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RESEARCH ARTICLE

Silica Supported MTSA Catalyst for the Synthesis of 5-Substituted-1*H*-tetrazole- A Green Chemistry Approach

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Abstract: We have developed simple, cost efficient and environmentally benign protocol for the synthesis of 5-substituted 1*H*-tetrazole via [2+3] cyclo addition reaction from organic nitrile and sodium azide in refluxing DMF by using heterogeneous catalyst as MTSA (Melamine tri sulphonic acid). The corresponding 5-substituted 1*H*-tetrazole were obtained in lower yield but when using silica supported MTSA the yield obtained 85% in 6 h. After completion of the reaction, the catalyst was recovered by filtration and reused with only a slight decrease of activity observed under the same reaction conditions. Various aliphatic and aromatic nitrile converted in corresponding 5-substituted 1*H*-tetrazole in excellent yield without any contamination.

Keywords: 5-Substituted-1*H*-tetrazole, Aryl nitriles, Sodium azide, MTSA, Silica, Supported, Catalysis

Introduction

Tetrazoles which represent a significant class of heterocycles have attracted considerable interest in recent years because of their wide utility. Tetrazoles are heterocyclic compounds having a five membered ring containing one carbon and four nitrogen atoms. Tetrazoles are used in coordination chemistry as ligands, in medicinal chemistry as stable surrogates for carboxylic acids and in materials applications, including explosives, rocket propellants and agriculture[1-9]. An advantage of tetrazolic acids over carboxylic acids is that they are resistant to many biological metabolic degradation pathways[3]. The preparations of substituted tetrazoles have been the subject of intense investigation especially from the nitrile functionality, which is widely recognized as a useful intermediate in organic synthesis. The most widely used method of preparation for 5-substituted 1*H*-tetrazoles is [2+3] cycloaddition of azide anion to organic nitriles and many methods are reported in the literature.

Numbers of new catalysts have also been investigated till date and among those which serve the purpose are copper sulphate[10], amine salt[11], Sb_2O_3 [12], $B(C_6H_5)_3$[13], $CdCl_2$[14] ceric ammonium nitrate[15], $Et_3n.HCl$[16], $CuFe_2O_3$[17], $FeCl_3.SiO_2$[18], ferric hydrogen sulphate[19], reusable clay[20], metal

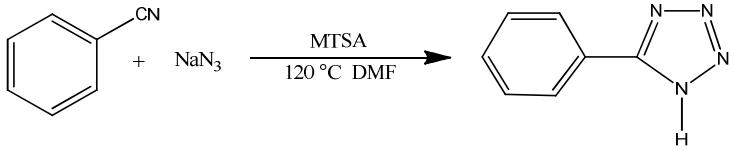
modified clay catalyst[21], tungstate[22], nano TiO_2[23], silica supported lanthanum tri phalate[24], silver nano particle[25], ZnS[26], Nano ZnS/Co_3O_4[27], natural and reusable natrolite zeolite[28] by using NaN_3 Or $TMSN_3$ The most convenient method to prepared 5-substituted-1*H*-tetrazoles is via [2+3] cycloaddition reaction by using azide to and corresponding of nitriles. These all the catalysts drawback is one of that harsh reaction condition, long reactions times, use of toxic and corrosive reagents, difficulty to separation and recovery the catalyst, expensive and explosive along with volatile.

Thus, we developed new an advance technique in the context of synthetic methodology towards mentioned class of biologically important molecules using silica supported melamine trisulphonic acid (SMTSA) to prepared 5-substituted-1*H*-tetrazole. This method is convenient simple work, cheap and not toxic reaction, use of SMTSA as a mild Lewis acid catalyst, ease of separation and reusability of the catalyst in comparison to homogenous systems and good generality and efficiency towards a wide of range of substrates.

In an effort to develop an innovative and efficient heterogeneous catalytic system for [2+3] cycloaddition between benzonitrile and sodium azide to yield 5-phenyl-1*H*-tetrazole, we have examined various parameters such as efficiency of the catalyst and its reusability, effective catalyst loading, solvent and temperature effect.

Results and Discussion

In the present work on the application of silica supported MTSA in the organic reactions, we decided to carry out the reaction of benzonitrile and sodium azide catalyzed by silica supported MTSA as a recyclable catalyst.



