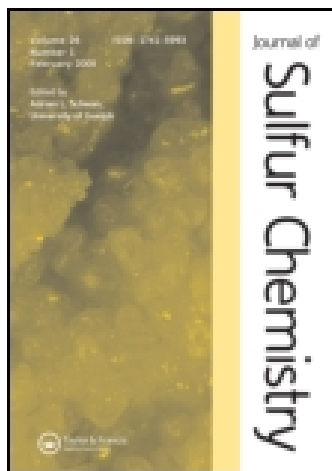


This article was downloaded by: [Monash University Library]

On: 05 October 2014, At: 09:28

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Sulfur Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gsrp20>

### Synthesis of 2-arylbenzothiazoles using nano $\text{BF}_3/\text{SiO}_2$ as a reusable and efficient heterogeneous catalyst under mild conditions

Hossein Naeimi<sup>a</sup> & Arash Heidarneshad<sup>a</sup>

<sup>a</sup> Department of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan, 87317, I.R. Iran

Published online: 14 May 2014.

To cite this article: Hossein Naeimi & Arash Heidarneshad (2014) Synthesis of 2-arylbenzothiazoles using nano  $\text{BF}_3/\text{SiO}_2$  as a reusable and efficient heterogeneous catalyst under mild conditions, Journal of Sulfur Chemistry, 35:5, 493-501, DOI: [10.1080/17415993.2014.917377](https://doi.org/10.1080/17415993.2014.917377)

To link to this article: <http://dx.doi.org/10.1080/17415993.2014.917377>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

## Synthesis of 2-arylbenzothiazoles using nano $\text{BF}_3/\text{SiO}_2$ as a reusable and efficient heterogeneous catalyst under mild conditions

Hossein Naeimi\* and Arash Heidarneshad

Department of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan, 87317, I.R. Iran

(Received 28 October 2013; accepted 18 April 2014)

2-Arylbenzothiazoles were synthesized via condensation of 2-aminothiophenol and different aldehydes catalyzed by nano silica-supported boron trifluoride (nano  $\text{BF}_3/\text{SiO}_2$ ) as an efficient and reusable catalyst in high yields and short reaction times. The reactions proceeded at room temperature under mild conditions to afford 2-arylbenzothiazole derivatives. The pure products were identified and characterized by physical and spectroscopic data such as IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and Mass spectroscopy.



**Keywords:** 2-arylbenzothiazoles; nano- $\text{BF}_3/\text{SiO}_2$ ; synthesis; 2-aminothiophenol; aldehydes

### 1. Introduction

The synthesis, reactions and biological properties of benzothiazoles and compounds containing the benzothiazole nucleus constitute a significant part of modern heterocyclic chemistry.[1] They are well known for their biological and pharmaceutical activities such as antitumor, antiparkinsonism,[2] antimalarial, anticonvulsant, antihemintic, antifungal and analgesic. Several methods for the synthesis of 2-arylbenzothiazoles have been developed.[3,4] In general, benzothiazoles have been synthesized by the condensation of 2-aminothiophenol with carboxylic acid derivatives.[5] On the other hand, the most general approaches for 2-arylbenzothiazoles include the following; (1) oxidative cyclization of phenolic Schiff bases derived from the condensation of 2-aminothiophenols and aldehydes using various oxidants such as  $\text{Sc}(\text{OTf})_3$ -molecular oxygen [6] and pyridinium chlorochromate,[7] and (2) the condensation of 2-aminothiophenols with carboxylic acids under microwave irradiation in the presence of a Lewis acid.[8–11] Despite their

\*Corresponding author. Email: [naeimi@kashanu.ac.ir](mailto:naeimi@kashanu.ac.ir)

potential utility, 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, the development of a facile and mild general method to overcome these shortcomings remains a challenge for organic chemists in the synthesis of 2-arylbenzothiazoles.[12,13]

In this study, in continuation of our interest on the synthesis of 2-arylbenzothiazoles,[14] and using  $\text{BF}_3$  as a catalyst in organic reactions,[15] we decided to explore the ability of nano  $\text{BF}_3/\text{SiO}_2$  as a mild and non-toxic Lewis acid catalyst for the synthesis of 2-arylbenzothiazoles. Therefore, nano  $\text{BF}_3/\text{SiO}_2$  was used as a new catalyst for the synthesis of 2-arylbenzothiazoles by the condensation reaction of 2-aminothiophenol with aromatic aldehydes at room temperature under mild conditions.

