Received: 15 February 2019 | Revised: 24 March 2019 | Accepted: 26 March 2019

DOI: 10.1002/aoc.4955



REVIEW

WILEY Applied Organometallic Chemistry

# Synthesis and structures of copper complexes bearing unsymmetric derivatives of (*R,R*)-1,2-diaminocyclohexane: An efficient catalyst for asymmetric Henry reaction

Juhyun Cho[1] | Min Kyung Chun[1] | Saira Nayab[2] | Jong Hwa Jeong[1]

[1]Department of Chemistry and Green-Nano Materials Research Center, Kyungpook National University, 1370 Sankyuk-dong, Taegu 702-701, Republic of Korea

[2]Department of Chemistry, Shaheed Benazir Bhutto University, Sheringal, Dir (Upper), Khyber Pakhtunkhwa, Islamic Republic of Pakistan

**Correspondence**
Jong Hwa Jeong, Department of Chemistry and Green-Nano Materials Research Center, Kyungpook National University, 1370 Sankyuk-dong, Taegu,702-701, Republic of Korea.
Email: jeongjh@knu.ac.kr

**Funding information**
Basic Science Research Program through the National Research Foundation of Korea, Grant/Award Number: NRF-2017R1D1A3B03030670

A series of Cu (II) complexes bearing asymmetric derivatives of (*R,R*)-1,2-diaminocyclohexane were synthesised and characterised. The X-ray structures of the complexes showed distorted square planar geometry. The catalytic activities of *in situ*-generated copper acetate complexes in the presence of 10 mol% of *N,N*-diisopropylethylamine were evaluated in the asymmetric Henry reaction. The current catalysts showed high enantioselectivity (up to 99%) for (*S*)-1-nitro-4-phenylbutan-2-ol from the reaction of 3-phenylpropanal and nitromethane.

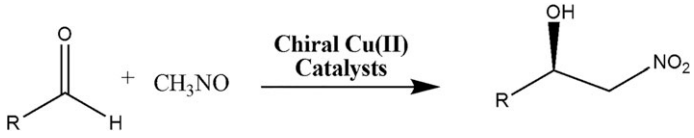
**KEYWORDS**
(*S*)-β-nitroalcohols, copper complexes, enantioselective Henry reaction, unsymmetrical chiral diamines

## 1 | INTRODUCTION

The asymmetric Henry reaction is one of the most significant and versatile organic transformation reactions for the synthesis of β-nitroalcohols (Scheme 1).[1] This reaction has received much attention in synthetic chemistry[2–4] because the resulting β-nitroalcohols can be conveniently converted into many valuable building blocks, such as β-aminoalcohols, 1,2-diamines and α-hydroxy carboxylic acids.[5–8] Although this reaction has been known for over a century,[9] Shibasaki's and co-workers pioneering work[10–14] on its asymmetric version attracted the attention of the synthetic community. Since then, a great number of metal-based catalysts[15,16] and organocatalysts[17–19] have been successfully established in the development of asymmetric Henry reactions. In particular, chiral Cu-based complexes have received particular attention given the wide structural variability of the chiral ligands, excellent chelating ability, ease of handling and ready availability.[20–29] For example, Bandini *et al.* applied a series of $C_2$-symmetrical oligothiophene ligands for this reaction.[30] Blay and co-workers applied $C_1$-symmetric camphor-derived amino pyridine ligands and observed high enantioselectivity.[31] Similarly, sparteine, oxazolines, imines and amine ligand-based copper complexes have also been successfully exploited for this reaction (Scheme 1).[32–35]

The Skarzewski group successfully applied chiral complexes derived from (*R,R*)-1,2-diaminocyclohexane to efficiently control the stereochemical outcomes in the asymmetric Henry reaction.[36] Since then, efforts have been devoted toward synthesising new Cu (II) complexes based on (*R,R*)-1,2-diaminocyclohexane with various pendant groups, to effectively control the stereochemical




**SCHEME 1** Asymmetric Henry reaction

outcomes.[37–41] However, the structural properties and specifically X-ray structural studies of these complexes have been insufficiently studied. Further, the asymmetrical ligand framework represents an attractive option because of its diverse structural properties.[42–44] The potential merits of the (*R*,*R*)-1,2-diaminocyclohexane framework and recent promising results in the asymmetric Henry reaction for Cu (II) complexes supported by such ligands, as reported by our group, encouraged us to evaluate asymmetrical chiral diamines based on the (*R*,*R*)-1,2-diaminocyclohexane backbone.[45–47] Although impressive progress has been achieved, there remains a need for new catalysts for the asymmetric Henry reaction of aldehydes with nitromethane. Herein, we describe the synthesis, structure and catalytic performance of Cu complexes containing asymmetric derivatives of the (*R*,*R*)-1,2-diaminocyclohexane-bearing backbone in the asymmetric Henry reaction.

## 2 | EXPERIMENTAL

### 2.1 | Materials and physical measurements

All manipulations involved in the synthesis of ligands ($L^1$–$L^4$) and their corresponding Cu (II) complexes, $[L^nCuCl_2]_n$ ($L^n = L^1$–$L^4$; $n = 1$ or 2), where $L^1$ is (1*R*,2*R*)-$N^1$,$N^2$-dibenzylcyclohexane-1,2-diamine, $L^2$ is (1*R*,2*R*)-$N^1$-benzyl-$N^2$-((naphthalen-1-yl)methyl)cyclohexane-1,2-diamine, $L^3$ is (1*R*,2*R*)-$N^1$-benzyl-$N^2$-((naphthalen-2-yl)methyl)cyclohexane-1,2-diamine and $L^4$ is (1*R*,2*R*)-$N^1$-benzyl-$N^2$-((anthracene-9-yl)methyl) cyclohexane-1,2-diamine, were performed using benchtop techniques in the air, unless otherwise specified. (1*R*,2*R*)-*N*-Benzylcyclohexane-1,2-diamine, 1-naphthylaldehyde, 2-naphthylaldehyde, 9-anthracenealdehyde, $CuCl_2{\cdot}2H_2O$, benzaldehyde, 3-phenylpropanal and diisopropylethylamine ($^iPr_2Net$) were obtained from Aldrich Chemical. NMR solvents were purchased from Sigma Aldrich and stored over 3 Å molecular sieves. Various solvents such as MeOH, $CH_2Cl_2$, $Et_2O$, EtOH, *n*-hexane (*n*-Hex) and ethyl acetate were purchased from high-grade commercial suppliers. $L^1$ and its corresponding Cu (II) complex, $[L^1CuCl_2]$, have been synthesised according to the reported methods.[44]

$^1$H- and $^{13}$C-NMR spectra were recorded on a Bruker Avance Digital 500-NMR spectrometer (Bruker, Billerica, MA, USA), and chemical shifts were recorded in ppm units ($\delta$) relative to residual protium in the deuterated solvents ($CDCl_3$, $\delta = 7.26$). Coupling constants were reported in Hertz (Hz). Data were recorded as m = multiplet, br = broad, s = singlet, d = doublet, t = triplet and q = quartet. For the homonuclear decoupling NMR spectroscopy, Bruker Avance digital 500-NMR spectrometer was used. Infrared spectra (IR) (neat) were recorded on Bruker FT/IR-Alpha and the data were reported in cm $^{-1}$. Elemental analyses were determined using the EA 1108-Elemental Analyzer at the Chemical Analysis Laboratory of the Centre for Scientific Instruments of Kyungpook National University. Enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC) with a chiral OD-H column and AD-H column using HPLC grade isopropanol (IPA) and *n*-Hex as eluting solvents.

