Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 121–123

Sodium dithionite in the regioselective reduction of the *ortho*-positioned nitro group in 1-R-2,4-dinitrobenzenes

Michael D. Tsymliakov, Anita I. Maksutova, Elena N. Bezsonova, Daria V. Zakharova, Yuri K. Grishin, Victor A. Tafeenko, Sergey E. Sosonyuk and Natalia A. Lozinskaya

Table of content

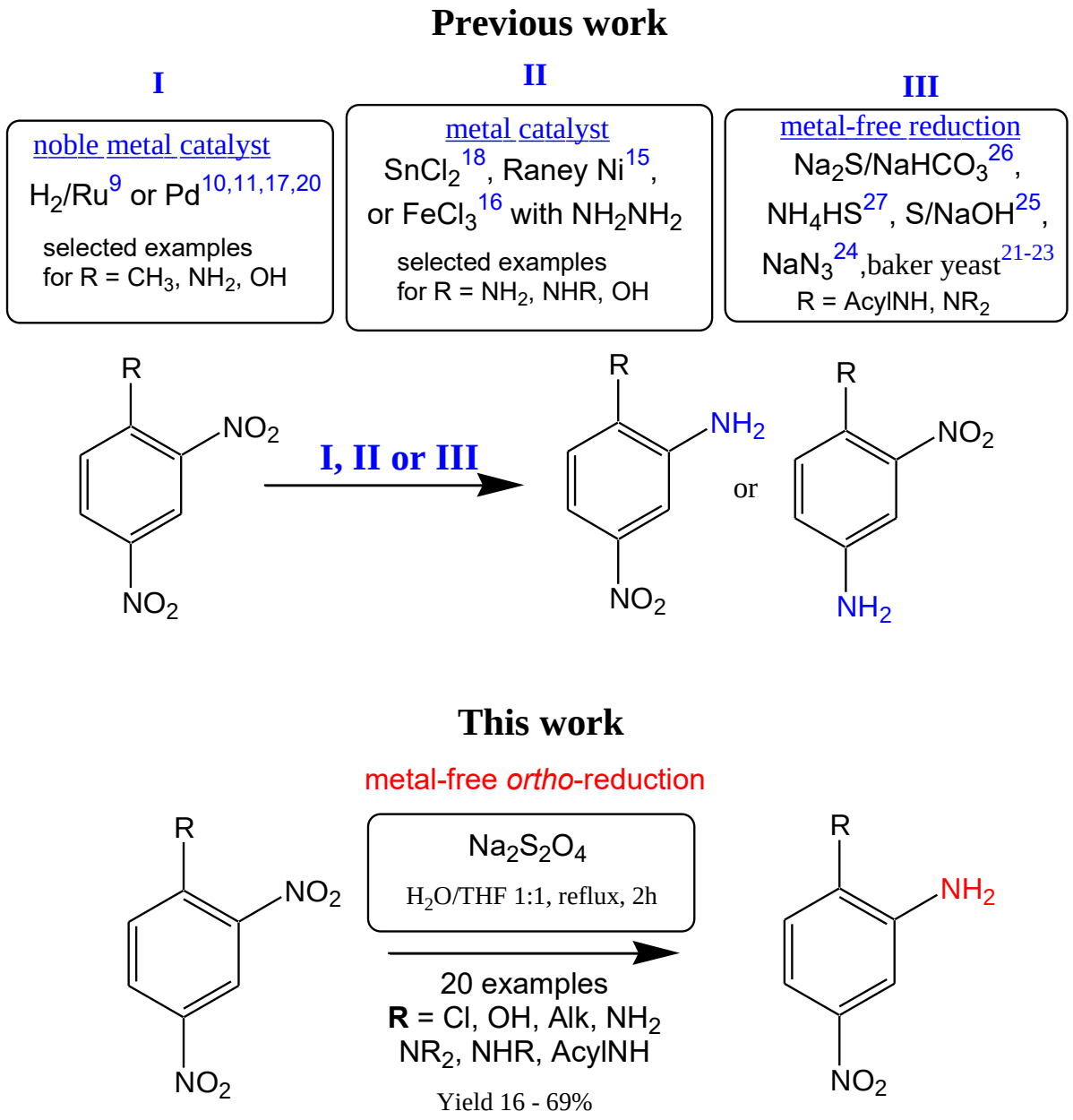


Figure S1

1. General Methods and Materials

All reaction temperatures correspond to internal temperatures unless otherwise noted. Solvents for extraction and chromatography were purified by standard procedures prior to use. Reactions were monitored by thin layer chromatography (TLC) carried out on Merck TLC silica gel plates (60 F254), using UV light for visualization. Column chromatography purification was performed using Merck silica gel 60 (particle size 0.040-0.060 mm). Elemental analysis of synthesized compounds was performed on CNH analyzer 'Carlo-Erba' ER-20. ^{1}H and ^{13}C NMR spectra were recorded on spectrometer Agilent 400-MR (400.0 MHz for ^{1}H; 100.6 MHz for ^{13}C) at room temperature; chemical shifts were measured with reference to the protonated residuals of solvents ($CDCl_3$, δ_H=7.24 ppm, δ_C=77.0 ppm; DMSO-d_6, δ_H=2.50 ppm, δ_C=39.50 ppm). Chemical shifts (δ) are given in ppm, spin-spin coupling constants (J) are reported in Hz; multiplicities are indicated by s (singlet), d (doublet), t (triplet), q(quadruplet), dd (doublet of doublets), m (multiplet). The melting points were measured in open capillaries and are presented without

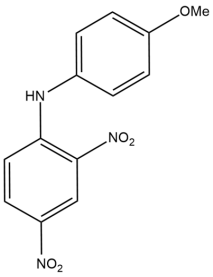
correction. High resolution mass spectra (HRMS) were measured on a Thermo Scientific LTQ Orbitrap instrument using nanoelectrospray ionization (nano-ESI). Various dinitrobenzenes used to obtain compounds **2n**, **3a-3c** were purchased from Merck and used without purification. 5,7-Dinitroisatin was synthesized according to the known procedure [S1].

2. Substituted 2,4-dinitroanilines 1a-m, 4a (general procedure)

Compounds were synthesized according to published procedure [S2] with modification:

To a solution of 1-chloro-2,4-dinitrobenzene (DNCB, 3.000 g, 14.82 mmol) in EtOH (30 mL) was added triethylamine (1.80 g, 2.47 mL, 17.78 mmol) and the corresponding primary or secondary amine (17.78 mmol), and the mixture was then stirred on reflux for the specified time. The reaction mixture was cooled, and the colored precipitate was filtered on a sintered glass filter. The precipitate was washed with EtOH (15 mL), cooled to 0 °C and washed with water (2×15 mL). Drying the precipitate in air for 24 h gave the desired products.

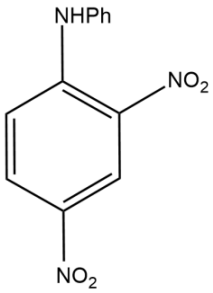
***N*-(4-Methoxyphenyl)-2,4-dinitroaniline** [S3] **1a** was obtained from *p*-anisidine (3.00 g, 25 mmol), reflux for 2 h, bright orange solid, yield 3.56 g (62%),



M.p. 142°C (from ethanol), M.p. (lit.) [S4] 141°C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (s, 3H), 7.01-7.05 (m, 3H), 7.21-7.26 (m, 2H), 8.15 (dd, *J*=2.7, 9.6, 1H), 9.19 (d, *J*=2.7, 1H), 9.89 (s, 1H).

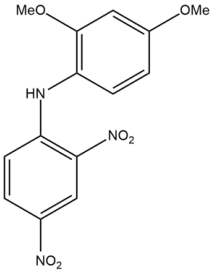
2,4-Dinitro-*N*-phenyl-aniline [S5] **1b** was obtained from aniline (1.10 ml, 12.5 mmol), reflux for 24 h, bright orange solid, yield 1.60 g (81%),



M.p. 156.4°C (from ethanol), M.p. (lit.)[S6] 158-159°C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, *J* = 9.5, 1H), 7.31-7.33 (m, 2H), 7.38-7.41 (m, 1H), 7.49-7.54 (m, 2H), 8.17 (dd, *J* = 2.7, 9.5, 1H), 9.17 (d, *J* = 2.7, 1H), 9.99 (br.s, 1H)

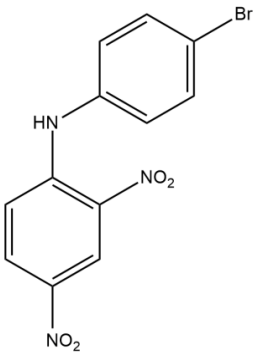
***N*-(2,4-Dimethoxyphenyl)-2,4-dinitroaniline 1c** was obtained from 2,4-dimethoxyaniline (1.91 g, 12.5 mmol), reflux for 2 h, brown solid, yield 2.00 g (63%),



M.p. 208.9°C (from ethanol), M.p. (lit.)[S7] 209 - 210°C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3H), 3.87 (s, 3H), 6.57 (dd, *J* = 2.6, 8.6, 1H), 6.60 (d, *J* = 2.6, 1H), 6.93 (d, *J* = 9.6, 1H), 7.21 (d, *J* = 8.6, 1H), 8.13 (dd, *J* = 2.7, 9.6, 1H), 9.18 (d, *J* = 2.6, 1H), 9.1 (br.s, 1H)

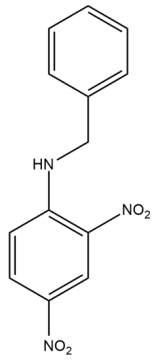
***N*-(4-Bromophenyl)-2,4-dinitroaniline 1d** was obtained from *p*-bromoaniline (2.15 g, 12.5 mmol), reflux for 24 h, dark orange solid, yield 2.11 g (63%)



M.p. 151.7-155.9°C (from ethanol), M.p. (lit.)[S8] 152-153°C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 9.5, 1H), 7.21 (d, *J* = 8.6, 2H), 7.63 (d, *J* = 8.6, 2H), 8.19 (dd, *J* = 2.6, 9.5, 1H), 9.17 (d, *J* = 2.6, 1H), 9.89 (br.s, 1H)

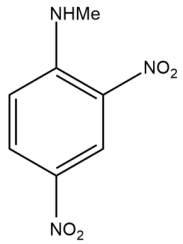
***N*-Benzyl-2,4-dinitroaniline**[S9] **1e** was obtained from $BnNH_2$ (2.59 ml, 23.7 mmol), reflux for 5 h, bright yellow solid, yield 4.67 g (87%),



M.p. 223-229°C (from ethanol), M.p. (lit.)[S10] 146°C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.66 (d, *J*=6.1, 2H), 6.92 (d, *J*=9.5, 1H), 7.34-7.44 (m, 5H), 8.24 (dd, *J*=2.7, 9.5, 1H), 8.93 (br. s, 1H), 9.17 (d, *J*=2.7, 1H)

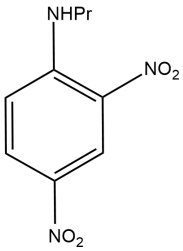
***N*-Methyl-2,4-dinitroaniline**[S9] **1f** was obtained from $MeNH_2$*HCl (5.00 g, 75 mmol), reflux for 2 h, bright yellow solid, yield 9.52 g (98%),



M.p. 175°C (from ethanol), M.p. (lit.)[S9] 171°C;

^{1}H NMR (400 MHz, DMSO-d_6): δ 3.04 (d, *J*=5.0, 3H), 7.11 (d, *J*=9.6, 1H), 8.25 (dd, *J*=2.7, 9.6, 1H), 8.81 (d, *J*=2.7, 1H), 8.9 (br.d, *J*=5.0, 1H).

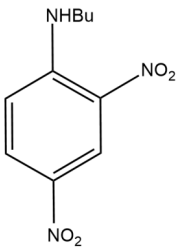
2,4-Dinitro-*N*-*n*-propylaniline[S3] **1g** was obtained from *n*-propylamine (1 ml, 12.5 mmol), reflux for 2 h, yellow solid, yield 2.13 g (96%),



M.p. 97°C (from ethanol), M.p. (lit.)[S11] 98-100°C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (t, *J*=7.4, 3H), 1.78-1.87 (m, 2H), 3.37-3.42 (m, 2H), 6.93 (d, *J*=9.5, 1H), 8.26 (dd, *J*=2.6, 9.5, 1H), 8.58 (br.s, 1H), 9.12 (d, *J*=2.6, 1H)

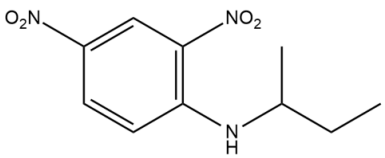
***N*-Butyl-2,4-dinitroaniline**[S9] **1h** was obtained from *n*-butylamine (1.25 ml, 12.5 mmol), reflux for 2 h, yellow solid, yield 2.26 g (96%).



M.p. 87.5-91.6°C (from ethanol), M.p. (lit.)[S9] 89-90°C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (t, *J* = 7.3, 3H), 1.46-1.55 (m, 2H), 1.74-1.81 (m, 2H), 3.40-3.45 (m, 2H), 6.93 (d, *J* = 9.5, 1H), 8.26 (dd, *J* = 2.4, 9.5, 1H), 8.56 (br.s, 1H), 9.12 (d, *J* = 2.7, 1H)

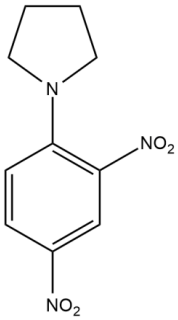
***N*-*sec*-Butyl-2,4-dinitroaniline 1i** was obtained from *sec*-butylamine (0.45 g, 6.2 mmol), reflux for 2 h, yellow solid, yield 0.60 g (51%),



M.p. 72.4°C (from ethanol), M.p. (lit.) 54 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (t, *J* = 7.5, 3H), 1.35 (d, *J* = 6.4, 3H), 1.68-1.78 (m, 2H), 3.71-3.77 (m, 1H), 6.93 (d, *J* = 9.6, 1H), 8.24 (dd, *J* = 2.6, 9.6, 1H), 8.54 (br.s, 1H), 9.13 (d, *J* = 2.6, 1H)

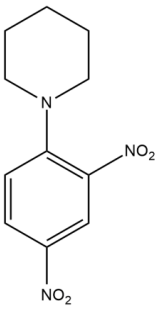
***N*-(2,4-Dinitrophenyl)pyrrolidine**[S9] **1j** was obtained from pyrrolidine (1.26 g, 17.78 mmol), reflux for 5 h, bright yellow solid, yield 3.42 g (98%),



M.p. 105.1°C (from ethanol), M.p. (lit.)[S9] 66°C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05-2.08 (m, 4H), 3.33-3.36 (m, 4H), 6.90 (d, *J*=9.5, 1H), 8.18 (dd, *J*=2.7, 9.5, 1H), 8.60 (d, *J*=2.7, 1H)

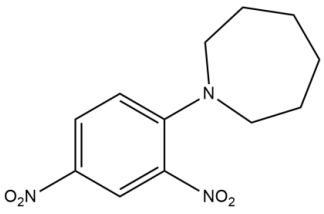
***N*-(2,4-Dinitrophenyl)piperidine**[S9] **1k** was obtained from piperidine (1.50 g, 17.62 mmol), reflux for 5 h, orange solid, yield 4.15 g (94%),



M.p. 91-92.5°C (from ethanol), M.p. (lit.)[S9] 91-92.5°C;

^{1}H NMR (400 MHz, $CDCl_3$): 1.67-1.78 (m, 6H), 3.23-3.29 (m, 4H), 7.09 (d, *J*=9.4, 1H), 8.21 (dd, *J*=2.8, 9.4, 1H), 8.68 (d, *J*=2.8, 1H)

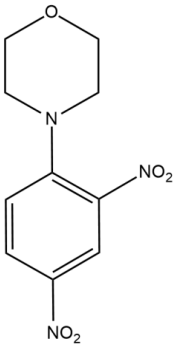
***N*-(2,4-Dinitrophenyl)azepane**[S12] **1l** was obtained from azepane **(**1.835 g, 18.5 mmol), reflux for 2.5 h, bright yellow solid, yield 3.460 g (88%),



M.p. 102°C (from ethanol), M.p. (lit.)[S12] 100-102°C

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.6-1.62 (m, 4H), 1.82-1.90 (m, 4H), 3.36-3.39 (m, 4H), 7.07 (d, *J* = 9.6, 1H), 8.17 (dd, *J* = 2.7, 9.6, 1H), 8.64 (d, *J* = 2.7, 1H).

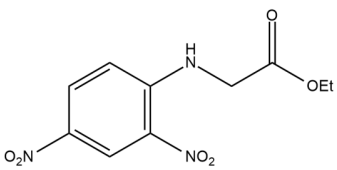
***N*-(2,4-Dinitrophenyl)morpholine**[S9] **1m** was obtained from morpholine (1.55 g, 17.78 mmol), reflux for 5 h, dark yellow solid, yield 3.54 g (95%),



M.p. 118°C (from ethanol), M.p. (lit.)[S9] 117-118°C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.26-3.28 (m, 4H), 3.85-3.87 (m, 4H), 7.12 (d, *J*=9.3, 1H), 8.3 (dd, *J*=2.3, 9.3, 1H), 8.70 (d, *J*=2.3, 1H)

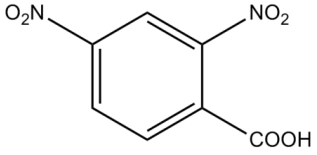
***N*-(2,4-Dinitrophenyl)glycine ethyl ester 4a** was obtained from glycine ethyl ester hydrochloride (4.136 g, 29.6 mmol), reflux for 5.5 h, light orange solid, yield 4.860 g (73%).



M.p. 142.9-143.4°C (from ethanol), M.p. (lit.)[S13] 142-144°C

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (t, *J* = 7.2, 3H), 4.19 (d, *J* = 5.1, 2H), 4.34 (q, *J* = 7.2, 2H), 6.79 (d, *J* = 9.4, 1H), 8.33 (dd, *J* = 2.7, 9.4, 1H), 8.98 (br.s, 1H), 9.19 (d, *J* = 2.7, 1H).

3. Synthesis of 2,4-dinitrobenzoic acid[S14]



To a suspension of finely ground 2,4-dinitrotoluene (2.345 g, 12.89 mmol) in conc. H_2SO_4 (*d* = 1.84, 25 ml), $K_2Cr_2O_7$ (4.548 g, 15.47 mmol) was added portionwise keeping the reaction temperature not higher than 60 °C. After the termination of self-heating, the mixture was stirred at room temperature for more 2 h. Crushed ice (25 g) was added. After the ice completely melted, the mixture was cooled to 0 °C, the precipitated product was filtered and washed with a little ice water until the green color of the washings disappeared. Beige solid, yield 1.480 g (54%).

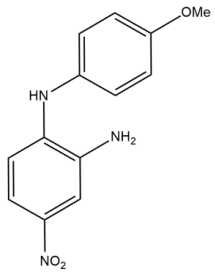
M.p. 169°C (from ethanol), M.p. (lit.) [S14] 181-182°C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J*=8.5, 1H), 8.57 (dd, *J*=8.5, 2.2, 1H), 8.77 (d, *J*=2.2, 1H)

4. Reduction of substituted 2,4-dinitroanilines 1a-m, 4a (general procedure)

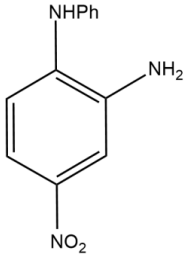
Dinitro compound (11.00 mmol) was added to a 1:1 THF/H_2O mixture (60 mL; THF was preliminarily distilled from alkali), then this solution or suspension was heated to reflux under intensive stirring. Sodium dithionite powder (9.560 g, 54.95 mmol) was added in small portions within 1 h, the mixture was refluxed for 2 h and cooled to room temperature. The reaction mixture finally appeared as two layers due to the salting effect of Na_2SO_4 formed from $Na_2S_2O_4$. The organic part was separated, the water layer was extracted with THF (1-2 times for aromatic derivatives, 4-5 times for others). The organic extracts were combined, dried over Na_2SO_4 and evaporated under reduced pressure followed by flash chromatography on silica gel (eluent EtOAc-light petroleum, 2:1).

***N*^{1}-(4-Methoxyphenyl)-4-nitro-1,2-benzenediamine**[S15] **2a** was obtained from *N*-(4-methoxyphenyl)-2,4-dinitroaniline **1a** (1.800 g, 6.26 mmol), bright orange solid, yield 0.824 g (52%).



M.p. 145.3°C (ethanol), M.p. (lit.)[S16] 144°C;

^{1}H NMR (400 MHz, DMSO-d_6): δ 3.74 (s, 3H), 5.36 (br.s, 2H), 6.75 (d, *J* = 8.9, 1H), 6.95 (d, *J* = 8.9, 2H), 7.12 (d, *J* = 8.9, 2H), 7.42 (dd, *J* = 2.6, 8.9, 1H), 7.51 (d, *J* = 2.6, 1H), 7.66 (br.s, 1H)

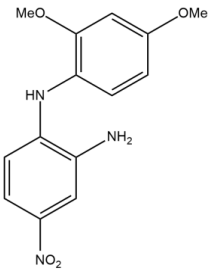


4-Nitro-*N*^{1}-phenyl-1,2-benzenediamine[S17] **2b** was obtained from *N*-phenyl-2,4-dinitroaniline **1b** (0.5 g, 1.95 mmol), light vinaceous solid, yield 0.152 g (35%),

M.p. 121.5°C (ethyl acetate/petroleum ether), M.p. (lit.)[S18] 130-131°C;

^{1}H NMR (400 MHz, DMSO-d_6): δ 4.33 (br.s, 2H), 6.92 (t, *J* = 7.3, 1H), 7.01 (d, *J* = 8.9, 1H), 7.02-7.07 (m, 2H), 7.18 (br.s, 1H), 7.20-7.28 (m, 2H), 7.44 (dd, *J* = 2.6, 8.9, 1H), 7.54 (d, *J* = 2.6, 1H).

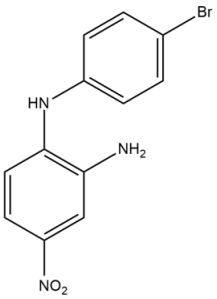
***N*^{1}-(2,4-Dimethoxyphenyl)-4-nitrobenzene-1,2-diamine 2c** was obtained from *N*-(2,4-dimethoxyphenyl)-2,4-dinitroaniline **1c** (0.571 g, 1.807 mmol), dark vinaceous solid, yield 0.153 g (30%),



M.p. 132°C (ethyl acetate/petroleum ether), M.p. (lit.)[S19] 131-132°C;

^{1}H NMR (400 MHz, DMSO-d_6): δ 3.74 (s, 3H), 3.77 (s, 3H), 5.36 (br.s, 2H), 6.30 (d, *J* = 8.9, 1H), 6.55 (dd, *J* = 2.6, 8.6, 1H), 6.69 (d, *J* = 2.6, 1H), 7.11 (d, *J* = 8.6, 1H), 7.16 (br.s, 1H), 7.38 (dd, *J* = 2.6, 8.9, 1H), 7.47 (d, *J* = 2.6, 1H). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 55.37, 55.56, 99.64, 104.95, 108.07, 109.80, 114.81, 121.34, 126.70, 135.44, 138.01, 140.80, 154.46, 157.96.

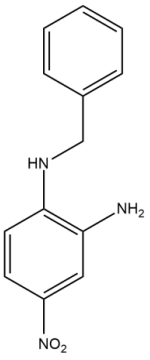
***N*^{1}-(4-Bromophenyl)-4-nitrobenzene-1,2-diamine 2d** was obtained from *N*-(4-bromophenyl)-2,4-dinitroaniline **1d** (0.500 g, 1.49 mmol), dark vinaceous solid, yield 0.071 g (16%)



M.p. 159.6°C (ethyl acetate/petroleum ether), M.p. (lit.)[S20] 158-160°C;

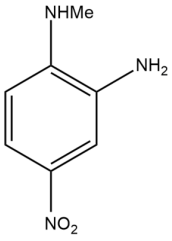
^{1}H NMR (400 MHz, DMSO-d_6): δ 5.45 (br.s, 2H), 7.05 (d, *J* = 8.8, 2H), 7.08 (d, *J* = 8.9, 1H), 7.41-7.46 (m, 3H), 7.57 (d, *J* = 2.7, 1H), 7.91 (s, 1H).

***N*^{1}-Benzyl-4-nitro-1,2-benzenediamine**[S21] **2e** was obtained from *N*-benzyl-2,4-dinitroaniline **1e** (1.6, 6 mmol), light vinaceous solid, yield 0.644 g (46%),



M.p. 146°C (ethyl acetate/petroleum ether), M.p. (lit.)[S18] 148°C;

^{1}H NMR (400 MHz, DMSO-d_6): δ 4.46 (d, *J* = 5.8, 2H), 5.23 (s, 2H), 6.38 (d, *J* = 9.5, 1H), 6.60 (br.t, *J* = 5.8, 1H), 7.21-7.26 (m, 1H), 7.32-7.33 (m, 4H), 7.40-7.43 (m, 2H). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 46.17, 107.47, 107.64, 115.60, 127.02, 127.16, 128.49, 134.76, 136.91, 138.85, 142.26.

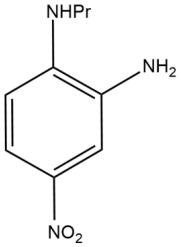


***N*^{1}-Methyl-4-nitro-1,2-benzenediamine**[S22] **2f** was obtained from *N*-methyl-2,4-dinitroaniline **1f** (0.648 g, 3.34 mmol), vinaceous solid, yield 0.148 g (27%),

M.p. 176.9-180.4°C (ethyl acetate/petroleum ether), M.p. (lit.)[S18] 178-180°C;

^{1}H NMR 400 MHz, DMSO-d_6): δ 2.82 (d, *J* = 4.4, 3H), 5.09 (br.s, 2H), 6.14 (br.d, *J*= 3.2, 1H), 6.40 (d, *J* = 8.8, 1H), 7.39 (d, *J* = 1.8, 1H), 7.54 (dd, *J* = 1.8, 8.8, 1H).

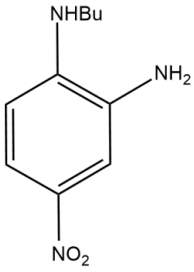
4-Nitro-*N*^{1}-*n*-propyl-1,2-benzenediamine[S23] **2g** was obtained from 2,4-dinitro-*N*-*n*-propylaniline **1g** (1.500 g, 6.76 mmol), dark red solid, yield 0.327 g (25%).



M.p. 105-106°C (ethanol), M.p. (lit.)[S24] 119-122 °C;

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 0.94 (t, *J* = 7.3, 3H), 1.56-1.65 (m, 2H), 3.10-3.15 (m, 2H), 5.16 (s, 2H), 5.90 (br.t, *J*=5.1, 1H), 6.44 (d, *J*=8.9, 1H), 7.39 (d, *J* = 2.4, 1H), 7.50 (dd, *J* = 2.4, 8.9, 1H). ^{13}C NMR (100.6 MHz, DMSO-d$_6$) δ: 11.58, 21.56, 44.68, 106.78, 107.19, 115.98, 134.39, 136.38, 142.66.

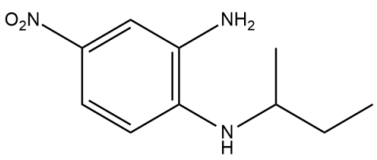
***N*^{1}-*n*-Butyl-4-nitro-1,2-benzenediamine**[S21] **2h** was obtained from *N*-*n*-butyl-2,4-dinitroaniline **1h** (1.500 g, 6.36 mmol), yellow solid, yield 0.38 g (29%),



M.p. 103-104°C (ethanol), M.p. (lit.)[S25] 108-109°C;

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 0.91 (t, *J*=7.3, 3H), 1.34-1.43 (m, 2H), 1.54-1.62 (m, 2H), 3.14-3.19 (m, 2H), 5.16 (br.s, 2H), 5.88 (br.t, *J*=5.1, 1H), 6.45 (d, *J*=8.9, 1H), 7.37 (d, *J*=2.7, 1H), 7.50 (dd, *J*=2.7, 8.9, 1H). ^{13}C NMR (100.6 MHz, DMSO-d$_6$) δ: 13.77, 19.82, 30.40, 42.60, 106.76, 107.13, 115.96, 134.40, 136.38, 142.65.

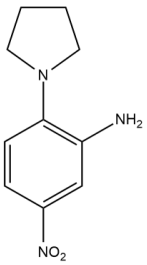
***N*^{1}-*sec*-Butyl-4-nitro-1,2-benzenediamine 2i** was obtained from *N*-*sec*-butyl-2,4-dinitroaniline **1i** (1.500, 5.12 mmol), bright yellow solid, yield 0.268 g (25%),



M.p. 82.6°C (ethyl acetate/petroleum ether) M.p. (lit.)[S5] 82-84°C

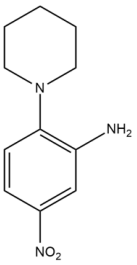
^{1}H NMR (400 MHz, DMSO-d$_6$): δ 0.87 (t, *J*=7.4, 3H), 1.13 (d, *J*=6.4, 3H), 1.43-1.60 (m, 2H), 3.49-3.54 (m, 1H), 5.17 (s, 2H), 5.58 (d, *J*=7.8, 1H), 6.45 (d, *J*=9.2, 1H), 7.37 (d, *J*=2.8, 1H), 7.50 (dd, *J*=2.8, 9.2, 1H).

5-Nitro-2-(1-pyrrolidinyl)aniline 2j was obtained from *N*-(2,4-dinitro-phenyl)pyrrolidine **1j** (2.000 g, 8.4 mmol), light red solid, yield 1.118 g (64%),



M.p. 76.6°C (ethanol), M.p. (lit.)[S26] 77°C;

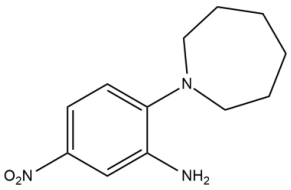
^{1}H NMR (400 MHz, DMSO-d$_6$): δ 1.84-1.87 (m, 4H), 3.26-3.29 (m, 4H), 5.04 (br.s, 2H), 6.72 (d, *J* = 8.8, 1H), 7.45 (dd, *J* = 2.8, 8.8, 1H), 7.49 (d, *J* = 2.8, 1H). ^{13}C NMR (100.6 MHz, DMSO-d$_6$) δ: 24.52, 49.59, 109.35, 114.11, 114.35, 139.57, 139.80, 144.26.



5-Nitro-2-(1-piperidinyl)aniline[S27] **2k** was obtained from *N*-(2,4-dinitrophenyl)piperidine **1k** (2.000 g, 7.97 mmol), orange solid, yield 1.029 g (52%),

M.p. 76.9°C (ethanol), M.p. (lit.)[S28] 82-83°C;

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 1.49-1.55 (m, 2H), 1.63-1.69 (m, 4H), 2.82-2.84 (m, 4H), 4.57 (br. s, 2H), 6.95 (d, *J* = 8.7, 1H), 7.42 (dd, *J* = 2.8, 8.7, 1H), 7.52 (d, *J* = 2.8, 1H)

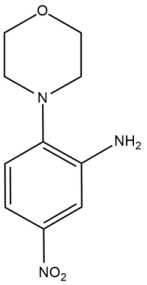


2-(1-Azepanyl)-5-nitroaniline 2l was obtained from *N*-(2,4-dinitrophenyl)azepane **1l** (1.000 g, 3.774 mmol), isolation by filtration through silica gel pad, orange solid, yield 0.284 g (32%),

M.p. 58.8°C (from ethanol), M.p. (lit.)[S12] 61°C;

^{1}H NMR (400 MHz, DMSO-d_6): δ 1.61-1.77 (m, 8H), 3.08-3.11 (m, 4H), 5.13 (br.s, 2H), 6.98 (d, *J* = 8.8, 1H), 7.41 (dd, *J*=2.8, 8.8, 1H), 7.52 (d, *J* = 2.8, 1H). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 26.59, 28.48, 53.17, 108.45, 112.56, 119.20, 142.09, 142.31, 147.13.

