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Highly efficient synthesis of 1- and 5-substituted 1*H*-tetrazoles using chitosan derived magnetic ionic liquid as a recyclable biopolymer-supported catalyst†

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A general method for the efficient synthesis of 1- and 5-substituted 1*H*-tetrazoles from nitriles and amines is described using chitosan supported magnetic ionic liquid nanoparticles (CSMIL) as a novel heterogeneous catalyst. The application of this catalyst allows the synthesis of a variety of tetrazoles in high yields at low temperature. This new magnetic catalyst has been prepared from chitosan (the most abundant biopolymer in nature and cheap industrial waste) and methyl imidazole (a widely available backbone of ionic liquids) which was reacted with $FeCl_3$ to obtain the CS–EMImFeCl_4 catalyst. This methodology illustrates a very simple procedure, with wide applicability, environmental friendliness and reusability of catalyst. The new catalyst was characterized using some different microscopic and spectroscopic techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), FTIR spectroscopy, and Raman spectroscopy. The novel catalyst has therefore a great potential to be used in green processes.

1. Introduction

It is quite obvious that wide application of tetrazoles, primarily in pharmaceutical chemistry as lipophilic spacers, metabolically stable surrogate for a carboxylic acid group,[1] antibacterial,[2] antifungal,[3] antiviral,[4] and antiulcer[5] agents have led to the development of new methods for synthesis of functionally substituted tetrazoles. The most important drugs containing a tetrazole ring are antihypertensive drugs Losartan and its analogues or the peptidase inhibitor CGS-26303 (Fig. 1).[6] In addition, tetrazoles have been successfully used in various material sciences and synthetic organic chemistry as analytical reagents[7] and synthons.[8] They have also important roles in coordination chemistry as a ligand for preparation of complex heterocyclic structures.[9] For example, proline-derived tetrazole is used as an enantioselective catalyst in asymmetric reactions.[10]

Tetrazole rings can be prepared in several ways, the most convenient method to achieve 5-substituted 1*H*-tetrazoles is [2+3]-cycloaddition of azide ion to the corresponding nitriles that many synthetic approaches towards them have been developed.[11]

Different homogenous and heterogeneous catalysts such as $AlCl_3$,[12] $BF_3.OEt_2$,[13] $ZrOCl_2$,[14] $Pd(PPh_3)_4$,[15] $Pd(OAc)_2$/ZnBr,[16] ZnO,[17] $ZnBr_2$,[18] $ZnCl_2$/tungstates,[19] Zn/Al hydrotalcite,[20] $Zn(OTf)_3$,[21] Zn hydroxyapatite,[22] ZnS,[23] Cu_2O,[24] $CdCl_2$,[25] $BaWO_4$, and natural zeolite[26] have been reported for the promotion of reaction between nitrile and NaN_3 or TMS-N_3. Very recently, Nagarkar *et al.* have reported nano ZnO/Co_3O_4 as a novel nano heterogeneous catalyst for synthesis of tetrazole from nitrile in DMF.[27]

Iron salts that are cheap, non-toxic, and environmentally friendly are a group of metal salts for synthesis of 1*H*-tetrazoles. Some research groups reported $FeCl_3$–SiO_2,[28] $Fe(OAc)_2$,[29] $Fe(HSO_4)_3$,[30] and γ-Fe_2O_3,[31] as heterogeneous catalysts for the synthesis of 5-substituted 1*H*-tetrazoles *via* cycloaddition of nitriles and azide in DMF at 120 °C.

Although a wide range of 5-substituted 1*H*-tetrazoles are known, only a few valuable attempts have been made to facilitate their synthetic procedures. Most of these approaches consist of acid-catalyzed cycloaddition between isocyanides and hydrazoic acid[32] or cyclization between primary amines,

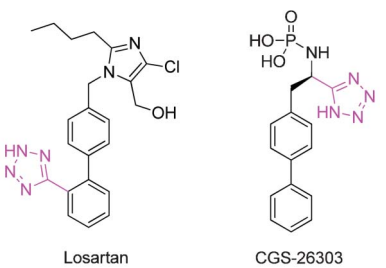

Fig. 1 The structure of Losartan and CGS-26303.

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triethyl *ortho*-formate, and sodium azide using AcOH, PCl_5, $In(OTf)_3$, $Yb(OTf)_3$, SSA, $[HBIm]BF_4$, and recently natrolite zeolite as catalyst.[33] Although all of these methods are worthwhile, a number of them have one or more of the following drawbacks: the use of DMF as solvent, tedious workup of the reaction mixture, refluxing for a prolonged period of time, high reaction temperature (up to 130 °C), expensive moisture-sensitive reaction conditions, toxic metals, difficulty in separation and recovery of the catalyst and the presence of hydrazoic acid which is highly toxic and explosive. Hence, it is of great practical importance to develop a more efficient and also environmentally benign method that avoids all of these drawbacks.

During the past decade, the development of nanocatalysis for excellent chemical synthesis of materials have been the subject of considerable research attention, because of some advantages of nano catalysts compared to bulk materials, such as a large surface-to-volume ratio, high selectivity and activity, low energy consumption, and long lifetime. Nanocatalysts are typically supported on silica or alumina, for stability toward sintering, but recently, nanoparticles made from natural materials particularly polysaccharides are attracting increasing interest as environmentally benign polymeric supports because of their outstanding physical and biological properties.[34] Among biopolymers, chitosan (CS, Fig. 2) is a potential excellent material as a support for catalytic applications in heterogeneous molecular catalysis, due to its chemical reactivity, unique three-dimensional structure, presence of hydroxyl and amino groups, excellent chelating and mechanical properties.[35] Zhao *et al.* developed CS-NMe_3Cl as an active catalyst for cycloaddition of CO_2[36] and recently, Sun *et al.* reported chitosan functionalized ionic liquid as a recyclable biopolymer-supported catalyst for the same reaction.[37] Yuanchen and co-workers found that chitosan supported L-proline can be used as a heterogeneous organocatalyst to catalyze the asymmetric Henry reaction in aqueous media.[38] In addition, different research groups have reported chitosan as a green and recyclable, heterogeneous organocatalyst for C–C bond forming reactions such as Henry reaction, Aldol condensation, Claisen–Schmidt condensation, Knoevenagel condensation and Michael addition.[39]

