Res Chem Intermed
DOI 10.1007/s11164-013-1529-x

An economic, simple and convenient synthesis of 2-aryl/heteroaryl/styryl/alkylbenzothiazoles using SiO_2–HNO_3

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Received: 22 August 2013 / Accepted: 30 December 2013

Abstract The present work was undertaken to develop an economic method for the synthesis of 2-aryl/heteroaryl/styryl/alkylbenzothiazoles mediated by SiO_2–HNO_3. In this report, we have demonstrated the catalytic potential of SiO_2–HNO_3 for the oxidative condensation of 2-aminothiophenol and aldehydes. Instant reaction at room temperature under solvent-free condition, high substrate to catalyst ratio 50:1 (by weight), practical application by large-scale synthesis, and excellent yields are the main advantages of the present protocol.

Keywords 2-Aminothiophenol · Aldehydes · 2-Aryl/heteroaryl/styryl/alkylbenzothiazoles · Nitric acid · Silica gel

Introduction

2-Aryl/styryl/alkylbenzothiazoles are an important class of heterocyclic compounds due to their wide range of applications [1–9] in medicinal, industrial, and agricultural chemistry, material chemistry, and nonlinear optics. For this reason, synthesis of this heterocyclic moiety has attracted much attention and many methods [10–34] have been developed (Scheme 1). Out of these, the most popular approach involves the direct condensation of 2-aminothiophenol with aryl

Electronic supplementary material The online version of this article (doi:10.1007/s11164-013-1529-x) contains supplementary material, which is available to authorized users.

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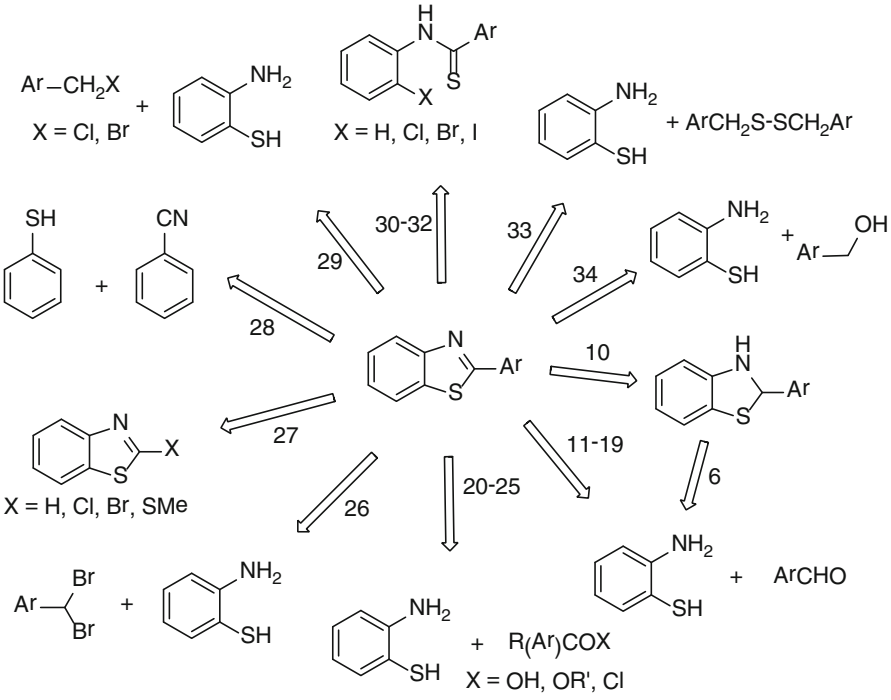
Published online: 23 January 2014

aldehydes under oxidative conditions [11–19]. However, the utility and practical applicability of the above methods suffer from certain disadvantages such as expensive catalysts [27, 31, 32], prolonged reaction times [17, 21, 31, 32], poor yields [33], by-products [28], high reaction temperature [17, 30, 32], tedious procedure [26, 31, 32], and usage of toxic organic solvents [22, 29, 31, 34]. Recently, green protocols have been extensively studied [35–38], which would provide a more convenient and efficient technique for the production of the benzothiazole skeleton.

