Electronic Supplementary Material (ESI) for ChemComm.


# Access to 1H-indazoles, 1H-benzoindazoles and 1H-azaindazoles from (het)aryl azides: a Staudinger-aza-Wittig tandem reaction leading to N-N bond formation?

*T. Alaime[1,2], M. Daniel[1,2], M.-A. Hiebel[2], E. Pasquinet[1], F. Suzenet[2], G. Guillaumet[2]*

[1]CEA, DAM, Le Ripault, F-37260 Monts, France

[2]Institut de Chimie Organique et Analytique, UMR-CNRS 7311, LRC CEA M09, 45067 Orléans, France

# SUPPORTING INFORMATION

**General Comments.**

The reactions were monitored by thin-layer chromatography (TLC) analysis using silica gel (60 F254) plates. Compounds were visualized by UV irradiation. Flash column chromatography was performed on silica gel 60 (230−400.13 mesh, 0.040 0.063 mm). Melting points (mp [°C]) were taken on samples in open capillary tubes and are uncorrected. The infrared spectra of compounds are given in $cm^{-1}$. $^{1}H$ and $^{13}C$ NMR spectra were recorded at 250 MHz ($^{13}C$, 62.9MHz) or at 400 MHz ($^{13}C$, 100.62 MHz). Chemical shifts are given in parts per million using tetramethylsilane (TMS) as internal standard. Coupling constants (*J*) are reported in Hertz (Hz). High-resolution mass spectra (HRMS) were performed on a quadrupole analyzer.

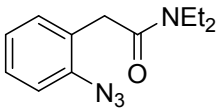
Dry acetonitrile was obtained from a dry station GT S100 immediately prior to use. The amount of water in acetonitrile is regularly checked (Karl Fisher) and is below 20 ppm.

Kornblum's solution: To prepare 50mL, dissolve 15g of urea in 40mL of water and add 10mL of acetic acid.

The azido precursors **1a**, **1b**, **1f**, **1g**, **4**, **13** were synthesized according to the following literature.[17,18].

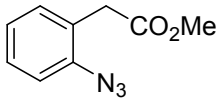
**FORMATION of 1c-1e, 1h-1l**

**Formation of 1d**



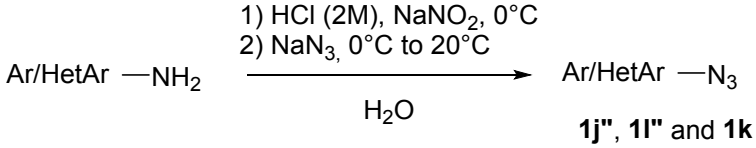

*2-(2-Azidophenyl)-N,N-diethylacetamide (**1d**).* The procedure[1] with 2-(2-azidophenyl)acetic acid[2] (200 mg) was followed to provide after purification with column chromatography (eluent = 1:1 ethyl acetate/pentane) 223mg (85 %) **1d** as an orange oil; IR $\bar{\nu}$ ($cm^{-1}$) 2973, 2119, 1639, 1451, 1283, 748; $^{1}H$ NMR (250 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 2H), 7.18 – 7.06 (m, 2H), 3.62 (s, 2H), 3.37 (dq, *J* = 14.4, 7.1 Hz, 4H), 1.15 (dt, *J* = 10.1, 7.1 Hz, 6H) ; $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 169.7 (C), 138.1 (C), 131.1 (CH), 128.3 (CH), 127.4 (C), 125.0 (CH), 118.1 (CH), 42.4 ($CH_2$), 40.5 ($CH_2$), 35.5 ($CH_2$), 14.4 ($CH_3$), 13.1 ($CH_3$); HRMS (ESI) : $[M+H]^+$ calcd. 233.1396 for $C_{12}H_{17}N_4O$, found 233.1397.

**Formation of 1e**



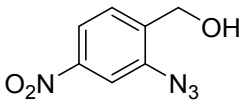

*Methyl 2-(2-azidophenyl)acetate (**1e**).* To a solution of 2-azidophenylacetic acid[2] (2.110 g, 1equiv.) in methanol (0,32M) at 0°C, under argon, was slowly added thionyl chloride (1.5equiv.). The mixture was then allowed to react at room temperature overnight. After concentration under reduced pressure, the residue was dissolved in dichloromethane, washed with water and brine, dried over $MgSO_4$ and concentrated under reduced pressure. The desired compound **1e** was obtained without any further purification with 94% yield (2.140 g) as a brown oil; IR $\bar{\nu}$ ($cm^{-1}$) 2118, 1736, 1490, 1284, 1158, 745, $^{1}H$ NMR (250 MHz, $CDCl_3$) δ 7.33 (ddd, *J* = 8.0, 7.5, 1.7 Hz, 1H), 7.23 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.17 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.11 (td, *J* = 7.5, 1.2 Hz, 1H), 3.71 (s, 3H, $CH_3$), 3.62 (s, 2H, $CH_2$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 171.5, 138.6, 131.4, 128.7, 125.6, 124.8, 118.1, 52.1, 36.4.

**General procedure for the preparation of 1j" 1l" and 1k.**

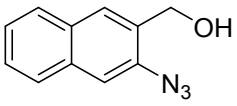



**1j"**, **1l"** and **1k**

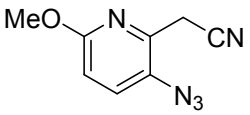
To a solution of the aromatic amine (1 equiv.; 0.7 M) in hydrochloric acid (2 M) at 0°C was slowly added a solution of sodium nitrite (1.2equiv.) in water (4.2M). After 5 min of stirring, a solution of sodium azide (2.0 equiv.) and sodium acetate (3.0 equiv.) in water (2 M) was slowly added. The mixture was then allowed to react at room temperature for 4 h. The mixture was extracted three times with dichloromethane and the combined organic phase was washed with water and brine, dried over MgSO4. After concentration under reduced pressure, the product was purified by flash chromatography on silica gel.




(*2-Azido-4-nitrophenyl)methanol (**1j"**)*. The general procedure with commercial (2-amino-4-nitrophenyl)methanol (2.940 g) was followed to provide was followed to provide after purification with column chromatography (eluent = 1:1 ethyl acetate/pentane) 2.390 g (71 %) of **1j"** as a beige solid; $^{1}$H NMR (250 MHz, $CDCl_3$) δ 8.02-8.04 (m, 2H), 7.66 (d, *J* = 8.7 Hz, 1H), 4.74 (s, 2H, $CH_2$), 2.00 (br s, 1H, OH); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 148.5, 139.3, 130.5, 129.3, 120.3, 113.3, 61.1 ($CH_2$).

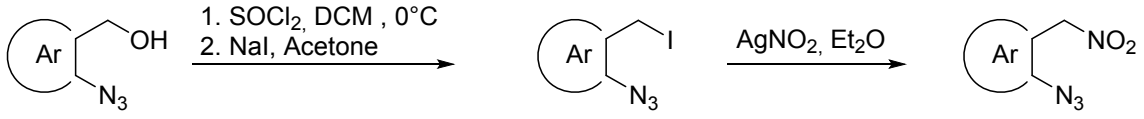



*(3-Azidonaphthalen-2-yl)methanol (**1l"**).* The general procedure with (3-aminonaphthalen-2-yl)methanol[3] (900 mg) was followed to provide after purification with column chromatography (eluent = 1:1 ethyl acetate/pentane) 858 mg (83 %) of **1l"** as a beige solid; mp= 95-96 °C; IR $\bar{\nu}$ ($cm^{-1}$)3234; 2101; 1501; 1285; 1005; 864; 735; $^{1}$H NMR (250 MHz, $CDCl_3$) δ 7.86 – 7.72 (m, 3H), 7.57 – 7.39 (m, 3H), 4.79 (s, 2H), 2.15 (br s, 1H, OH); $^{13}$C NMR (63 MHz, $CDCl_3$) δ 136.5 (q), 133.5 (q), 131.4 (q), 131.1 (q), 128.3 (CH), 127.9 (CH), 127.0 (CH), 126.5 (CH), 125.8 (CH), 115.5 (CH), 62.2 ($CH_2$).




*2-(3-Azido-6-methoxypyridin-2-yl)acetonitrile (**1k**)*. The general procedure with 2-(3-amino-6-methoxypyridin-2-yl)acetonitrile (500mg) was followed to provide 152mg (27%) of **1k** as a beige solid; mp= 92-93°C; $^{1}$H NMR (250 MHz, $CDCl_3$) δ 7.39 (d, J = 8.8 Hz, 1H), 6.77 (d, J = 8.8 Hz, 1H), 3.93 (s, 3H, $CH_3$), 3.76 (s, 2H, $CH_2$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.8, 136.7, 128.1, 126.5, 115.3, 111.0, 53.0, 21.3; HRMS (ESI) : $[M+H]^+$ calcd. 190.0723 for $C_8H_8N_5O$, found 190.0723.

**General procedure for the preparation of 1c, 1h, 1i, 1j and 1l.**

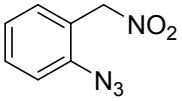



**1h"**, **1i"**,**1j"** and **1l"** **1c'**, **1h'**, **1i'**,**1j'** and **1l'** **1c**, **1h**, **1i**,**1j** and **1l**

The corresponding alcohol derivative (1.0 equiv.) was dissolved in anhydrous dichloromethane (0.2M) at 0°C before the slow addition of thionyl chloride (1.2equiv.). After 3 h at 0°C, the reaction was concentrated under reduced pressure and the residue was dissolved in anhydrous acetone (0.75M). Sodium iodide (1.5 equiv.) was added and the reaction was left at room temperature for 12h under inert atmosphere. Then, the reaction was filtered through celite pad, which was rinsed twice with acetone. After concentration under reduced pressure, the residue was dissolved in dichloromethane and filtered a second time through celite pad rinsed twice with dichloromethane. The filtrate is washed with a saturated solution of thiosulfate sodium and brine, dried over $MgSO_4$ and concentrated under reduced pressure to yield to the corresponding iodinated products **1h'**, **1i' 1j'** and 1l' without further purification.

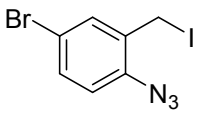
In a flask coated with aluminum foil, a suspension of silver nitrite (1.5equiv, 0.22M) in $Et_2O$ was made and cooled to 0°C before slowly adding a solution of the benzylic iodide compound (0.22 M). The

reaction mixture was kept at 0°C for 3h and then allowed to return at room temperature for 20h. After filtration over a celite pad, a solution of sodium methanolate in methanol (1.1 equiv., 1M) is added at 10°C. The resulted precipitate was filtered and dissolved in a minimum volume of water. The pH of the solution was corrected to 4 by using a Kornblum solution (6M) at 0°C. The resulted precipitate was filtered, washed with water and dried under vacuum to yield to the corresponding products **1c**, **1h**, **1i**, **1j** and **1l**.



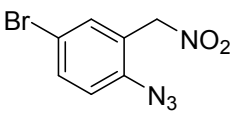

*1-Azido-2-(nitromethyl)benzene (**1c**)*.

The general procedure with **1c'**[4] (1.000 g) was followed to provide 290 mg (42 %) of **1c** as a yellow solid; mp= 47-48 °C; IR $\bar{\nu}$ ($cm^{-1}$) 2132, 1557, 1540, 1300, 763; $^1$H NMR (250 MHz, Chloroform-*d*) δ 7.52 (t, J = 7,5 Hz, 1H), 7.38 (d, J = 7.5 Hz, 1H), 7.20-7.27 (m, 2H), 5.46 (s, 2H, $CH_2$); NMR (101 MHz, DMSO-$d_6$) δ (ppm) 140.1 (C), 132.6 (CH), 131.8 (CH), 125.2 (CH), 120.9 (C), 118.6 (CH), 74.70 ($CH_2$).



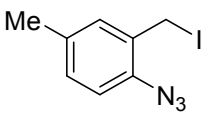

*1-Azido-4-bromo-2-(iodomethyl)benzene (**1h'**)*

The general procedure with (2-azido-5-bromophenyl)methanol[5] (3.54 g) was followed to provide 3.460 g (87 %) of **1h'** as a yellow solid; mp= 66-67 °C; IR $\bar{\nu}$ ($cm^{-1}$) 2115, 2078, 1486, 1473, 1299, 807; $^1$H NMR (250 MHz, $CDCl_3$) δ 7.47 (d, *J* = 2.3 Hz, 1H), 7.41 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 4.32 (s, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 137.4 (C), 133.4 (CH), 132.4 (CH), 132.3 (CH), 120.3 (CH), 117.6 (C), -1.5 ($CH_2$).



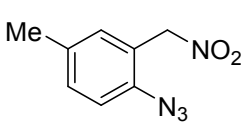

*1-Azido-4-bromo-2-(nitromethyl)benzene (**1h**).*

The general procedure with **1h'** (1.920 g) was followed to provide 575 mg (40 %) of **1h** as a yellow solid; mp= 63-64 °C; IR $\bar{\nu}$ ($cm^{-1}$) 2124, 2087, 1550, 1289, 820; $^1$H NMR (250 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 2.1, 8.0 Hz, 1H), 7.52 (d, *J* = 2.1 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 5.40 (s, 2H, $CH_2$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.4 (C), 135.4 (CH), 134.7 (CH), 122.6 (C), 120.2 (CH), 117.8 (C), 74.0 ($CH_2$).



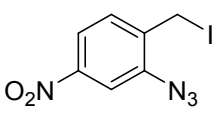

*1-Azido-2-(iodomethyl)-4-methylbenzene (**1i'**)*.

The general procedure with (2-azido-5-methylphenyl)methanol[6] (1.000 g) was followed to provide 1.650 g (99 %) of **1i'** as a brown oil; IR $\bar{\nu}$ ($cm^{-1}$) 2918, 2115, 2078, 1496, 1293, 1158, 806; $^1$H NMR (250 MHz, $CDCl_3$) δ 7.13-7.16 (m, 1H), 7.10-7.11 (m, 1H), 7.00-7.02 (m, 1H), 4.38 (s, 2H, $CH_2$), 2.32 (s, 3H, $CH_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 135.5 (C), 135.0 (C), 131.3 (CH), 130.4 (CH), 130.2 (C), 118.7 (CH), 20.8 ($CH_3$), 0.57 ($CH_2$).




*1-Azido-4-methyl-2-(nitromethyl) benzene (**1i**).*

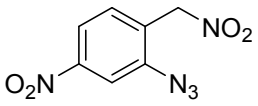
The general procedure with **1i'** (137 mg) was followed to provide 57 mg (57 %) of **1i** as a yellow solid; mp= 61-62 °C; IR $\bar{\nu}$ ($cm^{-1}$) 2927, 2128, 2101, 1549, 1537, 1302, 823; $^1$H NMR (250 MHz, $CDCl_3$) δ 7.51 (d, *J* = 3.0 Hz, 1H), 7.42 (dd, *J* = 2.2, 8.5 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 5.38 (s, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 137.3 (C), 135.2 (C), 133.1 (CH), 132.4 (CH), 120.7 (C), 118.5 (CH), 74.8 ($CH_2$), 20.8 ($CH_3$).




*2-Azido-1-(iodomethyl)-4-nitrobenzene (**1j'**).*

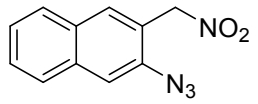
The general procedure with **1j"** (1.200 g) was followed to provide 1.230 g (66%) of **1j'** as a yellow solid; mp= 78-79 °C; IR $\bar{\nu}$ ($cm^{-1}$) 2118, 1512, 1342, 1288, 1137, 870, 812, 743, 724; $^1$H NMR (250 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.1 Hz, 1H), 7.92 (dd, *J* = 2.1 Hz, 8.4 Hz, 1H),

7.50 (d, *J* = 8.4 Hz, 1H), 4.41 (s, 2H, $CH_2$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 148.0, 139.7, 137.3, 131.1, 119.9, 113.6, -2.8 ($CH_2$).



*2-Azido-4-nitro-1-(nitromethyl)benzene (**1j**).*

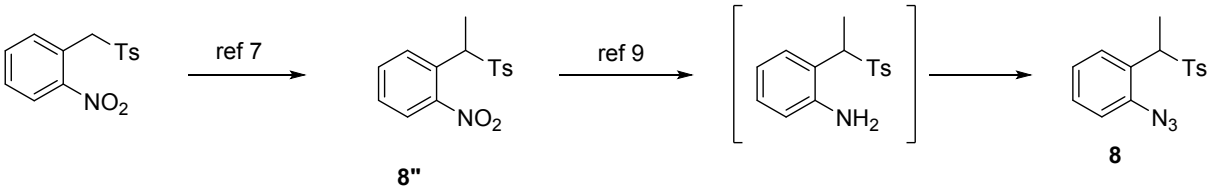
The general procedure with **1j'** (137 mg) was followed to provide 59% yield (57mg) of **1j** as a white solid; mp= 90-91°C; IR $\bar{\nu}$ ($cm^{-1}$) 3071, 2125, 1553, 1520, 1345, 1275; 1150, 881, 814; 733; $^1$H NMR (250 MHz, $CDCl_3$) δ 8.10 (d, *J* = 2.2 Hz, 1H), 8.06 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 5.52 (s, 2H).; $^{13}$C NMR (101 MHz, $CDCl_3$) δ 149.9 (C), 142.1 (C), 133.6 (CH), 126.6 (C), 119.9 (CH), 113.6 (CH), 73.8 ($CH_2$).



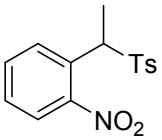
*2-Azido-3-(nitromethyl)naphthalene (**1l**).*

The general procedure with **1l"** (300 mg) was followed to provide 103 mg (30 % over the two steps) of **1l** as a beige solid; mp= 71-72°C; IR $\bar{\nu}$ ($cm^{-1}$) 2111, 1549, 1363, 1287, 875, 753, 697; $^1$H NMR (250 MHz, $CDCl_3$) δ 7.88 – 7.78 (m, 3H), 7.63 – 7.54 (m, 2H), 7.53 – 7.45 (m, 1H), 5.59 (s, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 137.31 (q), 134.74 (q), 133.17 (CH), 1320.62 (q), 128.45 (CH), 128.33 (CH), 126.71 (CH), 126.41 (CH), 120.54 (q), 116.07 (CH), 75.2 (CH2).

**Preparation of 8**

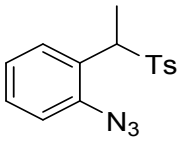



**8"** **8**



*1-Nitro-2-(1-tosylethyl)benzene (**8"**).*

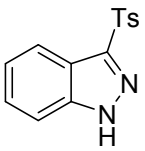
The procedure[7] with 1-nitro-2-(tosylmethyl)benzene[8] (1,634 g) was followed to provide after purification with column chromatography (eluent = 2:8 ethyl acetate/pentane) 1,410 g (82%) of **8"** as a light pink solid; mp= 96-97°C; IR $\bar{\nu}$ ($cm^{-1}$) 2105, 1530, 1226, 734; $^1$H NMR (250 MHz, DMSO-$d_6$) 7.99 – 7.85 (m, 1H), 7.85 – 7.58 (m, 3H), 7.53 – 7.32 (m, 4H), 5.32 (q, *J* = 7.0 Hz, 1H), 2.39 (s, 3H), 1.65 (d, *J* = 7.0 Hz, 3H); $^{13}$C NMR (63 MHz, DMSO-$d_6$) 150.0 (C), 145.0 (C), 133.3, 133.3, 130.1 (CH), 129.9 (CH), 129.9 (CH), 128.5 (CH), 127.1 (C), 124.9 (CH), 57.9 (CH), 21.1 ($CH_3$), 14.0 ($CH_3$); HRMS (ESI) **:** $[M+H]^+$ calcd. 306.0794 for $C_{15}H_{16}NO_4S$, found 309.791.



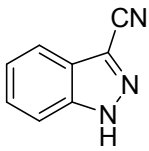
*1-Azido-2-(1-tosylethyl)benzene (**8**).*

The procedure[9] with **8"** (1,347 g) was followed to provide the amino intermediate which was directly used in the general procedure for the formation of azido compound to provide after purification with column chromatography (eluent = 3:2 ethyl acetate/pentane) 543mg (41% 2 steps) of **8** as a pale orange solid; mp= 107-108°C; IR $\bar{\nu}$ ($cm^{-1}$) 2116, 1492, 1299, 1141, 761; $^1$H NMR (250 MHz, DMSO-$d_6$) δ 7.50 – 7.26 (m, 6H), 7.20 (td, *J* = 7.7, 1.3 Hz, 1H), 7.08 (dd, *J* = 7.7, 1.3 Hz, 1H), 4.66 (q, *J* = 7.1 Hz, 1H), 2.33 (s, 3H), 1.55 (d, *J* = 7.2 Hz, 3H); $^{13}$C NMR (63 MHz, DMSO) δ 144.5 (C), 138.5 (C), 134.2 (C), 130.3 (CH), 129.3 (CH), 129.2 (CH), 128.6 (CH), 125.1 (CH), 125.1 (C) , 118.5 (CH), 57.7 (CH), 21.0 ($CH_3$), 13.0 ($CH_3$); HRMS (ESI) **:** $[M+Na]^+$ calcd. 324.0777 for $C_{15}H_{15}N_3NaO_2S$, found 324.0777.

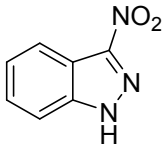
**General procedure for the preparation of 3a-l.** In a dry flask under argon, **1a-l** (1.0 equiv.) was dissolved in anhydrous acetonitrile (0.12M) before adding triphenylphosphine (1.1 equiv.). The resulting mixture was stirred at room temperature up to total consumption of the starting material (3-4h). *tert*-Butylnitrite (4.0 equiv.) was then added and the mixture was left at room temperature for 20 h. After concentration under reduced pressure, the product was purified by flash chromatography on silica gel.



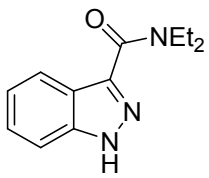
*3-Tosyl*-1H-*indazole* ***(3a)***. The general procedure with **1a** (70 mg) was followed to provide after purification with column chromatography (eluent = 3:7 ethyl acetate/pentane) 45 mg (69%) of **3a** as a white solid. mp = 167 C ; IR $\bar{\nu}$ ($cm^{-1}$) 3263, 2924, 1594, 1369, 1312, 1300, 1289, 1141, 1084, 721, 684; $^1$H NMR (250 MHz, DMSO-$d_6$) δ 14.20 (br s, 1H, NH), 8.04 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.30 (m, 4H), 2.35 (s, 3H, $CH_3$); $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 144.5 (C), 143.3 (C), 140.9 (C), 138.1 (q), 130.1 (2xCH), 127.4 (CH), 127.1 (2xCH), 123.53 (CH), 119.7 (q), 119.5 (CH), 111.5 (CH), 21.02 ($CH_3$); HRMS (ESI) **:** $[M+H]^+$ calcd 273.0692 for $C_{14}H_{13}N_2O_2S$, found 273.0693.



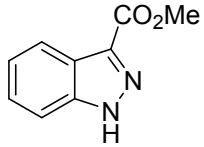
*3-Cyano-1H-indazole (**3b**).*[10] The general procedure with **1b** (70 mg) was followed to provide after purification with column chromatography (eluent = 4:6 ethyl acetate/pentane) 51 mg (92 %) of **3b** as a white solid; mp=129-130 °C (lit. 140-141°C); $^1$H NMR (250 MHz, $CDCl_3$) δ 11.21 (br s, 1H, NH), 7.88 (d, *J* = 7,7 Hz, 1H), 7.69 (d, J = 7,7 Hz, 1H), 7.55 (t; *J* = 7,6 Hz, 1H), 7.39 (t; *J* = 7.6 Hz, 1H).



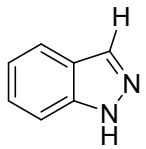
*3-Nitro-1H-indazole (**3c**)*. The general procedure with **1c** (35 mg) was followed to provide after purification with column chromatography (eluent = 4:6 ethyl acetate/pentane) 28 mg (87 %) of **3c** as a white solid; mp= 205°C (lit. 205°C)[11]; IR $\bar{\nu}$ ($cm^{-1}$) 3195, 1531, 1478, 1381, 1321, 1249, 1065, 831, 743; $^1$H NMR (250 MHz, DMSO-d6) δ 14.50 (br s, 1H, NH), 8.15 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.60 (t; *J* = 7.6 Hz, 1H), 7.51 (t; *J* = 7.6 Hz, 1H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 148.0, 141.3, 127.9, 125.2, 119.8, 115.1, 111.8; HRMS (ESI) **:** $[M+H]^+$ calcd 164.0454 for $C_7H_6N_3O_2$, found 164.0454.



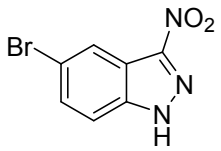
N,N-*Diethyl-1H-indazole-3-carboxamide (**3d**)*. The general procedure with **1d** (220 mg) was followed to provide after purification with column chromatography (eluent = 3:7 ethyl acetate/pentane) 145 mg (71 %) of 71% **3d** as a yellow solid (145mg). mp= 174-174.5°C (lit. 172.5-174°C)[12]; IR $\bar{\nu}$ ($cm^{-1}$)3147, 3107, 3063, 2989, 2972, 2927, 1594, 1579, 1493, 1454, 1434, 746 ; $^1$H NMR (250 MHz, DMSO-$d_6$) δ 13.42 (br s, 1H, NH), 7.97 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.58 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.40 (ddd, *J* = 8.3, 6.8, 1.1 Hz, 1H), 7.19 (ddd, *J* = 8.0, 6.8, 1.0 Hz, 1H), 3.74 (d, *J* = 7.0 Hz, 2H, $CH_2$), 3.51 (d, *J* = 7.5 Hz, 2H, $CH_2$), 1.19 (t, *J* = 7.0 Hz, 6H, 2x$CH_3$) ; $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 162.7 (q), 140.1 (q), 139.3 (q), 126.4 (CH), 122.8 (q), 121.6 (CH), 121.4 (CH), 110.3 (CH), 42.5 ($CH_2$), 40.0 ($CH_2$), 14.7 ($CH_3$), 12.9 ($CH_3$) ; HRMS (ESI) : $[M+H]^+$ calcd. 218.1287 for $C_{12}H_{16}N_3O$, found 218.1288.



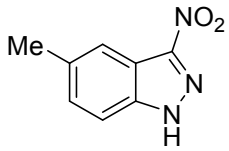
*Methyl 1H-indazole-3-carboxylate (**3e**)*.[13] The general procedure with **1e** (76 mg) was followed to provide after purification with column chromatography (eluent = 2:8 ethyl acetate/pentane) 53 mg (77 %) yield of **3e** as a white solid; mp= 169°C (lit. 170-171°C); IR $\bar{\nu}$ ($cm^{-1}$) 3159, 2106, 1783, 1462, 1230, 1148, 1128, 1067, 745, 734; $^1$H NMR (250 MHz, DMSO-$d_6$) δ 13.93 (br s, 1H, NH), 8.08 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.45 (dd, *J* = 8.2, 6.8 Hz, 1H), 7.31 (dd, *J* = 8.2, 6.8 Hz, 1H)., 3.08 (s, 3H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 163.0, 141.1, 135.2, 126.9, 123.1, 122.3, 121.2, 111.3, 51.8.



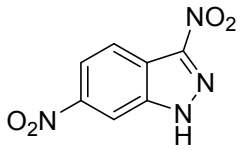
1H-*Indazole (**3f**).*[14] The general procedure with **1f** (62 mg) was followed to provide after purification with column chromatography (eluent = 2:8 ethyl acetate/pentane) 24 mg (51 %) of **3f** as a white solid; mp= 145-146°C (lit. 145-146°C); IR $\bar{\nu}$ ($cm^{-1}$) 3178, 1622, 1504, 1367, 1004, 952; 847, 746; $^1$H NMR (250 MHz, $CDCl_3$) δ 13.04 (br s, 1H, NH), 8.06 (s, 1H), 7.75 (d, *J* = 8,3 Hz, 1H), 7.53 (d, *J* = 8,3 Hz, 1H), 7.33 (t, *J* = 7,3 Hz, 1H), 7.10 (t, *J* = 7,3 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) 140.0, 133.5, 126.0, 122.9, 120.6, 120.3, 110.2.



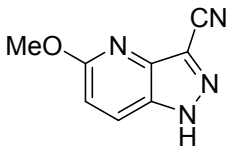
*5-Bromo-3-nitro-1H-indazole (**3h**)* The general procedure with **1h** (50 mg) was followed to provide after purification with column chromatography (eluent = 4:6 ethyl acetate/pentane) 41 mg (87 %) of **3h** as a white solid; mp= 236°C (decomp.); IR $\bar{\nu}$ ($cm^{-1}$) 3233, 1584, 1532, 1490, 1386, 1289, 915, 787; $^1$H NMR (250 MHz, DMSO-$d_6$) δ 14.65 (s, 1H), 8.28 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.78 (dd, *J* = 9.0, 0.8 Hz, 1H), 7.71 (dd, *J* = 9.0, 1.8 Hz, 1H).; $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 140.3, 131.1, 122.2, 118.2, 116.8, 114.3; HRMS (ESI) : $[M+H]^+$ calcd. 241.9560 for $C_7H_5BrN_3O_2$, found 241.9959.



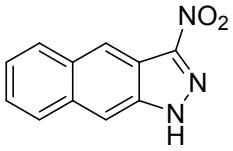
*5-Methyl-3-nitro-1H-indazole (**3i**).* The general procedure with **1i** (75 mg) was followed to provide after purification with column chromatography (eluent = 2:8 ethyl acetate/pentane) 58 mg (84 %) of **3i** as a yellow solid; mp= 190°C (decomp.); IR $\bar{\nu}$ ($cm^{-1}$) 3255, 1588, 1504, 1384, 1307, 1248, 1178, 941, 852, 797, 729; $^1$H NMR (250 MHz, DMSO-$d_6$) δ 14.4 (br s, 1H, NH), 7.94 (s, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 1H), 2.50 (s, 3H, $CH_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 148.2, 140.7, 135.7, 130.7, 119.3, 116.2, 112.3, 21.7; HRMS (ESI) **:** $[M+H]^+$ calcd. 178.0611 for $C_8H_8N_3O_2$, found 178.0612.



*3,6-Dinitro-1H-indazole (**3j**)*. The general procedure with **1j** (40 mg) was followed to provide after purification with column chromatography (eluent = 2:8 ethyl acetate/pentane) 21 mg (57 %) of **3j** as a white solid; mp= 251-252°C (decomp.) (lit.241 - 243 °C)[15]; IR $\bar{\nu}$ ($cm^{-1}$) 1514, 1394, 1348, 1321, 1055, 887, 822, 791, 739; $^1$H NMR (250 MHz, $CDCl_3$) δ 11.19 (br s, 1H, NH), 8.61 (s, 1H), 8.50 (d, *J* = 9.0 Hz, 1H), 8.35 (d, *J* = 9.0 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 162.4, 121.2, 114.3, 53.9.

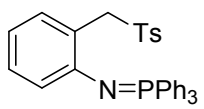


*5-Methoxy-1H-pyrazolo[4,3-*b*]pyridine-3-carbonitrile (**3k**)*. The general procedure with **1k** (98 mg) was followed to provide after purification with column chromatography (eluent = 2:8 ethyl acetate/pentane) 72 mg (80 %) of **3k** as a pale orange solid; mp= 220°C (decomp.); IR $\bar{\nu}$ ($cm^{-1}$) 3267, 2250, 1584, 1510, 1452, 1372, 1278, 1084 ,1010, 954, 817, 757; $^1$H NMR (250 MHz, $CDCl_3$) δ 7.80 (d, *J* = 9.1 Hz, 1H), 6.94 (d, *J* = 9.1 Hz, 1H), 4.06 (s, 3H, $CH_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 162.5, 138.6, 130.9, 124.4, 116.9, 114.2, 114.1, 54.1; HRMS (ESI) **:** $[M+H]^+$ calcd. 175.0614 for $C_8H_7N_4O$, found 175.0614.

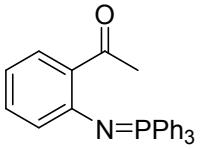


*3-Nitro-1H-benzo*[f]*indazole (**3l**)* The general procedure with **1l** (50 mg) was followed to provide after purification with column chromatography (eluent = 1:1 ethyl acetate/pentane) 21 mg (40 %) of **3l** as an orange solid. mp=269-270°C (decomp.); IR $\bar{\nu}$ ($cm^{-1}$) 3192, 3056, 1533, 1502, 1486, 1377, 1298, 853, 734; $^1$H NMR (250 MHz, DMSO-$d_6$) 14.62 (br s, 1H, NH), 8.86 (s, 1H), 8.37 (s, 1H), 8.27 – 8.20 (m, 1H), 8.19 – 8.12 (m, 1H), 7.68 – 7.44 (m, 2H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 139.9 (q), 132.5 (q), 130.9 (q), 129.1 (CH), 128.1 (CH), 126.8 (CH), 125.4 (CH), 119.1 (CH), 115.6 (q), 108.2 (CH); HRMS (ESI) **:** $[M+H]^+$ calcd. 214.0611 for $C_{11}H_8N_3O_2$, found 214.0611.

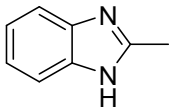
**General procedure for the preparation of 2a, 5 and 14.** Azide (1.0 equiv.) was dissolved in anhydrous acetonitrile (0.12M) under argon. Then triphenylphosphine (1.1 equiv.) was added and the resulting mixture was stirred at room temperature until total consumption of starting material (3-4h). For compound **5** a precipitate appeared. This precipitate was filtered and triturated with 5mL of cold acetonitrile to yield the corresponding iminophosphorane without any further purification. For compounds **2a** and **14** the solvent was evaporated and the crude mixture purified on flash chromatography to yield the corresponding product.



