

Supporting Information

Piperazinylpyrimidine modified MCM-41 for the ecofriendly synthesis of benzothiazoles by the simple cleavage of disulfide in presence of molecular O₂

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A. Materials and instrumentation

The ^1H - and ^{13}C -NMR analyses were carried out on Bruker-Advanced Digital 300 MHz instrument with d_6 -DMSO with TMS as an internal reference. IR spectra were recorded in KBr pellets in reflection mode on a Perkin Elmer RX-1 FTIR spectrophotometer. CHN analysis was performed using a Perkin-Elmer 2400 Series II CHN analyzer. X-ray single crystal analysis was performed in a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator. Nitrogen adsorption/desorption isotherms were obtained using a Quantachrome Autosorb 1C at 77 K. Prior to gas adsorption, all the samples were degassed for 2 h at 403 K. Transmission electron microscopic images were recorded on a JEOL 2010 TEM operated at 200 kV. X-ray diffraction patterns of the powder sample were obtained with a Seifert P3000 diffractometer using Cu Ka ($\lambda = 0.15406$ nm) radiation. N_2 sorption, TEM, XRD, and CHN analysis were carried out at Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India. Carbon 13 CP MAS NMR and ^{29}Si MAS NMR was referenced with respect to external TMS and 10-12 kHz speed in BRUKER DSX-300 solid state NMR spectrometer in NMR Research Centre, IISc, Bangalore-560012.

B. Preparation of MCM-41 mesoporous silica

In a typical procedure, cetyltrimethyl ammonium bromide (CTAB) (8.8 g) was dissolved in a mixture of water (208 mL) and aqueous ammonia (96 mL, 35 %) at 35 °C in a polypropylene bottle. To this solution, TEOS (40 mL) was added slowly from a dropping funnel under stirring. After further stirring for 3 h, the gel formed was aged in a closed container at room temperature for 24 h. The product was washed with water and air dried. The template was removed by calcination at 550 °C for 6 h in a continuous flow of air, and the obtained material is designated as MCM-41.

C. Preparation of MCM-41 supported 3-chloropropane (1)

The surface modification of the MCM-41 by post synthesis grafting method was achieved by reacting the silanols of the MCM-41 with 3-chloropropyltrimethoxysilane (Aldrich) under nitrogen atmosphere. 20 mmol of 3-chloropropyltrimethoxysilane was slowly added to a dry acetonitrile solution containing 10 g of MCM-41 and refluxed for 24 h under N_2 . The material was filtered after cooling to ambient temperature, washed with dry acetone and dichloromethane. Soxhlet extraction was carried out for 24 h in dichloromethane (DCM) to remove occluded

organosilane. The sample was dried in vacuum for 10 h and characterized by solid state ^{13}C CP MAS NMR spectrum and CHN analysis.

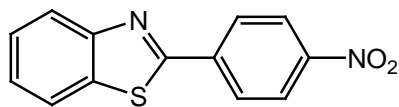
D. Preparation of MCM-41 supported piperazinyipyrimidine (MCM-PP) catalyst (3)

In a typical procedure 5g of 3-chloropropane anchored MCM-41 (**1**) was reacted with 10 mmol of 2-(piperazin-1-yl)pyrimidine (**2**) in dry acetonitrile under reflux for 18h in presence of 1mmol triethylamine. The liberated HCl was removed through a CaCl_2 drying tube under reduced pressure to a water trap. The solid was washed successively with water (10 times), ethanol (3 times) and dried at 110°C for 3h. No precipitate was obtained on treatment of silver nitrate solution with the aqueous extract of the solid after washing it ten times with distilled water. The aforesaid observation conclusively proved the absence of Cl^- on the solid catalyst after thorough washing with distilled water. The as prepared MCM-41 supported piperazinyipyrimidine catalyst was abbreviated as **MCM-PP (3)**.

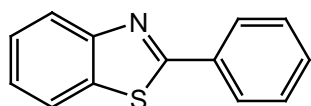
E. General procedure for the synthesis of the 2-arylbenzothiazoles (6)

All the reactions were carried out in round bottomed flask equipped with a magnetic stirrer and a reflux condenser. In a typical reaction a mixture of ortho-aminothiophenol disulfides (**4**) (1 mmol) and different aldehydes (**6**) (1 mmol) in EtOH (4 ml) were refluxed on a water bath for 4h using 20 mg **MCM-PP (3)** and 1 mmol iodine. The completion of the reaction was indicated by the disappearance of the starting materials in thin layer chromatography. After completion of the reaction, the little excess of EtOH was evaporated to dryness. The crude product was taken in dichloromethane and washed with an aqueous solution of sodium metabisulphite to free it from any unreacted iodine. The DCM was evaporated in rotary evaporator and the crude product was further purified by silica gel column chromatography using EtOAc/petroleum ether (4%/96% v/v) as eluent.

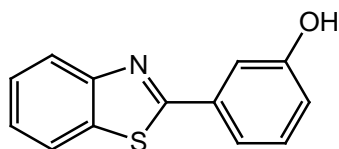
F. Spectroscopic characterization of 6a-6o



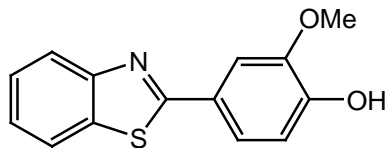
2-(4-nitrophenyl)benzo[d]thiazole (6a, Table 1, entry 1): White solid; m.p. 228-230 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr): 3436, 2372, 1520, 1343, 852 and 764 cm^{-1} ; ^1H NMR, CDCl_3 , 300 MHz) δ : 8.39 (d, $J = 8.4$ Hz, 2H), 8.29 (d, $J = 7.8$ Hz, 2H), 7.99 (dd, $J = 7.5$ Hz and 1.2 Hz, 1H), 7.59 (dt, $J = 7.2$ Hz and 1.2 Hz, 1H), 7.49 (dt, $J = 7.2$ Hz and 1.2 Hz, 1H); ^{13}C NMR (CDCl_3 , 75 MHz), δ : 165.6, 154.0, 149.3, 138.8, 135.6, 128.9, 127.6, 126.9, 125.1, 124.0, 123.1; Anal. Calcd for $\text{C}_{13}\text{H}_8\text{N}_2\text{O}_2\text{S}$: C, 60.93; H, 3.15; N, 10.93%. Found: C, 60.97; H, 3.14; N, 10.90%.



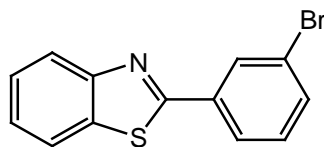
2-phenylbenzo[d]thiazole (6b, Table 1, entry 2): White solid; m.p. 112-114 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr): 3064, 1554, 1479, 1433, 1314, 1283, 1253, 1225, 1159, 1070, 963, 766, 729, and 686 cm^{-1} ; ^1H NMR, CDCl_3 , 300 MHz) δ : 8.14-8.08 (m, 3H), 7.92 (d, $J = 7.2$ Hz, 1H), 7.53-7.48 (m, 4H), 7.40 (dt, $J = 7.5$ Hz and 1.2 Hz, 1H); ^{13}C NMR (CDCl_3 , 75 MHz), δ : 168.1, 154.2, 135.1, 133.6, 130.9, 129.0, 127.6, 126.3, 125.2, 123.2, 121.6; Anal. Calcd for $\text{C}_{13}\text{H}_9\text{NS}$: C, 73.90; H, 4.29; N, 6.63%. Found: C, 73.92; H, 4.29; N, 6.64%.



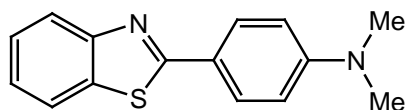
3-(benzo[d]thiazol-2-yl)phenol (6c, Table 1, entry 3): White solid; m.p. 160-162 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr): 3059, 2373, 1595, 1442, 1220, and 771 cm^{-1} ; ^1H NMR (DMSO-d_6 , 300 MHz) δ : 9.92 (br s, 1H), 8.13 (d, $J = 7.8$ Hz, 3H), 8.05 (d, $J = 7.8$ Hz, 1H), 7.58-7.35 (m, 5H), 6.99-6.95 (m, 1H); ^{13}C NMR (CDCl_3 , 75 MHz), δ : 167.8, 158.5, 154.0, 134.9, 134.5, 131.0, 127.1, 126.0, 123.3, 122.7, 119.0, 118.6, 113.9; Anal. Calcd for $\text{C}_{13}\text{H}_9\text{NOS}$: C, 68.70; H, 3.99; N, 6.16%. Found: C, 68.73; H, 3.98; N, 6.15%.



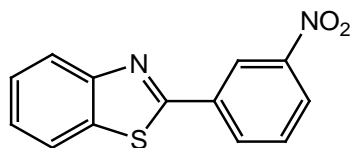
4-(benzo[d]thiazol-2-yl)-2-methoxyphenol (6d, Table 1, entry 4): White solid; m.p. 161-163 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr): 2929, 2371, 1469, 1429, 1282, and 764 cm^{-1} ; ^1H NMR (DMSO- d_6 , 300 MHz) δ : 9.86 (br s, 1H), 8.07 (d, $J = 7.5$ Hz, 1H), 8.00 (d, $J = 7.8$ Hz, 1H), 7.64 (d, $J = 2.1$ Hz, 1H), 7.53–7.37 (m, 3H), 7.95 (d, $J = 8.1$ Hz and 1.3 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz), δ : 168.0, 154.1, 150.5, 148.6, 134.7, 126.9, 125.4, 124.8, 122.8, 122.5, 121.8, 116.4, 110.6, 56.2; Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{NO}_2\text{S}$: C, 65.35; H, 4.31; N, 5.44%. Found: C, 65.33; H, 4.30; N, 5.46%.



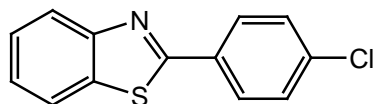
2-(3-bromophenyl)benzo[d]thiazole (6e, Table 1, entry 5): White solid; m.p. 84-86 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr): 3436, 2374, 1775, 1562, 1417, 1343, and 764 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ : 8.30 (s, 1H), 8.11 (d, $J = 8.1$ Hz, 1H), 8.02 (dd, $J = 8.4$ Hz and 1.2 Hz, 1H), 7.94 (dd, $J = 7.2$ Hz and 1.2 Hz, 1H), 7.64 (dd, $J = 8.1$ Hz and 1.2 Hz, 1H), 7.54 (t, $J = 7.5$ Hz, 1H), 7.46-7.36 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz), δ : 166.1, 154.0, 135.5, 135.1, 133.8, 130.5, 130.3, 126.5, 126.1, 125.6, 123.5, 123.2, 121.7; Anal. Calcd for $\text{C}_{13}\text{H}_8\text{BrNS}$: C, 53.81; H, 2.78; N, 4.83%. Found: C, 53.87; H, 2.75; N, 4.87%.



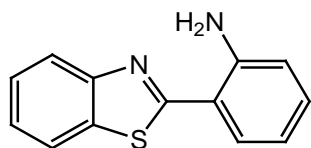
4-(benzo[d]thiazol-2-yl)-N,N-dimethylbenzenamine (6f, Table 1, entry 6): White solid; m.p. 160-162 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr): 3053, 2900, 2815, 1609, 1486, 1430, 1369, 1314, 1227, 1188, 1012, 963, 943, 817, and 752 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ : 7.99-7.96 (m, 3H), 7.86 (dd, $J = 7.8$ Hz and 1.2 Hz, 1H), 7.46 (dt, $J = 7.2$ Hz and 1.2 Hz, 1H), 7.32 (dt, $J = 7.8$ Hz and 0.9 Hz, 1H), 6.77 (dd, $J = 9.3$ Hz and 1.8 Hz, 2H), 3.08 (s, 6H); ^{13}C NMR (CDCl_3 , 75 MHz), δ : 168.8, 154.4, 152.2, 134.5, 128.9, 125.9, 124.2, 122.3, 121.4, 121.3, 111.7, 40.1; Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{S}$: C, 70.83; H, 5.55; N, 11.01%. Found: C, 70.86; H, 5.53; N, 11.04%.



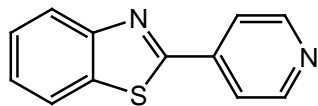
2-(3-nitrophenyl)benzo[d]thiazole (6g), Table 1, entry 7): White solid; m.p. 181-182 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr): 2372, 1528, 1343, 1219, and 771 cm^{-1} ; ^1H NMR (DMSO- d_6 , 300 MHz) δ : 8.81 (s, 1H), 8.50 (dd, $J = 7.8$ Hz and 1.2 Hz, 1H), 8.41 (dd, $J = 8.4$ Hz and 1.2 Hz, 1H), 8.22 (dd, $J = 8.1$ Hz and 1.2 Hz, 1H), 8.15 (d, $J = 7.8$ Hz, 1H), 7.89 (t, $J = 8.1$ Hz, 1H), 7.64-7.51 (m, 2H); ^{13}C NMR (CDCl $_3$, 75 MHz), δ : 165.3, 153.8, 148.9, 135.2, 134.7, 133.9, 131.7, 127.5, 126.7, 126.1, 123.8, 123.1, 121.6; Anal. Calcd for $\text{C}_{13}\text{H}_8\text{N}_2\text{O}_2\text{S}$: C, 60.93; H, 3.15; N, 10.93%. Found: C, 60.95; H, 3.16; N, 10.91.



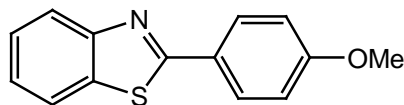
2-(4-chlorophenyl)benzo[d]thiazole (6h), Table 1, entry 8): White solid; m.p. 115-117 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr): 3055, 2990, 1646, 1569, 1506, 1589, 1474, 1434, 1399, 1315, 1251, 1227, 1174, 1089, 1012, 971, 828, and 753 cm^{-1} ; ^1H NMR, DMSO- d_6 , 300 MHz) δ : 8.13-8.03 (m, 3H), 7.92 (dd, $J = 8.1$ Hz and 1.2 Hz, 1H), 7.55-7.39 (m, 4H); ^{13}C NMR (CDCl $_3$, 75 MHz), δ : 166.6, 154.1, 137.0, 135.1, 132.1, 129.3, 128.7, 126.5, 125.4, 123.3, 121.6; Anal. Calcd for $\text{C}_{13}\text{H}_8\text{ClNS}$: C, 63.54; H, 3.28; N, 5.70%. Found: C, 63.58; H, 3.29; N, 5.73%.



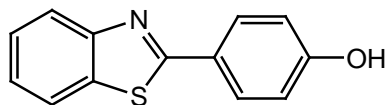
2-(benzo[d]thiazol-2-yl)benzenamine (6i), Table 1, entry 9): White solid; m.p. 160-162 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr): 3435, 3321, 2924, 2371, 1601, 1521, 1475, 1430, 1282, 972, 824, and 752 cm^{-1} ; ^1H NMR, DMSO- d_6 , 300 MHz) δ : 7.97 (d, $J = 8.4$ Hz, 1H), 7.88 (d, $J = 8.4$ Hz, 1H), 7.71 (dd, $J = 8.0$ Hz and $J = 1.5$ Hz, 1H), 7.46 (dt, $J = 7.2$ Hz and 1.2 Hz, 1H), 7.36 (dt, $J = 7.8$ Hz and 1.2 Hz, 1H), 7.26-7.20 (m, 1H), 6.81-6.72 (m, 2H), 6.40 (m, 2H); ^{13}C NMR (CDCl $_3$, 75 MHz), δ : 165.3, 153.8, 145.9, 134.9, 131.6, 130.3, 126.0, 124.9, 122.4, 121.2, 116.9, 116.8; Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{S}$: C, 69.00; H, 4.45; N, 12.38%. Found: C, 69.06; H, 4.47; N, 12.35%.



