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A family of ligand and anion dependent structurally diverse Cu(II) Schiff–base complexes and their catalytic efficacy in O–arylation reaction in ethanolic medium†

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Abstract

Two nitrato bridged dinuclear systems $[Cu_2(L1)_2(NO_3)_3]NO_3.H_2O$ (**1**) and $[Cu_2(L2)_2(NO_3)_3]NO_3.MeOH$ (**2**); five monomeric complexes *viz.* $[Cu(L3)(NO_3)]NO_3$ (**3**), $[Cu(L4)(NO_3)]NO_3$ (**4**), $[Cu(L5)(NO_3)]NO_3$ (**5**), $[Cu(L6)(NO_3)NO_3]$ (**7**), $[Cu(L7)(NO_3)]NO_3$ (**8**) and one hetero bi–bridged (phenoxido and water) dinuclear complex $[Cu_2(L2)_2(H_2O)_2](ClO_4)_4.4H_2O$ (**6**) have been synthesized and characterized by several physicochemical methods (L1 = 1–(N–3–methoxysalicylideneimino)–ethane–2–piperazine, L2 = 1– (N–3–ethoxysalicylideneimino)–ethane–2–piperazine, L3 = 1–(N–4′–ethoxy–α– methylasalicylideneimino)–ethane–2–piperazine, L4 = 1–(N–5′–chloro–α– methylasalicylideneimino)–ethane–2–piperazine, L5 = 1–(N–5–chlorosalicylideneimino)– ethane–2–

piperazine, L6 = 1–(N–4–methoxysalicylideneimino)–ethane–2–piperazine and L7 = 1–(N–4′–

methoxy–α–methylasalicylideneimino)–ethane–2–piperazine). X–ray structural analysis showed

that complexes **1** and **2** are discrete dinuclear species where the pentacoordinated metal centers

are bridged through nitrate ion. In **3**, **4**, **5** and **8** monomeric copper center experience a square

pyramidal geometry with a weak axial Cu–O bond. In **7** monomeric copper center experience

distorted octahedral geometry with two coordinated nitrate anions. However, in **6** two copper

center coordinates in different manner (one square–pyramidal and other is distorted octahedral)

and bridged through a phenoxido group and a water molecule. All complexes efficiently catalyze

C–O coupling reaction under homogeneous condition at 80 °C to afford unsymmetrical diaryl

ethers using nitroarenes act as an excellent electrophile. Notably, the reaction is carried out in

ethanol medium which facilitates to avoid toxic wastes. Structurally diverse copper(II) Schiff–

base complexes have rarely been used systematically in catalytic C–O coupling reaction.

1. Introduction

Diaryl ethers are ubiquitous structural motifs that represent a large number of natural

biologically active compounds (K13, perrottetin, teicoplanin and vancomycin) (Scheme 1) and

they are also important in polymer industries.[1–8] Classically, these compounds have been

synthesized via copper–catalyzed Ullmann type cross–coupling reactions of aryl halides and

phenols at very high temperature (125–220ºC) that requires stoichiometric amount of catalyst.[9–11]

Low to moderate yields are often obtained following these classic method. Recently attempts

have been made to develop of new synthesis route of diaryl ethers under milder reaction

condition.[6,10–22] Buchwald, Hartwig and Beller developed palladium catalyzed processes for C–O

cross–coupling reactions under mild condition.[23–28] In spite of palladium catalyzed methods are

being highly active their prospect in application in large scale reaction for industrial production

is limited owing to high expense of palladium and its toxicity as well as need of using phosphorated ligands in the process.[29,30] In 1998, Chen, Lam and Evans developed a new route to build carbon–heteroatom bonds, using arylboronic acid instead of aryl halides which produces undesirable by–products.[31–33] This problem is difficult to mitigate as phenylboronic acids release water through triphenylboroxime formation and enhances phenol formation from phenylboronic acid that leads to competition between phenol and phenolic derivatives for O–arylation.[34–38] Copper–based catalysts have been developed for O–arylation reaction of nitroarenes to achieve diaryl ethers.[2,7] In this study we demonstrated that cheap nitroarenes resolve the problem of unwanted by–product formation.

Selection of suitable metal salts and multidentate ligands are very important as they play dominant role in the control and adjustment of the architecture of coordination complexes.[39–42] Coordination chemistry of Schiff–base ligand is particularly interesting as selection of suitable amine and aldehyde/ketone, which can afford steric and electronic influence originated from different substituents groups, may create structural and functional variations.[43–46] These types of structural diversity have significant impact in the field of catalysis,[47–48] magnetism,[49–50] and DNA cleavage study.[51] Ramadan *et al.* studied oxidase catalytic activity of mononuclear and dinuclear Cu(II) complexes towards the aerobic oxidation of vitamin C.[47] Enantioselective cyclopropanation of styrene is efficiently catalyzed by monomeric and dimeric Cu(II) chiral Schiff–base complexes.[48] Lin *et al.* used structurally diverse copper complexes as catalyst for copolymerization of carbon dioxide and cyclohexene oxide.[52] Copper(II) Schiff–base complexes containing Cu_2O_2 moiety have also been investigated exhaustively with reference to their catecholase activity.[53–58] We have employed copper(II) Schiff–base complexes in catalytic olefin epoxidation reaction in homogeneous and heterogeneous conditions.[59–62] Nevertheless, catalytic

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efficacy of Cu(II) Schiff–base complexes *vis–à–vis* their structural diversities has rarely been explored. We are particularly interested to explore the catalytic efficacy of structurally diverse Schiff–base copper complex in coupling reaction.

We report here the syntheses and crystal structures of a family of structurally diverse copper(II) Schiff–base complexes and their application in catalytic O–arylation reaction. All the complexes efficiently catalyze O–arylation reaction of phenolic derivatives with nitroarenes in ethanol medium under milder condition. For practical applications, copper(II)–based catalysts are promising alternative by virtue of their low cost and insensitivity to air as well as their ability to cut down undesirable byproducts in O–arylation reaction. To our knowledge, there have been only very few reports in which copper(II) Schiff–base complex being used to catalyze C–O coupling reaction.[63–64]

2. Experimental section

2.1. Materials

N–(2–ethylamino)piperazine, *o*–vanilline, 3–ethoxysalicylaldehyde, 5–chlorosalicylaldehyde, 4′–ethoxy–2′–hydroxyacetophenone, 5′–chloro–2′–hydroxyacetophenone, 4–methoxysalicylaldehyde and 4′–methoxy–2′–hydroxyacetophenone were purchased from Aldrich. Solvents (analytical grade), cesium carbonate, copper(II) nitrate trihydrate, copper(II) perchlorate hexahydrate, substituted phenols and other chemicals were purchased from Merck (India) Pvt. Ltd. Solvents were dried before use.

2.2. Physical measurements

Elemental analysis was performed using the Perkin–Elmer 240C elemental analyzer. Fourier transform–infrared spectra of KBr pellets were measured on a Perkin–Elmer SPECTRUM II

FTIR spectrometer. The UV−Vis spectral measurements were carried out using a Shimadzu UV−Vis 1700 spectrophotometer. Thermogravimetric differential thermal analysis (TG–DTA) measurements were performed using a PerkinElmer (Singapore) Pyris Diamond TG/DTA unit. The heating rate was programmed at 4 °C min^{-1} with a protecting stream of N_2 flowing at a rate of 150 mL min^{-1}. The powder X–ray diffraction (XRD) patterns of samples were recorded on a Bruker D8 Advance diffractometer using CuKα radiation (λ = 1.54Å). ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance DPX 300 NMR (300 MHz) and 600 MHz spectrometer. Mass spectra were measured on a Waters XEVO–G2QTOF#YCA351 high resolution Mass Spectrometer.

