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MCM-41-SO_3H as an efficient reusable nano-ordered heterogeneous catalyst for the synthesis of divers 1- & 5-substituted 1*H*-tetrazoles

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Abstract. An improved and efficient method for the synthesis of 1- & 5-substituted 1*H*-tetrazole derivatives was described in the presence of nano-ordered MCM-41-SO_3H as an effective heterogeneous catalyst. This metal-free protocol, [2 + 3] cycloaddition of sodium azide to various nitriles or ethyl *N*-phenyl formimidate intermediate under mild reaction conditions, provides a wide range of 1*H*-tetrazoles in good to excellent yields. The catalyst was reused five times without significant loss of catalytic activity.

1. Introduction

Tetrazoles are poly nitrogen electron-rich heterocyclic compounds that have been known for over a hundred years. Five-membered doubly unsaturated tetrazole rings contain one carbon and four nitrogen atoms. Tetrazole-containing molecules have a wide range of applications in organic synthesis as precursors of various nitrogen-containing heterocyclic compounds (triazoles, oxazolidones, and thiazoles) [1,2], in material science as rocket propellants and explosives [3], in coordination chemistry as ligands [4], and in medicinal chemistry as isosteric replacements for carboxylic acid (Figure 1) [5]. In addition to this application, they are used as herbicides, fungicides [6], and plant growth regulators in the agricultural field.

According to the important properties of tetrazole functionality as biologically active molecules mentioned earlier, considerable attention has been dedicated to the development of environmentally friendly methodologies to synthesize these compounds over the past decades.

Literature reviews indicate that the Huisgen 1,3-Dipolar Cycloaddition of a dipolarophile (e.g., nitrile moiety) with a 1,3-dipolar structure (e.g., sodium azide) in the presence of a broad variety of homogeneous or heterogeneous catalysts such as $CdCl_2$ [7], $Pd(OAc)_2/ZnBr_2$ [8], ZnO, $ZnBr_2$, $ZnCl_2$/tungstates, Zn/Al hydrotalcite, $ZnCl_2/AlCl_3$/silica, $Zn(OTf)_2$, Zn hydroxyapatite, ZnS, $Cu(OAc)_2$, Cu_2O, nano ZnO/Co_3O_4, $FeCl_3$-SiO_2, $Fe(OAc)_2$, nano $CuFe_2O_4$, $BF_3.OEt_2$, $InCl_3$, I_2, $(CH_3)_2SnO$, NH_4Cl, TBAF, TBAB, $AgNO_3$, Ag-NPs, copper triflates, β-cyclodextrin, cuttlebone, COY zeolites, Silica Sulfuric Acid, $Pd(PPh_3)_4$, WAlPO-5 microspheres, Fe_3O_4@SiO_2/salen of Cu(II), $B(C_6F_5)_3$, $AlCl_3$, Zn-Cu alloy, CAES, $CuSO_4.5H_2O$, and cutlleboneand $In(OTf)_3$ is a general current mechanism for the synthesis of 1*H*-tetrazol derivatives [9-20].

Furthermore, one of the most important methods for synthesis of tetrazoles is the reaction of substituted amines with triethyl orthoformate and sodium azide [21-27].

However, the most common reported methods

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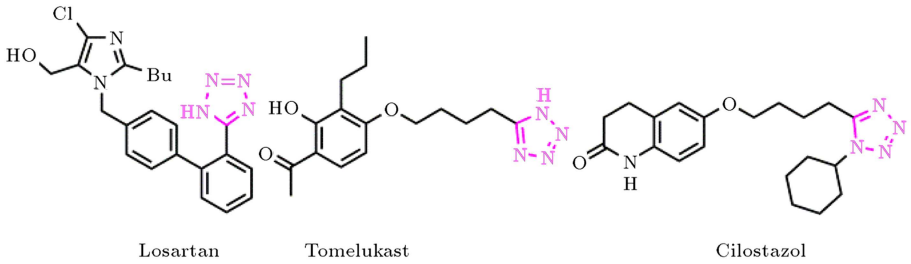


Figure 1. Tetrazole-based biologically active compounds.

suffer from drawbacks such as the use of a catalyst containing transition metals, harsh and stringent reaction conditions (e.g., volatile or highly corrosive solvents), metal and expensive catalase, longer reaction time, and low yields [9,13-14]. Thus, obviation of these limitations is urgent to develop a simple and efficient synthetic method for obtaining diverse 1*H*-tetrazoles. In this context, one of the fundamental aspects of the development of a new alternative is decreasing pollution in chemical synthesis leading to the elimination of environmental pollution. The development of the as-silica-based mesoporous materials (MCMs) with a hexagonal array, large surface areas (> 1000 $m^2.g^{-1}$), large pore volume (up to 0.99 cm^3 g^1), and excellent hydrothermal, thermal, mechanical, and chemical stability has attracted significant attention to replacing homogeneous catalytic systems [28].

On the other hand, to overcome the low acid strength of mesoporous silicas, different methods including replacement part of Si atoms in the matrix by metal ions, such as Al, B, Fe, and Zr, or by anchoring inorganic sulfonic acid (-SO_3H) have been described [29].

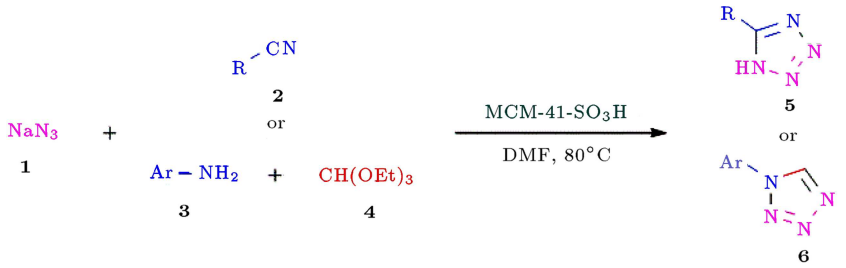
Herein, we wish to report a new metal-free protocol for the synthesis of 1-& 5-substituted 1*H*-tetrazoles from a wide variety of nitrile and ethyl *N*-phenyl formimidate intermediates using MCM-41 as an effective solid acid catalyst (Scheme 1).

2. Results and discussion

At the beginning, to evaluate the reaction conditions, cycloaddition reaction of sodium azide (**1**, 1.3 mmol) with benzonitrile (**2e**, 1 mmol) was chosen as the model reaction under a variety of conditions (Table 1). Our initial attempts to synthesize 5-phenyl-1*H*-tetrazole **5e** in the absence of any catalyst in various solvents even at high temperature have been all disadvantageous to the reaction. However, DMF exhibits higher performance in comparison to other solvents such as DMSO, H_2O, CH_3CN, 1,4-dioxane, and $CHCl_3$. Therefore, we found that the addition of polar solvent and the presence of a catalyst for the reaction progress were both necessary. As expected, the desired product **5e** formation was observed in moderate yield when a catalytic amount of Al-MCM-41, B-MCM-41, Zn-MCM-41, Fe-MCM-41, MCM-41-SO_3H, and MCM-41-3-aminopropyl-SO_3H (30 mg) was used in DMF at 80°C (Table 1, entries 1-6). However, MCM-41-SO_3H was the best choice. In the next step, the temperature increased from 80 to 120°C. However, no significant difference was observed in yield (Table 1, entry 7). Subsequently, to check the effect of catalyst loading, the model reaction was carried out in the presence of 50, 75, and 100 mg of MCM-SO_3H (Table 1, entries 8, 9, and 10). An increase in the yield was obtained by changing the catalyst loading from 30 to 50 mg.

In an effort to develop better reaction conditions, different solvents, such as DMSO, H_2O, CH_3CN, $CHCl_3$, 1,4-dioxan, and toluene (Table 1, entries 11-16), were screened for cycloaddition reaction in the presence of MCM-41SO_3H as an effective catalyst. The result indicated that the desired product was obtained in low yield as compared with DMF. It is noteworthy that, due to explosive properties of sodium azide, the neat reaction condition was not examined.

The results reported in Table 1 highlight the specific role of MCM-41-SO_3H in the synthesis of



Scheme 1. Synthesis of 1- & 5-substituted 1*H*-tetrazoles (**5, 6**) catalyzed by MCM-41-SO_3H mesoporous solid acid.

Table 1. Optimization of the reaction conditions for the preparation of 5-phenyl-1*H*-tetrazole (**5e**)[a].

Entry	Catalyst	Loading (mg)	Solvent	Temp. (°C)	Yield[b] (%)
1	Al-MCM-41	30	DMF	80	35
2	B-MCM-41	30	DMF	80	50
3	Zn-MCM-41	30	DMF	80	40
4	Fe-MCM-41	30	DMF	80	40
5	MCM-41-SO_3H	30	DMF	80	70
6	MCM-41-AP-SO_3H[c]	30	DMF	80	65
7	MCM-41-SO_3H	30	DMF	120	90
8	MCM-41-SO_3H	50	DMF	80	90
9	MCM-41-SO_3H	75	DMF	80	92
10	MCM-41-SO_3H	100	DMF	80	85
11	MCM-41-SO_3H	50	DMSO	80	72
12	MCM-41-SO_3H	50	H_2O	80	38
13	MCM-41-SO_3H	50	CH_3CN	80	43
14	MCM-41-SO_3H	50	$CHCl_3$	Reflux	Trace
15	MCM-41-SO_3H	50	1,4-dioxan	80	Trace
16	MCM-41-SO_3H	50	toluene	80	Trace

[a]Reaction conditions: sodium azide (1, 1.3 mmol), benzonitrile (2, 1 mmol), solvent (2 mL), time (2 h), and required amount of the catalysts;

[b] the yields refer to the isolated product **5e**; and

[c] MCM-41-3-aminopropyl-SO_3H.

tetrazoles. Therefore, according to catalyst loading of 50 mg and temperature of 80°C, as optimized conditions, obtained results were applied to different aliphatic and aromatic nitriles (**2a-n**). The results are presented in Table 2.

Generally, the electronic and steric hindrance of nitrile has a negligible effect on the yield of the desired product. Nonetheless, it is observed that unsubstituted and electron-withdrawing groups on the aromatic nitrile compounds normally favor the increasing rate of cycloaddition to azides (Table 2, entries 1-5).

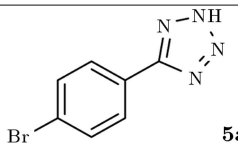
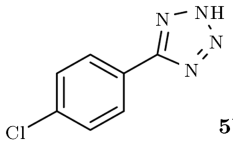
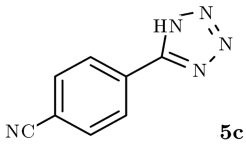
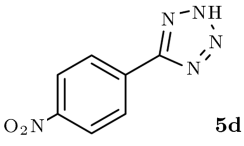
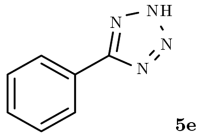
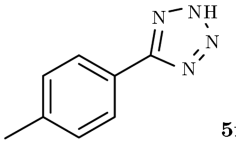
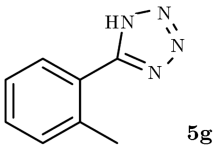
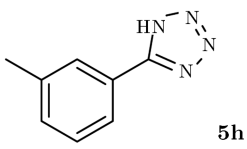
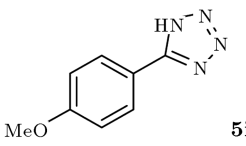
In comparison to aromatic nitriles, a wide range of alkyl nitriles, such as 4-chloro benzyl cyanide, benzyl cyanide, and malononitrile, react with NaN_3 under the optimized reaction conditions with subsided yield (Table 2 entries 12-14).

In the next step, to demonstrate the scope of this new and impressive methodology to amine compounds (**3a-k**), the optimized reaction conditions were developed to the synthesis of 1-substituted 1*H*-tetrazoles (**6a-k**). The results are summarized in Table 3. Again, good to excellent yields were obtained for the desired products. It is noteworthy that ethyl *N*-phenyl formimidate intermediate required shorter reaction times compared to nitrile compounds. The results suggested that aromatic anilines containing electron donating groups, particularly in the para positions, such as $-OMe$, $-CH_3$, $-NH_2$, and benzyl amine, took a short reaction time for easy treatment with triethyl orthoformate and sodium azide to produce 1-aryl-1*H*-tetrazoles in high yields (Table 3, entries 6, 9, and 11).

Recovery and reuse of the catalyst are another useful advantage of catalytic processes in different aspects such as environmental protection debate, costs of the catalyst, and toxicity. Therefore, we intended to check the reusability of the MCM-41-SO_3H catalyst in five consecutive runs for the synthesis of 5-phenyl-1*H*-tetrazoles under optimized conditions (Table 4). As shown in Table 4, the MCM-41-SO_3H catalyst promotes the reaction with the high and robust catalytic activity each time.

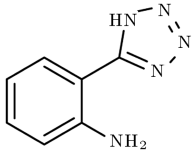
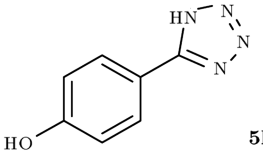
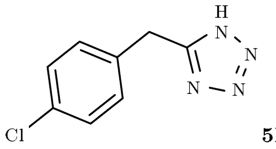
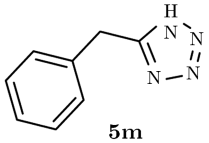
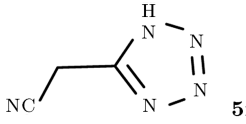
Finally, compared to various catalysts reported

Table 2. One-pot synthesis of 5-substituted 1*H*-tetrazole derivatives in the presence of MCM-41-SO_3H[a].

Entry	Substrate 2	Product[b] 5	Time (min)	Yield[c] (%)	m.p.[d] (Obsd)	m.p.[d] (Lit)
1	4-bromobenzonitrile **2a**	 **5a**	120	85	235-236	234-235 [32]
2	4-chlorobenzonitrile **2b**	 **5b**	120	90	258-260	262-264 [33]
3	4-cyanobenzonitrile **2c**	 **5c**	100	90	195-197	192 [34]
4	4-nitrobenzonitrile **2d**	 **5d**	120	80	220-222	218-219 [35]
5	benzonitrile **2e**	 **5e**	120	90	214-216	214-216 [36]
6	4-methylbenzonitrile **2f**	 **5f**	120	80	247-249	251-252 [44]
7	2-methylbenzonitrile **2g**	 **5g**	180	80	153-155	149-151 [22]
8	3-methylbenzonitrile **2h**	 **5h**	120	90	145-147	149-150 [37]
9	4-methoxybenzonitrile **2i**	 **5i**	150	80	230-232	231-233 [45]

[a] Reaction conditions: sodium azide (1, 1.3 mmol), nitrile compounds (2, 1 mmol), MCM-41-SO3H (50 mg) in DMF (2 mL) at 80 °C for the time shown in Table 2; [b] all compounds are known, and their structures were established from their spectral data and melting points as compared with authentic samples or literature values; [c] isolated yield; and [d] melting point.

Table 2. One-pot synthesis of 5-substituted 1*H*-tetrazole derivatives in the presence of MCM-41-SO_3H[a] (continued).

Entry	Substrate 2	Product[b] 5	Time (min)	Yield[c] (%)	m.p.[d] (Obsd)	m.p.[d] (Lit)
10	2-aminobenzonitrile **2j**	 **5j**	180	75	135-137	135-137 [39]
11	4-hydroxybenzonitrile **2k**	 **5k**	150	90	225-227	228-231 [40]
12	(4-chlorophenyl) acetonitrile **2l**	 **5l**	180	80	222-224	225 [23]
13	Benzyl cyanide **2m**	 **5m**	180	85	120-122	117-119 [33]
14	Malononitrile **2n**	 **5n**	180	75	110-112	116-118 [46]

[a] Reaction conditions: sodium azide (1, 1.3 mmol), nitrile compounds (2, 1 mmol), MCM-41-SO3H (50 mg) in DMF (2 mL) at 80 °C for the time shown in Table 2; [b] all compounds are known, and their structures were established from their spectral data and melting points as compared with authentic samples or literature values; [c] isolated yield; and [d] melting point.

earlier, [3+2] cycloaddition reaction of benxonitriles with sodium azide in the presence of MCM-41-SO_3H, provides 5-phenyl-1*H*-tetrazole (**5e**) (Table 5). According to Table 5, many proposed that catalytic methods would take a very long reaction time to achieve suitable yields and would use hazardous or expensive catalysts and a tedious work-up procedure.

3. Conclusion

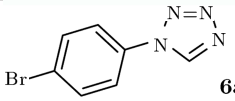
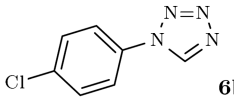
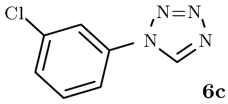
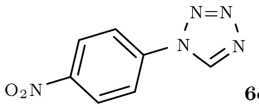
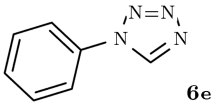
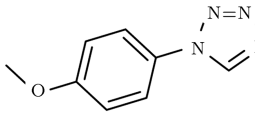
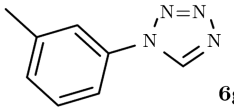
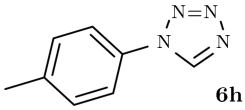
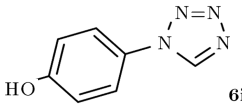
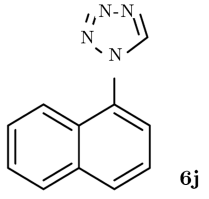
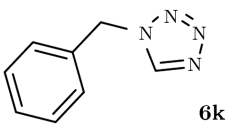
In conclusion, an innovative and highly efficient methodology was developed for the synthesis of divers 1-& 5-substituted 1*H*-tetrazoles using reusable MCM-41-SO_3H as the nonporous heterogeneous catalyst under mild reaction conditions. This strategy enjoys good to excellent yields, metal-free conditions, short reaction times, low cost, regiospecific products, lower number of reaction and work-up steps, and operational simplicity.

4. Experimental

4.1. Materials and techniques

All solvents, reagents, and chemicals were obtained from Merck (Germany) and Fluka (Switzerland) companies. FTIR spectra of samples were determined by an ABB Bomem MB-100 FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were determined by a Bruker (Avance DRX-400) spectrometer using DMSO as a solvent and TMS as an internal standard at room temperature.

Table 3. One-pot synthesis of 1-substituted 1*H*-tetrazole derivatives in the presence of MCM-41-SO_3H[a].

Entry	Substrate 3	Product[b] 6	Time (min)	Yield[c] (%)	m.p.[d] (Obsd)	m.p.[d] (Lit)
1	4-bromoaniline **3a**	 **6a**	120	85	170-172	168-170 [41]
2	4-choloromoaniline **3b**	 **6b**	120	80	151-153	157-158 [24]
3	3-choloromoaniline **3c**	 **6c**	100	90	140-141	137-139 [25]
4	4-nitromoaniline **3d**	 **6d**	120	80	195-197	199-200 [41]
5	Aniline **3e**	 **6e**	90	85	66-67	65-66 [42]
6	4-methoxyaniline **3f**	 **6f**	90	95	117-119	117-118 [43]
7	3-methylaniline **3g**	 **6g**	120	85	50-52	53-55 [24]
8	4-methylaniline **3h**	 **6h**	80	90	98-100	94-95 [42]
9	4-aminophenol **3i**	 **6i**	100	80	208-210	210-211 [47]
10	1-naphthylamine **3j**	 **6j**	100	90	95-97	98 [27]
11	Benzylamine **3k**	 **6k**	90	95	51-53	48-50 [26]

[a]Reaction conditions: sodium azide (1, 1.3 mmol), amine compounds (2, 1 mmol), triethyl orthoformate (1 mmol), and MCM-41-SO_3H (50 mg) in DMF (2 mL) at 80°C for the time shown in in the table; [b] all compounds are known, and their structures were established from their spectral data and melting points as compared with authentic samplesor literature values; [c] isolated yield; and [d] meltting point.

Table 4. Recovery and reuse of the MCM-41-SO_3H catalyst[a].

	Run				
	1	2	3	4	5
Yield	90	85	85	83	79

[a]Reaction conditions: sodium azide (1, 1.3 mmol), benzonitrlie (2, 1 mmol), and MCM-SO_3H (50 mg) in DMF (2 mL) at 80°C, 2 h.

4.1.1. General synthesis procedure for MCM-41-SO_3H
MCM-41 mesoporous silica was synthesized according to the previously reported method [29]. A suction flask of 100 mL was charged with MCM-41 (1 g) and CH_2Cl_2 (15 mL) equipped with a dropping funnel containing chlorosulfonic acid ($ClSO_3H$, 2 ml) and gas inlet tube for conducting HCl gas over a NaOH solution. After adding all of $ClSO_3H$ in a dropwise way, the solvent was evaporated under reduced pressure to obtain MCM-41-SO_3H as a light gray solid [30,31].

4.1.2. General procedure for 5a-5n
A mixture of nitrile compounds (1 mmol), sodium azide (1.3 mmol), MCM-41-SO_3H (50 mg), and DMF (2 mL) was taken in a screw-capped vial and stirred at 80 °C temperature until completion of the reaction. The reaction progress was tracked by Thin Layer Chromatography (TLC). After completion of the reaction, the reaction mixture was filtered to remove the catalyst, and the mixture was diluted with ethyl acetate (20 mL) and acidified with 1N HCl to pH = 4. The resulting organic layer was separated, and the extraction procedure was repeated two times with ethyl acetate (3 × 20 mL). The organic layers were washed with brine solution two times, dried over anhydrous $MgSO_4$, and evaporated under vacuum. To obtain higher purification, the crude material was chromatographed on SiO_2 column chromatography.

4.1.3. General procedure for 6a-k
A mixture of amine compounds (1 mmol), triethyl orthoformate (1 mmol), sodium azide (1.3 mmol), MCM-41-SO_3H (50 mg), and DMF (2 mL) was taken in a screw-capped vial and stirred at 80°C temperature until completion of the reaction. The reaction progress was tracked by Thin Layer Chromatography (TLC) (EtOAc/*n*-hexane, 1:3). After completion of the reaction, the reaction mixture was filtered to remove the catalyst, and the crude products were extracted with ethyl acetate (3 × 20 mL). The organic layers were washed with brine solution two times, dried over anhydrous $MgSO_4$, and evaporated under vacuum. To obtain higher purification, the crude material was chromatographed on SiO_2 column chromatography (hexane-EtOAc, 1:1).

4.2. Selected spectral data

5-(4-bromophenyl)-1*H*-tetrazole (5a)

Pale yellow crystals; m.p. 235-236°C (Lit. [32] 234-235°C); IR (KBr): ν = 3430, 3090, 3033, 2900, 2847, 1612, 1488, 1459, 1165, 1100, 1004, 829 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 ppm) δ: 7.52 (d, 2H, J = 8.42 Hz, Ar), 8.04 (d, 2H, J = 8.2 Hz, Ar).

5-(4-chlorophenyl)-1*H*-tetrazole (5b)

Colorless crystals; m.p. 258-260°C (Lit. [33] 261-263°C); IR (KBr): ν = 3410, 3071, 2992, 2936, 2809, 2725, 1621, 1492, 1461, 1431, 1387, 1350, 1164, 1102, 1057, 830 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 ppm) δ: 7.66 (d, 2H, J = 8.45 Hz, Ar), 8.01 (d, 2H, J = 8.45 Hz, Ar).

Table 5. Comparison of various catalysts in [3+2] cycloaddition reaction of nitriles with sodium azide.

Entry	Catalyst	Solvent	Temp. (°C)	Time (h/or min)	Yield (%)	Ref.
1	Silica sulfuric acid	DMF	Reflux	5 h	88	[20]
2	Chitosan derived magnetic ionic liquid	-	70	7 h	87	[23]
3	Mesoporous ZnS	DMF	120	36 h	96	[48]
4	Fe_3O_4@SiO_2/Salen Cu(II)	DMF	120	7 h	90	[17]
5	Zn Hydroxyapatite	DMF	120	12 h	78	[49]
6	CoY zeolite	DMF	29	14 h	90	[46]
7	Cuttlebone	DMSO	110	20 min	98	[50]
8	Imidazole-based zwitterionic-type molten salts	-	120	12 h	84	[51]
9	$CuFe_2O_4$	DMF	120	12 h	82	[45]
10	MCM-41-SO_3H	DMF	80	120 min	90	This Work

4-(1*H*-tetrazol-5-yl)benzonitrile (5c)

White solid; m.p. 195-197°C (Lit. [34] 195); IR (KBr): ν = 3148, 3090, 3015, 2923, 2859, 2760, 2609, 2229, 1590, 1558, 1488, 1438, 1283, 1155, 1021, 981, 950, 848, 754, 555 cm^{-1}; ^1H NMR (500 MHz; DMSO-d_6 ppm): δ: 8.20 (d, 2H, J = 8.60 Hz), 8.05 (d, 2H, J = 8.30 Hz).

5-(4-nitrophenyl)-1*H*-1,2,3,4-tetrazole (5d)

Yellow solid; m.p. 220-222°C (Lit. [35] 218-219); IR (KBr): ν = 3451, 3329, 3240, 3112, 3085, 2978, 2903, 2823, 2662, 1565, 1528, 1492, 1357, 1344, 1320, 1145, 1110, 992, 864, 855, 732, 711 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 ppm): δ: 8.34 (d, J = 8.6 Hz, 2H, Ph), 8.48 (d, J = 8.8 Hz, 2H, Ph).

5-phenyl-1*H*-tetrazole (5e)

Colorless crystals, m.p. 214-216°C (Lit. [36] 214-216°C); IR (KBr): ν = 3130, 3100, 2982, 2921, 2825, 2692, 2610, 2561, 2492, 1618, 1567, 1490, 1413, 1171, 1059 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6 ppm) δ: 7.62-7.77 (m, 3H, Ar), 8.04-8.29 (m, 2H, Ar).

5-(*p*-tolyl)-1*H*-tetrazole (5f)

Colorless crystals; m.p. 247-249°C (Lit. [53]. 251-252°C); IR (KBr): ν = 3048, 2976, 2968, 2977, 1601, 1488, 823 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 ppm): δ: 2.38 (s, 3H), 7.39 (d, J = 8.12 Hz, 2H, Ar), 7.93 (d, J = 8.12 Hz, 2H, Ar).

5-(o-tolyl)-1*H*-tetrazole (5g)

Colorless crystals; m.p. 153-155°C (Lit. [22] 149-151°C); IR (KBr): ν = 3330, 3112, 2899, 2773, 2615, 2501, 1728, 1631, 1492, 1162, 1043, 802, 741 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 ppm): δ: 7.73 (d, J= 7.74 Hz, 1H, Ar), 7.59 (t, J = 7.58 Hz, 1H, Ar), 7.45 (d, J = 7.77 Hz, 1H, Ar), 7.37 (t, J = 7.60 Hz, 1H, Ar).

5-(m-tolyl)-1*H*-tetrazole (5h)

Colorless crystals; m.p. 145-147°C (Lit. [37] 149-150°C); IR (KBr): ν = 3120, 3061, 2912, 2871, 2753, 2617, 2491, 1728, 1605, 1486, 1150, 1064, 1038, 802, 741 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 ppm): δ: 2.6 (s, 3H), 7.32-7.47 (m, 2H, Ar), 7.81 (d, J = 8.0 Hz, 1H, Ar), 7.85 (s, 1H, Ar).

5-(4-methoxyphenyl)-1*H*-tetrazole (5i)

White solid; m.p. 230-232°C (Lit. [38] 231-233). FT-IR (KBr): ν = 3430, 2938, 2751, 2659, 1620, 1510, 1449, 1411, 1301, 1270, 1184, 1035, 811, 752 cm^{-1}; ^1H NMR (500 MHz; DMSO-d_6 ppm): δ: 7.90 (d, 2H, J = 8.8 Hz), 7.10 (d, 2H, J = 8.8 Hz), 3.84 (s, 3H), 3.95 (brs, 1H, NH).

2-(1*H*-tetrazol-1-yl)aniline (5j)

Pale yellow solid; m.p. 135-137°C (Lit. [39] 135-137°C); IR (KBr): ν = 3421, 3369, 1631, 1562, 1495, 1459, 1317, 1258, 1154, 1076, 1028 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 ppm): δ: 7.80 (d, J = 7.19 Hz, 1H, Ph), 7.39 (t, J = 8.13 Hz, 1H, Ph), 6.92 (d, J = 8.44 Hz, 1H, Ar), 6.90 (t, J = 7.4 Hz, 1H, Ar).

4-(1*H*-tetrazol-5-yl)phenol (5k)

White solid; m.p. 208-210°C (Lit. [40] 210-211°C); IR (KBr): ν = 3249, 3106, 3070, 3022, 3000-2200, 1620, 1600, 1522, 1470, 1416, 1285, 834, 757, 515 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 ppm): δ: 6.98 (d, J = 8.4 Hz, 2H, Ph), 7.88 (d, J = 8.8 Hz, 2H, Ph), 10.15 (br s, 1H, OH).

5-benzyl-1*H*-tetrazole (5m)

White solid; m.p. 120-122°C (Lit. [33] 117-119°C); IR (KBr): ν = 3112, 3033, 2979, 2948, 2867, 2780, 2695, 2596, 1771, 1710, 1642, 1551, 1537, 1501, 1459, 1244, 1112, 1075, 773, 730, 691 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 ppm) δ: 4.28 (s, 2H, CH_2), 7.31 (s, 5H, Ph).

1-(4-boromophenyl)-1*H*-tetrazole (6a)

White solid; m.p. 170-172°C (Lit. [41] 168-170°C); ^1H NMR (500 MHz, $CDCl_3$ ppm) δ: 6.95-6.98 (d, 2H), 7.38-7.43 (d, 2H), 8.11 (s, 1H).

1-(4-Chlorophenyl)-1*H*-tetrazole (6b)

White solid; m.p. 151-153°C (Lit. [24] 157-158°C); ^1H NMR (500 MHz, $CDCl_3$ ppm) δ: 7.01-7.06 (d-2H), 7.30-7.34 (d-2H), 8.06 (s-1H).

1-phenyl-1*H*-tetrazole (6e)

Pale yellow solid; m.p. 66-67°C (Lit. [42] 65-66°C); ^1H NMR (500 MHz, $CDCl_3$ ppm) δ: (7.06-7.59 (m, 5H, Ar), 8.27 (s, 1H).

1-(4-methylphenyl)-1*H*-tetrazole (6f)

Pale yellow solid; m.p. 117-119°C (Lit. [43] 117-118°C); ^1H NMR (500 MHz, $CDCl_3$ ppm) δ: 3.72 (s, 3H), 6.90 (d, 2H, J = 8.95 Hz, Ar), 7.52 (d, 2H, J = 8.95 Hz, Ar), 8.19 (s, 1H).

1-(4-methylphenyl)-1*H*-tetrazole (6h)

Pale yellow solid; m.p. 98-100°C (Lit. [42] 94-95°C); ^1H

NMR (500 MHz, $CDCl_3$ ppm) δ: 2.28 (s, 3H), 6.89 (d, 2H, $J = 8.55$ Hz, Ar), 7.50 (d, 2H, $J = 8.50$ Hz, Ar), 8.20 (s, 1H).

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