

Discrete Benzotriazole-Copper(II) Complexes in Chelated and Non-Chelated Coordination Modes: Structural Analysis and Catalytic Application in Click and A³ Coupling Reactions

Sharmila Pandey*^[a, b] and Tanmoy Mandal^[a]

Two copper(II) complexes with benzotriazole-based ligands having pyridyl and quinolinyl arms were synthesized in good yields and characterized fully via spectroscopic and crystallographic techniques. The crystal structures of the complexes revealed different coordination environments around copper(II)

Introduction

The importance of N-donor ligands in the diverse and multifaceted chemistry of Cu is remarkable. The versatility of copper chemistry stems from the easy access of a variety of oxidation states such as Cu⁰, Cu¹, Cu¹¹, and Cu¹¹¹ which eventually facilitates several catalytic processes involving radical as well as twoelectron routes.^[1] The N-donor ligands possessing modular electronic and steric properties are particularly suitable in stabilizing such variable oxidation states of Cu, thus justifying their immense significance in efficient operation of the relevant catalytic cycles. Among several N-donor heterocyclic ligands, benzotriazole-based motifs,^[2,3,4,5] owing to some excellent attributes such as inexpensive, simple, stable, and ready accessibility, have been well-explored as suitable auxiliary ligands in various Cu-catalyzed organic syntheses. In addition to exhibiting very good σ -donor property, these nitrogen-enriched benzotriazole ligands also act as excellent π -acceptors, and thus they are able to stabilize low-valent Cu(I) intermediates which are key to several catalytic reactions. In fact, recently Vargas and Kostakis established the unique properties of this class of ligands as efficient charge sinks due to the availability of extended π -conjugation as well as uncoordinated N atoms within the ligand backbone, which facilitates stabilization of low oxidation states of Cu, such as Cu(I), during reductive catalysis.^[5] Notably, a balanced σ -donating and π -accepting capability is expected to be the key in such reductive catalysis. For example, Cu(I)-MIC (MIC = mesoionic carbene) complexes

[a] Dr. S. Pandey, T. Mandal Department of Chemistry Indian Institute of Science Education and Research (IISER) Bhopal Bhopal 462 066, India E-mail: sharmila.pandey@gmail.com
[b] Dr. S. Pandey School of Sciences SAGE University Bhopal Bhopal 462 022, India

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202100103 centers. The difference in structure was due to the steric effect of the ligands, which resulted in an octahedral and a square pyramidal geometry of the resulting complexes in the solid state. Both the air-stable complexes were utilized as precatalysts in catalytic click reactions and A³ coupling.

were found to be better catalysts than Cu(I)-NHC (NHC = N-heterocyclic carbene) complexes in copper-catalyzed azidealkyne cycloaddition (CuAAC) reactions, probably due to stronger σ -donating and π -accepting efficiency of the former ligands than the later ones.^[6] On the other hand, with regard to the π -acceptor property, cyclic (alkyl)(amino)carbenes (CAACs) are known to be very strong π -acceptor ligands.^[7,8] Eventually, catalytic CuAAC reactions were slow with Cu–CAAC complexes, and these ligands were even utilized to isolate Cu(I) acetylide complexes which are potential catalytic intermediates in the CuAAC reactions.^[7,9]