Caution! *Perchlorate salts of metal complexes coordinated with organic ligands are potentially explosive. It should be handled with care and only a small amount of material should be prepared.*

2.3. Synthesis of the Schiff–base ligands L1, L2, L3, L4, L5, L6 and L7

The Schiff–base **L1** was prepared by mixing 20 mL ethanolic solution of N–(2–ethylamino)piperazine (0.491 g, 4 mmol) and *o*–vaniline (0.608 g, 4 mmol) together in a flat bottom flask. The mixture was then refluxed for 30 min. The resulting yellow colored solution was then cooled to room temperature. Ethanol was then separated almost completely from the mixture using a rotary evaporator. The amine N–(2–ethylamino)piperazine was mixed with 3–ethoxysalicylaldehyde, 4′–ethoxy–2′–hydroxyacetophenone, 5′–chloro–2′–hydroxyacetophenone, 5–chlorosalicylaldehyde, 4–methoxysalicylaldehyde and 4′–methoxy–2′–hydroxyacetophenone to synthesize ligands **L2**, **L3**, **L4**, **L5, L6** and **L7** respectively. All ligands were characterized by ^{1}H and ^{13}C NMR, HRMS and elemental analysis (see ESI).

2.4. Synthesis of the complex 1

A 10 mL ethanolic solution of $Cu(NO_3)_2.3H_2O$ (0.24 g, 1 mmol) was added dropwise to a 10 mL ethanolic solution of L1 (1 mmol). The resulting deep green mixture was kept undisturbed without stirring at room temperature. On slow evaporation of the filtrate, dark green cube shaped crystals appeared in a day. They were collected by filtration and washed first with mother liquor then with few drops of diethylether. Yield ca. 81% based on the metal. The phase purity of bulk **1** was confirmed by powder XRD (Fig. S14, ESI) and elemental analysis. Elemental analysis Calcd. C 35.94, H 4.74, N 14.97; found C 35.9, H 4.7, N 14.9.

2.5. Synthesis of the complexes 2–8

All complexes were synthesized by following the similar procedure to that of **1**, using **L2**, **L3**, **L4**, **L5, L6** and **L7**, respectively, for complexes **2**, **3**, **4**, **5, 7** and **8** instead of **L1**. The crystals which separated were deep green in color. Complex **6** was prepared by same procedure only selecting **L2** as ligand and $Cu(ClO_4)_2.6H_2O$ instead of $Cu(NO_3)_2.3H_2O$. The single crystals of **6** were light green in color. Yield of these complexes are ca. 86, 73, 76, 57, 79 and 83% respectively based on the metal. The phase purities of the complexes were confirmed by powder XRD (Fig. S15–21, ESI) and elemental analysis. Elemental analysis for **2** Calcd. C 38.71, H 5.24, N 14.56; found C 38.7, H 5.2, N 14.5; for **3** Calcd. C 40.21, H 5.26, N 14.62; found C 40.2, H 5.2, N 14.6; for **4** Calcd. C 35.83, H 4.30, N 14.92; found C 35.8, H 4.2, N, 14.9; for **5** Calcd. C 34.29, H 3.98, N 15.38; found C 34.3, H 3.9, N 15.4; for **6** Calcd C 30.80, H 4.83, N 7.18; found C 30.8, H 4.8, N 7.1; for **7** Calcd C 37.31, H 5.22, N 14.50; found C 37.3, H 5.2, N 14.4).

2.6. X–ray crystallography

X–ray diffraction data for all compounds were collected on a Bruker Smart Apex CCD X–ray diffractometer using graphite–monochromated Mo–Kα radiation (λ = 0.71073 Å). Integrated intensities and cell refinement were determined with the SAINT[65] software package using a

narrow–frame integration algorithm. An empirical absorption correction[66] (SADABS) was applied. The structure was solved by direct methods and refined using a full–matrix least–squares technique against F2 with the anisotropic displacement parameters for non–hydrogen atoms, with the programs SHELXS97 and SHELXL97.[67] Hydrogen atoms were placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. In the final difference Fourier maps there were no noteworthy peaks other than the ghost peaks surrounding the metal centers. A summary of the crystal data and relevant refinement parameters are given in Table 1.

2.7. Catalytic reactions

Fixed amount of Cu(II) complex (1 mol%) was added to a round–bottom flask that contained a solution of 4–nitrobenzaldehyde (0.151 g, 1 mmol), phenol (0.094 g, 1 mmol) and K_2CO_3 (0.326 g, 1 mmol) in ethanol (4 mL). The reaction mixture was refluxed at 80 °C for 8 h. The reaction conversion was monitored by TLC (thin layer chromatography) method. After 8 h the reaction mixture was cooled to room temperature and the mixture was extracted with water and diethyl ether (2 × 15 mL). The organic layers thus collected were combined and washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (mesh 60−120) using an n–hexane/ethyl acetate mixture as the eluent to give the desired product. The product was characterized by ^{1}H, ^{13}C–NMR, HRMS and elemental analysis then compared with literature data. To study progress of the reaction mixtures were collected at desired interval and products have been isolated following the above procedure (Fig. 3 and 4).

3. Results and discussion

3.1. Synthesis

The Schiff–base ligand L1 and L2 were prepared by the 1:1 condensation of 3–methoxysalicylaldehyde and 3–ethoxysalicylaldehyde with N–(2–ethylamino)piperazine in ethanol solution respectively. Ethanolic solution of the ligand was allowed to react with copper(II) nitrate salt to prepare bis–complexes, $[Cu_2(L1)_2(NO_3)_3]NO_3.MeOH$ (**1**) and $[Cu_2(L2)_2(NO_3)_3]NO_3.MeOH$ (**2**). Absence of any electron donating functional group at 3–position of salicylaldehyde and/or 2–hydroxyacetophenone produced monomer complexes, e.g. $[Cu(L3)(NO_3)]NO_3$ (**3**), $[Cu(L4)(NO_3)]NO_3$ (**4**), $[Cu(L5)(NO_3)]NO_3$ (**5**), $[Cu(L6)(NO_3)_2]MeOH$ (**7**) and $[Cu(L7)(NO_3)]NO_3$ (**8**). Here nitrate anions also have some contribution for structure direction. It shows three different modes in **1** and **2**, as a bridging agent, terminal capping and also as a charge balancing ion. In **3–5, 7** and **8** it only acts as a capping and charge balancing agent. In all the above seven complexes Schiff–base ligand showed tridentate (NNO donor) coordination. When copper(II) perchlorate salt was used instead of copper(II) nitrate L2 affords a hetero–bridged dinuclear complex, $[Cu_2(L2)_2(H_2O)_2](ClO_4)_4.4H_2O$ (**6**), where L2 acts as both tri– and tetra–dentate (NNO and N_2O_2 donor, respectively) chelating ligand. Besides, phenoxide and water oxygen bridged two different copper centers. In **6** water molecules are in three different environments, as bridging or simple coordinating ligand and as water of crystallization. In all Schiff–base ligands proton liberated from phenolic OH group bonded to nitrogen atom of piperazine ring to form Zwitter ionic neutral molecule. Synthetic routes of complexes (**1–8**) are given in Scheme 2.

3.2. Thermal analysis

Thermogravimetric analysis confirmed that complexes **1–5** and **7** were thermally stable up to ~ 185 °C as shown in Fig. S1 and S2 (see ESI). The TG curve indicated that **1** and **2** starts to lose water molecules from the beginning and mass loss of approximately 2.02 and 1.91% have shown

upto a temperature 140 °C. This mass loss was well in agreement with the theoretical values 1.93

and 1.87 % for **1** and **2** respectively, corresponds to the loss of one molecule of crystalline water.

Corresponding DTA (differential thermal analysis) curve showed endothermic peak for both

compounds at ~ 75 °C. Compounds **3–5** and **7** experienced no such loss for deaquation, however,

after 180 °C (230 °C for **7**) all the compounds showed continuous mass loss up to 800 °C due to

decomposition showing two exothermic peaks at ~ 230 °C and ~ 410 °C in DTA curves.

Thermogravimetric analysis of complex **6** was performed upto a temperature 200 °C, further

heating was avoided as it contains explosive perchlorate anions (Fig. S2, see ESI). TG curve of **6**

showed mass loss from room temperature which continued up to 200 °C. This mass loss

corresponds to the liberation of water of crystallization and thereafter coordinated water

molecules. Corresponding DTA curve showed two broad endothermic peaks at ~ 62 and 148 °C.