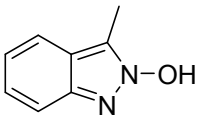

*1,1,1-Triphenyl-N-(2-(tosylmethyl)phenyl)-l5-phosphanimine (**2a**)*. The general procedure with **1a** (210 mg) was followed to provide after purification with column chromatography (eluent = 3:7 ethyl acetate/pentane) 310 mg (83 %) of **2a** as a white solid; mp= 171-172°C , IR $\bar{\nu}$ ($cm^{-1}$) 3063, 2907, 1482, 1351, 1124, 733; $^1$H NMR (250 MHz, DMSO-$d_6$) δ 7.76 – 7.41 (m, 17H), 7.30 – 7.19 (m, 1H), 7.19 – 7.03 (m, 2H), 6.73 (ddd, *J* = 8.0, 7.3, 1.8 Hz, 1H), 6.52 (td, *J* = 7.4, 1.2 Hz, 1H), 6.19 – 6.06 (m, 1H), 4.91 (s, 2H), 2.22 (s, 3H).; $^{13}$C NMR (63 MHz, DMSO-$d_6$) δ 150.3, 143.6, 137.0, 132.1, 131.9, 131.6, 130.6, 129.2, 129.1, 128.9, 128.7, 128.5, 128.0, 121.6, 121.2, 120.0, 116.2, 57.2 ($CH_2$), 21.02 ($CH_3$); HRMS (ESI) : [M+H]+ calcd 522.1651 for $C_{32}H_{29}NO_2PS$ found 522.1648.




*1-(2-((Triphenyl-l5-phosphanylidene)amino)phenyl)ethan-1-one (**5**)*. The general procedure with **4** (210 mg) was followed, the resulted precipitate was filtered and triturated with cold acetonitrile (5 mL) to provide 360 mg (70 %) of **5** as a white solid; mp= 120°C; IR $\bar{\nu}$ ($cm^{-1}$) 1645, 1585, 1436, 1260, 1106, 744; $^1$H NMR (250 MHz, DMSO-$d_6$) δ 7.84 – 7.49 (m, 15H), 7.35 – 7.23 (m, 1H), 6.89 (ddd, *J* = 8.1, 7.2, 1.9 Hz, 1H), 6.54 (td, *J* = 7.4, 1.0 Hz, 1H), 6.35 (dt, *J* = 8.2, 1.2 Hz, 1H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 203.29, 150.85, 134.97, 134.59, 132.23, 132.19, 132.13, 131.97, 131.23, 130.47, 129.15, 128.96, 128.89, 128.71, 128.67, 122.35, 122.15, 116.22, 31.36 ($CH_3$); HRMS (ESI) **:** $[M+H]^+$ calcd. 396.1511 for $C_{26}H_{23}NOP$, found 396.1512.

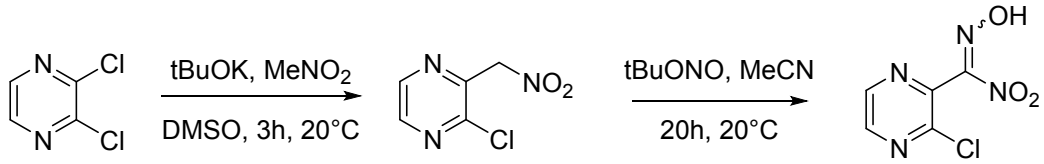



*2-Methyl-1H-benzo[*d*]imidazole (**14**)*[16]. The general procedure with **13** (132 mg) was followed in refluxing acetonitrile for 48h to provide after purification with column chromatography (eluent = 6:4 ethyl acetate/pentane) 79 mg (71 %) of **14** as a white solid; mp = 174-175°C (lit. 175-176°C)[15]; IR $\bar{\nu}$ ($cm^{-1}$) 3062, 2784, 2536, 1500, 1385, 1269, 1027, 729; $^1$H NMR (250 MHz, DMSO-$d_6$) δ 12.15 (s, 1H), 7.52 – 7.35 (m, 2H), 7.14 – 7.05 (m, 2H), 2.47 (s, 3H); HRMS (ESI) **:** $[M+H]^+$ calcd. 133.0760 for $C_8H_9N_2$, found 133.0757.

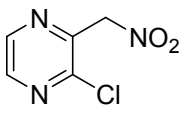



*3-Methyl-2H-indazol-2-ol (**15**)*[17]. The reaction was performed with **13** (100 mg) in refluxing toluene for 24h to provide after purification with column chromatography (eluent = 5% methanol in dichloromethane) 71mg (93%) of **15** as a light brown solid; mp = 174-175°C (lit 173-175°C)[17]; IR $\bar{\nu}$ ($cm^{-1}$) 3432, 1004, 758; $^1$H NMR (250 MHz, DMSO-$d_6$) δ 13.22 (br s, 1H, OH), 7.62 (dt, *J* = 8.3, 1.2 Hz, 1H), 7.45 (dt, *J* = 8.6, 1.0 Hz, 1H), 7.22 (ddd, *J* = 8.6, 6.8, 1.2 Hz, 1H), 7.02 (ddd, *J* = 8.3, 6.8, 1.0 Hz, 1H), 2.51 (s, 3H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 140.1 (C), 124.9 (CH), 122.1 (C), 119.8 (CH), 119.3 (CH), 118.8 (C), 115.1 (CH), 8.3 (CH3).; HRMS (ESI) **:** $[M+H]^+$ calcd. 149.0709 for $C_8H_9N_2O$, found 149.0709.

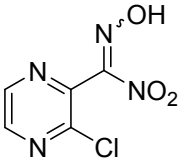
**Preparation of 10 and 11:**




**10** **11**

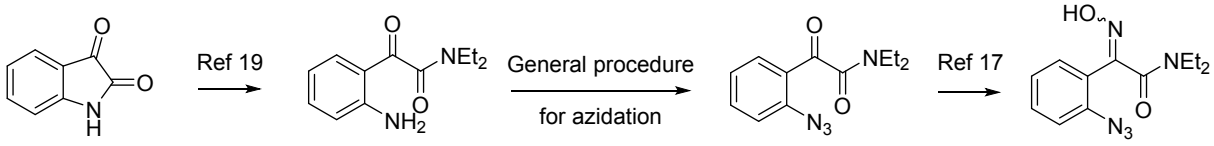


*2-Chloro-3-(nitromethyl)pyrazine (**10**).* In a dry flask was added to a solution of tBuOK (1.57 g; 14 mmol; 2 equiv.) in DMSO (10mL) the nitromethane (0.80mL; 14 mmol; 2 equiv.). Then the commercially available 2,3-Dichloropyrazine (1.00 g; 7 mmol; 1 equiv.) was slowly added and the resulting mixture was stirred for 3 hours at 20 °C. The reaction mixture was poored into 20 mL of iced water, the aqueous phase was washed three times with 20 mL of $Et_2O$, acidified with a Kornblum solution (6M) to pH=4 and extracted three times with 20 mL of $Et_2O$. The organic phase was dried under $MgSO_4$ and concentrated under reduced pressure to provide 720mg (62%) of **10** as a red oil without further purification; $^1$H NMR (250 MHz, $CDCl_3$) δ 8.58 (d, *J* = 2.5 Hz, 1H), 8.48 (d, *J* = 2.5 Hz, 1H), 5.81 (s, 2H).; $^{13}$C NMR (101 MHz, $CDCl_3$) 150.1 (C), 145.2 (CH), 144.2 (C), 142.8 (CH), 77.5 (CH2)

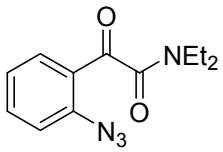


*(Z and E isomers mixture) 3-Chloropyrazin-2-yl(nitro)methanone oxime (**11**).* In a dry flask under argon was added **10** (96mg; 0.55 mmol; 1equiv.) and dry MeCN (2 mL). Then tBuONO (0.27 mL; 2.21 mmol; 4 equiv.) was added and the mixture stirred at 20 °C for 20 h. The mixture was filtrated on celite pad and purified with column chromatography (eluent = 8:2 pentane/ethyl acetate) to provide 39mg (35%) of **11** as a pale yellow solid; mp = 121-123 °C; $^1$H NMR (250 MHz, DMSO-$d_6$) δ 8,67 (d, J = 2,4 Hz, 1H); 8,74 (d, J = 2,4 Hz, 1H); 8,78 (d, J = 2,4 Hz, 1H); 8,81 (d, J = 2,4 Hz, 1H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 152.8 (C), 147.9 (C), 146.8 (CH), 146.7 (CH), 143.8 (CH), 143.3 (CH), 139.0 (C), 138.0 (C), 111.8 (C); HRMS (ESI) **:** $[M+H-HNO2]^+$ calcd. 155.9959 for $C_5H_3ClN_3O$, found 155.9959; [2M+H-2HNO2] calcd. 310.9846 for $C_{10}H_5Cl_2N_6O_2$, found 310.9844.

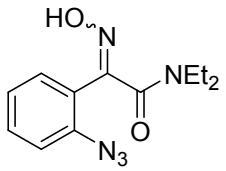
**Preparation of 12:**




**12"** **12'** **12**



*2-(2-Azidophenyl)-N,N-diethyl-2-oxoacetamide (**12'**)*. The reaction was performed with **12''** (840mg) following the general procedure for the generation of azido compound. The product appeared to precipitate in the reaction medium and was directly filtrated and washed with water to provide 830mg (88%) of **12'** as a red solid; mp = 78-79 °C; IR $\bar{\nu}$ ($cm^{-1}$)2975, 2145 2126, 2106, 1666, 1634, 1472, 758; $^1$H NMR (250 MHz, DMSO-$d_6$) δ 8.08 – 7.77 (m, 1H), 7.69 – 7.51 (m, 1H), 7.32 – 7.12 (m, 2H), 3.53 (q, *J* = 7.1 Hz, 2H), 3.29 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) 189.6 (C), 167.3 (C), 140.7 (C), 135.2 (CH), 131.9 (CH), 126.2 (C), 125.3 (CH), 119.3 (CH), 42.1 ($CH_2$), 38.9 ($CH_2$), 13.8 ($CH_3$), 12.2 ($CH_3$).; HRMS (ESI) **:** $[M+H]^+$ calcd. 247.1189 for $C_{12}H_{15}N_4O_2$, found 247.1190.

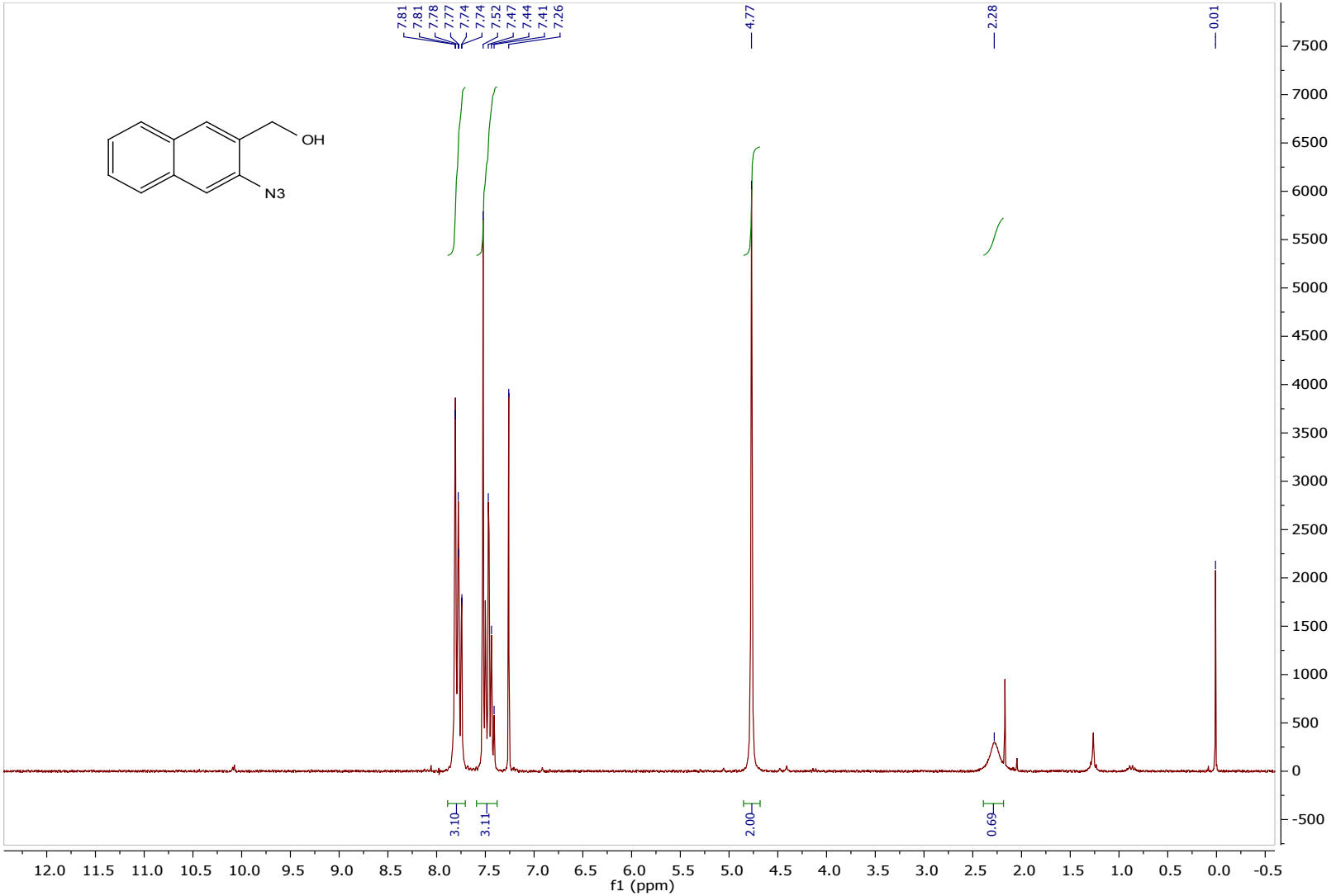


*2-(2-Azidophenyl)-N,N-diethyl-2-(hydroxyimino)acetamide (**12**)*. The procedure[17] with **12'** (750mg) was followed to provide after purification with column chromatography (eluent = 3:7 ethyl acetate/pentane) 406 mg (52%) of **12** as an orange solid; mp = 110-111 °C (decomp.); IR $\bar{\nu}$ ($cm^{-1}$) 3148, 2989, 2937, 1624, 1596, 1435, 1116, 719; $^{1}H$ NMR (250 MHz, $CDCl_3$) δ 8.76 (s, 1H, OH), 7.65 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.49 – 7.35 (m, 1H), 7.24 – 7.08 (m, 2H), 3.56 (q, *J* = 7.1 Hz, 2H, $CH_2$), 3.36 (q, *J* = 7.1 Hz, 2H, $CH_2$), 1.23 (t, *J* = 7.1 Hz, 3H, $CH_3$), 1.17 (t, *J* = 7.1 Hz, 3H, $CH_3$).,; $^{13}C$ NMR (63 MHz, $CDCl_3$) δ 163.5 (C), 152.3 (C), 137.8 (C), 131.3 (CH), 130.5 (CH), 125.2 (CH), 123.5 (C), 119.3 (CH), 42.5 ($CH_2$), 38.3 ($CH_2$), 13.7 ($CH_3$), 12.4 ($CH_3$); HRMS (ESI) **:** $[M+H]^+$ calcd. 262.1298 for $C_{12}H_{16}N_5O_2$, found 262.1301.

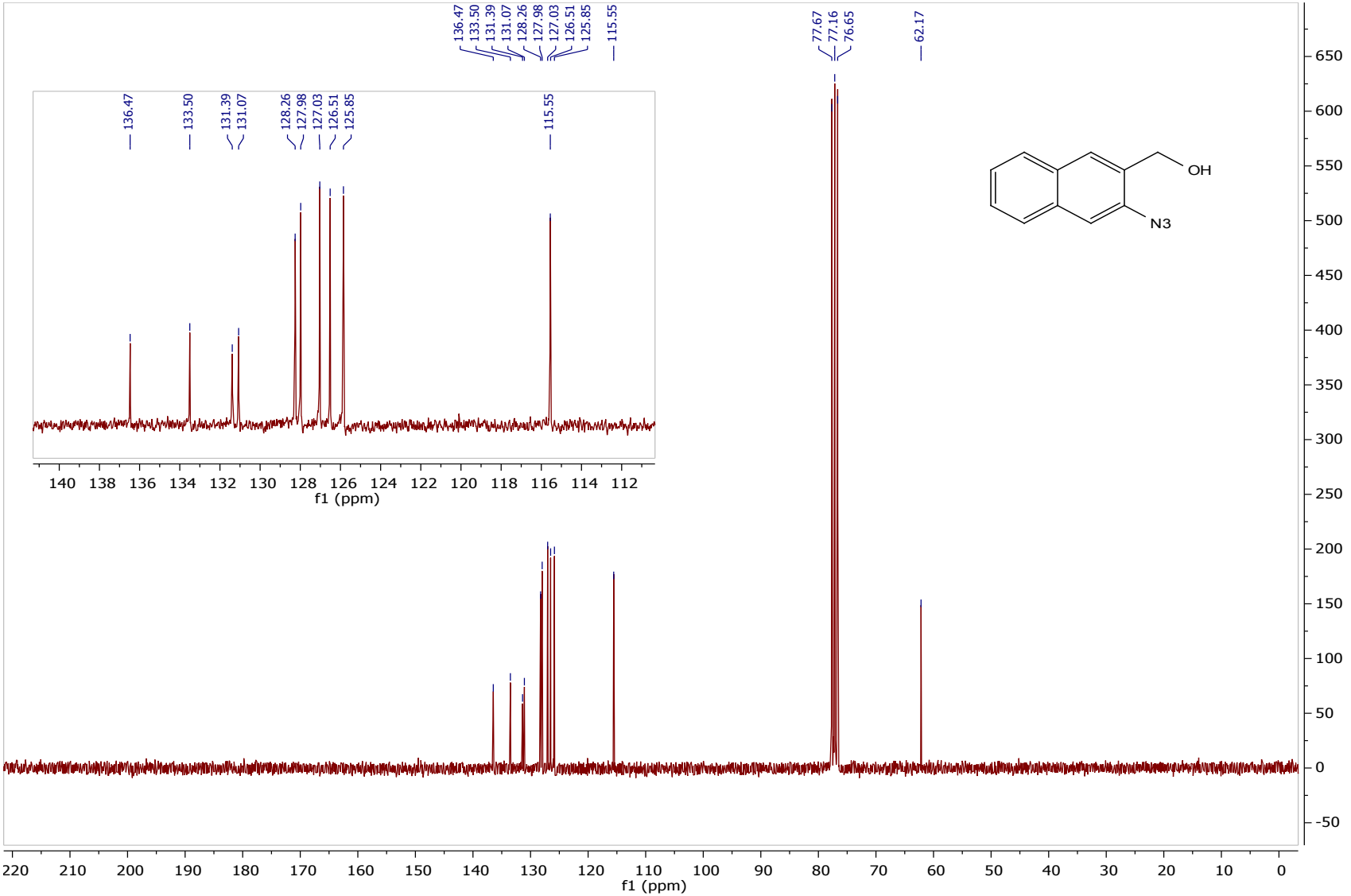
**References:**


1. Rathore, V.; Sattar, M.; Kumar, R.; Kumar, S. *J. Org. Chem.* **2016**, *81*, 9206.
2. Schwarzer, D. D.; Gritsch, P. J.; Gaich, T. *Angew. Chem. Int. Ed.* **2012**, *51*, 11514.
3. Taffarel, E.; Chirayil, S.; Thummel, R. P. *J. Org. Chem.* **1994**, *59*, 823.
4. Alajarín, M.; López-Lázaro, A.; Vidal, A.; Berná, J. *Chem. - Eur. J.* **1998**, *4*, 2558.
5. Sabbatini, P.; Wellendorph, P.; Høg, S.; Pedersen, M. H. F.; Bräuner-Osborne, H.; Martiny, L.; Frølund, B.; Clausen, R. P. *J. Med. Chem.* **2010**, *53*, 6506.
6. Thompson, W. J.; Jones, J. H.; Lyle, P. A.; Thies, J. E. *J. Org. Chem.* **1988**, *53*, 2052.
7. Nguyen, Q.; Nguyen, T.; Driver, T. G. *J. Am. Chem. Soc.* **2013**, *135*, 620.
8 Takahashi, M.; Suga, D. *Synthesis* **1998**, 986.
9. Culshaw, J. D.; Eden, J. M.; Ford, S. J.; Hayter, B.; Perkins, D. R.; Pike, K. G. *Synlett* **2012**, *23*, 1816.
10. Senecal, T. D.; Shu, W.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2013**, *52*, 10035.
11. Cohen-Fernandes, P.; Habraken, C. L. *J. Org. Chem.* **1971**, *36*, 3081.
12. Schwarzer, D. D.; Gritsch, P. J.; Gaich, T. *Angew. Chem. Int. Ed.* **2012**, *51*, 11514.
13. Buchstaller, H.-P.; Wilkinson, K.; Burek, K.; Nisar, Y. *Synthesis* **2011**, 3089.
14. Coşkun, N.; Çetin, M. *Tetrahedron* **2007**, *63*, 2966.
15. Wrzeciono; U; Linkowska, E. *Pharmazie*, **1980**, *35*, 593.
16. Butler, R. N.; Fitzgerald, K. J. *J. Chem. Soc.* **1989**, 155.
17. Takada, K.; Kan-Woon, T.; Boulton, A. J. *J. Org. Chem.* **1982,** *47*, 4323.
18. (a) Takahashi, M.; Suga, D. *Synthesis* **1998**, 986; (b) Benati, L.; Bencivenni, G.; Leardini, R.; Nanni, D.; Minozzi, M.; Spagnolo, P.; Scialpi, R.; Zanardi, G. *Org. Lett.* **2006**, *8*, 2499; (c) Alajarín, M.; Bonillo, B.; Orenes, R.-A.; Ortín, M.-M.; Vidal, A. *Org. Biomol. Chem.* **2012**, *10*, 9523; (d) Schwarzer, D. D.; Gritsch, P. J.; Gaich, T. *Angew. Chem. Int. Ed.* **2012**, *51*, 11514; (e) Stokes, B. J.; Vogel, C. V.; Urnezis, L. K.; Pan, M.; Driver, T. G. *Org. Lett.* **2010**, *12*, 2884.
19. Arifuzzaman, Md.; Kandahary, R. K.; Islam, Md. R.; Duddeck, H.; Gomez, E *J. Bangladesh Chem. Soc*. **2008**, *21*, 81

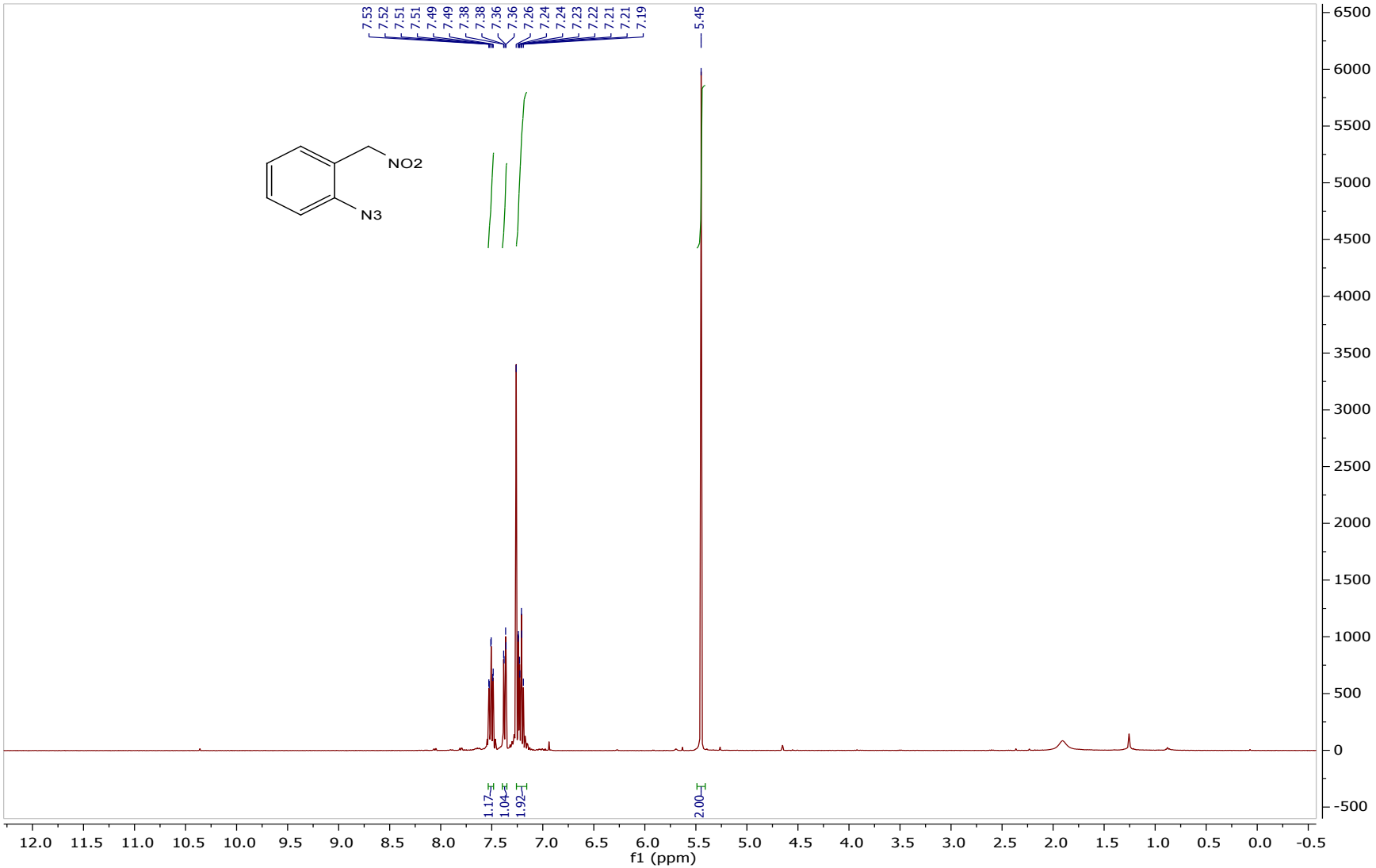
$^{1}$H NMR spectrum **1l”** (250 MHz, $CDCl_3$)



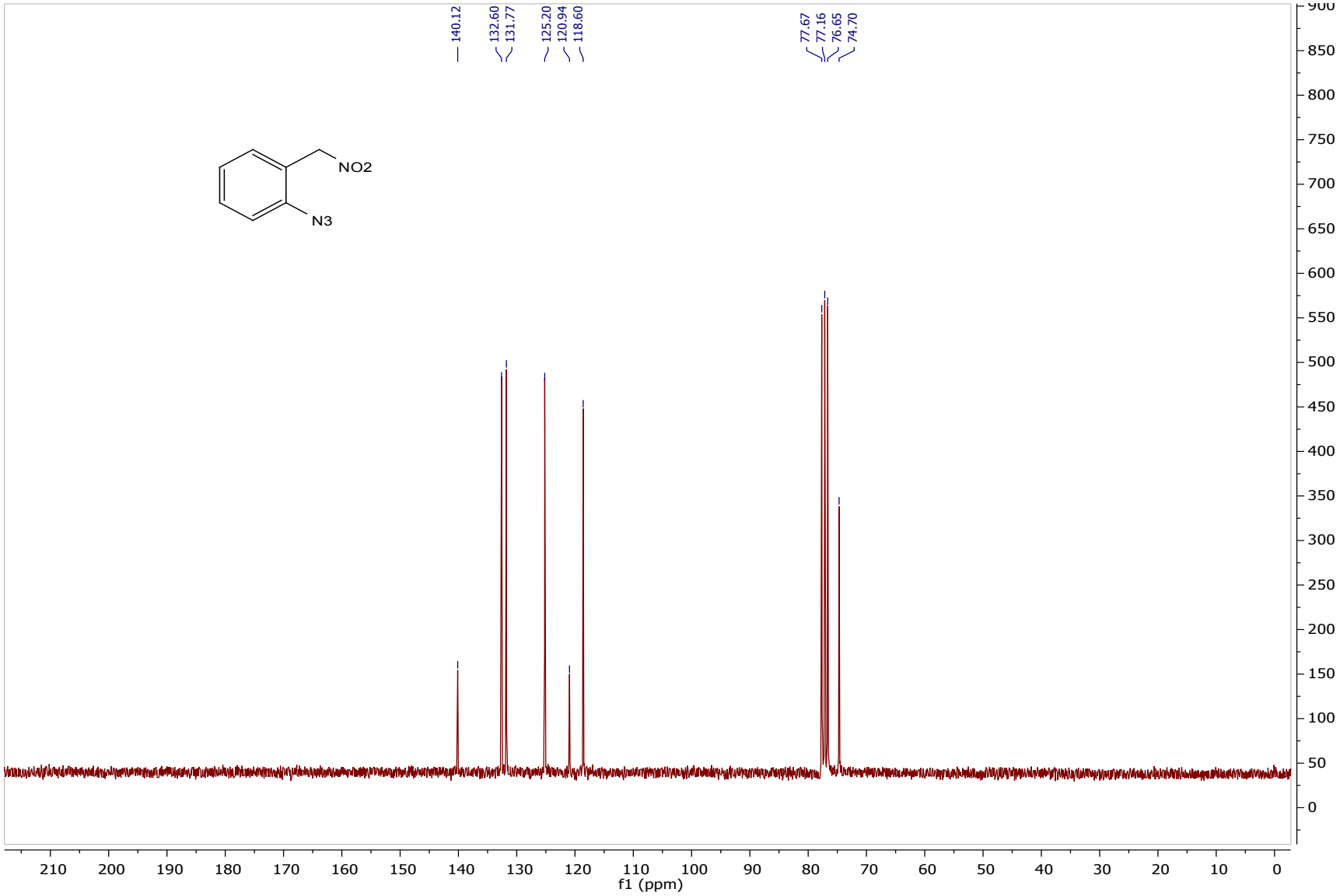
$^{13}$C NMR spectrum **1l”** (101 MHz, $CDCl_3$)



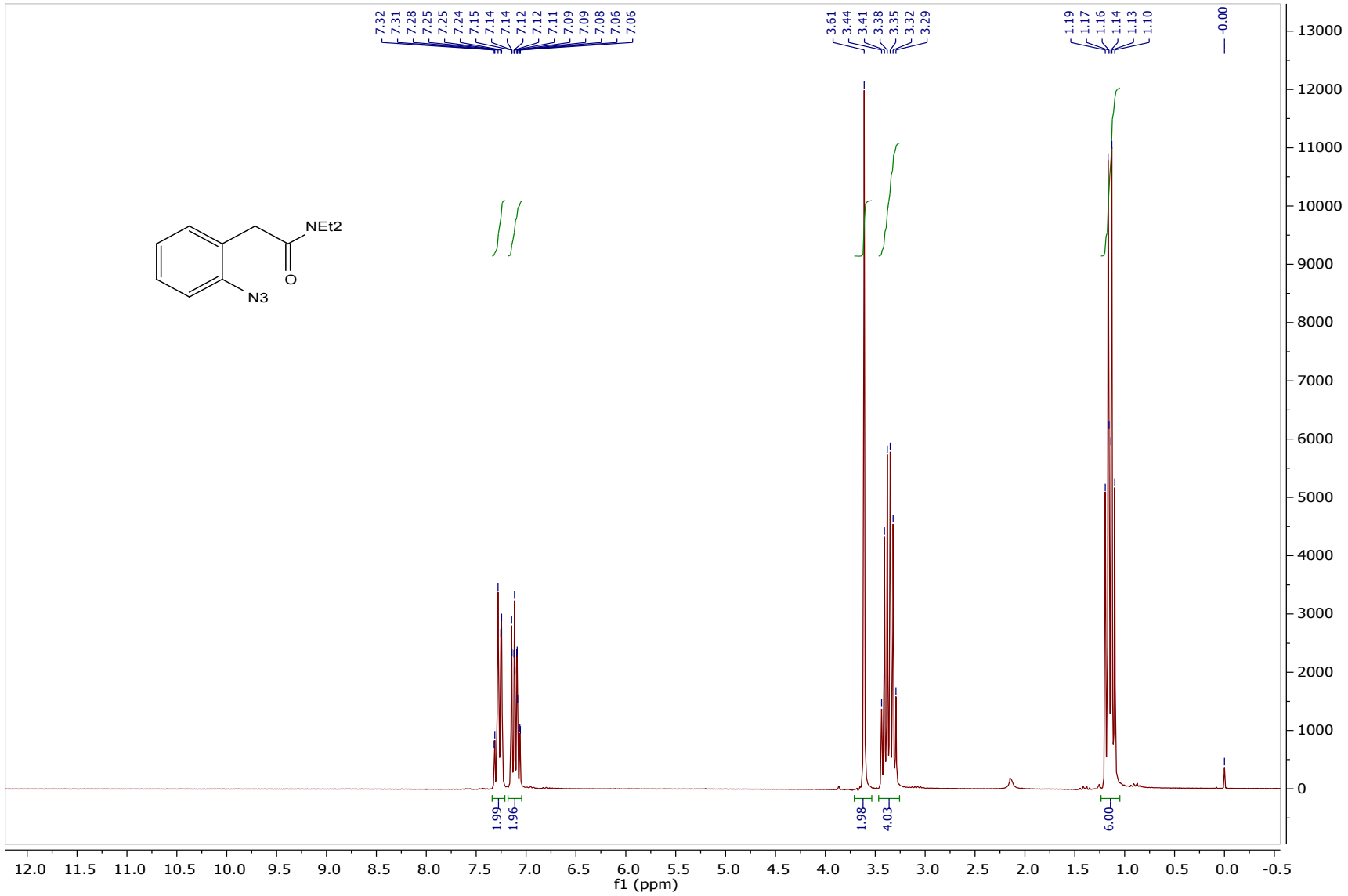
$^{1}$H NMR spectrum **1c** (250 MHz, $CDCl_3$)