## 2. Results and discussion

In this research, we have developed a synthetic method using nano  $\text{BF}_3/\text{SiO}_2$  as a reusable, efficient and eco-friendly solid acid catalyst for synthesis of 2-arylbenzothiazoles from 2-aminothiophenol and aldehydes in excellent yields at room temperature (Scheme 1).



Scheme 1. Synthesis of 2-arylbenzothiazoles.

The dimension of nano catalyst was observed with the scanning electron microscope (SEM). The size of the synthesized  $\text{BF}_3/\text{SiO}_2$  nanoparticles was confirmed to be about 18–39 nm by scanning electron microscopy (Figure 1).

We first screened a number of different catalysts in the reaction of 4-nitrobenzaldehyde with 2-aminothiophenol (reaction model) such as different Lewis acids, different reagents supported on solid materials, nano crystalline  $\text{TiO}_2$  and acidic alumina. The results are shown in Table 1.

When the reaction was carried out in the presence of nano  $\text{BF}_3/\text{SiO}_2$  as a catalyst, the product was obtained in excellent yields and short reaction times (Table 1, Entry 8). On the other hand, the same reaction using other catalysts gave the products in low yields even after prolonged reaction time.

In order to optimize the reaction in terms of yield and reaction time, we examined the efficiency of different reaction media and catalyst amounts in the condensation reaction of 4-nitrobenzaldehyde (1 mmol) with 2-aminothiophenol in ethanol solution. The results are given in Table 2.

In order to ascertain the scope and limitation of this method, the reaction of 2-aminothiophenol and several substituted aromatic aldehydes using the optimized method was examined at room temperature. By considering the above results, conversion of different aromatic aldehydes to the corresponding 2-arylbenzothiazoles using nano  $\text{BF}_3/\text{SiO}_2$  as a catalyst was investigated. The results of these reactions are summarized in Table 3.

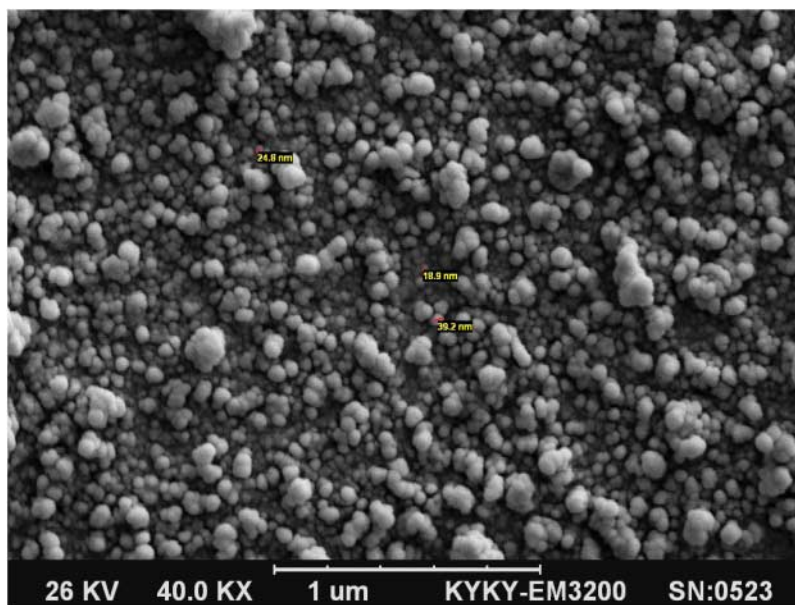
Figure 1. SEM image of nano  $\text{BF}_3/\text{SiO}_2$ .

Table 1. Screening of catalyst in the reaction of 4-nitrobenzaldehyde with 2-aminothiophenol.

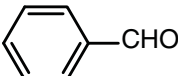
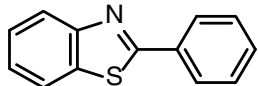
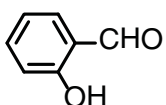
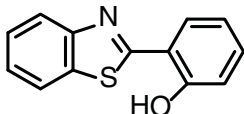