3.3. Spectroscopic analysis

In the IR spectra of complexes **1–8** the characteristic vibration band of azomethine $v(C=N)$ group

were observed at around 1600 cm^{-1} (Fig. S3 and S4). Peaks observed in the range 3060–2610

cm^{-1} were due to the stretching vibration of methyl ($-CH_3$), methylene ($-CH_2-$) and aromatic C–

H bonds. The appearance of strong band for the phenolic C–O group near 1210 cm^{-1} in IR

spectrum of the compounds indicates the presence of the phenolic oxygen atom. The presence of

a broad band at *ca.* 3450 cm^{-1} for **1–2** and 3500 cm^{-1} for **6** indicates the presence of water

molecules. In complexes **1–5, 7** and **8** the characteristic, strong peaks for stretching vibrations of

nitrate molecules appeared at ~ 1440 cm^{-1} (v_5), 1380 cm^{-1} (v_1) and 1020 cm^{-1} (v_2). Two strong

peaks appearing at 1100 cm^{-1} (v_3) and 915 cm^{-1} (v_4) for **6** were ascribed to the characteristic

vibration bands of uncoordinated perchlorate anions.

Electronic absorption spectra of all the complexes and ligands were recorded in ethanol medium (Fig. S5–S7, see ESI). The free ligand L1 showed three intra–ligand charge transfer bands at 416, 292 and 220 nm, which were significantly shifted to lower wavelength in complex **1** (Fig. S6, see ESI). Ligand L2 showed intra–ligand charge transfer bands at 370, 293 and 218 nm, amongst them first band were shifted to lower wavelength and other bands to higher wavelength upon complexation both in case of **2** and **6** (Fig. S6, see ESI). Rest of the ligands L3, L4, L5, L6 and L7 also showed three intra–ligand charge transfer bands; amongst them first two bands were shifted to lower wavelength and other band remain in the same position in complexes **3**, **4**, **5, 7** and **8**. The spectra showed a single absorption band at 639, 638, 620, 624, 641, 632, 641 and 622 nm for complexes **1**–**8**, respectively. The position of these bands were typical of d–d transition for Cu(II) complex.[68] For all the complexes bands appearing in the region 290–310 nm were attributed to a π–π* transition within the ligand[69] and the other bands appeared around 390 nm was due to L $\rightarrow$ M charge transfer transition.

3.4. Crystal structure of complexes (1–7)

Complexes **1** and **2** containing 3–methoxy– and 3–ethoxy– derivatives of Schiff–base are isostructural. The crystal structures confirm the chair conformation of the piperazine ring in both complexes. N_2O donor Schiff–base binds Cu(II) centers in a tridentate manner (Fig. 1). Both complexes crystallize in the monoclinic space group *C2/c* and consist of a centrosymmetric dinuclear cationic $[Cu_2(Lx)_2(NO_3)_3]^+$ (x = 1 or 2) moiety as shown in Fig. 1a and 1b respectively. Selected bond distance and angles are collated in Table S1 (see ESI). Copper centers feature a 5 coordinated square pyramidal geometry in both compounds as Addison parameter of (τ = |b – a|/60° where b and a are the two largest angles around the central atom; τ = 0 and 1 for perfect square pyramidal and trigonal bipyramidal geometries, respectively) **1** and **2** are 0.022 and 0.038

respectively.[70] The axial position is occupied by oxygen atom (O(6)) of bridged nitrato group with the long distance (Table S1). Three donor atoms (O(2), N(1) and N(2) in **1** and O(1), N(1) and N(3) in **2**) from chelating ligand occupy three equatorial positions and other one is occupied by oxygen atom (O(3)) from terminal nitrate group. Apart from that a weak interaction is found from oxygen atom (O(4)) of terminal nitrato group at the distances 2.734(7) and 2.651(4) for **1** and **2**, respectively. Intermolecular H–bonding gives further stability to both **1** and **2** (Table S4, see ESI). Fig. S8 and S9 shows both **1** and **2** afford a 2D supramolecular network.

Structure determination reveals that complex **3** consists of cationic monomer (Fig. 2a) and it crystallizes in a monoclinic space group $P2_1/c$. The selected bond lengths and angles are summarized in Table S2. The copper center is five–coordinated with an elongated square–pyramidal (4+1) geometry. A oxygen atom (O(23)) from the nitrato group coordinates axially at a very long distance 2.5440(15) Å. The Addison parameter of the copper center is 0.069, indicating its square pyramidal geometry. Copper(II) complex with similar structure was observed in case of Schiff–base derived from 4′–methoxy–2′–hydroxyacetophenone (complex **8** in our case) instead of 4′–ethoxy–2′–hydroxyacetophenone.[71] Complex **3** gains further stabilization through intermolecular H–bonding and a 1D supramolecular chain has been found (Table S4, see ESI) where, uncoordinated anionic nitrate molecule plays important role to form this zigzag chain (Fig. S10).

Single crystal X–ray structure determination reveals that complexes **4** and **5** are also cationic monomer like **3** and crystallizes in a monoclinic space group $P2_1/c$ (Fig. 2b and 2c respectively). In both of them Cu(II) ion features a pentacoordinated square pyramidal geometry where a oxygen atom (O(20), O(19) for **4** and **5** respectively) of the coordinated nitrato group occupies the axial position with a long distance of 2.550(3) and 2.5440(15) Å (Table S2). The

Addison parameters of the copper centers are 0.067 and 0.108 for **4** and **5** respectively, indicating their square pyramidal geometry. Both **4** and **5** forms 1D zigzag supramolecular structure through intermolecular H–bonding like complex **3** (Table S4, Fig. S11 and S12 respectively; see ESI).

Complex **6** consist discrete dinuclear unit of copper(II) (Fig. 2d). Selected bond parameters and angles are given in Table S3. The complex contains two different [CuL2] units, two coordinated water molecules and four uncoordinated perchlorate anions with four crystalline water molecules. Cu(1) atom features a pentacoordinated coordination sphere with square–pyramidal geometry. The equatorial plane is formed by the two nitrogen atoms N(12) and N(15), and the bridged phenoxido oxygen atom (O(1)) of one Schiff–base (tetradentate). An oxygen atom O(41) from the bridged water molecule completes the basal plane. Another terminal water molecule (O42) occupies the axial position at a distance 2.233(3) Å (Fig. 2d). The Addison parameter of Cu(1) is 0.052, indicating its square pyramidal geometry. The basal positions of octahedral Cu(2) atom is occupied by two nitrogen atoms N(32) and N(35), and a phenoxido oxygen atom O(21) of neighboring Schiff–base ligand. The fourth position of the equatorial plane and one elongated epical position are occupied by the bridged phenoxido oxygen atom (O(1)) and ethoxide oxygen atom (O(8)) of the tetradentate Schiff–base ligand. The bridged oxygen atoms of water molecule (O(41)) coordinates to the elongated side to complete the distorted octahedral geometry around Cu(2) with the bond distance 2.493(2) Å. The Cu----Cu distance in **6** is much closer (3.227) than other two dimers **1** and **2** (6.08 and 6.18, respectively). In **1** and **2** nitrates act as $\mu_{1,3}$ bridging ligand but in **6** phenoxide and water has no other option than to bind in $\mu_{1,1}$ bridging mode. This probably is the cause for two copper centers to come closer. Crystalline water and perchlorate anions give the complex further stability through inter–

molecular H–bonding (Table S4, see ESI). Numerous examples of mixed bi–bridged complexes containing phenoxido, alkoxido or hydroxido ligand featuring Cu_2O_2 or Cu_2O_3 moieties have been reported so far, however, there is no example of Cu(II) Schiff–base complex in which two copper centers are bridged through mixed phenoxido/water bridges. In this count complex (**6**) is a unique example.

Last member of the family, compound **7** crystallizes in a monoclinic space group $P2_1/c$. Copper center is five–coordinated with square–pyramidal geometry where three donor atoms of the Schiff–base ligand (O(4), N(2) and N(3)) occupy the basal plane. An oxygen atom (O(1)) of coordinated nitrato group binds copper center to complete the equatorial plane. Second oxygen atom (O(8)) from second coordinated nitrato group coordinates axially at a long distance 2.484(3) Å. The structure is quite similar with compounds **3**, **4** and **5**, but the difference is in weak interaction originates from oxygen atom (O(3)) of one nitrate, at a distance 2.734(7), coordinates axially to copper center. This minute structural change in 7 generates 2D supramolecular structure through H–bonding (Table S4, Fig. S13 see ESI).

