Searching for novel reusable biomass-derived solvents: furfuryl alcohol/water azeotrope as medium for the waste-minimized copper-catalysed azide-alkyne cycloaddition

Dace Rasina,[a] Aurora Lombi,[a] Stefano Santoro,[a] Francesco Ferlin,[a] and Luigi Vaccaro*[a]

[a] Laboratory of Green Synthetic Organic Chemistry, CEMIN – Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia Via Elce di Sotto, 8, 06123 Perugia, Italy
E-mail: luigi.vaccaro @unipg.it; Web: www.dcbb.unipg.it/greensoc

SUPPORTING INFORMATION

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General Information

Unless otherwise stated, all solvents and reagents were used as obtained from commercial sources without further purification. GC analyses were performed by using a Hewlett-Packard HP 5890A equipped with a capillary column DB-35MS (30 m, 0.53 mm), a FID detector and hydrogen as gas carrier. GC-EIMS analyses were carried out by using a Hewlett-Packard HP 6890N Network GC system/5975 Mass Selective Detector equipped with an electron impact ionizer at 70 eV. NMR spectra were recorded on a Bruker DRX-ADVANCE 400 MHz (^{1}H at 400 MHz and ^{13}C at 100.6 MHz) in $CDCl_3$ or DMSO-D6 using TMS as the internal standard.
All azides and non-commercially available alkynes were prepared according to methods reported in the

General procedure for the synthesis of 1,5-disubstituted 1,2,3-triazoles

Imidazole (14 mg, 20 mol%), sodium ascorbate (20 mg, 10 mol%) and copper(II) sulfate pentahydrate (5 mg, 2 mol%) were dissolved in 5 mL of furfuryl alcohol (20 wt%) water mixture, in a screw-capped vial equipped with a magnetic stirrer. Alkyne (1 mmol) and azide (1 mmol) were added and the resulting heterogeneous mixture was stirred vigorously at 30 °C, until GC analysis indicated complete consumption of the reactants.
*Isolation procedure **A**:* Product was collected by filtration, washed with 10 mL of distilled water and dried in vacuum to afford of pure product.
*Isolation procedure **B**:* Solvent was decanted and 5 mL of ice-cold water was added to oily residue to precipitate the product that was collected by filtration, washed with 10 mL of distilled water and dried in vacuum to afford pure product.
*Isolation procedure **C**:* Solvent was decanted and 10 mL of water and 10 mL of EtOAc was added. Organic phase was separated, washed with brine, dried over Na_2SO_4 and evaporated. The crude mixture was purified by column chromatography to afford pure product.

Calculation of *E*-factor

Our protocol for the preparation of 3c (Scheme 2): (0.027 mol, yield 91%)= $[(4.06_{(\text{azide } \mathbf{1a})} + 2.79_{(\text{alkyne } \mathbf{2a})} + 0.367_{(\text{imidazole})} + 0.535_{(\text{Na-asc})} + 0.135_{(\text{CuSO4})} + 27_{(\text{FA/H2O})} + 20_{(\text{H2O for washing})}) - (6.20_{(\text{isolated product } \mathbf{3c})} + 21.87_{(\text{recovered solvent})}]/ 6.20_{(\text{isolated product } \mathbf{3c})}$ = **4.3.**

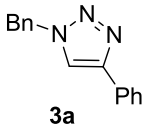
Typically CuAAC reactions are performed in water and some organic co-solvent. We calculated *E*-factor for three representative orotocols using classical reaction conditions and work-up procedures using *t*BuOH/H_2O solvent system done by Sharpless and Fokin, for DCM/H_2O solvent system and solvent free conditions.

Reference	Procedure	E-factor
Vsevolod V. Rostovtsev, Luke G. Green, Valery V. Fokin K. Barry Sharpless ACIE 2002, 41, No. 14, 2596	General procedure (entry 11, Table 1): 17-ethynylestradiol (888 mg, 3 mmol) and (S)-3-azidopropane-1,2-diol (352 mg, 3 mmol) were suspended in a **1:1 mixture of water and tert-butyl alcohol** (12 mL). **Sodium ascorbate** (0.3 mmol, 300 _L of freshly prepared 1_ solution in water) was added, followed by **copper(II) sulfate pentahydrate** (7.5 mg, 0.03 mmol, in 100 _L of water). The heterogeneous mixture was stirred vigorously overnight, at which point it cleared and TLC analysis indicated complete consumption of the reactants. The reaction mixture was diluted with water (50 mL), cooled in ice, and the white **precipitate was collected by filtration**. After washing the precipitate with cold water (2x25 mL), it was dried under	**96-195 (avg 150)** (11 substrates)

	vacuum to afford 1.17g (94%) of pure product as an off-white powder.	
Bo-Young Lee, So Ra Park, Heung Bae Jeon* and Kwan Soo Kim, Tetrahedron Letters 47 (2006) 5105	Typical procedure reported: To a solution of phenylacetylene (100 mg, 0.75 mmol) and benzyl azide (9, 80 mg, 0.83 mmol) **in CH_2Cl_2** (0.7 mL) **and H_2O** (0.7 mL) were added **$CuSO_4$*5H_2O** (9.3 mg, 0.04 mmol) and **sodium ascorbate** (22 mg, 0.11 mmol). The resulting solution was stirred for 7 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 (5 mL) and H_2O (5 mL). The organic layer was separated, dried over $MgSO_4$, and concentrated. The residue was **purified by flash column chromatography** (hexane/EtOAc, 2:1) to give the corresponding 1,2,3-triazole (170 mg, 97%) as a white solid.	**20-67 (avg 53)** (12 substrates) solvents used in column chromatography have not been included because sufficient details were not reported
Laura Rinaldi, Katia Martina, Francesca Baricco, Laura Rotolo and Giancarlo Cravotto Molecules **2015**, 20, 2837	The milling jar (50 mL; stainless steel) were equipped with 1500 milling balls (d = 2 mm, stainless steel) and 48 medium balls (d = 5 mm, stainless steel). Afterwards the alkyne (1 mmol), the azide (1 mmol) and **Cu powder** (1 mmol, 63 mg) were added in the given order. Milling was accomplished at 650 rpm for 5 min. After cooling of the milling jar to room temperature, the crude products were filtered on Büchner funnel with a sintered glass disc using **diethyl acetate (3 × 10 mL).** The solvent was evaporated in vacuum, the crude products were dried and analyzed by GC-MS, 1H-, 13C-NMR spectroscopy and MALDI-TOF mass spectrometry after dissolution in an appropriate solvent.	**71-155 (avg 115)** (12 substrates)

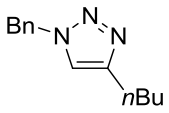
Spectral Data

1-Benzyl-4-phenyl-1H-1,2,3-triazole 3a. Isolated by procedure A, yield 159 mg (68 %), white powder with m. p.: 126-127 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 5.64 (s, 2H). 7.27-7.45 (m, 8H), 7.85 (d, *J* = 7.5 Hz, 2H), 8.62 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-D6) δ: 53.5, 122.0, 125.6, 128.3 (2 overlapping signals), 128.6, 129.2, 129.3, 131.1, 136.5, 147.2. IR ($CHCl_3$, cm^{-1}): 3013, 1467, 1356, 1226, 1209, 1074, 1048, 755, 695. GC-EIMS (m/z, %): 89 (35), 91 (63), 116 (89), 180 (21), 206 (100), 207 (20), 235 (26).



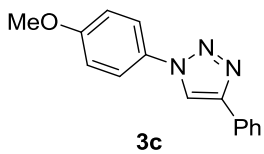
3a

1-Benzyl-4-butyl-1H-1,2,3-triazole 3b. Isolated by procedure B, yield 171 mg (79 %), white powder with m. p.: 62-63 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 0.86 (t, *J* = 7.3 Hz, 3H), 1.19-1.38 (m, 2H), 1.45-1.62 (m, 2H), 2.58 (t, *J* = 7.5 Hz, 2H), 5.51 (s, 2H), 7.20-7.42 (m, 5H), 7.86 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-D6) δ: 14.1, 22.1, 25.1, 31.5, 53.1, 122.4, 128.2, 128.4, 129.2, 136.8, 147.7. IR ($CHCl_3$, cm^{-1}): 3011, 2961, 2874, 1551, 1497, 1353, 1124, 1047, 798, 697. GC-EIMS (m/z, %): 65 (11), 91 (100), 92 (10), 173 (15), 215 (1).



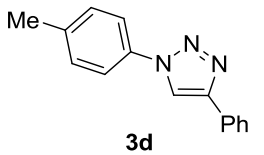
3b

1-(4-Methoxyphenyl)-4-phenyl-1H-1,2,3-triazole 3c. Isolated by procedure A, yield 6.02 g (91 %), light yellow powder with m.p. 160-161 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 3.81 (s, 3H), 7.14 (d, *J* = 8.7 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.93 (d, *J* = 7.5 Hz, 2H), 9.15 (s, 1H). ^{13}C NMR (100 MHz, DMSO-D6) δ: 56.0, 115.3, 120.0, 122.1, 125.8, 128.6, 129.4, 130.5, 130.9, 147.6, 159.8. IR ($CHCl_3$, cm^{-1}): 3017, 2848, 1613, 1519, 1257, 1042, 834. GC-EIMS (m/z, %): 116 (17), 152 (23), 180 (60), 181 (27), 208 (93), 223 (100), 251 (2).



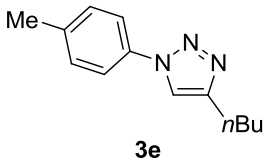
3c

4-Phenyl-1-p-tolyl-1H-1,2,3-triazole 3d. Prepared by procedure A, yield 205 mg (87 %), light yellow powder with m.p. 166-168 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 2.38 (s, 3H), 7.30-7.56 (m, 5H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.93 (d, *J* = 7.3 Hz, 2H), 9.22 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-D6) δ: 21.0, 119.9, 120.3, 125.8, 128.6, 129.4, 130.7, 130.8, 134.9, 138.8, 147.7. IR ($CHCl_3$, cm^{-1}): 3154, 3013, 1609, 1520, 1227, 1042, 993, 797. GC-EIMS (m/z, %): 89 (16), 116 (14), 165 (23), 206 (65), 207 (100), 235 (2).



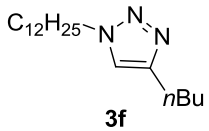
3d

4-Butyl-1-*p*-tolyl-1H-1,2,3-triazole 3e. Isolated by procedure B, yield 739 mg (81 %), light yellow powder with m.p. 53-55 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 0.90 (t, *J* = 7.3 Hz, 3H), 1.34-1.36 (m, 2H), 1.61-.64 (m, 2H), 2.35 (s, 3H), 2.76-2.67 (m, 2H), 7.35 (d, *J* = 7.4 Hz, 2H), 7.74 (d, *J* = 7.4 Hz, 2H), 8.50 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-D6) δ: 14.1, 21.0, 22.2, 25.1, 31.4, 120.0, 120.3, 130.6, 135.1, 138.2, 148.5. IR ($CHCl_3$, cm^{-1}): 3013, 2961, 2932, 2862, 1519, 1467, 1224, 1207, 1044, 990, 798. GC-EIMS (m/z, %): 65 (11), 91 (32), 144 (100), 145 (13), 186 (11), 215 (1).



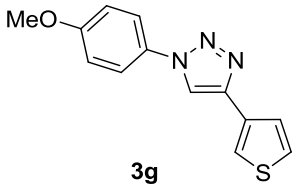
3e

4-Butyl-1-dodecyl-1H-1,2,3-triazole 3f. Isolated by procedure A, yield 237 mg (81 %), white powder with m.p. 51-52 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 0.77-0.92 (m, 6H), 1.11-1.36 (m, 20H), 1.46-1.62 (m, 2H), 1.68-1.81 (m, 2H), 2.57 (t, *J* = 7.5 Hz, 2H), 4.24 (t, *J* = 6.9 Hz, 2H), 7.78 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-D6) δ: 14.1, 14.4, 22.1, 22.5, 25.1, 26.2, 28.8, 29.1, 29.29, 29.32, 29.4 (2 overlapping signals), 30.1, 31.6, 31.7, 49.5, 122.0, 147.2. IR ($CHCl_3$, cm^{-1}): 2916, 2853, 1550, 1461, 1373, 1228, 1202, 1041, 756, 673. GC-EIMS (m/z, %): 82 (25), 96 (32), 110 (54), 111 (32), 124 (40), 126 (26), 138 (37), 152 (100), 166 (70), 180 (37), 194 (28), 222 (50), 236 (39), 250 (51), 251 (26), 293 (26).



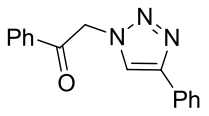
3f

1-(4-Methoxyphenyl)-4-(thiophen-3-yl)-1H-1,2,3-triazole 3g. Isolated by procedure A, yield 223 mg (87 %), pale yellow powder with m.p. 161-163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.87 (s, 3H), 7.02 (d, *J* = 8.4 Hz, 2H), 7.41 (s, 1H), 7.52 (d, *J* = 3.8 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.76 (s, 1H), 8.02 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 55.6, 114.8, 117.7, 121.4, 122.2, 125.8, 126.5, 130.4, 131.6, 144.4, 159.9. IR ($CHCl_3$, cm^{-1}): 3019, 1520, 1257, 1227, 1206, 1043, 719, 672. GC-EIMS (m/z, %): 96 (16), 122 (18), 186 (47), 187 (33), 214 (85), 229 (100), 257 (3).



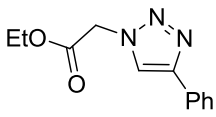
3g

1-Phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethanone 3h. Isolated by procedure A, yield 251 mg (95 %), yellow powder with m.p. 172-175 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 6.26 (s, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.73 (t, *J* = 7.2 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 2H), 8.10 (d, *J* = 7.5 Hz, 2H), 8.53 (s, 1H). ^{1}H NMR (100.6 MHz, DMSO-D6) δ: 56.5, 123.5, 125.6, 128.3, 128.7, 129.4, 129.5, 131.2, 134.6, 134.7, 146.8, 192.6. IR ($CHCl_3$, cm^{-1}): 3013, 1707, 1598, 1468, 1227, 796, 752, 664. GC-EIMS (m/z, %): 77 (94), 91 (34), 102 (44), 103 (83), 105 (100), 119 (42), 130 (99), 206 (63), 207 (35), 234 (31), 263 (39).



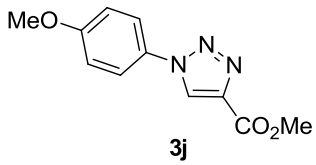
3h

Ethyl 2-(4-phenyl-1H-1,2,3-triazol-1-yl)acetate 3i. Isolated by procedure A, yield 185 mg (80 %), white powder with m.p. 99-101 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 1.22 (t, *J* = 7.1 Hz, 3H), 4.19 (q, *J* = 7.0 Hz, 2H), 5.44 (s, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.85 (d, *J* = 7.5 Hz, 2H), 8.55 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-D6) δ: 14.4. 51.0, 62.0, 123.2, 125.6, 128.4, 129.4, 131.0, 146.9, 167.7. IR ($CHCl_3$, cm^{-1}): 3151, 3027, 3013, 1755, 1467, 1232, 1198, 1022, 777. GC-EIMS (m/z, %): 77 (36), 89 (27), 91 (35), 102 (72), 103 (74), 105 (27), 116 (100), 118 (49), 130 (70), 131 (68), 160 (27), 203 (25), 231 (50).



3i

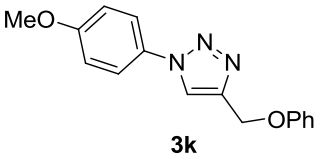
Methyl 1-(4-methoxyphenyl)-1H-1,2,3-triazole-4-carboxylate 3j. Isolated by procedure A, yield 197 mg (91 %), white powder with m.p. 138-140 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 3.80 (s, 3H), 3.86 (s, 3H), 7.10 (d, *J* = 8.9 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H), 9.34 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-D6) δ: 52.3. 56.0, 115.3, 122.6, 127.4, 129.8, 139.8, 160.13, 161.06. IR ($CHCl_3$, cm^{-1}): 3159, 3022, 2955, 2841, 1724, 1612, 1553,



3j

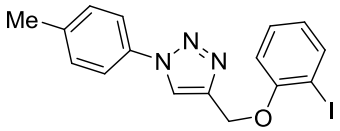
1520, 1439, 1351, 1254, 1218, 1149, 1037, 832, 756 GC-EIMS (m/z, %): 76 (15), 131 (18), 132 (19), 134 (15), 146 (100), 147 (20), 158 (17), 162 (21), 173 (36), 174 (90), 176 (16), 190 (67), 233 (40).

1-(4-Methoxyphenyl)-4-(phenoxymethyl)-1H-1,2,3-triazole 3k. Isolated by procedure A, yield 255 mg (91 %), pale yellow powder with m.p. 117-119 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 3.82 (s, 3H), 5.21 (s, 2H), 6.94-6.97 (m, 1H), 7.07 (d, *J* = 7.7 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.29-7.33 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 8.85 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-D6) δ: 56.0, 61.4, 115.1, 115.3, 121.4, 122.3, 123.3, 130.0, 130.4, 144.1, 158.5, 159.8. IR ($CHCl_3$, cm^{-1}): 3013, 2840, 1599, 1519, 1496, 1265, 1257, 1210, 1040, 834, 672. GC-EIMS (m/z, %): 77 (13), 117 (18), 145 (25), 160 (100), 161 (11), 281 (8).



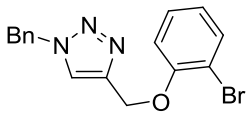
3k

4-((2-Iodophenoxy)methyl)-1-p-tolyl-1H-1,2,3-triazole 3l. Isolated by procedure A, yield 365 mg (93 %), light yellow powder with m.p. 97-99 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 2.37 (s, 3H), 5.29 (s, 2H), 6.76-6.79 (m, 1H), 7.26-7.28 (m, 1H), 7.38-7.40 (m, 3H), 7.77-7.79 (m, 3H), 8.90 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-D6) δ: 21.0, 62.6, 87.2, 113.7, 120.5, 123.3, 123.6, 130.2, 130.7, 134.7, 138.9, 139.6, 143.9, 157.1. IR ($CHCl_3$, cm^{-1}): 3013, 1582, 1520, 1220, 1209, 1046, 797, 755, 671. GC-EIMS (m/z, %): 91 (30), 143 (29), 144 (100), 236 (36), 264 (32).



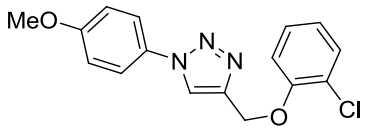
3l

1-Benzyl-4-((2-bromophenoxy)methyl)-1H-1,2,3-triazole 3m. Isolated by procedure B, yield 296 mg (86 %), white powder with m.p. 78-80 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 5.23 (s, 2H), 5.62 (s, 2H), 6.88-6.92 (m, 1H), 7.30-7.37 (m, 7H), 7.55-7.57 (m, 1H), 8.30 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-D6) δ: 53.3, 62.6, 111.6, 114.8, 122.8, 125.3, 128.4, 128.6, 129.2, 129.4, 133.5, 136.5, 143.1, 154.7. IR ($CHCl_3$, cm^{-1}): 3153, 3013, 1586, 1479, 1463, 1247, 1127, 1051, 1009, 795, 671. GC-EIMS (m/z, %): 91 (100), 144 (65), 145 (16), 172 (20), 173 (12), 264 (51), 344 (1), 345 (1).



