Ce-Catalyzed Regioselective Synthesis of Pyrazoles from 1,2-Diols via Tandem Oxidation and C-C/C-N Bond Formation

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General information

All reactions are carried out in oven dried round bottom flask under oxygen atmosphere with oxygen ballon. Commercially available chemicals of reagents grade are used throughout the work without any further purification. All chemicals were purchased from Sigma Aldrich, Spectrochem. Pvt. Ltd., Avra and SRL chemicals, India. TLC plates (Aluminium Sheet Silica gel 60 F 254) were purchased from Merck and were visualized under a UV lamp. Solvents are evaporated *in vacuo* using Buchi R-100 Rotavapor (equipped with I-100 Pro Interface, B-100 heating bath and F-100 recirculating chiller). IR spectra were recorded using Shimadzu IR Affinity1 spectrophotometer. All NMR spectra were performed on Brucker Avance 400 MHz spectrometer in $CDCl_3$ using TMS as internal standard. Coupling constants are reported in hertz (Hz). Melting points are uncorrected.

General procedure for synthesis of hydrazone derivatives[1-6]

Following the reported methods, aryl aldehydes were added to a solution of arylhydrazines in ethanol and if required few drops of acetic acid were added. After stirring, diarylhydrazone derivatives **1a-1ab** were formed, separated by vacuum filtration and if necessary purified by crystallization.

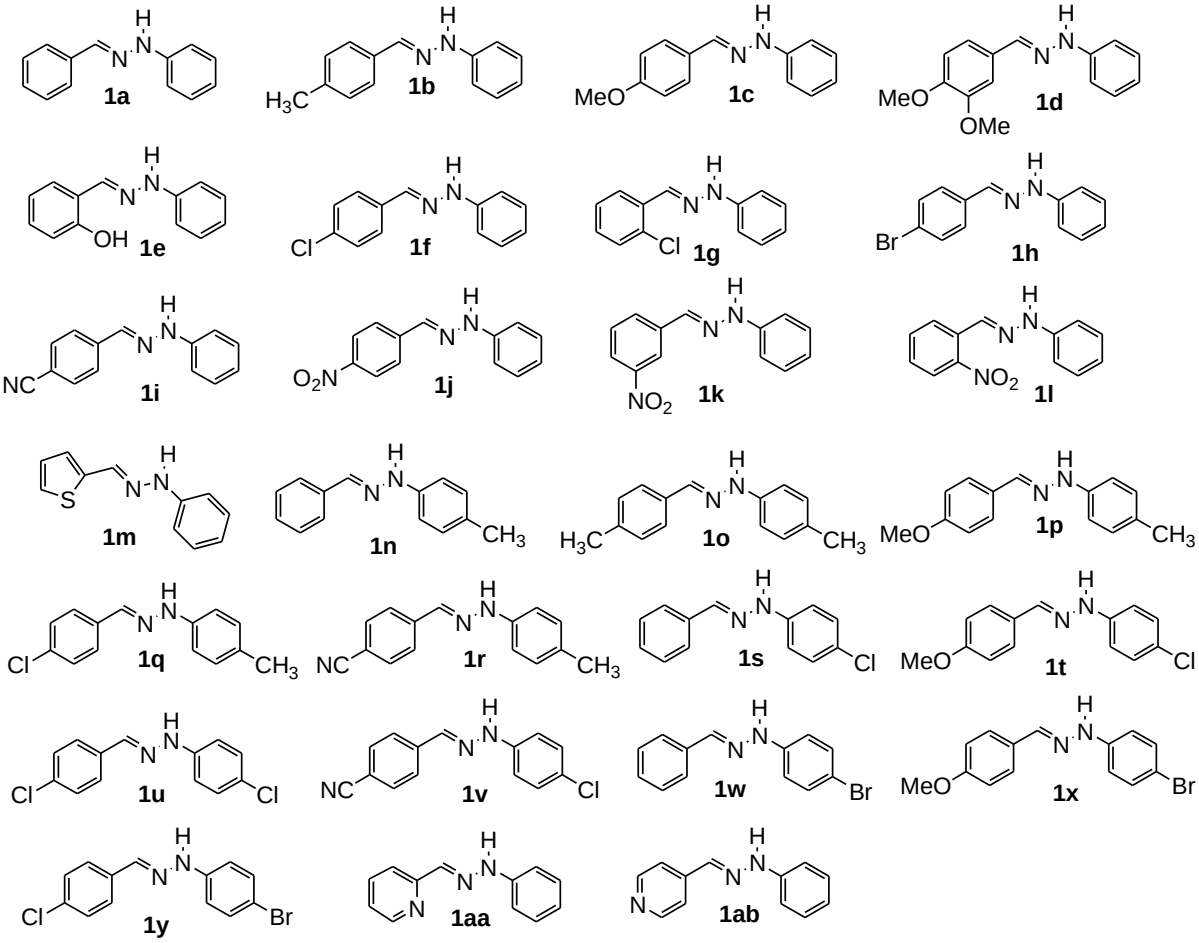
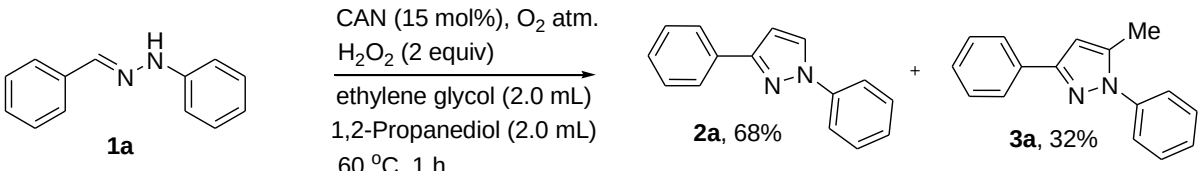


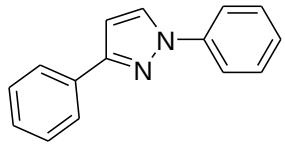
Table 1: Competition experiment



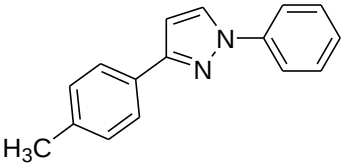
General procedure for the synthesis pyrazoles

To a 50 mL one neck RB, hydrazone derivative **1** (0.51 mmol) was dissolved in diol (3 mL) at rt. To the above mixture, CAN (15 mol %) and 50% aqueous H_2O_2 (1.02 mmol) were added sequentially. The resulting solution was stirred for appropriate temperature (60-80 °C) in a pre-heated oil bath under O_2 atmosphere. Progress of the reaction was monitored by thin layer chromatography. After completion of the reaction, the crude reaction mixture was extracted with DCM (3 x 30 mL). The organic phase was washed with water, dried over anhy. Na_2SO_4 and filtered. The solvent was removed in vacuo by rotary vacuum evaporator and the crude mixture was purified over silica gel column chromatography using petroleum ether and ethyl acetate as eluent.

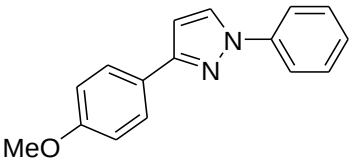
Characterization data



1,3-Diphenyl-1*H*-pyrazole (2a).[7] Following general procedure, hydrazone **1a** (100 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 0.7 h to afford the corresponding 1,3-diphenyl-1*H*-pyrazole **2a** (92 mg, 82% yield) as a white crystalline solid. M.P.: 81-82 °C. IR (KBr): 1598, 1524, 1504, 1455, 1362 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.98-7.94 (m, 3H), 7.83-7.80 (m, 2H), 7.53-7.44 (m, 4H), 7.40-7.30 (m, 2H), 6.80 (d, 1H, J = 2.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 140.2, 133.1, 129.4, 128.6, 128.0, 128.0, 126.3, 125.8, 119.0, 105.0. Anal.Calcd.for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72; Found: C, 81.68; H, 5.47; N, 12.81.

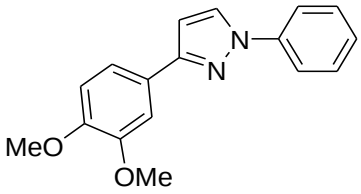


1-Phenyl-3-p-tolyl-1*H*-pyrazole (2b).[8] Following general procedure hydrazone **1b** (107 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 2 h to afford the corresponding 1-Phenyl-3-p-tolyl-1*H*-pyrazole **2b** (83 mg, 70% yield) as a white crystalline solid. M.P.: 77-78 °C. IR (KBr): 3035, 2926, 1599, 1510, 1445, 1387 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, 1H, J = 2.4 Hz), 7.85-7.79 (m, 4H), 7.49 (t, 2H, J = 7.6 Hz,), 7.33-7.26 (m, 3H), 6.77 (d, 1H, J = 1.6 Hz), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 140.2, 137.8, 130.3, 129.4, 129.3, 127.9, 126.2, 125.7, 119.0, 104.8, 21.3. Anal.Calcd.for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96; Found: C, 82.09; H, 6.05; N, 11.98.

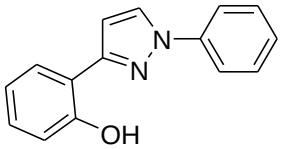


3-(4-Methoxyphenyl)-1-phenyl-1*H*-pyrazole (2c).[9] Following general procedure hydrazine **1c** (115 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 0.5 h to afford the corresponding 3-(4-Methoxyphenyl)-1-phenyl-1H-pyrazole **2c** (82 mg, 64% yield) as a white

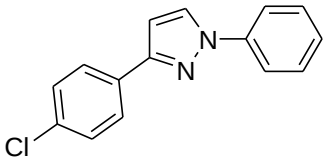
crystalline solid. M.P.: 102-104 °C. IR (KBr): 3142, 3058, 2959, 1595, 1510, 1453 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, 1H, J = 2.8 Hz), 7.90-7.84 (m, 2H), 7.80-7.76 (m, 2H), 7.48 (t, 2H, J = 7.6 Hz), 7.31 (d, 1H, J = 7.6 Hz), 7.00-6.98 (m, 2H), 6.73 (d, 1H, J = 2.8 Hz), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 152.8, 140.2, 129.3, 127.8, 127.1, 126.1, 125.9, 118.9, 114.0, 104.5, 55.3. Anal.Calcd.for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19; Found: C, 76.81; H, 5.65; N, 11.22.



3-(3,4-Dimethoxyphenyl)-1-phenyl-1*H*-pyrazole (2d). Following general procedure hydrazone **1d** (131 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 0.7 h to afford the corresponding 3-(3,4-dimethoxyphenyl)-1-phenyl-1*H*-pyrazole **2d** (103 mg, 72% yield) as a yellow solid. M.P.: 98-100 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, 1H, J = 2.4 Hz), 7.80 (d, 2H, J = 1.2 Hz), 7.56-7.40 (m, 4H), 7.33-7.29 (m, 1H), 6.95 (d, 1H, J = 8.4 Hz), 6.74 (d, 1H, J = 2.8 Hz), 4.01 (s, 3H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 149.1, 149.1, 140.2, 129.4, 128.0, 126.2, 126.1, 119.0, 118.5, 111.1, 108.7, 104.7, 55.9, 55.9. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{16}N_2O_2$ 281.1290, found 281.1300. Anal.Calcd.for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99; Found: C, 72.89; H, 5.72; N, 9.95.

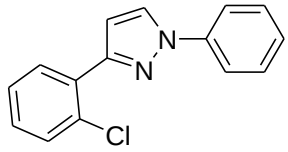


2-(1-Phenyl-1*H*-pyrazol-3-yl) phenol (2e).[10] Following general procedure hydrazone **1e** (108 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 0.5 h to afford the corresponding 2-(1-Phenyl-1*H*-pyrazol-3-yl) phenol **2e** (73 mg, 61% yield) as a white crystalline solid. M.P.: 102 °C. IR (KBr): 3142, 3051, 2952, 2921, 2854, 1620, 1598, 1522, 1507, 1450 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 10.84 (s, 1H), 8.00 (d, 1H, J = 2.8 Hz), 7.72 (d, 2H, J = 1.2 Hz), 7.70 (d, 1H, J= 0.8), 7.66-7.49 (m, 2H), 7.35 (t, 1H, J = 7.2), 7.30 (d, 1H, J = 1.6Hz,), 7.28-7.26 (m, 1H),7.10- 7.08 (m, 1H), 6.99-6.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 152.9, 139.3, 129.6, 127.7, 126.8, 126.5, 119.3, 118.8, 117.2, 116.2, 104.5. Anal.Calcd.for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86; Found: C, 76.28; H, 5.14; N, 11.83.

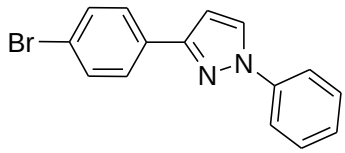


3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazole (2f).[9] Following general procedure hydrazone **1f** (118 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 1.5 h to afford the corresponding 3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazole **2f** (86 mg, 66% yield) as a white crystalline solid. M.P.: 117-118 °C. IR (KBr): 3052, 2924, 1595, 1440, 1412 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, 1H, J = 2.8 Hz), 7.90-7.84 (m, 2H), 7.80-7.76 (m, 2H), 7.52-

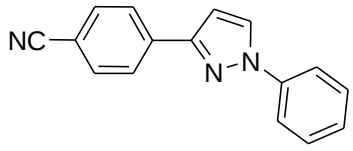
7.46 (m, 2H), 7.44-7.40 (m, 2H), 7.34-7.32 (m, 1H), 6.77 (d, 1H, *J* = 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 140.1, 133.7, 131.6, 129.4, 128.8, 128.1, 127.0, 126.5, 119.1, 104.9. Anal.Calcd.for $C_{15}H_{11}ClN_2$: C, 70.73; H, 4.35; N, 11.00; Found: C, 70.81; H, 4.38; N, 10.98.



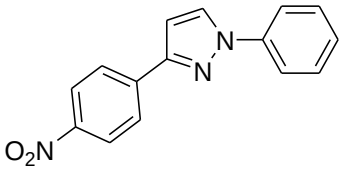
3-(2-chlorophenyl)-1-phenyl-1*H*-pyrazole (2g).[7] Following general procedure hydrazone **1g** (118 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 1 h to afford the corresponding 3-(2-chlorophenyl)-1-phenyl-1*H*-pyrazole **2g** (75 mg, 58% yield) as a white crystalline solid. M.P.: 134-136 °C. IR (KBr): 3051, 1598, 1502, 1448, 1385 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, 1H, *J* = 2.8 Hz), 7.97 (d, 1H, *J* = 7.2 Hz), 7.80 (d, 2H, *J*= 8.4 Hz), 7.41-7.47 (m, 3H), 7.38-7.28 (m, 3H), 7.03 (d, 1H, *J*= 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 140.0, 132.4, 132.1, 130.7, 130.3, 129.4, 129.0, 127.1, 126.9, 126.5, 119.2, 109.0. Anal.Calcd.for $C_{15}H_{11}ClN_2$: C, 70.73; H, 4.35; N, 11.00; Found: C, 70.78; H, 4.37; N, 11.04.



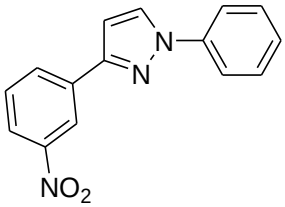
3-(4-Bromophenyl)-1-phenyl-1*H*-pyrazole (2h).[9] Following general procedure hydrazone **1h** (140 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 2 h to afford the corresponding 3-(4-bromophenyl)-1-phenyl-1H-pyrazole **2h** (107 mg, 70% yield) as a white crystalline solid. M.P.: 122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, 1H, J = 2.4 Hz), 7.84-7.76 (m, 4H), 7.58-7.56 (m, 2H), 7.49 (t, 2H, *J* = 8.0 Hz), 7.32 (t, 1H, *J* = 7.2 Hz), 6.77 (d, 1H, *J* = 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 140.1, 132.1, 131.7, 129.4, 128.2, 127.3, 126.5, 121.9, 119.1, 104.9. Anal.Calcd.for $C_{15}H_{11}BrN_2$: C, 60.22; H, 3.71; N, 9.36; Found: C, 60.12; H, 3.68; N, 9.41.



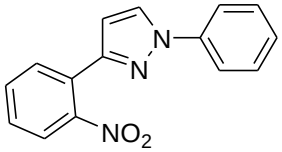
4-(1-Phenyl-1*H*-pyrazol-3-yl)benzonitrile (2i). Following general procedure hydrazone **1i** (113 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 3 h to afford the corresponding 4-(1-Phenyl-1H-pyrazol-3-yl)benzonitrile **2i** (106 mg, 85% yield) as a white crystalline solid. M.P.: 155-157 °C. IR (KBr): 3120, 3062, 3045, 2919, 2852, 2226, 1605, 1557, 1505, 1450 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-8.00 (m, 3H), 7.79 (d, 2H, *J* = 8.00 Hz), 7.72 (d, 2H, *J* = 8.4 Hz), 7.54-7.48 (m, 2H), 7.35 (t, 1H, *J* = 7.2 Hz), 6.84 (d, 1H, *J* = 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 139.8, 137.4, 132.5, 129.5, 128.5, 126.9, 126.1, 119.2, 119.1, 111.1, 105.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{16}H_{11}N_3$ 246.1031, found 246.1022. MS (ESI): m/z (relative intensity) 246 ($[M + H]^+$, 100).



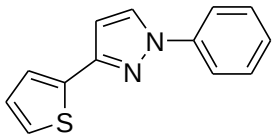
3-(4-Nitrophenyl)-1-phenyl-1*H*-pyrazole (2j).[11] Following general procedure hydrazone **1j** (123 mg, 0.51mmol) was mixed with ethylene glycol and stirred for 3 h to afford the corresponding 3-(4-Nitrophenyl)-1-phenyl-1*H*-pyrazole **2j** (84 mg, 62% yield) as a yellow crystalline solid. M.P.: 139-140 °C. IR (KBr): 1597, 1556, 1506, 1456, 1419, 1335 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, 2H, J = 8.8 Hz), 8.10 (d, 2H, J = 8.8 Hz), 8.04 (d, 1H, J = 2.4 Hz), 7.80 (d, 2H, J = 7.6 Hz), 7.52 (t, 2H, J = 8.0 Hz), 7.40-7.34 (m, 1H), 6.90 (d, 1H, J = 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 147.3, 139.8, 139.4, 129.5, 128.6, 127.0, 126.2, 124.1, 119.2, 105.9. Anal.Calcd.for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.18; N, 15.84; Found: C, 67.86; H, 4.22; N, 15.87



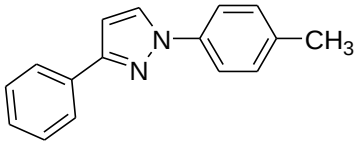
3-(3-Nitrophenyl)-1-phenyl-1*H*-pyrazole (2k).[11] Following general procedure hydrazone **1k** (123 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 1.5 h to afford the corresponding 3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazole **2k** (68 mg, 50% yield) as a yellow crystalline solid. M.P.: 110-111 °C. IR (KBr): 1596, 1518, 1455, 1345 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, 1H, J = 1.6 Hz), 8.30-8.18 (m, 2H), 8.03 (m, 1H, J = 2.4 Hz), 7.84-7.80 (m, 2H), 7.64-7.50 (m, 3H), 7.38-7.34 (m, 1H), 6.88 (d, 1H, J = 2.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 148.7, 139.9, 134.9, 131.5, 129.6, 129.5, 128.5, 126.8, 122.5, 120.6, 119.1, 105.3. Anal.Calcd.for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.18; N, 15.84; Found: C, 67.88; H, 4.20; N, 15.81.



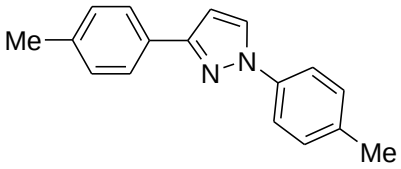
3-(2-Nitrophenyl)-1-phenyl-1*H*-pyrazole (2l).[11] Following general procedure hydrazone **2l** (123 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 3 h to afford the corresponding 3-(2-Nitrophenyl)-1-phenyl-1*H*-pyrazole **2l** (73 mg, 54 % yield) as a yellowish crystalline solid. M.P.: 80-82 °C. IR (KBr): 1599, 1503, 1342, 1271 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, 1H, J = 2.4 Hz), 7.87-7.85 (m, 1H), 7.78-7.73 (m, 3H), 7.65-7.61 (m, 1H), 7.52-7.46 (m, 3H), 7.34-7.28 (m, 1H), 6.64 (d, 1H, J = 2.4Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 148.2, 139.8, 131.8, 130.8, 129.4, 128.6, 127.9, 127.1, 126.7, 123.6, 119.1, 107.0. Anal.Calcd.for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.18; N, 15.84; Found: C, 67.82; H, 4.17; N, 15.89



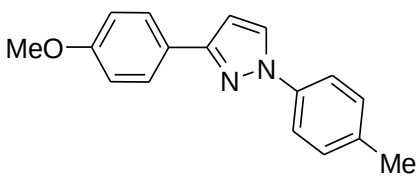
1-Phenyl-3-(thiophen-2-yl)-1*H*-pyrazole (2m).[7] Following general procedure hydrazone **1m** (103 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 3 h to afford the corresponding 1-Phenyl-3-(thiophen-2-yl)-1*H*-pyrazole **2m** (29 mg, 25% yield) as a white crystalline solid. M.P.: 65-66 °C. IR (KBr): 3067, 2921, 1598, 1558, 1506, 1461, 1374 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, 1H, J = 2.4 Hz), 7.82-7.74 (m, 2H), 7.52-7.42 (m, 3H), 7.34-7.29 (m, 2H), 7.14-7.08 (m, 1H), 6.70 (d, 1H, J = 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 139.9, 136.3, 129.4, 128.0, 127.4, 126.4, 124.9, 124.2, 119.1, 105.1 Anal.Calcd.for $C_{13}H_{10}N_2S$: C, 69.00; H, 4.45; N, 12.38; S, 14.17; Found: C, 69.08; H, 4.48; N, 12.34; S, 14.21.



3-Phenyl-1-p-tolyl-1*H*-pyrazole (2n).[7] Following general procedure hydrazone **1n** (107 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 1 h to afford the corresponding 3-Phenyl-1-p-tolyl-1*H*-pyrazole **2n** (62 mg, 52% yield) as a white crystalline solid. M.P.: 110-112 °C. IR (KBr): 3146, 3028, 1605, 1520, 1452, 1390 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.96-7.93 (m, 3H), 7.67 (d, 2H, J = 8.4 Hz), 7.46 (t, 2H, J= 8.8 Hz), 7.37 (d, 1H, J= 7.6 Hz), 7.29 (d, 2H, J= 7.6 Hz), 6.78 (d, 1H, J= 2.4 Hz), 2.4 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 138.0, 136.1, 133.2, 129.9, 128.6, 127.9, 127.9, 125.8, 119.0, 104.7, 20.9. Anal.Calcd.for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96; Found: C, 82.08; H, 6.05; N, 11.99

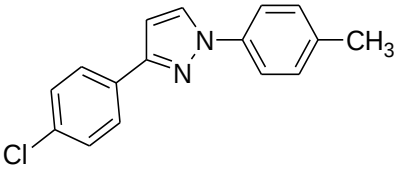


1,3-Di(4-tolyl)-1*H*-pyrazol (2o).[8] Following general procedure hydrazone **1o** (114 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 1 h to afford the corresponding 1,3-di(4-tolyl)-1*H*-pyrazol **2o** (53 mg, 42% yield) as a white crystalline solid. M.P.: 137-138 °C. IR (KBr): 2918, 2840, 1557, 1501, 1456, 1396 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, 1H, J = 2.0 Hz), 7.83 (d, 1H, J = 8.0 Hz), 7.66 (d, 2H, J = 8.0 Hz), 7.30-7.24 (m, 4H), 6.75 (d, 1H, J = 2.0 Hz), 2.41 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 138.0, 137.7, 136.0, 130.4, 129.9, 129.3, 127.8, 125.7, 119.0, 104.5, 21.3, 20.9. Anal.Calcd.for $C_{17}H_{16}N_2$: C, 82.22; H, 6.49; N, 11.28; Found: C, 82.28; H, 6.47; N, 11.25. MS (ESI): m/z (relative intensity) 249 ($[M + H]^+$, 100).

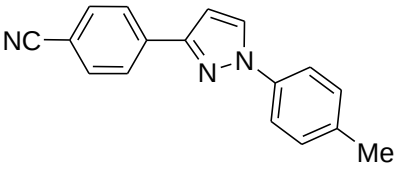


3-(4-Methoxyphenyl)-1-(4-tolyl)-1*H*-pyrazole (2p).[8] Following general procedure hydrazone **1p** (122 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 2 h to

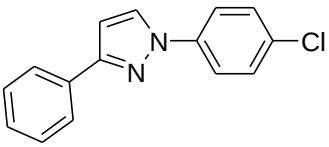
afford the corresponding 3-(4-methoxyphenyl)-1-(4-tolyl)-1*H*-pyrazole **2p** (73 mg, 54% yield) as a white crystalline solid. M.P.: 157-158 °C. IR (KBr): 3073, 2907, 2865, 1597, 1558, 1504, 1443 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, 1H, J = 2.5 Hz), 7.84 (d, 2H, J = 8.8 Hz,), 7.65 (d, 2H, J = 8.5 Hz,), 7.26 (d, 2H, J = 8.2 Hz), 6.98 (d, 2H, J = 8.8 Hz), 6.68 (d, 1H, J = 2.5 Hz), 3.86 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 152.5, 138.0, 135.9, 129.9, 127.8, 127.0, 126.0, 118.9, 114.0, 104.2, 55.3, 20.9. Anal.Calcd.for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60; Found: C, 77.32; H, 6.12; N, 10.63



3-(4-Chlorophenyl)-1-p-tolyl-1*H*-pyrazole (2q). Following general procedure hydrazone **1q** (125 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 1.5 h to afford the corresponding 3-(4-Chlorophenyl)-1-p-tolyl-1*H*-pyrazole **2q** (33 mg, 24% yield) as a white crystalline solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, 1H, J = 2.4 Hz), 7.90-7.84 (m, 2H), 7.65 (d, 2H, J= 8.4 Hz), 7.44-7.40 (m, 2H), 7.29 (d, 2H, J= 6.4 Hz), 6.75 (d, 1H, J= 2.4 Hz), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 137.8, 136.3, 133.6, 131.7, 129.9, 128.8, 128.1, 127.0, 119.0, 104.7, 20.9. Anal.Calcd.for $C_{16}H_{13}ClN_2$: C, 71.51; H, 4.88; N, 10.42; Found: C, 71.45; H, 4.92; N, 10.48. MS (ESI): m/z (relative intensity) 268 ($[M]^+$, 100).

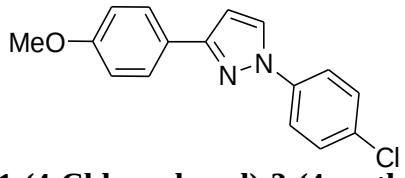


4-(1-p-tolyl-1*H*-pyrazol-3-yl) benzonitrile (2r). Following general procedure hydrazone **1r** (120 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 1 h to afford the corresponding 4-(1-p-tolyl-1*H*-pyrazol-3-yl) benzonitrile **2r** (108 mg, 82% yield) as a white crystalline solid. M.P.: 133-135 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, 2H, J = 8.0 Hz), 7.96 (d, 1H, J = 2.0 Hz), 7.71 (d, 2H, J = 8.0 Hz), 7.65 (d, 2H, J = 8.0 Hz), 7.30 (d, 2H, J = 8.4 Hz), 6.82 (d, 1H, J = 2.4 Hz), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 137.6, 137.6, 136.8, 132.5, 130.0, 128.5, 126.1, 119.1, 119.1, 111.0, 105.3, 21.0. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{13}N_3$ 260.1187, found 260.1178. MS (ESI): m/z (relative intensity) 260 ($[M + H]^+$, 100).

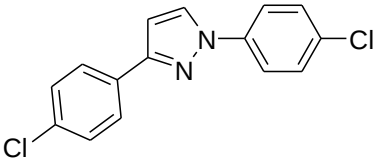


1-(4-Chlorophenyl)-3-phenyl-1*H*-pyrazole (2s).[7] Following general procedure hydrazone **1s** (118 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 1 h to afford the corresponding, 1-(4-Chlorophenyl)-3-phenyl-1*H*-pyrazole **2s** (78 mg, 60% yield) as a white crystalline solid. M.P.: 131-133 °C. IR (KBr): 3060, 1595, 1531, 1504, 1492, 1450 cm^{-1}. ^1H

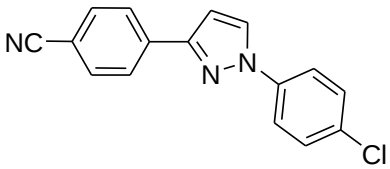
NMR (400 MHz, $CDCl_3$): δ 7.93 (t, 3H, J = 2.4 Hz,), 7.76-7.72 (m, 2H), 7.48-7.44 (m, 2H), 7.40-7.34 (m, 3H), 6.81 (d, 1H, J = 2.8 Hz,). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 138.7, 132.8,131.7,129.5, 128.7,128.2, 127.90, 125.8, 120.1, 105.4. Anal.Calcd.for $C_{15}H_{11}ClN_2$: C, 70.73; H, 4.35; N, 11.00; Found: C, 70.83; H, 4.41; N, 11.04.



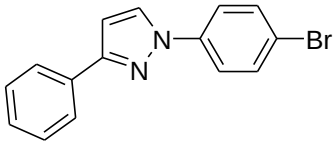
1-(4-Chlorophenyl)-3-(4-methoxyphenyl)-1*H*-pyrazole (2t).[12] Following general procedure hydrazone **1t** (133 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 1 h to afford the corresponding 1-(4-Chlorophenyl)-3-(4-methoxyphenyl)-1*H*-pyrazole **2t** (65 mg, 45% yield) as a white crystalline solid. M.P.: 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, 1H, J = 2.0 Hz), 7.85 (d, 2H, J = 8.4 Hz), 7.72 (d, 2H, J = 8.8 Hz), 7.44 (d, 2H, J = 8.8 Hz), 6.99 (d, 2H, J = 8.8 Hz), 6.73 (d, 1H, J = 2.4 Hz), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 153.0, 138.7, 131.5, 129.4, 127.8, 127.1, 125.6, 119.9, 114.1, 104.9, 55.3. Anal.Calcd.for $C_{16}H_{13}ClN_2O$: C, 67.49; H, 4.60; N, 9.84; Found: C, 67.52; H, 4.62; N, 9.88.



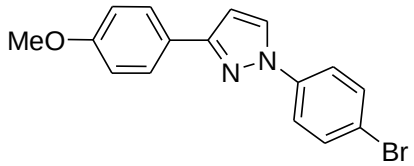
1,3-Bis(4-chlorophenyl)-1*H*-pyrazole (2u).[7] Following general procedure hydrazone **1u** (135 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 1 h to afford the corresponding, 1,3-Bis(4-chlorophenyl)-1*H*-pyrazole **2u** (106 mg, 72% yield) as a white crystalline solid. M.P.: 135-136 °C. IR (KBr): 3144, 3047,1595, 1564, 1501, 1442, 1420 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (t, 1H, J = 2.4 Hz), 7.86-7.84 (m, 2H), 7.73-7.70 (m, 2H), 7.46-7.40 (m, 4H), 6.76 (t, 1H, J = 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 138.6, 133.9, 131.9, 131.3, 129.5, 128.8, 128.0, 127.0, 120.1, 105.3. Anal.Calcd.for $C_{15}H_{10}Cl_2N_2$: C, 62.30; H, 3.49; N, 9.69; Found: C, 62.41; H, 3.52; N, 9.73.



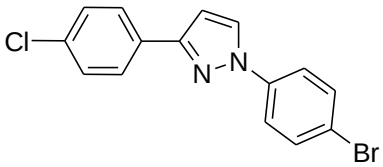
4-(1-(4-Chlorophenyl)-1*H*-pyrazol-3-yl) benzonitrile (2v). Following general procedure hydrazone **1v** (130 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 1 h to afford the corresponding 4-(1-(4-Chlorophenyl)-1*H*-pyrazol-3-yl) benzonitrile **2v** (117 mg, 82% yield) as a gummy mass. IR (KBr): 3149, 3057, 2914, 2857, 2235, 1651, 1611, 1561, 1510, 1450 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-7.96 (m, 3H), 7.73 (d, 4H, J = 8.0 Hz), 7.47 (d, 2H, J = 8.4 Hz), 6.85 (d, 1H, J = 0.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 138.4, 137.2, 132.5, 132.4, 129.6, 128.4, 126.2, 120.2, 119.0, 111.3, 105.9. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{16}H_{10}ClN_3$ 280.0641, found 280.0638 Anal.Calcd.for $C_{16}H_{10}ClN_3$: C, 68.70; H, 3.60; N, 15.02; Found: C, 68.74; H, 3.58; N, 15.08.



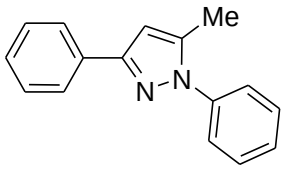
1-(4-Bromophenyl)-3-phenyl-1*H*-pyrazole (2w).[9] Following general procedure hydrazone **1w** (140 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 1 h to afford the corresponding 1-(4-Bromophenyl)-3-phenyl-1*H*-pyrazole **2w** (88 mg, 58% yield) as a white crystalline solid. M.P.: 134-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.92 (m, 3H), 7.70-7.67 (m, 2H), 7.62-7.59 (m, 2H), 7.48- 7.36 (m, 2H), 7.28 (s, 1H), 6.81 (d, 1H, J = 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 139.2, 132.8, 132.4, 128.7, 128.2, 127.8, 125.8, 120.3, 119.4, 105.4. Anal.Calcd.for $C_{15}H_{11}BrN_2$: C, 60.22; H, 3.71; N, 9.36; Found: C, 60.14; H, 3.74; N, 9.43



1-(4-Bromophenyl)-3-(4-methoxyphenyl)-1*H*-pyrazole (2x)[13]. Following general procedure hydrazone **1x** (155.4 mg, 0.51 mmol) was mixed with ethylene glycol and stirred for 2 h to afford the corresponding 1-(4-bromophenyl)-3-(4-methoxyphenyl)-1*H*-pyrazole **2x** (75.478 mg, 45% yield) as a white crystalline solid. M.P.: 187-188 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, 1H, J = 1.2 Hz), 7.85 (d, 2H, J = 8.8 Hz), 7.67 (d, 2H, J = 8.8 Hz), 7.59 (d, 2H, J = 8.8 Hz), 6.99 (d, 2H, J = 8.4 Hz), 6.73 (d, 1H, J = 1.2 Hz), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 153.0, 139.2, 132.4, 127.7, 127.1, 125.6, 120.2, 119.2, 114.1, 105.0, 55.3. Anal.Calcd.for $C_{16}H_{13}BrN_2O$: C, 58.38; H, 3.98; N, 8.51; Found: C, 58.47; H, 3.95; N, 8.57.

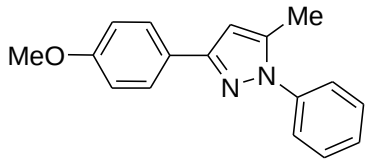


1-(4-Bromophenyl)-3-(4-chlorophenyl)-1*H*-pyrazole (2y).[11] Following general procedure hydrazone **1y** (158 mg, 0.51mmol) was mixed with ethylene glycol and stirred for **3 h** to afford the corresponding 1-(4-bromophenyl)-3-(4-chlorophenyl)-1*H*-pyrazole **2y** (116 mg, 68% yield) as a white crystalline solid. M.P.: 134-135 °C. IR (KBr): 3154, 2314, 1593, 1498, 1417, 1319 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, 1H, J = 2.4 Hz), 7.85 (d, 2H, J = 8.4 Hz), 7.70-7.58 (m, 4H), 7.42 (d, 2H, J = 8.4 Hz), 6.77 (d, 1H, J = 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 139.0, 133.9, 132.4, 131.3, 128.8, 128.0, 127.1, 120.4, 119.6, 105.4. Anal.Calcd.for $C_{15}H_{10}BrClN_2$: C, 54.00; H, 3.02; N, 8.40; Found: C, 54.07; H, 3.06; N, 8.45.

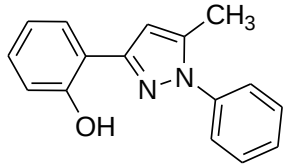


5-Methyl-1,3-diphenyl-1*H*-pyrazole (3a).[7] Following general procedure hydrazone **1a** (100

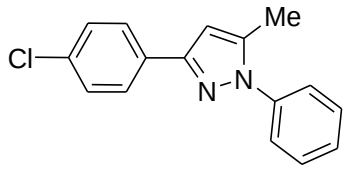
mg, 0.51 mmol) was mixed with 1,2- propanediol and stirred for 0.5 h to afford the corresponding, 5-Methyl-1,3-diphenyl-1*H*-pyrazole **3a** (62 mg, 52% yield) as a liquid. IR (neat): 3060, 2923, 1597, 1548, 1500, 1456 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.91-7.86 (m, 2H), 7.58-7.48 (m, 4H), 7.46-7.38 (m, 3H), 7.36-7.31 (m, 1H), 6.56 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 140.1, 139.9, 133.3, 129.1, 128.5, 127.7, 127.6, 125.7, 125.0, 104.3, 12.5. Anal.Calcd.for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96; Found: C, 82.11; H, 6.05; N, 11.99.



3-(4-Methoxyphenyl)-5-methyl-1-phenyl-1*H*-pyrazole (3b).[7] Following general procedure hydrazone **1c** (115 mg, 0.51 mmol) was mixed with 1,2-propanediol and stirred for 0.7 h to afford the corresponding, 3-(4-Methoxyphenyl)-5-methyl-1-phenyl-1*H*-pyrazole **3b** (74 mg, 55% yield) as a colourless solid. M.P.: 98-100 °C. IR (KBr): 3059, 2957, 1598, 1523, 1500, 1453, 1433, 1404 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.82-7.80 (m, 2H), 7.56-7.46 (m, 4H), 7.43-7.38 (m, 1H), 6.98-6.94 (m, 2H), 6.48 (d, 1H, J = 0.8 Hz), 3.86 (s, 3H), 2.39 (d, 3H, J = 0.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 151.3, 140.1, 139.9, 129.0, 127.5, 127.0, 126.0, 124.9, 113.9, 103.9, 55.3, 12.5. Anal.Calcd.for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60; Found: C, 77.24; H, 6.13; N, 10.62.

