Article

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Titanium Tetrabutoxide (TTBO) as Efficient Catalyst for Rapid One Pot Synthesis of 2-Arylbenzothiazoles under Mild Conditions

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An effective strategy has been developed for rapid and efficient one pot synthesis of 2-arylbenzothiazoles from readily available 2-aminothiophenol and aromatic aldehydes catalyzed by TTBO in high yields and short reaction times. This strategy allows access to a structurally diverse array of products for further manipulation. The reactions were preceded under mild conditions to afford 2-arylbenzothiazole derivatives. The pure products were identified and characterized by physical and spectroscopic data such as; IR, ^{1}H NMR and ^{13}C NMR.

Keywords: Titanium tetrabutoxide; 2-Arylbenzothiazoles; Lewis acid; 2-Aminothiophenol; Synthesis; Catalyst.

INTRODUCTION

Benzothiazole is a heterocyclic compound, weak base, having varied biological activities and still of great scientific interest now a days. They are widely found in bioorganic and medicinal chemistry with application in drug discovery. Benzothiazoles are known to inhibit several enzymes such as acetyl cholinesterase,[1] mon-amine oxidase,[2,3] lipoxygenase, lysophosphatidic acid acyltransferase-β,[4] aldose reductase, cyclooxygenase,[5] carbonic anhydrase, HCV helicase, and protease.[6] Other recognized pharmacological activities of benzothiazoles include antitumor,[7] antimicrobial, antioxidant and antiglutamate.[8] Various benzothiazoles such as 2-arylbenzothiazole received much attention due to unique structure and its uses as radioactive amyloid imagining agents[9] and anticancer agents.[10] The most useful synthesis of benzothiazoles include condensation of 2-aminobenzenethiol with carboxyl derivatives,[11] cyclization of ortho-haloanilides,[12] the radical cyclization of thioacylbenzanilides,[13] DMP mediated intramolecular cyclization of thioformanilides.[14] The direct condensation of 2-aminothiophenol with aromatic aldehyde[15,16] under microwave irradiation[17] in the presence of various catalysts such as $MnSiO_2$, *P*-TsOH or graphite supported on solid minerals I_2/DMF, 1-phenyl-3-methylimidazolium bromide[PmIm]Br, O_2 or H_2O_2 in the presence of $Sc(OTf)_3$, cerium(IV) ammonium nitrate(CAN). Despite their potential utility, some of these methods are not environmentally friendly and suffer from one or more disadvantages for example hazardous reaction conditions, complex work-up and purification, strongly acidic conditions, high temperatures, use of toxic metal catalysts and long reaction times. Therefore, in the development of facile and mild general method to overcome these short comings remains a challenge for organic chemists in the synthesis of 2-arylbenzothiazoles.[18-27]

In this study, in continuation of our interest on the synthesis of 2-arylbenzothiazoles, we decided to explore ability of Lewis acids as suitable catalysts for synthesis of significant and benefit 2-arylbenzothiazoles. Therefore, a number of different Lewis acids was used for synthesis of 2-arylbenzothiazoles through condensation reaction of 2-aminothiophenol with aromatic aldehydes under mild conditions.

RESULTS AND DISCUSSION

A number of methods are reported for the synthesis of heterocyclic compounds by using different catalysts. In this research, in order to the development of novel synthetic methodologies using Lewis acids as catalyst, we have found that TTBO can be efficient catalyst for synthesis of 2-arylbenzothiazoles from 2-aminothiophenol and aldehydes in excellent yields under mild conditions (Scheme 1).

To achieve the best results in terms of yields and reaction times we examined the efficiency of different reaction media and catalyst amounts in condensation reaction of 4-nitrobenzaldehyde with 2-aminothiophenol as a reaction model in ethanol solution. In order to find the optimum re-

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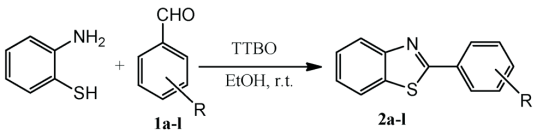
Scheme 1 Synthesis of benzothiazole derivatives from 2-aminothiophenol and aldehydes



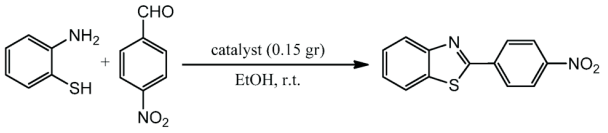
action conditions for the condensation reaction, preliminary efforts were mainly focused on the evaluation of different Lewis acids. So a number of different Lewis acids was examined on the model reaction, the results are shown in Table 1. As can be seen in this Table, when the reaction was carried out in the presence of TTBO as catalyst, the products were obtained in excellent yields and very short reaction times, while, the reaction using the other catalysts were occurred in lower yields and longer reaction times (Table 1, entry 12 *vs* entries 1-11).

