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Electronic Supplementary Information

Grindstone chemistry: protic ionic liquid catalysed substrate–tunned green synthesis of 1,2-disubstituted and 2-substituted benzimidazoles with outstanding selectivity.

Swapan Majumdar,[‡*] Mithun Chakraborty,[‡] Nabeyndu Pramanik[§] and Dilip K. Maiti[§*]
[‡]Department of Chemistry, Tripura University, Suryamaninagar 799 022, India; Tel: +91-381-2379070
Fax: 00913812374802; E-mail: smajumdar@tripurauniv.in
[§]Department of Chemistry, University of Calcutta, 92 A P C Ray Road, Kolkata 700 009, India. Fax: +91-33-2351-9755; Tel: +91-33-2350-9937; E-mail: dkmchem@caluniv.ac.in

1. Materials and methods.

All reagents were purchased from commercial suppliers and used without further purification, unless otherwise specified. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Reported melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra (Bruker Advance 300) were recorded at ambient temperature using 300 MHz spectrometers (300 MHz for ^{1}H and 75 MHz for ^{13}C). Chemical shift is reported in ppm from internal reference tetramethylsilane and coupling constant in Hz. Proton multiplicities are represented as s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet). Infrared spectra were recorded on FT-IR spectrometer (Perkin Elmer Spectrum 100) in thin film using KBr. HR-MS data were acquired by electron spray ionization technique on a Q-tof-micro quadriple mass spectrophotometer (Bruker).

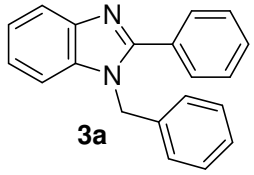
2. General procedure for synthesis of 1,2-disubstituted benzimidazole.

A mixture of o-phenylenediamine (10 mmol), aromatic aldehyde (22 mmol), and protic ionic liquid **II** (5 mol%) was grinded by means of mortar and pastel in open air at room temperature for appropriate time given in figure 1 (approximately 30 – 120 min). After completion of the reaction as revealed by TLC, the residue was poured on crushed ice and the solid was filtered washed thoroughly with water. The product was re-crystallized from ethanol-water to obtain the pure product.

3. General procedure for synthesis of 2-disubstituted benzimidazole.

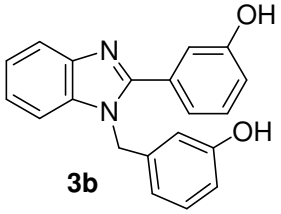
A mixture of o-phenylenediamine (1 mmol), aromatic aldehyde (1.2 mmol), and protic ionic liquid **II** (5 mol%) was grinded by means of mortar and pastel in open air at room temperature for appropriate time given in Table 2 (usually 30 - 360 min depending upon the nature of aldehydes). After completion of the reaction as revealed by TLC, the residue was poured on crushed ice and the solid was filtered washed thoroughly with water. For carbohydrate based substrates products were purified by column chromatography using ethyl acetate and hexane as eluent. The product was re-crystallized from ethanol-water to obtain analytically pure product.

The structures of the products were confirmed by IR, NMR spectral data and were compared with the melting point reported in literature for known compounds.



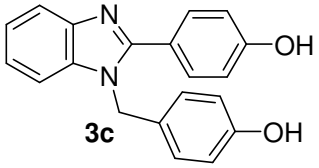
3a

2-Phenyl-1-benzyl 1H-1,3-benzimidazole (3a): Yield: 72%; m. p. 134–136 ^{o}C; lit.[1] m. p. 134^{0}C; ^{1}H (300 MHz, DMSO-d$_6$) δ 8.18-8.15 (m, 3H), 7.72-7.42 (m, 4H), 7.28-7.20 (m, 5H), 6.99-6.97 (m, 2H), 5.56 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ 152.7, 142.2, 136.4, 135.4, 129.6,129.3, 128.5, 128.4, 126.9, 125.9, 125.5, 122.5, 121.7, 118.8, 110.5, 46.9.



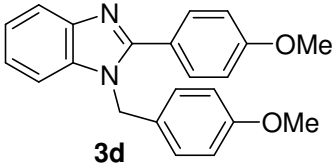
3b

2-(3-hydroxyphenyl)-1-(3-Hydroxybenzyl)-1*H*-benzimidazole (3b): Yield 80%; yellow solid, m. p. 250-251 °C, lit. [3]m. p. 253 ^{o}C; ^{1}H-NMR (300 Hz, DMSO-d$_6$) δ 9.76 (bs, 1H), 9.43 (bs, 1H), 7.71 (d, *J* = 6.3 Hz, 1H), 7.37-7.04 (m, 7H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 7.5 Hz, 1H), 6.47 (d, *J* = 6.9 Hz, 1H), 6.37 (bs, 1H), 5.47 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ 157.2, 152.8, 142.1, 137.9, 135.4, 130.7, 129.3, 122.1, 121.6, 118.9, 118.7, 116.4, 116.1, 115.5, 113.9, 112.2, 110.6, 46.9.



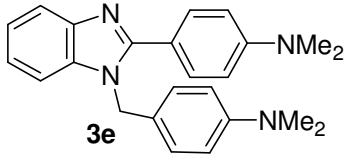
3c

2-(4-hydroxyphenyl)-1-(4-Hydroxybenzyl)-1*H*-benzimidazole (3c): Yield 78%; light yellow solid, m. p. 221 °C, lit.[3] m. p. 222 ^{o}C; ^{1}H-NMR (300 Hz, DMSO-d$_6$) δ 10.02 (s, 1H), 9.46 (s, 1H), 7.69-7.57 (m, 3H), 7.43 (d, *J* = 5.7 Hz, 1H), 7.23-7.20 (m, 2H), 6.94-6.84 (m, 4H), 6.70-6.67 (m, 2H), 5.44 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ 158.3, 156.2, 153.1, 142.2, 135.3, 130.1, 127.0, 126.6, 121.6, 121.3, 120.3, 118.3, 115.0, 114.9, 116.1, 114.9, 110.4, 46.5.



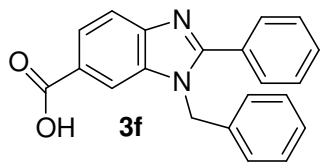
3d

2-(4-methoxyphenyl)-1-(4-methoxybenzyl)-1*H*-benzimidazole (3d): Yield: 70%; white powder, m. p. 130 ^{o}C, lit. [4] m. p. 130 ^{o}C; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ 7.84 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.20–7.30 (m, 3H), 7.01 (d, *J* = 8.01 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.38 (s, 2H), 3.78 (s, 3H), 3.84 (s, 3H),



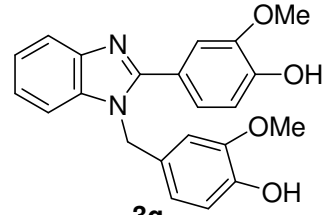
3e

1-(4-*N*,*N*-Dimethylaminobenzyl)-2-(4-*N*,*N*-dimethylaminophenyl)-1*H*-1,3-benzimidazole (3e): Yield 76%; m. p. 253-255 ^{o}C, lit. [1] m. p. 252^{o}C; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ 7.73 (d, *J* = 8 Hz, 1H); 7.55 (d, *J* = 9 Hz, 2H); 7.70-7.05 (m, 3H); 6.96 (d, *J* = 9 Hz, 2H), 6.70-6.55 (m, 4H); 2.93 (s, 3H); 2.86 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ 155.0, 151.2, 149.9, 143.1, 136.3, 130.2, 126.9, 124.2, 122.2, 119.1, 117.1, 112.7, 111.7, 110.4, 48.0, 40.5, 40.1.



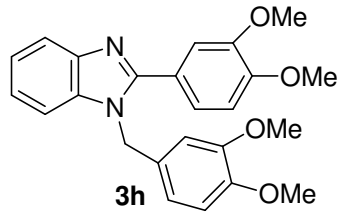
3f

1-benzyl-2-phenyl- 1H-1,3-benzimidazole-6-carboxylic acid (3f)[new]: Yield: 75 %; dirty white solid; m. p. 254°C; IR (KBr) 3548, 3469, 3416, 1677, 1616, 1560, 1441 and 1227 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 8.06 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.81-7.74 (m, 3H), 7.55 (s, 3H), 7.32-7.24 (m, 3H), 7.01 (d, *J* = 7.2 Hz, 2H), 5.67 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.3, 161.2, 151.0, 140.8, 140.5, 135.2, 134.3, 133.9, 133.8, 133.6, 132.7, 130.6, 130.5, 129.1, 123.9, 117.7, 53.1; HRMS calcd. for $C_{21}H_{16}N_2O_2$ 328.1212 found 328.1215



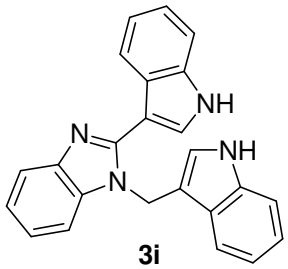
3g

1-(4-Hydroxy-3-methoxybenzyl)-2-(4-hydroxy-3-methoxyphenyl)-1H-1,3-benzimidazole (3g): Yield 81%; m. p. 184–185 °C, lit.[3] m. p. 184–186 °C; ^1H NMR (300 MHz, DMSO-d_6): δ 9.53 (s, 1H), 8.95 (s, 1H), 7.64 (bs, 1H), 7.45 (bs, 1H), 7.23–7.15 (m, 4H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.67-6.60 (m, 2H), 6.35 (d, *J* = 7.8 Hz, 1H); 5.41 (s, 2H), 3.69 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6,) δ 153.1, 147.7, 147.2, 147.1, 145.4, 142.1, 135.5, 127.4, 121.7, 121.4, 120.6, 118.4, 118.0, 115.1, 112.5, 110.4, 110.2, 55.0.



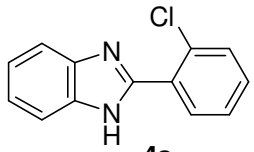
3h

1-(3, 4-dimethoxybenzyl)-2-(3,4-dimethoxyphenyl)-1H-1,3-benzimidazole (3h): Yield 75%; white needles, m. p. 168-169 °C, lit. [3] m. p. 171-173 °C; ^1H NMR (300MHz, DMSO-d_6) δ 7.66 (m, 1H); 7.44 (m,1H), 7.27-7.19 (m, 4H), 7.09-7.06 (m, 1H), 6.83 (m, 1H), 6.73 (bs, 1H), 6.44 (d, *J* = 8.1 Hz, 1H), 5.47 (s, 2H), 3.81 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6,) δ 152.6, 149.5, 148.3, 147.5, 142.0, 135.4, 128.9, 121.9, 121.4, 118.3, 117.4, 111.9, 111.3, 110.2, 109.6, 54.9, 46.9.



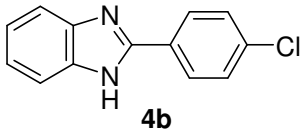
3i

2-(3-Indolyl)-1-(3-indolylmethyl)-1H-1,3-benzimidazole (3i)[new: Yield: 90 %; beige solid, m. p. 234-236 °C; IR (KBr) 3423, 2921, 1642, 1572, 1450, 1424 and 1105 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 12.22 (s, 1H), 11.76 (s, 1H), 8.58 (d, *J* = 6.3Hz, 1H), 7.94 (s, 1H), 7.75 (d, *J*= 6.3Hz, 1H), 7.64 (d, *J* = 2.7 Hz, 1H), 6.28 (d, *J* = 3.6Hz, 1H), 7.40-7.08 (m, 8H), 6.91 (t, *J* = 7.5 Hz, 1H), 5.89 (S, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 150.1, 143.8, 136.8, 136.5,136.1, 127.0, 126.8, 126.0, 124.0, 122.8, 121.9, 120.0, 119.3, 118.8, 118.7, 118.3, 112.5, 112.2, 110.9, 110.9, 105.6. HRMS calcd for $C_{24}H_{18}N_4+H^+$: 363.1611 found 363.1620.



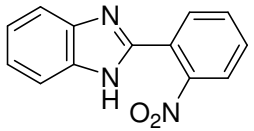
4a

2-(2-chlorophenyl)-1H-1,3-benzimidazole (4a): Yield 72%; m. p.229 °C, lit.[5] m. p. 230-231 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.03 (s, 1H), 8.21 (d, *J* = 8.7 Hz, 2H), 7.66-7.56 (m, 4H), 7.25 (bs, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 148.5, 146.8, 132.1, 130.4, 123.8, 122.4.



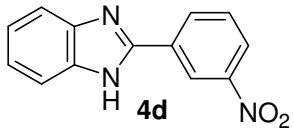
4b

2-(4-chlorophenyl)-1H-1,3-benzimidazole (4b): Yield 82%; m. p. 288 °C; lit.[5]m. p. 288-291 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.03 (s, 1H), 8.21 (d, *J* = 8.7 Hz, 2H), 7.66–7.56 (m, 4H), 7.25 (bs, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 149.6, 143.2, 134.5, 134.0, 128.5, 127.6, 122.2, 121.3, 118.4, 110.9.



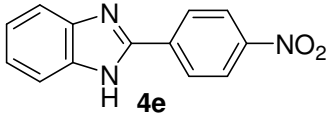
4c

2-(2-Nitrophenyl)-1H-1,3-benzimidazole (4c): Yield: 79%; light yellow solid, m. p. 230 °C; lit.[6] m. p. 232 °C ; ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.09 (s, 1H), 8.07-7.99 (m, 2H), 7.91- 7.65 (m, 4H), 7.28 (bs, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 148.5, 146.8, 132.1, 130.4, 123.8, 122.4.



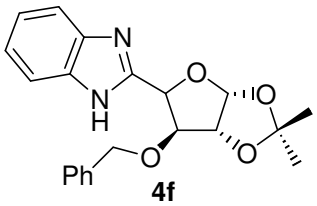
4d

2-(3-Nitrophenyl)-1H-1,3-benzimidazole* (4d) *: Yield 81%; light yellow solid, m. p. 199 °C, lit.[7] m. p. 200-202 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.45 (bs, 1H), 8.99 (d, *J* = 7.2 Hz, 1H), 8.58 (d, *J* = 7.8 Hz, 1H), 8.33 (m, 1H), 7.85 (m, 1H), 7.69-7.58 (m, 2H), 7.45-7.25 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 150.9, 148.8, 133.1, 132.9, 131.7, 131.2, 125.0, 123.5, 121.5.



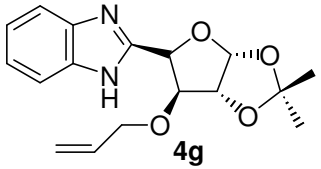
4e

2-(4-Nitrophenyl) benzimidazole (**4e**):Yield 85, light yellow solid, m. p. above 300 °C, lit.[5]m. p. 308-310 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.3(s, 1H), 7.8 - 6.6 (m, 8H).



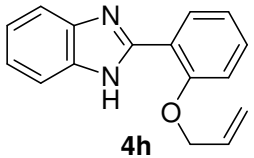
4f

2-(3-*O*-benzyl 1,2-*O*-isopropyledine-α-D-xylofuranoside)-1H-1,3-benzimidazole (4f[)new: Yield: 77%; beige solid; m. p. 210 °C; $[\alpha]_D^{26}$ -55.32 (c 0.47, $CHCl_3$); IR (KBr) ν_{max}3445, 1646, 1559, 1437, 1384 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (bs, 2H), 7.28 (bs, 2H), 7.17 (bd, 3H), 6.89 (d, *J* = 6 Hz, 2H), 6.08 (bs, 1H), 5.68 (bs 1H), 4.72 (bs, 1H), 4.44-4.37 (m, 2H), 4.18 (d, *J* = 11.1 Hz, 1H), 1.55 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 136.7, 128.4, 128.0, 127.7, 122.9, 112.7, 105.3, 83.7, 83.2, 77.7, 73.5, 26.9, 26.3; HRMS calcd for ($C_{21}H_{22}N_2O_4$ + H^+) 367.1652; found: 367.1647



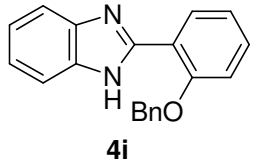
4g

2-(3-*O*-allyl 1,2-*O*-isopropyledine-α-D-xylofuranoside)-1H-1,3-benzimidazole (4g)new: Yield: 65%; white powder; m. p. 152 °C; $[\alpha]_D^{25}$ -36.00 (c 1.000, $CHCl_3$); IR (KBr) ν_{max}3445, 1633, 1600, 1557, 1437, 1378, 1306, 1273, 1221, 1165 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.61 (bs, 2H), 7.28 (bs, 2H), 6.08 (d, *J* = 3.0 Hz, 1H), 5.62 (d, *J* = 2.1 Hz, 1H), 5.60-5.52 (m, 1H), 5.06-4.97 (m, 2H), 4.70 (d, *J* = 3 Hz, 1H), 4.32 (s, 1H), 3.85 (dd, *J* = 12.6, 5.4 Hz, 1H), 3.65 (d, *J* = 12.6, 5.4 Hz, 1H), 1.54 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 133.4, 122.7, 117.9, 112.6, 105.2, 83.3, 83.2, 77.7, 71.7, 26.9, 26.3; HRMS calcd for $C_{17}H_{20}N_2O_4$+H+: 317.1409, found:.317.1402.



