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NANO SILICA BORON SULFURIC ACID AS A DUAL BRØNSTED/LEWIS SOLID ACID FOR THE SYNTHESIS OF 5-SUBSTITUTED-1*H*-TETRAZOLES

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Abstract: An efficient method for the synthesis of 5-substituted-1*H*-tetrazoles in the presence of nano silica boron sulfuric acid as an effective heterogeneous nanocatalyst is reported. The yields of the obtained tetrazoles were good to excellent and the reaction times were also acceptable.

Keywords: Cycloaddition, Nano silica boron sulfuric acid, Heterogeneous nanocatalyst, Organic nitriles, Sodium azide, Tetrazoles

Introduction

Tetrazoles are important class of nitrogen-rich heterocycles with a wide range of applications in organic synthesis, coordination and medicinal chemistry[i-iii]. They are extensively used in agriculture as herbicides and fungicides, material sciences and nanostructured compounds[iv-vi]. Tetrazoles have also been frequently used as stabilizers in photography[vii-ix]. The nitrogen content of tetrazoles is 80%, which is the largest percent among the heterocyclic compounds. Therefore, tetrazoles and their derivatives have been explored as the main constituents in various explosives and propellant compounds[vii].

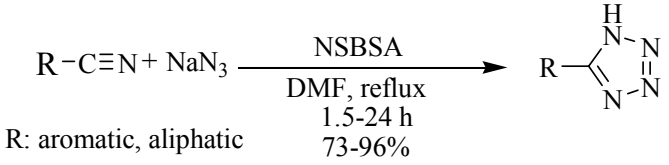
Tetrazoles were synthesized for the first time in 1885, by J. A. Bladin[x]. Since then, many attempts have been made to develop more efficient and eco-friendly methods for the construction of tetrazole frameworks[x-xiii]. The [3+2] cycloaddition reaction between hydrazoic acid and cyanide derivatives that is one of the most efficient routes is well known. Unfortunately, hydrazoic acid is highly explosive and toxic. Practically, the use of sodium azide as a substrate in place of the hydrazoic acid would be convenient; however, the [3+2] cycloaddition energy barrier is significantly lower with hydrazoic acid than with azide ion. To overcome this energy limitation, syntheses have been designed either to control the hydrazoic acid formation or to use a large excess of azide ions in the presence of metal catalysts or strong Lewis acids.

In recent years, considerable efforts have been devoted to explore more efficient catalysts for the synthesis of 5-substituted-1*H*-tetrazoles from nitriles and azide ion. Hence, a great number of catalysts such as nanoZnO, nanoCuO, tetrabutylammonium hydrogen sulfate

(TBAHS), Cu-MCM-41 nanoparticles, organoaluminumazieds, CoY/zeolite, OSU-6, $Cu(OAc)_2$, NH_4OAc, $[Pd(OAc)_2]$dabco/$ZnBr_2$, mesoporousZnS, $CuSO_4.5H_2O$, $H_2SO_4@SiO_2$ have been introduced[i-vi,xiv-xxii]. Although, a plenty of these methods are efficient, but the limitations and disadvantages of some of them realized from their long reaction times, low yields, harsh reaction conditions, expensive reagents, toxic and stringent metal catalysts, tedious separation procedures. Therefore, it is of great importance to introduce more efficient catalysts and also develop more benign methods to avoid these drawbacks.

The successful application of heterogeneous catalysts in organic transformations is well documented. So, most practical catalysts are designed to be porous and possess large specific surface area. In this regard, heterogeneous catalysts, especially micelle-templated silica and other mesoporous high surface area support materials, play more serious roles in chemical transformations catalyzed by solid acids[xxiii-xxix]. It is shown that the grafting of sulfuric groups to the silica support decreases their reactivity by lowering the amount of reactant diffusion to the surface of catalyst[xxx]. To have a dispersible heterogeneous catalyst in solution as a pseudo-homogeneous catalyst two practical solutions have been suggested. One way is to use of nano scale silica support. The other way is to introduction of Lewis acidic sites in proximity of Brønsted sites, which is known as Brønsted/Lewis Aicd Synergy; BLAS[xxx]. Thus, this method may cause an enhancement of acidic power of Brønsted sites. So, to increase the reactivity of solid acids using these two strategies could be effective.

