J. Chem. Sci. Vol. 129, No. 3, March 2017, pp. 289–294. © Indian Academy of Sciences.
DOI 10.1007/s12039-017-1240-3

RAPID COMMUNICATION

1,2,3-Triazole N(2)-coordinated C–O coupling: Access to *ortho* aryloxyl 1,4-diaryl 1,2,3-triazoles

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MS received 8 September 2016; accepted 23 January 2017

Abstract. CuI-catalyzed selective Ullmann C–O coupling of 1,4-disubstituted 1,2,3-triazole bromides with phenols were achieved through the coordination of N(2) atom. The *ortho* C–Br bond in N(1) aryl can be selectively coupled with phenols, while other C–Br bonds remain inert, generating *ortho* aryloxyl 1,4-diaryl 1,2,3-triazoles.

Keywords. 1, 2, 3-Triazole; coordinated; C–O coupling.

1. Introduction

The diaryl ether motif is found in numerous bioactive natural products, such as the antitumor riccardin C (A in Figure 1),[1] the hormone thyroxin (B in Figure 1),[2] and the antibiotic piperazinomycin (C in Figure 1),[3] as well as in non-natural useful agrochemicals, such as resveratrol analogues of D and E (Figure 1) possessing phytoalexin biological activities.[4] Owing to their wide applications in life and materials sciences, diaryl ethers have thus attracted much attention from organic chemists and the most applied and universal methods remain metal-mediated cross-couplings of aryl halides with phenols.[5] Pioneered by Ullmann, such coupling reactions have undergone a major improvement with the discovery of adequate and versatile Pd-[6] and Cu-based[7] catalytic systems. Since then, much work has focused on enriching the pool of the coupling partners. Though the nucleophilic components have been widely developed and mainly include a variety of carbon, nitrogen, oxygen, and sulfur sources with a variety of chemical environments,[8] reports on the electrophilic substrates are extremely rare. It is clear that the development of new electrophilic substrates for Ullmann reaction is highly desirable.

Meanwhile, with the development of Sharpless's highly efficient Cu-catalyzed 1,3-diplar cycloaddition of terminal alkyne with azide, various 1,2,3-triazole derivatives including *mono*-,[9] *di*-,[10] and *tri*-[11] substituted molecules were thus constructed, which greatly promoted the progress of its application, especially in biological and material fields.[12] However, most methodologies still met some troubles for the preparation of target molecules with complicated structures. Recently, direct modification of 1,2,3-triazoles emerges as a beautiful means for the construction of various 1,2,3-triazoles, especially with complicated fragments. Kuang group explored various modifications of 2-monosubstituted 1,2,3-triazoles including halogenation, arylation, alkoxylation, acylation, and acyloxylation, generating corresponding functionalized target molecules.[13] The acyloxylation and akenylation of 1,4-disubstituted 1,2,3-triazoles were also explored by Wu, Liu, and Correa groups,[14] and the substrates were mainly limited to 1-benzyl or 1-alkyl 1,2,3-triazoles which were favored for the coupling process involving electronic and steric aspects. In all of above modifications, it is N(3) of the 1,2,3-triazole ring which served as the donor atom to the catalyst center. For some unknown reasons, there is no report about selective *ortho* aryloxylation on 1-aryl in 1,4-diaryl 1,2,3-triazoles directed by N(2) of heterocycle, generating diaryl ether motif. Notably, some 1,2,3-triazole derivatives bearing diaryl ether motif, like D and E in Figure 1, possess good cytotoxic/antiproliferative effects.[4]

Herein, we would like to report an efficient, selective Ullmann C–O coupling reaction of 1,4-diaryl 1,2,3-triazole bromides, in which the *ortho* C–Br bond in N(1) aryl could be selectively aryloxylated while other C–Br bonds remain inert, probably owing to the coordination of the N(2) atom in the 1,2,3-triazole ring.

*For correspondence

2. Experimental

2.1 *Materials and Methods*

All commercially available reagents and solvents were purchased (Aladdin and Bokachem, China) and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AM-400 MHz spectrometer. Chemical shifts are reported relative to internal tetramethylsilane (0.00 ppm) for ^{1}H, and $CDCl_3$ (77.0 ppm) for ^{13}C. High resolution mass spectra were obtained using a Finnigan-NAT GC/MS/DS 8430 spectrometer. Flash column chromatography was performed on 300–400 mesh silica gel.