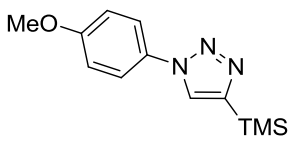
3m

4-((2-Chlorophenoxy)methyl)-1-(4-methoxyphenyl)-1H-1,2,3-triazole 3n. Isolated by procedure A, yield 265 mg (84 %), white powder with m.p. 108-110 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 3.81 (s, 3H), 5.30 (s, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 8.9 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.38-7.42 (m, 2H), 7.80 (d, *J* = 8.9 Hz, 2H), 8.84 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-D6) δ: 56.0, 62.4, 114.9, 115.3, 122.0, 122.3, 122.4, 123.5, 128.7, 130.4, 130.5, 143.6, 153.8, 159.8. IR ($CHCl_3$, cm^{-1}): 3158, 3018, 2840, 1612, 1591, 1519, 1485, 1254, 1220, 1064, 1043, 834, 671. GC-EIMS (m/z, %): 117 (12), 145 (20), 160 (100), 161 (11), 315 (3).



3n

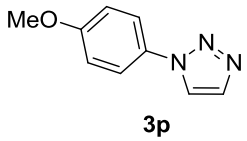
1-(4-Methoxyphenyl)-4-(trimethylsilyl)-1H-1,2,3-triazole 3o. Isolated by procedure C, yield 169 mg (68 %), white powder with m.p. 67-70 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 0.29 (s, 9H), 3.80 (s, 3H), 7.10 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 8.71 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-D6) δ: -0.6, 56.0, 115.2, 122.3,



3o

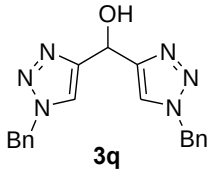
129.1, 130.5, 146.3, 159.5. IR ($CHCl_3$, cm^{-1}): 3013, 2962, 2839, 1613, 1519, 1302, 1252, 1227, 1171, 1109, 1043, 987, 845, 665. GC-EIMS (m/z, %): 176 (12), 204 (100), 205 (18), 219 (13), 247 (1).

1-(4-Methoxyphenyl)-1H-1,2,3-triazole 3p. After full conversion of 1-azido-4-methoxybenzene to 1-(4-methoxyphenyl)-4-(trimethylsilyl)-1H-1,2,3-triazole **3o**, tetrabutylammonium fluoride hydrate (630 mg, 2 mmol) was added and reaction stirred at 30 °C for 21 h. Product isolated by procedure C, yield 118 mg (67 %), bright yellow powder with m.p. 79-81 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 3.81 (s, 3H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.91 (s, 1H), 8.69 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-D6) δ: 56.0. 115.3, 122.3, 123.6, 130.6, 134.6, 159.7. IR ($CHCl_3$, cm^{-1}): 3165, 3009, 2833, 1607, 1518, 1461, 1249, 1041, 984, 823. GC-EIMS (m/z, %): 77 (22), 92 (11), 104 (23), 132 (100), 133 (10), 147 (36), 175 (29).



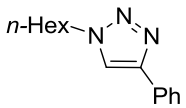
3p

Bis(1-benzyl-1H-1,2,3-triazol-4-yl)methanol 3q. Isolated by procedure A, yield 282 mg (82 %), white powder with m.p. 180-182 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 5.56 (s, 4H), 5.90 (d, *J* = 3.8 Hz, 1H), 6.01 (d, *J* = 3.8 Hz, 1H), 7.32-7.36 (m, 10H), 8.04 (s, 2H). ^{13}C NMR (100.6 MHz, DMSO-D6) δ: 53.1, 61.7, 123.2, 128.5, 128.6, 129.2, 136.6, 150.4.



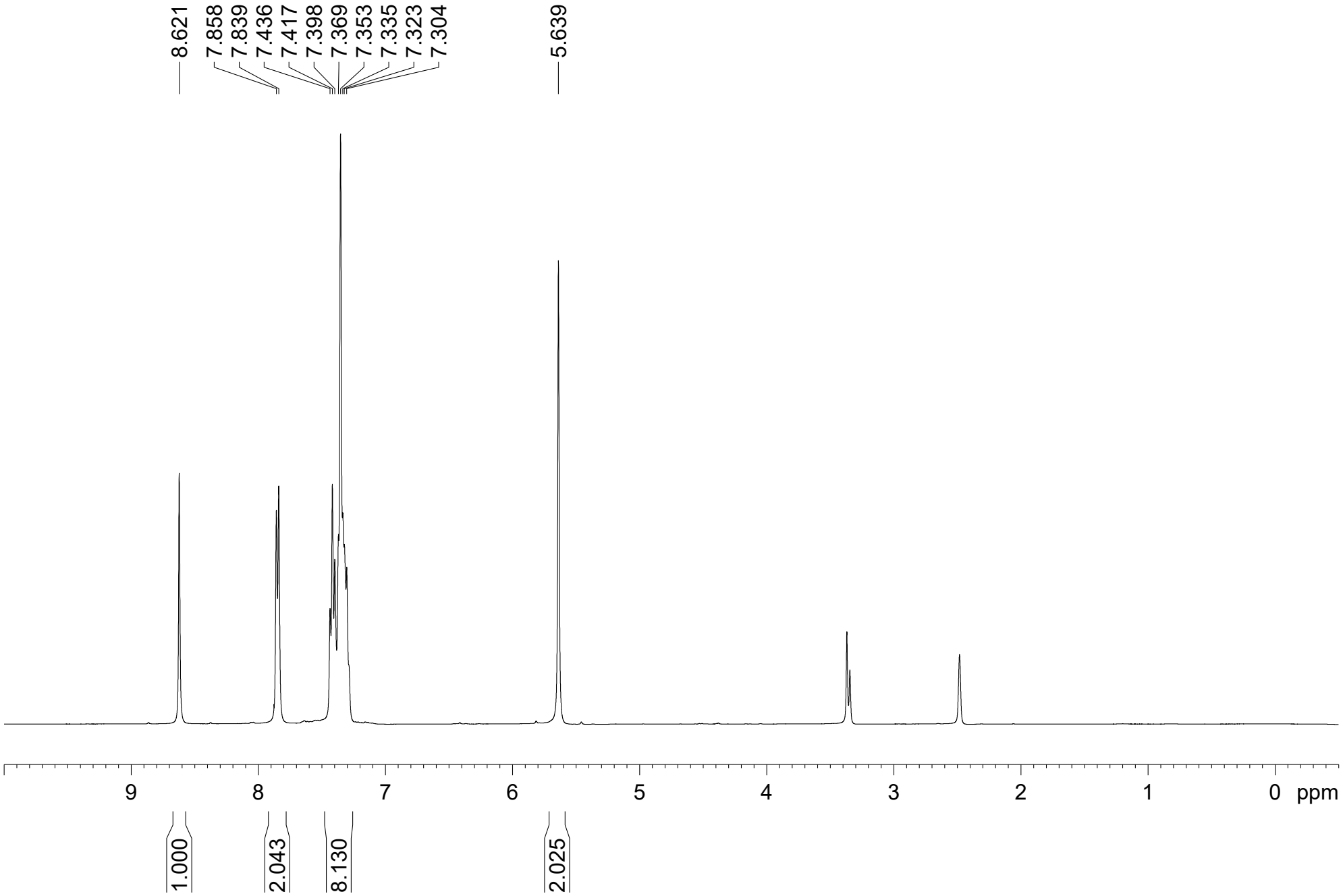
3q

1-Hexyl-4-phenyl-1H-1,2,3-triazole 3r. Imidazole (14 mg, 20 mol%), sodium ascorbate (20 mg, 10 mol%) and copper(II) sulfate pentahydrate (5 mg, 2 mol%) were dissolved in 5 mL of furfuryl alcohol (20 wt%) water mixture. Phenylacetylene (0.110 mL, 1 mmol) and 1-bromohexane (0.140 mL, 1 mmol) were suspended in the catalyst solution. After addition of sodium azide (130 mg, 2 mmol) the heterogeneous mixture was stirred vigorously at 60 °C for 48 h. After cooling to room temperature solvent was decanted and 10 mL of ice-cold water was added to the oily residue to precipitate product. This was collected by filtration, washed with 10 mL distilled water, 10 mL hexane and dried in vacuum to afford 121 mg (53 %), light brown powder with m.p. 72-76 °C. ^{1}H NMR (400 MHz, DMSO-D6) δ: 0.60-1.01 (m, 3H), 1.07-1.43 (m, 6H), 1.66-1.96 (m, 2H), 4.36 (t, *J* = 6.5 Hz, 2H), 7.30 (t, *J* = 7.1 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.83 (d, *J* = 7.5 Hz, 2H), 8.55 (s, 1H). ^{13}C NMR (100.6 MHz, DMSO-D6) δ: 14.3, 22.3, 26.0, 30.0, 31.0, 50.0, 121.6, 125.5, 128.2, 129.3, 131.4, 146.7. IR ($CHCl_3$, cm^{-1}): 3009, 2926, 2853, 1612, 1467, 1228, 1077, 745, 673. GC-EIMS (m/z, %): 89 (22), 102 (26), 103 (22), 104 (24), 116 (30), 117 (100), 130 (25), 144 (28), 145 (27), 172 (29), 200 (40), 229 (44).

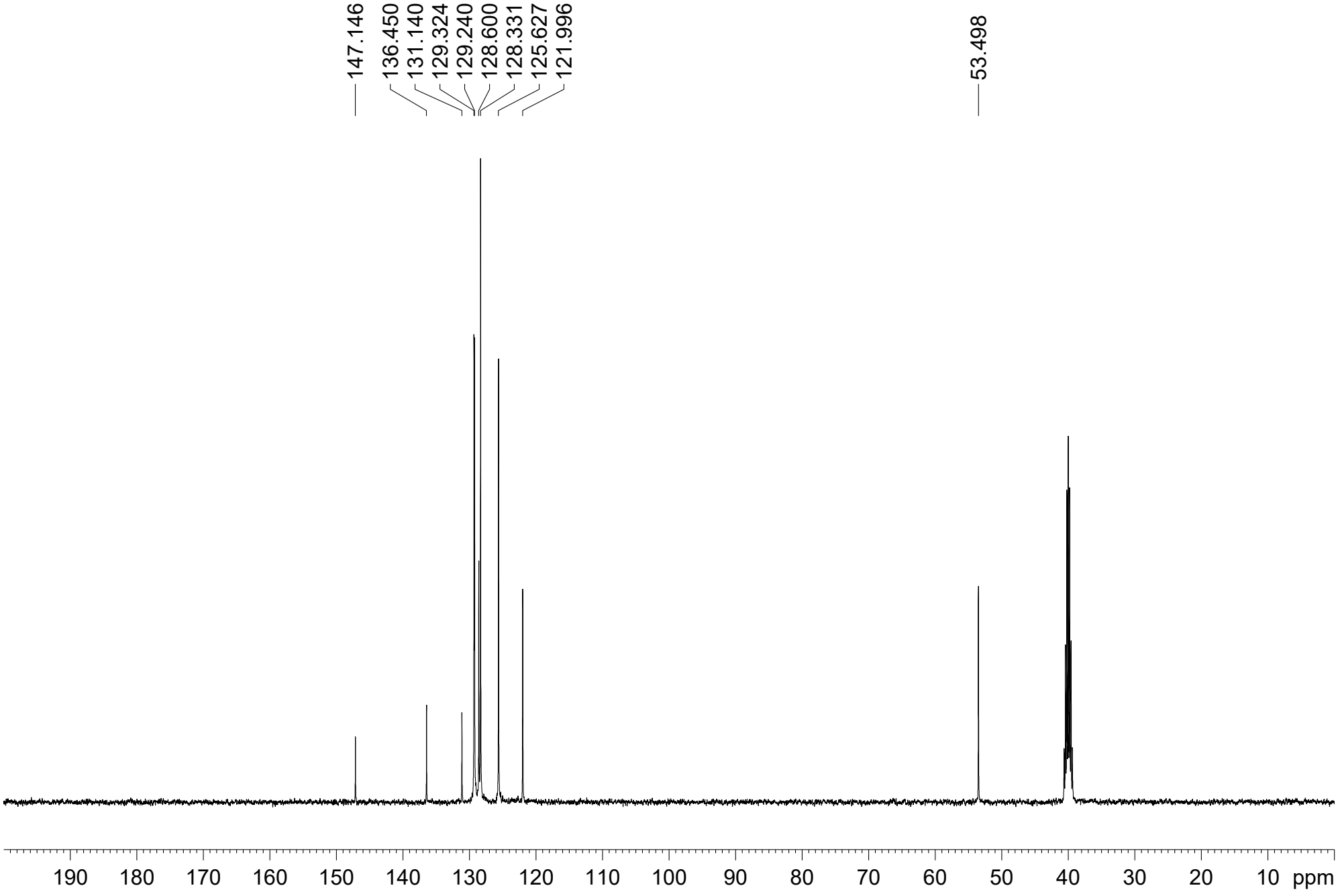


3r

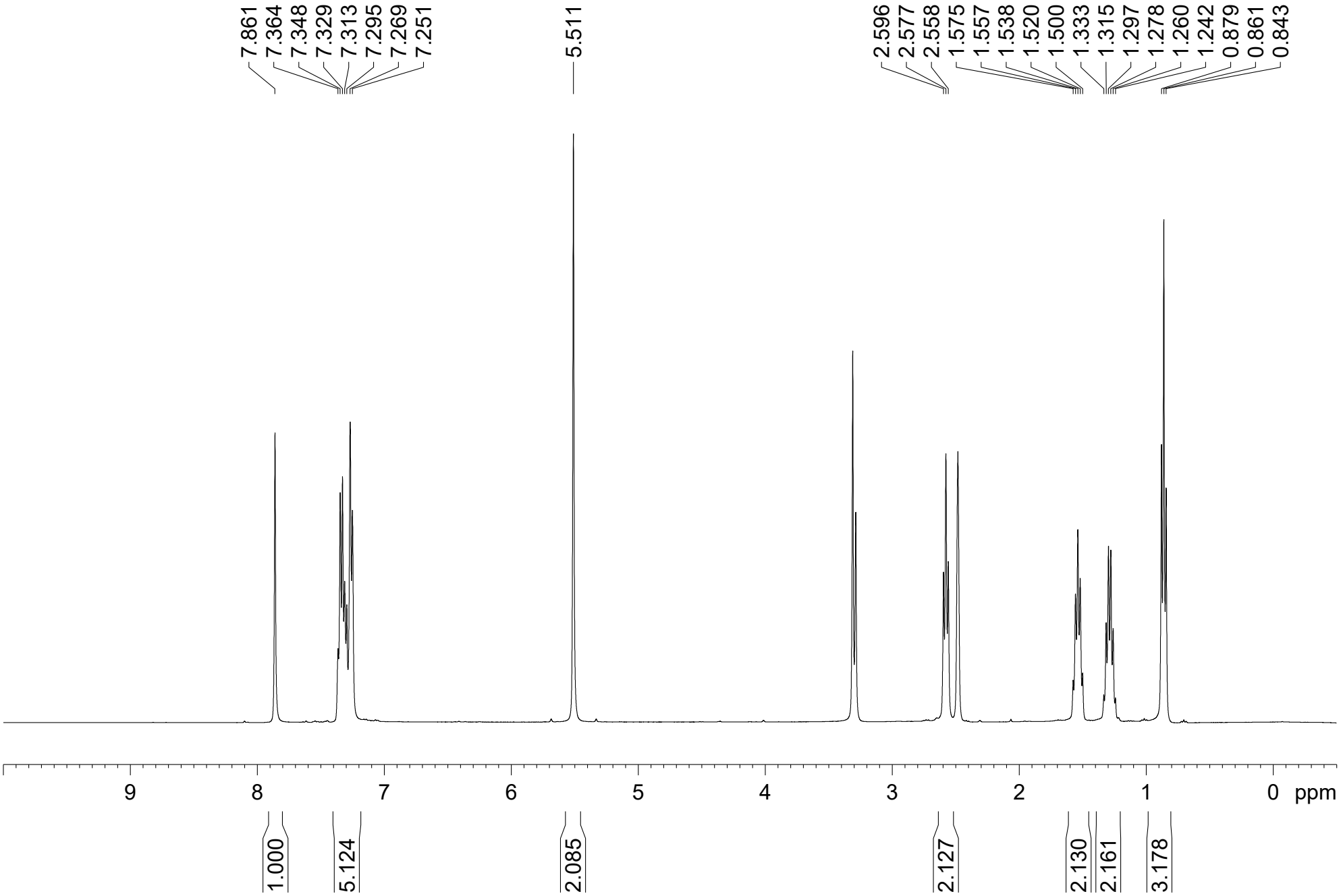
1−Benzyl−4−phenyl−1H−1,2,3−triazole (3a)



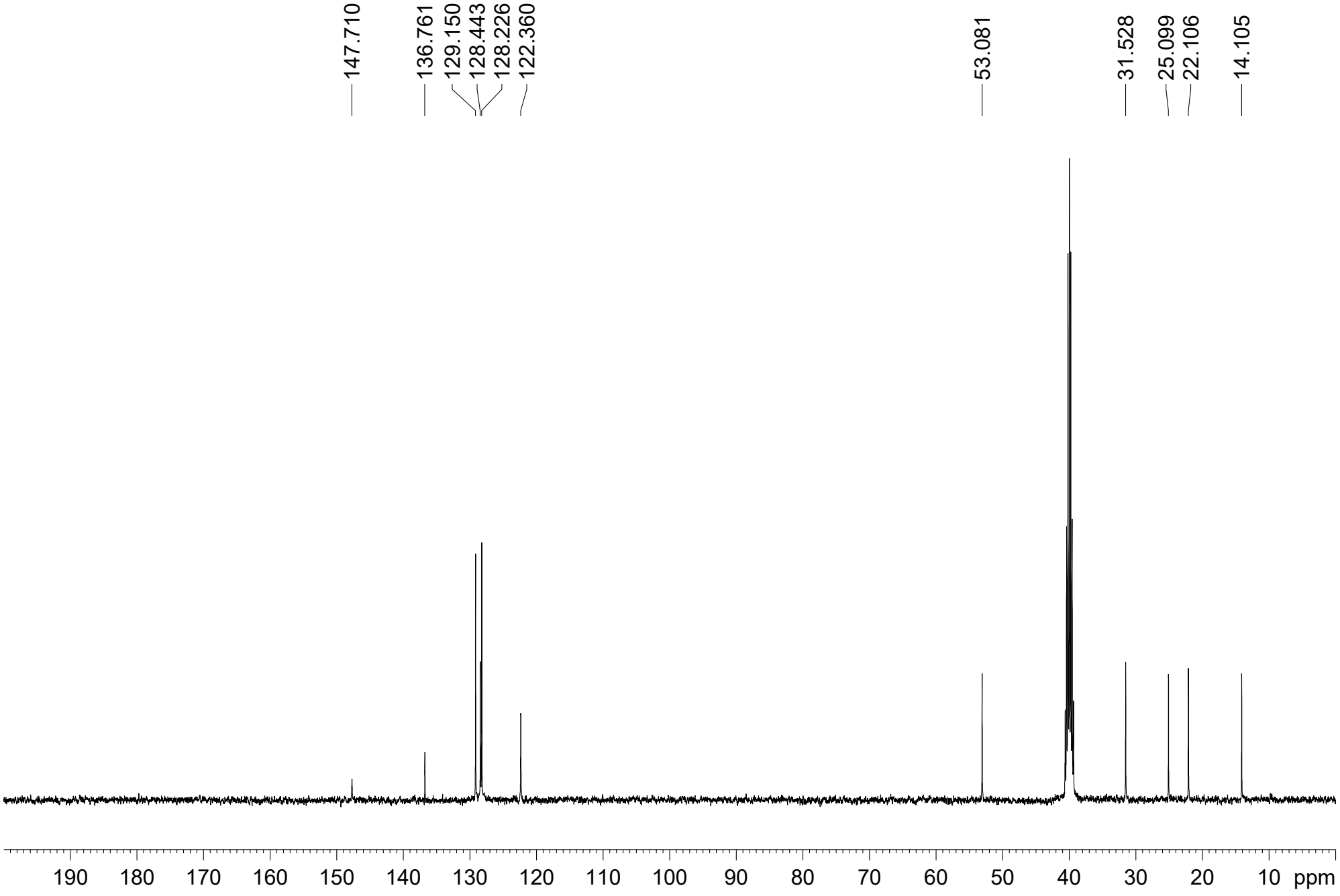
1−Benzyl−4−phenyl−1H−1,2,3−triazole (3a)