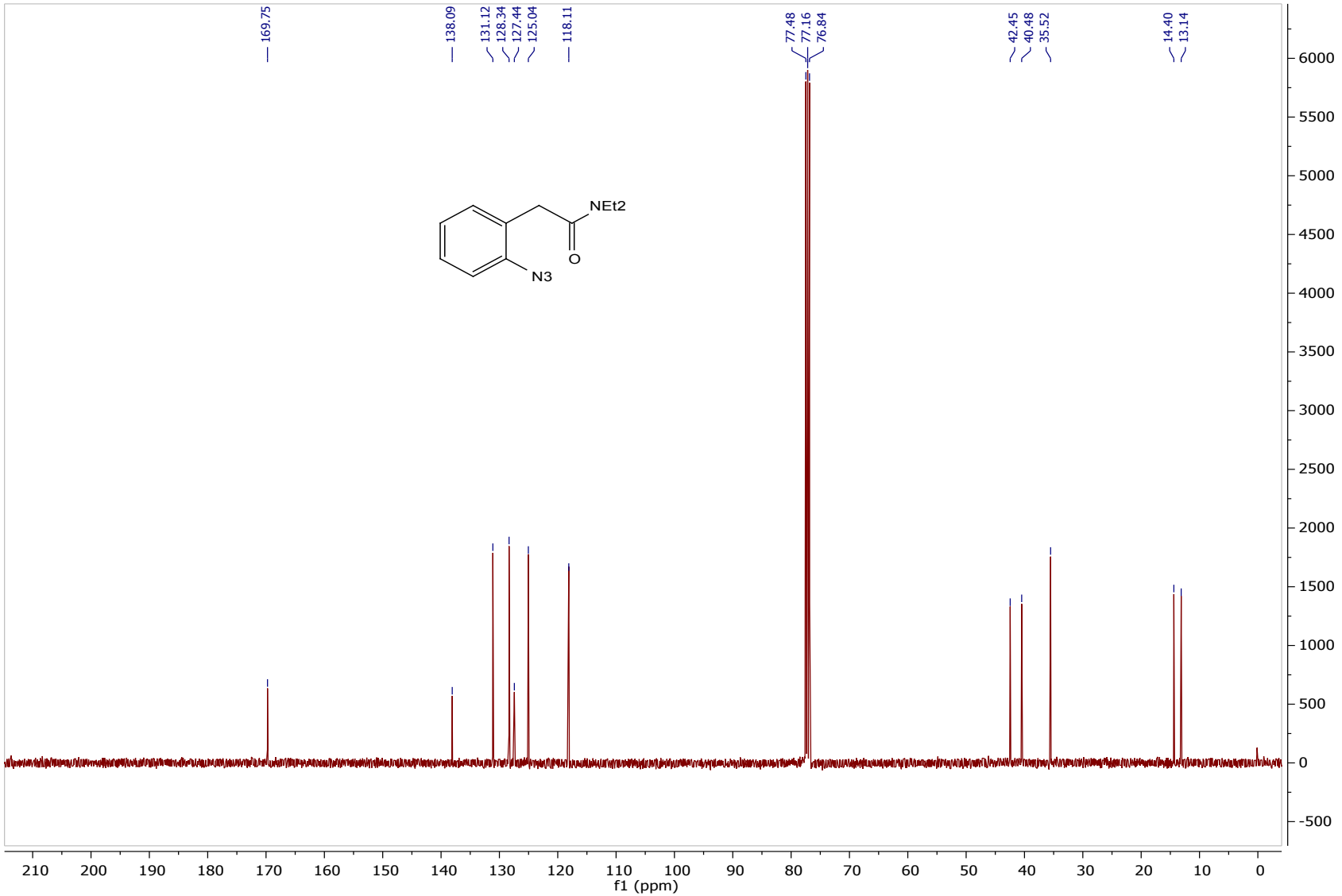
$^{13}C$ NMR spectrum **1c** (101 MHz, $CDCl_3$)



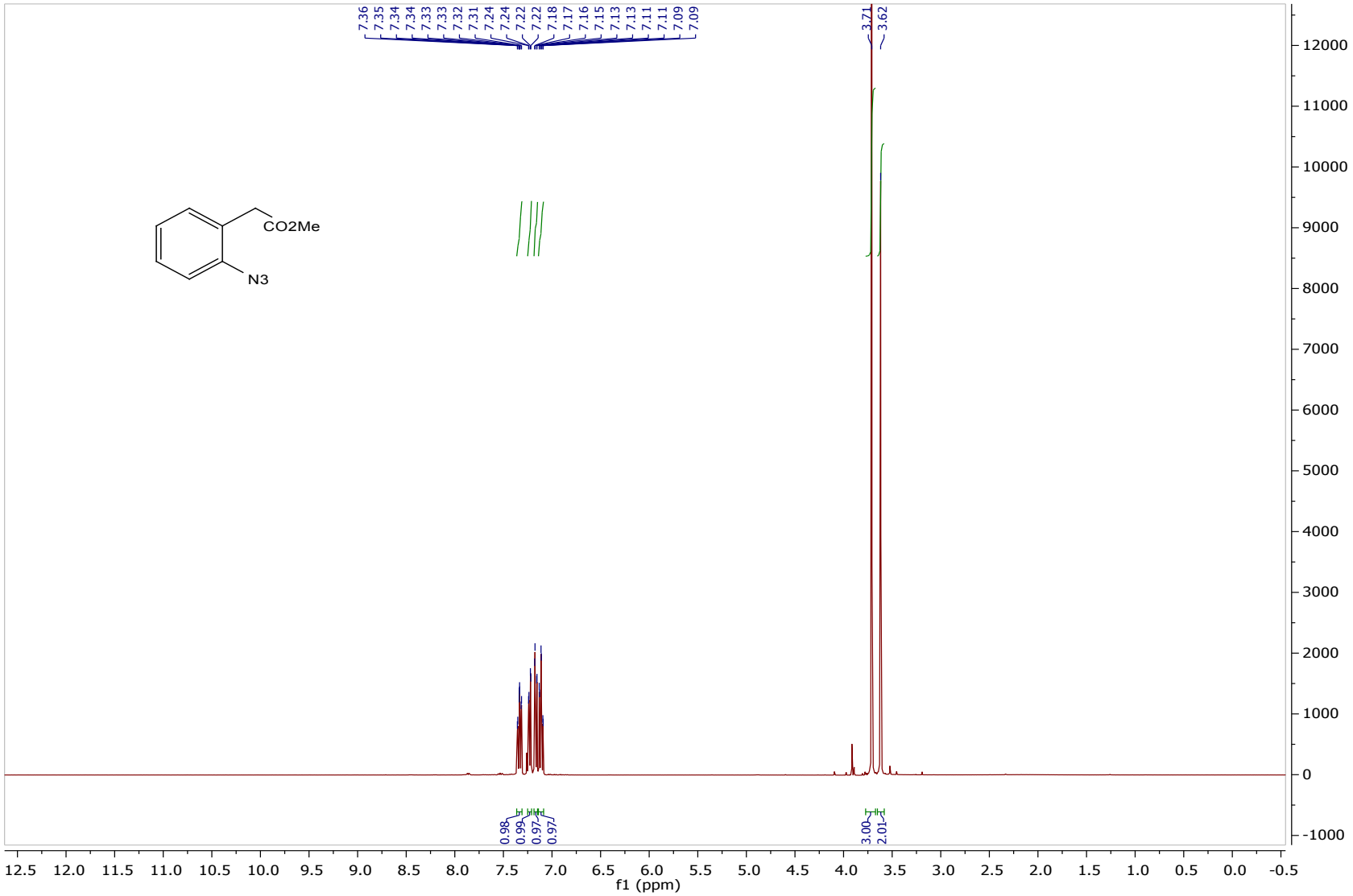
$^{1}$H NMR spectrum **1d** (250 MHz, DMSO-$d_6$)



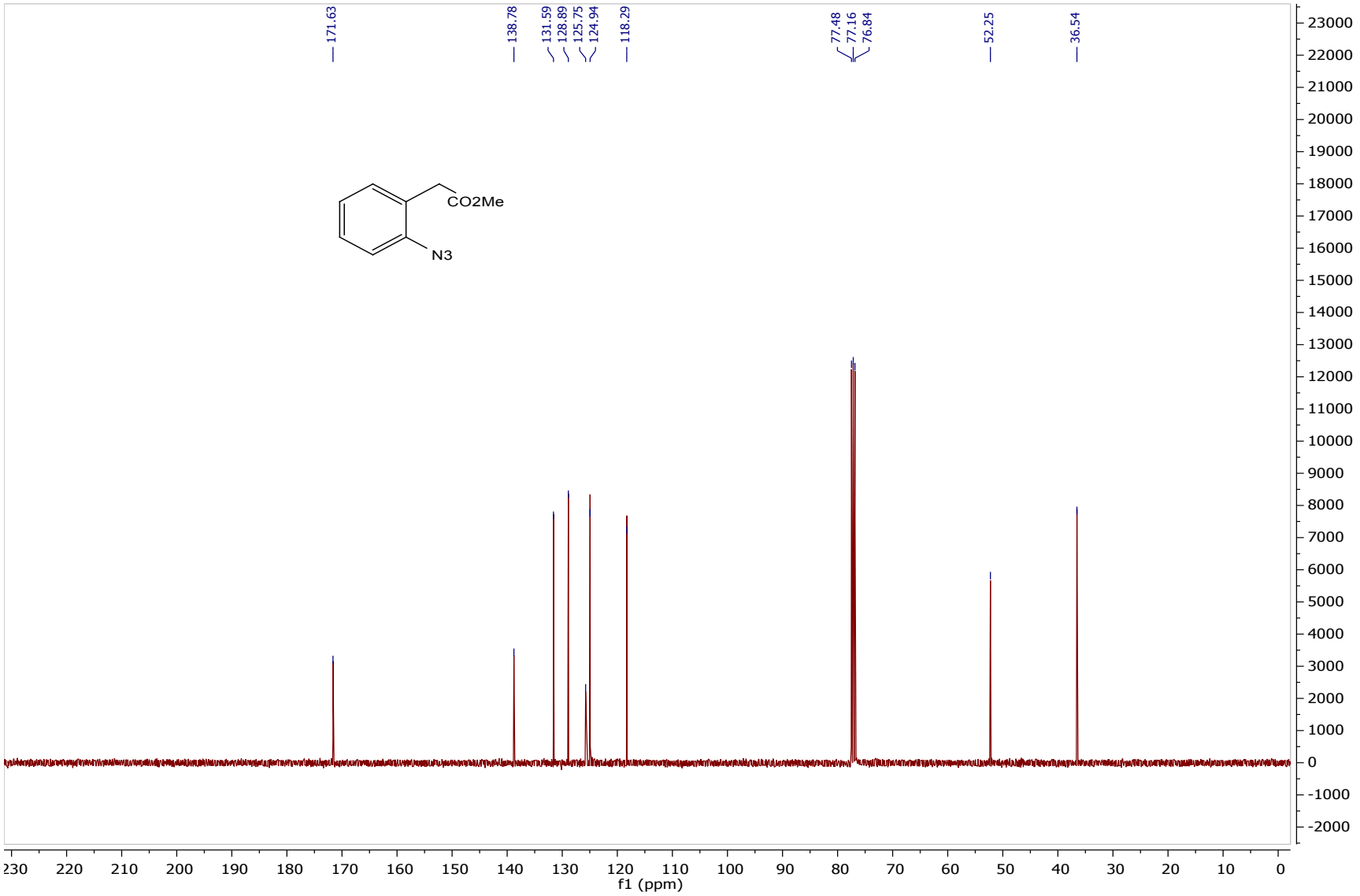
$^{13}$C NMR spectrum **1d** (101 MHz, $CDCl_3$)



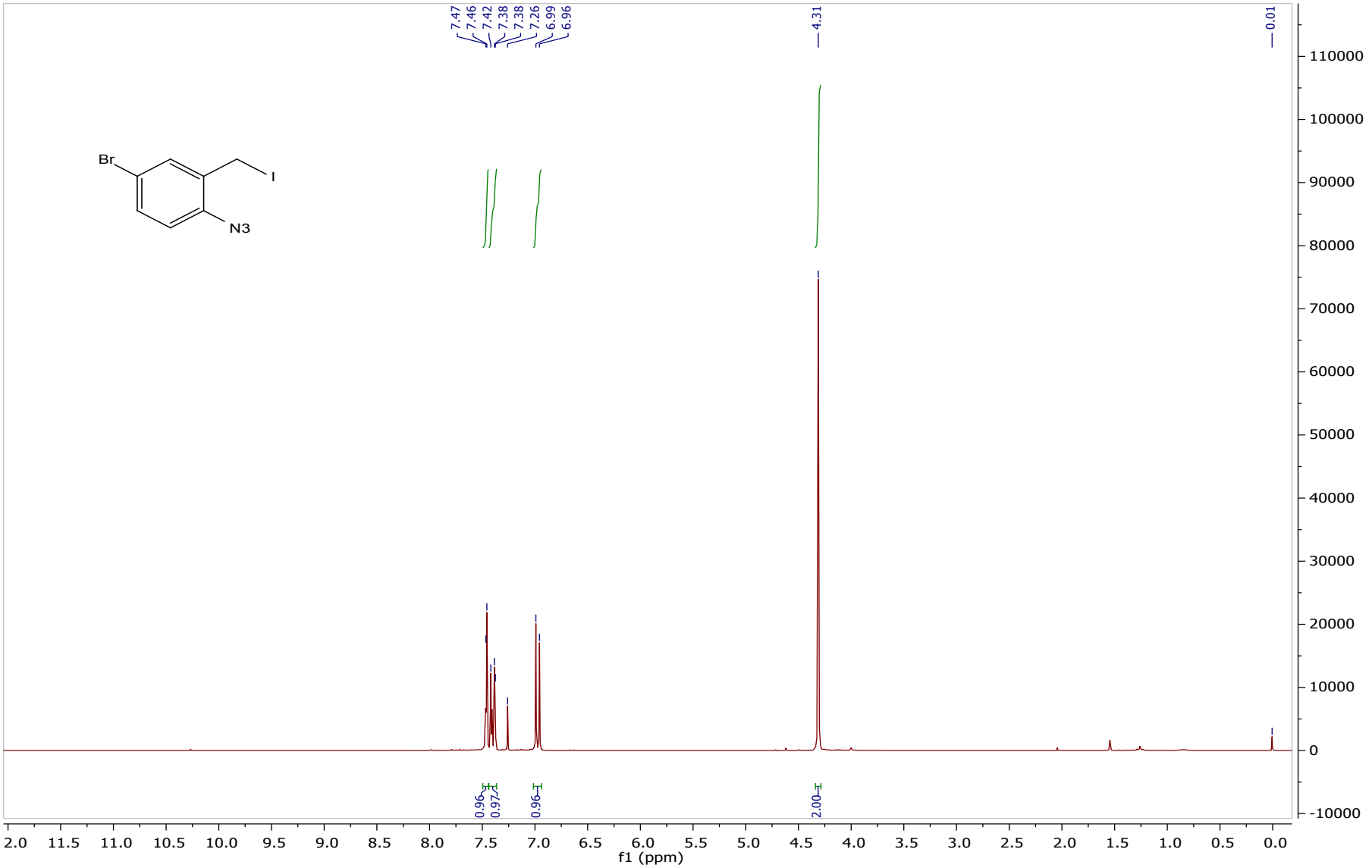
$^{1}$H NMR spectrum **1e** (250 MHz, $CDCl_3$)



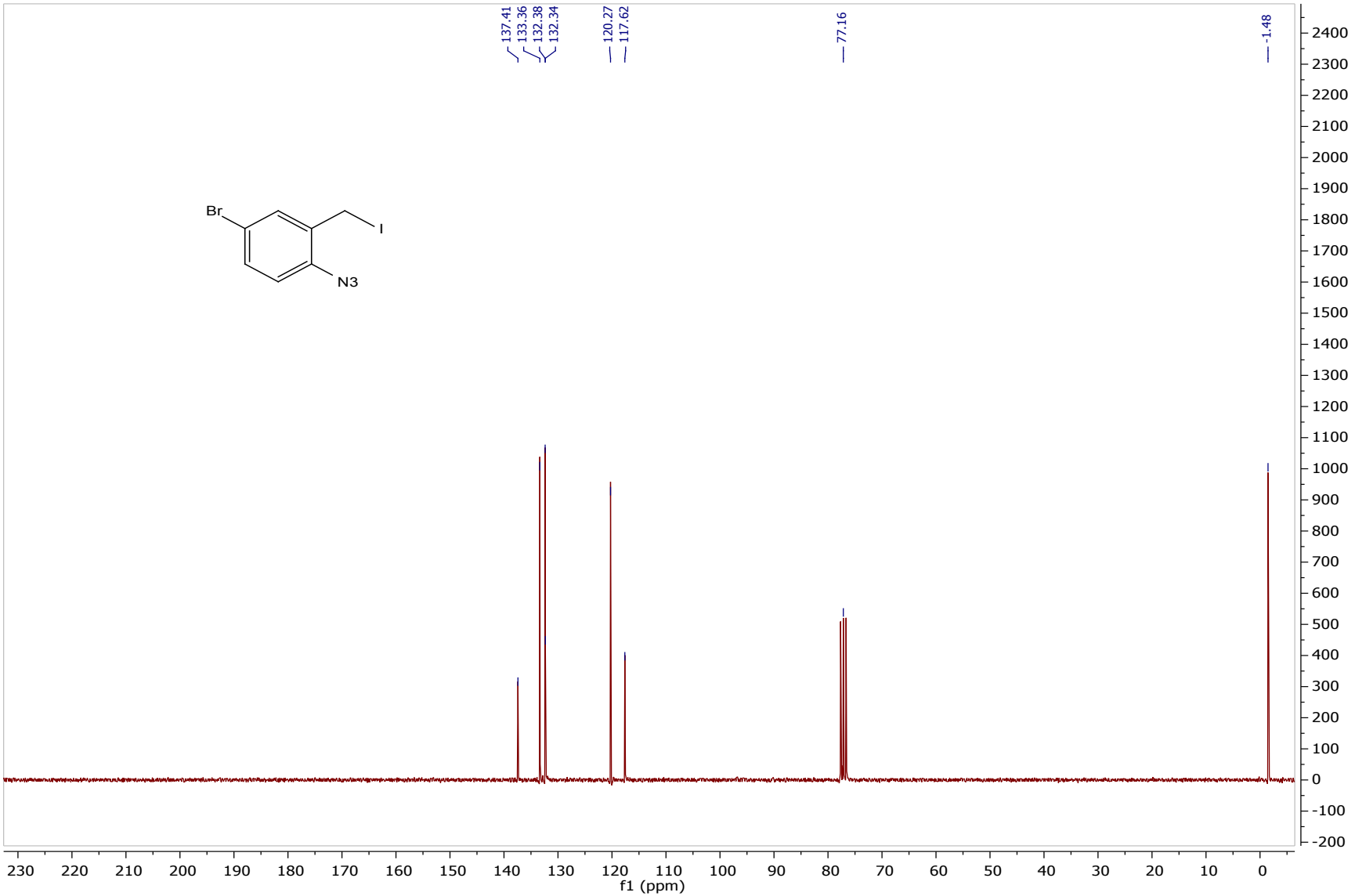
$^{13}C$ NMR spectrum **1e** (101 MHz, $CDCl_3$)



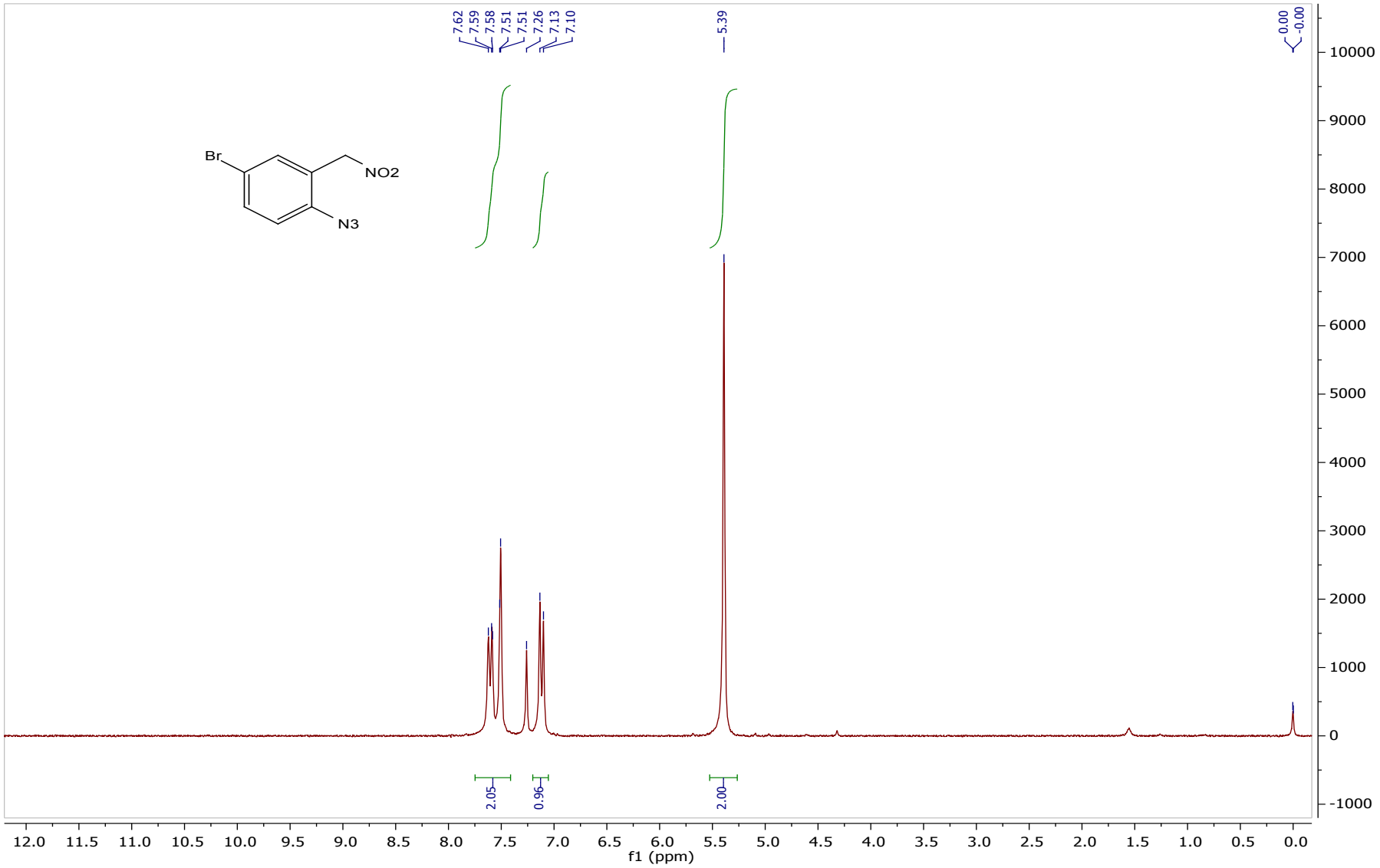
$^{1}$H NMR spectrum **1h'** (250 MHz, $CDCl_3$)



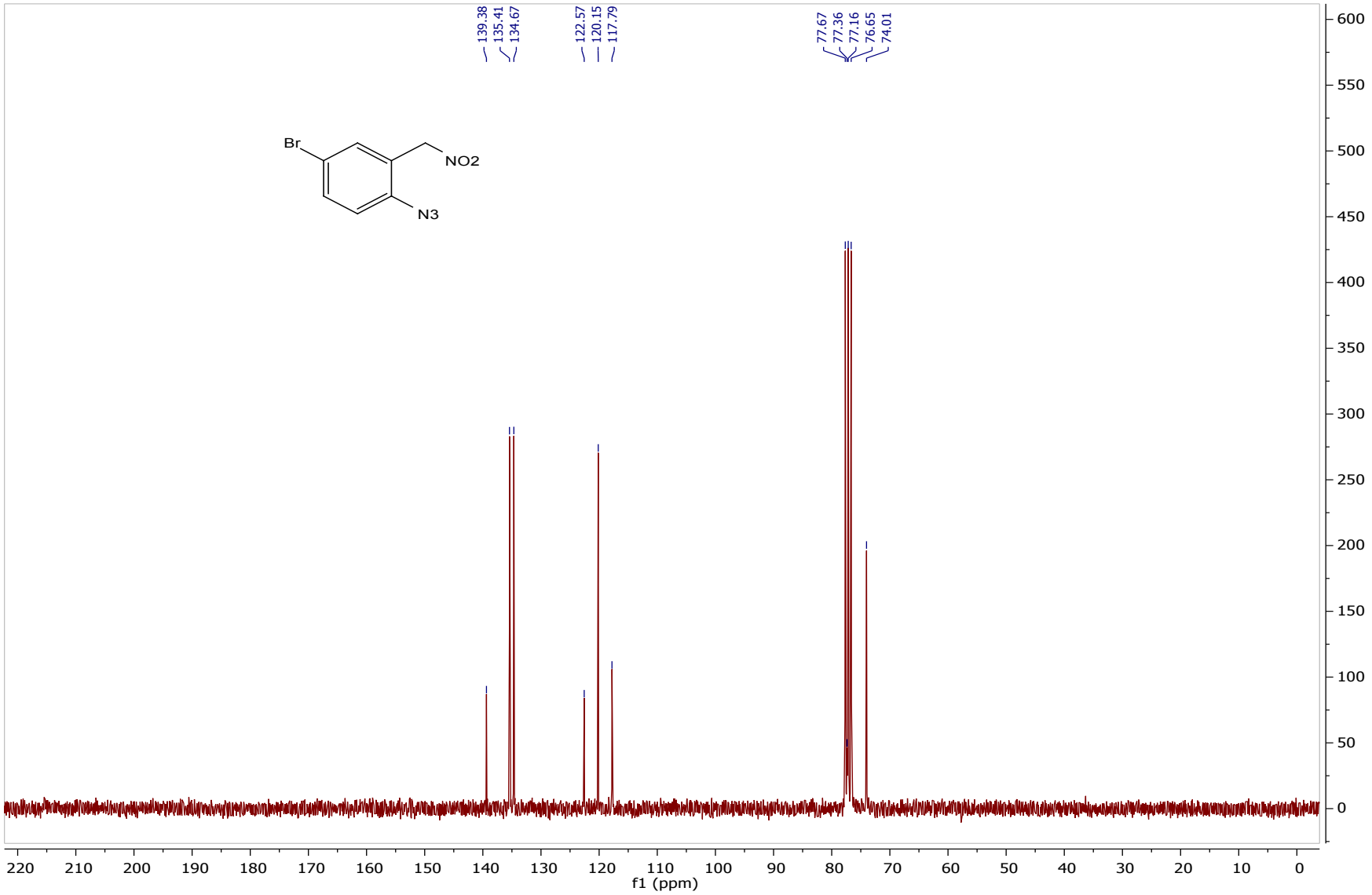
$^{13}C$ NMR spectrum **1h'** (101 MHz, $CDCl_3$)



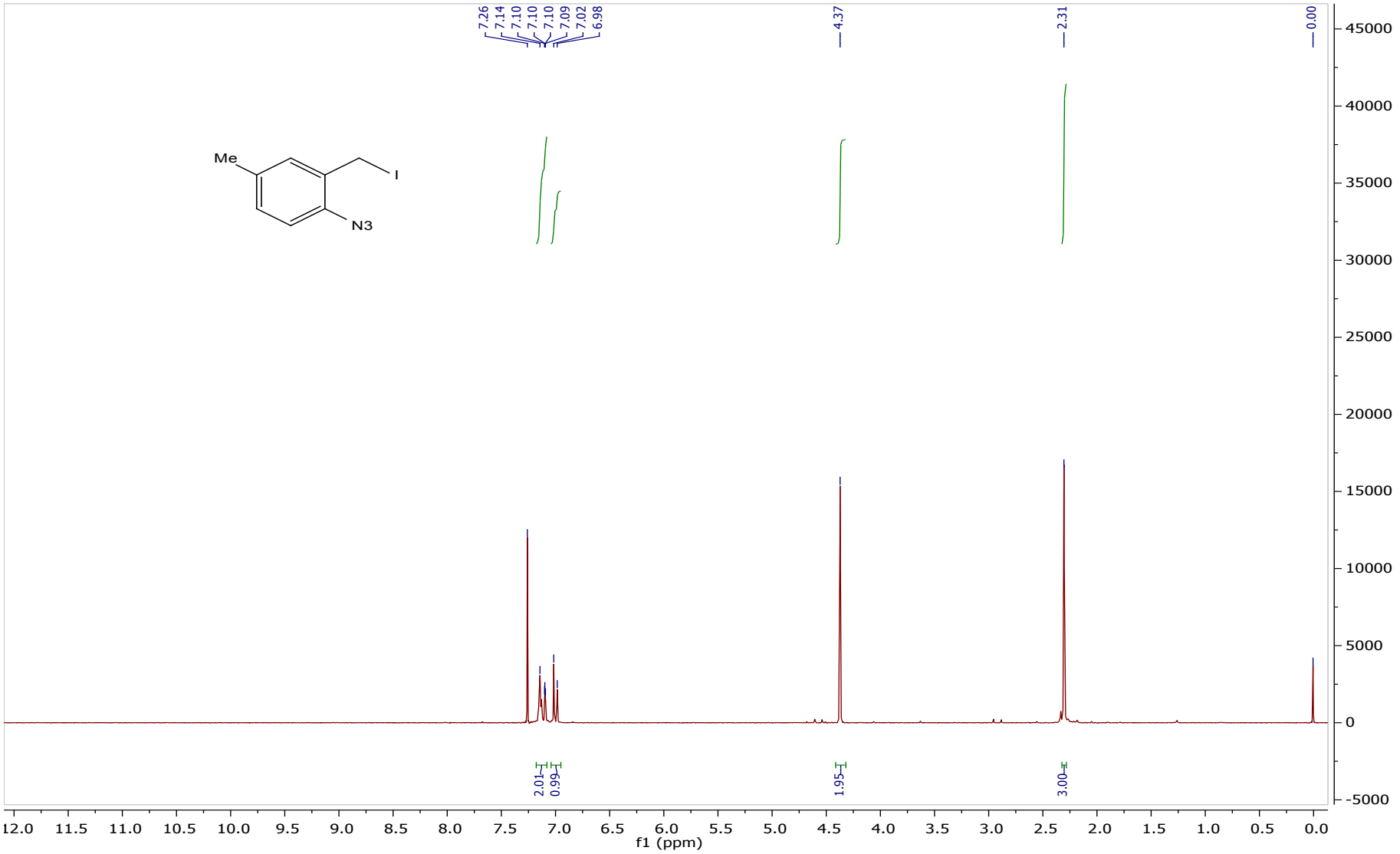
$^{1}$H NMR spectrum **1h** (250 MHz, $CDCl_3$)



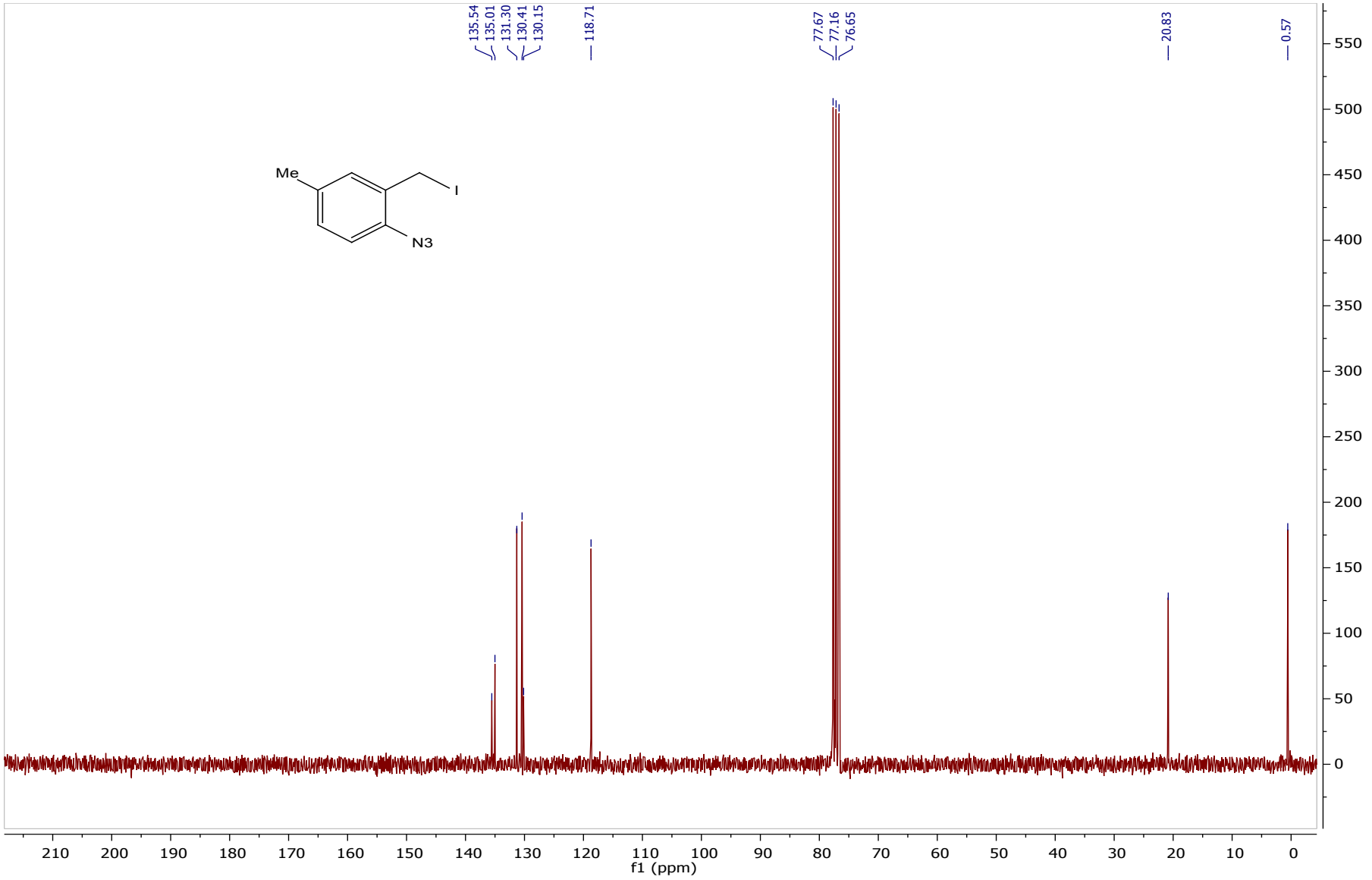
$^{13}$C NMR spectrum **1h** (101 MHz, $CDCl_3$)