Scheme 1. Synthesis of 5-phenyl 1*H*-tetrazole by using MTSA

Table 1. Results of reactions of MTSA with different portions of benzonitrile and sodium azide

No.	Benzonitrile/ NaN_3	Mol % of MTSA	Temp./time, h	Solvent	Yield, %[b]
1	1:1	5	120/8	DMF	2
2	1:2	5	RT/4	few drop DMF	0.2
3	1:2	5	120/8	DMF	10
4	1:2	10	120/5	DMF	16
5	1:2	15	120/5	DMF	18
7	1:3	5	120/24	DMF	25
8	1:3	5	RT	without solvent	Nil
9	1:3	5	RT/24	DMF	3
10	1:3	5	120/24	DMSO	24
11	1:3	10	120/6	DMSO	28
12	1:3	10	120/5	DMF	31
13	1:3	15	120/5	DMF	36
14	1:3	20	120/5	DMF	43
15	1:3	30	120/5	DMF	24

b:isolated yield

Initially, the reaction was carried out by using only melamine trisulphonic acid (MTSA) with different portions of benzonitrile, sodium azide and various solvent at decided temperature. The result is summarized in Table 1. The reaction was monitored by TLC showed no significant outcome found of the reaction carried out. The synthesis of 5-phenyl-1*H*- tetrazole using MTSA using varied amount of benzonitrile/ NaN_3 in the ratio of1:1 to 1:3 and mol% of MTSA ranging from 5% to 30% were applied. When using up to 1:3 ratio of benzonitrile: NaN_3 with polar solvent of DMF and 5 to 15 mol% of MTSA, no significant yield was obtained. (Table 1, entries 1 to 8). Then we increased the proportion of MTSA applying similar condition the yield 43% was achieved where benzonitrile/ NaN_3 used in 1:3 proportion using 20 mol% of MTSA at 120 ℃ and DMF as a solvent (Table1, entry 14). Further it was observed that increase in the mol% of the catalyst maintaining similar condition showed decrease in the yield.

Thus, by not getting considerable amount of yield in case of only using MTSA as a catalyst, we tried to modify this reaction in which we made silica supported melamine trisulphonic acid (SMTSA). This was used to carry out synthesis of 5-substituted-1*H*-tetrazole via [2+3] cycloaddition between various aromatic nitriles and sodium azide. The effect of solvent, reaction temperature and time on the reaction was systematically investigated and the results are summarized in Table 2. The optimized reaction conditions in presence of MTSA-SiO_2 for the reaction were found to be under solvent-free condition for 12 h at the temperature of 120 ^oC. Thus, MTSA-SiO_2 was used as a catalyst in the present work. In order to elucidate the role of MTSA-SiO_2 as catalyst, a controlled reaction was conducted using benzonitrile and sodium azide by using DMF.

Table 2. The effect of solvent, reaction temperature and time on the reaction synthesis[a]

Entry	Solvent	Mol ratio of SiO_2-MTSA, %	Mol ratio of benzonitrile: NaN_3	Temp/time	Yield, %[b]
1	Neat	25	1:2	120/24	1
2	DMSO	25	1:2	120/10	50
3	DMF	25	1:2	120/7	57
4	Ethanol	25	1:2	60/24	45
5	1,4-Dioxane	50	1:3	100/24	40
6	DCM	50	1:3	80/24	42
7	THF	50	1:3	120/9	60
8	**DMF**	**50**	**1:3**	**120/6**	**85**
9	Water	50	1:3	100/48	Nil
10	DMF	50	1:3	r.t/48	Nil
11	Ethanol	50	1:3	60/24	48
12	DMSO	50	1:3	120/8	75
13	Neat	50	1:3	120/24	3

[a]*Cycloaddition reaction of benzonitrile and sodium azide with different catalysts in DMF as a reaction medium.* [b]*Isolated yields*

In order to find the optimum reaction conditions for the [2+3] cycloaddition between sodium azide and various aromatic nitriles, preliminary efforts were mainly focused on the evaluation of different solvents. The model reaction was carried out between in the presence of MTSA-SiO_2 catalyst under different solvents and at different temperatures and results are shown in Table 2.