Over recent years, supported reagents [39, 40] have occupied an important place in the realm of synthetic organic chemistry, mainly because of the advantages over unsupported reagents such as cleaner reactions, easier work-up, high yield, milder conditions, reduced reaction times, and above all environmentally benign.

Nitric acid supported on a silica gel (SiO_2–HNO_3) catalyst is an inexpensive and easily available oxidizing reagent that possesses high efficiency in organic transformations [41, 42]. With our continuing interest in the development of new methodologies [43] and in a quest to design an economic method, here, we selected the SiO_2–HNO_3 as a catalyst for oxidative cyclocondensation of 2-aminothiophenol with various aldehydes for the synthesis of 2-aryl/heteroaryl/styryl/alkylbenzothiazoles under solvent-free conditions.



Scheme 1 Strategies for synthesis of 2-arylbenzothiazoles

Experimental

Chemicals used

All chemicals were commercial products. High purity grade *o*-aminothiophenol (Acros) and aldehydes (Sigma-Aldrich, Himedia, Spectrochem, SDFCL) were used.

Preparation of catalyst

In a conical flask, 10 ml conc. HNO_3 was added to 5 g silica gel (Acme's; 100–200 mesh size) and stirred for 10 min. Filtering produced a white solid which was kept in an oven for 10 min at 120 °C to activate the catalyst.

Acidity of reagents The neutralization titration gave us the acidity of 0.080352 g (NaOH)/1 g SiO_2–HNO_3.

General procedure for the synthesis of 2-aryl/heteroaryl/styryl/alkylbenzothiazoles 3

To a mixture of 2-aminothiophenol **1** (2.0 mmol) and aryl/heteroaryl/styryl/alkyl aldehyde **2** (2.0 mmol) in a vial was added SiO_2–HNO_3 (2 wt% to the aldehyde) and shaken at room temperature. Instantly, an exothermic reaction occurred with completion of the reaction (TLC) and the reaction mixture became a yellowish-orange solid that was directly chromatographed over a silica gel column to afford pure 2-aryl/heteroaryl/styryl/alkylbenzothiazole **3** (Table 3). The spectral data of some selected compounds are given below:

2-(Phenyl)benzothiazole, 3a: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.09–8.15 (m, 3H), 7.93 (d, 8.1 Hz, 1H), 7.38–7.54 (m, 5H)

2-(*p*-Tolyl)benzothiazole, **3b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.08 (d, $J = 8.4$ Hz, 1H), 8.01 (d, $J = 8.1$ Hz, 2H), 7.91 (d, $J = 8.1$ Hz, 1H), 7.47–7.53 (m, 1H), 7.36–7.41 (m, 1H), 7.32 (d, $J = 8.1$ Hz, 2H), 2.45 (s, 3H).

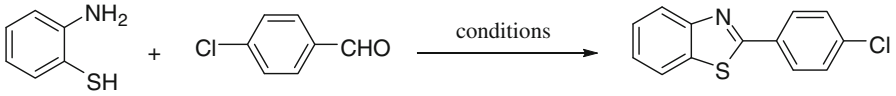
2-(2-Methoxyphenyl)benzothiazole, **3d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.04–8.07 (m, 3H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.34–7.52 (m, 2H), 7.027 (d, 8.7 Hz, 2H), 3.9 (s, 3H).

2-(2-Hydroxyphenyl)benzothiazole, 3h: ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.98 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.49–7.52 (m, 1H), 7.36–7.42 (m, 2H), 7.10 (d, $J = 8.5$ Hz, 1H), 6.94–6.97 (m, 1H).

2-(4-Fluorophenyl)benzothiazole, 3i: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.07–8.17 (m, 3H), 7.92 (d, 8.4 Hz, 1H), 7.38–7.55 (m, 2H), 7.17–7.24 (m, 2H).

