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An efficient synthetic approach towards a single diastereomer of (2*R*,3*R*)-N^2,N^3-bis((*S*)-1-phenylethyl)butane-2,3-diamine via metalation and demetalation

Juhyun Cho[1] · Saira Nayab[2] · Jong Hwa Jeong[1]

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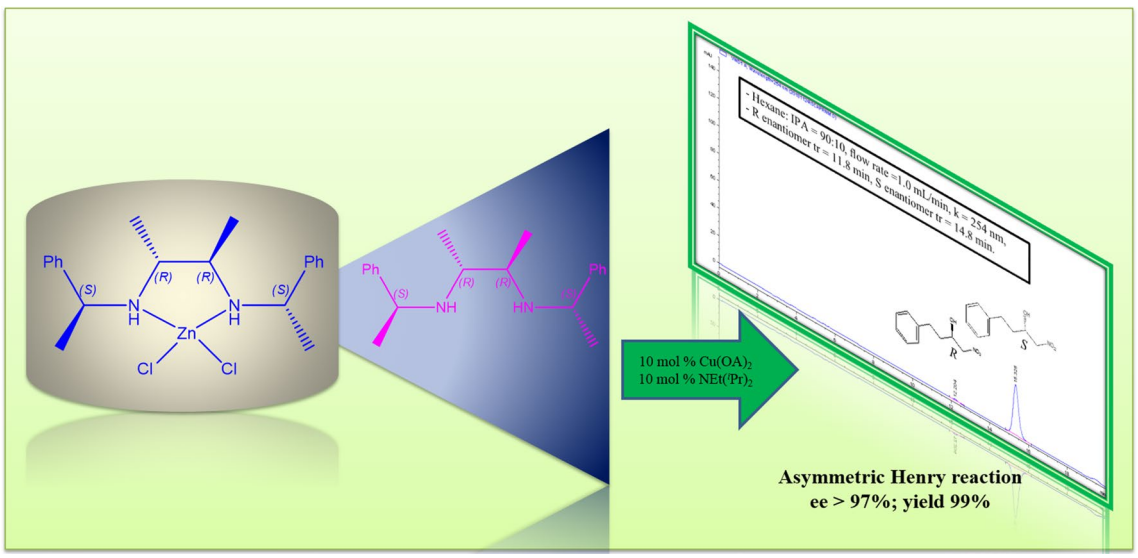
Abstract

A facile synthetic approach has been adopted towards the synthesis of (2*R*,3*R*)-N^2,N^3-bis((*S*)-1-phenylethyl)butane-2,3-diamine via demetalation of its dichloro Zn(II) complex, which itself was separated from a mixture of diastereomeric Zn(II) complexes by fractional crystallization. The synthesized chiral 1,2-diamine ligand was evaluated as a chiral auxiliary for the Cu(II)-catalysed asymmetric Henry reaction of 3-phenylpropanal and nitromethane, yielding (*S*)-1-nitro-4-phenylbutan-2-ol in excellent yields (up to 99%) and enantioselectivities (up to 97%).

Graphic abstract

A facile synthetic approach towards (2*R*,3*R*)-N^2,N^3-bis((*S*)-1-phenylethyl)butane-2,3-diamine (**2b**) via fractional crystallization and demetalation of its Zn(II) complex has been adopted. **2b** served as a highly enantioselective pro-ligand with $Cu(OAc)_2$ for asymmetric Henry reaction of 3-phenylpropanal and nitromethane in the presence of base with 97% > ee and 99% yield.



Introduction

Chiral 1,2-diamines have emerged as powerful tools for the synthesis of catalysts and bioactive compounds [1–7]. Diamines, especially C_2-symmetric diamines, have been utilized as chiral auxiliaries for a wide array of asymmetric

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chemical transformations [8–10]. For example, they have been used to develop a variety of innovative chiral catalysts for reactions such as oxidations, reductions, and hydrogenations. Additionally, they have also been used in a variety of carbon–carbon bond-forming reactions such as allylic alkylation, metathesis, Michael addition, aldol, cycloaddition, and ring-opening reactions [11–22]. The prevalence of the diamine motif in catalysts and bioactive compounds has led to the advancement of synthetic methodology for chiral diamines [23–29]. However, when using these methods, several limitations arise: limited scope, necessity for resolution, proper temperature control, and low yields [30]. Due to these limitations, it is a challenge to develop facile and efficient synthetic routes towards diverse chiral diamines that are enantiomerically pure; such an approach would greatly facilitate the development of new diamine-based catalysts and drugs. In previous years, we explored the generation of an enantiopure ligand by demetalation of its enantiopure metal complex. This was achieved in an economic manner by fractional crystallization from a mixture of two diastereomeric Zn(II) complexes [31]. Herein, we describe the synthetic procedure to afford (2*R*,3*R*)-N^2,N^3-bis((*S*)-1-phenylethyl) butane-2,3-diamine through the metalation and demetalation of Zn(II) complexes. A preliminary catalytic study of this ligand in Cu-catalysed asymmetric Henry reactions is also presented.

