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Green Chemistry

Cite this: *Green Chem.*, 2011, **13**, 3499

www.rsc.org/greenchem

PAPER

Green synthesis of the 1-substituted 1*H*-1,2,3,4-tetrazoles by application of the Natrolite zeolite as a new and reusable heterogeneous catalyst†

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Received 6th March 2011, Accepted 4th October 2011
DOI: 10.1039/c1gc15245a

An efficient method for the preparation of 1-substituted 1*H*-1,2,3,4-tetrazoles is reported using Natrolite zeolite as a natural and heterogeneous catalyst under solvent-free conditions. This method has the advantages of high yields, simple methodology and easy work-up. The catalyst can be recovered by simple filtration and reused in good yields.

Introduction

Tetrazoles have received considerable attention because of their wide range of applications in pharmaceuticals, information recording systems, photography and explosives and rocket propellants.[1,2] They are important ligands for many useful transformations and also precursors for a variety of nitrogen-containing heterocycles.[3,4]

Among tetrazoles, 1-substituted tetrazoles have received much attention because of their wide utility.[1b,1e] However, the lack of convenient methods for the preparation of 1-substituted tetrazoles strongly restricts their potential application in medical practice. Although many 5-substituted tetrazoles are known, only very few 1-substituted tetrazoles have been described.[5,6]

The acid-catalyzed cycloaddition between isocyanides and hydrazoic acid or trimethyl azide has long been one of the main routes for the synthesis of 1-substituted tetrazoles, which often include a number of steps and are insufficiently effective.[7,8] One of the most promising methods of synthesis for 1-substituted tetrazoles involves the reaction of amines with ethyl orthoformate or orthocarboxylic acid ester and sodium azide in the presence of acetic acid, trifluoroacetic acid or PCl_5, ionic liquid and DMSO and ytterbium triflate in highly polar solvents.[9]

Earlier reported methods for the synthesis of tetrazoles suffer from drawbacks, such as the use of expensive and toxic reagents, application of high boiling solvents, low yields, long reaction times, harsh reaction conditions, difficulty in obtaining and/or preparing the starting materials, tedious work-up, and the presence of hydrazoic acid, which is highly toxic, explosive and volatile.[10]

A substitute for hydrazoic acid is a mixture of sodium azide and ammonium chloride in DMF as a solvent.[2d] Combining azides and acids may yield gaseous HN_3, which is toxic and flammable. Also, the reaction mixture in DMF must be heated to 150 °C for several hours to several days. An additional disadvantage of DMF is its solubility in both organic solvents and water, thus removing DMF from tetrazole is difficult. From the standpoint of 'green chemistry', significant efforts have been made to find an alternative to organic solvents, such as solvent-free conditions, which are industrially important due to reduced pollution, low cost, and simplicity in processing and handling.[11]

The first principle of green chemistry states that it is better to prevent waste production than to treat waste or clean it up after it has been created.[11g] In our methods, tetrazoles were prepared by application of stoichiometric amounts of sodium azide (2.0 mmol) and amine (2.0 mmol) under solvent-free conditions. So, after completion of the reaction, there is no sodium azide residue in the reaction mixture, which can form a heavy-metal azide or potentially explosive hydrazoic acid and its toxic vapours. Sodium azide is not explosive except when heated near its decomposition temperature (300 °C) or reacted with metals. Compared to the reported methods, our method is convenient, fast, safe and is easy to work-up.

