

Supporting information

Phosphoric acid/titanium oxide-zirconium oxide as an effective reusable nanocatalyst for microwave-promoted synthesis of 2-arylbenzothiazole derivatives under irradiation

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General procedure for the synthesis of 2-arylbenzothiazoles with the catalyst of 30% wt. of phosphoric acid under microwave condition

In a 50 ml beaker, 2 mmol of 2-aminothiophenol and 2 mmol of aromatic aldehyde (4-nitrobenzaldehyde as a model reaction), each totally dissolved in 5 ml of ethanol solvent, were transferred, and 0.04 g of the arranged catalyst containing 30% wt. of phosphoric acid was included to it, and the response vessel was illuminated in a microwave oven with a power of 300 W. to monitor the progress of the reaction, TLC (thin-layer chromatography) was used. Upon completion of the reaction, the reaction mixture was dispersed in the ethyl acetate, filtered, and the catalyst was washed several times with ethyl acetate and acetone. Then, the catalyst was placed in an oven at 90°C for one hour and then placed in a furnace at 550°C for 4 hours. Finally, the washed catalyst was the preserved for use in subsequent reactions. The final products were recrystallized and purified using ethanol after solvent evaporation. The gotten products are recognized by physical and spectroscopic data and compared with the literature

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2-Phenylbenzothiazole (4a): white solid (84% yield); m.p_{rep.} (°C) = 110-112 °C; m.p_{lit.} (°C) = 111-112 °C³⁴; IR (KBr, ν , cm^{-1}): 3066, 3017, 2835, 1608, 1587, 1476, 1430, 830, 763; ¹H NMR (400 MHz, CDCl₃)/ δ ppm: 7.02-7.06 (t, 1H, J=7.6 Hz, Ar-H) 7.23 (d, 1H, J=8.4 Hz, Ar-H), 7.56-7.70 (m, 5H, Ar-H) 7.93 (d, 1H, J=7.6 Hz, Ar-H) 8.41 (d, 1H, J=8.4 Hz, Ar-H); MS (EI, m/z): 211 (M⁺, 42), 197 (8), 182 (40), 171 (6), 143 (11.9), 125 (100), 108 (18), 87 (83), 79 (44), 69 (9.4), 58 (70), 47(51).

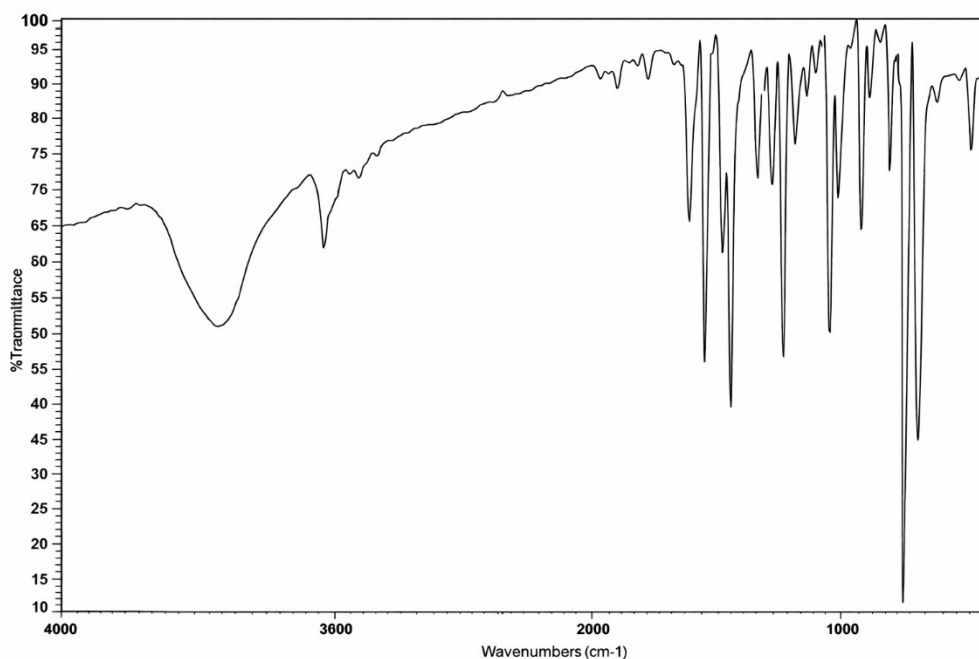


Figure S1. The FT-IR of **3a**

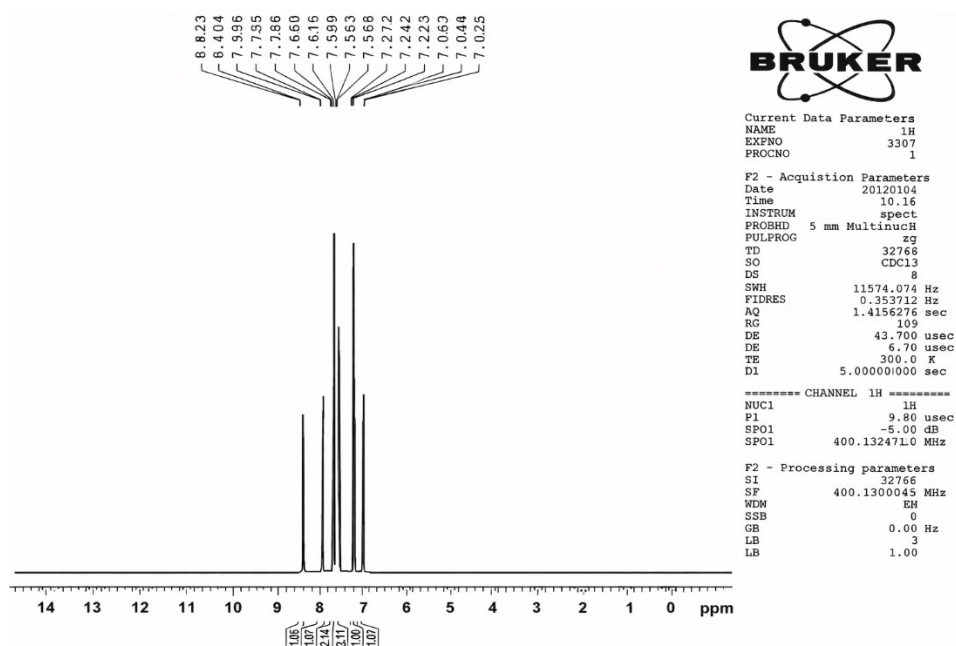


Figure S2. The ^1H NMR of 3a

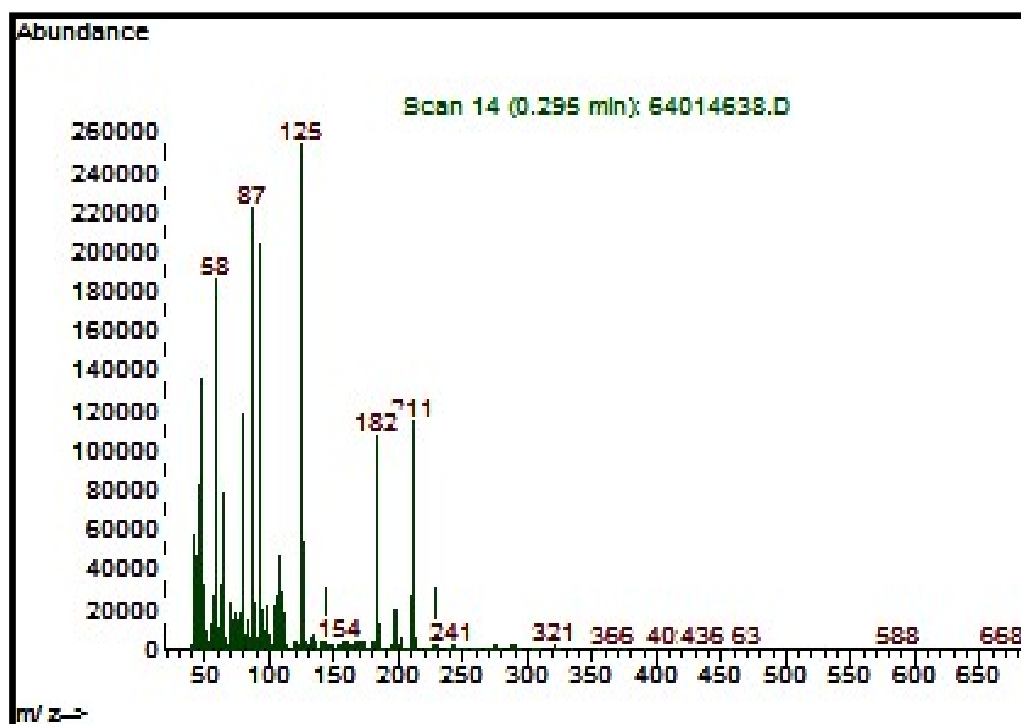


Figure S3: The MS of 3a

2-(2-Hydroxyphenyl)-benzothiazole (3b): Yellow solid; $m.p_{\text{rep.}} = 127\text{-}128\text{ }^\circ\text{C}$; $m.p_{\text{lit.}} = 126\text{-}128\text{ }^\circ\text{C}$ ³⁴; IR (KBr, ν , cm^{-1}): 3285, 3090, 2900, 1619, 1590, 1490,

1423, 874, 7517; $^1\text{H NMR}$ (400 MHz, CDCl_3)/ δ ppm: 6.95-699 (t, 1H, $J=8.0$ Hz, Ar-H) 7.12 (d, 1H, $J=8.0$ Hz, Ar-H), 7.38-7.44 (m, 2H, Ar-H) 7.50-7.54 (t, 1H, $J=8.4$ Hz, Ar-H) 7.71 (d, 1H, $J=8.0$ Hz, Ar-H) 7.92 (d, 1H, $J=8.4$ Hz, Ar-H) 8.01 (d, 1H, $J=8.0$ Hz, Ar-H) 12.54 (s, 1H, OH); $^{13}\text{C NMR}$ / (100 MHz, CDCl_3)/ δ ppm: 116.80, 117.88, 119.54, 121.52, 122.19, 125.56, 126.70, 128.43, 132.60, 132.77, 151.84, 157.96, 169.39; **MS (EI, m/z)**: 217 (M^+ , 1.8), 200 (37), 183 (5.7), 167 (16.5), 136 (100), 124 (81), 107 (78), 97 (13), 77 (50), 65 (30), 51 (18), 41(3).