Experimental section

General consideration and materials

The alkylation of diimine using MeLi was carried out using the standard Schlenk techniques and glove box under argon. THF was dried over Na/benzophenone ketyl, while CH_2Cl_2 was dried over CaH_2 and deoxygenated by distillation under argon prior to use. Degas water was prepared by freeze and thaw process. Ethanol (EtOH), methanol (MeOH), *n*-hexane (*n*-Hex), ethyl acetate (EA), isopropanol (IPA), and diethyl ether (Et_2O) were purchased from high-grade commercial supplier and used as received. Starting materials, MeLi (1.5 M in diethyl ether), (*S*)-methyl benzyl amine, Glyoxal (40% aqueous solution), $ZnCl_2$, $Cu(OAc)_2$, NaCN, and *N*,*N*-diisopropylethylamine ($^iPr_2NEt$) were purchased from Aldrich. NMR solvents were purchased from Aldrich and stored over 3-Å molecular sieves. The synthesis of **1** was carried out according to reported method [32].

Instrumentation

^1H (operating at 500 MHz) and ^{13}C (operating at 125 MHz) NMR spectra were recorded on a Bruker Avance Digital 500-NMR spectrometer (Bruker, Billerica, MA), and chemical shifts were recorded in ppm units (δ) 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 600-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 excesses (ee) were determined by HPLC with chiral OD-H and AD-H columns using HPLC-grade IPA and *n*-Hex as eluting solvents.

Synthetic procedures

Synthesis of N^2,N^3-bis(1-phenylethyl)butane-2,3-diamine (2)

The analogous method as reported in the literature was applied for synthesis of **2** [33]. The grafting of methyl group at ethylene backbone resulted in **2** as a mixture of *SRRS, SSSS* diastereomers in ratio of 1:0.7. The separation of resultant diastereomers via column chromatography was not possible even after several trials. Thus, the crude ligand was subjected in next reaction without separation of diastereomers.

Synthesis of 3*b*

EtOH (10 mL) solution of crude ligand **2** (4.00 g, 13.49 mmol) was treated with EtOH (10 mL) solution of $ZnCl_2$ (1.83 g, 13.49 mmol) at ambient temperature for overnight. The precipitated solid was filtered and subsequently washed with cold EtOH (10.00 mL × 2) and Et_2O (5.00 mL × 2) to get a mixture of two diastereomeric Zn(II) complexes as a final product (5.19 g, 89%). Fractional crystallization was carried out for the separation of two diastereomeric complexes using EtOH. The pure **3b** was separated from **3a** as a fine crystalline product [(**3b**: 4.50 g, 77%)]. The solubility of **3a** in various organic solvents makes it impractical to precipitate and separate it from mother liquor in appreciable and quantitative amount. Characterization data for **3b**: Anal. Calcd. for $C_{20}H_{28}Cl_2N_2Zn$: C, 55.51; H, 6.52; N, 6.47. Found: C, 55.54; H, 6.55; N, 6.49. ^1H NMR (500 MHz, $CDCl_3$) δ 7.42–7.32 (m, 4H, Ar*H*), 7.35–7.32 (m, 2H, Ar*H*), 7.23–7.21 (m, 4H, Ar*H*), 4.16 (sext, 2H, $J = 6.7$, 12.13 Hz, $Ph(CH)_2(NH)_2$), 2.83–2.80 (m, 2H, $CH_3(CH)_2$), 1.58 (br s, 2H, $(NH)_2$), 1.69 (d, 6H, $J = 6.7$ Hz, $PhCH(CH_3)_2$), 1.26 (d, 6H, $J = 6.7$ Hz, $NHCH(CH_3)_2$. ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2 (2C), 129.4 (4C), 128.2 (4C), 125.7 (2C), 55.1 (2C), 54.6 (2C), 24.9 (2C), 15.0

(2C). IR (solid neat; cm^{-1}): ν(N–H) 3458 w; ν(C–H) 3242 w; ν(C=C), 1648 s; ν_{bend}(C–H sp^3) 1435 m; ν_{bend}(C–H sp^2) 935 m.

Synthesis of (2*R*,3*R*)-N^2,N^3-bis(*S*-1-phenylethyl) butane-2,3-diamine, (2*b*)