Recently, magnetic ionic liquids are attracting increasing interest as environmentally benign reaction media for various organic synthesis,[40] catalysis,[41] *etc*.[42] Further, magnetic ionic liquid offers several advantages, such as extremely low volatility, high thermal stability, non flammability and high ionic conductivity. These advantages and nontoxic nature of magnetic ionic liquid show its potential as a catalyst in organic synthesis. It is also reported that magnetic ionic liquids could be separated from other solvents by a combination of magnetic field and conventional methods such as filtration, ultracentrifugation, and adsorption.[43]

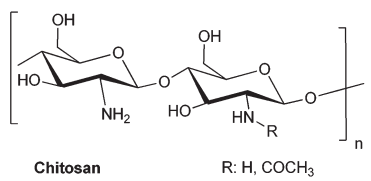
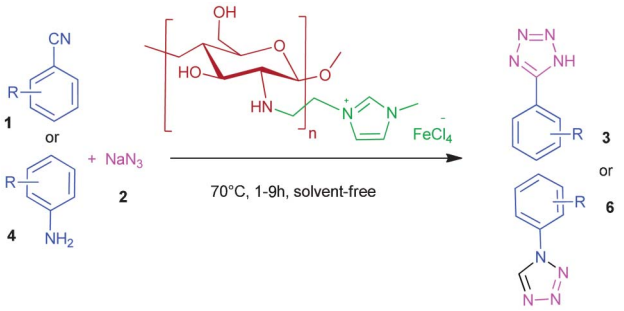


Fig. 2 The general structure of chitosan (CS).



Scheme 1 Synthesis of 1- and 5-substituted 1*H*-tetrazoles in the presence of chitosan supported magnetic ionic liquid (CSMIL).

In this work, to combine the benefits of ILs and heterogeneous catalysts, we reveal a new magnetic biopolymer supported heterogeneous catalyst based on nanometre scale which can be applied for different organic functional group transformations in green processes. Therefore, we focused our attention on a simple, green, and efficient method for synthesis of biologically active 1- and 5-substituated 1*H*-tetrazoles from a wide variety of nitriles and amines in high yields and very short reaction time (Scheme 1). Lower cost, operational simplicity, high yields, and the possibility of easy recovery of catalyst are the advantages of this new method.

2. Results and discussion

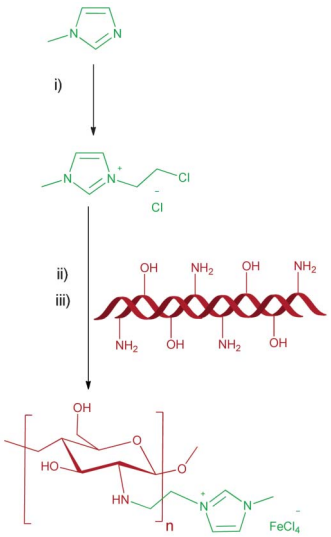
2.1. Catalyst preparation

Chitosan supported magnetic ionic liquid nanoparticles (CSMIL) as a new catalyst was prepared based on the following procedure (Scheme 2) (see the experimental section).

2.2. Optimization of reaction

The first step for the 5-substituted 1*H*-tetrazoles synthetic approach involved optimization of the reaction conditions and exploration of the catalytic activity of chitosan supported magnetic ionic liquid nanoparticles. In order to delineate the standard operating condition, for our initial screening experiments, the catalytic activities of different catalysts were examined in the model reaction. The choice of the iron salt as a catalyst is of great importance for the generation of tetrazole, therefore, the effect of various solvents, as well as of different reaction temperature on the reaction of 4-nitrobenzonitrile **1g** and sodium azide **2** has been studied. The catalytic performances of different iron salt catalysts are shown in Table 1.

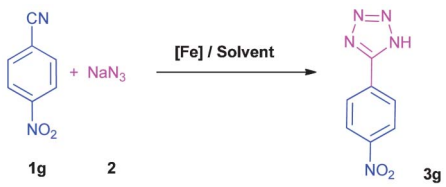
It was confirmed by the results that no addition product is obtained when the reaction is carried out without catalyst



Scheme 2 Preparation of chitosan supported ethyl methyl imidazole tetrachloroferrate nanoparticles (CS-EMImFeCl$_4$); i) 1,2-dichloroethane, acetone, reflux, ii) chitosan, isopropanol, 75 °C, iii) anhydrous FeCl$_3$.

