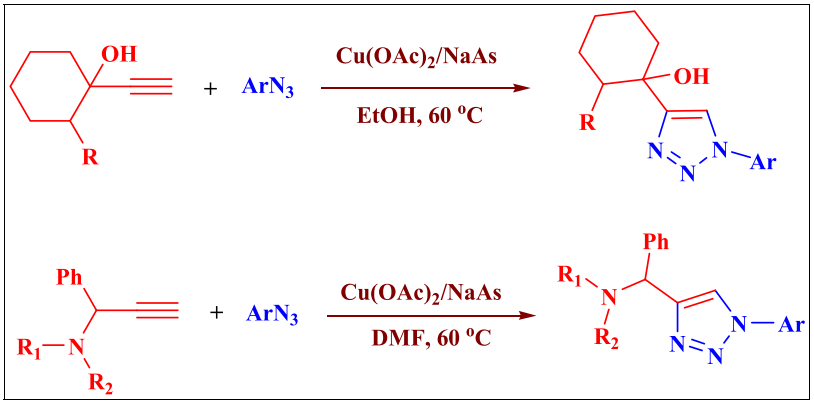
Synthesis of 1,4-Disubstituted 1,2,3-Triazoles via 1,3-Dipolar Cycloaddition/C–N Coupling of Propargyl Alcohols/amines and Aryl Azides

Mohammad Bakherad,* Ahmad Kakavand Ghalenoei, and Ali Keivanloo

Faculty of Chemistry, Shahrood University of Technology, Shahrood, Iran
*E-mail: m.bakherad@yahoo.com
Received May 5, 2018
DOI 10.1002/jhet.3325
Published online 00 Month 2018 in Wiley Online Library (wileyonlinelibrary.com).



1,4-Disubstituted 1,2,3-triazoles are prepared through the 1,3-dipolar cycloaddition of propargyl (alcohols/amines) and aryl azides in the presence of a mixture of $Cu(OAc)_2.H_2O$ and NaAs as the catalyst. This method offers the advantages of mild experimental conditions, operational simplicity, and high-to-excellent reaction yields.

J. Heterocyclic Chem., **00,** 00 (2018).

INTRODUCTION

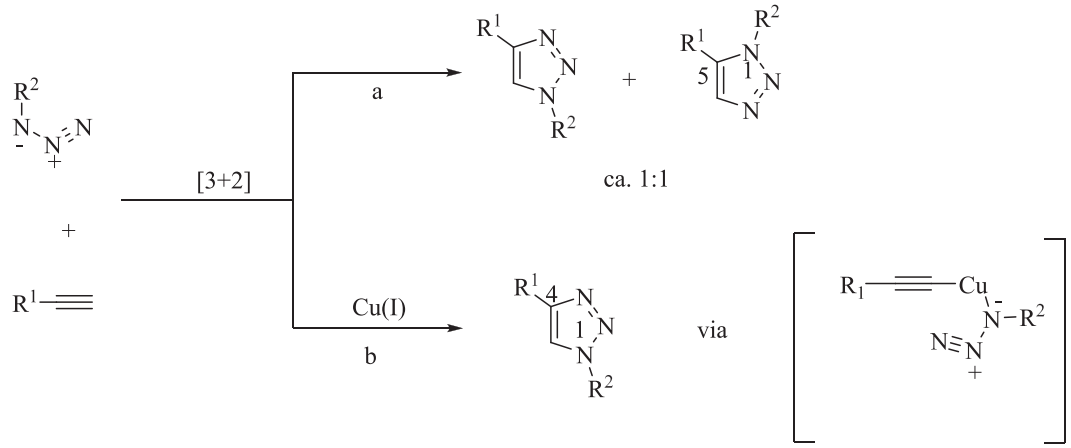
It has been noticed that triazol has different usages in research works as a building block for complex chemical compounds like pharmaceutical drugs such as the antibacterial, antifungal, antiviral, anticancer, antimicrobial, antidepressant, anticonvulsant, central nervous system modulators, and anti-inflammatory ones [1–5]. Several methods have been claimed for the synthesis of 1,2,3-triazoles. A widespread method used for the synthesis of 1,2,3-triazoles is the addition of organoazides to alkynes [6–17]. This well-appointed method is utilized for the synthesis of the 1,2,3-triazol system based on the thermal 1,3-dipolar Huisgen cycloaddition of organic azides with alkynes (Scheme 1). The Huisgen 1,3-dipolar cycloaddition of organic azides to alkynes is one of the most significant synthetic ways to the 1,2,3-triazol derivatives [18], applied as dyes, photostabilizers, biochemicals, and agrochemicals [19–21]. This transformation indicates a high chemoselectivity because many functional groups do not respond to azides or alkynes.

However, Huisgen cycloaddition usually requires a high-reaction temperature and results in the formation of a mixture of 1,4- and 1,5-regioisomers. In 2002, the Sharpless [22] and Meldal [23] teams have independently claimed that copper catalysts dramatically fasten the reaction and make it totally regioselective to the 1,4-regioisomer [c]. The copper-catalyzed region selective 1,3-dipolar cycloaddition ("click reaction") is now used for the syntheses of various complex materials [24–28].

Recently, various copper catalysts such as Cu_2O [29], CuI [30,31], $CuSO_4.5H_2O$ [32,33], CuBr $(PPh_3)_3$ [34], polymeric imidazole-Cu (II) [35], Cu/SiO_2 [36], Cu/C [37], and polymer-capped Cu/Cu_2O [38] have been investigated for this purpose. In this letter, we wish to report the synthesis of new derivatives of 1,4-disubstituted 1,2,3-triazol via 1,3-dipolar cycloaddition/C–N coupling of propargyl (alcohols/amines) and aryl azides in the presence of a mixture of $Cu(OAc)_2.H_2O$ and NaAs at 60°C in ethanol as the solvent.

The nitrogen ligands allow the use of copper catalysts in reduced amounts compared with the original classic catalyst ($Cu(OAc)_2.H_2O$ and sodium ascorbate), which is still the most commonly utilized catalyst but in much larger quantities that are often even stoichiometric or superior to stoichiometry [39]. Ligands have been applied to (a) avoid the formation of unreactive polynuclear copper(I) acetylides; (b) render ease coordination of the azide to the copper center at the ligand exchange step; and (c) develop the solubility of the copper complex to gain higher solution concentrations of the necessary Cu(I)-species [40]. A number of researchers have effectively decreased the required amount of the copper catalyst for the click reactions by the usage of ligands

Scheme 1. Synthesis of 1,2,3-triazol system based on thermal 1,3-dipolar Huisgen cycloaddition of organic azides with alkynes.



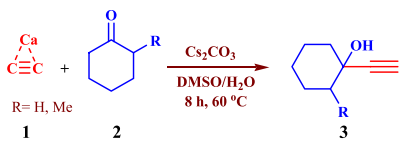
[41–43]. Recently, Deraedt *et al*. have used the dendrimer ligand to decrease the copper catalyst used to the ppm scale in simple click reactions [44].