CH_2Cl_2 (20 mL) solution of **3b** (4.00 g, 9.24 mmol) was treated with aqueous solution (10 mL) of NaCN (3.17 g, 64.68 mmol) and stirred for 2 h at ambient temperature. The clear organic layer was separated, dried over $MgSO_4$, and concentrated to yield **2a** as light yellow oil (2.45 g, 90%). Anal. Calcd. for $C_{20}H_{28}N_2$: C, 81.03; H, 9.52; N, 9.45. Found: C, 81.08; H, 9.51; N, 9.49%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.22 (m, 8H, Ar*H*), 7.17–7.13 (m, 2H, Ar*H*), 3.75 (q, 2H, J = 6.5, 18.34 Hz, Ph(C*H*)$_2$), 2.01–1.98 (m, 2H, NH(C*H*)$_2$), 1.50 (br s, 2H, (N*H*)$_2$), 1.24 (d, 6H, J = 6.5 Hz, PhCH(CH_3)$_2$), 0.82 (d, 6H, J = 6.5 Hz, NHCH(CH_3)$_2$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 128.3, 126.8, 126.7, 55.1, 55.0, 25.5, 16.5. IR (oily liquid neat; cm^{-1}): ν(N–H) 3300 w; ν(C–H) 3060 w; ν(C=C), 1651 s; ν_{bend}(C–H sp^3) 1449 m; ν_{bend}(C–H sp^2) 910 m.

General procedure for Henry reaction

A 20-mL flask was charged with $Cu(OAc)_2$ (0.0908 g, 0.50 mmol) and (2*R*,3*R*)-N^2,N^3-bis((*S*)-1-phenylethyl) butane-2,3-diamine (0.148 g, 0.50 mmol) in IPA (10.00 mL) and stirred at room temperature for 1 h to get in situ-generated diacetato Cu(II) complexes, and the resultant solution was applied to Henry reaction. Then, nitromethane (CH_3NO_2) (1.00 mL, 20.00 mmol) was added and stirred for 10 min followed by the addition of benzaldehyde (0.50 mL, 5.00 mmol) or 3-phenylpropanal (0.65 mL, 5.00 mmol). Finally, ^{i}Pr$_2$NEt (0.62 g, 0.50 mmol) was added in the previous mixture which acts as an effective co-catalyst and stirred for prescribed time at room temperature [34, 35]. The reaction progress was monitored by thin-layer chromatography (TLC). Upon completion, the reaction mixture was evaporated and the crude product was purified by column chromatography using AcOEt/*n*-Hex eluent.

