An efficient green protocol for the synthesis of 2-substituted benzothiazole under solvent and catalyst free condition

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Abstract

Direct one step synthesis of benzothiazole from o-amino thiophenol and carboxylic acid is described without using solvent and catalyst. The salient features of this method include novel route, simple procedure, no coupling agents or commercial oxidants/ additives, no dehydrating agent, no waste product formed (only by-product being water), easy purification and high yield. Moreover, the easy set-up and purification tasks of this sustainable method make it appealing for bulk industry applications.

Key Word: - *o*-amino thiophenol, carboxylic acids, benzothiazole, solvent free, catalyst free

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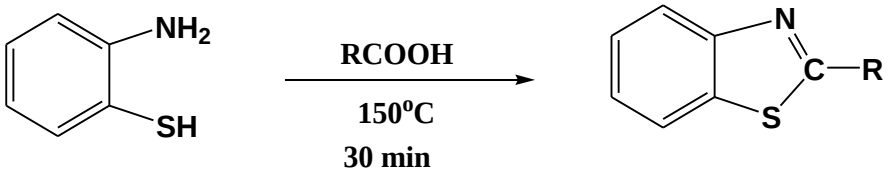
INTRODUCTION

The 2-substituted benzothiazole structure is useful in the field of medicinal and biological chemistry. The benzothiazolyl system possesses highly selective and potent antitumor activity. Also, 2-(4-dimethylamino phenyl)-benzothiazole is an integral component used for the treatment of alzheimer disease. The presence of the benzothiazole nucleus is essential in the thermally stable rigid-rod polymers with high tensile strength and modulus. They have also found applications in industry as antioxidants, antifungal vulcanization accelerators, and as a dopant in a light–emitting organic electroluminescent device.[1-3] Thus, the synthesis of benzothiazole posses a great challenge to synthetic chemists. In general, benzothiazoles have been synthesized by condensation of 2-aminothiophenol with carboxylic acid derivatives,[4] one pot reaction of 2-aminothiophenol with β-chlorocinam aldehydes using pTsOH, [5] condensation of 2-amino thiophenol with acid chlorides,[6] esters,[7] arylation of benzothiazoles with aryl bromides at 150°C in a sealed tube catalyzed by $Pd(OAc)_2$, Cs_2CO_3 and CuBr with $P(t\text{-}Bu)_3$ as ligand,[8] multistep synthetic approaches of 2-arylbenzo thiazoles[9] or Suzuki biaryl coupling of 2-arylbenzothiazoles with aryl boronic acid.[10]



On the other hand, the most general synthetic approach for synthesis of 2-arylbenzothiazoles involves condensation of 2- amino thiophenols with aldehydes using various oxidants such as MnO_2/SiO_2[11], pTsOH or graphite on the surface of solid mineral supports under microwave irradiation [12], I_2/DMF[13], 1-phenyl-3-methylimidazolium bromide [PmIm]Br under microwave irradiation[14], activated carbon (Shirasagi KL or Darco® KB) under oxygen atmosphere[15], O_2 or H_2O_2 in the presence of $Sc(OTf)_3$ [16], CAN [17], electro oxidation [18], direct condensation of 2-aminothiophenol with aromatic aldehydes under microwave irradiation [19], Dowex 50W [20], $H_2O_2/Fe(NO_3)_3$ [21], solid

heteropoly acid supported on silica gel ($Cu_3/2PMo_{12}O_{40}/SiO_2$) [22], alum ($KAl(SO_4)_2.12H_2O$) [23], Bakers yeast[24], trichloroisocyanuric acid [25], perchloric acid-doped polyaniline [26] and tungstophosphoric acid impregnated zirconium phosphate [27]. However, many of these procedures are associated with one or more disadvantages such as the use of toxic, expensive catalyst, hazardous and carcinogenic solvents, e.g., nitro benzene and dioxane, multistep processes, and loss of the catalyst. Therefore, it was felt that there is an urgent need to overcome the above limitations by developing an efficient, simple and green methodology for the synthesis of benzothiazoles.

