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Cu-catalyzed Asymmetric Henry Reaction Promoted by Chiral Camphor Schiff Bases

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Highlights

- Cu-camphor Schiff base complexes were firstly investigated as catalysts in asymmetric Henry reaction
- The diastereoisomeric Schiff bases **5a** and **5a'** were successfully isolated and gave completely converse absolute configuration of catalyzed products when it used in the Henry reaction as ligand, respectively.
- The chiral camphor Schiff base **5a**, together with CuCl, showed high efficiency in catalyzed asymmetric Henry reactions between various aldehydes and nitromethane.

Abstract

Five novel chiral camphor Schiff bases have been synthesized and utilized as ligands in asymmetric Henry reaction between nitromethane and aldehydes. The diastereoisomeric Schiff bases 5a and 5a' were separated successfully and gave completely different absolute configurations in the reaction. The reactions were carried out with CuCl-Schiff base 5a complex under mild condition with good yields and enantioselectivities. This is the first time that camphor-derivated Schiff bases were used as ligands in asymmetric Henry reaction.

Keywords: Camphor；Schiff base; Henry reaction; Copper complex; enantioselectivity.

1. Introduction

The Henry (nitroaldol) reaction is an attractive C-C bond-forming reaction in which

a nitroalkane compound is added to an aldehyde or ketone to obtain primarily a *β*-nitroalcohol, which may be subsequently converted into synthetically useful derivatives such as carboxylic acids, aldehydes, *α*-hydroxy ketones, amino alcohols, azides, sulphides and other useful compounds by FGT (Functional Group Transformation)[1]. Significantly, chiral amino alcohols obtained by reduction of chiral *β*-nitroalcohols have been found widespread utility as chiral ligands in asymmetric catalysis, and as an important building block of natural products as well as pharmaceuticals[2]. Due to the importance of chiral *β*-nitroalcohols in organic synthesis, considerable efforts have been focused on the development of catalytic enantioselective version of the Henry reaction on the basis of the use of coordinating complexes of transition metals or lanthanides with chiral ligands[3]. In particular, chiral copper complexes have received particular attention in terms of wide structural variability of the chiral ligands (bisoxazolines[4], amino alcohols[5], diamines[6], sulfonamides[7], aminopyridines[8], Schiff bases[9] etc.), low toxicity, low cost, excellent chelating ability, ease of handling and ready availability. Chiral Schiff bases and their complexes with transition metals are one of the most studied chiral catalysts and have been extensively applied in asymmetric synthesis[10]. *D*-(+)-camphor plays an important role in the asymmetric synthesis in terms of its low cost, rigid structure and convenience to transform into synthetically useful derivatives. Chiral camphor derived Schiff base has already been reported in enantioselective trimethylsilylcyanation of aldehydes[11]. But the report of chiral camphor derived Schiff bases used in enantioselective Henry reaction is still rare. We have paid much attention to modifying the novel chiral frame of camphor and studying their applications in asymmetric reaction[12]. Therefore, the development of new chiral camphor Schiff bases and investigation on its activities in Cu-catalyzed enantioselective Henry reaction are proceeding in our laboratory. The results are recorded here.

2. Experimental section

2.1 General

All the starting materials and reagents were obtained from commercial sources and

used directly without further purification. The solvents were purified by standard techniques. The reactions were monitored by thin layer chromatography (TLC). Flash column chromatography was carried out on silica gel (200-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE-300 and Bruker AVANCE-400 spectrometers (with TMS as an internal standard). Melting points were recorded on a melting point apparatus and uncorrected. Optical rotations were measured on a Rudolph Autopol IV-T polarimeter in the indicated solvent. Enantiomeric excesses were determined using Shimadzu LC-20AT high performance liquid chromatography with a chiralcel OD-H column.

*2.2 General procedure for the preparation of diastereoisomers **5a** and **5a'***

Camphor amino ketone **1** (1.53g, 10 mmol) was added to a 50 mL round-bottomed flask containing 10 mL methanol, then cooled to -15ºC. Sodium borohydride (0.95g, 25 mmol) was slowly added portionwise to the flask over 20 minutes. The mixture was stirred overnight at -15ºC, then warmed to room temperature naturally and stirred for additional 3h, subsequently, removed the methanol under reduced pressure, added the H_2O (10 mL), and extracted with dichloromethane (3 x 10 mL). The combined organic solution was dried over Na_2SO_4, filtered and concentrated under vacuum. The mixed diastereoisomer of amino alcohol **2** was obtained (1.29g, 83%).

The produced diastereoisomeric amino alcohol **2** (0.78g, 5 mmol), the 4-hydroxy-salicylaldehyde **4a** (0.69g, 5 mmol) and anhydrous sodium sulfate (1.42g, 10 mmol) were suspended in dry ethanol (35 mL). The mixture was stirred at reflux for 12h, and then the solvent was evaporated under reduced pressure to obtain crude product. Diastereoisomer **5a** and **5a'** were obtained in 74% (1.02g) and 20% (0.28g) yield by purification the crude product through flash column chromatography on a silica gel using petroleum ether and ethyl acetate as eluent.

