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Development of one pot three component synthesis of 1,4-substituted, 1,2,3-triazoles, employing green catalyst

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Abstract: An efficient and eco-friendly protocol for the synthesis of 1,4-substituted-1*H*-1,2,3-triazoles was achieved employing D-glucosamine as a green ligand with CuI as catalyst. An advantage, of high water solubility, of the ligand facilitates easy catalyst removal. All the products were formed in good yields and were characterized by advanced spectral data.

Keywords: D-glucosamine; 1,4-substituted-1*H*-1,2,3-triazoles; CuI; aryl halides;eco-friendly.

1. Introduction

1,2,3-Triazoles are important five-membered nitrogen heterocycles, involved in a wide range of industrial applications such as agrochemicals, corrosion inhibitions, dyes, optical brighteners and biologically active agents.[1] Earlier, the compounds were in general prepared by the coupling of alkynes and azides to form a mixture of 1,4-substituted- and 1,5-substituted-1,2, 3-triazoles at high temperature.[2] The recent important investigations lead to the 'click' chemistry approach.[3]

The Huisgen 1,3-dipolar cycloaddition[4] of azides and alkynes resulting in 1,2,3-triazoles is one of the most powerful click reactions. Several members of the 1,2,3- triazole family have indeed shown interesting biological properties, such as anti-allergic,[5] anti-bacterial,[6] and anti- HIV activity.[7] Additionally, 1,2,3-triazoles are found in herbicides, fungicides, and dyes.[8] The recently discovered copper(I) catalysis of this transformation,[9] which accelerates the reaction up to 10^7 times, has placed it in a class of its own and has enabled many novel applications.[10]

Cu(I)-catalyzed ligation of organic azides and terminal alkynes has gained much research applications. Exclusive regioselectivity, wide substrate scope, mild reaction conditions, and very high yields[11] have made a choice for making permanent connections by means of 1,4- disubstituted 1,2,3-triazoles. Although organic azides are generally safe compounds, those of low molecular weight can be unstable and, therefore, difficult to handle.[12]

Recently, enormous progress has been achieved in the field of asymmetric synthesis using carbohydrate derivatives as chiral auxiliaries.[13] The cheapness, possession of multiple chiral centers and high environmental friendly nature of monosaccharide molecules have driven us to explore their capabilities as ligands in transition metal-catalyzed organic reactions. A few reports on D-glucosamine and D-glucose as ligands for the copper-catalyzed synthesis of aniline and phenol through C–N and C–O bond formation; is investigated.[14]

To the best of our knowledge, no attempt has been made for the use of D-glucosamine as ligand in copper (I)-catalyzed Huisgen cycloaddition process. Herein, we report an efficient and ecofriendly

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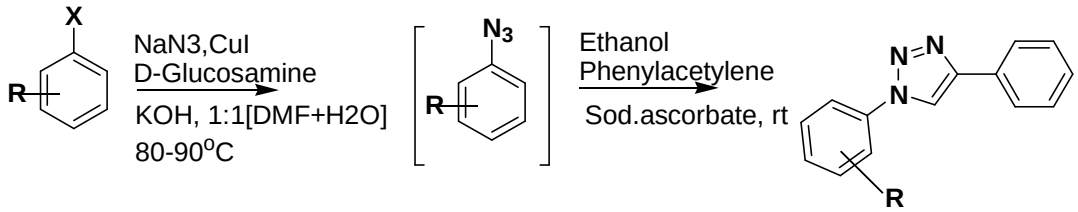
one-pot three-component reaction to form 1,4-disubstituted 1,2,3-triazoles. Reaction of various halides, **(1a-1p)** sodium azide with phenyl acetylene in D-glucosamine/ CuI(KOH/DMF:H_2O) afforded corresponding 1,4-substituted-1,2,3-triazoles (**2a-2p)** in good to excellent yields (Figure **1**) using aryl substituted iodo/ bromo benzenes (**1a-1p**), sixteen 1,4-substituted 1,2,3-triazoles were synthesized (**2a-2p**). The synthesized compounds were purified by chromatography and crystallised from ethanol. The structures of **2a-2p** were well characterised by advanced spectroscopic data.