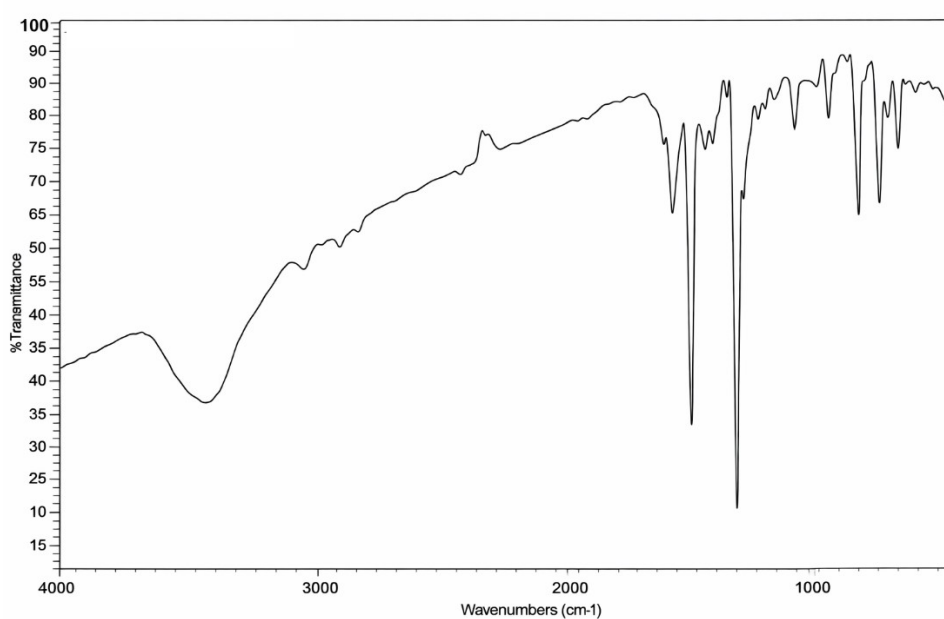


Figure S4. The FT-IR of **3b**

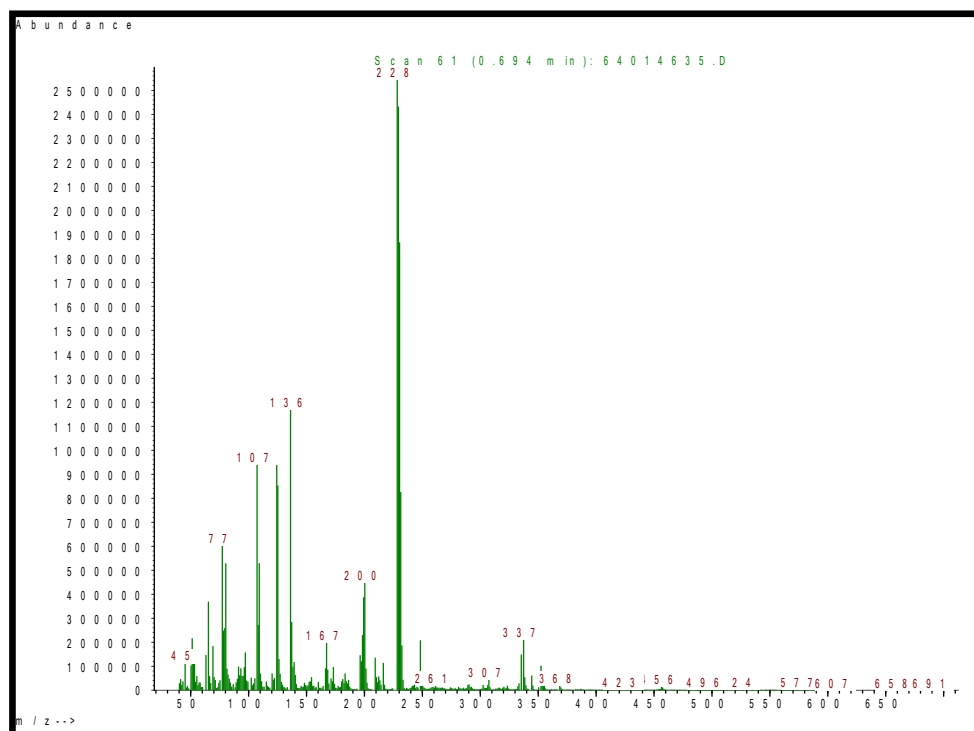


Figure S7: The MS of 3b

2-(4-Methoxyphenyl)-benzothiazole (3c): White solid; m.p_{rep.} = 120-122 °C; m.p_{lit.} = 120-122 °C³⁴; IR (KBr, ν , cm^{-1}): 3021, 3048, 2837, 1609, 1590, 1483, 1249, 830; ¹H NMR (400 MHz, CDCl₃)/ δ ppm: 3.90 (s, 3H, OCH₃) 7.04 (d, 2H, J=10.0 Hz, Ar-H) 7.34 (t, 2H, J=8.0 Hz, Ar-H) 7.57 (t, 1H, J=8.0 Hz, Ar-H) 7.74 (d, 1H, J=8.0 Hz, Ar-H) 8.21 (d, 2H, J=10.0 Hz, Ar-H); ¹³C NMR/ (100 MHz, CDCl₃)/ δ ppm: 55.47, 114.38, 121.53, 122.83, 124.81, 126.23, 126.42, 129.13, 134.86, 154.21, 161.94, 167.89; **MS (EI, m/z):** 243 (12.5), 242 (38), 241 (M⁺, 100), 226 (15.8), 198 (23), 171 (3.5), 154 (5.4), 139 (0.8), 127 (1.6), 108 (2.8), 82 (2.8), 69 (6.9).

