An "on-water" exploration of CuO nano particle catalysed synthesis of 2-aminobenzothiazoles

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General information:

All the reagents were commercial grade and purified according to the established procedures. Organic extracts were dried over anhydrous sodium sulphate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (60–120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25mm). NMR spectra were recorded in $CDCl_3$ and DMSO–d_6 with tetramethylsilane as the internal standard for ^{1}H NMR (400 MHz) $CDCl_3$ and DMSO–d_6 solvent as the internal standard for ^{13}C NMR (100 MHz). Mass spectra were recorded using WATERS MS system, Q–tof premier and data analyzed using Mass Lynx 4.1. Specific rotations were recorded on Perkin Elmer instruments model 343 polarimeter. Elemental analysis was performed with a Perkin Elmer 2400 elemental analyzer. Melting points were recorded on Buchi B-545 melting point apparatus and are uncorrected. IR spectra were recorded in KBr or neat on a Nicolet Impact 410 spectrophotometer.

Crystallographic Description:

Crystal data were collected with Bruker Smart Apex-II CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) at 298 K. Cell parameters were retrieved using SMART [a] software and refined with SAINT[a] on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS[b]. The structure was solved by direct methods implemented in SHELX-97[c] program and refined by full-matrix least-squares methods on F2. All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. colorless crystals were isolated in rectangular shape from acetonitrile at room temperature.

a. SMART V 4.043 Software for the CCD Detector System; Siemens Analytical Instruments Division: Madison, WI, 1995.
b. SAINT V 4.035 Software for the CCD Detector System; Siemens Analytical Instruments Division: Madison, WI, 1995.
c. Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen (Germany), **1997**

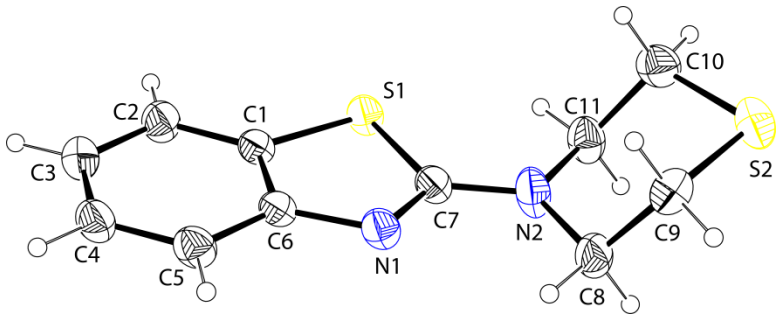


Fig. 3 ORTEP view of **2-Thiomorpholinobenzo[*d*]thiazole (1b)**

Crystallographic description of 2-Thiomorpholinobenzo[*d*]thiazole (1b): $C_{11}H_{12}N_2S_2$, crystal dimensions 0.42 x 0.35 x 0.28 mm, M_r = 236.37, monoclinic, space group P 21/c, a = 10.130(2), b = 8.1511(15), c = 13.600(2) Å, α = 90°, β = 93.902(10)°, γ = 90 °, V = 1120.4(3) Å^3, Z = 4, ρ_{calcd} = 1.401 mg/m^3, μ = 0.442 mm^{-1}, F(000) = 496.0, reflection collected / unique = 2761 / 2255, refinement method = full-matrix least-squares on F^2, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0379, wR_2 = 0.1007, R indices (all data): R_1 = 0.0469, wR_2 = 0.1069, goodness of fit = 1.070. CCDC-876212 for **2-Thiomorpholinobenzo[*d*]thiazole (1b)** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

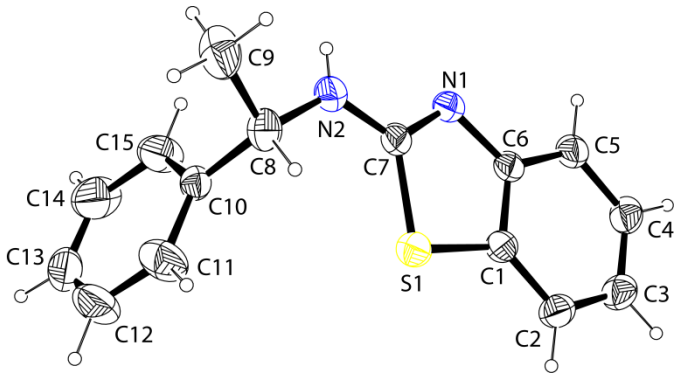


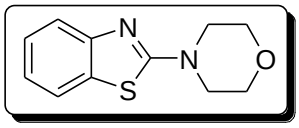
Fig. 3 ORTEP view of ***N*-((*R*)-1-phenylethyl)benzo[d]thiazol-2-amine (10q)**

Crystallographic description of *N*-((*R*)-1-phenylethyl)benzo[d]thiazol-2-amine (10q): $C_{15}H_{13}N_2S$, crystal dimensions 0.45 x 0.34 x 0.25 mm, M_r = 253.34, tetragonal, space group I 41, a = 14.9330(16), b = 14.9330(16), c = 12.2771(16) Å, α = 90°, β = 90°, γ = 90 °, V = 2737.7(5) Å^3, Z = 8, ρ_{calcd} = 1.229 mg/m^3, μ = 0.220 mm^{-1}, F(000) = 1064.0, reflection collected / unique = 2726 / 2243, refinement method = full-matrix least-squares on F^2, final R indices [$I > 2\sigma(I)$]: R_1

= 0.0553, wR_2 = 0.1214, *R* indices (all data): R_1 = 0.0641, wR_2 = 0.1302, goodness of fit = 1.019. CCDC-829313 for ***N*-((*R*)-1-phenylethyl)benzo[d]thiazol-2-amine (10q)** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

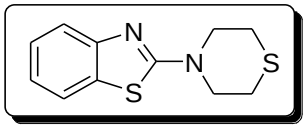
Spectral Data

2-Morpholinobenzo[*d*]thiazole (1a):



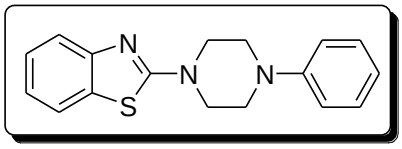
White solid; M.p. 120–122 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.59 (t, 4H, J = 4.4 Hz), 3.80 (t, 4H., J = 4.4 Hz), 7.07 (t, 1H, J = 7.6 Hz), 7.28 (t, 1H, J = 8.0 Hz), 7.57 (dd, 2H, J_1 = 6.4 Hz, J_2 = 4.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 48.6, 66.3, 119.4,120.9, 121.8, 126.2, 130.7, 152.6, 169.1; IR (KBr): 2918, 2854, 1591, 1537, 1441, 1377, 1289, 1229, 1113, 1067, 1032, 945, 859, 756 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{12}N_2OS$ $(M+H)^+$ 221.0743; found 221.0749.

2-Thiomorpholinobenzo[*d*]thiazole (1b):



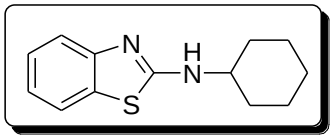
Yellow solid; M.p. 98-99 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.71 (t, 4H, J = 5.2 Hz), 3.93 (t, 4H, J = 4.8 Hz), 7.06 (t, 1H, J = 7.2 Hz), 7.28 (t, 1H, J = 8.0 Hz), 7.52 (d, 1H, J = 8.0 Hz), 7.57 (d, 1H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.7, 51.4, 119.3, 120.9, 121.7, 126.2, 130.8, 152.8, 168.2; IR (KBr): 3059, 2936, 2858, 1599, 1531, 1444, 1385, 1359, 1313, 1218, 1054, 1020, 899, 750 cm^{-1}; Anal. calcd for $C_{11}H_{12}N_2S_2$: C 55.90, H 5.12, N 11.85; found C 55.88, H 5.17, N 11.79.

2-(4-Phenylpiperazine-1-yl)benzo[d]thiazole (1c):



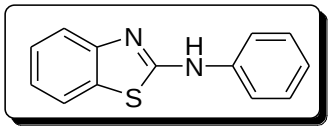
White solid; M.p. 165–167 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.32 (t, 4H, *J* = 5.2 Hz), 3.80 (t, 4H, *J* = 5.2 Hz), 6.92 (t, 1H, *J* = 7.2 Hz), 6.97 (d, 2H, *J* = 8.4 Hz), 7.10 (t, 1H, *J* = 7.2 Hz), 7.28–7.33 (m, 3H), 7.57–7.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 48.4, 49.2, 117.0, 119.4, 120.8, 120.9, 121.7, 126.2, 129.4, 131.0, 151.1, 152.9, 168.8; IR (KBr): 3054, 2838, 1594, 1539, 1504, 1444, 1230, 1158, 1024, 935, 754, 724 cm^{-1}; Anal. calcd for $C_{17}H_{17}N_3S$: C 69.12, H 5.80, N 14.22; found C 69.07, H 5.86, N 14.16.

Benzothiazol-2-yl-cyclohexyl-amine (1d):



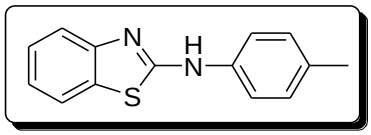
White solid; M.p. 107–108 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.17–1.46 (m, 5H), 1.61–1.65 (m, 1H), 1.73–1.79 (m, 2H), 2.10 (m, 2H), 3.53 (s, 1H), 5.70 (brs, 1H), 7.05 (t, 1H, *J* = 8.0 Hz), 7.25–7.29 (m, 1H), 7.51 (d, 1H, *J* = 8.0 Hz), 7.56 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 24.9, 25.6, 33.4, 54.8, 118.8, 119.8, 120.9, 121.4, 123.4, 126.0, 129.2, 167.1; IR (KBr) 3202, 3017, 2927, 2852, 1590, 1538, 1445, 1365, 1345, 1248, 1209, 1076, 885, 804, 746, 720 cm^{-1}; Anal. calcd for $C_{13}H_{16}N_2S$: C 67.20, H 6.94, N 12.06; found C 67.16, H 6.98, N 11.99.

_N_-Phenylbenzo[d]thiazol-2-amine (1e):



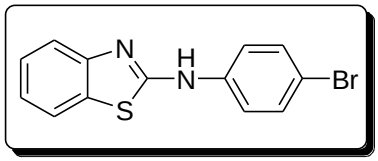
Grey solid; M.p. 156-158 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.11–7.19 (m, 2H), 7.31 (t, 1H, *J* = 8 Hz), 7.40 (t, 2H, *J* = 8 Hz), 7.50 (d, 2H, *J* = 8.8 Hz), 7.54 (d, 1H, *J* = 8 Hz), 7.61 (d, 1H, *J* = 8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 119.4, 120.7, 121.1, 122.5, 124.7, 126.3, 129.8, 130.0, 140.2, 151.5, 165.4; IR (KBr) 3234, 3187, 3128, 3053, 2996, 2935, 1625, 1602, 1571, 1558, 1466, 1429, 1248, 1224, 921, 744, 720, 688, 592 cm^{-1}; Anal. calcd for $C_{13}H_{10}N_2S$: C 69.00, H 4.45, N 12.38; found C 69.05, H 4.51, N 12.32.

Benzothiazol-2-yl-p-tolyl-amine (1f):



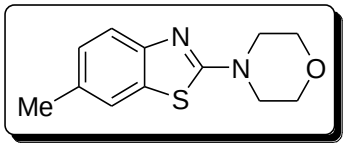
White solid; M.p. 177–178 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.37 (s, 3H), 7.12 (t, 1H, *J* = 8.0 Hz), 7.21 (d, 2H, *J* = 8.0 Hz), 7.29 (t, 1H, *J* = 8.0 Hz), 7.35–7.40 (m, 2H), 7.50 (d, 1H, *J* = 8.0 Hz), 7.60 (d, 1H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 21.1, 119.2, 121.0, 121.5, 122.4, 126.3, 129.7, 130.3, 134.9, 137.5, 151.5, 166.3; IR (KBr) 3183, 3029, 2914, 1624, 1572, 1514, 1447, 1404, 1330, 1271, 1247, 919 cm^{-1}; Anal. calcd for $C_{14}H_{12}N_2S$: C 69.97, H 5.03, N 11.66; found C 69.92, H 5.07, N 11.63.

Benzothiazol-2-yl-(4-bromo-phenyl)-amine (1g):



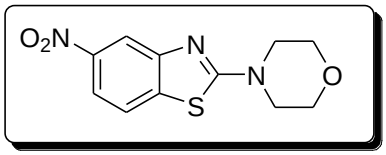
White solid; M.p. 217–218 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6) δ (ppm) 7.15 (t, 1H, *J* = 7.6 Hz), 7.32 (t, 1H, *J* = 7.2 Hz), 7.43 (d, 2H, *J* = 8.8 Hz), 7.61 (d, 1H, *J* = 8.0 Hz), 7.66 (d, 1H, *J* = 8.0 Hz), 7.76 (d, 2H, *J* = 8.8 Hz), 10.34 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6) δ (ppm) 114.1, 119.9, 120.2, 120.9, 122.8, 126.1, 130.6, 131.8, 140.4, 152.5, 161.9; IR (KBr) 3174, 3069, 2956, 2899, 1619, 1584, 1562, 1454, 1448, 1445, 1311, 1298, 1270, 1246, 1226, 1076 cm^{-1}; Anal. calcd for $C_{13}H_9BrN_2S$: C 51.16, H 2.97, N 9.18; found C 51.12, H 2.94, N 9.25.

6-Methyl-2-morpholinobenzo[*d*]thiazole (2a):



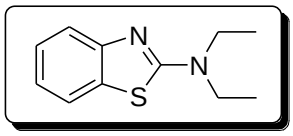
Pale white; Mp 134–136 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.37 (s, 3H), 3.56 (t, 4H, *J* = 4.8 Hz), 3.79 (t, 4H, *J* = 4.8 Hz), 7.09 (d, 1H, *J* = 8.0 Hz), 7.39 (s, 1H), 7.44 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.4, 48. 6, 66.4, 119.1, 120.9, 127.4, 130.8, 131.6, 150.4, 168.6; IR (KBr): 2963, 2912, 2856, 1599, 1575, 1544, 1464, 1434, 1352, 1281, 1235, 1113, 1026, 943, 811 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{14}N_2OS$ $(M+H)^+$ 235.1035; found 235.1035.

2-Morpholino-5-nitrobenzo[d]thiazole (3a):



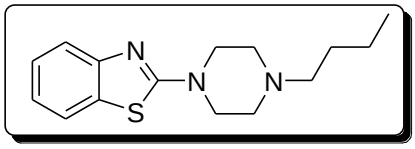
Yellow solid; M.p. 172–174 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.68 (t, 4H, *J* = 5.2 Hz), 3.86 (t, 4H, *J* = 5.2 Hz), 7.70 (d, 1H, *J* = 8.8 Hz), 7.97 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.4 Hz), 8.35 (ds, 1H, *J* = 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 48.6, 66.2, 114.0, 116.3, 120.9, 138.0, 147.1, 153.0, 170.4; IR (KBr) 3095, 3064, 3019, 2979, 2913, 2866, 1602, 1539, 1531, 1508, 1343, 1228, 1119, 815, 738, 723 cm^{-1}; Anal. calcd for $C_{11}H_{11}N_3O_3S$: C 49.80, H 4.18, N 15.84; found C 49.83, H 4.14, N 15.78.

***N,N*-Diethylbenzo[d]thiazol-2-amine (4h):**



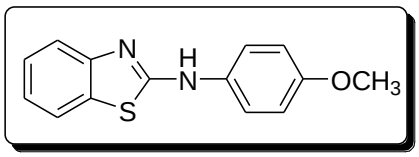
Pale yellow solid; M.p. 113-114 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.26 (m, 6H), 3.55 (m, 4H), 7.03 (t, 1H, *J* = 8.0 Hz), 7.27 (t, 1H, *J* = 8.0 Hz), 7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 12.9, 45.4, 118.6, 120.6, 120.7, 125.8, 130.7, 153.3, 167.4; IR (KBr): 3056, 2972, 2931, 2862, 1596, 1561, 1542, 1444, 1360, 1315, 1260, 1135, 1079, 1013, 750 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{14}N_2S$ $(M+H)^+$ 207.0687; found 207.0687.

2-(4-Butylpiperazin-1-yl)benzo[d]thiazole (4i):



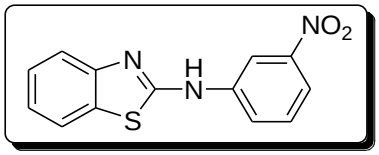
White solid; M.p. 92-93 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.94 (t, 3H, *J* = 7.2 Hz), 1.35 (sextet, 2H, *J* = 7.6 Hz), 1.51 (quin, 2H, *J* = 7.2 Hz), 2.40 (t, 2H, *J* = 7.6 Hz), 2.57 (t, 4H, *J* = 5.2 Hz), 3.66 (t, 4H, *J* = 5.2 Hz), 7.07 (t, 1H, *J* = 7.6 Hz), 7.29 (t, 1H, *J* = 7.6 Hz), 7.55 (d, 1H, *J* = 8.0 Hz), 7.60 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.2, 20.9, 29.1, 48.5, 52.7, 58.6, 119.2, 120.9, 121.5, 126.2, 130.9, 152.9, 168.9; IR (KBr): 3047, 2955, 2935, 2860, 2814, 1601, 1544, 1445, 1347, 1291, 1245, 1235, 1127, 749, 722 cm^{-1}; Anal. Calcd for $C_{15}H_{21}N_3S$: C 65.41, H 7.69, N 15.26; found C 65.35, H 7.63, N 15.19.

Benzothiazol-2-yl-(4-methoxy-phenyl)-amine (4j):



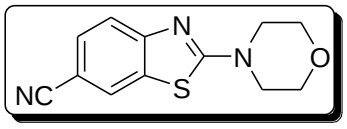
Grey solid; M.p. 160–161 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.84 (s, 3H), 6.95 (d, 2H, *J* = 8.8 Hz), 7.12 (t, 1H, *J* = 7.2 Hz), 7.31 (t, 1H, *J* = 7.2 Hz), 7.40 (d, 2H, *J* = 8.8 Hz), 7.54 (d, 1H, *J* = 8.0 Hz), 7.59 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 55.8, 115.0, 119.3, 121.0, 122.3, 124.1, 126.3, 130.3, 133.1, 152.0, 157.6, 166.8; IR (KBr): 3181, 2835, 1619, 1572, 1511, 1444, 1414, 1241, 1037, 918 cm^{-1}; Anal. calcd for $C_{14}H_{12}N_2OS$: C 65.60, H 4.72, N 10.93; found C 65.64, H 4.69, N 10.99.

_N_-(3-Nitrophenyl)benzo[d]thiazol-2-amine (4k):



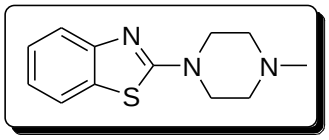
Yellow solid; M.p. 189–190 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ (ppm) 7.23–7.26 (m, 1H), 7.41 (t, 1H, *J* = 8.0 Hz), 7.54 (t, 1H, *J* = 8.0 Hz), 7.70 (d, 1H, *J* = 8.0 Hz), 7.74 (d, 1H, *J* = 8.0 Hz), 7.96 (t, 2H, *J* = 7 Hz), 8.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ (ppm) 111.7, 115.5, 119.3, 120.0, 122.1, 123.0, 125.2, 129.0, 129.7, 141.3, 147.9, 151.3, 160.6; IR (KBr): 3226, 3181, 3073, 2947, 1619, 1567, 1532, 1460, 1445, 1351, 1243, 885, 745, 718 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_9N_3O_2S$ $(M+H)^+$ 272.0488; found 272.0472.

2-Morpholinobenzo[d]thiazole-6-carbonitrile (6a):



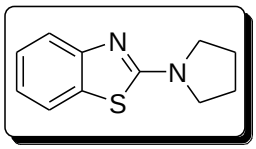
White solid; M.p. 173–175 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.57 (t, 4H, *J* = 4.8 Hz), 3.74 (t, 4H, *J* = 4.4 Hz), 7.42 (s, 2H), 7.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 48.5, 66.0, 103.9, 119.3, 124.9, 130.0, 131.1, 155.9, 162.5, 171.0; IR (KBr): 2906, 2861, 2224, 1526, 1554, 1434, 1325, 1286, 1226, 1194, 1118, 1067, 1028, 949, 838 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{11}N_3OS$ $(M+H)^+$ 246.0702; found 246.0649.

2-(4-Methylpiperazin-1-yl)benzo[d]thiazole (7l):



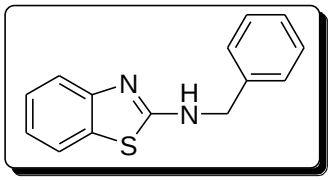
White solid; M.p. 94-95 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.36 (s, 3H), 2.55 (t, 4H, *J* = 5.2 Hz), 3.67 (t, 4H, *J* = 5.2 Hz), 7.08 (t, 1H, *J* = 8.0 Hz), 7.30 (t, 1H, *J* = 7.2 Hz), 7.55–7.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 46.2, 48.2, 54.2, 119.1, 120.7, 121.4, 126.0, 130.8, 152.7, 168.7; IR (KBr): 3052, 2938, 2884, 2844, 2807, 1593, 1530, 1445, 1375, 1334, 1293, 1214, 1140, 1002, 748, 726 cm^{-1}; Anal. Calcd for $C_{12}H_{15}N_3S$: C 61.77, H 6.48, N 18.01; found C 61.74, H 6.45, N 18.07.

