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Chitosan-SO_3H: A Green Approach to 2-Aryl/Heteroaryl Benzothiazoles under Solvent-Free Conditions at Room Temperature

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An efficient green protocol have been developed for the synthesis of 2-aryl/heteroaryl benzothiazole derivatives by intramolecular cyclocondensation of 2-mercaptoaniline with various substituted aryl/heteroaryl aldehydes using chitosan-SO_3H as an efficient biocompatible and reusable heterogenous solid acid catalyst in presence of air under solvent free conditions at room temperature. ^1H NMR and ^{13}C NMR spectra recorded are in agreement with the reported data.

Keywords: Green synthesis, Chitosan-SO_3H, Benzothiazoles, Intramolecular cyclocondensation, Solvent-free condition.

INTRODUCTION

Benzothiazole ring is a fused bicyclic ring often constructed from acyclic reactants [1]. This core nucleus bearing N and S atoms at symmetrical position have been studied extensively owing to their interesting pharmacological activities. Especially, among those 2-arylbenzothiazoles (Fig. 1) are of great interest as these structural frameworks have proved to be as an important class of biological active motifs and hence play a pivotal role in the field of medicinal and industrial chemistry. They are the basic constituents of several antitumor, anticonvulsant, antiviral and anticancer drugs [2].

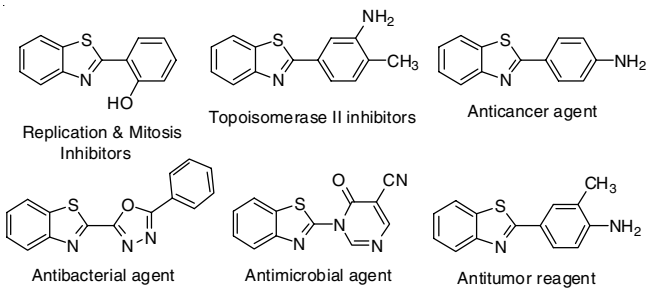


Fig: 1. Biological activity profile of certain 2-substituted benzothiazole scaffolds [Ref. 3]

Traditionally, the common synthetic strategies to construct these bioactive compounds relies on majorly condensation of 2-mercaptoaniline with aldehydes, β-diketones, carboxylic acids, acid chlorides or esters *via* Hofmann synthesis [4], oxidative intramolecular cyclization of thiobenzanilides *via* Jacobson cyclization [5] and palladium-catalyzed coupling of 2-bromobenzothiazole with arylboronic acids *via* Suzuki biaryl coupling [6].

However, many of the reported methods are quite effective and useful, but suffer by using acidic reagents or hazardous organic solvents that are not environmentally compatible. Moreover, harsh reaction conditions, multistep process, longer reaction times, higher temperatures, use of expensive reagents, metal oxidants and produce a large amounts of waste with observed side product formation are the other drawbacks of these methodologies. Consequently, there is a need to overcome the above limitations by developing an efficient, simple and green methodology for the synthesis of 2-substituted benzothiazoles in terms of selectivity, reusability and biocompatibility.

Recently, the direction of science and technology has been shifting more towards eco-friendly, natural product resources and reusable catalysts. Thus natural biopolymers have emerged as potential candidates for preparing solid acid support catalysts enabling high selectivity of the reactions under solvent-free conditions [7]. Researchers have demonstrated that solvent-free organic syntheses are generally faster, selective, higher yielding with cleaner products, environmentally benign and involve simple operational procedure as compared to the classical reactions [8]. To the best of our knowledge, as far as

concerned to the literature revealed there are no reports found using this present methodology. We wish to report herein a simple procedure for the synthesis of 2-substituted benzothiazoles using chitosan-SO_3H as a reusable solid acid catalyst under solvent-free conditions at room temperature with high selectivity.

Chitosan is a linear polyamine derivative briefed as [poly-(β-1/4)-2-amino-2-deoxy-D-glucopyranose] obtained by partial and controlled deacetylation of chitin [9]. Chitosan can easily be subjected to a variety of chemical modifications. One such chemical modification is sulfonation at the reactive amine function to produce chitosan-SO_3H (CS-SO_3H) and has been used as a solid acid catalyst in many organic reactions [10]. Prompted by these reports, we herein report CS-SO_3H as an efficient, reusable heterogeneous solid acid catalyst for the synthesis of 2-aryl/heteroaryl benzothaizole derivatives under solvent free conditions at room temperature.