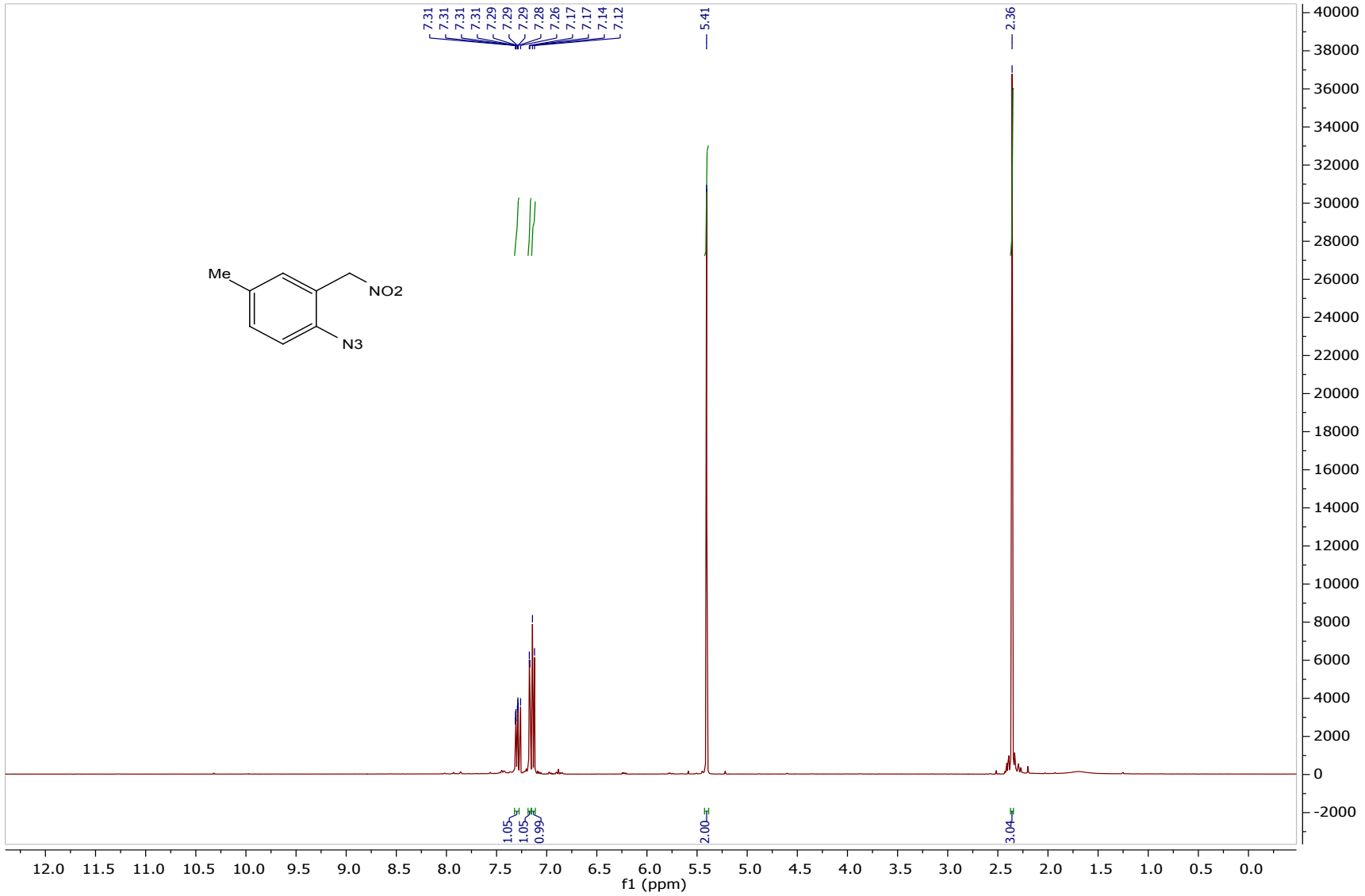
$^{1}$H NMR spectrum **1i'** (250 MHz, $CDCl_3$)



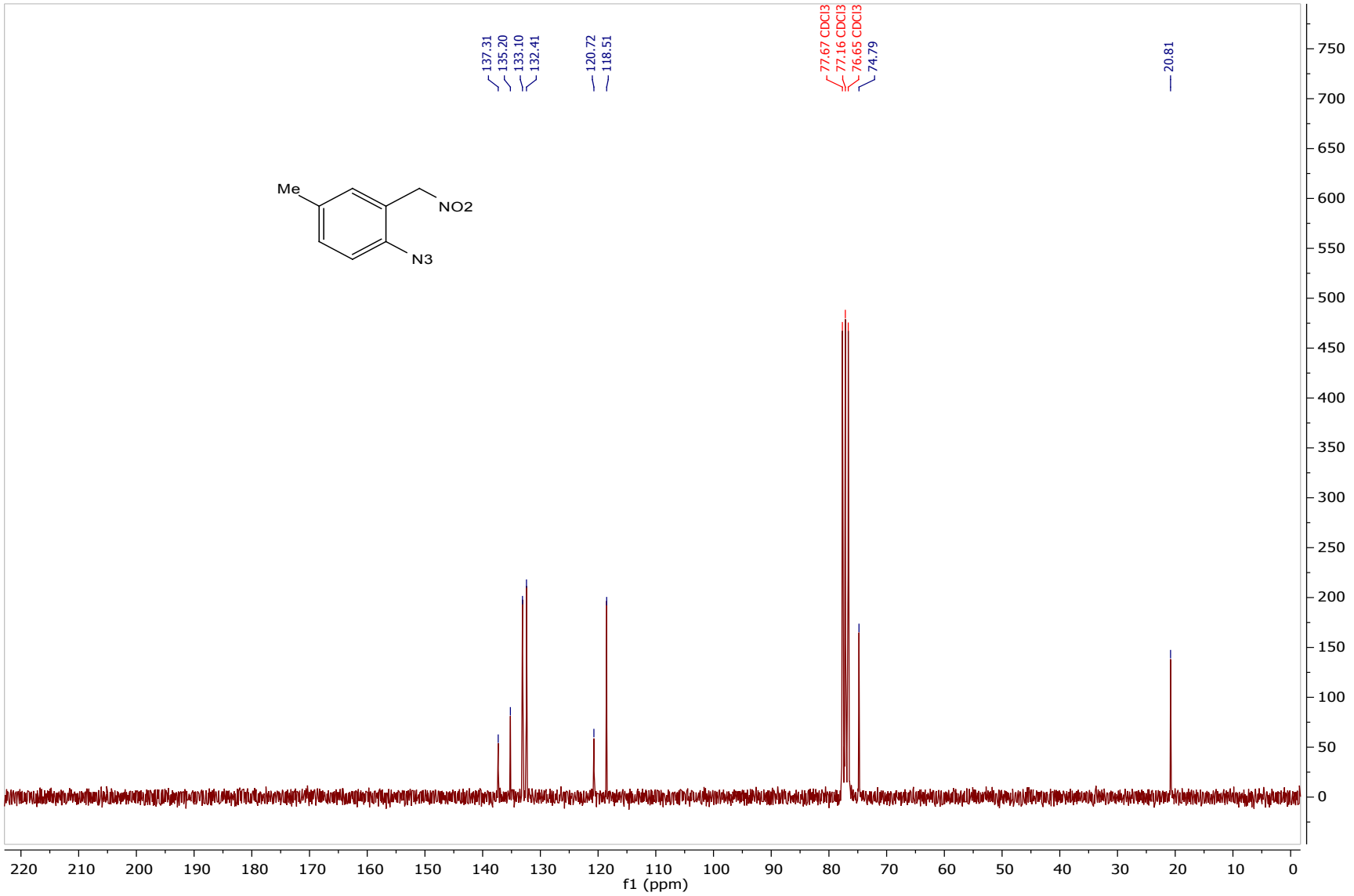
$^{13}C$ NMR spectrum **1i'** (101 MHz, $CDCl_3$)


135.54
135.01
131.30
130.41
130.15
118.71
77.67
77.16
76.65
20.83
0.57
Me
I
N3
550
500
450
400
350
300
250
200
150
100
50
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

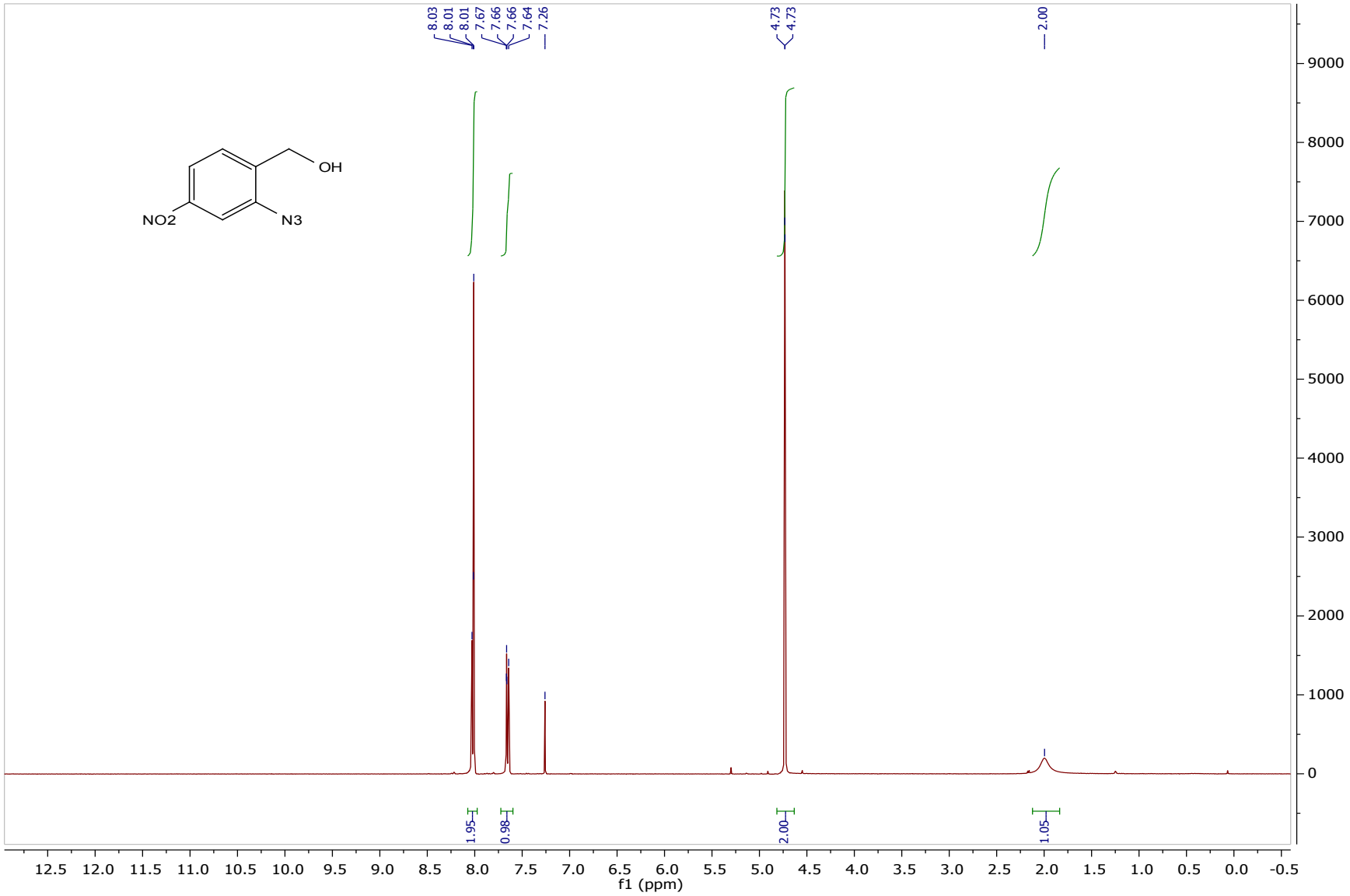
$^{1}$H NMR spectrum **1i** (250 MHz, $CDCl_3$)



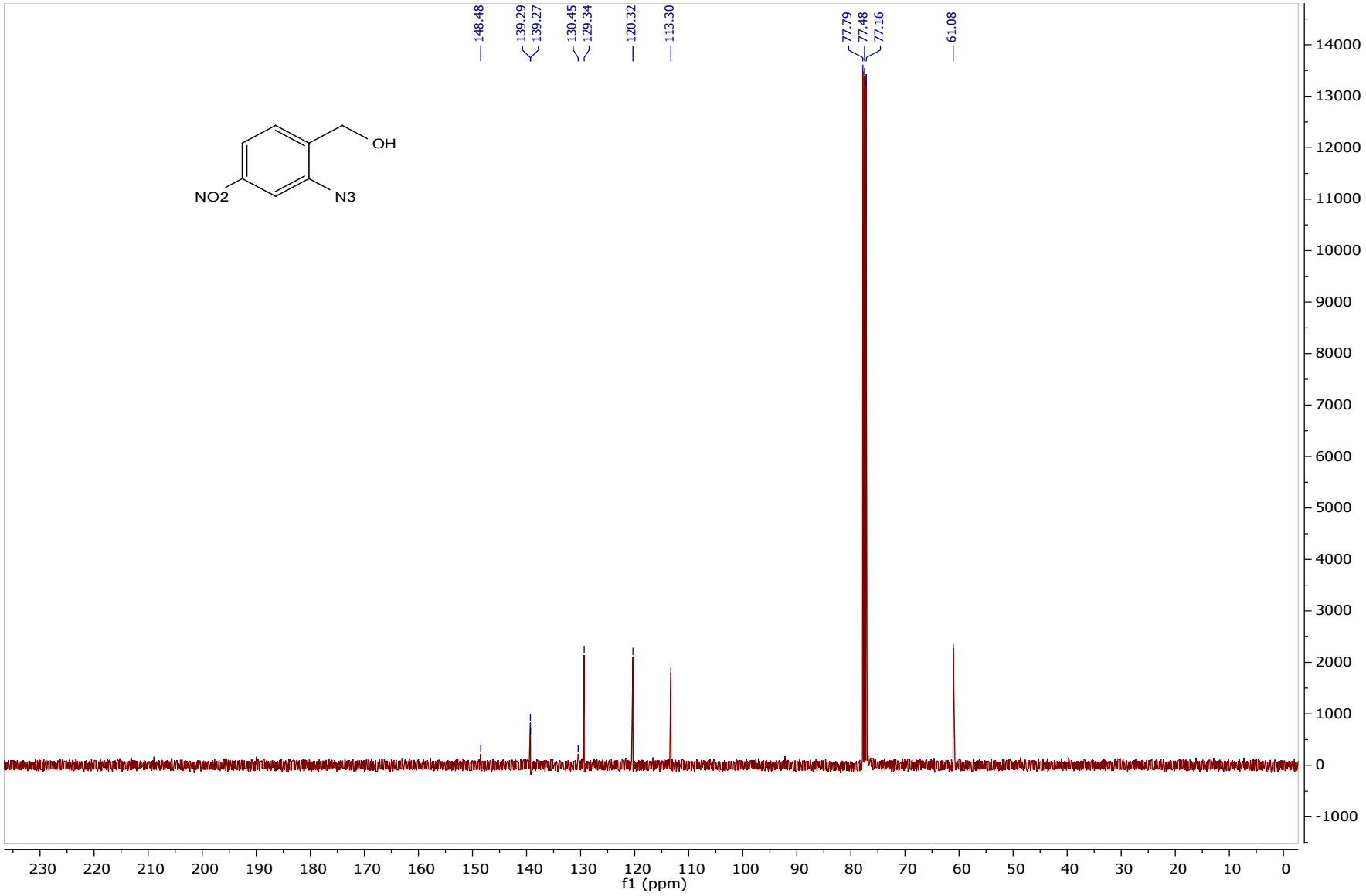
$^{13}C$ NMR spectrum **1i** (101 MHz, $CDCl_3$)



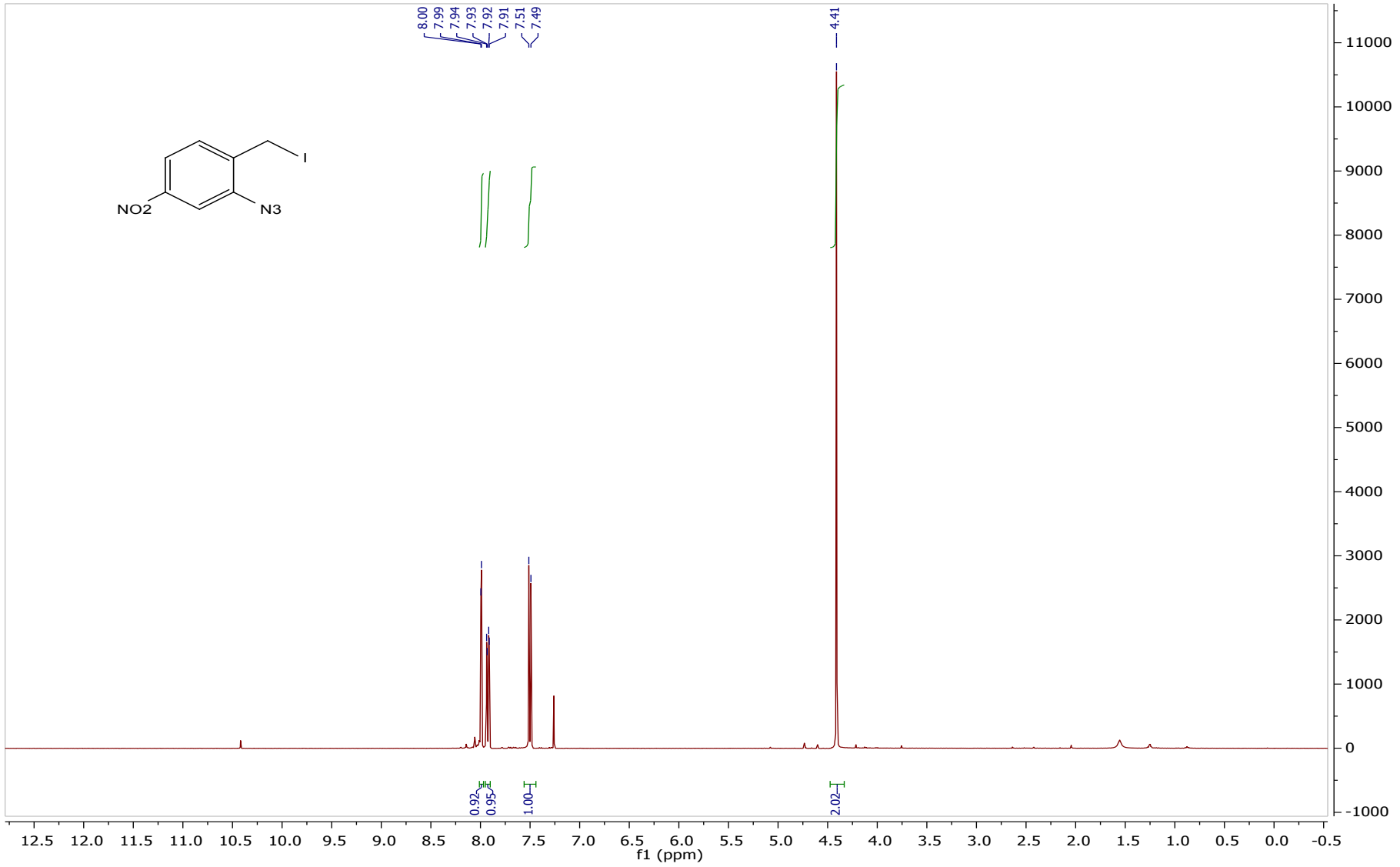
$^{1}$H NMR spectrum **1j"** (250 MHz, $CDCl_3$)



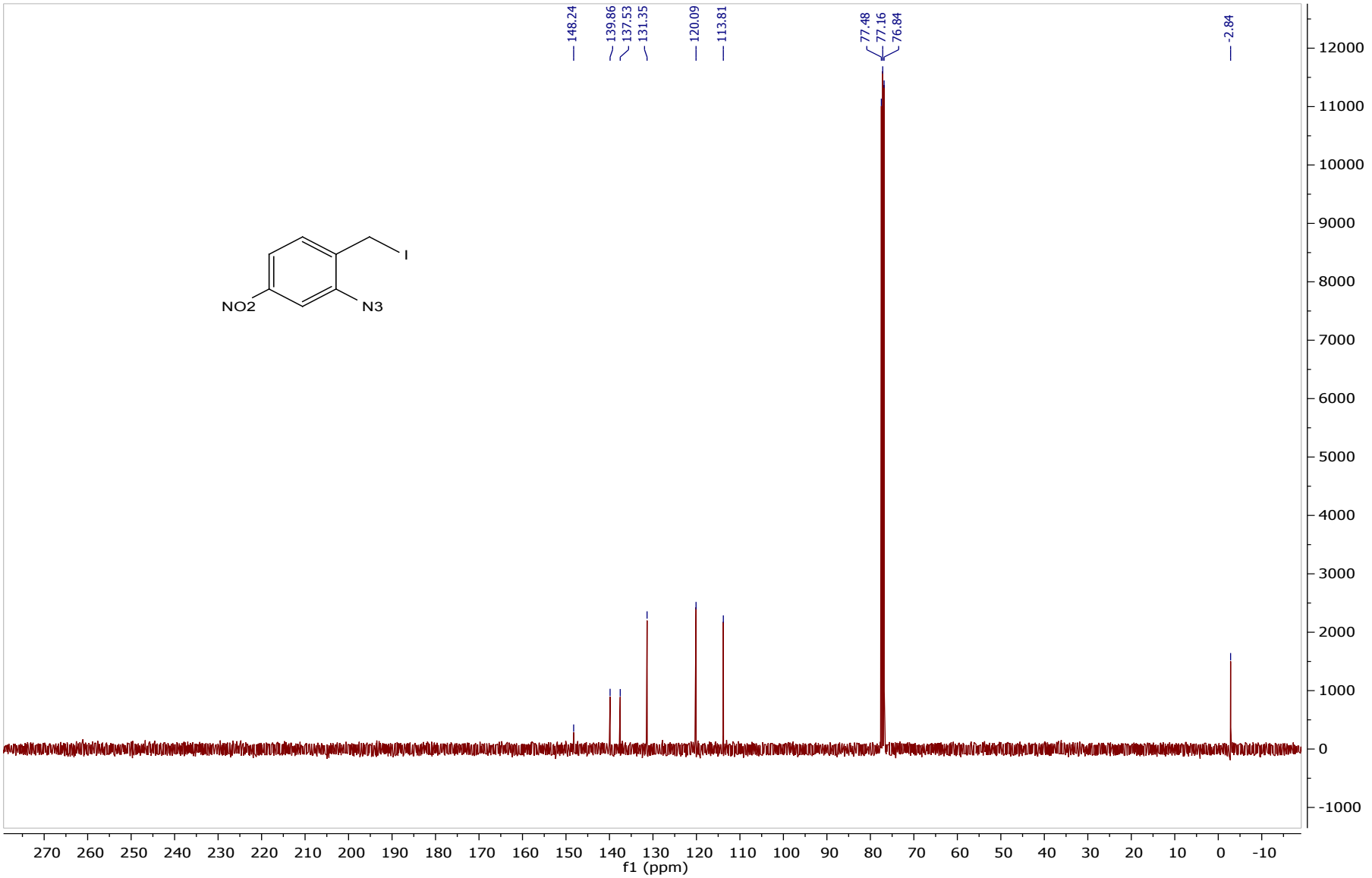
$^{13}C$ NMR spectrum **1j"** (101 MHz, $CDCl_3$)


148.48
139.29
139.27
130.45
129.34
120.32
113.30
77.79
77.48
77.16
61.08
OH
NO2
N3
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

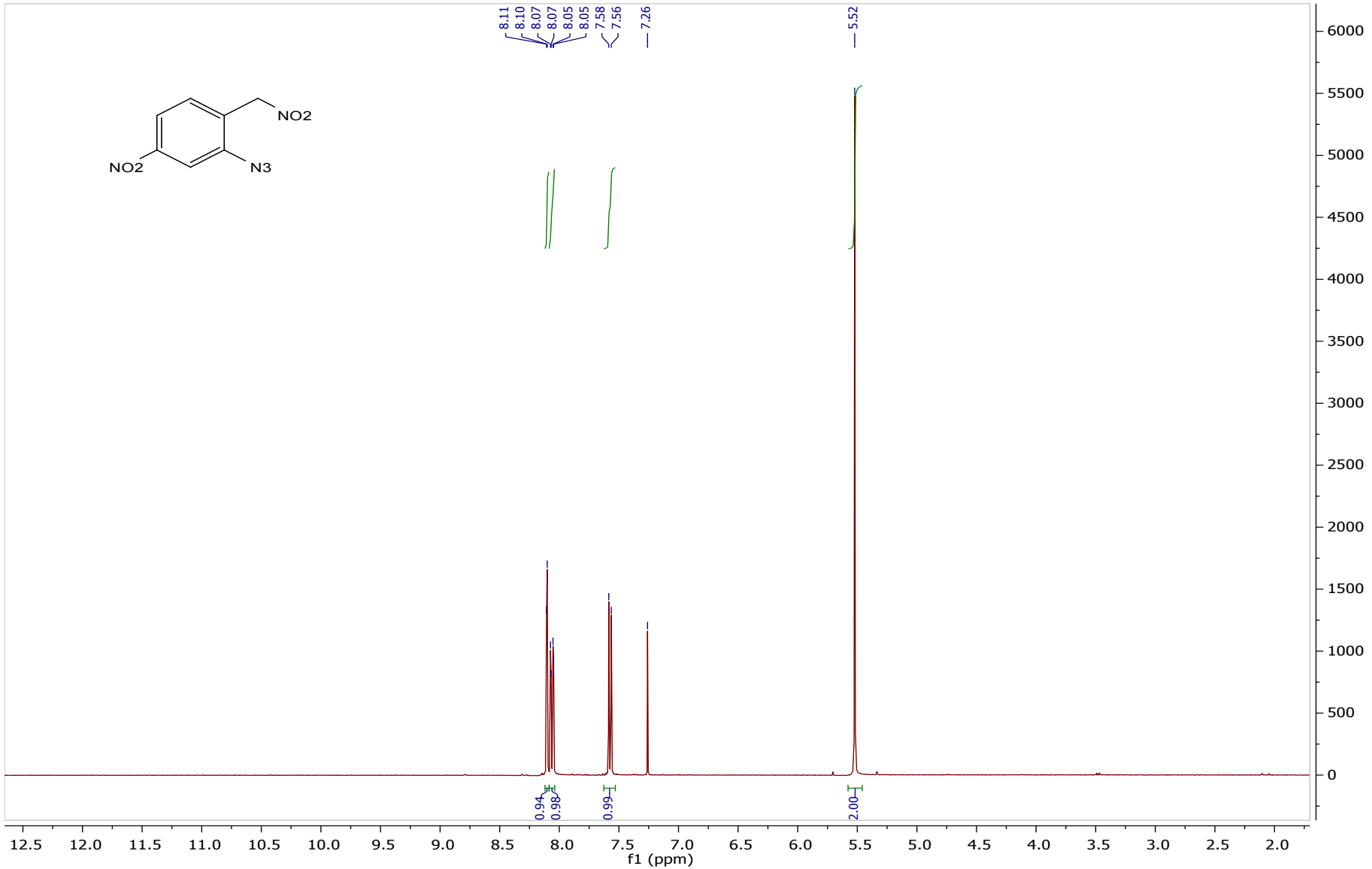
$^{1}$H NMR spectrum **1j'** (250 MHz, $CDCl_3$)



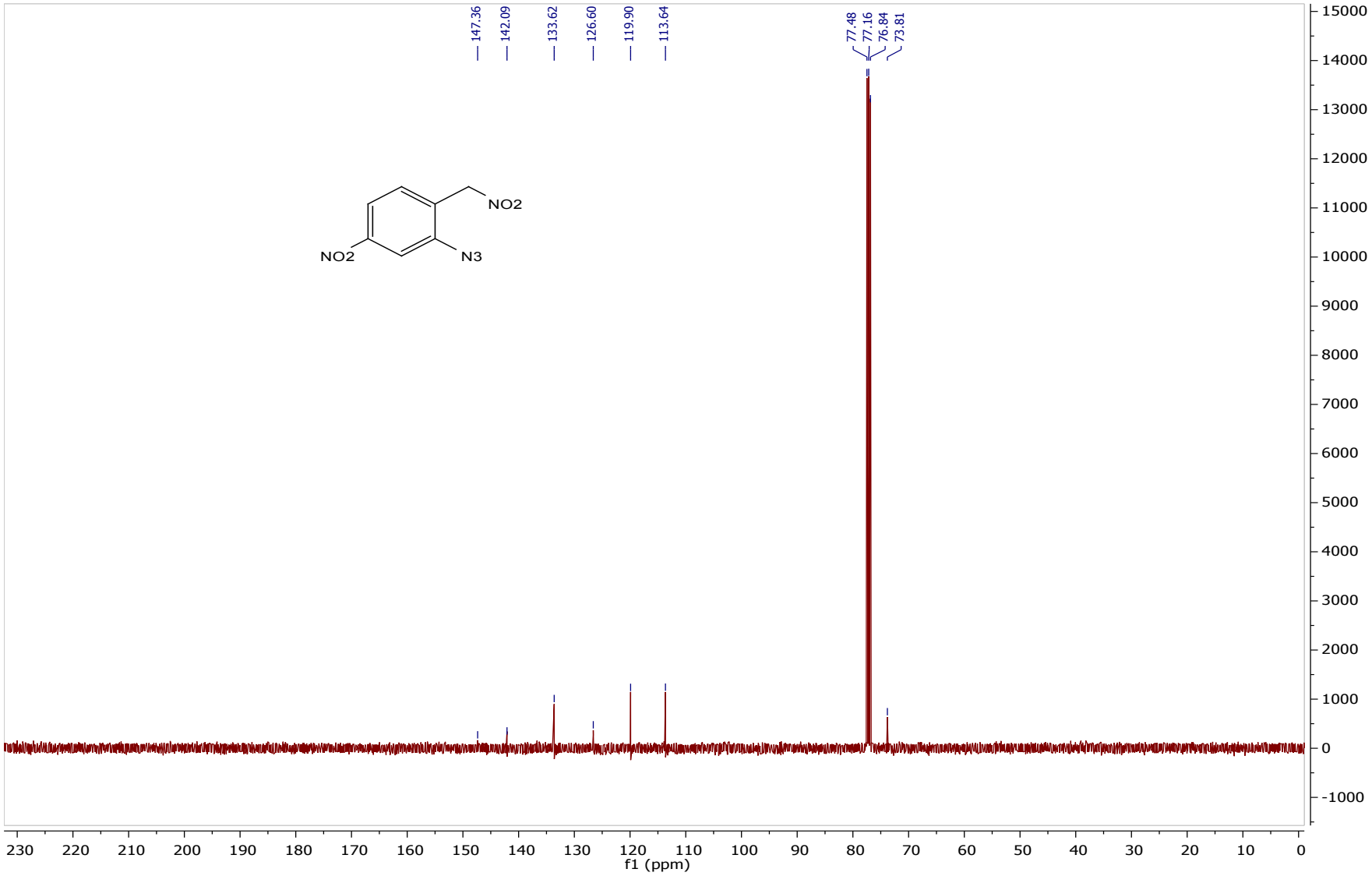
$^{13}$C NMR spectrum **1j'** (101 MHz, $CDCl_3$)