2-(2,4-Difluorophenyl)benzothiazole, **3j**: ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.41–8.49 (m, 1H), 8.10 (d, $J = 8.0$ Hz, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.51–7.54 (m, 1H), 7.40–7.43 (m, 1H), 6.97–7.07 (m, 2H); ^{13}C NMR (101 MHz $CDCl_3$,): δ (ppm) 165.47 (d, $J = 10$ Hz), 162.01–163.00 (m), 159.46–160.17 (m), 152.39 (s), 135.42 (d, $J = 8$ Hz), 131.05-131.18 (m), 126.37 (s), 125.34 (s), 123.19 (s), 121.46 (s), 112.28–112.49 (m), 104.65 (t, $J = 25$ Hz).

Table 1 Screening conditions[a]



1 **2m** **3m**

Entry	Catalyst	Time (min)	Yield (%)[a]
1	Catalyst-free	540	14
2	HNO_3 (conc.)	180	76
3	SiO_2–HNO_3	2	87
4	SiO_2 [39]	180	12
5	SiO_2/MW [19]	5	78
6	$Co(No_3)_2{\cdot}6H_2O$[15]	60	74
7	$Bi(NO_3)_2$ [12, 16]	120	79
8	$Ni(NO_3)_2{\cdot}6H_2O$[15]	180	75
9	H_2O_2/CAN [34]	30	83
10	I_2 [13, 36]	60	74
11	NBS [16]	300	71
12	$CuCl_2$ [16]	300	53
13	PTSA [16]	180	78
14	H_3PO_4 [16]	180	72
15	$HClO_4$ [44]	240	80
16	H_2SO_4 (conc.) [16]	300	67
17	SiO_2–H_2SO_4 [37, 38]	108	77

Reaction conditions: 1 (2 mmol), 2 m (2 mmol), catalyst (10 wt% to aldehyde **2m**)

[a] Isolated yield

2-(2,5-Difluorophenyl)benzothiazole, 3k: ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.11–8.16 (m, 2H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.51–7.54 (m, 1H), 7.41–7.44 (m, 1H), 7.12–7.22 (m, 2H); ^{13}C NMR (101 MHz $CDCl_3$,): δ (ppm) 159.66–160.04 (m), 157.56–157.83 (m), 155.32 (d, $J = 4$ Hz), 152.26 (s), 137.81 (d, $J = 7$ Hz), 126.49 (s), 125.62 (s), 123.44 (s), 121.52 (s), 118.48–118.81 (m), 117.45–117.78 (m), 115.51–115.81 (m).

2-(4-Chlorophenyl)benzothiazole, 3m: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.04–8.14 (m, 3H), 7.93 (d, $J = 7.8$ Hz, 1H), 7.48–7.55 (m, 3H), 7.39–7.45 (m, 1H).

2-(4-Nitrophenyl)benzothiazole, **3o**: ^{1}H NMR (300 MHz, $CDCl_3$,): δ (ppm) 8.38 (d, $J = 9.0$ Hz, 2H), 8.29 (d, $J = 9.0$ Hz, 2H), 8.16 (d, $J = 8.1$ Hz, 1H), 7.98 (d, $J = 7.8$ Hz, 1H), 7.55–7.60 (m, 1H), 7.46–7.51 (m, 1H).

Results and discussion

We began our study by the examination of various catalysts for the current reaction using 2-aminothiophenol **1** and 4-chlorobenzaldehyde (**2m**) in a 1:1 ratio as

