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Methionine-Coated Fe_3O_4 Nanoparticles: An Efficient and Reusable Nanomagnetic Catalyst for the Synthesis of 5-Substituted 1*H*-Tetrazoles

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Abstract—Methionine-coated Fe_3O_4 nanoparticles, a magnetically reusable and environmentally friendly heterogeneous catalyst, was synthesized. The new catalyst was characterized by FT-IR spectra, XRD, SEM, and EDX analysis and was used to catalyze the cycloaddition of nitriles and sodium azide in DMSO at 120°C to give the corresponding 5-substituted 1*H*-tetrazoles. Methionine-coated Fe_3O_4 nanoparticles proved to be highly efficient for this organic reaction. The catalyst can be easily separated and reused several times without loss of activity. The proposed procedure also offers several benefits such as quick reaction, high yields, clean process, low-cost heterogeneous catalyst, low loading of catalyst, and simple operation.

Keywords: tetrazoles, methionine, heterogeneous catalyst, magnetically recoverable catalyst

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INTRODUCTION

Tetrazoles constitute an essential class of heterocyclic compounds that have gained much interest due to wide range of their use in medicine [1–4]. For example, tetrazole ring is present in various biologically active compounds such as antibiotics, antiviral (i.e., HIV) [5], antiplatelet [6], cardiazol [7], and "sartan" family drugs. Heterocyclic compounds containing a tetrazole moiety are also used in materials science [8], coordination chemistry [9], and as plant growth regulators in agriculture [10].

Accordingly, it is important to search for efficient methods of synthesis of 5-substituted 1*H*-tetrazoles. The commonly employed method involves the [3+2]-cycloaddition reaction between nitriles and azides. Other routes for the synthesis of tetrazoles include the use of thioamides, imidoyl chlorides, oximes, heterocumulenes, ketones, amines, alkenes, or isocyanides as starting materials in the presence of azide ion source [5]. These procedures utilize numerous catalysts such as Pd catalysts [11], CuI [12], Cu_2O [13], ZnO [14], $CuFe_2O_4$ [15], $CuSO_4 \cdot 5H_2O$ [16], $Fe(OAc)_2$ [17], Fe_3O_4@chitin [18], Cu-MCM-41 [19], $InCl_3$ [20], $AgNO_3$ [21], $FeCl_3/SiO_2$ [22], $ZnCl_2$ [23], $ZrOCl_2 \cdot 8H_2O$ [24], $B(C_6H_5)_3$ [25], DPPA/DBU [26], $BaWO_4$ [27], $Ln(OTf)_3/SiO_2$ [28], Zn–Cu alloy [29], $I_2/NaHSO_4/SiO_2$ [30], mesoporous ZnS nanospheres [31], COY zeolite [32], cuttlebone [33], and P_2O_5 [34]. Recently, a few research teams have also used microwave irradiation to shorten the reaction time [35–39].

Based on the facts mentioned above and in continuation of our research program on the synthesis of heterogeneous catalysts and heterocyclic compounds [40–44], we now report the synthesis of methionine-coated Fe_3O_4 nanoparticles as a novel, efficient, and recyclable heterogeneous catalyst with high catalytic activity. Furthermore, recent developments of heterogeneous catalysts, especially magnetic nanoparticle-supported catalysts, have become an important line of research in organic synthesis [40]. These magnetic nanoparticles can be easily separated from the reaction medium by an external magnet and repeatedly used.

