q).

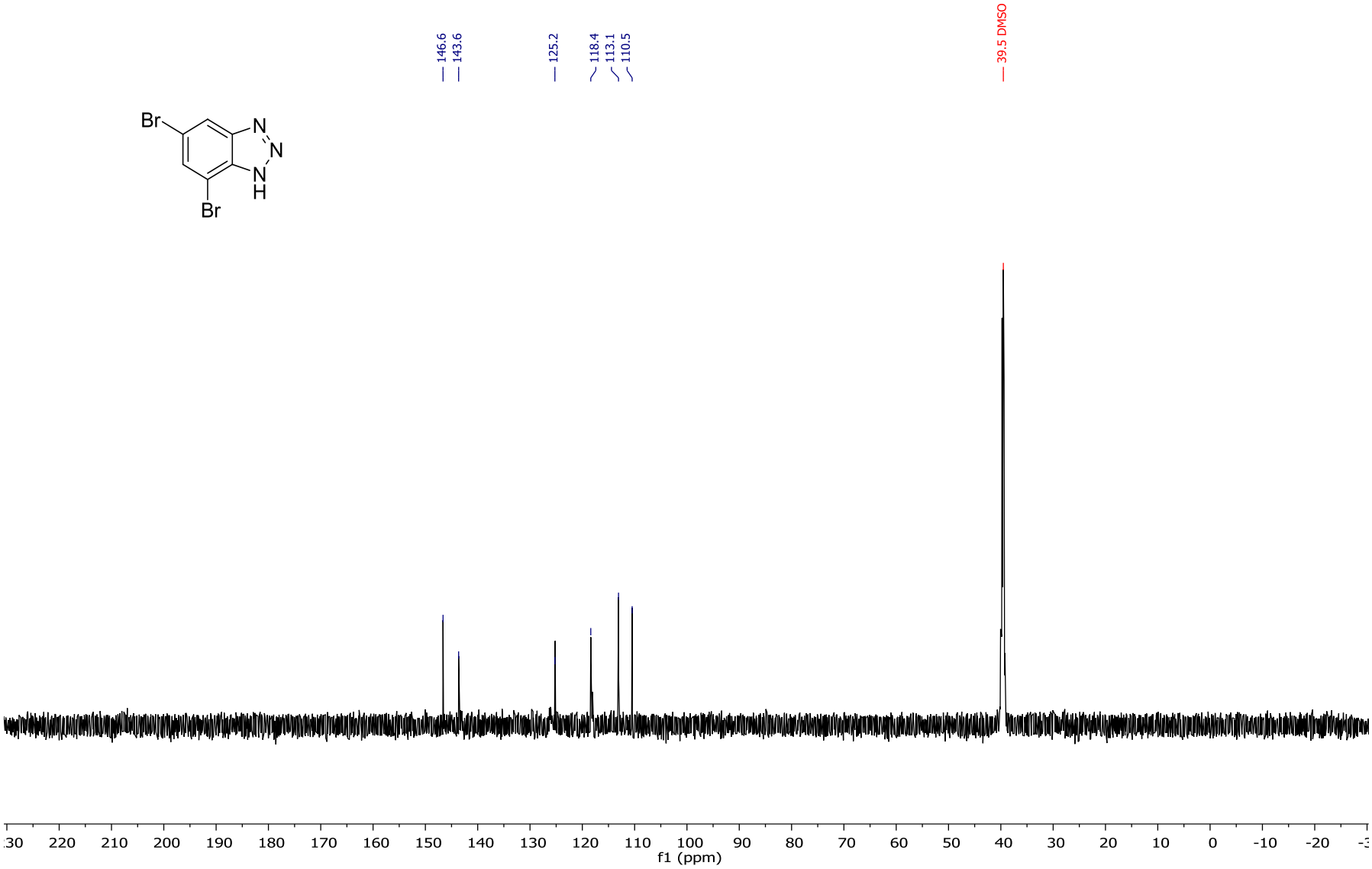


Figure S145. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 5,7-dibromo-1H-benzo[d][1,2,3]triazole (3q).

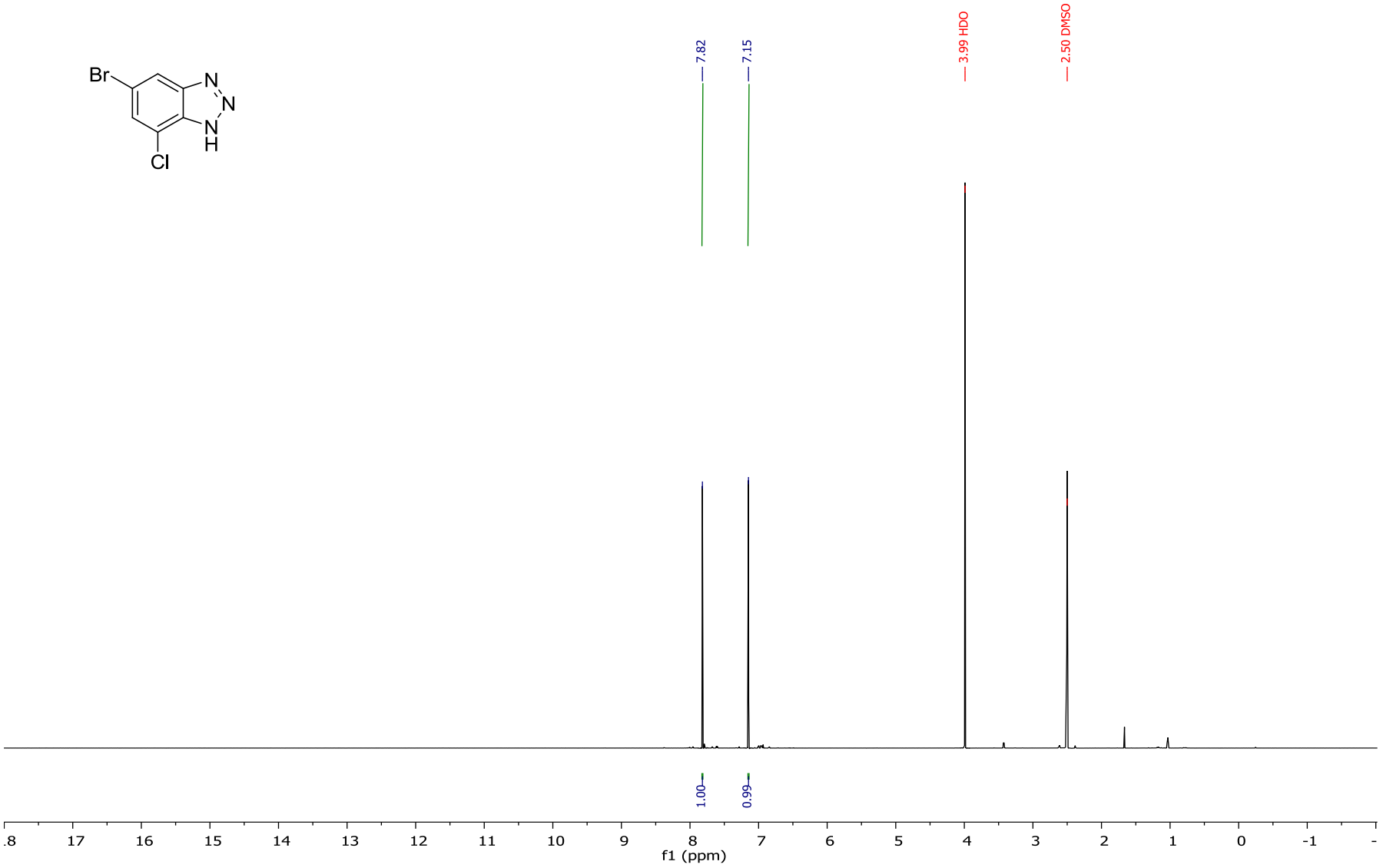


Figure S146. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 5-bromo-7-chloro-1H-benzo[d][1,2,3]triazole (3r).

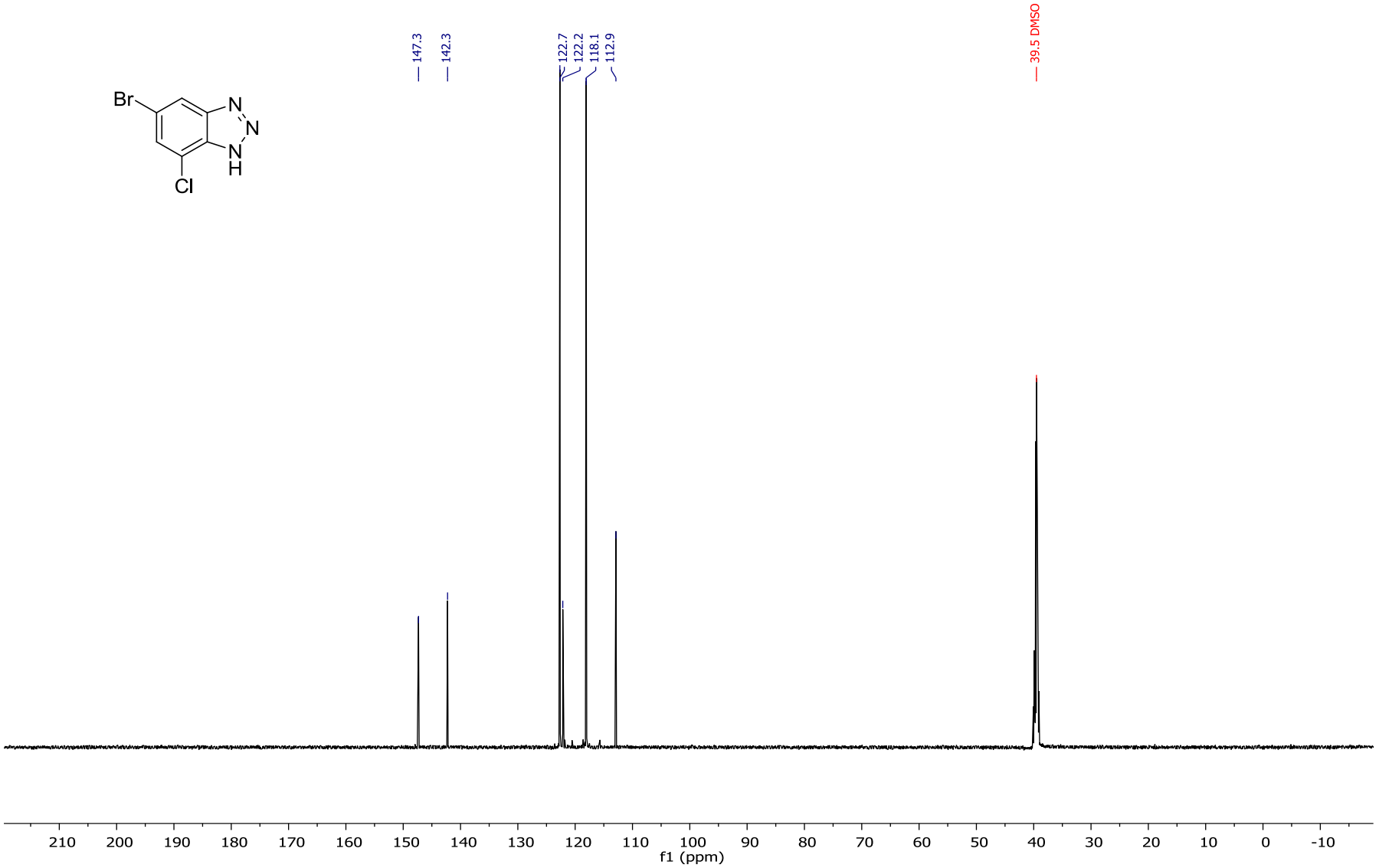


Figure S147. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 5-bromo-7-chloro-1H-benzo[d][1,2,3]triazole (3r).