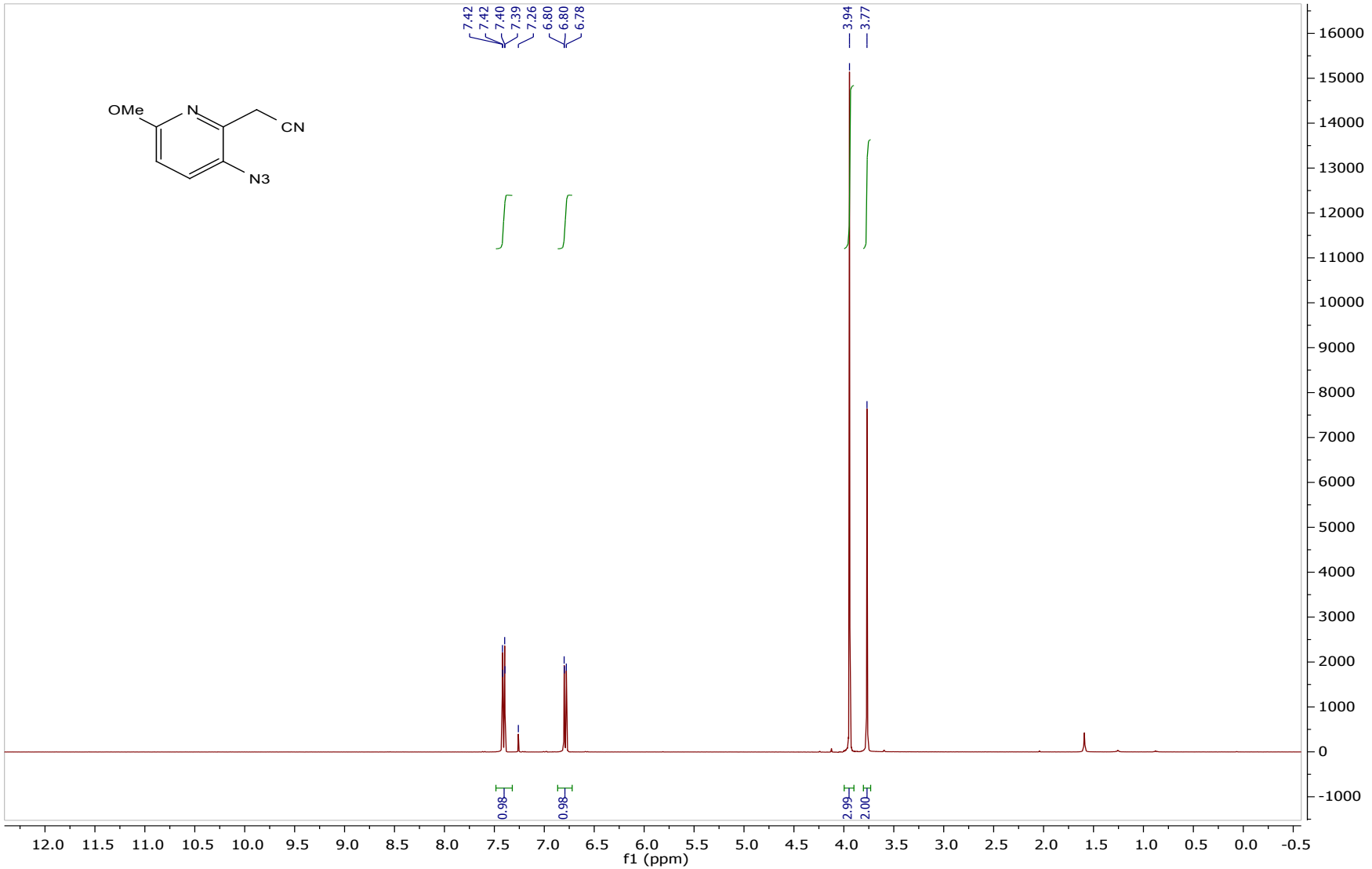
$^{1}$H NMR spectrum **1j** (250 MHz, $CDCl_3$)



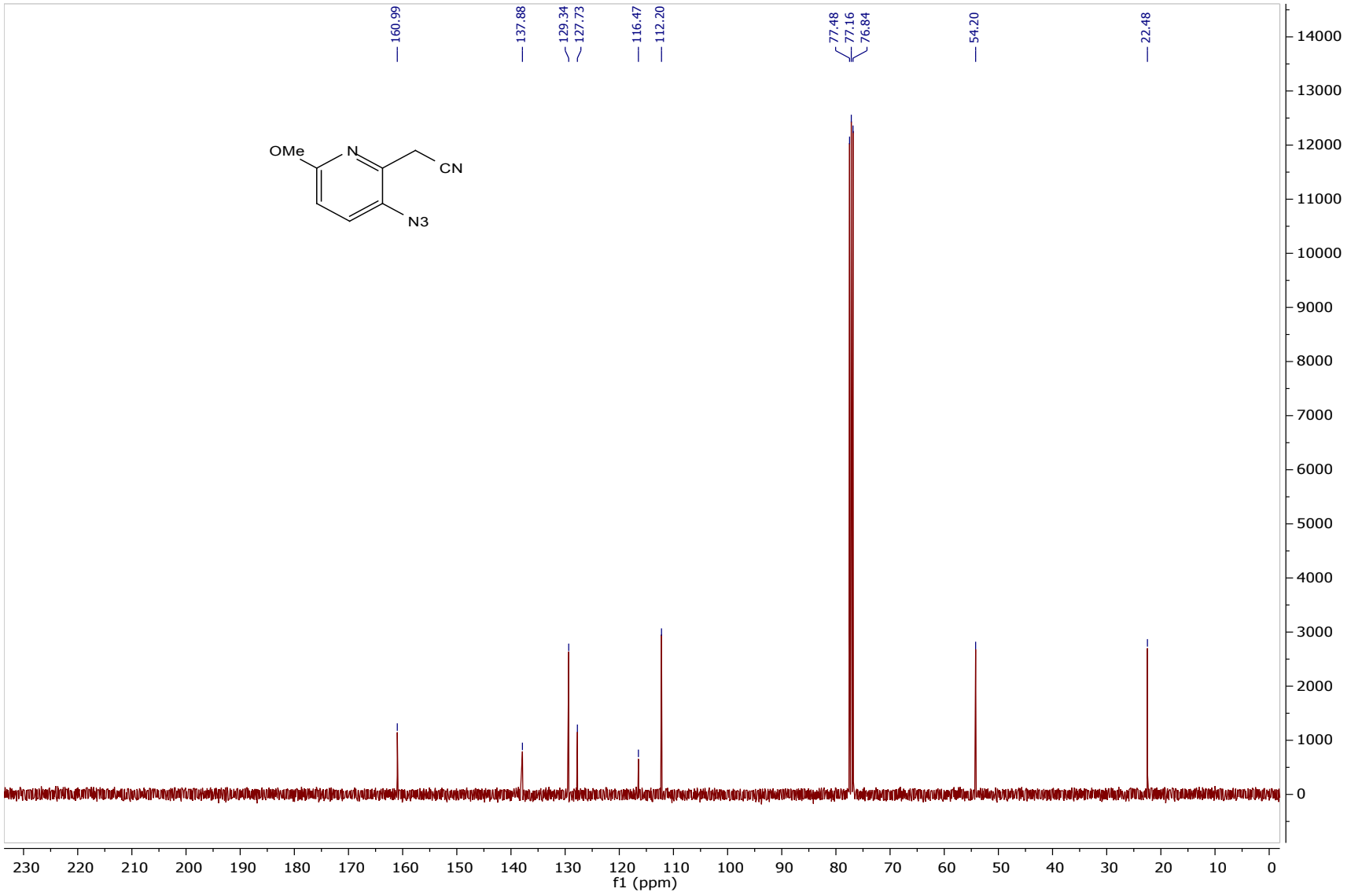
$^{13}C$ NMR spectrum **1j** (101 MHz, $CDCl_3$)



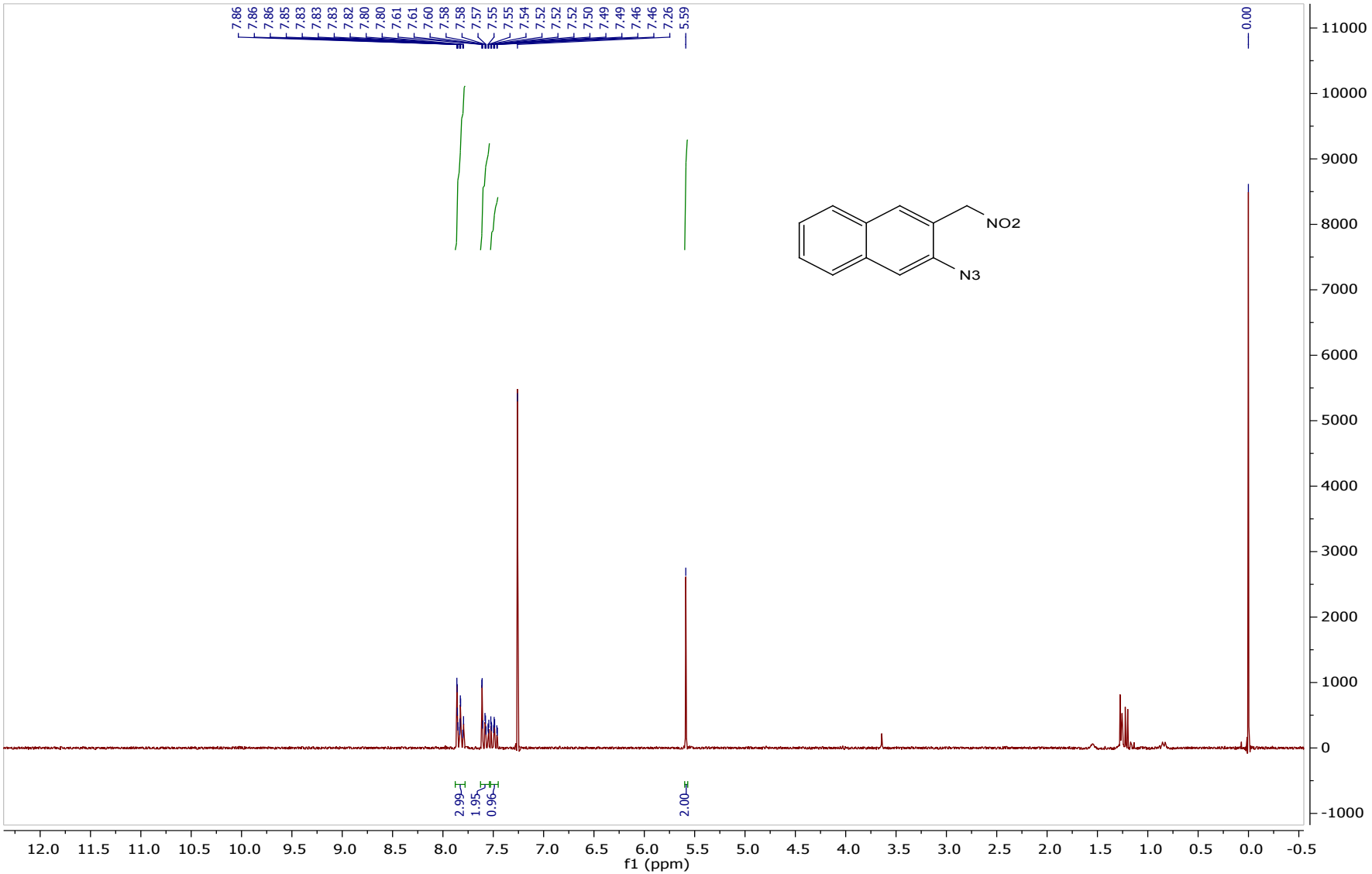
$^{1}$H NMR spectrum **1k** (250 MHz, $CDCl_3$)



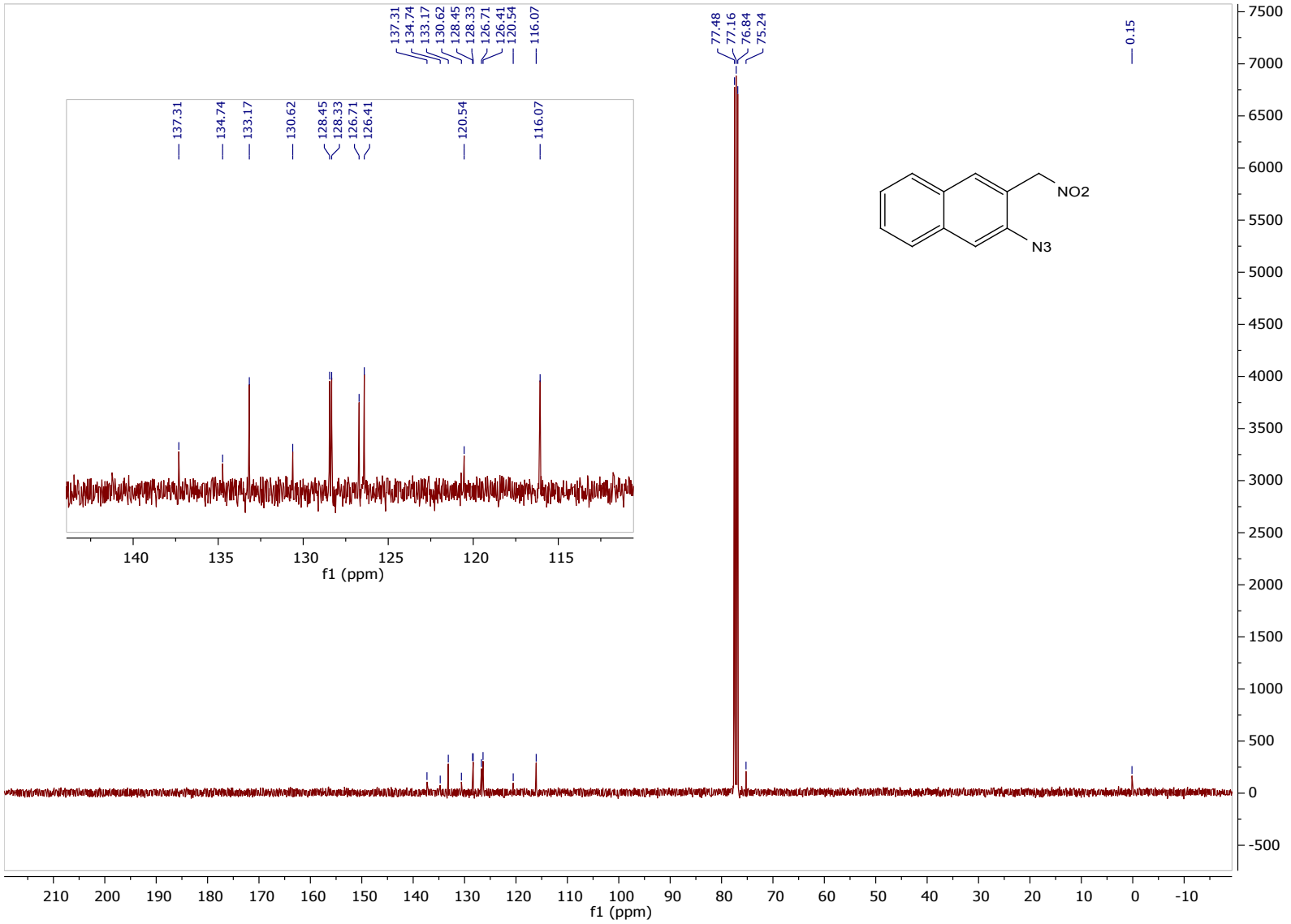
$^{13}C$ NMR spectrum **1k** (101 MHz, $CDCl_3$)



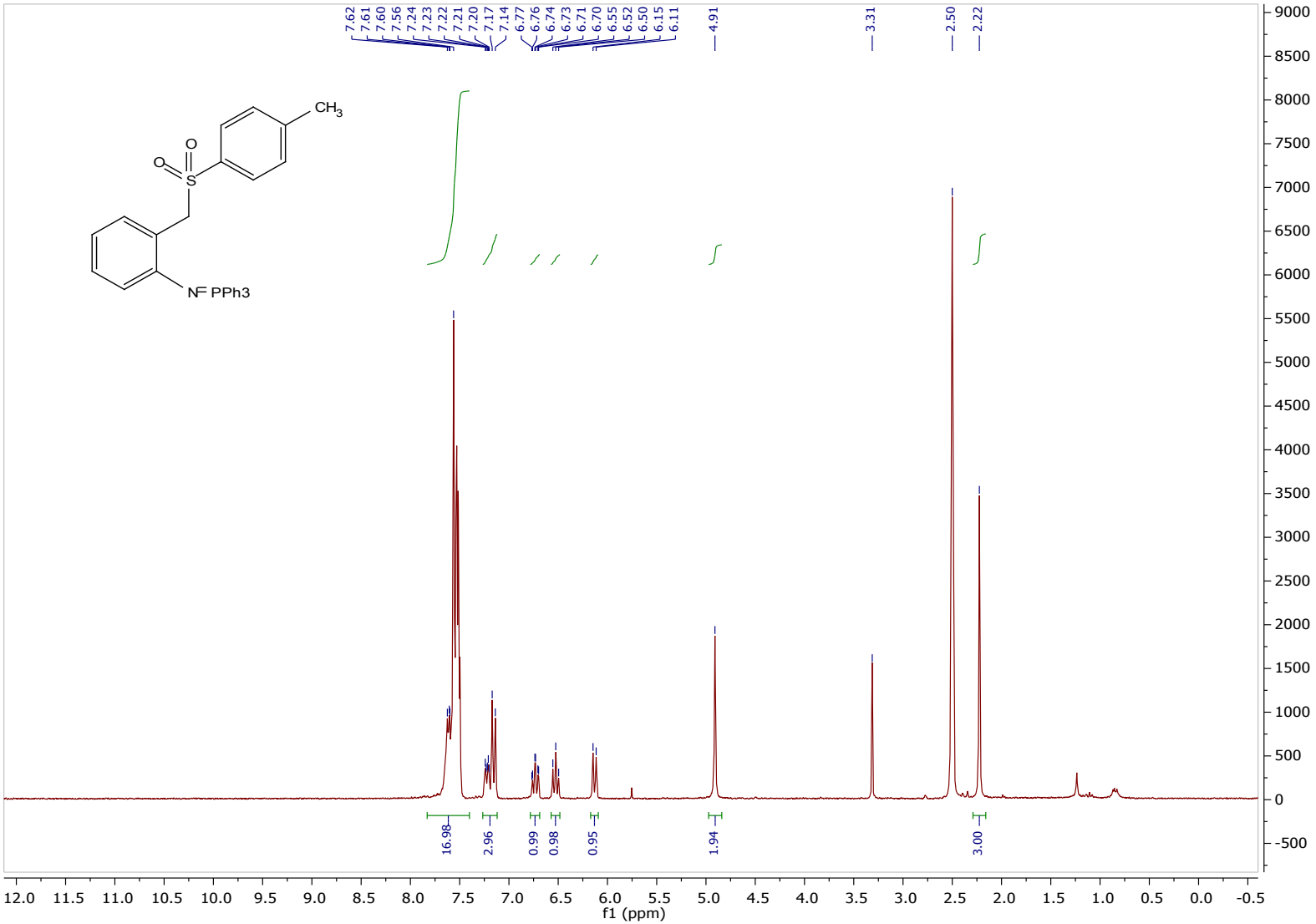
$^{1}$H NMR spectrum **1l** (250 MHz, $CDCl_3$)



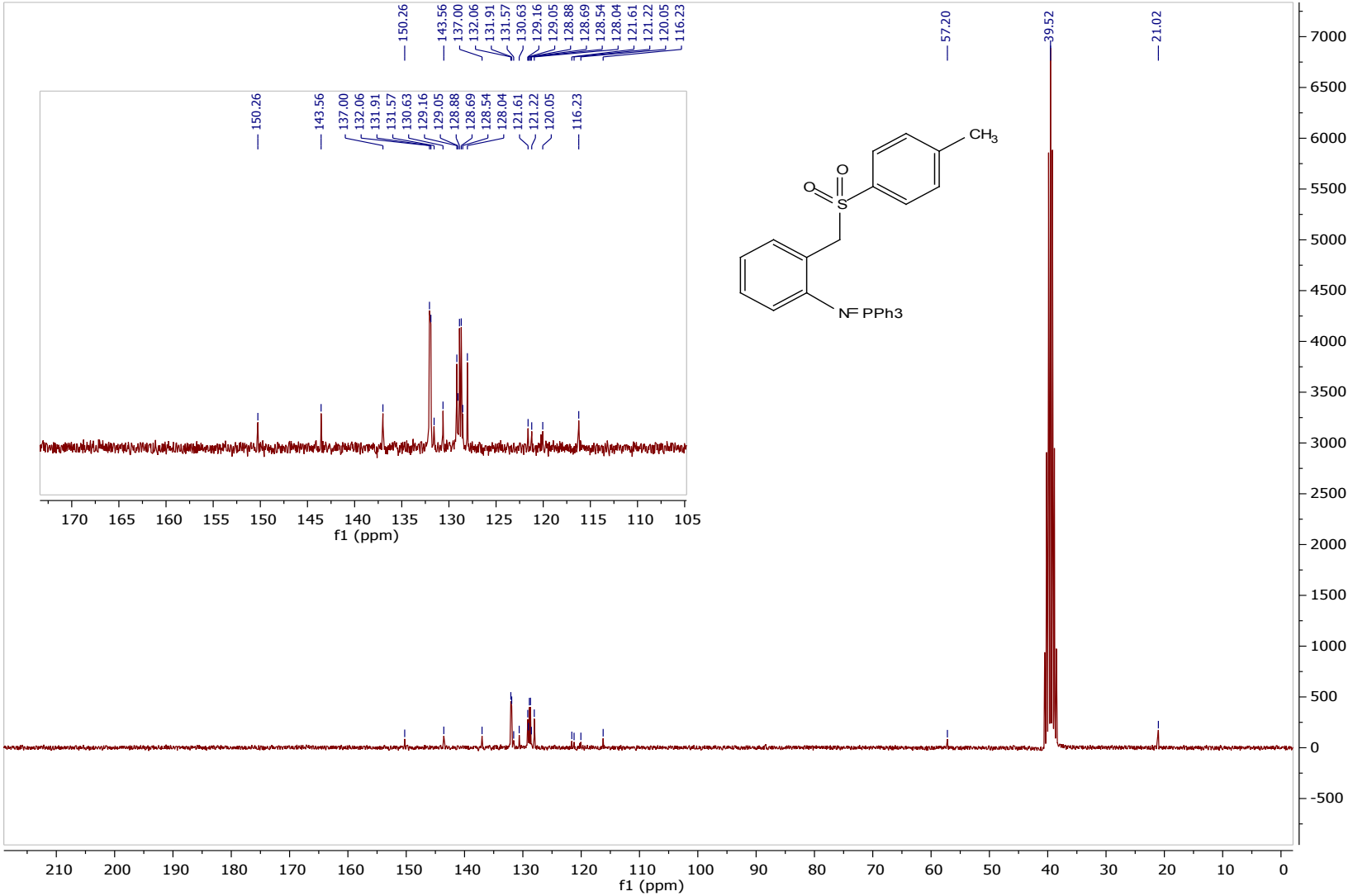
$^{13}C$ NMR spectrum **1l** (101 MHz, $CDCl_3$)



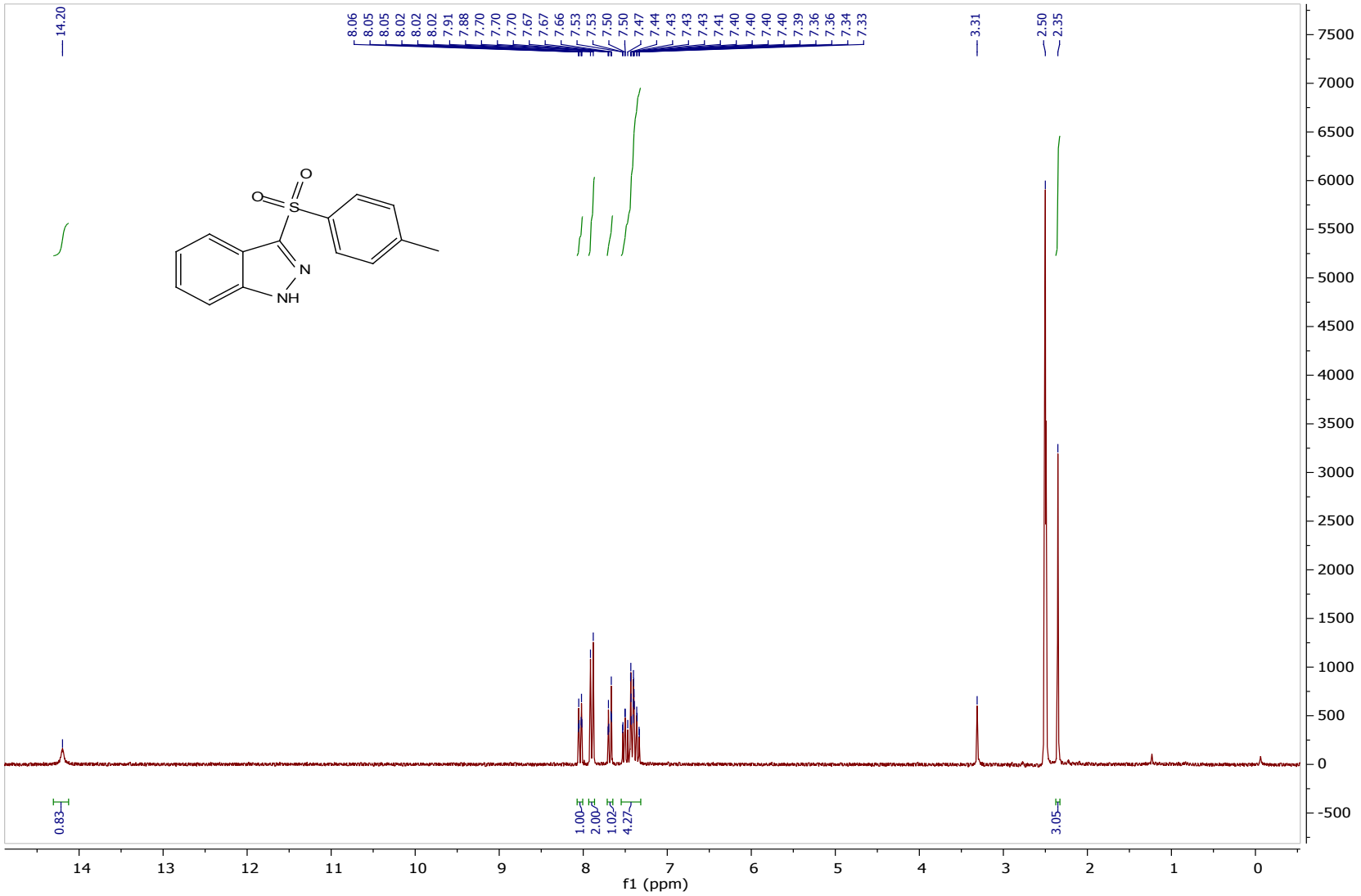
$^{1}$H NMR spectrum **2a** (250 MHz, DMSO-$d_6$)



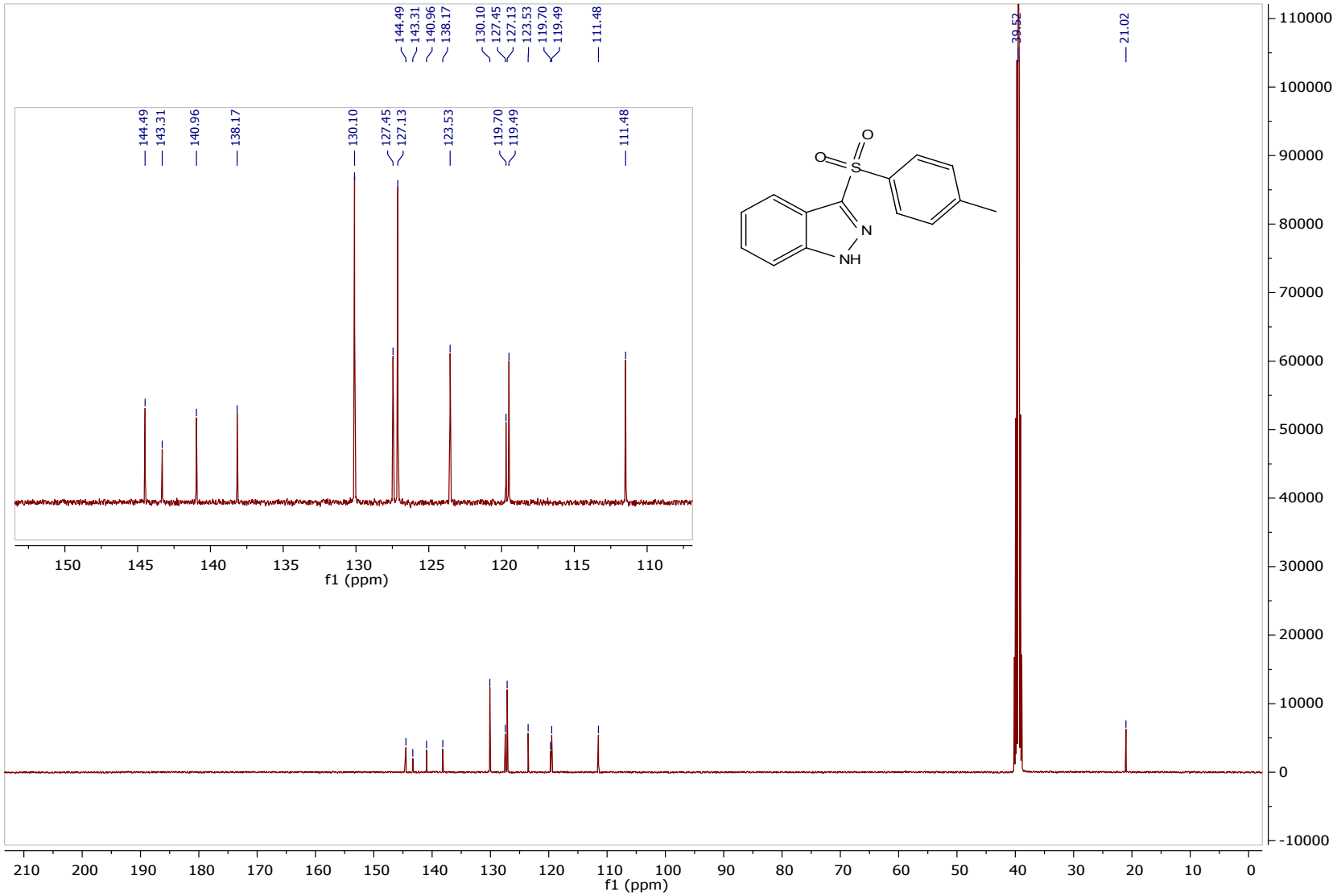
$^{13}$C NMR spectrum **2a** (101 MHz, DMSO-$d_6$)



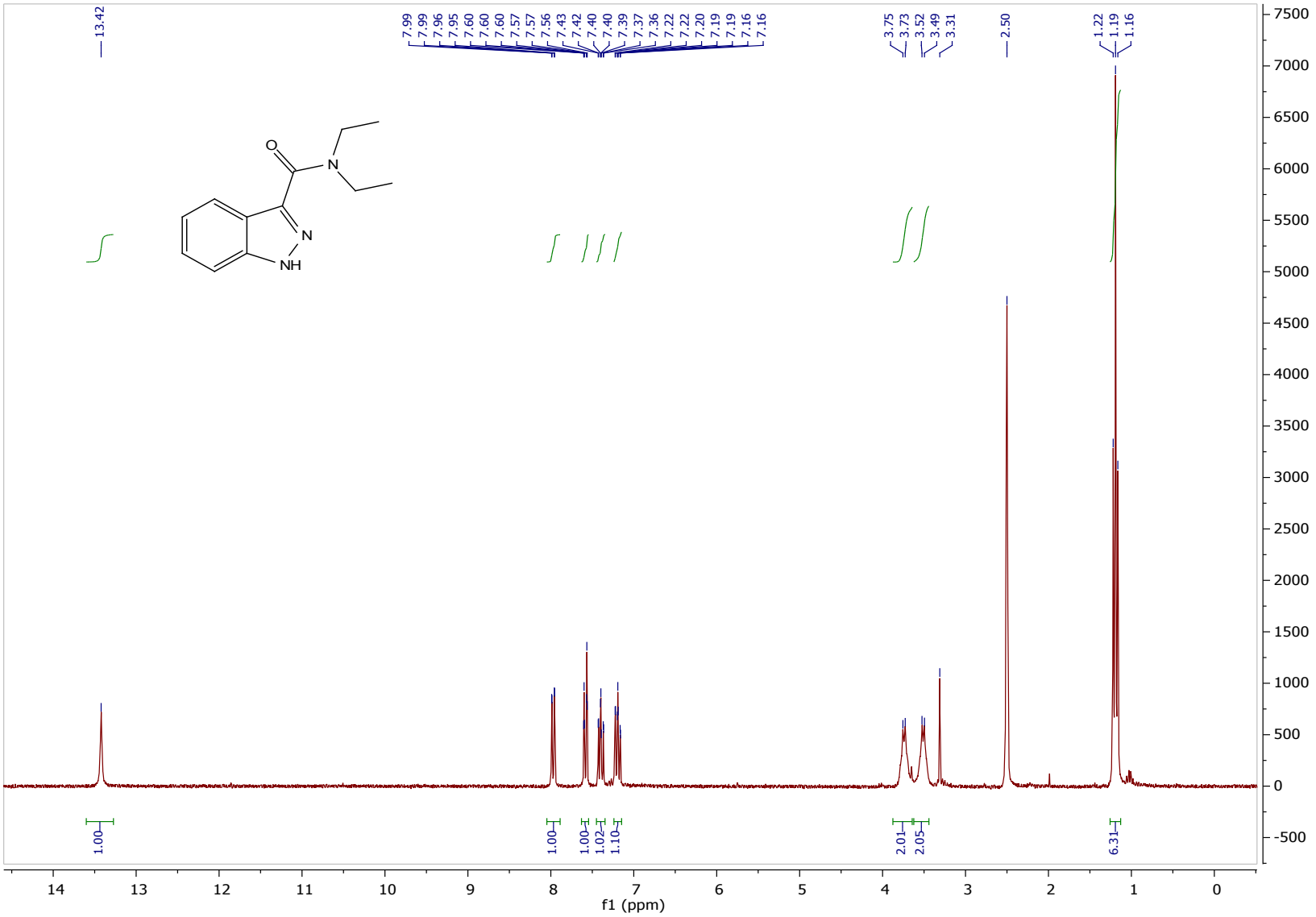
$^{1}$H NMR spectrum **3a** (250 MHz, DMSO-$d_6$)



