Supporting Information

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$Zn(OAc)_2{\cdot}2H_2O$: An efficient catalyst for the one-pot synthesis of 2-substituted benzothiazoles

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S1: Experimental Section

Materials and Methods

All of the compounds were obtained from commercial sources and utilized without undergoing any further purification processes. Before being used, the solvents for chromatography go through the distillation process. In $CDCl_3$, ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using Bruker UXNMR FT-300 MHz (Avance) devices. The tetramethylsilane (δ 0.0) internal standard serves as the reference point against which chemical shifts are compared and represented as parts per million. At a temperature of 200 ^0C and an energy of 70 eV, electron-impact mass spectra were obtained using a VG 7070H Micromass mass spectrometer. For the purpose of recording melting points, an electrothermal melting point equipment has been utilized. The IR spectra were obtained by employing potassium bromide pellets and a Perkin Elmer 240-C instrument in the collection process. The analytical TLC for all reactions was performed on plates that had been pre-coated by Merck (silica gel 60F-254 on glass). In order to perform column chromatography, acme silica gel was utilized (100-200 mesh).

S2: General procedure for the synthesis of 2-substituted benzothiazoles (3a-p, Table 3)

A mixture of aldehyde (**2**, 1 mmol), 2-aminothiophenol (**1**, 1 mmol), and $Zn(OAc)_2•2H_2O$ (5 mol%) was thoroughly heated at 80 °C in an open atmosphere until the overall mixture turned into a solid and progress of the reaction was monitored by TLC for the time specified in Table 3. After completion, the solid was washed with water, and the product was crystallized from ethanol or purified by column chromatography using a short silica-gel column (60-120 Mesh, 20% EtOAc/petroleum ether mixture). Each product (**3**) was adequately characterized with the help of FT-IR, NMR, and mass spectrum analysis, and the results were compared with those found in the relevant literature.

S3: Spectral data for all compounds

*2-Phenyl-1, 3-Benzothiazole (**3a**):* White solid, mp 112-113 ^oC; IR (KBr, cm^{-1}): 3065, 1970, 1510, 1478, 1433, 1313, 1259, 1225, 1158, 1070, 962, 728, 698, 622; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.04-8.11 (m, 3H), 7.88 (1H), 7.48-7.52 (m, 3H), 7.36-7.39 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.09, 154.21, 135.12, 133.67, 130.99, 129.04, 127.60, 126.35, 125.22, 123.29, 121.65; MS (EI): *m/z* 212.23 [M+1]

*6-Methyl-2-phenylbenzo[d]thiazole (**3b**):* Yellow solid, mp 125-126 ^oC. IR (KBr, cm^{-1}): 3020, 2915, 2845, 1509, 1479, 1441, 1312, 1255, 967, 766, 650; ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, J = 6.6, 2.9 Hz, 2H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.67 (s, 1H), 7.47 (dd, *J* = 4.9, 1.6 Hz, 3H), 7.29 (d, *J* = 8.3 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 152.2, 135.4, 135.2, 133.7, 130.8, 129.0, 128.0, 127.5, 122.7, 121.4, 21.6.

*6-Methoxy-2-phenylbenzo[d]thiazole (**3c**):* White solid, mp 116-117 ^oC. IR (KBr, cm^{-1}): 3020, 2915, 2845, 1509, 1479, 1460, 1260, 1225, 1115, 1058, 1023; ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (m, 2H), 7.98 (d, *J* = 8.9 Hz, 1H), 7.48 (dd, *J* = 5.3, 1.7 Hz, 3H), 7.34 (d, *J* = 1.9 Hz, 1H), 7.11 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 157.8, 148.7, 136.5, 133.8, 130.5, 129.0, 127.3, 123.7, 115.7, 104.2, 55.8.

*6-Bromo-2-phenylbenzo[d]thiazole (**3d**):* Yellow solid; mp 151-152 ºC; IR (KBr): ν 3067, 3047, 3015, 2362, 1968, 1903, 1584, 1536, 1477, 1434, 1394, 1302, 1247, 1222, 1090, 1073, 971, 816, 756, 671 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.09 (s, 1H), 8.06 (d, *J* = 8.59 Hz, 1H), 8.03 (dd, *J* = 7.41, 2.12 Hz, 2H), 7.92 (d, *J* = 8.59 Hz, 1H), 7.48-7.51 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 168.63, 152.90, 136.64, 133.13, 131.35, 129.89, 129.13, 127.61, 124.29, 124.18, 118.80

*2-Phenyl-6-(trifluoromethyl)benzo[d]thiazole (**3e**):* Yellow solid, mp 156-157 ºC. IR (KBr, cm^{-1}): 3658, 2921, 1318, 1115, 839; ^1H NMR (300 MHz, $CDCl_3$): δ 8.20 (s, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 8.11 (dd, *J* = 7.4, 2.1 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.50-7.54 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2, 156.1, 135.1, 133.1, 131.7, 129.2, 127.8, 127.3, 124.2, 123.5, 123.3, 119.32.

*2-(4-Methylphenyl)-1,3-Benzothiazole (**3f**):* White solid, mp 82-83°C. IR (KBr, cm^{-1}): 3091, 2955, 1659, 1579, 1537, 1259, 1222, 864, 797; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.93-8.04 (m, 2H), 7.38-7.53 (m, 4H), 7.27-7.37 (m, 2H), 2.29-2.33 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 153.2, 139.2, 134.9, 128.9, 127.9), 127.5, 124.7, 123.2, 122.1, 118.9, 21.4; MS (EI): *m/z* 225.12 [M^+]

*2-(4-Methoxyphenyl)-1,3-Benzothiazole (**3g**):* White solid, mp 120-121 °C; IR (KBr, cm^{-1}): 3058, 1638, 1529, 1430, 1358, 1236, 1231, 856, 769, 723; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.94 (s, 1H), 7.83-7.88 (m, 3H), 7.44-7.47 (m, 1H), 7.22 (s, 1H), 7.17-7.19 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.93, 161.99, 154.13, 134.83, 126.24, 121.52, 114.40, 55.46; MS (EI): *m/z* 241.26 [M^+]

*2-(4-Chlorophenyl)-1,3-Benzothiazole (**3h**):* White solid, mp 118-119 °C. IR (KBr, cm^{-1}): 3055, 3032, 2990, 1945, 1893, 1589, 1509, 1474, 1432, 1314, 1250, 1222, 1085, 1013, 963, 828, 729, 689; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.06 (s, 1H), 7.79-7.85 (m, 3H), 7.71 (m, 2H), 7.35-7.38 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6, 154.0, 137.1, 135.0, 132.1, 130.9, 129.3, 128.7, 126.5, 125.4, 123.3, 121.7; MS (EI): *m/z* 245.33 [M^+]

*2-(4-Hydroxyphenyl)-1,3-Benzothiazole (**3i**):* White solid, mp 228-230 °C. IR (KBr, cm^{-1}): 3371, 3022, 1644, 1579, 1571, 1223, 892, 753, 719; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.98 (s, 1H), 7.81-7.86 (m, 3H), 7.41 (s, 1H), 6.89-7.29 (m, 3H), 2.48 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 157.2, 153.9, 134.3, 128.2, 127.6, 126.8, 124.1, 122.6, 122.1, 115.4; MS (EI): *m/z* 227.09 [M^+]

*2-(4-N,N-dimethylaminophenyl)benzothiazole (**3j**):* Brown crystals, mp 171-172 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.98 (dd, *J* = 7.0 Hz, J = 2.0 Hz, 3H), 7.83-7.86 (m, 1H), 7.42-7.45 (m, 1H), 7.3.-7.33 (m, 1H), 6.74 (dd, *J* = 2.0 Hz, *J* = 7.0 Hz, 2H), 3.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 154.4, 152.1, 134.5, 128.8, 125.9, 124.1, 122.2, 121.3, 111.6, 40.1; MS (ESI): *m/z* (%) 255 ([M+H]$^+$, 100).

*2-(4-Cynophenyl)-1,3-Benzothiazole (**3k**):* White solid, mp 172-173 °C, IR (KBr, cm^{-1}): 3062, 2224, 1471, 1432, 1407, 1314, 1250, 963, 838, 729; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.29 (m, 1H), 7.92-7.97 (m, 4H), 7.81 (m, 1H), 7.61-7.56 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.3, 154.1, 137.5, 135.3, 132.8, 127.9, 126.8, 126.3, 124.5, 122.5, 122.9, 122.1, 118.3, 114.2; MS (EI): *m/z* 236.27 [M^+]

*2-(3-Nitrophenyl)-1,3-benzothiazole (**3l**):* Yellow crystals, mp 112-113 °C. IR (KBr, cm^{-1}): ν 3080, 3035, 1612, 1580 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.84 (s, 1H), 8.44 (d, 1H), 8.41 (d, 1H), 8.24 (d, 1H), 8.16 (d, 1H), 7.88 (t, 1H), 7.60 (t, 1H), 7.54 (t, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.8, 153.8, 148.6, 135.2, 135.1, 132.9, 130.0, 126.8, 126.0, 125.1, 123.7, 122.2, 121.8 ppm; MS (EI): *m/z* 256.0 (M^+, 100)

*2-Isobutylbenzothiazole (**3m**):* Colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.98-8.01 (m, 1H, ArH), 7.84-7.87 (m, 1H, ArH), 7.43-7.48 (m, 1H), 7.35-7.38 (m, 1H), 3.00 (d, *J* = 7.2 Hz, 2H), 2.25 (m, 1H), 1.06 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 153.2, 135.2, 125.8, 124.6, 122.5, 121.4, 43.2, 29.7, 22.4; MS (ESI): *m/z* (%) 192 ($[M+H]^+$, 100)

*2-(Pyridin-4-yl)benzo[d]thiazole (**3n**):* White solid, mp 136-137 ºC. IR (KBr, cm^{-1}): 3658, 3038, 2920, 1408, 758. ^1H NMR (400 MHz, $CDCl_3$) δ= 8.78 (s, 2H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.93 (m, 3H), 7.53 (m, 1H), 7.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ =165.0, 154.0, 150.7, 140.5, 135.2, 126.8, 126.2, 123.9, 121.9, 121.3

*2-(2-Furan-2-yl)-1,3-Benzothiazole (**3o**):* Pale solid, mp 101-102 °C; IR (KBr, cm^{-1}): 3012, 1684, 1353, 1284, 1180, 1038, 876, 812, 748, 726; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.03-8.06 (m, 1H), 7.85-7.87 (m, 1H), 7.84-7.86 (m, 1H), 7.33-7.58 (m, 2H), 7.15 (m, 1H), 6.56-6.57 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.6, 153.7, 148.8, 144.7, 134.3, 126.3, 124.3, 121.6, 112.6, 111.5; MS (EI): *m/z* 201.13 [M^+]

*2-(2-Thiophen-2-yl)-1,3-Benzothiazole (**3p**):* Pale solid, mp 99-100 °C. IR (KBr, cm^{-1}): 3137, 1682, 1362, 1248, 1159, 1031, 869, 848, 762, 722; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.86-8.06 (m, 2H), 7.52-7.69 (m, 1H), 7.50-7.69 (m, 1H), 7.15-7.48 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.4, 153.7, 137.3, 134.7, 129.3, 128.7, 126.5, 125.2, 123.0, 121.5; MS (EI): *m/z* 217.13 [M^+]