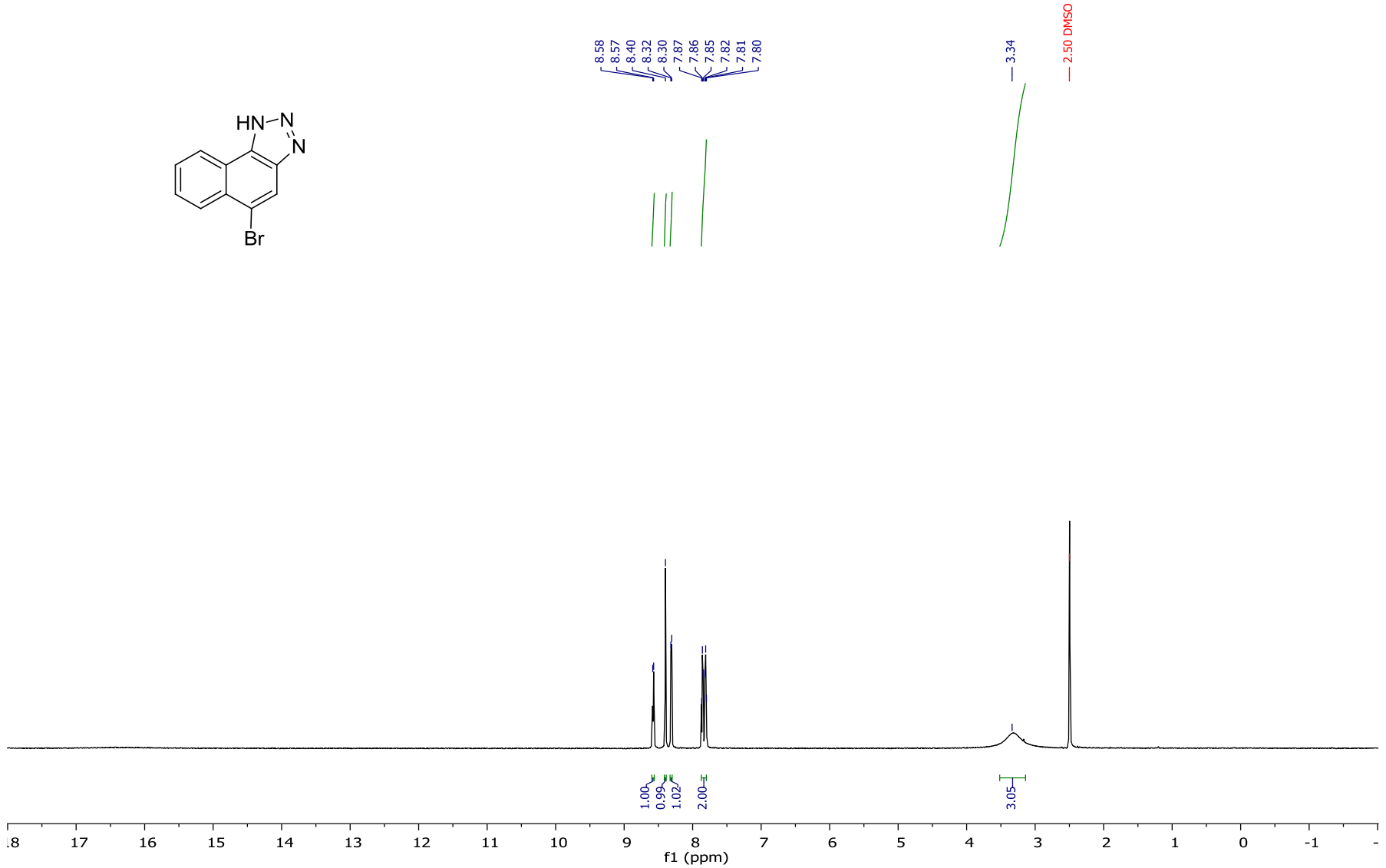


Figure S148. ^{1}H NMR (600 MHz, DMSO-d_6) of 5-bromo-1H-naphtho[1,2-d][1,2,3]triazole (3s).

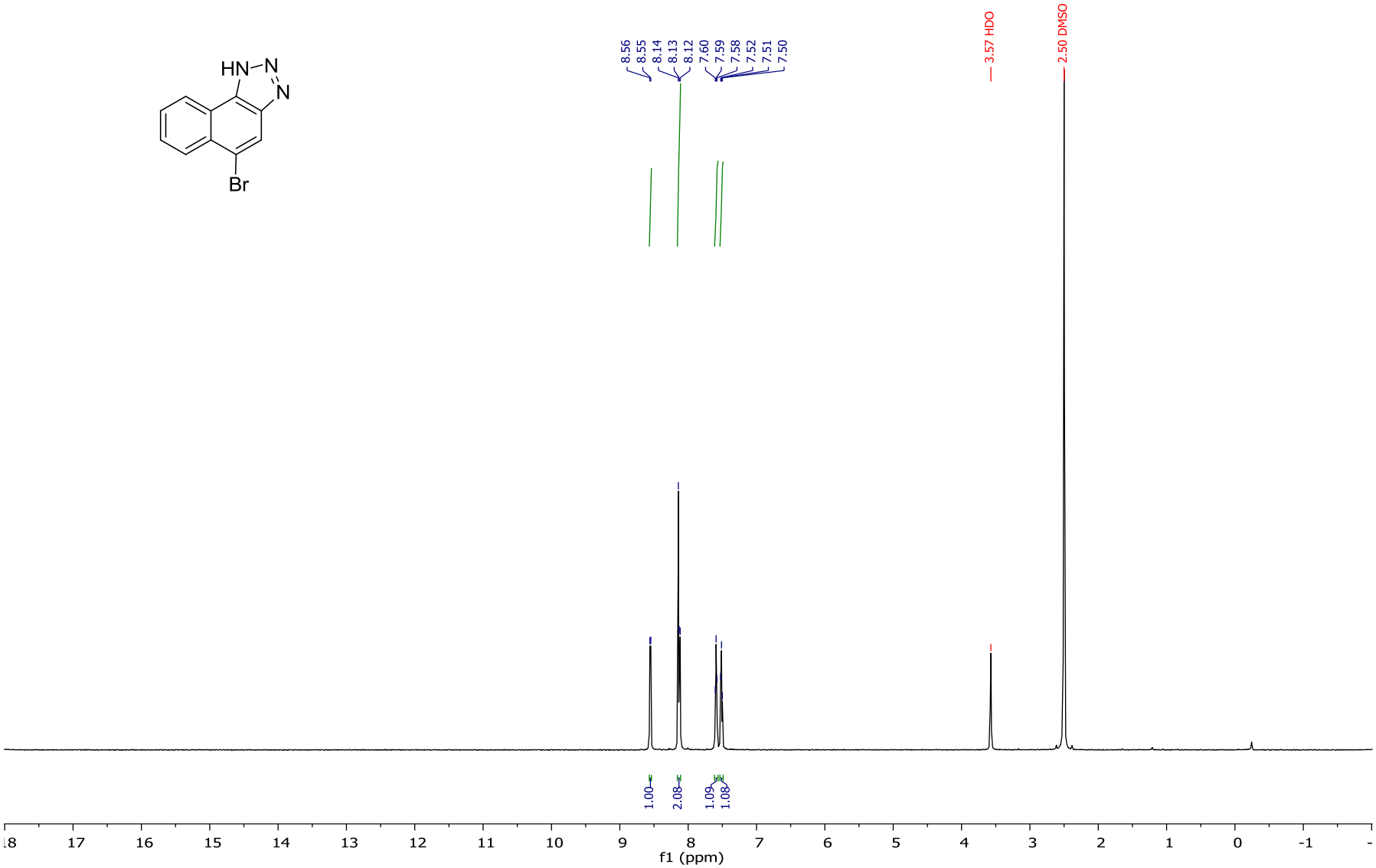


Figure S149. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 5-bromo-1H-naphtho[1,2-d][1,2,3]triazole (3s).

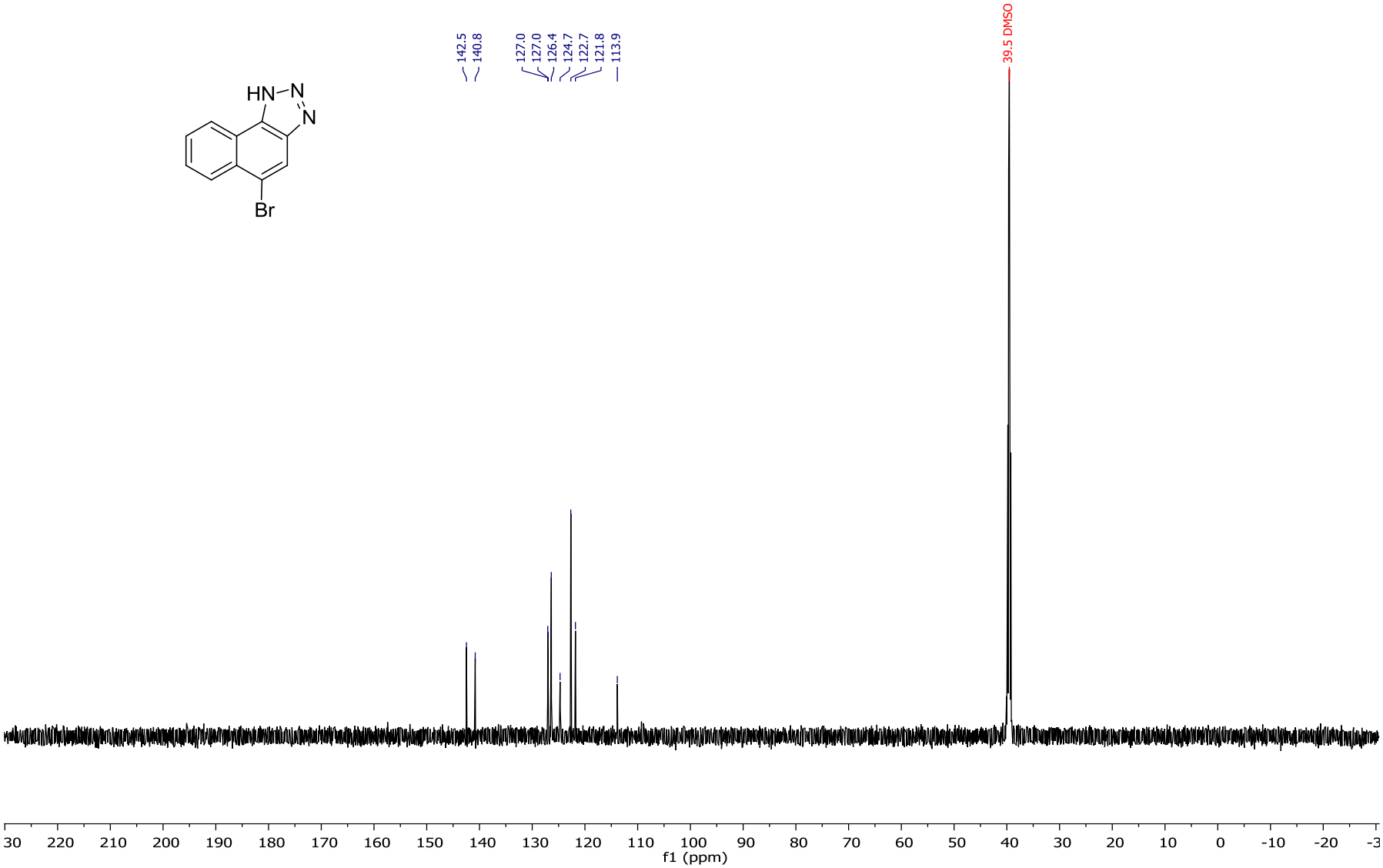


Figure S150. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 5-bromo-1H-naphtho[1,2-d][1,2,3]triazole (3s).

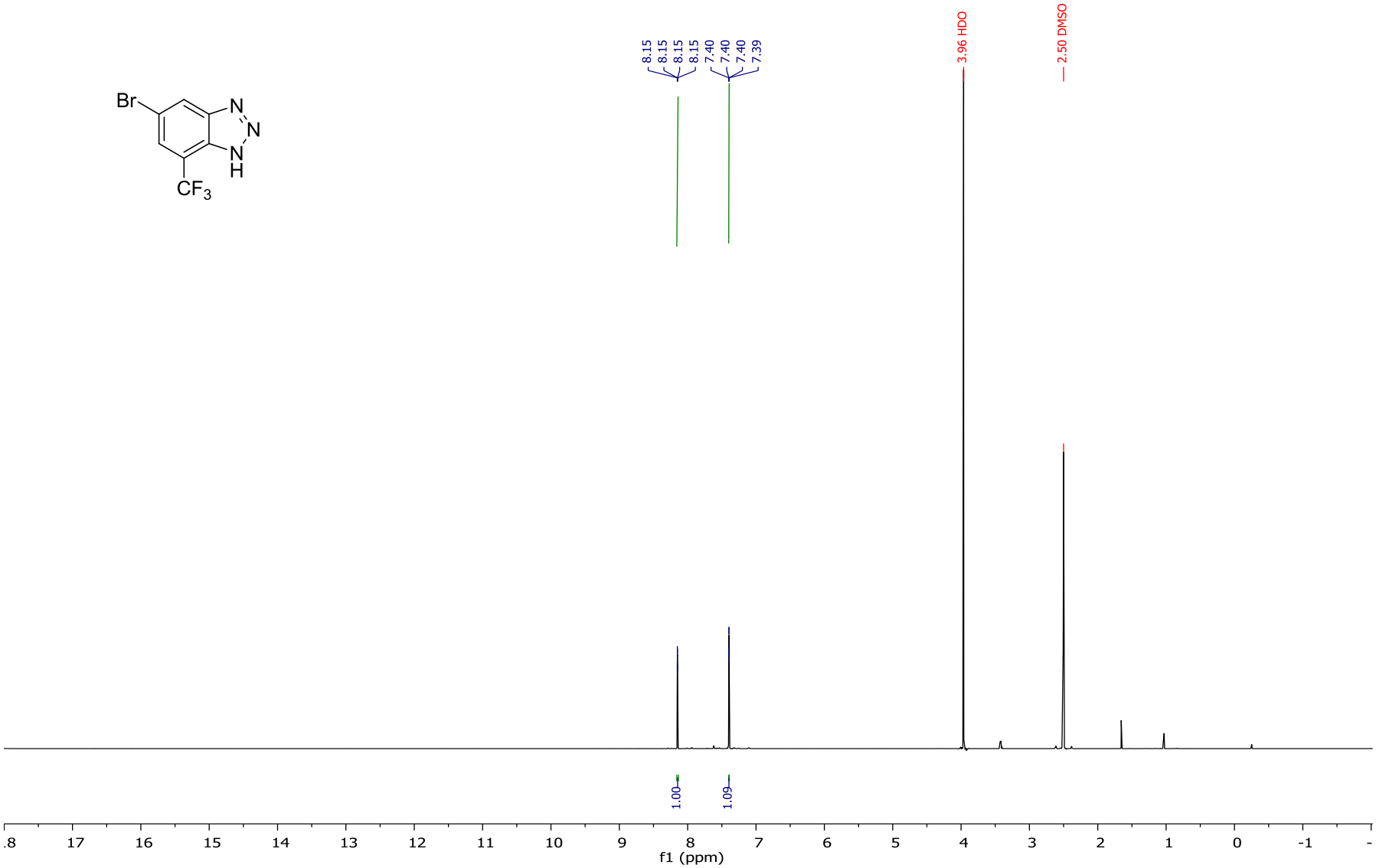


Figure S151. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 5-bromo-7-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (3t).

