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A rapid metal free synthesis of 5-substituted-1*H*-tetrazoles using cuttlebone as a natural high effective and low cost heterogeneous catalyst†

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A convenient, rapid and metal free synthesis of 5-substituted-1*H*-tetrazoles is described by [3 + 2] cycloaddition reaction of nitriles with sodium azide. The reaction was catalyzed by cuttlebone in DMSO at 110 °C. Cycloaddition reaction of nitriles with sodium azide happened in the presence of mesoporous cuttlebone by "electrophilic activation" of nitriles through hydrogen bond formation between the cuttlebone and nitrile. Cuttlebone as a natural low cost heterogeneous catalyst with high porosity, high flexural stiffness, high compressive strength and high thermal stability affords 5-substituted-1*H*-tetrazoles rapidly with high efficiency.

Introduction

Tetrazoles have been known for over a hundred years. They are an important and useful class of heterocycles with a wide range of applications in medicinal chemistry,[1–8] coordination chemistry[9] and material science.[10] Tetrazoles as precursors of different nitrogen containing heterocycles (triazoles, oxazolidones and thiazoles)[9a,11] have been studied as lipophilic spacers,[12] ion and peptide chelating agents,[13] *cis*-peptide bond mimics[14] and catalysts in asymmetric synthesis.[15] Because of their usefulness, research on the catalytic preparation of tetrazoles has attracted great attention. The first method involves the [3 + 2] cycloaddition of an azide with a nitrile which was reported by Hantzsch and Vagt in 1901.[16] So far, most of the reported methods contain the cycloaddition of nitrile with an azide moiety, under the influence of several efficient catalysts. For a long time proton acid-catalyzed cycloaddition was the main routes to 5-substituted-1*H*-tetrazoles which was suffered from explosion of large amounts of harmful hydrazoic acid.[17–27] Some of different homogenous and heterogeneous catalyst systems were also applied in 5-substituted-1*H*-tetrazoles synthesis *via* cycloaddition of nitrile with azide. Numbers of these new catalysts are $Pd(OAc)_2/ZnBr_2$,[28] ZnO,[29] $ZnBr_2$,[30] $ZnCl_2$/tungstates,[31] Zn/Al hydrotalcite,[32] $Zn(OTf)_2$,[33] Zn hydroxyapatite,[34] ZnS,[35] Cu_2O,[36] nano ZnO/Co_3O_4,[37] $FeCl_3$–SiO_2,[38] $Fe(OAc)_2$,[39] $Fe(HSO_4)_3$,[40] nano $CuFe_2O_4$,[41] $CdCl_2$,[42] $BF_3 \cdot OEt_2$,[43] $InCl_3$,[44] I_2,[45] $(CH_3)_2SnO$,[46] TBAFza,[47] $AgNO_3$,[48] copper triflates,[49] β-cyclodextrin,[50] COY zeolites,[51] $Pd(PPh_3)_4$,[52] AgNPs,[53] WAlPO-5 microspheres,[54] Fe_3O_4@SiO_2/salen of Cu(II),[55] $CuFe_2O_4$ nano particles,[41] $B(C_6F_5)_3$,[56] $AlCl_3$,[57] Zn–Cu alloy,[58] CAES,[59] $CuSO_4 \cdot 5H_2O$,[60] $In(OTf)_3$.[61] But, in this ways, there are problems including the use of expensive and toxic metals, high-cost reagents, long reaction times (several hours to days) in combination with high reaction temperatures, strong Lewis acids, low yield, harsh reaction conditions, boring work-ups and difficulty in separation and recovery of the catalyst.

Today, as employing the metal catalysts are not always eco-friendly and because of this, serious environmental pollution often results,[62] and also because of the strict environmental legislation, there is a huge demand for metal-free, green and safe synthetic methods that not only reduce the use of toxic and corrosive reagents and stop the formation of inorganic wastes but also leading to high yield of the desired product.[63] In continuation of our studies and to promote the methods of tetrazoles preparation,[59,60] herein we report an efficient rapid metal free synthesis of 5-substituted-1*H*-tetrazoles in the presence of mesoporous cuttlebone as a new green heterogeneous catalyst with super catalytic activity.

Results and discussion

Cuttlebone signifies a special class of ultra-light weight, high stiffness and high permeability cellular biomaterials, which was provided from cuttlefish with an efficient means of maintaining neutral buoyancy at considerable habitation depths.[64,65] Cuttlebone as a natural material possessing the multifunctional properties with high porosity, high flexural stiffness, high compressive strength and high thermal stability functions as a rigid buoyant tank in animal. Cuttlebone with an inorganic–organic composite framework composed of aragonite, protein and β-chitin.[66,67] Following our interest in the synthesis of 5-substituted-1*H*-tetrazoles, we speculated on the possibility of

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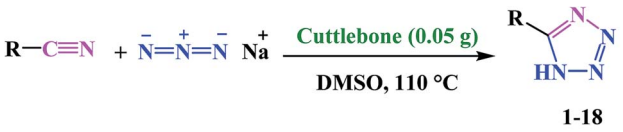


R = Ph, 4-BrC_6H_4, 4-ClC_6H_4, 4-CNC_6H_4, 4-$NO_2C_6H_4$, 2-NH_2 5-$NO_2C_6H_3$, 4-$EtOC_6H_4$, 3,5-di-$MeOC_6H_4$, 3-MeC_6H_4, 4-OHC_6H_4, 2-OHC_6H_4, 9-phenanthrene, 2-thiophene, 4-pyridine, 2-pyridine, $(CH_3)_2CHCH_2$, $(CH_3)_2CH(CH_2)$, $PhCH_2$

Scheme 1 Synthesis of different structurally 5-substituted-1*H*-tetrazoles in the presence of cuttlebone in DMSO.

using cuttlebone to achieve 5-substituted-1*H*-tetrazoles by [3 + 2] cycloaddition reaction of nitriles with sodium azide (Scheme 1).

Cuttlebone was taken out from cuttlefish (*Sepia esculenta*),[64,65,68,69] which is commonly found in saltwater beaches like Persian Gulf in Iran. This sample was in a fairly good condition with minimal external damage. In order to remove pollution on the surface of cuttlebone, the catalyst was powdered, washed with distilled water and dried at 100 °C for 2 h.