Propargyl (alcohols/amines) were prepared according to a reported procedure [45]. On one hand, the treatment of calcium carbide **1** with various aldehydes or ketones **2** in dimethyl sulfoxide (DMSO)/H_2O (50:1) in the presence of Cs_2CO_3, as a base, afforded propargyl alcohols **3** in good yields (Scheme 2). On the other hand, the reaction of calcium carbide **1**, benzaldehyde **4**, an amine **5**, and CuI (as the catalyst) in CH_3CN at 80°C afforded a propargyl amine **6** in a good yield (Scheme 3).

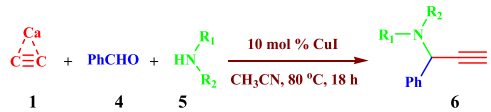
Then, we chose the reaction of a propargyl alcohol (R=H, **3a**) (1 equiv.) with 1-azido-4-nitrobenzene **7b** (1 equiv.), as a model reaction, using 10 mol% of $Cu(OAc)_2.H_2O$ and 20 mol% of sodium ascorbate as the catalyst. The effects of solvent, ligand, reaction temperature, and catalyst concentration were studied, and the results obtained were tabulated in Table 1. As shown in this table, the click reaction was most effective in the presence of 10 mol% of $Cu(OAc)_2.H_2O$ and 20 mol% of sodium ascorbate in ethanol at 60°C, giving the product **8b** with an excellent yield (95%) (Table 1, entry 12). Also, the effect of temperature on the click reaction was checked, and the results obtained were tabulated in Table 1. Increasing the temperature did not improve the reaction yield (Table 1, entry 13). It is obvious that at room temperature, a low product yield was formed (Table 1, entry 14). Moreover, increasing the amount of catalyst to 20 mol% showed no substantial improvement in the yield (Table 1, entry 15). However, decreasing the loading of the catalyst to 5 mol% lowered the reaction yield dramatically (Table 1, entry 16).

A large amount of a heavy metal catalyst is used in the classic copper-catalyzed click reactions, whereas Cu salts are toxic, pollute the biologically relevant compounds, and their complete removal from the reaction products is difficult. This problem inhibits the utilization of the click reactions in the biomedicine science. In order to decrease the amount of the copper catalyst, we decided to use the Schiff base ligands salen (L1), salophen (L2), metformine (L3) and ethylenediamine (L4), and O-phenylenediamine (L5), as additive in the reaction. Surprisingly, in the presence of L2 and with 2.5 mol% of $Cu(OAc)_2.H_2O$, this reaction proceeded accordingly and was completed to gain the estimated outcome in a 95% yield (Table 1, entry 22). As a result, the most suitable cases were 2.5 mol% of $Cu(OAc)_2.H_2O$, 5 mol% of sodium ascorbate, and 2.5 mol% of salophen (L2) at 60°C in ethanol (Table 1, entry 22).

Scheme 2. Synthesis of propargyl alcohols by reaction of calcium carbide with various ketones in dimethyl sulfoxide (DMSO)/H_2O. [Color figure can be viewed at wileyonlinelibrary.com]



Scheme 3. Synthesis of propargyl amines by reaction of calcium carbide, benzaldehyde, and an amine in CH_3CN. R_1R_2NH, dimethylamine, diethylamine, diperidine, morpholine. [Color figure can be viewed at wileyonlinelibrary.com]



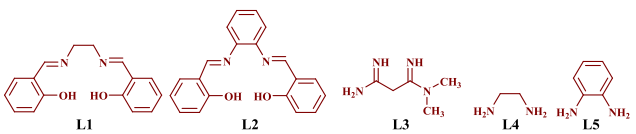
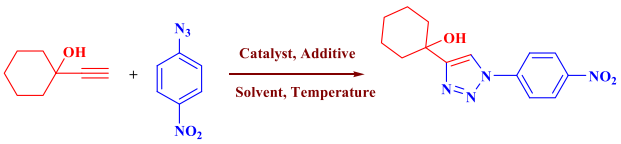


Table 1

Effects of various amounts of catalyst and solvent, and temperature and ligand on reaction of propargyl alcohol **3a** with 1-azido-4-nitrobenzene **7b**.[a] [Color table can be viewed at wileyonlinelibrary.com]



3a **7b** **8b**

Entry	Catalyst (mol%)	Additive	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
1[c]	CuI (10)	–	CH_3CN	60	4	81
2	CuI (10)	–	DMF	60	4	80
3	CuI (10)	–	H_2O	60	5	70
4	CuI (10)	–	EtOH	60	4	89
5	$CuSO_4.5H_2O$ (10)	–	CH_3CN	60	4	76
6	$CuSO_4.5H_2O$ (10)	–	DMF	60	6	74
7	$CuSO_4.5H_2O$ (10)	–	H_2O	60	10	65
8	$CuSO_4.5H_2O$ (10)	–	EtOH	60	6	85
9	$Cu(OAc)_2.H_2O$ (10)	–	CH_3CN	60	3	87
10	$Cu(OAc)_2.H_2O$ (10)	–	DMF	60	4	82
11	$Cu(OAc)_2.H_2O$ (10)	–	H_2O	60	5	78
12	$Cu(OAc)_2.H_2O$ (10)	–	EtOH	60	2	95
13	$Cu(OAc)_2.H_2O$ (10)	–	EtOH	78	2	95
14	$Cu(OAc)_2.H_2O$ (10)	–	EtOH	RT	10	64
15	$Cu(OAc)_2.H_2O$ (20)	–	EtOH	60	2	96
16	$Cu(OAc)_2.H_2O$ (5)	–	EtOH	60	10	63
17	$Cu(OAc)_2.H_2O$ (5)	L1	EtOH	60	2	75
18	$Cu(OAc)_2.H_2O$ (5)	L2	EtOH	60	2	96
19	$Cu(OAc)_2.H_2O$ (5)	L3	EtOH	60	2	77
20	$Cu(OAc)_2.H_2O$ (5)	L4	EtOH	60	2	82
21	$Cu(OAc)_2.H_2O$ (5)	L5	EtOH	60	2	80
22	$Cu(OAc)_2.H_2O$ (2.5)	L2	EtOH	60	2	95
23	$Cu(OAc)_2.H_2O$ (1)	L2	EtOH	60	4	77
24	$Cu(OAc)_2.H_2O$ (2.5)	L2	EtOH	RT	5	80

DMF, dimethylformamide; RT, room temperature.
[a]Reaction conditions: compound **3a** (1.0 mmol), 1-azido-4-nitrobenzene **7b** (1.0 mmol), copper salt, sodium ascorbate (twice the amount of copper salt), ligand (equal to copper salt), solvent (5 mL).
[b]Isolated yield.
[c]Without sodium ascorbate.

In order to explore the scope and generality of this protocol, a number of propargyl alcohols **3a–b** were reacted with aryl azied **8a–i** in the presence of $Cu(OAc)_2.H_2O$ at 60°C in ethanol. The desired products, 1,4-disubstitued 1,2,3-triazoles **8a–i**, were obtained in moderate-to-good yields. The results obtained are shown in Table 2. As shown in this table, the click reactions of compound **3** with aryl azides bearing an electron-donating (Table 2, entries 7 and 8) or electron-withdrawing group were obtained in high yields.

