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Syntheses of 5-Substituted 1*H*-Tetrazoles Catalyzed by Reusable CoY Zeolite

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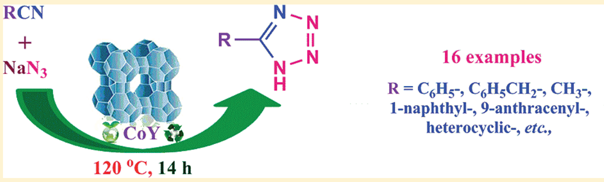
S *Supporting Information*

ABSTRACT: A simple and efficient route for the synthesis of 5-substituted 1*H*-tetrazoles catalyzed by CoY zeolite is reported. The salient features of this atom-economical, cost-effective, and high-yield cobalt-catalyzed protocol are aerobic conditions, lower reaction time, and milder reaction conditions without additives. Other advantages include experimental ease of manipulation, safer alternative to hazardous, corrosive, and polluting conventional Lewis acid catalysts, recovery, and reusability with consistent catalytic activity. The results are rationalized by proposing a suitable mechanism.



Tetrazoles are nitrogen-rich compounds, covering a wide range of applications.[1] They are used in pharmaceuticals as lipophilic spacers and metabolically stable surrogates for the carboxylic acid group and *cis*-amide bond,[1a] as antifoggants in photographic materials,[1b] in information recording systems,[1c] in biomedical applications,[1d] in agriculture,[1e] and in materials science applications including propellants[1f] and explosives.[1g] Tetrazole moieties are also important synthons in synthetic organic chemistry.[1h] For example, proline-derived tetrazole is used as an enantioselective catalyst in asymmetric synthesis and multicomponent reactions and as ligands in coordination chemistry.

Conventional synthesis of 5-substituted 1*H*-tetrazoles via [3 + 2] cycloaddition of azide to the corresponding nitriles, first reported by Hantzsch and Vagt,[2] suffered from drawbacks including use of expensive and toxic metal−organic azide complexes such as tin or silicon,[3] highly moisture-sensitive reaction conditions, and use of amine salts, strong Lewis acid,[4] and hydrazoic acid which are extremely toxic, water-sensitive, explosive, and volatile.[5] Later, Demko and Sharpless reported an innovative and safe procedure in water with Zn salts as catalysts.[6] Stoichiometric amounts of inorganic salts and metal complexes[7] as catalysts, use of $TMSN_3$ and TBAF[8] instead of metal salts under solvent-free conditions in micellar media and ionic liquids, and use of various catalysts[9] such as $BF_3 \cdot OEt_2$,[4] $Pd(OAc)_2/ZnBr_2$,[9a] $Yb(OTf)_3$,[9b] $Zn(OTf)_3$,[9c] $AlCl_3$,[9d] and $Pd(PPh_3)_4$[9e] were also employed for the same purpose. However, a drawback of these homogeneous catalytic processes is difficulty in separation and recovery of the catalysts. Therefore, heterogeneous alternatives are highly desirable and have attracted increasing attention. Several heterogeneous catalytic systems[10,11] using nanocrystalline ZnO, Zn/Al HT,[10a] Zn hydroxyapatite,[10b] Cu_2O,[11a,b] Sb_2O_3, $FeCl_3-SiO_2$,[11c] $CdCl_2$,[11d] $BaWO_4$, γ-Fe_2O_3,[11e] ZnS,[11f] and natural natrolite zeolite[11g] were reported. These methods require a large excess of sodium azide, higher temperature, longer reaction time, and expensive metals. In spite of this, the cycloaddition is too slow to be synthetically useful except when potent electron-withdrawing groups activate the nitrile component and for aliphatic nitriles. Thus, the development of environmentally friendly alternatives is desirable for the synthesis of tetrazoles.

Since the pioneering work of Kharasch, cobalt has been extensively used as catalyst for many transformations[12] associated with homocoupling, cross-coupling, radical cyclizations, Vollhardt [2 + 2 + 2] and [2 + 2] cycloaddition reactions, Nicholas reaction, Pauson− Khand reaction, and Heck-type reactions. Zeolite-encapsulated cobalt clusters are the first shape-selective Fischer−Tropsch (F−T) catalysts.[12b] Cobalt as a biological constituent of organometallic species via coenzyme B_{12}, can be used as replacement for the corrosive Lewis acid and expensive metals Pd, Pt, and Cu, making the process more practical and viable. Cobalt complexes can also undergo a facile switch among several oxidation states (Co^{III}, Co^{II}, Co^{I}, and Co^{0}), resulting in a high reactivity with good catalytic active sites.