RESULTS AND DISCUSSION

Magnetite nanoparticles were coated by methionine residues in a one-pot aqueous reaction. The FT-IR spectra of Fe_3O_4 nanoparticles and methionine-coated magnetite Fe_3O_4 nanoparticles are shown in Fig. 1. For Fe_3O_4 nanoparticles, the characteristic Fe–O band is observed at 580 cm^{-1}. The broad band at 3358 cm^{-1}

was attributed to OH groups [45, 46]. In the methionine-coated magnetite Fe_3O_4 nanoparticles, the original bands of Fe_3O_4 nanoparticles are observed. In addition, new bands are present at around 1600 and 1390 cm^{-1}, which correspond to C=O and C–O stretching vibrations, respectively, of the amino acid residues. The band at 2870 cm^{-1} was assigned to C–H stretching vibrations of methionine on Fe_3O_4 nanoparticles [47]. It can also be seen that the band around 3400 cm^{-1} becomes more intense after functionalization due to overlap of N–H and O–H stretching bands.

The XRD pattern of methionine-coated Fe_3O_4 nanoparticles is shown in Fig. 2. The XRD data prove the crystalline phase of Fe_3O_4, and the pattern is consistent with the standard magnetite pattern (JCPDS no. 89-4319) [48]. Accordingly, one can conclude that the modification process does not affect the crystalline structure of Fe_3O_4. Figure 3 illustrates the morphology of functionalized Fe_3O_4 nanoparticles. As can be seen, the particle size is distributed from ~40 to 500 nm.

The EDS analysis was performed to probe the elemental composition of both Fe_3O_4 NPs and methionine-coated magnetite nanoparticles (Fig. 4). For pure magnetite, peaks related to Fe and O can be observed in the EDX spectra. In the case of functionalized Fe_3O_4 NPs, new peaks of C and S appeared due to methionine residues. However, the Fe and O peaks are the main constituents of functionalized nanoparticles. These results confirmed the existence of methionine and Fe_3O_4 in these nanoparticles. Methionine-coated magnetite nanoparticles were very stable, and nanoparticles did not precipitate over a long time.

Detailed bonding structure of the amino acid residues on the Fe_3O_4 surface was elucidated by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and by in situ IR absorption spectroscopy [49]. On the basis of the obtained results, possible binding mode of the amino acid to magnetite nanoparticles is shown in Fig. 5. The amino acid residues are linked to the Fe_3O_4 surface through the carboxy groups.

Following our interest in the preparation of catalysts for the synthesis of heterocycles [50], methionine-coated Fe_3O_4 nanoparticles were used as a novel heterogeneous catalyst to produce 5-substituted 1*H*-tetrazoles by reaction of aromatic nitriles with sodium azide (Scheme 1). To optimize the conditions, the cycloaddition of benzonitrile (**1a**) and sodium azide was chosen as a model reaction. Table 1 shows the effect of different factors, viz., the amount of the catalyst, solvent nature, and temperature, on the yield of 5-phenyl-

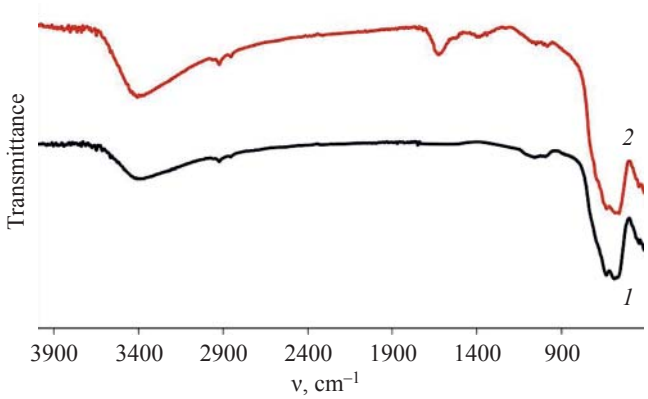


Fig. 1. FT-IR spectra of (*1*) Fe_3O_4 nanoparticles and (*2*) methionine-coated Fe_3O_4 NPs.