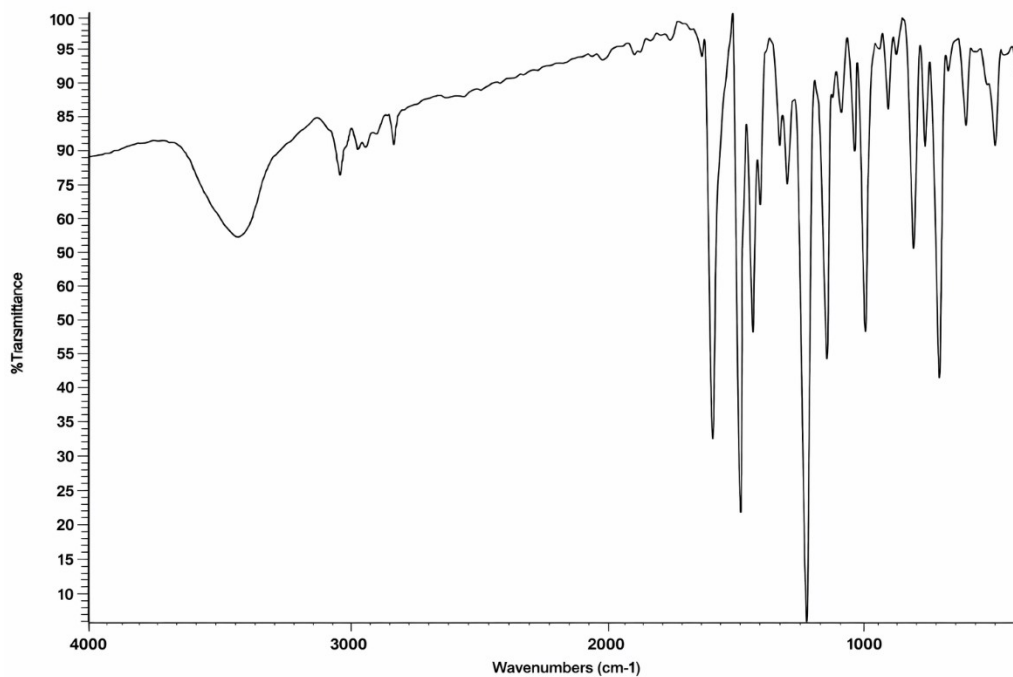


Figure S8. The FT-IR of 3c

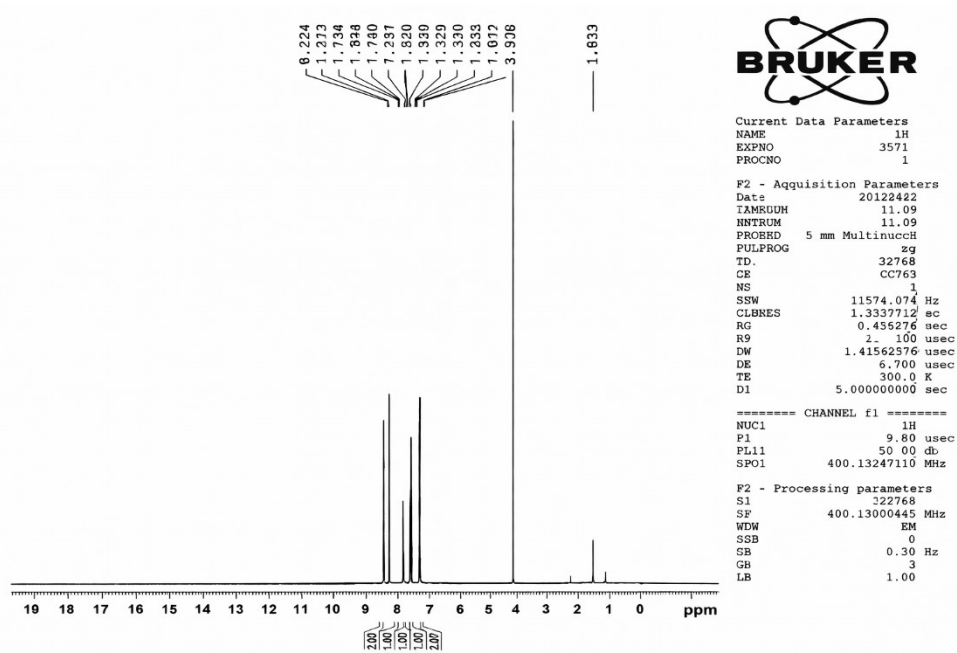


Figure S9. The ^1H NMR of 3c

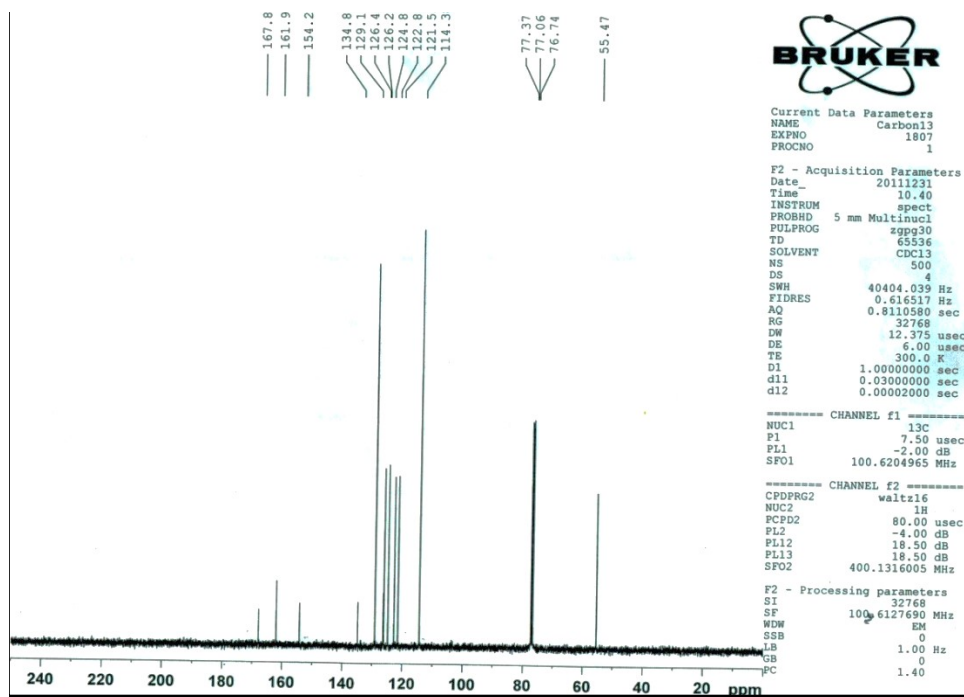


Figure S10. The ^{13}C NMR of **3c**

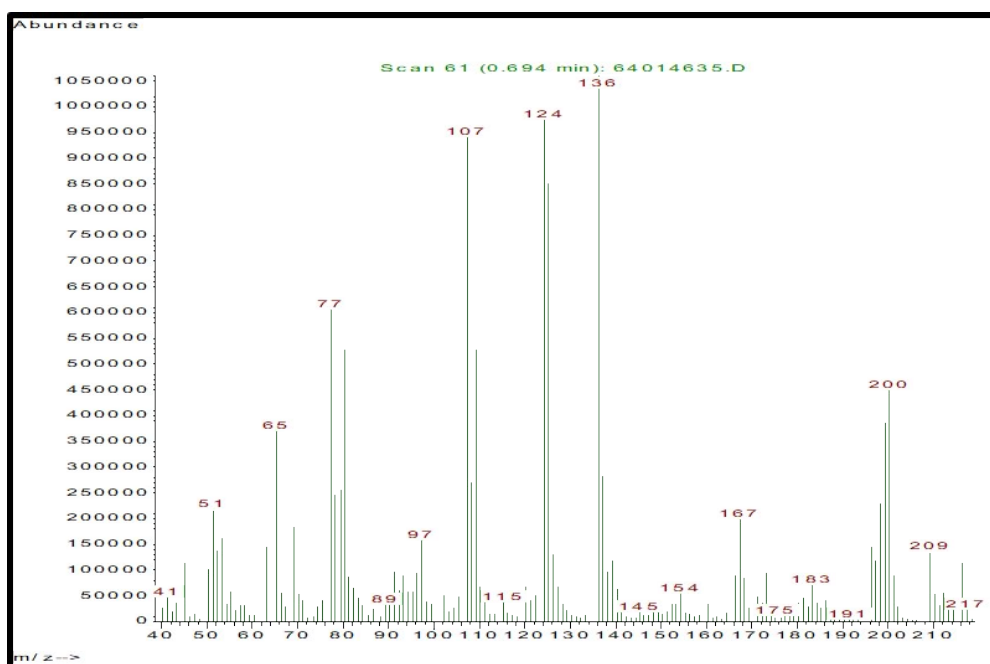


Figure S11. The MS of **3c**

2-(3-Chlorophenyl)benzothiazole (3d): White solid; $m.p_{\text{rep}}$: 125-127 $^{\circ}\text{C}$; $m.p_{\text{lit}}$: 126-128 $^{\circ}\text{C}$ ³⁴; IR (KBr, ν , cm^{-1}): 3053, 1628, 1501, 1457, 731; ^1H NMR (400 MHz, CDCl_3)/ δ (ppm): 8.23-8.21 (m, 1H), 8.15 (d, $J=8.0$ Hz, 1H), 7.96 (d, $J=8.0$ Hz, 1H), 7.52-7.56 (m, 2H), 7.41-7.46 (m, 3H).