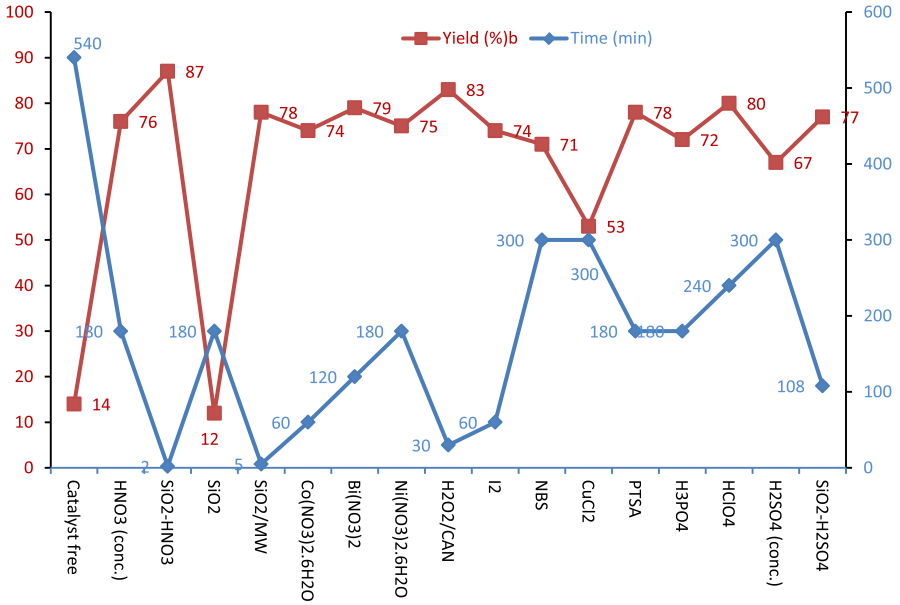


Fig. 1 Graphical representation of screening conditions

Table 2 Optimization of reaction conditions with different ratios of the SiO_2–HNO_3 catalyst for the synthesis of 2-(4-chlorophenyl)benzothiazole **3m**

Entry	Aldehyde 2 m:SiO_2–HNO_3 weight ratio	Reaction condition	Yield (%)[a]
1	50:1	rt/solvent-free	98
2	50:2	rt/solvent-free	97
3	50:3	rt/solvent-free	97
4	50:5	rt/solvent-free	95
5	50:10	rt/solvent-free	71
6	50:20	rt/solvent-free	63
7	50:1	rt/MeOH/10 min	89
8	50:1	rt/CH_3CN/15 min	88
9	50:1	rt/CH_2Cl_2/25 min	81

[a] Product was isolated by column chromatography

substrate (Table 1). In an initial experiment, using traditional conditions, equimolar amounts of 2-aminothiophenol **1** and 4-chlorobenzaldehyde (**2m**) were kept at room temperature with occasional shaking which resulted in a sluggish reaction. After 9 h, only 14 % of product 2-(4-chlorophenyl)benzothiazole (**3m**), was obtained (Table 1, entry 1). To improve the product yield and to optimize the reaction conditions, nitric acid was used in catalytic amount (10 mol%). Under parallel reaction conditions, the speed of the reaction was accelerated, even though in a still unsatisfactory yield (76 %; Table 1, entry 2). We subsequently changed the

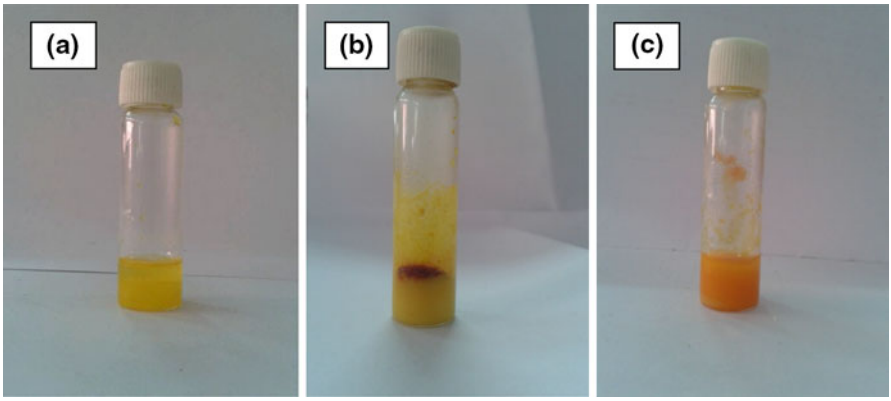


Fig. 2 **a** Reaction after mixing of 2-aminothiophenol and salicylaldehyde. **b** Reaction after adding a pinch of SiO_2–HNO_3. **c** Reaction with excess of SiO_2–HNO_3

