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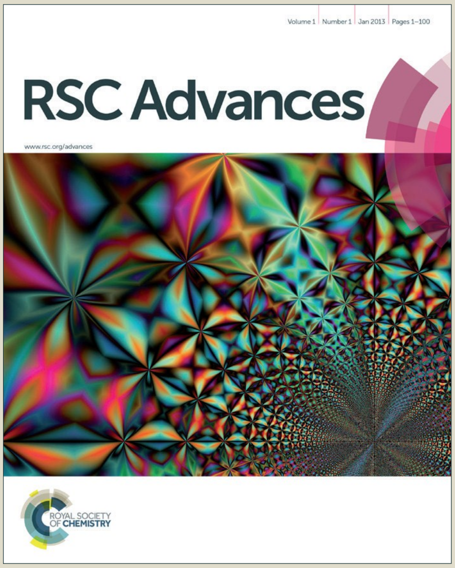

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A binuclear Cu(I) complex as novel catalyst towards direct synthesis of N–2–aryl–substituted–1,2,3–triazoles from chalcones

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A binuclear Cu(I) complex containing N',N'-bis{(1H-indol-3-yl)methylene}oxalohydrazide (H_2bioh) ligand has been synthesized and characterized. The molecular structures of the synthesized compounds have been determined by single crystal X–ray diffraction. The crystal structures are stabilized by inter– and intra–molecular π–π stacking and C−H···π interactions. The Cu(I)-complex has successfully been employed as an efficient catalyst for one–pot operation involving the azide–chalcone click reaction and subsequent arylation has been developed. The complex exhibits excellent catalytic activity with significantly low catalyst loading. The over all process is insensitive to air and moisture and can be manipulated under ambient temperature with operational ease.

1. Introduction

The Click chemistry is the most straight forward and atom economical approach for the synthesis of 1,2,3–triazoles.[1] Owing to its fidelity and compatibility, this strategy has been widely used in chemical biology, material science, and medicinal chemistry.[2] Most of the reported click reactions are two–component, employing organic azides and alkynes. In this system, the organic azides need to be synthesized in advance, and the potential hazards of organic azides, especially in isolation or purification processing, can be problematic. Thus, it is desirable to develop efficient methods that use sodium azide for direct cycloaddition.

The synthesis and functionalization of triazole derivatives is an attractive area of research. Recently described methods for the catalytic direct functionalization of triazole and its derivatives have also been found attractive but are mainly limited to the N–1 position.[3] One important group of triazole derivatives is the N–2–aryl/alkyl triazoles. In N–2–aryl triazoles the two aromatic rings adopt coplanar conformation and thus posses a typical electron density distribution, and exhibit unique photonic properties.[4] It has been well documented that the N–2 substitution is a major challenge for triazoles due to the lower relative electron density at the internal nitrogen atom (N–2) as compared to the two terminal nitrogen atoms (N–1 and N–3). The efforts have been made by Sharpless and others to further advance this difficult N–2 functionalization of triazoles.[5] Despite of these achievements, a facile preparation of N–2–substituted triazoles with low copper loading under mild conditions remains challenging.

The Cu(I) species necessary for the click reaction is often generated *in situ* either by employing Cu(II) in conjunction with a reducing agent such as ascorbate,[6] or via the comproportionation of Cu(II) and Cu(0). Additionally, 1,2,3–triazoles and other compounds have been employed as stabilizing ligands for Cu(I), inhibiting the oxidation and disproportionation of the ion while retaining its catalytic activity.[7] Various genuine Cu(I) catalysts that do not require a sacrificial reductant are also known. The advantage of ligated Cu(I), particularly with nitrogen ligands, being the rate accelerator, for instance with the efficient polytriazoles[8] and tris(2–aminoethyl)amine derivatives.[9] The nitrogen ligands allow the use of Cu(I) catalysts in reduced amounts (most often of the order of 1%) compared to the original, simple, and practical catalyst $CuSO_4$ + sodium ascorbate that is still the most commonly utilized catalyst but in much larger quantities.[10] Although Cu(I) may be obtained directly from the utilization of Cu(I) salts and coordination complexes,[11] the thermodynamically unstable Cu(I) either disproportionates to Cu(II) and Cu(0) or oxidizes to Cu(II). Moreover, when Cu(I) halides are employed as azide–alkyne cycloaddition catalysts in organic solvents, significant amounts of undesired side–products are generated.[12] Owing to the cytotoxicity associated with Cu(I), several groups have endeavored to minimize the copper concentration while maintaining high reaction rates.[13]

