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A C G publications

Org. Commun. xx:xx (2017) xx-xx

organic communications

Lanthanum (III) nitrate hexahydrate catalyzed one-pot synthesis of 2-arylbenzothiazoles under mild reaction conditions

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(Received August 02, 2017; Revised September 13, 2017; Accepted September 28, 2017)

Abstract: An efficient one pot synthesis of 2-arylbenzothiazole derivatives through condensation of aldehydes and 2-aminothiophenol in the presence of catalytic amount of $La(NO_3)_3 \cdot 6H_2O$ under mild reaction conditions was developed. The key advantages of this protocol are short reaction time, high to excellent yields, simple work up, inexpensive catalyst and simple separation of pure product.

Keywords: Aromatic aldehyde; 2-aminothiophenol; Lanthanum (III) nitrate hexahydrate.

1. Introduction

Chemistry of heterocyclic compounds is one of the leading research subjects in organic chemistry. Heterocyclic compounds are widely distributed in nature and are essential for life. They play a vital role in metabolism of all living cells. There are vast numbers of pharmacologically active heterocyclic compounds, many of which are in regular clinical use. Nitrogen, sulfur and oxygen containing five membered heterocyclic compounds have occupied enormous significance in the field of drug discovery process. Benzothiazole and its derivatives are often found in heterocyclic compounds, which exhibit a variety of biological activities, such as anti-viral, [1] anti-bacterial,[2] anti-fungal,[3] anti-microbial, [4] anti-Parkinson,[5] anti-cancer[6] and anti-tumor.[7] Moreover, they are also used as drugs for treatment of diabetes.[8] Benzothiazole unit is found in *zopolrestat* [9] and *riluzole*,[10] which are used to treat diabetes.

Due to their wide range of synthetic, industrial and pharmacological applications, synthesis of substituted benzothiazoles has become a focus of intense research in recent years. Several synthetic methodologies have been developed for the synthesis of 2-substituted benzothiazoles, including

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The article was published by ACG Publications
www.acgpubs.org/OC/index.htm © Published online 10/07/2017 EISSN:1307-6175
DOI: http://doi.org/10.25135/acg.oc.29.17.08.044

condensation of 2-aminothiophenol with substituted nitriles, carboxylic acids, aldehydes, acyl chlorides and esters, followed by an oxidation. Different catalysts were reported to be applied for the synthesis of these heterocycles like silica gel,[11] HBF_4-SiO_2,[12] bakers' yeast,[13] CAN,[14] copper-catalyzed Tandem Reaction,[15] $K_2S_2O_8$,[16-17] SDS,[18] PEG-400,[19] L-proline,[20] PTSA,[21] CTAB,[22] acetic acid,[23] silica sulfuric acid,[24] PCC/silica,[25] SBA-Pr-SO_3H,[26] sulfamic acid,[27] vanadium(IV)salen,[28] $FeCl_3$/montmorillonite K-10,[29] ammonium chloride,[30] $Sm(OTf)_3$,[31-32] BF_3/SiO_2,[33] lithium bromide,[34] Ag_2CO_3/Celite,[35] Fe_3O_4@SiO_2/collagen,[36] ruthenium (I) complexes,[37] $VOSO_4$,[38] $Co(NO_3)_2$ $6H_2O$,[39] $Fe(NO_3)_3$:$9H_2O$,[40] $Bi(NO_3)_3$,[41] $CuSO_4$,[42] $Zn(OTf)_2$[43] and $LaCl_3$.[44]

However, many of these methods suffer from one or more of the drawbacks such as requirement of strong acidic conditions, long reaction times, low yields, tedious work-up procedures, requirement of excess amounts of reagent and use of toxic reagents, catalysts or solvents. Therefore, there is a strong demand for a highly efficient and environmentally benign method.

Lanthanum (III) nitrate have recently attracted much attention in organic transformations due to its high acidity, thermal stability, low toxicity, low cost and good stability, Furthermore, current literature reveals that Lanthanum (III) nitrate has been utilized as an effective catalyst in the synthesis of 4-(3*H*)-quinazolinones under solvent-free conditions, chiral tetrahydroquinolino pyranose derivatives, chemoselective deprotection of acetonides, chemoselective protection of amines as *N*-benzyloxycarbonyl derivatives, acetylation of alcohols, phenols and amines with acetic anhydride and synthesis of α-amino nitriles.[45-50]

In continuation of our ongoing research to develop novel methodologies in synthetic organic chemistry, [51-53] we report herein an efficient, low cost and environmentally benign protocol for the synthesis of 2-arylbenzothiazole using Lanthanum (III) nitrate hexahydrate catalyst under mild reaction condition.