2.2.1 4-(((1S,2R,4R)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-ylimino)methyl) benzene-1,3-diol **5a**

Pale yellow solid, 1.02g, yield: 74%, mp: 220 – 221.8℃, $[\alpha]_D^{20}$ =-174.59°(c 0.95,

CH_2Cl_2); ^{1}H NMR (400 MHz, DMSO) δ 14.63 (s, 1H), 9.90 (d, J = 22.4 Hz, 1H), 8.26 (d, J = 6.0 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 6.09 (dd, J = 8.8, 2.0 Hz, 1H), 5.98 (d, J = 2 Hz, 1H), 5.24 – 5.25 (m, 1H), 3.75 – 3.78 (m, 1H), 1.91 – 1.94 (m, 1H), 1.76 – 1.83 (m, 4H), 1.19 – 1.31 (m, 2H), 1.12 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 171.6, 163.0, 162.2, 134.2, 111.2, 105.9, 103.6, 75.6, 71.4, 47.3, 42.4, 40.4, 28.44, 26.6, 19.7, 19.7. HRMS (ESI, M+H$^+$) calcd. for $C_{16}H_{22}NO_3$ 276.1594, found 276.1599.

2.2.2 4-(((1S,2S,4R)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-ylimino)methyl) benzene-1,3-diol **5a'**

Pale yellow solid, 0.28 g, yield: 20%, mp: 226.4 – 227.8℃, $[\alpha]_D^{20}$ =-216^o (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO) δ 14.65 (s, 1H), 9.92 (s, 1H), 8.24 (s, 1H), 7.21 (d, J = 8.4 Hz, 1H), 6.24 (dd, J = 8.4, 2.3 Hz, 1H), 6.14 (d, J = 2.2 Hz, 1H), 4.97(d, J = 5.3Hz, 1H), 4.15 (t, J = 4.9Hz, 1H), 2.25 – 2.31 (m, 2H), 1.75 – 1.90 (m, 1H), 1.69 – 1.71 (m, 1H), 1.42 – 1.49 (m, 2H), 1.08 (d, J = 3.4 Hz, 1H), 1.05 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 166.1, 163.9, 162.1, 133.8, 112.1, 106.9, 103.1, 74.8, 73.3, 49.1, 42.9, 40.6, 28.1, 21.9, 20.2, 18.9. HRMS (ESI, M+H$^+$) calcd. for $C_{16}H_{22}NO_3$ 276.1600, found 276.1599.

2.3 General procedure for the preparation of the chiral camphor amino alcohol ***2a***[12]

Solid $CeCl_3$•$7H_2O$ (2.60g, 7 mmol) was added to a solution of the chiral camphor isocyanate **3** (5.01g, 28 mmol) in 100 mL of dry methanol in 250 mL single-necked flask at 0℃. The mixture was cooled to -78℃, slowly added solid sodium borohydride (5.30g, 140 mmol) portionwise over 1h, then continuously stirred at -78℃ for one more hour. After that, the reaction mixture was warmed to -40℃ and continuously stirred for 2h, then naturally warmed to 25℃. 6N KOH (50 mL) was added to the remaining slurry which was obtained by removing the methanol from the reaction mixture under reduced rotation. The resulting mixture was heated to reflux for 3h, cooled to room temperature, and extracted with dichloromethane (100mL) for three times. The combined organic phases were dried over anhydrous sodium sulfate,

filtered, concentrated to obtain a white crude camphor amino alcohol. The optically pure camphor amino alcohol **2a** (2.83g, 65%) was obtained after separating the crude camphor amino alcohol by column chromatography.

2.4 General procedure for the preparation of the chiral camphor Schiff base ligands

Chiral camphor amino alcohol **2a** (0.62g, 4 mmol), the corresponding salicylaldehyde derivatives **4a**-**4f** (4 mmol) and anhydrous sodium sulfate (1.14g, 8 mmol) were dissolved in dry ethanol (30 mL). The mixture was stirred at reflux for 12h, and then the solvent was evaporated under reduced pressure. The crude product was purified to obtain the final product by flash column chromatography on a silica gel using petroleum ether and ethyl acetate as eluent.

2.4.1 4-(((1S,2R,4R)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-ylimino)methyl) benzene-1,3-diol ***5a***

Pale yellow solid, 0.83g, yield: 75%.

2.4.2 (1S,2R,4R)-1-(4-butoxy-2-hydroxybenzylideneamino)-7,7-dimethylbicyclo-[2.2.1]heptan-2-ol ***5b***

Yellow solid, 1.03 g, yield: 78%, mp: 78 – 79.2℃, $[\alpha]_D^{20}$ =-197.67° (c 1.0, CH_2Cl_2), ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.21 (s, 1H), 7.54 (s, 1H), 6.61 – 6.64 (m, 1H), 5.98 – 6.01 (m, 2H), 5.12 (s, 1H), 3.83 – 3.89 (m, 3H), 1.94 – 1.96 (m, 1H), 1.66 – 1.85 (m, 6H), 1.39 – 1.44 (m, 2H), 1.15 – 1.20 (m, 5H), 0.86 – 0.90 (m, 3H), 0.70 – 0.73 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 164.5, 159.8, 133.3, 110.1, 105.1, 102.0, 75.9, 70.4, 66.5, 47.0, 41.9, 38.9, 30.1, 26.5, 25.8, 18.7, 18.5, 18.2, 12.8. HRMS (ESI, $M+H^+$) calcd. for $C_{20}H_{30}NO_3$ 332.2220, found 332.2225.

