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Heterogeneous Copper Nanoparticle on Charcoal (Cu/C) Mediated Efficient Synthesis of 1-Substituted 1*H*-Tetrazoles under Solvent Free Condition

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1-substituted 1*H*-tetrazoles were efficiently synthesized under solvent-free conditions from the reaction of primary amines, triethylorthoformate, and sodium azide in the presence of Cu/C as a heterogeneous catalyst. Various amines including aromatic and heteroaromatic amines were used to afford the corresponding products in good to excellent yields. The characterization of corresponding products were also performed applying several analysis techniques such as infrared spectroscopy, ^{1}H NMR, ^{13}C NMR and elemental analyses. The catalyst can be recycled and reused for five times without noticeable loss of its activity. This procedure has various benefits including high yields, low cost, fast reaction and reusability of the catalyst.

Keywords: Tetrazole derivatives, Cu/C, Heterogeneous catalyst, Multicomponent reaction, Solvent-free conditions

INTRODUCTION

Tetrazoles are a group of nitrogenous heterocyclic compounds with a five-membered ring including one carbon and four nitrogen atoms, respectively. These heterocyclic systems are unknown in the nature [1]. Tetrazoles have attracted considerable attention due to their unique and broad range of applications in photography [2], agriculture [3], information recording systems in material science [2] and medicinal chemistry as lipophilic spacers and carboxylic acid surrogates [4]. Applications of tetrazoles in pharmaceutical field include antibacterial [5], antifungal [6], antiallergic [7], anti-inflammatory [5], anticonvulsant [8], analgesic [9], anticancer [10] and antiviral activity [11]. Tetrazole compounds are also widely used as ligands in coordination chemistry [12], as rocket propellants and explosives [13].

Although there are various methods for tetrazole synthesis, [3+2] cycloaddition between nitriles and organic azides can be considered the most straightforward method [14-21]. Tetrazoles may also be synthesized *via* cyclization reaction between primary amines, or their salts with an orthocarboxylic acid ester and sodium azide. A wide spectrum of potential applications has led to a continuous search for new and more efficient approaches to obtain new structures and original synthetic methodologies. One of the modified synthesis methods for 1-substituted 1*H*-tetrazoles includes cyclizations from an amine, triethylorthoformate and sodium azide using variety of catalysts such as $In(OTf)_3$ [22], SSA [23], $Yb(OTf)_3$ [24], $[Hbim]BF_4$ [25] and natrolite zeolite [26].

However, a number of these methods have some shortcomings such as low yields, use of toxic and high boiling point solvent, long reaction time, harsh reaction conditions and using toxic and expensive reagents. Thus, there is still a need for more efficient protocols for synthesis of 1-substituted 1*H*-tetrazole derivatives. Recently one-pot conversion of organic compounds using non-toxic and inexpensive reagents has gained much more interest in organic chemistry[27].

We have reported copper nanoparticles on charcoal (Cu/C) as a superb heterogeneous catalyst for synthesis of triazole [28], propargylamine [29], benzimidazole [30], 2-Amino-3-cyanopyridine [31] and indazole derivatives [32].

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As part of our research program directed toward new protocols for the synthesis of organic compounds [33-49], in the present study, we exploit recyclable copper nanoparticles on charcoal (Cu/C) for synthesis of 1-substituted 1*H*-tetrazoles from a wide variety of aromatic amines with triethylorthoformate and sodium azide under solvent free condition.

EXPERIMENTAL

Instrumentation, Materials and General Experimental Details

All chemical materials were either synthesized in our laboratories or were purchased from Fluka, Aldrich and Merck companies and used without further purification. The used activated carbon was also purchased from Merck (Catalog No. 109631, 0.3-0.5 mm). NMR spectra were recorded in pure deuterated DMSO-d_6 and $CDCl_3$ solvents on a BrukerAvance DPX-250 (^{1}H NMR 250 MHz, 300 MHz and ^{13}C NMR 62.5 MHz, 75 MHz) with tetramethylsilane (TMS) as internal standards. FT-IR (KBr) spectra were recorded with a Shimadzu FTIR-8300 spectrophotometer. Elemental analyses were performed with a Thermo Finnigan CHNS-O 1112 series analyzer. Melting points measured in open capillary tubes in an Electrothermal IA 9000 and are uncorrected. The purity determination of the substrates and reaction monitoring was accomplished *via* TLC on silica gel PolyGram SILG/UV 254 nm plates (from Merck Company).