Copper-catalyzed azide-alkyne cycloaddition (CuAAC), popularly known as "click reaction"^[10] and aldehyde-amine-terminal alkyne multicomponent reaction (MCR), popularly known as "A³-coupling",^[11] are regarded as high-utility catalytic processes in synthetic chemistry (Figure 1a). The products of these two reactions - 1,2,3-triazoles and propargylamines respectively, are extremely useful chemicals in various applications.^[12,13,14] Previous studies disclosed that the click reaction, in the absence of any catalyst, is sluggish, and requires harsh conditions, and more importantly, it produces a mixture of both 1,4- and 1,5disubstituted 1,2,3-triazoles without any regioselectivity.^[10] However, the presence of a Cu(I) catalyst, results in a dramatic improvement of both rate and regioselectivity of the same reaction, yielding 1,4-disubstituted 1,2,3-triazoles under mild reaction conditions. To avoid handling of unstable Cu(I) species, often Cu(II) salts/compounds are used for in situ generation of Cu(I) species. In further improvement, to overcome the instability issues related to unprotected Cu(I) species, various ligands are mixed with Cu(II) precursors. N-containing ligands, and especially the nitrogen-containing heterocyclic ligands are one of the most popular ligands in Cu-catalyzed click reactions.^[10] Similarly, as the A³-coupling reaction also proceeds through a Cu(I) intermediate, the significance of N-heterocyclic ligands is obviously very important in this reaction too. It is noteworthy to mention that the application of pre-formed Cu(II)-precursor complexes in these transformations are still underexplored, in comparison to in situ protocols.^[11]





Figure 1. (a) Model click reaction and A³ coupling; (b) reported Cu(II)benzotriazole-based coordination polymer used as catalyst; (c) two discrete Cu(II)-benzotriazole based complexes 1 and 2 having variable ligand coordination, used as catalysts in this study.

From the above perspectives, it would be interesting to design and apply pre-formed well-defined benzotriazole-based ligand-bound Cu(II) complexes as pre-catalysts for CuAAC and A³-coupling reactions. Notably, Kostakis et al. recently used coordination polymers of Cu(II) with substituted benzotriazole ligands in these two high-utility catalytic reactions (Figure 1b).^[3,4] Motivated by the above background, we sought to explore discrete, molecular Cu(II)-benzotriazole complexes in CuAAC and A³-coupling reactions. In this study, we utilized 1heteroaryl-substituted benzotriazole ligands, BTZ-2P and BTZ-2Q, to synthesize two new Cu(II)-complexes - 1 with chelated BTZ-2P and 2 with non-chelated BTZ-2O coordination modes and investigated their catalytic applications in these reactions (Figure 1c).^[5] Both the air-stable complexes were found to be effective in the click as well as A³-coupling reactions. These results are in support of the fact that benzotriazole-based ligands are efficient to stabilize the low oxidation state Cu(I), which is the key intermediate for these reactions.

Results and Discussion

Syntheses of ligands and complexes

Treatment of benzotriazole with 2-bromopyridine and 2choroguinoline, as per our previously reported protocol, afforded the desired ligands - 1-(pyridine-2-yl)-1H-benzo [d][1,2,3]triazole (BTZ-2P) and 1-(quinoline-2-yl)-1H-benzo [d][1,2,3]triazole) (BTZ-2Q) respectively, in excellent yields (> 90%).^[2b] The air-stable Cu(II) complexes $[Cu(BTZ-2P)_2(ClO_4)_2]$ (1) and $[Cu(BTZ-2Q)_2(CH_3CN)_2(H_2O)](ClO_4)_2$ (2) were isolated in good yields (82% for 1 and 74% for 2) by reacting the ligands BTZ-2P and BTZ-2Q respectively with Cu(ClO₄)₂.6H₂O in CH₃CN (Scheme 1). These complexes were first analyzed by electronspray ionization mass spectrometry (ESI-MS) to get insight into their probable structural formulations in solution. The ESI-MS spectrum of complex 1 exhibited a major intense peak at m/z =455.0808 with the expected isotopic pattern (Figure S5, Supporting Information), which may be assigned to $[Cu^{!}(BTZ-2P)_{2}]^{+}$ fragment, plausibly generated under mass spectrometric conditions through dissociation of the two ClO_{4}^{-} anionic ligands and in situ reduction of Cu(II) to Cu(I). On the other hand, complex 2 displayed three peaks at m/z = 407.9712, m/z =555.1128 and m/z = 654.0608 with the expected isotopic patterns (Figure S6), which may correspond to the [Cu^{II}(BTZ- $2Q)(CIO_4)]^+$, $[Cu^{I}(BTZ-2Q)_2]^+$ and $[Cu^{II}(BTZ-2Q)_2(CIO_4)]^+$ fragments respectively, present under mass spectrometric conditions. From the above studies, it was apparent that there were two BTZ-2P and BTZ-2Q ligands attached to the Cu center in 1 and 2 respectively. To evaluate the exact binding modes (monodentate or bidentate) of these ligands as well as the exact geometry around the central metal center, single crystal X-ray diffraction (SCXRD) studies were undertaken (vide infra). Further, electronic and electron paramagnetic resonance (EPR) spectroscopic analyses were performed to examine the structural integrity correlation of 1 and 2 both in solution and under solid-state conditions.