2.4.3 (1S,2R,4R)-1-(3,5-di-tert-butyl-2-hydroxybenzylideneamino)-7,7-dimethylbicyclo[2.2.1]heptan-2-ol ***5c***

Yellow solid, 1.28 g, yield: 86%, mp: 149 – 150℃, $[\alpha]_D^{20}$ =-51.34° (c 0.4, CH_2Cl_2), ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.97 (s, 1H), 8.46 (s, 1H), 7.40 (s, 1H), 7.14 (s, 1H),

3.85 (d, *J* = 6.0 Hz, 1H), 2.15 (s, 1H), 1.88 – 2.10 (m, 5H), 1.45 (s, 9H), 1.32 (s, 9H), 1.25 – 1.30 (m, 5H), 0.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 158.6, 140.0, 137.1, 127.1, 126.2, 118.1, 78.8, 74.8, 48.1, 43.7, 39.8, 35.1, 34.2, 31.5, 29.5, 28.0, 27.1, 20.2, 20.0. HRMS (ESI, M+H$^+$) calcd. for $C_{24}H_{38}NO_2$ 372.2897, found 372.2906.

2.4.4 (1S,2R,4R)-1-(5-bromo-2-hydroxybenzylideneamino)-7,7-dimethylbicyclo [2.2.1]heptan-2-ol ***5d***

Yellow solid, 1.12 g, yield: 83%, mp: 101.4 – 105℃, $[\alpha]_D^{20} = -74.56°$ (c 0.98, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.22 (s, 1H), 8.27 (s, 1H), 7.34 – 7.38 (m, 2H), 6.81 (d, *J* = 8.8 Hz, 1H), 3.90 (dd, *J* = 8.0, 3.6 Hz, 1H), 2.46 (s, 1H), 2.04 – 2.10 (m, 1H), 1.88 – 2.00 (m, 4H), 1.23 – 1.34 (s, 5H), 0.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4, 163.0, 139.7, 135.6, 133.8, 120.4, 119.8, 108.7, 78.3, 74.4, 48.4, 43.5, 40.1, 27.7, 27.0, 19.8. HRMS (ESI, M+H$^+$) calcd. for $C_{16}H_{21}BrNO_2$ 338.0750, found 338.0755.

2.4.5 (1S,2R,4R)-1-(2-hydroxy-3-methylbenzylideneamino)-7,7-dimethylbicyclo [2.2.1]heptan-2-ol ***5e***

Yellow solid, 0.87g, yield: 80%, mp: 148.8 – 149.6℃, $[\alpha]_D^{20} = -55.26°$ (c 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.20 (s, 1H), 8.39 (s, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.77 (t, *J* = 7.2 Hz, 1H), 3.86 (dd, *J* = 8.0, 3.6 Hz, 1H), 2.38 (s, 1H), 2.28 (s, 3H), 2.03 – 2.08 (m, 1H), 1.87 – 2.00 (m, 4H), 1.23 – 1.33 (s, 5H), 0.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 160.7, 133.5, 129.3, 126.5, 118.1, 117.8, 78.7, 74.6, 48.2, 43.6, 40.0, 28.0, 27.1, 20.1, 19.9, 15.6. HRMS (ESI, M+H$^+$) calcd. for $C_{17}H_{24}NO_2$ 274.1802, found 274.1807.

2.5 General procedure for the addition of nitromethane to aldehydes

Under a nitrogen atmosphere, the ligand **5a** (13.8 mg, 0.05mmol, 10 mol %) and CuCl (5.0 mg, 0.05 mmol, 10 mol %) were suspended in anhydrous *tert*-butanol (2.0 mL). The reaction mixture was stirred for 2h at room temperature, added

nitromethane (0.54 mL, 20 mmol) and continuously stirred for additional 0.5h, then added the aldehyde (0.5 mmol). The reaction mixture was stirred for a specified period at room temperature, and then the volatile components were removed under reduced pressure to obtain the crude product. It was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to obtain the pure product. The enantiomeric excess of the product was determined by HPLC analysis. The absolute configurations of the products were assigned by comparison to literature values.

2.5.1 (R)-1-(4-Nitropheny)-2-nitroethanol ***7a***[13]

Off-white solid, 95 mg, 90% yield, 84% e.e., HPLC (Chiralcel OD-H, *n*-hexane / *i*-PrOH 85:15, 1.0 mL/min, 254 nm): t_R (major) = 22.4 min, t_R (minor) = 27.3 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.24 (m, 2H), 7.62 – 7.64 (m, 2H), 5.60 – 5.62 (m, 1H), 4.60 –4.62 (m, 2H), 3.72 (s, 1H).

2.5.2 (R)-1-(3-Nitropheny)-2-nitroethanol ***7b***[14]

Brown solid, 87 mg, 82% yield, 80% e.e., HPLC (Chiralcel OD-H, *n*-hexane / *i*-PrOH 90:10, 1.0 mL/min, 254 nm): t_R (major) = 35.3 min, t_R (minor) = 39.7 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.13 – 8.16 (m, 1H), 7.70 – 7.72 (m, 1H), 7.52 –7.56 (m, 1H), 5.55 (t, J = 3.6 Hz, 1H), 4.54 – 4.56 (m, 2H), 3.23 (s, 1H).

2.5.3 (R)-1-(2-Nitropheny)-2-nitroethanol ***7c***[13]

Off-white solid, 85 mg, 80% yield, 68% e.e., HPLC (Chiralcel OD-H, *n*-hexane / *i*-PrOH 90:10, 1.0 mL/min, 254 nm): t_R (major) = 20.2 min, t_R (minor) = 22.4 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 8.02 (m, 1H), 7.87 – 7.89 (m, 1H), 7.66 – 7.70 (m, 1H), 7.49 – 7.51 (m, 1H), 5.97 – 5.99 (m, 1H), 4.78 – 4.82 (m, 1H), 4.46 – 4.52 (m, 1H), 3.18 (s, 1H).