In recent years there has been a tremendous interests in various chemical transformations performed under the heterogeneous catalysis.[12] Moreover, application of the inorganic solid acids, especially zeolites, has received considerable attention due to their unique physical and chemical properties, such as shape, selectivity, acidic and basic nature and thermal stability.[13a] Natrolite zeolite, $Na_2[Al_2Si_3O_{10}]\cdot 2H_2O$, is one of the fibrous zeolites with the framework constructed from chains of corner-sharing Al and Si oxygen tetrahedra.[13b]

In continuation of our work on the synthesis of tetrazoles and the application of heterogeneous reagents,[5,14] we hereby report a new protocol for the preparation of 1-substituted tetrazoles from a wide variety of primary amines with sodium azide and triethyl orthoformate under solvent-free conditions

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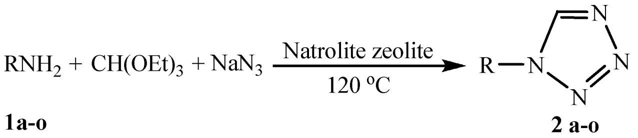
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1gc15245a



Scheme 1

using Natrolite zeolite[14a,15a,b] as a reusable and natural catalyst (Scheme 1).

Results and Discussion

The reaction of aniline and triethyl orthoformate with sodium azide in the presence of Natrolite zeolite were carried out in various temperatures and catalyst amounts under solvent-free conditions to optimize the reaction conditions (Fig. 1). In the absence of catalyst at 120 °C, no reaction was carried out, even after 6 h. The optimum amount of Natrolite zeolite was found to be 0.02 g in the presence of amine (2.0 mmol), sodium azide (2.0 mmol) and orthoformate (2.4 mmol) in 4 h. Increasing the amount of Natrolite zeolite to more than 0.02 g showed no substantial improvement in the yield, while decreasing the catalyst reduced the yield to 0.015, 0.01 and 0.007 g.

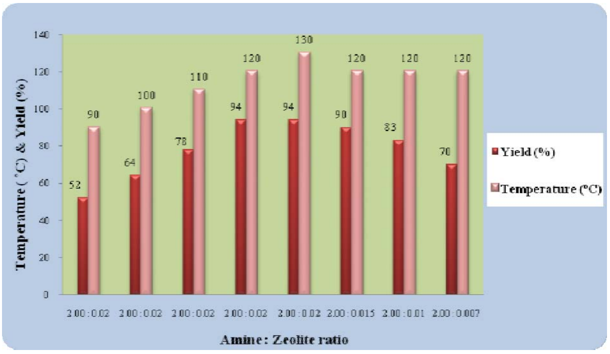


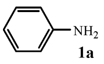
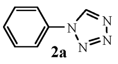
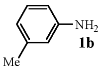
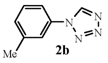
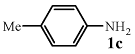
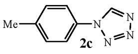
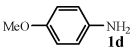
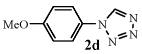
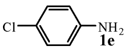
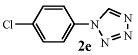
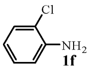
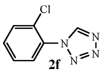
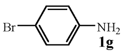
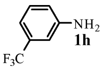
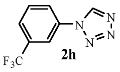
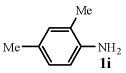
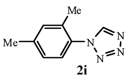
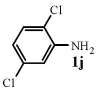
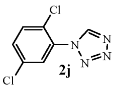
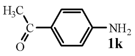
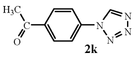
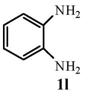
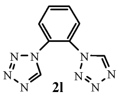
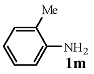
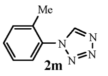
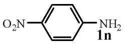
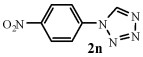
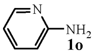
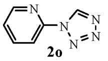
Fig. 1 Optimization of the amount of Natrolite zeolite and temperature.

A variety of amines possessing both electron-releasing and electron-withdrawing groups were employed (Table 1). According to the table, the nature of the substituent on the benzene ring did not affect the reaction time and the yields were excellent. Due to the presence of the two NH_2 groups, **1l** interestingly afforded the double-addition product (Table 1, entry 12).