Recently, we have successfully used nano silica boron sulfuric acid(NSBSA) as an efficient heterogeneous nanocatalyst in Baeyer-Villiger oxidation of ketones[xxiii]. Herein, on the basis of our previous experience, we wish to report nano silica boron sulfuric acid(NSBSA)mediated synthesis of 5-substituted-1*H*-tetrazoles from organic nitriles and sodium azide (**Scheme 1**).



Scheme 1. Synthesisof 5-substituted-1*H*-tetrazoles from nitriles and sodium azides catalyzed by nano silica boron sulfuric acid (NSBSA).

Result and discussion

The mostconvenient route for the synthesis of 5-substituted-1*H*-tetrazoles is via [3+2] dipolar cycloaddition reaction between organic nitriles and an azide moiety. In 2001, Demko and Sharpless reported a cycloaddition reaction between organic nitriles and sodium azide in the presence of $ZnBr_2$[xxxi]. In continuation of our recent works in developing environmentally friendly synthetic methods in click chemistry[xxxii,xxxiii], we used nano silica boron sulfuric acid(NSBSA)as an efficient nanocatalyst for the synthesis of 5-substituted-1*H*-tetrazoles from organic nitriles and sodium azide (**Scheme 1**).

Characterization of the Catalyst:

The boron sulfuric acid (BSA) was prepared from the reaction of chlorosulfonic acid with boric acid in chloroform at room temperature. Then, the prepared BSA was reacted with nano silica to produce nano silica boron sulfuric acid (NSBSA)[xxxiv]. The catalyst was characterized by PXRD, SEM, and energy-dispersive X-ray (EDX) mapping techniques**.** Powder X-ray diffraction pattern of the prepared NSBSA is shown in (**Figure 1**). According to PXRD pattern the peaks observed at 2θ= 25.09 and 27.91° are assigned to NSBSA. These peaks assigned to Si-O and B-O bonds in the crystalline structure of NSBSA. The presence and distribution of boron sulfuric centers in the silica support is confirmed by EDX mapping. The

results show uniform distribution of sulfur, oxygen and silicon atoms over the structure of the NSBSA (**Figure 2**). Also, SEM images of the particles showed spherical shaped morphology with an average particle size of about 36 nm (**Figure 3**).

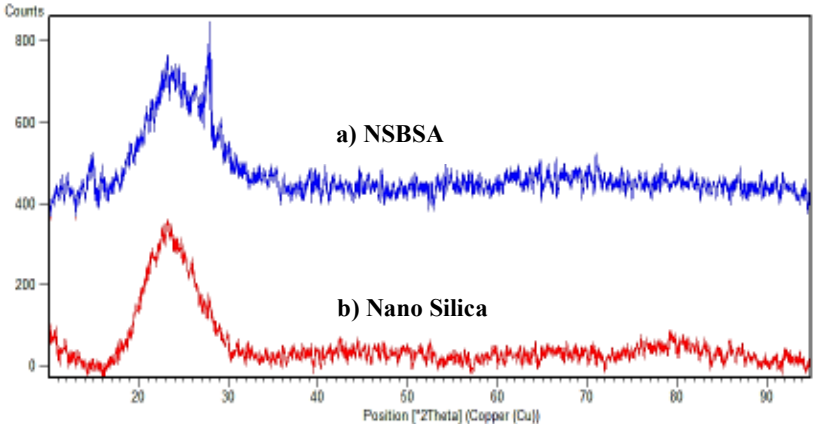


Figure 1.PXRD pattern of the nano silica boron sulfuric acid (NSBSA).