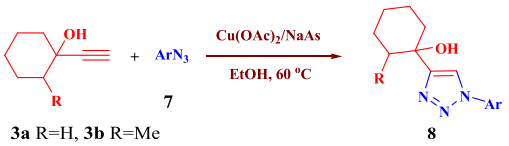
The structural assignments of compounds **8a–i** are based on the NMR spectroscopic and mass analysis data. The ^1H NMR spectrum for compound **8b** showed two doublets at δ 8.24 and δ 8.45, which were assigned to the four protons on the phenyl ring. Moreover, the singlet at δ 8.87 was due to the triazol ring. In the aliphatic region, we observed a singlet at δ 5.13, which is related to the OH group, and the three multiples at δ 1.40, 1.75, and 1.94 were assigned to the cyclohexanone group.

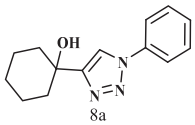
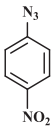
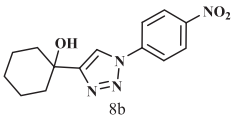
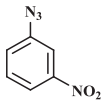
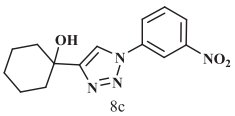
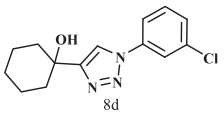
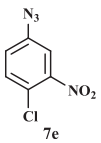
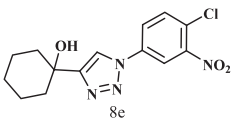
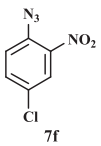
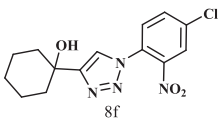
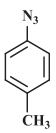
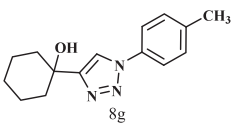
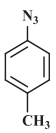
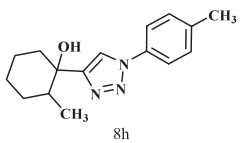
To extend the scope of our work, we next investigated the click reaction of propargyl amines **6** with aryl azides **7**, which afforded new 1,4-disubstituted 1,2,3-triazoles **9** in a good yield.

Initially, we chose the click reaction of *N*,*N*-diethyl-1-phenylprop-2-yn-1-amine **6a** with 1-azido-4-nitrobenzene **7a** in the presence of 5 mol% of $Cu(OAc)_2.H_2O$ and 10 mol% of sodium ascorbate as the model reaction. In order to find the optimal reaction conditions for the synthesis of compound **9a**, the effects of various solvents, catalysts, and ligands were studied, and the results obtained were tabulated in Table 3. As shown in this table, the reaction was most effective in the presence of 2.5 mol% of

Table 2

Synthesis of new 1,4-disubstituted 1,2,3-triazoles.[a] [Color table can be viewed at wileyonlinelibrary.com]

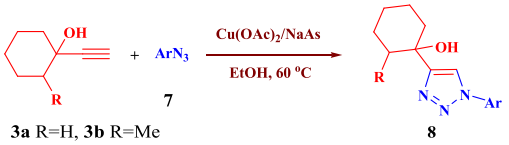


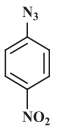
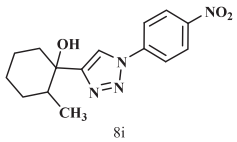
Entry	Propargyl alcohol	Aryl azide	Time (h)	Product	Yield[b] (%)
1	**3a**	 **7a**	3	 8a	93
2	**3a**	 **7b**	2	 8b	95
3	**3a**	 **7c**	5	 8c	82
4	**3a**	 **7d**	6	 8d	83
5	**3a**	 **7e**	8	 8e	75
6	**3a**	 **7f**	8	 8f	70
7	**3a**	 **7g**	3	 8g	98
8	**3b**	 **7h**	6	 8h	95

(*Continues*)

Table 2

(*Continued*)

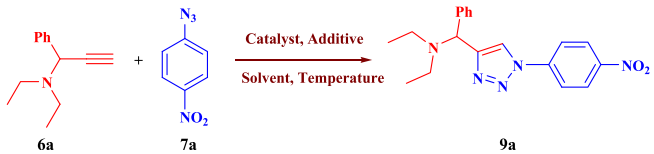


Entry	Propargyl alcohol	Aryl azide	Time (h)	Product	Yield[b] (%)
9	**3b**	 **7i**	5	 8i	80

[a]Reaction conditions: **3** (1 mmol), **7** (1 mmol), $Cu(OAc)_2.H_2O$ (2.5 mol%), sodium ascorbate (5 mol%), salophen (2.5 mol%), ethanol (5 mL), 60°C.
[b]Isolated yield.

Table 3

Effects of various catalysts and solvents and temperature and ligands on reaction of compound **6a** with 1-azido-4-nitrobenzene **7a**.[a] [Color table can be viewed at wileyonlinelibrary.com]



Entry	Catalyst (mol%)	Additive	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
1[c]	CuI (10)	–	CH_3CN	Reflux	6	76
2	CuI (10)	–	DMF	60	6	80
3	CuI (10)	–	H_2O	Reflux	6	70
4	CuI (10)	–	EtOH	Reflux	6	85
5	$CuSO_4.5H_2O$ (10)	–	CH_3CN	Reflux	5	81
6	$CuSO_4.5H_2O$ (10)	–	DMF	60	8	83
7	$CuSO_4.5H_2O$ (10)	–	H_2O	Reflux	8	60
8	$CuSO_4.5H_2O$ (10)	–	EtOH	Reflux	8	78
9	$Cu(OAc)_2.H_2O$ (10)	–	CH_3CN	Reflux	5	86
10	$Cu(OAc)_2.H_2O$ (10)	–	DMF	60	2	95
11	$Cu(OAc)_2.H_2O$ (10)	–	H_2O	Reflux	5	67
12	$Cu(OAc)_2.H_2O$ (10)	–	EtOH	Reflux	6	77
13	$Cu(OAc)_2.H2O$ (10)	–	DMF	90	3	95
14	$Cu(OAc)_2.H_2O$ (10)	–	DMF	RT	8	56
15	$Cu(OAc)_2.H_2O$ (20)	–	DMF	60	2	97
16	$Cu(OAc)_2.H_2O$ (5)	–	DMF	60	10	72
17	$Cu(OAc)_2.H_2O$ (5)	L1	DMF	60	3	97
18	$Cu(OAc)_2.H_2O$ (5)	L2	DMF	60	3	79
19	$Cu(OAc)_2.H_2O$ (5)	L3	DMF	60	3	67
20	$Cu(OAc)_2.H_2O$ (5)	L4	DMF	60	3	80
21	$Cu(OAc)_2.H_2O$ (5)	L5	DMF	60	3	75
22	$Cu(OAc)_2.H_2O$ (2.5)	L1	DMF	60	3	97
23	$Cu(OAc)_2.H_2O$ (1)	L1	DMF	60	4	80

DMF, dimethylformamide; RT, room temperature.
[a]Reaction conditions: compound **6a** (1.0 mmol), 1-azido-4-nitrobenzene **7a** (1.0 mmol), copper salt, sodium ascorbate (twice the amount of copper salt), ligand (equal copper salt), solvent (5 mL).
[b]Isolated yield.
[c]Without sodium ascorbate.