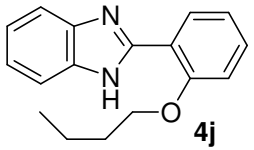
4h

2-(2-allyloxy phenyl)-1H-1,3-benzimidazole (4h)new: Yield: 75%; white needles; m. p. 240-242 °C; IR (KBr) ν_{max} 3422, 3043, 2723, 598, 1560, 1522, 1456, 1399, 1350, 1330, 1289, 1270, 1247, 1223, 1164, 1125, 1098, 1078 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.55 (bs, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 6.47 (2, 2H), 6.38 9m, 2H), 6.24 (m, 2H), 6.13 (d, *J* = 8.4 Hz, 1H), 5.37-5.20 (m, 1H), 4.63 (m, 2H), 3.87 (d, *J* = 5.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8, 149.8, 132.3, 131.4, 130.2, 122.5, 121.9, 119.3, 118.1, 69.7; HRMS calcd for $C_{16}H_{14}N_2O + H^+$): 251.1179; found: 251.1173.



4i

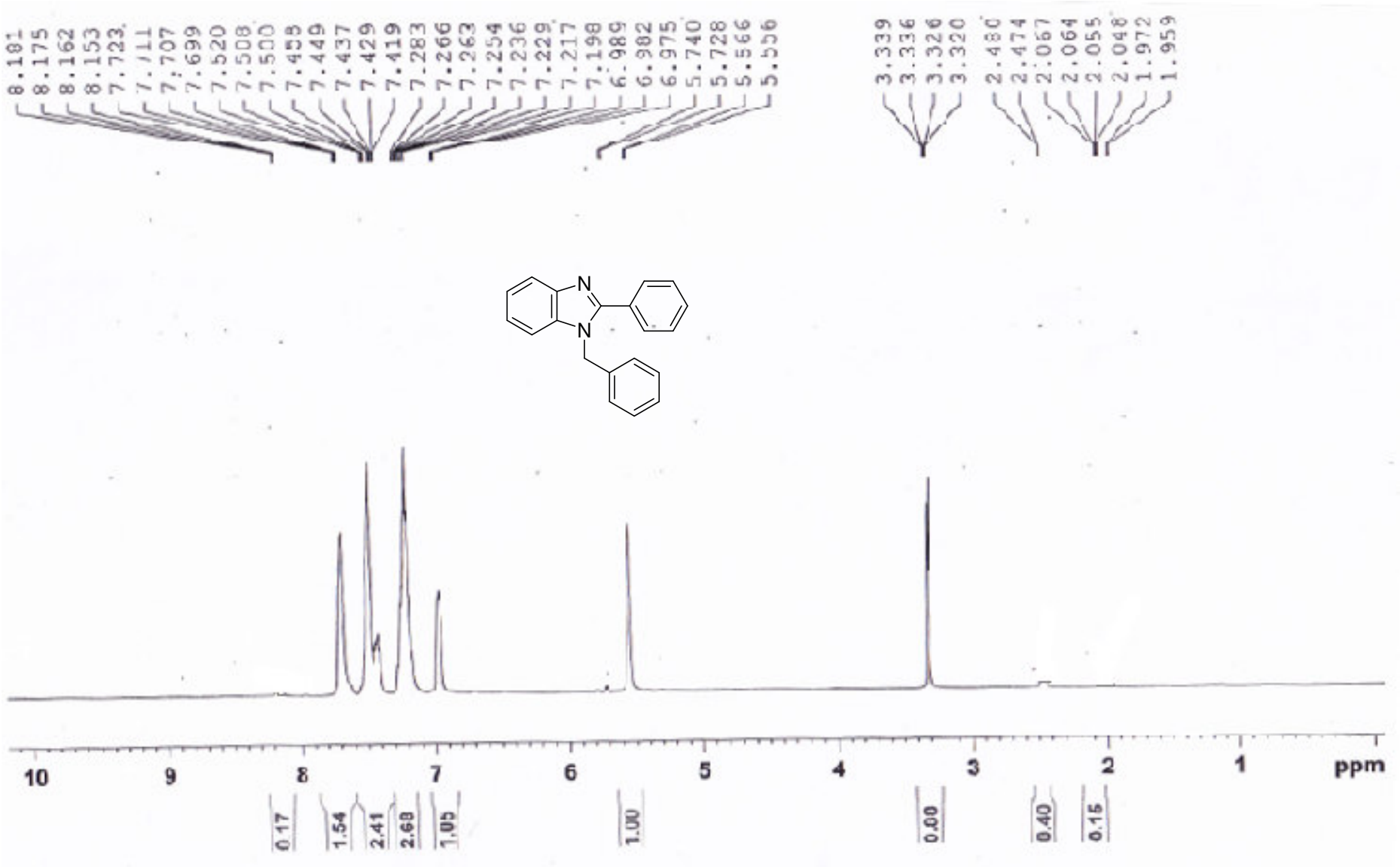
2-(2-benzyloxy phenyl)-1H-1,3-benzimidazole (4i)new: Yield: 81%; amorphous solid; m. p. 244 °C; IR (KBr) ν_{max} 3434, 2852, 1629, 1584, 1556, 1495, 1455, 1387, 1352, 1297, 1240, 1219, 1137 cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$) δ 10.55 (bs, 1H), 8.57 (d, *J* = 7.8 Hz, 2H), 7.28 (s, 5H), 7.24 (m, 1H), 7.16 (m, 2H), 7.04 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.07(s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 149.6, 135.8, 131.0, 129.9, 128.8, 128.5, 127.5, 122.3, 121.8, 118.1, 114.4, 112.7, 71.0; HRMS calcd for ($C_{20}H_{16}N_2O + H^+$): 301.1335; found: 301.1333.



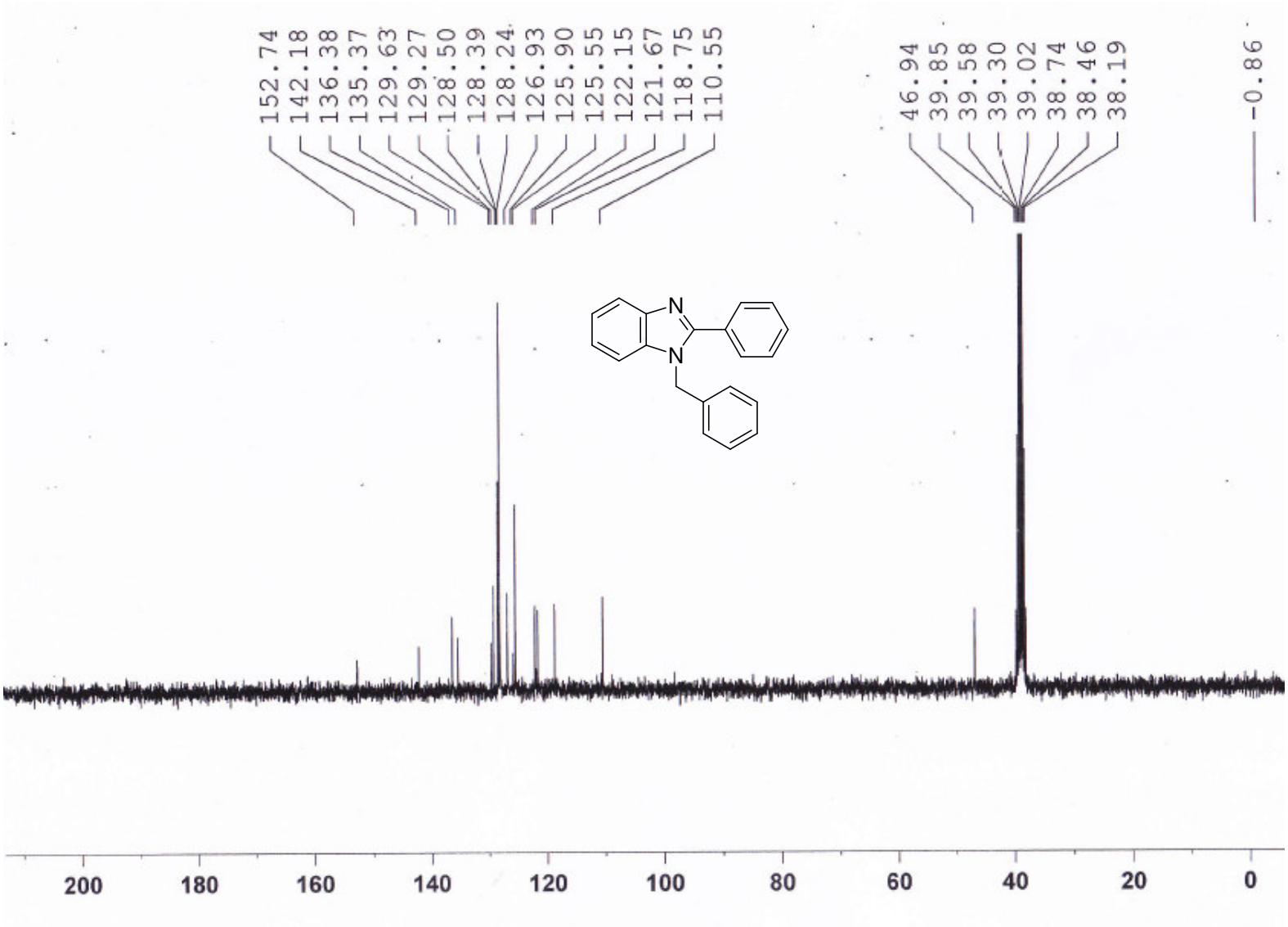
4j

2-(2-n-butyloxy phenyl)-1H-1,3-benzimidazole (4j): Yield: 71%; white needles; m. p. 148 -150 °C; IR (KBr) ν_{max} 3418, 3068, 2958, 2932, 2872, 1620, 1602, 1589, 1557, 1489, 1455, 1446, 1394, 1311, 1282, 1243, 1164, 1092, 1067 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.61 (d, *J*= 7.8 Hz, 1H), 7.67 (bs, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.29 (bs, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 4.25 (t, *J* = 7.5 Hz, 2H), 2.04-1.95 (m, 2H), 1.67-1.52 (m, 2H), 1.08 (t, *J* = 7.5 Hz, 3H); ^{13} NMR (75 MHz, $CDCl_3$) δ 156.3, 150.0, 131.3, 130.2, 122.6, 121.6, 68.8, 31.3, 19.5, 13.8; HRMS calcd for ($C_{17}H_{18}N_2O$+H^+): 267.1492; found: 267.1486

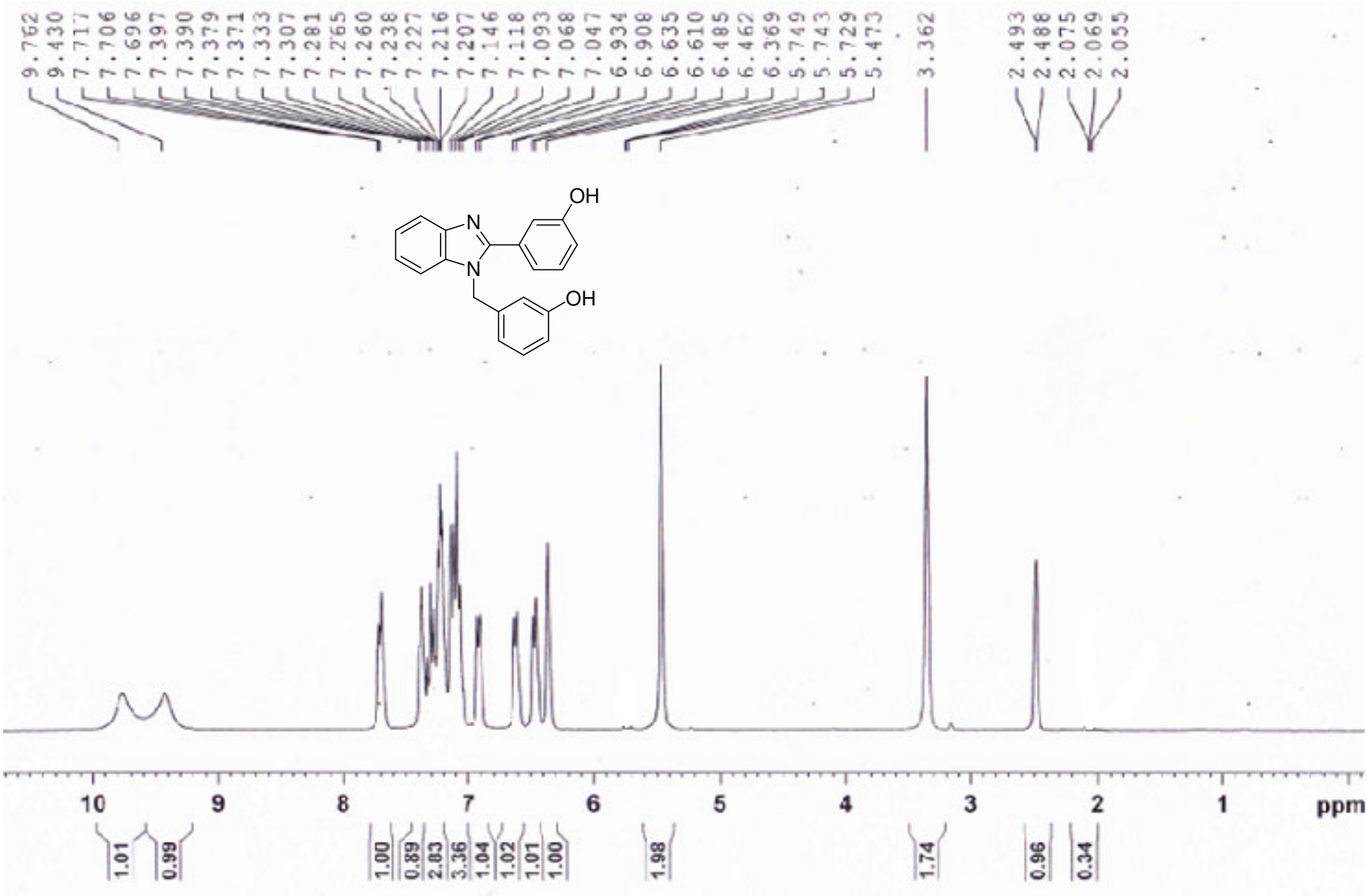
^{1}H NMR spectra of **3a** (300 MHz, DMSO-d_6)



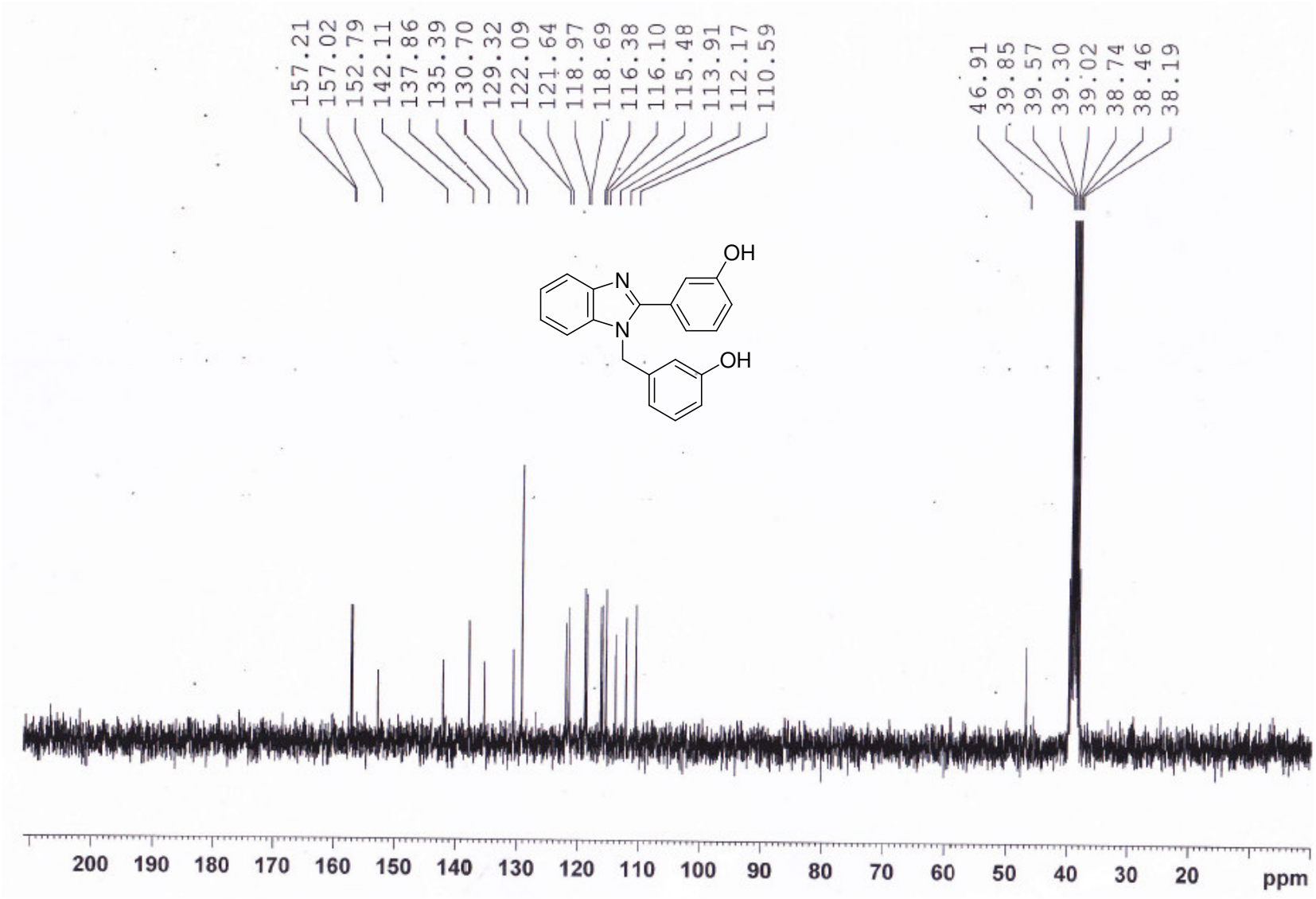
^{13}C NMR spectra of **3a** (75 MHz, DMSO-d_6)