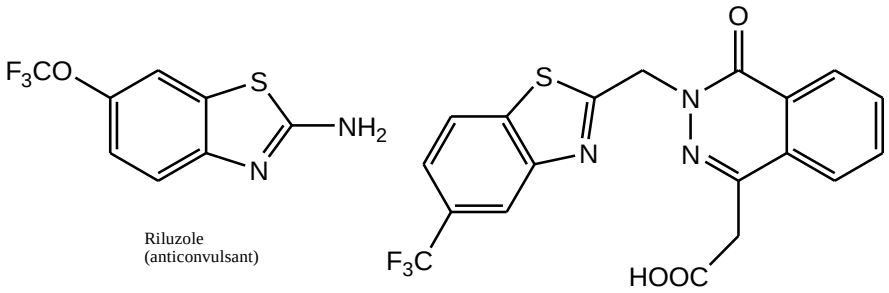


Figure 1. Benzthiazole containing important commercial drugs

2. Experimental

2.1. Materials and Apparatus

The chemicals and solvents were purchased from commercial suppliers (Merck, S.D. fine and Spectrochem) and they were used without purification prior to use. Melting points were recorded by open tube capillary method and are uncorrected. The progress of the reaction and the purity of the compounds were monitored by thin-layer chromatography (TLC), using analytical silica gel plates (Merck 60 F250). ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 and 100 MHz, respectively. NMR spectra were obtained in $CDCl_3$ solutions and are reported as parts per million (ppm) downfield from tetramethylsilane (TMS) as internal standard and the coupling constants (*J*) are expressed in Hertz (Hz). Mass spectra were recorded on a macro mass spectrometer, applying electrospray ionization (ESI) method. To see the spectra of compounds please see the supporting infotmation (Figure S1-S18).

2.2 General Procedure for the Synthesis of 2-Aryl benzothiazole:

$La(NO_3)_3.6H_2O$ (15 mol%) was added to a stirred solution of the aldehyde (1.0 mmol) and 2-aminothiophenol (1.0 mmol) in ethanol (5 mL) and the mixture was stirred at room temperature for appropriate time (Table 2). The progress of the reaction was monitored by thin layer chromatography (TLC) (Hexane: Ethyl acetate, 8:2). After the reaction was completed, the pure products were isolated by filtration. The solid product was purified by recrystallization from ethanol. Selected spectral data of compounds are given below.

*2-(4-Methylphenyl)-benzothiazole (**3b**) (Table 2 entry 3b)* White solid; IR (KBr) ν (cm^{-1}): 3026, 2811, 2343, 1606, 1581, 1520, 1361, 1297, 1258, 1152, 1034, 951, 867 and 659 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: δ 8.00-8.06 (3H, m, Ar-H), 7.96 (1H, d, *J* = 8.0 Hz, Ar-H),7.51 (1H, t, *J* = 8.4 Hz, Ar-H), 7.41 (1H, t, *J* = 8.4 Hz, Ar-H), 7.36 (2H, d, *J* = 8.1 Hz, Ar-H) , 2.45 (3H, s, -CH_3) , ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: δ 168.0, 154.2, 141.6, 135.0, 131.0, 129.7, 127.3, 126.2, 125.0, 122.9, 121.6 and 21.2; MS: *m/z* 225.1234 $[M + 1]^+$

*2-(4-Methoxyphenyl)-benzothiazole (**3c**) (Table 2 entry 3c)* White solid; IR (KBr) ν (cm^{-1}): 3021, 3048, 2837, 1609, 1590, 1483, 830; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.03-8.08 (3H, m, Ar-H) 7.91 (1H, d, *J*=8.0 Hz, Ar-H),7.48 (1H, t, , *J*=8.0 Hz, Ar-H), 7.37 (1H, t, *J*=8.0 Hz, Ar-H), 7.02 (2H, d, *J*=8.4 Hz, Ar-H), 3.89 (3H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm:, 167.6, 162.0, 154.3, 134.9, 129.0, 126.3, 126.1, 124.7, 122.7, 121.5, 114.3, 55.4; MS: *m/z* 242.0649 $[M + 1]^+$