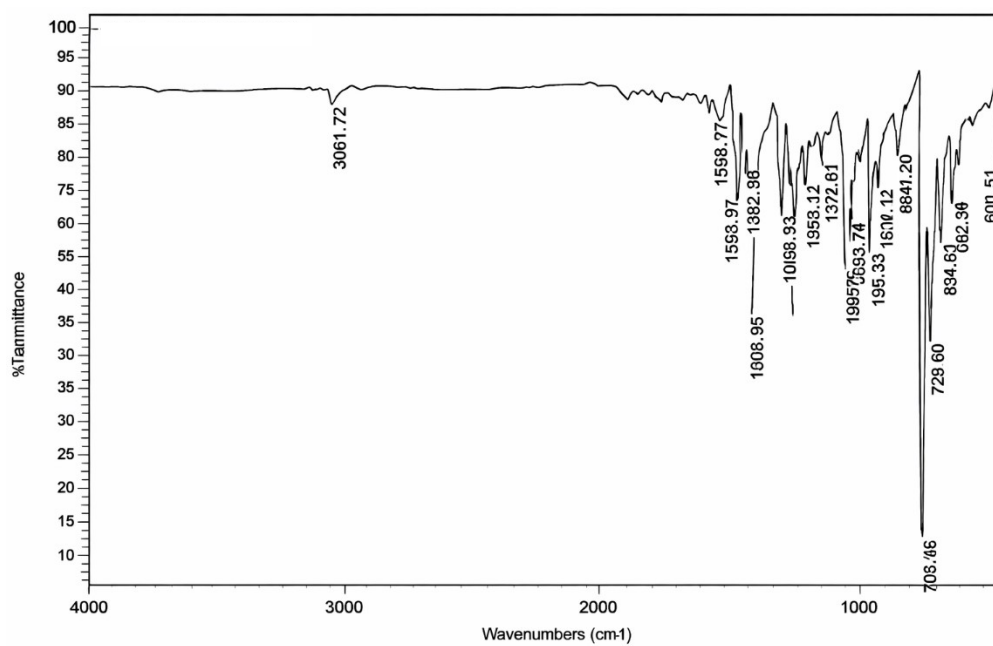


Figure S12. The FT-IR of **3d**

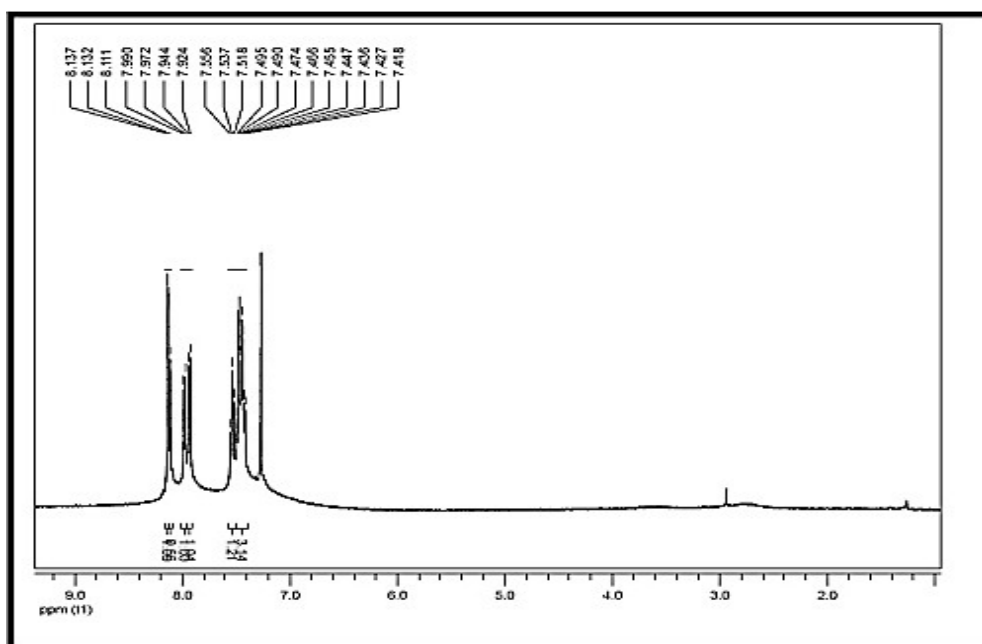


Figure S13. The ^1H NMR of **3d**

2-(4-Methylphenyl)-benzothiazole (3e): White solid; $m.p_{\text{rep.}} = 82\text{-}84\text{ }^\circ\text{C}$; $m.p_{\text{lit.}} = 83\text{-}85\text{ }^\circ\text{C}$ ³⁴; IR (KBr, ν , cm^{-1}): 3024, 2905, 1610, 1519, 1480, 1435, 1383, 1312, 821, 759; ^1H NMR (400 MHz, CDCl_3)/ δ ppm: 2.45 (s, 3H, CH₃) 7.34-736 (m,

4H, Ar-H) 7.54-7.59 (m, 1H, Ar-H) 7.75 7.78 (m, 1H, Ar-H) 8.14-8.16 (m, 2H, Ar-H).

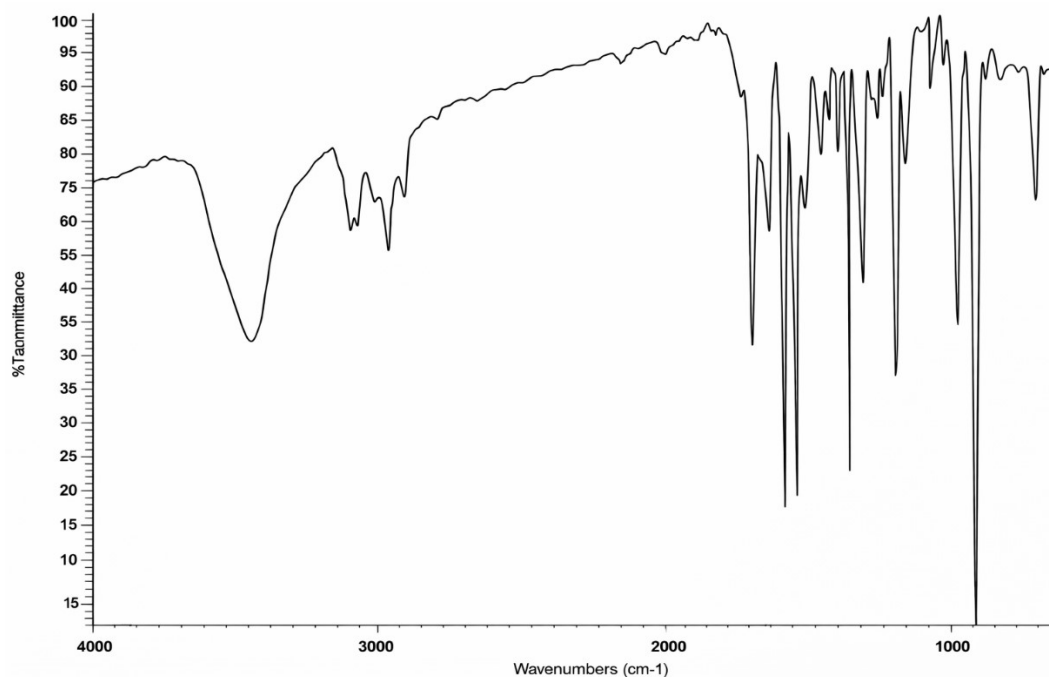


Figure S14. The FT-IR of 3e

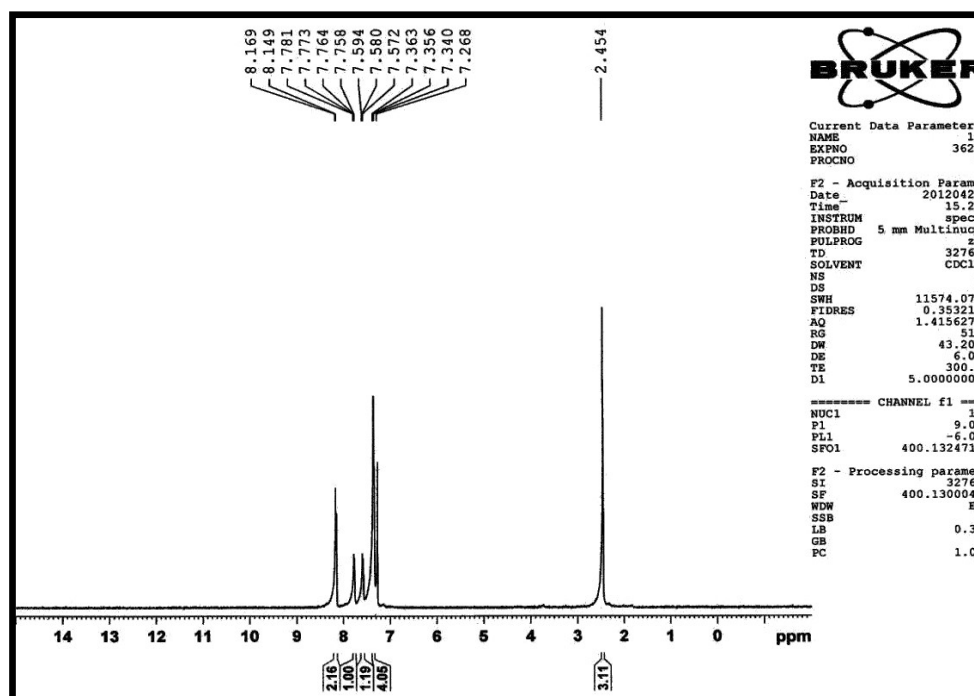


Figure S15. The ¹H NMR of 3e

2-(2-Chlorophenyl)-benzothiazole (3f): Colorless solid; m.p.= 72-74 °C; m.p._{lit.}=72-74 °C³⁵; IR (KBr, ν , cm⁻¹): 3061, 1597, 1557, 1481, 756; ¹H NMR

2-(4-Chlorophenyl)-benzothiazole (3g): Yellow solid; m.p.= 114-116 °C; m.p_{lit.}= 116-118 °C³⁵; IR (KBr, ν , cm^{-1}): 3055, 2358, 1560, 1455, 1430, 1317, 1275, 1060, 965, 750, 725; ¹H NMR (400 MHz, CDCl₃)/ δ ppm: 7.37-7.39 (m, 2H, Ar-H) 7.51-7.53 (d, 2H, J=7.6 Hz, Ar-H) 7.58 7.61 (m, 1H, Ar-H) 7.77-7.79 (m, 1H, Ar-H) 8.19-8.22 (d, 2H, J=7.6 Hz, Ar-H).

