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Research paper

Application of asymmetric Henry reaction by copper(II) complexes containing (*R*,*R*)-1,2-diaminocyclohexane with naphthyl and thiophenyl substituents

Juhyun Cho [a], Jong Hwa Jeong [a,*], Hyosun Lee [a,*], Jungkyu K. Lee [a], Saira Nayab [b]

[a] Department of Chemistry and Green-Nano Materials Research Center, Kyungpook National University, 80 Daehakro, Bukgu, Daegu 41566, Republic of Korea
[b] Department of Chemistry, Shaheed Benazir Bhutto University, Sheringal Dir (U), Khyber Pakhtunkhwa, Pakistan

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ABSTRACT

A series of Cu(II) complexes containing C_1-symmetric thiophene derivatives of (1*R*,2*R*)-*N*1-(naphthalen-2-ylmethyl)cyclohexane-1,2-diamine, namely $\mathbf{L^1}$, $\mathbf{L^2}$ and $\mathbf{L^3}$ were synthesized and characterized. These complexes had distorted square-planar geometries around the Cu(II) center. High yield (99%) and excellent enantioselectivity (>99%) for (*S*)-1-nitro-4-phenylbutan-2-ol from the reaction of 3-phenylpropanal and nitromethane was obtained using $\mathbf{[L^1Cu(OAc)_2]}$ or $\mathbf{[L^3Cu(OAc)_2]}$ with 10 mol% of diisopropylethylamine (DIPEA) within 24 h. The catalytic systems also demonstrated good activity and moderate to high enantioselectivity for aliphatic aldehydes.

1. Introduction

The asymmetric Henry reaction proved to be an important C—C bond formation reaction resulting in enantiomerically enriched *β*-nitro alcohols, which are valuable intermediates in the synthesis of biologically interesting molecules [1,2]. Notably, the resulting nitroaldol products can be reduced to vicinal amino alcohols, a common structural motif found in many pharmaceuticals and long-chain lipids [3–7]. Since the pioneering work of Shibasaki in 1992 [8], several studies have focused on the development of chiral C_2-symmetric ligands for the Cu-catalyzed asymmetric Henry reaction; these ligands have excellent asymmetric-induction ability [9–15]. For example, high activities and moderate to high enantioselectivities have been obtained using salan-type [16–18], BOX-type [9,10,19], diamine [12–15,20,21], amino-sulfonamide [22,23] and bistetracarboline amides [24]-based C_2-symmetric frameworks in the asymmetric Henry reaction. More recently, chiral C_1-symmetric ligands based on unsymmetrical substitutions of these above-mentioned scaffolds [25-29] and several new synthetic systems [6,30–34] have also been investigated in the copper-catalyzed Henry reaction. However many of these catalytic systems display poor enantioselectivity together with low product yields when using aliphatic aldehydes as substrates [29,35]. Thus, the development of effective catalytic systems is still desired for this class of substrate. In this regard Arai and co-workers demonstrated that C_1-symmetric chiral imidazolidine-pyridine[36] and (*R*,*R*)-1,2-diphenylethylenediamine derived Cu(OAc)$_2$ complexes [25] proved to be efficient catalyst for the Henry reaction, giving the various nitroaldols with high yields and over 90% ee. More recently, Panov and Novakova groups independently studied Cu(II) initiators supported with C_1-symmetric 2-(pyridin-2-yl)imidazolidin-4-one[37] and 2-(pyridine-2-yl)imidazolidine-4-thione [38] ligands, respectively, which demonstrated moderate to high yields and enantioselectivities in asymmetric Henry reaction. Similarly, we recently reported the generation of Cu(II) complexes based on the C_1-symmetric (1*R*,2*R*)-*N*-benzylcyclohexane-1,2-diamine motif that resulted in high product yields and superior enantioselectivities (>99%) [39]. The nature of the ligand framework and attached substituents is a pivotal factor governing the efficiency of catalysts in the asymmetric Henry reaction. The utility of thiophene-based ligands in this reaction has been investigated by several groups. Mansawat et al. showed that homochiral amino alcohols carrying the *N*-2-thienyl methyl substituent provided moderate yields and good enantioselectivities [40], and Bandini et al. used a C_2-symmetric diamino ligand with oligothienyl groups [41]. We recently explored the influence of the methylthiophenyl moiety on the level of asymmetric induction (enantiomeric excess [ee] up to 92%) in the Henry reaction. Therein, we introduced an unsymmetrical scaffold by incorporating thiophenyl moieties in the (1*R*,2*R*)-*N*1-

* Corresponding authors.
E-mail addresses: jeongjh@knu.ac.kr (J.H. Jeong), hyosunlee@knu.ac.kr (H. Lee).

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(naphthalylcyclohexane)-1,2-diamine fragment [42]. The synthesis, X-ray structures, and application in the asymmetric Henry reaction of Cu (II) complexes supported with these unsymmetrical thiophenyl derivatives of (1*R*,2*R*)-*N*1-naphthalylcyclohexane-1,2-diamine are discussed herein.

2. Experimental

2.1. Materials and methods

All manipulations involved in the synthesis of ligands (L^1–L^3) and their corresponding Cu(II) complexes, **[L^nCuCl$_2$]** (L^n = L^1–L^3), were performed using bench-top techniques in air unless otherwise specified. (*R*,*R*)-1,2-Diaminoniumcyclohexane mono-(L)-(+)-tartrate salt, 2-naphthylaldehyde, 2-naphthylaldehyde, 2-thiophenecarboxaldehyde, 3-thiophenecarboxaldehyde, 5-methyl-2-thiophenecarboxaldehyde, copper (II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$), benzaldehyde, 3-phenylpropionaldehyde, butyraldehyde, 3-methylbutanal, and diisopropylethylamine (DIPEA) were obtained from Sigma–Aldrich. Solvents for nuclear magnetic resonance (NMR) measurements were purchased from Sigma–Aldrich and stored over 3-Å molecular sieves. Various solvents, such as methanol (MeOH), dichloromethane (CH_2Cl_2), diethyl ether, ethanol, *n*-hexane (*n*-hex), and ethyl acetate (EtOAc), were purchased from high-grade commercial suppliers and used as received.

Proton (^{1}H; operating at 500 MHz) and carbon-13 (^{13}C; operating at 125 MHz) NMR spectra were recorded on a Bruker Avance Digital 500-NMR spectrometer (Bruker, Billerica, MA). Chemical shifts are reported in δ units relative to residual ^{1}H in the deuterated solvent ($CDCl_3$, δ = 7.26 ppm). Coupling constants are reported in Hertz (Hz). Data are reported as m = multiplet, br = broad, s = singlet, d = doublet, t = triplet, and q = quartet. Fourier transform-infrared (FTIR) spectra of neat samples were recorded on a Bruker FT/IR-Alpha instrument, and the data are reported in cm^{-1}. Elemental analyses were determined using the EA 1108 Elemental Analyzer at the Chemical Analysis Laboratory of the Center for Scientific Instruments of Kyungpook National University. Enantiomeric excess was determined by HPLC using Chiralcel OD-H and Chiralpak AD-H columns with various proportions of HPLC-grade isopropanol (IPA) and *n*-hexane as eluting solvents. The ligands designed in the current study are the thiophene derivatives of (1*R*,2*R*)-*N*1-(naphthalen-2-ylmethyl)cyclohexane-1,2-diamine: (1*R*,2*R*)-*N*1-(naphthalen-2-ylmethyl)–*N*2-(thiophen-2-ylmethyl)cyclohexane-1,2-diamine (**L^1**), (1*R*,2*R*)-*N*1-((5-methylthiophen-2-yl)methyl)–*N*2-(naphthalen-2-ylmethyl)cyclohexane-1,2-diamine (**L^2**), and (1*R*,2*R*)-*N*1-(naphthalen-2-ylmethyl)–*N*2-(thiophen-3-ylmethyl)cyclohexane-1,2-diamine (**L^3**).