The suggested Natrolite zeolite catalyzed transformation mechanism is shown in Scheme 2, in which the Lewis acidity of the catalyst probably has an important role in the promotion of the cyclization process. The breakdown of triethyl orthoformate in the presence of the catalyst facilitates the elimination of ethanol, as well as the formation of the imidoylazide intermediate,[5,17,18,19] which will produce the final 1-substituted 1*H*-1,2,3,4-tetrazole upon cyclization.

The second principle of green chemistry states that the synthetic systems should be focused to improve the atom economy or atom efficiency by the employment of equimolar amounts of starting materials.[11g] Atom economy (AE) is a useful concept for estimating the environmental impacts of starting materials in a reaction to reach a desired product.[20]

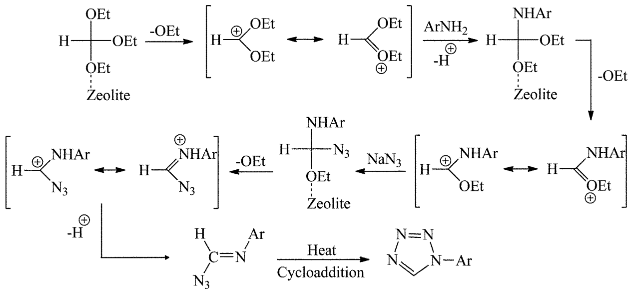
Table 1 Formation of 1-substituted tetrazoles **2a–o** *via* primary amines **1a–o**

Entry	Substrate	Product	Yield[a] (%)	Ref.
1	 **1a**	 **2a**	94, 91[b]	7*b*,9*c*,16,17
2	 **1b**	 **2b**	89	9*c*
3	 **1c**	 **2c**	83	9*c*,16,17
4	 **1d**	 **2d**	82	7*b*,16
5	 **1e**	 **2e**	93	9*c*,16
6	 **1f**	 **2f**	80	9*c*,17
7	 **1g**	 **2g**	82	This work
8	 **1h**	 **2h**	81	This work
9	 **1i**	 **2i**	85	This work
10	 **1j**	 **2j**	83	This work
11	 **1k**	 **2k**	85	16
12	 **1l**	 **2l**	86	This work
13	 **1m**	 **2m**	85	This work
14	 **1n**	 **2n**	86	7*b*
15	 **1o**	 **2o**	81	9*c*,16

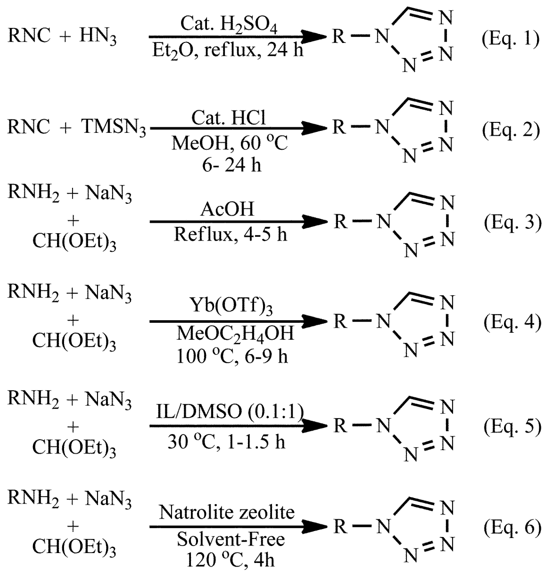
[a] Yields are after work-up. [b] Yield after the fifth cycle.

A number of synthetic methods have been reported in recent years for the preparation of 1-substituted tetrazoles (Scheme 3, equations 1–5). From the view point of atom economy, the present methodology (Scheme 3, equation 6) compared with those reported in the literature (Scheme 3 and Table 2).

Disadvantages of equation (1):[8] Application of large excess amounts of hydrazoic acid (highly toxic, explosive and volatile), low yield, long reaction times (24 h), harsh reaction conditions



Scheme 2



Scheme 3

and use of sulfuric acid, which is toxic, extremely corrosive, and cannot be easily recovered and recycled.