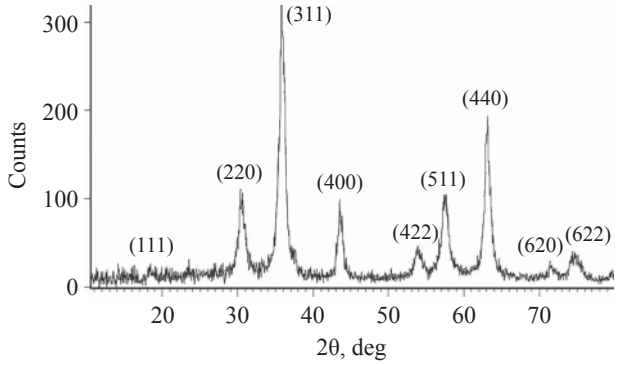


Fig. 2. XRD pattern of Met-Fe_3O_4 NPs.

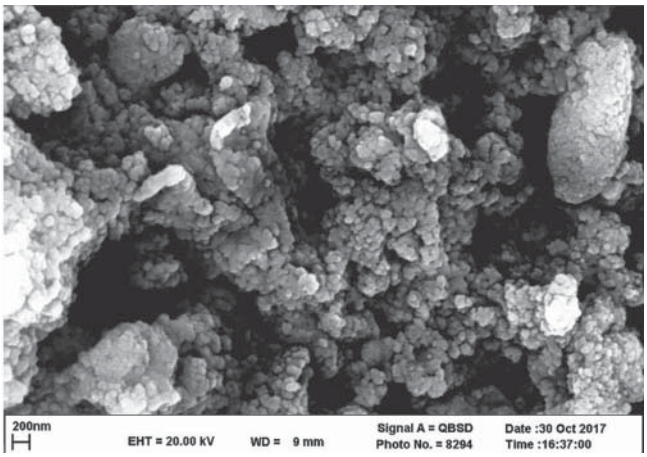


Fig. 3. SEM image of distributed Met-Fe_3O_4 nanoparticles.

1*H*-tetrazole (**2a**). In the absence of a catalyst, 5-phenyl-1*H*-tetrazole was obtained in 32% yield (Table 1, entry no. 1). Among the variety of the solvents tested (Table 1, entry nos. 2–6), the best result was obtained in DMSO. Other solvents, such as H_2O, DMF, MeCN, and $CHCl_3$ gave the required product in a low yield despite prolonged reaction time. At a lower temperature (100°C, Table 1, entry no. 7), the reaction