### 2.2 | Synthesis of ligands and Cu (II) complexes

#### 2.2.1 | (1*R*,2*R*)-$N^1$-benzyl-$N^2$-((naphthalen-1-yl)methyl)cyclohexane-1,2-diamine ($L^2$)

$L^2$ was prepared by treating (1*R*,2*R*)-*N*-benzylcyclohexane-1,2-diamine (1.73 g, 8.47 mmol) with 1-naphthylaldehyde (1.32 g, 8.47 mmol) in MeOH. The resultant solution was refluxed for 5 days. The residue obtained after solvent evaporation was treated with distilled water and $CH_2Cl_2$. The organic phase was separated and dried over $MgSO_4$, and concentrated to obtain an imine intermediate (2.72 g, 94%). The imine moiety was further reduced by treating with $NaBH_4$ (0.45 g, 11.9 mmol) in MeOH (50 ml). After being stirred for 12 hr at ambient conditions, the solvent was removed under reduced pressure. The resultant residue was extracted with $CH_2Cl_2$ followed by washing with water (10 ml × 3). The combined organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure to get $L^2$ as a light yellow oil (2.60 g, 95%). Anal. calcd for $C_{24}H_{28}N_2$: C, 83.68; H, 8.19; N, 8.13; found: C, 83.78; H, 8.22; N, 8.17%. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.05 (d, 1H, naph), 7.76 (d, 1H, naph), 7.67 (d, 1H, naph), 7.40–7.30 (m, 4H, naph), 7.16–7.09 (m, 5H, Ph), 4.13 (q, $J = 12.82$ Hz, 2H, $CH_aCH_b$), 3.62 (q, $J = 13.12$ Hz, 2H,

$CH_aCH_b$), 2.89 (br, N-H), 2.82–2.14 (m, 2H, CyH), 2.25–2.06 (m, 2H, CyH), 1.70–1.65 (m, 2H, CyH), 1.25–1.12 (m, 2H, CyH), 1.06–0.94 (m, 2H, CyH); $^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 140.88, 136.51, 133.86, 131.89, 128.58, 128.19 (2C, Ph), 127.95 (2C, Ph), 127.64, 126.59, 126.05, 125.97, 125.50, 125.31, 124.01, 61.45, 61.09, 50.89, 49.03, 31.67, 31.54, 25.10, 24.97; IR (oil neat; cm $^{-1}$): 3293 (m), 3059 (m), 2924 (s), 2852 (s), 1597 (m), 1509 (m), 1451 (s), 1357 (m), 1113 (w), 776 (s), 731 (s), 697 (s).

### 2.2.2 | (1*R*,2*R*)-$N^1$-benzyl-$N^2$-((naphthalen-2-yl)methyl)cyclohexane-1,2-diamine ($L^3$)

$L^3$ was prepared by an identical procedure as described for $L^2$, except utilising 2-naphthylaldehyde (1.32 g, 8.47 mmol) to obtain a light yellow imine intermediate (2.79 g, 96%). Further reduction was the same as described for $L^2$ using $NaBH_4$ (0.46 g, 12.2 mmol) to obtain the amine product (2.54 g, 90%). Anal. calcd for $C_{24}H_{28}N_2$: C, 83.68; H, 8.19; N, 8.13; found: C, 83.70; H, 8.20; N, 8.16%. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 7.74–7.67 (m, 4H, naph), 7.38–7.36 (m, 3H, naph), 7.25–7.14 (m, 5H, Ph), 3.86 (q, $J$ = 13.43 Hz, 2H, $CH_aCH_b$), 3.71 (q, $J$ = 13.12 Hz, 2H, $CH_aCH_b$), 2.22 (m, 2H, CyH), 2.13 (m, 2H, CyH), 1.88 (br, 2H, N-H), 1.65 (m, 2H, CyH), 1.20–1.12 (m, 2H, CyH), 1.03–0.93 (m, 2H, CyH); $^{13}$C-NMR (500 MHz, $CDCl_3$): $\delta$ 141.00, 138.52, 133.43, 132.56, 128.31 (2C, Ph), 128.04 (2C, Ph), 127.92, 127.65, 127.60, 126.73, 126.64, 126.20, 125.87, 125.39, 60.85 (2C, N-$CH_2$), 50.94, 50.83, 31.56, 31.51, 25.02, 24.99. IR (oil neat; cm$^{-1}$): 3298 (m), 3053 (m), 2924 (s), 2852 (s), 1600 (m), 1494 (m), 1451 (s), 1336 (m), 1203 (w), 1123 (w), 855 (w), 813 (s), 739 (s), 697 (s).

### 2.2.3 | (1*R*,2*R*)-$N^1$-benzyl-$N^2$-((anthracen-9-yl)methyl)cyclohexane-1,2-diamine ($L^4$)

$L^4$ was prepared by an identical procedure as described for $L^2$, except utilising 9-anthracenecarboxaldehyde (3.03 g, 14.7 mmol) to obtain imine (5.62 g, 97%). Further reduction follows the same procedure as stated for $L^2$ using $NaBH_4$ (0.81 g, 21.45 mmol) to obtain diamine as a yellow solid (5.48 g, 97% yield). Anal. calcd for $C_{28}H_{30}N_2$: C, 85.25; H, 7.66; N, 7.10; found: C, 85.32; H, 7.70; N, 7.15%. $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.41 (s, 1H, anth), 8.35 (m, 2H, anth), 8.02 (m, 2H, anth), 7.47 (m, 4H, anth), 7.19–7.16 (m, 5H, Ph), 4.73 (q, $J$ = 11.90 Hz, 2H, $CH_aCH_b$), 3.70 (q, $J$ = 12.82 Hz, 2H, $CH_aCH_b$), 2.58–2.52 (m, 2H, CyH), 2.29–2.20 (m, 2H, CyH), 1.94 (br, 2H, N-H), 1.89–1.79 (m, 2H, CyH), 1.44–1.32 (m, 2H, CyH), 1.34–1.09 (m, 2H, CyH); $^{13}$C-NMR (125 MHz, $CDCl_3$): $\delta$ 140.81, 132.10, 131.59, 130.26 (2C, anth), 129.06 (2C, anth), 128.16 (2C, Ph), 127.92 (2C, Ph), 127.0, 126.98 (2C, anth), 126.56, 125.98, 124.85 (2C, anth), 124.85 (2C, anth), 62.32, 61.23, 50.95, 43.38, 32.17, 31.67, 25.28, 25.06; IR (oil neat; cm$^{-1}$): 3294 (m), 3229 (m), 3051 (m), 2923 (s), 2850 (s), 1621 (m), 1488 (m), 1444 (s), 1337 (m), 1202 (w), 1092 (s), 884 (s), 729 (s), 700 (s).