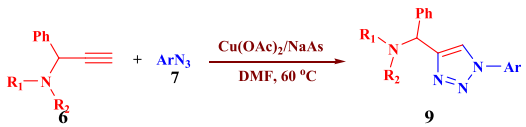
$Cu(OAc)_2.H_2O$, 5 mol% of sodium ascorbate, and 2.5 mol% of salen (L1) at 60°C in dimethylformamide, giving the desired product with a 97% yield (Table 3, entry 22).

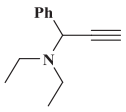
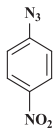
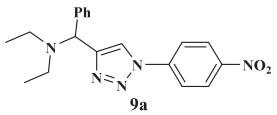
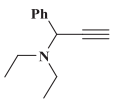
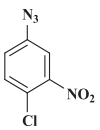
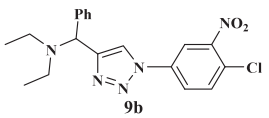
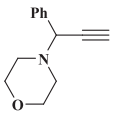
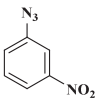
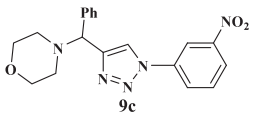
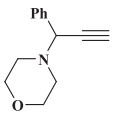
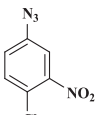
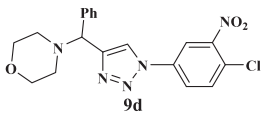
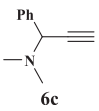
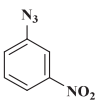
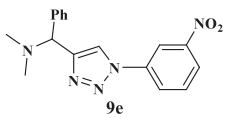
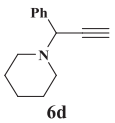
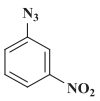
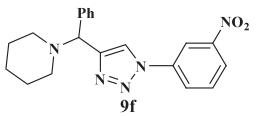
Using the aforementioned optimized conditions, the scope of the aryl azides was then examined. As shown in Table 4, various aryl azides performed well in the developed catalytic system. The corresponding products were isolated in good-to-high yields. The electronic effects of the substituents in aryl azides seemed to have a little effect on the reaction (Table 4).

The copper-catalyzed click reaction mechanism comprises the multi-general steps shown in Scheme 4: (a) formation of copper(I) acetylide A; this step occurs through a π-alkyne copper complex intermediate; (b) the

Table 4

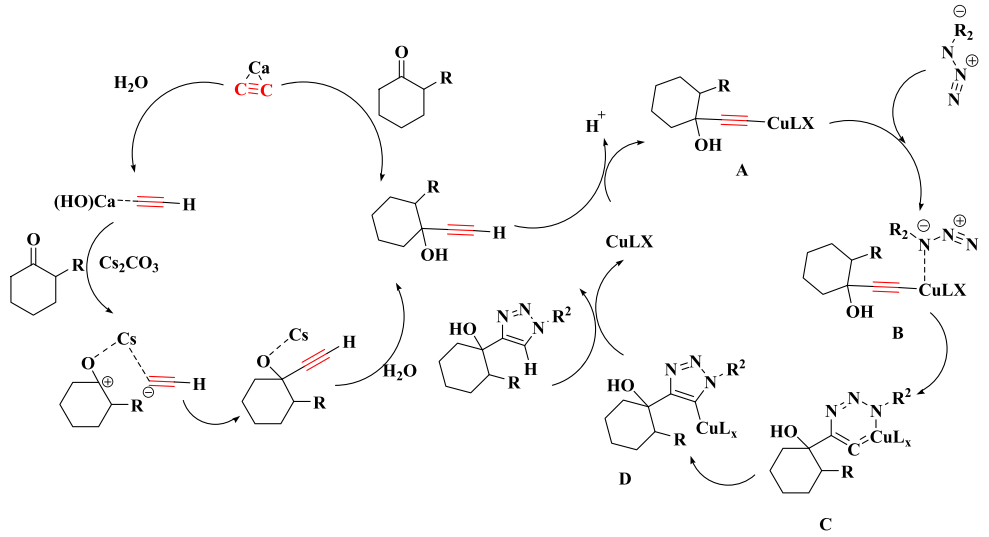
Synthesis of new 1,4-disubstituted 1,2,3-triazoles.[a] [Color table can be viewed at wileyonlinelibrary.com]



Entry	Propargyl amine	Aryl azide	Time (h)	Product	Yield[b] (%)
1	 6a	 7a	3	 9a	97
2	 6a	 7b	5	 9b	90
3	 6b	 7c	6	 9c	90
4	 6b	 7b	6	 9d	85
5	 6c	 7c	3	 9e	83
6	 6d	 7c	6	 9f	87

[a]Reaction conditions: compound **6** (1.0 mmol), aryl azide **7** (1.0 mmol), copper acetate (2.5 mol%), sodium ascorbate (5 mol%), salen (2.5 mol%), dimethylformamide (3 mL), 60°C.
[b]Isolated yield.

Scheme 4. Proposed mechanism for copper-catalyzed click reactions. [Color figure can be viewed at wileyonlinelibrary.com]



azide is activated by coordination to copper(I), framing intermediate B; (c) the first C–N bond formation affords the six-membered ring copper metallacycle C; (d) cyclization takes place to yield the copper triazol intermediate D; (e) proteolysis of the Cu–C bond gives the triazol product and regenerates the catalyst. Each stage involves a multi-nuclear Cu species [46].

In conclusion, we demonstrated an efficient and successful click reaction protocol for the synthesis of new 1,4-disubstituted 1,2,3-triazoles via 1,3-dipolar cycloaddition/C–N coupling of propargyl alcohols/amines and aryl azides. This methodology offers several advantages like one-pot synthesis of a wide range of 1,2,3-triazol derivatives starting from propargyl alcohols/amines, simple reaction conditions, and readily available starting materials.

EXPERIMENTAL

General. The solvents and reagents used were all supplied from Merck (Darmstadt, Germany) or Fluka (Switzerland) and used without any further purification. Melting points were recorded on a thermocouple digital melting point apparatus. Fourier transform infrared spectra were obtained as potassium bromide pellets in the range of 400–4000 cm^{-1} on a Bomem MB series spectrometer (Germany). NMR spectra were recorded on a Bruker 300 MHz ^1H NMR, 75 MHz ^{13}C NMR spectrometer (Billerica, MA). Mass spectra were recorded on a 5975C spectrometer supplied from Agilent Technologies Company (Santa Clara, CA).

General procedure for coupling reaction to synthesize propargyl alcohols (3). To a vial was added 163 mg of Cs_2CO_3 (0.5 mmol), 200 mg CaC_2 (2.5 mmol), cyclohexanone (1 mmol), and 3 mL (DMSO/H_2O, 50:1). The mixture was bubbled with argon for 10 min, and the reaction was stirred at 60°C for 8 h. The resulting product was extracted with 20 mL ethyl acetate. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*, and the crude product obtained was purified by column chromatography (hexane/ethyl acetate: 5/1) [41].