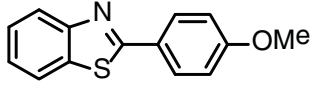
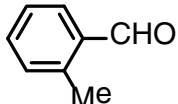
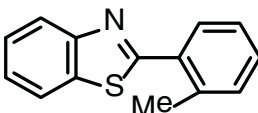
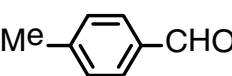
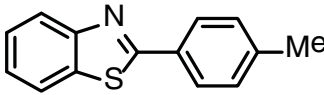
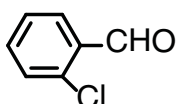
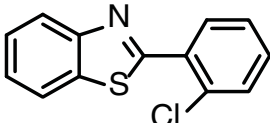
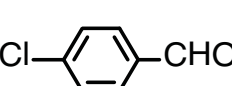
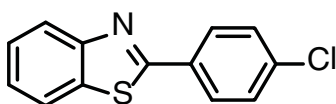
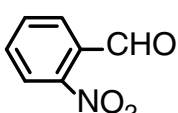
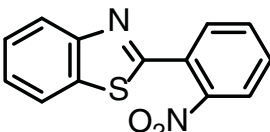
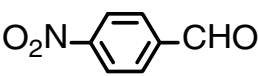
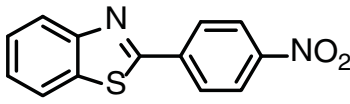
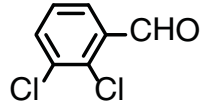
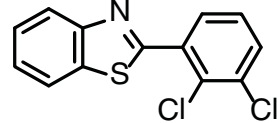
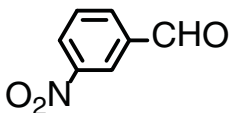
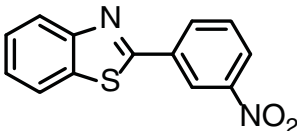
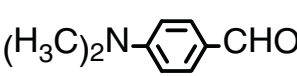
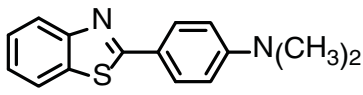
Entry	Catalyst	Time (min)	Yield <sup>a</sup> (%)
1	$\text{AlCl}_3$	15	48
2	$\text{FeCl}_3$	15	62
3	$\text{Al}_2\text{O}_3$	15	25
4	$\text{SSA}^b$	15	85
5	Nano $\text{TiO}_2$	15	7
6	$\text{BF}_3(\text{Et}_2\text{O})$	15	70
7	Nano $\text{SiO}_2$	15	35
8	Nano $\text{BF}_3/\text{SiO}_2$	15	92

<sup>a</sup>Isolated yield.<sup>b</sup>Silica sulphuric acid.Table 2. Synthesis of 2-arylbenzothiazoles catalyzed by nano  $\text{BF}_3/\text{SiO}_2$  under various conditions.

Entry	Nano $\text{BF}_3/\text{SiO}_2(\text{g})$	Catalyst (mol% $\text{BF}_3$ )	Solvent	Yield <sup>a</sup> (%)
1	0.03	15	$\text{CH}_3\text{CN}$	48
2	0.03	15	$\text{CH}_3\text{CN}$	70
3	0.03	15	$\text{CH}_3\text{CN}$	76
4	0.03	15	$\text{EtOH}$	55
5	0.03	15	$\text{EtOH}$	82
6	0.03	15	$\text{EtOH}$	85
7	0.03	15	$\text{CH}_2\text{Cl}_2$	50
8	0.03	15	$\text{CH}_2\text{Cl}_2$	72
9	0.03	15	$\text{CH}_2\text{Cl}_2$	80
10	0.04	20	$\text{EtOH}$	92
11	0.05	25	$\text{EtOH}$	95
12	0.06	30	$\text{EtOH}$	95

<sup>a</sup>Isolated yields based on starting materials.

Table 3. Synthesis of 2-arylbenzothiazoles using nano  $\text{BF}_3/\text{SiO}_2$  as a catalyst (0.05 g, 25 mol %  $\text{BF}_3$ ) in EtOH at room temperature.

Entry	Substrate	Product	M.P. (°C)	Time (min)	Yield <sup>a</sup> (%)
1			111–112	30	85
2			127–128	35	87
3			120–122	35	95
4			53–55	40	62
5			82–84	25	80
6			72–74	30	85
7			114–116	25	90
8			94–96	40	78
9			227–229	20	95
10			118–120	30	73
11			181–183	30	91
12			160–162	45	84

<sup>a</sup>Isolated yields.

Table 4. Synthesis of 2-(4-Nitrophenyl)-benzothiazole with recovered catalyst.

