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Eco-friendly synthesis of 2-substituted benzothiazoles catalyzed by silica sulfuric acid

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Abstract 2-Substituted benzothiazoles have been synthesized via one-pot reaction from aromatic aldehydes and *o*-aminothiophenol catalyzed by silica sulfuric acid in absolute methanol at room temperature. The remarkable advantages offered by this method are an environmentally friendly and reusable catalyst, a simple procedure, mild conditions, short reaction times, and good to excellent yields of products.

Keywords Benzothiazoles · *o*-Aminothiophenol · Aldehydes · Silica sulfuric acid

Introduction

Benzothiazole and their derivatives are often found in heterocyclic compounds, which exhibit a variety of biological activities [1, 2], such as a cathepsin S inhibitor [3], an HIV reverse transcriptase inhibitor [4], an anticancer agent [5], and an orexin-1 receptor antagonist [6]. They can also be used in industry as antioxidants, vulcanization accelerators, and as a dopant in light-emitting organic electroluminescent devices [7–9]. Because of their importance, the synthesis of substituted benzothiazoles has become a focus of synthetic organic chemistry. A number of methods have been reported for the synthesis of benzothiazoles. One of the classic methods for the synthesis of 2-aryl benzothiazoles is the condensation of *o*-aminothiophenol with substituted nitriles [10], carboxylic acids [11–15], acyl chlorides [16, 17], and esters [18]. Subsequently, because of the availability of a

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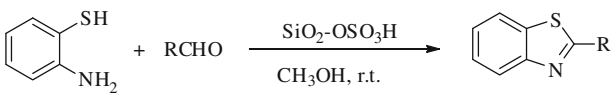
vast number of aldehydes, several improved protocols have been developed for the synthesis of benzothiazoles via the condensation of *o*-aminothiophenol with aldehydes. Various oxidative reagents, such as 4-methoxy-TEMPO [19], cetyltrimethyl ammonium bromide [20], $KAl(SO_4)_2{\cdot}12H_2O$ [21], H_2O_2/CAN [22], H_2O_2/HCl [23], NaOAc [24], poly[4-diacetoxyiodo] styrene [25], $Sc(OTf)_3$ [26], trichloroisocyanuric acid [27], I_2 [28], $HClO_4$/PANI [29], silica gel [30], PTSA [31], activated carbon-molecular oxygen [32], ionic liquid [33], Bakers' yeast [34], SDS [35], glucose oxidase–peroxidase [36], P_2O_5 [37], Dowex 50W [38], $Fe(HSO_4)_3$ [39], etc., have all been used as oxidants in the reaction. However, many of these methodologies are associated with one or more disadvantages such as expensive reagents, drastic reaction conditions, low yields, tedious work-up procedures, and co-occurrence of several side reactions. Therefore, a more effective and environmentally friendly process is needed.

Recently, silica sulfuric acid has attracted a great deal of attention due to its unique properties and potential applications in organic synthesis. It is a good proton source in terms of convenience, cheapness, easy production, insolubility to all organic solvents and can be selected as an excellent candidate for sulfuric acid or chlorosulfonic acid replacement in organic reactions [40]. As reported in previous papers, silica sulfuric acid has been used as an efficient catalyst in a number of organic reactions with the advantage that it is reusable and has minimal environmental impact [41–46]. Considering the above points and in continuation of our work on the synthesis of heterocyclic compounds [47, 48], we report here a green, mild, and practical method for the synthesis of 2-substituted benzothiazoles from *o*-aminothiophenol and aldehydes at room temperature (Scheme 1).

Results and discussion

To examine the effect of reaction conditions on the synthesis of title compounds, the condensation of *o*-aminothiophenol (**1**) and benzaldehyde (**2a**) was selected as the model reaction. The results are summarized in Table 1.