2.2. Synthesis of CMN [(1R,2R)-N^1-(naphthalen-2-ylmethyl) cyclohexane-1,2-diamine]

2-Naphthaldehyde (7.02 g, 45.0 mmol) solution in CH_2Cl_2 (200 mL) was added dropwise into (1*R*,2*R*)-(+)-1,2-cyclohexanediamine L-Tartrate (12.0 g, 45.0 mmol) solution of 2 N NaOH (30 mL). After being stirred for 3 days, the organic layer was extracted and over $MgSO_4$. The solution was concentrated to get imine product as ivory solid (10.3 g, 40.9 mmol). For reduction of imine moiety, the above mentioned ivory solid (10.3 g, 40.9 mmol) was dissolved in MeOH (95%, 100 mL) followed by the addition of $NaBH_4$ (2.32 g, 61.3 mmol) slowly and stirred for 12 h. The solvent as removed and the resultant residue was treated with distilled water (10 mL) to get rid of any excess $NaBH_4$. The product was extracted with CH_2Cl_2 (30 mL) and the organic layer was dried over $MgSO_4$. The solvent was removed to get crude yellow oil which was purified by column (EA: MeOH, 3:1, R_f = 0.28 (mono-sub), 0.57 (di-sub)) to provide pure (1*R*,2*R*)-N^1-(naphthalen-2-ylmethyl)cyclohexane-1,2-diamine. (Yellow oil, 4.68 g, 18.4 mmol, 40% yield). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 7.83–7.75 (m, 4H, naph-C**H**), 7.48–7.43 (m, 3H, naph-C**H**), 4.11 (d, *J* = 13.1 Hz, 1H, NHC$\boldsymbol{H_a}$H$_b$), 3.87 (d, *J* = 13.4 Hz, 1H, NHCH$_a$$\boldsymbol{H_b}$), 2.44–2.39 (m, 1H, Cy-CH), 2.22–2.11 (m, 2H, Cy-C$\mathbf{H_2}$), 1.92–1.87 (m, 1H, Cy-C**H**), 1.77–1.67 (m, 2H, Cy-C$\mathbf{H_2}$), 1.62 (br, 3H, N**H**), 1.34–1.18 (m, 2H, Cy-C$\mathbf{H_2}$), 1.14–1.01 (m, 2H, Cy-C$\mathbf{H_2}$) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 137.7, 132.5, 131.6, 126.9, 126.6, 126.6, 125.7, 125.3, 124.8, 124.4 (1C, 2naph-**C**), 62.4 (1C, Cy-**C**), 54.4 (1C, NH-**C**H$_2$), 50.2, 35.1, 30.5, 24.5, 24.3 (1C, Cy-**C**); FTIR (liquid neat; cm^{-1}): ν(N-H) 3349 (w); ν(sp^3 C-H) 2922 w; ν(C═C) 1632 m; ν(C═C)antisym and ν(C═C)*sym* 1599(w) and1447(w); δ(-C-H sp^3) 1361 m; ν(N—C) 1225 m; δ(C—H sp^2) 855 w.

2.3. Synthesis protocols

2.3.1. Synthesis of L^1

2-Thiophenecarboxaldehyde (0.8 g, 7.0 mmol) was added to a solution of CMN (1.8 g, 7.0 mmol) in MeOH (95%, 50 mL). The reaction mixture was refluxed for 4 days. The solvent was removed to obtain a yellow oil as the imine product (2.4 g, 6.8 mmol, yield 98%). The imine product was reduced by dissolving in MeOH (95%, 50 mL) followed by the addition of $NaBH_4$ (0.6 g, 17.0 mmol). After stirring for 12 h, the solvent was evaporated and the resulting crude solid was treated with distilled water (10 mL). The organic layer was extracted with CH_2Cl_2 (30 mL). The solvent was evaporated to obtain a light-yellow oil as the final product (2.40 g, yield 98%). Analysis calculated for $C_{22}H_{26}Cl_2N_2S$ (%): C, 75.38; H, 7.48; N, 7.99. Found: C, 75.35; H, 7.47; N, 7.95. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 7.83–7.76 (m, 4H, Naph-C**H**), 7.50–7.43 (m, 3H, Naph-C**H**), 7.21–7.19 (m, 1H, Thiophen-C**H**), 6.95 (m, 1H, Thiophen-C**H**), 6.91 (m, 1H, Thiophen-C**H**), 4.13 (d, *J* = 14 Hz, 1H, C$\mathbf{H_A}$CH$_B$), 4.09 (d, *J* = 13.4 Hz, 1H, C$\mathbf{H_c}$CH$_d$), 3.89 (d, *J* = 14 Hz, 1H, CH$_A$C$\mathbf{H_B}$), 3.85 (d, *J* = 13.4 Hz, 1H, CH$_c$C$\mathbf{H_d}$), 2.38–2.26 (m, 2H, Cy-**H**), 2.24–2.13 (m, 2H, Cy-**H**), 1.93 (br, 2H, N—**H**), 1.74 (m, 2H, Cy-**H**), 1.27–1.21 (m, 2H, Cy-**H**), 1.13–0.99 (m, 2H, Cy-**H**) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ = 145.3, 138.5, 133.5, 132.6, 127.9, 127.7, 127.6, 126.7, 126.5, 126.26, 125.9, 125.4, 124.3, 124.2, 60.7, 60.6, 50.9, 45.6, 31.6, 25.06, 24.9. IR (liquid neat; cm^{-1}): ν(N-H) 3299 (w); ν(sp^3 C-H) 2925 w; ν(C═C) 1654 m; ν(C═C)antisym and ν(C═C)*sym* 1508 w and1447 w; δ(-C-H sp^3) 1359 m; ν(N—C) 1211 m; δ(C—H sp^2) 815 w.

2.3.2. Synthesis of L^2

An analogous method to that described for **L^1** was adopted for the synthesis of **L^2** except using CMN (1.8 g, 7.0 mmol) and 5-methylthiophene-2-carboxaldehyde (0.90 g, 7.0 mmol). The imine product (2.5 g, 6.8 mmol) was treated with $NaBH_4$ (0.6 g, 17 mmol) to obtain the amine product as a yellow oil (2.5 g, 6.8 mmol, yield 98%). Analysis calculated for $C_{23}H_{28}N_2S$ (%): C, 75.78; H, 7.74; N, 7.68. Found: C, 75.77; H, 7.73; N, 7.65. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 7.84–7.79 (m, 4H, Naph-C**H**), 7.52–7.43 (m, 3H, Naph-C**H**), 6.87–6.68 (m, 1H, Thiophene-C**H**), 6.66–6.57 (m, 1H, Thiophene-C**H**), 4.09 (d, *J* = 13.4 Hz, 1H, C$\mathbf{H_A}$CH$_B$), 4.04 (d, *J* = 14 Hz, 1H, C$\mathbf{H_c}$CH$_d$), 3.84 (d, *J* = 13.4 Hz, 1H, CH$_A$C$\mathbf{H_B}$), 3.81 (d, *J* = 14 Hz, 1H, CH$_c$C$\mathbf{H_d}$), 2.44 (s, 3H, Thiophene-C$\mathbf{H_3}$), 2.37–2.32 (m, 1H, Cy-**H**), 2.30–2.25 (m, 1H, Cy-**H**), 2.23–2.19 (m, 1H, Cy-**H**), 2.16–2.13 (m, 1H, Cy-**H**), 1.96 (br, 2H, N—**H**), 1.75–1.72 (m, 2H, Cy-**H**), 1.27–1.21 (m, 2H, Cy-**H**), 1.14–1.00 (m, 2H, Cy-**H**). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ = 142.7, 138.6, 138.5, 133.4, 127.9, 127.6, 126.6, 126.2, 125.82, 125.4, 125.3, 124.7, 124.4, 124.1, 60.7, 60.3, 52.6, 50.91, 45.9, 31.5, 25.0, 15.5, 15.3. IR (liquid neat; cm^{-1}): ν(N-H) 3305 (w); ν(sp^3 C-H) 2925 w; ν(C═C) 1627 m; ν(C═C)antisym and ν(C═C)*sym* 1525 w and 1448 w; δ(-C-H sp^3) 1357 m; ν(N—C) 1226 m; δ(C—H sp^2) 854 w.