2-(Pyrrolidin-1-yl)benzo[*d*]thiazole (7m):



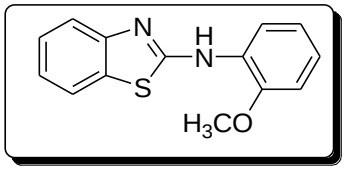
White solid; M.p. 101–103 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.04 (m, 4H), 3.57 (s, 4H), 7.02 (t, 1H, *J* = 7.6 Hz), 7.26 (t, 1H, *J* = 8.0 Hz), 7. 57 (t, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 25.8, 49.8, 118.9, 120.9, 121.2, 126.2, 130.6, 153.2, 165.6; IR (KBr): 2924, 2851, 16, 1544, 1442, 1363, 1314, 1278, 1166, 1119, 853 cm^{-1}. Anal. Calcd for $C_{11}H_{12}N_2S$: C 64.67, H 5.92, N 13.71; found C 64.61, H 5.96, N 13.76.

_N_-Benzylbenzo[d]thiazol-2-amine (7n):



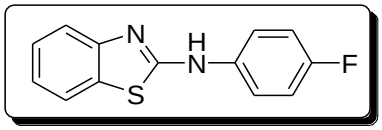
White solid; M.p. 163–165 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.63 (s, 2H), 6.36 (brs, 1H), 7.08 (t, 1H, *J* = 7.2 Hz), 7.25–7.47 (brm, 7H), 7.57 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 49.6, 119.1, 121.0, 121.8, 126.2, 127.9, 128.1, 129.0, 130.6, 137.7, 152.5, 167.9; IR (KBr) 3183, 3085, 2980, 2897, 2853, 1620, 1574, 1447, 1355, 1268, 972, 743, 724, 698, 673 cm^{-1}; Anal. calcd for $C_{14}H_{12}N_2S$: C 69.97, H 5.03, N 11.66; found C 69.93, H 5.06, N 11.59.

_N_-(2-Methoxyphenyl)benzo[d]thiazol-2-amine (7o):



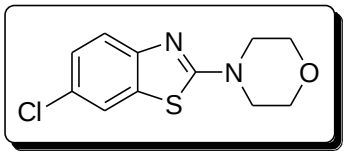
Grey solid; M.p. 146-148 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.86 (s, 3H), 6.88–6.90 (m, 1H), 7.01–7.04 (m, 2H), 7.15 (t, 1H, *J* = 8 Hz), 7.34 (t, 1H, *J* = 8 Hz), 7.63 (d, 1H, *J* = 8 Hz), 7.68 (d, 1H, *J* = 8 Hz), 8.26–8.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 55.9, 110.4, 118.1, 120.1, 120.9, 121.3, 122.7, 123.1, 126.2, 129.6, 130.5, 148.1, 152.2, 162.5; IR (KBr) 3469, 3177, 3074, 2934, 1612, 1566, 1443, 1433, 1255, 1114, 1018, 755 cm^{-1}; Anal. calcd for $C_{14}H_{12}N_2OS$: C 65.60, H 4.72, N 10.93; found C 65.54, H 4.77, N 10.86.

_N_-(4-Fluorophenyl)benzo[d]thiazol-2-amine (7p):



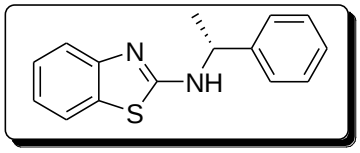
White solid; M.p. 196-197 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ (ppm) 7.03 (t, 2H, J = 8.4 Hz), 7.13 (t, 1H, J = 7.6 Hz), 7.31 (t, 1H, J = 8 Hz), 7.62 (d, 2H, J = 8 Hz), 7.71–7.75 (m, 2H), 9.65 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ (ppm) 115.2, 115.4, 119.3, 120.0, 120.1, 120.4, 122.0, 125.6, 130.2, 136.8, 152.2, 162.5; IR (KBr) 3443, 3194, 3136, 3054, 2910, 1626, 1574, 1511, 1455, 1445, 1216, 921, 834, 745, 722 cm^{-1}; Anal. calcd for $C_{13}H_9FN_2S$: C 63.92, H 3.71, N 11.47; found C 63.98, H 3.76, N 11.42.

6-Chloro-2-morpholinobenzo[*d*]thiazole (9a):



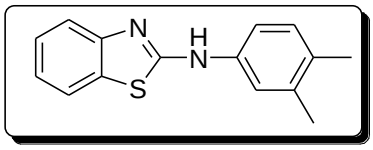
White solid; M.p. 122–124 ^{o}C ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.56 (t, 4H, J = 4.8 Hz), 3.81 (t, 4H, J = 4.8 Hz), 7.18 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.0 Hz), 7.43 (d, 1H, J = 8.4 Hz), 7.69 (d, 1H, J = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 48.6, 66.3, 119.4, 121.5, 121.9, 129.0, 132.1, 153.8, 170.1; IR (KBr): 3051, 2978, 2902, 2855, 1737, 1587, 1530, 147, 1375, 1325, 1279, 1234, 1142, 1116, 1070, 1035, 885, 872, 808, 678 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{11}N_2OSCl$ $(M+H)^+$ 255.0446; found 255.0448.

_N_-((_R_)-1-Phenylethyl)benzo[d]thiazol-2-amine (10q):



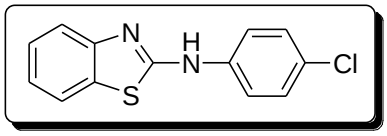
Yellow solid; M.p. 160-161 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.61 (d, 3H, *J* = 6.8 Hz), 4.75 (q, 1H, *J* = 6.8 Hz), 7.02 (t, 1H, *J* = 7.6 Hz), 7.21–7.27 (m, 2H), 7.31 (t, 2H, *J* = 7.6 Hz), 7.38, (d, 2H, *J* = 7.6 Hz), 7.47-7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 24.0, 55.8, 118.9, 121.0, 121.5, 126.0, 126.3, 127.7, 128.9, 130.7, 143.2, 152.1, 167.8; IR (KBr) 3444, 3178, 3077, 2965, 1605, 1569, 1556, 1445, 1309, 1271, 1207, 1141, 1122, 751, 700 cm^{-1}; Anal. calcd for $C_{15}H_{14}N_2S$: C 70.83, H 5.55, N 11.01; found C 70.78, H 5.49, N 10.98.

_N_-(3,4-Dimethylphenyl)benzo[d]thiazol-2-amine (10r):



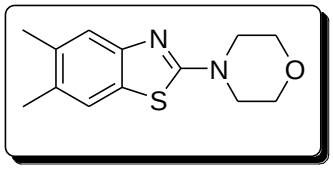
White solid; M.p. 140-142 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.27 (s, 3H), 2.28 (s, 3H), 7.10-7.17 (m, 2H), 7.22 (brs, 2H), 7.30 (t, 1H, *J* = 7.6 Hz), 7.53 (d, 1H, *J* = 8.4 Hz), 7.60 (d, 1H, *J* = 8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 19.4, 20.1, 118.9, 119.1, 121.0, 122.1, 123.0, 126.2, 129.9, 130.8, 133.5, 137.9, 138.2, 151.6, 166.7; IR (KBr) 3436, 3227, 3183, 1623, 1569, 1467, 1272, 1249, 887, 737, 717 cm^{-1}; Anal. calcd for $C_{15}H_{14}N_2S$: C 70.83, H 5.55, N 11.01; found C 70.78, H 5.58, N 10.95.

_N_-(4-Chlorophenyl)benzo[d]thiazol-2-amine (10s):



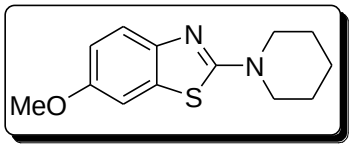
White solid; M.p. 114-116 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ (ppm) 7.19 (t, 1H, J = 8 Hz), 7.34–7.38 (m, 3H), 7.50 (d, 2H, J = 8.8 Hz), 7.64 (t, 2H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$ DMSO-d_6): δ (ppm) 119.2, 119.3, 120.2, 122.0, 125.5, 126.3, 128.4, 130.0, 139.2, 151.9,161.6; IR (KBr) 3444, 3054, 1567, 1474, 1434, 1315, 1250, 1089, 1012, 964, 828, 756, 731, 692 cm^{-1}; Anal. calcd for $C_{13}H_9ClN_2S$: C 59.88, H 3.48, N 10.74; found C 59.96, H 3.45, N 10.69.

6,6-Dimethyl-2-morpholinobenzo[d]thiazole (11a):



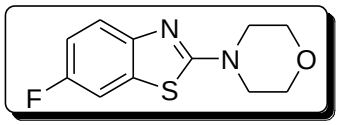
Brown solid; M.p. 156–158 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.30 (s, 3H), 2.31 (s, 3H), 3.59 (t, 4H, J = 5.2 Hz), 3.83 (t, 4H, J = 4.8 Hz), 7.37 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 20.0, 20.3, 48.7, 66.4, 120.3, 121.2, 128.0, 130.7, 135.1, 151.1, 168.9; IR (KBr) 2966, 2892, 2857, 1530, 1443, 1375, 1283, 1227, 1114, 1020, 899, 857 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{16}N_2OS$ $(M+H)^+$ 249.1161; found 249.1164.

6-Methoxy-2-(piperdin-1-yl)benzo[*d*]thiazole (12t):



White solid; M.p. 96–97 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.63 (brs, 6H), 3.51 (brs, 4H), 3.76 (s, 3H), 6.87 (dd, 1H, *J* = 8.4, 2.4 Hz), 7.11 (s, 1H), 7.44 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 24.2, 25.3, 49.6, 55.8, 105.2, 113.4, 119.2, 131.6, 147.8, 154.8, 167.6; IR (KBr): 2934, 2922, 2849, 1588, 1534, 1440, 1382, 1332, 1257, 1234, 1209, 1120, 1018, 749 cm^{-1}; Anal. Calcd for $C_{13}H_{16}N_2OS$: C 62.87, H 6.49, N 11.28; found C 62.81, H 6.56, N 11.21.

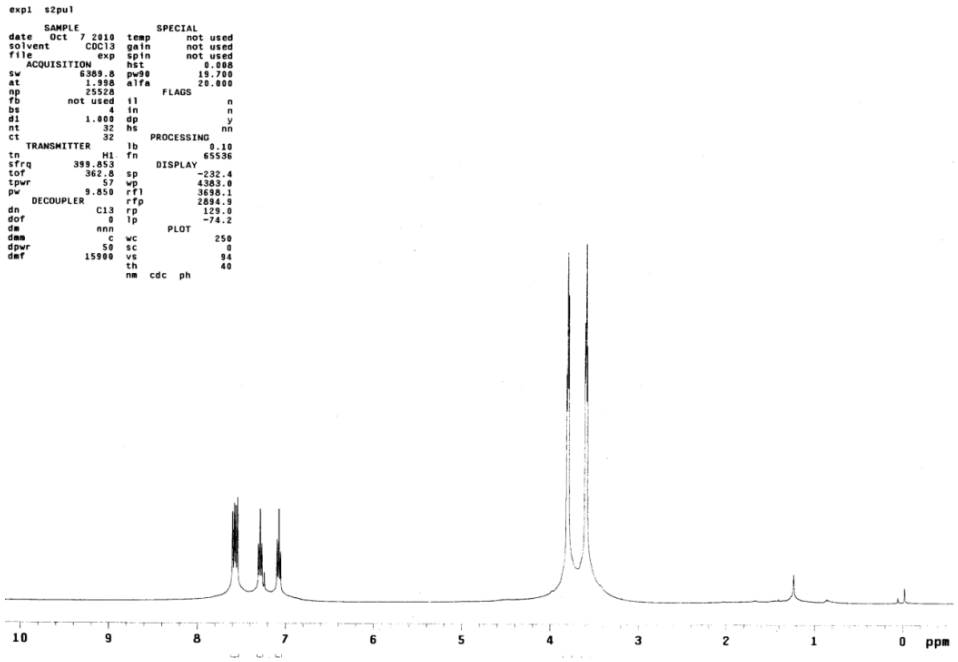
6-Fluoro-2-morpholinobenzo[*d*]thiazole (13a):



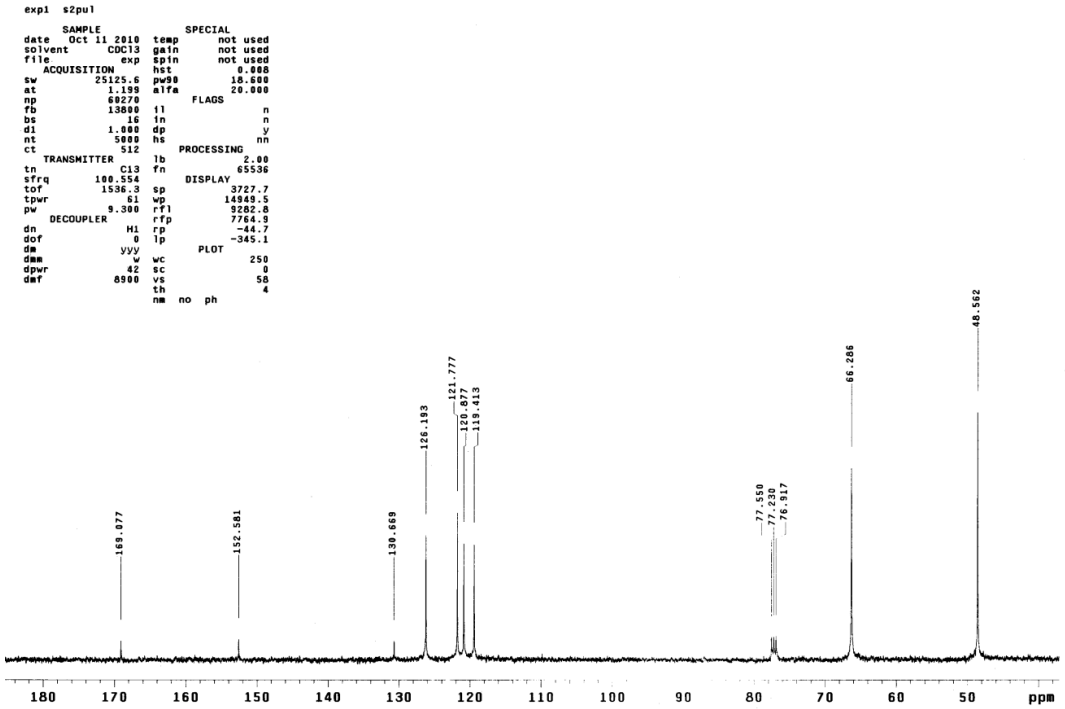
White solid; M.p. 157–158 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.51 (t, 4H, *J* = 4.8 Hz), 3.75 (t, 1H, *J* = 4.4 Hz), 6.97 (m, 1H), 7.25 (m, 1H), 7.44 (m, 1H); ^{13}CNMR (100 MHz, $CDCl_3$): δ (ppm) 48.4, 66.2, 107.4, 107.7, 113.7, 113.9, 119.7, 119.8, 131.3, 131.4, 148.9, 157.0, 159.4, 168.6; IR (KBr): 2982, 2901, 2863, 1673, 1597, 1538, 1459, 1376, 1343, 1287, 1234, 1181, 1111, 1073, 1029, 948, 920, 844 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{11}N_2OSF$ $(M+H)^+$ 239.0655; found 239.0651.

Spectra

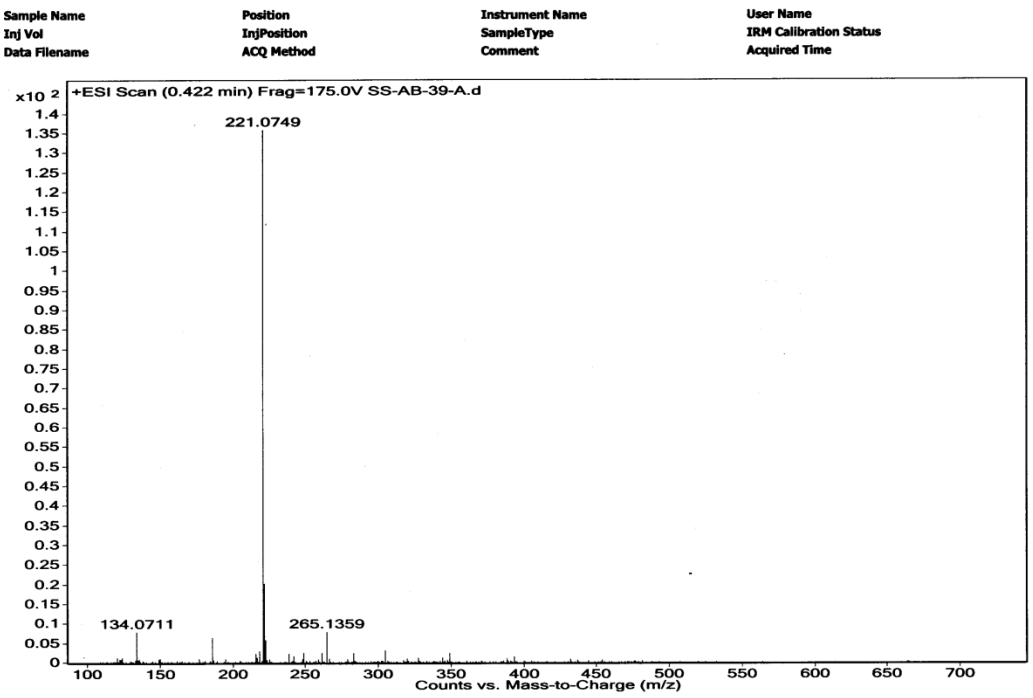
2-Morpholinobenzo[*d*]thiazole (1a): ^{1}H NMR (400 MHz, $CDCl_3$):



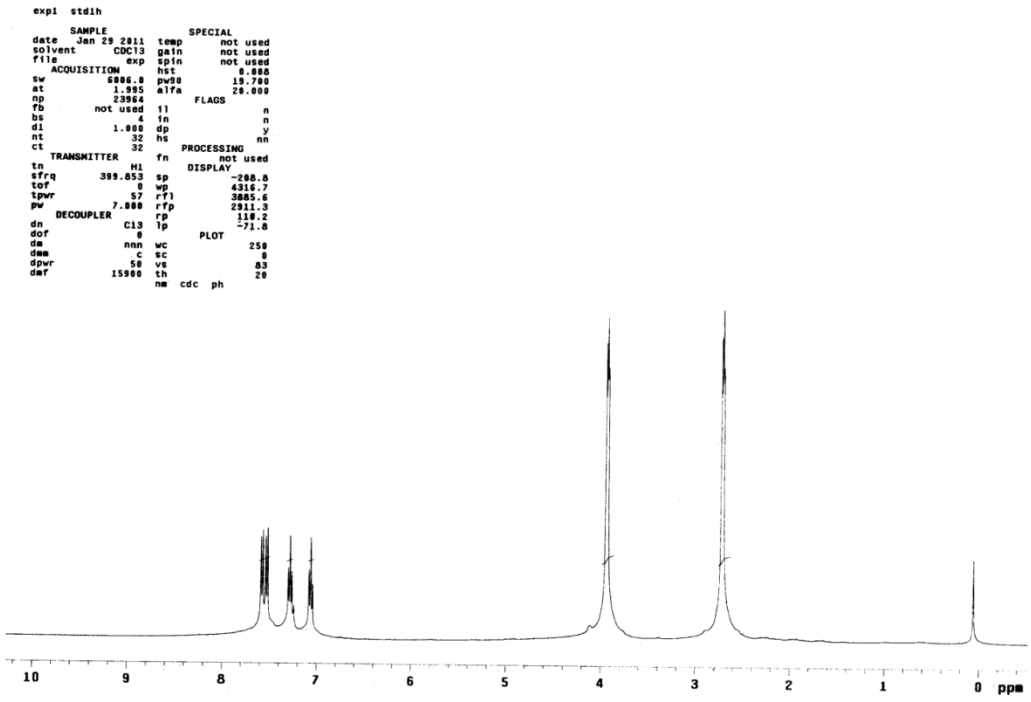
2-Morpholinobenzo[*d*]thiazole (1a):^{13}C NMR (100 MHz, $CDCl_3$):



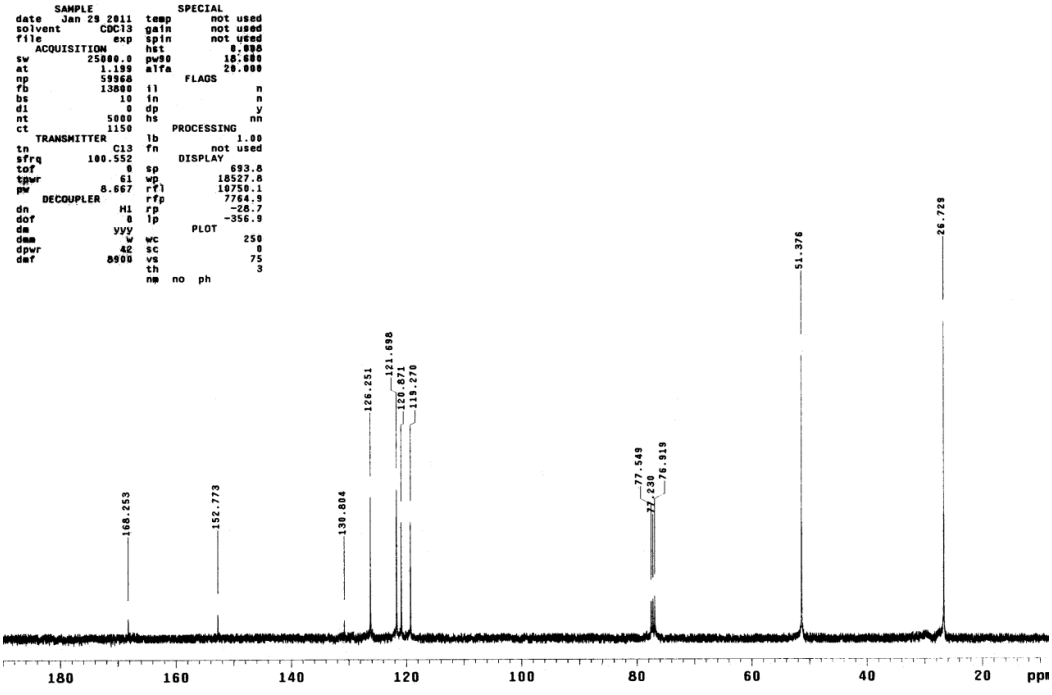
2-Morpholinobenzo[*d*]thiazole (1a): MASS SPECTRA:



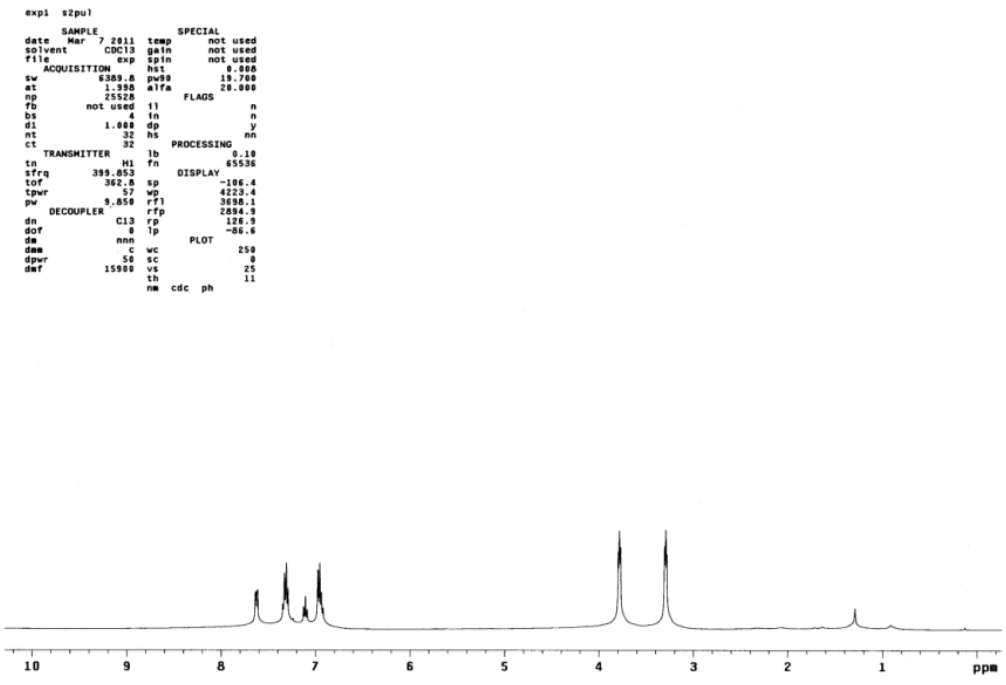
2-Thiomorpholinobenzo[*d*]thiazole (1b): ^{1}H NMR (400 MHz, $CDCl_3$):



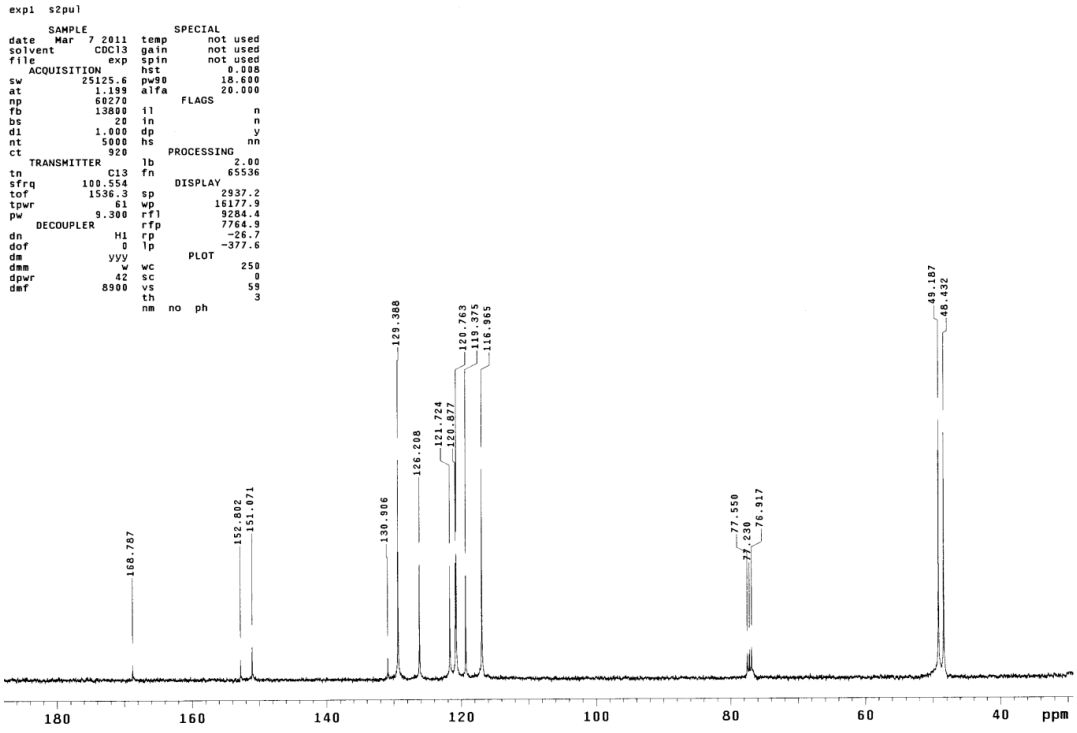
2-Thiomorpholinobenzo[*d*]thiazole (1b): ^{13}C NMR (100 MHz, $CDCl_3$):



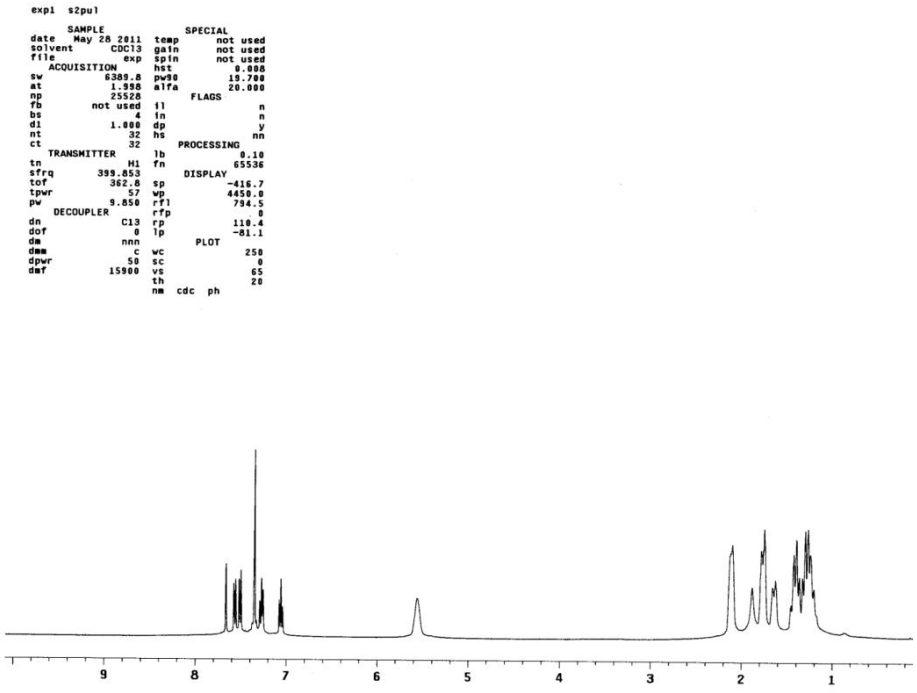
2-(4-Phenylpiperazine-1-yl)benzo[d]thiazole (1c): ^{1}H NMR (400 MHz, $CDCl_3$):



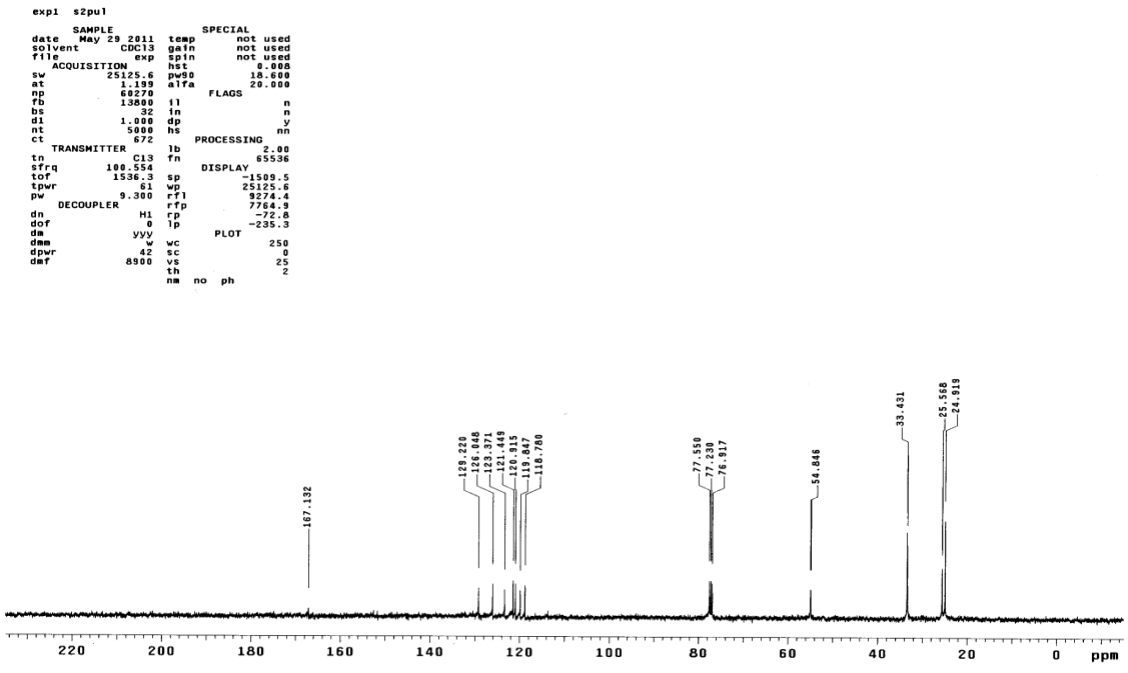
2-(4-Phenylpiperazine-1-yl)benzo[d]thiazole (1c): ^{13}C NMR (100 MHz, $CDCl_3$):



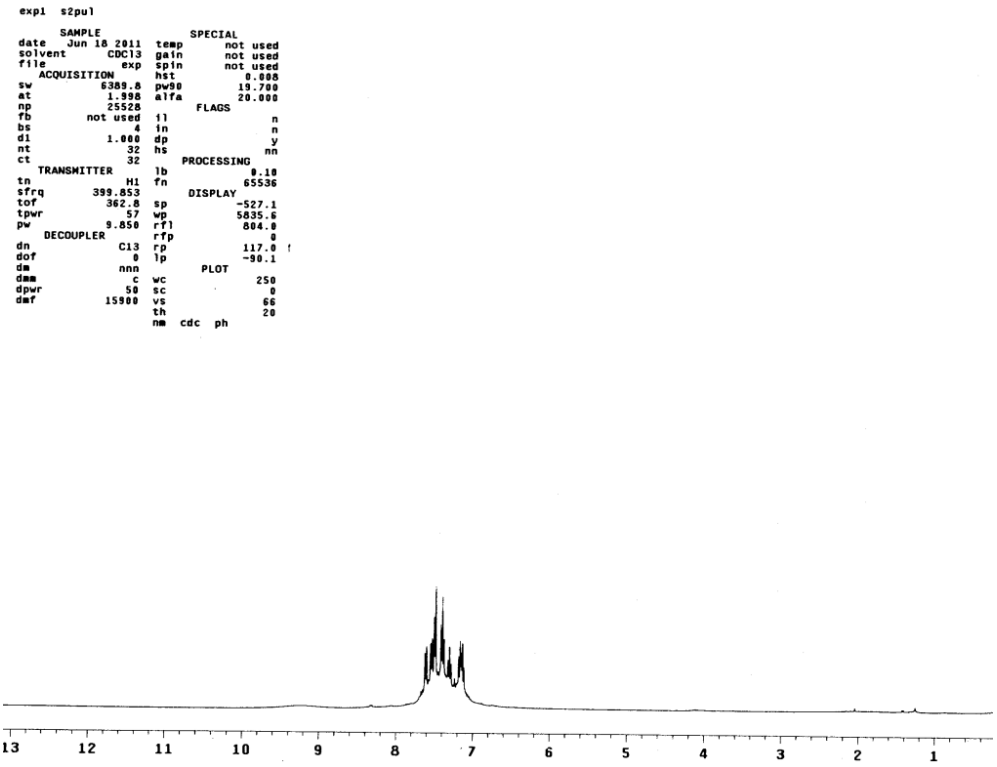
Benzothiazol-2-yl-cyclohexyl-amine (1d): ^{1}H NMR (400 MHz, $CDCl_3$):



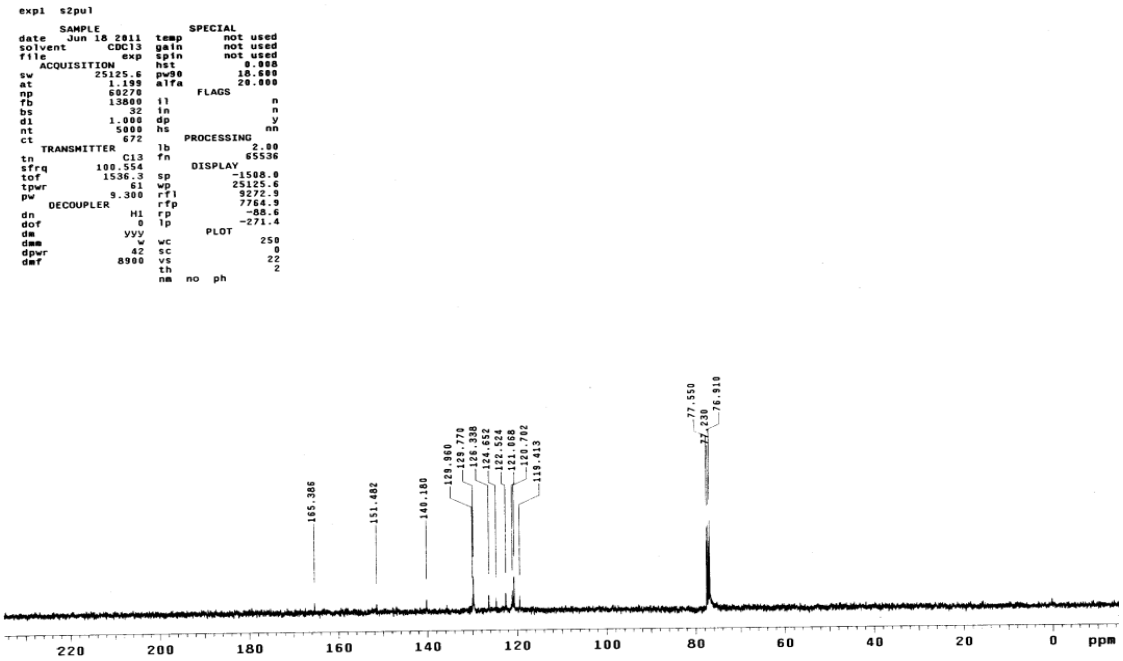
Benzothiazol-2-yl-cyclohexyl-amine (1d): ^{13}C NMR (100 MHz, $CDCl_3$):



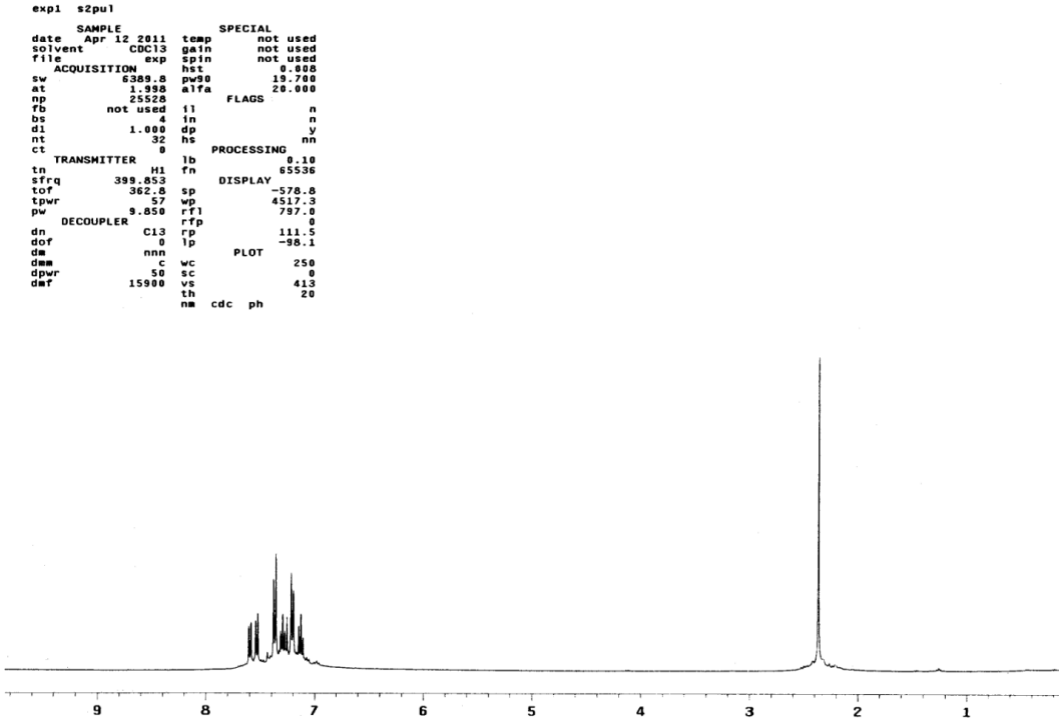
***N*-Phenylbenzo[d]thiazol-2-amine (1e): ^{1}H NMR (400 MHz, $CDCl_3$):**



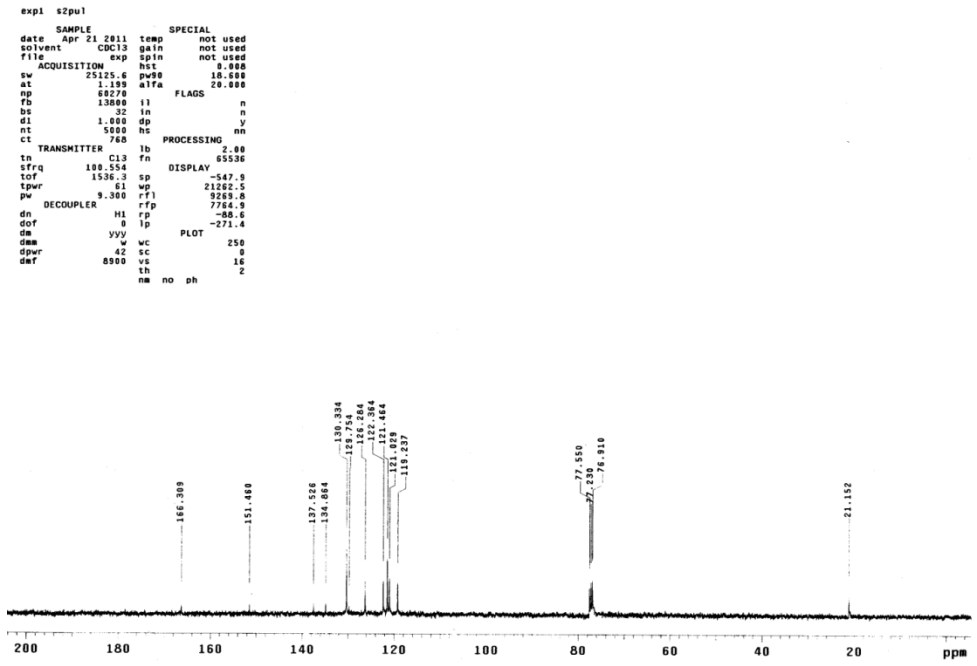
***N*-Phenylbenzo[d]thiazol-2-amine (1e): ^{13}C NMR (100 MHz, $CDCl_3$):**



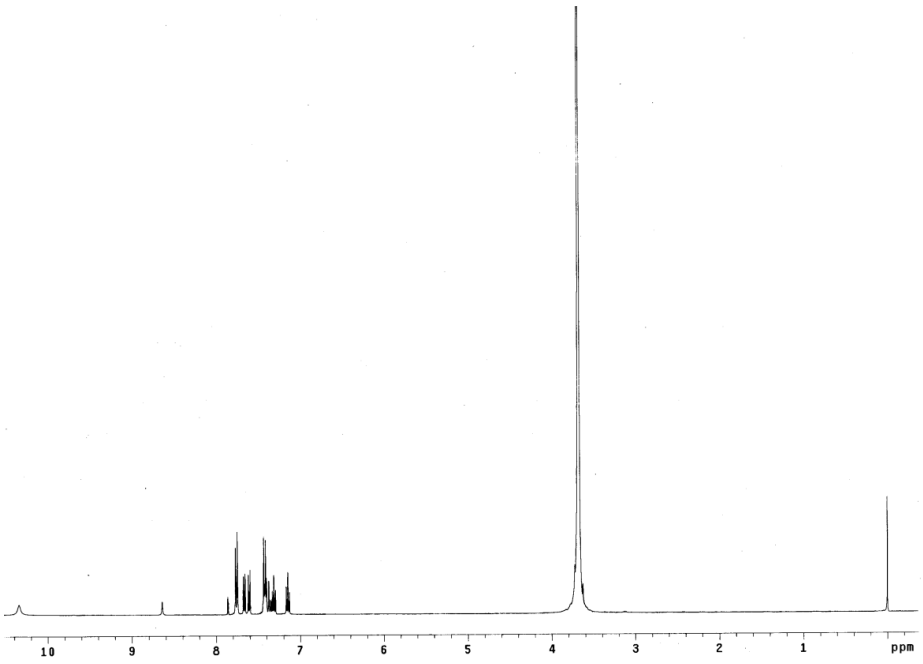
Benzothiazol-2-yl-p-tolyl-amine (1f): ^{1}H NMR (400 MHz, $CDCl_3$):