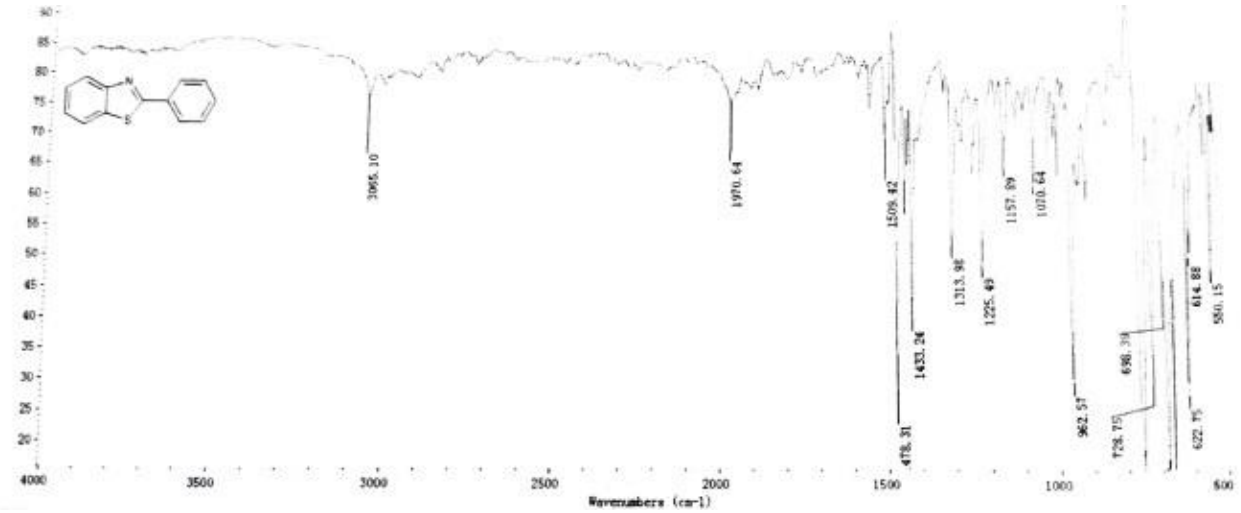

Figure S1: IR Spectrum of compound **3a**

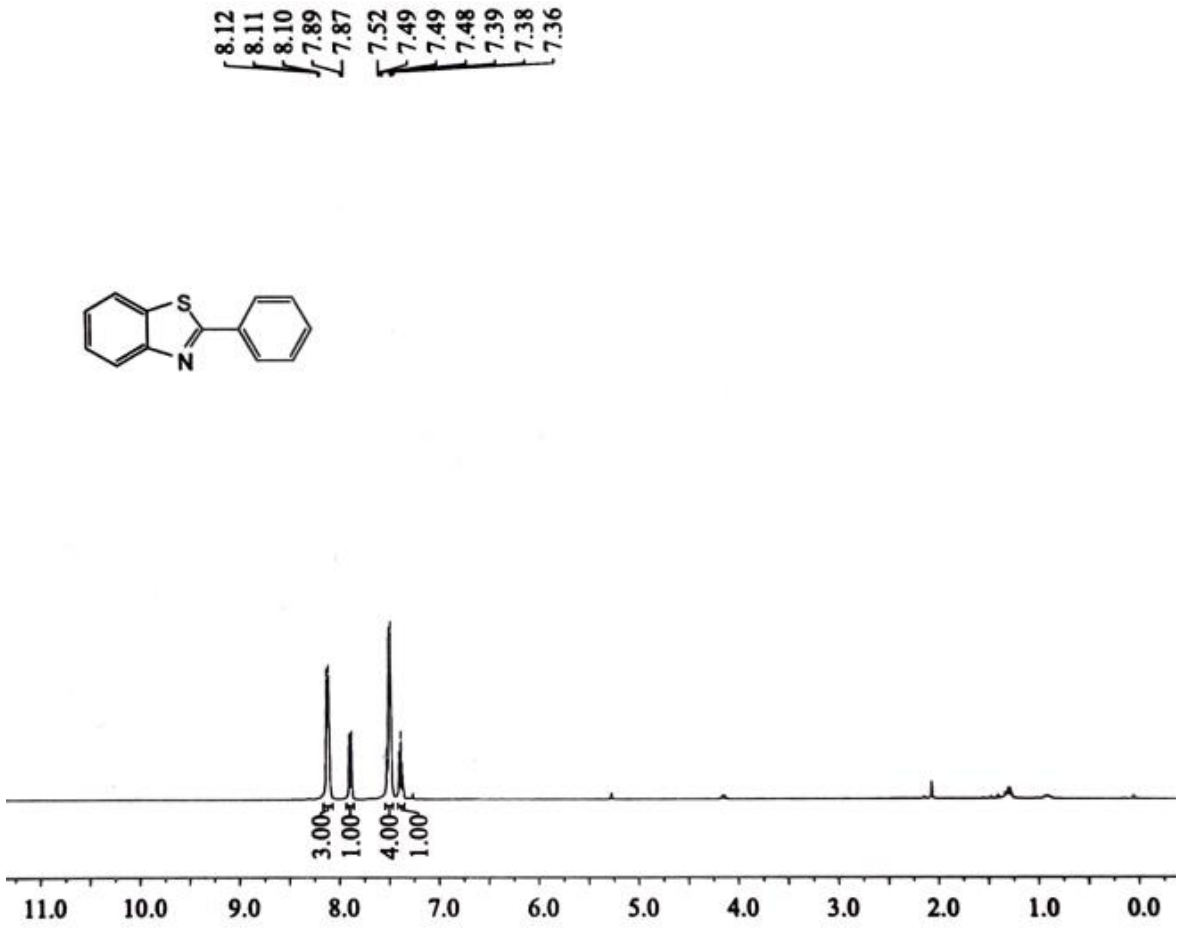

Figure S2: ^{1}H NMR Spectrum of compound **3a**

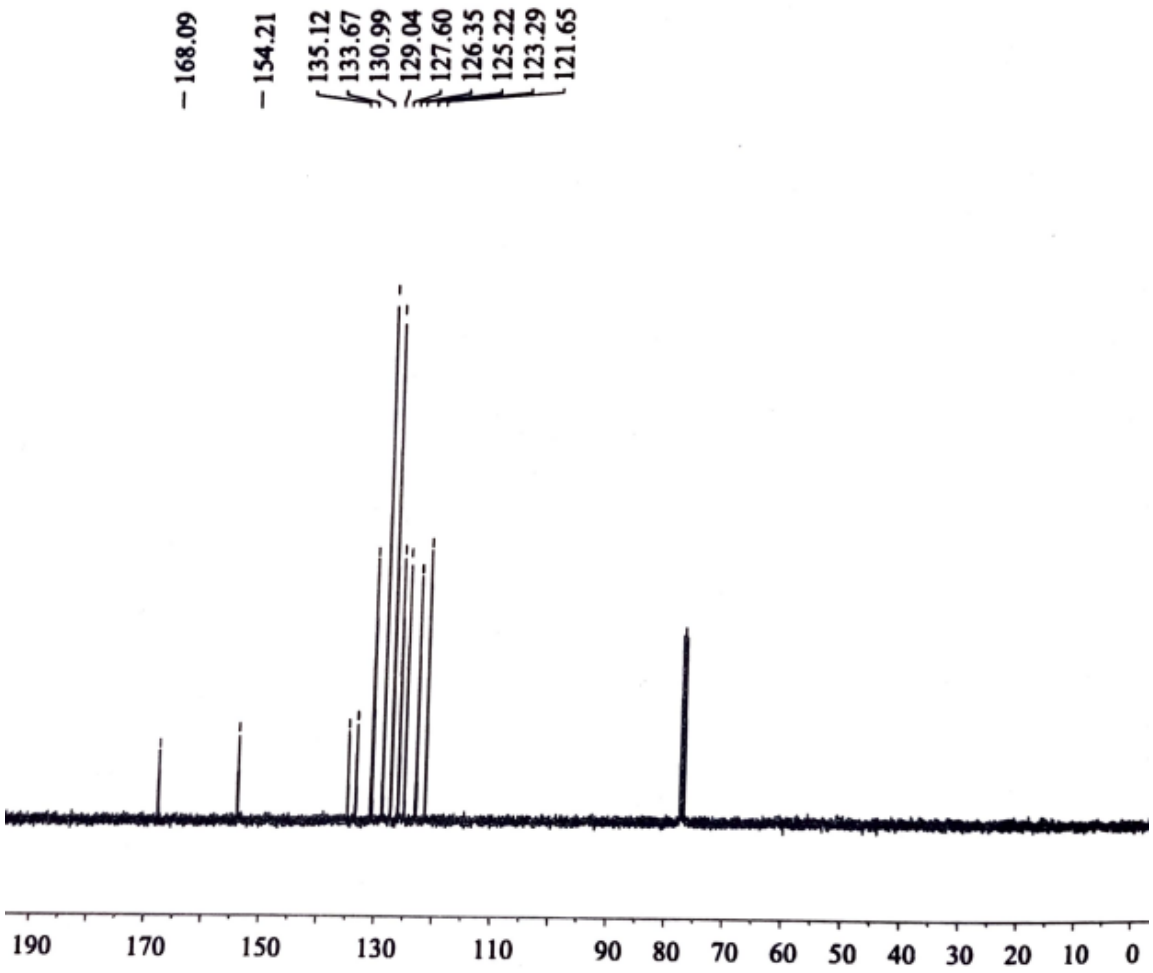

Figure S3: ^{13}C NMR Spectrum of compound **3a**

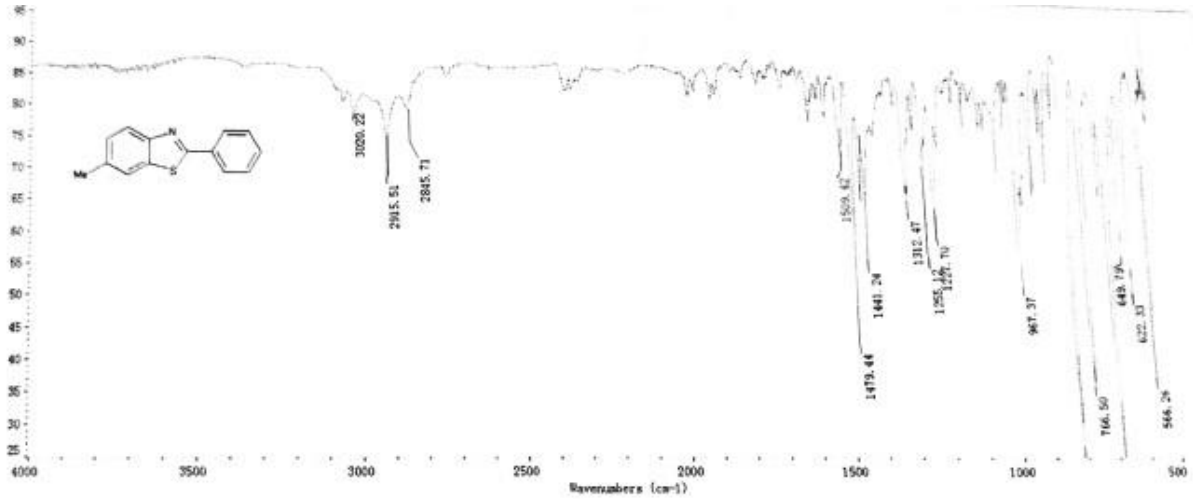

Figure S4: IR Spectrum of compound **3b**

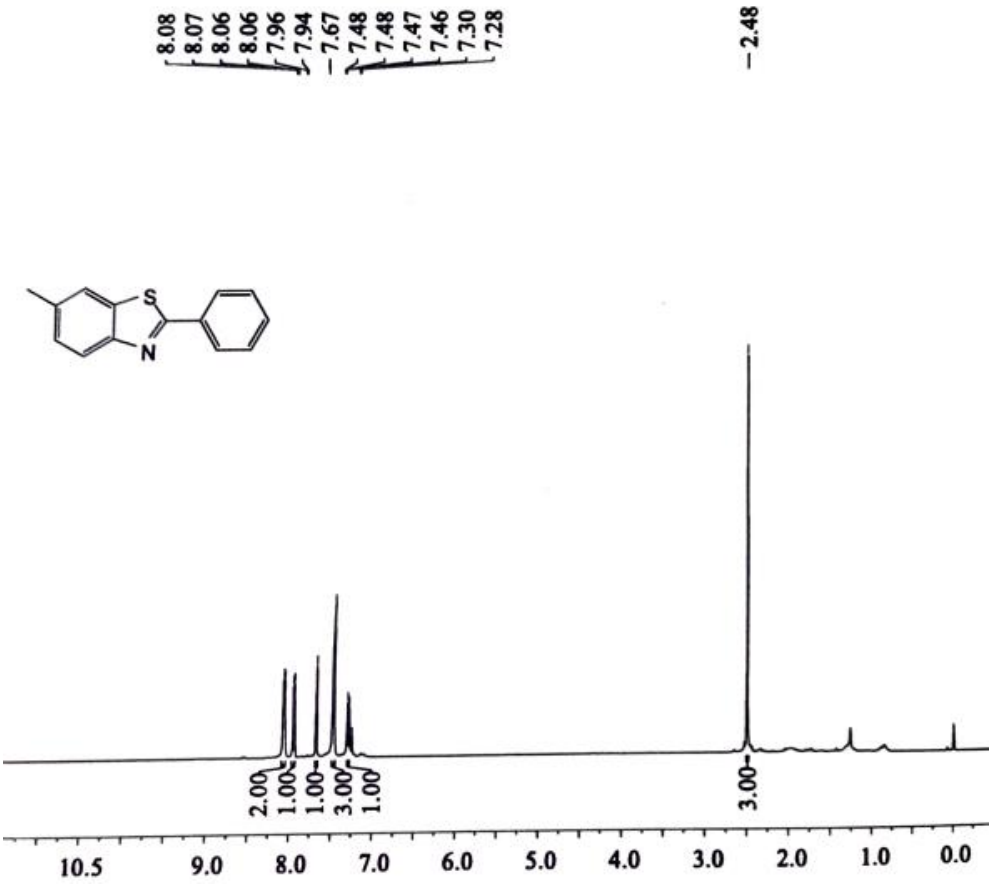

Figure S5: ^{1}H NMR Spectrum of compound **3b**

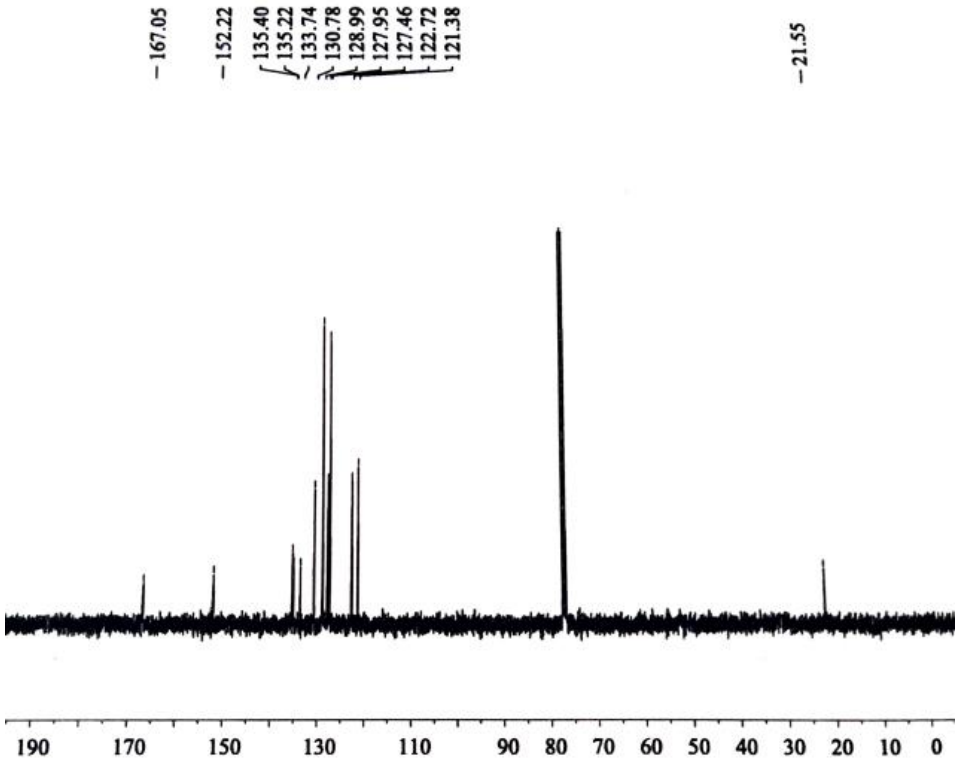