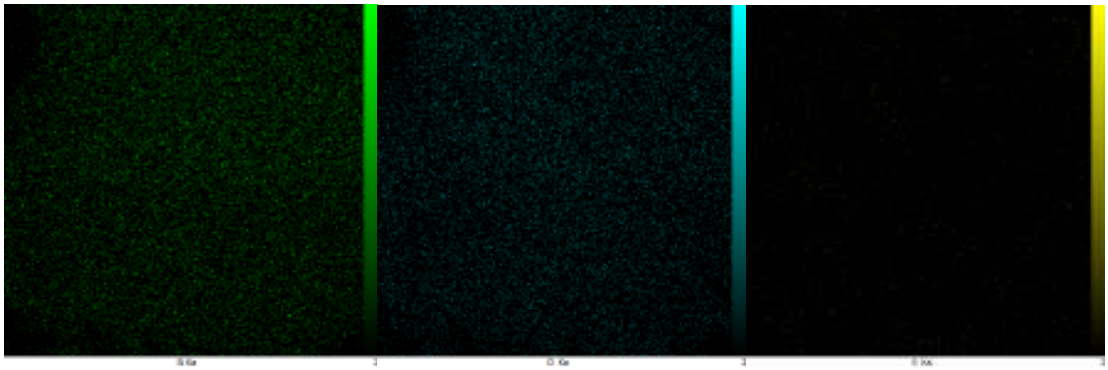


Figure 2.EDX mapping of the nano silica boron sulfuric acid (NSBSA).

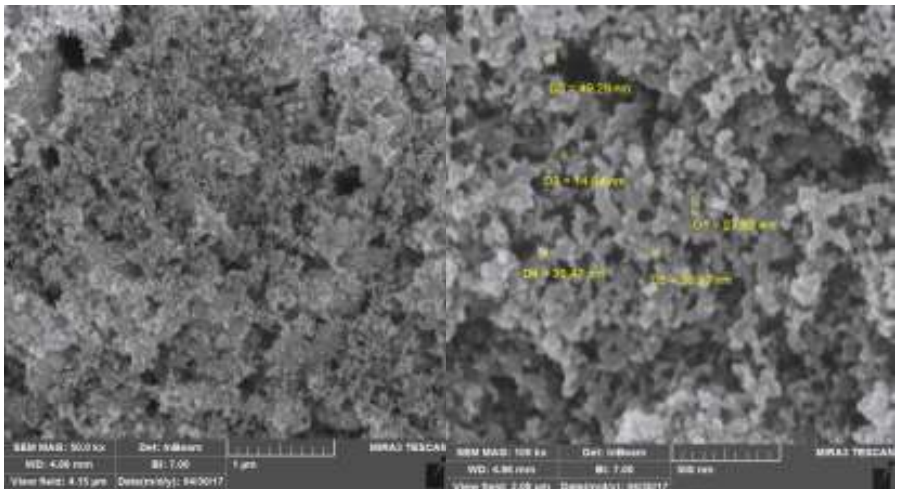


Figure 3.SEM images of the nano silica boron sulfuric acid (NSBSA).

To optimize the reaction conditions, initially, the reaction of benzonitrile with sodium azide was selected as a model reaction. Therefore, to develop a better catalytic system, various reaction parameters such as type of solvent, catalytic loading and temperature were investigated. During our optimization studies, the effect of different types of solvents e.g.

nonpolar, polar protic and polar aprotic solvents was screened (**Table 1**). Noticeably, the reaction was very sensitive to the type of solvent. No product was obtained in chloroform. H_2O, ethanol, methanol and DMSO were effective, but the yields were low, even though the reaction was prolonged up to 24 h (**Table 1**, entries 1-5). Drastic reduction of the catalytic activity of NSBSA and yields of reactions may be attributed to the coordination of donor solvents such as H_2O, ethanol, methanol with empty orbitals of boron atoms. So, it seems that boron atoms may have a key role in the reactivity of NSBSA. As shown in Table 1, in terms of time and yield of tetrazole formation, among the various solvents studied, DMF was found to be the best. Hence, DMF was applied for all other reactions.