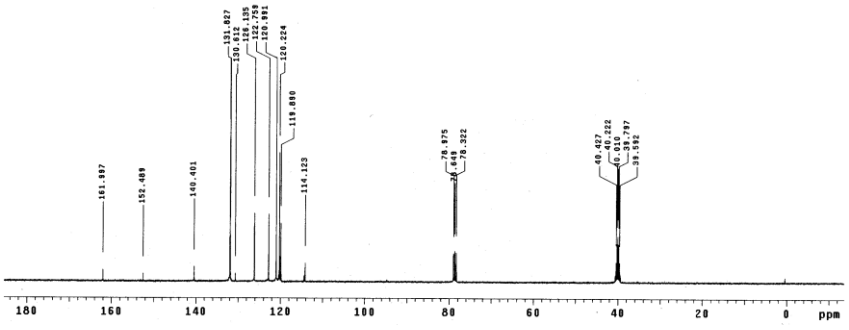
Benzothiazol-2-yl-*p*-tolyl-amine (1f): ^{13}C NMR (100 MHz, $CDCl_3$):



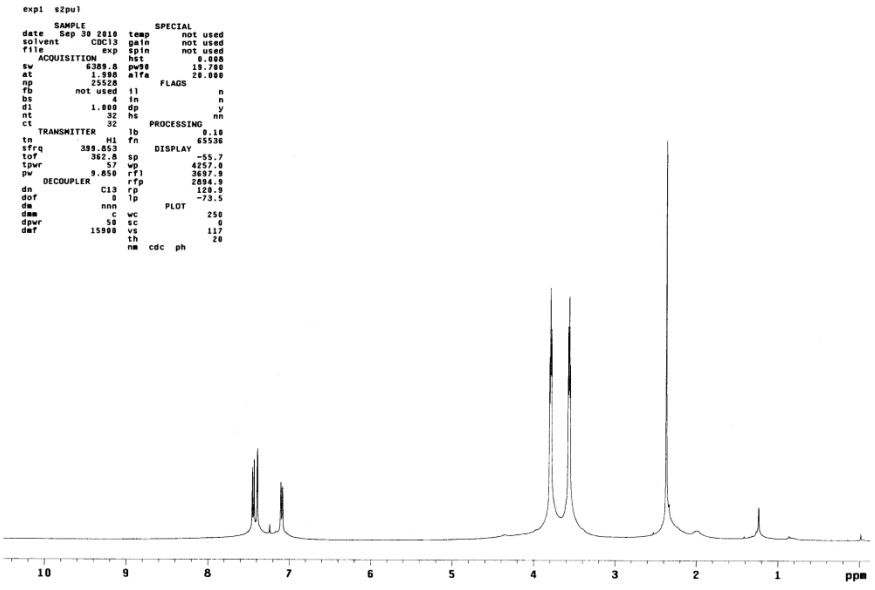
Benzothiazol-2-yl-(4-bromo-phenyl)-amine (1g): ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6)



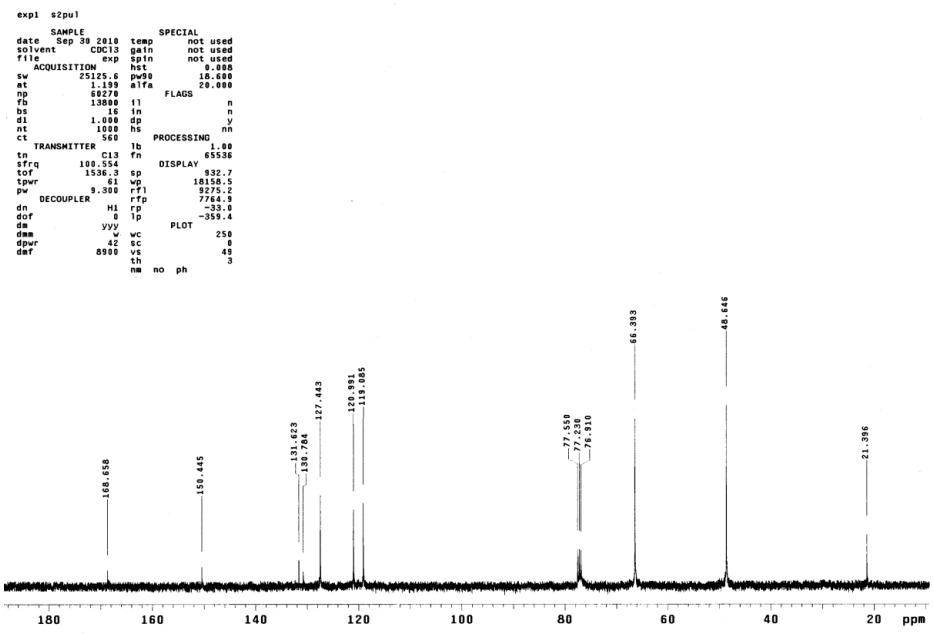
Benzothiazol-2-yl-(4-bromo-phenyl)-amine (1g): ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6)



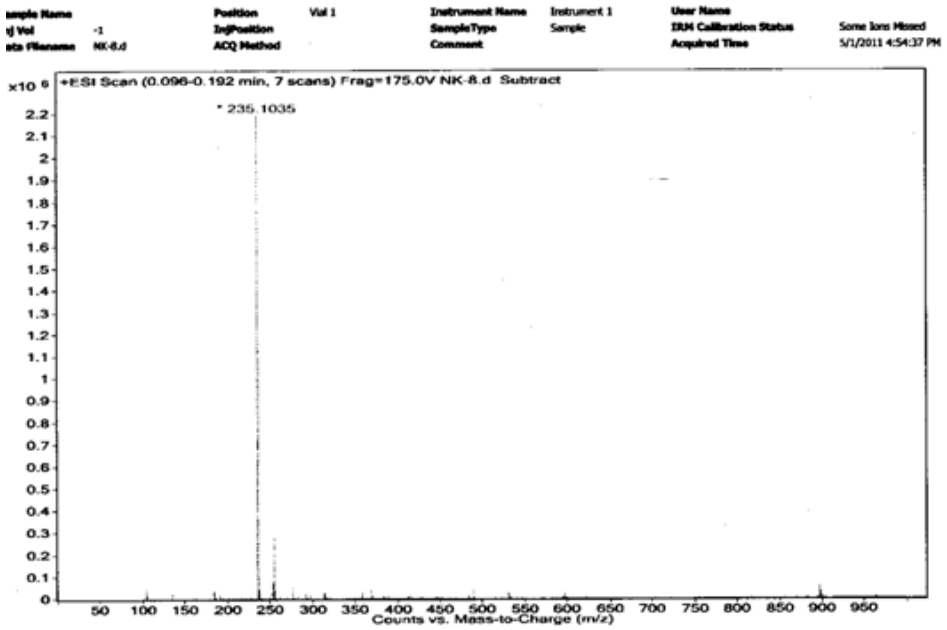
6-Methyl-2-morpholinobenzo[*d*]thiazole (2a): ^{1}H NMR (400 MHz, $CDCl_3$):



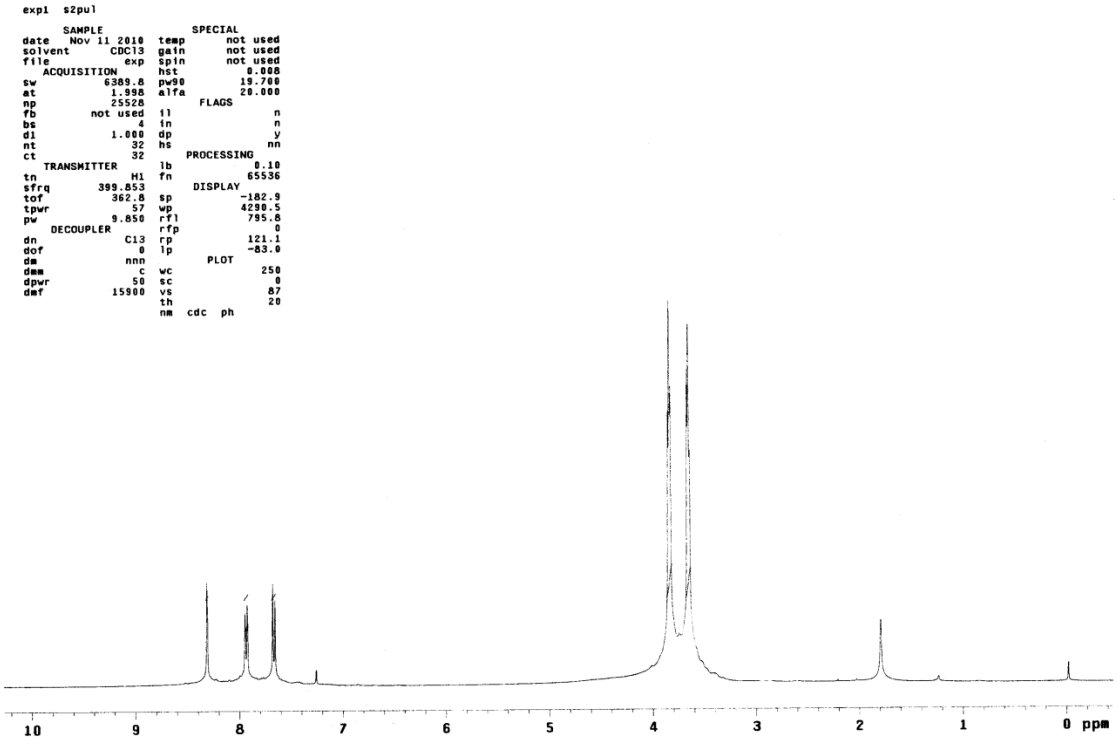
6-Methyl-2-morpholinobenzo[*d*]thiazole (2a): ^{13}C NMR (100 MHz, $CDCl_3$):



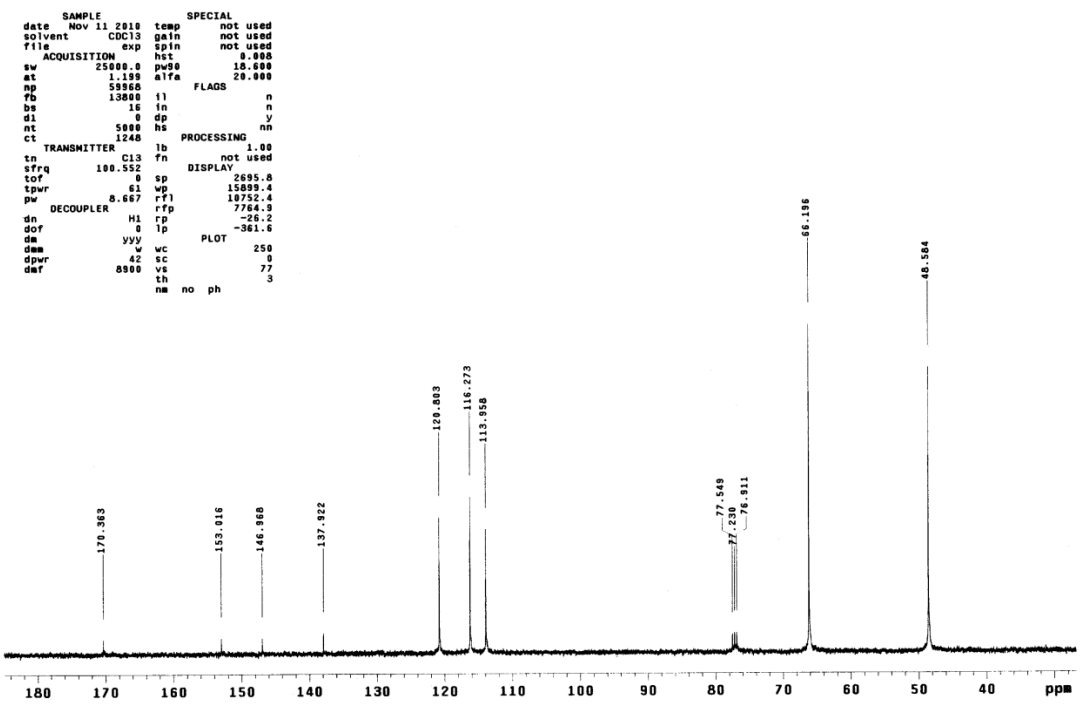
6-Methyl-2-morpholinobenzo[*d*]thiazole (2a): MASS SPECTRA:



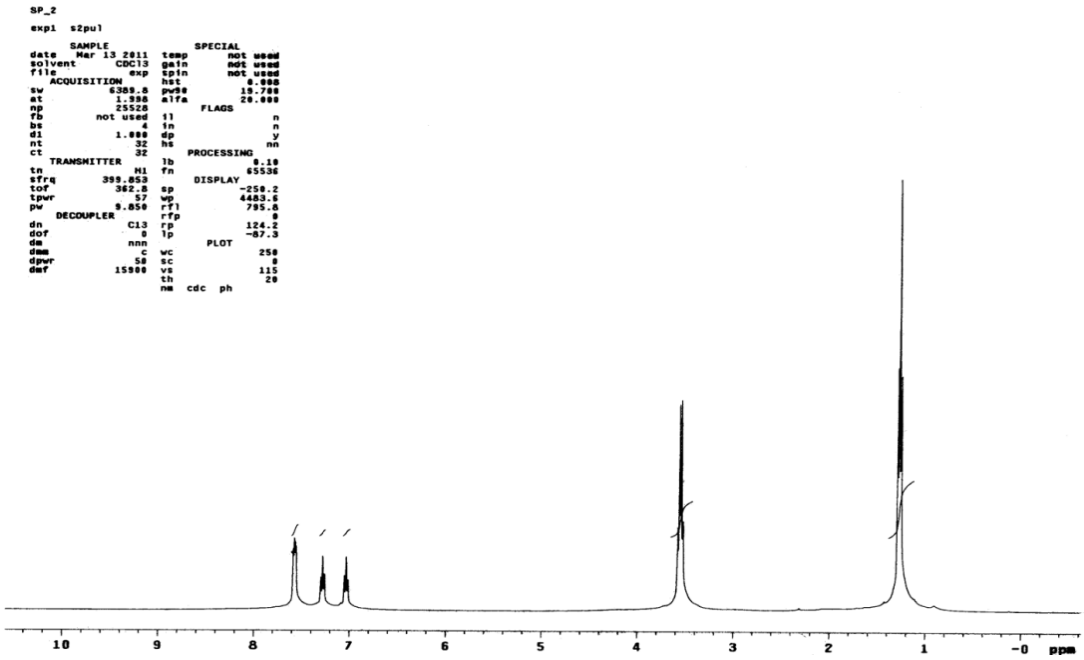
2-Morpholino-5-nitrobenzo[d]thiazole (3a): ^{1}H NMR (400 MHz, $CDCl_3$):



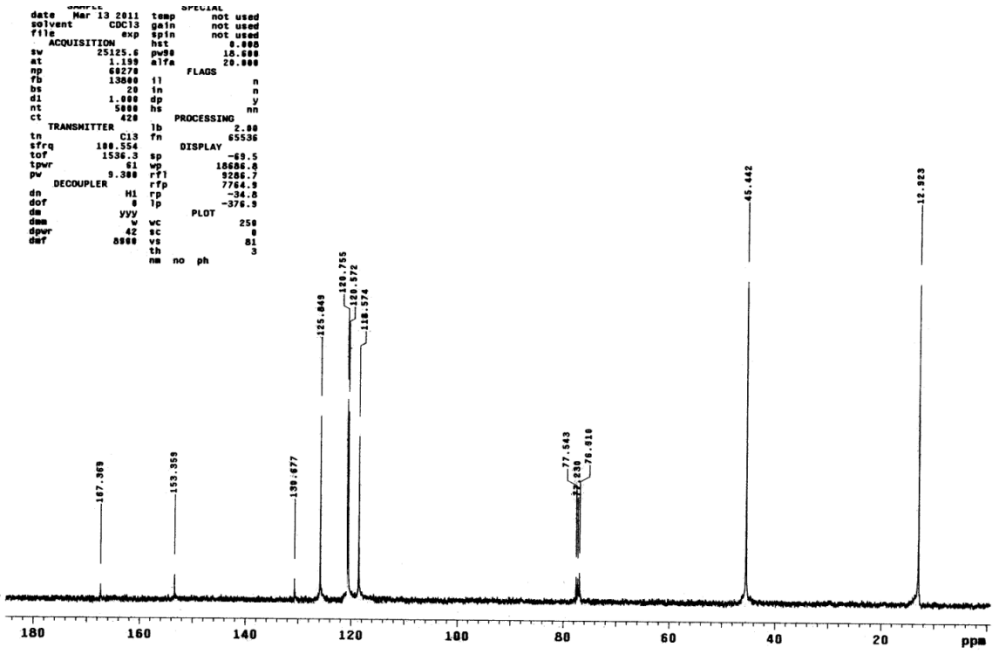
2-Morpholino-5-nitrobenzo[d]thiazole (3a): ^{13}C NMR (100 MHz, $CDCl_3$):



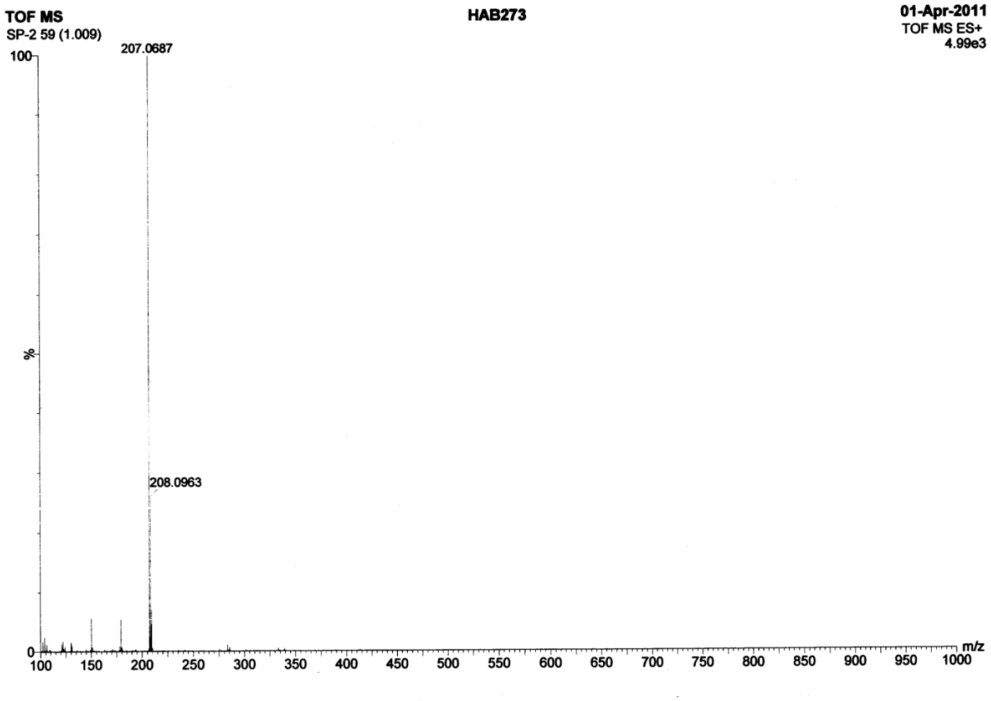
***N*,*N*-Diethylbenzo[d]thiazol-2-amine (4h): ^{1}H NMR (400 MHz, $CDCl_3$):**



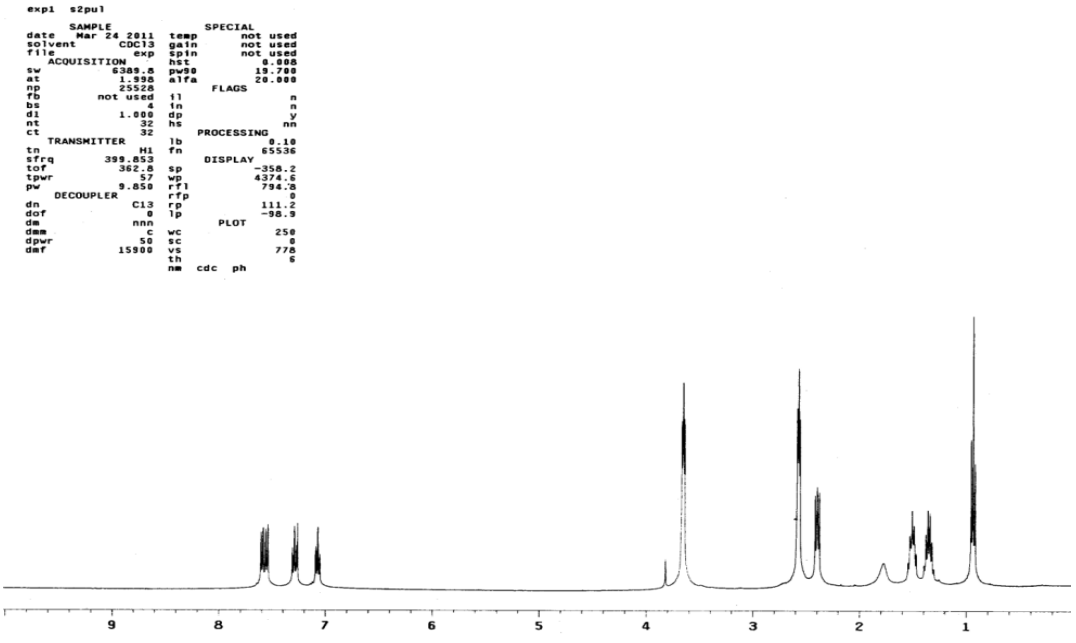
***N*,*N*-Diethylbenzo[d]thiazol-2-amine (4h): ^{13}C NMR (100 MHz, $CDCl_3$):**