In the studies regarding the effect of temperature and solvents, the above reaction was conducted in the presence of silica sulfuric acid with various solvents such as EtOH, $CH_3COOC_2H_5$, CH_2Cl_2, CH_3CN, THF, $CHCl_3$, and CH_3OH at room or reflux temperature. The results indicated that the solvents and temperature had a significant effect on the product yield (Table 1). In general, non-polar solvents such as ethyl acetate afforded low yields either at room or reflux temperature. The best conversion was observed when the reaction was performed in CH_3OH at room temperature. The yield of 2-phenylbenzothiazole (**3a**) was 85.2 % at rt (Entry 7)



1 **2(a-r)** **3(a-r)**

Scheme 1 Synthesis of 2-substituted benzothiazoles

Table 1 The effect of solvent and temperature on the synthesis of 2-phenylbenzothiazole (**3a**)

Entry	Solvent	Time (h)	Amount of catalyst (mg)	Isolated yield (%)	
				A	B
1	C_2H_5OH	2	200	74.9	73.9
2	$CH_3COOC_2H_5$	2	200	73.7	60.1
3	CH_3CN	2	200	84.6	67.5
4	CH_2Cl_2	2	200	77.4	77.9
5	THF	2	200	72.0	76.4
6	$CHCl_3$	2	200	63.9	81.8
7	CH_3OH	2	200	64.4	85.2
8	CH_3OH	2	150		75.6
9	CH_3OH	2	100		85.7
10	CH_3OH	2	50		68.2
11	CH_3OH	2	0		50.0
12	CH_3OH	2	200		75.9[a]
13	CH_3OH	2	100		73.5[b]

Reaction conditions: *o*-aminothiophenol (1.0 mmol), benzaldehyde (1.0 mmol), solvent (5 mL)

A reflux, *B* stirred at room temperature

[a] Under ultrasound

[b] Operated in nitrogen atmosphere

while at reflux temperature the reaction can be completed in 64.4 % yield (Entry 7) within the same reaction time. So, we chose room temperature as the reaction temperature. Moreover, we found that the yields were obviously affected by the amount of silica sulfuric acid. When 200, 150, 100, 50, and 0 mg of silica sulfuric acid were used, the yields were 85.2, 75.6, 85.7, 68.2, and 50.0 %, respectively (Table 1, Entries 7–11). Therefore, 100 mg silica sulfuric acid was sufficient; however, utilizing 200 mg of silica sulfuric acid did not significantly increase the yield. In addition, in the absence of catalyst, the reaction gave an unsatisfactory yield of 2-phenylbenzothiazole (**3a**) (Table 1, Entry 11). The above results showed that silica sulfuric acid was essential for high yield, and the best results were obtained when the reaction was carried out with 100 mg silica sulfuric acid at room temperature. We also observed the effect of ultrasound irradiation on the reaction. **3a** was obtained in 75.9 % yield under ultrasound irradiation at 25–30 °C (Table 1, Entry 12). When the reaction was run under a nitrogen atmosphere, 2-phenylbenzothiazole (**3a**) was obtained in 73.5 % yield (Table 1, Entry 13). These results suggest that oxygen played an oxidant role in this reaction.

Recyclability of the catalyst was also investigated. After completion of the reaction of *o*-aminothiophenol (**1**) and benzaldehyde (**2a**), the catalyst was separated by filtration, thoroughly washed with ethyl acetate, and dried at room temperature for 4 h. The recovered catalyst was then added to fresh substrates under the same experimental conditions for three runs, our observations revealing that as the number of the recycle of catalyst increases the activity decreases (Table 2).

Table 2 Synthesis of 2-phenylbenzothiazole (**3a**) with recovered catalyst

Cycle	Fresh	First	Second	Third
Yield (%)[a]	85.7	78.5	74.8	72.3

[a] Isolated yield

Under the optimized reaction conditions, a range of 2-substituted benzothiazoles **3a–r** was synthesized catalyzed by silica sulfuric acid at room temperature. The results are summarized in Table 3. Most products described here have been previously reported in the literature [11–39]. As shown in Table 3, the condensation of *o*-aminothiophenol with a series of aromatic aldehydes afforded 2-substituted benzothiazoles in excellent yields catalyzed by silica sulfuric acid in absolute methanol. The reaction proceeded very cleanly at room temperature and no undesirable side reactions were observed. Aromatic aldehydes bearing an electron-withdrawing functionality, such as a nitro group, showed obviously weaker reactivity than those containing electron-neutral or electron-donating groups. No corresponding product was obtained when the substrate was 2-nitrobenzaldehyde or 2,4-dinitrobenzaldehyde (Table 3, Entries 19, 20) in this experiment.