3.5. Catalytic activity study

Initially, optimization studies for C–O coupling reaction was undertaken using p–methylphenol and p–nitrobenzaldehyde as substrates and complex **1** as catalyst under various reaction conditions as given in Table 2. To begin with we explored the effect of solvents since solvent plays important role in transition–metal catalyzed transformation. Among different solvents, highest yield of product was obtained in DMF (entry 1). Though, ethanol was selected (entry 14) for environmental concern. It was generally found that O–arylation reaction was much faster with Cs_2CO_3 than with K_2CO_3 or Na_2CO_3 due to higher solubility of Cs_2CO_3.[72] However, use of K_2CO_3 will be more economic than Cs_2CO_3 for large scale production. Other bases such as KOH,

Na$_2$CO$_3$, CH$_3$COONa, *tert*–BuOK, and DABCO showed slower formation of 4–formayl–4′–

methyldiphenylether after 8 hour (entries 8–12). Cheap K$_2$CO$_3$ showed satisfactory yield and has

been chosen for the O–arylation reaction (entry 14). Isolated yield increased sharply with the

increase of reaction temperature (entries 14–16). The copper concentration in the reaction

mixture was another important factor to investigate. Thus, the O–arylation reaction was carried

out in the presence of 0.1, 0.2, 0.5, 1 and 2 mol% of catalyst (entries 17–21). A maximum

conversion was achieved with 1 mol% of catalyst in 8 hours as shown in Fig. 3 and 4. Notably

isolated yields were not up to the mark in lower concentration of catalyst. Besides, increasing in

catalyst concentration beyond 1 mol% the reaction rate was not enhanced significantly. No

reaction occurred in the absence of catalyst in 8 hours (entry 13) as well as no induction period

was observed in all the reactions (Fig. 3 and 4). A mixture of copper nitrate salt and ligand L1 as

well as copper nitrate salt itself has been used as catalyst which afforded a moderate to low

conversion in coupling reaction (Table 2; entry 21 and 22). Thus the optimum condition of the

catalytic reaction was as follows: K$_2$CO$_3$ (base), ethanol (solvent), 1 mol% catalyst and reaction

temperature 80 °C.

Under the optimized reaction conditions, the scope and applicability of the coupling

reaction using *p*–nitrobenzaldehyde with substituted phenol to unsymmetrical diaryl ethers were

investigated (Table 3). At first, impact of electronic properties of the aryl moiety of phenols on

the yield of catalytic reactions was evaluated using various substitutions on phenol moiety.

Results obtained in test reactions demonstrate that electronic properties of phenols affect the

product yield (Table 3, entries 1–5). Substituted phenols possessing electron donating methyl

group accelerates the reaction to yield product in higher amount in comparison to simple phenol.

Though, *p*–methylphenol showed higher yield than *o*–methylphenol indicating yield being

affected by the steric effects of substitution also (Table 3, entries 2 and 3). Besides, catalysts were capable of activating less nucleophilic phenols (2–naphthol and 1–naphthol) to react with *p*–nitrobenzaldehyde and afforded good yields (Table 3, entries 6 and 7 respectively). We have investigated reactions of *p*–nitrobenzonitrile, and *o*– or *p*–dinitrobenzene with different phenols and collected in Table 3. Notably they also exhibit almost same yields with same trends in catalytic reaction. Progress of O–arylation reaction for *p*–nitrobenzaldehyde and *p*–nitrobenzonitrile with *p*–methylphenol catalyzed by complex **1** was given in Fig. 3. The coupling reactions of electron–deficient phenols with aryl halides have been challenging as the corresponding phenolates are weak nucleophile.[73] Recently, Li *et al.* reported the O–arylation of *p*–hydroxyacetophenone with *p*–fluorobenzonitrile in DMF medium at 90 °C temperature under N$_2$ atmosphere.[74] Buchwald and his group also studied the reactivity of some electron–deficient phenols in C–O coupling at 100–110 °C. However, in all the above reported processes aryl halides were used as electrophile. For the first time, the results presented here demonstrate that *p*–nitrobenzonitrile can behave as an electrophile in O–arylation of *p*–hydroxyacetophenone and can afford very good yield in ethanolic medium.

   All the copper(II) Schiff–base complexes (**1**–**8**) efficiently catalyzed the O–arylation reactions. The turn over frequency calculation demonstrates catalytic efficacy of complex **6** is better than other monomeric and dimeric complexes. Two nitrato–bridged dimers **1** and **2** were less efficient than others may be due to higher coordination number. Five monomers (**3**, **4**, **5**, **7** and **8**) were little bit less efficient than **6**. Amongst the monomers **7** shows lowest efficiency which may be due to the steric–crowding around metal center. To test the stability of the complexes in reaction medium HRMS spectra of all compounds have been recorded in ethanol medium. Mass spectra confirm that both monomeric and dimeric complexes are stable in boiling

ethanol (see ESI). We compared efficacy of our catalyst with some Cu(II) salts, Cu(II) salts with amine and a previously reported nitrato–bridged 1D Cu(II) Schiff–base complex[61] under the optimized reaction condition and results were summarized in Table S5 (see ESI). Even a cursory look at Table S5 it will be clear that Cu(II) salts act as poor catalyst but their activity increases in presence of amine may be due to *in situ* formation of metal–amine chelate. Catalytic efficiency (TOF) of the previously reported nitrato–bridged complex showed close efficiency to that of the monomer catalysts.

A plausible mechanism has been suggested based on the previous reports.[75] According to recent studies on the mechanism of the copper–catalyzed N–arylation reactions, it assumes that the reaction proceeds with the initial nucleoplilic substitution (NuH) over the copper complex (Scheme 3). The base used here abstracts the N–H proton from the heterocycle, thereby generating a nucleophile. Then oxidative addition of the nitroarene ($ArNO_2$) occurs through coordination with the Cu atom followed by reductive elimination to give the desired N–arylated heterocycles (Scheme 3).

4. Conclusion

Seven structurally diverse copper complexes containing mono– and dimeric structure, depending on the nature of Schiff–base ligands or copper salts, have been synthesized and fully characterized by X–ray single–crystal structural analyses. Their molecular structures differ in the solid state under the influence of varied stereo–electronic character of Schiff–base ligands with copper salt used. Dinuclear complex **6** exhibits a hitherto unknown structure of Cu(II) Schiff–base complex in which two copper centers are bridged through mixed phenoxido/water bridges. All complexes are highly active to catalyze the C–O coupling reactions of phenols with *p*–nitrobenzaldehyde/*p*–nitrobenzonitrile in environmentally benign solvent, ethanol. The result

presented here is the rare example of C–O coupling reactions which are being catalyzed by copper(II) Schiff–base complex. Notably, catalysts are efficient enough to activate electron–deficient phenols towards O–arylation reaction to afford diarylethers. This catalytic procedure also resolves the problem of unwanted by-product formation by using cheaper variety of substrate, nitroarenes. Further investigations on the synthesis of structurally diverse Schiff–base complexes and their application as catalysts in other organic reactions are currently on progress in our laboratory.

Acknowledgement

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Captions:

Scheme 1 Selected bioactive compounds featuring arylether moiety

Scheme 2 Synthesis route of complexes **1–8**

Scheme 3 Plausible mechanism of the reaction

Fig. 1 ORTEP diagram of complexes **1** (a) and **2** (b)

Fig. 2 ORTEP diagram of complexes **3** (a), **4** (b), **5** (c), **6 (**d) and **7** (e)

Fig. 3 Plot showing progress of O–arylation reaction for *p*–nitrobenzaldehyde (■) and *p*–nitrobenzonitrile (●) with *p*–methylphenol catalyzed by complex **1**

Fig. 4 Plot showing progress of O–arylation reaction catalyzed by **1**, **3** and **6** using *p*–nitrobenzaldehyde and *p*–methylphenol as reactant