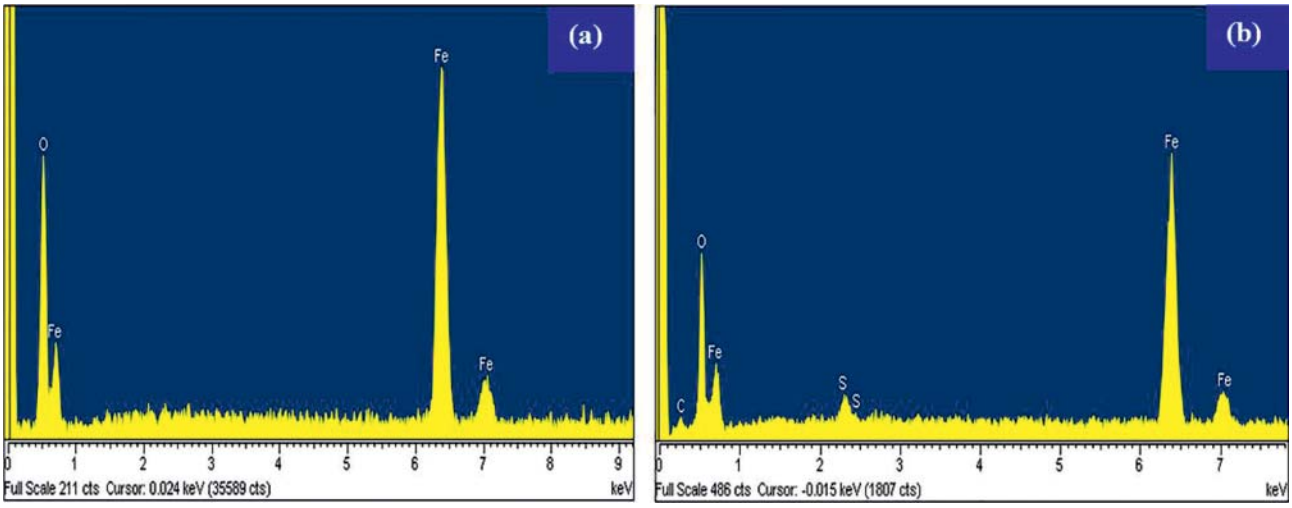


Fig. 4. EDX spectra of (a) Fe_3O_4 and (b) Met-Fe_3O_4 NPs.

progressed slowly. To examine the effect of catalyst loading, the reaction was carried out in DMSO at 120°C in the presence of 0.05, 0.07, and 0.03 g of Met-Fe_3O_4 NPs. The largest yield of **2a** was achieved using 0.05 g of the catalyst in DMSO (Table 1, entry no. 2). Further increase of the amount of the catalyst did not accelerate the reaction (Table 1, entry no. 8). In contrast, lower catalyst loading decreased the yield even after longer reaction time (Table 1, entry no. 9).

To demonstrate the catalytic effect of methionine-coated Fe_3O_4 nanoparticles, the synthesis of **2a** was also performed using Fe_3O_4 NPs and methionine separately. As shown in Table 1, 100% conversion was achieved after 10 min in the presence of methionine-coated Fe_3O_4 nanoparticles (entry no. 2). Methionine taken alone as catalyst gave the product in medium yield (70%, entry no. 10), whereas only 55% of **2a** was obtained using Fe_3O_4 nanoparticles alone (entry no. 11). Therefore, methionine-coated Fe_3O_4 nanoparticles can be proposed as an efficient solid acid catalyst for the synthesis of 5-substituted 1*H*-tetrazoles.

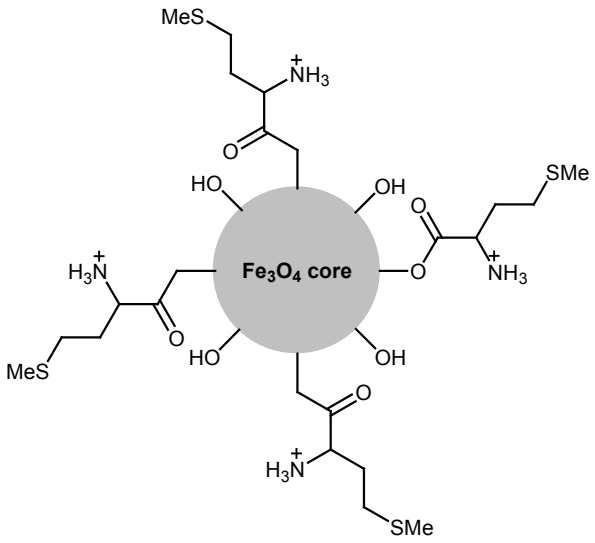
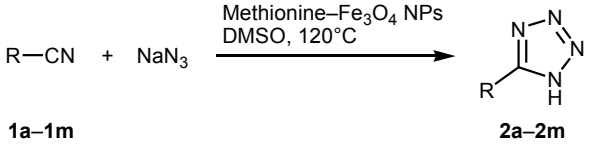


Fig. 5. Possible bonding structure of Met-Fe_3O_4 nanoparticles.

Various substituted benzonitriles **1a**–**1k** were reacted with sodium azide in the presence of 0.05 g of methionine-coated Fe_3O_4 nanoparticles in DMSO at 120°C (Table 2). The rate of the reaction and product yields depended on the substituent in the aromatic ring of the initial nitrile. Aromatic nitriles **1b**–**1d** containing electron-withdrawing substituents such as Br, Cl, and NO_2 gave the corresponding tetrazoles **2b**–**2d** with excellent yields in short reaction time (Table 2). Aromatic nitriles **1e**–**1k** with electron-donating groups (Me, OMe, OEt, OH, NMe_2) were also successfully converted into tetrazoles **2e**–**2k** but with longer reaction time. Moreover, aliphatic nitrile such as 4-methylpentanenitrile (**1m**) smoothly reacted under the optimized conditions to afford tetrazole **2m** in 85% yield.

