

Supporting Information

Facile and direct halogenation of 1,2,3-triazoles promoted by KX-Oxone system under transition metal free conditions

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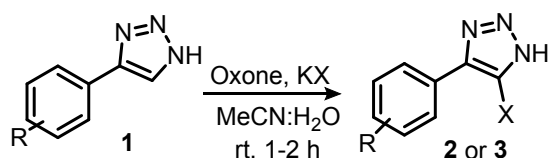
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Material and Methods General Information:

All reactions were carried out in oven-dried glassware, all compounds were fully characterized by spectroscopic data. The NMR spectra were recorded on JEOL -400 spectrometers, (^1H : 400 MHz, ^{13}C : 100 MHz), and were referenced to the residual peaks of CDCl_3 at 7.26 ppm, DMSO-d_6 at 2.5 ppm (^1H NMR), CDCl_3 at 77.23 ppm (^{13}C NMR) and DMSO-d_6 at 38.89 - 40.14 (septate, ^{13}C NMR) Chemical shifts (δ) are expressed in ppm, and J values are given in Hz. Data are reported as follows: Chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, db = doublet broad, m = multiplet), coupling constant (Hz), and integration. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF254. The melting points (m.p.) were determined on digital melting point apparatus and are uncorrected. Mass measurement was performed on Agilent QTOF mass spectrometer with electron spray ionization (ESI) as the ion source. Column chromatography was carried out using commercially available silica gel (230-400 mesh) under pressure. Materials Unless otherwise indicated, all reagents were obtained from commercial suppliers used without further purification. PE refers to Petroleum ether (b.p. 60-90 °C) and EA refers to ethyl acetate, and all reaction solvents were freshly distilled prior to use.

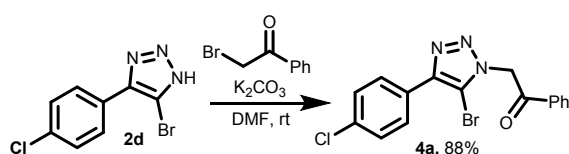
All the 1,2,3 *NH* triazole starting materials were synthesized using the procedure given in literature¹.

General Procedure for Halogenation of triazoles



To a 25 ml reaction flask, was added NH-1,2,3 triazole **1** (100 mg, 1 equiv. 0.689 mmol), oxone (1.1 equiv., 0.758 mmol), KX (1.1 equiv., 0.758mmol) followed by MeCN:H₂O (1:1, 2 ml). The mixture was stirred at room temperature for 1-2 hours. The progress of reaction was monitored by TLC. After the completion of reaction, the mixture was quenched with water, extracted with ethyl acetate. The combined organic layers were dried over sodium sulphate, concentrated under reduced pressure and purified by column chromatography to afford product **2** or **3**

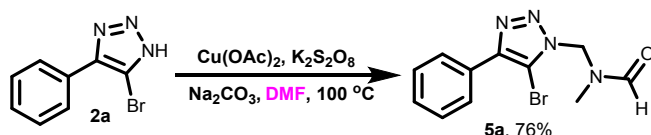
Reaction of 2d with Phenacyl bromide



A mixture of **2a** (100 mg, 0.389 mmol), phenacyl bromide (77 mg, 0.389mol), and K_2CO_3 (1 equiv.) in DMF (5 mL) was stirred at room temperature for 4 hours. The progress of reaction was monitored by TLC. After the completion of reaction, the resultant mixture was cooled to room temperature, poured into ice cold water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 , concentrated under reduced pressure and purified by column chromatography to obtain the desired product as white solid.

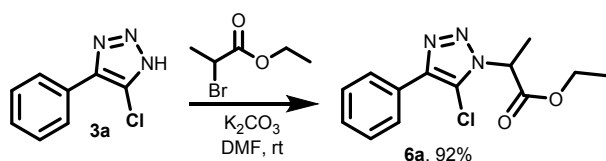
Reaction of 2a with Dimethyl formamide

A mixture of **2a** (100 mg, 0.44 mmol), copper acetate (79.9 mg, 0.08 mmol), $K_2S_2O_8$ (238 mg, 0.88 mmol) and Na_2CO_3 (51.2 mg, 0.48 mmol) in DMF (5 mL) was stirred at 100 °C for 6 hours. The progress of reaction was monitored by TLC. After the completion of reaction, the resultant mixture was cooled to room temperature, poured into ice cold water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 , concentrated under reduced pressure and purified by column chromatography to obtain the desired product as yellow solid.



Reaction of 3a with 2-bromo ethyl propionate

A mixture of **3a** (100 mg, 0.558 mmol), 2-bromo ethyl propionate (100 mg, 0.558 mmol), and K_2CO_3 (1 equiv.) in DMF (5 mL) was stirred at room temperature for 4 hours. The progress of reaction was monitored by TLC. After the completion of reaction, the resultant mixture was cooled to room temperature, poured into ice cold water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 , concentrated under reduced pressure and purified by column chromatography to obtain the desired product as colourless oil.



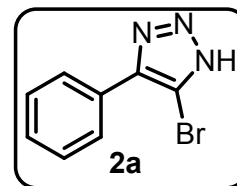
References:

1. (a) X. J. Quan, Z. H. Ren, Y. Y. Wang and Z. H. Guan, *Org. Lett.*, 2014, **16**, 5728; (b) R. Hui, M. Zhao, M. Chen, Z. Ren and Z. Guan, *Chin. J. Chem.* 2017, **XX**, 1. (c) L. Yang, Y. Wu, Y. Yang, C. Wen and J.P. Wan, *Beilstein J. Org. Chem.* 2018, **14**, 2348.

Spectroscopic Data

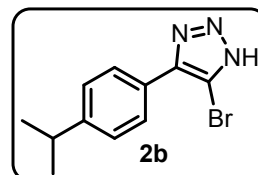
5-bromo-4-phenyl-1H-1,2,3-triazole (2a):

White solid; M.p. 140-142 °C; Yield – 96% (148 mg); R_f = 0.6 (20% in EtOAc/PE); $^1\text{H-NMR}$ (400 MHz, CDCl_3); δ = 7.42-7.52 (m, 3H), 7.91-7.95 (m, 2H), 12.14 (s, 1H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3); δ = 118.7, 126.9, 128.1, 128.8, 128.9, 131.9; MS (ESI): m/z calcd for $\text{C}_8\text{H}_6\text{BrN}_3$ 222.97, found 223.97 [M+H], 225.97 [M+H+2].



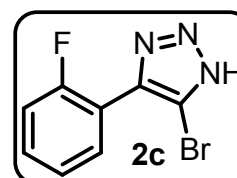
5-bromo-4-(4-isopropylphenyl)-1H-1,2,3-triazole (2b):

White solid; M.p. 106-108 °C; Yield – 91% (129 mg); R_f = 0.6 (20% in EtOAc/PE); $^1\text{H-NMR}$ (400 MHz, DMSO - d_6); δ = 1.14 (d, J = 6.80 Hz, 6H), 2.80-2.91 (m, 1H), 7.29 (d, J = 6.4 Hz, 2H), 7.72 (s, 2H); $^{13}\text{C-NMR}$ (100 MHz, DMSO - d_6); δ = 23.6, 33.2, 119.2, 126.4, 126.6, 126.9, 143.7, 149.1; MS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{12}\text{BrN}_3$ 265.02, found 266.03 [M+H], 268.02 [M+H+2].



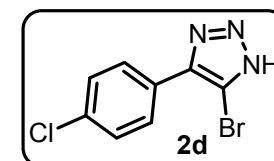
5-bromo-4-(2-fluorophenyl)-1H-1,2,3-triazole (2c):

Yellow liquid; Yield – 90% (133 mg); R_f = 0.5 (20% in EtOAc/PE); $^1\text{H-NMR}$ (400 MHz, CDCl_3); δ = 7.12-7.25 (m, 2H), 7.37-7.45 (m, 1H), 7.68 (td, J_1 = 7.5, J_2 = 1.7 Hz, 1H), 13.51 (s, 1H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3); δ = 115.41 (d, J = 13 Hz), 116.22 (d, J = 21.6 Hz), 121.6, 124.34 (d, J = 3.4 Hz), 130.5, 131.42 (d, J = 8.6 Hz), 137.8, 159.57 (d, J = 249.6 Hz); MS (ESI): m/z calcd for $\text{C}_8\text{H}_5\text{BrFN}_3$ 240.97, found 241.97 [M+H], 243.97 [M+H+2].



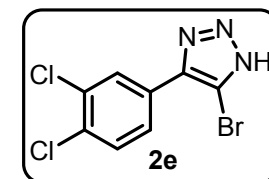
5-bromo-4-(4-chlorophenyl)-1H-1,2,3-triazole (2d):

White solid; M.p. 196-198 °C; Yield – 92% (132 mg); R_f = 0.4 (20% in EtOAc/PE); $^1\text{H-NMR}$ (400 MHz, DMSO - d_6); δ = 7.57 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 15.62 (s, 1H); $^{13}\text{C-NMR}$ (100 MHz, DMSO - d_6); δ = 119.5, 127.8, 128.6, 128.9, 133.6, 142.7; MS (ESI): m/z calcd for $\text{C}_8\text{H}_5\text{BrClN}_3$ 256.93, found 257.93 [M+H], 259.93 [M+H+2], 261.93 [M+H+4].



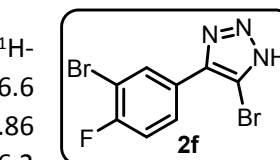
5-bromo-4-(3,4-dichlorophenyl)-1H-1,2,3-triazole (2e):

White solid; M.p. 168-170 °C; Yield – 91% (125 mg); R_f = 0.3 (10% in EtOAc/PE); $^1\text{H-NMR}$ (400 MHz, DMSO - d_6); δ = 7.78-7.82 (m, 1H), 7.82-7.87 (m, 1H), 8.05 (d, J = 1.9 Hz, 1H); $^{13}\text{C-NMR}$ (100 MHz, DMSO - d_6); δ = 127.4, 128.9, 130.0, 131.7, 132.1, 132.2, 132.5, 133.3; MS (ESI): m/z calcd for $\text{C}_8\text{H}_4\text{BrCl}_2\text{N}_3$ 290.90, found 291.92 [M+H], 293.92 [M+H+2], 295.92 [M+H+4], 297.92 [M+H+6].



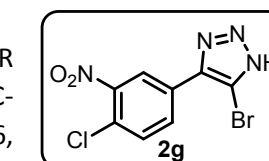
5-bromo-4-(3-bromo-4-fluorophenyl)-1H-1,2,3-triazole (2f):

White solid; M.p. 130-132 °C; Yield – 89% (118 mg); R_f = 0.6 (20% in EtOAc/PE); $^1\text{H-NMR}$ (400 MHz, DMSO - d_6); δ = 7.51 (t, J = 8.7 Hz, 1H), 7.87 (s, 1H), 8.10 (dd, J_1 = 6.6 Hz, J_2 = 2.2 Hz, 1H); $^{13}\text{C-NMR}$ (100 MHz, DMSO - d_6); δ = 109.07 (d, J = 22.1 Hz), 117.86 (d, J = 23 Hz), 119.8, 127.7, 128.95 (d, J = 7.7 Hz), 132.2, 142.1, 158.96 (d, J = 246.2 Hz); MS (ESI): m/z calcd for $\text{C}_8\text{H}_4\text{Br}_2\text{FN}_3$ 318.88, found 319.88 [M+H], 321.87 [M+H+2], 323.87 [M+H+4].



5-bromo-4-(4-chloro-3-nitrophenyl)-1H-1,2,3-triazole (2g):

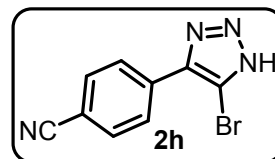
Yellow solid; 76-78 °C Yield – 81% (109 mg); R_f = 0.3 (20% in EtOAc/PE); $^1\text{H-NMR}$ (400 MHz, DMSO - d_6); δ = 7.81-7.85 (m, 1H), 8.05-8.10 (m, 1H), 8.40 (s, 1H); $^{13}\text{C-NMR}$ (100 MHz, DMSO - d_6); δ = 117.7, 124.0, 125.8, 129.5, 132.2, 132.9, 140.6,



148.1; MS (ESI): m/z calcd for $C_8H_4BrClN_4O_2$ 301.92, found 302.91 [M+H], 304.92 [M+H+2]. 306.92 [M+H+4].

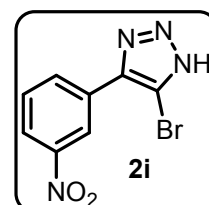
4-(5-bromo-1H-1,2,3-triazol-4-yl)benzonitrile (2h):

White solid; 192-194 °C; Yield – 85% (124 mg); R_f = 0.4 (10% in EtOAc/PE); 1H -NMR (400 MHz, DMSO - d_6); δ = 7.91-7.96 (m, 2H), 7.99-8.10 (m, 2H); ^{13}C -NMR (100 MHz, DMSO - d_6); δ = 111.4, 118.6, 119.6, 127.5, 127.7, 132.9, 133.1; MS (ESI): m/z calcd for $C_9H_5BrN_4$ 247.96, found 248.96 [M+H], 250.97 [M+H+2].



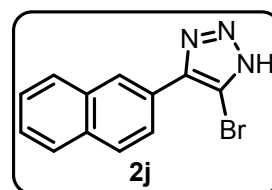
5-bromo-4-(3-nitrophenyl)-1H-1,2,3-triazole (2i):

Yellow solid; M.p. 184-186 °C; Yield – 82% (116 mg); R_f = 0.4 (10% in EtOAc/PE); 1H -NMR (400 MHz, DMSO - d_6); δ = 7.71-7.81 (m, 1H), 8.21-8.28 (m, 2H), 8.61 (t, J = 1.9 Hz, 1H); ^{13}C -NMR (100 MHz, DMSO - d_6); δ = 120.0, 121.0, 123.5, 130.4, 130.7, 132.9, 141.5, 148.0; MS (ESI): m/z calcd for $C_8H_5BrN_4O_2$ 267.95, found 268.96 [M+H], 270.95 [M+H+2].



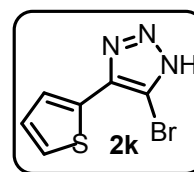
5-bromo-4-(naphthalen-2-yl)-1H-1,2,3-triazole (2j):

White solid; M.p. 136-138 °C; Yield – 88% (123 mg); R_f = 0.5 (20% in EtOAc/PE); 1H -NMR (400 MHz, DMSO - d_6); δ = 7.45-7.60 (m, 1H), 7.61-7.80 (m, 4H), 7.99 (d, J = 7.6 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H); ^{13}C -NMR (100 MHz, DMSO - d_6); δ = 126.1, 126.5, 126.9, 127.9, 128.3, 128.4, 128.6, 129.1, 129.6, 131.2, 132.1, 143.5; MS (ESI): m/z calcd for $C_{12}H_8BrN_3$ 272.99, found 273.99 [M+H], 275.98 [M+H+2].



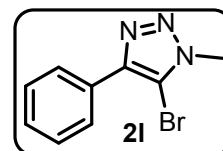
5-bromo-4-(thiophen-2-yl)-1H-1,2,3-triazole (2k):

White solid; M.p. 86-88 °C; Yield – 91% (138 mg); R_f = 0.6 (20% in EtOAc/PE); 1H -NMR (400 MHz, DMSO - d_6); δ = 7.29-7.34 (m, 1H), 7.48 (s, 1H), 7.73 (d, J = 4.0 Hz, 1H), 12.34 (s, 1H); ^{13}C -NMR (100 MHz, DMSO - d_6); δ = 114.2, 120.0, 126.9, 130.5, 133.3, 140.7; MS (ESI): m/z calcd for $C_6H_4BrN_3S$ 228.93, found 229.94 [M+H], 231.93 [M+H+2].



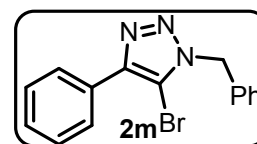
5-bromo-1-methyl-4-phenyl-1H-1,2,3-triazole (2l):

Colourless oil; Yield – 74% (110 mg); R_f = 0.5 (5% in EtOAc/PE); 1H -NMR (400 MHz, $CDCl_3$); δ = 4.22 (s, 3H), 7.40-7.50 (m, 3H), 7.89-7.94 (m, 2H); ^{13}C -NMR (100 MHz, $CDCl_3$); δ = 42.3, 119.3, 127.1, 128.5, 128.7, 129.0, 145.3; MS (ESI): m/z calcd for $C_9H_8BrN_3$ 236.99, found 237.99 [M+H], 239.99 [M+H+2].



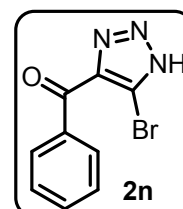
1-benzyl-5-bromo-4-phenyl-1H-1,2,3-triazole (2m):

Colourless oil; Yield – 72% (96 mg); R_f = 0.6 (5% in EtOAc/PE); 1H -NMR (400 MHz, $CDCl_3$); δ = 5.58 (s, 2H), 7.33-7.43 (m, 6H), 7.43-7.49 (m, 2H), 7.94 (d, J = 7.0 Hz, 2H); ^{13}C -NMR (100 MHz, $CDCl_3$); δ = 59.4, 119.9, 127.2, 128.1, 128.3, 128.5, 128.8, 129.0, 129.6, 134.5, 145.6; MS (ESI): m/z calcd for $C_{15}H_{12}BrN_3$ 313.02, found 314.03 [M+H], 316.03 [M+H+2].



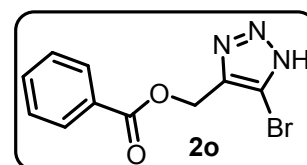
(5-bromo-1H-1,2,3-triazol-4-yl)(phenyl)methanone (2n):

Yellow oil; Yield – 55% (80 mg); R_f = 0.6 (10% in EtOAc/PE); 1H -NMR (400 MHz, $CDCl_3$); δ = 7.50 (t, J = 7.7 Hz, 2H), 7.60-7.65 (m, 1H), 7.88 (d, J = 8.3 Hz, 2H); ^{13}C -NMR (100 MHz, $CDCl_3$); δ = 109.1, 128.0, 128.8, 133.8, 134.5, 182.8; MS (ESI): m/z calcd for $C_9H_6BrN_3O$ 250.96, found 251.96 [M+H], 253.96 [M+H+2].



(5-bromo-1H-1,2,3-triazol-4-yl)methyl benzoate (2o):

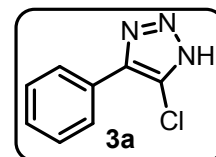
Yellow oil; Yield – 57% (78 mg); R_f = 0.7 (5% in EtOAc/PE); 1H -NMR (400 MHz, $CDCl_3$); δ = 5.59 (s, 2H), 7.70-7.76 (m, 2H), 7.87 (t, J = 7.6 Hz, 2H), 8.15-8.18 (m,



2H); ^{13}C -NMR (100 MHz, CDCl_3); δ = 56.3, 126.0, 128.3, 128.8, 129.0, 133.6, 165.2; MS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{12}\text{BrN}_3$ 280.98, found 281.98 [M+H], 283.98 [M+H+2].

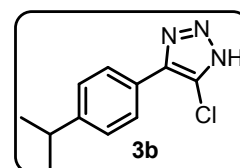
5-chloro-4-phenyl-1H-1,2,3-triazole (3a):

White solid; M.p. 144-146 $^{\circ}\text{C}$; Yield – 88% (109 mg); R_f = 0.5 (20% in EtOAc/PE); ^1H -NMR (400 MHz, DMSO - d_6); δ = 7.43-7.49 (m, 1H), 7.49-7.55 (m, 2H), 7.82-7.87 (m, 2H), 15.62 (s, 1H); ^{13}C -NMR (100 MHz, DMSO - d_6); δ = 127.1, 127.9, 128.8, 128.9, 129.2, 134.3; MS (ESI): m/z calcd for $\text{C}_8\text{H}_6\text{ClN}_3$ 179.03, found 180.03 [M+H], 182.03 [M+H+2].



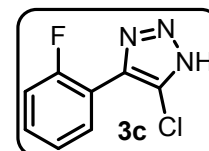
5-chloro-4-(4-isopropylphenyl)-1H-1,2,3-triazole (3b):

White solid; M.p. 126-128 $^{\circ}\text{C}$; Yield – 80% (95 mg); R_f = 0.7 (20% in EtOAc/PE); ^1H -NMR (400 MHz, DMSO - d_6); δ = 1.11 (d, J = 7.0 Hz, 6H), 2.75-2.88 (m, 1H), 7.27 (d, J = 7.5 Hz, 2H), 7.66 (d, J = 5.6 Hz, 2H); ^{13}C -NMR (100 MHz, DMSO - d_6); δ = 24.1, 33.6, 127.1, 127.3, 128.2, 132.2, 142.3, 149.8; MS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{12}\text{ClN}_3$ 221.07, found 222.08 [M+H], 224.07 [M+H+2].



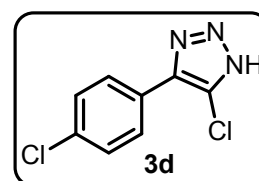
5-chloro-4-(2-fluorophenyl)-1H-1,2,3-triazole (3c):

Yellow liquid; Yield – 84% (101 mg); R_f = 0.3 (10% in EtOAc/PE); ^1H -NMR (400 MHz, DMSO - d_6); δ = 7.14-7.27 (m, 2H), 7.38-7.46 (m, 1H), 7.68-7.74 (m, 1H); ^{13}C -NMR (100 MHz, DMSO - d_6); δ = 115.06 (d, J = 21 Hz), 116.22 (d, J = 21 Hz), 124.42 (d, J = 3.3 Hz), 125.1, 130.1, 131.37 (d, J = 8.2 Hz), 134.9, 159.56 (d, J = 250.1 Hz); MS (ESI): m/z calcd for $\text{C}_8\text{H}_5\text{ClFN}_3$ 197.02, found 198.03 [M+H], 180.03 [M+H+2].



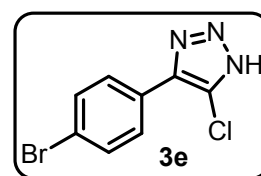
5-chloro-4-(4-chlorophenyl)-1H-1,2,3-triazole (3d):

White solid; M.p. 226-228 $^{\circ}\text{C}$; Yield – 89% (106 mg); R_f = 0.3 (10% in EtOAc/PE); ^1H -NMR (400 MHz, DMSO - d_6); δ = 7.58 (d, J = 8.3 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H); ^{13}C -NMR (100 MHz, DMSO - d_6); δ = 127.9, 128.8, 129.5, 132.8, 134.1, 140.4; MS (ESI): m/z calcd for $\text{C}_8\text{H}_5\text{Cl}_2\text{N}_3$ 212.99, found 213.99 [M+H], 215.99 [M+H+2], 217.99 [M+H+4].



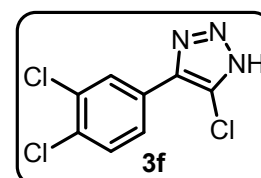
4-(4-bromophenyl)-5-chloro-1H-1,2,3-triazole (3e):

Orange solid; M.p. 151-152 $^{\circ}\text{C}$; Yield – 88% (101 mg); R_f = 0.5 (10% in EtOAc/PE); ^1H -NMR (400 MHz, DMSO - d_6); δ = 7.63 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.6 Hz, 2H); ^{13}C -NMR (100 MHz, DMSO - d_6); δ = 122.3, 127.3, 128.5, 128.8, 131.9, 132.7; MS (ESI): m/z calcd for $\text{C}_8\text{H}_5\text{BrClN}_3$ 256.94, found 257.94 [M+H], 259.94 [M+H+2], 261.94 [M+H+4].



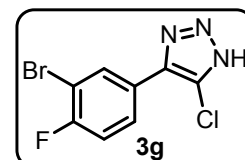
5-chloro-4-(3,4-dichlorophenyl)-1H-1,2,3-triazole (3f):

White solid; M.p. 120-122 $^{\circ}\text{C}$; Yield – 82% (95 mg); R_f = 0.5 (10% in EtOAc/PE); ^1H -NMR (400 MHz, DMSO - d_6); δ = 7.65-7.69 (m, 1H), 7.71-7.76 (m, 1H), 7.92 (d, J = 2 Hz, 1H); ^{13}C -NMR (100 MHz, DMSO - d_6); δ = 126.0, 127.1, 128.5, 131.7, 132.1, 132.2, 132.4, 132.7; MS (ESI): m/z calcd for $\text{C}_8\text{H}_4\text{Cl}_3\text{N}_3$ 246.95, found 247.95 [M+H], 249.95 [M+H+2], 251.95 [M+H+4], 253.95 [M+H+6].



4-(3-bromo-4-fluorophenyl)-5-chloro-1H-1,2,3-triazole (3g):

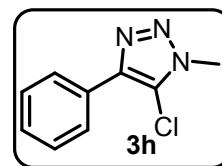
Yellow liquid; Yield – 76% (86 mg); R_f = 0.6 (20% in EtOAc/PE); ^1H -NMR (400 MHz, DMSO - d_6); δ = 7.45 (t, J = 8.7 Hz, 1H), 7.79 (s, 1H), 8.01 (dd, J_1 = 6.8, J_2 = 2.4 Hz, 1H); ^{13}C -NMR (100 MHz, DMSO - d_6); δ = 109.07 (d, J = 22.1 Hz), 117.86 (d, J = 23



Hz), 119.8, 127.7, 128.95 (d, $J = 7.7$ Hz), 132.2, 142.1, 158.96 (d, $J = 246.2$ Hz); MS (ESI): m/z calcd for $C_8H_4Br_1ClFN_3$ 274.93, found 275.93 [M+H], 277.93 [M+H+2], 279.93 [M+H+4].

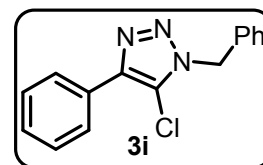
5-chloro-1-methyl-4-phenyl-1H-1,2,3-triazole (3h):

Colourless oil; Yield – 80% (86 mg); $R_f = 0.6$ (20% in EtOAc/PE); 1H -NMR (400 MHz, $CDCl_3$); $\delta = 4.19$ (s, 3H), 7.38-7.49 (m, 3H), 7.88-7.93 (m, 2H); ^{13}C -NMR (100 MHz, $CDCl_3$); $\delta = 42.5, 126.9, 128.7, 128.85, 128.88, 133.0, 142.9$; MS (ESI): m/z calcd for $C_9H_8ClN_3$ 193.04, found 194.04 [M+H], 196.03 [M+H+2].



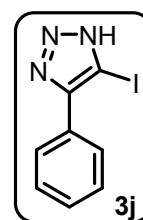
1-benzyl-5-chloro-4-phenyl-1H-1,2,3-triazole (3i):

Colourless oil; Yield – 78% (117 mg); $R_f = 0.6$ (20% in EtOAc/PE); 1H -NMR (400 MHz, $CDCl_3$); $\delta = 5.55$ (s, 2H), 7.34-7.43 (m, 6H), 7.43-7.49 (m, 2H), 7.92-7.96 (m, 2H); ^{13}C -NMR (100 MHz, $CDCl_3$); $\delta = 59.5, 128.3, 128.4, 128.6, 128.7, 128.8, 128.9, 129.8, 133.5, 134.6, 143.2$; MS (ESI): m/z calcd for $C_{15}H_{12}ClN_3$ 269.03, found 270.63 [M+H], 272.03 [M+H+2].



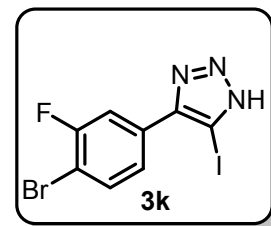
5-iodo-4-phenyl-1H-1,2,3-triazole (3j):

Semi solid; Yield – 78% (145 mg); $R_f = 0.5$ (20% in EtOAc/PE); 1H -NMR (400 MHz, $CDCl_3$); $\delta = 7.41$ -7.54 (m, 3H), 7.83 (d, $J = 7.3$ Hz, 2H), 15.65 (s, 1H); ^{13}C -NMR (100 MHz, $CDCl_3$); $\delta = 127.3, 128.7, 129.1$; MS (ESI): m/z calcd for $C_8H_6IN_3$ 270.96, found 271.96 [M+H].



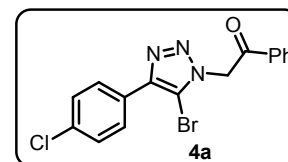
4-(4-bromo-3-fluorophenyl)-5-iodo-1H-1,2,3-triazole (3k):

Colourless oil; Yield – 72% (110 mg); $R_f = 0.5$ (20% in EtOAc/PE); 1H -NMR (400 MHz, $CDCl_3$); $\delta = 7.41$ -7.54 (m, 3H), 7.83 (d, $J = 7.3$ Hz, 2H), 15.65 (s, 1H); ^{13}C -NMR (100 MHz, $CDCl_3$); $\delta = 108.6$ (d, $J = 20$ Hz), 117.3 (d, $J = 22$ Hz), 126.8 (d, $J = 5.2$ Hz), 128.7, 129.8, 130.7 (d, $J = 80$ MHz), 144.2, 158.02 (d, $J = 244.4$ Hz); MS (ESI): m/z calcd for $C_8H_4BrFIN_3$ 366.86 found 367.86 [M+H], 369.86 [M+H+2].



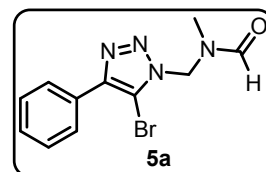
2-(5-bromo-4-(4-chlorophenyl)-1H-1,2,3-triazol-1-yl)-1-phenylethan-1-one (4a):

White solid; M.p. 138-140 °C; Yield – 88% (128 mg); $R_f = 0.6$ (5% in EtOAc/PE); 1H -NMR (400 MHz, $CDCl_3$); 5.92 (s, 2H), 7.51-7.61 (m, 4H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.83 (d, $J = 11.0$ Hz, 2H), 7.97 (d, $J = 8.5$ Hz, 2H); ^{13}C -NMR (100 MHz, $CDCl_3$); $\delta = 61.0, 120.9, 123.3, 127.9, 128.1, 128.9, 129.2, 131.8, 134.0, 134.6, 145.6, 190.3$; MS (ESI): m/z calcd for $C_{16}H_{11}BrClN_3O$ 374.98, found 375.98 [M+H], 377.98 [M+H+2], 379.98 [M+H+4].



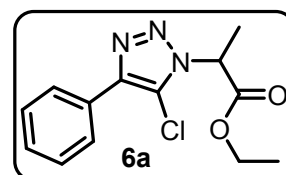
N-((5-bromo-4-phenyl-1H-1,2,3-triazol-1-yl)methyl)-N-methylformamide (5a):

Yellow solid; M.p. 68-70 °C; Yield – 76% (100 mg); $R_f = 0.4$ (50% in EtOAc/PE); 1H -NMR (400 MHz, DMSO - d_6); $\delta = 2.78$ (s, 3H), 6.00 (s, 2H), 7.45-7.55 (m, 3H), 7.81-7.87 (m, 2H), 8.48 (s, 1H); ^{13}C -NMR (100 MHz, DMSO - d_6); $\delta = 29.4, 68.1, 127.5, 128.6, 129.4, 129.8, 132.4, 146.0, 164.4$; MS (ESI): m/z calcd for $C_{11}H_{11}BrN_4O$ 294.01, found 295.02 [M+H], 297.02 [M+H+2].