Table 1 Crystal data and refinement details of compounds **1–7**

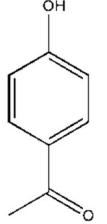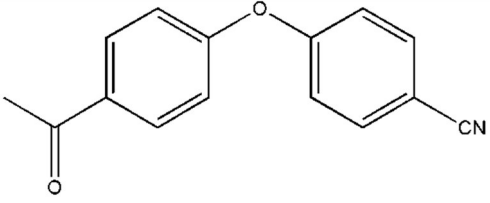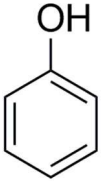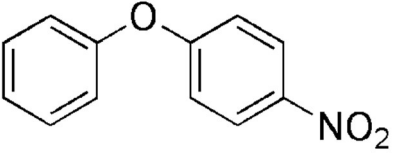| Complex	1	2	3	4	5	6	7
Formula	$C_{28}H_{42}Cu_2N_{10}O_{18}$	$C_{31}H_{47}Cu_2N_{10}O_{16.50}$	$C_{16}H_{25}CuN_5O_8$	$C_{14}H_{20}ClCuN_5O_7$	$C_{13}H_{18}ClCuN_5O_7$	$C_{30}H_{56}Cl_4Cu_2N_6O_{25}$	$C_{15}H_{25}CuN_5O_9$
Formula Weight	933.82	950.86	478.95	469.34	455.31	1169.68	482.95
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space Group	$C2/c$	$C2/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	15.3483(9)	15.2074(4)	23.3712(6)	22.6374(13)	22.0294(6)	9.1817(4)	12.0035(5)
b (Å)	12.7358(8)	12.6983(3)	6.5538(2)	6.6010(4)	6.6638(2)	11.7822(5)	9.5610(4)
c (Å)	19.0760(11)	20.2333(5)	12.8896(3)	12.4456(7)	12.1691(3)	22.0042(10)	18.1151(8)
α (°)	90	90	90	90	90	86.723(2)	90
β (°)	92.446(4)	91.6930(10)	90.7490(10)	97.759(2)	98.658(2)	89.312(2)	105.715(3)
γ (°)	90	90	90	90	90	83.934(2)	90
V (Å^3)	3725.4(4)	3905.51(17)	1974.13(9)	1842.71(19)	1766.06(8)	2363.19(18)	2001.28(15)
Z	4	4	4	4	4	2	4
D_{calc} (gcm^{-3})	1.665	1.617	1.611	1.692	1.712	1.644	1.603
μ (mm^{-1})	1.234	1.176	1.163	1.380	1.437	1.217	1.151
R_{int}	0.0811	0.0322	0.039	0.049	0.025	0.032	0.059
Unique data	4116	4348	5305	3871	5396	12608	4521
Data with $I > 2(I)$	2247	3525	4114	3487	4483	8436	2859
R_1 ($I > 2(I)$)	0.0756	0.0620	0.0346	0.0397	0.0329	0.0492	0.0480
wR_2 ($I > 2(I)$)	0.2470	0.1570	0.0877	0.0839	0.0843	0.1329	0.1307
(GOF) on F^2	1.032	1.056	1.037	1.202	1.038	1.028	0.965
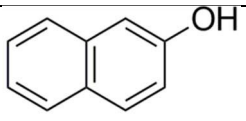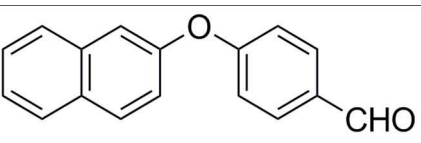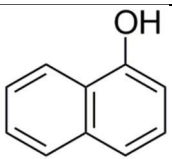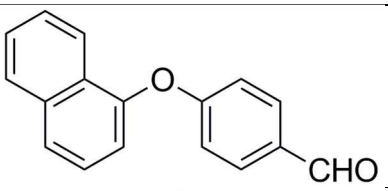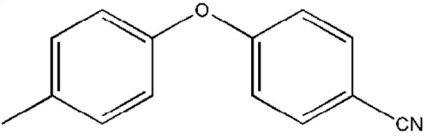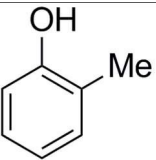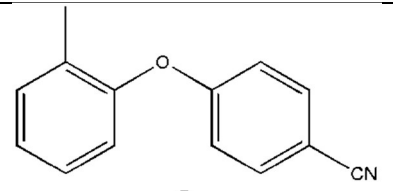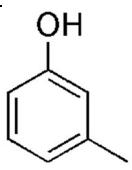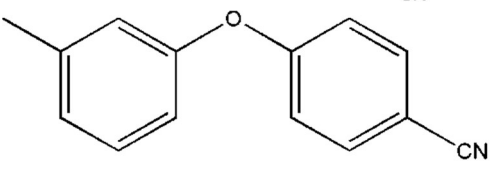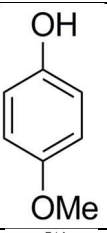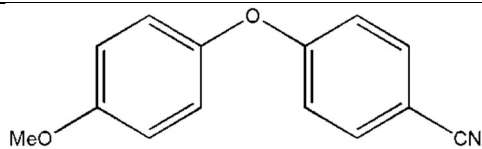
Table 2 Optimization of reaction conditions[a]
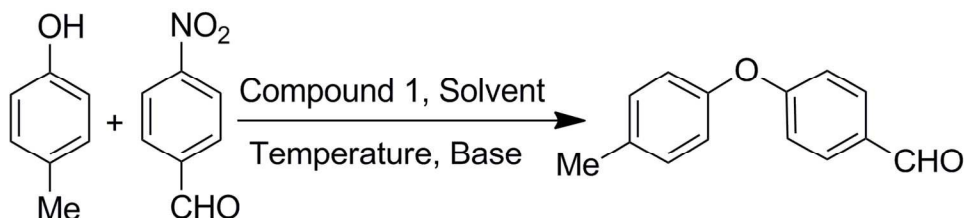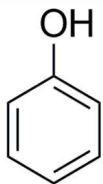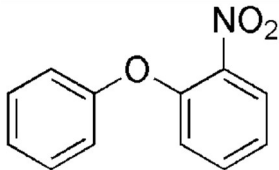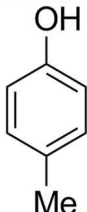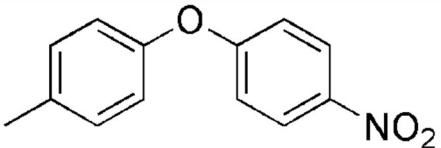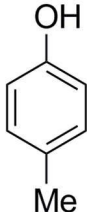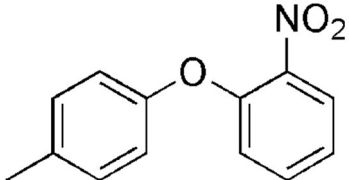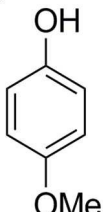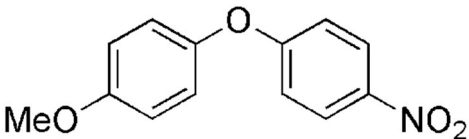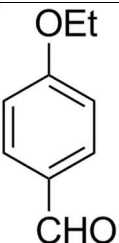
Entry	Catalyst	Base	Solvent	Yield[b] (%)
1	Compound **1**	K_2CO_3	DMF	97
2	Compound **1**	K_2CO_3	DMSO	87
3	Compound **1**	K_2CO_3	Toluene	18
4	Compound **1**	K_2CO_3	Acetonitrile	36
5	Compound **1**	K_2CO_3	Methanol	73
6	Compound **1**	K_2CO_3	Ethyleneglycol	70
7	Compound **1**	K_2CO_3	Dioxane	42
8	Compound **1**	KOH	Ethanol	62
9	Compound **1**	Na_2CO_3	Ethanol	64
10	Compound **1**	CH_3COONa	Ethanol	0
11	Compound **1**	tBuOK	Ethanol	18
12	Compound **1**	DABCO	Ethanol	0
13	–	K_2CO_3	Ethanol	0
14	Compound **1**	K_2CO_3	Ethanol	88
15	Compound **1**	K_2CO_3	Ethanol	21[c]
16	Compound **1**	K_2CO_3	Ethanol	57[d]
17	Compound **1**	K_2CO_3	Ethanol	12[e]
18	Compound **1**	K_2CO_3	Ethanol	28[f]
19	Compound **1**	K_2CO_3	Ethanol	62[g]
20	Compound **1**	K_2CO_3	Ethanol	88[h]
21	$Cu(NO_3)_2.3H_2O$ + L1	K_2CO_3	Ethanol	41
22	$Cu(NO_3)_2.3H_2O$	K_2CO_3	Ethanol	8

[a] Reaction condition: *p*–nitrobenzaldehyde (1.1 mmol), *p*–methylphenol (1.0 mmol), base (1.2 mmol), catalyst (1 mol%), solvent (3 mL) at 80 °C for 8 h. [b] Isolated yield. [c] Temperature was 30 °C and [d] 50 °C. [e] 0.1 Mol% compound **1**. [f] 0.2 Mol% compound **1**. [g] 0.5 Mol% compound **1**. [h] 2 Mol% compound **1**.