In according to the Table 1, the results related to different Lewis acids were indicated that TTBO as catalyst plays a critical role in this reaction and was highly effective catalyst for condensation reaction of different aldehydes with 2-aminothiophenol. Thus, TTBO was used as the preferred catalyst for further studies. The catalytic role of TTBO can be chelating the oxygen of carbonyl group by Ti, and also acting as a base to generate the thiolate anion that let to release the nucleophilisity of sulfur atom. So the effect of catalyst amount on this reaction was studied in Table 2. Also, it was found that with increase the amount of TTBO, yield of the desired 2-arylbenzothiazole increased. Hence 6.6 mol% of TTBO catalyst was chosen as the optimum concentration of catalyst in this reaction. The results are shown in Table 2.

After the optimization of TTBO amount as catalyst, to demonstrate the generality and scope of this method, it was examined the condensation reaction with a number of different aldehydes and 2-aminothiophenol at room temperature. The results of these reactions are summarized in Table 3.

As it is shown in Table 3, the yields of aldehydes with EWG groups like *p*-NO_2 (entry 9) is more than the aldehydes with EDG groups like *o*-Me (entry 4). Certain atoms or groups of atoms can add or withdrawal electron density to a system. Electron withdrawing groups (EWG) remove electron density from a system and tend to stabilize anions or electron rich structures and electron donating groups (EDG) add electron density to a system and tend to stabilize

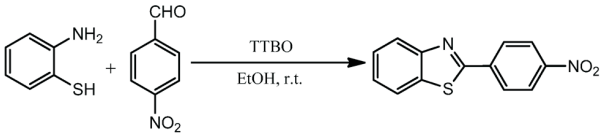
Table 1. Effect of various Lewis acids on the reaction of 4-nitrobenzaldehyde with 2-aminothiophenol



Entry	Catalyst	Time (min)	Yield[a] (%)
1	$AlCl_3$	15	48
2	$FeCl_3$	20	7
3	$Cu(OAc)_2.2H_2O$	20	25
4	$Zn(OAc)_2$	15	30
5	Al_2O_3	25	30
6[b]	SSA	10	80
7	Nano TiO_2	20	10
8	$BF_3(Et_2O)$	15	70
9	Nano SiO_2	25	40
10	SiO_2	25	15
11	P_2O_5/SiO_2	15	65
12[c]	TTBO	Immed.	90

[a] Isolated yield.
[b] Silica sulfuric acid.
[c] Titanium tetrabutoxide.

Table 2. Effect of TTBO[a] as Lewis acid catalyst on the reaction of 4-nitrobenzaldehyde with 2-aminothiophenol



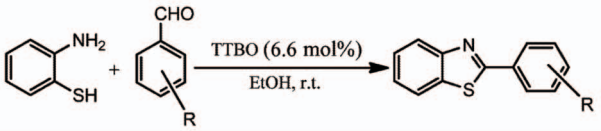
Entry	TTBO loading (mol%)	Yield[b] (%)
1	1.1	50
2	2.2	62
3	3.3	75
4	4.4	80
5	5.5	90
6	6.6	95
7	7.7	95
8	8.8	92

[a] Titanium tetrabutoxide.
[b] Isolated yield.

cations or electron poor systems. In other hand, the steric hindrance, or crowdedness around the electrophile, is an important factor that influences reactivity.