All tetrazoles **2a**–**2m** were reported previously; they were characterized by spectral and analytical data and also by comparison of their melting points with the reported values. For example, The IR spectra of all compounds **2a**–**2m** showed absorption bands at 3100–

Scheme 1.



1a–1m **2a–2m**

For R, see Table 2.

Table 1. Synthesis of 5-phenyl-1*H*-tetrazole (**2a**) under different conditions

Entry no.	Solvent	Catalyst	Catalyst loading, g	Time, h	Temperature, °C	Yield, %
1	DMSO	–	–	5	120	32
2	DMSO	Met-Fe_3O_4 NPs	0.05	10 min	120	100
3	DMF	Met-Fe_3O_4 NPs	0.05	2	120	70
4	H_2O	Mete-Fe_3O_4 NPs	0.05	2	Reflux	30
5	CH_3CN	Met-Fe_3O_4 NPs	0.05	2	Reflux	15
6	$CHCl_3$	Met-Fe_3O_4 NPs	0.05	2	Reflux	Traces
7	DMSO	Met-Fe_3O_4 NPs	0.05	10 min	100	85
8	DMSO	Met-Fe_3O_4 NPs	0.07	10 min	120	100
9	DMSO	Met-Fe_3O_4 NPs	0.03	30 min	120	65
10	DMSO	Methionine	0.05	30 min	120	70
11	DMSO	Fe_3O_4 NPs	0.05	1	120	55

Table 2. Synthesis of 5-substituted 1*H*-tetrazoles **2a**–**2m** in the presence of 0.05 g of Met-Fe_3O_4 NPs (DMSO, 120°C)

Compound no.	R	Reaction time, min	Yield, %	Melting point, °C	
				found	reported
2a	Ph	10	100	215	214 [26]
2b	4-BrC_6H_4	18	98	265–266	268–270 [51]
2c	4-ClC_6H_4	10	100	262	261–262 [33]
2d	4-$O_2NC_6H_4$	10	100	217–218	218–219 [33]
2e	4-MeC_6H_4	30	95	254	251–252 [19]
2f	3-MeC_6H_4	30	90	149–150	151–152 [52]
2g	4-$MeOC_6H_4$	55	90	230–231	229–230 [53]
2h	3,5-$(MeO)_2C_6H_3$	1 h	85	206	204–205 [33]
2i	4-$EtOC_6H_4$	1 h	90	234–235	234–235 [33]
2j	4-HOC_6H_4	1 h	85	233–234	234–235 [33]
2k	4-$Me_2NC_6H_4$	1 h	80	278–280	282–284 [54]
2l	Naphthalen-1-yl	1 h	90	214–215	212–214 [53]
2m	3-Methylbutyl	1 h	85	95	95–96 [33]

Table 3. Comparison of various catalysts for the synthesis of 5-phenyl-1*H*-tetrazole

Entry no.	Catalyst	Conditions (solvent, temperature, time)	Yield, %
1	COY zeolite [32]	DMF, 120°C, 14 h	90
2	Cuttlebone [33]	DMSO, 110°C, 20 min	98
3	Fe_3O_4@chitin [18]	Solvent-free, 110°C, 20 min	95
4	CAES [55]	DMSO, 130°C, 1 h	95
5	Zn/Al hydrocalcite [56]	DMF, 120–130°C, 12 h	84
6	$CuFe_2O_4$ [15]	DMF, 120°C, 12 h	92
7	DPPA/DBU [26]	Toluene, reflux, 16 h	93
8	TEA·HCl [57]	Toluene, 100°C, 24 h	90
9	Cu(II)/Fe_3O_4@APTMS-DFX [58]	DMSO, 120°C, 1 h	98
10	[*t*-$Bu_2Sn(OH)(H_2O)]_{22}$+2OTf^- [59]	H_2O, 85°C, 1 h	96
11	ChCl–$ZnCl_2$ [54]	140°C, 30 min	90
12	Methionine-Fe_3O_4 NPs [this work]	DMSO, 120°C, 10 min	100