2.3.3. Synthesis of L^3

An analogous method to that described for **L^1** was followed to synthesize **L^3** except using CMN (1.8 g, 7.0 mmol) and 3-thiophenecarboxaldehyde (0.8 g, 7.0 mmol) to obtain the imine product (2.4 g, 6.8 mmol, yield 98%). Further reduction of the imine product (2.4 g, 6.8 mmol) with $NaBH_4$ (0.6 g, 17 mmol) was done to obtain the final product as a yellow oil (2.40 g, yield 98%). Analysis calculated for $C_{22}H_{26}N_2$ (%): C,

75.38; H, 7.48; N, 7.99. Found: C, 75.37; H, 7.45; N, 7.97. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 7.84–7.76 (m, 4H, Naph-C**H**), 7.49–7.44 (m, 3H, Naph-C**H**), 7.28–7.26 (m, 1H, Thiophen-C**H**), 7.13–7.12 (m, 1H, Thiophen-C**H**), 7.06–7.05 (m, 1H, Thiophen-C**H**), 4.08 (d, J = 13.4 Hz, 1H, NC**H$_a$**H$_b$), 3.94 (d, J = 13.0 Hz, 1H, NC**H$_c$**H$_d$), 3.84 (d, J = 13.3 Hz, 1H, NCH$_a$**H$_b$**), 3.70 (d, J = 13.4 Hz, 1H, NCH$_c$**H$_d$**), 2.32–2.29 (m, 2H, Cy-C**H$_2$**), 2.24–2.20 (m, 1H, Cy-C**H**), 2.17–2.13 (m, 1H, Cy-C**H**), 1.97 (br, 2H, N**H**), 1.77–1.72 (m, 2H, Cy-C**H$_2$**), 1.28–1.22 (m, 2H, Cy-C**H$_2$**), 1.11–1.01 (m, 2H, Cy-C**H$_2$**). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ = 141.9, 138.4, 133.4, 132.6, 127.9, 127.6, 127.6, 127.5, 126.6, 126.2, 125.9, 125.6, 125.4, 121.1, 60.8, 60.7, 50.9, 45.8, 31.5, 31.3, 24.9, 24.9. IR (liquid neat; cm^{-1}): ν(N-H) 3298 (w); ν(sp^3 C-H) 2925 w; ν(C═C) 1667 m; ν(C═C)antisym and ν(C═C)*sym* 1508 w and 1448 w; δ(-C-H sp^3) 1336 m; ν(N—C) 1243 m; δ(C—H sp^2) 814 w.

2.3.4. Synthesis of [L^1CuCl_2]

A solution of **L^1** (1.0 g, 2.8 mmol) in CH_2Cl_2 (10 mL) was treated with a solution of $CuCl_2{\cdot}2H_2O$ (0.5 g, 2.8 mmol) in CH_2Cl_2 and stirred for 12 h at ambient temperature. The blue-green precipitate was isolated by filtration and oven-dried at 60 °C to obtain a crystalline solid as the final product (98% yield). Single crystals suitable for X-ray diffraction analysis were grown by slow evaporation of MeOH solution of **[L^{1}CuCl$_2$]**. Analysis calculated for $C_{22}H_{26}Cl_2CuN_2S$ (%): C, 54.48; H, 5.40; N, 5.78. Found: C, 54.38; H, 5.42; N, 5.79. IR (liquid neat; cm^{-1}): ν(N-H) 3216 (w); ν(sp^3 C-H) 2933 w; ν(C═C) 1630 m; ν(C═C)antisym and ν(C═C) *sym* 1518 w and 1448 w; δ(-C-H sp^3) 1365 m; ν(N—C) 1282 m; δ(C—H sp^2) 823 w; ν(M−N) 655 s.

2.3.5. Synthesis of [L^2CuCl_2]

An analogous method to that described for **[L^{1}CuCl$_2$]** was adopted for the synthesis of **[L^{2}CuCl$_2$]**, except using **L^2** and $CuCl_2{\cdot}2H_2O$ (0.5 g, 2.8 mmol) to obtain a blue-green solid as the final product (98% yield). Single crystals suitable for X-ray diffraction analysis were grown by slow evaporation of MeOH solution of **[L^{2}CuCl$_2$]**. Analysis calculated for $C_{23}H_{28}Cl_2CuN_2S$ (%): C, 55.36; H, 5.66; N, 5.61. Found: C, 55.33; H, 5.65; N, 5.59. IR (liquid neat; cm^{-1}): ν(N-H) 3212 (w); ν(sp^3 C-H) 2935 w; ν(C═C) 1600 m; ν(C═C)antisym and ν(C═C)*sym* 1518 w and 1444 w; δ(-C-H sp^3) 1365 m; ν(N—C) 1268 m; δ(C—H sp^2) 865 w; ν(M−N) 698 s.

2.3.6. Synthesis of [L^3CuCl_2]

An analogous method to that described for **[L^{1}CuCl$_2$]** was adopted for the synthesis of **[L^{3}CuCl$_2$]**, except using **L^3** and $CuCl_2{\cdot}2H_2O$ (0.5 g, 2.8 mmol) to obtain a blue-green solid as the final product (98% yield). Single crystals suitable for X-ray diffraction analysis were grown by slow evaporation of MeOH solution of **[L^{3}CuCl$_2$]**. Analysis calculated for $C_{22}H_{26}Cl_2CuN_2S$ (%): C, 54.48; H, 5.40; N, 5.78. Found: C, 54.45; H, 5.42; N, 5.81. IR (liquid neat; cm^{-1}): ν(N-H) 3157 (w); ν(sp^3 C-H) 2937 w; ν(C═C) 1600 m; ν(C═C)antisym and ν(C═C)*sym* 1509 w and 1448 w; δ(-C-H sp^3) 1365 m; ν(N—C) 1264 m; δ(C—H sp^2) 859 w; ν(M−N) 699 s.

2.4. X-ray crystallographic studies

X-ray-quality single crystals were mounted in thin-walled glass capillaries on an Enraf-Noius CAD-4 diffractometer with Mo *K*α radiation (λ = 0.71073 Å). Unit cell parameters were determined by least-squares analysis of 25 reflections. Intensity data were collected in the ω/2θ scan mode, and three standard reflections were monitored every hour during data collection. Empirical absorption corrections with ψ-scans were performed on the data using the ABSCALC program [43]. The structures were solved using direct methods and refined by full-matrix least-squares techniques on F^2 using the SHELX*L*-97 and SHELX*S*-97 program packages [44,45]. Absolute structures were confirmed using anomalous dispersion effects with Friedel pairs, which were not merged. All non-hydrogen atoms were refined anisotropically, except the disordered atoms and all hydrogen atoms were positioned geometrically using the riding model with fixed isotropic thermal factors. The crystallographic data and refinements of the complexes are summarized in Table S1.