2.5.4 (R)-1-(4-Fluorophenyl)-2-nitroethanol ***7d***[15]

Colorless oil, 67 mg, 72% yield, 73% e.e., HPLC (Chiralcel OD-H, *n*-hexane / *i*-PrOH 90:10, 1.0 mL/min, 254 nm): t_R (major) = 15.3 min, t_R(minor)= 17.9 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.34 (m, 2H), 7.00 – 7.04 (m, 2H), 5.37 – 5.40 (m, 1H), 4.40 – 4.52 (m, 2H), 2.85(s, 1H).

*2.5.5 (R)-1-(3-Fluorophenyl)-2-nitroethanol **7e***[13]

Colorless oil, 75 mg, 81% yield, 76% e.e., HPLC (Chiralcel OD-H, *n*-hexane / *i*-PrOH 90:10，1.0 mL/min, 254 nm): t_R (major) = 31.1 min, t_R (minor)=38.2 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.30 (m, 1H), 7.05 – 7.10 (m, 2H), 6.85 – 6.97 (m, 1H), 5.38 (t, *J* = 4.4 Hz, 1H), 4.45 – 4.50 (m, 2H), 3.0 (s, 1H).

*2.5.6 (R)-1-(4-Bromophenyl)-2-nitroethanol **7f***[13]

Colorless oil, 96 mg, 78% yield, 81% e.e., HPLC (Chiralcel OD-H, *n*-hexane / *i*-PrOH 90:10, 1.0 mL/min, 254 nm): t_R (major) =19.4 min, t_R (minor) = 24.9 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 2H), 5.36 (t, *J* = 4.4 Hz, 1H), 4.01 – 4.50 (m, 2H), 2.90 (s, 1H).

*2.5.7 (R)-1-(3-Bromophenyl)-2-nitroethanol **7g***[13]

Colorless oil, 92 mg, 75% yield, 83% e.e., HPLC(Chiralcel OD-H, *n*-hexane / *i*-PrOH 90:10，1.0 mL/min, 254 nm): t_R (major) = 19.8 min, t_R (minor) = 25.8 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.42 (s, 1H), 5.36 – 5.39 (m, 1H), 4.45 – 4.50 (m, 1H), 2.87 (s, 1H).

*2.5.8 (R)-1-(4-Chlorophenyl)-2-nitroethanol **7h***[13]

Colorless oil, 77 mg, 76% yield, 87% e.e., HPLC (Chiralcel OD-H, *n*-hexane / *i*-PrOH 90:10, 1.0 mL/min, 254 nm): t_R (major) =17.2 min, t_R (minor) = 21.1 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.39 (m, 4H), 5.44 – 5.46 (m, 1H), 4.48 – 4.60 (m, 2H), 2.68 (s, 1H).

*2.5.9 (R)-1-(3-Chlorophenyl)-2-nitroethanol **7i***[16]

Colorless oil, 69 mg, 68% yield, 74% e.e., HPLC (Chiralcel OD-H, *n*-hexane / *i*-PrOH 90:10，1.0 mL/min, 254nm): t_R (major) =18.4 min, t_R (minor)= 22.9 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.58 (m, 1H), 7.48 – 7.50 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.15 – 7.18 (m, 1H), 5.71 – 5.73 (m, 1H), 4.59 – 4.62 (m, 1H), 4.34 – 4.38 (m, 1H), 3.03 (s, 1H).

*2.5.10 (R)-1-(4-Trifluoromethylphenyl)-2-nitroethanol **7j***[17]

Colorless oil, 92 mg, 78% yield, 78% e.e., HPLC (Chiralcel OD-H, *n*-hexane / *i*-PrOH 90:10, 1.0 mL/min, 254 nm): t_R (major) =13.4 min, t_R (minor) =16.8 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.61 (m, 2H), 7.47 – 7.49 (m, 2H), 5.47 (t, *J* = 4.8

Hz, 1H), 4.48 – 4.52 (m, 2H), 3.00 (s, 1H).

2.5.11 (R)-1-(3-Trifluoromethylphenyl)-2-nitroethanol ***7k***[18]

Colorless oil, 80 mg, 68% yield, 86% e.e., HPLC (Chiralcel OD-H, *n*-hexane / *i*-PrOH 90:10, 1.0 mL/min, 254 nm): t_R (major) =12.7 min, t_R (minor)=14.4 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.71 (m, 4H), 5.53 – 5.56 (m, 1H), 4.53 – 4.64 (m, 2H), 2.99 (s, 1H).

2.5.12 (R)-4-(1-hydroxy-2-nitroethyl)benzonitrile ***7l***[19]

White solid, 79 mg, 82% yield, 81% e.e., HPLC (Chiralcel OD-H, *n*-hexane / *i*-PrOH 90:10, 1.0 mL/min, 254 nm): t_R (major) = 42.7 min, t_R (minor)= 49.5 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 10.8 Hz, 2H), 7.56 (d, J = 10.8 Hz, 2H), 5.55 (t, J = 5.6 Hz, 1H), 4.55 – 4.59 (m, 2H), 3.18 (s, 1H).

2.5.13 (R)-1-Phenyl-2-nitroethanol ***7m***[13]

Colorless oil, 63 mg, 75% yield, 66% e.e., HPLC (Chiralcel OD-H, *n*-hexane / *i*-PrOH 92:8, 0.8 mL/min, 254 nm): t_R (major) = 26.5 min, t_R (minor) = 32.7 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.59 (m, 1H), 7.23 – 7.32 (m, 3H), 5.76 (m, 1H), 4.58 – 4.62 (m, 1H), 4.35 – 4.41 (m, 1H), 2.98 (s, 1H).