A tremendous upsurge of interest has been evident recently in chemical transformations performed on solid supports,[13] which make the reaction processes convenient to perform (simple isolation of reaction products by filtration), faster, more economical, environmentally benign, and recyclable with minimal metallic waste. In this context, heterogeneous catalysis by zeolites with exchangeable metal cations possessing tunable larger pore sizes and inherent acid/base catalytic properties are excellent catalysts with their well-optimized isolated active sites providing greener alternatives to homogeneous catalysis.[14] Zeolite Y is a faujasite (FAU) type, microporous aluminosilicate built from infinitely extending three-dimensional network of SiO_4 and AlO_4 tetrahedra that are linked together through oxygen bridges. The presence of Al^{3+} instead of Si^{4+} creates a negative charge, which is

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Table 1. Synthesis of 5-Substituted 1*H*-Tetrazole with Various Catalysts[a]

entry	catalyst	time (h)	yield[b] (%)
1	HY	24	22
2	NaY	48	10
3	FeY	24	40
4	CoY	14	80
5	NiY	24	38
6	CuY	24	42
7	ZnY	24	45
8	CdY	24	38
9	AlY	24	45
10	SnY	24	45
11		48	nil

[a] Phenylacetonitrile (1 mmol), sodium azide (2.0 mmol), catalyst (20 mg), DMF, 120 °C. [b] Isolated yield.

Table 2. Catalytic Performance of CoY Zeolite under Various Reaction Conditions[a]

entry	catalyst	solvent	yield[b] (%)	TON[c]
1[d]	$CoCl_2 \cdot 6H_2O$	DMF	56	21
2[d]	$Co(NO_3)_2 \cdot 6H_2O$	DMF	nil	
3[d]	$Co(OAc)_2 \cdot 4H_2O$	DMF	nil	
4[d]	$CoSO_4 \cdot 7H_2O$	DMF	27	1
5	CoY	DMF	80	29
6	Co−K10 Mont.	DMF	72	26
7	Co/Al−HT	DMF	12	4
8	Co−Al−MCM41	DMF	10	3
9[e]	CoY	DMF	35, 80	15, 29
10	CoY	DMSO	58	18
11	CoY	toluene	55	18
12	CoY	EtOH	35	16
13	CoY	dioxan	50	17
14	CoY	THF	62	23
15	CoY	ACN	25	14
16[f]	CoY	DMF	50, 80	17, 29
17[g]	CoY	DMF	30, 80	8, 29
18[h]	CoY	DMF	30, 80	14, 29
19[i]	CoY	DMF	70, 80	24, 29

[a] Phenylacetonitrile (1 mmol), sodium azide (2 mmol), catalyst (20 mg), DMF (2 mL), 120 °C for 14 h. [b] Isolated yield. [c] Moles of tetrazole formed per mole of catalyst. [d] Reaction carried out with 0.01 g of cobalt salts. [e] Yield and TON of the reaction carried at 100 and 120 °C, respectively. [f] Yield and TON of the reaction carried for 12 and 14 h, respectively. [g] Yield and TON of the reaction carried with 10 mg and 20 mg of catalyst, respectively. [h] Yield and TON when the reaction carried with 1.0 and 2.0 mmol of sodium azide, respectively. [i] Yield and TON when the reaction carried with solvent 0.5 and 1 mL, respectively.

compensated by exchangeable transition-metal cations which, after dehydration, may occupy different sites in zeolite.

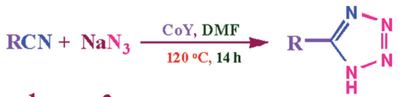
In continuation of our ongoing works on development of efficient, reusable supports, and catalysts using zeolites/clays[15] which are readily impregnated with metal ions, herein we report a simple, green, and efficient protocol for the synthesis of tetrazoles with environmentally friendly CoY zeolites as a novel catalyst. In the search toward ecocompatible and more economical transition-metal-catalyzed procedures, Cobalt-catalyzed reactions are promising,[12] as they are favorably comparable to nickel and palladium, although in the framework of sustainable development, cobalt is less interesting than iron or manganese. On the other hand, several reactions performed under cobalt catalysis are specific to this metal. For instance, iron-catalyzed cross coupling between aryl Grignard reagents and functionalized secondary alkyl bromides generally failed where as excellent yields are obtained under cobalt catalysis.