### 2.2.4 | (1*R*,2*R*)-$N^1$-benzyl-$N^2$-((naphthalen-1-yl)methyl)cyclohexane-1,2-diamine Zn (II) chloride [$L^2CuCl_2$]

$L^2$ (1.00 g, 2.90 mmol) was treated with $CuCl_2{\cdot}2H_2O$ (0.49 g, 2.90 mmol) in $CH_2Cl_2$ (20.0 ml) and stirred for 12 hr at ambient temperature. The solution was dried over $MgSO_4$ and concentrated to obtain a green solid. The resultant solid was washed with $Et_2O$ (5 ml × 3) to obtain the final product as a blue green powder (1.27 g, 91% yield). Anal. calcd for $C_{24}H_{28}Cl_2CuN_2$: C, 60.19; H, 5.89; N, 5.85; found: C, 60.25; H, 6.02; N, 5.88%; IR (solid neat; cm$^{-1}$): 3163 (m), 3057 (w), 2931 (s), 2857 (s), 1697 (m), 1453 (m), 1510 (m), 1396 (s), 1165 (m), 1097 (w), 930 (w), 778 (s), 748 (s), 701 (s).

### 2.2.5 | (1*R*,2*R*)-$N^1$-benzyl-$N^2$-((naphthalen-2-yl)methyl)cyclohexane-1,2-diamine Zn (II) chloride [$L^3CuCl_2$]

An analogous method was followed for the synthesis of **[$L^3CuCl_2$]** as described for **[$L^2CuCl_2$]**, except utilising $L^2$ (1.00 g, 2.90 mmol) to obtain a blue green powder as the final product (1.21 g, 87% yield). Anal. calcd for $C_{24}H_{28}Cl_2CuN_2$: C, 60.19; H, 5.89; N, 5.85; found: C, 60.22; H, 6.06; N, 6.00%; IR (solid neat; cm$^{-1}$): 3164 (m), 3058 (w), 2933 (s), 2858 (s), 1698 (m), 1600 (m), 1508 (m), 1451 (s), 111 (w), 931 (s), 749 (s), 700 (s).

### 2.2.6 | [(1*R*,2*R*)-$N^1$-benzyl-$N^2$-((anthracen-9-yl)methyl)cyclohexane-1,2-diamine(μ-chloro) Zn (II) chloride] $[L^4CuCl_2]_2$

An analogous method was followed for the synthesis of **$[L^4CuCl_2]_2$** as described for **[$L^2CuCl_2$]**, except utilising $L^3$ (1.14 g, 2.90 mmol) to obtain a dark green powder as the final product (1.24 g, 92% yield). Anal. calcd for $C_{54}H_{60}Cl_4Cu_2N_4$: C, 63.57; H, 5.72; N, 5.30; found: C, 63.59; H, 5.77; N, 5.36%; IR (solid neat; cm$^{-1}$): 3165 (m), 3047 (w), 2929 (s), 2856 (s), 1622 (m), 1495 (m), 1448 (s), 1396 (m), 1033 (w), 889 (s), 735 (s), 702 (s).

### 2.3 | X-ray crystallographic studies

X-ray-quality single crystals were mounted in thin-walled glass capillaries on an Enraf-Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by least-squares analysis of 25 reflections ($10° < \theta < 13°$). Intensity data were collected in the $\omega/2\theta$ scan mode, and three standard reflections were monitored every hour during data collection. Empirical absorption corrections with $\psi$-scans were performed on the data using the ABSCALC program.[47] The structures were solved using direct methods and refined using the full-matrix least-squares techniques on $F^2$ using *SHELXS*-97[48] and *SHELXL* program packages.[49] Absolute structures were confirmed using anomalous dispersion effects with Friedel pairs, which were not merged. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were positioned geometrically using the riding model with fixed isotropic thermal factors. The crystallographic data and refinements are summarised in Table 1.

### 2.4 | General procedure for asymmetric Henry reaction

A 50-ml flask was charged with 10 mol% of a dichloro Cu (II) complex in 10 ml of IPA and treated with silver acetate to generate the diacetato Cu (II) complex *in situ*. The resultant solution was applied to the Henry reaction. Then, nitromethane (0.53 ml, 10 mmol) and benzaldehyde or 3-phenylpropanal (5.0 mmol) were added followed by the addition of 10.0 mol% of *N*,*N*-diisopropylethylamine ($^i$Pr$_2$NEt) as a co-catalyst due to its good activity at −20°C.[50,51] After stirring for a specified time, reactions were quenched with 1.0 ml of 1 N HCl solution and then evaporated. The products were extracted with $CH_2Cl_2$ (3 × 20 ml), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure.

#### 2.4.1 | (*S*)-1-Phenyl-2-nitroethanol

The crude products were purified by column chromatography (30% EtOAc/hexane) to give a colorless oil as (*S*)-1-phenyl-2-nitroethanol.[44] $^1$H-NMR (500 Hz, $CDCl_3$): $\delta$ 7.30 (5H, m, Ar-*H*), 5.38 (1H, dd, C*H*), 4.51(1H, dd, C$H_2$), 4.41 (1H, dd, C$H_2$), 2.89 (1H, br s, O*H*). Enantiomeric excess (ee) was determined using HPLC on Chiracel OD-H column (*n*-Hex:IPA = 95:5; flow rate = 1.5 ml/min; $\lambda$ = 215 nm); *R* enantiomer $t_R$ = 18.4 min, *S* enantiomer $t_R$ = 22.3 min (Table 3).

#### 2.4.2 | (*S*)-1-Nitro-4-phenylbutan-2-ol

The crude products were purified by column chromatography (10% EtOAc/hexane) to give a colorless oil as (*S*)-1-nitro-4-phenylbutan-2-ol.[52,53] $^1$H-NMR (500 Hz, $CDCl_3$): $\delta$ 7.30 (5H, m, Ar-*H*), 5.38 (1H, dd, -C*H*), 4.51(1H, dd, C$H_2$), 4.41 (1H, dd, -C$H_2$), 2.89 (1H, br, s, -O*H*). Enantiomeric excess (ee) was determined using HPLC on Chiral AD-H column (*n*-Hex:IPA = 90:10; flow rate = 1.0 ml/min; $\lambda$ = 254 nm); *R* enantiomer $t_R$ (minor) = 11 min, *S* enantiomer $t_R$ (major) = 17 min (Table 3).

## 3 | RESULTS AND DISCUSSION

### 3.1 | Synthesis and chemical properties

The ligands studied in the current work were readily prepared by the condensation reaction of (1*R*,2*R*)-*N*-benzylcyclohexane-1,2-diamine with 1- or 2-naphthaldehyde and 9-anthracencarboxyaldehyde. Reduction of the imine moiety with $NaBH_4$ in anhydrous methanol afforded the corresponding reduced ligands. All synthesised ligands were characterised by multinuclear NMR spectroscopy. The disappearance of imine proton signals and the appearance of (-C$H_2$-) signals (as two quartets; $L^2$: 4.13, 3.62; $L^3$: 3.86, 3.71; $L^4$: 4.73, 3.70 ppm) in the NMR spectra of the reduced ligands confirmed the formation of the $C_1$-asymmetric diamines ($L^2$–$L^4$). Treating these ligands with $CuCl_2 \cdot 2H_2O$ at the 1:1 molar ratio gave their respective Cu (II) complexes, $\mathbf{[L^nCuCl_2]_n}$ ($L^n = L^2$–$L^3$; $n$ = 1 or 2) in high yield (up to 89%) at ambient temperature in $CH_2Cl_2$ (Scheme 2). These complexes were structurally characterised using IR spectroscopy, elemental analysis and X-ray diffraction. The IR spectra of the ligands were compared with those of the complexes, specifically in the N–H region. Characteristic broad N–H peaks in the IR spectra of the ligands ($L^2$–$L^4$) were observed at 3293, 3298 and 3294 $cm^{-1}$, while in the corresponding Cu (II) complexes the N–H absorption bands appeared at 3163, 3164 and 3165 $cm^{-1}$ for $\mathbf{[L^nCuCl_2]_n}$ ($L^n = L^2$–$L^4$; $n$ = 1 or 2).

