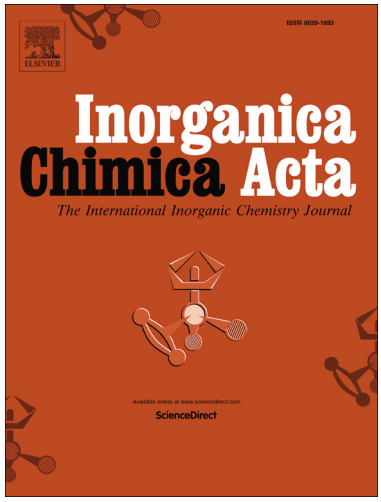

Research paper

Chiral 1,8-Naphthyridine Based Ligands: Syntheses and Characterization of Di- and Tetranuclear Copper (I) and Silver (I) Complexes

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Chiral 1,8-Naphthyridine Based Ligands: Syntheses and Characterization of Di- and Tetranuclear Copper (I) and Silver (I) Complexes

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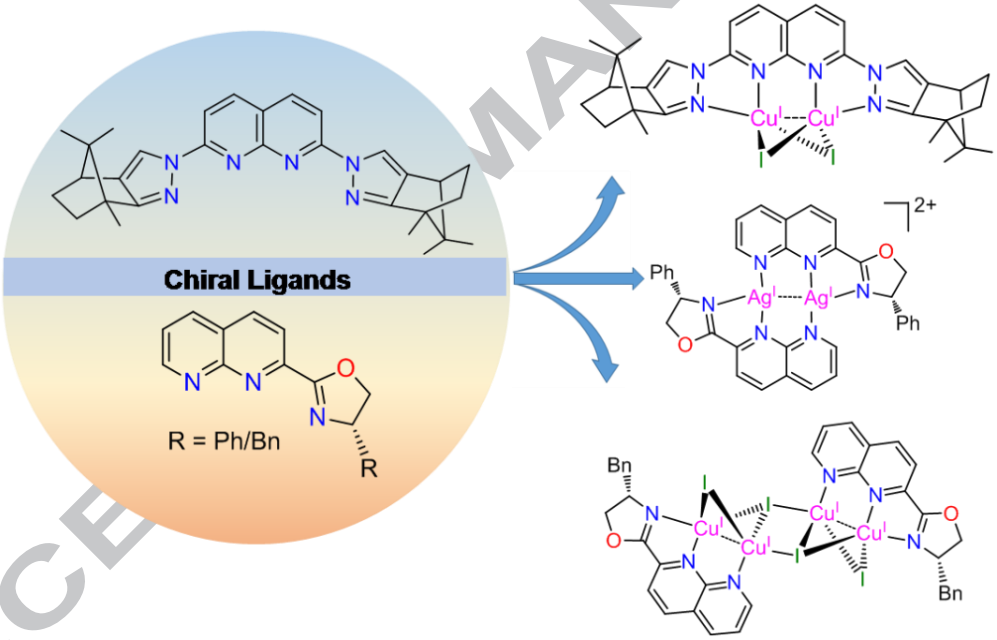
$ Dedicated to Prof. Rabindranath Mukherjee.

Highlights

- Naphthyridine-functionalized oxazoline and camphor-pyrazole chiral ligands are synthesized
- Di- and tetranuclear Cu(I) and Ag(I) complexes containing chiral ligands are structurally characterized
- Each ligand displays bridge-chelate coordination motif holding two metal centers in close proximity
- A combination of Cu salt and chiral camphor-pyrazole ligand affords appreciable yields for asymmetric transformations but with very low enantioselectivity

Graphical Abstract



Abstract

Oxazoline and camphor-pyrazole units are introduced on the 1,8-naphthyridine scaffold to access chiral ligands L^1, L^2 and L^3. Metalation of these chiral ligands with Cu(I) and Ag(I) precursors afforded di- and tetranuclear complexes $[Cu_4I_4(L^1)_2]$ (**1**), $[Cu_4I_4(L^2)_2]$ (**2**), $[Cu_2I_2(L^3)]$ (**3**), $[Cu_2I(L^2)_2](OTf)$ (**4**), $[Ag_2(L^1)_2](OTf)_2$ (**5**) and $[Ag_4(L^2)_4Br](OTf)_3$ (**6**), containing $[M_4X_n]$ (n = 1,4 and X = Br, I) or $[M_2X_n]$ (n = 0, 1, 2 and X = I) core. All complexes are structurally characterized. Naphthyridine-derived ligands reveal bridge-chelate coordination motif and hold two metal centers in close proximity. The tetranuclear complexes are dimer of dinuclear complexes bridged by the halides. Electronic absorption and emission spectra of copper complexes are reported. Catalytic utility of all complexes are examined for asymmetric transformations but they showed poor activity probably due to limited solubility and coordinative saturation at the metal centers. The best results are obtained with [L^3/Cu salt] combination for cyclopropanation of styrene, N-H bond insertion and nitroaldol (Henry) reactions with very low enantioselectivity.

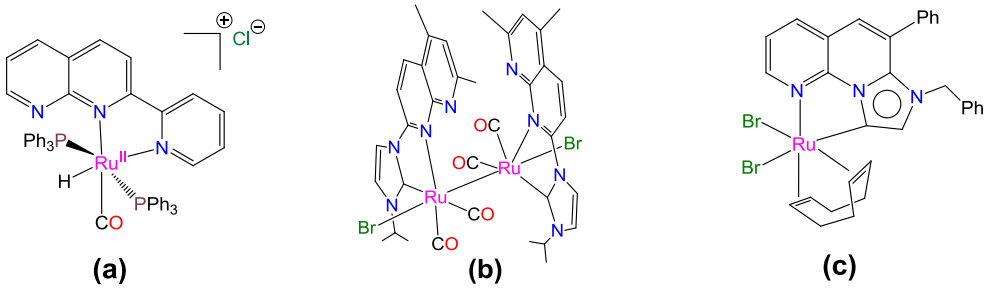
Keywords

1,8-naphthyridine, Chiral ligand, Oxazoline, Camphor-pyrazole, Copper and Silver Complexes

Introduction

1,8-naphthyridine (NP) is a useful scaffold with wide applications in coordination chemistry, supramolecular architectures, organometallics and biomedical sciences.[1]·[2]·[3]·[4] The *syn, syn* coordination motif of NP skeleton holds two metal centers in close proximity. Functionalization at 2 and 7 position of NP has afforded ligands with varied stereo-electronic properties capable of supporting a range of unusual bimetallic constructs. Uyeda group has reported a low-valent Ni(I)−Ni(I) complex [(NDI)Ni_2(C_6H_6)] stabilized by redox active naphthyridine−diimine (NDI) pincer ligand and studied different organic transformation reactions, including selective cyclotrimerization, hydrosilyation of terminal alkynes, strain-induced ring-opening reactions on dinickel platform.[5] Lippard and coworkers employed functionalized NP ligands to construct several bimetallic complexes involving 3d metals for mimicking metalloenzymes.[6] Diiron complexes supported by 2,7-bis{bis[2-(2-pyridyl)ethyl]aminomethyl}-1,8-naphthyridine (BPEAN) and its derivatives were used for studying O_2 activation.[7] Tilley group designed dinucleating 2,7-bis(di(2-pyridyl)fluoromethyl)-1,8-naphthyridine (DPFN) for the synthesis of several 3d metal complexes.[8] Further modification led to 2,7-bis(1,1-dipyridylethyl)-1,8-naphthyridine (dpen) which afforded an unusual $\mu-\eta 1:\eta 1$ acetonitrile-bridged dicopper complex that exhibits a three-center two-electron bonding interaction involving acetonitrile.[9] Suitably modified NP ligands have been used for making different dimetal and metal-chain complexes, studying inter-ligand electron transfers and a multitude of other purposes.[10]

We have developed a range of NP functionalized ligands over the years that are employed in coordination chemistry and catalysis.[11] Introduction of ferrocene unit to NP afforded ligands, which upon metalation with divalent transition metal ions provided an array of mixed-metal complexes.[12] A dipalladium(I) complex is accessed by amide-linked naphthyridine-ferrocene hybrid ligands featuring short metal–metal distance.[13] The presence of free nitrogen, offered by suitably designed NP scaffold, in the vicinity of a metal ion is exploited for water activation.[14] By using a pyridine-functionalized NP ligand (py-NP), the catalytic utility of $[RuH(CO)(py\text{-}NP)(PPh_3)_2]Cl$ for direct conversion of alcohols to the corresponding acids with alkaline water is studied (Scheme 1a).[15] Exploiting the same strategy, water-mediated oxidation of metal-coordinated olefin to carbonyl on an iridium center is reported by us.[16] An unsupported diruthenium (I,I) complex incorporating N-heterocyclic carbene (NHC) functionalized NP ligands is used for carbene transfer reaction at site *trans* to the metal-metal single bond (Scheme 1b).[17] A fused imidazo[1,2-a][1,8]naphthyridine based mesoionic NHC (MIC) ligand was designed that upon metalation afforded $[Ru(MIC)(COD)Br_2]$, which showed an excellent catalytic activity for selective C=C bond scission of olefins to aldehydes (Scheme 1c).[18] Recently, a ruthenium catalyst incorporating pyrazole-functionalized NP ligand is shown to catalyze oxidant-free and acceptor-less selective double dehydrogenation of primary amines to nitriles.[19]



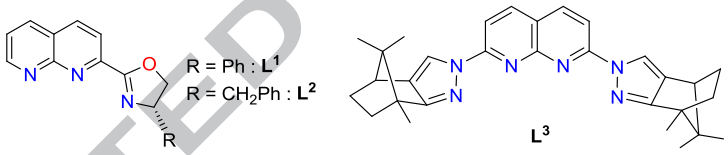
(a) *ACS Catal.* **2017** Water activation

(b) *Organometallics,* **2011** Carbene transfer reaction

(c) *JACS.* **2014** Oxidative cleavage of alkene

Scheme 1. Selected complexes containing 1,8-naphthyridine functionalized ligand scaffolds employed in catalysis.

Despite an impressive diversity of the NP ligands, chiral adaptions are rarely reported. Although pyridine derivatives containing chiral oxazoline[20], imidazoline[21] and camphor-pyrazole[22] are extensively used in asymmetric catalysis, only a handful of NP variants are known in the literature.[23] In our quest to expand the scope of NP ligands in deriving new structures and in organometallic catalysis, we have introduced oxazoline and camphor-pyrazole chiral auxiliaries to NP. Herein, we report the syntheses of naphthyridine based chiral ligands (**L^1**–**L^3**, Scheme 2). Use of appropriate stoichiometry of the ligands with different copper and silver precursors have afforded several di- and tetranuclear complexes. Catalytic asymmetric transformations are attempted using these newly synthesized complexes.



Scheme 2. Chiral oxazoline and camphor-pyrazole based NP ligands employed in this work.

Results and discussion

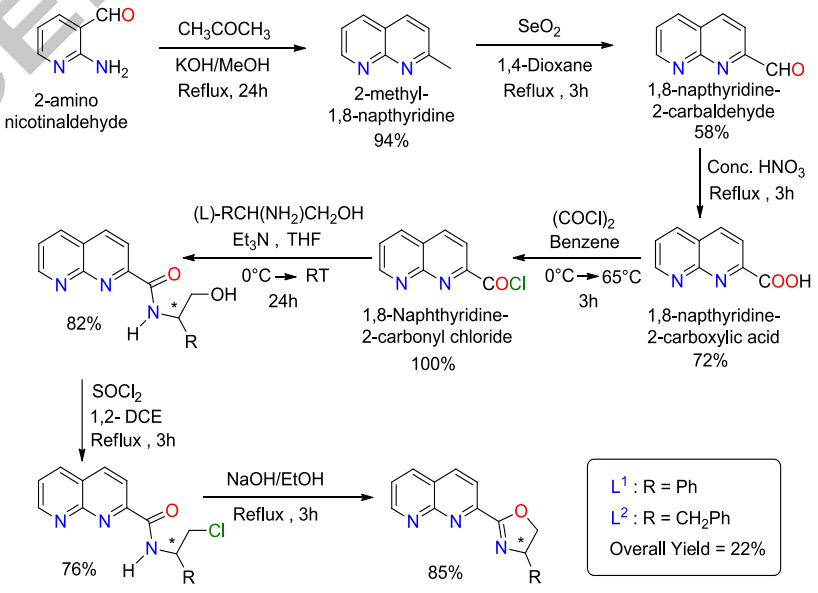
Syntheses of ligands L^1–L^3

Oxazoline unit was introduced to NP following a multi-step synthesis illustrated in Scheme 3. Several procedures are available in the literature to construct the oxazoline ring.[24] Coupling between appropriate carboxylic acid and optically active amino alcohol appears to be more general and convenient. At first, 1,8-napthyridine-2-carboxylic acid was synthesized following the literature procedure.[19,][25] It was then

converted to the corresponding carbonyl chloride by treatment with oxalyl chloride. Subsequent coupling with optically active amino alcohols produced hydroxy amide derivative. Chirality of the amino alcohol was incorporated to the ligand in this step. The hydroxy group of the amide derivative was then converted to a good chloro leaving group by treatment with $SOCl_2$. Base induced cyclization of chloro-amide in the final step gave the desired oxazoline ligands **L**^{1} and **L**^{2} in 22% overall yield.