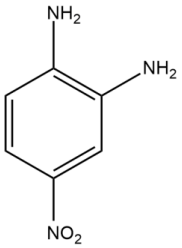
5-Nitro-2-(1-morpholinyl)aniline 2m was obtained from *N*-(2,4-dinitrophenyl)morpholine **1m** (3.500 g, 13.834 mmol), brown solid, yield 1.026 g (34%),



M.p. 147.9°C (ethyl acetate/petroleum ether), M.p. (lit.)[S29] 153°C;

^{1}H NMR (400 MHz, DMSO-d_6): δ 2.88-2.90 (m, 4H), 3.65-3.67 (m, 4H), 5.36 (br.s, 2H), 6.98 (d, *J* = 8.7, 1H), 7.43 (dd, *J* = 2.8, 8.7, 1H), 7.53 (d, *J* = 2.8, 1H)

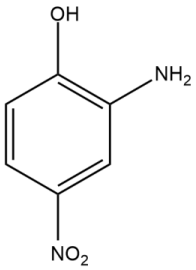
4-Nitrobenzene-1,2-diamine[S30] **2n** was obtained from 2,4-dinitroaniline **1n** (1.00 g, 4.51 mmol), light purple solid, yield 0.87 g (59%),



M.p. 202.6-203.4°C (ethyl acetate/petroleum ether), M.p. (lit.)[S31] 197-198°C;

^{1}H NMR (400 MHz, DMSO-d_6): δ 5.05 (br.s, 2H), 6.04 (br.s, 2H), 6.52 (d, *J* = 8.6, 1H), 7.39 (d, *J* = 2.7, 1H), 7.41 (dd, *J* = 2.7, 8.6, 1H). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ 108.5, 111.9, 116.1, 134.4, 137.3, 143.8.

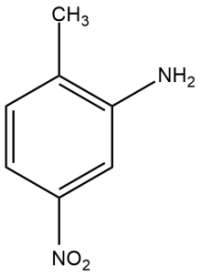
2-Amino-4-nitrophenol[S32] **3a** was obtained from2,4-dinitrophenol (1.000 g, 5.34 mmol), isolated by filtration through silica gel pad (eluent EtOAc:petroleum ether, 1:1), light brown solid, yield 0.534 g (69%).



M.p. 138-141°C (ethyl acetate/petroleum ether), M.p. (lit.)[S32] 141-142°C;

^{1}H NMR (400 MHz, DMSO-d_6): δ 5.19 (br.s., 2H), 6.78 (d, *J* = 8.6, 1H), 7.37 (dd, *J* = 2.6, 8.6, 1H), 7.45 (d, *J* = 2.6), 10.59 (brs, 1H). ^{13}C NMR (100.6 MHz, DMSO-d_6) 108.1, 113.6, 113.6, 138.1, 140.5, 151.5.

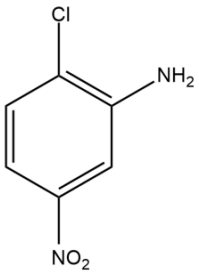
2-Amino-4-nitrotoluene[S33] **3b** was obtained from2,4-dinitrotoluene (2.000 g, 11 mmol), dark brown with green shade solid, yield 0.376 g (23%),



M.p. 70.3-72.8 (ethyl acetate/petroleum ether), M.p. (lit.)[S34] 103 - 105°C;

^{1}H NMR (400 MHz, DMSO-d_6): δ 2.30 (s, 3H), 5.52 (br.s, 2H), 6.79 (dd, *J* = 2.5, 8.3, 1H), 7.07 (d, *J* = 8.3, 1H), 7.14 (d, *J* = 2.5, 1H).

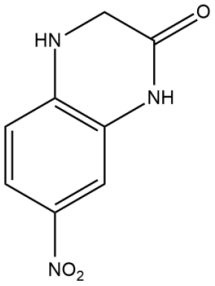
2-Amino-1-chloro-4-nitrobenzene[S35] **3c** was obtained from 1-chloro-2,4-dinitrobenzene 2.000 g (9.88 mmol), isolated by filtration through silica gel pad, light orange solid, yield 0.403 g (26%),



M.p. 119°C (ethyl acetate/petroleum ether), M.p. (lit.)[S36] 118.5°C;

^{1}H NMR (400 MHz, DMSO-d_6): δ 5.91 (br.s, 2H), 6.81 (dd, *J* = 2.8, 8.8, 1H), 7.10 (d, *J* = 2.8, 1H), 7.29 (d, *J* = 8.8, 1H).

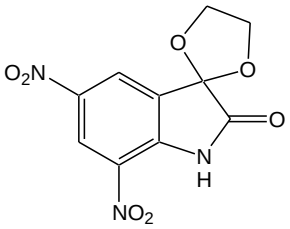
5. Synthesis of 7-nitro-3,4-dihydroquinoxalin-2(1*H*)-one (5)



7-Nitro-3,4-dihydroquinoxalin-2(1*H*)-one 5 was obtained from *N*-(2,4-dinitrophenyl)glycine ethyl ester **4a** (1.486 g, 5.58 mmol), brown solid, yield 0.366 g (34%). Compound **5** was also obtained from *N*-(2,4-dinitrophenyl)glycine (1.000 g, 4.15 mmol), yield 0.121 g (14%).

M.p. 268°C (ethyl acetate/petroleum ether), M.p. (lit.)[S37] 262-264°C (decomp.);
^{1}H NMR (400 MHz, DMSO-d_6): δ 3.99 (s, 2H), 6.64 (d, *J* = 8.7, 1H), 7.49 (br.s, 1H), 7.55 (s, 1H), 7.70 (d, *J* = 8.7, 1H), 10.63 (br.s, 1H).

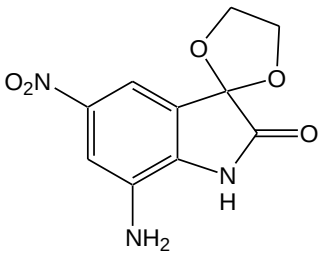
6. 5',7'-Dinitrospiro[1,3-dioxolan-2,3'-indol]-2'(1'*H*)-one (6')



A mixture of 5,7-dinitroisatin (1.000 g, 2.6 mmol), ethylene glycol (2.303 ml, 41.34 mmol) and TsOH (0.037 g) was refluxed in toluene with a Dean-Stark separator until no additional water was formed. Water was added to the reaction mixture, and the precipitate formed was filtered and washed with diethyl ether. Product **6'** appeared as brown solid, yield 0.880 g (74%). M.p. 243 - 245°C.

^{1}H NMR (400 MHz, DMSO-d_6): 4.34-4.43 (m, 4H), 8.52 (d, *J* = 2.3, 1H), 8.80 (d, *J* = 2.3, 1H), 11.84 (s, 1H). IR (nujol, cm^{-1}): 1309, 1533, 1340, 1559, 1610, 1663, 1766, 2904-3232.

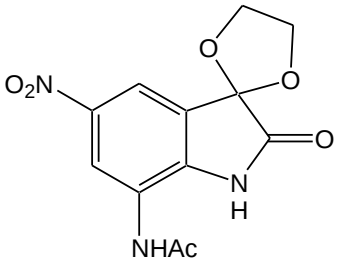
7. 7'-Amino-5'-nitrospiro[1,3-dioxolan-2,3'-indol]-2' (1'*H*)-one (7a)



To a solution of 5',7'-dinitrospiro[1,3-dioxolan-2,3'-indol]-2'(1'*H*)-one **6'** (0.200 g, 0.71 mmol) in THF/H_2O mixture (1:1, 10 ml), sodium dithionite powder (433 mg, 2.49 mmol) was added portionwise within 1 h under intensive stirring and reflux. The mixture was refluxed for another 2 h after dithionite addition (TLC control, R_f 0.6, eluent ethyl acetate). The solvent was evaporated, water (5 ml) was added to the dry residue, and the suspension was extracted with ethyl acetate (3×15 ml). The combined organic phase was dried under Na_2SO_4 and evaporated under reduced pressure. Amine **7a** was obtained as a light-yellow powder. Yield 0.073 g (41%). M.p. 178.0 – 178.9°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.30 (s, 4H), 4.92 (br.s, 2H), 7.42 (s, 1H), 7.57 (s, 1H), 10.59 (s, 1H), ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 66.26, 101.75, 108.54, 111.88, 125.30, 133.77, 134.63, 144.15, 174.88. IR (nujol, cm^{-1}): 1334, 1523, 1606-1653, 1729, 2852-3455, HRMS (ESI): Found:

$C_{10}H_9N_3O_5$. (M+H) 252.0615, calculated: 252.0615; Found: (M-H) 250.0462, calculated: 250.0458.

8. 7'-Acetylamino-5'-nitrospiro[1,3-dioxolan-2,3'-indol]-2'(1'*H*)-one[S38] **7b**



Compound **7a** (30 mg, 0.12 mmol) was dissolved in acetic anhydride (1.5 ml), and the mixture was vigorously stirred until precipitation of solid. The precipitate was filtered, washed with 2M HCl and dried in air. Product **7b** was obtained as a bright-orange powder. Yield 0.013 g (37%).

M.p. 187 - 189°C , M.p. (lit.)[S38] 185 – 190°C;

^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.08 (s, 3H), 4.35 (s, 4H), 8.00 (d, *J*=2.2, 1H), 8.48 (d, *J* = 2.2, 1H), 9.70 (s, 1H), 10.82 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 23.42, 66.06, 100.72, 116.40, 121.50, 122.35, 126.08, 141.50, 142.60, 168.95, 174.20. HRMS (ESI): found: $C_{12}H_{12}N_3O_6$ (M+H) 294.0719, calculated: 294.0721.

9. References

[S1] E. V. Zaryanova, N.A. Lozinskaya, O. V. Beznos, M.S. Volkova, N.B. Chesnokova, N.S. Zefirov, *Bioorg. Med. Chem. Lett.*, 2017, **27**, 3787.

[S2] M. Nagano, N. Carrillo, N. Otsubo, W. Hakamata, H. Ban, R.P. Fuller, N.K. Bashiruddin, C.F. Barbas, *Bioorg. Med. Chem.*, 2017, **25**, 5952.

[S3] S.R. Manne, J. Chandra, B. Mandal, *Org. Lett.*, 2019, **21**, 636.

[S4] N.M. Cullinane, O.E. Embrey, D.R. Davies, *Journal of the Chemical Society (Resumed)*, 1932, **6**, 2363.

[S5] S.R. Manne, J. Chandra, B. Mandal, *Org. Lett.*, 2019, **21**, 636.

[S6] W. Ozegowski, D. Krebs, M. Wunderwald, *Journal fur Praktische Chemie*, 1963, **20**, 166.

[S7] A.F. Pozharskii, V. V. Kuz'menko, A.M. Simonov, *Chem. Heterocycl. Compd. (N Y)*, 1971, **7**, 1036.

[S8] C. Willgerodt, *Berichte der deutschen chemischen Gesellschaft*, 1878, **11**, 601.

[S9] Y.S. Feng, L. Mao, X.S. Bu, J.J. Dai, H.J. Xu, *Tetrahedron*, 2015, **71**, 3827.

[S10] C.F. Bernasconi, *J. Org. Chem.*, 1967, **32**, 2947.

[S11] J.M. Gardiner, C.R. Loyns, C.H. Schwalbe, G.C. Barrett, P.R. Lowe, *Tetrahedron*, 1995, **51**, 4101.

[S12] H. Möhrle, M. Busch, *Arch. Pharm. (Weinheim)*, 1982, **315**, 333.

[S13] I.W. Harvey, M.D. McFarlane, D.J. Moody, D.M. Smith, *J. Chem. Soc. Perkin 1*, 1988, **1**, 681.

[S14] A. Preiss, M. Elend, S. Gerling, S. Tränckner, *Magnetic Resonance in Chemistry*, 2005, **43**, 736.

[S15] J.P. Henichart, J.L. Bernwr, V. Warin, F. Baert, *Tetrahedron*, 1980, **36**, 3535.

[S16] J.-P. Hénichart, J. Bernier, C. Vaccher, R. Houssin, V. Warin, F. Baert, *Tetrahedron Lett.*, 1979, **20**, 945.

[S17] G. Qian, F. Dai, H. Chen, M. Wang, M. Hu, C. Chen, Y. Yu, *RSC Adv.*, 2021, **11**, 3770.

[S18] W. Ozegowski, D. Krebs, M. Wunderwald, *Journal fur Praktische Chemie*, 1963, **20**, 166.

[S19] A.F. Pozharskii, V. V. Kuz'menko, A.M. Simonov, *Chem. Heterocycl. Compd. (N Y)*, 1971, **7**, 1036.

[S20] O. Neunhoeffer, A. Keiler, *Chem. Ber.*, 1958, **91**, 122.

[S21] H. YIN, K. CHENG, H. YIN, K. CHENG, *WO/2015/171951*, 2015.

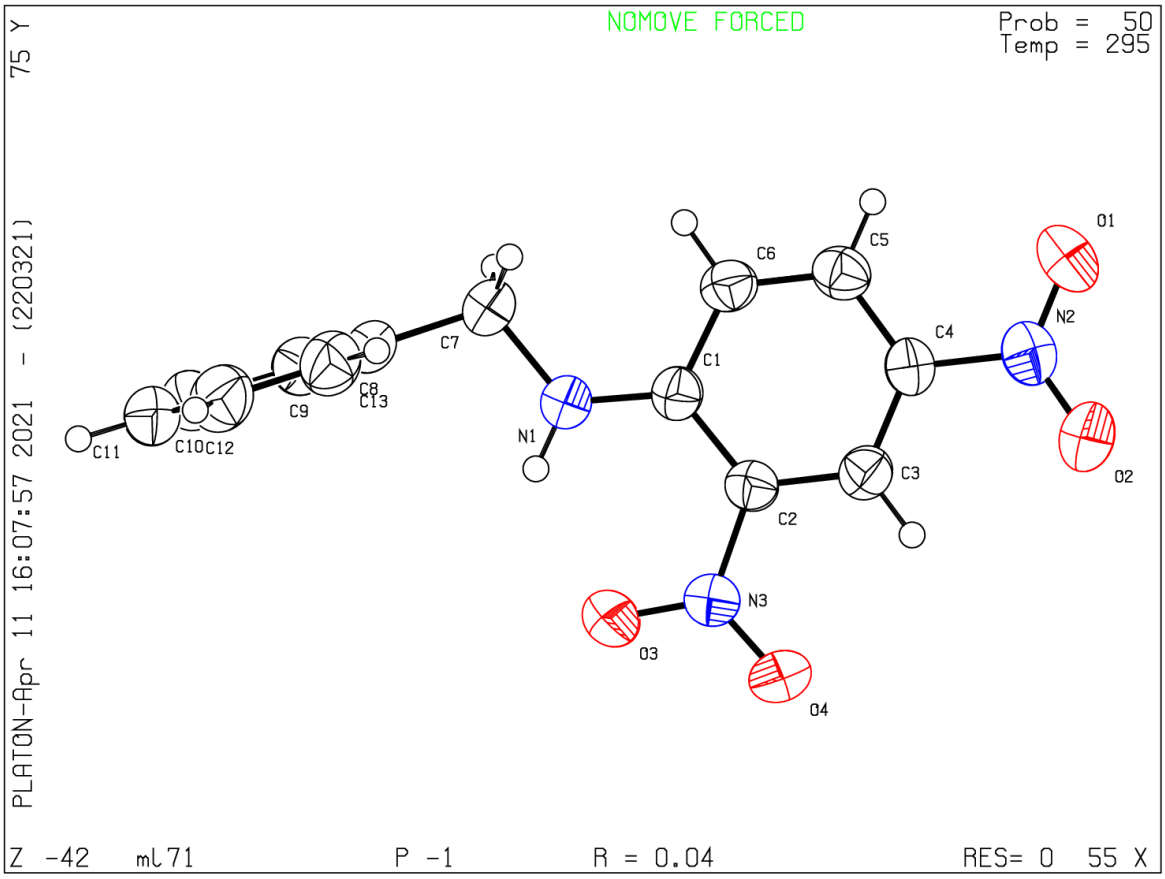
[S22] M. Bella, V. Milata, C. López, R.M. Claramunt, I. Alkorta, J. Elguero, *Spectroscopy Letters*, 2013, **46**, 91.

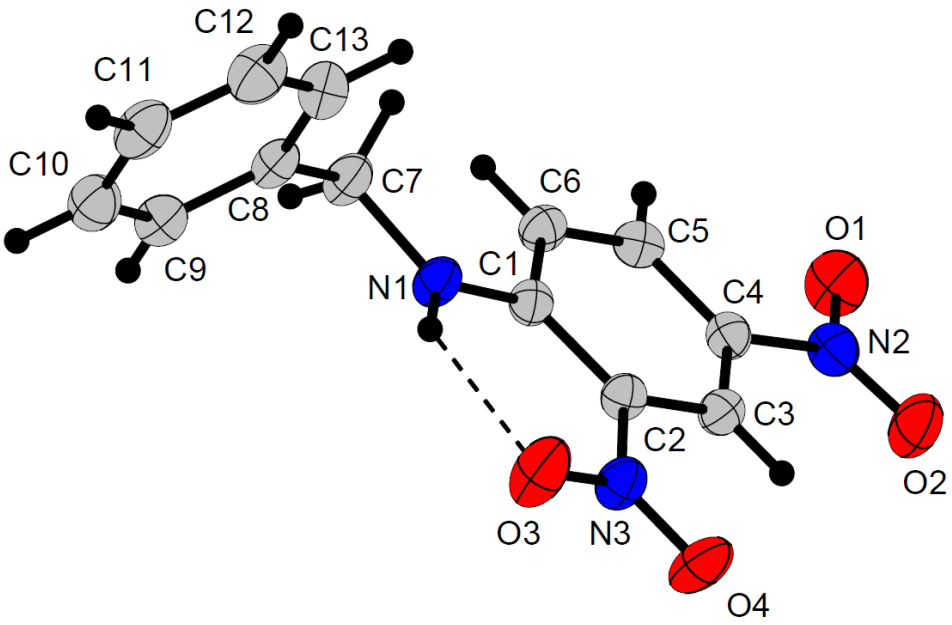
[S23] N. XI, M. LI, J. PENG, LI Xiaobo, T. ZHANG, HU Haiyang, CHEN Wuhong, C. BAI, D. KE, P. CHEN, N. XI, M. LI, J. PENG, LI Xiaobo, T. ZHANG, HU Haiyang, CHEN Wuhong, C. BAI, D. KE, P. CHEN, *WO/2019/099311*, 2019.

[S24] L. Joseph, J. Julca, *J. Org. Chem.*, 1962, **27**, 1101.

[S25] A.S. Burlov, V.N. Ikorskii, A.I. Uraev, Y. V. Koshchienko, I.S. Vasil'chenko, D.A. Garnovskii, G.S. Borodkin, S.A. Nikolaevskii, A.D. Garnovskii, *Russ. J. Gen. Chem.*, 2006, **76**, 1282.
[S26] J. Martin, O. Meth-Cohn, H. Suschitzky, *J Chem Soc Perkin 1*, 1974, **1**, 2451.
[S27] R.S. Begunov, T.N. Orlova, O. v Taranova, V.Y. Orlov, *J. Appl. Spectrosc.*, 2002, **69**, 807.
[S28] S. de Castro, R. Chicharro, V.J. Arán, *J. Chem. Soc. Perkin 1*, 2002, **1**, 790.
[S29] D.P. Ainsworth, H. Suschitzky, *Journal of the Chemical Society C: Organic*, 1966, 111.
[S30] Y. Liu, S. He, Z. Quan, H. Cai, Y. Zhao, B. Wang, *Green Chemistry*, 2019, **21**, 830.
[S31] S.P. Singh, S.S. Parmar, B.R. Pandey, *J. Heterocycl. Chem.*, 1977, **14**, 1093.
[S32] M. Imoto, Y. Matsui, M. Takeda, A. Tamaki, H. Taniguchi, K. Mizuno, H. Ikeda, *Journal of Organic Chemistry*, 2011, **76**, 6356.
[S33] Y. Monguchi, T. Maejima, S. Mori, T. Maegawa, H. Sajiki, *Chemistry - A European Journal*, 2010, **16**, 7372.
[S34] A. Cambanis, V. Dobre, I. Niculescu-Duvaz, *J. Med. Chem.*, 1969, **12**, 161.
[S35] S.S. Liu, X. Liu, L. Yu, Y.M. Liu, H.Y. He, Y. Cao, *Green Chemistry*, 2014, **16**, 4162.
[S36] W.N. White, T. Vogelmann, M. Morse, H.S. White, *J. Org. Chem.*, 1977, **42**, 162.
[S37] S.S. Berg, E.W. Parnell, *Journal of the Chemical Society (Resumed)*, 1961, 5275.
[S38] E. V. Zaryanova, A.A. Ignatov, N.A. Lozynskaya, *Tetrahedron*, 2017, **73**, 6887.

10. Figure S2. Crystal data for *N*-benzyl-2,4-dinitroaniline 1e





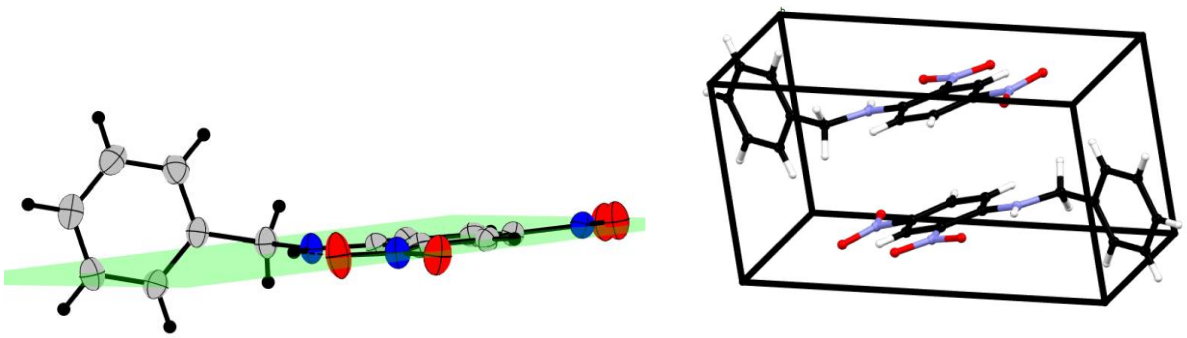


Table S1. Crystal data and structure refinement for **1e**.

Identification code	shelx	
Empirical formula	C13H11N3O4	
Formula weight	273.25	
Temperature	293(2) K	
Wavelength	1.54186 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.1232(5) E	α= 84.6350(10)°.
	b = 8.2598(6) E	β= 84.0150(10)°.
	c = 11.1839(8) E	γ = 72.9800(10)°.
Volume	624.40(8) $Å^3$	
Z	2	
Density (calculated)	1.453 Mg/m^3	
Absorption coefficient	0.932 mm^{-1}	
F(000)	284	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	3.983 to 70.663°.	
Index ranges	-7<=h<=8, -10<=k<=10, -13<=l<=9	
Reflections collected	6285	
Independent reflections	2211 [R(int) = 0.0496]	
Completeness to theta = 67.686°	93.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2211 / 0 / 186	
Goodness-of-fit on F^2	0.937	
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1118	
R indices (all data)	R1 = 0.0664, wR2 = 0.1226	
Extinction coefficient	0.019(2)	
Largest diff. peak and hole	0.217 and -0.288 $e.E^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for **1e**.

O(1)-N(2)	1.223(2)
O(2)-N(2)	1.227(2)
O(3)-N(3)	1.229(2)
O(4)-N(3)	1.222(2)
N(1)-C(1)	1.337(2)
N(1)-C(7)	1.460(2)
N(1)-H(1)	0.87(2)
N(2)-C(4)	1.447(3)
N(3)-C(2)	1.449(2)
C(1)-C(2)	1.422(3)
C(1)-C(6)	1.426(2)
C(2)-C(3)	1.380(3)
C(3)-C(4)	1.374(2)
C(3)-H(3)	0.9300
C(4)-C(5)	1.391(3)
C(5)-C(6)	1.362(3)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-C(8)	1.506(3)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.376(3)
C(8)-C(13)	1.379(3)
C(9)-C(10)	1.388(3)
C(9)-H(9)	0.9300
C(10)-C(11)	1.372(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.367(3)
C(11)-H(11)	0.9300
C(12)-C(13)	1.383(3)
C(12)-H(12)	0.9300
C(13)-H(13)	0.9300
C(1)-N(1)-C(7)	124.50(17)
C(1)-N(1)-H(1)	119.3(15)
C(7)-N(1)-H(1)	116.1(15)
O(1)-N(2)-O(2)	122.59(19)
O(1)-N(2)-C(4)	118.27(18)

O(2)-N(2)-C(4)	119.14(17)
O(4)-N(3)-O(3)	121.54(16)
O(4)-N(3)-C(2)	118.95(17)
O(3)-N(3)-C(2)	119.50(16)
N(1)-C(1)-C(2)	124.49(16)
N(1)-C(1)-C(6)	120.23(17)
C(2)-C(1)-C(6)	115.28(16)
C(3)-C(2)-C(1)	122.41(16)
C(3)-C(2)-N(3)	115.91(17)
C(1)-C(2)-N(3)	121.68(16)
C(4)-C(3)-C(2)	119.32(18)
C(4)-C(3)-H(3)	120.3
C(2)-C(3)-H(3)	120.3
C(3)-C(4)-C(5)	120.87(18)
C(3)-C(4)-N(2)	119.04(18)
C(5)-C(4)-N(2)	120.07(17)
C(6)-C(5)-C(4)	119.87(17)
C(6)-C(5)-H(5)	120.1
C(4)-C(5)-H(5)	120.1
C(5)-C(6)-C(1)	122.21(18)
C(5)-C(6)-H(6)	118.9
C(1)-C(6)-H(6)	118.9
N(1)-C(7)-C(8)	110.79(15)
N(1)-C(7)-H(7A)	109.5
C(8)-C(7)-H(7A)	109.5
N(1)-C(7)-H(7B)	109.5
C(8)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	108.1
C(9)-C(8)-C(13)	118.90(18)
C(9)-C(8)-C(7)	121.17(18)
C(13)-C(8)-C(7)	119.9(2)
C(8)-C(9)-C(10)	120.5(2)
C(8)-C(9)-H(9)	119.8
C(10)-C(9)-H(9)	119.8
C(11)-C(10)-C(9)	120.1(2)
C(11)-C(10)-H(10)	120.0
C(9)-C(10)-H(10)	120.0
C(12)-C(11)-C(10)	119.7(2)
C(12)-C(11)-H(11)	120.2
C(10)-C(11)-H(11)	120.2

C(11)-C(12)-C(13)	120.4(2)
C(11)-C(12)-H(12)	119.8
C(13)-C(12)-H(12)	119.8
C(8)-C(13)-C(12)	120.4(2)
C(8)-C(13)-H(13)	119.8
C(12)-C(13)-H(13)	119.8

Symmetry transformations used to generate equivalent atoms:

Table S3. Torsion angles [°] for **1e**.

C(7)-N(1)-C(1)-C(2)	175.09(17)
C(7)-N(1)-C(1)-C(6)	-5.5(3)
N(1)-C(1)-C(2)-C(3)	-177.88(17)
C(6)-C(1)-C(2)-C(3)	2.7(2)
N(1)-C(1)-C(2)-N(3)	2.3(3)
C(6)-C(1)-C(2)-N(3)	-177.17(15)
O(4)-N(3)-C(2)-C(3)	-2.1(3)
O(3)-N(3)-C(2)-C(3)	176.68(18)
O(4)-N(3)-C(2)-C(1)	177.76(17)
O(3)-N(3)-C(2)-C(1)	-3.5(3)
C(1)-C(2)-C(3)-C(4)	-1.6(3)
N(3)-C(2)-C(3)-C(4)	178.28(15)
C(2)-C(3)-C(4)-C(5)	-0.3(3)
C(2)-C(3)-C(4)-N(2)	178.15(16)
O(1)-N(2)-C(4)-C(3)	178.10(16)
O(2)-N(2)-C(4)-C(3)	-2.8(2)
O(1)-N(2)-C(4)-C(5)	-3.4(3)
O(2)-N(2)-C(4)-C(5)	175.69(16)
C(3)-C(4)-C(5)-C(6)	0.9(3)
N(2)-C(4)-C(5)-C(6)	-177.55(17)
C(4)-C(5)-C(6)-C(1)	0.4(3)
N(1)-C(1)-C(6)-C(5)	178.46(17)
C(2)-C(1)-C(6)-C(5)	-2.1(3)
C(1)-N(1)-C(7)-C(8)	-165.85(18)
N(1)-C(7)-C(8)-C(9)	-94.2(2)
N(1)-C(7)-C(8)-C(13)	86.2(2)
C(13)-C(8)-C(9)-C(10)	0.8(3)
C(7)-C(8)-C(9)-C(10)	-178.81(18)
C(8)-C(9)-C(10)-C(11)	-0.6(3)
C(9)-C(10)-C(11)-C(12)	-0.3(3)
C(10)-C(11)-C(12)-C(13)	0.9(3)
C(9)-C(8)-C(13)-C(12)	-0.2(3)
C(7)-C(8)-C(13)-C(12)	179.44(19)
C(11)-C(12)-C(13)-C(8)	-0.7(3)

Symmetry transformations used to generate equivalent atoms:

Table **S4**. Hydrogen bonds for **1e** [E and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(3)	0.87(2)	2.01(2)	2.642(2)	128(2)
C(5)-H(5)...O(4)#1	0.93	2.55	3.467(2)	170.8

Symmetry transformations used to generate equivalent atoms: #1 x,y+1,z

11. Figure S3. Crystal Data for *N*-(2,4-dinitrophenyl)azepane 1l

.

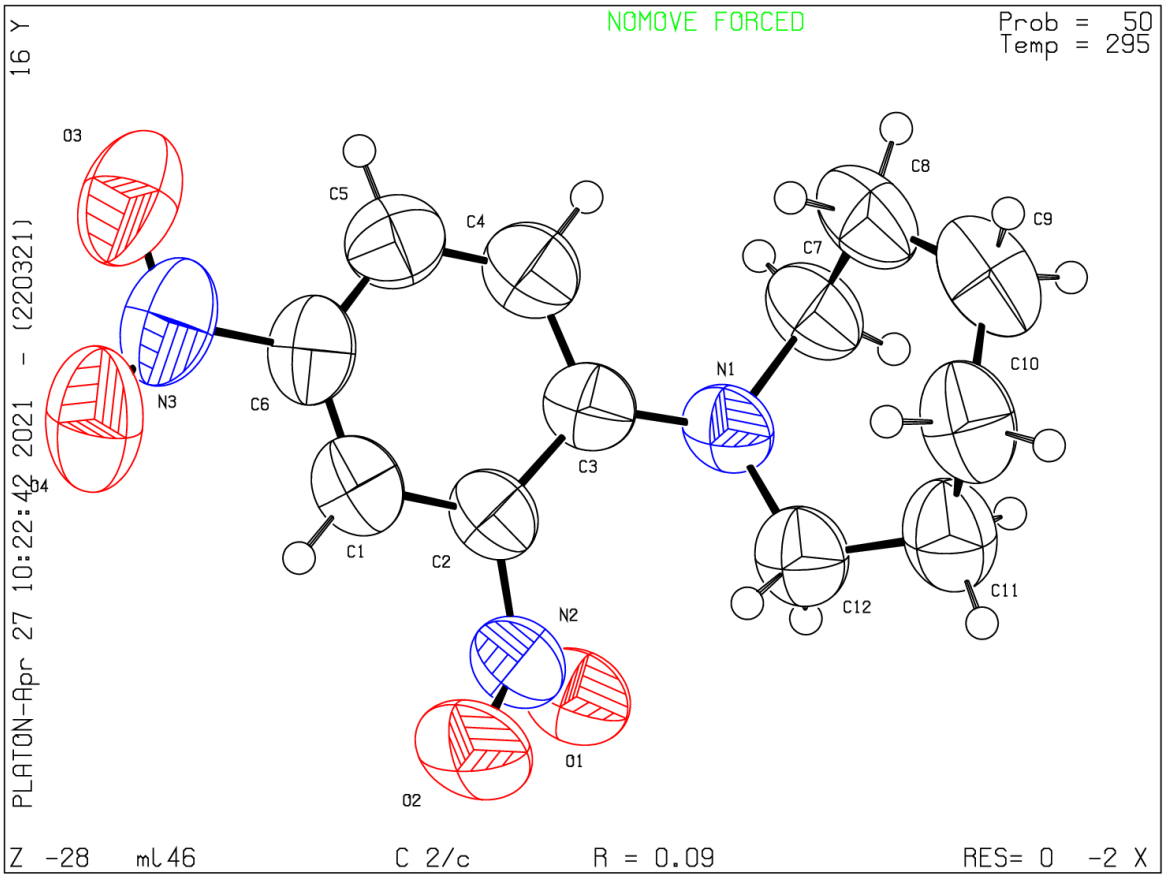


Table S5. Crystal Data and Structure Refinement for *N*-(2,4-dinitrophenyl)azepane **1l**

Identification code	ml46 (**1l**)	
Empirical formula	C12H15N3O4	
Formula weight	265.27	
Temperature	293(2) K	
Wavelength	1.54186 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 9.7940(10) Å	α= 90°.
	b = 28.913(6) Å	β= 92.810(10)°.
	c = 9.0490(10) Å	γ = 90°.
Volume	2559.4(7) $Å^3$	
Z	8	
Density (calculated)	1.377 Mg/m^3	
Absorption coefficient	0.883 mm^{-1}	
F(000)	1120	

Theta range for data collection	3.057 to 66.845°.
Index ranges	-11<=h<=8, -34<=k<=32, -7<=l<=10
Reflections collected	8038
Independent reflections	2234 [R(int) = 0.1832]
Completeness to theta = 66.845°	98.1 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2234 / 0 / 173
Goodness-of-fit on F^2	0.860
Final R indices [I>2sigma(I)]	R1 = 0.0871, wR2 = 0.2093
R indices (all data)	R1 = 0.1484, wR2 = 0.2683
Extinction coefficient	0.0011(4)
Largest diff. peak and hole	0.331 and -0.361 e.$Å^{-3}$

Table S6. Bond lengths [Å] and angles [°] for **1l**.