2.5. Asymmetric Henry reaction

A 25-mL flask was charged with 10 mol% of a dichloro Cu(II) complex **[L^{n}CuCl$_2$]** (L^n = L^1–L^3) in 10 mL of IPA and treated with silver acetate to generate the diacetato Cu(II) complex *in situ*; the resulting solution was applied to the Henry reaction. Then, nitromethane (0.53 mL, 10 mmol) and aldehyde (5.0 mmol) were added, followed by addition of 10.0 mol% of DIPEA as co-catalyst due to its good activity at –20 °C [30,46]. After stirring for a specified time, reactions were quenched with 1.0 mL of 1 N HCl solution and then evaporated to dryness. The products were extracted by CH_2Cl_2 (3 × 20 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude products were purified by column chromatography. Yields of isolated products (β-nitroalcohols) are based on weight obtained. The purity of isolated product were assessed by ^{1}H NMR spectroscopy. The enantiomeric excess was determined by chiral HPLC analysis using Chiralpak AD-H and Chiralcel OD-H columns.

2.5.1. (S)-1-phenyl-2-nitroethanol

The crude products were purified by column chromatography (30% EtOAc/*n*-hexane) to provide (*S*)-1-phenyl-2-nitroethanol as a colorless oil [20]. ^{1}H NMR (500 Hz, $CDCl_3$): δ 7.30 (5H, m, Ph), 5.38 (1H, dd, –CH), 4.51(1H, dd, –CH_2), 4.41 (1H, dd, –CH_2), 2.89 (1H, br s, –OH) ppm. The enantiomeric excess was determined using HPLC on a Chiralcel OD-H column (*n*-hex:IPA 95:5; flow rate 1.5 mL/min; λ = 215 nm); *R* enantiomer tr = 17.1 min, *S* enantiomer tr = 21.5 min.

2.5.2. (S)-1-nitro-4-phenylbutan-2-ol

The crude products were purified by column chromatography (10% EtOAc/*n*-hexane) to provide (*S*)-1-nitro-4-phenylbutan-2-ol as a colorless oil [23,39,47]. ^{1}H NMR (500 Hz, $CDCl_3$): δ 7.30 (5H, m, Ar–H), 5.38 (1H, dd, –CH), 4.51(1H, dd, –CH_2), 4.41 (1H, dd, –CH_2), 2.89 (1H, br, s, –OH) ppm. The enantiomeric excess was determined using HPLC on Chiralcel OD-H column (*n*-hex:IPA 90:10; flow rate 1.0 mL/min; λ = 254 nm); *R* enantiomer t_R (minor) = 11.8 min, *S* enantiomer t_R (major) = 14.8 min.

2.5.3. (S)-1-nitropentan-2-ol

The crude products were purified by column chromatography (5% EtOAc/*n*-hexane) to provide (*S*)-1-nitropentan-2-ol as a light yellow oil [48]. ^{1}H NMR ($CDCl_3$): 0.98 (3H, t, J = 6.9 Hz), 1.50–1.59 (4H, m), 2.53 (1H, br s), 4.35–4.46 (3H, m) ppm. HPLC analysis: Chiralpak AD-H column (*n*-hexane:IPA 98:2), flow rate 1.0 mL/min, 215 nm); *R* enantiomer t_R (minor) = 63.7 min, *S* enantiomer t_R (major) = 103.3 min.

2.5.4. (S)-4-methyl-1-nitropentan-2-ol

The crude products were purified by column chromatography (5% EtOAc/*n*-hexane) to provide (S)-4-methyl-1-nitropentan-2-ol as a light yellow oil [49]. ^{1}H NMR ($CDCl_3$): 0.95–1.01 (m, 6H, –CH(CH_3)$_2$), 1.21–1.30 (m, 1H, –CH_2–), 1.50–1.56 (m, 1H, –CH_2–), 1.81–1.91 (m, 1H, –CH–), 2.50 (brs, 1H, –OH), 4.37–4.45 (m, 3H, –CH_2NO_2, –CHOH–) ppm. HPLC analysis: Chiralpak AD-H column (*n*-hexane:IPA 95:5, flow rate 0.5 mL/min, λ = 210 nm); *R* enantiomer t_R (minor) = 27.42 min, *S* enantiomer t_R (major) = 37.22 min.

3. Results and discussion

3.1. Synthetic methods and physical properties

The C_1-symmetric derivatives served as an important building block and provided metal complexes of variable coordination geometries and

nuclearities. Scheme 1 illustrates the synthesis of ligands *via* the condensation reaction of (1*R*,2*R*)-*N*1-(naphthalen-2-ylmethyl)cyclohexane-1,2-diamine[42] with 2- or 3-thiophenecarboxyaldehyde and 5-methyl-2-thiophenecarboxyaldehyde. Treatment of the imine with a stoichiometric amount of reducing agent in MeOH yielded the corresponding diamines (Scheme 1). The structures of the resulting ligands were characterized by ^{1}H and ^{13}C NMR, and elemental analysis. The (–CH_2–) unit of the thiophene ring and amine moiety appeared as a set of four doublets at 4.13–3.85 for L^1, 4.09–3.81 for L^2, and 4.08–3.70 ppm for L^3 (Fig. S1–S3). The ^{1}H NMR spectrum of L^2 clearly indicated a singlet at 2.44 ppm corresponding to the methyl protons attached to the thiophene ring. Similarly, the ^{13}C NMR spectra (Fig. S4–S6) of the ligands showed peaks that were consistent with the ligand formulation.