2.5.14 (R)-1-(4-Methoxyphenyl)-2-nitroethanol ***7n***[13]

Colorless oil, 44 mg, 45% yield, 69% e.e., HPLC (Chiralcel OD-H, *n*-hexane / *i*-PrOH 90:10, 0.8 mL/min, 254 nm): t_R (major)= 30.2 min, t_R (minor) = 38.1 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.25 (m, 2H), 6.80 – 6.86 (m, 2H), 5.30 – 5.34 (m, 1H), 4.49 – 4.55 (m, 1H), 4.37 – 4.42 (m, 1H), 3.73 (s, 3H), 2.78 (s, 1H).

2.5.15 (R)-1-Nitro-4-phenylbutan-2-ol ***7o*** [15]

Yellow oil, 64 mg, 66% yield, 48% e.e., HPLC (Chiralcel AD-H, *n*-hexane / *i*-PrOH 95:5, 1.0 mL/min, 254nm): t_r (major) = 33.5 min, t_r (minor) = 40.4 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.15 (m, 5H), 4.44 – 4.32 (m, 2H), 4.31 (s, 1H), 2.90 – 2.71 (m, 2H), 2.68 (s, 1H), 1.95 – 1.71 (m, 2H).

2.5.16 (R)-1-(4-Nitropheny)-2-nitroethanol (R)-1-Nitrooctan-2-ol ***7p***[20]

Colorless oil, 19 mg, 22% yield, 43% e.e., HPLC (Chiralcel AD-H, *n*-hexane / *i*-PrOH 95:5, 0.5 mL/min, 254nm): t_r (major) = 26.3 min, t_r (minor) = 37.7 min. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 4.50 – 4.38 (m,2H), 4.35 (m,1H), 2.42 (br,1H), 1.63 – 1.44 (m,3H), 1.36 (m,7H), 0.91 (t, J = 6.4 Hz,3H).

2.5.17 (R)-4-Methyl-1-nitropentan-2-ol: ***7q***[20]

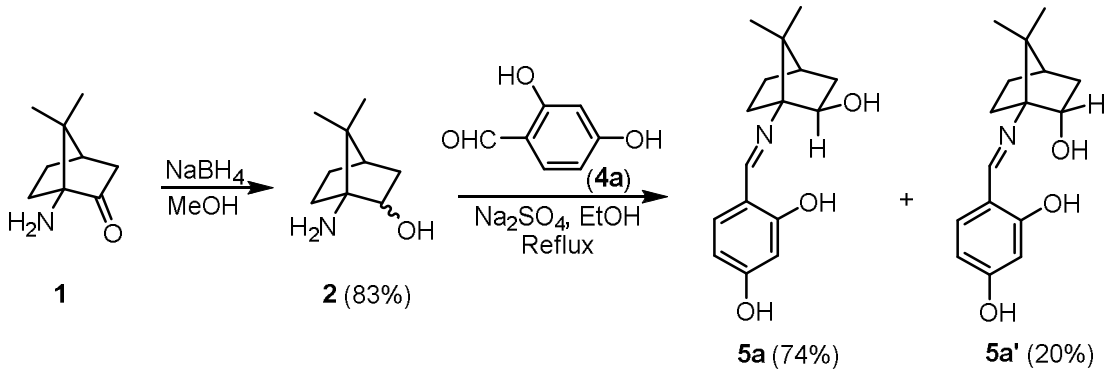
Colorless oil, 20 mg, 27% yield, 82% e.e., HPLC (Chiralcel AD-H, *n*-hexane / *i*-PrOH 95:5, 0.5 mL/min, 254nm): t_r (major) = 21.7 min, t_r (minor) = 31.1 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.47 – 4.31 (m, 3H), 2.57 (s, 1H), 1.91 – 1.78 (m, 1H), 1.52 (dd, J = 10.0, 4.9 Hz, 1H), 1.26 – 1.20 (m, 1H), 0.97 (t, J = 6.2 Hz, 6H).

2.5.18 (S)-1-(4-Nitropheny)-2-nitroethanol ***7a'***[13]

Yellow oil, 87 mg, 82% yield, 62% e.e., HPLC (Chiralcel OD-H, *n*-hexane / *i*-PrOH 85:15, 1.0 mL/min, 254nm): t_r (minor) = 22.2 min, t_r (major) = 26.3 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.24 (m, 2H), 7.62 – 7.64 (m, 2H), 5.60 – 5.62 (m, 1H), 4.60 –4.62 (m, 2H), 3.72 (s, 1H).

3. Results and discussion

The diastereoisomeric Schiff bases **5a** and **5a'** were prepared from 4-hydroxy-salicylaldehyde **4a** and diastereoisomers of amino alcohol (1*S*,4*R*)-1-amino-7,7-dimethylbicyclo[2.2.1]heptan-2-ol **2**, which were obtained by reduction of (1*S*,4*R*)-1-amino-7,7-dimethylbicyclo[2.2.1]heptan-2-one **1** in 83% yield (Scheme 1).