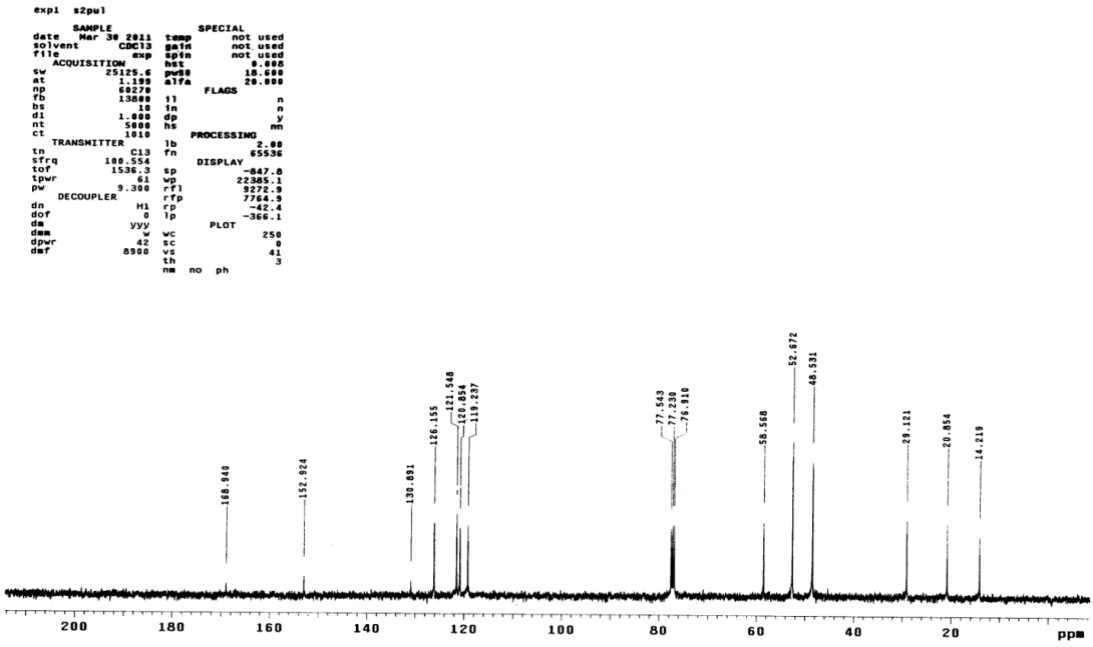
_N,N_-Diethylbenzo[d]thiazol-2-amine (4h): MASS SPECTRA:



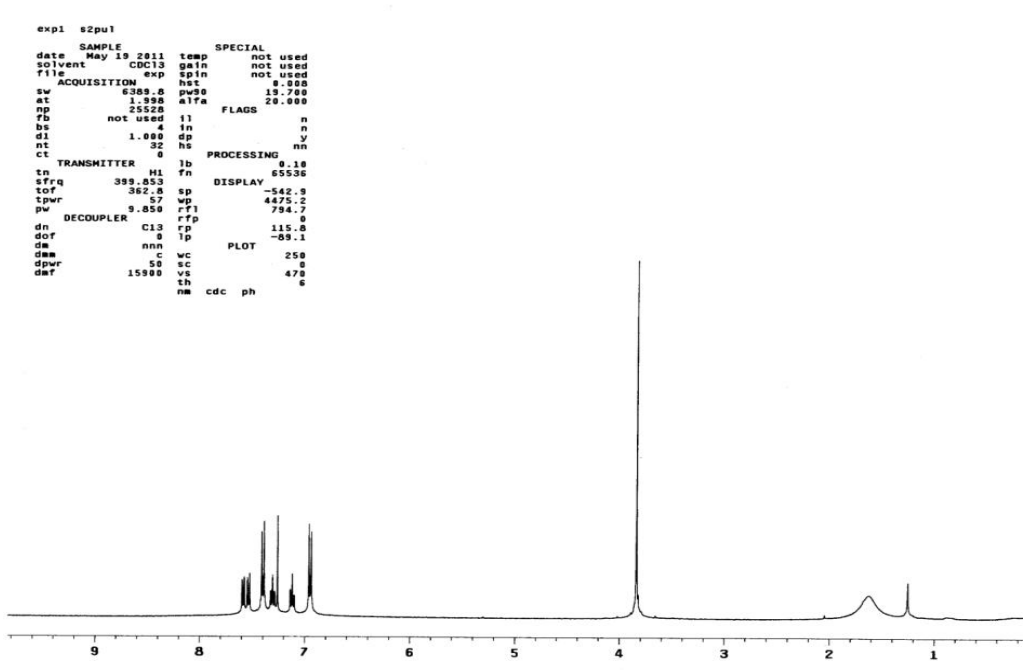
2-(4-Butylpiperazin-1-yl)benzo[d]thiazole (4i): ^{1}H NMR (400 MHz, $CDCl_3$):



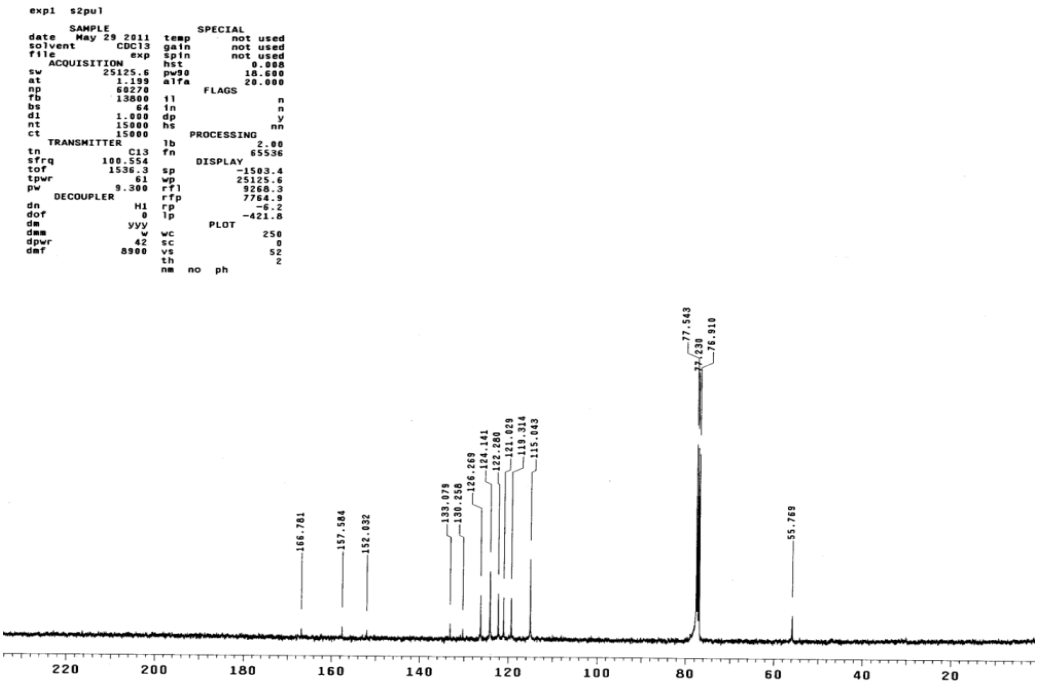
2-(4-Butylpiperazin-1-yl)benzo[d]thiazole (4i): ^{13}C NMR (100 MHz, $CDCl_3$):



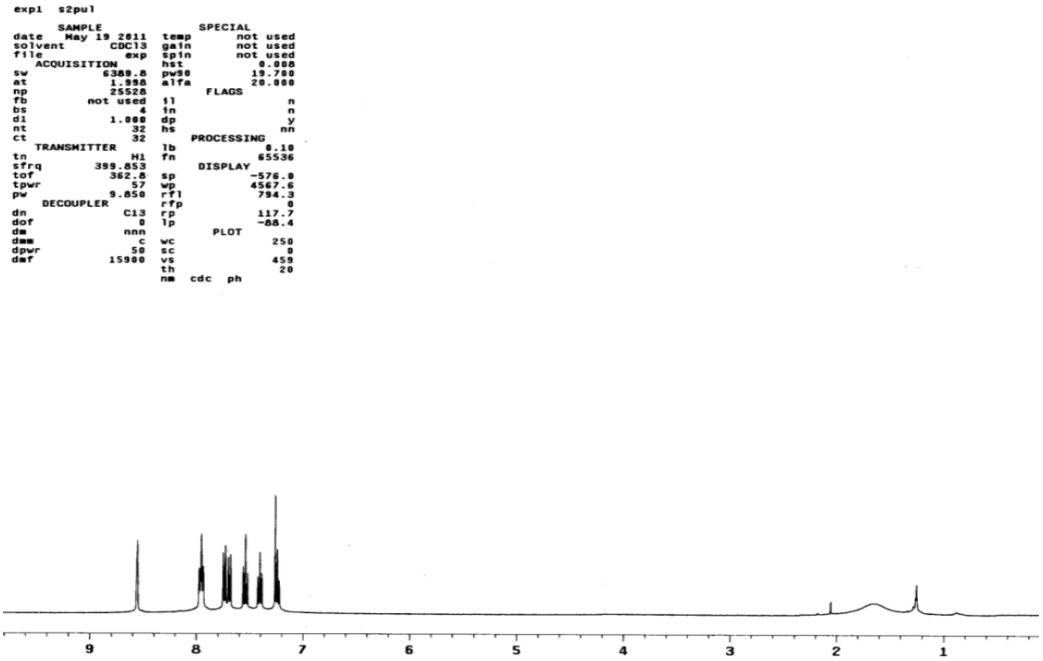
Benzothiazol-2-yl-(4-methoxy-phenyl)-amine (4j): ^{1}H NMR (400 MHz, $CDCl_3$):



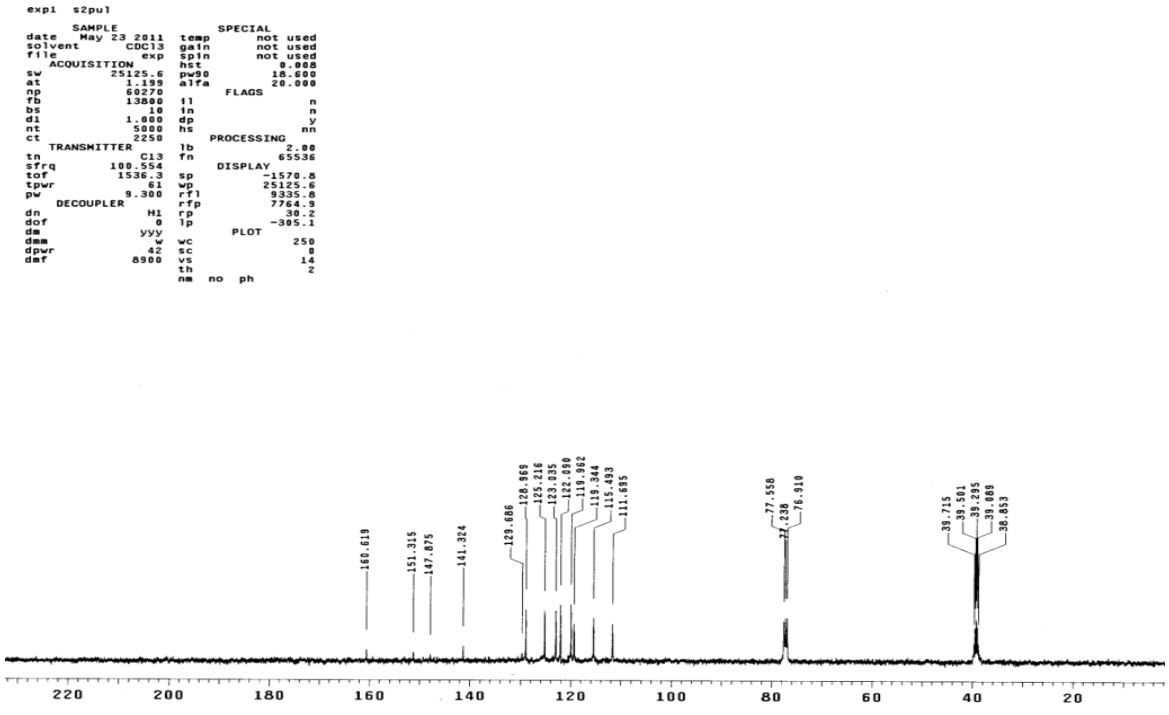
Benzothiazol-2-yl-(4-methoxy-phenyl)-amine (4j): ^{13}C NMR (100 MHz, $CDCl_3$):



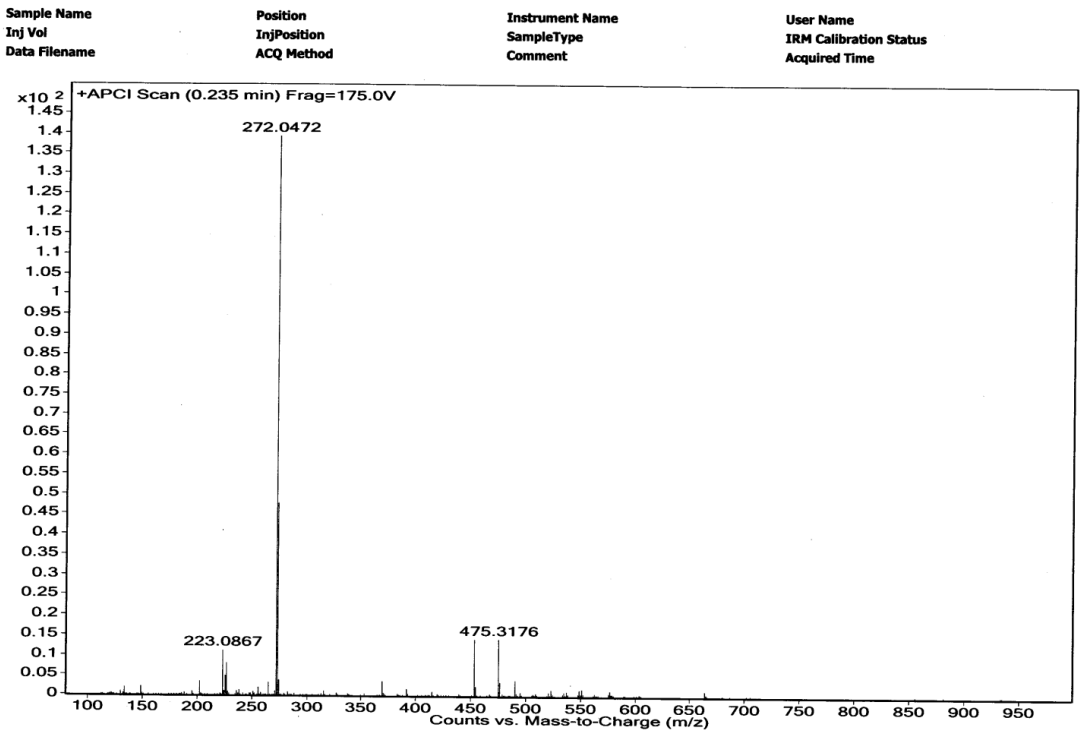
***N*-(3-Nitrophenyl)benzo[d]thiazol-2-amine (4k): ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6):**



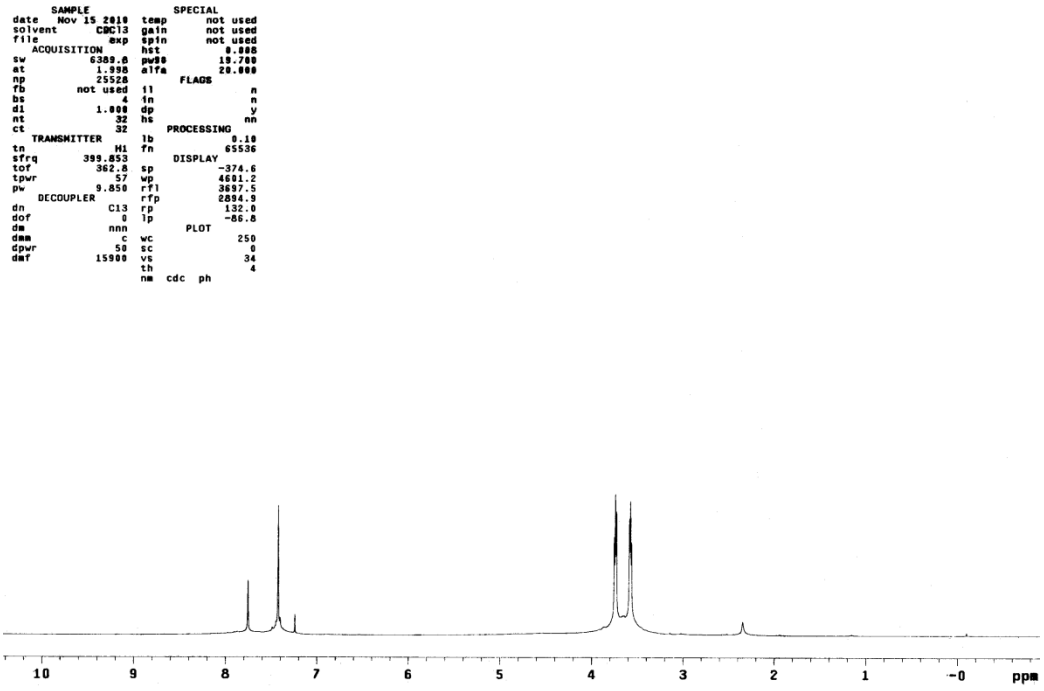
***N*-(3-Nitrophenyl)benzo[d]thiazol-2-amine (4k): ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6):**



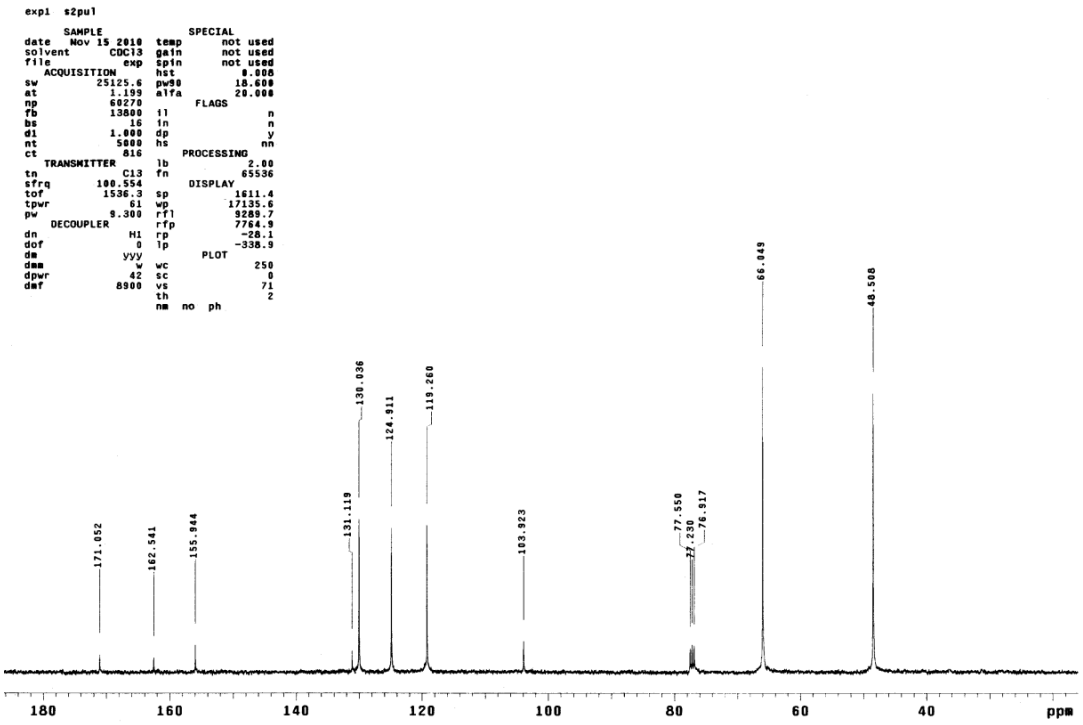
***N*-(3-Nitrophenyl)benzo[d]thiazol-2-amine (4k): MASS SPECTRA**



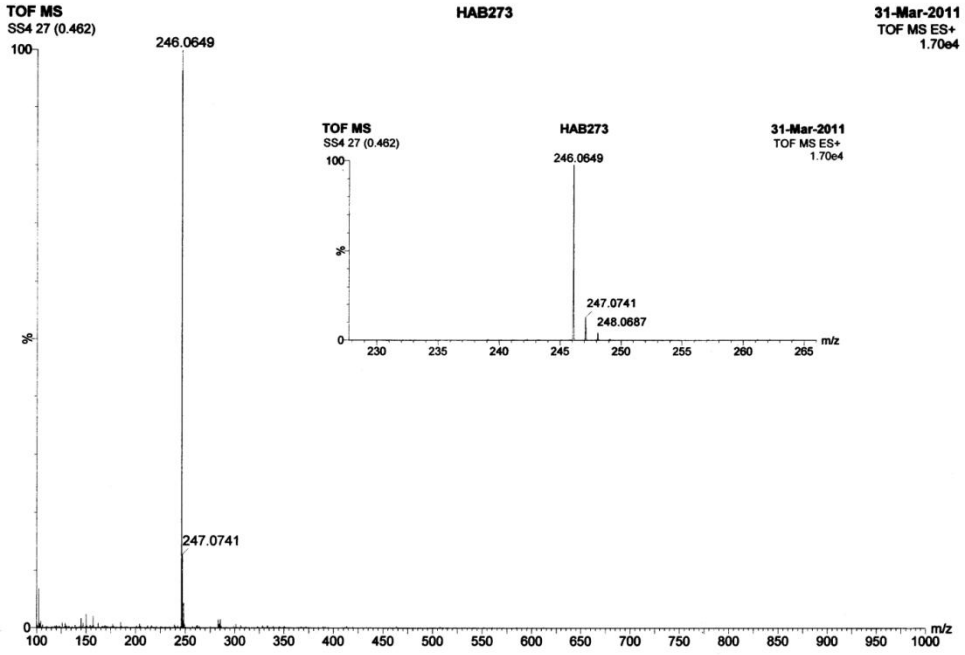
2-Morpholinobenzo[d]thiazole-6-carbonitrile (6a): ^{1}H NMR (400 MHz, $CDCl_3$):