General Procedure for Preparation of the 1-Substituted Tetrazoles

A mixture of amine (1 mmol), triethylorthoformate (1.5 mmol), sodium azide (1.3 mmol) and 1 mol% Cu/C (0.021 g) was taken in a round-bottomed flask and stirred at 100 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature and the catalyst was separated by filtration. The resulting mixture was then extracted by ethyl acetate (3 × 10 ml). The combined organic layers were dried over anhydrous Na_2SO_4. After evaporation of the solvent, some of the crude products were purified by recrystallization from n-hexane and other products through column chromatography to afford the corresponding pure product.

1-Phenyl-1H-tetrazole (1). White solid, m. p.: 63-64 °C (Lit. [50]: 63-66 °C). IR (KBr): 760 (m), 1319 (m), 1490 (m), 1679 (s), 3051 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.03-7.10 (m, 3H), 7.26-7.33 (m, 2H), 8.22 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 118.8, 123.4, 129.4, 145.3, 149.1. Anal. Calcd. for $C_7H_6N_4$ (146.151): C, 57.53; H, 4.14. Found: C, 57.49; H, 3.98.

1-m-tolyl-1H-tetrazole (2). White solid, m. p.: 52-54 °C (Lit. [51]: 52-54 °C). IR (KBr): 786 (m), 1323 (m), 1602 (m), 1682 (s), 2921 (w), 3158 (w) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.31 (s, 3H), 6.84-6.91 (m, 3H), 7.16-7.27 (m, 1H), 8.23 (s, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.7, 116.0, 120.3, 124.3, 129.2, 138.9, 145.4, 150.1. Anal. Calcd. for $C_8H_8N_4$ (160.176): C, 59.99; H, 5.03. Found: C 60.11, H 4.89.

1-(3-Methoxyphenyl)-1H-tetrazole (3)
White solid, m.p: 67-68 °C (Lit. [52]: 68-69 °C). IR (KBr): 786 (m), 1153 (s), 1299 (s), 1475 (m), 1668 (s), 2947 (w), 3005 (w) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.68 (s, 3H), 6.57-6.64 (m, 3H), 7.16-7.26 (m, 1H), 8.25 (s, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 55.4, 104.9, 109.4, 111.3, 130.1, 146.3, 150.1, 160.2. Anal. Calcd. for $C_8H_8N_4O$ (176.175): C, 54.54; H, 4.58. Found: C, 54.39; H, 4.71.

1-(4-Fluorophenyl)-1H-tetrazole (4). White solid, m. p.: 90-92 °C (Lit. [53]: 91-92 °C). IR (KBr): 829(s), 1242(s), 1330(m), 1522(s), 1642(w), 2960(m) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.97-6.99 (m, 4H), 8.05 (s, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 115.8, 116.2, 120.4, 141.4, 161.3. Anal. Calcd. for $C_7H_5FN_4$ (164.140): C, 51.22; H, 3.07. Found: C, 51.10; H, 2.96.

1-(3-Chlorophenyl)-1H-tetrazole (5). White solid, m. p.: 138-140 °C (Lit. [54]: 138-140 °C). IR (KBr): 774 (s), 857 (m), 1316 (s), 1592 (s), 1655 (s), 3065 (w) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.91 (d, 1H, J = 7.9 Hz), 7.04-7.09 (m, 1H), 7.20 (s, 1H), 7.24 (d, 1H, J = 7.5 Hz), 8.14 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 117.5, 119.3, 123.7, 130.3, 135.1, 146.1, 150.1. Anal. Calcd. for $C_7H_5ClN_4$ (180.594): C, 46.55; H, 2.79. Found: C, 46.68; H, 2.91.