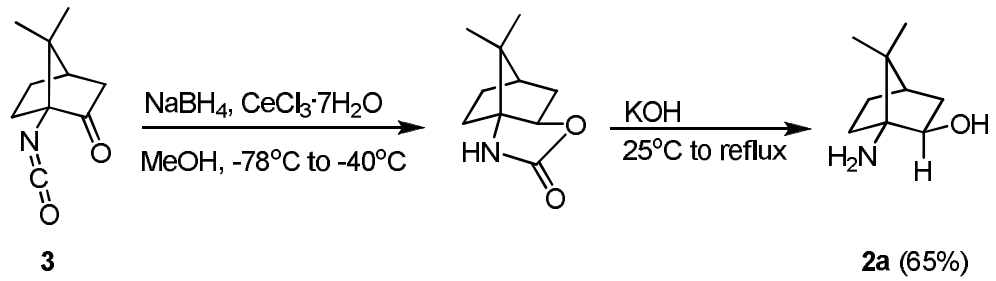


1 **2** (83%) **5a** (74%) **5a'** (20%)

Scheme 1. Preparation of diastereoisomer 5a and 5a'

At the beginning, we have not realized the strong effect of the configuration of 2-hydroxyl group in camphor frame on the enantioselective Henry reaction. The mixture diastereoisomer of amino alcohol was used directly to react with general aromatic aldehydes to obtain the diastereoisomer Schiff bases, both of the

diastereoisomer of amino alcohol **2** and diastereoisomer Schiff bases cannot be separated by simple methods. When the mixture of diastereoisomer Schiff bases was used as ligand to promote the enantioselectivity, no enantioselective results were observed in catalytic Henry reaction. When the aromatic aldehydes was changed to 4-hydroxy-salicylaldehyde **4a,** fortunately, the mixture of diastereoisomer Schiff bases **5a** and **5a'** can be separated by chromatography on silica gel for its different retention factors. The enantioselective results were produced using either a pair of diastereoisomer Schiff bases **5a** or **5a'** as a ligand in Henry reaction. With this result, enantiomerically pure amino alcohol (1*S*,2*R*,4*R*)-1-amino-7,7–dimethyl-bicylco[2.2.1] heptan-2-ol **2a** was synthesized by one-pot reaction starting from the chiral camphor isocyanate **3** (Scheme 2)[21] and converted to diastereoisomerically pure Schiff bases **5a**.

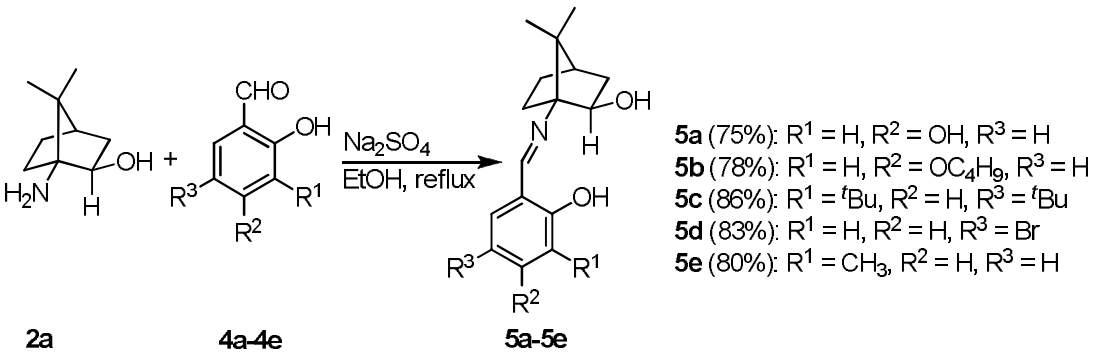


3 **2a** (65%)

Scheme 2. Prepration of enantiomerically pure aminol alcohol 2a

The structures of **5a** and **5a'** were confirmed by NMR and HRMS (see supporting information) as well as the comparison of rotation values with **5a** of a determined configuration synthesized by enantiomerically pure amino alcohol **2a**.

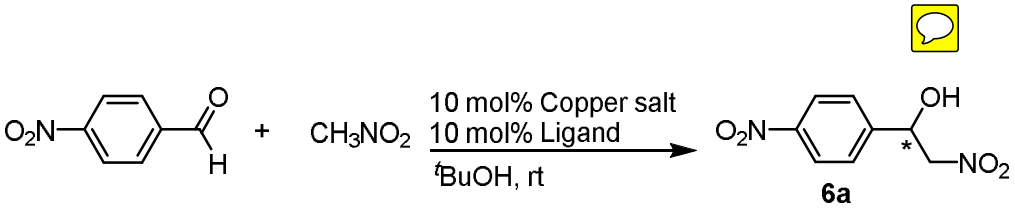
After learning the key factor to the enantioselective Henry reaction of chiral camphor amino alcohol, we established the preparation process of enantiomerically pure amino alcohol (1*S*,2*R*,4*R*)-1-amino-7,7-dimethylbicylco[2.2.1]heptan-2-ol **2a**. For investigation on the structure effect of chiral camphor Schiff bases, a serial of key enantiomerically pure amino alcohol Schiff bases **5a-5e** were prepared in high yields from amino alcohol **2a** and salicylaldehyde derivatives **4a-4e** (Scheme 3).



Scheme 3. Synthesis of chiral camphor Schiff bases 5a-5e

Reaction between 4-nitrobenaldehyde and nitromethane was selected as the model reaction to evaluate the performance of chiral camphor Schiff bases in the presence of CuCl in *tert*-butanol solvent (Table 1). The sequential investigations on the steric and electronic effects of the chiral camphor Schiff base showed that the chemical reactivity and enantioselectivity were closely related to the chiral backbone and the substituents of the Schiff base ligands. The performance of the ligand **5a,** with a hydroxyl group at the 4-position of salicylaldehyde moiety was the best, giving 90% yield and 84% e.e. value (Table 1, entry 1). While the enantioselectivity was decreased sharply to 46% e.e. when the hydroxyl group was changed to a more electron-donating butoxyl group (Table 1, entry 3). The Schiff base **5c** with two hindered *tert*-butyl substituents only generated 21% e.e. and 75% yield (Table 1, entry 4). Schiff base **5d** with a bromo substituent on *para* position to the hydroxyl of salicylaldehyde moiety afforded moderate enantioselectivity (Table 1, entry 5). Schiff base **5e** with a methyl group on *ortho* position to the hydroxyl of salicylaldehyde moiety generated 66% e.e. value due to the attribution of the steric effect (Table 1, entry 6). It is notable that Schiff base **5a'** affords the product with a completely different steric configuration compared to Schiff base **5a** (Table 1, entry 2).