Figure S6: ^{13}C NMR Spectrum of compound **3b**

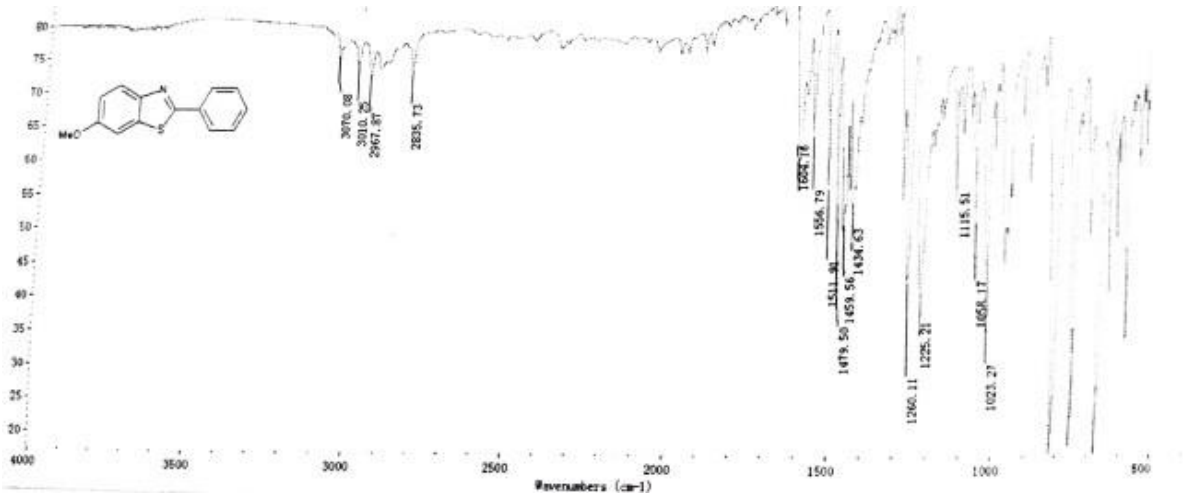

Figure S7: IR Spectrum of compound **3c**

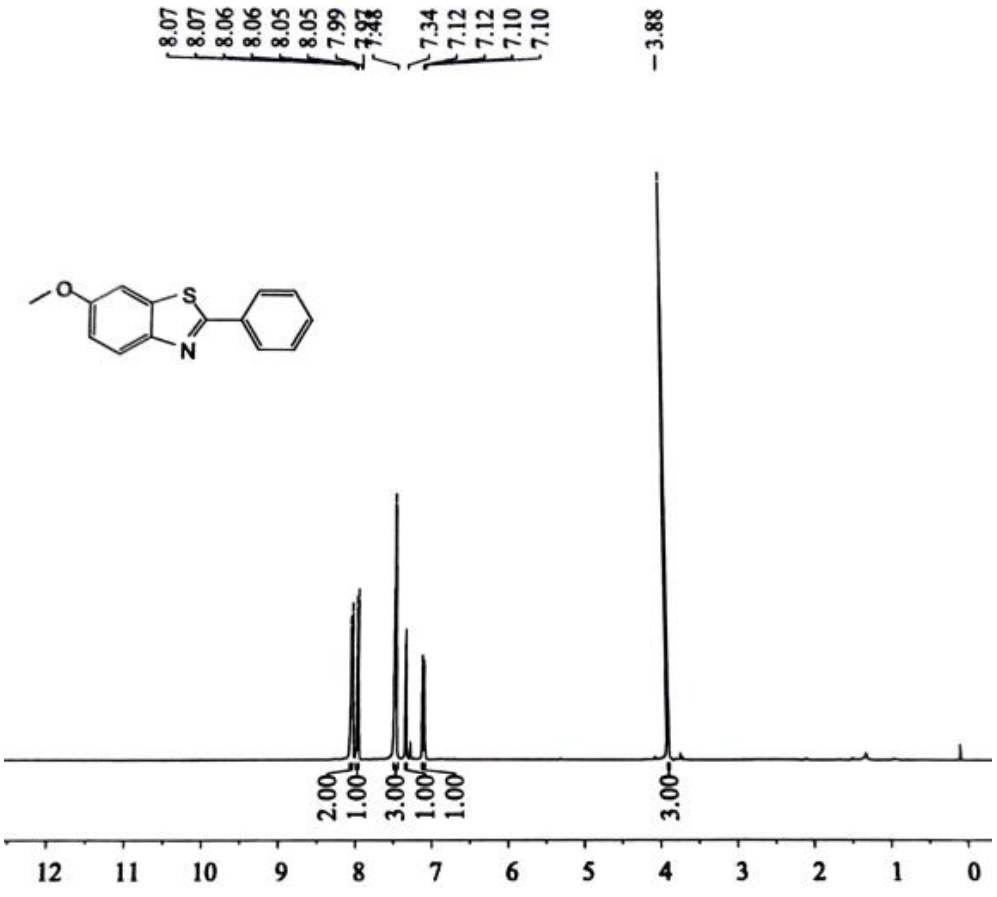

Figure S8: ^{1}H NMR Spectrum of compound **3c**

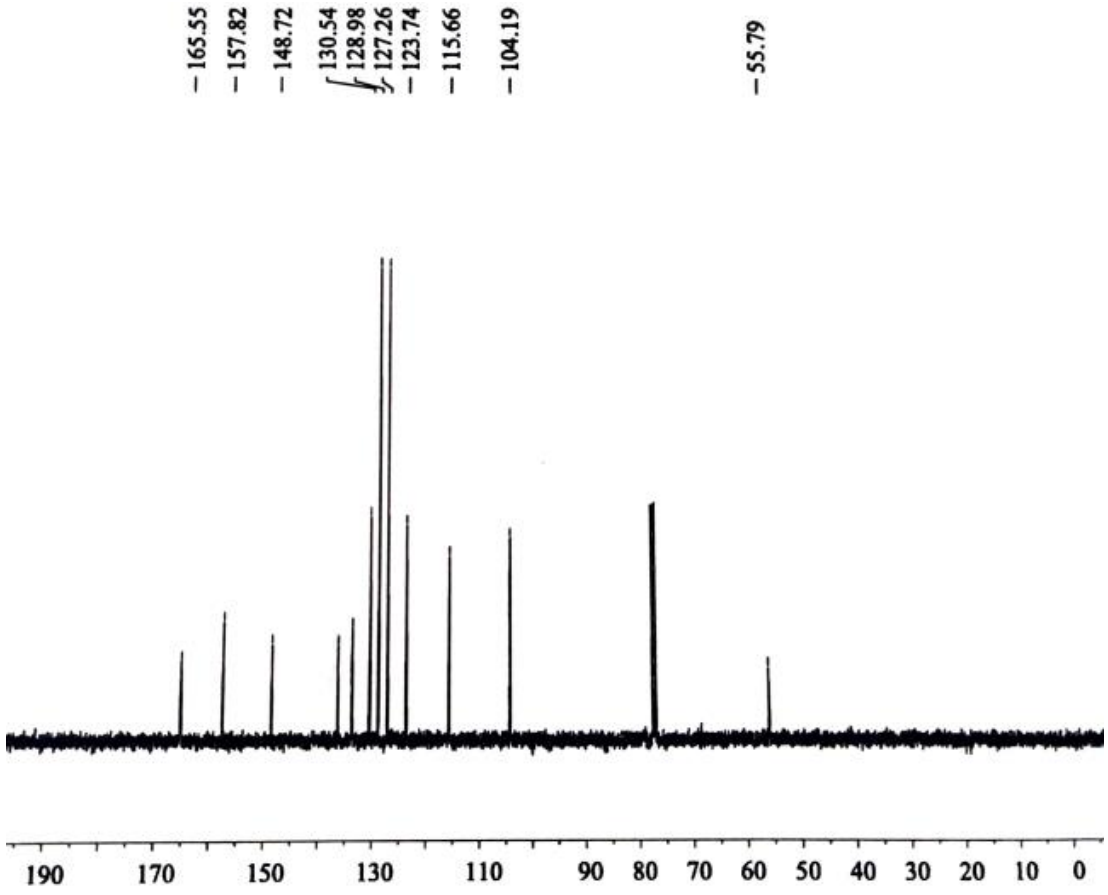

Figure S9: ^{13}C NMR Spectrum of compound **3c**

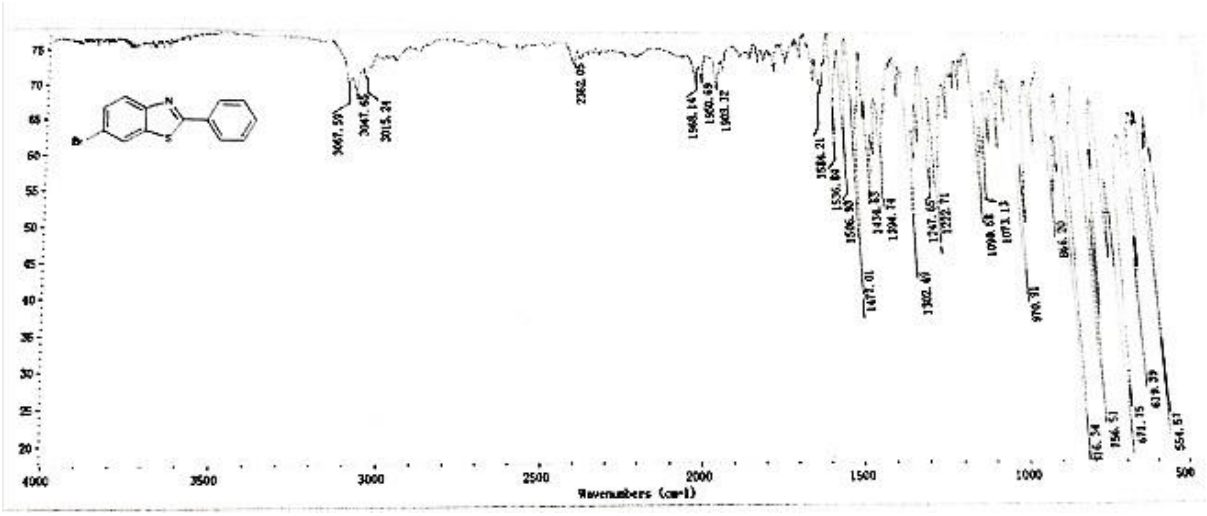

Figure S10: IR Spectrum of compound **3d**

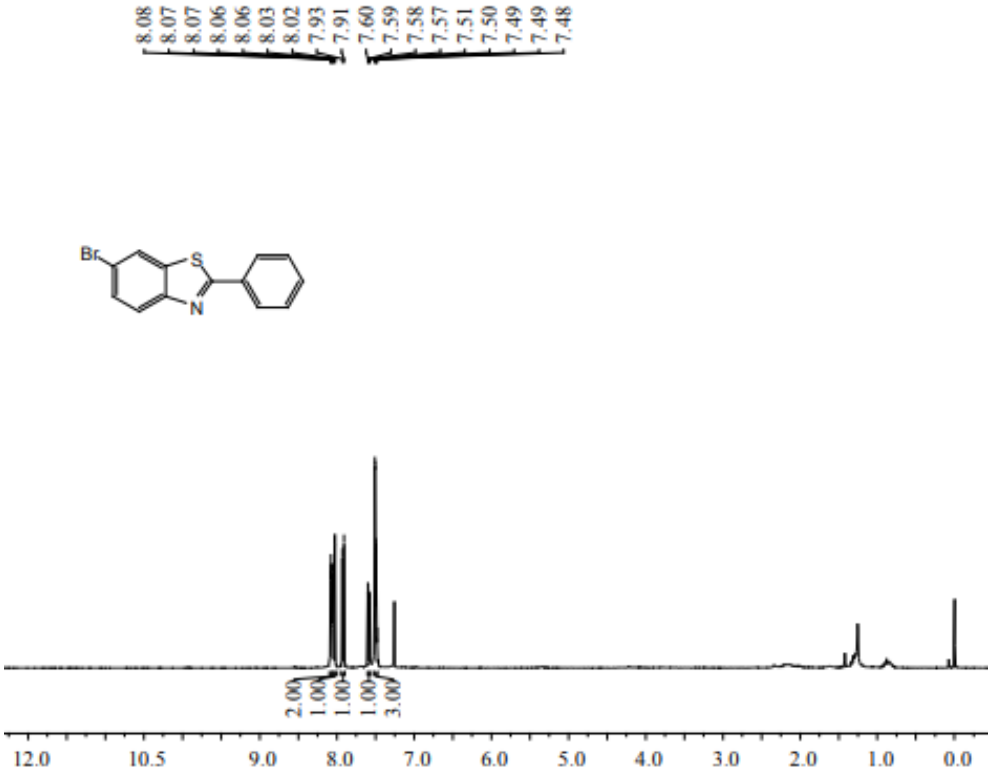

Figure S11: ^{1}H NMR Spectrum of compound **3d**

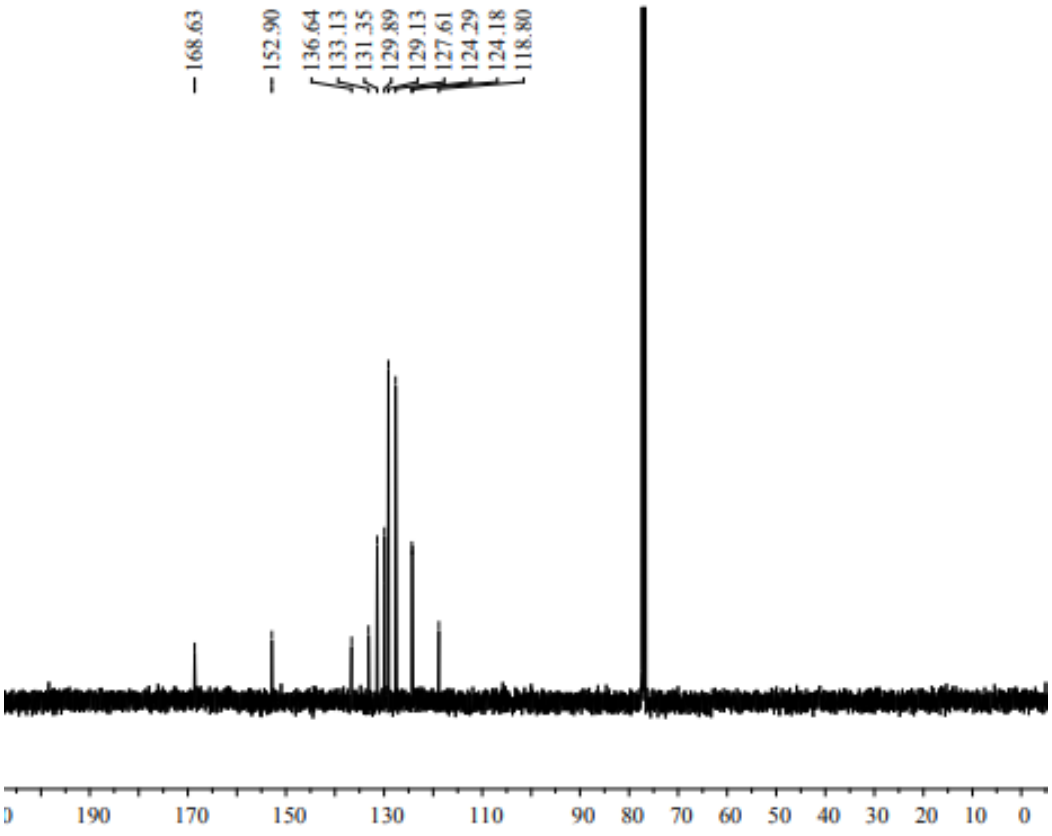