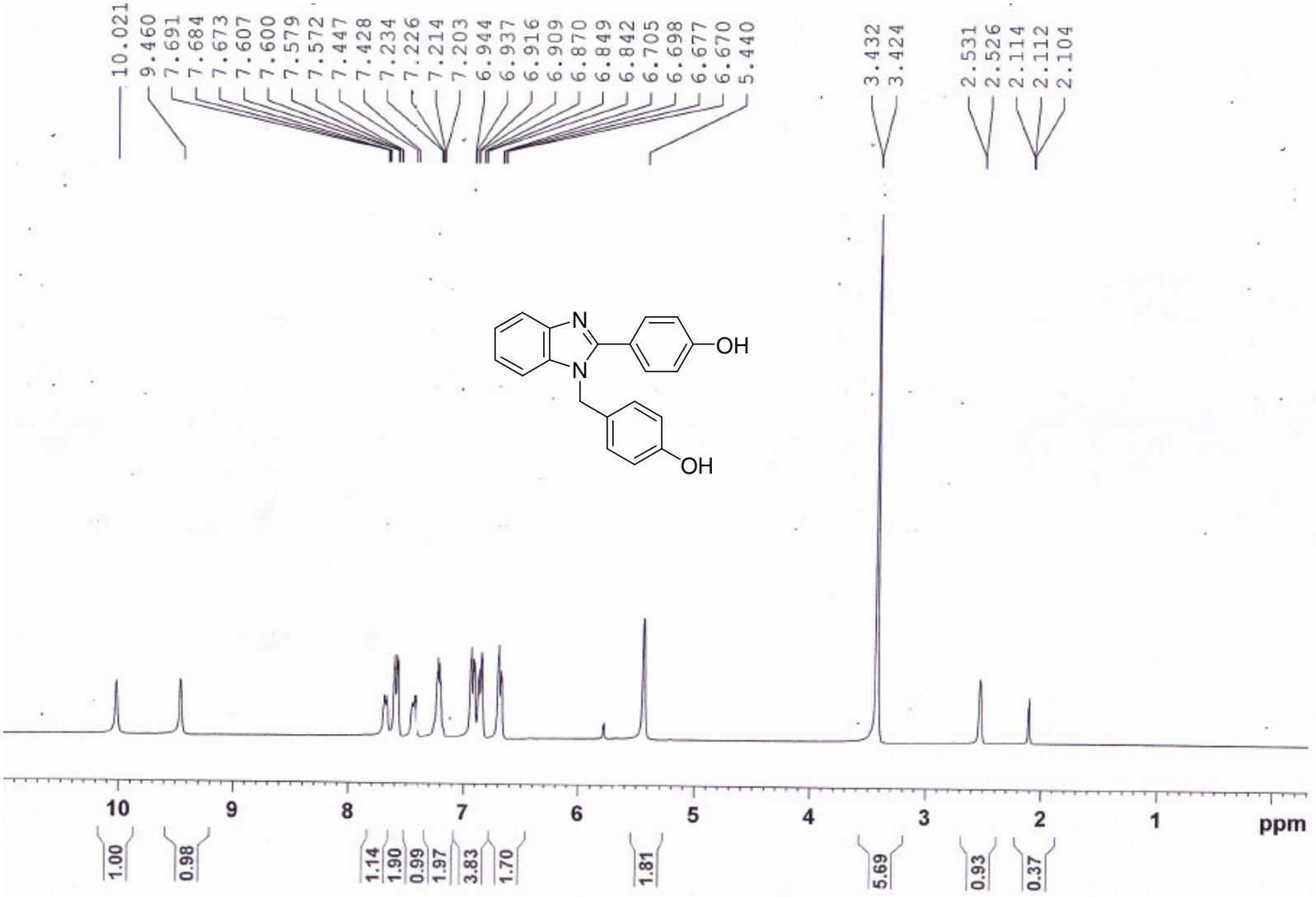
^{1}H NMR spectra of **3b** (300 MHz, DMSO-d_6)



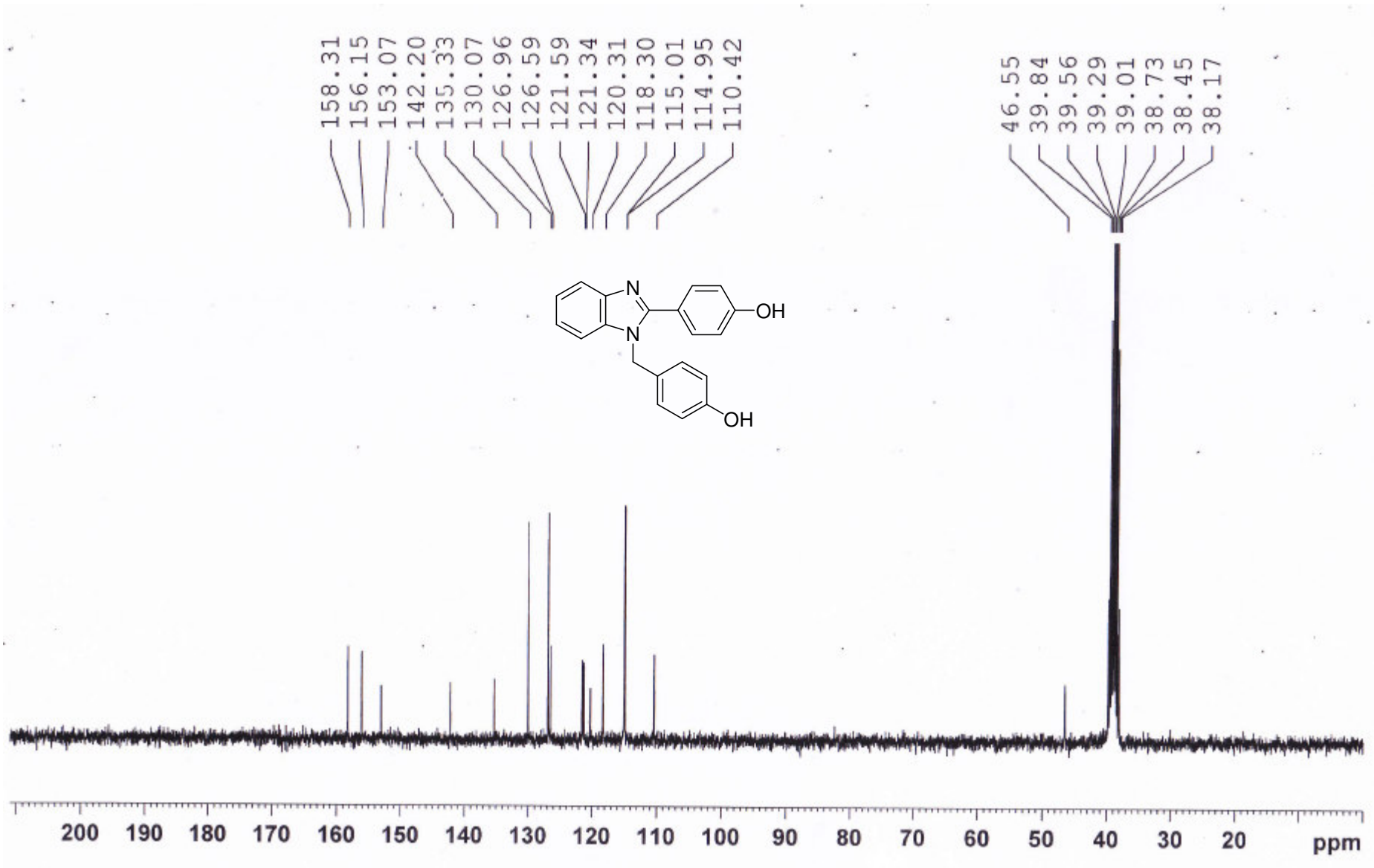
^{13}C NMR spectra of **3b** (75 MHz, DMSO-d_6)



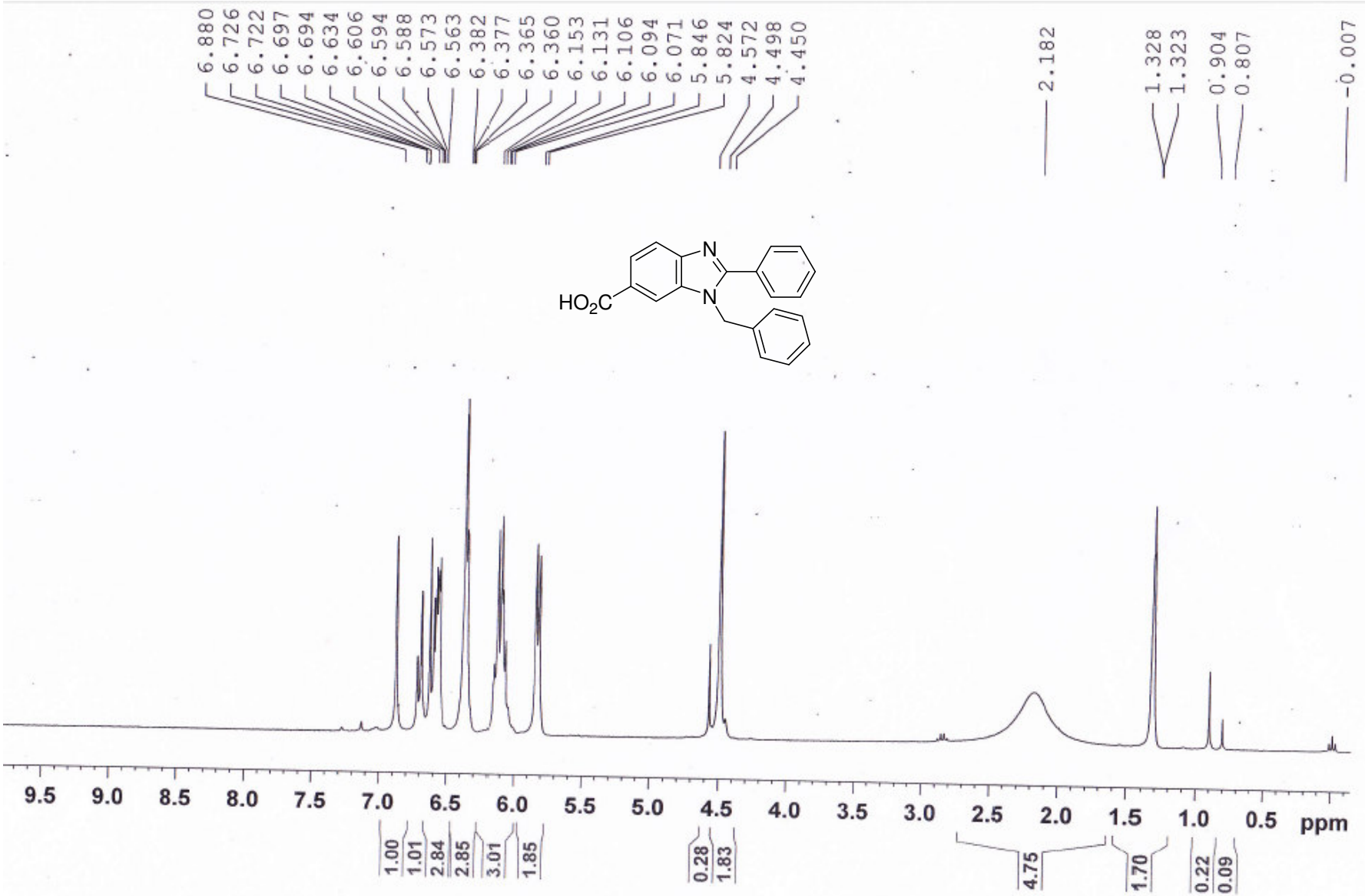
^{1}H NMR spectra of **3c** (300 MHz, DMSO-d_6)



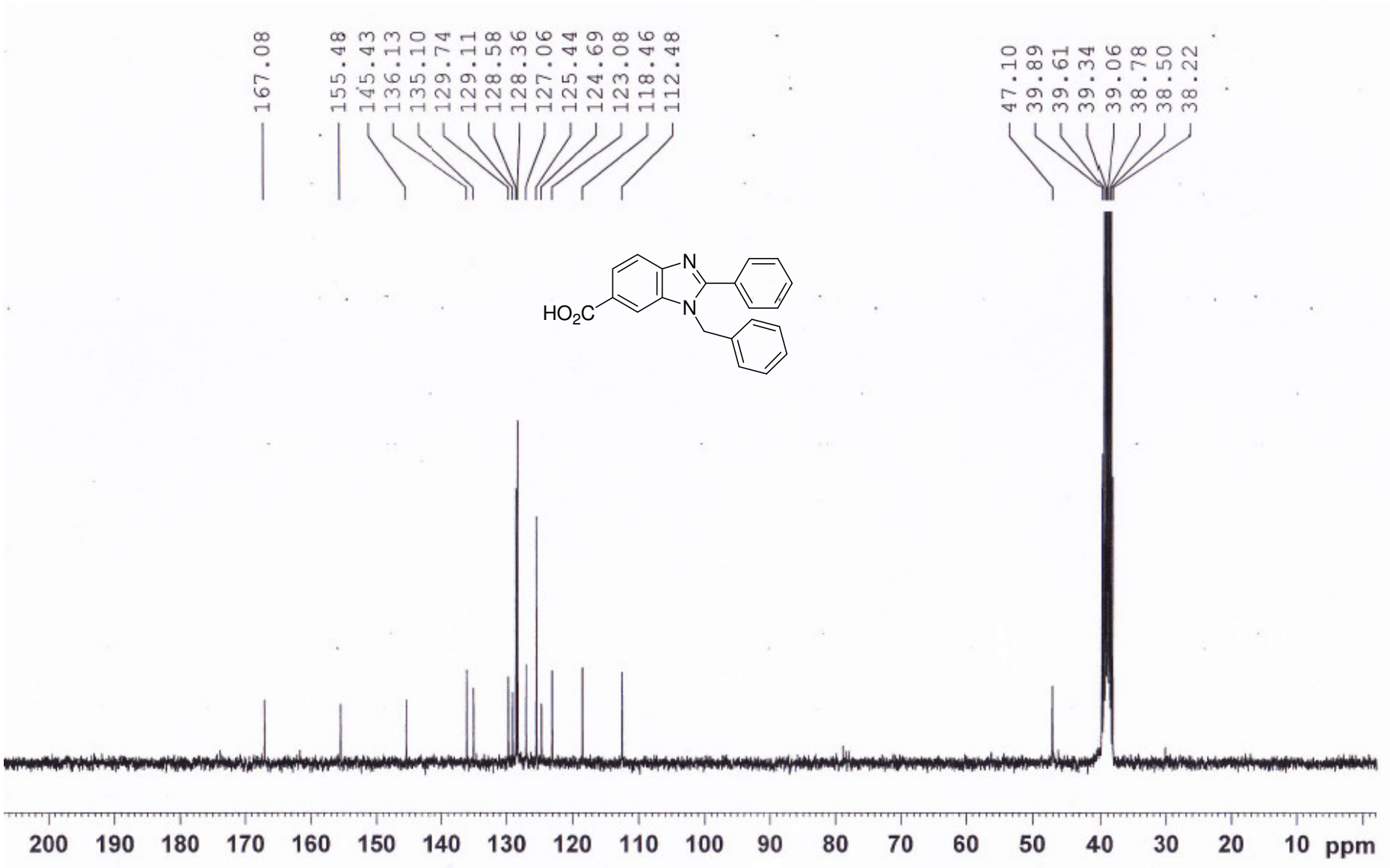
^{13}C NMR spectra of **3c** (75 MHz, DMSO-d_6)