2.2 *General synthetic procedures*

1,4-Diaryl 1,2,3-triazole **1** (0.3 mmol), phenol **2** (0.33 mmol), CuI (0.03 mmol), X-Phos (0.06 mmol), K_3PO_4 (0.6 mmol), and PhMe (2 mL) were added to a 15 mL pressure tube. Then the tube was sealed with a teflon screw cap and stirred at 100°C for 24 h. After consumption of 1,4-diaryl 1,2,3-triazole **1** (monitored by TLC analysis), the mixture was added to H_2O (15 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layer was washed with brine (3 × 5 mL), dried over Na_2SO_4 and concentrated under reduced pressure to afford a crude product. Purification by column chromatography on silica gel afforded the desired product **3**.

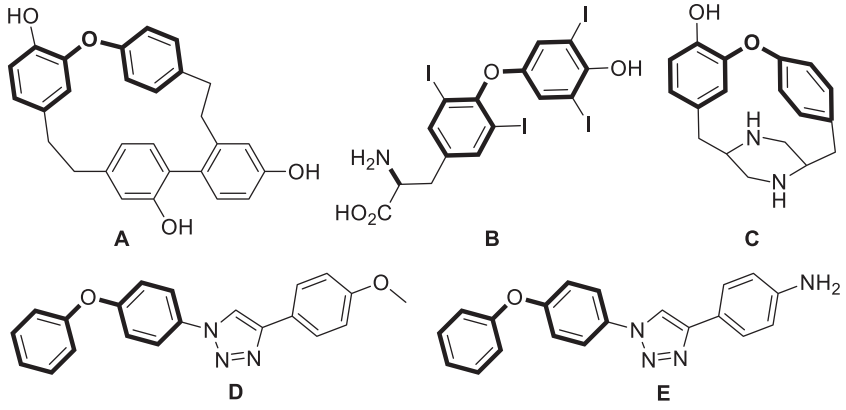
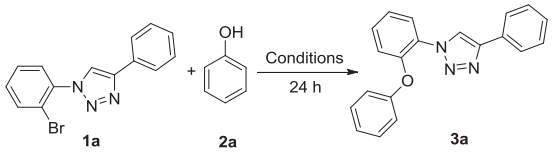


Figure 1. Bioactive structures bearing diaryl ether.

Table 1. Optimization of reaction conditions.[a]



Entry	Catalyst	Base	Ligand	Solvent	Temp. (°C)	**3a** (%)[b]
1	$Pd_2(dba)_3$	K_3PO_4	X-Phos	PhMe	100	57
2	CuI	K_3PO_4	X-Phos	PhMe	100	86
3	CuCl	K_3PO_4	X-Phos	PhMe	100	65
4	CuBr	K_3PO_4	X-Phos	PhMe	100	81
5	CuI	K_2CO_3	X-Phos	PhMe	100	78
6	CuI	Cs_2CO_3	X-Phos	PhMe	100	60
7	CuI	$K_2H\ PO_4$	X-Phos	PhMe	100	66
8	CuI	K_3PO_4	S-Phos	PhMe	100	56
9	CuI	–	–	PhMe	100	33
10	CuI	K_3PO_4	X-Phos	DMF	100	40
11	CuI	K_3PO_4	X-Phos	CH_3CN	100	
12	CuI	K_3PO_4	X-Phos	DMSO	100	13
13	CuI	K_3PO_4	X-Phos	PhMe	90	45
14	CuI	K_3PO_4	X-Phos	PhMe	110	78
15[c]	CuI	K_3PO_4	X-Phos	PhMe	100	81
16[d]	CuI	K_3PO_4	X-Phos	PhMe	100	81

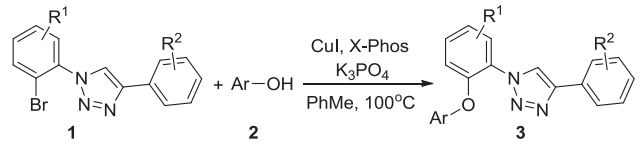
[a]Unless otherwise noted, the reaction conditions are as follows: 1,2,3-triazole bromide **1a** (0.3 mmol), phenol **2a** (0.33 mmol), catalyst (0.03 mmol), base (0.6 mmol), ligand (0.06 mmol), and solvent (2 mL). [b]Isolated yield. [c]CuI (0.015 mmol) and X-Phos (0.03 mmol) were used. [d]CuI (0.06 mmol) and X-Phos (0.12 mmol).