EXPERIMENTAL

^1H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) spectrometer by using $CDCl_3$ solvent and tetramethylsilane (TMS) as an internal standard. The FT-IR spectra were obtained with KBr pellets in the range 4000-400 cm^{-1} with a Perkin Elmer 550 spectrometer. Melting points were uncorrected and determined in open capillary tubes using sulphuric acid bath and Mass spectra on an Agilent LC-MS instrument giving only M^+ values in Q+1 mode. All starting materials, chitosan were purchased from TCI and Alfa-aesar.

General procedure for the preparation of 2-aryl/heteroaryl benzothiazoles catalyzed by chitosan-SO_3H: In a round bottom equipped flask 2-mercaptoaniline (**1**) (1 mmol), substituted aryl/heteroaryl aldehydes **2(a-o)** (1 mmol) and CS-SO_3H (2 mol %) is stirred at room temperature for 30 min in presence of oxygen balloon. The reaction was monitored by using TLC. Upon completion of the reaction, the reaction mass was quenched to absolute ethanol. The precipitated CS-SO_3H was filtered and reused for subsequent reactions. The filterate was concentrated and obtained the curde product. Further the crude product was recrystallized from ethanol and obtained pure products **3(a-o)**.

Physical and spectral data

2-Phenylbenzothiazole (3a): White solid, m.p.: 111-112 °C (Lit. [11] 110-111 °C); IR (KBr, ν_{max}, cm^{-1}): 3066, 3017, 2835, 1608, 1587, 1476,1430, 830, 763; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.37 (t, *J* = 8.0 Hz, 1H), 7.39-7.51 (m, 4H), 7.89 (d, *J* = 8.0 Hz, 1H), 8.06-8.10 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 121.59, 123.24, 125.16, 126.29, 127.56, 128.99, 130.93,133.64, 135.07, 154.16, 168.03; MS (*m/z*) $[M+H]^+$: 212.

2-(4-Methylphenyl)benzothiazole (3b): White solid; m.p.: 82-84 °C (Lit. [12] 83-85 °C); IR (KBr, ν_{max}, cm^{-1}): 3024, 2905, 1610, 1519, 1480, 1435, 1383, 1312, 821, 759; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.2, 154.2, 141.3, 135.0, 131.1, 129.7, 127.5, 126.2, 125.0, 123.1, 121.5, 21.4; MS (*m/z*) $[M+H]^+$: 226.

2-(4-Methoxyphenyl)benzothiazole (3c): White solid; m.p.: 120-122 °C (Lit. [13] 120-122 °C); IR (KBr, ν_{max}, cm^{-1}): 3021, 3048, 2837, 1609, 1590, 1483, 830; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.04 (d, *J* = 8.4 Hz, 3H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 3.88(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.8, 162.0, 154.3, 134.9, 129.1, 126.5, 126.1, 124.7, 122.8, 121.4, 114.4, 55.4; MS (*m/z*) $[M+H]^+$: 242.

2-(2-Hydroxyphenyl)benzothiazole (3d): Yellow solid; m.p.: 127-128 °C (Lit. [14] 126-128 °C); IR (KBr, ν_{max}, cm^{-1}): 3285, 3090, 2900, 1619, 1590, 1490, 1423, 874, 751; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 6.95-699 (t, 1H, *J* = 8.0 Hz, Ar-H) 7.12 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.38-7.44 (m,2H, Ar-H) 7.50-7.54 (t, 1H, *J* = 8.4 Hz, Ar-H) 7.71 (d, 1H, *J* = 8.0 Hz, Ar-H) 7.92 (d, 1H, *J* = 8.4Hz, Ar-H) 8.01 (d, 1H, *J* = 8.0 Hz, Ar-H) 12.54 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 116.8, 117.9, 119.5, 121.5, 122.2, 125.6, 126.7, 128.4, 132.6, 132.8, 151.8, 157.9, 169.4; MS (*m/z*) $[M+H]^+$: 228.