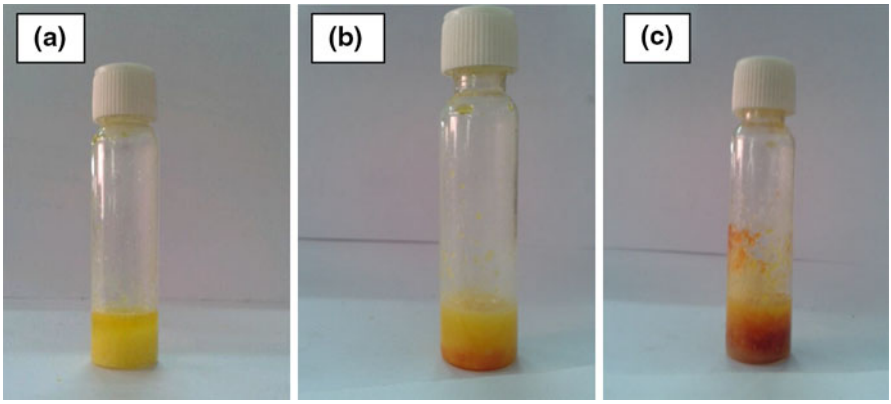


Fig. 3 **a** Reaction after mixing of 2-aminothiophenol and *p*-chlorobenzaldehyde. **b** Reaction after adding a pinch of SiO_2–HNO_3. **c** Reaction after adding excess of SiO_2–HNO_3

reagents from concentrated nitric acid to silica-supported nitric acid (SiO_2–HNO_3, 10 wt%), and a significant improvement was observed in the yield (87 %) after just 2 min (Table 1, entry 3). In order to determine the efficiency of SiO_2–HNO_3 as a catalyst, the same reaction was carried out with other commercially available catalysts [12, 13, 15, 16, 34, 36] (Table 1, entries 6–16) and SiO_2 alone [14, 32] (entries 4 and 5). The results are summarized in Table 1 which revealed that these systems gave lower yields of the product, even with high catalytic loadings, and, in the presence of SiO_2 alone, a very poor yield was obtained after 180 min at room temperature (12 %, entry 4). Graphical representations of yield and reaction times with different reagents are shown in Fig. 1.

A TGA experiment showed that the moisture contained in the freshly prepared SiO_2–HNO_3 was 58 %. Therefore, the catalyst SiO_2–HNO_3 was activated at 120 °C for 10 min, and we investigated the reaction using the same substrates (**1** and **2m**) in

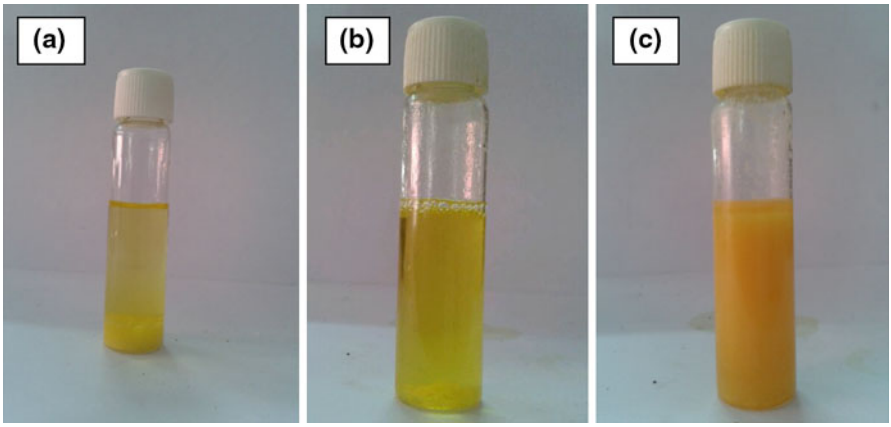


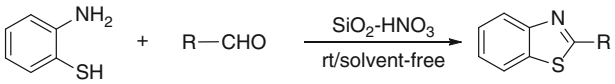
Fig. 4 **a** Reaction after mixing of 2-aminothiophenol and *p*-chlorobenzaldehyde in methanol. **b** Reaction after adding a pinch of SiO_2–HNO_3. **c** Reaction after adding excess of SiO_2–HNO_3