Table 1. Screening of various solvents for the reaction of benzonitrile with sodium azide under reflux condition in the presence of NSBSA.

entry	solvent	time (h)	yield (%)
1	H_2O	24	10
2	Ethanol	24	18
3	Methanol	24	24
4	$CHCl_3$	24	N.R
5	DMSO	24	35
6	DMF	2	92

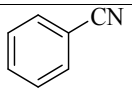
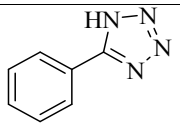
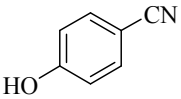
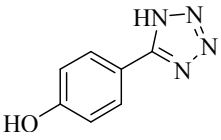
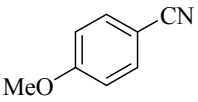
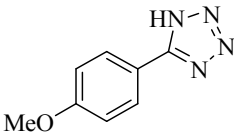
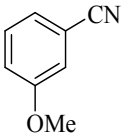
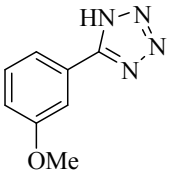
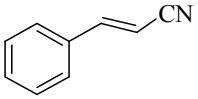
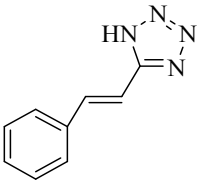
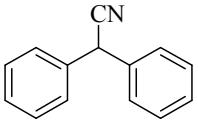
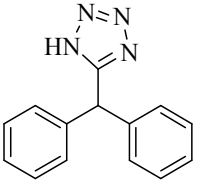
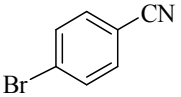
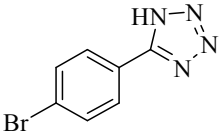
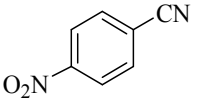
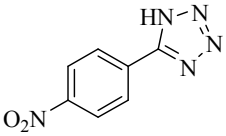
To evaluate the effect of catalyst loading on reaction rate, various amount of NSBSA was examined (**Table 2**). It is clearly seen that NSBSA plays an important role in [3+2] cycloaddition reaction of the benzonitrile with sodium azide. No product was obtained in the absence of catalyst (**Table 2**, entry 1). On the basis of the data of Table 2, the best results were achieved when the model reaction was carried out in the presence of 0.08 g of NSBSA (**Table 2**, entry 5). Lower conversions and longer reaction times were observed when amount of catalyst used was 0.02-0.06 g, whereas, further increase in the amount of catalyst, up to 0.1 g, did not show any significant improvement in the yield.

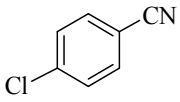
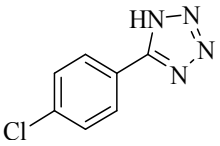
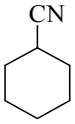
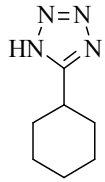
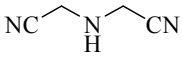
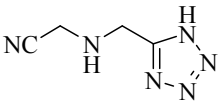
Table 2. Optimization of the amount of NSBSA for the reaction of benzonitrile with sodium azide in DMF under reflux condition.

entry	catalyst (g)	time (h)	yield (%)
1	None	24	N.R
2	0.02	3.5	69
3	0.04	2.5	75
4	0.06	2	83
5	0.08	2	92
6	0.1	2	92

Temperature was another important factor affecting the rate of reaction, which was also assessed. To study the effect of the temperature, the reaction was initially carried out at room temperature and then elevated to reflux condition. Notably, the reaction did not proceed at room temperature and no product was detected. So, refluxing the reaction mixture in DMF was the best choice. We next investigated the scope and generality of this method in the [3+2] cycloaddition reaction of various nitriles with sodium azide in the presence of NSBSA (**Table 3**).