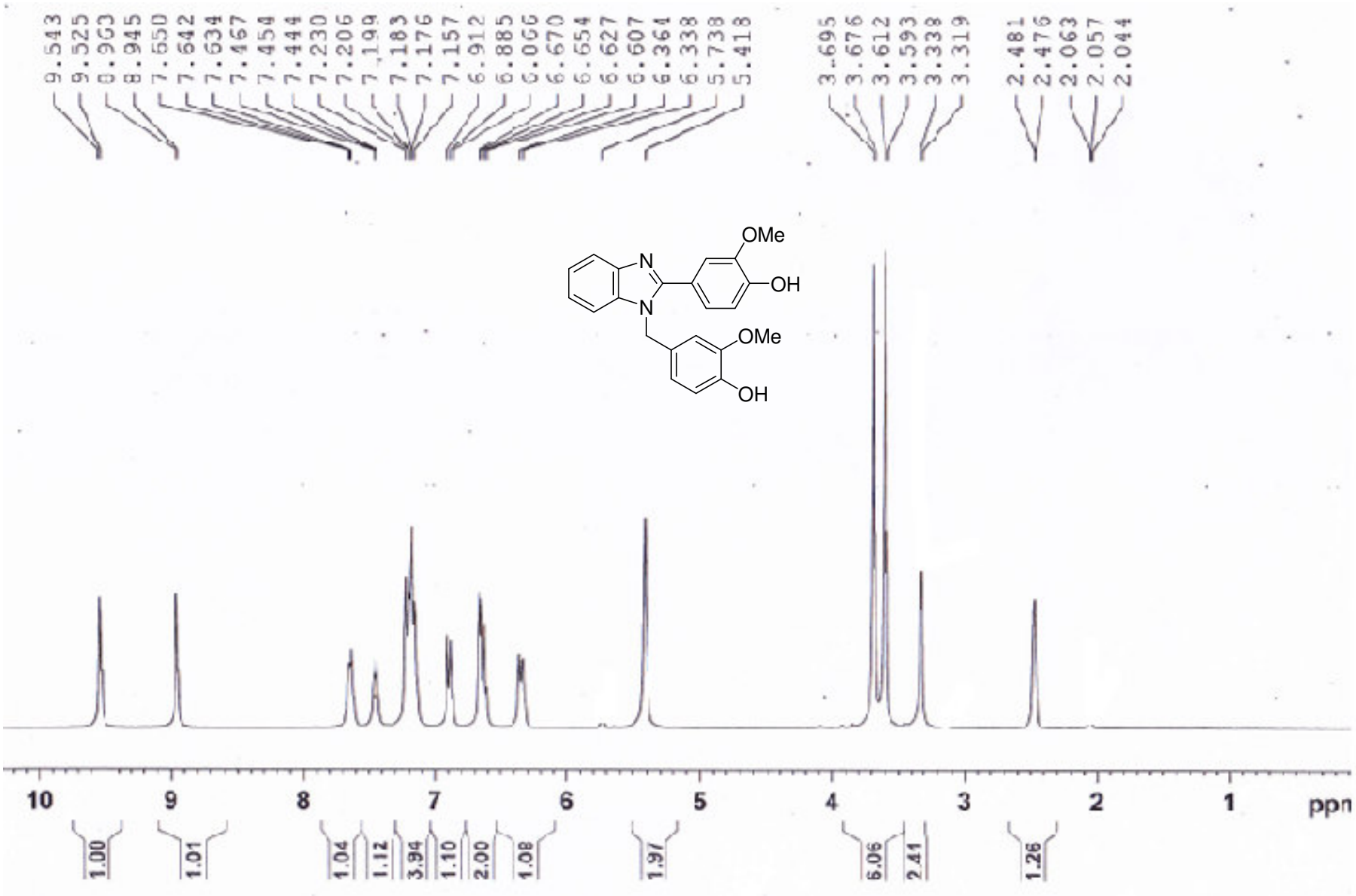
^{1}H NMR spectra of **3f** (300 MHz, DMSO-d_6



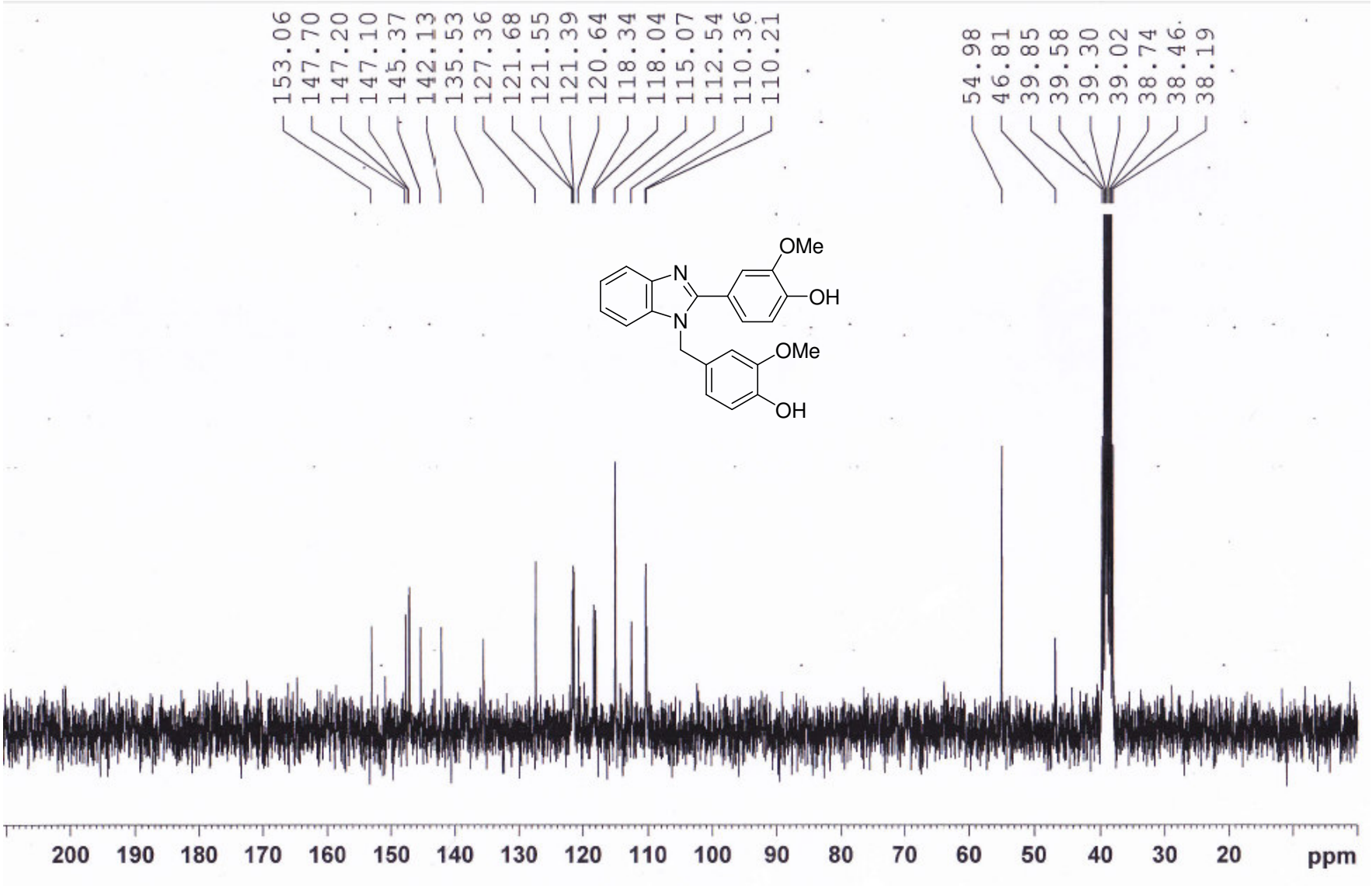
^{13}C NMR spectra of **3f** (75 MHz, DMSO-d_6)



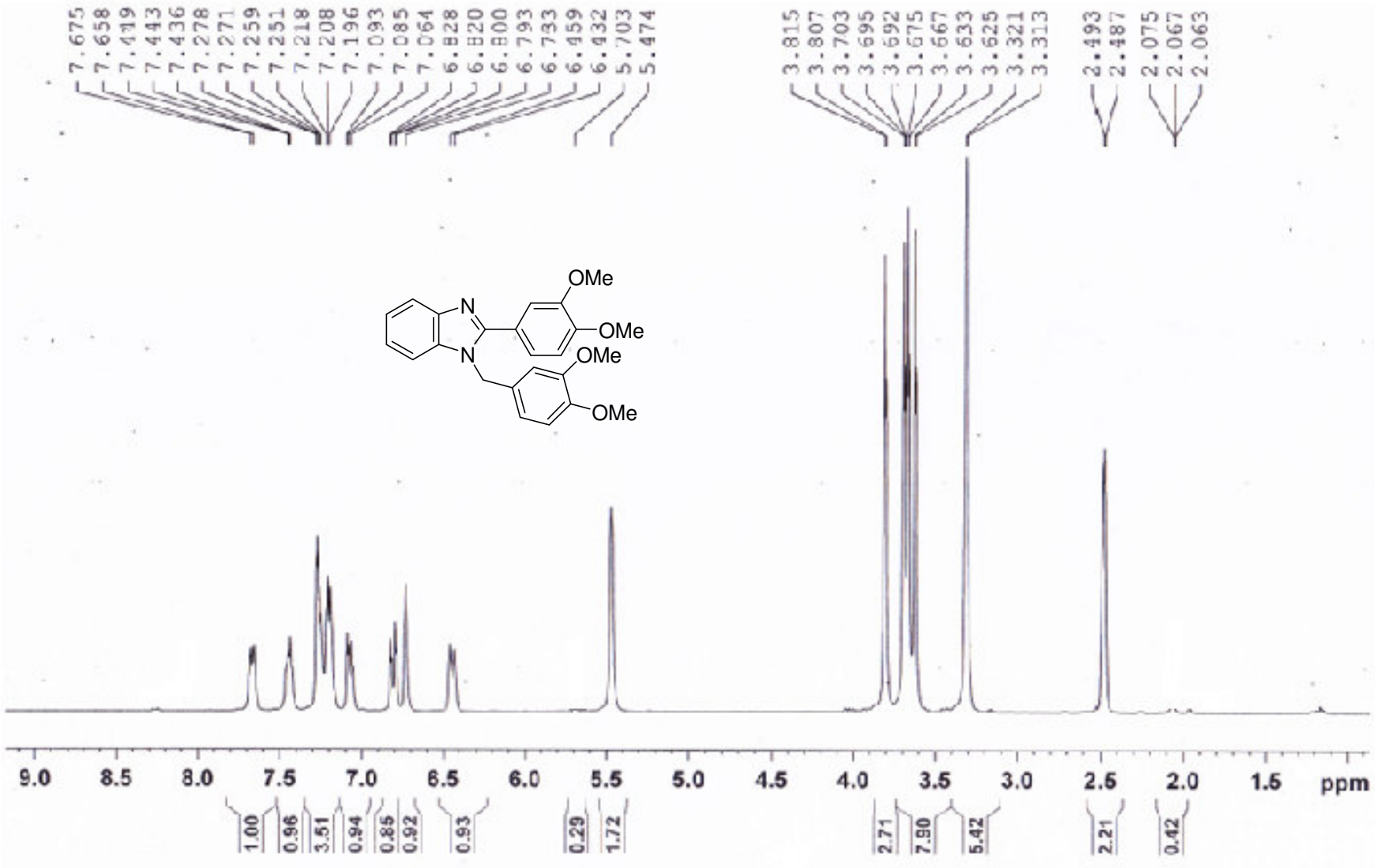
^{1}H NMR spectra of **3g** (300 MHz, DMSO-d_6)



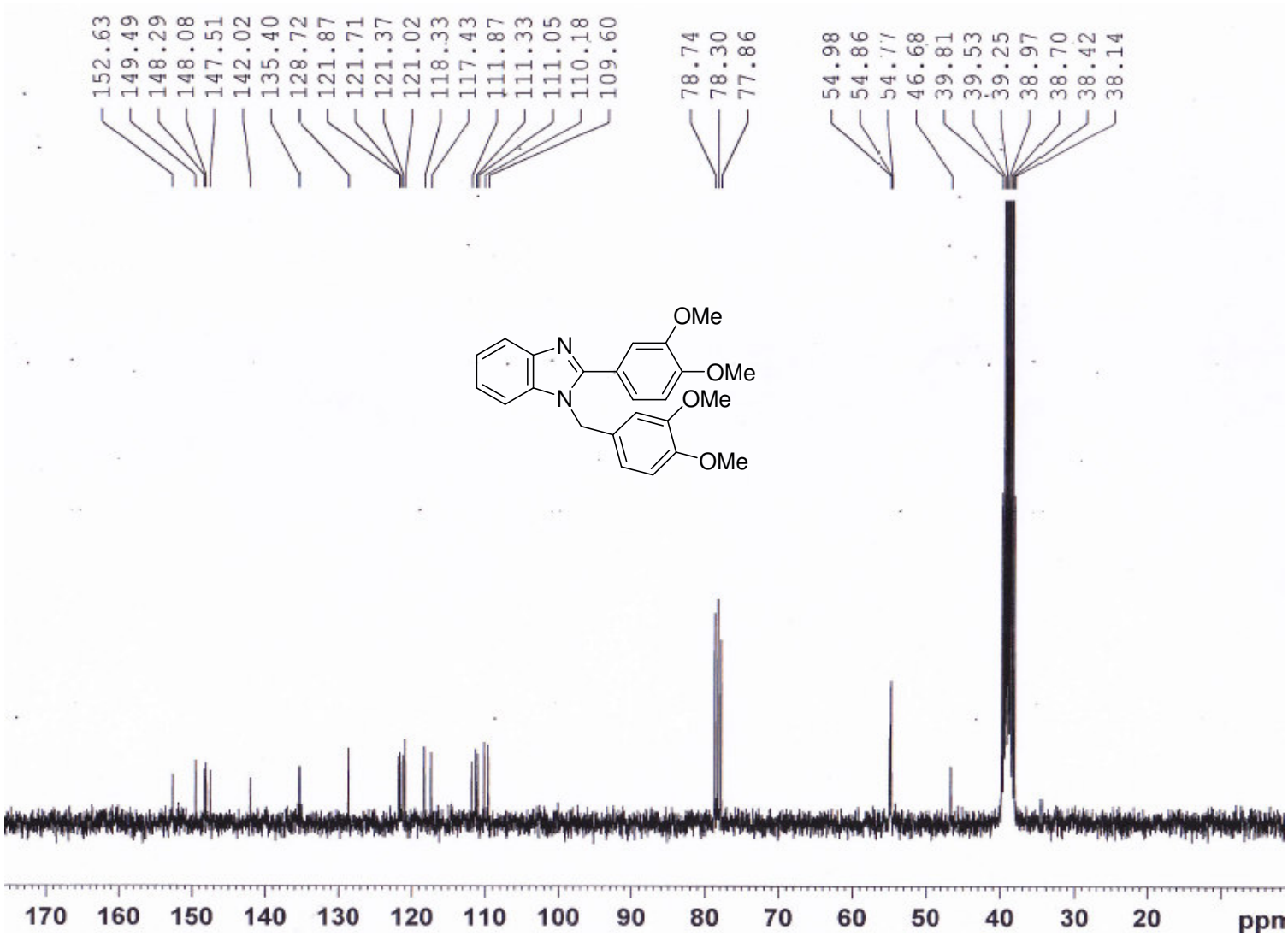
^{13}C NMR spectra of **3g** (75 MHz, DMSO-d_6)



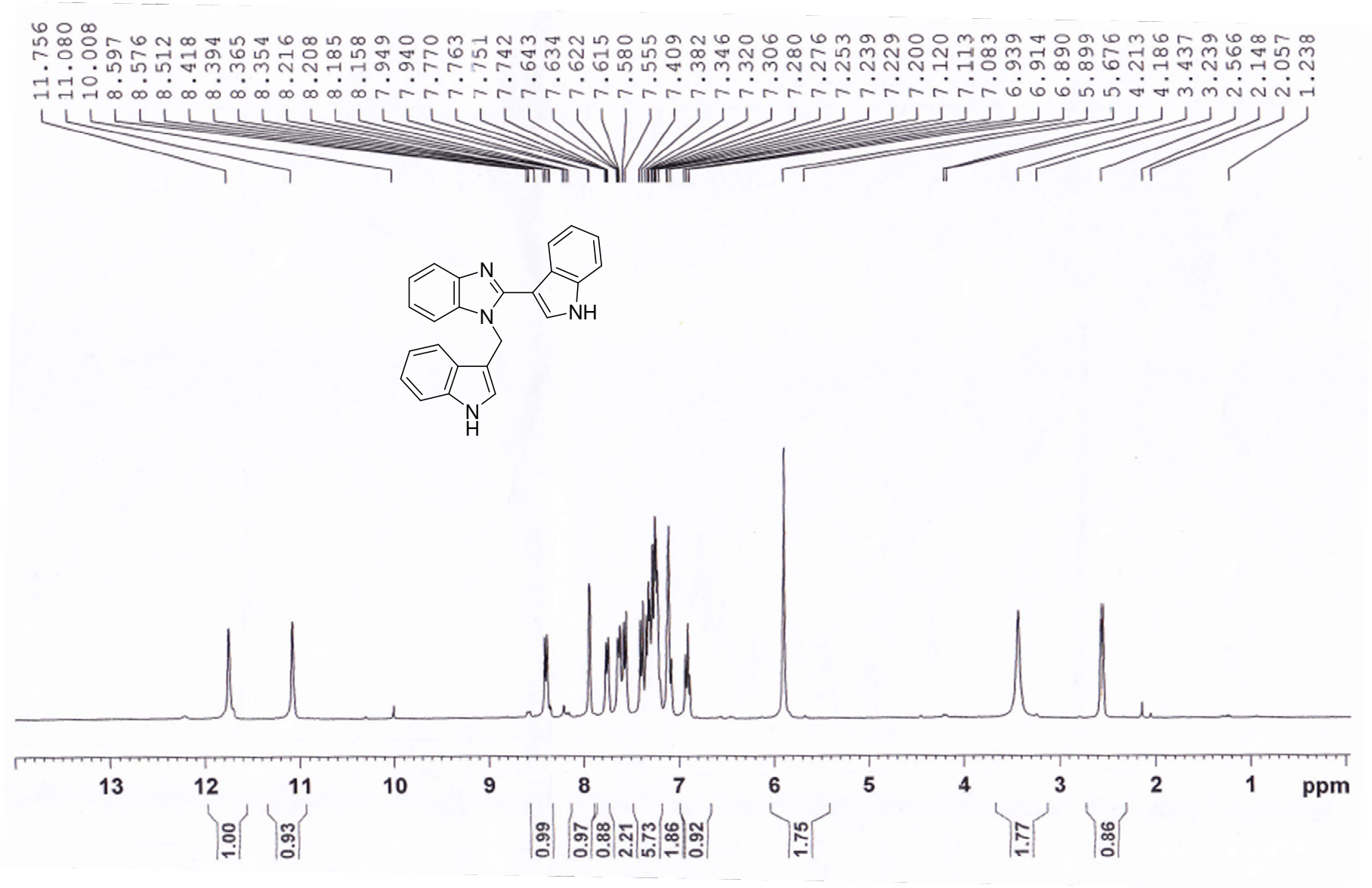
^{1}H NMR spectra of **3h** (300 MHz, DMSO-d_6)



