



## Original Research Article

## Benign synthesis of 5-substituted 1*H*-tetrazoles via [3+2] cycloaddition of nitriles and sodium azide employing SO<sub>3</sub>H-carbon as an efficient heterogeneous catalyst

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## KEYWORDS

Tetrazoles

[3+2] Cycloaddition

Nitriles

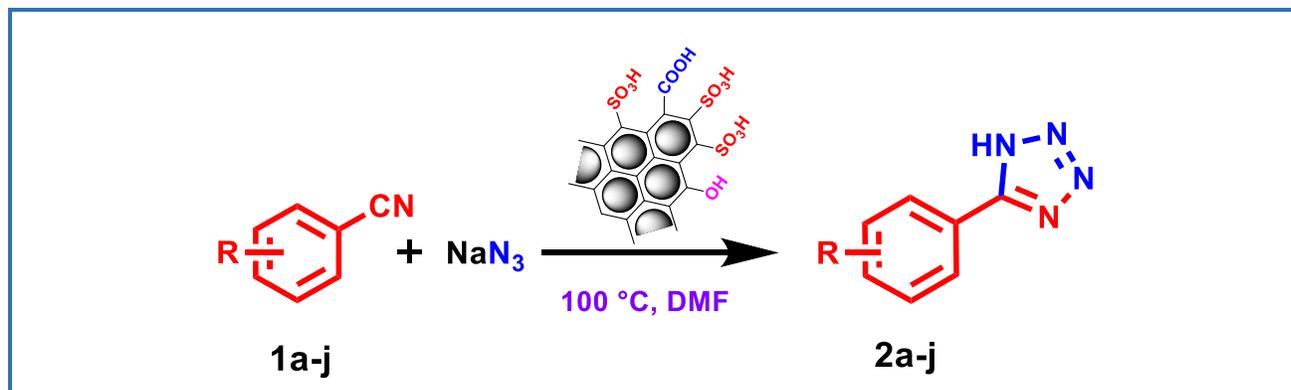
Sodium azide

SO<sub>3</sub>H-carbon catalyst

## ABSTRACT

A novel and green methodology was developed for the synthesis of 5-substituted 1*H*-tetrazoles by [3+2] cycloaddition of nitriles with sodium azide in DMF at 100 °C in the presence of highly stable, water resistant and recyclable nonmetallic SO<sub>3</sub>H-carbon catalyst derived from glycerol. The methodology was extended for the preparation of different 5-substituted 1*H*-tetrazoles from aryl nitriles having electron-donating as well as electron-releasing groups on the arene nucleus in good to excellent yields (85–95%) under optimum reaction conditions. The catalyst was recovered using simple filtration and, then, reused for five cycles without any loss of activity. The main advantages of this methodology are moderate temperature, easy purification of products, easy recovery, and reusability of the catalyst.

## Graphical Abstract



## Introduction

Tetrazoles are the compounds having nitrogen as a heteroatom with five membered cyclic structures. Tetrazoles play a significant role in coordination chemistry as ligands, in medicinal chemistry as stable surrogates for carboxylic acids and in materials applications; including, explosives, rocket propellants, and agriculture [1–7]. Tetrazole serves as precursors of nitrogen-containing heterocyclic compounds [8]. The synthetic tetrazole derivatives can show antifungal [9], antidiabetic [10], and anti-HIV [11] activities, and also can be used in the treatment of asthma [12]. Tetrazole-containing compounds can be used as valuable catalysts in asymmetric reactions. Chiral tetrazole catalyst, (S)-pyrrolidinyl tetrazole has been used [13] in the synthesis of flavanone derivatives, by enantioselective synthetic procedure and also imidazolidine-tetrazole catalyst has been used [14] in the Michael addition of nitroalkanes to  $\alpha$ -,  $\beta$ -unsaturated ketones with high enantiomeric excess.