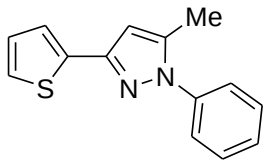


2-(5-Methyl-1-phenyl-1*H*-pyrazol-3-yl) phenol (3c).[7] Following general procedure hydrazone **1e** (108 mg, 0.51 mmol) was mixed with 1,2-propanediol and stirred for 4 h to afford the corresponding, 2-(5-Methyl-1-phenyl-1*H*-pyrazol-3-yl) phenol **3c** (38 mg, 30% yield) as a colourless liquid. IR (neat): 3132, 3102, 3055, 1618, 1597, 1548, 1500, 1458 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 11.01 (s, 1H), 7.62-7.58 (m, 1H), 7.54−7.48 (m, 4H), 7.47−7.40 (m, 1H), 7.27−7.20 (m, 1H), 7.07−7.01 (m, 1H), 6.97−6.90 (m, 1H), 6.62 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 151.5, 139.9, 139.1, 129.2, 129.2, 127.9, 126.4, 124.6, 119.2, 117.1, 116.4, 103.8, 12.4. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{16}H_{14}N_2O$ 251.1184, found 251.1192

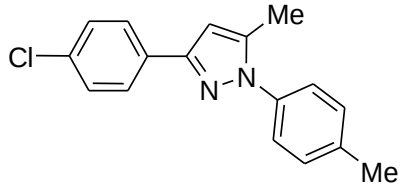


3-(4-Chlorophenyl)-5-methyl-1-phenyl-1*H*-pyrazole (3d).[11] Following general procedure hydrazine **1f** (118 mg, 0.51mmol) was mixed with 1,2-propanediol and stirred for 1 h to afford the corresponding, 3-(4-Chlorophenyl)-5-methyl-1-phenyl-1*H*-pyrazole **3d** (78 mg, 57% yield) as a white crystalline solid. M.P.: 80-81 °C. IR (KBr): 3058, 2920, 1598, 1548, 1500, 1452, 1398 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, 2H, J = 8.4 Hz), 7.54-7.50 (m, 4H), 7.42-7.36 (m, 3H), 6.52 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4,

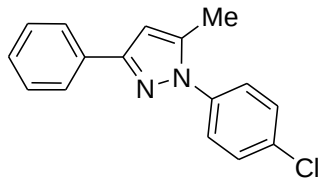
140.4, 139.8, 133.4, 131.8, 129.1, 128.7, 127.8, 126.9, 125.0, 104.3, 12.5. Anal.Calcd.for $C_{16}H_{13}ClN_2$: C, 71.51; H, 4.88; N, 10.42; Found: C, 71.58; H, 4.92; N, 10.47.



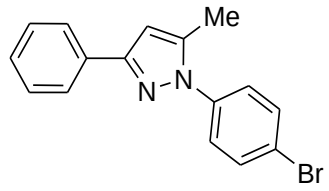
5-Methyl-1-phenyl-3-(thiophen-2-yl)-1*H*-pyrazole (3e).[7] Following general procedure hydrazone **1m** (103 mg, 0.51 mmol) was mixed with 1,2-propanediol and stirred for 0.7 h to afford the corresponding, 5-Methyl-1-phenyl-3-(thiophen-2-yl)-1*H*-pyrazole **3e** (37 mg, 30% yield) as a colourless liquid. IR (neat): 3067, 2961, 1596, 1566, 1532, 1500, 1425, 1375 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.56-7.46 (m, 4H), 7.44-7.36 (m, 2H), 7.27-7.24 (m, 1H), 7.10-7.04 (m, 1H), 6.46 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 140.2, 139.6, 136.6, 129.1, 127.7, 127.4, 125.0, 124.5, 123.8, 104.4, 12.5. Anal.Calcd.for $C_{14}H_{12}N_2S$: C, 69.97; H, 5.03; N, 11.66; S, 13.34; Found: C, 69.94; H, 5.08; N, 11.72; S, 13.37



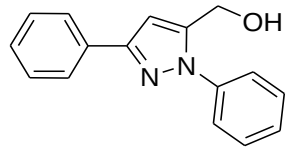
3-(4-Chlorophenyl)-5-methyl-1-p-tolyl-1*H*-pyrazole (3f). Following general procedure hydrazone **1q** (125 mg, 0.51 mmol) was mixed with 1,2-propanediol and stirred for 1 h to afford the corresponding, 3-(4-Chlorophenyl)-5-methyl-1-p-tolyl-1*H*-pyrazole **3f** (75 mg, 52% yield) as a gummy mass. IR (KBr): 3045, 2925, 2850, 1588, 1550, 1509, 1455, 1429, 1394 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.84-7.78 (m, 2H), 7.46-7.36 (m, 4H), 7.32-7.29 (m, 2H), 6.49 (d, 1H, J = 0.4 Hz), 2.4 (s, 3H), 2.37 (d, 3H, J = 0.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 140.4, 137.8, 137.3, 133.3, 131.9, 129.7, 128.7, 126.9, 124.9, 104.0, 21.1, 12.4.Anal.Calcd.for $C_{17}H_{15}ClN_2$: C, 72.21; H, 5.35; N, 9.91; Found: C, 72.15; H, 5.32; N, 9.94. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{15}ClN_2$ 283.1002, found 283.1003. MS (ESI): m/z (relative intensity) 282 ($[M]^+$, 100).



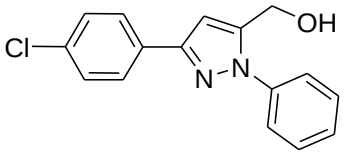
1-(4-Chlorophenyl)-5-methyl-3-phenyl-1*H*-pyrazole (3g). Following general procedure hydrazone **1s** (117 mg, 0.51 mmol) was mixed with 1,2-propanediol and stirred for 1 h to afford the corresponding, 1-(4-Chlorophenyl)-5-methyl-3-phenyl-1*H*-pyrazole **3g** (68 mg, 50 % yield) as a yellow oil. IR (neat): 3059, 2975, 2908, 2857, 1592, 1566, 1550, 1504 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, 1H, J = 7.6 Hz), 7.52-7.40 (m, 6H), 7.36-7.32 (m, 1H), 6.55 (s, 1H), 2.4 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 140.2, 138.4, 133.3, 133.1, 129.2, 128.6, 127.9, 126.0, 125.7, 104.8, 12.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{16}H_{13}ClN_2$ 269.0845, found 269.0849. MS (ESI): m/z (relative intensity) 268 ($[M]^+$, 100). Anal.Calcd.for $C_{16}H_{13}ClN_2$: C, 71.51; H, 4.88; N, 10.42; Found: C, 71.59; H, 4.94; N, 10.44.



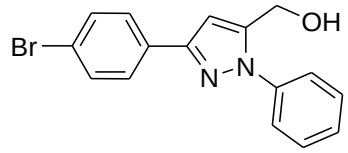
1-(4-Bromophenyl)-5-methyl-3-phenyl-1*H*-pyrazole (3h).[11] Following general procedure hydrazone **1w** (140 mg, 0.51 mmol) was mixed with 1,2-propanediol and stirred for **1 h** to afford the corresponding, 1-(4-Bromophenyl)-5-methyl-3-phenyl-1*H*-pyrazole **3h** (82 mg, 52% yield) as a gummy liquid. IR (neat): 3062, 2917, 1582, 1553, 1487, 1364 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, 2H, J = 7.6 Hz), 7.63 (d, 2H, J = 8.4 Hz), 7.46-7.30 (m, 5H), 6.56 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 140.2, 138.9, 133.0, 132.2, 128.6, 127.9, 126.3, 125.7, 121.2, 104.8, 12.6. Anal.Calcd.for $C_{16}H_{13}BrN_2$: C, 61.36; H, 4.18; N, 8.94; Found: C, 61.43; H, 4.22; N, 8.99.



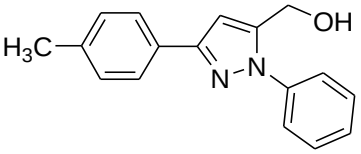
(1,3-Diphenyl-1*H*-pyrazol-5-yl) methanol (3i).[14] Following general procedure hydrazone **1a** (100 mg, 0.51 mmol) was mixed with glycerol and stirred for 6 h to afford the corresponding 1,3-Diphenyl-1*H*-pyrazol-5-yl) methanol **3i** (38 mg, 30% yield) as a green solid. M.P.: 99-100 °C. IR (KBr): 3299, 3069, 2878, 1590, 1501, 1369 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, 2H, J = 7.2 Hz), 7.67 (d, 2H, J = 8.0 Hz), 7.51 (t, 2H, J = 8.0 Hz), 7.48-7.32 (m, 4H), 6.78 (s, 1H), 4.70 (s, 2H), 1.96 (s, br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 143.3, 139.5, 132.8, 129.2, 128.6, 128.0, 127.9, 125.7, 124.5, 104.9, 55.8. Anal.Calcd.for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19; Found: C, 76.82; H, 5.67; N, 11.17.



(3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-5-yl)methanol (3j).[14] Following general procedure hydrazone **1f** (117 mg, 0.51 mmol) was mixed with glycerol and stirred for 3 h to afford the corresponding (3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-5-yl)methanol **3j** (54 mg, 37% yield) as a white solid. M.P.: 91-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, 2H, J = 8.4 Hz), 7.67 (d, 2H, J = 8.0 Hz), 7.56-7.48 (m, 2H), 7.44-7.38 (m, 3H), 6.76 (s, 1H), 4.72 (s, 2H), 1.98 (s, br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 143.4, 139.4, 133.7, 131.5, 129.3, 128.8, 128.1, 127.0, 124.5, 104.8, 55.8. Anal.Calcd.for $C_{16}H_{13}ClN_2O$: C, 67.49; H, 4.60; N, 9.84; Found: C, 67.56; H, 4.64; N, 9.89.



(3-(4-Bromophenyl)-1-phenyl-1*H*-pyrazol-5-yl)methanol (3k). Following general procedure hydrazone **1h** (140 mg, 0.51 mmol) was mixed with glycerol and stirred for 3 h to afford the corresponding, (3-(4-Bromophenyl)-1-phenyl-1*H*-pyrazol-5-yl)methanol **3k** (55 mg, 33% yield) as a gummy mass. IR (KBr): 3146, 2965, 2935, 2843, 1612, 1558, 1512, 1504, 1458 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, 2H, J = 8.0 Hz), 7.66 (d, 2H, J = 8.0 Hz), 7.58-7.50 (m, 4H), 7.46-7.40 (m, 1H), 6.76 (s, 1H), 4.71 (s, 2H), 1.80 (s, br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 143.4, 139.4, 131.9, 131.7, 129.3, 128.1, 127.3, 124.5, 121.9, 104.8, 55.8. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{16}H_{13}BrN_2O$ 329.0289, found 329.0293. MS (ESI): m/z (relative intensity) 329 ($[M]^+$, 100). Anal.Calcd.for $C_{16}H_{13}BrN_2O$: C, 58.38; H, 3.98; N, 8.51; Found: C, 58.45; H, 3.94; N, 8.56.



(1-Phenyl-3-p-tolyl-1*H*-pyrazol-5-yl)methanol (3l).[14] Following general procedure hydrazone **1b** (107 mg, 0.51 mmol) was mixed with glycerol and stirred for **3 h** to afford the corresponding (1-Phenyl-3-p-tolyl-1*H*-pyrazol-5-yl)methanol **3l** (38 mg, 28% yield) as a white crystalline solid. M.P.: 92-93 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, 2H, J = 7.6 Hz), 7.67 (d, 2H, J = 8.0 Hz), 7.54-7.48 (m, 2H), 7.44-7.38 (m, 1H), 7.26-7.22 (m, 2H), 6.75 (s, 1H), 4.71 (s, 2H), 2.4 (s, 3H), 1.92 (s, br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 143.1, 139.5, 137.8, 130.0, 129.3, 129.2, 127.8, 125.6, 124.5, 104.7, 55.8, 21.3. Anal.Calcd.for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60; Found: C, 77.24; H, 6.13; N, 10.62.

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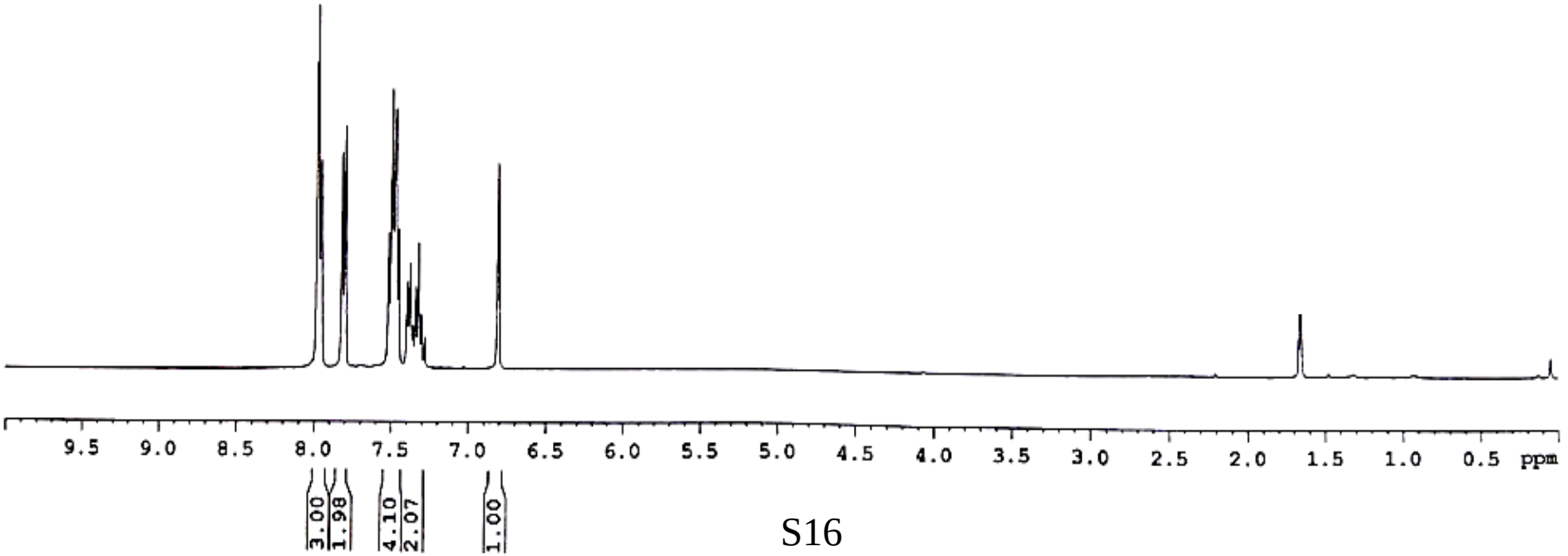
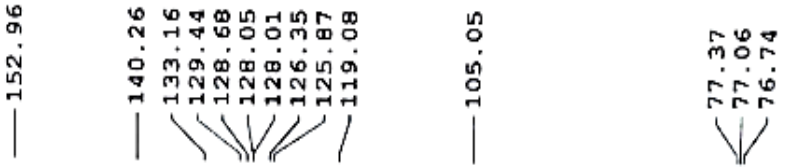
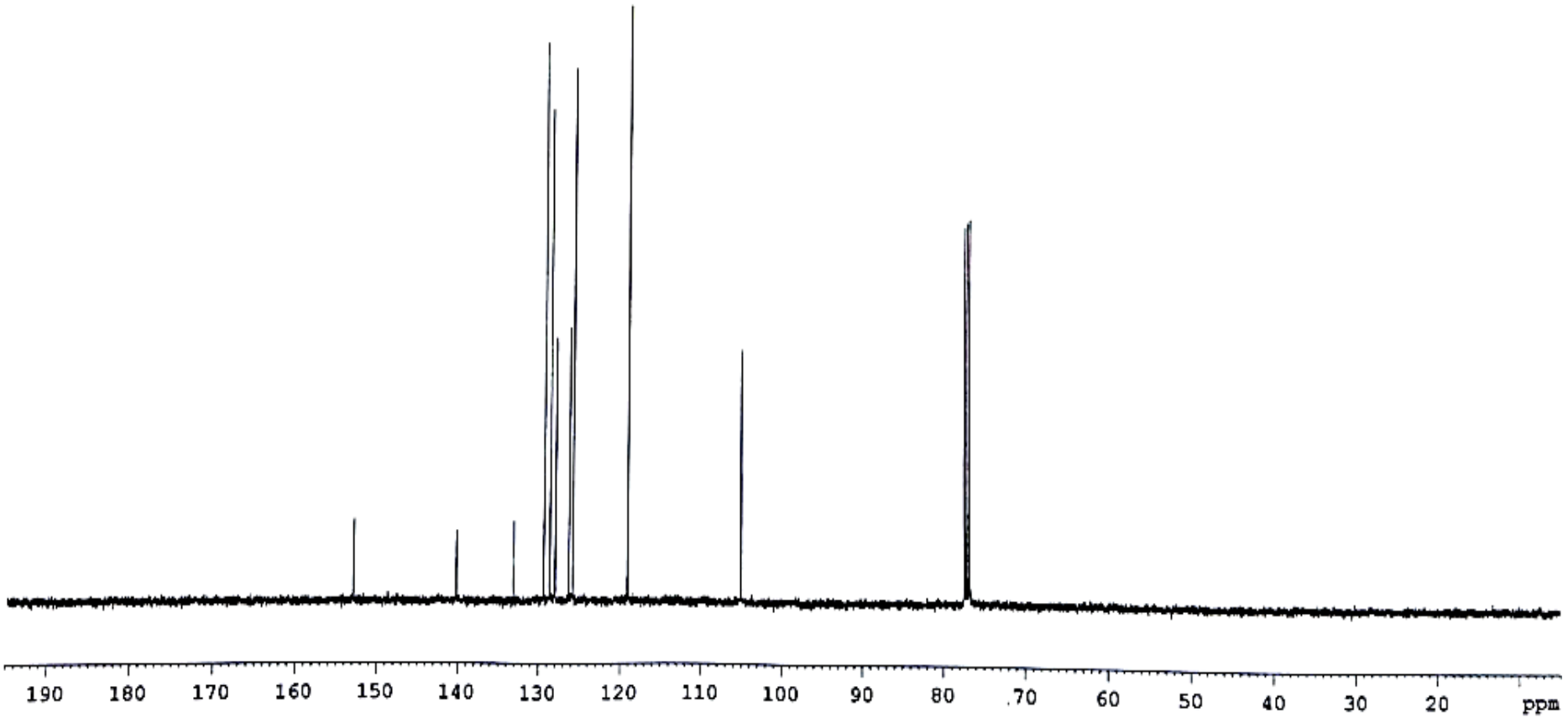
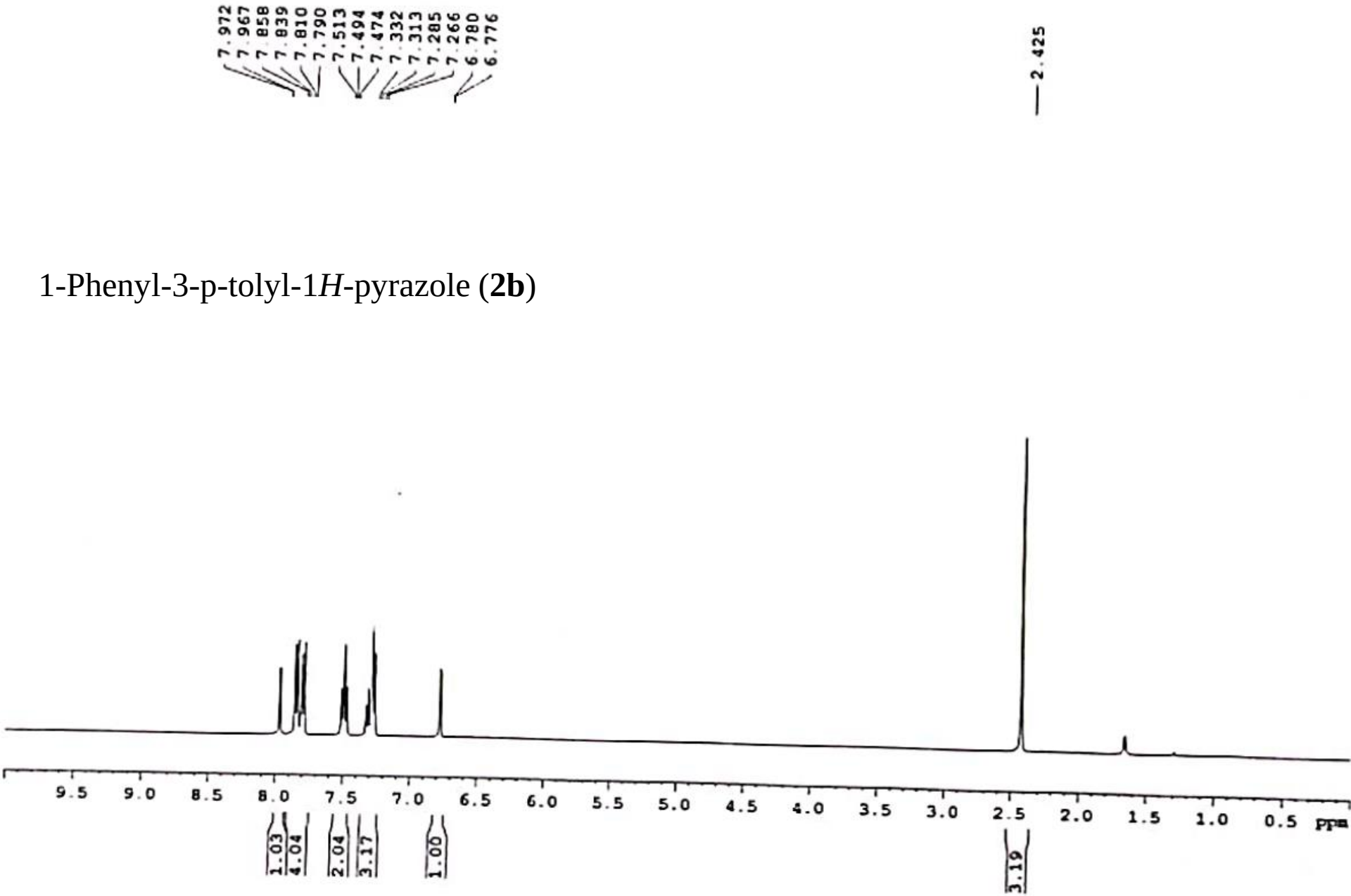
1,3-Diphenyl-1*H*-pyrazole (**2a**)



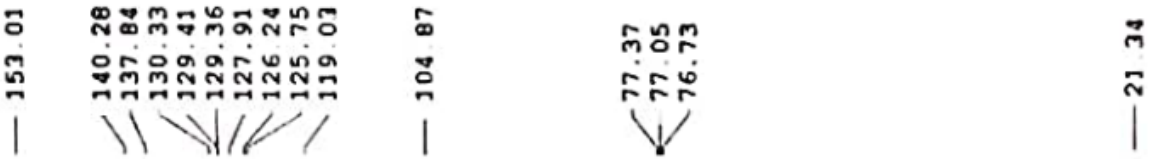


1,3-Diphenyl-1*H*-pyrazole (**2a**)

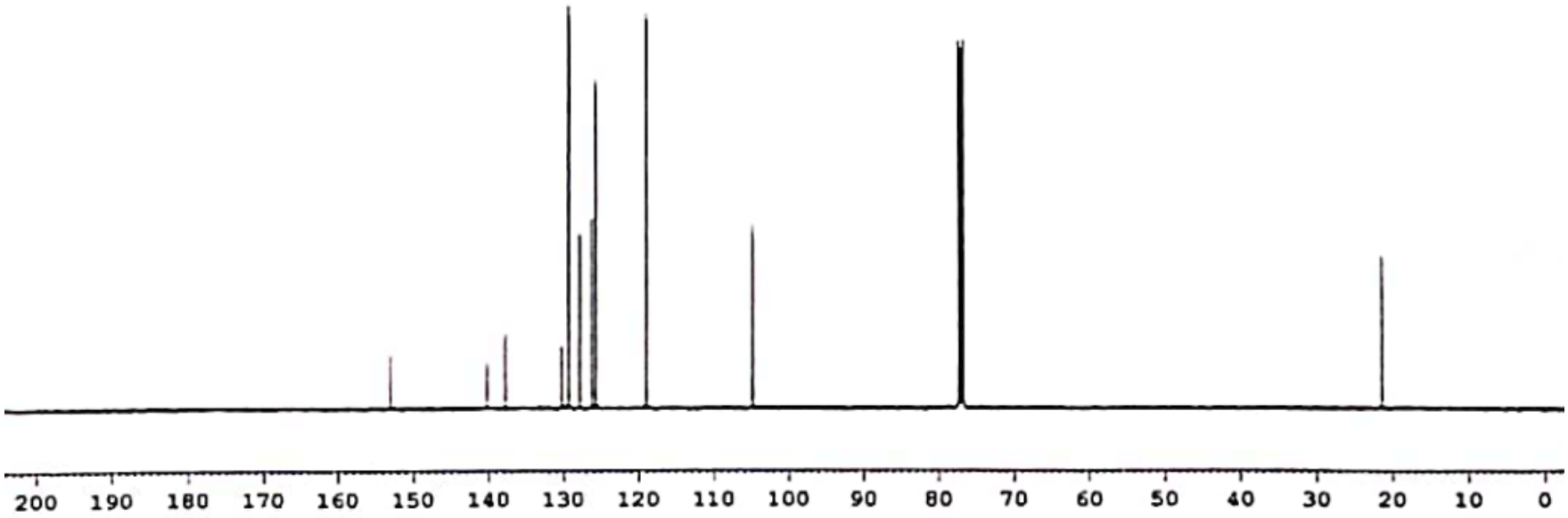


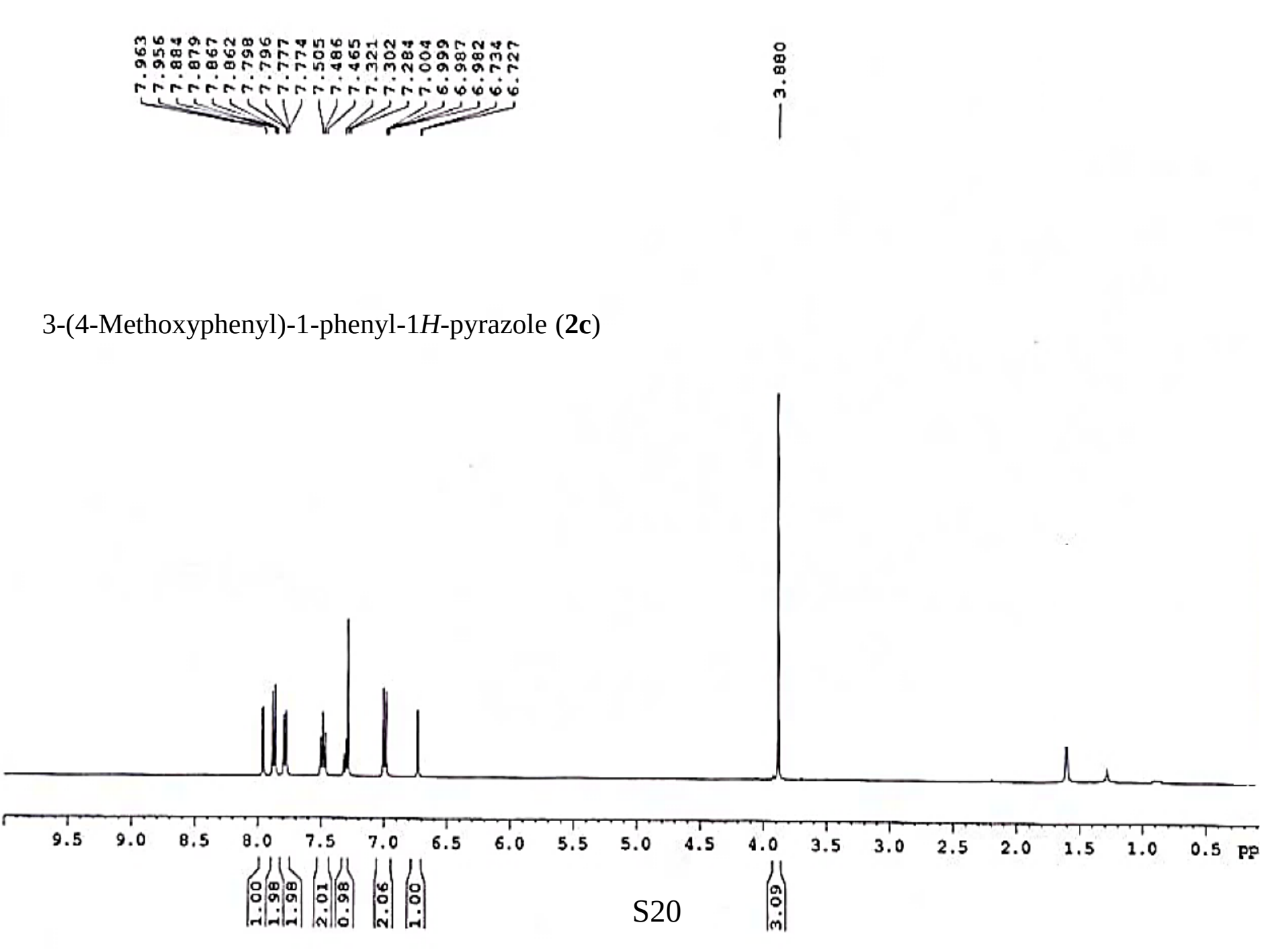


1-Phenyl-3-p-tolyl-1*H*-pyrazole (**2b**)



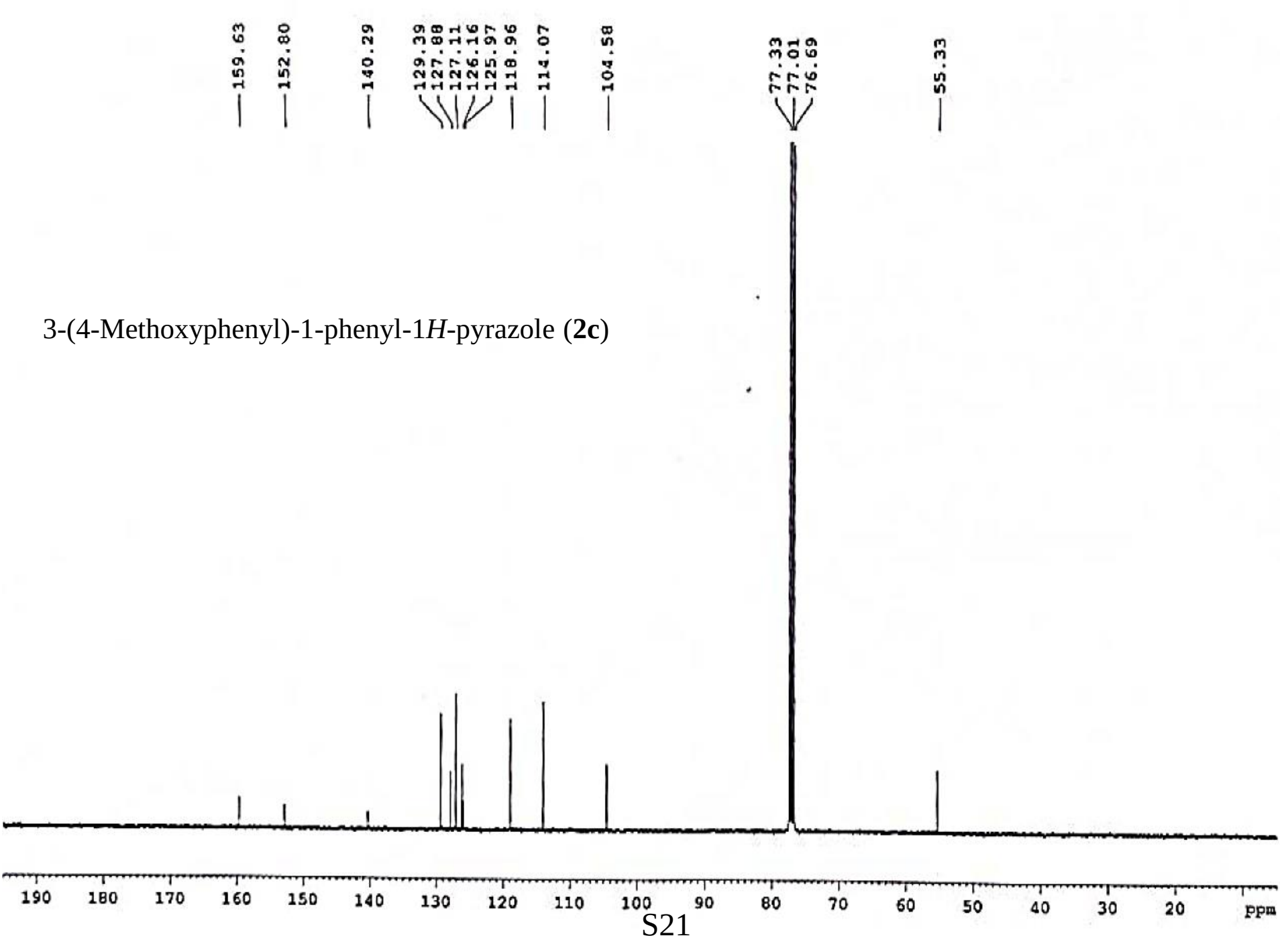
1-Phenyl-3-p-tolyl-1*H*-pyrazole (**2b**)

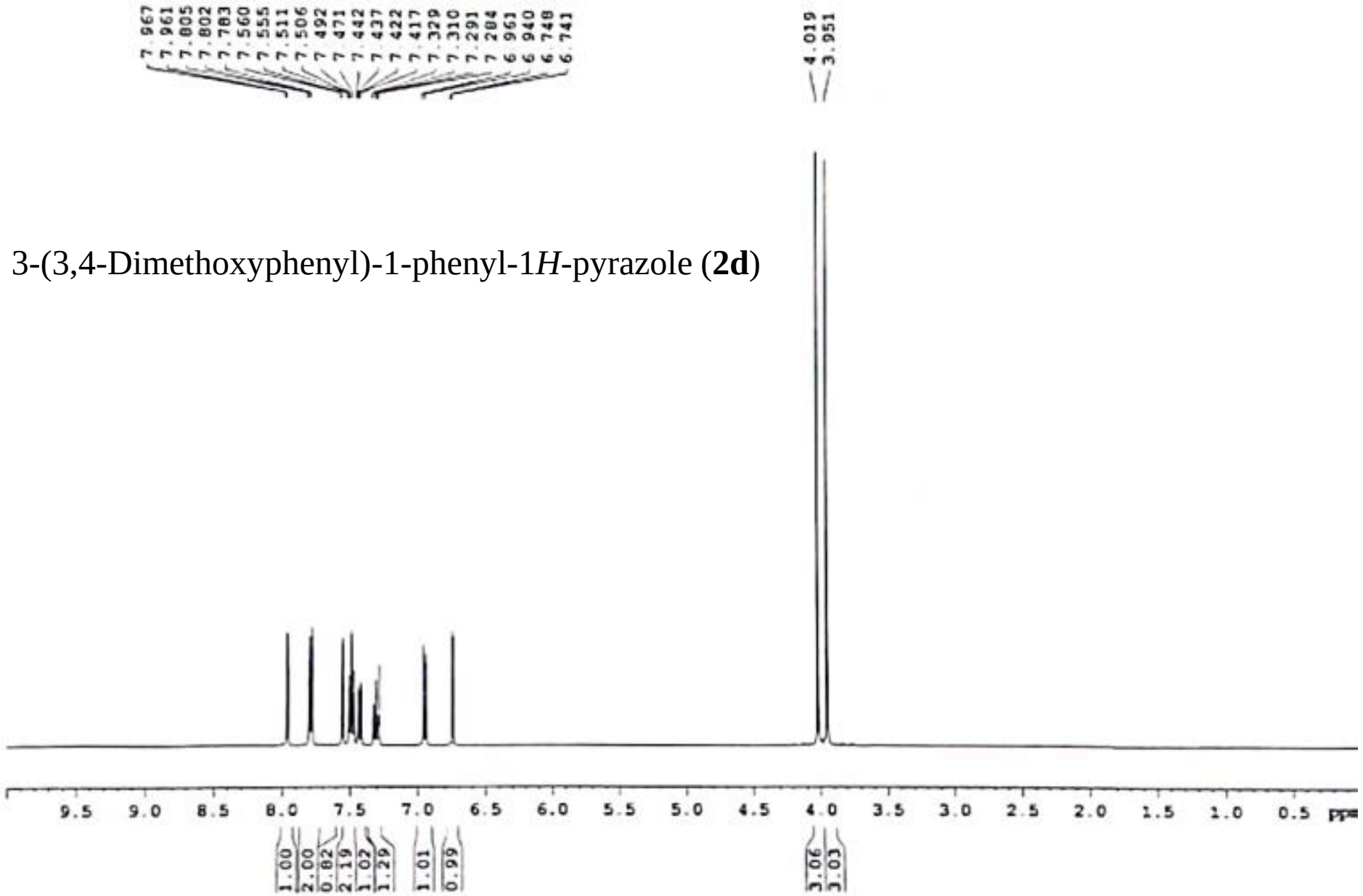




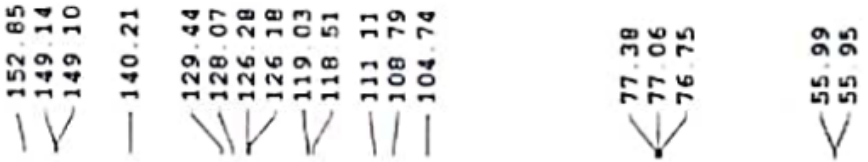
3-(4-Methoxyphenyl)-1-phenyl-1*H*-pyrazole (**2c**)

3-(4-Methoxyphenyl)-1-phenyl-1*H*-pyrazole (**2c**)