Table 3 The synthesis of 2-substituted benzothiazoles derivatives catalyzed by silica sulfuric acid

Entry	R	Product	Time (h)	Yield[a] (%)	mp (°C) [lit]
1	C_6H_5	**3a**	2.6	85.7	116–117 (112–114) [21]
2	2-ClC_6H_4	**3b**	4.2	73.8	81–83 (81–82) [1]
3	2-OHC_6H_4	**3c**	3.2	78.5	130–134 (129–131) [28]
4	2-$CH_3OC_6H_4$	**3d**	1.6	80.4	110–112 (120–122) [20]
5	4-ClC_6H_4	**3e**	1.8	76.8	116–120 (114–115) [21]
6	4-OHC_6H_4	**3f**	4.3	89.5	232–238 (231) [35]
7	4-$CH_3OC_6H_4$	**3g**	1.6	82.2	122–124 (121) [35]
8	4-$CH_3C_6H_4$	**3h**	2.3	89.2	82–86 (83) [21]
9	4-$(Me)_2NC_6H_3$	**3i**	0.7	73.8	184–186 (173) [35]
10	4-$NO_2C_6H_4$	**3j**	2.0	13.2	236–241 (231–232) [20]
11	3-ClC_6H_4	**3k**	2.7	82.8	97–100 (94–95) [29]
12	3-$NO_2C_6H_4$	**3l**	3.7	33.4	194–197 (185–186) [16]
13	4-OH-3-$MeOC_6H_3$	**3m**	2.3	79.8	180–183 (162–164) [38]
14	2-OH-3-$MeOC_6H_3$	**3n**	3.2	60.8	170–173 (162–163) [39]
15	3,4-$Cl_2C_6H_3$	**3o**	2.8	92.0	122–124 (118–120) [2]
16	2,4-$Cl_2C_6H_3$	**3p**	3.9	95.1	151–152 (144–145) [1]
17	3,4-$OCH_2OC_6H_3$	**3q**	2.0	81.9	126–128 (125–127) [20]
18	2-Furyl	**3r**	3.0	70.9	107–108 (106) [35]
19	2-$NO_2C_6H_4$	–	4.8[b]		
20	2,4-$(NO_2)_2C_6H_3$	–	5.0[b]		

[a] Isolated yield

[b] No reaction

According to the method catalyzed by 4-methoxy-TEMPO in presence of oxygen [19], the time and yield of **3a** were 9 h and 80 %, respectively, heating at 120 °C in xylene for the condensation of *o*-aminothiophenol and benzaldehyde, while the present procedure gave 85.7 % yield within 2 h (Table 3, Entry 1) at room temperature. In the reaction catalyzed by Bakers' yeast in DCM [34], **3h** was obtained in 67 % yield at room temperature for 24 h, whereas the present procedure afforded **3h** in 89.2 % yield within 2.3 h at room temperature (Table 3, Entry 8). Encouraged by these results, the condensation of furfuraldehyde (**2r**) and *o*-aminothiophenol (**1**) was also examined to extend the scope of this method, 2-(2-furanyl)benzothiazole (**3r**) was obtained in moderate yields(70.9 %) within 3.0 h (Table 3, Entry 18).

Conclusion

In conclusion, we have found an efficient and practical procedure for the preparation of 2-substituted benzothiazoles catalyzed by silica sulfuric acid at room temperature. Compared to the classical method, the remarkable advantages offered by this are milder conditions, shorter reaction times, higher yields, non-corrosive, non-polluting, and employing a reusable catalyst. The cheapness and availability of the reagents, and the simple procedure and work-up make this method attractive for large-scale operations.

Experimental

Apparatus, materials and measurements

All chemicals were obtained from commercial suppliers and were used without further purification, and melting points were uncorrected. Silica sulfuric acid was obtained according to the method reported in the literature [42]. The ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded on a Bruker AVANCE III 600 spectrometer using TMS as internal standard and DMSO-d_6 or $CDCl_3$ as solvent.

General procedure for synthesis of 2-substituted benzothiazoles

Aromatic aldehydes (**2**, 1.0 mmol) and *o*-aminothiophenol (**1**, 1.0 mmol) were dissolved in absolute methanol (5 mL) in a 25-mL round bottomed flask. Silica sulfuric acid (100 mg) was then added and the mixture was stirred in oil bath at room temperature for a period time as indicated in Tables 1, 2, and 3 (reaction was continued until aromatic aldehydes disappeared as indicated by TLC). The reactant was dissolved in ethyl acetate. The catalyst was removed by filtration and washed with ethyl acetate. The solvent was evaporated under reduced pressure. The crude product was subjected to column chromatography on silica gel (200–300 mesh) and eluted with petroleum ether or the mixture of petroleum ether and ethyl acetate.