The model reaction was carried out by taking the mixture of benzonitrile with sodium azide in the presence of cuttlebone. Table 1 gives the details about the amount of cuttlebone, molar ratios of benzonitrile/NaN_3, solvent and temperature which were used to optimize the reaction conditions. Only 30% addition product is obtained when the reaction is carried out without catalyst in DMSO at 140 °C (Table 1, entry 1), despite of prolonged reaction time. At the same reaction condition, 100% conversion was obtained after 20 min in the presence of cuttlebone (Table 1, entry 2). This result highlights the specific role of cuttlebone in [3 + 2] cycloaddition reaction of benzonitrile with sodium azide. In an effort to develop better reaction conditions, different solvents were screened for cycloaddition reaction in the presence of cuttlebone (Table 1, entries 3–9). Other solvents, such as DMF, toluene, H_2O, CH_3CN gave the desired product in low yield (Table 1, entries 4–6) but no product was obtained when the reaction was performed in 1,4-dioxane, CH_3NO_2 and $CHCl_3$ (Table 1, entries 7–9). As shown in Table 1 among the different solvents tested DMSO was found to be the solvent of choice for [3 + 2] cycloaddition reaction in the presence of cuttlebone. At lower reaction temperature (130 °C and 110 °C) the reaction was progressed as the same as at 140 °C (Table 1, entries 10–12). To investigate the effect of catalyst loading, the formation of 5-phenyl-1*H*-tetrazole was carried out in DMSO at 110 °C in the presence of 0.07 g and 0.03 g of catalyst. According to this study, increasing the catalyst loading did not lead to higher conversion (Table 1, entry 13), while lower catalyst loading has lessened the reaction yield even after longer reaction time (Table 1, entry 14). To improve [3 + 2] cycloaddition reaction, the effect of different molar ratio of benzonitrile/sodium azide was also examined in DMSO at 110 °C. It is noteworthy that additional amount of sodium azide cannot improve the reaction rate (Table 1, entry 15). By considering the cuttlebone structure[66,67] and to understand which segment of cuttlebone catalyzed [3 + 2] cycloaddition reaction, the optimized reaction conditions were applied on the cyclization of benzonitrile with sodium azide in the presence of $CaCO_3$ and freshly extracted β-chitin from cuttlebone[70] respectively (Table 1, entries 16 and 17). In comparison, a trace amount of product was produced in the presence of $CaCO_3$ while in the presence of β-chitin the reaction was completed after longer reaction time.

It can be seen from Table 2 that, admirable yields of the desired 5-substituted-1*H*-tetrazoles were obtained rapidly by using 0.05 g of cuttlebone in solution of 1 : 1 molar ratio of organic nitriles/NaN_3 in DMSO at 110 °C. The reaction times and product yields of aromatic nitriles bearing electron

Table 1 Synthesis of 5-phenyl-1*H*-tetrazole in the presence of different amounts of cuttlebone, different molar ratios of benzonitrile/NaN_3 in various solvents at different temperatures

Entry	Molar ratio (benzontrile/NaN_3)	Catalyst (g)	Solvent	Temperature (°C)	Time (h)	Isolated yield (%)
1	1 : 1	—	DMSO	140	10	30
2	1 : 1	0.05	DMSO	140	20 min	98
3	1 : 1	0.05	DMF	140	2	65
4	1 : 1	0.05	CH_3CN	Reflux	2	10
5	1 : 1	0.05	Toluene	Reflux	2	5
6	1 : 1	0.05	H_2O	Reflux	2	10
7	1 : 1	0.05	CH_3NO_2	Reflux	2	0
8	1 : 1	0.05	1,4-Dioxane	Reflux	2	0
9	1 : 1	0.05	$CHCl_3$	Reflux	2	0
10	1 : 1	0.05	DMSO	130	20 min	98
11	1 : 1	0.05	DMSO	110	20 min	98
12	1 : 1	0.05	DMSO	100	20 min	95
13	1 : 1	0.07	DMSO	110	20 min	98
14	1 : 1	0.03	DMSO	110	2	65
15	1 : 1/5	0.05	DMSO	110	20 min	98
16[a]	1 : 1	0.05	DMSO	110	20 min	Trace
17[b]	1 : 1	0.05	DMSO	110	20/40 min	85/98

[a] The reaction was performed in the presence of $CaCO_3$. [b] The reaction was performed in the presence of freshly extracted β-chitin from cuttlebone.

Table 2 Synthesis of different structurally 5-substituted-1*H*-tetrazoles in the presence of cuttlebone in DMSO

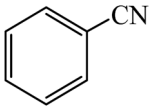
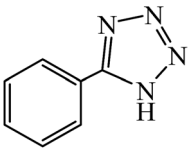
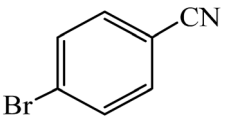
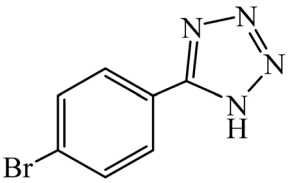
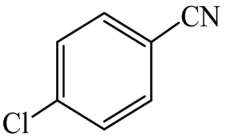
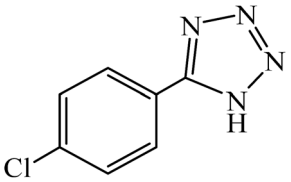
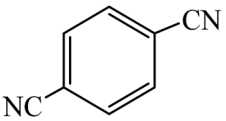
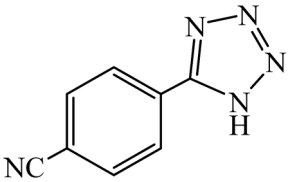
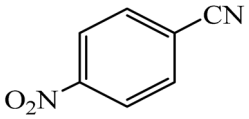
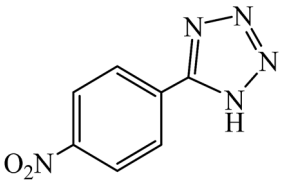
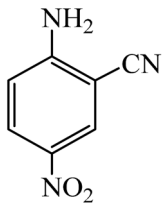
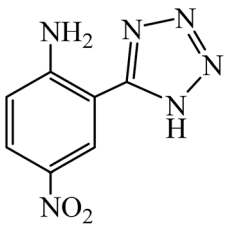
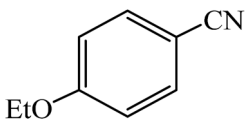
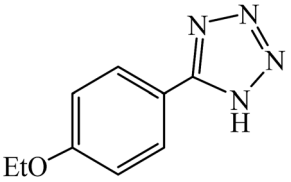
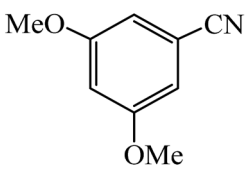
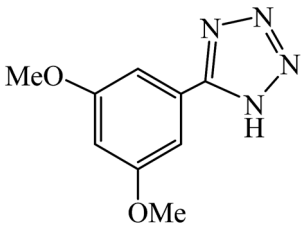
Entry	Substrate	Product	Time (min)	Isolated yield (%)
1			20	98
2			30	95
3			15	97
4			18	98
5			15	98
6			50	96
7			40	90
8			2 (h)	95