(Table 1, entry 1), despite prolonged reaction time, thus highlighting the specific role of iron salt catalyst. In the presence of iron(II), (III) salts such as Fe(HSO$_4$)$_3$, FeCl$_3$, FeCl$_3$–SiO$_2$ and Fe(OAc)$_2$, application of high boiling point organic solvent (DMF) is vital at high temperature (sometimes as high as 130 °C) in long reaction times (Table 1, entries 2–5). It was observed a decrease in the reaction time using (BMIm)Cl ionic liquid as a solvent system for FeCl$_3$ as a catalyst and so on, this observation motivated us to check magnetic ionic liquid (BMIm)FeCl$_4$ as a reaction medium instead of FeCl$_3$/BMImCl. By Switching the solvent from DMF to (BMIm)FeCl$_4$, complete conversion of the starting material was achieved within 8 h, but unfortunately the separation and reuse of the (BMIm)FeCl$_4$ from the products wasn't so perfect. Therefore, we decided to convert it to a heterogeneous catalyst by using chitosan as a supporting agent. So, after converting (BMIM)FeCl$_4$ to chitosan supported magnetic ionic liquid (CSMIL), we surprisingly found that the same reaction in the presence of CSMIL gave higher yield of the desired product (90%) in shorter reaction time (6 h) (Table 1, entries 14). The solvent has an inconspicuous influence on the yield and reaction time (Table 1, entries 9–12) and the best result was achieved in solvent free conditions. Additionally, we also investigated the effect of temperature (Table 1, entries 13–14) and amount of catalyst (Table 2) in solvent-free conditions. There was no appreciable increase in the yield by increase the reaction temperature. In contrast to previously reported reactions involving iron salts, the addition of DMF as a solvent and using high temperature were unnecessary. Different research groups established that the rate of cycloaddition reactions proceeding in solvents such as DMF, and this has been related to the stability of DMF at the high temperatures necessary for cycloaddition reactions,[44] so it seems reasonable to think that [EMIm]FeCl$_4$ ionic liquid supported on chitosan would be a good choice of catalyst/solvent instead of iron salts/DMF. Consequently, the optimal reaction conditions have been identified as 70 °C for 6 h in solvent free condition in the presence of 2.5 mmol% CSMIL.

Table 1 Catalytic activity of different iron salt catalysts on the synthesis of 5-substituted-1*H*-tetrazoles[a]



1g 2 3g

Entry[ref]	Catalyst	Solvent	Time (h)	*T* (°C)	Yield[b] (%)
1	No catalyst	DMF	24	120	—
2[30]	Fe(HSO$_4$)$_3$	DMF	18	120	96
3	FeCl$_3$	DMF : H$_2$O (9 : 1)	15	120	76
4[28]	FeCl$_3$–SiO$_2$	DMF	12	120	81
5[29]	Fe(OAc)$_2$	DMF : H$_2$O (9 : 1)	24	80	96
6	FeCl$_3$	(BMIm)Cl	10	120	78
7	—	(BMIm)FeCl$_4$	8	120	82
8	Chitosan	—	24	120	20
9	Nano CSMIL	EtOH	10	120	75
10	Nano CSMIL	MeCN	8	120	80
11	Nano CSMIL	DMSO	8	120	81
12	Nano CSMIL	DMF	8	120	85
13	Nano CSMIL	Neat	5	120	89
14	Nano CSMIL	Neat	6	70	90

[a] Reaction conditions: nitrile (1 mmol), NaN$_3$ (1.2 mmol), solvent (1 mL), chitosan supported EMIm FeCl$_4$ (2.5 mmol%). [b] Isolated yield.

Table 2 Effect of catalyst amount on the reaction between nitrile (1 mmol), NaN$_3$ (1.2 mmol), chitosan supported (EMIm)FeCl$_4$[a]

Entry	Amount of cat. (mmol%)	Yield[b] (%)
1	0.5	30
2	1.0	45
3	1.5	80
4	2.0	86
5	2.5	90
6	3.0	91

[a] Reaction conditions: *p*-nitro benzonitrile (1 mmol), NaN$_3$ (1.2 mmol), chitosan supported (EMIm)FeCl$_4$ (2.5 mmol%). [b] Isolated yield.

Table 3 Comparison of various heterogeneous catalysts with CSMIL in the synthesis of 5-substituted 1*H*-tetrazoles[a]

Entry[ref]	Catalyst	Solvent	Time (h)	*T* (°C)	Yield[b] (%)
1[22]	ZnHAP	DMF	12	120	78
2[20]	Zn/Al-HT	DMF	12	120	84
3[31]	Nano ZnO/Co$_3$O$_4$	DMF	12	120	90
4[33]	CoY zeolite	DMF	14	120	90
5	**Nano CSMIL**	**Neat**	**6**	**70**	**90**

[a] Reaction conditions: nitrile (1 mmol), NaN$_3$ (1.2 mmol), chitosan supported (EMIm)FeCl$_4$ (2.5 mmol%). [b] Isolated yield.

Table 4 Preparation of 5-substituted 1*H*-tetrazoles in the presence of nano chitosan supported [EMIm]$FeCl_4$[a]

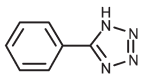
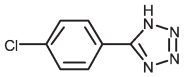
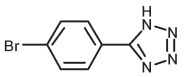
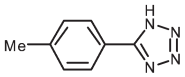
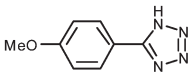
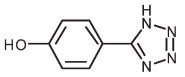
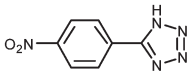
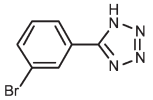
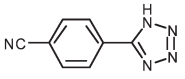
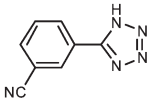
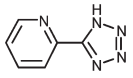
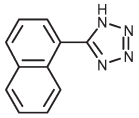
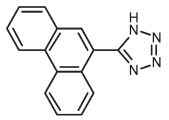
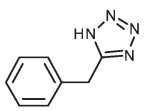
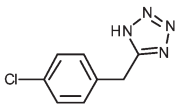
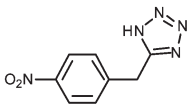
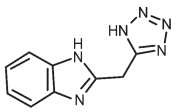
Entry[ref]	Product	Time (h)	Yield[b] (%)	M.P. (°C)
3a[11c,18]		7	87	215
3b[18,20]		7	84	262
3c[11e]		7	86	266
3d[11c,24]		8	87	248
3e[18]		8	82	230
3f[18]		8	81	234
3g[18,24]		6	90	218
3h[11e]		6.5	85	149
3i[20]		6	84	255
3j		6	89	213
3k[18]		6	90	211
3l[18,24]		6	90	264
3m[24]		8	83	215
3n[11e,24]		9	81	123

Table 4 (*Continued*)

Entry[ref]	Product	Time (h)	Yield[b] (%)	M.P. (°C)
3o[17,20]		8	83	225
3p[17,20]		7	85	184
3q		9	86	278

[a] Reaction conditions: nitrile compounds (1 mmol), NaN_3 (1.2 mmol), chitosan supported [EMIm]$FeCl_4$ (2.5 mmol%), 70 °C.
[b] Isolated yield.