N-((5-chloro-4-phenyl-1H-1,2,3-triazol-1-yl)methyl)-N-methylformamide (6a):

Colourless oil; Yield – 92% (144 mg); $R_f = 0.4$ (50% in EtOAc/PE); 1H -NMR (400 MHz, $CDCl_3$); $\delta = 1.22$ -1.31 (m, 3H), 1.93 (d, $J = 7.1$ Hz, 3H), 4.22 (q, $J = 7.1$ Hz, 2H), 5.29-5.37 (m, 1H), 7.37-7.48 (m, 3H), 7.91-7.96 (m, 2H); ^{13}C -NMR (100 MHz, $CDCl_3$); $\delta = 14.1, 16.5, 62.3, 63.1, 127.1, 128.4, 128.73, 128.79,$



128.99, 129.9, 169.1; MS (ESI): m/z calcd for $C_{13}H_{14}ClN_3O_2$ 279.08, found 280.08 [M+H], 282.08 [M+H+2].

Copies of 1H and ^{13}C NMR Spectrum

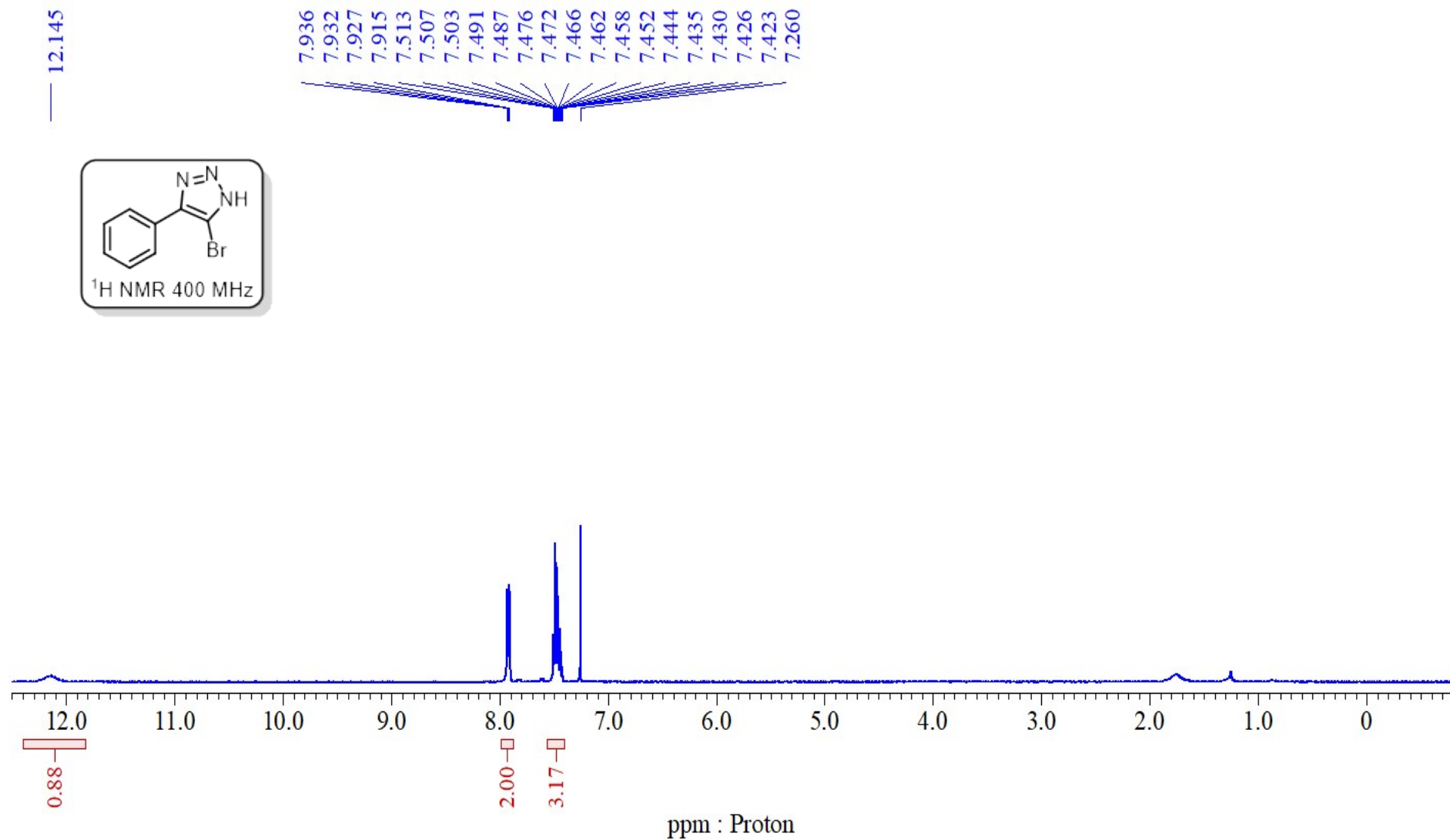


Fig. 1: ^1H NMR spectrum of 5-bromo-4-phenyl-1H-1,2,3-triazole (**2a**)

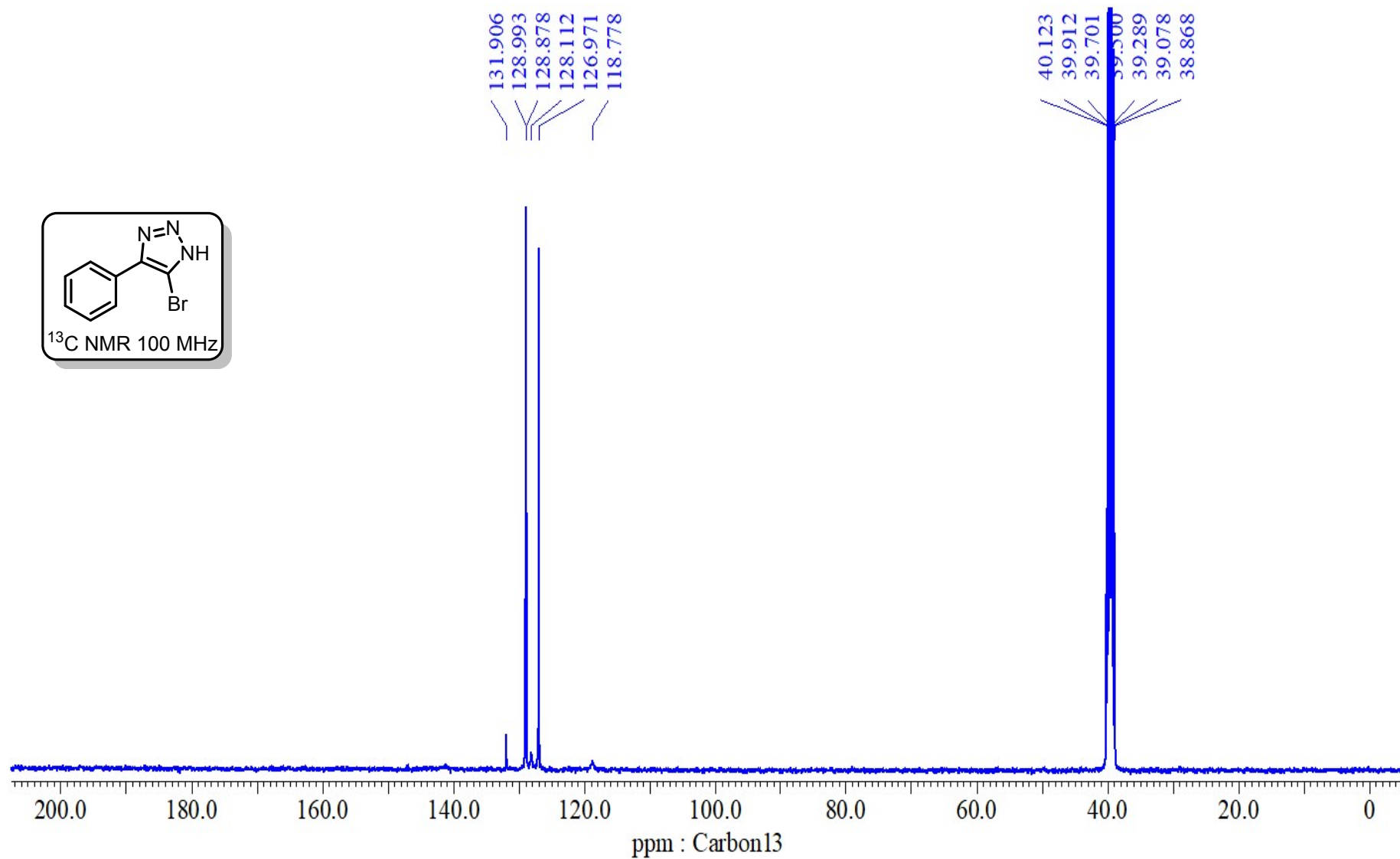


Fig. 2: ¹³C NMR spectrum of 5-bromo-4-phenyl-1H-1,2,3-triazole (**2a**)

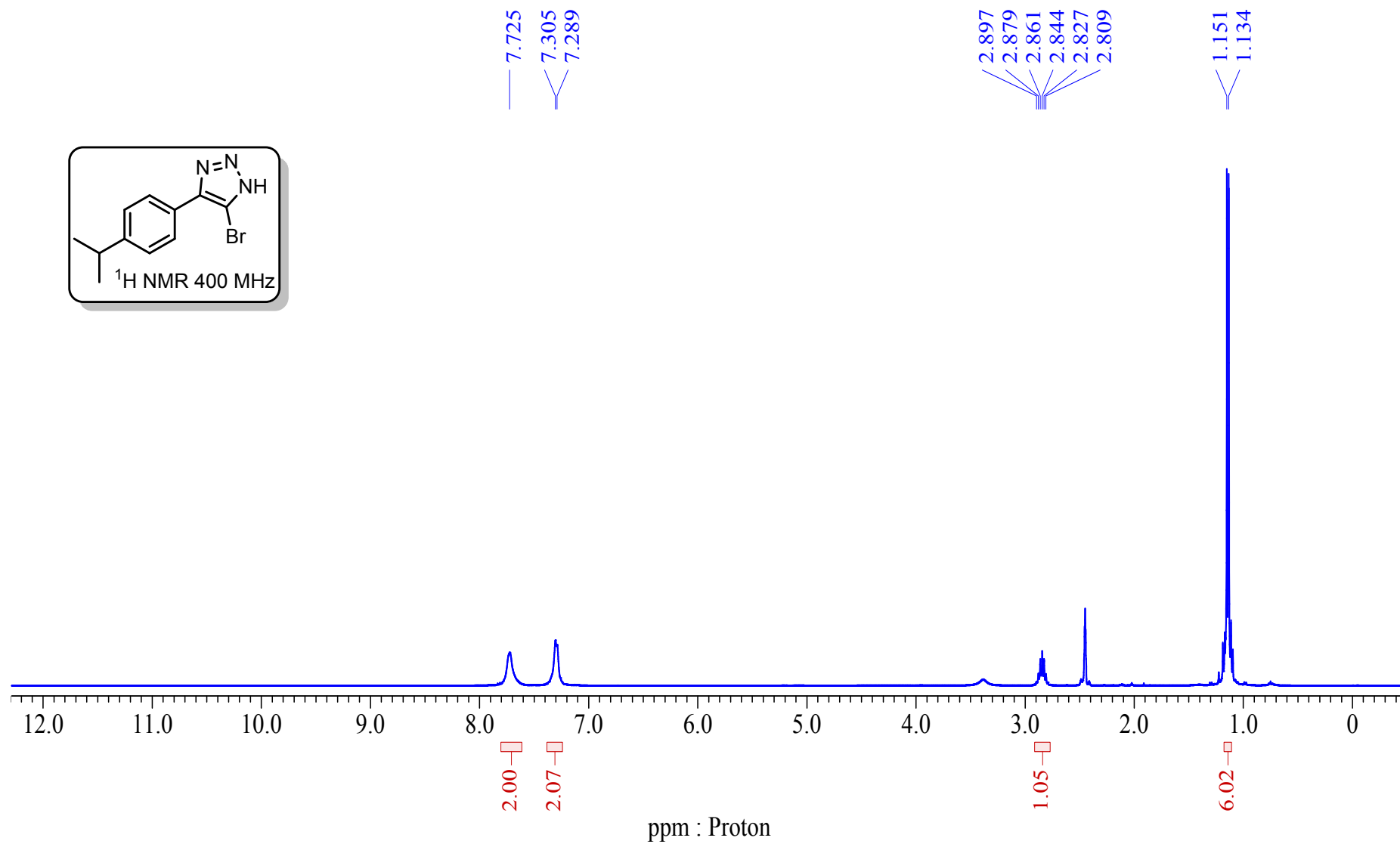


Fig. 3: ¹H NMR spectrum of 5-bromo-4-(4-isopropylphenyl)-1H-1,2,3-triazole (**2b**)

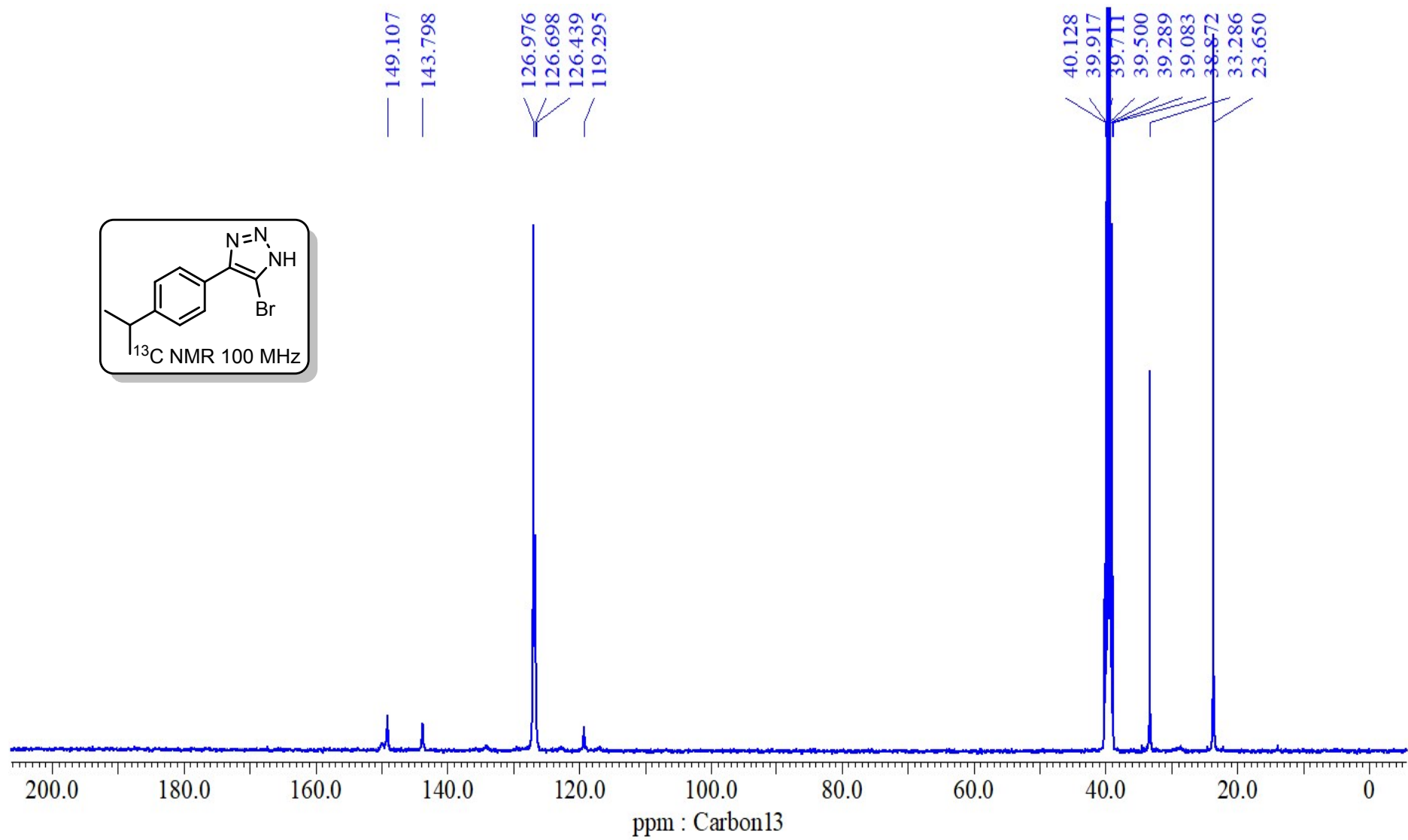


Fig. 4: ¹³C NMR spectrum of 5-bromo-4-(4-isopropylphenyl)-1H-1,2,3-triazole (**2b**)

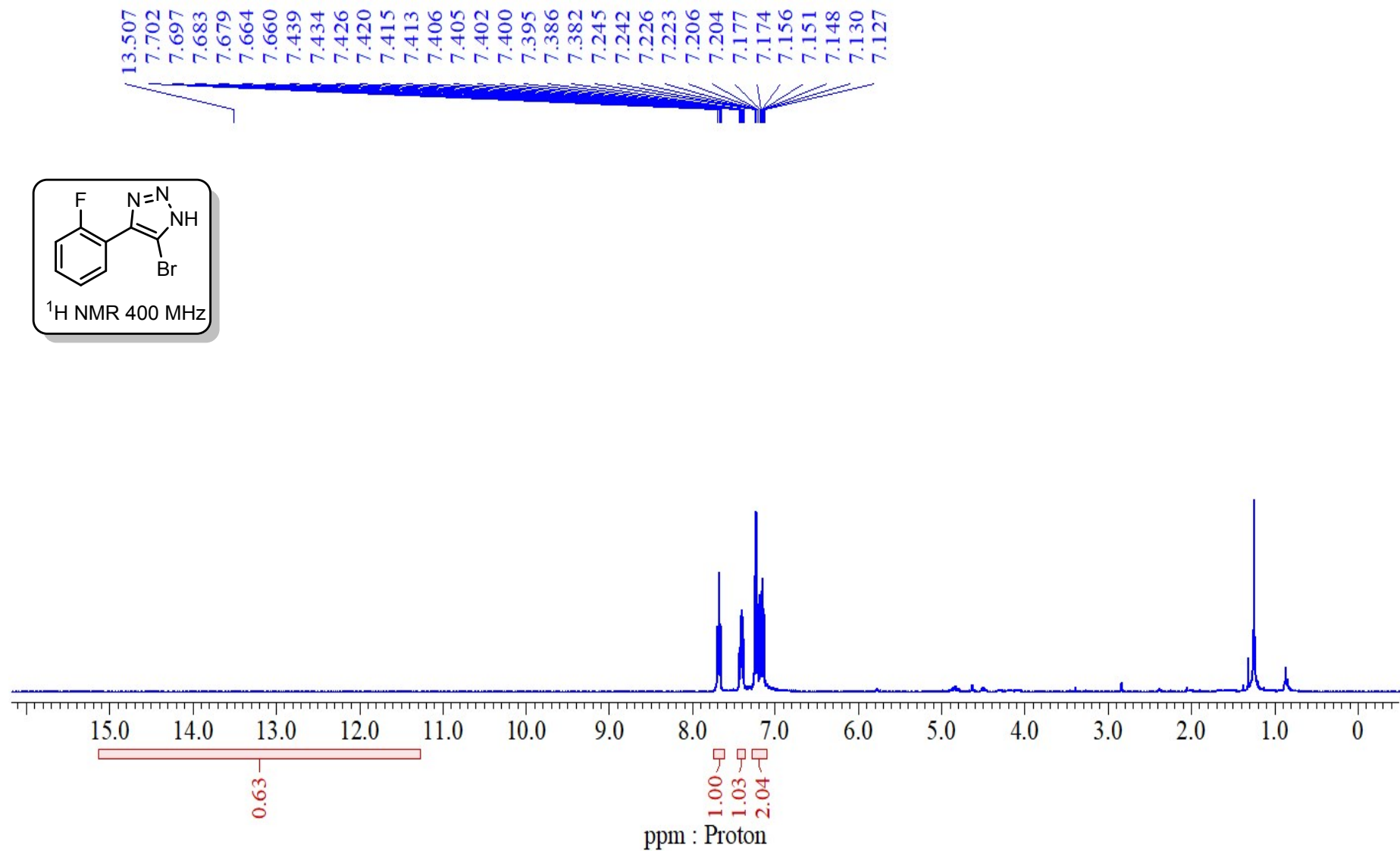


Fig. 5: ¹H NMR spectrum of 5-bromo-4-(2-fluorophenyl)-1H-1,2,3-triazole (2c)

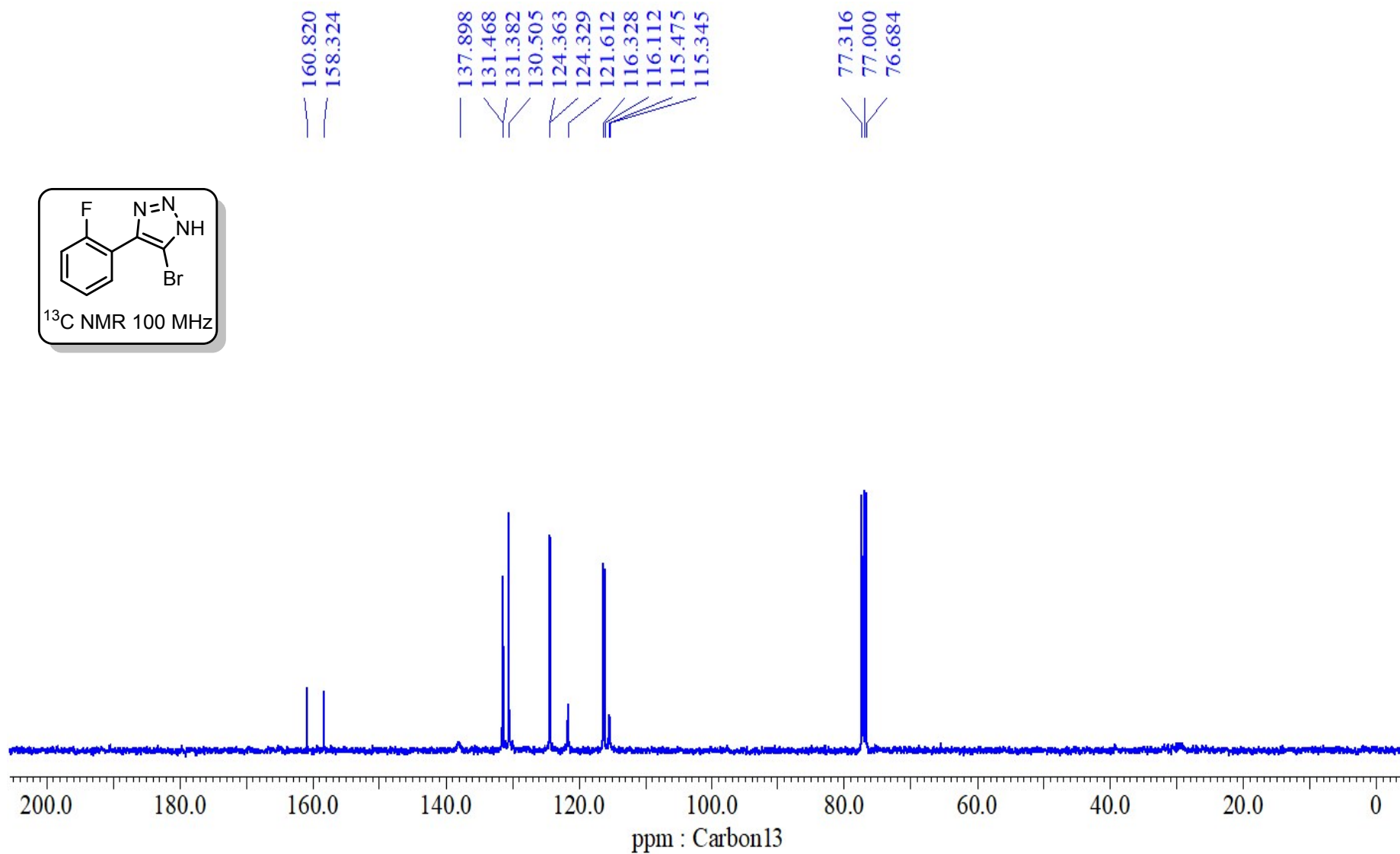


Fig. 6: ¹³C NMR spectrum of 5-bromo-4-(2-fluorophenyl)-1H-1,2,3-triazole (**2c**)

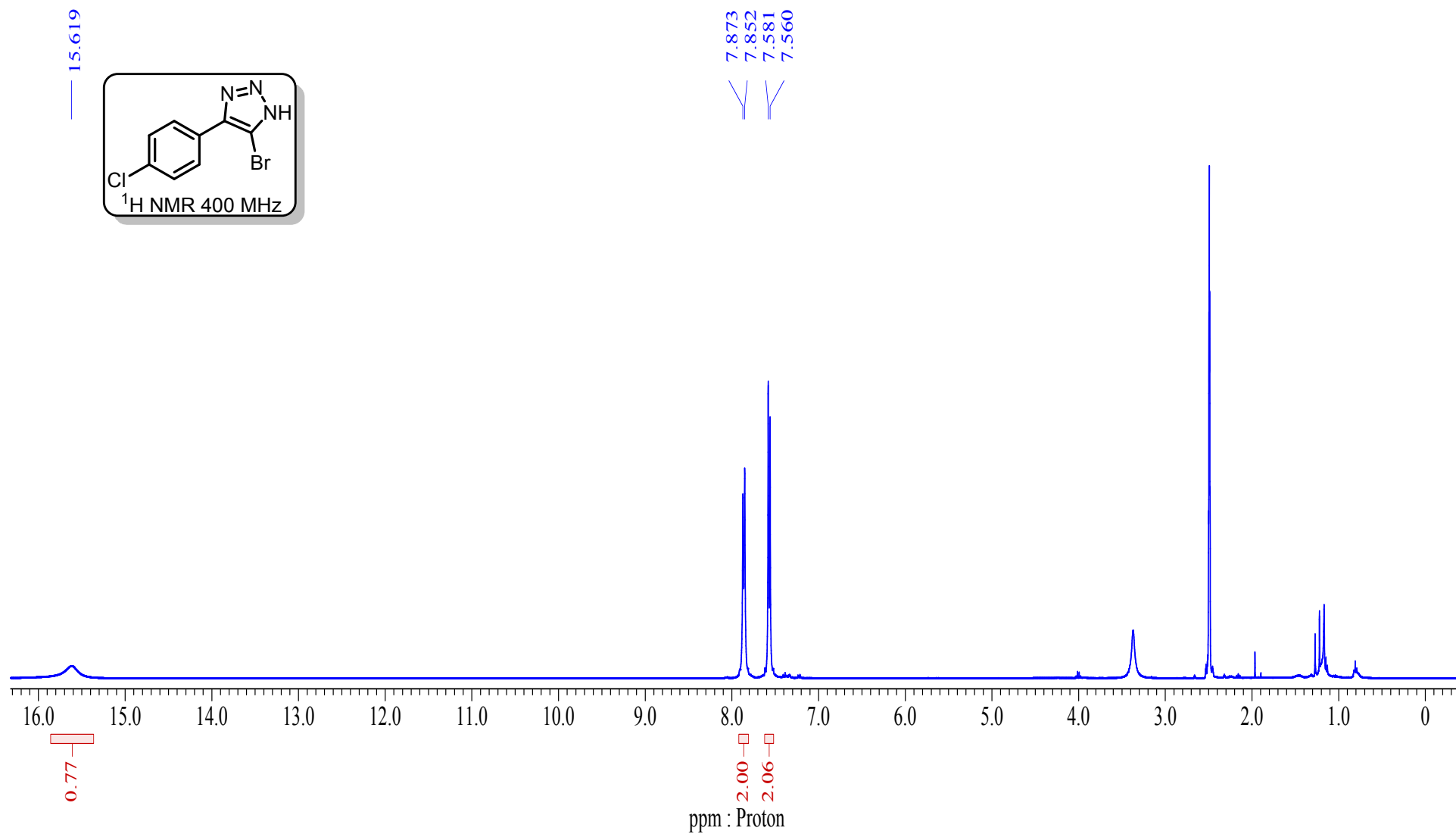


Fig. 7: ¹H-NMR spectrum of 5-bromo-4-(4-chlorophenyl)-1H-1,2,3-triazole (**2d**)

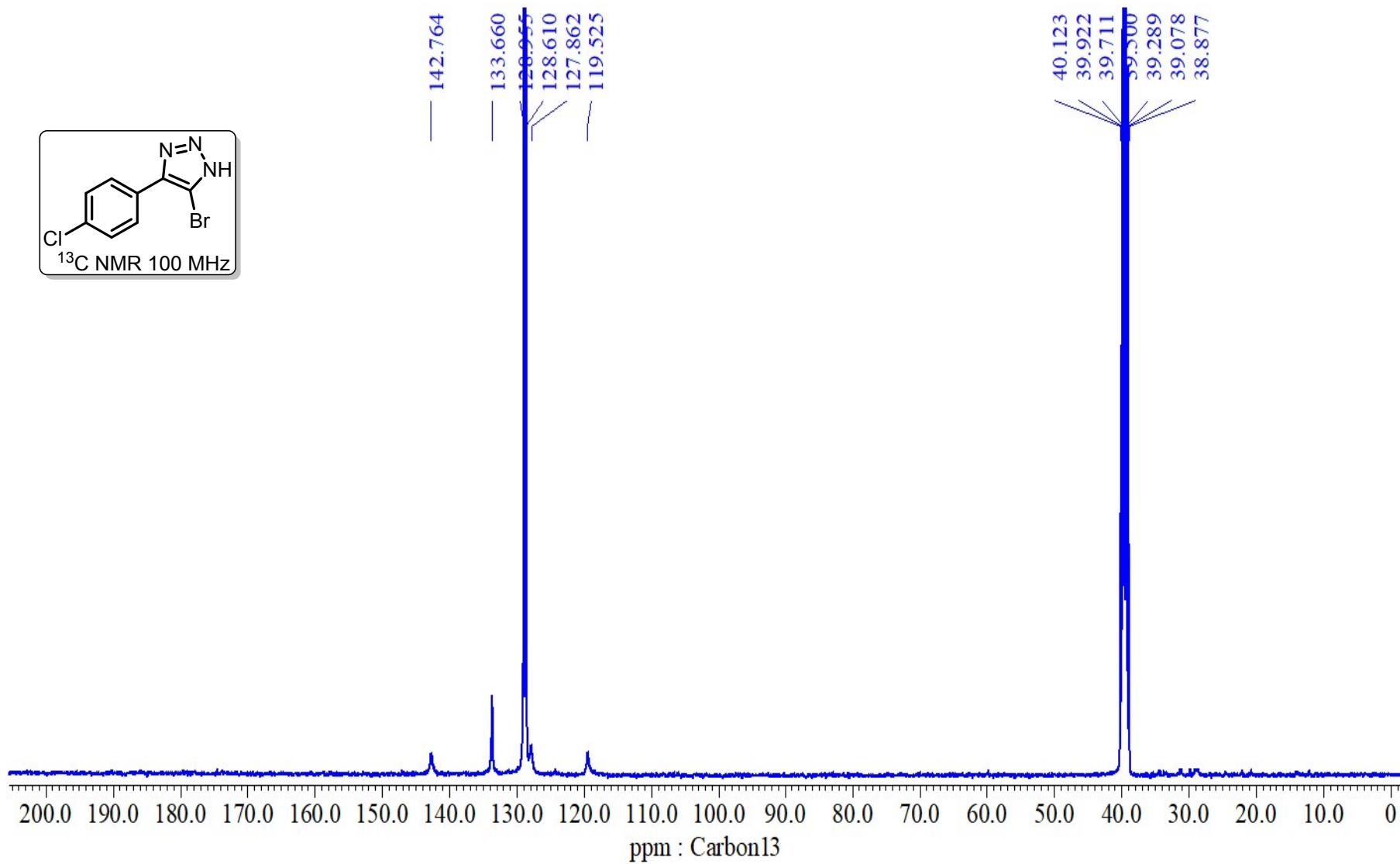


Fig. 8: ¹³C NMR spectrum of 5-bromo-4-(4-chlorophenyl)-1H-1,2,3-triazole (**2d**)