To optimize the reaction conditions and to explore the catalytic activity of cobalt-exchanged Y zeolite, phenylacetonitrile (**1i**) and sodium azide (**2**) were used as test substrates to yield 5-benzyltetrazole (**3i**), and the results are summarized in Table 1. CoY zeolite shows better catalytic performance than other metal ion exchanged zeolites such as Fe, Ni, Cu, Zn, Cd, Al, and Sn (Table 1, entries 3, and 5−10), and HY zeolite (Table 1, entry 1). Poor yield is obtained with unmodified solid support, NaY zeolite (Table 1, entry 2). No addition product is obtained when the reaction is carried out without catalyst (Table 1, entry 11), despite prolonged reaction time, thus highlighting the specific role of cobalt present in the solid support.

To identify the best cobalt source, catalytic activities of various cobalt forms are investigated under our experimental conditions. The results, including yields and turnover number (TON), are summarized in Table 2. Cobalt chloride has provided the desired product in low but promising yield (Table 2, entry 1). However, the separation and reuse of the catalyst pose problems due to its complete dissolution in DMF. Use of solid supports led to sharply ascending efficiencies in the synthesis of tetrazoles except for Co/Al-HT and Co−Al−MCM41 (Table 2, entries 5−8). Cobalt-exchanged zeolite is a better catalyst than others and gives a very high yield of tetrazoles (Table 2, entry 5). CoY zeolite was prepared by an ion-exchange method[16] and characterized[17] by powder XRD, SEM-EDX, ICP-AES, AAS analysis, UV-DRS, and FT-IR spectra. The XRD (see the Supporting Information, Figure S1) confirmed the dispersion of cobalt on NaY framework, the heterogeneity in shape, and highly crystalline nature of zeolite. The size and morphology of the catalyst were analyzed by SEM image (see the Supporting Information, Figure S2). The total cobalt content was found to be 7.06 atom % by EDX analyzer (see the Supporting Information, Figure S3). The UV−DRS spectra provided a “fingerprint” of the specific transition of cobalt environment in the zeolite, indicating the presence of cobalt in +2 state.[17] The three bands around 530, 574, and 634 nm were assigned to Co^{2+} in zeolite, which was absent in the unmodified solid support, NaY zeolite (see the Supporting Information, Figure S4). The results obtained from ICP-AES and AAS analyses also confirmed the presence of cobalt (7.06%) in CoY zeolite (see the Supporting Information). FT-IR spectra (see the Supporting Information, Figure S5) of recycled catalyst shows that the structural integrity remains unaltered after the reaction and thus proves the efficiency of cobalt exchanged zeolite as a recyclable catalyst.

The influence of other experimental parameters such as solvent, temperature, amount of catalyst, and reaction time was also optimized. The solvent has a prominent influence on the yield (Table 2, entries 10−15). The experimental results show that toluene, THF, and DMF are good solvents in sharply ascending efficiencies in the synthesis of tetrazoles, whereas a protic solvent namely ethanol is not suitable for this reaction. An increase in temperature from 100 to 120 °C accelerates the

Table 3. Synthesis of 5-Substituted 1*H*-Tetrazoles Catalyzed by CoY Zeolite[a]



1 2 3a-p

entry	R	product	yield[b] (%)	TON[c]
1	C_6H_5-	**3a**	90, 92[d]	37
2	*p*-ClC_6H_4-	**3b**	91	40
3	*p*-$NO_2C_6H_4$-	**3c**	95	40
4	*p*-$NH_2C_6H_4$-	**3d**	77	31
5	2- pyridinyl-	**3e**	92	37
6	4-pyridinyl-	**3f**	90	34
7	1-naphthyl-	**3g**	68	30
8	9-anthracenyl-	**3h**	62	26
9	$C_6H_5CH_2$-	**3i**	80	29
10	*p*-$NO_2C_6H_4CH_2$-	**3j**	91	37
11	*p*-$H_3COC_6H_4CH_2$-	**3k**	87	38
12	1-cyclohexenyl-CH_2-	**3l**	93	39
13[e]	CH_3-	**3m**	74	60
14[f]	$CNCH_2$-	**3n**	86	46
15[g]	*p*-$(CH_3)_2NC_6H_4$-	**3o**	nil	
16[g]	*p*-$OHC_6H_4CH{=}C(COOH)$-	**3p**	nil	

[a] Nitrile (1 mmol), sodium azide (2.0 mmol), catalyst (20 mg), DMF (1 mL) for 14 h at 120 °C. [b] Yield of isolated product. [c] Moles of tetrazole formed per mole of catalyst. [d] Yield of gram-scale reaction with benzonitrile (10 mmol), sodium azide (20.0 mmol). [e] Reaction carried for 20 h in a pressure tube. [f] Reaction carried in a pressure tube with 2 and 4.0 mmol of sodium azide. [g] Reaction carried at 140 °C.

reaction to give the desired product in high yield (Table 2, entry 9). Moderate to good yield is obtained on increasing the quantity of sodium azide from 1 equiv to 2 equiv (Table 2, entry 18). The effects of reaction times and the amount of catalyst on the reaction were also evaluated (Table 2, entries 16 and 17). There was no appreciable increase in the yield on prolonging the reaction time or increasing the amount of catalyst. Consequently, the optimal reaction conditions have been identified as 120 °C in DMF for 14 h.