Single crystal X-ray structures of 1 and 2

The exact mode of coordination of the ligands and the structure of the complexes were unambiguously confirmed via single crystal X-ray structure determination of **1** and **2**.



Scheme 1. Synthesis of the complexes 1 and 2.



Features of $[Cu(BTZ-2P)_2(CIO_4)_2]$ (1): A perspective view of the crystal structure of 1 is displayed in Figure 2. Some selected bond distances and angles are collected in Table 1. The crystal structure of 1 revealed a mononuclear complex where two **BTZ-2P** ligands were coordinated to the Cu(II) ion in bidentate fashion, occupying a square-based plane. The intra-ligand





Figure 2. ORTEP of 1 (top) and 2 (bottom) with 30% and 50% ellipsoid probability respectively. H atoms were removed for clarity.

Table 1 Calastad band lawstha (Å) and band analas

	1	2
Cu–N1 _{btz}	-	1.996(4)
Cu–N2 _{btz}	1.992(2)	-
Cu–N5 _{btz}	-	2.004(4)
Cu–N4 _{PY}	2.093(7)	
Cu01	2.413(2)	
Cu–O1S		1.958(4)
Cu–N1S		2.190(3)
Cu–N2S		2.190(3)
N2 _{BTZ} -Cu-N4 _{PY}	79.43(9)	
N1 _{BTZ} -Cu-N5 _{BTZ}		169.58(13)
N2 _{BTZ} -Cu-O1	88.43(10)	
N1 _{BTZ} -Cu-N1S		89.08(17)
N1 _{BTZ} -Cu-N2S		97.56(17)
N1 _{BTZ} -Cu-O1S		88.04(17)
N5 _{BTZ} -Cu-N1S		89.59(17)
N5 _{BTZ} -Cu-N2S		92.86(17)
N5 _{BTZ} -Cu-O1S		90.42(17)

the square-based plane around the Cu center showed the values of 79.43(9)° and 100.57(9)° respectively. Two perchlorate ions (ClO_4^{-}) were attached to Cu through one of the oxygen atoms of perchlorate anion in the axial positions thus making the complex octahedral and charge-neutral. The Cu-N_{BTZ} and Cu-N_{PY} distances were found to be 1.992(2) Å and 2.093(7) Å respectively. The structural features are supported by similar characteristics observed in a reported Cu(II) complex with benzotriazole ligands.^[2a] For example, the previously reported Cu-N_{BTZ} and Cu-N_{PY} distances were 2.047(2) Å and 2.034(2) Å respectively, whereas the intra-ligand $\angle N_{\text{BTZ}}$ -Cu-N_{PY} angle and the inter-ligand $\angle N_{BTZ}$ —Cu— N_{PY} angle of the square-based plane around the Cu center were reported as 80.34(8)° and 99.66(8)° respectively. The Cu–O1 (ClO₄) bond distance in **1** is 2.413(2) Å which is shorter than the Cu-O (ClO₄) distance of 2.453(2) Å found in a similar Cu(II) complex with a fused benzotriazole ligand.[15]