O(1)-N(2)	1.245(4)
O(2)-N(2)	1.232(4)
O(3)-N(3)	1.234(7)
O(4)-N(3)	1.224(6)
N(1)-C(3)	1.349(5)
N(1)-C(12)	1.459(5)
N(1)-C(7)	1.476(5)
N(2)-C(2)	1.448(6)
N(3)-C(6)	1.452(7)
C(1)-C(6)	1.363(7)
C(1)-C(2)	1.391(6)
C(1)-H(1)	0.9300
C(2)-C(3)	1.420(5)
C(3)-C(4)	1.417(7)
C(4)-C(5)	1.379(6)
C(4)-H(4)	0.9300
C(5)-C(6)	1.388(7)
C(5)-H(5)	0.9300
C(7)-C(8)	1.508(7)
C(7)-H(71)	0.9700
C(7)-H(72)	0.9700
C(8)-C(9)	1.512(8)
C(8)-H(81)	0.9700
C(8)-H(82)	0.9700
C(9)-C(10)	1.509(8)

C(9)-H(91)	0.9700
C(9)-H(92)	0.9700
C(10)-C(11)	1.508(8)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-C(12)	1.516(7)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700

C(3)-N(1)-C(12)	124.1(3)
C(3)-N(1)-C(7)	118.5(4)
C(12)-N(1)-C(7)	117.0(3)
O(2)-N(2)-O(1)	122.2(4)
O(2)-N(2)-C(2)	119.4(4)
O(1)-N(2)-C(2)	118.3(3)
O(4)-N(3)-O(3)	123.3(5)
O(4)-N(3)-C(6)	119.5(6)
O(3)-N(3)-C(6)	117.2(6)
C(6)-C(1)-C(2)	119.3(4)
C(6)-C(1)-H(1)	120.4
C(2)-C(1)-H(1)	120.4
C(1)-C(2)-C(3)	122.2(4)
C(1)-C(2)-N(2)	113.2(4)
C(3)-C(2)-N(2)	123.9(4)
N(1)-C(3)-C(4)	121.3(4)
N(1)-C(3)-C(2)	123.7(4)
C(4)-C(3)-C(2)	114.9(4)
C(5)-C(4)-C(3)	122.6(4)
C(5)-C(4)-H(4)	118.7
C(3)-C(4)-H(4)	118.7
C(4)-C(5)-C(6)	119.0(5)
C(4)-C(5)-H(5)	120.5
C(6)-C(5)-H(5)	120.5
C(1)-C(6)-C(5)	121.3(4)
C(1)-C(6)-N(3)	118.7(5)
C(5)-C(6)-N(3)	119.9(5)
N(1)-C(7)-C(8)	112.9(3)
N(1)-C(7)-H(71)	109.0

C(8)-C(7)-H(71)	109.0
N(1)-C(7)-H(72)	109.0
C(8)-C(7)-H(72)	109.0
H(71)-C(7)-H(72)	107.8
C(7)-C(8)-C(9)	114.6(5)
C(7)-C(8)-H(81)	108.6
C(9)-C(8)-H(81)	108.6
C(7)-C(8)-H(82)	108.6
C(9)-C(8)-H(82)	108.6
H(81)-C(8)-H(82)	107.6
C(10)-C(9)-C(8)	116.1(4)
C(10)-C(9)-H(91)	108.3
C(8)-C(9)-H(91)	108.3
C(10)-C(9)-H(92)	108.3
C(8)-C(9)-H(92)	108.3
H(91)-C(9)-H(92)	107.4
C(11)-C(10)-C(9)	114.6(4)
C(11)-C(10)-H(10A)	108.6
C(9)-C(10)-H(10A)	108.6
C(11)-C(10)-H(10B)	108.6
C(9)-C(10)-H(10B)	108.6
H(10A)-C(10)-H(10B)	107.6
C(10)-C(11)-C(12)	116.2(5)
C(10)-C(11)-H(11A)	108.2
C(12)-C(11)-H(11A)	108.2
C(10)-C(11)-H(11B)	108.2
C(12)-C(11)-H(11B)	108.2
H(11A)-C(11)-H(11B)	107.4
N(1)-C(12)-C(11)	115.4(4)
N(1)-C(12)-H(12A)	108.4
C(11)-C(12)-H(12A)	108.4
N(1)-C(12)-H(12B)	108.4
C(11)-C(12)-H(12B)	108.4
H(12A)-C(12)-H(12B)	107.5

Symmetry transformations used to generate equivalent atoms:

Table S7. Torsion angles [°] for **1l**.

C(6)-C(1)-C(2)-C(3)	4.4(6)
C(6)-C(1)-C(2)-N(2)	-166.7(4)
O(2)-N(2)-C(2)-C(1)	-43.8(5)
O(1)-N(2)-C(2)-C(1)	132.6(4)
O(2)-N(2)-C(2)-C(3)	145.3(4)
O(1)-N(2)-C(2)-C(3)	-38.3(5)
C(12)-N(1)-C(3)-C(4)	163.2(4)
C(7)-N(1)-C(3)-C(4)	-9.4(5)
C(12)-N(1)-C(3)-C(2)	-14.1(6)
C(7)-N(1)-C(3)-C(2)	173.3(3)
C(1)-C(2)-C(3)-N(1)	168.3(4)
N(2)-C(2)-C(3)-N(1)	-21.6(6)
C(1)-C(2)-C(3)-C(4)	-9.2(5)
N(2)-C(2)-C(3)-C(4)	160.9(4)
N(1)-C(3)-C(4)-C(5)	-170.7(4)
C(2)-C(3)-C(4)-C(5)	6.8(6)
C(3)-C(4)-C(5)-C(6)	0.2(7)
C(2)-C(1)-C(6)-C(5)	3.4(6)
C(2)-C(1)-C(6)-N(3)	178.9(3)
C(4)-C(5)-C(6)-C(1)	-5.7(6)
C(4)-C(5)-C(6)-N(3)	178.8(4)
O(4)-N(3)-C(6)-C(1)	1.6(7)
O(3)-N(3)-C(6)-C(1)	-179.8(4)
O(4)-N(3)-C(6)-C(5)	177.2(4)
O(3)-N(3)-C(6)-C(5)	-4.2(6)
C(3)-N(1)-C(7)-C(8)	85.8(5)
C(12)-N(1)-C(7)-C(8)	-87.4(5)
N(1)-C(7)-C(8)-C(9)	76.4(5)
C(7)-C(8)-C(9)-C(10)	-51.9(6)
C(8)-C(9)-C(10)-C(11)	63.1(7)
C(9)-C(10)-C(11)-C(12)	-85.1(6)
C(3)-N(1)-C(12)-C(11)	-142.8(4)
C(7)-N(1)-C(12)-C(11)	29.9(5)
C(10)-C(11)-C(12)-N(1)	47.9(6)

Symmetry transformations used to generate equivalent atoms:

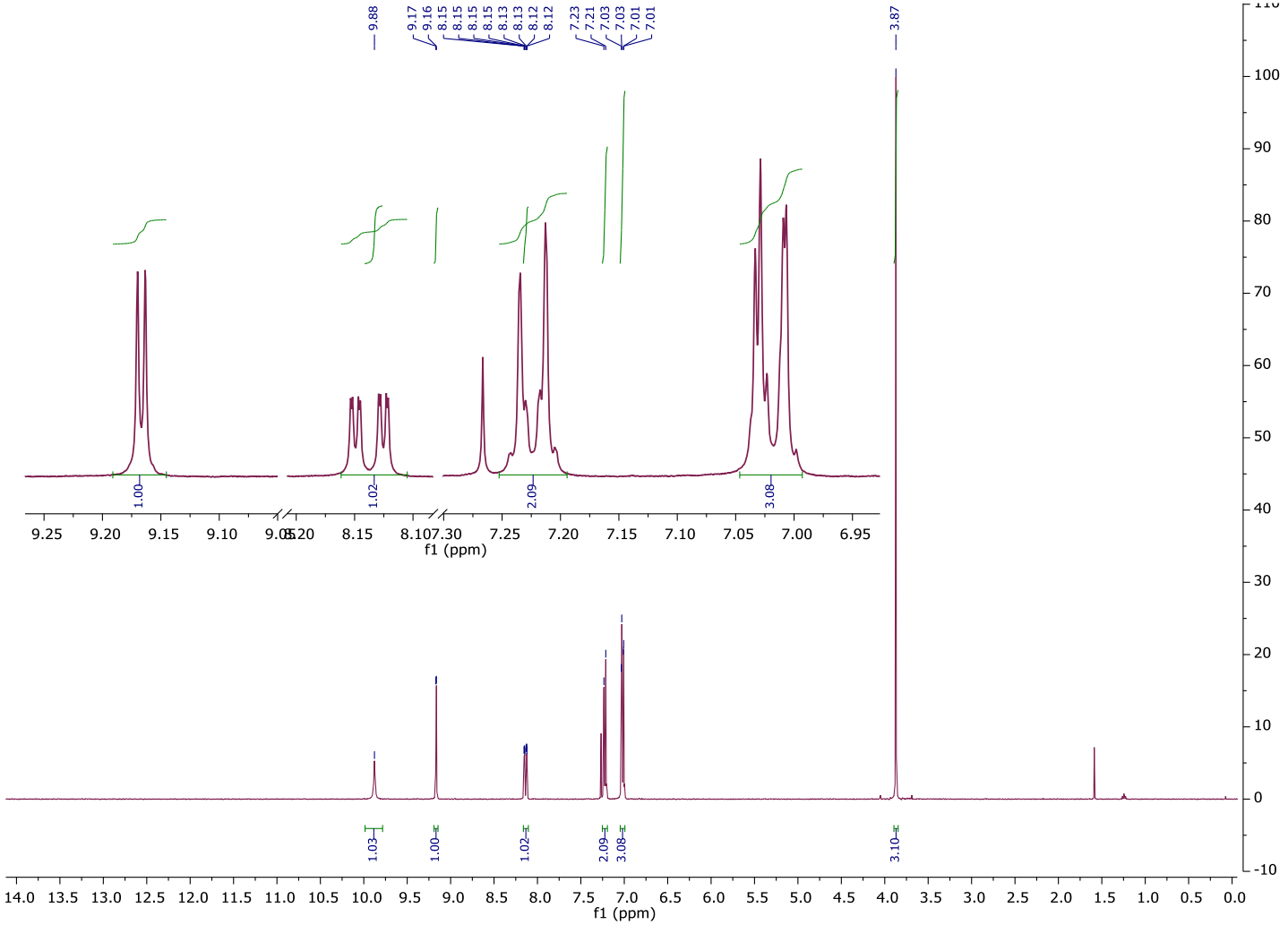
Table S8. Hydrogen bonds for **1l** [Å and °].

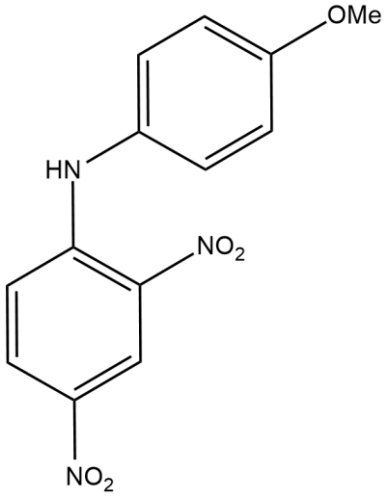
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(7)-H(71)...O(3)#1	0.97	2.61	3.340(7)	132.1
C(8)-H(82)...O(3)#1	0.97	2.66	3.307(7)	124.6
C(12)-H(12B)...N(2)	0.97	2.39	2.890(6)	111.5

Symmetry transformations used to generate equivalent atoms:

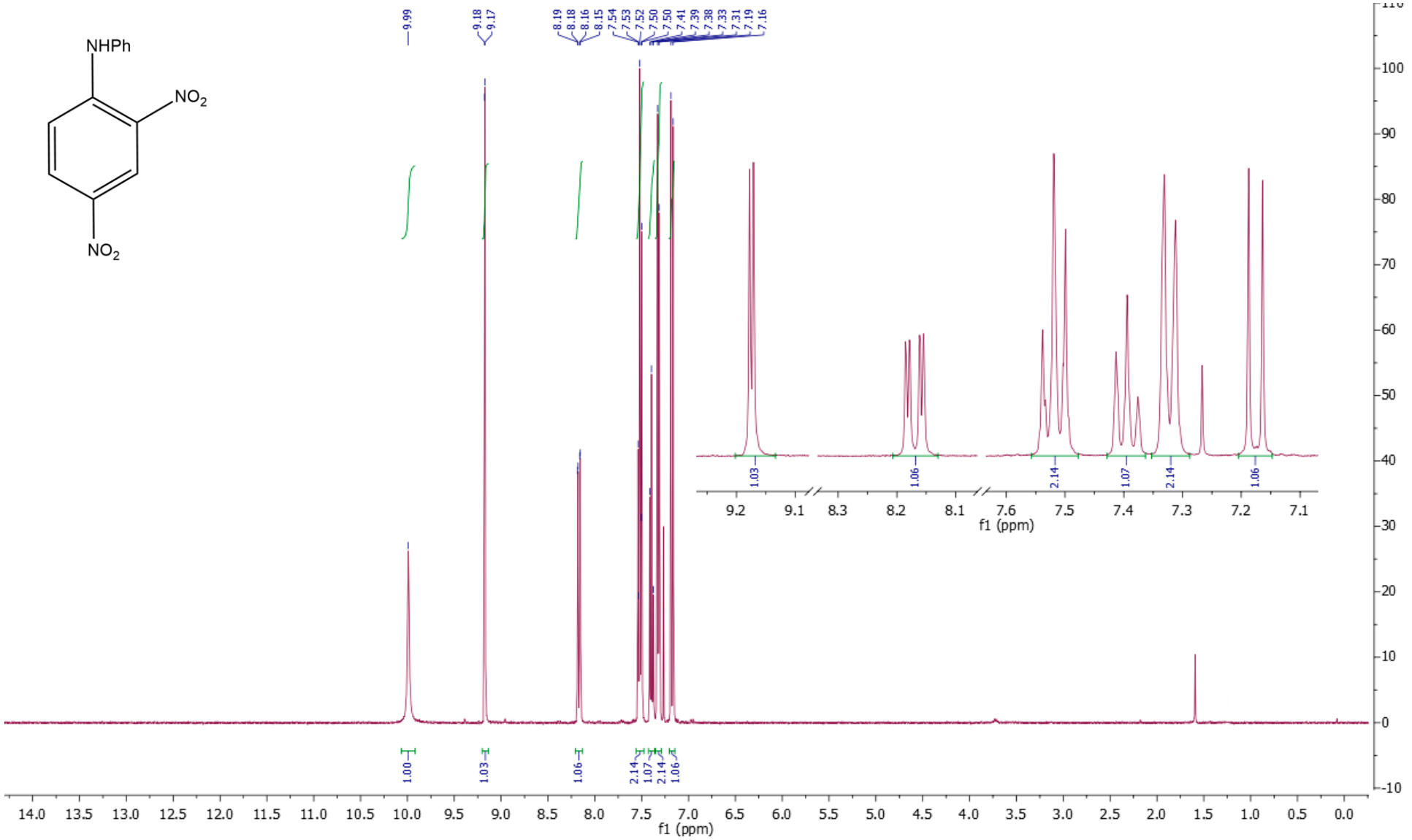
#1 x+1/2,-y+1/2,z-1/2

12. NMR Data of synthesized compounds

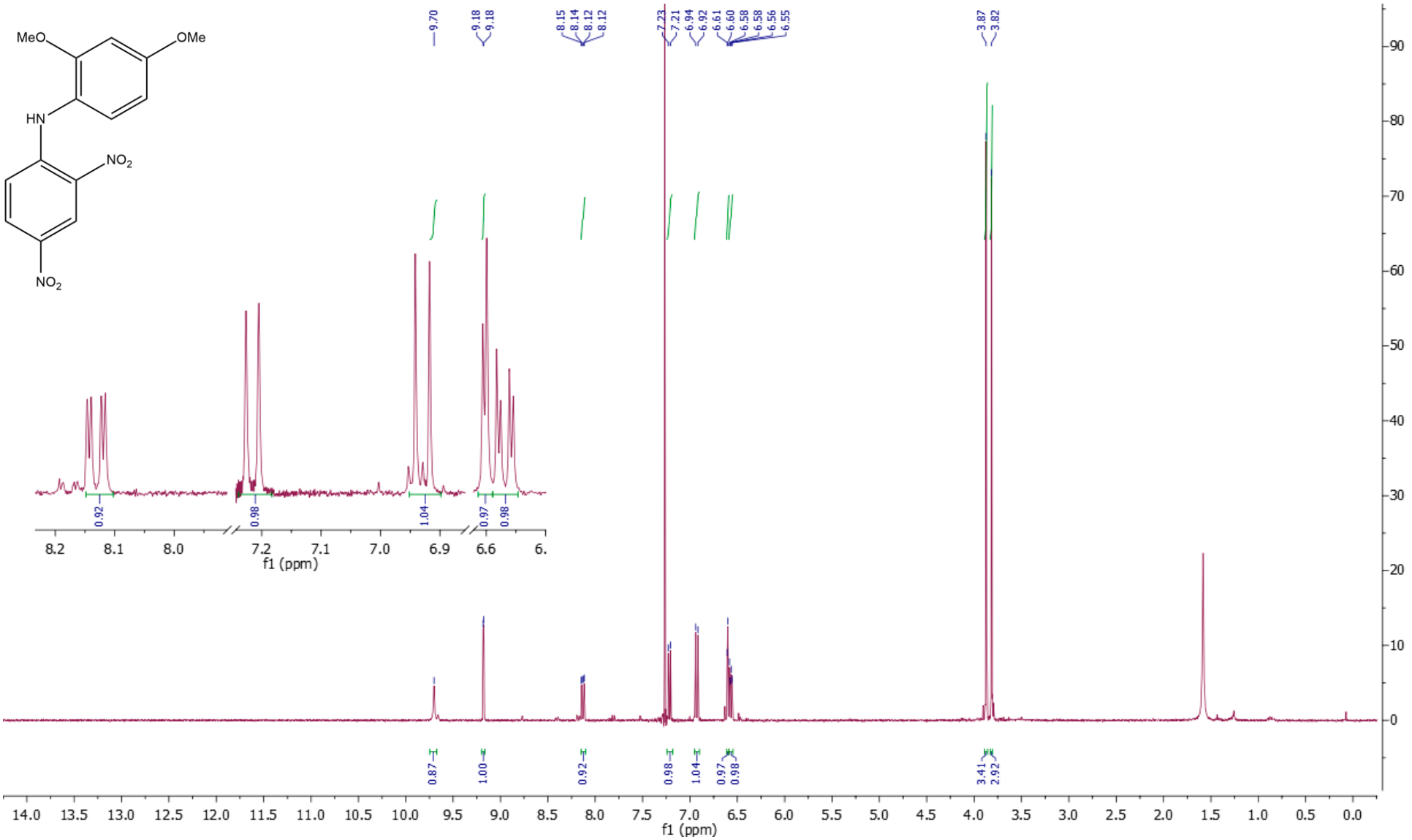




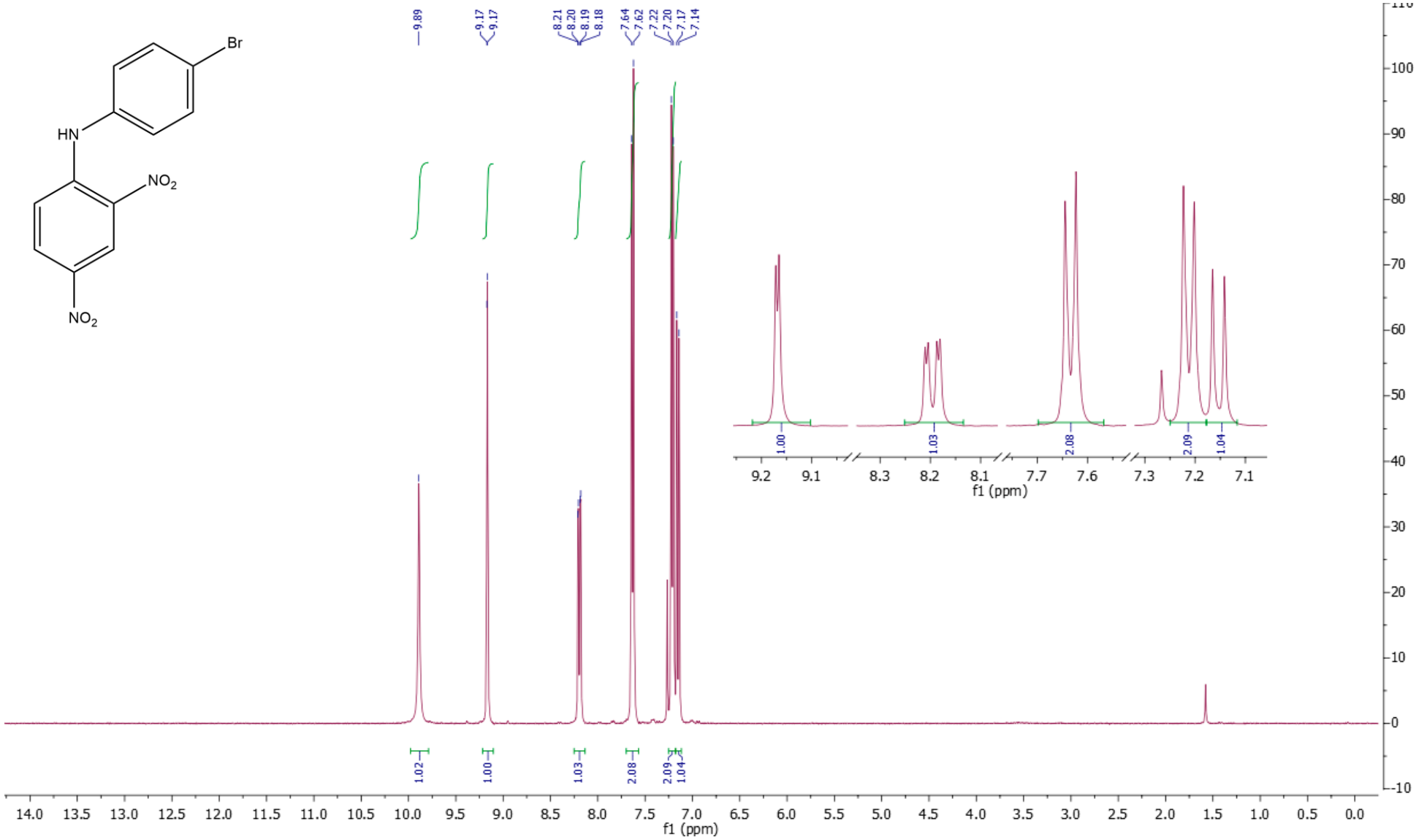
^{1}H NMR spectrum ($CDCl_3$) of *N*-(4-methoxyphenyl)-2,4-dinitroaniline **1a**



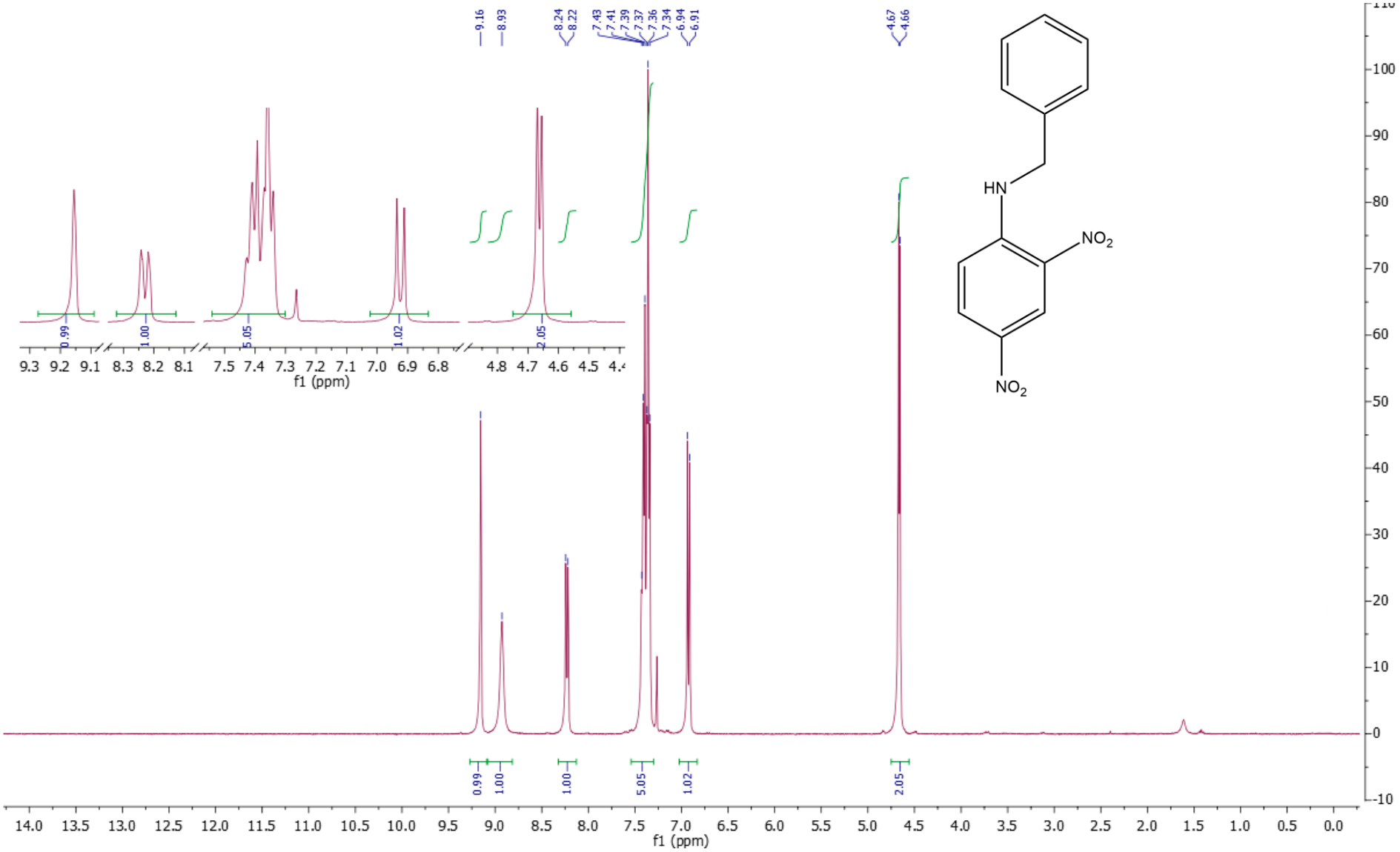
^{1}H NMR spectrum ($CDCl_3$) of 2,4-dinitro- *N*-phenylaniline **1b**



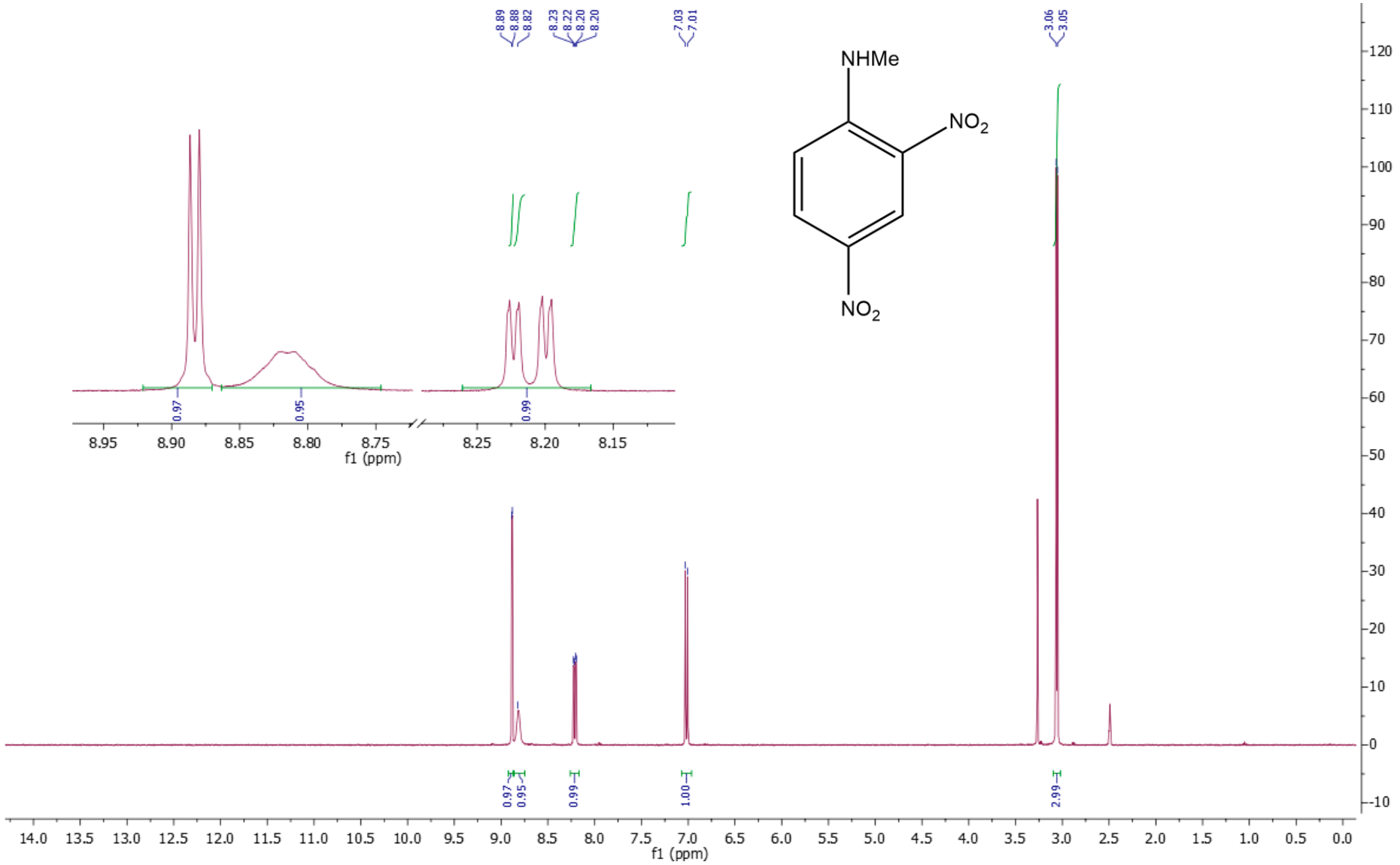
^{1}H NMR spectrum ($CDCl_3$) of *N*-(2,4-dimethoxyphenyl)-2,4-dinitroaniline **1c**