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Heterocyclic Schiff bases contain a number of coordination sites in addition to >C=N–, forming more stable bi–, tri– or poly–nuclear metal complexes. It has also been observed that the binuclear complexes of transition metal ions show better catalytic efficiency than those of corresponding mononuclear ones due to the synergic effect of two metal ions.[14] In view of the potential catalytic applications offered by the binuclear metal complexes of acyldihydrazone Schiff bases, and as a part of our recent investigations on the catalytic application of transition metals[15] and their complexes;[16] we have synthesized and characterized a novel binuclear copper(I) complex with H_2bioh ligand. The catalytic efficiency of the above complex has successfully been explored for N–2–aryl–1,2,3–triazole synthesis.

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2. Experimental

2.1 Synthesis of ligand

The ligand, N',N'–bis{(1H–indol–3–yl)methylene}oxalo hydrazide (H_2bioh) was synthesized by reacting 50 mL aqueous solution of oxalic acid dihydrazide (10 mmol, 1.18 g) with 50 mL methanolic solution of indole–3–carboxaldehyde (20 mmol, 2.90 g) in 1:2 molar ratio in a round bottom flask. A light yellow colored product was obtained by stirring the reaction mixture for 5 h at room temperature. The product was filtered on a Buckner funnel and washed several times with water followed by methanol, and dried in a desiccator over anhydrous calcium chloride at room temperature. Single crystal of the ligand was obtained by slow evaporation of its solution in a mixture of dichloromethane and DMSO solvents at room temperature. Yield (85%). M.p. >300 ºC. *Anal*. Calc. for $C_{20}H_{16}N_6O_2$ (372): C, 64.51; H, 4.33; N, 22.57. Found: C, 64.35; H, 4.35; N, 22.45%. IR (ν cm^{-1}, KBr): ν(NH) 3263b; ν(C=O) 1667s; ν(C=N) 1578m; ν(N−N) 989w. ^1H NMR (DMSO-d_6; δ ppm): 11.90 (s, NH); 11.65 (s, NH, indole moiety); 8.73 (s, CH); 8.25–7.13 (Ar-H). ^{13}C NMR (DMSO-d_6; δ ppm): 166.62 (>C=O); 158.33 (>C=N); 156.12–111.57 (aromatic carbons).

2.2 Synthesis of the Cu(I) complex

The Cu(I) complex of N',N'-bis{(1H-indol-3-yl)methylene} oxalohydrazide (H_2bioh) was synthesized by reacting 50 mL methanolic solution of the ligand H_2bioh (1 mmol, 0.334 g) with 50 mL solution of bis-(triphenylphosphine)copper(I) nitrate (2 mmol, 1.3 g) in dichloromethane in 2:1 (M:L) molar ratio. The reaction mixture was continuously stirred on a magnetic stirrer for 24 h at room temperature. The product was crystallized from the above solution by evaporating the solvent slowly at room temperature. Yellow crystal, yield (70%). M.p. 185 ºC. *Anal*. Calc. for $C_{94}H_{84}Cu_2N_8O_{10}P_4$ (1736.67): Cu, 7.31; C, 64.95; H, 4.84; N, 6.45. Found: Cu, 7.28; C, 64.76; H, 4.85; N, 6.41%. IR (ν cm^{-1}, KBr): ν (NH) 3258b; ν (C=O) 1634m; ν (C=N) 1553m; ν (N−N) 1020w. ^1H NMR (DMSO–d_6; δ ppm): 11.95 (s, NH); 11.67 (s, NH, indole moiety); 8.76 (s, CH); 8.24–7.14 (m, Ar-H). ^{13}C NMR (DMSO–d_6; δ ppm): 155.97 (C=O); 147.90 (C=N); 137.05–111.34 (aromatic carbons); ^{31}P NMR (DMSO–d_6; δ ppm): 10.71.