2-(4-Bromophenyl)benzothiazole (3e): White solid; m.p.: 129-131 °C (Lit. [15] 130-132 °C); IR (KBr, ν_{max}, cm^{-1}): 1503, 1392, 1311, 1224, 968, 820, 754, 722, 477; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.06 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.64- 7.60 (m, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 166.7, 154.1, 135.0, 132.5, 132.2, 128.9, 126.5, 125.4, 125.4, 123.3, 121.6; MS (*m/z*) $[M+H]^+$: 289.

2-(4-Chlorophenyl)benzothiazole (3f): White solid; m.p.: 114-116 °C (Lit. [16] 116-118 °C); IR (KBr, ν_{max}, cm^{-1}): 3055, 2358, 1560, 1455, 1430, 1317, 1275, 1060, 965, 750, 725; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 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}C NMR (100 MHz, $CDCl_3$, ppm) δ 121.8, 123.1, 125.2, 126.8, 129.1, 129.8, 132.7, 135.2, 137.1,154.4, 166.2; MS (*m/z*) $[M+H]^+$: 247.

2-(4-Fluorophenyl)benzothiazole (3g): White solid; m.p.: 97-98 °C (Lit. [15] 98-100 °C); IR (KBr, ν_{max}, cm^{-1}): 1710, 1520, 1362, 1226, 1092,967, 837, 756, 728, 499; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.09-8.04 (m, 3H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.20-7.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 166.2 (d, *J* = 101.9 Hz), 163.2, 154.1, 135.0, 130.0 (d, *J* = 3.1 Hz), 129.5 (d, *J* = 8.6 Hz), 126.4, 125.2, 123.2, 121.6, 116.1 (d, *J* = 22.0 Hz); MS (*m/z*) $[M+H]^+$: 230.

2-(4-Trifluoromethylphenyl)benzothiazole (3h): White solid; m.p.: 160-162 °C (Lit. [17] 160-162 °C); IR (KBr, ν_{max}, cm^{-1}): 1483, 1434, 1323, 1110, 970,839, 760, 620, 439; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.21 (d, *J* = 8.3 Hz, 2H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.0, 154.0, 136.8, 135.2, 132.3 (q, *J* = 32.6 Hz), 127.8, 126.7, 126.0 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 270.8 Hz), 123.6, 121.7; MS (*m/z*) $[M+H]^+$: 280.

2-(3-Nitrophenyl)benzothiazole (3i): White solid; m.p.: 181-183 °C (Lit. [18] 181-182 °C); IR (KBr, ν_{max}, cm^{-1}): 3039,

2936, 1522, 1460, 1345, 1103, 1041, 851, 750; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.94 (s, 1H), 8.43 (d, *J* = 7.6 Hz, 1H), 8.34 (d, *J* = 7.6 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 164.9, 153.9, 148.7, 135.3, 135.2, 133.0, 130.1, 126.8, 126.0, 125.1, 123.7, 122.3, 121.8; MS (*m/z*) $[M+H]^+$: 257.

2-(3-Bromo-4-methylphenyl)benzothiazole (3j): White solid, m.p.: 115 -117 °C. (Lit. [19] 115-117 °C); IR (KBr, ν_{max}, cm^{-1}): 1472,1433, 1375, 1310, 1284, 973, 824, 756, 724, 433; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.29 (d, *J* = 1.4 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 166.3, 154.0, 141.0, 135.0, 132.9, 131.2, 131.0, 126.4, 126.3, 125.5, 125.3, 123.2, 121.6; MS (*m/z*) $[M+H]^+$: 303.

2-(Naphthalen-2-yl)benzothiazole (3k): White solid; m.p.: 125-127 °C (Lit. [20] 126-128 °C); IR (KBr, ν_{max}, cm^{-1}): 1496, 1453, 1361, 1311, 981, 934, 852, 829, 747, 728, 476; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.56 (d, *J* = 1.2 Hz, 1H), 8.20 (dd, *J* = 8.7 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.98-7.86 (m, 4H), 7.56-7.49 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 1H; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.1, 154.2, 135.1, 134.6, 133.2, 131.0; MS (*m/z*) $[M+H]^+$: 262.