Table 2 (*Contd.*)

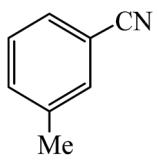
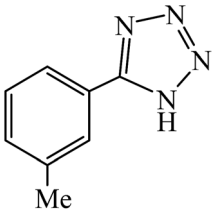
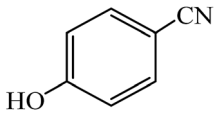
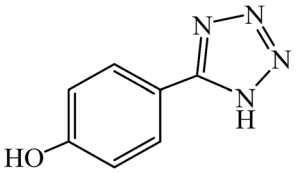
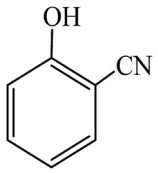
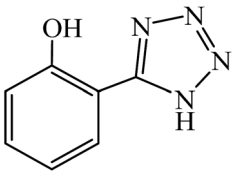
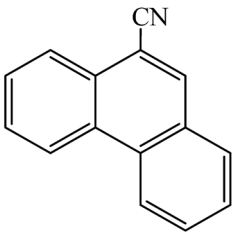
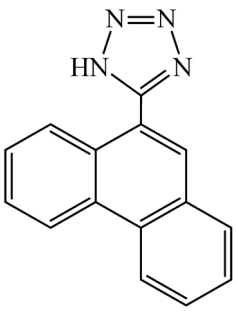
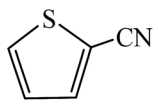
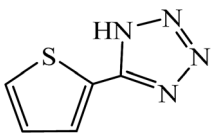
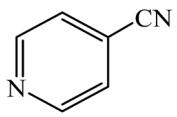
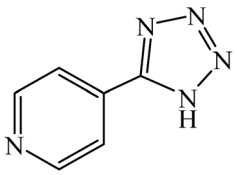
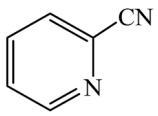
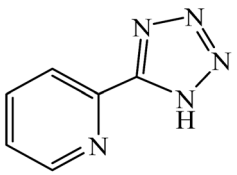
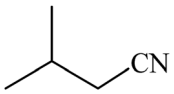
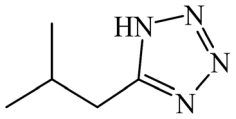
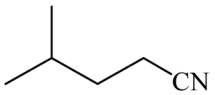
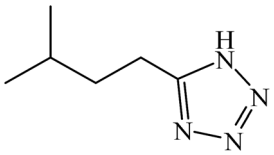
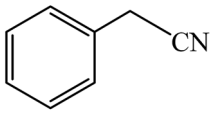
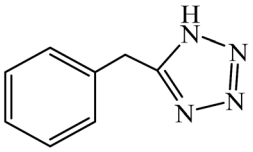
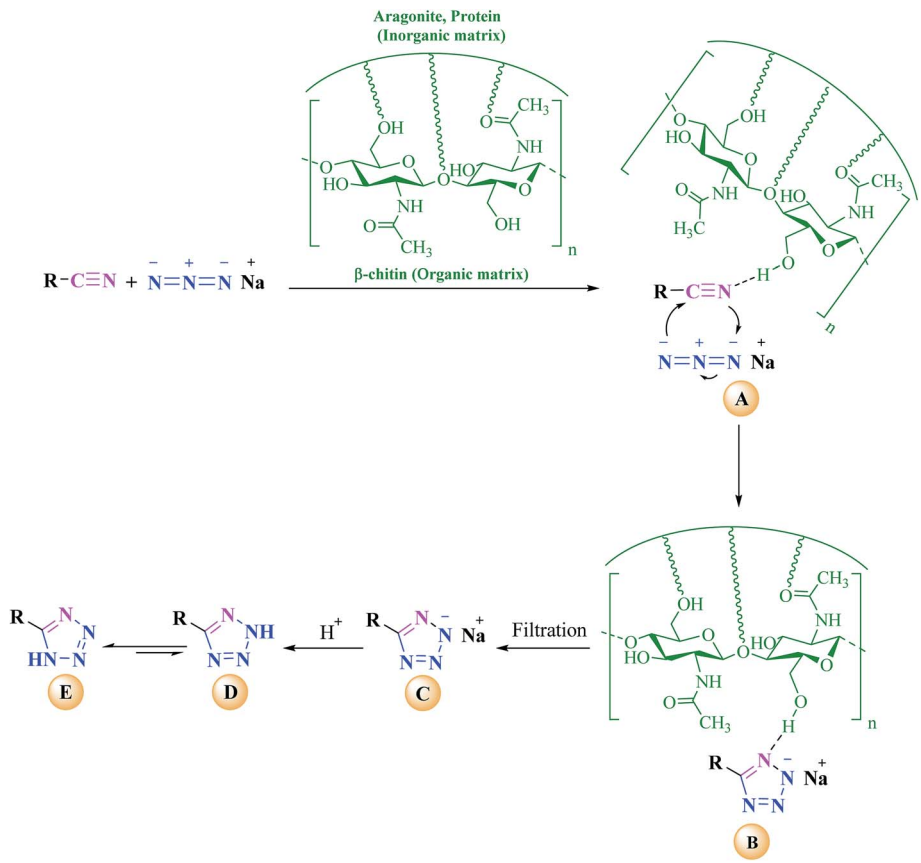
Entry	Substrate	Product	Time (min)	Isolated yield (%)
9			2 (h)	95
10			1 (h)	87
11			40	95
12			2 (h)	85
13			40	90
14			30	97
15			40	92
16			1.5 (h)	95

Table 2 (*Contd.*)

Entry	Substrate	Product	Time (min)	Isolated yield (%)
17			1.5 (h)	95
18			1 (h)	98

withdrawing and electron donating groups have a significant difference, because of the obvious difference in electrophilic character of nitrile. The aromatic nitriles containing electron withdrawing substituents such as –Cl, –Br, –CN, $–NO_2$ at *para* position took less time (15–30 min) for complete conversion of starting material (Table 2, entries 2–5). 2-Amino-5-nitrobenzonitrile results the desired product in longer reaction time due to steric effect and electron donation of $–NH_2$ substitution at *ortho* position (Table 2, entry 6). Moreover, aromatic rings with electron donating groups ($–NH_2$, $–OCH_3$, CH_3, $–OCH_2CH_3$ and –OH) gave the corresponding tetrazoles in high yields, although longer reaction times (40 min to 2 h) were required (Table 2, entries 7–11). Interestingly, aryl nitrile containing a free hydroxy group at *ortho* or *para* positions gave desired product in high yield after 1 h or 40 min respectively (Table 2, entries 10 and 11). Hydroxy group at *ortho* position render inductive effect which accelerates the cycloaddition reaction of 2-hydroxybenzonitrile. Phenanthrene-9-carbonitrile



Scheme 2 Proposed mechanism for the synthesis of 5-substituted-1*H*-tetrazoles in the presence of cuttlebone.