Disadvantages of equation (2):[7b] *In situ* formation of hydrazoic acid (highly toxic, explosive and volatile), use of hydrochloric acid (toxic, corrosive and homogeneous reagent that cannot easily be recovered and reused) and application of organic solvents. Trimethylsilyl azide is a highly flammable substance and incompatible with the presence of moisture, strong oxidizing agents and strong acids. It is toxic by inhalation, in contact with eye, skin and if swallowed or when it is exposed to water. Also, isocyanides are toxic and very reactive with any materials containing active hydrogens, such as water, alcohol, amines, bases and acids. Therefore, working with these materials is very hard. In addition, a by-product of this reaction is trimethylsilane (Me_3SiH), which is a toxic and flammable substance and may cause flash fire and target organ damage.

Disadvantages of equation (3):[9e] *In situ* formation of hydrazoic acid (highly toxic, explosive and volatile), application of large excess amounts of glacial acetic acid, which is homogeneous and cannot easily be recovered and reused.

Disadvantage of equation (4):[9c] Application of a volatile organic solvent ($CH_3OC_2H_4OH$).

Disadvantage of equation (5):[9d] Application of a high boiling point organic solvent (DMSO) leading to complicated isolation and recovery procedures.

Table 2 The Atomic Economy comparison of the present methodology with other methods for the synthesis of 1-substituted tetrazoles

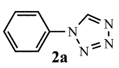
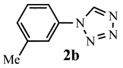
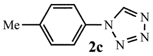
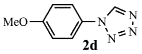
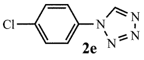
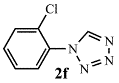
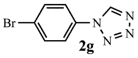
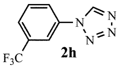
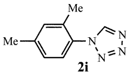
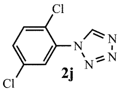
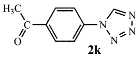
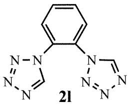
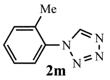
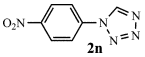
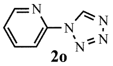
Entry	Equation	Desired product	Yield[a] (%)	AE (%)
1	1	 2a	16	100
	2		67	58.39
	4		85	47.71
	5		86	47.71
	6		94	47.71
2	1	 2b	34	100
	4		89	49.99
	5		89	49.99
	6		89	49.99
3	1	 2c	88	100
	4		91	49.99
	5		88	49.99
	6		83	49.99
4	1	 2d	35	100
	2		92	62.91
	5		85	52.37
	6		82	52.37
5	1	 2e	32	100
	4		88	52.99
	5		88	52.99
	6		93	52.99
6	1	 2f	41	100
	4		82	52.99
	6		80	52.99
7	6	 2g	82	58.42
8	6	 2h	81	57.21
9	6	 2i	85	52.09
10	6	 2j	83	57.31
11	6	 2k	85	54.02
12	6	 2l	86	66.66
13	6	 2m	85	49.99

Table 2 (*Contd.*)

Entry	Equation	Desired product	Yield[a] (%)	AE (%)
14	2	 2n	77	64.71
	6		86	54.41
15	6	 2o	81	47.88

[a] Yields are after work-up.

Advantages of equation (6): None of the above mentioned disadvantages are observed. Also, the application of Natrolite zeolite as a natural, benign, inexpensive and non-corrosive heterogeneous catalyst represents an interesting synthetic route with relatively high atom economy. The only by-product of this reaction is ethanol, which is a green solvent.

