Supplementary Information:

Facile One-pot Synthesis of 2-Arylbenzothiazoles Catalyzed by $\text{H}_3\text{PO}_4/\text{TiO}_2\text{-ZrO}_2$ (1/1) under Solvent-free Conditions

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EXPERIMENTAL

Materials and Methods

Chemicals were purchased from the Merck, Fluka and Aldrich Chemical Companies in high purity. All of the materials were of commercial reagent grade. The aromatic aldehydes and *o*-aminothiophenol were purified by standard procedures.

The FT-IR spectra were obtained with potassium bromide pellets in the range 400-4000 cm^{-1} with a Perkin Elmer 550 spectrometer. Melting points were determined in open capillaries using an Electro thermal MK₃ apparatus and are uncorrected. The SEM image was recorded by a SERON (AIS-2100) scanning electron microscopy. All ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 MHz. The NMR spectra were obtained in CDCl_3 solutions and are reported as parts per million (ppm) downfield from tetramethylsilane (TMS) as internal standard. The abbreviations used are: singlet(s), doublet (d), triplet (t) and multiplet (m). Mass spectra were recorded on an Agilent Technology (HP) MS Model: 5973 Network Mass Selective Detector, instrument by Electron Impact (EI) Ionization mode with an ionization voltage of 70 eV. The completion of the reaction was monitored by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company).

General procedure for preparation of the catalyst

$\text{TiO}_2\text{-ZrO}_2$ (1/1) was used as the support, which was prepared by the sol-gel method^[31, 32]. Zirconium (IV)isopropoxide (70%wt. solution in 2-propanol) andtitanium (IV) *n*-butoxide (99%) were used as the precursors,and 2, 4-pentandione (H-acac) as the complexingagent. Appropriate amounts of zirconium propoxideand titanium n-butoxide were dissolved in

the solvent, *n*-butanol. The solution was heated to 60 °C. The components were thoroughly mixed. Then the solution was cooled down to room temperature, and H-acac as the complexing agent was added. Then the clear solution was hydrolyzed with deionized water containing cetylpyridinium bromide (CPB) surfactant (mol surfactant/mol alkoxide = 0.1). The solutions were left overnight to hydrolyze the alkoxides, yielding transparent gels. The transparent gels were dried at 110 °C to remove water and solvent, and then calcined at 500 °C for 5 h to remove the organics. The support was denoted as ZrO₂-TiO₂ (1/1)-CPB. Then a series of catalysts with varying H₃PO₄ contents were prepared by impregnating calculated amounts of H₃PO₄ dissolved in deionized water on the TiO₂-ZrO₂ (1/1)-CPB support. The impregnated catalysts were dried at 110 °C for 12 h and then calcined in air at 500 °C for 6 h.^[30, 33]

General procedure for the synthesis of 2-arylbenzothiazoles catalyzed by H₃PO₄/TiO₂-ZrO₂ (1/1)

A mixture of 2-aminothiophenol (1 mmol, 0.995 g), aldehyde (1 mmol) and nano H₃PO₄-TiO₂-ZrO₂ (1/1) (40 mg, 30 wt% H₃PO₄) were added in a beaker and the reaction mixture was mixed properly with the help of glass rod under solvent-free condition at room temperature. The progress of the reaction was monitored by TLC (ethyl acetate:hexane, 4:6). After completion of the reaction, the reaction mixture was dispersed in ethyl acetate (5 mL), filtered and the catalyst was washed several times with ethyl acetate and acetone. Then, the filtrate was evaporated under reduced pressure to isolate a solid residue, and recrystallized from hot ethanol (10 mL) to afford the corresponding products. All of the 2-arylbenzothiazole products were characterized by IR, ¹H NMR, ¹³C NMR and Mass spectroscopy and identified by comparison of their physical and spectral data with those of authentic samples.^[34, 35]

2-Phenyl-benzothiazole. White solid; m.p.= 110-112 °C (m.p.= 111-112 °C) ^[34]; IR (KBr)/ $\nu(\text{cm}^{-1})$: 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) 7.25 (t, 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); ¹³C NMR/ (100 MHz, CDCl₃)/ δ ppm: 121.5, 123.4, 125.1, 126.4, 127.6, 128.9, 130.8, 133.9, 135.1, 155.1, 168.0; 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).