 $\angle N_{BTZ}$ —Cu—N_{PY} angle and the inter-ligand $\angle N_{BTZ}$ —Cu—N_{PY} angle of

Features of [Cu(BTZ-2Q)₂(CH₃CN)₂(H₂O)](ClO₄)₂ (2): In contrast to the complex 1, the crystal structure of [Cu(BTZ- $2Q_{2}(CH_{3}CN)_{2}(H_{2}O)(CIO_{4})_{2}$ (2) showed a square pyramidal geometry around Cu(II) ion. A perspective view of the structure is depicted in Figure 2, and some selected bond distances and angles are tabulated in Table 1. Interestingly, the structure of 2 revealed that the mononuclear complex consisted of two BTZ-2Q ligands bound to the central Cu(II) ion trans to each other via a monodentate fashion through the most basic nitrogen atom of the benzotriazole ring, farthest from the quinoline motif of the ligand. The guinoline nitrogen remained free of coordination to the Cu(II) ion plausibly due to the subtle steric factor of the fused benzene ring adjacent to the nitrogen atom of the quinoline scaffold.^[2a] The formation of N₂₀-Cu-N_{BTZ}-type chelate in 2 similar to the complex 1 was thus disfavored due to the inhibition of coordination of the guinoline nitrogen to the Cu center. It was also found previously by Steel et al. that the nitrogen atom of the pendant isoguinoline of a similar benzotriazole-based ligand did not coordinate to the Cu(II) ion and remained free.^[2a] Apart from the above distinguished coordination features of the ligand BTZ-2Q in 2, there were some additional salient characteristics present around the metal center. One acetonitrile was attached to the Cu(II) ion at the apical position while another coordinated acetonitrile and a coordinated water molecule occupied the remaining two trans positions of the square plane, thus leading to a square pyramidal geometry around the metal center. The two ${\it \angle N_{BTZ}}{\rm -}Cu{\rm -}N_{CH3CN}$ angles in the square plane were found to be 89.08(17)° and 89.59(17)° while the two $\angle N_{BTZ}$ –Cu–O_{H2O} angles in the square plane showed the values of $88.04(17)^\circ$ and 90.42(17)°, thus suggesting a very little deviation from the idealized value of 90°. In addition, the apical CH₃CN ligand also maintained approximately 90° angles to each of the four ligands occupying the square plane (Table 1). While the two Cu-N_{BTZ} bond distances were almost equal 1.996(4) Å and 2.004(4) Å, the apical Cu-N_{CH3CN} bond (2.190(3) Å) was found to be longer than the equatorial Cu-N_{CH3CN} bond (1.997(4)Å) as expected.



The Cu– N_{BTZ} bond distances were almost similar as reported for this type of copper complex with benzotriazole-based ligand.^[2a] Notably, unlike the coordination polymers reported in literature with this kind of chelating ligand backbones,^[3] the compound **2** existed clearly as a discrete molecule as evident from the presence of free quinoline nitrogen atoms in the crystal packing diagram (Figure S4).

EPR spectroscopy of 1 and 2 in the solid state

EPR spectrum of complex 1 in the solid state at room temperature exhibited a shoulder at $g_{\parallel} \approx 2.360$ and an intense signal at $g_{\perp} \approx$ (Figure 3A). On the other hand, the EPR spectrum of complex 2 consisted of a weak shoulder at $g_{\parallel} \approx 2.230$ accompanied by an adjacent intense peak at $g_{\perp} \approx 2.066$ (Figure 3B). For both the complexes, the trend of $g_{\parallel} > g_{\perp} > g_e$ ($g_e = 2.0023$) suggested an axial symmetry of the Cu(II) ion having the unpaired electron in the d_x^{2-2} orbital, thus confirming a common square-based geometry around the metal center. The difference in the patterns and g values were consistent with an octahedral geometry for 1 and a square-pyramidal geometry for 2, in line with the literature reports.^[16] These results were therefore corroborated with the observed crystal structures for 1 and 2.

