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SUPPLEMENTARY MATERIAL

A novel method for the synthesis of benzothiazole heterocycles catalyzed by copper-diamsar complex loaded on SBA-15 in water media

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1. Preparation of SBA-15

SBA-15 was prepared by the procedure previously explained by Zhao et al..[24] In summary, P123 (2.00 g) was first dissolved in solution of deionised water (15.00 g) and HCl (60.00 g, 2 M) under vigorous stirring. Then, tetraethyl orthosilicate (4.25 g) was added into the solution, and stirring at 40 ˚C for 24 h. After that, the solution was heated at 100 ˚C for another 24 h. The product was filtered off, washed and dried at room temperature, and calcined at 600 ˚C for 8 hours to remove the surfactant molecules. SBA-15 was activated by refluxing in hydrochloric acid (6 M) for 6 h, to hydrolyse the siloxane Si–O–Si bonds to Si–OH species for better anchoring of the copper complex. The sample was then washed thoroughly with deionized water and heated at 120 ˚C under vacuum overnight.

2. Preparation of diamsar[25] (Scheme 1)

2.1. Preparation of tri(ethylenediamine) cobalt(III) chloride,[26] compound 4

Ethylanediamine (61 mL, 30 %) was added to HCl (17 mL, 6 N), after which a solution of cobalt chloride 6-hydrate (24 g) in water (75 mL) was added to the partially neutralized ethylanediamine. The cobalt was oxidized by blowing a violent stream of air through the solution for 3 hours. The solution was first evaporated to a volume of 15 mL; next HCl (37 %, 15 mL) and ethanol (30 mL) were added to it. The residue was cooled in an ice bath, filtered, washed with ethanol and and dried, respectively. The yield was 89%.

2.2. Synthesis of [Co-(1,8-dinitro)-sarcophagine],Cl_3 complex, compound 5

The complex of tri(ethylenediamine) cobalt(III) chloride dihydrate **4** (1 eq, 2.00 g) was first dissolved in a solution of water (3 mL) and aqueous formaldehyde (37 %, 10.4 eq, 4.5 mL). Next, nitromethane (1.06 mL) was added to the solution. The reaction mixture was cooled to 4 ºC in an ice-water bath. Then, a solution of aqueous sodium hydroxide (4 M, 3.45 eq, 5 mL) was cooled to 4 ºC and added to the above prepared solution. This new solution was stirred in an ice-water bath until it rapidly changed to a deep violet-brown color from the initial orange color and the reaction temperature was raised to 35 ºC. After 15 minutes, when the temperature was dropped to 20 ºC, concentrated HCl (60 mmol, 5 mL) was added to the solution. Finally, the solution was cooled in an ice bath and after an hour, the orange residue was filtered, washed with methanol, and dried to give the product in 70 %.

2.3. Synthesis of [Co-(1,8-diammonium) sarcophagine],Cl_5 complex, compound 6

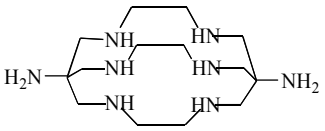
A solution of concentrated hydrochloric acid (145 eq, 12 mL) and ethanol (6 mL) was added to stannous chloride dihydrate (13 eq, 3.00 g) in a round bottomed flask. The solution was stirred magnetically and heated to 70 ˚C until it became clear. Then, the complex of [Co(dinosar)]Cl_3 **5** (1 eq, 600 mg) was added to the solution under vigorous stirring. The reaction mixture was heated at 70 ˚C for 4 h while the colour of the solution turned green from orange/brown. After addition of 6 mL water to the solution, it was cooled at room temperature for 15 minutes. Later the flask was immersed in an ice-water bath and the orange product was filtered and dried. The [Co(diamsar)]Cl_5 **6** complex was obtained in 60% yield.

2.4. Synthesis of diamino-sarcophagine (diamsar), compound 7

Sodium hydroxide (2.11 eq, 77 mg) was dissolved in deoxygenated water (7 mL) and nitrogen was purged to the solution for eliminating oxygen. The bubbling continued for 30 minutes. Then, [Co(diamsar)]Cl_5 complex **6** (1 eq, 500 mg) and cobalt (II) chloride 6-hydrate (1.01 eq, 118 mg) were dissolved in the basic solution. After homogenization of the solution, sodium cyanide (17.7 eq, 783 mg) was added to the prepared solution under vigorous stirring. The mixture was heated to 70 °C and vigorously stirred under nitrogen until the solution turned almost yellow (7 h). The solution was dried under air flow, and the residue was extracted with boiling acetonitrile. The total extract volume was reduced under vacuum, and cooled to -10 °C to precipitate white crystals of the product. The product was recovered by filtration and dried. The Diamino-sarcophagine compound **7** was obtained with a yield around 56%.

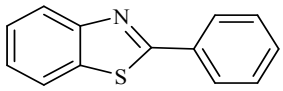
3. Sellected spectroscopic data

Diamsar (7)



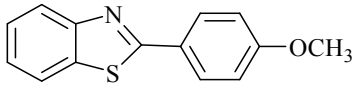
White solid. Yield 60%; IR (KBr) *w* 3400, 3048, 3012, 2810, 2720. ^{1}H NMR (400 MHz, D_2O) δ 2.69 (s, 12H), 2.76 (s, 12H). ^{13}C NMR (400MHz, D_2O) δ 48.15, 51.78, 57.40. GC-MS (EI): 315.3 $(M + H)^+$

2-Phenyl-benzothiazole (10a)



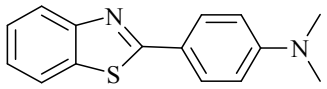
White solid. Yield 90%; mp: 110-114 °C. FTIR (KBr) *w* 3050, 1615, 1519, 1388, 950. ^{1}H NMR (400 MHz, DMSO-d_6) *δ* 7.46-7.60 (m, 5H), 8.07-8.17 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 122.8, 123.3, 126.0, 127.1, 127.6, 129.9, 131.9, 133.2, 134.8, 153.9, 167.8.

2-(4-Methoxyphenyl)benzothiazole (10b)



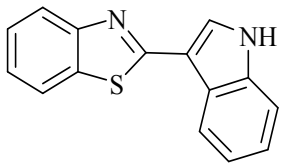
White solid. Yield 85%; mp: 288-290 °C. FTIR (KBr) *w*: 3383, 1615, 1430, 1310, 810, 610. ^{1}H NMR (300 MHz, DMSO-d_6) *δ* 3.8 (S, 3H) 7.08 (d, *j* = 8.3, 2H), 7.39 (t, j = 7.5, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.98-8.08 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6) *δ*: 55.4, 114.7, 122.1, 122.4, 125.0, 125.5, 126.4, 128.8, 134.2, 153,6, 161,7. 167.1.

2-(4-Dimethylamino phenyl)benzothiazole (10c)



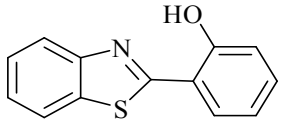
White solid. Yield 85%; mp: 166-168 °C. FTIR (KBr) *w* 3050, 1460, 1300, 1615, 1100, 820. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.03 (s, 6H), 6.84 (d, J = 9.2 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.89-7.95 (m, 3H), 8.05 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 40.2, 111.7, 121.4, 122.3, 124.2, 126.0, 128.9, 134.6, 152.2, 154.4, 168.8.

2-(1H-indol-3-yl)benzothiazole (10d)



White solid. Yield 85%; mp: 174-177 °C. FTIR (KBr) *w* 3510, 3055, 1355, 1650, 1000, 800. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09-7.34 (m, 5H), 7.70-7.85 (m, 3H), 8.28 (t, J = 3.5 Hz, 1H), 10.98 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 110.4, 112.3, 120.7, 121.1, 121.5, 121.7, 122.7, 124.2, 124.5, 126.1, 128.9, 133.0, 136.8, 153.7, 162.9.

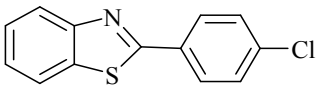
2-(2-Hydroxyphenyl)benzothiazole (10e)



Light blue solid. Yield 88%; mp: 132-134 °C. FTIR (KBr) *w* 3550, 3057, 2923, 1621, 1589, 1483, 1315, 1165, 1033, 973, 871, 742. ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.98-7.09 (m, 2H), 7.38-

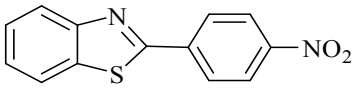
7.56 (m, 3H), 8.03-8.17 (m, 3H), 11.56 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 116.9, 118.3, 119.7, 122.0, 122.1, 125.1, 125.4, 126.4, 128.5, 132.4, 134.2, 151.4, 156.2, 165.2.

2-(4-Chlorophenyl)benzothiazole (10f)



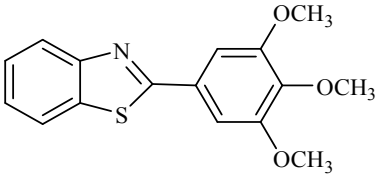
White solid. Yield 90%; mp: 114-116 ºC. FTIR (KBr) *w* 3054, 1508, 1474, 1399, 965, 828, 756. ^{1}H NMR (400 MHz, DMSO-d6) δ 7.48 (dd, J = 7.2 Hz, 0.7 Hz, 1H), 7.56 (dd, J = 6.8 Hz, 1.2 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 8.06-8.15 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d6) δ 122.8, 123.4, 126.2, 127.2, 129.3, 129.9, 132.1, 135.0, 136.4, 153.4, 166.4.

2-(4-Nitrophenyl)benzothiazole (10g)



Light yellow solid. Yield 88%; mp: 227-229 °C. FTIR (KBr) *w* 3060, 1797, 1520, 1350, 954, 810. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.55 (m, 1H), 7.63 (m, 1H), 8.20 (dd, J = 24.8 Hz, 8.0 Hz, 2H), 8.39 (m, 4H).