It seems that nanostructure can be a good candidate as a catalyst, because their surface area increases dramatically and are even dispersible in solution to form an emulsion to increase the diffusion rate. The catalyst activity of CSMIL presumably is related to: (1) nanostructured nature of the catalyst and (2) catalytic activity of amine or hydroxyl groups of the polysaccharide of chitosan for activating the starting materials. Additionally, we found the recyclability of this catalyst by using magnetic field or *via* solvent extraction of the product from the reaction mixture.

The optimum amount of nanocatalyst loading in this reaction, was found to be 2.5 mmol % (Table 2, entry 5). By lowering the catalyst loading to 0.5–2.0 mmol%, the desired product was obtained in low yield (Table 2, entries 1–4) while with increasing of the catalyst loading to 3.0 mmol% has no significant effect on reaction rate and isolated yield of product (Table 2, entry 6).

Many methods directed towards synthesis of 1*H*-tetrazole have therefore been developed; the present methodology was compared to non iron salt catalysts, summarized in Table 3. This method has the distinction of providing a green nano biopolymer-supported catalyst, and has attracted much interest in relation to the available methods catalyzed by different catalysts; because this method was undertaken at 70 °C, with high yields in short reaction time. It can be seen that 81–90% yield of products is obtained at 70 °C in the presence of 2.5 mmol% CSMIL after 6 h whereas 78–90% yield is obtained at 120 °C in prolonged time in the presence of other catalysts such as ZnHAP, Zn/Al-HT, and nano ZnO/Co_3O_4. Additionally, this is the first report of 5-substituated tetrazole synthesized in solvent-free conditions and low temperature instead of DMF as solvent.

Aiming to extend the scope of our methodology, we next used different nitriles as the substrates for this reaction. The results are summarized in Table 4. As the entries in Table 4 reveal, the catalysis proceeded well for a wide variety of aryl

nitriles, providing the corresponding tetrazoles in high yields. The results showed that an electron donating group or an electron withdrawing group on benzonitrile does not have a notable effect and gives good yield.

Therefore, the best performing catalyst to achieve 5-substituted 1*H*-tetrazoles is the nano CSMIL catalyst, delivering excellent yields up to 90%. After this pioneering example, we proceeded to investigate the scope of 1*H*-tetrazole synthesis from another starting materials utilizing CSMIL as catalyst to ensure versatility of this catalyst with a wide scope of substrates.

With the new catalyst at hand, we conducted a reaction of *p*-methyl aniline with triethyl *ortho*-formate, and sodium azide in the presence of 2.5 mmol% of chitosan supported $EMImFeCl_4$ catalyst (Table 5). In comparison with the other reported catalysts in literature, we observed that the nano CSMIL catalyst gives better yield in shorter reaction time and lower temperature than $In(OTf)_3$, SSA, $[HBIm]BF_4$, and natrolite zeolite.

Under these conditions with 2.5 mmol% of CSMIL under solvent-free conditions, various aromatic, hetero aromatic, and aliphatic amines reacted with triethyl *ortho*-formate, and sodium azide to furnish 1-substituted 1*H*-tetrazoles in moderate to excellent yields (Scheme 3, Table 6). All known compounds were characterized by comparing their physical and spectral data with those reported in the literature.

2.3. Characterization of chitosan supported $EMImFeCl_4$ (CSMIL)

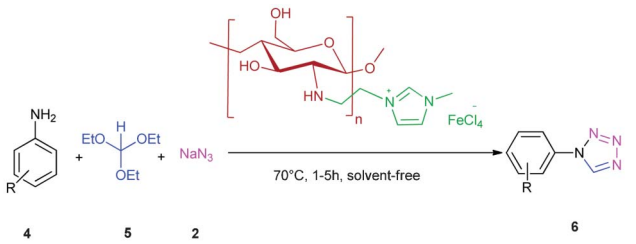
The CSMIL catalyst was characterized using some different microscopic and spectroscopic techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), FT-IR and Raman spectroscopies. To characterize the functionalized chitosan ionic liquid, first of all, we used the FT-IR spectrum. The FT-IR spectrum of native chitosan and functionalized chitosan ionic liquid sample are shown in Fig. 3.

The results show that the band at about 3200–3500 cm^{-1} was attributed to the OH and NH stretching vibrations, and the band at about 1535–1658 cm^{-1} is related to the bending vibration absorption peak of N–H. Two absorption bands at ~897 and 1156 cm^{-1} are related to the chitosan structure. But, after functionalization, the bending vibration absorption peak of N–H at about 1530–1660 cm^{-1} disappeared, which was assigned to the secondary amine. There are peaks at about 1145 cm^{-1}, which were assigned to the characteristic absorption of N–CH_2 in functionalized chitosan. There are three main peaks (CH_2: 1405–1465, 880–900, C=N stretching vibrations: 2215–2240, C=C stretching vibrations: 1585–1625) are related to imidazolium ionic liquid. In this spectrum the two bands appearing at ~394 and 145 cm^{-1} can be assigned with certainty to the two predicted (Fe–Cl) bands. Previous works have shown that the iron–chloride stretches occur above 300 cm^{-1} and that the iron–chloride bending modes occur below 150 cm^{-1}.[45]

Vibrational Raman spectra of CSMIL in the range 100–500 cm^{-1} show the previously observed symmetric Fe–Cl bond stretch vibrations of $[FeCl_4]$ at ~113 and 331 cm^{-1}.[46] This assignment provides further verification of the presence of the $[FeCl_4]$ anion. Raman (Fig. 4) showed the structural change of chitosan after supporting ionic liquid and converting to CSMIL that all functional groups identified are presented in Table 7.