1a-1p **2a-2p**

X= I, R=(a) H, (b) 4-NO_2, (c) 2-NO_2,4-CH_3, (d) C_6H_5, (e) 2-CH_3, (f) 4-OCH_3, (g) 3-OCH_3, (h) 4-NH_2, (i) 2-NH_2;

X=Br, R= (j) 3-NO_2, (k) 4-$COCH_3$, (l) 3-$COCH_3$, (m) 4-CN, (n) 2-OCH_3, (o)4-OCH_3, (p) 4-NH_2

Figure 1. Synthesis of 1,4-substituted-1*H*-1, 2, 3-triazoles

2. Results and Discussions

In our initial efforts to optimize the reaction conditions, different organic solvents were screened to get the product in good yields. The results are presented in table **1**. From table **1**, it is evident that DMF/H_2O (1:1) solvent system in KOH resulted in high yields. In this reaction, temperature plays a vital role in formation of product. After formation of azide, the reaction mixture at kept to room temperature as formation of triazoles occurred at room temperature only. If temperature increases about 90°C, formation of azide decreases drastically. Hence all the reactions are carefully carried out at the optimized temperature conditions.

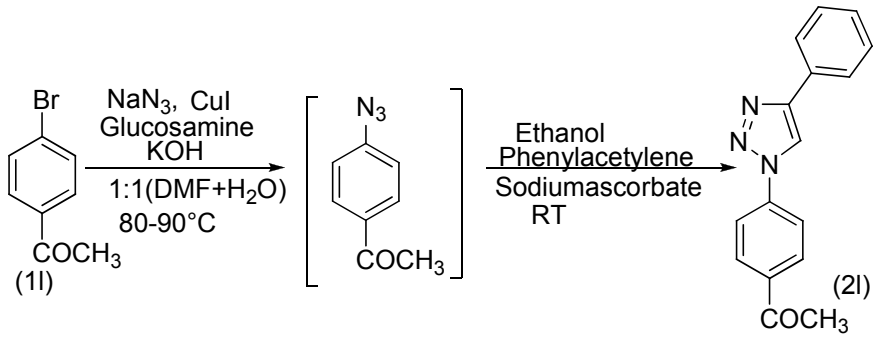


Figure 2. Formation of triazoles occurred at room temperature

Table 1. Optimization of solvent system and bases for the synthesis of triazoles at 80-90^{o}C

Entry	Solvent/H_2O(1:1)	Base	Time(hrs)	Yield(%) [a]
1	DMF	KOH	12	90
2	DMSO	KOH	16	20
3	THF	KOH	20	15
4	Acetone	KOH	36	00
5	Dioxane	KOH	36	00
6	DMF	CS_2CO_3	24	86
7	DMF	Na_2CO_3	24	82
8	DMF	K_2CO_3	24	80
9	DMF	$NaHCO_3$	24	63
10	DMF	NaOH	13	74

[a] Yields are compared to isolated products

After attaining the optimum reaction conditions, the role of suitable copper salt was examined. Four different copper salts viz) $CuSO_4$, CuCl, CuBr, CuI were tested and the results were presented in table **2**. It was observed from the table 2 that among the tested copper salts, CuI showed the best yields.

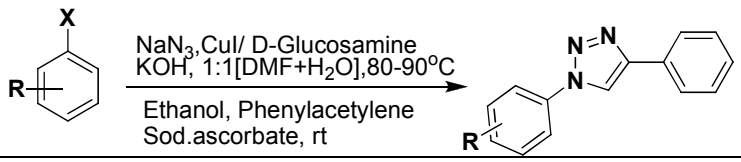
Table 2. Effect of copper salts in the formation of 1, 2, 3-triazoles