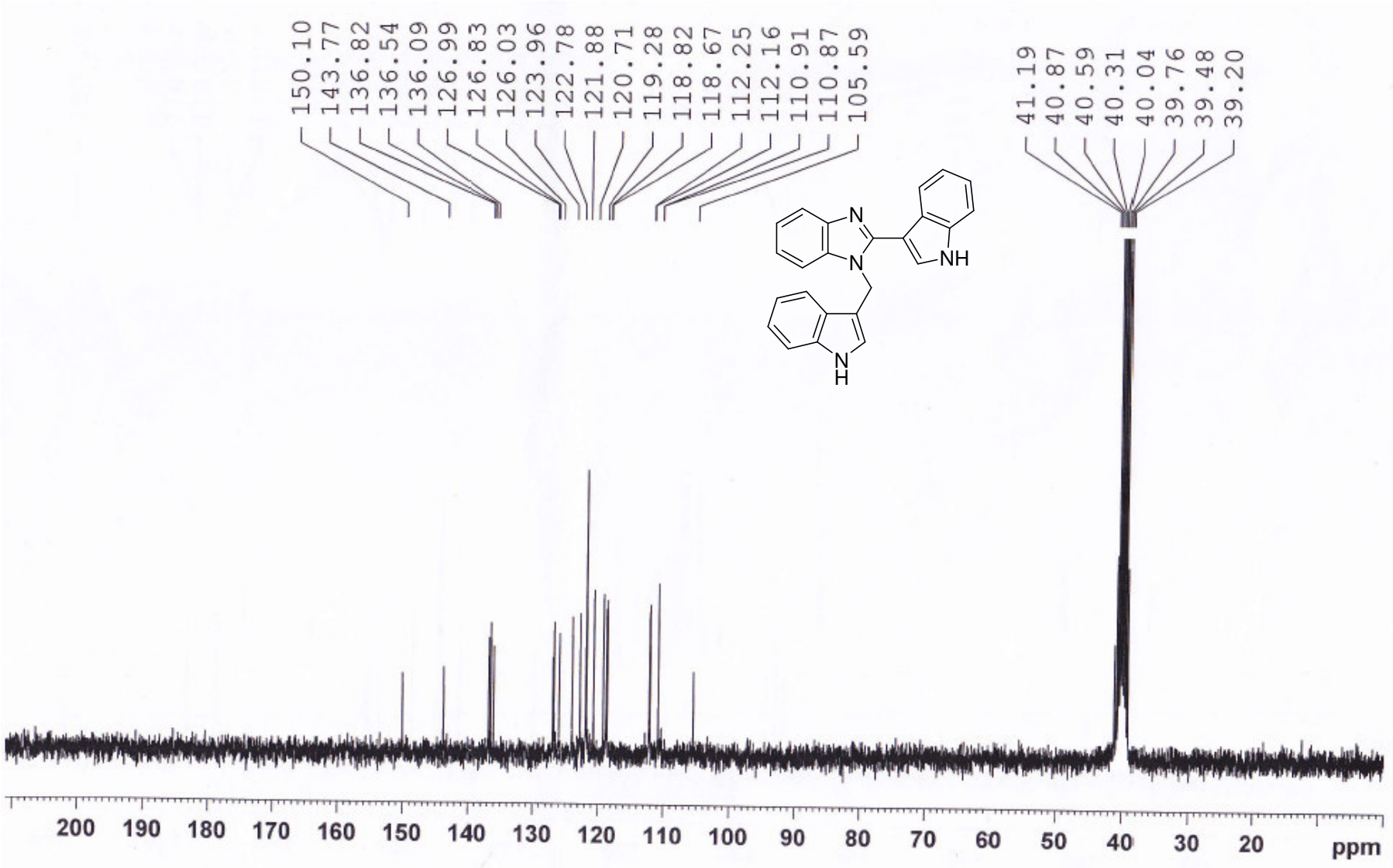
^{13}C NMR spectra of **3h** (75 MHz, DMSO-d_6)



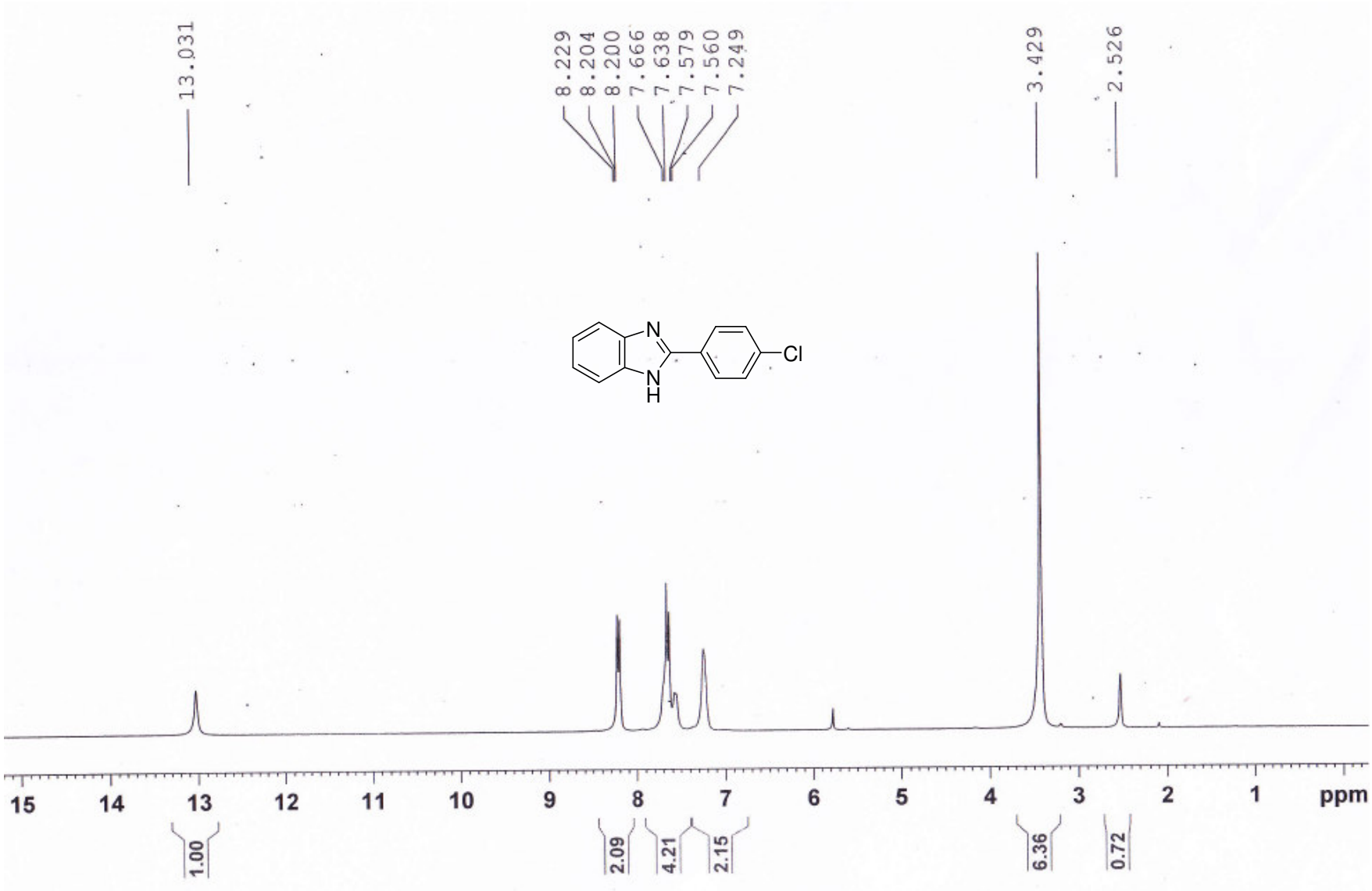
^{1}H NMR spectra of **3i** (300 MHz, DMSO-d_6)



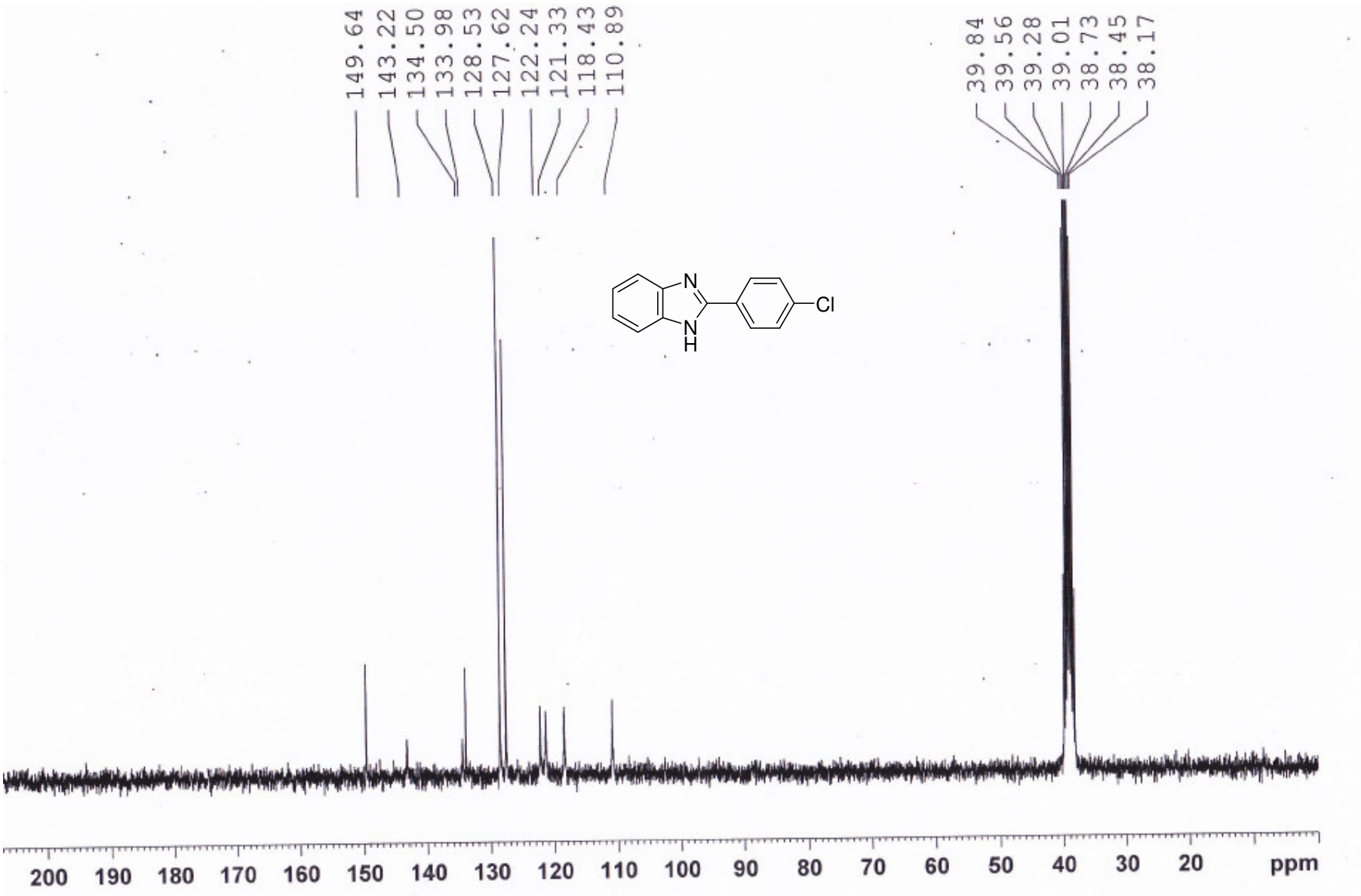
^{13}C NMR spectra of **3i** (75 MHz, DMSO-d_6)



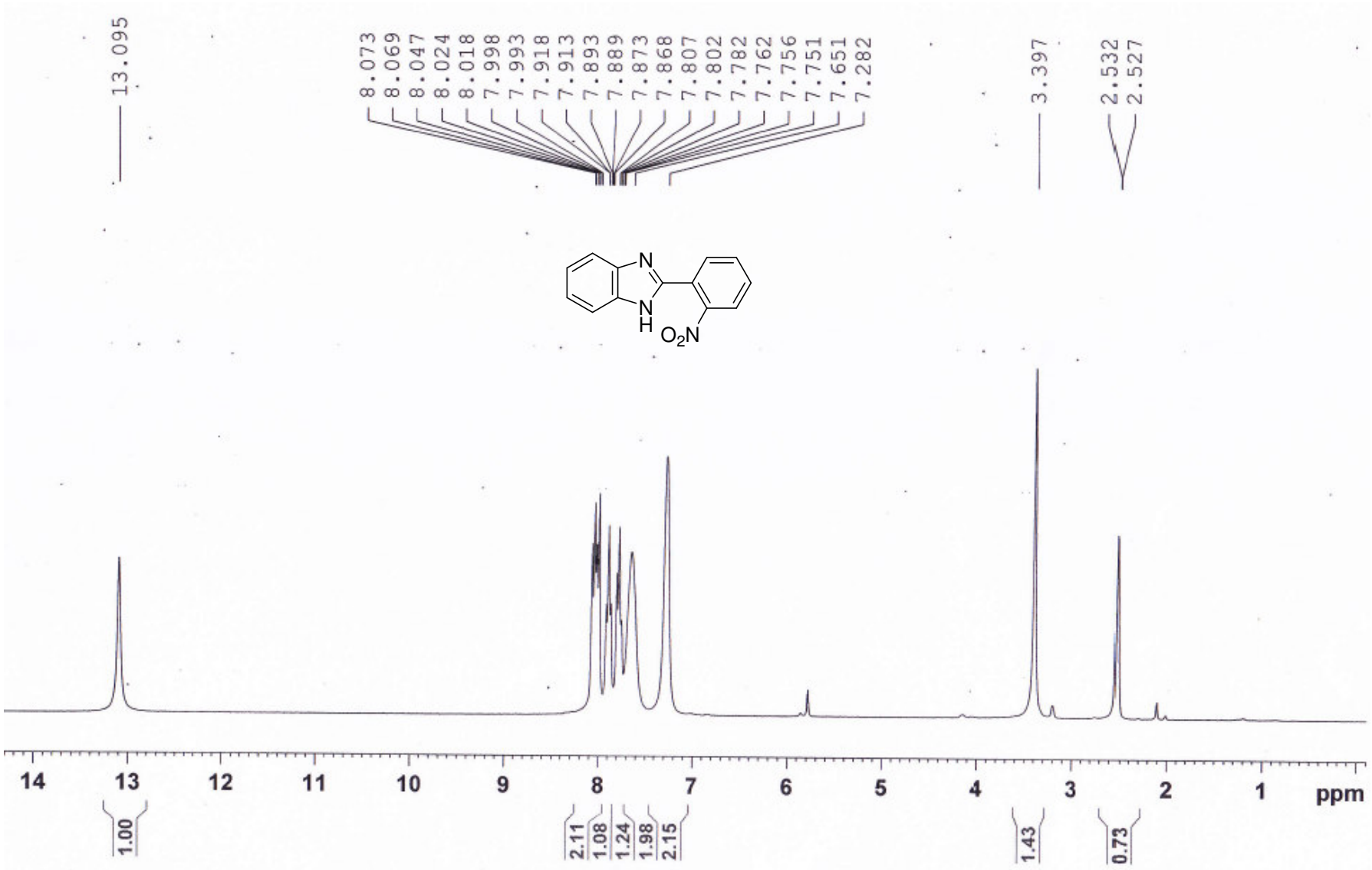
^{1}H NMR spectra of **4b** (300 MHz, DMSO-d_6)