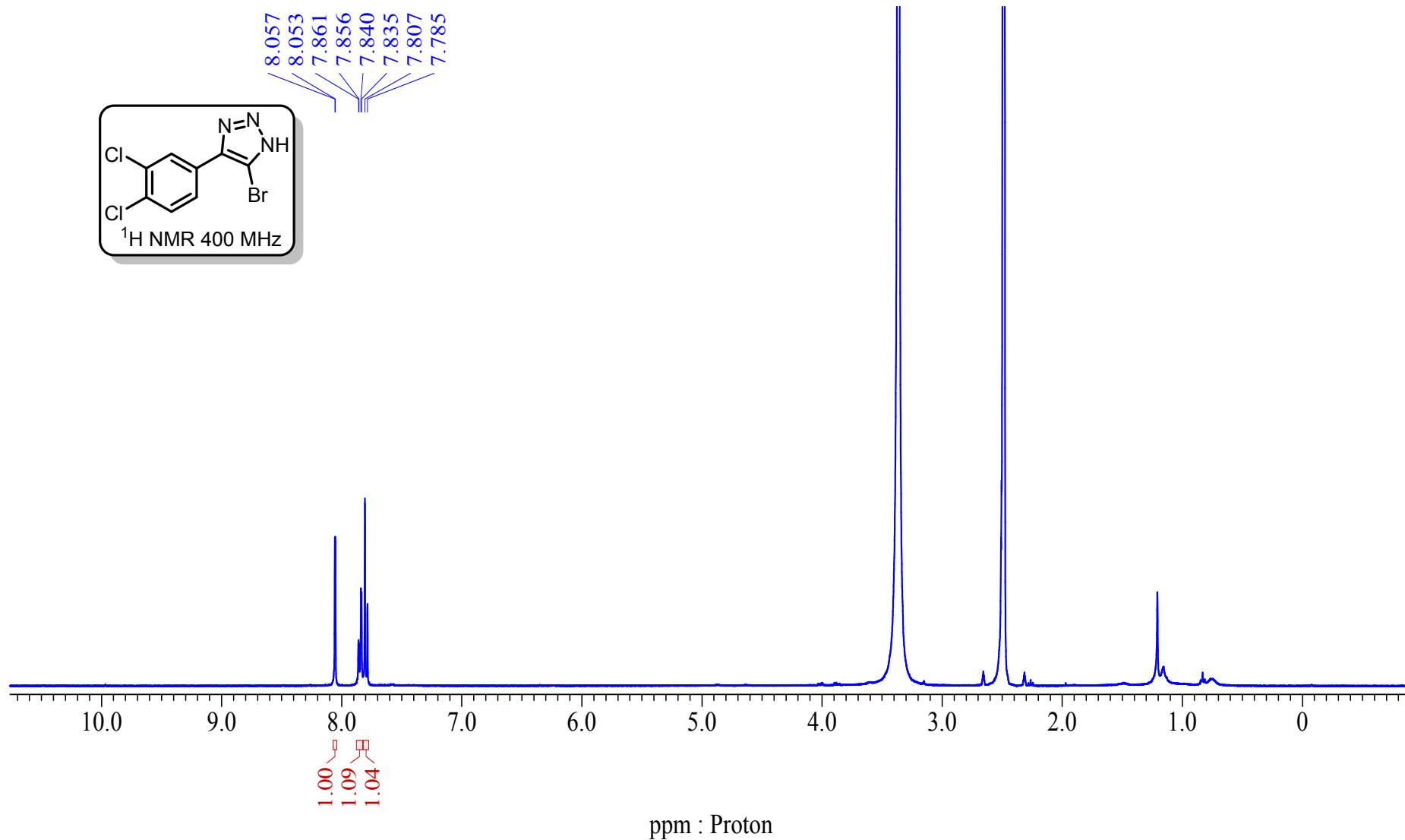


Fig. 9: ^1H NMR spectrum of 5-bromo-4-(3,4-dichlorophenyl)-1H-1,2,3-triazole (**2e**)

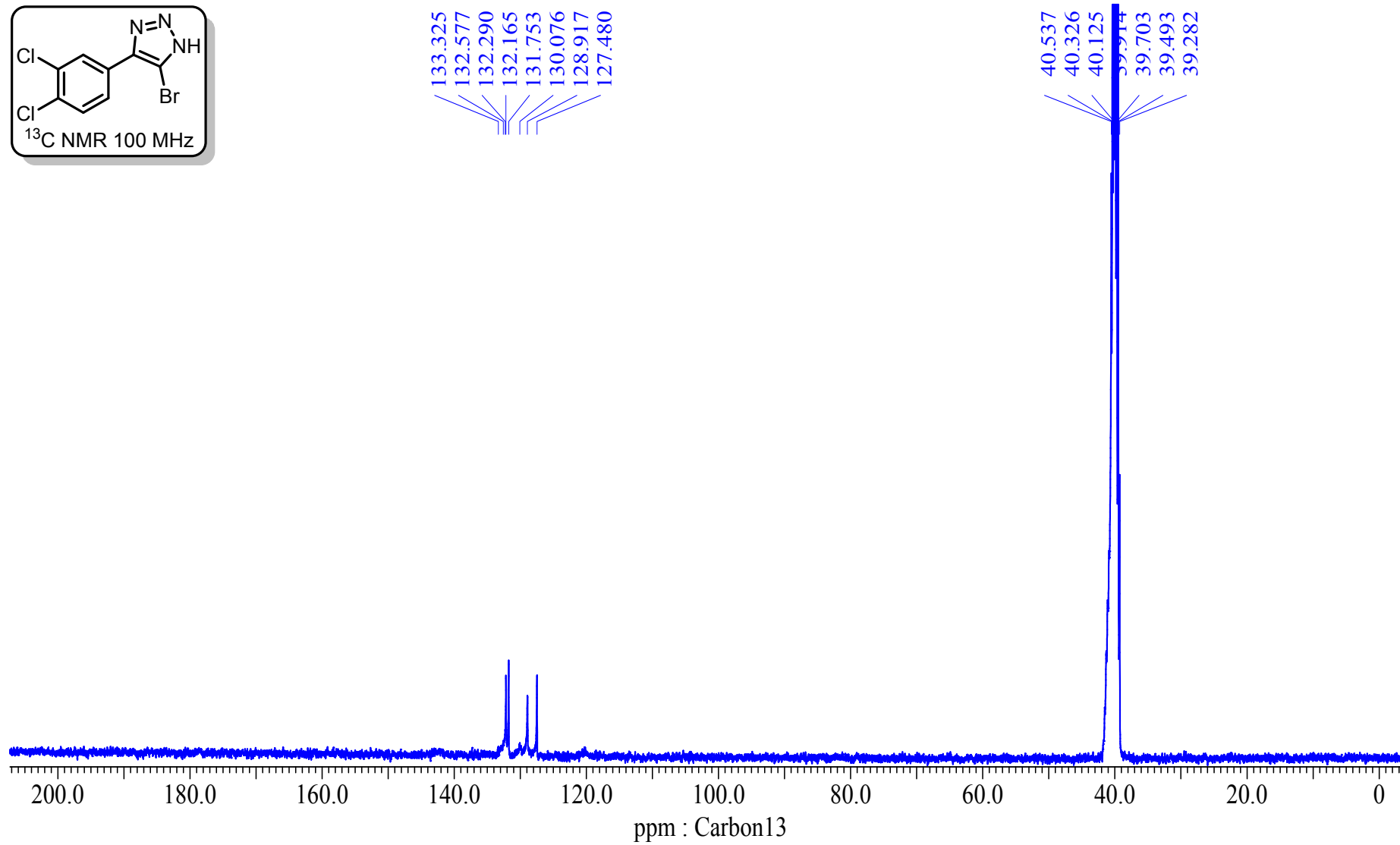
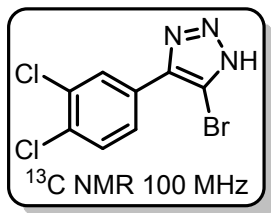


Fig. 10: ¹³C NMR spectrum of 5-bromo-4-(3,4-dichlorophenyl)-1H-1,2,3-triazole (**2e**)

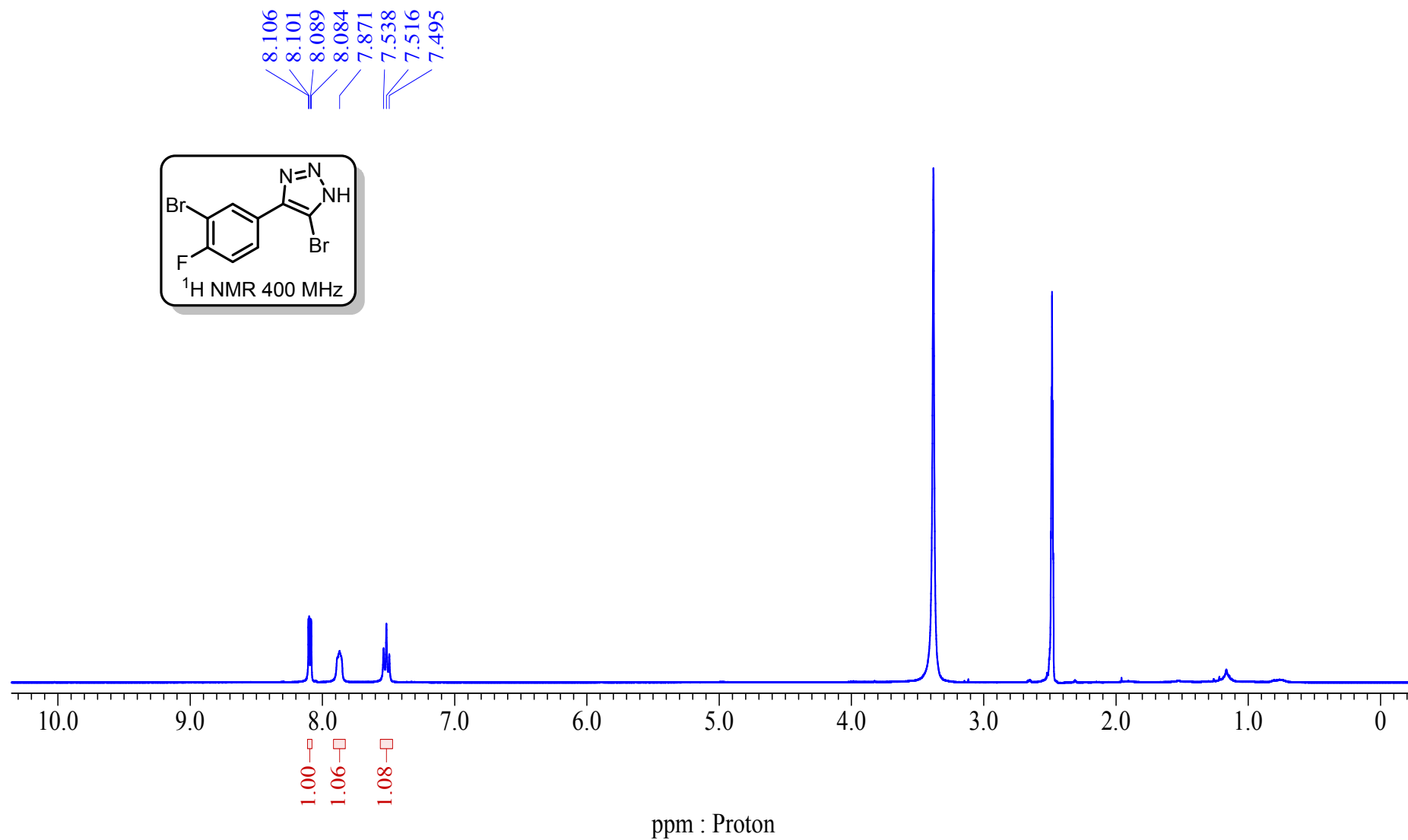


Fig. 11: ¹H NMR spectrum of 5-bromo-4-(3-bromo-4-fluorophenyl)-1H-1,2,3-triazole (**2f**)

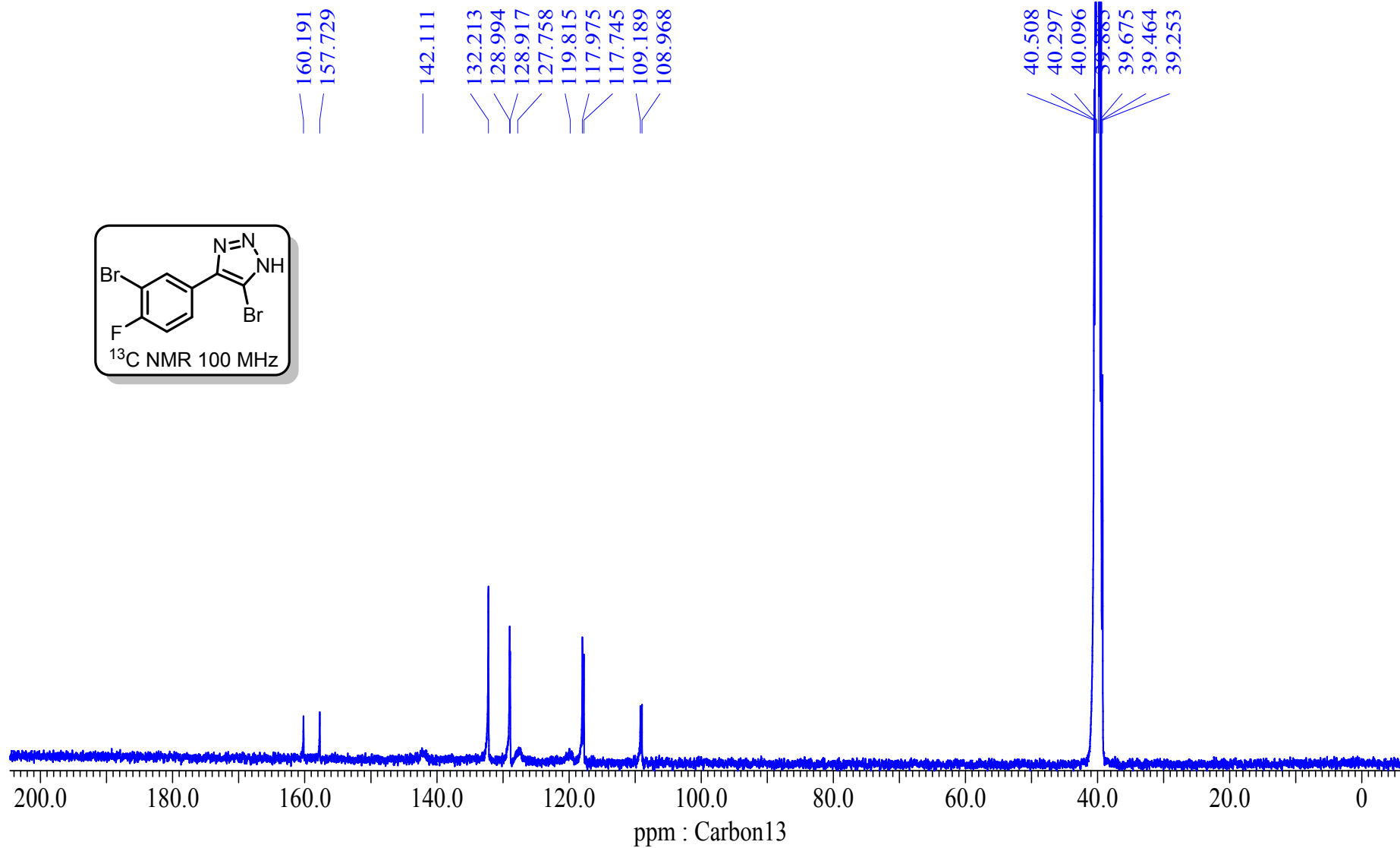


Fig. 12: ¹³C NMR spectrum of 5-bromo-4-(3-bromo-4-fluorophenyl)-1H-1,2,3-triazole (**2f**)

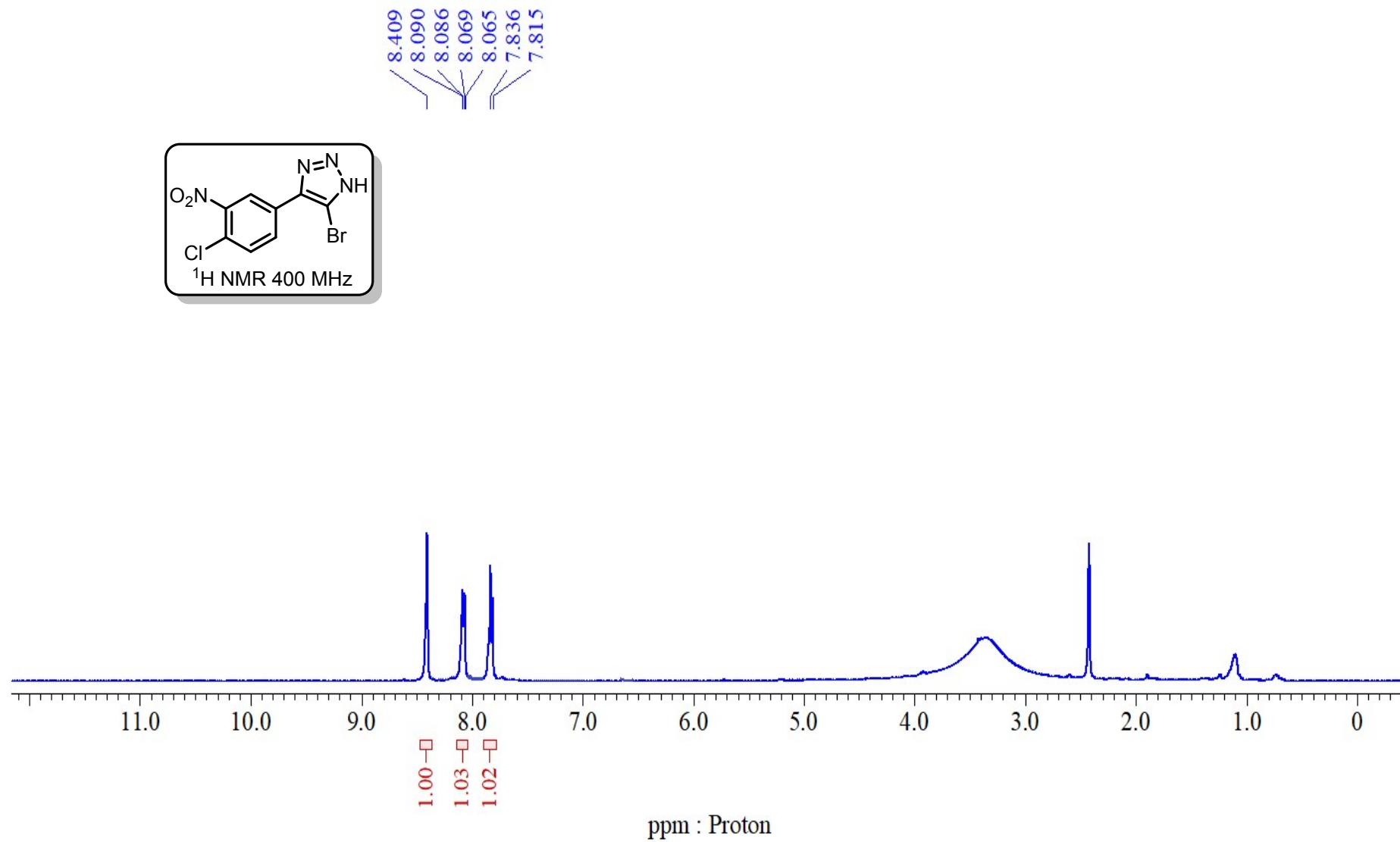


Fig. 13: ¹H NMR spectrum of 5-bromo-4-(4-chloro-3-nitrophenyl)-1H-1,2,3-triazole (**2g**)

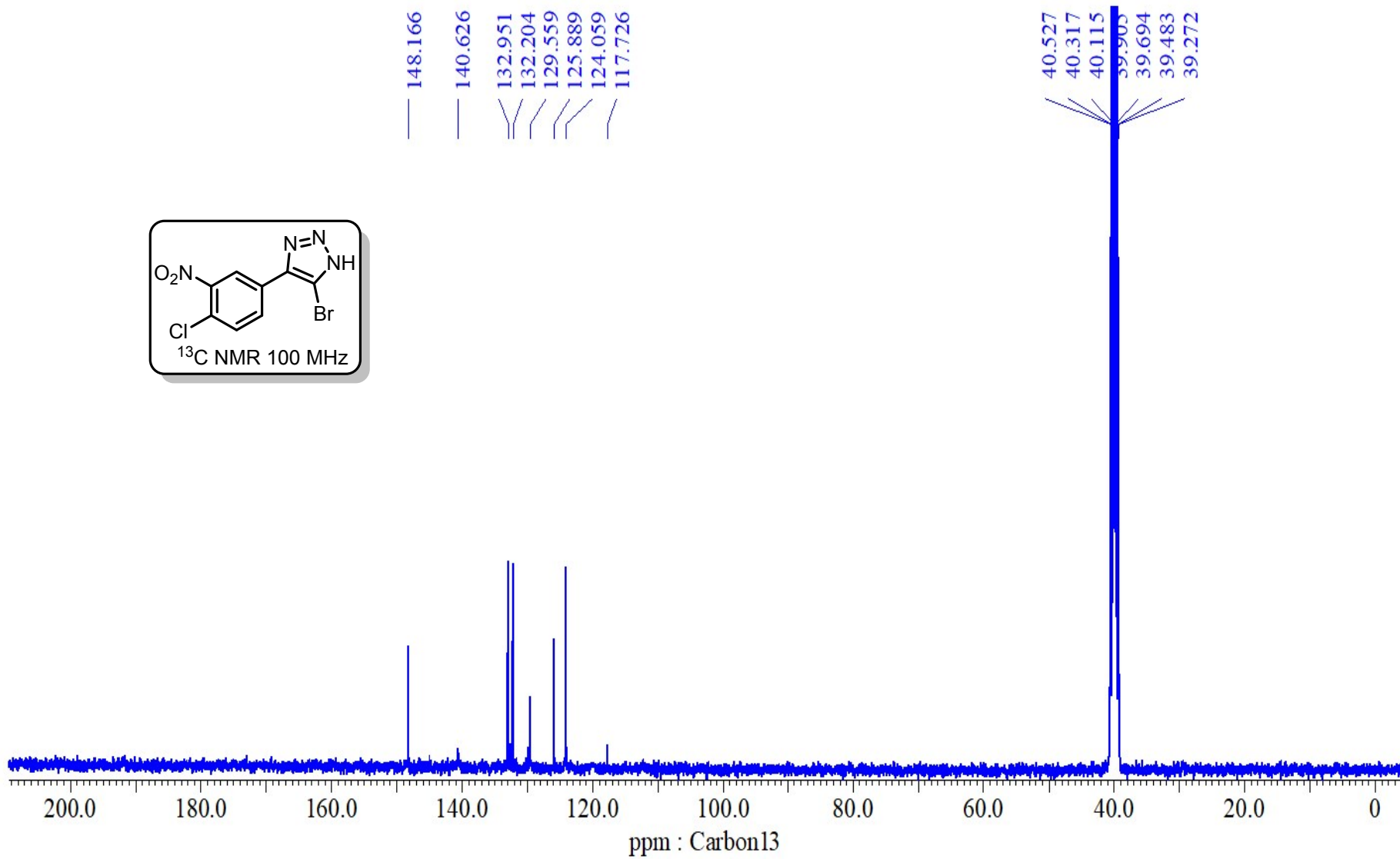


Fig. 14: ¹³C NMR spectrum of 5-bromo-4-(4-chloro-3-nitrophenyl)-1H-1,2,3-triazole (**2g**)

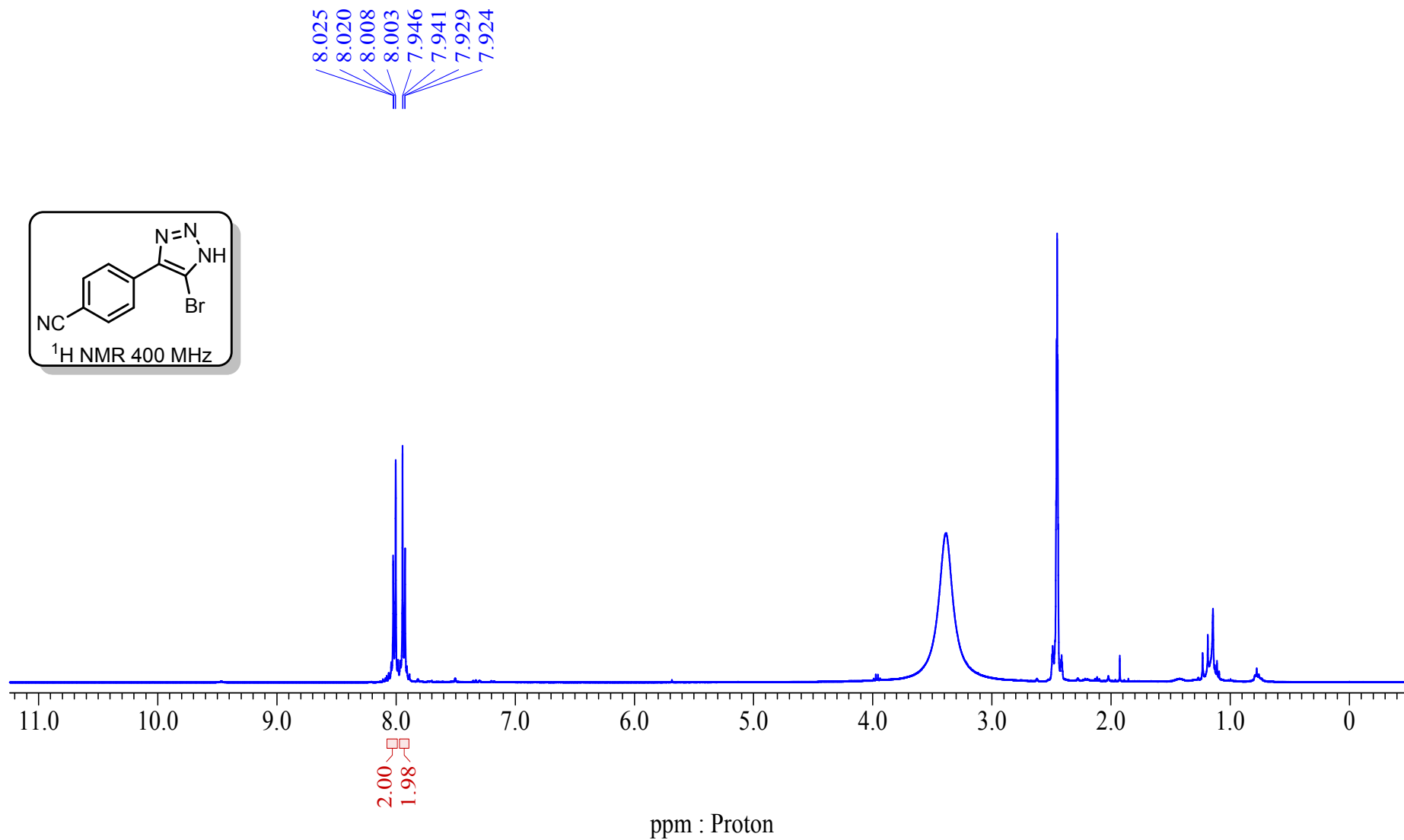


Fig. 15: ¹H NMR spectrum of 4-(5-bromo-1H-1,2,3-triazol-4-yl)benzonitrile (**2h**)

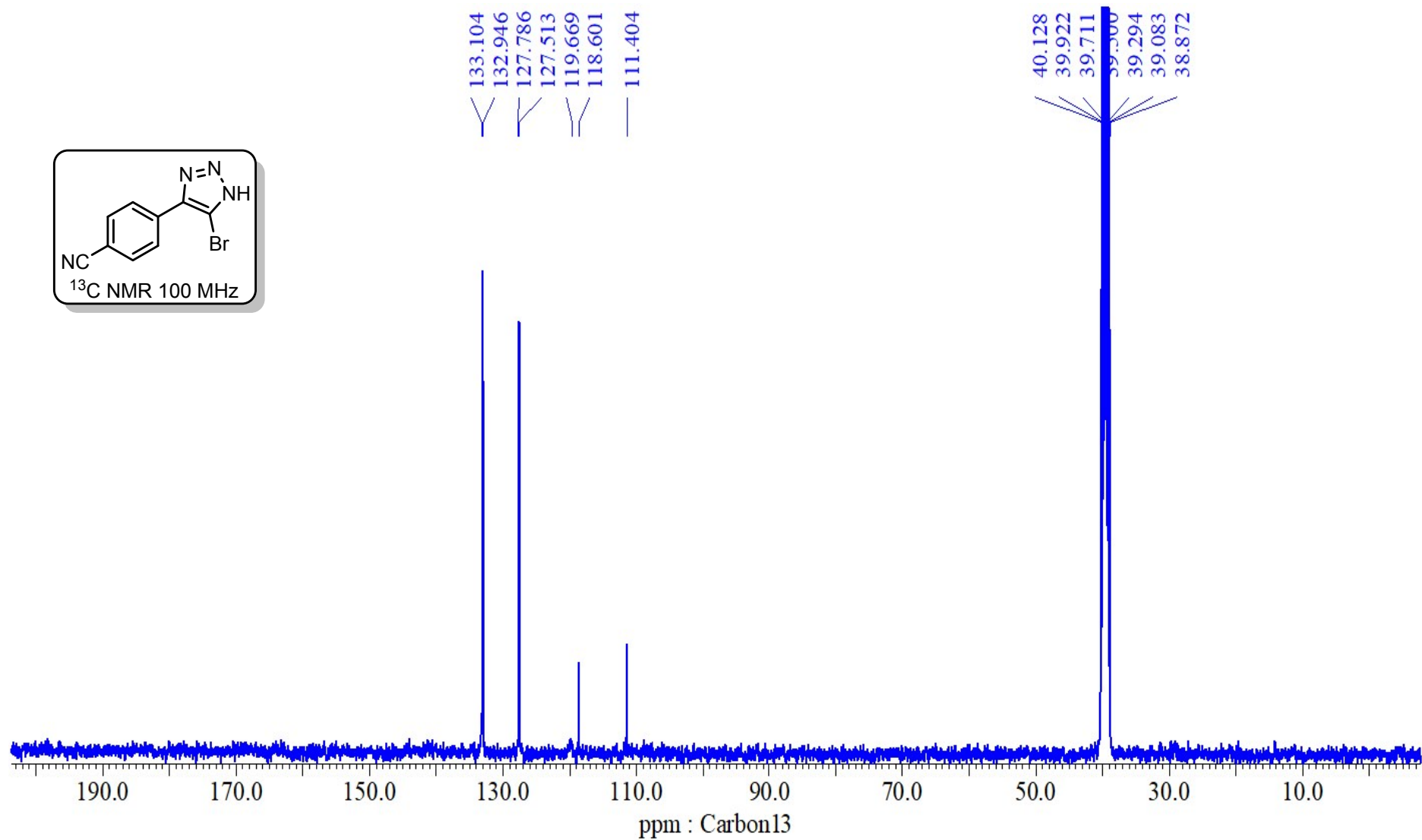


Fig. 16: ¹³C NMR spectrum of 4-(5-bromo-1H-1,2,3-triazol-4-yl)benzonitrile (**2h**)