### 3.2 | Description of the X-ray crystal structures

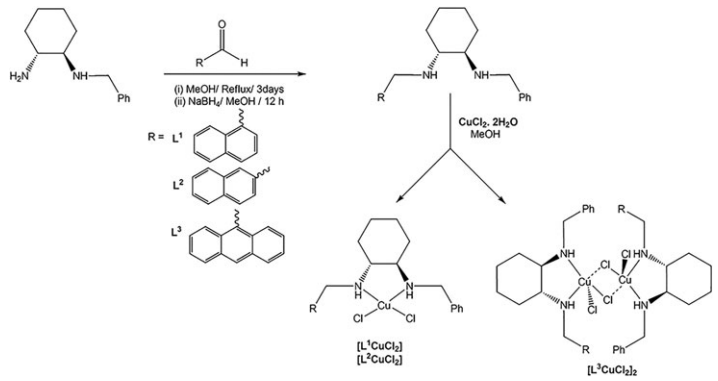
X-ray-quality single crystals of $\mathbf{[L^3CuCl_2]}$ were obtained by slow diffusion of diethyl ether ($Et_2O$) into ethanol (EtOH) solutions, whereas those of $\mathbf{[L^4CuCl_2]_2}$ were grown by slow diffusion of $Et_2O$ into an EtOH:$CH_2Cl_2$ (1:1) mixture at room temperature. The ORTEP diagrams depicting the Cu (II) complexes with the atom numbering scheme at the 30% probability level are shown in Figures 1

**TABLE 1** Crystal data and structural refinement for Cu (II) complexes

| | $[L^3CuCl_2]\cdot CH_3CH_2OH$ | $[L^4CuCl_2]_2\cdot CH_2Cl_2\cdot CH_3CH_2OH$ |
|---|---|---|
| Empirical formula | $C_{24}H_{28}Cl_2CuN_2\cdot CH_3CH_2OH$ | $C_{56}H_{60}Cl_4Cu_2N_4\cdot CH_2Cl_2\cdot CH_3CH_2OH$ |
| Formula weight | 524.99 | 1188.95 |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Temperature (K) | 293(2) | 293(2) |
| Crystal system | Orthorhombic | Triclinic |
| Space group | $P2_12_12_1$ | $P_1$ |
| Unit cell dimensions | | |
| $a$ (Å) | 11.0408(7) | 9.3835(9) |
| $b$ (Å) | 12.6512(8) | 12.3640(11) |
| $c$ (Å) | 18.1672(17) | 14.2534(14) |
| $\alpha$ (°) | 90 | 69.459(7) |
| $\beta$ (°) | 90 | 73.952(9) |
| $\gamma$ (°) | 90 | 71.731(8) |
| Volume (Å$^3$), $Z$ | 2537.6(3), 4 | 1444.5(2), 1 |
| Density (calcd) (mg/m$^3$) | 1.374 | 1.367 |
| Absorption coefficient (mm$^{-1}$) | 1.092 | 1.056 |
| $F$ (000) | 0.1213 | 618 |
| Crystal size (mm) | $0.50\times0.45\times0.40$ | $0.48\times0.45\times0.35$ |
| $\theta$ range for data collection | 1.96 to 25.48 | 1.55 to 25.48 |
| Index ranges | $13\le h\le 13$; $-15\le k\le 15$; $-21\le l\le 21$ | $-11\le h\le 11$; $-14\le k\le 14$; $-17\le l\le 17$ |
| Reflections collected | 5399 | 10 783 |
| Independent reflections | 4708 [$R$ (int) = 0.0185] | 10 732 [$R$ (int) = 0.0020] |
| Reflections observed ($>2\sigma$) | 3557 | 8142 |
| Data completeness | 1.000 | 0.998 |
| Max. and min. transmission | 0.6692 and 0.6112 | 0.7087 and 0.6310 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 4708/0/291 | 10 732/5/651 |
| Final $R$ indices [$I>2\sigma(I)$] | $R_1 = 0.0390$ $wR_2 = 0.1213$ | $R_1 = 0.0452$ $wR_2 = 0.1285$ |
| $R$ indices (all data) | $R_1 = 0.0658$ $wR_2 = 0.1478$ | $R_1 = 0.0676$ $wR_2 = 0.1373$ |
| Absolute structure parameter | 0.03(2) | 0.080(14) |
| Largest diff. peak and hole ($e$/Å$^3$) | 0.380 and − 0.258 | 0.877 and − 0.396 |

and 2; selected bond lengths and angles are given in Table 2. The crystal systems were orthorhombic with space group $P2_12_12_1$ for **$[L^3CuCl_2]\cdot CH_3CH_2OH$**, and triclinic with space group $P_1$ for **$[L^4CuCl_2]_2\cdot CH_2Cl_2\cdot CH_3CH_2OH$**. All attempts to obtain suitable crystals of **$[L^2CuCl_2]$** for X-ray crystallographic studies failed.

X-ray diffraction analysis revealed that **$[L^3CuCl_2]$** existed as a monomeric complex. The central metal atom in **$[L^3CuCl_2]$** was four-coordinated and adopted a distorted square planar geometry (Figure 1). The Cu–N bond distances were 2.030(3) and 2.018(4) Å. A slight difference between the Cu–N(1) and Cu–N(2) lengths is attributed to the different substituents attached to the nitrogen atoms of the (*R*,*R*)-1,2-diaminocyclohexane backbone. However, these Cu–N bond distances are similar to other reported values.[44–46,54] Similarly, the Cu–Cl bond distances were in the range of 2.223(1)–2.227(2) Å, which is slightly shorter than the Cu–Cl lengths found in the dichloro Cu (II) complex of *N*,*N*′-di (methoxybenzyl)-(*R*,*R*)-1,2-diaminocyclohexane.[45] The Cl1–Cu–Cl2 angle of 95.70(6)° is much larger than the 83.85(14)° N1–Cu–N2 angle of **$[L^3CuCl_2]$**. These angles are smaller than we previously reported for the same




**SCHEME 2** Synthetic route of ligands ($L^2$–$L^4$) and their corresponding Cu (II) complexes, $\mathbf{[L^nCuCl_2]_n}$ ($L^n$ = $L^2$–$L^4$; $n$ = 1or 2)