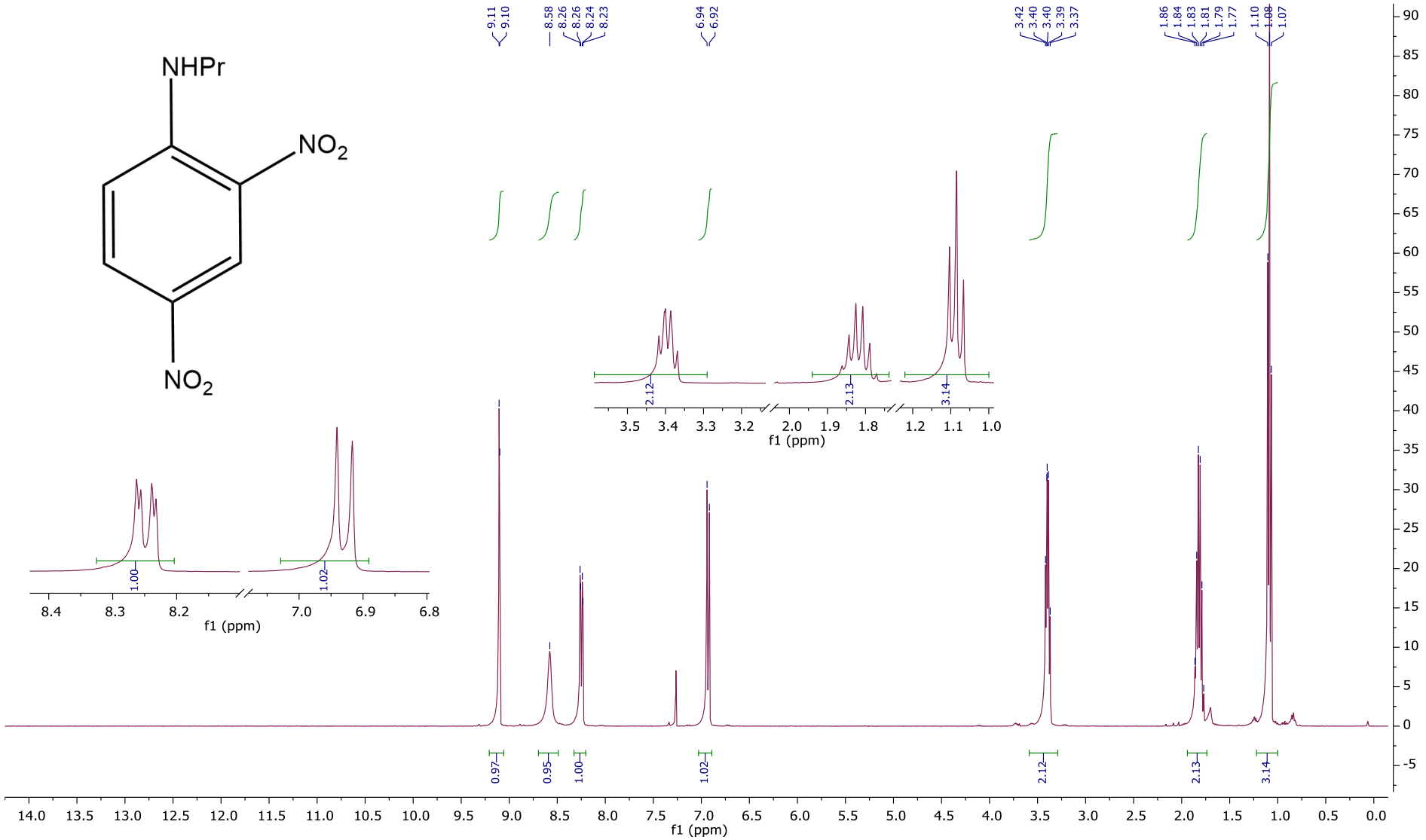
^{1}H NMR spectrum ($CDCl_3$) of *N*-(4-bromophenyl)-2,4-dinitroaniline **1d**



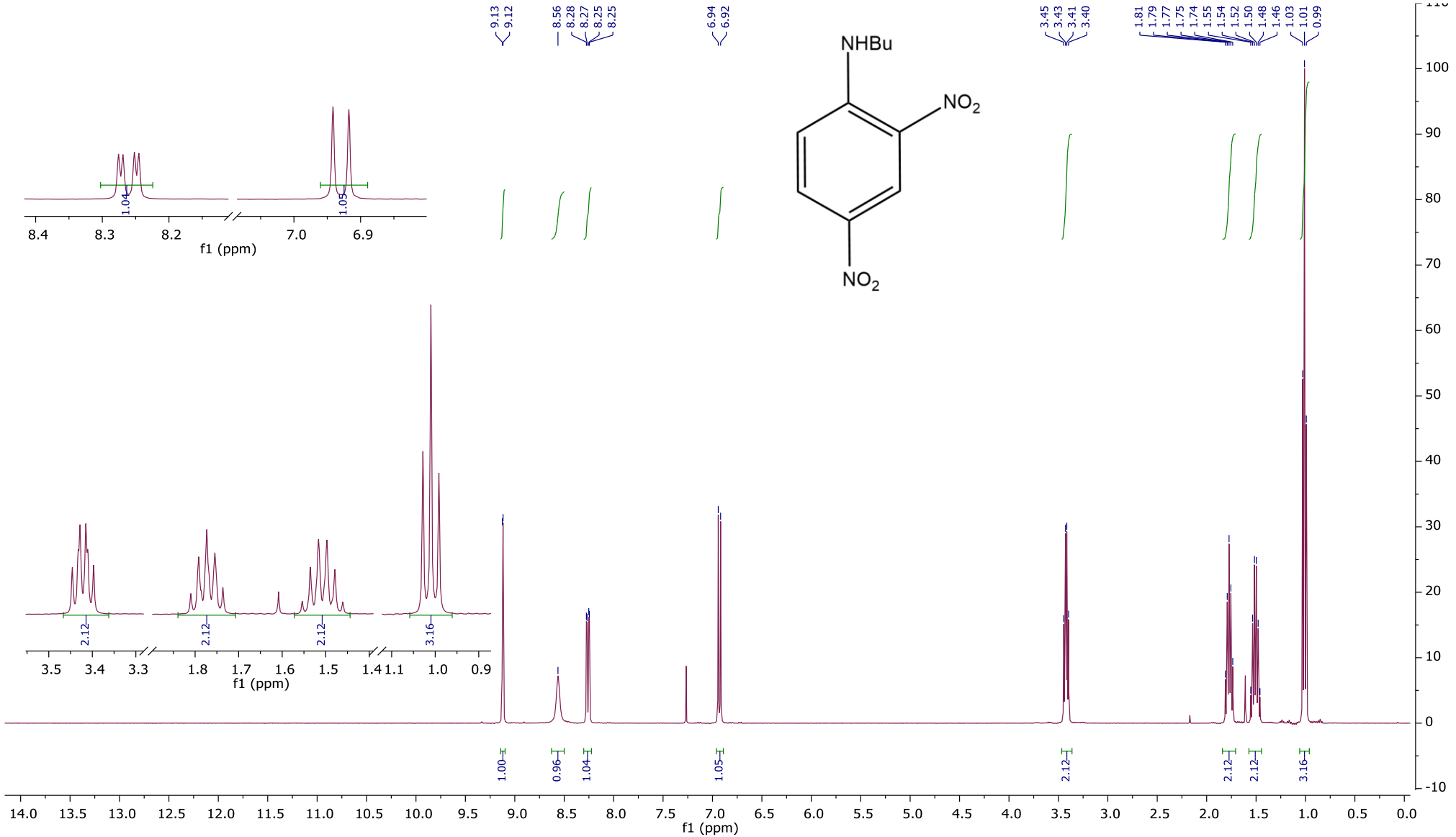
^{1}H NMR spectrum ($CDCl_3$) of *N*-benzyl-2,4-dinitroaniline **1e**



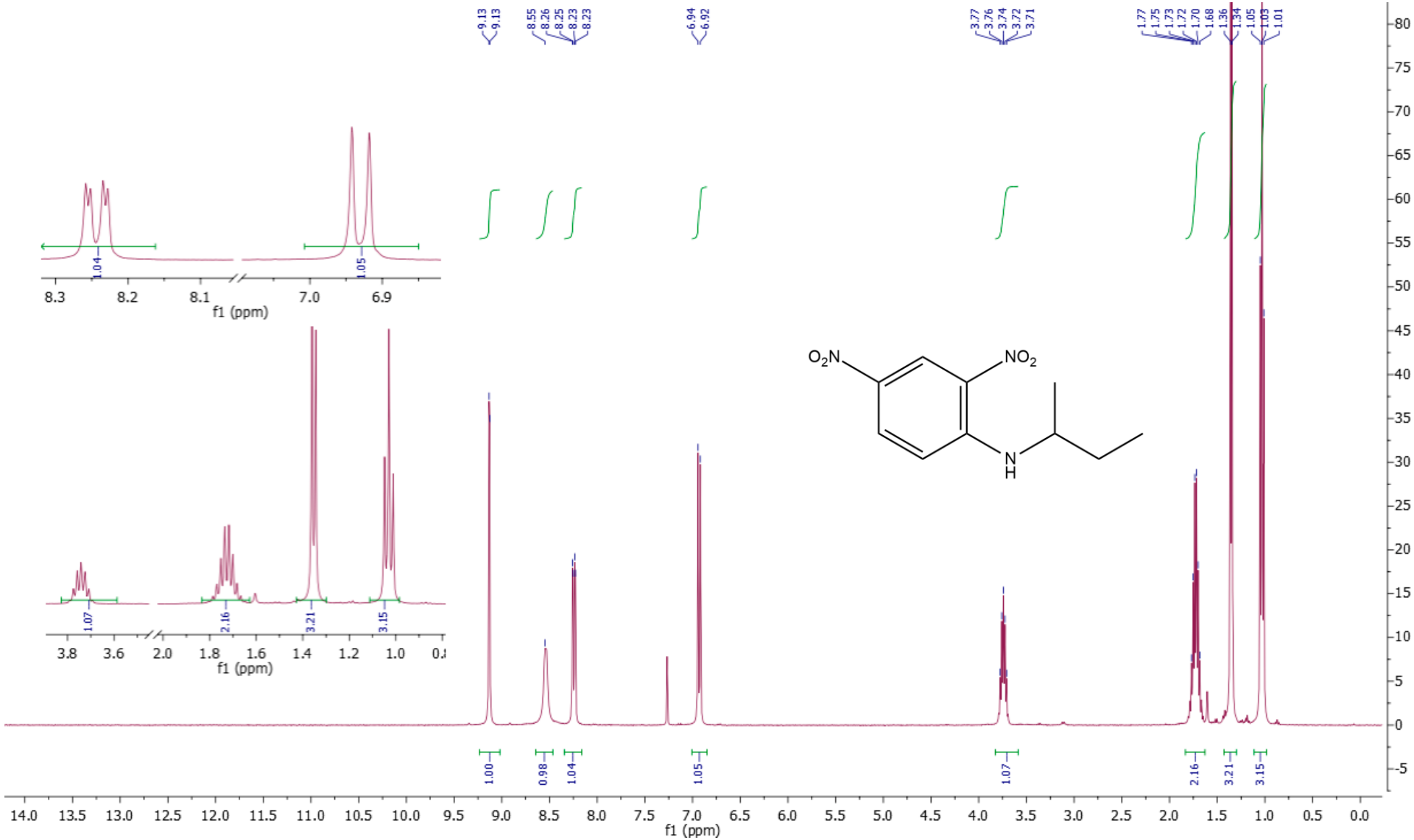
^{1}H NMR spectrum ($CDCl_3$) of *N*-methyl-2,4-dinitroaniline **1f**



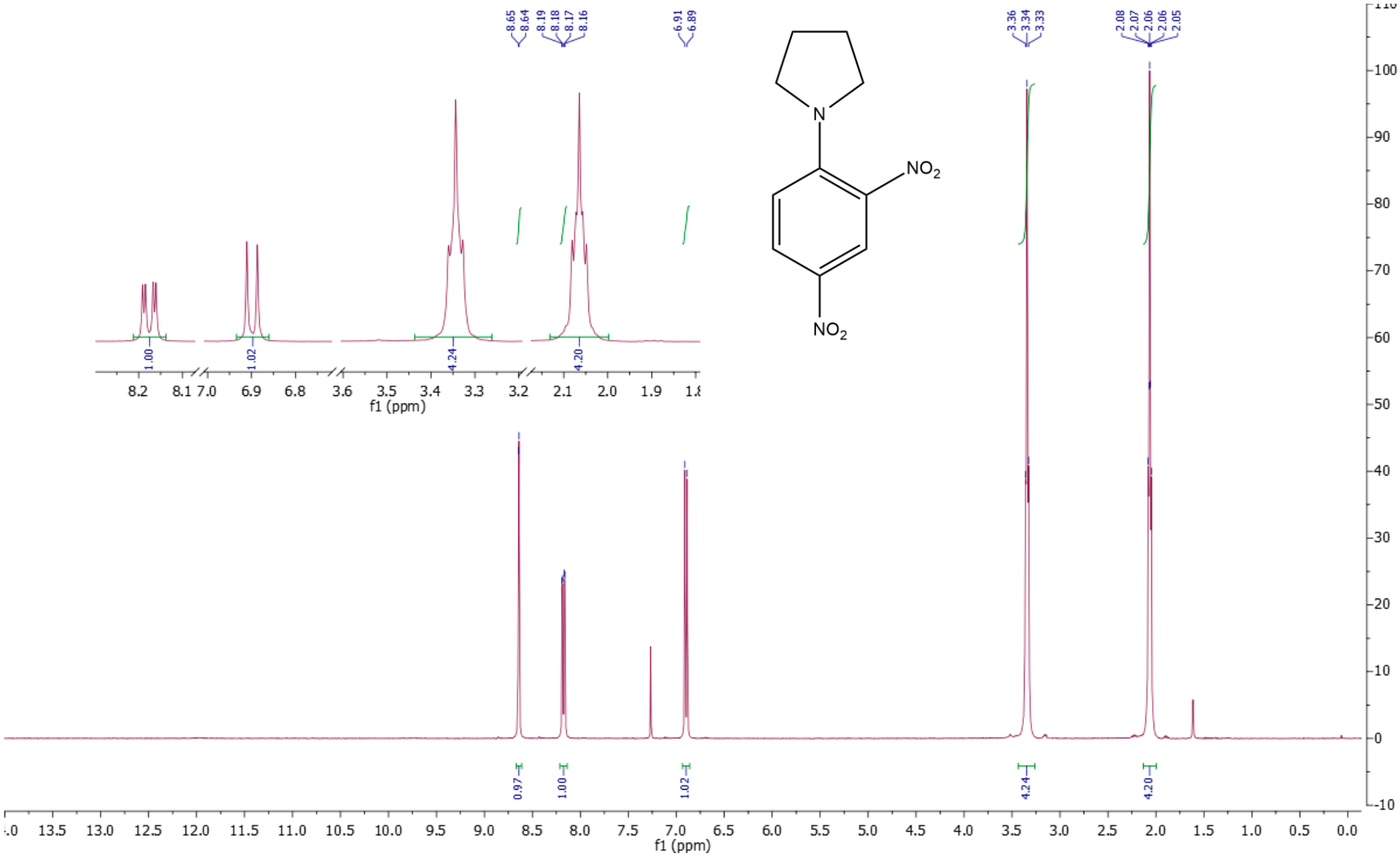
^{1}H NMR spectrum ($CDCl_3$) of 2,4-dinitro-*N*-propylaniline **1g**



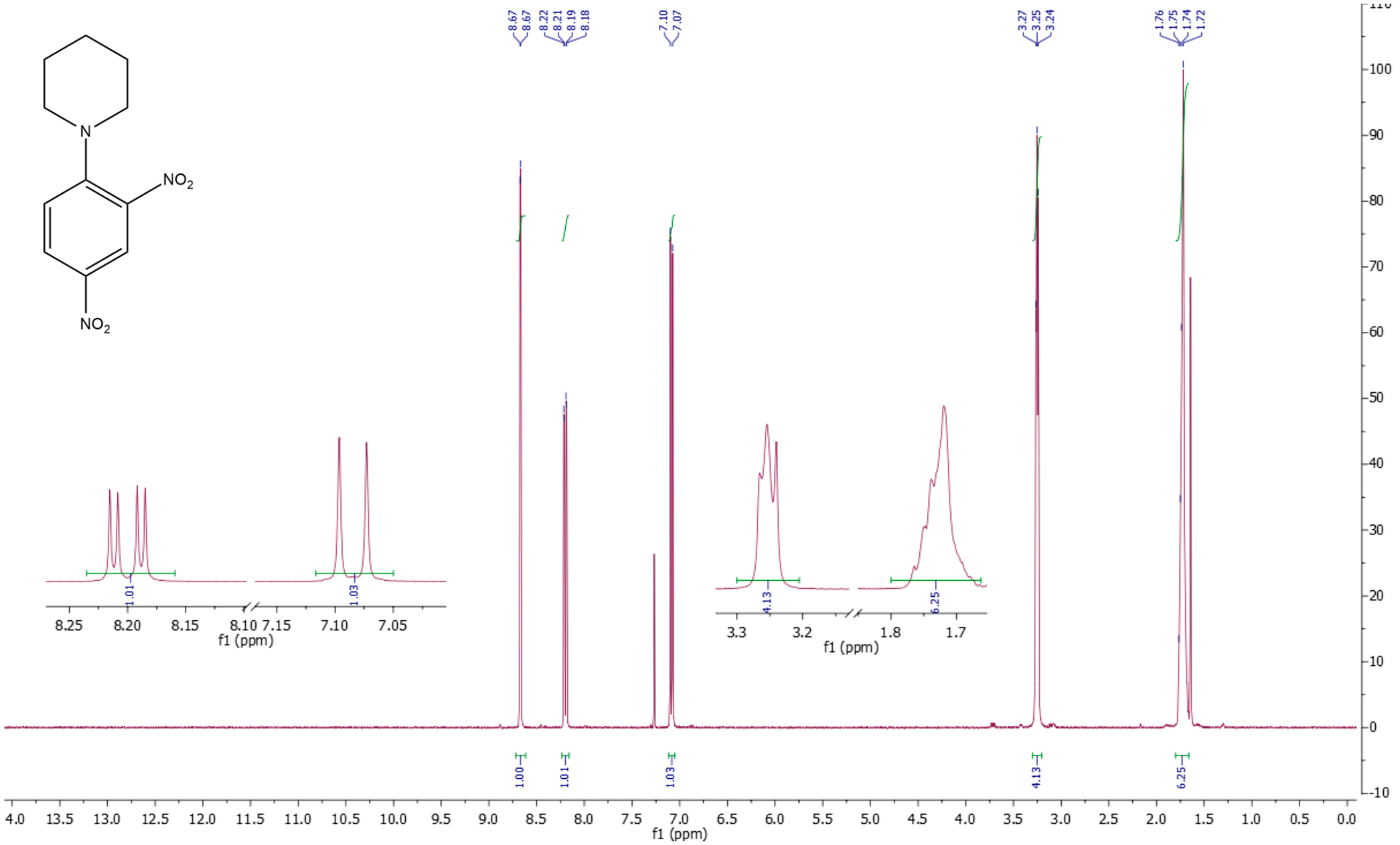
^{1}H NMR spectrum (CDCl3) of *N*-butyl-2,4-dinitroaniline **1h**



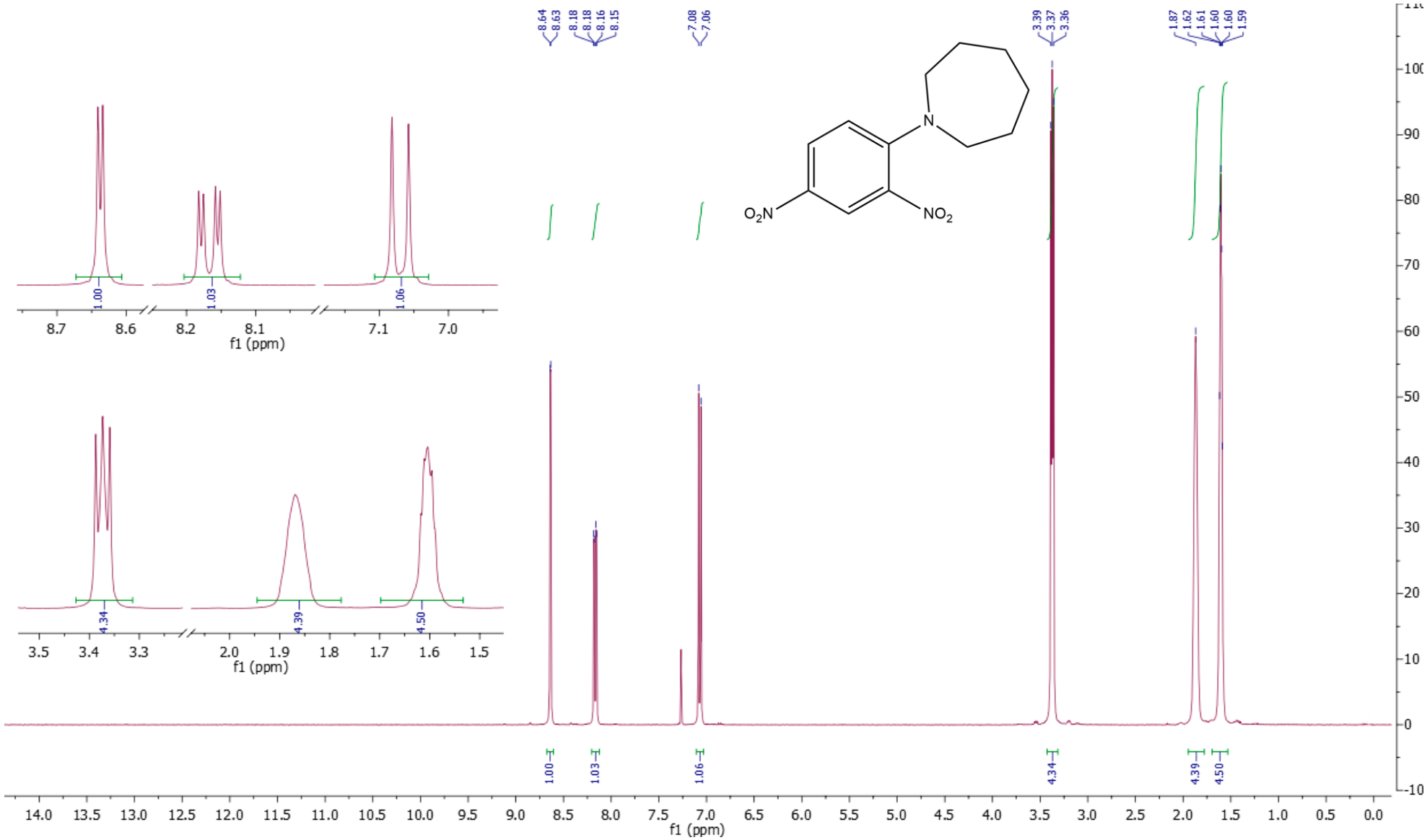
^{1}H NMR spectrum ($CDCl_3$) of *N*-sec-butyl-2,4-dinitroaniline **1i**



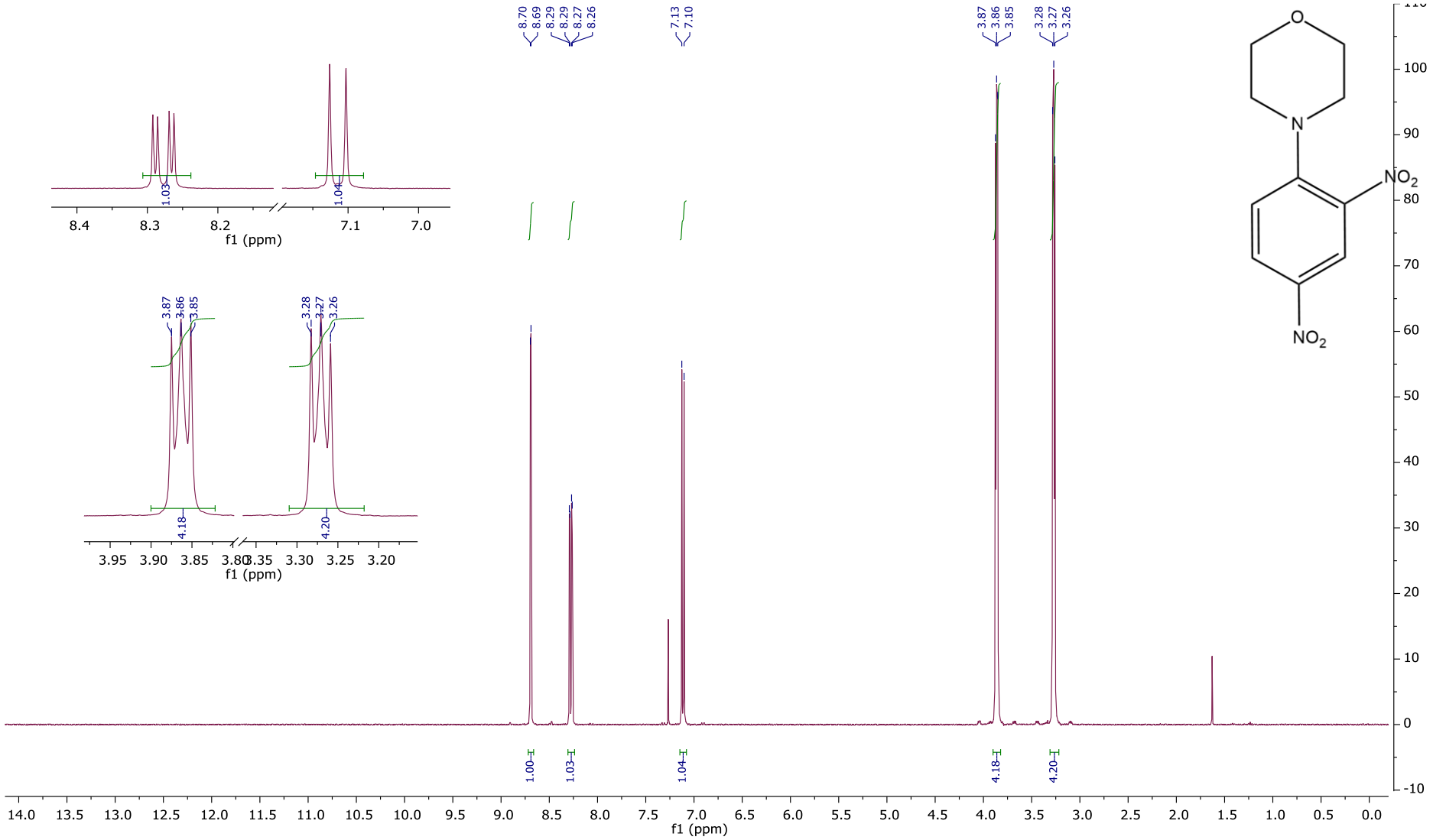
^{1}H NMR spectrum ($CDCl_3$) of *N*-(2,4-dinitrophenyl)pyrrolidine **1j**



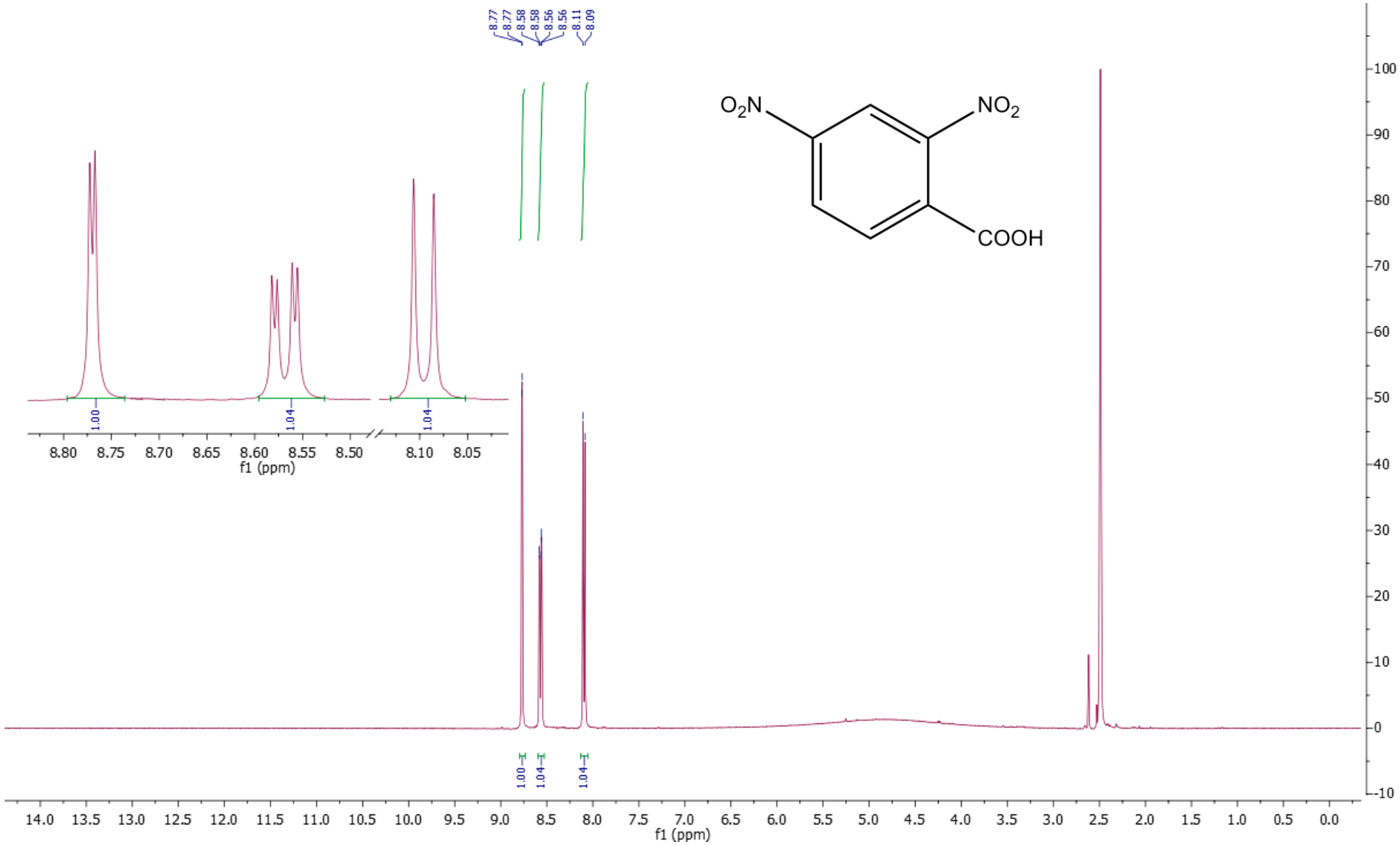
^{1}H NMR spectrum ($CDCl_3$) of *N*-(2,4-dinitrophenyl)piperidine **1k**



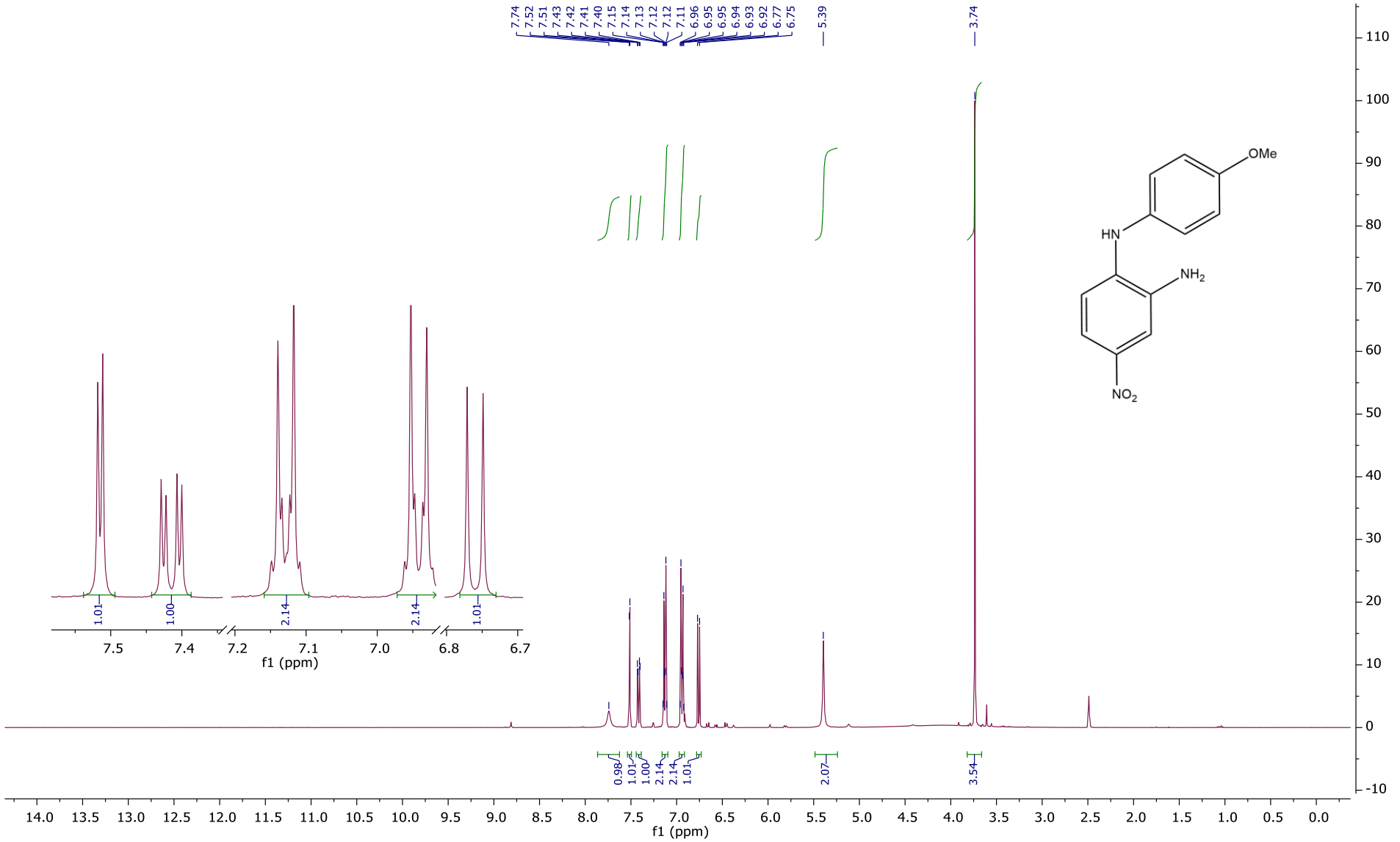
^{1}H NMR spectrum (CDCl3) of *N*-(2,4-dinitrophenyl)azepane **1l**