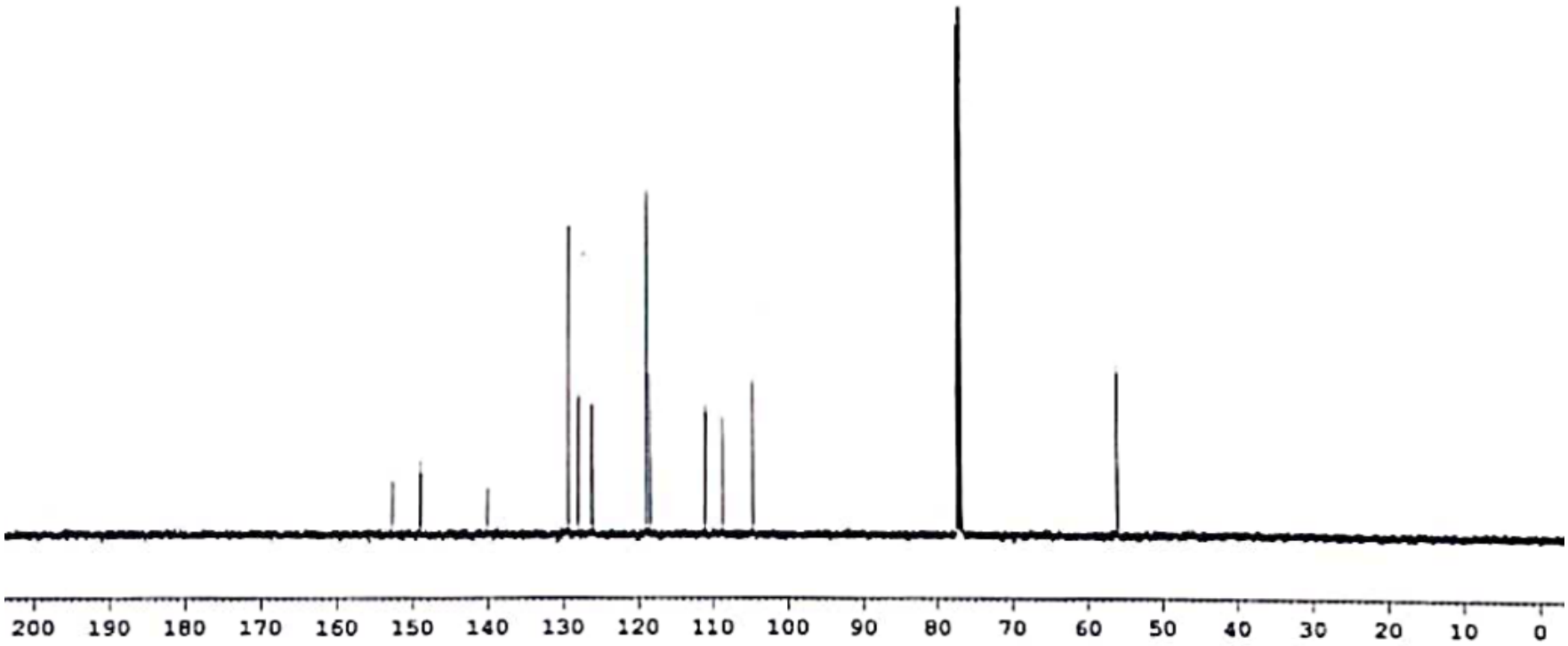


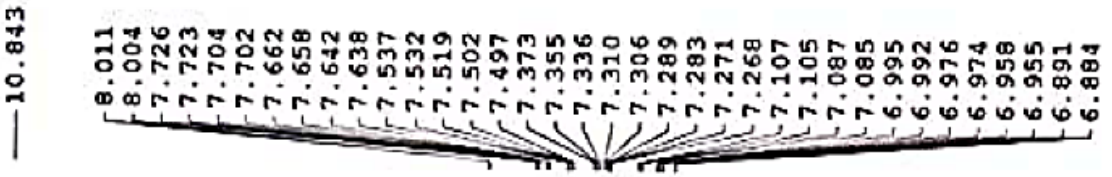


3-(3,4-Dimethoxyphenyl)-1-phenyl-1*H*-pyrazole (**2d**)

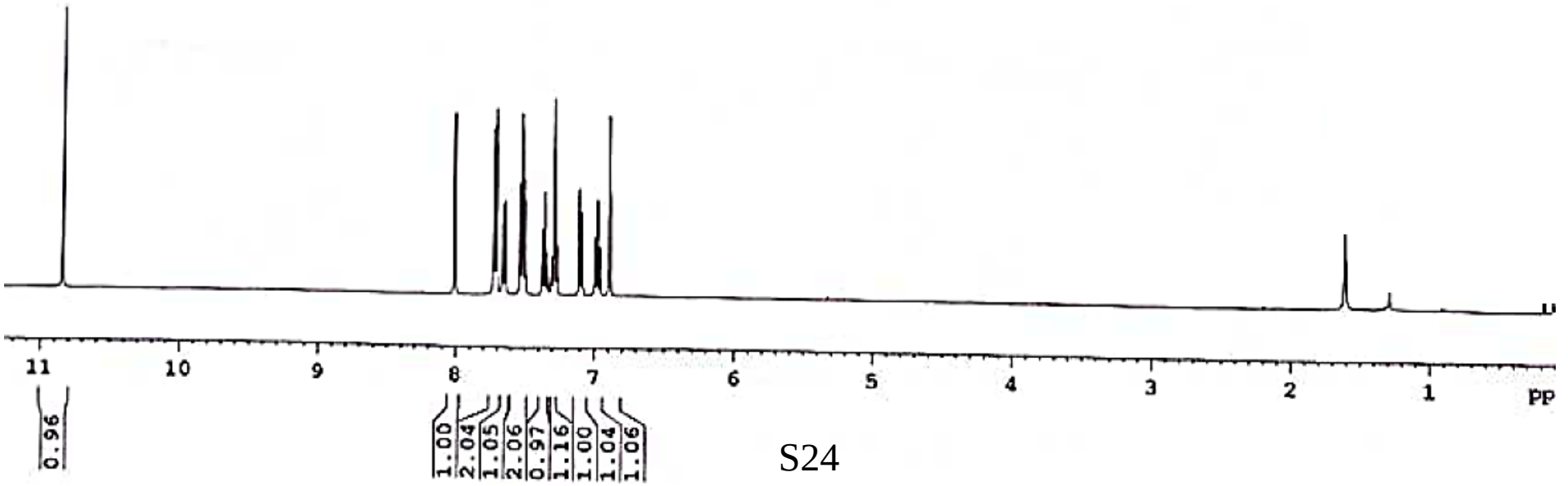


3-(3,4-Dimethoxyphenyl)-1-phenyl-1*H*-pyrazole (**2d**)

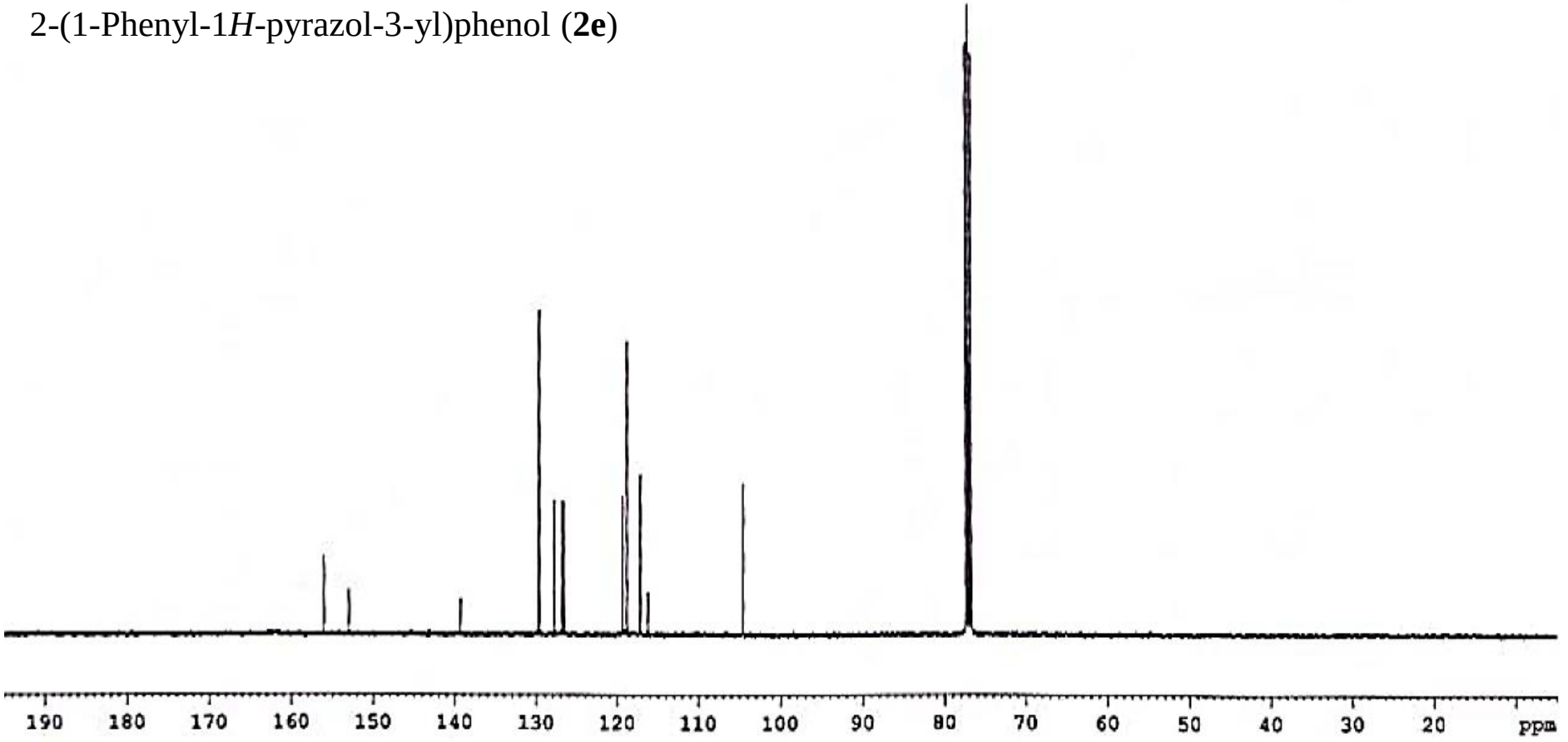


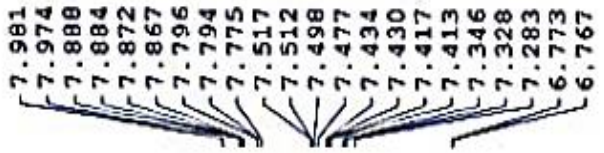


2-(1-Phenyl-1*H*-pyrazol-3-yl)phenol (**2e**)

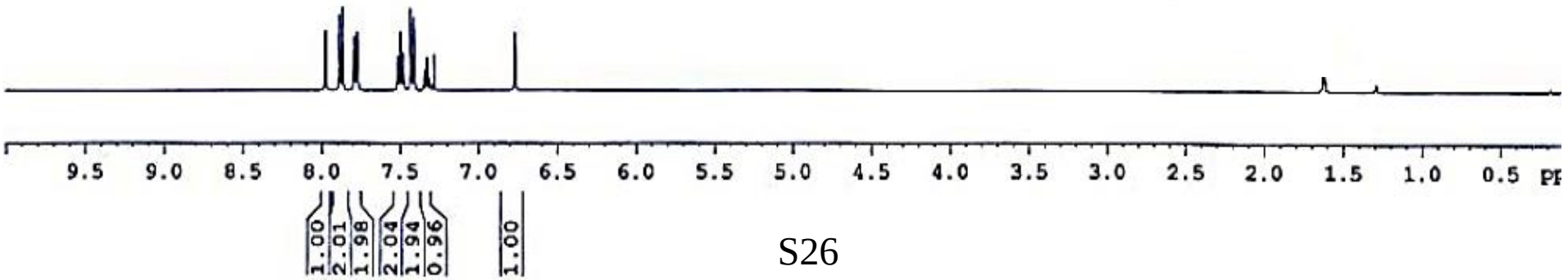


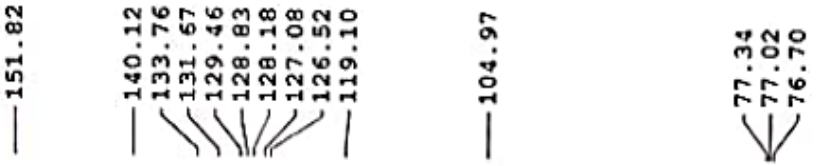
2-(1-Phenyl-1*H*-pyrazol-3-yl)phenol (**2e**)



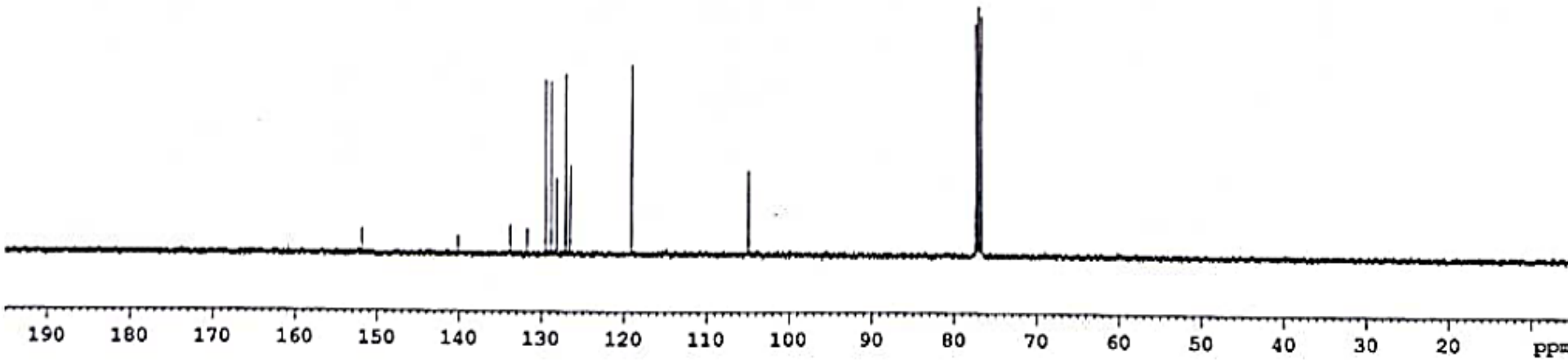


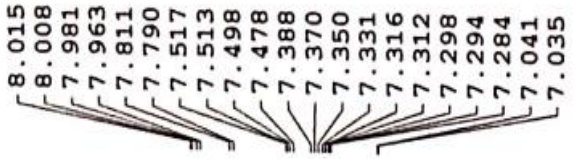
3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazole (**2f**)



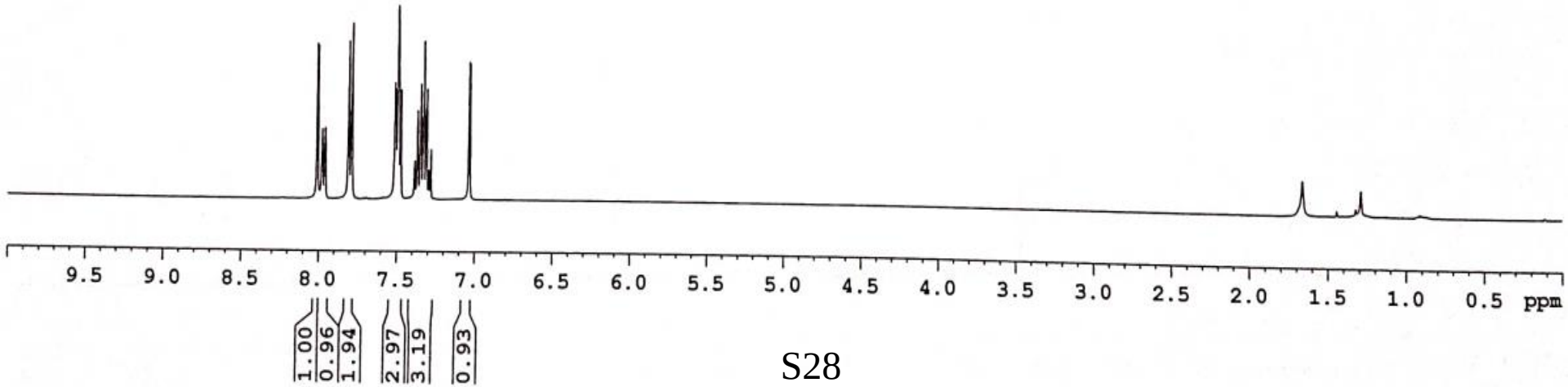


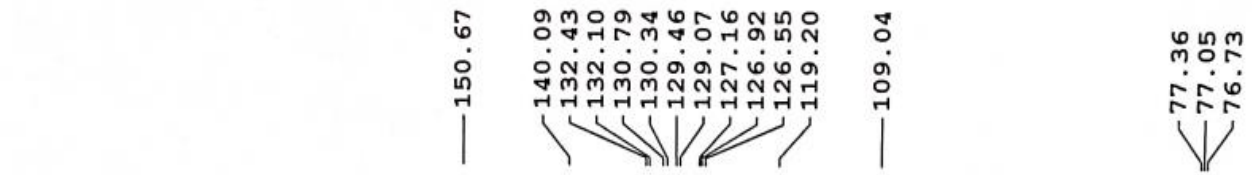
3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazole (**2f**)



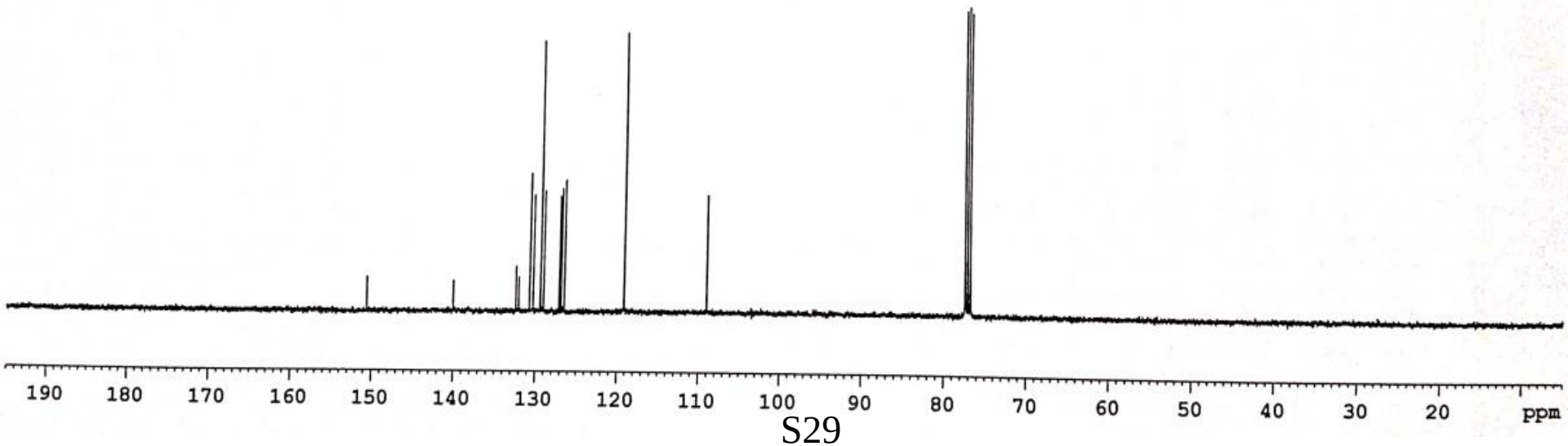


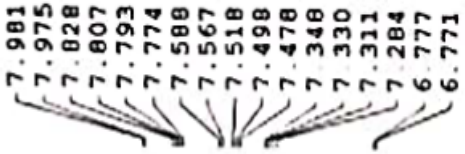
3-(2-Chlorophenyl)-1-phenyl-1*H*-pyrazole (**2g**)



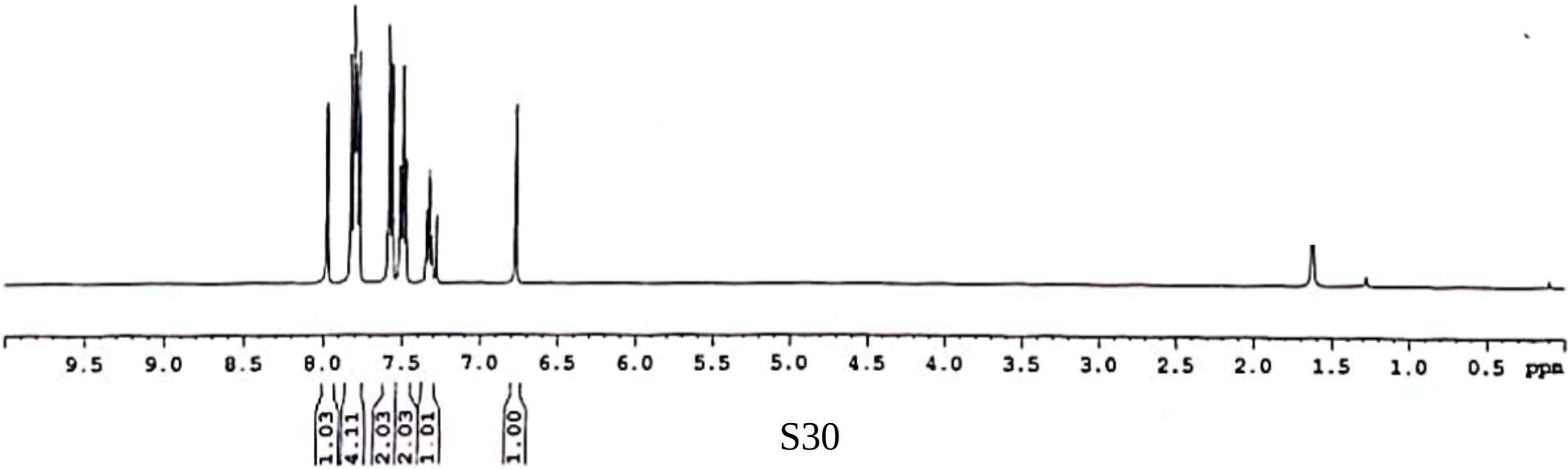


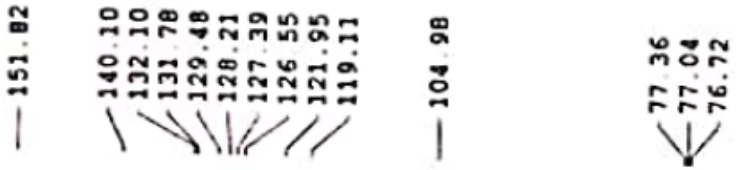
3-(2-Chlorophenyl)-1-phenyl-1*H*-pyrazole (**2g**)



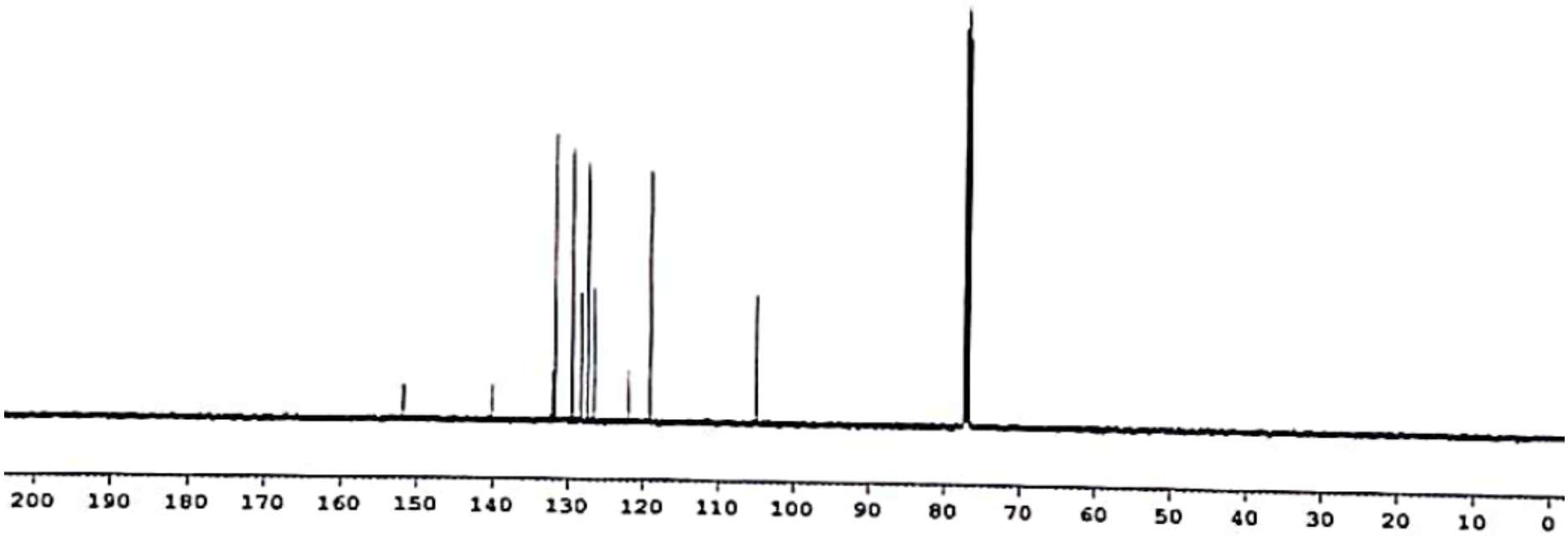


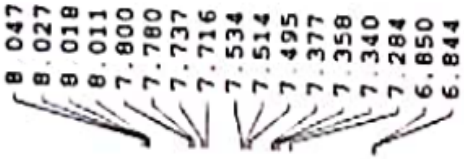
3-(4-Bromophenyl)-1-phenyl-1*H*-pyrazole (**2h**)



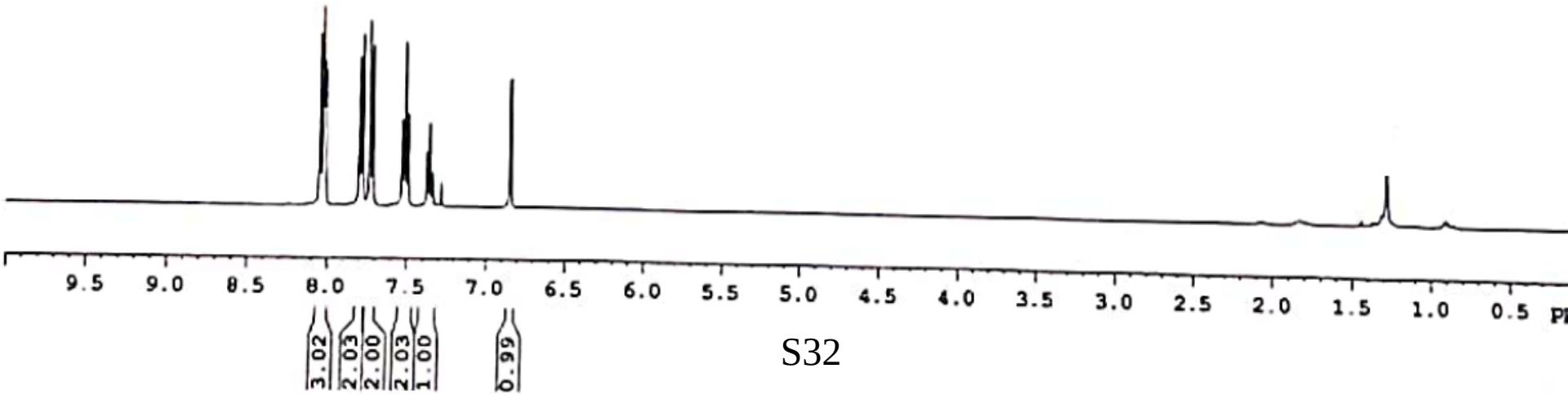


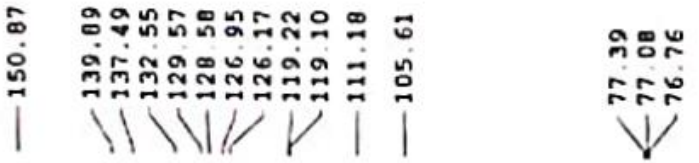
3-(4-Bromophenyl)-1-phenyl-1*H*-pyrazole (**2h**)



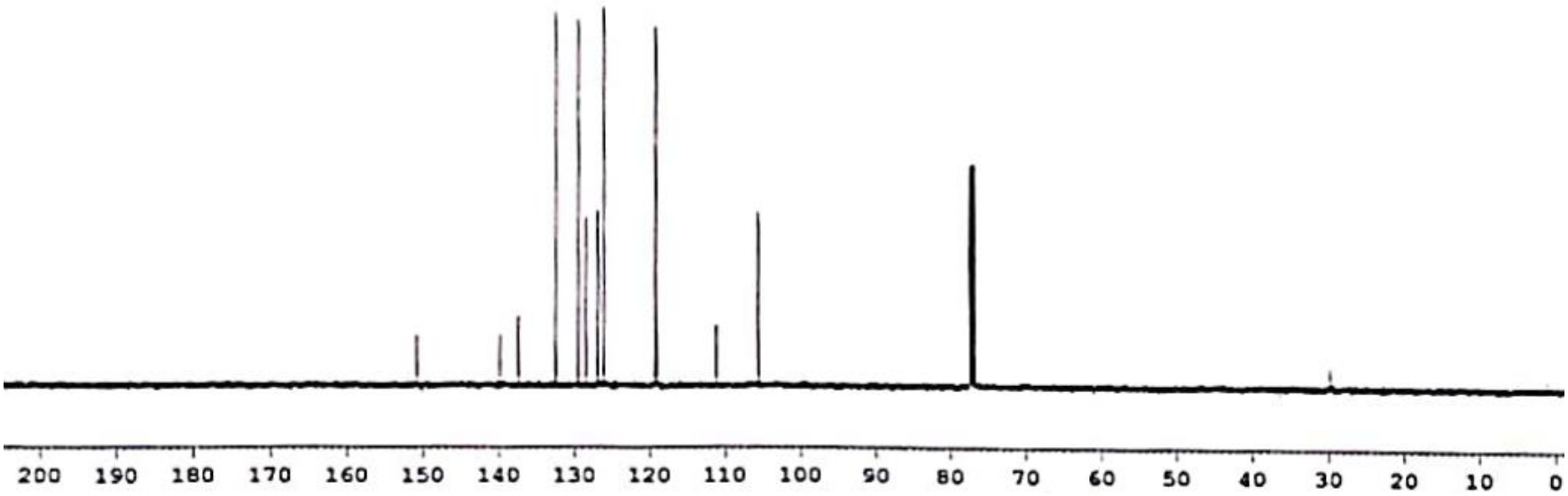


4-(1-Phenyl-1*H*-pyrazol-3-yl)benzonitrile (**2i**)

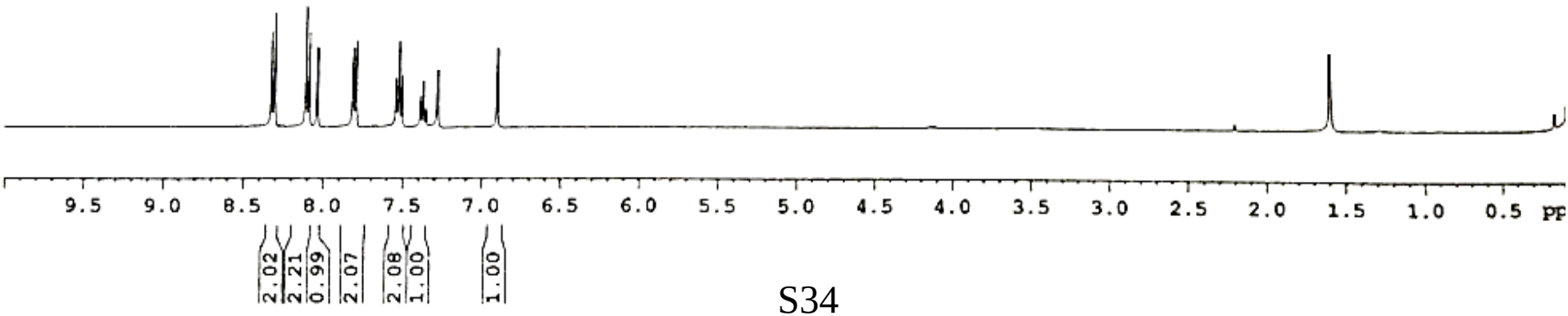




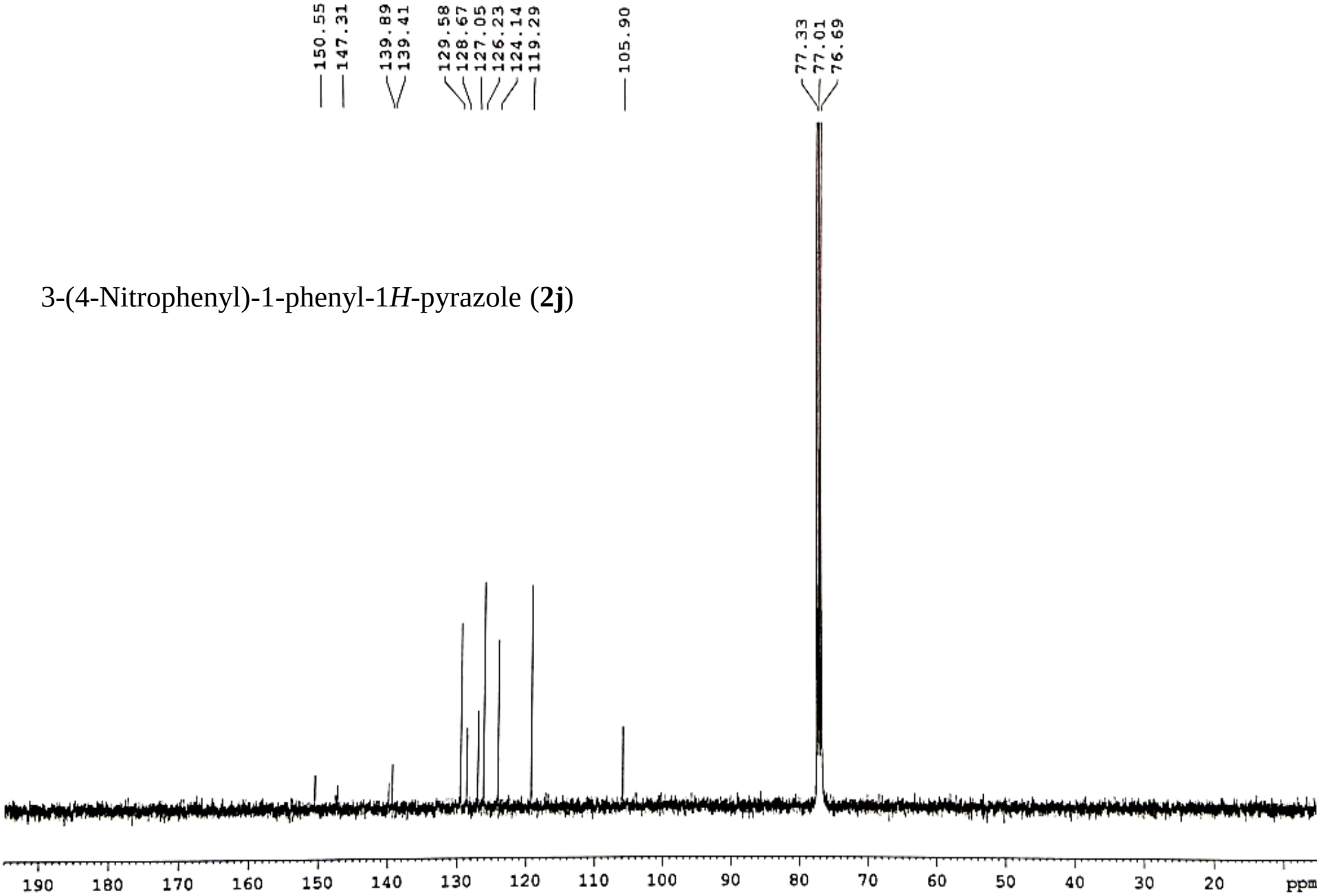
4-(1-phenyl-1*H*-pyrazol-3-yl)benzonitrile (**2i**)

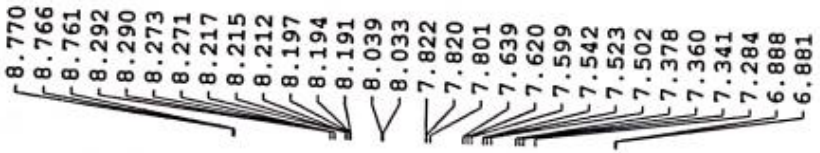


3-(4-Nitrophenyl)-1-phenyl-1*H*-pyrazole (**2j**)

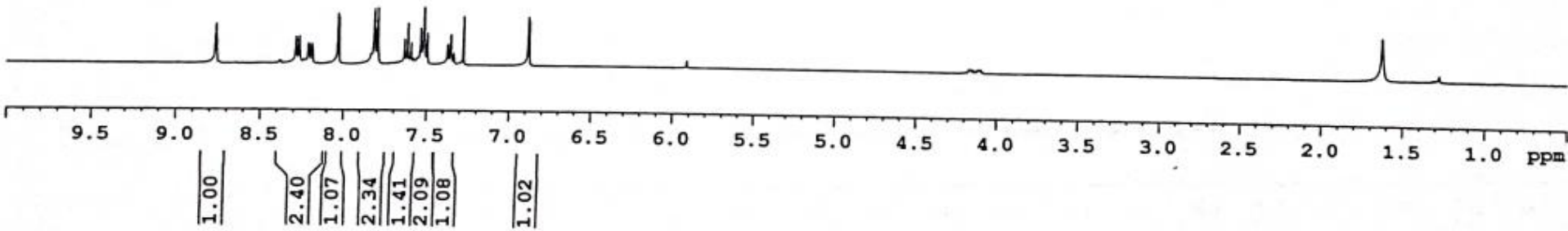


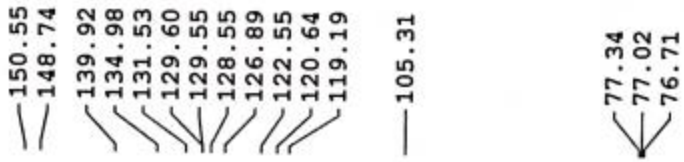
3-(4-Nitrophenyl)-1-phenyl-1*H*-pyrazole (**2j**)



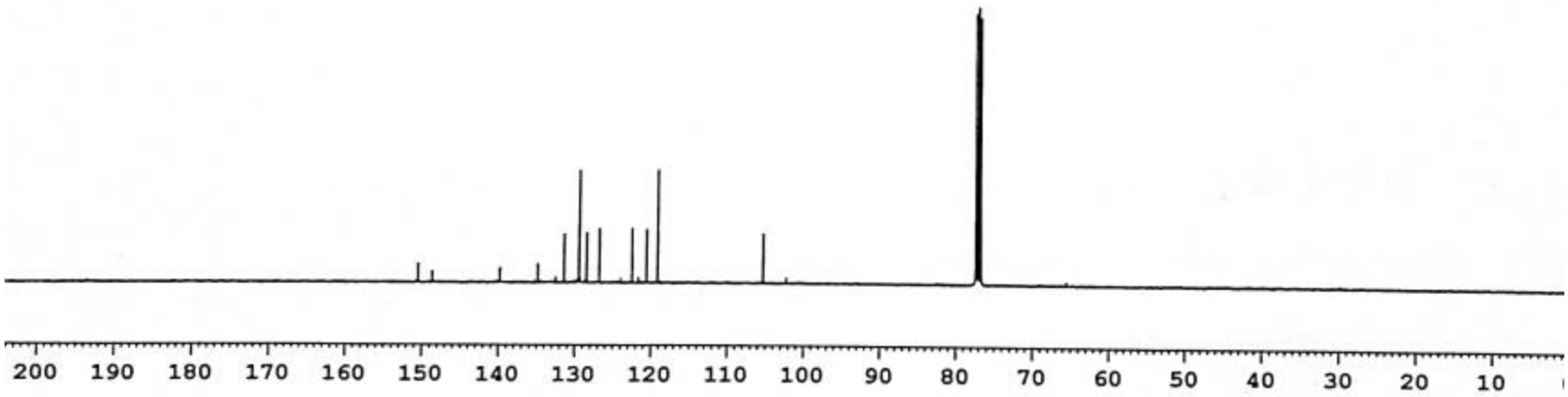


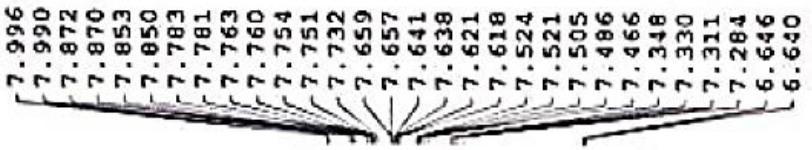
3-(3-Nitrophenyl)-1-phenyl-1*H*-pyrazole (**2k**)