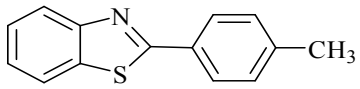
2-(3,4,5-Trimethoxyphenyl)benzothiazole (10h)



Light yellow solid. Yield 92%; mp: 146-148 °C. FTIR (KBr) *w* 3160, 1615, 1310, 1246, 1058, 950. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.77 (s, 3H), 3.93 (s, 6H), 7.35 (s, 2H), 7.47 (dd, J =

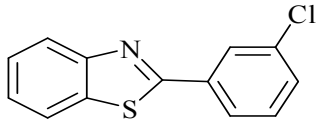
6.0 Hz, 1.2 Hz, 1H), 7.56 (dd, *J* = 6.8 Hz, 1.2 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.14 (dd, *J* = 7.2 Hz, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 56.6, 60.72, 104.88, 122.7, 123.2, 125, 9, 127.1, 128.7, 135.0, 140.6, 153.0, 153.8, 167.6.

2-(4-Methylphenyl)benzothiazole (10i)



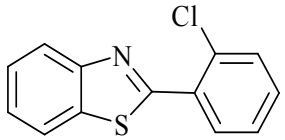
Light yellow solid. Yield 88%; mp: 81-84 °C. FTIR (KBr) *w* 3058, 3023, 2850, 1483, 1360, 1286, 1253, 959. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 (d, *J* = 7.9 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.50-7.53 (m, 1H), 7.38-7.41 (m, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.5, 121.6, 123.1, 125.0, 126.3, 127.5, 129.7, 131.0, 134.9, 141.5, 154.2, 168.3.

2-(3-Chlorophenyl)benzothiazole (10j)



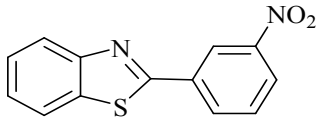
Yellow solid. Yield 89%; mp: 93-94 °C. FTIR (KBr) *w* 3053, 1622, 1588, 1473, 1294, 1232, 1161, 943, 886, 732. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.62 (m, 4H), 7.98 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 8.06 (s, 1H), 8.13 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ 122.4, 123.0, 125.8, 125.9, 126.3, 126.8, 131.0, 131.2, 134.0, 134.6, 134.7, 153.3, 165.5.

2-(2-Chlorophenyl)benzothiazole (10k)

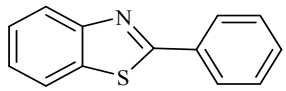


White crystals. Yield 87%; mp: 80-82 °C. FTIR (KBr) *w* 3055, 1590, 1492, 1317, 1271, 1061, 966, 748. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.47 (m, 3H), 7.52-7.57 (m, 2H), 7.97 (d, J = 8.1 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.24 (m, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 121.3, 123.4, 125.4, 126.2, 127.1, 130.7, 131.1, 131.7, 132.2, 132.6, 136.0, 152.4, 164,1.

2-(3-Nitrophenyl)benzothiazole (10l)



Light yellow solid. Yield 88%; mp: 182-184 °C. FTIR (KBr) *w* 3085, 1558, 1530, 1363, 1345, 987, 810, 761. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm); 7.36-7.49 (m, 2H), 7.67 (t, J = 8.1 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 8.27 (d, J = 8.1 Hz, 1H), 8.34 (d, J = 7.8 Hz, 1H), 8.84 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 121.1, 122.4, 123.2, 125.4, 126.0, 126.9, 131.1, 133.3, 134.2, 134.7, 148.3, 153.2,164.9,.



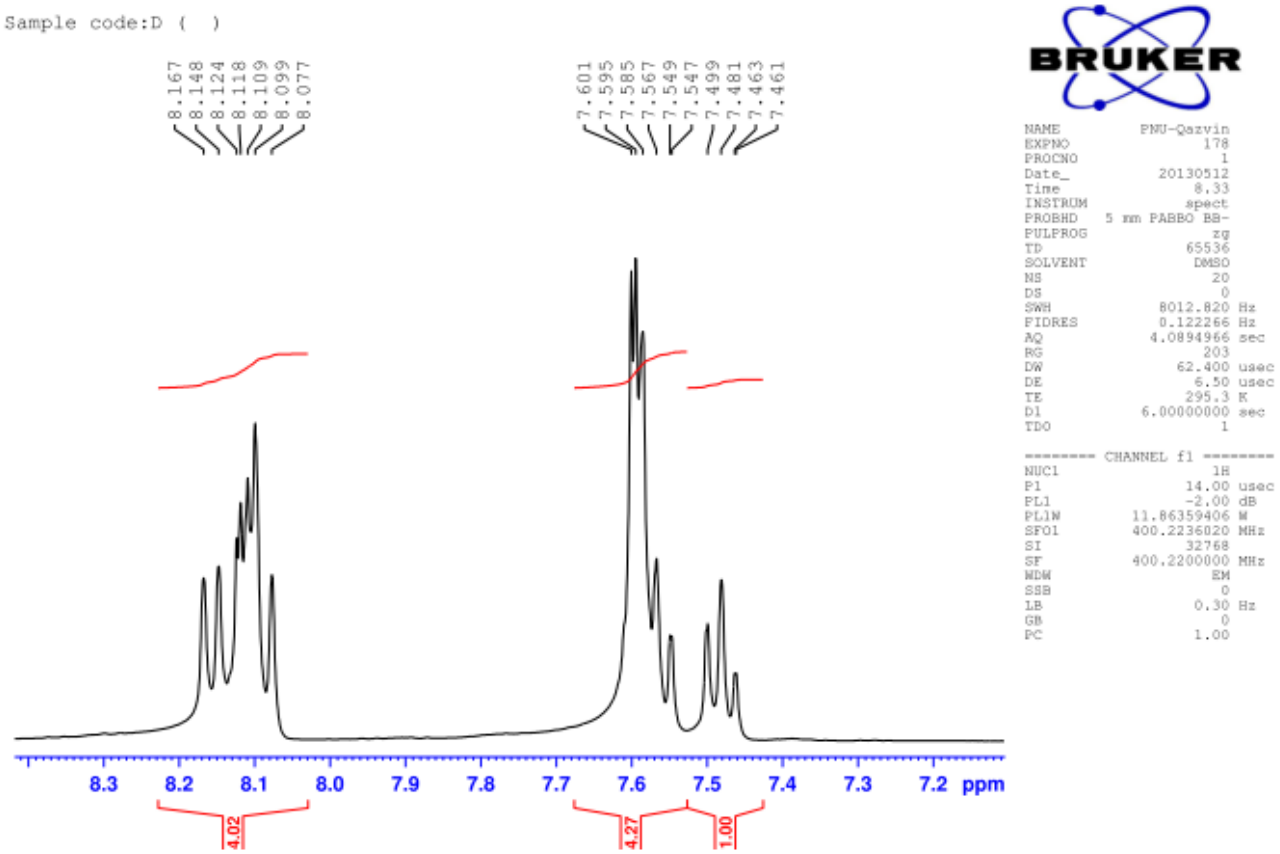
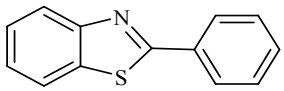


Figure S1. ^{1}H NMR of 2-phenyl-benzothiazole (**10a**)



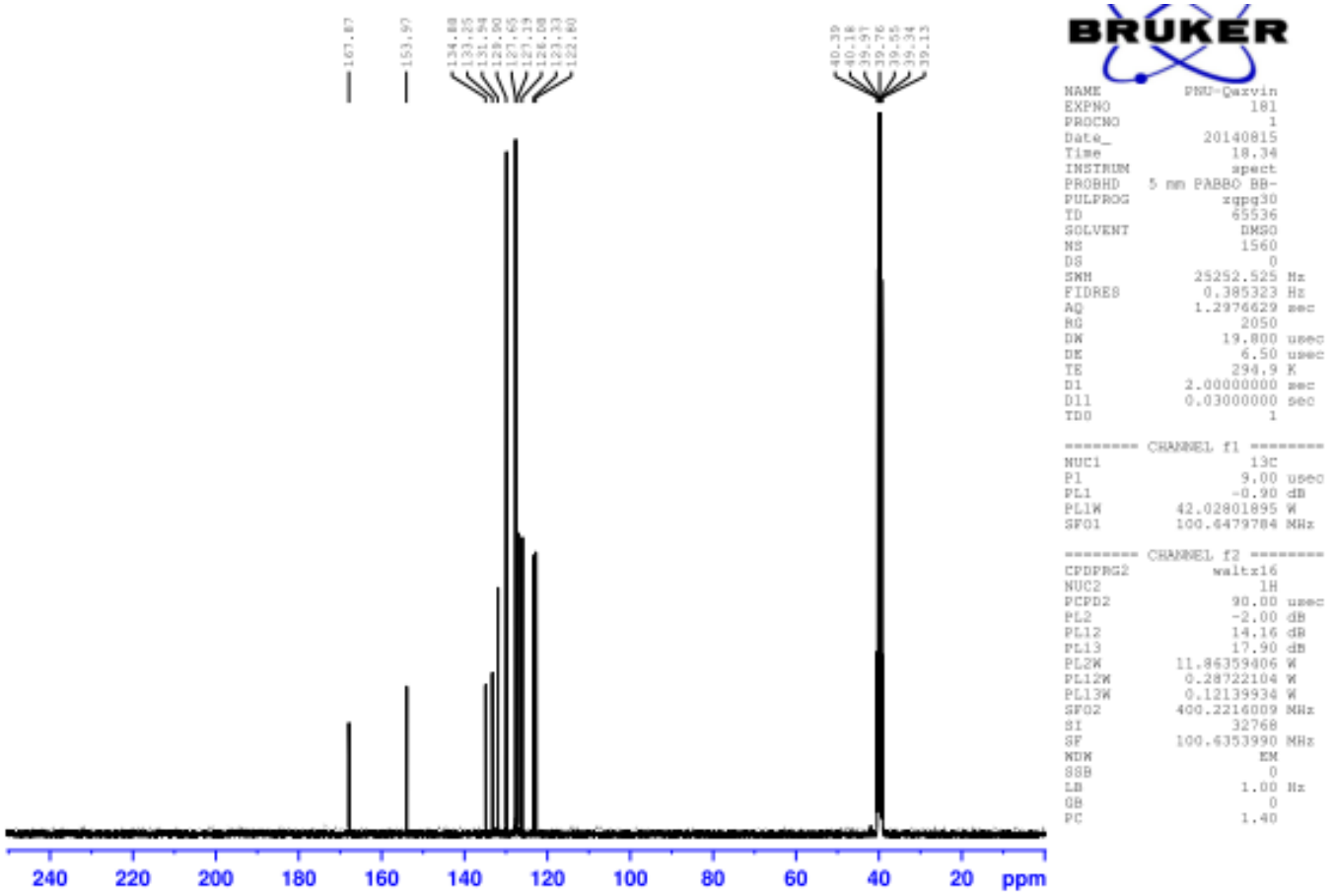
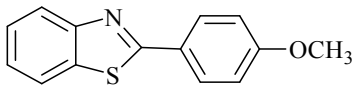