Table 3 O–arylation of *p*–nitrobenzaldehyde with phenols[a]

Aryl alcohol + [*p*-nitrobenzaldehyde, R=–CN/–CHO] $\xrightarrow[\text{80 °C, EtOH, K}_2\text{CO}_3]{\text{Catalyst (1 mol \%)}}$ Aryl–O–C₆H₄–R

(R=−CN/−CHO)
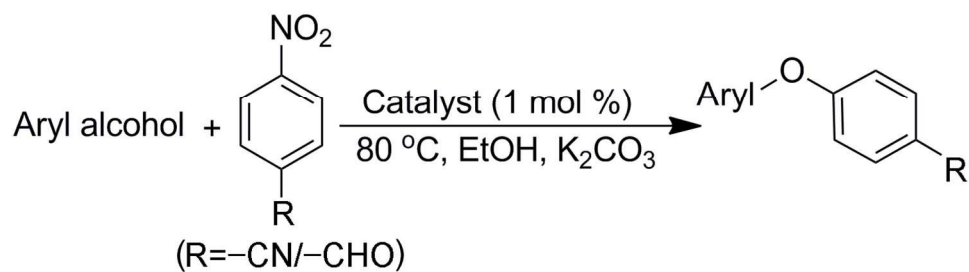
Entry	Aryl alcohol	Product	Catalyst	Yield[c] (wt%)	TOF[d] (h⁻¹)
1	OH (phenol)	phenyl ether–CHO	**1**	81	5
			2	81	5
			3	88	11
			4	84	11
			5	84	11
			6[b]	94	16
			7	78	10
			8	87	11
2	OH, Me (p-cresol)	product–CHO	**1**	88	6
			2	88	6
			3	93	12
			4	91	12
			5	92	12
			6	97	16
			7	83	10
			8	89	11
3	OH, Me (o-cresol)	product–CHO	**6**	92	15
4	OH, Me (m-cresol)	product–CHO	**6**	94	16
5	OH (4-ethylphenol)	product–CHO	**6**	95	16

Entry	Substrate	Product			
6	naphthalen-2-ol (OH)	naphthyl-O-C6H4-CHO	6	84	14
7	naphthalen-1-ol (OH)	naphthyl-O-C6H4-CHO	6	89	15
8	4-methylphenol (OH, Me)	Me-C6H4-O-C6H4-CN	6	98	16
9	2-methylphenol (OH, Me)	o-Me-C6H4-O-C6H4-CN	6	90	15
10	3-methylphenol (OH)	m-Me-C6H4-O-C6H4-CN	6	96	16
11	4-methoxyphenol (OH, OMe)	MeO-C6H4-O-C6H4-CN	6	98	16
12[e]	4-hydroxyacetophenone (OH)	MeCO-C6H4-O-C6H4-CN	6	43	5
13	phenol (OH)	C6H5-O-C6H4-NO2	6	93	15

| 14			**6**	85	14
15			**6**	97	16
16			**6**	90	15
17			**6**	98	16
18	EtOH		**1** **2** **3** **4** **5** **6** **7** **8**	–	–