Both ligands were characterized by different spectroscopic techniques. The ^{1}H NMR spectrum of **L**^{1} (Fig. S8) shows five naphthyridine protons at the downfield region ranging from δ 8.24–9.21 ppm. Five phenyl protons appear together at δ 7.34–7.39 ppm. The proton at the chiral center appears at δ 5.51 ppm, whereas peaks at δ 4.97 and 4.47 ppm correspond to two diastereototopic CH_2 protons. The ESI–MS spectrum shows a signal at *m/z* 276.1136 that is assigned for $[M+H]^+$.

A similar ^{1}H NMR spectrum is observed for **L**^{2} with additional diastereotopic benzylic CH_2 protons at δ 3.28 and 2.81 ppm (Fig. S9). The ESI–MS spectrum at *m/z* 290.1290 corresponds to the $[M+H]^+$ ion.

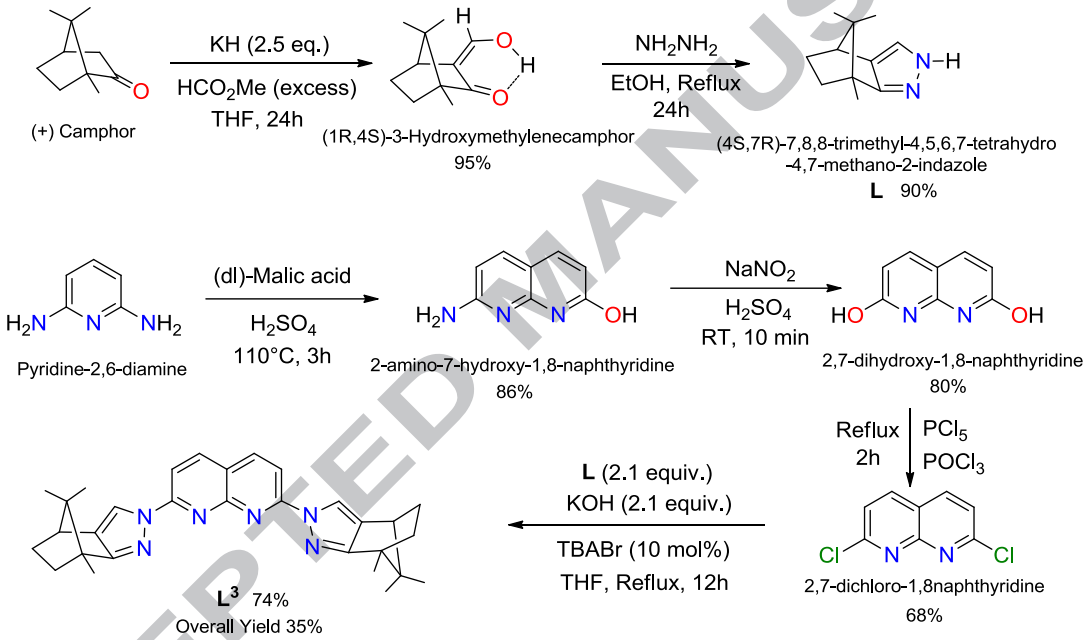


Scheme 3. Synthesis of oxazoline based ligands **L**^{1} and **L**^{2}.

Synthesis of **L^3** involves coupling between 2,7-dichloro-1,8-naphthyridine[26] with two equivalents of camphor-pyrazole [27] (Scheme 4). At first, commercially available optically active (+)-camphor was converted to 1,3-dicarbonyl compound, which remains predominantly in the enol form, by treatment with excess methyl formate and KH. In the next step, (1R,4S)-3-Hydroxymethylenecamphor was treated with hydrazine hydrate to form camphor-pyrazole ring (**L**). In a separate synthesis, treatment of 2,6-diaminopyridine with (*dl*)-malic acid in conc. H_2SO_4 produced 2-amino-7-hydroxy-1,8-naphthyridine which after diazotization by $NaNO_2$ in conc. H_2SO_4 gave 2,7-dihydroxy-1,8-naphthyridine. It was then converted to 2,7-dichloro-1,8-naphthyridine by treatment with PCl_5 and $POCl_3$ in refluxing condition. Finally, two equivalents of **L** was refluxed with one equivalent of 2,7-dichloro-1,8-naphthyridine in THF in presence of two equivalents of KOH and 10 mol% of tetrabutylammonium bromide (TBABr) as catalyst to produce ligand **L^3** in 35% overall yield.

^{1}H NMR spectrum in $CDCl_3$ discloses symmetric structure for the ligand **L^3** (Fig. S10). One camphor-pyrazole proton and two naphthyridine protons of the symmetric half appear as two singlets respectively at δ = 8.46 and 8.09 ppm in a ratio 1:2. This is in contrast to two separate doublets exhibited by similar naphthyridine based ligands. In $CDCl_3$, the naphthyridine and pyrazole units remain *trans* to each other (as in X-ray structure), thereby allowing intramolecular H-bonding interaction between pyrazole nitrogen and naphthyridine hydrogen (see Fig. S10). As a result, the *meta*-hydrogen is deshielded and appears together with *para*-hydrogen as a singlet. However, this

degeneracy is removed when the spectrum is recorded in a mixed solvent 1:1 $CD_3OD/CDCl_3$. The ligand adapts a *cis* configuration supported by intermolecular hydrogen bond interactions with methanol molecules (Fig. S11). Consequently, two naphthyridine protons are observed as two doublets. The aliphatic region contains three distinct singlets for three methyl groups, one multiplet for CH proton at the downfield region and four multiplets for four diastereotopic CH_2 protons. The ESI–MS spectrum at m/z 479.2925 corresponds to the $[M+H]^+$ ion.



Scheme 4. Synthesis of **L**^{3}.

Ligand **L**^{3} was also characterized by X-ray crystallography. The molecular structure of **L**^{3} (Fig.1) reveals anti-planar conformation of the naphthyridine and camphor-pyrazole rings. It reveals the possibility of hydrogen bonding interaction between N and H atoms involving both the naphthyridine and camphor-pyrazole rings (N1···H9, N4···H2, N2···H20, N6···H7).

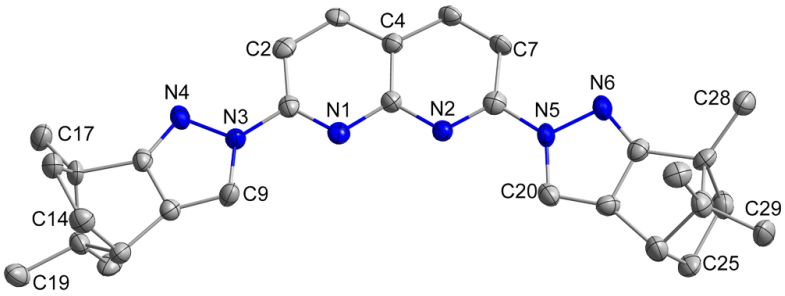
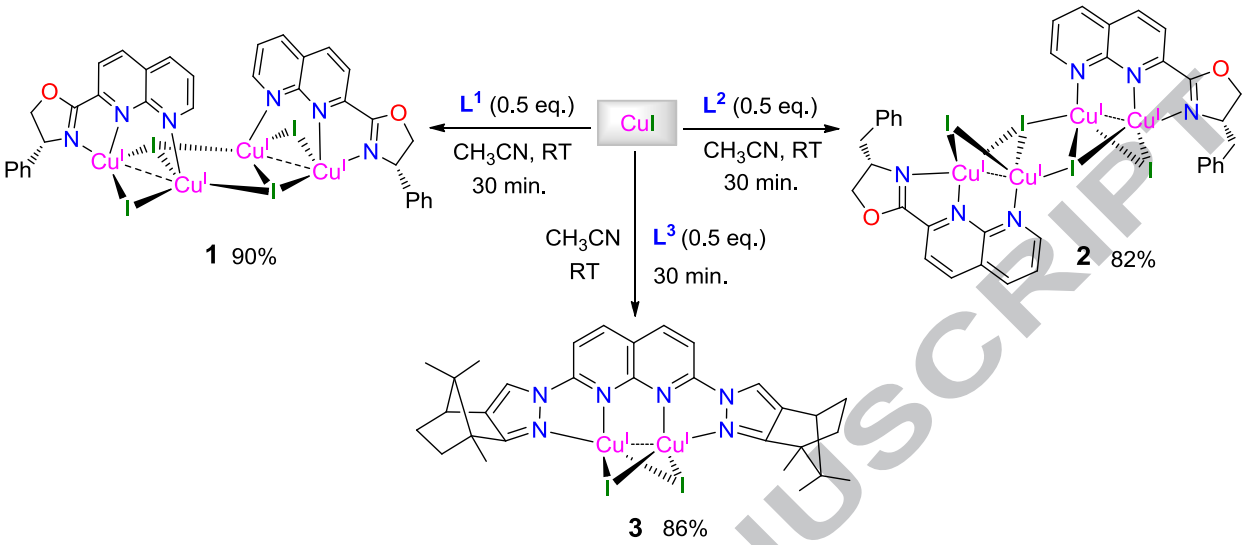


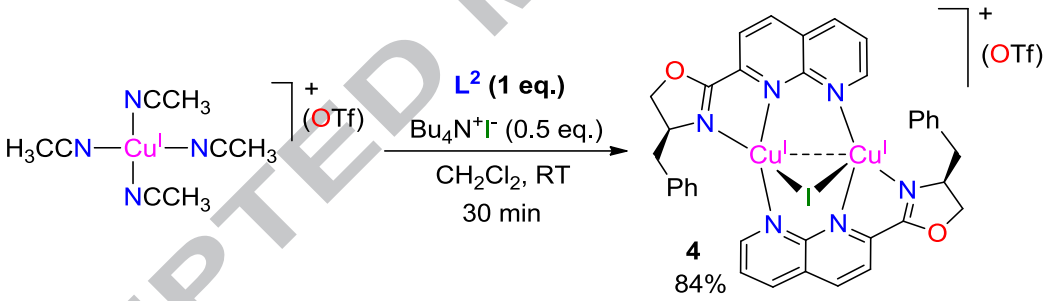
Fig. 1. Molecular structure of $\mathbf{L^3}$ with important atoms labeled. Hydrogen atoms have been omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level.

Cu and Ag complexes 1–6

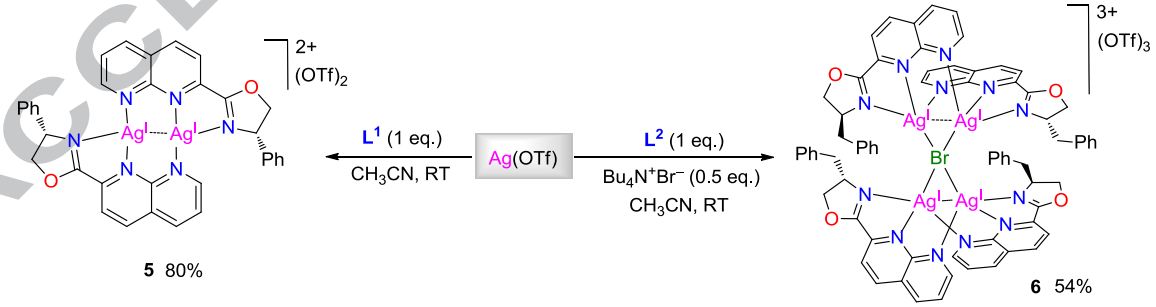
Treatment of $\mathbf{L^1}$–$\mathbf{L^3}$ separately with CuI in acetonitrile in a molar ratio 1:2 at room temperature afforded complexes $[Cu_4I_4(L^1)_2]$ (**1**), $[Cu_4I_4(L^2)_2]$ (**2**) and $[Cu_2I_2(L^3)]$ (**3**), within 30 minutes as dark red solids in high yields of 90%, 82% and 86%, respectively (Scheme 5). Use of $[Cu(CH_3CN)_4](OTf)$ with $\mathbf{L^2}$ in a ratio 1:1 and subsequent anion exchange with tetrabutylammonium iodide resulted in the formation of discrete dinuclear iodide-bridged complex $[Cu_2(L^2)_2(I)](OTf)$ (**4**) in 84% yield (Scheme 6). Similar types of iodide-bridged di- and tetranuclear copper complexes with chiral Pybox ligands are reported in literature.[28] Treatment of $\mathbf{L^1}$ and $\mathbf{L^2}$ ligands with Ag(OTf) in a molar ratio 1:1 produced disilver complex $[Ag_2(L^1)_2](OTf)_2$ (**5**) (80% yield) and bromide-bridged tetrasilver complex $[Ag_4(L^2)_4(Br)](OTf)_3$ (**6**) (54% yield) respectively (Scheme 7). Same reaction with $\mathbf{L^3}$ ligand resulted in the formation of insoluble polymeric metal complex which could not be characterized.