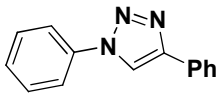
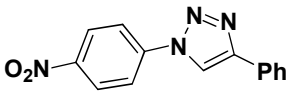
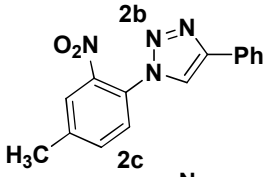
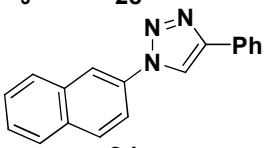
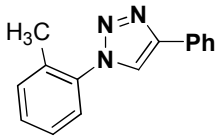
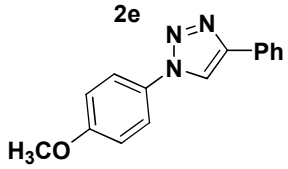
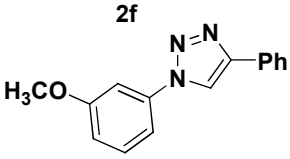
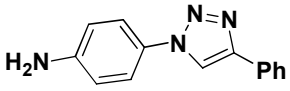
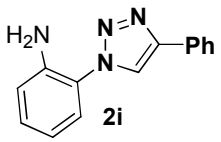
Entry	Copper salt	Time(hrs)	Yield (%)
1	CuI	12	90
2	CuBr	16	78
3	CuCl	18	72
4	$CuSO_4$	24	45

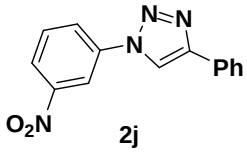
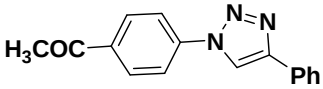
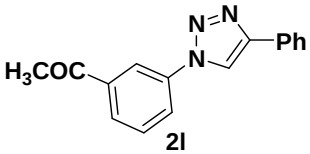
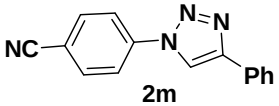
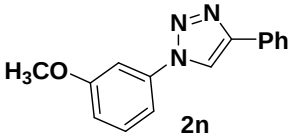
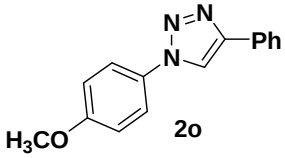
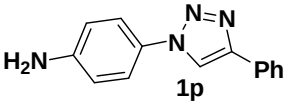
A variety of structurally varied aryl halides were easily converted into 1,4-substituted-1, 2, 3- triazoles employing D-glucosamine/CuI(KOH/DMF:H_2O) catalyst at room temperature. The results were presented in table **3**.The presence of electron withdrawing groups on aryl halides took less reaction times and yields more than the electron donating groups. It is observed that substituted iodobenzenes are more reactive than the bromobenzenes. After completion of the reaction (monitored by TLC), all the products were purified by coloumn chromatography and the pure compounds were recrystallized from ethanol. The purity of the compounds was checked by HPLC found (>99%). The pure compounds thus obtained were duly characterized by advanced spectroscopic techniques.

In the IR spectra of synthesized compounds, stretching vibrations from 1300-1500 cm^{-1} corresponds to -N=N group confirms the formation of triazole ring. In ^{1}H NMR spectra, a characteristic peak at δ 7.9-8.2 range corresponds to the –CH proton of triazole ring which confirms the formation of 1,2,3-triazole.

Table 3. Reaction between Aryl halides and NaN_3 in the synthesis of triazoles



S.No	X	R	Product	Time(hrs)	Yield(%)
1	I	H **1a**	 **2a**	22	67
2		4-NO_2 **1b**	 **2b**	11	96
3		2-NO_2,4-Me **1c**	 **2c**	15	93
4		C_6H_5 **1d**	 **2d**	21	71
5		2-CH_3 **1e**	 **2e**	20	70
6		4-OCH_3 **1f**	 **2f**	18	75
7		3-OCH_3 **1g**	 **2g**	20	74
8		4-NH_2 **1h**	 **2h**	20	78
9		2-NH_2 **1i**	 **2i**	21	76

S.No	X	R	Product	Time(hrs)	Yield(%)
10	**Br**	3-NO_2 **1j**	 **2j**	16	92
11		4-$COCH_3$ **1k**	 **2k**	12	90
12		3-$COCH_3$ **1l**	 **2l**	15	85
13		4-CN **1m**	 **2m**	17	88
14		2-OCH_3 **1n**	 **2n**	20	65
15		4-OCH_3 **1o**	 **2o**	18	66
16		4-NH_2 **1p**	 **1p**	24	61