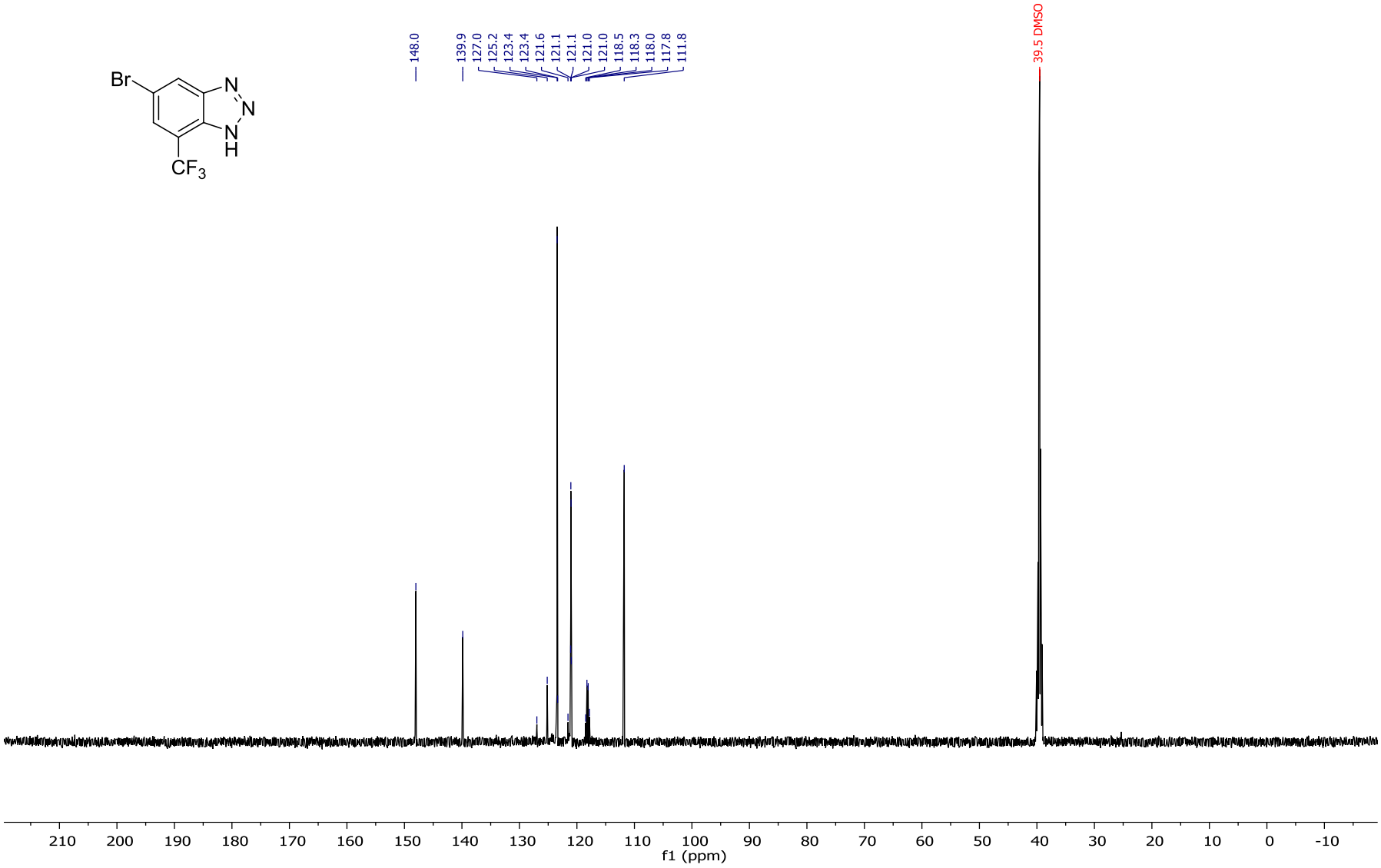


Figure S152. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 5-bromo-7-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (3t).

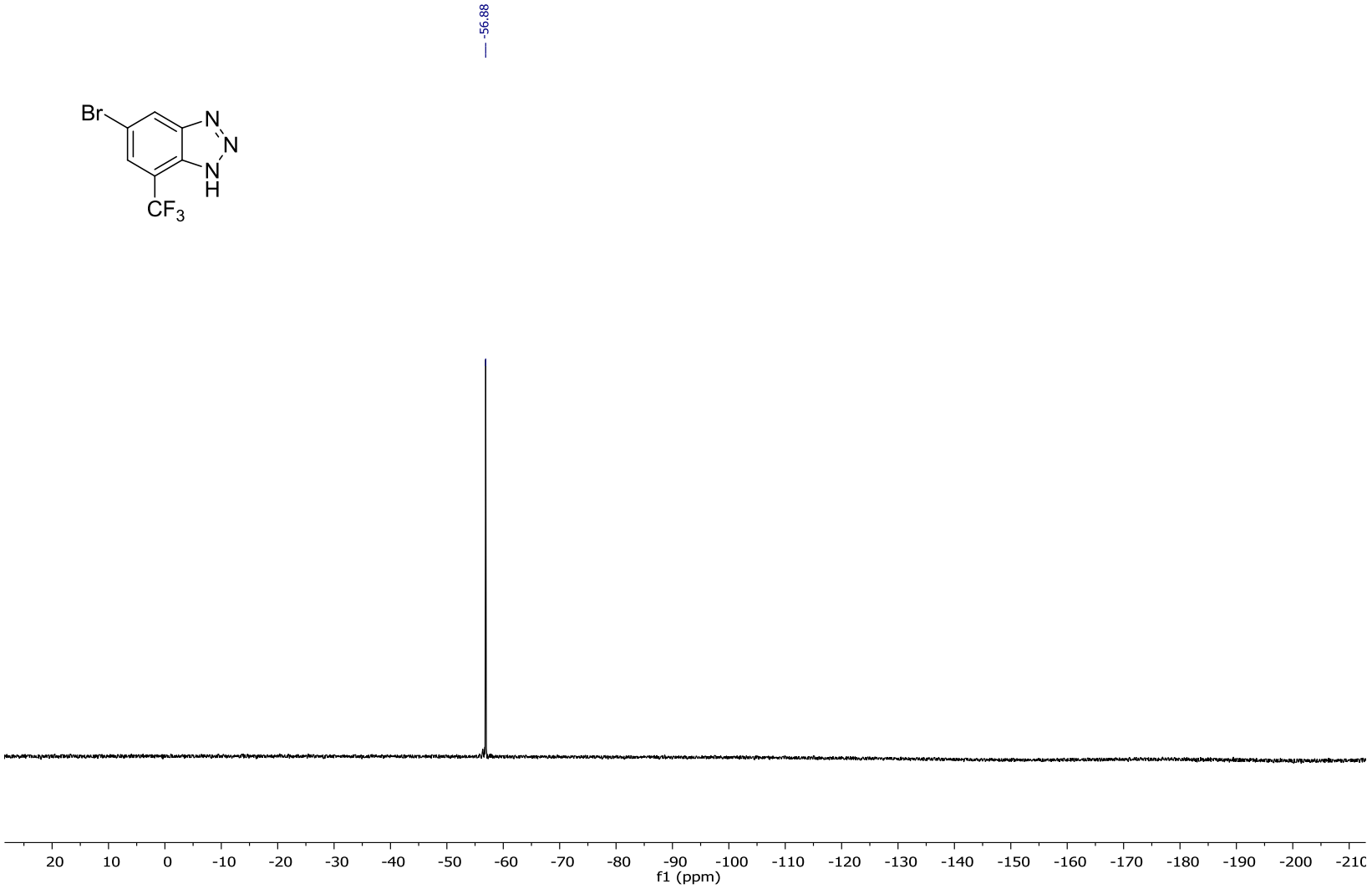


Figure S153. ^{19}F NMR (188 MHz, DMSO-d_6 + NaOH/D_2O) of 5-bromo-7-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (3t).

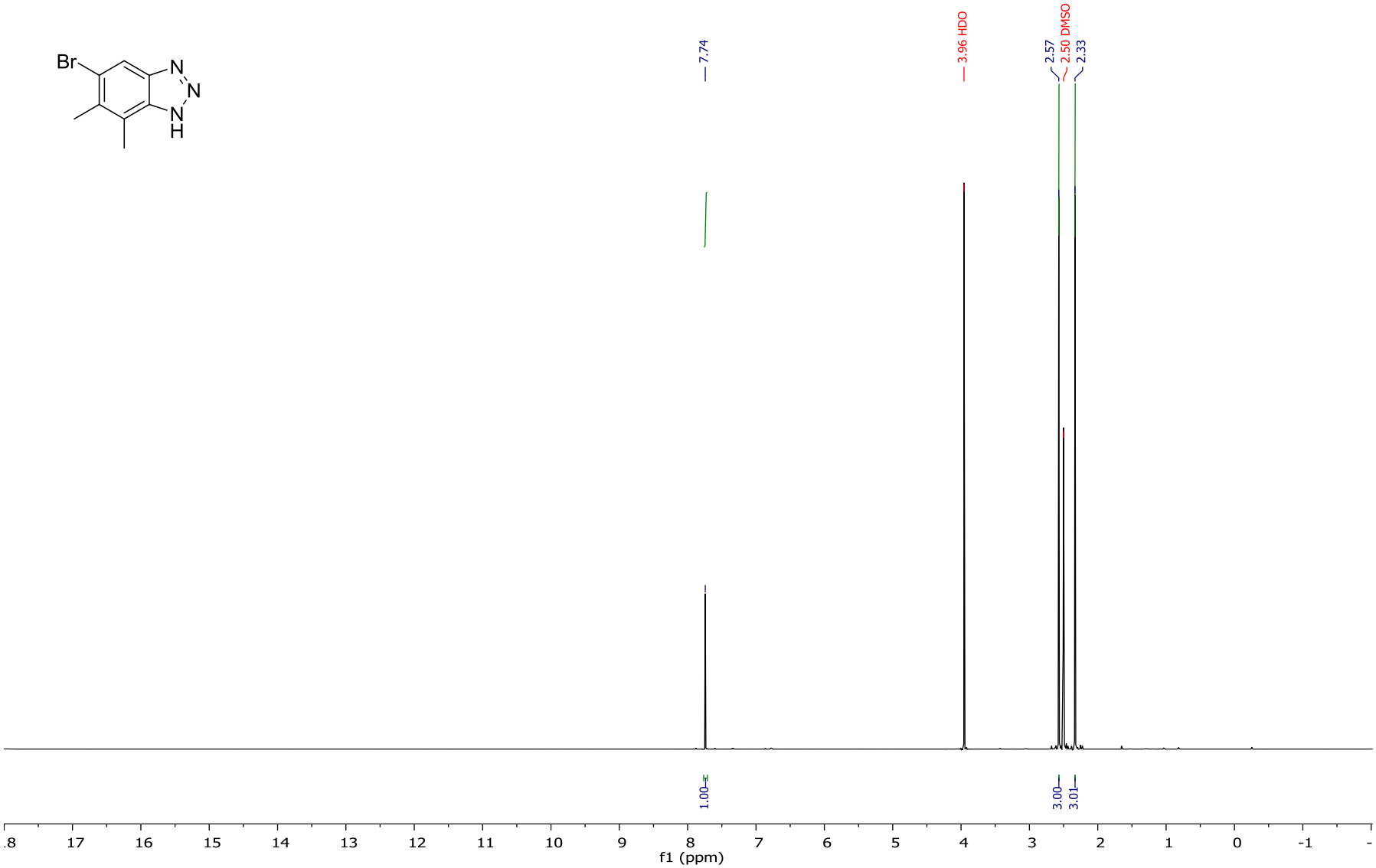


Figure S154. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 5-bromo-6,7-dimethyl-1H-benzo[d][1,2,3]triazole (3u).

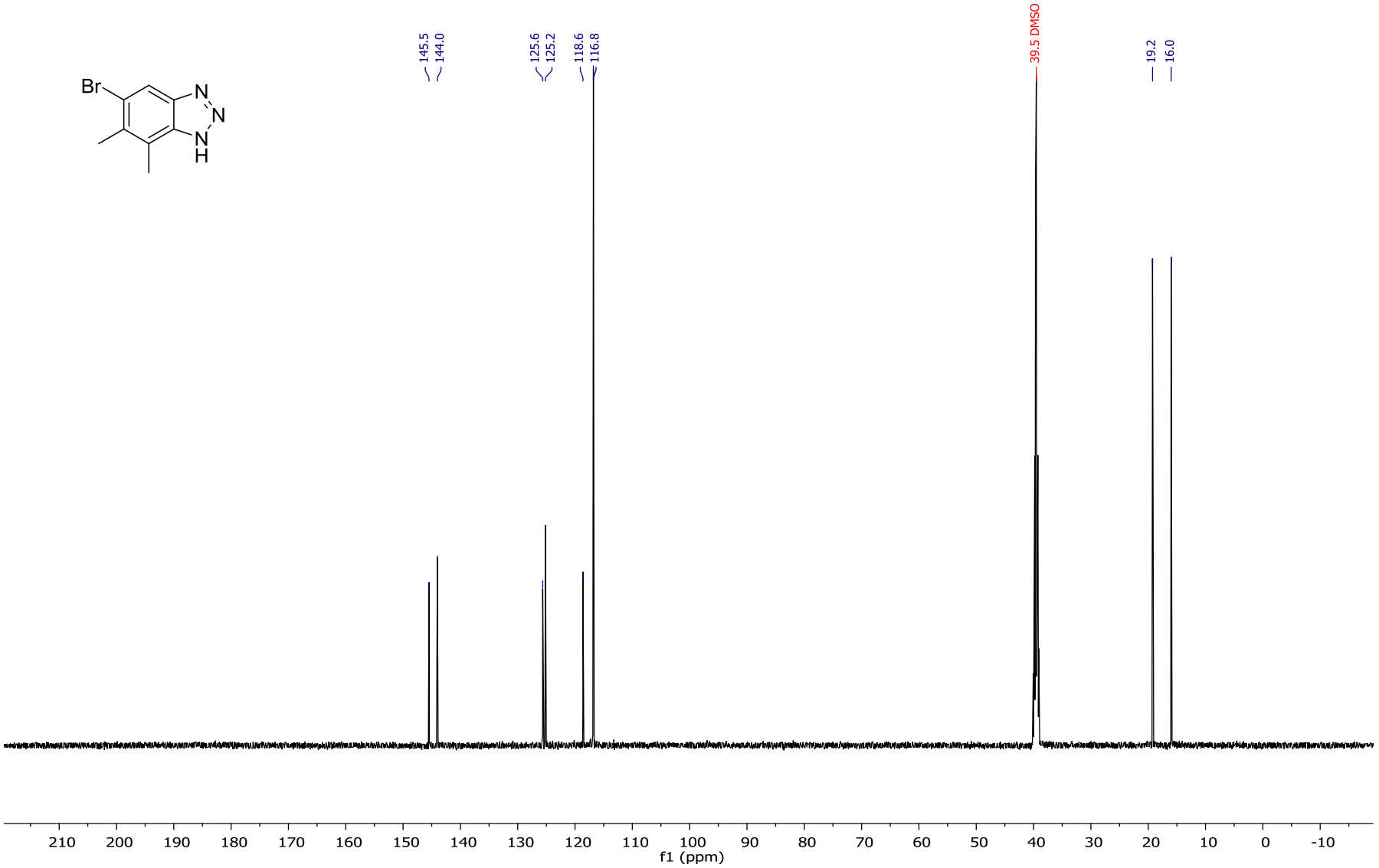


Figure S155. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 5-bromo-6,7-dimethyl-1H-benzo[d][1,2,3]triazole (3u).