2-(2-Hydroxyphenyl)-benzothiazole. Yellow solid; m.p.= 127-128 °C (m.p.= 126-128 °C) ^[34]; IR (KBr)/ $\nu(\text{cm}^{-1})$: 3285, 3090, 2900, 1619, 1590, 1490, 1423, 874, 751; ¹H NMR (400 MHz, CDCl₃)/ δ ppm: 6.95-6.99 (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); ¹³C NMR/ (100 MHz, CDCl₃)/ δ ppm: 116.8, 117.9, 119.5, 121.5, 122.2, 125.6, 126.7, 128.4, 132.6, 132.8, 151.8, 157.9, 169.4; 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).

2-(4-Metoxyphenyl)-benzothiazole. White solid; m.p.= 120-122 °C (m.p.= 120-122 °C) ^[35]; IR (KBr)/ $\nu(\text{cm}^{-1})$: 3021, 3048, 2837, 1609, 1590, 1483, 830; ¹H NMR (400 MHz, CDCl₃)/ δ ppm: 3.89 (s, 3H, OCH₃) 7.015 (d, 2H, J =10.0 Hz, Ar-H) 7.36 (t, 1H, J =8.0 Hz, Ar-H) 7.48 (t, 1H, J =8.0 Hz, Ar-H) 7.89 (d, 1H, J =8.0 Hz, Ar-H) 8.04-8.06 (d, 3H, J =10.0 Hz, Ar-H); ¹³C NMR/ (100 MHz, CDCl₃)/ δ ppm: 55.5, 114.4, 121.5, 122.8, 124.8, 126.2, 126.4, 129.1, 134.9, 154.2, 161.9, 167.9; 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).

2-(4-Nitrophenyl)-benzothiazole. Yellow solid; m.p.= 227-229 °C (m.p.= 226-228 °C) ^[35]; IR (KBr)/ $\nu(\text{cm}^{-1})$: 3042, 2937, 1520, 1461, 1342, 1106, 851, 762; ¹H NMR (400 MHz, CDCl₃)/ 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); ¹³C NMR/ (100 MHz, DMSO) / δ ppm: 121.8, 123.9, 124.3, 126.2, 126.9, 128.2, 133.1, 135.4, 148.8, 154.0, 164.9.

2-(2,3-Dichlorophenyl)-benzothiazole. White solid; m.p.= 118-120 °C (m.p.=119-121°C) ^[34]; IR (KBr)/ $\nu(\text{cm}^{-1})$: 3020, 2900, 1635, 1512, 1470, 1432, 1348, 780; ¹H NMR (400 MHz, CDCl₃)/ 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); ¹³C NMR/ (100 MHz, CDCl₃) / 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).

2-(2-Nitrophenyl)-benzothiazole. Brown solid; m.p.= 94-96 °C (m.p.= 95-97 °C) ^[34]; IR (KBr)/ $\nu(\text{cm}^{-1})$: 3033, 2930, 1545, 1466, 1349, 1111, 880, 851, 762; ¹H NMR (400 MHz, CDCl₃)/ δ ppm: 7.53-7.55 (m, 2H, Ar-H) 7.59 (d, 1H, $J=7.6$ Hz, Ar-H) 7.84-7.89 (m, 2H, Ar-H) 7.97-7.99 (m, 1H, Ar-H) 8.02-8.04 (d, 2H, $J=7.6$ Hz, Ar-H); ¹³C NMR/ (100 MHz, DMSO) / δ ppm: 120.8, 122.2, 124.3, 125.0, 126.0, 126.9, 128.9, 133.1, 136.1, 138.9, 143.8, 157.0, 164.1.