Absorption spectroscopy of 1 and 2 in solution

The absorption spectra of $[Cu(BTZ-2P)_2(ClO_4)_2]$ (1) and $[Cu(BTZ-2Q)_2(CH_3CN)_2(H_2O)](ClO_4)_2$ (2) were recorded in CH₃CN in the range of 220–800 nm (Figure 3C, Figure 3D). The spectra of the complexes exhibited very weak absorption bands originated from d-d transitions, apart from the very intense bands originated from the intra-ligand π - π * transitions. The spectrum of 1 displayed a very weak and broad d-d band centered at 680 nm (observed in ~1 M CH₃CN) plausibly from a combination of $d_z^2 \rightarrow d_x^{2-y^2}$ and $d_{xy} \rightarrow d_x^{2-y^2}$ and $d_{xz} \rightarrow d_x^{2-y^2}$ transitions in O_h geometry. On the other hand, the complex 2 showed a



Figure 3. Solid-state EPR (A–B) and solution-state electronic (C–D) spectra of 1 and 2.

similar very weak and broad d-d band centered at 760 nm (observed in ~1 M CH₃CN). However, according to previous literature reports, typical square pyramidal or distorted square pyramidal Cu(II) complexes generally display a weak band over a broad region of 550–650 nm,^[17] while typical trigonal bipyramidal Cu(II) systems generally feature a broad band at $\lambda > 800$ nm.^[17] Based on these observations, it can be argued that in CH₃CN solution, the complex **2** likely existed in a relatively more stable trigonal bipyramidal structure, although in the solid state it maintained the square-pyramidal geometry.

Catalytic application of 1 and 2

The complexes 1 and 2 were used as precatalysts for two different types of catalytic reactions, namely click reaction and A³-coupling. The two systems turned out to be highly efficient precatalysts in both the catalytic processes, thus demonstrating the successful application of the discrete molecular Cu(II) complexes in such reactions. The similar reactivity and catalytic efficiency of the two catalysts in both the reactions suggested the involvement of similar Cu(I) catalytic intermediates with little difference in electronic perturbation from the two ligands BTZ-2P and BTZ-2O to the metal centre during the catalytic conditions. In accordance with the recent findings of Cu(I)catalyzed click reactions,^[9,18] a bimetallic pathway along with a traditional monometallic pathway were proposed in the present CuAAC reactions by 1 and 2 (Figure S47, Supporting Information). The generation of active Cu(I) species from the starting Cu(II) complexes via single electron transfer (SET) pathway was hypothesized in line with the proposal recently provided by Vargas and Kostakis with similar Cu(II) complexes.^[5] The active Cu(I) intermediates might involve monodentate-coordinated BTZ-2P and BTZ-2Q via the benzotriazole nitrogen, thus making the two catalytic systems very similar in terms of activity. A similar structural change during the reduction process might plausibly be the main reason behind the similar catalytic activity observed for both 1 and 2-catalyzed A³ coupling as well (Figure S47, Supporting Information).

Click reaction toward synthesis of 1,2,3-triazoles

As already mentioned, click reaction leads to synthesis of various 1,4-disubstituted 1,2,3-triazoles which are not only used to connect readily accessible building blocks containing various functional groups but also used in pharmaceutical applications for biological activity^[12] as well as material sciences^[13] For conducting the azide-alkyne click reaction, the organic azide partner was generated in situ in the reaction medium, by the reaction of the corresponding alkyl halide with sodium azide. Further reaction of the azide with the suitable alkyne partner in the presence of 1 or 2 led to the formation of the desired triazole products in good yields (Scheme 2). Reaction conditions were chosen according to previous report by Kostakis et al. using Cu(II)-coordination polymers as precatalysts.^[3] A number of *para*-substituted benzyl halides were successfully utilized in





Scheme 2. Catalytic application of 1 and 2 in azide-alkyne click reaction. Yields (%) are shown in parentheses with 1 and 2 respectively.

the reaction, thus tolerating the functional groups such as methoxy, nitro and vinyl (3a-3d). Normal straight chain alkyl halide also gave good yield of product with phenyl acetylene (3e). In addition to aromatic alkyne, aliphatic alkyne was also found to be successful in the reaction (3f-3h).