Entry	Time (min)	Yield <sup>a</sup> (%)
1	20	95
2	20	92
3	20	90
4	20	85
5	20	82

<sup>a</sup>Isolated yields.

This reaction was also carried out with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  as a Lewis acid for comparison with nano  $\text{BF}_3/\text{SiO}_2$  as a catalyst. Unfortunately,  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  is a liquid that fumes in the air and reacts with moisture to form hydrofluoric acid making its use inconvenient and laborious. In addition, the yields of products using nano  $\text{BF}_3/\text{SiO}_2$  as a catalyst are considerably higher than  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  and it is clear that it is the preferred catalyst. As can be seen from Table 3, the products were obtained in 62–95% yields and in reaction times of 20–45 min. In this reaction, the Lewis acid nano  $\text{BF}_3/\text{SiO}_2$  catalyst activates the carbonyl group via coordination with the oxygen atom to accelerate the nucleophilic attack of the amino group at the carbon atom of the carbonyl group.

The structure of the products was confirmed by spectroscopic methods such as IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and Mass spectroscopy. In the IR spectra, the stretching frequency of aromatic  $\text{C}=\text{C}$  bonds is observed in the region between 1475 and 1600  $\text{cm}^{-1}$ . In the  $^1\text{H}$  NMR spectra, the proton of  $-\text{OH}$  group in 2-(2-hydroxyphenyl)-benzothiazole appeared at 12.54 ppm. The signals at 6.95–8.94 are assigned to  $\text{CH}=\text{CH}$  of the aromatic rings. The hydrogen atoms of the methoxy group have a chemical shift of 3.89 ppm, and the signal around 6.77–6.79 ppm is assigned to the  $-\text{N}(\text{CH}_3)_2$  group. In the  $^{13}\text{C}$  NMR spectra, the aromatic carbons absorb at 110–169 ppm and the signal of 55.47 is assigned to the  $-\text{OCH}_3$  group. The mass spectra (Electron Impact (EI)) of products have shown the corresponding molecular ion peak.

**Reusability of the nano  $\text{BF}_3/\text{SiO}_2$  catalyst:** In the next step of our study, our attention was directed toward evaluating the reusability and recycling potential of nano  $\text{BF}_3/\text{SiO}_2$  in these reactions. After each run, conducted for the 20 min indicated in Table 4, the catalyst was filtered from the product and washed with acetone, then dried at 90 °C for 2 hours and reused in the next reaction cycle using the optimized conditions for an additional 20 min. The recovered catalyst was active although a gradual decline was observed in its activity as its time of use was increased (Table 4).

### 3. Conclusion

In summary, a facile and mild procedure for the synthesis of 2-arylbenzothiazoles has been developed using the condensation reaction of 2-aminothiophenol and aromatic aldehydes with nano  $\text{BF}_3/\text{SiO}_2$  as an efficient, eco-friendly and reusable heterogeneous catalyst. The main advantages of the present synthetic protocol are mild conditions, high yields, short reaction times and easy reaction work up procedure.

## 4. Experimental section

### 4.1. Chemicals

Chemicals were purchased from the Merck, Fluka and Aldrich Chemical Companies in high purity. All of the materials were of commercial reagent grade. The solvents were purified by standard procedure.

## 4.2. Apparatus

The FT-IR spectra were obtained with potassium bromide pellets in the range 400–4000  $\text{cm}^{-1}$  with a Perkin Elmer 550 spectrometer. Melting points were determined in open capillaries using an Electrothermal MK<sub>3</sub> apparatus and are uncorrected. All  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 MHz. The NMR spectra were obtained in  $\text{CDCl}_3$  solutions and are reported as parts per million (ppm) downfield from tetramethylsilane as an 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 EI ionization mode with an ionization voltage of 70 eV. The SEM of nano catalyst was performed on a KYKY EM 3200 SEM instrument. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company).