*2-(4-Chlorophenyl)-benzothiazole (**3d**) (Table 2 entry 3d)* Yellow solid; IR (KBr) ν (cm^{-1}): 3051, 2326, 1600, 1434, 1372, 1313, 1168, 1064, 945, 821; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.06 (1H, d, *J*=8.2 Hz, Ar-H), 8.01 (2H, d, *J*=8.5 Hz, Ar-H), 7.89 (1H, d, *J*=8.0 Hz, Ar-H), 7.47 (3H, m, Ar-H), 7.40-7.36 (1H, m, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 166.5, 154.0, 137.0, 135.0, 132.1, 129.2, 128.7, 126.4, 125.4, 123.3, 121.6; MS: *m/z* 246.0143 $[M + 1]^+$

*2-(4-N,N-Dimethylphenyl)-benzothiazole (**3g**) (Table 2 entry 3g)* Yellow solid; IR (KBr) ν (cm^{-1}): 3052, 1600, 1435, 1372, 1313, 1168, 1037, 946, 821; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.86 (2H, d, *J*=8.5 Hz); 7.62 (1H, d, *J*=7.8 Hz); 7.16 (1H, t, *J*=7.7 Hz); 7.08 (1H, t, *J*=7.6 Hz); 7.02 (1H, d, *J*=7.6Hz); 6.75 (2H, d, *J*=8.9 Hz); 3.07(6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 159.59, 152.7, 149.7, 131.8, 130.8, 128.8, 126.5, 125.8, 125.5, 124.4, 117.1, 111.5, 40.1; MS: m/z 254.09, 157.9, 131.9, 114.0, 102.1, 86.2, 72.4

*2-(4-Bromophenyl)-benzothiazole (**3k**) (Table 2 entry 3k)* White solid; IR (KBr) ν (cm^{-1}): 3000, 1400-1600. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm : 8.11 (1H, d, *J* = 8.0 Hz, Ar-H), 8.0 (2H, d, *J* = 8.5 Hz, Ar-H), 7.94 (1H, d, *J* = 8.0 Hz, Ar-H), 7.67 (2H, d, *J* = 8.5 Hz, Ar-H),7.55 (1H, t, *J* = 8.0 Hz, Ar-H),7.44 (1H, t, *J* = 8.0 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm : 167.1, 154.5, 135.4, 133.0, 132.6, 129.3, 126.9, 125.8, 125.8 , 123.7, 122.0; MS: *m/z* 289.9638 $[M + 1]^+$

*2-(3-Nitrophenyl)-benzothiazole (**3m**) (Table 2 entry 3m)* Yellow solid; IR (KBr) ν (cm^{-1}): 3080, 3035, 1612, 1580; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm: 8.95 (1H, d *J* = 8.0 Hz), 8.45 (1H, d, J = 8.0 Hz, 1H), 8.36 (1H, d, *J* = 8.0 Hz), 8.15 (1H, d, *J* = 8.0 Hz), 7.98 (1H, d, *J* = 8.0 Hz), 7.73 (1H, t, *J*=7.9 Hz), 7.59 (1H, *J*=7.5 Hz), 7.49 (1H, *J*=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm : 164.9, 153.9, 148.7, 135.3, 135.1, 133.0, 130.1, 126.8, 126.0, 125.2, 123.7, 122.3, 121.8, MS: m/z 257.0379 $[M + 1]^+$

3. Results and Discussion

To explore the use of Lanthanum (III) nitrate hexahydrate as a catalyst, a reaction of benzaldehyde **2** and 2- aminothiophenol **1** was conducted as a standard model reaction for the preparation of 2-arylbenzothiazoles (**3a-3n**) (Scheme 1). The reaction in the absence of catalyst did

not give any desired product. To determine the exact amount of the catalyst, we investigated the model reaction using different concentrations of Lanthanum (III) nitrate hexahydrate (Table 1). During this study, we observed that 15 mol% Lanthanum (III) nitrate hexahydrate was proved to be an efficient catalyst to conduct the reaction smoothly. With these optimized reaction conditions, effect of different solvents such as methanol, dichloromethane, acetonitrile, THF, ethanol, aqueous ethanol and water was investigated (entries 1-7, Table 1). Among the tested solvents, ethanol was found to be superior over the other tested solvents in terms of both yield and reaction time (Table 1 Entry 10) for this transformation.