Table 1.Screening of the Schiff base ligands and copper salts in the asymmetric Henry reaction[a]



6a

Entry	Copper salt	Ligand	Yield[b] (%)	ee[c] (%)	Config[d]
1	CuCl	**5a**	90	84	*R*
2	CuCl	**5a'**	82	62	*S*
3	CuCl	**5b**	89	46	*R*
4	CuCl	**5c**	75	21	*R*
5	CuCl	**5d**	88	59	*R*
6	CuCl	**5e**	85	66	*R*
7	$Cu(OAc)_2{\cdot}H_2O$	**5a**	92	66	*R*
8	$CuCl_2{\cdot}6H_2O$	**5a**	NR	-	-
9	$Cu(OTf)_2$	**5a**	52	53	*R*
10	CuBr	**5a**	75	65	*R*
11[e]	CuCl	**5a**	92	83	*R*
12[f]	CuCl	**5a**	79	80	*R*
13[g]	CuCl	**5a**	90	83	*R*

[a] All the reaction were carried out with 0.5 mmol *p*-nitrobenzaldehyde and 10 mmol nitromethane in 2 mL ^{t}BuOH in the presence of 10 mol% copper salt and 10 mol% ligand at room temperature for 24 h.

[b] Isolated yield.

[c] Determined by HPLC analysis on a chiralcel OD-H column.

[d] By comparison with the literature data.

[e] 10 mol% CuCl and 20 mol% **5a** were used.

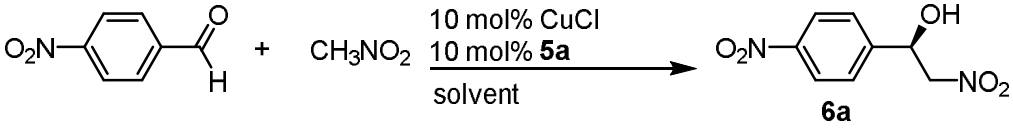
[f] 5 mol% CuCl and 5 mol% **5a** were used.

[g] 15 mol% CuCl and 15 mol% **5a** were used.

Then, the effects of different copper salts were evaluated using Schiff base **5a** as a ligand in 10 mol% catalyst loading with 1:1 ratio of copper salt and ligand. Amongst them, $Cu(OAc)_2{\cdot}H_2O$ generated a high chemical yield but moderate e.e. value, 92% yield and 66% e.e. (Table 1, entry 7). $CuCl_2{\cdot}6H_2O$ showed completely no performances both in activity and selectivity (Table 1, entry 8). Both $Cu(OTf)_2$ and CuBr displayed moderate chemical yield and enantioselectivity (Table 1, entries 9-10). CuCl proved to be the best copper catalyst, affording the corresponding product with high chemical yield and excellent e.e. value. When the ratio of copper metal to ligand was changed to 1:2, the chemical yield and e.e. value of the reaction remained almost

unchanged (Table 1, entry 11). Furthermore, when the catalyst loading was reduced to 5 mol% with 1:1 ratio of copper salt and ligand, a distinct decrease in chemical yield was observed (Table 1, entry 12). No improvement in chemical yield and e.e. value was observed when the catalyst loading was increased to 15 mol% (Table 1, entry 13). Thus, 10 mol% of catalyst loading in 1:1 ratio of CuCl/Schiff base **5a** was selected as the most efficient catalyst for the selected model reaction.

Table 2 Screening of the solvents in the asymmetric Henry reaction[a]



6a

Entry	Solvent	Temp.	Yield[b] (%)	ee[c] (%)
1	^{t}BuOH	rt	90	84
2	EtOH	rt	80	65
3	^{i}PrOH	rt	89	69
4	THF	rt	85	41
5	DMF	rt	91	37
6	CH_3CN	rt	89	43
7	DCM	rt	85	55
8	Toluene	rt	69	66
9	Dioxane	rt	75	39
10	Ethylene glycol	rt	62	13
11	^{i}PrOH	0°C	70	74
12	^{i}PrOH	-20°C	51	83

[a] All the reaction were carried out with 0.5 mmol *p*-nitrobenzaldehyde and 10 mmol nitromethane in 2 mL solvent in the presence of 10 mol% CuCl and 10 mol% **5a**.

[b] Isolated yield.

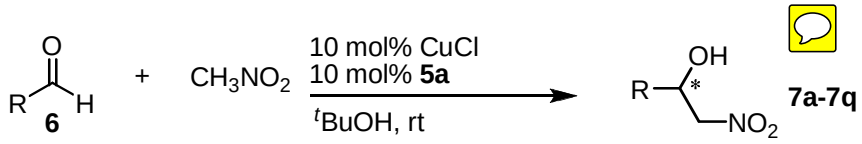
[c] Determined by HPLC analysis on a chiralcel OD-H column.