Figure S2. ^{13}C NMR of 2-phenyl- benzothiazole (**10a**)



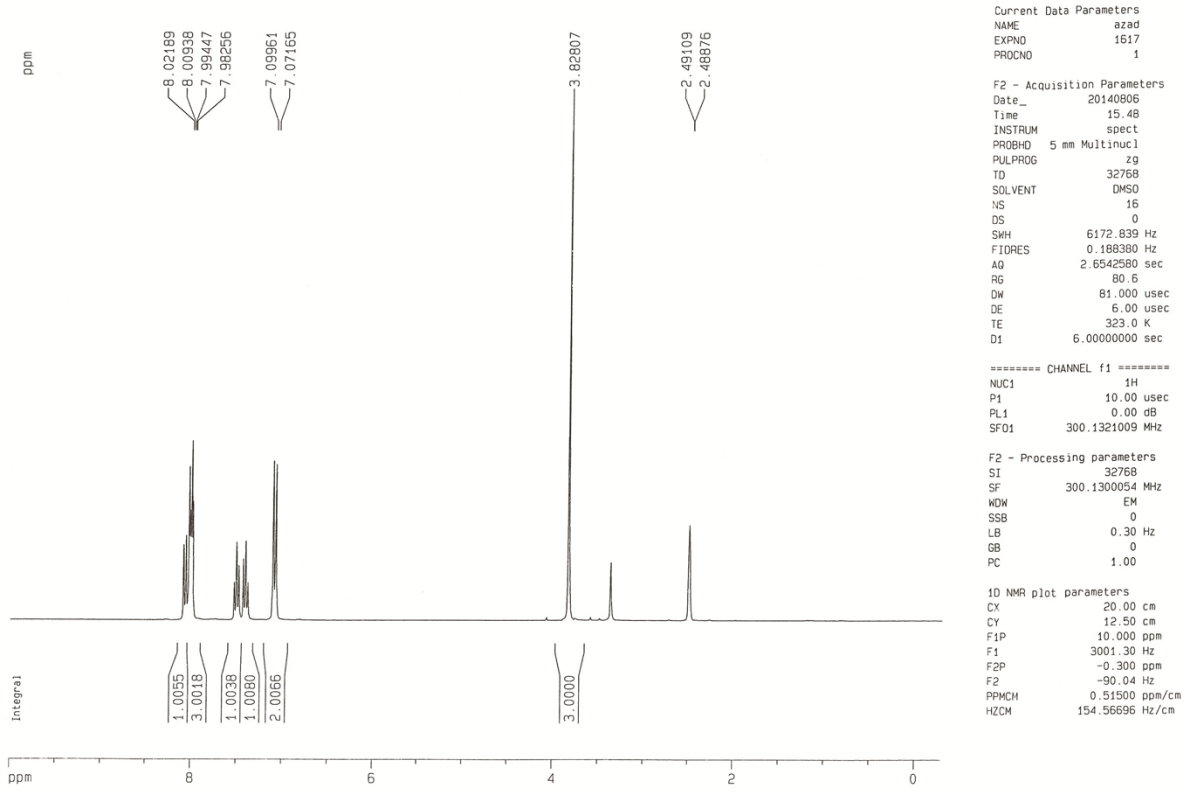
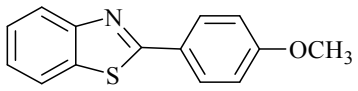


Figure S3. ^{1}H NMR of 2-(4-methoxyphenyl)benzothiazole (**10b**)



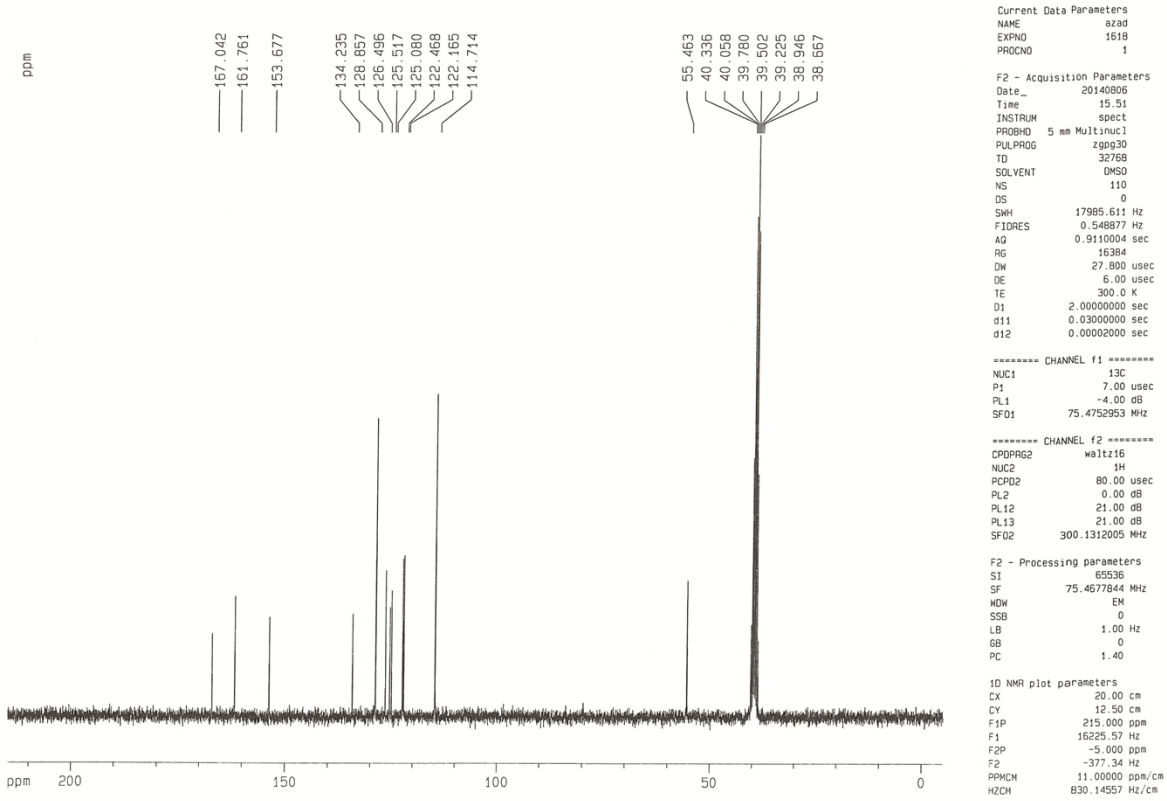
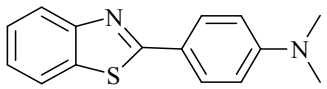


Figure S4. ^{13}C NMR of 2-(4-methoxyphenyl)benzothiazole (**10b**)



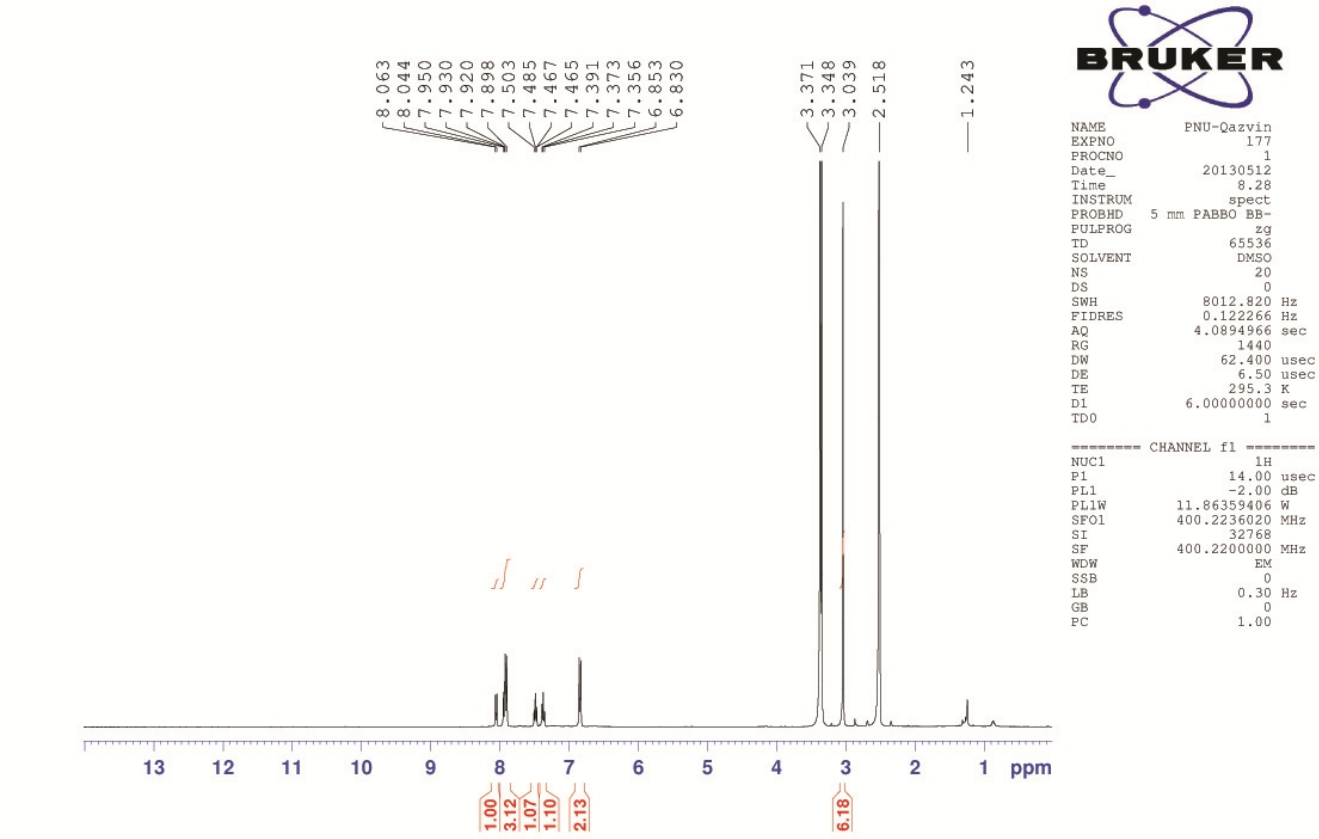
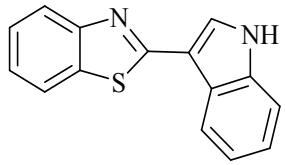