3. Experimental

3.1.General Synthesis of 1,4-substituted-1,2,3-triazoles: To a mixture of *p*-bromoacetophenone (0.5 mmol) and NaN_3 (1.5 mmol) was added a solution of CuI (0.05 mmol), Glucosamine hydrochloride(0.05 mmol) (ligand), KOH (1.5 mmol) in H_2O-DMF (1:1). The reaction mixture was stirred at 90^oC for 10 h up to the formation of azide (check TLC). After formation of azide, the reaction mixture was cooled to room temperature. To this mixture; sodium ascorbate (1.0 mmol), phenylacetylene (2.0 mmol) were added in ethanol (2 mL) then stirred at room temperature for 2 h. After completion of the reaction (monitored by TLC), the reaction mixture was poured into cold water and the products were extracted with dichloromethane. The organic layer was dried ($MgSO_4$) and the products were collected under reduced pressure. The crude product thus obtained was recrystallized from EtOH or MeOH and purity of the compound was checked by HPLC (>99%). All the compounds were well characterized by IR, NMR and Mass spectroscopic techniques.

3.2. Spectral Data Of The Compounds:

3.2.1. 1,4-diphenyl-1H-1,2,3-triazole (2a) : IR(KBr pellet): 1630 cm^{-1}, 1610 cm^{-1}, 1380 cm^{-1}, 1320 cm^{-1}, 1100 cm^{-1}; ^{1}H NMR (400 MHz / $CDCl_3$) δ ppm): 8.21(1H, s), 7.46(2H, d, *J* = 7.6Hz),

7.34(2H,m), 7.30 (5H, s), 7.26(1H, t, *J* = 7.6Hz) ; ^{13}C NMR (22. 5 MHz / $CDCl_3$) δ ppm:149.9, 132.4, 129.6, 128.8, 128.3, 125.8 , 120.4; Mass-ESI: 221.10 (M+1).

3.2.2. 1-(4-nitrophenyl)-4-phenyl-1H-1,2,3-triazole (2b): IR(KBr pellet): 1800 cm^{-1}, 1630 cm^{-1} ,1550 cm^{-1} ,1450 cm^{-1}, 1350 cm^{-1},1320 cm^{-1}, 1100 cm^{-1}; ^{1}H NMR (400MHz / $CDCl_3$) δ ppm: 8.14(1H,s), 8.3(1H,s), 7.93(2H,d, *J* = 8.0Hz), 7.56(2H,s), 7.39(2H,d, *J* = 7.4Hz); 7.37(1H,t, *J* = 7.4Hz); ^{13}C NMR (22. 5 MHz / $CDCl_3$) δ ppm:): 147.5, 147.0, 133.5 ,133.3, 132.1, 131.5, 128.5, 128.2, 126.4, 120.0; Mass-ESI: 225.07(M+1).

3.2.3. 1-(4-methyl-2-nitrophenyl)-4-phenyl-1H-1,2,3-triazole (2c): IR(KBr pellet): 1620 cm^{-1}, 1600 cm^{-1}, 1550 cm^{-1}, 1450 cm^{-1}, 1350 cm^{-1}, 1300 cm^{-1}, 1100 cm^{-1}; ^{1}H NMR (400 MHz / $CDCl_3$) δ ppm): 8.10, (1H. s), 7.9(1H, s), 7.51(2H, d, *J* = 7.8Hz), 7.40(1H, s), 7.34 (2H, m), 7.30(1H, d, *J* = 7.2Hz) 7.20(1H, t, *J* = 7.2Hz) 2.30 (3H, s) ; ^{13}C NMR (22. 5 MHz / $CDCl_3$) δ ppm:): 146.0, 133.2, 132.5, 131.7, 130.1 ,129.5, 128.1, 127.2, 123.5, 23.0; Mass-ESI: 281.10(M+1).