Scheme 5. Syntheses of copper complexes **1**–**3**.



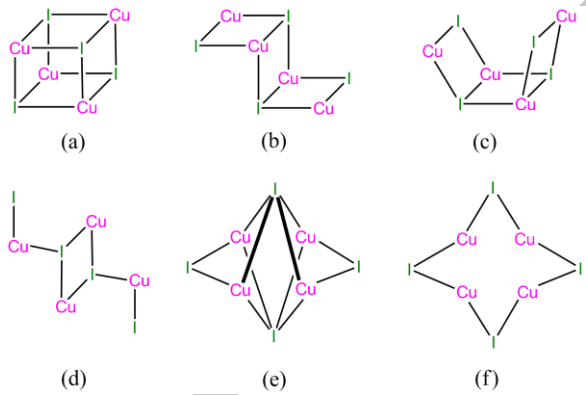
Scheme 6. Synthesis of copper complex **4**.



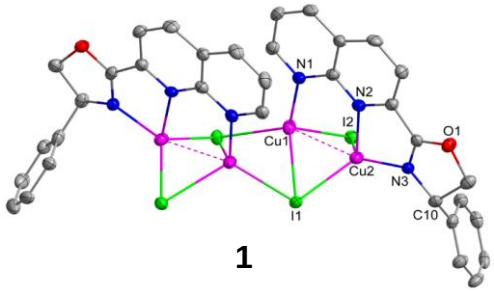
Scheme 7. Syntheses of silver complexes **5** and **6**.

Complexes **1**–**6** were characterized by single crystal X-ray crystallography which shows tetranuclear structures for complexes **1**, **2** and **6**, and discrete dinuclear structures for complexes **3**, **4** and **5** (Fig. 2) Molecular structures of complexes **1** and **2**, depicted in Fig. 2, contain $[Cu_4I_4]$ core, but the disposition of the ligands in two complexes are opposite. Complex **1** crystallizes in an orthorhombic chiral space group $P2_12_12$, whereas complex **2** crystallizes in triclinic $P1$ space group. Careful examination of the crystal structure of **1** reveals a crystallographically imposed C2 axis which passes through the midpoint between two central copper atoms. As a result, only half of the molecule of **1** appears in the asymmetric unit, whereas complex **2** does not retain any symmetry element and therefore the asymmetric unit contains the full molecule. Both complexes show distorted 'step-type' geometry of $[Cu_4I_4]$ unit (Scheme 8b) that is most common among other geometries exhibited by various copper complexes having $[Cu_4I_4]$ core (Scheme 8).[29] The copper atoms in both complexes show different coordination environment. The terminal copper atoms are coordinated to two bridging iodide ions and two nitrogen atoms (proximal nitrogen of naphthyridine and nitrogen in the oxazoline ring) of the ligand, while the central copper atoms are bonded to three bridging iodides and a distal nitrogen atom of the naphthyridine unit. The structures also contain two different types of bridging iodides (two iodides are doubly (μ_2) bridged and the other two are triply (μ_3) bridged). The short Cu···Cu distances in both complexes range between 2.38(1)–2.593(4) Å, which are less than the sum of the van der Waals radii (2.80 Å)[30] indicating closed shell interaction between the two copper centers. Molecular structure of complex **3** shows the butterfly-shaped discrete $[Cu_2I_2]$[31] core with Cu···Cu distance 2.558(2) Å.

The molecular structure of **4** (Fig. 2) consists of two copper centers spanned by two naphthyridine ligands and one bridging iodide. One triflate anion was located in the asymmetric unit. The two copper centers reside in distorted tetrahedral environment with a Cu···Cu separation of 2.6189(9) Å. It crystallizes in an orthorhombic $P2_12_12_1$ chiral space group. The Cu1–I1–Cu2, N1–Cu1–N5, N2–Cu2–N4 and N1–Cu1–I1 angles are 59.35(2), 132.82(17), 129.46(17) and 115.17(12)° respectively.

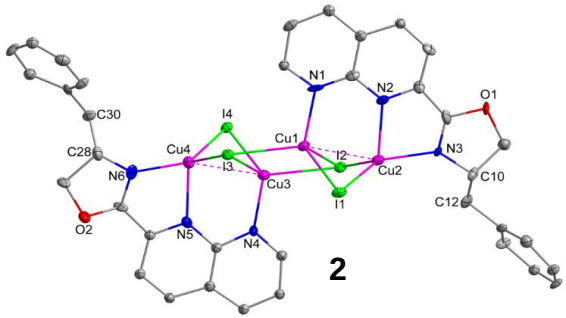


Scheme 8. Some common geometries of $[Cu_4I_4]$ unit.



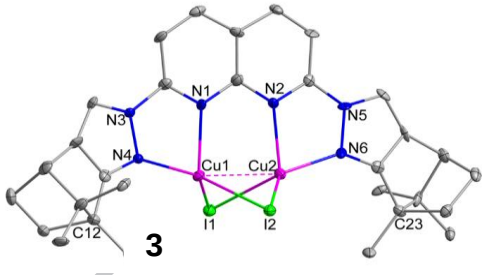
1

Cu1···Cu2 2.5381(8), Cu1···Cu1′ 2.9463(11). I1–Cu1–I2 99.851(19), I1–Cu2–I2 113.74(2), Cu2–I1–Cu1′–I2′ 10.6(1)



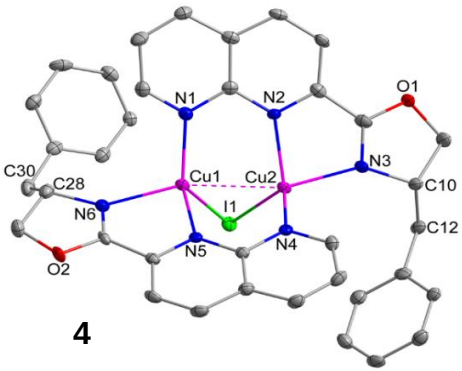
2

Cu1···Cu2 2.574(4), Cu3···Cu4 2.593(4), Cu1···Cu3 2.724(2), I1–Cu1–I2 101.02(11), I1–Cu2–I2 109.44(15), I3–Cu3–I4 99.78(11), I3–Cu4–I4 107.53(14), Cu2–I2–Cu1–I3 21.6(2)



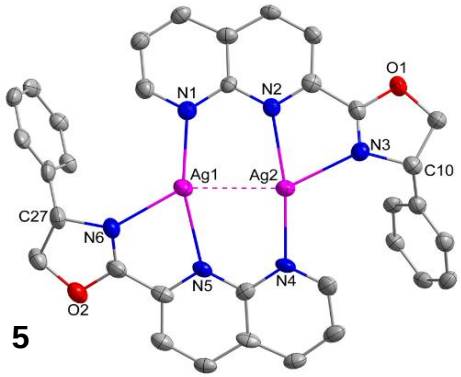
3

Cu1···Cu2 2.558(2), Cu1–I1–Cu2 58.46(5), Cu1–I2–Cu2 61.79(5), Cu1–N1–C1–N3 0.9(1), Cu2–N2–C8–N5 4.4(1)



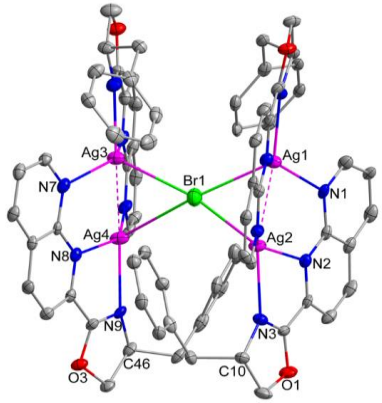
4

Cu1···Cu2 2.6189(9), Cu1–I1–Cu2 59.35(2), N1–Cu1–N5 132.82(17), N2–Cu2–N4 129.46(17), N1–Cu1–I1 115.17(12), N2–Cu2–I1 106.70(12), N1–Cu1–Cu2–N2 6.3(1)



5

Ag1···Ag2 2.8238(12), N1–Ag1–N5 161.1(3), N2–Ag2–N4 169.6(3), N1–Ag1–Ag2–N2 1.0(1), N5–Ag1–Ag2–N4 5.3(2)



6

Ag···Ag 2.8024(11) Å, Ag1–Br1 2.8139(16), Ag2–Br1 2.7202(15), Ag2–N2 2.543(8), Ag2–N3 2.288(9), Ag2–Br1–Ag1 60.82(3), Ag4–Br1–Ag3 58.96(3)

Fig. 2. Molecular structure of **1-6** with important atoms labeled. All the hydrogen atoms are omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level. Important bond distances (Å) and angles (deg) are given below each structure.

Molecular structure of **5** consists of two silver centers bridged by two naphthyridine moieties that are *trans* to each other. Two silver centers reside in a distorted square planar arrangement of ligands with Ag···Ag distance of 2.8238(12) Å.[32] Compound **5** crystallizes in monoclinic $P2_1$ chiral space group. The important bond and dihedral angles are: N1–Ag1–N5 161.1(3)°, N2–Ag2–N4 169.6(3)°; N1–Ag1-Ag2-N2 1.0(1)° and N5-Ag1-Ag2-N4 5.3(2)°. The crystal structure of tetrasilver(I) complex **6** exhibits two dimeric silver units that are bridged by a central bromide ion. Each disilver unit is bridged by two naphthyridine ligands *trans* to each other in a distorted tetrahedral arrangement around the two silver centers. The Ag···Ag distance is 2.8024(11) Å.

Due to poor solubility in common organic solvents, NMR spectroscopic data of complexes **1** and **2** could not be obtained. However, other complexes show ^{1}H and ^{13}C NMR spectra very similar to the corresponding free ligands (see experimental section). ESI–MS spectra of complexes show signals at *m/z* = 802.9774 for $[Cu_2I(L^1)_2]^+$ in **1**, 830.9941 for $[Cu_2I(L^2)_2]^+$ in **2**, 731.0501 for $[M–I]^+$ in **3**, 831.0107 for $[M–OTf]^+$ in **4**, 914.9477 for $[M–OTf]^+$ in **5** and 941.0102 for $[Ag_2(L^2)_2(OTf)]^+$ in **6**, respectively (Fig. S16).

Electronic spectra

Electronic absorption spectra of ligands **L^1–L^3** and complexes **1**–**6** were recorded in dichloromethane at room temperature in the range 200–800 nm. The λ_{max} with the corresponding ε values are summarized in Table **1**.

Table 1. Electronic absorption data for ligands $\mathbf{L^1}$–$\mathbf{L^3}$, and complexes **1**–**6** in CH_2Cl_2 at room temperature.

Compounds	Absorption Data λ_{max}[nm] ($\varepsilon \times 10^{-3}$[$mol^{-1}dm^3cm^{-1}$])
$\mathbf{L^1}$	255 (15.1), 314 (14.9), 319 (14.8)
$\mathbf{L^2}$	262 (11.5), 316 (12.8), 327 (11.6)
$\mathbf{L^3}$	274 (92.8), 360 (55.1), 378 (83.2)
1	305 (16.6), 312 (16.7), 445 (1.6)
2	314 (13.1), 396 (2.1)
3	264 (50.1), 293(35.0), 368 (30.1), 386 (42.9)
4	300 (24.8), 472 (4.6)
5	238 (20.4), 268 (9.9), 312 (10.0), 321 (11.2)
6	248 (7.8), 281 (6.2), 322 (15.0)

Ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ exhibit multiple $\pi \rightarrow \pi^*$ transitions between λ= 255–327 nm (Fig. S17). The absorptions observed in the UV region ranging from 238–322 nm for complexes **1**, **2**, **4**, **5** and **6** are ascribed to ligand-centered $\pi \rightarrow \pi^*$ transitions (Fig. 3). No absorption peak is observed for complexes **5** and **6** in the visible region, whereas complexes **1** and **2** show absorption tails ranging from 386–512 nm. These low energy absorptions are assigned to metal to ligand charge transfer (MLCT) transitions mixed with halogen to ligand charge transfer (XLCT) transitions, and are therefore assigned to (X+M)LCT states.[33] Complex **4** shows absorption peak around 472 nm with high ε value. This corresponds to halide to metal charge transfer transition and it overshadows the MLCT and XLCT transitions observed for complexes **1** and **2**. Ligand $\mathbf{L^3}$ shows $\pi \rightarrow \pi^*$ transitions at 274, 360 and 378 nm with high ε values (Fig. S17). These high ε values stem probably from the extensive π-delocalization between naphthyridine and

camphor-pyrazole rings. Complex **3** exhibits similar type of absorption spectrum (Fig. 3) of free $\mathbf{L^3}$ ligand.