The different aldehydes were reacted with 2-aminothiophenol without any significant difference in the reaction time to give the corresponding 2-arylbenzothiazole derivatives in good yields (Table 3). All the products were synthesized in good to excellent yields and characterized

Table 3. Synthesis of 2-arylbenzothiazoles using TTBO as a catalyst in EtOH



Entry	Substrate (1a-l)	Product (2a-l)	M.P. (°C)	M.P. (°C) [Ref]	Yield[a] (%)
1	H	**2a**	110-112	111-112 [28]	85
2	*o*-OH	**2b**	127-128	126-128 [28]	87
3	*p*-OMe	**2c**	120-122	120-122 [29]	95
4	*o*-Me	**2d**	53-55	54-56 [28]	62
5	*p*-Me	**2e**	82-84	83-85 [28]	80
6	*o*-Cl	**2f**	72-74	72-74 [29]	85
7	*p*-Cl	**2g**	114-116	116-118 [29]	90
8	*o*-NO_2	**2h**	94-96	95-97 [28]	78
9	*p*-NO_2	**2i**	227-229	226-228 [29]	95
10	*2,3*-Cl	**2j**	118-120	119-121 [28]	90
11	*m*-NO_2	**2k**	181-183	181-182 [29]	91
12	*p*-$N(CH_3)_2$	**2l**	160-162	160-162 [28]	84

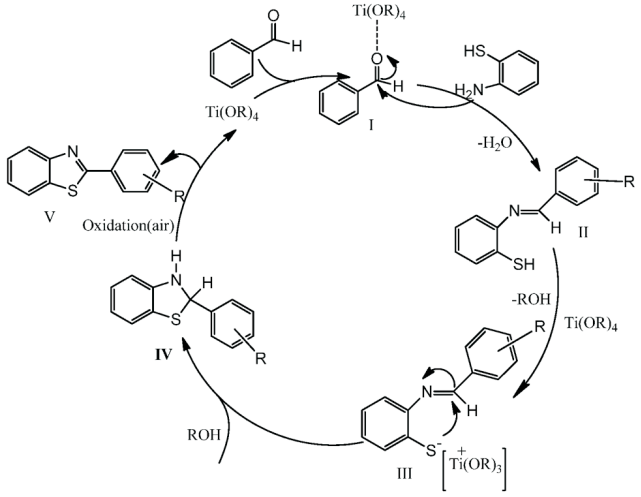
[a] Isolated yields.

with physical and spectroscopic data such as, FT-IR, ^{1}H NMR and ^{13}C NMR.

The proposed reaction mechanism

The proposed reaction mechanism for synthesis of 2-arylbenzothiazoles is shown in Scheme 2. In this reaction, TTBO as a strong Lewis acid can be activated the carbonyl group of aldehyde I for initial nucleophilic attack of NH_2 group to aldehyde to form a Schiff base intermediate II. On the other hand, the catalyst can be absorbed hydrogen atom from intermediate II followed by nucleophilic attack of thiolate anion to C=N resulted the intermediate IV. Then, the subsequent oxidation of IV in the presence of air oxygen to furnish 2-arylbenzothiazoles as product V (Scheme 2).

Scheme 2 The proposed reaction mechanism



CONCLUSIONS

In conclusion, we have explored a useful and practical approach to 2-arylbenzothiazoles with a facile and mild procedure by condensation reaction of 2-aminothiophenol and aromatic aldehydes using TTBO as an efficient catalyst. The main advantages of the present synthetic protocol are mild, high yields, short reaction times and easy reaction work up procedure.

EXPERIMENTAL

The chemicals and TTBO as catalyst were purchased from the Fluka and Merck Chemical Companies in high purity. All of the materials were of commercial grade. 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 Electrothermal MK_3 apparatus and are uncorrected. All ^{1}H 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). The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates

(from Merck Company).

General procedure for synthesis of 2-arylbenzothiazoles catalyzed by TTBO: TTBO (0.18 gr) was added to a mixture of 2-aminothiophenol (8 mmol, 0.995 gr) and aldehyde (9 mmol) in ethanol (10 mL) as solvent in a beaker and the reaction mixture was properly mixed with the help of glass rod and stirred in ambient temperature and the progress of the reaction was monitored by TLC (ethyl acetate: n-hexane, 6:4), after completion of the reaction the mixture was cooled and dichloromethane (2 × 15 mL) was added to the mixture for extracting the product. Then, the filtrate was evaporated under reduced pressure to isolate a solid residue, and recrystallized from ethanol (10 mL) to afford the corresponding products.

General procedure for synthesis of 2-arylbenzothiazoles catalyzed by solid Lewis acids: A mixure of 2-aminothiophenol (8 mmol, 0.995 gr), aldehyde (9 mmol) and different Lewis acids (0.15 gr) that are shown in Table 1, were added in ethanol (10 mL) as solvent in a beaker and the reaction mixture was properly mixed with the help of glass rod and stirred in ambient temperature for the time indicated in Table 1. The progress of the reaction was monitored by TLC (ethyl acetate:hexane, 6:4), after completion of the reaction the solvent was removed under reduced pressure, then the mixture was cooled and dichloromethane (15 mL) was added to the mixture and filtered to remove the catalyst. Then the filtrate was evaporated under reduced pressure to isolate a solid residue, and recrystallized from ethanol (10 mL) to afford the corresponding products.