General procedure for synthesis of propargyl amines (6). General procedure for A^3 coupling: A mixture of calcium carbide (1.2 mmol, 77 mg), benzaldehyde (1.0 mmol, 106 mg), diisopropylamine (1.5 mmol, 151.5 mg), and CuI catalyst (0.1 mmol, 20.0 mg) was added to a reaction tube (10 mL) with 2 mL CH_3CN. After stirring at 80°C for 18 h, the mixture was diluted with H_2O (10 mL), and the aqueous layer was extracted with diethyl ether (2 × 10 mL), dried over Na_2SO_4, and concentrated under vacuum to give the crude product. This crude product was further purified by column chromatography on silica gel (ethyl acetate/hexane, 1:4) to afford the corresponding pure aminopropyne [42].

General procedure for synthesis of 2-subsituted-1-(1-aryl-1*H*-1,2,3-triazol-4-yl) cyclohexanol (8a–i). 1-Ethynylcyclohexan-1-ol (1.5 mmol), an aryl azide (1 mmol), $Cu(OAc)_2.H_2O$ (10 mol%), and sodium ascorbate (20 mol%) were mixed in ethanol at 60°C. The mixture was extracted with ethyl acetate (3 × 10 mL), dried over Na_2SO_4, and concentrated under vacuum to give the crude product. The crude product was further purified by column chromatography on silica gel (ethyl acetate/hexane, 1:4) to afford the corresponding pure 1,2,3-triazol as the eluent (Table 2).

1-(1-Phenyl-1*H*-1,2,3-triazol-4-yl)cyclohexan-1-ol (8a). Yellow solid; mp 178–180°C; ^1H NMR (300 MHz, DMSO-d_6): δ 1.41–1.62 (m, 4H, CH_2 of cyclohexane), 1.69–1.81 (m, 4H, CH_2 of cyclohexane), 1.92–1.96 (m,

2H, CH_2 of cyclohexane), 5.06 (s, 1H, OH), 7.47 (t, J = 9 Hz, 1H, CH aromatic), 7.59 (t, J = 9 Hz, 2H, CH aromatic), 7.93 (d, J = 9 Hz, 2H, CH aromatic), 8.62 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.00, 25.42, 38.12, 73.81, 117.69, 122.14, 127.74, 130.06, 136.32, 153.13; IR (KBr): 3369, 3099, 3057, 2933, 2854, 1595, 1549, 1498, 1068 cm^{-1}; MS (EI), *m/z* $[M]^+$ 244.14; *Anal*. Calcd for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04; N, 17.27%; Found: C, 69.25; H, 7.19; N, 17.35%.

1-(1-(4-Nitrophenyl)-1H-1,2,3-triazol-4-yl)cyclohexan-1-ol (8b). Light brown solid; mp 209–210°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.34–1.47 (m, 4H, CH_2 of cyclohexane), 1.70–1.81 (m, 4H, CH_2 of cyclohexane), 1.93–1.96 (m, 2H, CH_2 of cyclohexane), 5.13 (s, 1H, OH), 8.25 (d, J = 8.9 Hz, 2H, CH aromatic), 8.44 (d, J = 8.9 Hz, 2H, CH aromatic), 8.87 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz, DMSO-d_6): δ 22.10, 25.65, 38.00, 68.41, 120.29, 120.69, 126.04, 141.53, 146.87, 157.87; IR (KBr): 3224, 3116, 3074, 2939, 2854, 1597, 1527, 1442, 1047 cm^{-1}; MS (EI), *m/z* $[M]^+$ 289.2; *Anal*. Calcd for $C_{14}H_{16}N_4O_3$: C, 58.32; H, 5.59; N, 19.43%; Found: C, 58.22; H, 5.41; N, 19.34%.

1-(1-(3-Nitrophenyl)-1H-1,2,3-triazol-4-yl)cyclohexan-1-ol (8c). Yellow solid; mp 194–195°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.32–1.98 (m, 10H, CH_2 of cyclohexane), 5.07 (s, 1H, OH), 7.89 (t, J = 7.95 Hz, 1H, CH aromatic), 8.30 (d, J = 7.5 Hz, 1H, CH aromatic), 8.43 (d, J = 7.5 Hz, 1H, CH aromatic), 8.75 (s, 1H), 8.90 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz, DMSO-d_6): δ 22.16, 25.68, 38.05, 68.41, 114.86, 120.33, 123.19, 126.19, 131.95, 137.88, 149.01, 157.60; IR (KBr): 3220, 3119, 3054, 2925, 2830, 1585, 1519, 1438, 1051 cm^{-1}; MS (EI), *m/z* $[M]^+$ 289.2; *Anal*. Calcd for $C_{14}H_{16}N_4O_3$: C, 58.32; H, 5.59; N, 19.43%; Found: C, 58.30; H, 5.55; N, 19.39%.

1-(1-(3-Chlorophenyl)-1H-1,2,3-triazol-4-yl)cyclohexan-1-ol (8d). White solid; mp 201–203°C; ^{1}H NMR (300 MHz, $CDCl_3$): ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.30–1.47 (m, 4H, CH_2 of cyclohexane), 1.66–1.81 (m, 4H, CH_2 of cyclohexane), 1.92–1.99 (m, 2H, CH_2 of cyclohexane), 5.07 (s, 1H, OH), 7.54 (d, J = 9 Hz, 1H, CH aromatic), 7.62 (t, J = 7.5 Hz, 1H, CH aromatic), 7.95 (d, J = 6 Hz, 1H, CH aromatic), 8.08 (t, J = 7.5 Hz, 1H, CH aromatic), 8.74 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz, DMSO-d_6): δ 22.15, 25.67, 38.05, 68.38, 118.07, 119.97, 120.03, 128.59, 132.08, 134.66, 138.33, 157.35; IR (KBr): 3226, 3103, 3059, 2933, 2854, 1668, 1591, 1485, 1153 cm^{-1}; MS (EI), *m/z* $[M]^+$ 278.2; *Anal*. Calcd for $C_{14}H_{16}ClN_3O$: C, 60.54; H, 5.81; N, 15.13%; Found: C, 60.67; H, 5.96; N, 15.25%.

1-(1-(4-Chloro-3-nitrophenyl)-1H-1,2,3-triazol-4-yl) cyclohexan-1-ol (8e). Light yellow solid; mp 197–198°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.46–1.56 (m, 4H, CH_2 of cyclohexane), 1.66–1.81 (m, 4H, CH_2 of cyclohexane), 1.93–2.00 (m, 2H, CH_2 of cyclohexane), 5.09 (s, 1H, OH), 8.02 (d, J = 8.7 Hz, 1H, CH aromatic), 8.32 (d, J = 8.8 Hz, 1H, CH aromatic), 8.72 (s, 1H, CH aromatic), 8.84 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz, DMSO-d_6): δ 22.13, 25.66, 38.06, 68.42, 117.12, 120.35, 124.50, 124.83, 133.59, 136.48, 148.59, 157.73; IR (KBr): 3216, 3112, 3041, 2917, 2821, 1585, 1519, 1437, 1101 cm^{-1}; MS (EI), *m/z* $[M]^+$ 323.2; *Anal*. Calcd for $C_{14}H_{15}ClN_4O_3$: C, 52.10; H, 4.68; N, 17.36%; Found: C, 52.21; H, 4.78; N, 17.44%.