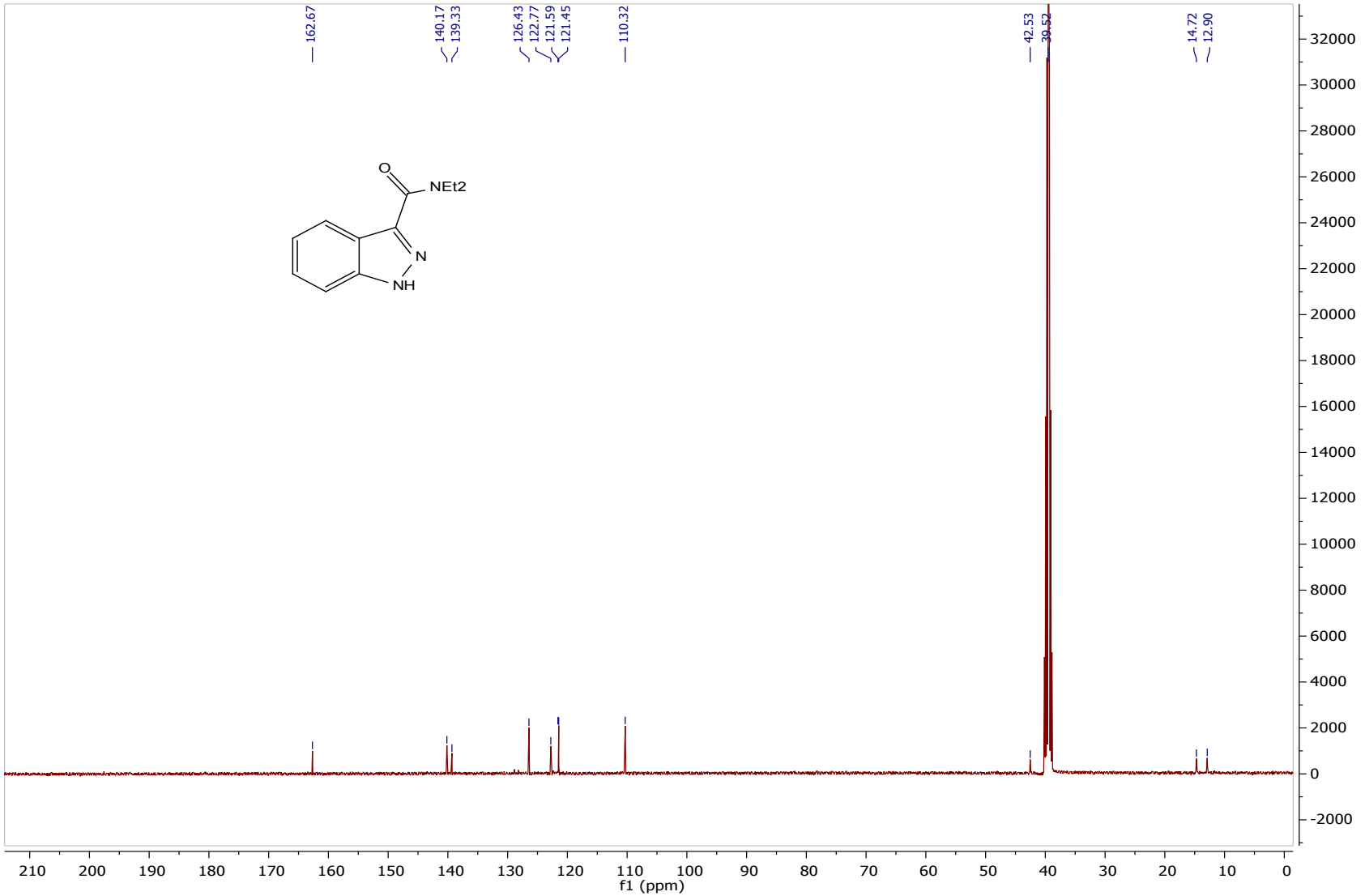
$^{13}$C NMR spectrum **3a** (101 MHz, DMSO-$d_6$)



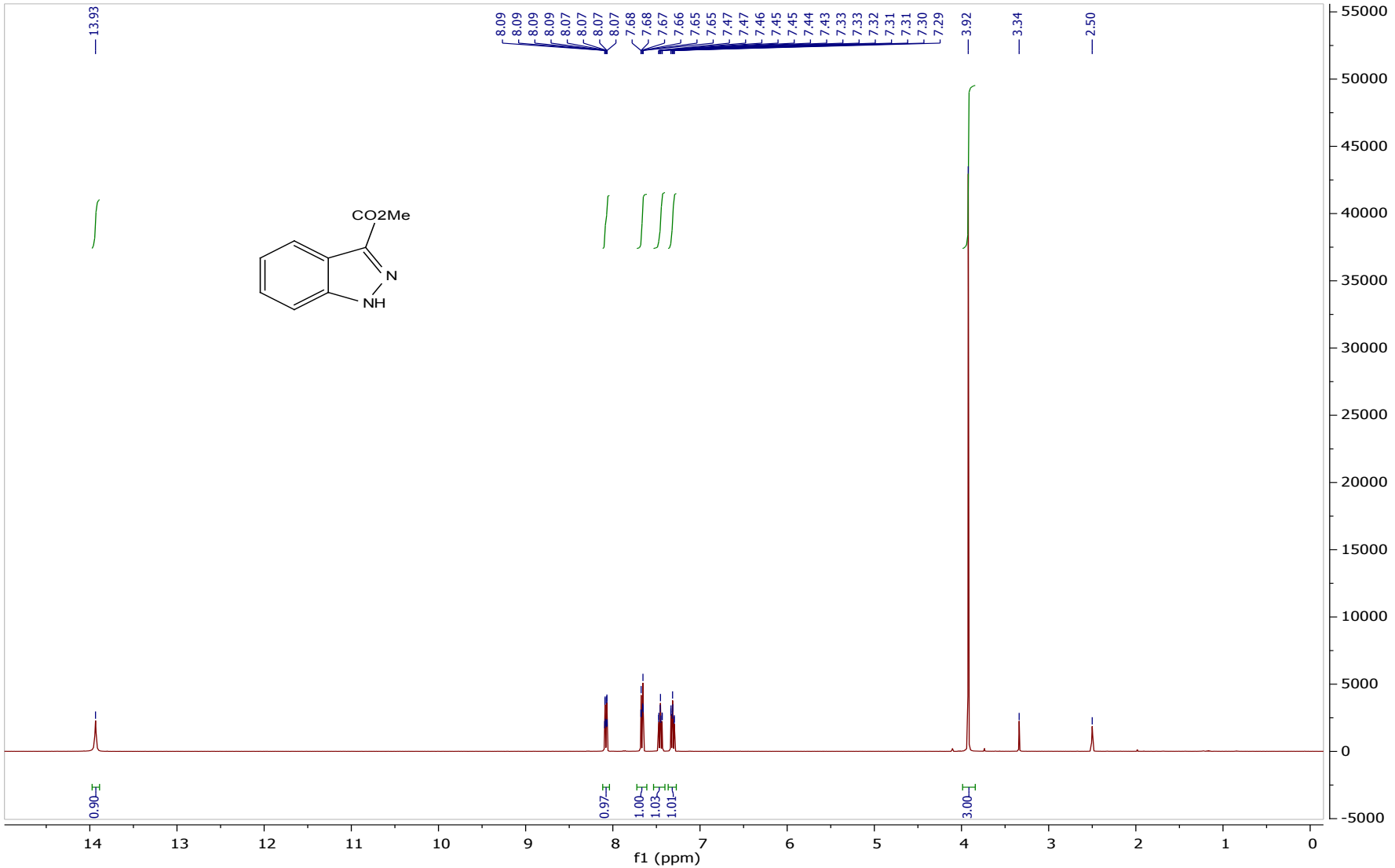
$^{1}$H NMR spectrum **3d** (250 MHz, DMSO-$d_6$)



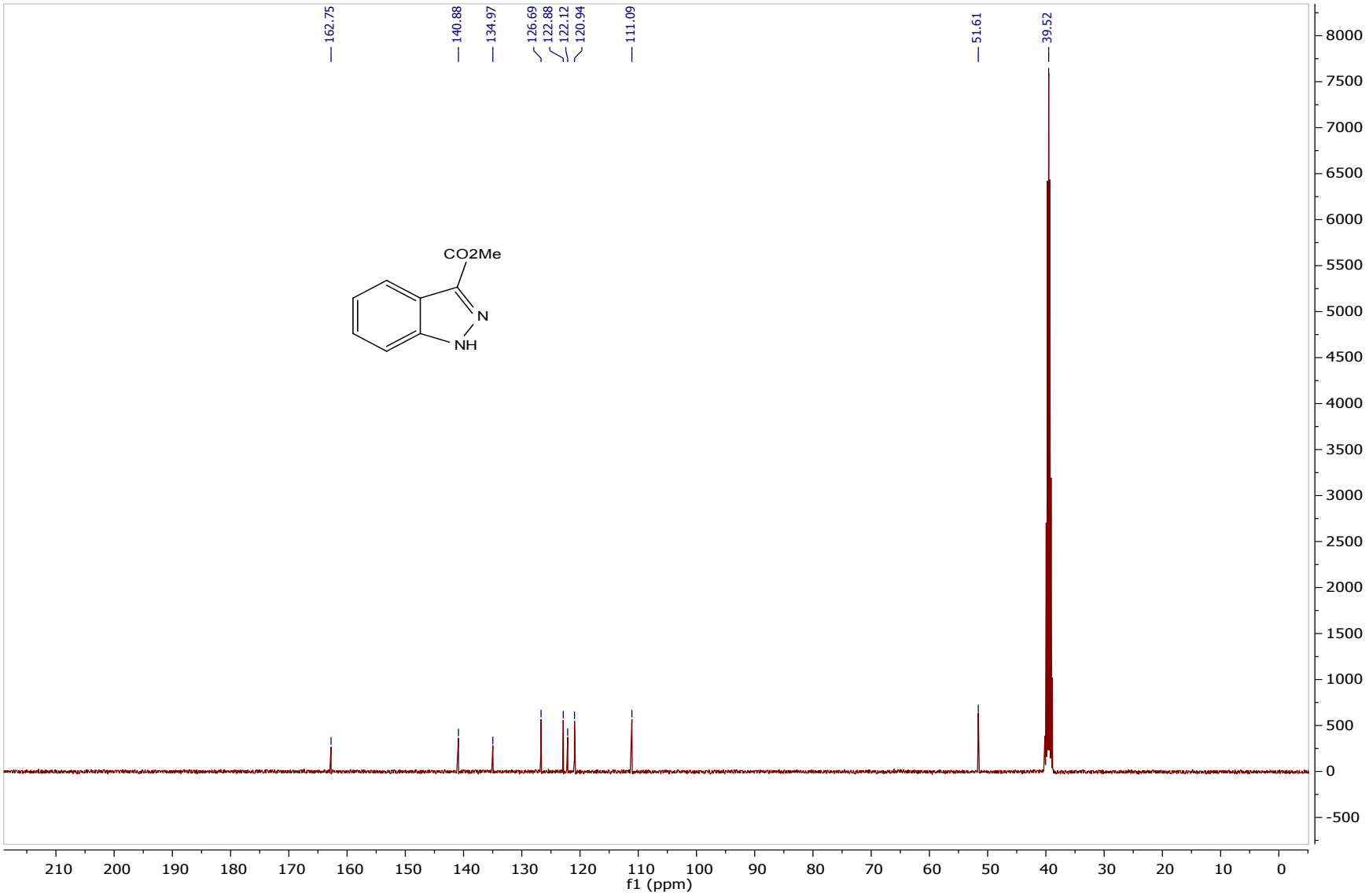
$^{13}$C NMR spectrum **3d** (101 MHz, DMSO-$d_6$)



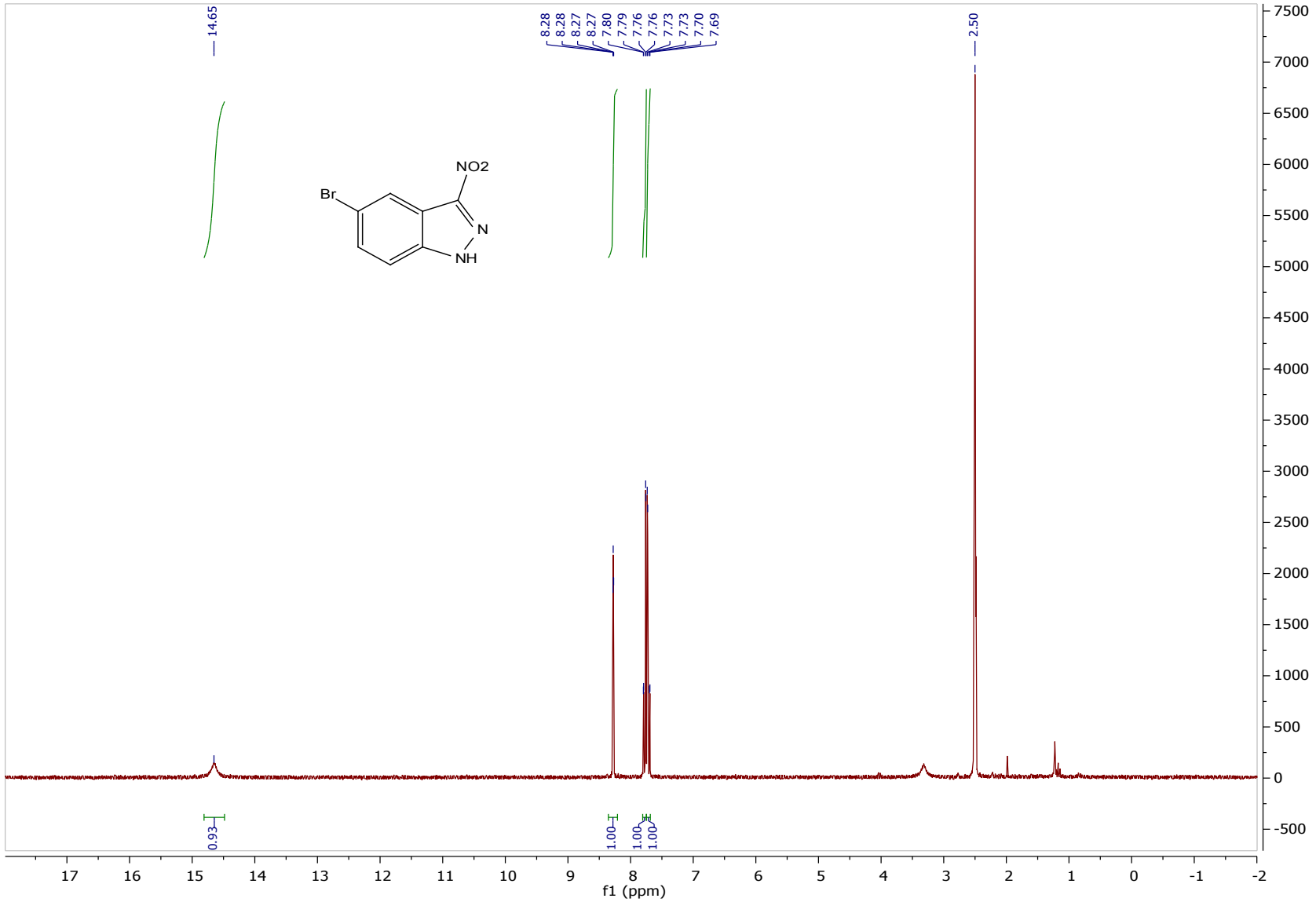
$^{1}$H NMR spectrum **3e** (250 MHz, DMSO-$d_6$)



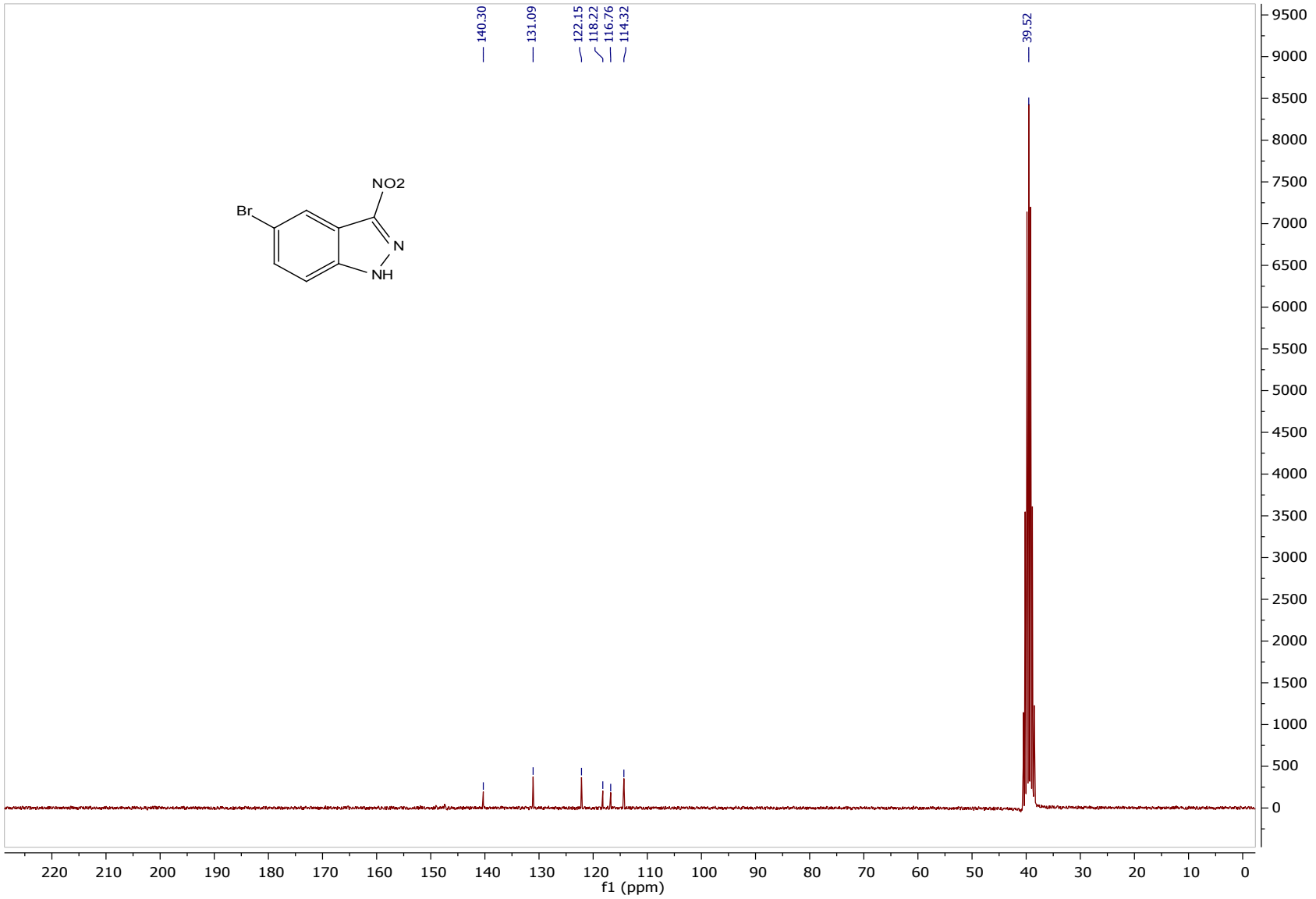
$^{13}$C NMR spectrum **3e** (101 MHz, DMSO-$d_6$)



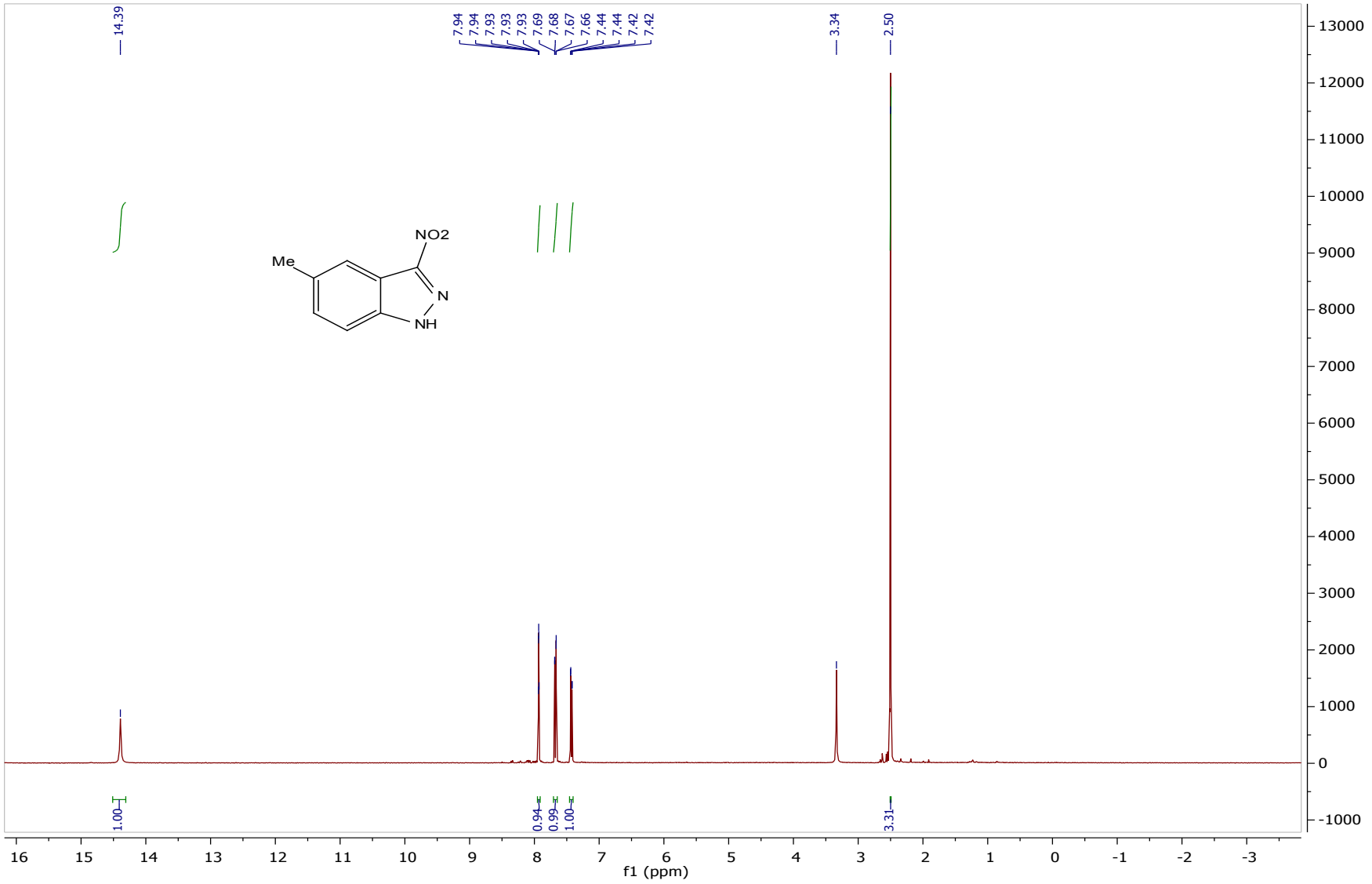
$^{1}$H NMR spectrum **3h** (250 MHz, DMSO-$d_6$)



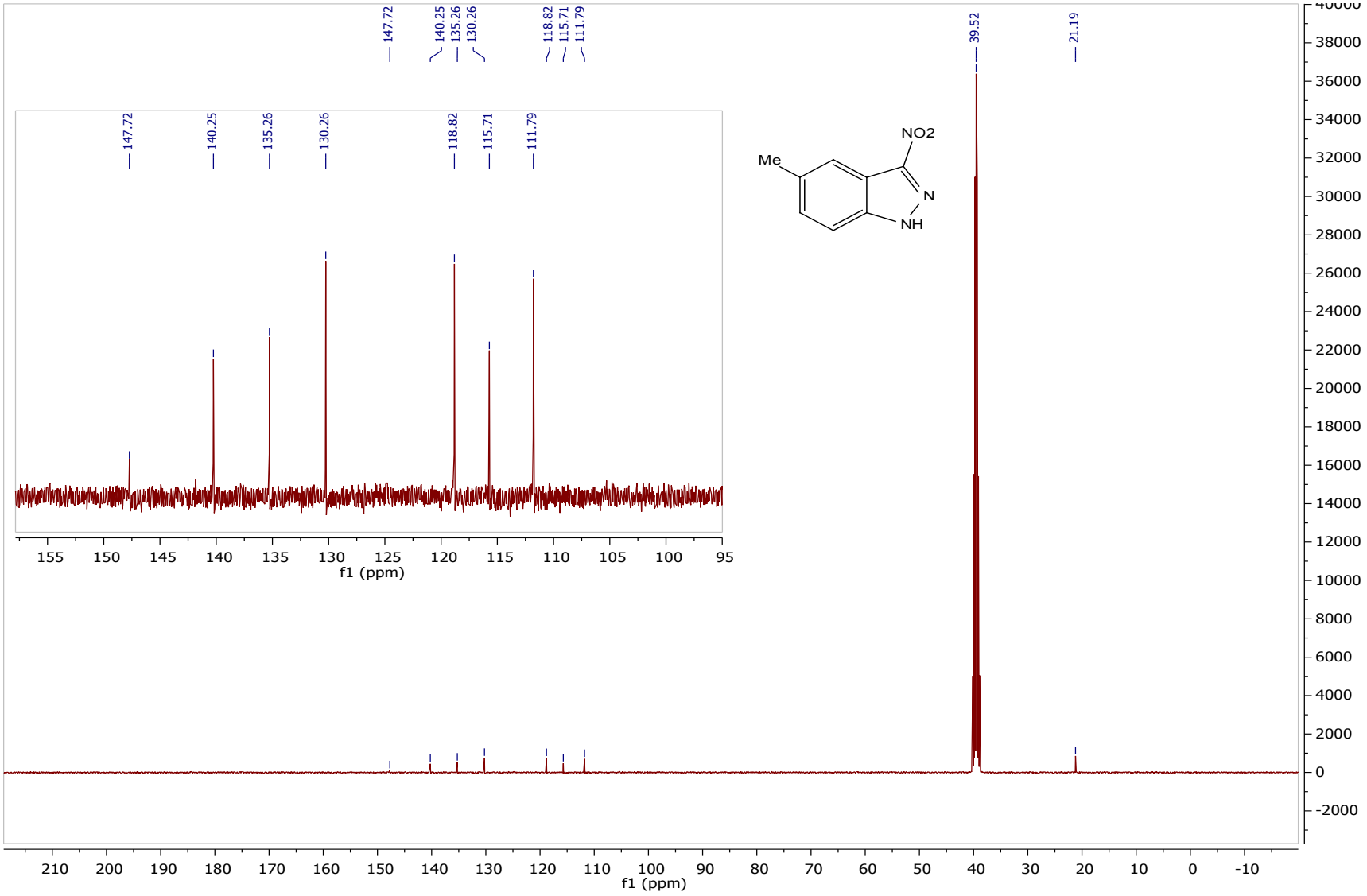
$^{13}$C NMR spectrum **3h** (101 MHz, DMSO-$d_6$)



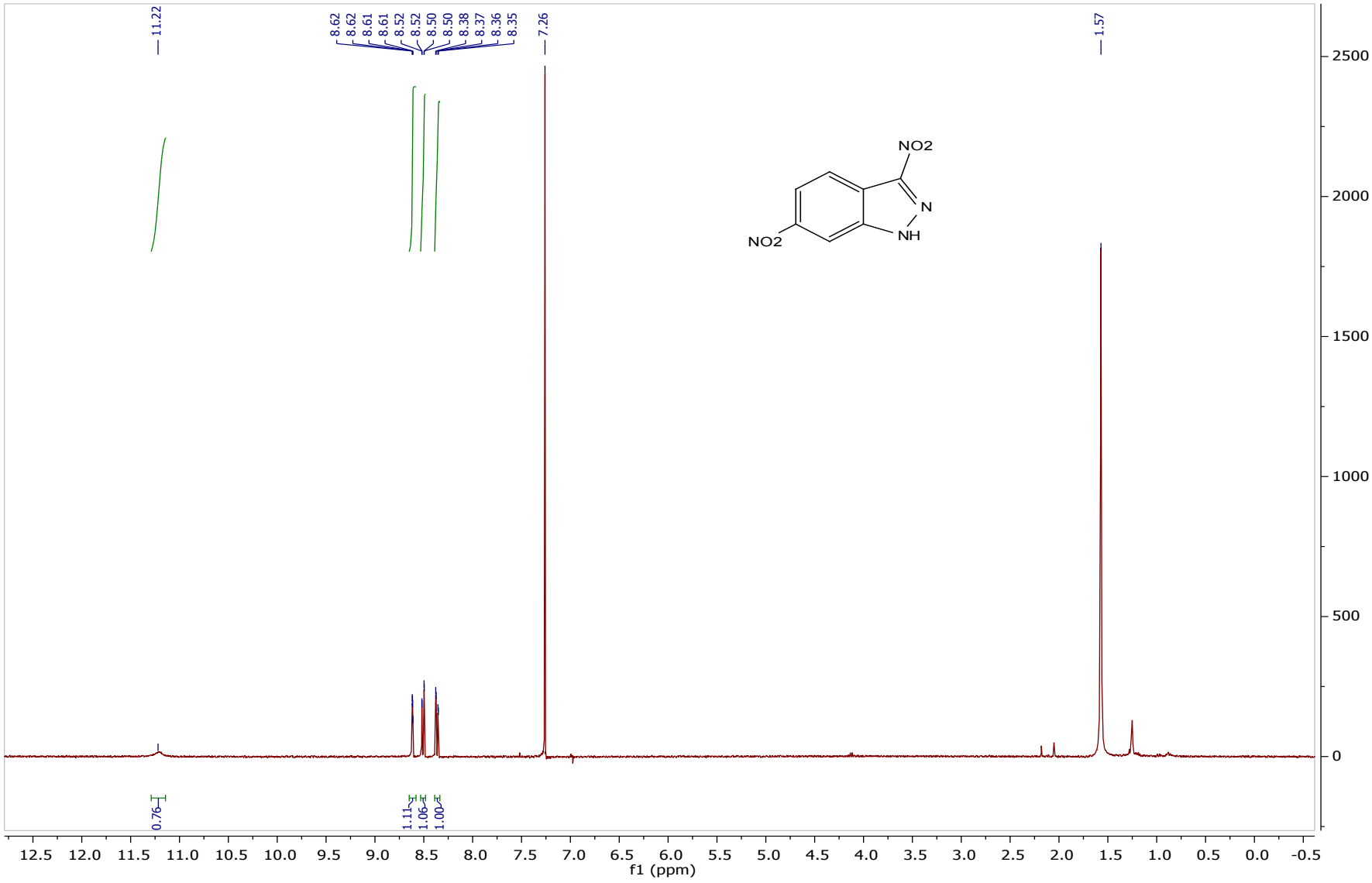
[1]H NMR spectrum **3i** (250 MHz, DMSO-$d_6$)



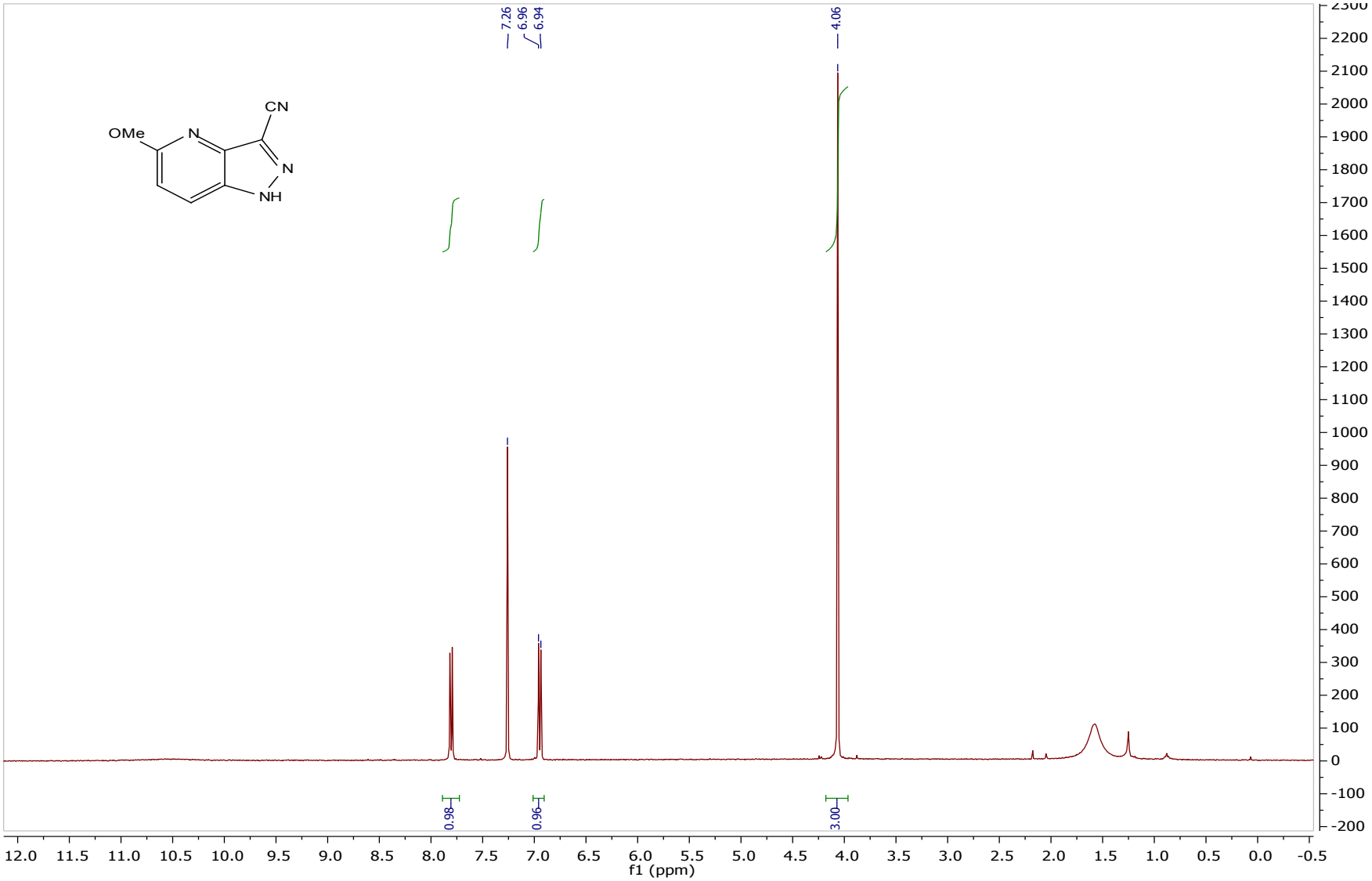
$^{13}$C NMR spectrum **3i** (101 MHz, DMSO-$d_6$)