Photoluminescence properties of copper complexes **1-4** were studied. When a dichloromethane solution of **1-4** is excited at 340 nm at room temperature, emission maxima at 404, 400, 380 and 381 nm were observed, respectively. The tetranuclear copper complexes **1** and **2** with $[Cu_4I_4]$ core showed emission spectra at lower energy compared to dinuclear analogs **3** and **4** (Fig. S18).

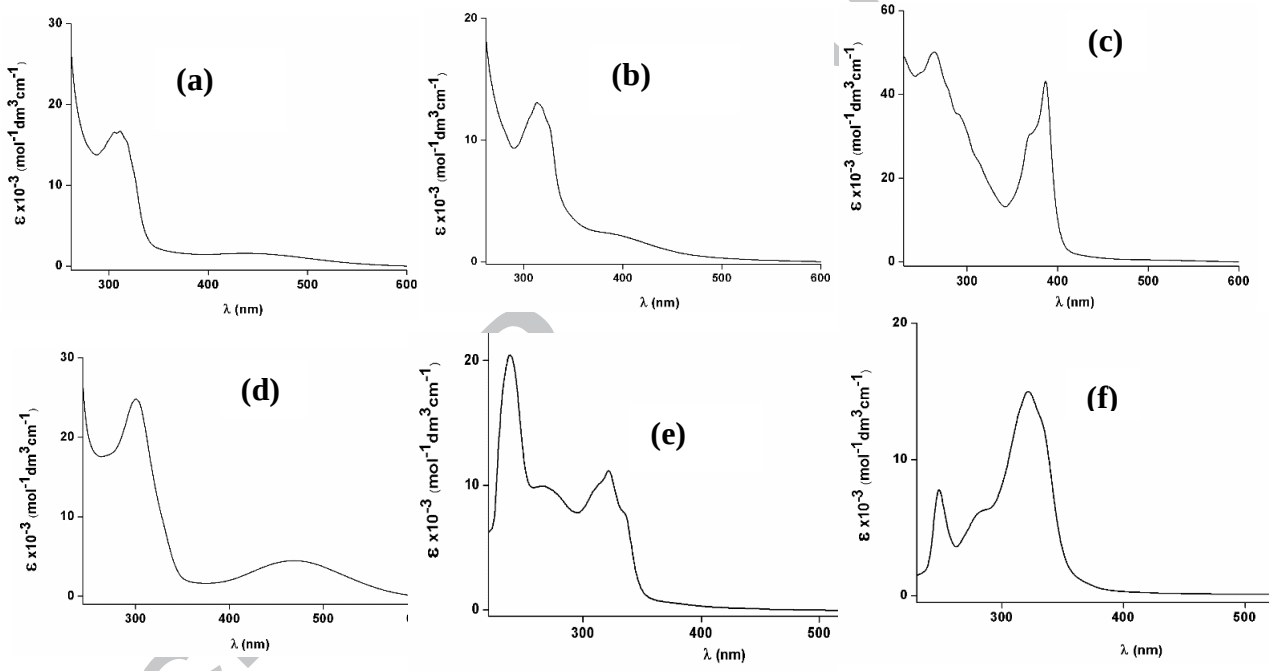
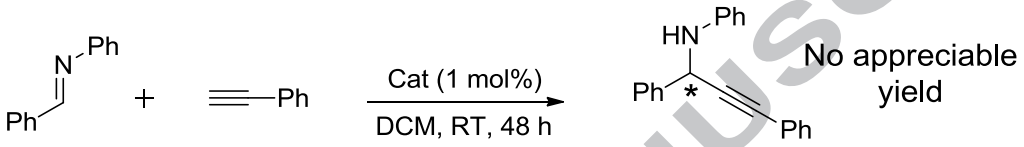


Fig. 3. UV–Vis spectra of complexes (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5** and (f) **6**.

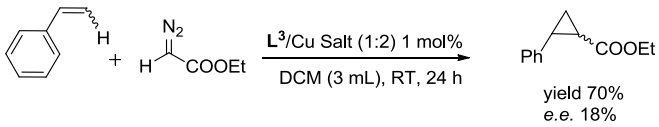
Attempted catalytic studies

Copper and silver salts in combination with variety of chiral ligands have been employed in asymmetric transformation reactions.[34] At first, we examined the catalytic activity of di- and tetranuclear complexes **1-6** for enantioselective addition of phenylacetylene to N-benzylideneaniline to form propargylamine (Scheme 9, Table S2)[35]. Unfortunately none of these complexes had shown satisfactory results.



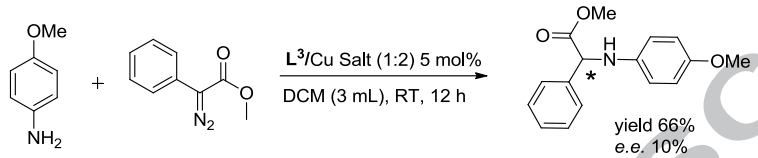
Scheme 9. Enantioselective synthesis of (1,3-Diphenyl-2-propynyl) aniline.

Further, copper complexes **1-4** are found catalytically sluggish for cyclopropanation – a most commonly performed reaction for Cu catalysts.[36] The low solubility of the complexes and coordinative saturation at the metal centers are likely responsible for the inactivity.[28b] A viable remedy is *in situ* generation of a coordinatively unsaturated and catalytically active species. Accordingly, cyclopropanation reaction was attempted with combination of copper salts and chiral ligands (**L**^{1}, **L**^{2} and **L**^{3}) (Table S3). The best result was obtained with **L**^{3}/[Cu(OTf)] for cyclopropanation of styrene with ethyl diazoacetate (EDA) to give 70% yield after 24 h (Scheme 10, Table S3, entry 7).



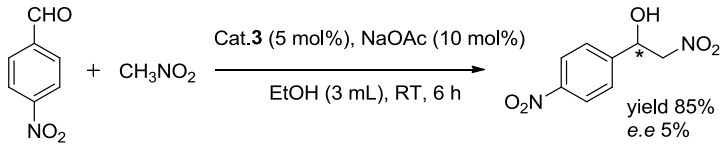
Scheme 10. Cyclopropanation of styrene.

Similarly, the **L^3**/[Cu(CH$_3$CN)$_4$](OTf) (1:2) (5 mol%) combination afforded N-H insertion product in moderate yield of 66% for the reaction of 4-methoxy aniline (0.5 mmol) with methyl phenyldiazoacetate (0.5 mmol) in DCM at room temperature after 12 h (Scheme 11). However, poor enantioselectivity was observed (10-18% *e.e*).



Scheme 11. N-H insertion reaction catalyzed by **L^3**/ [Cu(CH$_3$CN)$_4$](OTf).

In view of the catalytic activity of the **L^3**/Cu combination, nitroaldol (Henry) reaction[37] was examined with complex **3**. Reaction of p-nitro benzalehyde (1 mmol) with nitromethane (10 mmol) catalyzed by **3** (5 mol%) and NaOAc (10 mol%) in dry EtOH (3 mL) at room temperature for 6 h gave the corresponding 2-nitro-1-(4-nitrophenyl)ethanol in 85% yield. However, the enantioselectivity again was very low (Scheme 12). In absence of NaOAc, no product formation was observed even after 24 h of stirring. It is reasonable to assume that the additive NaOAc creates unsaturation at the copper centers and thus allows the reaction to proceed.



Scheme 12. Nitroaldol (Henry) reaction catalyzed by **3**.

Summary and Concluding Remarks

Oxazoline and camphor-pyrazole derived chiral 1,8-naphthyridine ligands are synthesized and characterized by spectroscopic techniques. Several di- and tetranuclear complexes are accessed by treating Cu(I) or Ag(I) salts with these ligands. All complexes are fully characterized including X-ray crystallography. Each naphthyridine-derived ligand displays bridge-chelate coordination behavior and holds two metal centers in close proximity. Use of metal-halide precursors or addition of external halides fulfills the metal coordination sites and thus allows easy isolation of the metal complexes. These complexes are found to be catalytically inactive for a number of organometallic transformations. Coordinative saturation at the metal centers blocks the substrate approach and thus impedes the activity. A combination of Cu salt/ligand was found to catalyze cyclopropanation of styrene, N-H insertion and nitroaldol (Henry) reactions affording good yields. However, chiral side arms on the naphthyridine scaffold failed to afford noticeable enantioselectivity. Clearly, the choice of metal precursors, ligand geometry and reaction conditions need to be probed carefully to achieve better activity and enantioselectivity. The purpose of this report is to draw attention on naphthyridine based chiral ligands for asymmetric transformations on a dimetal construct.

Experimental Section

General Procedures

All reactions were carried out under nitrogen atmosphere with the use of standard Schlenk-line techniques unless stated otherwise and at room temperature (30 °C).

Glass wares were flame–dried under vacuum prior to use. Solvents were dried by conventional methods prior to use. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL JNM–LA 500 MHz and JEOL JNM–LA 400 MHz spectrometer. Chemical shift values were referenced to the residual signals of the deuterated solvents. ESI–MS were recorded on a Waters Micro mass Quattro Micro triple-quadruple mass spectrometer. Infrared spectra were recorded on a Bruker Vertex 70 FTIR spectrophotometer in the ranges from 400 to 4000 cm^{-1}. UV–Vis spectra were recorded using a JASCO V–670 UV–Vis absorption spectrophotometer. Emission spectra were recorded using a Fluorolog FL3-21(Horiba Jobin Yvon) spectrofluorometer equipped with a xenon flash lamp and also using a PTI Quanta Master Model QM-4 scanning spectrofluorometer equipped with a 75-watt xenon lamp, emission and excitation monochromators, excitation correction unit, and a PMT detector for both visible and NIR regions. The GC-MS experiments were performed on an Agilent 7890A GC and 5975C MS. HPLC analyses were performed on an Agilent 1200 series HPLC system using a Daicel chiral column.

Materials

2-Aminonicotinaldehyde[25] and optically active amino alcohols such as (*S*)-phenylglycinol, (S)-phenylalaninol were prepared according to the literature procedures.[38] 2,6-Diaminopyridine, (*dl*)-malic acid, KH (30% suspension in mineral oil), SeO_2, TBABr, TBAI, $NaNO_2$, PCl_5, hydrazine hydrate were purchased from Sigma-Aldrich. Metal precursors, such as $[Cu(CH_3CN)_4](OTf)$[39], Ag(OTf)[40] were prepared following the literature procedure reported earlier and CuI was purchased from Sigma-

Aldrich. Oxalyl chloride, $SOCl_2$, $POCl_3$, and methyl formate were purchased from local supplier and distilled before use.

Syntheses of oxazoline based ligands L^1 and L^2

1,8-Naphthyridine-2-carbonyl chloride. To a suspension of 1,8-naphthyridine-2-carboxylic acid (2 g, 0.011 mol) in dry benzene (50 mL), was added oxalyl chloride (1.4 mL, 0.017 mol) drop wisely at 0 ºC. Then few drops of DMF were added and the reaction began immediately. It was then slowly brought to room temperature and heated at 65ºC for 3 h until the gas evolution subsided. The solvent and excess oxalyl chloride was removed under reduced pressure to afford a light yellow residue of 1,8-Naphthyridine-2-carbonyl chloride in almost quantitative yield which was directly used for the next step without further purification.