2-(Thiophen-2-yl)benzothiazole (3l): White solid; m.p.: 92-94 °C (Lit. [21] 93-95 °C); IR (KBr, ν_{max}, cm^{-1}): 3096, 3056, 1542, 1476, 1312, 1222, 912, 852, 826, 762, 714; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 3.2 Hz, 1H), 7.51-7.45 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.3, 153.7, 137.4, 134.7, 129.2, 128.5, 128.0, 126.4, 125.2, 123.0, 121.4; MS (*m/z*) $[M+H]^+$: 218.

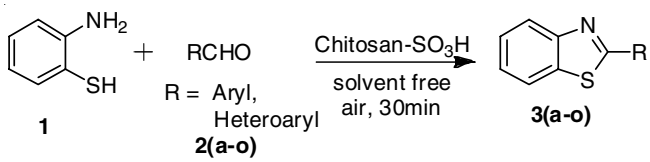
2-(Pyridin-3-yl)benzothiazole (3m): White solid; m.p.: 135-137 °C (Lit. [22] 137-138 °C); IR (KBr, ν_{max}, cm^{-1}): 3050, 3032, 1586, 1574, 1426, 1310, 1234, 964, 814, 766, 702; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.28 (d, *J* = 1.6 Hz, 1H), 8.70 (dd, *J* = 0.8, 4.4 Hz, 1H), 8.37-8.34 (m, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz), 7.53-7.49 (m, 1H), 7.43-7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 164.5, 153.9, 151.5, 148.5, 134.9, 134.5, 129.6, 126.6, 125.6, 123.7, 123.4, 121.7; MS (*m/z*) $[M+H]^+$: 213.

2-(Pyridin-4-yl)benzothiazole (3n): White solid; m.p.: 131-133 °C (Lit. [23] 132-134 °C); IR (KBr, ν_{max}, cm^{-1}): 1433, 979, 758, 728, 720; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.96-7.95 (m, 3H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 165.1, 154.0, 150.7, 140.5, 135.2, 126.8, 126.2, 123.9, 121.8, 121.2; MS (*m/z*) $[M+H]^+$: 213.

2-(Furan-2-yl)benzothiazole (3o): Yellow solid; m.p.: 100-102 °C (Lit. [22] 102-104 °C); IR (KBr, ν_{max}, cm^{-1}): 3144, 3122, 3050, 1598, 1578, 1434, 1246, 1114, 898, 748,730; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.57 (dd, *J* = 1.5, 7.4 Hz, 1H), 7.17 (d, *J* = 6.9 Hz, 1H), 7.35 (dt, *J* = 1.0, 8.3 Hz, 1H), 7.47 (dt, *J* = 1.0, 8.3 Hz, 1H), 7.55-7.59 (m, 1H), 7.86 (d, *J* = 7.3 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 111.3, 112.4, 121.4, 123.0, 125.1, 126.4, 134.1, 144.6, 148.6, 153.6, 157.4; MS (*m/z*) $[M+H]^+$: 202.

RESULTS AND DISCUSSION

In continuation of our research on synthetic applications of green catalysts [24] for pharmacologically active heterocyclic compounds herein we wish to report a simple synthesis of 2-aryl/heteroaryl benzothiazoles by condensation of 2-mercaptoaniline with various substituted aryl/heteroaryl aldehydes under solvent-free conditions catalyzed by CS-SO_3H at room temperature as depicted in **Scheme-I**.



Scheme-I: Synthesis of 2-aryl/heteroaryl benzothiaozles

Initially, we selected our catalyst of choice chitosan-SO_3H (CS-SO_3H) and is prepared by following the reported procedure [10a]. To demonstrate the green protocol, we selected 2-mercaptoaniline (**1**) and simple benzaldehyde (**2a**) as the model reaction in presence of CS-SO_3H (50 mol %) as a catalyst in ethanol at room temperature in presence of air balloon and achieved the cyclized compound **3(a)** in 60 % yield (Table-1, entry-1). The analytical data of the obtained compound was in agreement with the reported data [11].