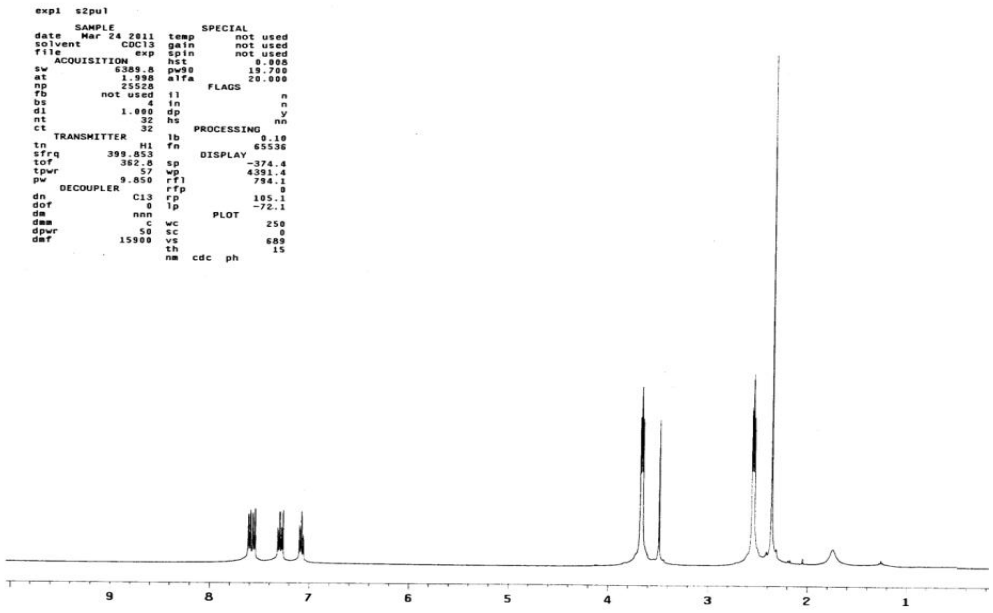
2-Morpholinobenzo[d]thiazole-6-carbonitrile (6a): ^{1}C NMR (100 MHz, $CDCl_3$):



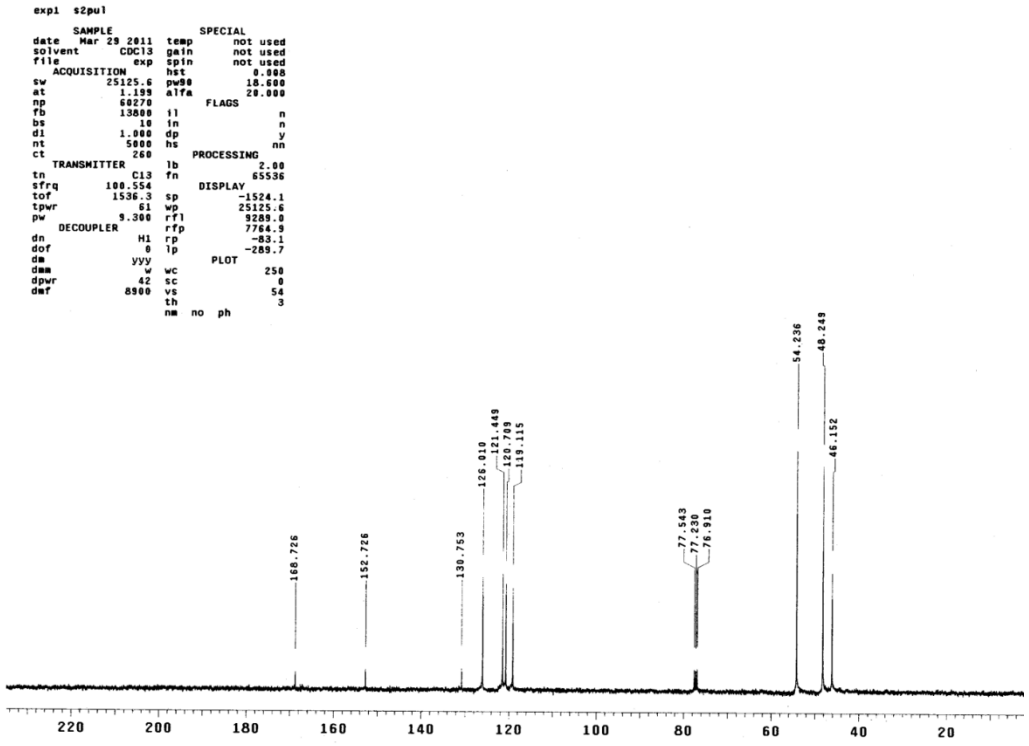
2-Morpholinobenzo[d]thiazole-6-carbonitrile (6a): MASS SPECTRA



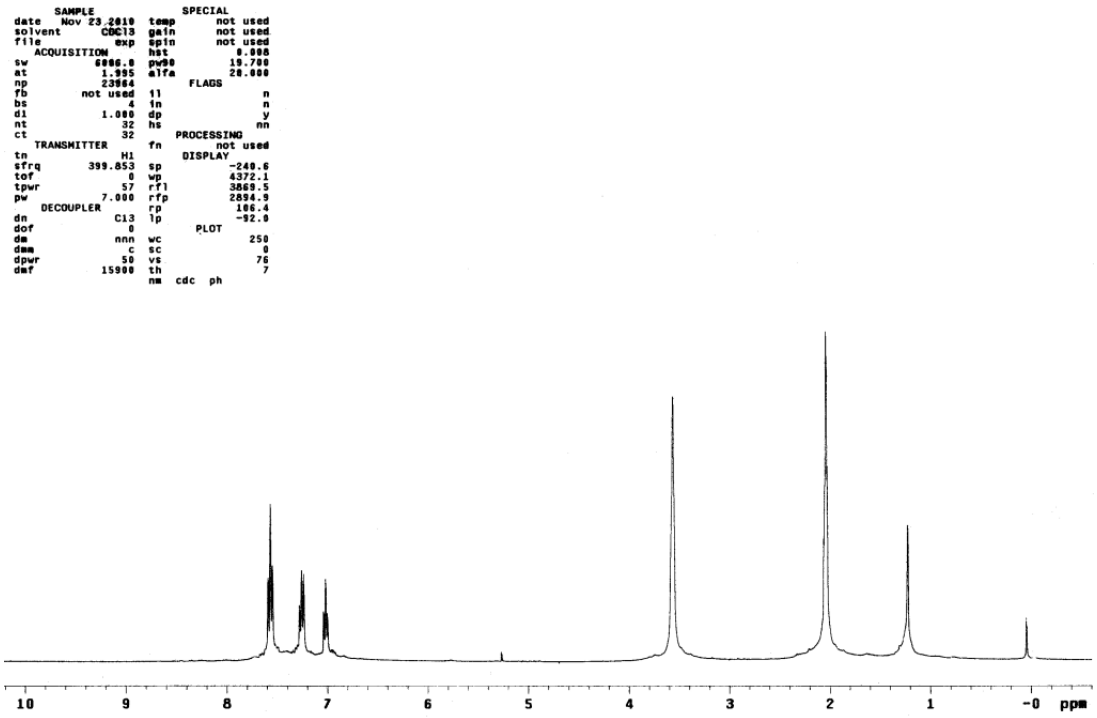
2-(4-Methylpiperazin-1-yl)benzo[d]thiazole (7l): ^{1}H NMR (400 MHz, $CDCl_3$):



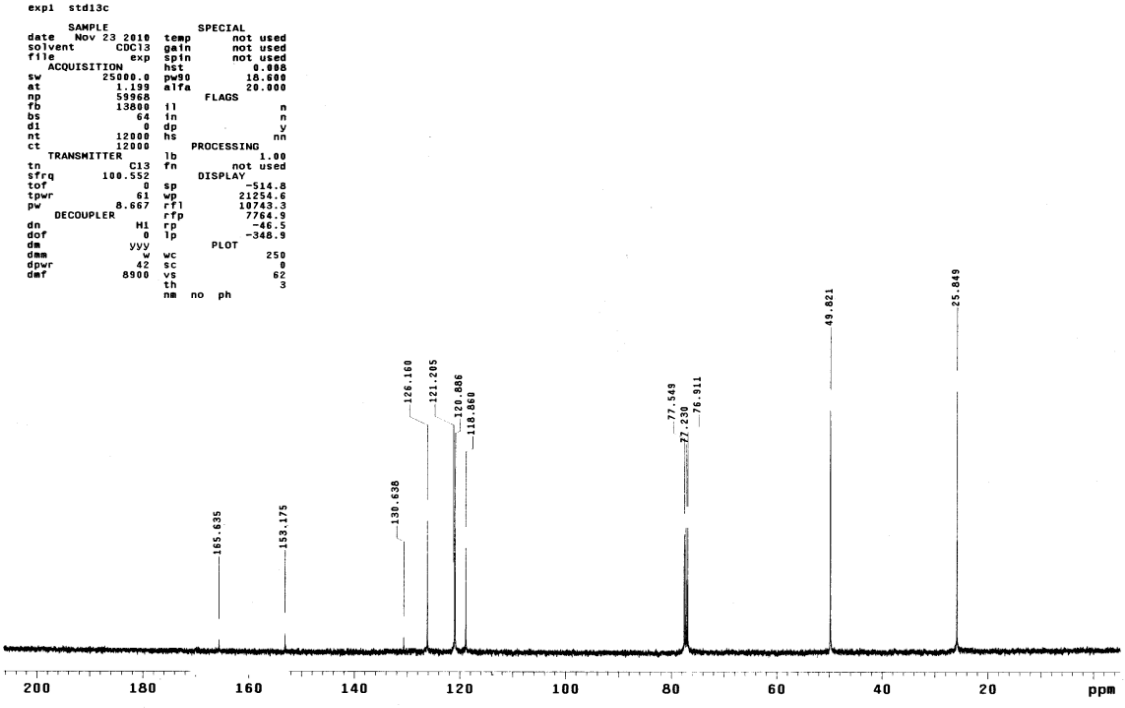
2-(4-Methylpiperazin-1-yl)benzo[d]thiazole (7l): ^{13}C NMR (100 MHz, $CDCl_3$):



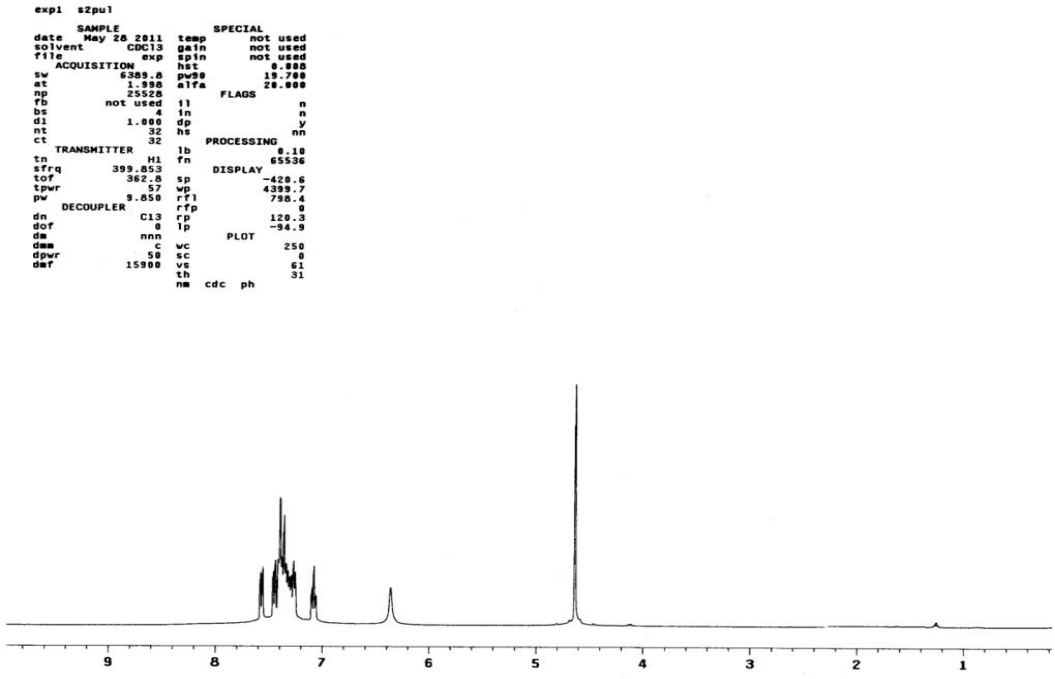
2-(Pyrrolidin-1-yl)benzo[*d*]thiazole (7m): ^{1}H NMR (400 MHz, $CDCl_3$):



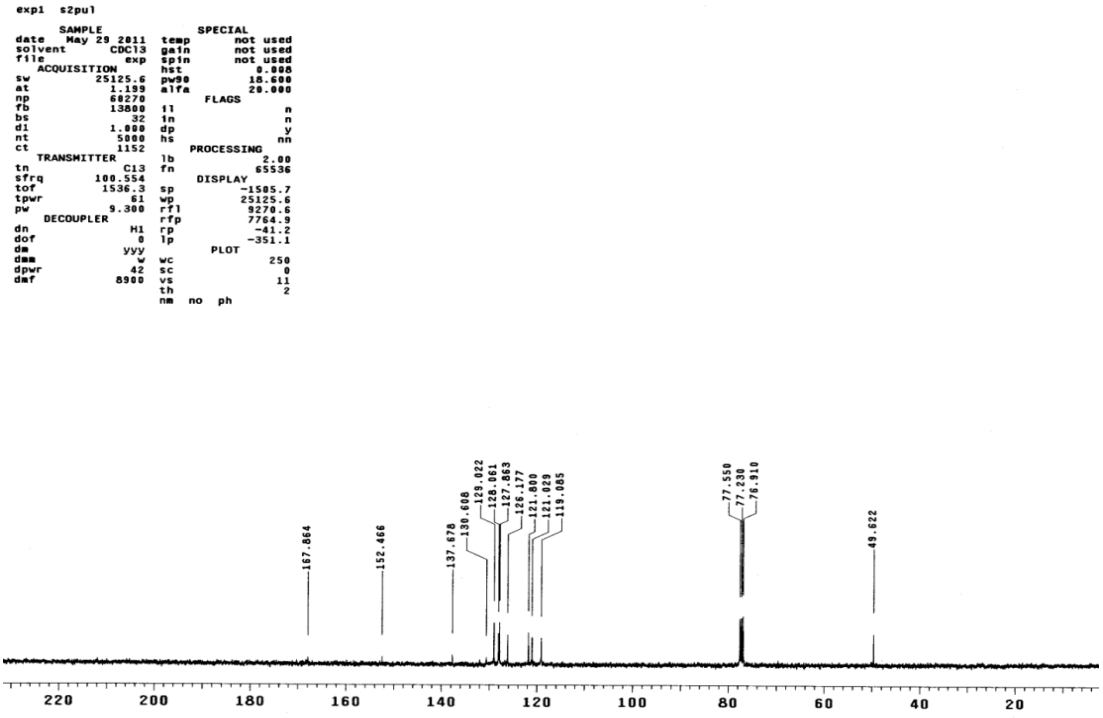
2-(Pyrrolidin-1-yl)benzo[*d*]thiazole (7m): ^{13}C NMR (100 MHz, $CDCl_3$):



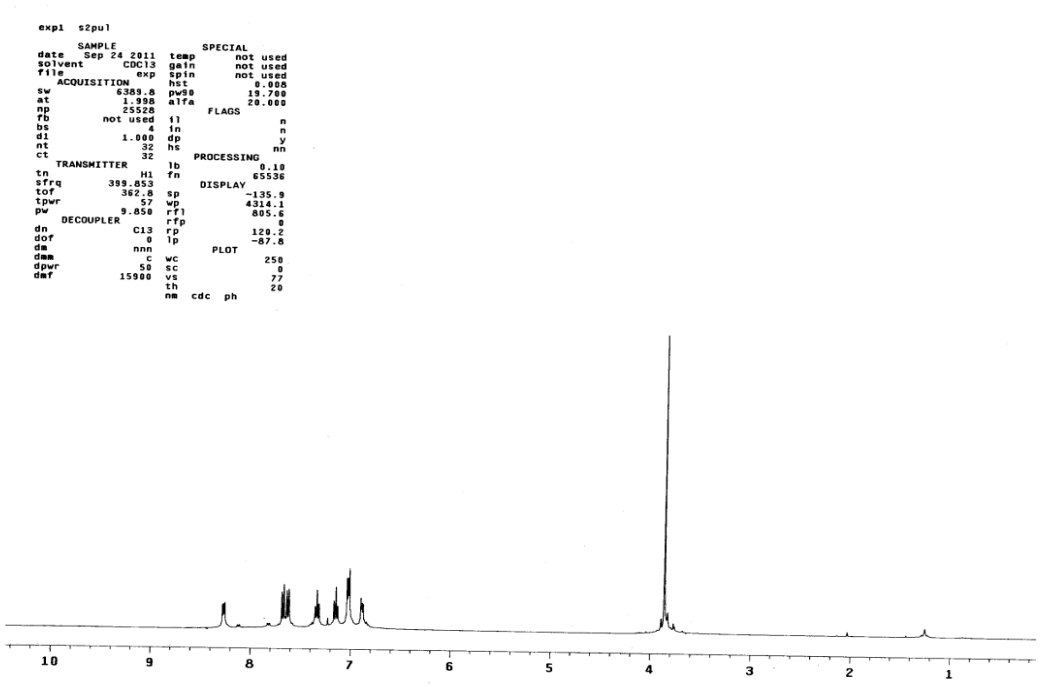
***N*-Benzylbenzo[d]thiazol-2-amine (7n): ^{1}H NMR (400 MHz, $CDCl_3$):**



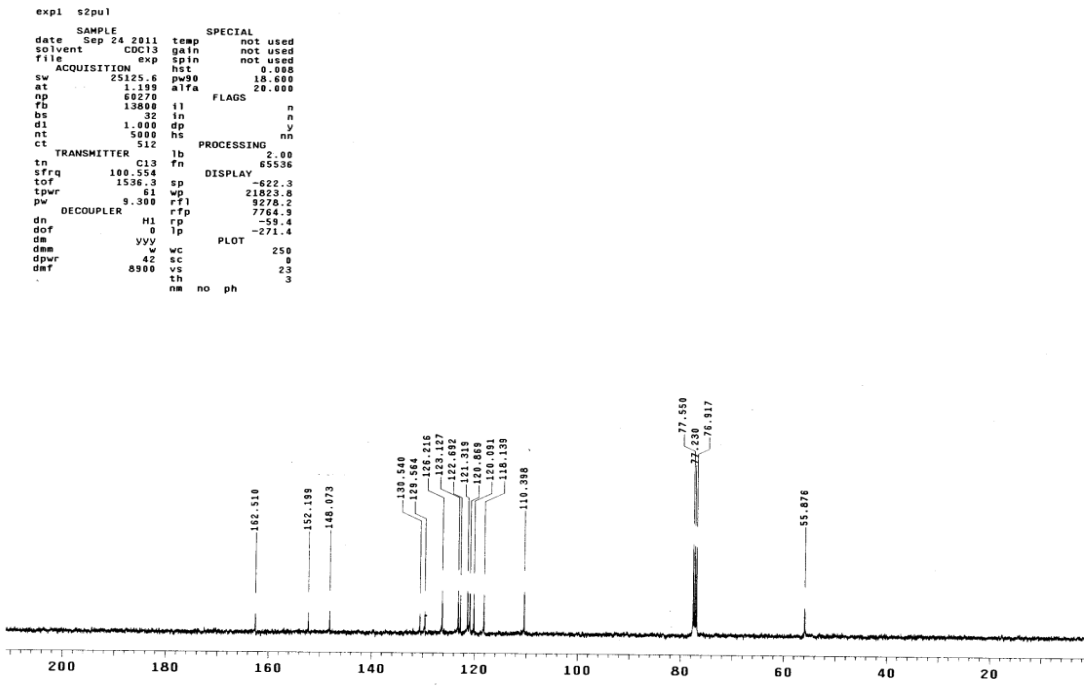
***N*-Benzylbenzo[d]thiazol-2-amine (7n): ^{13}C NMR (100 MHz, $CDCl_3$):**



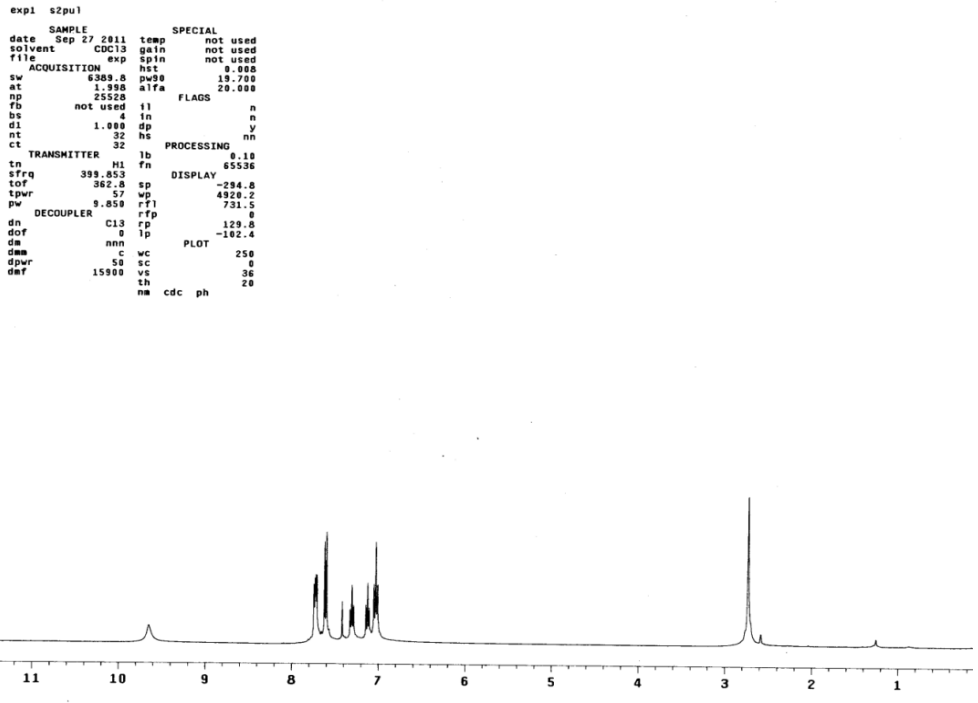
***N*-(2-Methoxyphenyl)benzo[d]thiazol-2-amine (7o): ^{1}H NMR (400 MHz, $CDCl_3$):**