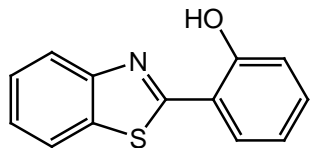
2-(pyridin-4-yl)benzo[d]thiazole (6j, Table 1, entry 10): White solid; m.p. 180-182 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr): 3435, 2372, 1522, 1343, 851 and 764 cm^{-1} ; ^1H NMR, CDCl_3 , 300 MHz) δ : 8.72-8.69 (m, 2H), 8.07 (t, $J = 10.2$ Hz, 1H), 7.89-7.83 (m, 3H), 7.53-7.35 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz), δ : 164.8, 153.7, 150.5, 140.1, 135.0, 126.5, 125.9, 123.7, 121.6, 120.9; Anal. Calcd for $\text{C}_{12}\text{H}_8\text{N}_2\text{S}$: C, 67.90; H, 3.80; N, 13.20%. Found: C, 67.95; H, 3.82; N, 13.23%.



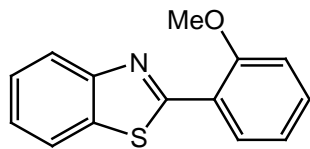
2-(4-methoxyphenyl)benzo[d]thiazole (6k, Table 1, entry 11): White solid; m.p. 120-122 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr) 2835, 1605, 1521, 1485, 1434, 1412, 1310, 1260, 1226, 1172, 1114, 1027, 969, 833, 758, and 730 cm^{-1} ; ^1H NMR, DMSO-d_6 , 300 MHz) δ : 8.09-8.06 (m, 3H), 7.90 (d, $J = 7.8$ Hz, 1H), 7.50 (t, $J = 7.8$ Hz, 1H), 7.38 (t, $J = 8.1$ Hz, 1H), 7.03 (dd, $J = 7.8$ Hz and 1.8 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz), δ : 167.9, 161.9, 154.2, 134.9, 129.1, 126.5, 126.2, 124.8, 122.8, 121.5, 114.4, 55.5; Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{NOS}$: C, 69.68; H, 4.59; N, 5.80%. Found: C, 69.66; H, 4.58; N, 5.82%.



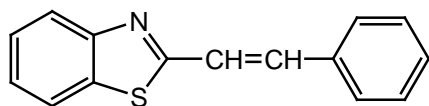
4-(benzo[d]thiazol-2-yl)phenol (6l, Table 1, entry 12): White solid; m.p. 225-227 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr): 3436, 2366, 1601, 1479, 1308, 1256, 1171, 1025, 832, and 760 cm^{-1} ; ^1H NMR (DMSO-d_6 , 300 MHz) δ : 9.93 (brs, 1H), 8.07 (d, $J = 8.1$ Hz, 1H), 7.99-7.92 (m, 3H), 7.50 (t, $J = 7.2$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 1H), 6.94 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (DMSO-d_6 , 75 MHz), δ : 167.9, 161.0, 154.2, 134.6, 129.5, 126.9, 125.4, 124.5, 122.8, 122.6, 116.6; Anal. Calcd for $\text{C}_{13}\text{H}_9\text{NOS}$: C, 68.70; H, 3.99; N, 6.16%. Found: C, 68.72; H, 3.99; N, 6.17%.



2-(benzo[d]thiazol-2-yl)phenol (6m, Table 1, entry 13): White solid; m.p. 124-226 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr): 3437, 2923, 2372, 1580, 1477, 1210, 742 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ : 8.04 (d, $J = 7.8$ Hz), 7.94 (d, $J = 8.1$ Hz, 1H), 7.72 (d, $J = 7.2$ Hz, 1H), 7.54 (t, $J = 7.2$, 1H), 7.47-7.32 (m, 2H), 7.14 (d, $J = 9.0$ Hz, 1H), 6.96 (t, $J = 8.1$ Hz, 1H); ^{13}C NMR (CDCl_3 , 75 MHz), δ : 169.1, 158.2, 152.2, 132.8, 128.5, 126.6, 125.6, 122.3, 121.5, 119.5, 117.5, 116.5; Anal. Calcd for $\text{C}_{13}\text{H}_9\text{NOS}$: C, 68.70; H, 3.99; N, 6.16%. Found: C, 68.74; H, 3.99; N, 6.14%.

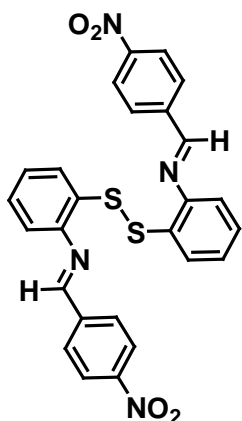


2-(2-methoxyphenyl)benzo[d]thiazole (6n, Table 1, entry 14): White solid; m.p. 101-103 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr): 3435, 2932, 2372, 1586, 1458, 1427, 1286, 1246, 1013, and 754 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ : 8.50 (d, $J = 7.8$ Hz, 1H), 8.07 (dt, $J = 8.4$ Hz, 1H), 7.89 (d, $J = 7.8$ Hz, 1H), 7.48-7.30 (m, 3H), 7.10 (t, $J = 7.5$ Hz, 1H), 7.01 (d, $J = 8.0$ Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 163.1, 157.2, 152.2, 136.1, 131.7, 129.5, 125.8, 124.5, 122.8, 122.3, 121.1, 121.1, 111.7, 55.7; Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{NOS}$: C, 69.68; H, 4.59; N, 5.80%. Found: C, 69.66; H, 4.58; N, 5.80%.



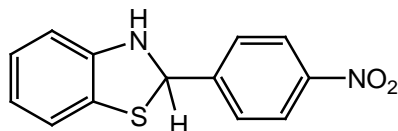
2-styrylbenzo[d]thiazole (6o, Table 1, entry 15): White solid; m.p. 110-112 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr): 3436, 1628, 1438, 1177, and 955 cm^{-1} ; ^1H NMR, DMSO-d_6 , 300 MHz) δ : 8.00 (d, $J = 8.1$ Hz, 1H), 7.87 (d, $J = 8.1$ Hz, 1H), 7.61-7.57 (m, 2H), 7.52-7.36 (m, 7H); ^{13}C NMR (CDCl_3 , 75 MHz), δ : 167.0, 153.8, 137.6, 135.4, 134.3, 129.4, 128.9, 127.4, 126.3, 125.3, 122.9, 122.1, 121.5; Anal. Calcd for $\text{C}_{15}\text{H}_{11}\text{NS}$: C, 75.91; H, 4.67; N, 5.90%. Found: C, 75.94; H, 4.66; N, 5.91%.

G. Spectral data of intermediates 7 and 12



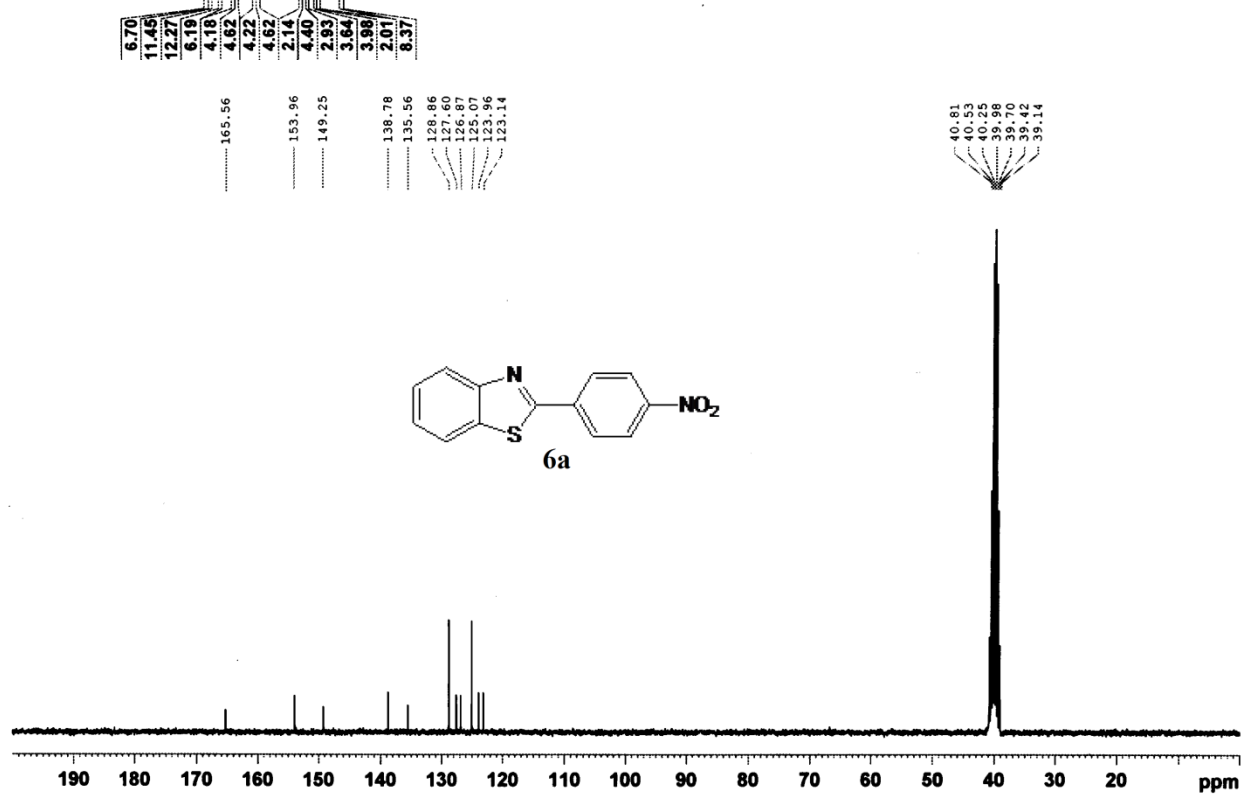
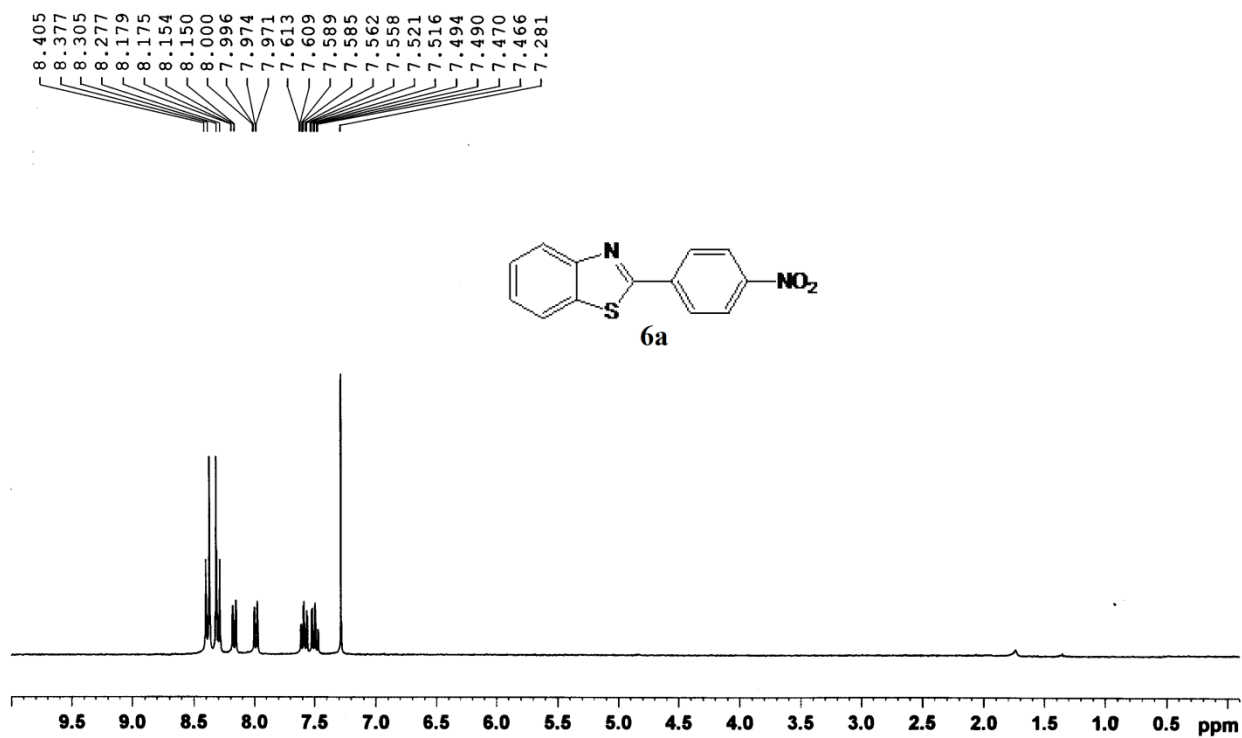
(15E)-N-(4-nitrobenzylidene)-2-(2-((E)-2-(4-nitrobenzylideneamino)phenyl)disulfanyl)benzenamine (7):