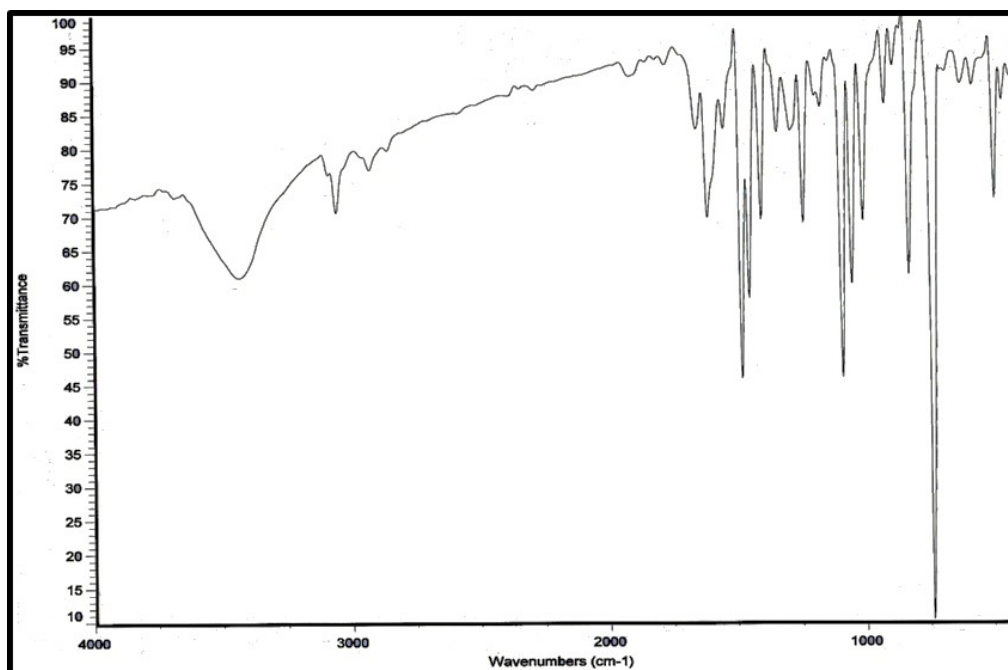


Figure S18. The FT-IR of 3g

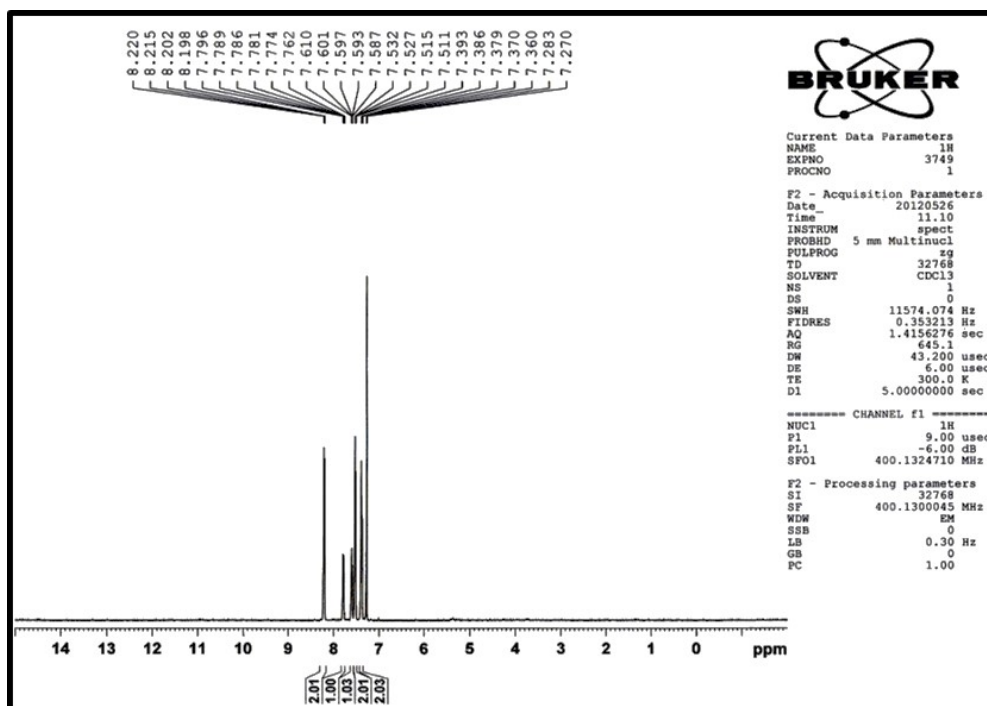


Figure S19. The ^1H NMR of **3g**

2-(4-Fluorophenyl)benzothiazole (3h): yellow solid; m.p_{rep.}: 99-101 °C m.p lit.: 101-103 °C³⁴; ; IR (KBr, ν , cm^{-1}): 3436, 1602, 1518, 1480, 759; ^1H NMR (400 MHz, CDCl_3)/ δ (ppm): 8.06-8.12 (m, 3H), 7.91 (d, $J=8.0$ Hz, 1H), 7.51 (t, $J=7.2$ Hz, 1H), 7.40 (t, $J=7.2$ Hz, 1H), 7.20 (t, $J=8.4$ Hz, 2H).

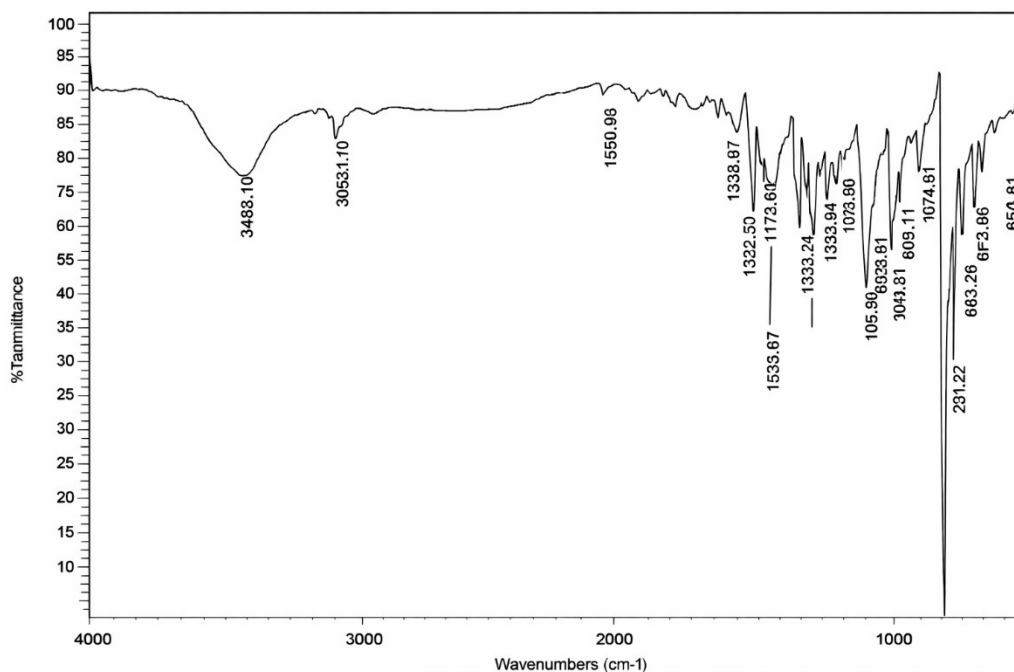


Figure S20. The FT-IR of **3h**

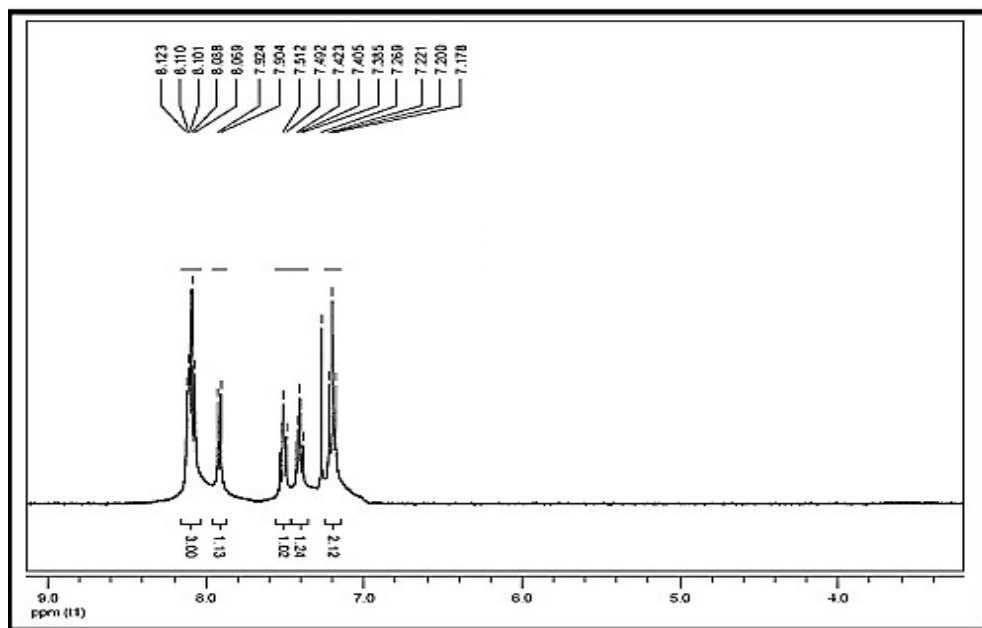


Figure S21. The ^1H NMR of **3h**

2-(4-Nitrophenyl)-benzothiazole (3i): Yellow solid; $m.p_{\text{rep.}} = 227\text{-}229\text{ }^\circ\text{C}$; $m.p. = 226\text{-}228\text{ }^\circ\text{C}$ ³⁵; **IR (KBr, ν , cm^{-1}):** 3042, 2937, 1520, 1461, 1342, 1106, 851, 762; **^1H NMR (400 MHz, CDCl_3)/ δ ppm:** 7.45-7.49 (t, 1H, $J=7.2$ Hz, Ar-H) 7.54-7.58 (t, 1H, $J=7.2$ Hz, Ar-H) 7.97 (d, 1H, $J=7.6$ Hz, Ar-H) 8.14 (d, 1H, $J=7.6$ Hz, Ar-H) 8.27 (d, 2H, $J=8.0$ Hz, Ar-H) 8.36 (d, 2H, $J=8.0$ Hz, Ar-H).