To understand the scope and generality of CoY zeolite catalyzed [3 + 2] cycloaddition reaction, various structurally divergent benzonitriles were employed as substrates. As depicted in Table 3, various aromatic, heteroaromatic and aliphatic nitriles were tested. All reactions proceeded to completion within 14 h, and tetrazoles were isolated in moderate to excellent yields. The isolated yield obtained for gram-scale reaction was comparable to that for small-scale reaction (Table 3, entry 1). This demonstrates the potential utility of this method for preparative purposes. The aromatic benzonitriles give moderate to good yields (Table 3, entries 1–8). The best results are obtained with nitriles containing an electron-withdrawing substituent (Table 3, entries 2 and 3) than with an electron-donating substituent (Table 3, entry 4). Heteroaromatic nitriles such as 2-pyridinecarbonitrile and 4-pyridinecarbonitrile gave the corresponding tetrazoles in excellent yields (Table 3, entries 5 and 6). Moderate yield was obtained in the reaction of sterically demanding cyanoanthracene and cyanonaphthalene (Table 3, entries 7 and 8). Among aliphatic nitriles, acetonitrile provided moderate yield with longer reaction time without any additives (Table 3, entry 13).[18] Malononitrile afforded only monoaddition product even on addition of 2 equiv of sodium azide (Table 3, entry 14). Phenylacetonitrile, 4-nitrophenylacetonitrile, 4-nitrophenylacetonitrile, and 1-cyclohexenylacetonitrile provided moderate to good yields with shorter reaction time (Table 3, entries 9–12) than the methods reported previously.[8,10] CoY catalyst exhibited negligible activity for *N*,*N*-dimethylbenzonitrile, and α-cyano-4-hydroxycinnamic acid (Table 3, entries 15 and 16) despite prolonged reaction time because azide ion would not add to the cyanide group of the nitriles of carboxylic acid and electron-rich nitriles, respectively.[19] All synthesized tetrazoles were characterized by ^1H and ^{13}C NMR, FT-IR, and UV–vis spectroscopy. The IR spectra of synthesized compounds showed a sharp absorption at 3421 cm^{-1} (N–H) and group of bands at 1455 (C–H), 1285 (N–N=N–), 1208, 1120, and 1048 cm^{-1} caused by the presence of secondary amino group and tetrazole ring and absence of band at 2200 cm^{-1} due to CN group.

Table 4. Sheldon Test Carried out with CoY Zeolite Catalyzed Synthesis of 5-Substituted 1*H*-Tetrazoles[a]

	yield[b] (%)		
catalyst	**7h**	**7 + 7h**	reused catalyst (TON)[c]
CoY	35.4	38.2	79.8 (29)

[a] Phenylacetonitrile (1 mmol), sodium azide (2.0 mmol), catalyst (20 mg), DMF (1 mL) at 120 °C. [b] HPLC yield. [c] Moles of tetrazole formed per mole of catalyst.

Table 5. Reusability of CoY Zeolite in the Synthesis 5-Substituted 1*H*-Tetrazoles[a]

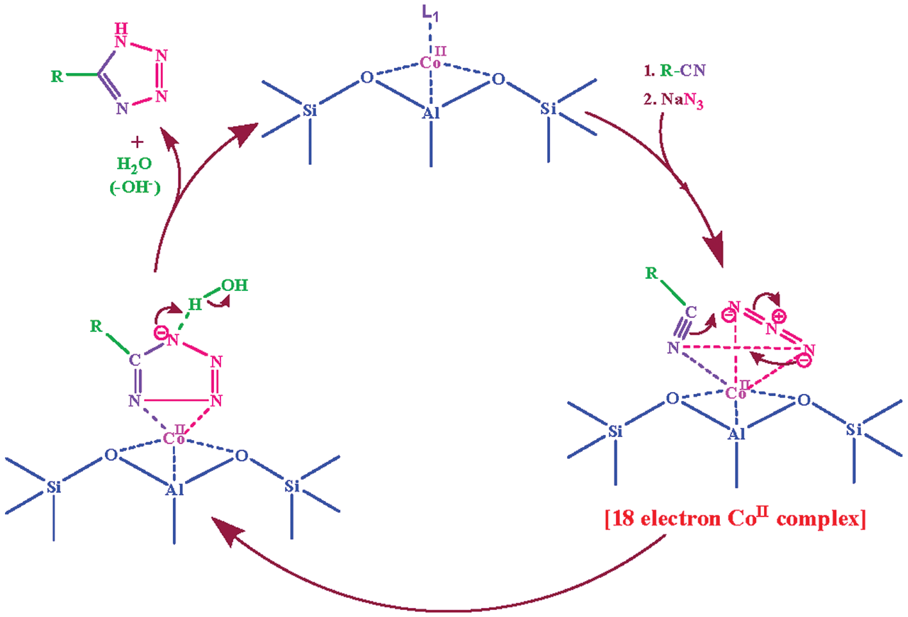
run[b]	first	second	third	fourth	fifth
yield (%)	80	78	79	77.4	77.5
TON[c]	29	29	29	28	29