Synthesis of the tetrazoles is based on the addition of azide ions to organic nitriles in the presence of the catalyst with a suitable solvent. Several methods have been reported in the literature for the synthesis of these compounds using different metal-based catalysts such as cadmium [15], copper [16–18], iron [19, 20], palladium [21], aluminum [22], zinc [23], silver (Silver benzoate) [24], titanium (TiO<sub>2</sub>) [25], and tungstates [26]. Recently, lanthanide-based catalysts (Yb(OTf)<sub>3</sub>, CAN) were also used in the tetrazole synthesis [27]. Also, some other heterogeneous catalysts, such as COY zeolites [28] and acid catalysts [29] have been used to synthesize the tetrazole via cycloaddition. Recently, *K.M. Khan* et al. [30] reported a one-pot preparation of tetrazoles starting from benzaldehydes which proceeds *via* non isolable nitrile intermediate. However, some of these protocols suffer from certain drawbacks such as prolonged reaction times, high temperatures, and being water-intolerant. To overcome these problems, the development of a clean protocol utilizing more eco-friendly and green catalysts with high catalytic activity and short reaction times for the production of tetrazoles has gained prominent attention. The demand of eco-efficient benign procedure promoted us to develop an expedition method for the synthesis of tetrazoles.

The carbon-based solid acid catalysts derived from natural resources have gained more attraction in recent years, due to their advantages including, high efficiency, sustainability, ease of product separation, eco-friendly, and reusability over homogeneous catalysts [31–34]. In this context, our group reported a sustainable methodology for the development of the highly stable and water resistant SO<sub>3</sub>H-carbon catalyst [35, 36] from glycerol (biodiesel by-product) and also from the glycerol pitch (Waste from fat splitting industry). The SO<sub>3</sub>H-carbon catalyst exhibited excellent catalytic properties for different organic transformations [37–40] due to strong acid sites of the

sulfonic acid functional groups in addition to its high thermal stability and recyclability. In continuation of exploring the catalytic applications of the SO<sub>3</sub>H-carbon, in this research study, we report a new synthetic method for the preparation of 5-substituted 1*H*-tetrazole derivatives by the cycloaddition of various substituted benzonitriles with sodium azide in DMF at 100 °C (Scheme 1) in excellent yields.

## Experimental

### *Materials and methods*

All the chemicals used in this study were purchased from M/s. SD Fine Chemicals Pvt. Ltd., Mumbai, India. All the solvents were of analytical grade. Reaction was monitored on silica gel TLC plates (Coated with TLC grade silica gel, obtained from Merck) employing iodine vapors for the detection of spots. Melting points of the products were recorded using Barnstead Electro thermal 9200 instrument. IR spectra were recorded on a PerkinElmer FT-IR Spectrum BX. Mass spectra were recorded using electron spray ionization-mass spectrometry (ESI-MS). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker UXNMR (Operating at 500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C NMR) spectrometer using DMSO-d<sub>6</sub>. Chemical shifts  $\delta$  are reported relative to TMS ( $\delta = 0.0$ ) as an internal standard and coupling constants (*J*) are given in Hz.

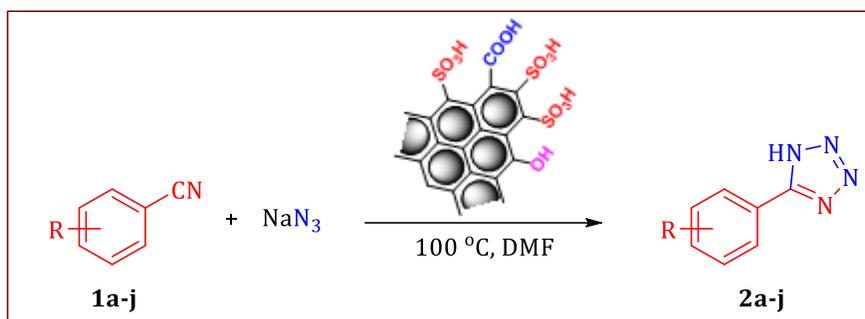
### *Preparation of SO<sub>3</sub>H-carbon catalyst*