Figure S5. ^{1}H NMR of 2-(4-dimethylamino phenyl)benzothiazole (**10c**)



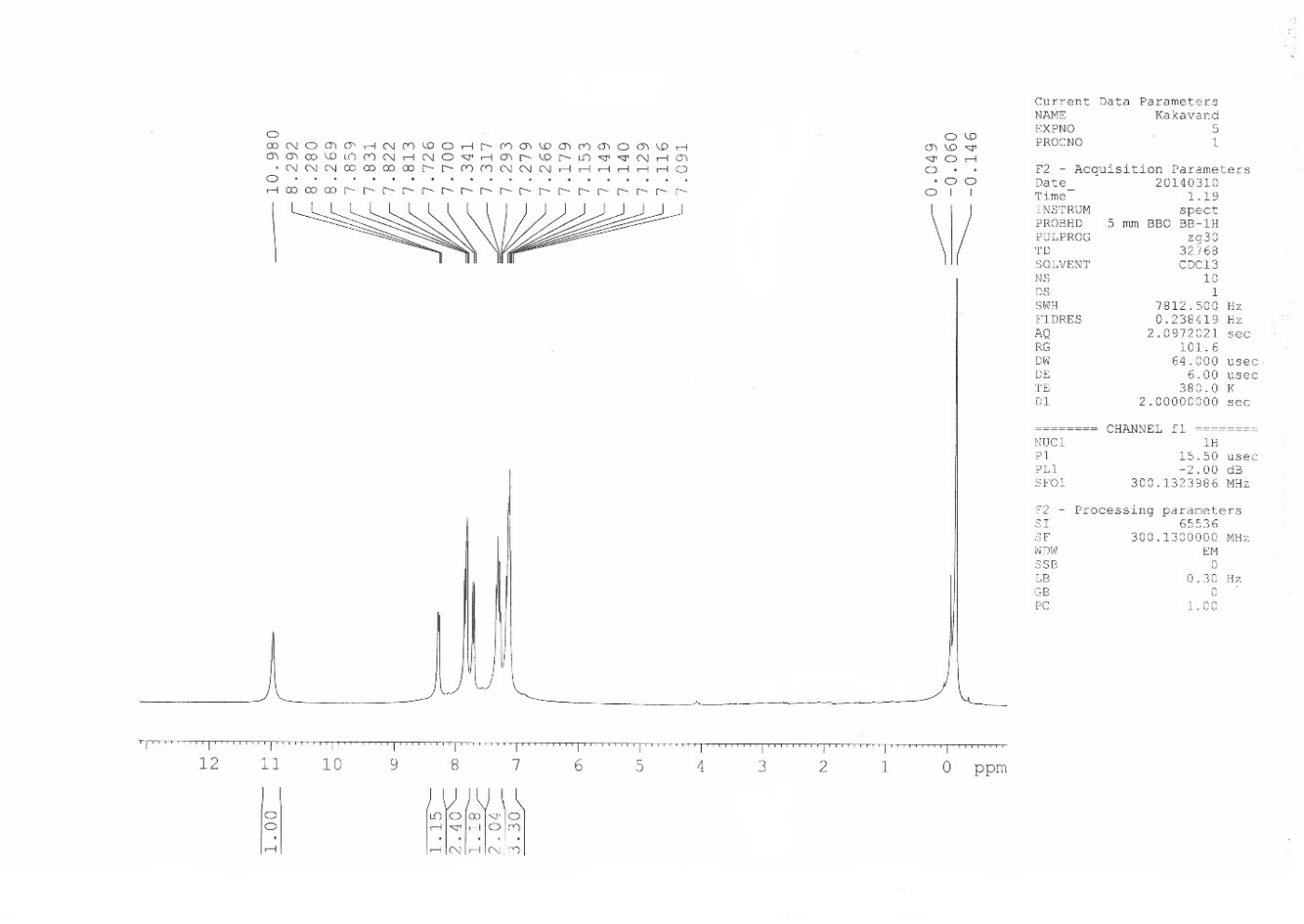
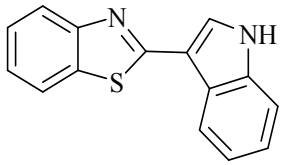


Figure S6. ^{1}H NMR of 2-(1H-indol-3-yl)benzothiazole (**10d**)



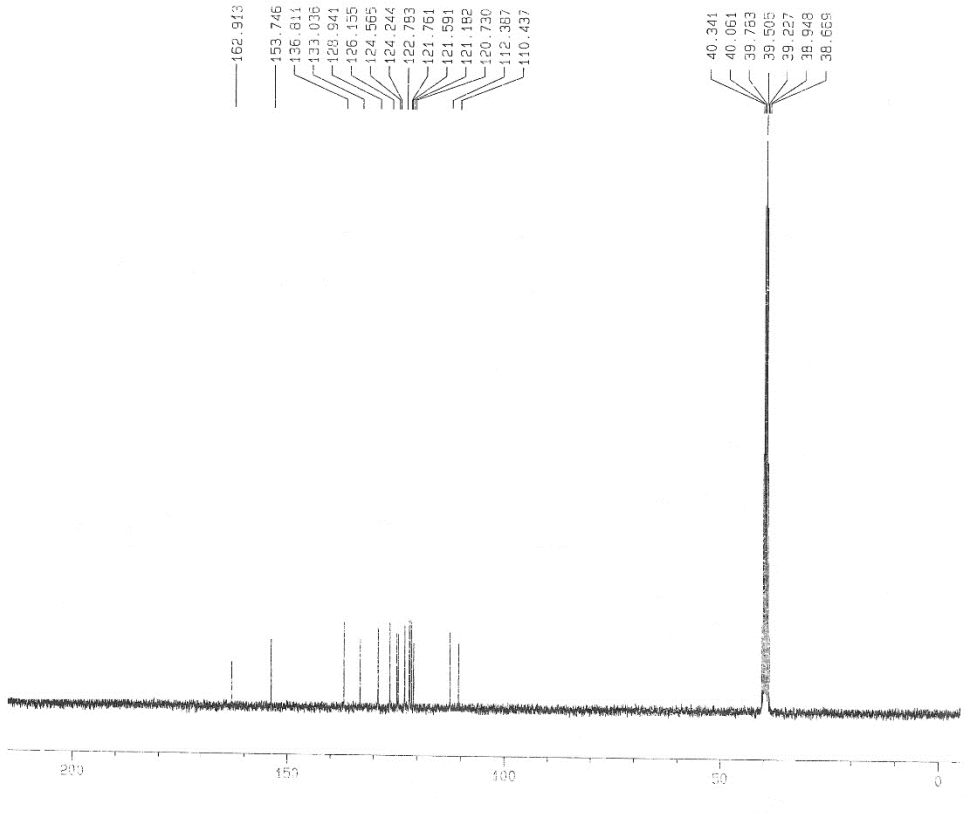


Figure S7. ^{13}C NMR of 2-(1H-indol-3-yl)benzothiazole (**10d**)

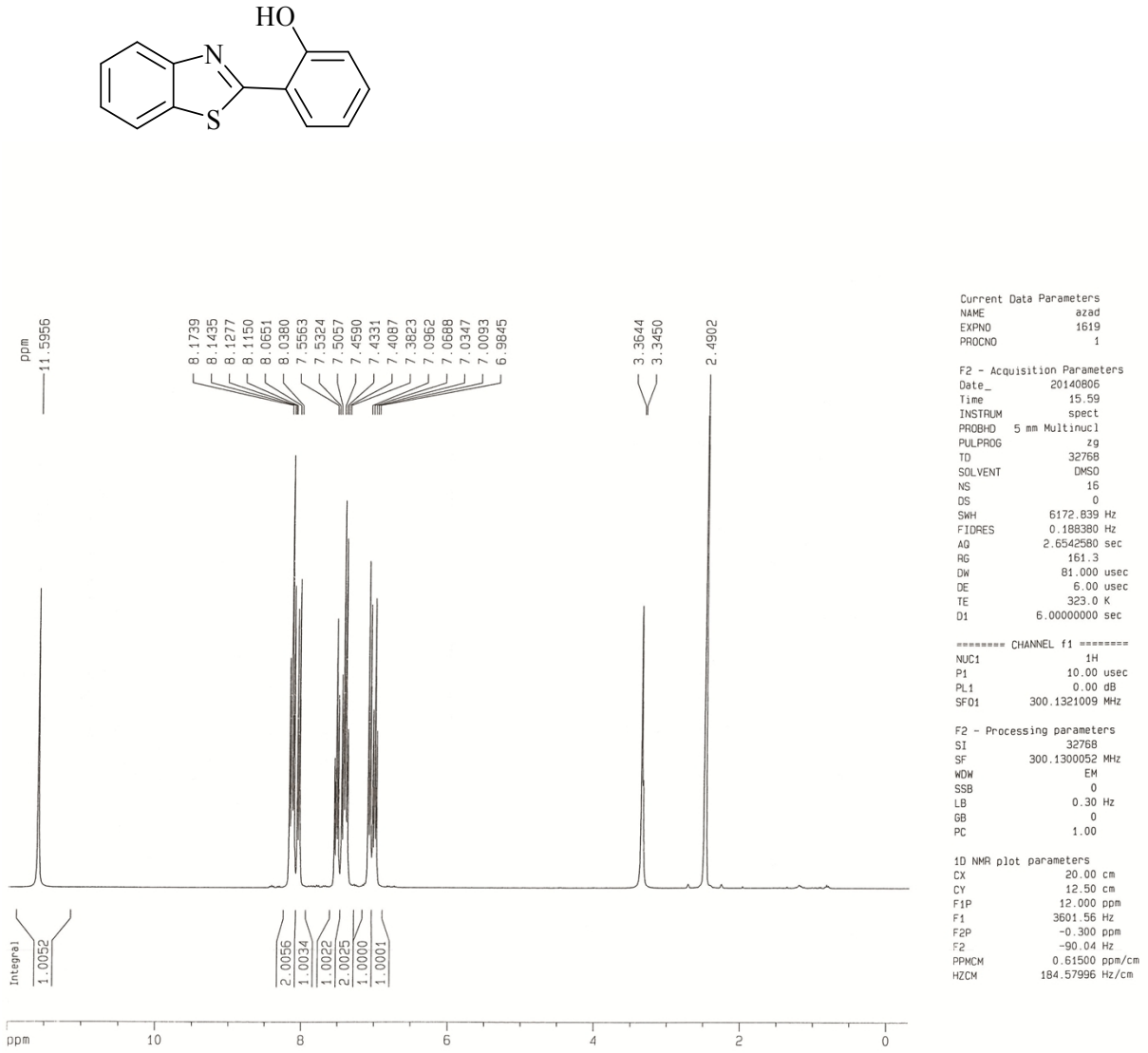
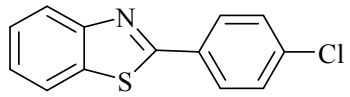