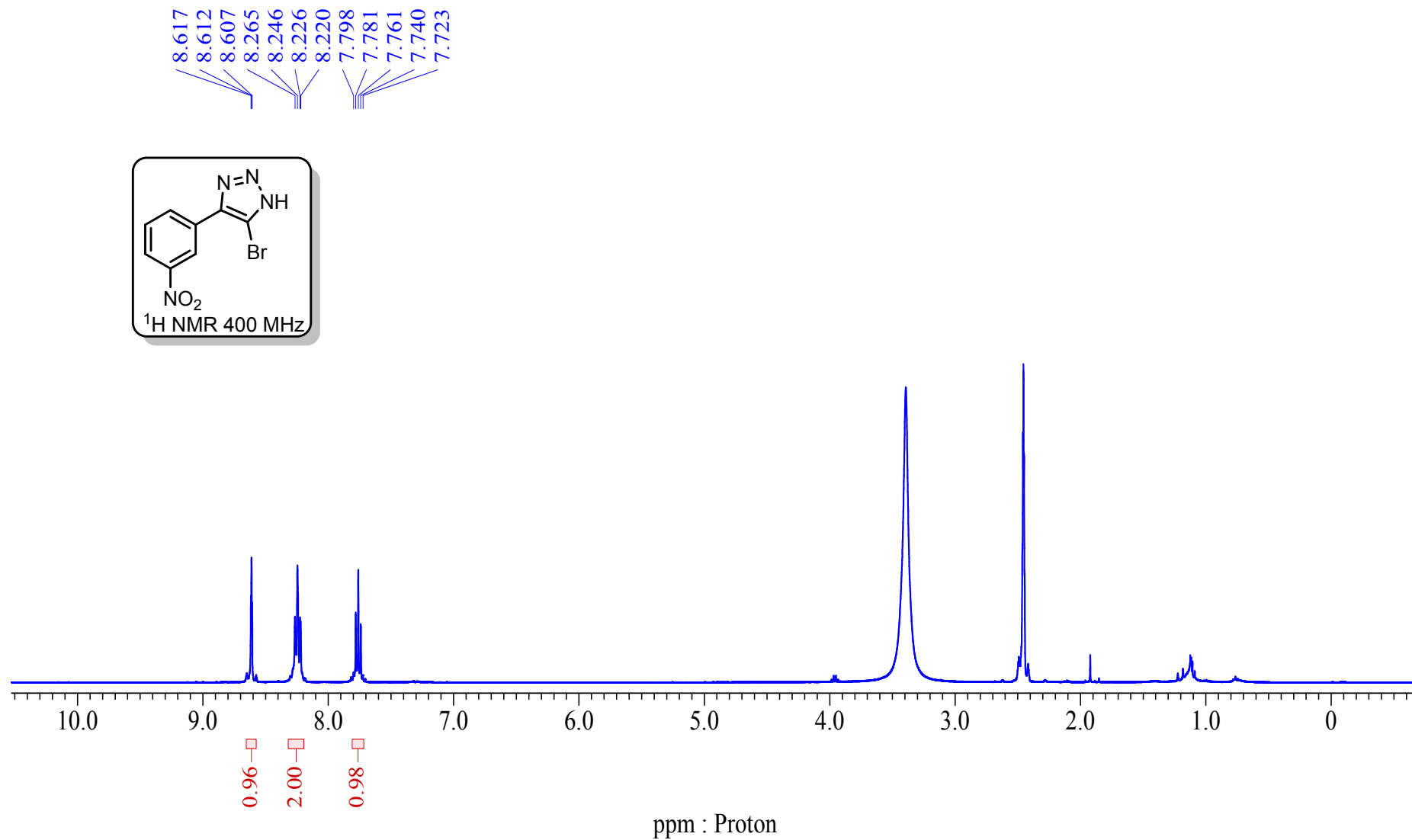


Fig. 17: ¹H NMR spectrum of 5-bromo-4-(3-nitrophenyl)-1H-1,2,3-triazole (**2i**)

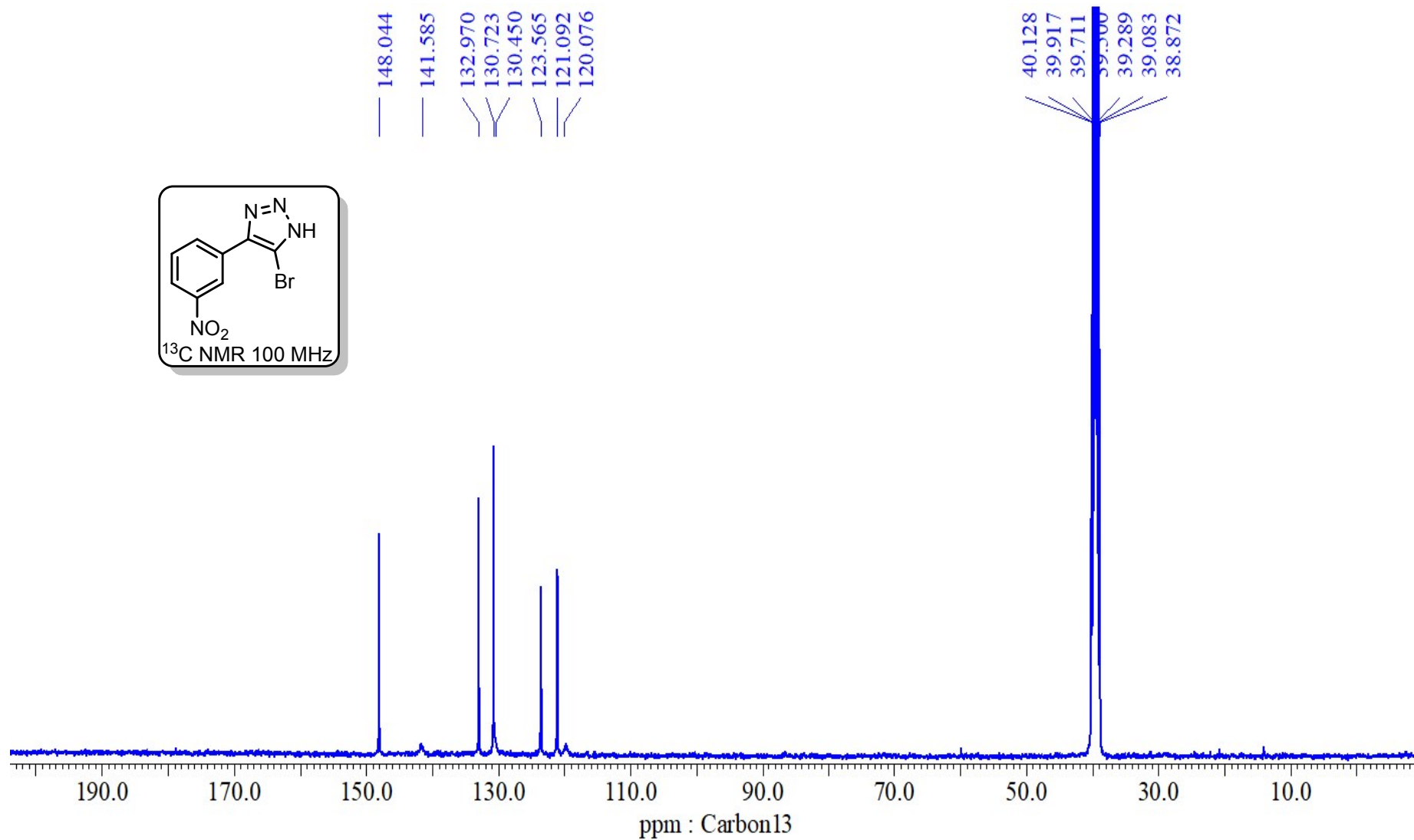


Fig. 18: ¹³C NMR spectrum of 5-bromo-4-(3-nitrophenyl)-1H-1,2,3-triazole (**2i**)

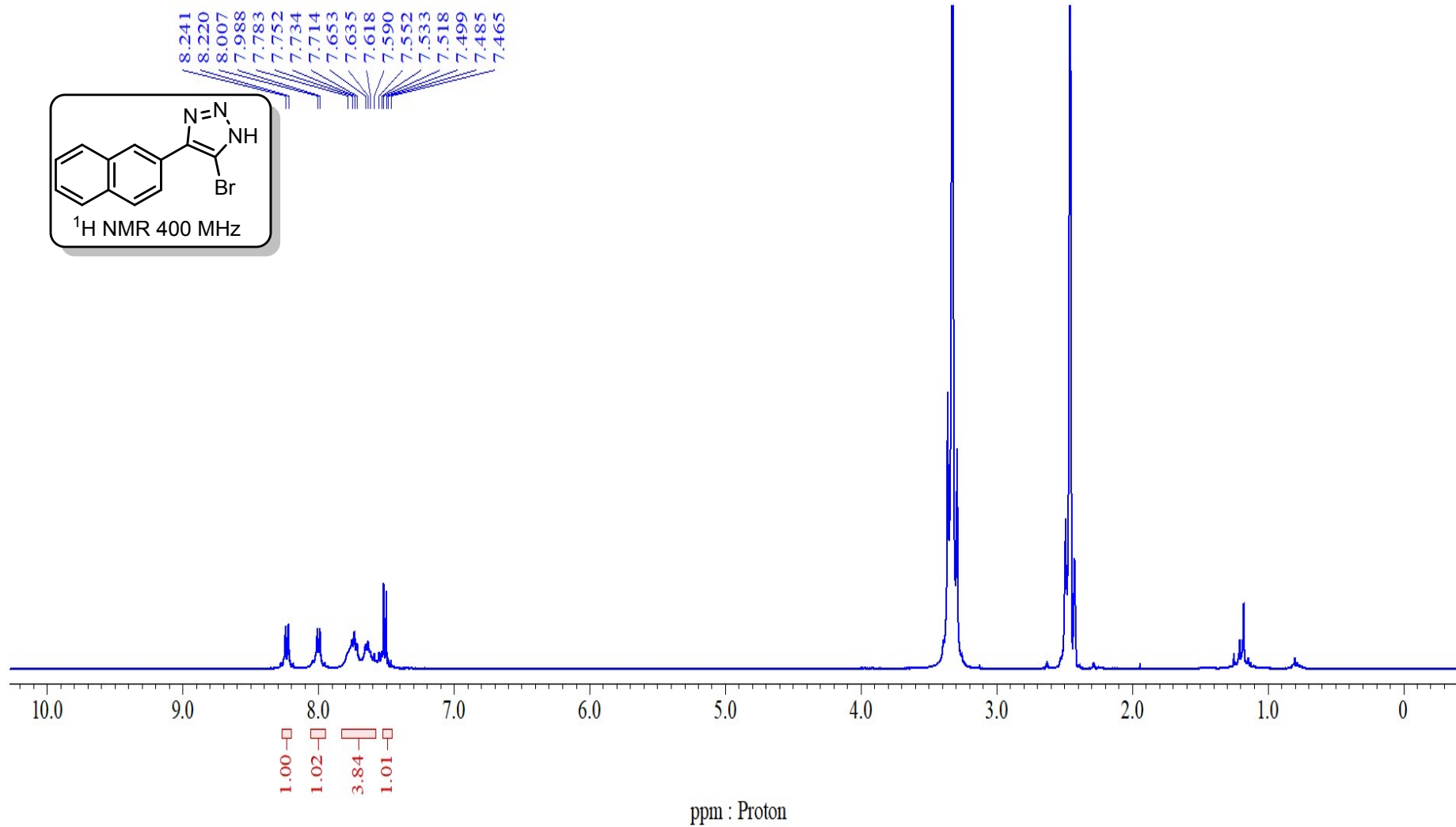


Fig. 19: ¹H NMR spectrum of 5-bromo-4-(naphthalen-2-yl)-1H-1,2,3-triazole (**2j**)

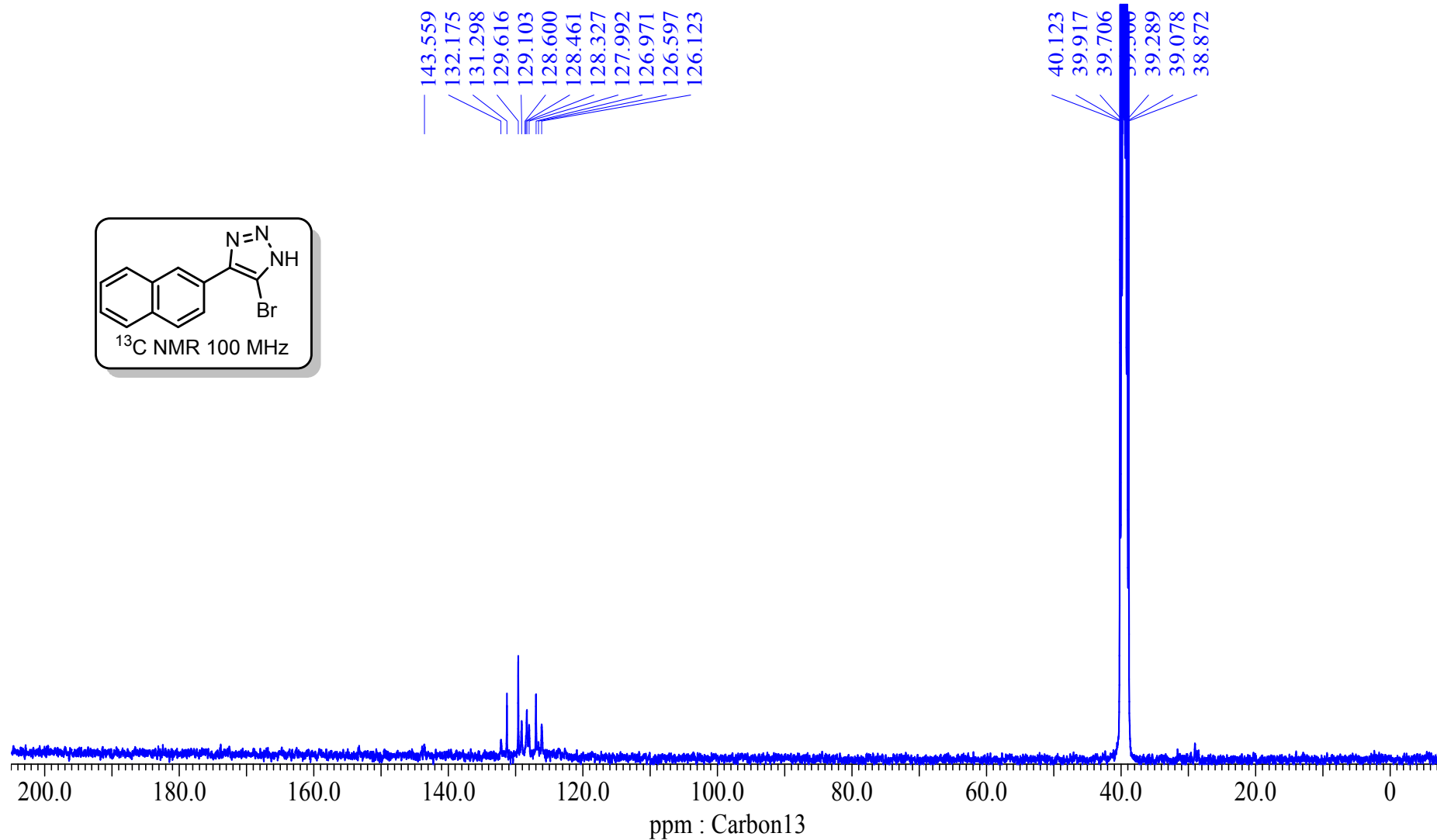


Fig. 20: ¹³C NMR spectrum of 5-bromo-4-(naphthalen-2-yl)-1H-1,2,3-triazole (2j)

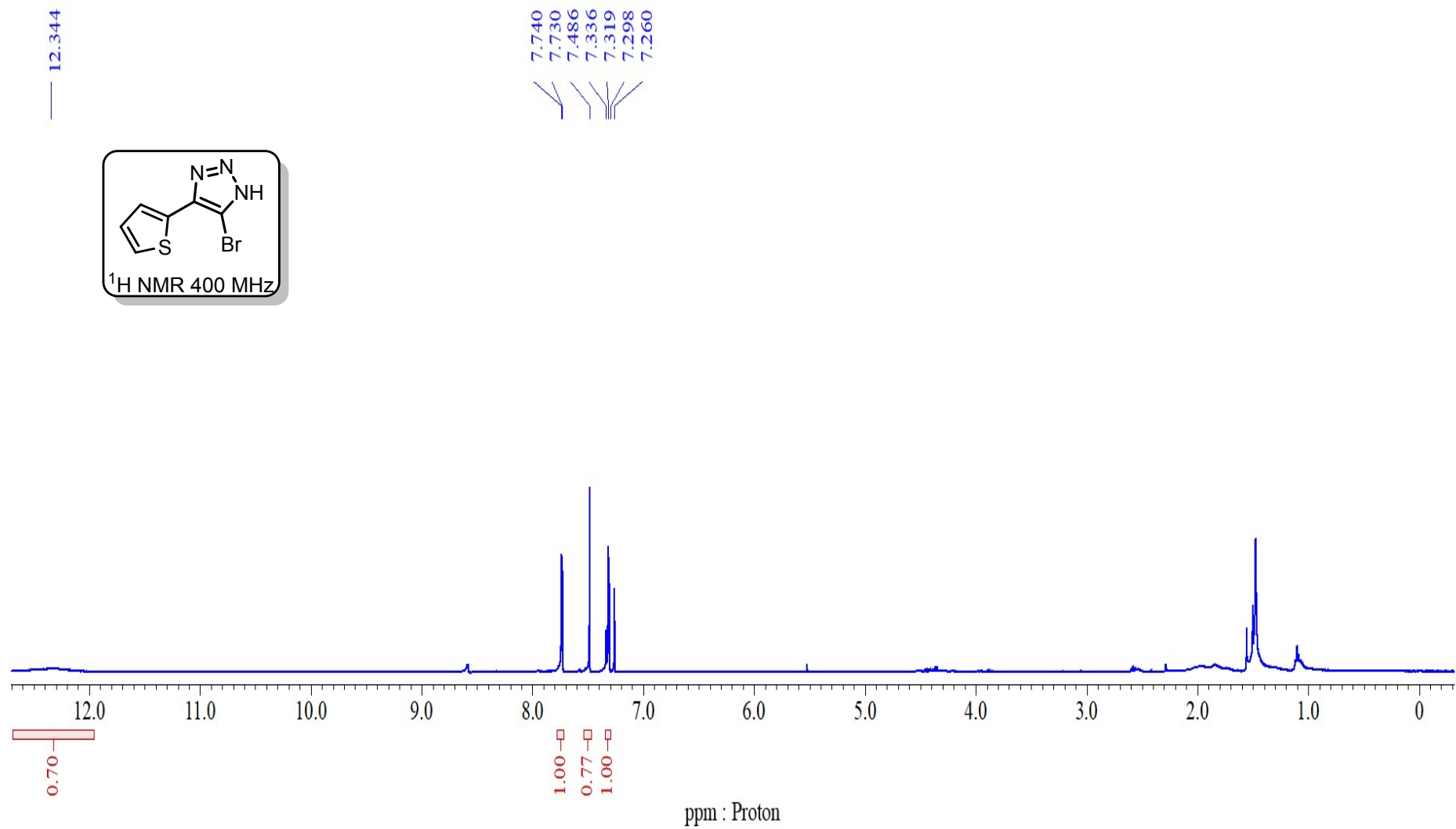


Fig. 21: ¹H NMR spectrum of 5-bromo-4-(thiophen-2-yl)-1H-1,2,3-triazole (**2k**)

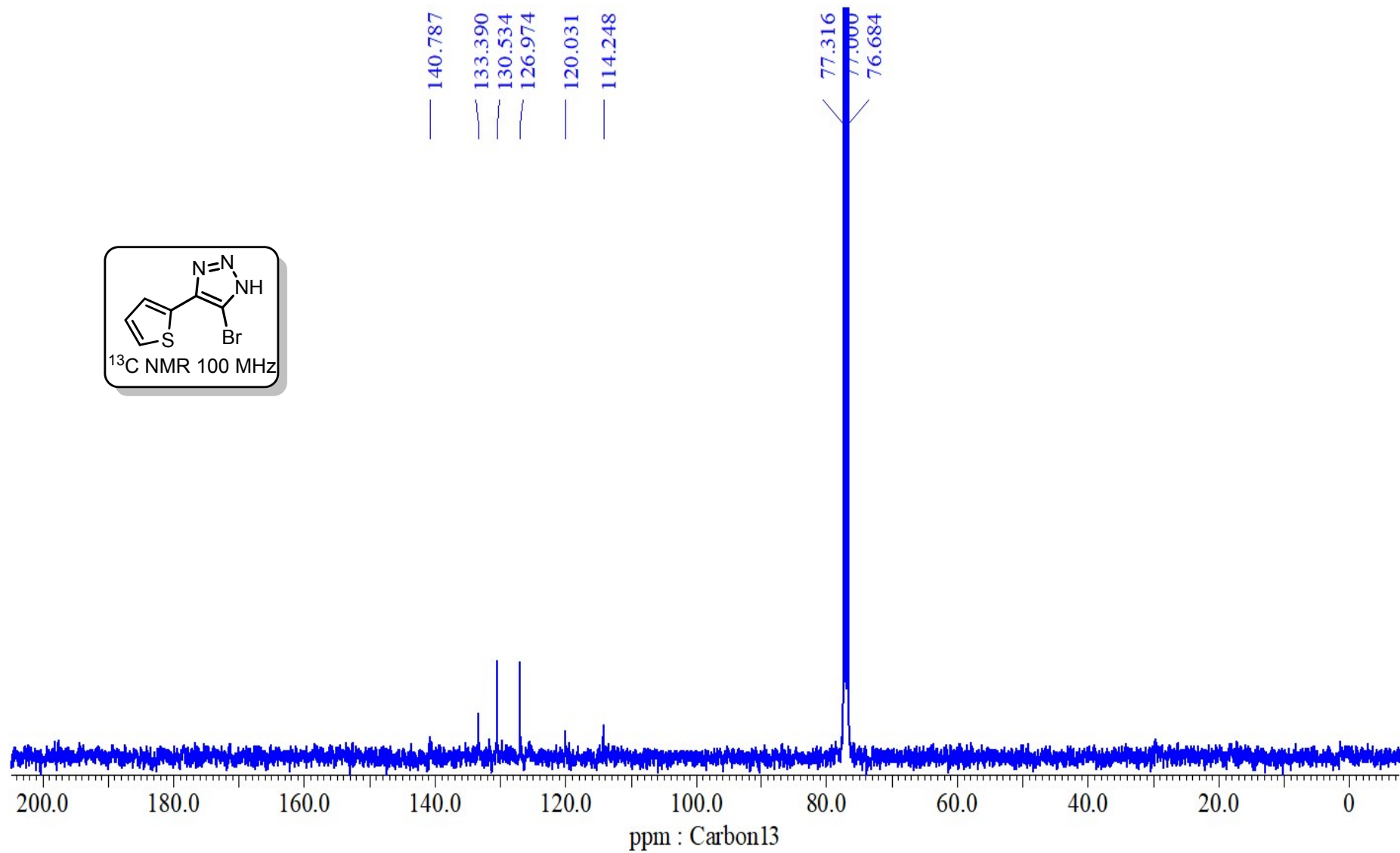


Fig. 22: ¹³C NMR spectrum of 5-bromo-4-(thiophen-2-yl)-1H-1,2,3-triazole (**2k**)

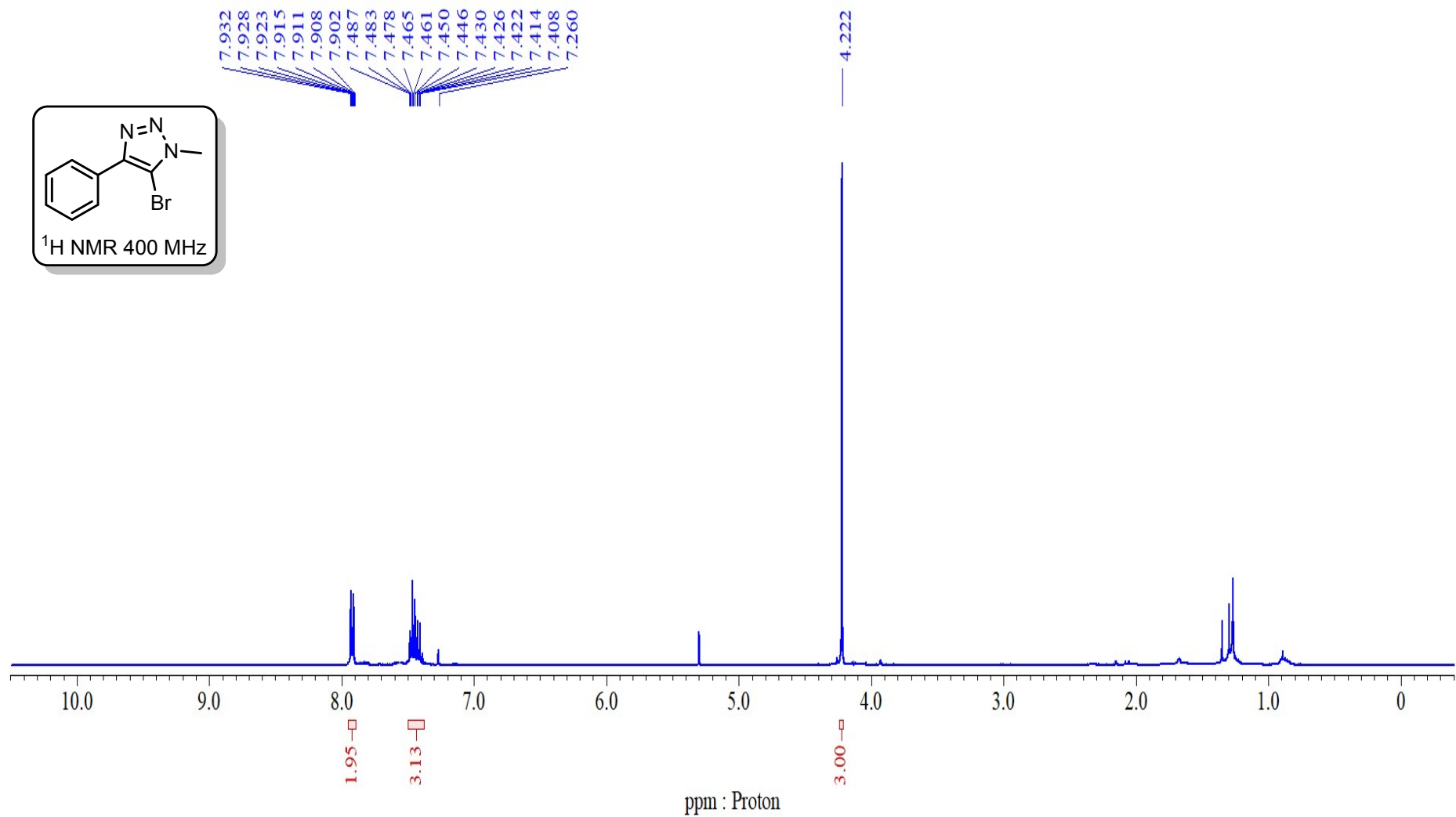


Fig. 23: ¹H NMR spectrum of 5-bromo-1-methyl-4-phenyl-1H-1,2,3-triazole (**21**)

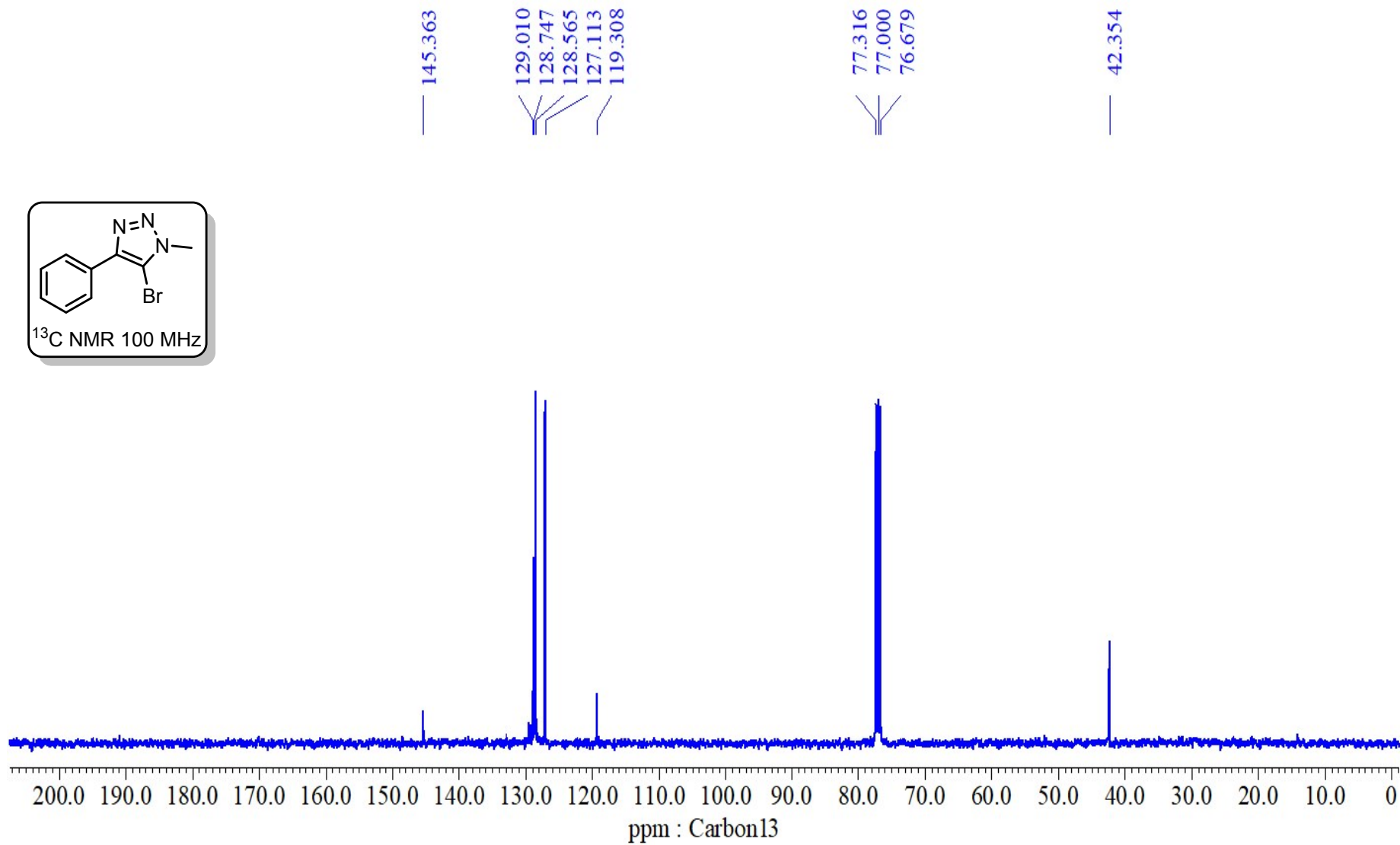
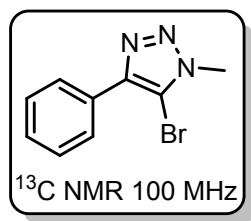


Fig. 24: ¹³C NMR spectrum of 5-bromo-1-methyl-4-phenyl-1H-1,2,3-triazole (**2I**)