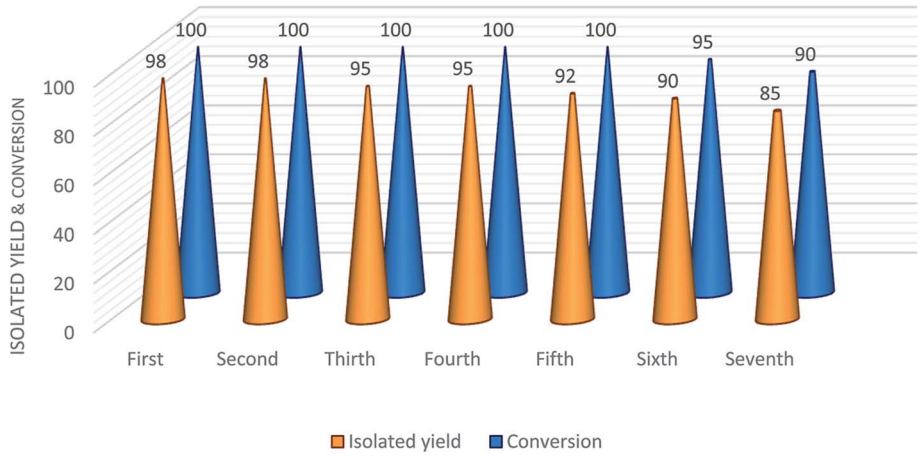


Fig. 1 [3 + 2] Cycloaddition reactions of benzonitrile with sodium azide in the presence of reused cuttlebone.

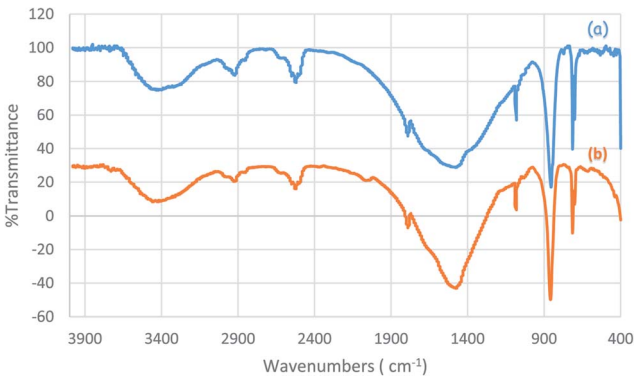


Fig. 2 FT-IR spectrum of cuttlebone and 6th recovered cuttlebone.

with steric hindrance at 9 position produced the corresponding tetrazole after 2 h (Table 2, entry 12). Similarly, heteroaryl nitriles were found to be extremely reactive substrate affording the relative tetrazole rapidly in the presence of cuttlebone (Table 2, entries 13–15). We next examined the cycloaddition of alkyl nitriles such as 3-methylbutanenitrile, 4-methylpentanenitrile and 2-phenylacetonitrile with azide ion in the presence of cuttlebone. It was found that alkyl nitriles in the presence of cuttlebone reacted smoothly to give the corresponding 1*H*-tetrazoles in excellent yields after 1–1.5 h (Table 2, entries 16–18). The results obtained from Table 2 indicate that [3 + 2] cycloaddition reaction of nitriles with sodium azide in the presence of cuttlebone proceeds rapidly irrespective of the electronic nature of nitrile compound.

FT-IR spectroscopy of all purified products revealed an absorption band at 3485–3329 cm^{-1} (N–H) and group of bands at 1469–1430 cm^{-1} (scissoring bending C–H), 1293–1233 cm^{-1} (N–N=N–), 1189–1110 and 1106–1041 cm^{-1} (tetrazole ring) and absence of band at 2200 cm^{-1} due to CN group. In ^{1}H NMR and ^{13}C NMR spectra, a signal at 16.9 and 161–155 ppm are assigned to the NH and quaternary carbon NH–C=N respectively.

All of the products were known compounds and characterized by the FT-IR spectroscopy, mass spectrometry and comparison of their melting points with known compounds. The structure of selected products was further confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy.

A plausible mechanism for the reaction methodology under current development is shown in Scheme 2. The fact that after a long reaction time, lower yield of product was observed in the absence of cuttlebone (Table 1, entry 1) established the catalytic activity of cuttlebone in [3 + 2] cycloaddition reactions of various organic nitriles with sodium azide. Although the role of cuttlebone in [3 + 2] cycloaddition reaction is not clear definitively, it is speculated that a ternary complex **A** among nitrile compound, azide ion and cuttlebone (β-chitin as organic segment of catalyst) would be generated in the transition state immediately as shown in Scheme 2. In accordance with Scheme 2 the following steps are postulated to occur: the hydrogen bonding of β-chitin with nitrogen atom of nitrile compound accelerates the cyclization step *via* increasing the electrophilicity of nitrile group. The [3 + 2] cycloaddition between the C≡N bond of nitrile compound and azide ion takes place readily to form the intermediate **B**. After removing the catalyst by simple filtration, **C** was produced as sodium salt which upon acidic work-up, leads to formation of **D** and **E**. Finally the more stable tautomer **E** (5-substituted-1*H*-tetrazole) was obtained as major product. Further investigation on the elucidation of the mechanism and scope of this reaction are currently underway in our laboratory.