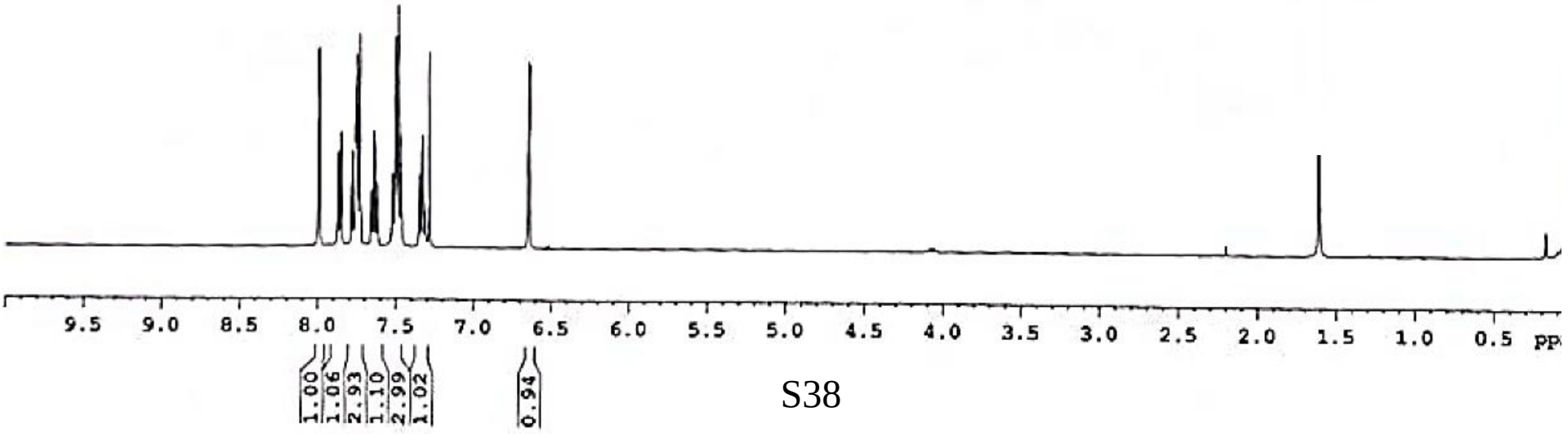


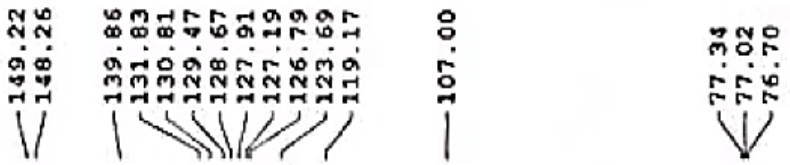
3-(3-nitrophenyl)-1-phenyl-1*H*-pyrazole (**2k**)



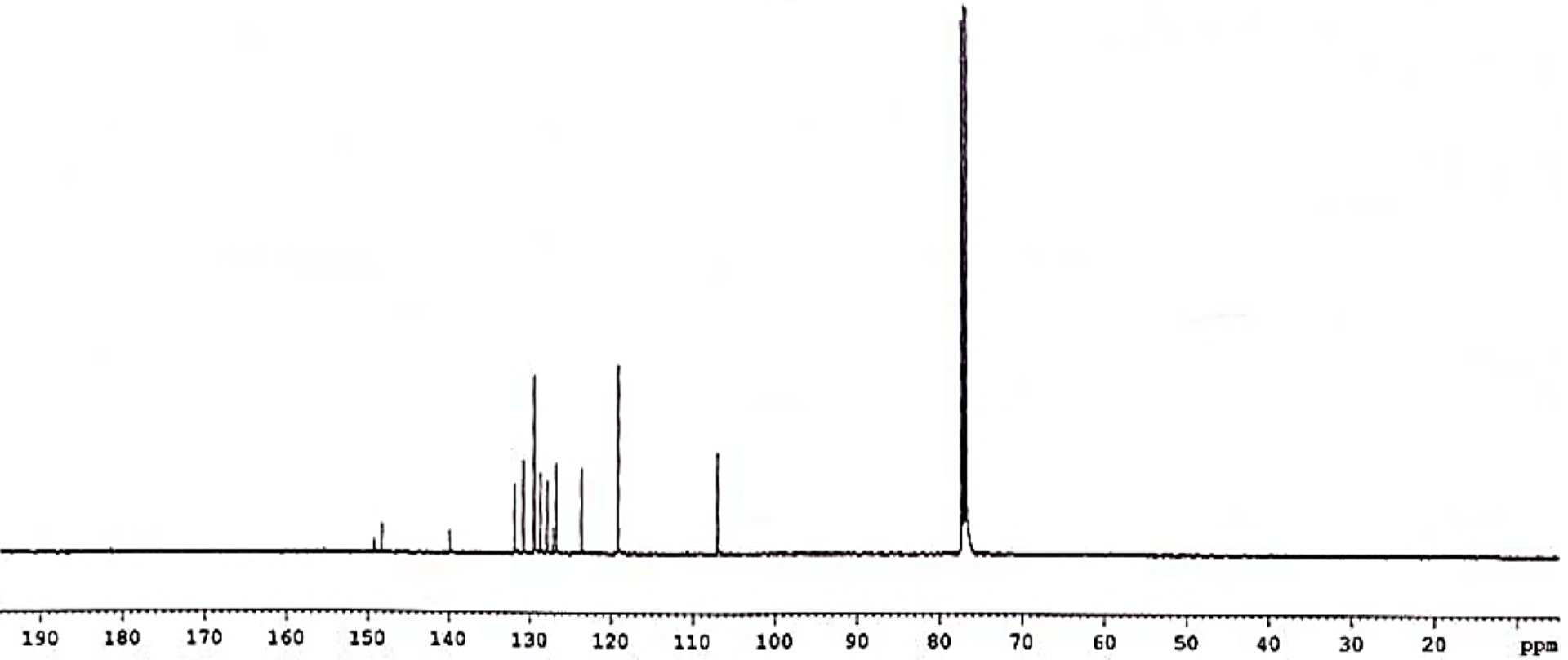


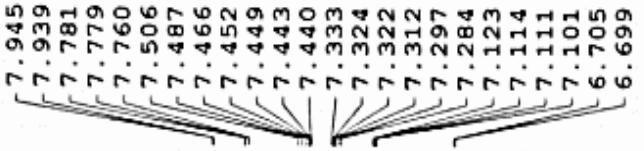
3-(2-Nitrophenyl)-1-phenyl-1*H*-pyrazole (**2l**)



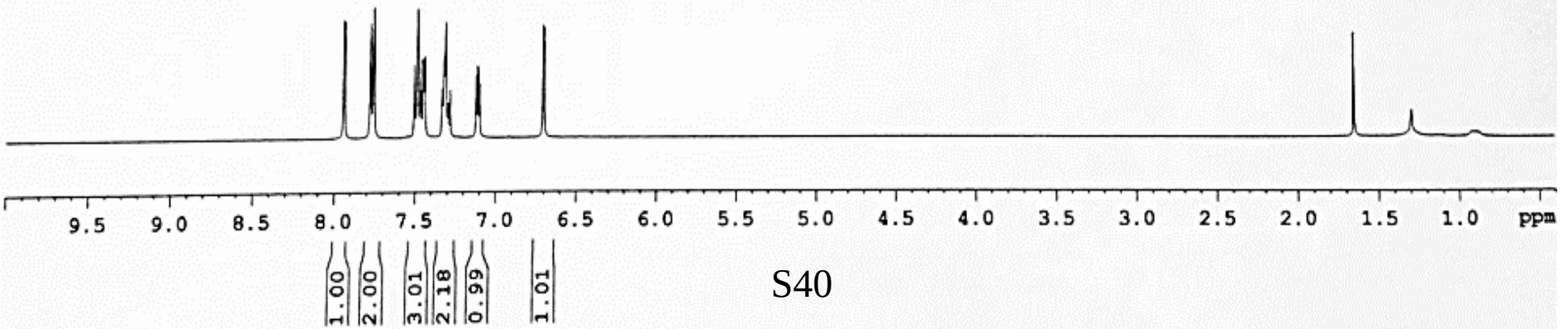


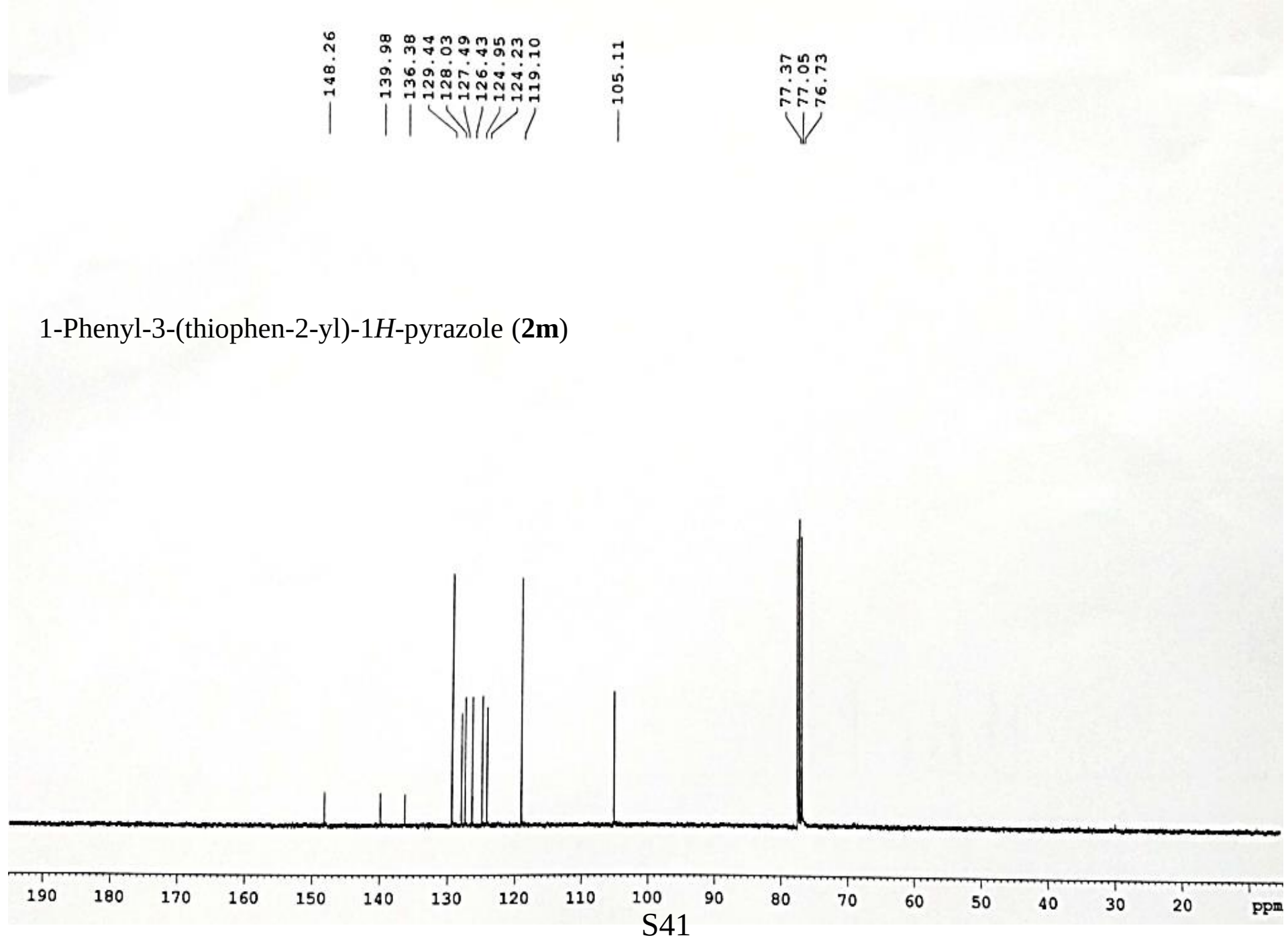
3-(2-Nitrophenyl)-1-phenyl-1*H*-pyrazole (**2l**)





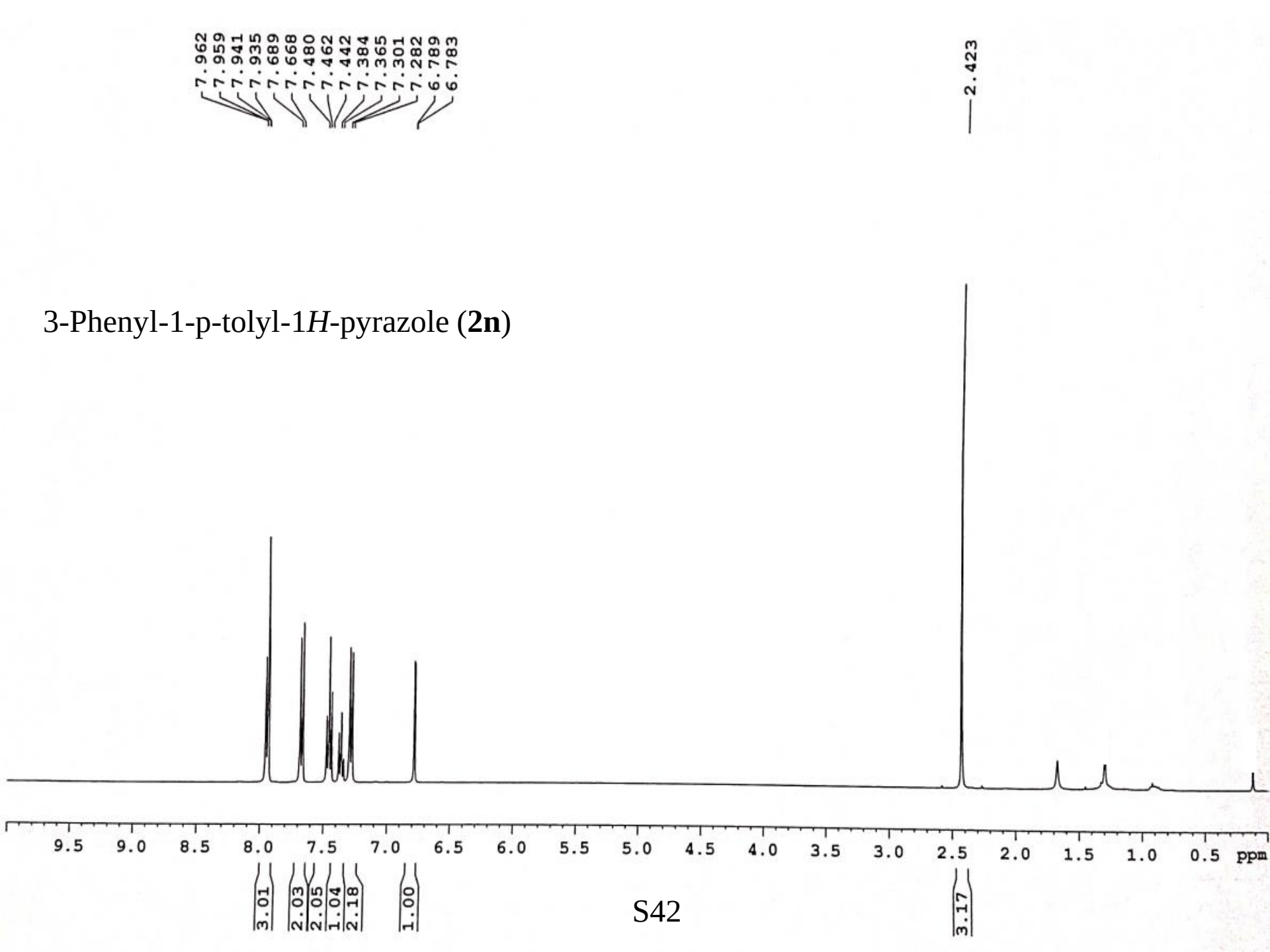
1-Phenyl-3-(thiophen-2-yl)-1*H*-pyrazole (**2m**)

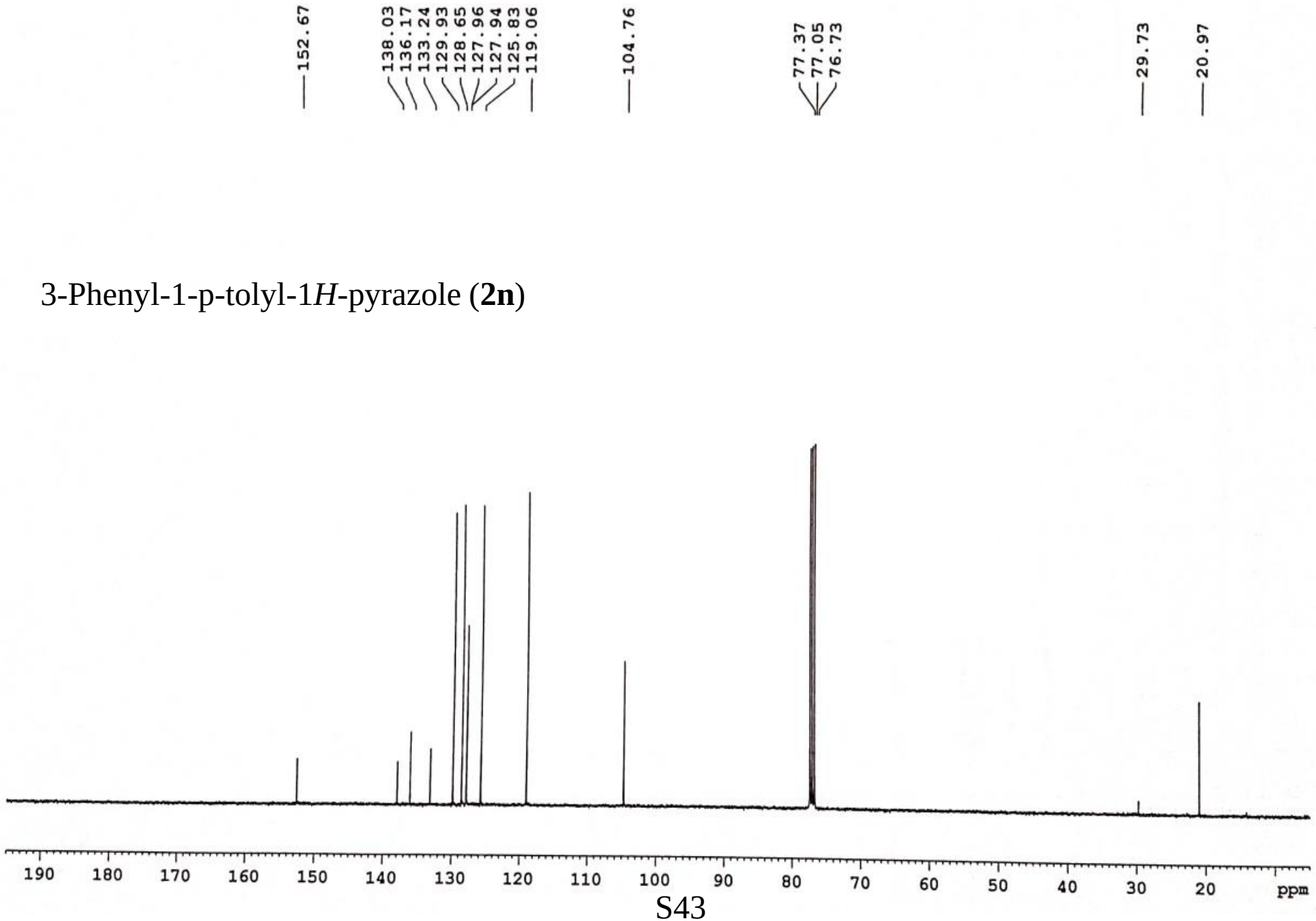




1-Phenyl-3-(thiophen-2-yl)-1*H*-pyrazole (**2m**)

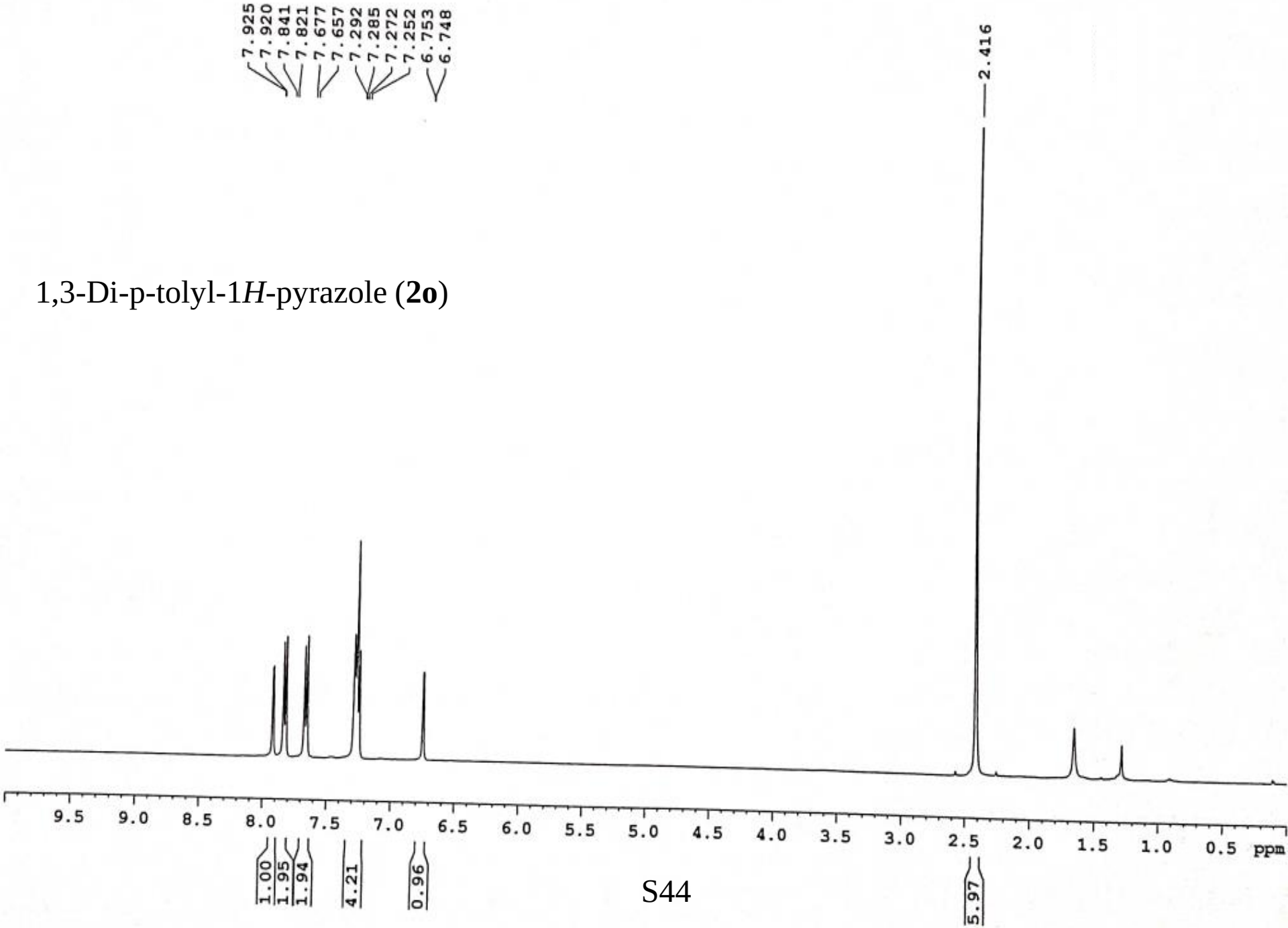
3-Phenyl-1-p-tolyl-1*H*-pyrazole (**2n**)

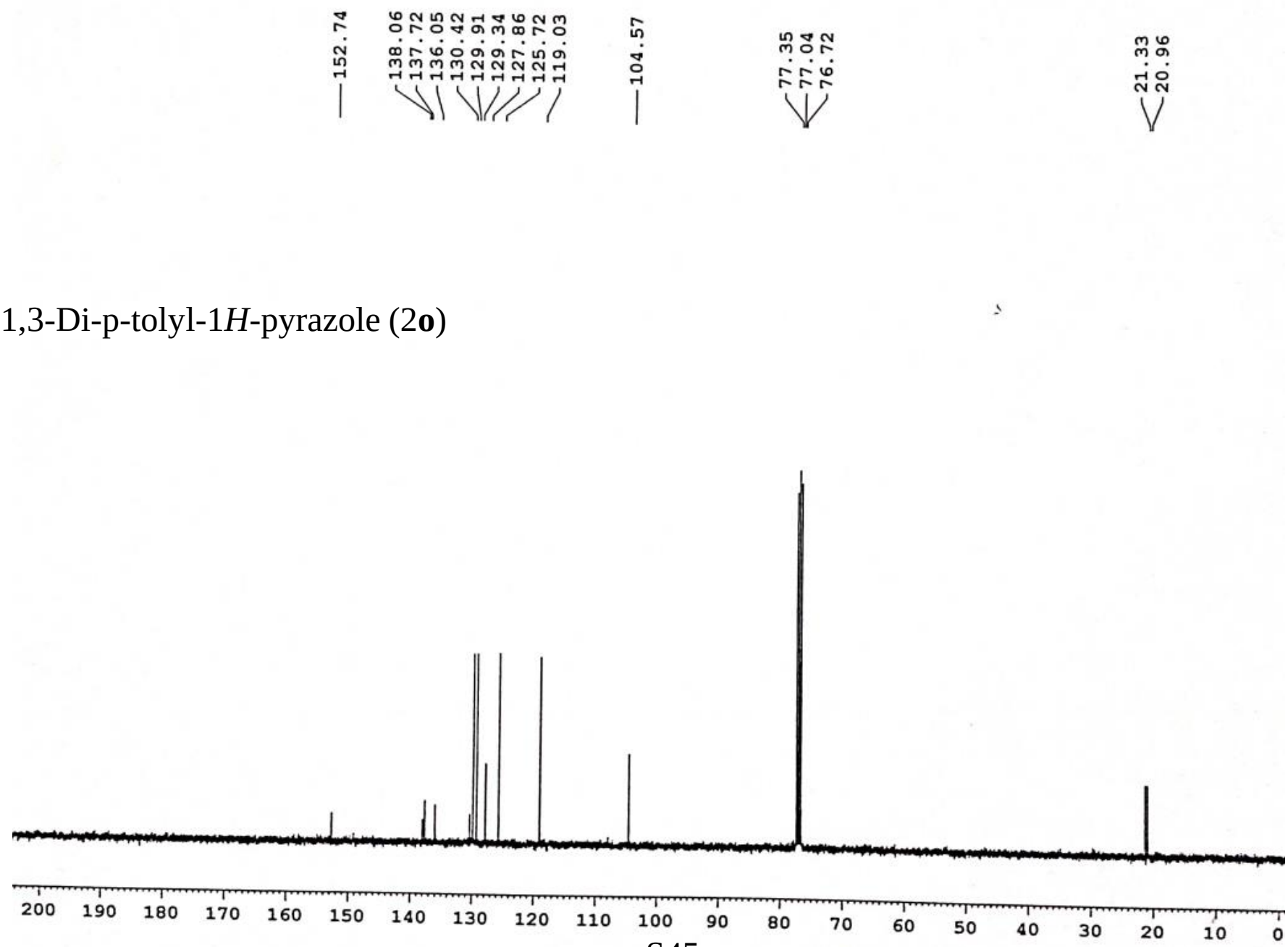




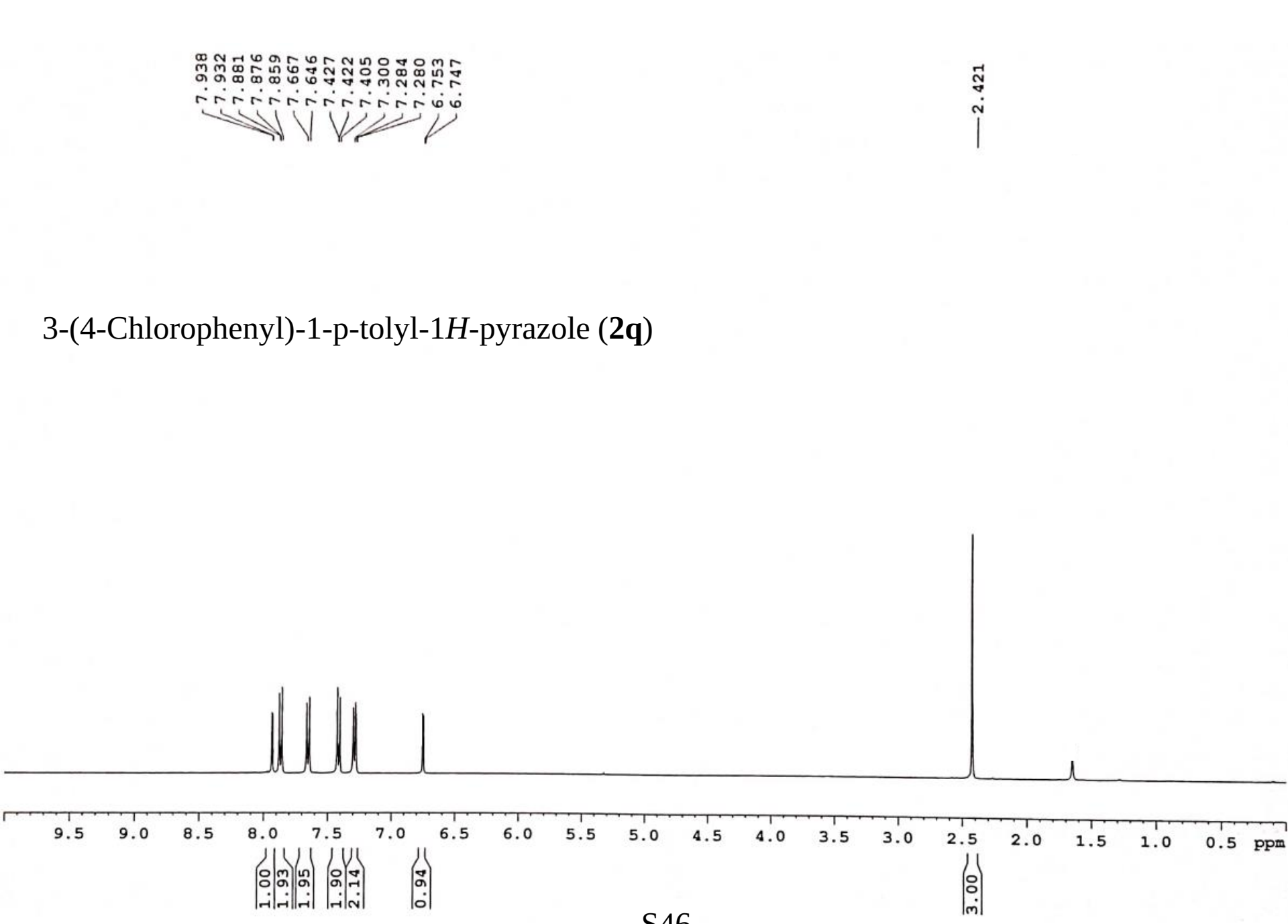
3-Phenyl-1-p-tolyl-1*H*-pyrazole (**2n**)

1,3-Di-p-tolyl-1*H*-pyrazole (**2o**)

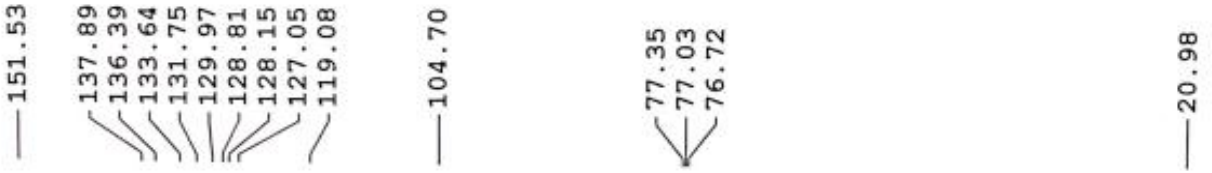




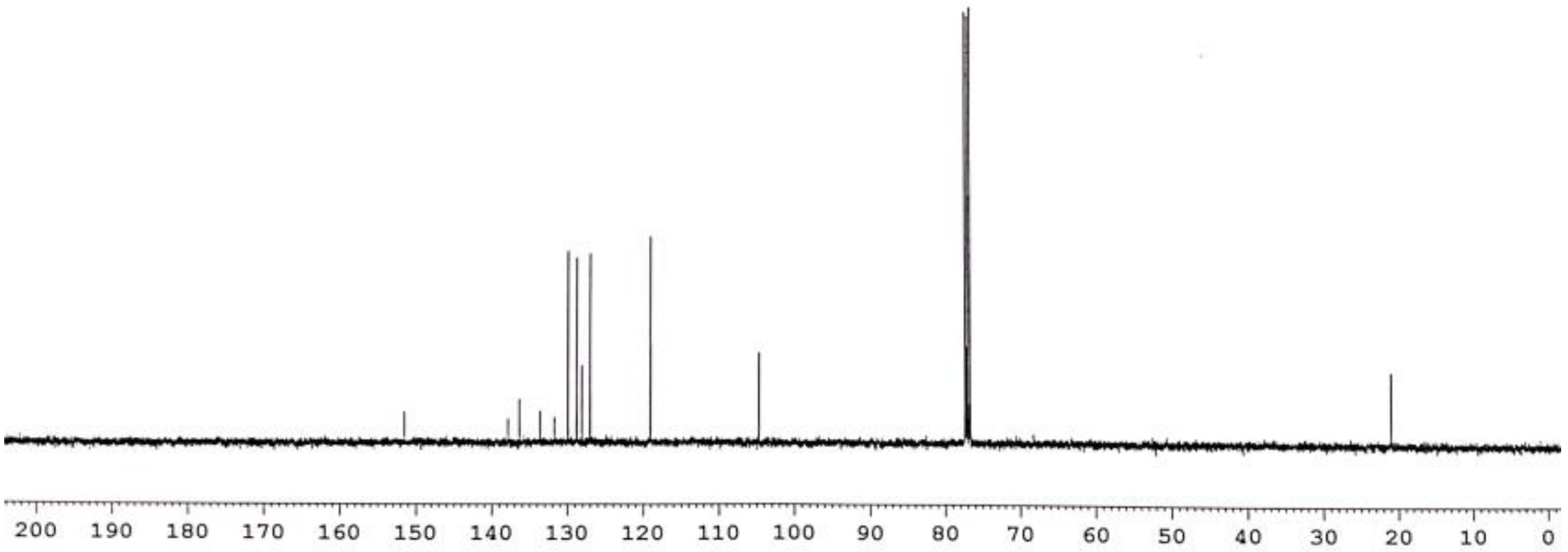
1,3-Di-p-tolyl-1*H*-pyrazole (2**o**)

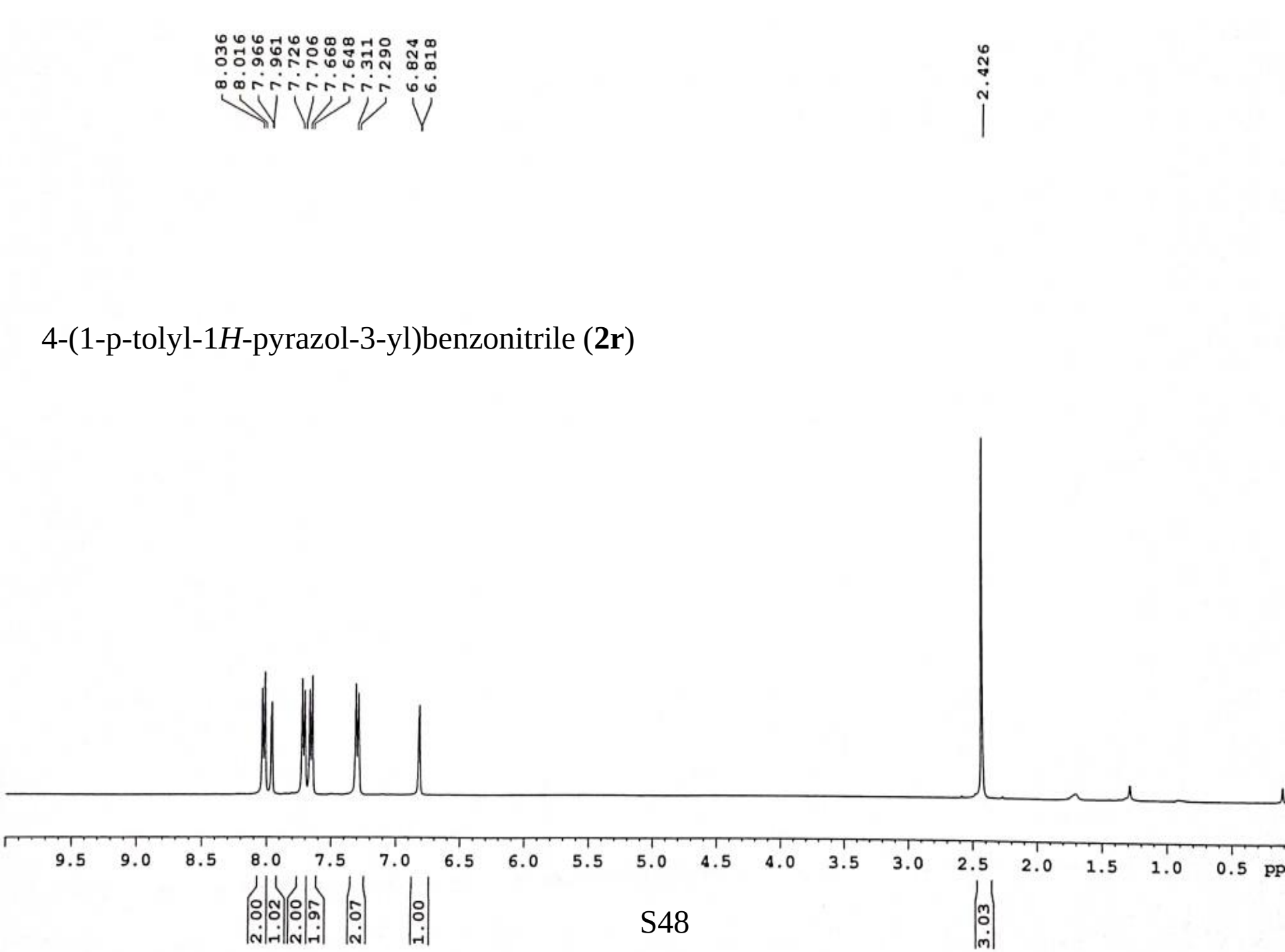


3-(4-Chlorophenyl)-1-p-tolyl-1*H*-pyrazole (**2q**)