Figure S12: ^{13}C NMR Spectrum of compound **3d**

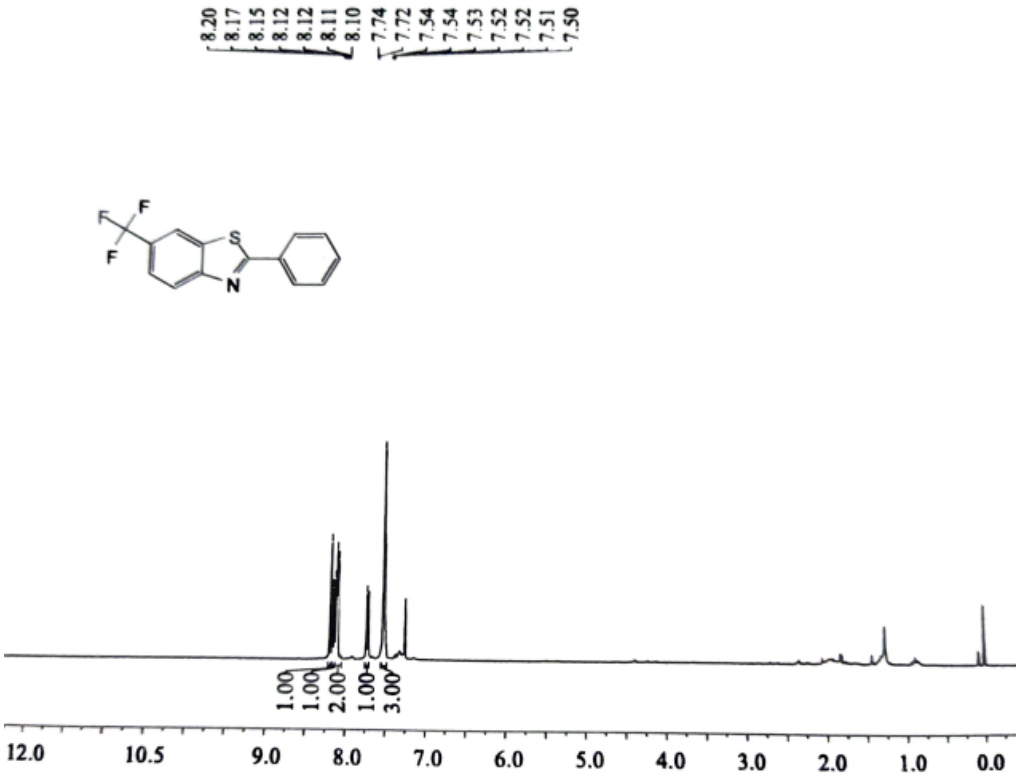

Figure S13: ^{1}H NMR Spectrum of compound **3e**

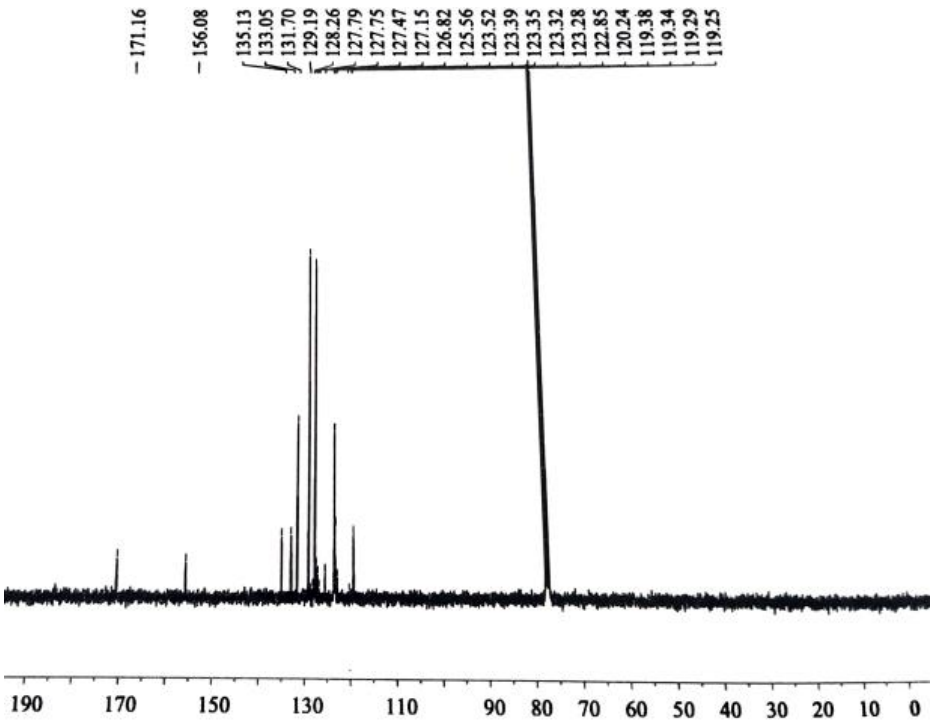

Figure S14: ^{13}C NMR Spectrum of compound **3e**

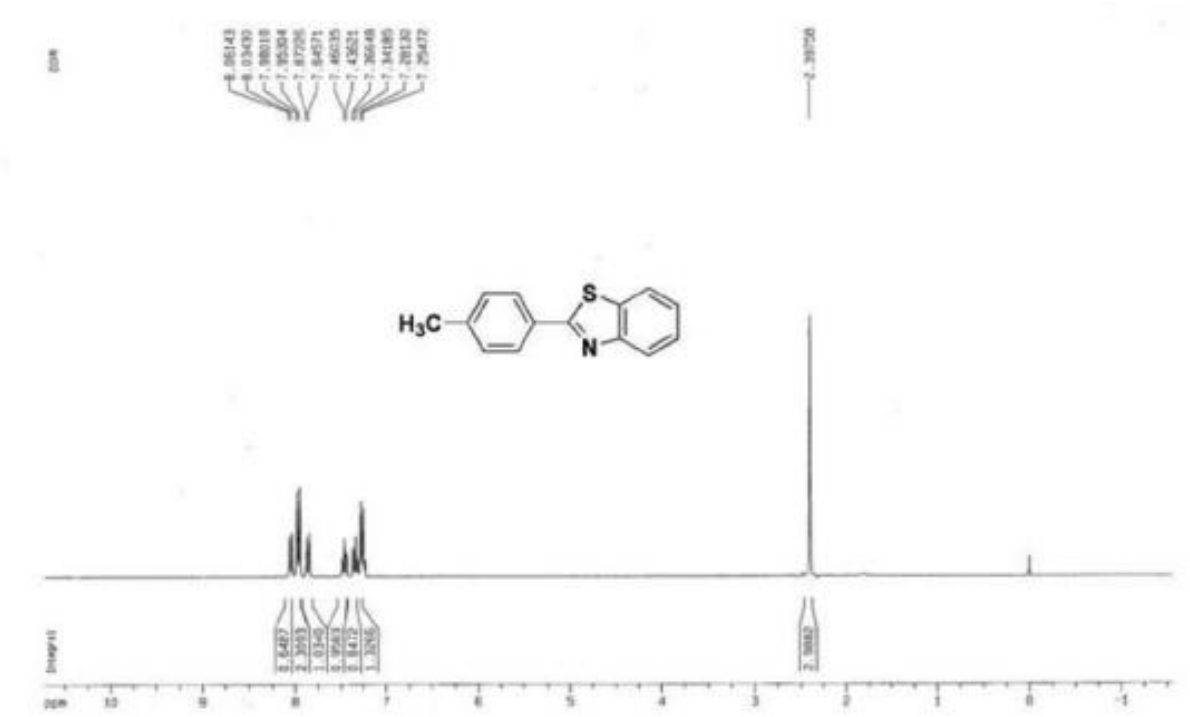

Figure S15: ^{1}H NMR Spectrum of compound **3f**

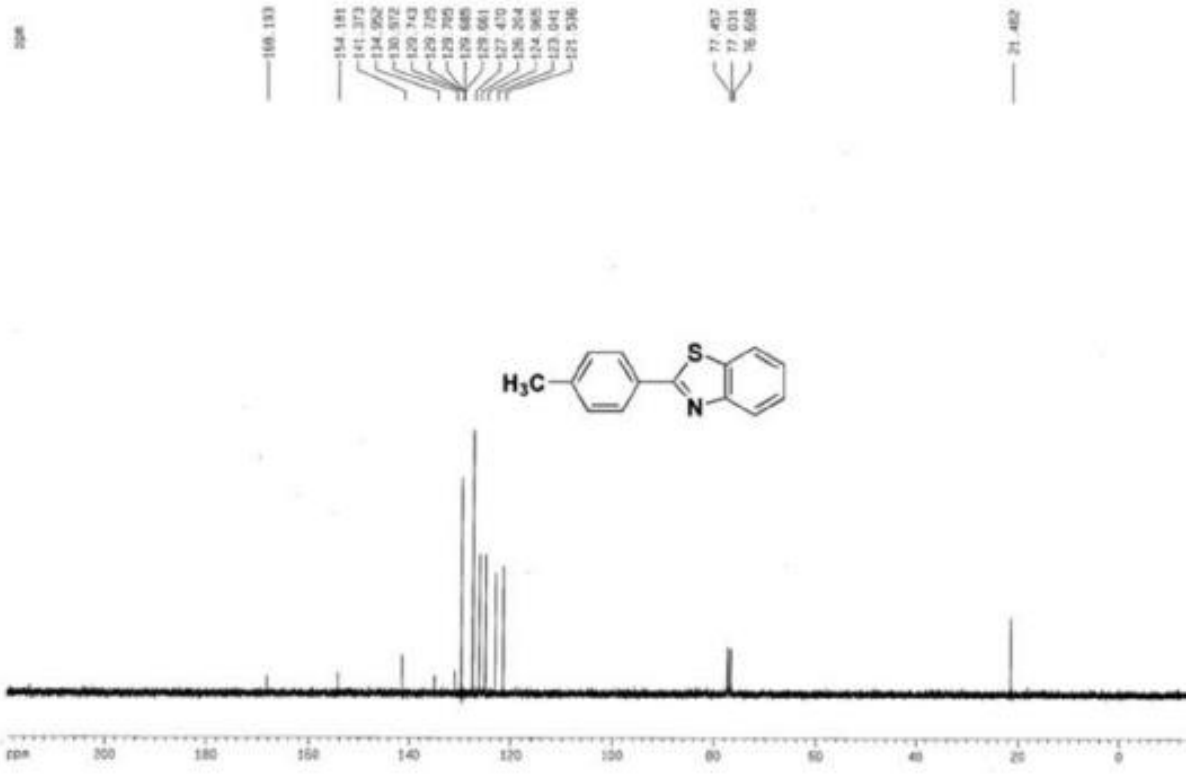

Figure S16: ^{13}C NMR Spectrum of compound **3f**

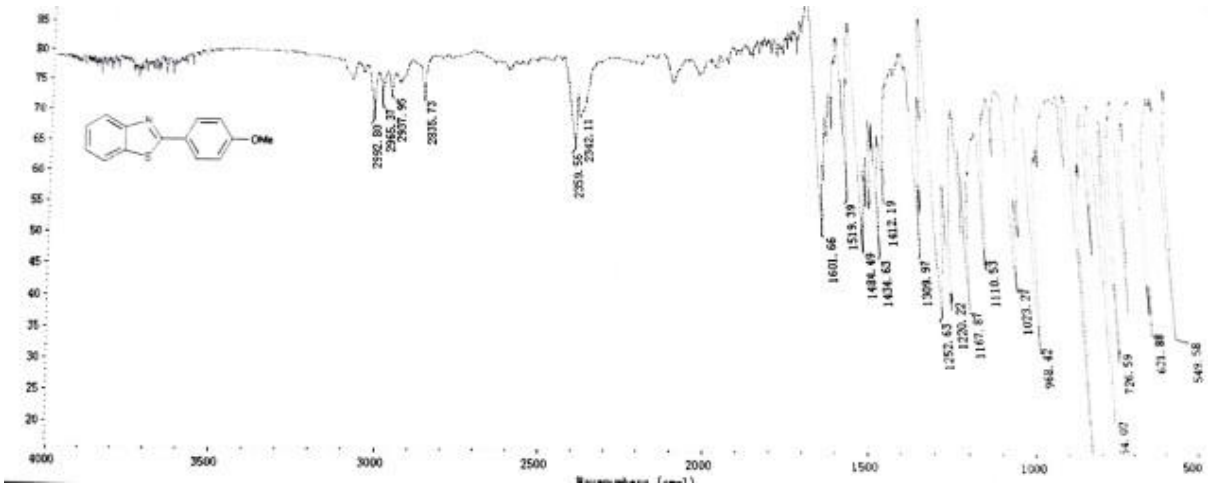

Figure S17: IR Spectrum of compound **3g**