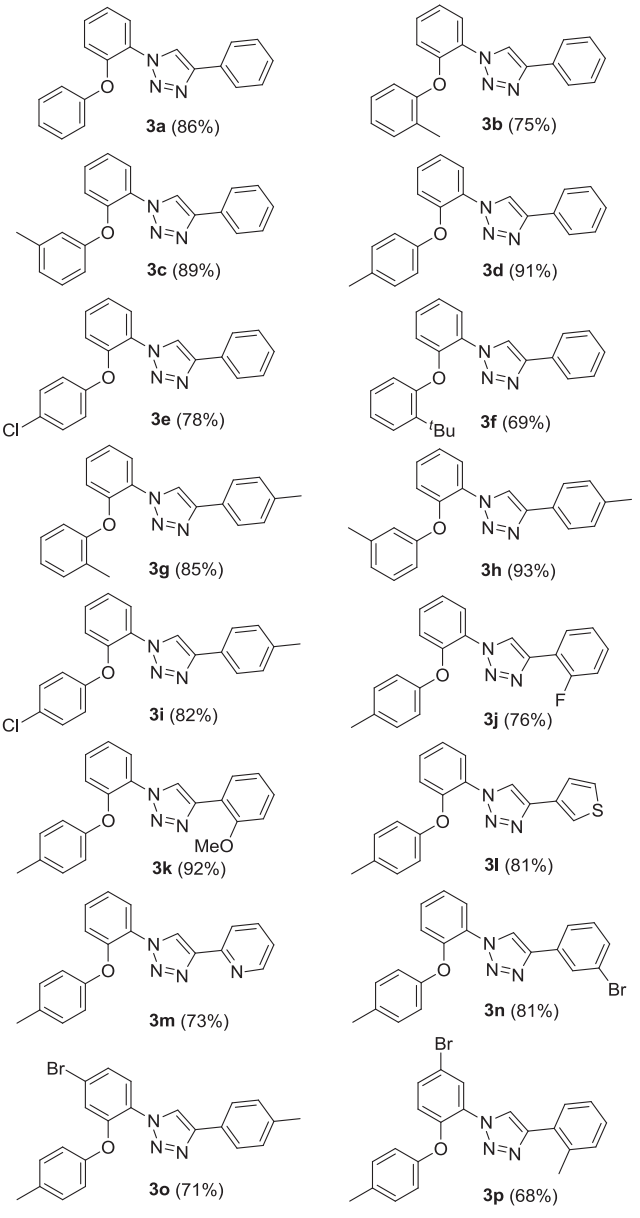
3. Results and Discussion

In our initial study, 1-(2-bromine phenyl)-4-phenyl-1,2,3-triazole (**1a**) and phenol (**2a**) were chosen as model substrates for optimization of the reaction conditions. We investigated the effects of catalyst, base, ligand, solvent and temperature, as summarized in Table 1. A moderate 57% yield of the product 4-phenyl-1-(2-(2-phenoxyphenyl)-1*H*-1,2,3-triazole **3a** was obtained when the reaction was catalyzed by $Pd_2(dba)_3$ (0.1 equiv.), using K_3PO_4 (2 equiv.) as the base, and 2-(dicyclohexylphosphino)-2′,4′,6′-triisopropylbiphenyl (X-Phos) (0.2 equiv.) as the ligand in solvent of PhMe under 100°C (Table 1, entry 1). After some tests on palladium catalysts, we focused our attention on cuprous salts. To our delight, an excellent 86% yield was reached if inexpensive CuI was used as the catalyst instead of $Pd_2(dba)_3$ (Table 1, entry 2). Other cuprous salts such as CuCl and CuBr are not so efficient for this reaction (Table 1, entries 3–4). Further, screening of bases showed that K_3PO_4 is the best choice as only lower yields could be obtained when K_2CO_3, Cs_2CO_3, or K_2HPO_4 was chosen for the system (Table 1, entries 5–7). The ligands also played important roles in this Ullmann C–O coupling reaction. The yield decreased to 56% when 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (S-Phos) was used instead of X-Phos and only 33% yield could be obtained in the absence of ligand (Table 1, entries 8–9). We found that the solvents such as DMF, CH_3CN, and DMSO were substantially less effective and no target molecules were detected in the system involved CH_3CN, in which the starting materials could be recovered (Table 1, entries 10–12). The yield did not improve when we adjusted the temperature to a lower 90°C or a higher 110°C, respectively (Table 1, entries 13–14). 0.1 Equivalent of CuI seems essential for this selective C–O coupling as the yields reduced to 81% when 5% mmol CuI was used instead, and more CuI loading seemed unnecessary (Table 1, entries 15–16).