2-(3-Nitrophenyl)-benzothiazole. Colourless solid; m.p.=181-183 °C (m.p.=181-182 °C) ^[35]; IR (KBr)/ $\nu(\text{cm}^{-1})$: 3039, 2936, 1522, 1460, 1345, 1103, 1041, 851, 750; ¹H NMR (400 MHz, CDCl₃)/ δ ppm: 7.50-7.53 (m, 1H, Ar-H) 7.57-7.59 (m, 1H, Ar-H) 7.84-7.88 (m, 1H, Ar-H)

8.11-8.14 (m, 1H, Ar-H) 8.18-8.21 (m, 1H, Ar-H) 8.37-8.40 (m, 1H, Ar-H) 8.47-8.49 (m, 1H, Ar-H) 8.80 (s, 1H, Ar-H); ^{13}C NMR/ (100 MHz, DMSO) / δ ppm: 121.9, 122.4, 123.3, 125.2, 126.1, 126.8, 128.7, 131.1, 133.6, 134.4, 147.8, 153.0, 162.2.

2-(4-Methylphenyl)-benzothiazole. White solid; m.p.= 82-84 °C (m.p.= 83-85 °C) ^[34]; IR (KBr)/ $\nu(\text{cm}^{-1})$: 3024, 2905, 1610, 1519, 1480, 1435, 1383, 1312, 821, 759; ^1H NMR (400 MHz, CDCl_3)/ δ ppm: 2.45 (s, 3H, CH_3) 7.34-7.36 (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); ^{13}C NMR/ (100 MHz, CDCl_3) / δ ppm: 23.6, 110.4, 120.3, 121.8, 123.3, 128.6, 132.7, 143.1, 155.6, 160.8, 165.1.

2-(4-Chlorophenyl)-benzothiazole. Yellow solid; m.p.= 114-116 °C (m.p.= 116-118 °C) ^[35]; IR (KBr)/ $\nu(\text{cm}^{-1})$: 3055, 2358, 1560, 1455, 1430, 1317, 1275, 1060, 965, 750, 725; ^1H NMR (400 MHz, CDCl_3)/ 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); ^{13}C NMR/ (100 MHz, CDCl_3) / δ ppm: 121.8, 123.1, 125.2, 126.8, 129.1, 129.8, 132.7, 135.2, 137.1, 154.4, 166.2.

2-(4-N, N-Dimethylphenyl)-benzothiazole. Brown solid; m.p.= 160-162 °C (m.p.=160-162 °C) ^[34]; IR (KBr)/ $\nu(\text{cm}^{-1})$: 3355, 2358, 1598, 1478, 1210, 1017, 965, 743; ^1H NMR (400 MHz, CDCl_3)/ δ ppm: 3.08 (s, 6H, $-\text{N}(\text{CH}_3)_2$) 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, $J=8.0$ Hz, Ar-H); ^{13}C NMR/ (100 MHz, CDCl_3) / δ ppm: 39.8, 111.1, 121.1, 122.0, 124.1, 126.8, 128.7, 135.2, 152.1, 154.4, 168.2.

2-(2-Chlorophenyl)-benzothiazole. Colorless solid; m.p.= 72-74 °C (m.p.=72-74 °C) ^[35]; IR (KBr)/ $\nu(\text{cm}^{-1})$: 2955, 1538, 1502, 1421, 1242, 1117, 965, 750, 733; ^1H NMR (400 MHz,

CDCl₃)/ δ ppm: 7.38-7.49 (m, 4H, Ar-H) 7.58-7.60 (m, 1H, Ar-H) 7.63-7.65 (m, 1H, Ar-H) 7.66-7.68 (m, 1H, Ar-H) 8.15-8.18 (m, 1H, Ar-H); ¹³C NMR/ (100 MHz, CDCl₃) / δ ppm: 111.8, 123.1, 124.2, 125.8, 128.2, 129.9, 131.7, 134.2, 137.1, 143.5, 154.4, 162.2.