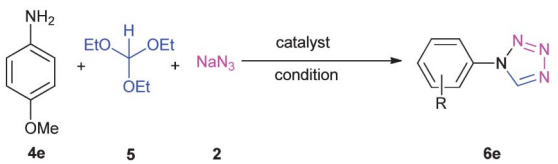
In this study, Dynamic light scattering (DLS) was used for particle size analyzing of the catalyst. The average diameter of CSMIL is evaluated to be about 80 nm which is shown in Fig. 5. The histogram was proposed according to the results obtained from the SEM images. According to the SEM image (Fig. 6), the morphology of CSMIL is regularly spherical and arranged in an approximately good orderly manner with nano sized particles and its TEM picture showed the average size of the particles entrapped in the chitosan framework to be around 80–85 nm (Fig. 7).

It is worth noting that one of the most important features of this nano catalyst is easy recyclability by using magnetic field or *via* solvent extraction of the product from the reaction mixture. The possibility of recycling the catalyst was tested by use of the reaction of 4-nitrobenzonitrile and sodium azide under optimized conditions. This catalyst can be successfully recycled by different methods such as adsorption by using a strong magnetic field (1T), centrifuge method, and filtration. Therefore, the use of a magnet to recover ILs from reaction mixtures will be very useful and have great potential. So, when the reaction was completed, the reaction mixture was cooled to room temperature and diluted with ethyl acetate, the CSMIL was separated from the reaction mixture by use of a magnet



Scheme 3 Synthesis of 1-substituted 1*H*-tetrazoles in the presence of chitosan supported magnetic ionic liquid (CSMIL).

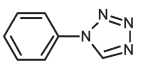
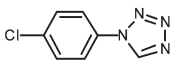
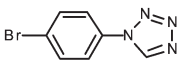
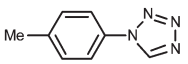
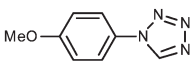
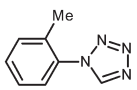
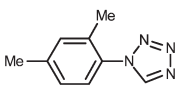
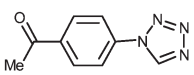
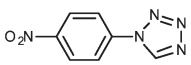
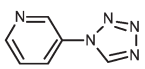
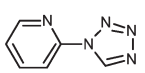
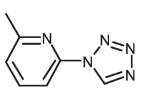
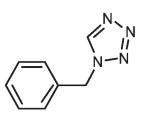
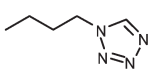
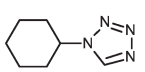
Table 5 Comparison of various catalysts in synthesis of 1-substituated tetrazoles[a]



Entry[ref]	Catalyst	Solvent	Time (h)	*T* (°C)	Yield[b] (%)
1[33]	Silica sulfuric acid	Neat	5	120	95
2	Natrolite zeolite	Neat	4	120	82
3[33]	$In(OTf)_3$	Neat	1.5	100	89
4[33]	$[HBIm]BF_4$	Neat	0.33	100	91
5	**Nano CSMIL**	**Neat**	**1**	**70**	**92**

[a] Reaction conditions: *p*-methoxy aniline **4d** (1 mmol), NaN_3 **2** (1 mmol), triethyl *ortho*-formate **5** (1.2 mmol). [b] Isolated yield.

Table 6 Preparation of 1-substituted 1*H*-tetrazoles in the presence of chitosan supported $EMImFeCl_4$[a]

Entry[ref]	Product	Time (h)	Yield[b] (%)	M.P. (°C)
6a[33b,d,f]		2.5	86	64
6b[33b,d,f]		2	84	153
6c[33f]		2	83	170
6d[33b,d,f]		1.5	88	92
6e[32c,33d,f]		1	91	115
6f[33f]		1.5	89	152
6g[33f]		1	91	133
6h[33d]		3.5	78	175
6i[33b,f]		3.5	73	200
6j[33b,d]		3.5	80	77
6k[33d]		3.5	81	128
6l[33d]		3	85	106
6m[33d]		2.5	78	130
6n[33e]		5	75	144
6o[33e]		5	76	170

[a] Reaction conditions: amine compounds **4** (1 mmol), NaN_3 **2** (1 mmol), triethyl *ortho*-formate **5** (1.2 mmol), CSMIL (2.5 mmol%), 70 °C. [b] Isolated yield.

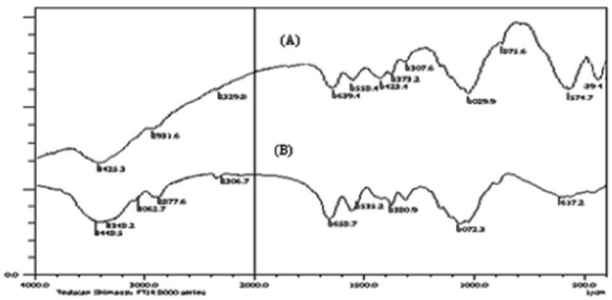


Fig. 3 Comparison between FT-IR spectra of chitosan supported magnetic ionic liquid nanoparticles (A) and pure chitosan (B).

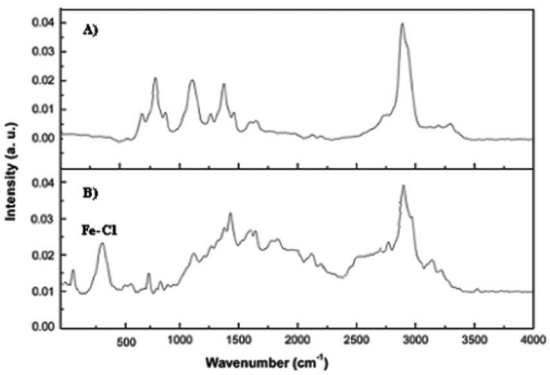


Fig. 4 Vibrational Raman spectra of chitosan (A) and CSMIL (B).