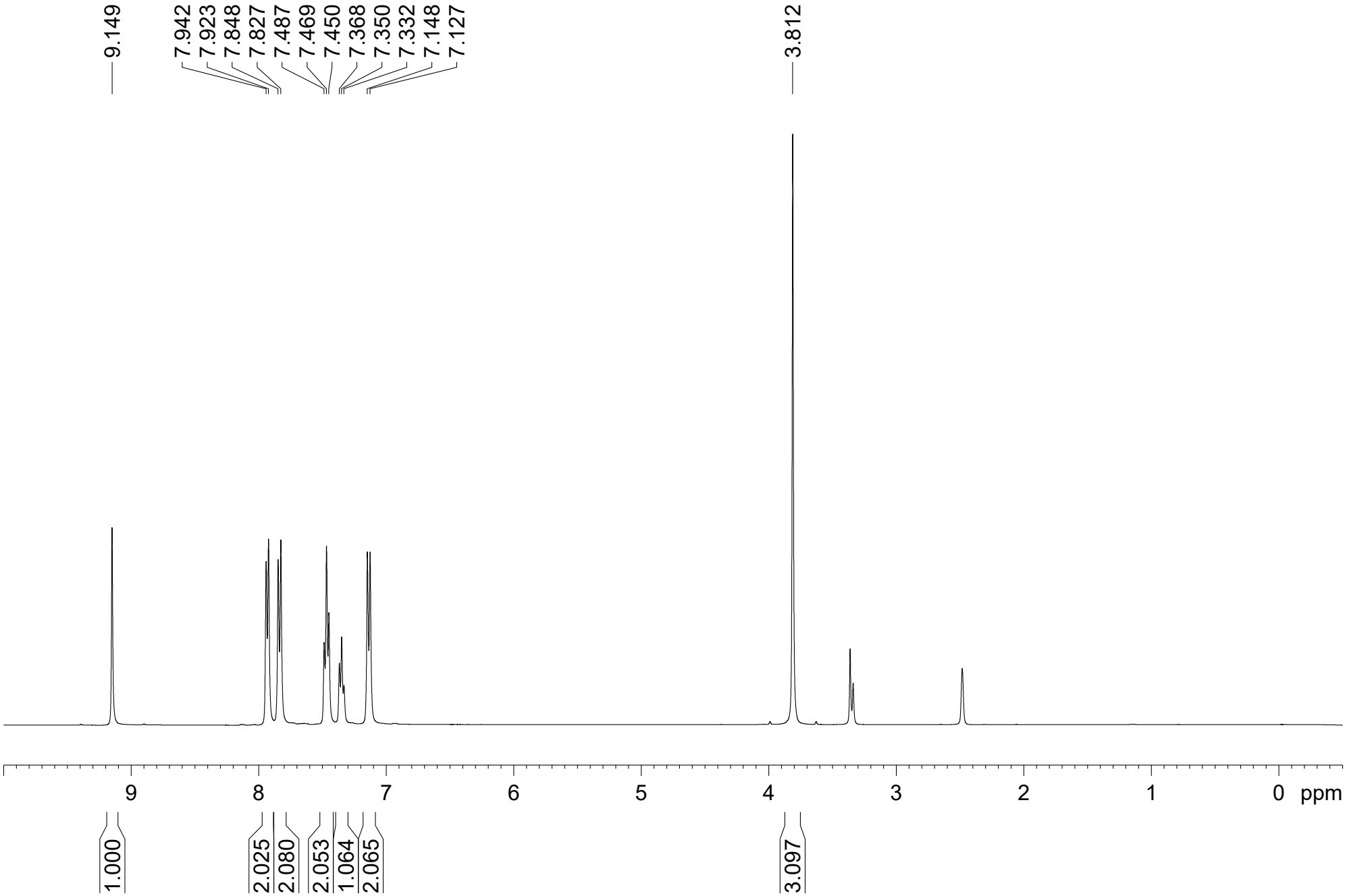
1−Benzyl−4−butyl−1H−1,2,3−triazole (3b)



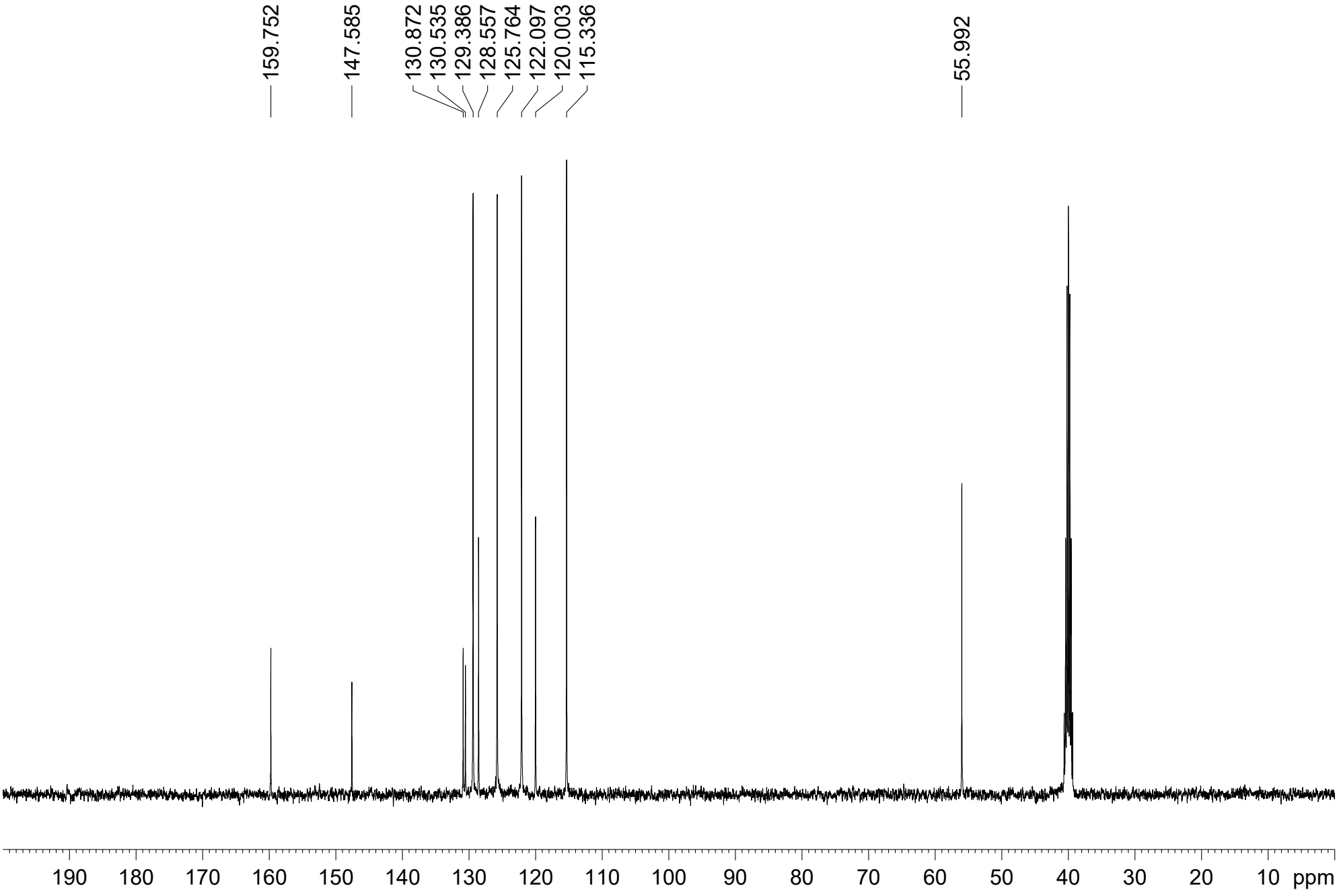
1−Benzyl−4−butyl−1H−1,2,3−triazole (3b)



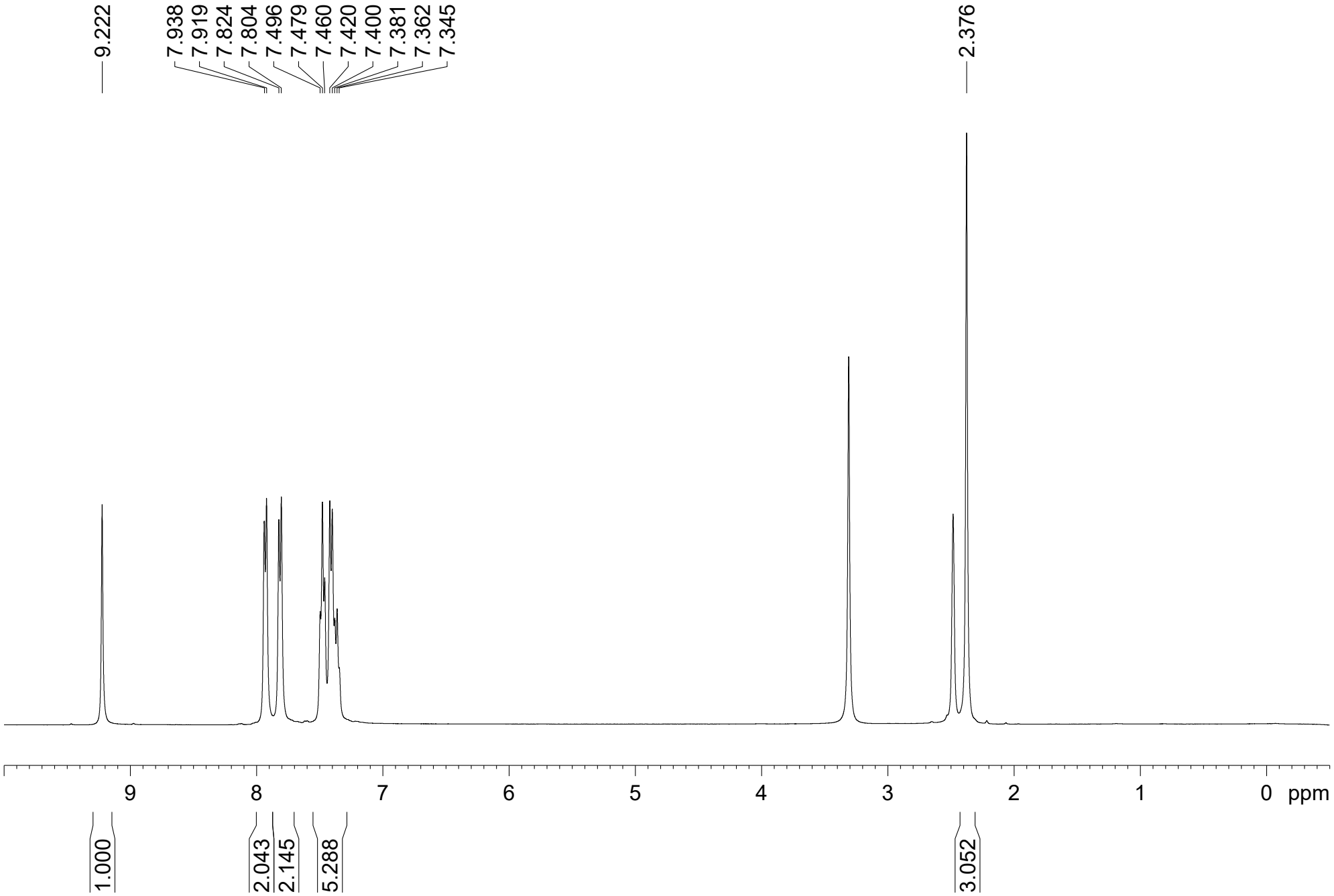
1−(4−Methoxyphenyl)−4−phenyl−1H−1,2,3−triazole (3c)



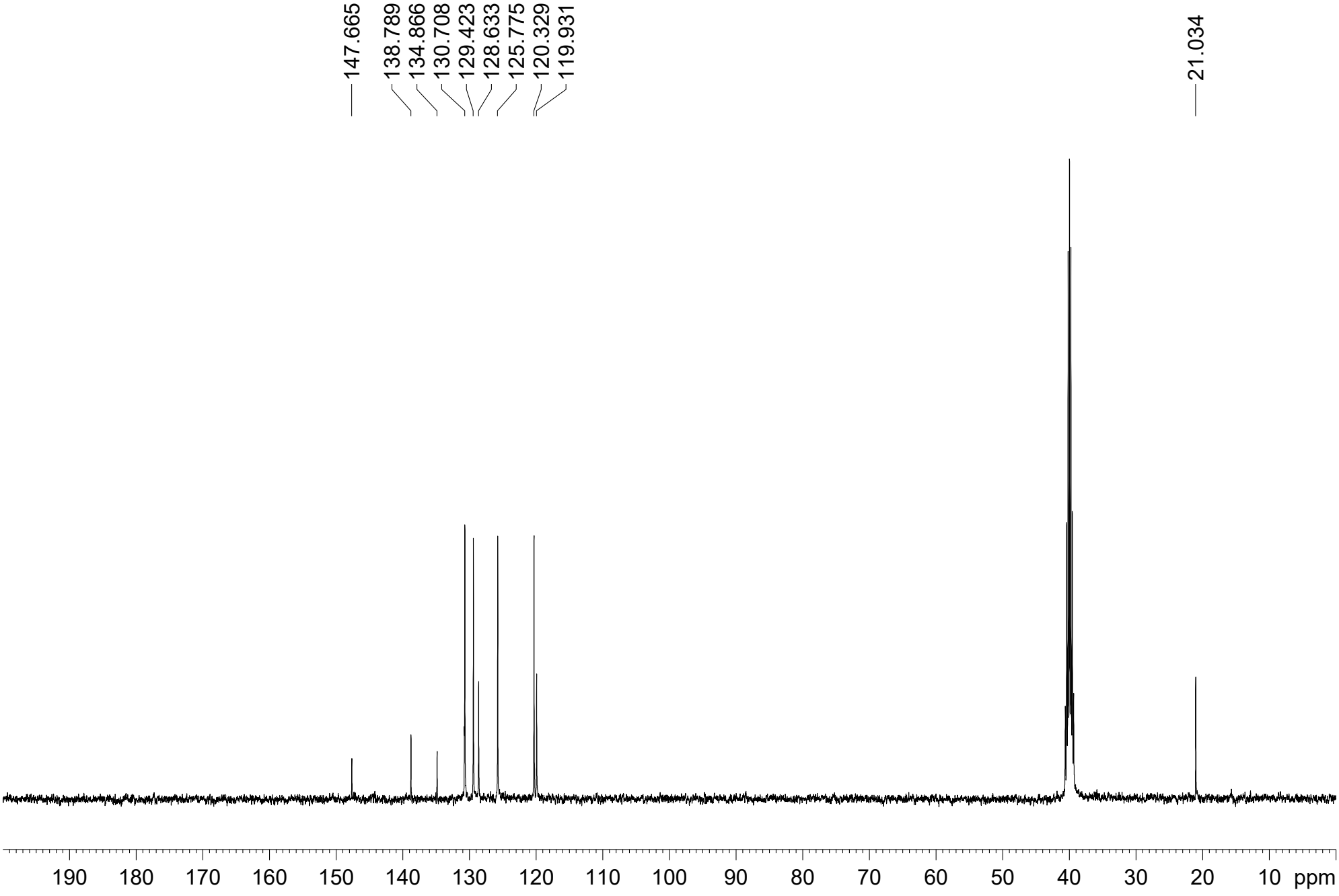
1−(4−Methoxyphenyl)−4−phenyl−1H−1,2,3−triazole (3c)



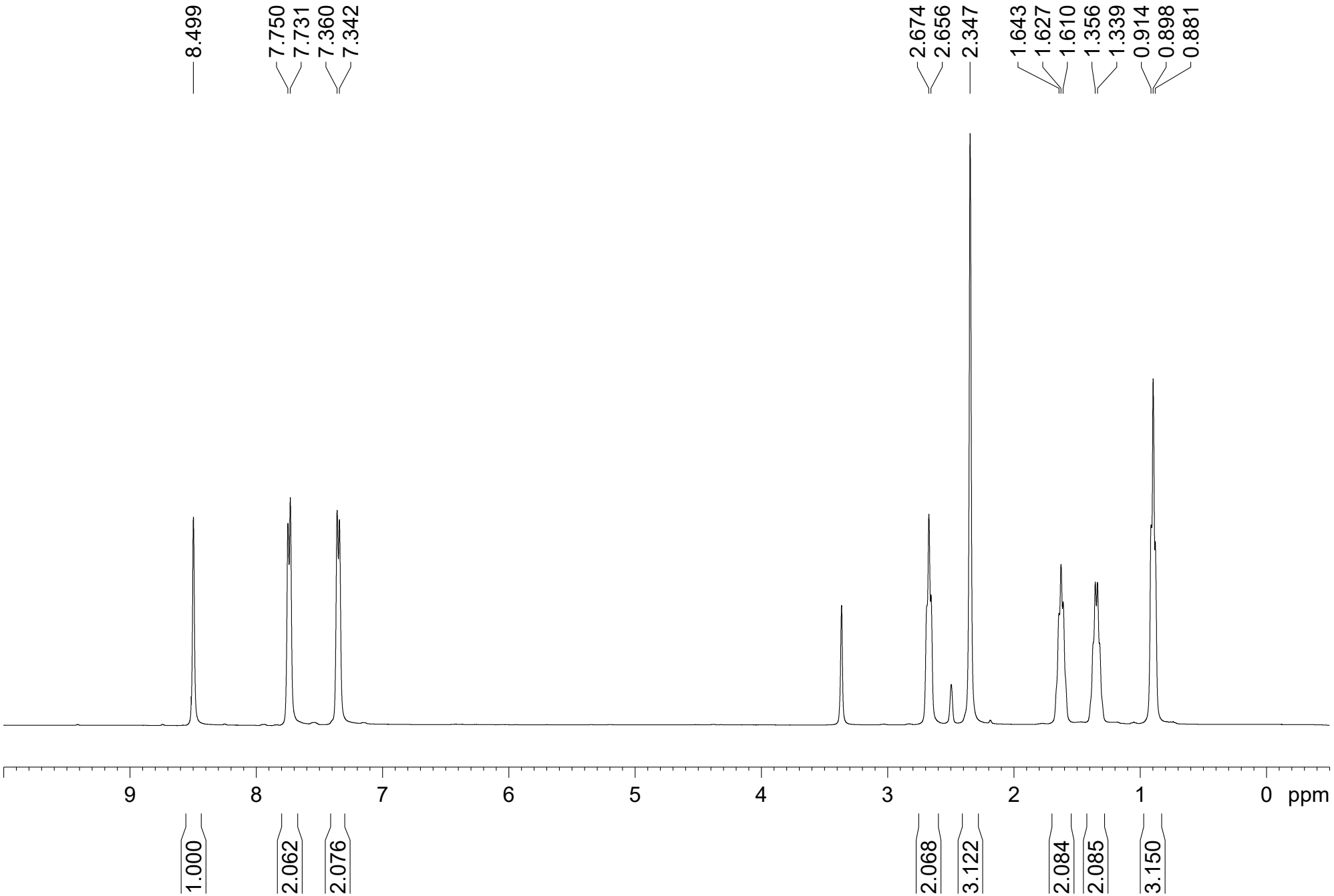
4−Phenyl−1−p−tolyl−1H−1,2,3−triazole (3d)