A mixture of glycerol (10 g) and concentrated sulphuric acid (30 g) were taken in a 500 mL glass beaker and gently heated on hotplate from ambient temperature to 220 °C for 20 min, in order to facilitate in situ partial carbonization and sulfonation. The reaction mixture was allowed at that temperature for about 20 min till the foaming was ceased. The resultant black crystalline product was washed with hot water under agitation till the wash water becomes neutral to pH. The partially crystalline product was filtered and dried in an oven at 120 °C for 2 h to ensure free of moisture to obtain glycerol-based carbon acid catalyst (4.67 g). The carbon acid catalyst was found to have acid density of 8.19 mmol/g, and surface area of 0.21 m<sup>2</sup>/g [40].

### *General procedure for the synthesis 5-substituted 1H-tetrazoles*

A mixture of benzonitrile (103 mg, 1 mmol), sodium azide (97.5 mg, 1.5 mmol) and SO<sub>3</sub>H-carbon catalyst (10 mg, 10 wt% of nitrile) in dry DMF (5 mL) was stirred at 100 °C in seal tube for 6 h. The progress of the reaction was monitored by TLC and after completion of the reaction, the catalyst was separated by simple filtration, washed with ethyl acetate. The filtrate was treated with ethyl acetate (30 mL) and ammonium chloride solution (30 mL) and stirred vigorously. The organic layer was

separated and the aqueous layer was again extracted with ethyl acetate (20 mL). The combined organic layer was washed with water, brine and dried over anhydrous sodium sulfate and, then, was evaporated under reduced pressure to give the product. The product was purified by the column chromatography. All the products were characterized by comparing their m.p, FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR with that of the reported [16, 17, 19, 41, 42]. The recovered catalyst was washed with methanol and dried in oven at 120 °C for 1 h and reused for the next cycle of reaction.



**Scheme 1.** SO<sub>3</sub>H-Carbon catalyzed synthesis of 5-substituted 1H-tetrazoles

#### The selected spectral data

##### 5-Phenyl 1H-tetrazole (2a)

Solid, yield 92%, mp 214–216 °C, IR (KBr) ( $\nu_{\text{max}}$ / cm<sup>-1</sup>): 3406, 3129, 3056, 2984, 1608, 1560, 1473, 1403, 1258, 1158, 1060, 988, 786 and 688.  $^1\text{H}$  NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  6.78–6.87 (s, 2H), 6.29–6.43 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  155.8, 131.2, 129.4, 127, 124.5.

##### 5-(4-Methoxyphenyl) 1H-tetrazole (2c)

Solid, yield 88%, mp 230–236 °C, IR (KBr) ( $\nu_{\text{max}}$ / cm<sup>-1</sup>): 3436, 3087, 3019, 2934, 2853, 2745, 1613, 1502, 1449, 1403, 1261, 1175, 1038, 854, 751, 696 and 615.  $^1\text{H}$  NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  6.73–6.79 (d, 2H,  $J = 7.1$ ), 5.85–5.95 (d, 2H,  $J = 7.4$ ).  $^{13}\text{C}$  NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  161.5, 155.2, 128.7, 116.6, 114.8, 55.5.

##### 5-(4-Bromophenyl) 1H-tetrazole (2h)

Solid, yield 91%, mp 264–266 °C, IR (KBr) ( $\nu_{\text{max}}$ / cm<sup>-1</sup>): 3436, 2689, 2248, 2121, 1657, 1480, 1052, 823, 762 and 620.  $^1\text{H}$  NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  6.72–6.86 (d, 2H,  $J = 6.7$ ), 6.50–6.65 (d, 2H,  $J = 5.7$ ).  $^{13}\text{C}$  NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  155.7, 132.5, 129.0, 124.7, 124.1.