### 4.2.1. Preparation of nano $\text{BF}_3/\text{SiO}_2$ as catalyst

For preparation of nano  $\text{BF}_3/\text{SiO}_2$ , to a mixture of 0.65 g nano-silicagel and 5 ml chloroform, 0.35 g  $\text{BF}_3$  (0.65 ml of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ) was added drop-wise to the reaction mixture over a period of 70 min at room temperature with stirring. Then after completion of the reaction,  $\text{Et}_2\text{O}$  and  $\text{CHCl}_3$  were evaporated from the reaction mixture by heating to obtain dry nano  $\text{BF}_3/\text{SiO}_2$ . [16–18]

### 4.2.2. General procedure for the synthesis of 2-arylbenzothiazoles catalyzed by nano $\text{BF}_3/\text{SiO}_2$

To a mixture of 2-aminothiophenol (1 mmol, 0.995 g) and aldehyde (1 mmol) in ethanol (10 ml), nano  $\text{BF}_3/\text{SiO}_2$  (0.05 g, 25 mol%  $\text{BF}_3$ ) was added in a beaker and the reaction mixture was mixed properly with the help of a glass rod and stirred in ambient temperature for the time indicated in Table 3. The progress of the reaction was monitored by TLC (ethylacetate: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 and the catalyst residue was washed with acetone and reused. All of the 2-arylbenzothiazole products were identified by physical and spectroscopic data as follows.

4.2.2.1. *2-(2-Hydroxyphenyl)-benzothiazole*. Yellow solid; m.p. = 127–128°C (m.p. = 126–128°C) [19]; IR (KBr)/ $\nu(\text{cm}^{-1})$ : 3285, 3090, 2900, 1619, 1590, 1490, 1423, 874, 751;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )/ $\delta$  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);  $^{13}\text{C}$  NMR/(100 MHz,  $\text{CDCl}_3$ )/ $\delta$  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).

4.2.2.2. *2-Phenyl-benzothiazole*. White solid; m.p. = 110–112°C (m.p. = 111–112°C) [19]; IR (KBr)/ $\nu(\text{cm}^{-1})$ : 3066, 3017, 2835, 1608, 1587, 1476, 1430, 830, 763;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )/ $\delta$  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);  $^{13}\text{C}$  NMR/(100 MHz,  $\text{CDCl}_3$ )/ $\delta$  ppm: 121.50, 123.38, 125.07, 126.36, 127.58, 128.91, 130.77, 133.89, 135.11, 155.05,



167.98. MS (EI,  $m/z$ ): 211 (M<sup>+</sup>, 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).

4.2.2.3. *2-(4-Methoxyphenyl)-benzothiazole*. White solid; m.p. = 120–122°C (m.p. = 120–122°C) [20]; IR (KBr)/ $\nu(\text{cm}^{-1})$ : 3021, 3048, 2837, 1609, 1590, 1483, 830;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )/ $\delta$  ppm: 3.89 (s, 3H,  $\text{OCH}_3$ ) 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);  $^{13}\text{C}$  NMR/(100 MHz,  $\text{CDCl}_3$ )/ $\delta$  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<sup>+</sup>, 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).

4.2.2.4. *2-(4-Nitrophenyl)-benzothiazole*. Yellow solid; m.p. = 227–229°C (m.p. = 226–228°C) [20]; IR (KBr)/ $\nu(\text{cm}^{-1})$ : 3042, 2937, 1520, 1461, 1342, 1106, 851, 762;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )/ $\delta$  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);  $^{13}\text{C}$  NMR/(100 MHz, DMSO)/ $\delta$  ppm: 121.85, 123.94, 124.32, 126.24, 126.94, 128.23, 133.1, 135.40, 148.8, 154.0, 164.90.

4.2.2.5. *2-(2,3-Dichlorophenyl)-benzothiazole*. White solid; m.p. = 118–120°C (119–121) [19]; IR (KBr)/ $\nu(\text{cm}^{-1})$ : 3020, 2900, 1635, 1512, 1470, 1432, 1348, 780;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )/ $\delta$  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);  $^{13}\text{C}$  NMR/(100 MHz,  $\text{CDCl}_3$ )/ $\delta$  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. MS (EI,  $m/z$ ): 281 (0.7), 280 (M<sup>+</sup>, 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).

4.2.2.6. *2-(3-Nitrophenyl)-benzothiazole*. Colorless solid; m.p. = 181–183°C (m.p. = 181–182°C) [20]; IR (KBr)/ $\nu(\text{cm}^{-1})$ : 3039, 2936, 1522, 1460, 1345, 1103, 1041, 851, 750;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )/ $\delta$  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);  $^{13}\text{C}$  NMR/(100 MHz, DMSO)/ $\delta$  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.

4.2.2.7. *2-(2-Nitrophenyl)-benzothiazole*. Brown solid; m.p. = 94–96°C (m.p. = 95–97°C) [19]; IR (KBr)/ $\nu(\text{cm}^{-1})$ : 3033, 2930, 1545, 1466, 1349, 1111, 880, 851, 762;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )/ $\delta$  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);  $^{13}\text{C}$  NMR/(100 MHz, DMSO)/ $\delta$  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.