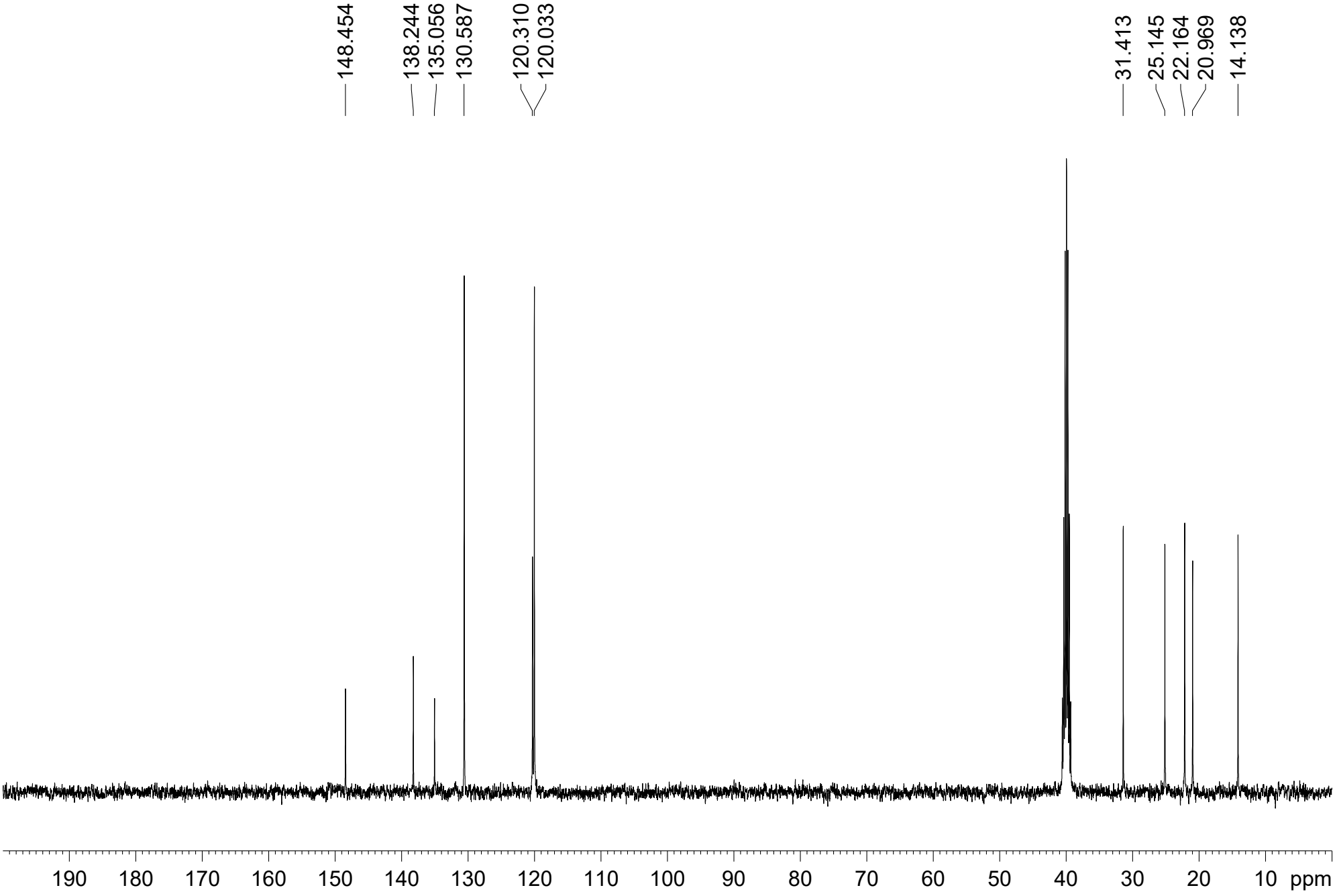
4−Phenyl−1−p−tolyl−1H−1,2,3−triazole (3d)



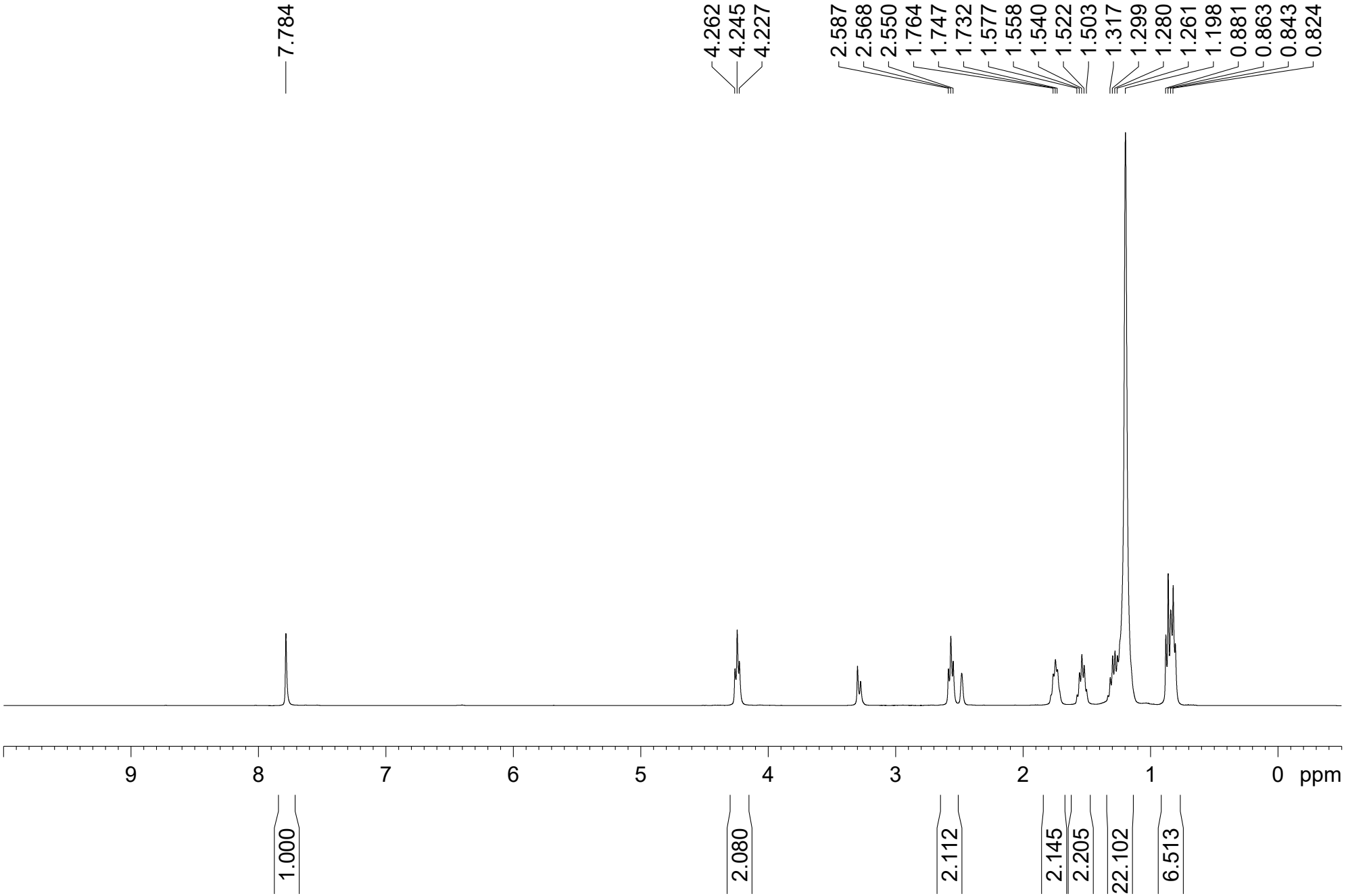
4−Butyl−1−p−tolyl−1H−1,2,3−triazole (3e)



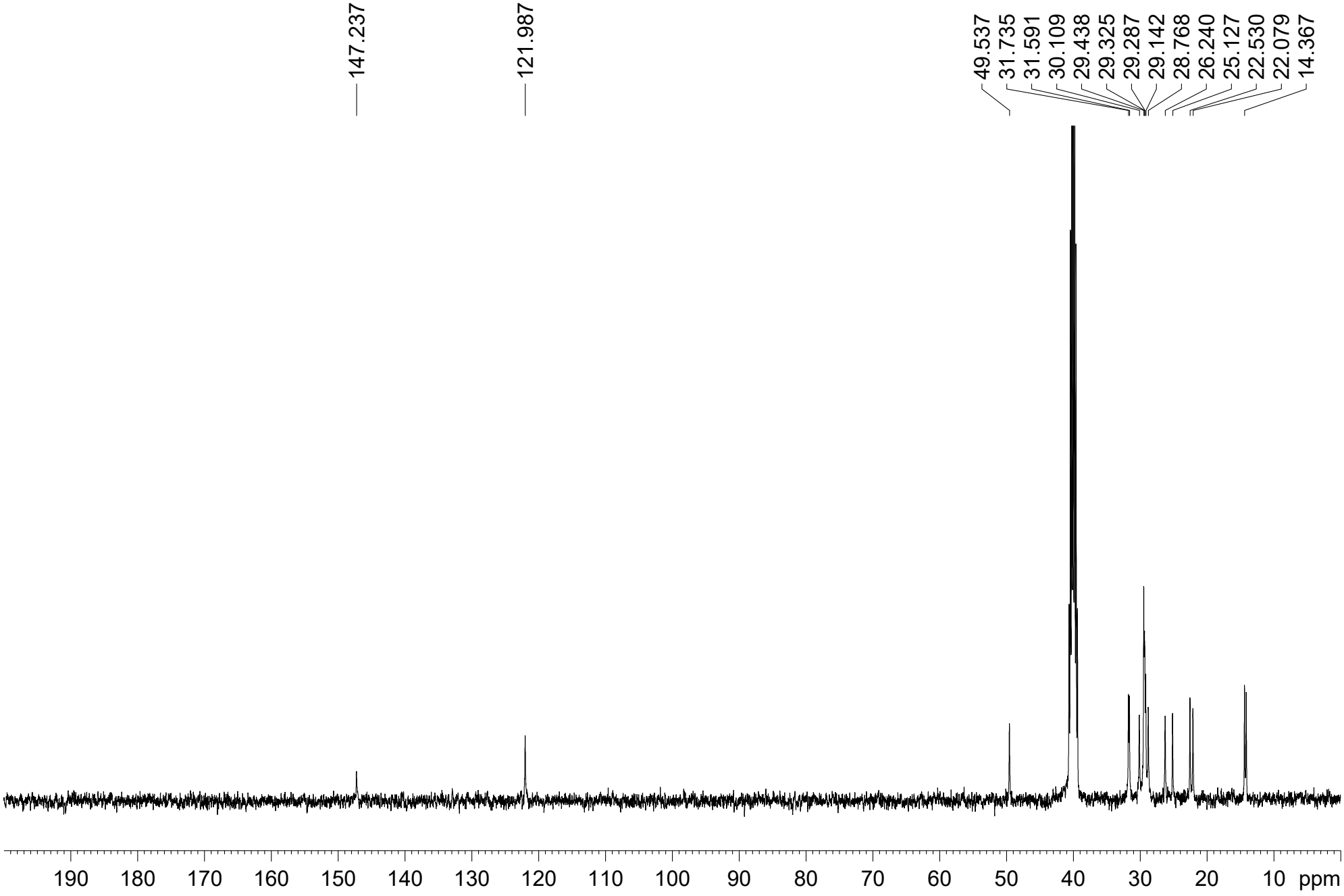
4−Butyl−1−p−tolyl−1H−1,2,3−triazole (3e)



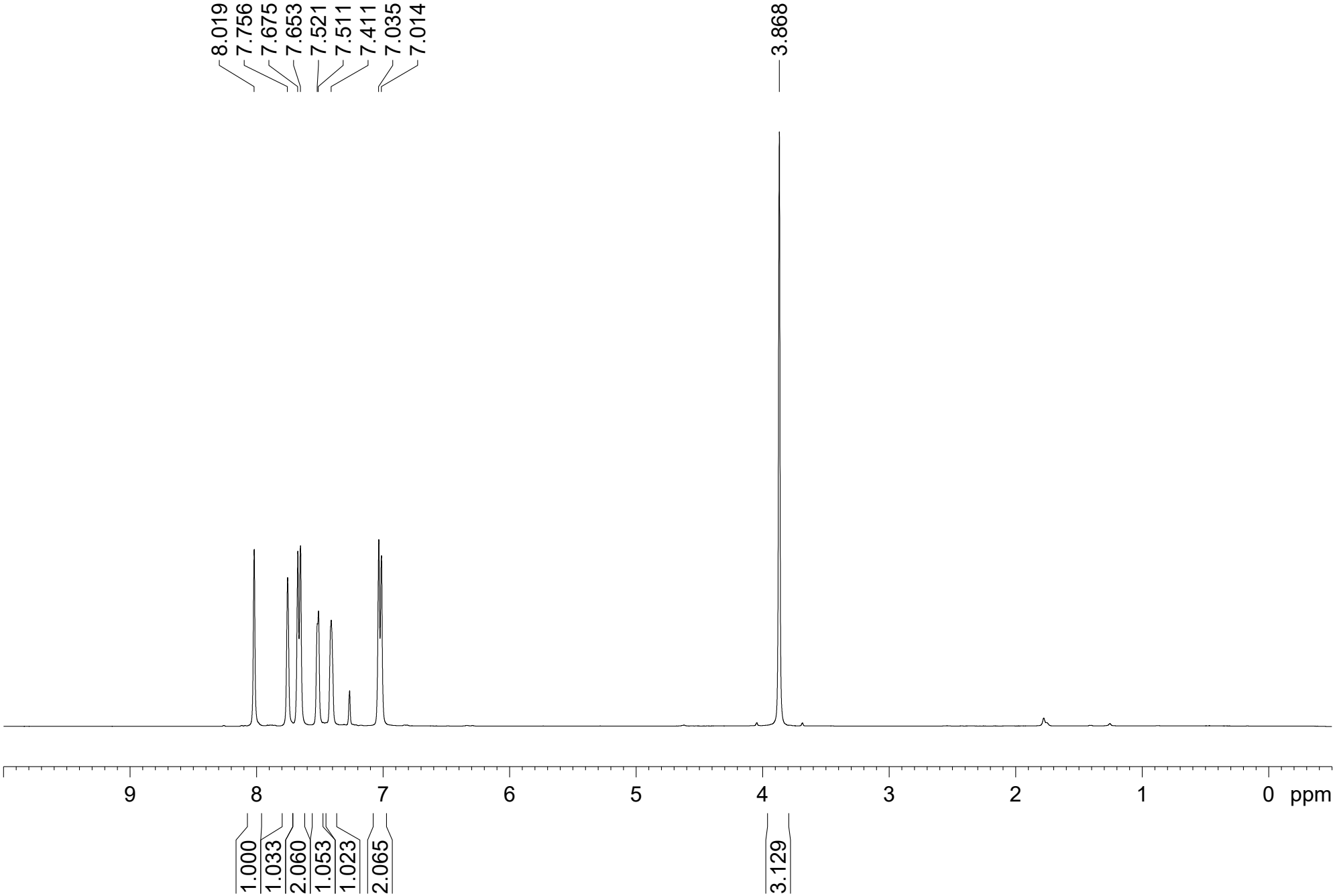
4−Butyl−1−dodecyl−1H−1,2,3−triazole (3f)



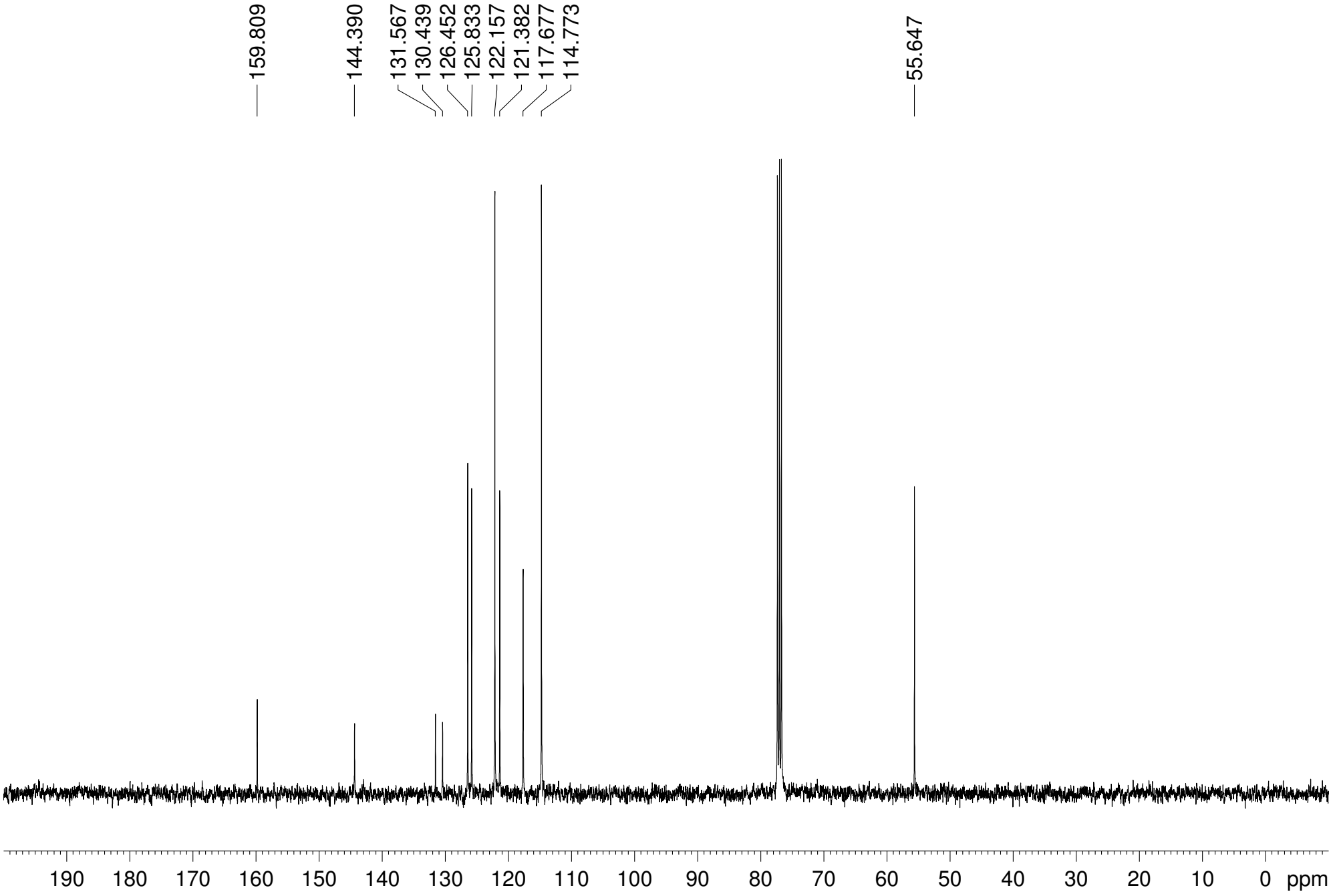
4−Butyl−1−dodecyl−1H−1,2,3−triazole (3f)