Table 7 Raman excitation frequencies for functional groups present in the catalyst

Group	Char. Freq. (cm^{-1})	Char. Freq. (cm^{-1})
1	Methylene: C–C, C–H	2850–2960
2	Amine: NH_2 (primary)	Pair of peaks, 3350 and 3270
3	Amine: NH (secondary)	3350–3310
4	Alcohol: C–OH	3600–3200
5	Ether: C–O–C	1100
6	N–C stretch vibration	791
7	Fe–Cl stretch	331, 113

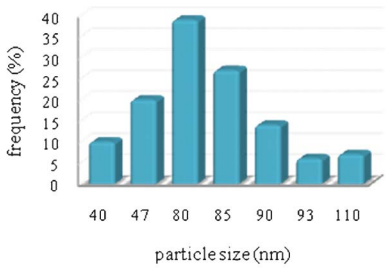


Fig. 5 Histogram representing the size distribution of CSMIL.

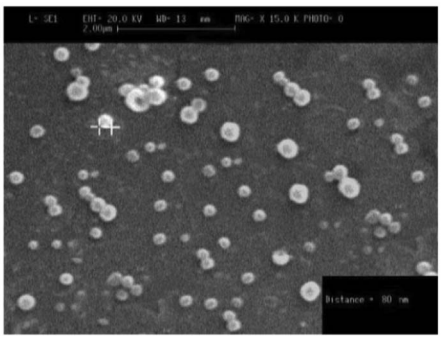


Fig. 6 SEM image of CSMIL.

during 5–10 min. The recycled catalyst was washed with ether for three times and can be used for another cycle. This catalyst was recycled and reused five times which was accompanied by the loss of its catalytic activity. The results are shown in Table 8.

For finding the reason of this observation, we have studied the SEM pictures of the recovered catalyst. SEM picture of the recovered nanoparticles after the fourth run showed gelification of chitosan that is obvious in Fig. 8.

We believe that the gelification of chitosan can easily cover the particles of the magnetic ionic liquid in the surface of chitosan.

To explore the catalyst leaching from the supported catalyst and maybe migration to the liquid phase, the reaction of 4-nitrobenzonitrile (1 mmol) with sodium azide (1.2 mmol) catalyzed by CSMIL (2.5 mmol%) was carried out at 70 °C under solvent-free conditions. When the reaction time reached 3 h, hot ethyl acetate was added and the CSMIL was easily removed using a magnetic force. The solution was averagely divided into two parts (A_1 and A_2). The corresponding product of A_1 was obtained with a 43% yield. Moreover, the neat A_2 was reacted under the above conditions for another 3 h to afford the product in 44% yield, which was similar to A_1 and less than normal (90%; Table 4, entry 3g). Therefore, these above results convinced us that the leaching of CSMIL was negligible in the catalytic process.

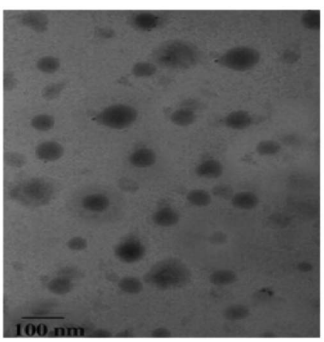
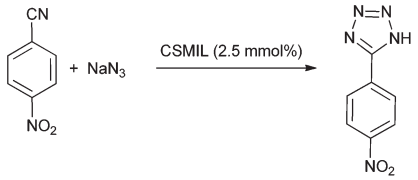


Fig. 7 TEM picture of the CSMIL.

Table 8 Recycling of magnetic ionic liquid supported on chitosan for the reaction of 4-nitrobenzonitrile with sodium azide



Run	1[a]	2[a]	3[a]	4[a]	5[a]
Time for completion of the reaction /h	6(3.5)	6(3.5)	6.5(4)	6.5(4)	7(4.5)

[a] The data shown in parentheses refer to the reaction times for synthesis of 1-substituted tetrazoles from 4-nitroaniline.

Conclusions

In summary, we have successfully developed a novel nano magnetic biopolymer-supported catalyst as an efficient, inexpensive and non-corrosive catalyst for synthesis of 5-substituted 1*H*-tetrazoles from nitriles and 1-substituted 1*H*-tetrazoles from amines under solvent-free conditions. This operationally simple method does not require the use of toxic organic solvents. Moreover, this recyclable catalyst offers advantages like its ease of operation, high efficiency, low cost, and capability for large-scale synthesis. Current efforts in our research group are attempting to expand the application of CSMIL for catalyzed organic reactions.

Experimental section

General considerations

Chitosan was purchased from Zhejiang Jinke (Golden Shell). The degree of deacetylation was 90% and average molecular weight was 5×10^4. Other chemicals were purchased from Fluka, Merck and Aldrich chemical companies. For recording ^{1}H NMR spectra we used a Brucker (250 MHZ) Avanc DRX in pure deuterated DMSO-d_6 and $CDCl_3$ solvents with tetramethyl silane (TMS) as the internal standard. Mass spectra were

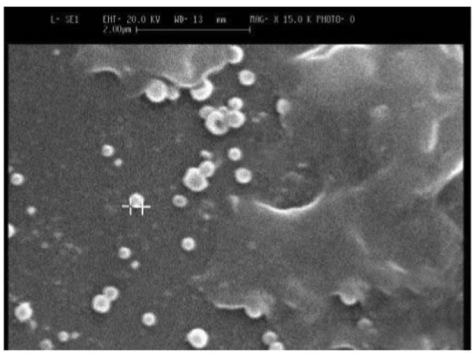


Fig. 8 SEM picture of the recovered CSMIL after the fifth run.

recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at 70 eV. FT-IR spectroscopy (Shimadzu FT-IR 8300 spectrophotometer), was employed for characterization of the compounds. The scanning electron micrograph for CSMIL catalyst was obtained by SEM instrumentation (SEM, XL-30 FEG SEM, Philips, at 20 kV). Melting points were determined in open capillary tubes in a Barnstead Electrothermal 9100 BZ circulating oil melting point apparatus. The reaction monitoring was accomplished *via* TLC on silica gel PolyGram SILG/UV254 plates.