the presence of different ratios of the activated SiO_2–HNO_3 catalyst under the same reaction conditions (Table 2). We found, to our surprise, that the activated SiO_2–HNO_3 catalyst dramatically enhanced the reaction rate and reactions could be accomplished just by shaking the reaction partners at room temperature to furnish the desired product (**3m**) (Figs. 2b, 3b) in excellent yields (95–98 %; Table 2, entries 1–4). It was important to note that, in excess amounts of the catalyst, the reaction mixture became a red-colored paste (Figs. 2c, 3c) and resulted (**3m**) in lower yields (71 %, entry 5; and 63 %, entry 6). Thus, a ratio of 50:1::aldehyde:SiO_2–HNO_3 (2 wt% of SiO_2–HNO_3 to aldehyde, entry 1) was found to be optimum for this reaction and no side product was observed. Finally, using the optimum amount of catalyst, this reaction was also studied in solution phase conditions. Although, good yields were obtained in solution phase conditions, they required a longer reaction time (Table 2, entries 7–9) (Fig. 4b) than the reaction time in solvent-free condition (entry 1).

Using the optimal reaction conditions (SiO_2–HNO_3 catalyst 2 wt% to the aldehyde, solvent-less, room temperature), the applicability of the activated SiO_2–HNO_3 catalyst was then explored for the preparation of a series of 2-aryl/heteroaryl/styryl/alkylbenzothiazoles, **3(a–w)** by the reactions of 2-aminothiophenol **1** with various substituted aryl/heteroaryl/styryl/alkyl aldehydes, **2(a–w)** (Table 3). The results demonstrated that the SiO_2–HNO_3 catalyst was found to be compatible with both electron-donating and electron-withdrawing groups on the aromatic ring of the aldehydes, and no significant substituent effect was observed on the yields of the products. The structures of all synthesized benzothiazoles were supported by their IR, ^{1}H NMR and melting point.

In order to demonstrate the practical application of this protocol on a preparative scale, we carried out some reactions of 2-aminothiophenol (**1**) with 4-methylbenzaldehyde (**2b**), 2-hydroxybenzaldehyde (**2h**), 4-chlorobenzaldehyde (**2m**) and 4-nitrobenzaldehyde (**2o**) separately, on a grams scale (20 mmol). As expected,

Table 3 Synthesis of 2-aryl/heteroaryl/styryl/alkylbenzothiazoles **3(a–w)** using the SiO_2–HNO_3 catalyst



