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Research Note
Silica Boron Sulfonic Acid as Heterogeneous and Highly Efficient Solid Acid Catalyst For the Preparation of Hantzsch 1,4-dihydropyridines Under Solvent-Free

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Abstract

Silica boron sulfonic acid [SiO_2–$B(OSO_3H)_3$] as an inexpensive, reusable, and Lewis and Brønsted acid catalyst was successfully synthesized, and used for the one-pot three-components synthesis of biologically active substituted Hantzsch 1,4-dihydropyridine derivatives in the absence of solvent at 90ºC. Silica boron sulfonic acid is attractive and efficient, because it plays in two role as a Lewis acid (by boron atom) and also as a Brønsted acid (by OSO_3H group), which can have a better effect in reaction. The reaction was carried out under solvent-free and mild conditions. Silica boron sulfonic acid can be recovered and reused for at least five consecutive runs.

Keywords: Lewis and Brønsted acidic; Hantzsch Reaction; 1,4-dihydropyridine; Solvent-free; One-pot condensation.

Introduction

Multi component reactions (MCRs) are described by three or more reactants connecting in a one-pot process to produce a single product [1-2]. They are economically and environmentally convenient due to multi-step synthesis commonly make a large quantity of waste because the complex isolation actions often include uneasy, poisonous and dangerous solvents after each step [3]. MCRs like the Ugi [4], Mannich [5], Biginelli [6], Passerini [7], and Hantzsch [8] are very important in the organic reactions, and provide a wide variety of heterocyclic compound. For instance, the Hantzsch reaction provides 1,4-dihydropyridine (DHP) derivatives serve as an important class of compounds. The preparation of 1,4-dihydropyridine (DHP) derivatives have received significant attention in recent years because of their wide range of medicinally important compounds such as antidiabetic, antiatherosclerotic, vasodilator, bronchodilator, geroprotective, and hepatoprotective [9]. These heterocyclic molecules have been widely used as a chemosensitizer in tumor therapy and as cerebral antiischemic agents in the treatment of Alzheimer’s disease [10], as calcium channel blockers for the treatment of cardiovascular diseases [11]. On the other hand, 1,4-dihydropyridine (DHP) derivatives beneficial and appropriate as synthetic tools for reducing imines to amines [12]. In 1881, Arthur Hantzsch started his work for the first time [8], several new methods have been reported for the preparation of dihydropyridine, including the use of Ni nanoparticles [13], Silica

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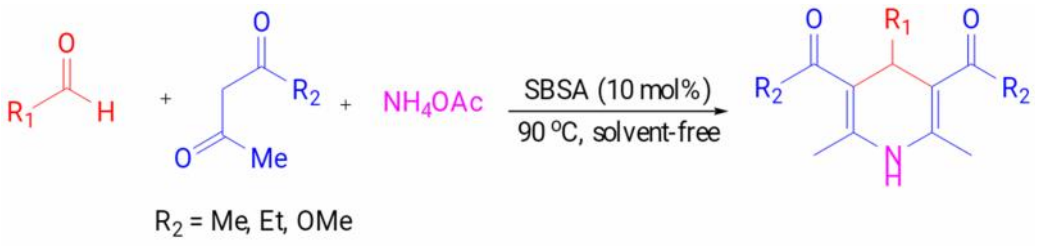


Scheme 1. Silica boron sulfonic acid-catalysed synthesis of the Hantzsch 1,4-dihydropyridines