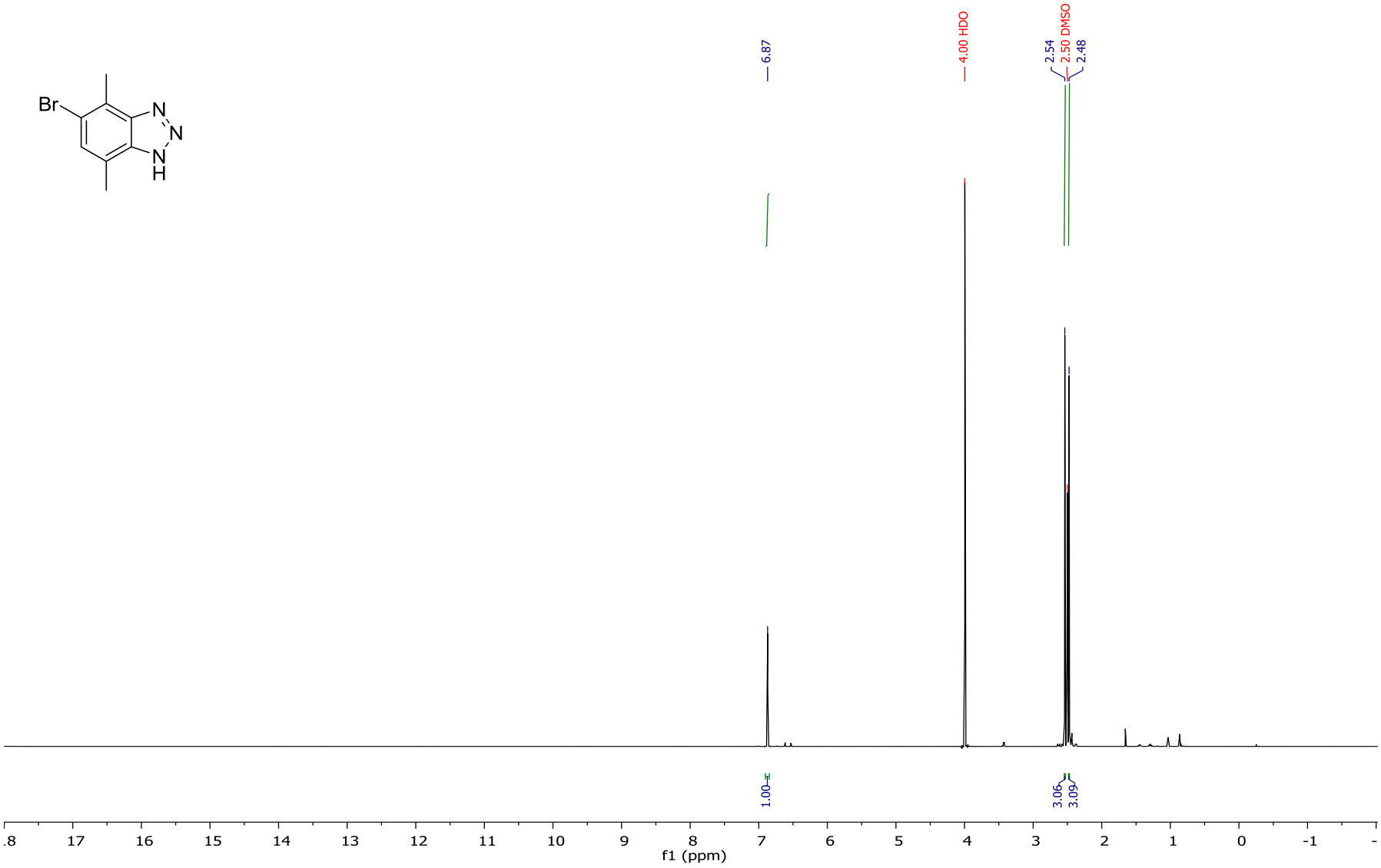


Figure S156. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 5-bromo-4,7-dimethyl-1H-benzo[d][1,2,3]triazole (3v).

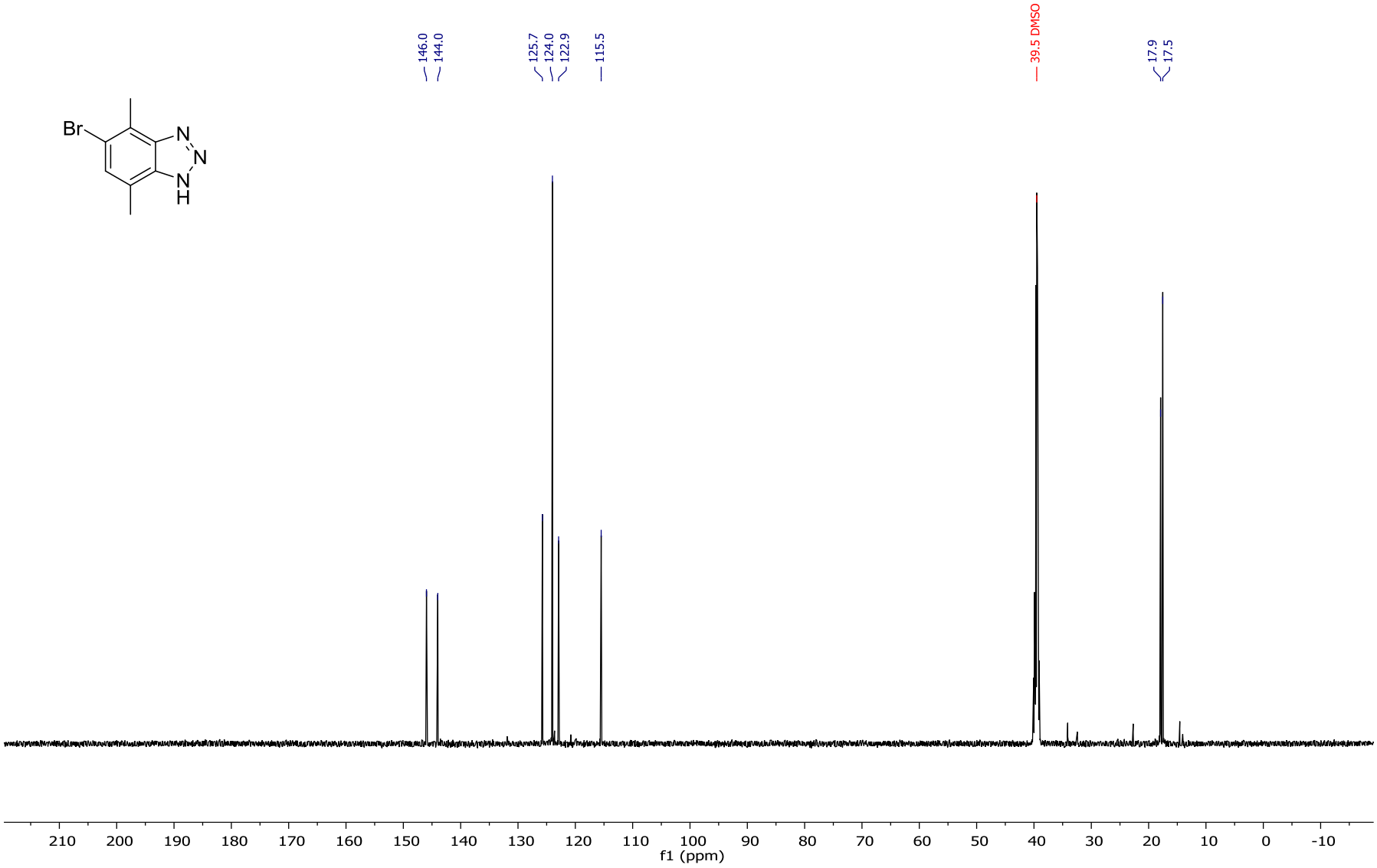


Figure S157. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 5-bromo-4,7-dimethyl-1H-benzo[d][1,2,3]triazole (3v).

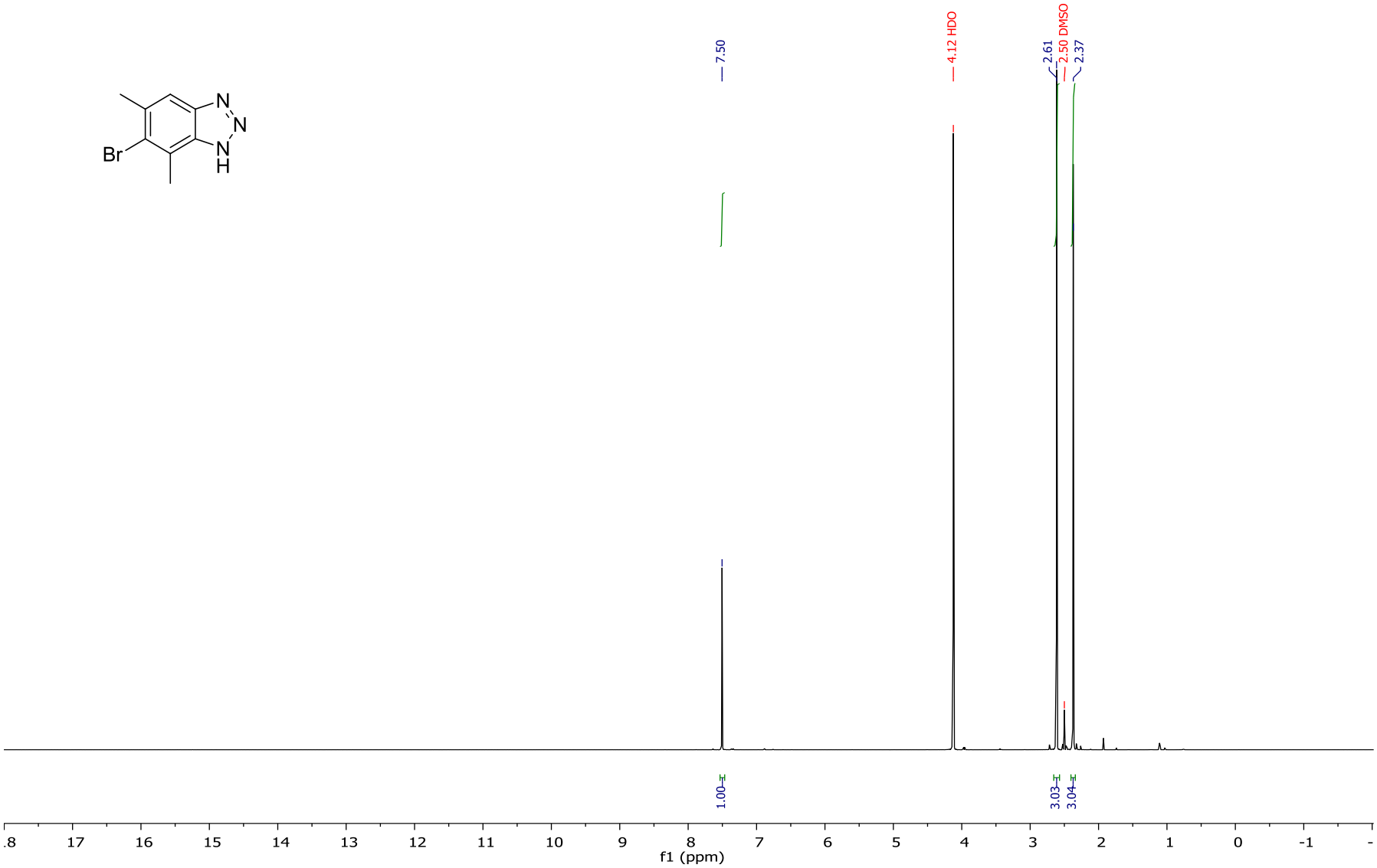


Figure S158. ^{1}H NMR (600 MHz, DMSO-d_6 + NaOH/D_2O) of 6-bromo-5,7-dimethyl-1H-benzo[d][1,2,3]triazole (3w).