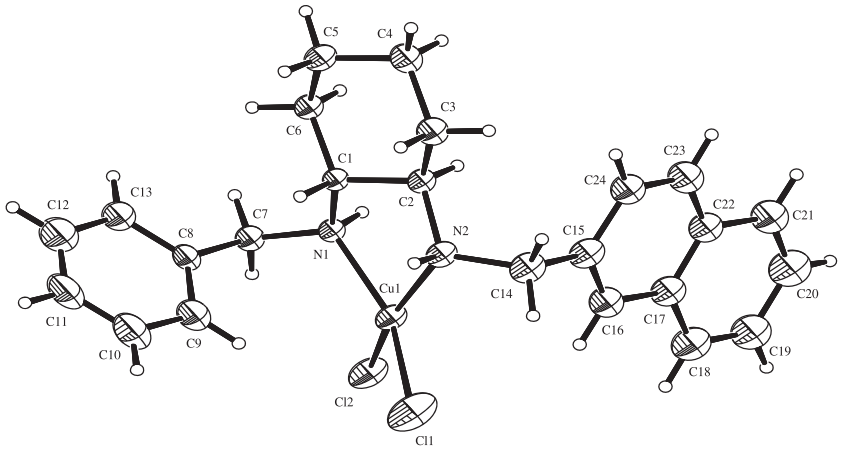



**FIGURE 1** The ORTEP drawing of $\mathbf{[L^3CuCl_2]}$ with the atom numbering scheme. Displacement ellipsoids are drawn at 30% probability level

ligand.[46] The N1–Cu–Cl2 and N2–Cu–Cl1 angles were 94.3(1)° and 93.3(1)°, respectively. The angle between the Cl1–Cu–Cl2 and N1–Cu–N2 planes was 29.6(2)°, which illustrates the deviation from the ideal geometry.

Surprisingly, the $\mathbf{[L^4CuCl_2]_2}$ complex was dimeric despite having the bulky anthracene pendent group on the ligand backbone. One explanation for this dimeric structure is that both the benzyl and anthracene moieties bent away from the metal center, in contrast to monomeric $\mathbf{[L^3CuCl_2]}$ where the 2-naphthyl and benzyl moieties were in a back-and-forth orientation (Figures 1 and 2).

The $Cu^{2+}$ ion in $\mathbf{[L^4CuCl_2]_2}$ adopted a distorted square planar geometry by coordinating with two nitrogen atoms of the (*R*,*R*)-1,2-diaminocyclohexane backbone in a chelating manner, and with one terminal and one bridging chloro ligand. The Cu–N [2.037(5)–2.043(6) Å] and Cu–Cl [2.253(2)–2.2972(2) Å] bond lengths were well within the expected range.[36,54,55] The 2.7239(2)–2.7239(2) Å distance between Cu1···Cl3 and Cu2···Cl1 in $\mathbf{[L^4CuCl_2]_2}$ suggests a weak interaction **(**Table 2). However, the N–Cu–N [84.20(2)–84.7(2)°], Cl1–Cu1–Cl2 [93.16(7)°] and Cl3–Cu2–Cl4 [91.69(8)°] angles were smaller than we previously reported with $C_2$-symmetric ligands.[44–46,54] The angles between the Cu1–C1l–Cl2 and Cu1–N1–N2 planes ranged from 6.5(2)° to 9.8(2)°.

The complexation of the metal to the ligand framework having the stereogenic centers $R_C$ and $R_C$ derived from the (*R*,*R*)-1,2-diaminocyclohexane backbone hindered inversion of the nitrogen atoms, and thus induced chirality therein. The $\mathbf{[L^3CuCl_2]}$ complex was obtained as an enantiopure complex, where both nitrogens were in the $R_N$ configuration. However, the induced nitrogen chirality in the two asymmetric units in $\mathbf{[L^4CuCl_2]_2}$ was $R_N$,$R_N$ and $R_N$,$S_N$. Such a diastereomeric configuration in two asymmetric units of a dimer is rarely observed.[46,56] Figure 2 shows that this selective *R*,*S*-coordination of one asymmetric unit of the dimeric structure is due to the pseudo-axial orientation of the benzyl moiety at N1, and to pseudo-equatorial orientation of the anthracene moiety at N2. The hydrogen atoms of the chiral carbons and nitrogens were in the head-to-tail conformation in $\mathbf{[L^3CuCl_2]}$ (Figure 1). In contrast, the hydrogen atoms of the chiral carbons and nitrogens were in the head-to-tail arrangement around Cu1 while in the head-to-head conformation around Cu2 in $\mathbf{[L^4CuCl_2]_2}$ (Figure 2).

## 3.3 | Catalytic activities of the Cu (II) complexes in the Henry reaction

The catalytic efficacy of *in situ*-generated diacetato Cu (II) complexes in the asymmetric Henry reaction between benzaldehyde or 3-phenylpropanal and nitromethane,

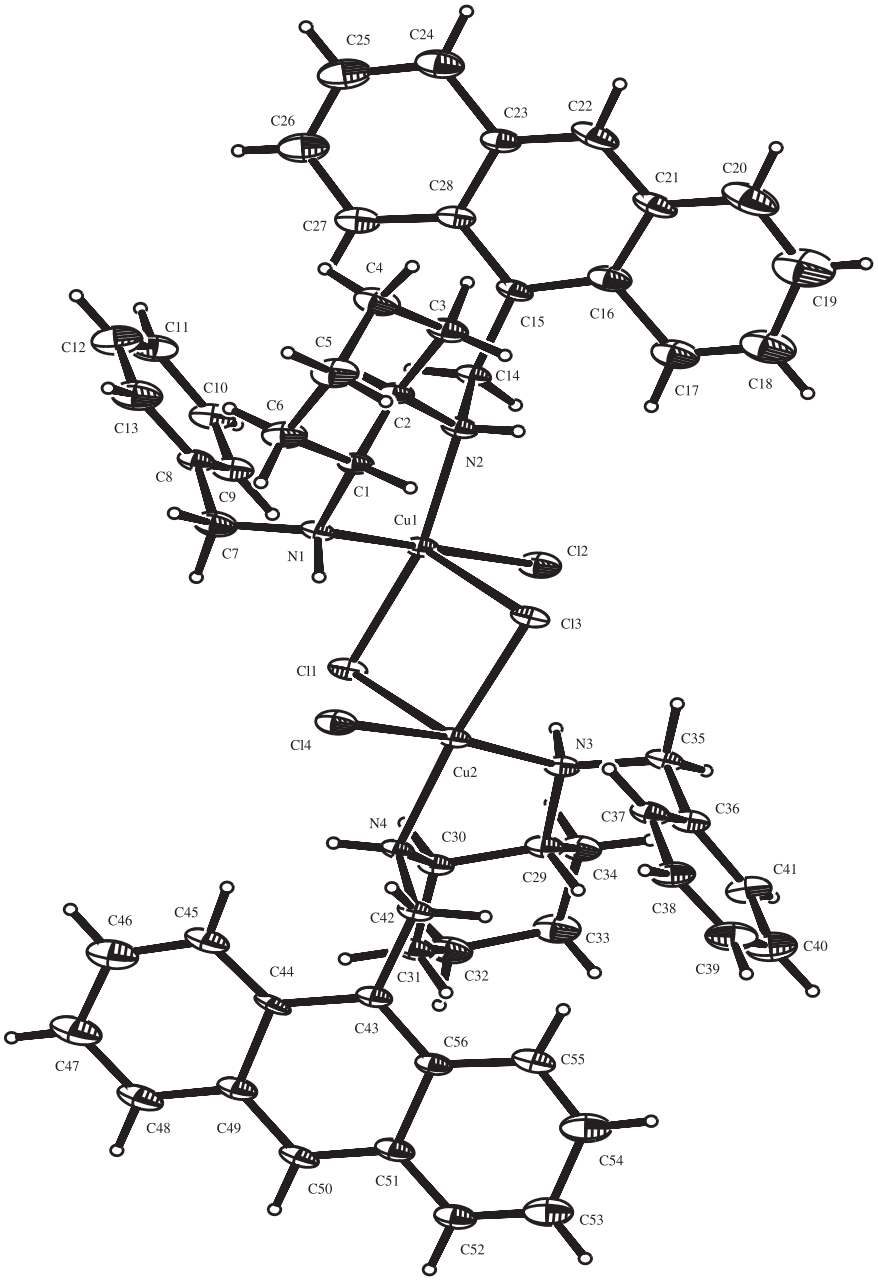



**FIGURE 2** The ORTEP drawing of $[L^4CuCl_2]_2$ with the atom numbering scheme. Displacement ellipsoids are drawn at 30% probability level