sulphuric acid [14], Triphenylphosphine [15], [PS-IM$(CH_2)_4SO_3H$][HSO_4] [16], Cerium(IV) ammonium nitrate [17], TMSCl–NaI [18], I_2 [19], 1-Methyl-3-(2-(sulfooxy)ethyl)-1H-imidazol-3-ium chloride [20], $Hf(NPf_2)_4$ in $C_{10}F_{18}$ [21], $Yb(OTf)_3$ [22], Fe_3O_4 MNPs [23], Grinding [24], ASA [25], Phospho sulfonic acid [26], Solar thermal energy [27], Conventional heating [28], Metal triflates [29], and A Microwave-assisted bismuth nitrate [30]. All these methods suffer from such as refluxing ethanol, performances under certain special conditions, unsatisfactory yields, long reaction times, the use of high temperatures and volatile organic solvents, poor agreement with the green chemistry protocols, and use of expensive, non-available or toxic catalysts. Therefore, search for finding simple, clean, inexpensive, and solvent-free reaction conditions methods for the preparation of 1,4-dihydropyridine (DHP) derivatives under solvent-free conditions without reflux conditions is still of significance. Boron sulfonic acid [$B(OSO_3H)_3$] as highly efficient, inexpensive, and heterogeneous reusable solid acid catalyst can act as a Lewis acid and Brønsted acid catalyst, which this behavior can be help to the better effect it. Boron sulfonic acid (BSA) supported on silica gel for use more convenient. In the past decades, solid acid catalysts are very important and highly efficient in organic transformations, because, these catalysts are appropriate from two opinion economic and environmental. Boron sulfonic acid (BSA) as attractive and heterogeneous reusable solid acid catalyst was designed, and low-cost and easily method synthesized for the first time by kiasat and *et al.*, and was used in various organic transformations [31-42] silica boron sulfonic acid is inexpensive and easily obtained, stable and storable, easily recycled and reused for several times with consistent activity.

In continuation of our effort toward the synthesis of catalysts, and their application in organic synthesis [32-34], and as a result of global interest in the ongoing research towards the development of environmentally friendly methods for the synthesis of organic compounds, We wish to introduce a new and Lewis and Brønsted solid acid catalyst as a solid acid catalyst in the low cost and eco-friendly for the one-pot, three-component synthesis of biologically active substituted Hantzsch 1,4-dihydropyridine under solvent-free conditions (Scheme 1).

Materials and Methods

In this study, silica boron sulfonic acid (SBA) was prepared according to the literature procedure [32-33]. All the solvents, aldehydes, ammonium acetate, and 1,3-Dicarbonyl compounds were purchased from Sigma–Aldrich (USA) and Merck. The products were separated and purified by different chromatographic techniques and identified by comparing their IR and ^{1}H and ^{13}C NMR spectra and melting point against standard samples. Progress of reactions was monitored by TLC (Silica gel 60 F254)..

General procedure for the preparation of 1,4-dihydropyridines

To a mixture of substituted aromatic aldehydes (1 mmol), 1,3-dicarbonyl compounds (2 mmol) and ammonium acetate (1.5 mmol) in the presence of SBSA (10 mol%) was heated for indicated time in Table 3. After completion of the reaction, $CHCl_3$ (2 × 10 mL) was added to the mixture and filtered, then the solid material [SiO_2–$B(OSO_3H)_3$] was again washed with $CHCl_3$ (2 × 5 mL) and collected for reuse. Finally, the raw product was recrystallized (EtOH–H_2O solution) to provide pure of 1,4-dihydropyridine derivatives with excellent yields (84–97%).