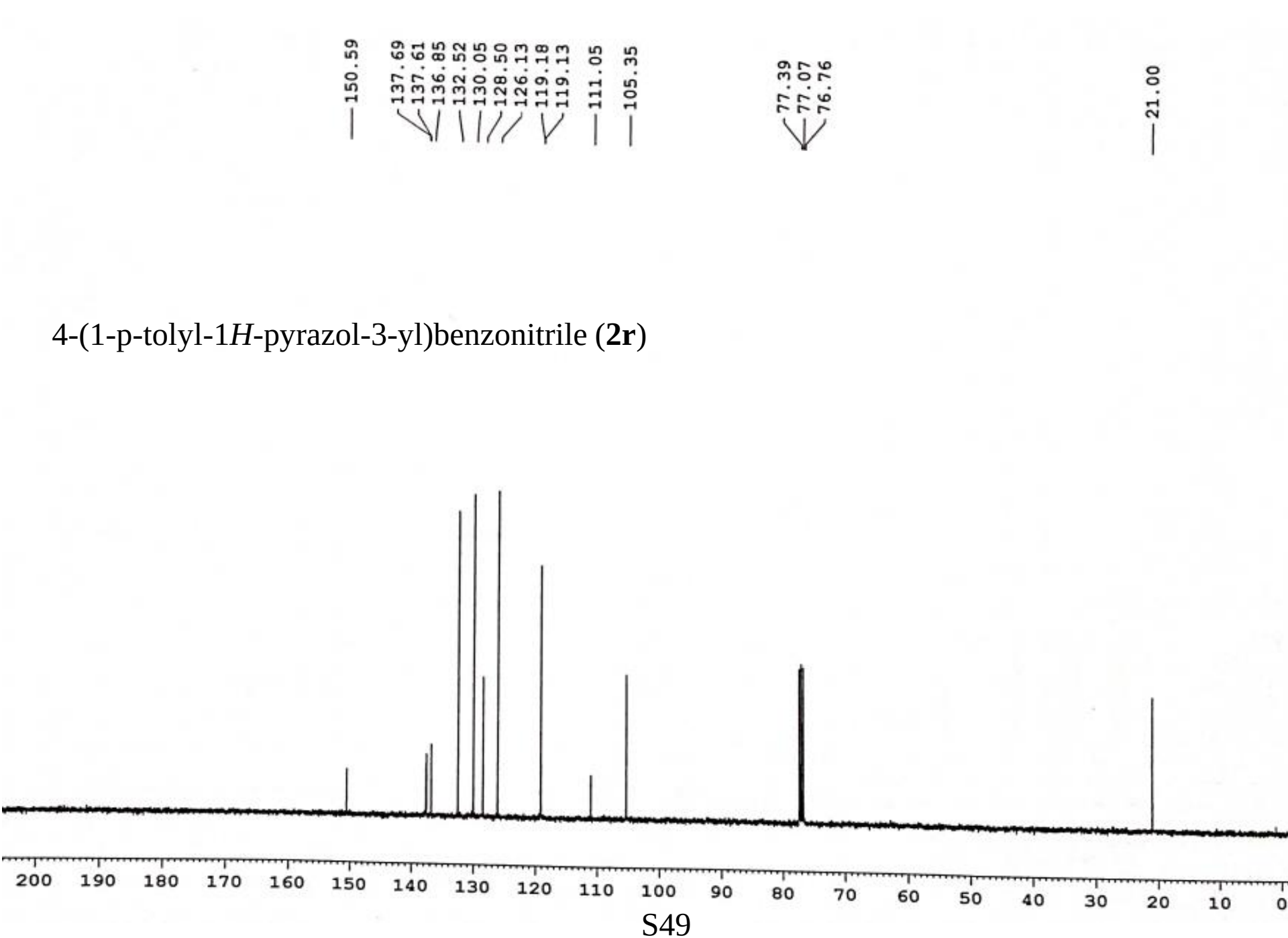


3-(4-Chlorophenyl)-1-p-tolyl-1*H*-pyrazole (**2q**)



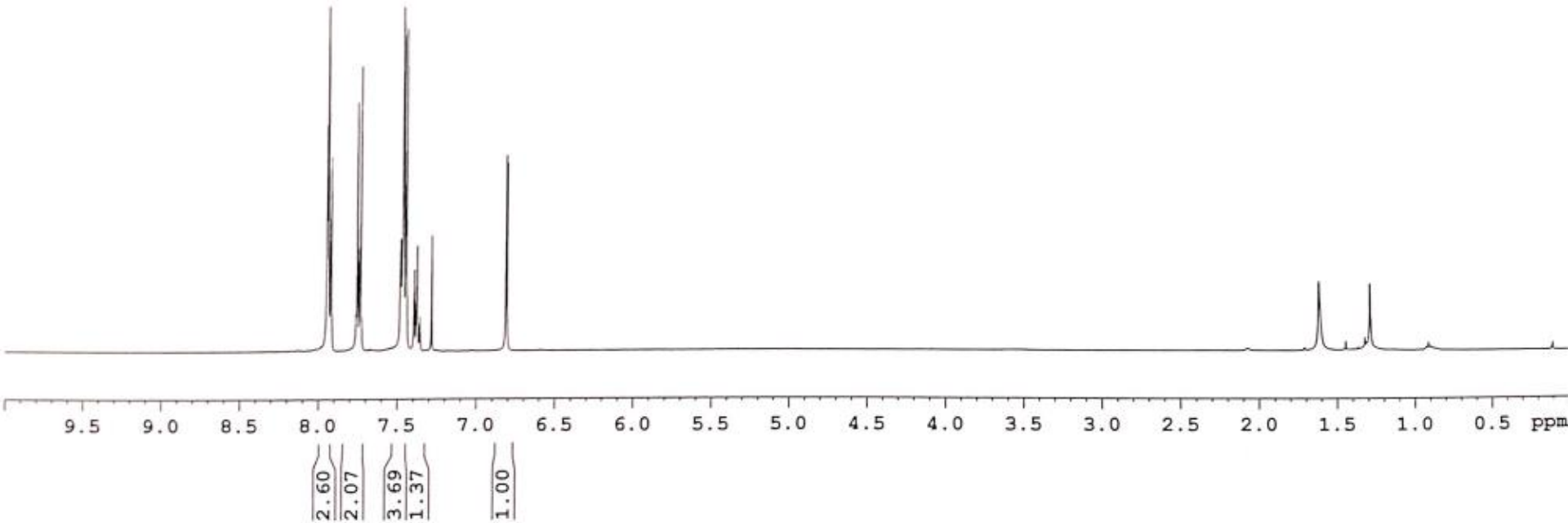


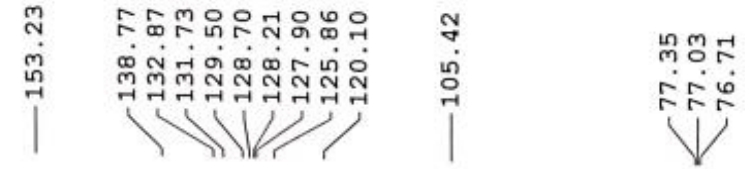
4-(1-p-tolyl-1*H*-pyrazol-3-yl)benzonitrile (**2r**)



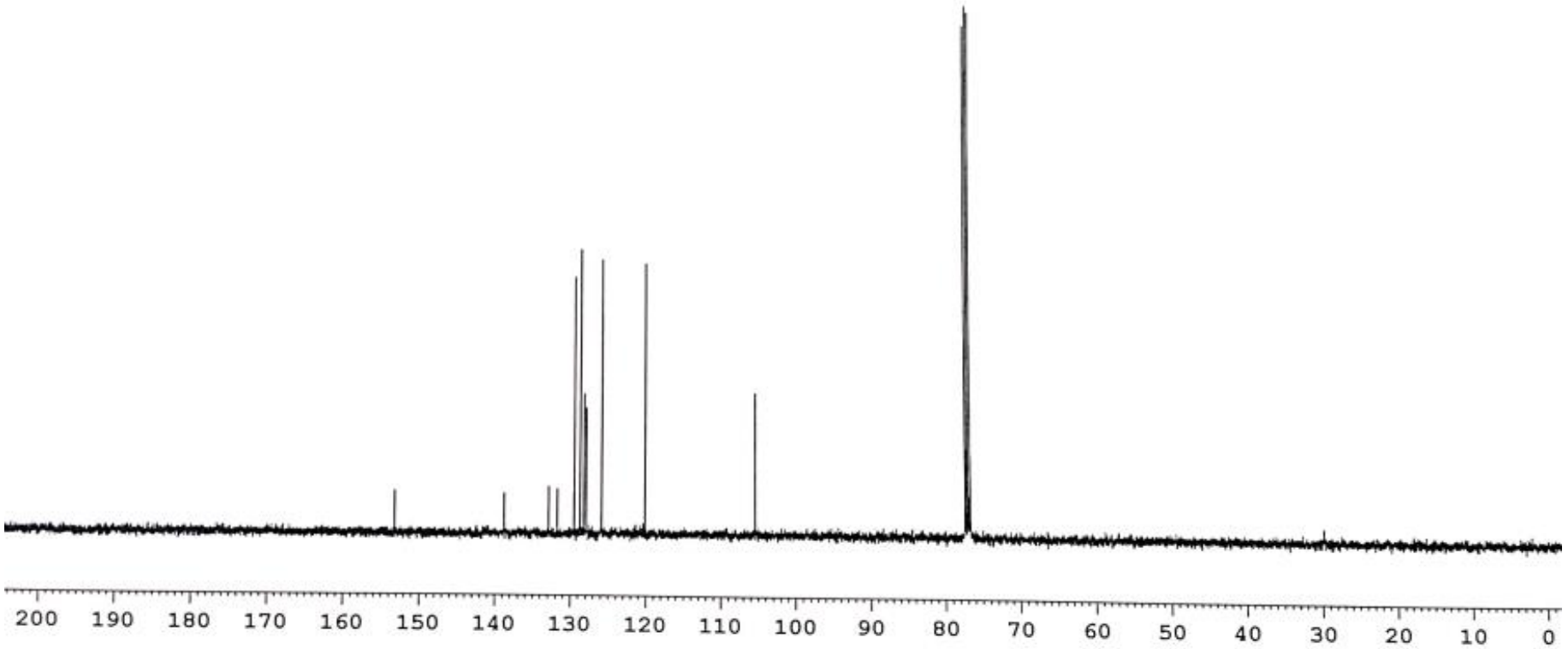
4-(1-p-tolyl-1*H*-pyrazol-3-yl)benzonitrile (**2r**)

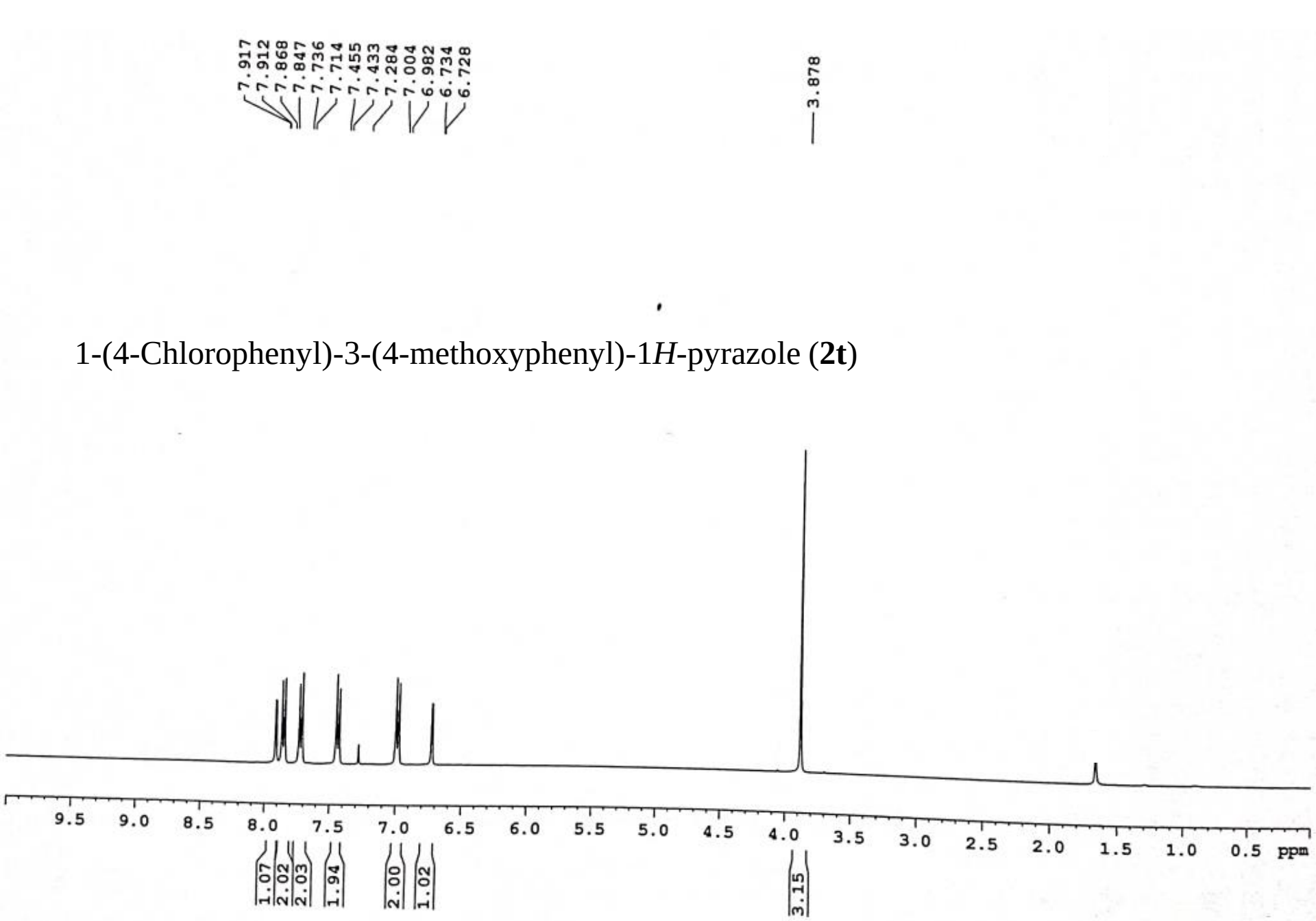
1-(4-Chlorophenyl)-3-phenyl-1*H*-pyrazole (**2s**)



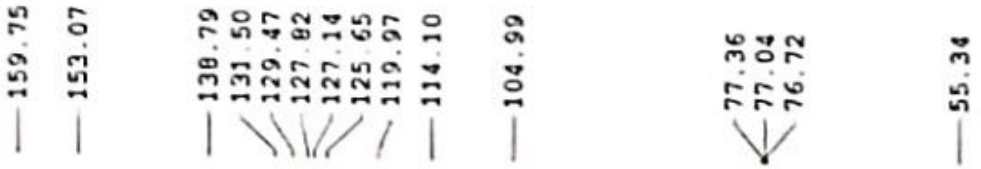


1-(4-Chlorophenyl)-3-phenyl-1*H*-pyrazole (**2s**)

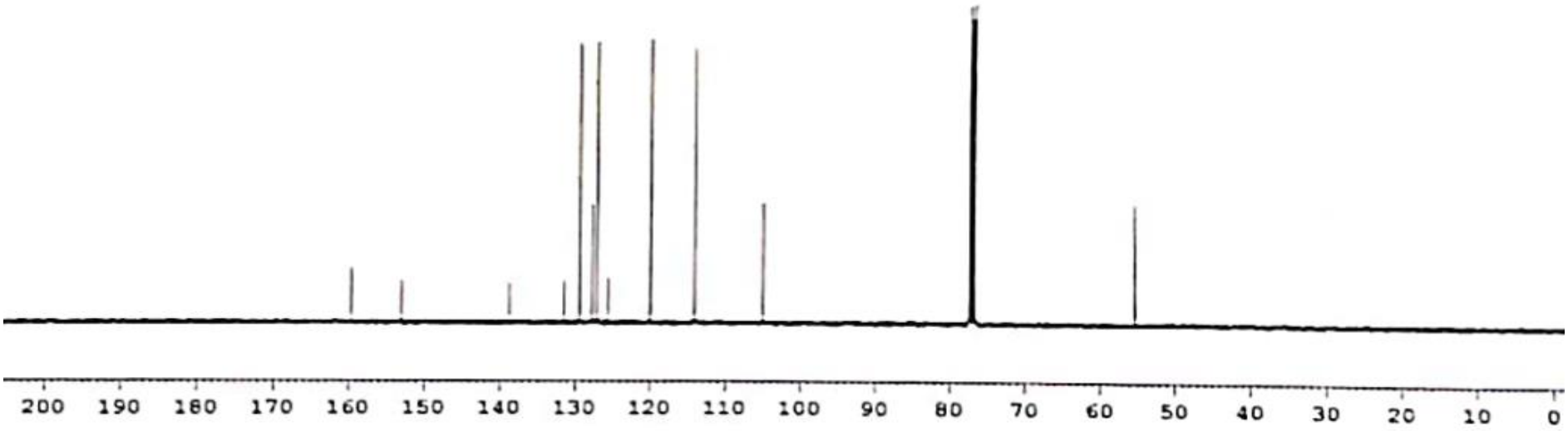


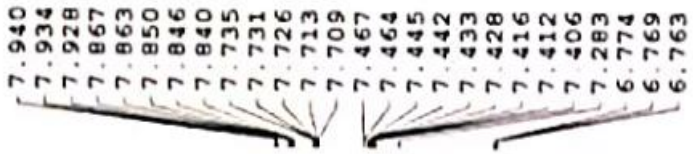


1-(4-Chlorophenyl)-3-(4-methoxyphenyl)-1*H*-pyrazole (**2t**)

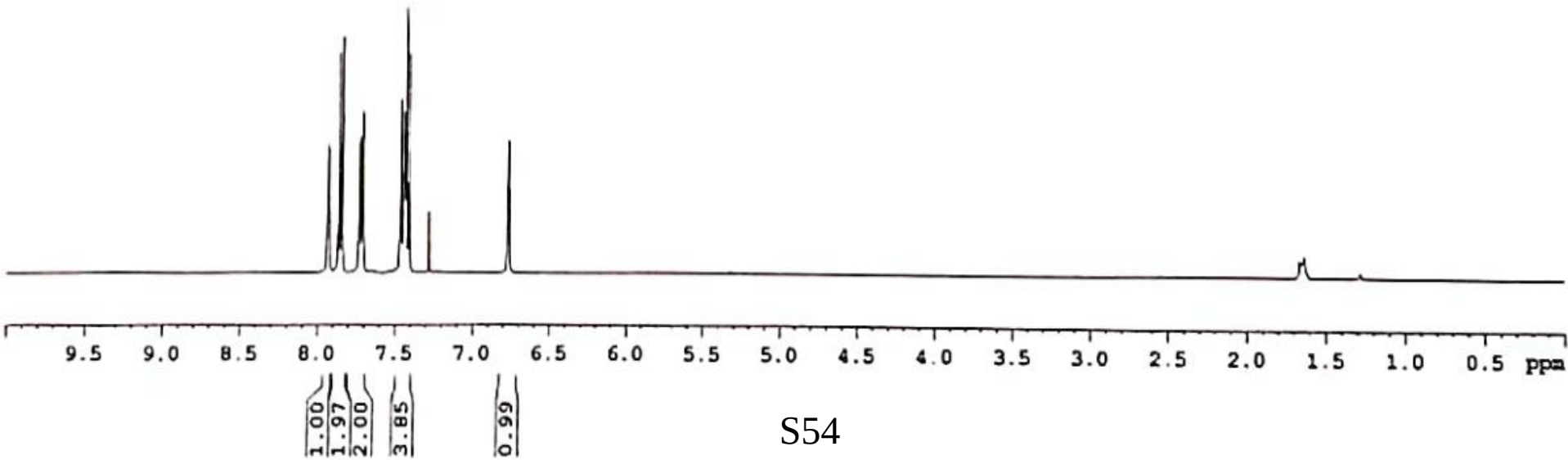


1-(4-Chlorophenyl)-3-(4-methoxyphenyl)-1*H*-pyrazole (**2t**)

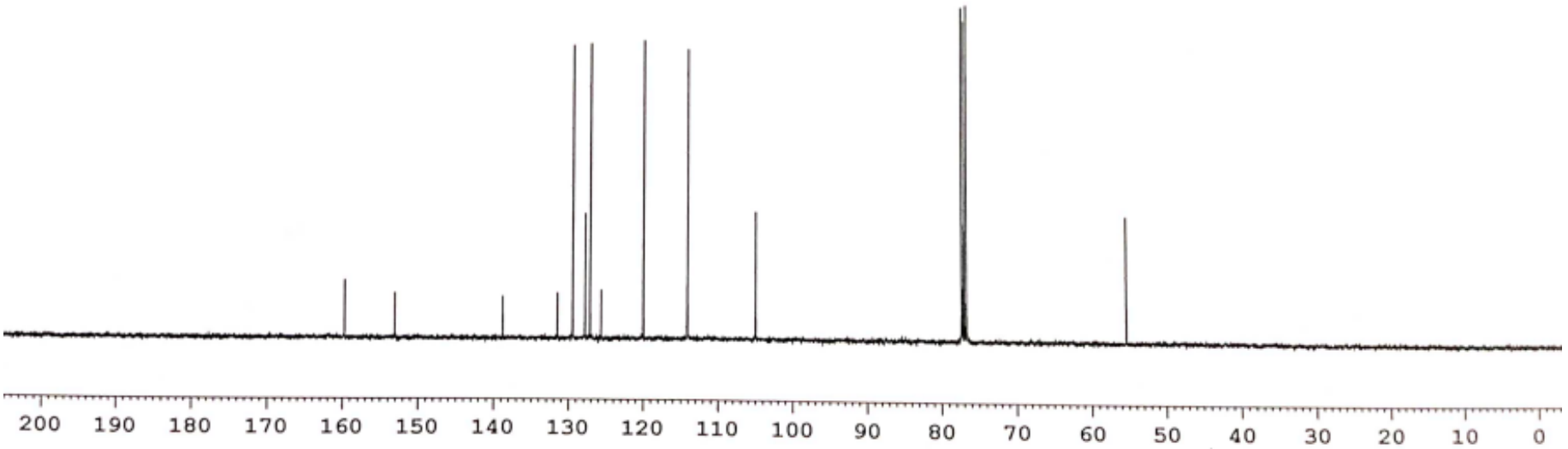


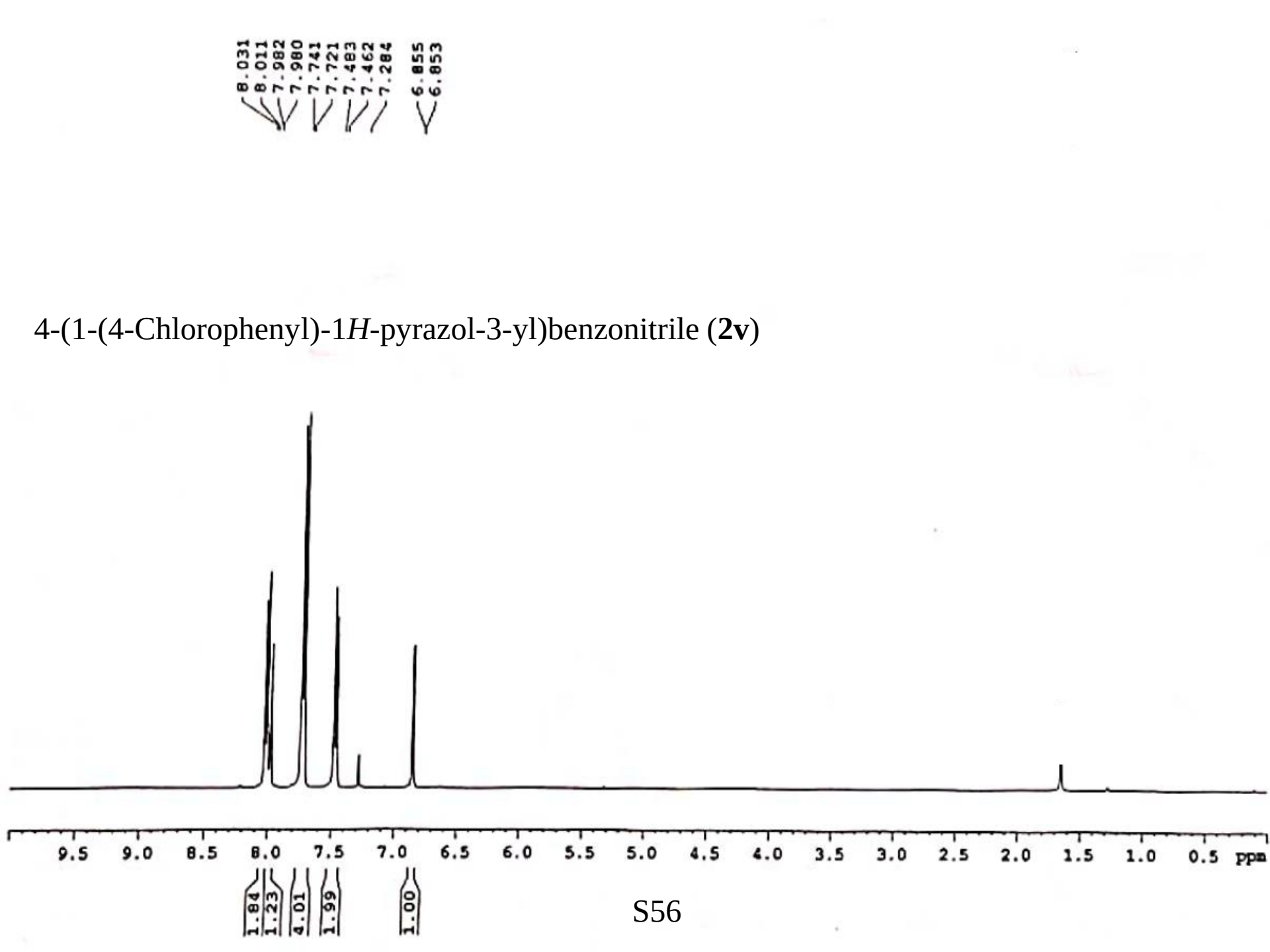


1,3-Bis(4-chlorophenyl)-1*H*-pyrazole (**2u**)

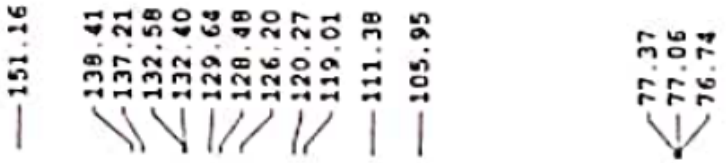


1,3-Bis(4-chlorophenyl)-1*H*-pyrazole (**2u**)

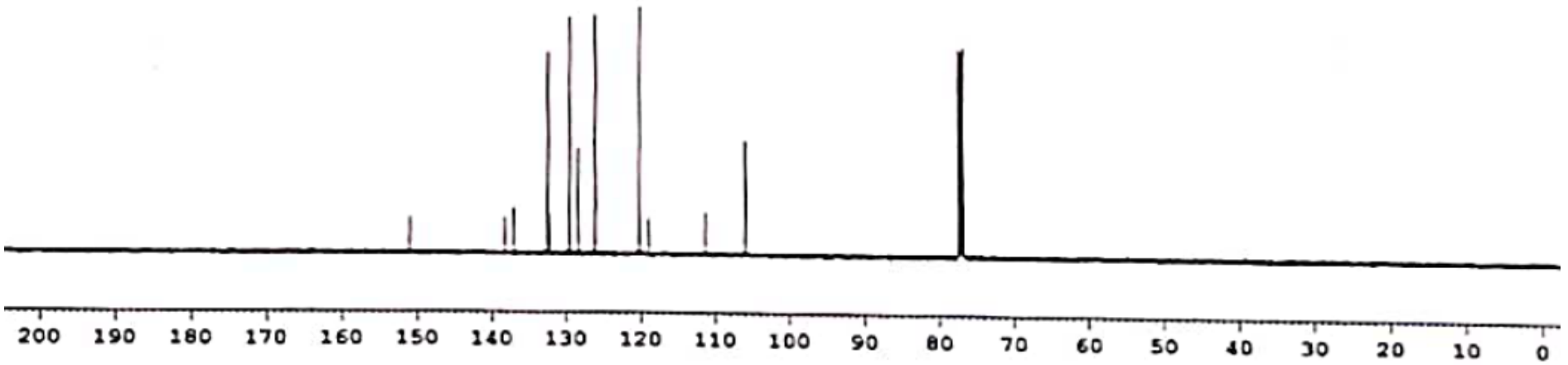


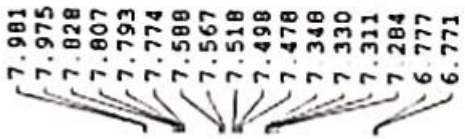


4-(1-(4-Chlorophenyl)-1*H*-pyrazol-3-yl)benzonitrile (**2v**)

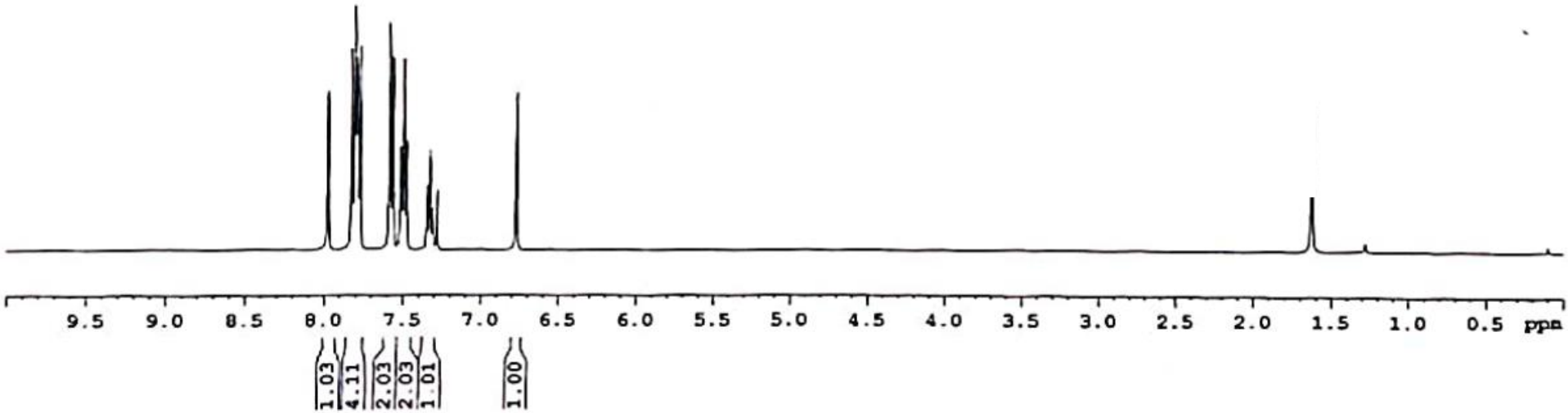


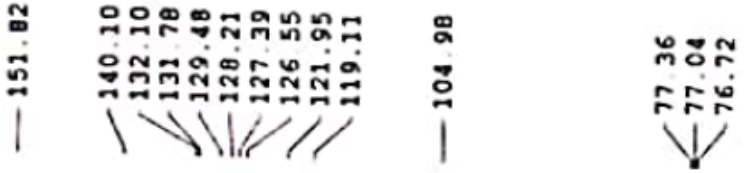
4-(1-(4-Chlorophenyl)-1*H*-pyrazol-3-yl)benzonitrile (**2v**)



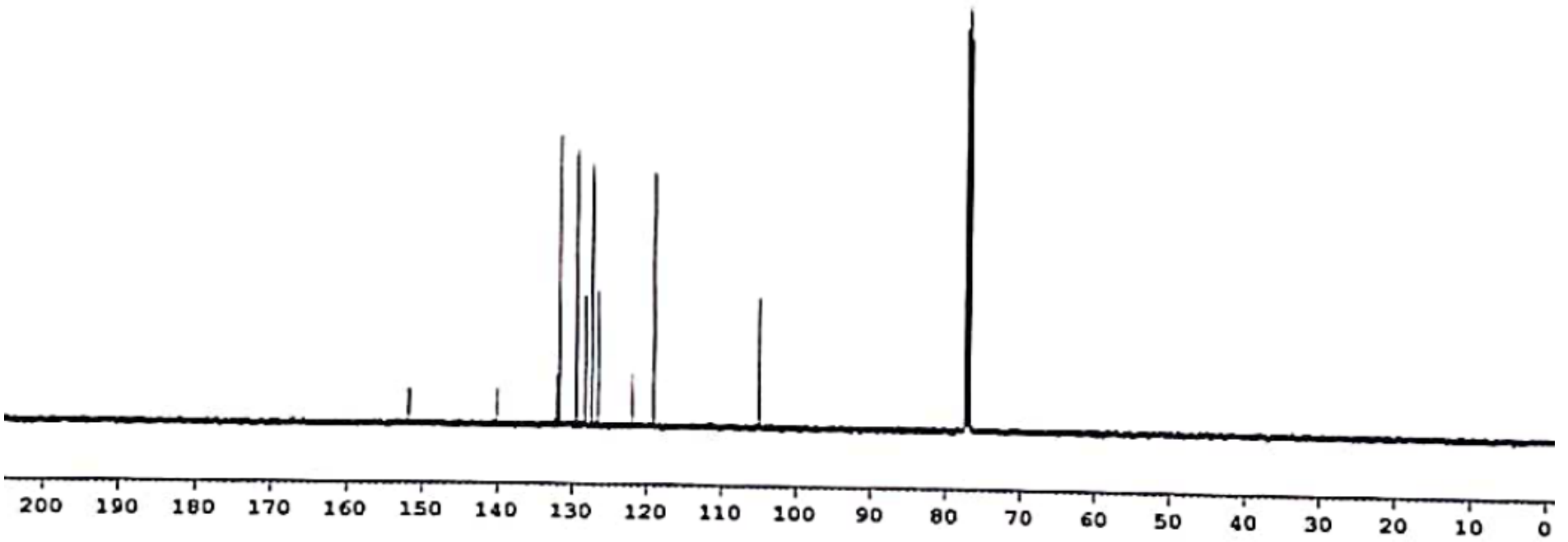


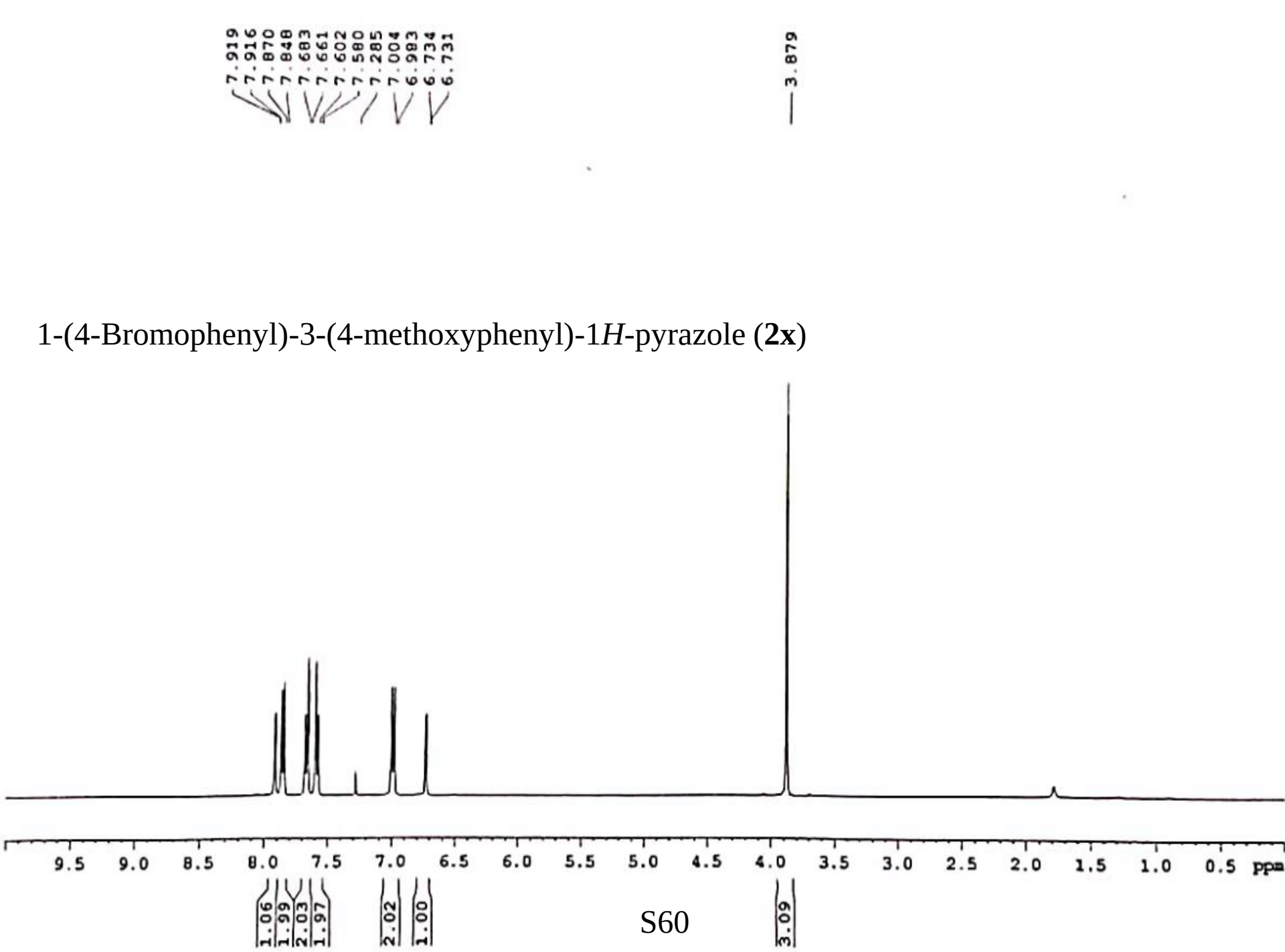
1-(4-Bromophenyl)-3-phenyl-1*H*-pyrazole (**2w**)