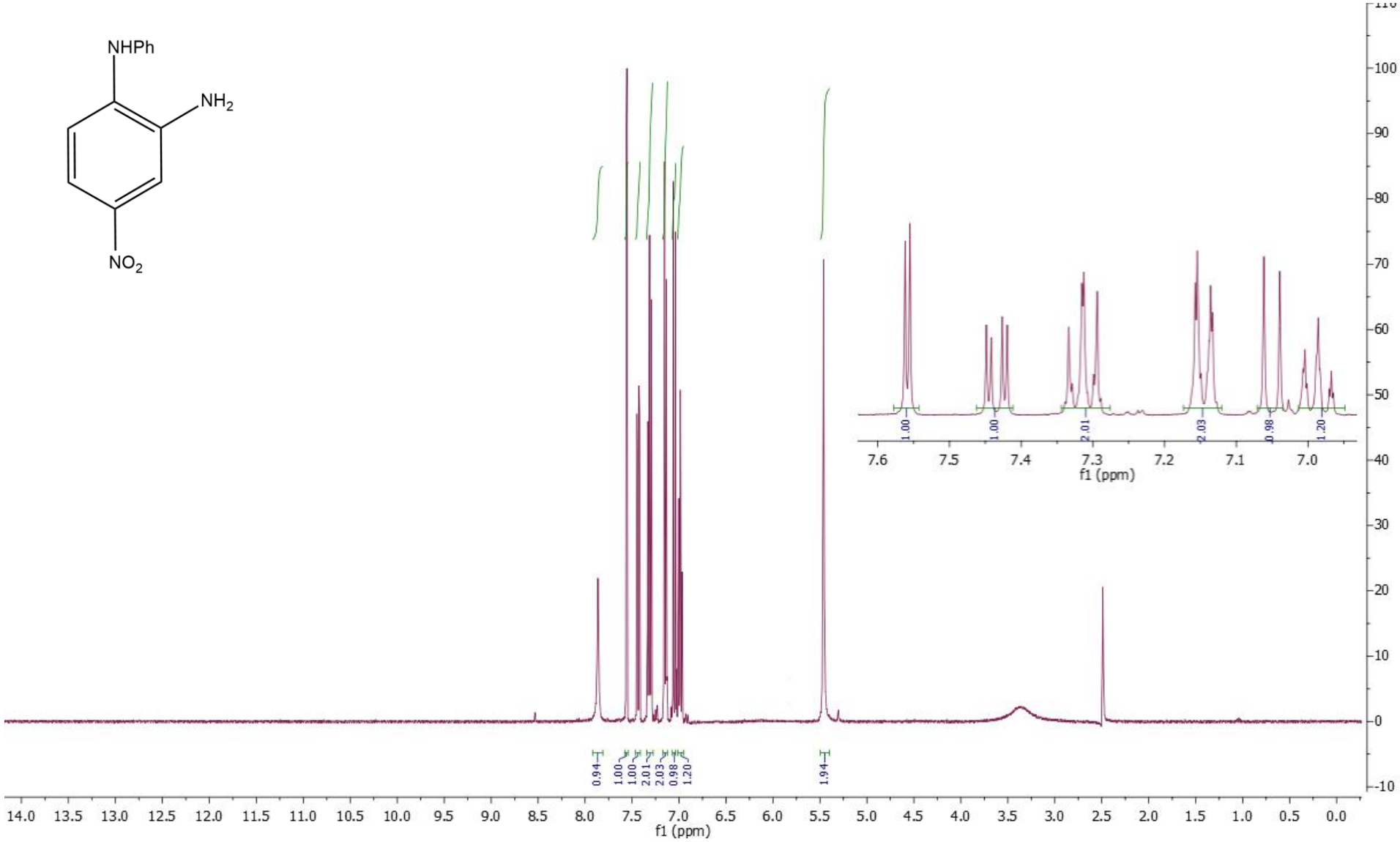
^{1}H NMR spectrum ($CDCl_3$) of *N*-(2,4-dinitrophenyl)morpholine **1m**



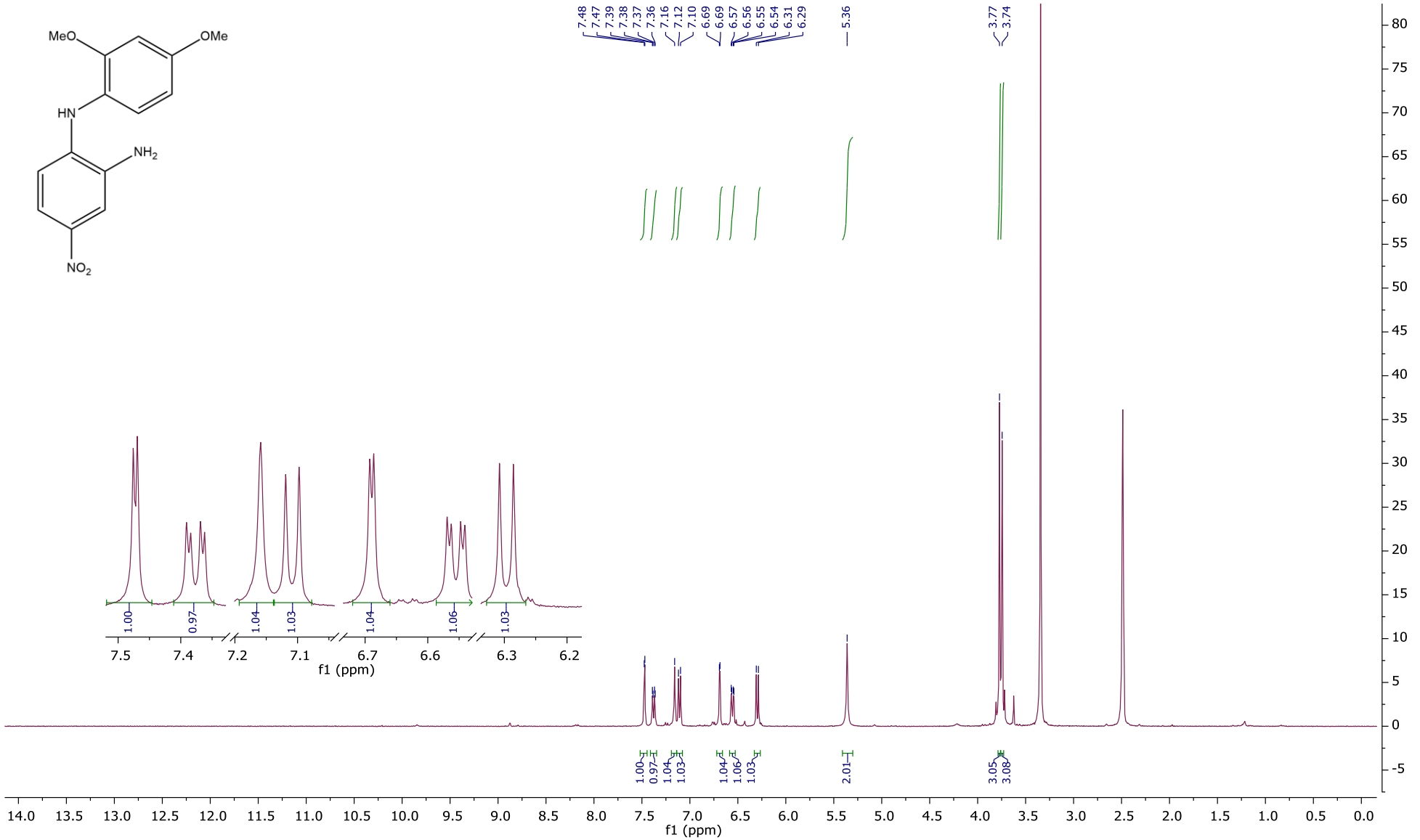
^{1}H NMR spectrum (DMSO-d_6) of 2,4-dinitrobenzoic acid



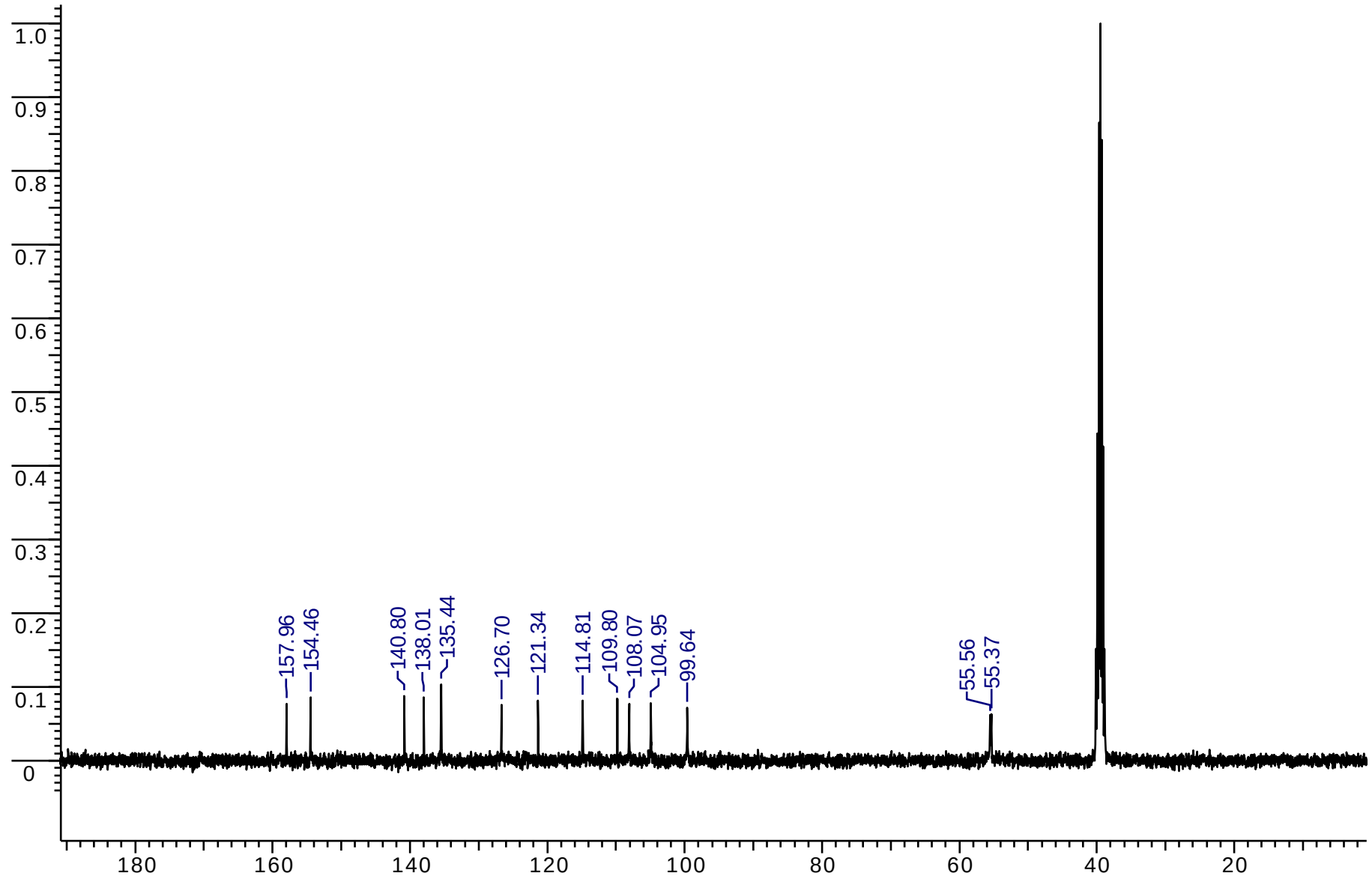
^{1}H NMR spectrum (DMSO-d$_6$) of N^1-(4-methoxyphenyl)-4-nitrobenzene-1,2-diamine **2a**



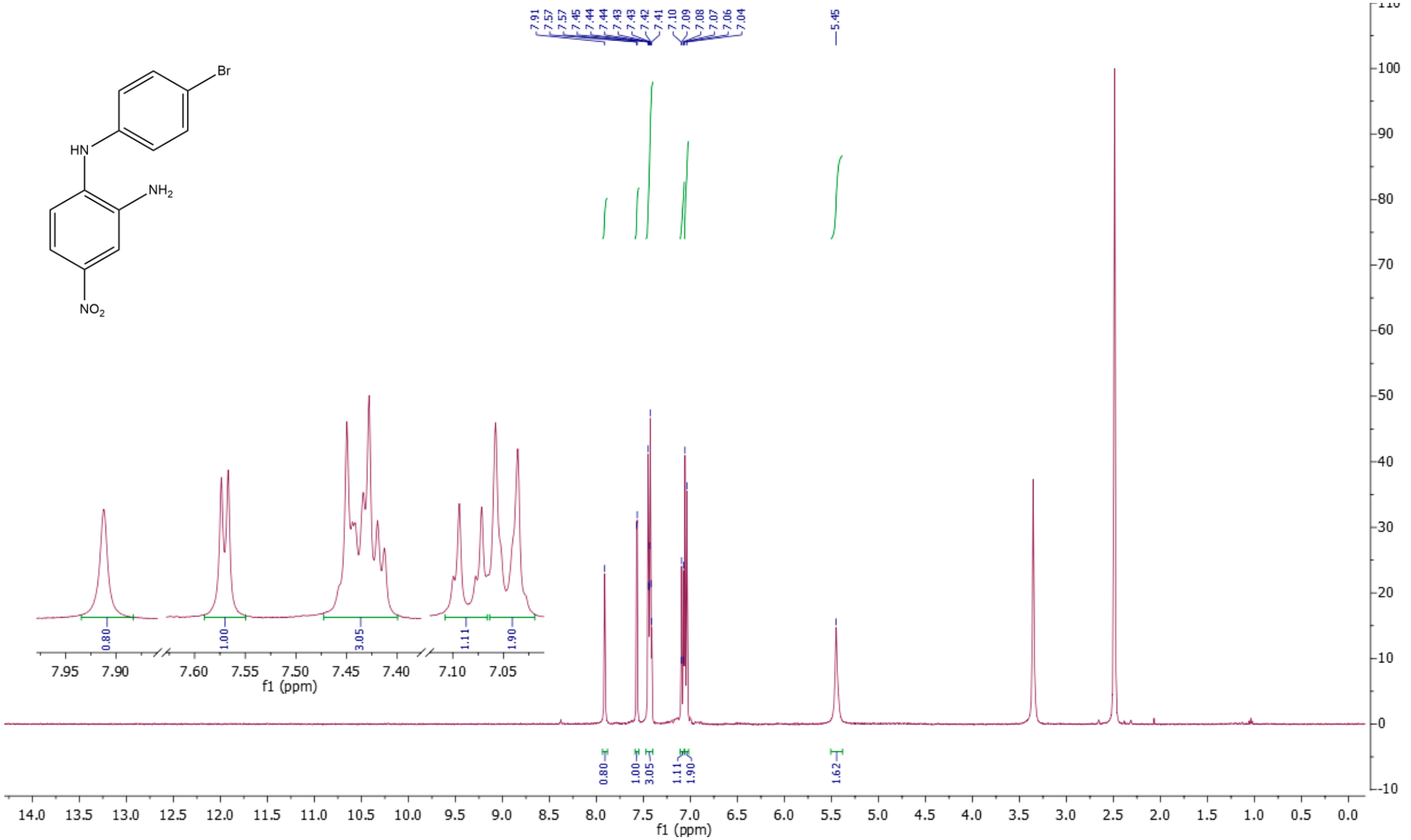
^{1}H NMR spectrum (DMSO-d$_6$) of 4-nitro-*N*^{1}-phenylbenzene-1,2-diamine **2b**



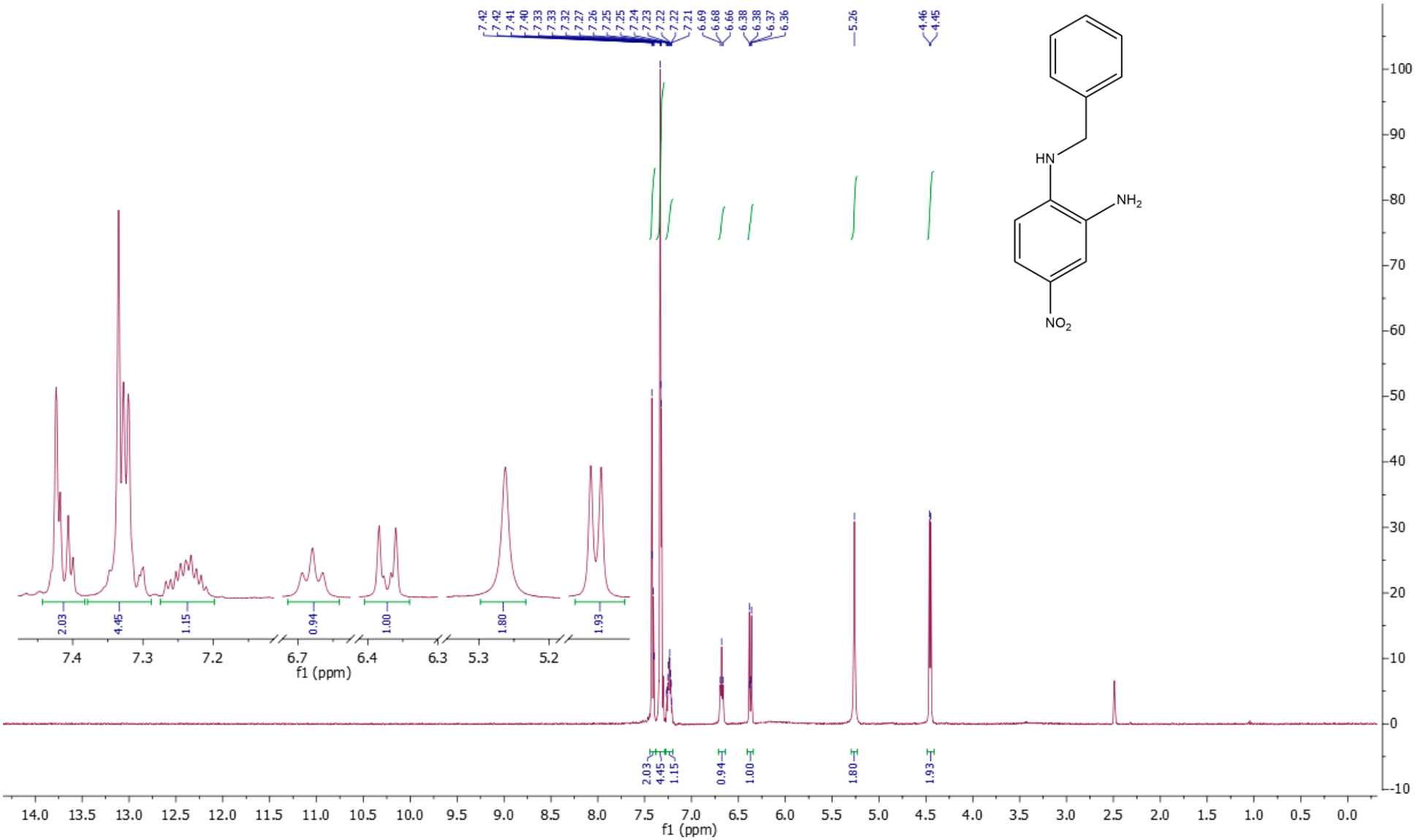
^{1}H NMR spectrum (DMSO-d$_6$) of *N*^{1}-(2,4-dimethoxyphenyl)-4-nitrobenzene-1,2-diamine **2c**



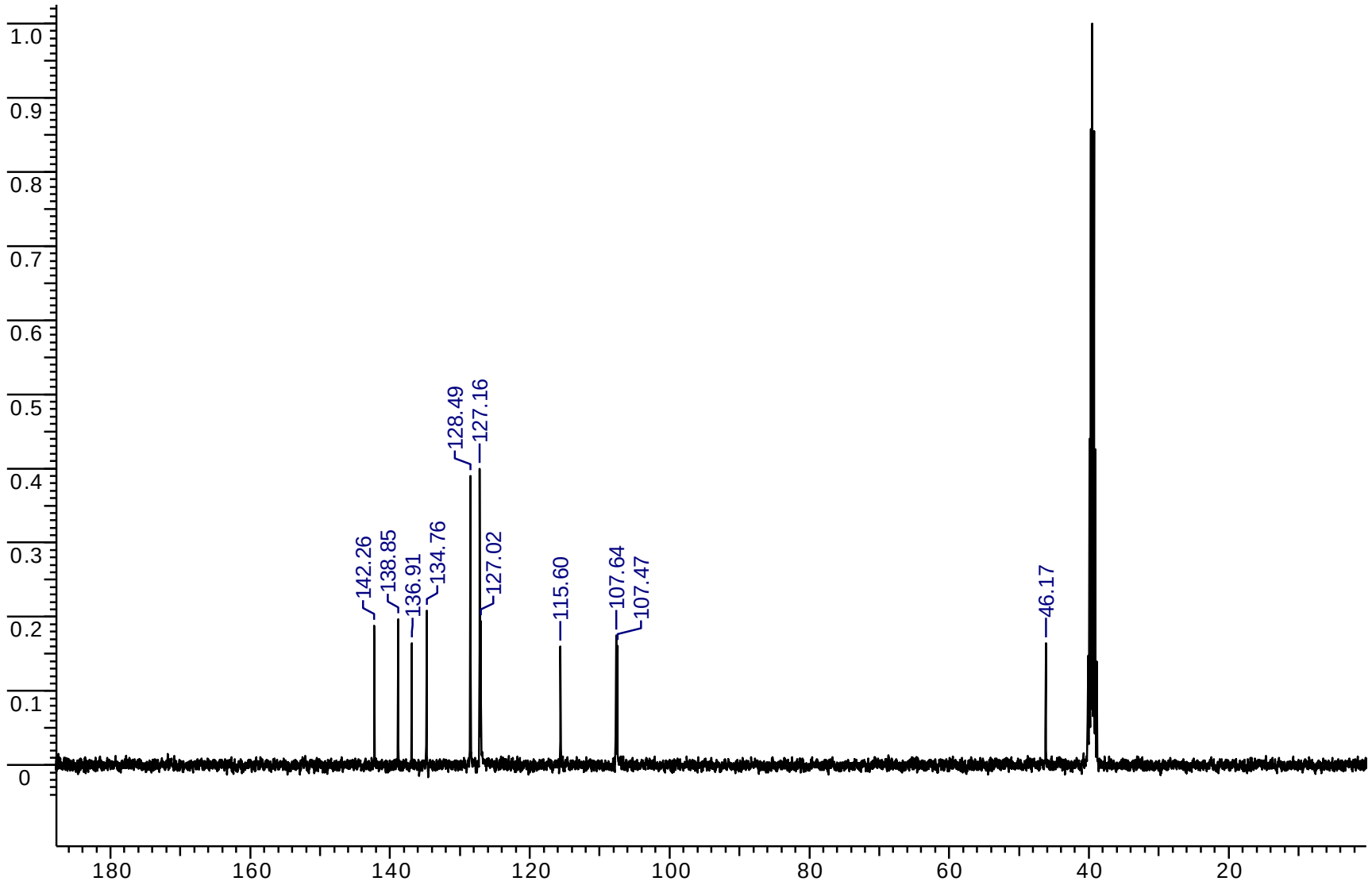
^{13}C NMR spectrum (DMSO-d$_6$) *N*^{1}-(2,4-dimethoxyphenyl)-4-nitrobenzene-1,2-diamine **2c**



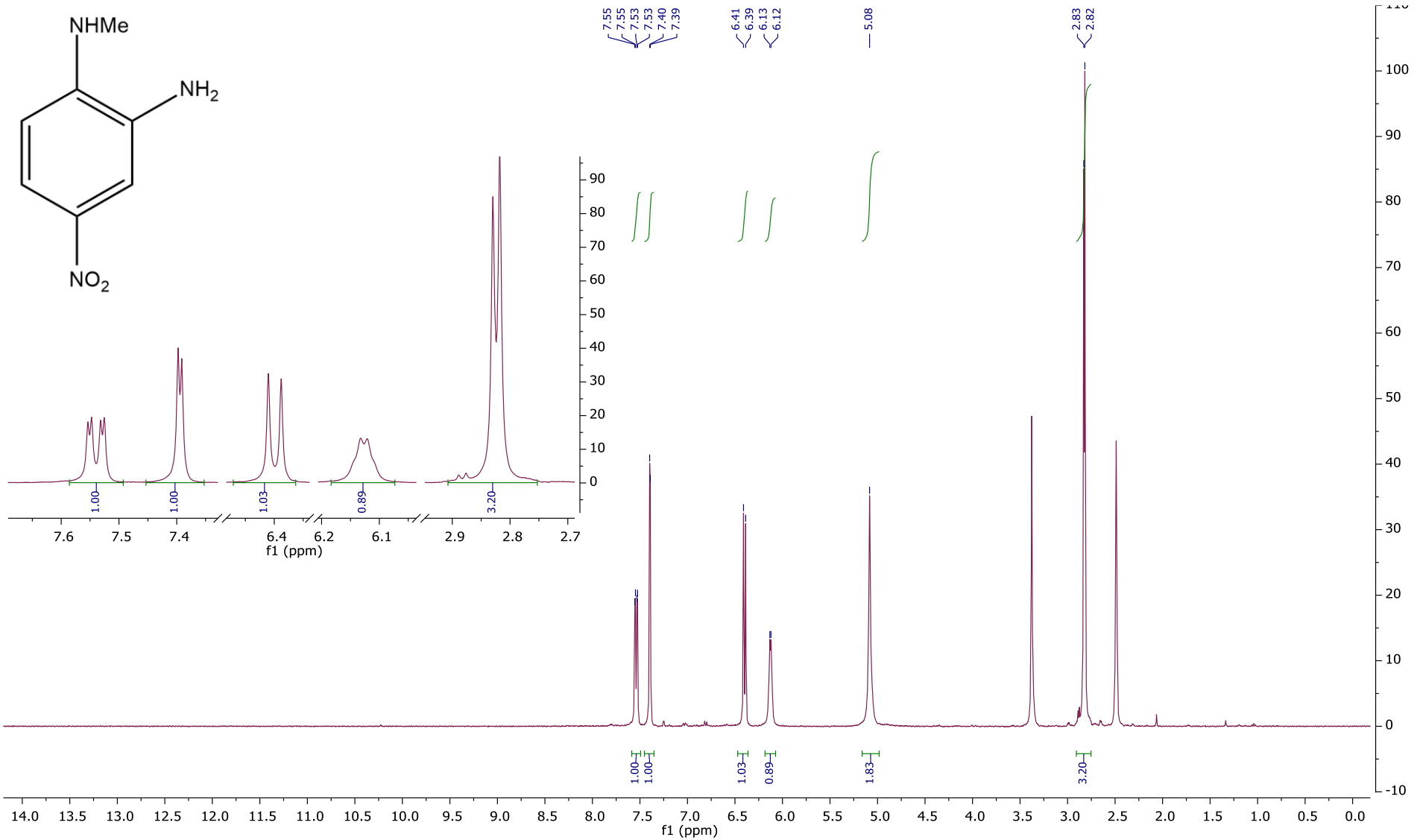
^{1}H NMR spectrum (DMSO-d$_6$) of *N*^{1}-(4-bromophenyl)-4-nitrobenzene-1,2-diamine **2d**



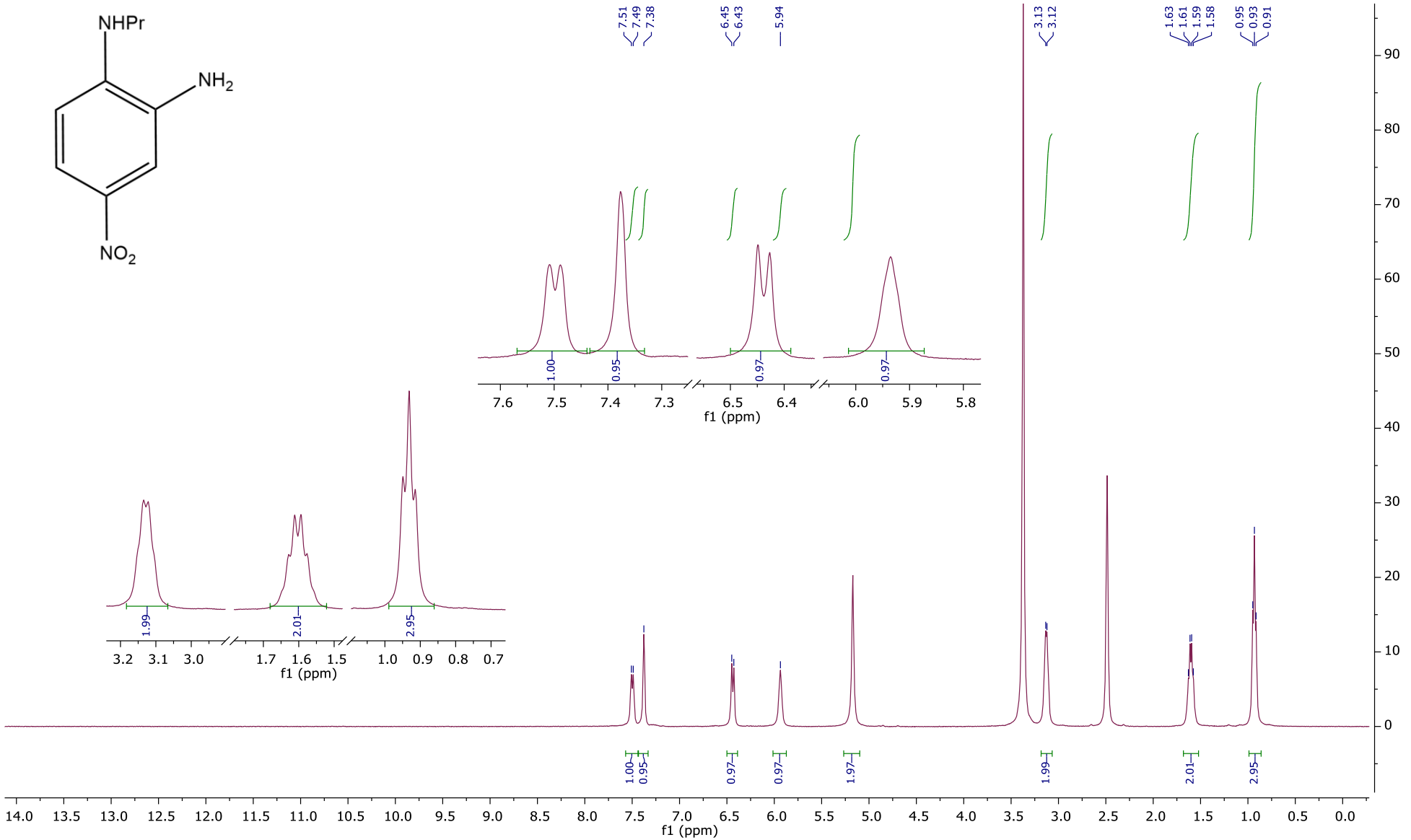
^{1}H NMR spectrum (DMSO-d$_6$) of *N*^{1}-benzyl-4-nitrobenzene-1,2-diamine **2e**