1-(4-Bromophenyl)-1H-tetrazole (6). White solid, m. p.: 176-178 °C (Lit. [51]: 176-180 °C). IR (KBr): 767 (m), 821 (m), 1392 (m), 1534 (m), 1672 (s), 3258 (m) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.98 (dd, 2H,

J_1 = 2.1 Hz, J_2 = 6.7 Hz), 7.47 (dd, 2H J_1 = 2.1 Hz, J_2 = 6.7 Hz), 8.37 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 120.6, 121.5, 131.9, 132.8, 135.9, 158.7, 162.5. Anal. Calcd. for $C_7H_5BrN_4$ (225.046): C, 37.36; H, 2.24. Found: C, 37.22; H, 2.36.

1-(3,5-Dichlorophenyl)-1H-tetrazole (7). White solid, m. p.: 126-128 °C (Lit. [50]: 127-128 °C). IR (KBr): 788 (s), 839 (m), 1166 (m), 1587 (s), 1667 (s), 3075 (m) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.01 (d, 1H, J = 1.6 Hz), 7.17 (d, 1H, J = 1.6 Hz), 7.51 (d, 1H, J = 1.7 Hz), 8.38 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.8, 118.2, 124.9, 135.4, 138.5, 158.9, 161.9. Anal. Calcd. for $C_7H_4Cl_2N_4$ (215.039): C 39.10, H 1.87. found: C, 38.95; H, 1.73.

1-(Naphthalen-1-yl)-1H-tetrazole (8). White solid, m. p.: 180-182 °C (Lit. [55]: 181-183 °C). IR (KBr): 771 (m), 1388 (m), 1550 (m), 1658 (s), 3224 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (d, 1H, J = 7.2 Hz), 7.44-7.63 (m, 2H), 7.73 (d, 1H, J = 8.1 Hz), 7.80 (d, 1H, J = 8.4 Hz), 7.85-8.04 (m, 2H), 8.30 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 125.5, 125.7, 126.2, 126.3, 126.6, 126.8, 127.1, 128.6, 134.3, 159.8, 163.9. Anal. Calcd. for $C_{11}H_8N_4$ (196.208): C, 67.34; H 4.11. Found: C, 67.19; H, 4.23.

1-(3-(1H-tetrazol-1-yl)phenyl)ethan-1-one (9). White solid, m. p.: 147-148 °C (Lit. [56]: 147-148 °C). IR (KBr): 800(s), 1269(s), 1418(s), 1558(s), 1668(s), 1700(s), 3000(w), 3079(m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.61 (s, 3H), 7.41-7.50 (m, 1H), 7.70-7.76 (m, 1H), 7.94 (d, 1H, J = 8.1 Hz), 8.06 (s, 1H), 8.43 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.8, 119.4, 124.8, 125.2, 129.5, 137.6, 159.9, 162.8, 198.4. Anal. Calcd. for $C_9H_8N_4O$ (188.186): C, 57.44; H, 4.28. Found: C, 57.41; H, 4.41.

2-(1H-tetrazol-1-yl)benzo[d]thiazole (10). White solid, m. p.: 255-257 °C. IR (KBr): 747 (m), 1123 (s), 1436 (s), 1598 (s), 3059 (w) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.32 (t, 1H, J = 7.2 Hz), 7.43 (d, 1H, J = 6.6 Hz), 7.79 (d, 1H, J = 7.5 Hz), 7.95-8.03 (m, 1H), 8.69 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 121.3, 121.8, 122.5, 124.3, 126.8, 133.2, 134.0, 151.8. Anal. Calcd. for $C_8H_5N_5S$ (203.225): C, 47.28; H, 2.48. Found: C, 47.15; H, 2.59.