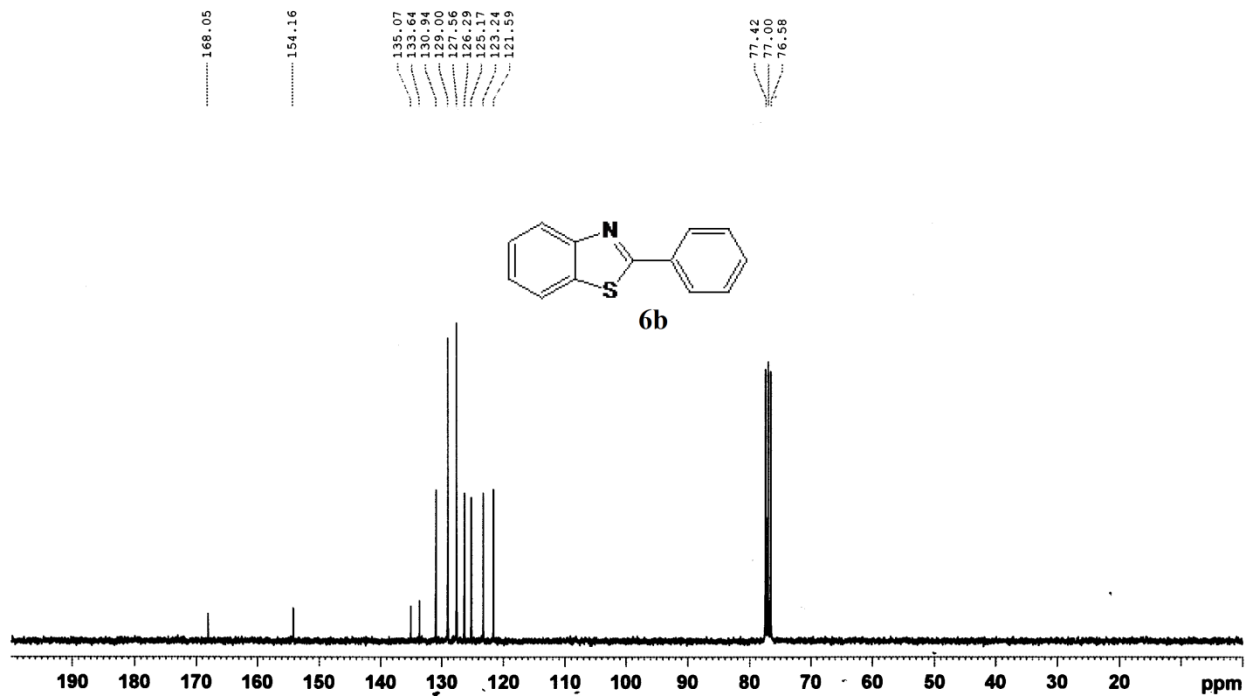
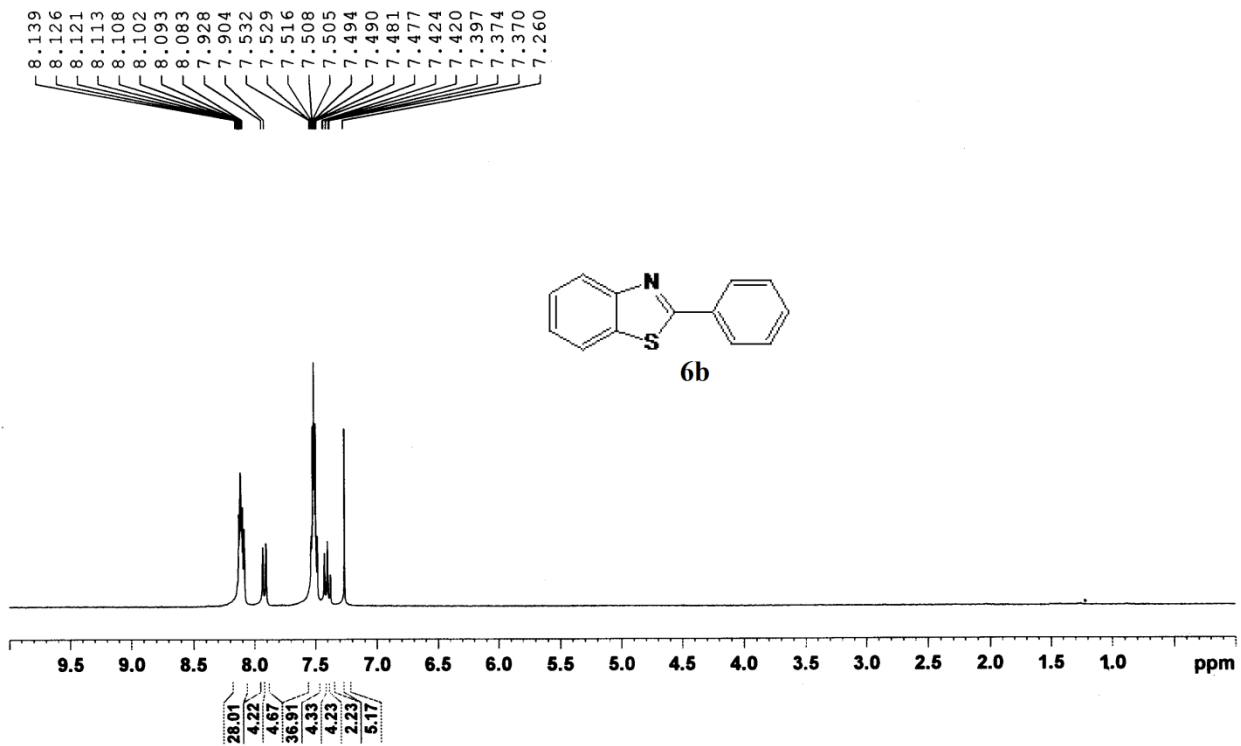
Yellow solid; mp 158–160 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr) 1598, 1569, 1549, 1529, 1461, 1434, 1372, 1168, 946, 821, 758, 523, 463 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.04-7.07 (m, (2 \times 1)H), 7.13-7.19 (m, (2 \times 2)H), 7.61 (d, $J=6.3$ Hz, (2 \times 1)H), 8.08 (d, $J=8.4$ Hz, (2 \times 2)H), 8.27 (d, $J=8.7$ Hz, (2 \times 2)H), 8.53 (s, (2 \times 1)H); ^{13}C NMR (75 MHz, CDCl_3) δ 116.8, 123.8, 126.1, 127.0, 127.8, 129.5, 132.7, 141.0, 147.6, 149.3, 156.8; Anal. Calcd for $\text{C}_{26}\text{H}_{18}\text{N}_4\text{O}_4\text{S}_2$: C, 60.69; H, 3.53; N, 10.89%. Found: C, 60.70; H, 3.54; N, 10.90%.

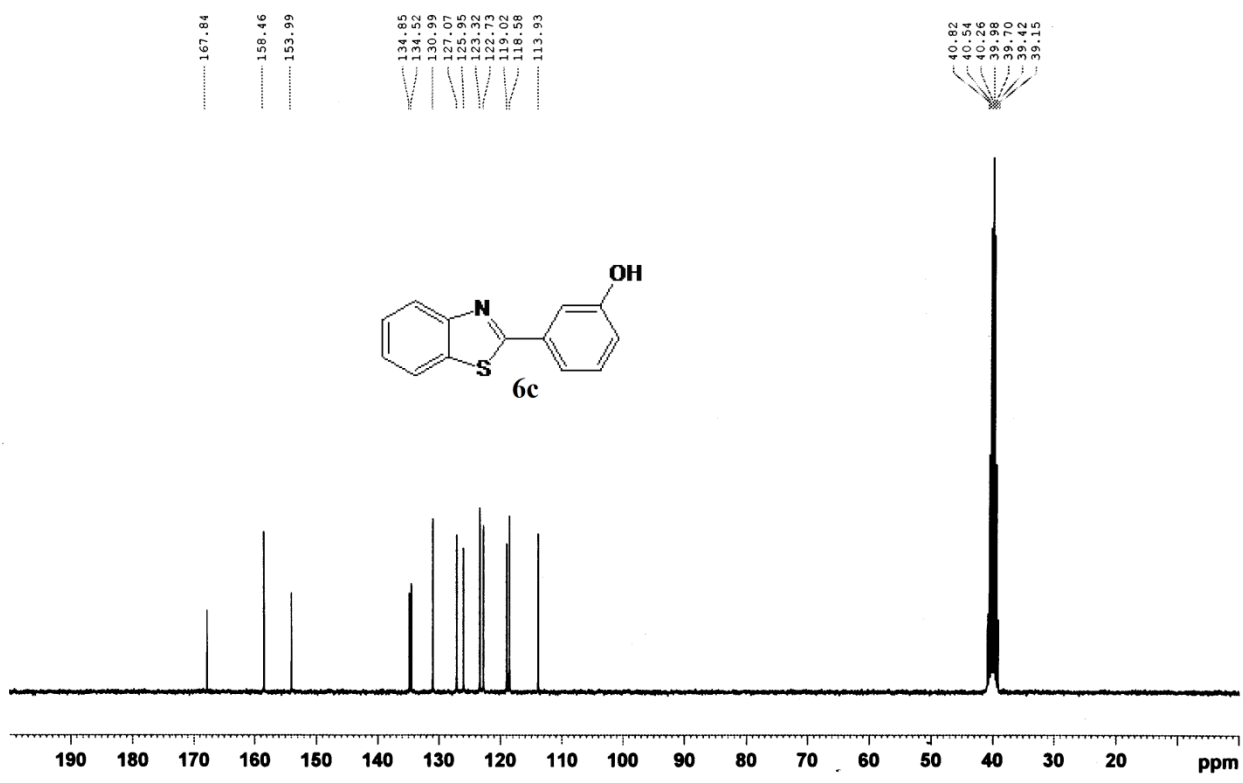
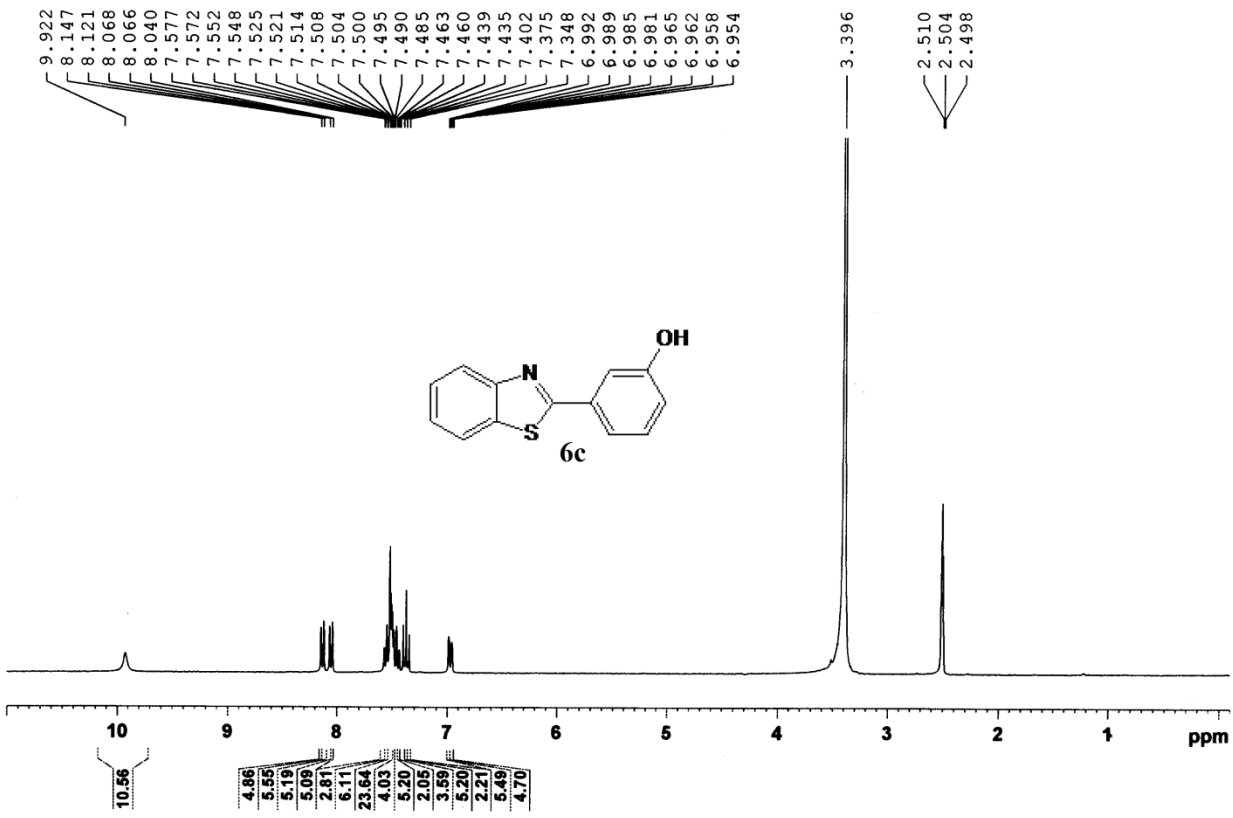


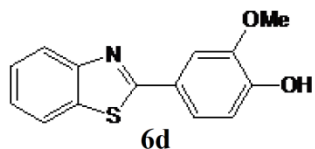
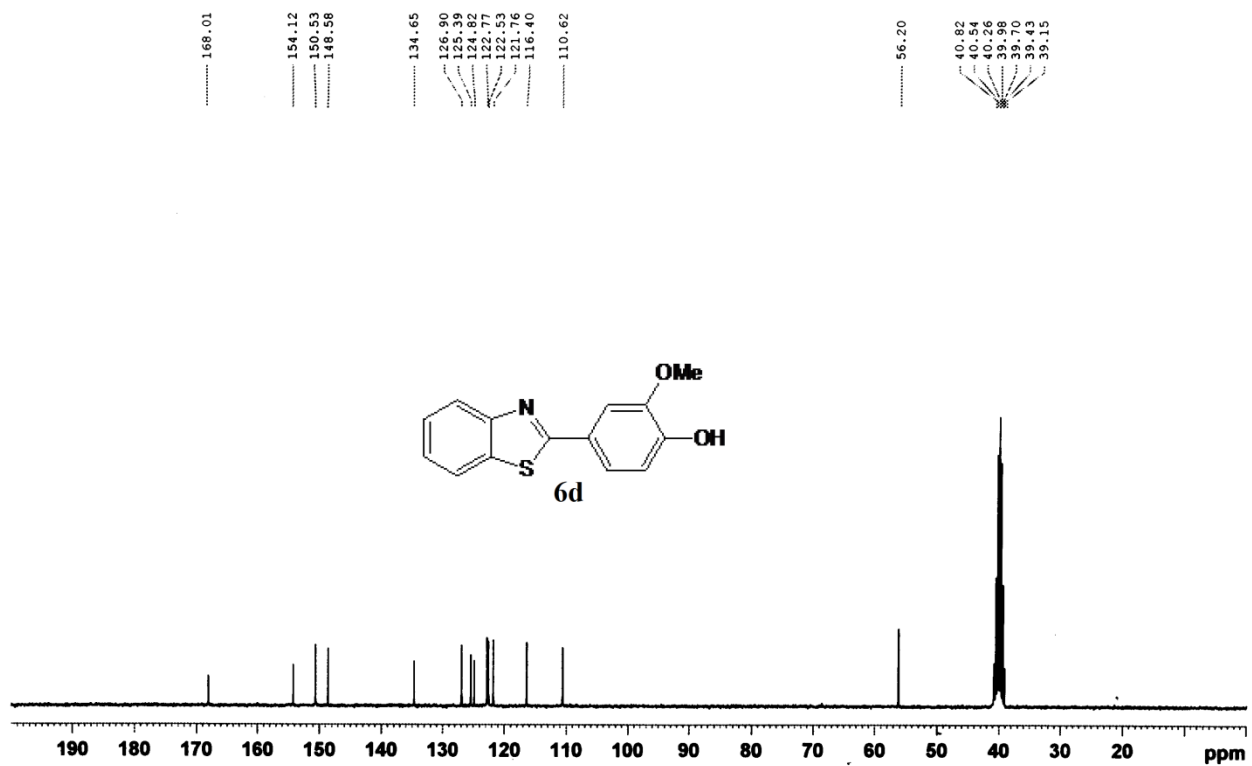
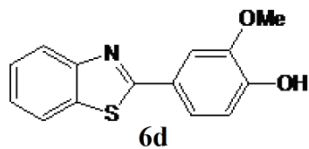
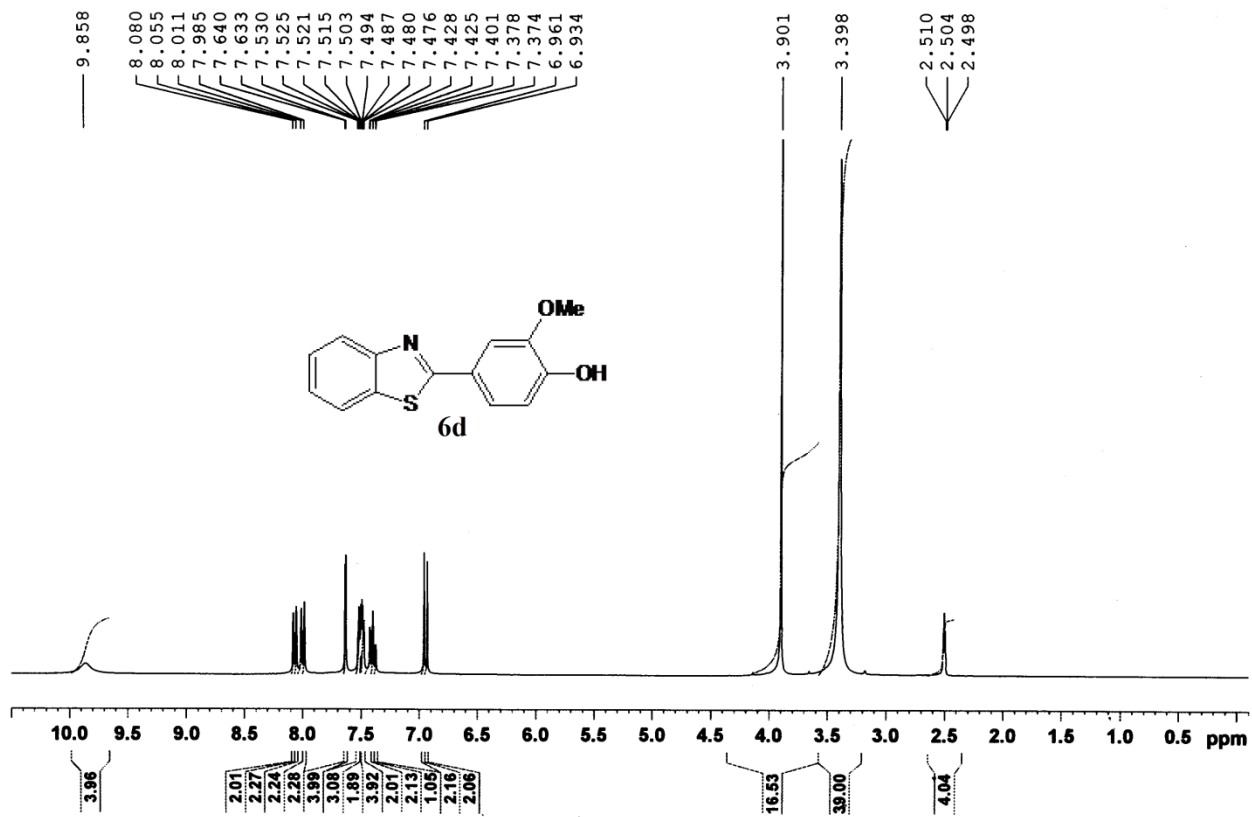
2,3-dihydro-2-(4-nitrophenyl)benzo[d]thiazole (12): White solid; m.p. 228-230 °C (recrystallized from EtOAc/DCM, equal volume); IR (KBr): 3333, 2371, 1595, 1515, 1340, 853, and 756 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ : 8.21 (d, $J = 9.3$ Hz, 2H), 7.68 (d, $J = 8.7$ Hz, 2H), 7.07-6.97 (m, 2H), 6.84-6.73 (m, 2H), 6.43 (d, $J = 3.9$ Hz, 1H), 4.52 (br s, 1H); ^{13}C NMR (CDCl_3 , 75 MHz), δ : 149.3, 147.9, 145.8, 127.2, 126.0, 125.9, 124.1, 121.8, 121.5, 110.5, 68.3; Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$: C, 60.45; H, 3.90; N, 10.85%. Found: C, 60.49; H, 3.91; N, 10.83%.