(*S*)-N-(2-hydroxy-1-phenylethyl)-1,8-naphthyridine-2-carboxamide. (*S*)-Phenylglycinol (1.51 g, 0.011 mol) was dissolved in dry THF (100 mL) and the solution was chilled to 0°C. Then, triethylamine (3.9 mL, 0.028 mol) was added to the solution. Subsequently, a suspension of 1,8-naphthyridine-2-carbonyl chloride (prepared in the previous step) in dry THF was added portion wise during 30 minutes. Then the mixture was slowly brought to room temperature and stirred at room temperature for additional 24 h. After that it was evaporated, taken in dichloromethane and extracted with saturated aqueous sodium bicarbonate solution. After further extraction of the aqueous phase with dichloromethane, the combined organic phases were dried over anhydrous Na_2SO_4 and evaporated again to get a brown residue. The residue was then purified by silica gel column chromatography using ethyl acetate/petroleum ether as eluent to obtain (*S*)-N-(2-hydroxy-1-phenylethyl)-1,8-naphthyridine-2-carboxamide as colorless

powder. Yield: 2.76 g (82 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.17 (br, 1H), 9.04 (d, *J* = 6.3 Hz, 1H), 8.35 (br, 2H), 8.29 (d, *J* = 7.2 Hz, 1H), 7.58–7.61 (m, 1H), 7.42–7.45 (m, 2H), 7.30–7.33 (m, 2H), 7.23–7.26 (m, 1H), 5.33–5.37 (m, 1H), 4.06–4.12 ppm (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.1, 154.3, 153.8, 152.9, 139.0, 138.9, 137.8, 128.9, 127.9, 127.1, 124.3, 123.4, 120.6, 66.3, 56.7 ppm; IR (KBr): ν = 3375 (s), 3293 (br, m), 3057 (w), 3024 (w), 2925 (w), 1675 (vs), 1601 (s), 1531 (vs), 1491 (vs), 1446 (m), 1423 (m), 1336 (w), 1295 (w), 1249 (w), 1162 (w), 1063 (s), 848 (m), 792 cm^{-1} (s); MS (ESI; CH_3CN): *m/z* 294.1247 $[M+H]^+$, 316.1075 $[M+Na]^+$.

(*S*)-N-(1-hydroxy-3-phenylpropan-2-yl)-1,8-naphthyridine-2-carboxamide. Synthetic procedure was same as for (*S*)-N-(2-hydroxy-1-phenylethyl)-1,8-naphthyridine-2-carboxamide with 1,8-naphthyridine-2-carboxylic acid (2 g, 0.011 mol) and (*S*)-2-amino-3-phenylpropan-1-ol (1.66 g, 0.011 mol). Yield: 2.80 g (80 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.18 (d, *J* = 3.1 Hz, 1H), 8.68 (d, *J* = 8.3 Hz, 1H), 8.38 (d, *J* = 8.3 Hz, 1H), 8.35 (d, *J* = 8.3 Hz, 1H), 8.30 (d, *J* = 7.4 Hz, 1H), 7.60–7.62 (m, 1H), 7.24–7.31 (m, 4H), 7.16–7.18 (m, 1H), 4.42–4.49 (m, 1H), 3.87 (dd, *J* = 11.6 Hz, 3.7 Hz, 1H), 3.77 (dd, *J* = 11.3 Hz, 5.5 Hz, 1H), 3.02–3.10 ppm (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.9, 154.1, 153.6, 153.1, 139.0, 138.1, 138.0, 129.4, 128.6, 126.6, 124.3, 123.4, 120.6, 63.8, 53.8, 37.3 ppm; IR (KBr): ν = 3373 (s), 3299 (br, m), 3060 (w), 3027 (w), 2937 (w), 1662 (vs), 1603 (s), 1526 (vs), 1492 (vs), 1454 (m), 1421 (m), 1368 (w), 1296 (w), 1253 (w), 1162 (w), 1046 (s), 859 (m), 796 cm^{-1} (s); MS (ESI, CH_3CN): *m/z* 308.1393 $[M+H]^+$, 330.1212 $[M+Na]^+$.

(*S*)-N-(2-chloro-1-phenylethyl)-1,8-naphthyridine-2-carboxamide. To a solution of (*S*)-N-(2-hydroxy-1-phenylethyl)-1,8-naphthyridine-2-carboxamide (2 g, 6.82 mmol) in

dry 1,2-dichloroethane (50 mL), freshly distilled $SOCl_2$ (5 mL, 68.2 mmol) was added drop wise at room temperature and the resulting mixture was refluxed for 3 h until the gas evolution subsided. Then, it was cooled to room temperature and solvent and excess $SOCl_2$ were removed under reduced pressure. The residue was taken in dichloromethane and extracted cautiously with saturated aqueous solution of Na_2CO_3. The combined organic phase was dried over anhydrous Na_2SO_4 and evaporated to obtain a brown residue which was purified by silica gel column chromatography using 50% ethyl acetate/petroleum ether as eluent. A colorless crystalline product was obtained. Yield: 1.62 g (76 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.20–9.22 (m, 1H), 8.90 (d, *J* = 7.7 Hz, 1H), 8.45 (dd, *J* = 8.3 Hz, 2Hz, 1H), 8.40 (dd, *J* = 8.3 Hz, 2.3 Hz, 1H), 8.30 (d, *J* = 8 Hz, 1H), 7.59–7.62 (m, 1H), 7.45–7.47 (m, 2H), 7.36–7.39 (m, 2H), 7.30–7.33 (m, 1H), 5.54–5.58 (m, 1H), 3.97–3.99 ppm (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.5, 154.6, 154.2, 152.4, 139.1, 138.3, 137.2, 128.9, 128.1, 126.9, 124.4, 123.1, 120.4, 54.9, 46.8 ppm; IR (KBr): ν = 3371 (s), 3056 (w), 3026 (w), 2958 (w), 1670 (vs), 1603 (s), 1520 (vs), 1492 (vs), 1450 (m), 1373 (w), 1346 (w), 1293 (w), 1232 (w), 1130 (w), 862 (m), 793 (m), 700 cm^{-1} (s); MS (ESI, CH_3CN): *m/z* 312.0909 $[M+H]^+$.

(*S*)-N-(1-chloro-3-phenylpropan-2-yl)-1,8-naphthyridine-2-carboxamide. Same as for (*S*)-N-(2-chloro-1-phenylethyl)-1,8-naphthyridine-2-carboxamide with (S)-N-(1-hydroxy-3-phenylpropan-2-yl)-1,8-naphthyridine-2-carboxamide (2 g, 6.51 mmol) and $SOCl_2$ (4.7 mL, 65.1 mmol). Yield: 1.6 g (75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.23 (d, *J* = 4.6 Hz, 1H), 8.60 (d, *J* = 8.9 Hz, 1H), 8.44 (dd, *J* = 7.9 Hz, 2.8 Hz, 1H), 8.40 (dd, *J* = 8.5 Hz, 3 Hz, 1H), 8.34 (d, *J* = 8 Hz, 1H), 7.63–7.65 (m, 1H), 7.28–7.32 (m, 4H), 7.20–7.23 (m, 1H), 4.67–4.72 (m, 1H), 3.77 (dd, *J* = 11.3 Hz, 4 Hz, 1H), 3.62 (dd, *J* = 11.3 Hz,

4.9 Hz, 1H), 3.06–3.16 ppm (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.4, 154.2, 153.7, 152.8, 139.1, 138.1, 137.0, 129.4, 128.8, 126.9, 124.5, 123.5, 120.6, 51.9, 46.3, 37.8 ppm; IR (KBr): ν = 3373 (s), 3060 (w), 3028 (w), 2958 (w), 1678 (vs), 1603 (s), 1520 (vs), 1491 (vs), 1448 (m), 1420 (w), 1345 (w), 1293 (w), 1235 (w), 1157 (w), 1128 (w), 860 (m), 792 (s), 701 cm^{-1} (s); MS (ESI, CH_3CN); *m/z* 326.1068 $[M+H]^+$.

(*S*)-2-(1,8-naphthyridin-2-yl)-4-phenyl-4,5-dihydrooxazole (L^1). To a solution of (S)-N-(2-chloro-1-phenylethyl)-1,8-naphthyridine-2-carboxamide (1.6 g, 5.13 mmol) in dry ethanol (50 mL), 5.6 mL of 1(N) ethanolic NaOH (5.6 mmol) solution was added drop wise and the solution was refluxed for 3 h under N_2 atmosphere. Then the solvent was removed by rotary evaporation and the residue was passed through a column packed with silica gel using 3% MeOH/DCM as eluent. A nice white powder was obtained. Yield: 1.2 g ,(85 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.21 (dd, *J* = 4.3 Hz, 2 Hz, 1H; NP), 8.40 (d, *J* = 8.3 Hz, 1H; NP), 8.29 (d, *J* = 8.3 Hz, 1H; NP), 8.24 (dd, *J* = 8.1 Hz, 2 Hz, 1H; NP), 7.54–7.57 (m, 1H; NP), 7.34–7.39 (m, 5H; Ph), 5.51 (dd, *J* = 10.3 Hz, 8.6 Hz, 1H; CH), 4.97 (t, 8.6 Hz, 1H; CH_2), 4.47 ppm (t, *J* = 8.6 Hz, 1H; CH_2); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.2, 155.5, 154.5, 149.9, 141.7, 138.1, 136.8, 129.0, 128.0, 126.9, 123.8, 123.3, 122.2, 75.6, 70.5 ppm; IR (KBr): ν = 3440 (br), 3043 (w), 3023 (w), 3010 (w), 2960 (w), 2924 (w), 2896 (w), 2856 (w), 1638 (s), 1600 (s), 1549 (m), 1496 (m), 1448 (m), 1368 (s), 1334 (m), 1260 (m), 1124 (s), 1097 (vs), 1034 (m), 967 (m), 865 (s), 804 cm^{-1} (s); MS (ESI, CH_3CN): *m/z* 276.1136 $[M+H]^+$; $[\alpha]_D^{25}$ = –175.4 (*c* 0.33, $CHCl_3$).

(*S*)-4-Benzyl-2-(1,8-naphthyridin-2-yl)-4,5-dihydrooxazole (L^2). Same as for (S)-N-(2-chloro-1-phenylethyl)-1,8-naphthyridine-2-carboxamide with (S)-N-(1-chloro-3-phenylpropan-2-yl)-1,8-naphthyridine-2-carboxamide (1.6 g, 4.91 mmol) and 5.4 mL of

1(N) ethanolic NaOH (5.4 mmol) solution. Yield: 1.2 g ,(84 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.18 (dd, *J* = 4.3 Hz, 2 Hz, 1H; NP), 8.30 (d, *J* = 8.3 Hz, 1H; NP), 8.27 (d, *J* = 8.3 Hz, 1H; NP), 8.22 (dd, *J* = 8.3 Hz, 2 Hz, 1H; NP), 7.52–7.54 (m, 1H; NP), 7.21–7.32 (m, 5H; Ph), 4.67 – 4.74 (m, 1H, CH), 4.52 (t, *J* = 8.6 Hz, 1H, CH_2), 4.30 (t, *J* = 8.6 Hz, 1H; CH_2), 3.28 (dd, *J* = 13.7 Hz, 5.4 Hz, 1H; CH_2), 2.81 ppm (dd, *J* = 13.7 Hz, 8.9 Hz, 1H; CH_2); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.6, 155.5, 154.6, 150.0, 138.0, 137.8, 136.8, 129.4, 128.7, 126.8, 123.7, 123.2, 122.0, 72.8, 68.4, 41.8 ppm; IR (KBr): ν = 3406 (br), 3044 (w), 3024 (w), 3010 (w), 2956 (w), 2922 (w), 2910 (w), 1637 (vs), 1600 (vs), 1552 (m), 1495 (s), 1451 (m), 1370 (s), 1295 (m), 1260 (m), 1232 (m), 1119 (s), 1098 (s), 1089 (s), 1065 (m), 1037 (m), 968 (s), 863 (s), 771 cm^{-1} (s); MS (ESI, CH_3CN); *m/z* 290.1290 $[M+H]^+$; $[\alpha]_D^{25}$ = –61.8 (*c* 0.33, $CHCl_3$).

Synthesis of L^3

(1*R*,4*S*)-3-Hydroxymethylenecamphor and (4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2-indazole were prepared according to the literature procedure starting from (+)-camphor.[27] 2-Amino-7-hydroxy-1,8-naphthyridine, 2,7-dihydroxy-1,8-naphthyridine and 2,7-dichloro-1,8-naphthyridine were also prepared according to the literature procedures known but with little modification.[26]

2-Amino-7-hydroxy-1,8-naphthyridine. 2,6-Diaminopyridine (20 g, 0.18 mol) and (*dl*)-malic acid (27 g, 0.2 mol) were placed into a 500 mL three-neck round bottomed flask fitted with an addition funnel, thermometer, and mechanical stirrer. The stirred mixture was cooled in an ice-water bath and concentrated sulfuric acid (100 mL) was added drop-wise. The rate of addition was controlled to maintain an internal temperature ≤ 45 °C during the addition. Next, the addition funnel was replaced by a reflux condenser and

the slurry was heated to an internal temperature of 110°C for 3 h. The solution was transferred to a 1L beaker, cooled to 0°C by an ice-water bath and was made basic (pH = 8) by careful addition of NH_4OH_{aq} (300 mL). The crude brown solid was collected by vacuum filtration and was washed on the filter-paper with water (2 L). The solid was triturated with 1:9 (v:v) water: methanol and again collected by vacuum filtration, affording 7-amino-2-hydroxy-1,8-naphthyridine as a tan powder. Yield: 25 g (86%). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.91 (br s, 1H), 7.65 (d, J = 9.5, 1H), 7.65 (d, J = 8, 1H), 7.03 (br s, 2H), 6.34 (d, J = 8.5, 1H), 6.12 ppm (d, J = 9.2, 1H); ^{13}C NMR (126 MHz; DMSO-d_6): δ = 163.8, 160.6, 150.4, 139.8, 137.4, 114.8, 105.3, 105.0 ppm; MS (ESI; CH_3OH): m/z 162.0664 ($[M+H]^+$).