However, there are no examples of the solvent and catalyst free synthesis of benzothiazoles. Here in, we wish to disclose a novel protocol for the rapid synthesis of a variety of biologically significant benzothiazoles without using catalyst and solvent. The reaction was carried out at 150°C temperature for 30 minutes, using o-amino thiophenol (1 mmol) and carboxylic acid (1 mmol). The results are summarized in Table 1. As shown in Table 1, aromatic, aliphatic and unsaturated carboxylic acids with o-amino thiophenol react without any significant difference to give the corresponding benzothiazole in good yield. Best results were obtained when the reaction mixture was heated at 150°C at 30 min. This method offers several advantages such as high conversions, shorter reaction times, cleaner reaction profiles, solvent and catalyst free conditions, simple experimental and work-up procedure make our methodology a valid contribution to the existing processes in the field of benzothiazole derivative synthesis.

EXPERIMENTAL SECTION

Chemicals were procured from Aldrich Chemical Co. Reactions were monitored and purity of the products was checked by thin layer chromatography (TLC). TLC was performed on Merck 60 F-254 silica gel plates with visualization by UV-light. Melting points were determined in capillary tubes in silicon oil bath using a Veego melting point apparatus and are uncorrected. ^1H (300 MHz) NMR and ^{13}C (75 MHz) NMR spectra were recorded on Varian mercury XL-300 and Bruker spectrometer instruments. Chemical shifts are reported from internal tetramethyl silane standard and are given in δ units. The solvent for NMR spectra was $CDCl_3$ and DMSO-d_6. Infra red spectra were taken on Shimadzu FTIR – 408 in KBr. The mass spectra were recorded on Shimadzu GC-MS QP 2010A mass spectrometer with an ionization potential of 70 eV. Column chromatography was performed on silica gel (230–400 mesh) supplied by Acme Chemical Co. The chemicals and solvents used were laboratory grade and were purified as per literature methods.

General Procedure for the synthesis 2-substituted benzothiazole

In a 50 ml round bottom flask, a mixture of o-amino thiophenol (1 mmol) and carboxylic acids (1 mmol) were mixed and was heated at 150°C for 30 min without solvent or catalyst. To this ethyl acetate (25 ml) was added and washed with dilute ammonia. The organic phase was separated, dried with Na_2SO_4 and concentrated in vacuum to get the crude product which was purified by silica gel column Chromatography using 1:1 ethyl acetate: hexane. All the known compounds were characterized by comparing their Physical constant (MPs) and spectral data (IR, ^1H NMR and ^{13}C NMR) with those of reported compounds.

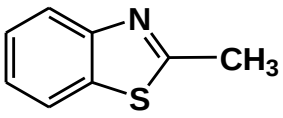
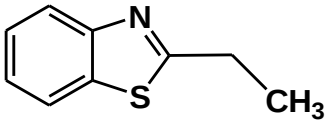
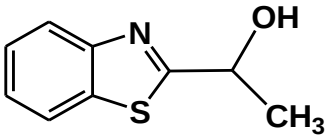
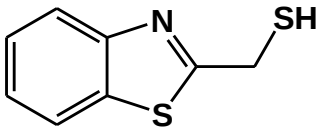
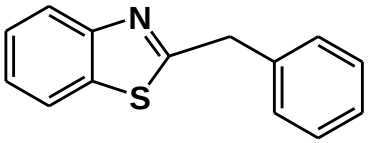
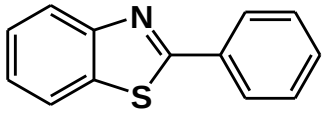
RESULT AND DISCUSSION

