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ORIGINAL PAPER

Rapid, green, and catalyst-free one-pot three-component syntheses of 5-substituted 1*H*-tetrazoles in magnetized water

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Abstract The catalyst-free multi-component reactions of aldehydes, malononitrile, and sodium azide at a relatively low temperature in magnetized water provided 5-substituted 1*H*-tetrazoles in high-to-excellent yields. This method offers the advantages of short reaction times, low costs, quantitative reaction yields, simple work-up, green, and no need for any organic solvent.

Keywords Magnetized water · Catalyst-free · Green method · 5-Substituted 1*H*-tetrazoles

Introduction

Attention to tetrazole chemistry has increased in the recent years, chiefly as a consequence of the role played by this heterocyclic functionality in medicinal chemistry as a metabolically-stable alternative for carboxylic acid functionalities [1]. Further significant applications of tetrazoles can be found in materials science, coordination chemistry, and as intermediates in a range of synthetic transformations [2–4]. Various methods have been developed for the synthesis of 5-substituted 1*H*-tetrazoles. A known procedure for the synthesis of 5-substituted 1*H*-tetrazoles involves treatment of primary amines with *ortho*- carboxylic acid ester/sodium azide and employment of metallic triflates or imidazolium ionic liquids [5–7]. However, a lot of these protocols have some drawbacks like the use of toxic metals, strong Lewis acids, and expensive reagents, low product yield, drastic reaction conditions, and presence of hydrazoic acid that is toxic and explosive. Moreover, all of the known methods use organic solvents, specifically the dipolar aprotic ones like DMF [8]. Therefore, the development of a suitable and safe process for the synthesis of new tetrazole derivatives is an appealing goal for investigation.

The design and exploration of novel catalyst-free methods for pharmacological agents in aqueous media is an ideal option and a major challenge for chemists to reduce the ecological problems and economic burdens [9]. In this context, domino multi-component reactions (MCRs), which can take place in aqueous media, have been considerably followed in the past few years because of their effective atom economy and green characteristics [10]. These reactions are efficient in preparing highly-functionalized small organic molecules from readily-available starting materials in one step with inherent flexibility for producing molecular diversity and complexity coupled with minimization of cost, time, labor, and waste production [11]. Moreover, these reactions frequently yield excellent regio- and chemo-selectivities [12].

Among the commonly-used solvents in organic synthesis, water is quite non-toxic, and it is the most economical, most abundant, safest, and most environmentally friendly medium. Sometimes water shows a higher reactivity and selectivity in comparison with the other conventional organic solvents because of its strong hydrogen-bonding ability [13]. These characteristics allow water to act as a solvent, a reactant or a catalyst, which is different from

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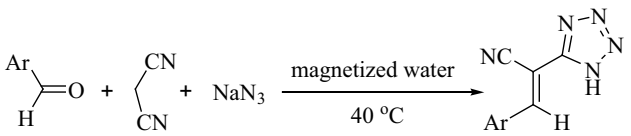
those spotted in the conventional organic solvents. Since the innovative studies carried out on the Diels–Alder reactions by Breslow [14], there has been a growing realization that organic reactions can go ahead well in aqueous media and suggest benefits over those taking place in organic solvents [15]. However, most chemical reactions could not be performed in water, as a solvent, since they need the presence of reagents, catalysts or energy.

From the 1950s, we have known that water can be magnetized when exposed to a magnetic field, although the effect is very small [16–18]. Based on the literature surveys carried out on magnetized water during the last few years, most researchers have been interested in studying the magnetic field effects on the properties of water [19, 20], especially the hydrogen bond distribution [21, 22]. On the other hand, various researchers have studied the effects of magnetized water on the morphology of precipitated calcium carbonate [23], TiO_2-based varistors [24], and synthesis of manganese oxide nano-crystals [25]. Recently, we have reported the synthesis of pyrano[2,3-c]pyrazoles and pyrano[4′,3′:5,6] pyrazolo[2,3-d]pyrimidines in magnetized water, as a green solvent [26]. Herein, we wish to report, for the first time, a catalyst-free, rapid, simple, and green synthetic method for the synthesis of 5-substituted 1*H*-tetrazoles via the one-pot multi-component reaction (MCR) of aldehydes, malononitrile, and sodium azide in magnetized water (Scheme 1).

Our extensive literature survey showed that there are only a few reports related to the synthesis of (*E*)-(1*H*-tetrazole-5-yl) acrylonitrile derivatives **4** using a three-component domino reaction of an aldehyde, malononitrile, and sodium azide [27–32]. Safaei-Ghomi et al. [31] have reported that this transformation can be completed in the presence of 6 mol% of NiO nanoparticles in DMF at 70 °C for 6 h. Although this method was quite useful, it had some limitations such as the use of catalyst and organic solvent, long reaction time, and harsh reaction conditions. Also, Dabiri et al. have describes the catalyst-free synthesis of 5-substituted 1*H*-tetrazoles **4** with 63–81% product yield in water at 50 °C for 24–31 h [32]. In this method, Dabiri et al. found that water was the best solvent with respect to the reaction yield, which could be ascribed to the existence of powerful hydrogen bond interactions at the organic phase-water interface, which stabilizes the reaction intermediate [33]. Therefore, according to the results obtained by Dabiri et al., we attempted to carry out the catalyst-free synthesis of 5-substituted 1*H*-tetrazoles **4** using magnetized water, as a solvent, which helped to lower the reaction time and increase the yield of the target product.



Scheme 1 Synthesis of 5-substituted 1*H*-tetrazoles in magnetized water

Magnetized water was prepared using a static magnetic system of 6000 G [26] field strength with a flow rate of 500 mL s^{-1} at different magnetic field time exposures (Fig. 1). Moreover, doubly distilled water, which was deionized by a Millipore Q-Plus 185 system, was used in the experiments.

Initially, we used the three-component reaction of benzaldehyde **1a**, malononitrile **2**, and sodium azide **3** as a model reaction to explore the suitable reaction conditions. As indicated in Table 1 (entries 1–3), the magnetization time plays a critical role in obtaining a high-yield product **4a**. The best product yield **4a** was found in water magnetized in 5 min and for a reaction time of 15 min at 40 °C (Table 1, entry 2). Dabiri et al. reported that this transformation could be completed in water at 50 °C for 24 h [28]. During the optimization process, the reaction temperature was varied between 25 and 60 °C, with 40 °C giving the optimal reaction enhancement. Moreover, to demonstrate the efficiency and practicability of this method in the synthesis of these types of molecules, the model reaction was carried out in a scale of 50 mmol. As expected, the desired product could be obtained with 96% yield in 15 min (Table 1, entry 6). We performed the model reaction using with 2 equivalent of sodium azide. Increasing of amount of sodium azide did not improve the product yield (Table 1, entry 7). Also the above three-component reaction was carried out in doubly distilled water to establish the real efficacy of magnetized water. As shown in Table 1, only a low product yield was obtained even after the reaction time was prolonged to 2 h (Table 1, entry 8).

A number of researchers have reported that when the applied magnetic field is removed from the magnetized water, its magnetization effect does not disappear immediately, and can be maintained for a relatively long period of

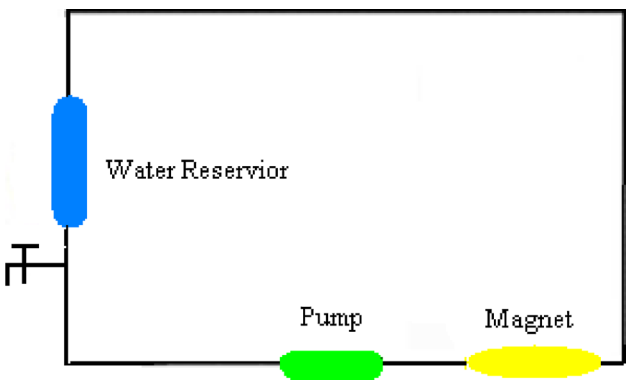


Fig. 1 Pilot for solvent magnetizing apparatus

Table 1 Synthesis of (*E*)-3-phenyl-2-(1*H*-tetrazole-5-yl) acrylonitrile **4a** under various conditions

Entry	Solvent	Magnetization time (min)	Temp. (°C)	Reaction time (min)	Yield (%)[a]
1	Magnetized water	2	40	60	80
2	Magnetized water	5	40	15	97
3	Magnetized water	10	40	15	97
4	Magnetized water	5	60	15	97
5	Magnetized water	5	25	120	60
6	Magnetized water	5	40	15	96[b]
7	Magnetized water	5	40	15	97[c]
8	Doubly distilled water	Non-magnetized	40	120	20

Reaction conditions: benzaldehyde (1.0 mmol), malononitrile (1.0 mmol), sodium azide (1.0 mmol), solvent (4 mL)

[a] Isolated yield

[b] 50 mmol scale

[c] 2 mmol of NaN_3

Table 2 Synthesis of (*E*)-3-phenyl-2-(1*H*-tetrazole-5-yl) acrylonitrile **4a** at different times after water magnetization

Entry	Time after completion of magnetic exposure (h)	Yield (%)[a]
1	0 (freshly-magnetized water)	97
2	2	97
3	4	95
4	6	85
5	8	70
6	10	50

Reaction conditions: aldehyde (1.0 mmol), malononitrile (1.0 mmol), sodium azide (1.0 mmol), magnetized water (4 mL), magnetization time (5 min), reaction time (15 min), 40 °C

[a] Isolated yield

time. This phenomenon is referred to as the "memory effect" of magnetized water, i.e. how long water magnetization effect remains after completion of the magnetic exposure [34]. Therefore, we examined the memory effect of magnetized water. The model reaction was performed in magnetized water at different times after completion of the magnetic exposure. After a magnetic exposure of 5 min, magnetized water was left standing for different time periods. It was found that magnetized water kept its magnetization property for up to 4 h, and a reaction performed in water magnetized for some time was as acceptable as that carried out in a freshly-magnetized water with a high reaction yield (Table 2).

Following our study to synthesize 5-substituted 1*H*-tetrazoles via a multi-component Knoevenagel condensation/1,3-dipolar cycloaddition reaction, the best conditions (Table 1, entry 2) were applied to various aromatic aldehydes and hetero-aromatics to give the related (*E*)-(1*H*-tetrazol-5-yl)acrylonitriles **4** in high-to-excellent yields and stereo-selectivity (Table 3). The details of the stereo-chemical structure determination have been described earlier by Dabiri and coworkers [32]. As shown in Table 3, aromatic aldehydes having electron-withdrawing groups reacted at faster rates compared with those having electron-releasing groups. Since no acid or metal-containing catalysts were used, our system allowed the use of acid-labile substrates. For example, 4-*N,N*-dimethyl amino benzaldehyde, which tends to poison acids or metal-containing species by means of acid–base interaction or coordination, can be converted to the desired product in high yields without damage to the tertiary amine group (Table 3, entry 5). Furthermore, furfural, which is known as an acid-sensitive species, was also proved to be applicable in magnetized water (Table 3, entry 13), indicating the usefulness of our methodology.

Notably, at the beginning of the reactions, a solution that seemed to be transparent was observed because aldehydes, malononitrile, and sodium azide were soluble in magnetized water. The latter formed a product, which was found to be insoluble in magnetized water. At the end of the reaction, a large amount of a solid product was formed. This made stirring of the reaction mixture difficult.

As mentioned earlier, applying a magnetic field to water causes several changes in it, one of which is a change in the hydrogen bond distribution in magnetized water compared with that for normal water. The characteristic properties of water are chiefly due to its 3D hydrogen bonding network. An external magnetic field can weaken or even partly break the inter-molecular hydrogen bonds in water, and thus increase the number of monomer water molecules, which may result in some biological effects [35–38]. Yin et al. have shown that weakening of the hydrogen bonds and the Van der Waals forces between water molecules in magnetized water contribute to the amount of its evaporation [39]. Nakagawa et al. have examined the effect of magnetic

Table 3 Synthesis of 5-substituted 1*H*-tetrazoles **4**

Entry	Ar	Product	Time (min)	Yield (%)	M.p. (°C) Lit. [ref.]
1	Ph	**4a**	15	97	167–168 (168–170) [32]
2	4-OH–C_6H_4	**4b**	15	95	159–161 (159–161) [32]
3	4-Me–C_6H_4	**4c**	15	90	158–159
4	4-MeO–C_6H_4	**4d**	20	93	150–151 (153–155) [31]
5	4-Me_2N–C_6H_4	**4e**	20	95	171–172
6	3,5-$(OMe)_2$–4-OH–C_6H_2	**4f**	20	90	157–158
7	2,3,4-$(OMe)_3$–C_6H_2	**4g**	20	93	95–96
8	4-Br–C_6H_4	**4h**	10	97	160–161 (165–167) [32]
9	2,4-$Cl_2C_6H_3$	**4i**	10	91	142–143
10	2-NO_2–C_6H_4	**4j**	10	93	132–133
11	3-NO_2–C_6H_4	**4k**	10	97	97–98
12	4-NO_2–C_6H_4	**4l**	10	98	163–164 (166–168) [32]
13	2′-Furanyl	**4m**	20	92	253–254
14	2′-thiophenyl	**4n**	20	94	85–86
15	2′-Pyridinyl	**4o**	25	90	185–186

Reaction conditions: Aldehyde (1.0 mmol), malononitrile (1.0 mmol), sodium azide (1.0 mmol), magnetization time (5 min), magnetized water (4 mL), at 40 °C

Isolated yield

field on water vaporization. They have found that the applied magnetic field enhances water vaporization into the air [40]. Moreover, Toledo et al. have proved the effect of an external magnetic field on the physical and chemical properties of water through an experimental procedure and a theoretical one. They have found that an external magnetic field influences the hydrogen bond networks. They have pointed out the existence of a competition between the intra- and intermolecular hydrogen bond networks in water, which weakens the stronger intra-cluster hydrogen bonds, breaks the larger clusters, and forms the smaller ones with the stronger inter-cluster hydrogen bonds [41]. Therefore, the number of hydrogen bonds between the magnetized water molecules and the reacting molecules increases. Thus we think that the hydrogen bonds between the molecules of magnetized water and the molecules of the substrates and intermediates involved in a reaction are responsible for the reaction activation.

A plausible mechanism for the synthesis of 5-substituted 1*H*-tetrazole **4a** from benzaldehyde **1a**, malononitrile **2**, and sodium azide **3**, is shown in Scheme 2. Magnetized water plays a major role in its promoting activity for the formation of intermediate (**I**), which is readily prepared in situ by the Knoevenagel condensation of benzaldehyde **1a** with the highly active CH acidic malononitrile **2**. Finally, the 1,3-dipolar cycloaddition reaction between the C≡N group of phenylidenemalononitrile and azide ion followed by tautomerization yielded 5-substituted 1*H*-tetrazole **4a**.

A comparative study of the reaction conditions for the synthesis of (*E*)-3-phenyl-2-(1*H*-tetrazole-5-yl) acrylonitrile **4a** using the methods given in Table 4 and reported in the present article demonstrate that the present protocol is indeed superior to several of the other protocols. As shown in Table 4, most of the listed methodologies suffer from some limitations such as use of catalysts, elevated temperatures and the prolonged reaction times.

Conclusion

A novel, efficient, catalyst-free, green, and convenient method was proposed for the one-pot three-component synthesis of 5-substituted 1*H*-tetrazoles in magnetized water. This method not only offers substantial improvements in the reaction rates and yields but also avoids the use of catalysts or solvents. In addition, the promising points for the presented methodology are its efficiency, generality, high yield, short reaction time, clean reaction profile, simple work-up procedure, and finally, agreement with the green chemistry protocols, making it a useful and attractive process for the synthesis of 5-substituted 1*H*-tetrazoles. This protocol employs magnetized water as an inherently-safe and a low-cost reaction medium in organic synthesis. Moreover, the presented method can be used in large-scale syntheses.

Experimental

Aldehydes, malononitrile, and sodium azide were purchased from Merck, Fluka or Aldrich. Melting points were determined using an electro-thermal C14500 apparatus. All the known compounds were identified by comparing their

Scheme 2 Plausible mechanism for synthesis of (*E*)-3-phenyl-2-(1*H*-tetrazole-5-yl) acrylonitrile **4a**

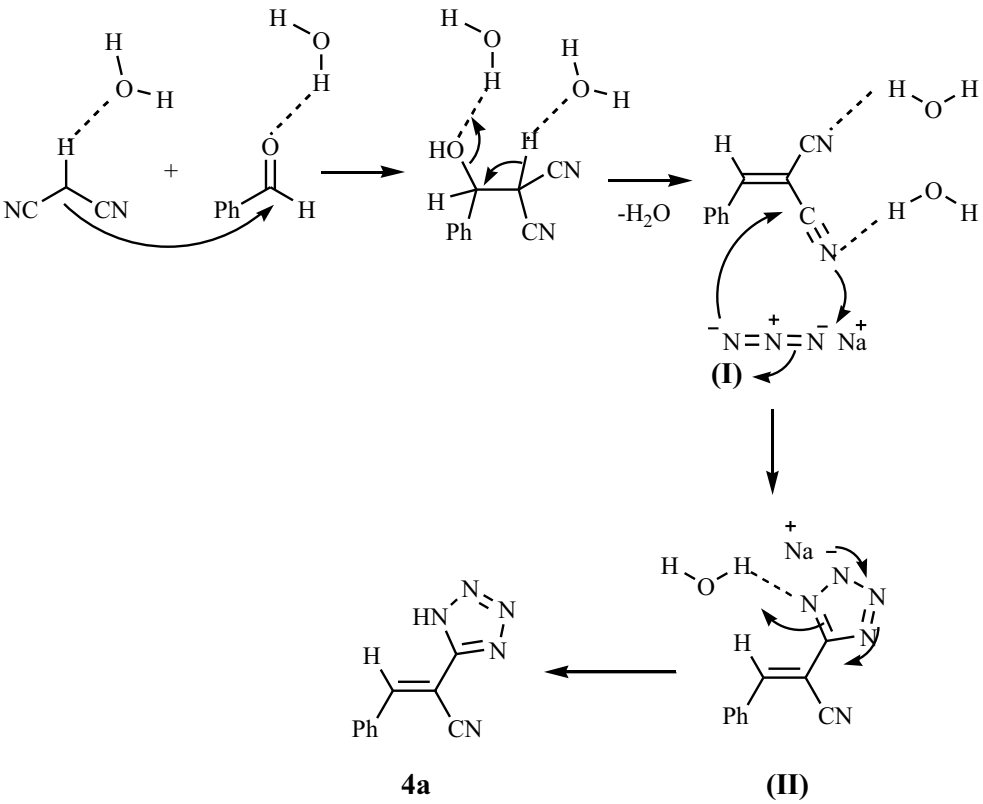


Table 4 Comparison of reaction conditions of magnetized water with the most recent reported catalyst for the synthesis of (*E*)-3-phenyl-2-(1*H*-tetrazole-5-yl) acrylonitrile **4a**

Entry	Catalyst	Solvent	Temp (°C)	Time	Yeild (%)	References
1	$[BMIM]N_3$	–	100	10 h	80	[1]
2	SMA/Microwaves	H_2O	50	15 min	93	[2]
3	ZrP_2O_7	DMF	70	6 h	91	[5]
4	Nano-NiO	DMF	70	6 h	90	[4]
5	Catalyst-free	H_2O	50	24 h	81	[3]
6	Catalyst-free	Magnetized water	40	15 min	97	Present work

melting points and ^{1}H NMR data with those in the authentic samples. ^{1}NMR spectra were recorded on a Bruker 300 (300 MHz ^{1}H, 75 MHz ^{13}C) spectrometer. ^{1}H NMR signals were reported relative to Me_4Si (δ 0.0) or residual $CHCl_3$ (δ 7.26). ^{13}C NMR signals were reported relative to $CDCl_3$ (δ 77.16). Multiplicities were described using the following abbreviations: s = singlet, d = doublet, t = triplet, and m = multiplet.