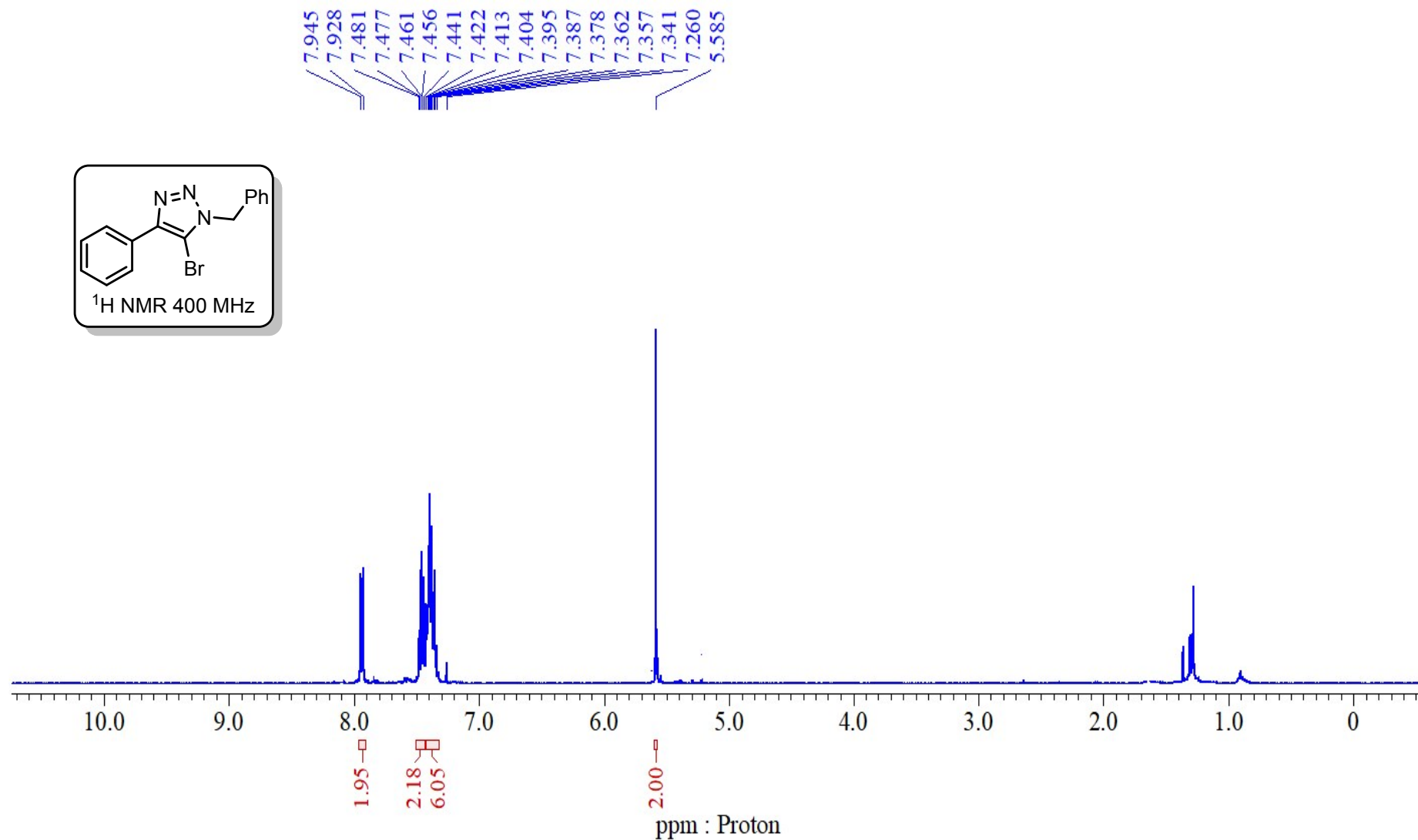


Fig. 25: ¹H NMR spectrum of 1-benzyl-5-bromo-4-phenyl-1H-1,2,3-triazole (**2m**)

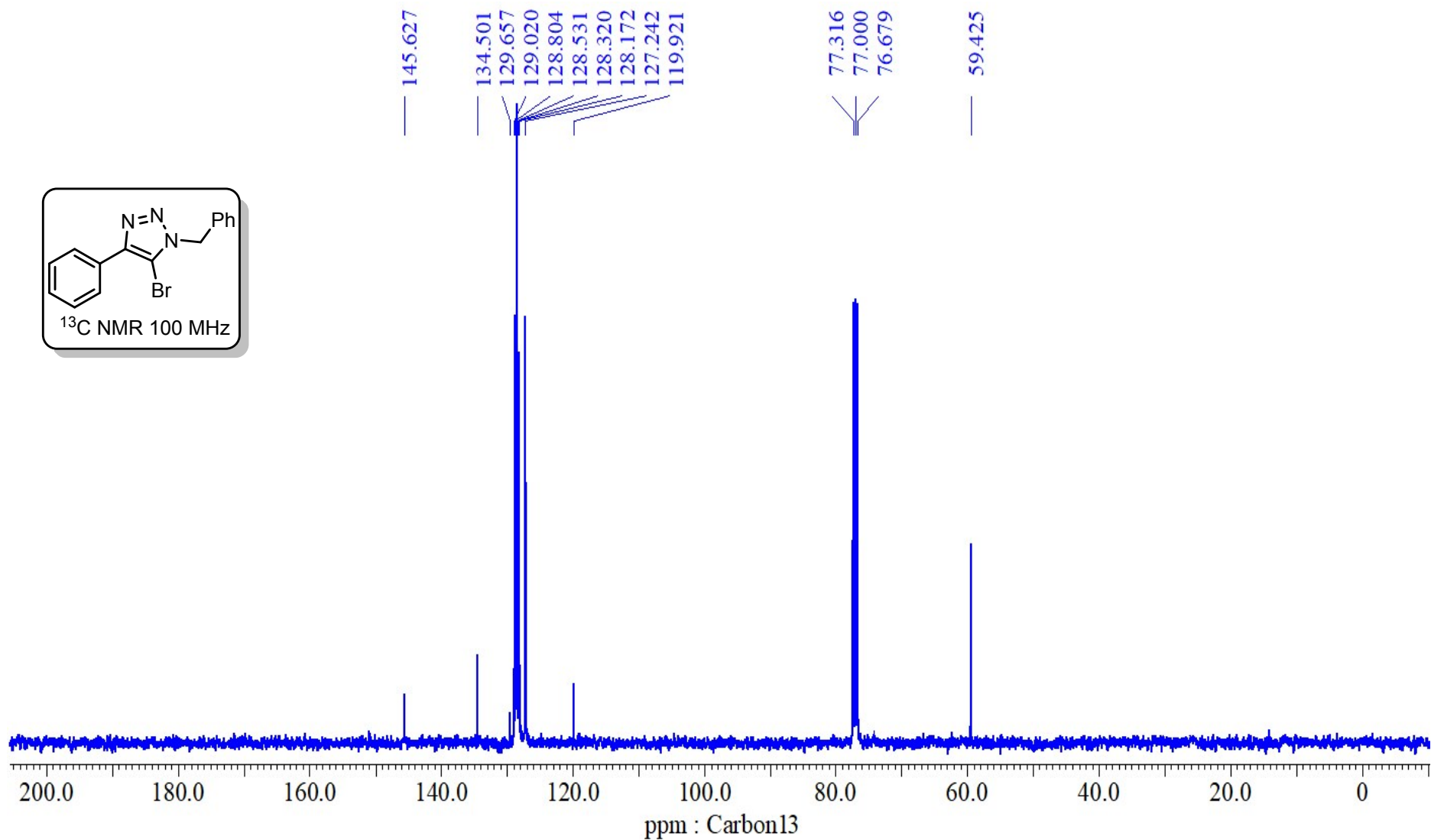


Fig. 26: ¹³C NMR spectrum of 1-benzyl-5-bromo-4-phenyl-1H-1,2,3-triazole (**2m**)

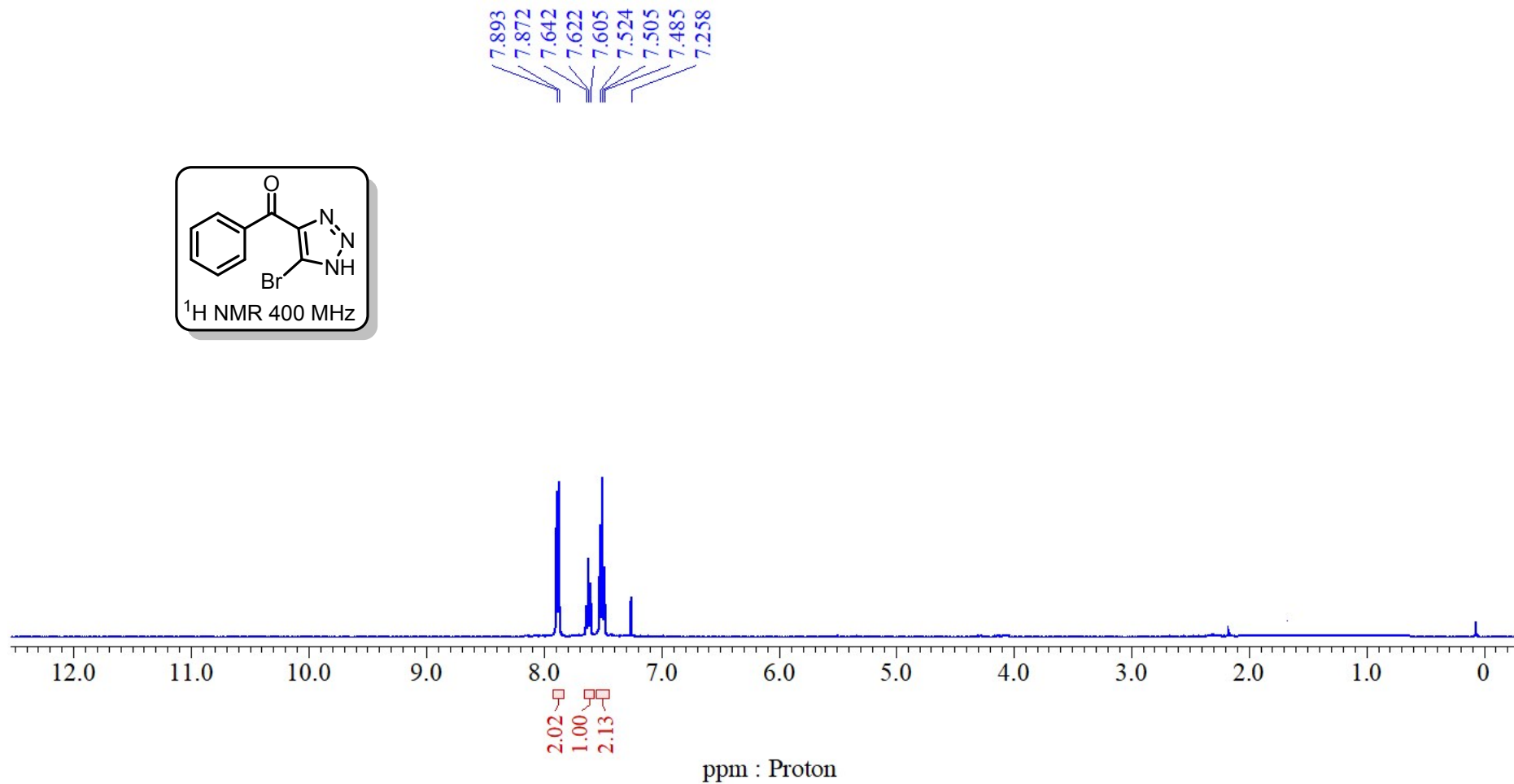


Fig. 27: ¹H NMR spectrum of (5-bromo-1H-1,2,3-triazol-4-yl)(phenyl)methanone (**2n**)

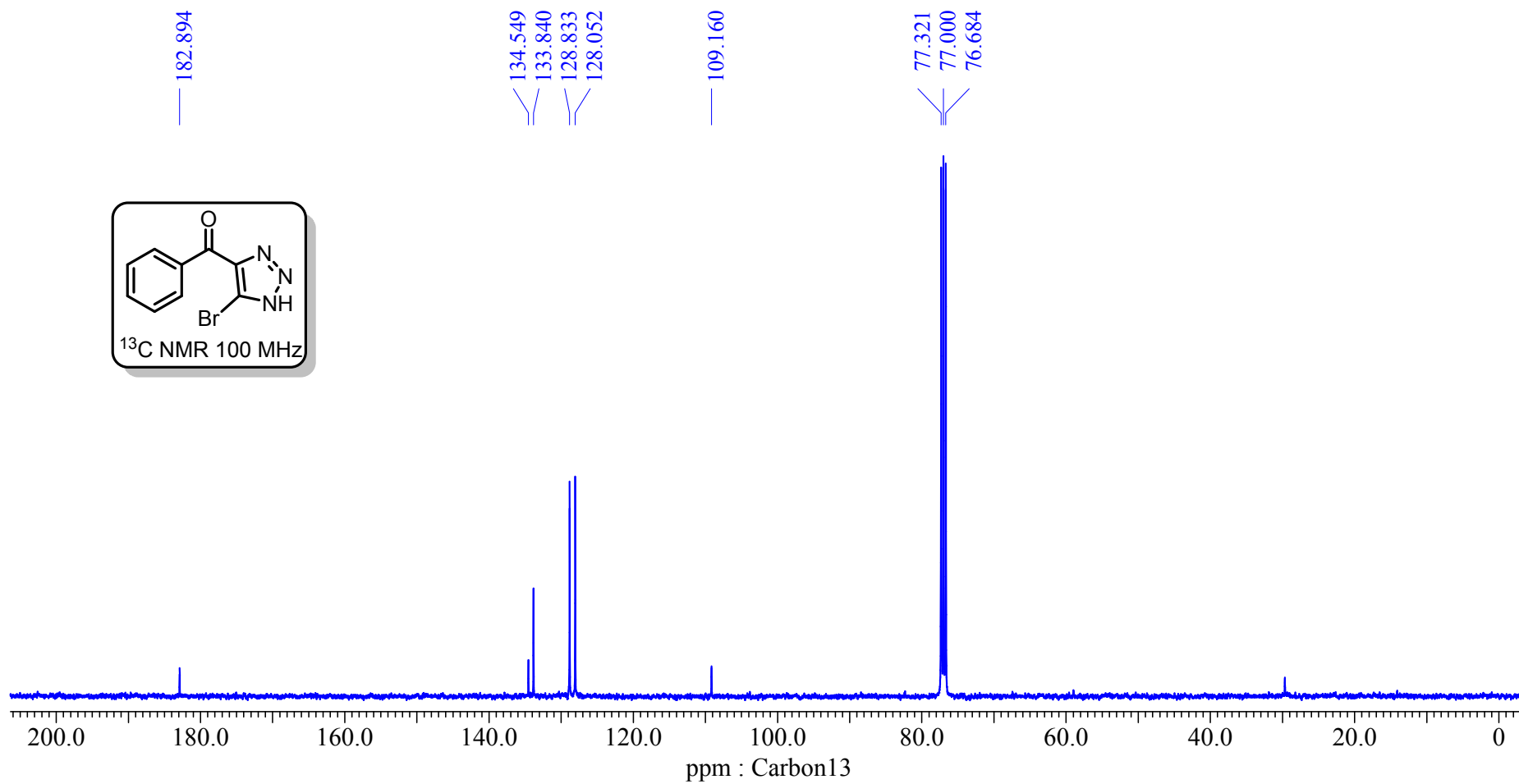


Fig. 28: ¹³C NMR spectrum of 1-benzyl-5-bromo-4-phenyl-1H-1,2,3-triazole (**2n**)

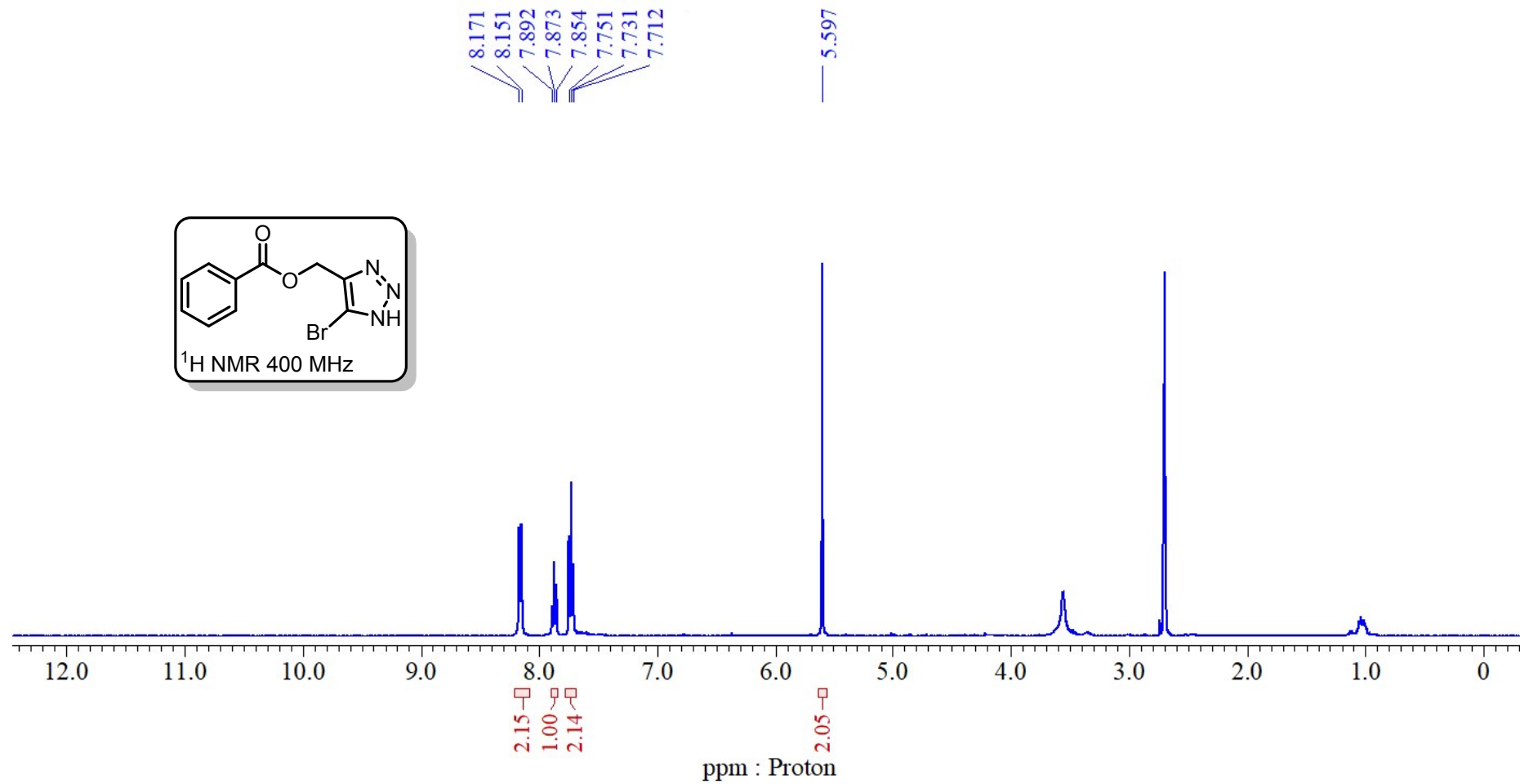


Fig. 29: ¹H NMR spectrum of (5-bromo-1H-1,2,3-triazol-4-yl)methyl benzoate (**2o**)

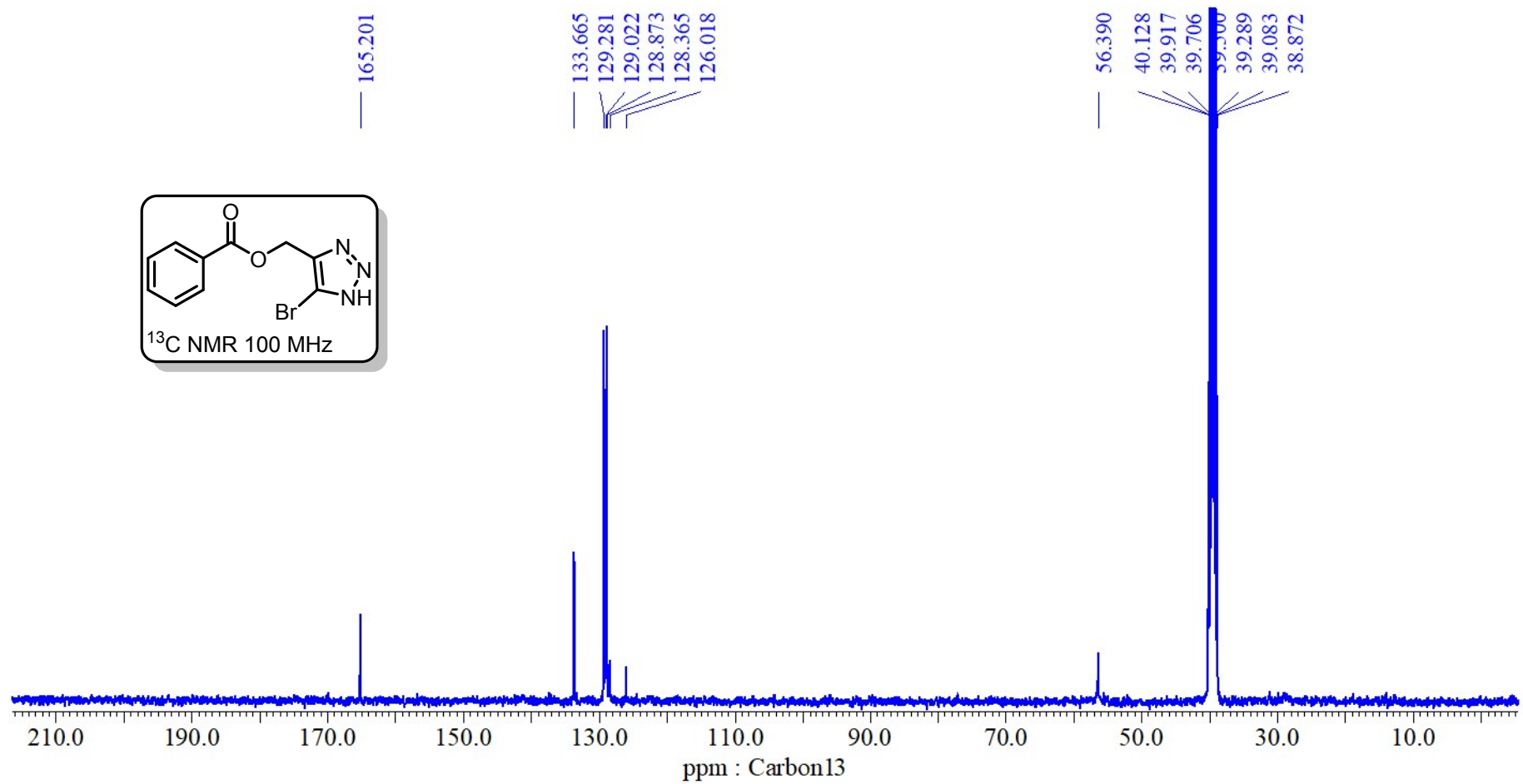


Fig. 30: ¹³C NMR spectrum of (5-bromo-1H-1,2,3-triazol-4-yl)methyl benzoate (**2o**)

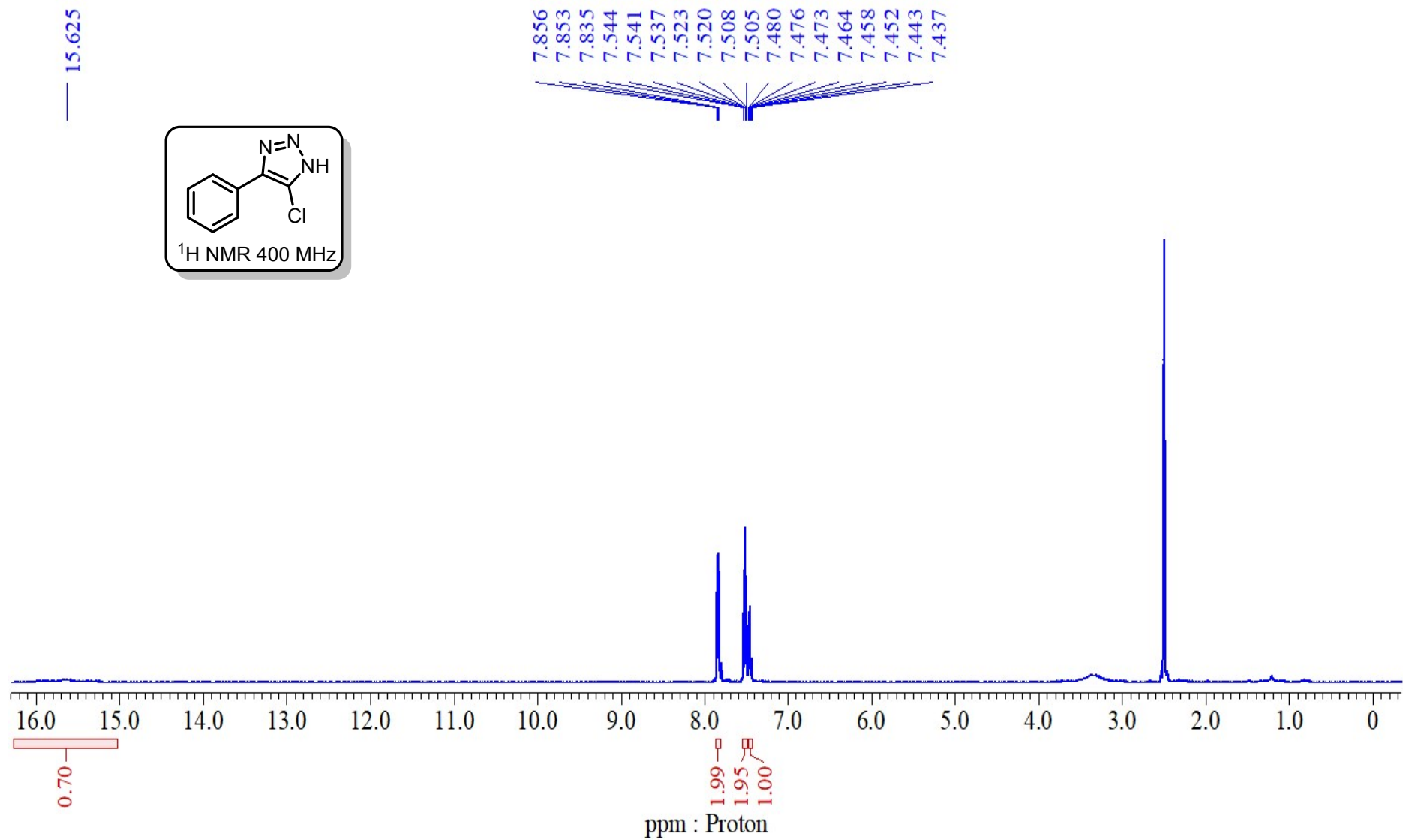


Fig. 31: ¹H NMR spectrum of 5-chloro-4-phenyl-1H-1,2,3-triazole (**3a**)

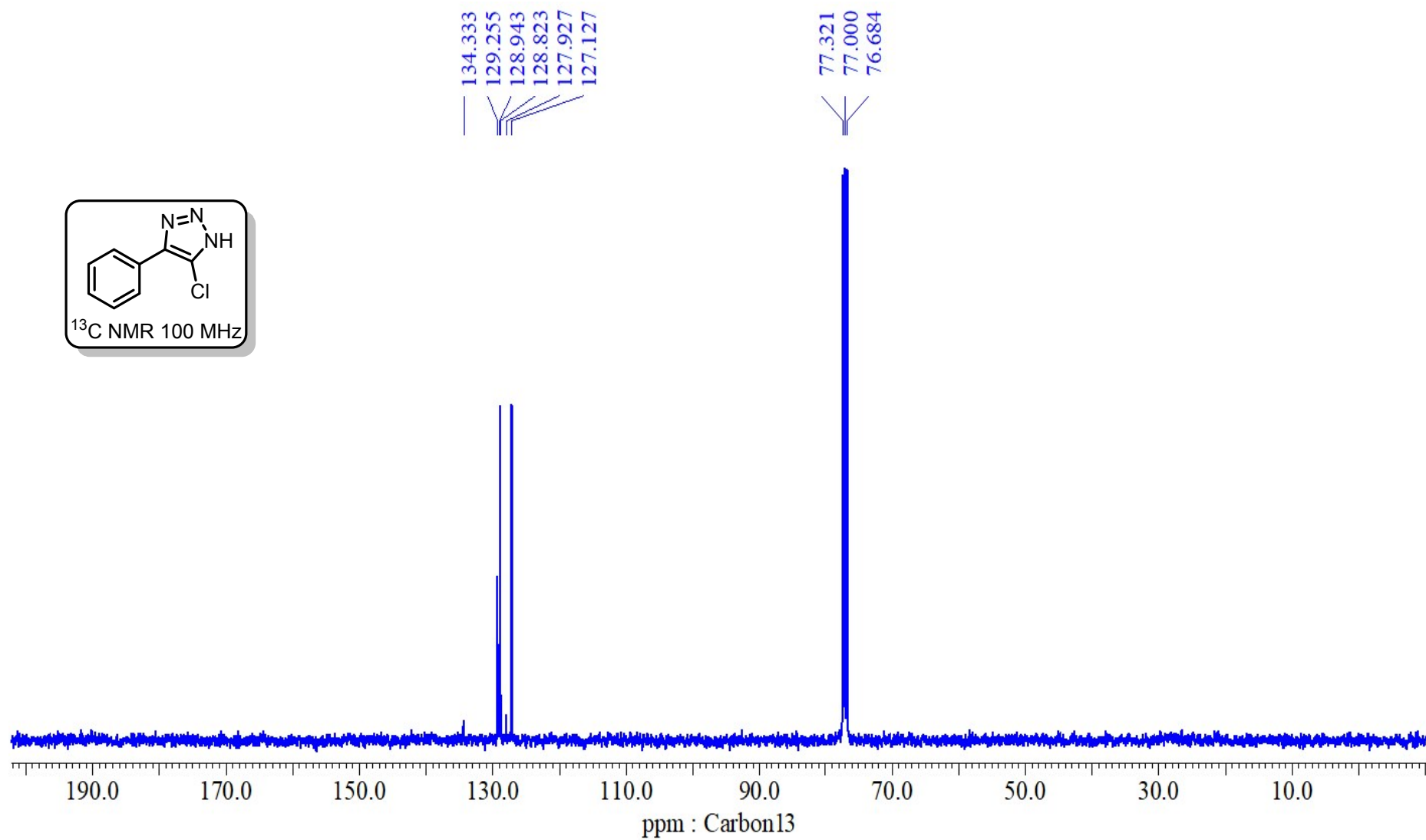


Fig. 32: ¹³C NMR spectrum of 5-chloro-4-phenyl-1H-1,2,3-triazole (**3a**)