2,7-Dihydroxy-1,8-naphthyridine. 2-Amino-7-hydroxy-l,8-naphthyridine (10 g, 62 mmol) was ground to a fine powder and added to concentrated sulfuric acid (80 mL), and then sodium nitrite (5 g, 74mmol) was added. The mixture was allowed to stand for 10 min, poured over crushed ice, and allowed to stand for 10 min. Excess acid was neutralized with sodium carbonate, and then the solution was acidified with glacial acetic acid (pH = 3), giving 2,7-dihydroxy-1,8-naphthyridine as a brown powder. Yield = 8 g (80%). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.54 (d, J = 8.9 Hz, 2H), 5.98 (d, J = 9.1 Hz, 2H), 3.31 ppm (brs, 2H); ^{13}C NMR (126 MHz; DMSO-d_6): δ = 166.2, 149.8, 139.4, 112.6, 102.0 ppm; MS (ESI; CH_3OH): m/z 163.05 ($[M+H]^+$).

2,7-Dichloro-1,8-naphthyridine. A mixture of 2,7-dihydroxy-l,8-naphthyridine (6 g, 37 mmol), phosphorus pentachloride (15.4 g, 74 mmol) and freshly distilled phosphorus oxychloride (100 mL) were refluxed at 100 ºC for 2 h. After that, excess $POCl_3$ was removed by distillation and the remaining concentrated solution (5 mL) was poured into

a beaker containing crushed ice. Then, the solution was made alkaline (pH = 9) with saturated aqueous solution of sodium carbonate. A brown precipitate was appeared and it was collected by vacuum filtration and dried under high vacuum. This was then extracted with chloroform (150 mL) using soxhlet extractor apparatus for two days. Finally, the solvents were removed by rotary evaporation and dried under vacuum to give a light yellow powder. Yield 5 g (68%). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.58 (d, J = 8.5 Hz, 2H), 7.76 ppm (d, J = 8.5 Hz, 2H); ^{13}C NMR (126 MHz; DMSO-d_6): δ = 170.2, 150.6, 139.8, 112.6, 102.4 ppm; MS (ESI; CH_3OH): m/z 198.9834 ($[M+H]^+$).

2,7-Bis{(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2-indazol-1-yl}-1,8-naphthyridine (L^3). (4*S*,7*R*)-7,8,8-Trimethyl-4,5,6,7-tetrahydro-4,7-methano-2-indazole (3.7 g, 21 mmol), KOH (1.2 g, 21.4 mmol) and tetrabutyl ammonium bromide (320 mg, 1 mmol) were taken in a 250 mL RB and dissolved in dry tetrahydrofuran (100 mL) by stirring at room temperature during 1h. Then, 2,7-dichloro-1,8-naphthyridine (2 g, 10 mmol) was added in one portion into the solution and it was refluxed under nitrogen for 12 h. The initially formed brown solution started precipitating out as the reaction progressed. After the completion of reaction, it was cooled to room temperature and evaporated completely by rotary evaporation. Then, it was extracted with CH_2Cl_2/H_2O and the organic layer was collected over anhydrous Na_2SO_4. Finally, the dichloromethane layer was again evaporated to brown mass and purified by column chromatography (Silica gel, 10% EtOAc/hexane as eluent) to obtain white powder. Yield 3.5 g (74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.46 (s, 2H; CH_{Pz}), 8.09 (s, 4H; NP), 2.87 (d, J = 4 Hz, 2H; CH), 2.10–2.16 (m, 2H; CH_2), 1.89–1.95 (m, 2H; CH_2), 1.42–1.48 (m, 2H; CH_2), 1.35 (s, 6H; Me), 1.27–1.32 (m, 2H; CH_2), 1.00 (s, 6H, Me), 0.72 (s, 6H, Me);

^{1}H NMR (400 MHz, $CD_3OD+CDCl_3$): δ = 8.29 (s, 2H; CH_{Pz}), 8.22 (d, J = 9.8 Hz, 2H; NP), 7.97 (d, J = 8.7 Hz, 2H; NP), 2.82 (d, J = 3.6 Hz, 2H; CH), 2.09–2.17 (m, 2H; CH_2), 1.88–1.95 (m, 2H; CH_2), 1.33–1.39 (m, 2H; CH_2), 1.28 (s, 6H; Me), 1.19–1.25 (m, 2H; CH_2), 0.96 (s, 6H; Me), 0.66 (s, 6H; Me); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 171.2, 153.8, 138.4, 130.8, 119.9, 118.1, 111.9, 59.8, 50.6, 46.7, 33.5, 27.4, 20.7, 18.7, 10.7 ppm; ^{13}C NMR (100 MHz, $CD_3OD+CDCl_3$): δ = 173.8, 156.5, 142.0, 133.3, 121.8, 121.0, 113.9, 62.2, 52.8, 49.5, 35.9, 29.6, 22.4, 20.6, 12.2 ppm; IR (KBr) ν = 3452 (br), 2959 (w), 2869 (w), 1598 (m), 1368 (s), 1288 (m), 932 cm^{-1} (m); MS (ESI; $CHCl_3$) *m/z* 479.2925 ($[M+H]^+$); $[\alpha]_D^{25}$ = +139.1 (*c* 0.33, $CHCl_3$).

Syntheses of metal complexes

$[Cu_4I_4(L^1)_2]$ (1)

CuI (50 mg, 0.263 mmol) was dissolved in 10 mL dry acetonitrile and 36 mg of (*S*)-2-(1,8-naphthyridin-2-yl)-4-phenyl-4,5-dihydrooxazole (**L^1**; 0.131 mmol) was added directly to the solution at room temperature. Immediately after the addition, the color of the solution became red and the compound started precipitating and completed within 30 minutes. Then, it was washed with diethyl ether (10 mL×3) and dried under vacuum to afford **1** as dark red microcrystalline solid. Yield: 78 mg (90%, based on Cu). Block shaped X-ray-quality red crystals of **1** were grown by layering ethereal solution of **L^1** onto an acetonitrile solution of CuI inside an 8 mm o.d. vacuum-sealed glass tube. IR (KBr): ν = 3424 (br), 3050 (w), 2924 (w), 2897 (w), 1633 (w), 1597 (s), 1553 (m), 1503 (m), 1496 (m), 1468 (m), 1449 (s), 1424 (s), 1382 (s), 1329 (m), 1266 (m), 1192 (m), 1159 (s), 1131 (m), 1049 (m), 970 (m), 942 (m), 926 (m), 859 (m), 781 (s), 698 (s). MS (ESI; CH_3CN): *m/z* 1182.6453 for $[Cu_4I_3(L^1)_2]^+$, 802.9774 for $[Cu_2I(L^1)_2]^+$.

$[Cu_4I_4(L^2)_2]$ (2)

Complex **2** was synthesized following the same procedure described for the synthesis of **1** with CuI (50 mg, 0.263 mmol) and 38 mg of (*S*)-4-benzyl-2-(1,8-naphthyridin-2-yl)-4,5-dihydrooxazole (**L^2**; 0.131 mmol). Yield: 72 mg (82%, based on Cu). Block shaped X-ray-quality red crystals of **2** were grown by layering ethereal solution of **L^2** onto an acetonitrile solution of CuI inside an 8 mm o.d. vacuum-sealed glass tube. IR (KBr): ν = 3450 (br), 3056 (w), 3026 (w), 2897 (w), 1630 (w), 1595 (s), 1552 (m), 1494 (m), 1450 (s), 1425 (m), 1386 (s), 1290 (m), 1162 (s), 1123 (m), 1053 (m), 967 (m), 944 (m), 935 (m), 862 (m), 787 (s), 700 cm^{-1} (m); MS (ESI; CH_3CN): *m/z* 1210.6594 for $[Cu_4I_3(L^2)_2]^+$, 830.9941 for $[Cu_2I(L^1)_2]^+$.

$[Cu_2I_2(L^3)]$ (3)

CuI (50 mg, 0.263 mmol) was dissolved in 10 mL dry acetonitrile and 63 mg of 2,7-Bis{(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2-indazol-1-yl}-1,8-naphthyridine (**L^3**; 0.131 mmol) was added directly to the solution at room temperature. Immediately after the addition, the color of the solution became light brown and the compound started precipitating from solution. The precipitation completed within 30 minutes. After the completion of the reaction, the excess solvent was filtered out and the precipitate was washed with diethyl ether (10mL×3). Finally, the precipitate was dried under vacuum to afford **3** as brown powder. Yield: 96 mg (86%, based on Cu). Needle shaped X-ray-quality red crystals of **3** were grown by layering of petroleum ether onto an dichloromethane solution of **3** inside an 8 mm o.d. vacuum-sealed glass tube. ^1H NMR (400 MHz, CD_2Cl_2): δ = 8.31 (d, *J* = 8.7 Hz, 2H; NP), 7,73 (s, 2H; CH_{Pz}), 7.47 (d, *J*

= 9.2 Hz, 2H; NP), 2.92 (d, *J* = 4.1 Hz, 2H; CH), 2.15–2.23 (m, 2H; CH_2), 1.96–2.023 (m, 2H; CH_2), 1.53 (s, 6H; Me), 1.46–1.52 (m, 2H; CH_2), 1.03 (s, 6H; Me), 0.76 ppm (s, 6H; Me); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 170.2, 149.5, 139.9, 133.5, 119.0, 118.7, 109.6, 60.4, 51.1, 32.9, 29.7, 27.2, 20.4, 18.5, 10.1 ppm; IR (KBr): ν = 3440 (br, w), 2959 (w), 2869 (w), 1598 (m), 1524 (m), 1493 (m), 1446 (m), 1382 (s), 1368 (s), 1288 (m), 932 cm^{-1} (m); MS (ESI; CH_2Cl_2); *m/z* 731.0501 $[M–I]^+$.

$[Cu_2I(L^2)_2](OTf)$ (4)

$[Cu(CH_3CN)_4](OTf)$ (50 mg, 0.133 mmol) was dissolved in 10 mL of dry CH_2Cl_2 and 40 mg of (*S*)-4-benzyl-2-(1,8-naphthyridin-2-yl)-4,5-dihydrooxazole (**L^2**; 0.138 mmol) was added directly to the solution at room temperature. Immediately after the addition, the color of the solution became brown. After 30 minutes of stirring at room temperature under nitrogen atmosphere, tetrabutylammonium iodide (25 mg, 0.067 mmol) was added as an external source of iodide. Immediately, the color of the solution was changed to red from brown. The stirring was continued for additional 15 minutes. The solution was then concentrated to a small volume under reduced pressure and 10 mL diethyl ether was added while stirring to get a red precipitate. The precipitate was washed with diethyl ether (3 × 10 mL) and dried under vacuum to afford **4** as dark red microcrystalline solid.Yield: 55 mg (84%, based on Cu). Needle shaped X-ray-quality crystals were grown by layering petroleum ether onto a dichloromethane solution of **4** inside an 8 mm o.d. vacuum-sealed glass tube. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.94 (br, s, 2H; NP), 8.65 (d, *J* = 8.3 Hz, 2H; NP), 8.52 (d, *J* = 8.0 Hz, 2H; NP), 8.13 (d, *J* = 8.2 Hz, 2H; NP), 7.48 (d, *J* = 7.3 Hz, 4H; Ph), 7.11–7.22 (m, 6H; Ph), 5.14–5.20 (m, 2H; CH), 5.06–5.09 (m, 2H; CH_2), 4.67–4.70 (m, 2H; CH_2), 3.12–3.17 ppm (m, 2H; CH_2); ^{13}C

NMR (125 MHz, CD_2Cl_2): δ = 165.7, 155.5, 150.9, 145.4, 140.7, 138.9, 136.7, 129.9, 128.7, 126.9, 126.6, 125.6, 121.6, 75.7, 67.5, 40.9 ppm; IR (KBr): ν = 3491 (br), 3060 (w), 2901 (w), 1639 (w), 1602 (m), 1555 (w), 1508 (w), 1469 (w), 1451 (m), 1427 (w), 1383 (m), 1263 (vs), 1223 (m), 1154 (s), 1031 (s), 972 (m), 954 (w), 853 (m), 784 (m), 758 (m), 706 (m), 637 (s); MS (ESI; CH_3CN): *m/z* 831.0107 for $[M–OTf]^+$.

$[Ag_2(L^1)_2]$ $(OTf)_2$ (5)

AgOTf (50 mg, 0.195 mmol) was dissolved in 10 mL of dry CH_3CN and 54 mg of (*S*)-2-(1,8-naphthyridin-2-yl)-4-phenyl-4,5-dihydrooxazole (**L^1**; 0.196 mmol) was added directly to the solution at room temperature. Then, the solution was stirred for one hour. After that, the solution was concentrated to a small volume under reduced pressure and 10 mL diethyl ether was added while stirring to get a yellowish-white precipitate. The precipitate was washed further with diethyl ether (3 × 10 mL) and dried under vacuum to afford **5** as yellowish-white powder. Yield: 82 mg (80%, based on Ag). Block shaped pale yellow colored X-ray-quality crystals were grown by layering petroleum ether onto a dichloromethane solution of **5** inside an 8 mm o.d. vacuum-sealed glass tube. ^{1}H NMR (500 MHz, CD_3CN): δ = 8.87 (d, *J* = 5.8 Hz, 2H; NP), 8.63 (d, *J* = 8.2 Hz, 2H; NP), 8.45 (d, *J* = 8.2 Hz, 2H; NP), 8.11 (d, *J* = 8.2 Hz, 2H; NP), 7.53–7.56 (m, 2H; NP), 6.91–6.96 (m, 6H; Ph), 6.82–6.85 (m, 4H, Ph), 5.42–5.46 (m, 2H; CH), 5.02–5.06 (m, 2H; CH_2), 4.39–4.43 ppm (m, 2H; CH_2); ^{13}C NMR (125 MHz, CD_3CN): δ = 164.8, 157.1, 151.4, 147.0, 141.7, 140.3, 139.4, 128.3, 126.6, 125.6, 124.7, 122.2, 77.7, 69.3 ppm; IR (KBr): ν = 3511 (br, w), 3064 (w), 1651 (m), 1605 (m), 1560 (m), 1456 (m), 1376 (m), 1278 (vs: OTf), 1157 (s), 1053 (s), 637 (s); MS (ESI; CH_3CN): *m/z* 914.9477 for $[M–OTf]^+$.

$[Ag_4(L^2)_4Br](OTf)_3$ (6)

AgOTf (50 mg, 0.195 mmol) was dissolved in 10 mL of dry CH_3CN and 56 mg of (*S*)-4-benzyl-2-(1,8-naphthyridin-2-yl)-4,5-dihydrooxazole (**L^2**; 0.194 mmol) was added directly to the solution at room temperature. Then, the solution was stirred for one hour. After that, 32 mg tetrabutylammonium bromide (TBABr, 0.099 mmol) was added and the solution was stirred again for additional 30 minutes to exchange the anion. Next, the solution was concentrated to a small volume under reduced pressure and 10 mL diethyl ether was added while stirring to get a yellowish-white precipitate. The precipitate was washed further with diethyl ether (3 × 10 mL) and dried under vacuum to afford **6** as pale yellow powder.Yield: 54 mg (54%, based on Ag). Block shaped pale yellow colored X-ray-quality crystals were grown by layering petroleum ether onto a dichloromethane solution of **6** inside an 8 mm o.d. vacuum-sealed glass tube. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.91 (br s, 2H; NP), 8.76 (d, *J* = 8.5 Hz, 2H; NP), 8.61 (d, *J* = 8.2 Hz, 2H; NP), 8.33 (d, *J* = 8.5 Hz, 2H; NP), 7.75–7.78 (m, 2H; NP), 7.17–7.24 (m, 6H; Ph), 6.75–6.79 (m, 4H; Ph), 5.06–5.11 (m, 2H, CH_2), 4.88–4.97 (m, 2H; CH), 4.58–4.62 (m, 2H; CH_2), 3.10–3.15 (m, 2H; CH_2), 2.93–2.99 ppm (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 165.1, 158.7, 150.8, 147.5, 142.1, 139.9, 137.3, 129.3, 129.0, 128.3, 126.3, 125.3, 122.6, 76.3, 66.9, 41.5 ppm; IR (KBr): ν = 3478 (br, w), 3064 (w), 1651 (m), 1604 (m), 1558 (m), 1455 (m), 1378 (m), 1260 (vs: OTf), 1157 (s), 1030 (s), 637 (s); MS (ESI; CH_3CN): *m/z* 941.0102 for $[Ag_2(L^2)_2(OTf)]^+$.

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References

References

[1] For examples of reviews, see: (a) V.P. Litvinov, Russ. Chem. Rev. 73 (2004) 637; (b) L.A. Oro, M.A. Ciriano, J.J. Perez-Torrente, B.E. Villarroya, Coord. Chem. Rev. 193 (1999) 941; (c) J.K. Bera, N. Sadhukhan, M. Majumdar, Eur. J. Inorg. Chem. (2009) 4023; (d) Y. Sato, S. Nishizawa, K. Yoshimoto, T. Seino, T. Ichi-hashi, K. Morita, N. Teramae, Nucleic Acids Res. 37 (2009) 1411.

[10] (a) R.H. Cayton, M.H. Chisholm, J.C. Huffman, E.B. Lobkovsky, J. Am. Chem. Soc. 113 (1991) 8709;(b) C.H. Chien, J.C. Chang, C.Y. Yeh, G.H. Lee, J.M. Fang, S.M. Peng, Dalton Trans. (2006) 2106;(c) C.H. Chien, J.C. Chang, C.Y. Yeh, G.H. Lee, J.M. Fang, Y. Song, S. M. Peng, Dalton Trans. (2006) 3249; (d) S.A. Hua, G.C. Huang, I.P. Liu, Z.J. Kuo, C.H. Jiang, C.L. Chiu, C.Y Yeh, G.H. Leea, S.M. Peng, Chem. Commun. 46 (2010) 501; (e) S.A. Hua, I.P.C. Liu, H. Hasanov, G.C. Huang, R.H. Ismayilov, C.L. Chiu, C.Y. Yeh, G.H. Lee, S.M. Peng, Dalton Trans. 39 (2010) 3890; (f) R. H. Ismayilov, W.Z, Wang, G.H. Lee, C.Y. Yeh, S.A. Hua, Y. Song, M.M. Rohmer, M. Bénard, S.M. Peng, Angew. Chem. Int. Ed. 50 (2011) 2045; (g) B.-S. Liao, Y.-H. Liu, S.-M. Peng, S.-T. Liu, Dalton Trans. 41 (2012) 1158; (h) M. Majumdar, S. Saha, I. Dutta, A. Sinha, J.K. Bera, Dalton Trans. 46 (2017) 5660.

[11] (a) A. Sinha, S.M.W. Rahaman, M. Sarkar, B. Saha, P. Daw, J. K. Bera, Inorg. Chem. 48 (2009) 11114; (b) S.K. Patra, N. Sadhukhan, J.K. Bera, Inorg. Chem. 45 (2006) 4007; (c) M. Majumdar, S.K. Patra, M. Kannan, K.R. Dunbar, J.K. Bera, Inorg. Chem. 47 (2008) 2212; (d) M. Sarkar, P. Daw, T. Ghatak, J.K. Bera, Chem. Eur. J. 20 (2014) 16537; (e) B. Saha, S.M.W. Rahaman, P. Daw, G. Sengupta, J.K. Bera, Chem. Eur. J. 20 (2014), 6542; (f) R.K. Das, M. Sarkar, S.M.W. Rahaman, H. Doucet, J.K. Bera, Eur. J. Inorg. Chem. (2012) 1680; (g) I. Dutta, A. Sarbajna, P. Pandey, S.M.W. Rahaman, K. Singh, J.K. Bera, Organometallics 35 (2016) 1505; (h) I. Dutta, S. De S. Yadav, R. Mondol, J.K. Bera, J. Organomet. Chem. 849-850 (2017) 117; (i) G. Sengupta, P. Pandey, S. De, R. Ramapanicker, J.K. Bera, Dalton Trans. 47, (2018) 11917.

[12] (a) N. Sadhukhan, S.K. Patra, K. Sana, J.K. Bera, Organometallics 25 (2006) 2914; (b) N. Sadhukhan, J.K. Bera, Inorg. Chem. 48 (2009) 978; (c) S.K. Patra, S.M.W. Rahaman, M. Majumdar, A. Sinha, J.K. Bera, Chem. Commun. (2008) 2511.

[13] R.K. Das, B. Saha, S.M.W. Rahaman, J.K. Bera, Chem. Eur. J. 16 (2010) 14459.

[14] P. Daw, A. Sinha, S.M.W. Rahaman, S. Dinda, J.K. Bera, 31 Organometallics (2012) 3790.

[15] A. Sarbajna, I. Dutta, P. Daw, S. Dinda, S.M.W. Rahaman, A. Sarkar, J.K. Bera, ACS Catal. 7 (2017) 2786.

[16] T. Ghatak, M. Sarkar, S. Dinda, I. Dutta, S.M.W. Rahaman, J.K. Bera, J. Am. Chem. Soc. 137 (2015) 6168.

[17] B. Saha, T. Ghatak, A. Sinha, S.M.W. Rahaman, J.K. Bera, Organometallics 30 (2011) 2051.

[18] P. Daw, R. Petakamsetty, A. Sarbajna, S. Laha, R. Ramapanicker, J.K. Bera, J. Am. Chem. Soc. 136 (2014) 13987.

[19] I. Dutta, S. Yadav, A. Sarbajna, S. De, M. Hölscher, W. Leitner, J.K. Bera, J. Am. Chem. Soc. 140 (2018) 8662.

[2] (a) W.R. Tikkanen, E. Binamira–Soriaga, W.C. Kaska, P.C. Ford, Inorg. Chem. 22 (1983) 1147; (b) W.R. Tikkanen, E. Binamira–Soriaga, W.C. Kaska, P.C. Ford, Inorg. Chem. 23 (1984) 141; (c) A.T. Baker, W.R. Tikkanen, W.C. Kaska, P.C. Ford, Inorg. Chem. 23 (1984) 3254; (d) J.P. Collin, A. Jouaiti, J.P. Sauvage, W.C. Kaska, M.A. McLoughlin, N.L. Keder, W.T.A. Harrison, G.D. Stucky, Inorg. Chem. 29 (1990) 2238; (e) C.S. Campos–Fernández, X. Ouyang, K.R. Dunbar, Inorg. Chem. 39 (2000) 2432; (f) B.-C. Tsai, Y.-H. Liu, S.-M. Peng, S.-T. Liu, Eur. J. Inorg. Chem. (2016) 2783; (g) C.-H. Lee, C.-L. Wu, S.-A. Hua, Y.-H. Liu, S.-M. Peng, S.-T. Liu, Eur. J. Inorg.Chem. (2015) 1417; (h) W.-H. Tang, Y.-H. Liu, S.-M. Peng, S.-T. Liu, J. Organomet. Chem. 775 (2015) 94.

[20] (a) H. Brunner, U. Obermann, Chem. Ber. 122 (1989) 499; (b) H. Brunner, P. Brandl, Tetrahedron: Asymmetry 2 (1991) 919; (c) H. Brunner, C. Henrichs, Tetrahedron: Asymmetry 6 (1995) 653; (d) H. Brunner, R. Störiko, B. Nuber, Tetrahedron: Asymmetry 9 (1998) 407; (e) H. Nishiyama, H. Sakaguchi, T. Nakamura, M. Horihata, M. Kondo, K. Itoh, Organometallics 8 (1989) 846; (f) H. Nishiyama, M. Kondo, T. Nakamura, K. Itoh, Organometallics 10 (1991) 500; (g) H. Nishiyama, S.–B. Park, K. Itoh, Tetrahedron: Asymmetry 3 (1992) 1029; (h) H. Nishiyama, S. Yamaguchi, M. Kondo, K. Itoh, J. Org. Chem. 57 (1992) 4306; (i) H. Nishiyama, S. Yamaguchi, S.–B. Park, K. Itoh, Tetrahedron: Asymmetry 4 (1993) 143; (j) H. Nishiyama, Y. Itoh, H. Matsumoto, S. Park, K. Itoh, J. Am. Chem. Soc. 116 (1994) 2223; (k) S. Park, N. Sakata, H. Nishiyama, Chem. Eur. J. 2 (1996) 303.