## Results and discussion

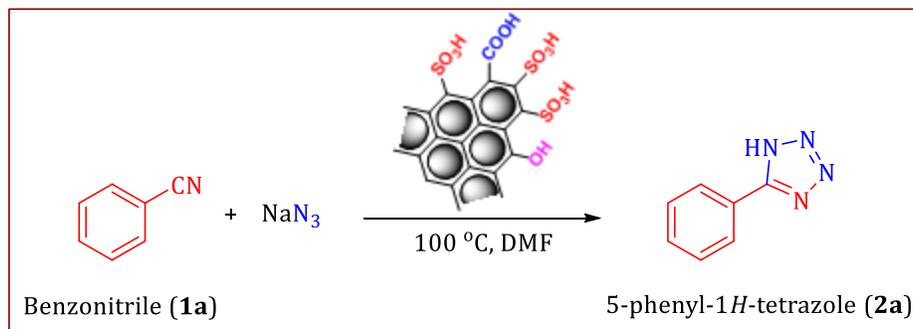
First, we have studied a standard model reaction using benzonitrile **1a** (1 eq) and sodium azide (1 eq) at 100 °C in DMF without catalyst. In this sense, no product was formed even after 10 h of heating. The same reaction was performed in the presence of carbon acid catalyst (10 wt% of substrate) at 100 °C in DMF (10 mL) for 6 h which resulted the corresponding 5-phenyl 1*H*-tetrazole (**2a**) in 75% isolated yield (As shown in [Scheme 2](#)). This reveals that the presence of the carbon acid catalyst is to perform the reaction, hence, the catalytic activity of SO<sub>3</sub>H-carbon catalyst was observed in the model reaction. Next, in order to evaluate the effect of mole ratio of the benzonitrile (**1a**) and sodium azide, we investigated the reaction under similar conditions and found out that the use of excess amount of azide (1.5 eq) over benzonitrile (1 eq) was advantageous for obtaining higher yield of 5-phenyl 1*H*-tetrazole (**2a**) in 92% isolated yield in 6 h. Hence, further reactions were performed with 1:1.5 molar ratio of nitrile and sodium azide.

Afterwards, we investigated the effect of the solvent on the reaction under similar conditions using various solvents like DMSO, DMF, THF, Toluene, ACN and water. From this study it was found that, the reaction did not proceed in toluene and only 60% of the product was formed along with several unwanted side products in DMSO. Whereas, THF gave the desired product in low yield and only a trace amount of the product was observed in ACN and water, after substantial experimentation with different solvents, DMF was found to be superior in resulting 5-phenyl 1*H*-tetrazole (**2a**) in higher isolated yield of 92% as compared to other solvents.

The effect of SO<sub>3</sub>H-carbon catalyst loading on the yield of 5-phenyl 1*H*-tetrazole (**2a**) was studied by varying catalyst amounts ranging from 5 to 20 wt% of benzonitrile, keeping the reaction temperature at 100 °C and molar ratios of benzonitrile to NaN<sub>3</sub> as 1:1.5 for 6 h and the results are depicted in [Figure 1a](#). The data clearly indicated that the yield of the product increased to a maximum of 92% at 10 wt% of the catalyst loading as the further increase of loading to 15 and 20 wt% didn't show any considerable increase. Hence, the catalyst amount 10 wt% of benzonitrile was found to be the optimal quantity and sufficient to push the reaction towards the maximum yield of 5-phenyl 1*H*-tetrazole (**2a**).