3.2.4. 1-(naphthalen-4-yl)-4-phenyl-1H-1,2,3-triazole (2d): IR(KBr pellet) : 1640 Cm^{-1}, 1600 Cm^{-1} 1500 Cm^{-1} , 1200 Cm^{-1}, 1100 Cm^{-1}; ^{1}H NMR (400 MHz / $CDCl_3$) δ ppm): 8.1 (1H, s) 7.71(2H, m), 7.62(1H,d, *J* = 7.2Hz), 7.48(2H,d, *J* = 7.2Hz), 7.40(2H,m), 7.33(4H,m), 7.15(1H, m); ^{13}C NMR (22. 5 MHz / $CDCl_3$) δ ppm:149.8, 138.0, 130.4,130.2,128.8,128.3, 125.8, 121.2, 117.0; Mass-ESI :128.11(M+1).

*3.2.5. 4-phenyl-1-o-tolyl-1H-1,2,3-triazole (2e)***:** IR (KBr pellet): 2921.5 cm^{-1} ,1628 cm^{-1}, 1620 cm^{-1}, 1485 cm^{-1}, 1271.9 cm^{-1}, 1260.8 cm^{-1}, ^{1}H NMR (400 MHz / $CDCl_3$) δ ppm): 8.20 (1H, s) 7.47(2H, m), 7.34(2H, m), 7.25(1H, t, *J* = 7.6Hz), 7.21(1H, m), 7.20(1H, m) 7.10(1H,d, *J* = 7.6Hz) ; ^{13}C NMR (22. 5 MHz / $CDCl_3$) δ ppm:147.0, 133.2, 132.5, 131.2, 130.1 ,129.1, 128.0, 127.2, 14.5; Mass-ESI: 236.11(M+1).

3.2.6. 1-(4-methoxyphenyl)-4-phenyl-1H-1,2,3-triazole (2f): IR (KBr pellet): 1617 cm^{-1}, 1603.7 cm^{-1}, 1430.9 cm^{-1}, 1316.1 cm^{-1}, 1146.8 cm^{-1}, 1124.4 cm^{-1}.;^{1}H NMR (400 MHz / $CDCl_3$) δ ppm): 8.11(1H,s), 7.46(2H,d, *J* = 7.8Hz), 7.34(2H,d, *J* = 7.4Hz), 7.26(1H,t, *J* = 7.4Hz), 7.20(2H,d, *J* = 7.8Hz), 6.60(2H,m), 3.82(3H,s), ^{13}C NMR (22. 5 MHz / $CDCl_3$) δ ppm:): 149.1, 132.4, 130.2, 129.5, 129.1, 128.3, 125.8, 56.6 ; Mass-ESI: 252.11(M+1).

3.2.7. 1-(3-methoxyphenyl)-4-phenyl-1H-1,2,3-triazole (2g) : IR(KBr pellet): 1640 cm^{-1}, 1600 cm^{-1} , 1400 cm^{-1}, 1300 cm^{-1}, 1100 cm^{-1}, 1000 cm^{-1}; ^{1}H NMR (400 MHz / $CDCl_3$) δ ppm): 7.9(1H,s), 7.40(2H,d, *J* = 8.0Hz), 7.34(2H,m), 7.30(1H,t, *J* = 8.0Hz), 7.20(2H,m), 6.8(2H,d, *J* = 7.6Hz), 3.8(3H,s); ^{13}C NMR (22. 5 MHz / $CDCl_3$) δ ppm:): 160.0, 147.1, 131.10, 130.0, 129.5, 129.2, 128.5, 128.2, 127.5, 120.2, 112.0, 54.5; Mass-ESI : 252.11 (M+1).

3.2.8. 4-(4-phenyl--1H-1,2,3-triazol-1-yl)benzenamine (2h): IR(KBr pellet): 1680 cm^{-1}, 1600 cm^{-1}, 1450 cm^{-1}, 1300 cm^{-1}, 1100 cm^{-1}.;^{1}H NMR (400 MHz / $CDCl_3$) δ ppm): 8.13(1H,s), 7.38(2H,d, *J* = 8.1Hz), 7.30(2H,dd, *J* = 7.4Hz), 7.15(1H,m), 7.12(2H,dd, *J* = 7.6Hz), 6.40(2H,dd, *J* = 7.4Hz), 4.0(2H,br,s); ^{13}C NMR (22. 5 MHz / $CDCl_3$) δ ppm:): 147.2, 131.1, 130.4, 128.5, 128.1, 127.2, 117.1, 115.5 ;Mass-ESI: 237(M+1).

3.2.9. 2-(4-phenyl--1H-1,2,3-triazol-1-yl)benzenamine (2i): IR(KBr pellet): 3350 cm^{-1} 1620 cm^{-1}, 1600 cm^{-1}, 1450 cm^{-1}, 1100 cm^{-1}, ;^{1}H NMR (400 MHz / $CDCl_3$) δ ppm): 8.0 (1H, s), 7.48 (2H,dd, *J* = 7.6Hz), 7.32 (2H,m), 7.22 (1H,t, *J* = 7.8Hz), 7.0 (1H,d, *J* = 7.6Hz), 6.6 (2H,m), 6.5 (1H,m), 4.0 (2H,br. s); ^{13}C NMR (22.5 MHz / $CDCl_3$) δ ppm:): 150.1,147.0, 132.1, 129.3,128.5, 128.1, 126.3,120.2, 117.1, 114.3; Mass-ESI :237.11(M+1).

3.2.10. 1-(3-nitrophenyl)-4-phenyl-1H-1,2,3-triazole (2j): IR(KBr pellet): 1603.8 cm^{-1}, 1580 cm^{-1}, 1384.6 cm^{-1}, 1348.2 cm^{-1}, 1172.5 cm^{-1}, ; ^{1}H NMR (400 MHz / $CDCl_3$) δ ppm): 8.31(1H, d, *J* = 7.8Hz) 8.11(1H, s) 7.70(1H,d, *J* = 7.8Hz) 7.60(2H,m) 7.52(2H, d, *J* = 6.8Hz), 7.36(2H, m), 7.26(1H, t, *J* =

7.0Hz); ^{13}C NMR (22. 5 MHz / $CDCl_3$) δ ppm:):, 150.0 , 133.8, 132.5, 131.9, 129.2, 129.0, 126.8, 114.4; Mass-ESI: 267.08(M+1).

3.2.11. 1-(4-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyl)ethanone (2k): IR(KBr pellet):1745.4 cm^{-1},1619.5 cm^{-1} , 1591.6 cm^{-1}, 1479.7 cm^{-1} ,1356.6 cm^{-1} ,1174.6 cm^{-1}**;** ^{1}H NMR (400 MHz / $CDCl_3$) δ ppm: 8.22(1H,s) 7.80(2H,m); 7.54(2H,m), 7.52 (2H,m), 7.32(2H,m), 7.26 (1H,s), 2.50 (3H, s); ^{13}C NMR (22. 5 MHz / $CDCl_3$) δ ppm: 198.8 , 135.2, 132.1, 131.2, 131.0, 129.2, 128.9, 126.2, 29.2 ;Mass -ESI : 264.11(M+1).

3.2.12. 1-(3-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyl)ethanone (2l): IR(KBr pellet) : 2890 cm^{-1}, 1715 cm^{-1}, 1620 cm^{-1}, 1600 cm^{-1}, 1400 cm^{-1}, 1300 cm^{-1}, 1100 cm^{-1}; ^{1}H NMR (400 MHz / $CDCl_3$) δ ppm): 8.15(1H, s), 7.9 (1H, d, *J* = 7.2Hz), 7.79(1H, s), 7.82(1H, d, *J* = 7.6Hz), 7.50(2H, d, *J* = 7.2Hz), 7.29 (2H, m), 7.19(1H, m),7.15(1H,d, *J* = 7.6Hz), 2.49(3H, s); ^{13}C NMR (22. 5 MHz / $CDCl_3$) δ ppm:): 198.1,147.7, 137.6, 135.4, 132.4, 129.0, 128.5, 128.1, 127.5, 127.1, 28.2;Mass-ESI: 264.11(M+1).

3.2.13. 4-(4-phenyl-1H-1,2,3-triazol-1-yl)benzonitrile (2m): IR(KBr pellet): 2200 cm^{-1} : 1650 cm^{-1}, 1620 cm^{-1}, 1450 cm^{-1}, 1300 cm^{-1}, ^{1}H NMR (400 MHz / $CDCl_3$) δ ppm): 8.1(1H, s), 7.52(2H, d, *J* = 7.8Hz), 7.46(2H,d, *J* = 7.6Hz) 7.44(2H. d, *J* = 7.8Hz), 7.34(2H, m)7.20(1H, t, *J* = 7.6Hz); ^{13}C NMR (22. 5 MHz / $CDCl_3$) δ ppm:): 146.0, 134.1, 133.1, 132.0, 131.5, 129.5, 128.4, 127.7 , 114.7, 110.0; Mass-ESI: 246.09 (M+1).

3.2.14. 1-(3-methoxyphenyl)-4-phenyl-1H-1, 2, 3-triazole (2n): IR(KBr pellet) : 1593 cm^{-1}, 1400 cm^{-1},1274 cm^{-1}1250 cm^{-1} 1200 cm^{-1}, 1178.3 cm^{-1}, , ^{1}H NMR (400 MHz / $CDCl_3$) δ ppm: 8.31 (1H, s), 7.45 (2H, d, *J* = 7.6Hz) 7.31(2H, m), 7.25(1H, m), 7.22(1H, t, *J* = 7.6Hz), 7.20(1H, d, *J* = 6.8Hz), 6.80(2H, d, *J* = 6.8Hz), 3.90(3H,s) ; ^{13}C NMR (22. 5 MHz / $CDCl_3$) δ ppm:): 148.1, 147.0,132.0,131.2,130.1,129.2, 128.5, 128.4, 127.2,115.0,114.2, 55.0; Mass-ESI: 252.11(M+1).

3.2.15. 1-(4-methoxyphenyl)-4-phenyl-1H-1,2,3-triazole (2o): IR(KBr pellet):1 620 cm^{-1}, 1600 cm^{-1}, 1400 cm^{-1}, 1350 cm^{-1}, 1300 cm^{-1}, 1100 cm^{-1}.;^{1}H NMR (400 MHz / $CDCl_3$) δ ppm: 8.12 (1H, s), 7.38(2H, d, *J* = 7.8Hz), 7.35(2H, m), 7.28(2H,d, *J* = 7.8Hz), 7.24(1H, m), 6.79(2H,d, *J* = 7.2Hz), 3.82(3H, s); ^{13}C NMR (22. 5 MHz / $CDCl_3$) δ ppm:): 158.1, 147.1, 132.1, 131.4, 130.7, 129.0, 128.2, 127.1,115.0, 54.5; Mass-ESI: 252.11(M+1).

3.2.16. 4-(4-phenyl--1H-1,2,3-triazol-1-yl)benzenamine (2p): IR(KBr pellet):3342.6 cm^{-1},1593 cm^{-1}, 1518.18 cm^{-1}, 1283.9 cm^{-1}; ^{1}H NMR (400 MHz / $CDCl_3$) δ ppm): 8.1 (1H, s), 7.48(2H,d, *J* = 7.4Hz), 7.31(2H, m), 7.20(1H, t, *J* = 7.0Hz) 6.8(2H,d, *J* = 7.4Hz), 6.4(2H, d, *J* = 7.0Hz), 3.9(2H, br.s); ^{13}C NMR (22. 5 MHz / $CDCl_3$) δ ppm:): 149.2, 134.0, 132.0, 130.5, 129.5, 129.4, 129.2, , 128.5, 128.3 , 117.0, 115.5, 115.0 ;Mass-ESI: 237.11(M+1).

4. Conclusions

In conclusion, we report here for the first time an efficient protocol for the synthesis of 1, 4-substituted-1*H*-1,2,3-triazoles by employing D-glucosamine as a green ligand with CuI as catalyst. The notable advantages are; A green solvent (water) was partially used (50%) for the conversion of aryl halides to the corresponding triazoles in the presence of CuI and D-glucosamine, with NaN_3 as the nitrogen source. A mechanistic study showed that the first step is a copper-catalyzed C_{aryl}–N bond forming coupling reaction between the aryl halide and sodium azide to give the aryl azide *in situ*, which further cyclized to the triazole in the presence of sodium ascorbate and phenyl acetylene. The insolubility of D-glucosamine in organic solvents and its high solubility in water help the catalyst removal from the product amine by a simple water workup.

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