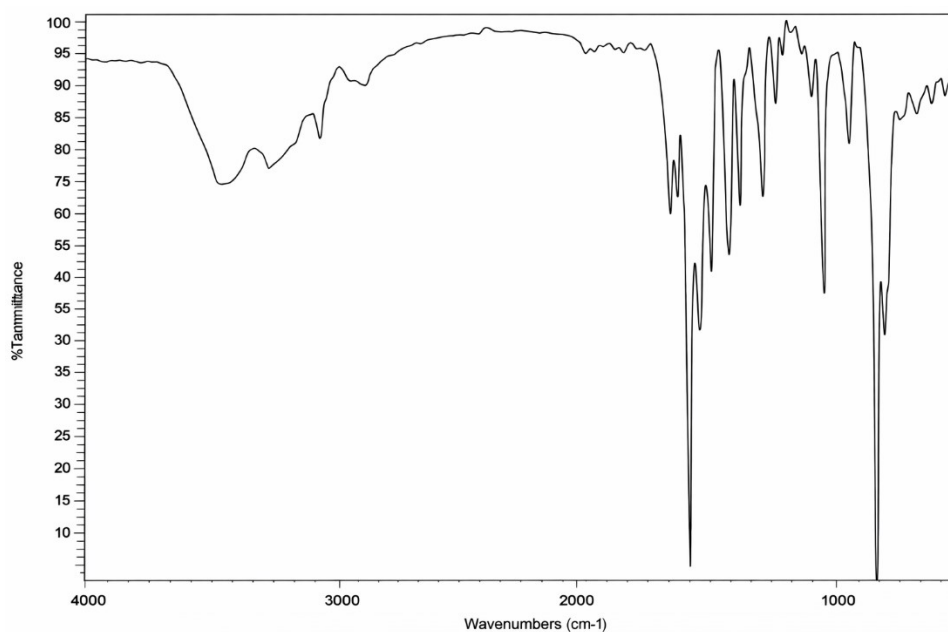


Figure S22. The FT-IR of **3h**

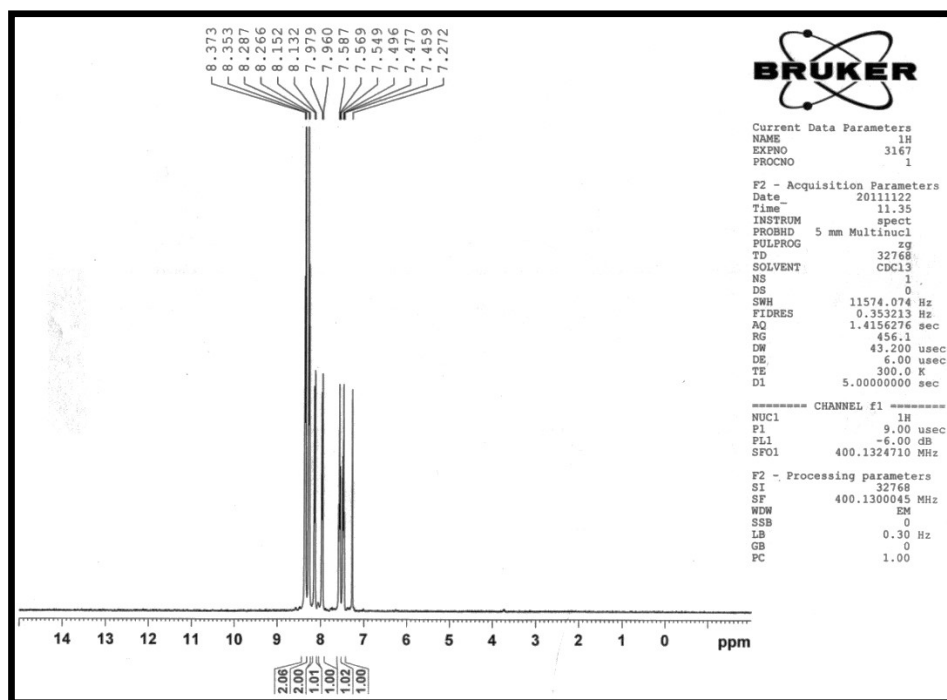


Figure S23. The ^1H NMR of **3h**

2-(2,3-Dichlorophenyl)-benzothiazole (3j): White solid; $m.p_{\text{rep.}} = 118\text{-}120\text{ }^\circ\text{C}$; $m.p_{\text{lit.}} = 119\text{-}121\text{ }^\circ\text{C}$ ³⁴; **IR (KBr, ν , cm^{-1}):** 3020, 2900, 1635, 1512, 1470, 1432, 1348, 780; **^1H NMR (400 MHz, CDCl_3)/ δ ppm:** 7.35-7.39 (t, 1H, $J=8.0$ Hz, Ar-H) 7.45-7.49 (t, 1H, $J=8.0$ Hz, Ar-H) 7.54-7.58 (t, 1H, $J=8.0$ Hz, Ar-H) 7.62 (d, 1H, $J=8.0$ Hz, Ar-H) 7.98 (d, 1H, $J=8.0$ Hz, Ar-H) 8.07 (d, 1H, $J=8.0$ Hz, Ar-H) 8.15 (d, 1H, $J=8.0$ Hz, Ar-H); **^{13}C NMR/ (100 MHz, CDCl_3) / δ ppm:** 117.8, 118.1, 123.3, 124.5, 127.1, 128.1, 128.7, 129.3, 129.9, 130.9, 131.7, 146.0, 149.0; **MS (EI, m/z):** 281 (0.7), 280 (M^+ , 1.2), 244 (3.9), 230 (100), 212 (31), 199 (16.7), 171 (4.3), 157 (1.6), 143 (1.3), 125 (14), 87 (30), 58 (22), 44 (9.6).