Spectral Data of the Selected Compounds: 2-(2-Hydroxyphenyl)-benzothiazole: Yellow solid; m.p. = 127-128 ^{o}C (m.p. = 126-128 ^{o}C);[28] IR (KBr)/ υ(cm^{-1}): 3285, 3090, 2900, 1619, 1590, 1490, 1423, 874, 751; ^{1}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}C NMR/ (400 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. **2-Phenyl-benzothiazole:** White solid; m.p. = 110-112 ^{o}C (m.p. = 111-112 ^{o}C);[28] IR (KBr)/ υ(cm^{-1}): 3066, 3017, 2835, 1608, 1587, 1476,1430, 830, 763; ^{1}H NMR (400 MHz, $CDCl_3$)/ 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); ^{13}C NMR/ (400 MHz, $CDCl_3$)/ δ ppm: 121.50, 123.38, 125.07, 126.36, 127.58, 128.91, 130.77, 133.89, 135.11, 155.05, 167.98. **2-(4-Metoxyphenyl)-benzothiazole:** White solid; m.p. = 120-122 ^{o}C (m.p. = 120-122 ^{o}C);[29] IR (KBr)/ υ(cm^{-1}): 3021, 3048, 2837, 1609, 1590, 1483, 830; ^{1}H NMR (400 MHz, $CDCl_3$)/ δ ppm: 3.89 (s, 3H, OCH_3), 7.015 (d, 2H, *J* = 8.8 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* = 8.8 Hz, Ar-H); ^{13}C NMR/ (400 MHz, $CDCl_3$)/ 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. **2-(4-Nitrophenyl)-benzothiazole:** Yellow solid; m.p. = 227-229 ^{o}C (m.p. = 226-228 ^{o}C);[29] IR (KBr)/ υ(cm^{-1}): 3042, 2937, 1520, 1461, 1342, 1106, 851, 762; ^{1}H 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); ^{13}C NMR/ (400 MHz, DMSO) / δ ppm: 121.85, 123.94, 124.32, 126.24, 126.94, 128.23, 133.1, 135.40, 148.8, 154.0, 164.90. **2-(2,3-Dichlorophenyl)-benzothiazole:** White solid; m.p. = 118-120 ^{o}C (m.p. = 119-121 ^{o}C);[28] IR (KBr)/ υ(cm^{-1}): 3020, 2900, 1635, 1512, 1470,1432, 1348, 780; ^{1}H 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/ (400 MHz, $CDCl_3$) / δ ppm: 117.77, 118.13, 123.30, 124.54, 127.10, 128.11, 128.73, 129.27, 129.95, 130.91, 131.67, 146.01, 149.00. **2-(3-Nitrophenyl)-benzothiazole:** Colourless solid; m.p. =181-183 ^{o}C (m.p. =181-182 ^{o}C);[29] IR (KBr)/ υ(cm^{-1}): 3039, 2936, 1522, 1460, 1345, 1103, 1041, 851, 750; ^{1}H NMR (400 MHz, $CDCl_3$)/ δ ppm: 7.47 (m, 1H, Ar-H), 7.56 (m, 1H, Ar-H), 7.71-7.79 (m, 1H, Ar-H), 7.97 (d, 1H, *J* = 7.6 Hz, Ar-H), 8.14 (m, 1H, Ar-H), 8.36 (m, 1H, Ar-H), 8.44 (d, 1H, *J* = 7.6 Hz, Ar-H), 8.95 (s, 1H, Ar-H); ^{13}C NMR/ (400 MHz, DMSO) / δ ppm: 121.90, 122.4, 123.32, 125.24, 126.11, 126.80, 128.75, 131.1, 133.63, 134.40, 147.8, 153.0, 162.23. **2-(2-Nitrophenyl)-benzothiazole:** Brown solid; m.p. = 94-96 ^{o}C (m.p. = 95-97 ^{o}C);[28] IR (KBr)/ υ(cm^{-1}): 3033, 2930, 1545, 1466, 1349, 1111, 880, 851, 762; ^{1}H NMR (400 MHz, $CDCl_3$)/ δ ppm: 7.44-7.56 (m, 2H, Ar-H), 7.64-7.73 (m, 2H, Ar-H), 7.81 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.93-7.96 (m, 2H, Ar-H), 8.09 (d, 1H, *J* = 7.6 Hz, Ar-H); ^{13}C NMR/ (400 MHz, DMSO) / δ ppm: 120.85, 122.18, 124.30, 124.98, 126.03, 126.94, 128.88, 133.12, 136.14, 138.90, 143.8, 157.0, 164.09. **2-(4-Methylphenyl)-benzothiazole:** White solid; m.p. = 82-84 ^{o}C (m.p. = 83-85 ^{o}C);[28] IR (KBr)/ υ(cm^{-1}): 3024, 2905, 1610, 1519, 1480, 1435, 1383, 1312, 821, 759; ^{1}H NMR (400 MHz, $CDCl_3$)/ δ ppm: 2.45 (s, 3H, CH_3), 7.34-736 (m, 4H, Ar-H), 7.54-759 (m, 1H, Ar-H), 7.75-7.78 (m, 1H, Ar-H), 8.14-8.16 (m, 2H, Ar-H); ^{13}C NMR/ (400 MHz, $CDCl_3$) / δ ppm: 23.6, 110.42, 120.33, 121.76, 123.34, 128.56, 131.65, 132.67, 143.15, 155.63, 160.83, 165.11. **2-(4-Chlorophenyl)-benzothiazole:** Yellow solid; m.p. = 114-