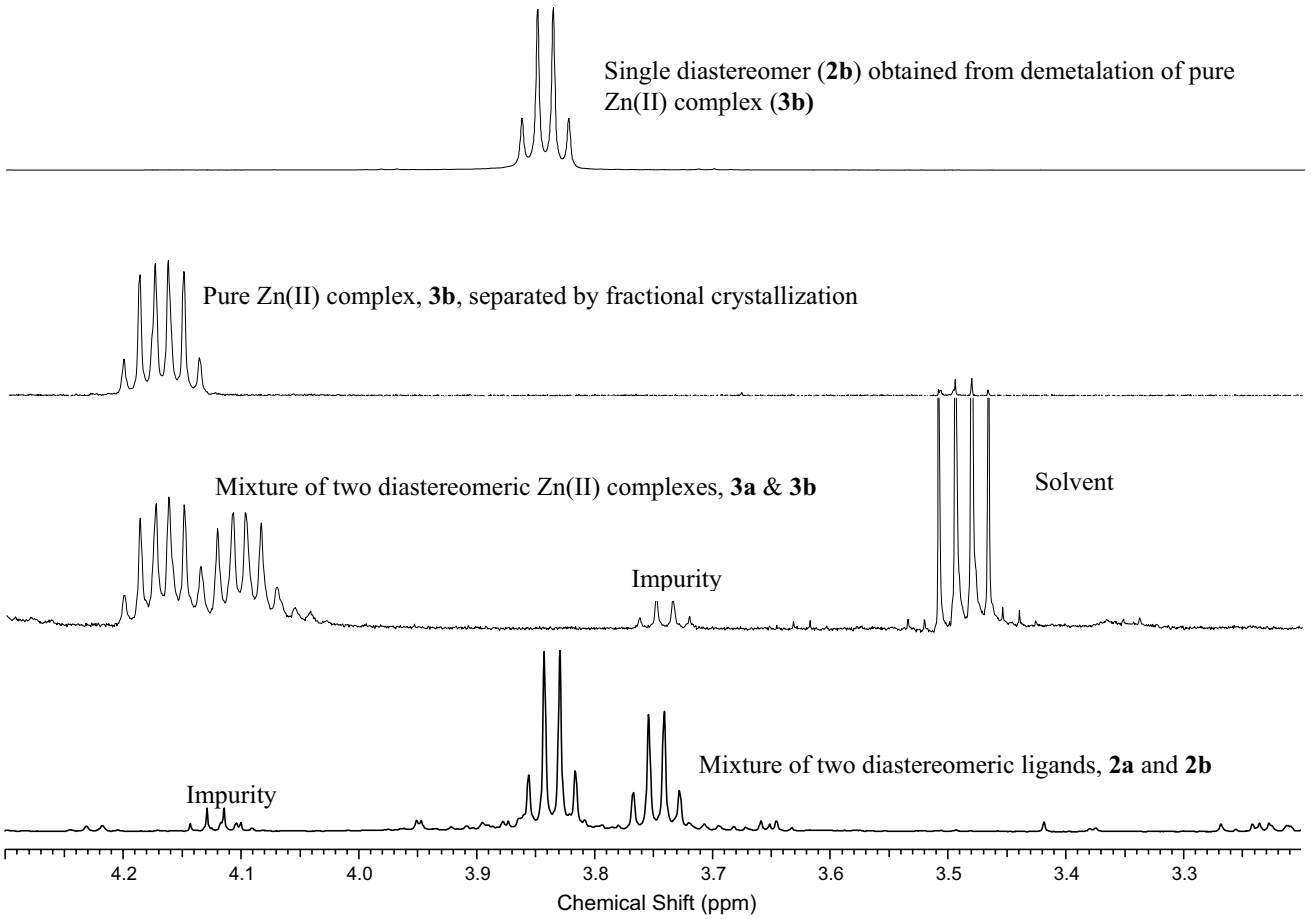


Fig. 1 Comparative view of ^{1}H NMR clearly demonstrating the methine protons region for various steps of separating process to obtain single diastereomer (**2b**) of **2**

Isolation and characterization of (*S*)-1-phenyl-2-nitroethanol

The crude products were purified by column chromatography (30% EtOAc/hexane) to give yellow oil as (*S*)-1-phenyl-2-nitroethanol [36]. ^{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). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2, 129.0, 128.9, 126.0, 81.2, 71.0. $[\alpha]_D^{20} = +14.8$ (c 2.4, $CHCl_3$) [37]. Enantiomeric excess (ee) was determined using HPLC on Chiracel OD-H column as reported earlier [38] (*n*-Hex: IPA = 95:5; flow rate = 1.5 mL/min; $\lambda = 215$ nm); *R* enantiomer $t_R = 17.4$ min, *S* enantiomer $t_R = 20.6$ min.

Isolation and characterization of (*S*)-1-nitro-4-phenylbutan-2-ol

The crude products were purified by column chromatography (10% EtOAc/hexane) to give a colourless needle-like solid as (*S*)-1-nitro-4-phenylbutan-2-ol [39, 40]. ^{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). ^{13}C NMR (125 Hz, $CDCl_3$): δ 140.64, 128.69, 128.45, 126.37, 80.58, 67.80, 35.15, 31.35. $[\alpha]_D^{25} = -13.26$ (c 2.2, CH_2Cl_2) [41]. Enantiomeric excess (ee) was determined using HPLC on AD-H column [37] (*n*-Hex: IPA = 95:5; flow rate = 1.5 mL/min; $\lambda = 254$ nm); *R* enantiomer $t_R = 12.2$ min, *S* enantiomer $t_R = 15.3$ min.