N-[2-(acetylamino)-4-(1H-tetraazol-1-yl)phenyl] acetamide (11). White solid, m. p.: 217-219 °C. IR (KBr): 738 (m), 1340 (s), 1417 (m), 1474 (m), 1515 (m), 1592 (w), 1630 (m), 2999 (w), 3107 (w). cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.54 (s, 6H), 7.62 (s, 1H), 8.04 (d, 2H, J = 8.7 Hz), 8.34 (s, 1H), 12.90 (s, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 15.3, 107.7, 111.4, 113.8, 114.3, 117.6, 139.8, 142.5, 156.6. Anal. Calcd. for $C_{11}H_{12}N_6O_2$(260.252): C, 50.77; H, 4.65. Found: C, 50.89; H, 4.72.

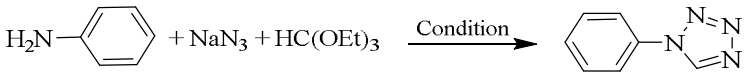
4-Methyl-7-(1H-tetrazol-1-yl)-2H-chromen-2-one (12). White solid, m. p.: 244-246 °C. IR (KBr): 842 (w), 1166 (w), 1264 (m), 1413 (m), 1586 (m), 1622 (m), 1691 (s), 2861 (w), 2925 (w) cm^{-1}. ^{1}H NMR (250 MHz, DMSO-d_6): δ = 2.37 (s, 3H), 6.24 (d, 1H, J = 5.7 Hz), 7.41-7.46 (m, 1H), 7.66-7.72 (m, 2H), 8.35 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 18.5, 103.8, 105.8, 112.9, 115.5, 126.6, 141.8, 153.5, 154.1, 160.9, 163.2. Anal. Calcd. for $C_{11}H_8N_4O_2$ (228.207): C, 57.89; H, 3.53. Found: C, 57.96; H, 3.39.

RESULTS AND DISCUSSION

The copper nanoparticle on charcoal (Cu/C) as catalyst was synthesized according to our previously published procedures (Scheme 1) [28]. The reaction of aniline, triethylorthoformate and sodium azide in the presence of Cu/C as a model reaction was carried out in various solvents, temperatures and with different catalysts to optimize the reaction conditions and the results are summarized in Table 1.

The model reaction was primarily performed in DMSO and a good yield of the product was obtained after 5 h (Table 1, entry 1). Whereas in DMF, the yield of the desired product decreased to 74% in the same hours (Table 1, entry 2). When the reaction was accomplished in 2-ethylhexanol, the product was obtained with a lower yield (Table 1, entry 3), while in PEG 200 and water as green solvents, the yield increased to 82% and 86% respectively after 4 h (Table 1, entries 4-5). The model reaction was then tested in solvent-free condition, and excellent yield of the product (92%) was obtained in the shortest reaction time (Table 1, entry 6). Also, the reaction in toluene led to the desired product with 73% yield after 7 h (Table 1, entry 7). The other organic solvents, such as acetone, ethyl acetate, chloroform, and THF, afforded the desired product in not satisfactory yields and prolonged reaction times (Table 1, entry 8-11). The reaction resulted in a lower yield when it was accomplished

Table 1. Effect of Various Conditions on Model Reaction



Entry	Solvent	Catalyst (mol%)	Temperature (ºC)	Time (h)	Yield (%)
1	DMSO	Cu/C (1)	100	5	81
2	DMF	Cu/C (1)	100	5	74
3	2-Ethylhexanol	Cu/C (1)	100	6	67
4	PEG 200	Cu/C (1)	100	4	82
5	H_2O	Cu/C (1)	Reflux	4	86
6	-	Cu/C (1)	100	1.5	92
7	Toluene	Cu/C (1)	100	7	73
8	Acetone	Cu/C (1)	Reflux	7	62
9	EtOAc	Cu/C (1)	Reflux	9	58
10	$CHCl_3$	Cu/C (1)	Reflux	9	63
11	THF	Cu/C (1)	Reflux	4	43
12	MeCN	Cu/C (1)	Reflux	5	72
13	MeOH	Cu/C (1)	Reflux	5	81
14	EtOH	Cu/C (1)	Reflux	5	79
15	-	Cu/C (1)	70	2	68
16	-	Cu/C (1)	120	1	95
17	-	Activated Charcoal	100	3	33
18	-	-	100	12	0
19	-	Cu/C (0.5)	100	2	84
20	-	Cu/C (2)	100	1.5	95
21	-	$CuSO_4$	100	2	58
22	-	$Cu(OAc)_2$	100	2	64
23		CuI	100	2.5	46