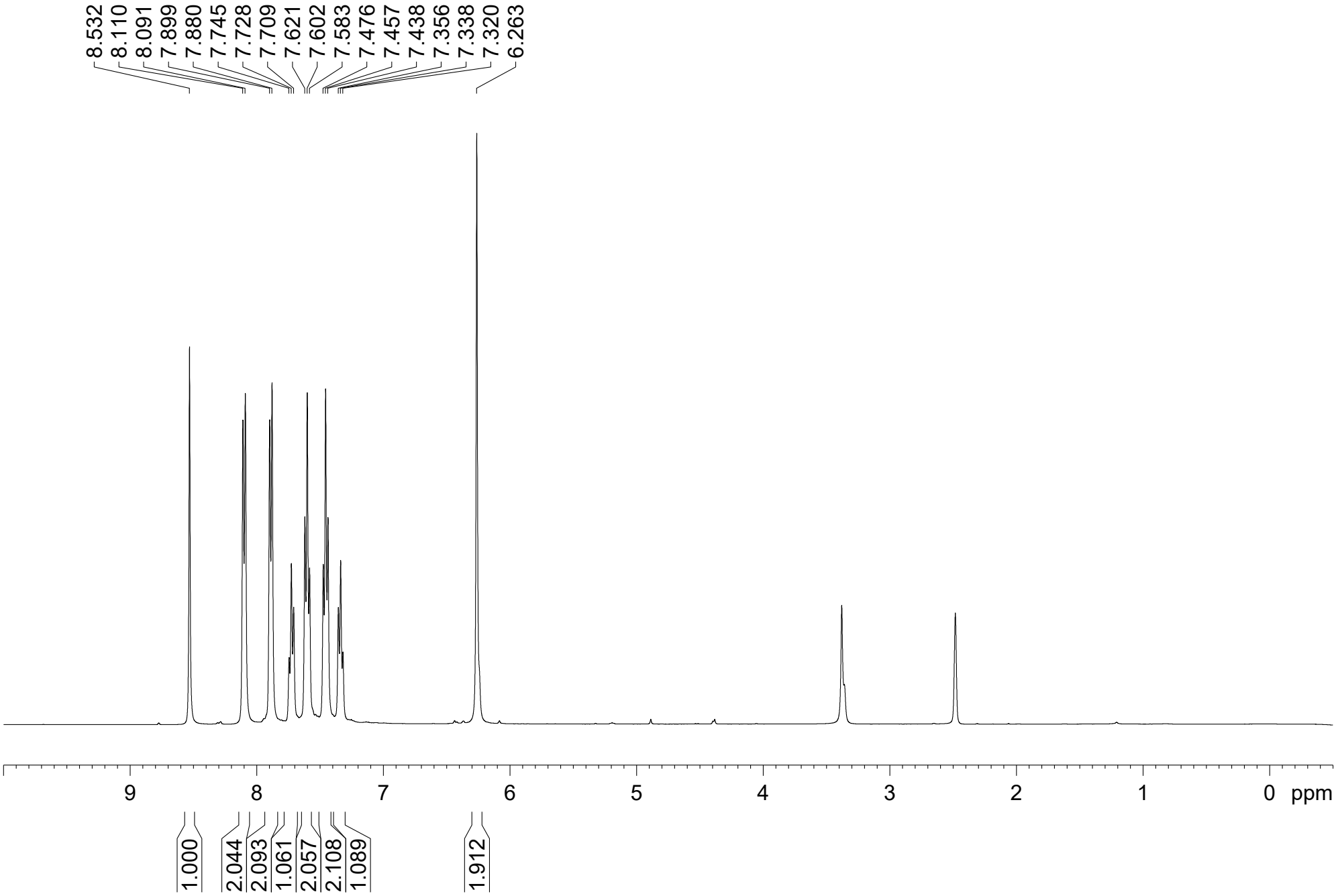
1−(4−Methoxyphenyl)−4−(thiophen−3−yl)−1H−1,2,3−triazole (3g)



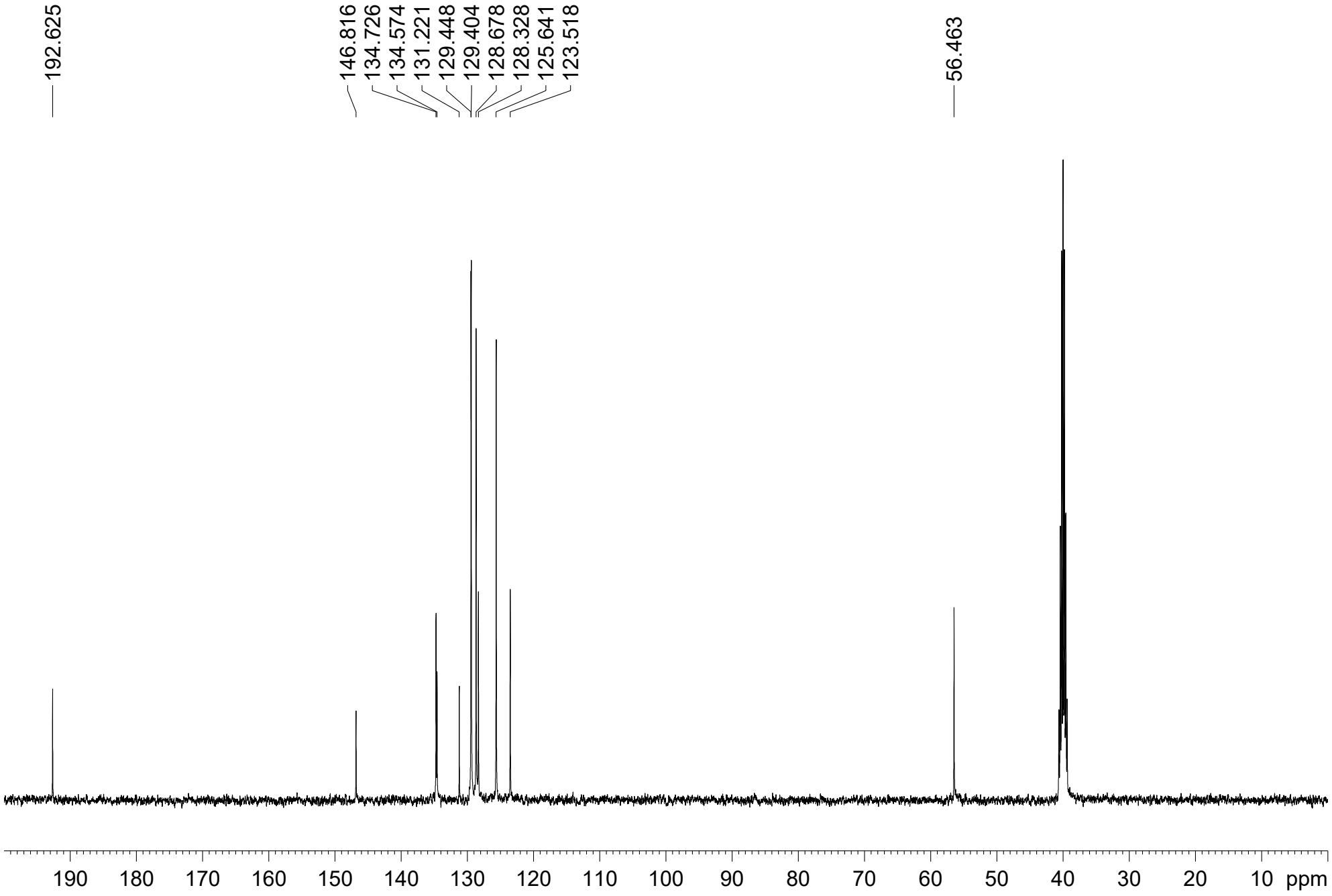
1–(4–Methoxyphenyl)–4–(thiophen–3–yl)–1H–1,2,3–triazole (3g)



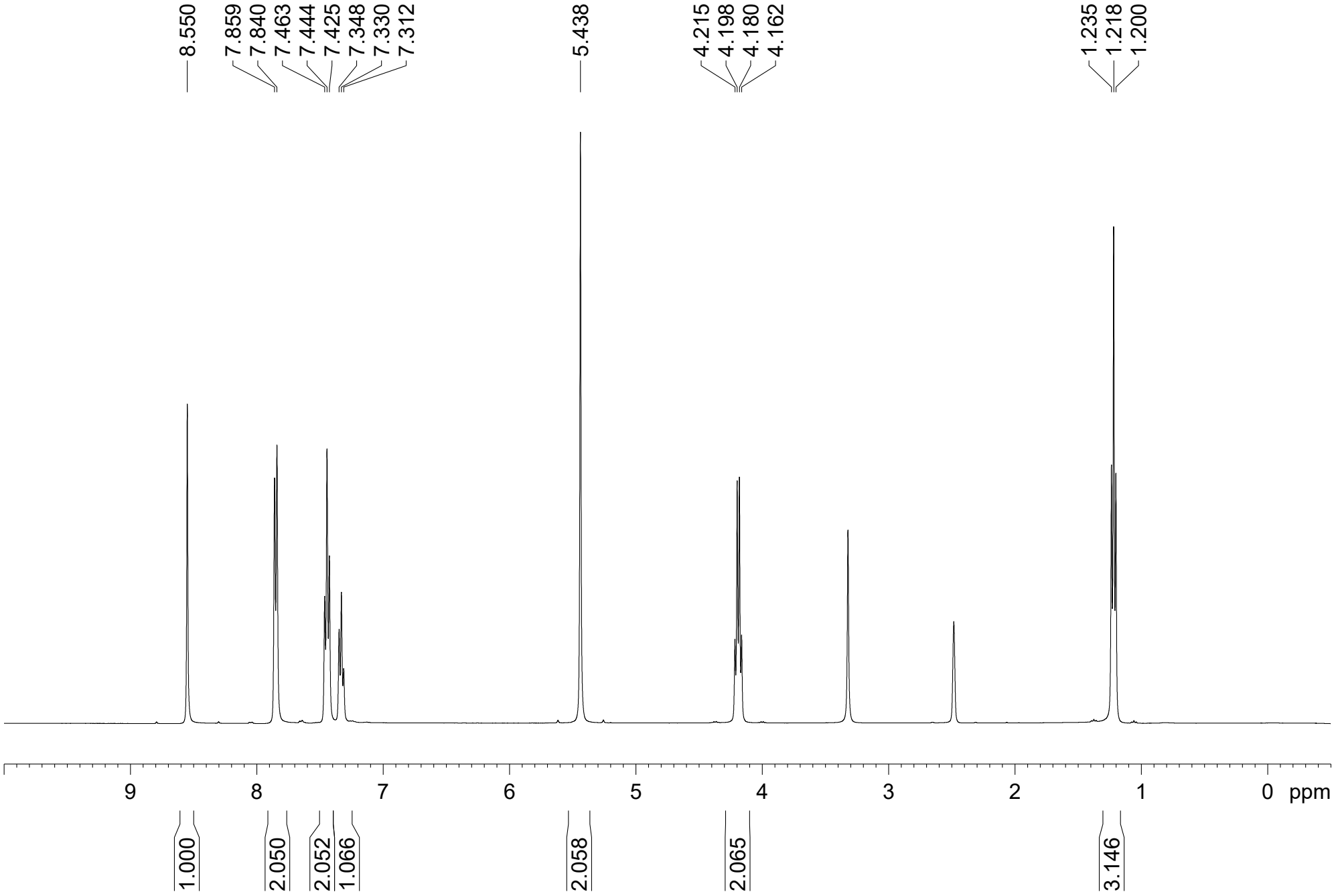
1−Phenyl−2−(4−phenyl−1H−1,2,3−triazol−1−yl)ethanone (3h)



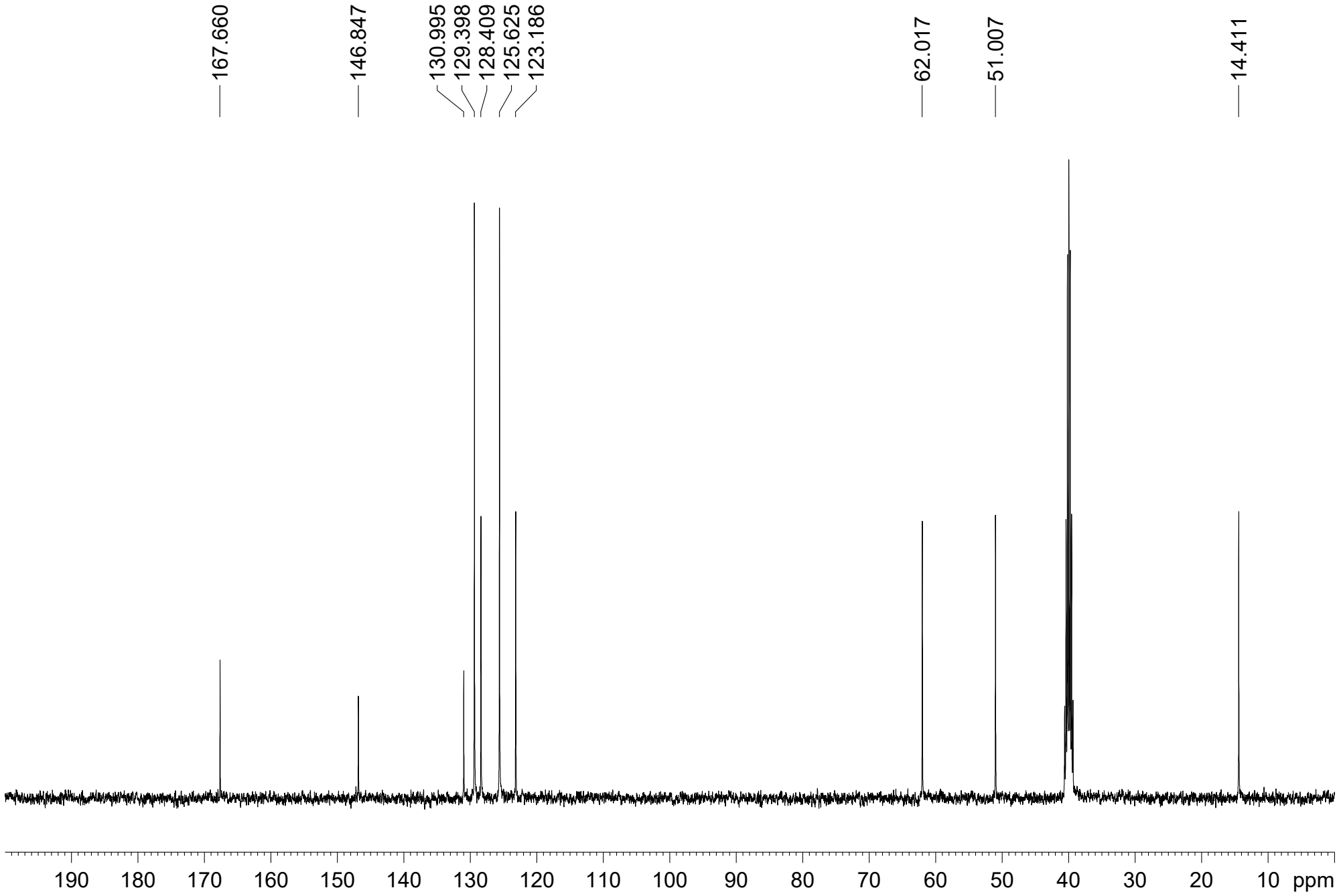
1−Phenyl−2−(4−phenyl−1H−1,2,3−triazol−1−yl)ethanone (3h)



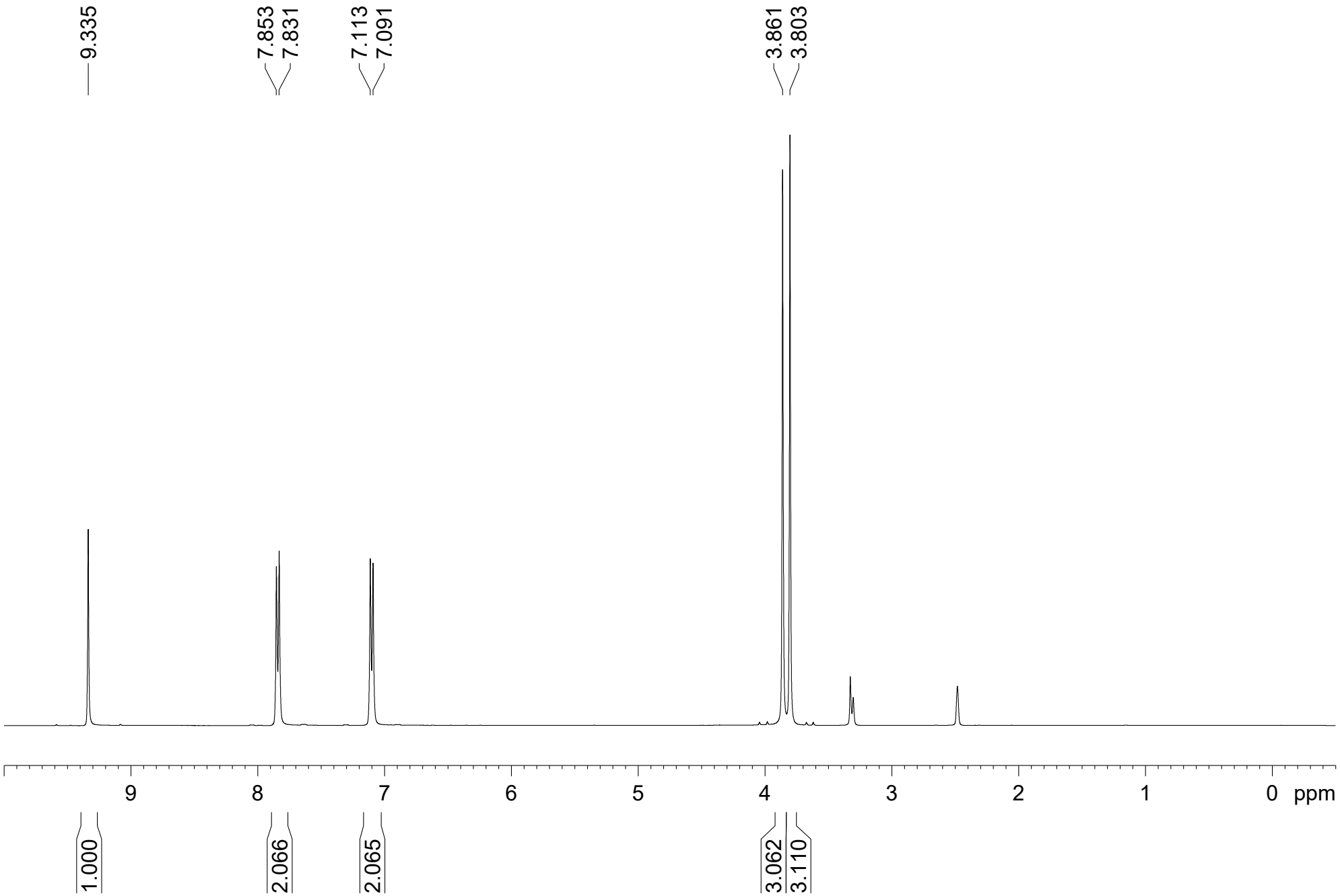
Ethyl 2−(4−phenyl−1H−1,2,3−triazol−1−yl)acetate (3i)



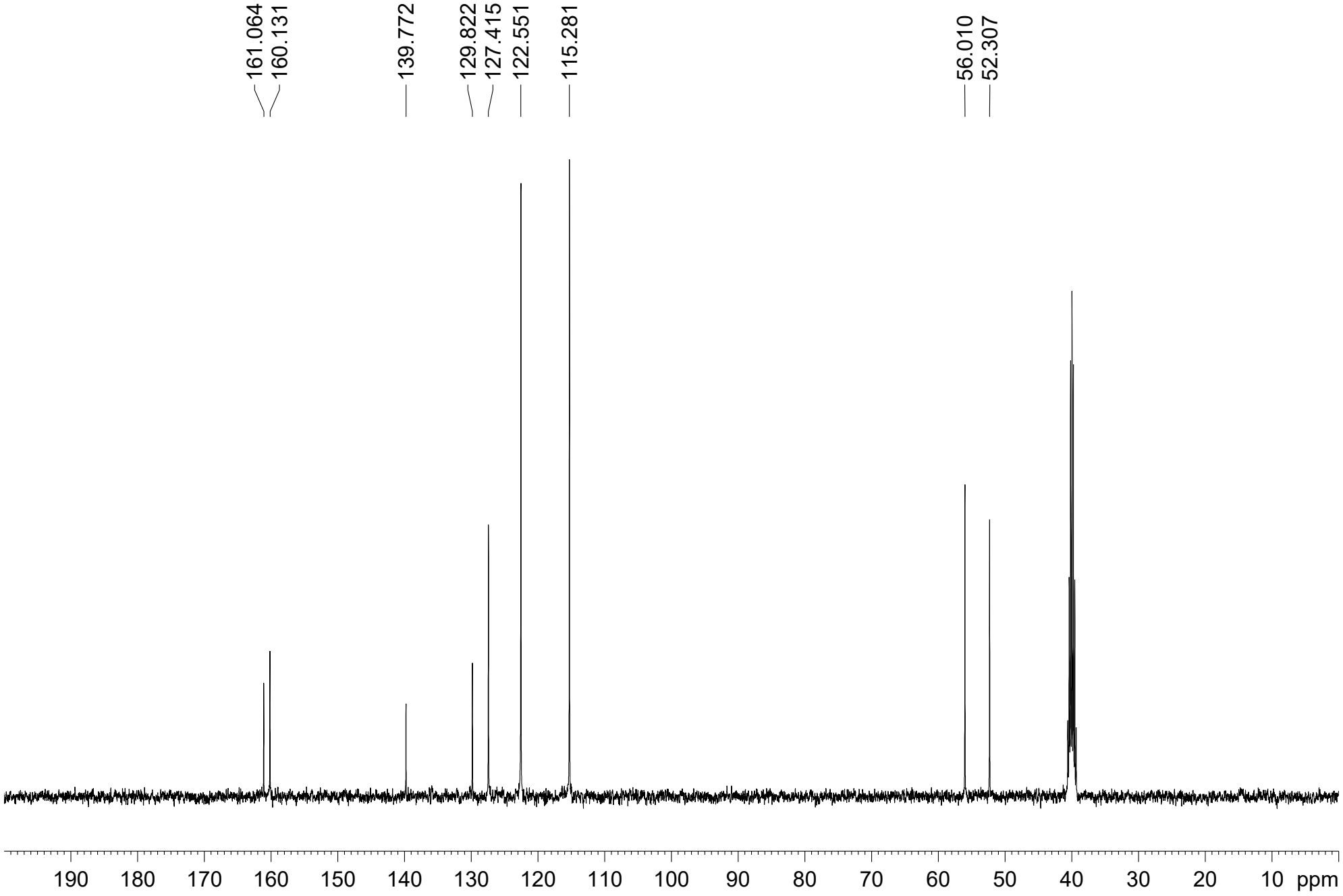
Ethyl 2−(4−phenyl−1H−1,2,3−triazol−1−yl)acetate (3i)