Table 1. Effect of solvent and catalyst evaluation in synthesis of 2-phenylbenzothiazole at room temperature[a]

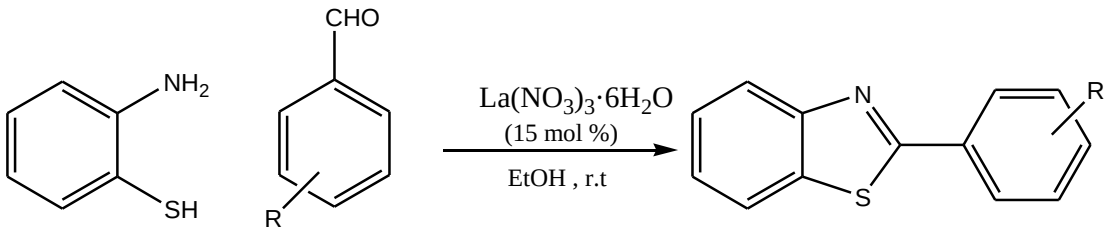
Entry	Solvent	Catalyst (mol %)	Time (min.)	Yield[b] (%)
1	THF	10	45	62
2	CH_3CN	10	45	72
3	CH_3OH	10	45	82
4	CH_2Cl_2	10	45	56
5	H_2O	10	45	60
6	EtOH:H_2O	10	45	68
7	EtOH	5	57	75
8	EtOH	7	50	80
9	EtOH	10	45	88
10	EtOH	15	30	94
11	EtOH	20	30	95

[a]Reaction conditions: benzaldehyde(1 mmol), 2-aminothiophenol (1 mmol), Lanthanum (III) nitrate hexahydrate (15 mol%) in ethanol (5 mL) at room temperature. [b]Isolated yield.

Encouraged by this result, in order to build the generality of the reaction, various aromatic aldehydes, posessing electron-donating and electron-withdrawing groups were converted to 2-arylbenzothiazole derivatives in good to excellent yields. All the results are summarized in Table 2.

In order to understand the efficiency and greenness of the method, we compared our results on the synthesis of 2-phenyl benzothiazole with the well-known data from the literature (Table 3). As shown in the Table 3, many of the previously reported methodologies suffer from one or more disadvantages such as requirement of excess amount of catalyst, high temperature, ultrasound irradiation, prolonged reaction time, and use of volatile and toxic organic solvents. Thus, the present method avoids the disadvantages of the previously reported methodologies.

The mechanism for 2-aryl benzothiazole formation is proposed in scheme 2. Lanthanum (III) nitrate hexahydrate appears to play a more efficient catalytic role due to strong oxophilicity. Initially, aldehyde molecules co-ordinate through their carbonyl oxygen atoms to the lanthanum ion and facilitate the nucleophilic attack. The reaction between an aldehyde and thiol leads to the formation of sulfonium ion intermediate. Then, intramolecular attack by the second group on C=S double bond followed by air oxidation gives the final product.



1 2 3a-n

Scheme 1. Synthesis of 2-arylbenzothiazole

Table 2. Synthesis of 2-arylbenzothiazole in the presence of Lanthanum (III) nitrate hexahydrate[a]