[a] Reactions are performed with phenylacetonitrile (1 mmol), sodium azide (2.0 mmol), catalyst (20 mg), DMF (1 mL) for 14 h at 120 °C. [b] After completion of the reaction, catalyst was filtered and washed three times with ethyl acetate, air-dried, activated at 450 °C, and reused for successive runs. [c] Moles of tetrazole formed per mole of catalyst.

In order to verify real heterogeneity of CoY zeolite, a Sheldon test[20] was performed to evaluate possible metal leaching. Thus, the reaction mixture after 7 h at 120 °C was filtered, and the filtrate was further heated at 120 °C for an additional 7 h. Sodium azide and phenylacetonitrile were further added to the recovered solid catalyst, and the mixture was heated at 120 °C for 14 h. The obtained results clearly indicated that there is no appreciable leaching of metal ions under the present reaction conditions (Table 4). The absence of leaching was also confirmed from chemical and ICP-AES analyses of the filtrate from the reaction mixture and also of the filtrate from a stirred solution of CoY in DMF (at 120 °C for 14 h) (for details, see the Supporting Information).

As recyclability is important for industrial applications of a good catalyst, reuse performance of CoY zeolite was investigated. It is noteworthy that the recovered catalyst was recycled by calcinating at 450 °C and even after the fifth cycle exhibited comparable activity with 77.5% yield and a turnover number of 29 as shown in Table 5. The reusability was also confirmed

Scheme 1. Plausible Mechanism for CoY Zeolite Catalyzed [3 + 2] Cycloaddition of Tetrazoles



by ICP-AES analysis of reused CoY zeolite, which proved the presence of 7.06% of cobalt, and this strongly supports the heterogeneous nature of CoY zeolite.

On the basis of the above results, and also in accordance with previous literature reports,[6] a plausible reaction pathway is proposed as shown in Scheme 1. The pink CoY zeolite (octahedral coordination) upon activation became blue because of tetrahedral coordination, which was strongly supported by UV−DRS spectra (see the Supporting Information, Figure S4). The three bands at 530, 574, and 634 nm were assigned to Co^{2+} in tetrahedral coordination in the zeolite framework. During the course of reaction, the color changed from blue to deep blue and then pink indicating a change in the coordination sphere, from tetrahedral to octahedral.

Co^{II} bound to zeolite Y (to trivalent Al) coordinated readily to the nitrile, and this is the dominant factor influencing [2 + 3] cycloaddition. It is relevant to note here that, in the study of azide−nitrile cycloaddition catalyzed by Zn^{2+}, Sharpless et al. reported that coordination of the nitrile substrate to the Lewis acidic zinc is the source of the catalysis in the formation of 1*H*-tetrazoles which is supported by model calculations using density functional theory and corroborated with experimental rate studies. Subsequent neucleophilic attack by azide (via azide binding to Co^{II} ensures the formation of an 18-e^- complex)[21] followed by hydrolysis produces tetrazole as the end product, with Co^{II} catalyst being released for the next cycle of reactions as its structural integrity remains unaltered (see the Supporting Information, Figure S5).

In conclusion, an efficient, atom-economical synthesis of 5-substituted 1*H*-tetrazoles is reported for the first time using the heterogeneous CoY zeolite. This simple, environmentally benign catalysis proceeds under aerobic conditions with no additives, tolerates various nitriles particularly for aliphatic nitriles, requires shorter reaction times with good to excellent yields, and gives a higher turnover number. The present [2 + 3] cycloaddition is associated with several advantages such as simpler procedure, milder reaction conditions, and an alternative to hazardous, corrosive, and polluting conventional Lewis acid catalysts. Its reusability with consistent activity for at least five cycles is also established, indicating CoY as a greener catalyst, it can substitute metal salts or other heterogeneous catalysts, and has potential value for industrial applications.