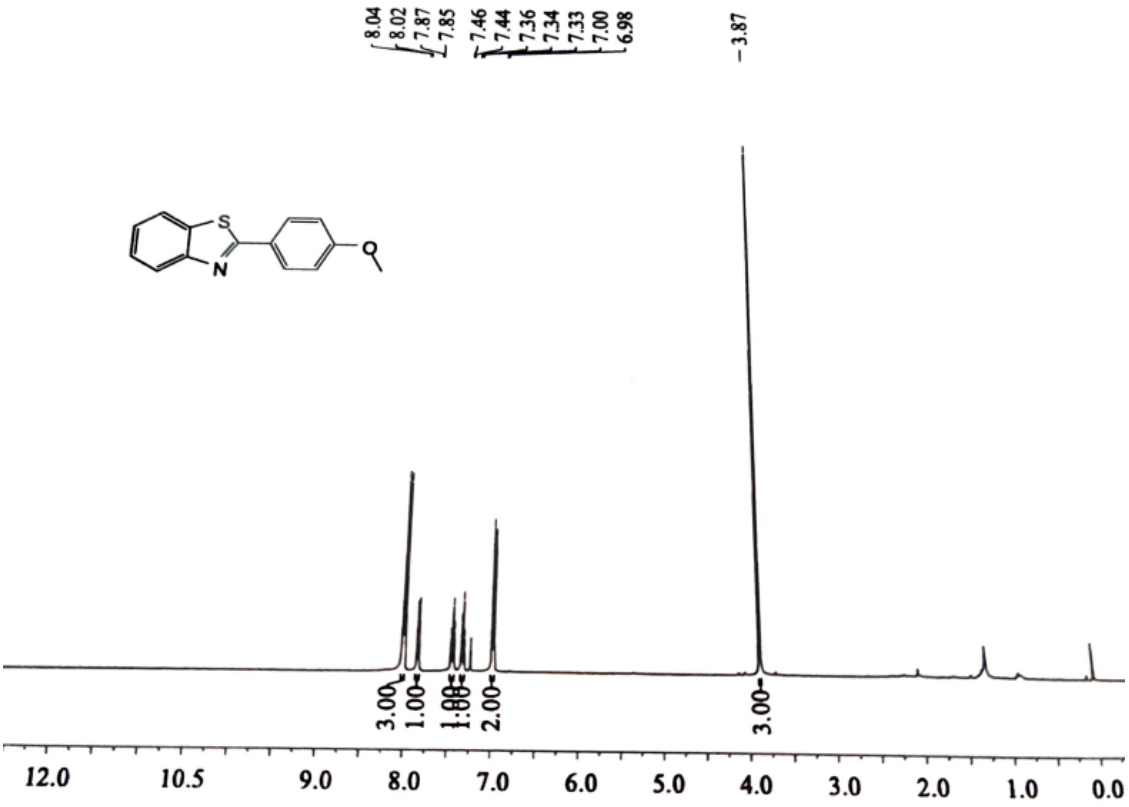

Figure S18: ^{1}H NMR Spectrum of compound **3g**

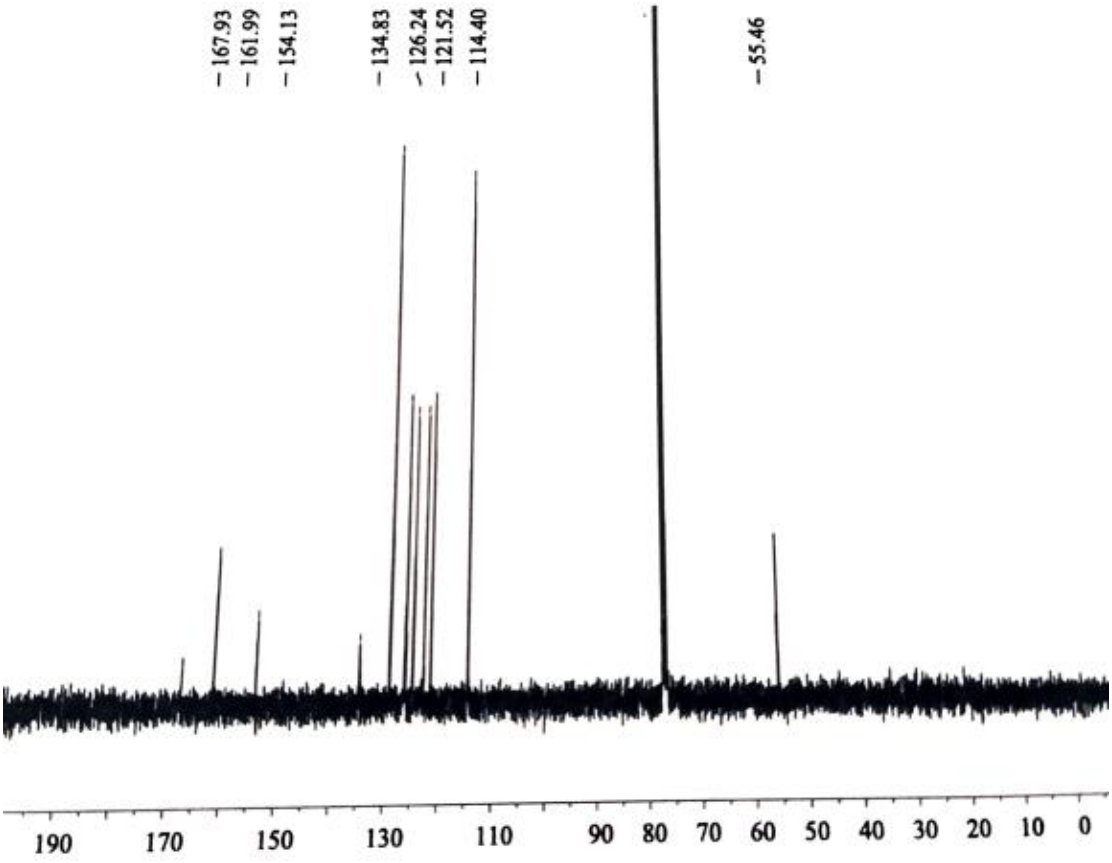

Figure S19: ^{13}C NMR Spectrum of compound **3g**

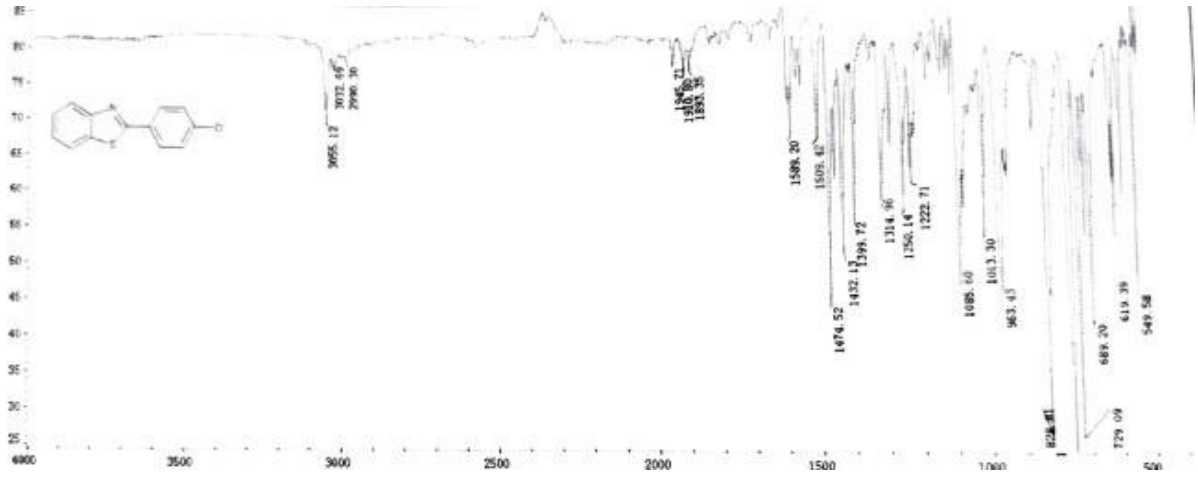

Figure S20: IR Spectrum of compound **3h**

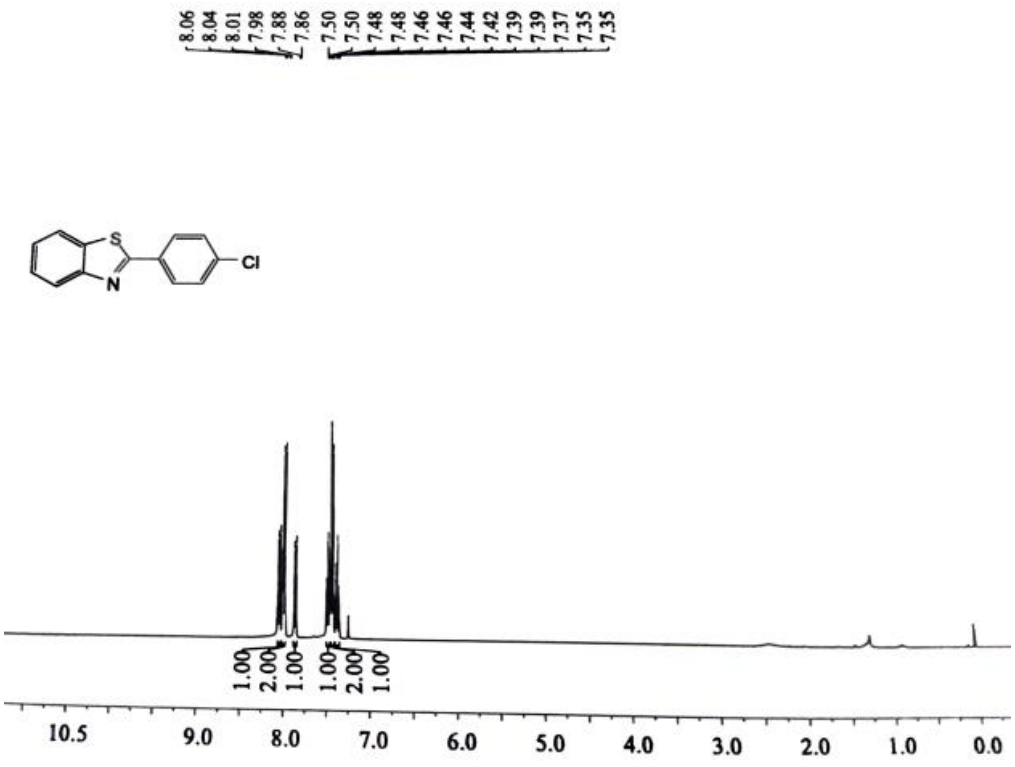

Figure S21: ^{1}H NMR Spectrum of compound **3h**

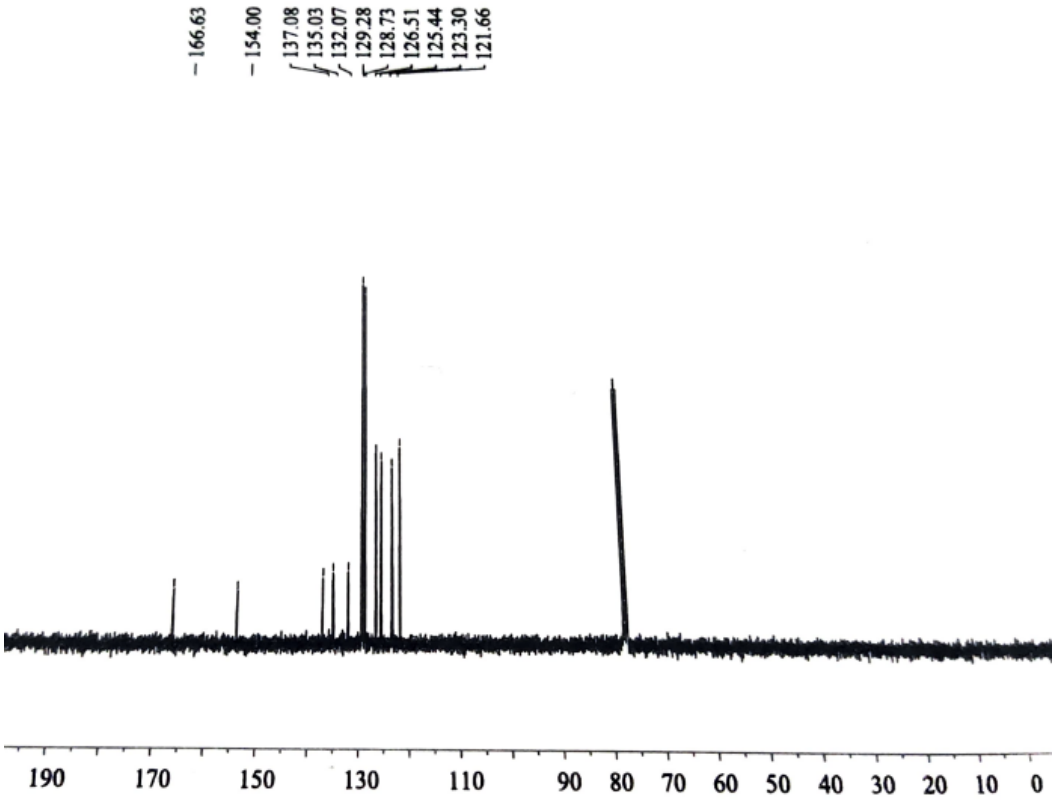

Figure S22: ^{13}C NMR Spectrum of compound **3h**

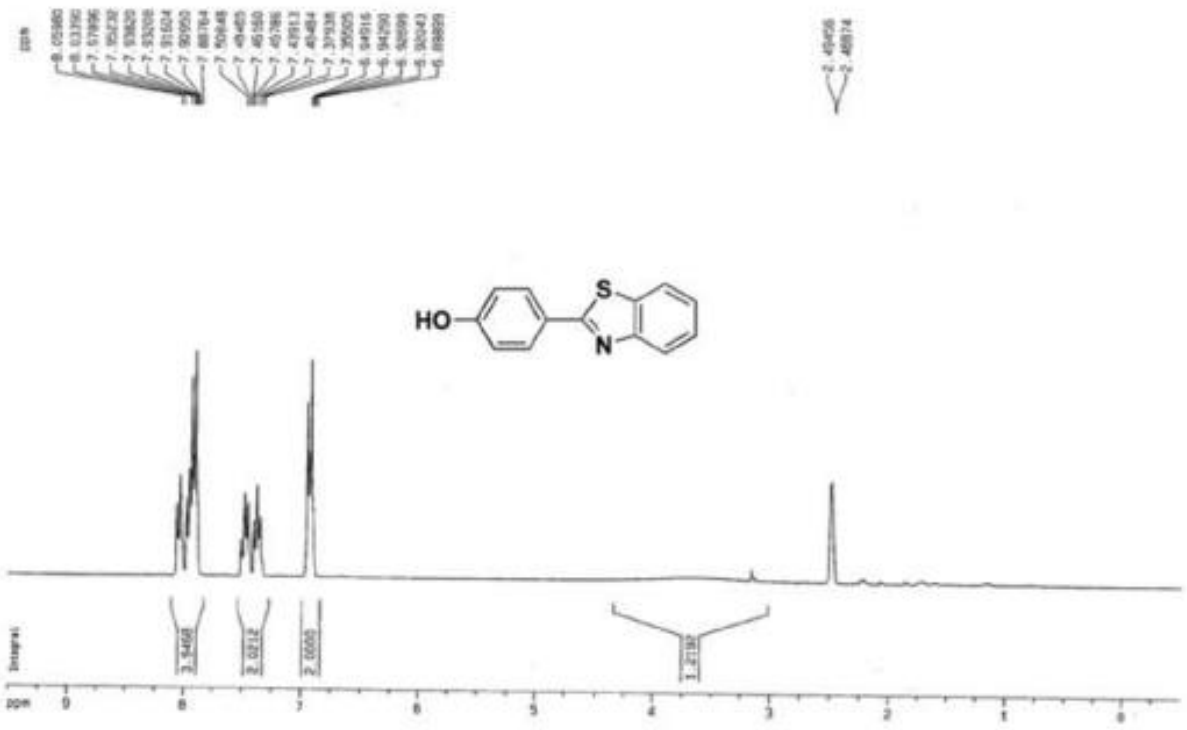