Figure S8. ^{1}H NMR of 2-(2-hydroxyphenyl)benzothiazole (**10e**)



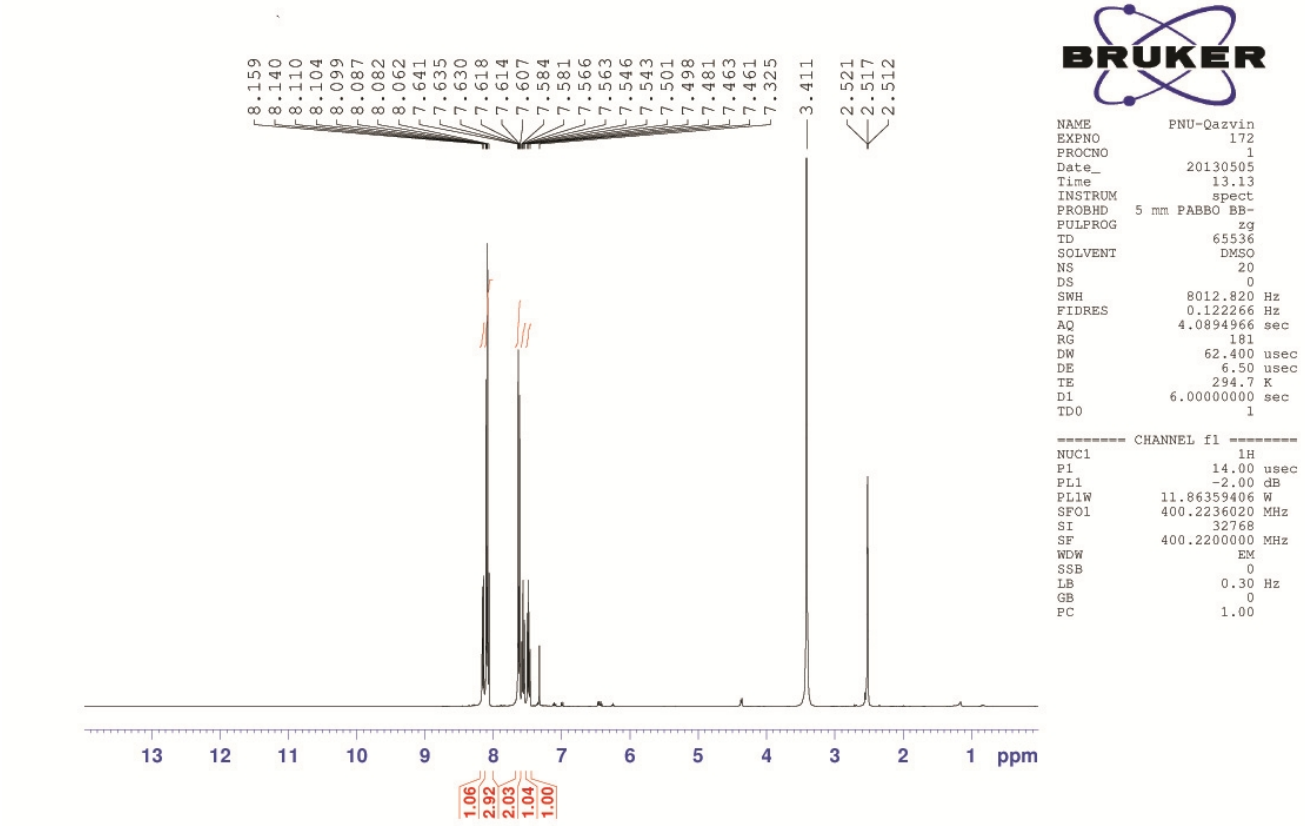
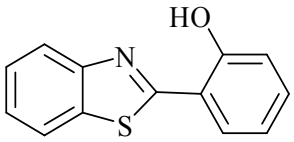


Figure S9. ^{1}H NMR of 2-(4-chlorophenyl)benzothiazole (**10f**)



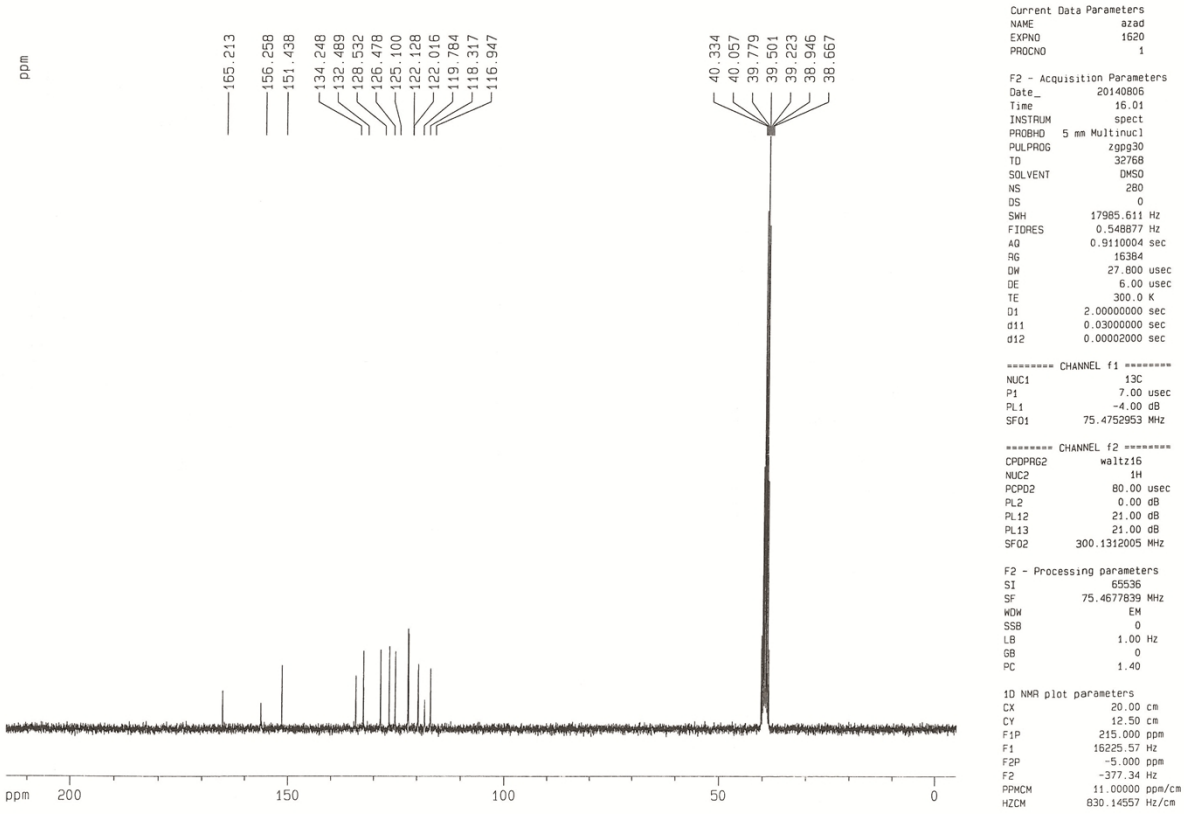
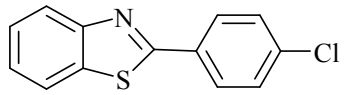


Figure S10. ^{13}C NMR of 2-(2-hydroxyphenyl)benzothiazole (**10e**)