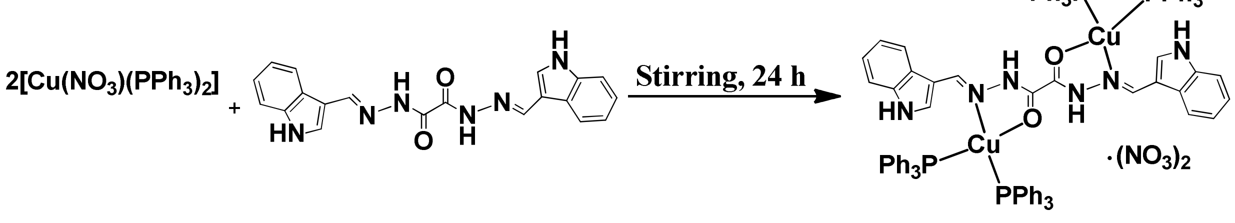
2.3 General procedure for the synthesis of N-2-aryl-substituted-1,2,3-triazoles

The chalcones (1 mmol), sodium azide (1 mmol), Cu(I) complex (1 mol %) and 3 mL DMF were taken in a 25 mL round bottom flask equipped with a stirrer. The reaction mixture was stirred at 50℃ for 10 h, and then 2,4-dinitrochlorobenzene/4-fluoronitro benzene (1 mmol) was added to the mixture. The reaction was continued further for 12 h at 100℃. After completion of the reaction, brine water (10 mL) was added and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure in a rotary evaporator. The crude product thus obtained, was purified using column chromatography (ethylacetate/hexane). All the products have been characterized based upon reported literature characteristics.

3. Results and discussion

It appears from the analytical data that reaction between the precursor bis–(triphenylphosphine)copper(I) nitrate and ligand H_2bioh occurs in 2:1 (M:L) molar ratio to give a binuclear Cu(I) complex (Scheme 1).

The complex is highly soluble in water, dichloromethane, ethanol, methanol, chloroform, chloroform, DMF and DMSO. It melts with decomposition at 185 ºC and shows molar conductance value of 59.35 Ω^{-1} mol^{-1} cm^2 at room temperature in the range of 1:1 electrolyte for 10^{-3} M solution in DMSO.



Scheme 1. Preparation of $[Cu_2(H_2bioh)(PPh_3)_4](NO_3)_2.2CH_3OH$

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3.1 Spectral characterization

The IR spectral bands observed at 3263, 1667, 1578 and 989 cm–1 in the free ligand are assigned to ν(N–H), ν(C=O), ν(C=N) and ν(N–N), respectively.16 In the complex, ν(C=O) and ν(C=N) occur at significantly lower wave numbers than the free ligand, indicating coordination of the >C=O and >C=N groups to metal.17 A considerable shift of ν(N–N) to higher wave number in the complex indicates the involvement of one of the nitrogen atoms of >N–N< moiety in bonding.18 The presence of ν(N–H) nearly at the same position in the complex as in the ligand shows non–participation of N–H group in bonding.

The 1H NMR spectrum of H2bioh in DMSO exhibits signals at 11.90 and 11.65 ppm due to >NH protons of −CONH and indole–NH, respectively (Fig. S1). In the Cu(I) complex, these protons occur almost at the same positions as in the ligand, suggesting non–participation of >NH group in bonding (Fig. S2). The −CH=N proton observed at 8.73 ppm in the ligand, shows downfield shift in the complex due to participation of −CH=N− group in bonding. The signals due to aromatic ring protons are observed in the region 8.24–7.14 ppm as multiplets in the ligand and complex.19 The 13C NMR spectrum exhibits a cluster of peaks between 156.13–111.57 ppm in the ligand and 137.05–111.34 ppm in the complex corresponding to carbons of the aromatic rings (Fig. S3). The signals observed at 158.33 and 166.62 ppm in the ligand are assigned to >C=N– and >C=O carbons, respectively. These signals show a considerable high field shift in the Cu(I) complex, suggesting the bonding of >C=N– and >C=O groups with metal (Fig. S4). The 31P NMR spectrum of the complex shows a peak at 10.71 ppm due to PPh3.