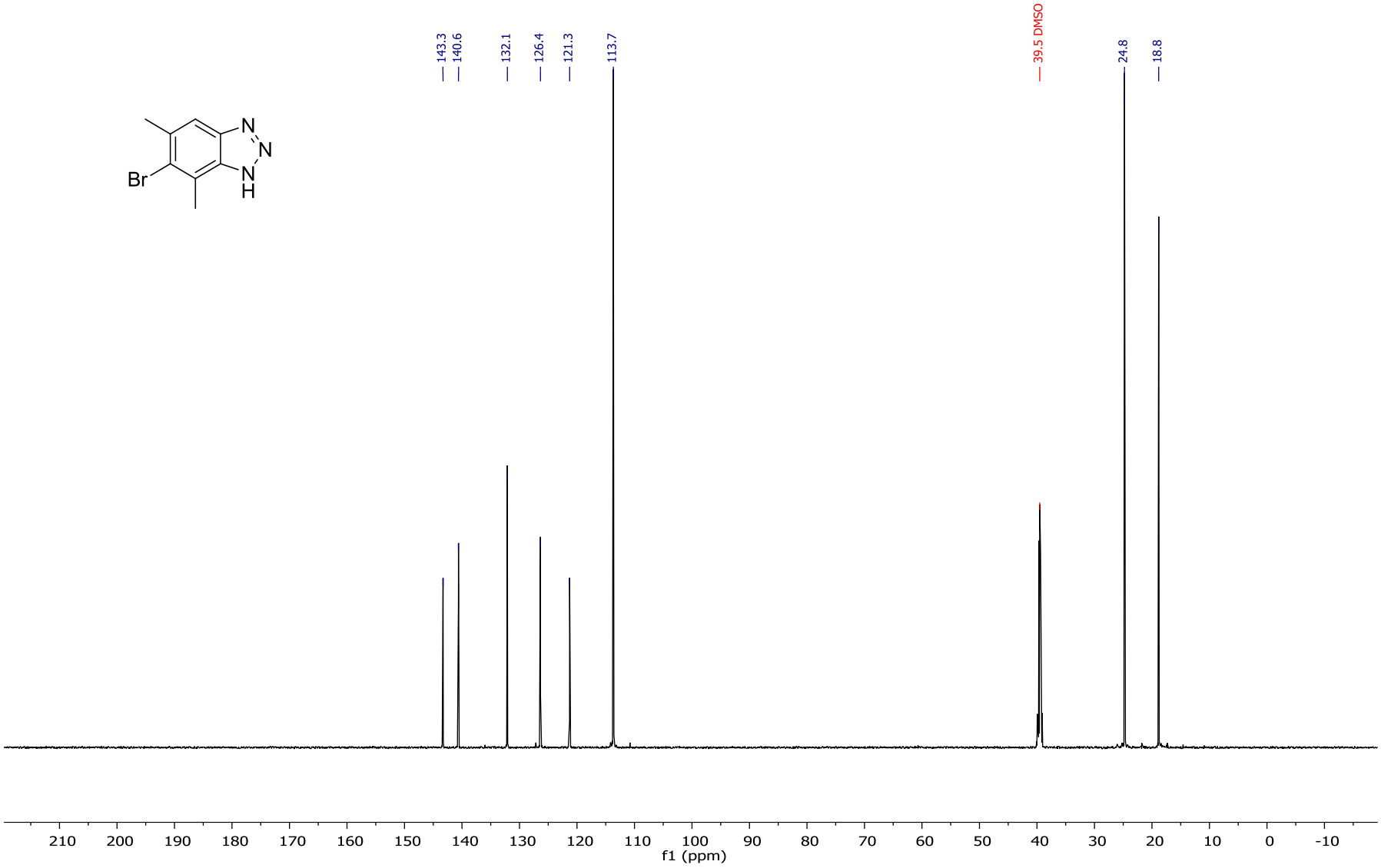


Figure S159. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d_6 + NaOH/D_2O) of 6-bromo-5,7-dimethyl-1H-benzo[d][1,2,3]triazole (3w).

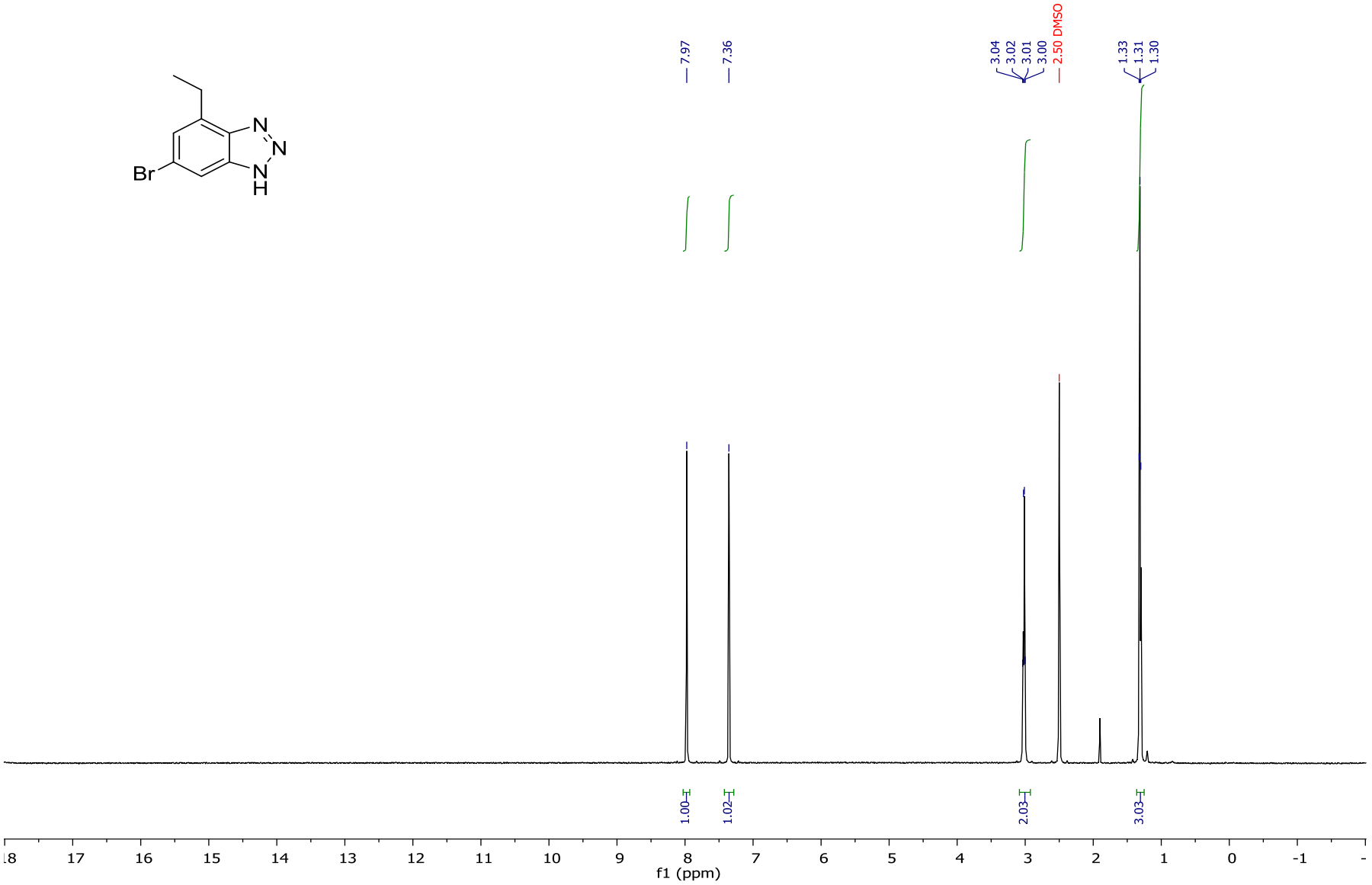


Figure S160. ^{1}H NMR (600 MHz, DMSO-d6) of 6-bromo-4-ethyl-1H-benzo[d][1,2,3]triazole (3x).

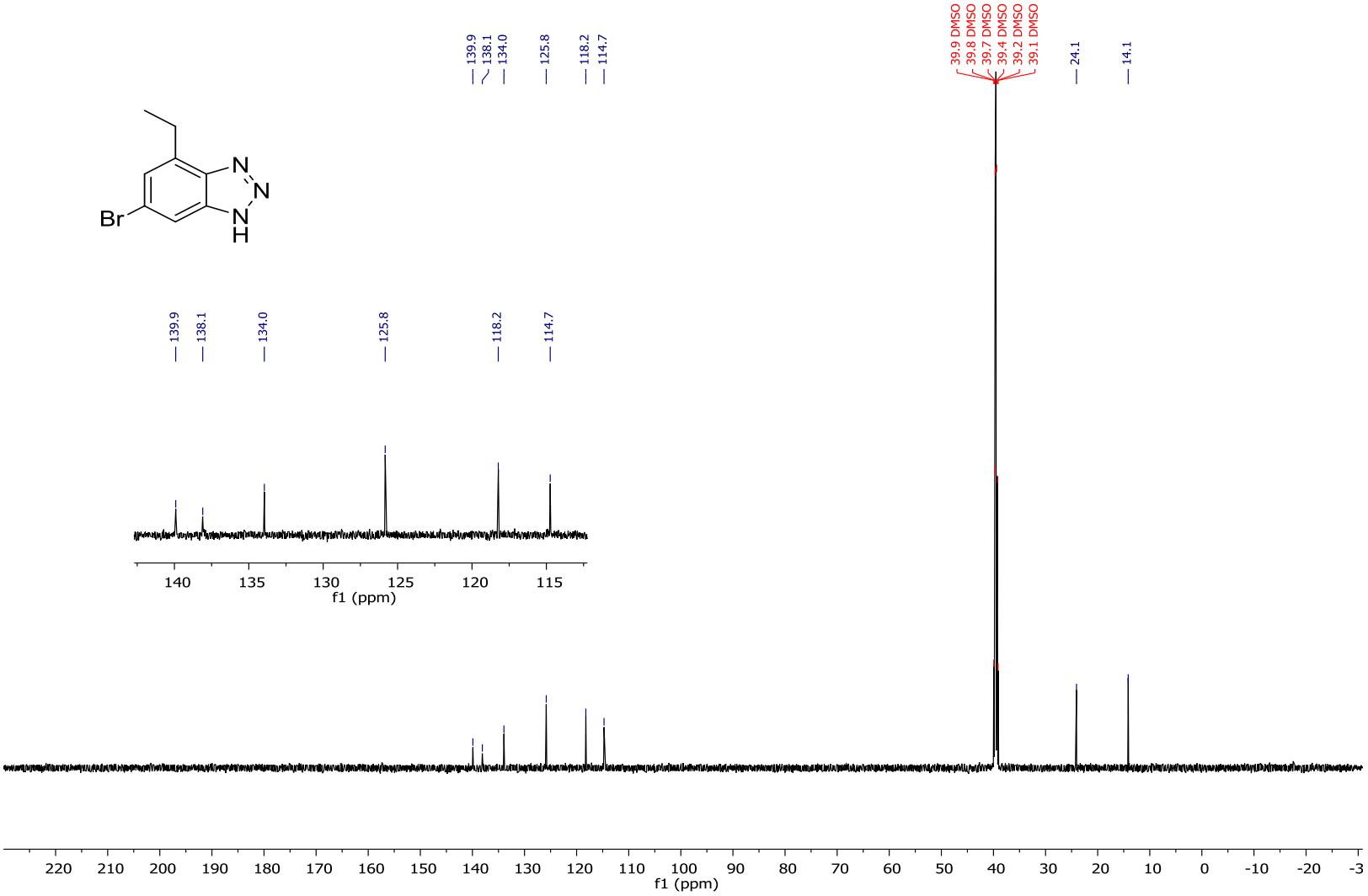


Figure S161. $^{13}C\{^{1}H\}$ NMR (151 MHz, DMSO-d6) of 6-bromo-4-ethyl-1H-benzo[d][1,2,3]triazole (3x).