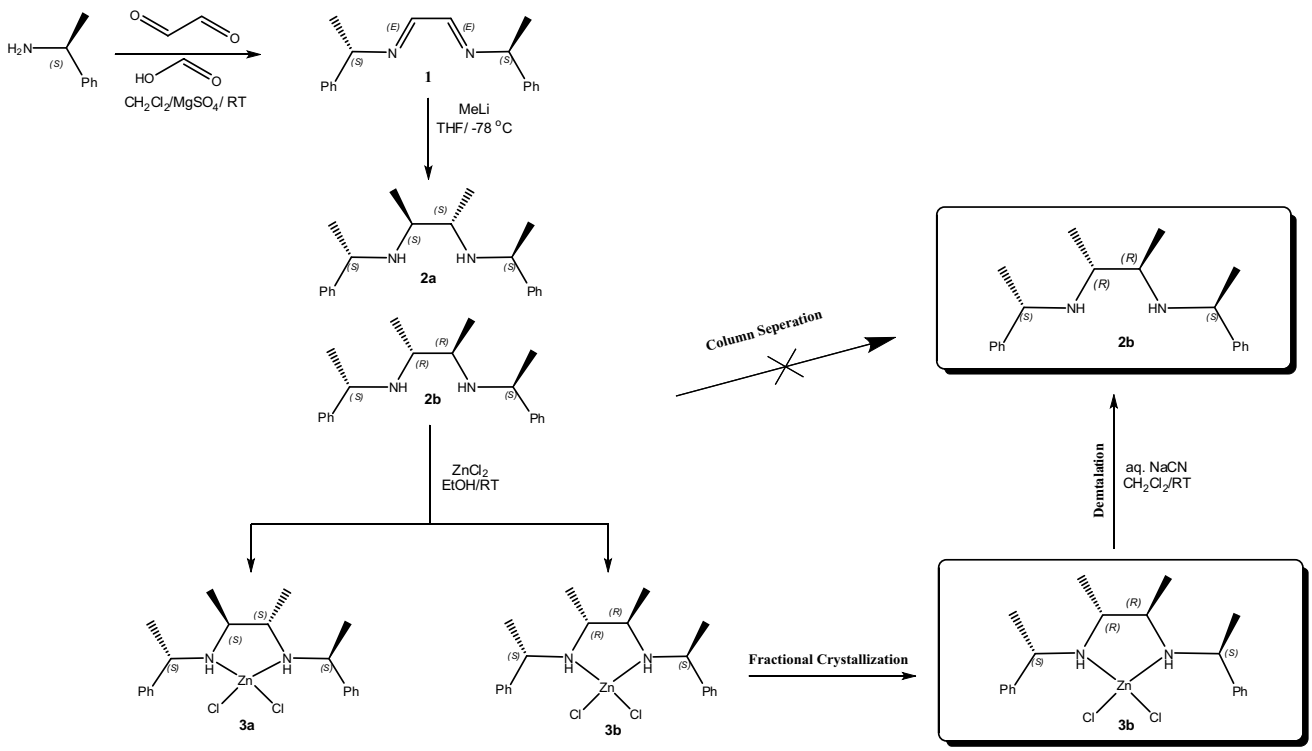
X-ray crystallography

The single X-ray crystals were obtained from slow evaporation of EtOH. An X-ray quality single crystal of **3b** was mounted in a thin-walled glass capillary on an Enraf-Noius CAD-4 diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by least-squares analysis of 25 reflections ($10° < \theta < 13°$). Intensity data were collected with θ range of 1.56°–25.47° in $\omega/2\theta$ scan mode. Three standard reflections were monitored every 1 h during data collection. The data were corrected for Lorentz–polarization effects and decay. Empirical absorption corrections with ψ-scans were applied to the data. Structures were solved by direct methods and refined by full-matrix least-squares refinement using the *SHELXL*-97 [42] and *SHELXL* program packages [43].

Results and discussion

Synthesis and physical properties

The synthesis of compounds **1** and **2** was carried out as reported previously [32, 33, 44]. Compound **2** was obtained



Scheme 1 Synthetic route of C_2-symmetric diamine with diastereomeric configurations (*SRRS*) and its dichloro Zn(II) complex

as a mixture of two diastereomers in the ratio of 1:0.7, as indicated by the ^{1}H NMR integration of two quartets for the Ph–C*H*-Me groups (Fig. 1). Purification using column chromatography was unsuccessful. The mixture of diastereomers (**2a** and **2b**) was ligated with $ZnCl_2$ in a ratio of 1:1, controlling the amount of EtOH, affording two diastereomeric Zn(II) complexes (**3a** and **3b**) in a ratio of 1:0.7 (Scheme 1). Opposite stereochemical outcomes have been achieved by incorporating methyl substituents onto the ethylene backbone; however, no diastereoselectivity for the (*SSSS*) configuration was observed [1]. These interesting stereochemical properties could be due to better accommodation of any steric clashes between methyl substituents on the ethylene backbone and the pendent moieties of the amine groups. Compounds **3a** and **3b** were separated using fractional crystallization in EtOH. Compounds **3a** and **3b**, in the *SSSS* and *SRRS* configurations, respectively, have different physical properties. Compound **3b** is sparingly soluble in EtOH and was easily crystallized from the more soluble diastereomer **3a**. Unfortunately, extensive crystallization trials using a variety of solvents did not afford compound **3a**.

The ^{1}H NMR spectrum of the isolated single diastereomeric Zn(II) complex **3b** showed a diagnostic sextet for the methine protons of the Ph–C*H*-Me group (Fig. 1). Complex **3b** was subjected to demetalation yielding compound **2b** as a final ligand. The isolated ligand **2b** and the Zn(II) complex **3b** were characterized by various spectroscopic techniques, including elemental analysis. The IR spectra of complex showed that the peak corresponding to aromatic C=C stretch and aromatic C–H bands shifts from the lower wavenumber to the higher wavenumber in comparison with its corresponding ligand. Elemental analysis of the synthesized ligand and its corresponding Zn(II) complex was consistent with the proposed structures in Scheme 1 and confirmed the purity of the isolated compounds. These compounds were stable in the air with long shelf life.

X-ray diffraction studies

The absolute stereochemistry and configuration of compound **2b** were confirmed by X-ray crystallographic studies of complex **3b**. The complex crystallized in an orthorhombic system with the $P2_12_12$ space group (Table 1). As expected, a distorted tetrahedral geometry was observed around the Zn(II) centre. Both the bond lengths and the angles agree well with those of complexes bearing an identical ligand (Table 2) [45–47]. The plane angle between Cl–Zn–Cl and N–Zn–N was found to be 82.38(7)°. Complexation of Zn with ligand **2b** resulted in a five-membered heterocyclic ring, restricting the freedom of the ligand's N atoms (increasing the N-inversion barrier) and inducing chirality, provided the nitrogen substituents were inequivalent [48, 49]. The resulting configurations of the N atoms were found to be (*S*,*S)* in complex **3b**. These results were contradictory to those of our previous studies, in which the N atoms were found to be in the (*R*,*R*) configuration [44]. The hydrogen atoms on the chiral carbons and nitrogens were in a head-to-tail conformation (Fig. 2). Furthermore, the resultant five-membered chelated ring (Zn–N–C–C–N) was solely in a δ conformation.