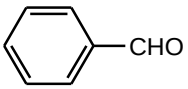
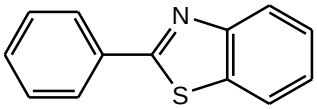
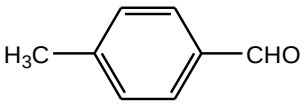
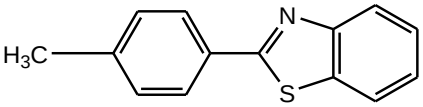
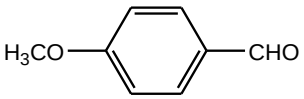
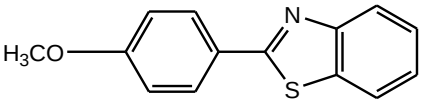
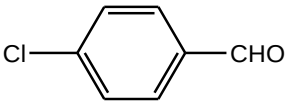
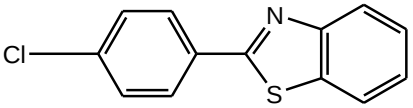
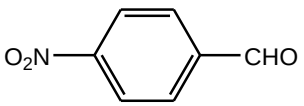
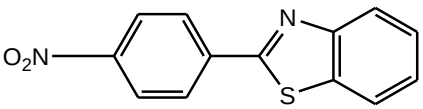
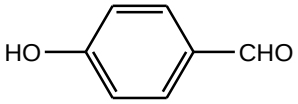
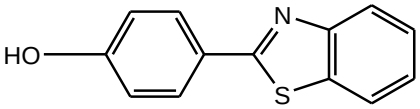
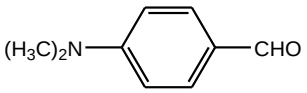
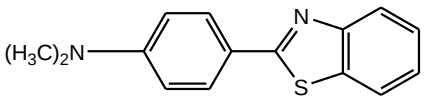
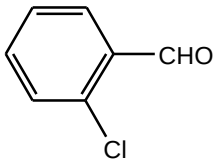
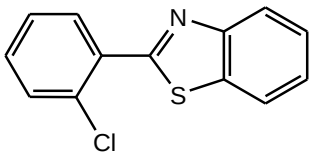
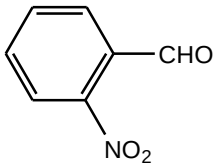
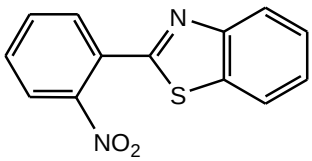
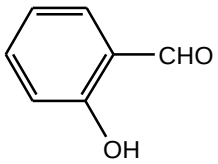
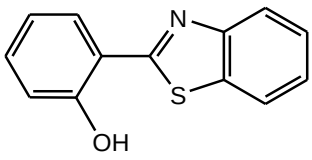
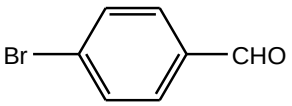
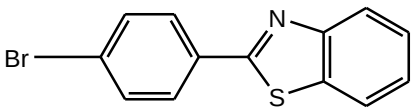
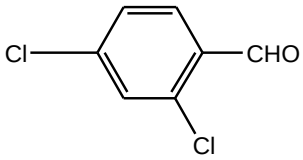
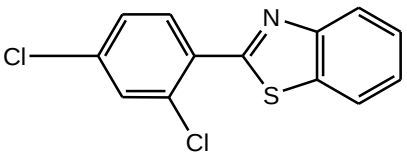
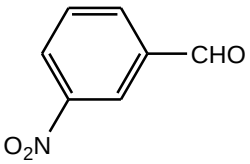
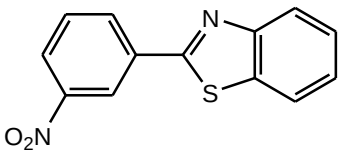
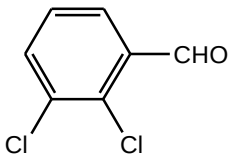
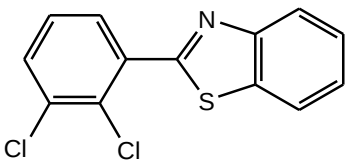
Entry	Aldehydes	Products	Time (min)	Yield[b] (%)	M.P °C [Ref.]
3a			30	94	112-114 [14]
3b			35	96	80–82 [27]
3c			35	94	125-126 [14]
3d			30	96	114–116 [27]
3e			32	96	224-226 [14]
3f			40	92	228–230 [27]