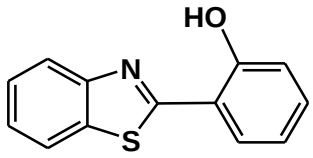
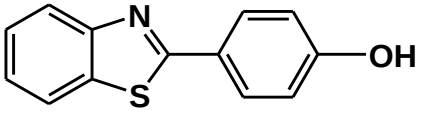
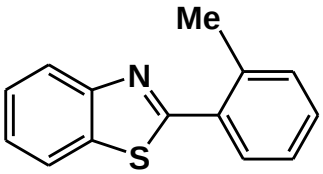
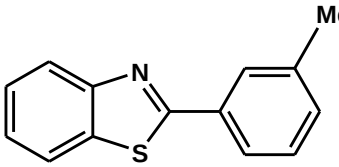
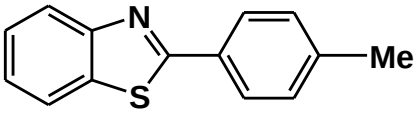
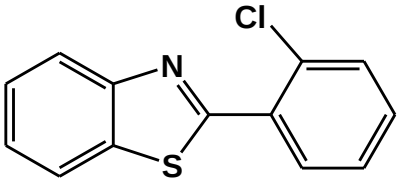
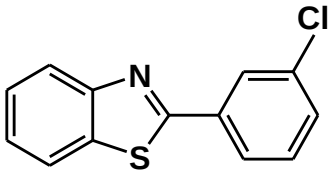
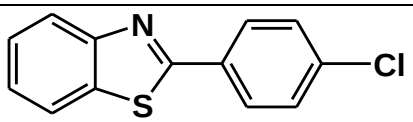
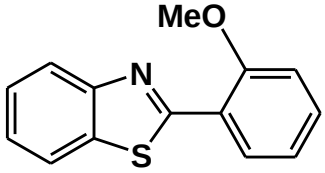
One aim of green chemistry is to decrease or eliminate the use of solvents and/or catalysts. There is no report regarding formation of benzthiazole by such method. Herein we wish to disclose a

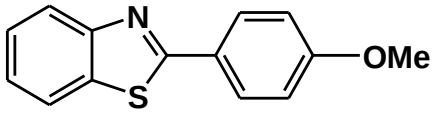
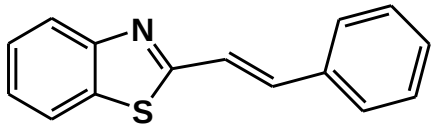
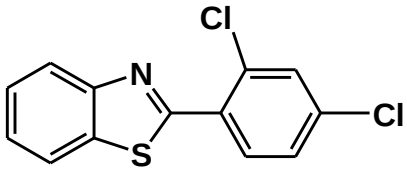
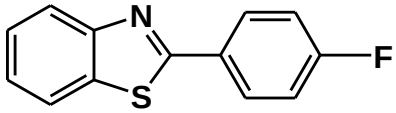
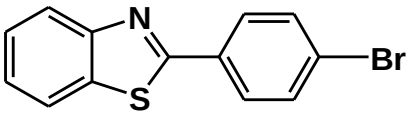
novel protocol for the rapid synthesis of variety of biologically significant, already reported benzothiazole except **2**, **3**,**4**, **5**, **7**, **10, 13** and **18**, without using solvent and catalyst (Scheme-I). The reaction was carried out at 150^{o}C for 30 min, using o-amino thiophenol and carboxylic acid. The generality of the reaction was demonstrated by condensation reaction of o-amino thiophenol with carboxylic acids containing different electron donating and electron withdrawing groups. The results are summarized in table 1.

As can be seen in table 1, aromatic and aliphatic carboxylic acid having melting point below 160^{o}C were converted to the corresponding benzothiazoles better yields compared with those having higher melting point. All reactions were carried out for 30 min. The time of reaction depended on the melting point of the carboxylic acids. Carboxylic acids in liquid state proceeded at faster rates than those in solid state.

Table 1: Synthesis of benzothiazole derivatives by dehydrative C-N and C-S bond formation method.

Code No.	R-COOH	Product	Yield (%)	M.P./B.P. °C Found [Reported] (Ref)
1	Acetic Acid		*90*	Yellow oil 238 – 240 °C
2	Propanoic Acid		*93*	Yellow oil 222-225 °C
3	Lactic Acid		*90*	Yellow oil 202-204 °C
4	Thio Glycolic acid		*88*	Yellow oil 240-242 °C
5	Phenyl Acetic Acid		*86*	76-78 °C
6	Benzoic Acid		*80*	114-115 °C [113-114 °C] [29]

7	2-Hydroxy Benzoic Acid		*77*	128-130 ºC
8	4-Hydroxy Benzoic Acid		*75*	227 ºC [227-228 ºC] [29]
9	2-Methyl Benzoic Acid		*80*	54 ºC [53-54 ºC] [28]
10	3-Methyl Benzoic Acid		*69*	90-93 ºC
11	4-Methyl Benzoic Acid		*60*	84-85 ºC [84-85 ºC] [29]
12	2-Chloro Benzoic cid		*55*	82 ºC [82-83 ºC] [20]
13	3-chloro benzoic acid		74	92-94 ºC
14	4-Chloro Benzoic Acid		*50*	118 ºC [117-118 ºC] [20]
15	2-Methoxy Benzoic Acid		*63*	103 ºC [101-102 ºC] [20]

16	4-Methoxy Benzoic Acid		68	120 ºC [119-121 ºC] [5]
17	Cinnamic Acid		55	112 ºC [110-112 ºC] [20]
18	2,4 dichloro benzoic aid		68	122 ºC
19	4-Fluro Benzoic Acid		78	100 ºC [98-99 ºC] [5]
20	4-Bromo Benzoic Acid		75	132-133 ºC [130-131 ºC] [20]

2-Methyl-1H- benzothiazole (1)

IR (KBr): 1718, 1600, 948, 740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.6 (s, 3H), 7.20 - 8.20 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 18.8, 115.1, 122.1, 122.5, 131.3, 139.1, 134.1, 151.3; ESI (m/z) : 150 (M+1), 149 (M^+).

2-Ethylbenzothiazole (2)

IR (KBr): 1722, 1600, 1450, 1550,748 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.28-8.00 (m, 4H, ArH), 3.10 (q, J = 7.2 Hz, 2H, CH_2CH_3), 1.43 (t, J = 7.2 Hz, 3H, CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.6, 153.2, 135.0, 125.9, 124.6, 122.5, 121.5, 27.8, 13.8; ESI (m/z) 164 (M+H), 163(M^+).

1(benzothiazole 2-yl) ethanol (3)

IR (KBr): 1718, 1600, 948, 740 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 1.50 (d, J = 7.2 Hz, 3H), 2.1 (s, 1H, OH), 4.0 (q, J = 7.2 Hz, 1H), 7.20 - 8.18 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 22.6, 70.1, 115.1, 122.1, 122.5, 134.1, 139.1, 134.2, 151.3. ESI (m/z) 180 (M+1), 179 (M^+).

benzothiazole 2-yl methane thiol (4)

IR (KBr): 1724, 1610, 1450, 1100, 1200, 950 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 4.19 (s, 2H), 7.20 -8.18 (m, 4H), 9.26 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 26.4, 114.1, 122.9, 123.8, 139.2, 134.9, 151.4; ESI (m/z) : 182 (M+1), 180 (M-1).

2-benzyl- benzothiazole (5)

IR (KBr): 1718, 1600, 948, 740 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 4.17 (s, 2H), 7.12 (m, 2H), 7.23 (m, 2H), 7.29 (m, 3H), 7.41 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 15.1, 123.3, 125.2, 128.5, 129.7, 130.3, 138.5, 136.1, 141.8, 152.7; ESI (m/z) 226 (M+1), 224 (M-1).

2-Phenyl benzothiazole (6)

IR (KBr) : 1718, 1600, 948, 740 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10-8.12 (m, 3H, ArH), 7.91(d, J = 8.5 Hz, 1H, ArH), 7.48-7.53 (m, 4H, ArH), 7.40 (d, J = 8.5 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$,) δ = 168.1, 154.1, 135.0, 133.6, 131.0, 129.1, 127.6, 126.3, 125.2, 123.2, 121.6; ESI (m/z) 212 (M+1), 211 (M^+).

2-(2-hydroxy phenyl) benzothiazole (7)

IR (KBr): 1718, 1600, 948, 740 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.04 - 8.26 (m, 4H), 7.28 (m, 2H), 7.65 (m, 2H), 4.01 (bs, 1H, OH); ^{13}C NMR (75 MHz, DMSO-d_6) : δ = 115.1, 116.2, 118.4, 121.1, 123.4, 130.7, 138.8, 152.3, 155.2, ESI (m/z) 227 (M+1), 225 (M-1).

2-(4-Hydroxyphenyl) benzothiazole (8)

IR (KBr): 1722, 1600, 1450, 1550,748 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ = 7.89-8.06 (m, 4H, ArH), 7.36-7.50 (m, 2H, ArH), 6.90-6.95 (m, 2H, ArH), 3.64 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.9, 170.1, 154.1, 134.5, 129.5, 126.8, 125.3, 124.4, 122.7, 122.5, 116.5. ESI (m/z) 228 (M+1), 227 (M^+).

2-(2-Methylphenyl)-benzothiazole (9)

IR (KBr): 1722, 1600, 1450, 1550,748 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.1 (d, J = 8.5 Hz, 1H, ArH), 7.90 (d, J = 8.5Hz, 1H, ArH), 7.75 (d, J =7.6 Hz, 1H, ArH), 7.50 (d, J =7.6 Hz, 1H, ArH), 7.26-7.41 (m, 4H, ArH), 2.65 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.1, 157.2, 152.1, 136.1, 131.7, 129.5, 125.8, 124.5, 122.7, 122.2, 121.2, 121.1, 111.6, 55.6; ESI (m/z) 226 (M+1), 225 (M^+).

2-(3-methylphenyl) benzothiazole (10)

IR (KBr): 1724, 1612, 1442, 1407, 1273, 958, 744 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.60 (s, 3H, Me), 7.17-8.20 (m, 8H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 21.3, 115.5, 119.4, 121.8, 122.8, 126.4, 129.7, 129.9, 130.5, 131.7, 134.8, 137.4, 144.1, 152.4; ESI (m/z) 226 (M+1), 225 (M^+).

2-(4-Methylphenyl)-benzothiazole (11)

IR (KBr): 1722, 1600, 1450, 1550,748 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.05 (d, J = 8.5 Hz, 1H, ArH), 7.97 (d, J = 8.5 Hz, 2H, ArH), 7.86 (d, J = 8.5 Hz, 1H, ArH), 7.44-7.46 (m, 1H, ArH), 7.34-7.37 (m, 1H, ArH), 7.27 (d, J = 8.5 Hz, 1H, ArH), 2.40 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.2, 154.2, 141.4, 135.0, 131.0, 129.7, 127.5, 126.2, 125.0, 123.0, 121.5, 21.5; ESI (m/z) 226 (M+1), 225 (M^+).

2-(2-chlorophenyl) benzothiazole (12)

IR (KBr): 1722, 1600, 1450, 1550,748 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): = δ 7.21 - 8.18 (m, 8H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 115.6, 123.1, 127.7, 128.3, 129.4, 130.2, 132.8, 138.1, 138.8, 152.3; ESI (m/z) 246 (M+1), 245(M^+).

2-(3- chlorophenyl) benzothiazole (13)

IR (KBr): 1724, 1612, 1442, 1407, 1273, 958, 744 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ = 7.17-7.21 (m, 4H), 7.51 – 7.73 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 21.3, 115.5, 119.4, 121.8, 122.8, 126.4, 129.7, 129.9, 130.5, 131.7, 134.8, 137.4, 144.1, 152.4; ESI (m/z) 246 (M+1).