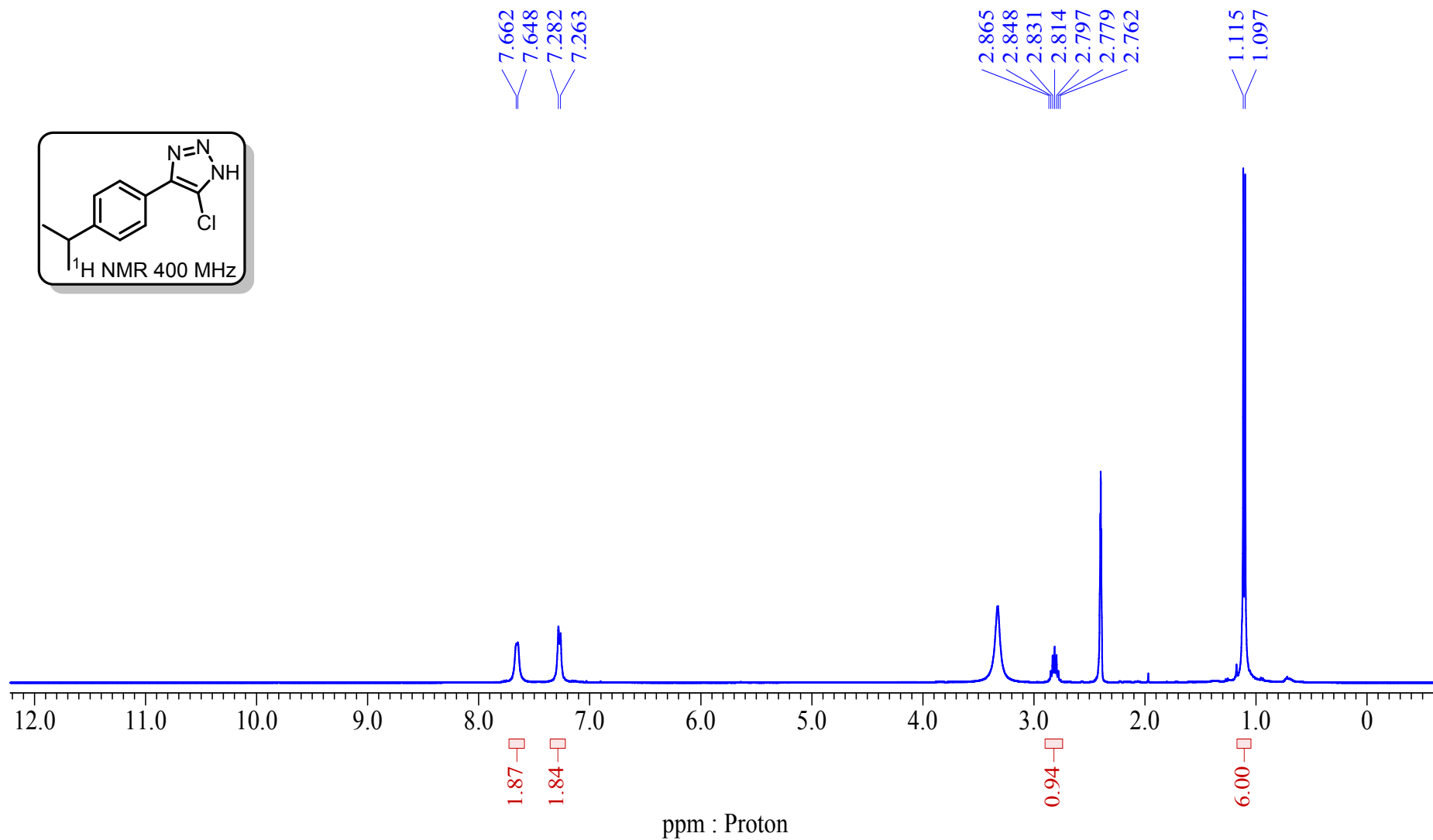


Fig. 33: ¹H NMR spectrum of 5-chloro-4-(4-isopropylphenyl)-1H-1,2,3-triazole (**3b**)

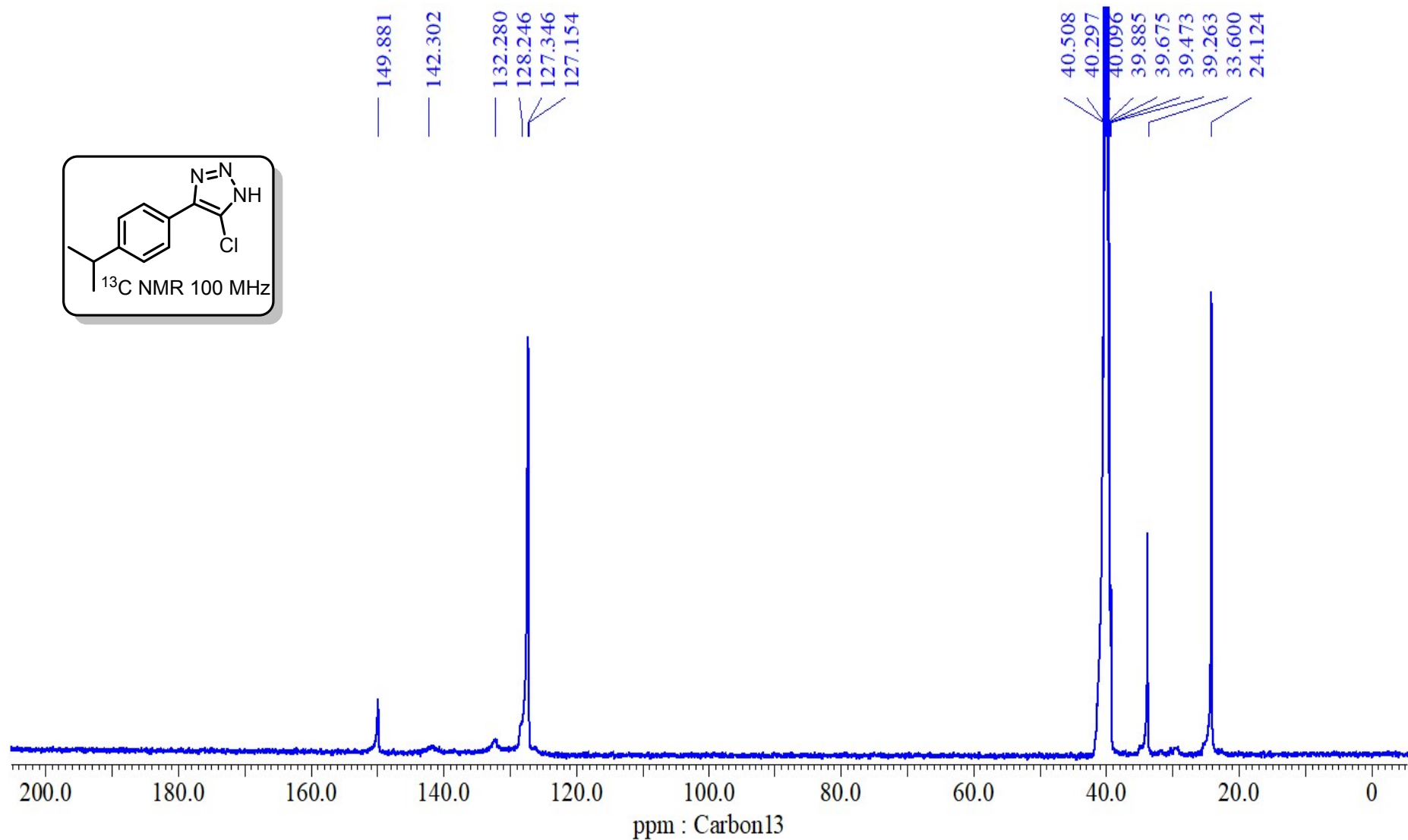


Fig. 34: ¹³C NMR spectrum of 5-chloro-4-(4-isopropylphenyl)-1H-1,2,3-triazole (**3b**)

7.731
7.728
7.712
7.694
7.445
7.441
7.432
7.427
7.413
7.407
7.393
7.389
7.260
7.257
7.241
7.238
7.222
7.219
7.193
7.172
7.169
7.166
7.146

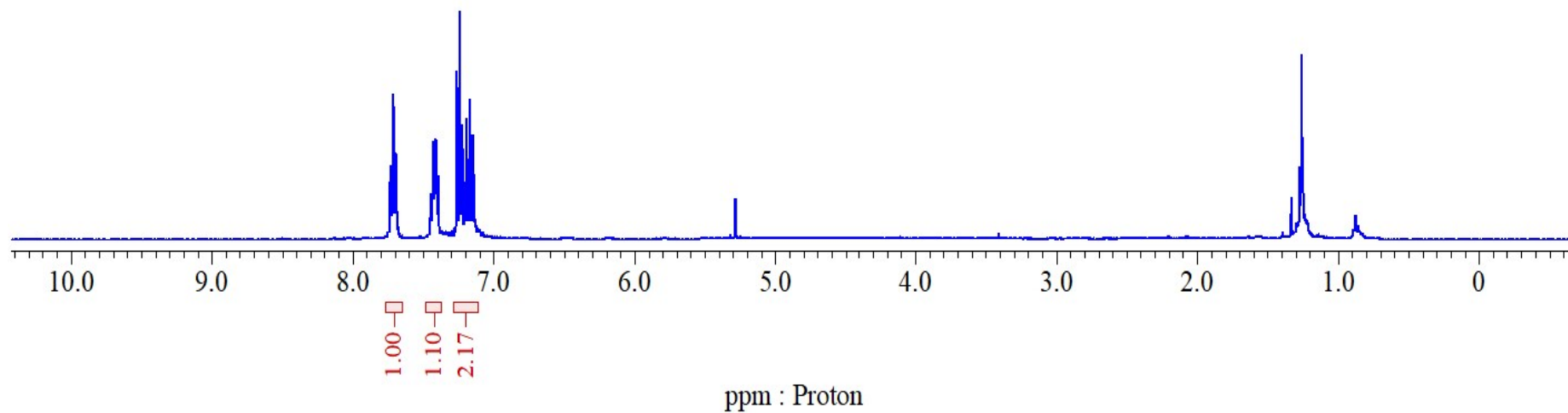
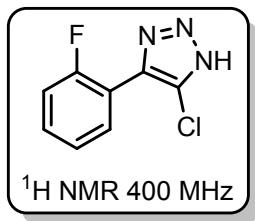


Fig. 35: ¹H NMR spectrum of 5-chloro-4-(2-fluorophenyl)-1H-1,2,3-triazole (**3c**)

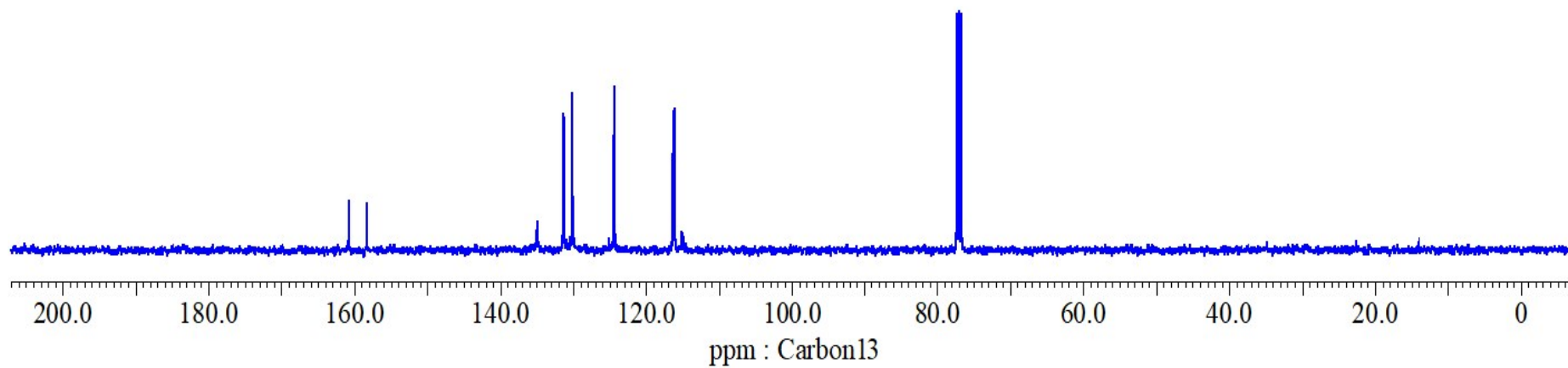
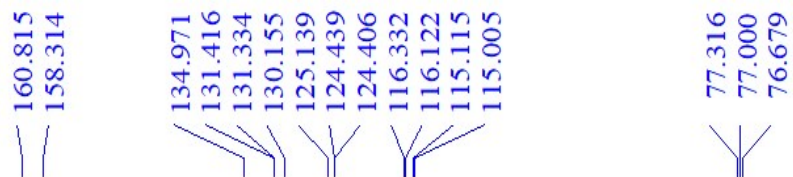
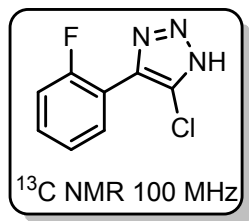


Fig. 36: ^{13}C NMR spectrum of 5-chloro-4-(2-fluorophenyl)-1H-1,2,3-triazole (**3c**)

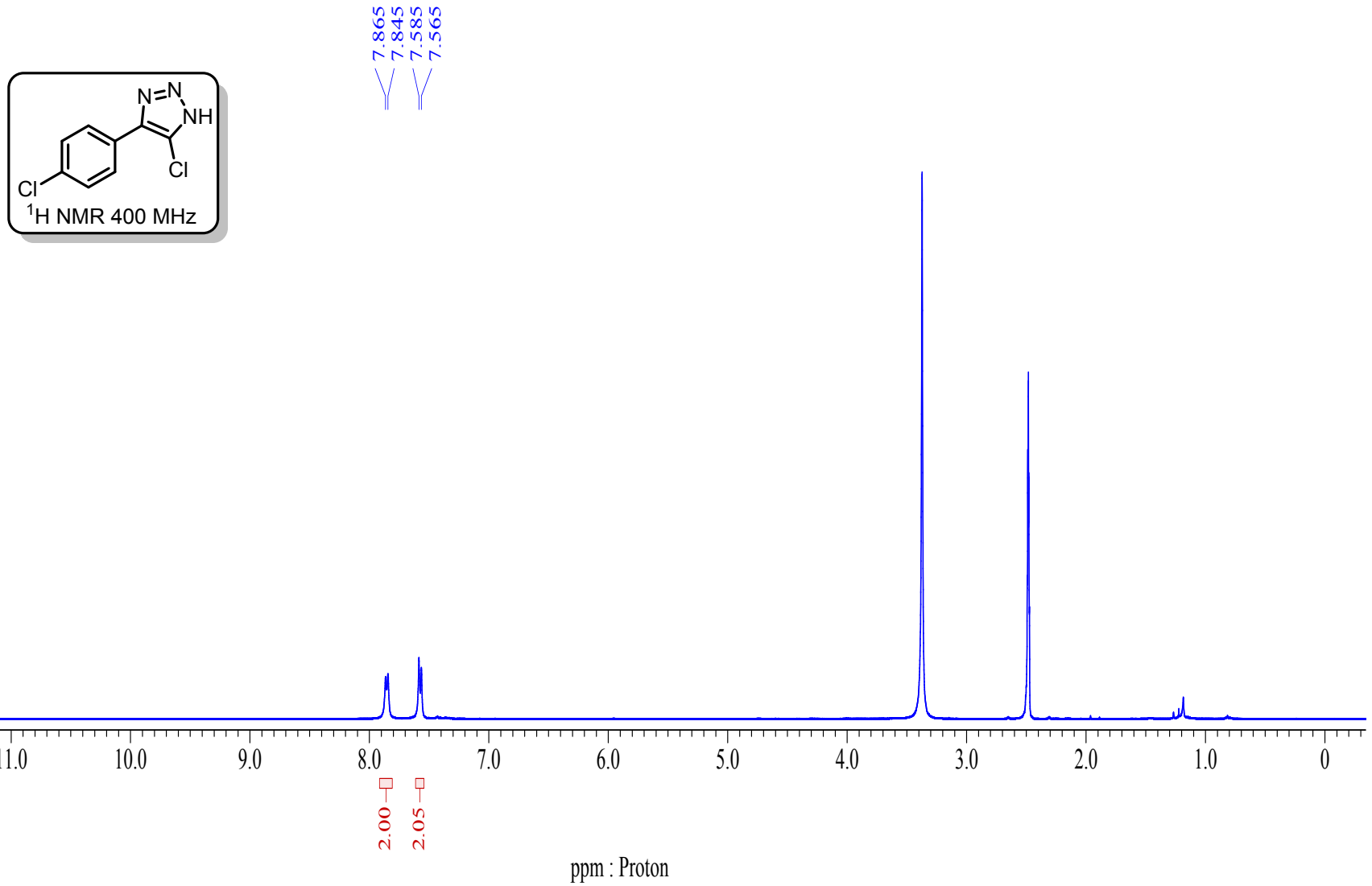


Fig. 37: ^1H NMR spectrum of 5-chloro-4-(4-chlorophenyl)-1H-1,2,3-triazole (**3d**)

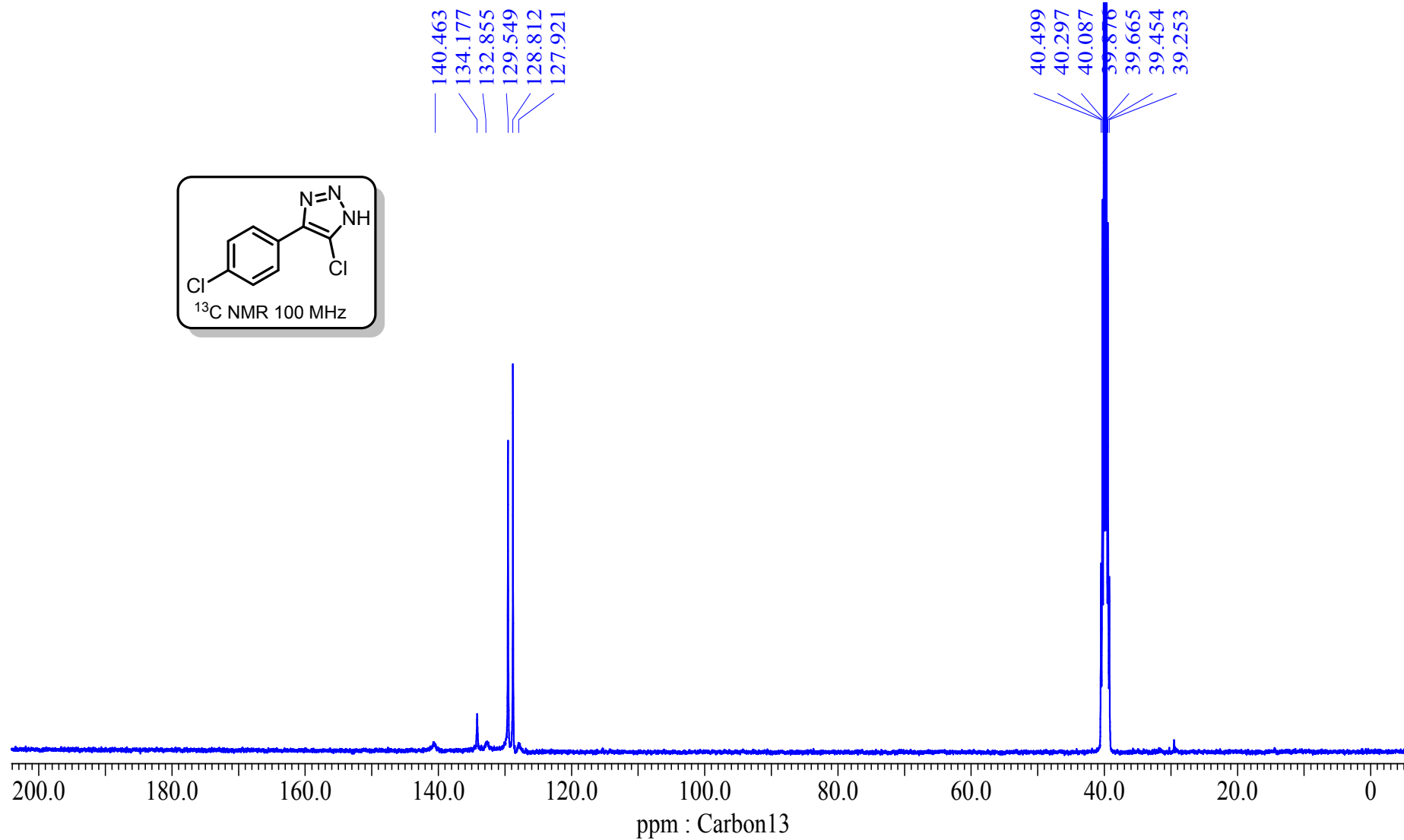
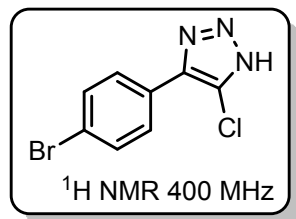


Fig. 38: ¹³C NMR spectrum of 5-chloro-4-(4-chlorophenyl)-1H-1,2,3-triazole (**3d**)



7.750
7.729
7.643
7.622

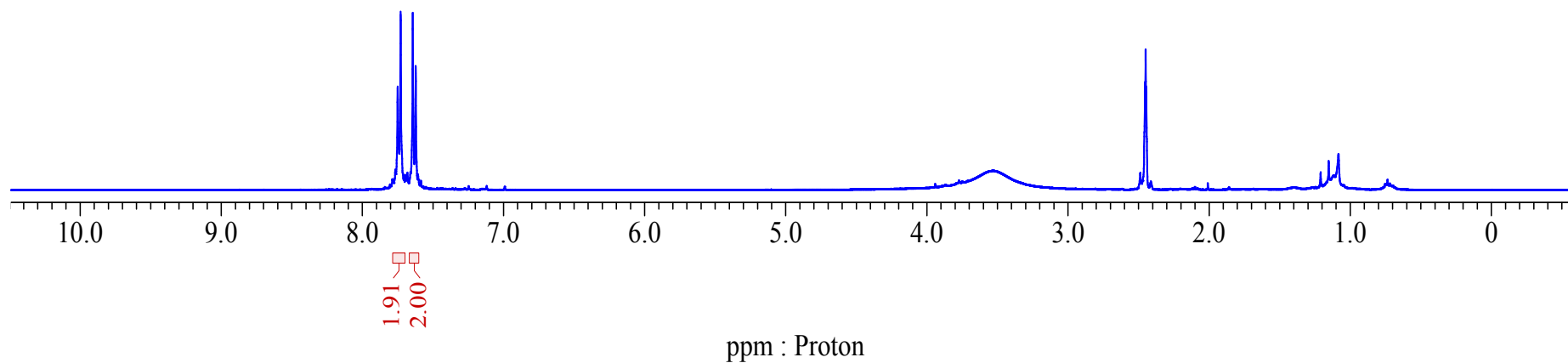


Fig. 39: ¹H NMR spectrum of 4-(4-bromophenyl)-5-chloro-1H-1,2,3-triazole (**3e**)

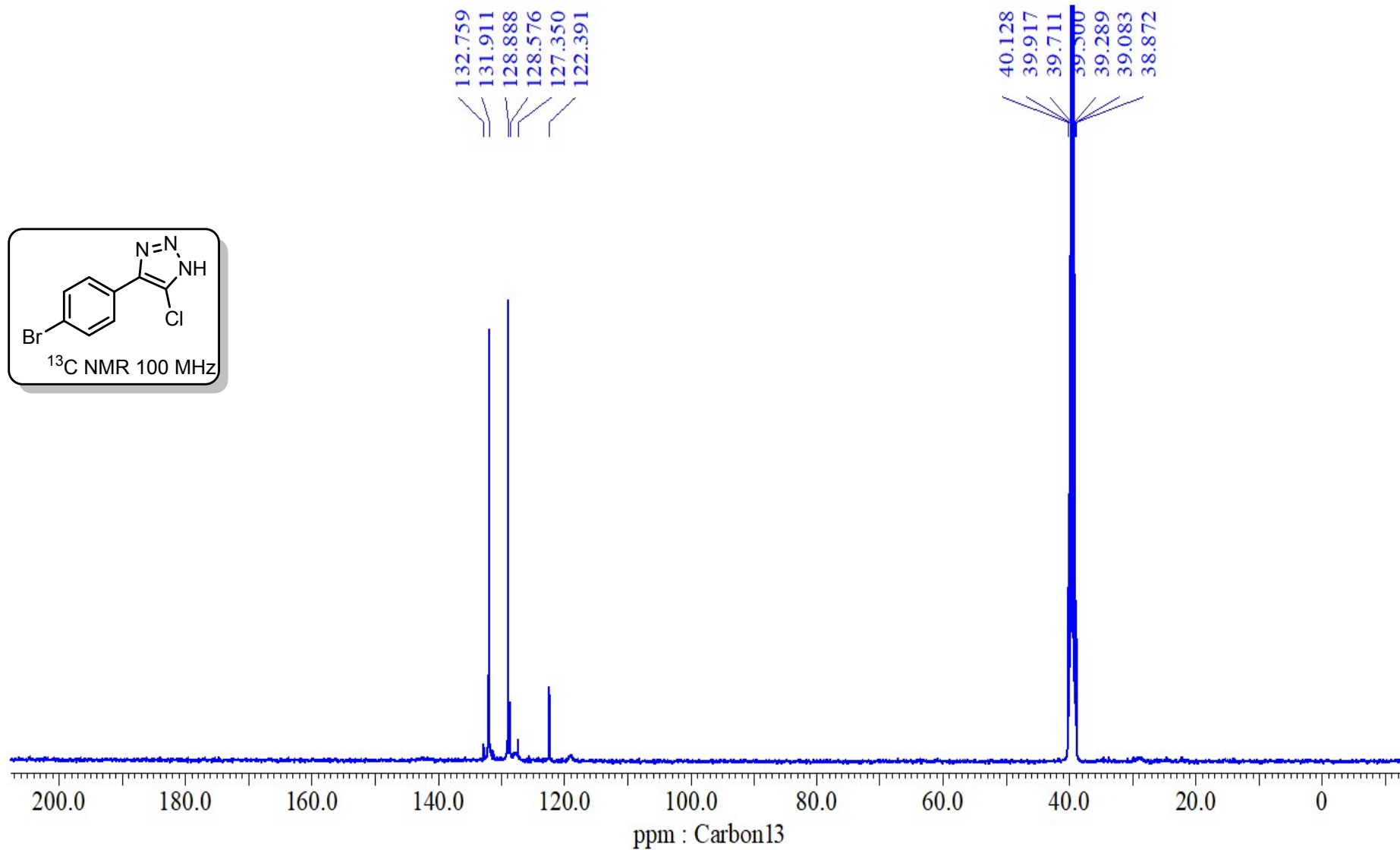


Fig. 40: ^{13}C NMR spectrum of 4-(4-bromophenyl)-5-chloro-1H-1,2,3-triazole (**3e**)

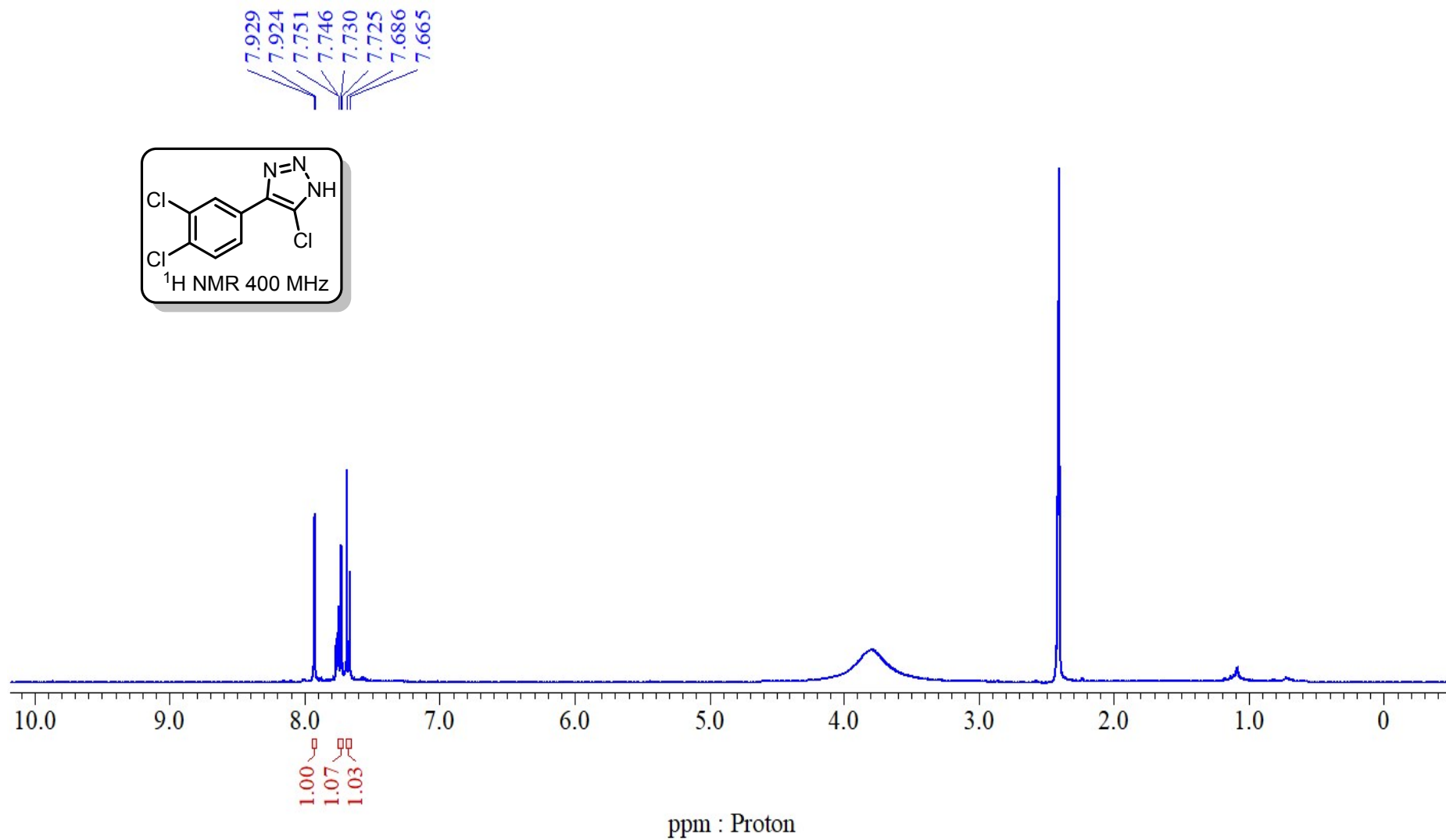


Fig. 41: ¹H NMR spectrum of 4-(3-bromo-4-fluorophenyl)-5-chloro-1H-1,2,3-triazole (**3f**)