Table 3. Nano silica boron sulfuric acid (NSBSA) mediated preparation of 5-substituted-1*H*-tetrazoles in DMF under reflux condition.

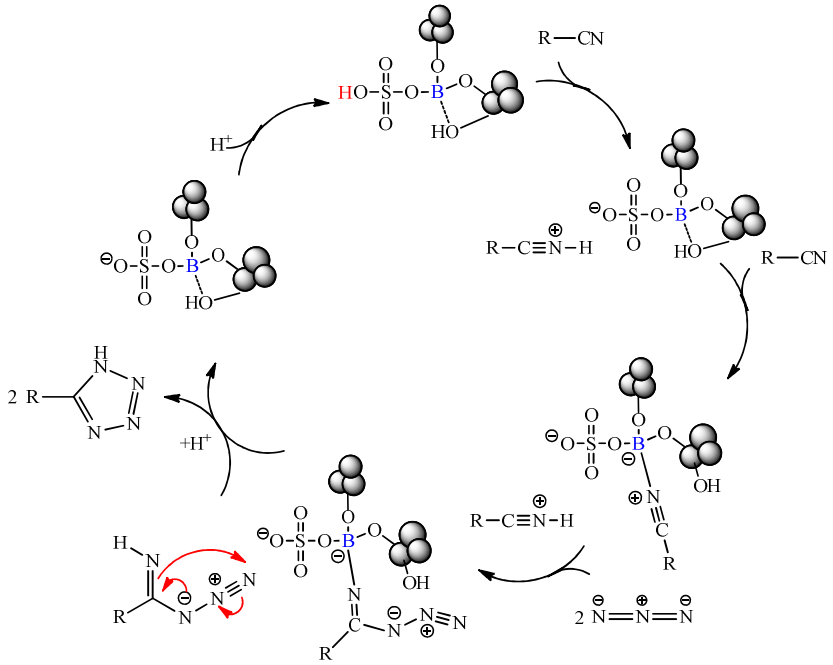
Entry	Nitrile	Tetrazole	Time (h)	Yield (%)	m.p Found(°C) M.P. Reported(°C)
1			2	92	215-217 [215-216][xxii]
2			24	78	232-233 [234-235][x]
3			24	88	228-230 [231-233][xxxi]
4			12	90	155-157 [156-158][xxii]
5			14	90	158-159 [155-156][xxxv]
6			12	94	163-164 [162-165][xxxvi]
7			12	73	267-269 [268-270][xxii]
8			1.5	96	218-220 [220-221][x]

9			2	94	250-253 [251-252][xxxvii]
10			1.5	95	105-107
11			2	87	oily

As shown in Table 3, a series of 5-substituted-1*H*-tetrazoles were prepared in good to high yields from various aromatic and aliphatic nitriles in the presence of NSBSAas a heterogeneous mesoporous catalyst. As expected, NSBSAshowed to be an appropriate nanocatalyst for the versatile synthesis of 5-substituted-1*H*-tetrazoles. All products are known compounds, which were identified by comparison of their spectral data (FT-IR, ^{1}H NMR, ^{13}C NMR) and physical properties such as melting points with those reported in the literature. At first, the disappearance of the spot of nitrile on the middle of TLC plate was observed. Furthermore, the FT-IR spectra revealed the disappearance of a medium and sharp stretching absorption band ofC≡N at 2150 cm^{-1}. In addition, the FT-IR spectra of the purified compounds showed the presence of some characteristic absorption bands corresponding to the NH group at 2159-3235 cm^{-1}, (-N-N=N-) at 1233-1293 cm^{-1}, 1041-1106 and 1110-1189 cm^{-1} due to tetrazole rings. Additionally, a ^{13}C NMR signal at 154-161 ppm is also assigned to the quaternary carbon of NH-C=N[xxi].