4.2.2.8. *2-(4-Methylphenyl)-benzothiazole*. White solid; m.p. = 82–84°C (m.p. = 83–85°C) [19]; IR (KBr)/ $\nu(\text{cm}^{-1})$ : 3024, 2905, 1610, 1519, 1480, 1435, 1383, 1312, 821, 759;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )/ $\delta$  ppm: 2.45 (s, 3H,  $\text{CH}_3$ ) 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);  $^{13}\text{C}$  NMR/(100 MHz,  $\text{CDCl}_3$ )/ $\delta$  ppm: 23.6, 110.42, 120.33, 121.76, 123.34, 128.56, 132.67, 143.15, 155.63, 160.83, 165.11.

4.2.2.9. *2-(4-Chlorophenyl)-benzothiazole*. Yellow solid; m.p. = 114–116°C (116–118) [20]; IR (KBr)/ $\nu(\text{cm}^{-1})$ : 3055, 2358, 1560, 1455, 1430, 1317, 1275, 1060, 965, 750, 725;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )/ $\delta$  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);  $^{13}\text{C}$  NMR/(100 MHz,  $\text{CDCl}_3$ )/ $\delta$  ppm: 121.8, 123.13, 125.17, 126.80, 129.10, 129.78, 132.67, 135.2, 137.1, 154.4, 166.21.

4.2.2.10. *2-(4-N, N-dimethylphenyl)-benzothiazole*. Brown solid; m.p. = 160–162°C (160–162) [19]; IR (KBr)/ $\nu(\text{cm}^{-1})$ : 3355, 2358, 1598, 1478, 1210, 1017, 965, 743;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )/ $\delta$  ppm: 3.08 (s, 6H,  $\text{N}(\text{CH}_3)_2$ ) 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);  $^{13}\text{C}$  NMR/(100 MHz,  $\text{CDCl}_3$ )/ $\delta$  ppm: 39.8, 111.13, 121.1, 122.0, 124.1, 126.78, 128.67, 135.2, 152.1, 154.4, 168.2.

4.2.2.11. *2-(2-Chlorophenyl)-benzothiazole*. Colorless solid; m.p. = 72–74°C (72–74) [20]; IR (KBr)/ $\nu(\text{cm}^{-1})$ : 2955, 1538, 1502, 1421, 1242, 1117, 965, 750, 733;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )/ $\delta$  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);  $^{13}\text{C}$  NMR/(100 MHz,  $\text{CDCl}_3$ )/ $\delta$  ppm: 111.8, 123.13, 124.17, 125.80, 128.19, 129.88, 131.67, 134.21, 137.1, 143.51, 154.4, 162.21.

4.2.2.12. *2-(2-Methylphenyl)-benzothiazole*. Yellow solid; m.p. = 53–55°C (m.p. = 54–56°C) [19]; IR (KBr)/ $\nu(\text{cm}^{-1})$ : 3040, 2980, 1598, 1550, 1451, 1244, 1115, 862, 754;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )/ $\delta$  ppm: 2.47 (s, 3H,  $\text{CH}_3$ ) 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);  $^{13}\text{C}$  NMR/(100 MHz,  $\text{CDCl}_3$ )/ $\delta$  ppm: 22.6, 112.13, 119.38, 120.53, 122.34, 126.17, 130.67, 144.15, 152.68, 159.93, 162.17.

## Funding

The authors are grateful to University of Kashan for supporting this work by [Grant No. 159148/18].

## Supplemental data

Supplemental data for this article can be accessed at <http://dx.doi.org/10.1080/17415993.2014.917377>.