Figure S23: ^{1}H NMR Spectrum of compound **3i**

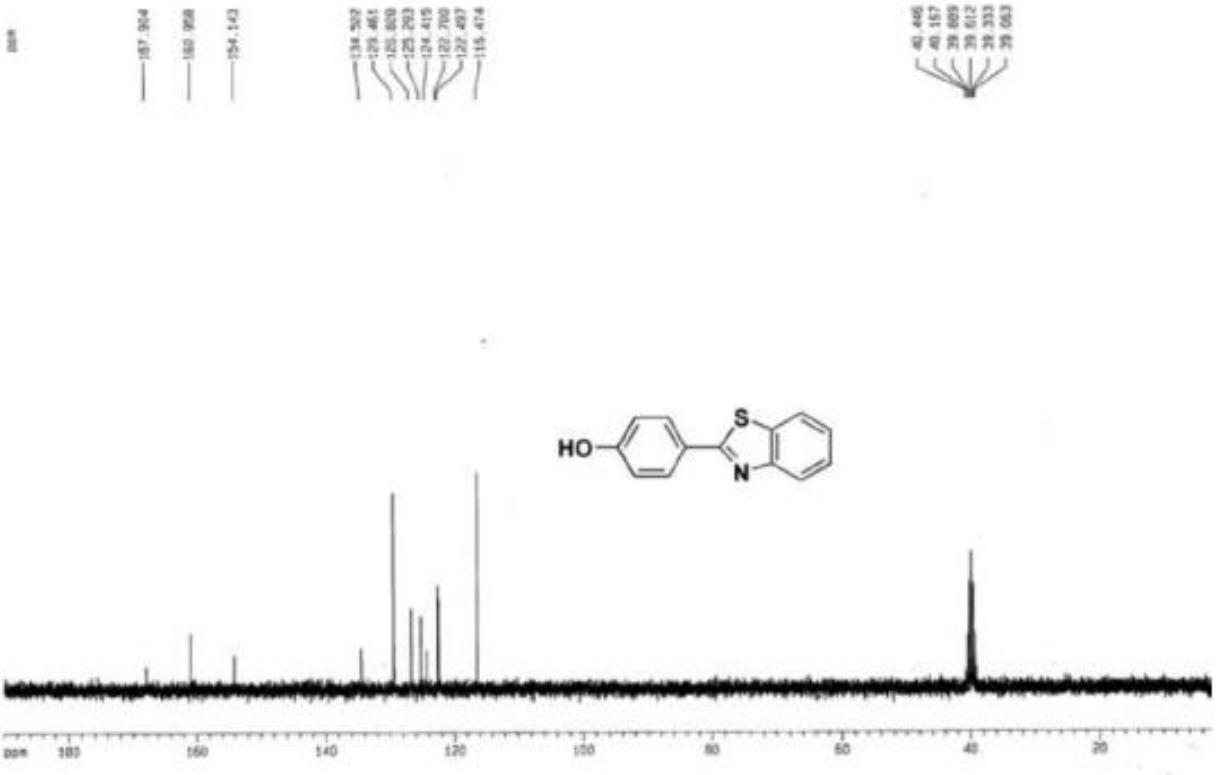

Figure S24: ^{13}C NMR Spectrum of compound **3i**

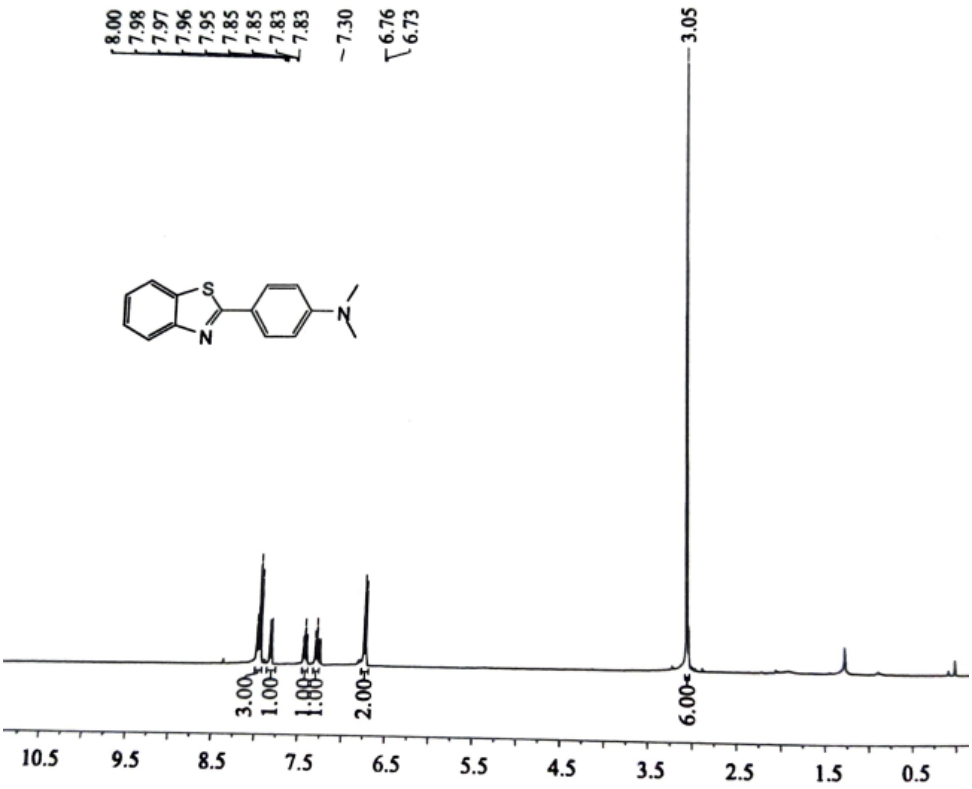

Figure S25: ^{1}H NMR Spectrum of compound **3j**

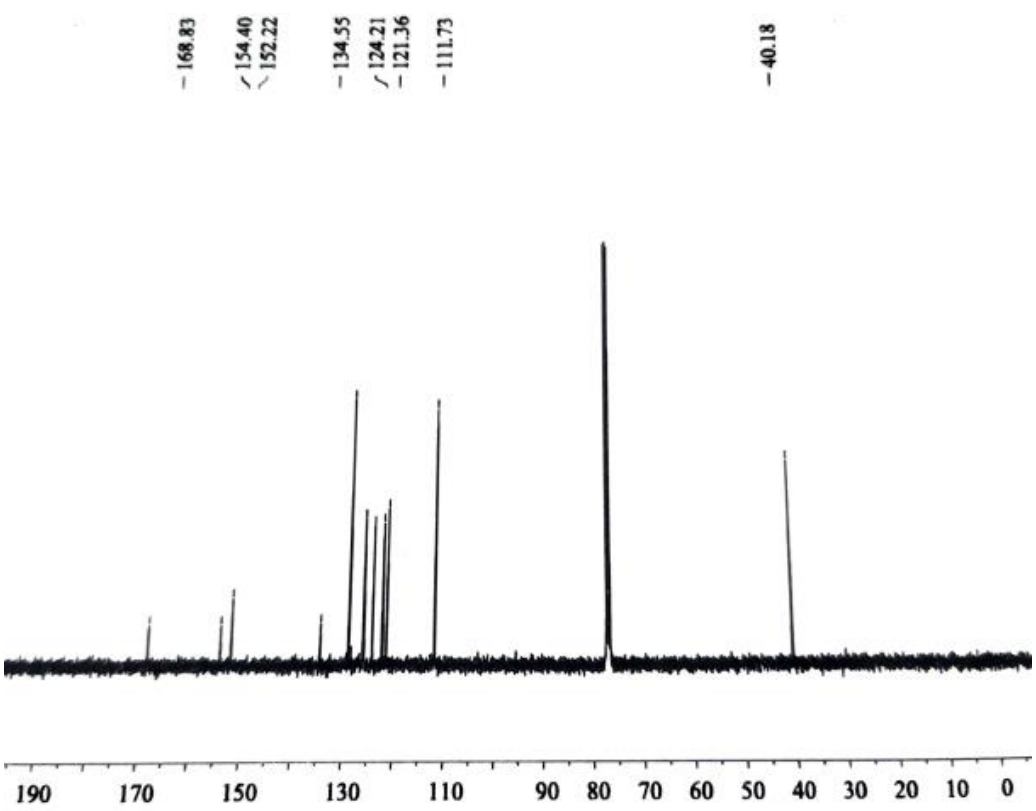

Figure S26: ^{13}C NMR Spectrum of compound **3j**

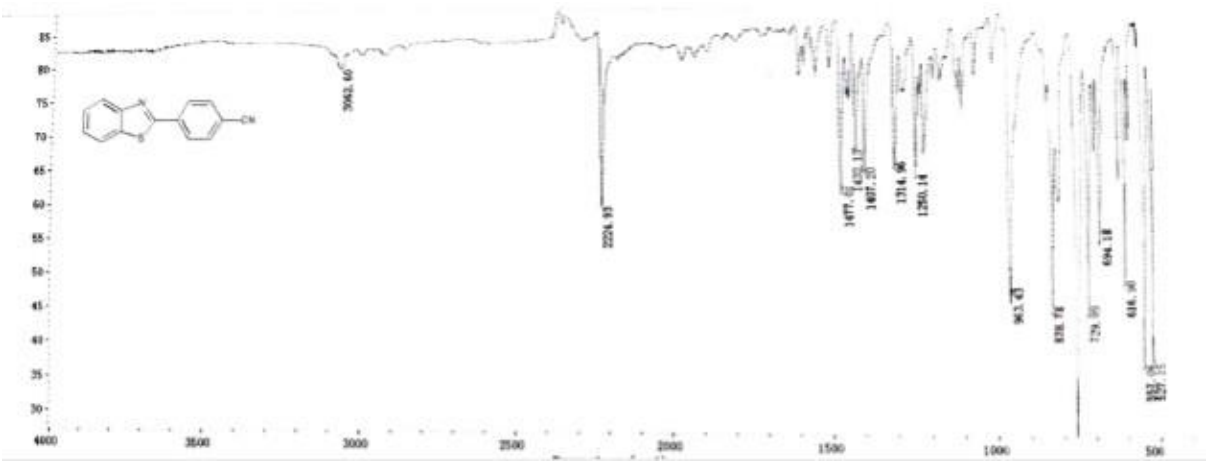

Figure S27: IR Spectrum of compound **3k**

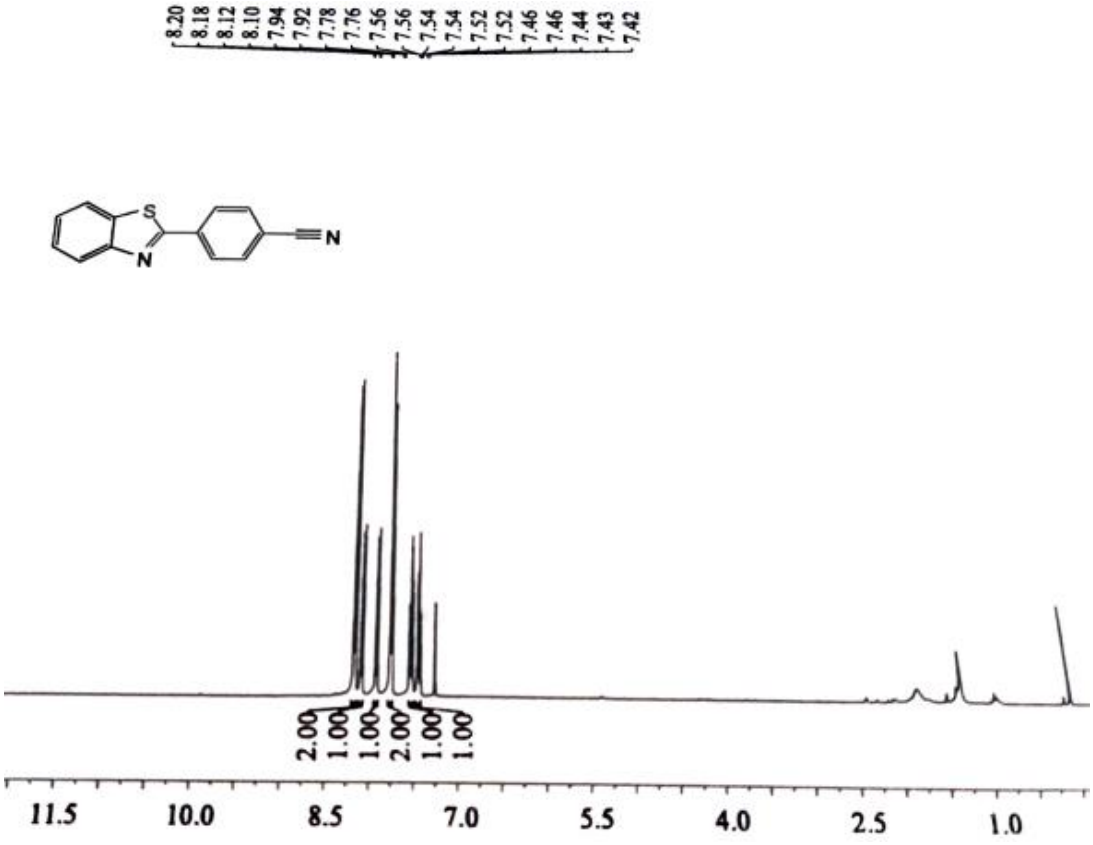

Figure S28: ^{1}H NMR Spectrum of compound **3k**