Table 1 Crystal data and structure refinement for **3b·H_2O**

Empirical formula	$C_{20}H_{28}Cl_2N_2Zn{\cdot}H_2O$
Formula weight	225.36
Wavelength (Å)	0.71073
Temperature (K)	293 (2)
Crystal system	Orthorhombic
Space group	$P2_12_12$
Unit cell dimensions	
a (Å)	7.4872 (7)
b (Å)	19.8981 (15)
c (Å)	7.4690 (6)
Volume (Å^3), *Z*	1112.74 (16), 2
Density (calcd.) (Mg/m^3)	1.345
Absorption coefficient (mm^{-1})	1.355
F (000)	472
Crystal size (mm)	0.45 × 0.25 × 0.25
θ range for data collection	2.05–25.47
Index ranges	$-9 \le h \le 9$; $-24 \le k \le 24$; $-9 \le l \le 9$
Reflections collected	2504
Independent reflections	2061 [*R*(int) = 0.0178]
Reflections observed ($> 2\sigma$)	1679
Data completeness	0.998
Max. and min. transmission	0.7282 and 0.5808
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2061/1/124
Goodness-of-fit (GOF) on F^2	1.044
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0265$ $wR_2 = 0.0655$
R indices (all data)	$R_1 = 0.043$ $wR_2 = 0.0691$
Absolute structure parameter	−0.005 (18)
Largest diff. peak and hole (e/Å^3)	0.203 and −0.240

Table 2 Selected bond lengths and angles for **3b·H_2O**

Bond lengths		Bond angles	
Zn1–N1$^{\#1}$	2.081 (2)	N1–Zn1–N1$^{\#1}$	86.57 (11)
Zn1–Cl1$^{\#1}$	2.2150	N1–Zn1–Cl1$^{\#1}$	112.14 (6)
N1–C2	1.484 (3)	N1$^{\#1}$–Zn1–Cl1$^{\#1}$	111.84 (6)
N1–C10	1.502 (3)	N1$^{\#1}$–Zn1–Cl1	112.14 (6)
C2–C3	1.515 (3)	N1–Zn1–Cl1	111.84 (6)
C10–C10$^{\#1}$	1.532 (5)	Cl1$^{\#1}$–Zn1–Cl1	118.09 (5)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, z$

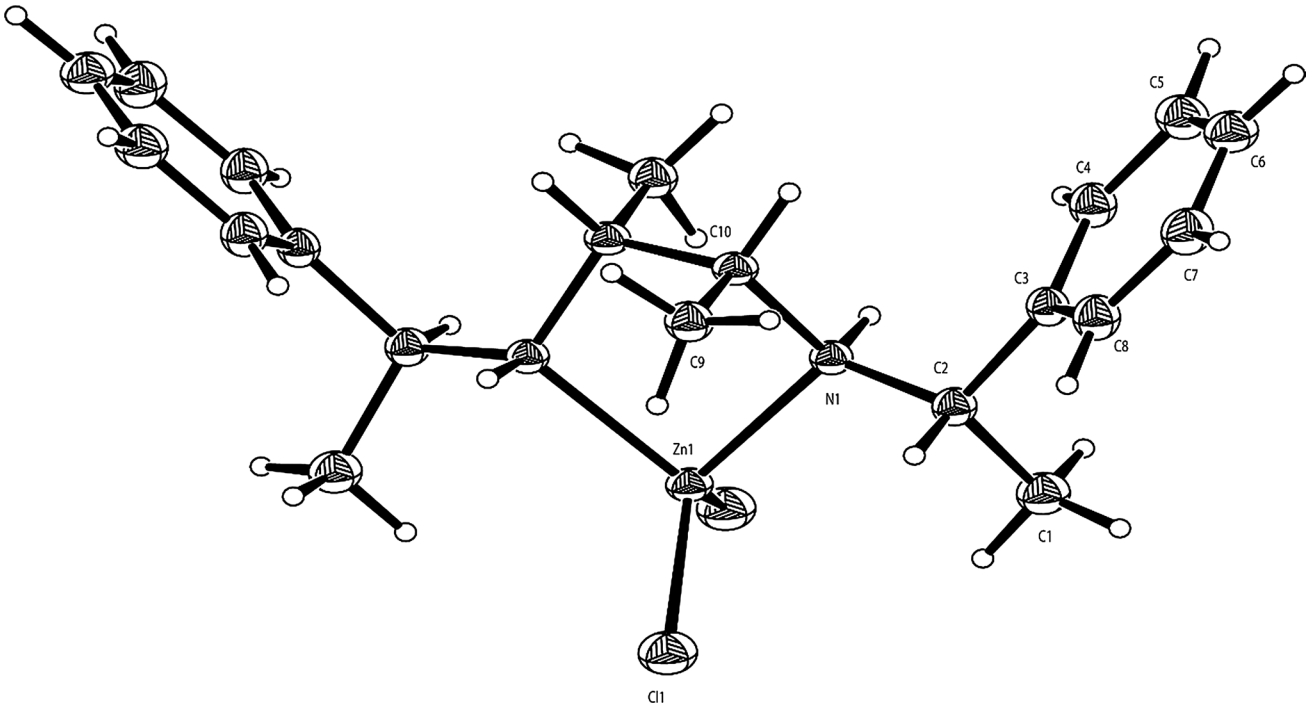


Fig. 2 ORTEP diagram of the molecular structure of complex **3b**. Thermal ellipsoids are drawn at the 30% probability level