All the products are known compounds and were identified by spectroscopic data (^{1}H NMR, ^{13}C NMR) and comparison of their physical properties (melt point) with the literature.

2-Phenylbenzothiazole (**3a**)

Light yellow crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 8.11–8.14 (m, 3H, ArH), 7.93 (d, $J = 8.0$ Hz, 1H, ArH), 7.51–7.54 (m, 4H, ArH), 7.42 (t, $J = 8.0$ Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 168.1, 154.2, 135.1, 133.6, 131.0, 129.0, 127.6, 126.34, 125.2, 123.3, 121.6.

2-(2-Chlorophenyl)benzothiazole (**3b**)

White crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 8.23–8.26 (m, 1H, ArH), 8.17 (d, $J = 8.1$ Hz, 1H, ArH), 7.98 (d, $J = 8.0$ Hz, 1H, ArH), 7.55–7.58 (m, 2H, ArH), 7.43–7.48 (m, 3H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 164.2, 152.5, 136.1, 132.8, 132.3, 131.8, 131.2, 130.8, 127.1, 126.3, 125.5, 123.5, 121.4.

2-(2-Hydroxyphenyl)benzothiazole (**3c**)

White crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 12.55 (s, 1H, OH), 8.00 (d, 1H, $J = 8.0$ Hz, ArH), 7.91 (d, 1H, $J = 7.9$ Hz, ArH), 7.71 (dd, 1H, $J_1 = 7.9$ Hz, $J_2 = 1.1$ Hz, ArH), 7.51–7.54 (m, 1H, ArH), 7.40–7.44 (m, 2H, ArH), 7.14 (dd, 1H, $J_1 = 8.3$ Hz, $J_2 = 0.8$ Hz, ArH), 6.97–6.99 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 169.4, 158.0, 151.9, 132.7, 132.6, 128.4, 126.7, 126.7, 125.5, 122.2, 121.5, 119.5, 117.9, 116.8.

2-(2-Methoxyphenyl)benzothiazole (**3d**)

Light yellow crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 8.58 (dd, 1H, $J_1 = 7.8$ Hz, $J_2 = 1.6$ Hz, ArH), 8.14 (d, $J = 8.2$ Hz, 1H, ArH), 7.96 (d, $J = 7.9$ Hz, 1H, ArH), 7.47–7.54 (m, 2H, ArH), 7.40 (t, $J = 7.3$ Hz, 1H, ArH), 7.17 (t, $J = 7.4$ Hz, 1H, ArH), 7.08 (d, $J = 8.3$ Hz, 1H, ArH), 4.07 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 163.1, 157.3, 152.2, 136.2, 131.8, 129.6, 125.9, 124.6, 122.8, 122.4, 121.2, 111.7, 55.7.

2-(4-Chlorophenyl)benzothiazole (**3e**)

White crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 8.09 (d, $J = 8.1$ Hz, 1H, ArH), 8.05 (d, $J = 8.5$ Hz, 2H, ArH), 7.92 (d, $J = 8.0$ Hz, 1H, ArH), 7.51–7.54 (m, 1H, ArH), 7.49 (d, 1H, $J = 8.6$ Hz, ArH), 7.41–7.44 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 166.6, 154.1, 137.1, 135.1, 132.1, 129.3, 128.7, 126.5, 125.4, 123.3, 121.7.

2-(4-Hydroxyphenyl)benzothiazole (**3f**)

Brown crystals, ^{1}H NMR (DMSO-d_6, 600 MHz): δ_H 10.25 (s, 1H, OH), 8.07 (d, $J = 7.9$ Hz, 1H, ArH), 7.98 (d, $J = 8.1$ Hz, 1H, ArH), 7.94 (d, $J = 8.5$ Hz, 2H, ArH), 7.49–7.51 (m, 1H, ArH), 7.39–7.41 (m, 1H, ArH), 6.94–6.96 (m, 2H, ArH); ^{13}C NMR (DMSO-d_6, 150 MHz): δ_C 167.9, 161.0, 160.8, 154.2, 134.6, 129.5, 126.9, 125.4, 124.6, 122.8, 122.6, 116.6, 116.5.