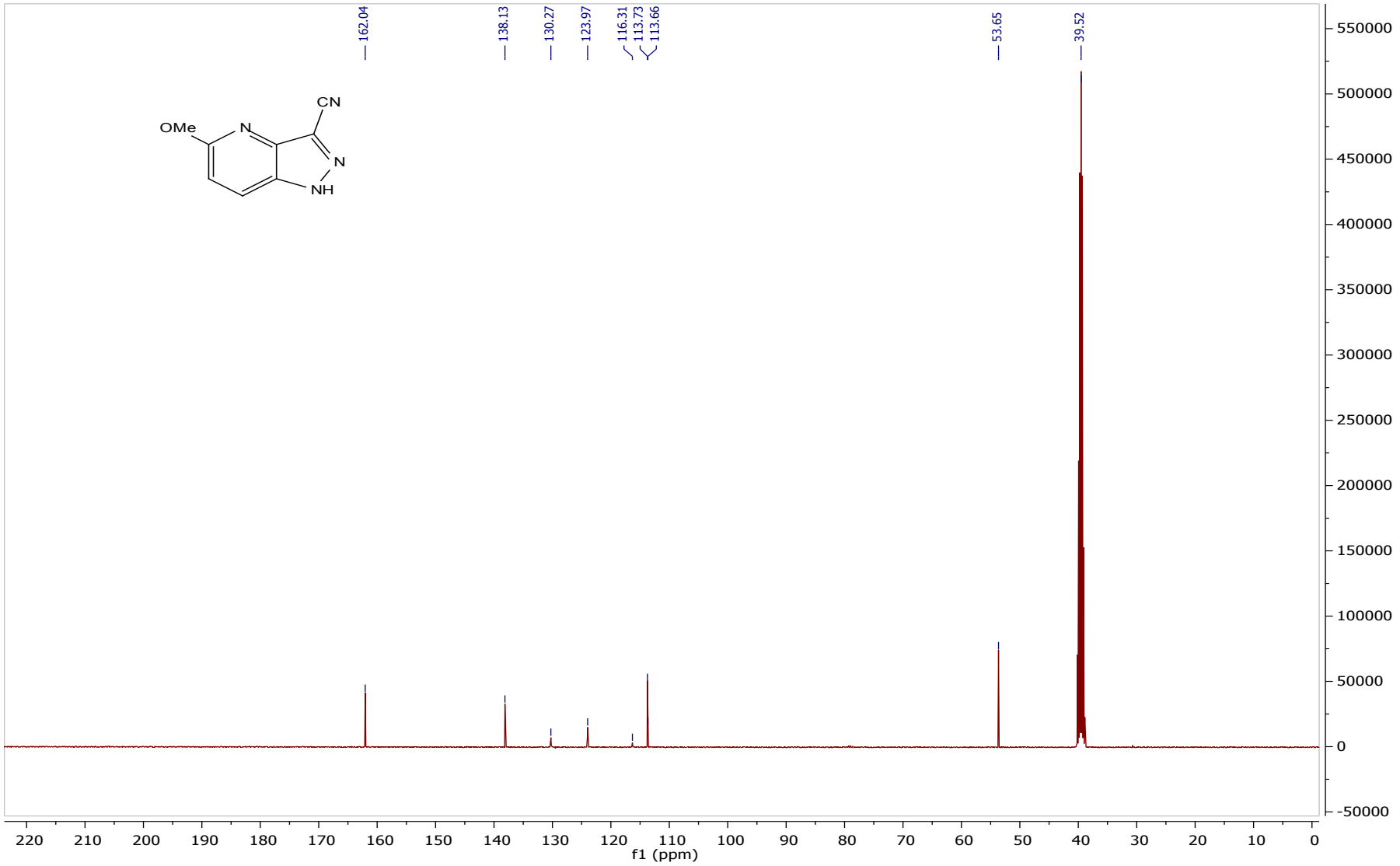
$^{1}$H NMR spectrum **3j** (250 MHz, $CDCl_3$)



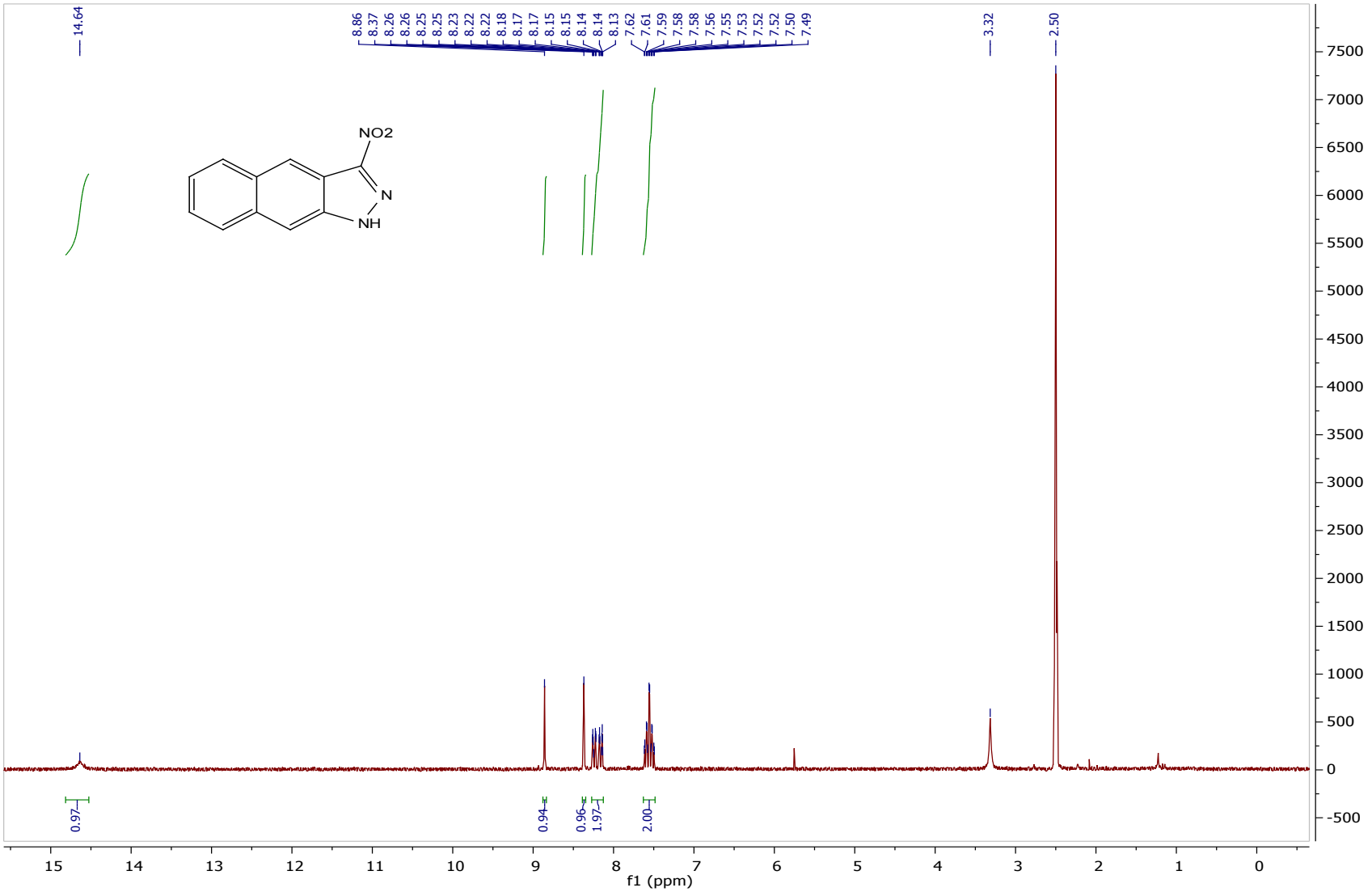
$^{1}$H NMR spectrum **3k** (250 MHz, $CDCl_3$)



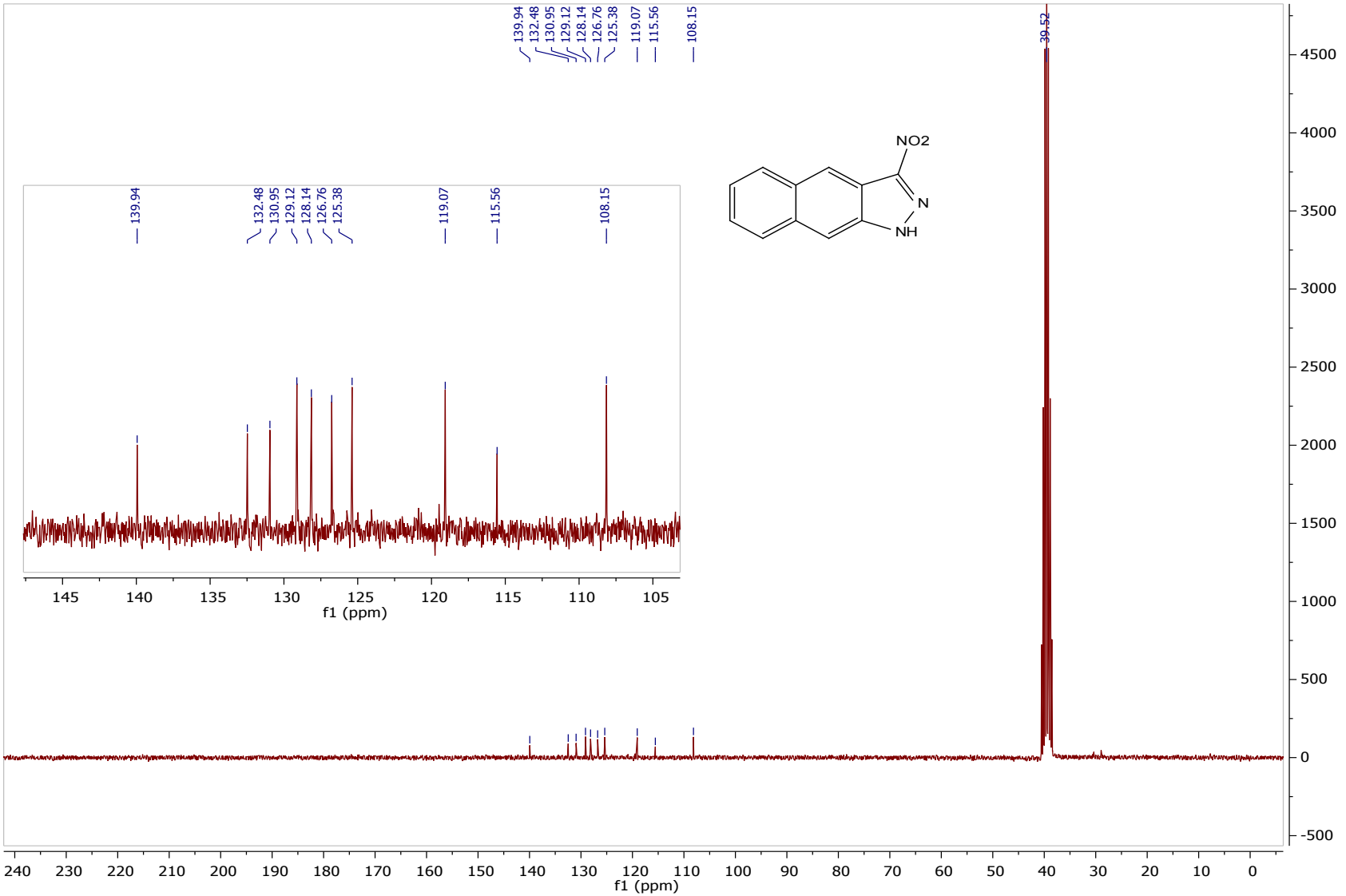
$^{13}$C NMR spectrum **3k** (101 MHz, $CDCl_3$)



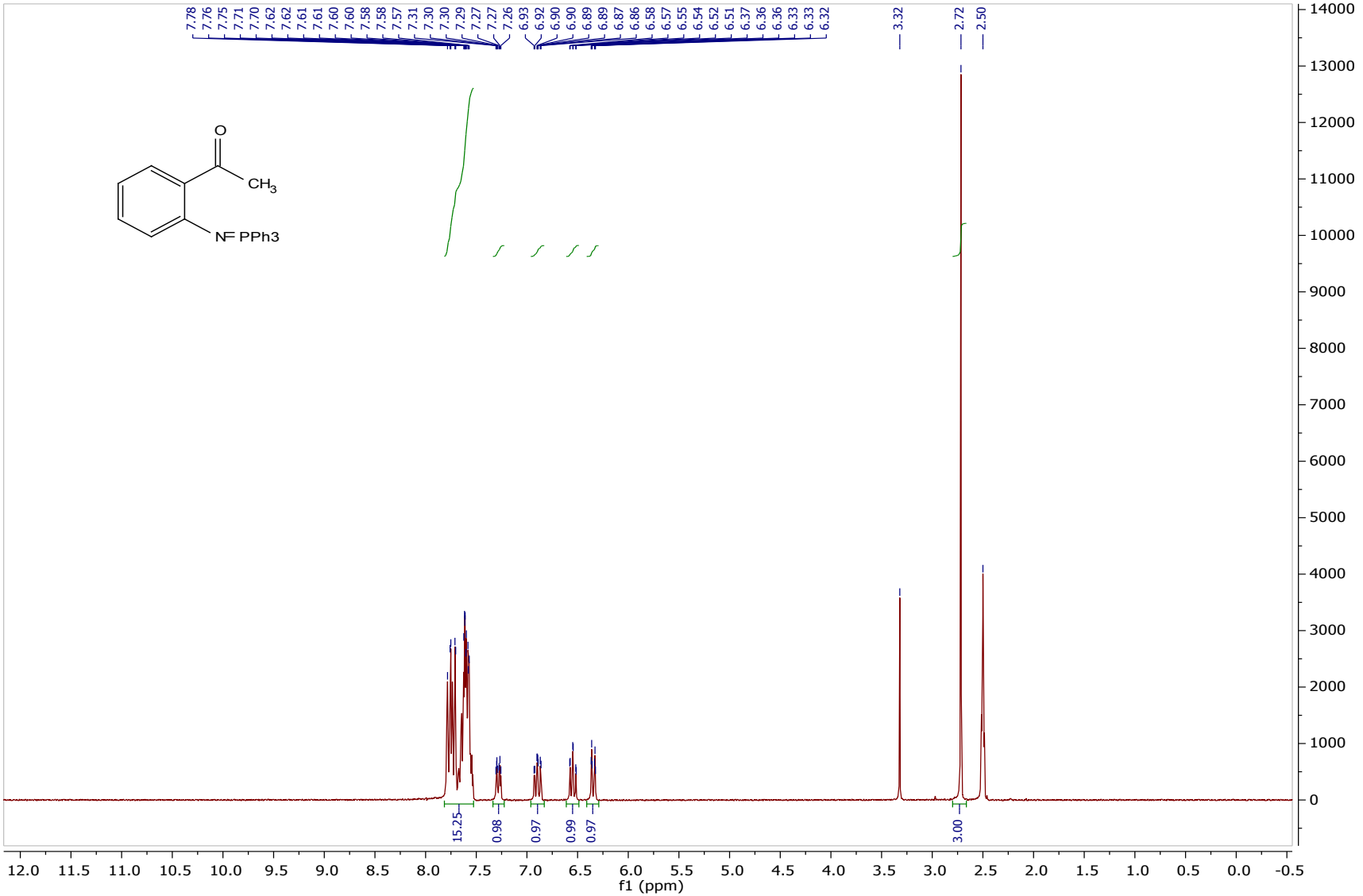
$^{1}$H NMR spectrum **3l** (250 MHz, DMSO-$d_6$)



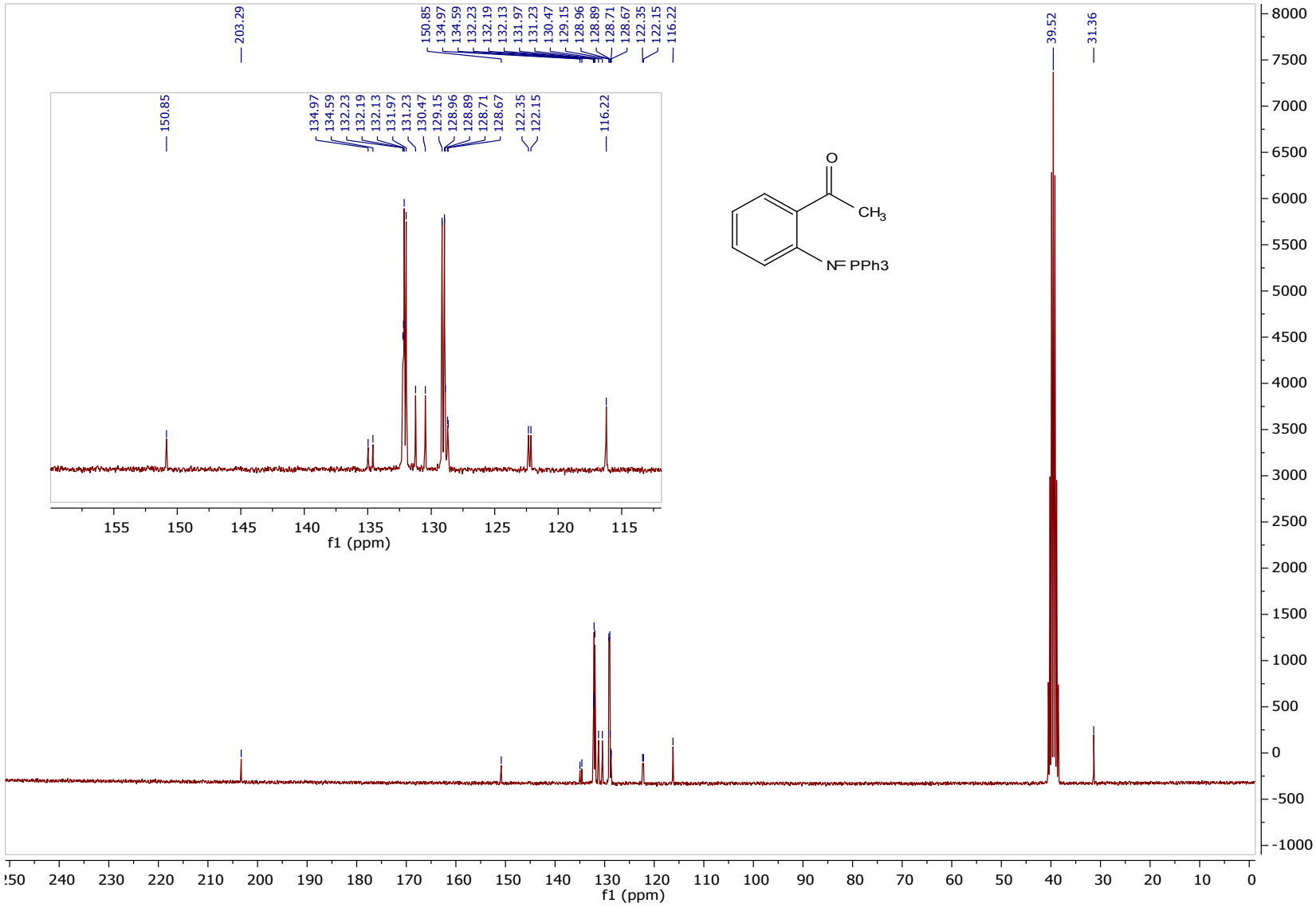
$^{13}$C NMR spectrum **3l** (101 MHz, DMSO-$d_6$)



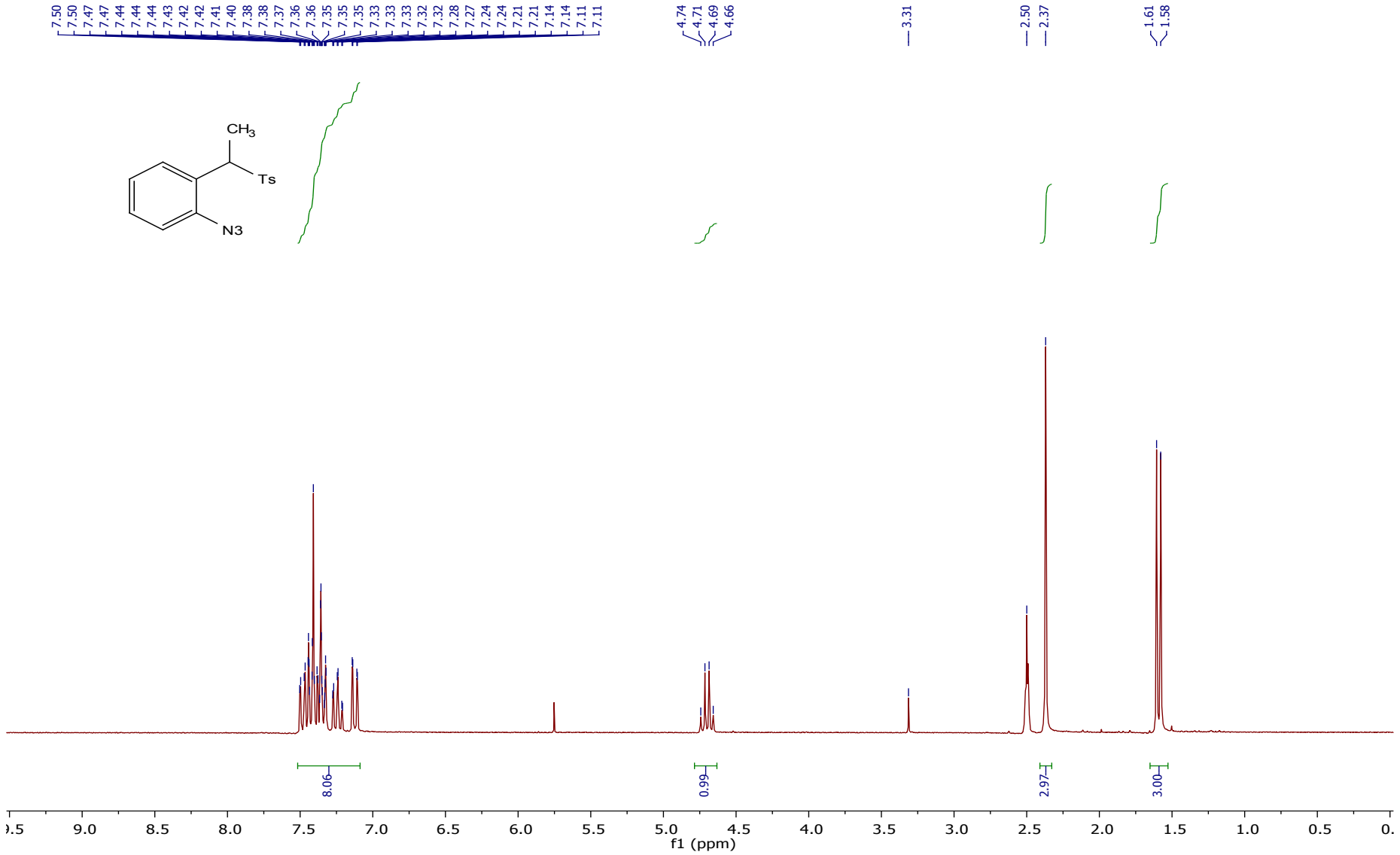
$^{1}$H NMR spectrum **5** (250 MHz, DMSO-$d_6$)



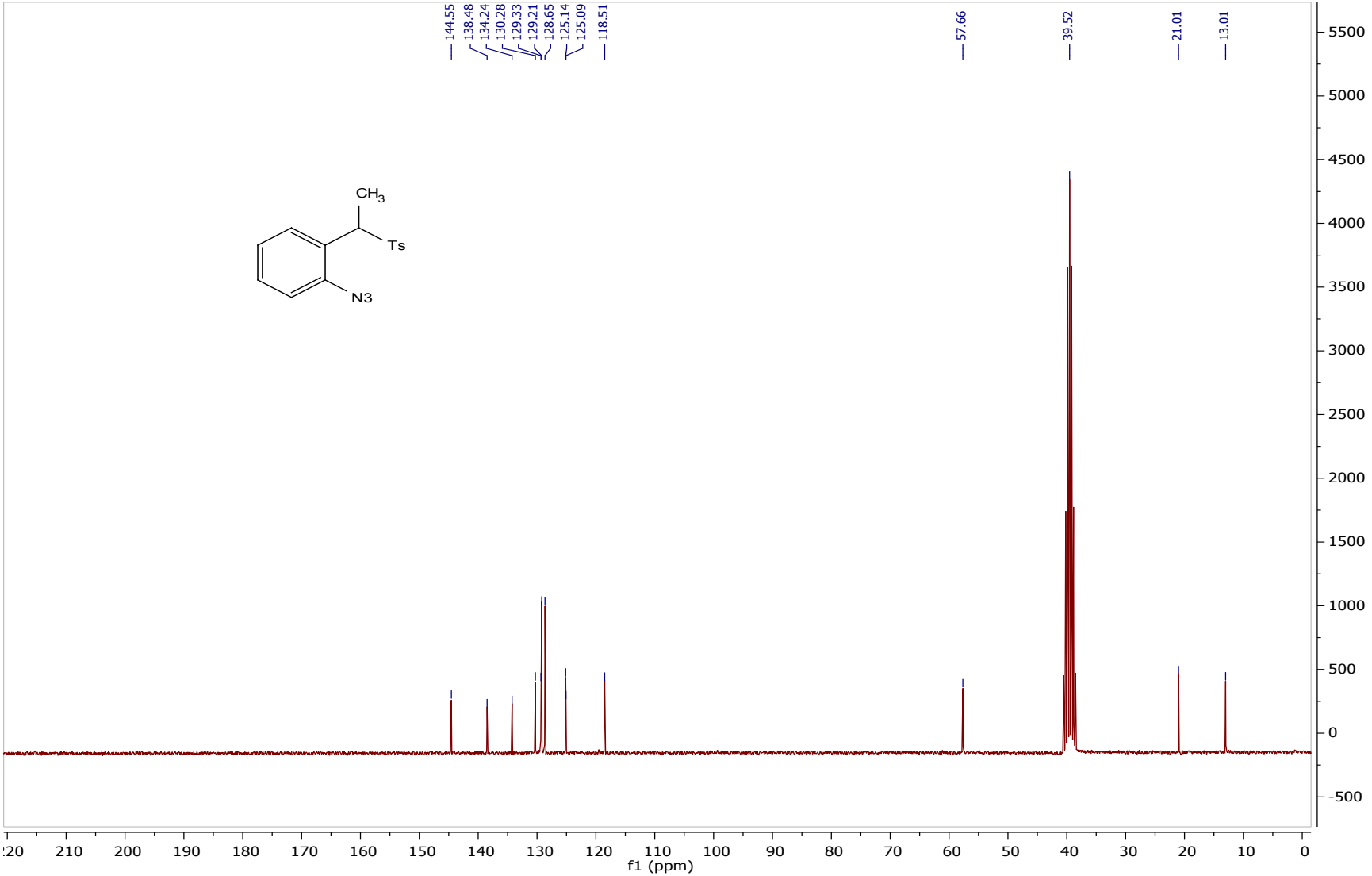
$^{13}$C NMR spectrum **5** (101 MHz, DMSO-$d_6$)



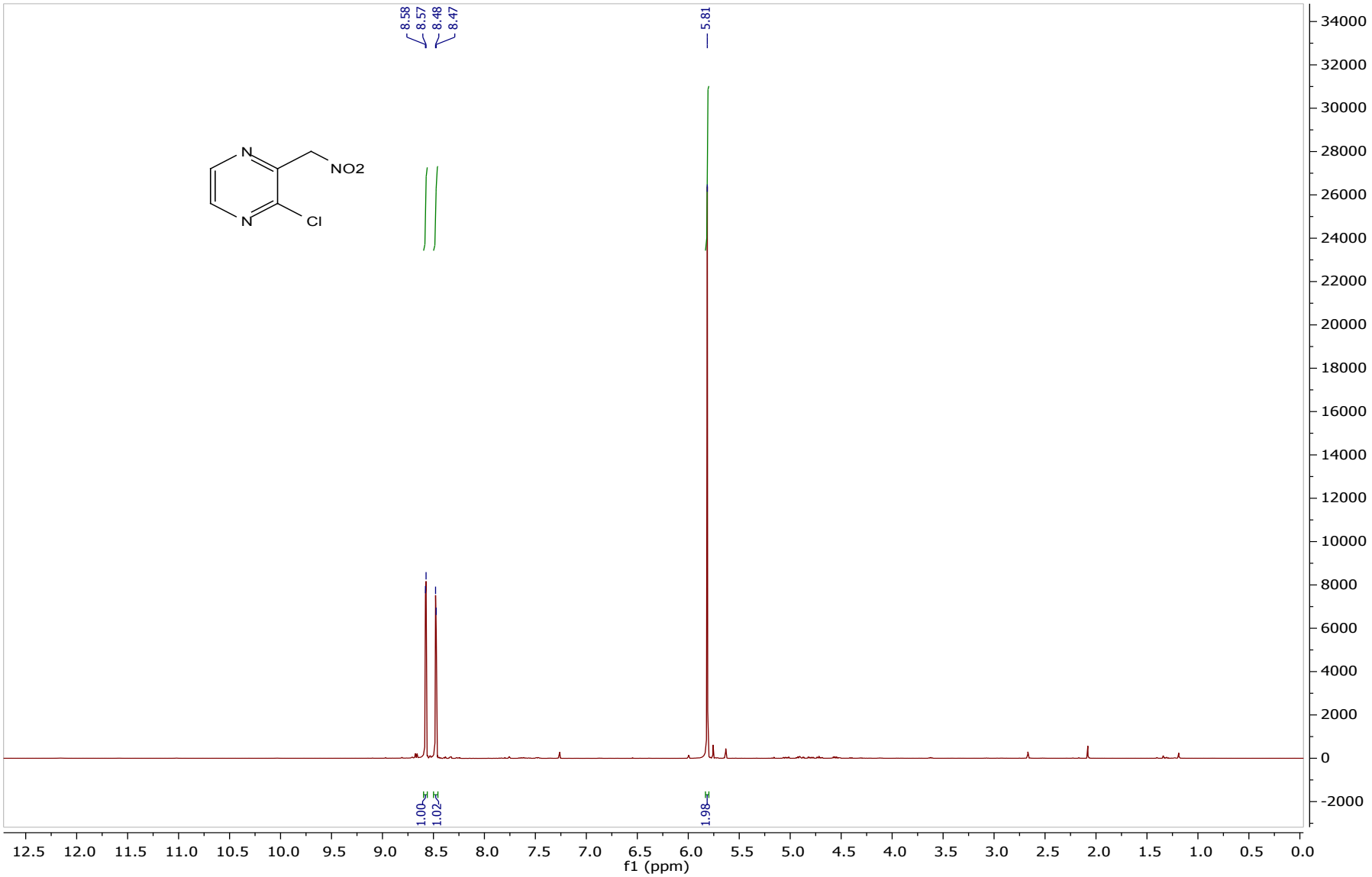
$^{1}$H NMR spectrum **8** (250 MHz, DMSO-$d_6$)