A³-coupling for the synthesis of propargylamines

To further evaluate the catalytic activity of the Cu complexes 1 and 2, the A³-coupling reaction was also explored (Scheme 3).



Scheme 3. Catalytic application of 1 and 2 in A^3 coupling reaction. Yields (%) are shown in parentheses with 1 and 2 respectively.

We employed previously reported reaction conditions utilized for Cu(II)-coordination polymers.^[4] In the present case, it was seen that both the Cu-complexes 1 and 2 resulted in significantly high yields (65-77%) of propargylamine products 4a-4l. Various para-substituted benzaldehydes (bromo, methyl, methoxy) were employed in this reaction to furnish good yields of the corresponding products (4b-4d, 4i-4k) which indicated the the tolerance of these groups under the reaction conditions. However, no electronic bias from the substituents of the aromatic aldehyde was observed on the yields of the final products. Moreover, the use of heteroarene aldehydes such as 4-pyridinecarboxaldehyde and 3-pyridinecarboxaldehyde also resulted in successful product formation (4e, 4f, 4l) when reacted with pyrrolidine and aromatic/aliphatic alkyne partners. Notably, comparable yields (in the range of 68-76%) were obtained with the heteroarene aldehydes as well similar to the aromatic aldehydes (in the range of 65-77%). Saturated aliphatic aldehyde also reacted efficiently to provide the corresponding product (4g) in 65% (with 1) and 68% (with 2) yields. Use of 1-octyne in place of aromatic alkyne, showed that the Cu catalysts 1 and 2 were effective for aliphatic alkyne also in the reaction with pyrrolidine and aldehyde resulting in the formation of the corresponding propargyl products (4h, 4i, 4j, 4k, 4l) in good vields.

Conclusion

In summary, pyridine- and guinoline-appended two benzotriazole-based N,N-chelating ligands, BTZ-2P and BTZ-2Q, were utilized successfully to yield two diverse coordination complexes of copper(II) - 1 and 2, wherein the BTZ-2P was bound to the copper(II) center in a cheating bidentate mode in an octahedral geometry whereas the BTZ-2Q was coordinated in a non-cheating monodentate coordination mode in a squarepyramidal structure in the solid state. X-ray crystal structures of both the complexes confirmed the above proposition. Solidstate EPR features of 1 and 2 were in good agreement with their X-ray structures. Solution-state electronic spectroscopic characteristics in CH₃CN at ambient temperature suggested an octahedral geometry for 1 while for 2, a likely conversion from square-pyramidal to trigonal bipyramidal structure was suggested. Finally, the catalytic application of both the copper complexes was successfully explored in click and A³ coupling reactions, thus suggesting the utility of these discrete Cu(II) systems as efficient precatalysts. The similarity in their catalytic performance in alcoholic solution under heating conditions cannot rule out the involvement of a similar active Cu(I)-species, both sterically and electronically, in both the cases. To the best of our knowledge, these are the first examples of benzotriazolebased discrete copper catalysts in click as well as A³ coupling reactions.^[5]



Experimental Section

Ligands BTZ-2P and BTZ-2Q were synthesized according to a previously published procedure. $^{\text{[2b]}}$

Synthesis of [Cu(BTZ-2P)₂(ClO₄)₂] (1)