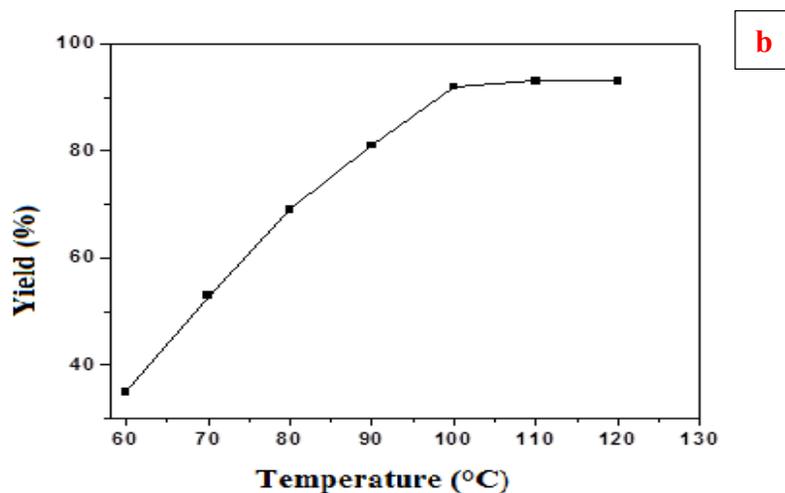
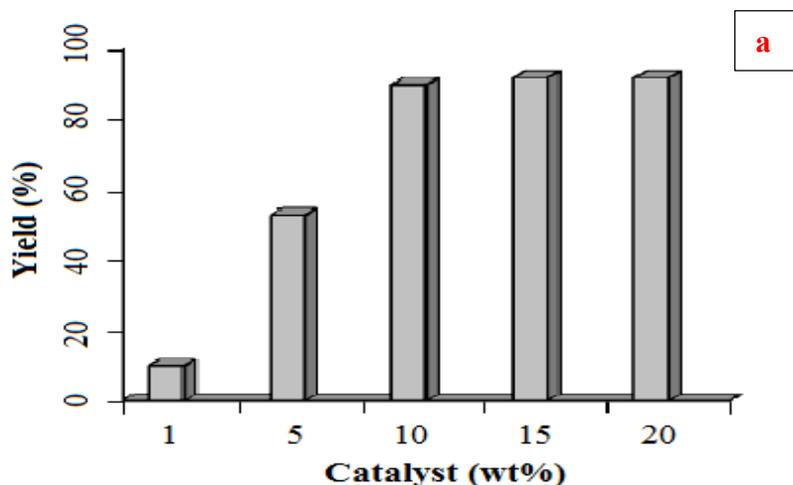
The effect of the reaction temperature on the [3+2]-cycloaddition reaction of benzonitrile (**1a**) with sodium azide was conducted at different temperatures ranging from 60 to 120 °C using a catalyst loading of 10 wt% for 6 h and the results are summarized in [Figure 1b](#). This study revealed that the increase of the reaction temperature from 60 to 100 °C accelerates the reaction towards the product formation while at 100 °C maximum 92% yield of 5-phenyl 1*H*-tetrazole (**2a**) was obtained. Further increase in temperature to 120 °C didn't showed any significant improvement in % yield of the product. Based on this study, the optimum reaction temperature for the [3+2] cycloaddition reaction of benzonitrile with sodium azide to obtain 92% yield of 5-phenyl 1*H*-tetrazole (**2a**) is 100

°C. In addition, the effect of the reaction period on the yield of tetrazoles was also studied by varying the reaction period from 4 to 12 h under similar reaction conditions. Consequently, the study revealed that, 6 h of reaction period is optimum to obtain the maximum yield of the 5-phenyl 1H-tetrazole (**2a**).



**Scheme 2.** Model [3+2]-cycloaddition reaction of benzonitrile with sodium azide in presence of  $\text{SO}_3\text{H}$ -Carbon catalyst

**Figure 1.** Effect of catalyst loading a) and reaction temperature b) on the yield of product

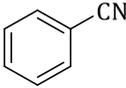
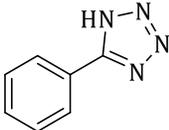