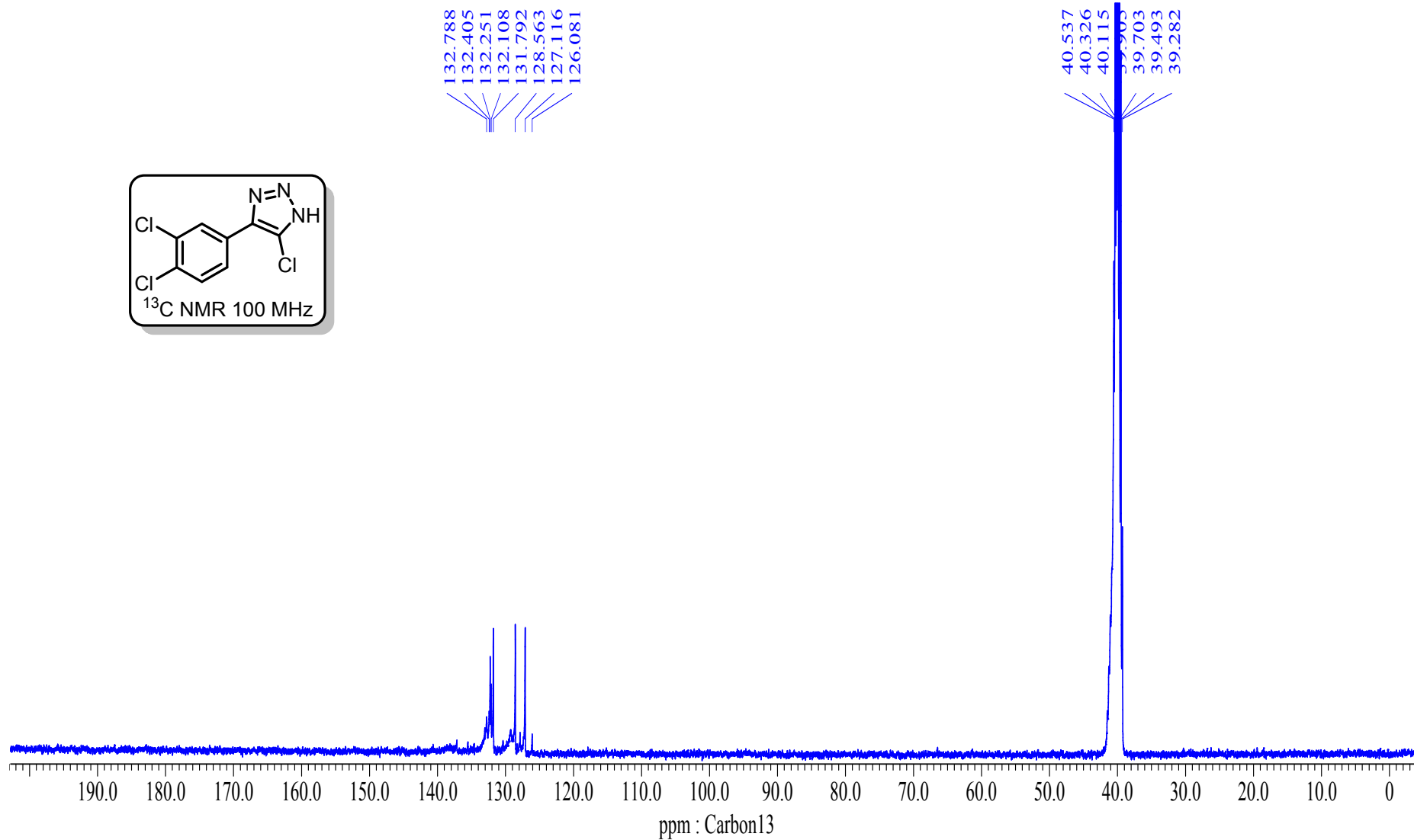


Fig. 42: ¹³C NMR spectrum of 5-chloro-4-(3,4-dichlorophenyl)-1H-1,2,3-triazole (**3f**)

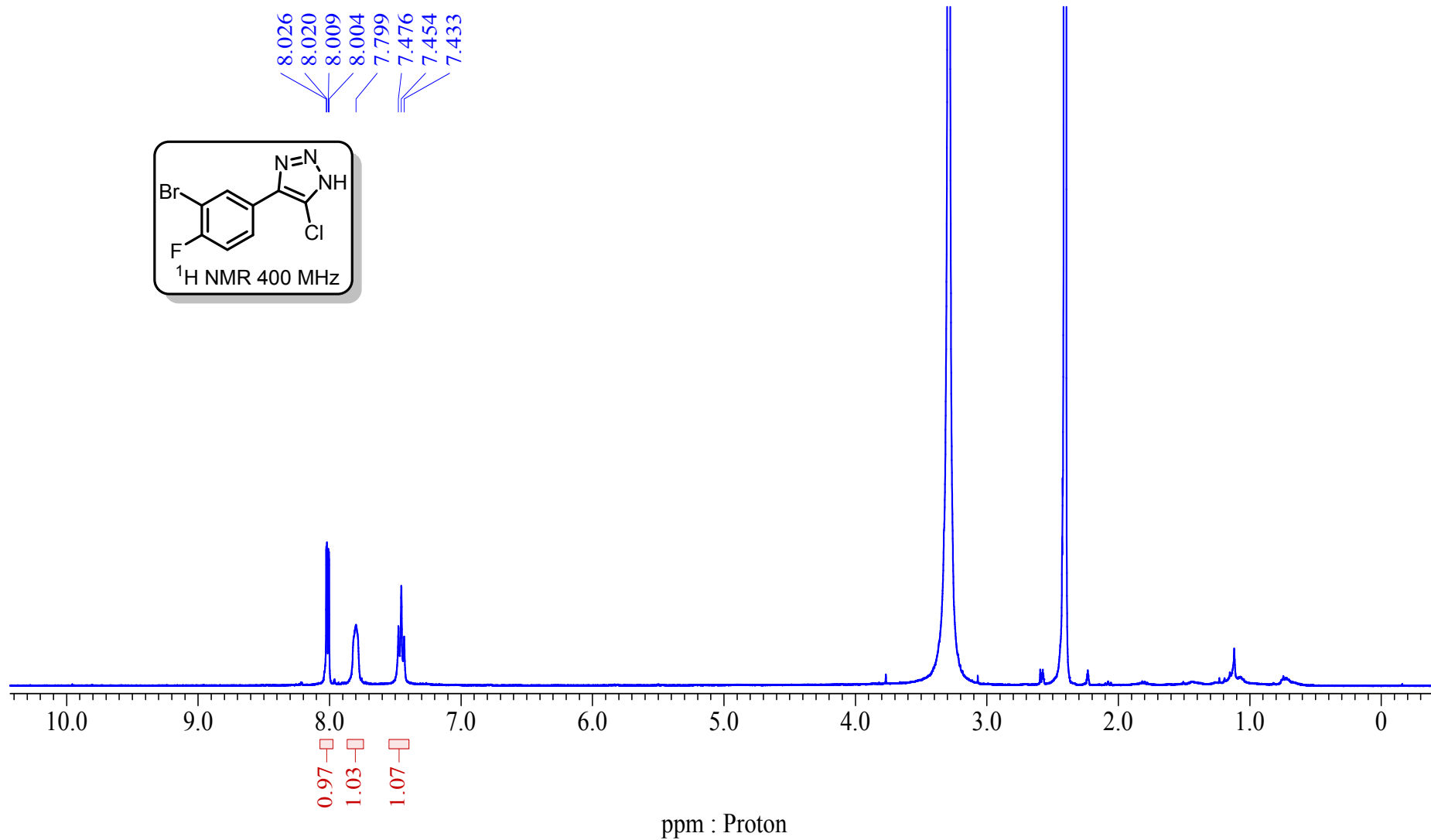


Fig. 43: ¹H NMR spectrum of 4-(3-bromo-4-fluorophenyl)-5-chloro-1H-1,2,3-triazole (**3g**)

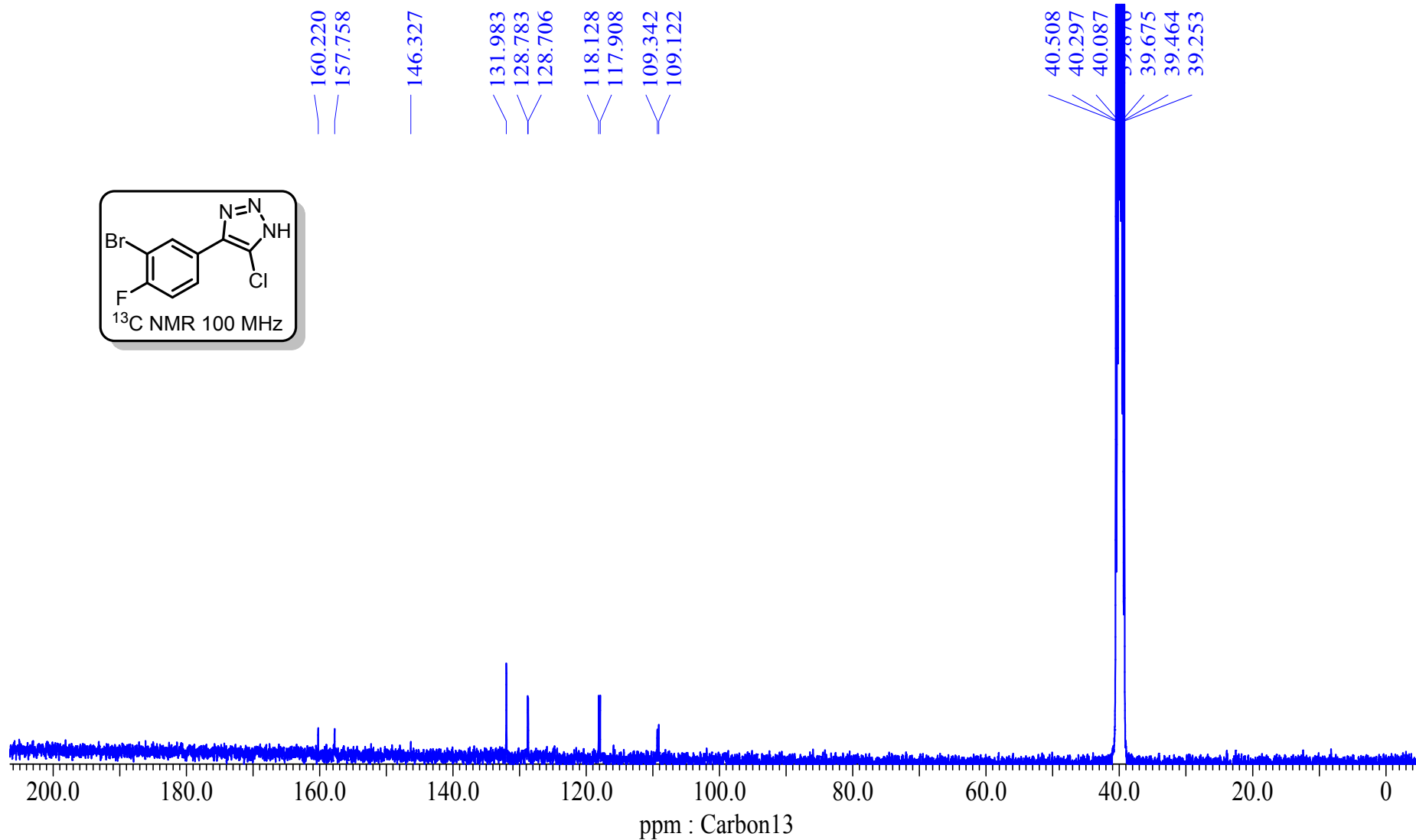


Fig. 44: ¹³C NMR spectrum of 4-(3-bromo-4-fluorophenyl)-5-chloro-1H-1,2,3-triazole (**3g**)

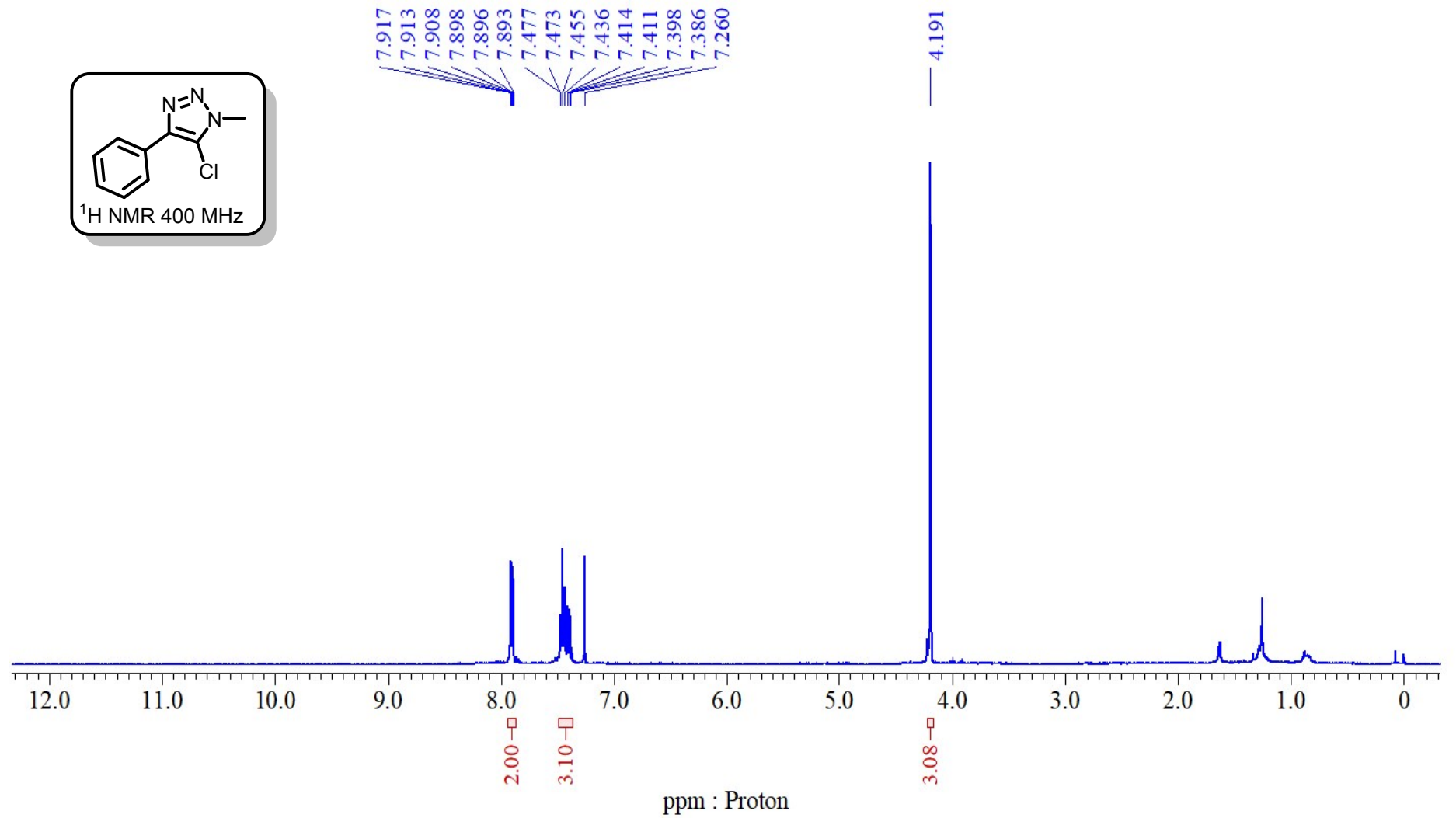


Fig. 45: ¹H NMR of 5-chloro-1-methyl-4-phenyl-1H-1,2,3-triazole (**3h**)

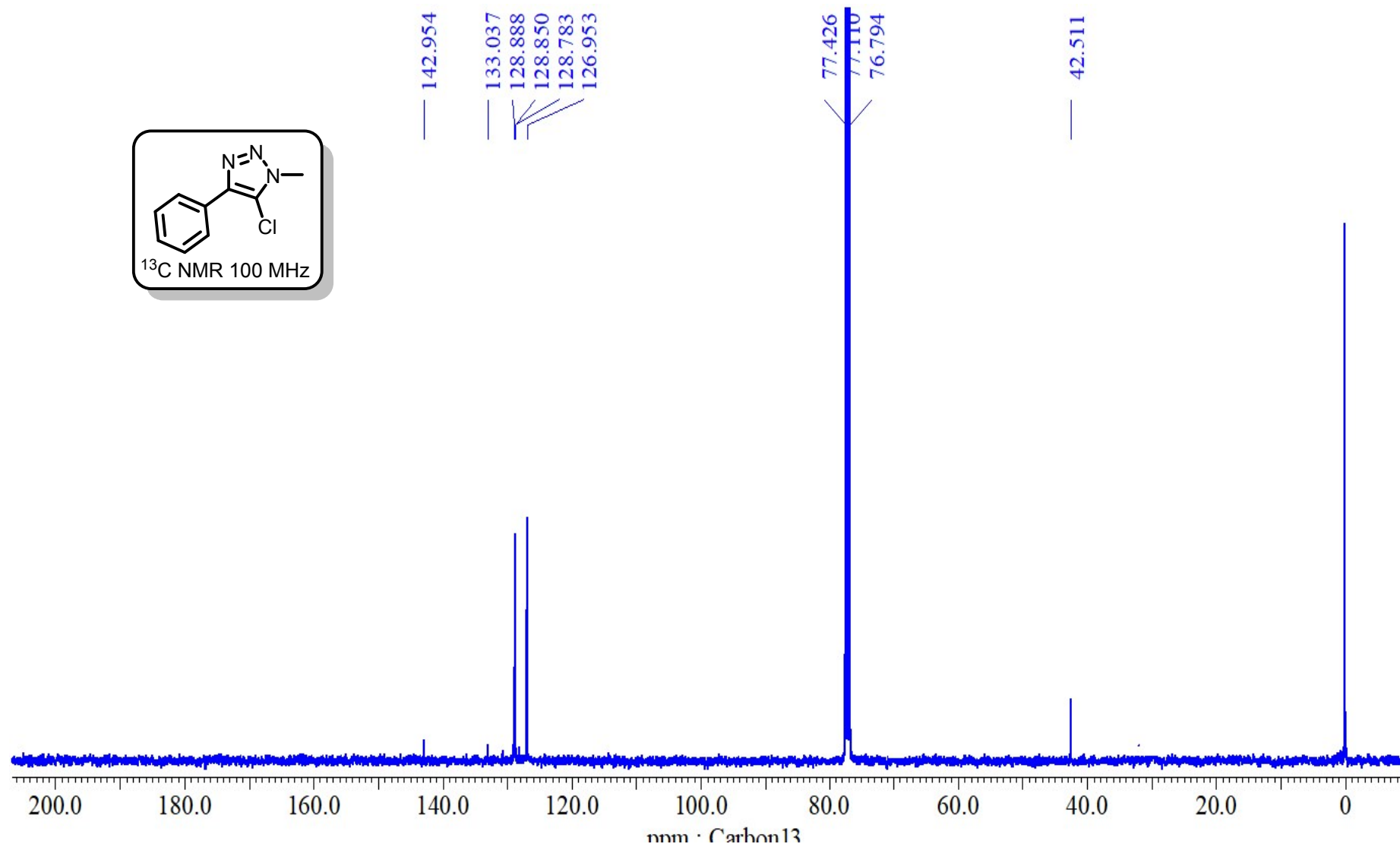
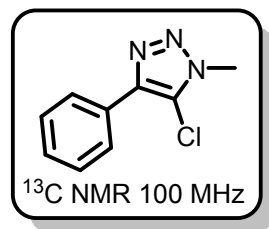


Fig. 46: ¹³C NMR of 5-chloro-1-methyl-4-phenyl-1H-1,2,3-triazole (**3h**)

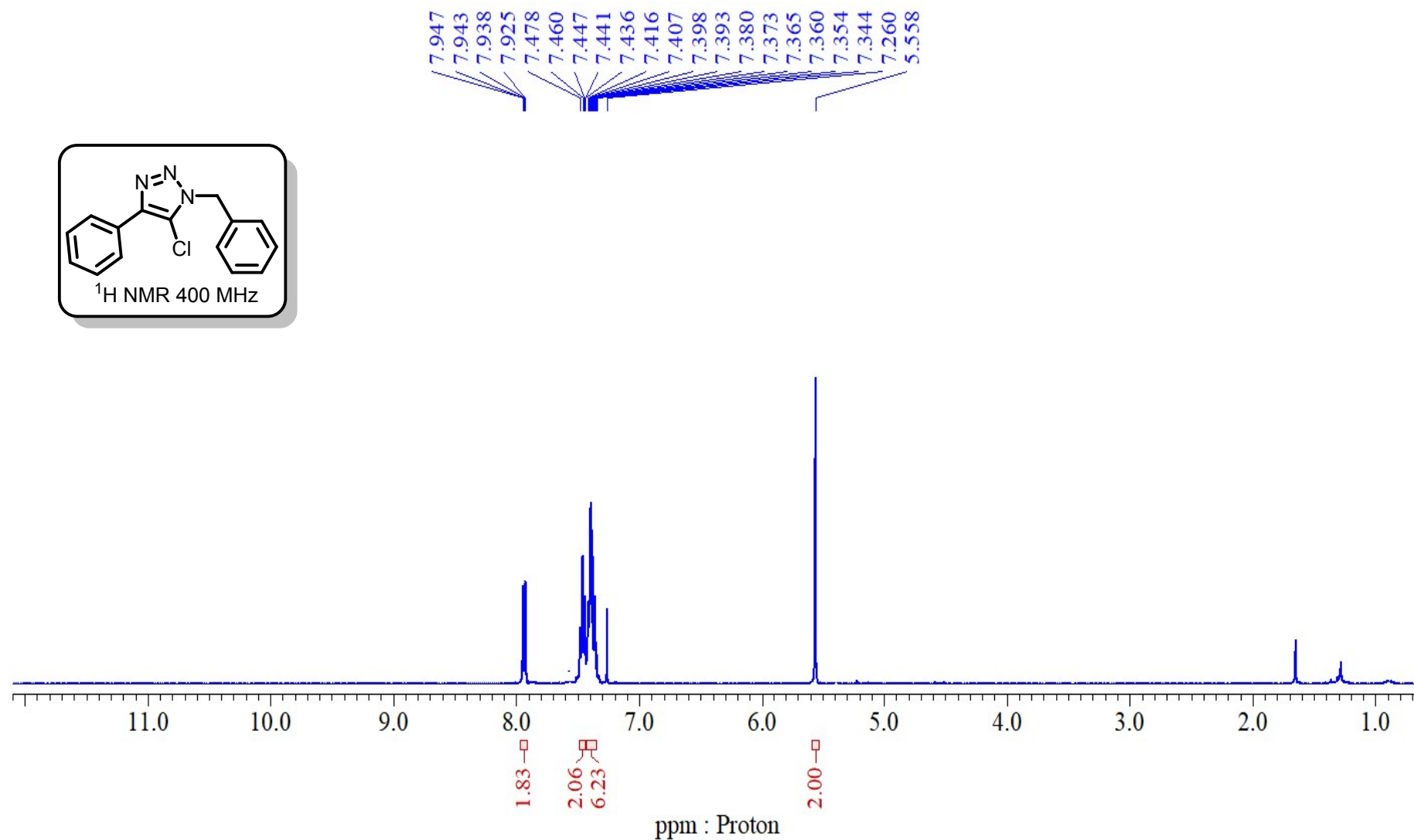


Fig. 47: ¹H NMR spectrum of 1-benzyl-5-chloro-4-phenyl-1H-1,2,3-triazole (**3i**)

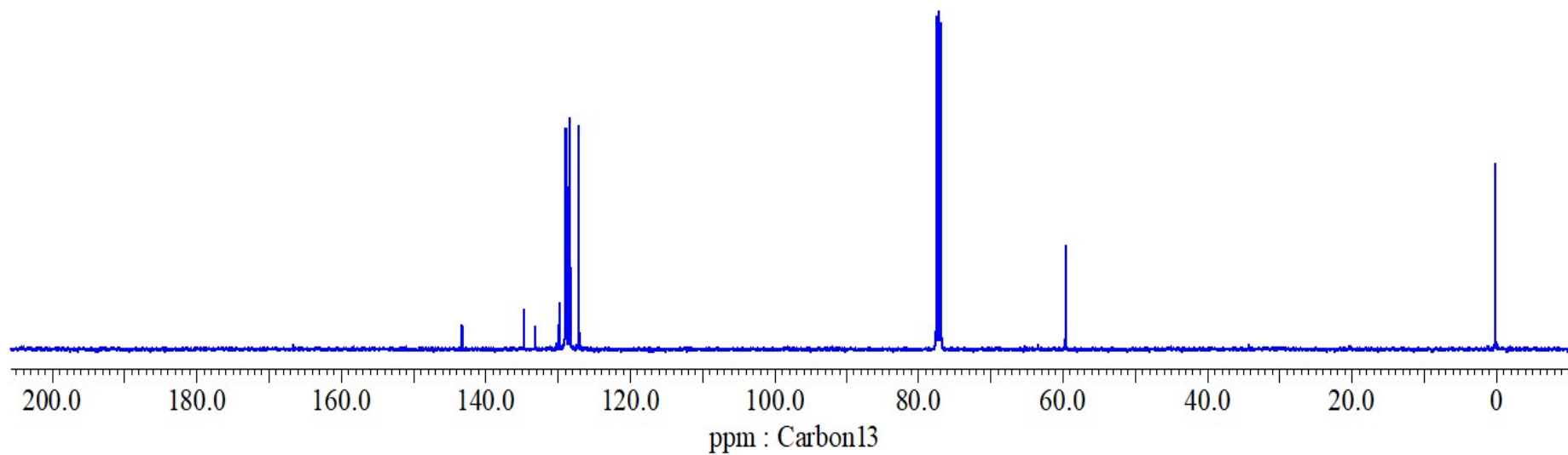
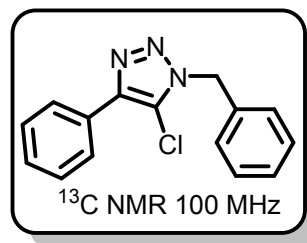


Fig. 48: ¹³C NMR spectrum of 1-benzyl-5-chloro-4-phenyl-1H-1,2,3-triazole (**3i**)

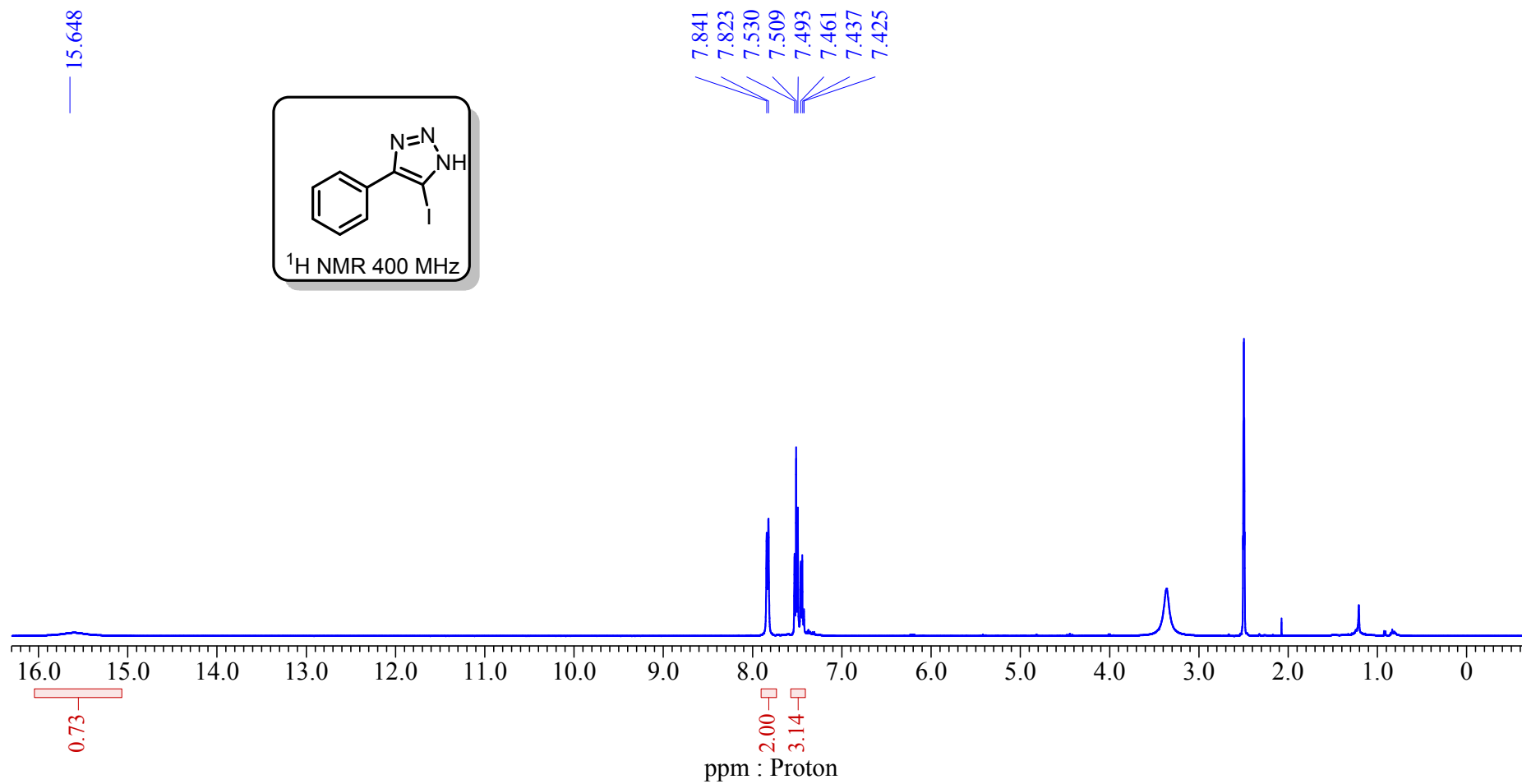


Fig. 49: ¹H NMR spectrum of 5-iodo-4-phenyl-1H-1,2,3-triazole (**3j**)

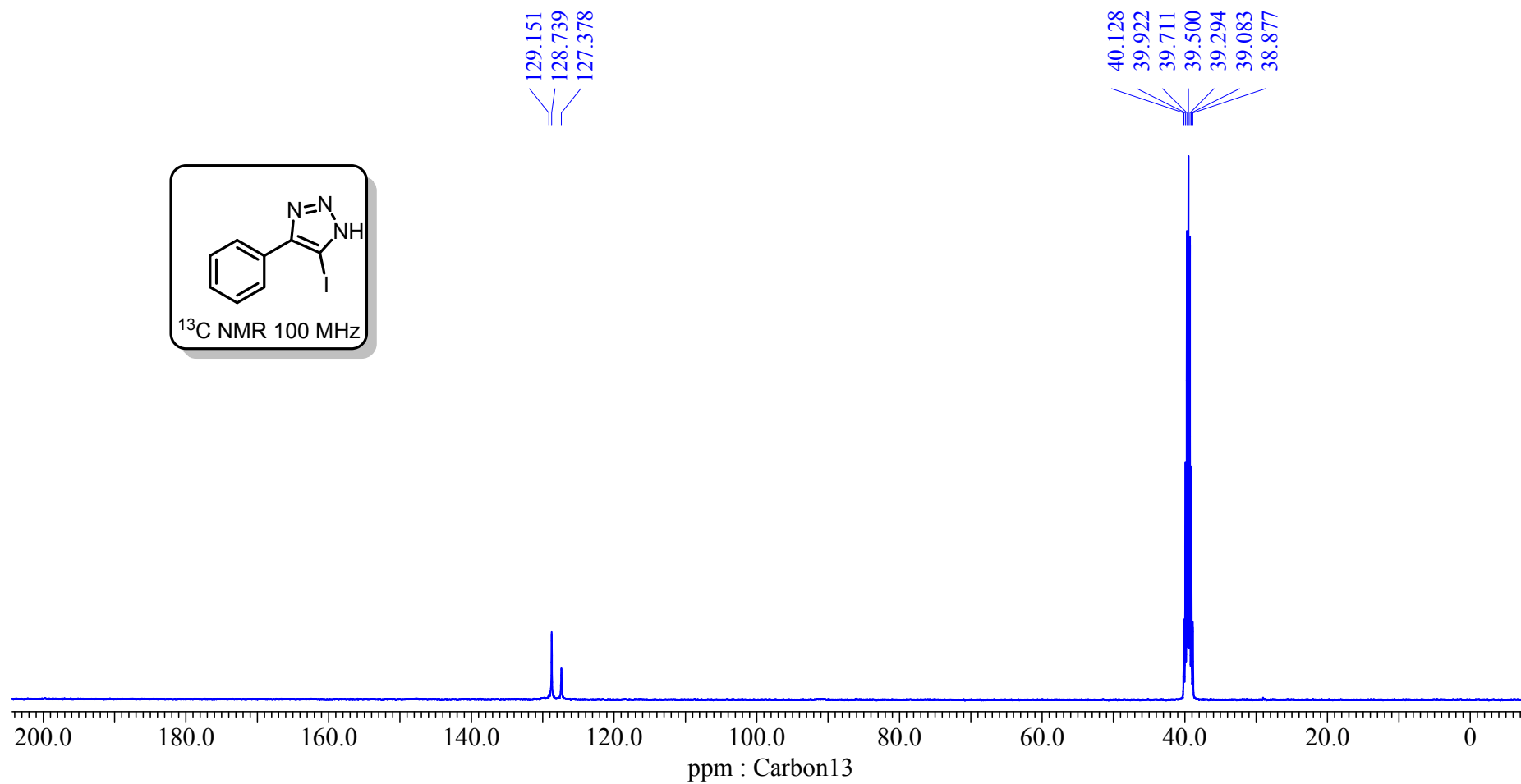


Fig. 50: ¹³C NMR spectrum of 5-iodo-4-phenyl-1H-1,2,3-triazole (**3j**)