1-(1-(4-Chloro-2-nitrophenyl)-1H-1,2,3-triazol-4-yl) cyclohexan-1-ol (8f). Yellow solid; mp 139–140°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.29–1.51 (m, 4H, CH_2 of cyclohexane), 1.70–1.85 (m, 4H, CH_2 of cyclohexane), 1.95–2.02 (m, 2H, CH_2 of cyclohexane), 5.15 (s, 1H, OH), 7.96 (d, J = 8.4 Hz, 1H, CH aromatic), 8.10 (d, J = 8.4 Hz, 1H, CH aromatic), 8.44 (s, 1H, CH of triazol), 8.55(s, 1H, CH aromatic); ^{13}C NMR (75 MHz, DMSO-d_6): δ 22.10, 25.65, 38.17, 68.44, 122.90, 125.83, 128.50, 129.01, 134.41, 135.05, 144.82, 157.07; IR (KBr): 3216, 3115, 3042, 2915, 2819, 1581, 1520, 1437, 1101 cm^{-1}; MS (EI), *m/z* $[M]^+$ 323.2; *Anal*. Calcd for $C_{14}H_{15}ClN_4O_3$: C, 52.10; H, 4.68; N, 17.36%; Found: C, C, 52.28; H, 4.74; N, 17.49%.

1-(1-(p-Tolyl)-1H-1,2,3-triazol-4-yl)cyclohexan-1-ol (8g). Brown solid; mp 148–150°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.37–1.52 (m, 4H, CH_2 of cyclohexane), 1.68–1.80 (m, 4H, CH_2 of cyclohexane), 1.92–1.95 (m, 2H, CH_2 of cyclohexane), 2.38 (s, 3H, CH_3) 5.02 (s, 1H, OH), 7.38 (d, J = 8.4 Hz, 2H, CH aromatic), 7.79 (d, J = 8.4 Hz, 2H, CH aromatic), 8.56 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz, DMSO-d_6): δ 22.16, 25.70, 38.12, 68.41, 88.197, 119.62, 120.13, 130.66, 135.06, 138.33, 157.14; IR (KBr): 3401, 3128, 3045, 2921, 2852, 1640, 1516, 1445, 1110 cm^{-1}; MS (EI), *m/z* $[M]^+$ 258.2; *Anal*. Calcd for $C15H_{19}N_3O$: C, 70.01; H, 7.44; N, 16.33%; Found: C, 70.12; H, 7.51; N, 16.47%.

2-Methyl-1-(1-(p-tolyl)-1H-1,2,3-triazol-4-yl)cyclohexan-1-ol (8h). White solid; mp 160–162; ^{1}H NMR (300 MHz, $CDCl_3$): ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.685 (dd, J = 6.9 Hz, 3H, CH_3), 1.30–1.55 (m, 3H, CH_2 of cyclohexane), 1.60–2.08 (m, 6H, CH_2 of cyclohexane), 2.35 (s, 3H, CH_3), 5.21 (s, 1H, OH), 7.37 (d, J = 8.4 Hz, 2H, CH aromatic), 7.72 (d, J = 8.7 Hz, 2H, CH aromatic), 8.32 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz, DMSO-d_6): δ 15.78, 23.69, 25.65, 29.83, 39.84, 41.80, 73.39, 88.19, 119.61, 120.11, 130.65, 135.04, 138.33, 157.12; IR (KBr): 3408, 3130, 3049, 2925, 2856, 1641, 1518, 1446, 1113 cm^{-1}; MS (EI), *m/z* $[M]^+$ 272.17; *Anal*. Calcd for $C_{16}H_{21}N_3O$: C, 70.82; H, 7.80; N, 15.49%; Found: C, 70.72; H, 7.69; N, 15.37%.

2-Methyl-1-(1-(4-nitrophenyl)-1H-1,2,3-triazol-4-yl) cyclohexan-1-ol (8i). Yellow solid; mp 126–128°C; ^{1}H NMR (300 MHz, $CDCl_3$): ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.833 (dd, J = 6.9 Hz, 3H, CH_3), 1.40–

1.55 (m, 3H, CH_2 of cyclohexane), 1.60–2.08 (m, 6H, CH_2 of cyclohexane), 5.21 (s, 1H, OH), 8.01 (d, J = 8.4 Hz, 2H, CH aromatic), 8.07 (s, 1H, CH of triazol), 8.44 (d, J = 8.7 Hz, 2H, CH aromatic); ^{13}C NMR (75 MHz, DMSO-d_6): δ 15.82, 23.70, 25.65, 29.85, 39.88, 41.88, 73.41, 119.09, 120.35, 125.54, 141.29, 147.11, 157.14; IR (KBr): 3365, 3134, 3089, 2925, 2856, 1599, 1516, 1448, 1107 cm^{-1}; MS (EI), m/z [M]$^+$ 272.17; *Anal*. Calcd for $C_{15}H_{18}N_4O_3$: C, 59.59; H, 6.00; N, 18.53%; Found: C, 59.46; H, 5.91; N, 18.45%.

General procedure for synthesis of (1-aryl-1H-1,2,3-triazol-4-yl)-N,N-dialkyl (phenyl) methanamine (9a–f). Propargyl amine **6** (1.0 mmol), an aryl azide (1.2 mmol), CuI (10 mol%), and *N*-ethyldiisopropylamine (15 mol%) were mixed in dimethylformamide at 60°C. The mixture was extracted with diethyl ether (2 × 10 mL), dried over Na_2SO_4, and concentrated under vacuum to give the crude product. This crude product was further purified by column chromatography on silica gel (ethyl acetate/hexane, 1:4) to afford the corresponding pure title compounds. All products gave satisfactory spectroscopic data.

N-Ethyl-N-((1-(4-nitrophenyl)-1H-1,2,3-triazol-4-yl)(phenyl) methyl) ethanamine (9a). White solid; mp 97–98°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.99 (t, 6H, $2CH_3$), 2.32–2.44 (m, 2H, CH_2), 2.52–2.61 (m, 2H, CH_2), 5.22 (s, 1H, CH), 7.26 (t, J = 7.2 Hz, 1H, CH aromatic), 7.34 (t, J = 7.2 Hz, 2H, CH aromatic), 7.48 (d, J = 7.5 Hz, 2H, CH aromatic), 8.28 (d, J = 7.75 Hz, 2H, CH aromatic), 8.45 (d, J = 9.3 Hz, 2H, CH aromatic) 9.03 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz, DMSO-d_6): δ12.54, 31.175, 43.52, 61.44, 120.86, 122.39, 126.01, 127.51, 128.60, 128.68, 141.42, 141.81, 146.98, 149.08; IR (KBr): 3130, 3093, 2951, 2858, 1624, 1535, 1452, 1346, 1198 cm^{-1}; MS (EI), m/z [M]$^+$ 352.2; *Anal*. Calcd for $C_{19}H_{21}N_5O_2$: C, 64.94; H, 6.02; N, 19.93%; Found: C, 64.83; H, 5.97; N, 19.86%.