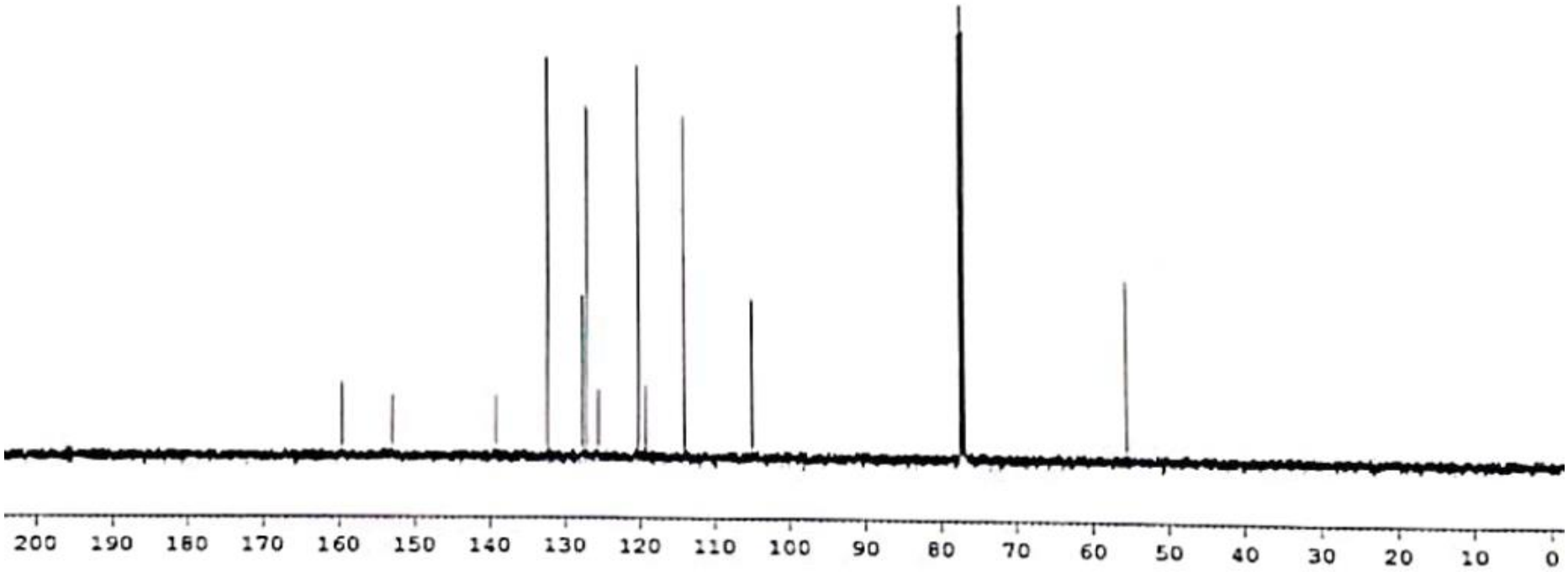
1-(4-Bromophenyl)-3-phenyl-1*H*-pyrazole (**2w**)

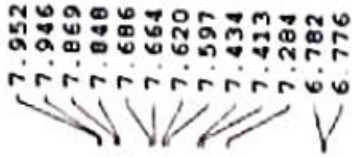




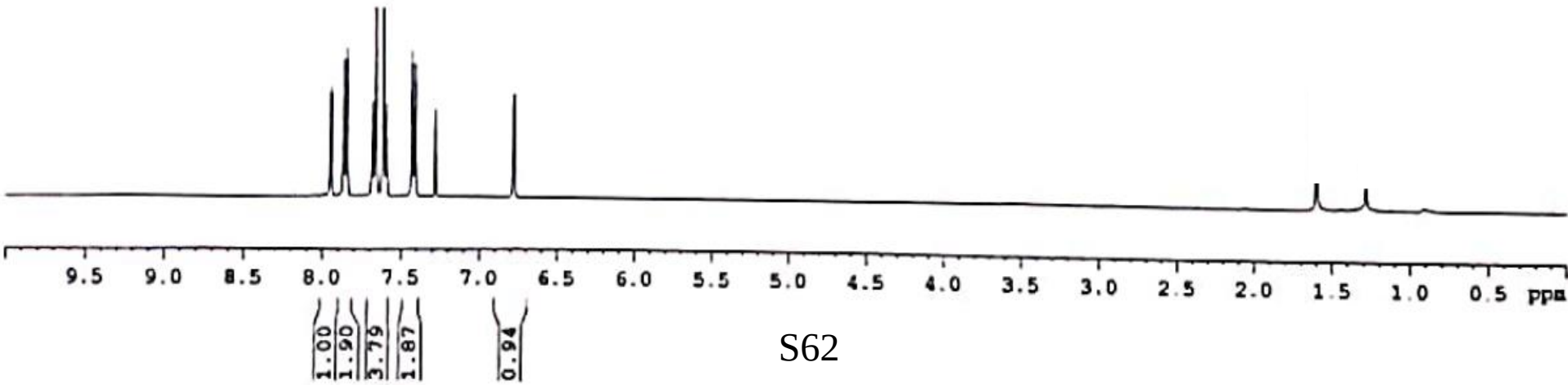
1-(4-Bromophenyl)-3-(4-methoxyphenyl)-1*H*-pyrazole (**2x**)

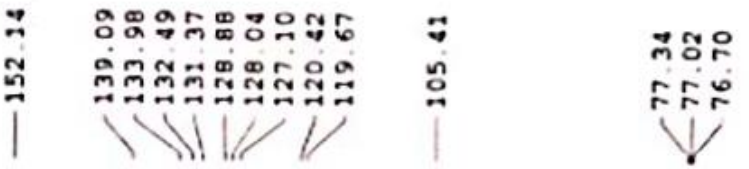
1-(4-Bromophenyl)-3-(4-methoxyphenyl)-1*H*-pyrazole (**2x**)



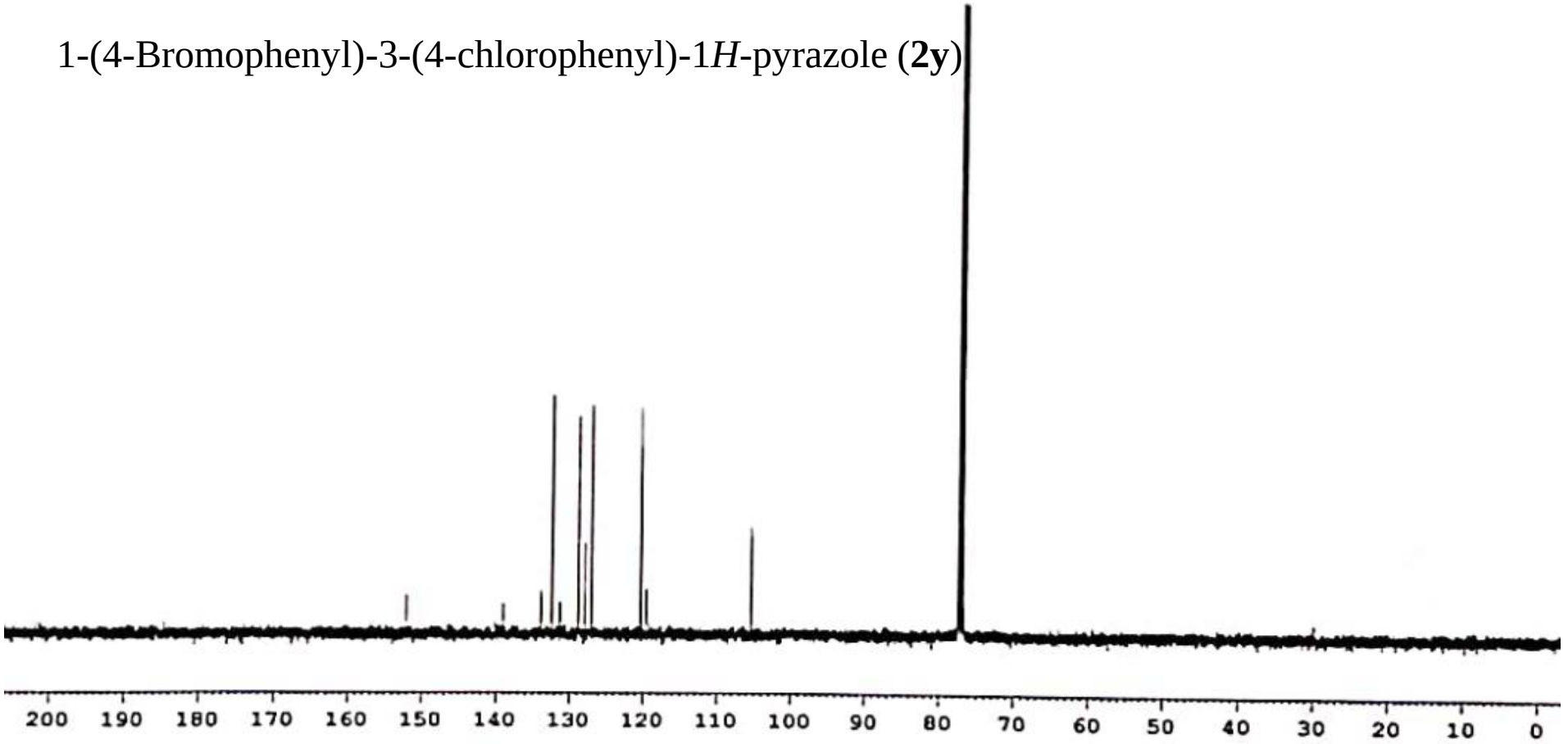


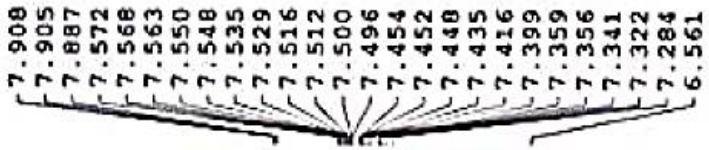
1-(4-Bromophenyl)-3-(4-chlorophenyl)-1*H*-pyrazole (**2y**)

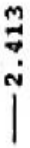




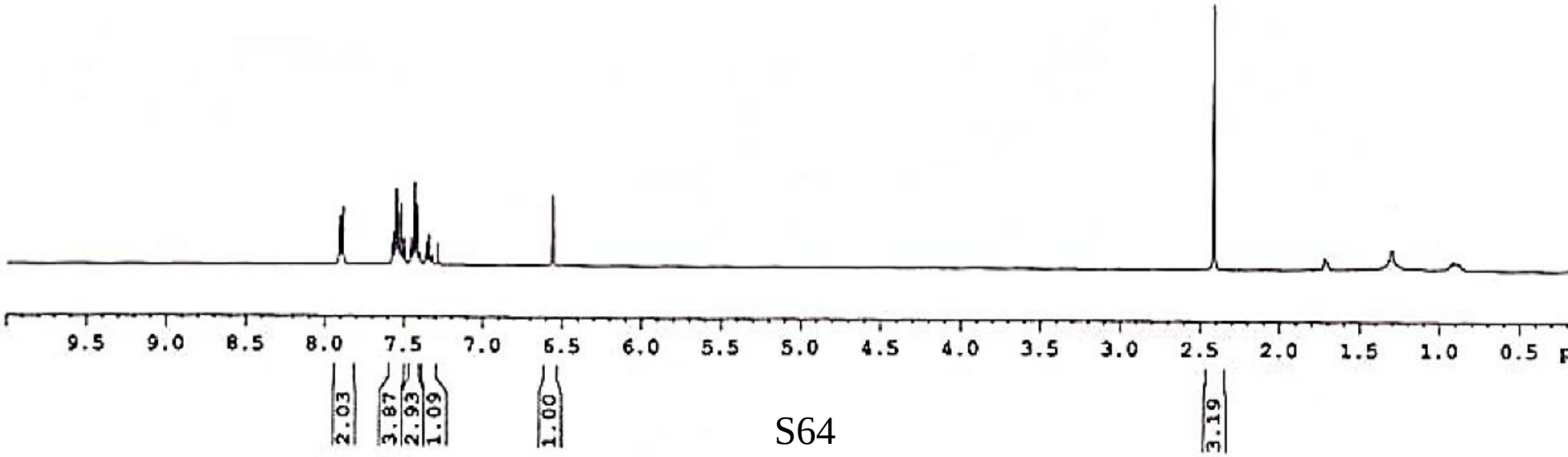
1-(4-Bromophenyl)-3-(4-chlorophenyl)-1*H*-pyrazole (**2y**)

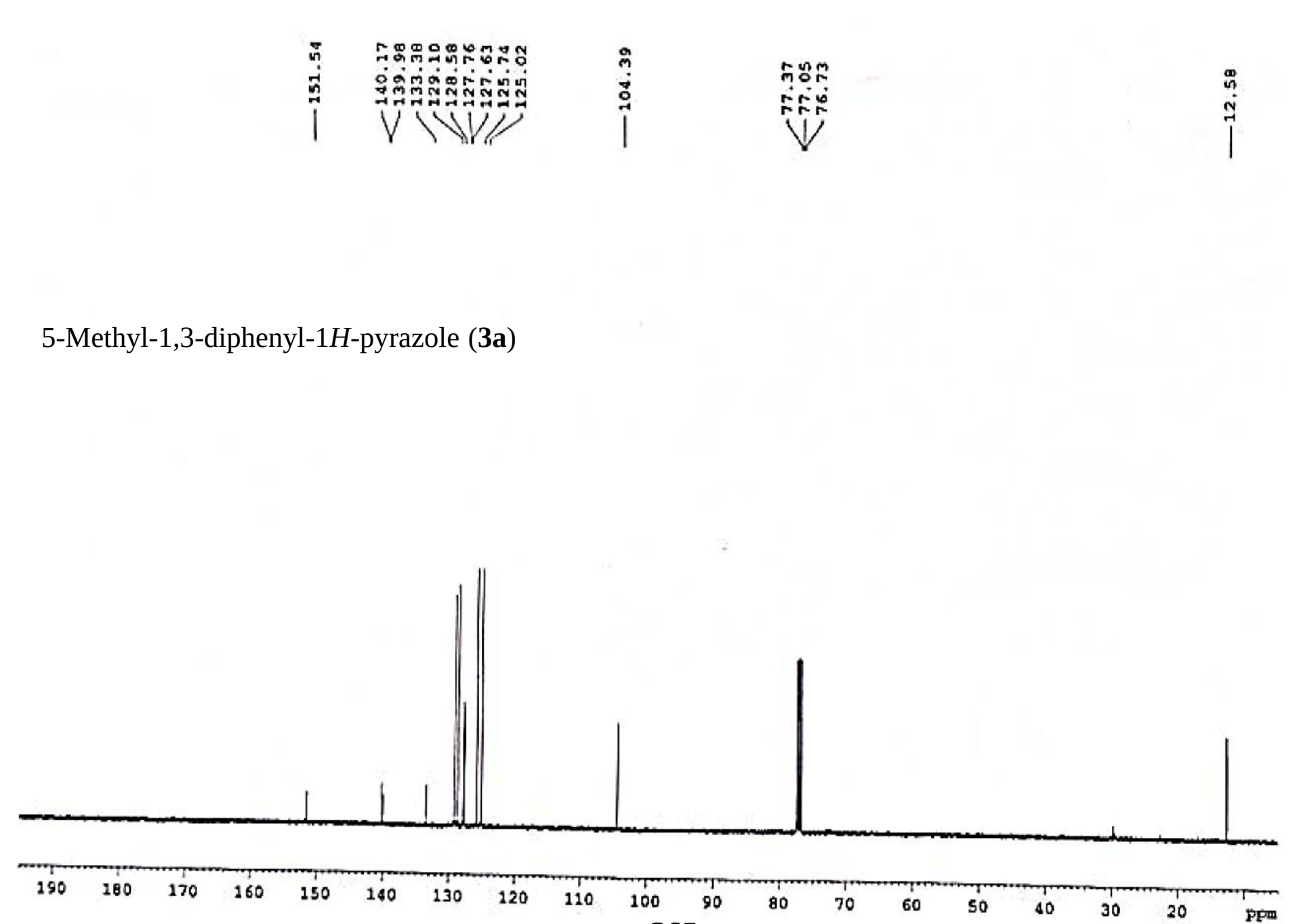




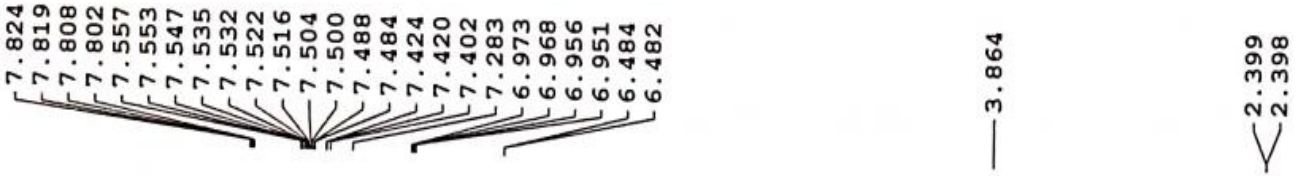


5-Methyl-1,3-diphenyl-1*H*-pyrazole (**3a**)

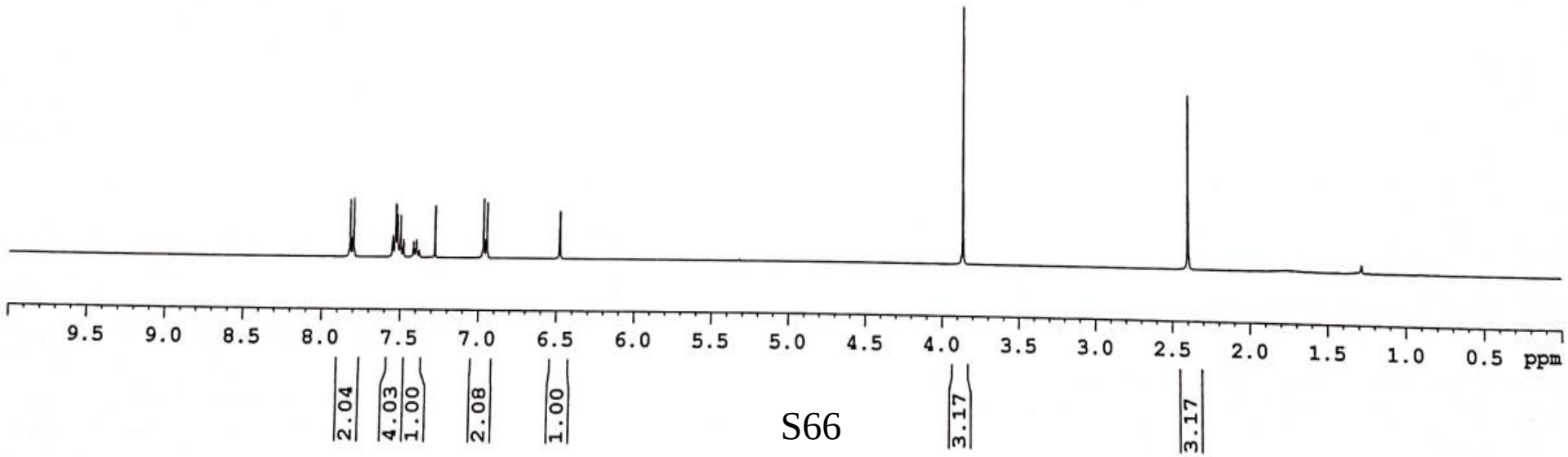




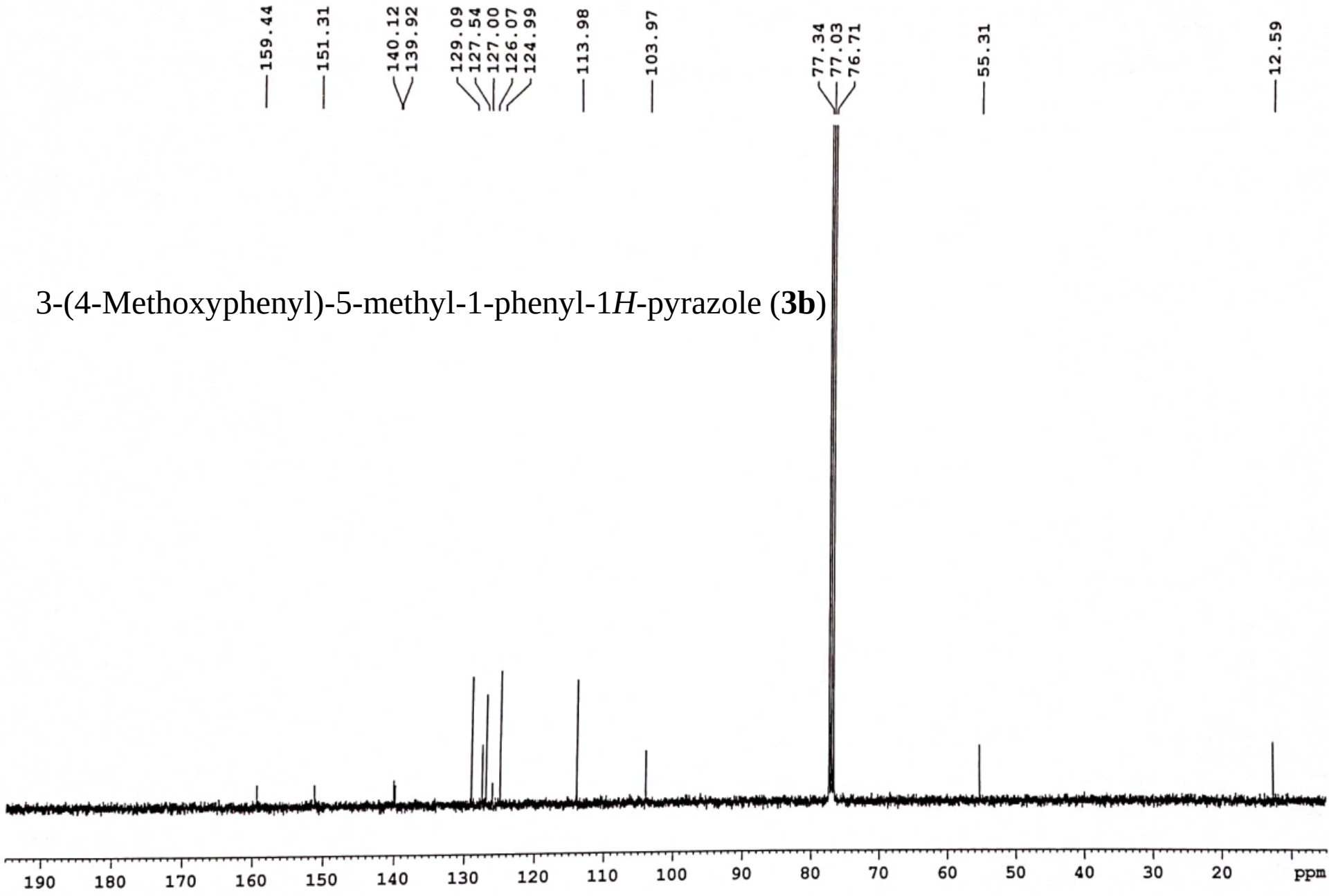
5-Methyl-1,3-diphenyl-1*H*-pyrazole (**3a**)

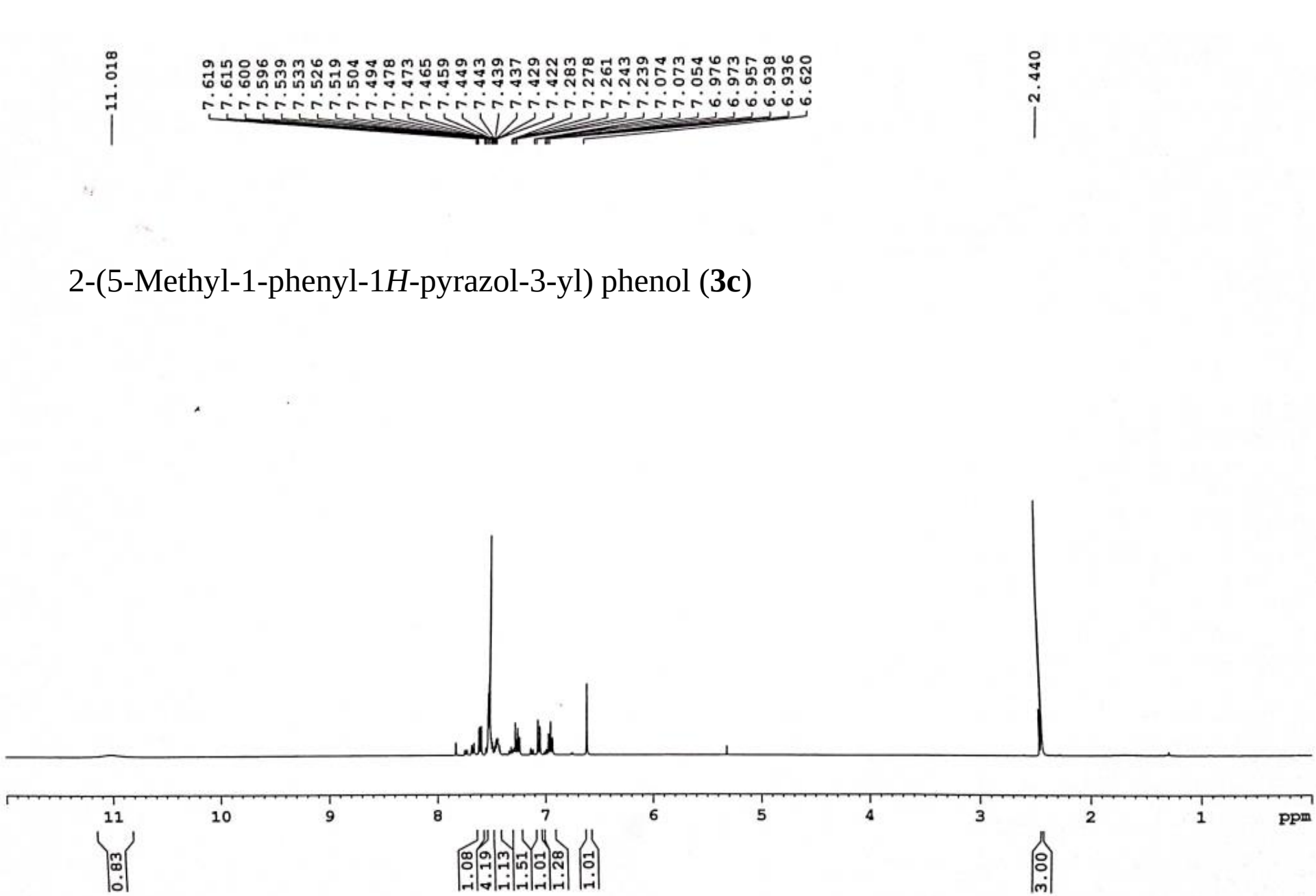


3-(4-Methoxyphenyl)-5-methyl-1-phenyl-1*H*-pyrazole (**3b**)

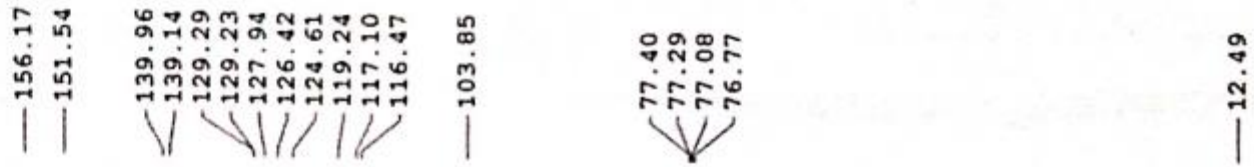


3-(4-Methoxyphenyl)-5-methyl-1-phenyl-1*H*-pyrazole (**3b**)

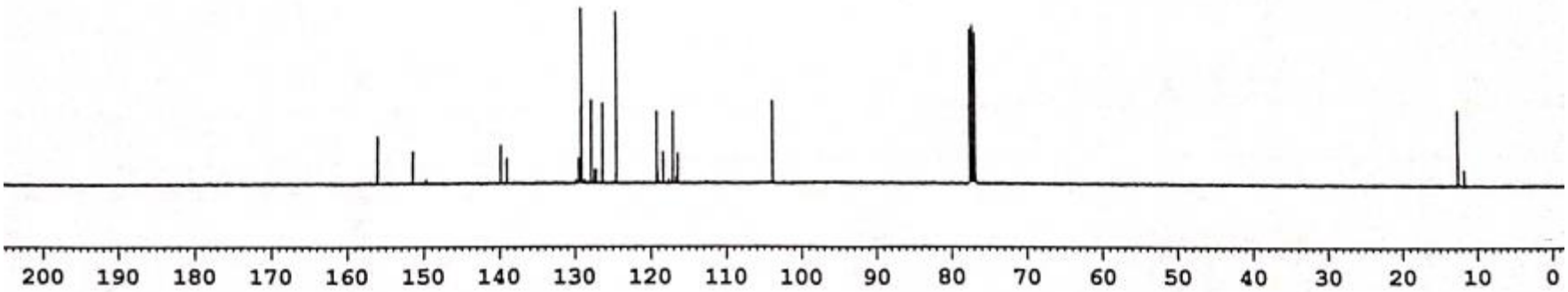




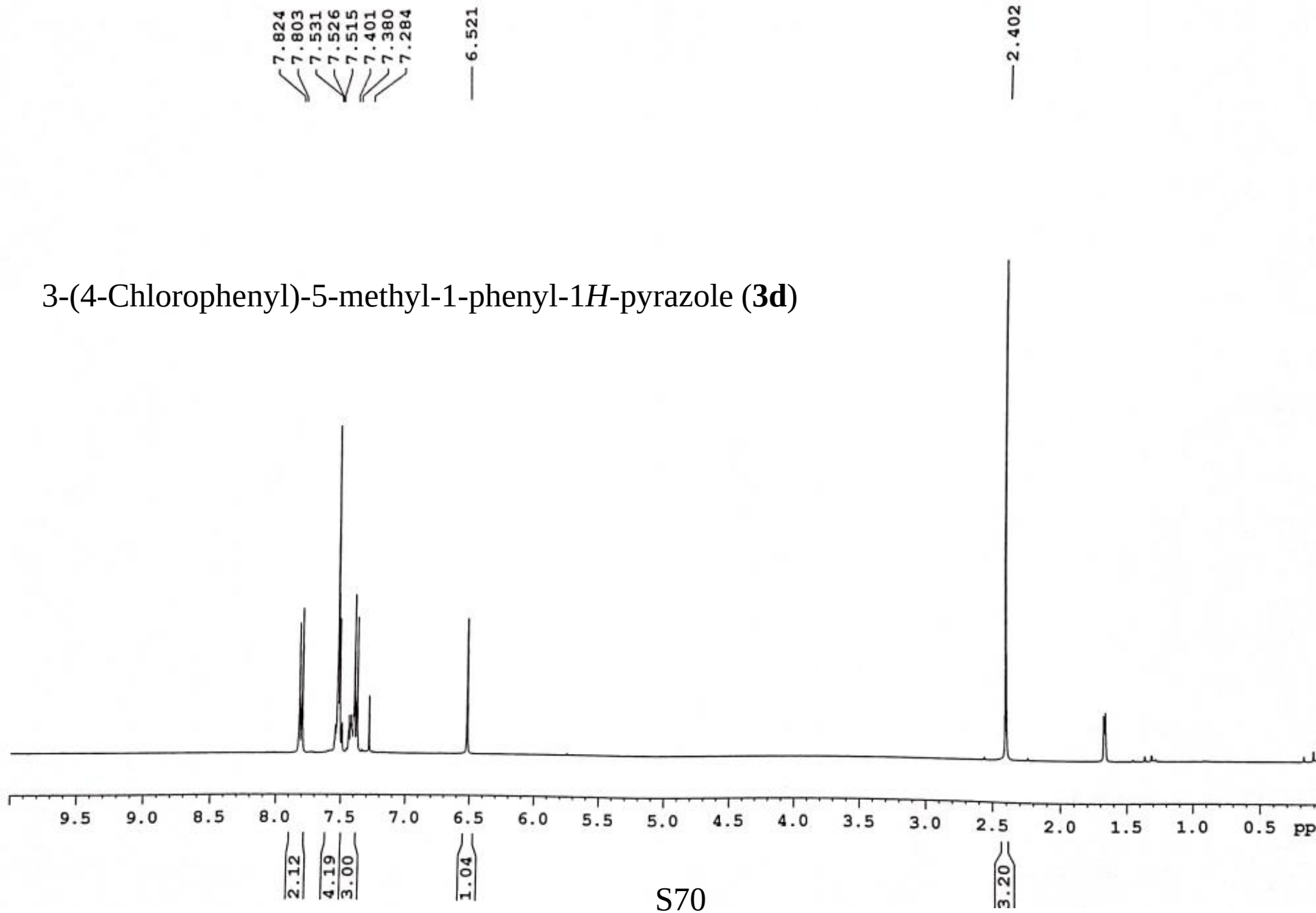
2-(5-Methyl-1-phenyl-1*H*-pyrazol-3-yl) phenol (**3c**)



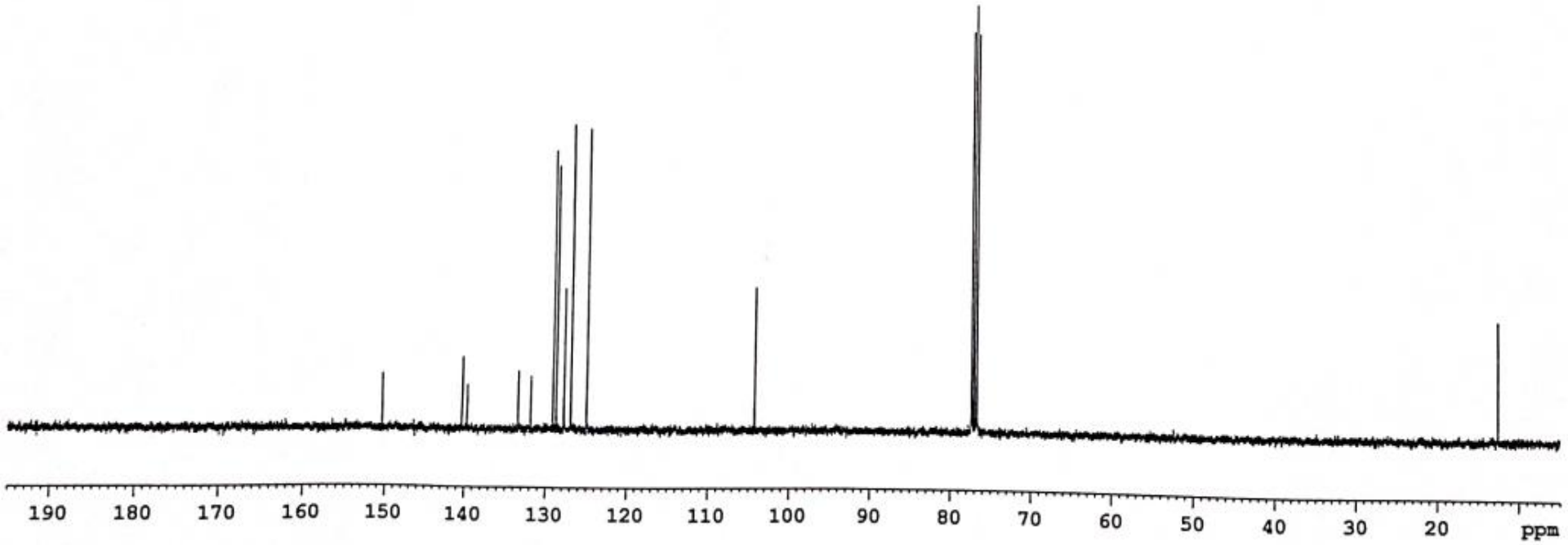
2-(5-Methyl-1-phenyl-1*H*-pyrazol-3-yl) phenol (**3c**)



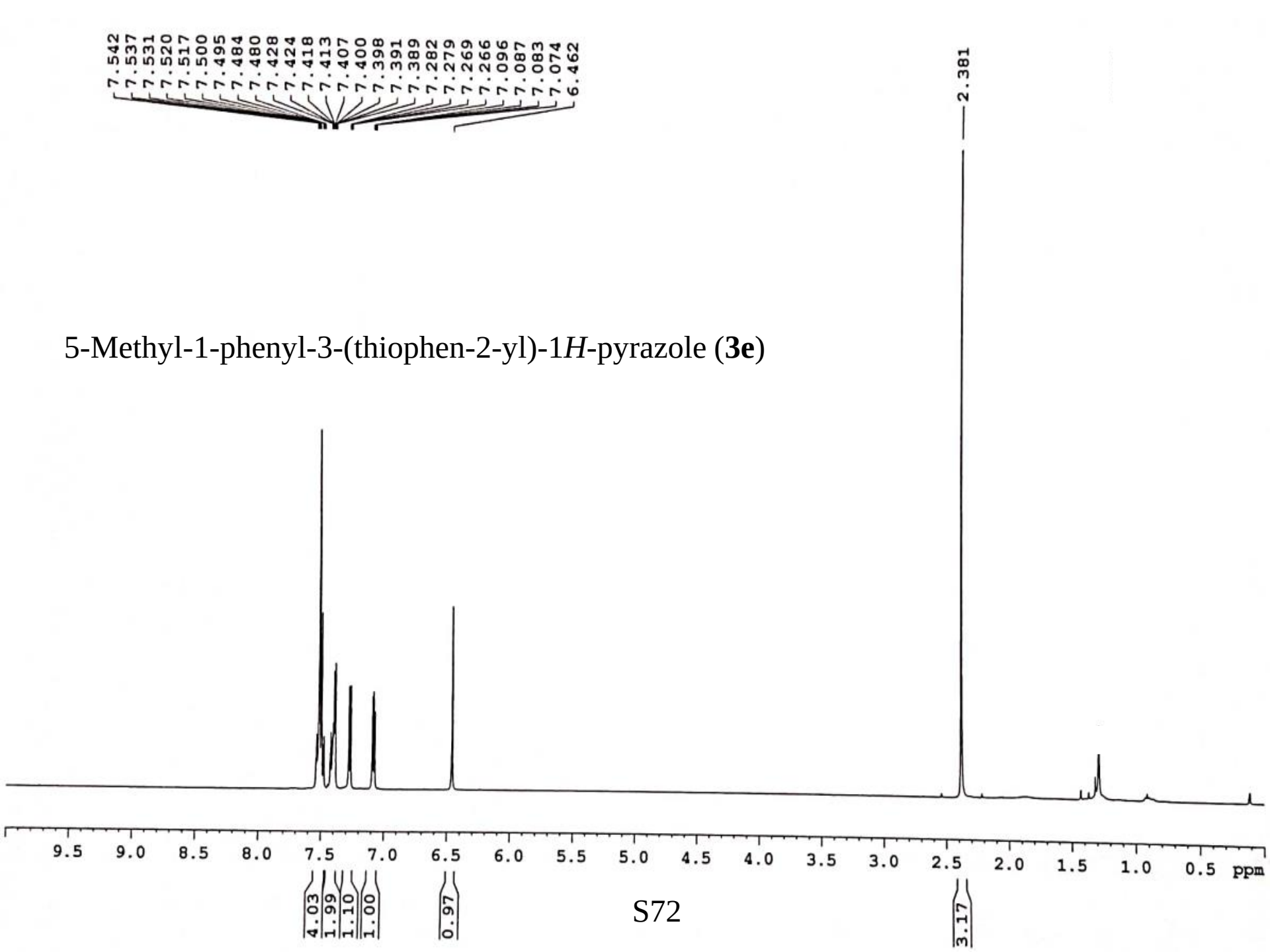
3-(4-Chlorophenyl)-5-methyl-1-phenyl-1*H*-pyrazole (**3d**)