Table 3 Four-coordinate geometry indices (τ_4) for **3b** and representative examples from the literature

Complexes	Geometry	τ_4	References
Square planar (D_{4h})[a]	Square planar	0.00	[50]
[(L-a)ZnCl$_2$][b]	Tetrahedral	0.866	[51, 52]
[(L-c)ZnCl$_2$][c]	Tetrahedral	0.885	[52]
3b	Tetrahedral	0.920	This work
Tetrahedral (T_d)[a]	Tetrahedral	1.00	[50]

[a]See Ref. [50]

[b]See Refs. [51, 52]

[c]See Ref. [52]

The geometric parameters for the 4-coordinated complexes, τ_4, as improved simple metrics for quantitatively evaluating the geometry are presented in Table 3 [50]. τ_4 values for perfect tetrahedron are 1.00 and zero for perfect square planar geometry. The degree of distortion based on bond angles around Zn(II) centre using these structural indexes has been observed. τ_4 value of **3b** was observed to be 0.920, which is closer to 1 rather than zero. Thus, the geometry of **3b** can be best described as distorted tetrahedron geometry.

Asymmetric Henry reaction

One of the challenging tasks in the advancement of catalytic asymmetric Henry reaction is the development of new chiral ligands with improved catalyst efficiency and enantioselectivity. Copper with a variety of C_2-symmetric diamines displayed promising results in an asymmetric Henry reaction yielding enantio-enriched β-nitroalcohols with excellent yields and moderate to high enantioselectivities [44, 49, 53, 54]. The catalytic efficacy of in situ-generated copper acetate complex in asymmetric Henry reaction between

Scheme 2 Schematic representation of asymmetric Henry reaction catalysed by in situ-generated [**2b-Cu(OAc)$_2$**]

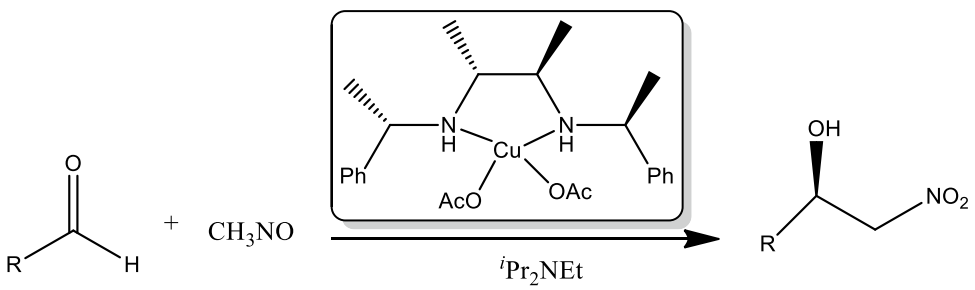


Table 4 Asymmetry Henry reaction catalysed by **2b** and $Cu(OAc)_2$

Run[a]	Substrate	Time (h)	Yield (%)[b]	ee(%)[c]	Config.[d]
1	Benzaldehyde	24	99	44	(*S*)
2	3-Phenylpropanal	24	99	97	(*S*)

[a]Reactions were carried out 5.0 mmol scale aldehyde, 10 mol% of $Cu(OAc)_2$, 10 mol% of chiral ligand **2b**, 10 mol% of $^{i}Pr_2NEt$, 2 equiv. of CH_3NO_2 in IPA (10 mL) at 25 °C

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

[c]ee was determined by Chiralcel HPLC analysis using chiral OD-H and chiral AD-H columns