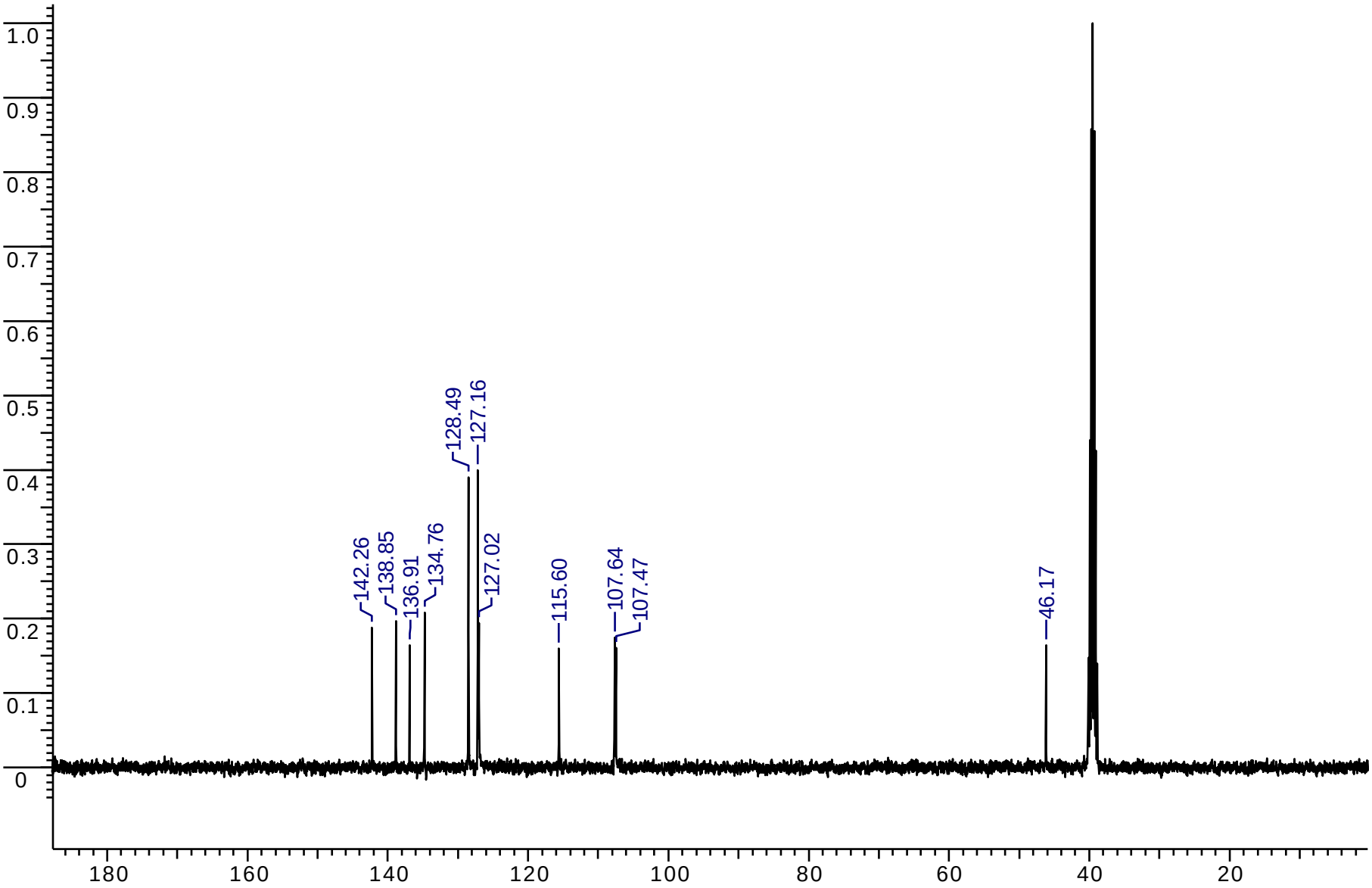
^{13}C NMR spectrum (DMSO-d$_6$) *N*^{1}-benzyl-4-nitrobenzene-1,2-diamine **2e**



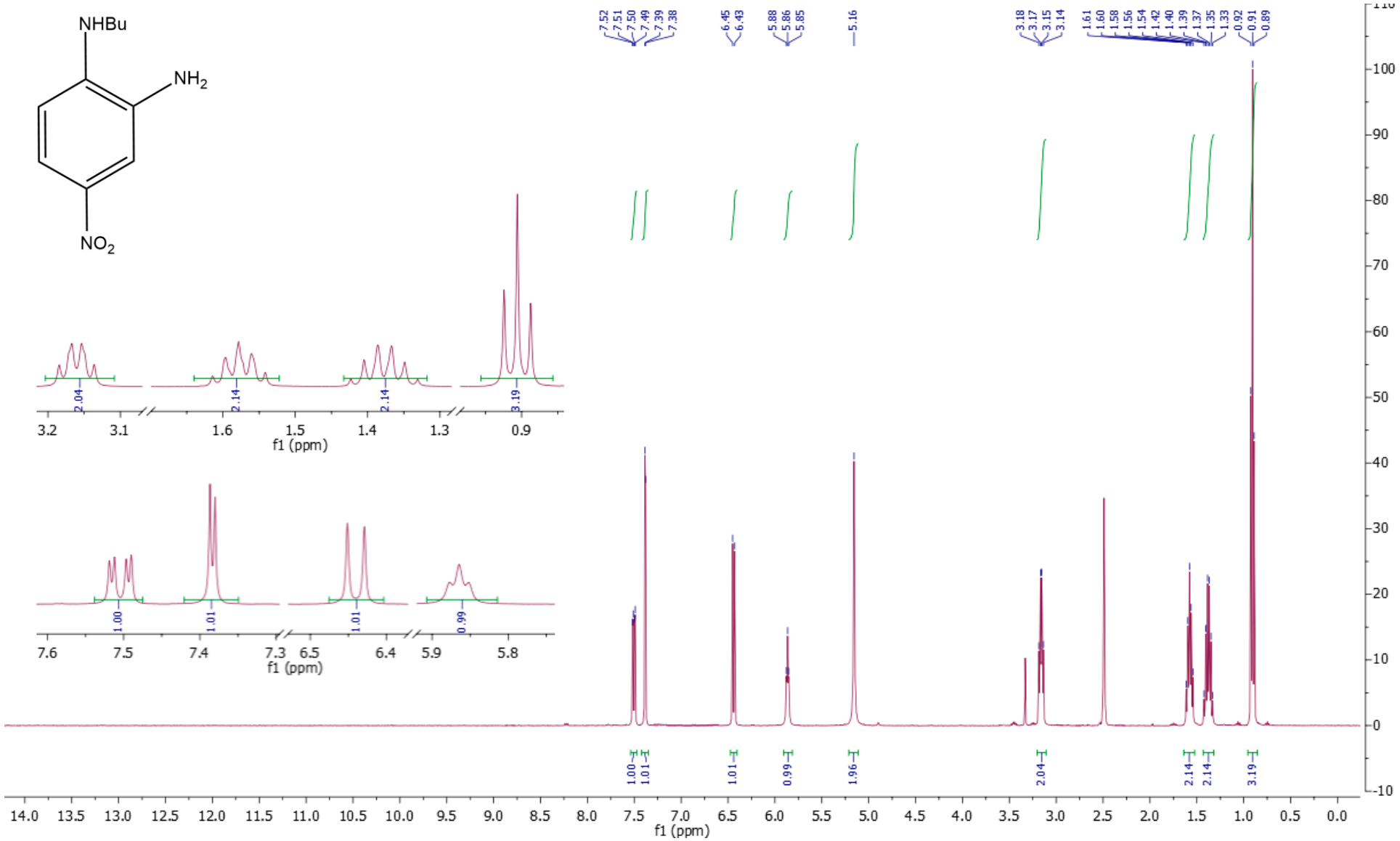
^{1}H NMR spectrum (DMSO-d$_6$) of *N*^{1}-methyl-4-nitrobenzene-1,2-diamine **2f**



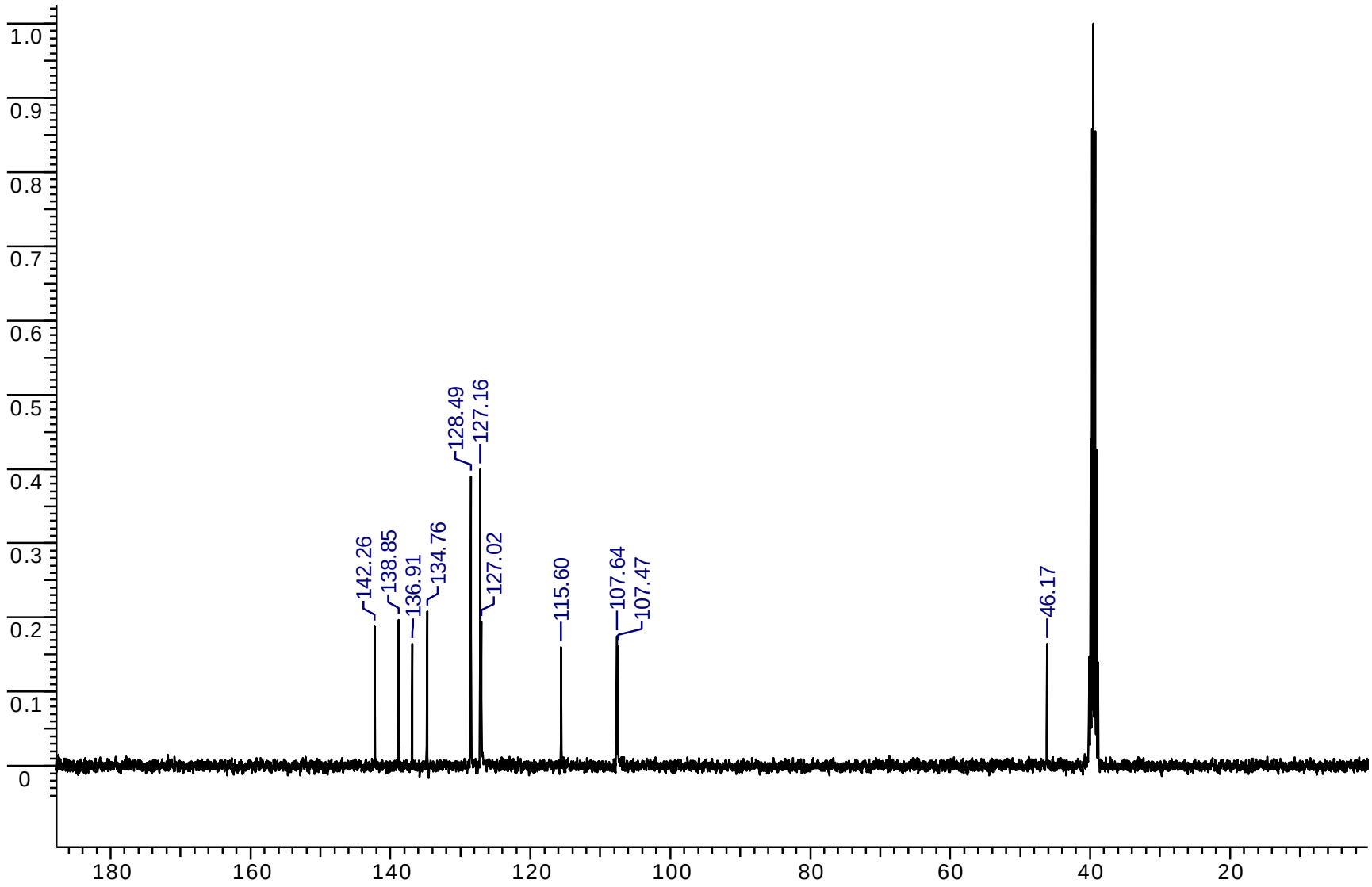
^{1}H NMR spectrum (DMSO-d$_6$) of 4-nitro-*N*^{1}-*n*-propylbenzene-1,2-diamine **2g**



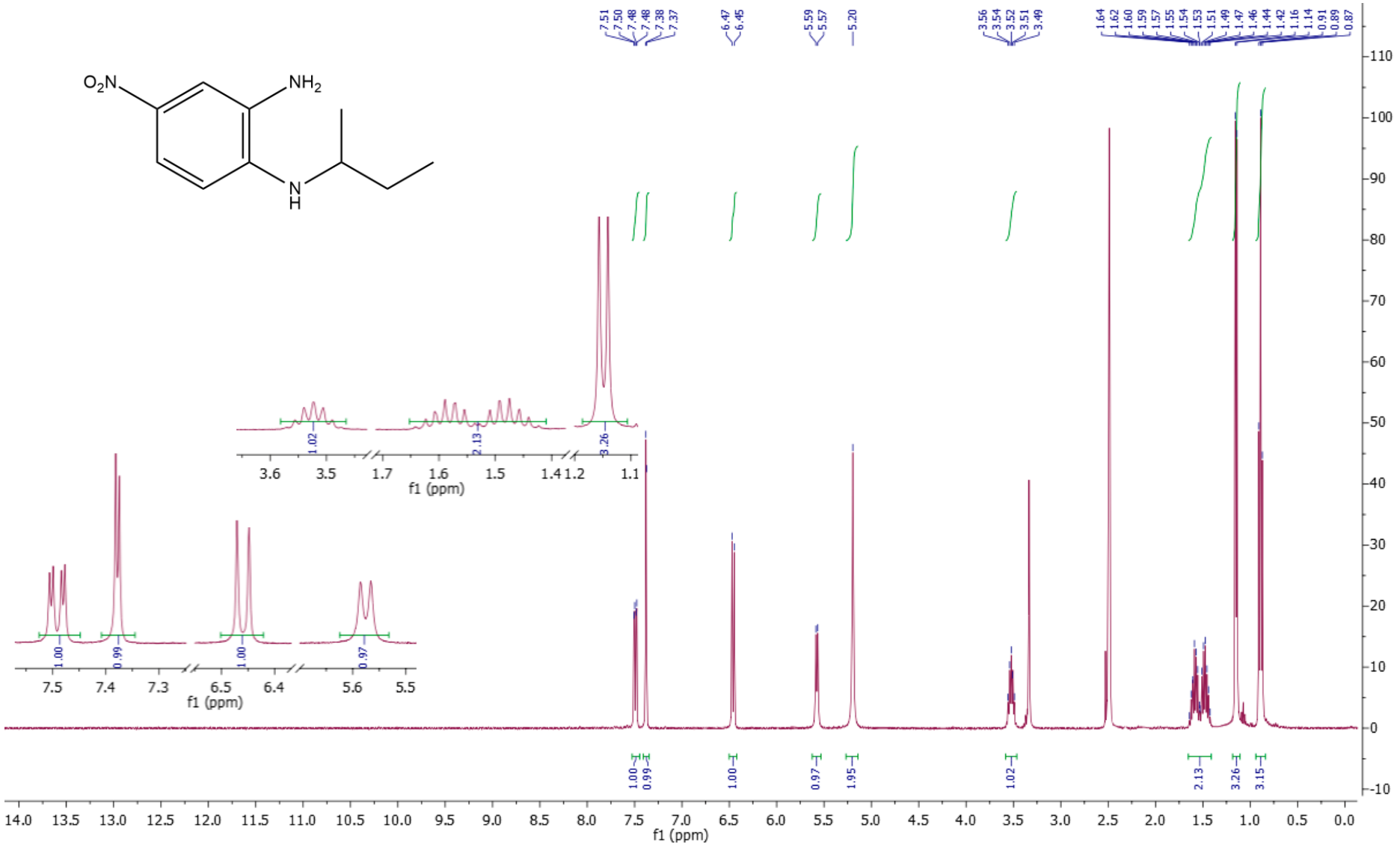
^{13}C NMR spectrum (DMSO-d$_6$) 4-nitro-*N*^{1}-*n*-propylbenzene-1,2-diamine **2g**



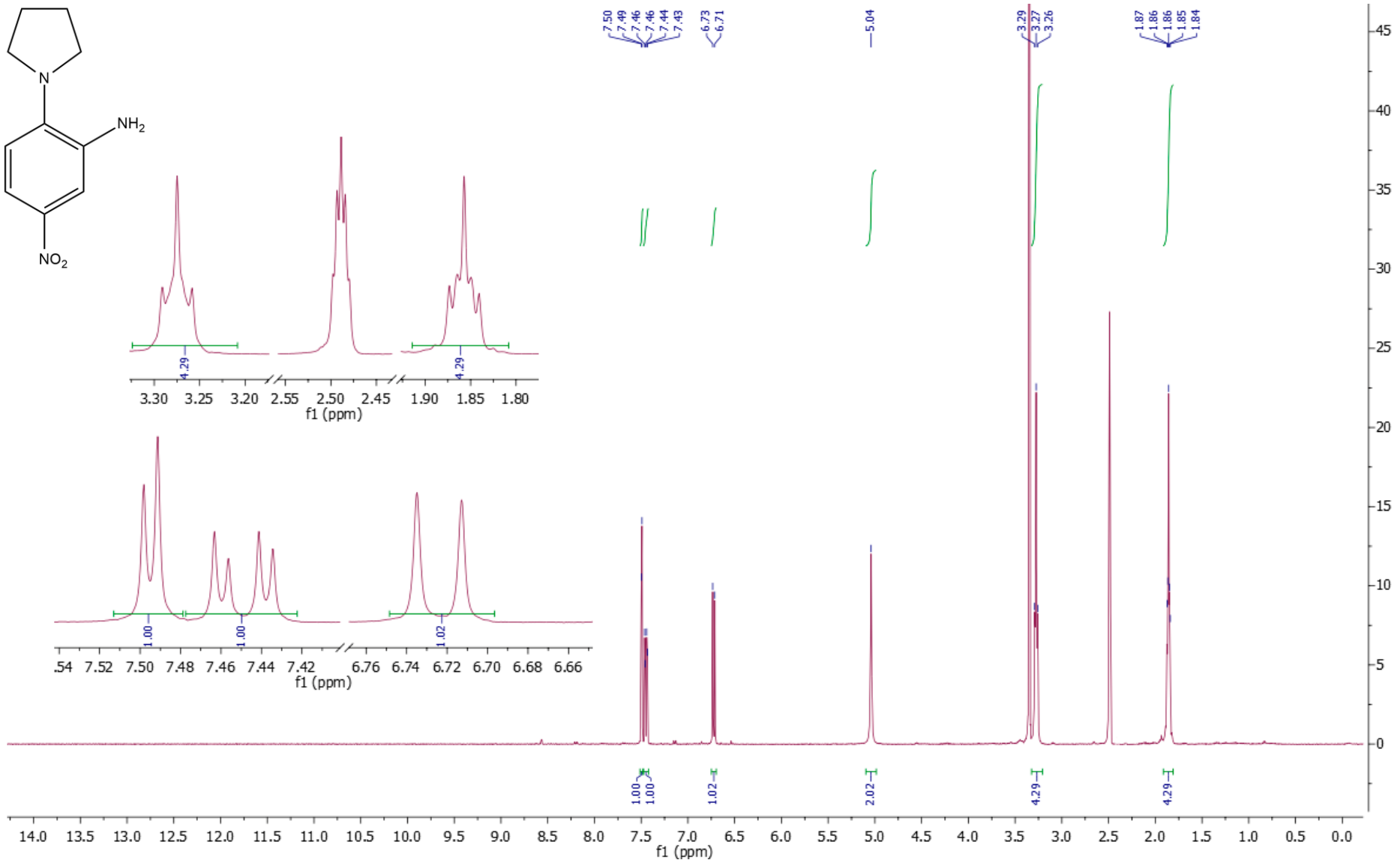
^{1}H NMR spectrum (DMSO-d$_6$) of *N*^{1}-*n*-butyl-4-nitrobenzene-1,2-diamine **2h**



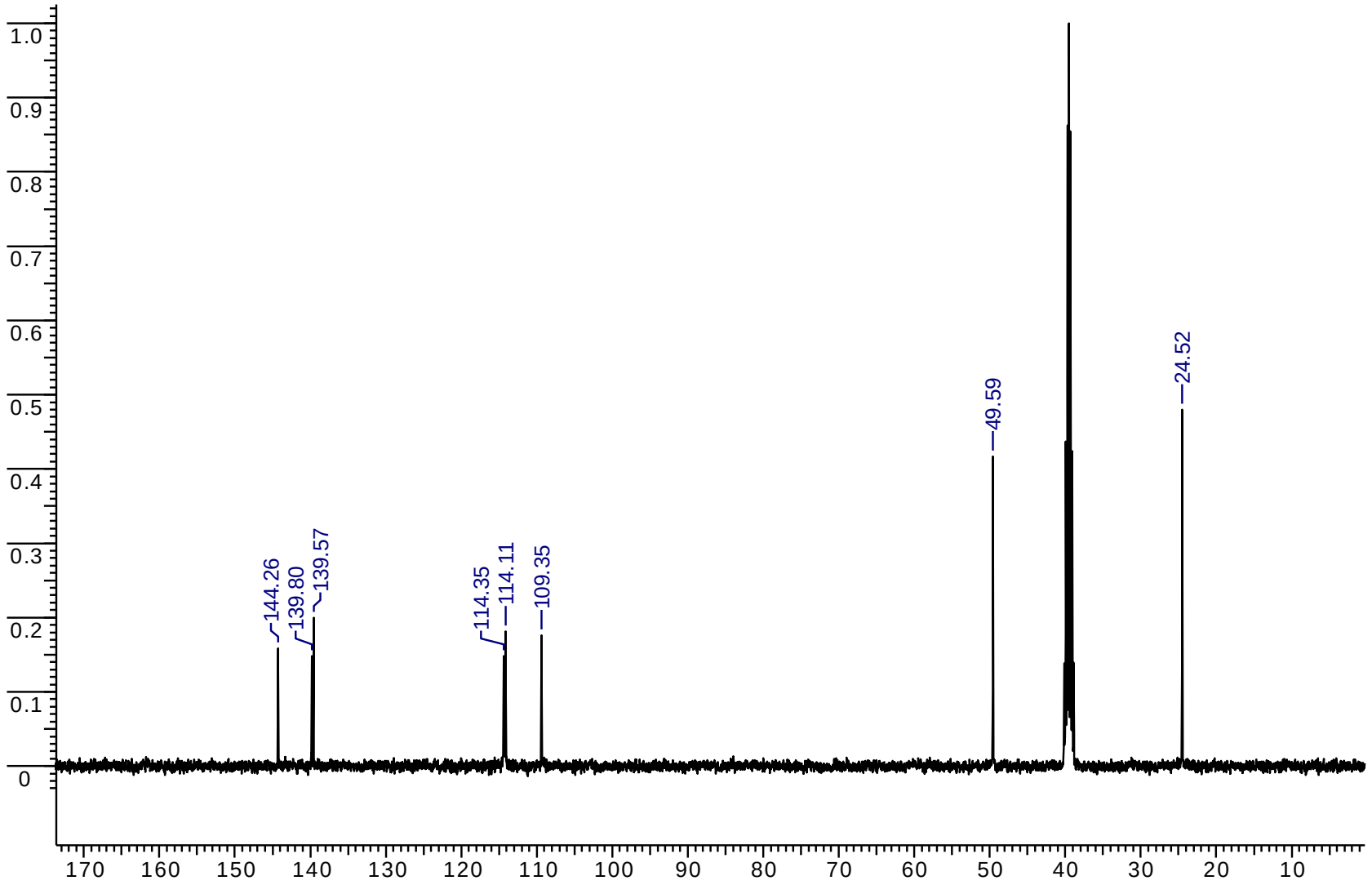
^{13}C NMR spectrum (DMSO-d$_6$) *N*^{1}-n-butyl-4-nitrobenzene-1,2-diamine **2h**



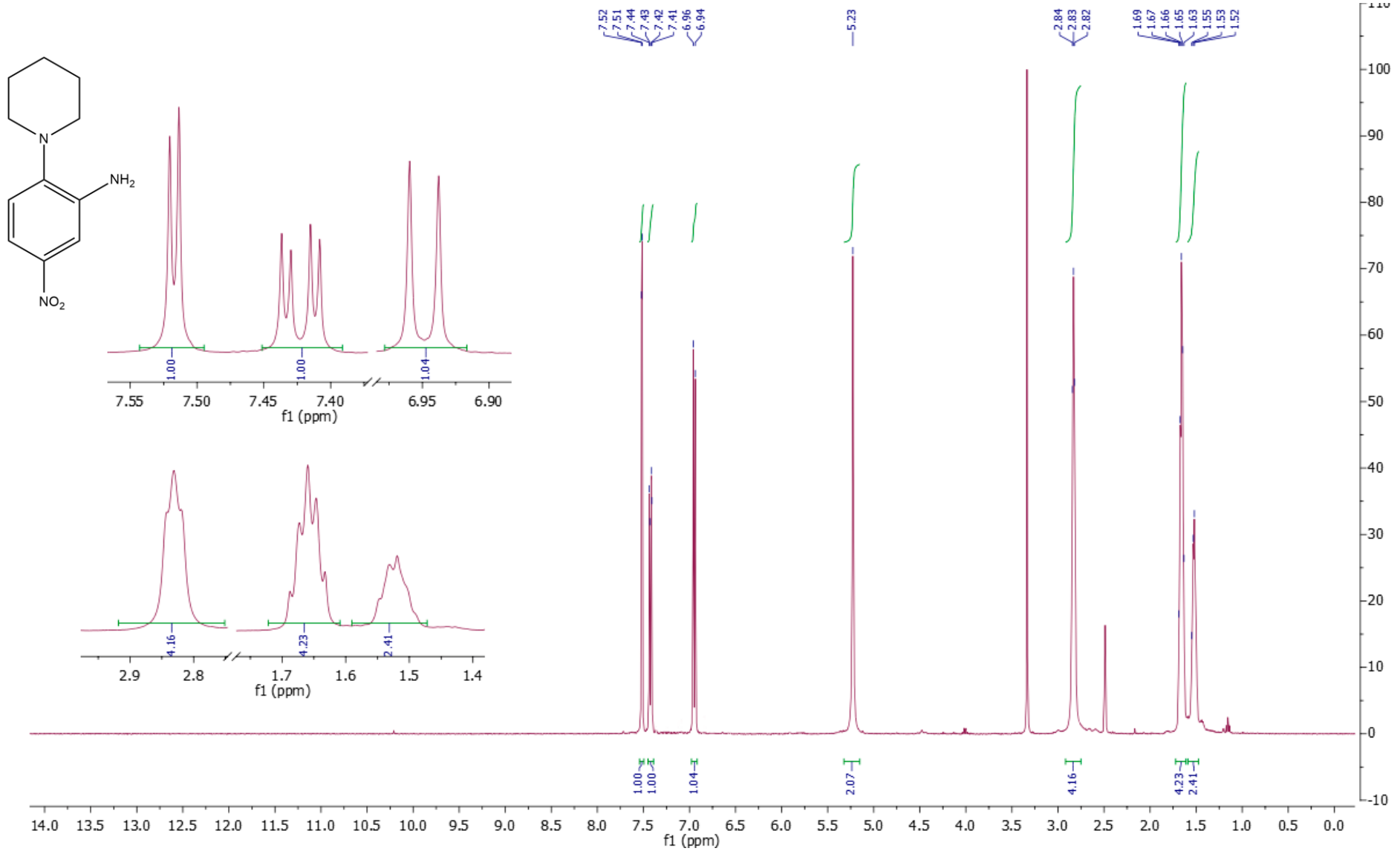
^{1}H NMR spectrum (DMSO-d$_6$) of *N*^{1}-sec-butyl-4-nitrobenzene-1,2-diamine **2i**



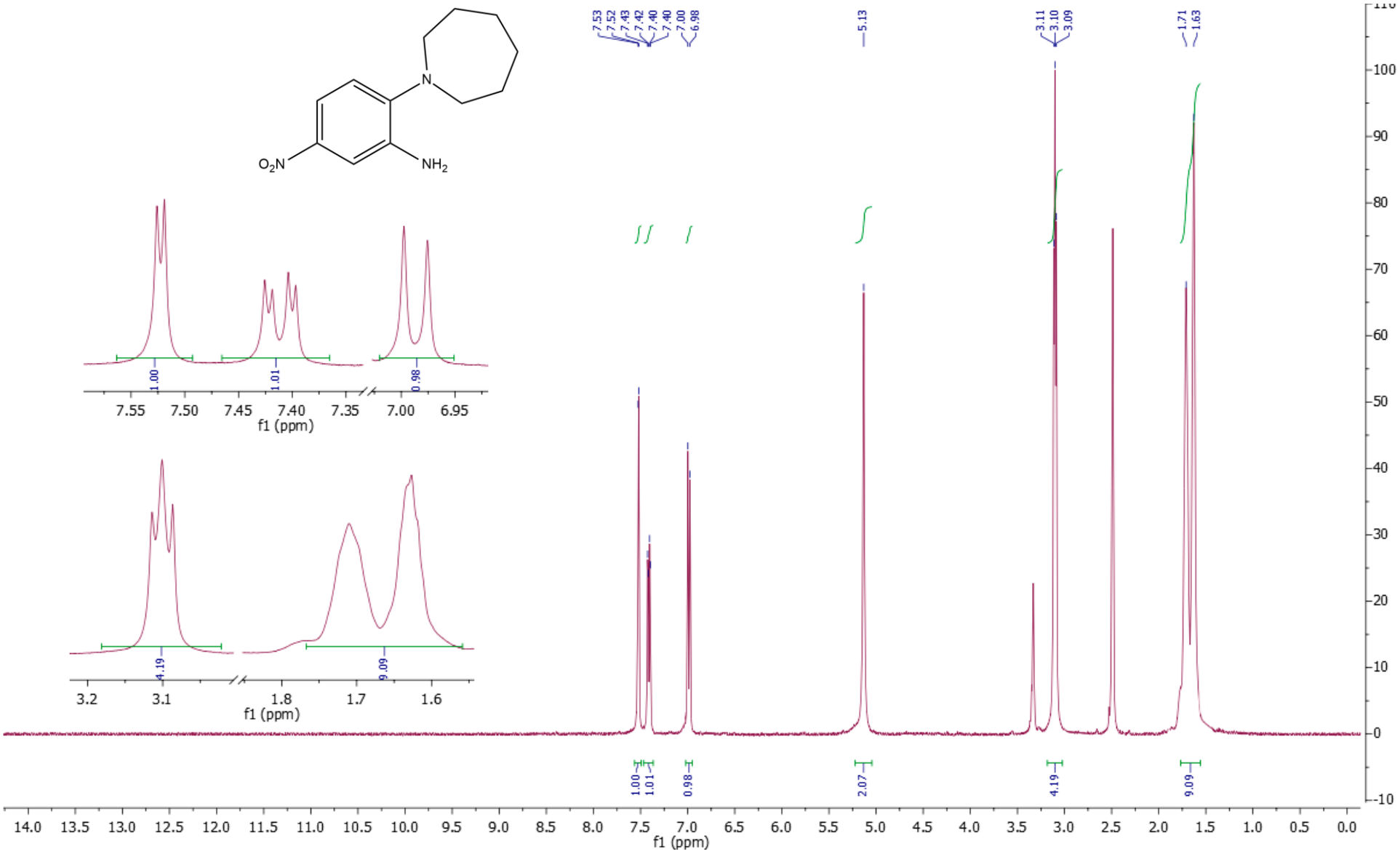
^{1}H NMR spectrum (DMSO-d_6) of 5-nitro-2-(1-pyrrolidinyl)aniline **2j**



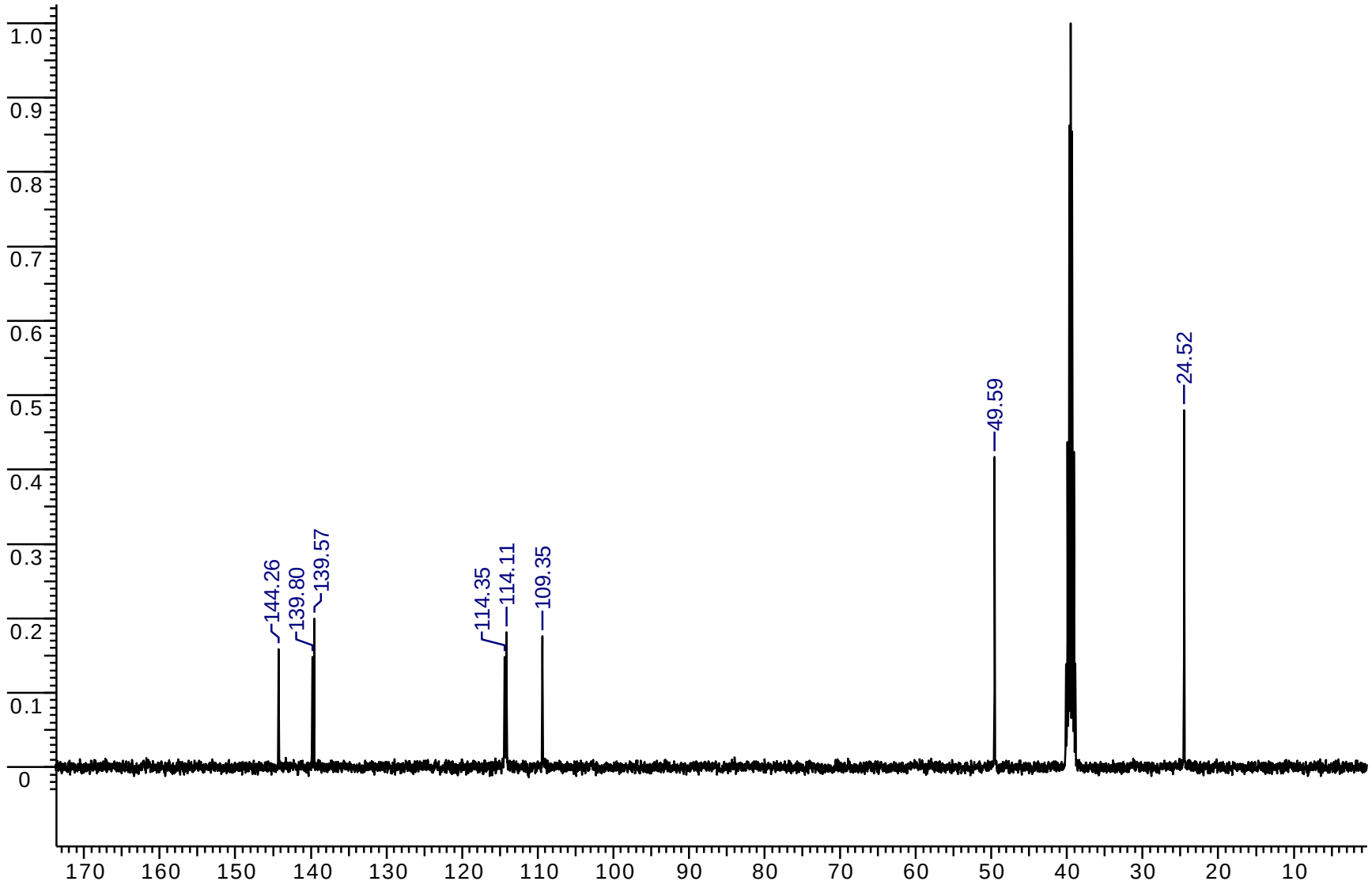
^{13}C NMR spectrum (DMSO-d$_6$) 5-nitro-2-(1-pyrrolidinyl)aniline **2j**