■ EXPERIMENTAL SECTION

Preparation and Characterization of Cobalt-Exchanged Zeolite. NaY zeolite powder was purchased and used as such. The physio-chemical parameters of NaY zeolite are 2.43 Si/Al ratio, unit cell size 24.65 Å and surface area, m^2/g: 900 with supercages of a diameter of ca. 1.3 nm. Cobalt-exchanged zeolite was prepared from NaY zeolite by an ion-exchange method and was characterized by powder XRD, EDX, ICP-AES, AAS analyses, and UV−DRS spectra.

The structure of NaY zeolite was found to be retained as observed from the retention of all the characteristic peaks in XRD patterns after cobalt-exchange process. The diffraction patterns of the zeolite samples show the reflections in the range 5−35°, typical of zeolites. This suggests that cobalt is highly dispersed on the NaY framework. The sharp intense peaks at 15.54°, 23.52°, and 31.15° show the good crystallinity of the zeolite material.

The SEM image (see the Supporting Information, Figure S2) shows that the surface consists of CoY zeolite granules with sizes ranging from 0.5 to 10 μm. It is noted that the shape of CoY grains is heterogeneous in nature.

Typical Procedure for the Preparation of 5-Substituted 1*H*-Tetrazole. CoY zeolite was added (0.02 g) to a mixture of phenylacetonitrile (1 mmol) and sodium azide (2 mmol) in DMF (1 mL) and stirred at 120 °C for 14 h. After completion of reaction (monitored by thin-layer chromatography, TLC), the reaction mixture was treated with ethyl acetate (10 mL), the catalyst was filtered, and the filtrate was washed with distilled water. The organic layer was treated with 5 N HCl (10 mL) and stirred vigorously. The resultant organic layer was separated, and the aqueous layer was again extracted with ethyl acetate (10 mL). The combined organic layers were washed with water, dried over anhydrous sodium sulfate, and concentrated to give the crude solid crystalline 5-benzyltetrazole. Column chromatography silica gel (60−120 mesh) afforded pure tetrazole. All products were characterized by ^{1}H and ^{13}C NMR, FT-IR, UV−vis, and emission spectra, which were in agreement with literature.[6a,8,10,22−28]

Characterization of 5-Phenyl-1H-tetrazole[6a] *(Table 3, Entry 1).* Compound **3a** was prepared according to the general procedure and recrystallized from ethanol to give a white solid (90% yield): mp 215−216 °C; UV−vis (EtOH) λ_{max} 209, 243, 274 nm; emission (EtOH, λ_{exci} = 274 nm) λ_{emi} 395 nm; FT-IR (KBr) γ cm^{-1} 3419, 2924, 2827, 2717, 2656, 1620, 1600, 1460, 1350, 1383, 1163, 1057, 765; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS, δ ppm) 3.92 (br s, 1H), 7.58 (m, 3H), 8.12 (m, 2H).

Characterization of 5-(p-Chlorophenyl)-1H-tetrazole[10a] *(Table 3, Entry 2).* Compound **3b** was prepared according to the general procedure and recrystallized from ethanol to give a white solid (91% yield): mp 261−263 °C; UV−vis (EtOH) λ_{max} 214, 254 nm; emission (EtOH, λ_{exci} = 254 nm) λ_{emi} 416 nm; FT-IR (KBr) γ cm^{-1} 3419, 2927, 2816, 2723, 1602, 1457, 1437, 1383, 1350, 1161, 1095, 1055, 875, 765; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS, δ ppm) 7.64 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS, δ ppm) 123.1, 128.7, 129.5, 135.9, 155.0.

Characterization of 5-(p-Nitrophenyl)-1H-tetrazole[8,10a] *(Table 3, Entry 3).* Compound **3c** was prepared according to the general procedure and recrystallized from ethanol to give a white solid (95% yield): mp 219−221 °C; UV−vis (EtOH) λ_{max} 219, 289 nm; emission (EtOH, λ_{exci} = 289 nm) λ_{emi} 452 nm; FT-IR (KBr) γ cm^{-1} 3421, 2933, 2818, 2719, 1627, 1599, 1273, 1174, 1016, 929, 852; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS, δ ppm) 3.44 (br s, 1H), 7.60 (m, 2H), 8.04 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS, δ ppm) 124.2, 126.9, 129.4, 131.2, 155.3.