[3 + 2] Cycloaddition reaction of organic nitriles with sodium azide in the presence of cuttlebone was vigorously dependent on physical form of the catalyst. Excellent yield of product was obtained in the presence of fine powdered cuttlebone, while 5-phenyl-1*H*-tetrazole was obtained in 20% yield in the presence of non-powdered cuttlebone. On the basis of the results obtained from Table 1 (entries 16 and 17), organic segment of cuttlebone (β-chitin) has an essential role in catalytic activity of cuttlebone. So, in the presence of β-chitin (which was extracted from cuttlebone according the method reported previously)[70] the reaction was completed after longer reaction time, and in the presence of $CaCO_3$ (as inorganic segment of cuttlebone) a trace amount of product was produced. Performing the reaction in the presence of β-chitin suffered from long reaction time and

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

Entry	Catalyst	Solvent	Temp. °C	Time (h)	Yield (%)
1	Mesoporous ZnS[35]	DMF	120	36	96
2	Silica sulfuric acid[71]	DMF	Reflux	5	88
3	Imidazole-based zwitterionic-type molten salts[72]	—	120	12	84
4	Chitosan derived magnetic ionic liquid[73]	—	70	7	87
5	$AgNO_3$ (ref. 48)	DMF	120	5	83
6	CoY zeolite[74]	DMF	120	14	90
7	Fe_3O_4@SiO_2/Salen Cu(II)[55]	DMF	120	7	90
8	Zn/Al hydrocalcite[32]	DMF	120–130	12	84
9	Zn hydroxyapatite[34]	DMF	120	12	78
10	AgNPs[53]	DMF	120	8	92
11	$B(C_6F_5)_3$ (ref. 56)	DMF	120	8	94
12	CAES[59]	DMSO	130	1	95
13	$CuSO_4 \cdot 5H_2O$[60]	DMSO	140	1	98
14	Cuttlebone	DMSO	110	20 min	98

tedious work-up procedure, because of gelation of β-chitin in the reaction mixture. Also, β-chitin is not reusable catalyst in [3 + 2] cycloaddition reaction. Interestingly, cuttlebone matrix improved the catalytic activity of β-chitin significantly with providing easy and simple removing of catalyst which could be reusable several times (Fig. 1).

Recyclability is important for industrial application of a catalyst. Therefore, the reuse performance of cuttlebone was investigated. After completion of [3 + 2] cycloaddition reaction of benzonitrile with sodium azide, cuttlebone was separated by simple filtration from the reaction mixture, washed with distilled water and ethanol several times to remove the organic products. The catalyst was dried at 100 °C for 1 h. The heterogeneous catalyst was used for 6 successive times in the new experiments without dramatic yield loss and generate product with purity similar to that obtained in the first run (Fig. 1).

The FT-IR spectrum of cuttlebone and the 6th recovered cuttlebone was shown in Fig. 2. As can be seen, the shape, position and relative intensity of all characteristic peaks are well preserved. The results indicate no considerable changes were observed on the chemical structure of functional groups and the hydrogen bonding network (Fig. 2).

In comparison, [3 + 2] cycloaddition reaction of nitriles with sodium azide in the presence of cuttlebone affords 5-sustituted-1*H*-tetrazole rapidly in high yield than the earlier reported catalysts (Table 3). As can be seen from Table 3, all of the previously reported methods suffer from long reaction times to achieve suitable yields as well as use of strong Lewis acids, expensive and toxic metals and tedious work-up procedure.

Experimental

General

The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an Avatar 370 FT-IR Therma Nicolet spectrometer. The NMR spectra were provided on Brucker Avance 100 and 400 MHz instruments in acetone-d_6, DMSO-d_6 and CD_3CN. Elemental analyses were performed using a Thermo Finnegan Flash EA 1112 Series instrument. Mass spectra were recorded with Agilent Technologies (HP) 5973 Network Mass Selective Detector, Shimadzu GC-MS-QP5050 instruments and a CH7A Varianmat Bremem instrument (Germany) at 70 eV. Elemental compositions were determined with a Leo 1450 VP scanning electron microscope equipped with an SC7620 energy dispersive spectrometer (SEM-EDS) presenting a 133 eV resolution at 20 kV. All of the products were known compounds and characterized by the FT-IR spectroscopy and comparison of their melting points with known compounds. The structure of selected products was further confirmed by ^{1}H NMR, ^{13}C NMR spectroscopy, and mass spectrometry. Cuttlebone was taken out from cuttlefish (*Sepia esculenta*),[64,65,68,69] which is commonly found in saltwater beaches like Persian Gulf in Iran.

Pre-preparation of cuttlebone

In order to remove pollution on the surface of cuttlebone, the catalyst was powdered, washed with distilled water and dried at 100 °C for 2 h.

Characterization of cuttlebone

Cuttlebone was identified by FT-IR spectroscopy, scanning electron microscope and energy dispersive spectrum (SEM-EDS). The FT-IR spectrum of the cuttlebone (*Sepia esculenta*) shows absorption bands between 3440–699 cm^{-1} (Fig. 3). The observed absorptions bands for aragonite phases (calcium carbonate) in cuttlebone structure are due to the planar CO_3^{-2} ion. There are four vibrational modes in the free CO_3^{-2} ion:[75] the symmetric stretching vibration of the carbonate ion at about 1082 cm^{-1} (ν_1); the out-of-plane bending absorption at about 857 cm^{-1} (ν_2); the asymmetric stretching vibrations at about 1400–1500 cm^{-1} (ν_3); the split in-plane bending vibrations at about 700 cm^{-1} (ν_4). Also, as shown in the FT-IR spectrum of cuttlebone (Fig. 3), the bands at 3448 and 3318 cm^{-1} are