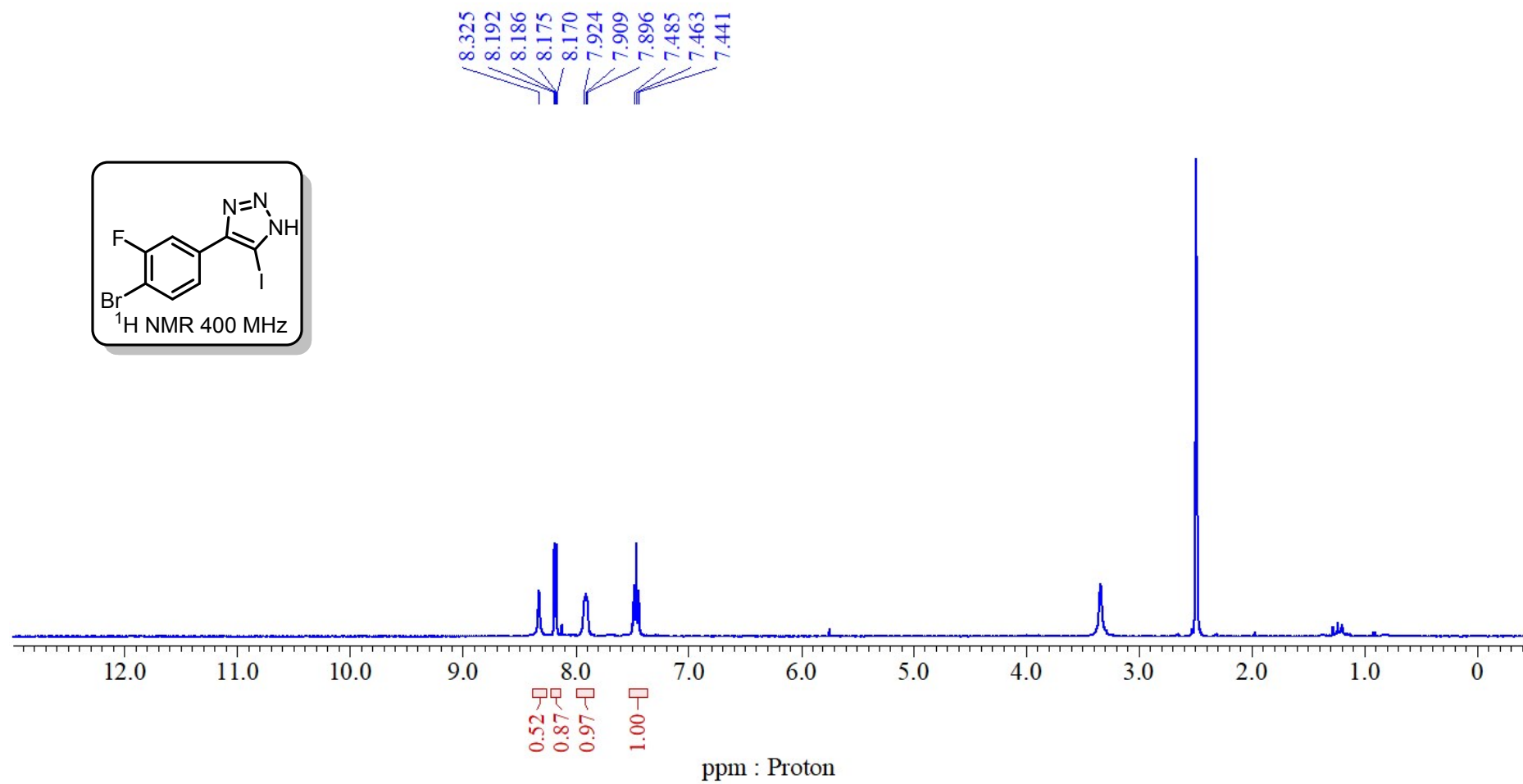


Fig. 51: ¹H NMR spectrum of 4-(4-bromo-3-fluorophenyl)-5-iodo-1H-1,2,3-triazole (**3k**)

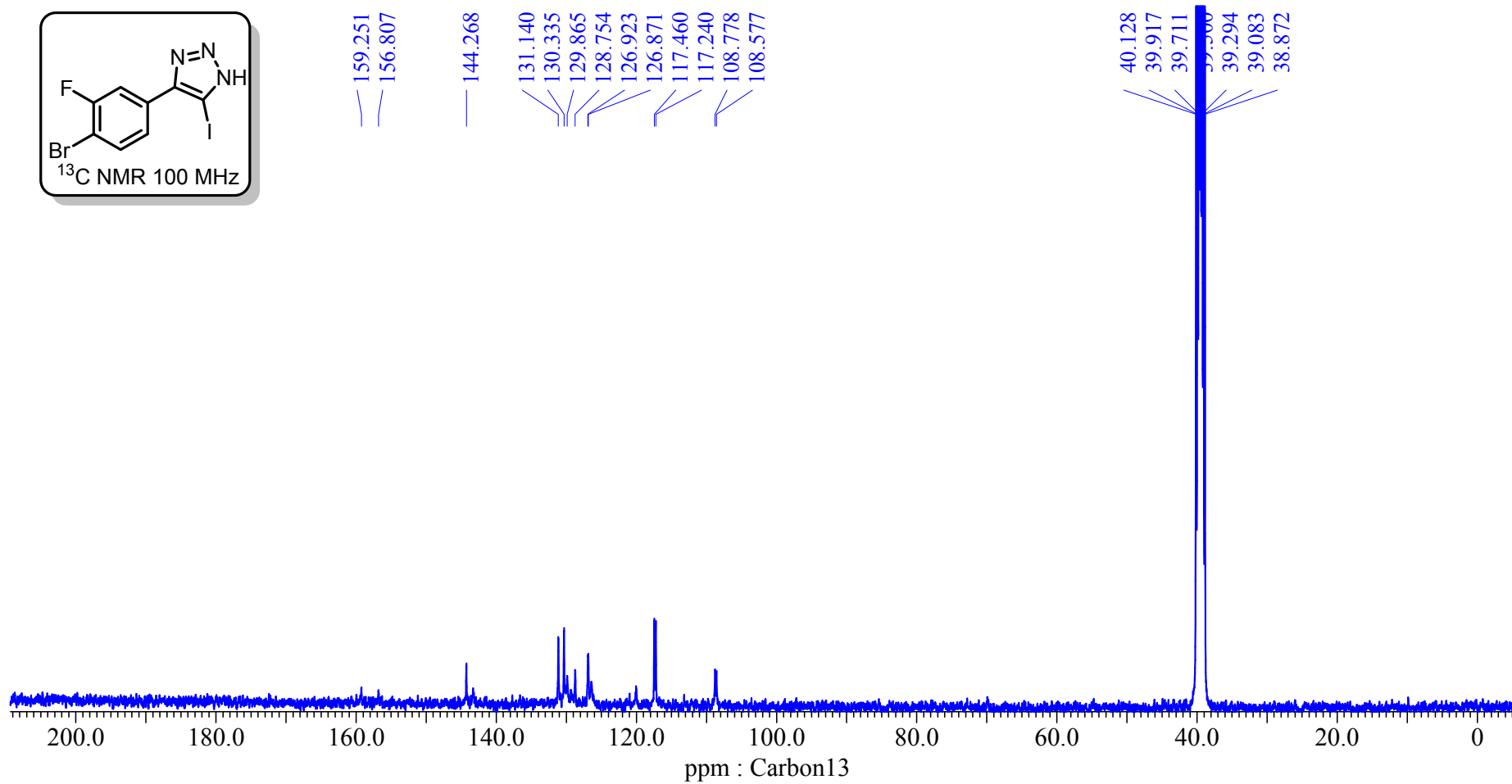


Fig. 52: ¹³C NMR spectrum of 4-(4-bromo-3-fluorophenyl)-5-iodo-1H-1,2,3-triazole (**3k**)

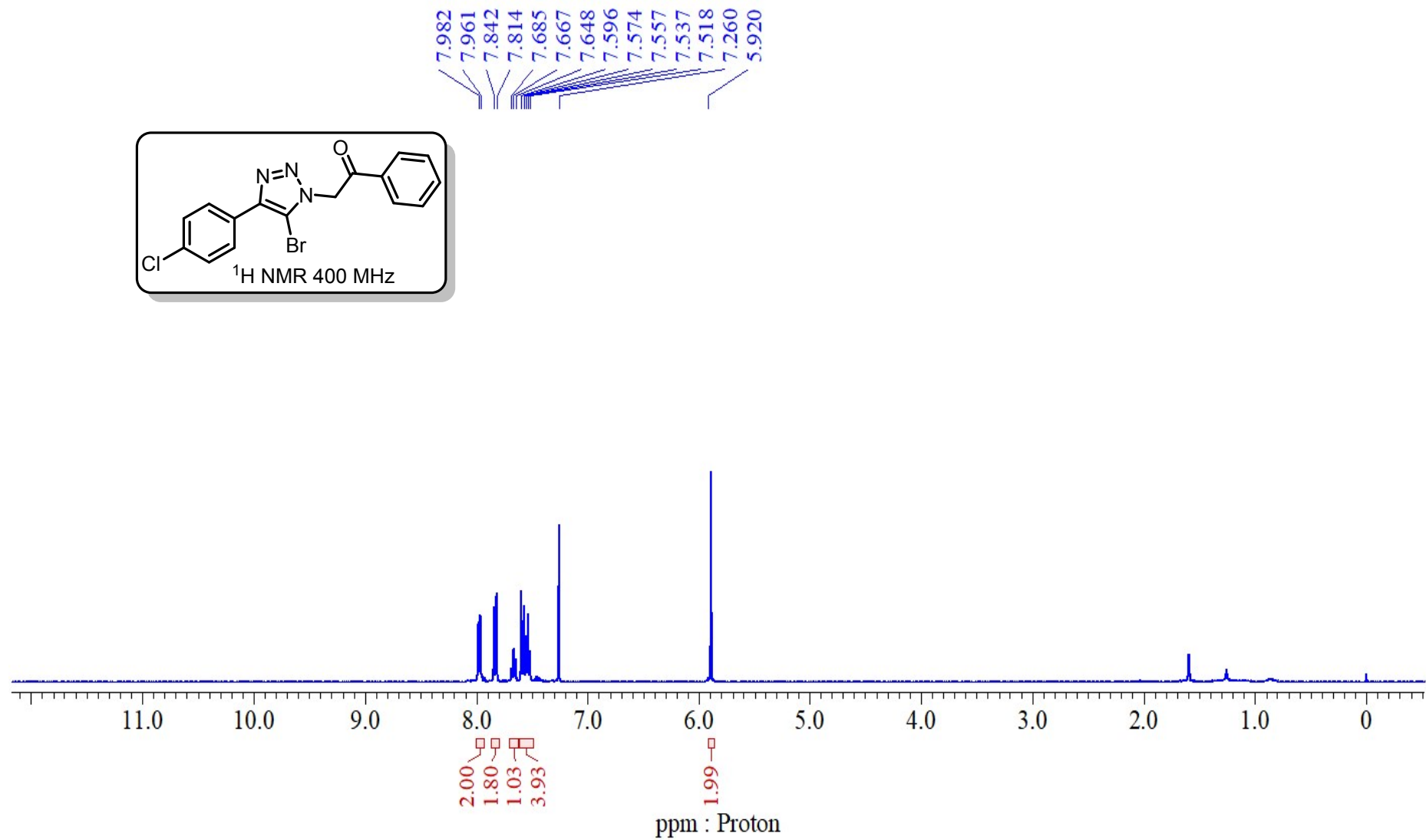


Fig. 53: ¹H NMR spectrum of 2-(5-bromo-4-(4-chlorophenyl)-1H-1,2,3-triazol-1-yl)-1-phenylethan-1-one (**4a**)

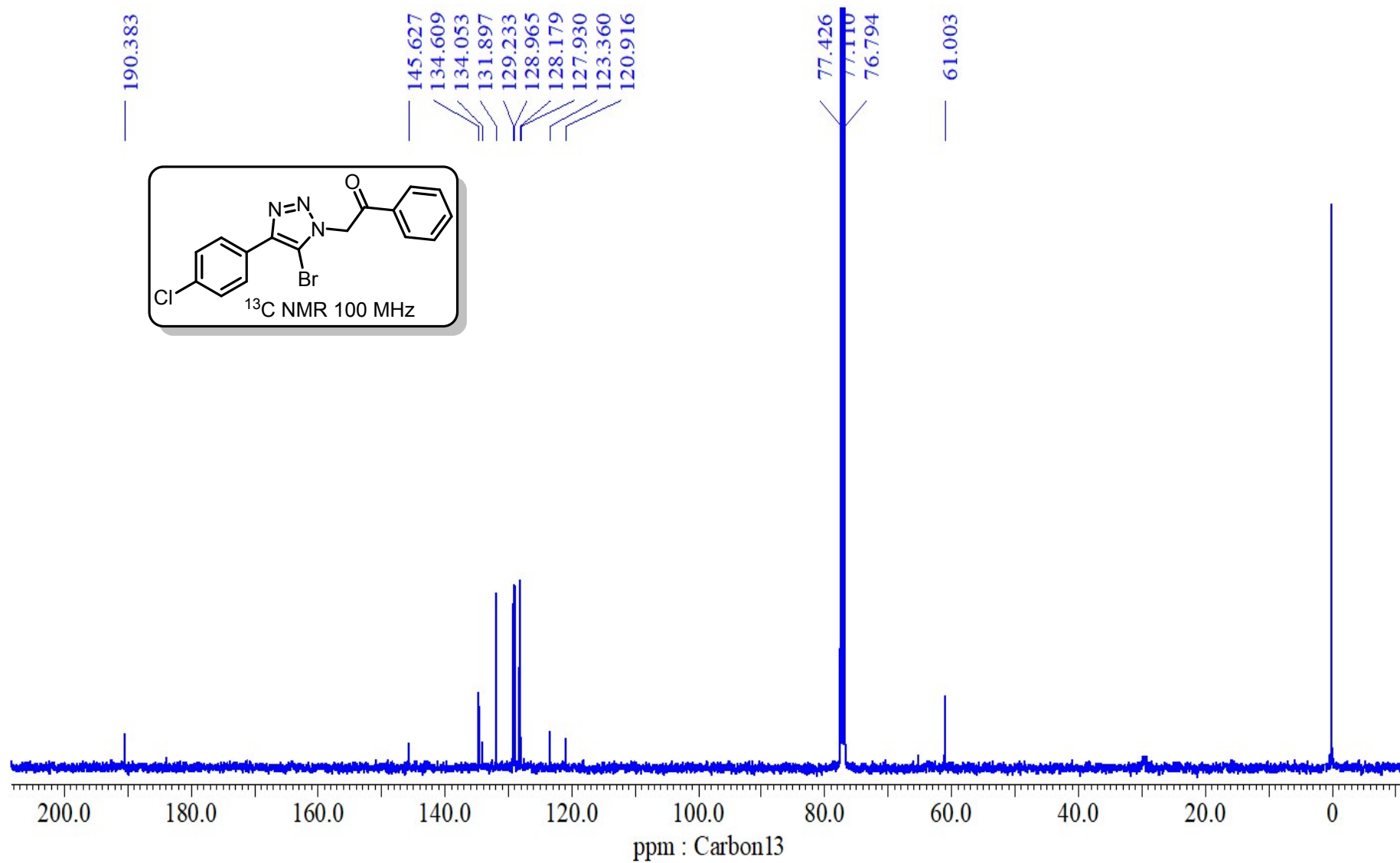


Fig. S4: ¹³C NMR spectrum of 2-(5-bromo-4-(4-chlorophenyl)-1H-1,2,3-triazol-1-yl)-1-phenylethan-1-one (**4a**)

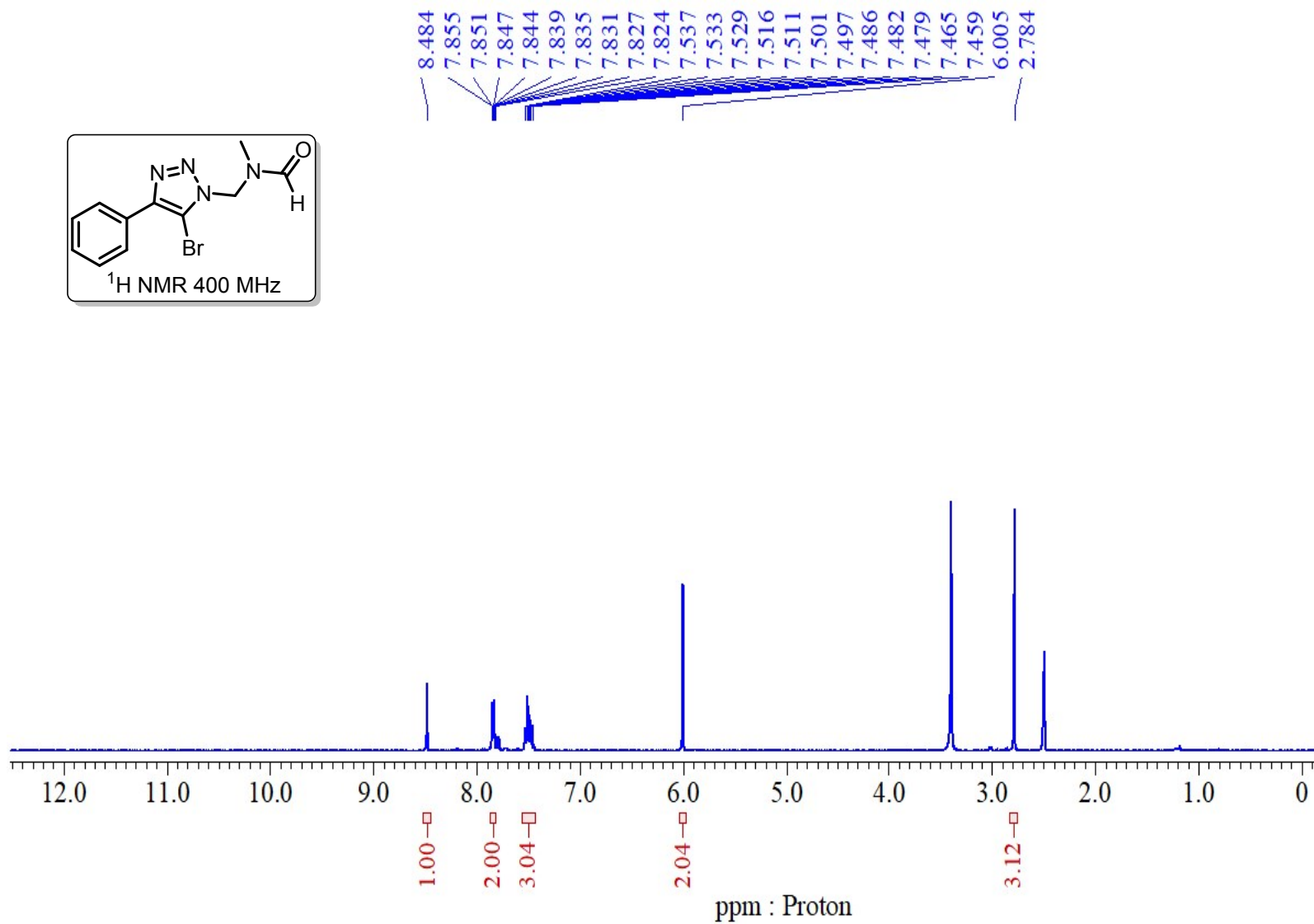


Fig. 55: ¹H- NMR spectrum of N-((5-bromo-4-phenyl-1H-1,2,3-triazol-1-yl)methyl)-N-methylformamide (**5a**)

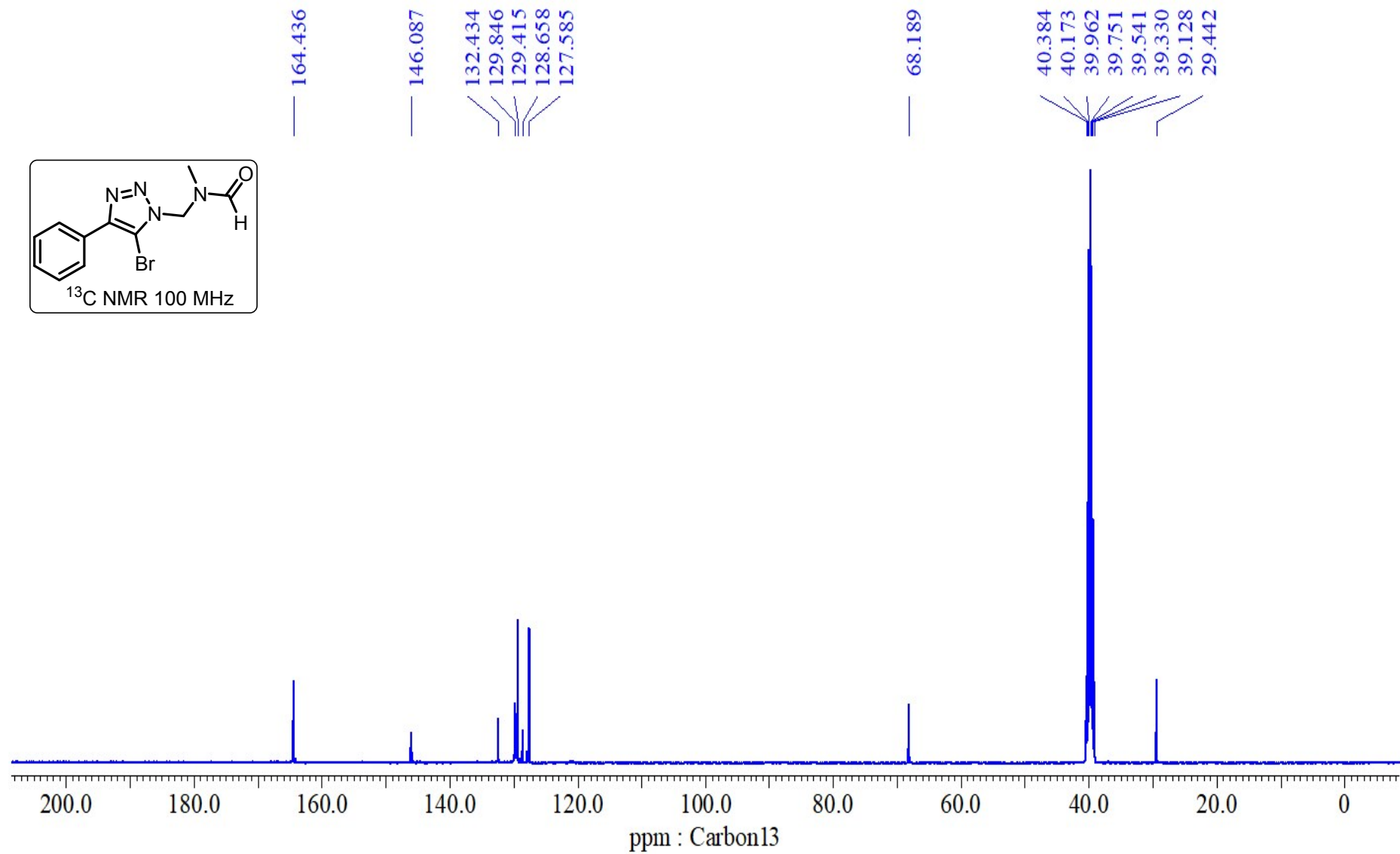


Fig. 56: ¹³C- NMR spectrum of N-((5-bromo-4-phenyl-1H-1,2,3-triazol-1-yl)methyl)-N-methylformamide (**5a**)

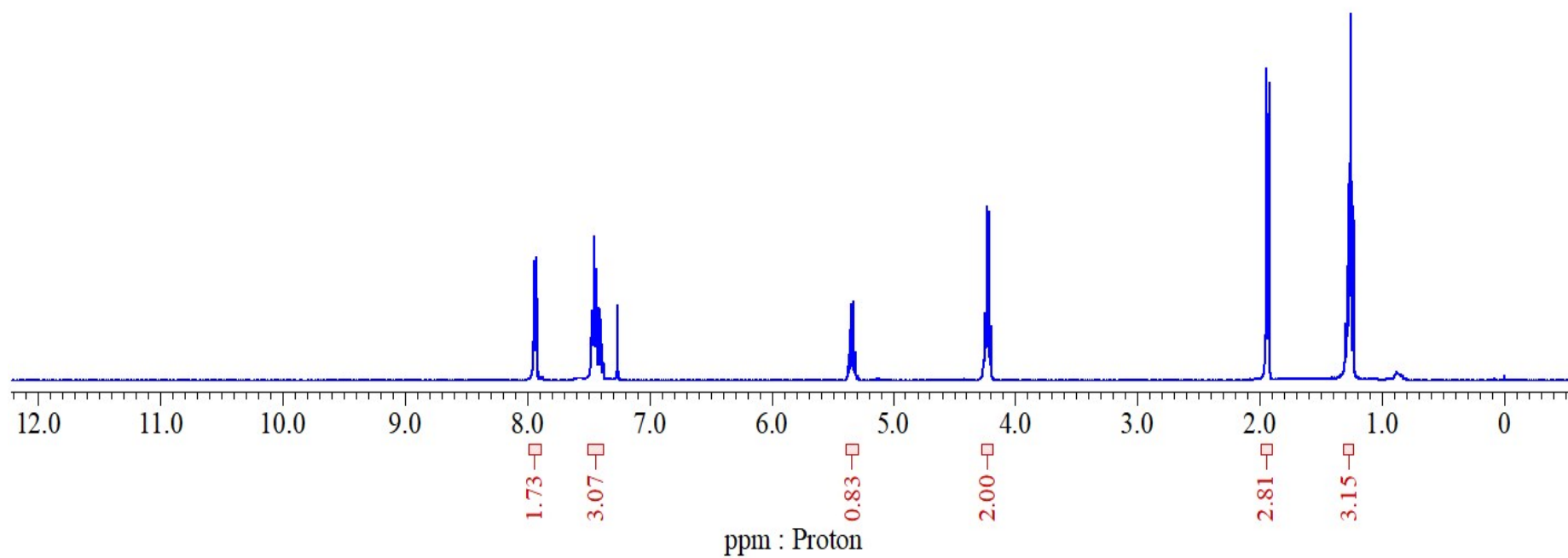
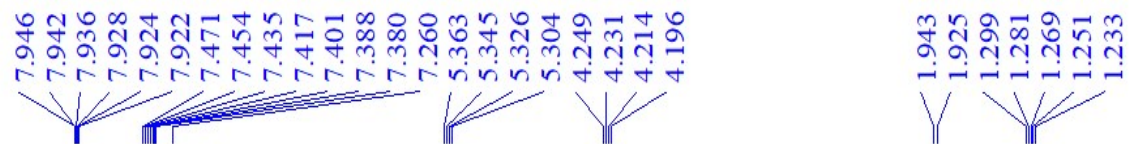
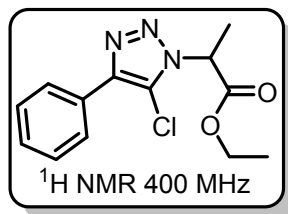


Fig. 57: ¹H NMR spectrum of ethyl 2-(5-bromo-4-phenyl-1H-1,2,3-triazol-1-yl)propanoate (**6a**)

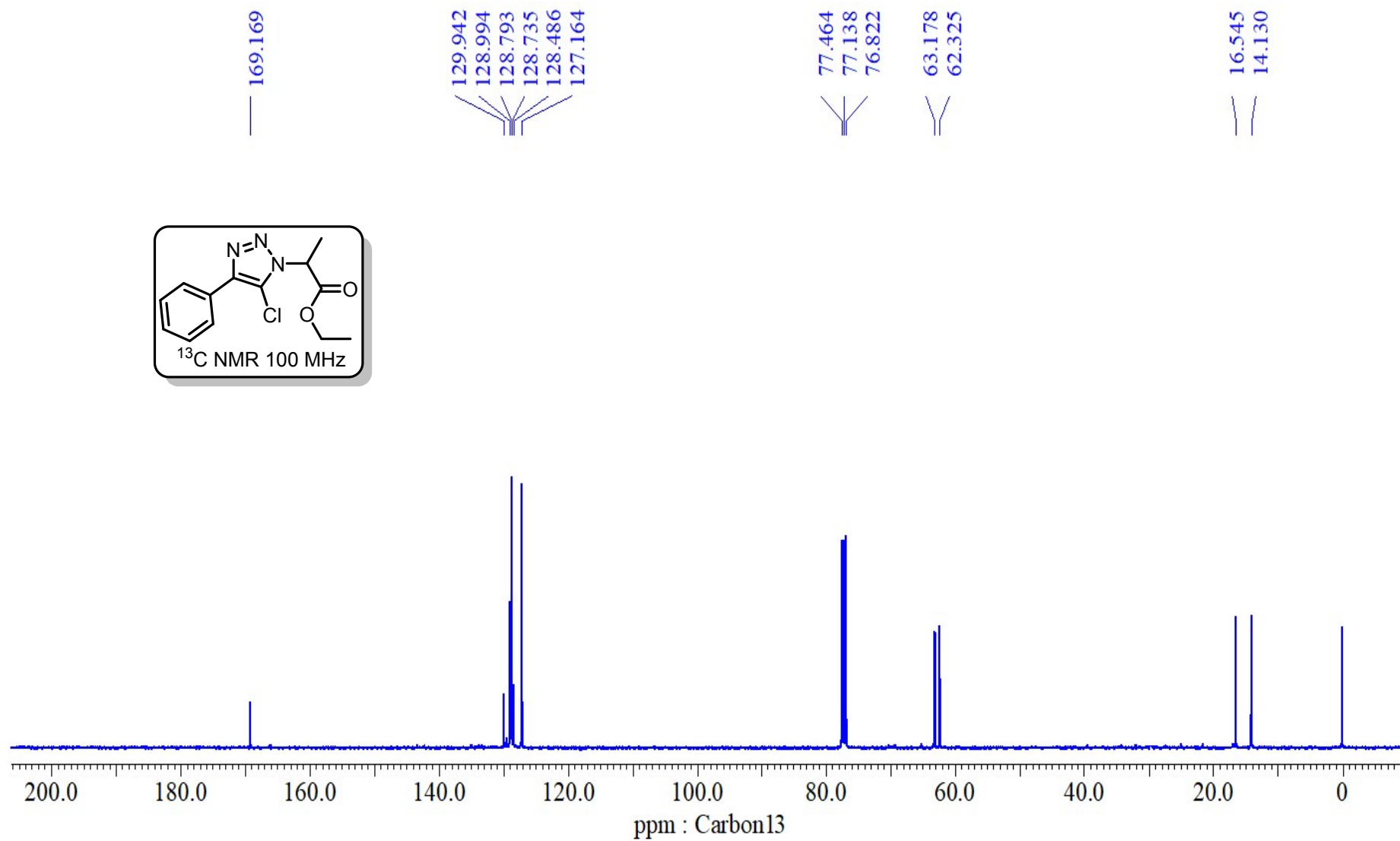


Fig. 58: ¹³C NMR spectrum of ethyl 2-(5-bromo-4-phenyl-1H-1,2,3-triazol-1-yl)propanoate (**6a**)