2-(2-Methylphenyl)-benzothiazole. Yellow solid; m.p.= 53-55 °C (m.p.= 54-56 °C) ^[34]; IR (KBr)/ ν (cm⁻¹): 3040, 2980, 1598, 1550, 1451, 1244, 1115, 862, 754; ¹H NMR (400 MHz, CDCl₃)/ δ ppm: 2.47 (s, 3H, CH₃) 7.35-7.37 (m, 3H, Ar-H) 7.41-7.45 (t, 1H, *J*=8.0Hz, Ar-H) 7.58-7.60 (m, 1H, Ar-H) 7.77-7.79 (m, 1H, Ar-H) 8.05-8.07 (d, 1H, *J*=8.0Hz, Ar-H) 8.08 (d, 1H, *J*=8.0Hz, Ar-H); ¹³C NMR/ (100 MHz, CDCl₃) / δ ppm: 22.6, 112.1, 119.4, 120.5, 122.3, 126.2, 130.7, 144.1, 152.7, 159.9, 162.2.

Spectroscopic data:

IR (KBr)/ $\nu(\text{cm}^{-1})$:of 2-(2-Hydroxyphenyl)-benzothiazole

¹H NMR (400 MHz, CDCl₃) of 2-(2-Hydroxyphenyl)-benzothiazole

¹H NMR (400 MHz, CDCl₃) of 2-(2-Hydroxyphenyl)-benzothiazole

¹³C NMR/ (100 MHz, CDCl₃) of 2-(2-Hydroxyphenyl)-benzothiazole

Mass spectra of 2-(2-Hydroxyphenyl)-benzothiazole

IR (KBr)/ $\nu(\text{cm}^{-1})$:of 2-phenyl-benzothiazole

¹H NMR (400 MHz, CDCl₃) of 2-phenyl-benzothiazole

¹H NMR (400 MHz, CDCl₃) of 2-phenyl-benzothiazole

¹³C NMR/ (100 MHz, CDCl₃) of 2-phenyl-benzothiazole

Mass spectra of 2-phenyl-benzothiazole

IR (KBr)/ $\nu(\text{cm}^{-1})$: of 2-(4-Methoxyphenyl)-benzothiazole

¹H NMR (400 MHz, CDCl₃) of 2-(4-Methoxyphenyl)-benzothiazole

¹³C NMR/ (100 MHz, CDCl₃) of 2-(4-Metoxyphenyl)-benzothiazole

Mass spectra of 2-(4-Methoxyphenyl)-benzothiazole

¹H NMR (400 MHz, CDCl₃) of 2-(4-Nitrophenyl)-benzothiazole

¹H NMR (400 MHz, CDCl₃) of 2-(4-Nitrophenyl)-benzothiazole

¹H NMR (400 MHz, CDCl₃) of 2-(4-Methylphenyl)-benzothiazole

¹H NMR (400 MHz, CDCl₃) of 2-(4-chlorophenyl)-benzothiazole

IR (KBr)/ $\nu(\text{cm}^{-1})$:of 2-(2,3-diChlorophenyl)-benzothiazole

¹H NMR (400 MHz, CDCl₃) of 2-(2,3-diChlorophenyl)-benzothiazole

¹H NMR (400 MHz, CDCl₃) of 2-(2,3-diChlorophenyl)-benzothiazole

¹³C NMR/ (100 MHz, CDCl₃) of 2-(2,3-diChlorophenyl)-benzothiazole

¹³C NMR/ (100 MHz, CDCl₃) of 2-(2,3-diChlorophenyl)-benzothiazole

Mass spectra of 2-(2,3-diChlorophenyl)-benzothiazole

¹H NMR (400 MHz, CDCl₃) of 2-(2-Nitrophenyl)-benzothiazole

¹H NMR (400 MHz, CDCl₃) of 2-(3-Nitrophenyl)-benzothiazole

¹H NMR (400 MHz, CDCl₃) of 2-(3-Nitrophenyl)-benzothiazole

IR (KBr)/ $\nu(\text{cm}^{-1})$: of 2-(4-N, N-Dimethylphenyl)-benzothiazole

¹H NMR (400 MHz, CDCl₃) of 2-(4-N, N-Dimethylphenyl)-benzothiazole