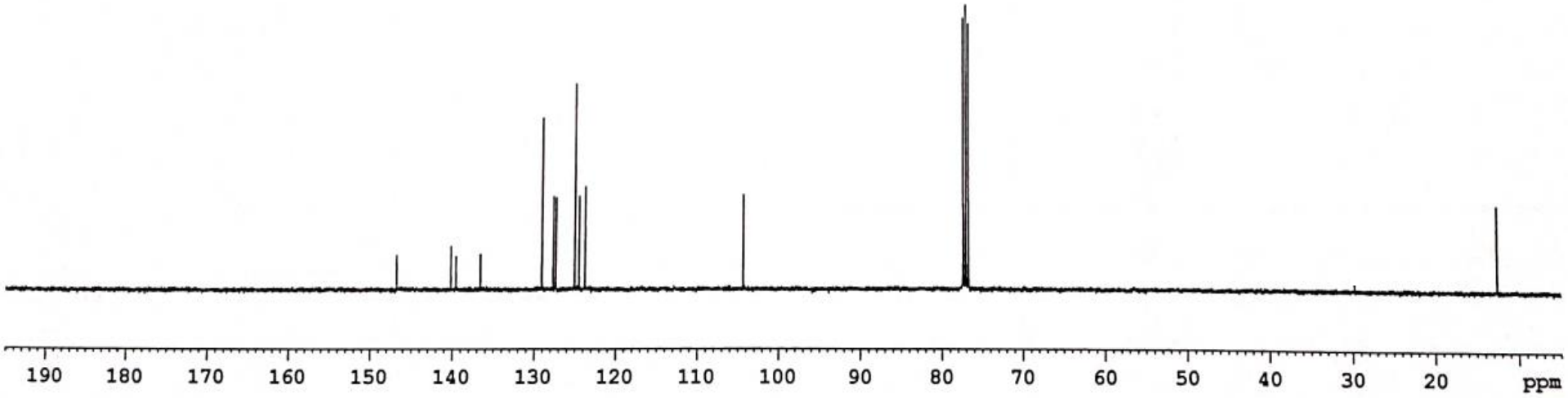
3-(4-Chlorophenyl)-5-methyl-1-phenyl-1*H*-pyrazole (**3d**)

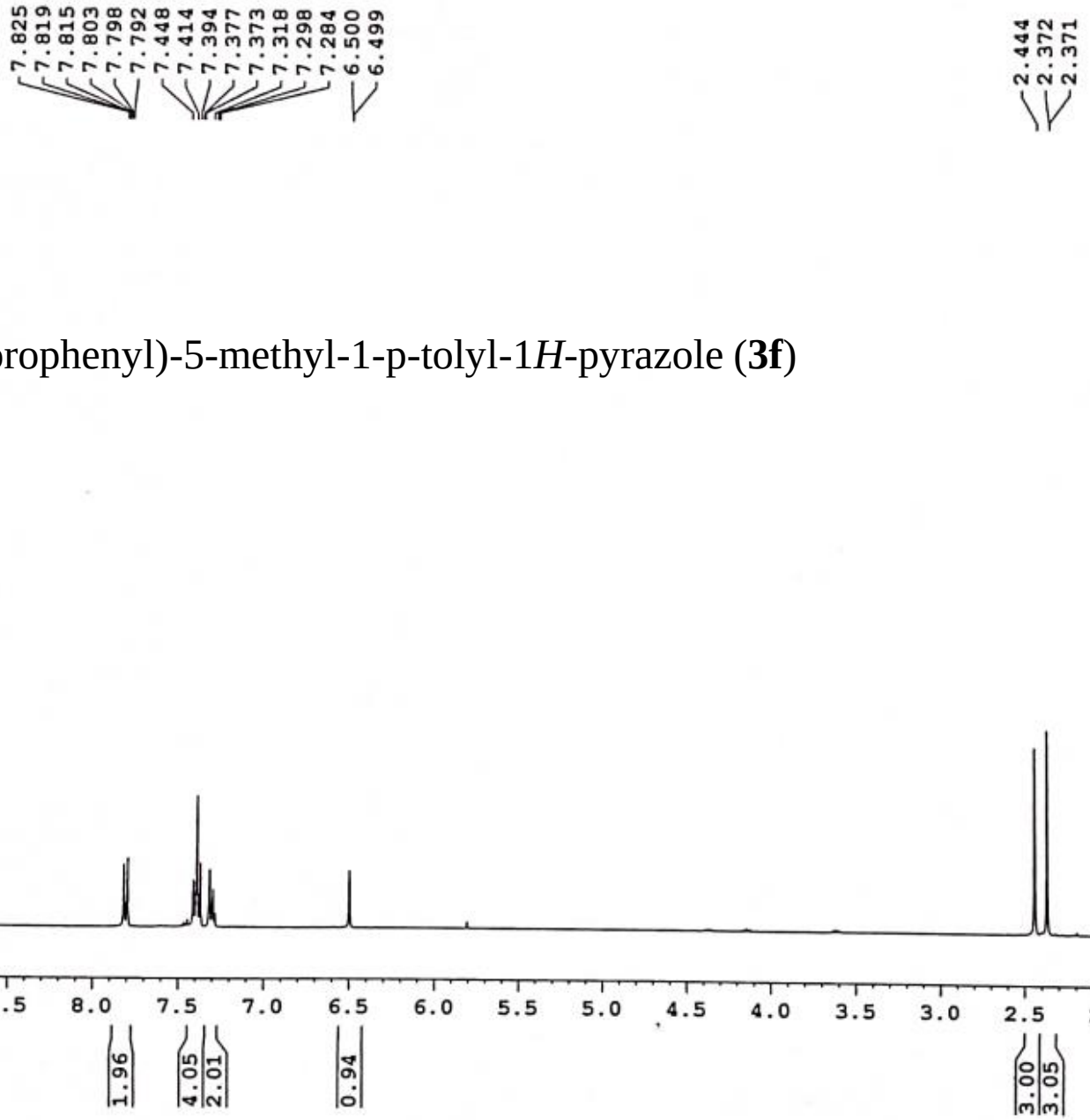


5-Methyl-1-phenyl-3-(thiophen-2-yl)-1*H*-pyrazole (**3e**)

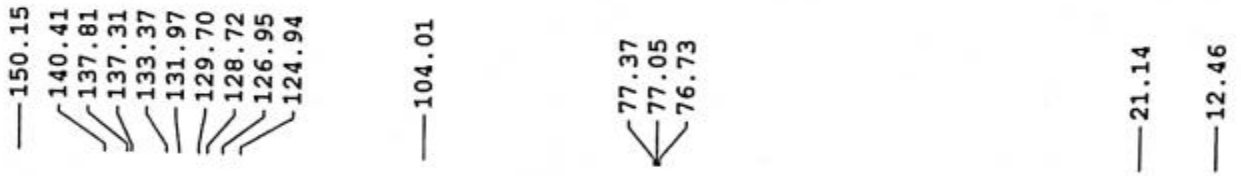


5-Methyl-1-phenyl-3-(thiophen-2-yl)-1*H*-pyrazole (**3e**)

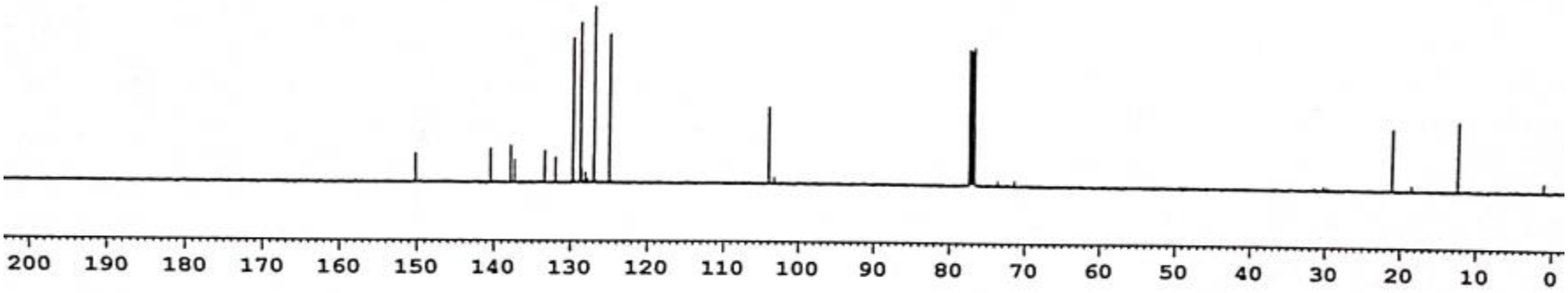


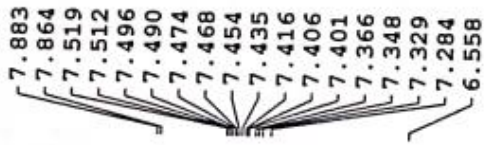


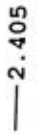
3-(4-Chlorophenyl)-5-methyl-1-p-tolyl-1*H*-pyrazole (**3f**)



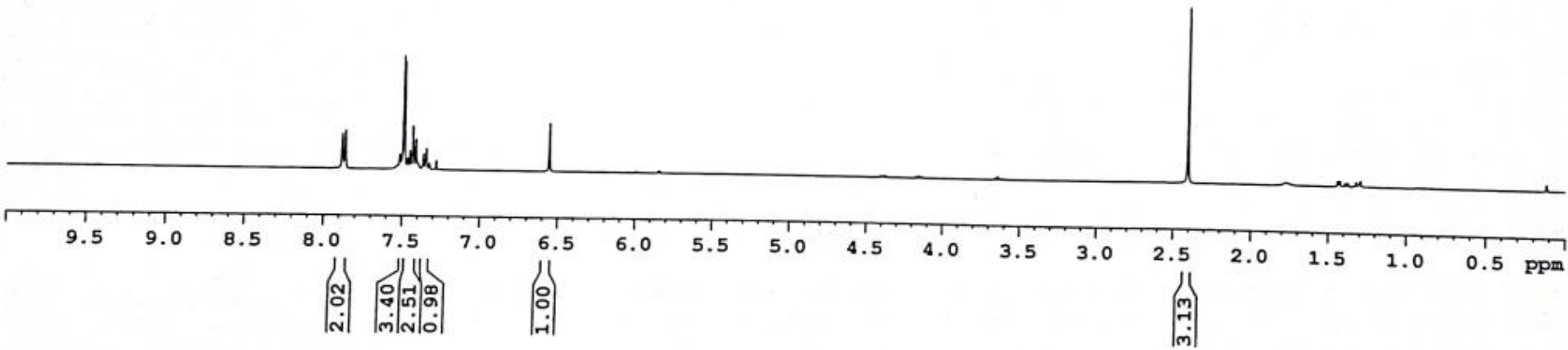
3-(4-Chlorophenyl)-5-methyl-1-p-tolyl-1H-pyrazole (**3f**)



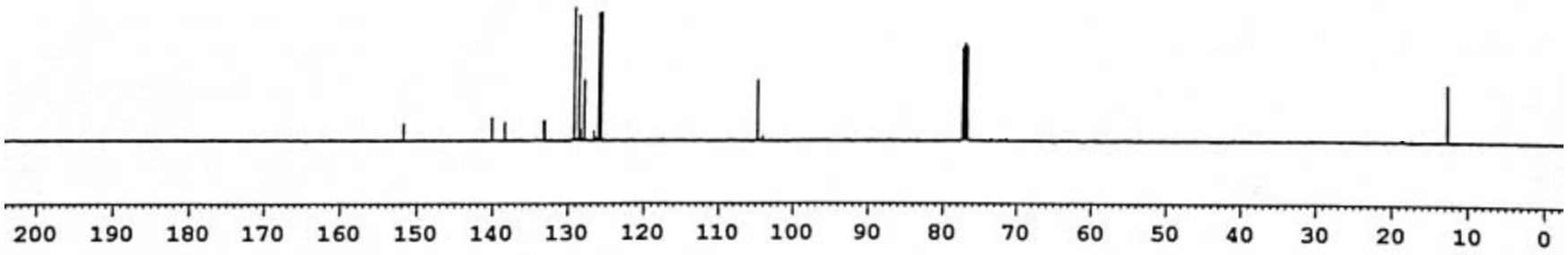


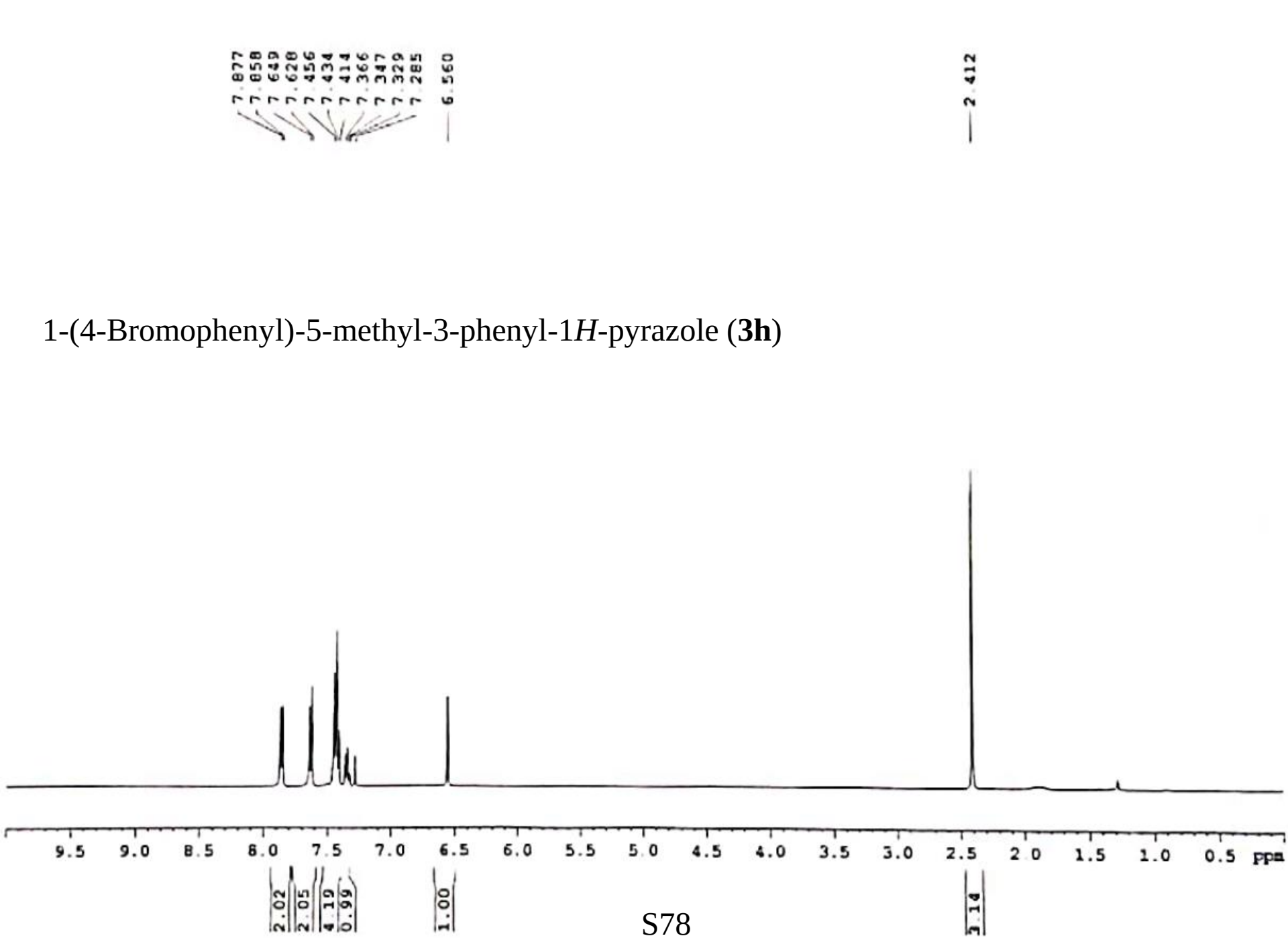


1-(4-Chlorophenyl)-5-methyl-3-phenyl-1*H*-pyrazole (**3g**)

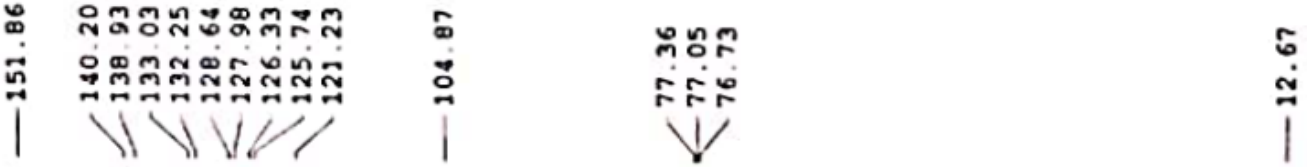


1-(4-Chlorophenyl)-5-methyl-3-phenyl-1*H*-pyrazole (**3g**)

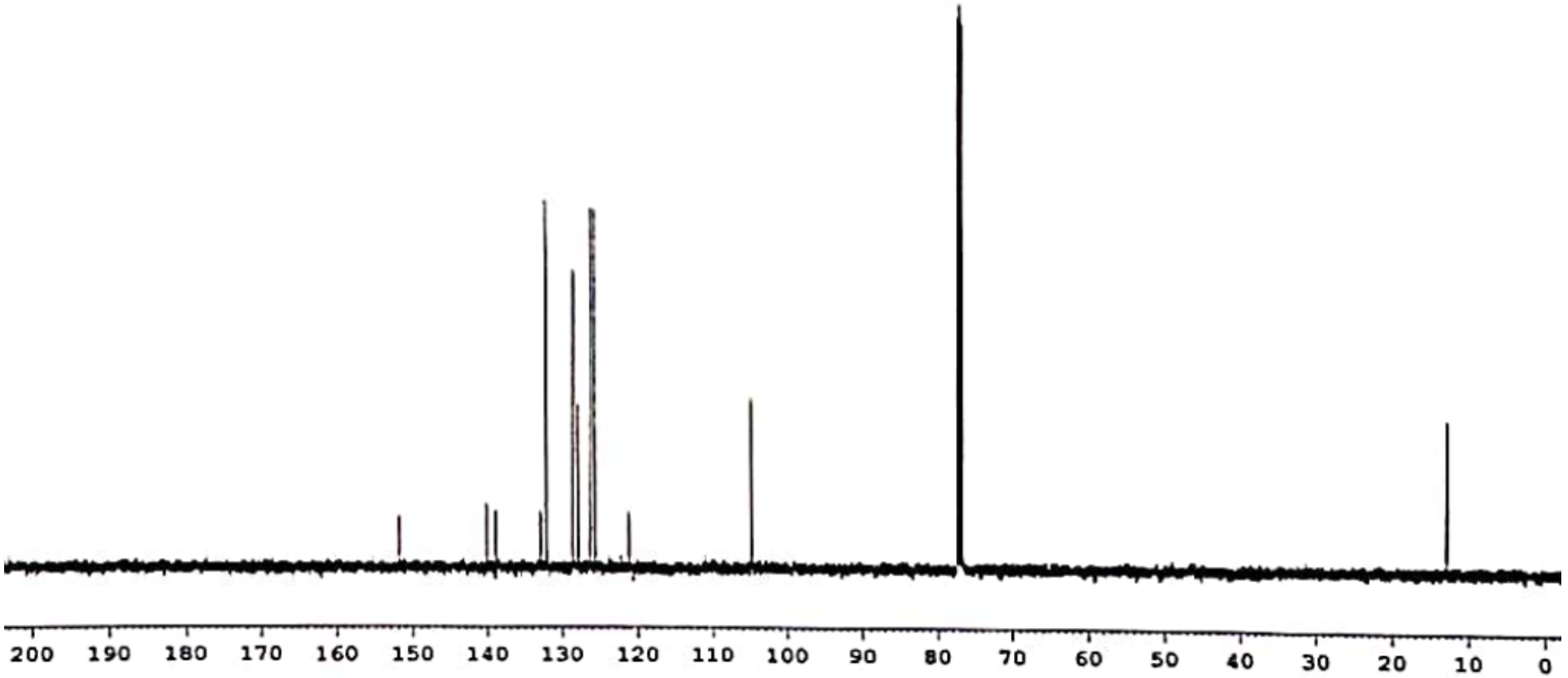


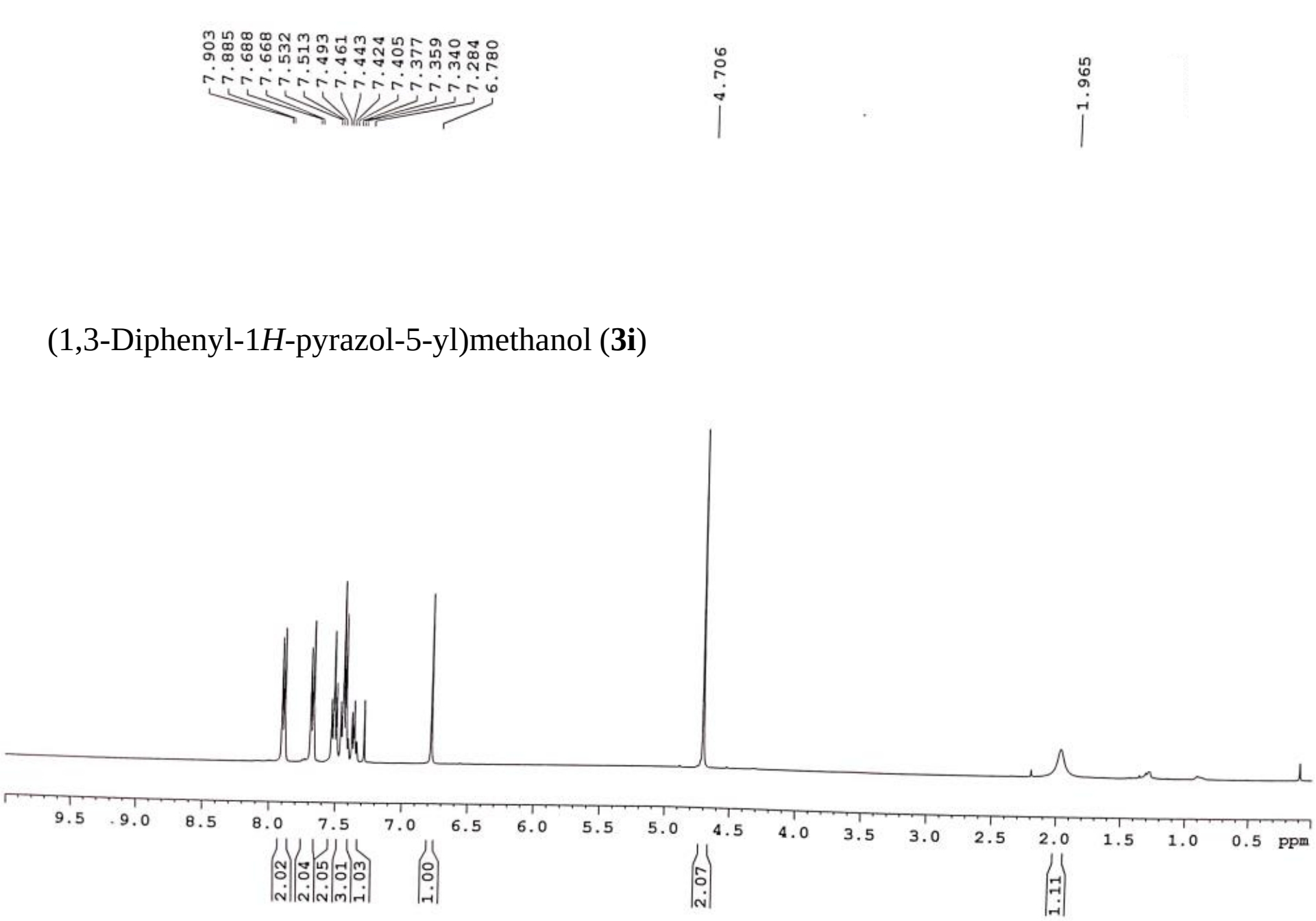


1-(4-Bromophenyl)-5-methyl-3-phenyl-1*H*-pyrazole (**3h**)



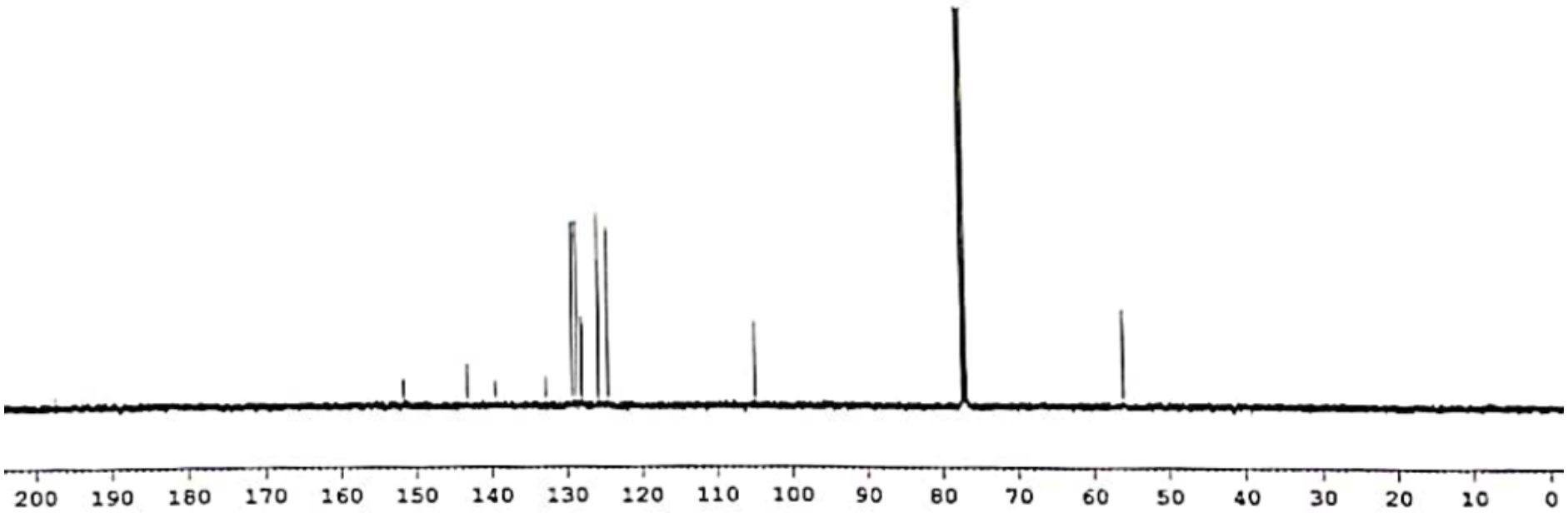
1-(4-Bromophenyl)-5-methyl-3-phenyl-1*H*-pyrazole (**3h**)

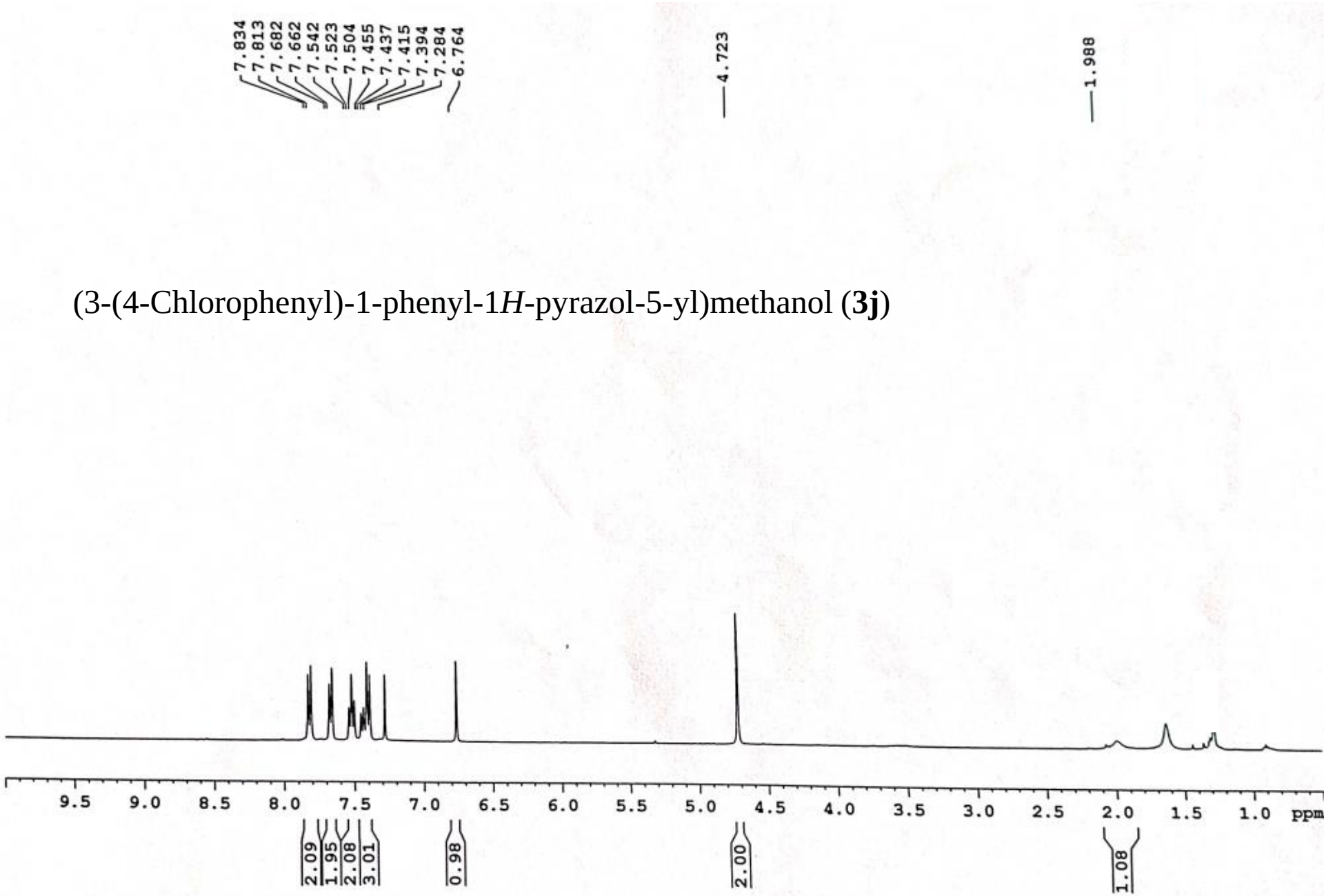




(1,3-Diphenyl-1*H*-pyrazol-5-yl)methanol (**3i**)

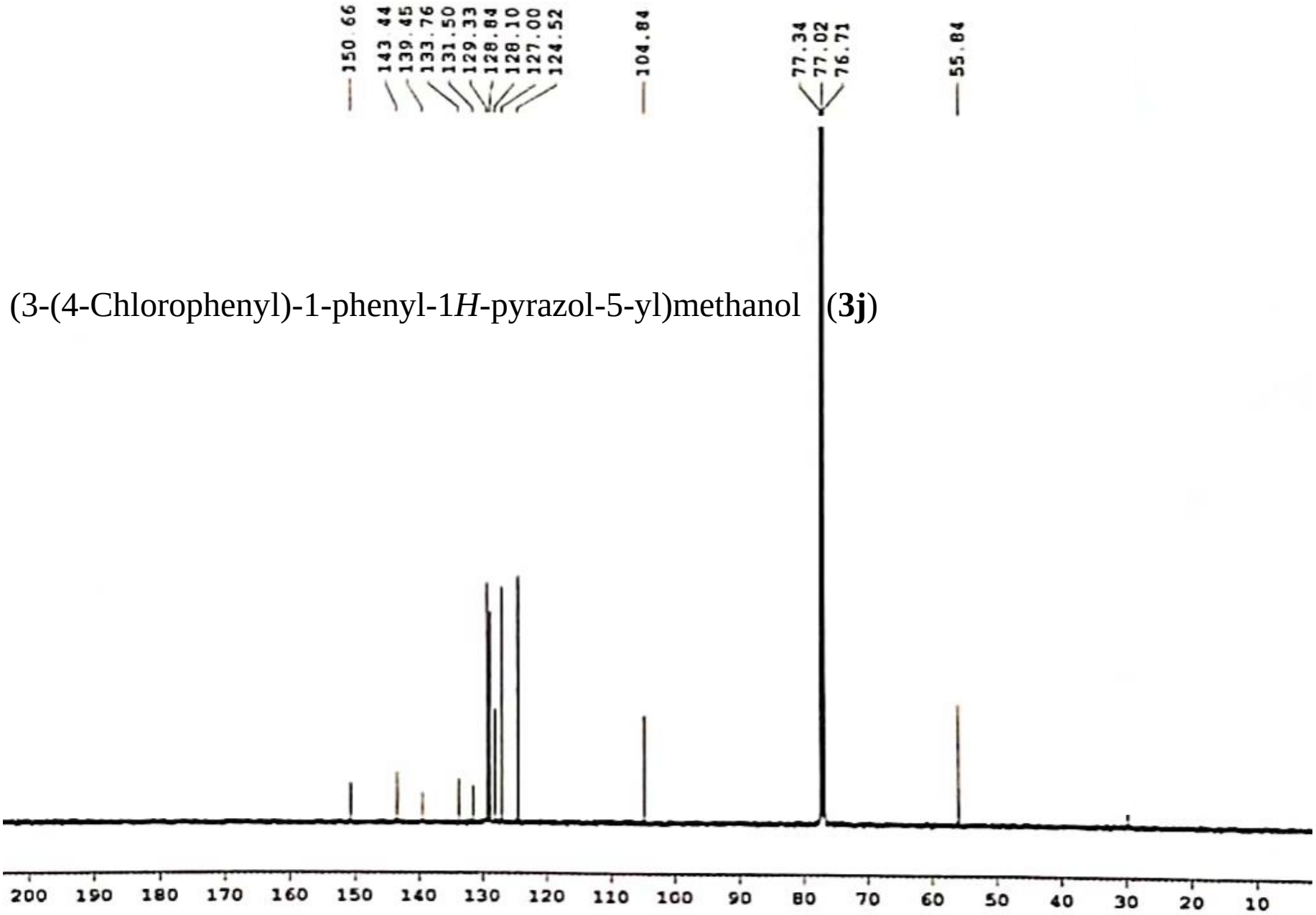
(1,3-Diphenyl-1*H*-pyrazol-5-yl)methanol (**3i**)

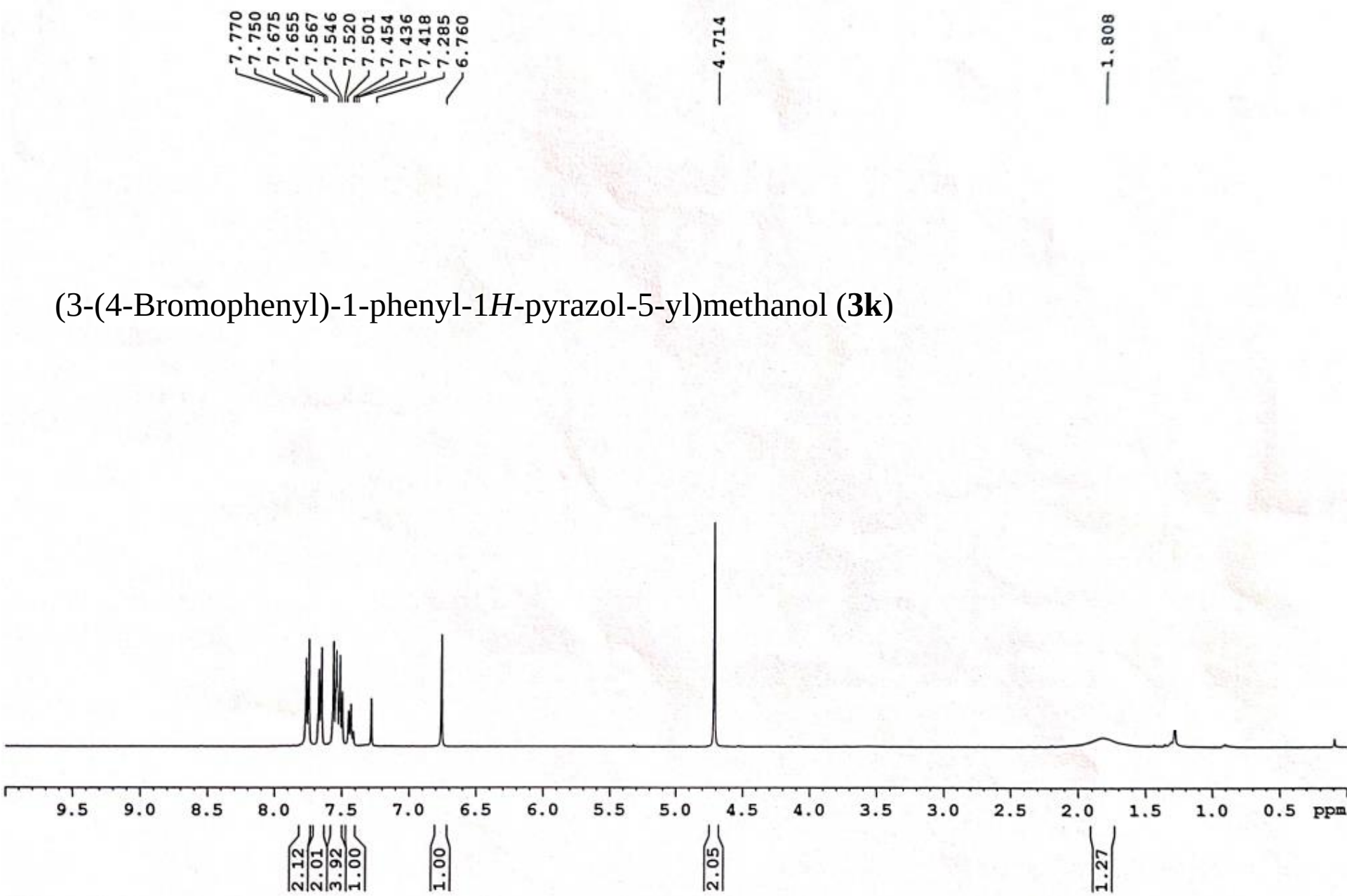




(3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-5-yl)methanol (**3j**)