Preparation of magnetized water

A magnetic treatment apparatus was assembled as shown in Fig. 1. This apparatus is equipped with a powerful magnet 6000 G. A centrifugal pump was used to circulate water in the system. Water was treated in the system for 5 min, and then 100 mL of this magnetized water was used in the current work.

General procedure for synthesis of (*E*)-(1*H*-tetrazol-5-yl)acrylonitrile derivatives (4a–o)

To a 10-mL round-bottomed flask equipped with a magnetic stirrer bar and containing magnetized water (4 mL, with magnetization time of 5 min), were added an aldehyde (1.0 mmol), malononitrile (1.0 mmol, 0.067 g), and sodium azide (1.0 mmol, 0.065 g). The reaction mixture was stirred at 40 °C, and the reaction progress was monitored by TLC using chloroform as the eluent. After completion of the reaction, the precipitate formed was filtered and purified by recrystallization from ethanol to afford the desired product (Table 3).

(*E*)-3-(4-Methylphenyl)-2-(1*H*-tetrazole-5-yl) acrylonitrile (4c)

M.p., 158–159 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 3H,CH_3), 7.3 (d, J = 8.1 Hz, 2H, Ar), 7.70 (s, 1H, CH), 7.78 (d, J = 8.1 Hz, 2H, Ar–H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.0, 81.2, 112.8, 114.0, 128.4, 130.4, 130.9, 146.4, 159.7 ppm; Anal. Calcd. for $C_{11}H_9N_5$: C: 62.55; H: 4.29; N: 33.16; found: C: 62.68; H: 4.37; N: 33.29.

(*E*)-3-(4-*N*,*N*-dimethylaminophenyl)-2-(1*H*-tetrazole-5-yl) acrylonitrile (4e)

M.p., 171–172 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.12 (s, 6H, CH_3), 6.64 (d, J = 9.0 Hz, 2H, Ar), 7.39 (s, 1H, CH), 7.74 (d, J = 9.0 Hz, 2H, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.2, 71.6, 111.6, 115.0, 116.0, 119.2, 133.8, 154.2, 158.0 ppm; Anal. Calcd. for $C_{12}H_9N_6$: C: 59.99; H: 5.03; N: 34.98; found: C: 60.12; H: 5.13; N: 34.86.

(*E*)-3-(3,5-Dimethoxy-4-hydroxyphenyl)-2-(1*H*-tetrazole-5-yl) acrylonitrile (4f)

M.p., 157–158 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.91 (s, 6H,OCH_3), 6.42 (br, 1H, OH), 7.19 (s, 1H, Ar), 7.23 (s, 1H, Ar), 7.59 (s, 1H, CH) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.5, 78.4, 109.3, 113.6, 114.3, 122.7, 141.5, 147.3, 159.4 ppm; Anal. Calcd. for $C_{12}H_{11}N_5O_3$: C: 52.75; H: 4.06; N: 25.63; found: C: 52.62; H: 4.17; N: 25.80.

(*E*)-3-(2,3,4-Trimethoxyphenyl)-2-(1*H*-tetrazole-5-yl) acrylonitrile (4g)

M.p., 95–96 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.84 (s, 3H,OCH_3), 3.95 (s, 3H,OCH_3), 3.98 (s, 3H,OCH_3), 6.75 (d, J = 9.3 Hz, 1H, Ar), 8.06 (s, 1H, CH), 8.10 (d, J = 9.3 Hz, 1H, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.4, 61.0, 62.1, 78.7, 107.8, 113.5, 114.8, 118.2, 124.7, 141.7, 153.6, 154.5, 159.7 ppm; Anal. Calcd. for $C_{13}H_{13}N_5O_3$: C: 54.35; H: 4.56; N: 24.38; found: C: 54.50; H: 4.65; N: 24.51.