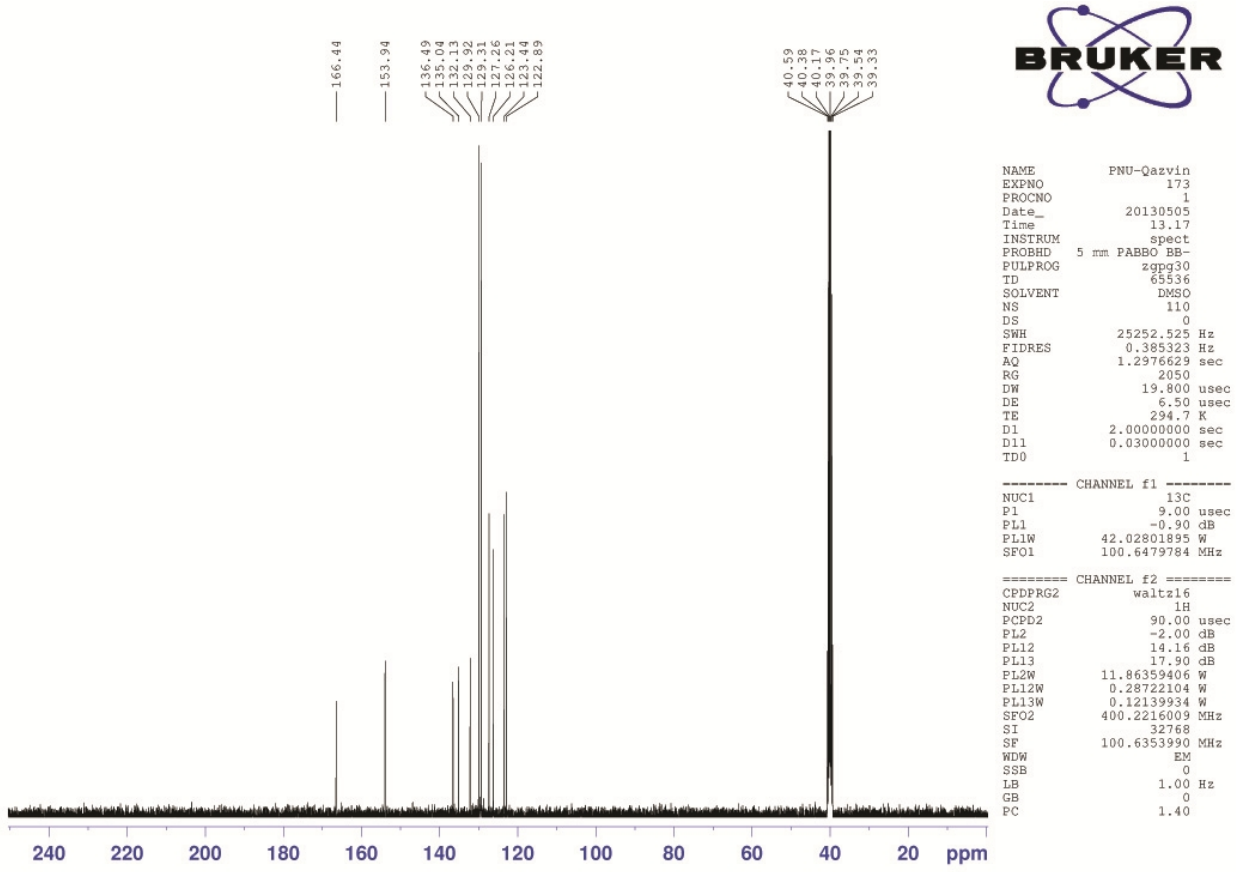
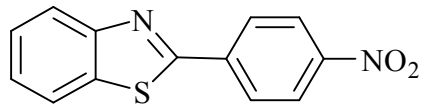


Figure S11. ^{13}C NMR of 2-(4-chlorophenyl)benzothiazole (**10f**)



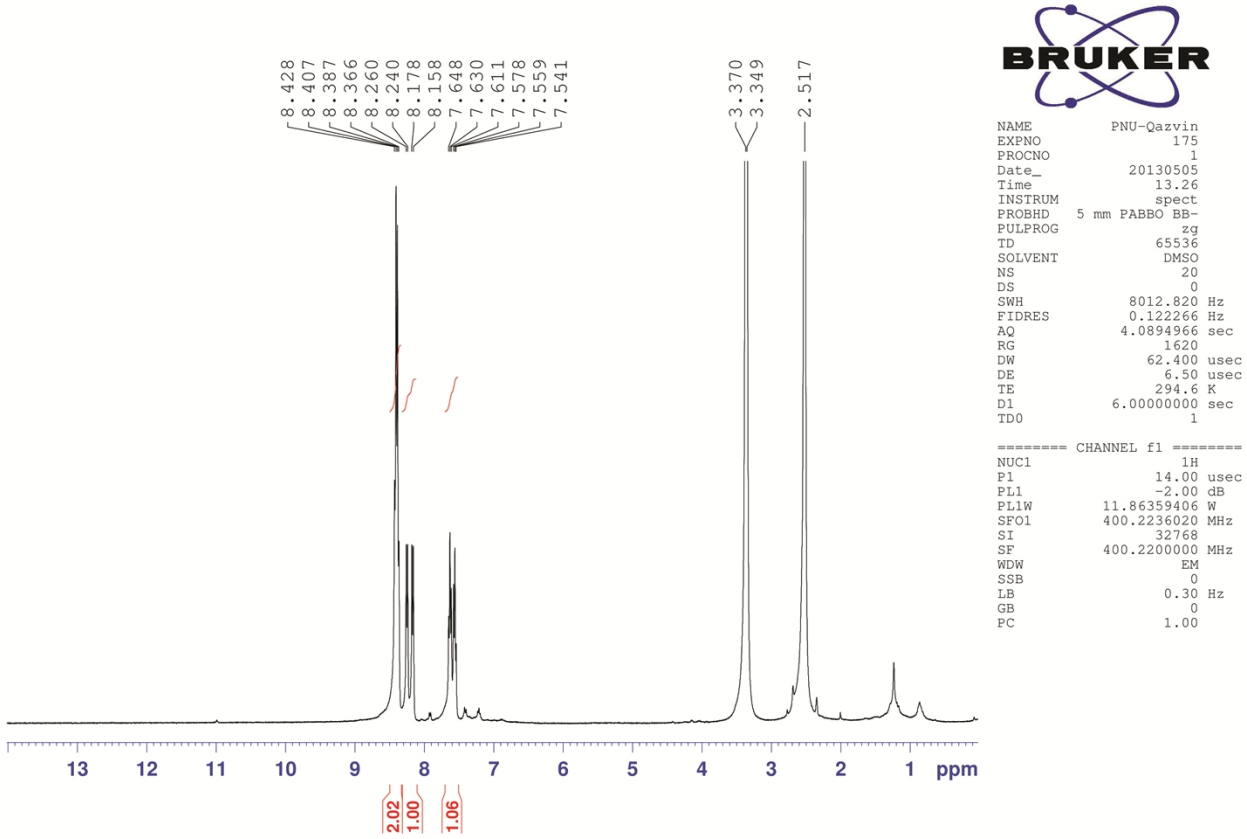
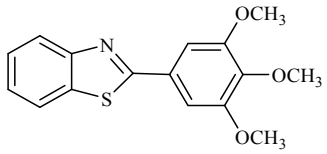


Figure S12. ^{1}H NMR of 2-(4-nitrophenyl)benzothiazole (**10g**)



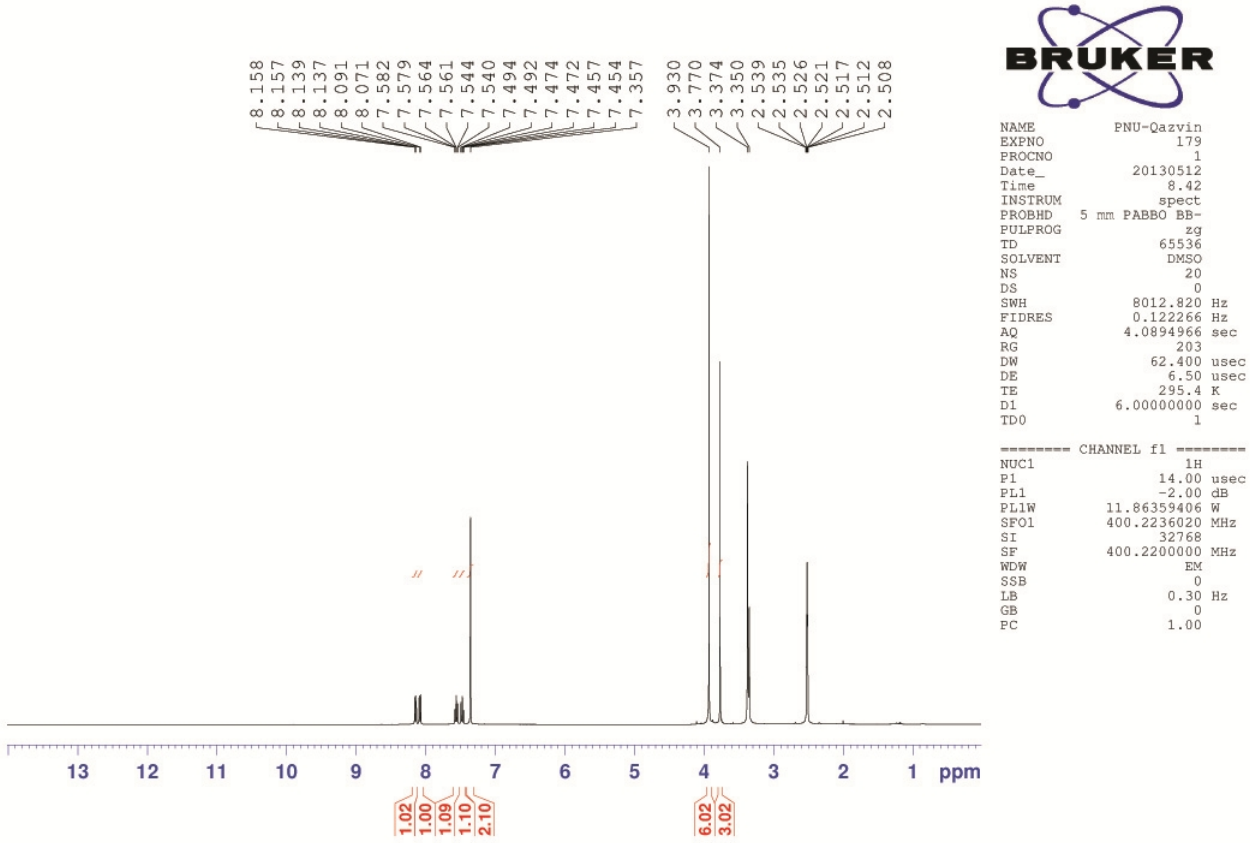


Figure S13. ^{1}H NMR of 2-(3,4,5-trimethoxyphenyl)benzothiazole (**10h**)