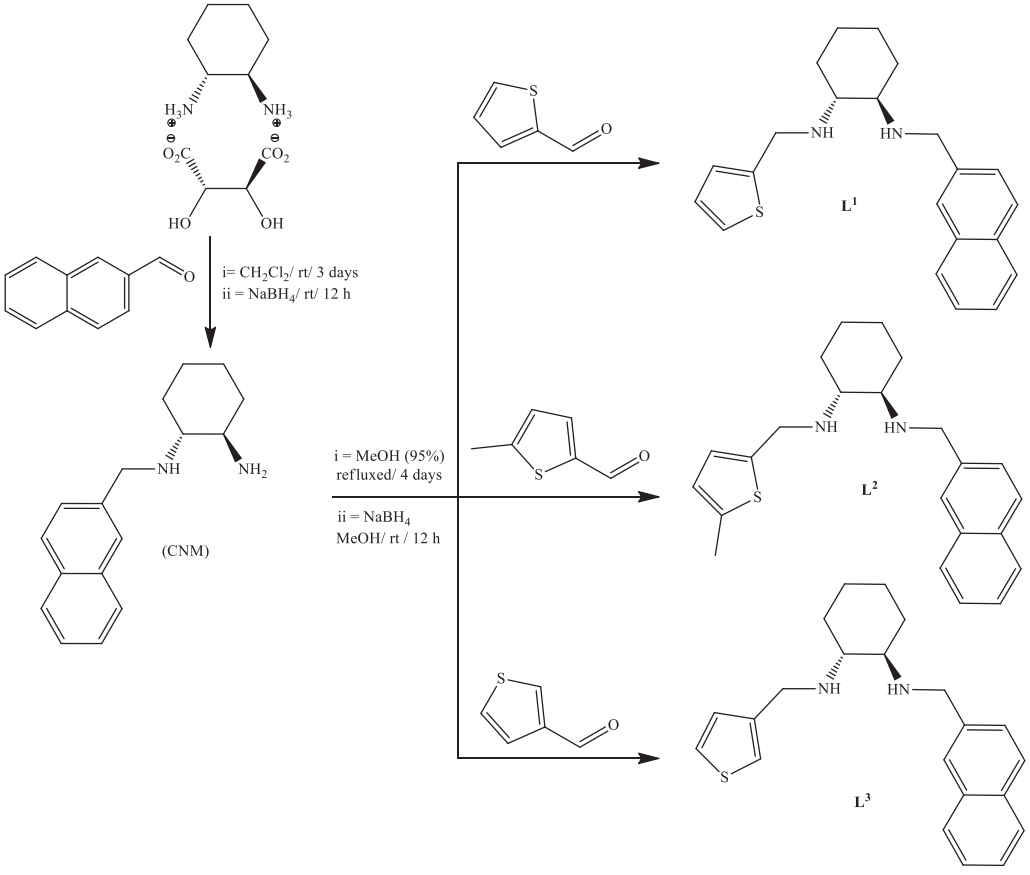
The direct coordination of these ligands to $CuCl_2{\cdot}2H_2O$ at the 1:1 M ratio furnished the corresponding dichloro Cu(II) complexes **[L^nCuCl$_2$]** (L^n = L^1–L^3) in high yield (98%) (Scheme 2). The FTIR spectra of the ligands (L^n = L^1–L^3) were compared with those of the corresponding Cu (II) complexes (Figs. S7–S12). Characteristic bands assigned to the sp^3 ν(N—H) and ν(C═C) bond stretching vibrations were observed at 2865–2949 and 1638–1663 cm^{-1}, respectively, in **[L^nCuCl$_2$]** (L^n = L^1–L^3). The symmetric and antisymmetric ν(C═C) stretching vibration bands, ν_{sym}(C═C) and ν_{asym}(C═C), of the thiophene ring appeared at 1456, 1467, and 1510 cm^{-1}. The ν(N—H) bands assigned to the amine moieties were shifted to lower wavenumbers in the spectra of the Cu(II)-complexes compared with the corresponding ligands, which suggested back-donation and the participation of nitrogen atoms in bonding [50]. Similarly, the typical sp^3 and sp^2 ν(C—H) stretching bands appeared at the frequencies reported in the literature. The presence of these absorption bands confirmed the involvement of amine nitrogens in chelating the Cu(II) center. Additionally, elemental analysis data for the synthesized Cu(II) complexes were consistent with the structures proposed in Scheme 2. The synthesized Cu(II) complexes were stable in air and could be stored for months at room temperature without appreciable degradation.

3.2. Single-crystal X-ray studies

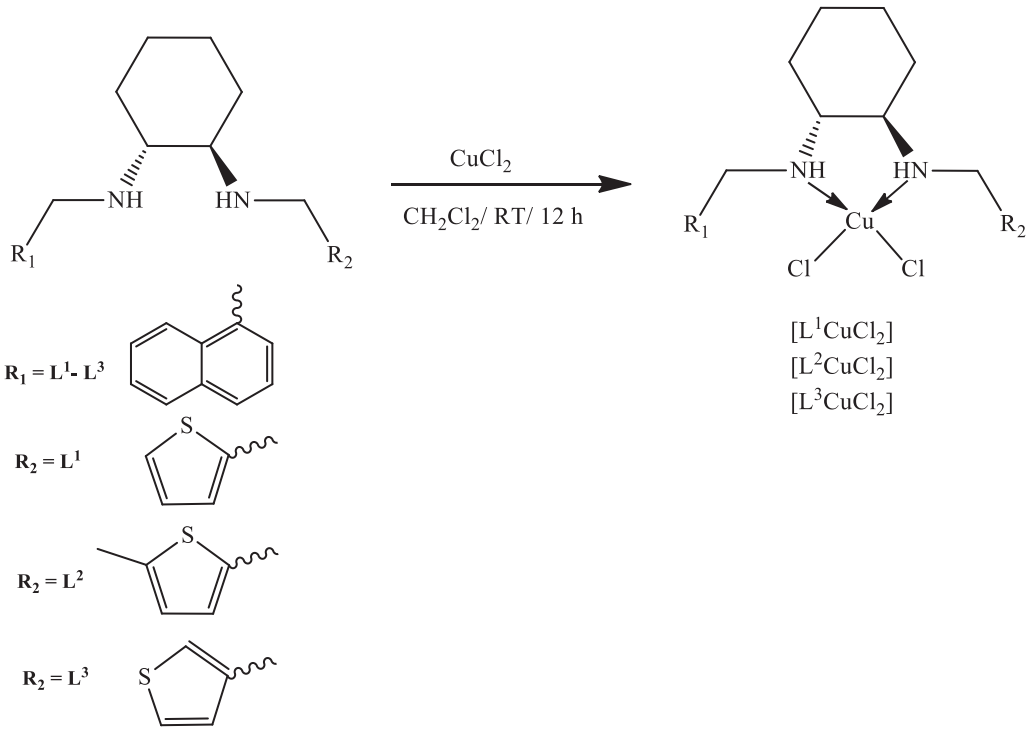
Single-crystal X-ray crystallographic analysis were carried out to determine the geometries of the obtained Cu(II) complexes. Slow evaporation of MeOH solutions of the complexes provided crystals suitable for X-ray analysis. The ORTEP diagrams of **[L^1CuCl$_2$]**, **[L^2CuCl$_2$]**, and **[L^3CuCl$_2$]** are presented in Figs. 1–3, and the bond lengths and angles of the complexes are provided in Table 1. The **[L^nCuCl$_2$]·CH$_3$OH** (L^n = L^1 – L^3) complexes crystallized in the orthorhombic crystal system with $P2_12_12_1$ space group.

The central metal atom in **[L^nCuCl$_2$]** (L^n = L^1–L^3) was tetra-coordinated and adopted a square-planar geometry. The Cu–N_{amine} bond lengths were in the range of 2.032(2)–2.0652(1) Å [20,21]. There was a slight difference between the Cu–N(1) and Cu–N(2) lengths, which might be due to the different substituents attached to the nitrogen atoms of the (*R*,*R*)-1,2-diaminocyclohexane backbone. However, these geometric parameters are within the acceptable range reported for similar Cu(II) complexes [20,21,39,51]. The Cu–N(2) bond length increased by approximately 0.013 Å in the order **[L^3CuCl$_2$]** < **[L^1CuCl$_2$]** < **[L^2CuCl$_2$]**. These results are in agreement with our previously reported Cu(II) complex [52], in which the presence of methyl substituents at the thiophene moieties affected the bond lengths. The average Cu–Cl bond length was 2.3290 Å, which is consistent with structural data obtained for similar Cu(II) complexes [53].

However, these lengths are slightly shorter than the Cu–$Cl_{terminal}$ lengths reported for Cu(II) complexes bearing C_2-symmetric ligands, such as *N*,*N*′-di(methoxybenzyl)-(*R*,*R*)-1,2-diaminocyclohexane Cu(II) dichloride [20], (*R*,*R*)-*N*,*N*′-(bis)methyl-naphthalenylmethyl-1,2-diaminocyclohexanes [52], and bis(5-methylthiophene-2-ylmethyl)



Scheme 1. Synthetic route of thiophene derived ligands (L^n = L^1–L^3) based on (1*R*,2*R*)-*N*1-(naphthalen-2-ylmethyl)cyclohexane-1,2-diamine framework.



Scheme 2. Synthesis of C_1-symmetric Cu(II)-complexes, **[L^{n}CuCl$_2$]** (L^n = L^1 – L^3), based on thiophene derivatives of (1*R*,2*R*)-*N*1-(naphthalen-2-ylmethyl)cyclohexane-1,2-diamine.