The results revealed that, DMF was found to be a superior one in terms of reaction time and the product yield among the solvents screened (Table 2, entry 8). An attempt was also made to catalyze the reaction in the absence of solvent but outcome was not promising (Table 2, entry 1). Polar solvents like ethanol produced 45% and 48% yields even after 24 h by using different mol proportion of benzonitrile, sodium azide and MTSA -SiO_2 (Table 2, entries 4 and 11). DMSO was also used as a solvent at various mol ratios but the yield was found to be lower than using DMF. (Table 2, entries 2 and 12). When using 1,4 dioxane produced only 40% (Table 2, entry 5). This cycloaddition did not progress well while using chloro solvents such as chloroform or dichloromethane as medium (Table 2, entry 6). When, THF was employed as the reaction medium, the cycloaddition product was obtained in 60% yield in 9 h (Table 2, entry 7). Cycloaddition reaction also carried out at room temperature by using DMF as solvent and same amount of catalyst but there was no product obtained (Table 2, entry 10). The reaction was also tried in water, but the yield of the desired product was very low (Table 2, entry 9). As far the study carried out denoted that 50% mol ratio of catalyst with 1:3 benzonitrile: NaN_3 used in [2+3] cycloaddition reaction was found to be essential.

Table 3. Effect of different weight of catalyst[a]

No.	Catalyst weight, g	Yield, %[b]
1	0.02	8
2	0.04	15
3	0.06	20
4	0.08	46
5	0.1	54
6	0.12	55
7	0.14	58
8	0.16	60
9	0.18	77
10	**0.20**	**85**
11	0.22	75
12	0.24	66

[a]Reaction of benzonitrile (1 mmol) with sodium azide (3 mmol) at 120 °C [b]Isolated yield

Amount of silica supported MTSA also played a vital role in this cycloaddition reaction. When benzonitrile was treated with sodium azide using 0.02 to 0.1 g SMTSA in DMF, the 5-phenyl-1*H*-tetrazole was isolated by increasing yield (Table 3, entries 1-5). The catalyst amount was 0.12, the product was obtained 55% (Table 3, entry 6). The yield was improved to 60% when the reaction was carried out in the presence of 0.16 g of SMTSA (Table 3, entry 8). In an attempt to improve the conversion and yield, the reaction was repeated using 0.20 g of SMTSA as a catalyst. Pleasantly, this resulted in complete conversion of benzonitrile into 5-phenyl-1*H*-tetrazole within 6 h in excellent yield. Further improvement of yields was not observed on increasing the loading of the catalyst (Table 3, entry 10). Hence 0.20 g of catalyst was considered as an optimum catalyst concentration. Among the various solvents tested, DMF was found to be the best solvent giving maximum yields of the desired product. Whereas, while increasing the catalyst amount, the time required for the completion of the reaction was increased with lesser yield. The optimum amount of SiO_2 - MTSA was found to be 0.2 g in the presence of nitrile (1 mmol) and sodium azide (3 mmol) in DMF (6 mL) for the cycloaddition reaction under study.

We investigated the substrate scope and generality of the protocol by employing structurally divergent benzonitriles bearing activating and deactivating groups and few aromatic and heteroaromatic including aliphatic nitriles. The methodology worked well for most of the nitriles which gave excellent yields over and around 80% and all the reactions proceeded to completion within 6 hours.