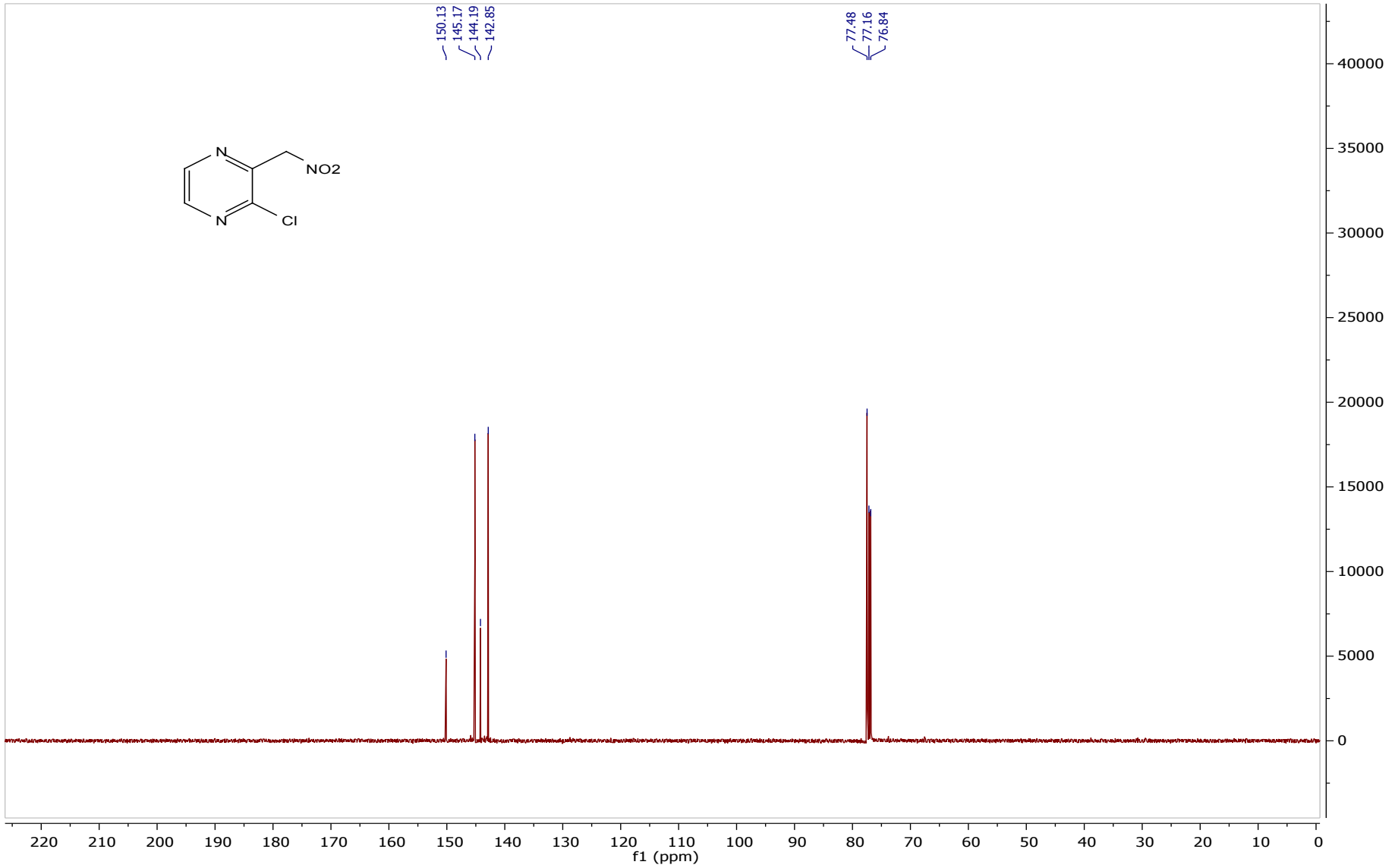
$^{13}$C NMR spectrum **8** (101 MHz, DMSO-$d_6$)



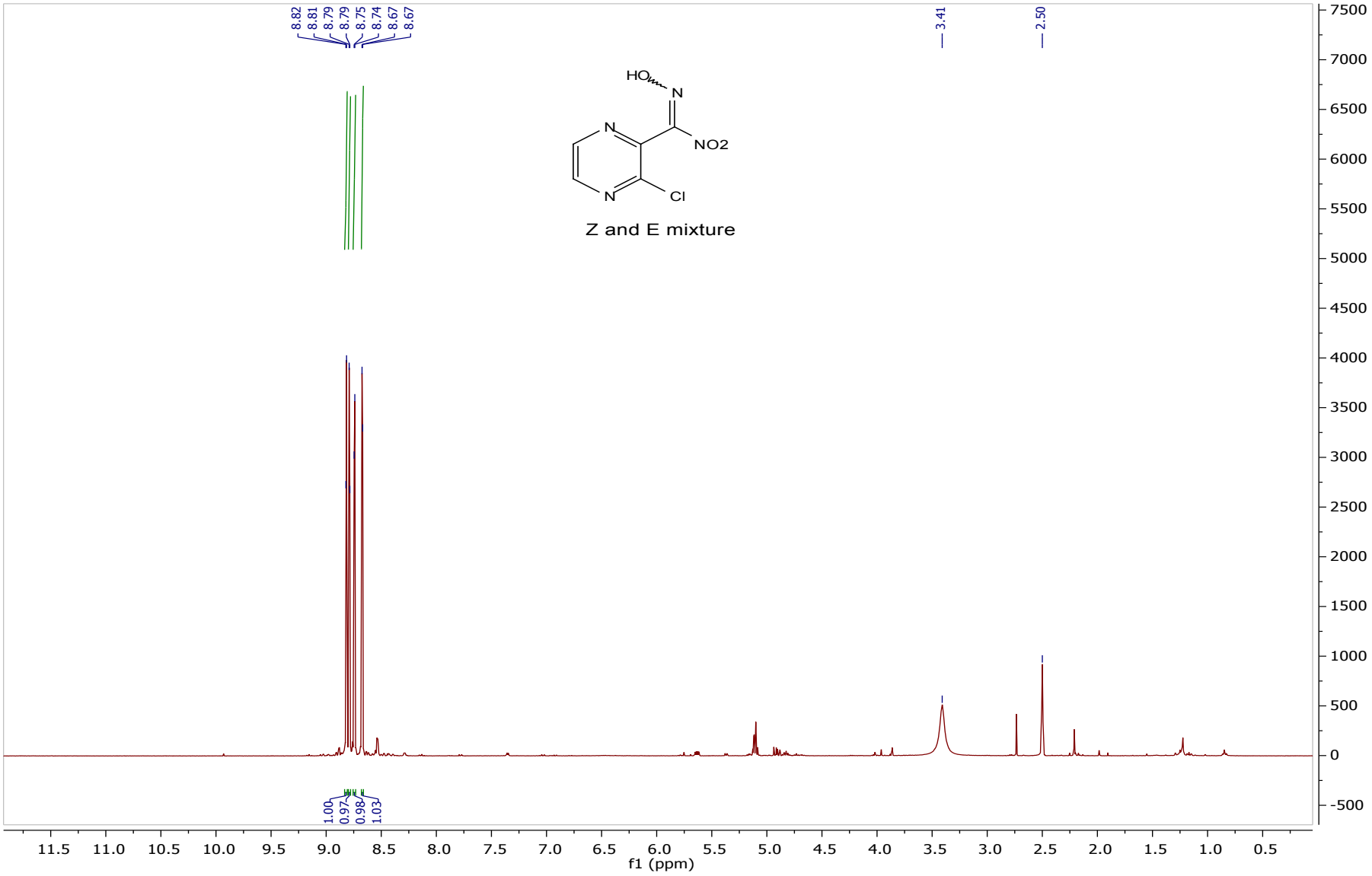
[1]H NMR spectrum **10** (250 MHz, DMSO-$d_6$)



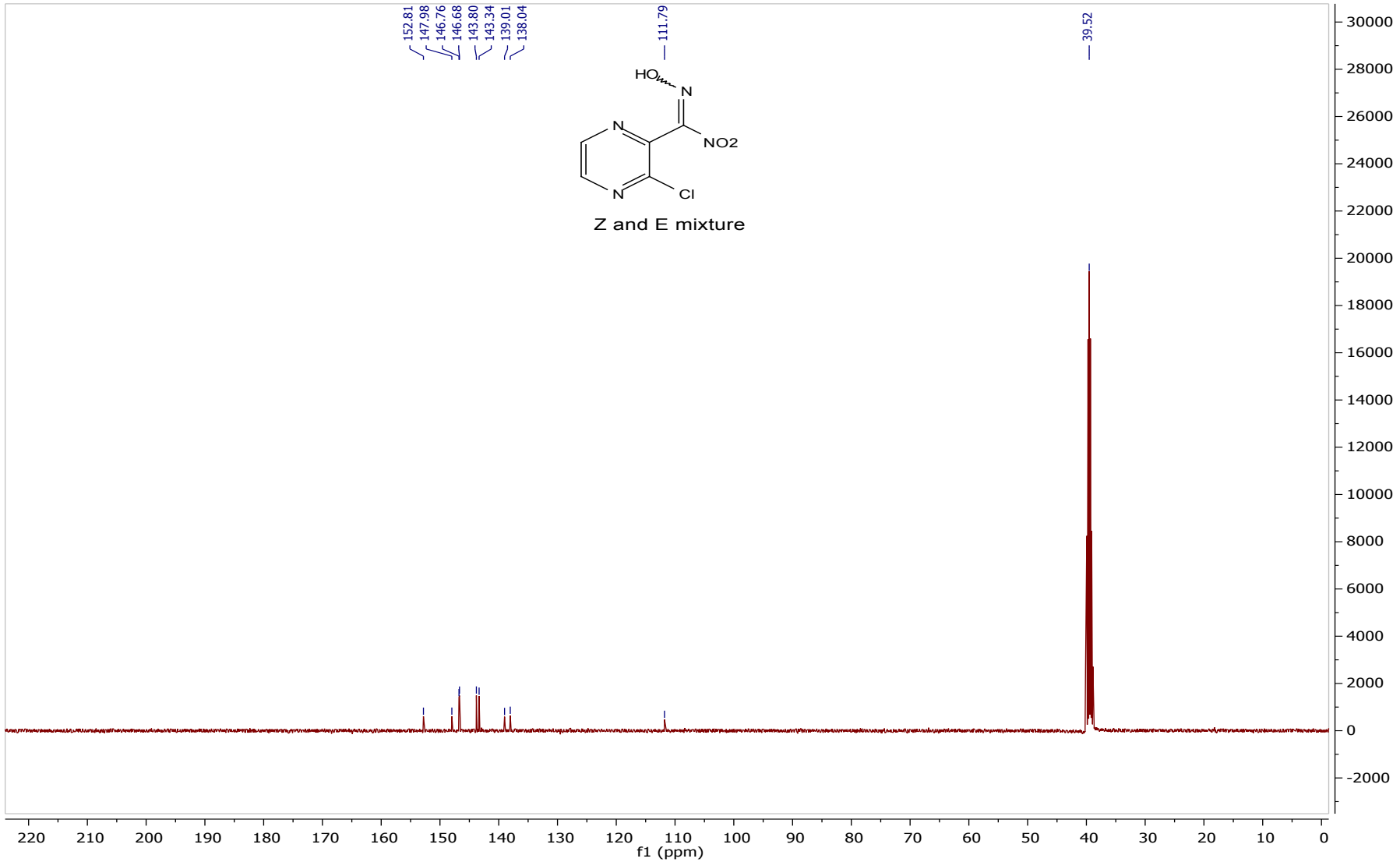
$^{13}$C NMR spectrum **10** (101 MHz, DMSO-$d_6$)



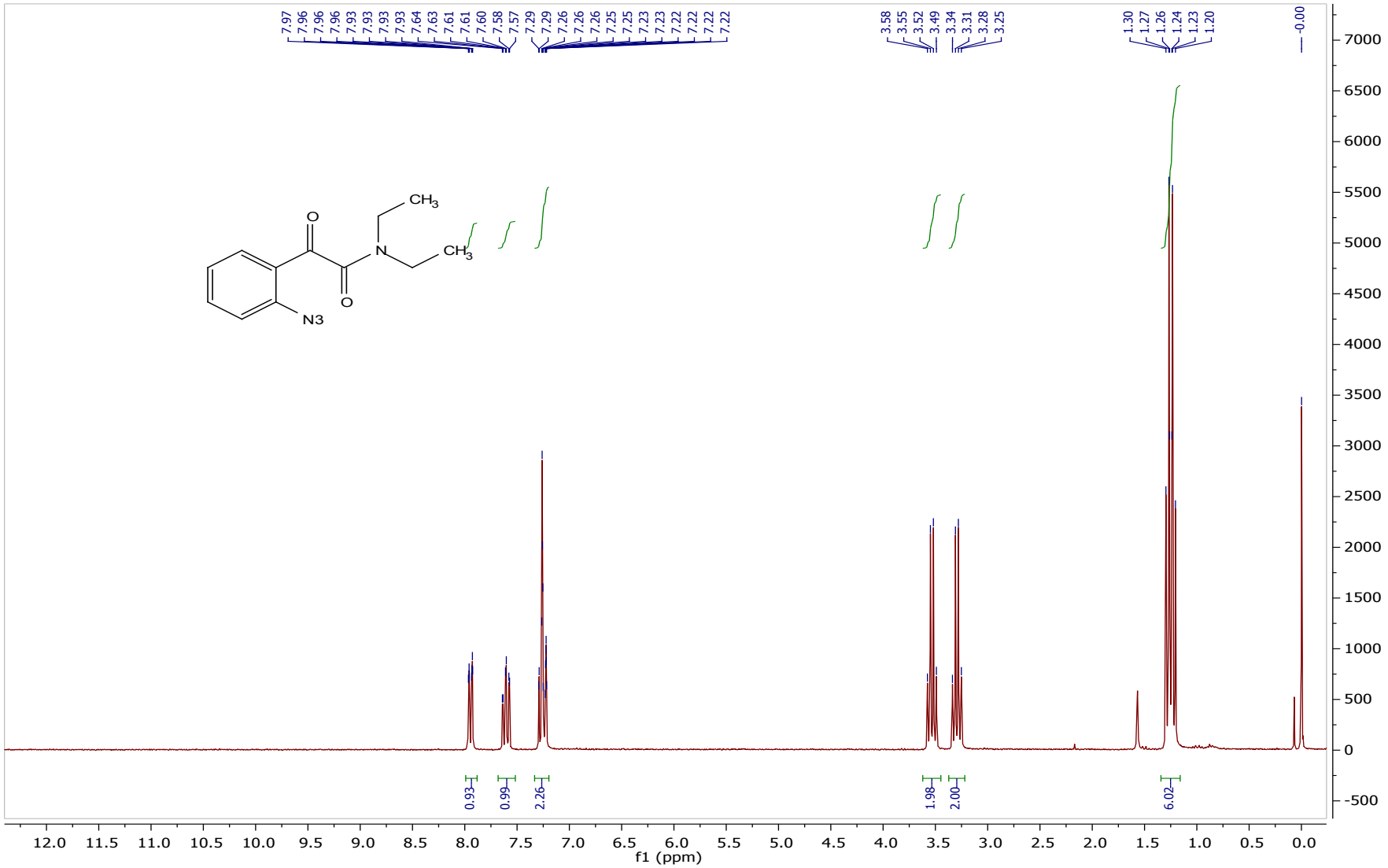
[1]H NMR spectrum **11** (250 MHz, DMSO-$d_6$)



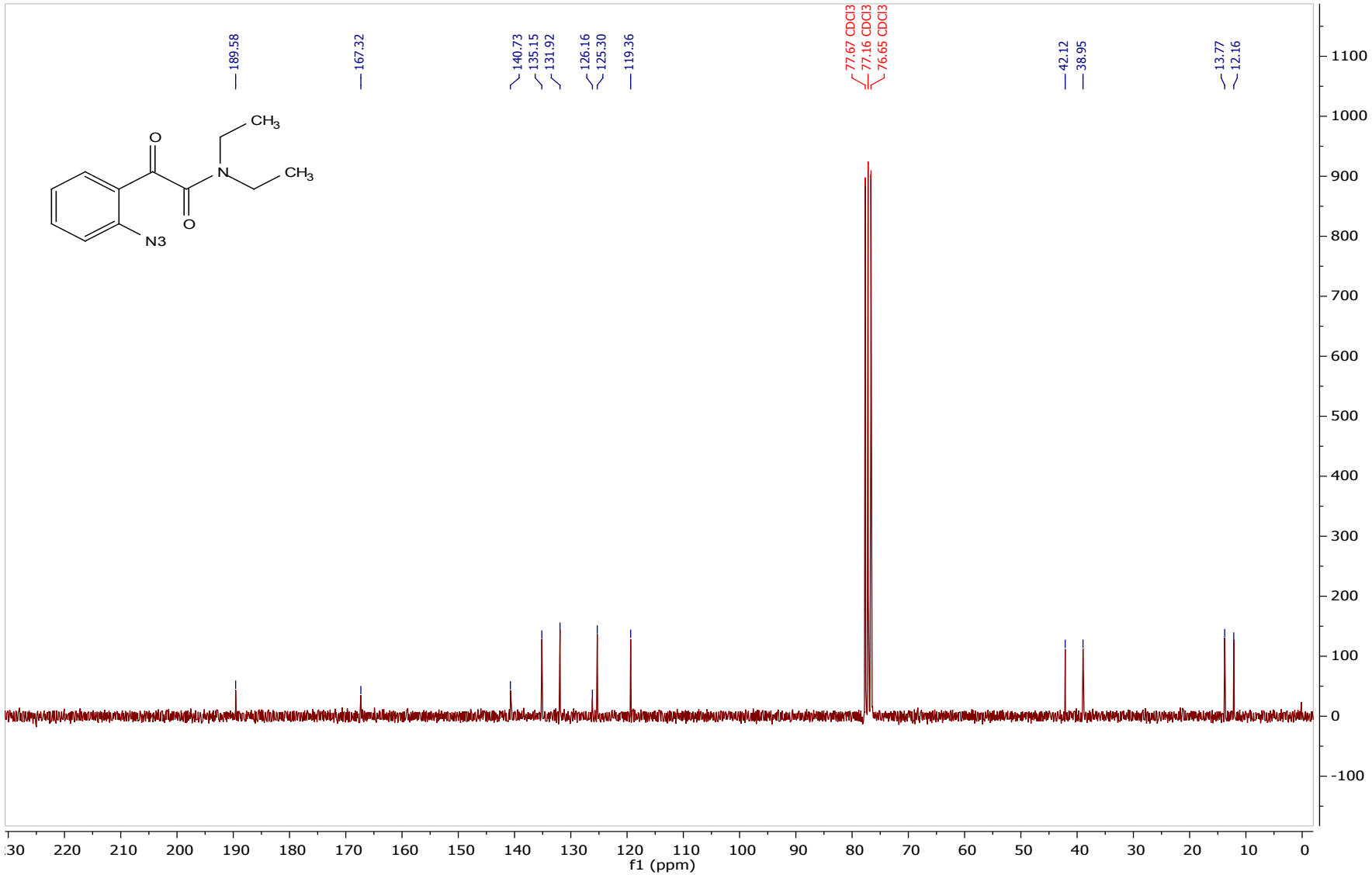
$^{13}$C NMR spectrum **11** (101 MHz, DMSO-$d_6$)



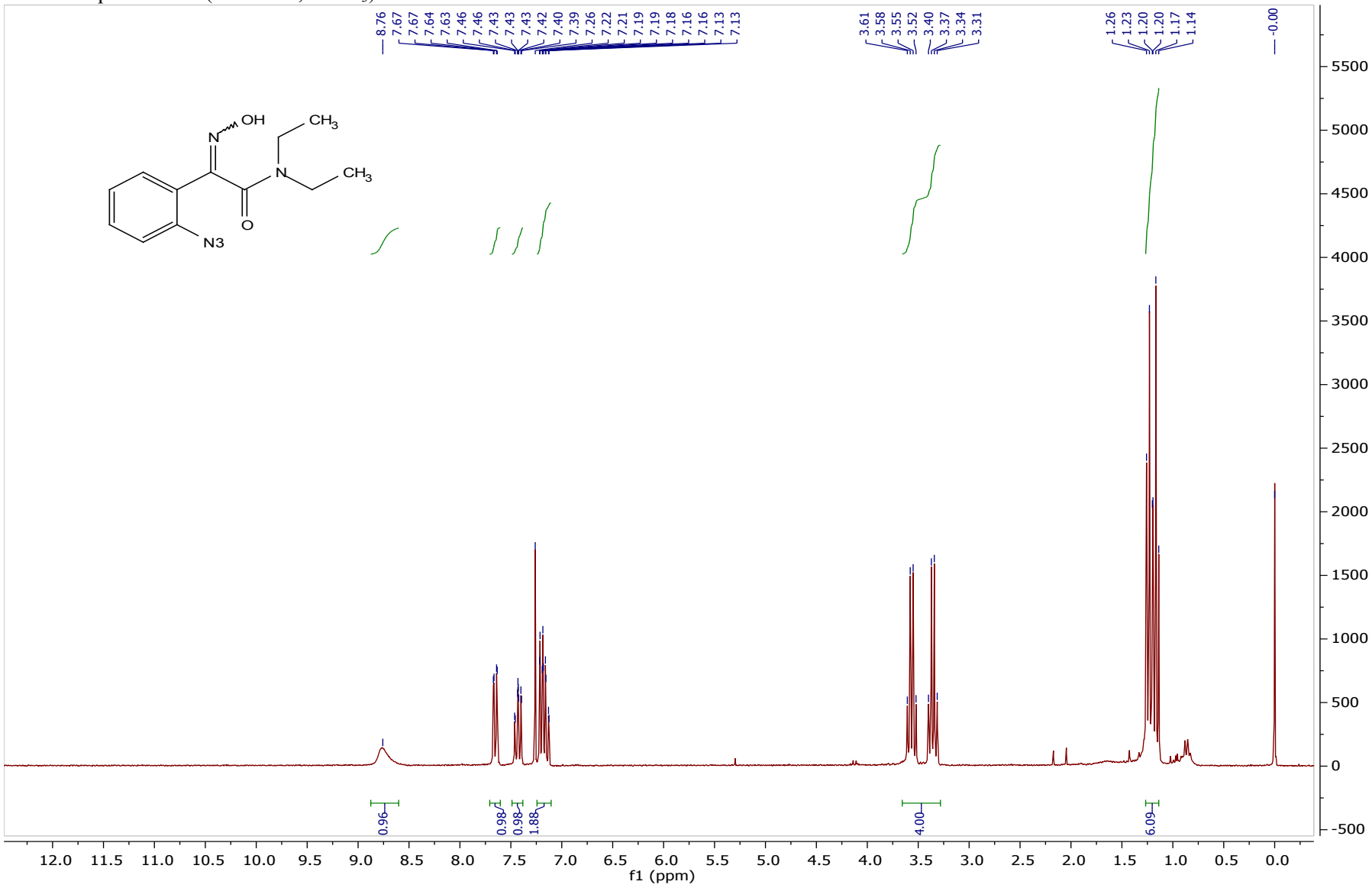
$^{1}$H NMR spectrum **12'** (250 MHz, DMSO-$d_6$)



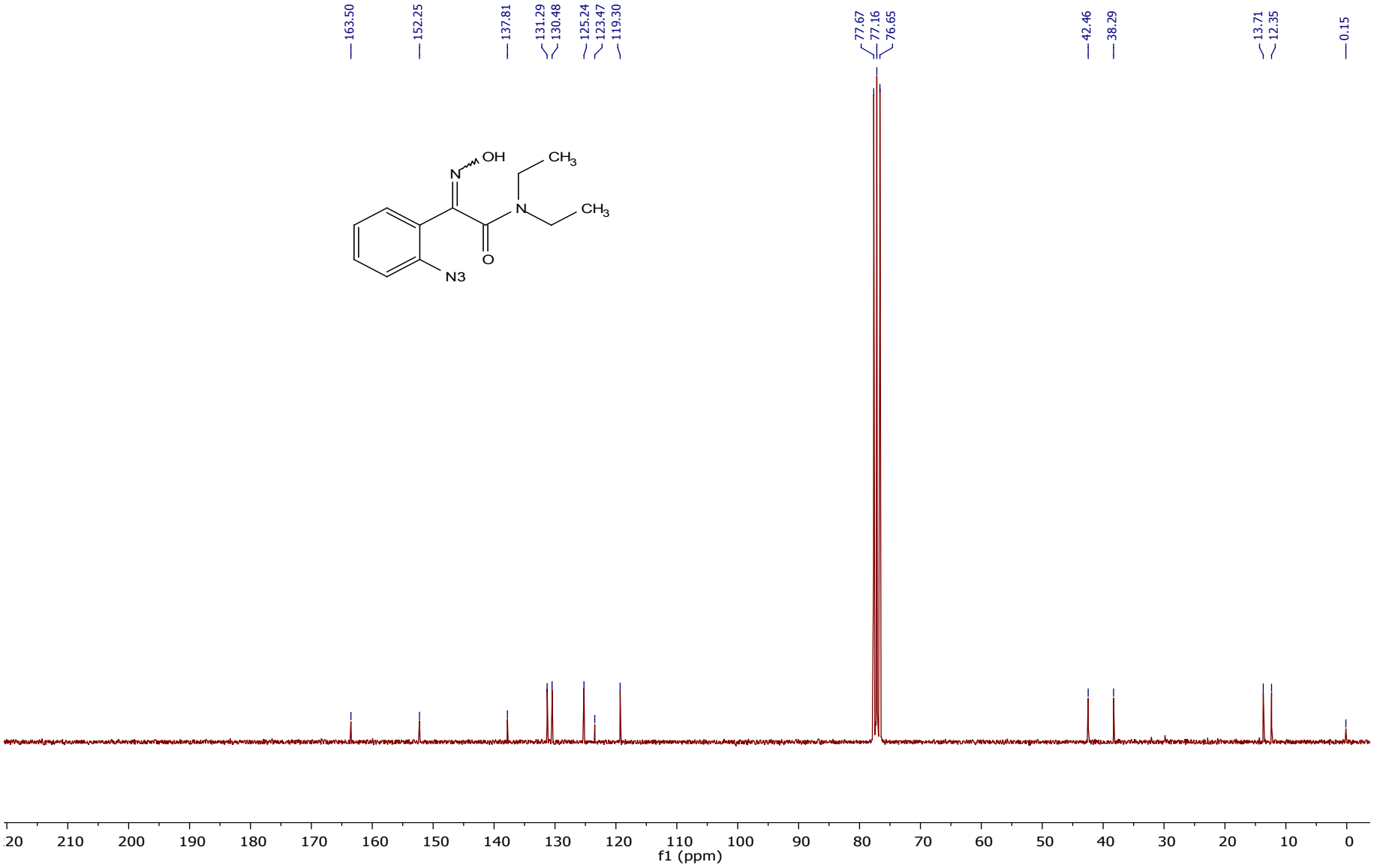
$^{13}$C NMR spectrum **12'** (101 MHz, DMSO-$d_6$)



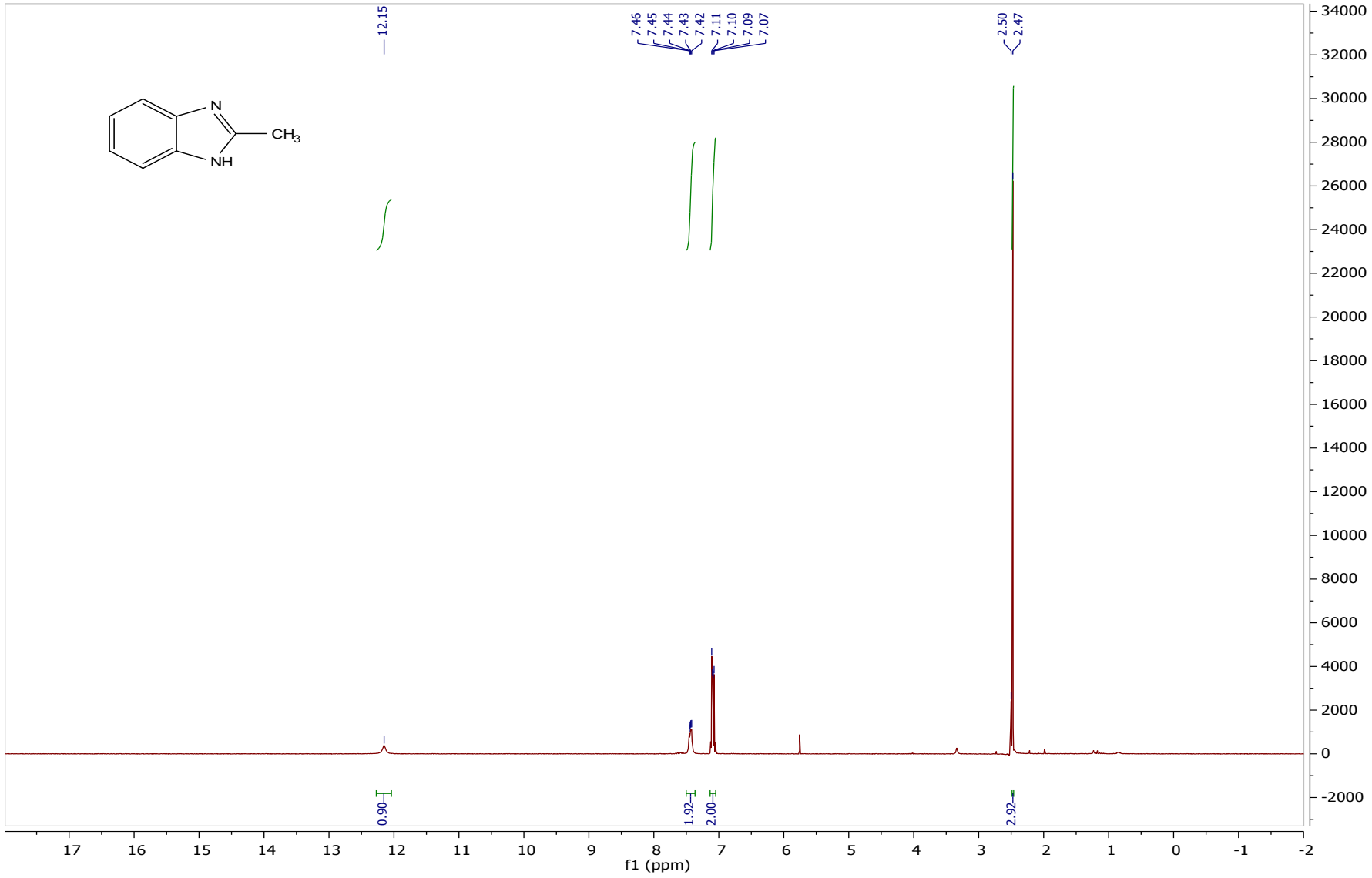
$^{1}$H NMR spectrum **12** (250 MHz, $CDCl_3$)



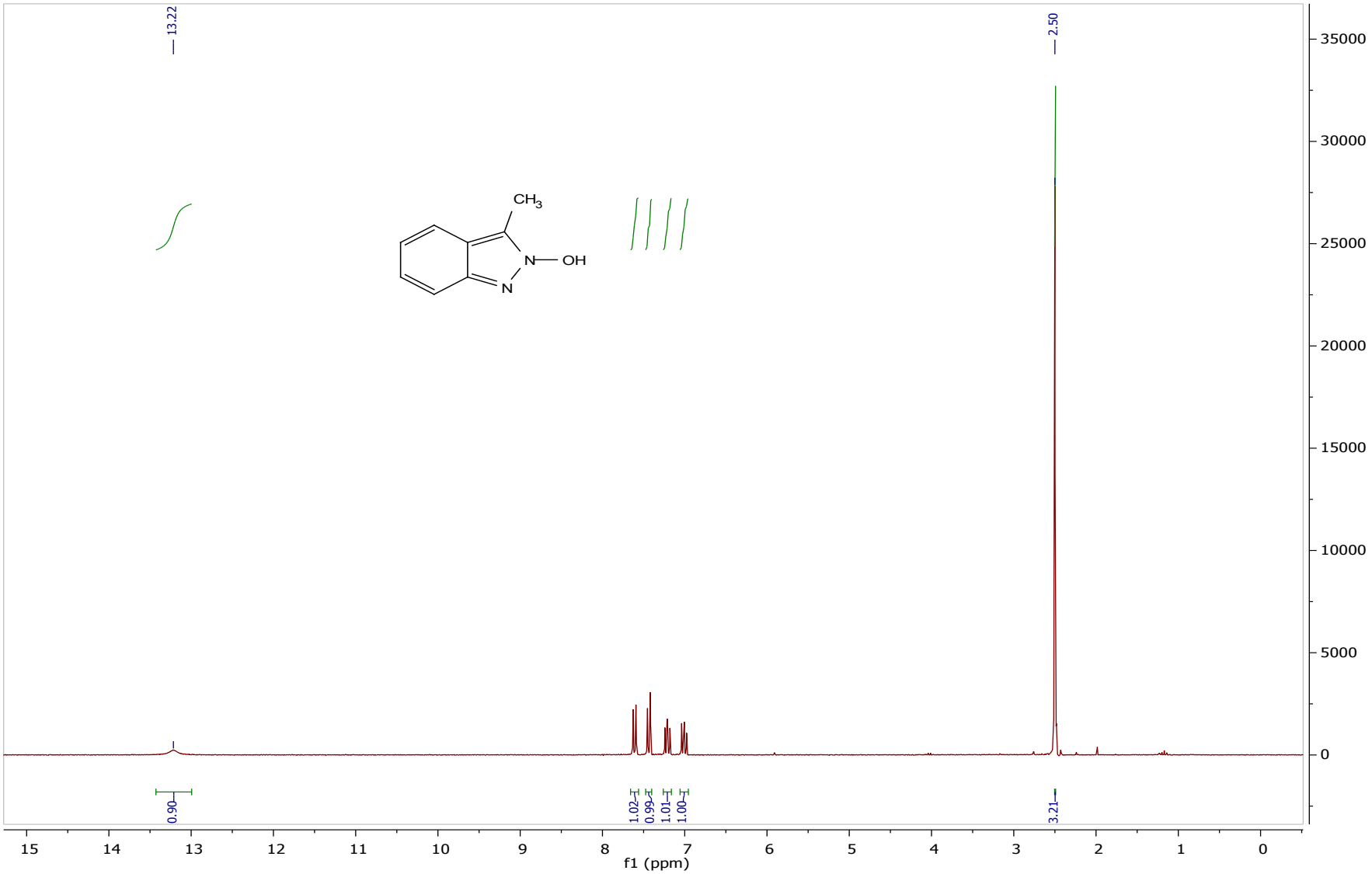
$^{13}$C NMR spectrum **12** (101 MHz, $CDCl_3$)



$^{1}$H NMR spectrum **14** (250 MHz, DMSO-$d_6$)



$^{1}$H NMR spectrum **15** (250 MHz, DMSO-$d_6$)



$^{13}$C NMR spectrum **15** (63 MHz, DMSO-$d_6$)