Preparation of the CS-EMImFeCl$_4$

The CS supported 1-ethyl-3-methyl imidazolium chlorate (CS-EMImCl) were synthesized according to the reported procedure in liturature.[37]

At first, *N*-methyl imidazole (10 mL, 25 °C) was dropped very slowly into a mixture of 1,2-dichloroethane (30 mL, 25 °C) and acetone (25 mL) in a 100 mL three-necked flask. The reactants were magnetically stirred at reflux for 24 h. After filtration, the solid product was washed by acetone for four times and then dried under vacuum at 60 °C for 12 h. Secondly, CS (4 g), 1-(2-chloroethyl)-3-methyl imidazolium chloride solution (10 g of 60 wt%) and isopropanol (30 mL) were added into a 100 mL three-necked flask. The reactants were magnetically stirred at 75 °C for 24 h. When the reaction was complete, the product was precipitated by the addition of ethanol into the reaction mixture, followed by filtration. Then, it was washed with anhydrous ethanol, and dried under vacuum at 80 °C for 24 h using phosphoric anhydride as a desiccant. The loading of EMImCl in CS-EMImCl was 2.9 mmol g^{-1} determined by N and Cl elemental analysis with Elemental Analyzer. After preparation of the CS-EMImCl, it was mixed with equimolar amounts of anhydrous $FeCl_3$ at 30 °C for 3 h, as a result a dark brown solid was obtained. The obtained catalyst was washed with small portions of anhydrous ethanol, and dried under vacuum at 60 °C for 24 h.

General procedure for the synthesis of 5-substituted-1*H*-tetrazoles by a [3+2]-cycloaddition reaction

A solution of nitrile (1 mmol) and sodium azide (1.5 mmol) in the presence of 2.5 mmol% of CSEMImFeCl$_4$, was stirred at 70 °C; after completion of the reaction (TLC), the reaction mixture was cooled to room temperature and diluted with ethyl acetate (3 × 20 mL). The catalyst was removed by using magnetic field or filtration and then, the resulting solution was washed with 1 N HCl and the combined ethyl acetate fractions were evaporated. The crude products thus obtained were purified by column chromatography (silica gel, 200–300 mesh; ethyl acetate/petroleum ether, 1:5–1:3). All products were characterized by ^{1}H, ^{13}C NMR, FT-IR, and melting point which were in agreement with literature. We have reported the spectral data of some aromatic and heteroaromatic synthesized compounds.

5-(4-Chlorophenyl)-1*H*-tetrazole (3b). White solid (84% yield); m.p. 261–262 °C. ^{1}H NMR (250 MHz, DMSO-d$_6$): δ 7.72 (d, J = 8.6 Hz, 2H), 8.12 (d, J = 8.6 Hz, 2H) ppm. ^{13}C NMR (62.5 MHz, DMSO-d$_6$): δ 123.5, 129.3, 130.2, 136.3, 156.4 ppm. FT-IR (KBr) (ν_{max} cm^{-1}): 3423, 2931, 2822, 2745, 1612, 1468, 1445, 1398, 1356, 1173, 1089, 1043, 878, 773 cm^{-1}. Anal. Calcd for $C_7H_5ClN_4$. Calcd. C, 46.55; H, 2.79; N, 31.02. Found, C, 46.13; H, 2.51; N, 30.80.

2-(1*H*-Tetrazol-5-yl)pyridine (3k). White solid (90% yield); m.p. 210–211 °C. ^{1}H NMR (250 MHz, DMSO-d$_6$): δ 7.69 (m, 1H), 8.23 (m, 1H), 8.21 (d, J = 8.2 Hz, 1H), 8.78 (d, J = 5.0 Hz, 1H) ppm. ^{13}C NMR (62.5 MHz, DMSO-d$_6$): δ 120.4, 138.4, 137.8, 150.6 ppm. FT-IR (KBr) (ν_{max} cm^{-1}): 3434, 2865, 2716, 1635, 1596, 1510, 1383, 1367, 1045, 867 cm^{-1}. Anal. Calcd for $C_6H_5N_5$ Calcd. C, 48.98; H, 3.43; N, 47.60. Found, C, 48.45; H, 3.20; N, 47.31.

5-(Naphthalen-1-yl)-1*H*-tetrazole (3l). White solid (90% yield); m.p. 264–267 °C. ^{1}H NMR (250 MHz, DMSO-d$_6$): δ 7.66–7.81 (m, 3H), 7.91–8.03 (m, 1H), 8.09–8.12 (m, 1H), 8.19–8.23 (m, 1H), 8.62–8.72 (m, 1H) ppm. ^{13}C NMR (62.5 MHz, DMSO-d$_6$): δ 125.9, 126.7, 127.9, 128.0, 128.8,131.3, 132.8, 169.0 ppm. FT-IR (KBr) (ν_{max} cm^{-1}): 3429, 3061, 2817, 2720, 1628, 1601, 1523, 1491, 1385, 1358, 1252, 1128, 1100, 958, 869 cm^{-1}. Anal. Calcd for $C_{11}H_8N_4$. Calcd. C, 67.34; H, 4.11; N, 28.55. Found, C, 67.00; H, 3.91; N, 28.11.