[a]Reaction condition: aniline (1 mmol), triethylorthoformate (1.5 mmol), sodium azide (1.3 mmol) and Cu/C (1 mol%). [b]Isolated yields.

in acetonitrile (Table 1, entry 12). The model reaction was completed in methanol and ethanol with 81% and 79% yield of the target product, respectively, after 5 h (Table 1, entries 13-14). According to these results, solvent-free reaction condition is the best synthetic protocol.

In order to optimize the reaction temperature, the model reaction was conducted at different temperatures under solvent-free condition. When the model reaction was carried out at 70 ºC, the yield was not satisfactory (Table 1, entry 15). In spite of the increase in reaction temperature from 100 ºC to 120 ºC, there was no considerable effect on the reaction in terms of yield and reaction time (Table 1, entry 16). The yield decreased to 33% when activated charcoal was used (Table 1, entry 17). No significant progress was observed in the absence of the catalyst (Table 1, entry 18). These results suggest that the proposed catalyst is effective for this transformation.

The effect of catalyst loading was also studied by performing the model reaction at different amounts of the catalyst. When the reaction was carried out in the presence of 0.5 mol% of the catalyst, the desired product was obtained with 84% yield (Table 1, entry 19). Increasing the amount of catalyst to 2 mol% was not effective (Table 1, entry 20). A comparative study of a variety of catalysts was carried out to distinguish the superiority of Cu/C over some other catalysts. By using $CuSO_4$ as a copper source, the yield of the desired product decreased to 58% (Table 1, entry 21). The results showed that a moderate yield (64%) could be obtained in the presence of $Cu(OAc)_2$ (Table 1, entry 22). Also, the model reaction was tested with CuI and a decrease in the yield was observed (Table 1, entry 23).

After optimization of the reaction conditions, we examined the generality of the present protocol by accomplishing the reaction of different amines with triethylorthoformate and sodium azide in the presence of Cu/C under solvent-free condition. The results are tabulated in Table 2. Amines carrying different functional groups were subjected to the coupling reactions and in all cases, a high yield of the desired product was obtained. It was observed that under similar conditions, a wide range of anilines containing electron-withdrawing as well as electron-donating groups such as fluoro, chloro, methoxy, methyl, and nitro underwent condensation in short reaction times with high isolated yields.

2-Methyl aniline reacts similarly with aniline to provide the corresponding tetrazoles (Table 2, entry 2). The success with 2-methyl aniline encouraged us to test the reactivity of other electron-rich amines under these conditions. Supreme yield was obtained for 3-methoxy aniline (Table 2, entry 3). Anilines with halo substituents in *meta* and *para* positions reacted well, providing the corresponding products in moderately good yields (Table 2, entries 4-7).