All known compounds were characterized by comparing their physical and spectral data with those reported in the literature. The structures of the 1-substituted tetrazoles were in agreement with their IR and NMR spectra. In the IR spectra of the 1-substituted tetrazoles, the NH_2 peaks were disappeared and one strong absorptions band was detected (C=N stretching band, ~1640–1690 cm^{-1}). The 1-substituted tetrazoles are generally acidic substances and the relevant proton signal will be shifted to downfield (see Fig. 1 and ^1H NMR data), so the peak at δ = 7.80–8.30 ppm can be attributed to the proton of the tetrazole ring. The carbon of the tetrazole ring can be seen at about δ = 141–157.2 ppm in the ^{13}C NMR.[5,6,9,14a,14e,16]

Catalyst reuse and stability

The catalyst recycling is an important step as it reduces the cost of the process. The reusability of the Natrolite zeolite catalyst was checked in the reaction of different anilines with sodium azide and orthoformate under the reaction conditions (Table 1, entry 1). In a typical experiment, after completion of the reaction, Natrolite zeolite was isolated by simple filtration, washed with water (10 mL) and ethanol (5 mL) three times, dried and successively used 5 times without any significant loss of activity (yields: ~91–94%). The XRD patterns before and after the reaction revealed that the zeolite retained its crystallinity throughout.

Conclusion

In conclusion, we have developed an efficient procedure for the preparation of 1-substituted tetrazoles using Natrolite zeolite as a natural and reusable heterogeneous catalyst. This method has the advantages of high yields, simple methodology and easy work-up in which the chromatographic separation is not necessary to get the pure compounds.

Experimental

All reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. Products were characterized by comparison of their physical and spectral data with authentic samples. The NMR spectra were recorded in DMSO and acetone. ^1H NMR spectra were recorded on a Bruker Avance DRX 90 and 300 MHz instruments. The chemical shifts (δ) are reported in ppm relative to the TMS as an internal standard and J values are given in Hz. ^{13}C NMR spectra were recorded at 24.5 and 75 Hz. FT-IR (KBr) spectra were recorded on a Perkin-Elmer 781 spectrophotometer. Melting points were taken in open capillary tubes with a BUCHI 510 melting point apparatus and were uncorrected. The elemental analysis was performed using Heraeus CHN-*O*-Rapid analyzer. TLC was performed on silica gel polygram SIL G/UV 254 plates. Natural Iranian Natrolite zeolite was obtained from the Hormak area (city of Zahedan, province of Sistan & Baluchestan, Iran).[14a]

Catalyst characterization

The natural Natrolite zeolite was characterized by using powder XRD, SEM and FT-IR spectroscopy. Also, X-ray powder diffraction was applied for its phase purity in which the pattern is completely matched with that of the Natrolite zeolite.[15a] The actual phases for this catalyst were silicon oxide cristabolite-SiO_2 (cubic) and aluminum silicate zeolite. The composition of the natural zeolite is $Na_2[Al_2Si_3O_{10}]\cdot 2H_2O$.[15a] The SiO_2/Al_2O_3 ratio of the material is 1.77 corresponding to a Natrolite zeolite.[15c]

In the relevant FT-IR spectra (Electronic Supporting Information†), peaks 950–1200 cm^{-1} are probably related to the Si–O–Si and Si–O–Al vibrations, peaks 3619, 3440 and 1640 cm^{-1} to the presence of zeolitic water and peaks 500–800 cm^{-1} to the pseudo-lattice vibrations.[14a,15a] Above 1500 cm^{-1}, the familiar bending HOH will appear at 1640 cm^{-1}, while their asymmetric and symmetric stretching appear at 3440, and 3619 cm^{-1}, respectively.

The SEM pictures for this new type of zeolite are given in Fig. 2. The surface of the natural zeolite specimens is highly heterogeneous due to the coexistence of different zeolite phases together with other crystalline and amorphous materials. Crystals of various shapes and sizes, together with amorphous masses, incorporate into the friable grains. Their size is in the range 1–50 μm.