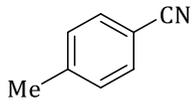
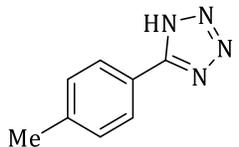
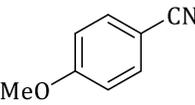
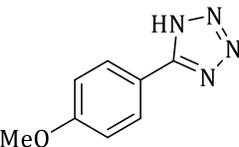
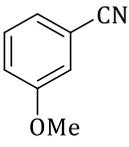
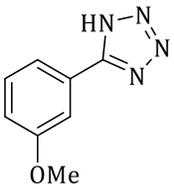
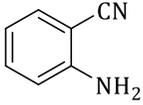
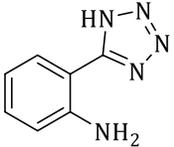
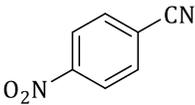
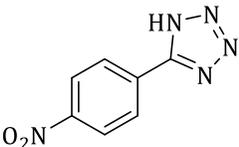
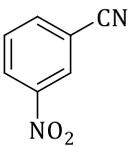
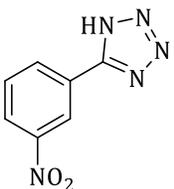
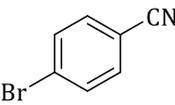
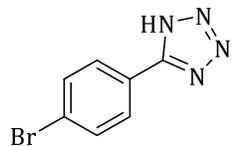
From the above study, the optimum reaction conditions for the synthesis of 5-phenyl 1*H*-tetrazole (**2a**) in excellent isolated yield (92%) were found to be: benzonitrile (1 mmol), sodium azide (1.5 mmol), SO<sub>3</sub>H-carbon catalyst (10 wt% of nitrile), DMF solvent, temperature 100 °C and the reaction time of 6 h (Table 1, entry 1). Furthermore, the scope and generality of this protocol was investigated under optimum reaction conditions for the [3+2] cycloaddition reaction of the substituted benzonitriles (**1b-h**) with sodium azide in order to obtain the corresponding tetrazole derivatives (**2b-h**) in good to excellent yields. The results are summarized in Table 1. Various substituents presented on the benzonitriles, such as nitro, bromo, amino and methoxy were well tolerated and produced corresponding tetrazoles in excellent yields under these conditions. More importantly, the aromatic nitriles with electron-withdrawing groups like nitro, bromo showed better reactivity (Table 1, entries 6-8) than electron-donating groups like methoxy, amino (Table 1, entries 3-5). Next, we extended this procedure to the preparation of pyridine and benzyl based tetrazoles derivatives **2i** and **2j**, by [2+3] cycloaddition reaction of corresponding nitriles **1i** and **1j** with sodium azide in very good yields (Table 1, entries 9 and 10). All the products were characterized by comparing their m.p, FT-IR and <sup>1</sup>H and <sup>13</sup>C NMR with that of the reported ones.

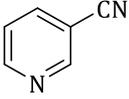
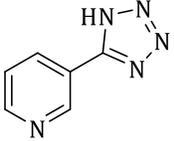
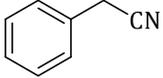
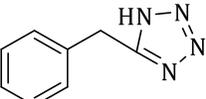
#### Reusability of the catalyst

The reusability of a catalyst which is one of its most important benefits makes it useful for commercial application. Reusability of SO<sub>3</sub>H-carbon catalyst for the [3+2] cycloaddition reaction of benzonitrile (**1a**) with sodium azide was investigated (Figure 2) in DMF under the optimized conditions at 100 °C for 6 h to obtain 5-phenyl 1*H*-tetrazole (**2a**) in 92% yield. After completion of the reaction, the catalyst was recovered by filtration, washed with methanol and dried in oven at 120 °C for 1 h. The catalyst was reused for 5 cycles and it was found that the catalytic activity maintained with ~92% conversion in first of the three cycles and marginally reduced from 90% to 88% in the last two cycles due to the loss in the recovery. This study demonstrated that the catalyst was highly active, stable, and recyclable up to fifth cycle without any significant loss of activity.