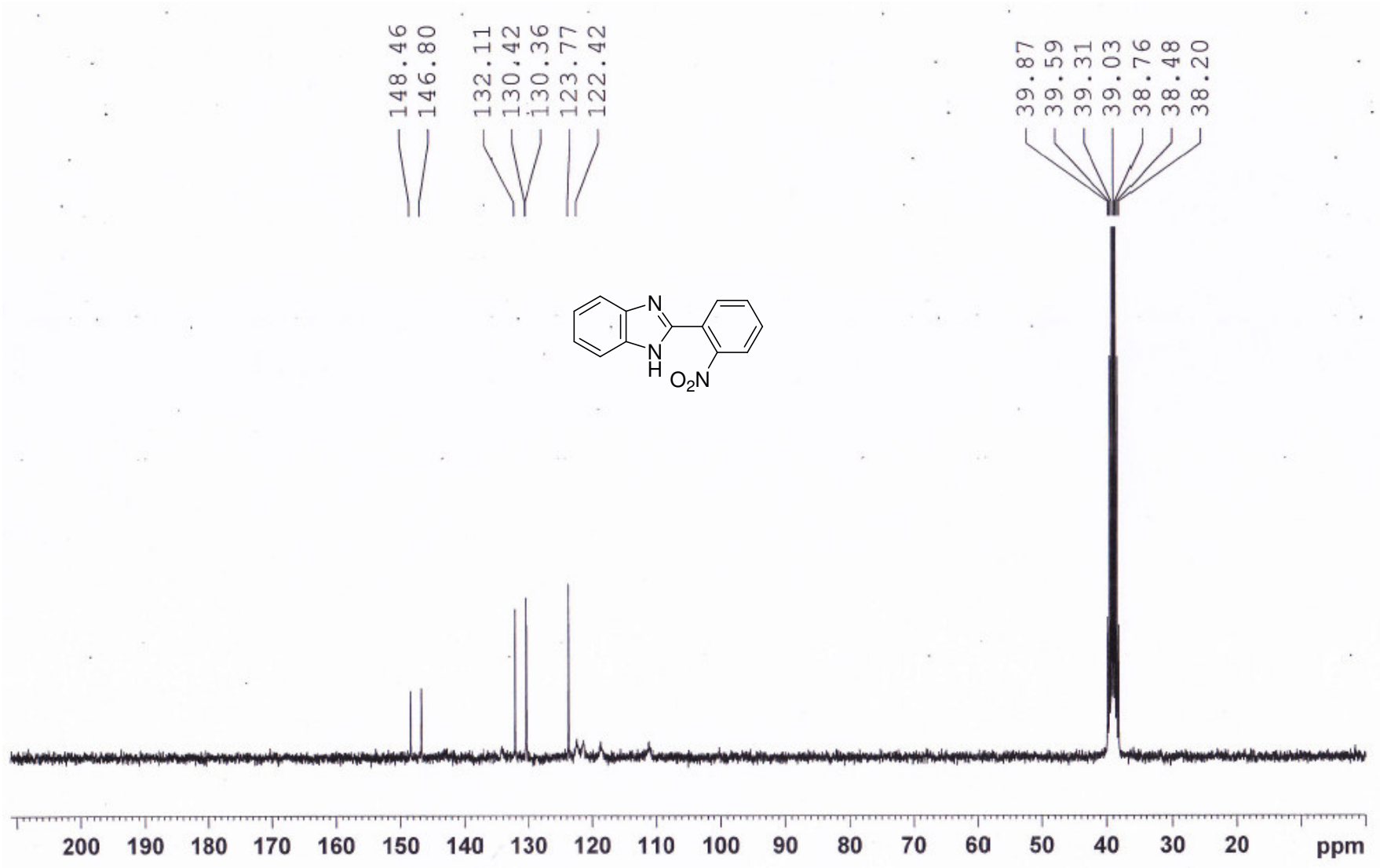
^{13}C NMR spectra of **4b** (75 MHz, DMSO-d_6)



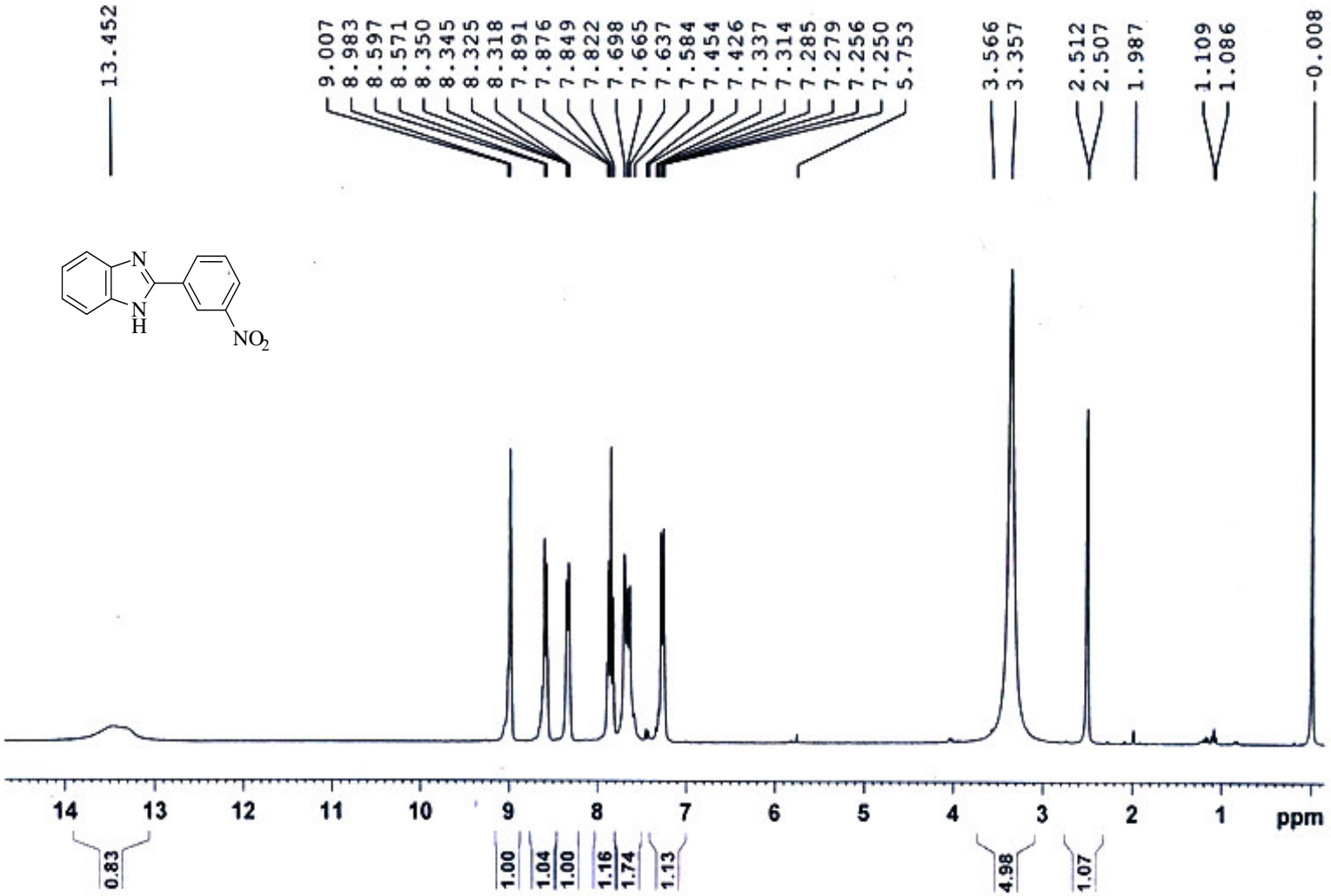
^{1}H NMR spectra of **4c** (300 MHz, DMSO-d_6)



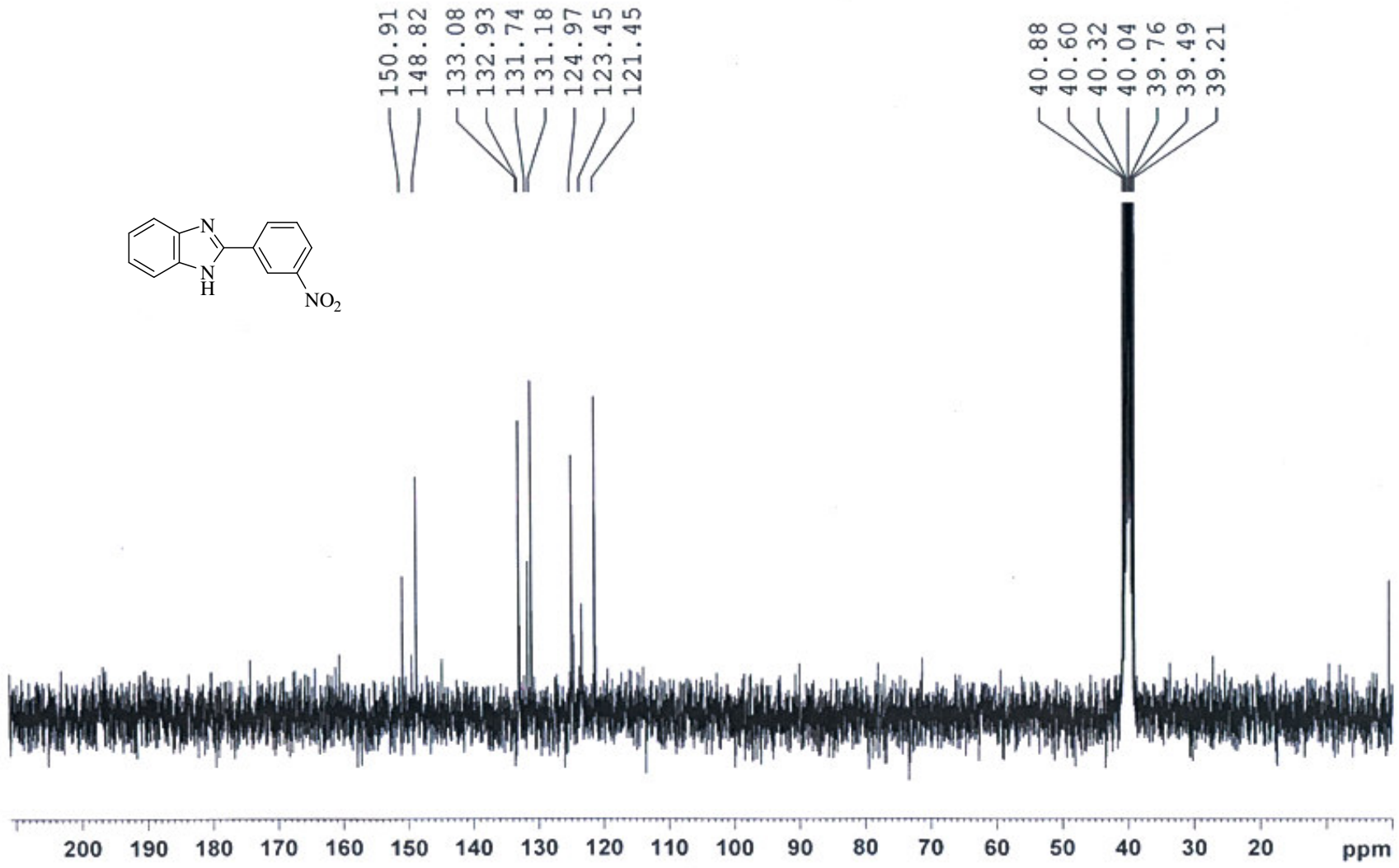
^{13}C NMR spectra of **4c** (75 MHz, DMSO-d_6)



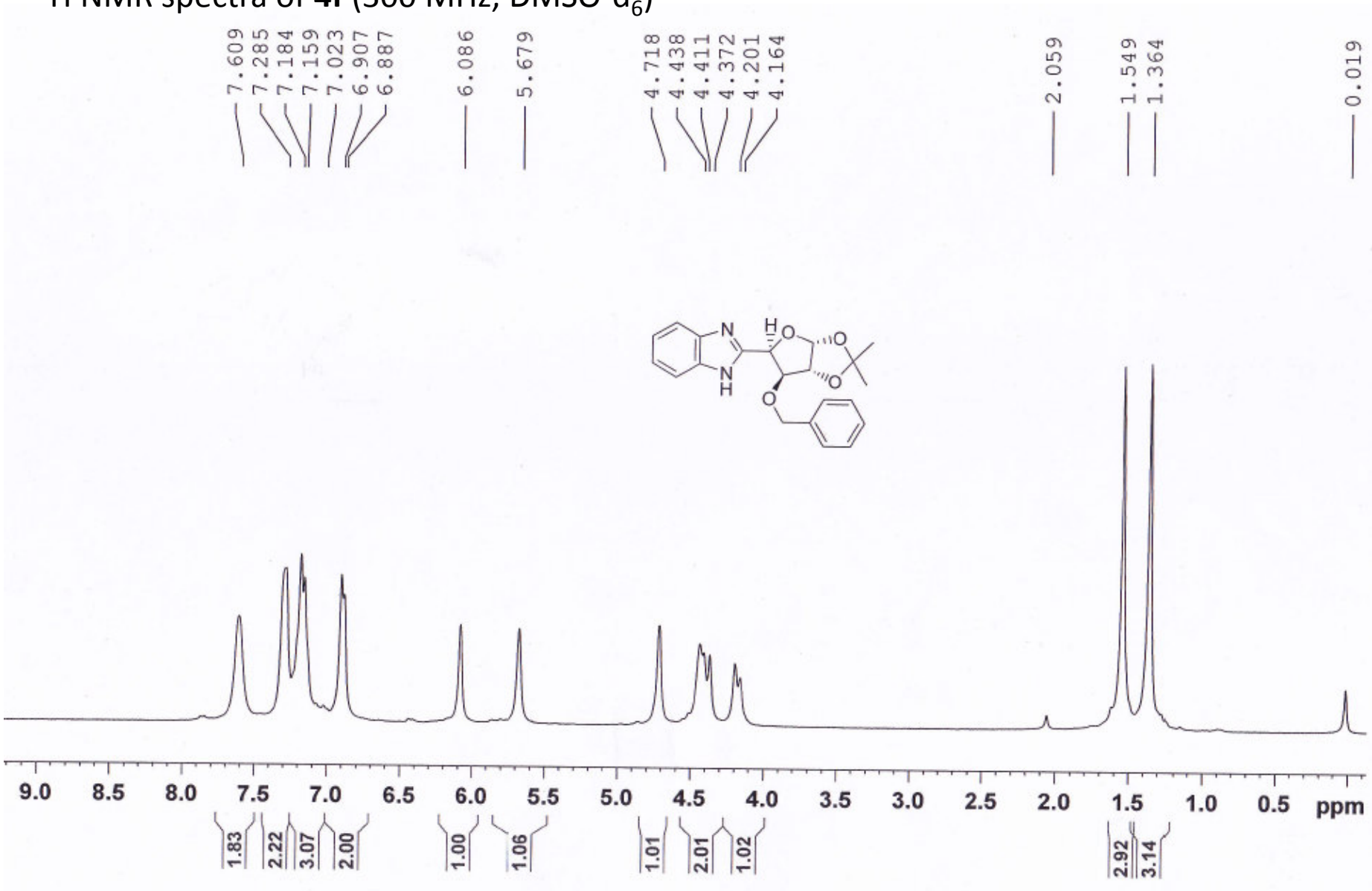
^{1}H NMR spectra of 4d (300MHz, DMSO-d_6)



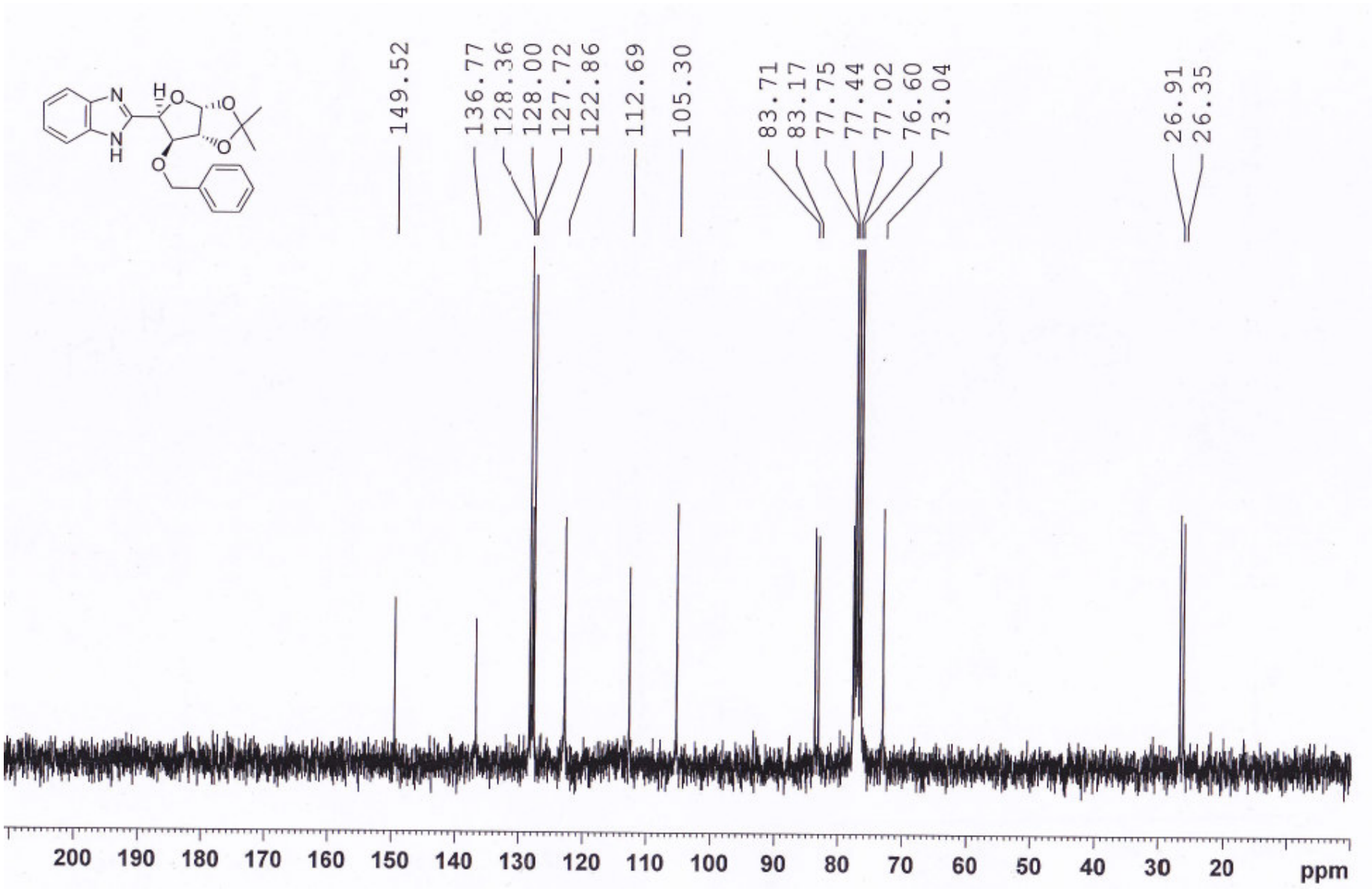
^{13}C NMR spectra of 4d (75 MHz, DMSO-d_6)