116 °C (m.p. = 116-118 °C);[29] IR (KBr)/ υ(cm^{-1}): 3055, 2358, 1560, 1455, 1430, 1317, 1275, 1060, 965, 750, 725; ^{1}H NMR (400 MHz, $CDCl_3$)/ δ ppm: 7.37-739 (m, 2H, Ar-H), 7.51-753 (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/ (400 MHz, $CDCl_3$) / δ ppm: 121.8, 123.13, 125.17, 126.80, 129.10, 129.78, 132.67, 135.2, 137.1, 154.4, 166.21. **2-(4-N,N-dimethylphenyl)-benzothiazole:** Brown solid; m.p. = 160-162 °C (m.p. = 160-162 °C);[28] IR (KBr)/ υ(cm^{-1}): 3355, 2358, 1598, 1478, 1210, 1017, 965, 743; ^{1}H NMR (400 MHz, $CDCl_3$)/ δ ppm: 3.08 (s, 6H, -$N(CH_3)_2$), 6.77-6.79 (d, 2H, *J* = 8 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 Hz, Ar-H); ^{13}C NMR/ (400 MHz, $CDCl_3$) / δ ppm: 39.8, 111.13, 121.1, 122.0, 124.1, 126.78, 128.67, 132.25, 135.2, 152.1, 154.4, 168.2. **2-(2-Chlorophenyl)-benzothiazole:** Colorless solid; m.p. = 72-74 °C (m.p. = 72-74 °C);[28] IR (KBr)/ υ(cm^{-1}): 2955, 1538, 1502, 1421, 1242, 1117, 965, 750, 733; ^{1}H NMR (400 MHz, $CDCl_3$)/ δ ppm: 7.38-7.49 (m, 4H, Ar-H), 7.58-760 (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); ^{13}C NMR/ (400 MHz, $CDCl_3$) / δ ppm: 111.8, 123.13, 124.17, 125.80, 128.19, 129.88, 131.67,133.14, 134.21, 137.1, 143.51, 154.4, 162.21. **2-(2-Methylphenyl)-benzothiazole:** Yellow solid; m.p. = 53-55 °C (m.p. = 54-56 °C);[28] IR (KBr)/ υ(cm^{-1}): 3040, 2980, 1598, 1550, 1451, 1244, 1115, 862, 754; ^{1}H NMR (400 MHz, $CDCl_3$)/ δ ppm: 2.47 (s, 3H, CH_3), 7.35-7.37 (m, 3H, Ar-H), 7.41-7.45 (t, 1H, *J* = 8 Hz, 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 Hz, Ar-H), 8.08 (d, 1H, *J* = 8 Hz, Ar-H); ^{13}C NMR/ (400 MHz, $CDCl_3$) / δ ppm: 22.6, 112.13, 119.38, 120.53, 122.34, 126.17, 128.34, 129.12, 130.67,132.47, 144.15, 152.68, 159.93, 162.17.

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