**Table 1.** SO<sub>3</sub>H-Carbon catalyzed synthesis of tetrazoles from nitriles<sup>a</sup>

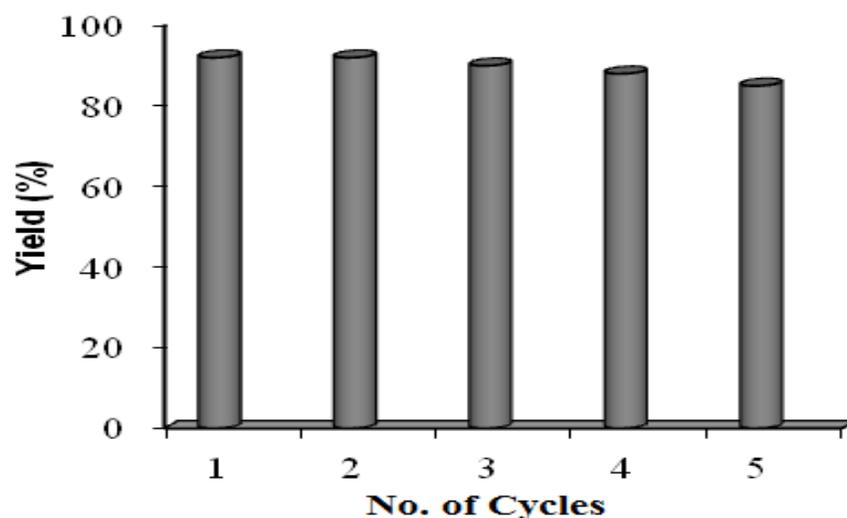
Entry	Nitrile	Tetrazole	Time (h)	Yield (%)	M.p. (°C) [lit.]	
1	 <b>1a</b>	 <b>2a</b>	6	92	214-216	213-214 [17]

2	 <b>1b</b>	 <b>2b</b>	6	87	245-247	248-249 [16]
3	 <b>1c</b>	 <b>2c</b>	6.5	88	230-232	231-233 [16]
4	 <b>1d</b>	 <b>2d</b>	6.5	85	156-158	157-159 [17]
5	 <b>1e</b>	 <b>2e</b>	6.5	88	204-206	202-205 [19]
6	 <b>1f</b>	 <b>2f</b>	5	95	218-220	219-221 [16]
7	 <b>1g</b>	 <b>2g</b>	5.5	92	144-145	145-146 [41]
8	 <b>1h</b>	 <b>2h</b>	5	91	264-266	264-265 [17]

9			5.5	89	238-240	239-240 [42]
	<b>1i</b>	<b>2i</b>				
10			6	90	121-122	123-124 [16]
	<b>1j</b>	<b>2j</b>				

<sup>a</sup> Reaction conditions: Nitriles (**1a-j**) (1 mmol), NaN<sub>3</sub> (1.5 mmol), DMF (10 mL), SO<sub>3</sub>H-carbon catalyst (10 wt% of nitrile), temperature (100 °C)

<sup>b</sup> Isolated yields



**Figure 2.** Reusability of the SO<sub>3</sub>H-carbon catalyst

## Conclusion

We have developed a simple and highly efficient protocol for the synthesis of the 5-substituted 1*H*-tetrazoles (**2a-j**) from nitriles (**1a-j**) by treating it with sodium azide using the highly stable SO<sub>3</sub>H-carbon catalyst derived from glycerol. The promising points for the presented methodology are high efficiency, short reaction time, cleaner reaction profile, easy work up, and highly yielding process and recyclability of the catalyst which make this procedure a potential alternative to the existing methods. This method might have a great number of other applications, as the catalyst is cheap and easy to prepare from glycerol.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

## Supporting Information

Additional supporting information related to this article can be found, in the online version, at [http://www.ajgreenchem.com/article\\_68043.html](http://www.ajgreenchem.com/article_68043.html)

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