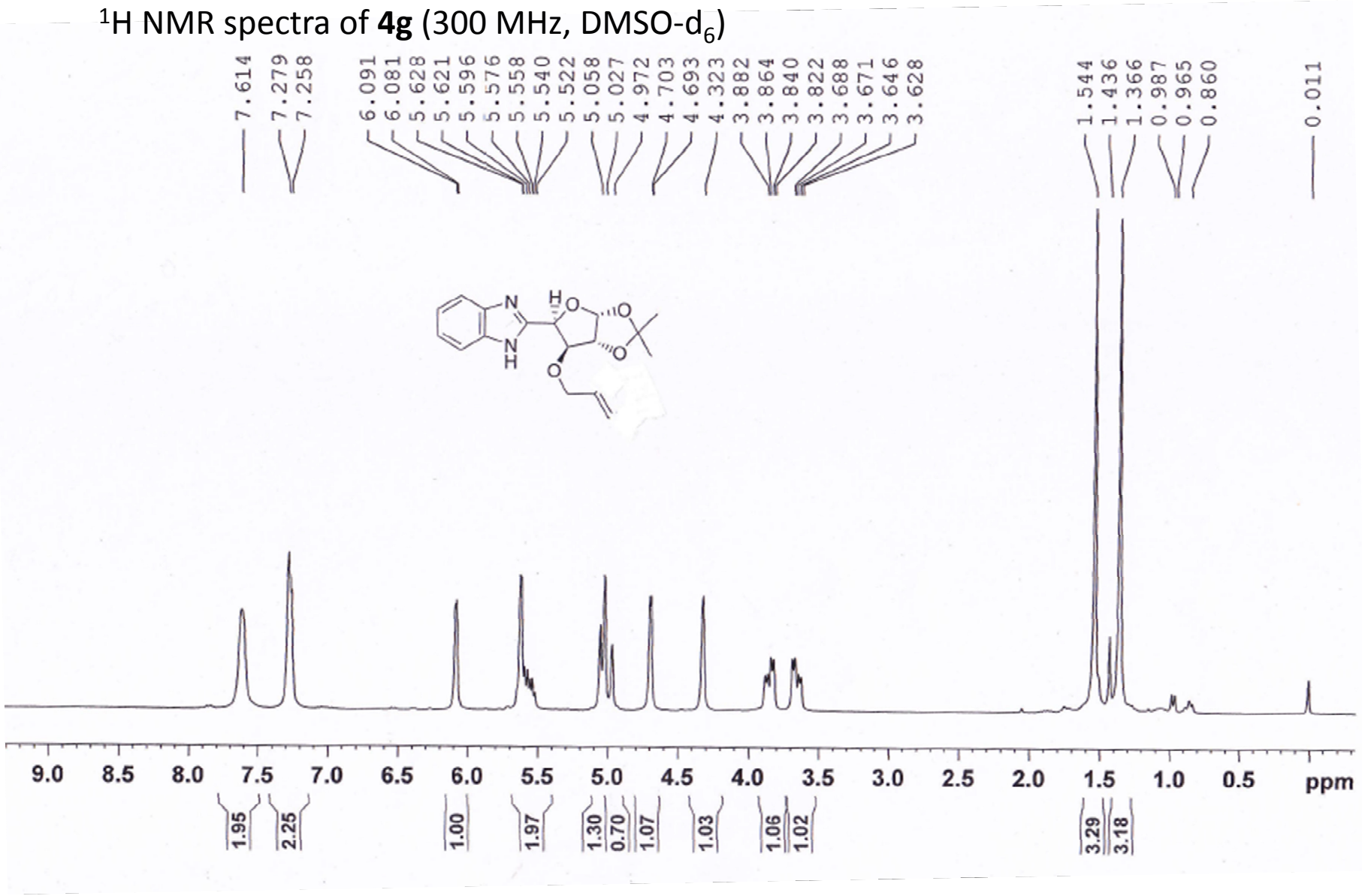
^{1}H NMR spectra of **4f** (300 MHz, DMSO-d_6)



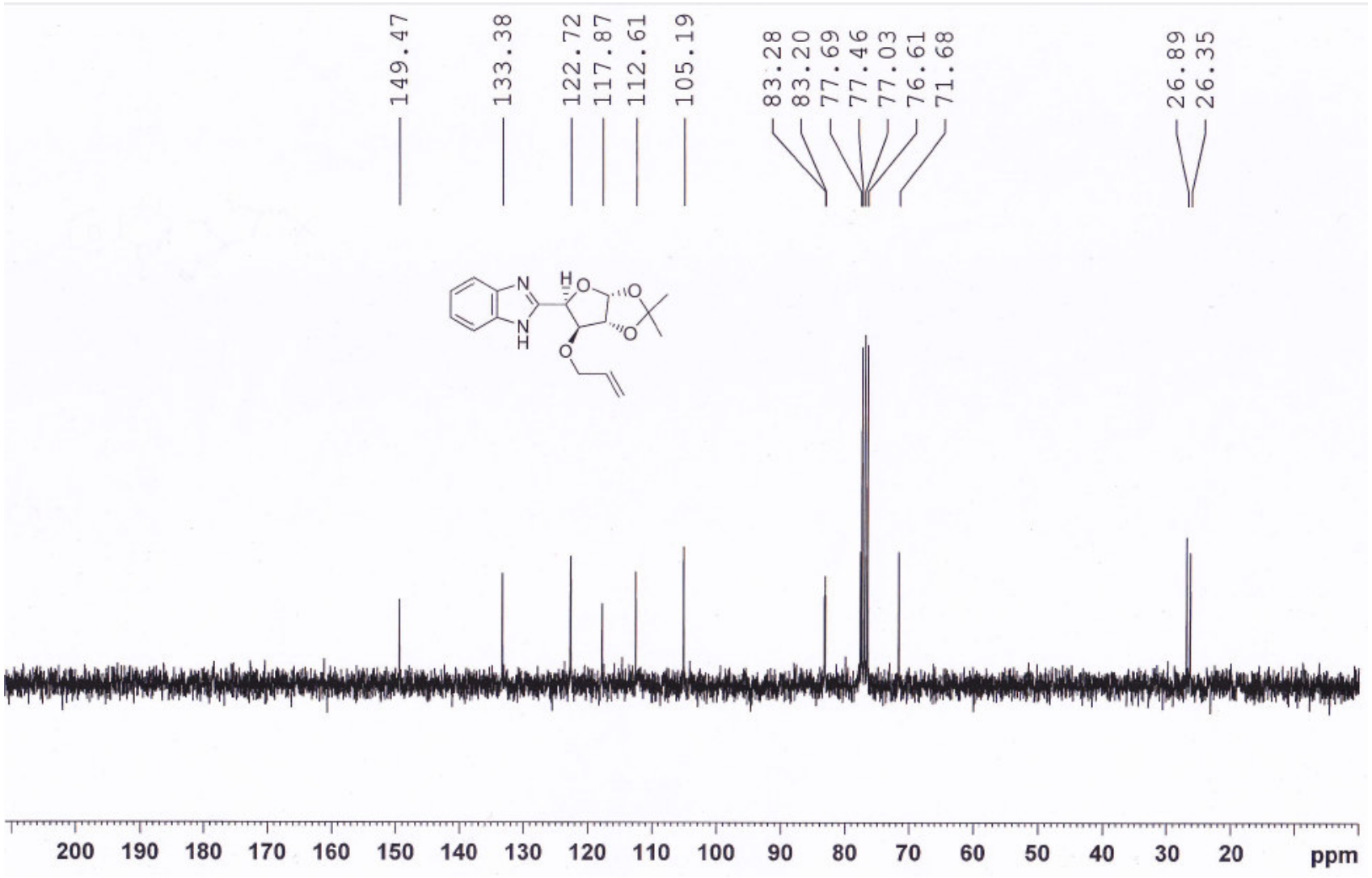
^{13}C NMR spectra of **4f** (75 MHz, DMSO-d_6)



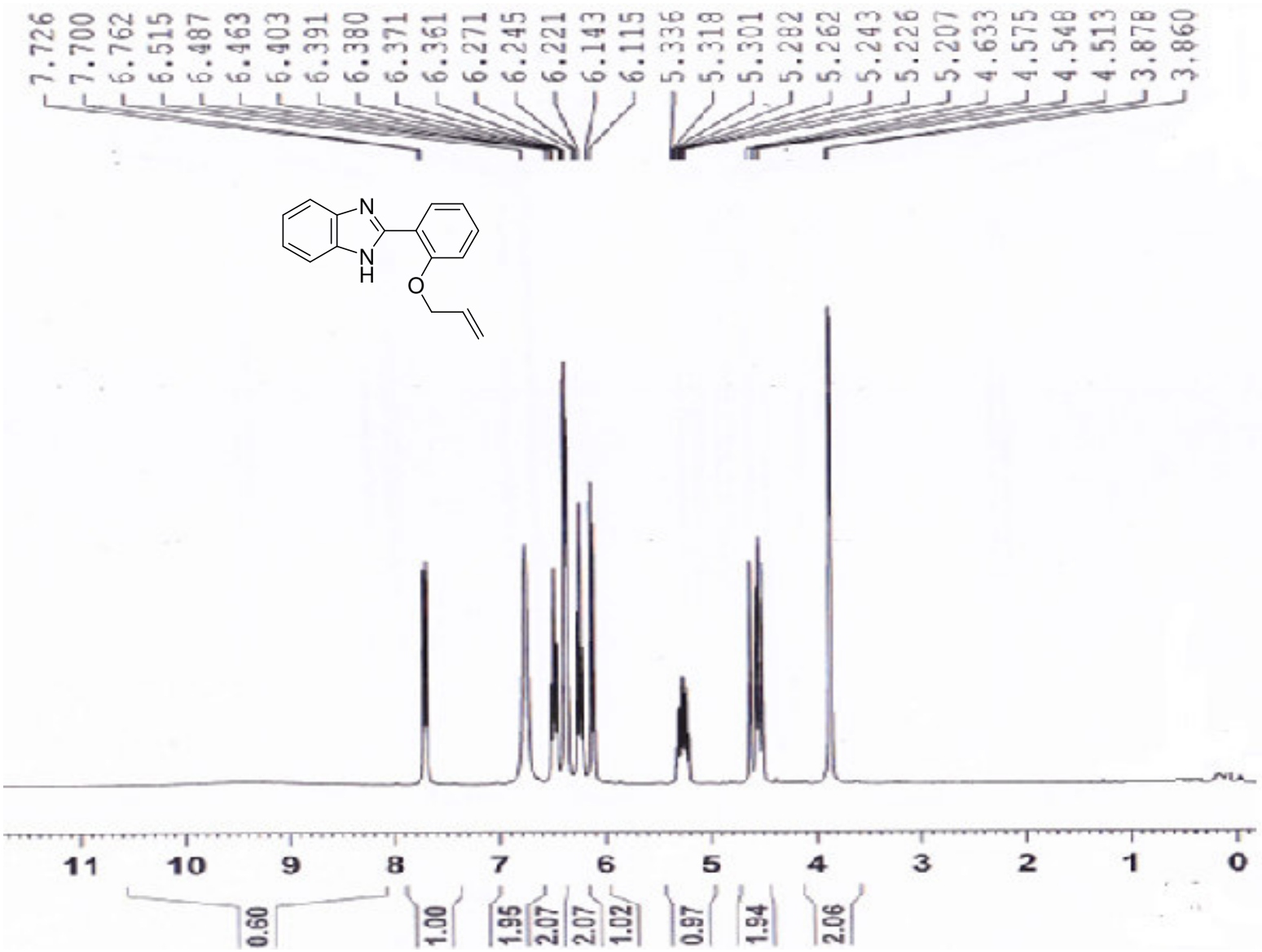
^{1}H NMR spectra of **4g** (300 MHz, DMSO-d_6)



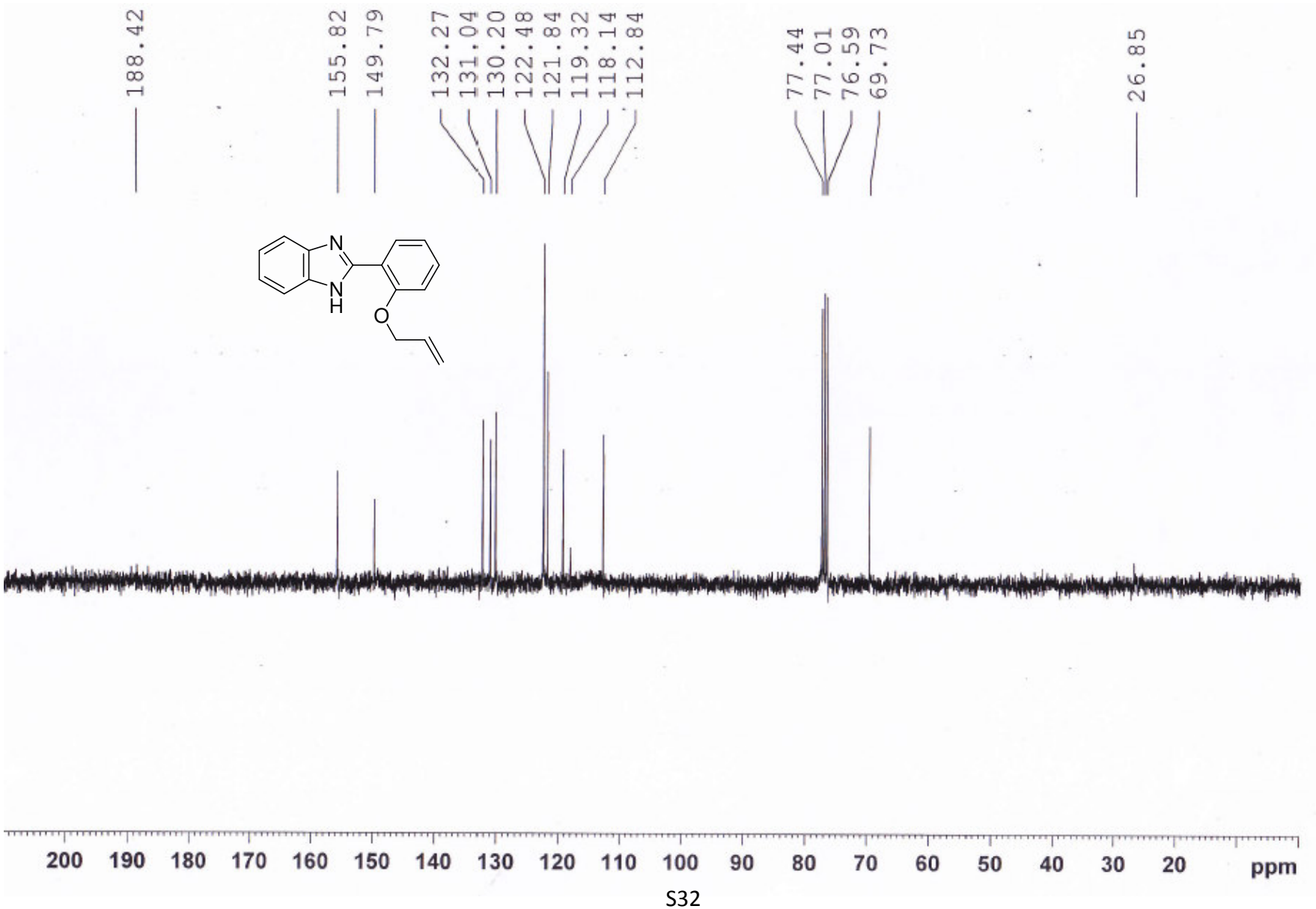
^{13}C NMR spectra of **4g** (75 MHz, DMSO-d_6)