## References

- [1] Horton DA, Bourne GT, Smythe ML. The combinatorial synthesis of bicyclic privileged structures or privileged substructures Chem Rev. 2003;103(3):893–930.
- [2] Benzzaous A, Boroud T, Dubedat P, Boireau A, Stutzmann J, Gross C, Riluzole prevents MPTP-induced parkinsonism in the rhesus monkey: a pilot study. Eur J Pharmacol. 1995;284:299–307.
- [3] Sharghi H, Omid A. Methanesulfonic acid/ $\text{SiO}_2$  as an efficient combination for the synthesis of 2-substituted aromatic and aliphatic benzothiazoles from carboxylic acids. Synth Commun. 2009;39:860–867.
- [4] Alagile D, Baldwin RM, Tamagnan GD. One-step synthesis of 2-arylbenzothiazole ('BTA') and benzoxazole precursors for in vivo imaging of  $\beta$ -amyloid plaques. Tetrahedron Lett. 2005;46:1349–1351.
- [5] Ben-Alloum A, Bakkas S, Soufiaoui M. Nouvelle Voie de Synthèse des 2-Arylbenzothiazoles Transfert d'Electrons Activé par Micro-ondes. Tetrahedron Lett. 1997;38:6395–6396.
- [6] Itoh T, Nagata K, Ishikawa H, Ohsawa A. Synthesis of 2-arylbenzothiazoles and imidazoles using scandium triflates as a catalyst for both a ring closing and oxidation steps. Heterocycles. 2004;63:2769–2783.
- [7] Praveen C, Kumar KH, Muralidharan D, Perumal PT. Oxidative cyclization of thiophenolic and phenolic Schiff's bases promoted by PCC: a new oxidant for 2-substituted benzothiazoles and benzoxazoles. Tetrahedron. 2008;64:2369–2374.
- [8] Chakraborti AK, Selvam C, Kaur G, Bahagat S. Carboxylic acids are converted to benzothiazoles by direct condensation with 2-aminothiophenol under microwave irradiation in the absence of solvent. Synlett. 2004;5:851–855.
- [9] Mutsushita H, Lee SH, Joung M, Clapham B, Janda KD. Smart cleavage reactions: the synthesis of benzimidazoles and benzothiazoles from polymer-bound esters. Tetrahedron Lett. 2004;45:313–316.

- [10] Fazaeli R, Aliyan H. A Heterogeneous catalyst for efficient and green synthesis of 2-arylbenzothiazoles and 2-arylbenzimidazoles. *Appl Catal A*. 2009;353:74–79.
- [11] Algul O, Kaessler A, Apcin Y, Yilmaz A, Jose J. Comparative studies on conventional and microwave synthesis of some Benzimidazole, Benzothiazole and Indole derivatives and testing on inhibition of Hyaluronidase. *Molecules*. 2008;13:736–748.
- [12] Ranu BC, Jana R, Dey S. An efficient and green synthesis of 2-arylbenzothiazoles in an ionic liquid, [pmIm]Br under microwave irradiation. *Chem Lett*. 2004;33:274–275.
- [13] Kawashita Y, Ueba C, Hayashi M. A simple synthesis of 2-arylbenzothiazoles and its application to palladium-catalyzed Mizoroki–Heck reaction. *Tetrahedron Lett*. 2006;47:4231–4233.
- [14] Naeimi H, Tarazian R. Efficient and facile catalyst-free one-pot synthesis and characterization of some novel bis(2-benzothiazole) derivatives. *J Heterocycl Chem*. 2013. .
- [15] Naeimi H, Moradi L. Microwave assisted direct ortho-acylation of phenol and naphthol derivatives by  $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$ . *Bull Chem Soc Jpn*. 2005;78:284–287.
- [16] Safari J, Banitaba SH, Khalili S.  $\text{BF}_3$ -nano  $\text{SiO}_2$  as a catalytic system for one-pot green synthesis of pyrophthalone derivatives under microwave conditions: 1st Nano Update. *Arab J Chem*. 2012;5:419–424.
- [17] Wilson K, Clark JH. Synthesis of a novel supported solid acid  $\text{BF}_3$  catalyst. *Chem Commun*. 1998;2135–2136.
- [18] Mirjalili BF, Bamoniri A, Akbari A. Nano- $\text{BF}_3 \cdot \text{SiO}_2$ : a reusable and eco-friendly catalyst for thioacetalization and trans-thioacetalization reactions. *Iran J Catal*. 2011;1(2):87–92.
- [19] Maleki B, Salehabadi H, Khodaverdian Moghaddam M. Room-temperature synthesis of 2-arylbenzothiazoles using sulfuric acid immobilized on silica as a reusable catalyst under heterogeneous condition. *Acta Chim Slov*. 2010;57:741–745.
- [20] Niralwad KS, Shingate BB, Shingare MS. Solid-phase synthesis of 2-arylbenzothiazole using silica sulfuric acid under microwave irradiation. *Bull Korean Chem Soc*. 2010;31(4):981–983.