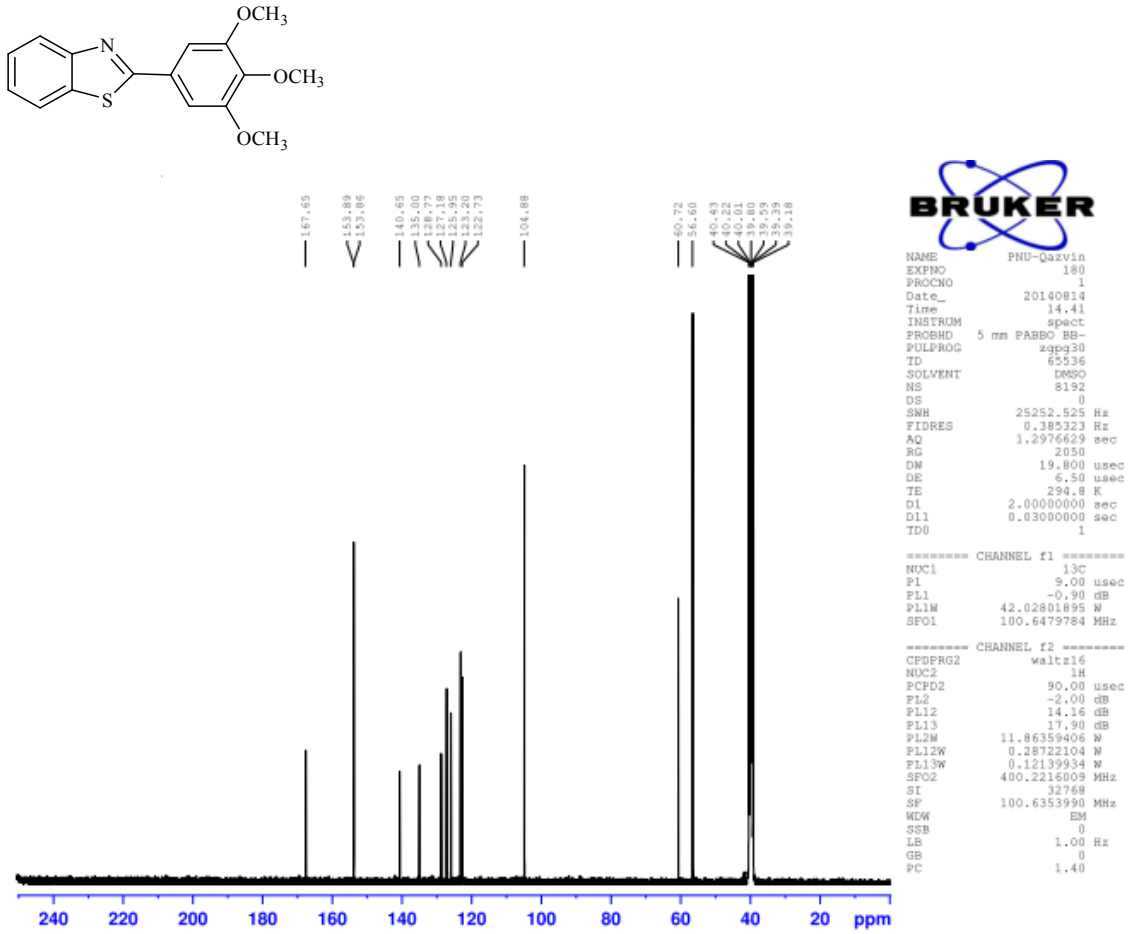
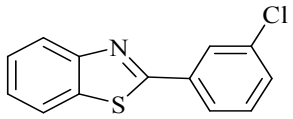


Figure S14. ^{13}C NMR of 2-(3,4,5-trimethoxyphenyl)benzothiazole (**10h**)



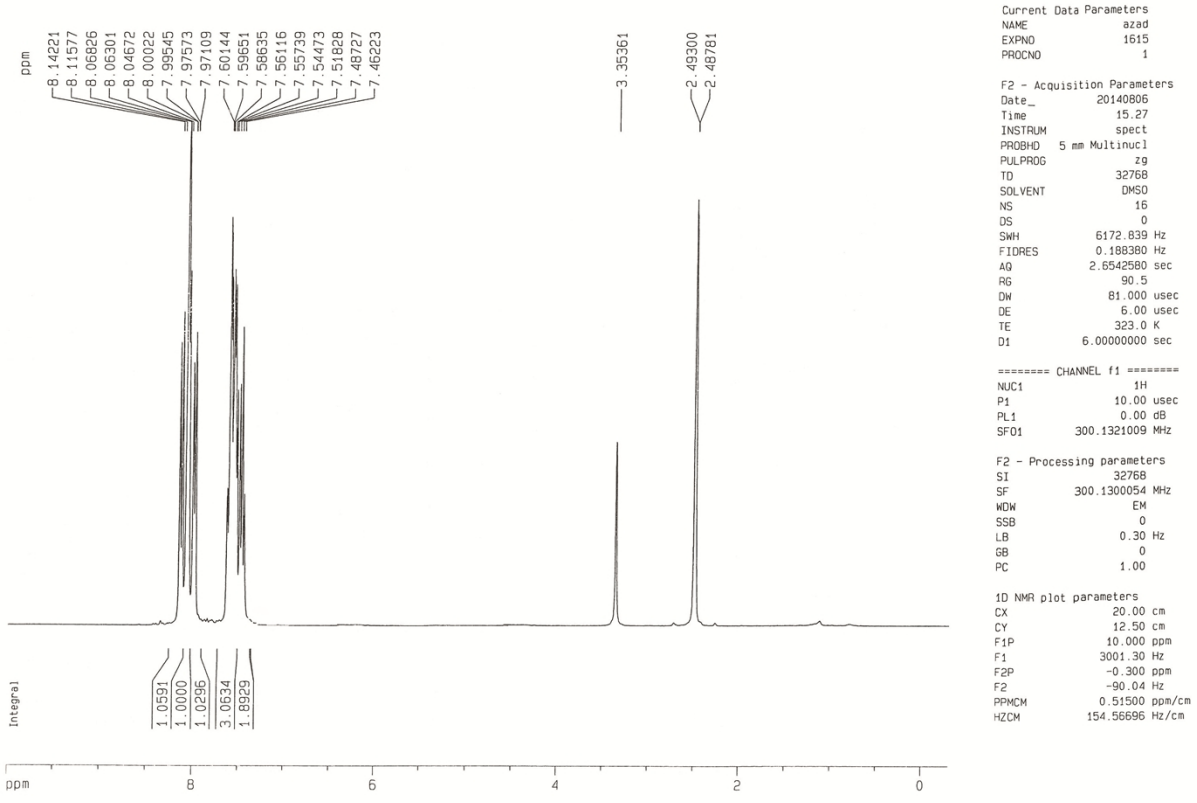
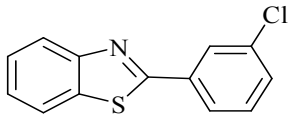


Figure S15. ^{1}H NMR of 2-(3-chlorophenyl)benzothiazole (**10j**)



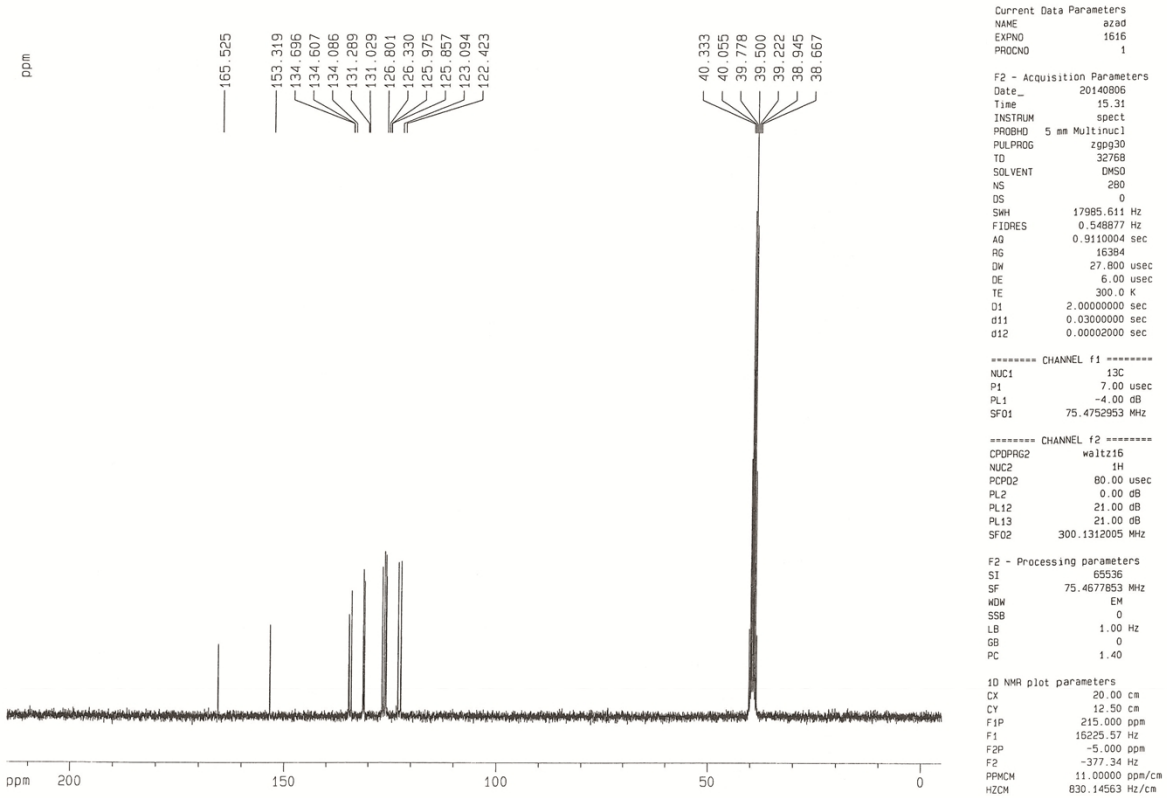


Figure S16. ^{13}C NMR of 2-(3-chlorophenyl)benzothiazole (**10j**)