Table 4. Silica supported MTSA catalyzed synthesis of 5-substituted tetrazoles

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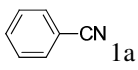
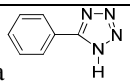
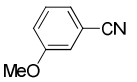
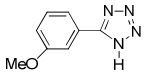
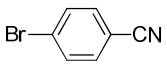
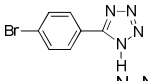
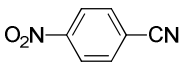
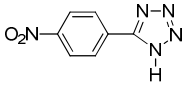
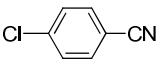
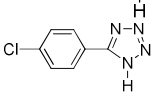
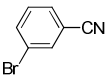
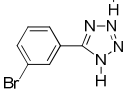
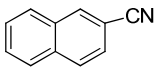
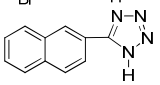
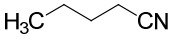
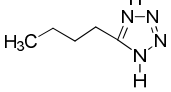
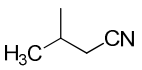
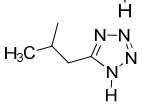
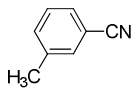
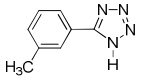
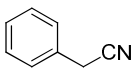
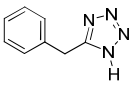
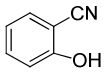
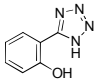
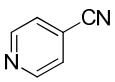
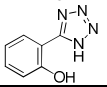
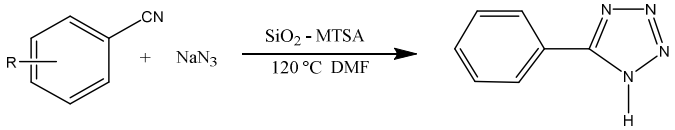
1	 1a	 2a	6	210-215	83
2			6	155-160	80
3			5	277-278	80
4			5	215-220	82
5			5	245-250	83
6			6	175-180	76
7			5	200-205	84
8			6	90-95	75
9			6	50-55	73
10			6	145-150	84
11			5	115-120	80
12			8	179-182	78
13			7	254-255	79

[a]*The reaction between various nitriles (1 equiv.) and sodium azide (3 equiv.) was performed in the presence of SiO_2-MTSA (0.2 g) in DMF (6 mL) at 120 ℃.* [b]*Isolated yield*

As shown in scheme 2 different benzonitriles reacted with sodium azide without any significant difference in the reaction time to give the corresponding 5-substituted tetrazole and their derivatives in good yield. The method has the ability to tolerate other functional groups such as methoxy, methyl and halides. Among the various nitriles tested, the aromatic

nitriles with electron withdrawing substituent gave excellent yields in a very short time to conversion of nitrile compounds relatively and the desire product was obtained in excellent yield (Table 4, entries 3-7). Moreover, electron donating groups at ortho or meta position of aromatic ring gave the corresponding tetrazoles in high yields, although longer reaction times were required (Table 4, entries 2, 10 and 12). Likewise, aliphatic nitriles react similarly and provide good yields of the corresponding tetrazoles (Table 4, entries 8 and 9). While it was particularly noticed that hydroxy substitution at ortho position had given comparatively lower yield and longer reaction time may be due to steric effect (Table 4, entry 12). Other aryl nitriles such as phenyl acetonitrile also reacted easily to furnish the corresponding tetrazoles in 80%, respectively (Table 4, entry 11). Heterocyclic nitriles *i.e.* nicotinonitrile was also used as a substrate and found to be extremely reactive, affording the relative tetrazole in 79% yield after 7 h. The activity of nitrile compound towards azide ion plays an important role in this cycloaddition reaction. In comparison the cycloaddition reaction of aromatic nitriles with electron withdrawing substituent such as -Cl, -Br, -CN and -NO_2 is faster than the reaction of aromatic nitrile compound with electron donating substituent such as -NH_2, -OCH_3, -CH_3, -OCH_2CH_3 and -OH. From Table 4, it is evident that, excellent to good results were obtained with alkyl, aryl, despite the different activities of the nitrile derivatives.



Scheme 2. Synthesis of 5-phenyl-1*H*-tetrazole (**1**) in the presence of SiO_2.MTSA

The prime importance of heterogeneous catalyst over the homogeneous counterpart is its simplicity of separation and reusability without loss of activity. The reusability of catalyst is important for the large-scale operation and industrial point of view. Therefore, the recovery and reusability of SiO_2-MTSA was examined (Figure 1). In consequence with this, we successfully achieved the recovery of catalyst from reaction mixture by simple filtration and the solid residue obtained was subjected to centrifugal washing with ethanol (2x15 mL) by drying in an oven at 100 °C for 3-4 hours. This assisted in keeping the catalyst surface active. It is noteworthy, that the recycled catalyst retained optimum activity until 4th cycle after which a drop-in yield was observed.