[a] Reaction condition: *p*–nitrobenzaldehyde (1.1 mmol), aryl alcohol (1.0 mmol), K_2CO_3 (1.2 mmol), catalyst (1 mol%), EtOH (3 mL) at 80 °C for 8 h. [b] except for catalyst **6** (3 hours). [c] Isolated yield. [d] Mol. diaryl ether/mol. copper/ h. [e] 10 hours.
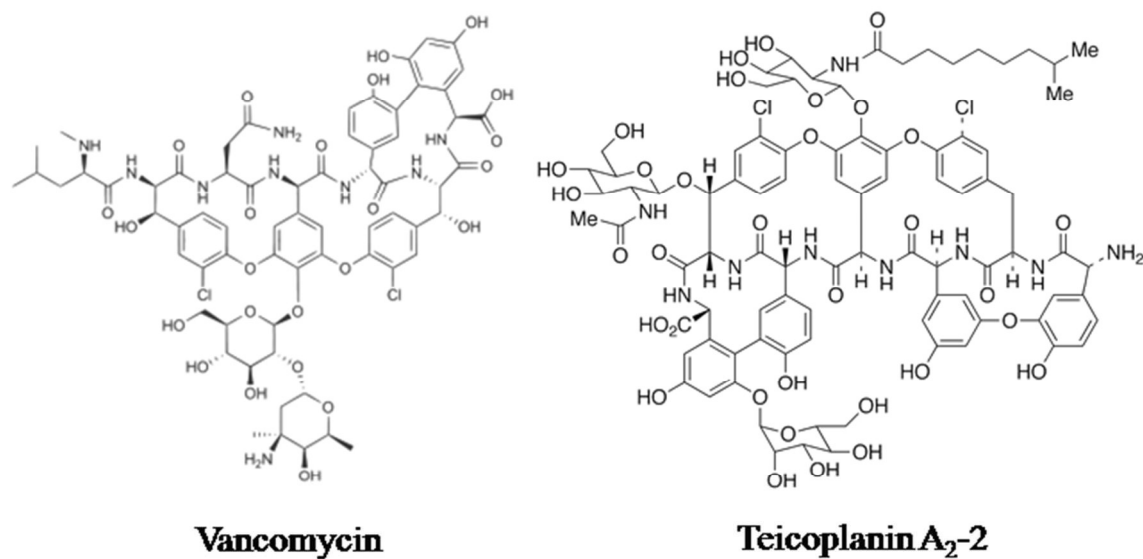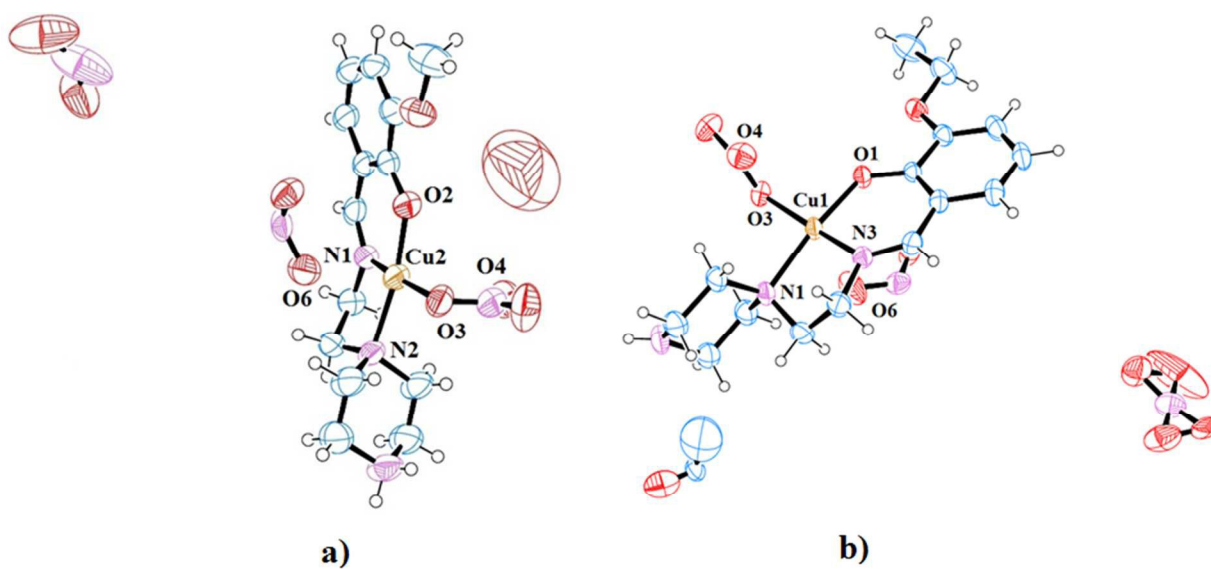
Scheme 1 Selected bioactive compounds featuring arylether moiety
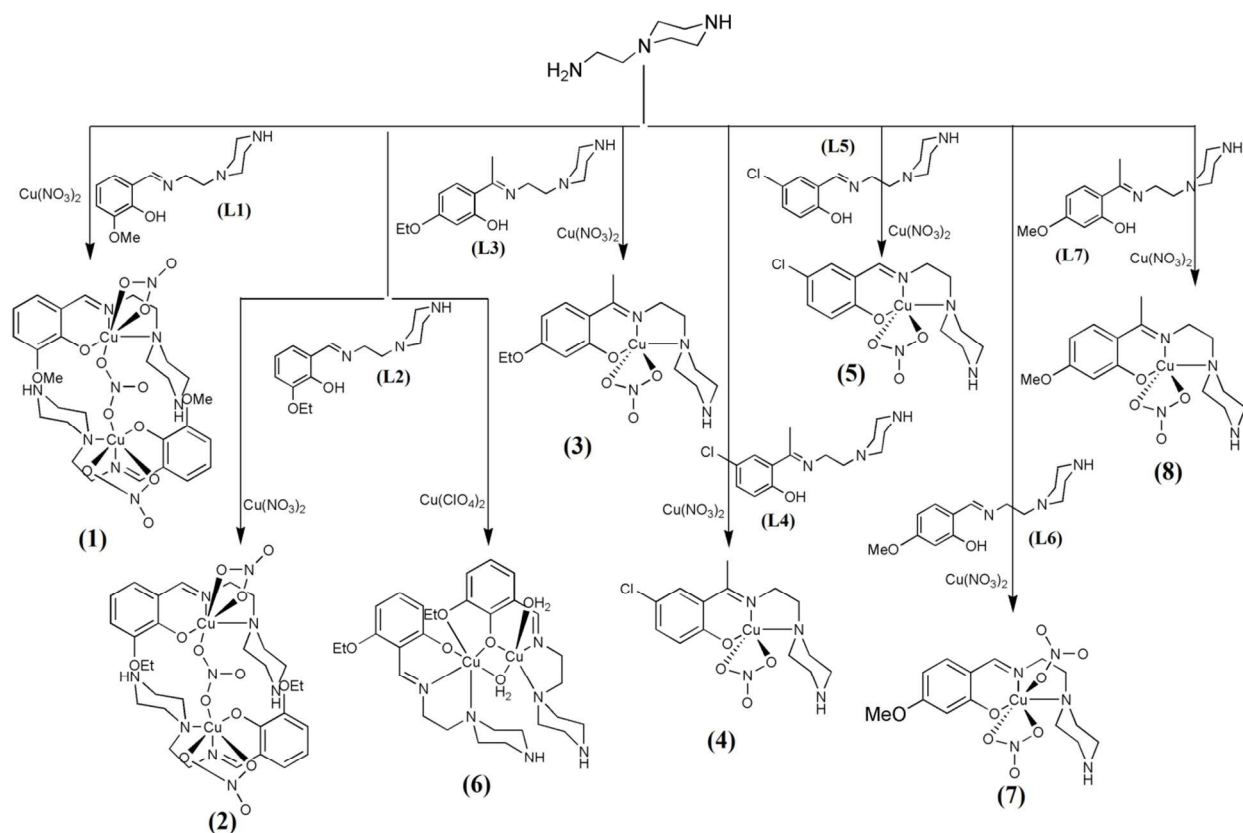
Scheme 2 Synthesis route of complexes **1–8**
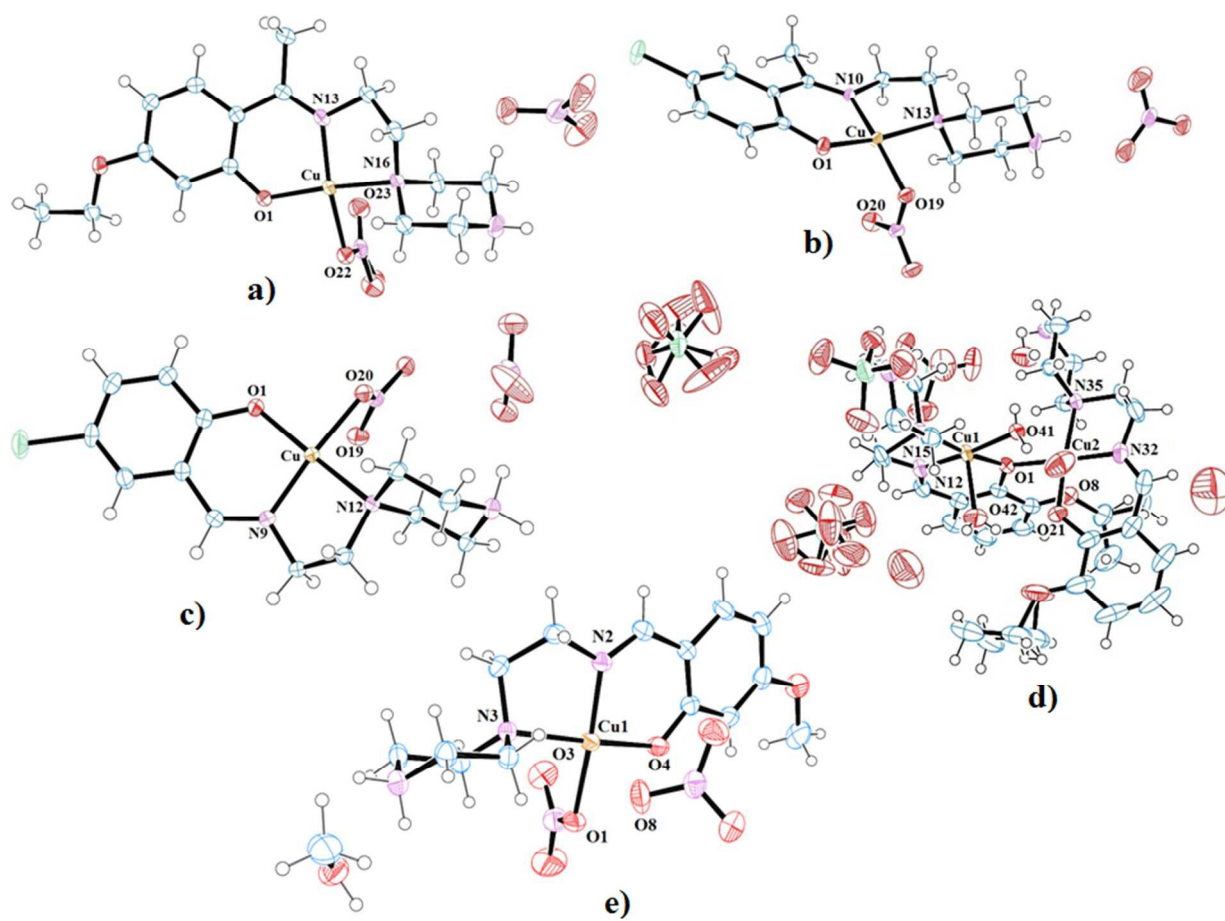
Scheme 3 Plausible mechanism of the reaction
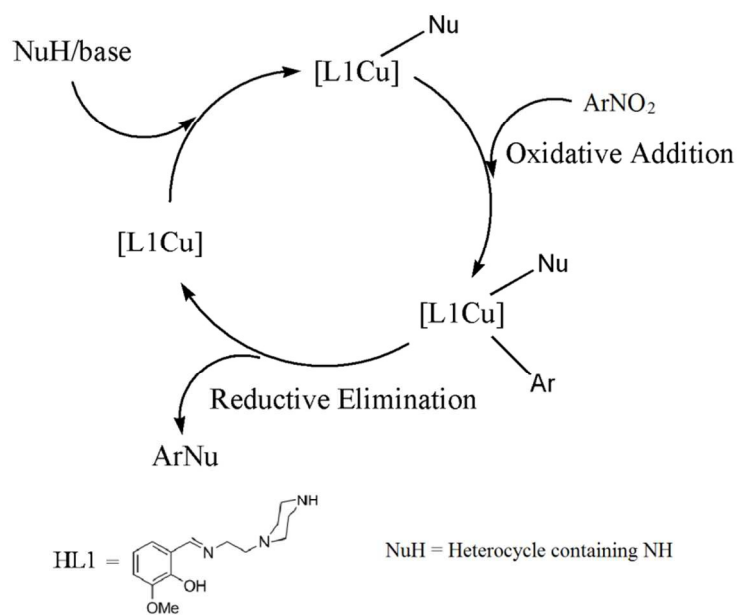
Fig. 1 ORTEP diagram of complexes **1** a) and **2** b)