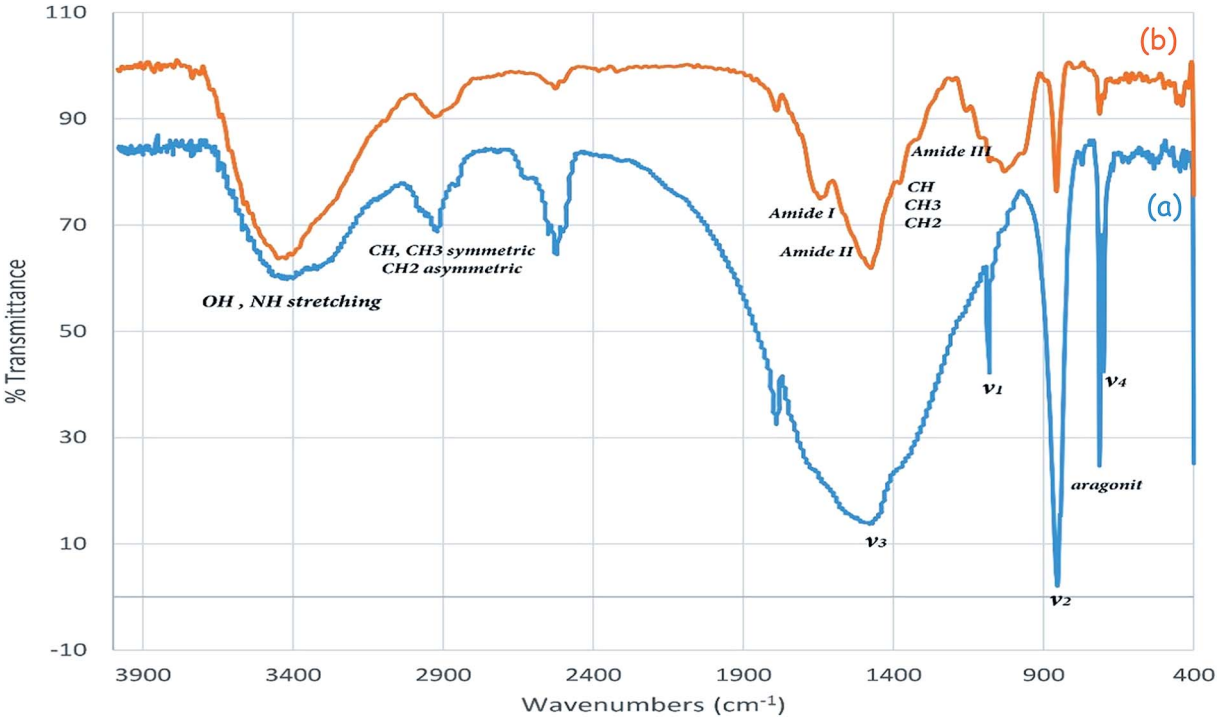


Fig. 3 FT-IR spectrum of the (a) cuttlebone and (b) extracted β-chitin from cuttlebone.

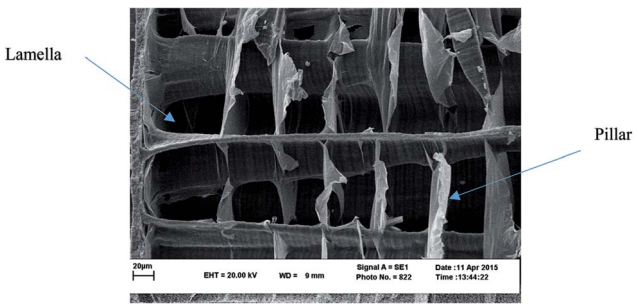


Fig. 4 SEM image of cuttlebone.

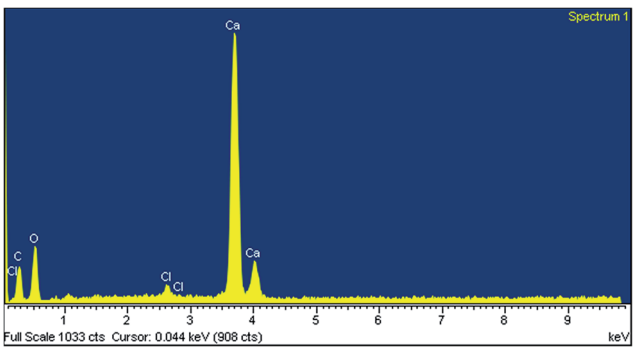


Fig. 6 EDS of finely powdered cuttlebone.

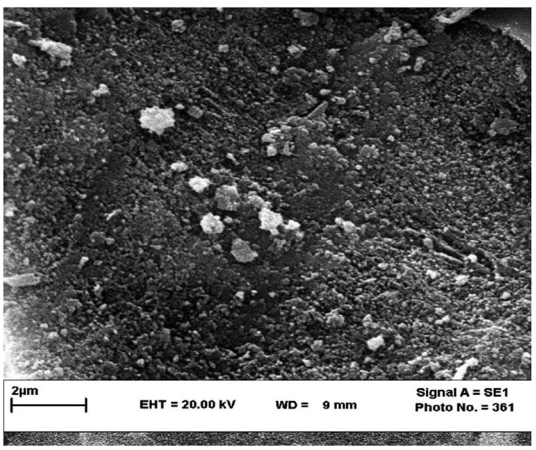


Fig. 5 SEM image of finely powdered cuttlebone.

attributed to the OH and NH stretching vibrations respectively, which are related to absorption bands of β-chitin segment of cuttlebone. The hydrogen bonding network of β-chitin in cuttlebone would change the shape and intensity of the above mentioned absorption bands. The absorption bands ranging from 2977 to 2855 cm^{-1} were related to symmetric stretching of CH, CH_3 and asymmetric stretching vibrations of CH_2. The CH bending, CH_3 symmetric deformation and CH_2 wagging bands were appeared at 1384 to 1312 cm^{-1}. The absorption bands at 1662 and 1644 cm^{-1} are assigned to amide I band (two types of hydrogen bonds in a C═O group with the NH group of the adjacent chain and the OH group of the inter-chain). Amide II band (in-plane N–H bending and C–N stretching mode) at about 1550 and 1360 cm^{-1} and amide III band (in-plane mode of the CONH group) are observed at 1315 cm^{-1}. The absorption bands

ranging from 1160 to 1030 cm^{-1} are attributed to the asymmetric bridge oxygen and C–O stretching vibrations.[76,77]

Scanning electronic microscopy (SEM) of transverse section of cuttlebone commonly reveals an approximately periodic microstructure. The most common base cell (or smallest representative volume element – RVE) has a bridge-like configuration (Fig. 4). This base cell geometry can be used to approximate the mechanical properties for cuttlebone.[66]

Also, as was shown in Fig. 5 scanning electronic microscopy (SEM) of finely powdered cuttlebone shows an amorphous morphology.

The energy dispersive spectrum (EDS) indicates the presence of Ca, C, O and Cl elements in cuttlebone structure (Fig. 6).

Typical procedure for the preparation of 5-phenyl-1*H*-tetrazole in the presence of cuttlebone

Finely powdered cuttlebone (0.050) was added to a mixture of benzonitrile (0.1031 g, 1 mmol) and sodium azide (0.0650 g, 1 mmol) in DMSO (2 mL) with stirring at room temperature. The reaction temperature was raised up to 110 °C for 20 min. The progress of the reaction was monitored by TLC. After completion of reaction (monitored by thin-layer chromatography, TLC), the reaction mixture was cooled and the catalyst was filtered. The filtrate was treated with HCl (4 N, 10 mL) and then ethyl acetate (2 × 10 mL). The resultant organic layer was washed with distilled water, dried over anhydrous sodium sulfate, and concentrated to give the crude solid crystalline 5-phenyl-1*H*-tetrazole. The crude product was recrystallized from *n*-hexane/ethylacetate (1 : 1) obtaining 0.1430 g of colourless crystals (98% isolated yield).