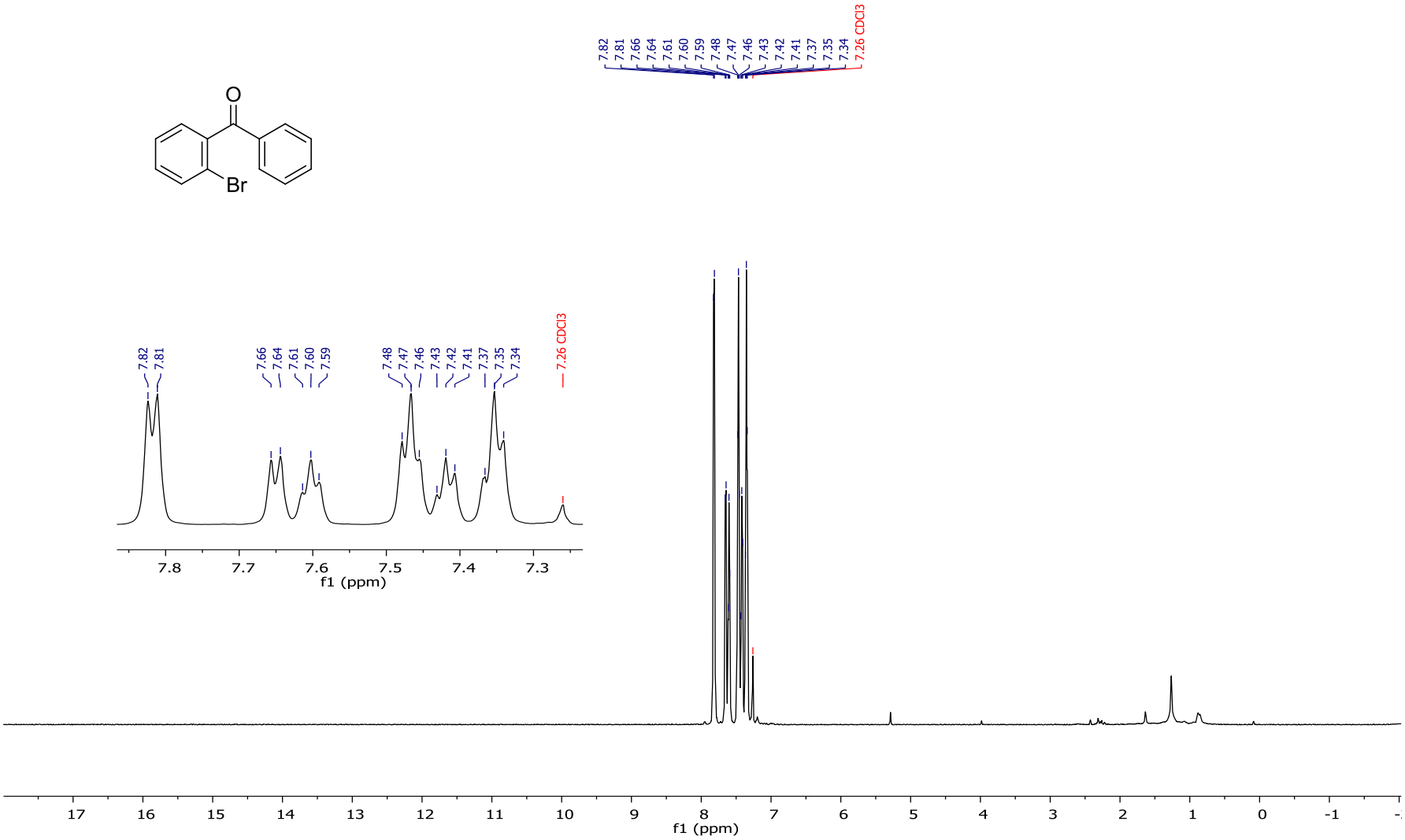


Figure S162. ^{1}H NMR (600 MHz, Chloroform-*d*) of (2-bromophenyl)(phenyl)methanone.

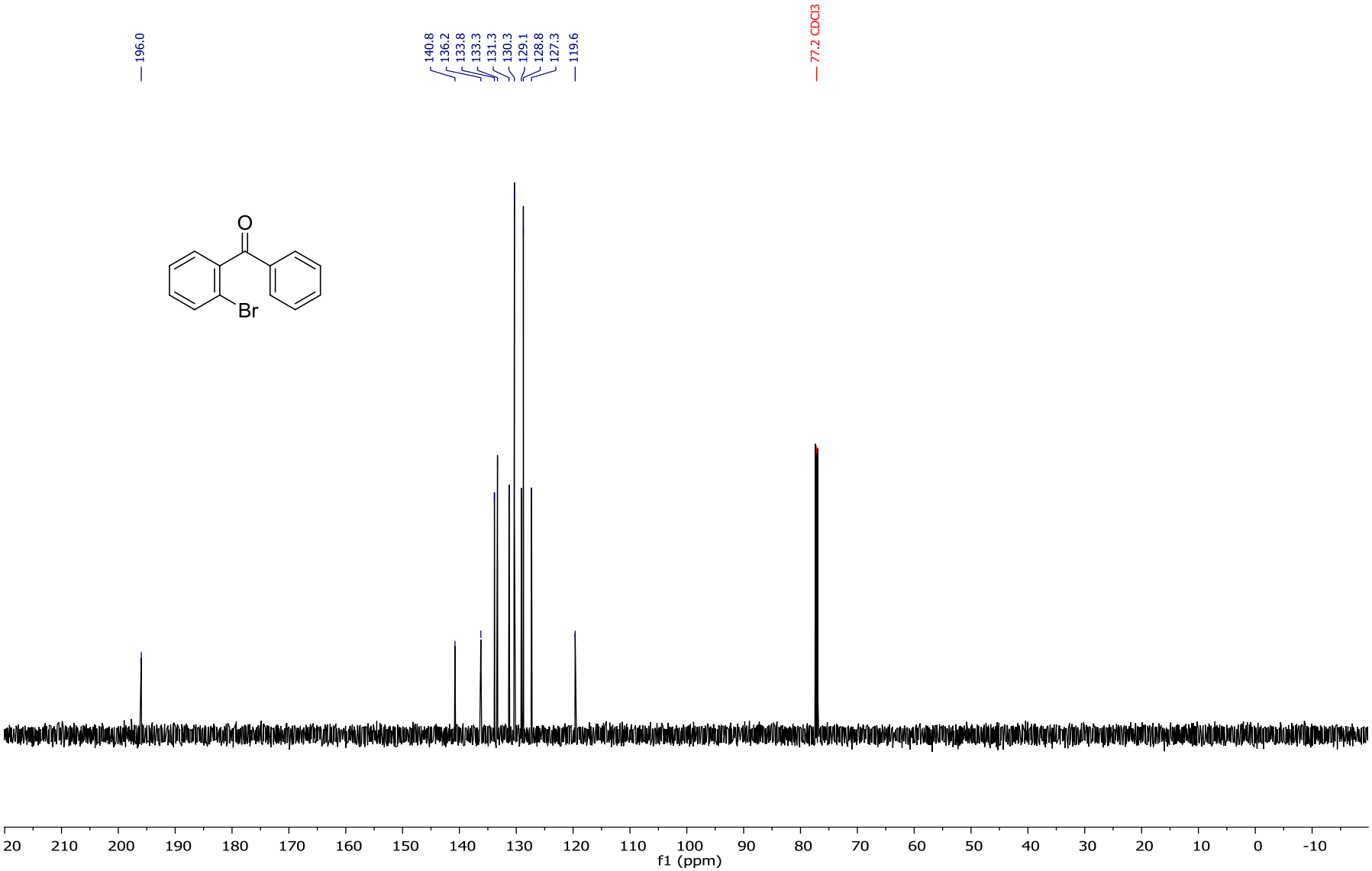


Figure S163. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of (2-bromophenyl)(phenyl)methanone.

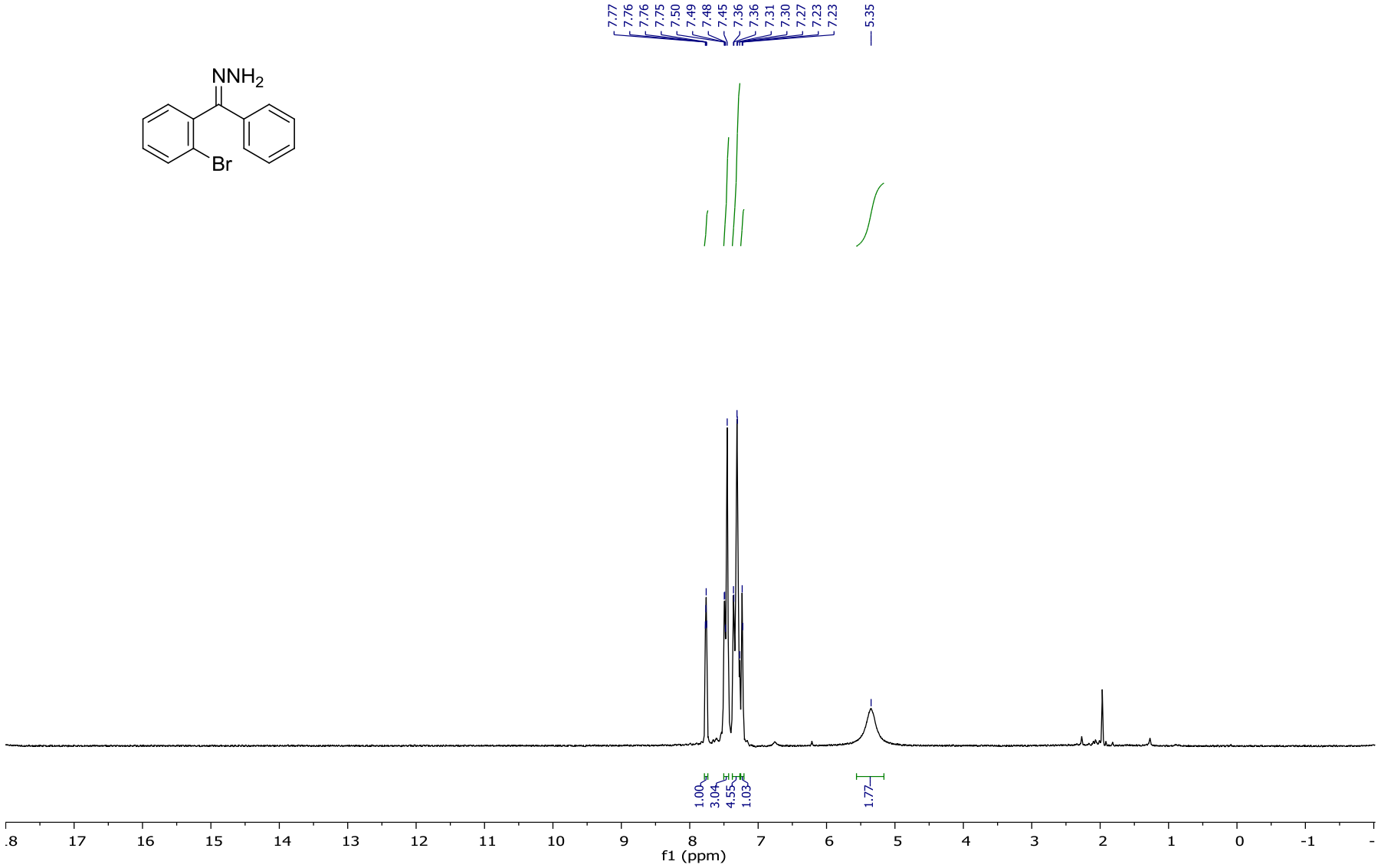


Figure S164. ^{1}H NMR (600 MHz, Chloroform-*d*) of ((2-bromophenyl)(phenyl)methylene)hydrazine.

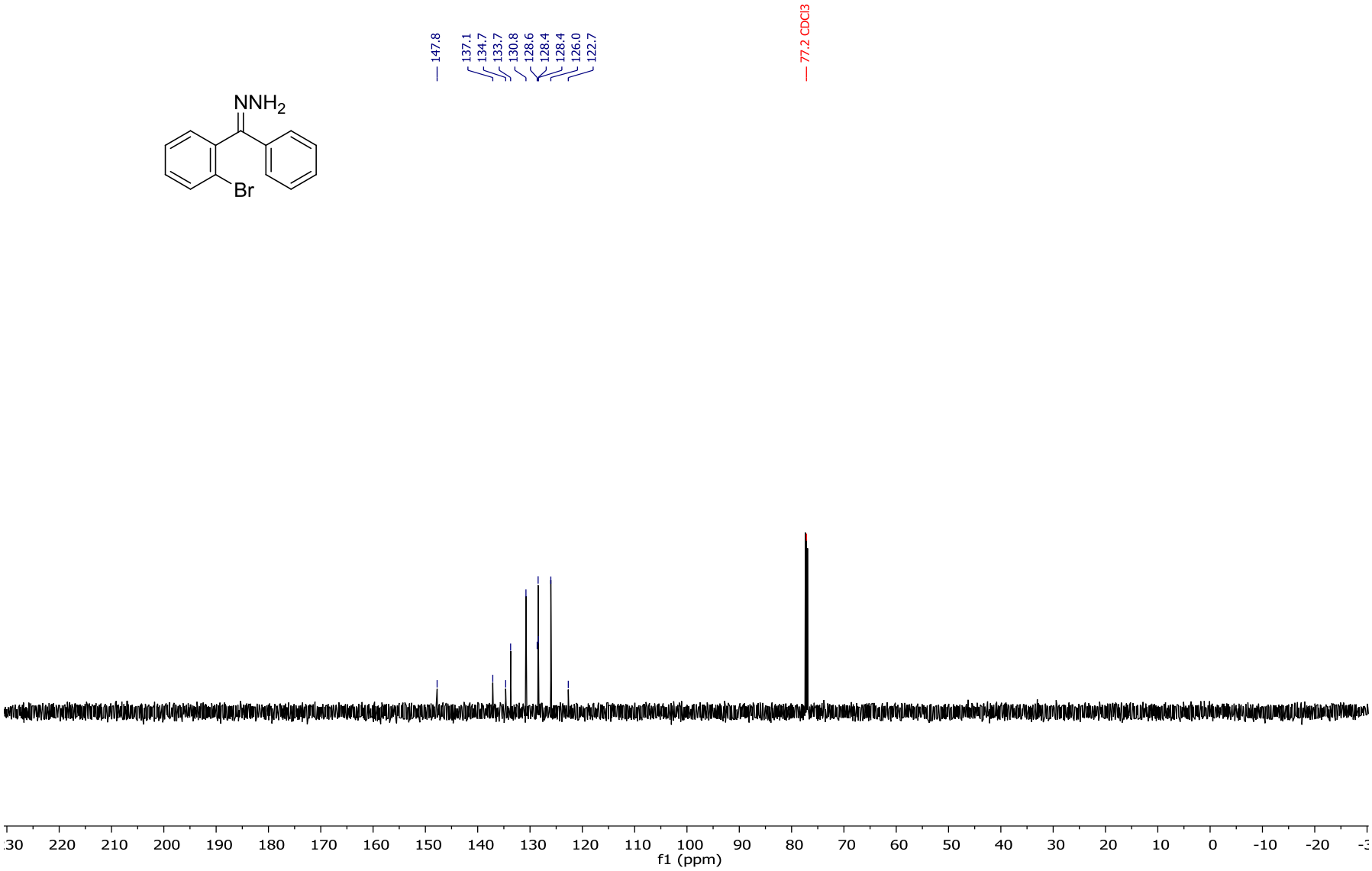


Figure S165. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of ((2-bromophenyl)(phenyl)methylene)hydrazine.