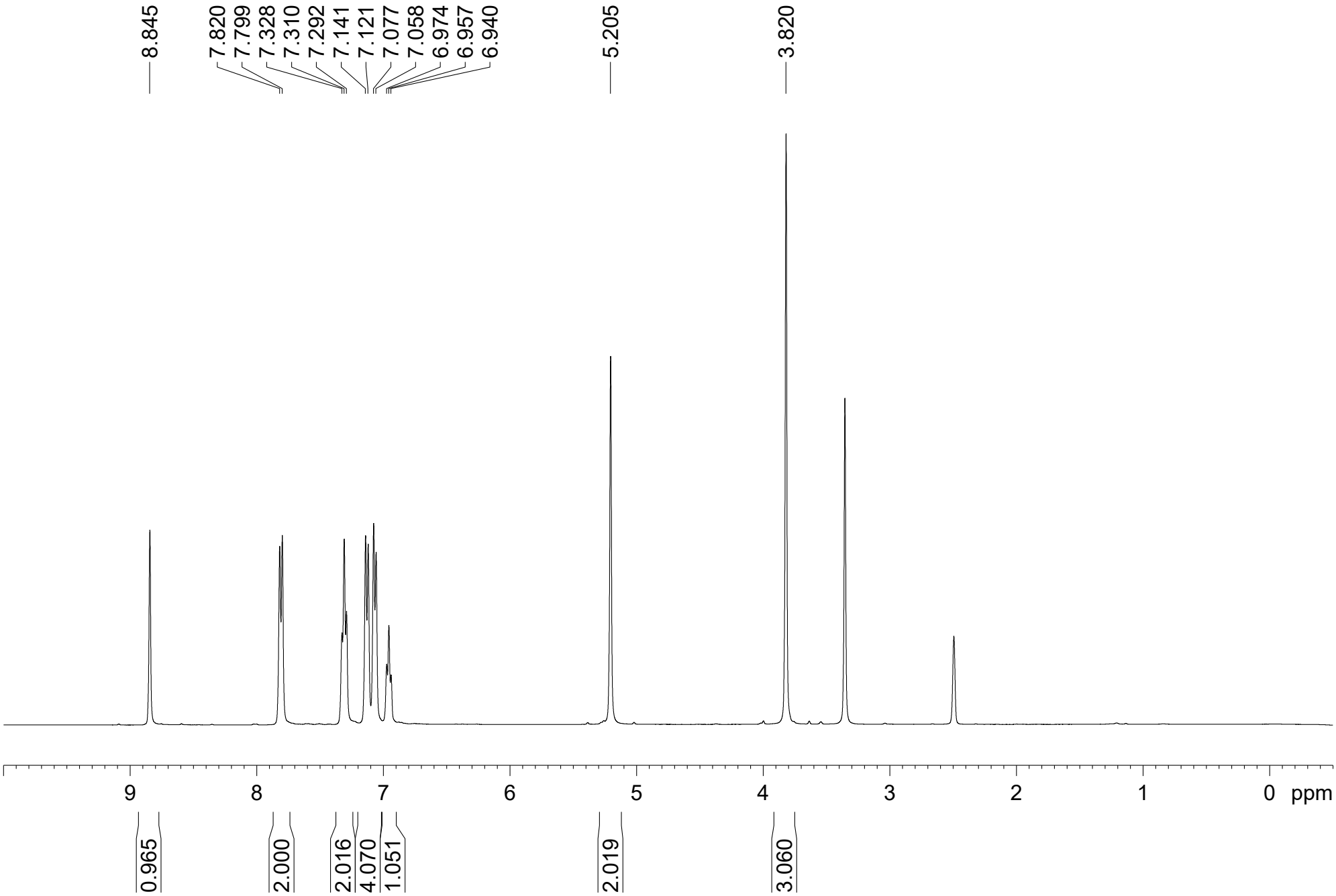
Methyl 1−(4−methoxyphenyl)−1H−1,2,3−triazole−4−carboxylate (3j)



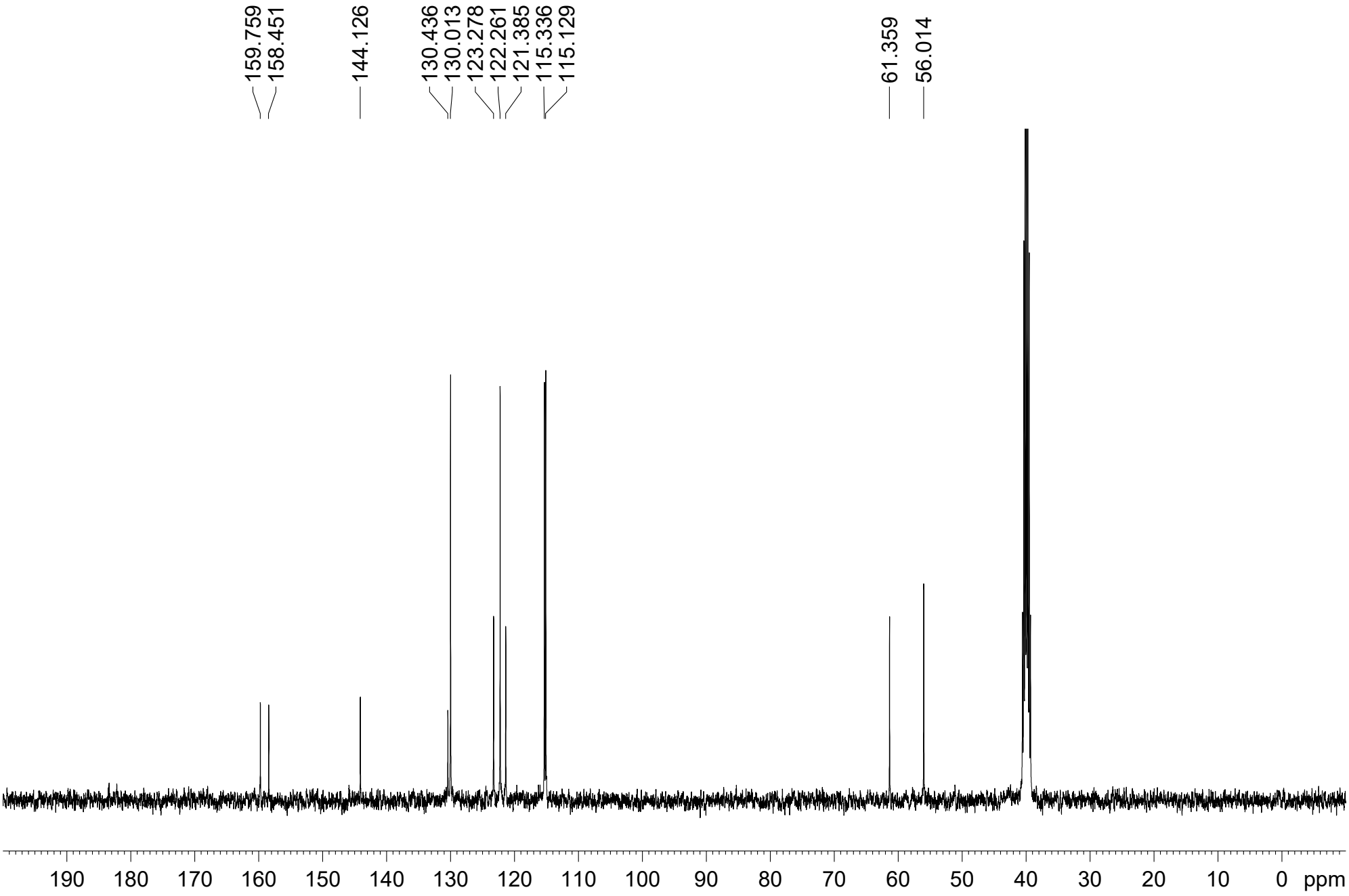
Methyl 1−(4−methoxyphenyl)−1H−1,2,3−triazole−4−carboxylate (3j)

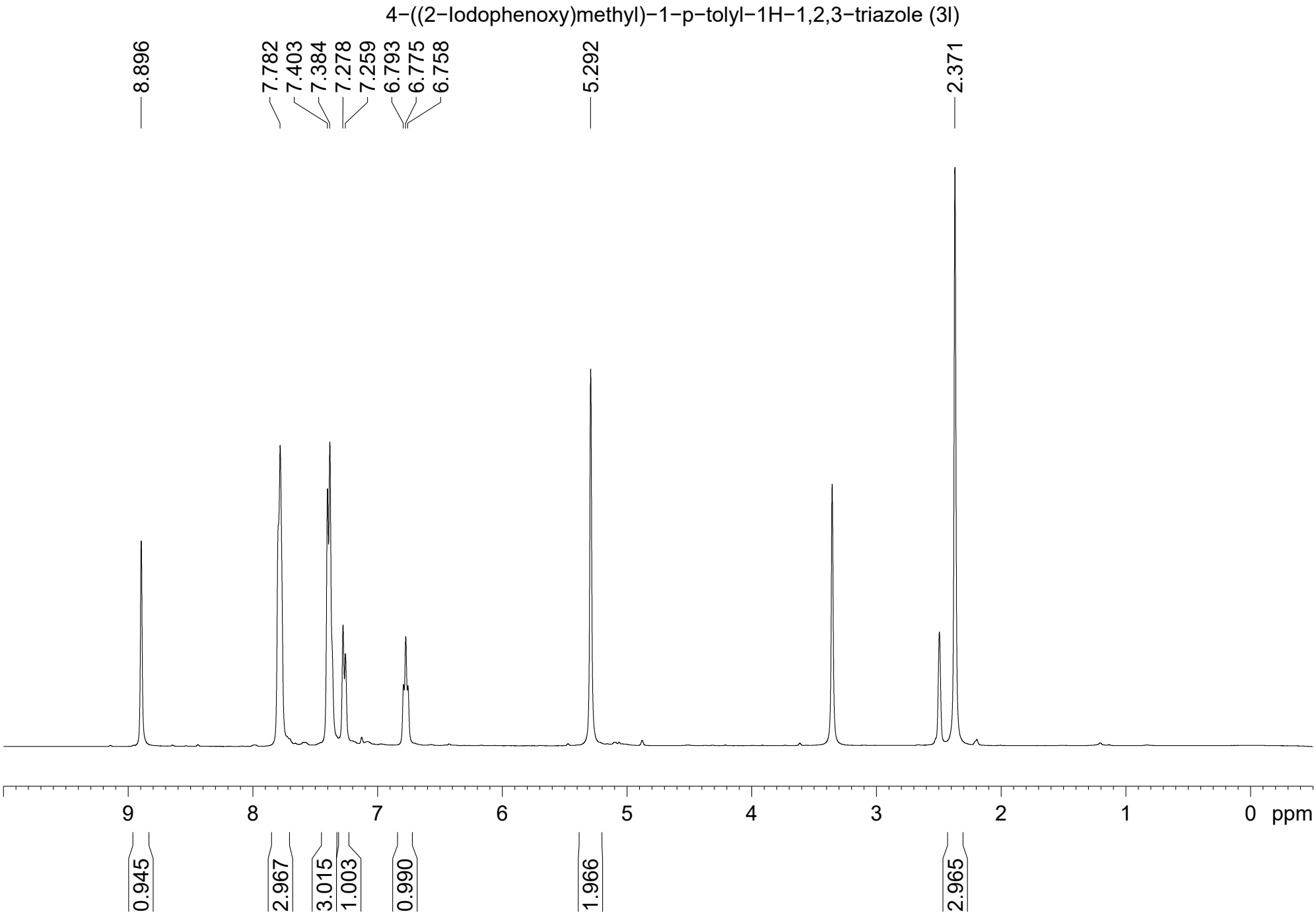


1−(4−Methoxyphenyl)−4−(phenoxymethyl)−1H−1,2,3−triazole (3k)

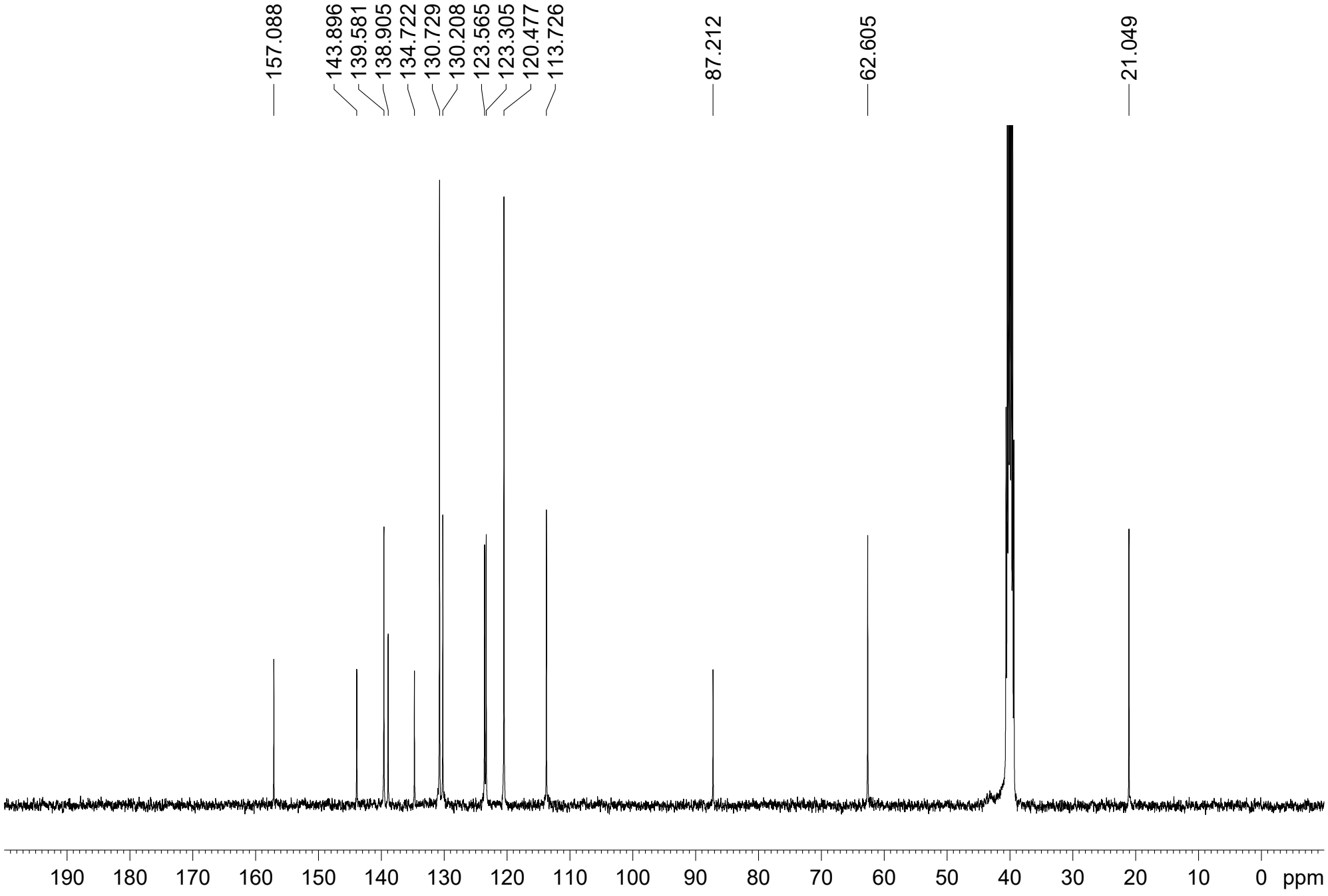


1−(4−Methoxyphenyl)−4−(phenoxymethyl)−1H−1,2,3−triazole (3k)

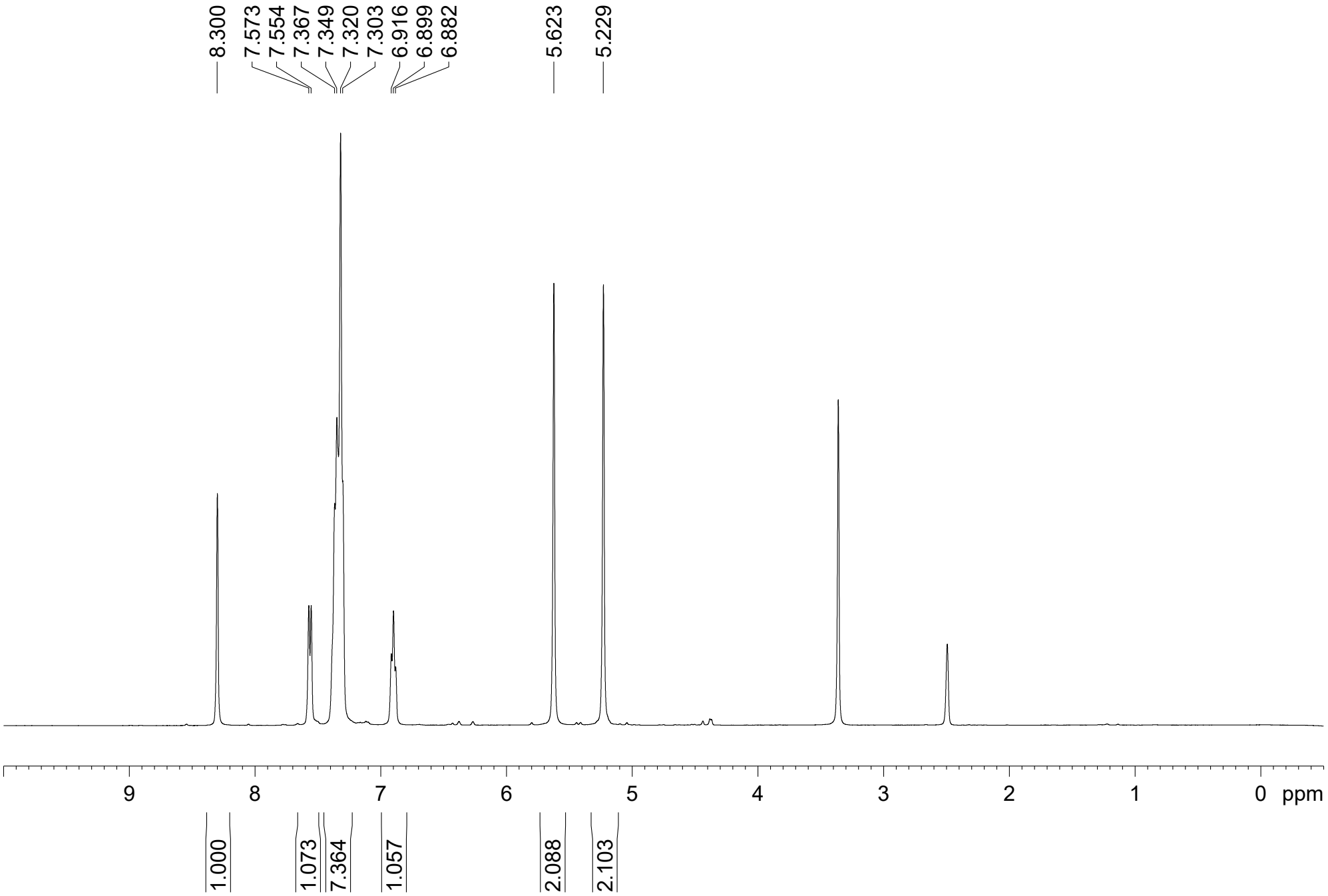



4−((2−Iodophenoxy)methyl)−1−p−tolyl−1H−1,2,3−triazole (3l)
8.896
7.782
7.403
7.384
7.278
7.259
6.793
6.775
6.758
5.292
2.371
9
8
7
6
5
4
3
2
1
0 ppm
0.945
2.967
3.015
1.003
0.990
1.966
2.965