2-(4-Methoxyphenyl)benzothiazole (**3g**)

Light yellow crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 8.06–8.07 (m, 3H, ArH), 7.90 (d, $J = 8.0$ Hz, 1H, ArH), 7.48–7.51 (m, 1H, ArH), 7.37–7.39 (m, 1H, ArH), 7.02–7.03 (m, 2H, ArH), 3.91 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 167.9, 161.9, 154.2, 134.9, 129.1, 126.5, 126.2, 124.80, 122.8, 121.5, 114.4, 55.5.

2-(4-Methylphenyl)benzothiazole (**3h**)

White crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 8.10 (d, $J = 7.9$ Hz, 1H, ArH), 8.02 (d, $J = 8.2$ Hz, 2H, ArH), 7.91 (d, $J = 8.0$ Hz, 1H, ArH), 7.50–7.53 (m, 1H, ArH), 7.38–7.41 (m, 1H, ArH), 7.32 (d, $J = 7.9$ Hz, 2H, ArH), 2.45 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 168.3, 154.2, 141.5, 134.9, 131.0, 129.7, 127.5, 125.02, 126.3, 123.1, 121.6, 21.5.

2-(4-*N*,*N*-dimethylphenyl)benzothiazole (**3i**)

Light yellow crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 8.02 (d, 1H, $J = 8.0$ Hz, ArH), 7.98–8.00 (m, 2H, ArH), 7.86 (d, 1H, $J = 8.4$ Hz, ArH), 7.45–7.48 (m, 1H, ArH), 7.32–7.34 (m, 1H, ArH), 6.75–6.78 (m, 2H), 3.07 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 168.8, 154.4, 152.2, 134.6, 128.9, 126.0, 124.2, 122.3, 121.4, 111.7, 40.2.

2-(4-Nitrophenyl) benzothiazole (**3j**)

Yellow crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 8.38 (d, $J = 8.6$ Hz, 2H, ArH), 8.30 (d, $J = 8.7$ Hz, 2H, ArH), 8.16 (d, $J = 8.2$ Hz, 1H, ArH), 7.98 (d, $J = 7.9$ Hz, 1H, ArH), 7.58 (t, $J = 7.4$ Hz, 1H, ArH), 7.49 (t, $J = 7.4$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 164.8, 154.1, 149.1, 139.2, 135.5, 128.2, 126.9, 126.2, 124.3, 123.9, 121.8.

2-(3-Chlorophenyl)benzothiazole (**3k**)

White crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 8.14 (t, 1H, $J = 1.8$ Hz ArH), 8.11 (d, 1H, $J = 8.2$ Hz, ArH), 7.96–7.97 (m, 1H, ArH), 7.93 (d, 1H, $J = 8.4$ Hz, ArH), 7.52–7.55 (m, 1H, ArH), 7.47–7.49 (m, 1H, ArH), 7.42–7.45 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 166.3, 154.0, 135.3, 135.2, 135.1, 130.9, 130.2, 127.4, 126.5, 125.7, 125.6, 123.5, 121.7.

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

Light yellow crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 8.93 (s, 1H, ArH), 8.42 (d, $J = 7.7$ Hz, 1H, ArH), 8.34 (dd, 1H, $J_1 = 8.1$ Hz, $J_2 = 1.3$ Hz, ArH), 8.13 (d, $J = 8.2$ Hz, 1H, ArH), 7.96 (d, $J = 8.0$ Hz, 1H, ArH), 7.70 (t, $J = 7.9$ Hz, 1H, ArH), 7.56 (t, $J = 7.5$ Hz, 1H, ArH), 7.47 (t, $J = 7.6$ Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 164.9, 153.9, 148.8, 135.3, 135.2, 133.0, 130.1, 126.8, 126.0, 125.1, 123.7, 122.3, 121.8.