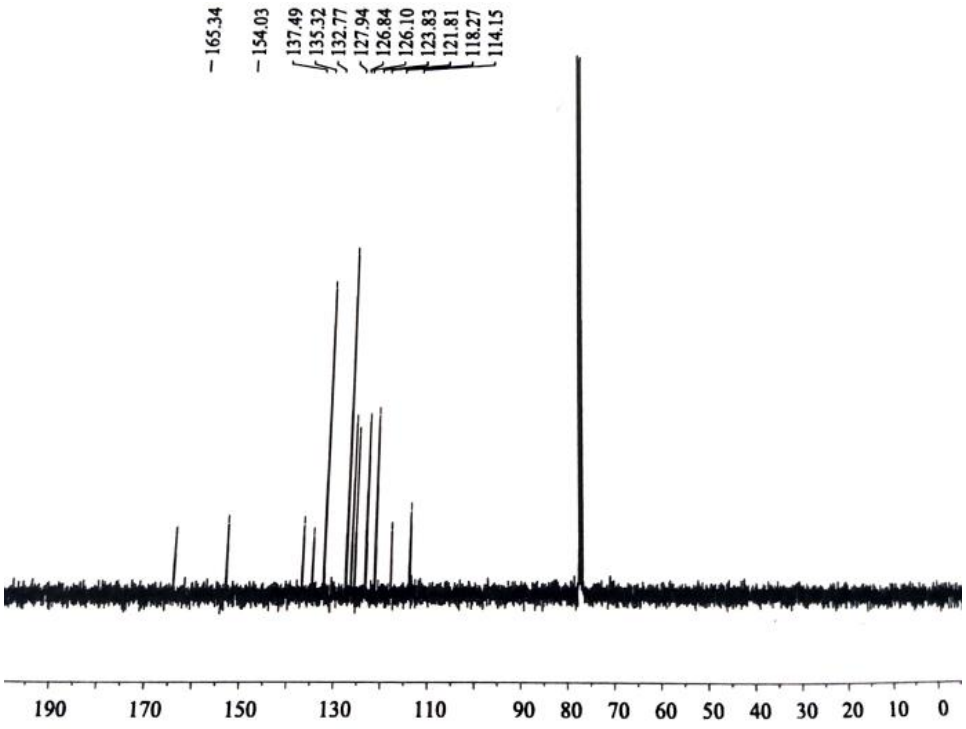

Figure S29: ^{13}C NMR Spectrum of compound **3k**

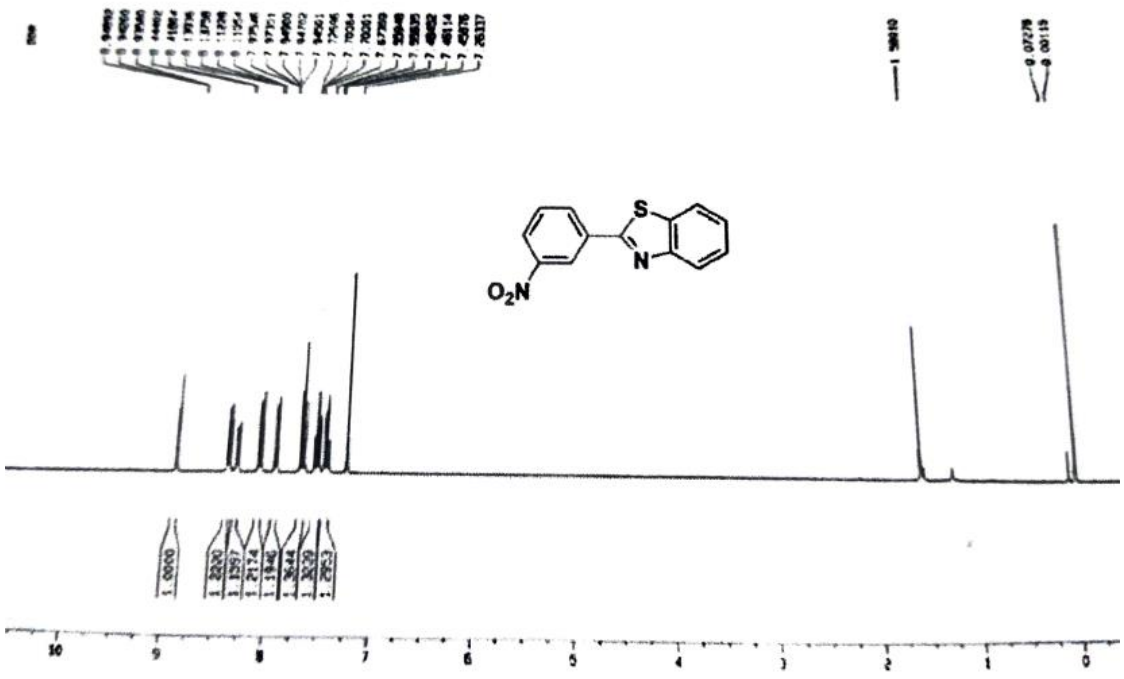

Figure S30: ^{1}H NMR Spectrum of compound **3l**

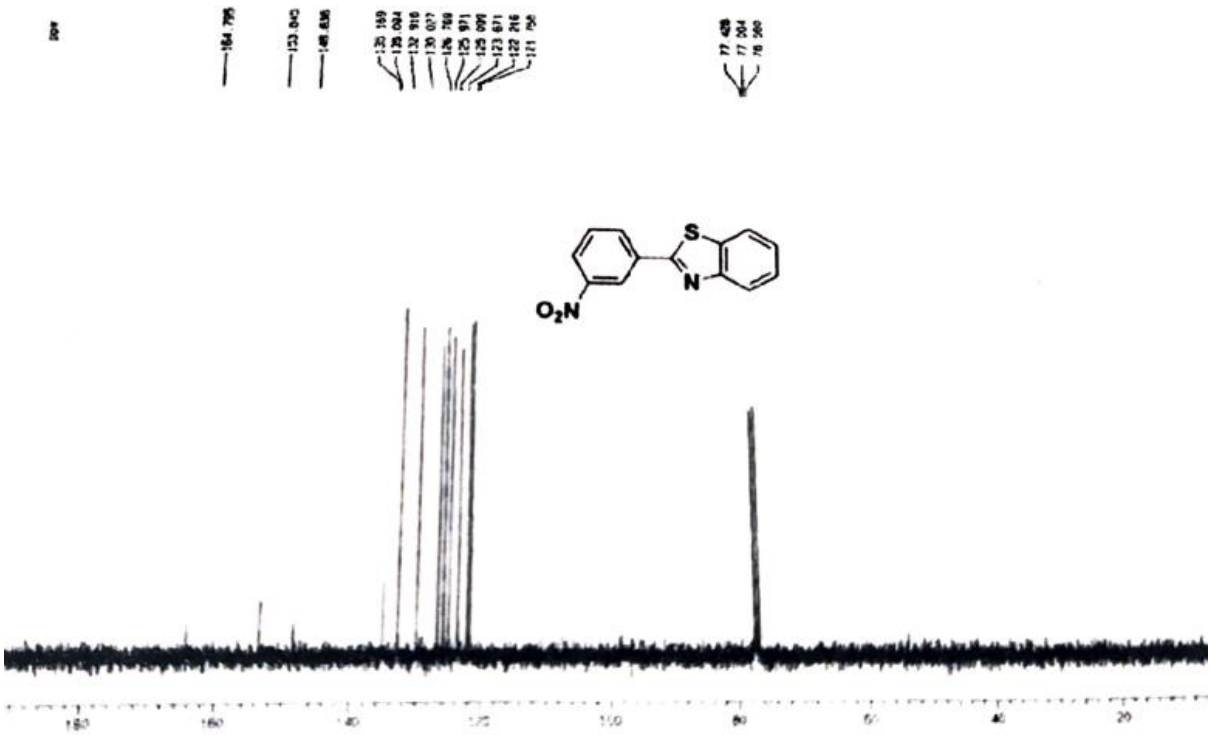

Figure S31: ^{13}C NMR Spectrum of compound **3l**

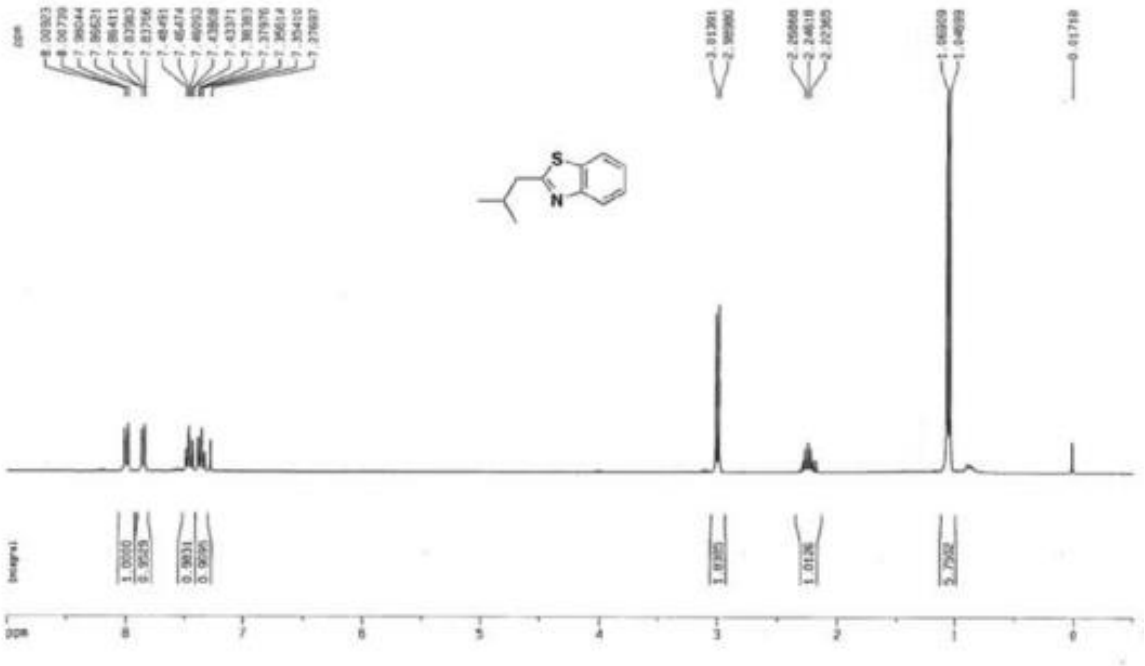

Figure S32: ^{1}H NMR Spectrum of compound **3m**

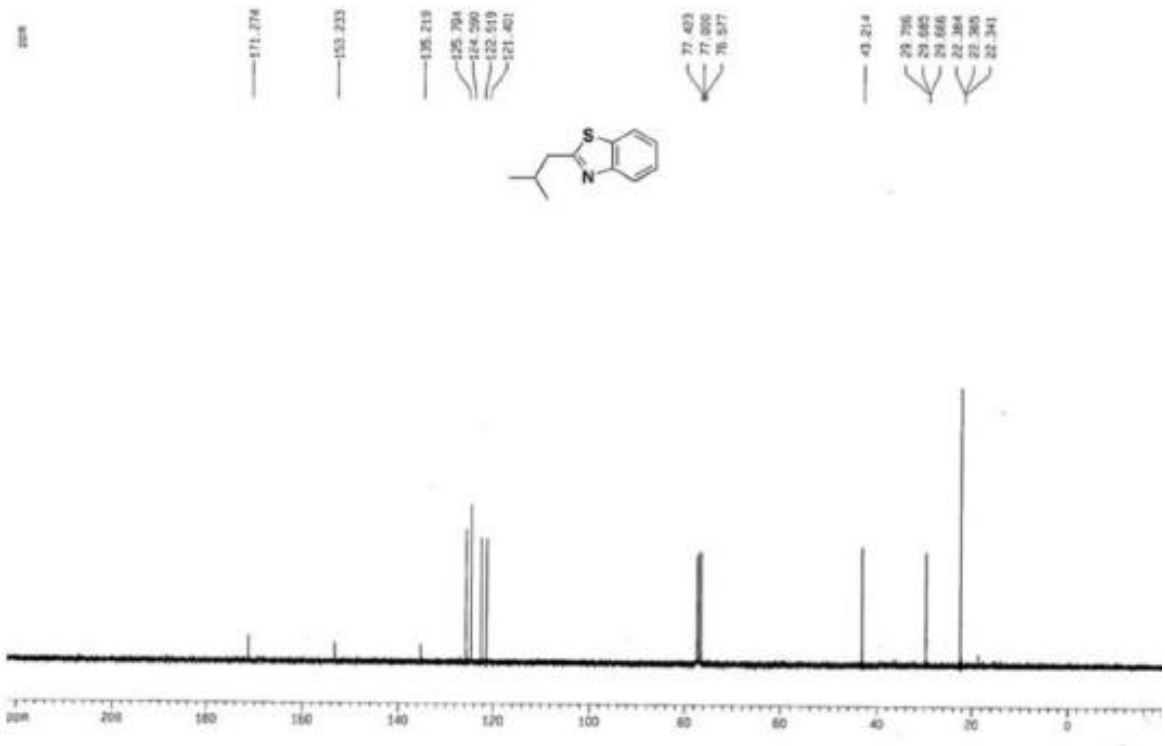

Figure S33: ^{13}C NMR Spectrum of compound **3m**

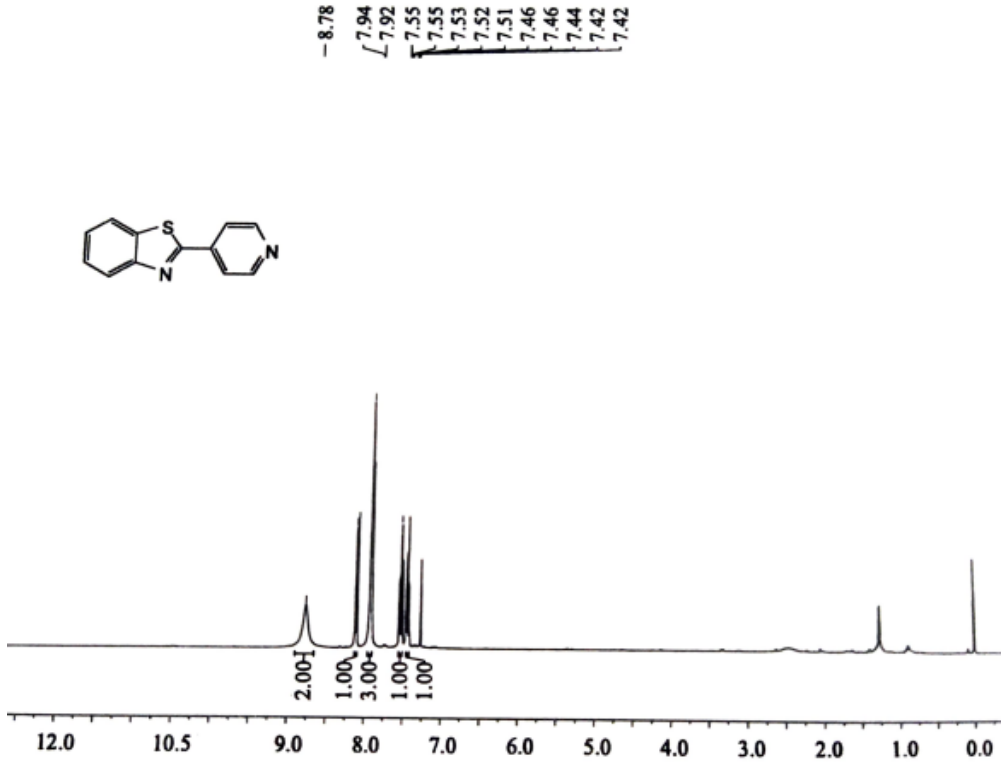