N-((1-(4-Chloro-3-nitrophenyl)-1H-1,2,3-triazol-4-yl) (phenyl)methyl)-N-ethylethan-amine (9b). Brown solid; mp 134–136°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.99 (t, 6H, CH_3), 2.34–2.43 (m, 2H, CH_2), 2.55–2.59 (m, 2H, CH_2), 5.20 (s, 1H, CH), 7.25 (t, J = 7.2 Hz, 1H, CH aromatic), 7.34 (t, J = 7.35 Hz, 2H, CH aromatic), 7.47 (d, J = 7.2 Hz, 2H, CH aromatic), 8.02 (d, J = 9 Hz, 1H, CH aromatic), 8.34 (d, J = 8.7 Hz, 1H, CH aromatic), 8.76 (s, 1H CH aromatic), 8.98 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz, DMSO-d_6): δ12.59, 43.49, 61.43, 117.26, 122.41, 124.61, 124.94, 127.51, 128.60, 128.68, 133.53, 136.34, 141.79, 148.52, 148.97; IR (KBr): 3157, 3086, 2968, 2927, 2817, 1597, 1516, 1454, 1342, 1171 cm^{-1}; MS (EI), m/z [M]$^+$ 386.2; *Anal*. Calcd for $C_{19}H_{20}ClN_5O_2$: C, 59.14; H, 5.22; N, 18.15%; Found: C, 59.20; H, 5.24; N, 18.21%.

4-((1-(3-Nitrophenyl)-1H-1,2,3-triazol-4-yl)(phenyl)methyl) morpholine (9c). Light yellow solid; mp 150–152°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.36 (m, 4H, CH_2 morpholine), 3.60 (m, 4H, CH_2 morpholine), 4.73 (s, 1H, CH), 7.28 (t, J = 7.2 Hz, 1H, CH aromatic), 7.36 (t, J = 7.35 Hz, 2H, CH aromatic), 7.53 (d, J = 7.2 Hz, 2H, CH aromatic), 7.89 (t, J = 8.25 Hz, 1H, CH aromatic), 8.32 (d, J = 8.1 Hz, 1H, CH aromatic), 8.44 (d, J = 8.1 Hz, 1H, CH aromatic) 8.78 (s, 1H, CH aromatic), 9.1 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz, DMSO-d_6): δ 51.98, 66.72, 67.46, 115.16, 122.34, 123.46, 126.49, 127.94, 128.93, 128.97, 131.91, 137.73, 140.33, 148.95, 149.41; IR (KBr): 3093, 2962, 2924, 2858, 1641, 1541, 1452, 1351, 1190 cm^{-1}; MS (EI), m/z [M]$^+$ 366.2; *Anal*. Calcd for $C_{19}H_{19}N_5O_3$: C, 62.46; H, 5.24; N, 19.17%; Found: C, 62.53; H, 5.33; N, 19.24%.

4-((1-(4-Chloro-3-nitrophenyl)-1H-1,2,3-triazol-4-yl)(phenyl) methyl) morpholine (9d). Yellow solid; mp 154–156°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.36 (m, 4H, CH_2 morpholine), 3.60 (m, 4H, CH_2 morpholine), 5.20 (s, 1H, CH), 7.29 (t, J = 7.2 Hz, 1H, CH aromatic), 7.37 (t, J = 7.00 Hz, 2H, CH aromatic), 7.51 (d, J = 7.0 Hz, 2H, CH aromatic), 8.01 (d, J = 9 Hz, 1H, CH aromatic), 8.32 (d, J = 8.7 Hz, 1H, CH aromatic), 8.74 (s, 1H, CH aromatic), 8.99 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz, DMSO-d_6): δ51.95, 66.74, 67.38, 117.37, 122.33, 124.68, 125.07, 127.94, 128.92, 128.94, 133.49, 136.35, 140.22, 148.51, 149.49; IR (KBr): 3171, 3095, 2958, 2921, 2812, 1591, 1518, 1450, 1345, 1191 cm^{-1}; MS (EI), m/z [M]$^+$ 400.2; *Anal*. Calcd for $C_{19}H_{18}ClN_5O_3$: C, 57.08; H, 4.54; N, 17.52%; Found: C, 57.16; H, 4.61; N, 17.55%.

N,N-*Dimethyl-1-(1-(3-nitrophenyl)-1H-1,2,3-triazol-4-yl)-1-phenylmethanamine (9e).* Yellow solid; mp 96–98°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.15 (s, 6H, $2CH_3$), 4.65 (s, 1H, CH), 7.26 (t, J = 7.2 Hz, 1H, CH aromatic), 7.35 (t, J = 7.00 Hz, 2H, CH aromatic), 7.50 (d, J = 7.0 Hz, 2H, CH aromatic), 7.88 (t, J = 8.1 Hz, 1H, CH aromatic), 8.32 (d, J = 8.7 Hz, 1H, CH aromatic), 8.45 (d, J = 8.7 Hz, 1H, CH aromatic), 8.79 (s, 1H, CH aromatic), 9.11 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz, DMSO-d_6): δ43.73, 67.94, 115.05, 122.11, 123.42, 126.37, 127.78, 128.74, 128.82, 131.93, 137.75, 141.29, 148.98, 149.96; IR (KBr): 3135, 3095, 2954, 2850, 1626, 1531, 1455, 1341, 1190 cm^{-1}; MS (EI), m/z [M]$^+$ 324.2; *Anal*. Calcd for $C_{17}H_{17}N_5O_2$: C, 63.15; H, 5.30; N, 21.66%; Found: C, 63.24; H, 5.37; N, 21.71%.

1-((1-(3-Nitrophenyl)-1H-1,2,3-triazol-4-yl)(phenyl)methyl) piperidine (9f). Yellow solid; mp 159–161°C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.36–1.37 (m, 2H, CH_2 of piperidine), 1.52 (m, 4H, CH_2 of piperidine), 2.34 (m, 4H, CH_2 of piperidine), 5.09 (s, 1H, CH), 7.26 (t, J = 7.05 Hz, 1H, CH aromatic), 7.34 (t, J = 7.35 Hz, 2H, CH aromatic), 7.48 (d, J = 7.2 Hz, 2H, CH aromatic), 7.88 (t, J = 8.25 Hz, 1H, CH aromatic), 8.32 (d, J = 8.1 Hz, 1H, CH aromatic), 8.45 (d, J = 8.1 Hz, 1H,

CH aromatic), 8.78 (s, 1H, CH aromatic), 9.04 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz, DMSO-d_6): δ 24.58, 26.18, 52.19, 67.31, 115.08, 122.21, 123.37, 126.41, 127.62, 128.73, 128.79, 131.90, 137.78, 140.90, 149.00, 149.51; IR (KBr): 3161, 3095, 2960, 2931, 2812, 1590, 1516, 1457, 1343, 1112 cm^{-1}; MS (EI), *m/z* $[M]^+$ 363.2; *Anal.* Calcd for $C_{20}H_{21}N_5O_2$: C, 66.10; H, 5.82; N, 19.27%; Found: C, 66.13; H, 5.89; N, 19.32%.

Acknowledgment. We wish to express our thanks to the Research Council of the Shahrood University of Technology for the financial support of this work.