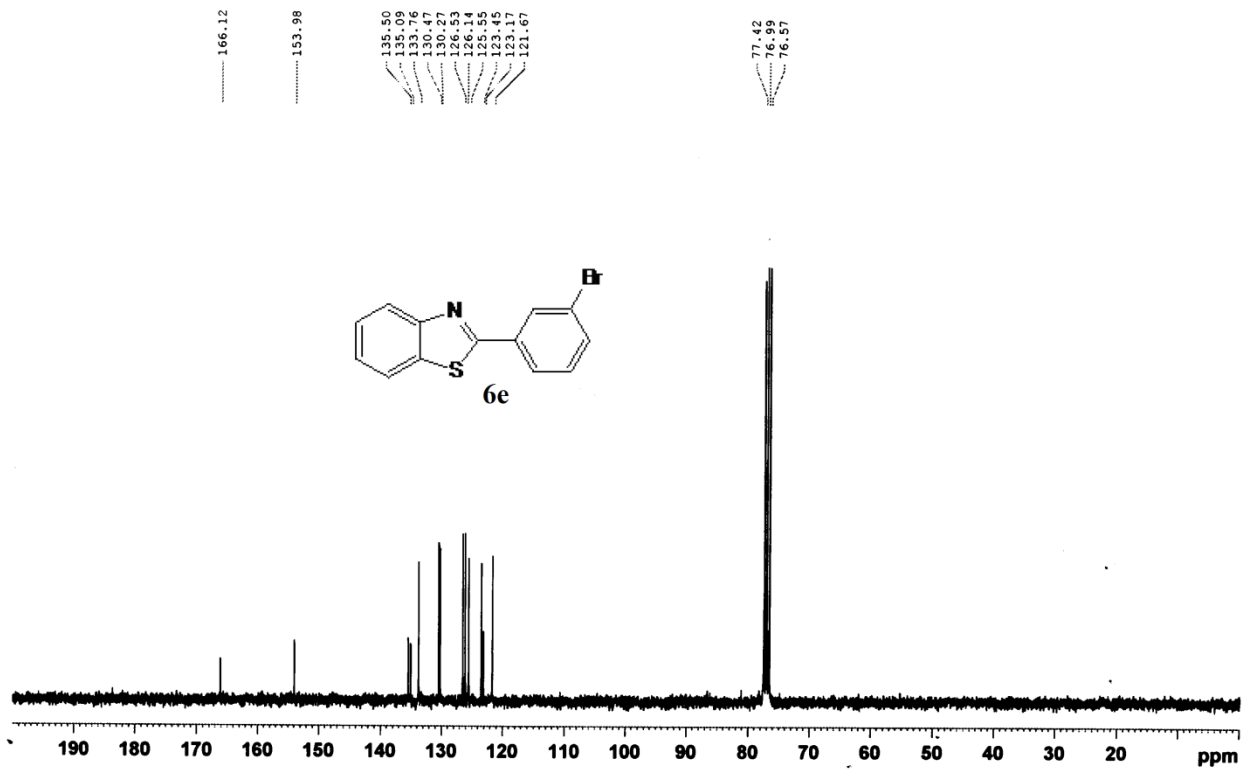
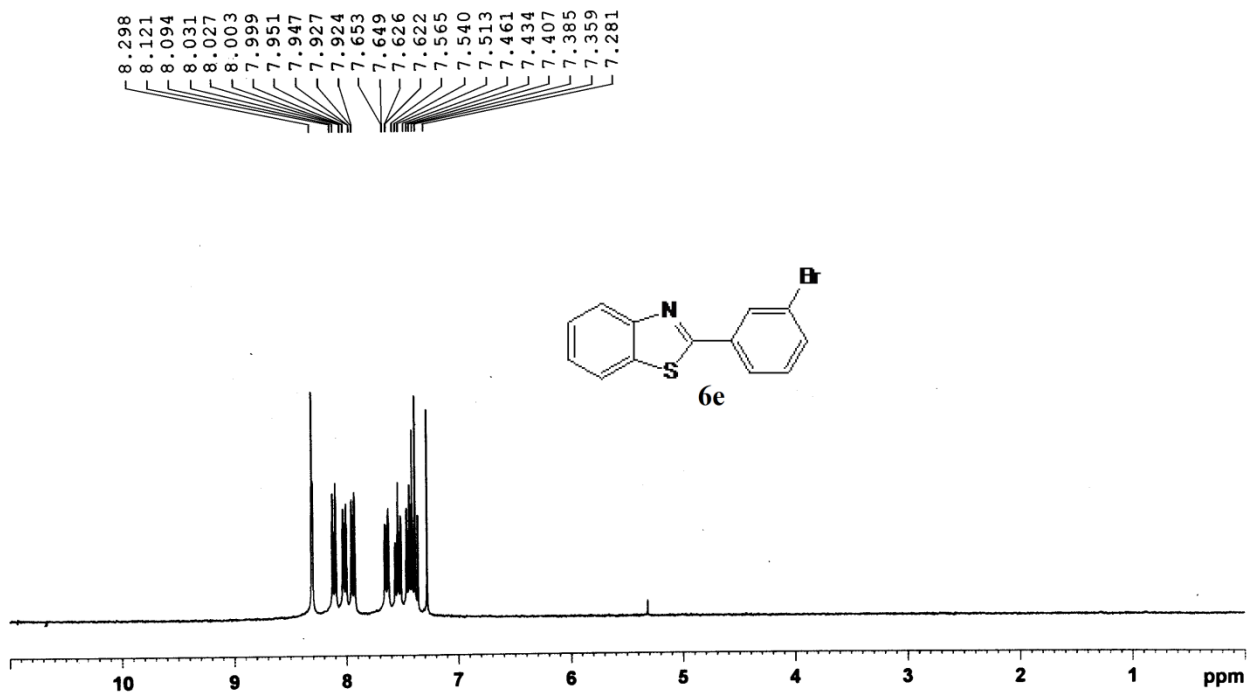
H. ¹H and ¹³C NMR Spectra of 6a-6o

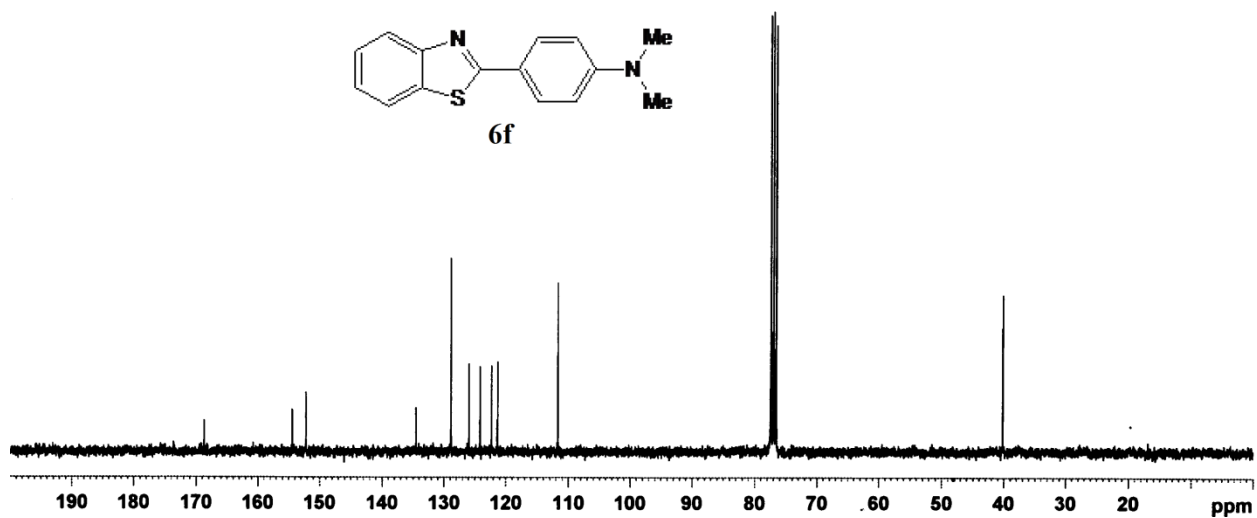
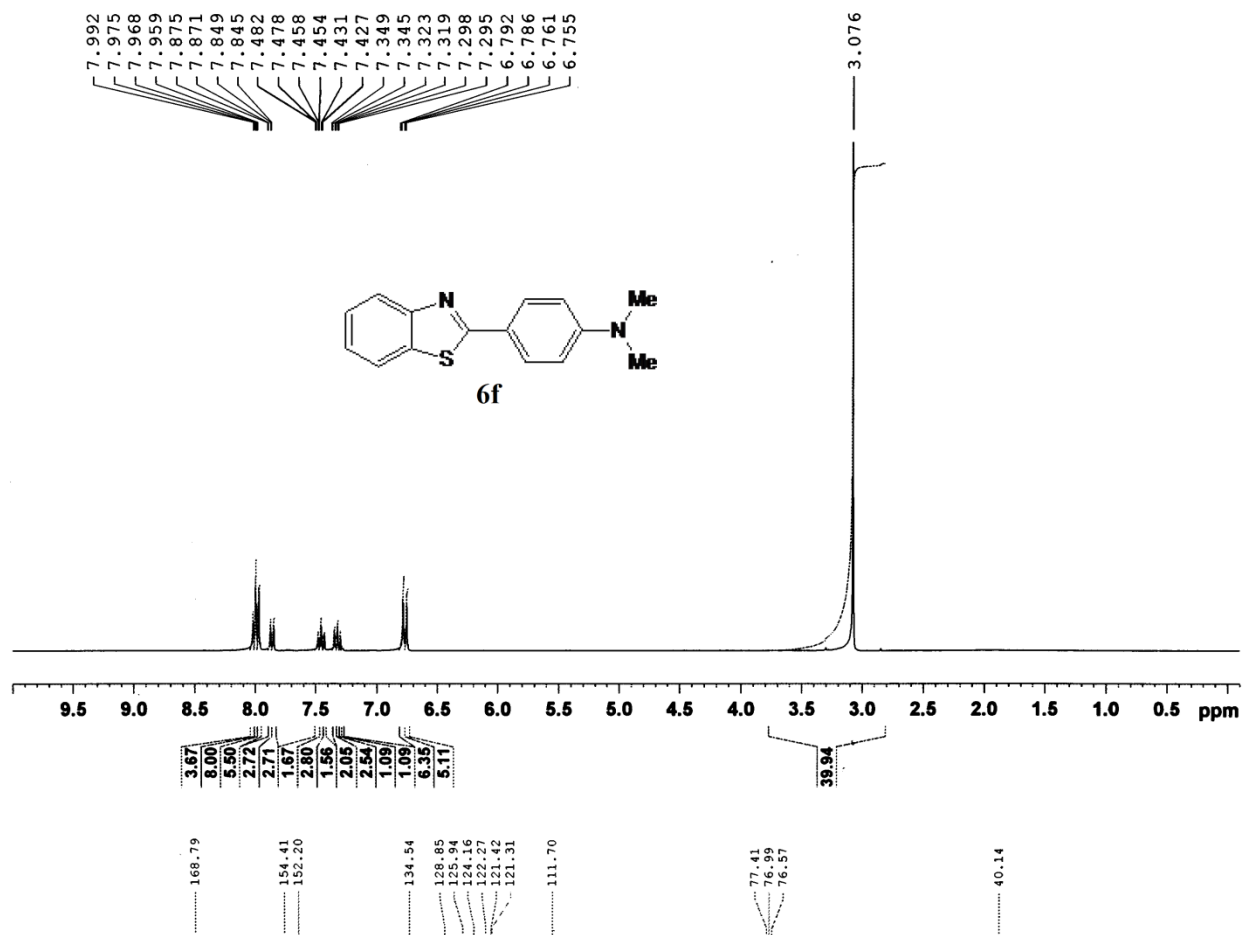