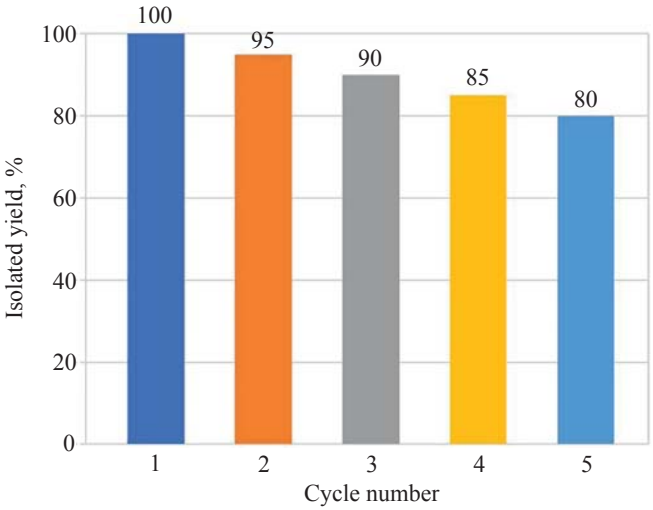


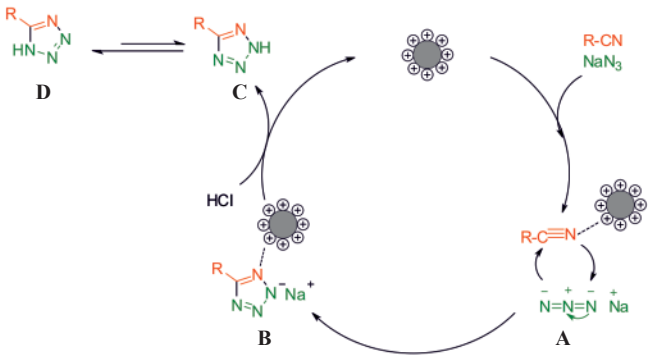
Fig. 6. Recyclability of Met-Fe_3O_4 NPs for the reaction of benzonitrile with sodium azide.

3400 (N–H) and 1000–1300 cm^{-1} (tetrazole ring), whereas no absorption band at 2240 cm^{-1} (C≡N) was observed.

In continue, we compared the reported methods with the other catalysts recently reported for synthesis tetrazole derivatives in the literature. As it is found (Table 3), the Met-Fe_3O_4 NPs are the more efficient catalysts than many of the methods reported in the literature for this reaction.

A plausible reaction mechanism is shown in Scheme 2. It has been proposed that the cycloaddition of nitriles and sodium azide is accelerated through the positive charge of the catalyst surface, which activates the nitrile for azide addition via hydrogen bonding of nanoparticles with the nitrile nitrogen atom. Initially, coordination of the nitrile nitrogen atom to Met-Fe_3O_4 NPs gives complex **A**, which accelerates the cyclization step by increasing the electrophilicity of the nitrile group. The [3+2]-cycloaddition involving the C≡N bond and azide ion occurs instantly to form intermediate **B**. Removal of the catalyst by simple filtration and acidic work-up gives tetrazole tautomers **C** and **D**. The more stable 1*H*-tautomer **D** is the major product.

Scheme 2.