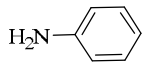
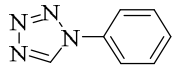
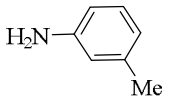
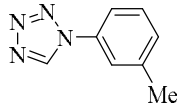
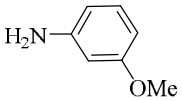
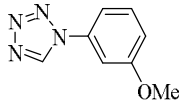
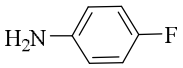
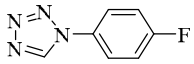
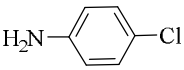
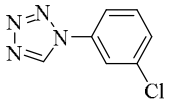
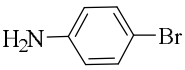
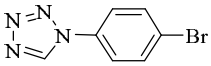
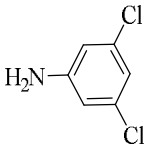
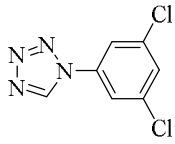
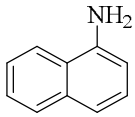
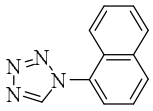
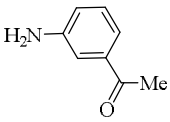
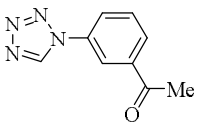
Sterically hindered aryl amines such as 1-aminonaphthalene also reacted without any problems to give the corresponding tetrazole 8 in a good yield (Table 2, entry 8). Compared with electron-withdrawing groups such as fluoro, chloro, and bromo present on the aromatic ring (Table 2, entries 4-7), 3-aminoacetophenone gave only 1*H*-tetrazole with carbonyl (ketone) functionality untouched (Table 2, entry 9). Heteroaromatic amine such as 2-aminobenzothiazole gave the corresponding tetrazole in good yields (Table 2, entry 10). Aromatic amine containing amide substituent gave the corresponding tetrazole in good yields (Table 2, entry 11). Finally, the capability of Cu/C mediated [3+2] cycloaddition leading to tetrazole coumarin was studied. For this purpose, 7-amino-4-methylcoumarin was converted into compound 12 in 63% yield within 5 h (Table 2, entry 12).

As recyclability is an important factor for an industrially accepted catalyst, reuse efficiency of Cu/C was investigated. It is noteworthy that the recovered catalyst was separated by filtration and reused, after the fifth cycle, the exhibited comparable activity is as shown in Fig. 1. The amount of Cu loaded in the catalyst used after five times was determined using elemental analysis (ICP) as 9.86% (w/w).

CONCLUSIONS

In summary, various tetrazoles have been synthesized from readily available primary amines, triethylorthoformate, and sodium azide using inexpensive and nontoxic Cu/C under solvent free condition at 100 °C, leading to a good to excellent yield. The catalyst is separable by simple filtration after completion of the reaction and can be used for at least five times without loss of catalytic activity. The easy synthesis of catalyst, elimination of toxic catalyst and solvent and a simple work-up procedure are significant benefits of the proposed method.

Table 2. Synthesis of Different Tetrazoles from Various Amines[a]

Entry	Amine	Product	Time (h)	Yield (%)[b]	Ref.
1		 1	1.5	92	[50]
2		 2	2	91	[51]
3		 3	2.5	88	[52]
4		 4	2	87	[53]
5		 5	3	78	[54]
6		 6	3	84	[51]
7		 7	3	64	[50]
8		 8	2.5	62	[55]
9		 9	2	71	[56]

[a]Reaction condition: aniline (1 mmol), triethylorthoformate (1.5 mmol), sodium azide (1.3 mmol) and Cu/C (1 mol%). [b]Isolated yields.

Table 2. Continued

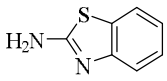
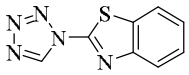
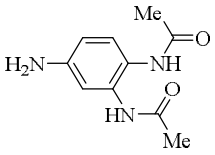
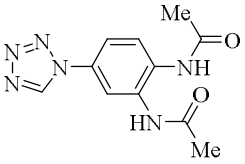
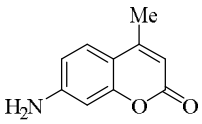
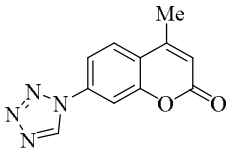
10		 10	4	74
11		 11	6	62
12		 12	5	63

Fig. 1. Catalytic activity of cu/c in five cycles for the synthesis of 1-substituted 1*H*-tetrazoles.

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