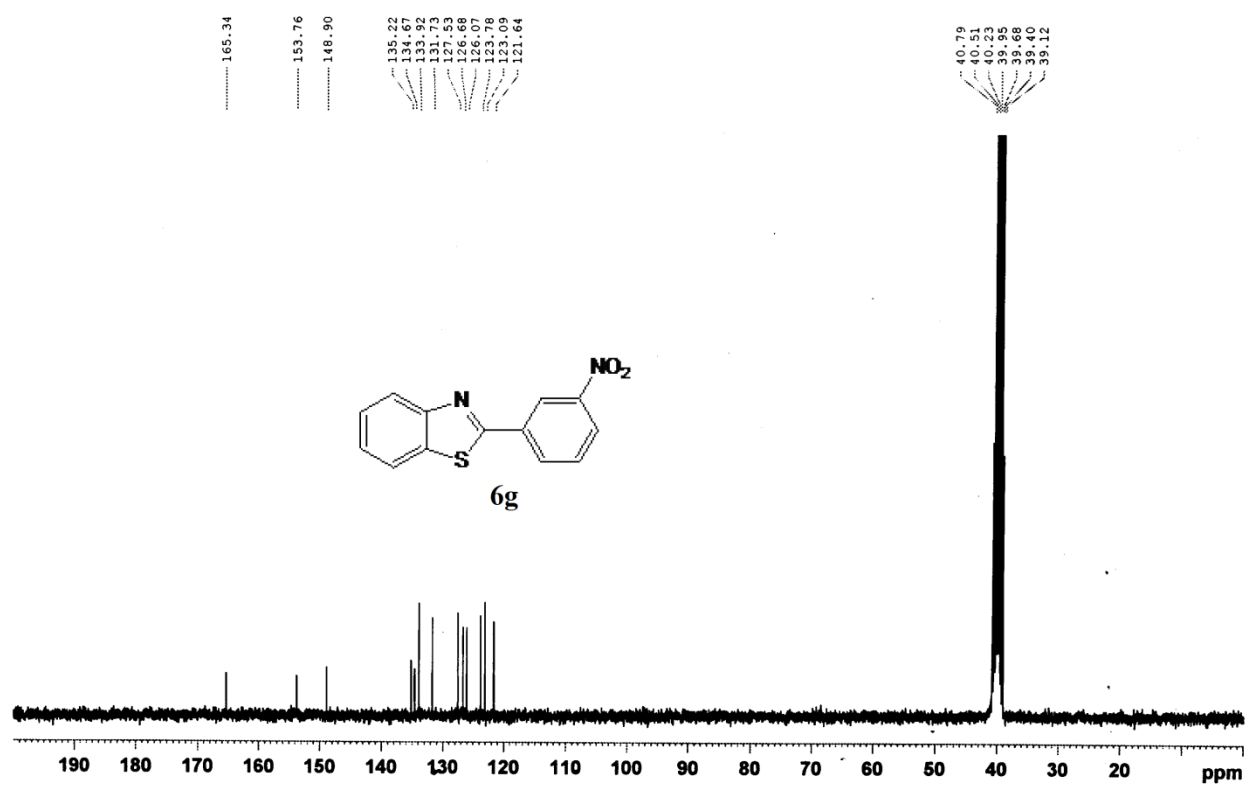
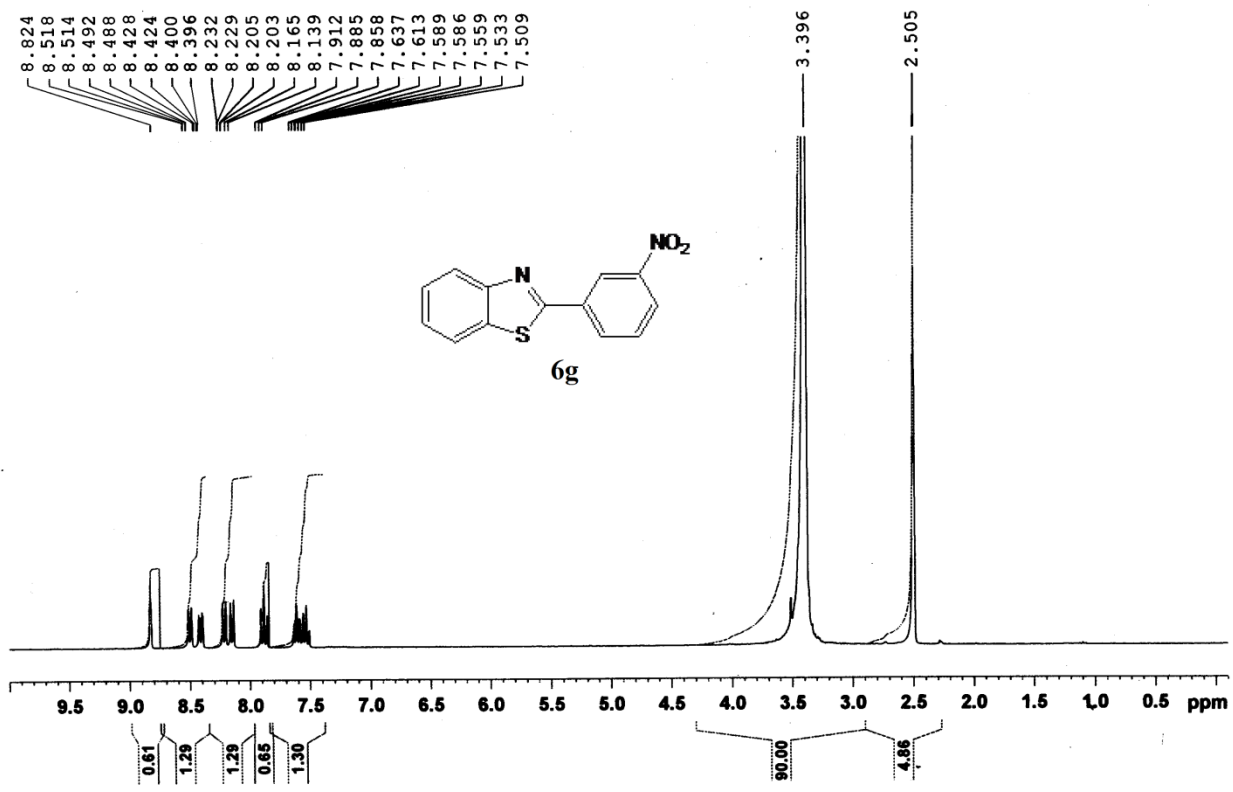




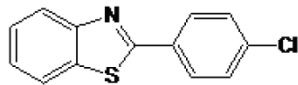




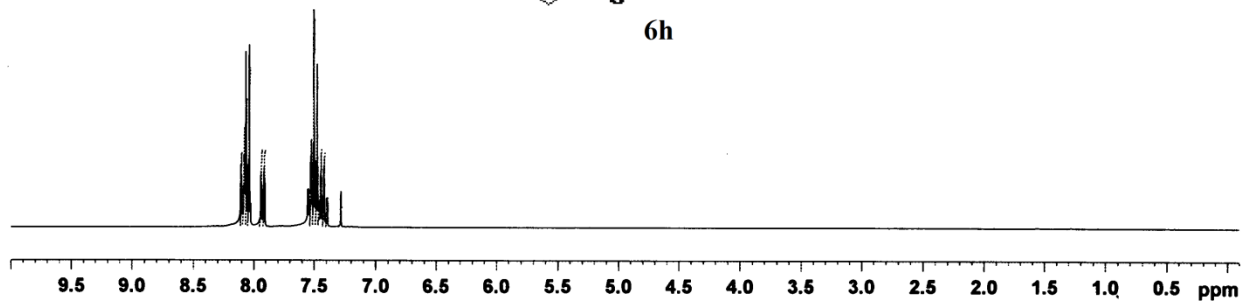




8.125
8.101
8.060
8.054
8.031
8.025
7.939
7.935
7.912
7.908
7.551
7.547
7.527
7.524
7.520
7.510
7.496
7.480
7.465
7.445
7.441
7.419
7.415
7.394
7.391
7.281

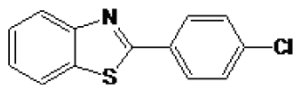


6h

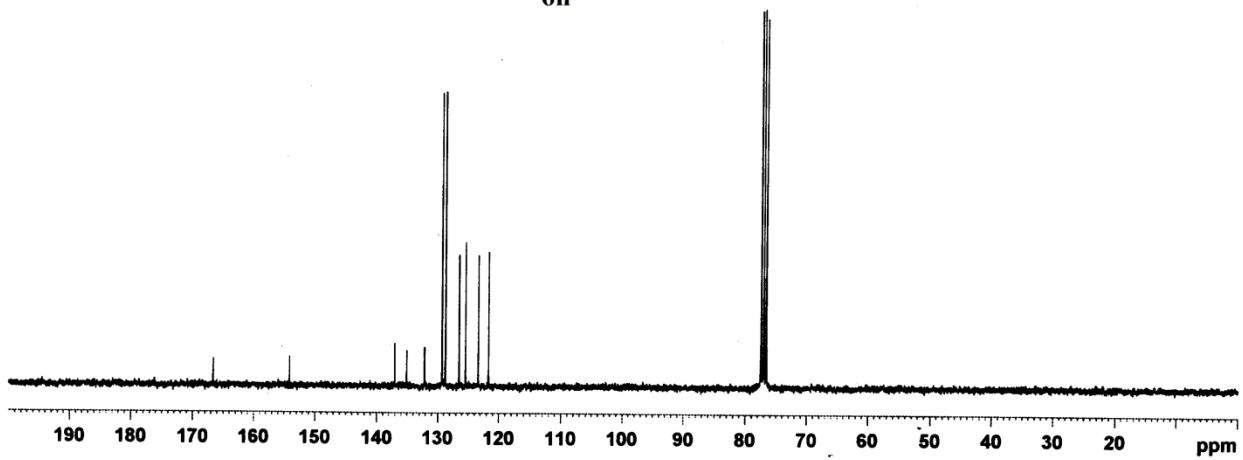


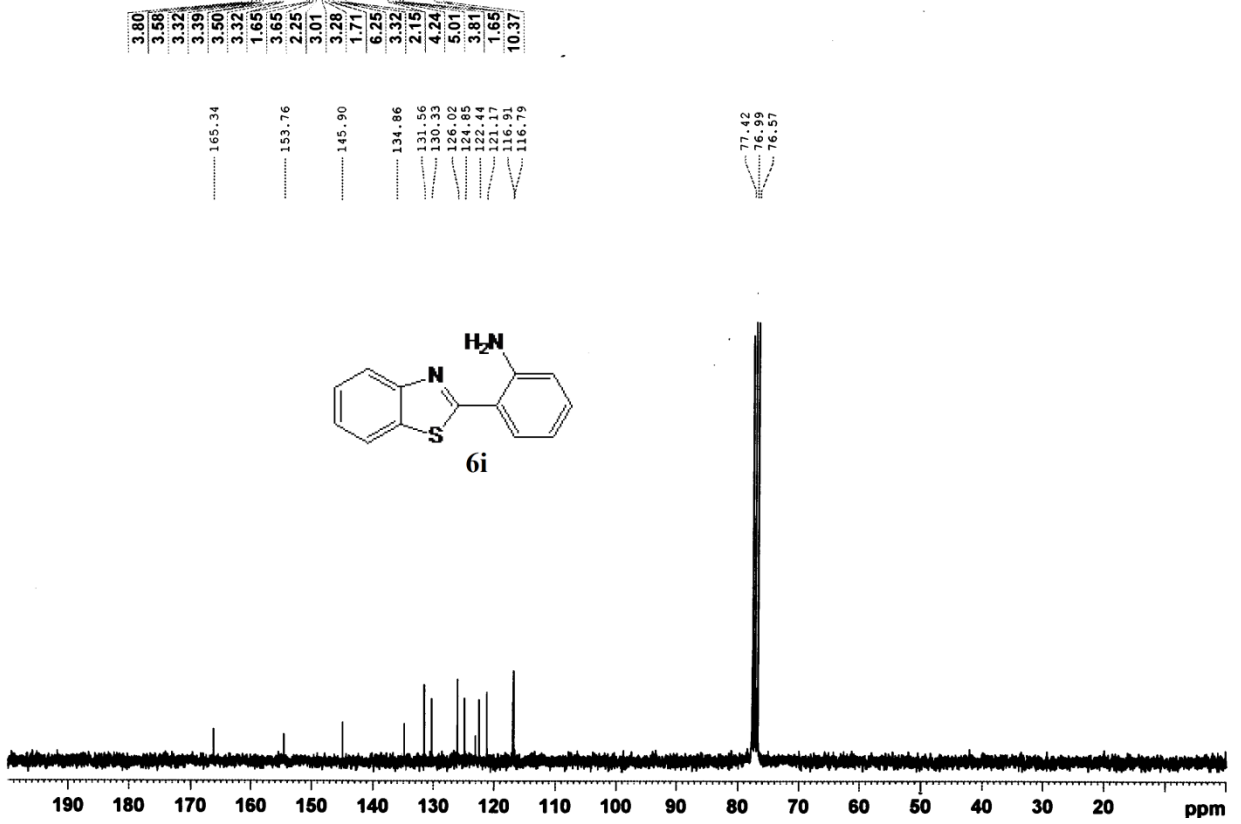
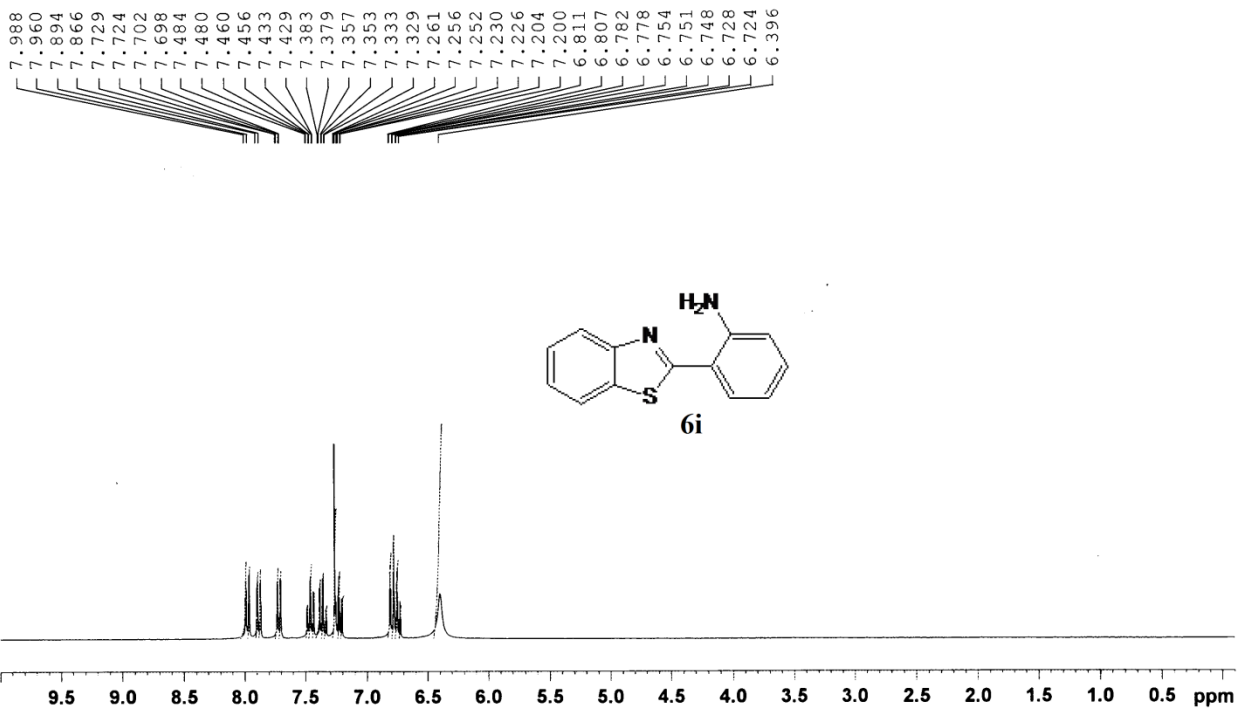
5.26
7.57
8.86
10.61
5.28
5.13
6.50
14.24
8.95
5.40
5.01
2.00
1.33