The solvent was generally vital for the activity of the catalyst, especially in asymmetric reaction. A series of solvents (e.g., *tert*-butanol, ethanol, THF, *iso*-propanol, DMF, acetonitrile, dichloromethane, toluene, dioxane, and ethylene glycol) were examined in the catalytic enantioselective Henry reaction between 4-nitrobenzaldehyde and nitromethane with 10 mol% catalyst loading using CuCl and Schiff base **5a** in 1:1 ratio at room temperature (Table 2). Amongst the screened

solvents, protic solvents, such as *tert*-butanol, ethanol, and *iso*-propanol were superior to aprotic solvents since it might coordinate the copper to enhance the enantioselectivity[22]. *tert*-Butanol was clearly optimal for this reaction with 90% yield and 84% e.e. (Table 1, entry 1).

The reaction temperature plays an important role in determining the reaction rate and enantioselectivity. The influence of the different temperature on the reaction results was examined using *iso*-propanol as a solvent. When the reaction was carried out at 0^{o}C, the chemical yield decreased sharply with a slightly enhanced enantioselectivity (Table 2, entry 11). By further decreasing the reaction temperature to -20^{o}C, 83% e.e. was observed, accompanied by only 51% chemical yield. Therefore, the combination of *tert*-butanol and room temperature was clearly the best choice for current reaction system.

Table 3 Asymmetric Henry reactions between nitromethane and various aldehydes[a]



Entry	6	Time (h)	Product	Yield[b] (%)	ee[c] (%)	*Config*[d]
1	4-nitrobenzaldehyde	24	**7a**	90	84	*R*
2	3-nitrobenzaldehyde	24	**7b**	82	80	*R*
3	2-nitrobenzaldehyde	36	**7c**	80	68	*R*
4	4-fluorobenzaldehyde	24	**7d**	72	73	*R*
5	3-fluorobenzaldehyde	36	**7e**	81	76	*R*
6	4-bromobenzaldehyde	36	**7f**	78	81	*R*
7	3-bromobenzaldehyde	36	**7g**	75	83	*R*
8	4-chlorobenzaldehyde	36	**7h**	76	87	*R*
9	3-chlorobenzaldehyde	36	**7i**	68	74	*R*
10	4-(trifluoromethyl)benzaldehyde	24	**7j**	78	78	*R*
11	3-(trifluoromethyl)benzaldehyde	36	**7k**	68	86	*R*
12	4-formylbenzonitrile	36	**7l**	82	81	*R*
13	benzaldehyde	36	**7m**	75	66	*R*
14	4-methoxybenzaldehyde	48	**7n**	45	69	*R*
15	3-phenyl propanal	48	**7o**	66	48	*R*
16	heptanal	48	**7p**	22	43	*R*
17	3-methylbutanal	48	**7q**	27	82	*R*

[a] All the reaction were carried out with 0.5 mmol *p*-nitrobenzaldehyde and 10 mmol nitromethane in 2 mL ^{t}BuOH in the presence of 10 mol% CuCl and 10 mol% **5a**.

[b] Isolated yield.

[c] Determined by HPLC analysis on a chiralcel OD-H or AD-H column.

[d] By comparison with the literature data.

With the identification of the optimal reaction condition, the scope of the asymmetric Henry reaction was investigated by treatment of various aldehydes with nitromethane in the presence of 10 mol% of CuCl/Schiff base **5a** 1:1 complex in *tert*-butanol at room temperature. The results are presented in Table 3. It clearly shows that the electronic properties of the substituent on the phenyl ring of aromatic aldehydes have a great effect on the chemical yield and enantioselectivity. In general, the aromatic aldehydes with electron-withdrawing groups generated the *β*-nitroalcohols in higher chemical yields and e.e. values compared with aromatic

aldehydes with electron-donating group. The bulky 2-nitrobenzaldehyde also successfully afforded the product **7c**, with 80% chemical yield and 68% e.e. (Table 3, entry 3). The aldehydes with halogenic substituent afforded adducts with good yields and enantioselectivities (Table 3, entries 4-9). However, aromatic aldehyde with electron-donating group provided poor reactivity and stereoselectivity (Table 3, entry 14). When the aromatic aldehydes were changed to aliphatic aldehydes, such as 3-phenyl propanal, heptanal and 3-methylbutanal, the catalytic reaction provided relative lower chemical yield or enantioselectivity (Table 3, entry 15-17). The steric configuration of all products is *R* configuration using Schiff base **5a** as the ligand. It is quite different with Mariusz J. Bosiak reported[11] trimethylsilylcyanation of aldehydes using Schiff bases ligand prepared from (1*R*,2*S*,3*R*,4*S*)-3-amino-1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-ol and salicylaldehydes, in which the aldehydes with electron-withdrawing groups shows lower e.e. value and the steric configurations of all products is disordered.

4. Conclusion

In summary, five novel chiral camphor Schiff bases have been synthesized. The diastereoisomers **5a** and **5a'** were separated successfully. The chiral camphor Schiff base **5a**, together with CuCl, showed high efficiency in asymmetric Henry reactions between nitromethane and various aldehydes, especially for the aromatic aldehydes. This is the first time that camphor-derivated Schiff bases were used as ligands in asymmetric Henry reaction. Notably, the absolute configuration of the products in Henry reaction can be easily regulated with diastereoisomers **5a** and **5a'**. *β*-Nitroaldols with *R* absolute configuration could be obtained using Schiff base **5a**, *β*-nitroaldols with *S* absolute configuration could be obtained with Schiff base **5a'**. Further modification of these ligands as well as applications in asymmetric catalysis is in progress in our laboratory.

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