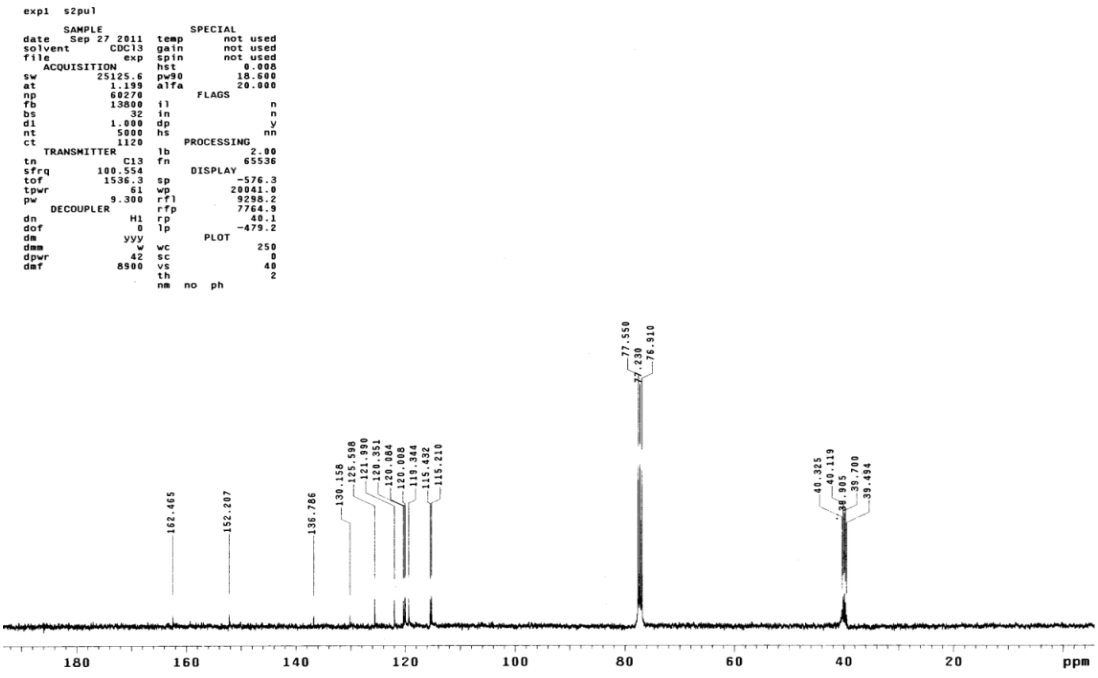
***N*-(2-Methoxyphenyl)benzo[d]thiazol-2-amine (7o): ^{13}C NMR (100 MHz, $CDCl_3$):**



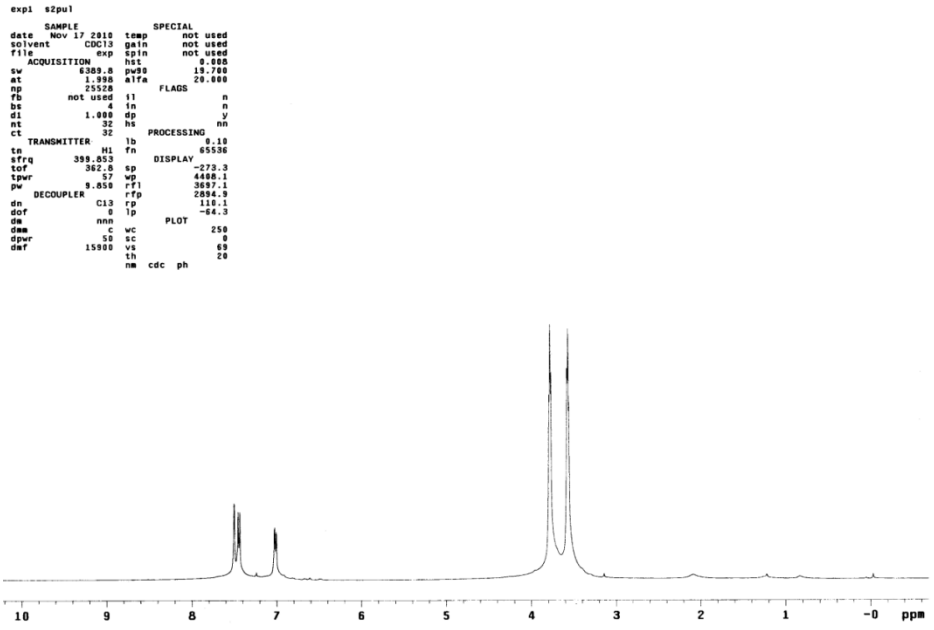
***N*-(4-Fluorophenyl)benzo[d]thiazol-2-amine (7p): ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6):**



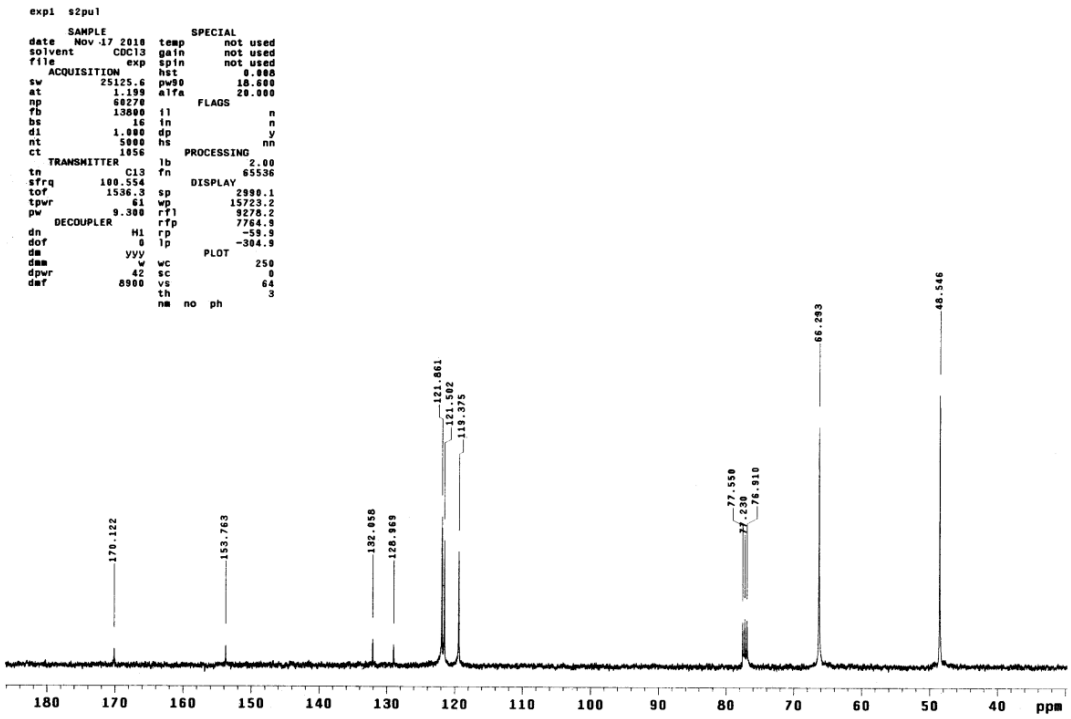
***N*-(4-Fluorophenyl)benzo[d]thiazol-2-amine (7p): ^{13}C NMR (400 MHz, $CDCl_3$+ DMSO-d_6):**



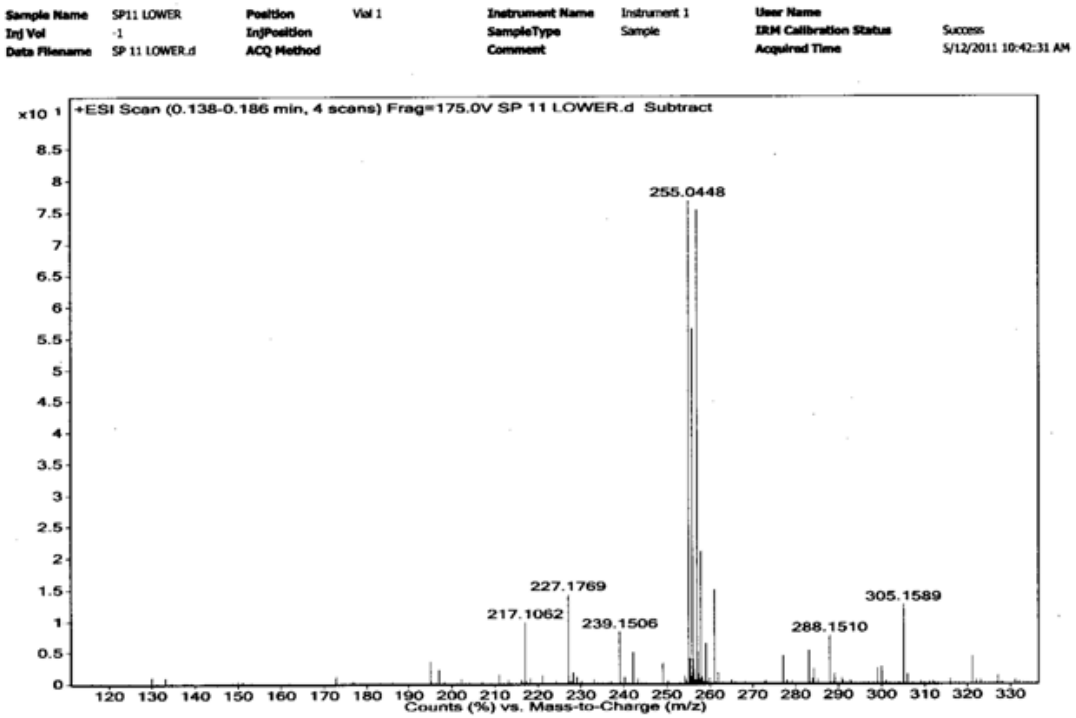
6-Chloro-2-morpholinobenzo[*d*]thiazole (9a): ^{1}H NMR (400 MHz, $CDCl_3$):



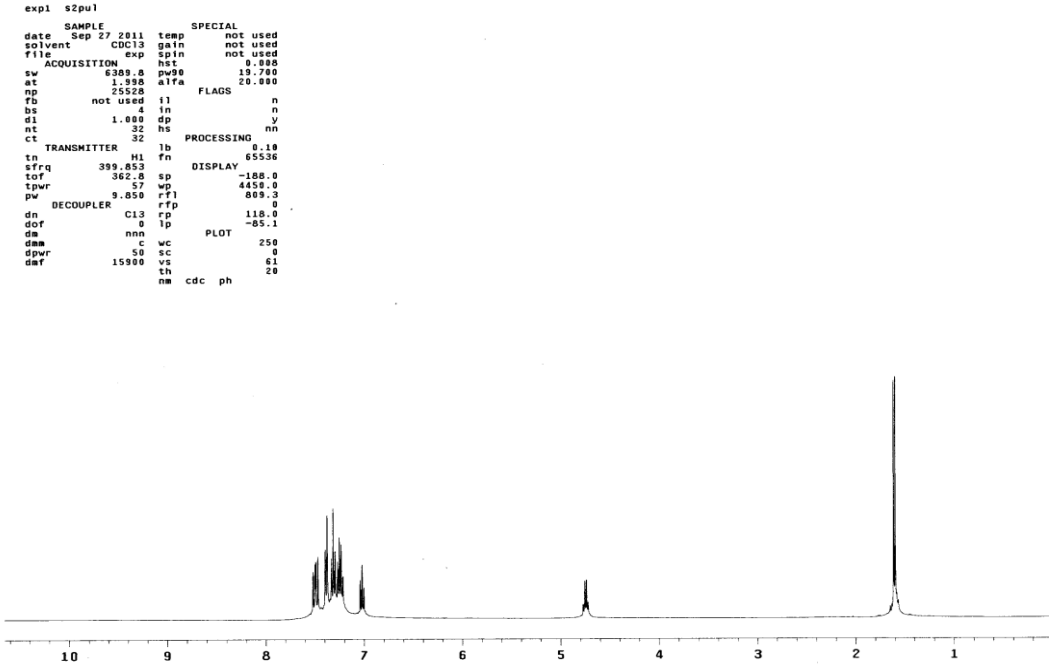
6-Chloro-2-morpholinobenzo[*d*]thiazole (9a): ^{13}C NMR (100 MHz, $CDCl_3$):



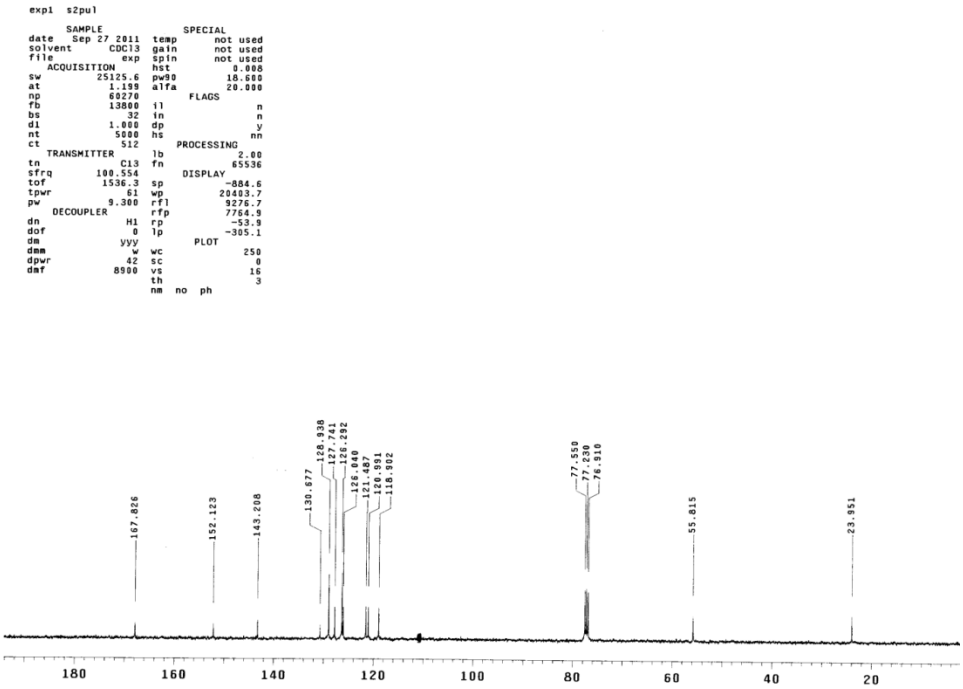
6-Chloro-2-morpholinobenzo[*d*]thiazole (9a): MASS SPECTRA:



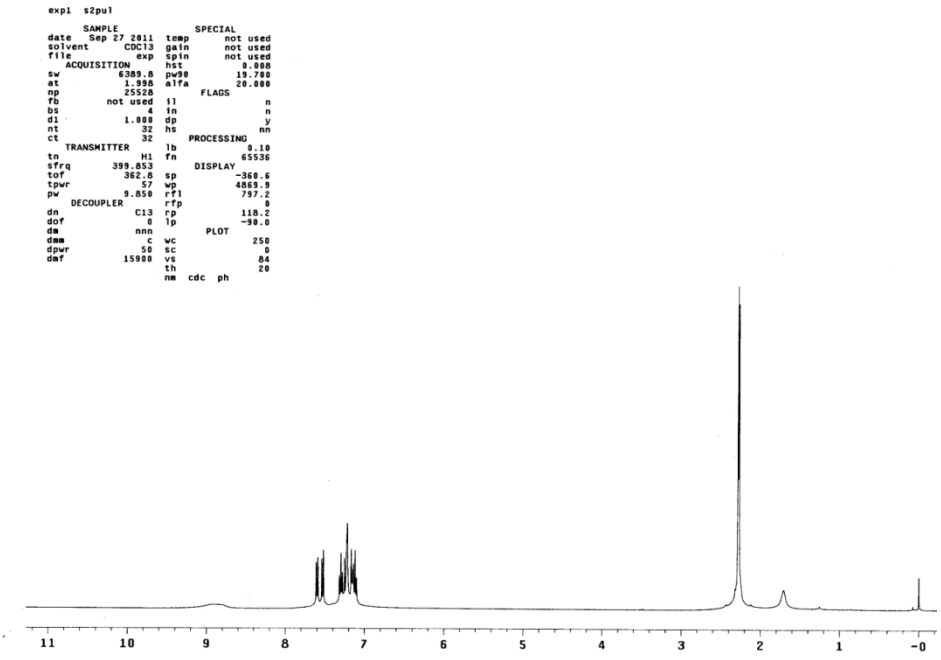
_N_-((_R_)-1-Phenylethyl)benzo[d]thiazol-2-amine (10q): ^{1}H NMR (400 MHz, $CDCl_3$):



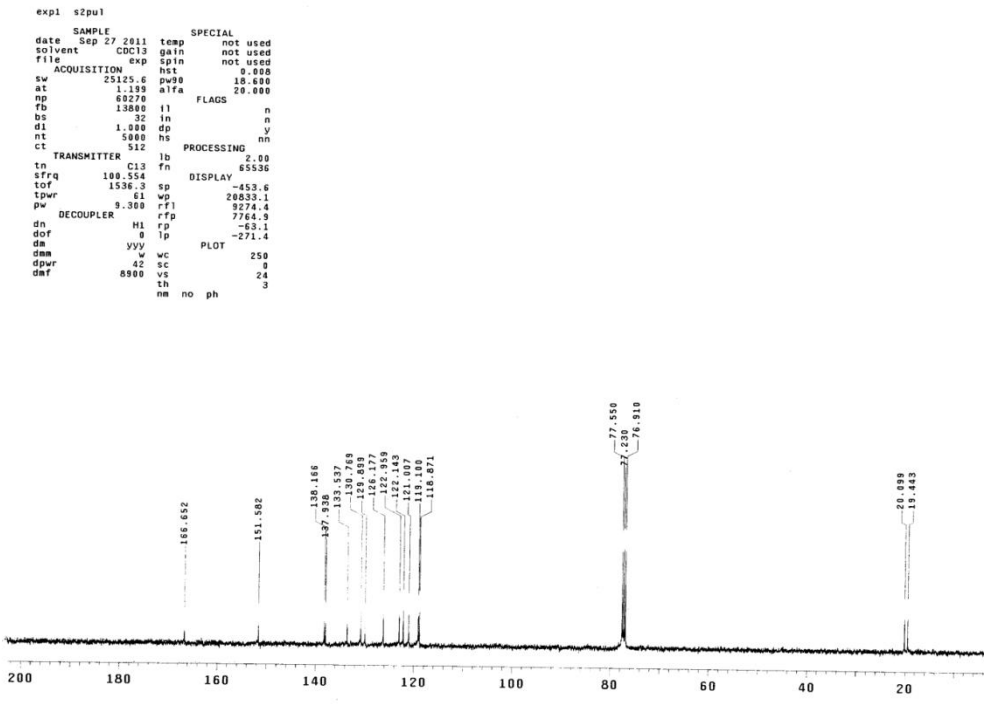
_N_-((_R_)-1-Phenylethyl)benzo[d]thiazol-2-amine (10q): ^{13}C NMR (100 MHz, $CDCl_3$):



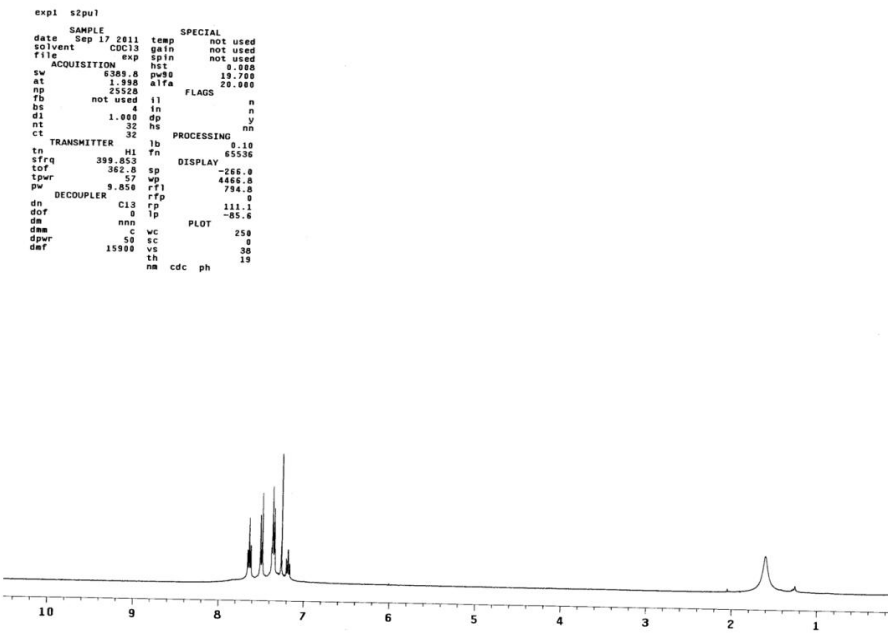
_N_-(3,4-Dimethylphenyl)benzo[d]thiazol-2-amine (10r): ^{1}H NMR (400 MHz, $CDCl_3$):