Under the optimized conditions (CuI, X-Phos, K_3PO_4, PhMe, 100°C, 24 h), the selective C–O coupling reactions were carried out with a range of 1,4-diaryl 1,2,3-triazole bromide **1** and phenol **2**, generating good to excellent yields. As shown in Table 2, phenols bearing various groups on its *ortho*, *meta*, or *para* position could all serve as good partners. The coupling of 1,2,3-triazole substrates containing $-CH_3$, –F, or –Br substituent on its 1- and 4-aryl could all go smoothly. It was observed that substituents on both phenol and triazole partners played a distinguishing influence on the reaction. Electron donating substituents are beneficial to this C–O coupling, leading good to excellent yields and electron withdrawing groups are unfavorable to this reaction (Table 2, **3c** and **3d** vs **3e**, **3g** and **3h** vs **3i**, **3j** vs **3k**). Steric hindrance also affects this reaction remarkably. Phenols bearing *ortho* substituent, especially *tert*-butyl, only generated lower yields (Table 2, **3b** and

Table 2. N(2)-coordinated C–O coupling of 1,4-diaryl 1,2,3-triazole bromides.[a,b]

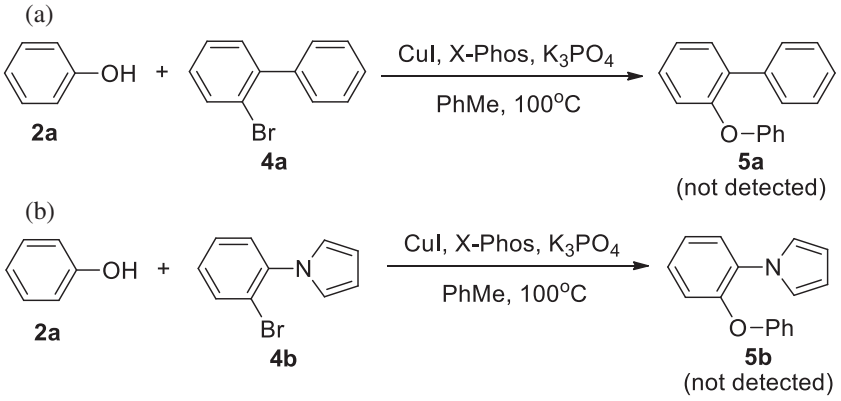




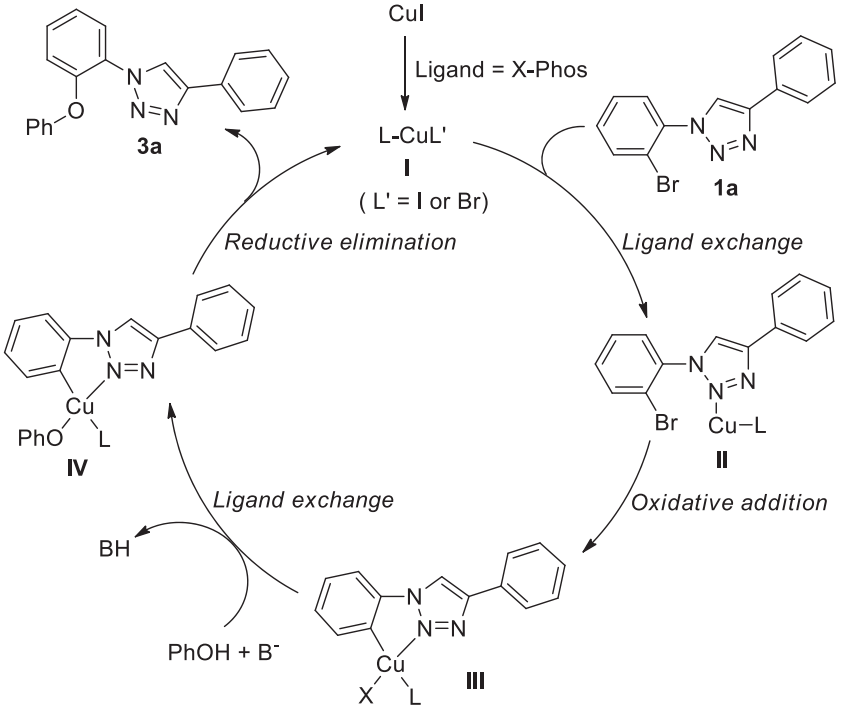
[a]Reaction conditions: 1,4-diaryl 1,2,3-triazole **1** (0.3 mmol), phenol **2** (0.33 mmol), CuI (0.03 mmol), X-Phos (0.06 mmol), K_3PO_4 (0.6 mmol), and PhMe (2 mL) were mixed and stirred at 100°C for 24 h. [b]Isolated yield.