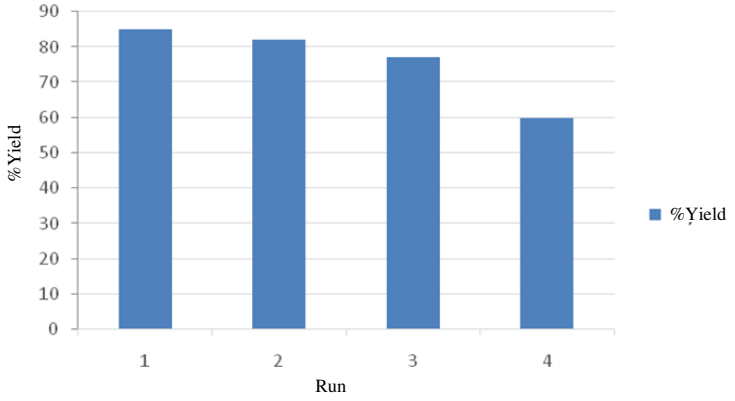


Figure 1. Reusability of SiO_2-MTSA

(Conditions:Benzonitriles (1 equiv.) and sodium azide (3 equiv.) was performed in the presence of SiO_2-MTSA (0.2 g) in DMF (6 mL) at 120 ℃

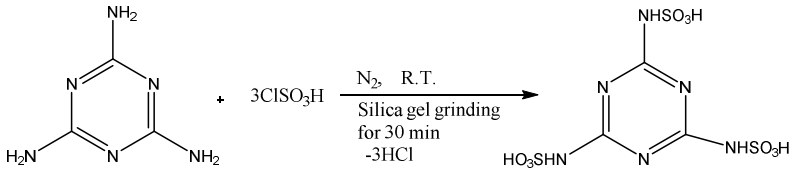
Reusability of SiO_2-MTSA

General procedure of 5-substituted-1H-tetrazole

Briefly, SMTSA (0.2 g) was added to the reaction mixture of the solution of benzonitrile (1 mmol) in DMF (6 mL) and sodium azide (3 mmol) with stirring for 6 h at 120 °C. The reaction was monitored by TLC (*n*-hexane:ethanol-9:1) and after completion of the reaction, the catalyst was removed by filtration and the filtrate was treated with ethyl acetate (20 mL) and 4 N HCl (20 mL) and stirred vigorously. The resultant organic layer was separated and the aqueous layer was extracted with ethyl acetate (10 mL). The combined organic layer was washed with water (8 mL) and concentrated it to give yield the crude white crystalline solid 5-phenyl tetrazole in 80-82% yield. The crude tetrazole was then recrystallized by mixture of solvents (50% ethyl acetate in hexane) and subsequently characterized by ^{1}H NMR, ^{13}C NMR, IR.

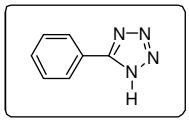
Preparation of silica supported melamine trisulphonic acid (SMTSA catalyst)[29]

A 250 mL suction flask charged with chlorosulfonic acid (10.5 g, ca. 6 mL, 90 mmol) in CH_2Cl_2 (10 mL) was equipped with a gas inlet tube for conducting HCl gas over an adsorbing solution *i.e*. water. Melamine (3.78 g, 30 mmol) was added in small portions over a period of 30 min. at room temperature under N_2(g). HCl gas evolved from the reaction vessel immediately. After completion of the addition of melamine, the mixture was shaken for 30 min; meanwhile, the residual HCl was eliminated by suction. Then the mixture was washed with excess CH_2Cl_2 to remove the unreacted chloro sulphonic acid. Finally, a white solid powder was obtained (~10 g, 91%). Then 18.2 g silica gel was added to this white solid and stirred those for 30 min. Finally, dried and grayish solid material was obtained (28.1 g). General scheme for synthesis of silica melamine trisulfonic acid is given in Scheme 3.