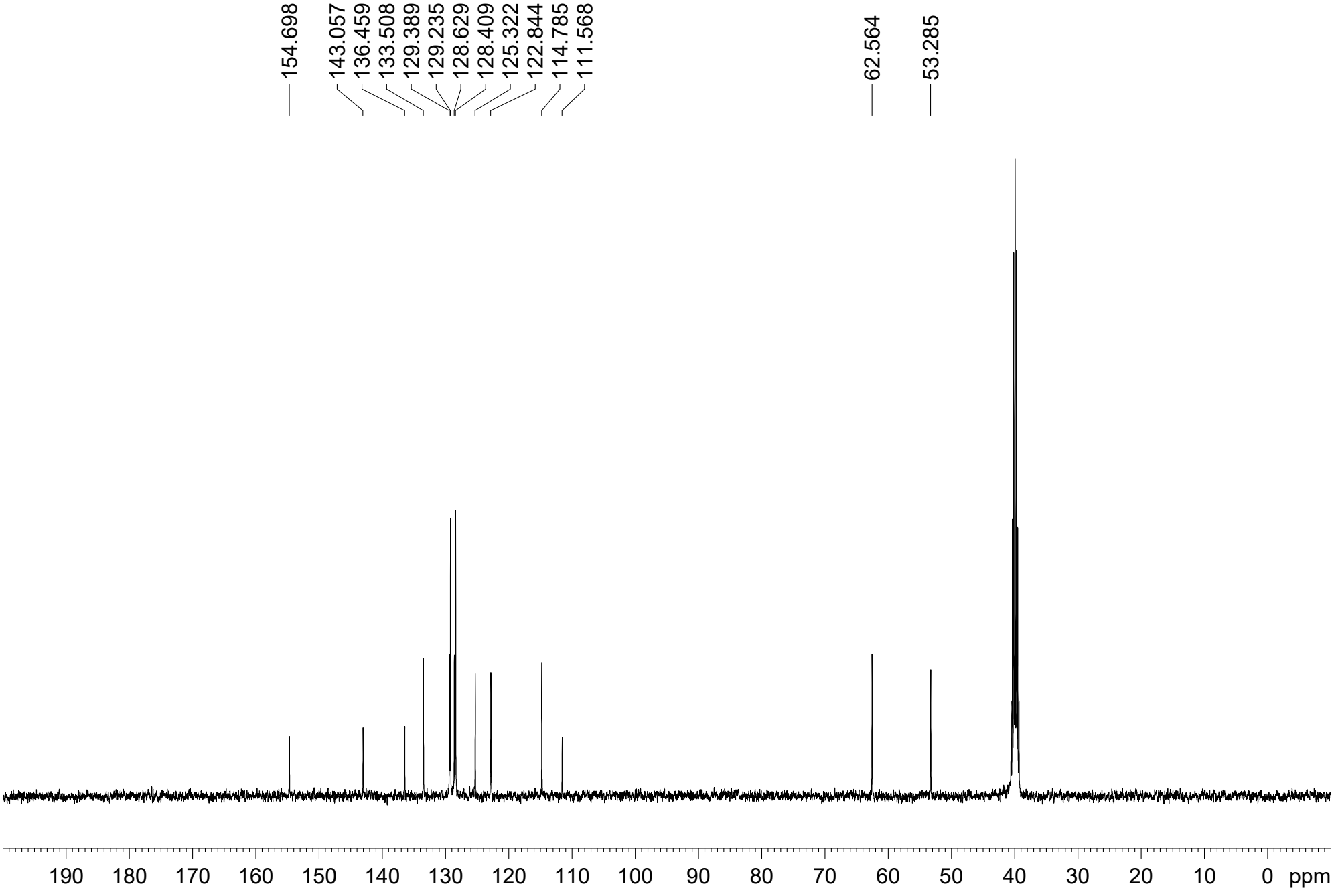
4−((2−Iodophenoxy)methyl)−1−p−tolyl−1H−1,2,3−triazole (3l)



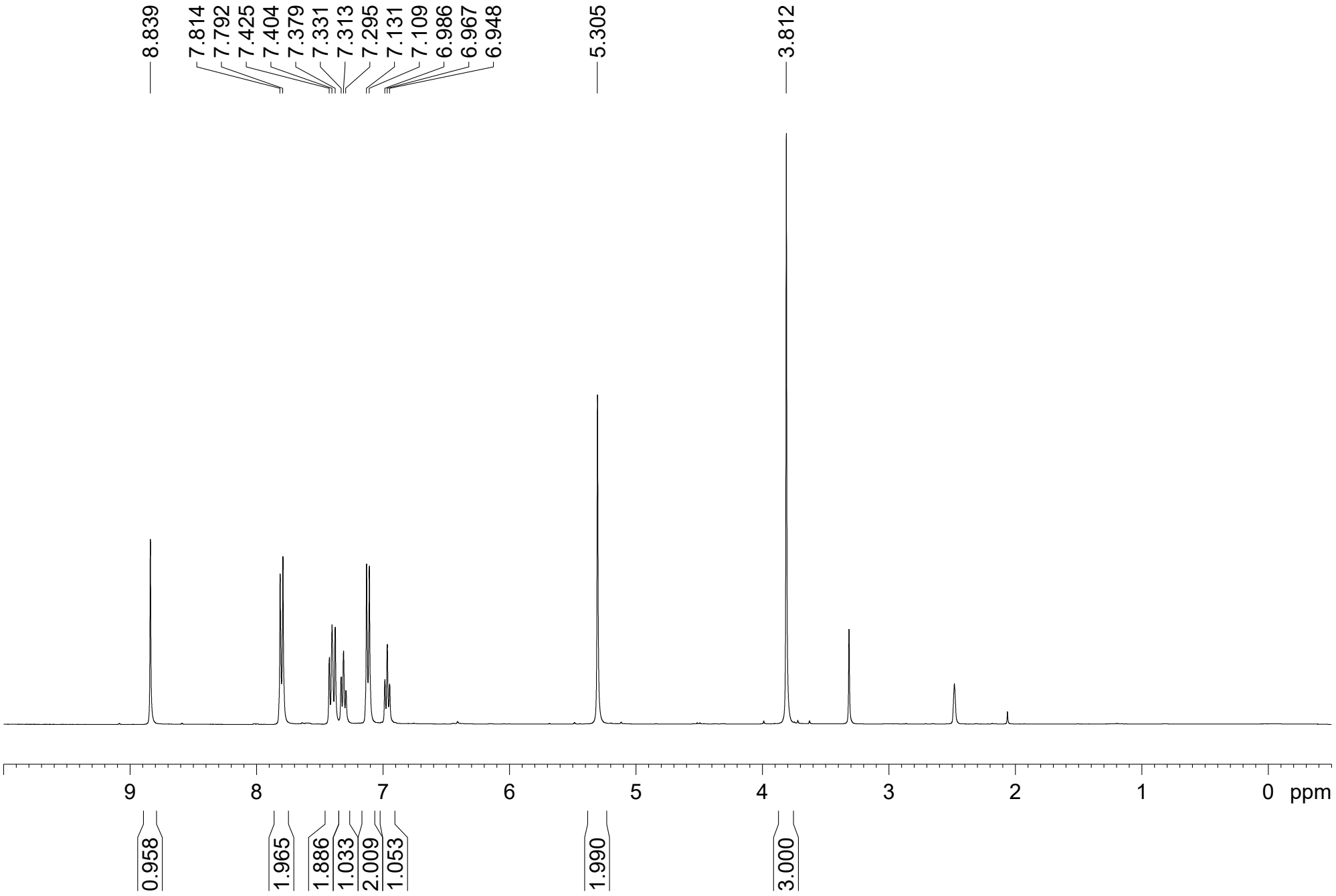
1−Benzyl−4−((2−bromophenoxy)methyl)−1H−1,2,3−triazole (3m)



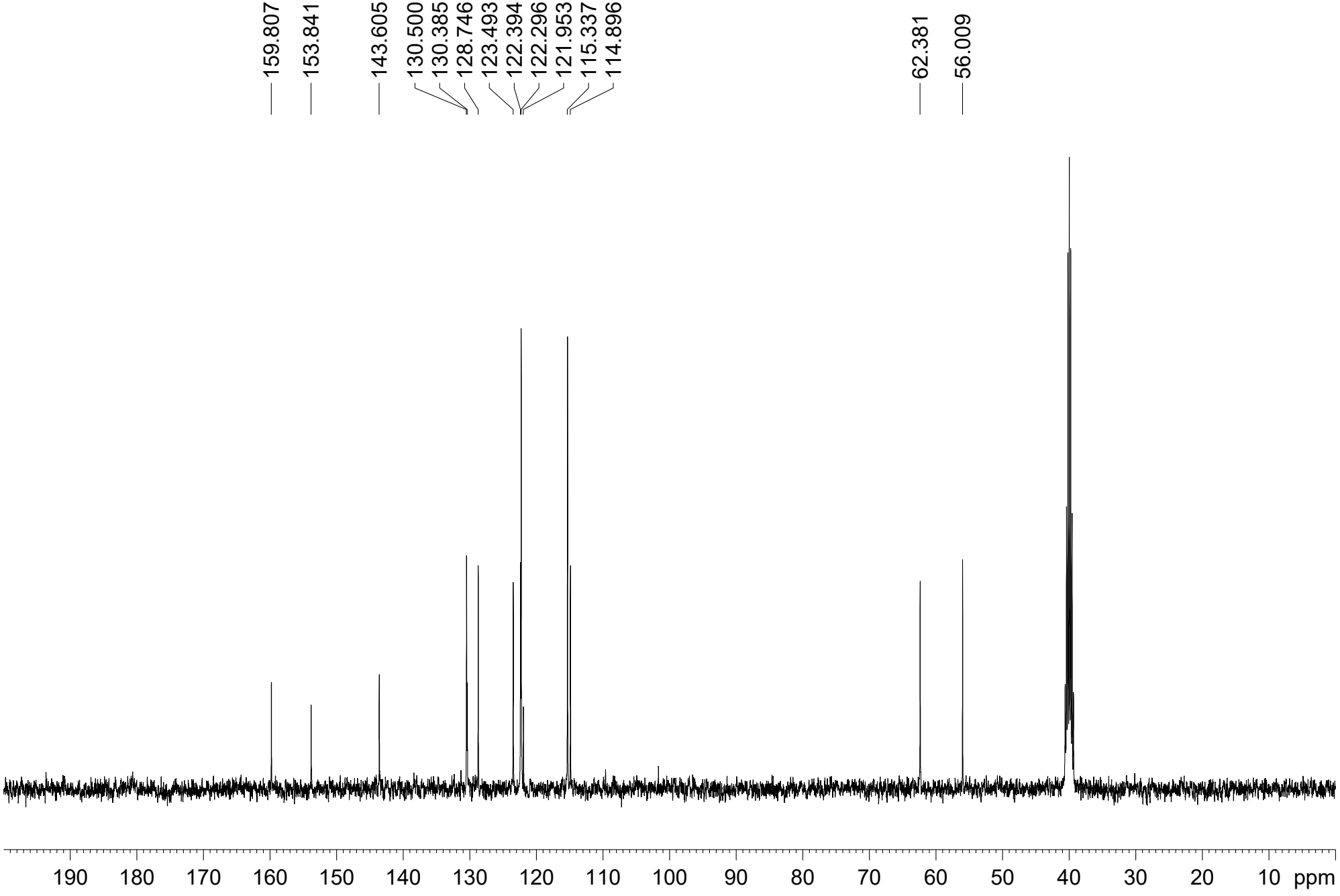
1−Benzyl−4−((2−bromophenoxy)methyl)−1H−1,2,3−triazole (3m)



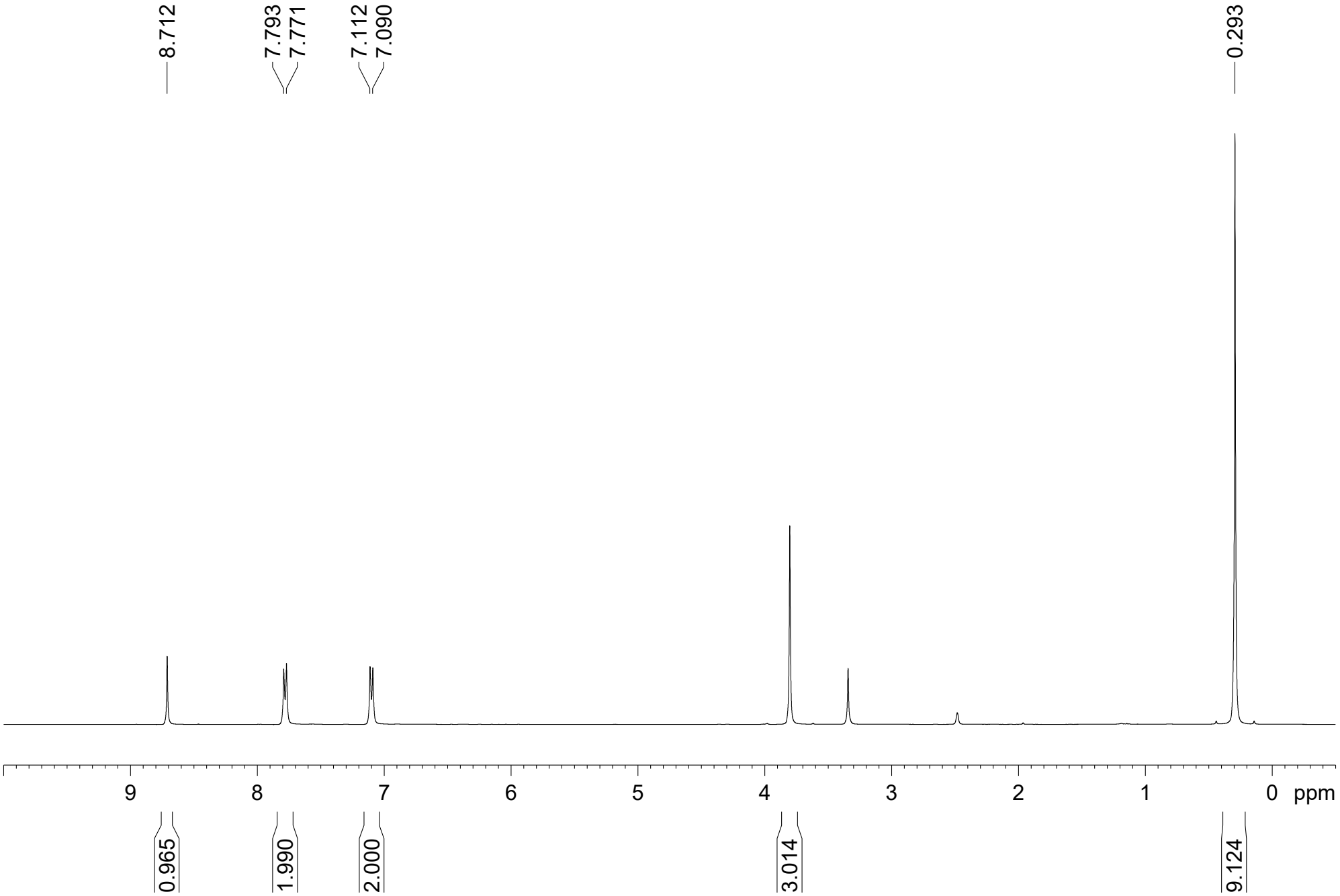
4−((2−Chlorophenoxy)methyl)−1−(4−methoxyphenyl)−1H−1,2,3−triazole (3n)



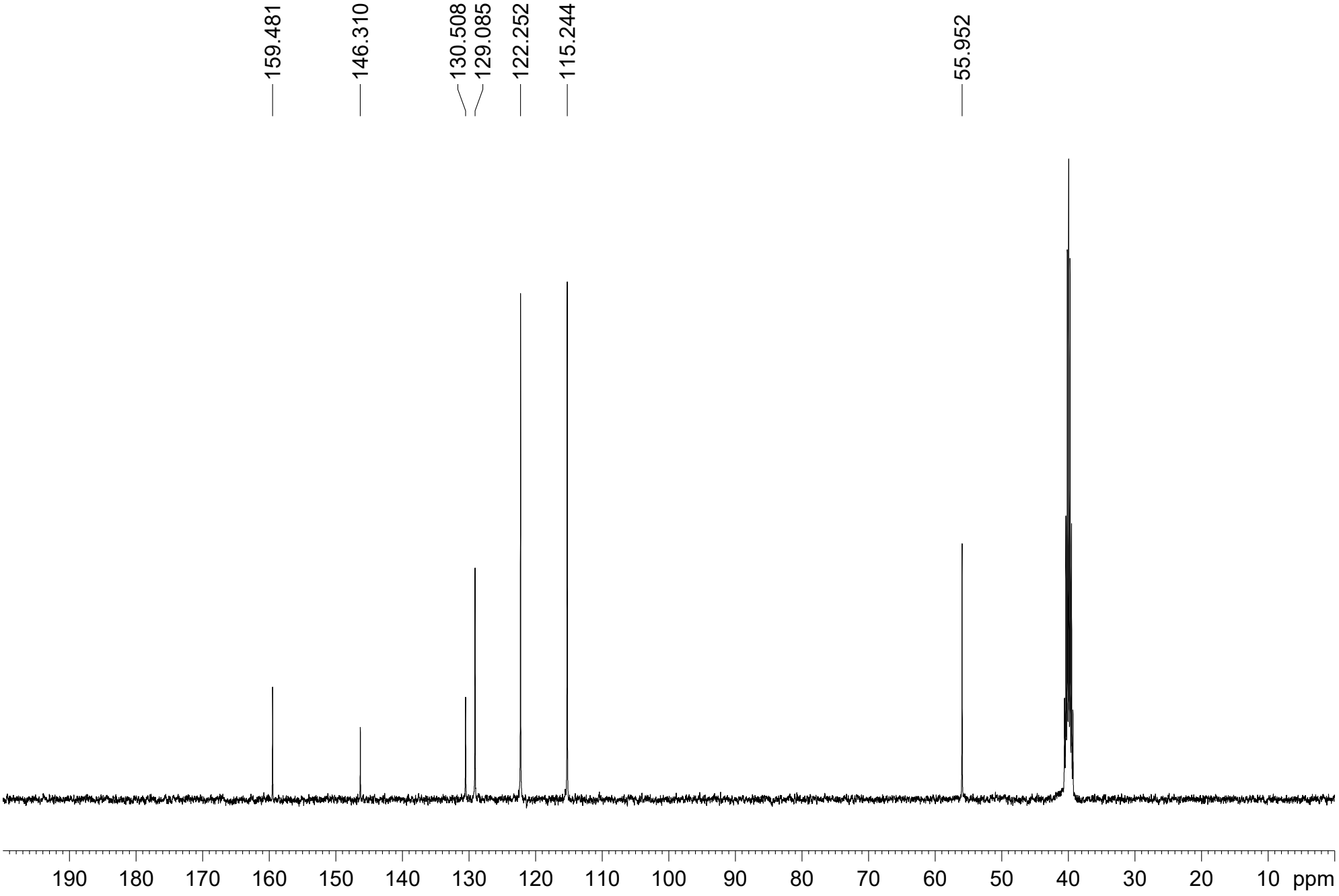
4−((2−Chlorophenoxy)methyl)−1−(4−methoxyphenyl)−1H−1,2,3−triazole (3n)