3f vs **3a**). The yields of the reactions of the 1,2,3-triazoles without *ortho* substituent could offer higher yields compared to the substrates bearing a −F or –CH_3 group adjacent to the triazole ring (Table 2, **3j** and **3p**). It should be noted that heterocyclic rings like pyridyl and thiazolyl were tolerated in the system and good yields were also obtained (Table 2, **3l** and **3m**). It is worth noting that substituent of −Br on *meta* or *para* position in the substrates was found to be perfectly compatible, which was probably owing to the effect of N(2) coordination of the 1,2,3-triazole ring (Table 2, **3n**–**p**). We also checked the reaction of 1,2,3-triazole chloride under the optimized conditions and coupling products were not detected, probably owing to the lower reaction activity of C–Cl bond compared to C–Br bond.

To evaluate role of the N(2) coordination of the 1,2,3-triazole ring, we carried out the reactions of phenol **2a** and some aryl bromides with comparable steric effect and electronic property while the coordination site is absent, such as 2-bromo-1,1′-biphenyl **4a** and 1-(2-bromophenyl)-1*H*-pyrrole **4b** as shown in Scheme 1 (reactions a and b). After the reactions were conducted under 100°C for 24 h, no coupled molecules of **5a** and **5b** were detected and the substrates **4a** and **4b** could be recovered. This result explained that the C–Br bond adjacent to the bulky groups could not react with phenol smoothly without the coordination effect of 1,2,3-triazole ring under the optimized conditions, which indicated that the N(2) coordination of the 1,2,3-triazole ring played an important role in this cross-coupling system.



Scheme 1. Experiments on coupling reactions.



Scheme 2. Proposed mechanism.

Based on our coupling results and literature reports,[5d,15] a possible Cu(I) / Cu(III) cycle is proposed, as shown in Scheme 1. Coordination of the N(2) in 1,2,3-triazole **1a** to the Cu(I) center of the active catalyst **I**, through a ligand exchange process, afforded the 1,2,3-triazole coordinated Cu(I) intermediate **II**, which then underwent intramolecular oxidative addition of the *ortho* C–Br bond to the Cu center, producing Cu(III) intermediate **III**. Subsequent ligand exchange occurred between phenol and halogen in the presence of base, generating aryloxyl-Cu(III)-triazole species **IV**. Finally, the desired product **3a** was formed through reductive elimination of **IV**, and the active catalyst **I** was released simultaneously (Scheme 2).

4. Conclusions

In conclusion, we have demonstrated CuI-catalyzed regioselective Ullmann C–O coupling of 1,4-diaryl 1,2,3-triazole bromide with phenol. The N(2) of the 1,2,3-triazole ring served as the coordinating atom and controlled the *ortho* selectivity. It provides a quick access to *ortho* aryl in 1,4-diaryl 1,2,3-triazoles, which are widely used in biological and material fields.

Supplementary Information (SI)

Experimental procedures, characterization data and all the NMR spectra are available at www.ias.ac.in/chemsci.

Acknowledgements

We are grateful for the financial support provided by the National Natural Science Foundation of China (Grant Nos. 21262020 and 21662020).

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