5-(Phenanthren-9-yl)-1*H*-tetrazole (3m). White solid (83% yield); m.p. 215–216 °C. ^{1}H NMR (250 MHz, DMSO-d$_6$): δ 7.50–7.70 (m, 4H), 7.99 (d, J = 8.3 Hz, 2H), 8.43 (d, J = 8.2 Hz, 2H), 8.52 (s, 1H) ppm.^{13}C NMR (62.5 MHz, DMSO-d$_6$): δ 125.3, 126.8, 128.2, 130.9, 131.8, 133.6, 134.0, 134.9, 161.0 ppm. FT-IR (KBr) (ν_{max} cm^{-1}): 3448, 3063, 2823, 2743, 1622, 1594, 1511, 1490, 1381, 1361, 1253, 1125, 1100, 969, 867 cm^{-1}. Anal. Calcd for $C_{15}H_{10}N_4$. Calcd. C, 73.16; H, 4.09; N, 22.75. Found, C, 73.00; H, 3.78; N, 22.15.

2-((2*H*-Tetrazol-5-yl)methyl)-1*H*-benzoimidazole (3q). White solid (86% yield); m.p. 278–279 °C. ^{1}H NMR (DMSO-d$_6$, 250 MHz): δ 3.84 (s, 2H), 7.80 (d, J = 7.1 Hz, 2H), 8.35 (t, J = 7.2 Hz, 2H), 10.85 (br s, 1H), 11.38 (br s, 1H) ppm. ^{13}C NMR (62.5 MHz, DMSO-d$_6$): δ 29.50, 127.58, 129.00, 131.75, 147.70, 155.00 ppm. FT-IR (KBr) (ν_{max} cm^{-1}): 3423, 2820, 2734, 1637, 1586, 1500, 1363,1312, 1047, 850 cm^{-1}. Anal. Calcd for $C_9H_8N_6$. Calcd. C, 53.99; H, 4.03; N, 41.98. Found, C, 53.21; H, 4.00; N, 41.39.

General procedure for the synthesis of 1-substituted-1*H*-tetrazoles from amines

The same procedure such as synthesis of 5-substituted-1*H*-tetrazoles from nitriles was done in the presence of amine (1 mmol), sodium azide (1.2 mmol), triethyl *ortho*-formate (1 mmol) and 2.5 mmol% of CSEMImFeCl$_4$.

After completion of the reaction, the catalyst was removed by using magnetic field or filtration and the resulting solution was washed with water and the combined ethyl acetate fractions were evaporated. Then a crystallization step was performed using EtOAc–hexane to afford the pure product.

1-(4-Bromophenyl)-1*H*-tetrazole (6c). White solid (83% yield); m.p. 183–184 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.00 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 7.5 Hz, 2H), 8.07 (s, 1H) ppm.^{13}C NMR (62.5 MHz, DMSO-d$_6$): δ 153.5, 137.0, 128.9, 125.3, 118.0 ppm. FT-IR (KBr) (ν_{max} cm^{-1}): 3532, 3167, 3058, 2863, 1675, 1591, 1575, 1488, 1415, 1319, 1284, 1235, 1200, 1153, 1100, 1098, 1013, 992, 834 cm^{-1}. Anal. calcd for $C_7H_5N_4Br$: C, 37.36; H, 2.24; N, 24.90. Found: C, 37.00; H, 2.11; N, 24.45.

1-(2,4-Dimethylphenyl)-1*H*-tetrazole (6g). White solid (91% yield); m.p. 133–135 °C. ^{1}H NMR (DMSO-d_6, 250 MHz): δ 6.87–7.67 (d, J = 6.0 Hz, 2H), 7.88 (s, 1H), 8.45 (s, 1H) ppm.^{13}C NMR (62.5 MHz, DMSO-d_6): δ 148.0, 131.6, 132.2, 128.1, 127.8, 121.5, 119.0, 20.1, 17.3 ppm. FT-IR (KBr) (ν_{max} cm^{-1}): 2923, 1657, 1612, 1493, 1301, 1205, 1132, 823 cm^{-1}. Anal. calcd for $C_9H_{10}N_4$:C, 68.56; H, 4.79; N, 26.65. Found: C, 68.13; H, 4.54; N, 26.55.

1-(4-Acetylphenyl)-1*H*-tetrazole (6h). Yellow solid (78% yield); m.p. 175–176 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.76 (s, 3 H), 7.78–7.97 (d, J = 8.7 Hz, 2 H), 8.12–8.31 (d, J = 8.7 Hz, 2 H), 9.32 (s, 1 H) ppm. ^{13}C NMR (62.5 MHz, DMSO-d_6): δ 26.58, 122.32, 131.12, 136.00, 138.67, 142.22, 194.11 ppm. FT-IR (KBr) (ν_{max} cm^{-1}): 3024, 1712, 1675, 1634, 1600, 1576, 1532, 1500, 1243, 1056, 976 cm^{-1}. Anal. Calcd for $C_9H_8N_4O$. Calcd, C, 57.44; H, 4.28; N, 29.77. Found, C, 57.21; H, 4.00; N, 29.41.

2-Methyl-6-(1*H*-tetrazol-1-yl)pyridine (6l). White solid (85% yield); m.p. 106–107 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.90 (s, 3 H), 7.21–7.43 (m, 1 H), 7.84–8.02 (m, 2 H), 9.32 (s, 1 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 123.4, 129.4, 130.2, 137.0, 155.3 ppm. FT-IR (KBr) (ν_{max} cm^{-1}): 3025, 1632, 1587, 1555, 1511, 1497, 1254, 1065, 973 cm^{-1}. Anal. Calcd for $C_7H_7N_5$. Calcd, C, 52.17; H, 4.38; N, 43.45. Found, C, 51.83; H, 4.01; N, 43.17.

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