with 10 mol% $i$Pr$_2$NEt as co-catalyst in IPA at −20°C, was examined. The results are summarised in Table 3. No product formed in the absence of $^i$Pr$_2$NEt. The recently developed double catalytic activation concept suggests that transition metal complexes (acting as Lewis acids) are not sufficiently powerful to form bonds through the single activation of nucleophiles; deprotonation of a nucleophile precursor with an amine base is needed to activate the reaction.[57] Therefore, the best results in terms of the yield and enantioselectivity of the corresponding $\beta$-nitroalcohol were achieved with the copper acetate complexes in the presence of 10 mol% $^i$Pr$_2$NEt as promoter.

The catalytic activity toward benzaldehyde and nitromethane followed an irregular trend in terms of ligand architecture, whereas for 3-phenylpropanal the observed activity was high for all complexes (> 97%). Thus, it was evident that the activity had not been significantly affected by the ligand architecture around the metal center, whereas the selectivity was significantly affected. The results in Table 3 indicate that when the copper acetate complex bearing $L^1$ was used as the catalyst for the reaction of 3-phenylpropanal with nitromethane, the activity (96%) and enantioselectivity (> 99%) for the resultant $\beta$-nitroalcohol was higher compared with the reaction with benzaldehyde under the same experimental conditions.[44] Based on our previous results, it was assumed that the dichloro Cu (II) complexes would require longer reaction times and have lower enantioselectivity compared with their diacetato

**TABLE 2** Selected bond lengths (Å) and bond angles (°) of Cu (II) complexes

| | | | |
|---|---|---|---|
| **$[L^3CuCl_2]$** | | | |
| Cu(1)-N(1) | 2.030(3) | N(1)-Cu(1)-N(2) | 83.8(1) |
| Cu(1)-N(2) | 2.018(4) | N(2)-Cu(1)-Cl(2) | 161.5 (1) |
| Cu(1)-Cl(1) | 2.227(2) | N(1)-Cu(1)-Cl(2) | 94.3(1) |
| Cu(1)-Cl(2) | 2.223(1) | N(2)-Cu(1)-Cl(1) | 93.3(1) |
| N(1)-C(1) | 1.491(5) | N(1)-Cu(1)-Cl(1) | 155.8(1) |
| N(2)-C(2) | 1.485(6) | Cl(2)-Cu(1)-Cl(1) | 95.70(6) |
| N(1)-C(7) | 1.493(6) | C(7)-N(1)-Cu(1) | 118.0(3) |
| N(2)-C(14) | 1.477 | C(14)-N(2)-Cu(1) | 116.7(3) |
| **$[L^4CuCl_2]_2$** | | | |
| Cu(1)-N(1) | 2.043(6) | N(1)-Cu(1)-N(2) | 84.7(2) |
| Cu(1)-N(2) | 2.037(5) | N(2)-Cu(1)-Cl(2) | 90.8(2) |
| Cu(1)-Cl(1) | 2.293(2) | N(1)-Cu(1)-Cl(2) | 172.6(2) |
| Cu(1)-Cl(2) | 2.280(2) | N(2)-Cu(1)-Cl(1) | 175.0(2) |
| Cu(1)-Cl(3) | 2.7239 | N(3)-Cu(2)-N(4) | 84.20(2) |
| Cu(2)-N(3) | 2.032(5) | Cl(1)-Cu(1)-Cl(2) | 93.16(7) |
| Cu(2)-N(4) | 2.050(6) | N(4)-Cu(2)-Cl(4) | 95.3(2) |
| Cu(2)-Cl(4) | 2.253(2) | Cl(4)-Cu(2)-Cl(3) | 91.69(8) |
| Cu(2)-Cl(1) | 2.724(2) | N(3)-Cu(2)-Cl(4) | 178.8(2) |
| Cu(2)-Cl(3) | 2.2972 | N(4)-Cu(2)-Cl(3) | 168.1(2) |

**TABLE 3** Asymmetry Henry reaction catalyzed by copper acetate complexes bearing unsymmetric chiral diamines

| Run[a] | Catalyst | Substrate | Time (days) | Yield (%)[b] | ee(%)[c] | Config.[d] |
|---|---|---|---|---|---|---|
| 1 | **$[L^1Cu(OAc)_2]$**[e] | Benzaldehyde | 4 | 84 | 84 | (*S*) |
| 2 | **$[L^1Cu(OAc)_2]$**[e] | 3-Phenylpropanal | 1 | 96 | > 99 | (*S*) |
| 3 | **$[L^2Cu(OAc)_2]$** | Benzaldehyde | 4 | 87 | 83 | (*S*) |
| 4 | **$[L^2Cu(OAc)_2]$** | 3-Phenylpropanal | 1 | 97 | > 99 | (*S*) |
| 5 | **$[L^3Cu(OAc)_2]$** | Benzaldehyde | 4 | 73 | 90 | (*S*) |
| 6 | **$[L^3Cu(OAc)_2]$** | 3-Phenylpropanal | 1 | 99 | > 99 | (*S*) |
| 7 | **$[L^4Cu(OAc)_2]_2$** | Benzaldehyde | 4 | 78 | 35 | (*S*) |
| 8 | **$[L^4Cu(OAc)_2]_2$** | 3-Phenylpropanal | 1 | 98 | 64 | (*S*) |

[a]Reactions were carried out 5.0 mmol scale aldehyde, 10 mol% of respective Cu (II) catalyst, 10 mol% of $^iPr_2Net$, 2 equiv. of $CH_3NO_2$ in IPA (10 ml) at −20°C for different time intervals.

[b]Yields of isolated alcohols were determined by $^1$H-NMR.

[c]Enantiomeric excess (ee) was determined by Chiralcel HPLC analysis using Chiral OD-H and Chiral AD-H columns.

[d]The absolute configuration of the major product was assigned by comparison with the literature values.[52,60]

[e]**$[L^1Cu(OAc)_2]$** was used previously and presented here for comparison.[44]

counterparts under identical experimental conditions. For this reason, the dichloro complexes were not subjected to the asymmetric Henry reaction in the current study.[46] A blank reaction performed in the absence of chiral complexes resulted in mild activity, with negligible enantioselectivity.