3.2 Crystal structure of H_2bioh ligand

The crystallographic data, structural refinement details, selected bond lengths, bond angles and hydrogen bonding parameters of H_2bioh and its Cu(I) complex are given in Table S1, S2 and S3, respectively. Fig. 1 shows ORTEP diagram of the ligand with atomic numbering scheme. The molecule displays an E configuration about the >C=N bond.[16] The C(10)–O(1) and C(9)–N(2) display bond distances of 1.236 (2) and 1.285 (3) Å , respectively as reported for double bonds.[16] The N(2)–N(3) bond distance is 1.390 Å, which is slightly shorter than the single bond distance (1.411 Å), indicating some double bond character.[20] All the C–C bond length (1.390 Å) and C–C–C bond angle (116.62º) of the indole ring as well as the C–N bond length (1.361 Å) and C–N–C angle (109.48º) are in accordance with a typical indole moiety.[21]

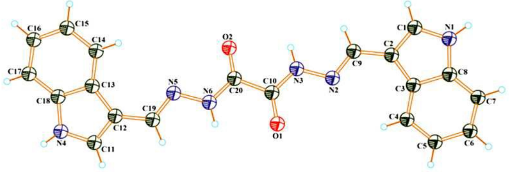


Fig. 1 ORTEP diagram of H_2bioh showing atomic numbering scheme (ellipsoids of 30% probability).

The molecular structure of the ligand is stabilized by inter–molecular H–bonding as well as inter–molecular C−H···π interactions. The inter–molecular H–bonding interactions N(1)−H(1A)···O(1) (2.10 Å), N(3)−H(3A)···O(1) (2.09 Å) and N(3)−H(3A)···O(1) (2.34 Å) form supra–molecular architectures on axis 'a' and 'c' (Fig. S5). The inter–molecular C−H···π interactions occur between the centroid of indole/phenyl ring and phenyl hydrogen with the contact distances of 2.974 and 3.398 Å (Fig. 2).[16]

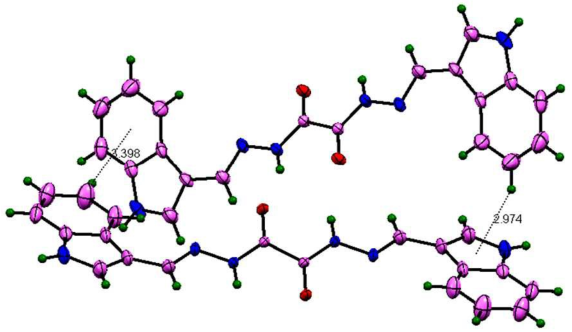


Fig. 2 Diagram showing intermolecular hydrogen bonding and intra–molecular C−H···π interactions along 'c' axis in H_2bioh.

3.3 Crystal structure of Cu(I) complex

Fig. 3 shows ORTEP diagram of the Cu(I) complex with atomic numbering scheme. In the binuclear complex, each metal centre is coordinated with NOP_2 core by using azomethine–nitrogen and a carbonyl–oxygen of H_2bioh ligand, and two phosphorous atoms of triphenylphosphine ligands. The two metal atoms in the complex are arranged in a trans manner to the coordinating sites of ligands. The average bond lengths in the complex are: C(9)–N(2) = 1.294(3), C(10)–O(1) = 1.228 (3) and N(2)–N(3) = 1.398(3) Å, respectively, which are longer or shorter than those of the corresponding distances in the ligand. The Cu–O(1) and Cu–N(2) bond distances are 2.197 (18) Å and 2.076 (2) Å, which fall in the range reported for Cu(I) tetrahedral complexes.[16] The C(9)–N(2) distance (1.294 Å) in the complex is significantly longer than the free ligand (1.285 Å) due to coordination of azomethine–N to the metal ion.

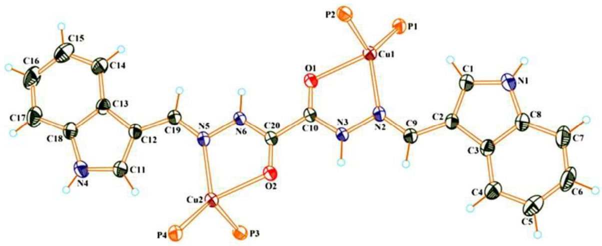


Fig. 3 ORTEP diagram of $[Cu_2(H_2bioh)(PPh_3)_4](NO_3)_2\cdot 2CH_3OH$ showing atomic numbering scheme with ellipsoids of 30% probability (phenyl rings, methanol and nitrate ions are omitted for clarity).