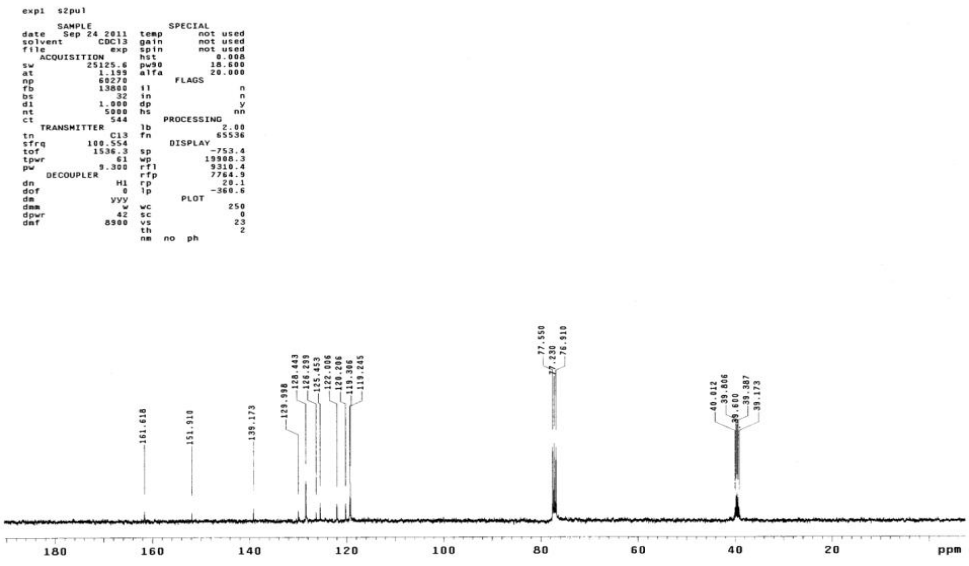
_N_-(3,4-Dimethylphenyl)benzo[d]thiazol-2-amine (10r): ^{13}C NMR (100 MHz, $CDCl_3$):



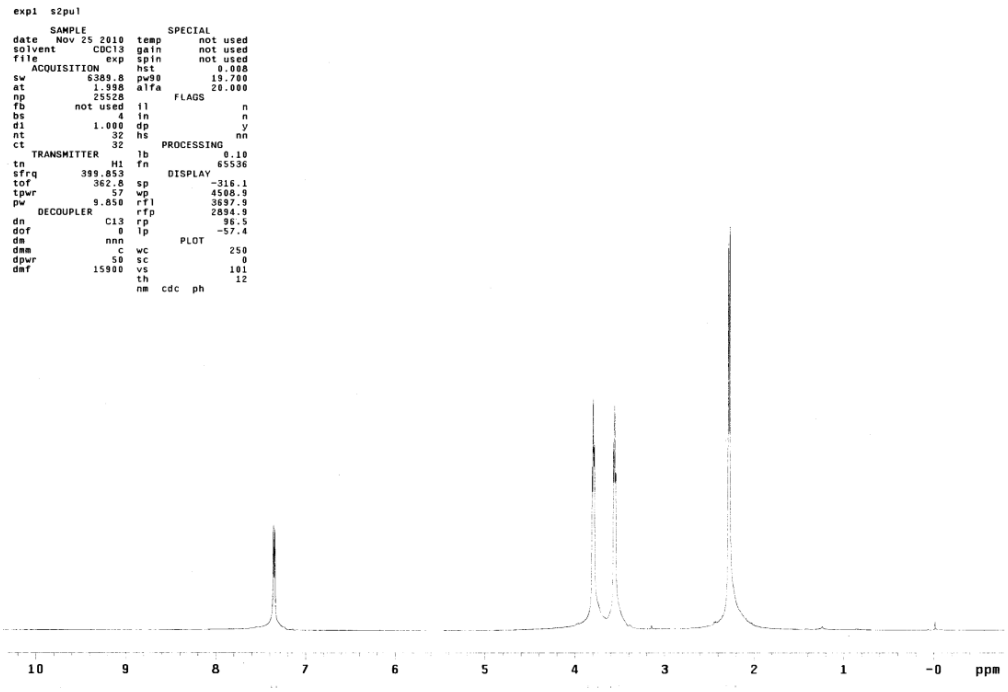
_N_-(4-Chlorophenyl)benzo[d]thiazol-2-amine (10s): ^{1}H NMR (400 MHz, $CDCl_3$):



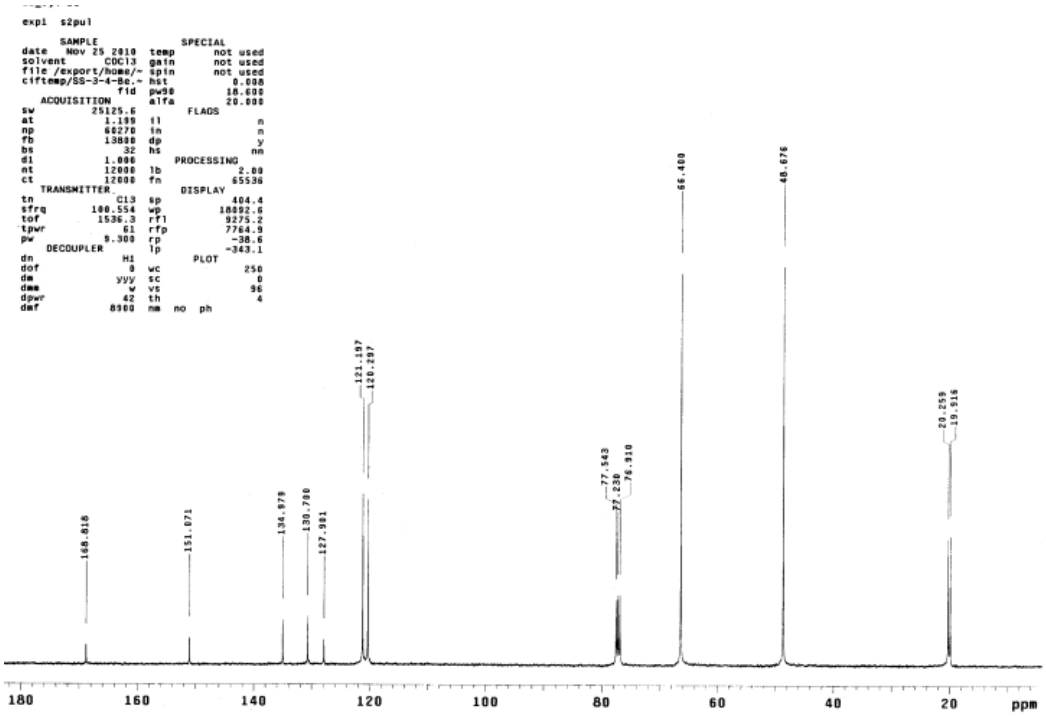
_N_-(4-Chlorophenyl)benzo[d]thiazol-2-amine (10s): ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6):



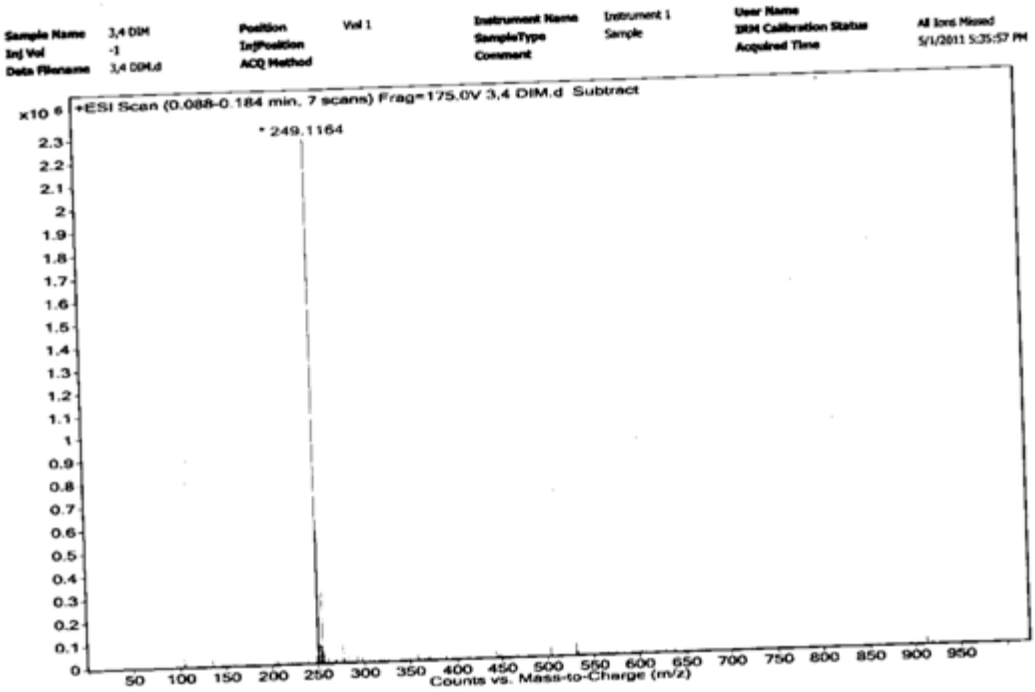
6,6-Dimethyl-2-morpholinobenzo[d]thiazole (11a): ^{1}H NMR (400 MHz, $CDCl_3$):



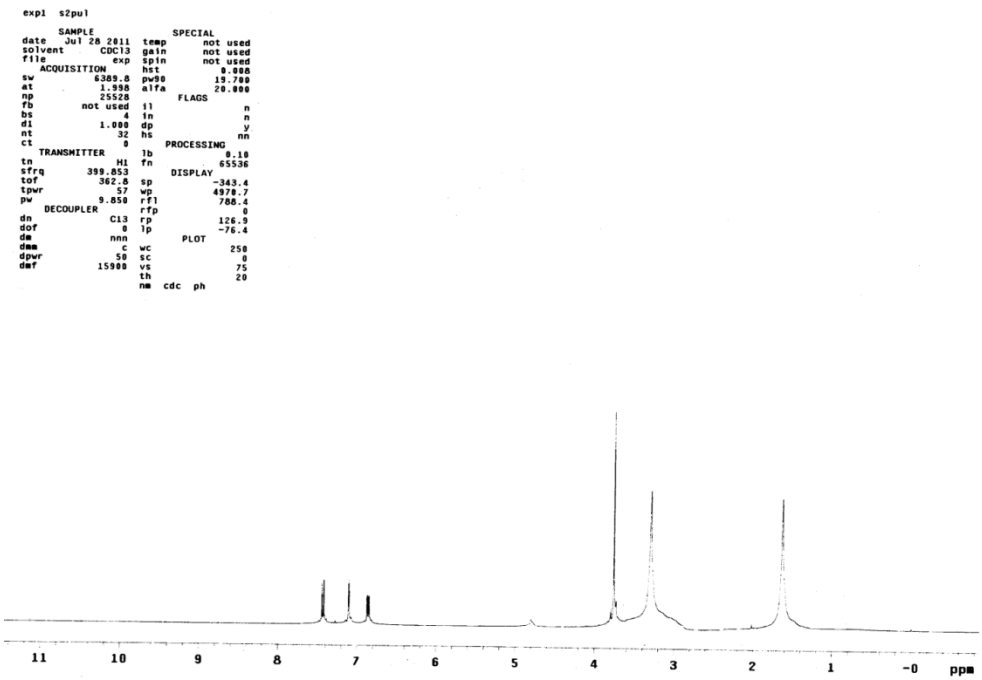
6,6-Dimethyl-2-morpholinobenzo[d]thiazole (11a): ^{13}C NMR (100 MHz, $CDCl_3$):



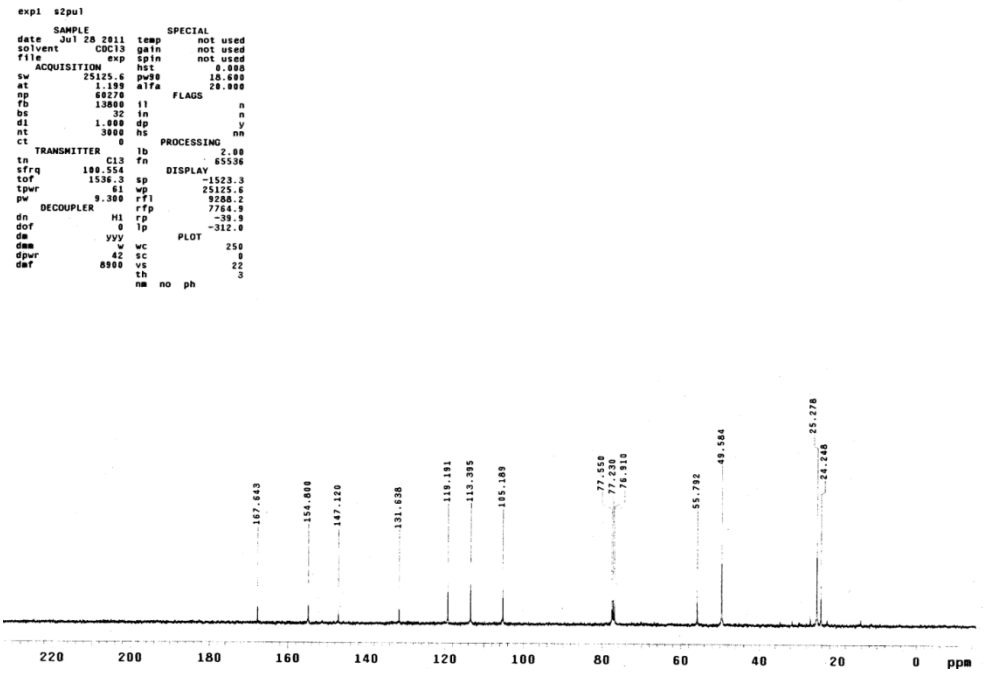
6,6-Dimethyl-2-morpholinobenzo[*d*]thiazole (11a) MASS SPECTRA:



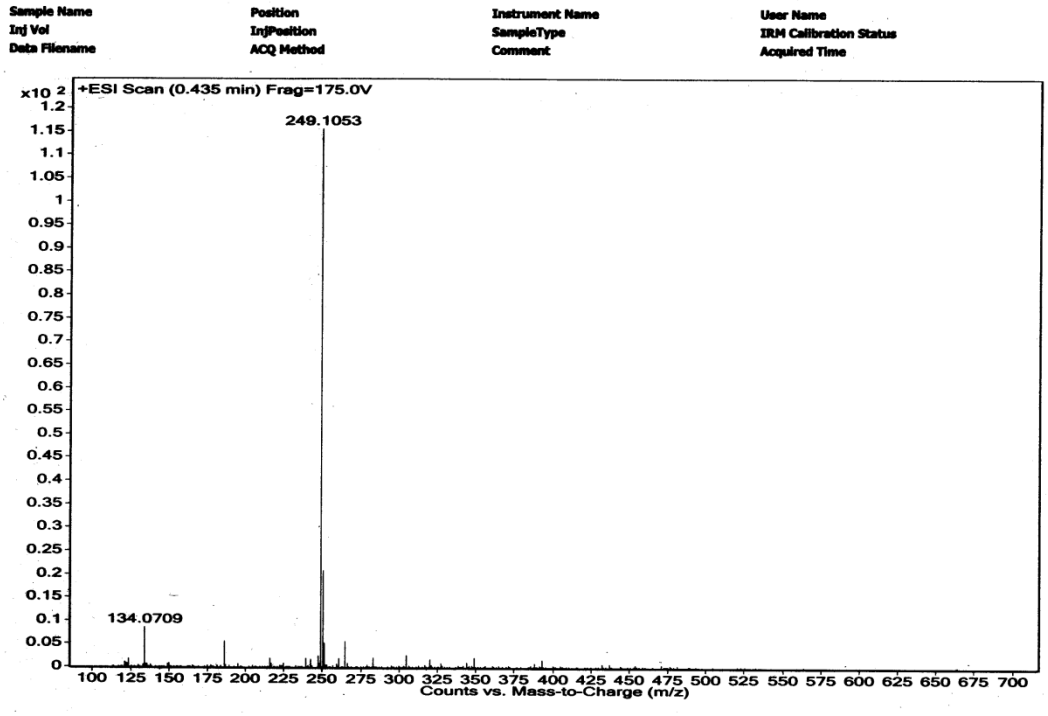
6-Methoxy-2-(piperdin-1-yl)benzo[*d*]thiazole (12t): ^{1}H NMR (400 MHz, $CDCl_3$):



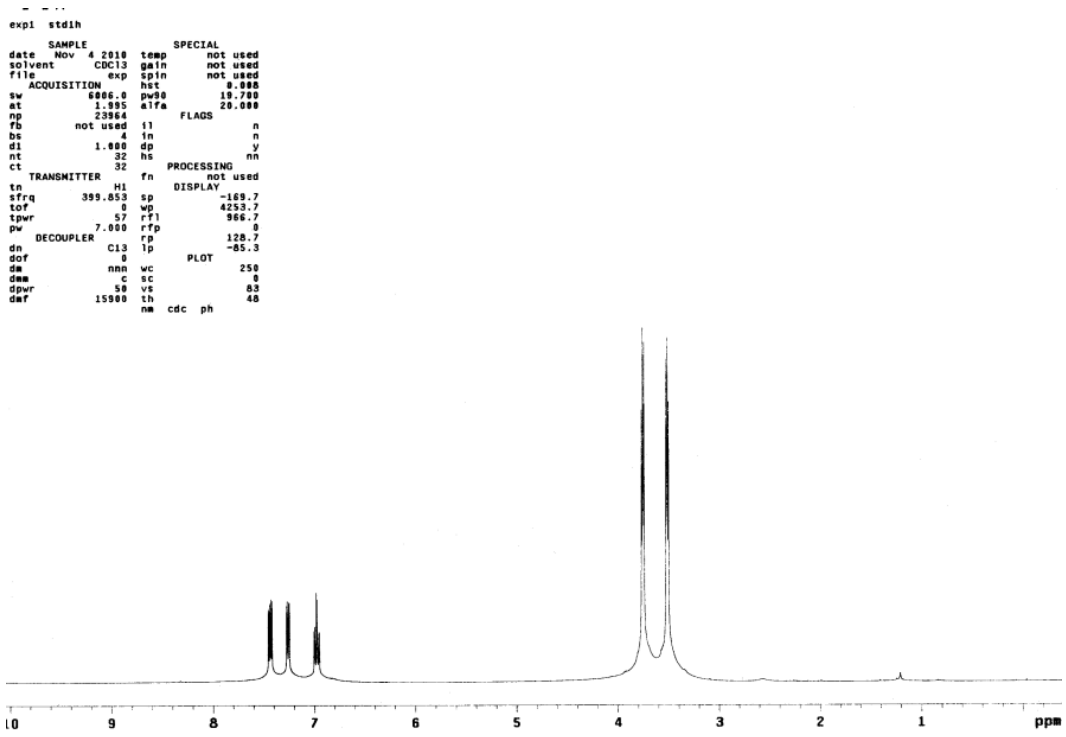
6-Methoxy-2-(piperdin-1-yl)benzo[*d*]thiazole (12t): ^{13}C NMR (100 MHz, $CDCl_3$):



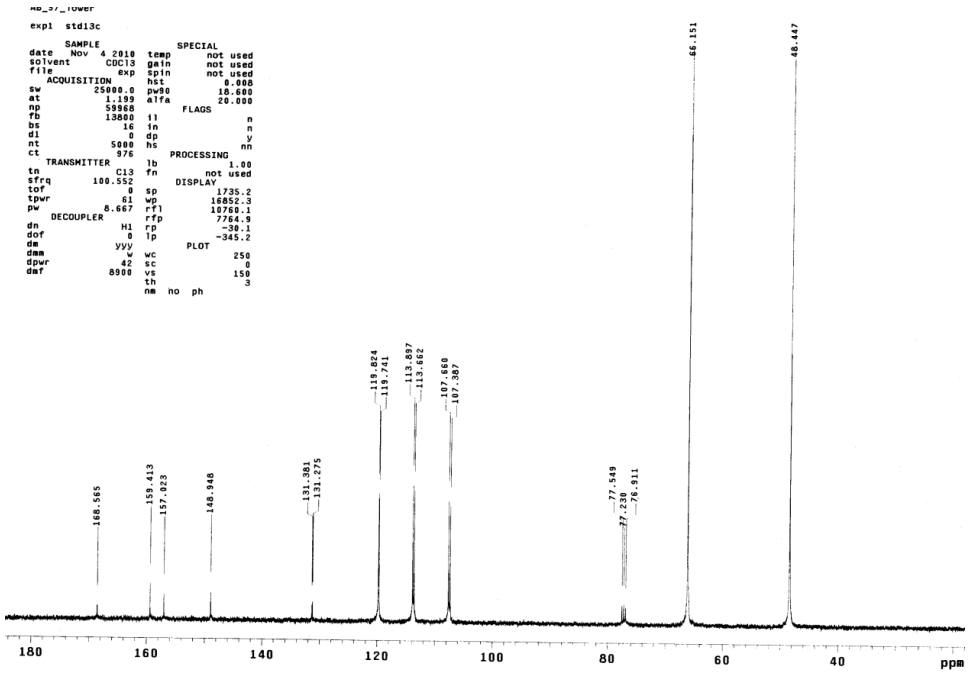
6-Methoxy-2-(piperdin-1-yl)benzo[*d*]thiazole (12t): MASS SPECTRA:



6-Fluoro-2-morpholinobenzo[*d*]thiazole (13a): ^{1}H NMR (400 MHz, $CDCl_3$):



6-Fluoro-2-morpholinobenzo[*d*]thiazole (13a): ^{13}C NMR (100 MHz, $CDCl_3$):



6-Fluoro-2-morpholinobenzo[*d*]thiazole (13a): MASS SPECTRA: