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GROUP 11 PINCER OXAZOLINE COMPLEXES

by

Mahroo Taghvaeem Seighalani

M.Sc., University of Guilan, Iran, 2005

A Thesis

Presented to Ryerson University

in partial fulfillment of the

requirements for the degree of

Master of Science

in the Program of Molecular Science

Toronto, Ontario, Canada, 2012
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GROUP 11 PINCER OXAZOLINE COMPLEXES

Mahroo Taghvaei Seighalani

Master of Science, Molecular Science, Ryerson University, 2012

Abstract

The synthesis and characterization of new copper pincer complexes via cyclometallation of potentially anionic pincer ligands with C₁ point group symmetry is reported. All of these complexes have been characterized by single crystal X-ray diffraction method, which confirms the proposed tridentate binding mode of pincer ligand and the formation of an amido N-Cu bond. The reactivity of two of the complexes was investigated towards C-C bond formation reaction, notably the Henry reaction. One of the complexes, which was derived from the achiral pincer ligand, is shown to be a suitable catalyst for the Henry reaction under the standard conditions. The Henry or nitroaldol reaction is one of the organic reactions which affords a C-C bond. The product of this reaction is a β -nitro alcohol which is formed by addition of a nitroalkane to a carbonyl compound.

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TO MY BELOVED ONE

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List of Abbreviations

Å	angstroms (10^{-10} metres)
br	broad
<i>n</i> Bu	<i>n</i> -butyl
<i>t</i> Bu	<i>tert</i> -butyl
CDCl ₃	deuterochloroform
COE	cyclooctene
COD	cycloocta-1,5-diene
d	doublet
dba	dibenzylideneacetone
DCM	dichloromethane
dd	doublet of doublets
DMF	<i>N,N'</i> -dimethylformamide
eq	equation
equiv	equivalent
Et	ethyl
EtOH	ethanol
HOAc	acetic acid
IR	infrared
m	multiplet or medium
mmol	millimole (s)
m. p.	melting point
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge Thermal Ellipsoid Plot
PA	picolinic acid
Ph	phenyl
rt	room temperature
s	singlet or strong
TCM	transcyclometalation
THF	tetrahydrofuran

TLC	thin layer chromatography
TM	transition metal or transmetalation
4-tol	4-methylphenyl
UV	ultraviolet
w	weak

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Introduction

1-Coordination Compound

1-1- Historical Background

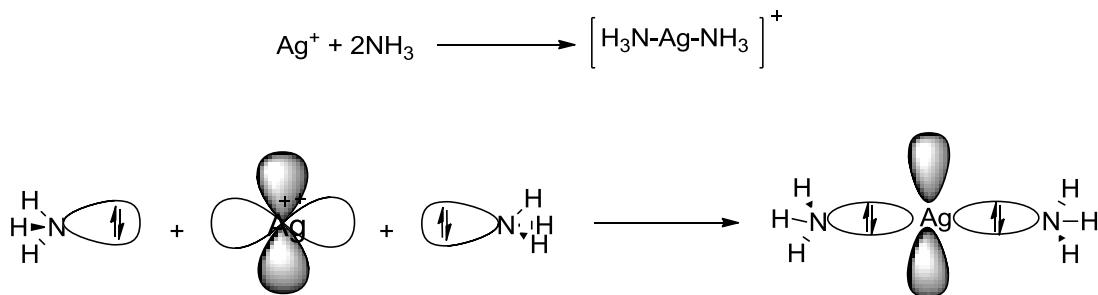
Studies and efforts on the preparation and characterization of what are now called coordination complexes, indeed, began in the nineteenth century.¹ Wolcott Gibbs and Frederick Genth published their research on the synthesis of ammonia-cobalt compounds such as $\text{Co}_2(\text{NH}_3)_8(\text{NO}_2)_4(\text{NO}_3)_2$ in 1857.² Following that, in 1875, Sophus Mads Jørgensen, a Danish chemist, reported some investigations in the field of coordination chemistry and even was considered as an explorer in this branch of chemistry. He also deduced the molecular structure of $\text{CoCl}_3 \cdot 6\text{NH}_3$ based on its freezing point and conductivity measurements.³ The octahedral configuration concept based on coordination number six was the hypothesis of Alfred Werner.³ In 1893, he correctly proposed the chemical structure of $[\text{Co}(\text{NH}_3)_6](\text{Cl})_3$ in which a Co^{3+} ion is surrounded by six NH_3 molecules in an octahedral geometry. The three chlorides are also involved in the overall complex as "free" (*i.e.*, non-coordinated) counter-anions.^{4, 5} Coordination chemistry is, therefore, the study of the interactions between a central, often metal, atom(s) and a certain number of molecules or ions that are directly bound to the metal and referred to as ligand.

1-2- Ligands: General

Ligand is defined as a molecule, element or ion which can have independent existence. This broad definition allows this term be used not only in chemistry, but also in molecular biology and biochemistry.¹ In chemistry however, a ligand is a molecule or ion in which donation of electron density facilitates coordination to a central atom. It should be noted that the availability of at least one lone pair of electrons is often a key aspect for a species to act as a ligand. Many ligands include heteroatoms such as N, O, S and P as the source of these electrons. Halogen ions are also a common source of ligands for metal and non-metal atoms. Moreover, large numbers of organic fragments can act as ligands or have the potential to be converted (*i.e.*, chemically modified) into ligands. One classic example of a ligand is the ammonia (NH_3) molecule which formally has one lone pair of electrons and hence can bind to a central atom (M) through donation of these electrons to a formally empty orbital on M.¹ However, ammonia is obviously not being considered to be a ligand until it is bound to such a central atom. The simplest coordination bond formation is represented in equation 1.



In another specific example ammonia acts as an electron donor to a metalloid acceptor (Ag^+) to form what is often termed a “coordinate” or “dative” bond (Scheme1).¹



Scheme 1. Formation of coordinated bond between ammonia and silver ion

1-2-1- Denticity and chelation

Many ligands contain more than one atom that can offer lone pair electron in their structures. As a result, these ligands can bind *via* more than one site to the central atom. According to this classification, a bi-dentate ligand has two, tri-dentate has three and in general poly-dentate ligands have more than two sites in the ligand to bind to a metal centre. Chelation happens where the ligand offers more than one lone pair through different atoms to attach to the same metal centre. A chelate ring is formed when a potentially chelating ligand binds to a metal centre from the non-coordinated (acyclic) system to one in which two different atoms have donated electrons to a metallic centre. Figure 1 shows an example of the carboxylate group in different coordination modes.¹

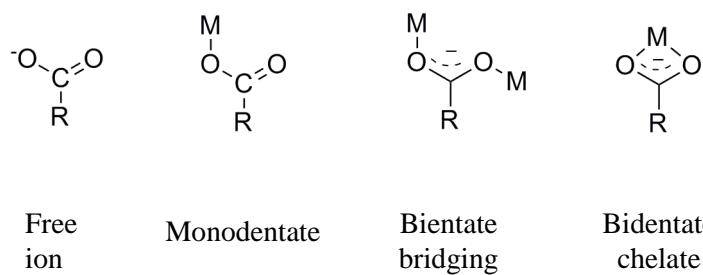
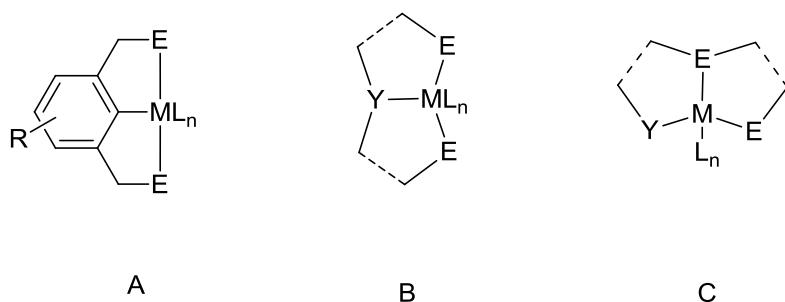


Figure 1. Carboxylate group in different coordination modes.

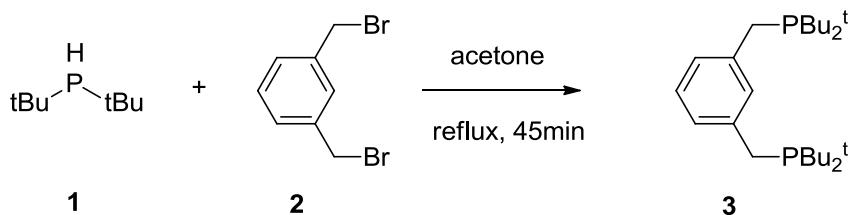
1-3- Pincer ligands

Pincer ligands are classified as tridentate binding agents in which one formally anionic centre (which can be either a C atom or other element) is linked to two other electron donating groups. These latter systems usually involve N, P, O, S and/or Se as source of electron pairs. Scheme 2 indicates the general class of pincer type ligands.⁶

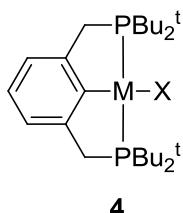


Scheme 2. Three general class of pincer ligands. (A) shows the general class of aryl pincer ligand M is an element bound to anionic centre and L is the ligand attached to the metal centre, (B) represents the more general pincer in which an anionic central donor atom Y can be a C or other atom attached to two other E donor atoms. Structure (C) is the type pincer form in which the formal anion does not have the central position.⁶

The first synthesis of pincer-type ligands was reported by Bernard L. Shaw and his group (Reaction 1.3.1). They reported that 1,3-bis((di-tert-butylphosphino) methyl) benzene (**3**) can undergo metallation to provide a novel type of tridentate chelating functions (**4**) (Scheme 3).⁷



Reaction 1.3.1



[MX(pcp)]

(M= Ni, Pd or Pt; X= Cl, Br, H, C≡CPh, or C≡N)

(M= Rh, X= C≡O)

Scheme 3. PCP pincer complex

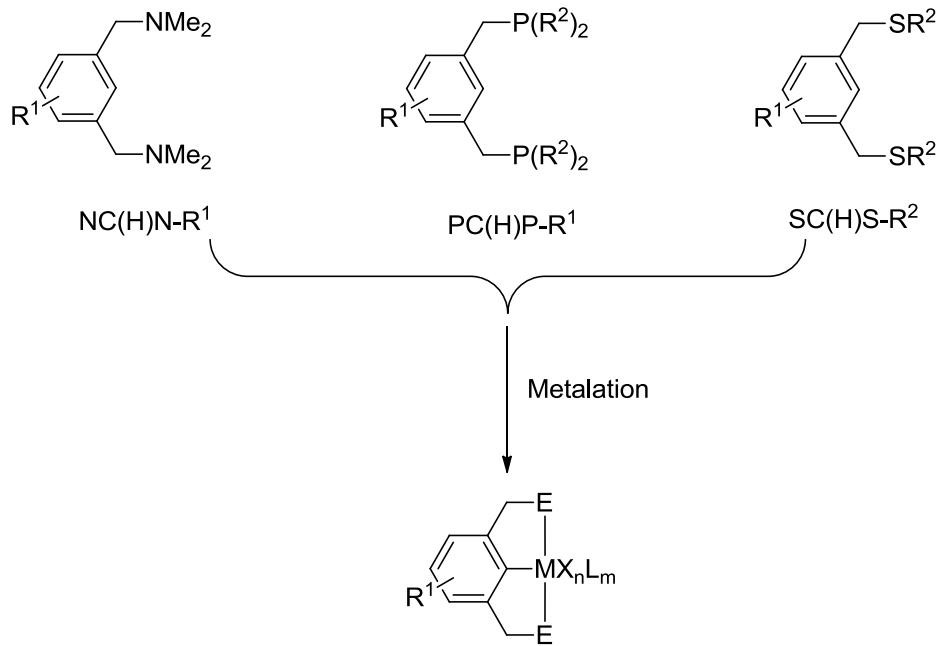
Pincer ligands have exhibited varied activities towards (transition) metals to generate the pincer complexes, various research groups have attempted the synthesis of these ligands. Distinct types of pincer ligands have been designed and synthesized by using either identical donor groups around the potential anionic centre or by altering the source of electron donors. As was mentioned earlier, a functional way of categorizing the various pincer ligands is based on the three atoms coordinating to the centre (transition metal), summarized as "ECE". For instance, in Scheme 2 with amino groups (E= NR₂) on the "side arms" is referred to as a NCN complex and with phosphines (E= PR₂) as a "PCP" complex. As a result, the combination of different electron donors can provide a variety of pincer ligand designs such as PCN, SCS, SCP, and SCN, etc.

However, the majority of research has been carried out with pincer ligands incorporating N, P and/or S donor atoms.

Due to their ability to bind to (transition) metals, pincer ligands are receiving a lot of attention among the organometallic community. Pincer ligand complexes have been used as catalysts in organic synthesis because they can introduce regio- and enantioselectivity in the products of organic reactions that they promote.⁸ As a result, pincer complexes are becoming very useful frameworks for a number of diverse applications. These related functions are described in detail in ref. 9.

1-4- Methodology for the Metalation of Pincer Ligands

Since pincer metal complexes are attracting much attention, the strategies for metalation of these ligands have played a significant role in the synthesis of such complexes. Scheme 4 shows some of different classes of aryl pincer ligands which undergo the metalation to give metal complexes.¹⁰



Scheme 4. Metalation of pincer ligands

Various methods for the metalation of pincer ligands and synthesis of new complexes have been disclosed. These methodologies either can include the formation of M-C σ -bonds or formation of a new bond between metal and another source of anion. This will be described in more detail below.

1-4-1- Direct Cyclometalation

Direct cyclometalation is a very effective method for the formation of a new bond between a (transition) metal and the potential anionic centre of pincer ligands (Figure 2).¹¹⁻¹²

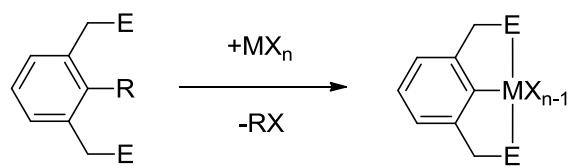
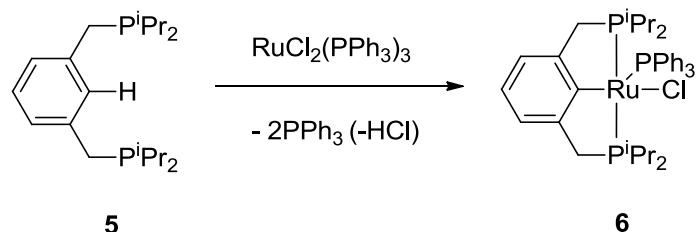


Figure 2. The direct cyclometallation reaction

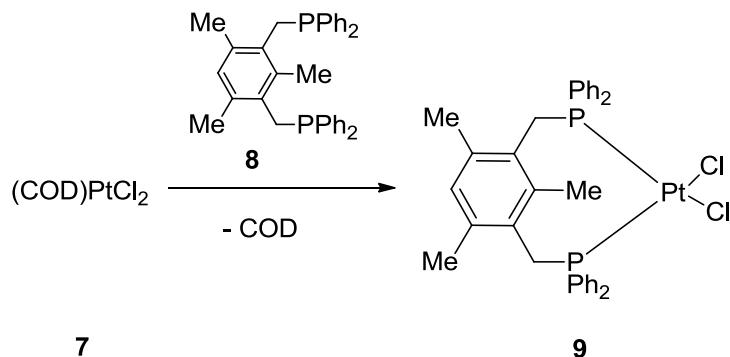
This method has been successfully used since 1976 for the synthesis of various complexes of Groups 9 (Rh, Ir) and 10 (Ni, Pd, Pt) especially for the PCP-type pincers.^{10, 14-16}

The reaction shown below (Reaction 1.4.1.1) is an example that demonstrates a pincer ligand **5** undergoing direct cyclometallation with RuCl₂(PPh₃)₃ to afford complex **6**.¹³



Reaction 1.4.1.1

Nevertheless, this method is not always a successful strategy for the metalation of pincer ligands. For example, as is shown in Reaction 1.4.1.2, compound **8** reacts with (COD)PtCl₂ (**7**) (COD = cycloocta-1,5-diene) to affords the non-cyclometallated monometallic complex **9**. Such materials have been considered as possible intermediates in the desired C-H and C-C bond activation processes.¹⁷



Reaction 1.4.1.2

1-4-2- Oxidative Addition

The oxidative addition reaction has been used to explain a category of reactions which is critical in catalysis and organometallic chemistry.¹⁸ Oxidative addition reactions result in a change in the formal oxidation state and coordination number of a metal centre. This is a very useful method especially for substituted pincer ligands. For example, EC(X) E type of pincer ligands (where X = Cl, Br, I and E is a donor group like NR₂) can be metalated via oxidative addition in cases where such precursors are resistant to direct cyclometalation (Figure 3).¹⁰

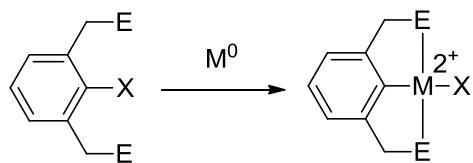


Figure 3. Oxidative addition to a pincer ligand

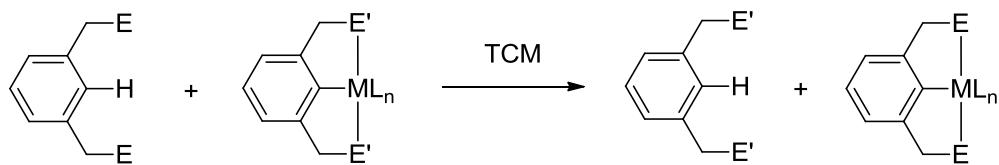
A variety of metal precursors have successfully been added to such ligands through the oxidative addition reaction to form pincer complexes. Some of the metal precursors that can be used for oxidative addition are including; $[\text{Ni}(\text{COD})_2]$, (COD = cycloocta-1,5-diene), $[\text{Ni}(\text{PPh}_3)_4]$, $[\text{Pd}_2(\text{dba})_3]$, (dba = dibenzylideneacetone), $[\text{Pt}(4\text{-tol})_2(\text{SEt}_2)]_2$, (4-tol = 4-methylphenyl), and $[\text{MCl}(\text{COE})_2]_n$, (COE = cyclooctene) with $\text{M} = \text{Rh}$ or Ir .¹⁹⁻²¹

1-4-3- Transcyclometalation

The term transmetalation (TM), in general, is used to describe a type of organometallic or organic reaction in which ligands are formally transported or exchanged from one metal to another. Equation 2 (below) depicts the general form of a transmetalation reaction in which R and R' can be an alkyl, allyl, alkynyl, aryl, halogen or pseudo-halogen group and M^1 and M^2 are transition metals where $\text{M}^1 \neq \text{M}^2$.

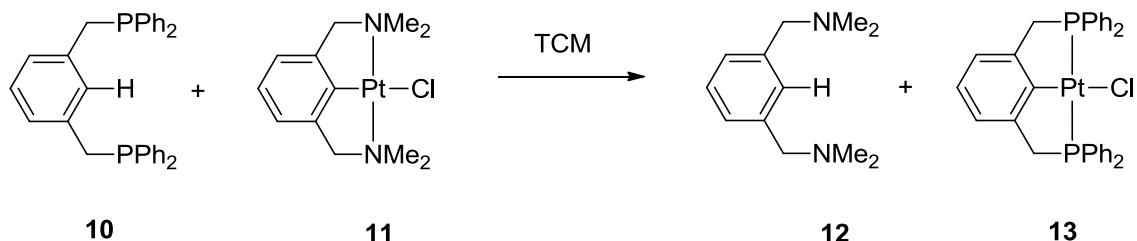


Trans-cyclometalation is a class of TM reaction which can be used as a method for formation of cyclometalated transition metal pincer complexes. Scheme 5 depicts the trans-cyclometalation (TCM) reaction with tridentate type of pincer ligands.^{10, 22}



Scheme 5. Transcyclometalation reaction

The very first example of transcyclometalation reaction to form a pincer complex was reported in 1989 by Michel Pfeffer and his group that described the cyclopalladation reactions of several sulfur-containing pincer ligands.²³ After that disclosure, several research groups have shown TCM reactions with various pincer ligands especially PCP and NCN type. For instance the TCM reaction of **10** with **11** affords **12** and [PtCl(PCP)] (**13** : Scheme 6).^{22,24}

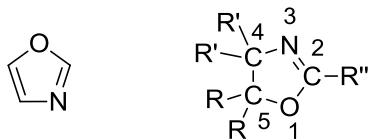


Scheme 6. Transcyclometalation between PCP pincer ligand and NCN pincer complex

1-5- Oxazolines; a Small Ring with High Capability

2-Oxazolines (**14b** in Figure 4) are a sub-class of oxazole heterocycles (**14a** in Figure 4) which are a part of the azole family and consist of a five-membered nitrogen heterocyclic ring compound bearing at least one other non-carbon atom. This atom can either be nitrogen, sulphur or oxygen.

A 2-oxazoline ring has a single oxygen atom and a single nitrogen atom separated by a sp²-hybridized carbon atom.²⁵

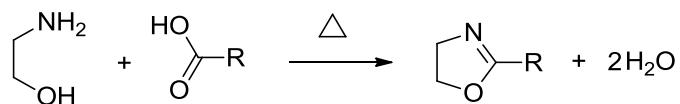


14a

14b

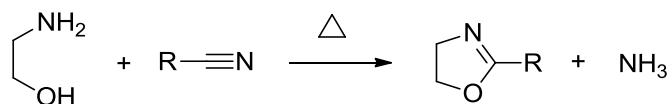
Figure 4. Oxazole and 2-oxazoline

The synthesis of oxazolines was first described in 1884 by Rudolf Andreasch. The ring system itself was not, however, identified correctly at that time. Five years later, Sigmund Gabriel presented the accepted structure of an oxazoline ring.⁶ Oxazolines can be synthesized by various methods which are mentioned in the literature.²⁵ A typical method involves the condensation of amino alcohols and carboxylic acids (Reaction 1.5.1) as one of the simplest and most inexpensive methods.²⁶



Reaction 1.5.1

For this purpose, NH₂ and OH groups of amino alcohol must be on adjoining carbon atoms and the carboxylic acid may either be aliphatic or aromatic.^{25, 26} However, the method which was mentioned above (Reaction 1.5.1), does not generally afford good yields. For improving the yield, alkynitriles (Reaction 1.5.2) can be used instead of carboxylic acids.²⁶



Reaction 1.5.2

The oxazoline ring can be easily prepared from natural available amino acids and synthetic amino alcohols, it can be extensively used in many numbers of organic reactions. Oxazolines have also been widely employed in many fields of chemistry, it can be used as a protecting group, coordinating ligand and activation moiety. Moreover, the ligating group of oxazoline occurs naturally in unidentified classes of microbacterial iron chelators.^{27, 28}

1-5-1- Pincer Oxazolines

As mentioned earlier, oxazolines can be used as a building block for the synthesis of pincer ligands. Bis-oxazolines (box's) are one of the most popular classes of pincer ligands.²⁹ These ligands (the general structure of bis-oxazolines is shown in the Figure 5) have two oxazoline rings in their structure which are separated by a spacer. In recent years box ligands have been widely used in asymmetric catalysis. Asymmetric catalysis, in general, includes of a cation (metal) coordinated to a ligand that is optically active and can produce a chiral compound.²⁹ Pincer oxazolines have also shown strong binding affinity towards transition metals.⁶

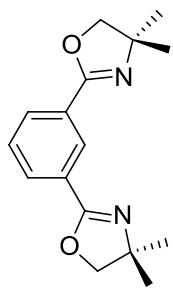
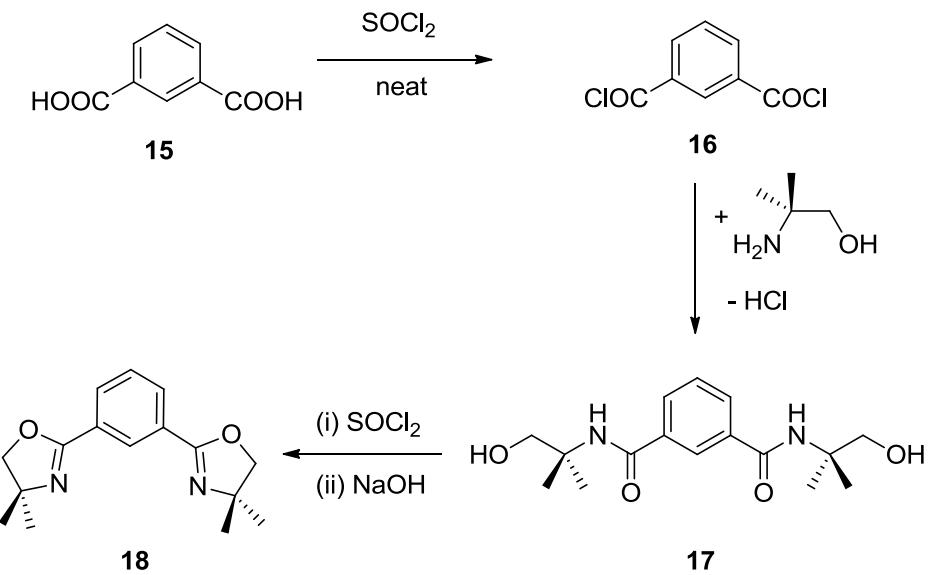


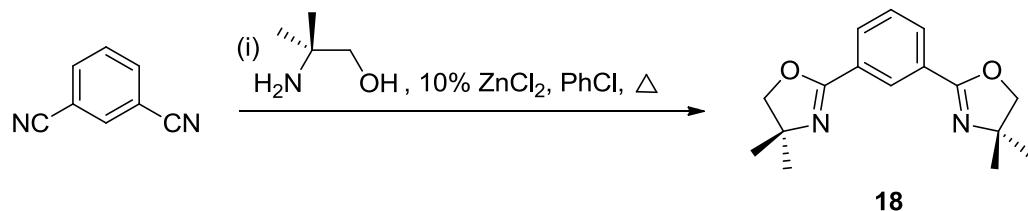
Figure 5. Bis-oxazoline

Several methods have been demonstrated in the literature for the synthesis of pincer bis-oxazolines.^{30, 31} One of the synthetic protocols for such synthesis is described in Scheme 7.³²



Scheme 7. Synthesis of Bis-oxazoline

This method, however, has some difficulties in the isolation of final product. An alternative "one-pot" method that provides improved yields uses anhydrous zinc dichloride as catalyst and 1,3-dicyanobenzene as a starting material.³³

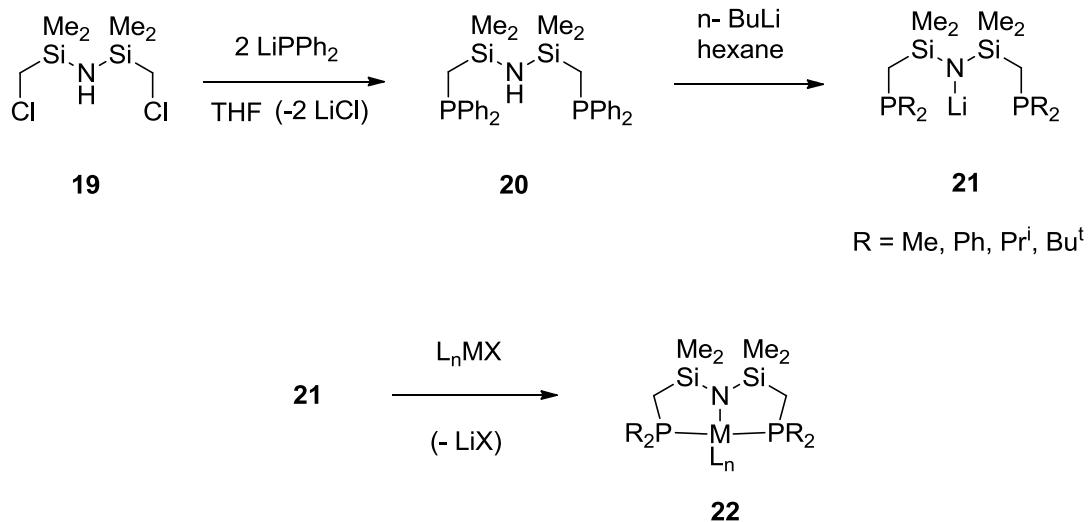


Reaction 1.5.1.4

The synthesized bis-oxazoline can be used as a starting material for transmetalation reactions with both main group metalloid elements (*e.g.*, tin) and transition metals.⁶ Nevertheless, the majority of the chemistry of the pincer bis-oxazoline ligand and its derivatives has been involved with asymmetric catalysis.^{34, 35}

1-5-2- Pincer Ligands with ENE Donors

A common aspect of all pincer ligands is the presence of a formal anionic source usually located on the central binding atom. This negatively charged atom tends to make a resulting complex more stable, particularly at higher temperatures. However, the source of this anion can be provided by atoms other than carbon. The Fryzuk group has reported several methods to synthesize pincer ligands with a N-H functionality as the source of such anions. One general formula of such ligand precursors is $(R_2PCH_2SiMe_2)_2-NH$.⁶ Fryzuk *et al.* has shown that 1,3-bis(chloromethyl)-tetramethyldisilizane (**19**) can be used as a starting material to synthesize such pincer ligands which are then used as precursors to bind to metals (Scheme 8)



Scheme 8. Synthesis of pincer ligand with N-H functionality

These "PNP"-type pincer ligands have been extensively developed and thus coordinated to Ni, Pd and Pt metal centres and then with other transition and main group metals.^{36- 40}

Since then, several research groups have combined the ideas of Fryzuk with those of the bis-oxazolines and hence designed and synthesized various bis-oxazoline derivatives containing other heterocycles such as carbazole, pyrrole and isoindoline. These latter ring systems contain a N-H bond as the potential source of an N-based anion (*i.e.*, following de-protonation). Some examples of pincer ligands derived from such bis-oxazolines are shown in Figure 6.^{6, 41}

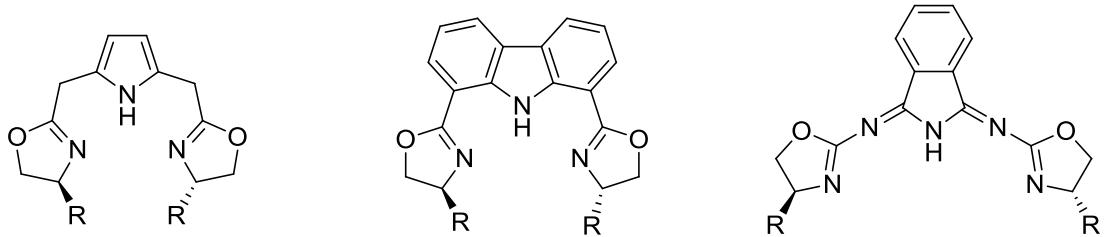


Figure 6. Pincer ligands containing N-H bond

Work with these ligands, however, is not fully developed yet but their high affinity towards the transition metals and the variety of complexes that they afford, suggest that this new class of pincers will have a promising future in coordination chemistry.

1-5-3- Pincer Ligands with Low Molecular Symmetry

Among the general category of PCP, NCN or NNN pincers, only a few of them have idealized molecular point group symmetry lower than C_2 (Figure 7).⁴²⁻⁴⁵ Indeed, the achiral pincer ligands typically have higher molecular symmetry (Figure 8).⁴²⁻⁴⁵

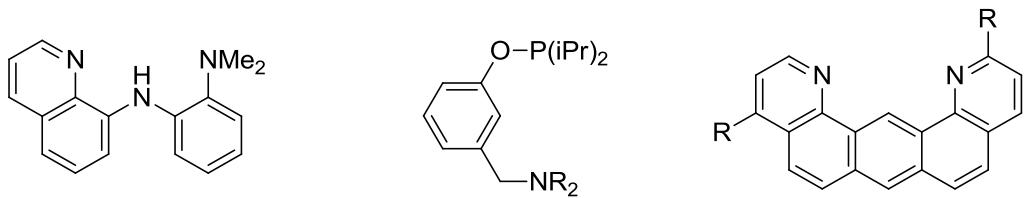


Figure 7. Pincer ligands with low symmetry

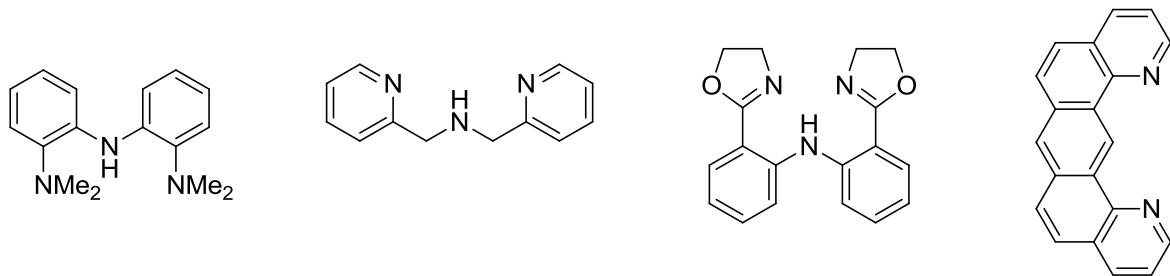
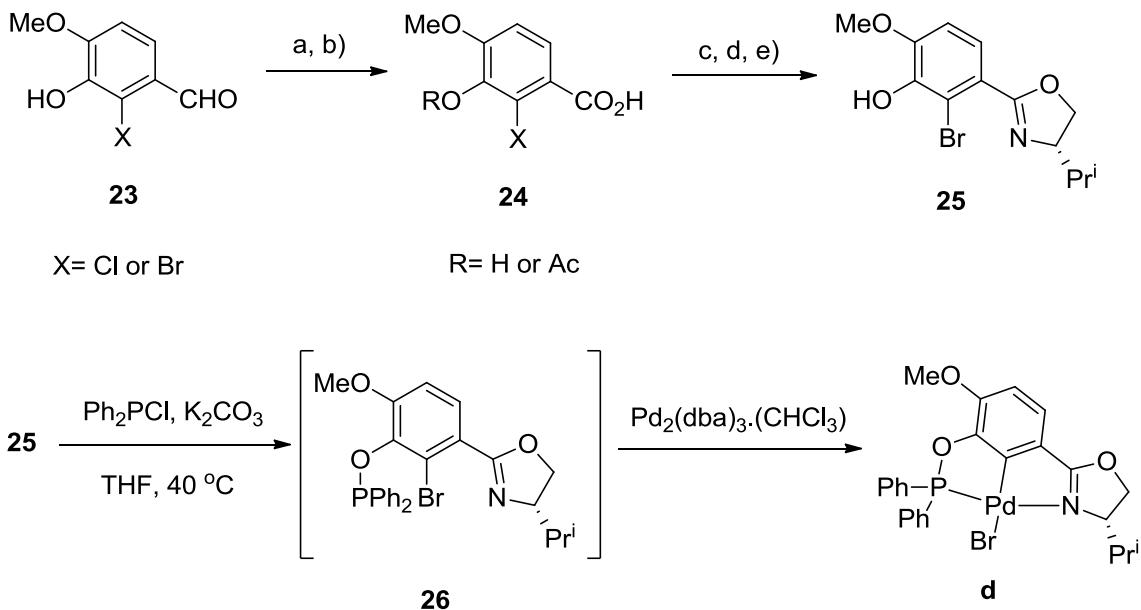


Figure 8. Symmetrical pincer ligand precursors

Oxazolines give an opportunity to elaborate both chiral and low symmetry ligand design methods. Pincer ligands with only a single (chiral or achiral) oxazoline ring have attracted much interest in recent years. Several research groups have described various synthetic methods to generate the ligands with formal C_1 or C_s molecular symmetry.

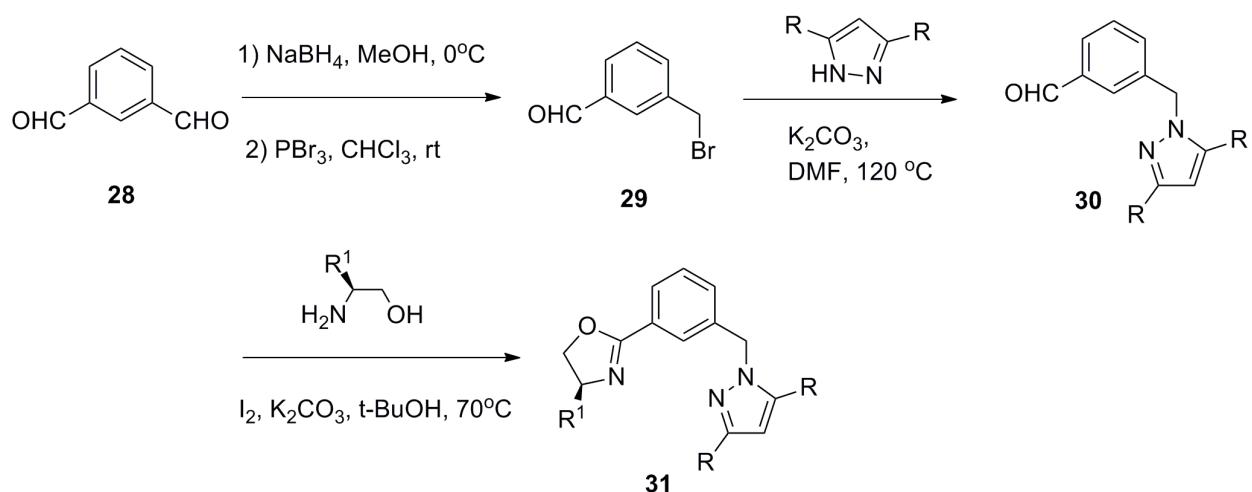
Motoyana *et al.* and Song and co-workers have reported the synthesis of PCN and NCN' types of pincer ligands which are of such low molecular symmetry. For example, [i-Pr-Phemox-OPPh₂]Br (**25**) can be synthesized from isovanillin (**23**) in six steps. Compound **25** then affords **27** upon metalation. (Scheme 9).⁴⁶



Reagents and conditions. (a) Ag_2O , $\text{NaOH}/\text{H}_2\text{O}$, 60°C , 10 min. (b) Ac_2O , H_2SO_4 , CH_2Cl_2 , r.t., 30 min. (c) SOCl_2 , 70°C , 3 h. (d) (S)-valinol, Et_3N , CH_2Cl_2 , 40°C , 1 h, then MsCl , 40°C , 1 h. (e) 1 N NaOH/MeOH , r.t., 10 h

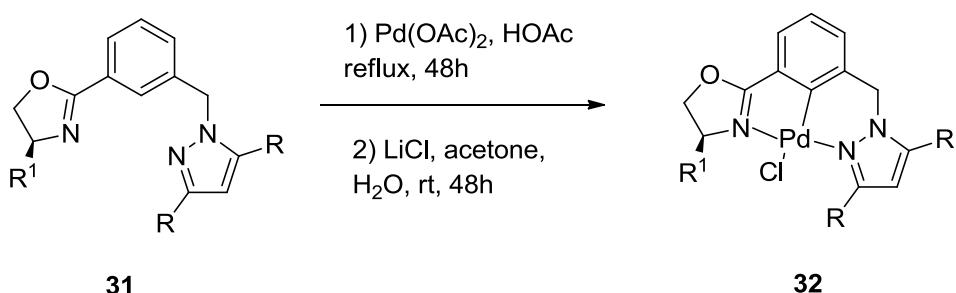
Scheme 9. Synthesis of low symmetry pincer ligand

Another example of an unsymmetrical NCN' pincer ligand is shown in Scheme 10 below. This molecule contains both an oxazoline and a pyrazole ring and can be synthesized from isophthalaldehyde in three steps.⁴⁷



Scheme 10. Synthesis of unsymmetrical NCN' pincer ligand

This potential pincer ligand (**31**) can undergo direct metallation with Pd(OAc)₂ in refluxing acetic acid (HOAc) to form the NCN' pincer palladium complex **32** (Reaction 1.5.3.1).⁴⁷

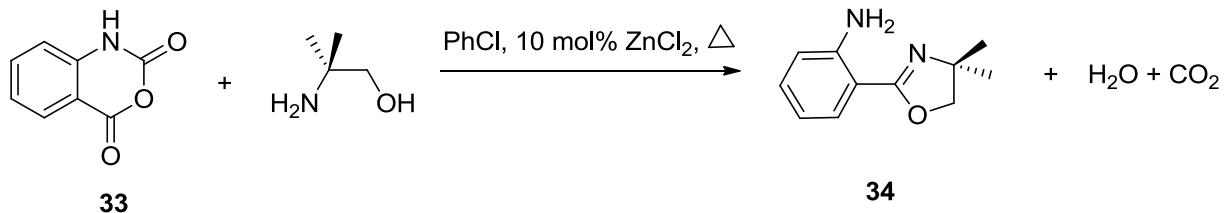


Reaction 1.5.3.1

1-5-4- N,N',N'' Pincer Oxazolines

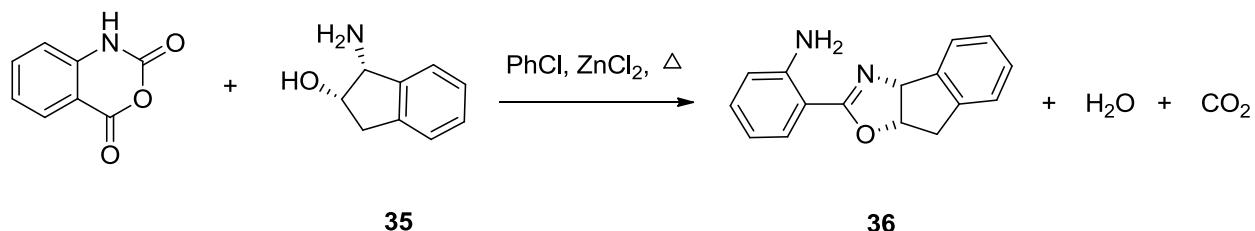
One advantage of using the oxazoline group for designing the N,N',N'' pincer ligands is the eligibility to induce both chirality and low symmetry at the same time. Since oxazolines have been shown to possess rich transition metal chemistry, design and synthesis of such ligands are attracting much interest. In many cases, enantioselective catalysis can result from the species which are containing such ligands.⁴⁸

One of the important starting materials to the synthesis of N,N',N'' pincer oxazoline ligands which is relevant to this research project is 2-(2'-anilinyl)-4,4-dimethyl-2-oxazoline (**34**) in Reaction 1.5.4.1). Compound **34** can be easily formed by the reaction between isatoic anhydride (**33**) and 2-amino-2-methyl-1-propanol in the presence of ZnCl₂ as a catalyst.⁴⁷



Reaction 1.5.4.1

Another ligand which has been used in this research as a chiral starting material is; (+)-indanyl-(2'-aminophenyl)-2-oxazoline (**36**). This compound can likewise be synthesized from the (1*R*, 2*S*)-*cis*-1-amino-2-indanol (**35**) under the same protocols as ligand **34** (Reaction 1.5.4.1.2).⁴⁷



Reaction 1.5.4.2

Both **34** and **36** have been used as the starting materials in the synthesis of both chiral **38** and achiral **39** low symmetry pincer oxazolines previously⁴⁸ and as a portion of this research project.

1-5-4-2- *N*-(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl)picolinamide (38)

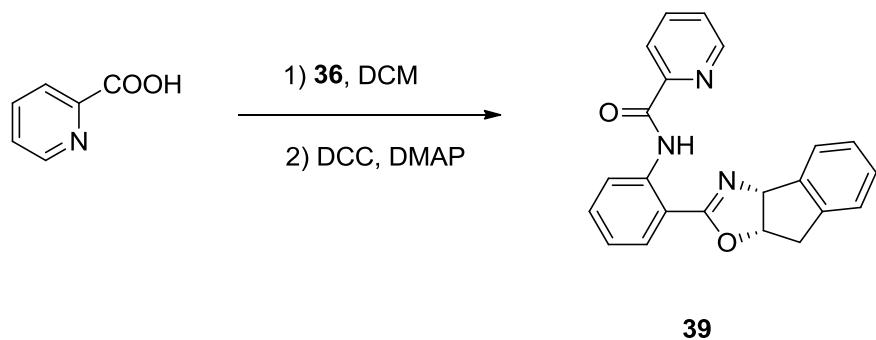
As mentioned above, research focusing on low symmetry pincer ligands has increased due to the fact that they can be used in enantioselective catalysis. Decken, Gossage and Yadav previously described one such formally C_1 -symmetric amide pincer ligand featuring an oxazoline and a pyridine group as the potential binding functionalities.⁴⁸ *N*-(2-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)picolinamide (**38**) can be synthesized *via* amide coupling of **34** with picolinic acid (**37**) (Reaction 1.5.4.2.1).⁴⁸



Reaction 1.5.4.2.1

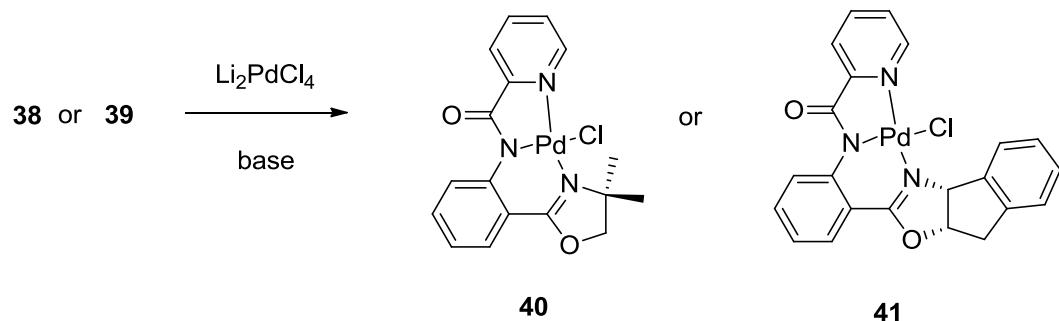
1-5-4-3- N-(2-((3Ar,8As)-8,8a-dihydro-3aH-indeno[1,2-d]oxazol-2-yl)phenyl)picolinamide (39)

In a same fashion as **38**, **39** can be synthesized upon amide coupling in presence of DCC and DMAP as coupling agents (Reaction 1.5.4.3.1).⁴⁸



Reaction 1.5.4.3.1

Both ligands **38** and **39** have shown to easily deprotonate on the reaction with Pd precursor to generate Pd-amido complexes (Reaction 1.5.4.3.2).⁴⁸ These materials contain a formally anionic pincer with the negative charge located at the central *N*-atom.



Reaction 1.5.4.3.2

1-6- Objective of Project

The cornerstone of this work presented in this thesis involves the study of coordination chemistry of oxazoline pincer ligands with Group 11 transition metals and study of their catalytic activities toward C-C bond formation. This work entails a study of alternative synthetic methods that are applied to synthesis of copper and gold pincer complexes. Following this discussion, the molecular structure of synthesized complexes will be described. At the end, the catalytic activity of some of the complexes was tested in the Henry reaction.

Chapter Two

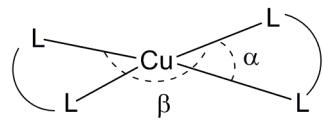
Copper

A large number of chemical structures that are found in the Cambridge Crystallographic Data Centre (CCDC) are transition metal complexes containing copper.^{49, 50} Despite the fact that the +2 oxidation state of copper is the most common one, other oxidation states including +1, +3 and +4 are known as well.^{49, 51} The number of reviews in which copper (II) compounds have been summarized is numerous,⁵²⁻⁵⁵ however, those which are specifically focused on Cu-pincer complexes are not well developed. The systems which will be discussed in this thesis are primarily four- and five-coordinated copper (II) pincer complexes containing an oxazoline ring.

2-1- General Aspects of Tetra-and Penta- coordinate Copper (II) Compounds

There are almost six hundred examples of datasets found in the CCDC which are crystal structure of tetra-coordinated copper (II) compounds reported in the literature.⁴⁹ Two idealized configurations are generally observed with this coordination number: square planar and tetrahedral and these two geometries occur in most cases with some degrees of distortion.⁵¹ One of the factors that can cause the distortion in the complexes is the size of ligand (sterics) and its denticity. Moreover, both electronic and steric hindrance of the coordinated atoms plays a significant role in the value of the L-Cu-L bond angles found in such metallocycles (Figure 9).

⁴⁹ The difference in covalent radii of the donating atoms can also cause differences in the value of such angles. For example, in copper complexes with coordination number four (Figure 9).^{56, 57} and the donor atoms are oxygen (radii [r] = 0.73 Å) mean value of the L-Cu-L intra ligand angle (α) is approximately 64°, for nitrogen (r = 0.75 Å), sulphur (r = 1.02 Å), and selenium (r = 1.16 Å) donors this angle is 67°, 77° and 79° respectively.⁴⁹



$$L = O, N, S, Se$$

Figure 9. General structure of four coordinated copper complexes

Copper complexes with coordination number five are less common than those with coordination number four. However, the number of fully characterized copper complexes with coordination number five is still over five hundred.^{49, 51} Two general types of geometries have been observed for this coordination number: idealized square pyramidal around the metal centre, which is more common and trigonal bipyramidal. In five coordinated systems (Figure 10), perfectly square-pyramidal geometry (Figure 10a) is associated with $\alpha = 90^\circ$ and $\beta = 180^\circ$. For ideally trigonal bipyramidal geometry (Figure 10b), α is 90° and β becomes 120° .

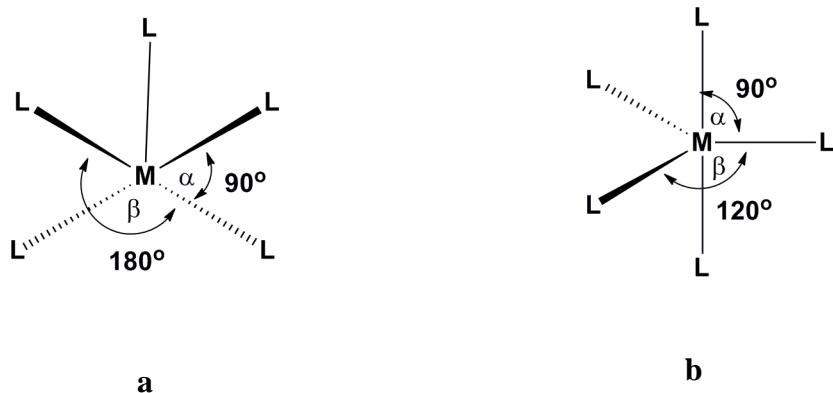


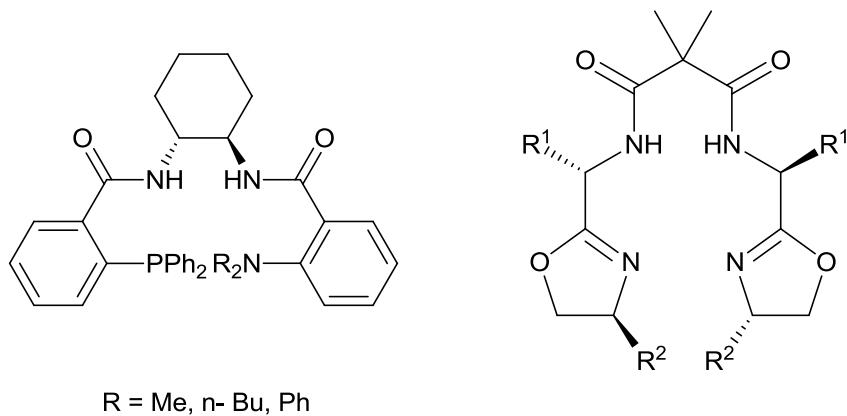
Figure 10. Five coordinated metal complexes

An examination of structurally characterised five-coordinate Cu(II) systems reveals that⁴⁹ of these two geometries, generally, the mean value of apical Cu-L bond lengths in these complexes are larger than the equatorial Cu-L bond distances. This value rises in the order of: 1.974 Å (N) < 1.976 Å (O) < 2.273 Å (S) < 2.285 Å (Cl) < 2.408 Å (Br) < 2.563 Å (I). For example; when L is nitrogen, Cu-N (equatorial) bond lengths (mean value) are approximately 2.01 Å vs. 2.25 Å for the corresponding apical Cu-L bond lengths.⁴⁹

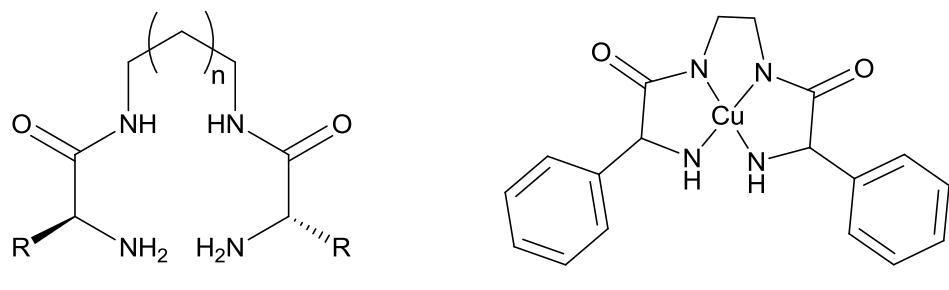
As is seen with the tetra-coordinated Cu(II) complexes, both steric and electronic effects of the ligands are significant parameters leading to the opening of the L-Cu-L bond angles in the metallocyclic ring complexes. No matter which geometry is taking place around the metal centre, this amount increases when the metallocyclic ring gets larger.^{49, 58}

2-3- Synthesis and Properties of Copper Amido Complexes

A major application of Cu compounds is the role that they play as industrial catalysts and their known roles in biochemical activity.⁴⁹ Amide (NR_2^-) base ligands (Scheme 11) have been extensively used for preparation of transition metal complexes particularly in the field of coordination and bioinorganic chemistry.⁵⁹⁻⁶² For example, some symmetrical bis(amino acids) (Scheme 12) have shown strong coordination activities towards copper(II) ions. Resulted copper complexes such as (**42** in Scheme 12) play a key role in bioinorganic chemistry.⁶³



Scheme 11. Tetradentate ligands containing amide group



Scheme 12

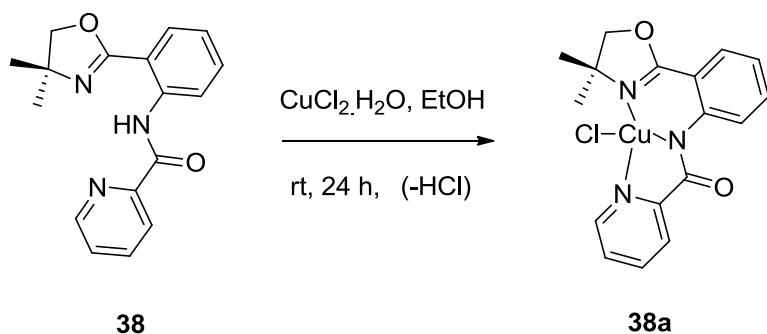
The research described in this chapter is focused mainly on the synthesis of Group 11 (copper especially) halide and pseudo-halide amido pincer complexes containing a single oxazoline unit. As stated earlier, (oxazoline) pincer ligands potentially can bind to a transition metal to make a complex. One of the advantages of using Cu in order to study complexation behaviour is that there is a possibility that copper halides could be used directly for metallation of pincer ligands described previously. This would involve N-H bond activation, which is technically easier than C-H bond activation, and the likely formal loss of HX. Hence, there

would be no need for any special metal precursors as copper(II) halides are readily available starting materials. This is in contrast to other pincer complexes such as those of Groups 9 and 10.^{64, 65-70}

2.3.1- Synthesis of Complex **38a**

The synthesis of amide **38** was performed according to Reaction 1.5.4.2.1 using the *in situ* produced (SOCl_2) acid chloride derivative of picolinic acid **37**, followed by low temperature addition of **34**. In a solution of 1 equiv. of ligand **38** in EtOH (95%) was added 1 equiv. of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ according to reaction (2.3.1.1). The green coloured mixture was then stirred at room temperature overnight. The reaction content was then filtered through a filter paper and then all volatiles were removed in *vacuo*. This process yielded the product **38a** as a green powder.

According to the previous work involving Pd precursors,⁴⁸ deprotonation of the N-H group is a possible reaction pathway. The IR data of compound **38a** indicated the possible presence of a C-N stretching vibration at 531 cm^{-1} . The absence of the N-H stretching band at 3309 and 3280 cm^{-1} suggested the formation of 1:1 adducts of ligand fragments with Cu^{2+} . In addition, the UV-Vis spectra of the compound **38a** exhibited only one absorption band for this compound at 342 nm ($\epsilon = 7792\text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$) which is presumably due to ligand to metal charge transfer (LMCT) transitions. This absorption band suggested the presence of Cu^{2+} species in the complex. To confirm the structural nature of this complex, however, a single crystal X-ray diffraction study was carried out on the synthesized species.



Reaction 2.3.1.1

A molecular representation of compound **38** is found in Figure 11. The X-ray diffraction data for complex **38a** is summarized in Table 2.1

Table 2.1. Summary of X-ray diffraction data of **38a**

Formula weight	393.32
Formula	C ₁₇ H ₁₆ Cl Cu N ₃ O ₂
Temperature (K)	150
Crystal system	Orthorhombic
Space group	<i>Pna2</i> ₁
Unit cell dimensions:	
<i>a</i> (Å)	12.5234(3)
<i>b</i> (Å)	14.3114(6)
β (°)	90.00
<i>c</i> (Å)	18.1160(8)
Volume (Å ³)	3246.9(2)
<i>Z</i>	8

The results indicate that **38a** is a monocopper complex strongly suggesting that it incorporates deprotonated **38**. The coordination sphere is completed by the presence of a single metal-bound Cl atom which occupies a position trans to the amido donor. Of note is the formal amido-Cu interaction in addition to the coordination of both pyridine and oxazoline groups forming five- and six-membered rings. The coordination geometry around the Cu atom is best described as distorted square planar in nature. Describing the structures of four-coordinated copper(II) complexes, however, can be a subjective endeavour especially when the structure is intermediate between the two most common four-coordinated geometries which are tetrahedral and square planar.

To determine the geometry around the metal centre the tao parameter, which was introduced by Addison, Reedijk and coworkers in 1984, can be helpful.⁷¹ This uses an empirical method based on bond angles to give a percentage of distortion and consequently a clear empirical method can be used to distinguish how close one particular structure is to the ideal extremes. In a transition metal complex with coordination number five (henceforth τ_5) this value, can be calculated using the two largest bond angles in the complex to give an index of the degree of trigonality (equation. 3).⁷²

$$\tau_5 = \frac{\beta - \alpha}{60} \quad \text{eq. 3}$$

This value for ideal trigonal bipyramidal structure with D_{3h} symmetry is 1.000; while an ideal square pyramidal structure with C_{4v} symmetry is zero (0.000).^{72, 73}

Similarly, R. P. Houser *et al.* proposed a simple geometry index for four-coordinated complexes inspired by Addison and Radjeek five-coordinated τ_5 index (equation 4).⁷²

$$\tau_4 = \frac{360 - (\beta + \alpha)}{141} \quad \text{eq. 4}$$

This parameter in the four-coordinated species for a perfect tetrahedral geometry is 1.000 and for the perfect square planar is 0.000.⁷²

Calculated τ_4 parameter for complex **38a** is 0.310 which is obviously closer to 0.000 than to 1.000. Therefore, the coordination geometry around the Cu atom is best described as distorted square planar which might be expected since the copper (II) is d⁹ and therefore possess an unpaired electron which can cause distortion according to the Jahn-Teller effect. Jahn-Teller distortion happens when the degenerate orbitals occupied unevenly in nonlinear molecules. Therefore, to reach to lower energy and being more stable the whole system distorts.

In the structurally characterized complex **38a**, the Cu-N_{pyridine}(1)B, Cu-N_{amide}(2)B and Cu-N_{oxazoline}(3)B bond lengths are 1.994(5), 1.941(5) and 1.980(5) Å respectively. The Cu-N_{amide} distance, however, is the shortest among the all three Cu-N bond lengths in the molecule. This difference may be attributed to the anionic coordination from the deprotonated N_{amide} donor as opposed to the neutral donation from the pyridine and oxazoline groups. The pyridine nitrogen Cu-N and the oxazoline nitrogen Cu-N bond lengths in the complex **38a** are similar in magnitude to the corresponding distances in complex [CuBr(pyoxal)₂]Br•H₂O (pyoxal: 2-pyridinyl-2-oxazoline) which are 2.011(4) and 2.169(4) Å respectively.⁷⁴ The amido nitrogen Cu-N bond

length is also comparable to an observed bond in the copper (II) complex containing tetradentate pyridine-based which is 1.921(2) Å.⁷⁵

The average Cu-N bond length, however, with this ligand set is 1.979 Å which is typical for tetracoordinated copper (II) metal centres with an N, N', N'', Cl ligand set.⁴⁹ The observed Cu-Cl bond length is 2.2318 Å. This bond length is close to the corresponding Cu-Cl bond distance in complex [Cu(2,6-bis(diisopropylaminomethyl)pyridine)Cl]₂CuCl₄ (in which copper has the coordination number four with one Cl trans to the pyridine nitrogen) which is 2.1970(6) Å.⁷⁶ The observed Cu-Cl bond length in complex **38a** is also in the expected range for Cu-X bond distance. The N(2)B-Cu-Cl(1)B and N(1)B-Cu(1)B-N(3)B bond angles are 157.22(16) and 153.7(2)° respectively. These values indicate that there is a distortion from ideal (180°) square planar geometry around the metal centre.

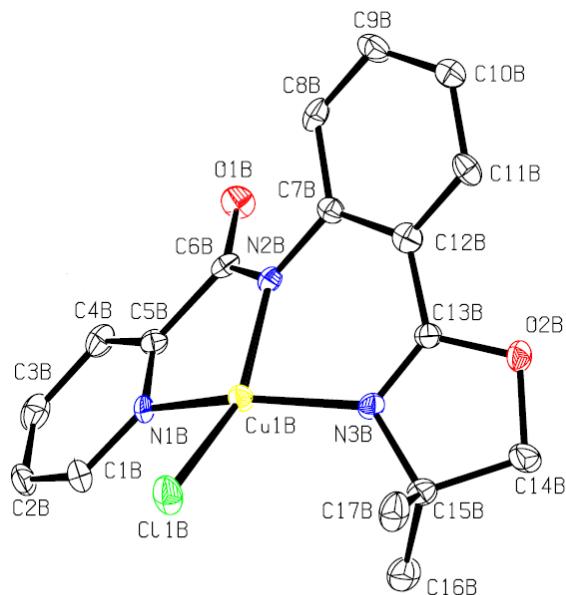
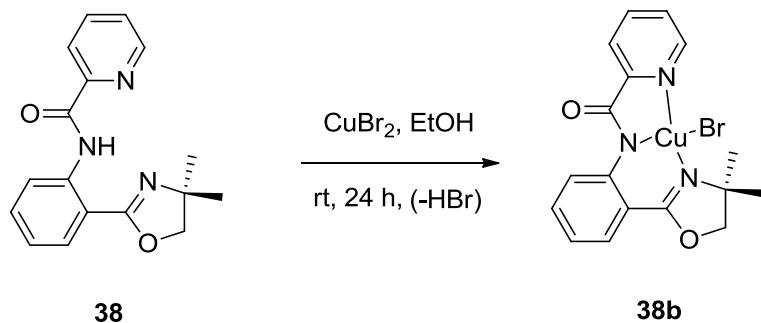


Figure 11: ORTEP representation of a unit cell molecule of complex **38a**

2-3-2- Synthesis of Complex 38b

A similar reaction, as described above, involving anhydrous CuBr₂ and **38** afforded green coloured powder as product. The reactivity of **38** and CuBr₂ in the reaction 2.3.2.2 clearly demonstrates the similarity of **38** in coordination with copper halides precursors. The corresponding Br analogue, **38b**, thus appears to be structurally and spectroscopically similar to the complex **38a**. The IR spectrum of **38b** is dominated by the absorbances typical of the compound **38** with the absence of N-H stretching band at 3309 and 3280 cm⁻¹. Elemental analysis data are also consistent with the proposed structure for **38b**.



Reaction 2.3.2.2

UV-Vis spectra of the compound **38b** showed only one absorption band at 348 nm ($\epsilon = 8022 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). This absorption band also suggested the presence of Cu^{2+} species in the complex.

The molecular structure of compound **38b** (Figure 12) was confirmed with X-ray crystallography. As the X-ray result indicated, complex **38b** demonstrated a distinct similarity to the compound **38a**. Complex **38b** crystallises in the $Pna2_1$ space group with eight molecules in

the unit cell. Cell angles (α , β and γ) are all 90° and cell lengths (a , b and c) are 12.5856(6), 14.4922(7) and 18.1596(6) Å respectively. The Cu-N_{pyridine}(1), Cu-N_{amide}(2) and Cu-N_{oxazoline}(3) bond lengths are 1.998(6), 1.945(6) and 1.970(6) Å, respectively. These bond lengths are very similar in magnitude to the corresponding distances in complex **38a**. It is also observed that the Cu-N_{amide} has the shorter distance among the Cu-N bond lengths in the complex. As expected, the Cu-Br bond length (2.3669 Å) in compound **38b** is slightly (0.1489 Å) longer than the Cu-Cl bond length in complex **38a**. This difference is possibly due to the larger atomic radius of Br versus Cl. The Cu-Br distance in the complex **38b** is to some extent close to the Cu-Br bond length (2.401 Å) which is reported for the complex [CuBr(pyoxaL₂)₂]Br•H₂O (pyoxaL: 2-pyridinyl-2-oxazoline).⁷⁵ As expected, the geometry of this compound is also distorted square planar as discussed earlier. A complete list of structure factors, bond lengths and bond angles can be found in Appendix B.

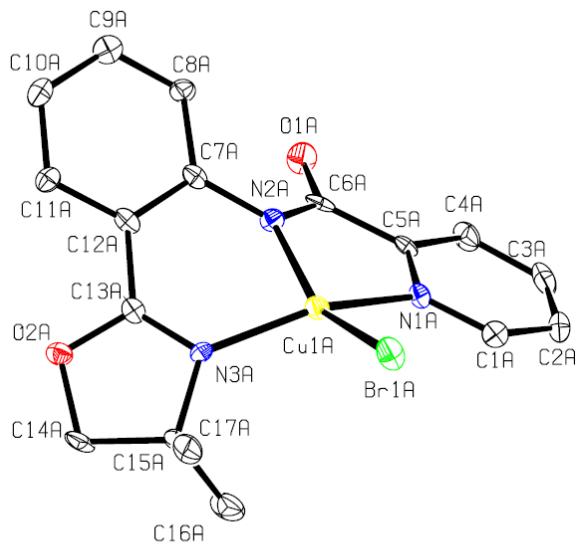
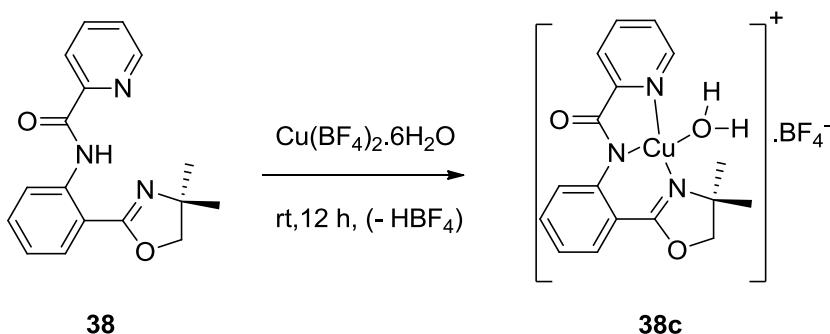


Figure 12: ORTEP view of complex **38b**

2-3-3- Synthesis of Complex 38c

A procedure similar to that used to make **38a** and **38b** was employed in the synthesis of the complex **38c**. Thus, 1 equiv. of **38** was dissolved in EtOH (95%) and 1 equiv. of Cu(BF₄)₂•6H₂O was then added directly, as blue coloured crystals to this mixture at room temperature. The formation of large quantities of a green precipitate was noted almost immediately. After 12 h, the reaction content was filtered through filter paper and yielded a green coloured powder which was washed with diethyl ether and dried in the open atmosphere (reaction 2.3.3.1).



Reaction 2.3.3.1

Elemental analysis of this compound matched the expected structure. The infrared spectrum of compound **38c** was consistent with its chemical formula as determined by elemental analysis and further confirmed by X-ray crystallography. The very strong and broad peaks at approximately 3400- 3200 cm⁻¹ in the vibration spectra rose from O-H stretching of either coordinated or uncoordinated water molecules. UV-Vis spectra of the compound **38c** showed only one absorption band at 344 nm ($\epsilon = 6772 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$). As expected, this absorption band suggested the presence of Cu²⁺ species in the complex.

Suitable crystals of compound **38c** belong to the monoclinic P2₁ space group. X-ray diffraction analysis of this compound showed that **38c** (Figure 13) is a mononuclear compound in which the copper atom is coordinated by three nitrogen atoms from the pincer ligand and one water molecule with BF₄⁻ as counter anion and a non-coordinated water molecule. One notable feature in this structure, however, is that copper (II) adopts coordination number five in the solid state (Figure 14). The fifth coordination site (apical) of the copper centre is occupied by the oxygen atom of a neighboring amide group. The calculated value of τ_5 (eq. 3) is 0.392 and the coordination environment of copper atom is distorted square-pyramidal from an idealized square-pyramidal geometry (in the solid state).

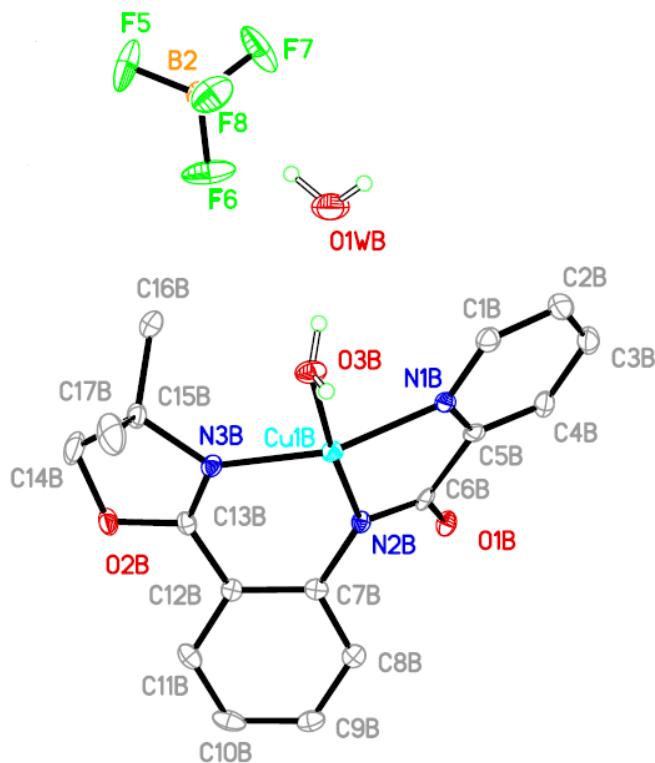


Figure 13. The ORTEP view of compound **38c**

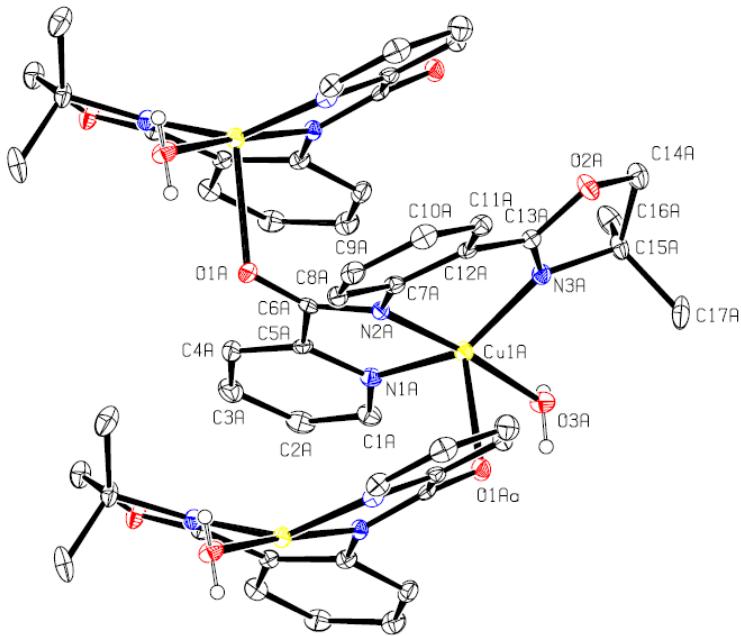


Figure 14: ORTEP view of overall structure of complex **38c**

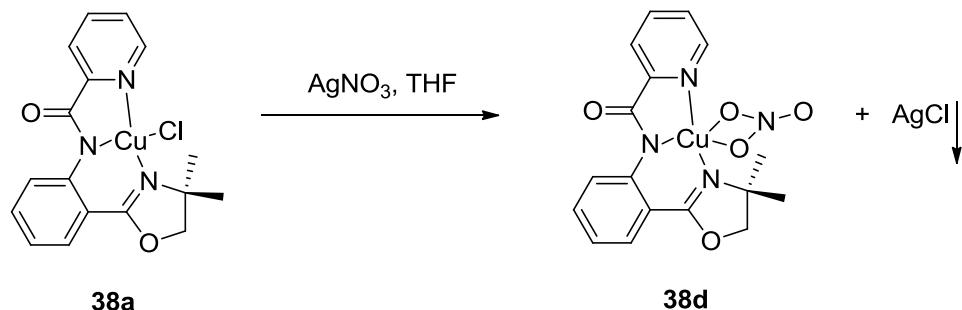
The Cu-O_{water}(3)A bond length is 1.971(3) Å which is expected for Cu-O bond distances.^{49, 77}

The Cu-O_{amide}(1)A bond length, being 2.298(2) Å, is much longer than that of typical Cu-O bond distances. As expected, the average of Cu-L(apical) bond lengths in the square-pyramidal geometry are generally longer than those of the equatorials.⁴⁹ The Cu-N distances of Cu-N(1)A, Cu-N(2)A, and Cu-N(3)A are 2.003(3), 1.953(3) and 1.988(3) Å respectively which are normal and consistent with those corresponding Cu-N bond lengths in of known complexes.^{74- 76}

A complete list of structure factors, bond lengths and bond angles of complex **38c** can be found in Appendix B.

2-3-4- Synthesis of Complex 3d

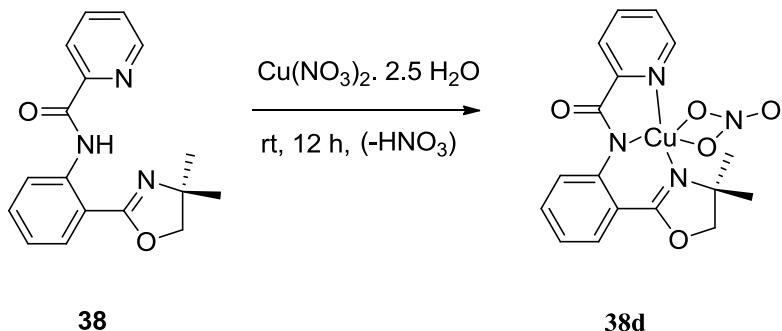
The synthesis of complex **38d** was accomplished using two different starting materials. In route A (reaction 2.3.4.1); 1 equiv. of complex **38a** was dissolved in THF and then followed by adding 1 equiv. of AgNO₃. The formation of a white precipitate(AgCl) was noticed after adding the silver nitrate.



Reaction 2.3.4.1

The white precipitate then was removed from the reaction content by filtration through filter paper. The remaining green coloured mixture then stirred for a further 4 h at room temperature. The mixture then was filtered by gravity filtration and all volatile components were removed by rotary evaporation. Compound **38d** was then obtained as green coloured powder.

In route B, 1 equiv. of Cu(NO₃)₂•2.5H₂O was added to the solution of 1 equiv. of **38** in the EtOH at room temperature. Formation of green precipitate was noted during this time. Stirring then continued for 12 h and after that reaction content filtered through a filter paper. The resulted green coloured powder was washed by diethyl ether and dried in an open atmosphere (Reaction 2.3.4.2).



Reaction 2.3.4.2

The infrared spectra of compound **38d** shows the strong and broad features at approximately 1560- 1330 cm⁻¹ which is related to N-O stretching and bending frequencies of a coordinated nitrate molecule⁷⁸. The IR results are consistent with its chemical formula as determined by elemental analysis. UV-Vis spectra of the compound **38d** indicated only one absorption band at 348 nm ($\epsilon = 15312 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). As expected, this absorption band suggested the presence of Cu²⁺ species in the complex.

The molecular structure of **38d** was confirmed by a single crystal X-ray analysis (Figure 15). Suitable crystals of complex **38d** belong to the monoclinic P2₁/c space group with two molecules in the unit cell. Cell angles (α , β and γ) are 90.00, 100.0840(15) and 90.00 ° and cell lengths (a , b and c) are 7.7793(3), 19.9956(5) and 10.9433(3) Å respectively.

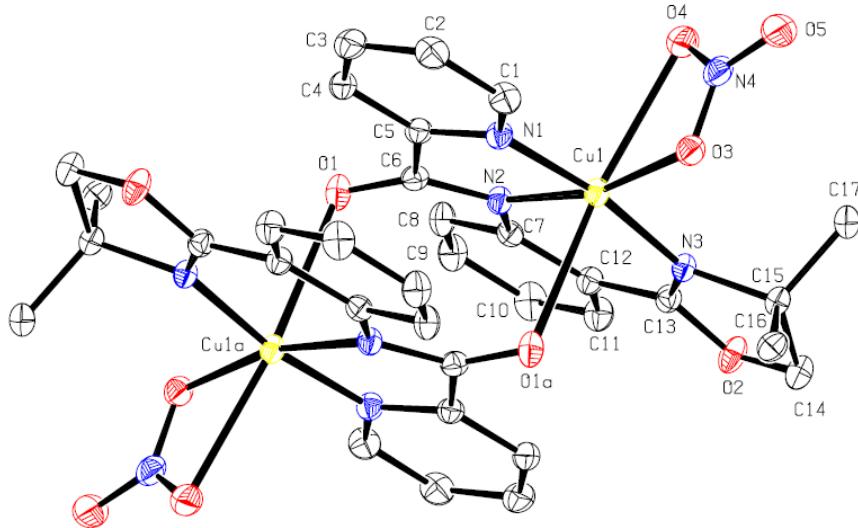


Figure 15: ORTEP view of complex **38d**

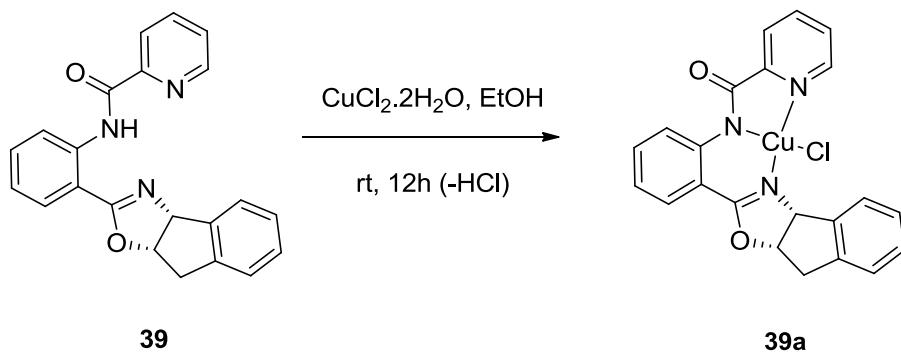
One notable feature in this structure is that Cu centre has coordination number of six. The copper atom in the **38d** is coordinated by three nitrogen atoms (one pyridine nitrogen atom, one amide nitrogen and one oxazoline nitrogen atom), two nitrate oxygen atoms and sixth coordination site is occupied by the amide oxygen atom of another molecule in the unit cell. The Cu-N distances at the equatorial positions are 1.983(3), 1.969(2) and 1.952(2) Å respectively. These bond lengths are comparable with the Cu-N distances in the six coordinate complex $[\text{Cu}(\text{NO}_3)(\text{MeOH})(\text{L}_4)](\text{NO}_3)$ in which these lengths are 1.983(4), 2.003(5) and 1.988(5) Å.⁷⁹ The average value of Cu-N bond lengths is, indeed, normal and consistent with those corresponding Cu-N bond lengths in known complexes.⁷⁴⁻⁷⁶ The Cu-O_{nitrate}(3) bond length is 2.016(2) Å which is typical for Cu-O distances¹ but Cu-O_{amide}(1) bond length (2.827 Å) is, however, longer in comparison to other Cu-O distances in the literature.^{1, 79} This suggests that

the Cu-O(1) interaction can be neglected. Thus the structure of compound **38d** may also be viewed as a distorted trigonal bipyramidal since the calculated τ_5 (eq. 3) value for this complex is 0.87.

A complete list of structure factors, bond lengths and bond angles of complex **38d** can be found in Appendix B.

2-3-5- Synthesis of Complex 39a

The chiral amide analogue **39** was prepared using PA (picolinic acid) and **36** under DCC-DMAP protocols (reaction 1.5.4.3.1, also experimental section).⁴⁸ The synthesis of compound **39a** was achieved dissolving 1 equiv. of **39** in EtOH (95%) followed by adding equimolar of CuCl₂.2H₂O at room temperature (Reaction 2.3.5.1).



Reaction 2.3.5.1

Formation of light green coloured precipitate was observed during the reaction. The resulting light green coloured product was then filtered through filter paper, washed with diethyl ether and dried in the open atmosphere.

The elemental analysis of compound **39a**, in combination with IR and UV-Vis data, strongly suggests the formation of a 1:1 adducts of the ligand fragments with Cu²⁺; specifically, loss of the IR stretching frequency assigned to the amide N-H implies the formation of an amido complex.

To confirm the molecular structure of this complex a single crystal X-ray diffraction study was carried out. A molecular representation of this material is found in Figure 16.

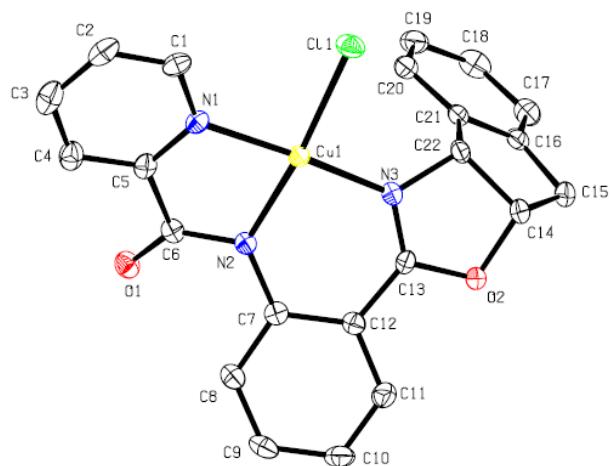


Figure 16: ORTEP view of complex **39a**

According to the X-ray data, mononuclear complex **39a** strongly suggests that it incorporates deprotonated **39**. Similar to the complex **38a**, the coordination sphere is completed by the presence of a single metal-bound Cl atom which occupies a position trans to the amido donor.

According to the τ_4 value (0.110) this complex is considered as slightly distorted square planar. The N(3)-Cu-N(1) and N(2)-Cu-Cl bond angles are 171.26 and 172.25°, respectively. These angles have a slight deviation from the 180° in the ideal square planar geometry. The Cu-N bond lengths in this complex are very similar in magnitude to the corresponding bond lengths in complex **38a**. The Cu-Cl bond distance (2.2289 Å) is slightly shorter than the same bond length in the complex **38a**. All Cu-N and Cu-Cl bond lengths, nevertheless, are typical for copper nitrogen and copper halogen bond distances. A complete list of structure factors, bond lengths and bond angles of complex **39a** can be found in Appendix B.

As it can be seen in Figure 17, **39a** is square planar for the directly attached groups. However, in the solid state, which is shown in Figure 16, is square pyramidal due to the intermolecular bond (2.506 Å) between the Cu(II) centres and the O of an adjacent amide group. This bond length, however, is comparable to the typical Cu-O distances.⁷⁹ Since Cu(II) is well-known to form both 4- and 5- coordinated species, this type of behaviour is unsurprising.

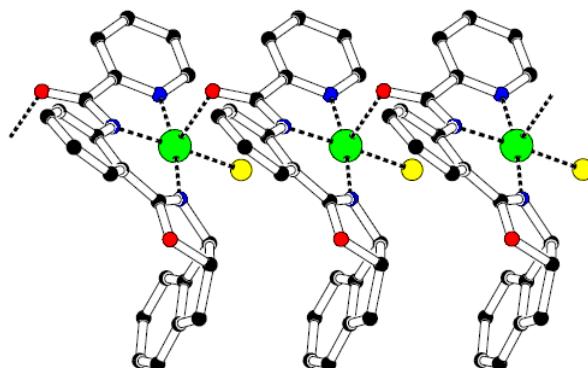
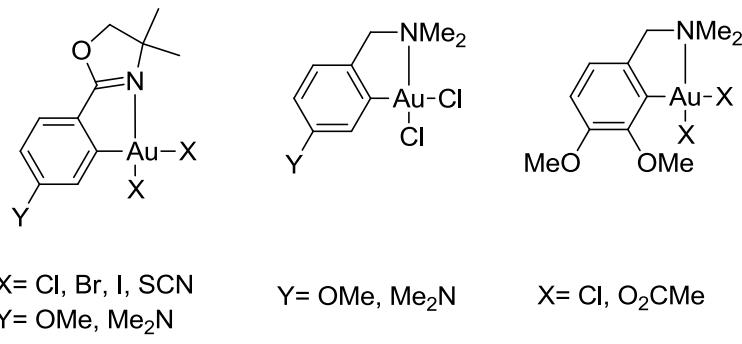


Figure 17. Molecular structure of compound **39a** in the solid state

2-4- An Introduction to Synthesis of Gold Pincer Complexes

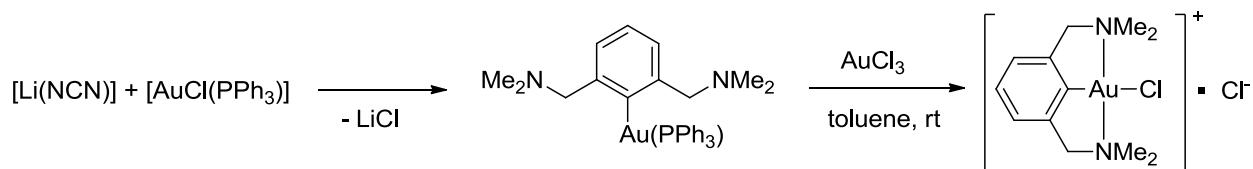
Group 11 metal complexes have been known as catalyst in various organic reactions, it was of interest to examine these with our materials. Au(I) and Au(III) species ,as catalysts, have attracted attention due to their versatility of applications that can be performed.⁸⁰ AuCl₃, which has been known as the most employed gold (III) catalyst, is a very hygroscopic, light sensitive, acidic and to some extent powerful oxidant species. Recently, however, the number of coordination and organometallic compounds has increased to offer some other alternatives to AuCl₃.^{80- 82}

R. V. Parish and his group have reported the synthesis of new complexes of [AuCl₂L], in which L is a chelating agent containing a phenyl group with a N-donor substituent such as an oxazoline or dimethylaminomethyl group (Scheme 13).^{83,84}



Scheme 13. Gold pincer complexes

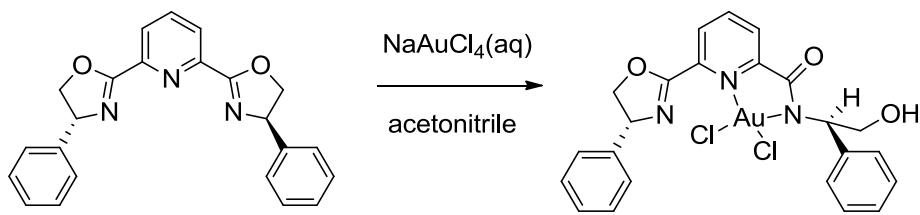
In another paper published by G. van Koten and his group describes the synthesis of a bis-(ortho-amine) aryl-gold(I) complex. The reaction of $[\text{AuCl}(\text{PPh}_3)]$ with $[\text{Li}(\text{NCN})]$ at -20°C in diethyl ether led to formation of the desired product in a good yield. This compound can further react with AuCl_3 at room temperature to afford the pincer type complexes (Reaction 2.4.1).⁸⁵



Reaction 2.4.1

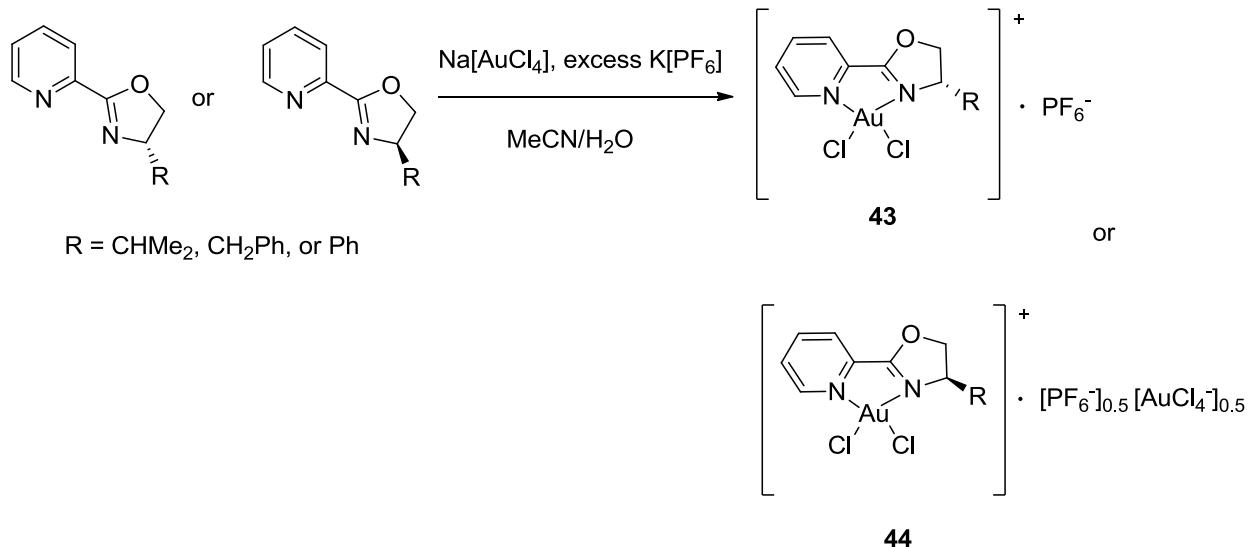
2-4-1-Gold complexes containing oxazoline ring

As it was mentioned previously, compounds containing a (chiral and/or achiral) oxazoline ring are becoming one of the most useful classes of catalysts in wide range of metal-catalyzed transformations. Nonetheless, gold derivatives bearing oxazoline containing ligands have not been extensively studied.⁸⁴ According to the research that has been done by A. Corma and his group, reaction of commercially available bis-[$(4R)$ -phenyl-2-oxazoline-2-yl]pyridine (Pybox) and an aqueous solution of NaAuCl_4 affords an unexpected ring-opened complex in which Au is coordinated to the nitrogen of pyridine and the nitrogen of ring opened oxazoline. This behaviour reveals that these molecules are affected easily by Lewis acids (especially gold species) under the certain experimental conditions (Reaction 2.4.1.1).⁸⁶



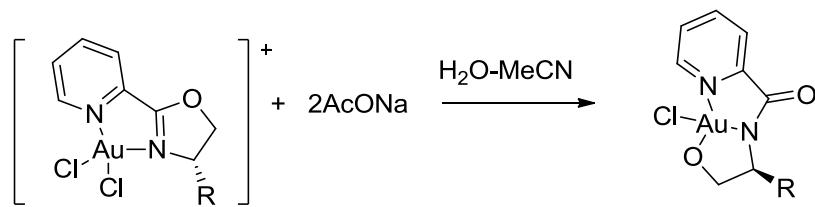
Reaction 2.4.1.1

Another synthesis of gold (III) derivatives was reported by an Italian research group in which pyridinyl-oxazolines(Pyox) have been used as ligand precursors (Reaction 2.4.1.2).⁸⁰



Reaction 2.4.1.2

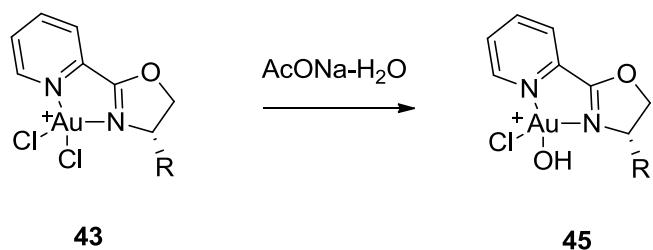
It has been seen that a further reaction of corresponding Au complex (**43**) with AcONa in order to generate the mononuclear dihydroxo- or dinuclear-oxo complexes did not work and yielded in a ring open product **46** (Reaction 2.4.1.3).



46

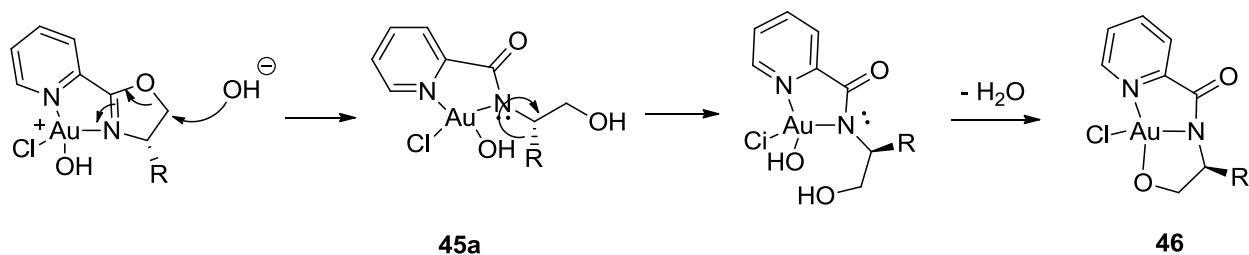
Reaction 2.4.1.3

Since this reaction (2.4.1.4) occurs in aqueous solution, the hydrolysis of $[\text{Au}(\text{pyox})\text{Cl}_2]^+$ (**43**) to give mono(hydroxo) complex is the first step (Reaction 2.4.1.4).⁸⁰



Reaction 2.4.1.4

Complex **45** it has been proposed that undergoes nucleophilic attack by OH^- at the 5-position of the oxazoline ring to give the intermediate **45a** which affords complex **46** after a condensation reaction (scheme 14).⁸⁰

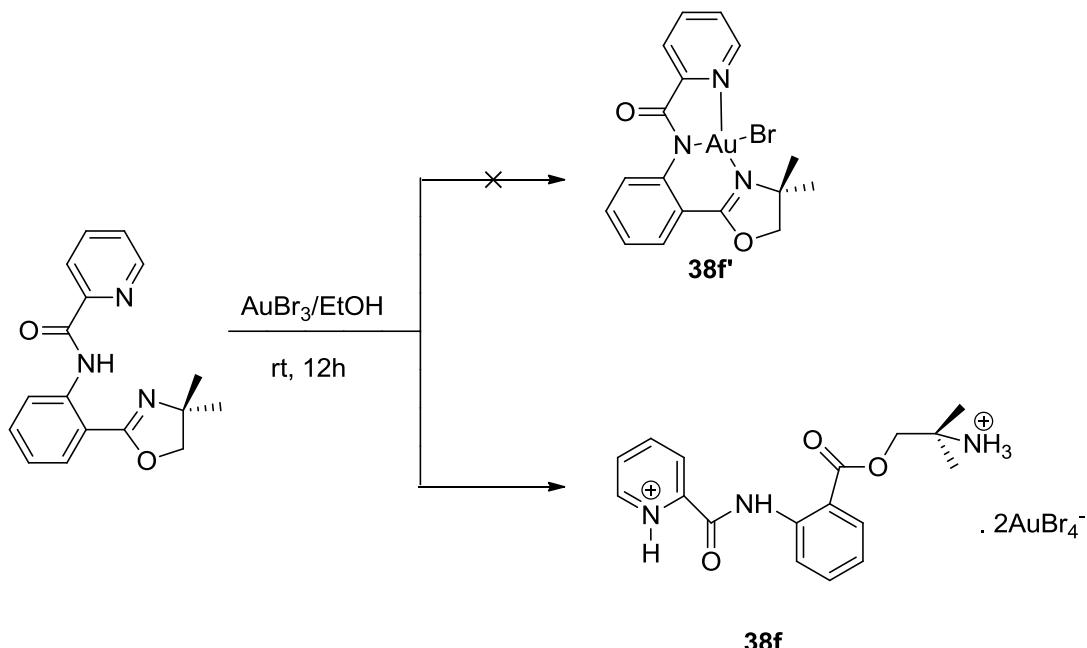


Scheme 14. Plausible reaction pathway for the formation of **46**

2-4-2-Synthesis of Complex **38f**

Several reactions were carried out in a same fashion as that of copper aimed to explore the coordination reactivity of pincer ligand **38** towards gold.

One equiv. of **38** was dissolved in EtOH and followed by adding 1 equiv. of AuBr₃ at room temperature. The dark orange coloured solution was stirred for 12 hours. The reaction contents were then filtered through filter paper and the resulting clear orange solution was left in an open atmosphere to evaporate all of the volatile components. Dark orange coloured solid was then formed. The IR spectrum of the obtained product is characterized by the presence of medium peaks at approximately 3300 and 3130 cm⁻¹ which can be assigned to the N-H groups. The resulting compound was then characterized by ¹H-NMR spectroscopy. The main feature of its ¹H-NMR spectrum is a slight downfield shift of all resonances of both the aromatic and oxazoline ring protons. The aromatic signals are found between 7.22 and 9.00 ppm. The oxazoline ring signals are at 1.69 and 4.61 ppm. Integration of the signals are consistent with the structure assigned to **38f**. The crystal structure of compound **38f** was then determined by X-ray diffraction methods to clarify the structural nature of this material. Since gold(III) usually shows square-planar geometry^{83, 87} it was expected to afford a complex such as **38f'**, as it outlined in the Scheme 15. The X-ray results show that in this case, the product of this reaction is in fact a ring-opened ammonium-ester cation **38f** with AuBr₄⁻ as anion.



Scheme 15. Formation of compound **38f**

The molecular structure of **38f** consists of two discrete AuBr_4^- units, one water molecule and the ammonium cation (Scheme 15 and Figure 18). The crystal system is determined to be triclinic and of space group *P1*. A complete list of structure factors, bond lengths and bond angles of complex **38f** can be found in Appendix B.

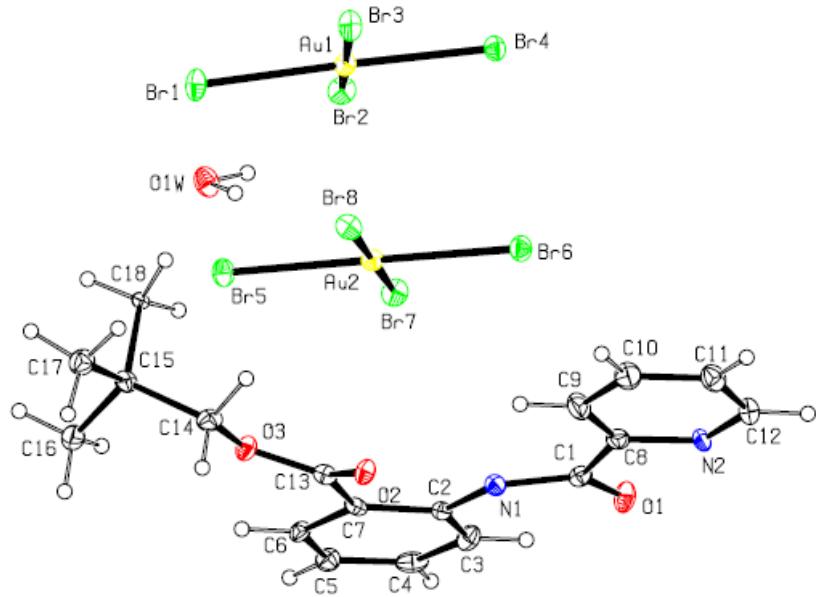
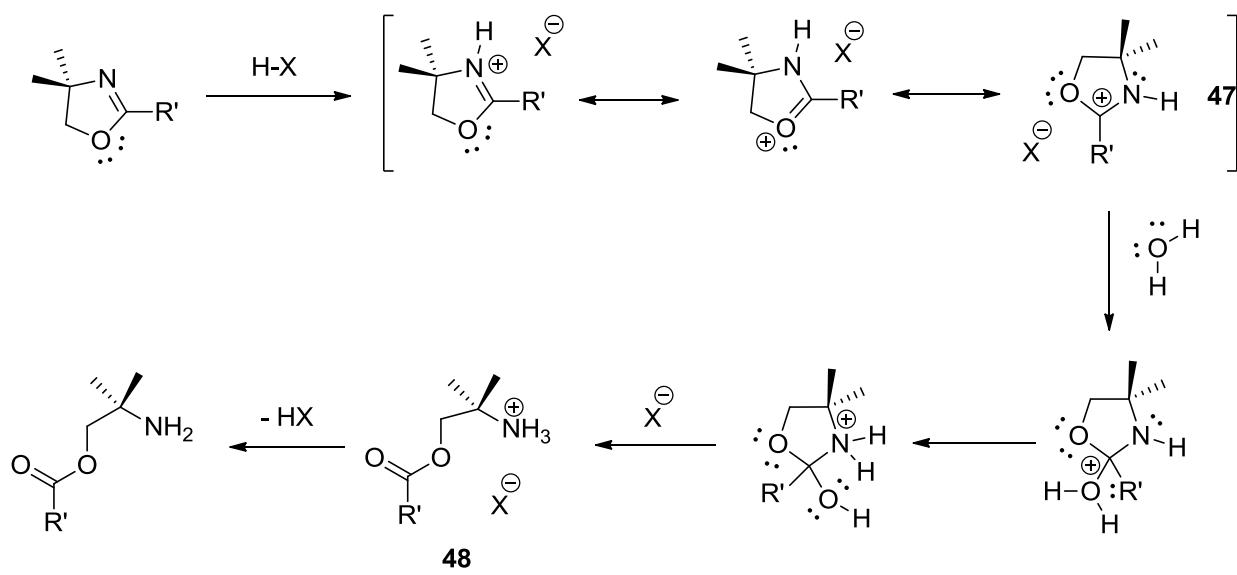


Figure 18: The molecular structure of Complex **38f**

The proposed mechanism of the reaction,⁸⁰ leading to **38f** is shown in scheme 16 and involves nucleophilic attack of the intermediate **47** by a second nucleophile (*e. g.* H₂O) which eventually leads to an ammonium intermediate **48** following the ring opening reaction.



Scheme 16. Plausible mechanism for formation of ring-open oxazoline

Reaction of ligand **38** with gold(III) bromide under basic condition, using 3 equiv of triethyl amine, also afford the same ring-open product. It is noted that by changing the nucleophile from water to a triethyl amine the product still remained unchanged. On the basis of these results here, sensibility to water, acid and base should be considered when using gold precursors in metalation of pincer ligands containing oxazoline rings.^{80, 88}

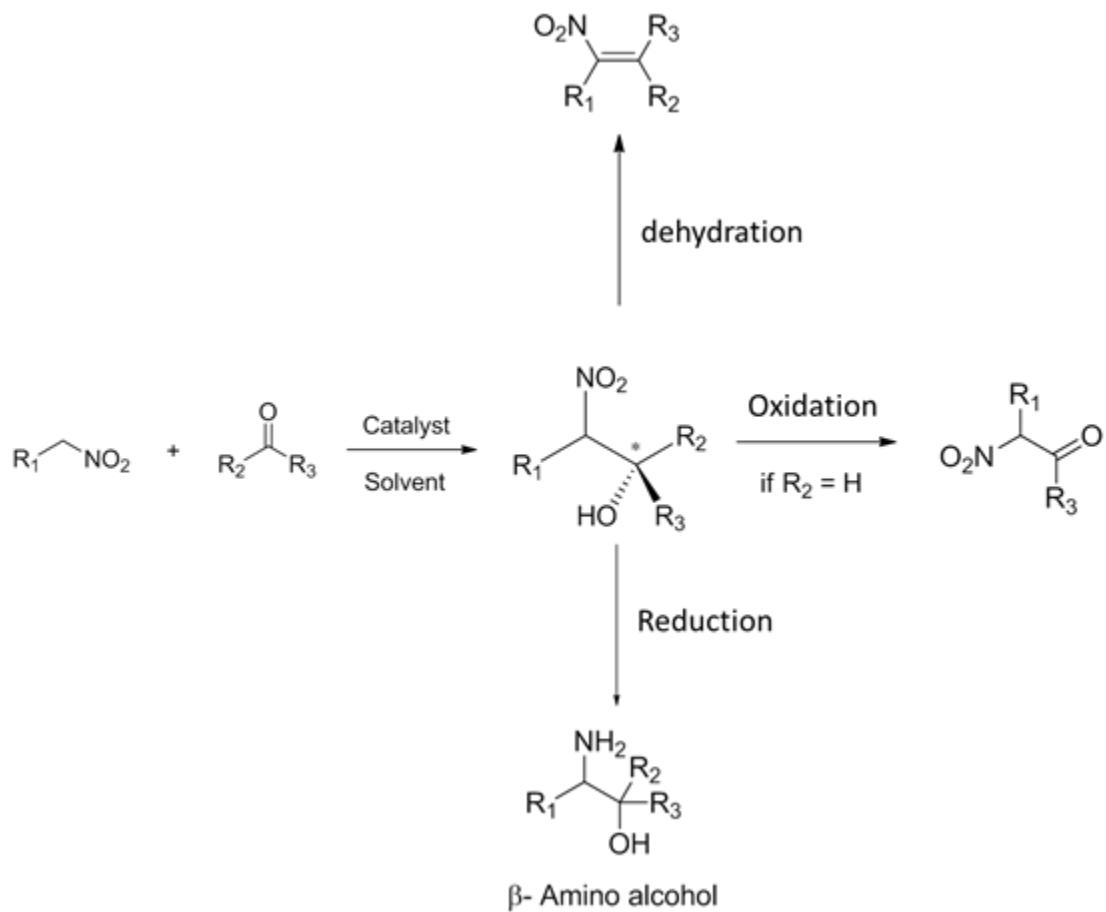
Chapter Three

3-1- Catalytic Activity of Oxazoline Complexes in Organic Reactions

Transition metal complexes, in general, have been widely used as catalysts in many organic and polymer syntheses.⁸⁹⁻⁹¹ Wilkinson's catalyst; ((PPh₃)₃RhCl) and Vaska's complex; (Ir(PPh₃)₂Cl(CO)) two some of the famous and classic examples of transition metal complexes. Complexes containing a chiral oxazoline ring, have attracted interests as catalyst in a wide range of metal-catalyzed reactions and transformations.⁹² Chiral compounds (a chiral compound is an object that is not identical to its mirror image) are very important in biological systems, pharmaceutical industry, organic and inorganic chemistry as well as biochemistry. The role of chirality in the pharmaceutical industry is crucial because different enantiomers or diastereomers have different biological activities.⁸⁹ Therefore, design, development and synthesis of asymmetric catalysis is very important since a small amount of catalyst can promote reactions and lead to the generation of chiral products.⁸⁹ A large number of these ligands can be synthesized from available chiral amino alcohols. As a result, the enantiocontrolling stereocentre exists on the carbon atom adjacent to the coordinated nitrogen of the oxazoline ring, and hence, it can be close enough to the metal active site to have a direct effect on the stereochemistry of the products.⁹²

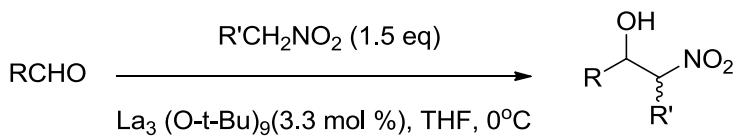
3-2-Nitro-Aldol (Henry) Reaction

The Henry reaction (which was discovered in 1895)⁹³ is one of the useful organic reactions that have been used for the formation of C-C bond.^{94, 95} The product of this reaction is a β -hydroxy-nitroalkane that can be used as a starting material in the synthesis of many valuable building blocks such as amino alcohols,⁹⁶ nitro alkenes and carbonyl compound like nitroketones (Scheme 17).⁸⁹



Scheme 17. Henry reaction

The applicability of this reaction depends on the type of catalyst which is used in the reaction. Choosing a suitable reaction is very critical to generate the stereogenic centre.⁹³ The initial research results on the asymmetric version of the nitroaldol (Henry) reaction have been reported by Shibasaki in 1992. They showed that rare earth metal alkoxides can be applied as catalysts (Reaction 3.2.2).⁹⁷



Reaction 3.2.2

Since then, several research groups have developed and tested new transition metal complex systems which contain the oxazoline unit in their structures. Evans and Jørgensen have showed Cu complexes containing bis-oxazoline ligand (Figure 19) that can be used as catalyst in the Henry reaction under the conditions which are outlined in Reactions 3.2.3 and 3.2.4.^{98,99}

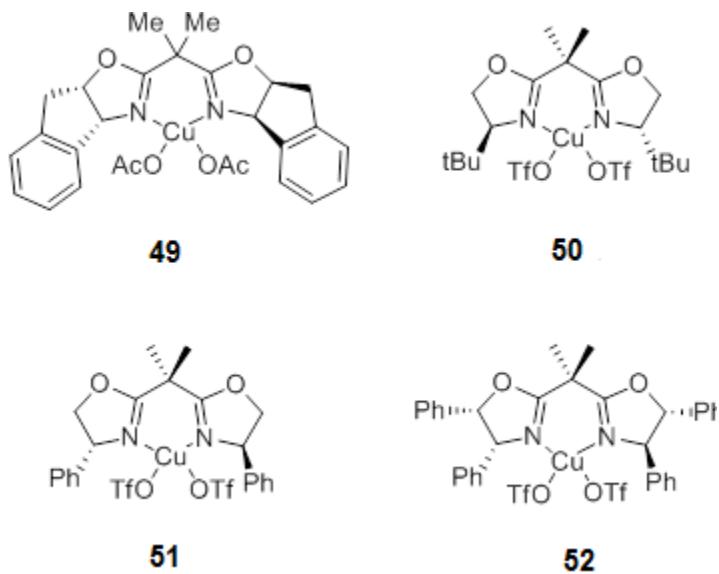
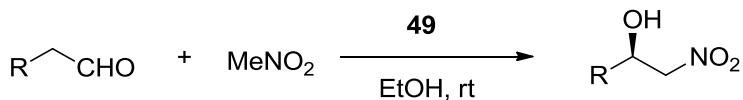
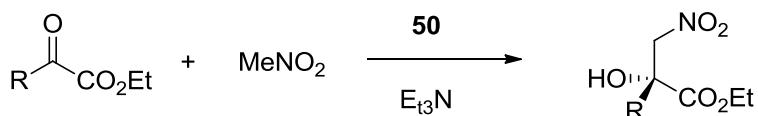


Figure 19. Copper complexes containing bis-oxazoline ligand



Reaction 3.2.3

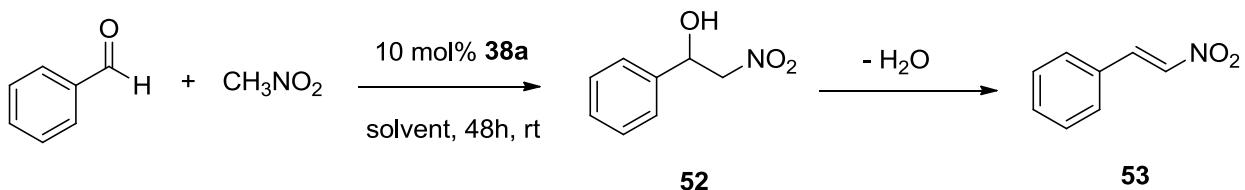


Reaction 3.2.4

There are many other examples have shown that the combination of various chiral ligands and metal ion, especially Cu(II), can catalyze the Henry reaction.^{91,99-101}

3-3- Study of Catalytic Activities of Novel Cu(II) Pincer Complexes in The Henry Reaction

Chiral complexes of copper have been found to be a suitable catalysts for the Henry reaction,¹⁰² the novel Cu(II) pincer complexes synthesized here were tested as catalysts in this reaction. In order to obtain optimized conditions, the achiral complexes **38a** and **38c** have been examined as catalysts in a series of solvents such as THF, EtOH, toluene, DCM and chloroform (Table 3.1). Henry reaction between benzaldehyde and nitromethane in combination with **38a** is described in the Reaction 3.3.1 below.



As it can be seen in the reaction, compound **52** can undergo dehydration to form **53**.⁶³

According to ¹H NMR data, when the reaction takes place in toluene, DCM and chloroform the product is **53**. However, less than 5% conversion to **52** can be achieved by using THF or EtOH as solvent.

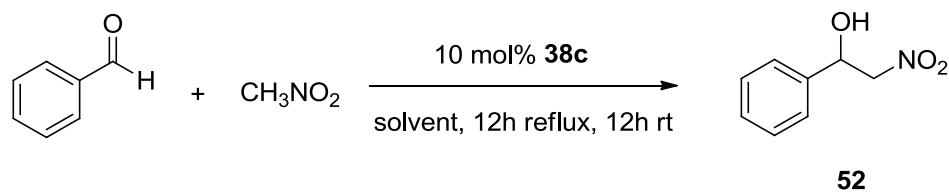
Table 3.1. Solvent effect on the catalyzed henry reaction with ligand **38a**

Molar ratio of reactants	Solvent	Catalyst(10 mol%)	Time (h)	Conv(%) to 52	Conv(%) to 53
1:1	THF	38a	48	< 5%	----
1:1	EtOH	38a	48	< 5%	----
1:1	Toluene	38a	48	----	34
1:1	DCM	38a	48	----	34
1:1	Chloroform	38a	48	----	----

The effect of temperature on the reaction of benzaldehyde and nitromethane with compound **38a** as catalyst was also tested. Heating the reaction at reflux in THF or ethanol for a period of 24 hours did not improve the results with this catalyst.

3.3.1- Henry reaction with compound **38c**

In related work, the use of complex **38c** as catalyst, in the conditions which outlined in reaction 3.3.1.1 and Table 3.2 did however, provide the corresponding β -hydroxy-nitroalkane product **52**.



Reaction 3.3.1.1

Table 3.2. Optimization of the reaction solvents and catalyst

Solvent	Molar ratio benzaldehyde: nitromethane	Catalyst	Time (h)	Yield(%) 52
THF	1:5	38c	24	25
EtOH	1:5	38c	24	20
acetonitrile	1:5	38c	24	20

The best reaction condition were determined to involve the use of 10 mol% of **38c** as catalyst in THF as solvent for 24 h (12 h reflux and 12 h rt). These reactions, however, resulted in only 25-20% yield of the product **52**. Complex **38c** exhibit the highest reactivity among the synthesized complexes and provide a racemic mixture of product **52**.

The effect of electron-withdrawing and electron-donating groups on the Henry reaction was also tested using 4-methoxy benzaldehyde and 4-nitrobenzaldehyde. Under the same condition as reaction 3.3.1.1, the electron- withdrawing group was found to provide the highest yield (49%).

With optimized reaction condition in hand, in order to see the effect of various synthesized copper complexes on the enantioselectivity, the chiral catalyst **39a** was tested in the same reaction conditions. Surprisingly, the chiral copper pincer complex **39a** did not afford any products. The structure of the ligand **39** may need further optimization to achieve the possible enantioselectivity. For instant, by altering the nature of the starting chiral amino alcohol various chiral oxazoline ligand can be developed. Further studies, hence, should aimed at designing new chiral ligands that can provide enantioselectivity for such transformations.

Conclusions

In conclusion, general synthetic methods for the synthesize of four- and five-coordinated $[(NN'N'')CuX]$ complexes $X = Cl, Br, OH_2$ and NO_3 , bearing N -(2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl) phenyl) picolinamide (**38**) and N -(2-((3aR, 8aS)-8, 8a-dihydro-3aH-indeno[1,2-d]oxazol-2-yl)phenyl) picolinamide (**39**) pincer ligands have been realised. Metalation of compound **38** with gold(III) salts under the same conditions, however, led to open-ring adducts. Such complexes can be readily prepared on large scales without the exclusion of air or moisture. All synthesized complexes were characterized by X-ray diffraction crystallography. These compounds can be used for C-C bond forming reaction, particularly Henry reaction.

Experimental

General

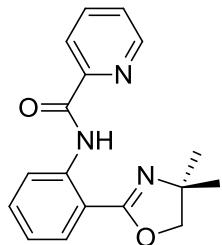
All reactions were carried out using standard bench-top laboratory techniques using commercially available, reagent grade solvents. All solvents were further purified by solvent purification system. Most of the reactions were performed under ambient temperature unless otherwise stated. Sensitive reactions were carried out under an atmosphere of dinitrogen gas using standard vacuum line Schlenk techniques. All starting materials and solvents were purchased commercially or synthesised according to the literature preparations.^{75, 76} ¹H NMR and ¹³C NMR were recorded from chloroform-*d* and acetone-*d*₆ solutions at 400 and 100.6 MHz using a Bruker Avance spectrometer. UV-Vis measurements were carried out in DCM solutions (C=10⁻⁴ g/mL) using a Perkin Elmer Lambda 20 spectrometer. IR spectra were obtained as KBr disks for all the solid complexes on Perkin Elmer Spectrum. Melting point was determined using Fisher Scientific melting point apparatus with maximum temperature of 300 °C.

The X-ray crystal structure determination of complexes **38a- 38f** and **39a** were performed by Dr. Alan J. Lough at the University of Toronto's crystallographic service centre.

Elemental analysis data were supplied by Atlantic Microanalytical of Atlanta, Georgia and are reported as percentages.

Synthesis of Compound 38

Thionyl choride (5.6 g, 50 mmol) was added dropwise to a stirred and cold (0°C) solution of picolinic acid (9.20 g, 75.0 mmol) and Et₃N (7.60 g, 75.0 mmol) in 35 mL of DCM. Stirring was continued for 30 min and then to this colourless mixture was added a solution of **34** (9.5 g, 50 mmol) in 20 mL of DCM at 0°C. The reaction content stirred for a further 3 h as the mixture warmed to room temperature. The reaction vessel was then left standing overnight. A saturated aqueous solution of Na₂HCO₃ was then added to the mixture (for neutralization) and subsequently followed by isolation of the organic layer. The organic layer then washed with water (3 × 15 mL) and then evaporated in *vacuo* (rotary evaporator). The obtained crude product was then purified by flash chromatography (SiO₂, 230-400 mesh) using hexane-ethyl acetate (5:1 v/v). The crystalline colorless solid product was obtained by dissolving the light yellow crude product in hot ethanol and cooling the mixture. Yield: 10.24 g (69%); mp 117 °C (lit.: 110 °C).⁴⁸ All IR and NMR data were consistent with the literature values.⁴⁸

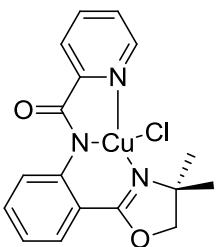


Synthesis of Compound 38a

In a 100 mL round-bottomed flask containing 20 mL of ethanol (95%), was added **38** (1.52 mmol, 0.450 g), directly as a solid to the flask at room temperature. The resulting solution was stirred until the ligand dissolved in the EtOH. CuCl₂.2H₂O (light yellow crystals, 0.26 g: 1.50 mmol) was then added to this mixture. The colour of the reaction mixture then turned from light yellow to dark green. Reaction mixture was then stirred for 24 h at room temperature. Subsequently, the mixture was filtered by gravity filtration through filter paper. The resulting green powder was then washed with diethyl ether (3 × 5 mL). The resulting green coloured product, in the form of a powder, was then dried on a rotary evaporator (Yield: 85%, 0.51 g). Crystalline material, in the form of green coloured crystals, were obtained by dissolving the product powder (0.2 g) in DCM (2 mL) and then layering this mixture with Et₂O (5 mL) and covering the top. Green crystals isolated from the vial after slow evaporation of solvent in a period time of one week.

IR (KBr: cm⁻¹): 3074(w), 2968(m), 1618(s), 1602(s), 1488(s), 1344(s), 750(s), 687(s), 531(m).

UV/Vis. (c = 0.00010 g/mL ; CH₂Cl₂): $\lambda_{\text{max}} = 342 \text{ nm}$, ($\epsilon = 7.8 \times 10^3$), Elemental Analysis calcd. for C₁₇H₁₆N₃ClCuO₂ (%): C 51.91, H 4.10, N 10.68; found: C 51.73, H 4.09, N 10.53.



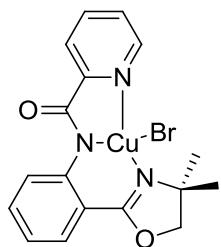
2-3- Synthesis of Compound 38b

Compound **38** (1.00 mmol, 0.340 g) was dissolved in 20 ml of ethanol (95%) and transferred to a 100 mL round-bottomed flask at room temperature. To this stirred mixture then was added CuBr₂, anhydrous, (0.20 g, 1.00 mmol) and stirring was continued for 24 h at room temperature. The dark green solution was then filtered by gravity filtration (through filter paper) and isolated solid then washed with diethyl ether (3×5 mL). The isolated green coloured product was then dried in vacuo (Yield: 89%, 0.39 g).

Green crystals suitable for X-ray diffraction were grown by dissolving the 0.2 g of the crude powder in 2 mL of DCM and then layering this mixture with Et₂O (5mL) and covering the top of the vial. Green crystals formed after 2 days.

IR (KBr cm⁻¹): 3074(w), 2969 (m), 1633 (s), 1615 (s), 1488 (s), 1346 (s), 749 (s), 686 (s), 531 (m)

UV/Vis. (c = 0.00010 g/mL ; CH₂Cl₂): $\lambda_{\text{max}} = 348$ nm, ($\varepsilon = 8.0 \times 10^3$), Elemental Analysis calcd. for C₁₇H₁₆N₃BrCuO₂ (%): C 44.8, H 3.98, N 9.22; found: C 46.39, H 3.70, N 9.37

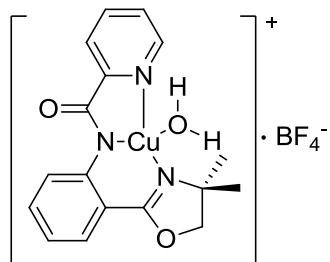


2-4- Synthesis of Compound 38c

To a mixture of 20 mL ethanol (95%) and ligand **38** (0.30 g, 1.00 mmol) in a 100 mL round-bottomed flask at the room temperature, was then added Cu(BF₄)₂.6H₂O (1.00 mmol, 0.36 g). The reaction mixture then stirred at room temperature for 12 h. The reaction content was then filtered twice by a gravity filtration. The clear green liquid was left under the fume hood to evaporate the solvent. Green needle shape crystalline was formed inside the solution by slow evaporation of volatile component. Green needle crystals then washed with diethyl ether (2 × 2 mL) and dried in open atmosphere. (Yield: 95%, 0.44 g)

IR (KBr cm⁻¹): 3348 (m), 3070 (m), 1612 (s), 1543 (s), 1486 (s), 1382 (s), 1077 (s), 758 (s), 688 (s), 662 (w).

UV/Vis. (c = 0.00010 g/mL; CH₂Cl₂): $\lambda_{\text{max}} = 344 \text{ nm}$, ($\epsilon = 6.8 \times 10^3$), Elemental Analysis calcd. for C₁₇H₁₈N₃CuO₃. BF₄. H₂O (%): C 44.13, H 3.92, N 11.18; found: C 48.48, H 3.81, N 13.23.



2-5- Synthesis of Compound 38d

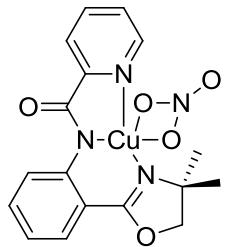
Route (a): Compound **38a** (0.50 mmol, 0.19 g) was dissolved in 10 mL of THF, AgNO₃ (0.50 mmol, 0.085 g) was then added to this stirring mixture. The stirring was then continued for 4 h at room temperature. The white precipitate of AgCl was removed from the mixture by a gravity filtration. The remaining green mixture left overnight to evaporate the volatile component in the

open atmosphere. The green powder was formed after all volatile solvents evaporate (Yield: 76%, 0.16 g). The green crystals suitable for X-ray crystallography were grown by dissolving the 0.1 g of green powder in 1 mL of DCM and then laying with 3 mL ethyl acetate and sealing the top. Crystals formed after 2-3 days.

Route (b): Compound **38** (1.00 mmol, 0.3 g) was dissolved in 15 ml EtOH (95%). Cu (NO₃)₂ (1.00 mmol, 0.19 g) was then added to this mixture at room temperature. The reaction content was then stirred for 12 h. Subsequently the green coloured precipitate, which was formed during the reaction, was isolated by a gravity filtration and dried on a rotary evaporator (Yield 90%, 0.19 g).

IR (KBr cm⁻¹): 2926 (m), 1626 (s), 1487 (s), 1338 (m), 1216 (m), 1126 (m), 1076 (m), 1013 (m), 755 (s), 687 (s), 538 (m), 458 (w).

UV/Vis. (c = 0.00010 g/mL ; CH₂Cl₂): $\lambda_{\text{max}} = 348 \text{ nm}$, ($\epsilon = 1.5 \times 10^4$), Elemental Analysis calcd. for C₃₄H₃₂N₈Cu₂O₁₀ (%): C 48.36, H 3.84, N 13.34; found: C 48.35, H 3.86, N 13.16

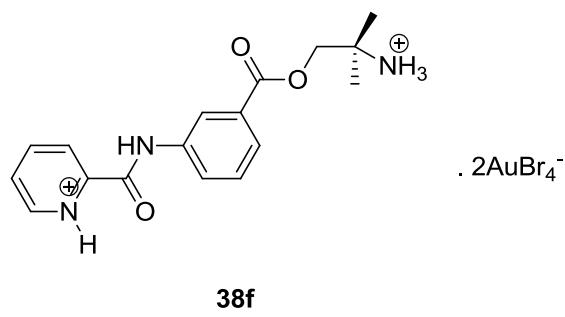


2-6- Synthesis of Compound 38f

Route a) AuBr₃, dark-red to black crystalline solid, (0.44 g, 1.00 mmole) was added to the mixture of **38** (0.34 g, 1.00 mmol) in 20 ml of EtOH (95%) at room temperature. The resulting deep orange- brown mixture stirred overnight. The reaction content was then filtered by gravity

filtration (through filter paper) and clear orange mixture left uncovered under the fume hood. Orange crystals were formed by solvent evaporation (Yield: 67%, 0.21 g).

Route b) Compound **38** (0.34 g, 1.00 mmol) was dissolved in 20 mL of 1,2-dichloroethane. To this mixture was then added triethylamine (0.303 g, 3.00 mmol) and the mixture stirred for 10 min. AuBr_3 (0.44 g, 1.00 mmol) was then added at room temperature to the reaction content and deep brownish color was resulted. Stirring was continued overnight. Solvent then removed under reduced pressure to yield a dark orange precipitate (Yield: 79%, 0.25 g). Orange crystals were grown by dissolving the 0.1 g of crude product in 1 mL of DCM and layering this mixture with ether and covering the top.

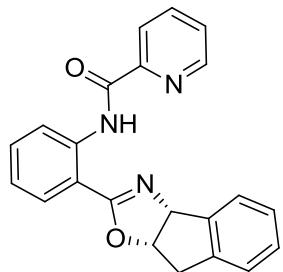


38f

2-7- Synthesis of Ligand **39**

Compound **36** (2.136 g, 11.2 mmol) and picolinic acid (1.674 g, 13.60 mmol) were added to chilled (10 °C) DCM (120 mL) in a 500 mL round-bottomed flask. The mixture was then stirred for 25 min at 0 °C. To this stirring mixture was then added DMAP (0.412 g, 3.2 mmol) and DCC (3.492 g, 16.8 mmol). Stirring was continued for a further 25 min at the same temperature. After that the cooling bath was removed and the reaction vessel warmed up to room temperature. The mixture

was stirring for 48 h and then filtered by a gravity filtration. The clear filtrate then washed with water (3×100 mL), 5% aq. HOAc (150 mL), and again water (3×50 mL). To the organic layer was then added drying agent (MgSO_4), filtered and all volatile solvents were removed on a rotary evaporator. The crude light beige product thus obtained was purified by recrystallization in hot ethanol. Yield: 61%, 2.4 g; mp 191 °C (lit.: 189 °C⁴⁸). All IR and NMR data were consistent with the literature values.⁴⁸

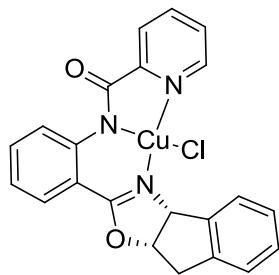


2-8- Synthesis of Complex 39a

In a 100 mL round-bottomed flask containing 20 mL EtOH (95%) was placed compound **39** (0.7 mmol, 0.25 g), directly in a form of solid, and was then stirred until it dissolved. To this resulted colourless mixture, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.17 g, 1.00 mmol) was then added at room temperature. Stirring was continued for further 12 h at room temperature. Resulted green precipitate was isolated by gravity filtration, washed with diethyl ether (3×5 mL) and dried on a rotary evaporator (Yield: 82%, 0.37 g). The green powder product was crystallized by dissolving the 0.2 g of green powder in 2 mL of DCM and then layering with diethyl ether (5 mL) and sealing the top.

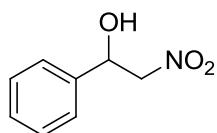
IR (KBr cm^{-1}): 2926 (m), 1626 (s), 1487 (s), 1338 (m), 1216 (m), 1126 (m), 1076 (m), 1013 (m), 755 (s), 687 (s), 538 (m), 458 (w).

UV/Vis. ($c = 0.00010$ g/mL ; CH_2Cl_2): $\lambda_{\max} = 349$ nm, ($\varepsilon = 7.6 \times 10^3$), Elemental Analysis calcd. for $\text{C}_{22}\text{H}_{16}\text{N}_3\text{ClCuO}_2$ (%): C 58.28, H 3.56, N 9.27; found: C 58.04, H 3.71, N 9.06



2-9- Synthesis of 2-nitro-1-phenylethanol (52)

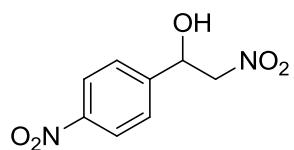
Catalyst **38c** (0.048 g, 0.1 mmol) was added directly to a mixture of benzaldehyde (0.106 g, 1.00 mmol) and nitromethane (0.305 g, 5.00 mmol) in 20 mL of THF at room temperature. The reaction content then refluxed for 24 h and subsequently was filtered through the Celite to obtain a clear light green solution. Purification was performed by TLC (Hexane-ethyl acetate 4:1). The compound **51** was obtained as light yellow oil (25%), ^1H NMR (400 MHz, CDCl_3) δ : 7.36- 7.39 (m, 5H, Ar-H), 5.48 (d, 1H), 4.43-4.54 (dd, 2H), 2.81 (s, 1H, OH). ^{13}C NMR (MHz, CDCl_3) δ : 131.12, 129.04, 128.98 ($\times 2$), 125.92 ($\times 2$), 81.22, 71.01



2-10- Synthesis of 2-nitro-1-(4-nitrophenyl) ethanol

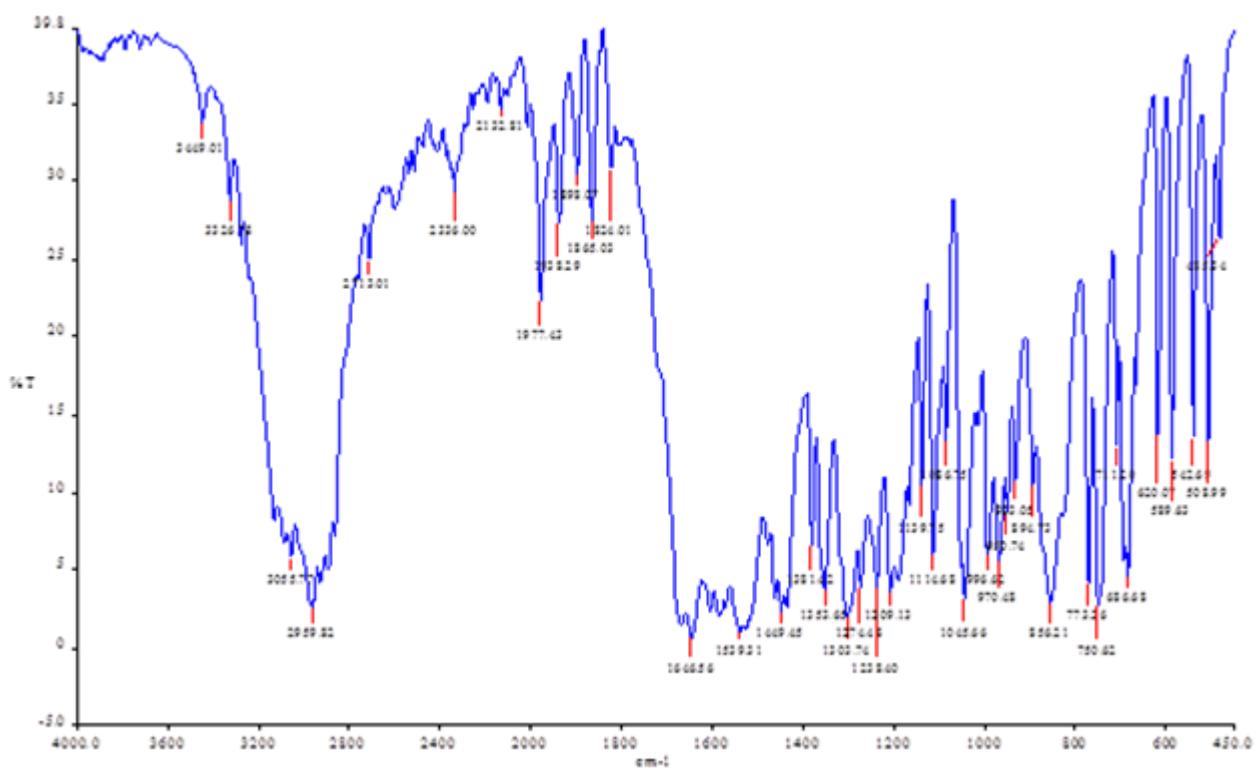
To a stirring mixture of para-nitrobenzaldehyde (0.151 g, 1.00 mmol) and nitromethane (0.305 g, 5.00 mmol) in 20 mL of THF was added catalyst **38c** at room temperature. The reaction content

then refluxed for 48 h and subsequently was filtered through filter paper twice to obtain a light green solution. The resulting liquid then was left overnight in an open atmosphere. Light green coloured solid was formed after solvent evaporation. Further purification was performed by TLC (DCM: ethyl acetate, 4:1). The title compound was obtained as a white colour solid 0.105 g (49%), ^1H NMR (400 MHz, CDCl_3) δ : 8.28 (d, 2H, $J = 8.68$ Hz, Ar-H), 7.64 (d, 2H, $J = 8.72$ Hz, Ar-H), 5.61 (m, 1H), 4.59 (dd, 2H, $J_1 = 6.68$ Hz, $J_2 = 8.28$ Hz), 3.27 (br, 1H, OH).

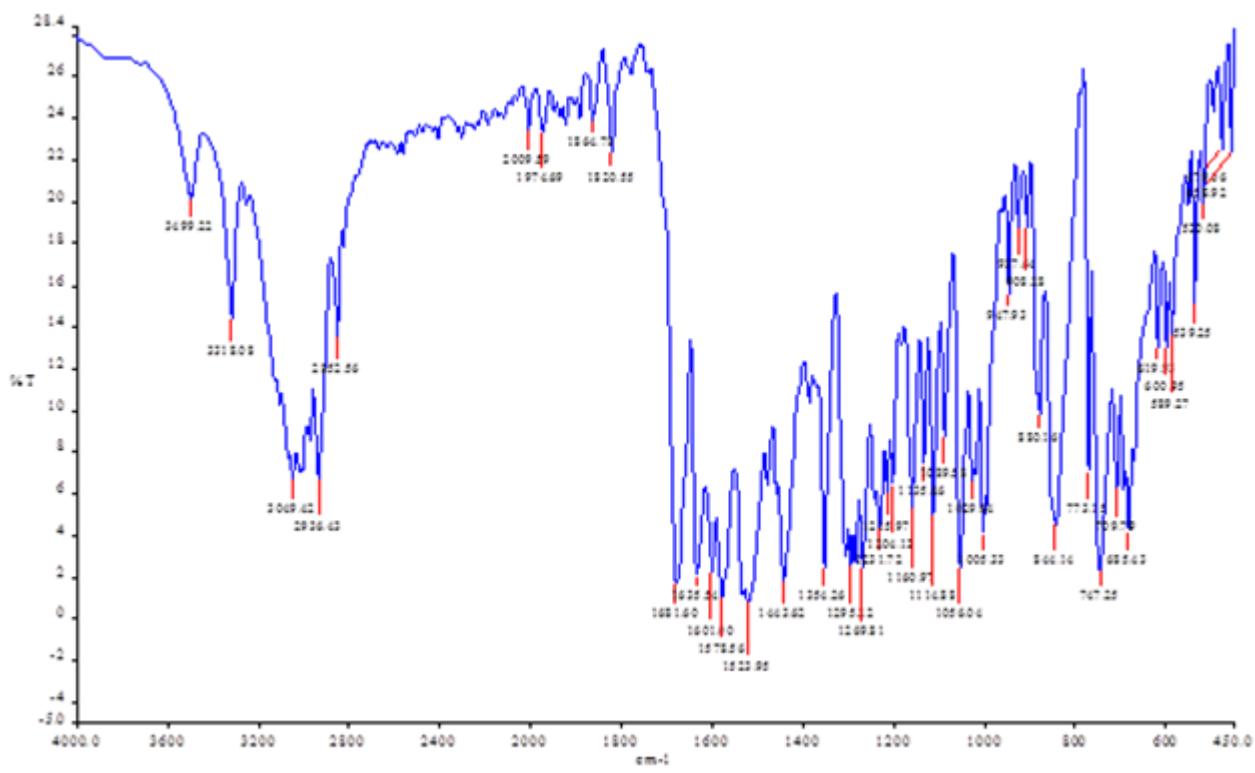


APPENDIX A

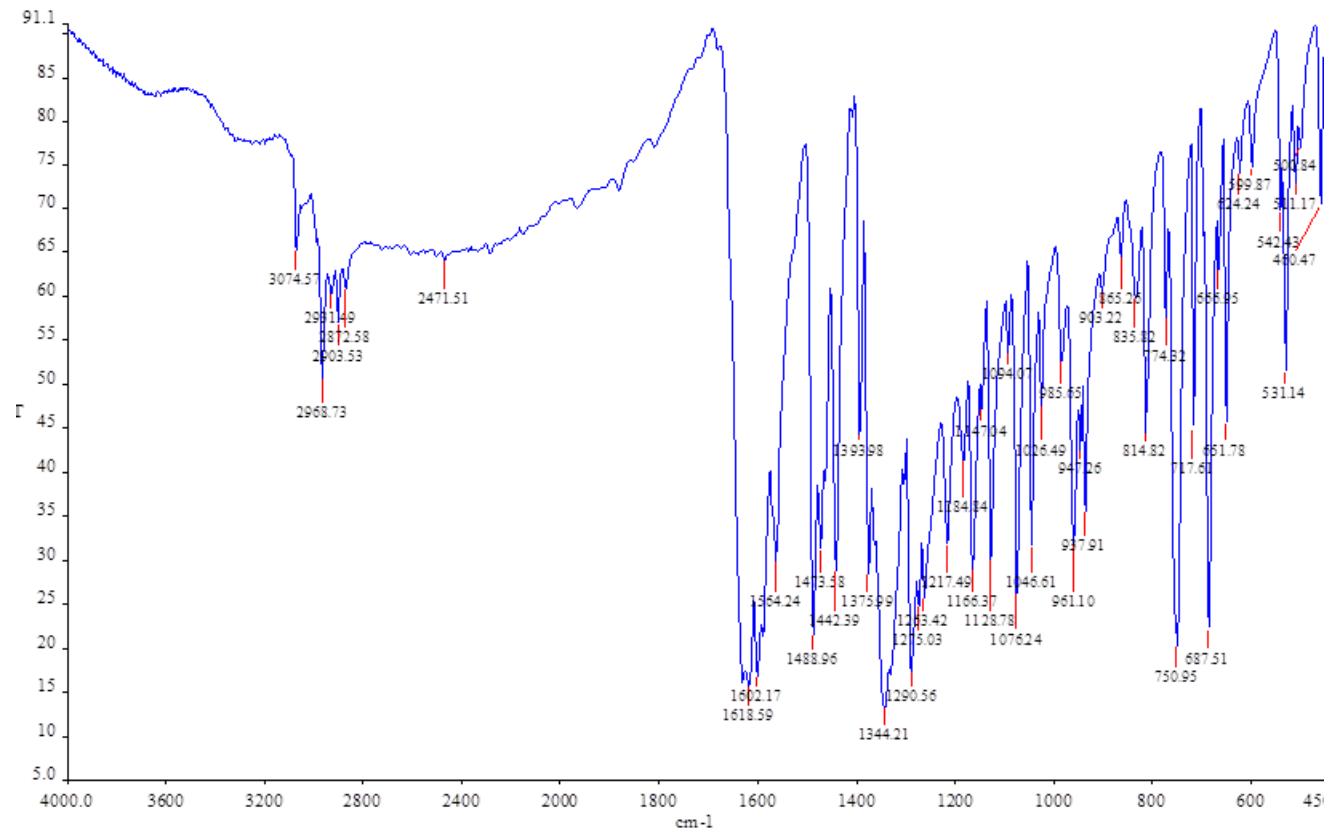
Infrared, UV-Vis and NMR data of the synthesized complexes



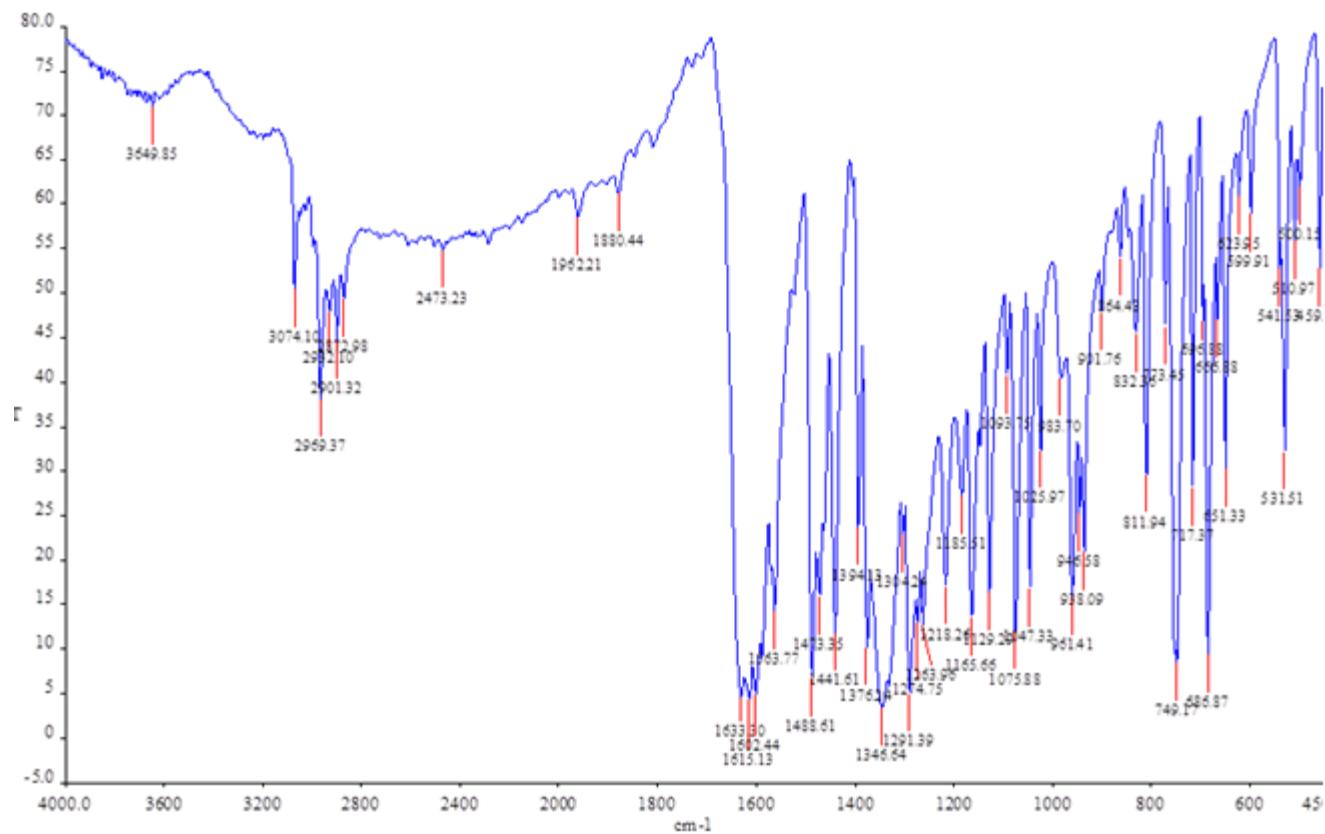
IR spectrum of Ligand **38** (KBr)



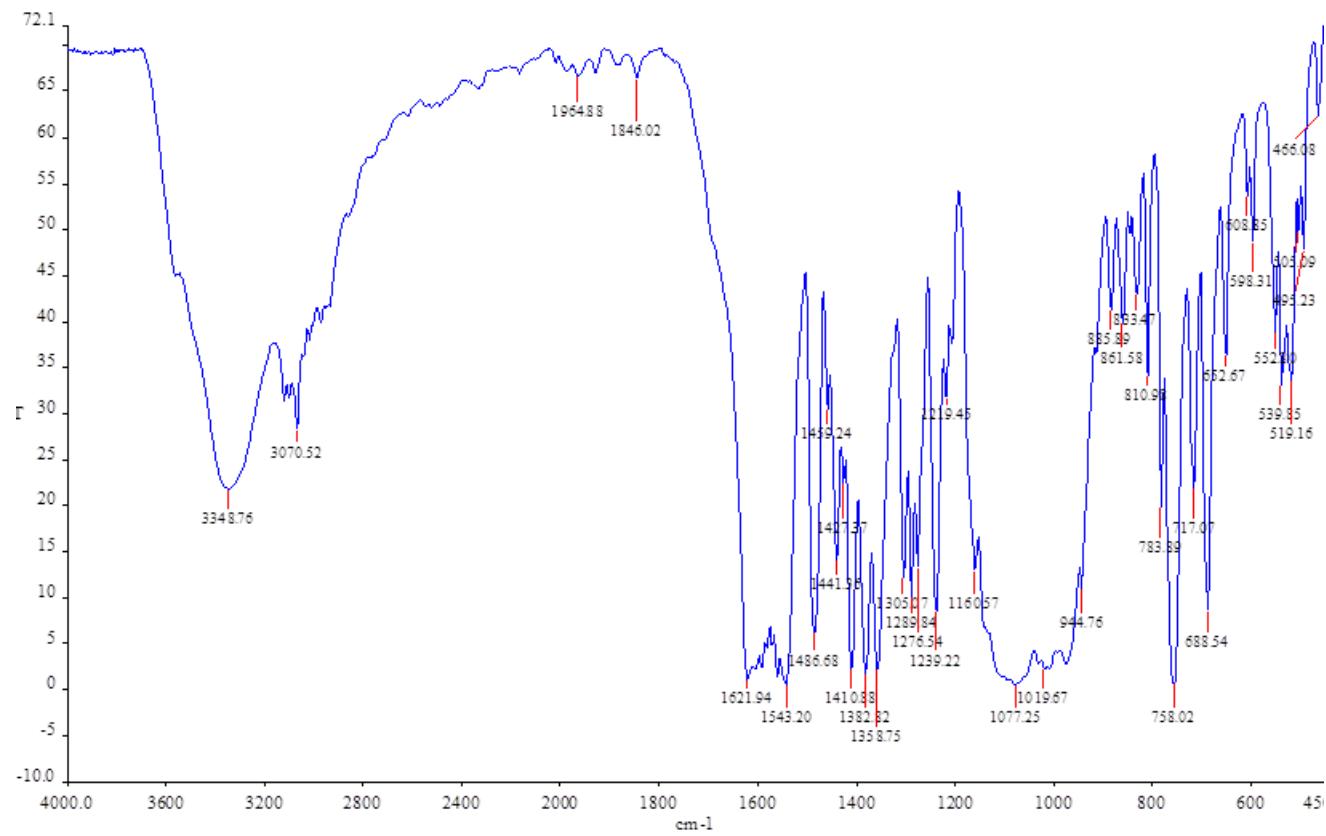
IR spectrum of Ligand **39** (KBr)



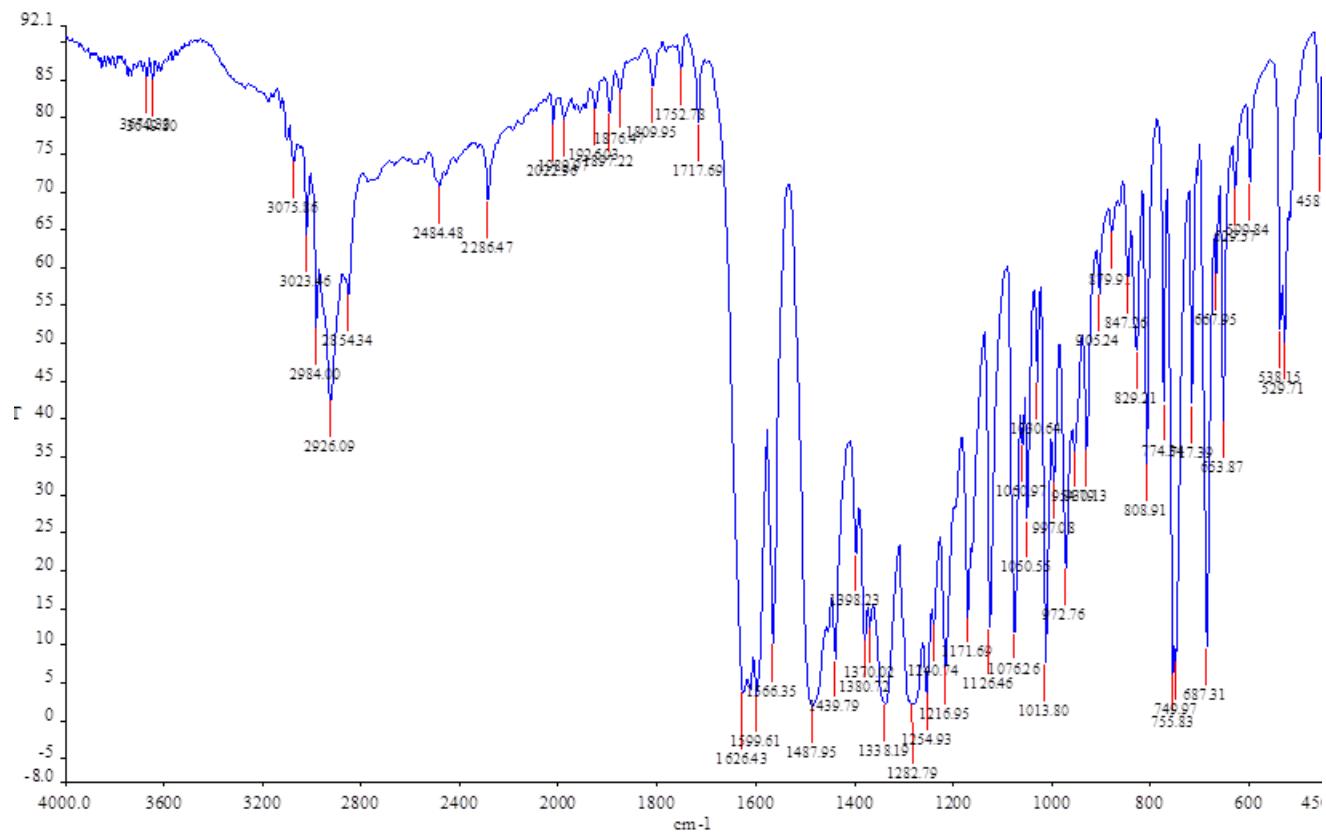
IR spectrum of compound **38a** (KBr)



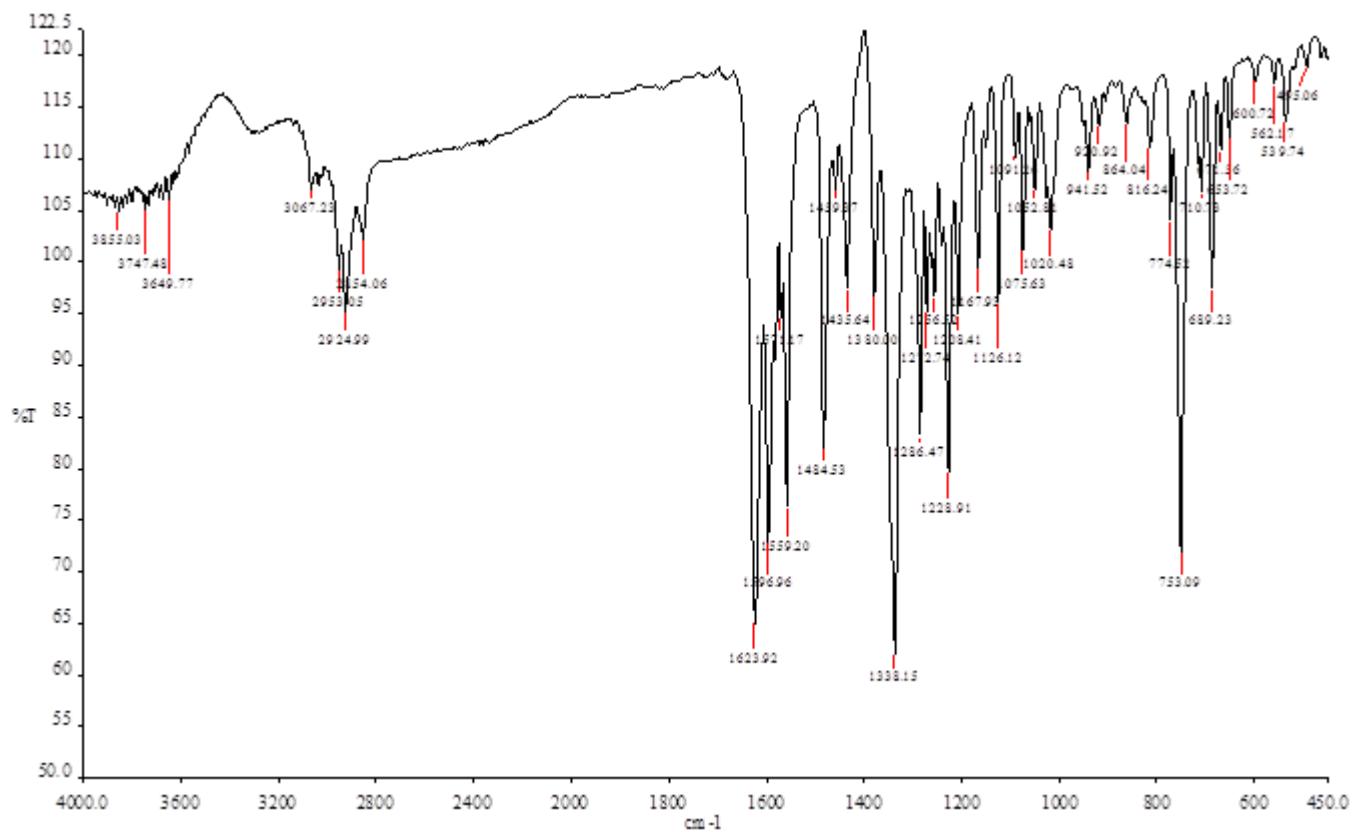
IR spectrum of compound **38b** (KBr)



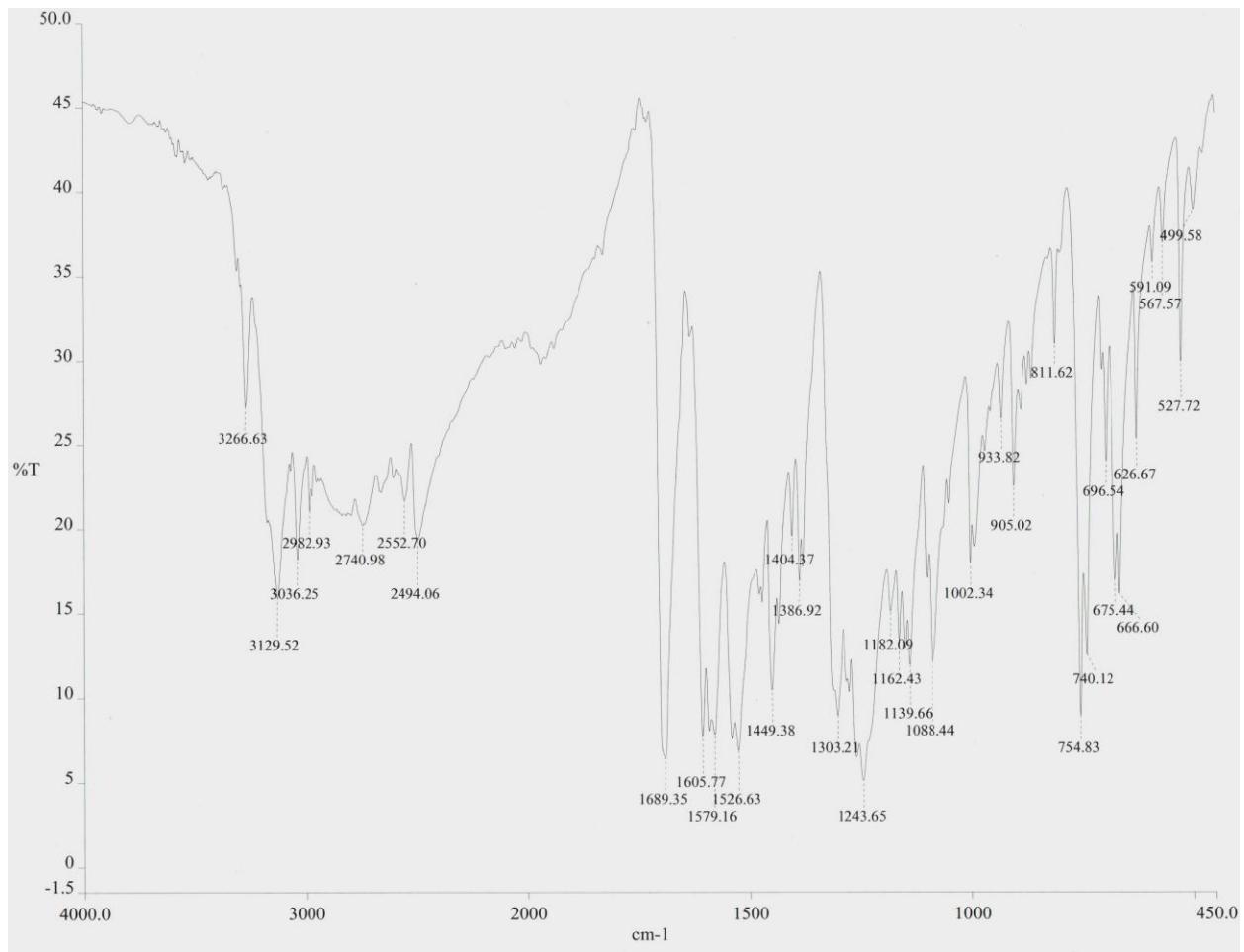
IR spectrum of compound **38c** (KBr)



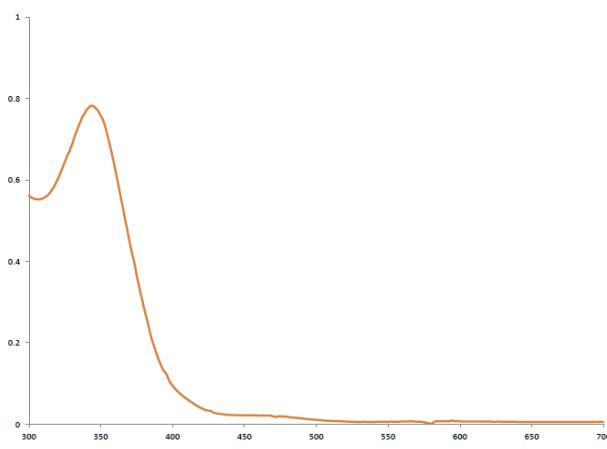
IR spectrum of compound **38d** (KBr)



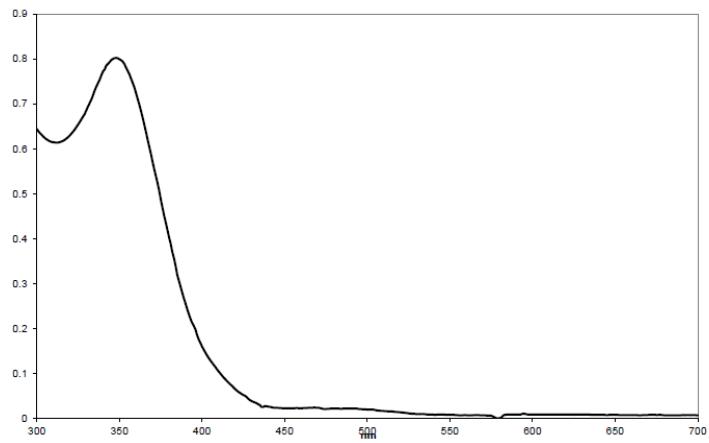
IR spectrum of compound **39a** (KBr)



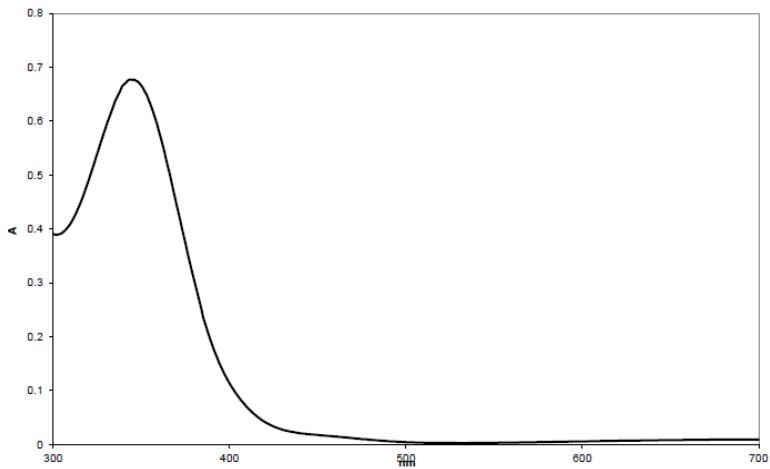
IR spectrum of compound **38f** (KBr)



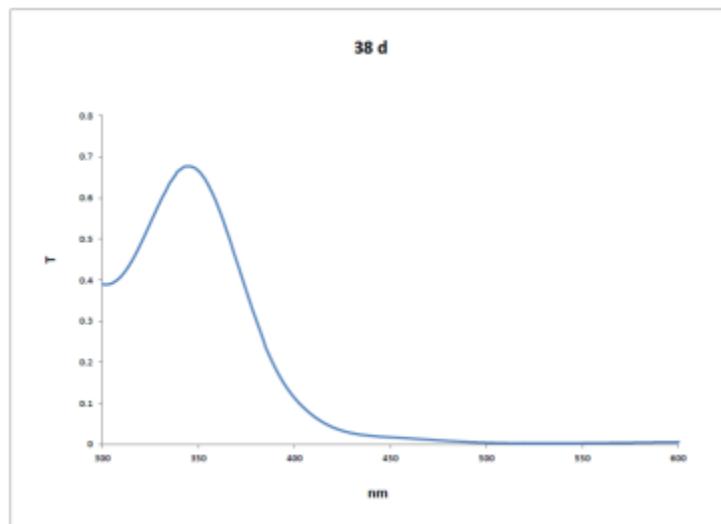
38a



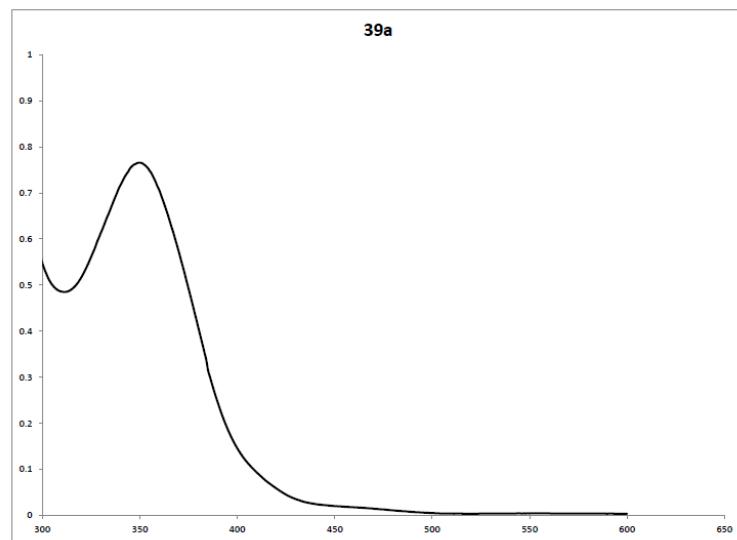
38b



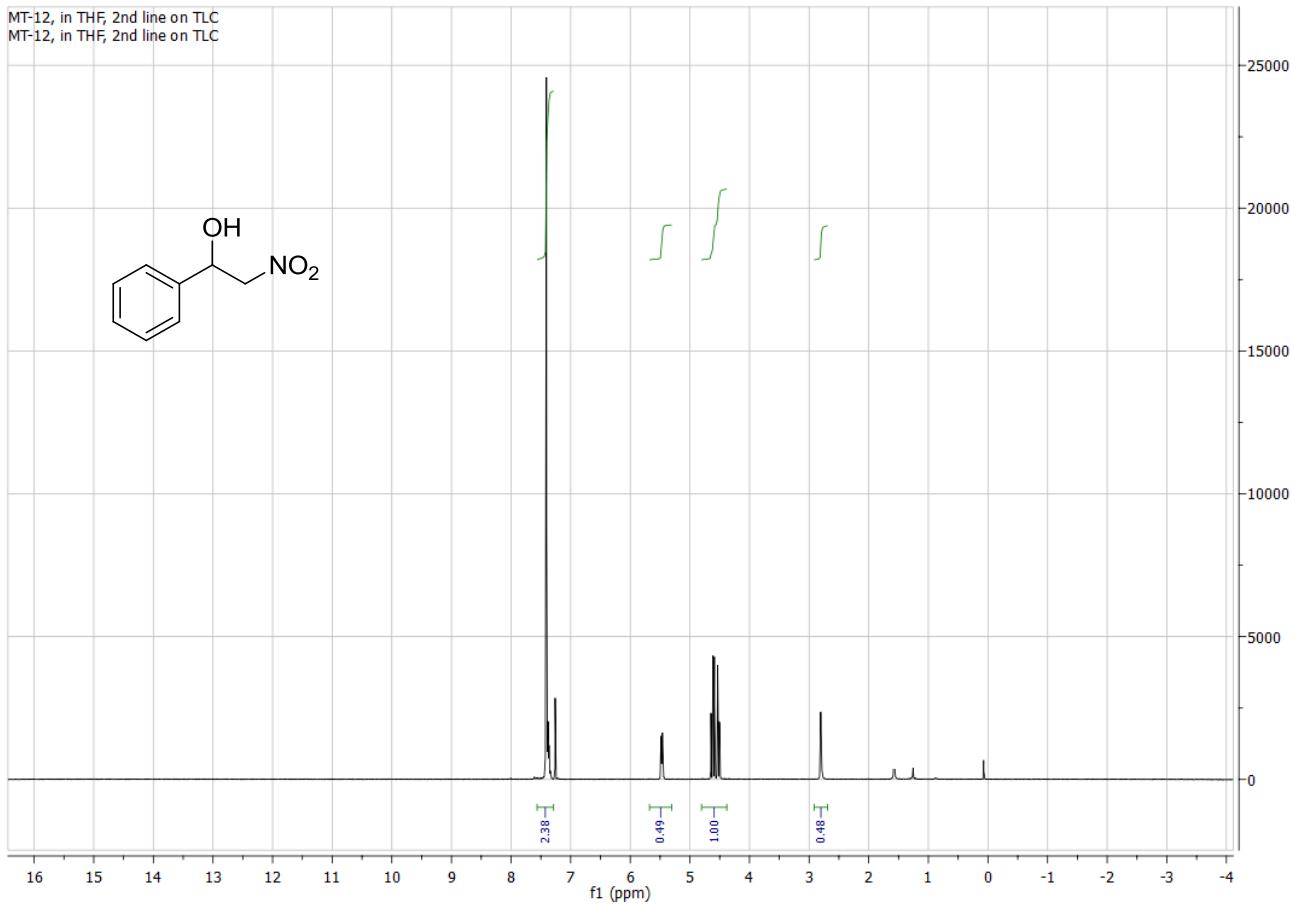
38c



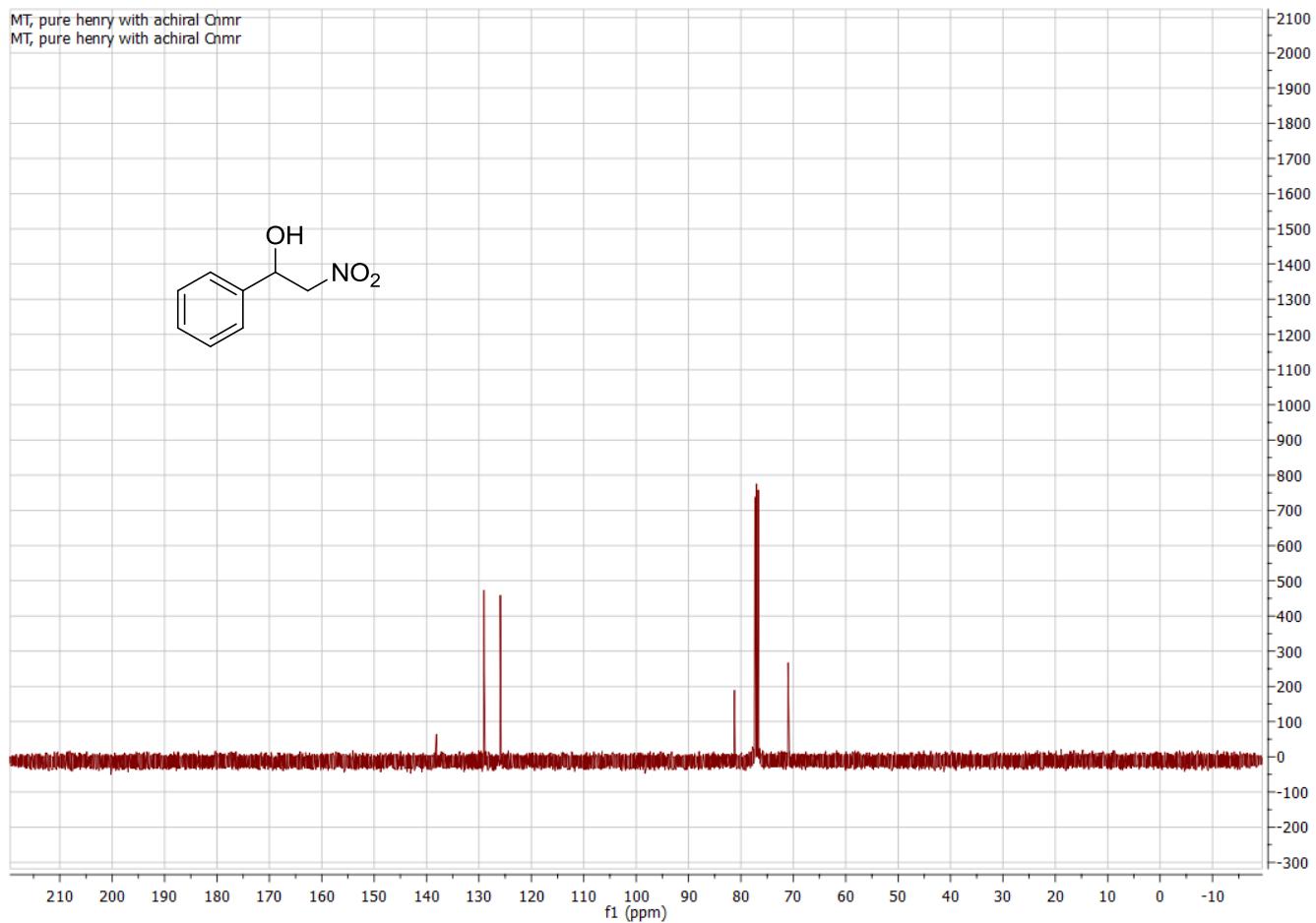
38d



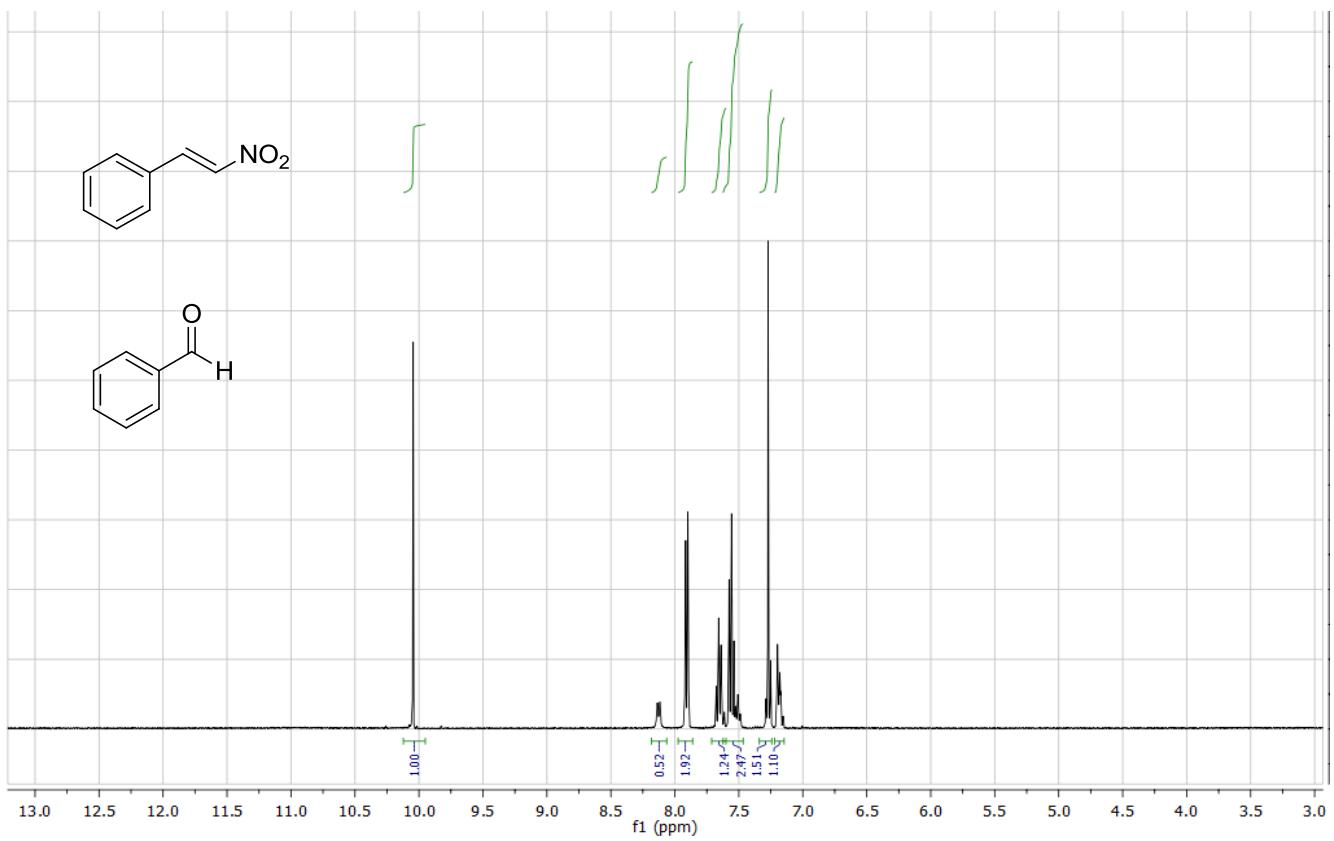
39a



^1H -NMR spectrum of compound **52** in CDCl_3



^{13}C -NMR spectrum of compound (CDCl_3)



¹H-NMR spectrum of compound **53** and unreacted benzaldehyde

APPENDIX B

Structure Determination Summary

Crystal data and structure refinement for **38a**

Empirical formula	<chem>C17H16ClCuN3O2</chem>	
Formula weight	393.32	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	$a = 12.5234(3)$ Å	$\alpha = 90^\circ$.
	$b = 14.3114(6)$ Å	$\beta = 90^\circ$.
	$c = 18.1160(8)$ Å	$\gamma = 90^\circ$.
Volume	3246.9(2) Å ³	
Z	8	
Density (calculated)	1.609 Mg/m ³	
Absorption coefficient	1.524 mm ⁻¹	
F(000)	1608	
Crystal size	0.20 x 0.12 x 0.10 mm ³	
Theta range for data collection	2.85 to 27.48°.	
Index ranges	-14<=h<=16, -17<=k<=18, -23<=l<=21	
Reflections collected	23332	
Independent reflections	7132 [R(int) = 0.0818]	
Completeness to theta = 27.48°	99.80%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.878 and 0.797	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7132 / 1 / 437	
Goodness-of-fit on F ²	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0548, wR2 = 0.1125	
R indices (all data)	R1 = 0.1325, wR2 = 0.1447	
Absolute structure parameter	-0.013(19)	
Largest diff. peak and hole	1.325 and -0.797 e.Å ⁻³	

Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³)

	x	y	z	U(eq)
Cu(1A)	5836(1)	4082(1)	7013(1)	26(1)
Cl(1A)	6490(1)	5050(1)	7866(1)	43(1)
O(1A)	5793(3)	3137(3)	4927(3)	35(1)
O(2A)	2927(3)	2957(3)	7531(2)	31(1)
N(1A)	7228(4)	3875(4)	6497(3)	28(1)
N(2A)	5246(4)	3783(3)	6032(3)	25(1)
N(3A)	4540(4)	3612(4)	7502(3)	28(1)
C(1A)	8200(5)	3993(4)	6776(4)	33(2)
C(2A)	9117(5)	3756(5)	6363(5)	38(2)
C(3A)	8990(6)	3404(5)	5650(5)	39(2)
C(4A)	7967(5)	3291(5)	5374(4)	34(2)
C(5A)	7110(5)	3545(4)	5812(4)	28(2)
C(6A)	5970(5)	3456(5)	5538(4)	27(2)
C(7A)	4183(5)	3866(4)	5862(4)	27(2)
C(8A)	3832(6)	4139(4)	5163(4)	30(2)
C(9A)	2771(6)	4247(5)	5003(4)	38(2)
C(10A)	1995(5)	4078(5)	5533(4)	31(2)
C(11A)	2308(5)	3791(4)	6234(4)	32(2)
C(12A)	3398(5)	3696(5)	6404(4)	28(2)
C(13A)	3676(5)	3423(4)	7154(4)	27(2)
C(14A)	3337(5)	2767(5)	8263(4)	42(2)
C(15A)	4453(5)	3243(5)	8274(4)	32(2)
C(16A)	5350(6)	2566(6)	8427(4)	48(2)
C(17A)	4454(6)	4046(5)	8829(4)	43(2)
Cu(1B)	1353(1)	5963(1)	7018(1)	25(1)
Cl(1B)	1996(1)	5090(1)	7926(1)	46(1)
O(1B)	1363(3)	6837(3)	4908(3)	34(1)
O(2B)	-1620(3)	7022(3)	7519(2)	31(1)
N(1B)	2755(4)	6123(3)	6511(3)	23(1)
N(2B)	785(4)	6242(3)	6045(3)	22(1)
N(3B)	33(4)	6431(3)	7493(3)	25(1)

C(1B)	3731(5)	6012(4)	6784(4)	32(2)
C(2B)	4641(5)	6256(4)	6382(4)	33(2)
C(3B)	4524(6)	6617(5)	5687(5)	38(2)
C(4B)	3513(5)	6707(5)	5391(4)	32(2)
C(5B)	2642(5)	6454(4)	5828(4)	25(2)
C(6B)	1516(5)	6526(4)	5535(4)	26(2)
C(7B)	-298(5)	6153(4)	5848(4)	24(2)
C(8B)	-617(6)	5887(4)	5146(4)	31(2)
C(9B)	-1681(5)	5754(4)	4984(4)	34(2)
C(10B)	-2474(5)	5905(5)	5501(4)	31(2)
C(11B)	-2167(5)	6189(5)	6205(4)	30(2)
C(12B)	-1087(5)	6302(4)	6387(4)	28(2)
C(13B)	-836(5)	6571(4)	7136(4)	25(2)
C(14B)	-1152(5)	7305(6)	8214(4)	38(2)
C(15B)	-108(5)	6747(5)	8274(4)	31(2)
C(16B)	820(5)	7331(5)	8512(4)	40(2)
C(17B)	-289(6)	5904(5)	8772(5)	42(2)

Bond lengths [Å] and angles [°] for **38a**

Cu(1A)-N(3A)	1.969(5)
Cu(1A)-N(2A)	1.970(5)
Cu(1A)-N(1A)	1.999(5)
Cu(1A)-Cl(1A)	2.2318(19)
O(1A)-C(6A)	1.218(8)
O(2A)-C(13A)	1.338(7)
O(2A)-C(14A)	1.449(8)
N(1A)-C(1A)	1.330(8)
N(1A)-C(5A)	1.336(9)
N(2A)-C(6A)	1.358(8)
N(2A)-C(7A)	1.372(8)
N(3A)-C(13A)	1.281(8)
N(3A)-C(15A)	1.498(8)
C(1A)-C(2A)	1.412(10)
C(1A)-H(1AA)	0.95
C(2A)-C(3A)	1.395(11)
C(2A)-H(2AA)	0.95
C(3A)-C(4A)	1.385(10)
C(3A)-H(3AA)	0.95
C(4A)-C(5A)	1.385(9)
C(4A)-H(4AA)	0.95
C(5A)-C(6A)	1.516(9)
C(7A)-C(8A)	1.396(10)
C(7A)-C(12A)	1.411(9)
C(8A)-C(9A)	1.370(9)
C(8A)-H(8AA)	0.95
C(9A)-C(10A)	1.387(10)
C(9A)-H(9AA)	0.95
C(10A)-C(11A)	1.390(10)
C(10A)-H(10A)	0.95
C(11A)-C(12A)	1.405(9)
C(11A)-H(11A)	0.95
C(12A)-C(13A)	1.456(10)
C(14A)-C(15A)	1.555(9)
C(14A)-H(14A)	0.99
C(14A)-H(14B)	0.99
C(15A)-C(16A)	1.509(9)
C(15A)-C(17A)	1.527(10)
C(16A)-H(16A)	0.98

C(16A)-H(16B)	0.98
C(16A)-H(16C)	0.98
C(17A)-H(17A)	0.98
C(17A)-H(17B)	0.98
C(17A)-H(17C)	0.98
Cu(1B)-N(2B)	1.941(5)
Cu(1B)-N(3B)	1.980(5)
Cu(1B)-N(1B)	1.994(5)
Cu(1B)-Cl(1B)	2.218(2)
O(1B)-C(6B)	1.235(8)
O(2B)-C(13B)	1.364(7)
O(2B)-C(14B)	1.448(8)
N(1B)-C(1B)	1.329(8)
N(1B)-C(5B)	1.332(9)
N(2B)-C(6B)	1.364(8)
N(2B)-C(7B)	1.408(8)
N(3B)-C(13B)	1.283(8)
N(3B)-C(15B)	1.494(8)
C(1B)-C(2B)	1.397(9)
C(1B)-H(1BA)	0.95
C(2B)-C(3B)	1.369(10)
C(2B)-H(2BA)	0.95
C(3B)-C(4B)	1.380(10)
C(3B)-H(3BA)	0.95
C(4B)-C(5B)	1.396(9)
C(4B)-H(4BA)	0.95
C(5B)-C(6B)	1.510(9)
C(7B)-C(8B)	1.386(10)
C(7B)-C(12B)	1.406(9)
C(8B)-C(9B)	1.378(10)
C(8B)-H(8BA)	0.95
C(9B)-C(10B)	1.382(10)
C(9B)-H(9BA)	0.95
C(10B)-C(11B)	1.393(10)
C(10B)-H(10B)	0.95
C(11B)-C(12B)	1.402(9)
C(11B)-H(11B)	0.95
C(12B)-C(13B)	1.444(10)
C(14B)-C(15B)	1.536(10)
C(14B)-H(14C)	0.99
C(14B)-H(14D)	0.99
C(15B)-C(16B)	1.495(9)
C(15B)-C(17B)	1.523(10)

C(16B)-H(16D)	0.98
C(16B)-H(16E)	0.98
C(16B)-H(16F)	0.98
C(17B)-H(17D)	0.98
C(17B)-H(17E)	0.98
C(17B)-H(17F)	0.98
N(3A)-Cu(1A)-N(2A)	91.3(2)
N(3A)-Cu(1A)-N(1A)	151.5(2)
N(2A)-Cu(1A)-N(1A)	82.7(2)
N(3A)-Cu(1A)-Cl(1A)	101.69(18)
N(2A)-Cu(1A)-Cl(1A)	153.73(16)
N(1A)-Cu(1A)-Cl(1A)	95.50(17)
C(13A)-O(2A)-C(14A)	108.2(5)
C(1A)-N(1A)-C(5A)	120.0(6)
C(1A)-N(1A)-Cu(1A)	127.0(5)
C(5A)-N(1A)-Cu(1A)	113.0(4)
C(6A)-N(2A)-C(7A)	122.0(6)
C(6A)-N(2A)-Cu(1A)	114.8(4)
C(7A)-N(2A)-Cu(1A)	123.2(4)
C(13A)-N(3A)-C(15A)	108.9(5)
C(13A)-N(3A)-Cu(1A)	123.1(5)
C(15A)-N(3A)-Cu(1A)	126.9(4)
N(1A)-C(1A)-C(2A)	120.8(7)
N(1A)-C(1A)-H(1AA)	119.6
C(2A)-C(1A)-H(1AA)	119.6
C(3A)-C(2A)-C(1A)	119.0(7)
C(3A)-C(2A)-H(2AA)	120.5
C(1A)-C(2A)-H(2AA)	120.5
C(4A)-C(3A)-C(2A)	118.9(7)
C(4A)-C(3A)-H(3AA)	120.6
C(2A)-C(3A)-H(3AA)	120.6
C(5A)-C(4A)-C(3A)	118.6(7)
C(5A)-C(4A)-H(4AA)	120.7
C(3A)-C(4A)-H(4AA)	120.7
N(1A)-C(5A)-C(4A)	122.7(7)
N(1A)-C(5A)-C(6A)	116.0(6)
C(4A)-C(5A)-C(6A)	121.4(7)
O(1A)-C(6A)-N(2A)	127.4(6)
O(1A)-C(6A)-C(5A)	120.0(6)
N(2A)-C(6A)-C(5A)	112.6(6)
N(2A)-C(7A)-C(8A)	122.2(6)
N(2A)-C(7A)-C(12A)	120.3(6)

C(8A)-C(7A)-C(12A)	117.4(6)
C(9A)-C(8A)-C(7A)	121.9(7)
C(9A)-C(8A)-H(8AA)	119
C(7A)-C(8A)-H(8AA)	119
C(8A)-C(9A)-C(10A)	120.9(7)
C(8A)-C(9A)-H(9AA)	119.6
C(10A)-C(9A)-H(9AA)	119.6
C(9A)-C(10A)-C(11A)	119.1(6)
C(9A)-C(10A)-H(10A)	120.4
C(11A)-C(10A)-H(10A)	120.4
C(10A)-C(11A)-C(12A)	120.1(7)
C(10A)-C(11A)-H(11A)	119.9
C(12A)-C(11A)-H(11A)	119.9
C(11A)-C(12A)-C(7A)	120.5(7)
C(11A)-C(12A)-C(13A)	117.6(6)
C(7A)-C(12A)-C(13A)	121.9(6)
N(3A)-C(13A)-O(2A)	116.5(6)
N(3A)-C(13A)-C(12A)	127.3(6)
O(2A)-C(13A)-C(12A)	116.2(6)
O(2A)-C(14A)-C(15A)	104.4(5)
O(2A)-C(14A)-H(14A)	110.9
C(15A)-C(14A)-H(14A)	110.9
O(2A)-C(14A)-H(14B)	110.9
C(15A)-C(14A)-H(14B)	110.9
H(14A)-C(14A)-H(14B)	108.9
N(3A)-C(15A)-C(16A)	110.1(6)
N(3A)-C(15A)-C(17A)	110.5(6)
C(16A)-C(15A)-C(17A)	111.2(6)
N(3A)-C(15A)-C(14A)	102.0(5)
C(16A)-C(15A)-C(14A)	112.9(7)
C(17A)-C(15A)-C(14A)	109.8(6)
C(15A)-C(16A)-H(16A)	109.5
C(15A)-C(16A)-H(16B)	109.5
H(16A)-C(16A)-H(16B)	109.5
C(15A)-C(16A)-H(16C)	109.5
H(16A)-C(16A)-H(16C)	109.5
H(16B)-C(16A)-H(16C)	109.5
C(15A)-C(17A)-H(17A)	109.5
C(15A)-C(17A)-H(17B)	109.5
H(17A)-C(17A)-H(17B)	109.5
C(15A)-C(17A)-H(17C)	109.5
H(17A)-C(17A)-H(17C)	109.5
H(17B)-C(17A)-H(17C)	109.5

N(2B)-Cu(1B)-N(3B)	91.2(2)
N(2B)-Cu(1B)-N(1B)	83.2(2)
N(3B)-Cu(1B)-N(1B)	153.7(2)
N(2B)-Cu(1B)-Cl(1B)	157.22(16)
N(3B)-Cu(1B)-Cl(1B)	99.83(17)
N(1B)-Cu(1B)-Cl(1B)	94.95(16)
C(13B)-O(2B)-C(14B)	106.5(5)
C(1B)-N(1B)-C(5B)	119.1(6)
C(1B)-N(1B)-Cu(1B)	128.7(5)
C(5B)-N(1B)-Cu(1B)	112.0(4)
C(6B)-N(2B)-C(7B)	120.1(6)
C(6B)-N(2B)-Cu(1B)	115.5(4)
C(7B)-N(2B)-Cu(1B)	124.4(4)
C(13B)-N(3B)-C(15B)	109.3(5)
C(13B)-N(3B)-Cu(1B)	122.7(5)
C(15B)-N(3B)-Cu(1B)	127.8(4)
N(1B)-C(1B)-C(2B)	121.8(7)
N(1B)-C(1B)-H(1BA)	119.1
C(2B)-C(1B)-H(1BA)	119.1
C(3B)-C(2B)-C(1B)	119.0(7)
C(3B)-C(2B)-H(2BA)	120.5
C(1B)-C(2B)-H(2BA)	120.5
C(2B)-C(3B)-C(4B)	119.4(7)
C(2B)-C(3B)-H(3BA)	120.3
C(4B)-C(3B)-H(3BA)	120.3
C(3B)-C(4B)-C(5B)	118.1(7)
C(3B)-C(4B)-H(4BA)	120.9
C(5B)-C(4B)-H(4BA)	120.9
N(1B)-C(5B)-C(4B)	122.4(6)
N(1B)-C(5B)-C(6B)	116.8(6)
C(4B)-C(5B)-C(6B)	120.8(6)
O(1B)-C(6B)-N(2B)	128.8(6)
O(1B)-C(6B)-C(5B)	119.6(6)
N(2B)-C(6B)-C(5B)	111.6(6)
C(8B)-C(7B)-C(12B)	118.4(6)
C(8B)-C(7B)-N(2B)	122.4(6)
C(12B)-C(7B)-N(2B)	119.1(6)
C(9B)-C(8B)-C(7B)	120.9(7)
C(9B)-C(8B)-H(8BA)	119.6
C(7B)-C(8B)-H(8BA)	119.6
C(8B)-C(9B)-C(10B)	121.9(7)
C(8B)-C(9B)-H(9BA)	119.1
C(10B)-C(9B)-H(9BA)	119.1

C(9B)-C(10B)-C(11B)	118.0(6)
C(9B)-C(10B)-H(10B)	121
C(11B)-C(10B)-H(10B)	121
C(10B)-C(11B)-C(12B)	121.0(7)
C(10B)-C(11B)-H(11B)	119.5
C(12B)-C(11B)-H(11B)	119.5
C(11B)-C(12B)-C(7B)	119.9(7)
C(11B)-C(12B)-C(13B)	117.5(6)
C(7B)-C(12B)-C(13B)	122.7(6)
N(3B)-C(13B)-O(2B)	115.3(6)
N(3B)-C(13B)-C(12B)	128.1(6)
O(2B)-C(13B)-C(12B)	116.6(5)
O(2B)-C(14B)-C(15B)	105.1(6)
O(2B)-C(14B)-H(14C)	110.7
C(15B)-C(14B)-H(14C)	110.7
O(2B)-C(14B)-H(14D)	110.7
C(15B)-C(14B)-H(14D)	110.7
H(14C)-C(14B)-H(14D)	108.8
N(3B)-C(15B)-C(16B)	110.5(6)
N(3B)-C(15B)-C(17B)	109.8(6)
C(16B)-C(15B)-C(17B)	112.8(6)
N(3B)-C(15B)-C(14B)	101.1(5)
C(16B)-C(15B)-C(14B)	113.0(6)
C(17B)-C(15B)-C(14B)	109.0(6)
C(15B)-C(16B)-H(16D)	109.5
C(15B)-C(16B)-H(16E)	109.5
H(16D)-C(16B)-H(16E)	109.5
C(15B)-C(16B)-H(16F)	109.5
H(16D)-C(16B)-H(16F)	109.5
H(16E)-C(16B)-H(16F)	109.5
C(15B)-C(17B)-H(17D)	109.5
C(15B)-C(17B)-H(17E)	109.5
H(17D)-C(17B)-H(17E)	109.5
C(15B)-C(17B)-H(17F)	109.5
H(17D)-C(17B)-H(17F)	109.5
H(17E)-C(17B)-H(17F)	109.5

Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **38a**

	U11	U22	U33	U23	U13	U12
Cu(1A)	22(1)	34(1)	21(1)	-1(1)	0(1)	-2(1)
Cl(1A)	43(1)	54(1)	31(1)	-12(1)	1(1)	-16(1)
O(1A)	39(3)	45(3)	22(3)	-7(2)	3(2)	-4(2)
O(2A)	23(2)	38(3)	32(3)	4(2)	2(2)	-4(2)
N(1A)	18(3)	34(3)	30(3)	0(3)	1(2)	-1(2)
N(2A)	25(3)	29(3)	20(3)	1(2)	2(3)	-2(2)
N(3A)	24(3)	36(3)	24(3)	1(3)	1(3)	-4(2)
C(1A)	32(4)	23(3)	44(5)	7(3)	-4(3)	-1(3)
C(2A)	21(4)	33(4)	61(6)	8(4)	0(4)	0(3)
C(3A)	37(4)	29(4)	49(6)	4(4)	13(4)	-1(3)
C(4A)	29(4)	31(4)	42(5)	9(3)	10(4)	2(3)
C(5A)	32(4)	23(3)	30(4)	4(3)	6(3)	-4(3)
C(6A)	25(4)	24(4)	33(5)	9(3)	2(3)	-4(3)
C(7A)	35(4)	24(4)	23(4)	-4(3)	-2(3)	-8(3)
C(8A)	36(4)	27(4)	26(4)	2(3)	0(3)	-2(3)
C(9A)	43(4)	39(4)	32(4)	3(4)	-15(4)	0(3)
C(10A)	24(4)	31(4)	39(5)	3(3)	-5(3)	1(3)
C(11A)	24(3)	24(4)	47(5)	-9(3)	6(4)	-2(3)
C(12A)	25(4)	28(4)	30(5)	-8(3)	-2(3)	-2(3)
C(13A)	26(3)	24(3)	30(5)	-4(3)	6(3)	1(3)
C(14A)	42(5)	53(5)	30(5)	13(4)	-4(3)	-16(4)
C(15A)	31(4)	48(5)	16(4)	4(3)	6(3)	0(3)
C(16A)	45(5)	60(5)	39(5)	16(4)	2(4)	9(4)
C(17A)	46(5)	59(5)	24(4)	-1(4)	5(4)	4(4)
Cu(1B)	23(1)	33(1)	20(1)	2(1)	0(1)	5(1)
Cl(1B)	47(1)	61(1)	29(1)	13(1)	5(1)	25(1)
O(1B)	36(3)	43(3)	23(3)	11(2)	4(2)	0(2)
O(2B)	26(2)	39(3)	28(3)	-2(2)	6(2)	8(2)
N(1B)	16(3)	27(3)	27(3)	-4(2)	3(2)	5(2)
N(2B)	24(3)	23(3)	18(3)	-2(2)	5(2)	1(2)
N(3B)	31(3)	29(3)	15(3)	1(2)	2(3)	5(3)
C(1B)	24(3)	34(4)	38(5)	0(3)	-1(3)	8(3)
C(2B)	19(3)	30(4)	49(5)	-5(4)	-5(3)	4(3)
C(3B)	38(4)	26(4)	50(6)	-9(4)	10(4)	-2(3)
C(4B)	34(4)	31(4)	30(4)	-4(3)	11(3)	-1(3)
C(5B)	25(3)	21(3)	30(4)	-5(3)	-2(3)	-3(3)
C(6B)	34(4)	22(3)	21(4)	-7(3)	1(3)	-1(3)
C(7B)	24(3)	21(4)	26(4)	3(3)	-3(3)	-1(3)

C(8B)	40(4)	27(4)	25(4)	-2(3)	11(4)	6(3)
C(9B)	35(4)	29(4)	39(5)	4(3)	-15(4)	2(3)
C(10B)	30(4)	32(4)	31(4)	3(3)	-4(3)	0(3)
C(11B)	20(3)	36(4)	33(4)	11(3)	1(3)	0(3)
C(12B)	33(4)	19(3)	33(5)	6(3)	-2(3)	-3(3)
C(13B)	24(3)	27(3)	23(5)	-2(3)	-1(3)	-1(3)
C(14B)	33(4)	60(5)	22(4)	2(4)	-2(3)	8(4)
C(15B)	32(4)	42(4)	20(4)	-2(3)	1(3)	3(3)
C(16B)	37(4)	51(5)	33(5)	-4(4)	9(3)	-1(4)
C(17B)	50(5)	45(5)	32(5)	7(4)	14(4)	13(4)

Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for
38a

	x	y	z	U(eq)
H(1AA)	8280	4239	7260	39
H(2AA)	9810	3836	6567	46
H(3AA)	9595	3244	5360	46
H(4AA)	7857	3043	4893	41
H(8AA)	4345	4253	4787	35
H(9AA)	2563	4441	4522	45
H(10A)	1261	4157	5419	38
H(11A)	1784	3660	6599	38
H(14A)	3401	2086	8349	50
H(14B)	2865	3038	8646	50
H(16A)	6032	2901	8427	72
H(16B)	5360	2082	8044	72
H(16C)	5239	2274	8910	72
H(17A)	5145	4367	8812	64
H(17B)	4335	3798	9327	64
H(17C)	3884	4487	8705	64
H(1BA)	3812	5759	7265	39
H(2BA)	5332	6173	6588	39
H(3BA)	5132	6803	5411	46
H(4BA)	3414	6935	4903	38
H(8BA)	-96	5794	4773	37
H(9BA)	-1876	5552	4503	41
H(10B)	-3205	5818	5380	37
H(11B)	-2698	6307	6568	35
H(14C)	-1635	7155	8630	46
H(14D)	-1006	7985	8217	46
H(16D)	1468	6948	8517	60
H(16E)	687	7576	9009	60
H(16F)	913	7853	8167	60
H(17D)	294	5456	8704	63
H(17E)	-969	5607	8643	63
H(17F)	-309	6108	9288	63

Crystal data and structure refinement for **38b**

Empirical formula	<chem>C17H16BrCuN3O2</chem>		
Formula weight	437.78		
Temperature	150(1) K		
Wavelength	0.71073 Å		
Crystal system	Orthorhombic		
Space group	P n a 21		
Unit cell dimensions	$a = 12.5856(6)$ Å	$\alpha = 90^\circ$.	
	$b = 14.4922(7)$ Å	$\beta = 90^\circ$.	
	$c = 18.1596(6)$ Å	$\gamma = 90^\circ$.	
Volume	3312.2(3) Å ³		
Z	8		
Density (calculated)	1.756 Mg/m ³		
Absorption coefficient	3.746 mm ⁻¹		
F(000)	1752		
Crystal size	0.22 x 0.14 x 0.14 mm ³		
Theta range for data collection	2.81 to 27.49°.		
Index ranges	-12<=h<=16, -18<=k<=18, -23<=l<=23		
Reflections collected	19220		
Independent reflections	7346 [R(int) = 0.0791]		
Completeness to theta = 27.49°	99.50%		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.601 and 0.516		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	7346 / 1 / 437		
Goodness-of-fit on F ²	0.983		
Final R indices [I>2sigma(I)]	R1 = 0.0507, wR2 = 0.0956		
R indices (all data)	R1 = 0.1410, wR2 = 0.1276		
Absolute structure parameter	-0.024(13)		
Largest diff. peak and hole	0.845 and -0.909 e.Å ⁻³		

Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³)

	x	y	z	U(eq)
Br(1A)	1566(1)	4902(1)	7297(1)	38(1)
Cu(1A)	934(1)	5946(1)	8199(1)	24(1)
O(1A)	887(4)	6866(4)	10283(3)	36(2)
O(2A)	-1926(4)	7128(4)	7680(3)	27(1)
N(1A)	2312(5)	6111(4)	8728(3)	23(2)
N(2A)	351(5)	6236(4)	9163(3)	22(2)
N(3A)	-330(5)	6452(4)	7702(3)	23(2)
C(1A)	3287(6)	5974(6)	8465(4)	28(2)
C(2A)	4193(6)	6210(6)	8872(5)	30(2)
C(3A)	4069(7)	6575(6)	9555(5)	38(3)
C(4A)	3054(7)	6689(6)	9840(5)	32(2)
C(5A)	2197(6)	6453(5)	9418(4)	20(2)
C(6A)	1069(7)	6545(6)	9672(4)	24(2)
C(7A)	-726(6)	6171(5)	9349(4)	22(2)
C(8A)	-1090(6)	5893(6)	10042(4)	26(2)
C(9A)	-2147(6)	5788(6)	10187(4)	32(2)
C(10A)	-2902(6)	5981(6)	9657(4)	30(2)
C(11A)	-2589(6)	6280(5)	8951(4)	25(2)
C(12A)	-1486(6)	6358(5)	8801(4)	24(2)
C(13A)	-1193(6)	6639(5)	8053(4)	23(2)
C(14A)	-1468(7)	7376(6)	6973(5)	32(2)
C(15A)	-424(6)	6825(6)	6940(4)	26(2)
C(16A)	542(7)	7415(7)	6752(5)	48(3)
C(17A)	-542(6)	6032(6)	6393(4)	38(2)
Br(1B)	6804(1)	5048(1)	7276(1)	39(1)
Cu(1B)	6176(1)	4041(1)	8201(1)	23(1)
O(1B)	6153(4)	3157(4)	10301(3)	30(1)
O(2B)	3298(4)	2874(4)	7683(3)	27(1)
N(1B)	7570(5)	3895(4)	8719(3)	24(2)
N(2B)	5592(5)	3747(4)	9169(3)	23(2)
N(3B)	4913(5)	3538(4)	7708(3)	20(2)
C(1B)	8545(6)	4023(6)	8459(4)	30(2)
C(2B)	9449(7)	3778(6)	8864(5)	37(2)
C(3B)	9296(7)	3403(7)	9550(5)	38(3)
C(4B)	8297(6)	3299(6)	9844(5)	32(2)
C(5B)	7434(6)	3557(6)	9410(5)	25(2)
C(6B)	6307(6)	3464(6)	9680(5)	26(2)

C(7B)	4509(6)	3813(5)	9341(4)	23(2)
C(8B)	4161(6)	4102(6)	10041(4)	28(2)
C(9B)	3103(7)	4200(6)	10184(4)	31(2)
C(10B)	2336(6)	4017(7)	9662(4)	30(2)
C(11B)	2662(6)	3726(5)	8961(4)	29(2)
C(12B)	3737(6)	3635(5)	8808(4)	24(2)
C(13B)	4039(6)	3354(5)	8052(4)	24(2)
C(14B)	3808(7)	2587(7)	7002(5)	39(3)
C(15B)	4797(6)	3202(6)	6923(4)	23(2)
C(16B)	5766(6)	2677(6)	6687(5)	36(2)
C(17B)	4546(6)	4013(6)	6438(4)	30(2)

Bond lengths [\AA] and angles [$^\circ$] for **38b**

Br(1A)-Cu(1A)	2.3669(12)
Cu(1A)-N(2A)	1.945(6)
Cu(1A)-N(3A)	1.970(6)
Cu(1A)-N(1A)	1.998(6)
O(1A)-C(6A)	1.225(9)
O(2A)-C(13A)	1.346(8)
O(2A)-C(14A)	1.453(9)
N(1A)-C(1A)	1.332(9)
N(1A)-C(5A)	1.355(9)
N(2A)-C(6A)	1.367(10)
N(2A)-C(7A)	1.399(9)
N(3A)-C(13A)	1.289(9)
N(3A)-C(15A)	1.490(9)
C(1A)-C(2A)	1.402(10)
C(2A)-C(3A)	1.357(12)
C(3A)-C(4A)	1.388(12)
C(4A)-C(5A)	1.367(11)
C(5A)-C(6A)	1.498(11)
C(7A)-C(8A)	1.398(10)
C(7A)-C(12A)	1.408(10)
C(8A)-C(9A)	1.364(10)
C(9A)-C(10A)	1.380(10)
C(10A)-C(11A)	1.410(10)
C(11A)-C(12A)	1.419(10)
C(12A)-C(13A)	1.464(11)
C(14A)-C(15A)	1.539(11)
C(15A)-C(16A)	1.524(12)
C(15A)-C(17A)	1.527(11)
Br(1B)-Cu(1B)	2.3611(13)
Cu(1B)-N(2B)	1.952(6)
Cu(1B)-N(3B)	1.964(6)
Cu(1B)-N(1B)	2.002(6)
O(1B)-C(6B)	1.228(9)
O(2B)-C(13B)	1.343(9)
O(2B)-C(14B)	1.455(9)
N(1B)-C(1B)	1.327(9)
N(1B)-C(5B)	1.359(10)
N(2B)-C(6B)	1.356(10)
N(2B)-C(7B)	1.402(9)
N(3B)-C(13B)	1.293(9)

N(3B)-C(15B)	1.512(8)
C(1B)-C(2B)	1.400(11)
C(2B)-C(3B)	1.374(12)
C(3B)-C(4B)	1.374(12)
C(4B)-C(5B)	1.394(11)
C(5B)-C(6B)	1.507(11)
C(7B)-C(12B)	1.396(10)
C(7B)-C(8B)	1.408(11)
C(8B)-C(9B)	1.365(11)
C(9B)-C(10B)	1.379(10)
C(10B)-C(11B)	1.402(10)
C(11B)-C(12B)	1.387(10)
C(12B)-C(13B)	1.482(10)
C(14B)-C(15B)	1.537(11)
C(15B)-C(16B)	1.501(11)
C(15B)-C(17B)	1.502(11)
N(2A)-Cu(1A)-N(3A)	91.6(3)
N(2A)-Cu(1A)-N(1A)	82.4(2)
N(3A)-Cu(1A)-N(1A)	151.2(3)
N(2A)-Cu(1A)-Br(1A)	152.6(2)
N(3A)-Cu(1A)-Br(1A)	101.11(19)
N(1A)-Cu(1A)-Br(1A)	96.75(18)
C(13A)-O(2A)-C(14A)	107.7(6)
C(1A)-N(1A)-C(5A)	119.0(6)
C(1A)-N(1A)-Cu(1A)	127.6(5)
C(5A)-N(1A)-Cu(1A)	113.3(5)
C(6A)-N(2A)-C(7A)	119.9(6)
C(6A)-N(2A)-Cu(1A)	115.4(5)
C(7A)-N(2A)-Cu(1A)	124.6(5)
C(13A)-N(3A)-C(15A)	108.5(6)
C(13A)-N(3A)-Cu(1A)	122.1(5)
C(15A)-N(3A)-Cu(1A)	128.6(5)
N(1A)-C(1A)-C(2A)	121.6(7)
C(3A)-C(2A)-C(1A)	118.9(8)
C(2A)-C(3A)-C(4A)	119.6(8)
C(5A)-C(4A)-C(3A)	119.1(8)
N(1A)-C(5A)-C(4A)	121.7(7)
N(1A)-C(5A)-C(6A)	114.7(6)
C(4A)-C(5A)-C(6A)	123.5(7)
O(1A)-C(6A)-N(2A)	127.8(8)
O(1A)-C(6A)-C(5A)	119.3(7)
N(2A)-C(6A)-C(5A)	112.9(7)

C(8A)-C(7A)-N(2A)	123.6(7)
C(8A)-C(7A)-C(12A)	118.0(7)
N(2A)-C(7A)-C(12A)	118.3(7)
C(9A)-C(8A)-C(7A)	121.7(7)
C(8A)-C(9A)-C(10A)	121.0(8)
C(9A)-C(10A)-C(11A)	120.2(7)
C(10A)-C(11A)-C(12A)	118.2(7)
C(7A)-C(12A)-C(11A)	120.9(7)
C(7A)-C(12A)-C(13A)	122.6(7)
C(11A)-C(12A)-C(13A)	116.5(7)
N(3A)-C(13A)-O(2A)	116.0(7)
N(3A)-C(13A)-C(12A)	127.8(7)
O(2A)-C(13A)-C(12A)	116.1(7)
O(2A)-C(14A)-C(15A)	104.1(6)
N(3A)-C(15A)-C(16A)	110.4(7)
N(3A)-C(15A)-C(17A)	109.8(7)
C(16A)-C(15A)-C(17A)	110.7(7)
N(3A)-C(15A)-C(14A)	102.7(6)
C(16A)-C(15A)-C(14A)	113.5(8)
C(17A)-C(15A)-C(14A)	109.4(7)
N(2B)-Cu(1B)-N(3B)	91.5(3)
N(2B)-Cu(1B)-N(1B)	83.3(2)
N(3B)-Cu(1B)-N(1B)	152.1(3)
N(2B)-Cu(1B)-Br(1B)	154.3(2)
N(3B)-Cu(1B)-Br(1B)	100.14(18)
N(1B)-Cu(1B)-Br(1B)	96.04(19)
C(13B)-O(2B)-C(14B)	105.4(6)
C(1B)-N(1B)-C(5B)	119.6(7)
C(1B)-N(1B)-Cu(1B)	129.0(5)
C(5B)-N(1B)-Cu(1B)	111.2(5)
C(6B)-N(2B)-C(7B)	120.9(6)
C(6B)-N(2B)-Cu(1B)	115.6(5)
C(7B)-N(2B)-Cu(1B)	123.5(5)
C(13B)-N(3B)-C(15B)	107.9(6)
C(13B)-N(3B)-Cu(1B)	123.0(5)
C(15B)-N(3B)-Cu(1B)	128.8(5)
N(1B)-C(1B)-C(2B)	122.0(8)
C(3B)-C(2B)-C(1B)	117.6(9)
C(4B)-C(3B)-C(2B)	121.6(9)
C(3B)-C(4B)-C(5B)	117.6(8)
N(1B)-C(5B)-C(4B)	121.4(7)
N(1B)-C(5B)-C(6B)	116.8(7)
C(4B)-C(5B)-C(6B)	121.7(8)

O(1B)-C(6B)-N(2B)	129.3(8)
O(1B)-C(6B)-C(5B)	118.7(7)
N(2B)-C(6B)-C(5B)	112.0(7)
C(12B)-C(7B)-N(2B)	120.7(7)
C(12B)-C(7B)-C(8B)	117.7(7)
N(2B)-C(7B)-C(8B)	121.6(7)
C(9B)-C(8B)-C(7B)	120.4(8)
C(8B)-C(9B)-C(10B)	122.2(7)
C(9B)-C(10B)-C(11B)	118.5(8)
C(12B)-C(11B)-C(10B)	119.7(7)
C(11B)-C(12B)-C(7B)	121.5(7)
C(11B)-C(12B)-C(13B)	117.5(7)
C(7B)-C(12B)-C(13B)	120.9(7)
N(3B)-C(13B)-O(2B)	117.2(7)
N(3B)-C(13B)-C(12B)	127.6(7)
O(2B)-C(13B)-C(12B)	115.2(7)
O(2B)-C(14B)-C(15B)	105.7(7)
C(16B)-C(15B)-C(17B)	113.6(7)
C(16B)-C(15B)-N(3B)	110.7(7)
C(17B)-C(15B)-N(3B)	108.7(7)
C(16B)-C(15B)-C(14B)	113.0(8)
C(17B)-C(15B)-C(14B)	109.7(7)
N(3B)-C(15B)-C(14B)	100.2(6)

Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **38b**

	U11	U22	U33	U23	U13	U12
Br(1A)	45(1)	44(1)	26(1)	-10(1)	-4(1)	17(1)
Cu(1A)	26(1)	27(1)	17(1)	-1(1)	-1(1)	3(1)
O(1A)	37(4)	48(5)	24(4)	-11(3)	-2(3)	2(3)
O(2A)	30(3)	29(4)	21(3)	3(3)	-2(3)	-1(3)
N(1A)	23(4)	20(4)	24(3)	-1(3)	-3(3)	4(3)
N(2A)	23(4)	27(4)	17(3)	-2(3)	-2(3)	-3(3)
N(3A)	22(4)	29(5)	17(4)	2(3)	7(3)	4(3)
C(1A)	30(5)	27(5)	28(5)	-2(4)	-1(3)	0(4)
C(2A)	22(4)	30(6)	39(6)	-2(4)	-3(4)	5(4)
C(3A)	31(5)	28(6)	54(7)	8(5)	-15(4)	5(4)
C(4A)	30(5)	36(6)	31(5)	1(4)	-14(4)	-3(4)
C(5A)	29(5)	7(4)	23(4)	4(3)	-4(4)	4(3)
C(6A)	44(5)	13(5)	15(5)	7(4)	-4(4)	2(4)
C(7A)	32(5)	13(5)	20(4)	-4(3)	-3(4)	6(4)
C(8A)	30(5)	29(5)	18(4)	-1(4)	3(4)	3(4)
C(9A)	37(5)	29(6)	30(5)	-7(4)	2(4)	-2(4)
C(10A)	25(5)	26(6)	39(5)	-5(4)	7(4)	-2(4)
C(11A)	23(4)	22(5)	29(5)	-3(4)	2(4)	-5(4)
C(12A)	32(5)	18(5)	21(5)	-3(4)	-9(4)	1(4)
C(13A)	26(4)	18(5)	23(5)	-4(4)	-5(4)	1(3)
C(14A)	51(6)	29(6)	14(5)	7(4)	1(4)	15(4)
C(15A)	26(5)	41(6)	11(4)	5(4)	-3(3)	6(4)
C(16A)	45(6)	60(7)	41(6)	21(5)	-18(5)	-11(5)
C(17A)	37(5)	54(7)	22(4)	0(5)	-12(4)	2(5)
Br(1B)	49(1)	45(1)	24(1)	10(1)	-6(1)	-23(1)
Cu(1B)	24(1)	25(1)	19(1)	2(1)	-1(1)	-4(1)
O(1B)	36(3)	34(4)	19(3)	10(3)	-4(3)	2(3)
O(2B)	21(3)	31(4)	29(3)	-2(3)	3(2)	-6(3)
N(1B)	27(4)	18(4)	26(4)	-3(3)	-1(3)	-4(3)
N(2B)	23(4)	23(4)	23(4)	0(3)	-5(3)	3(3)
N(3B)	26(4)	22(4)	11(3)	1(3)	2(3)	-3(3)
C(1B)	27(5)	23(5)	40(6)	-1(4)	-3(4)	-10(4)
C(2B)	29(5)	33(6)	50(6)	-12(5)	-3(4)	-4(4)
C(3B)	35(6)	33(7)	47(6)	1(5)	-12(5)	-2(4)
C(4B)	27(5)	33(6)	36(5)	-3(4)	-6(4)	-4(4)
C(5B)	23(4)	20(5)	32(5)	-5(4)	-5(4)	-1(4)
C(6B)	25(5)	24(6)	30(6)	-1(4)	-1(4)	-6(4)

C(7B)	28(5)	21(5)	19(4)	4(4)	-7(3)	-1(4)
C(8B)	28(5)	25(5)	31(5)	-9(4)	3(4)	-4(4)
C(9B)	46(6)	35(6)	14(4)	2(4)	5(4)	-3(4)
C(10B)	23(4)	41(6)	25(5)	3(4)	2(3)	9(4)
C(11B)	38(5)	23(5)	27(5)	11(4)	4(4)	1(4)
C(12B)	26(4)	27(5)	20(5)	2(4)	7(4)	11(4)
C(13B)	21(4)	25(5)	26(5)	0(4)	-3(4)	-3(3)
C(14B)	34(5)	54(7)	28(5)	-3(4)	2(4)	-6(5)
C(15B)	27(5)	26(5)	15(4)	-4(4)	2(3)	-3(4)
C(16B)	35(5)	48(7)	25(5)	-7(4)	2(4)	7(5)
C(17B)	30(5)	36(6)	25(5)	7(4)	-2(4)	7(4)

Hydrogen coordinates (x 10⁴) and isotropic displacement parameters (Å²x 10³)

	x	y	z	U(eq)
H(1AA)	3371	5710	7989	34
H(2AA)	4883	6116	8674	36
H(3AA)	4672	6752	9836	45
H(4AA)	2956	6927	10323	39
H(8AA)	-589	5774	10421	31
H(9AA)	-2366	5579	10659	38
H(10A)	-3635	5911	9769	36
H(11A)	-3102	6426	8586	30
H(14A)	-1330	8047	6946	38
H(14B)	-1948	7199	6564	38
H(16A)	1173	7022	6719	73
H(16B)	648	7880	7137	73
H(16C)	425	7724	6278	73
H(17A)	133	5697	6356	57
H(17B)	-735	6278	5909	57
H(17C)	-1099	5610	6564	57
H(1BA)	8632	4289	7985	36
H(2BA)	10143	3868	8671	45
H(3BA)	9896	3210	9829	46
H(4BA)	8199	3059	10327	38
H(8BA)	4667	4228	10416	33
H(9BA)	2887	4402	10658	38
H(10B)	1603	4086	9775	35
H(11B)	2149	3592	8593	35
H(14C)	3324	2675	6578	46
H(14D)	4014	1928	7027	46
H(16D)	6377	3096	6668	54
H(16E)	5646	2410	6199	54
H(16F)	5909	2181	7041	54
H(17D)	5162	4426	6418	45
H(17E)	3934	4347	6639	45
H(17F)	4378	3794	5941	45

Crystal data and structure refinement for **38c**

Empirical formula	$C_{17}H_{20}BCuF_4N_3O_4$
Formula weight	480.71
Temperature	150(1) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	$a = 24.1958(8)$ Å $\alpha = 90^\circ$. $b = 7.1369(2)$ Å $\beta = 113.353(1)^\circ$. $c = 24.6790(9)$ Å $\gamma = 90^\circ$.
Volume	3912.5(2) Å ³
Z	8
Density (calculated)	1.632 Mg/m ³
Absorption coefficient	1.184 mm ⁻¹
F(000)	1960
Crystal size	0.18 x 0.18 x 0.03 mm ³
Theta range for data collection	1.80 to 25.25°.
Index ranges	-28<=h<=28, -8<=k<=8, -29<=l<=29
Reflections collected	21115
Independent reflections	7020 [R(int) = 0.0607]
Completeness to theta = 25.25°	98.80%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6087
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	7020 / 0 / 590
Goodness-of-fit on F2	1.007
Final R indices [I>2sigma(I)]	R1 = 0.0452, wR2 = 0.0821
R indices (all data)	R1 = 0.0856, wR2 = 0.0965
Largest diff. peak and hole	0.422 and -0.434 e.Å ⁻³

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U(eq)
Cu(1A)	3298(1)	5000(1)	3165(1)	18(1)
O(1A)	1849(1)	6836(3)	1778(1)	23(1)
O(2A)	2791(1)	7349(4)	4430(1)	27(1)
O(3A)	4139(1)	4180(5)	3586(1)	24(1)
N(1A)	3352(1)	5179(4)	2378(1)	20(1)
N(2A)	2454(1)	5608(4)	2699(1)	17(1)
N(3A)	3253(1)	6192(4)	3875(1)	19(1)
C(1A)	3823(2)	4863(5)	2232(2)	24(1)
C(2A)	3799(2)	5210(5)	1674(2)	30(1)
C(3A)	3274(2)	5887(5)	1244(2)	32(1)
C(4A)	2784(2)	6214(5)	1388(2)	24(1)
C(5A)	2839(2)	5843(5)	1955(2)	19(1)
C(6A)	2325(2)	6143(5)	2142(2)	19(1)
C(7A)	2000(2)	5561(5)	2925(2)	19(1)
C(8A)	1409(2)	5016(5)	2574(2)	23(1)
C(9A)	977(2)	4916(5)	2807(2)	27(1)
C(10A)	1113(2)	5396(5)	3389(2)	27(1)
C(11A)	1694(2)	5929(5)	3745(2)	23(1)
C(12A)	2144(2)	5997(5)	3520(2)	17(1)
C(13A)	2750(2)	6497(5)	3926(2)	20(1)
C(14A)	3410(2)	7981(5)	4717(2)	28(1)
C(15A)	3757(2)	6847(5)	4432(2)	23(1)
C(16A)	4200(2)	8087(6)	4296(2)	36(1)
C(17A)	4062(2)	5149(6)	4806(2)	38(1)
Cu(1B)	2187(1)	1579(1)	6644(1)	19(1)
O(1B)	2500(1)	3558(3)	8267(1)	24(1)
O(2B)	3726(1)	4003(4)	6603(1)	29(1)
O(3B)	1668(2)	908(5)	5825(1)	30(1)
N(1B)	1488(1)	1787(4)	6888(1)	19(1)
N(2B)	2644(1)	2225(4)	7470(1)	18(1)
N(3B)	2822(1)	2737(4)	6423(1)	20(1)
C(1B)	904(2)	1483(5)	6571(2)	28(1)
C(2B)	468(2)	1904(5)	6784(2)	34(1)
C(3B)	636(2)	2621(5)	7341(2)	35(1)
C(4B)	1245(2)	2921(5)	7678(2)	26(1)
C(5B)	1657(2)	2502(5)	7437(2)	21(1)
C(6B)	2320(2)	2809(5)	7772(2)	21(1)

C(7B)	3279(2)	2191(5)	7753(2)	18(1)
C(8B)	3572(2)	1643(5)	8338(2)	24(1)
C(9B)	4192(2)	1534(5)	8603(2)	29(1)
C(10B)	4535(2)	2018(5)	8290(2)	32(1)
C(11B)	4259(2)	2565(5)	7713(2)	25(1)
C(12B)	3629(2)	2629(5)	7431(2)	19(1)
C(13B)	3359(2)	3111(5)	6808(2)	20(1)
C(14B)	3368(2)	4460(7)	5995(2)	48(1)
C(15B)	2793(2)	3328(6)	5828(2)	28(1)
C(16B)	2249(2)	4560(7)	5508(2)	50(1)
C(17B)	2807(2)	1611(7)	5478(2)	52(1)
F(1)	5435(1)	-765(3)	3399(1)	54(1)
F(2)	4784(1)	992(3)	3611(1)	59(1)
F(3)	5601(1)	-224(4)	4338(1)	66(1)
F(4)	5714(1)	2127(3)	3776(1)	42(1)
B(1)	5382(2)	546(7)	3790(2)	28(1)
F(5)	960(3)	8830(6)	4386(2)	74(2)
F(6)	1276(2)	7551(5)	5290(2)	66(2)
F(7)	339(2)	8551(6)	4855(3)	81(2)
F(5A)	593(11)	9330(30)	4308(10)	49(7)
F(6A)	1447(8)	8300(30)	4990(10)	47(7)
F(7A)	634(11)	8330(30)	5134(9)	38(6)
F(8)	646(1)	6015(3)	4501(1)	56(1)
B(2)	812(2)	7784(7)	4750(2)	33(1)
O(1WA)	5064(2)	5547(7)	3426(2)	49(1)
O(1WB)	723(2)	2954(6)	5221(2)	64(1)

Bond lengths [\AA] and angles [$^\circ$] for **38c**

Cu(1A)-N(2A)	1.953(3)
Cu(1A)-O(3A)	1.971(3)
Cu(1A)-N(3A)	1.988(3)
Cu(1A)-N(1A)	2.003(3)
Cu(1A)-O(1A)#1	2.298(2)
O(1A)-C(6A)	1.248(4)
O(1A)-Cu(1A)#2	2.298(2)
O(2A)-C(13A)	1.352(4)
O(2A)-C(14A)	1.451(4)
O(3A)-H(3OA)	0.77(4)
O(3A)-H(3OB)	0.78(5)
N(1A)-C(1A)	1.343(4)
N(1A)-C(5A)	1.352(5)
N(2A)-C(6A)	1.339(5)
N(2A)-C(7A)	1.416(4)
N(3A)-C(13A)	1.291(4)
N(3A)-C(15A)	1.505(5)
C(1A)-C(2A)	1.378(5)
C(1A)-H(1AA)	0.95
C(2A)-C(3A)	1.380(6)
C(2A)-H(2AA)	0.95
C(3A)-C(4A)	1.387(5)
C(3A)-H(3AA)	0.95
C(4A)-C(5A)	1.377(5)
C(4A)-H(4AA)	0.95
C(5A)-C(6A)	1.502(5)
C(7A)-C(8A)	1.401(5)
C(7A)-C(12A)	1.405(5)
C(8A)-C(9A)	1.380(5)
C(8A)-H(8AA)	0.95
C(9A)-C(10A)	1.383(5)
C(9A)-H(9AA)	0.95
C(10A)-C(11A)	1.383(5)
C(10A)-H(10B)	0.95
C(11A)-C(12A)	1.405(5)
C(11A)-H(11B)	0.95
C(12A)-C(13A)	1.455(5)
C(14A)-C(15A)	1.525(5)
C(14A)-H(14B)	0.99
C(14A)-H(14C)	0.99

C(15A)-C(17A)	1.525(5)
C(15A)-C(16A)	1.525(5)
C(16A)-H(16D)	0.98
C(16A)-H(16E)	0.98
C(16A)-H(16F)	0.98
C(17A)-H(17D)	0.98
C(17A)-H(17E)	0.98
C(17A)-H(17F)	0.98
Cu(1B)-N(2B)	1.951(3)
Cu(1B)-O(3B)	1.969(3)
Cu(1B)-N(3B)	2.001(3)
Cu(1B)-N(1B)	2.014(3)
Cu(1B)-O(1B)#3	2.267(2)
O(1B)-C(6B)	1.244(4)
O(1B)-Cu(1B)#4	2.267(2)
O(2B)-C(13B)	1.345(4)
O(2B)-C(14B)	1.441(5)
O(3B)-H(3OC)	0.77(5)
O(3B)-H(3OD)	0.77(5)
N(1B)-C(1B)	1.332(5)
N(1B)-C(5B)	1.349(5)
N(2B)-C(6B)	1.344(5)
N(2B)-C(7B)	1.413(5)
N(3B)-C(13B)	1.297(5)
N(3B)-C(15B)	1.504(5)
C(1B)-C(2B)	1.385(5)
C(1B)-H(1BA)	0.95
C(2B)-C(3B)	1.371(6)
C(2B)-H(2BA)	0.95
C(3B)-C(4B)	1.392(6)
C(3B)-H(3BA)	0.95
C(4B)-C(5B)	1.381(5)
C(4B)-H(4BA)	0.95
C(5B)-C(6B)	1.502(5)
C(7B)-C(8B)	1.388(5)
C(7B)-C(12B)	1.407(5)
C(8B)-C(9B)	1.380(5)
C(8B)-H(8BA)	0.95
C(9B)-C(10B)	1.385(6)
C(9B)-H(9BA)	0.95
C(10B)-C(11B)	1.368(6)
C(10B)-H(10A)	0.95
C(11B)-C(12B)	1.403(5)

C(11B)-H(11A)	0.95
C(12B)-C(13B)	1.453(5)
C(14B)-C(15B)	1.518(6)
C(14B)-H(14A)	0.99
C(14B)-H(14D)	0.99
C(15B)-C(17B)	1.508(6)
C(15B)-C(16B)	1.519(6)
C(16B)-H(16A)	0.98
C(16B)-H(16B)	0.98
C(16B)-H(16C)	0.98
C(17B)-H(17A)	0.98
C(17B)-H(17B)	0.98
C(17B)-H(17C)	0.98
F(1)-B(1)	1.386(5)
F(2)-B(1)	1.373(5)
F(3)-B(1)	1.358(5)
F(4)-B(1)	1.392(5)
F(5)-F(5A)	0.90(2)
F(5)-B(2)	1.322(6)
F(5)-F(6A)	1.54(2)
F(6)-F(6A)	1.12(2)
F(6)-B(2)	1.371(6)
F(6)-F(7A)	1.55(2)
F(7)-F(7A)	0.787(19)
F(7)-B(2)	1.381(6)
F(7)-F(5A)	1.78(2)
F(5A)-B(2)	1.49(2)
F(6A)-B(2)	1.458(19)
F(7A)-B(2)	1.25(2)
F(8)-B(2)	1.392(6)
O(1WA)-H(1W)	0.70(6)
O(1WA)-H(2W)	0.71(5)
O(1WB)-H(3W)	0.83(5)
O(1WB)-H(4W)	0.72(5)
N(2A)-Cu(1A)-O(3A)	174.56(13)
N(2A)-Cu(1A)-N(3A)	90.90(12)
O(3A)-Cu(1A)-N(3A)	93.88(13)
N(2A)-Cu(1A)-N(1A)	82.48(13)
O(3A)-Cu(1A)-N(1A)	94.53(13)
N(3A)-Cu(1A)-N(1A)	151.02(12)
N(2A)-Cu(1A)-O(1A) ^{#1}	95.98(11)
O(3A)-Cu(1A)-O(1A) ^{#1}	80.10(12)

N(3A)-Cu(1A)-O(1A)#1	107.65(10)
N(1A)-Cu(1A)-O(1A)#1	101.11(10)
C(6A)-O(1A)-Cu(1A)#2	117.8(2)
C(13A)-O(2A)-C(14A)	106.0(3)
Cu(1A)-O(3A)-H(3OA)	111(3)
Cu(1A)-O(3A)-H(3OB)	120(4)
H(3OA)-O(3A)-H(3OB)	114(5)
C(1A)-N(1A)-C(5A)	117.9(3)
C(1A)-N(1A)-Cu(1A)	129.7(3)
C(5A)-N(1A)-Cu(1A)	112.2(2)
C(6A)-N(2A)-C(7A)	120.6(3)
C(6A)-N(2A)-Cu(1A)	115.6(2)
C(7A)-N(2A)-Cu(1A)	123.7(3)
C(13A)-N(3A)-C(15A)	108.2(3)
C(13A)-N(3A)-Cu(1A)	122.7(3)
C(15A)-N(3A)-Cu(1A)	129.1(2)
N(1A)-C(1A)-C(2A)	122.3(4)
N(1A)-C(1A)-H(1AA)	118.9
C(2A)-C(1A)-H(1AA)	118.9
C(1A)-C(2A)-C(3A)	119.5(4)
C(1A)-C(2A)-H(2AA)	120.3
C(3A)-C(2A)-H(2AA)	120.3
C(2A)-C(3A)-C(4A)	118.8(4)
C(2A)-C(3A)-H(3AA)	120.6
C(4A)-C(3A)-H(3AA)	120.6
C(5A)-C(4A)-C(3A)	118.7(4)
C(5A)-C(4A)-H(4AA)	120.7
C(3A)-C(4A)-H(4AA)	120.7
N(1A)-C(5A)-C(4A)	122.8(4)
N(1A)-C(5A)-C(6A)	115.5(3)
C(4A)-C(5A)-C(6A)	121.7(4)
O(1A)-C(6A)-N(2A)	128.6(4)
O(1A)-C(6A)-C(5A)	118.5(3)
N(2A)-C(6A)-C(5A)	112.9(3)
C(8A)-C(7A)-C(12A)	118.4(3)
C(8A)-C(7A)-N(2A)	121.7(4)
C(12A)-C(7A)-N(2A)	119.9(3)
C(9A)-C(8A)-C(7A)	120.9(4)
C(9A)-C(8A)-H(8AA)	119.5
C(7A)-C(8A)-H(8AA)	119.6
C(8A)-C(9A)-C(10A)	120.8(4)
C(8A)-C(9A)-H(9AA)	119.6
C(10A)-C(9A)-H(9AA)	119.6

C(11A)-C(10A)-C(9A)	119.4(4)
C(11A)-C(10A)-H(10B)	120.3
C(9A)-C(10A)-H(10B)	120.3
C(10A)-C(11A)-C(12A)	120.7(4)
C(10A)-C(11A)-H(11B)	119.7
C(12A)-C(11A)-H(11B)	119.7
C(7A)-C(12A)-C(11A)	119.7(4)
C(7A)-C(12A)-C(13A)	122.6(3)
C(11A)-C(12A)-C(13A)	117.7(4)
N(3A)-C(13A)-O(2A)	115.9(3)
N(3A)-C(13A)-C(12A)	128.6(3)
O(2A)-C(13A)-C(12A)	115.5(3)
O(2A)-C(14A)-C(15A)	105.0(3)
O(2A)-C(14A)-H(14B)	110.7
C(15A)-C(14A)-H(14B)	110.7
O(2A)-C(14A)-H(14C)	110.7
C(15A)-C(14A)-H(14C)	110.7
H(14B)-C(14A)-H(14C)	108.8
N(3A)-C(15A)-C(17A)	109.1(3)
N(3A)-C(15A)-C(16A)	111.4(3)
C(17A)-C(15A)-C(16A)	112.4(3)
N(3A)-C(15A)-C(14A)	101.1(3)
C(17A)-C(15A)-C(14A)	111.4(3)
C(16A)-C(15A)-C(14A)	110.9(3)
C(15A)-C(16A)-H(16D)	109.5
C(15A)-C(16A)-H(16E)	109.5
H(16D)-C(16A)-H(16E)	109.5
C(15A)-C(16A)-H(16F)	109.5
H(16D)-C(16A)-H(16F)	109.5
H(16E)-C(16A)-H(16F)	109.5
C(15A)-C(17A)-H(17D)	109.5
C(15A)-C(17A)-H(17E)	109.5
H(17D)-C(17A)-H(17E)	109.5
C(15A)-C(17A)-H(17F)	109.5
H(17D)-C(17A)-H(17F)	109.5
H(17E)-C(17A)-H(17F)	109.5
N(2B)-Cu(1B)-O(3B)	175.40(13)
N(2B)-Cu(1B)-N(3B)	90.45(13)
O(3B)-Cu(1B)-N(3B)	93.88(13)
N(2B)-Cu(1B)-N(1B)	82.28(13)
O(3B)-Cu(1B)-N(1B)	93.17(14)
N(3B)-Cu(1B)-N(1B)	151.37(12)
N(2B)-Cu(1B)-O(1B)#3	95.40(11)

O(3B)-Cu(1B)-O(1B)#3	85.47(14)
N(3B)-Cu(1B)-O(1B)#3	98.93(10)
N(1B)-Cu(1B)-O(1B)#3	109.27(10)
C(6B)-O(1B)-Cu(1B)#4	118.5(2)
C(13B)-O(2B)-C(14B)	106.5(3)
Cu(1B)-O(3B)-H(3OC)	111(4)
Cu(1B)-O(3B)-H(3OD)	121(4)
H(3OC)-O(3B)-H(3OD)	115(5)
C(1B)-N(1B)-C(5B)	118.7(3)
C(1B)-N(1B)-Cu(1B)	129.2(3)
C(5B)-N(1B)-Cu(1B)	111.8(2)
C(6B)-N(2B)-C(7B)	119.4(3)
C(6B)-N(2B)-Cu(1B)	116.0(3)
C(7B)-N(2B)-Cu(1B)	124.6(2)
C(13B)-N(3B)-C(15B)	107.6(3)
C(13B)-N(3B)-Cu(1B)	122.7(3)
C(15B)-N(3B)-Cu(1B)	129.7(3)
N(1B)-C(1B)-C(2B)	122.2(4)
N(1B)-C(1B)-H(1BA)	118.9
C(2B)-C(1B)-H(1BA)	118.9
C(3B)-C(2B)-C(1B)	119.6(4)
C(3B)-C(2B)-H(2BA)	120.2
C(1B)-C(2B)-H(2BA)	120.2
C(2B)-C(3B)-C(4B)	118.6(4)
C(2B)-C(3B)-H(3BA)	120.7
C(4B)-C(3B)-H(3BA)	120.7
C(5B)-C(4B)-C(3B)	118.9(4)
C(5B)-C(4B)-H(4BA)	120.5
C(3B)-C(4B)-H(4BA)	120.5
N(1B)-C(5B)-C(4B)	122.1(4)
N(1B)-C(5B)-C(6B)	116.2(3)
C(4B)-C(5B)-C(6B)	121.7(4)
O(1B)-C(6B)-N(2B)	128.6(4)
O(1B)-C(6B)-C(5B)	119.0(3)
N(2B)-C(6B)-C(5B)	112.3(3)
C(8B)-C(7B)-C(12B)	118.5(4)
C(8B)-C(7B)-N(2B)	121.7(3)
C(12B)-C(7B)-N(2B)	119.8(3)
C(9B)-C(8B)-C(7B)	121.4(4)
C(9B)-C(8B)-H(8BA)	119.3
C(7B)-C(8B)-H(8BA)	119.3
C(8B)-C(9B)-C(10B)	120.0(4)
C(8B)-C(9B)-H(9BA)	120

C(10B)-C(9B)-H(9BA)	120
C(11B)-C(10B)-C(9B)	119.8(4)
C(11B)-C(10B)-H(10A)	120.1
C(9B)-C(10B)-H(10A)	120.1
C(10B)-C(11B)-C(12B)	121.0(4)
C(10B)-C(11B)-H(11A)	119.5
C(12B)-C(11B)-H(11A)	119.5
C(11B)-C(12B)-C(7B)	119.3(4)
C(11B)-C(12B)-C(13B)	118.6(3)
C(7B)-C(12B)-C(13B)	122.1(3)
N(3B)-C(13B)-O(2B)	116.3(4)
N(3B)-C(13B)-C(12B)	128.7(3)
O(2B)-C(13B)-C(12B)	115.0(3)
O(2B)-C(14B)-C(15B)	105.7(3)
O(2B)-C(14B)-H(14A)	110.6
C(15B)-C(14B)-H(14A)	110.6
O(2B)-C(14B)-H(14D)	110.6
C(15B)-C(14B)-H(14D)	110.6
H(14A)-C(14B)-H(14D)	108.7
N(3B)-C(15B)-C(17B)	109.2(3)
N(3B)-C(15B)-C(14B)	101.6(3)
C(17B)-C(15B)-C(14B)	111.2(4)
N(3B)-C(15B)-C(16B)	111.5(3)
C(17B)-C(15B)-C(16B)	112.6(4)
C(14B)-C(15B)-C(16B)	110.2(4)
C(15B)-C(16B)-H(16A)	109.5
C(15B)-C(16B)-H(16B)	109.5
H(16A)-C(16B)-H(16B)	109.5
C(15B)-C(16B)-H(16C)	109.5
H(16A)-C(16B)-H(16C)	109.5
H(16B)-C(16B)-H(16C)	109.5
C(15B)-C(17B)-H(17A)	109.5
C(15B)-C(17B)-H(17B)	109.5
H(17A)-C(17B)-H(17B)	109.5
C(15B)-C(17B)-H(17C)	109.5
H(17A)-C(17B)-H(17C)	109.5
H(17B)-C(17B)-H(17C)	109.5
F(3)-B(1)-F(2)	111.0(4)
F(3)-B(1)-F(1)	108.3(4)
F(2)-B(1)-F(1)	108.0(4)
F(3)-B(1)-F(4)	110.6(4)
F(2)-B(1)-F(4)	110.4(4)
F(1)-B(1)-F(4)	108.5(4)

F(5A)-F(5)-B(2)	81.9(14)
F(5A)-F(5)-F(6A)	128.0(17)
B(2)-F(5)-F(6A)	60.8(8)
F(6A)-F(6)-B(2)	70.9(10)
F(6A)-F(6)-F(7A)	105.1(12)
B(2)-F(6)-F(7A)	50.1(8)
F(7A)-F(7)-B(2)	63.4(16)
F(7A)-F(7)-F(5A)	105.2(18)
B(2)-F(7)-F(5A)	54.7(7)
F(5)-F(5A)-B(2)	61.3(12)
F(5)-F(5A)-F(7)	108.7(18)
B(2)-F(5A)-F(7)	49.0(7)
F(6)-F(6A)-B(2)	62.7(9)
F(6)-F(6A)-F(5)	114.7(14)
B(2)-F(6A)-F(5)	52.4(7)
F(7)-F(7A)-B(2)	82.2(18)
F(7)-F(7A)-F(6)	140(2)
B(2)-F(7A)-F(6)	57.6(10)
F(7A)-B(2)-F(5)	127.5(10)
F(7A)-B(2)-F(6)	72.3(11)
F(5)-B(2)-F(6)	113.0(5)
F(7A)-B(2)-F(7)	34.4(9)
F(5)-B(2)-F(7)	111.8(5)
F(6)-B(2)-F(7)	106.7(5)
F(7A)-B(2)-F(8)	119.4(10)
F(5)-B(2)-F(8)	108.7(4)
F(6)-B(2)-F(8)	107.6(4)
F(7)-B(2)-F(8)	109.0(4)
F(7A)-B(2)-F(6A)	103.9(13)
F(5)-B(2)-F(6A)	66.8(9)
F(6)-B(2)-F(6A)	46.4(8)
F(7)-B(2)-F(6A)	129.9(8)
F(8)-B(2)-F(6A)	118.9(8)
F(7A)-B(2)-F(5A)	101.4(12)
F(5)-B(2)-F(5A)	36.8(8)
F(6)-B(2)-F(5A)	135.8(9)
F(7)-B(2)-F(5A)	76.3(9)
F(8)-B(2)-F(5A)	112.9(9)
F(6A)-B(2)-F(5A)	96.9(11)
H(1W)-O(1WA)-H(2W)	113(6)
H(3W)-O(1WB)-H(4W)	110(6)

Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$)
for **38c**

	U11	U22	U33	U23	U13	U12
Cu(1A)	14(1)	20(1)	18(1)	-1(1)	5(1)	1(1)
O(1A)	21(2)	21(1)	20(2)	1(1)	1(1)	5(1)
O(2A)	19(2)	39(2)	22(2)	-11(1)	8(1)	-2(1)
O(3A)	17(2)	22(2)	33(2)	-2(1)	9(2)	-1(2)
N(1A)	18(2)	18(2)	23(2)	-2(2)	9(2)	0(1)
N(2A)	15(2)	18(2)	16(2)	-1(1)	5(2)	2(1)
N(3A)	17(2)	20(2)	19(2)	0(1)	4(2)	-1(1)
C(1A)	22(2)	25(2)	28(3)	-5(2)	12(2)	-1(2)
C(2A)	30(3)	29(2)	39(3)	-7(2)	22(3)	-1(2)
C(3A)	43(3)	31(2)	26(3)	-3(2)	19(3)	0(2)
C(4A)	29(3)	21(2)	19(2)	1(2)	6(2)	0(2)
C(5A)	19(2)	11(2)	23(2)	-2(2)	6(2)	1(2)
C(6A)	25(2)	11(2)	19(2)	-6(2)	5(2)	-3(2)
C(7A)	16(2)	16(2)	24(2)	-1(2)	7(2)	1(2)
C(8A)	20(2)	20(2)	24(2)	-4(2)	2(2)	1(2)
C(9A)	15(2)	26(2)	34(3)	0(2)	4(2)	1(2)
C(10A)	20(2)	28(2)	37(3)	4(2)	17(2)	-2(2)
C(11A)	22(2)	24(2)	25(3)	2(2)	12(2)	3(2)
C(12A)	14(2)	15(2)	21(2)	0(2)	6(2)	3(2)
C(13A)	23(2)	18(2)	19(2)	1(2)	7(2)	1(2)
C(14A)	22(2)	37(2)	23(3)	-4(2)	6(2)	-2(2)
C(15A)	17(2)	33(2)	17(2)	-5(2)	4(2)	-4(2)
C(16A)	30(3)	48(3)	31(3)	-14(2)	13(2)	-14(2)
C(17A)	29(3)	62(3)	16(2)	6(2)	3(2)	12(2)
Cu(1B)	19(1)	20(1)	17(1)	-1(1)	5(1)	-2(1)
O(1B)	32(2)	22(1)	20(2)	-3(1)	15(1)	-3(1)
O(2B)	20(2)	44(2)	24(2)	-2(1)	11(2)	-7(1)
O(3B)	26(2)	29(2)	24(2)	1(2)	-1(2)	-1(2)
N(1B)	18(2)	15(2)	24(2)	4(1)	7(2)	-1(1)
N(2B)	20(2)	18(2)	18(2)	-1(1)	8(2)	-3(1)
N(3B)	22(2)	23(2)	15(2)	-1(1)	7(2)	-2(2)
C(1B)	27(3)	25(2)	28(3)	4(2)	8(2)	-4(2)
C(2B)	25(3)	34(2)	42(3)	7(2)	12(2)	-1(2)
C(3B)	34(3)	29(2)	51(3)	12(2)	26(3)	5(2)
C(4B)	32(3)	23(2)	30(3)	2(2)	20(2)	0(2)
C(5B)	22(2)	13(2)	24(3)	6(2)	7(2)	3(2)
C(6B)	31(3)	9(2)	24(3)	6(2)	14(2)	-2(2)

C(7B)	22(2)	14(2)	18(2)	-7(2)	6(2)	0(2)
C(8B)	29(3)	21(2)	23(2)	-2(2)	11(2)	0(2)
C(9B)	33(3)	28(2)	20(2)	2(2)	5(2)	6(2)
C(10B)	21(2)	33(2)	29(3)	-11(2)	-4(2)	5(2)
C(11B)	21(2)	26(2)	30(3)	-11(2)	12(2)	-2(2)
C(12B)	21(2)	15(2)	19(2)	-5(2)	7(2)	-4(2)
C(13B)	21(2)	17(2)	26(2)	-3(2)	14(2)	0(2)
C(14B)	39(3)	83(4)	25(3)	13(3)	15(3)	-15(3)
C(15B)	21(2)	47(3)	17(2)	2(2)	9(2)	-4(2)
C(16B)	37(3)	67(3)	50(4)	36(3)	22(3)	7(3)
C(17B)	50(3)	79(4)	38(3)	-20(3)	28(3)	-10(3)
F(1)	73(2)	37(1)	64(2)	-12(1)	41(2)	3(1)
F(2)	29(2)	41(2)	106(3)	-6(2)	25(2)	6(1)
F(3)	65(2)	87(2)	33(2)	11(2)	5(2)	-31(2)
F(4)	42(2)	36(1)	51(2)	-3(1)	20(2)	-14(1)
B(1)	21(3)	32(3)	28(3)	-2(2)	7(3)	1(2)
F(5)	122(5)	73(3)	54(3)	-7(2)	62(3)	-41(3)
F(6)	76(3)	40(2)	40(3)	-8(2)	-23(2)	14(2)
F(7)	42(3)	69(3)	152(6)	-9(3)	60(4)	3(2)
F(8)	78(2)	45(2)	34(2)	-8(1)	9(2)	-10(2)
B(2)	30(3)	46(3)	23(3)	-5(3)	10(3)	-2(3)
O(1WA)	25(2)	44(2)	83(3)	-2(2)	26(2)	-6(2)
O(1WB)	33(3)	68(3)	72(3)	37(2)	1(2)	-3(2)

Hydrogen coordinates (x 10⁴) and isotropic displacement parameters (Å²x 10³)

	x	y	z	U(eq)
H(3OA)	4168(18)	3120(60)	3567(18)	27(14)
H(3OB)	4400(20)	4750(70)	3550(20)	59(19)
H(1AA)	4185	4383	2524	29
H(2AA)	4142	4986	1586	36
H(3AA)	3249	6124	856	38
H(4AA)	2417	6684	1101	29
H(8AA)	1305	4712	2171	28
H(9AA)	582	4513	2565	32
H(10B)	810	5360	3542	32
H(11B)	1789	6252	4145	28
H(14B)	3568	7739	5147	34
H(14C)	3441	9339	4652	34
H(16D)	4412	7336	4107	54
H(16E)	4492	8620	4664	54
H(16F)	3980	9102	4031	54
H(17D)	4262	4412	4601	56
H(17E)	3758	4373	4869	56
H(17F)	4360	5570	5187	56
H(3OC)	1640(20)	-160(70)	5790(20)	70(20)
H(3OD)	1380(20)	1470(60)	5650(20)	43(17)
H(1BA)	784	961	6188	33
H(2BA)	54	1697	6544	41
H(3BA)	343	2907	7495	42
H(4BA)	1376	3407	8067	31
H(8BA)	3341	1337	8560	29
H(9BA)	4383	1126	9001	35
H(10A)	4962	1971	8475	38
H(11A)	4496	2907	7501	30
H(14A)	3583	4118	5742	58
H(14D)	3277	5818	5951	58
H(16A)	1883	3791	5370	75
H(16B)	2291	5159	5169	75
H(16C)	2220	5525	5778	75
H(17A)	2445	858	5402	78
H(17B)	3165	865	5702	78
H(17C)	2820	1993	5101	78

H(1W)	5170(30)	6480(80)	3470(30)	90(30)
H(2W)	5300(30)	4890(70)	3490(30)	60(20)
H(3W)	710(20)	3790(60)	4990(20)	47(16)
H(4W)	430(20)	2530(70)	5130(20)	50(20)

Hydrogen bonds for **38c** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
O(3B)-H(3OC)...F(6)#5	0.77(5)	2.02(5)	2.718(5)	150(6)
O(3B)-H(3OD)...O(1WB)	0.77(5)	1.85(5)	2.623(5)	176(5)
O(1WA)-H(1W)...F(1)#6	0.70(6)	2.10(6)	2.790(5)	167(7)
O(1WA)-H(2W)...F(4)	0.71(5)	2.19(5)	2.846(6)	153(6)
O(1WB)-H(3W)...F(8)	0.83(5)	1.95(5)	2.775(5)	171(5)
O(1WB)-H(4W)...F(7)#7	0.72(5)	2.03(5)	2.723(6)	163(6)
O(3A)-H(3OA)...F(2)	0.77(4)	2.10(4)	2.746(4)	143(4)
O(3A)-H(3OB)...O(1WA)	0.78(5)	1.85(5)	2.612(5)	166(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y-1/2,-z+1/2 #2 -x+1/2,y+1/2,-z+1/2

#3 -x+1/2,y-1/2,-z+3/2 #4 -x+1/2,y+1/2,-z+3/2

#5 x,y-1,z #6 x,y+1,z #7 -x,-y+1,-z+1

Crystal data and structure refinement for **38d**.

Empirical formula	$C_{34}H_{32}Cu_2N_8O_{10}$	
Formula weight	839.76	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	$a = 7.7793(3)$ Å	$\alpha = 90^\circ$.
	$b = 19.9956(5)$ Å	$\beta =$ 100.0840(15)°.
	$c = 10.9433(3)$ Å	$\gamma = 90^\circ$.
Volume	$1675.95(9)$ Å ³	
Z	2	
Density (calculated)	1.664 Mg/m ³	
Absorption coefficient	1.343 mm ⁻¹	
F(000)	860	
Crystal size	0.30 x 0.15 x 0.10 mm ³	
Theta range for data collection	2.78 to 27.48°.	
Index ranges	$-10 \leq h \leq 10, -25 \leq k \leq 25, -4 \leq l \leq 14$	
Reflections collected	17177	
Independent reflections	3813 [R(int) = 0.090]	
Completeness to theta = 27.48°	99.50%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.931 and 0.728	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	3813 / 0 / 247	
Goodness-of-fit on F ²	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1026	
R indices (all data)	R1 = 0.0616, wR2 = 0.1113	
Largest diff. peak and hole	0.887 and -0.359 e.Å ⁻³	

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U(eq)
Cu(1)	969(1)	3966(1)	3814(1)	26(1)
O(1)	1426(3)	5929(1)	4528(2)	34(1)
O(2)	-3033(3)	3879(1)	829(2)	36(1)
O(3)	1773(3)	3019(1)	4201(2)	33(1)
O(4)	3472(3)	3420(1)	2997(2)	42(1)
O(5)	3766(4)	2387(1)	3639(3)	59(1)
N(1)	2562(4)	4265(1)	5332(2)	27(1)
N(2)	808(4)	4927(1)	3419(2)	26(1)
N(3)	-898(3)	3711(1)	2461(2)	25(1)
N(4)	3058(4)	2935(1)	3607(3)	39(1)
C(1)	3504(5)	3900(2)	6246(3)	35(1)
C(2)	4684(5)	4188(2)	7176(3)	38(1)
C(3)	4929(5)	4873(2)	7185(3)	38(1)
C(4)	3913(4)	5256(2)	6280(3)	31(1)
C(5)	2734(4)	4935(2)	5376(3)	27(1)
C(6)	1580(4)	5321(2)	4374(3)	27(1)
C(7)	-127(4)	5214(2)	2325(3)	26(1)
C(8)	113(5)	5887(2)	1999(3)	32(1)
C(9)	-818(5)	6167(2)	937(3)	36(1)
C(10)	-2030(5)	5796(2)	129(3)	39(1)
C(11)	-2259(5)	5134(2)	407(3)	35(1)
C(12)	-1327(4)	4835(2)	1489(3)	28(1)
C(13)	-1689(4)	4124(2)	1652(3)	27(1)
C(14)	-3320(5)	3197(2)	1213(3)	34(1)
C(15)	-1696(4)	3027(2)	2173(3)	28(1)
C(16)	-2207(5)	2717(2)	3337(3)	32(1)
C(17)	-441(5)	2574(2)	1623(3)	32(1)

Bond lengths [Å] and angles [°] for **38d**

Cu(1)-N(3)	1.952(2)
Cu(1)-N(2)	1.969(2)
Cu(1)-N(1)	1.983(3)
Cu(1)-O(3)	2.016(2)
Cu(1)-O(1)#1	2.827(3)
O(1)-C(6)	1.236(4)
O(2)-C(13)	1.347(4)
O(2)-C(14)	1.455(4)
O(3)-N(4)	1.295(4)
O(4)-N(4)	1.252(4)
O(5)-N(4)	1.224(3)
N(1)-C(5)	1.346(4)
N(1)-C(1)	1.347(4)
N(2)-C(6)	1.362(4)
N(2)-C(7)	1.410(4)
N(3)-C(13)	1.285(4)
N(3)-C(15)	1.513(4)
C(1)-C(2)	1.373(5)
C(1)-H(1A)	0.95
C(2)-C(3)	1.383(5)
C(2)-H(2A)	0.95
C(3)-C(4)	1.386(5)
C(3)-H(3A)	0.95
C(4)-C(5)	1.383(4)
C(4)-H(4A)	0.95
C(5)-C(6)	1.504(4)
C(7)-C(12)	1.409(4)
C(7)-C(8)	1.414(4)
C(8)-C(9)	1.376(4)
C(8)-H(8A)	0.95
C(9)-C(10)	1.388(5)
C(9)-H(9A)	0.95
C(10)-C(11)	1.376(5)
C(10)-H(10A)	0.95
C(11)-C(12)	1.409(4)
C(11)-H(11A)	0.95
C(12)-C(13)	1.465(4)
C(14)-C(15)	1.533(4)
C(14)-H(14A)	0.99
C(14)-H(14B)	0.99

C(15)-C(16)	1.530(4)
C(15)-C(17)	1.531(5)
C(16)-H(16A)	0.98
C(16)-H(16B)	0.98
C(16)-H(16C)	0.98
C(17)-H(17A)	0.98
C(17)-H(17B)	0.98
C(17)-H(17C)	0.98
N(3)-Cu(1)-N(2)	94.46(10)
N(3)-Cu(1)-N(1)	170.82(11)
N(2)-Cu(1)-N(1)	84.01(10)
N(3)-Cu(1)-O(3)	94.40(10)
N(2)-Cu(1)-O(3)	165.58(11)
N(1)-Cu(1)-O(3)	88.98(10)
N(3)-Cu(1)-O(1)#1	91.12(9)
N(2)-Cu(1)-O(1)#1	92.56(9)
N(1)-Cu(1)-O(1)#1	79.93(10)
O(3)-Cu(1)-O(1)#1	98.62(8)
C(13)-O(2)-C(14)	106.7(2)
N(4)-O(3)-Cu(1)	104.79(18)
C(5)-N(1)-C(1)	118.4(3)
C(5)-N(1)-Cu(1)	112.0(2)
C(1)-N(1)-Cu(1)	129.6(2)
C(6)-N(2)-C(7)	120.6(2)
C(6)-N(2)-Cu(1)	113.24(19)
C(7)-N(2)-Cu(1)	125.95(19)
C(13)-N(3)-C(15)	108.0(2)
C(13)-N(3)-Cu(1)	123.9(2)
C(15)-N(3)-Cu(1)	128.14(19)
O(5)-N(4)-O(4)	123.5(3)
O(5)-N(4)-O(3)	119.0(3)
O(4)-N(4)-O(3)	117.4(3)
N(1)-C(1)-C(2)	122.0(3)
N(1)-C(1)-H(1A)	119
C(2)-C(1)-H(1A)	119
C(1)-C(2)-C(3)	119.6(3)
C(1)-C(2)-H(2A)	120.2
C(3)-C(2)-H(2A)	120.2
C(2)-C(3)-C(4)	118.8(3)
C(2)-C(3)-H(3A)	120.6
C(4)-C(3)-H(3A)	120.6
C(5)-C(4)-C(3)	118.6(3)

C(5)-C(4)-H(4A)	120.7
C(3)-C(4)-H(4A)	120.7
N(1)-C(5)-C(4)	122.5(3)
N(1)-C(5)-C(6)	116.2(3)
C(4)-C(5)-C(6)	121.3(3)
O(1)-C(6)-N(2)	129.4(3)
O(1)-C(6)-C(5)	117.7(3)
N(2)-C(6)-C(5)	112.9(3)
C(12)-C(7)-N(2)	121.2(3)
C(12)-C(7)-C(8)	116.8(3)
N(2)-C(7)-C(8)	122.1(3)
C(9)-C(8)-C(7)	121.8(3)
C(9)-C(8)-H(8A)	119.1
C(7)-C(8)-H(8A)	119.1
C(8)-C(9)-C(10)	121.3(3)
C(8)-C(9)-H(9A)	119.3
C(10)-C(9)-H(9A)	119.3
C(11)-C(10)-C(9)	118.2(3)
C(11)-C(10)-H(10A)	120.9
C(9)-C(10)-H(10A)	120.9
C(10)-C(11)-C(12)	121.8(3)
C(10)-C(11)-H(11A)	119.1
C(12)-C(11)-H(11A)	119.1
C(11)-C(12)-C(7)	120.1(3)
C(11)-C(12)-C(13)	115.7(3)
C(7)-C(12)-C(13)	124.2(3)
N(3)-C(13)-O(2)	116.6(3)
N(3)-C(13)-C(12)	128.9(3)
O(2)-C(13)-C(12)	114.5(3)
O(2)-C(14)-C(15)	104.8(2)
O(2)-C(14)-H(14A)	110.8
C(15)-C(14)-H(14A)	110.8
O(2)-C(14)-H(14B)	110.8
C(15)-C(14)-H(14B)	110.8
H(14A)-C(14)-H(14B)	108.9
N(3)-C(15)-C(16)	110.5(2)
N(3)-C(15)-C(17)	110.6(3)
C(16)-C(15)-C(17)	111.3(3)
N(3)-C(15)-C(14)	101.6(2)
C(16)-C(15)-C(14)	110.9(3)
C(17)-C(15)-C(14)	111.6(3)
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5

H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **38d** The

anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [h^2 a^*{}^2 U^{11} + \dots + 2 h k a^* b^* U^{12}]$$

	U11	U22	U33	U23	U13	U12
Cu(1)	28(1)	21(1)	26(1)	0(1)	-2(1)	0(1)
O(1)	44(2)	24(1)	30(1)	-2(1)	-2(1)	-1(1)
O(2)	40(2)	30(1)	32(1)	2(1)	-12(1)	-7(1)
O(3)	31(1)	26(1)	40(1)	1(1)	1(1)	1(1)
O(4)	37(2)	33(1)	57(2)	-1(1)	11(1)	-3(1)
O(5)	37(2)	28(1)	108(3)	-3(2)	7(2)	9(1)
N(1)	27(1)	28(1)	26(1)	-1(1)	0(1)	1(1)
N(2)	27(1)	23(1)	25(1)	0(1)	1(1)	2(1)
N(3)	27(2)	22(1)	23(1)	-1(1)	1(1)	-2(1)
N(4)	27(2)	28(1)	57(2)	-3(1)	-5(1)	0(1)
C(1)	35(2)	37(2)	30(2)	3(1)	-2(1)	7(1)
C(2)	36(2)	45(2)	30(2)	3(2)	-2(2)	10(2)
C(3)	30(2)	51(2)	29(2)	-7(2)	-3(1)	-1(2)
C(4)	29(2)	36(2)	29(2)	-7(1)	4(1)	-2(1)
C(5)	24(2)	32(2)	25(1)	-2(1)	5(1)	0(1)
C(6)	23(2)	28(2)	29(2)	1(1)	3(1)	0(1)
C(7)	27(2)	25(1)	25(2)	2(1)	6(1)	3(1)
C(8)	43(2)	25(2)	26(2)	0(1)	4(2)	-1(1)
C(9)	51(2)	26(2)	31(2)	5(1)	8(2)	-2(2)
C(10)	53(2)	35(2)	26(2)	8(1)	0(2)	4(2)

C(11)	40(2)	35(2)	26(2)	1(1)	-2(2)	1(2)
C(12)	29(2)	26(2)	28(2)	0(1)	4(1)	-1(1)
C(13)	28(2)	29(2)	24(2)	-3(1)	3(1)	-3(1)
C(14)	37(2)	27(2)	34(2)	1(1)	-4(2)	-4(1)
C(15)	30(2)	25(2)	28(2)	-2(1)	3(1)	-5(1)
C(16)	32(2)	33(2)	31(2)	3(1)	4(1)	-5(1)
C(17)	40(2)	25(2)	31(2)	-3(1)	6(1)	-2(1)

Hydrogen coordinates (x 10⁴) and isotropic displacement parameters (Å² x 10³)

For **38d**

	x	y	z	U(eq)
H(1A)	3347	3429	6246	42
H(2A)	5330	3918	7811	45
H(3A)	5778	5077	7802	45
H(4A)	4023	5729	6280	38
H(8A)	940	6154	2528	38
H(9A)	-628	6622	752	43
H(10A)	-2683	5993	-596	46
H(11A)	-3069	4872	-145	42
H(14A)	-3439	2888	498	41
H(14B)	-4388	3170	1588	41
H(16A)	-2971	3026	3686	48
H(16B)	-1152	2632	3952	48
H(16C)	-2823	2295	3119	48
H(17A)	542	2451	2273	48
H(17B)	-5	2811	956	48
H(17C)	-1058	2168	1289	48

Crystal data and structure refinement for **38f**

Empirical formula	$C_{18}H_{21}Au_2Br_8N_2O_4$
Formula weight	1362.58
Temperature	147(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	$a = 8.0501(2)$ Å $\alpha = 78.7370(16)^\circ$. $b = 10.9273(3)$ Å $\beta = 87.8290(14)^\circ$. $c = 17.6282(5)$ Å $\gamma = 77.9940(14)^\circ$.
Volume	1487.54(7) Å ³
Z	2
Density (calculated)	3.042 Mg/m ³
Absorption coefficient	20.623 mm ⁻¹
F(000)	1226
Crystal size	0.18 x 0.10 x 0.07 mm ³
Theta range for data collection	2.59 to 27.52°.
Index ranges	-10≤h≤10, -14≤k≤14, -22≤l≤22
Reflections collected	28365
Independent reflections	6844 [R(int) = 0.0729]
Completeness to theta = 27.52°	99.60%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.501 and 0.266
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6844 / 0 / 318
Goodness-of-fit on F ²	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.0815
R indices (all data)	R1 = 0.0557, wR2 = 0.0872
Largest diff. peak and hole	1.610 and -2.384 e.Å ⁻³

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **38f**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Au(1)	8502(1)	7395(1)	1603(1)	19(1)
Au(2)	1022(1)	4074(1)	2828(1)	19(1)
Br(1)	8512(1)	6638(1)	393(1)	29(1)
Br(2)	11559(1)	7153(1)	1554(1)	28(1)
Br(3)	5422(1)	7832(1)	1618(1)	27(1)
Br(4)	8475(1)	8085(1)	2829(1)	24(1)
Br(5)	1614(1)	3471(1)	1572(1)	26(1)
Br(6)	442(1)	4662(1)	4084(1)	27(1)
Br(7)	4043(1)	3812(1)	3028(1)	27(1)
Br(8)	-2002(1)	4344(1)	2617(1)	25(1)
O(1)	10698(6)	1739(5)	5505(3)	29(1)
O(2)	7558(6)	1175(4)	3300(2)	22(1)
O(3)	8827(6)	1252(4)	2143(2)	23(1)
N(1)	9478(7)	1469(5)	4394(3)	21(1)
N(2)	7760(7)	2675(5)	6069(3)	22(1)
C(1)	9478(9)	1858(6)	5094(4)	22(2)
C(2)	10925(9)	994(6)	3975(4)	19(1)
C(3)	12567(9)	751(6)	4242(4)	25(2)
C(4)	13893(9)	285(6)	3794(4)	30(2)
C(5)	13614(9)	58(6)	3075(4)	25(2)
C(6)	12004(8)	315(6)	2792(4)	20(2)
C(7)	10608(8)	791(6)	3231(4)	20(2)
C(8)	7732(9)	2440(6)	5344(4)	23(2)
C(9)	6229(9)	2743(7)	4946(4)	31(2)
C(10)	4744(10)	3270(7)	5309(4)	32(2)
C(11)	4805(10)	3494(7)	6050(4)	29(2)
C(12)	6353(9)	3180(6)	6421(4)	25(2)
C(13)	8848(9)	1087(6)	2917(4)	22(2)
C(14)	7178(8)	1483(6)	1786(4)	24(2)
C(15)	7392(8)	1838(6)	918(4)	21(2)
C(16)	8829(10)	903(7)	615(4)	32(2)
C(17)	5747(9)	1911(7)	531(4)	30(2)
C(18)	7820(7)	3138(5)	733(3)	12(1)
O(1W)	5015(7)	4997(5)	970(3)	32(1)

Bond lengths [Å] and angles [°] for **38f**.

Au(1)-Br(2)	2.4204(7)
Au(1)-Br(4)	2.4208(7)
Au(1)-Br(3)	2.4251(7)
Au(1)-Br(1)	2.4330(7)
Au(2)-Br(7)	2.4201(7)
Au(2)-Br(8)	2.4243(7)
Au(2)-Br(6)	2.4254(7)
Au(2)-Br(5)	2.4332(7)
O(1)-C(1)	1.213(8)
O(2)-C(13)	1.215(7)
O(3)-C(13)	1.340(8)
O(3)-C(14)	1.444(8)
N(1)-C(1)	1.380(8)
N(1)-C(2)	1.416(8)
N(2)-C(12)	1.339(8)
N(2)-C(8)	1.355(8)
C(1)-C(8)	1.505(9)
C(2)-C(3)	1.375(10)
C(2)-C(7)	1.413(9)
C(3)-C(4)	1.374(9)
C(3)-H(3A)	0.95
C(4)-C(5)	1.375(10)
C(4)-H(4A)	0.95
C(5)-C(6)	1.360(9)
C(5)-H(5A)	0.95
C(6)-C(7)	1.408(9)
C(6)-H(6A)	0.95
C(7)-C(13)	1.489(9)
C(8)-C(9)	1.368(10)
C(9)-C(10)	1.403(10)
C(9)-H(9A)	0.95
C(10)-C(11)	1.380(10)
C(10)-H(10A)	0.95
C(11)-C(12)	1.377(10)
C(11)-H(11A)	0.95
C(12)-H(12A)	0.95
C(14)-C(15)	1.516(9)
C(14)-H(14A)	0.99
C(14)-H(14B)	0.99
C(15)-C(17)	1.494(9)

C(15)-C(18)	1.501(8)
C(15)-C(16)	1.530(9)
C(16)-H(16A)	0.98
C(16)-H(16B)	0.98
C(16)-H(16C)	0.98
C(17)-H(17A)	0.98
C(17)-H(17B)	0.98
C(17)-H(17C)	0.98
C(18)-H(18A)	0.98
C(18)-H(18B)	0.98
C(18)-H(18C)	0.98
O(1W)-H(1W)	0.94(7)
O(1W)-H(2W)	0.80(7)
Br(2)-Au(1)-Br(4)	89.76(2)
Br(2)-Au(1)-Br(3)	175.09(3)
Br(4)-Au(1)-Br(3)	89.22(2)
Br(2)-Au(1)-Br(1)	90.72(2)
Br(4)-Au(1)-Br(1)	178.21(3)
Br(3)-Au(1)-Br(1)	90.44(2)
Br(7)-Au(2)-Br(8)	179.56(3)
Br(7)-Au(2)-Br(6)	90.67(2)
Br(8)-Au(2)-Br(6)	89.68(2)
Br(7)-Au(2)-Br(5)	89.17(2)
Br(8)-Au(2)-Br(5)	90.48(2)
Br(6)-Au(2)-Br(5)	179.62(3)
C(13)-O(3)-C(14)	116.3(5)
C(1)-N(1)-C(2)	126.5(6)
C(12)-N(2)-C(8)	122.2(6)
O(1)-C(1)-N(1)	126.7(6)
O(1)-C(1)-C(8)	120.2(6)
N(1)-C(1)-C(8)	113.1(6)
C(3)-C(2)-C(7)	119.7(6)
C(3)-C(2)-N(1)	124.3(6)
C(7)-C(2)-N(1)	116.0(6)
C(4)-C(3)-C(2)	120.2(7)
C(4)-C(3)-H(3A)	119.9
C(2)-C(3)-H(3A)	119.9
C(3)-C(4)-C(5)	121.1(7)
C(3)-C(4)-H(4A)	119.5
C(5)-C(4)-H(4A)	119.5
C(6)-C(5)-C(4)	119.8(6)
C(6)-C(5)-H(5A)	120.1

C(4)-C(5)-H(5A)	120.1
C(5)-C(6)-C(7)	121.0(6)
C(5)-C(6)-H(6A)	119.5
C(7)-C(6)-H(6A)	119.5
C(6)-C(7)-C(2)	118.2(6)
C(6)-C(7)-C(13)	120.9(6)
C(2)-C(7)-C(13)	120.9(6)
N(2)-C(8)-C(9)	119.5(6)
N(2)-C(8)-C(1)	111.2(6)
C(9)-C(8)-C(1)	129.3(6)
C(8)-C(9)-C(10)	118.8(7)
C(8)-C(9)-H(9A)	120.6
C(10)-C(9)-H(9A)	120.6
C(11)-C(10)-C(9)	120.5(7)
C(11)-C(10)-H(10A)	119.7
C(9)-C(10)-H(10A)	119.7
C(12)-C(11)-C(10)	118.2(7)
C(12)-C(11)-H(11A)	120.9
C(10)-C(11)-H(11A)	120.9
N(2)-C(12)-C(11)	120.7(6)
N(2)-C(12)-H(12A)	119.7
C(11)-C(12)-H(12A)	119.7
O(2)-C(13)-O(3)	122.5(6)
O(2)-C(13)-C(7)	125.4(6)
O(3)-C(13)-C(7)	112.1(6)
O(3)-C(14)-C(15)	108.2(5)
O(3)-C(14)-H(14A)	110.1
C(15)-C(14)-H(14A)	110.1
O(3)-C(14)-H(14B)	110.1
C(15)-C(14)-H(14B)	110.1
H(14A)-C(14)-H(14B)	108.4
C(17)-C(15)-C(18)	108.0(6)
C(17)-C(15)-C(14)	109.0(6)
C(18)-C(15)-C(14)	108.4(5)
C(17)-C(15)-C(16)	111.1(5)
C(18)-C(15)-C(16)	108.1(5)
C(14)-C(15)-C(16)	112.0(6)
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(15)-C(18)-H(18A)	109.5
C(15)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(15)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
H(1W)-O(1W)-H(2W)	96(7)

Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **38f**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h2 a^* U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Au(1)	15(1)	23(1)	19(1)	-3(1)	0(1)	-4(1)
Au(2)	16(1)	20(1)	20(1)	-3(1)	2(1)	-3(1)
Br(1)	24(1)	46(1)	21(1)	-12(1)	3(1)	-8(1)
Br(2)	15(1)	35(1)	33(1)	-4(1)	0(1)	-4(1)
Br(3)	15(1)	41(1)	27(1)	-13(1)	1(1)	-5(1)
Br(4)	23(1)	27(1)	23(1)	-9(1)	-2(1)	-4(1)
Br(5)	23(1)	34(1)	24(1)	-10(1)	5(1)	-8(1)
Br(6)	29(1)	29(1)	22(1)	-7(1)	4(1)	-7(1)
Br(7)	16(1)	35(1)	31(1)	-6(1)	-1(1)	-3(1)
Br(8)	16(1)	28(1)	32(1)	-8(1)	2(1)	-4(1)
O(1)	21(3)	45(3)	21(3)	-9(2)	-5(2)	-5(2)
O(2)	21(3)	30(3)	16(2)	-3(2)	2(2)	-6(2)
O(3)	20(3)	29(3)	18(3)	-3(2)	-2(2)	-2(2)
N(1)	23(3)	19(3)	20(3)	-5(3)	1(2)	-5(2)
N(2)	31(4)	19(3)	19(3)	-9(3)	3(3)	-6(3)
C(1)	24(4)	20(4)	21(4)	0(3)	0(3)	-6(3)
C(2)	22(4)	15(3)	19(4)	-3(3)	1(3)	-2(3)
C(3)	24(4)	30(4)	22(4)	-1(3)	-1(3)	-10(3)
C(4)	19(4)	21(4)	43(5)	3(3)	-1(3)	1(3)
C(5)	22(4)	25(4)	25(4)	-3(3)	2(3)	0(3)
C(6)	19(4)	21(4)	17(3)	0(3)	-3(3)	0(3)
C(7)	22(4)	13(3)	25(4)	-5(3)	4(3)	-3(3)

C(8)	27(4)	18(4)	23(4)	-2(3)	4(3)	-5(3)
C(9)	32(4)	31(4)	30(4)	-14(4)	1(3)	1(3)
C(10)	32(5)	33(4)	32(4)	-8(4)	-1(3)	-5(4)
C(11)	29(4)	30(4)	31(4)	-10(4)	6(3)	-8(3)
C(12)	26(4)	30(4)	22(4)	-10(3)	2(3)	-7(3)
C(13)	21(4)	17(3)	27(4)	-5(3)	-1(3)	-3(3)
C(14)	17(4)	23(4)	28(4)	-2(3)	-1(3)	3(3)
C(15)	17(4)	21(4)	23(4)	-6(3)	7(3)	1(3)
C(16)	39(5)	30(4)	23(4)	-5(3)	0(3)	2(4)
C(17)	28(4)	31(4)	28(4)	-4(4)	0(3)	-3(3)
C(18)	10(3)	11(3)	14(3)	-3(3)	5(2)	-3(2)
O(1W)	29(3)	38(3)	33(3)	-15(3)	11(3)	-7(3)

Hydrogen coordinates (x 104) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)
for **38f**.

	x	y	z	U(eq)
H(3A)	12785	905	4737	30
H(4A)	15022	117	3986	35
H(5A)	14542	-277	2776	30
H(6A)	11819	171	2290	24
H(9A)	6192	2601	4433	37
H(10A)	3689	3473	5043	39
H(11A)	3805	3856	6297	35
H(12A)	6424	3323	6933	30
H(14A)	6397	2184	1977	29
H(14B)	6690	708	1916	29
H(16A)	8904	1151	52	48
H(16B)	8598	41	749	48
H(16C)	9906	918	851	48
H(17A)	4840	2485	752	45
H(17B)	5483	1059	611	45
H(17C)	5837	2237	-25	45
H(18A)	6830	3777	833	18
H(18B)	8139	3327	187	18
H(18C)	8771	3157	1058	18
H(1W)	4080(90)	4860(60)	1290(40)	30(20)
H(2W)	5480(100)	5280(70)	1270(50)	40(30)

Hydrogen bonds for **38f** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	\angle (DHA)
O(1W)-H(1W)...Br(5)	0.94(7)	2.72(7)	3.521(6)	143(5)
O(1W)-H(1W)...Br(2)#1	0.94(7)	2.98(7)	3.515(5)	118(5)
O(1W)-H(1W)...Br(7)	0.94(7)	3.06(7)	3.718(6)	129(5)
O(1W)-H(2W)...Br(3)	0.80(7)	2.96(7)	3.583(5)	136(7)
O(1W)-H(2W)...Br(8)#2	0.80(7)	3.06(8)	3.702(6)	140(7)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 x+1,y,z

Crystal data and structure refinement for **39a**.

Empirical formula	$C_{22} H_{16} Cl Cu N_3 O_2$		
Formula weight	453.37		
Temperature	150(2) K		
Wavelength	0.71073 Å		
Crystal system	Orthorhombic		
Space group	P 21 21 21		
Unit cell dimensions	$a = 5.0663(6)$ Å	$\alpha = 90^\circ$.	
	$b = 17.581(2)$ Å	$\beta = 90^\circ$.	
	$c = 20.534(3)$ Å	$\gamma = 90^\circ$.	
Volume	$1829.0(4)$ Å ³		
Z	4		
Density (calculated)	1.646 Mg/m ³		
Absorption coefficient	1.366 mm ⁻¹		
F(000)	924		
Crystal size	0.25 x 0.07 x 0.05 mm ³		
Theta range for data collection	1.52 to 27.61°.		
Index ranges	$-6 \leq h \leq 6, -22 \leq k \leq 22, -26 \leq l \leq 26$		
Reflections collected	17112		
Independent reflections	4241 [R(int) = 0.0448]		
Completeness to theta = 27.61°	99.80%		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.7456 and 0.6982		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	4241 / 0 / 263		
Goodness-of-fit on F ²	1.038		
Final R indices [I>2sigma(I)]	R1 = 0.0288, wR2 = 0.0608		
R indices (all data)	R1 = 0.0377, wR2 = 0.0634		
Absolute structure parameter	0.006(11)		
Largest diff. peak and hole	0.246 and -0.302 e.Å ⁻³		

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **39a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cu(1)	9677(1)	9209(1)	8400(1)	16(1)
Cl(1)	12333(1)	9318(1)	9297(1)	25(1)
O(1)	2776(3)	8553(1)	7632(1)	22(1)
O(2)	11551(4)	11084(1)	7298(1)	23(1)
N(1)	7994(4)	8264(1)	8731(1)	18(1)
N(2)	6969(4)	9108(1)	7706(1)	16(1)
N(3)	10777(4)	10189(1)	8055(1)	16(1)
C(1)	8852(5)	7795(2)	9204(1)	22(1)
C(2)	7577(6)	7122(2)	9342(1)	27(1)
C(3)	5328(6)	6926(2)	8999(1)	30(1)
C(4)	4428(5)	7420(1)	8524(1)	24(1)
C(5)	5801(4)	8082(1)	8403(1)	18(1)
C(6)	5015(5)	8621(1)	7867(1)	17(1)
C(7)	7019(5)	9463(1)	7091(1)	16(1)
C(8)	5458(5)	9214(2)	6570(1)	23(1)
C(9)	5780(5)	9499(2)	5945(1)	25(1)
C(10)	7684(6)	10043(2)	5811(1)	26(1)
C(11)	9189(5)	10319(2)	6317(1)	23(1)
C(12)	8860(5)	10050(1)	6959(1)	17(1)
C(13)	10427(5)	10412(1)	7463(1)	16(1)
C(14)	13185(5)	11326(2)	7850(1)	22(1)
C(15)	12547(5)	12145(1)	8041(1)	23(1)
C(16)	10589(5)	12061(1)	8589(1)	19(1)
C(17)	9088(5)	12624(2)	8886(1)	25(1)
C(18)	7301(5)	12415(2)	9365(1)	27(1)
C(19)	7025(5)	11657(2)	9551(1)	25(1)
C(20)	8581(5)	11096(2)	9266(1)	21(1)
C(21)	10371(5)	11304(1)	8791(1)	17(1)
C(22)	12216(4)	10804(1)	8400(1)	18(1)

Bond lengths [Å] and angles [°] for **39a**

Cu(1)-N(3)	1.944(2)
Cu(1)-N(2)	1.987(2)
Cu(1)-N(1)	1.988(2)
Cu(1)-Cl(1)	2.2898(7)
Cu(1)-O(1)#1	2.5060(18)
O(1)-C(6)	1.238(3)
O(2)-C(13)	1.355(3)
O(2)-C(14)	1.467(3)
N(1)-C(5)	1.337(3)
N(1)-C(1)	1.346(3)
N(2)-C(6)	1.351(3)
N(2)-C(7)	1.408(3)
N(3)-C(13)	1.289(3)
N(3)-C(22)	1.484(3)
C(1)-C(2)	1.377(4)
C(1)-H(1A)	0.95
C(2)-C(3)	1.383(4)
C(2)-H(2A)	0.95
C(3)-C(4)	1.384(4)
C(3)-H(3A)	0.95
C(4)-C(5)	1.379(3)
C(4)-H(4A)	0.95
C(5)-C(6)	1.506(3)
C(7)-C(8)	1.400(3)
C(7)-C(12)	1.417(3)
C(8)-C(9)	1.387(4)
C(8)-H(8A)	0.95
C(9)-C(10)	1.385(4)
C(9)-H(9A)	0.95
C(10)-C(11)	1.377(4)
C(10)-H(10A)	0.95
C(11)-C(12)	1.409(3)
C(11)-H(11A)	0.95
C(12)-C(13)	1.452(3)
C(14)-C(15)	1.528(4)
C(14)-C(22)	1.536(4)
C(14)-H(14A)	1
C(15)-C(16)	1.507(4)
C(15)-H(15A)	0.99
C(15)-H(15B)	0.99

C(16)-C(17)	1.390(4)
C(16)-C(21)	1.399(3)
C(17)-C(18)	1.386(4)
C(17)-H(17A)	0.95
C(18)-C(19)	1.394(4)
C(18)-H(18A)	0.95
C(19)-C(20)	1.391(4)
C(19)-H(19A)	0.95
C(20)-C(21)	1.381(3)
C(20)-H(20A)	0.95
C(21)-C(22)	1.514(3)
C(22)-H(22A)	1
N(3)-Cu(1)-N(2)	90.89(8)
N(3)-Cu(1)-N(1)	171.26(9)
N(2)-Cu(1)-N(1)	82.79(9)
N(3)-Cu(1)-Cl(1)	92.92(6)
N(2)-Cu(1)-Cl(1)	172.25(6)
N(1)-Cu(1)-Cl(1)	92.66(6)
N(3)-Cu(1)-O(1)#1	89.95(7)
N(2)-Cu(1)-O(1)#1	86.58(7)
N(1)-Cu(1)-O(1)#1	95.67(7)
Cl(1)-Cu(1)-O(1)#1	100.16(5)
C(13)-O(2)-C(14)	107.29(19)
C(5)-N(1)-C(1)	119.0(2)
C(5)-N(1)-Cu(1)	112.56(17)
C(1)-N(1)-Cu(1)	128.35(19)
C(6)-N(2)-C(7)	120.9(2)
C(6)-N(2)-Cu(1)	112.77(16)
C(7)-N(2)-Cu(1)	126.24(16)
C(13)-N(3)-C(22)	107.2(2)
C(13)-N(3)-Cu(1)	124.97(16)
C(22)-N(3)-Cu(1)	127.78(16)
N(1)-C(1)-C(2)	121.5(3)
N(1)-C(1)-H(1A)	119.2
C(2)-C(1)-H(1A)	119.2
C(1)-C(2)-C(3)	119.7(3)
C(1)-C(2)-H(2A)	120.1
C(3)-C(2)-H(2A)	120.1
C(2)-C(3)-C(4)	118.3(3)
C(2)-C(3)-H(3A)	120.8
C(4)-C(3)-H(3A)	120.8
C(5)-C(4)-C(3)	119.3(3)

C(5)-C(4)-H(4A)	120.3
C(3)-C(4)-H(4A)	120.3
N(1)-C(5)-C(4)	122.0(2)
N(1)-C(5)-C(6)	116.0(2)
C(4)-C(5)-C(6)	121.9(2)
O(1)-C(6)-N(2)	129.6(2)
O(1)-C(6)-C(5)	117.8(2)
N(2)-C(6)-C(5)	112.6(2)
C(8)-C(7)-N(2)	122.4(2)
C(8)-C(7)-C(12)	116.9(2)
N(2)-C(7)-C(12)	120.4(2)
C(9)-C(8)-C(7)	121.8(2)
C(9)-C(8)-H(8A)	119.1
C(7)-C(8)-H(8A)	119.1
C(10)-C(9)-C(8)	120.9(2)
C(10)-C(9)-H(9A)	119.5
C(8)-C(9)-H(9A)	119.5
C(11)-C(10)-C(9)	118.6(2)
C(11)-C(10)-H(10A)	120.7
C(9)-C(10)-H(10A)	120.7
C(10)-C(11)-C(12)	121.5(2)
C(10)-C(11)-H(11A)	119.3
C(12)-C(11)-H(11A)	119.3
C(11)-C(12)-C(7)	120.1(2)
C(11)-C(12)-C(13)	117.1(2)
C(7)-C(12)-C(13)	122.8(2)
N(3)-C(13)-O(2)	116.3(2)
N(3)-C(13)-C(12)	127.9(2)
O(2)-C(13)-C(12)	115.7(2)
O(2)-C(14)-C(15)	110.6(2)
O(2)-C(14)-C(22)	102.38(19)
C(15)-C(14)-C(22)	107.9(2)
O(2)-C(14)-H(14A)	111.8
C(15)-C(14)-H(14A)	111.8
C(22)-C(14)-H(14A)	111.8
C(16)-C(15)-C(14)	103.8(2)
C(16)-C(15)-H(15A)	111
C(14)-C(15)-H(15A)	111
C(16)-C(15)-H(15B)	111
C(14)-C(15)-H(15B)	111
H(15A)-C(15)-H(15B)	109
C(17)-C(16)-C(21)	120.3(2)
C(17)-C(16)-C(15)	128.2(2)

C(21)-C(16)-C(15)	111.6(2)
C(18)-C(17)-C(16)	118.7(3)
C(18)-C(17)-H(17A)	120.6
C(16)-C(17)-H(17A)	120.6
C(17)-C(18)-C(19)	120.9(3)
C(17)-C(18)-H(18A)	119.6
C(19)-C(18)-H(18A)	119.6
C(20)-C(19)-C(18)	120.4(3)
C(20)-C(19)-H(19A)	119.8
C(18)-C(19)-H(19A)	119.8
C(21)-C(20)-C(19)	118.8(2)
C(21)-C(20)-H(20A)	120.6
C(19)-C(20)-H(20A)	120.6
C(20)-C(21)-C(16)	120.9(2)
C(20)-C(21)-C(22)	128.8(2)
C(16)-C(21)-C(22)	110.3(2)
N(3)-C(22)-C(21)	111.93(18)
N(3)-C(22)-C(14)	104.0(2)
C(21)-C(22)-C(14)	103.94(19)
N(3)-C(22)-H(22A)	112.1
C(21)-C(22)-H(22A)	112.1
C(14)-C(22)-H(22A)	112.1

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z

Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **39a**.

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h2 a^* U11 + \dots + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Cu(1)	17(1)	14(1)	16(1)	1(1)	-2(1)	0(1)
Cl(1)	33(1)	21(1)	21(1)	1(1)	-10(1)	2(1)
O(1)	15(1)	26(1)	25(1)	-2(1)	-1(1)	0(1)
O(2)	31(1)	23(1)	17(1)	2(1)	-2(1)	-12(1)
N(1)	18(1)	19(1)	17(1)	2(1)	3(1)	1(1)
N(2)	16(1)	15(1)	17(1)	0(1)	-1(1)	1(1)
N(3)	15(1)	15(1)	18(1)	-1(1)	-1(1)	-1(1)
C(1)	23(1)	24(1)	18(1)	2(1)	4(1)	5(1)
C(2)	34(2)	22(1)	24(1)	5(1)	11(1)	6(1)
C(3)	34(2)	21(1)	36(2)	2(1)	13(1)	-1(1)
C(4)	23(1)	22(1)	28(1)	-3(1)	6(1)	-2(1)
C(5)	15(1)	18(1)	20(1)	-3(1)	8(1)	2(1)
C(6)	13(1)	17(1)	20(1)	-5(1)	3(1)	3(1)
C(7)	16(1)	14(1)	19(1)	-1(1)	1(1)	5(1)
C(8)	23(1)	23(1)	22(1)	-3(1)	-3(1)	-3(1)
C(9)	29(2)	26(1)	20(1)	-5(1)	-9(1)	1(1)
C(10)	38(2)	23(1)	15(1)	-1(1)	-2(1)	2(1)
C(11)	29(2)	19(1)	21(1)	1(1)	1(1)	-3(1)
C(12)	19(1)	14(1)	18(1)	-1(1)	-1(1)	2(1)
C(13)	17(1)	13(1)	18(1)	0(1)	5(1)	-1(1)
C(14)	19(1)	26(1)	21(1)	1(1)	-2(1)	-9(1)
C(15)	27(1)	19(1)	22(1)	3(1)	-4(1)	-9(1)
C(16)	22(1)	19(1)	17(1)	1(1)	-7(1)	-4(1)
C(17)	31(2)	16(1)	28(1)	2(1)	-10(1)	0(1)
C(18)	26(1)	27(2)	28(1)	-7(1)	-4(1)	8(1)
C(19)	24(2)	34(2)	18(1)	-2(1)	0(1)	-2(1)
C(20)	25(1)	19(1)	19(1)	1(1)	-3(1)	-3(1)
C(21)	19(1)	17(1)	16(1)	-1(1)	-4(1)	-3(1)
C(22)	17(1)	17(1)	20(1)	-1(1)	-4(1)	-4(1)

Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **39a**.

	x	y	z	U(eq)
H(1A)	10372	7931	9449	26
H(2A)	8240	6794	9671	32
H(3A)	4423	6464	9088	36
H(4A)	2880	7304	8282	29
H(8A)	4143	8840	6647	27
H(9A)	4678	9319	5604	30
H(10A)	7946	10222	5380	31
H(11A)	10477	10698	6232	28
H(14A)	15110	11254	7761	26
H(15A)	14151	12416	8189	27
H(15B)	11762	12426	7670	27
H(17A)	9284	13142	8764	30
H(18A)	6250	12794	9569	32
H(19A)	5767	11522	9874	30
H(20A)	8416	10580	9396	25
H(22A)	13704	10603	8670	21

Torsion angles [°] for **39a**.

N(2)-Cu(1)-N(1)-C(5)	-7.70(16)
Cl(1)-Cu(1)-N(1)-C(5)	165.99(16)
O(1)#1-Cu(1)-N(1)-C(5)	-93.52(16)
N(2)-Cu(1)-N(1)-C(1)	169.1(2)
Cl(1)-Cu(1)-N(1)-C(1)	-17.2(2)
O(1)#1-Cu(1)-N(1)-C(1)	83.3(2)
N(3)-Cu(1)-N(2)-C(6)	-158.17(16)
N(1)-Cu(1)-N(2)-C(6)	15.77(16)
O(1)#1-Cu(1)-N(2)-C(6)	111.94(16)
N(3)-Cu(1)-N(2)-C(7)	24.57(19)
N(1)-Cu(1)-N(2)-C(7)	-161.5(2)
O(1)#1-Cu(1)-N(2)-C(7)	-65.33(19)
N(2)-Cu(1)-N(3)-C(13)	-23.1(2)
Cl(1)-Cu(1)-N(3)-C(13)	163.6(2)
O(1)#1-Cu(1)-N(3)-C(13)	63.4(2)
N(2)-Cu(1)-N(3)-C(22)	158.84(19)
Cl(1)-Cu(1)-N(3)-C(22)	-14.41(19)
O(1)#1-Cu(1)-N(3)-C(22)	-114.57(19)

C(5)-N(1)-C(1)-C(2)	2.3(4)
Cu(1)-N(1)-C(1)-C(2)	-174.28(19)
N(1)-C(1)-C(2)-C(3)	-1.5(4)
C(1)-C(2)-C(3)-C(4)	0.0(4)
C(2)-C(3)-C(4)-C(5)	0.5(4)
C(1)-N(1)-C(5)-C(4)	-1.7(4)
Cu(1)-N(1)-C(5)-C(4)	175.40(19)
C(1)-N(1)-C(5)-C(6)	-178.0(2)
Cu(1)-N(1)-C(5)-C(6)	-0.9(3)
C(3)-C(4)-C(5)-N(1)	0.3(4)
C(3)-C(4)-C(5)-C(6)	176.4(2)
C(7)-N(2)-C(6)-O(1)	-21.1(4)
Cu(1)-N(2)-C(6)-O(1)	161.5(2)
C(7)-N(2)-C(6)-C(5)	157.5(2)
Cu(1)-N(2)-C(6)-C(5)	-19.9(2)
N(1)-C(5)-C(6)-O(1)	-167.2(2)
C(4)-C(5)-C(6)-O(1)	16.5(3)
N(1)-C(5)-C(6)-N(2)	14.0(3)
C(4)-C(5)-C(6)-N(2)	-162.3(2)
C(6)-N(2)-C(7)-C(8)	-14.6(3)
Cu(1)-N(2)-C(7)-C(8)	162.44(19)
C(6)-N(2)-C(7)-C(12)	171.3(2)
Cu(1)-N(2)-C(7)-C(12)	-11.6(3)
N(2)-C(7)-C(8)-C(9)	-171.1(2)
C(12)-C(7)-C(8)-C(9)	3.1(4)
C(7)-C(8)-C(9)-C(10)	0.3(4)
C(8)-C(9)-C(10)-C(11)	-2.6(4)
C(9)-C(10)-C(11)-C(12)	1.2(4)
C(10)-C(11)-C(12)-C(7)	2.4(4)
C(10)-C(11)-C(12)-C(13)	-176.2(2)
C(8)-C(7)-C(12)-C(11)	-4.4(3)
N(2)-C(7)-C(12)-C(11)	169.9(2)
C(8)-C(7)-C(12)-C(13)	174.1(2)
N(2)-C(7)-C(12)-C(13)	-11.6(3)
C(22)-N(3)-C(13)-O(2)	4.4(3)
Cu(1)-N(3)-C(13)-O(2)	-173.95(16)
C(22)-N(3)-C(13)-C(12)	-172.1(2)
Cu(1)-N(3)-C(13)-C(12)	9.5(4)
C(14)-O(2)-C(13)-N(3)	7.0(3)
C(14)-O(2)-C(13)-C(12)	-176.0(2)
C(11)-C(12)-C(13)-N(3)	-168.0(3)
C(7)-C(12)-C(13)-N(3)	13.5(4)
C(11)-C(12)-C(13)-O(2)	15.4(3)

C(7)-C(12)-C(13)-O(2)	-163.1(2)
C(13)-O(2)-C(14)-C(15)	-129.2(2)
C(13)-O(2)-C(14)-C(22)	-14.5(2)
O(2)-C(14)-C(15)-C(16)	95.9(2)
C(22)-C(14)-C(15)-C(16)	-15.4(3)
C(14)-C(15)-C(16)-C(17)	-170.6(2)
C(14)-C(15)-C(16)-C(21)	9.1(3)
C(21)-C(16)-C(17)-C(18)	-2.8(4)
C(15)-C(16)-C(17)-C(18)	176.9(2)
C(16)-C(17)-C(18)-C(19)	0.7(4)
C(17)-C(18)-C(19)-C(20)	1.2(4)
C(18)-C(19)-C(20)-C(21)	-0.9(4)
C(19)-C(20)-C(21)-C(16)	-1.2(4)
C(19)-C(20)-C(21)-C(22)	-178.2(2)
C(17)-C(16)-C(21)-C(20)	3.1(4)
C(15)-C(16)-C(21)-C(20)	-176.7(2)
C(17)-C(16)-C(21)-C(22)	-179.4(2)
C(15)-C(16)-C(21)-C(22)	0.9(3)
C(13)-N(3)-C(22)-C(21)	98.3(2)
Cu(1)-N(3)-C(22)-C(21)	-83.4(2)
C(13)-N(3)-C(22)-C(14)	-13.3(2)
Cu(1)-N(3)-C(22)-C(14)	165.05(16)
C(20)-C(21)-C(22)-N(3)	55.3(3)
C(16)-C(21)-C(22)-N(3)	-122.0(2)
C(20)-C(21)-C(22)-C(14)	166.9(2)
C(16)-C(21)-C(22)-C(14)	-10.4(3)
O(2)-C(14)-C(22)-N(3)	16.4(2)
C(15)-C(14)-C(22)-N(3)	133.2(2)
O(2)-C(14)-C(22)-C(21)	-100.8(2)
C(15)-C(14)-C(22)-C(21)	15.9(2)

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z

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