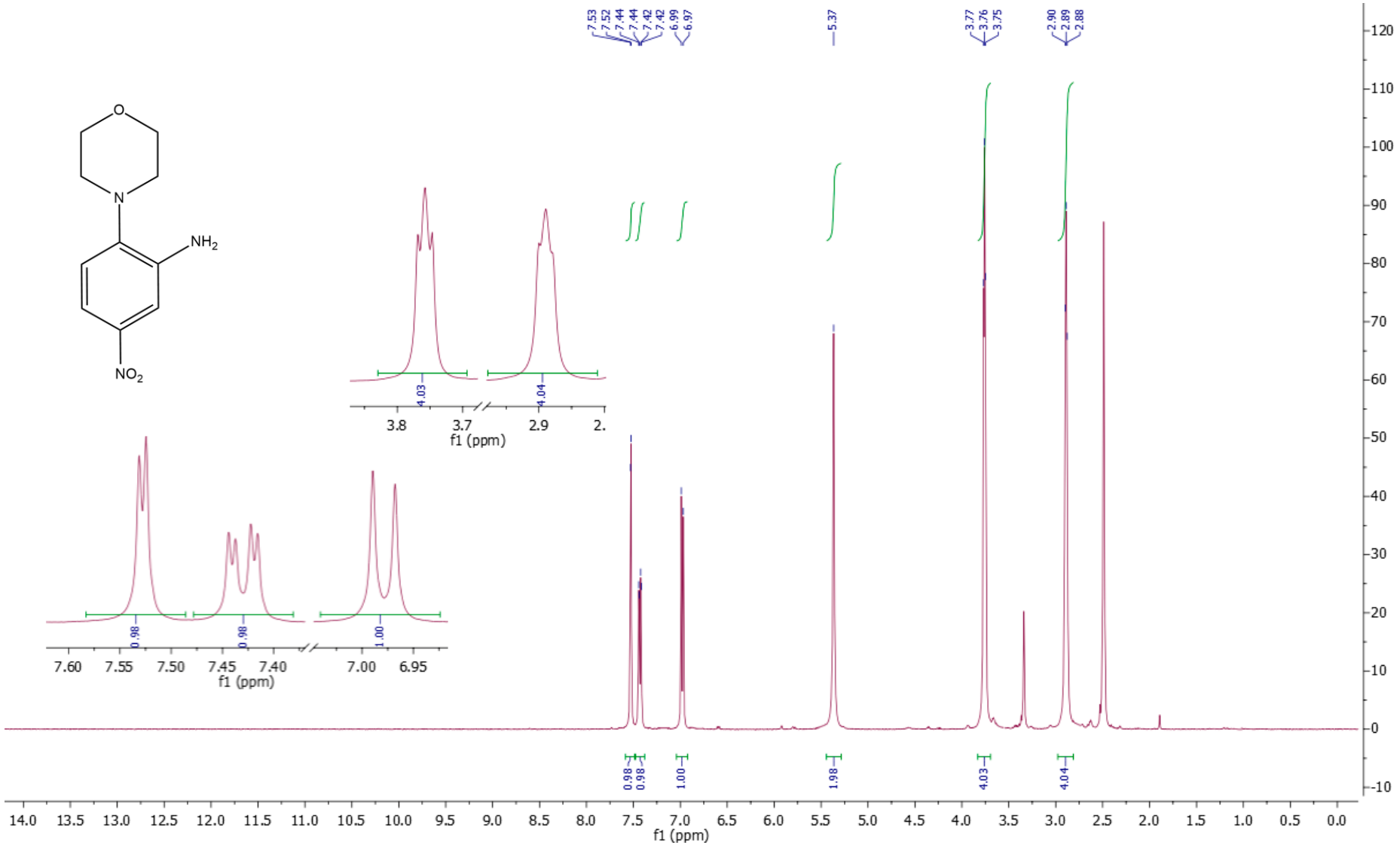
^{1}H NMR spectrum (DMSO-d_6) of 5-nitro-2-(1-piperidinyl)aniline **2k**



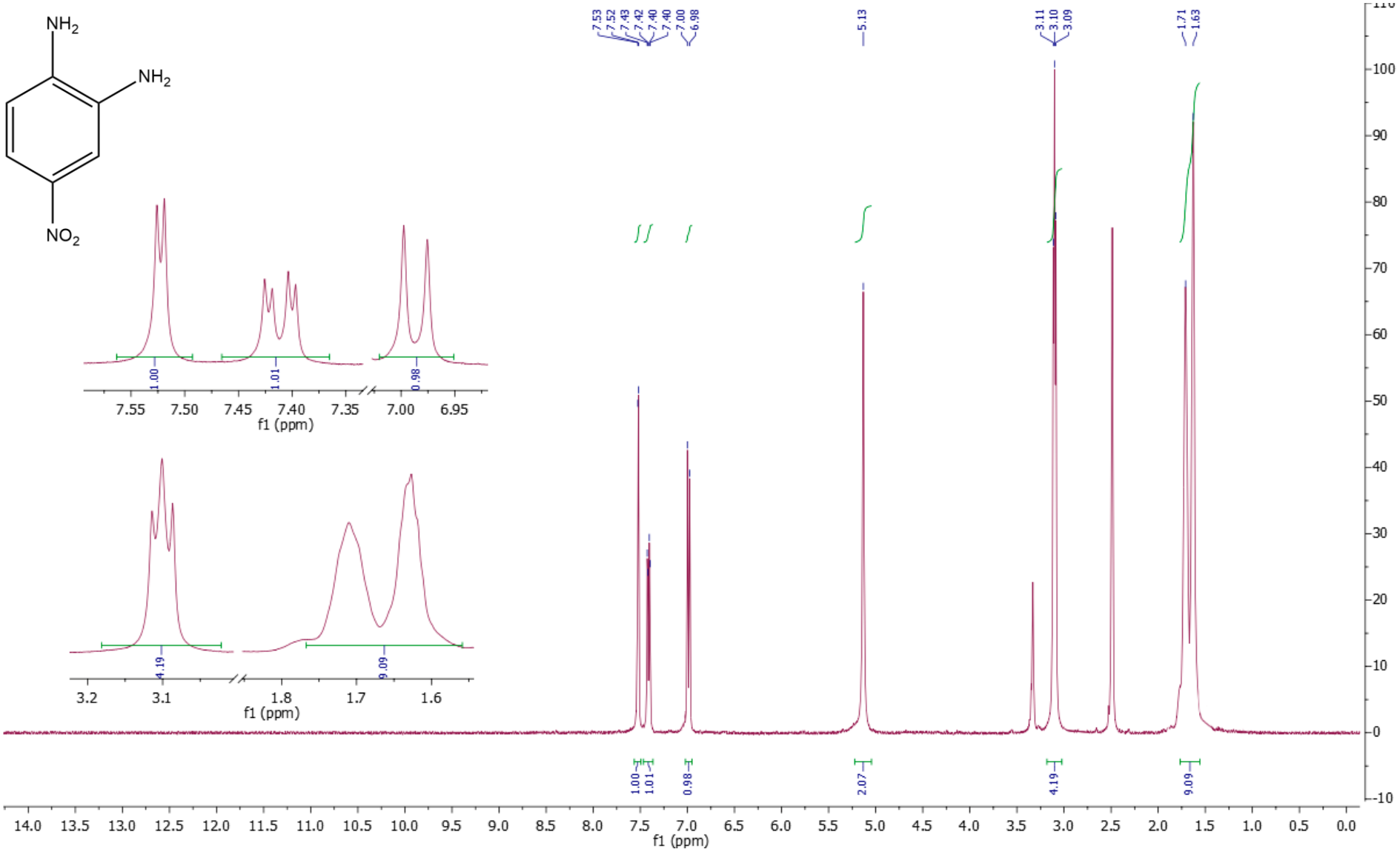
^{1}H NMR spectrum (DMSO-d_6) of 2-(1-azepanyl)-5-nitroaniline **2l**



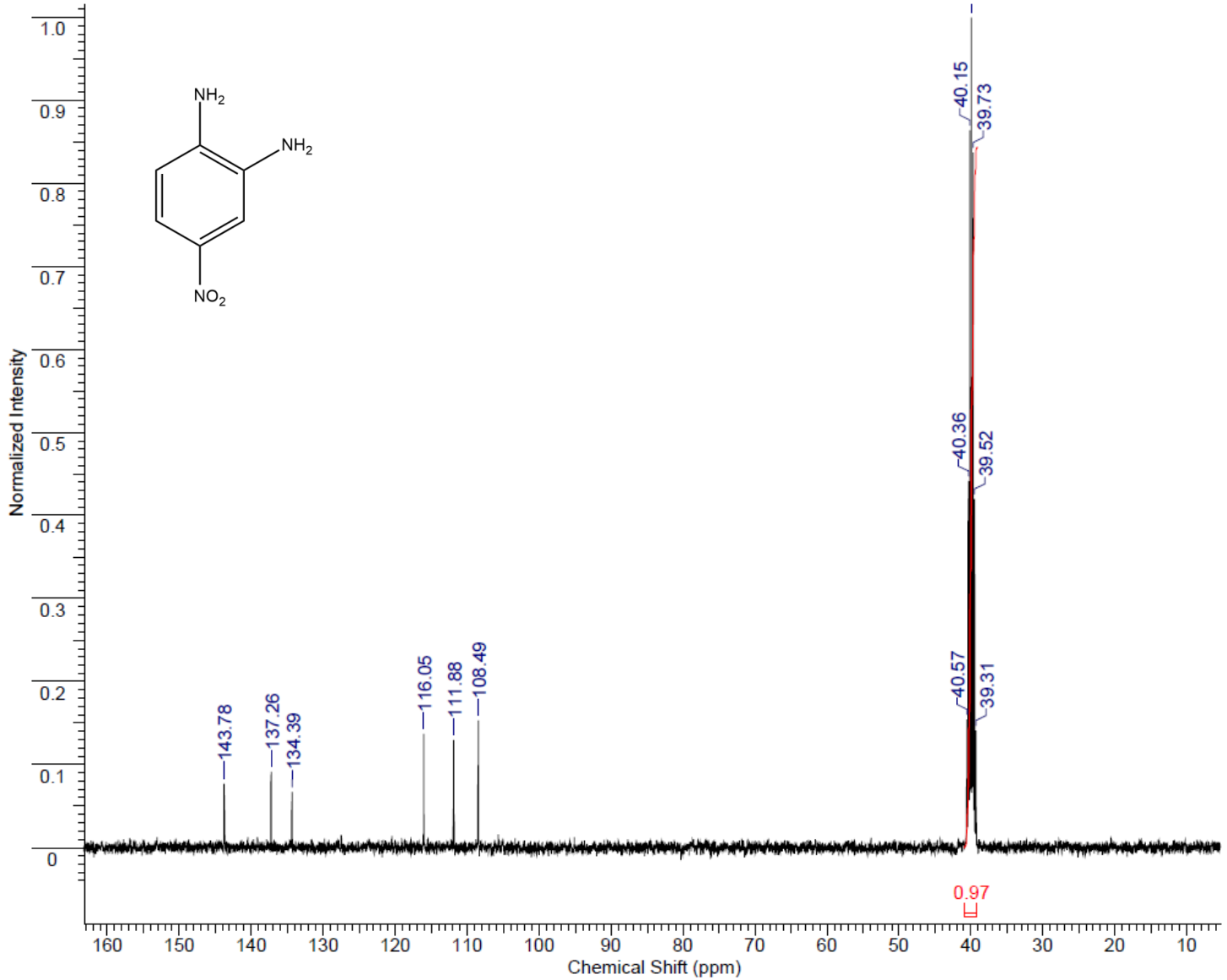
^{13}C NMR spectrum (DMSO-d$_6$) 2-(1-azepanyl)-5-nitroaniline **2l**



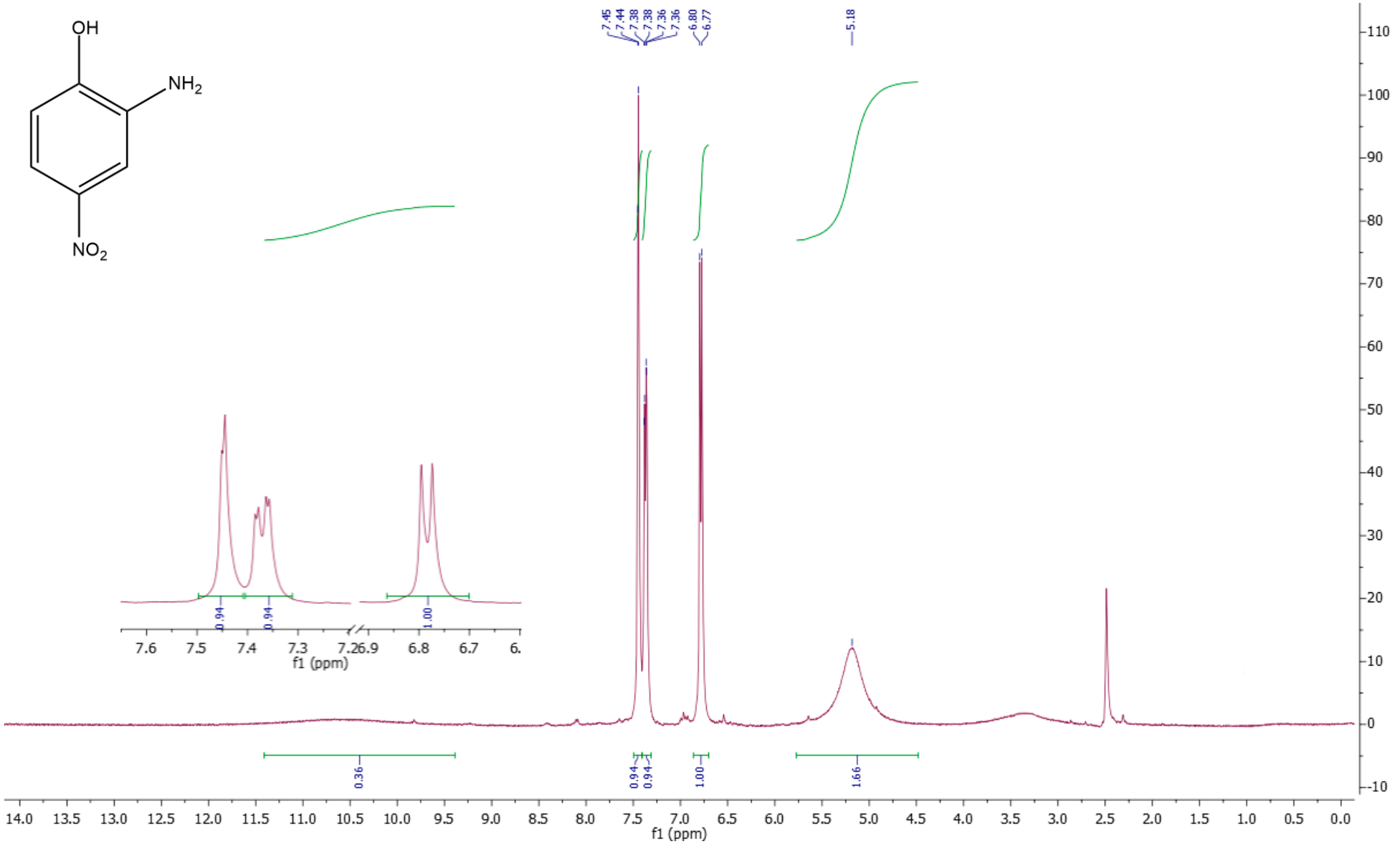
^{1}H NMR spectrum (DMSO-d_6) of 2-(1-morpholinyl)-5-nitroaniline **2m**



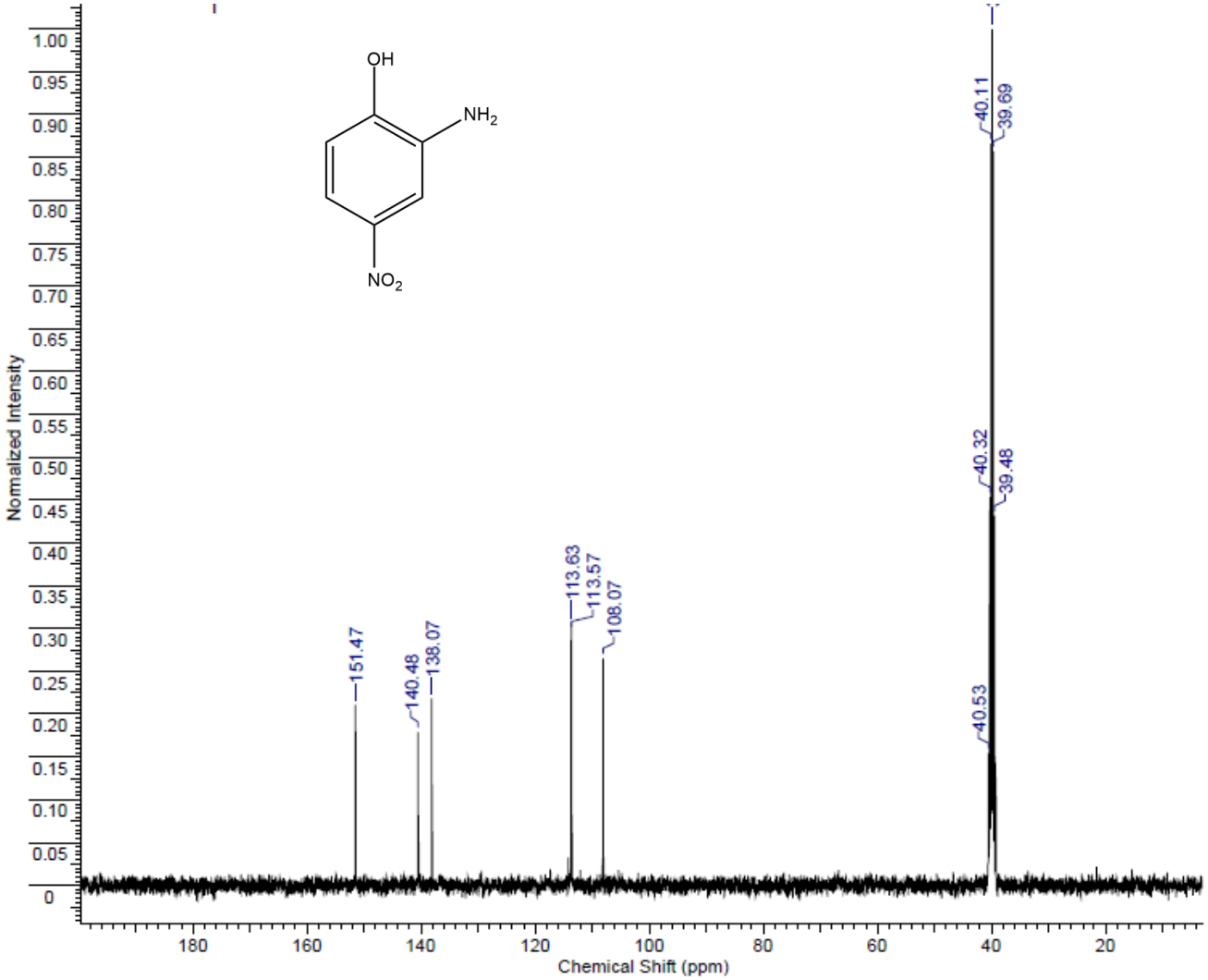
^{1}H NMR spectrum (DMSO-d_6) of 4-nitrobenzene-1,2-diamine **2n**



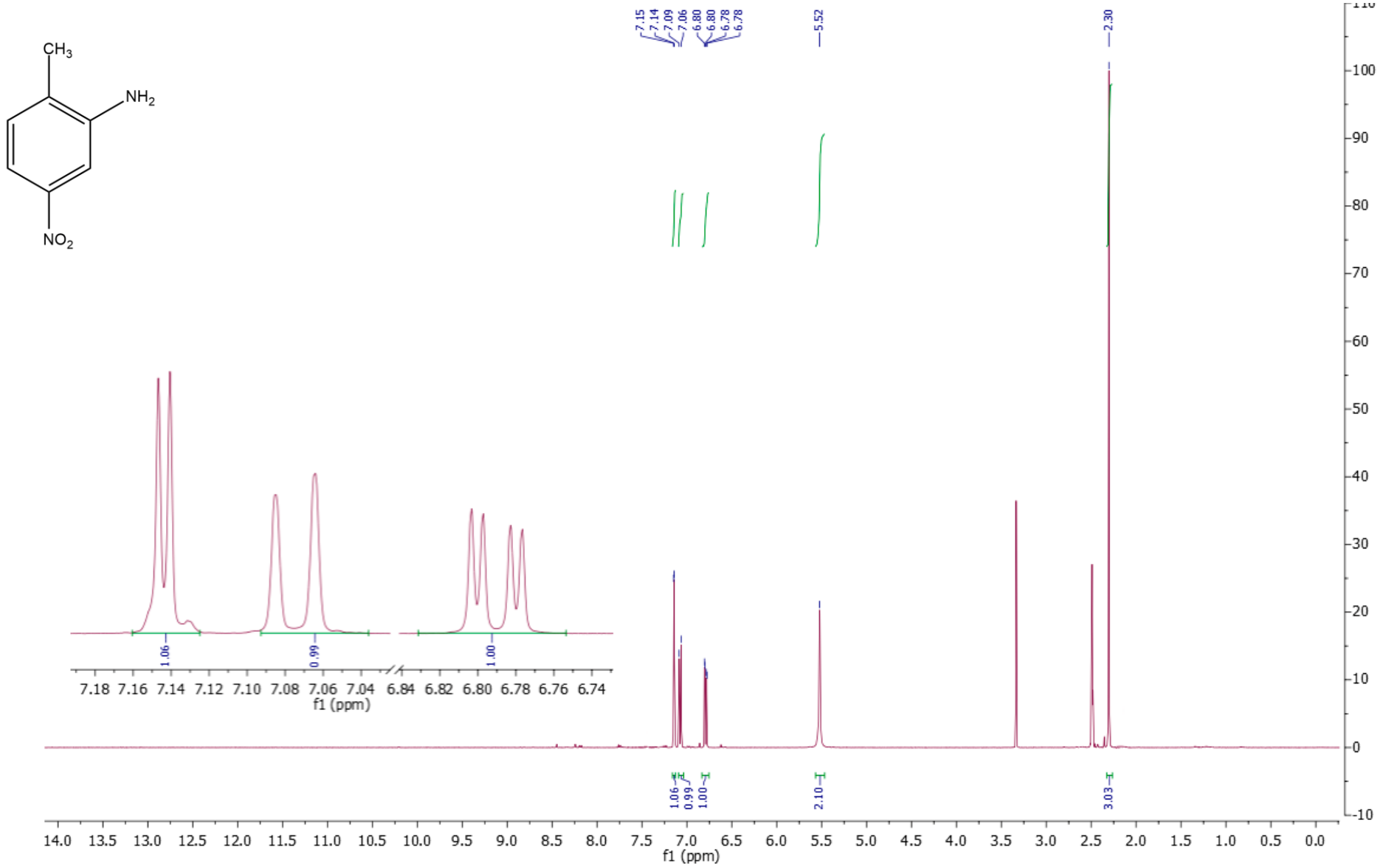
^{13}C NMR spectrum (DMSO-d$_6$) of 4-nitrobenzene-1,2-diamine **2n**



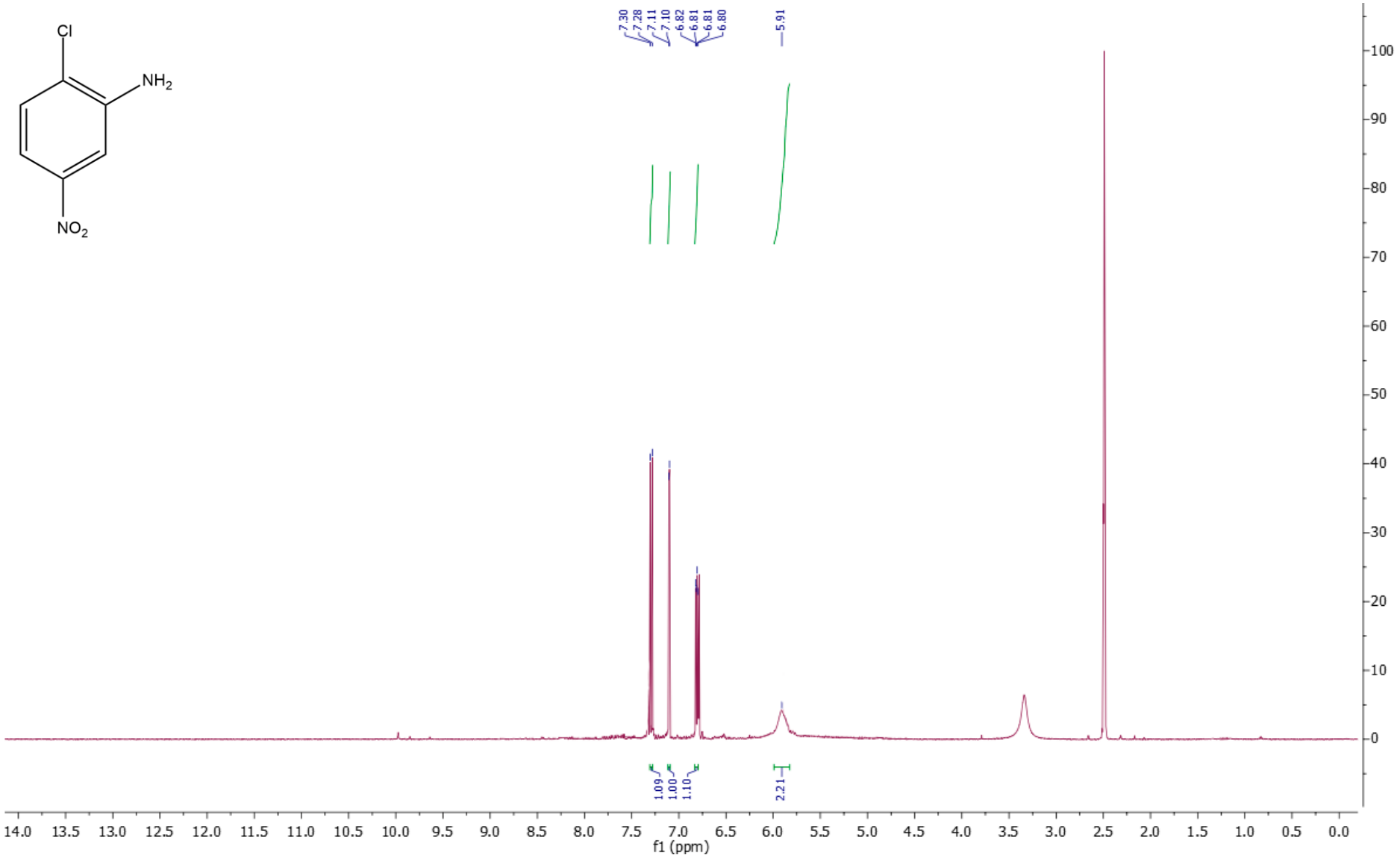
^{1}H NMR spectrum (DMSO-d$_6$) of 2-amino-4-nitrophenol **3a**



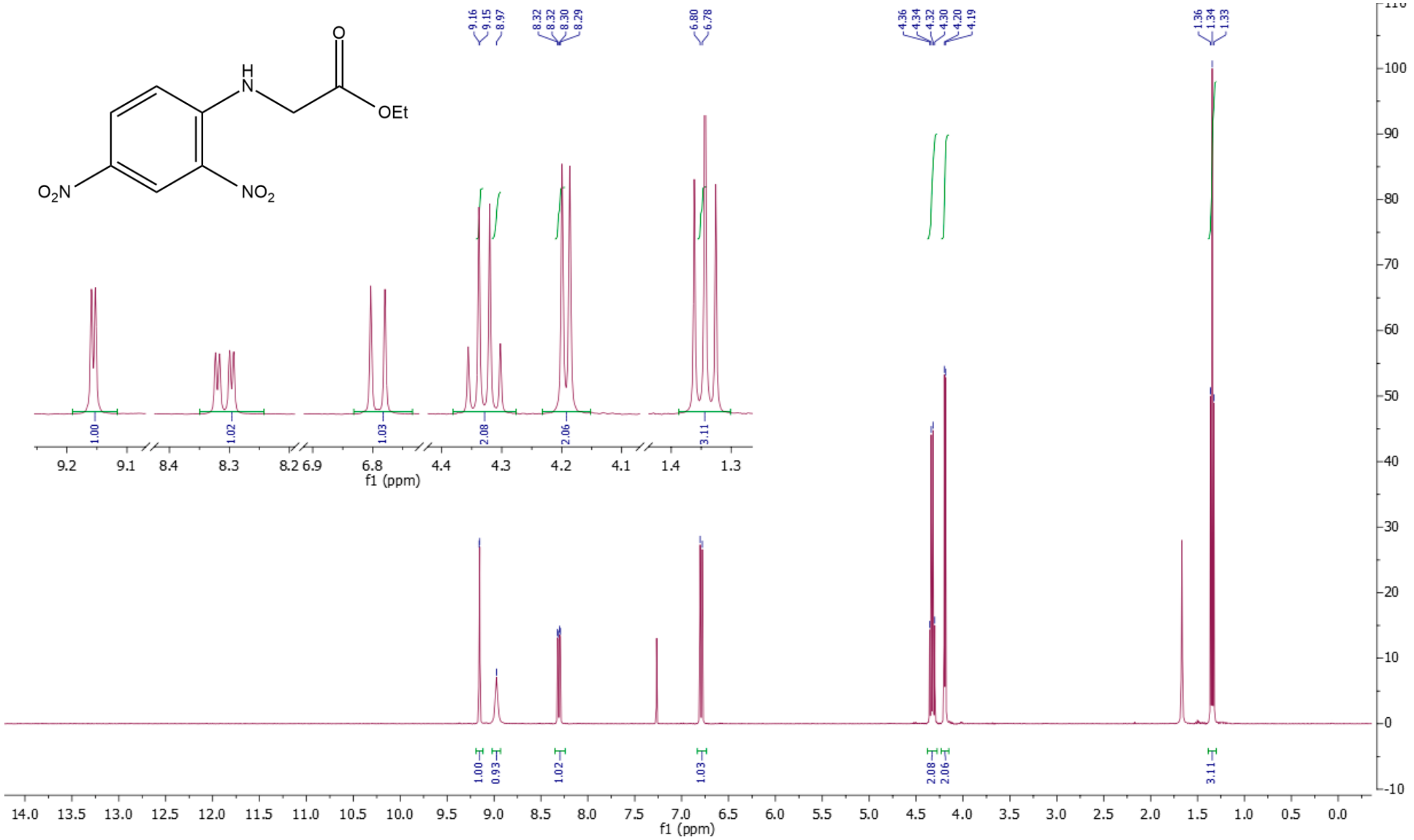
^{13}C NMR spectrum (DMSO-d_6) of 2-amino-4-nitrophenol **3a**