TABLE-1
OPTIMIZATION AND VARIATIONS (mol %) OF THE CATALYST AND SOLVENT EFFECT FOR THE SYNTHESIS OF 2-ARYL/HETEROARYL BENZOTHIAZOLES (**3a**)

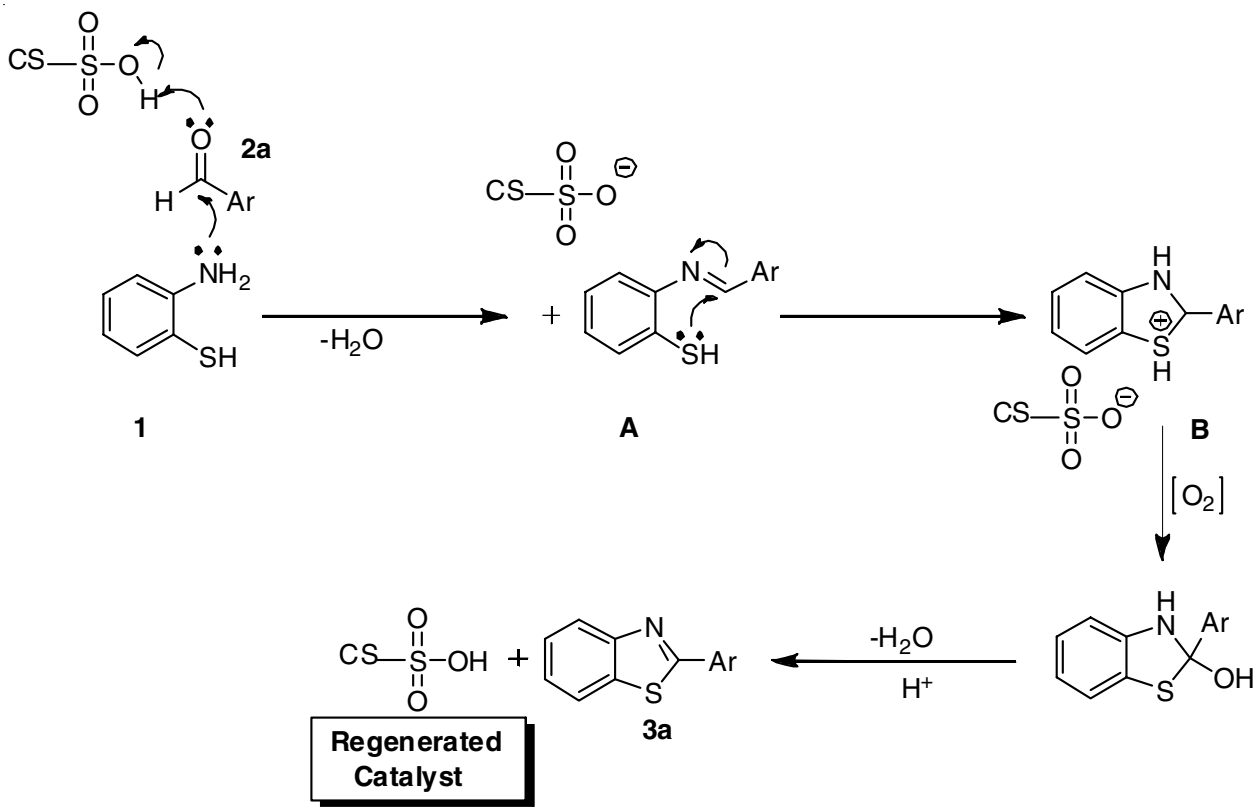
Entry	Catalyst	Mol (%)	Solvent	Time (min)[b]	Yield (%)[a]
1	CS-SO_3H	50	EtOH	60	60
2	CS-SO_3H	30	CH_3CN	50	65
3	CS-SO_3H	20	PEG-400	45	70
4	CS-SO_3H	10	THF	40	75
5	CS-SO_3H	5	Solvent less	30	80
6	CS-SO_3H	2	Solvent less	30	90
7	No catalyst	–	Solvent less	600	Trace

[a]Isolated yields; [b]All the reactions were performed at room temperature under oxygen balloon.