Remarkably, the activity of nitrile compound toward azide ion play an important role in [3+2] cycloaddition reactions. As shown in Table 3, in contrary to aromatic, best yields and times were obtained by aliphatic nitriles. In aromatic nitriles, the low yields accompanied with longer reaction times may be attributed to the significant resonance between the aromatic ring and cyano group, which decreases the electrophilic character of cyano group. In addition, aromatic compounds including electron donating and withdrawing substituents at *para*- or *meta*-positions showed no significant difference in product yields or reaction times (**Table 3**, entries 1-9). Maybe it could be attributed to the strongly withdrawing effect of cyano group that the presence of other groups does not affect considerably its behavior.

On the basis of related mechanisms of triazole and tetrazole formation in the presence of acidic catalysts reported in the literature[xxxi], a plausible mechanism may be proposed (**Scheme 2**). Mechanistically, it seems plausible to suppose that, initially, the nitrogen atom of nitrile compound may coordinate to the empty orbital of boron atoms or gets a proton of sulfuric units that can remarkably enhance its electrophilicity. Rationally, this complexation will accelerate the cyclization process. This claim is supported by the experimental facts that the reaction was not remarkably proceeded in the absence of NSBSA, even, after prolonged reaction time (**Table 2**, entry 1). After activation of cyano group by NSBSA, a [3+2] cyclization reaction between the C≡Nbond of nitrile compound and azide ion could take place readily. Finally, a stable 5-substituted-1*H*-tetrazole was obtained by an acidic work-up (**Scheme 2**).



Scheme 2.A proposed mechanism for the preparation of 5-substituted-1*H*-tetrazoles from nitriles and sodium azides in the presence of catalytic amount nano silica boron sulfuric acid (NSBSA).

The reusability capability and recovery of the applied catalyst was also examined in the model reaction. The applied NSBSA was successfully separated from the reaction mixture by centrifugation and reused three times with moderate loss of the catalytic activity (**Table 4**).

Table 4. Reusability test of nano silica boron sulfuric acid (NSBSA) in the model reaction[a].

	fresh	cycle 1	cycle 2	cycle 3
Yield (%)	92	83	78	72
Time (h)	2	2.5	2.5	3

[a] Reaction conditions: benzonitrile (1 mmol), NaN_3 (1.5 mmol), nano silica boron sulfuric acid(NSBSA)(0.08 g), DMF (5 mL) and reflux. [b] Isolated yield.

Experimental

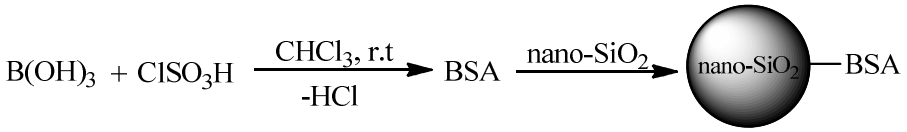
Materials and methods:

All reagents and solvents were obtained commercially and used without further purification. FT-IR spectra were recorded in KBr pellets at room temperature using St-jean Baptist Ave Bomem 450 instrument. FT-NMR Spectra (^{1}H and ^{13}C) were recorded on Bruker Avance DPX (400 MHz) in $CDCl_3$ with TMS as internal standard for protons and solvent signals as internal standard for carbon spectra. Chemical shift values are reported in δ (ppm) and coupling constants are given in Hz. The progress of all reactions was monitored by TLC on 2×5 cm pre-coated silica gel-60 F-254 plates of thickness of 0.25 mm (Merck). The chromatograms were visualized under UV 254-336 nm or by immersion in tanks of common chemical visualizer such as DNP, $H_2SO_{4(conc.)}$, I_2, etc.