Characterization of 5-(p-Aminophenyl)-1H-tetrazole[22] *(Table 3, Entry 4).* Compound **3d** was prepared according to the general procedure and recrystallized from ethanol to give a white solid (77% yield): mp 265−267 °C; UV−vis (EtOH) λ_{max} 218, 286 nm; emission (EtOH, λ_{exci} = 286 nm) λ_{emi} 434 nm; FT-IR (KBr) γ cm^{-1} 3485, 1622, 1510, 1457, 1407, 1377, 1191, 1139, 1056, 991, 837, 750; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS, δ ppm) 6.12 (br s, 3H), 6.59 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS, δ ppm) 113.4, 113.5, 133.3, 133.5, 152.9.

Characterization of 2-(1H-Tetrazol-5-yl)pyridine[6,10a] *(Table 3, Entry 5).* Compound **3e** was prepared according to the general procedure and recrystallized from ethanol to give a white solid (92% yield): mp 210−213 °C; UV−vis (EtOH) λ_{max} 214, 246 nm; emission (EtOH, λ_{exci} = 246 nm) λ_{emi} 401 nm; FT-IR (KBr) γ cm^{-1} 3417, 2818, 2724, 1623, 1599, 1512, 1384, 1350, 1039, 833; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS, δ ppm) 7.61 (m, 1H), 8.06 (m, 1H), 8.21 (d, *J* = 8 Hz, 1H), 8.78 (d, *J* = 4.8 Hz, 1H).

Characterization of 5-(4-Pyridyl)-1H-tetrazole[8] *(Table 3, Entry 6).* Compound **3f** was prepared according to the general procedure and recrystallized from ethanol to give a white solid (90% yield): mp 254−255 °C; UV−vis (EtOH) λ_{max} 214, 233, 271 nm; emission (EtOH, λ_{exci} = 271 nm) λ_{emi} 419 nm; FT-IR (KBr) γ cm^{-1} 3414, 2814, 2725, 1626, 1597, 1512, 1384, 1350, 1039, 833; ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS, δ ppm) 5.91 (d, *J* = 1.5 Hz, 2H), 6.26 (d, *J* = 3.9 Hz, 2H); ^{13}C NMR (75 MHz, D$_2$O, 25 °C, TMS, δ ppm) 119.1, 137.0, 137.3, 151.1.

Characterization of 5-(1-Naphthyl)-1H-tetrazole[23] *(Table 3, Entry 7).* Compound **3g** was prepared according to the general procedure and recrystallized from ethanol to give a white solid (68% yield): mp 264−267 °C; UV−vis (EtOH) λ_{max} 227, 288 nm; emission (EtOH, λ_{exci} = 288 nm) λ_{emi} 358 nm; FT-IR (KBr) γ cm^{-1} 3421, 3053, 2812, 2721, 1626, 1599, 1518, 1491, 1383, 1352, 1257, 1121, 1102, 966, 864; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS, δ ppm) 7.63−7.72 (m, 3H), 7.97−7.99 (m, 1H), 8.02−8.08 (m, 1H), 8.10−8.18 (m, 1H), 8.59−8.61 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, TMS, δ ppm) 125.3, 126.0, 127.4, 128.1, 128.5, 130.9, 133.3, 162.3.

Characterization of 5-(9-Anthracenyl)-1H-tetrazole[24] *(Table 3, Entry 8).* Compound **3h** was prepared according to the general procedure and recrystallized from ethanol to give a white solid (62% yield): mp 215−216 °C; UV−vis (EtOH) λ_{max} 215, 255 nm; emission (EtOH, λ_{exci} = 255 nm) λ_{emi} 446 nm; FT-IR (KBr) γ cm^{-1} 3441, 3058, 2819, 2731, 1616, 1597, 1518, 1491, 1373, 1357, 1259, 1120, 1101, 965, 863; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS, δ ppm) 7.48−7.64 (m, 4H), 7.94 (d, *J* = 8.1 Hz, 2H), 8.28 (d, *J* = 8.4 Hz, 2H), 8.47 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS, δ ppm) 125.0, 126.1, 128.8, 130.3, 132.5, 133.0, 133.2, 133.3, 162.8.

Characterization of 5-Benzyl-1H-tetrazole[8] *(Table 3, Entry 9).* Compound **3i** was prepared according to the general procedure and recrystallized from ethanol to give a white solid (80% yield): mp 123−125 °C; UV−vis (EtOH) λ_{max} 219, 257 nm; emission (EtOH, λ_{exci} = 257 nm) λ_{emi} 437 nm; FT-IR (KBr) γ cm^{-1} 3419, 2928, 2814, 2723, 1626, 1600, 1496, 1384, 1350, 1182, 1066, 831; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS, δ ppm) 4.29 (s, 2H), 7.20−7.56 (m, 5H), 8.52 (br s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS, δ ppm) 29.8, 127.7, 128.8, 129.1, 134.3, 156.1.