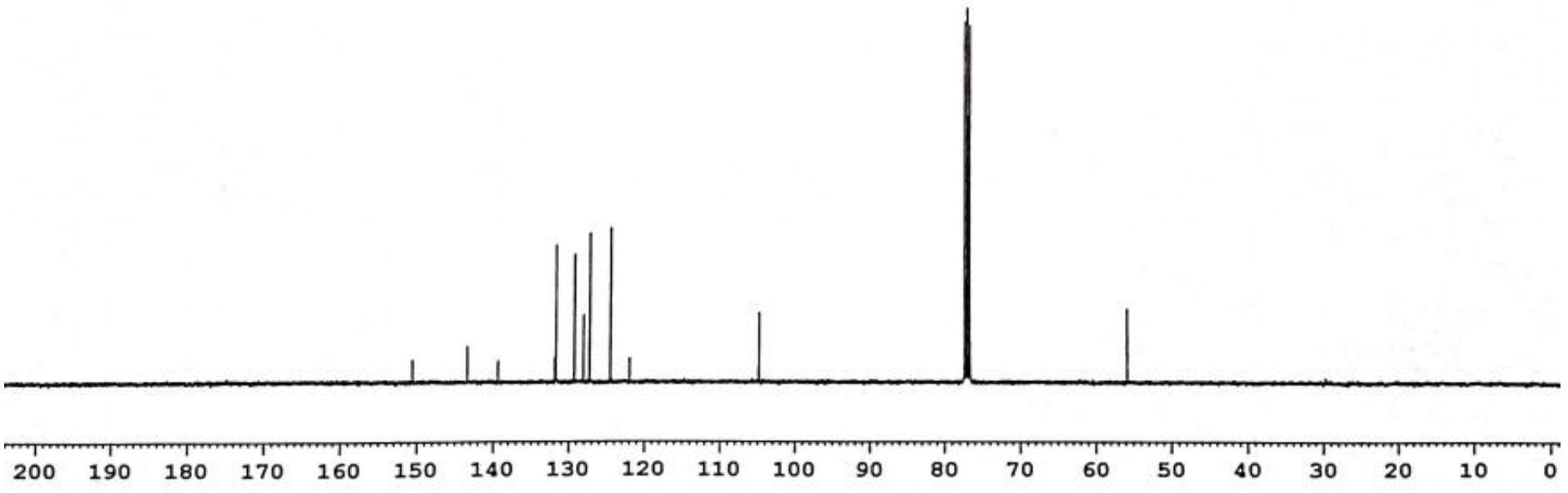
(3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-5-yl)methanol (**3j**)



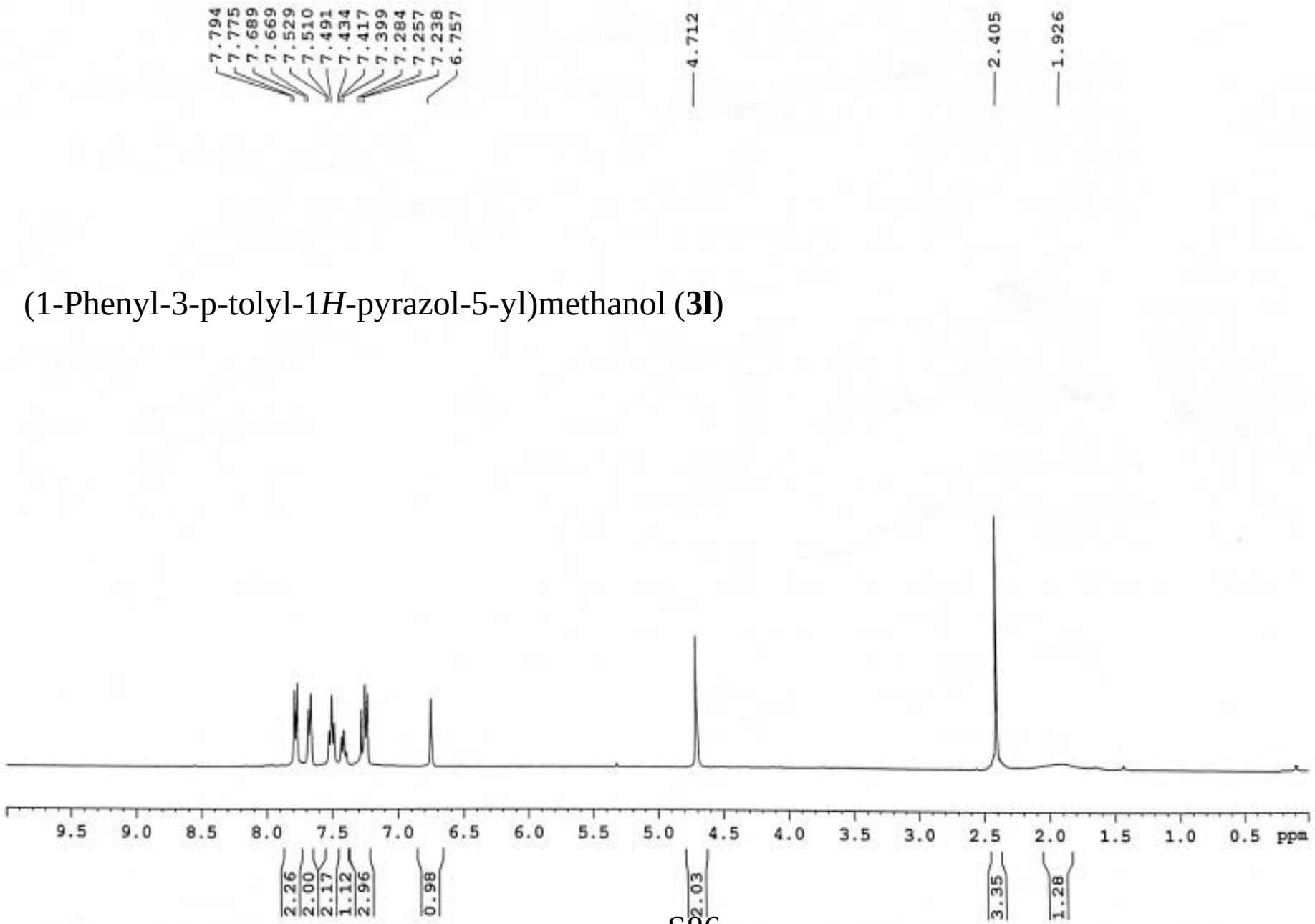


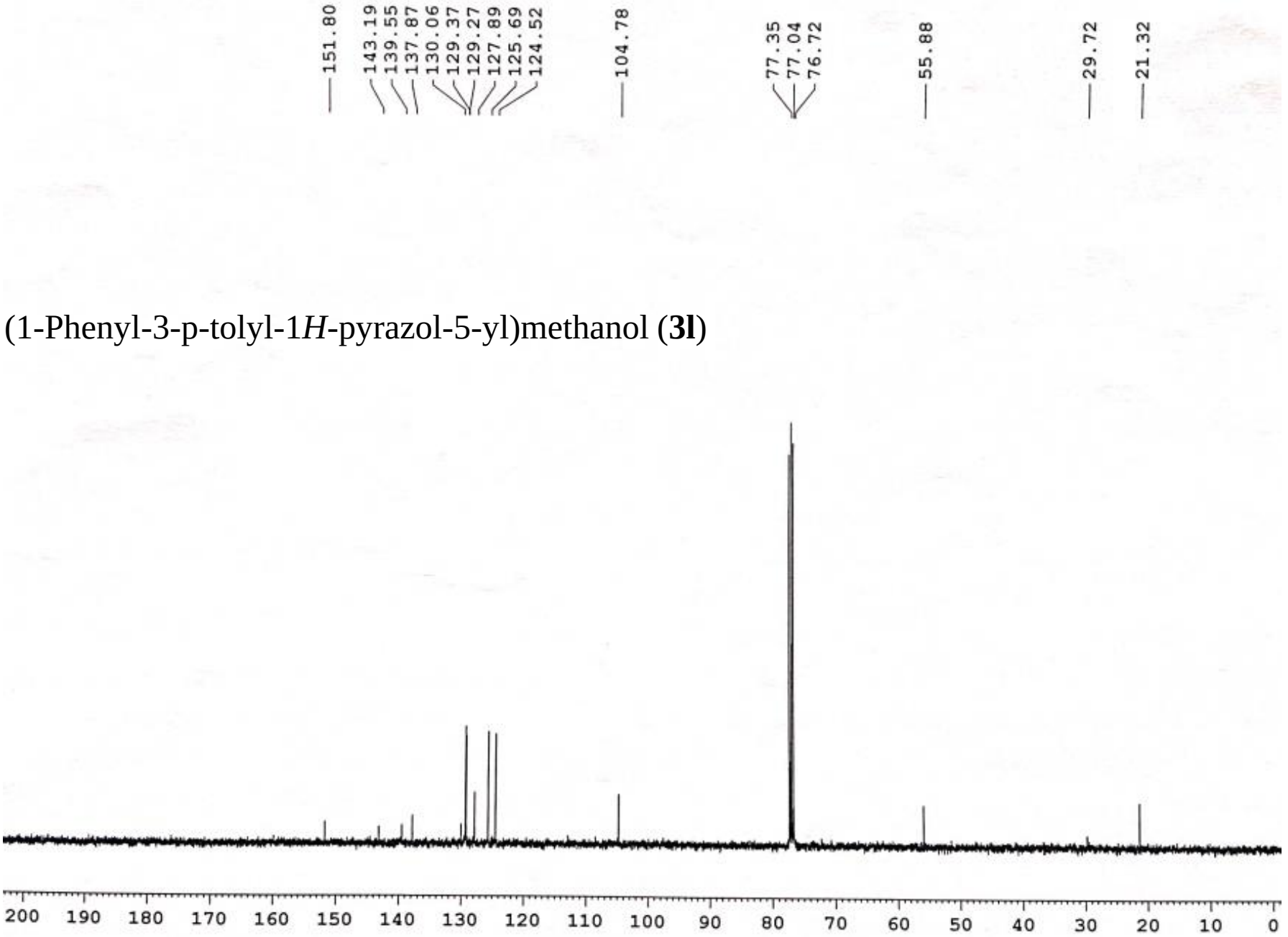
(3-(4-Bromophenyl)-1-phenyl-1*H*-pyrazol-5-yl)methanol (**3k**)

(3-(4-Bromophenyl)-1-phenyl-1*H*-pyrazol-5-yl)methanol (**3k**)



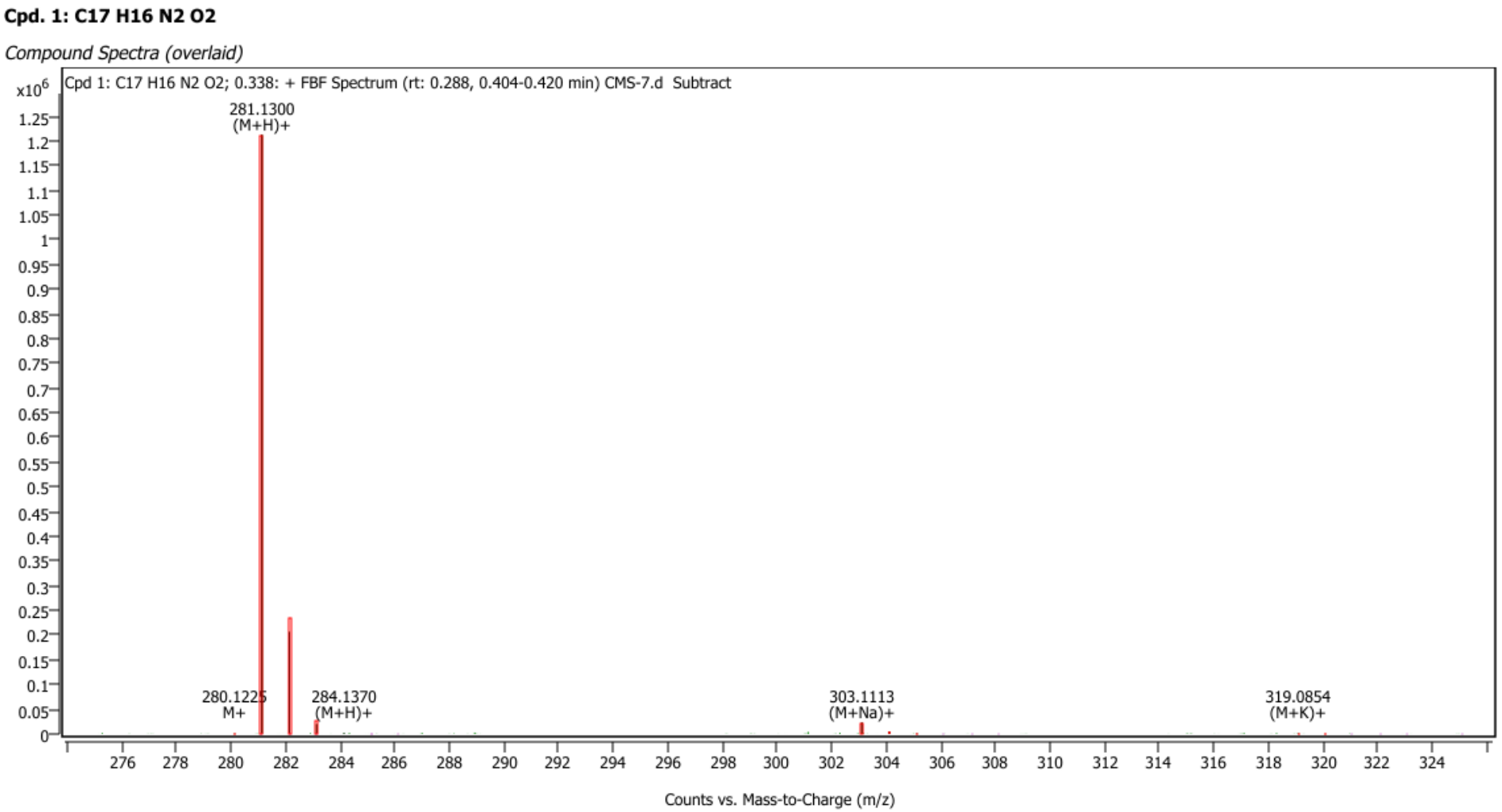
(1-Phenyl-3-p-tolyl-1*H*-pyrazol-5-yl)methanol (**3l**)



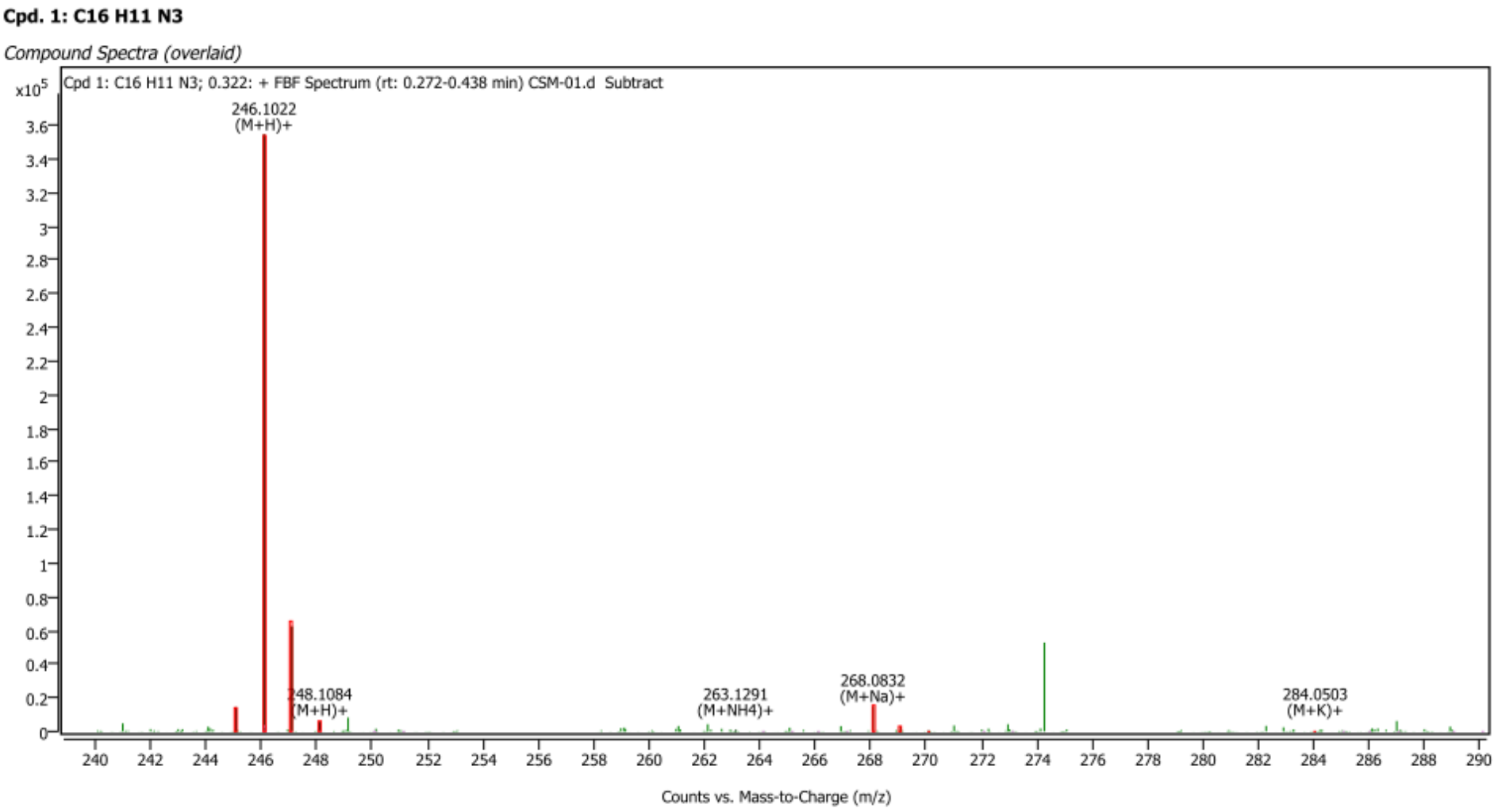


(1-Phenyl-3-p-tolyl-1*H*-pyrazol-5-yl)methanol (**3l**)

3-(3,4-Dimethoxyphenyl)-1-phenyl-1*H*-pyrazole (**2d**)



4-(1-phenyl-1*H*-pyrazol-3-yl)benzonitrile (**2i**)

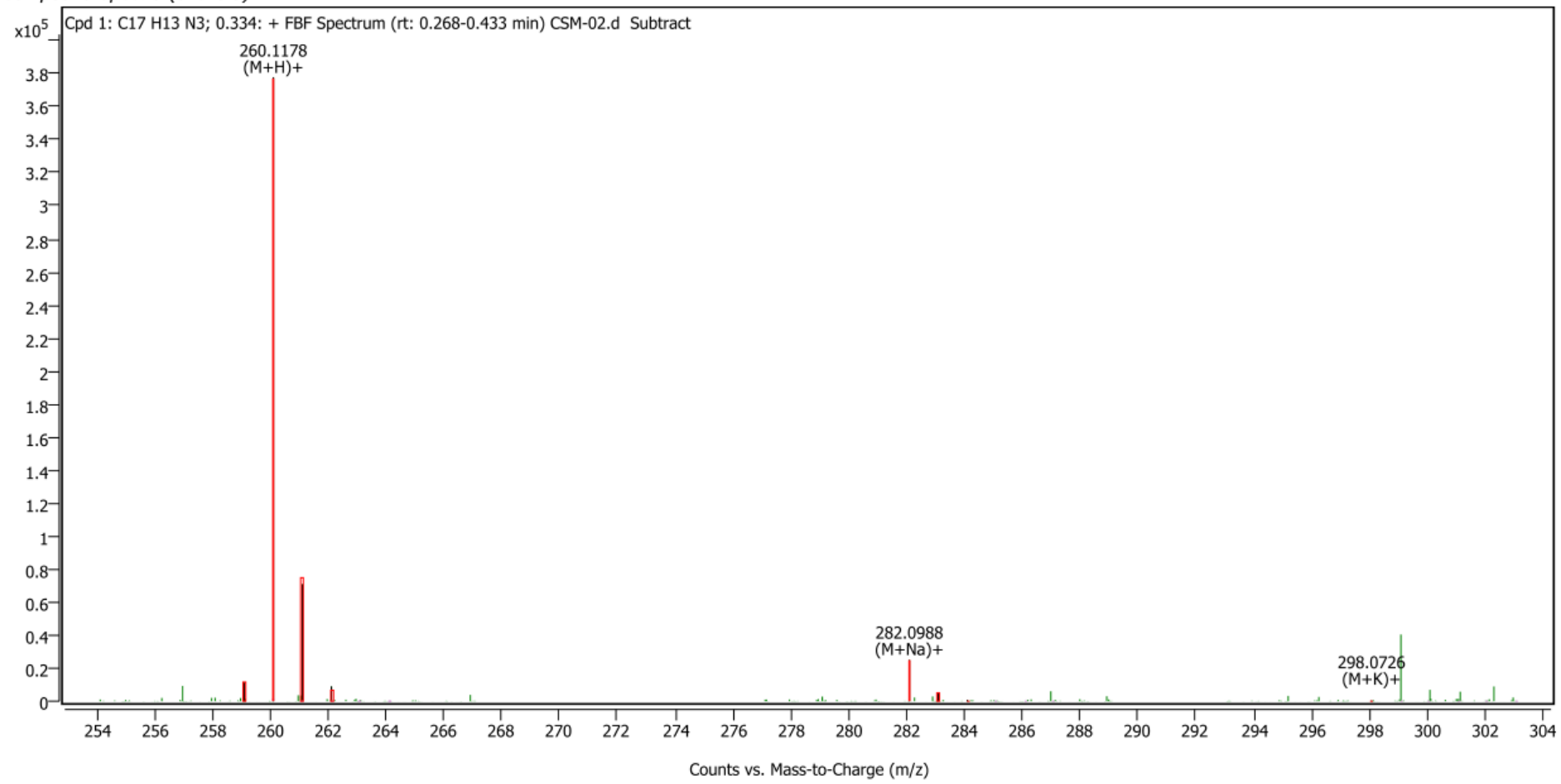


4-(1-p-tolyl-1*H*-pyrazol-3-yl)benzonitrile (**2r**)

Compound Details

Cpd. 1: C17 H13 N3

Compound Spectra (overlaid)

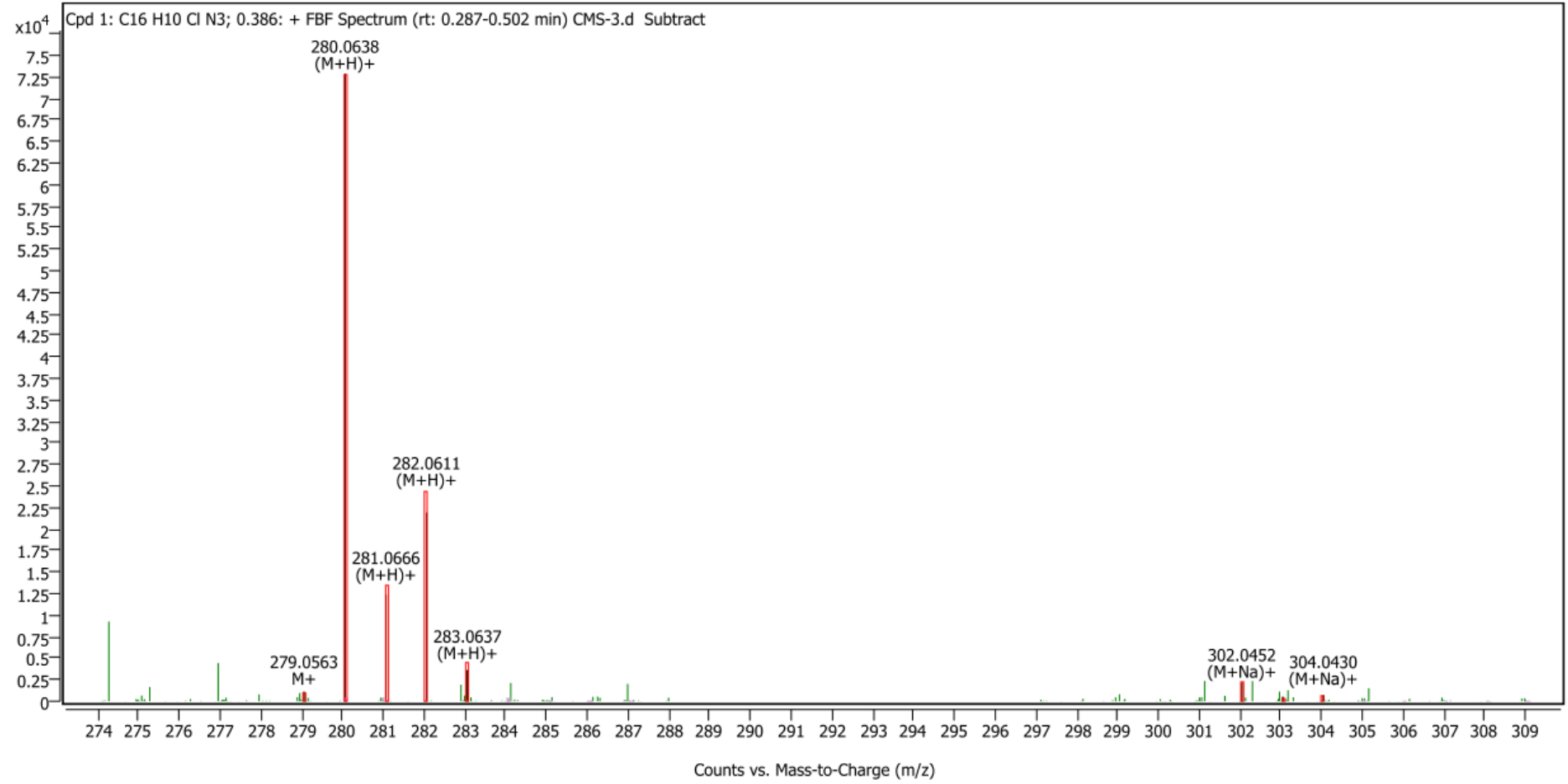


4-(1-(4-Chlorophenyl)-1*H*-pyrazol-3-yl)benzonitrile (**2v**)

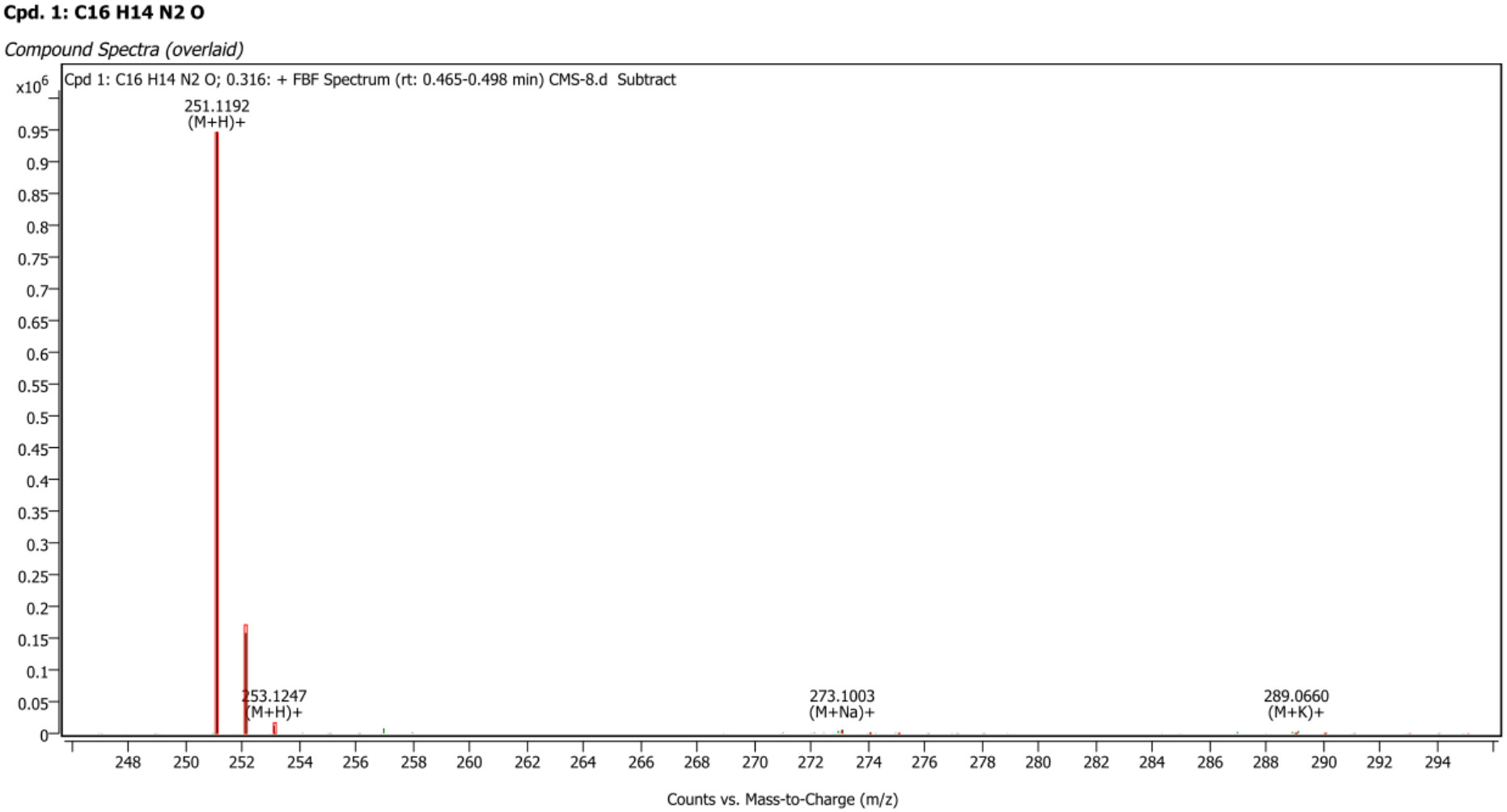
Compound Details

Cpd. 1: C16 H10 Cl N3

Compound Spectra (overlaid)



2-(5-Methyl-1-phenyl-1*H*-pyrazol-3-yl) phenol (**3c**)

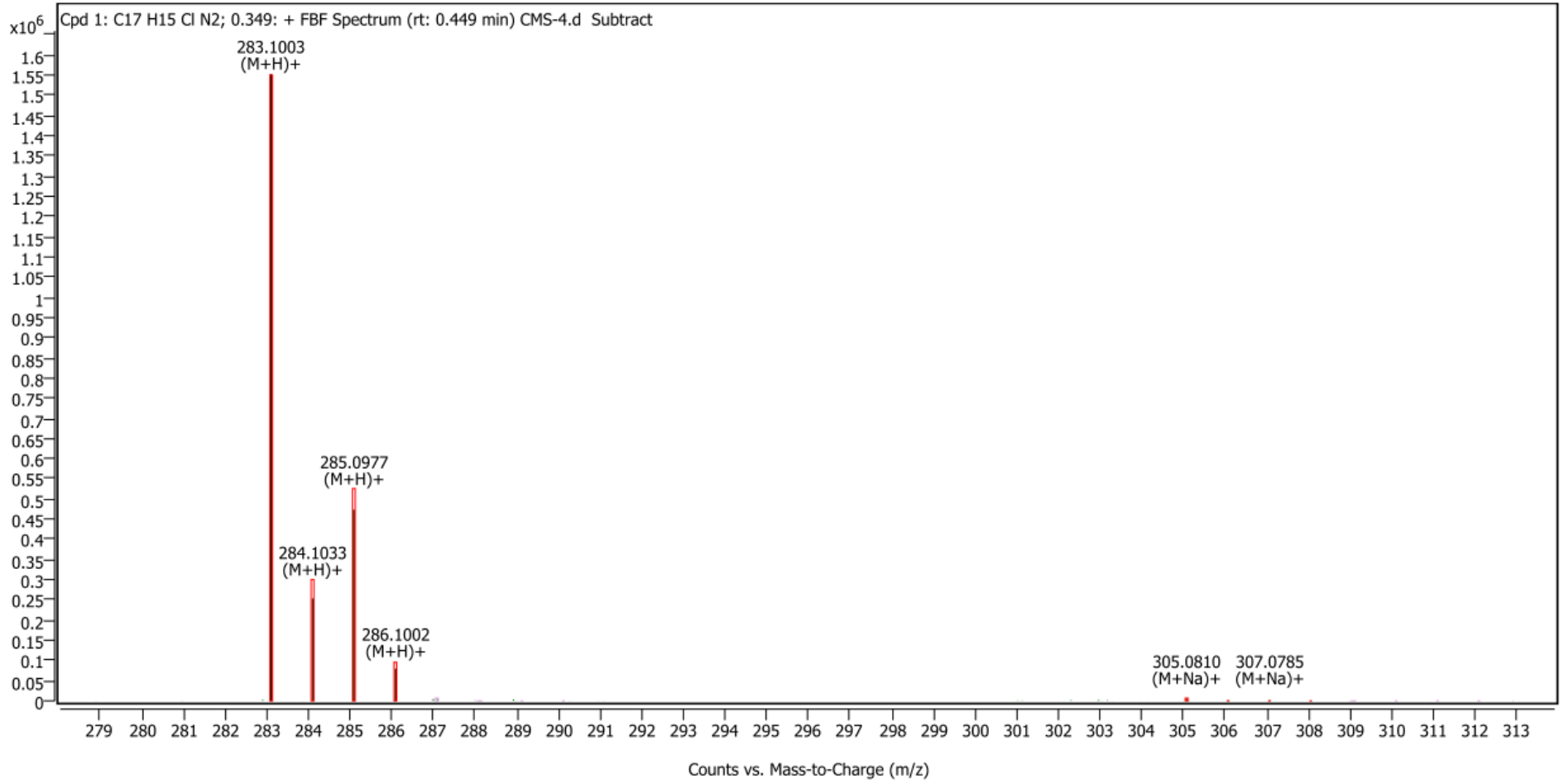


3-(4-Chlorophenyl)-5-methyl-1-p-tolyl-1*H*-pyrazole (**3f**)

Compound Details

Cpd. 1: C17 H15 Cl N2

Compound Spectra (overlaid)

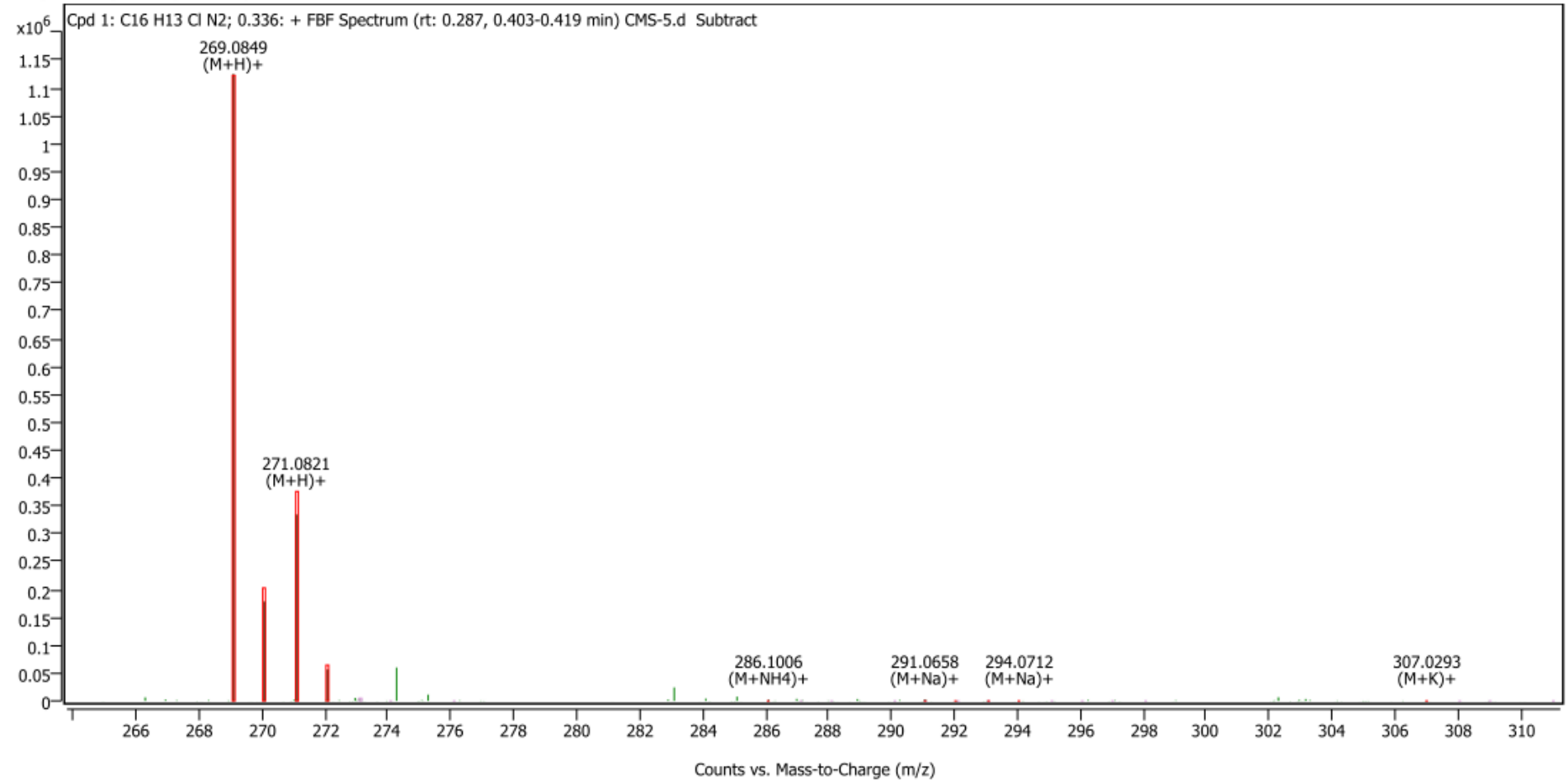


1-(4-Chlorophenyl)-5-methyl-3-phenyl-1*H*-pyrazole (**3g**)

Compound Details

Cpd. 1: C16 H13 Cl N2

Compound Spectra (overlaid)



(3-(4-Bromophenyl)-1-phenyl-1*H*-pyrazol-5-yl)methanol (**3k**)

Compound Details

Cpd. 1: C16 H13 Br N2 O

Compound Spectra (overlaid)