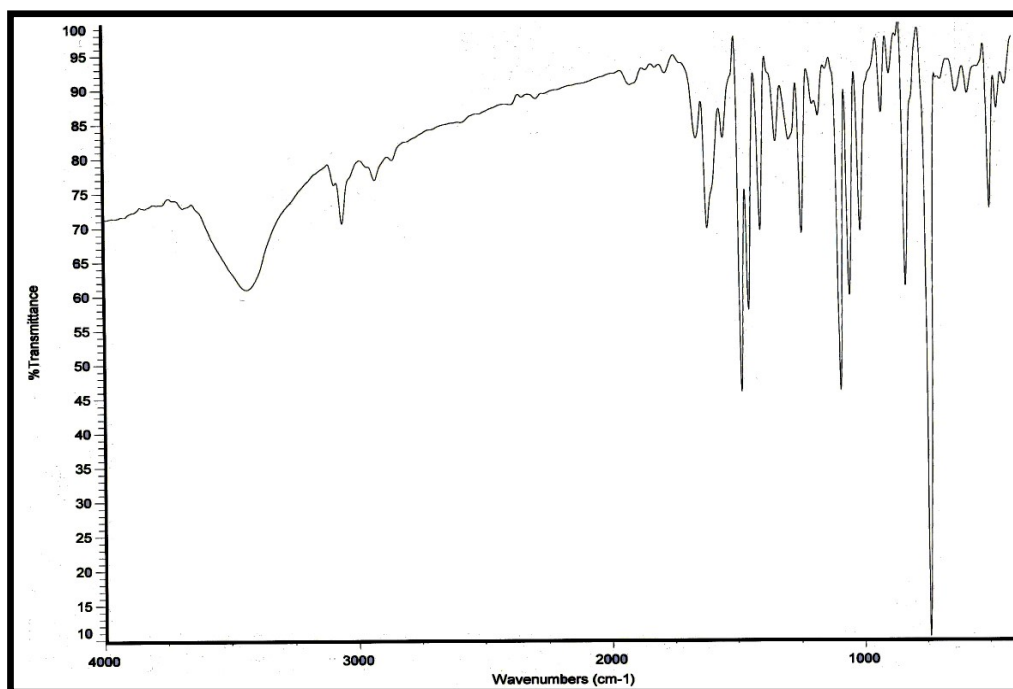


Figure S24. The FT-IR of 3j

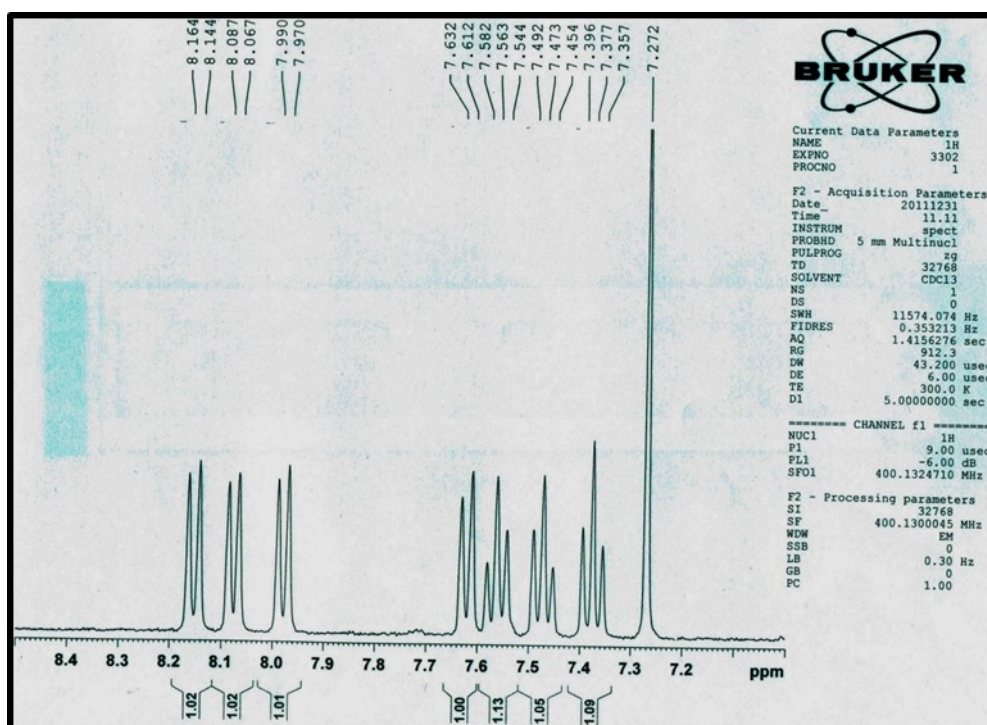


Figure S25. The ¹H NMR of 3j

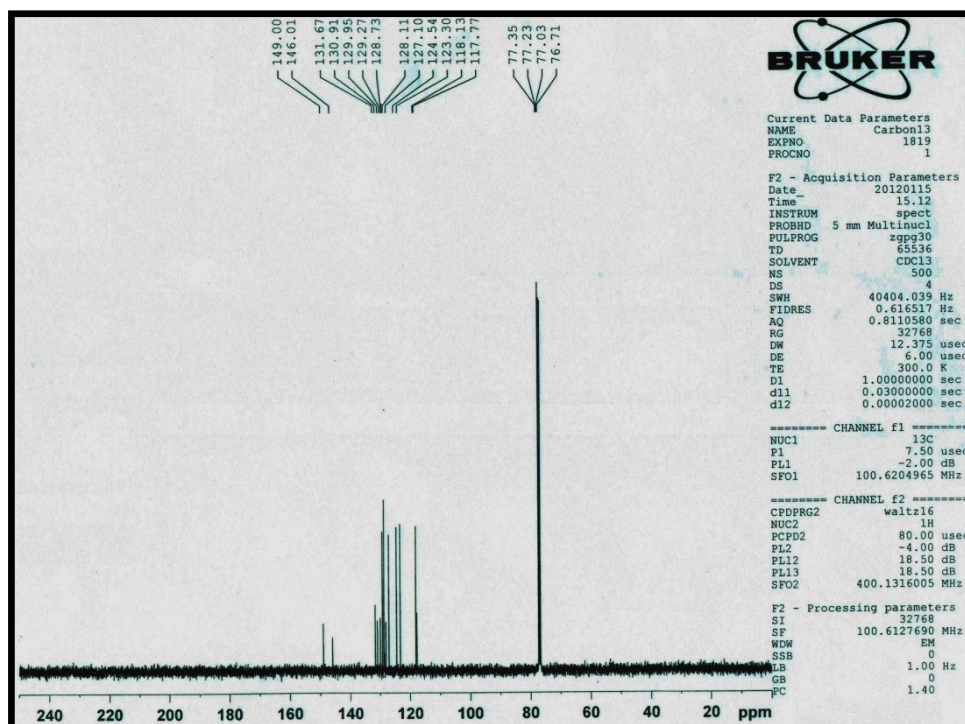


Figure S26. The ^{13}C NMR of **3j**

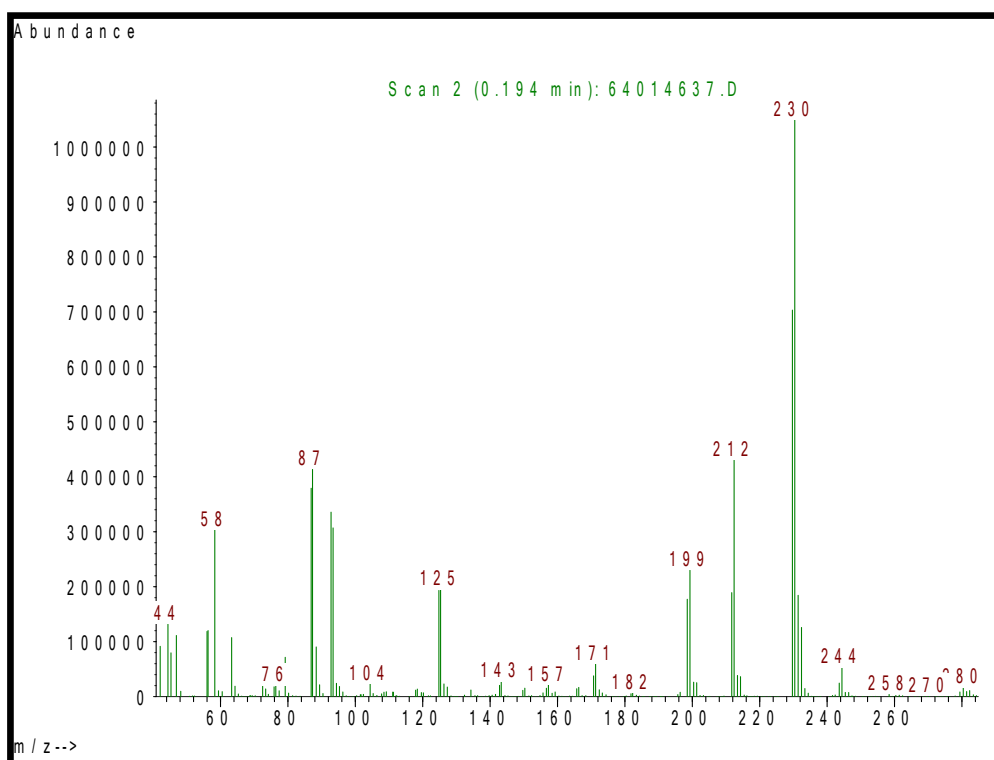


Figure S27: The MS of **3j**

2-(2,4-Dichlorophenyl)-benzothiazole (3k): Yellow solid; $m.p_{\text{rep.}} = 142\text{-}144\text{ }^{\circ}\text{C}$:
 $m.p_{\text{rep.}} = 140\text{-}143\text{ }^{\circ}\text{C}$ ³⁵; IR (KBr, ν , cm^{-1}): 3427, 3054, 1620, 1582, 1480, 752; ^1H
NMR (400 MHz, CDCl_3)/ δ (ppm): 8.26 (d, $J = 8.8$ Hz, 1H), 8.16 (d, $J = 8.0$ Hz,

1H), 7.97 (d, $J=8.0$ Hz, 1H), 7.57 (d, $J=2.0$ Hz, 1H), 7.54 (d, $J=7.2$ Hz, 1H), 7.46 (t, $J=8.0$ Hz, 1H), 7.42 (dd, $J=8.4$, 2 Hz, 1H).