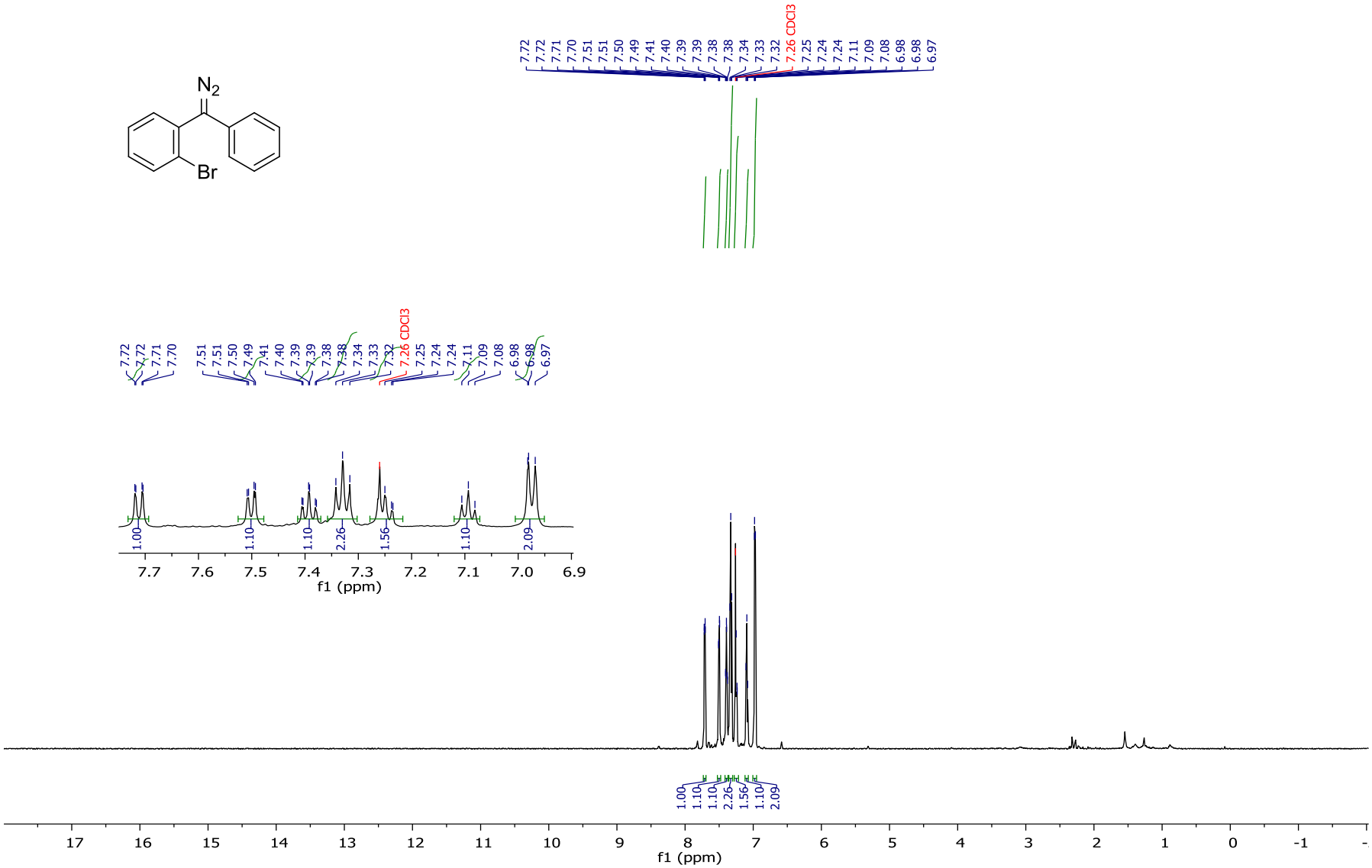


Figure S166. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-bromo-2-(diazo(phenyl)methyl)benzene (4).

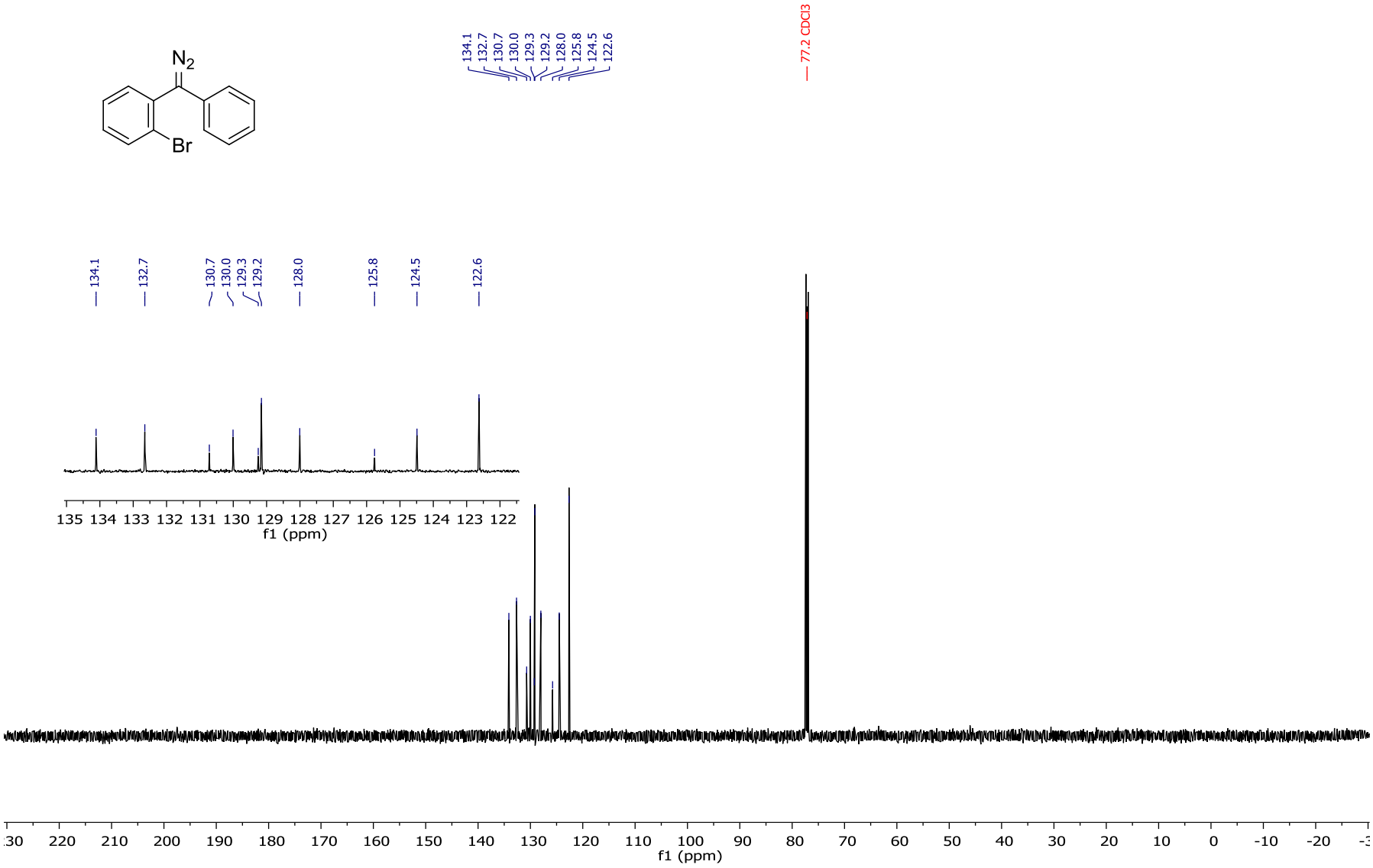


Figure S167. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-bromo-2-(diazo(phenyl)methyl)benzene (4).

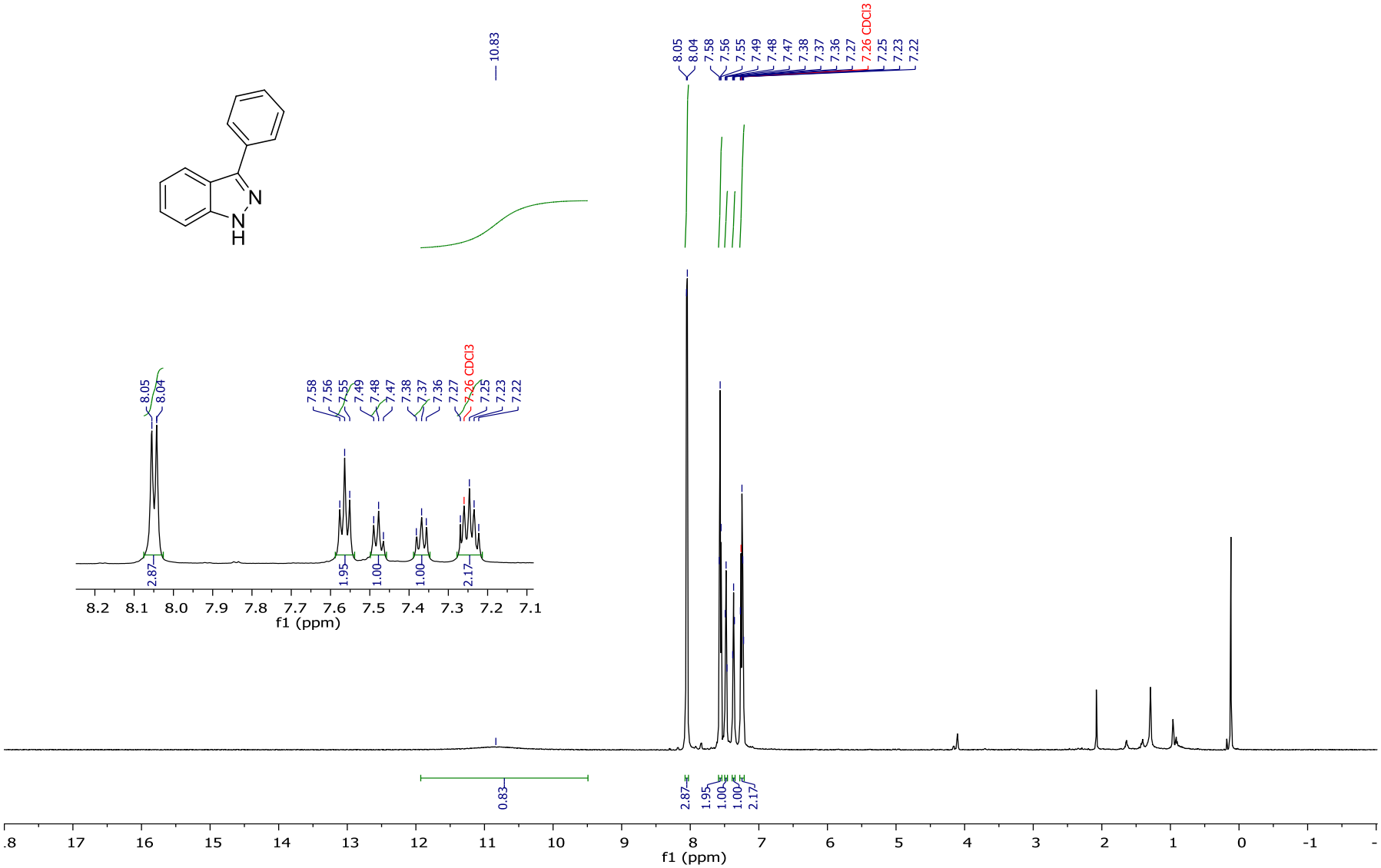


Figure S168. ^{1}H NMR (600 MHz, Chloroform-*d*) of 3-phenyl-1H-indazole (5).