The molecular structure of Cu(I)–complex is stabilized by a number of inter–molecular hydrogen bonding and intra–molecular C−H···π interactions (Fig. 4). The inter–molecular hydrogen bonding interactions form a supra–molecular architecture on axis ‘c’ (Fig. S6). The intra–molecular C−H···π interactions occur between a phenyl proton and the centroid of the phenyl ring with contact distances of 3.168, 3.289 and 3.386 Å. The C−H···π interactions also take place when phenyl protons approach the centroid of the chelate rings with contact distances of 2.968 and 3.183 Å (Fig. 4).[16]

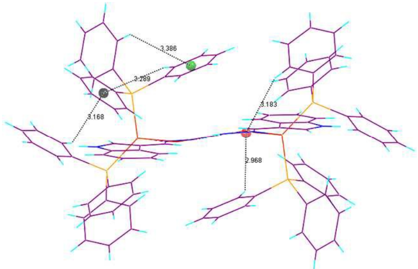
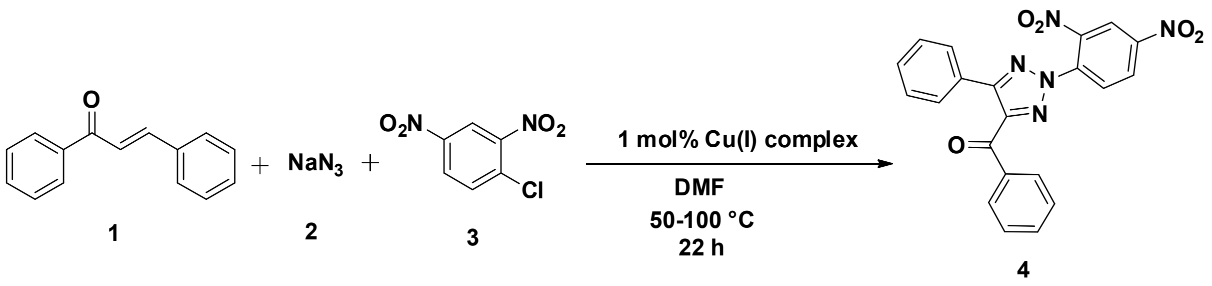


Fig. 4 Diagram showing intra–molecular C−H···π interactions along ‘c’ axis in the Cu(I)– complex.

3.4 Catalytic properties

The synthesized Cu(I)–complex has successfully been applied as a catalyst for the synthesis of N–2–aryl–1,2,3–triazoles through azide–chalcone oxidative cycloaddition and post–triazole arylation. The initial experiment was performed by using a model reaction between chalcone and sodium azide using 0.5 mol% of Cu(I)–complex under air for 10 h first, then 2,4–$(NO_2)_2$–C_6H_3Cl was added to the mixture. The reaction was continued further for 12 h to deliver the desired product **4a** with 67% yield (Table 1, entry 1). Further optimization of the reaction conditions resulted 84% product yield when 1 mol% Cu(I) complex was used as a catalyst (entry 2). Various solvents were also probed for their effect on the reaction yield and found DMF as the most suitable solvent (entries 4 and 5). The Cu(I)–precursor was also tested for its efficiency and found lower yield (entry 6). The ligand H_2bioh was failed to promote the reaction (entry 7).

Table 1 Effect of various parameters on reaction conditions



Entry	Catalyst mol (%)	Solvent	Yield (%)
1	Cu(I) complex (0.5)	DMF	67
2	**Cu(I) complex (1)**	**DMF**	**84**
3	Cu(I) complex (2)	DMF	84
4	Cu(I) complex (1)	CH_3CN	69
5	Cu(I) complex (1)	H_2O	n.r
6	$[Cu(PPh_3)_2]NO_3$ (5)	DMF	45
7	H_2bioh (5)	DMF	n.r

[a]Using chalcone (1 mmol), Sodium Azide (1 mmol, 65 mg), DMF (4 mL), Cu(I) complex (1 mol%), DMF (4 mL), at 50 °C under air for 10 h first, then 2,4–$(NO_2)_2$–C_6H_3Cl/4–$NO_2C_6H_4F$ (1 mmol) and DBU (1 equiv.) was added to the mixture, and the reaction continued further for 12 h at 100 °C . [b]Isolated yields.