Figure S34: ^{1}H NMR Spectrum of compound **3n**

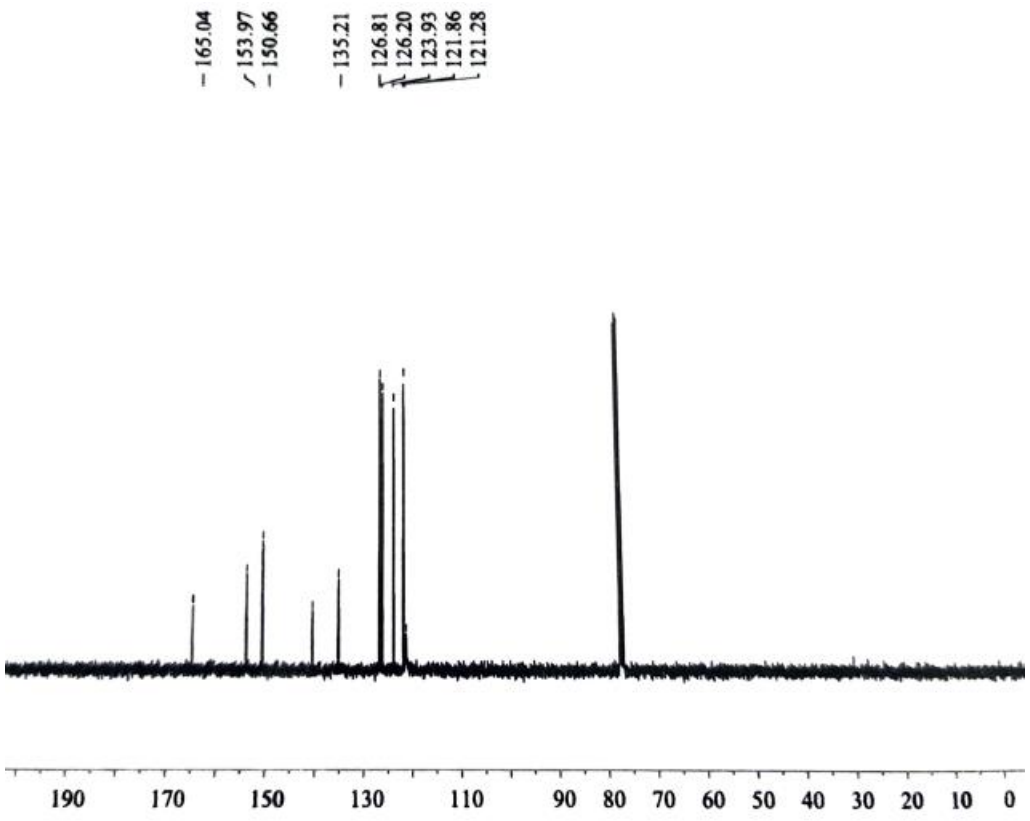

Figure S35: ^{13}C NMR Spectrum of compound **3n**

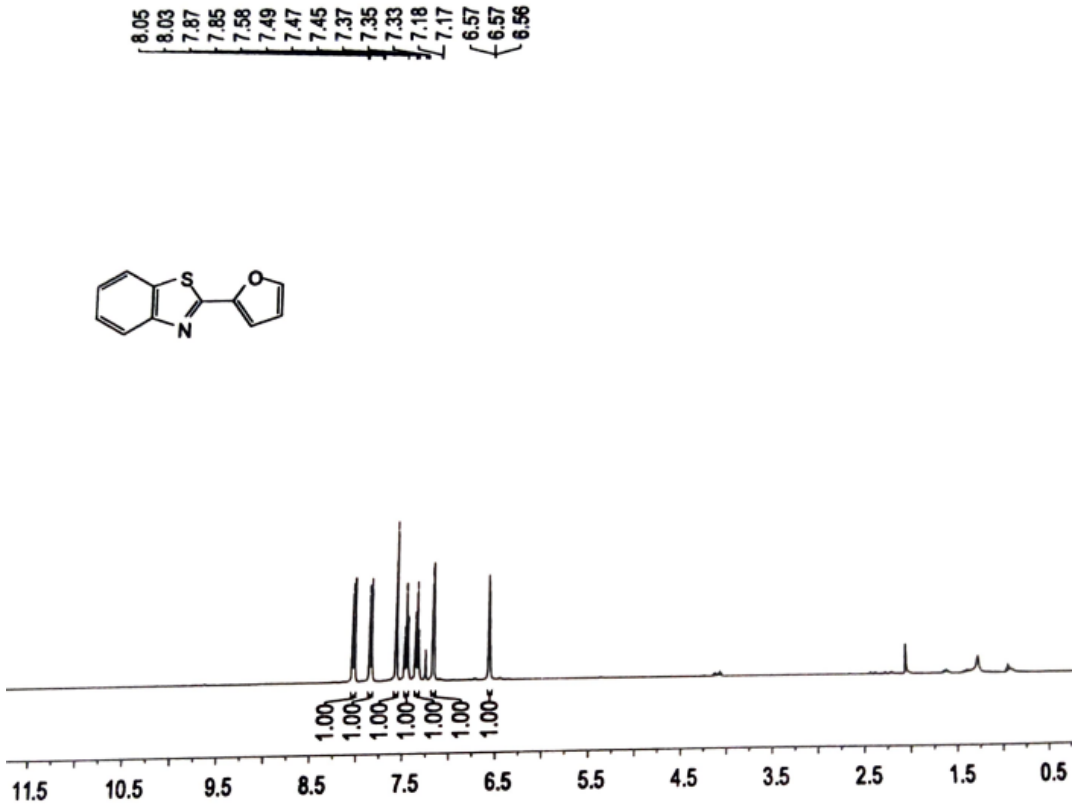

Figure S36: ^{1}H NMR Spectrum of compound **3o**

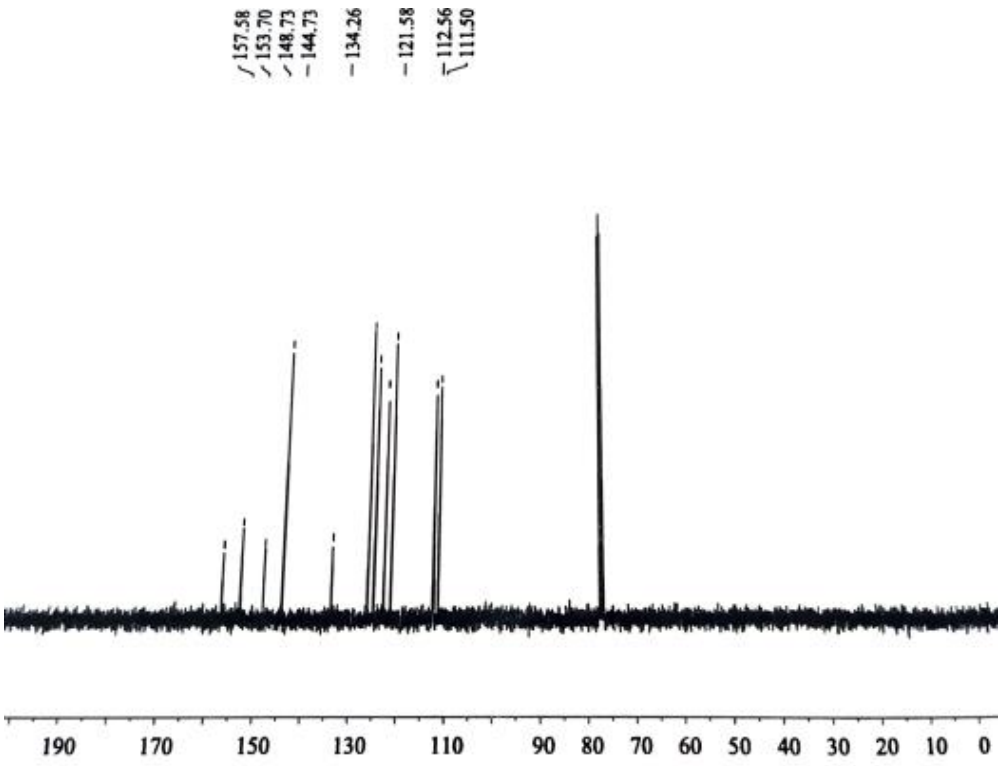

Figure S37: ^{13}C NMR Spectrum of compound **3o**

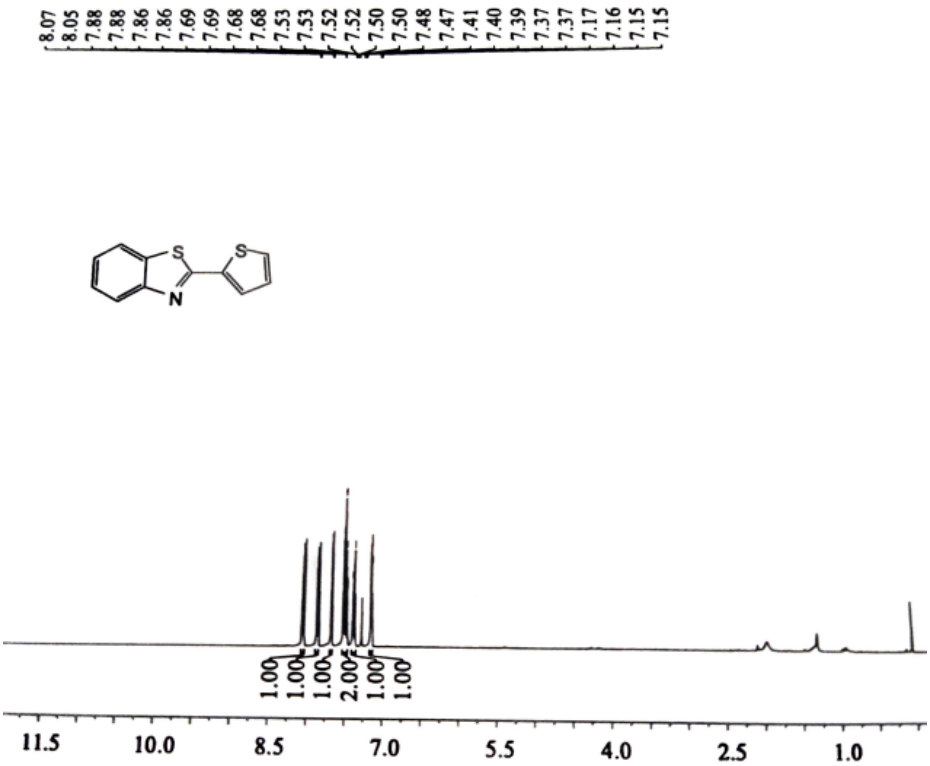

Figure S38: ^{1}H NMR Spectrum of compound **3p**

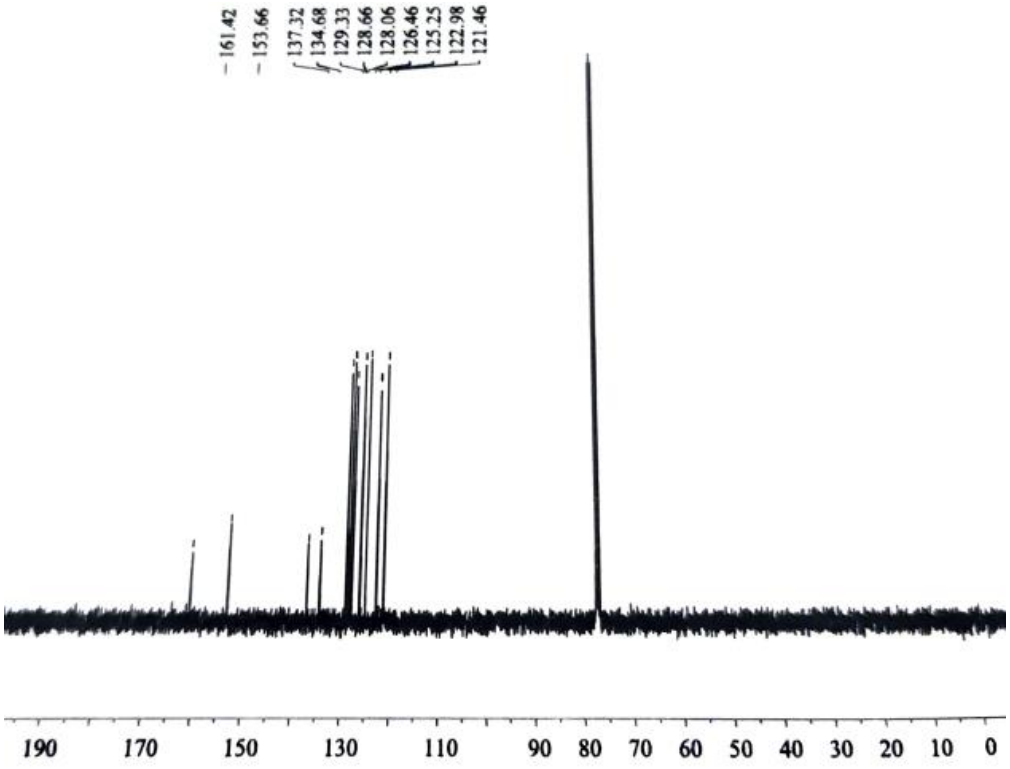

Figure S39: ^{13}C NMR Spectrum of compound **3p**