The chemical composition of silica and alumina was established by a wavelength dispersive XRF spectrophotometer (Electronic Supporting Information). Based on the XRF technique, the mineral content of the zeolitic material from quarry face was Natrolite 99.63% (w/w).[15b]

CAUTION

Although sodium azide is a valuable substance in organic synthesis, it is nonetheless a toxic, reactive and energetic material and appropriate safety precautions should be taken (for more information see the Electronic Supporting Information†).

Typical procedure for preparation of 1-substituted 1*H*-1,2,3,4-tetrazoles

Natrolite zeolite (0.02 g) was added to a mixture of amine (2.0 mmol), NaN_3 (2.0 mmol), triethyl orthoformate (2.4 mmol) and stirred at 120 °C for 4 h. After completion (as monitored by TLC), the reaction mixture was diluted with cold water (5 mL)

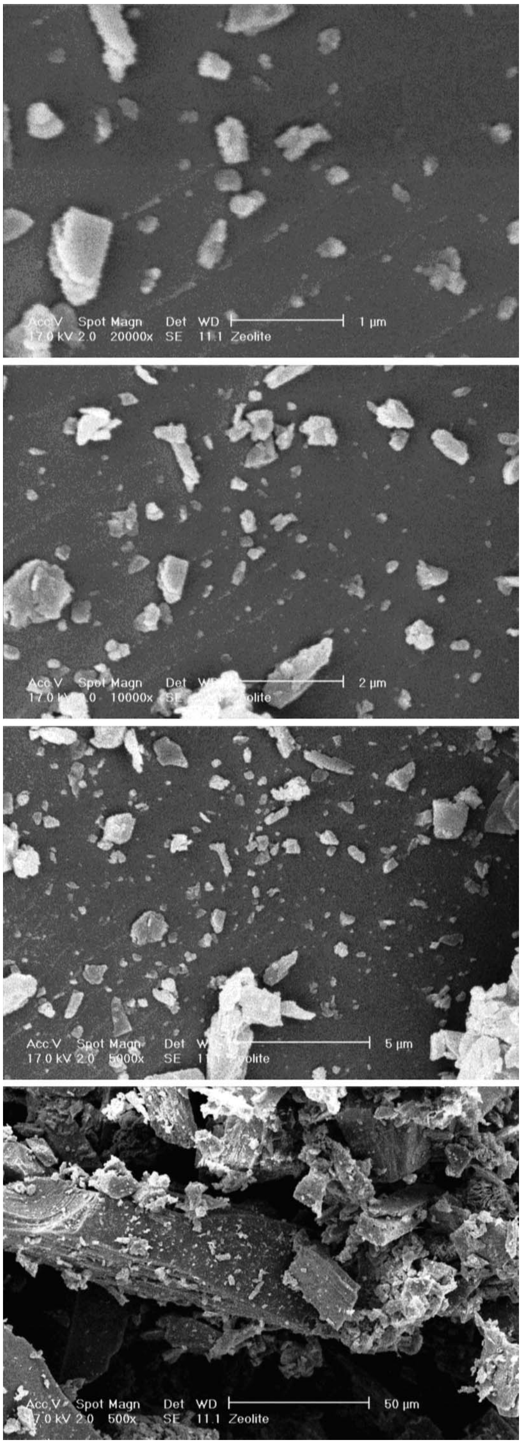


Fig. 2 Scanning electron microscopy analysis (SEM) of the Natrolite zeolite.

and extracted with ethyl acetate (3 × 10 mL). The catalyst was separated by filtration and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After concentration, a crystallizaton step was performed using EtOAc–hexane to afford the pure product. The physical data (mp, IR, NMR) of known compounds were found to be identical with those reported in the literature.[7b,9c,16]

The elemental analysis (CHN), IR, ^{1}H NMR and ^{13}C NMR data of the unknown 1-substituted tetrazoles (Table 1, entries 7–10 and 12–14) and ^{1}H NMR data of the known compounds (Table 1, entries 1–6, 11 and 15) are given below:

1-Phenyl-1*H*-1,2,3,4-tetrazole (2a, Table 1, entry 1). M.p. 65–66 °C (lit.[9c] 64–65 °C); ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.39–6.99 (m, 4H), 8.21 (s, 1H).