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

Entry	Compound	R	Yield (%)		Observed mp (°C)	Literature mp (°C)
			A[a]	B[b]		
1	**3a**	C_6H_5	86	93	112–114	112–113 [20]
2	**3b**	4-$CH_3C_6H_4$	86	91	84–86	85–86 [20]
3	**3c**	4-$OCH_3C_6H_4$	90	96	118–120	119–120 [20]
4	**3d**	2-$OCH_3C_6H_4$	89	93	100–102	102–103 [14]
5	**3e**	3,4-$(OCH_3)_2C_6H_3$	88	92	138–140	142–143 [14]
6	**3f**	4-OHC_6H_4	85	93	226–228	228–229 [20]
7	**3g**	3-OHC_6H_4	86	91	160–162	161–163 [22]
8	**3h**	2-OHC_6H_4	95	98	128–130	131 [22]
9	**3i**	4-FC_6H_4	94	98	102–104	101–102 [20]
10	**3j**	2,4-$F_2C_6H_3$	87	94	92–94	– [34]
11	**3k**	2,5-$F_2C_6H_3$	83	90	100–102	–
12	**3l**	4-$CF_3C_6H_4$	91	97	160–162	159–160 [26]
13	**3m**	4-ClC_6H_4	95	98	114–116	114–115 [20]
14	**3n**	4-BrC_6H_4	91	93	128–130	131–132 [20]
15	**3o**	4-$NO_2C_6H_4$	95	98	230–232	230–231 [20]
16	**3p**	4-Pyridyl	89	92	124–126	124–125 [37, 38]
17	**3q**	3-Pyridyl	90	92	124–126	123–124 [37, 38]
18	**3r**	2-Pyridyl	90	91	130–132	133–134 [37, 38]
19	**3s**	2-Furyl	89	91	100–102	102–103 [20]
20	**3t**	2-Thiophenyl	88	91	98–100	99–100 [20]
21	**3u**	2-Styryl	–	89[c]	92–94	– [17]
22	**3v**	2-(1-Phenylprop-1-en- 2yl)	–	87[c]	70–72	–
23	**3w**	2-Ethyl	–	90[c]	Oil	[19, 45]

Reaction conditions: 2-aminothiophenol (2 mmol), aldehyde (2 mmol), SiO_2–HNO_3 catalyst (2 wt% to aldehyde)

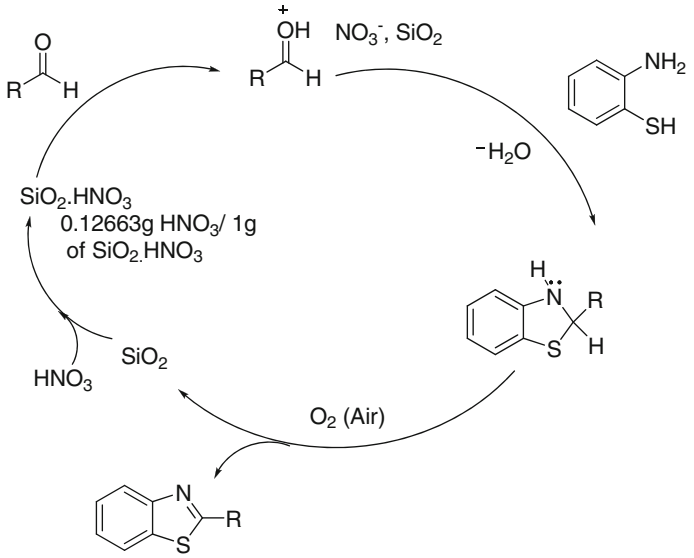
[a] Products were isolated by recrystallization using methanol

[b] Products were isolated by column chromatography

[c] Products were not isolated by recrystallization

the reactions proceeded smoothly to provide target compounds in high yield as obtained in the similar reaction on a milligrams scale (entries 2, 8, 13, and 15, respectively; Table 3), which expressed the practical utility of this method.

A possible mechanism was proposed for the synthesis of benzothiazoles as outlined in Scheme 2. It involves the initial condensation of the amino group



Scheme 2 Possible mechanism for the synthesis of 2-aryl/heteroaryl/styryl/alkylbenzothiazoles

($-NH_2$) on the carboxaldehyde group (C=O), activated by the SiO_2–HNO_3 catalyst, to form a Schiff base or benzothiazoline, and subsequent aerial oxidation furnished the products **3**(**a**–**w**).

Conclusion

In conclusion, we have developed a mild, economic, rapid and practical method for the synthesis of 2-aryl/heteroaryl/styryl/alkylbenzothiazoles in excellent yields. Highly efficient and easy preparation of SiO_2–HNO_3 catalyst make a valid contribution to the existing catalysts for the synthesis of benzothiazole derivatives.

Acknowledgment Financial support as a junior research fellowship by the Haryana State Council of Science and Technology is gratefully acknowledged for accomplishing this work.

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