2-(4-Chlorophenyl)benzothiazole (14)

IR (KBr): 1722, 1600, 1450, 1550,748 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.87-8.06 (m, 4H, ArH), 7.35-7.51 (m, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.8, 154.3, 137.2, 135.3, 132.3, 129.5, 128.9, 126.7, 125.6, 123.5, 121.8; ESI (m/z) 246 (M+1), 248 (M+2).

2-(2-Methoxyphenyl)-benzothiazole (15)

IR (KBr): 1718, 1600, 948, 740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.03-8.58 (m, 8H, ArH), 4.03 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.8, 156.9, 151.9, 135.8, 131.4, 129.2, 125.6, 124.3, 122.5, 120.9, 120.8, 111.4, 55.4; ESI (m/z) 242 (M+1).

2-(4-Methoxyphenyl)benzothiazole (16)

IR (KBr): 1722, 1600, 1450, 1550,748 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.04-8.07 (m, 3H, ArH), 7.90 (m, 1H, ArH), 7.48 (d, J = 8.5 Hz, 1H, ArH), 7.37 (d, J = 8.5 Hz, 1H, ArH), 7.01-7.04 (m, 2H, ArH), 3.90 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.0, 162.1, 154.4, 135.1, 129.3, 126.6, 126.4, 125.0, 123.0, 121.7, 114.5, 55.6; ESI (m/z) 242 (M+1), 241 (M^+).

2-Styrylbenzothiazole (17)

IR (KBr): 1722, 1600, 1450, 1550,748 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.36-7.98 (m, 11 H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.9, 153.9, 137.6, 135.4, 134.4, 129.4, 128.9, 127.4, 126.3, 125.3, 123.0, 122.2, 121.5; ESI (m/z) 238 (M+1).

2-(2, 4-dichlorophenyl) benzothiazole (18)

IR (KBr): 1724, 1612, 1442, 1407, 1273, 958, 744 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.18 - 8.06 (m, 7H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 21.3, 115.5, 119.4, 121.8, 122.8, 126.4, 129.7, 129.9, 130.5, 131.7, 134.8, 137.4, 144.1, 152.4; ESI (m/z) 281 (M+1).

2-(4-Fluorophenyl)benzothiazole (19)

IR (KBr): 1722, 1600, 1450, 1550,748 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.03-8.07 (m, 3H, ArH), 7.85 (d, J = 8.5 Hz, 1H, ArH), 7.47 (d, J = 8.0 Hz, 1H, ArH), 7.35 (d, J = 8.0 Hz, 1H, ArH), 7.15 (t, J = 8.5 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.9, 163.0 (d, $^1J_{C-F}$ = 250.3Hz), 154.3, 135.2, 130.1, 129.7 (d, $^3J_{C-F}$ = 7.0 Hz), 129.6, 125.4, 123.4 (d, $^4J_{C-F}$ = 2.9 Hz), 121.7, 116.3 (d, $^2J_{C-F}$ = 22.0 Hz). ESI (m/z) 230 (M+1)

2-(4-Bromophenyl)benzothiazole (20)

IR (KBr): 1722, 1600, 1450, 1550,748 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.37-8.08 (m, 8H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7, 154.1, 135.0, 132.5, 132.2, 128.9, 126.5, 125.5, 125.4, 123.3, 121.6; ESI (m/z) 291 (M+1), 289 (M+2).

CONCLUSION

A novel, simple, and efficient procedure for the synthesis of 2-substituted benzothiazole has been explored. Short reaction time, large-scale synthesis, easy and quick isolation of the products, excellent yield, solvent and catalyst free reaction are the main advantages of this procedure, which make this method more attractive. It is certainly a useful contribution to the present methodologies.

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