The loss of enantioselectivity with the $L^4$-bearing copper acetate complex was far more pronounced for both aldehydes compared with its analogs under the same experimental protocol. This decrease in selectivity is attributed to the different configurations of stereogenic nitrogens present in the $L^4$ copper acetate

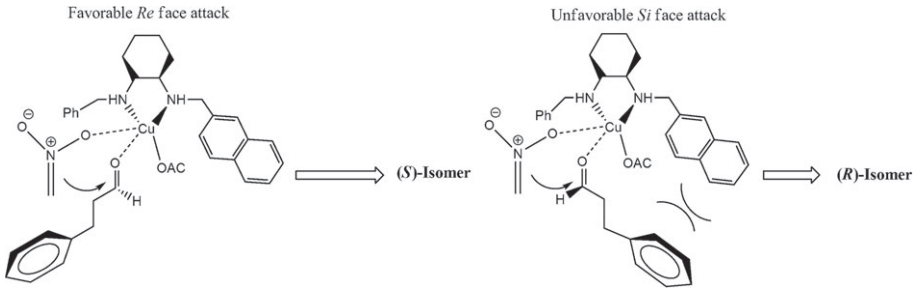



**FIGURE 3** Proposed transition states for the catalytic asymmetric Henry reaction with $L^3$-bearing copper acetate complex

complex. The enantioselectivity of the copper acetate complexes increased in the order of $\mathbf{L^4 < L^2 < L^1 < L^3}$ in the case of benzaldehyde, whereas for 3-phenylpropanal the selectivity increased in the order of $\mathbf{L^4 < L^2 \sim L^3}$. Thus, the anthracene-bearing copper acetate complex was less stereo-directing compared with the 1- and 2-naphthyl-bearing complexes for both benzaldehyde and 3-phenypropanal (Table 3; entries 7 and 8). The reaction catalyzed by these catalytic species resulted in *β*-nitroalcohols with an (*S*)-conformation at the stereogenic center, which is attributed to the favorable orientation of the phenyl group of the aldehyde and aromatic moieties of the ligand architecture.[33,35,58]

The stereo-chemical outcomes of the Henry reaction with diacetato Cu (II) complexes are in accord with the accepted model.[33,59] In this model, a pentavalent copper species is generated for maximum activation, which should attach to the aldehyde in the equatorial plane; nitronate ion, deprotonated by $^i Pr_2NEt$, should coordinate at the axial location. The nitronate generates a carbon–carbon bond with a carbonyl compound. The *Re* face of the carbonyl group of the aldehyde is more accessible to nitronate group attack, leading to the (*S*)-configuration product (Figure 3).

Compared with recently reported *in situ*-generated chiral Cu (II) complexes bearing *L*-proline,[60] our system showed superior activity, yielding (*S*)-1-nitro-4-phenylbutan-2-ol with superb enantioselectivity (Table 3). Similarly, the $L^3$-bearing copper acetate complex exhibited excellent activity (> 99% in 24 hr), as well as unusually high enantioselectivity (> 99%) for 3-phenylpropanal compared with well-known core-chiral bispidine-based copper complexes (88% yield; ee 97% in 48 hr for 3-phenylpropanal).[61] However, these complexes exhibited better activity (99%) and stereoselectivity (98%) for benzaldehyde compared with our current system. Comparison of catalysts in the current study revealed that proper orientation of pendant groups around the metal central is vital for efficient stereoselectivity. This stereoselectivity was superior to all other Cu (II) complexes bearing (*R*,*R*)-1,2-diaminocyclohexane derivatives tested to date in the asymmetric Henry reaction between 3-phenylpropanal and nitromethane. Hence, this work makes available a combination of complementary synthetic, structural and catalytic studies that provide a better knowledge of the promising, but as yet underdeveloped, chemistry of asymmetric Cu (II) complexes and their catalytic efficacy in the asymmetric Henry reaction.

## 4 | CONCLUSION

Copper (II) complexes bearing asymmetric derivatives of (*R*,*R*)-1,2-diaminocyclohexane were synthesised and characterised. The diacetato complexes were assessed toward the asymmetric Henry reaction of benzaldehyde or 3-phenylpropanal with nitromethane, to yield corresponding (*S*)-*β*-nitroalcohols in the presence of 10 mol% of $^i Pr_2NEt$. The most efficient enantioselective catalyst of the asymmetric Henry reaction was the $L^3$-bearing copper acetate complex, which provided (*S*)-enriched *β*-nitroalcohols with high yield and enantioselectivity (> 99%). Its enantiocatalytic activity was comparable with the best enantioselective catalysts to date for the Henry reaction between 3-phenylpropanal and nitromethane. The lower enantioselectivity found for the $L^4$-bearing complex corresponds to the diastereomeric configuration of its two nitrogen atoms; its activity remained unaffected.

## ACKNOWLEDGEMENTS

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF-2017R1D1A3B03030670).

## ORCID

*Jong Hwa Jeong* https://orcid.org/0000-0002-4473-1468

## REFERENCES

[1] C. Palomo, M. Oiarbide, A. Laso, *Eur. J. Org. Chem.* **2007**, *2007*, 2561.

[2] G. Chang-Sheng, P. Jian, *Chinese Eur. J. Org. Chem.* **2008**, *28*, 1193.

[3] C. Palomo, M. Oiarbide, A. Mielgo, *Angew. Chem. Int. Ed.* **2004**, *43*, 5442.

[4] A. Y. Sukhorukov, A. A. Sukhanova, S. G. Zlotin, *Tetrahedron* **2016**, *72*, 6191.

[5] F. A. Luzzio, *Tetrahedron* **2001**, *57*, 915.

[6] R. Ballini, M. Petrini, *Adv. Synth. Catal.* **2015**, *357*, 2371.

[7] M. Zhou, D. Dong, B. Zhu, H. Geng, Y. Wang, X. Zhang, *Org. Lett.* **2013**, *15*, 5524.

[8] B. Bauvois, M.-L. Puiffe, J.-B. Bongui, S. Paillat, C. Monneret, D. Dauzonne, *J. Med. Chem.* **2003**, *46*, 3900.

[9] L. Henry, *Bull. Acad. R. Belg.* **1896**, *32*, 33.

[10] H. Sasai, T. Suzuki, S. Arai, T. Arai, M. Shibasaki, *J. Am. Chem. Soc.* **1992**, *114*, 4418.

[11] H. Sasai, T. Tokunaga, S. Watanabe, T. Suzuki, N. Itoh, M. Shibasaki, *J. Org. Chem.* **1995**, *60*, 7388.

[12] M. Shibasaki, H. Sasai, T. Arai, *Angew. Chem. Int. Ed.* **1997**, *36*, 1236.

[13] K.-I. Yamada, S. J. Harwood, H. Gröger, M. Shibasaki, *Angew. Chem. Int. Ed.* **1999**, *38*, 3504.

[14] Z. Chen, H. Morimoto, S. Matsunaga, M. Shibasaki, *J. Am. Chem. Soc.* **2008**, *130*, 2170.

[15] D. Pavel, H. Lydie, S. Milos, *Curr. Org. Syn.* **2014**, *11*, 879.

[16] B. Karimi, D. Enders, E. Jafari, *Synthesis* **2013**, *45*, 2769.

[17] P. Chauhan, S. Mahajan, U. Kaya, D. Hack, D. Enders, *Adv. Synth. Catal.* **2015**, *357*, 253.

[18] J. V. Alegre-Requena, E. Marques-Lopez, R. P. Herrera, *Adv. Synth. Catal.* **2016**, *358*, 1801.