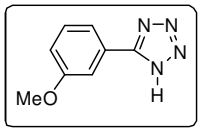
Scheme 3. Synthesis of silica melamine tri sulphonic acid

Physical, spectral and analytical data of compounds (Entry 1-13, Table 4)
5-Phenyl-1H tetrazole[30] ***(2a)***



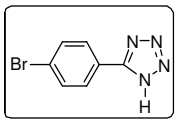
M.P. 210-215 ºC (Lit. 214-216 ºC); IR (KBr) νmax/cm^{-1}: 3130,3039, 2978, 2770, 2599, 2493, 1617, 1569, 1461, 1402, 1168, 1056, 730 ;^{1}H NMR (400 MHz, DMSO-d_6) d 7.61 , 8.05; ^{13}C NMR (100 MHz, DMSO-d_6) d 125.6, 126.4, 128.9, 130.7, 157.7; CHN ($C_7H_6N_4$) calc. (%): C (57.5), H (4.1), N (38.3); found (%): C (56.4), H (4.1), N (37.6).

5-(3-Methoxyphenyl)-1H-tetrazole[31] ***(2b)***



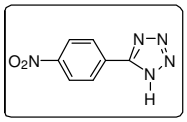
White solid, M.P. 155-160 °C (Lit.156-158°C). IR(KBr) νmax/cm^{-1}: 1490, 1564, 1711, 2843 ^{1}H NMR (500 Hz, DMSO-d_6):16.88 (brs, 1 H, N-H), 7.64–7.62 (m, 1 H, Ar-H),7.60–7.59 (m, 1 H, Ar-H), 7.53 (t, 1 H, J = 8.05 Hz,Ar-H), 7.17 (ddd, 1 H, J = 0.8, 2.55, 3.4 Hz, Ar-H), 3.86 (s, 3 H, CH_3-H) ppm ; CHN ($C_8H_8ON_4$) calc (%): ^{13}C NMR (125 Hz,DMSO-d_6): 159.7, 155.0, 130.6, 125.2, 119.1, 117.0, 112.0, 55.3 ppm.

5-(4-Bromophenyl)-1H-tetrazole[18] ***(2c)***



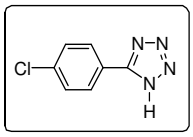
M.P. 277-279 ºC (Lit. 275-280 ºC); IR (KBr) νmax/cm^{-1}: 3090, 2903, 2849, 2730, 2630, 1654, 1484,1159, 1070, 1012, 745, 509; ^{1}H NMR (400 MHz, DMSO-d^6) d 7.80 (d, 2H, Ph), 7.95 (d, 2H, Ph);

5-(4-Nitrophenyl)-1H-tetrazole[18] ***(2d)***



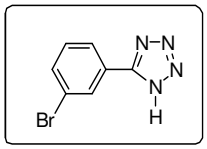
M.P. 215-220 ºC (Lit. 219-220 ºC); IR (KBr) νmax/cm^{-1}: 3450, 3100, 3095, 2978, 2903, 2819, 2676, 1568, 1100, 999, 730; ^{1}H NMR (400 MHz, DMSO-d$_6$) d 8.33(d, 2H, Ph), 8.49 (d, 2H, Ph)

5-(4-Chlorophenyl)-1H-tetrazole[18] ***(2e)***



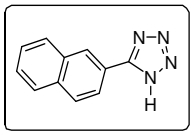
M.P. 261-262 ºC (Lit. 261-263 ºC); IR (KBr) νmax/cm^{-1}: 3092, 3060, 3007, 2978, 2907, 2851, 2725, 2622, 1609, 1564, 1486, 1160, 1096, 1053, 1020, 990, 833, 745, 508; ^{1}H NMR (400 MHz, DMSO-d$_6$) d 7.68 (d, 2H, J 8.4 Hz, Ph), 8.05 (d, 2H, J 8.8 Hz, Ph).

5-(3-Bromophenyl)-1H-tetrazole[18] ***(2f)***



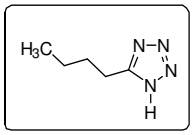
M.P. 153-154 ºC (Lit. 150-153 ºC); IR (KBr) νmax/cm^{-1}: 3450,3090, 2903, 2849, 2730, 2630, 1654, 1484, 1012, 745, 509; ^{1}H NMR (400 MHz, DMSO-d6) d 7.50 (d, 1H, Ph), 7.75 (d, 1H, Ph),8.02(dt, J=8.1Hz,1H)

5-(2-Naphthyl)-1H tetrazole[18] ***(2g)***



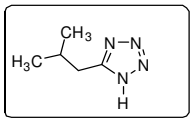
M.P. 200-205 °C (Lit 205-207) ; IR (KBr) νmax/cm^{-1} : 3421, 3053, 2812, 2721, 1626, 1599, 1518, 1491, 1383, 1352, 1257, 1121, 1102, 966, 864;^{1}H NMR (400 MHz, DMSO-d$_6$) δ (ppm): 8.67 (m, 1H), 8.12 (m, 2H), 8.06 (m, 1H), 7.99 (m, 1H), 7.61 (m, 2H).