Procedure for the preparation of nano silica boron sulfuric acid (NSBSA):

Theboron sulfuric acid (BSA) and nano silica were synthesized according to the methods in the references 30 and 34. A 500-mL suction flask was equipped with a constant pressure dropping funnel. The gas outlet was connected to a vacuum system through an adsorbing solution of alkali trap. Boric acid [$B(OH)_3$] (25 mmol, 1.55 g) in $CHCl_3$ (5 mL) was added to the suction flask. Then, Chlorosulfonic acid ($ClSO_3H$) (75 mmol, 8.74 g, 5 mL) in $CHCl_3$ (15

mL) was added drop-wise to the above flask, over a period of 30 min at room temperature. After completion of addition, the mixture was shaken for 4 h, while the residual HCl was eliminated by suction. Then, BSA was washed several times with dried CH_2Cl_2. Finally, BSA (4.62 g) was thoroughly mixed with nano silica (1:3) 13.86 g (**Scheme 3**).



Scheme 3. Synthesis of nano silica boron sulfuric acid (NSBSA) from nano silica, boroic acid and chlorosulfonic acid.

A typical procedure for the synthesis of 5-phenyl-1H-tetrazole:

In a 25 mL round-bottomed flask, benzonitrile (1 mmol, 0.1 mL) and sodium azide (1.5 mmol, 0.097 g) were dissolved in DMF (5 mL). Nano silica boron sulfuric acid (NSBSA) (0.08 g) was added to the reaction mixture and refluxed for 2 h. After completion of the reaction, i.e. disappearance of nitrile, as monitored by TLC (n-hexane/EtOAc, 4:1, V/V), the reaction vessel was cooled to room temperature. To separate the catalyst, the mixture was centrifuged. The centrifugate was decanted and washed with ethyl acetate. To eliminate any unreacted nitrile, HCl (5 M, 15 mL) was added until the reaction mixture became strongly acidic (pH 3). Then the reaction mixture was treated with ethyl acetate (30 mL) and stirred vigorously for 30 min. The resultant organic layer was extracted by n-hexane (3×50 mL) and washed with H_2O (2×50 mL). The solvent was dried by anhydrous $CaCl_2$ and evaporated by vacuo-rotary. A crude crystalline solid 5-phenyl-1H-tetrazole was obtained. To afford a pure product, the prepared tetrazole was recrystallized in hot ethanol. A white crystalline solid 0.134 g (92%, mp 215-217 °C) was obtained. The product was sufficiently pure, characterized by FT-IR, ^{1}H NMR and ^{13}C NMR and compared with reported spectral data in the literature (**Table 3**, entry 1).

5-phenyl-1H-tetrazole:

White solid; mp: 215-217 ^{o}C; FT-IR (KBr, cm^{-1}): *v* 3235-2159 (N-H stretch.), 1608 (aromatic C=C stretch.), 1562 (N-H bending.), 1486 (C=N stretch.), 1411 (C-N stretch.), 1256 (N=N stretch.), 1164, 1056, 992 (Ring tetrazole and amine 2^0), 695, 783; ^{1}H NMR (400 MHz, DMSO-d$_6$ δ / ppm): 16.85 (br, 1H, -NH), 8.1-8.06 (s, 2H, Ph), 7.69-7.63 (s, 3H, Ph); ^{13}C NMR (100 MHz, DMSO-d$_6$, *δ* / ppm): 155.88 (NH-C=N), 149.2, 131.12, 128.55, 125.06.

Conclusion

In summary, it can be claimed that we have developed a new application of NSBSAnanocomposite as an inexpensive, environmentally-friendly and efficient heterogeneous nanocatalyst for the synthesis of a broad range of aliphatic and aromatic 5-substituted-1*H*-tetrazoles in good to high yields. The procedure was simple and clean. It is also worth to emphasize that NSBSAwas easily prepared, recovered and reused. It is envisaged that the thermal and chemical stability as well as ease of recovery of NSBSAmakes it as a highly efficient and heterogeneous nanocatalyst, which is potentially suitable for further applications in organic syntheses and industrial requirements.

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