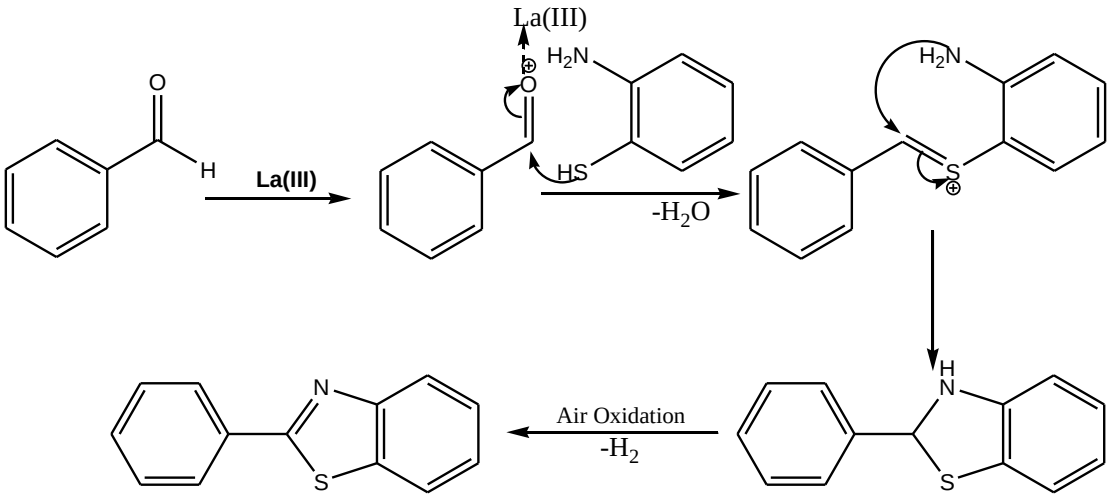
Table 2 Continued..

3g			35	95	172–174 [27]
3h			35	90	74-76 [14]
3i			35	91	122–123 [27]
3j			40	87	130–132 [27]
3k			35	95	130-132 [27]
3l			35	94	218-220 [36]
3m			35	91	182-184 [14]
3n			35	93	116-119 [33]

[a]Reaction conditions: Aromatic aldehyde (1 mmol), 2-aminothiophenol (1 mmol), Lanthanum (III) nitrate hexahydrate (15 mol%) at room temperature. [b]Isolated yield.

Table 3. Comparison of the activity of various catalysts for the synthesis of 2-arylbenzothiazole from the condensation of benzaldehyde and 2-aminothiophenol

Entry	Catalyst	Amount of catalyst	Condition	Time	Yield (%) [Ref.]
1	$Co(NO_3)_2\ 6H_2O$	2 mmol	DMF/80 °C	15 min	93 [39]
2	$Ni(NO_3)_2\ 6H_2O$	2 mmol	DMF/80 °C	90 min	85 [39]
3	$Fe(NO_3)_3{:}9H_2O$	5 mol %	$P(tBu)_3{:}HBF_4$ DMSO:H_2O, 120°C	24 h	89 [40]
4	$Bi(NO_3)_3$	0.15 mmol	aq.30 % H_2O_2 in ethanol, Reflux	20 min	90 [41]
5	$CuSO_4$	10 mol %	Glycerol /))))	70 min	91 [42]
6	$Sm(OTf)_3$	10 mol %	EtOH:H_2O, 50-60 °C	2-5 h	89 [31-32]
7	$Zn(OTf)_2$	10 mol %	Ethanol,Reflux	5 h	92 [43]
8	Fe_3O_4@SiO_2/Collagen	50 mg	EtOH, Reflux	1.5 h	70 [36]
9	$VOSO_4$	3 mol %	EtOH , r.t	60 min	92 [38]
10	BF_3/SiO_2	0.05g,25mol% BF_3	EtOH , r.t	30 min	85 [33]
12	$La(NO_3)_3{\cdot}6H_2O$	15 mol%	EtOH , r.t	30 min	94 Present work



Scheme 2. A plausible mechanism for synthesis of 2-arylbenzothiazoles in the presence of Lanthanum (III) nitrate hexahydrate

4. Conclusion

In summary, we have developed a facile, efficient and green method for the synthesis of 2-substituted benzothiazoles through condensation of aromatic aldehydes with 2-aminothiophenol in the presence of Lanthanum (III) nitrate hexahydrate under mild reaction conditions. Compare with the previously reported methodologies, the present protocol features simple work-up, environmentally benign, high yields and use of catalytic amount of a cheap catalyst.

Acknowledgements

Authors are pleased to acknowledge financial support received from Department of Science and Technology (SERB/F/4992/2013-14 dated 30/01/2013), New Delhi. Authors are also thankful to Principal, Kalikadevi (ACS) College, Shirur (Ka.) Dist. Beed for providing necessary laboratory facilities to carry out this work.

Supporting Information

Supporting Information accompanies this paper on http://www.acgpubs.org/OC

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