To test the versatility of the optimized reaction conditions, the reactions of a variety of chalcones were studied with sodium azide and 2,4–$(NO_2)_2$–C_6H_3Cl/4–$NO_2C_6H_4F$ (Table 2). Chalcones having various substituents *viz*. (*E*)-3-(phenyl)-1-phenylprop-2-en-1-one (3a), (*E*)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (3b), (*E*)-3-(4-chlorophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (3c), (*E*)-1-phenyl-3-(4-methoxy)prop-2-en-1-one (3d), (*E*)-1-(4-methoxyphenyl)-3-(4-nitrophenyl)prop-2-en-1-one (3e) and aryl fluorides/chlorides having electron-withdrawing groups were participated well in these reactions. The presence of an electron-withdrawing group on the aryl halide counterpart is necessary driving force for a successful post arylation. Functional groups appended to chalcones and aryl halides were also well tolerated in these reactions.

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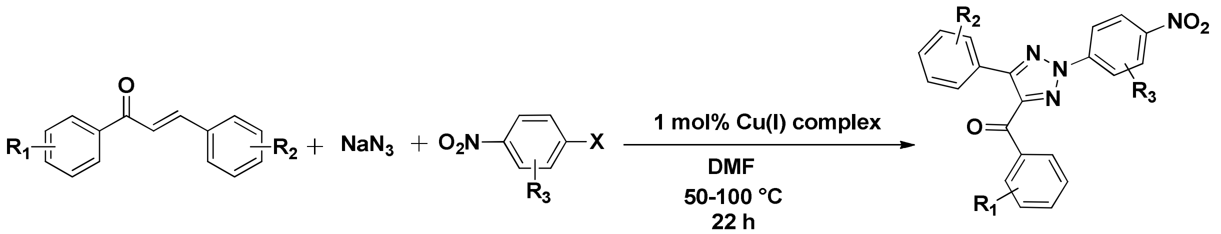
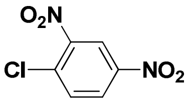
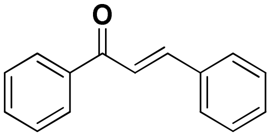
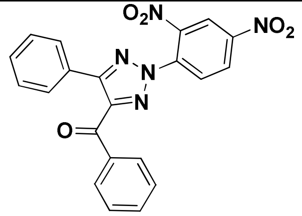
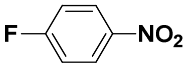
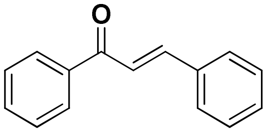
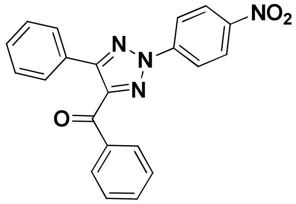
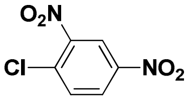
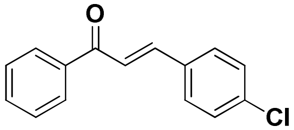
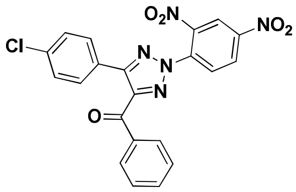
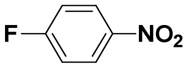
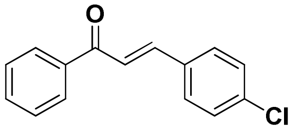
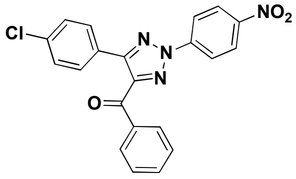
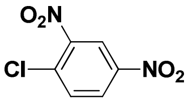
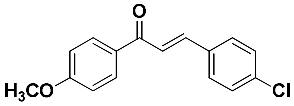
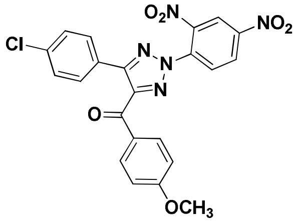
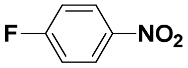
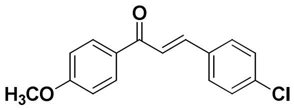
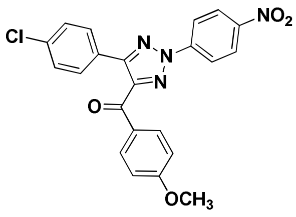
Table 2 Substrate scope for the copper catalyzed N–2–aryl–1,2,3–triazole synthesis[a]