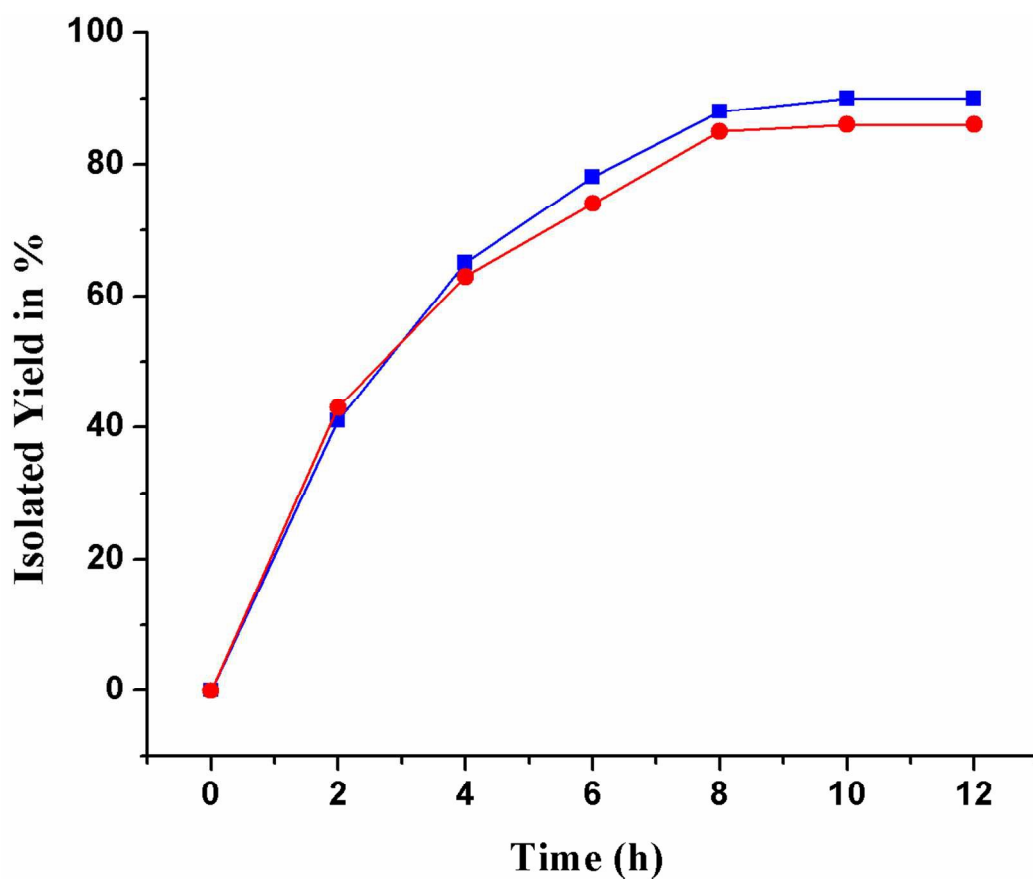Fig. 2 ORTEP diagram of complexes **3** a), **4** b), **5** c), **6** d) and **7** e)

Fig. 3 Plot showing progress of O–arylation reaction for *p*–nitrobenzaldehyde (■) and *p*–

nitrobenzonitrile (●) with *p*–methylphenol catalyzed by complex **1**
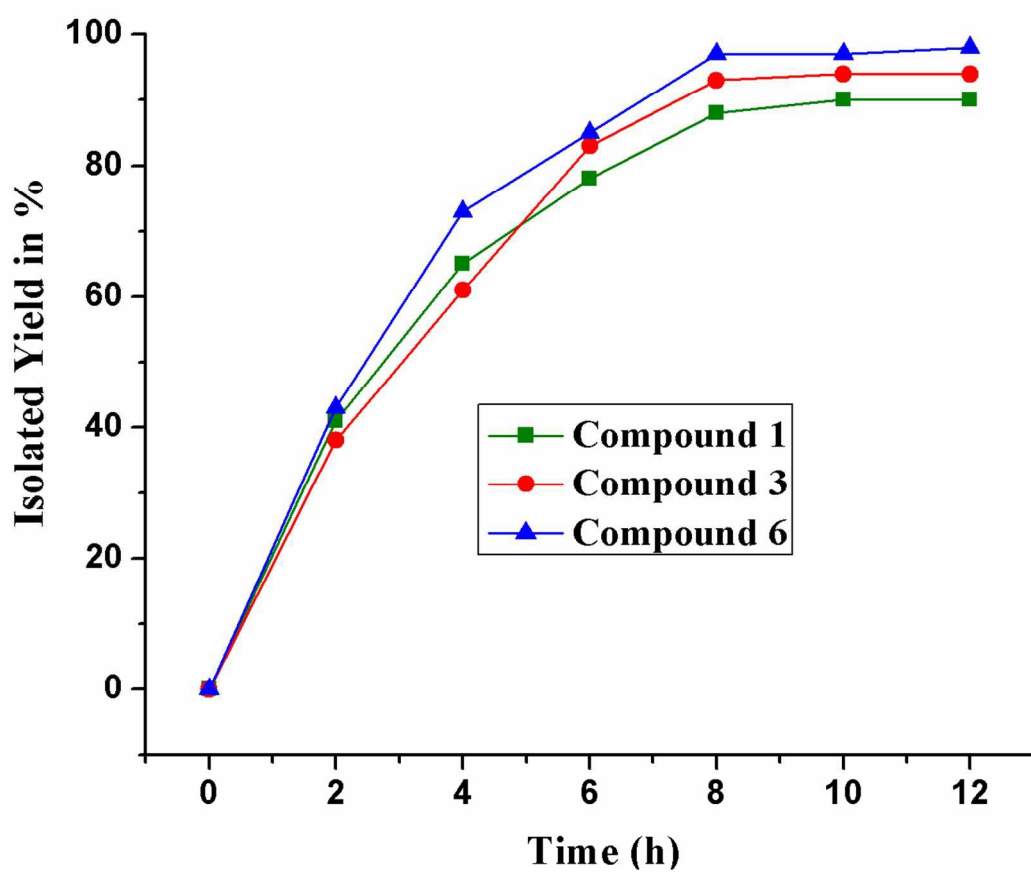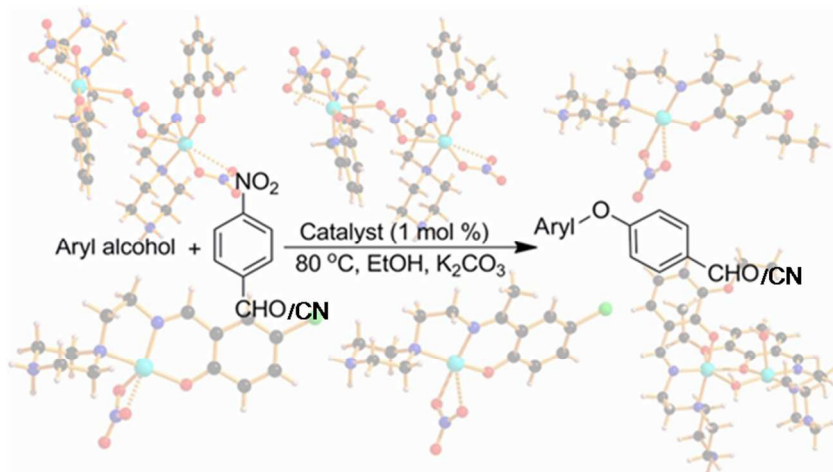
Fig. 4 Plot showing progress of O–arylation reaction catalyzed by **1**, **3** and **6** using *p*–

nitrobenzaldehyde and *p*–methylphenol as reactant

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Catalytic O-arylation reaction has been studied by employing a variety of copper(II) Schiff-base complexes under environmentally benign condition.