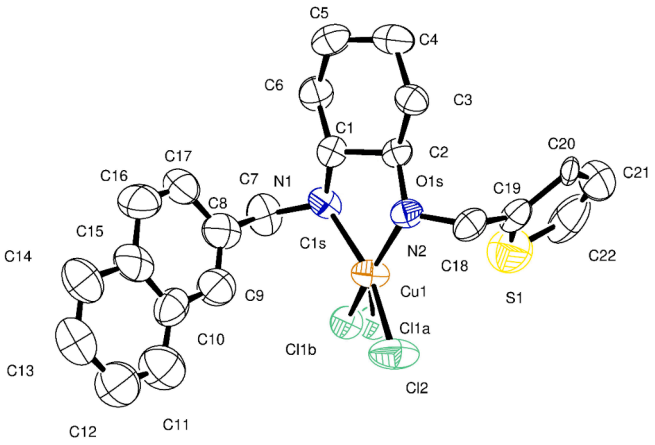


Fig. 1. An ORTEP drawing of **[L^{1}CuCl$_2$]** with thermal ellipsoids at 50% probability.

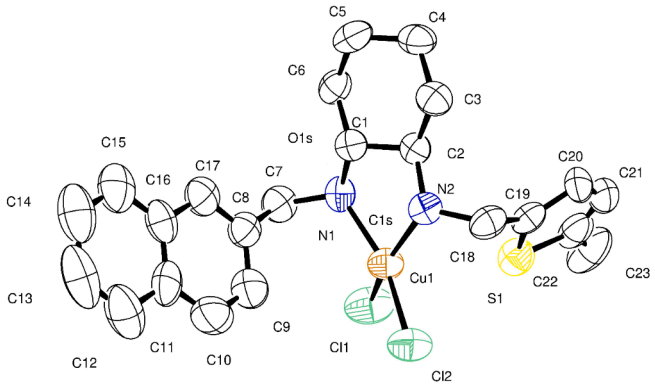


Fig. 2. An ORTEP drawing of **[L^{2}CuCl$_2$]** with thermal ellipsoids at 50% probability.

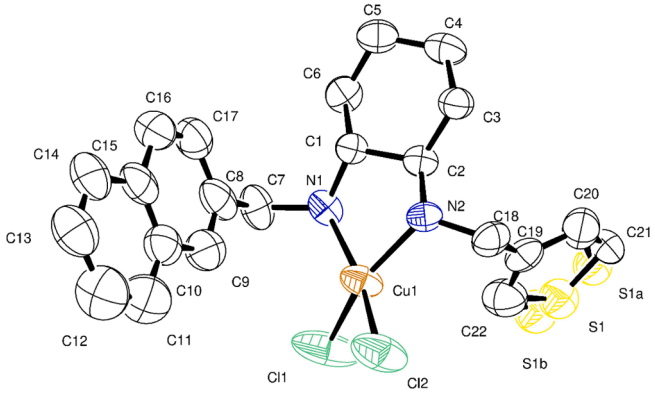


Fig. 3. An ORTEP drawing of **[L^{3}CuCl$_2$]** with thermal ellipsoids at 50% probability.

cyclohexane-1,2-diamine Cu(II) dichloride [21]. The data in Table 1 indicate that the Cu–Cl(2) bond length is longer in **[L^{2}CuCl$_2$]** than in its **[L^{1}CuCl$_2$]** analog. This discrepancy is attributed to the methyl substituents attached to the thiophene moiety in **[L^{2}CuCl$_2$]**.

The N(2)–Cu(1)–N(1) and N(3)–Cu(1)–N(2) bond angles in **[L^{n}CuCl$_2$]** (L^n = L^1–L^3) ranged from 78.89(2)° to 82.08(2)° and were affected by the substitution of the five-membered chelate ring [39,53]. The Cu center was attached to the (*R*,*R*)-1,2-diaminocyclohexane backbone derivative in a bidentate fashion and resulted in the formation of a five-membered chelate ring.

The average N_{amine}–Cu–N_{amine} bond angles for **[L^{n}CuCl$_2$]** (L^n = L^1–L^3) were in the range of 83.92(2)–84.31(6)° and hence deviated slightly from the 90° angle of an ideal square-planar geometry. Similarly, the N_{amine}–Cu–$Cl_{terminal}$ angles were 97.49(11)° for **[L^{1}CuCl$_2$]**, 97.40(6)° for **[L^{2}CuCl$_2$]**, and 96.02(7)° for **[L^{3}CuCl$_2$]**, which are reminiscent of similar square-planar tetra-coordinated Cu(II) complexes

Table 1
Selected bond lengths (Å) and angles (°) of $[L^nCuCl_2]$ ($L^n = L^1$–L^3).

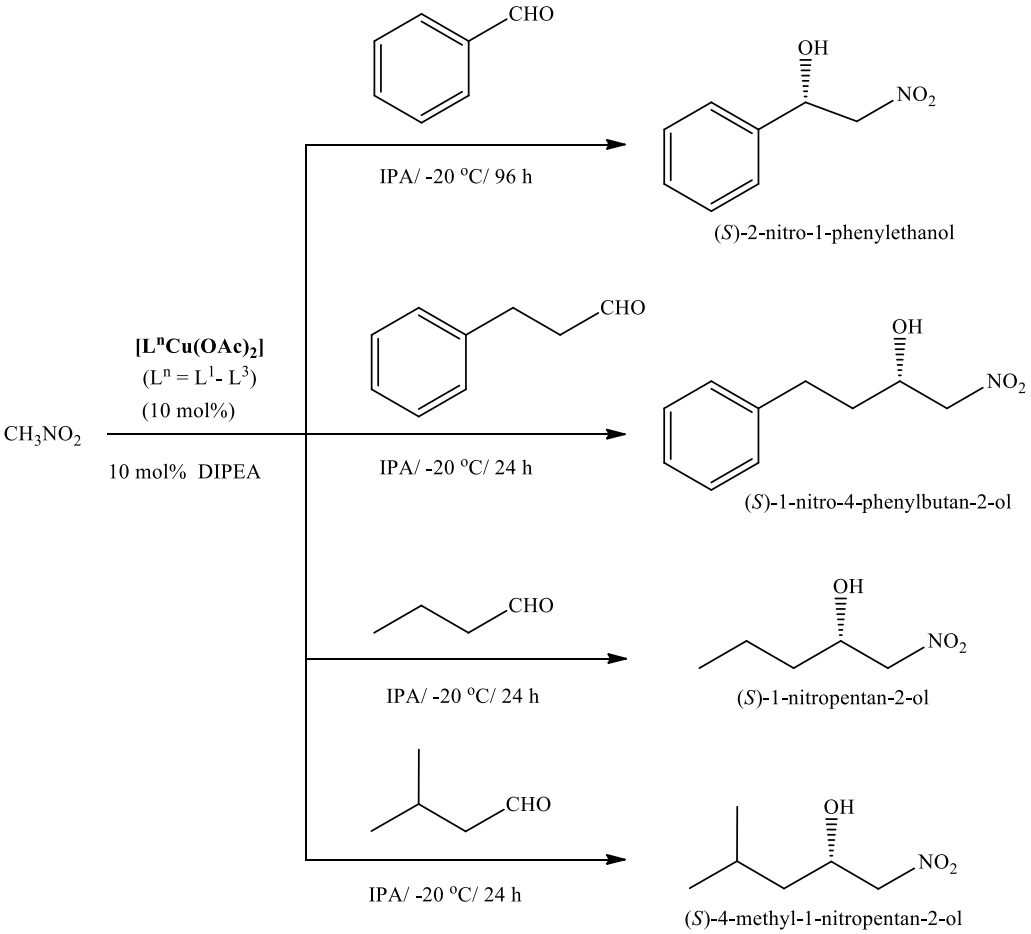
	$[L^1CuCl_2].CH_3OH$	$[L^2CuCl_2].CH_3OH$	$[L^3CuCl_2].CH_3OH$
Bond Lengths (Å)			
Cu-N1	2.026(5)	2.013(4)	2.009(4)
Cu-N2	2.034(5)	2.038(4)	2.025(4)
Cu-Cl1	2.228(4)	2.2284(15)	2.2226(17)
Cu-Cl2	2.2273(1)	2.2304(15)	2.2240(16)
N1-C1	1.493(7)	1.511(6)	1.487(6)
N2-C2	1.481(7)	1.478(5)	1.491(6)
N1-C7	1.484(8)	1.481(6)	1.491(6)
N2-C18	1.481(7)	1.485(5)	1.488(6)
Bond Angles (°)			
N1-Cu1-N2	83.91(19)	84.04(15)	84.31(15)
N2-Cu1-Cl2	93.60(14)	93.56(11)	94.06(11)
N2-Cu1-Cl1	150.77(17)	157.70(11)	154.96(13)
N1-Cu1-Cl2	159.09(17)	157.66(11)	159.31(13)
N1-Cu1-Cl1	97.72(17)	92.82(11)	93.94(12)
Cl2-Cu1-Cl1	97.49(11)	97.40(6)	96.02(7)
C7-N1-Cu1	115.2(5)	115.8(3)	116.3(3)
C18-N2-Cu1	118.0(4)	116.6(3)	114.7(4)