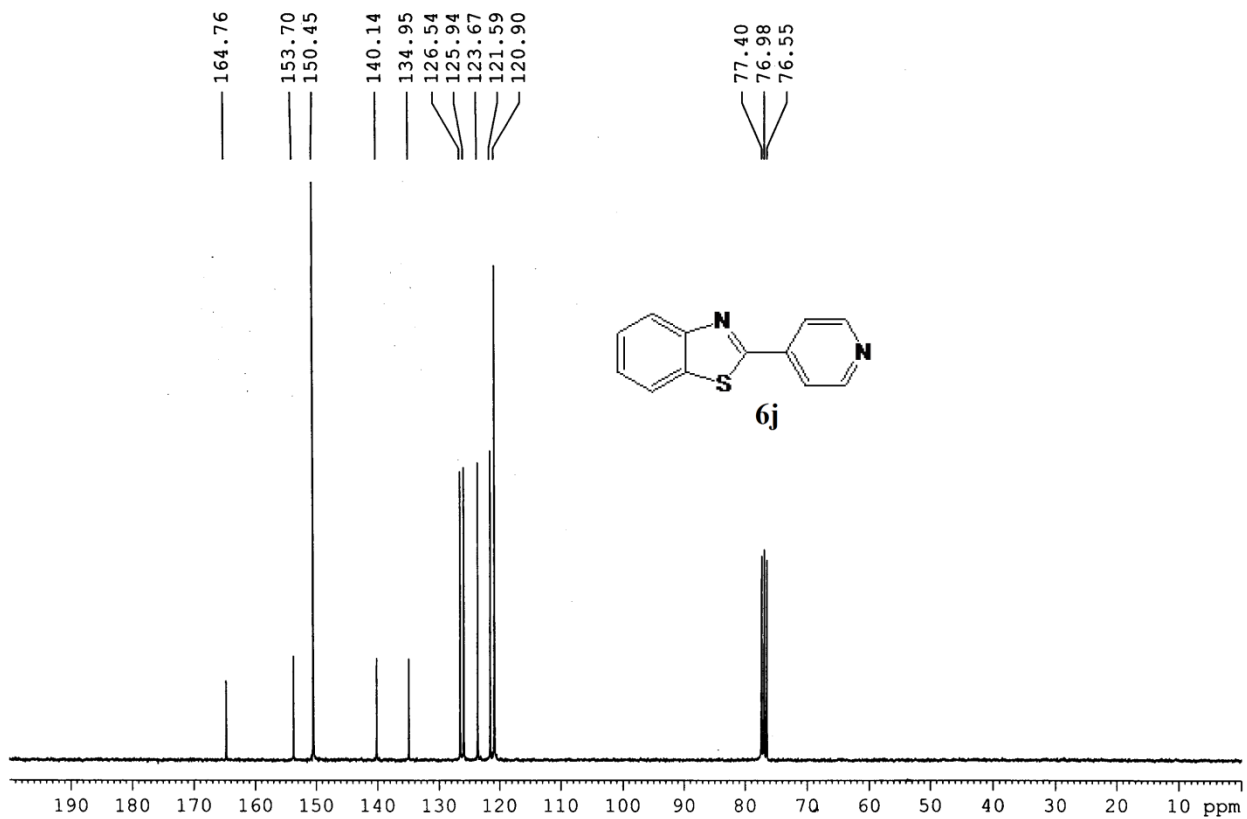
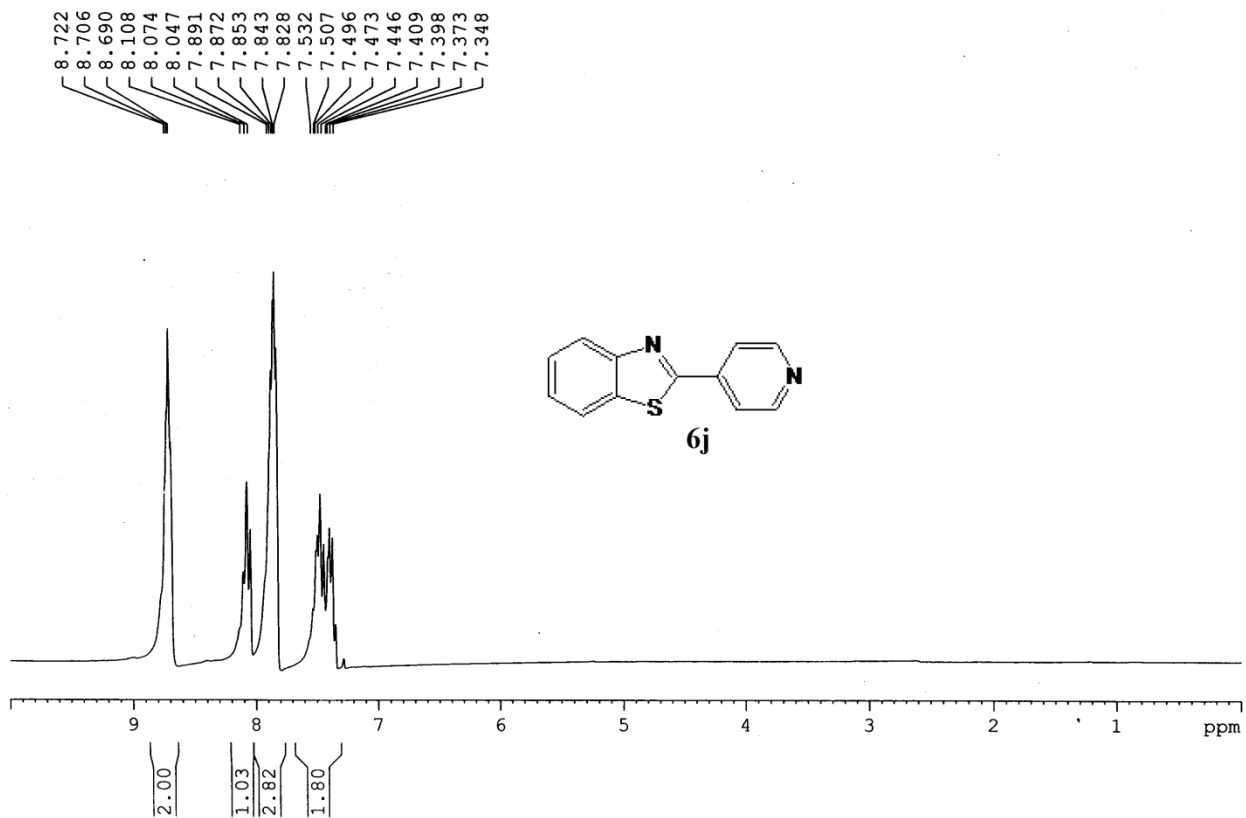
166.60
154.09
137.03
135.07
132.14
129.26
128.71
126.40
123.31
121.63
77.42
77.00
76.57

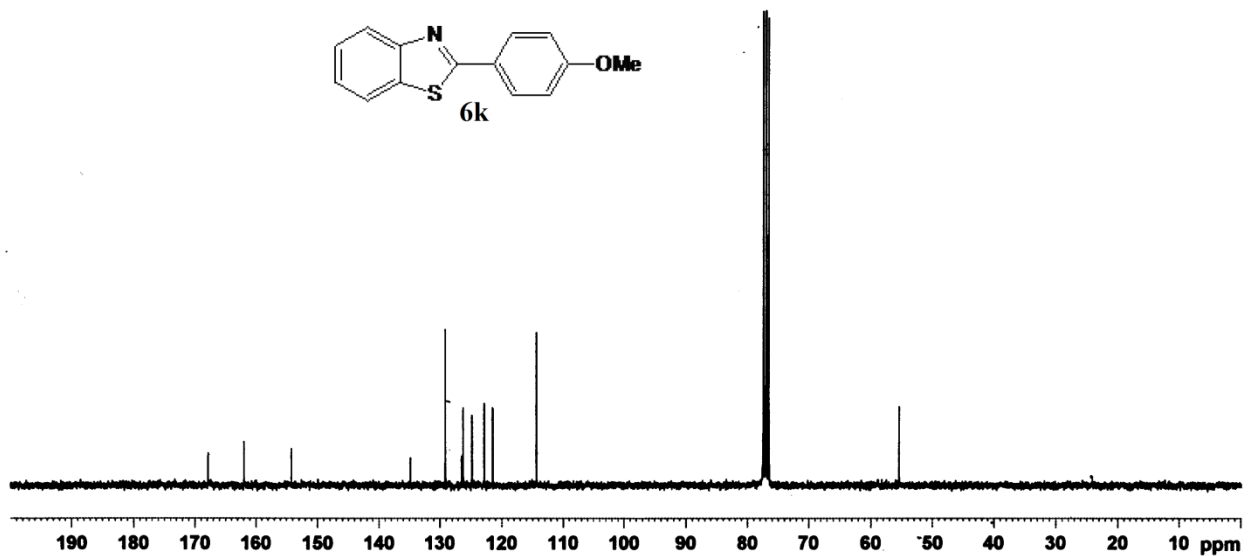
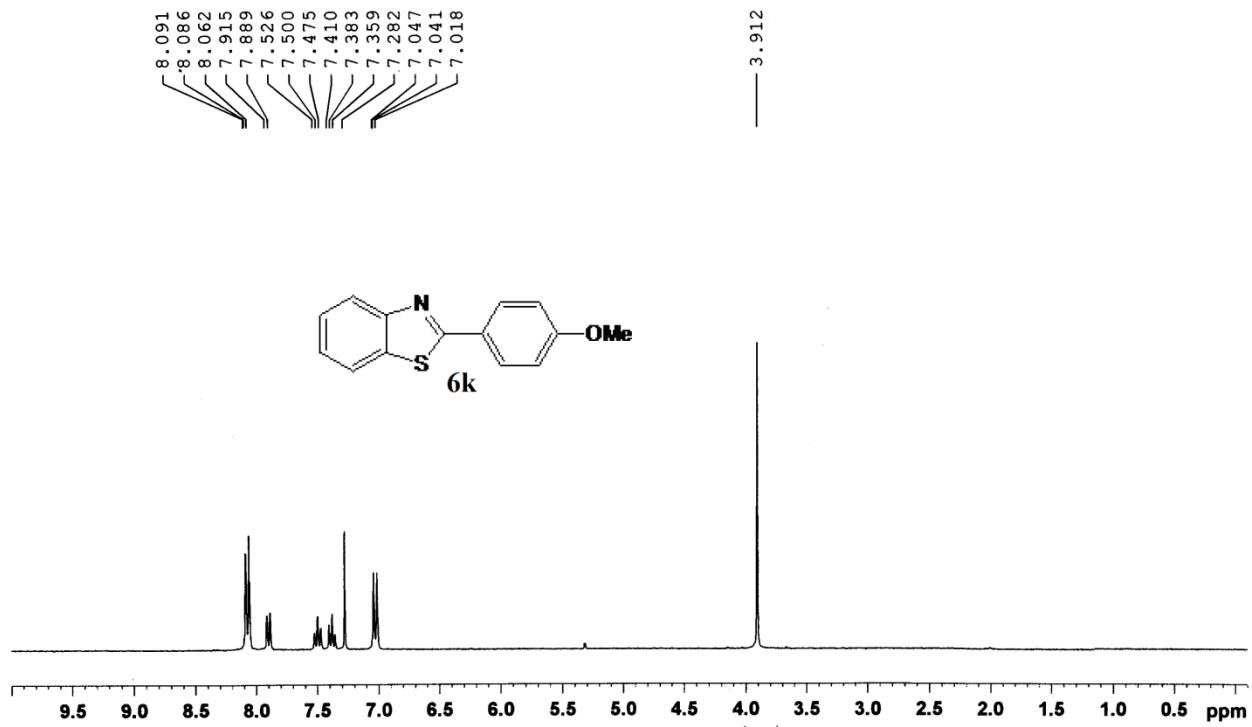


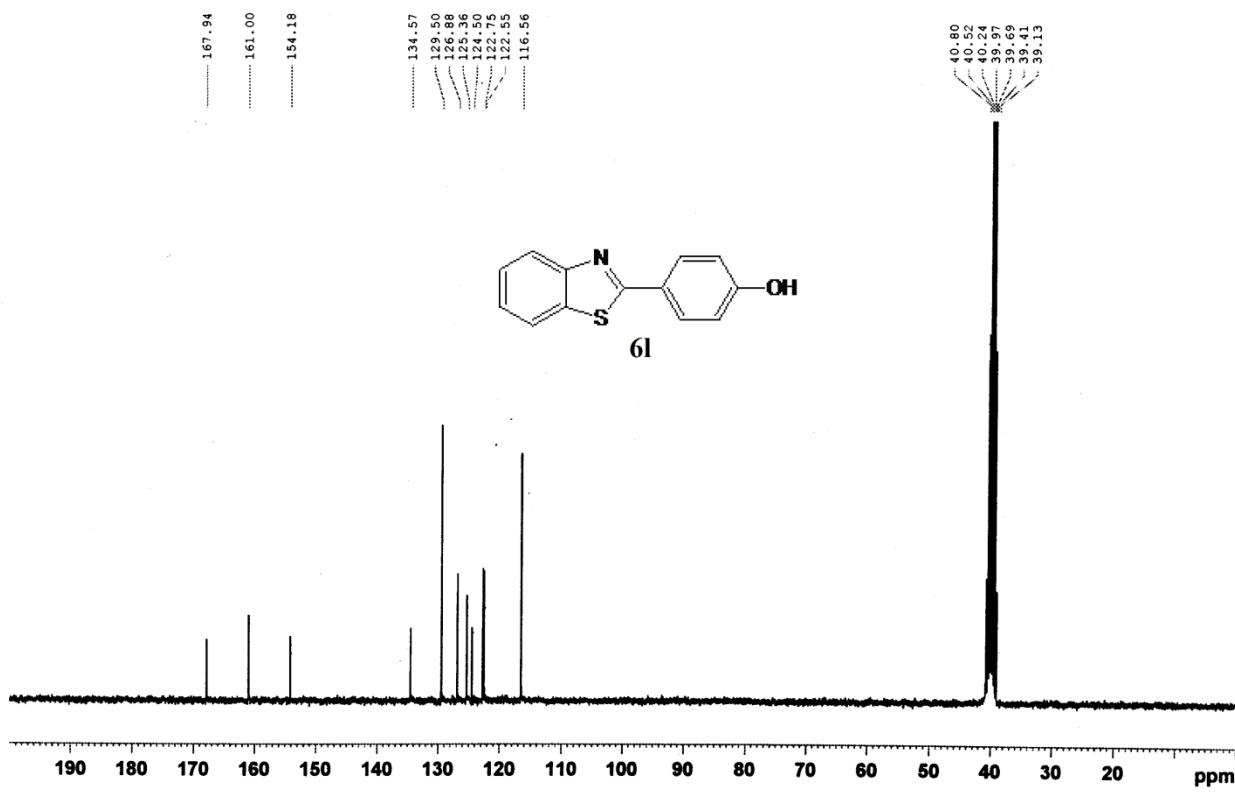
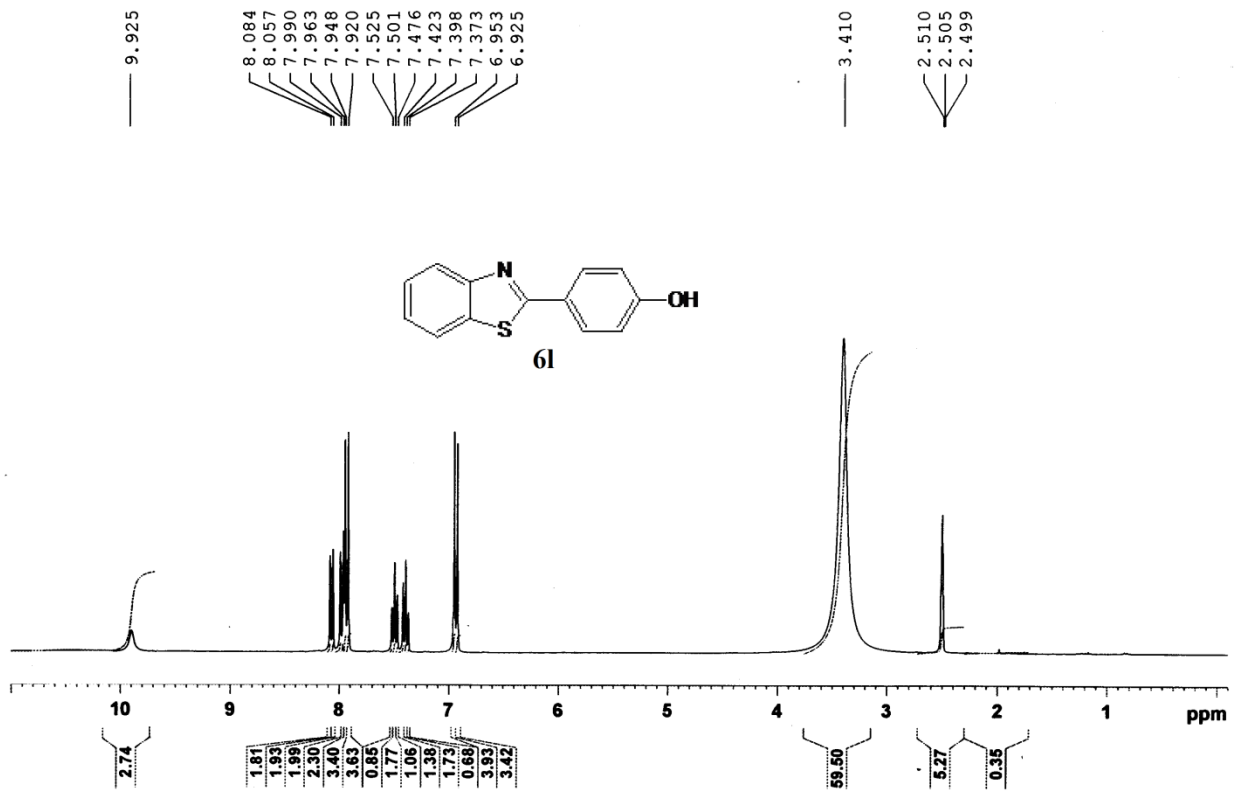
6h