5-(1-Pentyl)-1H tetrazole[31] ***(2h)***



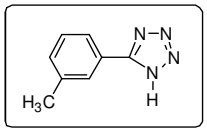
M.P. 90-95 °C (Lit 92-94); IR (KBr) νmax/cm^{-1}: 3414, 2854, 2204,1602, 1498, 1386, 1348, 837, 771; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ (ppm):3.71 (s, 2H), 7.84 (br s, 1H) d.1.00 (d, 6H, J 5 Hz, 2 CH$_3$),3.10 (t, 2H, J 6 Hz, -CH$_2$-).

5-Isobutyl-1H-tetrazole[31] ***(2i)***



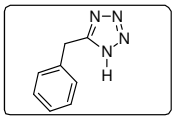
M.P. 50-55 ºC (Lit. 53.5-54 ºC); IR (KBr) νmax/cm^{-1}: 3089, 3063, 2971, 2901, 2845, 2765, 2729, 2633, 1605, 1482, 1454, 1430, 1156, 1075, 1053, 1017, 990, 829, 772,743, 502

5-(3-Methylphenyl)-1H-tetrazole[31] ***(2j)***



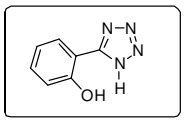
M.P. 145-150 ºC (Lit. 151-152 ºC); IR (KBr) νmax/cm^{-1}: 3120, 3061, 2979, 2917, 2871, 2746, 2611, 2490,1728, 1605, 1565, 1486, 1463, 1150, 1060, 1038, 802, 741, 705, 687; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ (ppm): 2.43 (s, 3H, CH$_3$), 7.40-7.90 (m, 4H, Ph).

5-Benzyl-1H-tetrazole[31] ***(2k)***



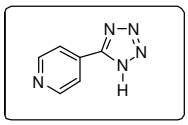
M.P. 115-120 ºC (Lit. 118-120 ºC); IR (KBr) νmax/cm^{-1}: 3109, 3031, 2984, 2945, 2863, 2778, 2704,2594, 1768, 1707, 1638, 1549, 1533, 1494, 1457, 1241, 1108, 1074, 772, 734, 695; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ (ppm):4.30 (s, 2H, -CH$_2$-), 7.31 (s, 5H, Ph).

5-(3-Hydroxyphenyl)-1H-tetrazole[15] ***(2l)***



M.P. 179-182 ºC (Lit. 178-180 ºC); IR (KBr) νmax/cm^{-1}: 3252, 3101, 3066, 3019, 3000-2200, 1615, 1599, 1511, 1466, 1413, 1282, 832, 752, 514; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ (ppm):6.97 (d, 2H, J 8.4 Hz, Ph), 7.87 (d, 2H, J 8.8 Hz, Ph), 10.20 (br s, OH).

4-(1H-Tetrazol-5-yl)pyridine[31] ***(2m)***



M.P. 254-255 ºC (Lit. 255-258 ºC); IR (KBr) νmax/cm^{-1}: 3485, 3264, 3099, 3035, 2966, 1624, 1529, 1435, 1388, 1123, 1096, 1042, 1022, 845, 730, 674, 593, 465.

Conclusion

SMTSA was successfully prepared and developed a mild, convenient and efficient protocol for the synthesis 5-substituted-1*H*-tetrazoles from nitriles and amines using silica supported melamine trisulphonic acid catalyst (SMTSA) efficient and recyclable catalyst. This method gives notable advantages such as easy separation of the catalyst excellent yields, short reaction times, non-toxic metal catalyst and simplicity of operation make this method a facile tool for the synthesis of tetrazoles.

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