(*E*)-3-(2,4-Dichlorophenyl)-2-(1*H*-tetrazole-5-yl) acrylonitrile (4i)

M.p., 142–143 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 (dd, J = 9.3, 1.8 Hz, 1H, Ar), 7.55 (d, J = 1.8 Hz, 1H, Ar); 8.11 (d, J = 8.4 Hz, 1H, Ar); 8.16 (s, 1H, CH) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 86.0, 111.7, 113.0, 127.5, 128.3, 130.1, 130.7, 137.1, 141.0, 154.6 ppm; Anal. Calcd. for $C_{10}H_5Cl_2N_5$: C: 45.14; H: 1.89; N: 26.32; found: C: 45.32; H: 1.98; N: 26.15.

(*E*)-3-(2-Nitroyphenyl)-2-(1*H*-tetrazole-5-yl) acrylonitrile (4j)

M.p., 132–133 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76–7.89 (m, 3H, Ar), 8.31 (d, J = 7.8 Hz, 1H, Ar), 8.43 (s, 1H, CH) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 88.5, 111.0, 112.2, 125.8, 126.7, 130.5, 133.4, 135.0, 146.8, 158.9 ppm; Anal. Calcd. for $C_{10}H_6N_6O_2$: C: 49.59; H: 2.50; N: 34.70; found: C: 49.73; H: 2.60; N: 34.88.

(*E*)-3-(3-Nitroyphenyl)-2-(1*H*-tetrazole-5-yl) acrylonitrile (4k)

M.p., 97–98 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (t, J = 8.1 Hz, 1H, Ar), 7.89 (s, 1H, CH), 8.31 (s, 1H, CH), 8.45 (dd, J = 8.1, 1.2 Hz, 1H, Ar), 8.64 (s, 1H, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 86.7, 111.6, 112.7, 125.5, 128.2, 131.0, 132.0, 134.9, 148.6, 157.0 ppm; Anal. Calcd. for $C_{10}H_6N_6O_2$: C: 49.59; H: 2.50; N: 34.70; found: C: 49.77; H: 2.41; N: 34.85.

(*E*)-3-(2-Furanyl)-2-(1*H*-tetrazole-5-yl) acrylonitrile (4m)

M.p., 253–254 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.68–6.70 (m, 1H, furan), 7.32 (d, J = 3.9 Hz, 1H, furan), 7.49 (s, 1H, CH), 7.78 (d, J = 1.8, Hz, 1H, furan) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 112.6, 113.8, 114.4, 123.5, 130.9, 143.1, 148.1, 149.6 ppm; Anal. Calcd. for $C_8H_5N_5O$: C: 51.34; H: 2.69; N: 37.42; found: C: 51.20; H: 2.57; N: 37.58.

(*E*)-3-(2-Thiophenyl)-2-(1*H*-tetrazole-5-yl) acrylonitrile (4n)

Mp., 85–88 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25–7.27 (m, 1H, thiophen), 7.78 (d, J = 3.9 Hz, 1H, thiophen), 7.85 (s, 1H, CH), 7.87 (d, J = 5.1 Hz, 1H, thiophen) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 112.9, 113.8, 129.0, 135.4, 136.9, 138.1, 151.0 ppm; Anal. Calcd. for $C_8H_5N_5S$: C: 47.28; H: 2.48; N: 34.46; S: 15.78; found: C: 47.44; H: 2.60; N: 34.62; S: 15.94.

(*E*)-3-(2-Pyridinyl)-2-(1*H*-tetrazole-5-yl) acrylonitrile (4o)

M.p., 185–186 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (t, J = 6.9 Hz, 1H, pyridine), 8.21 (d, J = 7.8 Hz, 1H, pyridine), 8.59 (d, J = 7.2 Hz, 1H, pyridine), 8.72 (d, J = 4.5 Hz, 1H, pyridine) 9.39 (s, 1H, CH) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 114.1, 116.1 122.2, 124.9, 129.9, 133.5, 136.4,

154.8 ppm; Anal. Calcd. for $C_9H_6N_6$: C: 54.54; H: 3.05; N: 42.41; found: C: 54.70; H: 3.19; N: 42.28.

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