Results and Discussion

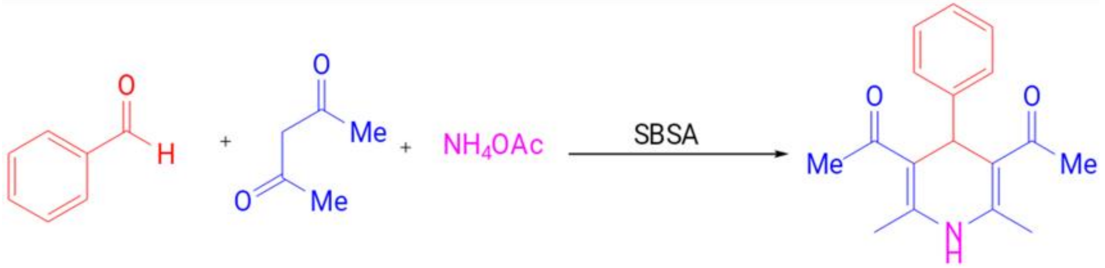
In this study, we want to report the application of silica boron sulfonic acid [SiO_2–$B(OSO_3H)_3$] as a tri-functional inorganic Lewis and Brønsted acid catalyst in the preparation of 1,4-dihydropyridines **4a-t** by the Hantzsch condensation reaction (Scheme 1). In the first step, for the optimization of the reaction conditions, the various effects such as amount of catalyst and reaction temperatures were investigated on the reaction of benzaldehyde (1 mmol) with acetyl acetone (2 mmol) and ammonium acetate (1.5 mmol) as a model reaction to provide 4-(phenyl)-2,6-dimethyl-1,4-dihydro-pyridine-3,5-dicarboxylate **4a** (Table 1).

The best result was obtained when the reaction was carried out in the 10 mol% of silica boron sulfonic at 90 ºC under solvent-free conditions (Table 1, entry 4). When 15 mol% of silica boron sulfonic acid was tested, the yield did not increase. But, on the other hand, the reaction time was longer (Table 1, entry 5). It is worth noting that, the reaction was carried out in the room temperature with 10 mol% amount of silica boron sulfonic acid. After 24 h, no product was obtained (Table 1, entry 11). When reactions were carried out with 10 mol% of silica boron sulfonic acid at 50 ºC and 60 ºC, reaction time was longer (3 h) and the yield was lower (Table 2, Entries 7-8).

For comparison, various solvents, such as dichloromethane, chloroform, ethyl acetate, acetone, *n*-hexane, acetonitrile, under reflux conditions, and solvent-free procedure, were investigated for model reaction to provide **4a**. The results are listed in Table 2. As can be seen from Table 2, inappropriate yields (30-54%) of **4a** was obtained by using these solvents after 4-6 h.

To compare the efficiency of silica boron sulfonic acid as catalyst for the reaction between benzaldehyde

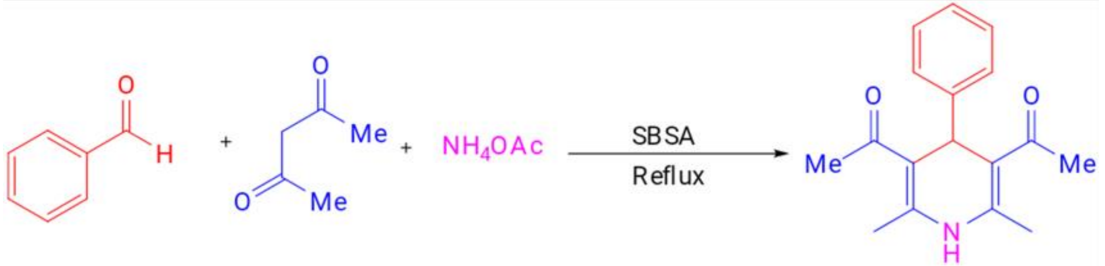
Table 1. Catalyst optimization in the synthesis of **4a**



Entry	Conditions	Catalyst amounts (%)	Time (h:min)	Yield (%)[a]
1	Solvent-free/90 ºC	1	04:00	Trace
2	Solvent-free/90 ºC	3	04:00	70
3	Solvent-free/90 ºC	5	01:10	80
4	Solvent-free/90 ºC	10	01:25	95
5	Solvent-free/90 ºC	15	01:30	90
6	Solvent-free/90 ºC	20	01:35	85
7	Solvent-free/50 ºC	10	03:00	75
8	Solvent-free/60 ºC	10	03:00	78
9	Solvent-free/80 ºC	10	01:30	92
10	Solvent-free/100 ºC	10	01:30	90
11	Solvent-free/r.t.	10	24:00	Trace

[a] Yield of isolated products.