We further explored the synthetic protocol and extended the scope of the reaction by varying the catalyst loadings and studied the effect of various solvents towards the reaction profile. Among the attempted conditions CS-SO_3H (2 mol %) under solvent free conditions at room temperature resulted the cyclized product in 90 % yield with high selectivity (Table-1, entry-6). The increased mol % of the catalyst towards the reaction is not satisfactory as depicted in (Table-1, entry: 1-4). In the absence of catalyst no formation of the expected product was detected even after prolonged hours (Table-1, entry-7).

Encouraged by the above appended results, we further explored the synthetic protocol and the scope of the reaction by employing substituted aryl/heteroaryl aldehydes functionalized with electron-rich and electron-deficient groups. The results were depicted in (Table-2, entries 2 to 15).

Clearly, all reactions worked well irrespective of the substrates present on the aldehydes even with electron-with-



Scheme-II: Sequential and plausible mechanistic pathway for the preparation of 2-aryl/heteroaryl benzothiazoles by using chitosan-SO_3H

TABLE-2
SYNTHESIS OF 2-ARYL/HETEROARYL BENZOTHIAZOLES USING CS-SO_3H AS A CATALYST UNDER SOLVENT FREE CONDITIONS AT ROOM TEMPERATURE

Entry	R-CHO	Products[a]	Time (min)[b]	Yields (%)[c]
1	C_6H_5	**3(a)**	30	90
2	4-$CH_3C_6H_4$	**3(b)**	25	92
3	4- $MeOC_6H_4$	**3(c)**	25	89
4	2-OHC_6H_4	**3(d)**	40	85
5	4-BrC_6H_4	**3(e)**	30	90
6	4-ClC_6H_4	**3(f)**	35	89
7	4-FC_6H_4	**3(g)**	30	88
8	4-$CF_3C_6H_4$	**3(h)**	35	89
9	3-$NO_2C_6H_4$	**3(i)**	40	87
10	3-Br-4-$CH_3C_6H_3$	**3(j)**	30	92
11	2-Naphthyl	**3(k)**	30	90
12	2-Thiophenyl	**3(l)**	35	89
13	3-Pyridyl	**3(m)**	30	92
14	4-Pyridyl	**3(n)**	30	90
15	2-Furanyl	**3(o)**	35	89

[a]All Products were characterized by ^1H NMR, ^{13}C NMR and Mass spectra. [b]The temperature for all the synthesized products is at room temperature. [c]Yields refer to isolated pure products.

drawing groups. The process successfully achieved the 2-aryl/heteroaryl benzothiazole derivatives (**3a-o**) (Table-2, entries 1-15) in good to excellent yields. After completion of the reaction the catalyst is easily separated by filteration and reused after activation at 120 °C for 3 h. The results obviously indicates no significant loss in its activity with that of fresh catalyst as depicted in Table-3.

A plausible mechanistic study is depicted in **Scheme-II**, showing the catalytic activation of the CS-SO_3H. The catalyst

TABLE-3
REUSE OF THE CATALYST FOR THE SYNTHESIS OF 2-ARYL/HETEROARYL BENZOTHIAZOLES

Run	1	2	3	4	5
Yield (%)[a]	92	92	91	90	90

[a]Isolated yields.

can possibly act as a convenient proton source which initiates the nucleophilic attack of NH_2 group on aldehyde carbonyl group activated by CS-SO_3H catalyst followed by the formation of an azomethine intermediate [**A**], followed by intramolecular cyclization to yield the intermediate [**B**], subsequent oxidation with O_2 from air and expulsion of H_2O to furnish the fully heteroaromatised product (**3a**) along with the regenerated CS-SO_3H.

Conclusion

We have demonstrated that chitosan-SO_3H catalyst is reusable and eco-friendly catalyst for the synthesis of 2-aryl/heteroaryl benzothiazoles. Nevertheless, without doubt the new process has significantly improved compared to those in the known literature in terms of high selectivity, short reactions times, excellent yields, no thermal heating, no metal oxidant, large substrate scope and without any waste generation or byproduct formation. Further no column chromatography is required. The process designed focuses on being environment friendly under green chemistry aspects.

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