[21] (a) S. Bhor, G. Anilkumar, M.K. Tse, M. Klawonn, C. Döbler, B. Bitterlich, A. Grotevendt, M. Beller, Org. Lett. 7 (2005) 3393; (b) K. Ma, J. You, Chem. Eur. J. 13 (2007) 1863; (c) M. Ishihara, H. Togo, Synthesis *(*2007) 1939; (d) I. Panov, P. Drabina, Z. Padělková, P. Šimůnek, M. Sedlák, J. Org. Chem. 76 (2011) 4787; (e) G. Anilkumar, S. Bhor, M.K. Tse, M. Klawonn, B. Bitterlich, M. Beller, Tetrahedron: Asymmetry 16 (2005) 3536; (f) A.J. Davenport, D.L. Davies, J. Fawcett, D.R. Russell, J. Organomet. Chem. 69 (2006) 13445; (g) A.J. Davenport, D.L. Davies, J. Fawcett, D.R. Russell, J. Chem. Soc. Perkin Trans. 1 (2001) 1500.

[22] (a) D.A. House, P.J. Steel, A.A. Watson, Aust. J. Chem. 39 (1986) 1525; (b) A. A. Watson, D.A. House, P.J. Steel, J. Org. Chem. 56 (1991) 4072; (c) H. Brunner, T. Scheck, Chem. Ber. 125 (1992) 701; (d) D.L. Christenson, C.J. Tokar, W.B. Tolman, Organometallics 14 (1995) 2148; (e) W. Fung, W. Cheng, W. Yu, C. Che, T.C.W. Mak, J. Chem. Soc. Chem. Commun. (1995) 2007. (f) A.A. Watson, D.A. House, P.J. Steel, Aust. J. Chem. 48 (1995) 1549; (g) C. Kashima, Y. Miwa, S. Shibata, H. Nakazono, J. Heterocyclic

Chem. 39 (2002) 1235; (h) A. Herrera, A. Briceño, T. Gonzalez, A. Linden, F.W. Heinemann, G. Agrifoglio, J. Pastrán, R. Dorta, Tetrahedron: Asymmetry 27 (2016) 759;(i) T.Godau, F. Platzmann, F.W. Heinemann, N. Burzlaff, Dalton Trans. (2009) 254.

[23] (a) C.J. Fahrni, A. Pfaltz, Helv. Chim. Acta. 81 (1998) 491; (b) C.J. Fahrni, A. Pfaltz, Helv. Chim. Acta. 81 (1998) 507; (c) C.J. Fahrni, Tetrahedron 54 (1998) 5465; (d) D. Das, R. Mal, N. Mittal, Z. Zhu, T.J. Emge, D.Seidel, Beilstein J. Org. Chem. 14 (2018) 2002.

[24] (a) J.A. Frump, Chem. Rev. 71 (1971) 483; (b) L. Mei, Z.J. Hai, S. Jie, Z.S. Ming, Y. Hao, H.K. Liang, J. Comb. Chem. 11 (2009) 220; (c) K. Nordström, E. Macedo, C. Moberg, J. Org. Chem. 62 (1997) 1604; (d) U. Bremberg, F. Rahm, C. Moberg, Tetrahedron: Asymmetry 9 (1998) 3437; (e) M. Redlich, M.M. Hossain, Tetrahedron Lett. 45 (2004) 8987.

[25] (a) C.S. Campos–Fernández, L.M. Thomson, J.R. Galán–Mascarós, X. Ouyang, K.R. Dunbar, Inorg. Chem. 41 (2002) 1523; (b) T.G. Majewicz, P. Caluwe, J. Org. Chem. 39 (1974) 720.

[26] G.R. Newkome, S.J. Garbis, V.K. Majestic, F.R. Fronczek, G. Chiari, J. Org. Chem. 46 (1981) 833.

[27] (a) D.D. LeCloux, C.J. Tokar, M. Osawa, R.P. Houser, M.C. Keyes, W.B. Tolman, Organometallics 13 (1994) 2855; (b) D.L. Jameson, R.K. Castellano, Inorg. Synth. 32 (1998) 55.

[28] (a) J. Díez, M.P. Gamasa, M. Panera, Inorg. Chem. 45 (2006) 10043; (b) M. Panera, J. Díez, I. Merino, E. Rubio, M.P. Gamasa, Inorg. Chem. 48 (2009) 11147.

[29] (a) Z. Deng, H. Qi, L. Huo, S.W. Ng, H. Zhao, S. Gao, Dalton Trans. 39 (2010) 10038; (b) G.F. Manbeck, W.W. Brennessel, C.M. Evans, R. Eisenberg, Inorg. Chem. 49 (2010) 2834; (c) Z. Liu, P.I. Djurovich, M.T. Whited, M.E. Thompson, Inorg. Chem. 51 (2012) 230; (d) M. Knorr, F. Guyon, A. Khatyr, C. Strohmann, M. Allain, S.M. Aly, A. Lapprand, D. Fortin, P.D. Harvey, Inorg. Chem. 51 (2012) 9917; (e) S. Naik, J.T. Mague, M.S. Balakrishna, Inorg. Chem. 53 (2014) 3864; (f) K. Chen, J. Shearer, V. J. Catalano, Inorg. Chem. 54 (2015) 6245.

[3] (a) V.P. Litvinov, Advances in Heterocyclic Chemistry 91 (2006) 189; (b) D.J. Brown, J.A. Ellman, E.C. Taylor, The Chemistry of Heterocyclic Compounds, The Naphthyridines; John Wiley, (2008); (c) R. Rosin, W. Seichter, A. Schwarzer, M. Mazik, Eur. J. Org. Chem. 2017 (2017) 6038; (d) A.J. Bailey, P.N. Horton, M.C. Grossel, CrystEngComm, 12 (2010) 4074; (e) L. Torre-Fernandez, S. Garcia-Granda, S. Goswami, Acta Crystallogr. Sect. A: Found. Crystallogr. 63 (2007) s154; (f) S.Z. Hu, C.F. Chen, Org. Biomol. Chem. 9 (2011) 5838; (g) C.-Y. Huang, K.-Y. Kuan, Y.-H. Liu, S.-M. Peng, S.-T. Liu, Organometallics 33 (2014) 2831; (h) B.-S. Liao, Y.-H. Liu, S.-M. Peng, K. R. R eddy, S.-H. Liu, P.-T. Chou, S.-T. Liu, Dalton Trans. 43 (2014) 3557; (i) M.-U. Hung, B.-S. Liao, Y.-H. Liu, S.-M. Peng, S.-T. Liu, Appl. Organomet. Chem. 2014, 28, 661.

[30] A. Bondi, J. Phys. Chem. 68 (1964) 441.

[31] H. Araki, K. Tsuge, Y. Sasaki, S. Ishizaka, N. Kitamura, Inorg. Chem. 46 (2007) 10032.

[32] C. Che, M. Tse, M.C.W. Chan, K. Cheung, D.L. Phillips, K. Leung, J. Am. Chem. Soc. 122 (2000) 2464.

[33] (a) K.R. Kyle, C.K. Ryu, J.A. DiBenedetto, P.C. Ford, J. Am. Chem. Soc. 113 (1991) 2954; (b) C.K. Ryu, M. Vitale, P.C. Ford, Inorg. Chem. 32 (1993) 869; (c) D. Tran, J.L. Bourassa, P.C. Ford, Inorg. Chem. 36 (1997) 439; (d) G.F. Manbeck, W.W. Brennessel, R. Eisenberg, Inorg. Chem. 50 (2011) 3431; (e) D.M. Zink, M. Bächle, T. Baumann, M. Nieger, M. Kühn, C. Wang, W. Klopper, U. Monkowius, T. Hofbeck, H. Yersin, S. Bräse, Inorg. Chem. 52 (2013) 2292.

[34] (a) K. Lauder, A. Toscani, N. Scalacci, D. Castagnolo, Chem. Rev. 117 (2017) 14091; (b) G. M. Borrajo-Calleja, E. de Julián, E. Bayón, J. Díez, E. Lastra, I. Merino, M.P. Gamasa, Inorg. Chem. 55 (2016) 8794; (c) H. Lebel, J-F. Marcoux, C. Molinaro, A.B. Charette, Chem. Rev. 103 (2003) 977; (d) N.R. Candeias, C.A.M. Afonso, Curr. Org. Chem., 13 (2009) 763; (e) S. Zhanga, Y. Lia, Y. Xua, Z. Wang, Chinese Chemical Letters 29 (2018) 873.

[35] In a typical experiment, a mixture of N-benzylideneaniline (0.5 mmol), phenylacetylene (0.75 mmol) and copper(I) or silver(I) complex (1 mol%) in dry and deoxygenated CH_2Cl_2 (5.0 mL) is stirred under a N_2 atmosphere at room temperature for 48 h. Then small aliquot was taken out and subjected to GC MS analysis.

[36] X. Zhao, Y. Zhang, J. Wang, Chem. Commun., 48 (2012) 10162.

[37] (a) D.A. Evans, D. Seidel, M. Rueping, H.W. Lam, J.T. Shaw, C.W. Downey, J. Am. Chem. Soc. 125 (2003) 12692; (b) K. Xu, G. Lai, Z. Zha, S. Pan, H. Chen, Z. Wang, Chem. Eur. J. 18 (2012) 12357; (c) S. Liu, C. Wolf, Org. Lett.10 (2008) 1831.

[38] M.J. McKennon, A.I. Meyers, J. Org. Chem. 58 (1993) 3568.

[39] (a) G.J. Kubas, Inorg. Synth. 19 (1979) 90. (b) J.W.L. Martin, G.J. Organ, K.P. Wainwright, K.D.V. Weerasuria, A.C. Willis, S.B. Wild, Inorg. Chem. 26 1987, 2963.

[4] (a) G.V. Bodrin, A.G. Matveeva, E.I. Goryunov, M.P. Pasechnik, R.R. Aysin, A.N. Turanov, V.K. Karandashev, E.D. Savin, A.S. Peregudov, Y.V. Nelyubina, V.K. Brel, Chemistry of Heterocyclic Compounds 52 (2016) 583; (b) A. Madaan, R. Verma, V. Kumar, A.T. Singh, S.K. Jain, M. Jaggi, Archiv der Pharmazie, 348 (2015) 837; (c) A.A. Fadda, S.A. El-Hadidy, K.M. Elattar, Synthetic Communications 45 (2015) 2765; (d) H. Wang, S. Wang, L. Cheng, L. Chen, Y. Wang, J. Qing, S. Huang, Y. Wang, X. Lei, Y. Wu, Z. Ma, L. Zhang, Y. Tang, ACS Med. Chem. Lett. 6 (2015) 977; (e) G. Y. Lesher, E. J. Froelich, M. D. Gruett, J. H. Bailey, R. P. Brundage, J. Med. Chem. 5 (1962) 1063.

[40] A. Mendía, E. Cerrada, M. Laguna, Inorg. Synth. 34 (2004) 86.

[5] (a) Y.-Y. Zhou, D.R. Hartline, T.J. Steiman, P.E. Fanwick, C. Uyeda, Inorg. Chem. 53 (2014) 11770; (b) T.J. Steiman, C. Uyeda, J. Am. Chem. Soc. 137 (2015) 6104; (c) S. Pal, C. Uyeda, J. Am. Chem. Soc. 137 (2015) 8042; (d) D.R. Hartline, M. Zeller, C. Uyeda, Angew. Chem. Int. Ed. 55 (2016) 6084; (e) Y.-Y. Zhou, C. Uyeda, Angew. Chem., Int. Ed. 55 (2016) 3171; (f) D.R. Hartline, M. Zeller, Christopher Uyeda, J. Am. Chem. Soc. 139 (2017) 13672; (g) H.R. Rounds, M. Zeller, C. Uyeda, Organometallics 37 (2018) 545; (h) A.K. Maity, M. Zeller, C. Uyeda, Organometallics 37 (2018) 2437.

[6] (a) C. He, S.J. Lippard, J. Am. Chem. Soc. 122 (2000) 184; (b) C. He, J.L. DuBois, B. Hedman, K.O. Hodgson, S.J. Lippard, Angew. Chem. Int. Ed. 40 (2001) 1484; (c) C. He, S.J. Lippard, Tetrahedron 56 (2000) 8245; (d) C. He, S.J. Lippard, Inorg. Chem. 39 (2000) 5225.

[7] (a) C. He, A.M. Barrios, D.Lee, J. Kuzelka, R.M. Davydov, S.J. Lippard, J. Am. Chem. Soc. 122 (2000) 12683; (b) C. He, S.J. Lippard, Inorg. Chem. 40 (2001) 1414; (c) J. Kuzelka, S. Mukhopadhyay, B. Spingler, S.J. Lippard, Inorg. Chem., 42 (2003) 6447.

[8] T.C. Davenport, T.D. Tilley, Dalton Trans. 44 (2015) 12244.

[9] (a) T.C. Davenport, T.D. Tilley, Angew. Chem. Int. Ed. 50 (2011) 12205; (b) T.C. Davenport, T.D. Tilley, Angew. Chem. 123 (2011) 12413.