[53]. Additionally, the complexation of the metal to the ligand framework with the stereogenic centers R_C, R_C derived from a (*R*,*R*)-1,2diaminocyclohexane backbone resulted in hindering nitrogen atom inversion and thus induced chirality therein. **$[L^nCuCl_2]$** ($L^n = L^1$–L^3) were obtained as enantiopure complexes in which both nitrogens have the R_N configuration. The hydrogen atoms of the stereogenic carbons and nitrogens in **$[L^nCuCl_2]$** ($L^n = L^1$–L^3) were in the head-to-tail conformation.

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

Our current work is targeted toward the C_1-symmetric Cu(II)-catalyzed asymmetric Henry reaction because of the diverse structural properties of asymmetrical ligand frameworks [54,55]. The catalytic activity of the diacetato derivatives, generated *in situ*, of the synthesized Cu(II) complexes in the asymmetric Henry reaction between nitromethane and various aldehydes with 10 mol% of DIPEA as base additive in IPA at –20 °C was examined (Scheme 3, Table 2). The use of DIPEA as a base for the asymmetric Henry reaction is well documented, and negligible product was observed when the reaction proceeded in the absence of DIPEA. It has been suggested that transition metal complexes (acting as Lewis acids) are not powerful enough to form bonds through the single activation of nucleophiles; thus, deprotonation of a nucleophile precursor with an amine base is needed to activate the reaction [56]. We previously reported that 10 mol% of DIPEA as promoter ensured the best results in term of yields and enantioselectivities of the corresponding *β*-nitroalcohol with copper acetate complexes **$[L^nCu(OAc)_2]$** ($L^n = L^1$–L^3).[21]

The screening of complexes toward benzaldehyde and nitromethane revealed lower yields of the resulting 2-nitro-1-phenylethanol, with activity increasing in the order **$[L^1Cu(OAc)_2]$** < **$[L^2Cu(OAc)_2]$** < **$[L^3Cu(OAc)_2]$**, whereas the enantioselectivities increased in the order **$[L^2Cu(OAc)_2]$** < **$[L^1Cu(OAc)_2]$** < **$[L^3Cu(OAc)]$**. No significant change in yield (>98%) of the resulting *β*-nitroalcohols was observed with **$[L^nCu(OAc)_2]$** ($L^n = L^1$–L^3) when 3-phenylpropanal was used as a substrate, with **$[L^3Cu(OAc)_2]$** showing superior enantioselectivity (>99%) (Table 2) (Figs. S13–S24). These results are consistent with our enantiomeric excess, consistent with reported studies.[61]



Scheme 3. Henry reaction of different aldehydes with CH_3NO_2 catalysed by **$[L^nCu(OAc)_2]$** ($L^n = L^1$–L^3) at –20 °C in the presence of 10 mol% of DIPEA.

Table 2
Screening diacetato Cu(II) complexes supported with (1*R*,2*R*)-*N*1-(naphthalen-2-ylmethyl)cyclohexane-1,2-diamine derivatives in asymmetric Henry reaction.

Catalyst	Entry		Aldehydes	Time (days)	Yields (%)[b]	ee(%)[c]	Config.[d]
Blank	[e]1	Me-NO_2	Ph-$(CH_2)_2$C(O)H	4	60	–	–
	[e]2	Me-NO_2	Ph-$(CH_2)_2$C(O)H	1	80	–	–
	[f]3	Me-NO_2	Ph-$(CH_2)_2$C(O)H	1	82	–	–
1	4	Me-NO_2	Ph-C(O)H	4	62	84	*S*
	5	Me-NO_2	Ph-$(CH_2)_2$C(O)H	1	98	99	*S*
	6	Me-NO_2	$CH_3(CH_2)_2$C(O)H	1	99	83	*S*
	7	Me-NO_2	$(CH_3)_2CHCH_2$C(O)H	1	93	74	*S*
2	8	Me-NO_2	Ph-C(O)H	4	68	77	*S*
	9	Me-NO_2	Ph-$(CH_2)_2$C(O)H	1	98	90	*S*
	10	Me-NO_2	$CH_3(CH_2)_2$C(O)H	1	99	88	*S*
	11	Me-NO_2	$(CH_3)_2CHCH_2$C(O)H	1	94	88	*S*
3	12	Me-NO_2	Ph-C(O)H	4	90	85	*S*
	13	Me-NO_2	Ph-$(CH_2)_2$C(O)H	1	99	>99	*S*
	14	Me-NO_2	$CH_3(CH_2)_2$C(O)H	1	99	82	*S*
	15	Me-NO_2	$(CH_3)_2CHCH_2$C(O)H	1	99	83	*S*

[a] 1 = **[L^1Cu(OAc)$_2$]**, 2 = **[L^2Cu(OAc)$_2$]**, 3 = **[L^3Cu(OAc)$_2$]**, 0.50 mmol of Cu(II)-initiator, 5.0 mmol aldehyde, 10.0 mmol of CH_3NO_2,10 mol% of DIPEA, solvent IPA (10 mL), temperature −20 °C.[b] Yields defined as weight of isolated *β*-nitro alcohols. [c] Enantiomeric excess (ee) was determined by chiral HPLC analysis using a Chiralcel OD-H and Chiralpak AD-H columns as per the reported protocol [20,23,47–49].[d] *S* enantiomer was the major product [59–61].[e] Experiments conducted in the absence of catalysts (blank reaction), 5.0 mmol aldehyde, 10.0 mmol of CH_3NO_2,10 mol% of DIPEA, solvent IPA (10 mL), temperature −20 °C . [f] Reaction performed in the absence of base DIPEA produced nitroalcohols with 82% yields with very low enantiomeric excess.

previous findings that unsymmetrical naphthyl derivatives of the (*R*,*R*)-1,2-diaminocyclohexane backbone showed excellent activity (99% in 24 h) and unusually high enantioselectivity (>99%) for the reaction between 3-phenylpropanal and nitromethane yielding (*S*)-1-nitro-4-phenylbutan-2-ol [39]. Longer reaction times and inferior enantioselectivities were anticipated for the dichloro Cu(II) complexes compared to their diacetato counterparts, based on our previous reports. Consequently, the dichloro complexes were not explored for the Henry reaction in our current study [39,53]. A blank reaction of nitromethane and benzaldehyde/3-phenylpropanal performed in the absence of the C_1-symmetric chiral Cu(II) complexes resulted in mild activity with negligible enantioselectivity (Table 2 entries 1 and 2). Additionally, experiment conducted in the absence of DIPEA produced (*S*)-1-nitro-4-phenylbutan-2-ol (Table 2 entry 3) in 88% yield with very low enantiomeric excess, consistent with reported studies [57].