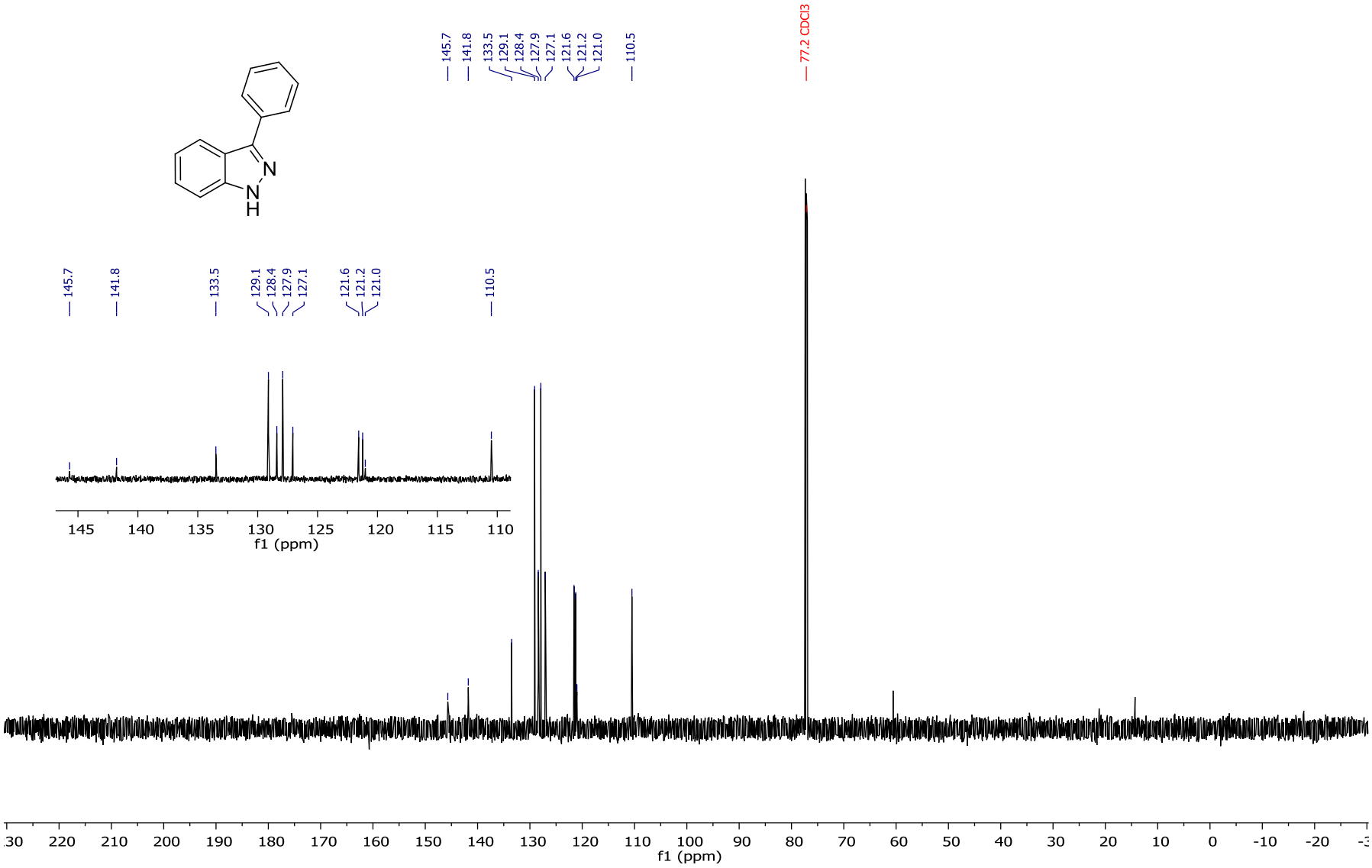


Figure S169. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 3-phenyl-1H-indazole (5).

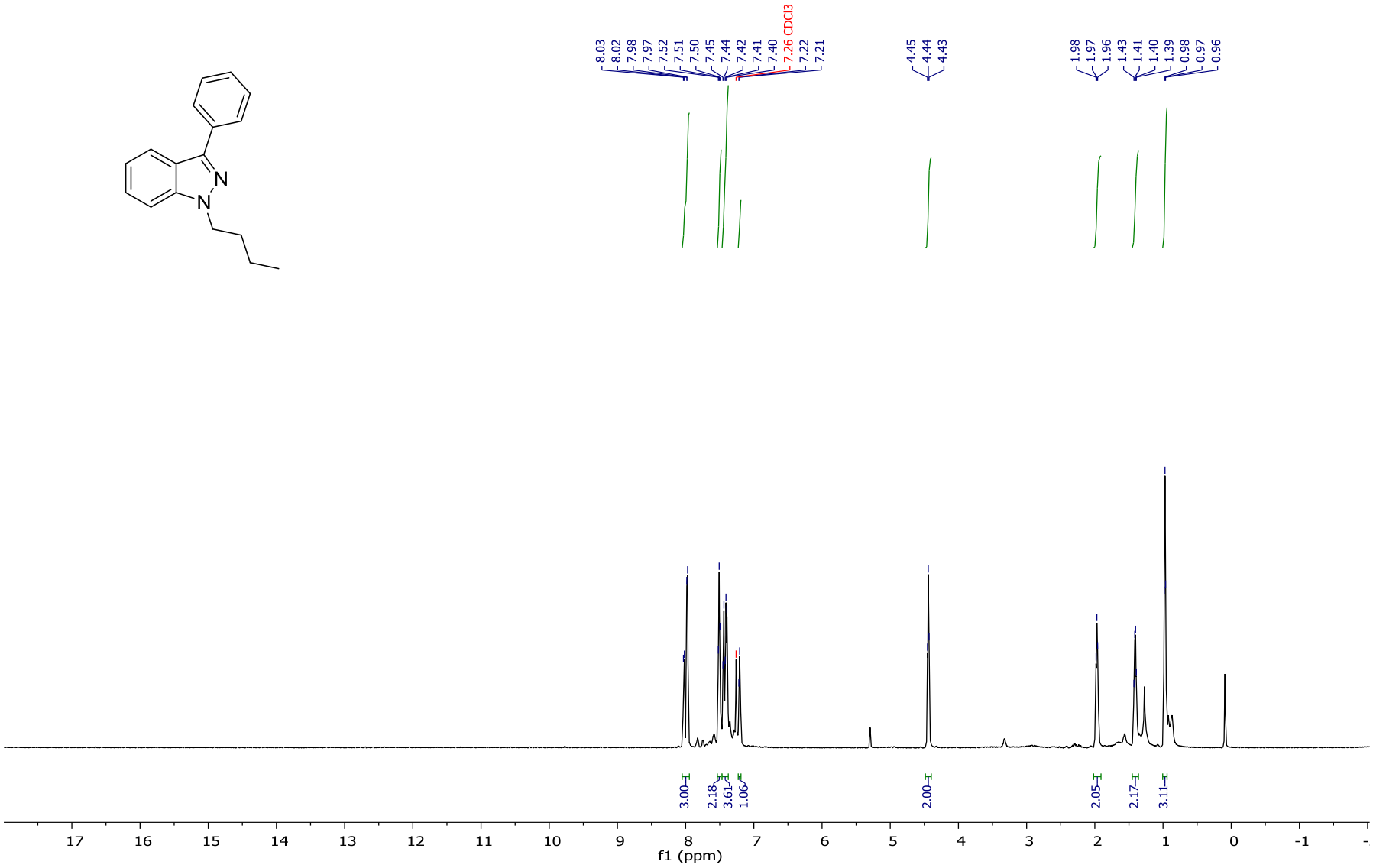


Figure S170. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-butyl-3-phenyl-1H-indazole (5a).

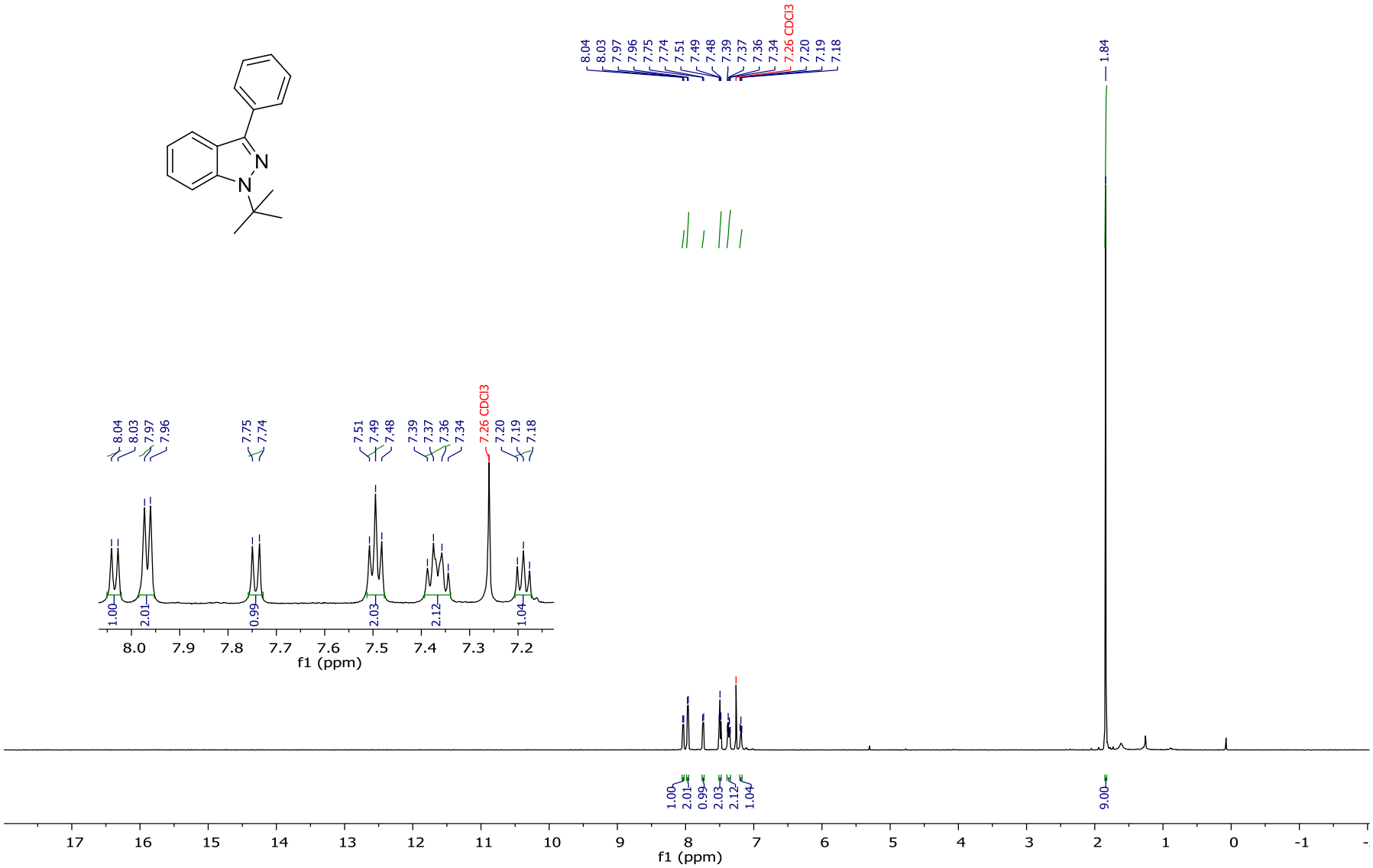


Figure S171. ^{1}H NMR (600 MHz, Chloroform-*d*) of 1-tert-butyl-3-phenyl-1H-indazole (5a).

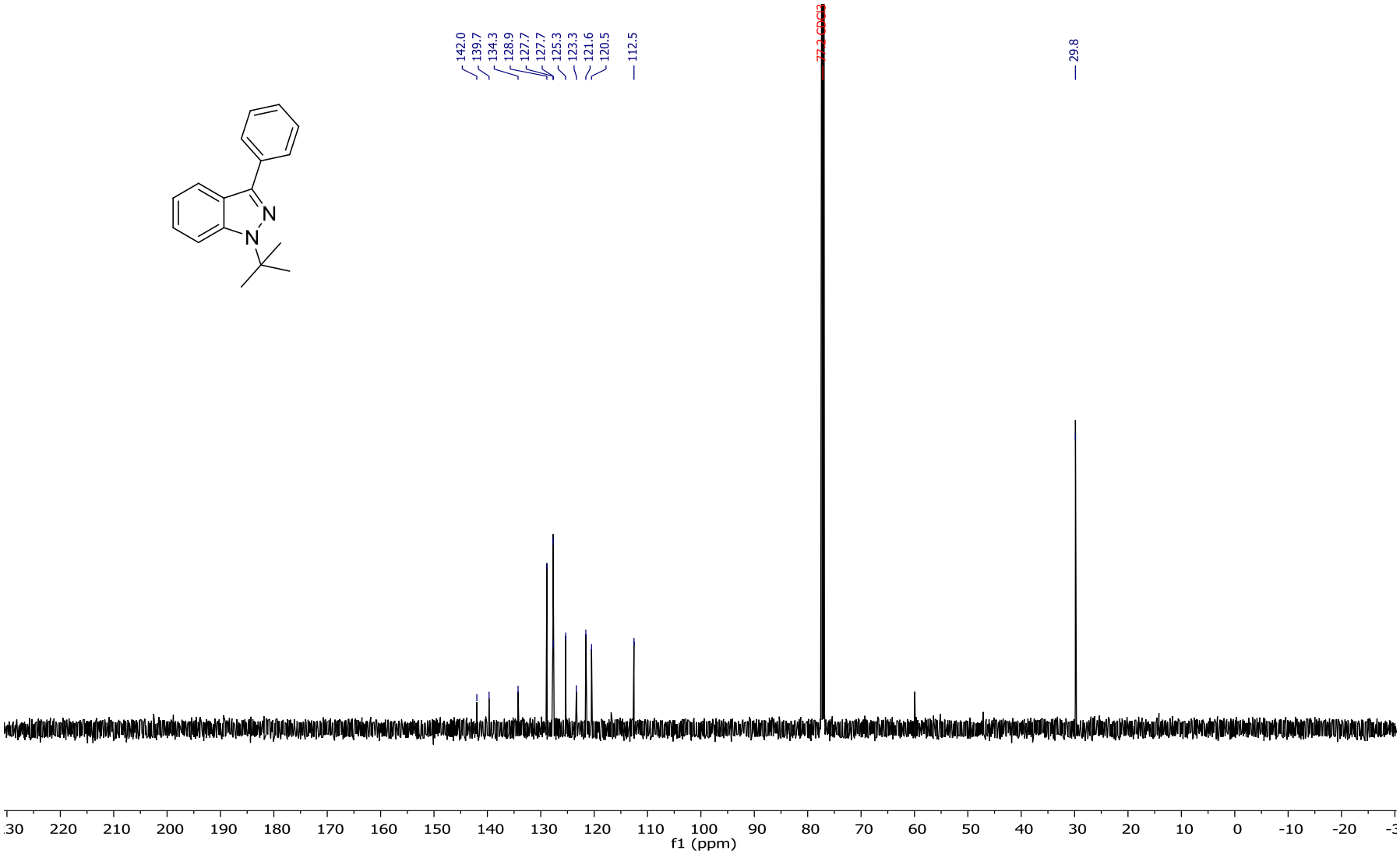


Figure S172. $^{13}C\{^{1}H\}$ NMR (151 MHz, Chloroform-d) of 1-tert-butyl-3-phenyl-1H-indazole (5b).

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