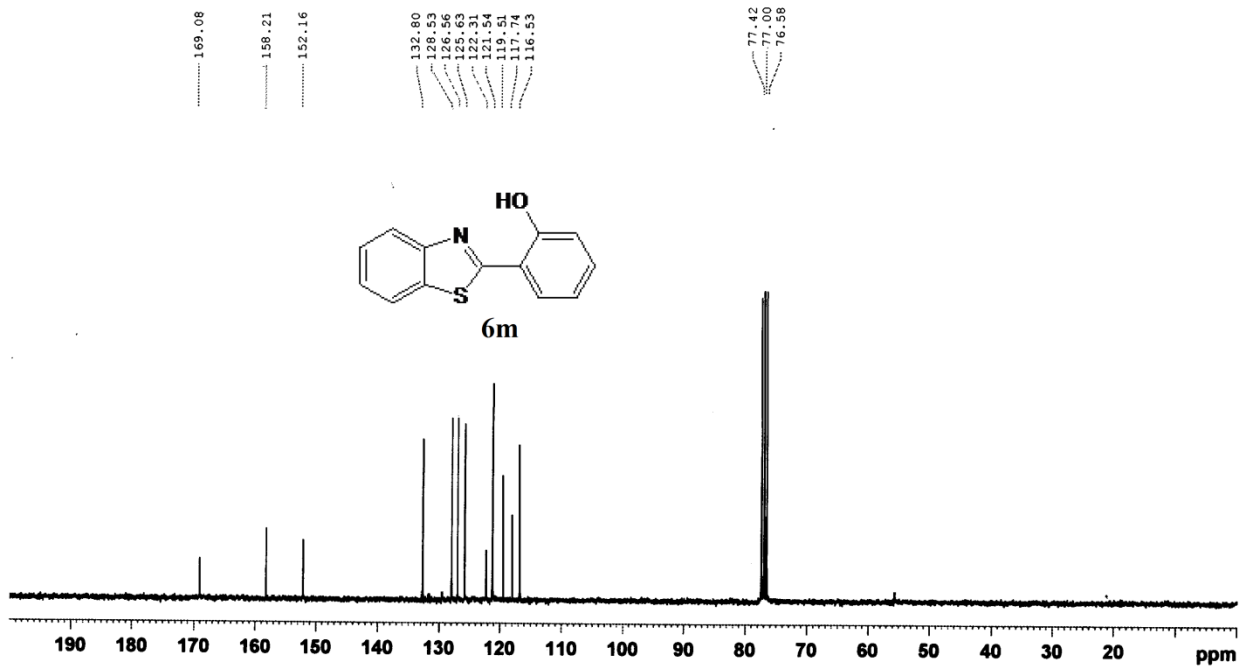
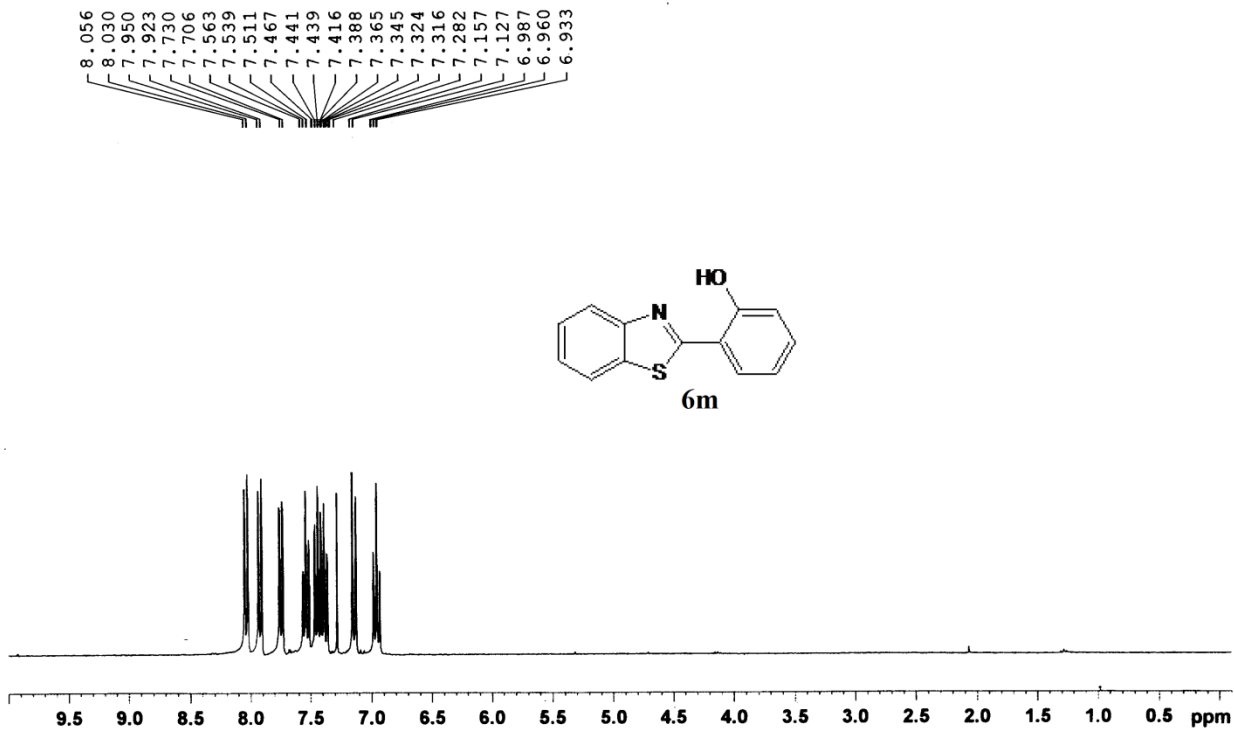


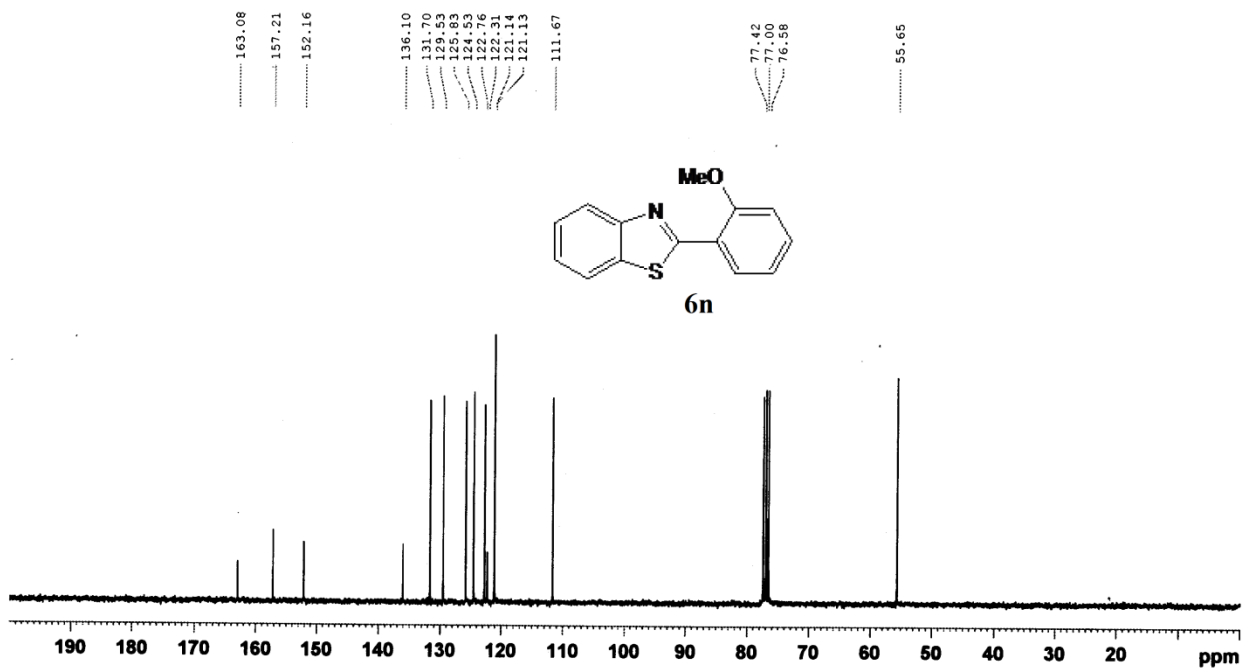
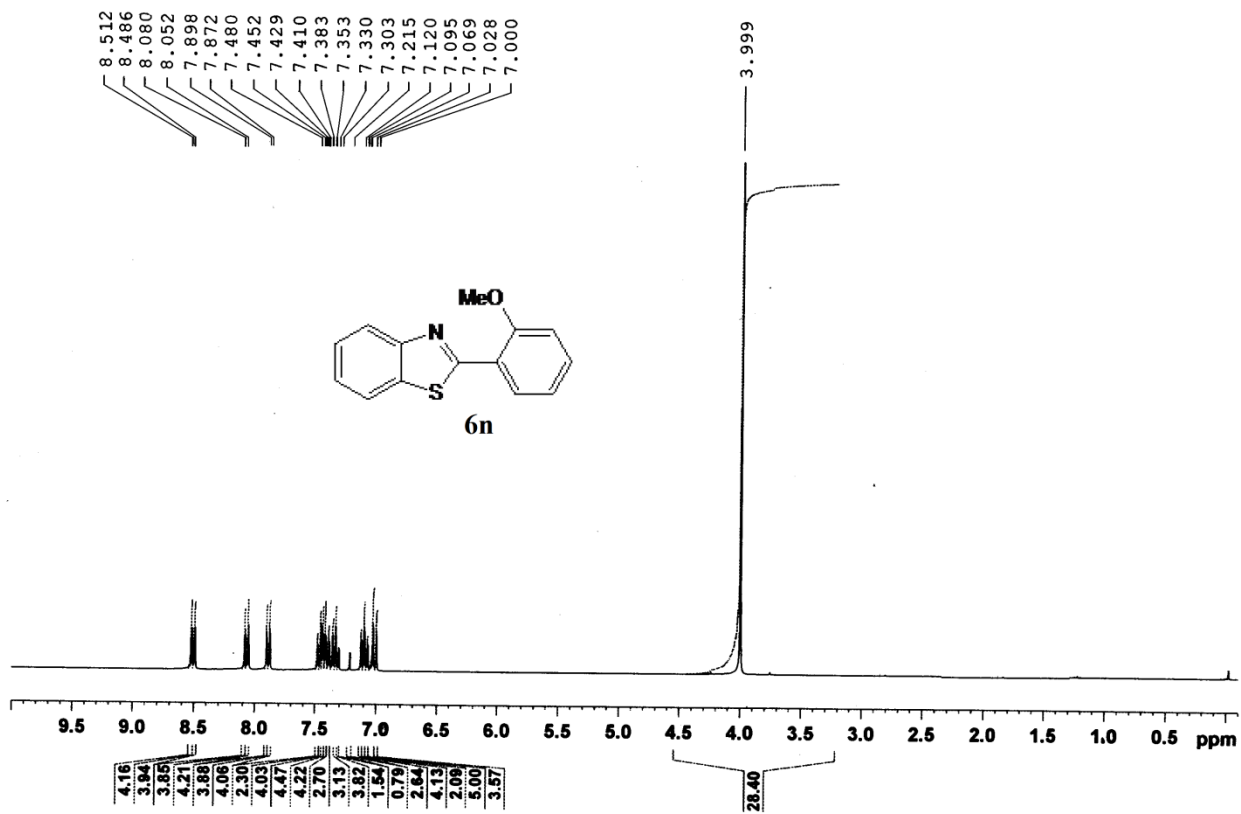


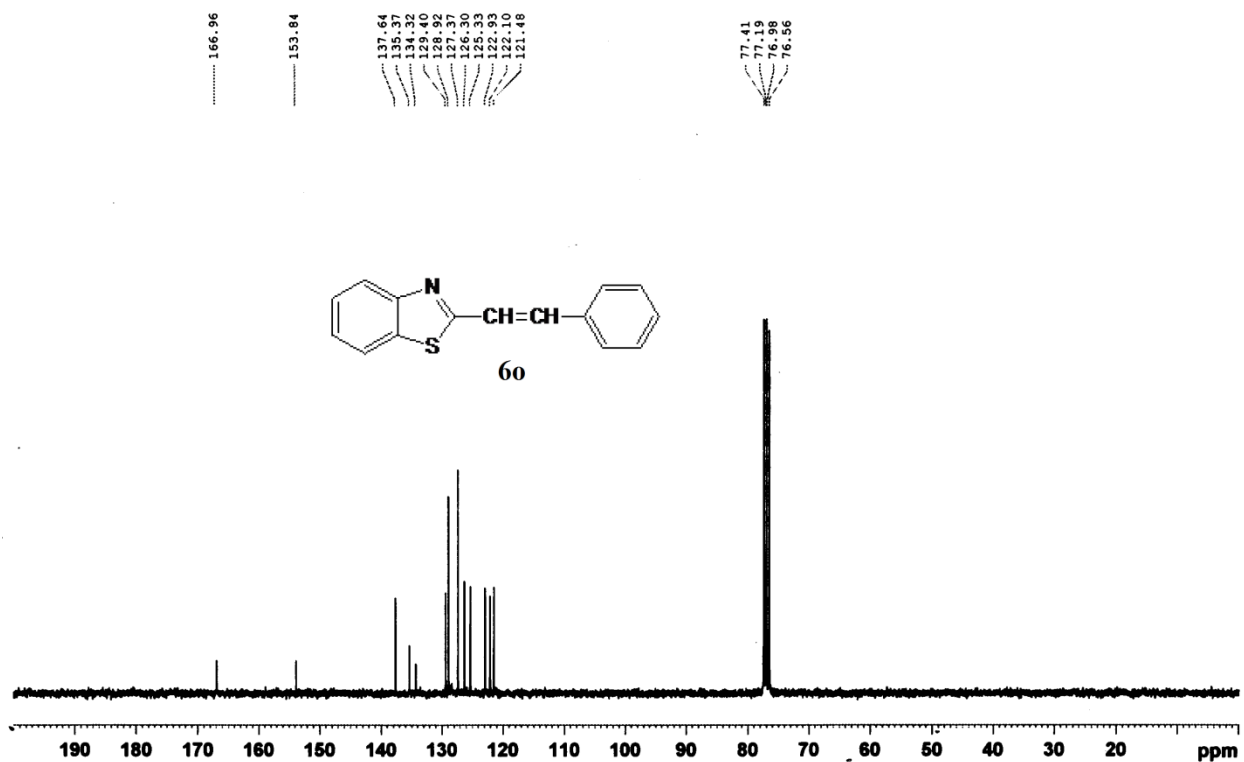
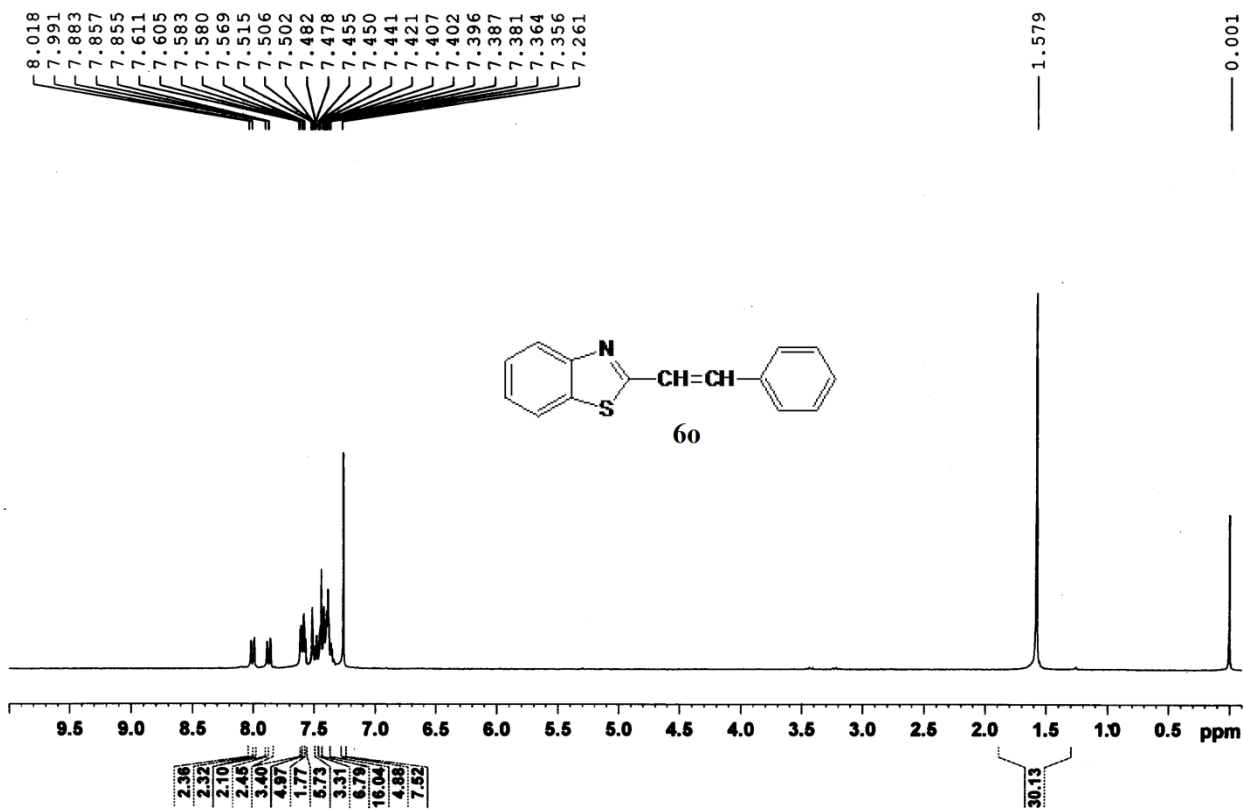