REFERENCES AND NOTES

[1] Kaku, Y.; Tsuruoka, A.; Kakinuma, H.; Tsukada, I.; Yanagisawa, M.; Naito, T. Chem Pharm Bull 1998, 46, 1125.

[2] Koltin, Y.; Hitchcock, C. A. Curr Opin Chem Biol 1997, 1, 176.

[3] Abdo, N. Y. M.; Kamel, M. M. Chem Pharm Bull 2015, 63, 369.

[4] Tang, R.; Jin, L.; Mou, C.; Yin, J.; Bai, S.; Hu, D.; Wu, J.; Yang, S.; Song, B. Chem Cen J 2013, 7, 30.

[5] Papadopoulou, M. V.; Bloomer, W. D.; Rosenzweig, H. S.; Ashworth, R.; Wilkinson, S. R.; Kaiser, M.; Andriani, G.; Rodriguez, A. Future Med Chem 2013, 5, 1763.

[6] Sha, C.-K.; Mohanakrishan, A. K.; Padwa, A.; Pearson, W. H. (Eds) Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products; Wiley: New York, 2003, pp. 623–680.

[7] Gothelf, K. V.; Jorgensen, K. A Chem Rev 1998, 98, 863.

[8] Mitali, C.; Praveen, S. G.; Arvind, K.; Diganta, S. Tetrahedron Lett 2018, 59, 397.

[9] Abdul, A. A.; Dhrubajyoti, G.; Amrita, K. C.; Alak, K. B.; Diganta, S. Bioorg Med Chem Lett 2017, 27, 3698.

[10] Mitali, C.; Abdul, A. A.; Ankur, B.; Diganta, S. J Chem Sci 2017, 129, 1211.

[11] Abdul, A. A.; Manashjyoti, K.; Mitali, C.; Diganta, S. Tetrahedron Lett 2016, 57, 5661.

[12] Manashjyoti, K.; Abdul, A. A.; Mitali, C.; Prakash, J. S.; Nageshwar, D. K.; Diganta, S. Chem Sel 2016, 1, 6016.

[13] Manashjyoti, K.; Abdul, A. A.; Mitali, C.; Prakash, J. S.; Diganta, S. Tetrahedron Lett 2016, 57, 4473.

[14] Abdul, A. A.; Mitali, C.; Diganta, S. Teterahedron Lett 2016, 57, 1711.

[15] Abdul, A. A.; Mitali, C.; Bishwajit, S.; Prakash, J. S.; Diganta, S. Tetrahedron Lett 2015, 56, 5892.

[16] Mitali, C.; Abdul, A. A.; Diganta, B.; Lakshi, S.; Diganta, S. New J Chem 2015, 39, 5902.

[17] Abdul, A. A.; Mitali, C.; Prakash, J. S.; Diganta, S. RSC Adv 2014, 4, 64388.

[18] Huisgen, R.; Padwa, A. 1,3-Dipolar Cycloaddition Chemistry; Wiley: New York, 1984; Vol.1, Ch 1, pp. 1–176.

[19] Alvarez, R.; Velazque, S.; San, F.; Aquaro, S.; De, C.; Perno, C. F.; Karlsson, A.; Balzarini, J.; Camarasa, M. J. J Med Chem 1994, 37, 4185.

[20] Genine, M. J.; David, D. A.; Anderson, J.; Barbachyn, M. R.; Emmert, D. E.; Garmon, S. A.; Graber, D. R.; Grega, K. C.; Hester, J. B.; Hutchinson, D. K.; Morris, J.; Reischer, R. J.; Ford, C. W.; Zurenko, G. E.; Hamel, J. C.; Schaadt, R. D.; Stapert, D.; Yagi, B. H. J. Med Chem 2000, 43, 953.

[21] Brik, A.; Lin, Y. C.; Elder, J.; Wong, C. H. Chem Biol 2002, 9, 891.

[22] Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. Angew Chem, Int Ed 2002, 41, No. 14.

[23] Tornøe, C. W.; Christensen, C.; Meldal, M. J Org Chem 2002, 67, 3057.

[24] Pachon, L. D.; Van Maarseveen, J. H.; Rothenberg, G. Adv Synth Catal 2005, 347, 811.

[25] Himo, F.; Lovell, T.; Hilgraf, R.; Rostovtsev, V. V.; Noodles, L.; Sharpless, K. B.; Fokin, V. V. J Am Chem Soc 2005, 127, 210.

[26] Valentin, O.; Valery, V. F.; Finn, M. G. Angew Chem, Int Ed 2005, 44, 2210.

[27] Sen, G. S.; Raja, K. S.; Kaltgrad, E.; Strable, E.; Finn, M. G. Chem Commun 2005 4315.

[28] Kim, J. Y.; Park, J. C.; Kang, H.; Song, H.; Park, K. H. Chem Commun 2010, 46, 439.

[29] Francisco, A.; Yanina, M.; Gabriel, R.; Miguel, Y. Synlett 2012, 23, 2179.

[30] Gary, A. M.; Jungyeob, H. Org Lett 2006, 13, 2767.

[31] Ilgen, F.; Konig, B. Green Chem 2009, 11, 848.

[32] Mukherjee, N.; Ahammed, S.; Bhadra, S.; Ranu, B. C. Green Chem 2013, 15, 389.

[33] Feldman, A. K.; Colasson, B.; Fokin, V. V. Org Lett 2004, 22, 3897.

[34] Lal, S.; Díez-Gonzalez, S. J Org Chem 2011, 76, 2367.

[35] Yamada, Y. M. A.; Sarkar, S. M.; Uozumi, Y. J Am Chem Soc 2012, 134, 9285.

[36] Veerakumar, P.; Velayudham, M.; Lub, K. L.; Rajagopal, S. Cat Sci Technol 2011, 1, 1512.

[37] Sharghi, H.; Khalifeh, R.; Doroodmand, M. M. Adv Synth Catal 2009, 351, 207.

[38] Abdulkin, P.; Moglie, Y.; Knappett, B. R.; Jefferson, D. A.; Yus, M.; Alonso, F.; Wheatley, A. E. H. Nanoscale 2013, 5, 342.

[39] Astruc, D.; Liang, L.; Rapakousiou, A.; Ruiz, J. Acc Chem Res 2011, 45, 630.

[40] Hein, J. E.; Fokin, V. V. Chem Soc Rev 2010, 39, 1302.

[41] Hong, V.; Presolski, S. I.; Ma, C.; Finn, M. Angew Chem Int Ed 2009, 48, 9879.

[42] Candelon, N.; Lastécouères, D.; Diallo, A. K.; Aranzaes, J. R.; Astruc, D.; Vincent, J. M. Chem Commun 2008 741.

[43] Liang, L.; Ruiz, J.; Astruc, D. Adv Syn Catal 2011, 353, 3434.

[44] Deraedt, C.; Pinaud, N. L.; Astruc, D. J. Am Chem Soc 2014, 136, 12092.

[45] Yin, N. S.; Dingyi, Y.; Yugen, Z. Green Chem 2718, 2013, 15.

[46] Ladomenou, K.; Nikolaou, V.; Charalambidis, G.; Coutsolelos, A. G. Coordination Chem Rev 2016, 306, 1.

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