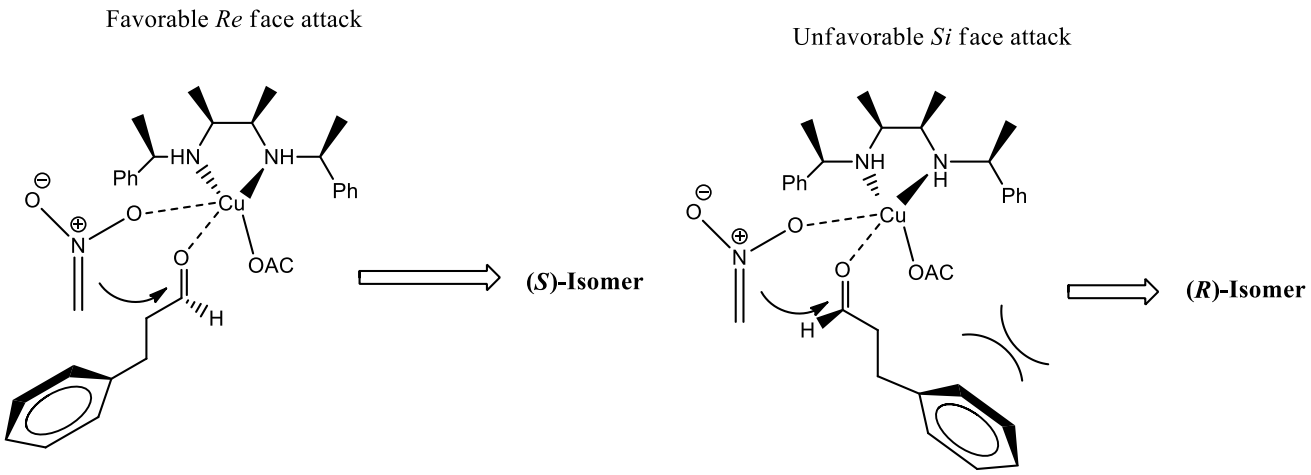
[d]The absolute configuration of the major product was assigned by comparison with the literature values [39]

benzaldehyde or 3-phenylpropanal and nitromethane with 10 mol % $^{i}Pr_2NEt$ as co-initiator in IPA at ambient temperature was examined (Scheme 2). The preliminary results for asymmetric Henry reaction are summarized in Table 4. The $Cu(OAc)_2$–**2b** complex exhibited excellent activity (99% in 24 h) and enantioselectivity (up to 97%) for the reaction between nitromethane and 3-phenylpropanal, yielding (*S*)-1-nitro-4-phenylbutan-2-ol. The reaction catalysed by in situ-generated Cu(II) species resulted in the corresponding *β*-nitroalcohols with an (*S*)-conformation, at the stereogenic centre, that might be due to the favourable orientation of the phenyl group of aldehydes and pendant moieties of the ligand architecture [54–56]. Moreover, the possible transition states of the reaction and their resultant stereochemical outcomes in asymmetric Henry reaction with **2b** as a ligand with $Cu(OAc)_2$ are proposed [55, 57] (Scheme 3).

Our current catalytic system showed superior activity (up to 99%) as well enantioselectivity (up to 97%) compared to well-known Cu(II) complexes for 3-phenylpropanal and nitromethane. For instance, the activity and selectivity of our current system are superior to recently reported in situ-generated chiral Cu(II) complexes bearing L-proline as the ligand [58]. Moreover, compared to well-known core-chiral bispidine-based copper complexes (with 88% yield; ee 97% in 48 h) [59], our system has shown improved activity and selectivity. However, although the Henry reaction between benzaldehyde and nitromethane showed activities of up to 99%, the enantiomeric excess was found to be only 44%. It was revealed that the diastereomeric conformation of the chiral centres (*SRRS*) in the ligand framework influences the stereochemical outcome of the asymmetric Henry reaction between 3-phenylpropanal and nitromethane. Detailed study towards asymmetric Henry reaction using a variety of aldehydes and nitromethanes to yield a library of *β*-nitroalcohols is underway in our laboratory. Further, the adopted strategy towards the synthesis of C_2-symmetric chiral diamine that possesses diastereomeric configurations (*SRRS*) is facile and paves the way towards the synthesis of variety of analogous.

Conclusions

In summary, an efficient approach has been adopted towards the synthesis of C_2-symmetric chiral diamine using demetalation of its dichloro Zn(II) complex, which itself was separated by fractional crystallization from a mixture of diastereomeric Zn(II) complexes. A Cu(II) acetate complex of the synthesized chiral diamine, generated in situ, was explored for its catalytic efficiency in an asymmetric Henry reaction. Excellent catalytic activity (up to 99% in 24 h) and enantioselectivity (up to 97%) for the reaction between nitromethane and 3-phenylpropanal, yielding (*S*)-1-nitro-4-phenylbutan-2-ol, were observed. The chiral diamine obtained in this study has considerable potential to be exploited in various



Scheme 3 Proposed model representing the transition states for the catalytic asymmetric Henry reaction with **$Cu(OAC)_2$-2b** system

metal-catalysed transformations. Further work is ongoing to modify the ligand architecture and to identify the scope of the synthesized ligand with a variety of substrates/aldehydes in asymmetric Henry reaction.

Supplementary Data

CCDC 1910912 contains the supplementary crystallographic data for **3b**. 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. Additionally, ^{1}H NMR, ^{13}C NMR and FT-IR spectra of ligand (**2b**), dichloro Zn(II) complex (**3b**), and resultant β-nitroalcohols are also presented in supplementary material.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict to interest.

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Affiliations

Juhyun Cho[1] · Saira Nayab[2] · Jong Hwa Jeong[1]

✉ Saira Nayab
drnayab@sbbu.edu.pk; sairanayab07@yahoo.com

✉ Jong Hwa Jeong
jeongjh@knu.ac.kr

[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, Pakistan