1-(3-Methylphenyl)-1*H*-1,2,3,4-tetrazole (2b, Table 1, entry 2). M.p. 53–55 °C (lit.[9c] 53–54 °C); ^{1}H NMR (90 MHz, $CDCl_3$): δ = 2.30 (s, 1H), 6.82–7.19 (m, 4H), 8.19 (s, 1H).

1-(4-Methylphenyl)-1*H*-1,2,3,4-tetrazole (2c, Table 1, entry 3). M.p. 94–95 °C (lit.[9c] 93–94 °C); ^{1}H NMR (90 MHz, $CDCl_3$): δ = 2.30 (s, 1H), 6.92–7.27 (m, 4H), 8.16 (s, 1H).

1-(4-Chlorophenyl)-1*H*-1,2,3,4-tetrazole (2e, Table 1, entry 5). M.p. 156–158 °C (lit.[9c] 157–158 °C); ^{1}H NMR (90 MHz, $CDCl_3$): δ = 6.96 (d, J = 6.8 Hz, 2H), 7.28 (d, J = 6.7 Hz, 2H), 8.09 (s, 1H).

1-(2-Chlorophenyl)-1*H*-1,2,3,4-tetrazole (2f, Table 1, entry 6). ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.10–7.44 (m, 4H), 8.07 (s, 1H).

1-(4-Bromophenyl)-1*H*-1,2,3,4-tetrazole (2g, Table 1, entry 7). M.p. 183–185 °C; FT-IR (Nujol) v 3527, 3151, 3045, 2855, 1660, 1589, 1575, 1483, 1402, 1312, 1291, 1224, 1205, 1173, 1101, 1073, 1003, 983, 827 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 6.90 (d, J = 8.7 Hz, 2H), 7.40 (d, J = 7.7 Hz, 2H), 8.07 (s, 1H); ^{13}C NMR (22.5 MHz, DMSO-d_6): δ = 152.4, 135.6, 128.2, 124.8, 117.6; Anal. calcd for $C_7H_5N_4Br$: C, 37.36; H, 2.24; N, 24.90. Found: C, 37.42; H, 2.26; N, 24.79.

1-(3-Trifluoromethylphenyl)-1*H*-1,2,3,4-tetrazole (2h, Table 1, entry 8). M.p. 125–127 °C; FT-IR (KBr): v 3275, 3220, 3140, 3005, 2981, 2940, 2840, 1620, 1585 cm^{-1}; ^{1}H NMR (90 MHz, DMSO-d_6): δ = 7.60–7.20 (m, 4H), 8.19 (s, 1H); ^{13}C NMR (22.5 MHz, DMSO-d_6): δ = 148.8, 145.1, 132.5, 131.0, 129.8, 121.9, 120.1, 115.7; Anal. calcd for $C_8H_5F_3N_4$: C, 44.87; H, 2.35; N, 26.16. Found: C, 44.80; H, 2.46; N, 26.33.

1-(2,4-Dimethylphenyl)-1*H*-1,2,3,4-tetrazole (2i, Table 1, entry 9). M.p. 133–135 °C; FT-IR (Nujol): v 2917, 1655, 1606, 1496, 1301, 1204, 1119, 811 cm^{-1}; ^{1}H NMR (90 MHz, DMSO-d_6): δ = 6.94–7.87 (d, J = 5.9 Hz, 2H), 7.80 (s, 1H), 8.69 (s, 1H); ^{13}C NMR (22.5 MHz, DMSO-d_6): δ = 147.7, 131.3, 130.7, 128.7, 126.7, 122.8, 118.8, 20.2, 17.8; Anal. calcd for $C_9H_{10}N_4$: C, 68.56; H, 4.79; N, 26.65. Found: C, 68.61; H, 4.70; N, 26.60.