[19] D.-Q. Ran, T.-H. Shen, X.-C. Zhou, J.-Q. Li, F.-N. Cui, C.-A. Ma, Q.-B. Song, *Russian J. Org. Chem.* **2013**, *49*, 849.

[20] J. D. White, S. Shaw, *Org. Lett.* **2012**, *14*, 6270.

[21] H. Naili, F. Hajlaoui, T. Mhiri, T. C. O. Mac-Leod, M. N. Kopylovich, K. T. Mahmudov, A. J. L. Pombeiro, *Dalton Trans.* **2013**, *42*, 399.

[22] R. Arunachalam, C. S. Aswathi, A. Das, R. I. Kureshy, P. S. Subramanian, *Chem. Plus Chem.* **2015**, *80*, 209.

[23] A. Karmakar, S. Hazra, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *New J. Chem.* **2014**, *38*, 4837.

[24] B. G. M. Rocha, T. C. O. Mac-Leod, M. F. C. Guedes da Silva, K. V. Luzyanin, L. M. D. R. S. Martins, A. J. L. Pombeiro, *Dalton Trans.* **2014**, *43*, 15 192.

[25] S. Hazra, A. Karmakar, M. d. F. C. Guedes da Silva, L. Dlhaň, R. Boča, A. J. L. Pombeiro, *New J. Chem.* **2015**, *39*, 3424.

[26] S. Zhang, Y. Li, Y. Xu, Z. Wang, *Chin. Chem. Lett.* **2018**, *29*, 873.

[27] P. Drabina, J. Hanusek, M. Sedlak, *Chem. Listy* **2016**, *110*, 602.

[28] L. Mei, Y. Hao, Z. J. Hai, H. K. Liang, P. W. Min, *Res. Chem. Intermediat.* **2009**, *35*, 123.

[29] M. Bandini, F. Piccinelli, S. Tommasi, A. Umani-Ronchi, C. Ventrici, *Chem. Commun.* **2007**, 616.

[30] G. Blay, L. R. Domingo, V. Hernandez-Olmos, J. R. Pedro, *Chem. Eur. J.* **2008**, *14*, 4725.

[31] H. Maheswaran, K. L. Prasanth, G. G. Krishna, K. Ravikumar, B. Sridhar, M. L. Kantam, *Chem. Commun.* **2006**, 4066.

[32] D. M. Du, S. F. Lu, T. Fang, J. X. Xu, *J. Org. Chem.* **2005**, *70*, 3712.

[33] D. A. Evans, D. Seidel, M. Rueping, H. W. Lam, J. T. Shaw, C. W. Downey, *J. Am. Chem. Soc.* **2003**, *125*, 12 692.

[34] M. D. Jones, C. J. Cooper, M. F. Mahon, P. R. Raithby, D. Apperley, J. Wolowska, D. Collison, *J. Mol. Catal. A: Chem.* **2010**, *325*, 8.

[35] R. Kowalczyk, L. Sidorowicz, J. Skarzewski, *Tetrahedron: Asymmetry* **2008**, *19*, 2310.

[36] M. Bandini, M. Benaglia, R. Sinisi, S. Tommasi, A. Umani-Ronchi, *Org. Lett.* **2007**, *9*, 2151.

[37] L.-L. Li, L. Liu, Y.-N. Pei, H.-J. Zhu, *Tetrahedron* **2014**, *70*, 9077.

[38] T. Arai, M. Watanabe, A. Fujiwara, N. Yokoyama, A. Yanagisawa, *Angew. Chem. Int. Ed.* **2006**, *45*, 5978.

[39] W. Jin, X. Li, Y. Huang, F. Wu, B. Wan, *Chem. Eur. J.* **2010**, *16*, 8259.

[40] F. Liua, S. Goua, L. Li, *Appl. Organomet. Chem.* **2014**, *28*, 186.

[41] P. Kocovský, S. Vyskocil, M. Smrcina, *Chem. Rev.* **2003**, *103*, 3213.

[42] S. Castillón, C. Claver, Y. Díaz, *Chem. Soc. Rev.* **2005**, *34*, 702.

[43] V. A. Pavlov, T. N. Pavlova, *Russ. Chem. Rev.* **2010**, *79*, 881.

[44] Q. T. Nguyen, J. H. Jeong, *Polyhedron* **2008**, *27*, 3227.

[45] S. E. Song, Q. T. Nguyen, J. J. Yu, H.-I. Lee, J. H. Jeong, *Polyhedron* **2014**, *67*, 264.

[46] J. Cho, G. H. Lee, S. Nayab, H. Lee, J. H. Jeong, *Polyhedron* **2015**, *99*, 198.

[47] P. McArdle, P. Daly, *ABSCALC*, National University of Ireland, Galway, Ireland **1999**.

[48] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112.

[49] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3.

[50] B. Qin, X. Xiao, X. Liu, J. Huang, Y. Wen, X. Feng, *J. Org. Chem.* **2007**, *72*, 9323.

[51] G. Blay, E. Climent, I. Fernandez, V. Hernandez-Olmos, J. R. Pedro, *Tetrahedron: Asymmetry* **2007**, *18*, 1063.

[52] Z. L. Guo, S. Zhong, Y. B. Li, G. Lu, *Tetrahedron: Asymmetry* **2011**, *22*, 238.

[53] G. Lai, F. Guo, Y. Zheng, Y. Fang, H. Song, K. Xu, S. Wang, Z. Zha, Z. Wang, *Chem. Eur. J.* **2011**, *17*, 1114.

[54] K. S. Kwon, S. Nayab, H. Lee, J. H. Jeong, *Polyhedron* **2014**, *77*, 32.

[55] S. H. Ahn, M. K. Chun, E. Kim, J. H. Jeong, S. Nayab, H. Lee, *Polyhedron* **2017**, *127*, 51.

[56] E. Rafii, B. Dassonneville, A. Heumann, *Chem. Commun.* **2007**, 583.

[57] S. Kanemasa, K. Ito, *Eur. J. Org. Chem.* **2004**, *2004*, 4741.

[58] C. Christensen, K. Juhl, R. G. Hazell, K. A. Jorgensen, *J. Org. Chem.* **2002**, *67*, 4875.

[59] A. Dixit, P. Kumar, G. D. Yadav, S. Singh, *Inorg. Chim. Acta* **2018**, *479*, 240. https://doi.org/10.1016/j.ica.2018.04.048

[60] D. Xu, Q. Sun, Z. Quan, W. Sun, X. Wang, *Tetrahedron: Asymmetry* **2017**, *28*, 954.

[61] D. Scharnagel, A. Miller, F. Prause, M. Eck, J. Goller, W. Milius, M. Breuning, *Chem. Eur. J.* **2015**, *21*, 12 488.

## SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

**How to cite this article:** Cho J, Chun MK, Nayab S, Jeong JH. Synthesis and structures of copper complexes bearing unsymmetric derivatives of (*R, R*)-1,2-diaminocyclohexane: An efficient catalyst for asymmetric Henry reaction. *Appl Organometal Chem*. 2019;e4955. https://doi.org/10.1002/aoc.4955

## APPENDIX

### SUPPLEMENTARY DATA

CCDC 1897111 & 1897112 contain the supplementary crystallographic data for **$[L^3CuCl_2]$** and **$[L^4CuCl_2]_2$**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.