The reusability of the catalyst was also investigated. After completion of the cycloaddition reaction, Met-Fe_3O_4 NPs were separated from the reaction mixture by an external magnet, washed with distilled water and hot ethyl acetate several times to remove organic products, dried at 70°C for 1 h, and used in the next cycle. As shown in Fig. 6, the nanocatalyst could be reused at least four times without considerable loss of activity.

EXPERIMENTAL

All materials and reagents were purchased from Merck and used without further purification. Methionine (98%) was purchased from Sigma–Aldrich. The melting points were determined with an Electrothermal Type 9200 melting point apparatus. The FT-IR spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer (Madison, WI). The ^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz instrument at room temperature using $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane as reference. The mass spectra (electron impact, 70 eV) were recorded with a Varian MAT CH7 instrument (Bremen). Elemental analysis was performed on a Thermo Finnigan Flash EA micro analyzer (Milan, Italy).

Synthesis of methionine-coated Fe_3O_4 nanoparticles. Methionine (1.3 g) was dissolved in 50 mL of deionized water, 1.3 g of Fe_3O_4 was added to the amino acid solution, and the mixture was stirred at 70°C for 3 h. The catalyst was separated from the solution using a magnet, washed with deionized water several times, and dried in an oven at 60°C overnight.

Typical procedure for the preparation of 5-phenyl-1*H*-tetrazole in the presence of methionine-coated Fe_3O_4 nanoparticles. A mixture of benzonitrile (**1a**, 1 mmol), sodium azide (1 mmol), and Met-Fe_3O_4 nanoparticles (0.05 g) in DMSO (5 mL) was stirred at 120°C. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled, the catalyst was separated from the mixture with an external magnet, and the solution was treated with 4 N aqueous HCl (10 mL) and ethyl acetate (2×10 mL). The combined extracts were washed with distilled water, dried over anhydrous sodium sulfate, and concentrated to give crystalline 5-phenyl-1*H*-tetrazole (**2a**). The product was recrystallized from *n*-hexane–ethyl acetate (1:1) to give white crystals.

The spectral data of some representative 5-substituted-1*H*-tetrazoles are given below.

5-Phenyl-1*H*-tetrazole (2a). White solid. IR spectrum, ν, cm^{-1}: 3125 (N–H), 3045, 2982, 2833, 2766, 2692, 2607, 2557, 1614, 1564, 1486, 1466, 1409, 1254 (N–N=N), 1164 (C–N), 1056, 988, 784. ^1H NMR spectrum, δ, ppm: 3.50 br.s (1H, NH), 7.62 s (3H, H_{arom}), 8.05 s (2H, H_{arom}). Mass spectrum: *m*/*z* 146 $[M]^+$. Found, %: C 57.53; H 4.15; N 38.32. $C_7H_6N_4$. Calculated, %: C 57.53; H 4.14; N 38.34.

5-(4-Bromophenyl)-1*H*-tetrazole (2b). Yellow solid. IR spectrum, ν, cm^{-1}: 3335 (N–H), 3089, 2996, 2845, 2725, 1652, 1605, 1483, 1275 (N–N=N), 1157 (C–N), 1054, 830. ^1H NMR spectrum, δ, ppm: 7.76–7.99 m (4H, H_{arom}). Mass spectrum: *m*/*z* 226/224 $[M]^+$. Found, %: C 37.70; H 2.85; N 24.60. $C_7H_5BrN_4$. Calculated, %: C 37.36; H 2.24; N 24.90.

5-(4-Nitrophenyl)-1*H*-tetrazole (2d). Yellow solid. IR spectrum, ν, cm^{-1}: 3440 (N–H), 3334, 3115, 2975, 2819, 1633, 1488, 1341, 1242 (N–N=N), 1140 (C–N), 995. ^1H NMR spectrum, δ, ppm: 3.21 br.s (1H, NH), 8.30–8.33 m (2H, H_{arom}), 8.45–8.48 m (2H, H_{arom}). Mass spectrum: *m*/*z* 191 $[M]^+$. Found, %: C 43.70; H 2.80; N 36.66. $C_7H_5N_5O_2$. Calculated, %: C 43.98; H 2.64; N 36.64.