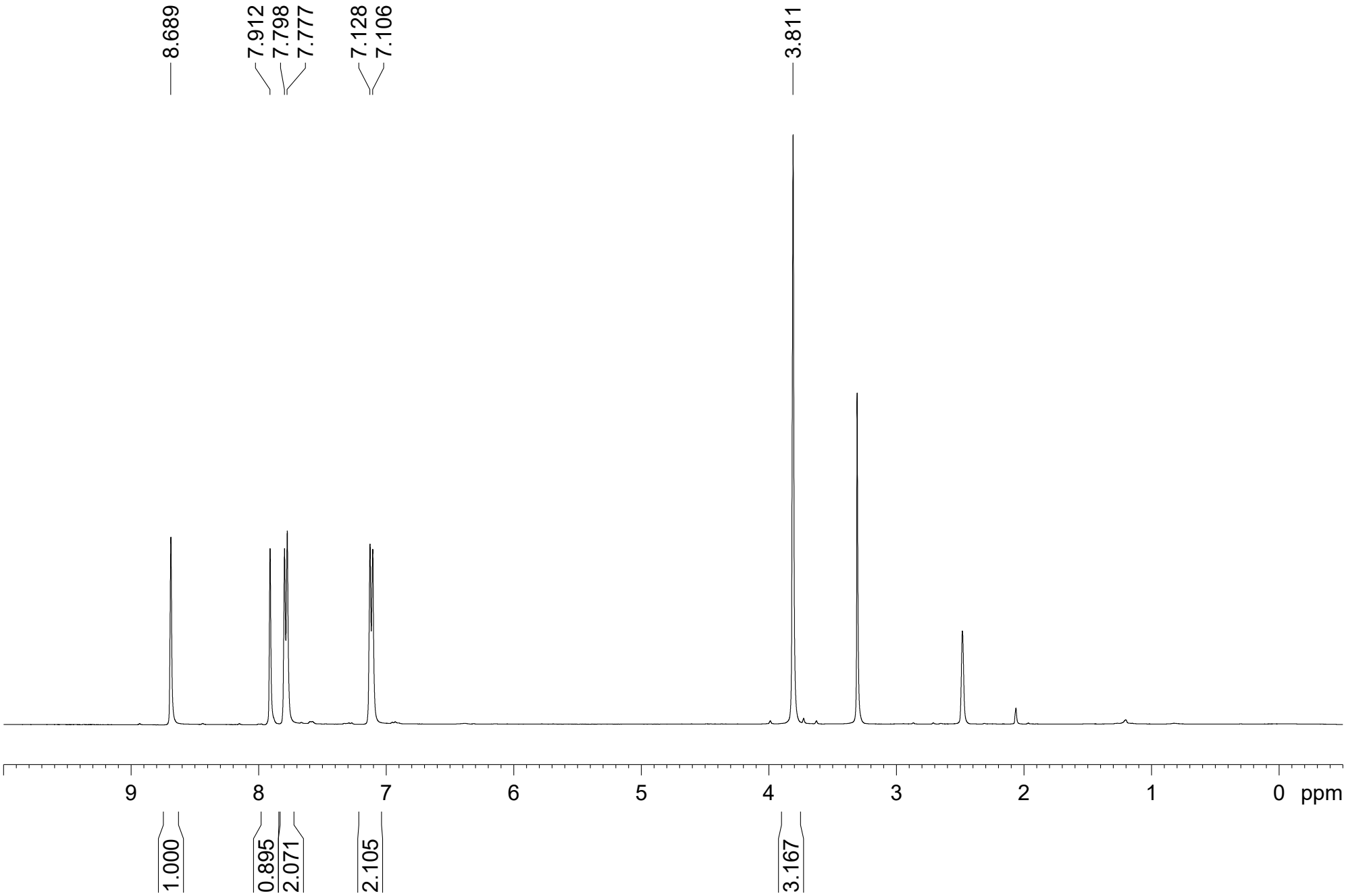
1−(4−Methoxyphenyl)−4−(trimethylsilyl)−1H−1,2,3−triazole (3o)



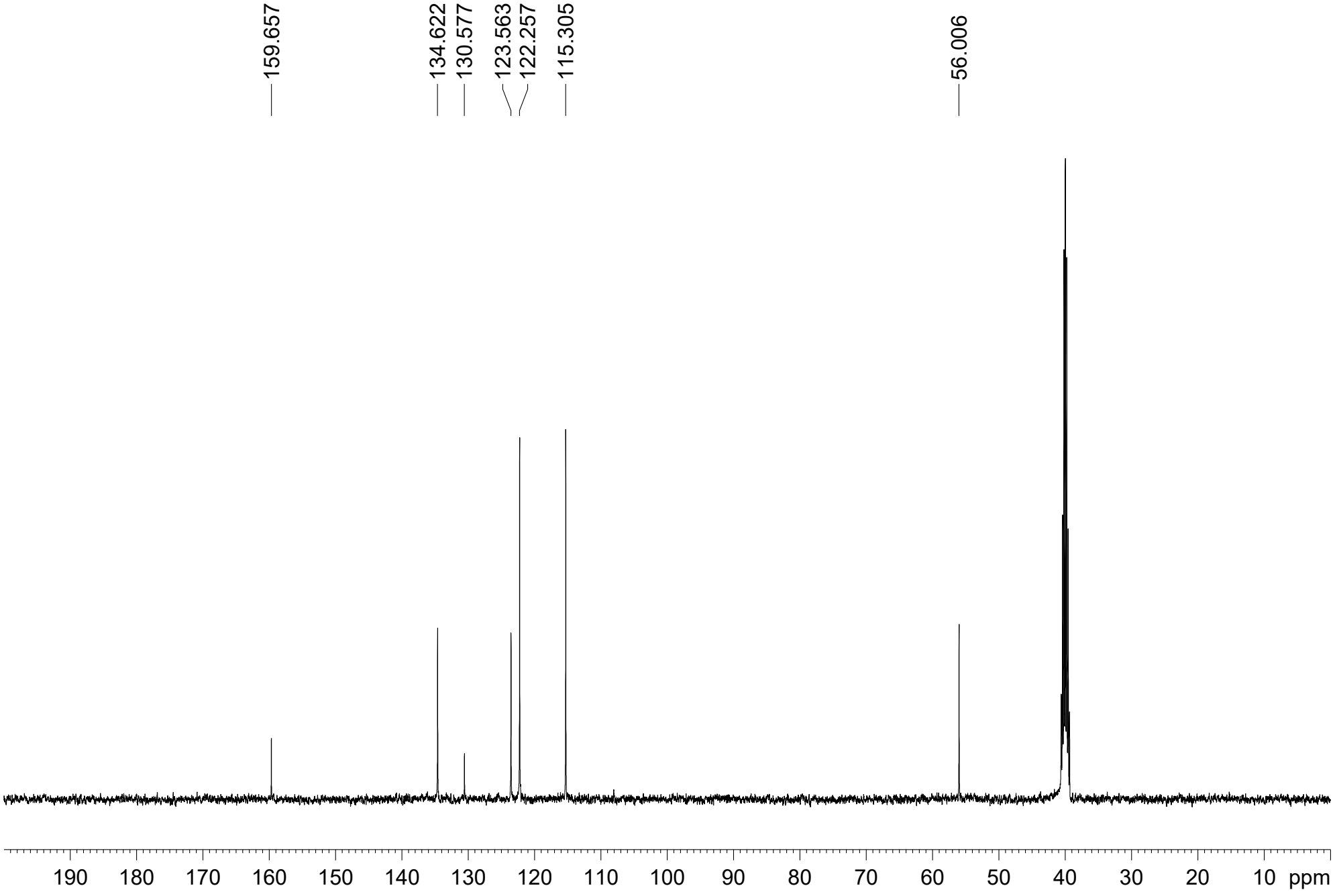
1−(4−Methoxyphenyl)−4−(trimethylsilyl)−1H−1,2,3−triazole (3o)



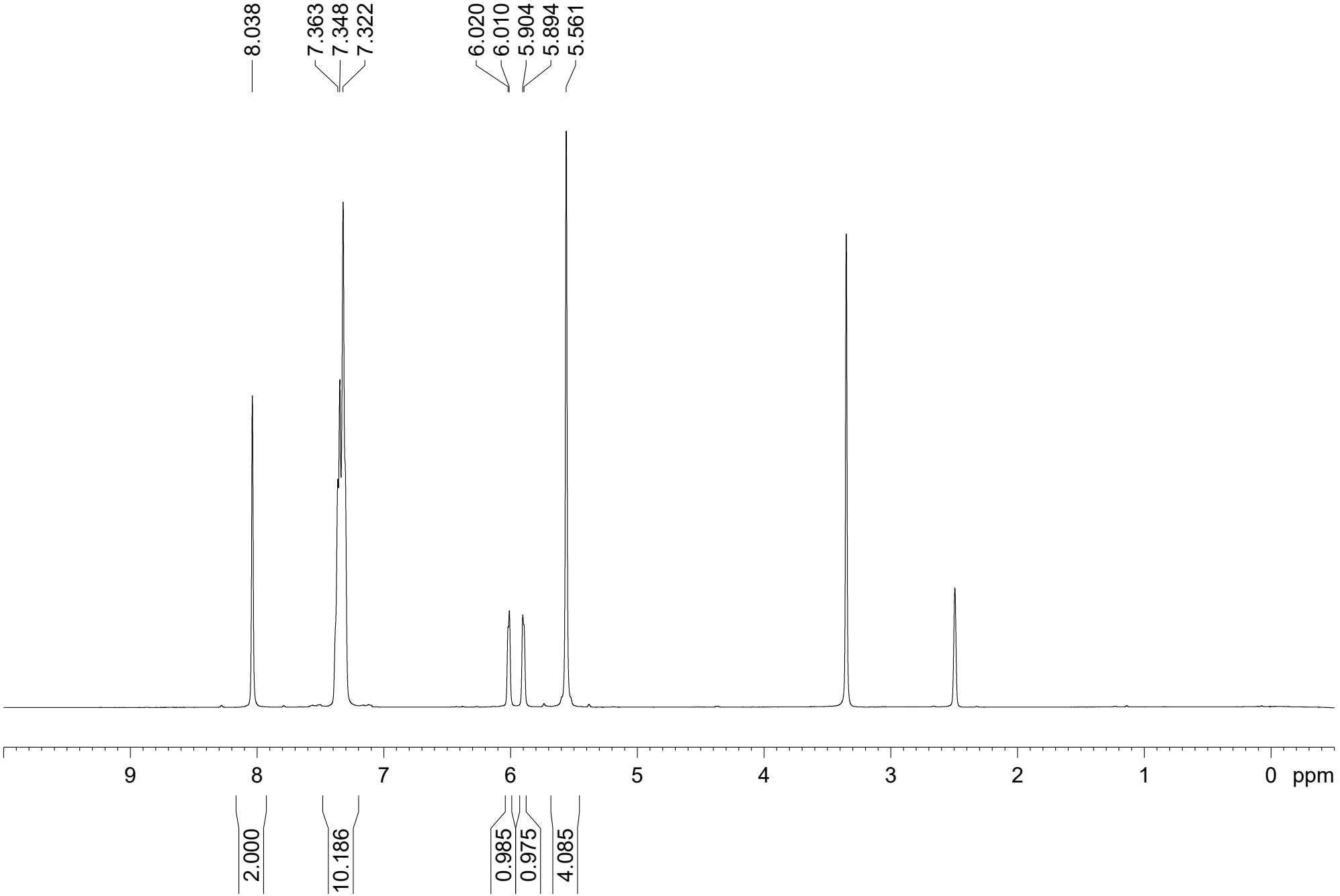
1−(4−Methoxyphenyl)−1H−1,2,3−triazole (3p)



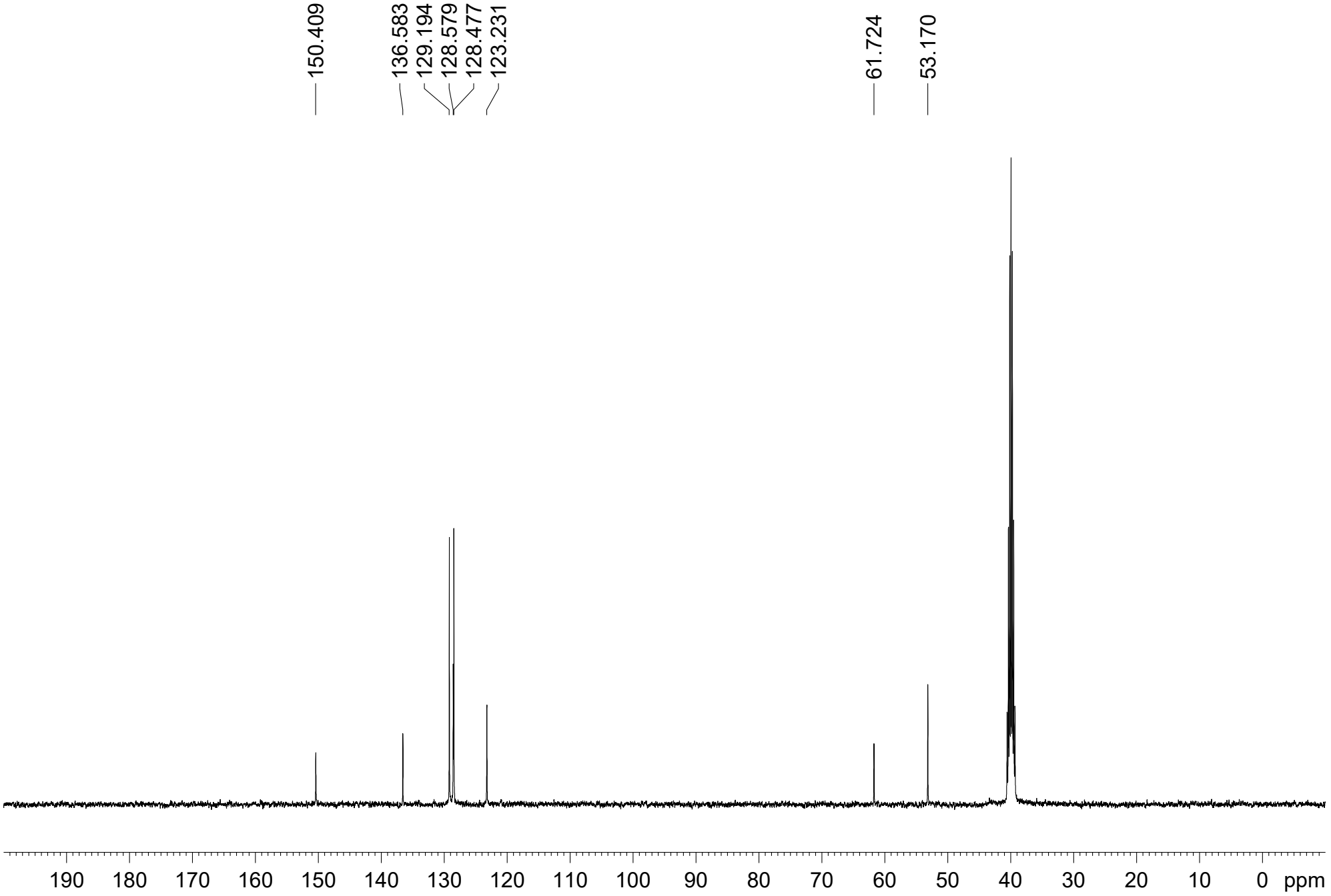
1−(4−Methoxyphenyl)−1H−1,2,3−triazole (3p)



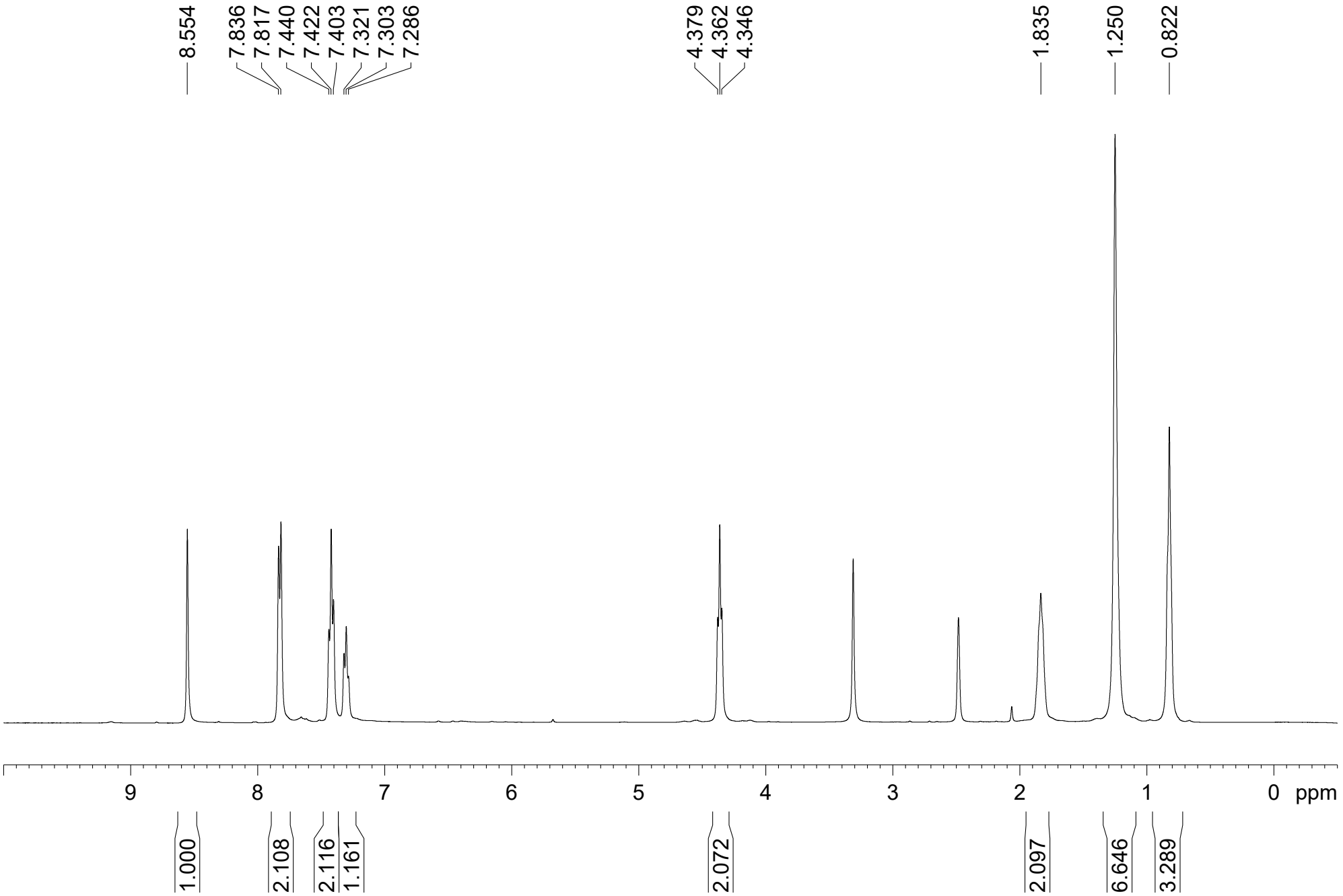
Bis(1−benzyl−1H−1,2,3−triazol−4−yl)methanol (3q)



Bis(1−benzyl−1H−1,2,3−triazol−4−yl)methanol (3q)



1−Hexyl−4−phenyl−1H−1,2,3−triazole (3r)



1−Hexyl−4−phenyl−1H−1,2,3−triazole (3r)