BTZ-2P (100 mg, 0.50 mmol) was taken in a round-bottom flask with 8 mL of CH₃CN. After that Cu(ClO₄)₂.6H₂O (92.5 mg, 0.25 mmol) was added to it. The reaction mixture was stirred for 15 min at room temperature. A green-colored precipitate appeared which was filtered and washed with diethyl ether. The green solid thus obtained was recrystallized from CH₃CN/Et₂O. Yield = 135 mg (82 %). Anal. Calcd for C₂₂H₁₆N₈CuCl₂O₈: C, 40.35; H, 2.46; N, 17.11. Found: C, 41.04; H, 2.23; N, 17.73. HRMS (ESI positive mode): *m/z* calcd for $[C_{22}H_{16}N_8CuCl_2O_8]^+$: 455.0808, found: 455.0808 for $[Cu^1(BTZ-2P)_2]^+$ fragment, present under mass spectrometric conditions.

Synthesis of [Cu(BTZ-2Q)₂(CH₃CN)₂(H₂O)](ClO₄)₂ (2)

BTZ-2Q (100 mg, 0.40 mmol) was taken in a round-bottom flask with 10 mL CH₃CN and then Cu(ClO₄)₂.6H₂O (74 mg, 0.20 mmol) was added to it. The reaction mixture was stirred for 1 h at 60 °C. The mixture was then filtered on celite pad to remove any insoluble material and the filtrate was evaporated. The green solid thus obtained was washed with diethyl ether and then recrystallized from CH₃CN/Et₂O. Yield = 155 mg (74%). Anal. Calcd for C₃₄H₂₈N₁₀CuCl₂O₉: C, 47.76; H, 3.30; N, 16.38. Found: C, 48.32; H, 3.27; N, 17.01%. HRMS (ESI positive mode): *m/z* calcd for [C₁₅H₁₀N₄CuClO₄]⁺: 407.9681, found 407.9712 for [Cu^{II}(**BTZ-2Q**)(ClO₄)]⁺ fragment; *m/z* calcd for [C₃₀H₂₀N₈CuClO₄]⁺: 654.0587, found 654.0608 for [Cu^{II}(**BTZ-2Q**)₂(ClO₄)]⁺ fragment.

Single crystal X-ray diffraction analysis of 1 and 2

Single crystals of 1 and 2 suitable for X-ray diffraction studies were grown by diffusion of diethyl ether into the concentrated acetonitrile solution of the respective complexes. Data collection was carried out on a Bruker SMART APEX II CCD diffractometer with graphite monochromated Mo K α (λ =0.71073 Å) radiation at low temperature. Structures were solved with direct methods using SHELXS-97 and refined with full-matrix least-squares on F² using SHELXL-97.^[19]

Catalytic CuAAC click reaction toward synthesis of 1,2,3-triazole derivatives

A mixture of organic chloride (1 mmol), sodium azide (1.1 mmol), alkyne (1.2 mmol) and Cu catalyst (5 mol% based on organic halide) in ethanol (5 mL) was placed in a sealed tube and was stirred at 78 °C for 24 h. After completion, the slurry was filtered through a short pad of silica. The filtrate was collected and evaporated under vacuum. The resulting residue was then loaded into a silica-gel column chromatograph and the triazole product was isolated using a hexane/EtOAc mixture (10/1, v/v) as the eluent.

Catalytic A³ coupling of aldehyde, amine, and acetylene toward synthesis of propargylamine derivatives

A mixture of aldehyde (1 mmol), amine (1.1 mmol), alkyne (1.2 mmol) and Cu catalyst (2 mol% based on aldehyde) in 2-propanol (5 mL) was placed in a sealed tube and stirred at $90\,^\circ$ C for

12 h. After completion, the slurry was filtered upon a short pad of silica. The filtrate was collected and evaporated under vacuum. The resulting residue was then loaded into a silica-gel column chromatograph and the product propargylamine was isolated using a hexane/EtOAc mixture (10/1, v/v) as the eluent.

Deposition Numbers 2048478 (for 1) and 2048479 (for 2) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Click reaction \cdot Coordination chemistry \cdot Copper $\cdot A^3$ coupling \cdot Structure elucidation

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