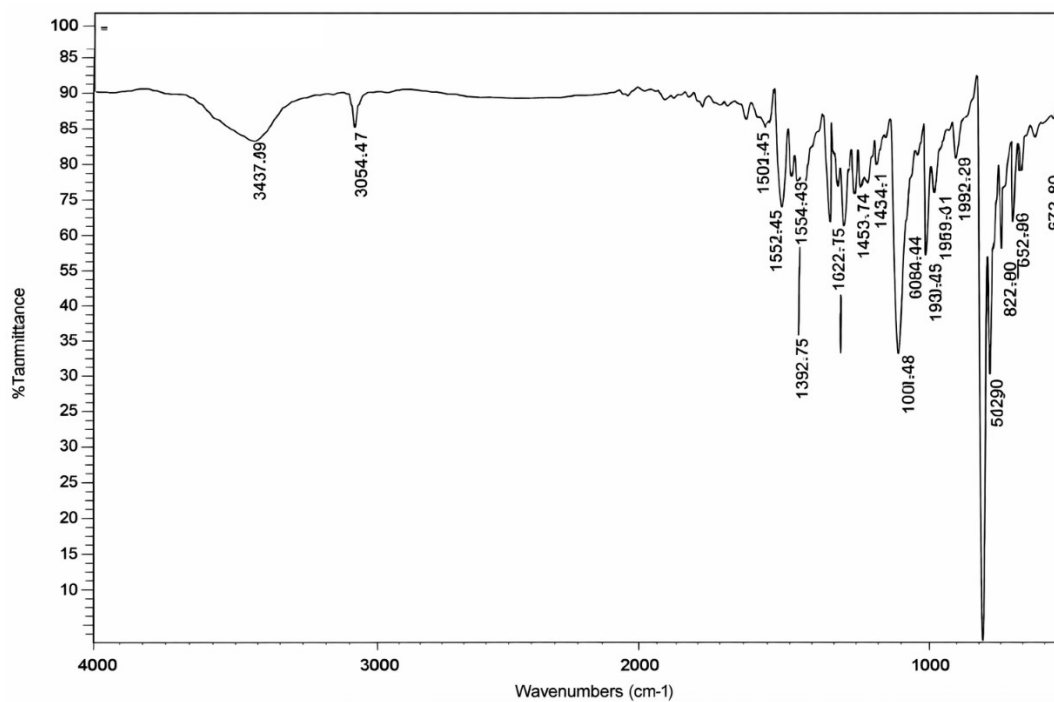


Figure S28. The FT-IR of **3k**

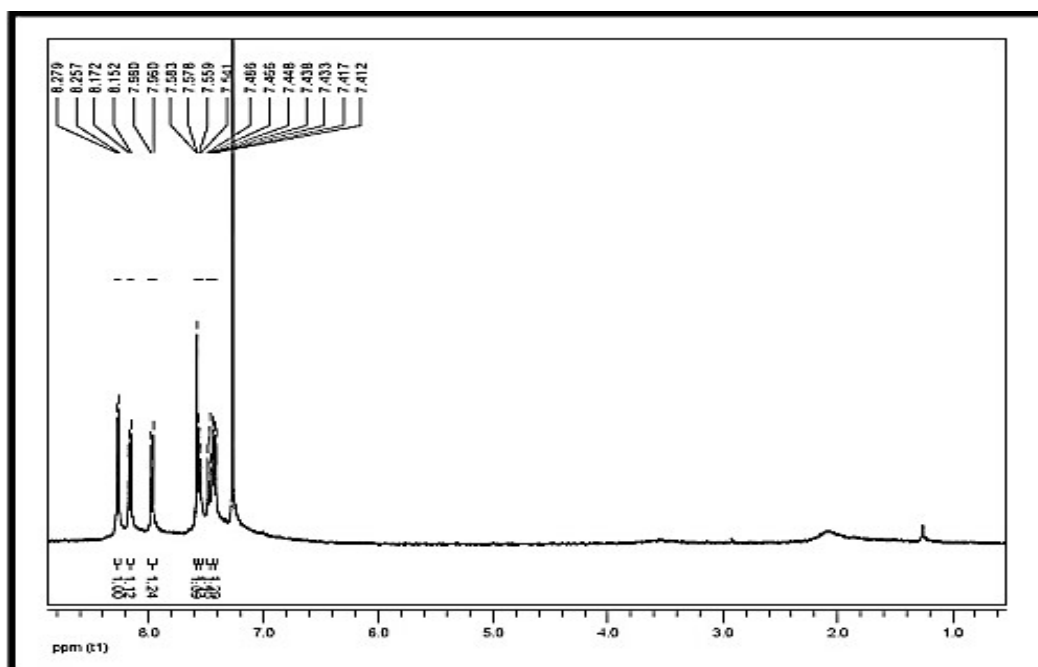


Figure S29. The ¹H NMR of **3k**

2-(4-N, N-Dimethylaminolphenyl)-benzothiazole (3I): Brown solid; m.p_{rep.}= 160-162 °C; m.p_{lit.}=160-162 °C³⁴; IR (KBr, ν , cm⁻¹): 3355, 2358, 1598, 1478, 1210, 1017, 965, 743; ¹H NMR (400 MHz, CDCl₃)/ δ ppm: 3.08 (s, 6H, -N(CH₃)₂) 6.77-6.79 (d, 2H, J=8.0 Hz, Ar-H) 7.27-7.31 (m, 2H, Ar-H) 7.52-7.54 (d, 1H, J=8.2 Hz, Ar-H) 7.70 (d, 1H, J=8.2 Hz, Ar-H) 8.11-8.13 (d, 2H, J=8.0Hz, Ar-H).

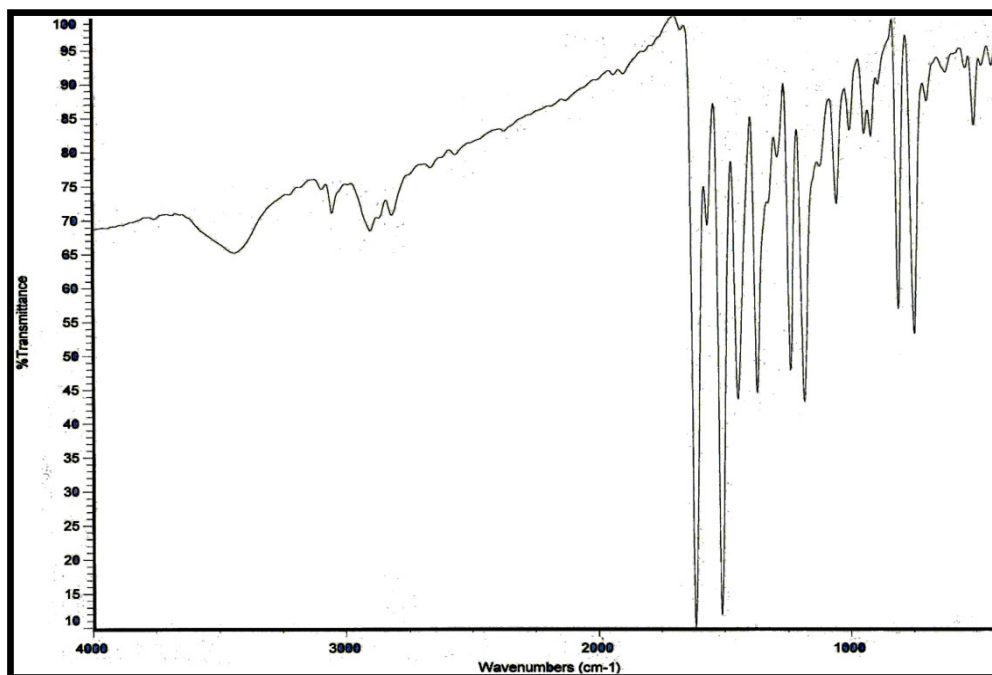


Figure S30. The FT-IR of 3I

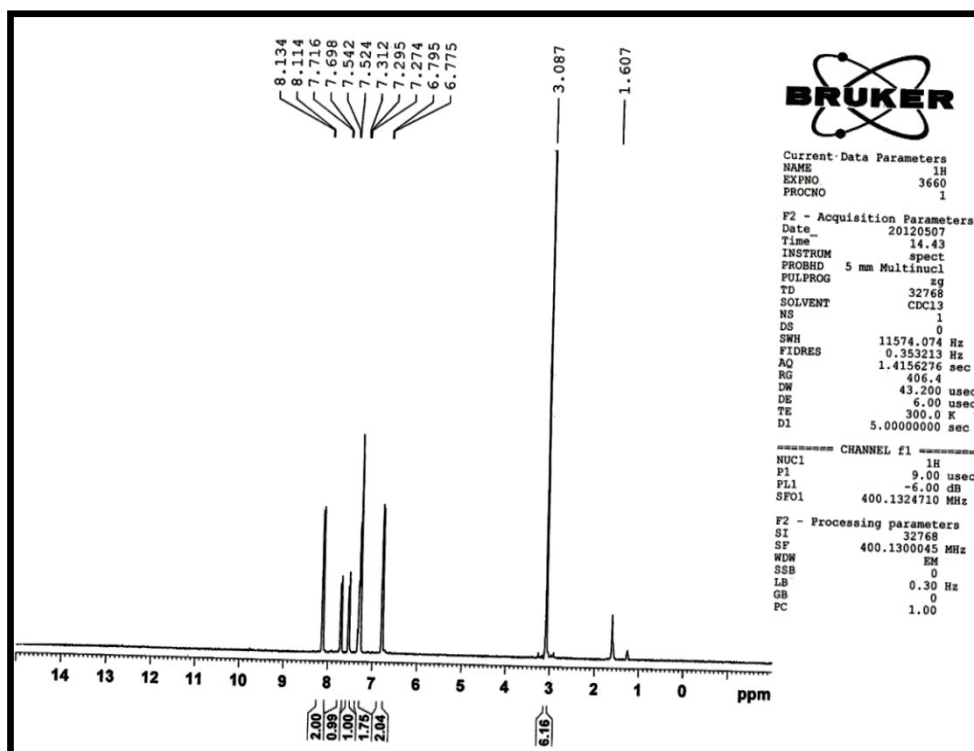


Figure S31. The ^1H NMR of **31**