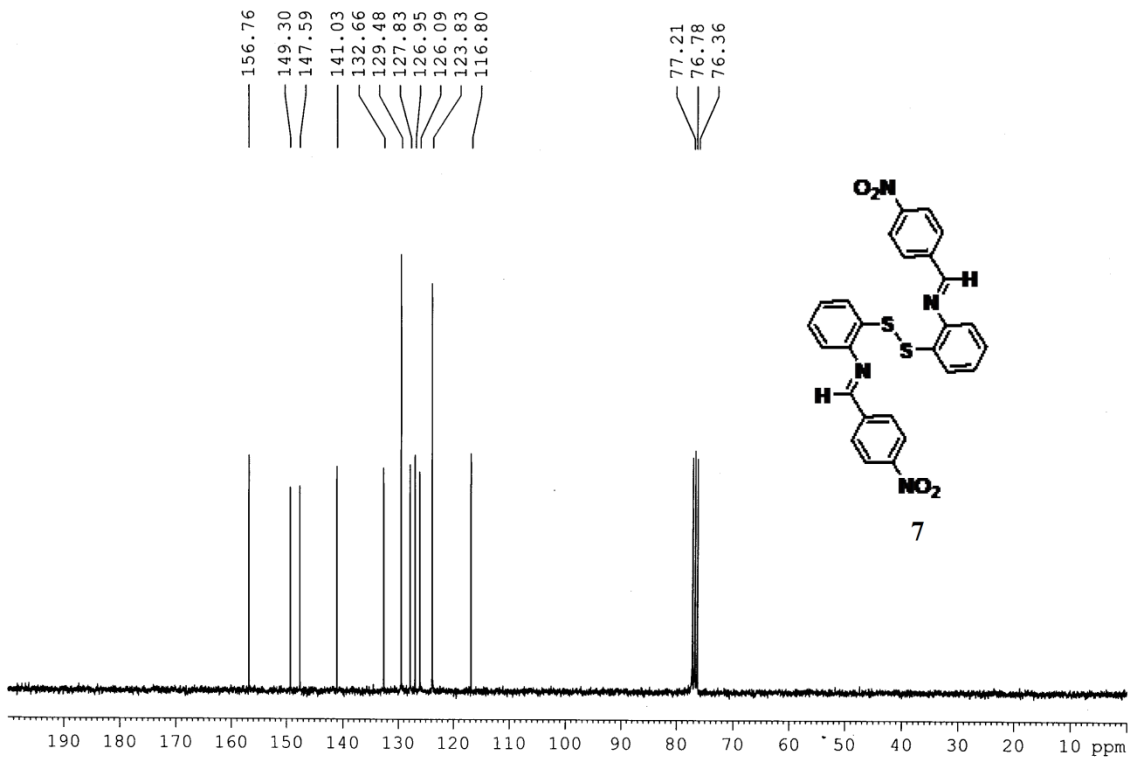
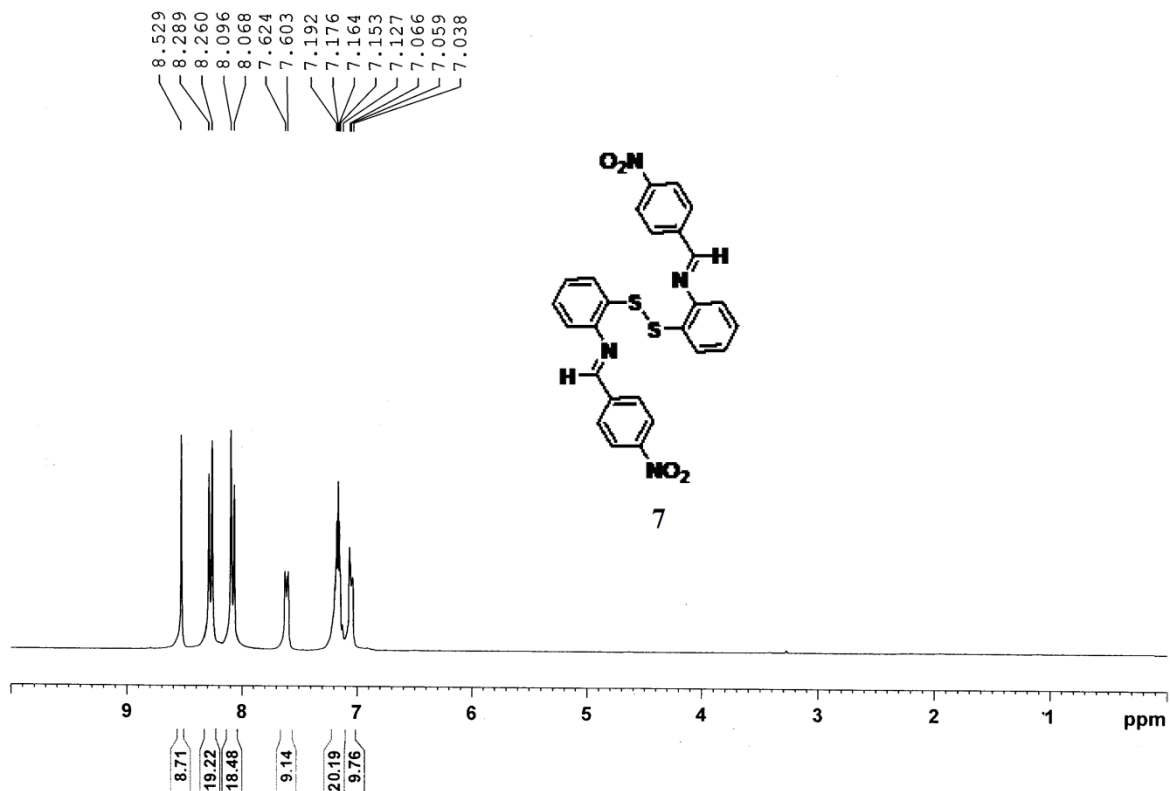


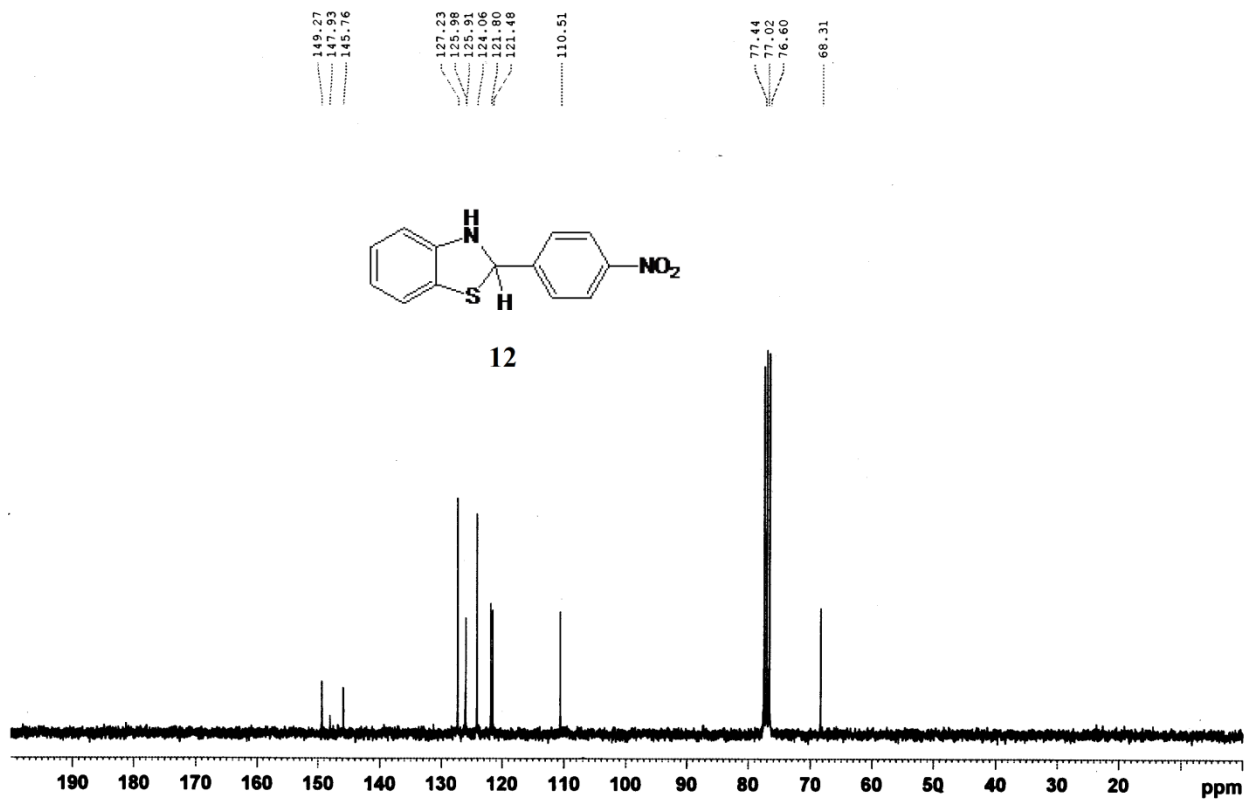
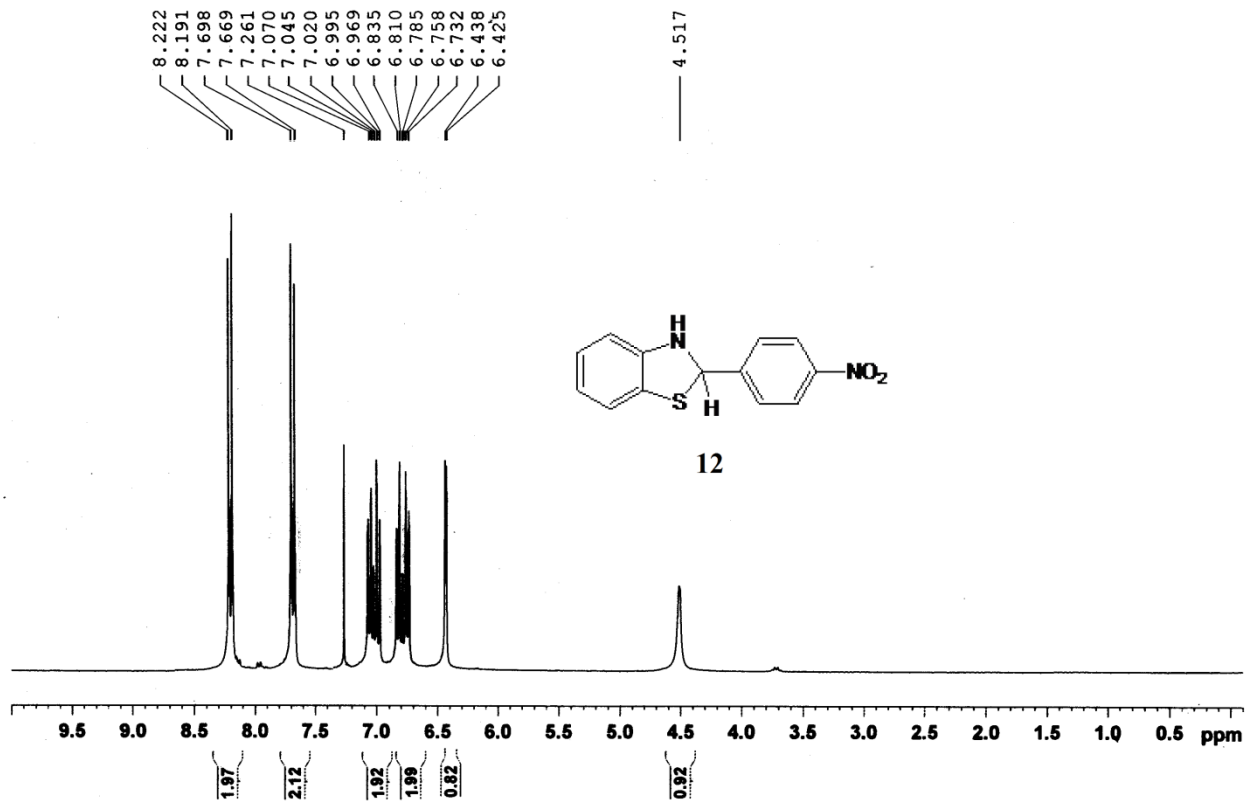






I. ^1H and ^{13}C NMR Spectra of intermediates 7 and 12





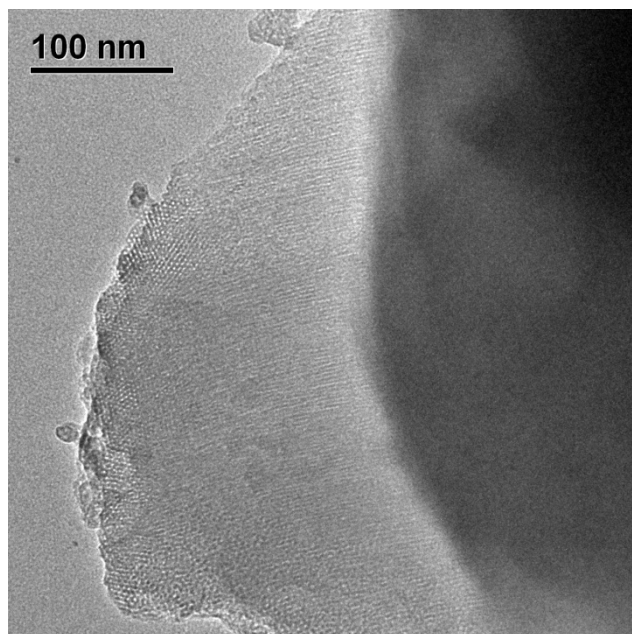


Figure S1. HRTEM image of the recycled **MCM-PP** catalyst.