5-Phenyl-1*H*-tetrazole (Table 2, entry 1). White solid; mp 214–216 °C (Lit.[75] 214–216 °C); FT-IR (KBr): ν_{max}/cm^{-1} 3125, 3043, 2982, 2913, 2835, 2765, 2692, 2606, 2557, 2488, 1613, 1563, 1485, 1465, 1409, 1163, 1056, 726, 703, 687; ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 7.61 (s, 3H, Ph), 8.05 (s, 2H, Ph); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ 124.6, 127.4, 129.9, 131.7, 155.7.

5-(4-Boromophenyl)-1*H*-tetrazole (Table 2, entry 2). White solid; mp 264–265 °C (Lit.[79] 265 °C); FT-IR (KBr): ν_{max}/cm^{-1} 3089, 3063, 2996, 2900, 2844, 2761, 2729, 2633, 1652, 1604, 1560, 1482, 1431, 1405, 1157, 1076, 1054, 1018, 829, 744, 502; ^{1}H NMR (100 MHz, DMSO-d_6, ppm) δ 8.00 (q, 4H, Ph); MS, *m*/*z* (%): 226 [M^+ + 2], 224 [M^+], 198 [(M^+ + 2) − N_2], 196 (100) [M^+ − N_2], 185 [(M^+ + 2) − N_3], 183 [M^+ − N_3].

5-(4-Chlorophenyl)-1*H*-tetrazole (Table 2, entry 3). White solid; mp 261–262 °C (Lit.[76] 261–263 °C). FT-IR (KBr): ν_{max}/cm^{-1} 3092, 3060, 3007, 2978, 2907, 2851, 2725, 2622, 2537, 2471, 1609, 1564, 1486, 1435, 1160, 1096, 1053, 1020, 990, 833, 745, 508; ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 7.68 (d, J = 8.4 Hz, 2H, Ph), 8.05 (d, J = 8.8 Hz, 2H, Ph); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ 123.5, 129.2, 130.0, 136.4, 155.3.

4-(1*H*-tetrazol-5-yl)benzonitrile (Table 2, entry 4). White solid; mp 190–191 °C (Lit.[80] 192 °C); FT-IR (KBr): ν_{max}/cm^{-1} 3150, 3092, 3013, 2928, 2861, 2758, 2610, 2231, 1585, 1560, 1494, 1433, 1279, 1153, 1014, 976, 944, 850, 749, 554; ^{1}H NMR (100 MHz, CD_3CN, ppm) δ 7.90 (d, J = 7.5 Hz, 2H, Ph), 8.20 (d, J = 7.5 Hz, 2H, Ph); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ 113.8, 118.6, 128.0, 129.1, 133.7, 155.6; MS, *m*/*z* (%): 171 [M^+], 142 (100) [M^+ − N_2], 114 [M^+ − 2N_2].

5-(4-Nitrophenyl)-1*H*-tetrazole (Table 2, entry 5). Yellow solid; mp 218–219 °C (Lit.[80] 219–220 °C). FT-IR (KBr): ν_{max}/cm^{-1} 3448, 3334, 3235, 3109, 3080, 2974, 2900, 2819, 2659, 1562, 1532, 1488, 1357, 1340, 1315, 1143, 1106, 995, 867, 853, 730, 710; ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 8.31 (d, J = 8.4 Hz, 2H, Ph), 8.46 (d, J = 8.8 Hz, 2H, Ph); ^{13}C NMR (100 MHz, DMSO-d_6. ppm) δ 125.1, 128.6, 131.0, 149.2, 155.9.

4-Nitro-2-(1*H*-tetrazol-5-yl)benzenamine (Table 2, entry 6). White solid; mp 268–270 °C (Lit.[81] 270–271 °C); FT-IR (KBr): ν_{max}/cm^{-1} 3411, 3321, 3199, 3084, 2937, 1645, 1616, 1572, 1477, 1325, 1278, 1141, 1041, 910, 831, 751, 722; ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 7.00 (d, J = 9.2 Hz, 1H, Ph), 7.94 (br s, 1H, NH), 8.10 (dd, J = 9.2, J = 2.4 Hz, 1H, Ph), 8.81 (d, J = 2.4 Hz, 1H, Ph); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ 104.4, 116.3, 126.1, 127.6, 136.3, 153.0, 154.4.

5-(4-Ethoxyphenyl)-1*H*-tetrazole (Table 2, entry 7). White solid; mp 234–235 °C (Lit.[60] 234–235 °C); FT-IR (KBr): ν_{max}/cm^{-1} 3145, 3101, 3060, 2986, 2921, 2868, 2737, 2647, 1613, 1505, 1470, 1394, 1293, 1262, 1189, 1056, 1041, 923, 827, 751, 653, 522; ^{1}H NMR (100 MHz, acetone-d_6, ppm) δ 1.40 (t, J = 5 Hz, 3H, –OEt), 4.20 (q, 2H, –OEt), 7.15 (d, J = 9.5 Hz, 2H, Ph), 8.07 (d, J = 9.5 Hz, 2H, Ph).

5-(3,5-Dimethoxyphenyl)-1*H*-tetrazole (Table 2, entry 8). White solid; mp 204–205 °C (Lit.[41] 204–206 °C); FT-IR (KBr): ν_{max}/cm^{-1} 3129, 3064, 3011, 2975, 2941, 2843, 2757, 2712, 2634, 1605, 1562, 1480, 1430, 1287, 1208, 1167, 1162, 1054, 827, 747; ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 3.84 (s, 6H, –OMe), 6.73 (t, J = 2 Hz, 1H, Ph), 7.21 (d, J = 2 Hz, 2H, Ph), 16.91 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ 56.0, 103.4, 105.3, 125.7, 156.3, 161.5; MS, *m*/*z* (%): 207 [M + H], 149 (100) [M^+ − 2N_2].

5-*m*-Tolyl-1*H*-tetrazole (Table 2, entry 9). White solid; mp 149–150 °C (Lit.[31] 151–152 °C); FT-IR (KBr): ν_{max}/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 (100 MHz, CD_3CN, ppm) δ 2.43 (s, 3H, CH_3), 7.40–7.90 (m, 4H, Ph).