These results clearly indicate that **[L^3Cu(OAc)$_2$]** is better stereo-directing compared with complexes bearing 2-thiophenyl and 5-methyl-2-thiophene pendant groups for both benzaldehyde and 3-phenypropanal (Table 2, entries 12 and 13). Using **[L^3Cu(OAc)$_2$]** as a catalyst for 3-phenylpropanal brought excellent activity (99%) and selectivity (>99%) compared with benzaldehyde under identical experimental protocols [39]. Compared with our previously studied C_2-symmetric (*R*,*R*)-*N*,*N*--bis(5-methylthiophen- 2-ylmethyl) cyclohexane-1,2-diamine based Cu(OAc)$_2$ complex which resulted in 70% yield of *β*-nitroalcohol with 92% enantioselectivity from reaction of nitromethane and benzaldehyde in the presence of 3 mol% DIPEA as a promoter [21], **[L^3Cu(OAc)$_2$]** with C_1-symmetric ligand architecture exhibited 90% yields for corresponding *β*-nitroalcohol with 87% ee (Table 2 entry 12).

Based on the conditions investigated, the catalytic protocol was extended to aliphatic aldehydes. The aliphatic aldehydes smoothly converted into their corresponding *β*-nitroalcohols with good to excellent yields. The length of the alkyl chain of the aldehyde moiety influenced the activity and enantioselectivity. In aliphatic aldehydes, a decrease in activity and enantioselectivity was observed with increasing aldehyde chain length. This contrasts with other findings in which the enantioselectivity increased with increasing aldehyde chain length [35]. These preliminary results reveal that the electron-donating methyl substituent in the pendant thiophenyl moiety in the L^2 complex significantly influenced the enantioselectivity of the 4-methyl-1-nitropentan-2-ol product compared with its analogs lacking methyl substituents in their respective thiophene moieties. Thus, **[L^2Cu(OAc)$_2$]** was better stereo-directing for both butyraldehyde and 3-methyl-butanal (Table 2 entries 10 and 11).

Interestingly, the Henry reaction catalyzed by these Cu(II) catalytic species resulted in the corresponding *β*-nitroalcohols with an (*S*)-configuration at the stereogenic center. This configuration may be due to the favorable orientation of the phenyl group of the aldehydes and the aromatic moieties of the ligand architecture [12,58–60]. The stereochemical outcomes (*S*)-enantiomer of the Henry reaction with these diacetato Cu(II) complexes are in agreement with the previous studies [5,12,25,39,61]. In this mechanism, the carbonyl oxygen atom is coordinated at one of the equatorial positions and the oxygen atom of nitromethane approaches the metal center from the axial side. The *Re* face (A) of the carbonyl group of the aldehyde is much more accessible to a nucleophilic group (nitromethane) than the *Si* face. This positioning of the reactants seems to be the most favorable orientation, taking into account steric and electronic considerations of neighboring coordination sites. Additionally, the attacking group will strongly increase repulsion between the aldehyde moiety and ligand substituents, as illustrated in transition state B of Fig. S25 [39]. The illustrated transition states for Henry reaction are also proposed to be supported by π-π interactions between the thiophenyl and phenyl moieties of ligand (Figure S25 A), which is additionally assisted by a charge-assisted hydrogen bonding (CAHB), as reported previously [62].

Compared with the chiral Cu(II)-complexes bearing L-proline[63] and core-chiral-bispidine ligands (88% yield; ee 97% in 48 h for 3-phenylpropanal) [64], the **[L^3Cu(OAc)$_2$]** complex displayed superior activity, providing (*S*)-1-nitro-4-phenylbutan-2-ol with excellent enantioselectivity (99% yield; >99% (*S*) ee in 24 h; Table 2 entry 13**)**. Interestingly, **[L^nCu(OAc)$_2$]** (L^n = L^1–L^3) performed less selectively toward benzaldehyde; consistent with the reported studies that chiral catalyst bearing cyclohexane-1,2-diamine ligands exhibits better enantioselectivity with aliphatic aldehydes compared with aromatic ones [65]. The C_1-symmetric Cu(II)-acetate complex bearing the pyridyl derivative of 1,2-diaminocyclohexane studied as an aliphatic aldehyde demonstrated lower activity and good enantioselectivity; the aldehyde with the *n*-butyl alkyl chain provided the corresponding *β*-nitroalcohol in 88% yield, 98% ee in 60 h, compared with our current system (94% yield, 88% ee in 24 h, Table 2 entry 11) [66]. Compared with (1*R*,2*R*)-*N*1-(4-methylpentan-2-yl)cyclohexane-1,2-diamine/Cu(OAc)$_2$·2H_2O/Et_3N for aliphatic aldehydes, the corresponding *β*-nitroalcohols were obtained in the (*S*)-configuration in low yields (38–53%) and enantioselectivities (75–86%) compared with our studied catalysts [29].

Similarly, compared with the *in situ*-generated Cu(II)-triflate complex of (1*S*,2*R*)-2-((5-methylthiophen-2-yl)methylamino-1-phenylpropanol [35] for aliphatic aldehydes, our current system gave superior results. Further investigation is being carried out on the catalytic applications of these complexes for the diastereoselective Henry reaction and other asymmetric reactions.

4. Conclusions

We synthesized Cu(II) complexes containing thiophene derivatives of the (1*R*,2*R*)-*N*1-naphthalylcyclohexane-1,2-diamine framework. The diacetato complexes were used in the asymmetric Henry reaction of aromatic and aliphatic aldehydes with nitromethane in the presence of 10 mol% of DIPEA to yield the corresponding β-nitroalcohols. All the studied C_1-symmetric **[L^{n}Cu(OAc)$_2$]** (L^n = L^1–L^3) complexes proved to be efficient enantioselective catalysts for the asymmetric Henry reaction between 3-phenylpropanal and nitromethane, resulting in (*S*)-1-nitro-4-phenylbutan-2-ol in high yield (99%), with **[L^{3}Cu(OAc)$_2$]** being produced β-nitroalcohols with highest ee (>99%). These results compare well with the best reported enantioselective Cu(II) catalysts of the Henry reaction between 3-phenylpropanal and nitromethane. Furthermore, the screening of **[L^{n}Cu(OAc)$_2$]** (L^n = L^1–L^3) for aliphatic aldehydes provided the corresponding β-nitroalcohols in excellent yields (up to 99%) and moderate to high enantioselectivities (up to 88%). With respect to ee, the best results were obtained with **[L^{2}Cu(OAc)$_2$]** for aliphatic aldehydes. This finding is attributed to the electron-donating effect of the methyl substituent.

CRediT authorship contribution statement

Juhyun Cho: Conceptualization, Data curation, Formal analysis. **Jong Hwa Jeong:** Funding acquisition, Investigation, Methodology, Project administration. **Hyosun Lee:** Validation, Visualization, Writing - original draft. **Jungkyu K. Lee:** Resources, Software, Supervision. **Saira Nayab:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2021.120492.

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