2-(3-Methoxy-4-hydroxyphenyl)benzothiazole (**3m**)

Brown crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 9.85 (s, 1H, OH), 8.06 (d, $J = 8.2$ Hz, 1H, ArH), 7.89 (d, $J = 7.9$ Hz, 1H, ArH), 7.75 (d, $J = 1.8$ Hz, 1H, ArH), 7.56 (dd, 1H, $J_1 = 8.2$ Hz, $J_2 = 1.9$ Hz, ArH), 7.48–7.51 (m,1H, ArH), 7.37–7.39 (m, 1H, ArH), 7.03 (d, $J = 8.2$ Hz, 1H, ArH), 4.00 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 168.2, 154.0, 148.6, 147.0, 134.8, 126.3, 126.2, 124.9, 122.7, 122.0, 121.5, 114.8, 109.3, 56.2.

2-(2-Hydroxy-4-methoxyphenyl)benzothiazole (**3n**)

Brown crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 9.85 (s, 1H, OH), 8.06 (d, $J = 8.1$ Hz, 1H, ArH), 7.89 (d, $J = 7.9$ Hz, 1H, ArH), 7.75 (d, $J = 1.4$ Hz, 1H, ArH), 7.56 (dd, 1H, $J_1 = 8.2$ Hz, $J_2 = 1.7$ Hz, ArH), 7.49 (t, $J = 7.6$ Hz, 1H, ArH), 7.38 (t, $J = 7.6$ Hz, 1H, ArH), 7.03 (d, $J = 8.2$ Hz, 1H, ArH), 3.99 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 168.2, 154.0, 148.6, 147.0, 134.8, 126.3, 126.2, 124.9, 122.7, 122.0, 121.5, 114.8, 109.3, 56.2.

2-(3,4-Dichlorophenyl)benzothiazole (**3o**)

White crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 8.23 (d, $J = 2.1$ Hz, 1H, ArH), 8.09 (d, $J = 8.2$ Hz, 1H, ArH), 7.93(d, $J = 7.9$ Hz, 1H, ArH), 7.90 (dd, 1H, $J_1 = 8.3$ Hz, $J_2 = 2.0$ Hz, ArH), 7.57 (d, $J = 8.3$ Hz, 1H, ArH), 7.52–7.55 (m, 1H, ArH), 7.43–7.45 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 165.0, 154.0, 135.1, 133.5, 131.0, 129.0, 126.7, 126.5, 125.7, 123.5, 121.7.

2-(2,4-Dichlorophenyl)benzothiazole (**3p**)

White crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 8.26 (d, $J = 8.5$ Hz, 1H, ArH), 8.15 (d, $J = 8.2$ Hz, 1H, ArH), 7.97 (d, $J = 8.0$ Hz, 1H, ArH), 7.55–7.58 (m, 2H, ArH), 7.45–7.48 (m, 1H, ArH), 7.42 (dd, 1H, $J_1 = 8.5$ Hz, $J_2 = 2.0$ Hz, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 163.0, 152.4, 136.6, 136.1, 133.3, 132.5, 130.8, 130.6, 127.6, 126.5, 125.7, 123.5, 121.4.

2-(3′,4′-Methylenedioxyphenyl)benzothiazole (**3q**)

Light yellow crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 8.05 (d, $J = 8.1$ Hz, 1H, ArH), 7.88 (d, $J = 7.9$ Hz, 1H, ArH), 7.61–7.64 (m, 2H, ArH), 7.48–7.51 (m, 1H, ArH), 7.37–7.40 (m, 1H, ArH), 6.92 (d, $J = 8.0$ Hz, 1H, ArH), 6.07 (s, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 167.6, 154.0, 150.1, 148.4, 134.8, 128.0, 126.3, 125.0, 122.9, 122.5, 121.5, 108.7, 107.5, 101.7.

2-(2-Furanyl)benzothiazole (**3r**)

Brown crystals, ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 8.08 (d, $J = 8.2$ Hz, 1H, ArH), 7.90 (d, $J = 7.9$ Hz, 1H, ArH), 7.62 (s, 1H, FuranH), 7.51 (t, $J = 7.3$ Hz, 1H, ArH), 7.40 (t, $J = 7.3$ Hz, 1H, ArH), 7.22 (d, $J = 2.8$ Hz, 1H, FuranH), 6.61 (d, $J = 1.5$ Hz, 1H, FuranH); ^{13}C NMR ($CDCl_3$, 150 MHz): δ_C 157.6, 153.7, 148.8, 144.7, 134.3, 126.5, 125.2, 123.1, 121.6, 112.5, 111.5.

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