5-(3-Methylphenyl)-1*H*-tetrazole (2f). White solid. IR spectrum, ν, cm^{-1}: 3303 (N–H), 3121, 2980, 2870, 2612, 1605, 1486, 1250 (N–N=N), 1150 (C–N), 890. ^1H NMR spectrum, δ, ppm: 2.50 s (3H, CH_3), 7.42 d (1H, H_{arom}, J = 7.6 Hz), 7.47–7.52 m (1H, H_{arom}), 7.83–7.89 m (2H, H_{arom}). Mass spectrum: *m*/*z* 160 $[M]^+$. Found, %: C 59.90; H 5.05; N 35.02. $C_8H_8N_4$. Calculated, %: C 59.99; H 5.03; N 34.98.

5-(4-Methoxyphenyl)-1*H*-tetrazole (2g). White solid. IR spectrum, ν, cm^{-1}: 3310 (N–H), 2930, 2653, 1620, 1445, 1278 (N–N=N), 1185 (C–N), 1034, 752. ^1H NMR spectrum, δ, ppm: 4.22 s (3H, OMe), 7.30 t (2H, H_{arom}, J = 7.6 Hz), 7.35 t (2H, H_{arom}, J = 7.6 Hz). Mass spectrum: *m*/*z* 175 $[M]^+$. Found, %: C 54.55, H 4.58, N 31.78. $C_8H_8N_4O$. Calculated, %: C 54.54; H 4.58; N 31.80.

5-(3,5-Dimethoxyphenyl)-1*H*-tetrazole (2h). White solid. IR spectrum, ν, cm^{-1}: 3130 (N–H), 3105, 2942, 2758, 1605, 1559, 1431, 1290 (N–N=N), 1166 (C–N), 1054, 846. ^1H NMR spectrum, δ, ppm: 3.85 s (6H, OMe), 6.72 t (1H, H_{arom}, J = 2.2 Hz), 7.22 d (2H, H_{arom}, J = 2.2 Hz), 16.91 br s (1H, NH). Mass spectrum: *m*/*z* 206 $[M]^+$. Found, %: C 52.44; H 4.85; N 27.17. $C_9H_{10}N_4O_2$. Calculated, %: C 52.42; H 4.89; N 27.17.

4-(1*H*-Tetrazol-5-yl)phenol (2j). White solid. IR spectrum, ν, cm^{-1}: 3252 (N–H), 3100, 3066, 3019, 3000–2220 (OH), 1615, 1599, 1511, 1466, 1413, 1285 (N–N=N), 835, 752, 514. ^1H NMR spectrum, δ, ppm: 6.95 d (2H, H_{arom}, J = 8.4 Hz), 7.87 d (2H, H_{arom}, J = 8.8 Hz), 10.00 br.s (1H, OH). Mass spectrum: *m*/*z* 162 $[M]^+$. Found, %: C 51.86; H 3.77; N 34.55. $C_7H_6N_4O$. Calculated, %: C 51.85; H 3.73; N 34.55.

5-(Naphthalen-1-yl)-1*H*-tetrazole (2l). White solid. IR spectrum, ν, cm^{-1}: 3412 (N–H), 3051, 2721, 1625, 1525, 1389, 1257 (N–N=N), 1131 (C–N), 965, 864. ^1H NMR spectrum, δ, ppm: 7.64–7.74 m (3H, H_{arom}), 7.97–8.0 m (1H, H_{arom}), 8.03–8.08 m (1H, H_{arom}), 8.12–8.19 m (1H, H_{arom}), 8.57–8.61 m (1H, H_{arom}). Mass spectrum: *m*/*z* 196 $[M]^+$. Found, %: C 67.34; H 4.10; N 28.56. $C_{11}H_8N_4$. Calculated, %: C 67.34; H 4.11; N 28.55.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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