Characterization of 5-(4-Nitrophenylacetonitrile)-1H-tetrazole[25] *(Table 2, Entry 10).* Compound **3j** was prepared according to the general procedure and recrystallized from ethanol to give a white solid (91% yield): mp 184−186 °C; UV−vis (EtOH) λ_{max} 217, 289 nm; emission (EtOH, λ_{exci} = 289 nm) λ_{emi} 421 nm; FT-IR (KBr) γ cm^{-1} 3421, 2933, 2818, 2719, 1627, 1599, 1273, 1174, 1016, 929, 852; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS, δ ppm) 2.54 (s, 2H), 5.25 (br s, 1H), 7.57−7.65 (m, 2H), 7.84−8.96 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS, δ ppm) 29.47, 127.44, 129.44, 131.27, 156.67.

Characterization of 5-(4-Methoxybenzyl)-1H-tetrazole[26] *(Table 3, Entry 11).* Compound **3k** was prepared according to the general procedure and recrystallized from ethanol to give a white solid (87% yield): mp 156−158 °C; UV−vis (EtOH) λ_{max} 217, 283 nm; emission (EtOH, λ_{exci} = 283 nm) λ_{emi} 394 nm; FT-IR (KBr) γ cm^{-1} 3415, 2962, 2814, 2718, 1627, 1600, 1247, 1178, 1383, 1350, 1111, 1033, 829; ^{1}H NMR (300 MHz, CDCl$_3$ and DMSO-d_6, 25 °C, TMS, δ ppm) 3.78 (s, 3H), 4.22 (s, 2H), 6.85 (d, *J* = 6.3 Hz, 2H), 7.21 (d, *J* = 6 Hz, 2H), 8.65 (br s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$ and DMSO-d_6, 25 °C, TMS, δ ppm) 28.9, 55.1, 114.1, 127.3, 129.3, 158.7.

Characterization of 5-(Cyclohexenylmethyl)-1H-tetrazole (Table 3, Entry 12). Compound **3l** was prepared according to the general procedure and recrystallized from ethanol to give white solid (93% yield): mp 180−182 °C; UV−vis (EtOH) λ_{max} 220 nm; emission (EtOH, λ_{exci} = 220 nm) λ_{emi} 428 nm; FT-IR (KBr) γ cm^{-1} 3427, 3139, 3002, 2931, 1571,1541, 1438, 1344, 1251, 1088, 840; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS, δ ppm) 1.56−1.60 (m, 4H), 1.92 (s, 2H), 2.02 (m, 2H), 3.55 (s, 2H), 5.54 (s, 1H), 7.76 (br s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C, TMS, δ ppm) 23.6, 26.2, 27.3, 30.1, 37.8, 122.9, 138.1, 157.5. Elemental Analysis Anal. Calcd for C$_8$H$_{12}$N$_4$: C, 58.51; H, 7.37; N, 34.12. Found: C, 58.64; H, 7.42; N, 34.12.

Characterization of 5-Methyl-1H-tetrazole[27] *(Table 3, Entry 13).* Compound **3m** was prepared according to the general procedure and recrystallized from ethanol to give a white solid (74% yield): mp 145−148 °C; UV−vis (EtOH) λ_{max} 210, 262 nm; emission (EtOH, λ_{exci} = 262 nm) λ_{emi} 443 nm; FT-IR (KBr) γ cm^{-1} 3443, 2945, 2814, 2723, 1628, 1247, 1600, 1489, 1180, 1095, 931, 767; ^{1}H NMR (300 MHz, D$_2$O, 25 °C, TMS, δ ppm) 1.84 (s, 3H), 8.32 (br s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, 25 °C, TMS, δ ppm) 22.1, 180.4.

Characterization of 5-Cyanomethyl-1H-tetrazole[28] *(Table 3, Entry 14).* Compound **3n** was prepared according to the general procedure and recrystallized from ethanol to give a white solid (86% yield): mp 116−118 °C; UV−vis (EtOH) λ_{max} 216, 262 nm; emission (EtOH, λ_{exci} = 262 nm) λ_{emi} 429 nm; FT-IR (KBr) γ cm^{-1} 3414, 2854, 2204, 1602, 1498, 1386, 1348, 837, 771; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS, δ ppm) 3.71 (s, 2H), 7.84 (br s, 1H).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. General methods, preparation of catalyst, and analytical data for all compounds **3a**−**n**. This material is available free of charge via the Internet at http://pubs.acs.org.

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