Entry	Aryl halide		Chalcone		Product		Yield (%)
1.		1a		3a		4a	84
2.		1b		3a		4b	81
3.		1a		3b		4c	75
4.		1b		3b		4d	73
5.		1a		3c		4e	82
6.		1b		3c		4f	79

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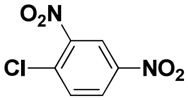
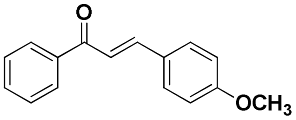
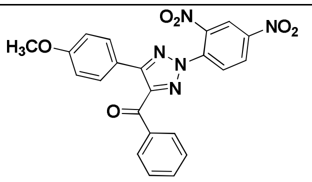
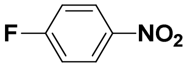
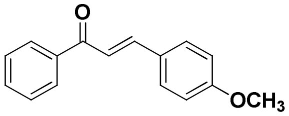
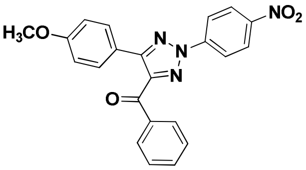
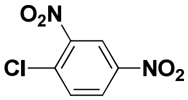
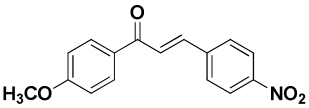
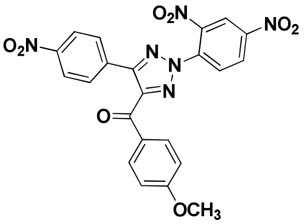
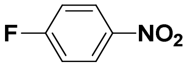
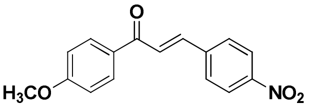
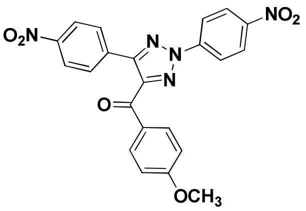
7.		**1a**		**3d**		**4g**	74
8.		**1b**		**3d**		**4h**	72
9.		**1a**		**3e**		**4i**	82
10.		**1b**		**3e**		**4j**	85

[a]Reaction conditions: Using chalcone (1 mmol), Sodium Azide (1 mmol, 65 mg), Cu(I) complex (1 mol%), DMF (4 mL), at 50 °C under air for 10 h first, then 2,4–$(NO_2)_2$–C_6H_3Cl/4–$NO_2C_6H_4F$ (1 mmol) and DBU (1 equiv.) was added to the mixture, and the reaction continued further for 12 h at 100 °C. [b]Isolated yields.

4. Conclusions

The present work describes the synthesis of a ligand N',N'–bis{(1H–indol–3–yl)methylene}oxalohydrazide (H_2bioh) and its Cu(I) complex and their characterization by various spectroscopic techniques. The molecular structures of the ligand and its Cu(I) complex have been determined by X–ray crystallography. The intermolecular π–π and C–H···π interactions are observed in the ligand as well as in its Cu(I) complex. The complex has a binuclear structure with a 4–coordinate tetrahedral geometry around each metal ion. The catalytic activity of the complex was successfully explored for the N–2–aryl–substituted–1,2,3–triazoles synthesis.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and spectral data for ligand. CCDC 984536 and 984537 contain the supporting information crystallographic data for the ligand H_2bioh and Cu(I) complex, respectively. These data can be obtained free of charge via the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Graphical Abstract

The binuclear Cu(I) complex as novel catalyst towards direct synthesis of N–2–aryl–substituted–1,2,3–triazoles from chalcones

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A binuclear Cu(I)–complex with N',N'−bis{(1H-indol-3-yl)methylene}oxalohydrazide is synthesized and characterized. The complex has been employed as a catalyst for one–pot operation involving the azide–chalcone click reaction and subsequent arylation.