Table 2. Solvent study in the synthesis of **4a** in reflux conditions



Entry	Catalyst amounts (%)	Time (h)	Yield (%)[a]
1	CH_2Cl_2	6	Trace
2	$CHCl_3$	5	Trace
3	EtOAc	4	54
4	Acetone	4	30
5	*n*-Hexane	4	50
6	CH_3CN	6	50

[a] Yield of isolated products.

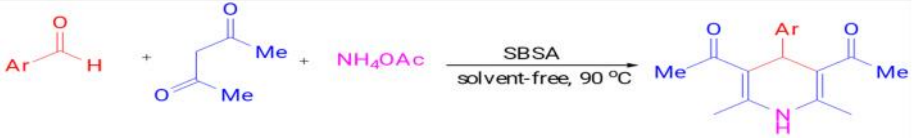
(1 mmol) with acetyl acetone (2 mmol) and ammonium acetate (1.5 mmol) in the presence different catalysts such as phthalic acid (Table 3, entry 1), oxalic acid (Table 3, entry 2), 4-methylpentanoic acid (Table 3, entry 3), isobutyric acid (Table 3, entry 4), and [2-(sulfooxy)ethyl]sulfamic acid (Table 3, entry 5) was examined (Table 3). It was observed that silica boron sulfonic acid exhibited high activity and the

Table 3. The model study for the synthesis of 4-(phenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **4a** in the presence of different catalysts

Entry	Catalyst	Time (h)	Yield (%)[a]
1	Phthalic acid	3	66
2	Oxalic acid	4	60
3	4-Methylpentanoic acid	6	45
4	Isobutyric acid	6	40
5	SESA	3	87

[a] Yield of isolated products.

Table 4. $SiO_2/B(OSO_3H)_3$ catalyzed Hantzsch synthesis of 1,4-dihydropyridines **4a-t**[a]



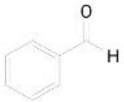
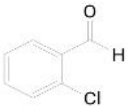
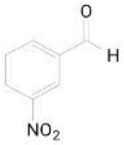
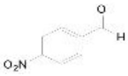
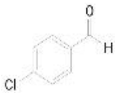
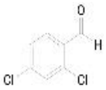
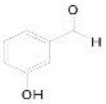
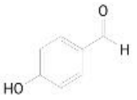
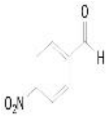
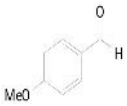
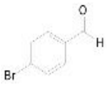
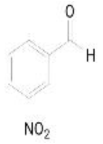
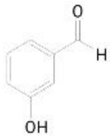
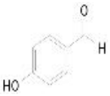
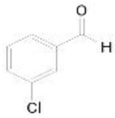
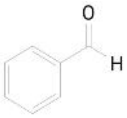
Entry	R₁	R₂	Product	Time (h:min)	Yield (%)[a]	Mp (°C)
1		Me	**4a**	01:25	95	170-172
2		Me	**4b**	00:40	95	143-144
3		Me	**4c**	00:40	93	195-196
4		Me	**4d**	01:40	90	197-200
5		Me	**4e**	01:15	88	143-145
6		Me	**4f**	01:40	95	380-382
7		OMe	**4g**	01:30	90	350-352

Table 4. Cntd

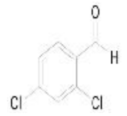
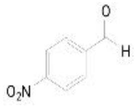
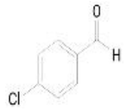
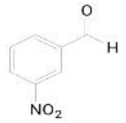
8		OMe	**4h**	00:35	89	404-405
9		OMe	**4i**	01:30	89	350-352
10		OMe	**4j**	02:51	90	170-173
11		OMe	**4k**	02:30	84	193-195
12		OMe	**4l**	02:30	93	239-241
13		OEt	**4m**	00:40	93	275-277
14		OEt	**4n**	01:45	89	224-226
15		OEt	**4o**	01:45	90	343-344
16		OEt	**4p**	01:10	87	156-157

corresponding product was performed in high yield and short reaction time. Then, various aldehyde (1 mmol) with acetyl acetone (2 mmol) and ammonium acetate (1.5 mmol) in the presence 10 mol% of silica boron sulfonic acid under solvent-free conditions at 90 ºC as a model reaction to provide biologically active substituted Hantzsch 1,4-dihydropyridine **4a-t** (Table 4).