4-(1*H*-Tetrazol-5-yl)phenol (Table 2, entry 10). White solid; mp 218–219 °C (Lit.[82] 219 °C); FT-IR (KBr): ν_{max}/cm^{-1} 3252, 3101, 3066, 3019, 3000–2200, 1615, 1599, 1511, 1466, 1413, 1282, 832, 752, 514; ^{1}H NMR (400 MHz, d_6 DMSO-d_6, ppm) δ 6.97 (d, J = 8.4 Hz, 2H, Ph), 7.87 (d, J = 8.8 Hz, 2H, Ph), 10.20 (br s, 2H, OH); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ 115.0, 116.6, 129.2, 155.2, 160.5.

2-(1*H*-Tetrazol-5-yl)phenol (Table 2, entry 11). White solid; mp 218–219 °C (Lit.[82] 219 °C); FT-IR (KBr): ν_{max}/cm^{-1} 3175, 2970, 2855, 2721, 2561, 1616, 1545, 1490, 1467, 1392, 1365, 1298, 1071, 999, 837, 745, 465; MS, *m*/*z* (%): 162 [M^+], 161 [M^+ − H], 133 (100) [M^+ − 2N_2].

5-(Phenanthren-9-yl)-1*H*-tetrazole (Table 2, entry 12). White solid; mp 241–242 °C (Lit.[83] 243–244 °C); FT-IR (KBr): ν_{max}/cm^{-1} 3105, 3076, 3016, 2978, 2878, 2830, 2724, 2686, 2622, 2590, 2520, 2478, 1612, 1565, 1450, 1399, 1246, 1112, 1053, 1038, 992, 934, 771, 737, 721, 424; ^{1}H NMR (100 MHz, DMSO-d_6. ppm) δ 7.79–7.82 (m, 4H, Ph), 8.08–8.20 (m, 1H, Ph), 8.40–8.52 (m, 2H,

Ph), 8.92–9.10 (m, 2H, Ph); Ms, *m*/*z* (%): 246 [M^+], 218 (100) [$M^+ - N_2$], 190 [$M^+ - 2N_2$].

5-(Thiophen-2-yl)-1*H*-tetrazole (Table 2, entry 13). White solid; mp 205–207 °C (Lit.[84] 205–207 °C); FT-IR (KBr): ν_{max}/cm^{-1} 3109, 3074, 2974, 2891, 2780, 2722, 2628, 2569, 2500, 2456, 1830, 1595, 1503, 1411, 1233, 1139, 1046, 962, 853, 740, 719; ^1H NMR (100 MHz, CD_3CN, ppm) δ 7.20–7.30 (m, 1H, tiophen), 7.67–7.80 (m, 2H, tiophen); Ms, *m*/*z* (%): 152 [M^+], 124 (100) [$M^+ - N_2$], 97 [$M^+ - 2N_2$].

4-(1*H*-Tetrazol-5-yl)pyridine (Table 2, entry 14). White solid; mp 255–258 °C (Lit.[78] 255–258 °C); FT-IR (KBr) ν_{max}/cm^{-1} 3485, 3264, 3099, 3035, 2966, 1624, 1529, 1435, 1388, 1123, 1096, 1042, 1022, 845, 730, 674, 593, 465.

2-(1*H*-Tetrazol-5-yl)pyridine (Table 2, entry 15). White solid; mp 211–213 °C (Lit.[76] 210–213 °C); FT-IR (KBr): ν_{max}/cm^{-1} 3088, 3060, 2959, 2929, 2864, 2737, 2692, 2622, 2582, 1728, 1602, 1557, 1483, 1449, 1405, 1284, 1158, 1068, 1024, 955, 795, 743, 726, 703, 637, 496; ^1H NMR (400 MHz, DMSO-d_6, ppm) δ 7.65 (s, 1H, Py), 8.10 (s, 1H, Py), 8.24 (d, $J = 6.4$ Hz, 1H, Py), 8.81 (s, 1H, Py); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ 123.1, 126.7, 138.7, 144.0, 150.6, 155.3.

5-Isobutyl-1*H*-tetrazole (Table 2, entry 16). White solid; mp 52–54 °C (Lit.[26b] 53.5–54 °C); FT-IR (KBr): ν_{max}/cm^{-1} 3089, 3063, 2971, 2901, 2845, 2765, 2729, 2633, 1605, 1482, 1454, 1430, 1156, 1075, 1053, 1017, 990, 829, 772, 743, 502.

5-Isopentyl-1*H*-tetrazole (Table 2, entry 17). White solid; mp 94 °C (Lit.[26b] 95–96 °C); FT-IR (KBr): ν_{max}/cm^{-1} 2962, 2931, 2874, 2709, 2618, 2482, 1867, 1583, 1553, 1469, 1404, 1110, 1048, 772. ^1H NMR (100 MHz, $CDCl_3$, ppm) δ 1.00 (d, *J* 5 Hz, 6H, 2 CH_3), 1.40–2.05 (m, 3H, –CH–, $-CH_2-$), 3.10 (t, *J* 6 Hz, 2H, $-CH_2-$).

5-Benzyl-1*H*-tetrazole (Table 2, entry 18). White solid; mp 117–119 °C (Lit.[85] 118–120 °C); FT-IR (KBr): ν_{max}/cm^{-1} 3109, 3031, 2984, 2945, 2863, 2778, 2704, 2594, 1768, 1707, 1638, 1549, 1533, 1494, 1457, 1241, 1108, 1074, 772, 734, 695; ^1H NMR (100 MHz, CD_3CN, ppm) δ 4.30 (s, 2H, $-CH_2-$), 7.31 (s, 5H, Ph).

Conclusion

In conclusion, a convenient and highly efficient metal free synthesis of 5-substituted-1*H*-tetrazoles has been developed by reacting nitriles with sodium azide in the presence of cuttlebone as a green and effective catalyst. This new type of low cost and reusable catalyst plays a crucial role by "electrophilic activation" of nitrile through hydrogen bond formation between cuttlebone and nitrile. Excellent yields of product, short reaction time, elimination of dangerous and harmful hydrazoic acid, avoidance of toxic metal derivatives, a simple work-up procedure, simple pre-preparation, and easy handling of the catalyst are the notable and valuable features of this metal free methodology. This procedure can be used to convert aryl, heteroaryl and alkyl nitriles, sterically hindered *ortho*-substituted aryl nitriles, organic nitriles containing bulky aryl groups and halo aryl nitriles to corresponding 5-substituted-1*H*-tetrazoles. Thus, it provides a better and more practical alternative to the existing methodologies.

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