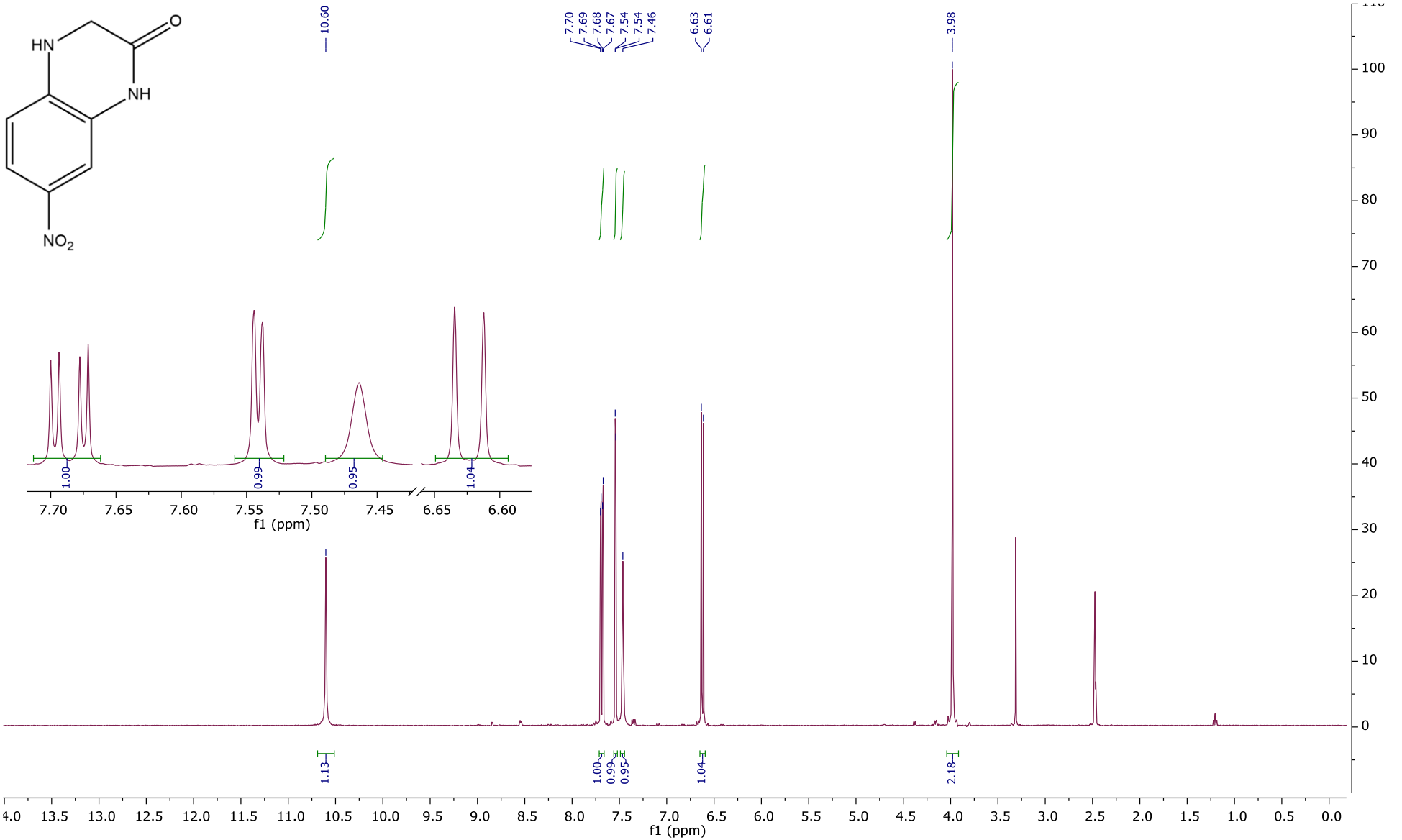
^{1}H NMR spectrum (DMSO-d_6) of 2-amino-4-nitrotoluene **3b**



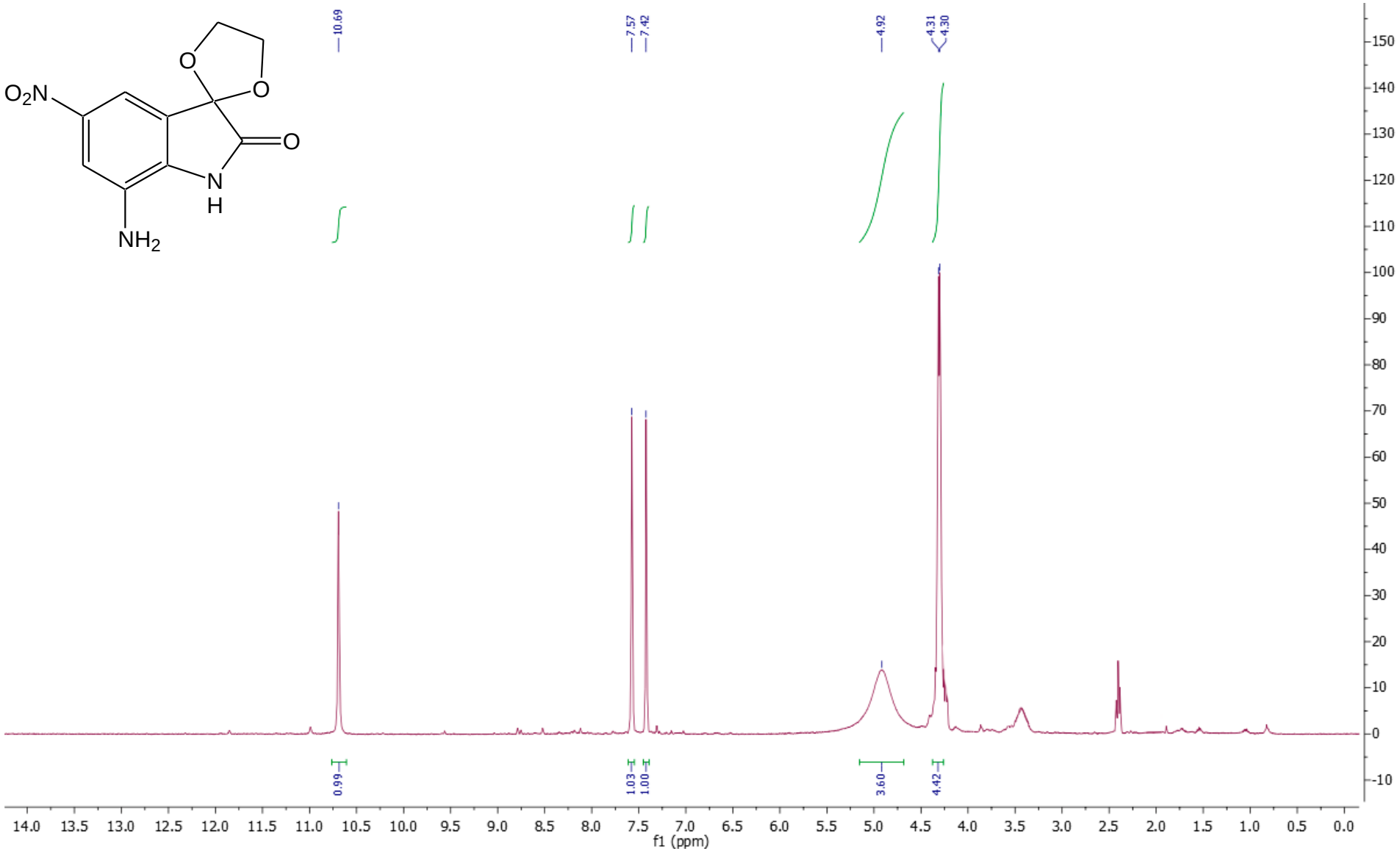
^{1}H NMR spectrum (DMSO-d_6) of 2-amino-1-chloro-4-nitrobenzene **3c**



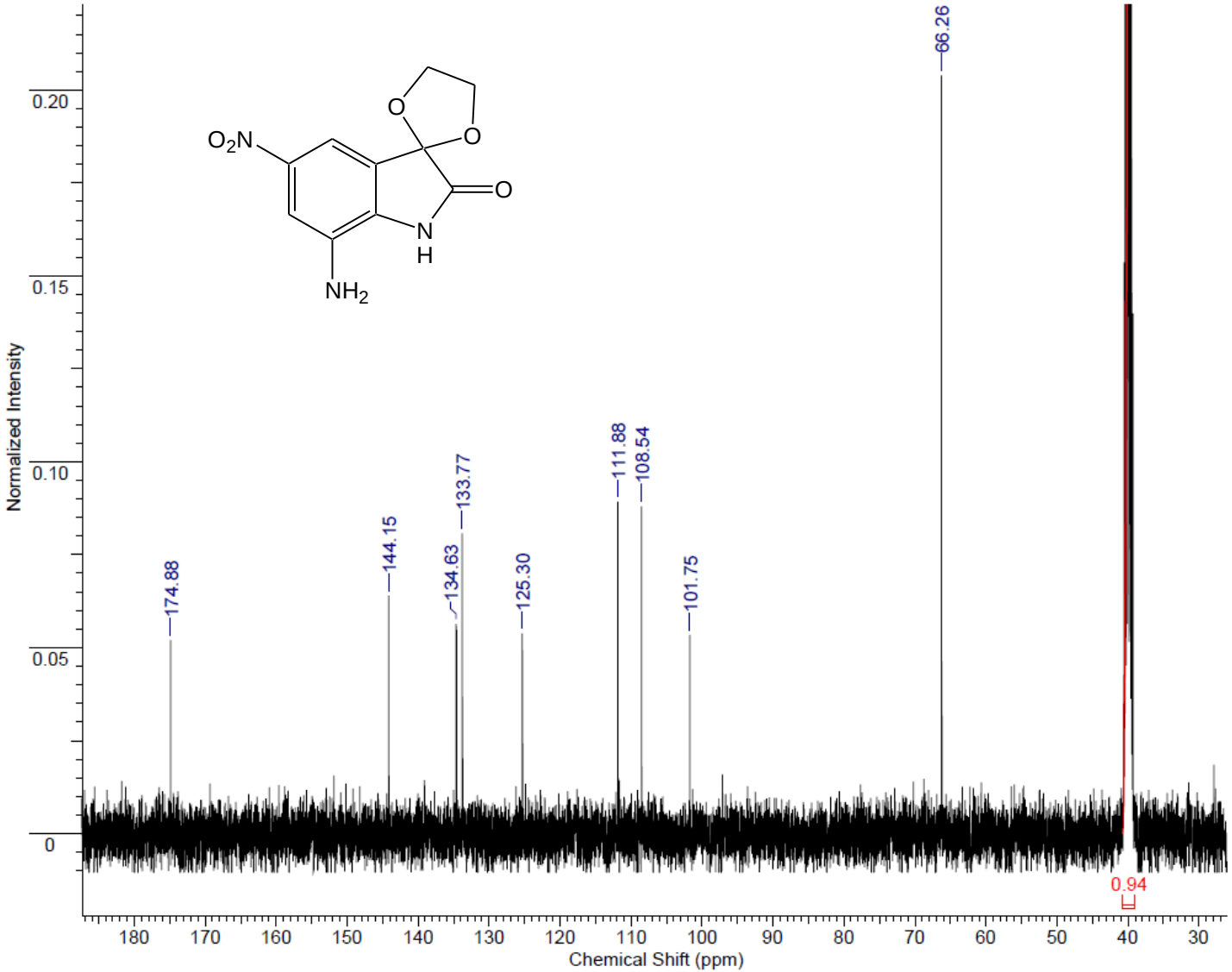
^{1}H NMR spectrum ($CDCl_3$) of *N*-(2,4-dinitrophenyl)glycine ethyl ester **4a**



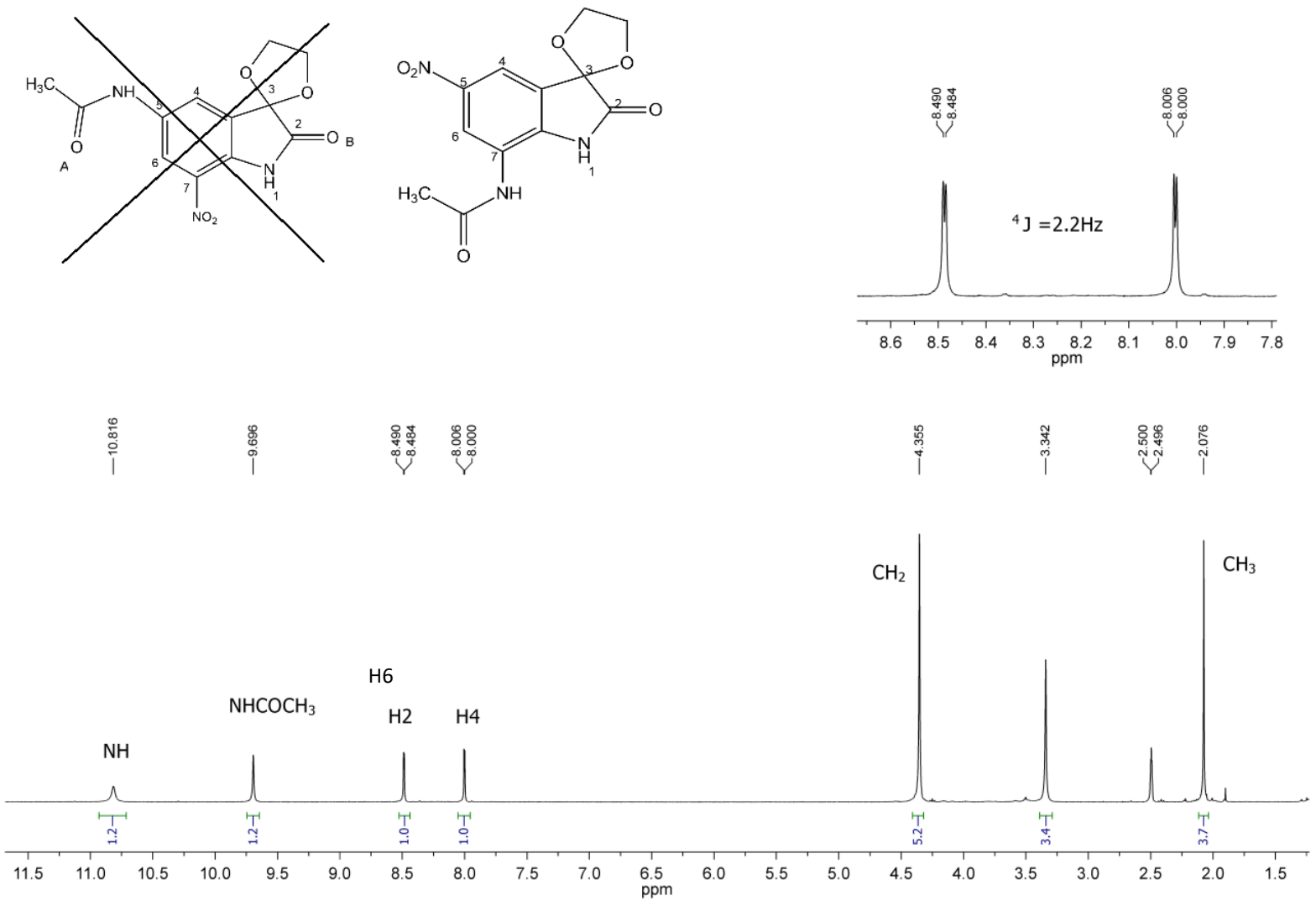
^{1}H NMR spectrum (DMSO-d$_6$) of 7-nitro-3,4-dihydroquinoxalin-2(1*H*)-one **5**



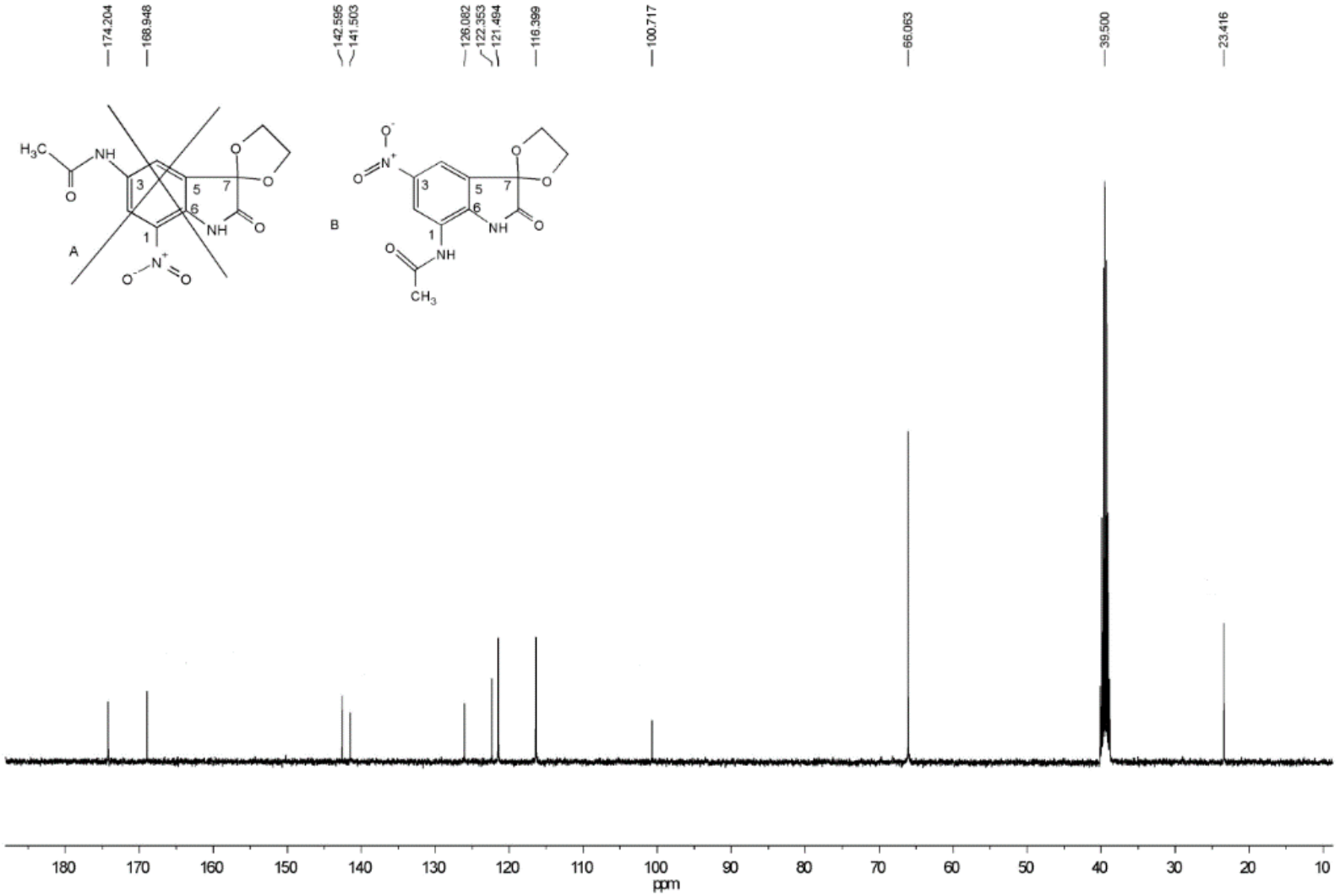
^{1}H NMR spectrum (DMSO-d_6) of 7'-amino-5'-nitrospiro[1,3-dioxolan-2,3'-indol]-2'(1'*H*)-one **7a**



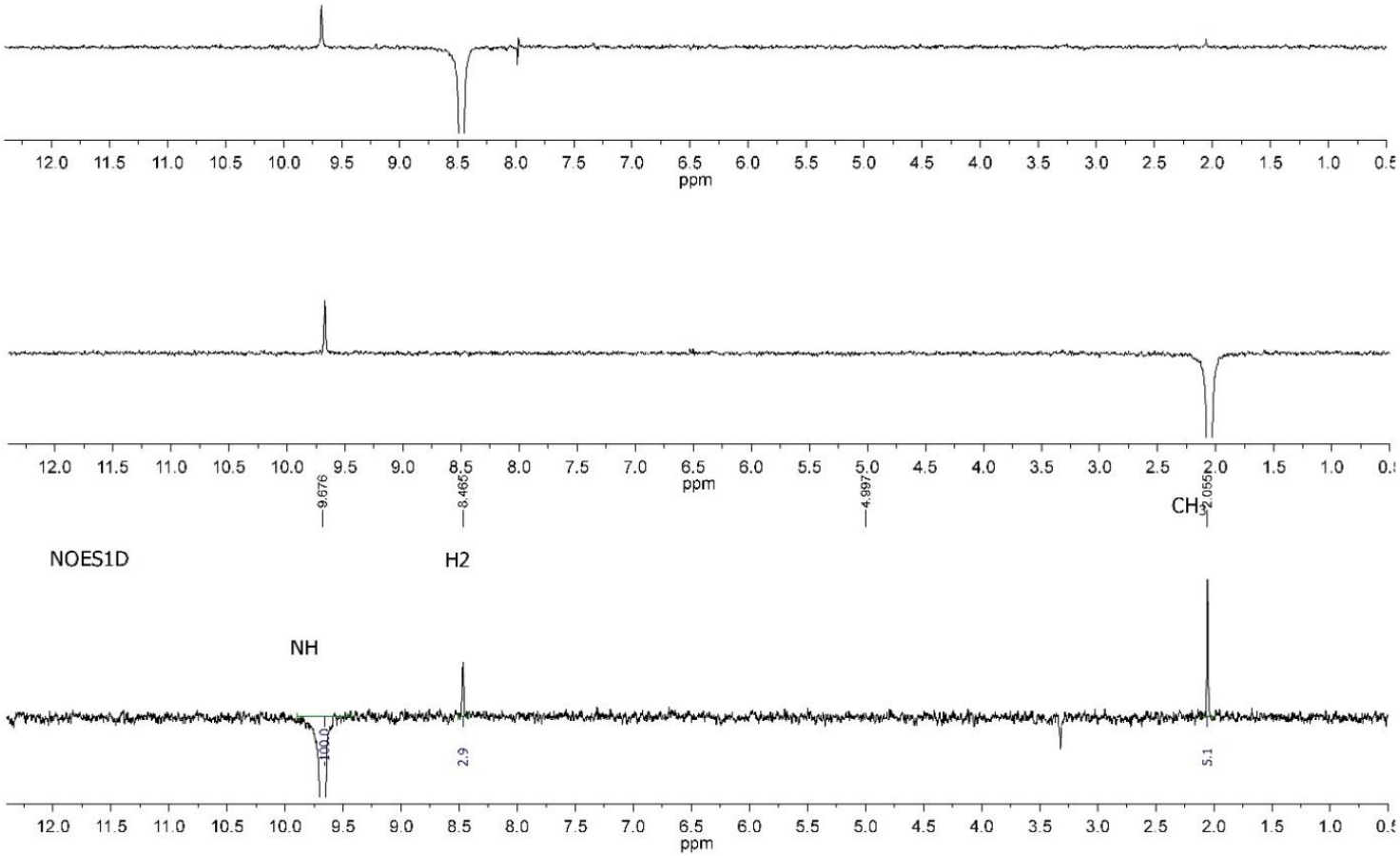
^{13}C NMR spectrum (DMSO-d_6) of 7'-amino-5'-nitrospiro[1,3-dioxolan-2,3'-indol]-2'(1'*H*)-one **7a**

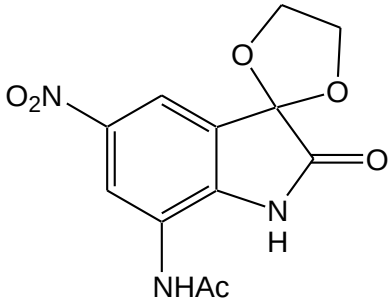


^{1}H NMR spectrum (DMSO-d_6) of 7'-acetylamino-5'-nitrospiro[1,3-dioxolan-2,3'-indol]-2'(1'*H*)-one **7b**

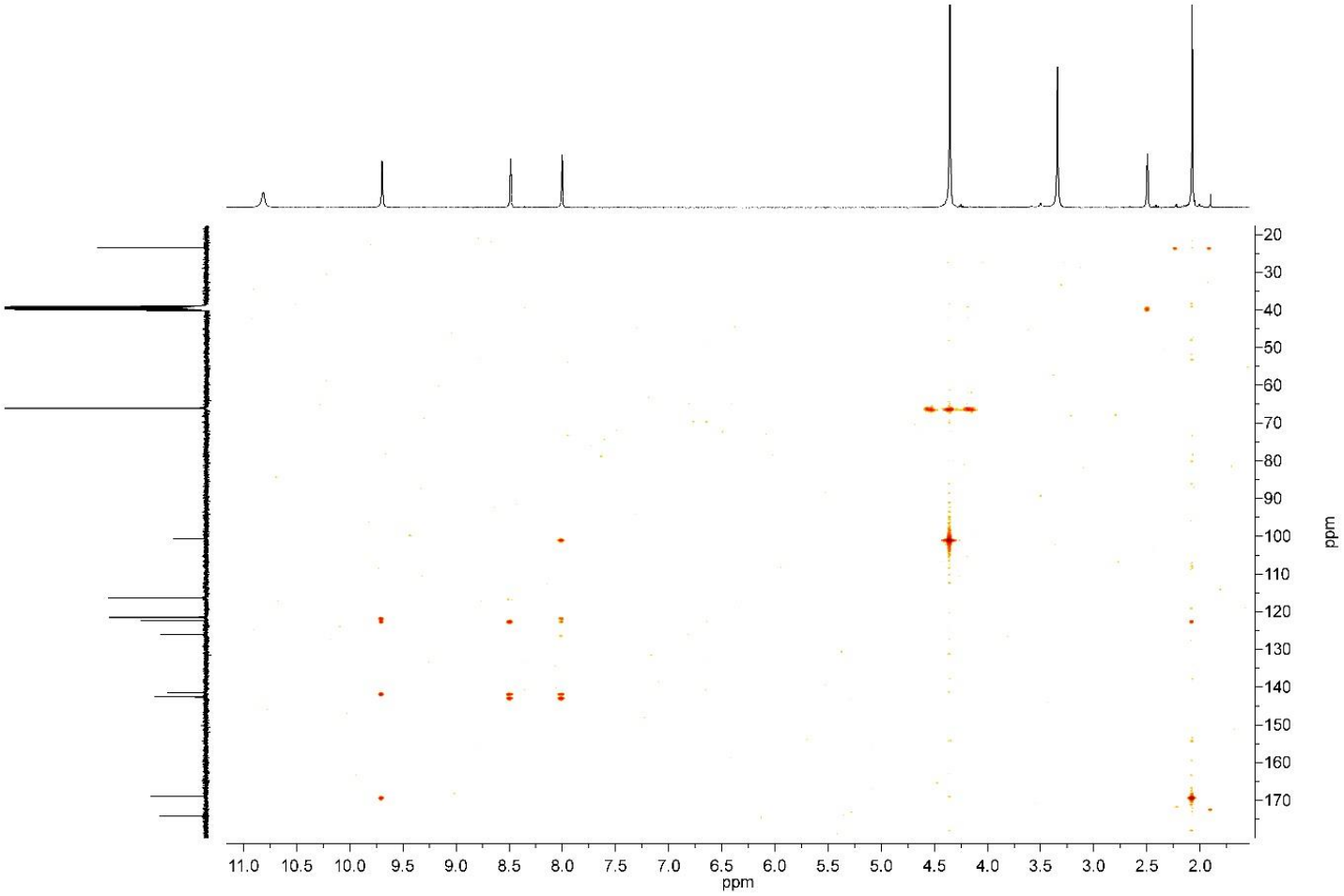


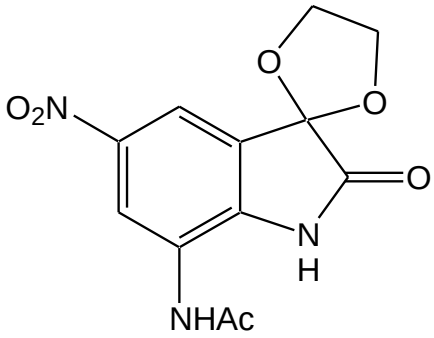
^{13}C NMR spectrum (DMSO-d$_6$) of 7'-acetylamino-5'-nitrospiro[1,3-dioxolan-2,3'-indol]-2'(1'*H*)-one **7b**



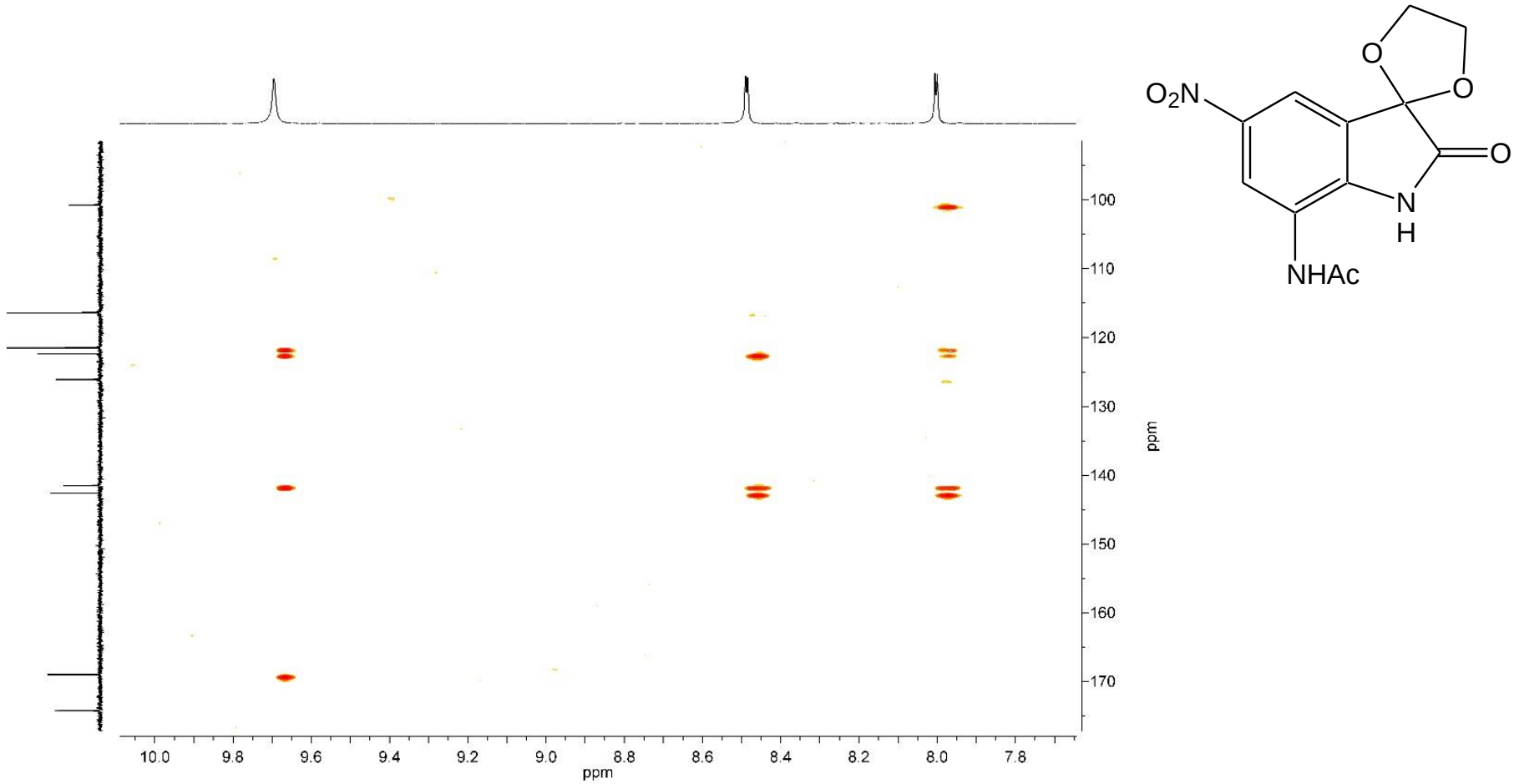


NOESY1D spectrum (DMSO-d_6) of 7'-acetylamino-5'-nitrospiro[1,3-dioxolan-2,3'-indol]-2'(1'*H*)-one **7b**





gHMBC spectrum (DMSO-d_6) of 7'-acetylamino-5'-nitrospiro[1,3-dioxolan-2,3'-indol]-2'(1'*H*)-one **7b**



gHMBC spectrum (DMSO-d_6) (low-field fragment) of 7'-acetylamino-5'-nitrospiro[1,3-dioxolan-2,3'-indol]-2'(1'*H*)-one **7b**