1-(2,5-Dichlorophenyl)-1*H*-1,2,3,4-tetrazole (2j, Table 1, entry 10). M.p. 99–105 °C; FT-IR (Nujol): v 3387, 2854, 1649, 1575, 1523, 1466, 1416, 1377, 1295, 1094, 1045, 802 cm^{-1}; ^{1}H NMR (90 MHz, DMSO-d_6): δ = 6.89–7.05 (m, 1H), 7.24–7.54 (m, 1H), 7.62 (s, 1H), 8.03 (s, 1H); ^{13}C NMR (22.5 MHz, DMSO-d_6): δ = 157.1, 149.3, 132.1, 130.3, 124.6, 123.5, 120.3; Anal. calcd for $C_7H_4Cl_2N_4$: C, 39.09; H, 1.87; N, 26.06. Found: C, 39.13; H, 1.85; N, 26.13.

1-(4-Acethylphenyl)-1*H*-1,2,3,4-tetrazole (2k, Table 1, entry 11). ^{1}H NMR (90 MHz, $CDCl_3$): δ = 2.59 (s, 3H), 7.09–8.00 (m, 4H), 8.29 (s, 1H).

1,1′-(1,2-Phenylene)bis(1*H*-1,2,3,4-tetrazole) (2l, Table 1, entry 12). M.p. 167–169 °C; FT-IR (Nujol): ν 3108, 3003, 2940, 1618, 1587, 1476, 1457, 1408, 1364, 1299, 1271, 1245, 1201, 1133, 1002, 956, 886, 767, 744, 634, 626 cm^{-1}; ^{1}H NMR (90 MHz, DMSO-d$_6$): $\delta = 7.12$– 7.69 (m, 4H), 8.30 (s, 2H); ^{13}C NMR (22.5 MHz, DMSO-d$_6$): $\delta = 141.9$, 138.1, 121.7, 115.3; Anal. calcd for $C_8H_6N_8$: C, 44.85; H, 2.82; N, 52.32. Found: C, 44.65; H, 2.71; N, 53.25.

1-(2-Methylphenyl)-1*H*-1,2,3,4-tetrazole (2m, Table 1, entry 13). M.p. 150–153 °C; FT-IR (Nujol): ν 3010, 2869, 1666, 1592, 1569, 1488, 1467, 375, 1304, 1221, 1186, 1112, 1049, 997, 934, 834, 782, 752, 722 cm^{-1}; ^{1}H NMR (90 MHz, DMSO-d$_6$): $\delta = 3.38$ (s, 3H), 6.88–7.17 (m, 4H), 7.86 (s, 1H); ^{13}C NMR (22.5 MHz, DMSO-d$_6$): $\delta = 147.8$, 144.6, 130.0, 128.8, 126.5, 122.6, 118.9, 17.8; Anal. calcd for $C_8H_8N_4$: C, 59.99; H, 5.03; N, 34.98. Found: C, 60.05; H, 4.95; N, 34.92.

1-(4-Nitrophenyl)-1*H*-1,2,3,4-tetrazole (2n, Table 1, entry 14). ^{1}H NMR (90 MHz, acetone-d$_6$): $\delta = 7.57$ (d, $J = 8.7$ Hz, 2H), 8.23 (d, $J = 8.8$ Hz, 2H), 8.52 (s, 1H).

1-(2-pyridine)-1*H*-1,2,3,4-tetrazole (2o, Table 1, entry 15). M.p. 128–130 °C (lit.[9c] 129–130 °C); ^{1}H NMR (90 MHz, CDCl$_3$): $\delta = 6.86$–8.52 (m, 4H), 9.29 (s, 1H).

Acknowledgements

We gratefully acknowledge the financial support from the Bu-Ali Sina University, Hamedan, 6517838683 Iran.

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