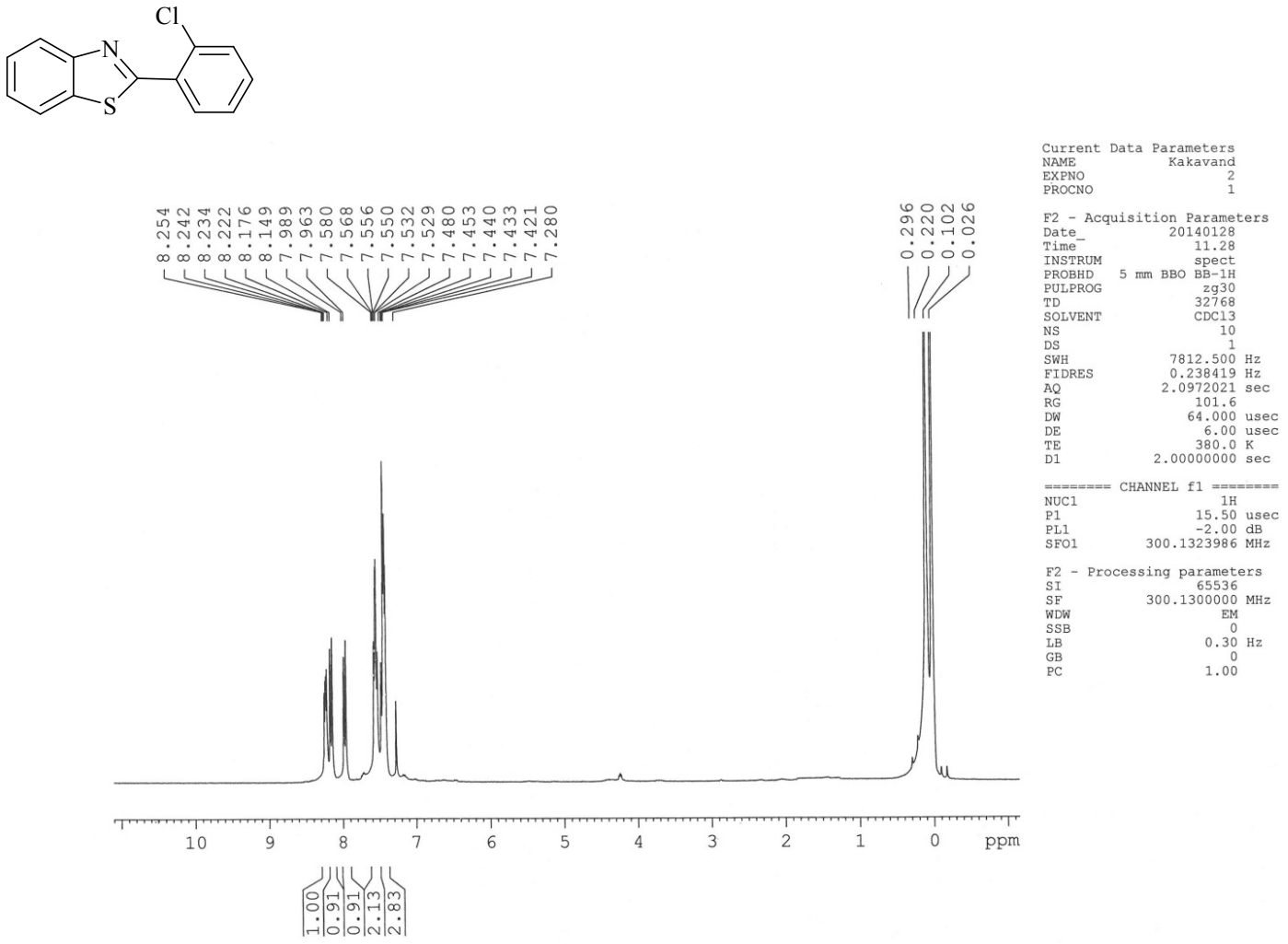
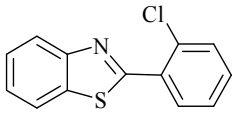


Figure S17. ^{1}H NMR of 2-(2-chlorophenyl)benzothiazole (**10k**)



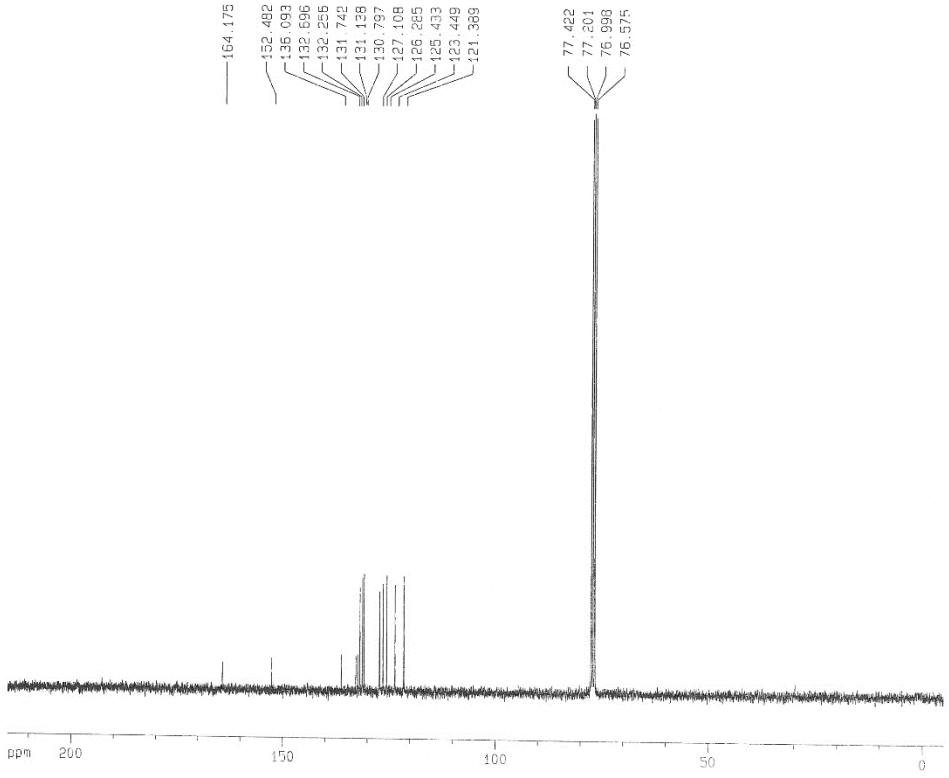
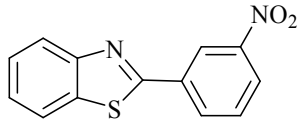


Figure S18. ^{13}C NMR of 2-(2-chlorophenyl)benzothiazole (**10k**)



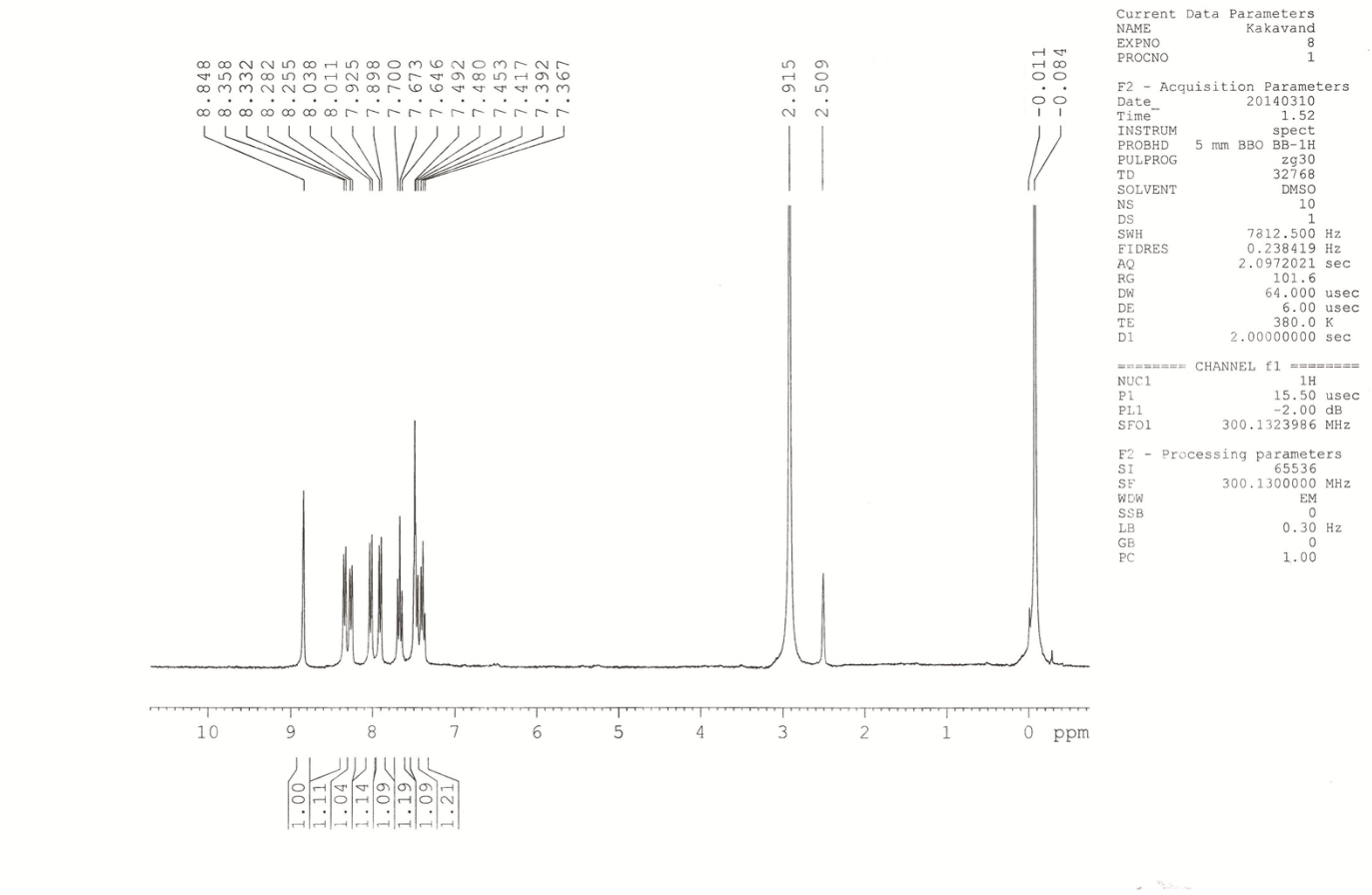


Figure S19. ^{1}H NMR of 2-(3-nitrophenyl)benzothiazole (**10l**)