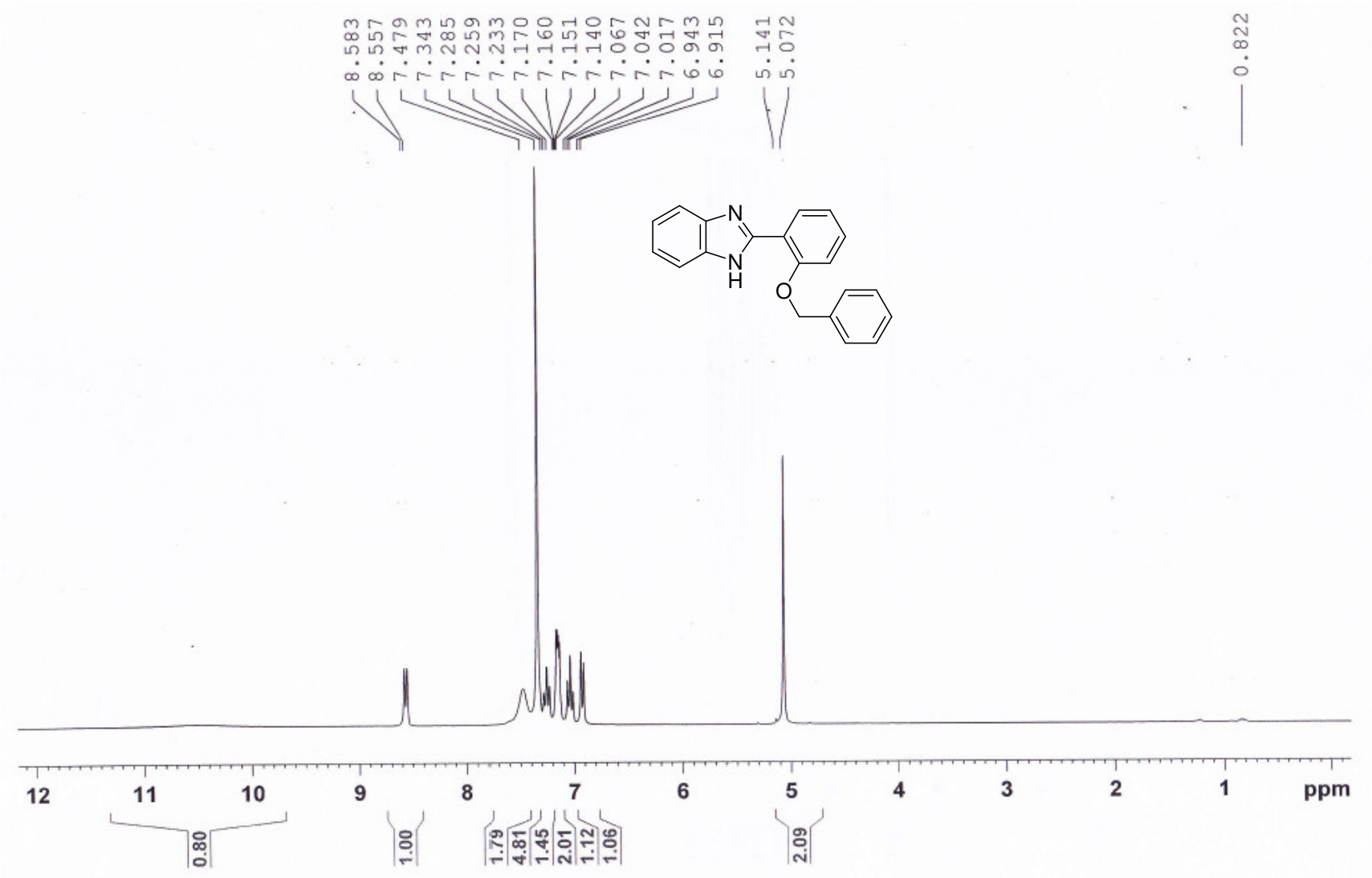
^{1}H NMR spectra of **4h** (300 MHz, DMSO-d_6)



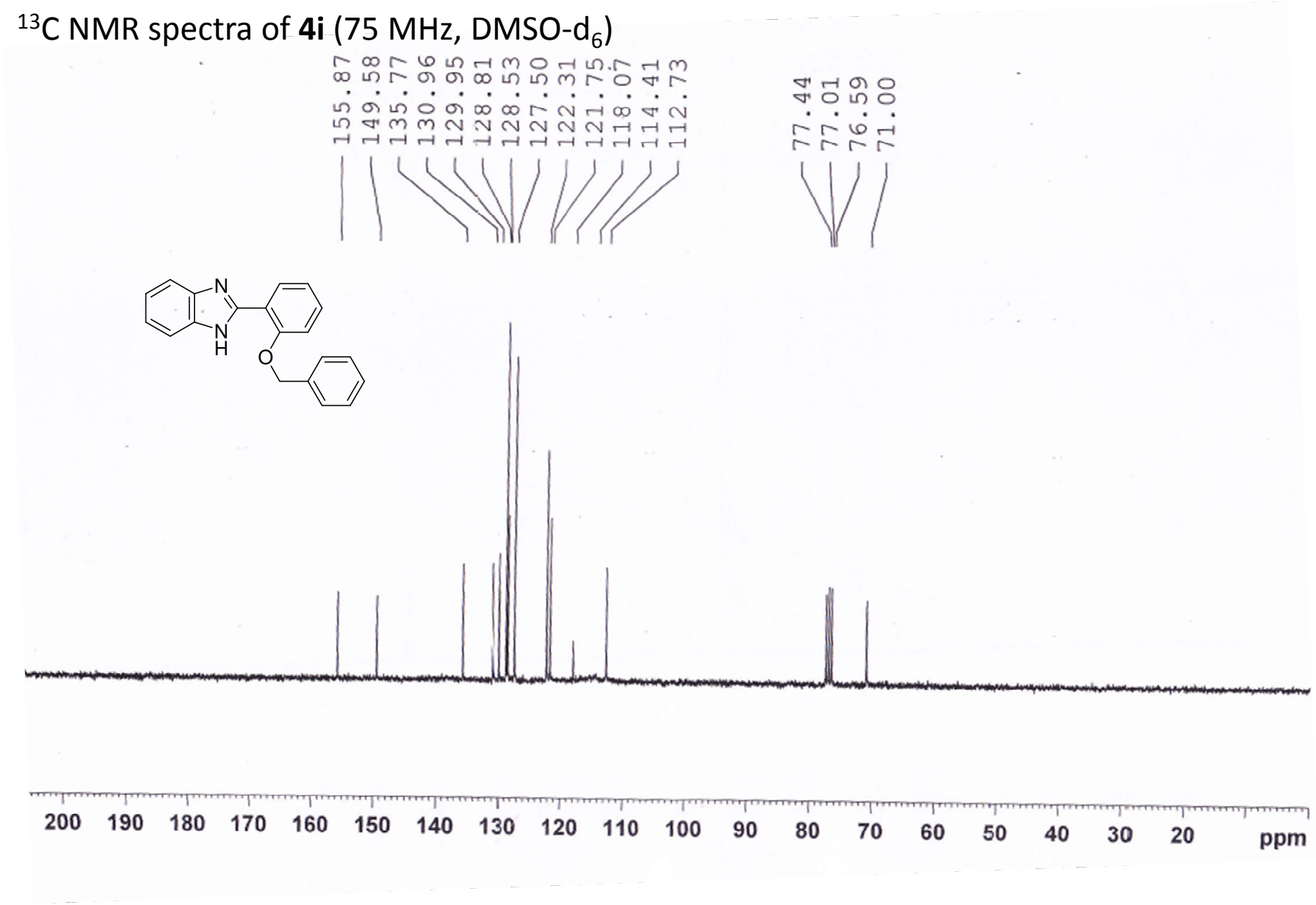
^{13}C NMR spectra of **4h** (75 MHz, DMSO-d_6)



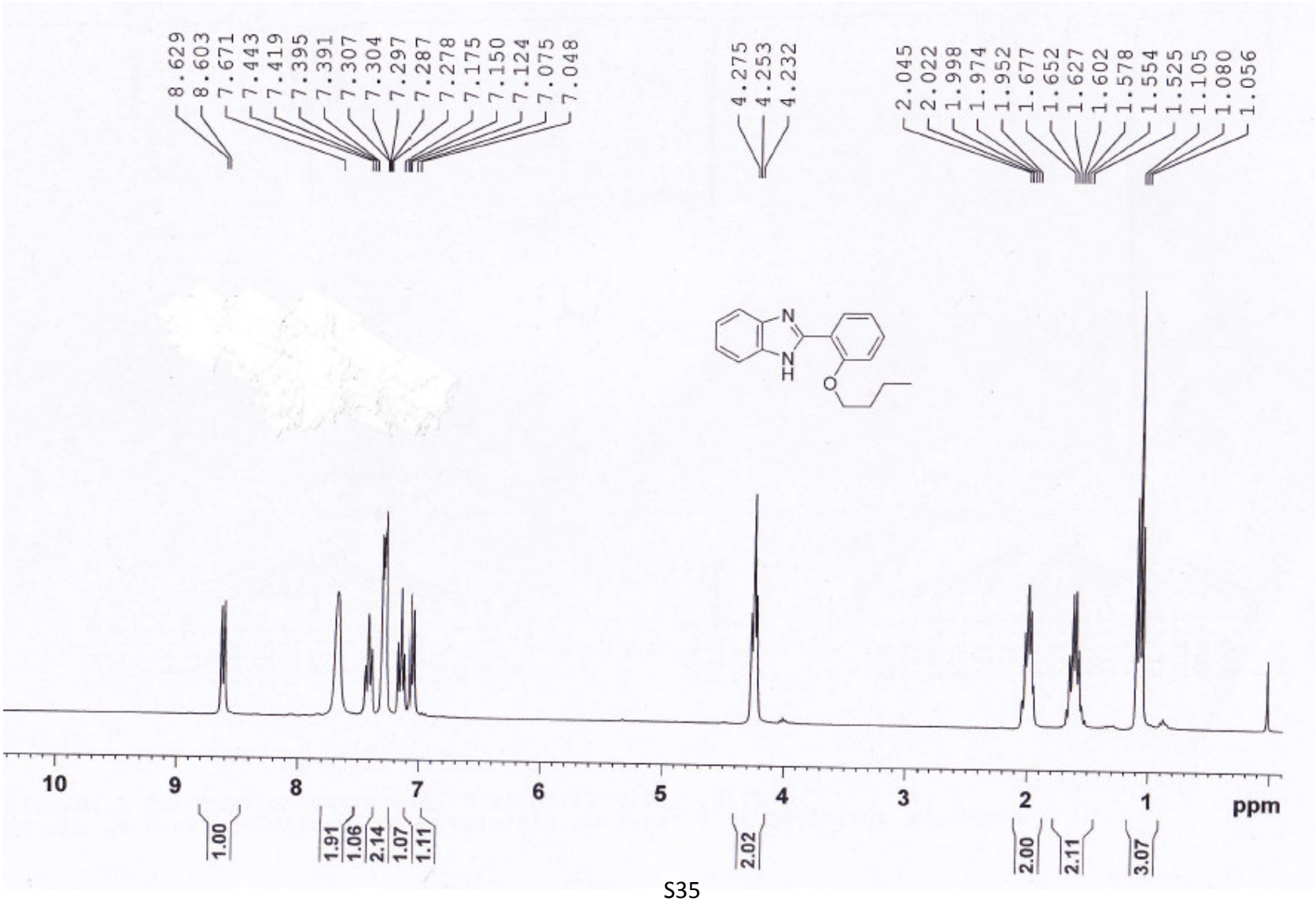
^{1}H NMR spectra of **4i** (300 MHz, DMSO-d_6)



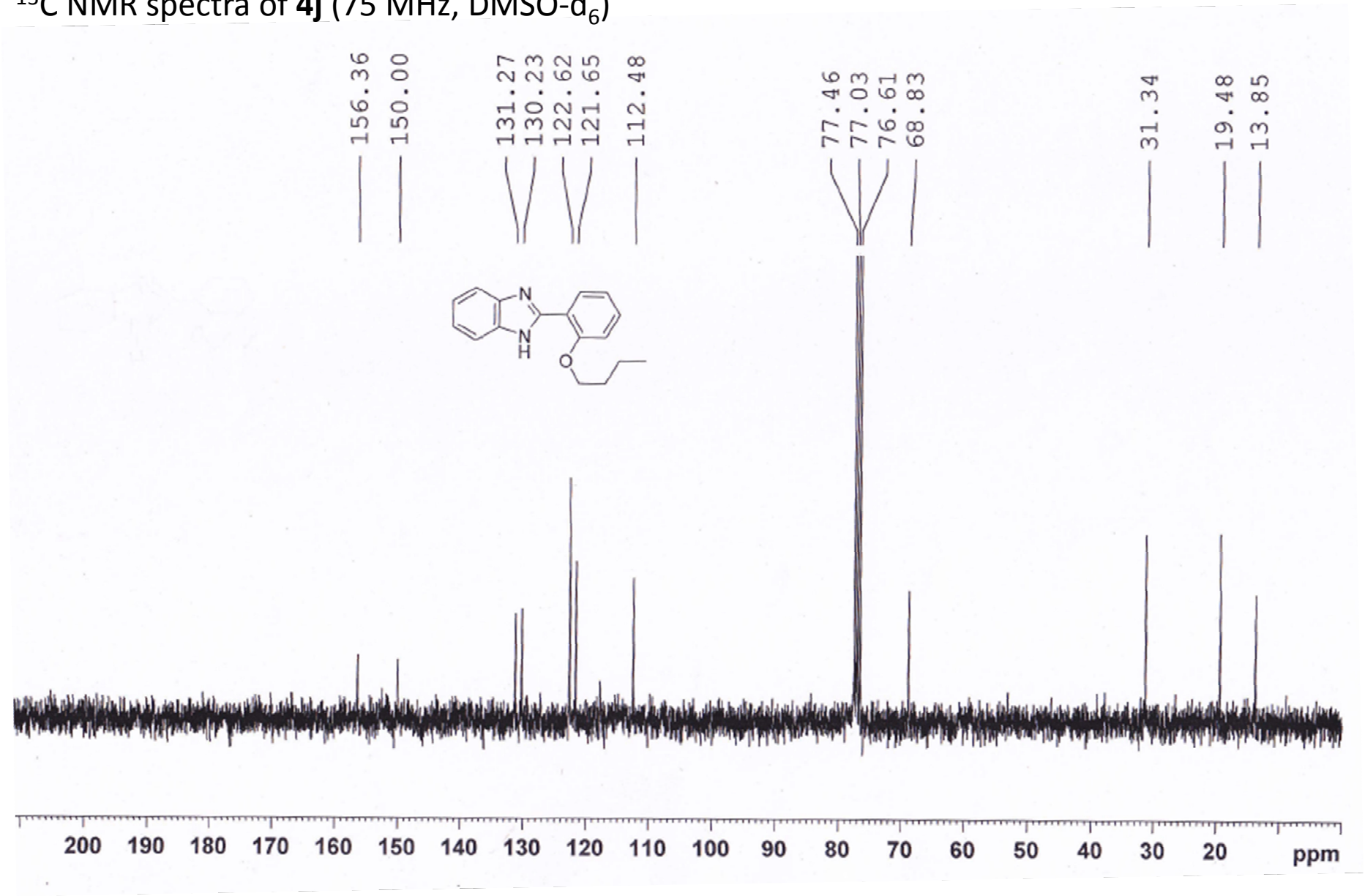
^{13}C NMR spectra of **4i** (75 MHz, DMSO-d_6)



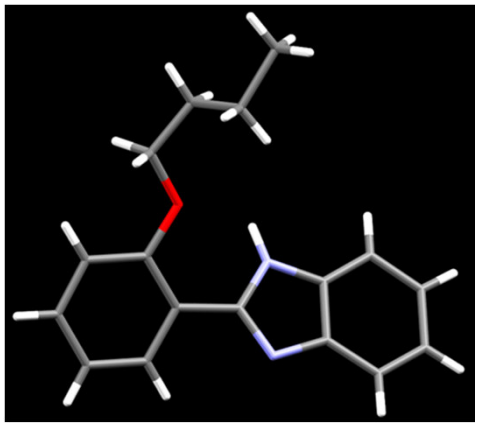
^{1}H NMR spectra of **4j** (300 MHz, DMSO-d_6)



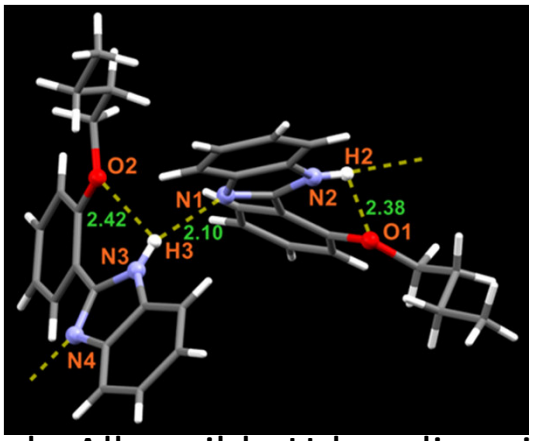
^{13}C NMR spectra of **4j** (75 MHz, DMSO-d_6)



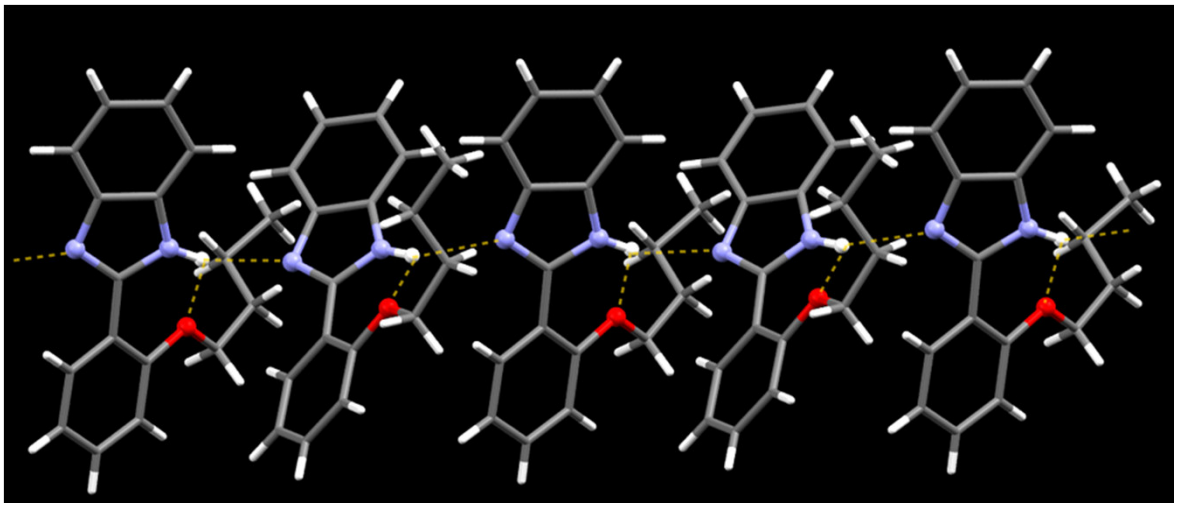
Crystal structure of 4j:



a. Single crystal structure of **4j**



b. All posible H-bonding site and their distance in **4j**



c. H-bonding network in **4j**

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