As can be seen from Table 4, in all cases, various substitutions in the aryl group of aldehydes (electron-donating and electron-withdrawing) such as methoxy, nitro, hydroxy, and chlorogroups with various 1,3-dicarbonyl compounds gave high yields of products in short reaction time. The structures of all known products **4a-t** were deduced and compared with those of authentic samples from their melting points, ^{1}H NMR, ^{13}C NMR, and FT-IR spectral data.

One of the advantages of this method as a heterogeneous catalyst is the reusability of the catalyst. This action is a very important topic in industry, environmental protection, and green chemistry. To test

Table 4. Cntd

17		OEt	**4q**	01:40	97	364-366
18		OEt	**4r**	02:05	90	124-126
19		OEt	**4s**	02:15	90	144-145
20		OEt	**4t**	01:30	92	174-176

[a] All products were characterized by melting point, ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy and comparison with these reported in the literature.
[b] Yield of isolated products.

this, the reaction of benzaldehyde with acetyl acetone/ ethyl acetoacetate and ammonium acetate under solvent-free conditions at 90 °C to provide **4a** and **4m**. As shown in Table 5, the silica boron sulfonic acid was reused for five times without any loss of catalytic activity in the yields.

The efficiency of this work in the synthesis of Hantzsch 1,4-dihydropyridines is compared with other catalysts reported in the literature, based on the reaction time, temperature, yield of product, and solvent is shown in Table 6.

Conclusion

Boron sulfonic acid supported on silica gel as an inexpensive and tri-functional inorganic Lewis and Brønsted acid catalyst were successfully prepared using a cost-effective and convenient one-step procedure. It was successfully used for preparation of 1,4-dihydropyridines.The present methodology offers several advantages such as reusability of catalyst, low

Table 5. The reusability of SBSA for the preparation of compound **4a** and **4m**

Compound	**Yield (%) (cycle 1)**	**Yield (%) (cycle 2)**	**Yield (%) (cycle 3)**	**Yield (%) (cycle 4)**	**Yield (%) (cycle 5)**
4a	95	92	90	90	87
4m	93	91	88	87	85

Table 6. Comparison of the results of the synthesis of Hantzsch 1,4-dihydropyridines catalyzed by our new catalyst with those obtained by the recently reported catalysts

Entry	**Conditions**	**Time (h)**	**Yield (%)**	**Re.**
1	SiO_2-SO_3H/ solvent-free/ 60 °C	4.5-7	83-95	14
2	SiO_2-$NaHSO_4$/ CH_3CN/ room temperature	5-8	75-90	15
3	silica sulphuric acid/ solvent-free/ 80 °C	2-60 min	80-98	18
4	Triphenylphosphine/ EtOH/ reflux	5-5	72-95	17
5	CAN/ EtOH/ room temperature	2-3	84-94	19
6	I_2/ solvent-free/ 25-40 °C	25 min-4 h	85-99	21
7	$Hf(NPf_2)_4$ in $C_{10}F_{18}$/ solvent-free/ 60 °C	2-8	82-96	23
8	$Yb(OTf)_3$/ EtOH/ room temperature	2-8	85-94	24
9	Fe_3O_4 MNPs/ solvent-free/ 80 °C	5-46 min	72-95	25
10	Alumina sulfuric acid/ MeOH/ 70 °C	5 h	82-89	27
11	SiO_2–$B(OSO_3H)_3$/ solvent-free/ 90 °C	35 min-2.51 h	84-97	-

catalyst loading, easy work-up, good to excellent yield of products **4a**-**4f**, short reaction time, and economic viability of the silica boron sulfonic acid.

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