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Enantioselective Henry reaction catalyzed by a novel L-(+)-aspartic acid-derived Schiff base ligand and Cu(II) ion

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Mild and efficient enantioselective Henry reactions of nitromethane with various aldehydes were catalyzed by a novel L-(+)-aspartic acid-derived Schiff base ligand in the presence of Cu(II) ions, affording the corresponding adducts in high yields (up to 96%) and enantioselectivities (up to 92% ee).

Key Words: Enantioselective Henry reaction, chiral Schiff base, L-(+)-aspartic acid

Introduction

The Henry (nitroaldol) reaction is a well-known tool for the building of a C-C bond.[1] The resulting products of this reaction, a coupling between nitroalkanes and carbonyl groups, can be converted into many valuable building blocks depending on the different requirements in the synthesis of natural products and other useful compounds.[2−6] For the asymmetric Henry reaction,[7] recent work focusing on the development of various metal-based catalysts has been reported by the groups of Shibasaki,[8] Trost,[9] Evans,[10] and others,[11,12] although organocatalysts[13] have also been employed.

Chiral amino acid-derived Schiff bases have frequently been used in catalytic asymmetric Henry reactions.[14−19] For example, Wang[20] prepared tridentate amino alcohol-based Schiff base ligands starting from phenylalanine (D and L) and obtained enantioselectivities of up to 96% ee for the Henry reaction in the presence of Cu^{2+} ions. Although many similar chiral ligands derived from natural amino acids have found applications as catalysts in asymmetric reactions, there are only a few examples of L-(+)-aspartic acid-derived ligands in the

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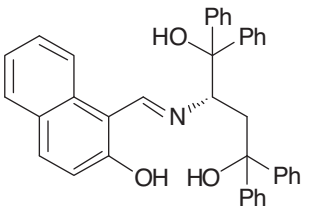
literature, and their application only includes the copper-catalyzed cyclopropanation of styrene.[21] We herein report a mild and efficient enantioselective Henry reaction catalyzed by Cu(II) ions and a novel chiral Schiff base ligand (**L**) (Figure 1), which can be readily prepared from L-(+)-aspartic acid in a 3-step procedure.



L

Figure 1. L-(+)-aspartic acid-derived Schiff base ligand.

Experimental

All chemicals were purchased from Merck, Sigma-Aldrich, Alfa Aesar, and Fluka and were used without any purification. Solvents were used as received from commercial suppliers. Silica gel F_{254} (Merck 5554) precoated plates were used for thin layer chromatography. For column chromatography, silica gel 60 (Merck 7743) was used. IR spectra were recorded using a PerkinElmer 100. ^{1}H-NMR and ^{13}C-NMR spectra were carried out using a 400-MHz Varian NMR spectrometer at ambient temperature. Melting points were recorded with an electrothermal digital melting point apparatus. Optical rotations were determined using a Rudolph Research Analytical AUTOPOL I automatic polarimeter. HPLC analyses were performed using a Chiralcel OD-H column.

Preparation of (S)-dimethyl-2-aminosuccinate (1)

$SOCl_2$ (12 mL) was added dropwise to a suspension of L-(+)-aspartic acid (354 mg, 2.66 mmol) in 60 mL of methanol at 0 °C. The resulting colorless solution was refluxed until all L-(+)-aspartic acid had been consumed. Methanol was evaporated in vacuo and water (5 mL) was added. Saturated $NaHCO_3$ was then added dropwise (pH = 8) and the mixture was extracted with ethyl acetate. The organic phase was dried with Na_2SO_4 and filtered. Ethyl acetate was evaporated to give the title compound as yellow oil (82% yield). IR (NaCl): 3385, 2956, 2851, 1738, 1438, 1366, 1203 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 3.84 (dd, J= 7.6, 4.8 Hz, 1H), 3.76 (s, 3H, CH_3), 3.71(s, 3H, CH_3), 2.82 (dd, J= 16.4, 4.8 Hz, 1H), 2.71 (dd, J= 16.4, 7.6 Hz, 1H), 1.88 (bs, 2H, -NH_2). ^{13}C-NMR (400 MHz, $CDCl_3$) δ (ppm): 174.7, 171.8, 52.5, 52.0, 38.9. Anal. Calcd. for $C_6H_{11}O_4N$ (%): C 44.72, H 6.88, N 8.69; Found: C 43.86, H 6.04, N 9.01. $[\alpha]_D^{25}$ = +60.2 (c 0.156, ethyl acetate).

Preparation of (S)-2-amino-1,1,4,4-tetraphenylbutane-1,4-diol (2)

To a solution of L-(+)-aspartic acid dimethyl ester (**1**) in dry ether was added excess freshly prepared PhMgBr solution in dry ether. The resulting solution was refluxed until all L-(+)-aspartic acid dimethyl ester had been consumed. The reaction was quenched with saturated NH_4Cl solution. The product was extracted with ether-water and the organic phase was dried with Na_2SO_4 and filtered, and then the ether fraction was evaporated in

vacuo. The crude product was purified with column chromatography (1:3 ethyl acetate:hexane) to give the title compound as white crystals (78% yield). Mp 145.9-149.5 °C. IR (NaCl): 3376, 1491, 1596, 1447, 700 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.12-7.41 (m, 20H, Ar-H), 3.65 (dd, J= 10.8, 1.2 Hz, 1H), 2.60 (bs, -OH), 2.44 (dd, J= 14.4, 1.2 Hz, 1H), 2.05 (dd, J= 14, 10.8 Hz, 1H). ^{13}C-NMR (400 MHz, $CDCl_3$) δ (ppm): 128.8, 128.6, 128.2, 128.1, 127.4, 127.2, 126.9, 126.8, 126.7, 125.96, 125.91, 125.8, 81.4, 78.2, 55.2, 40.1. Anal. Calcd. for $C_{28}H_{27}O_2N$ (%): C 82.12, H 6.65, N 3.42; Found: C 82.22, H 6.62, N 3.39. $[\alpha]_D^{25}$ = -3.15 (c 1.27, ethyl acetate).

Preparation of (2S)-2-{(E)-[(2-hydroxynaphthalen-1-yl)methylidene]amino}-1,1,4,4-tetraphenylbutane-1,4-diol (L)

A solution of (S)-2-amino-1,1,4,4-tetraphenyl butane-1,4-diol (200 mg, 0.49 mmol) (**2**) and 2-hydroxy-1-naphthaldehyde (84 mg, 0.49 mmol) in 20 mL of ethanol was refluxed for 5 h. Ethanol was evaporated in vacuo. The product was crystallized (dichloromethane-hexane) to give the title compound as yellow crystals (98% yield). Mp 118-120 °C (subl.). IR (KBr): 3266, 3058, 3028, 1629, 1544, 1519, 1492, 1447, 1350, 1265, 1164, 1053, 838, 748, 669 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.71 (s, 1H, -CH=N), 7.51-7.13 (m, 21H, Ar-H), 7.01 (t, J= 7.2 Hz, 1H, Ar-H), 6.94 (t, J= 7.2 Hz, 2H, Ar-H), 6.75 (t, J= 7.2 Hz, 1H, Ar-H), 6.63 (d, J= 9.6 Hz, 1H, Ar-H), 4.38 (d, J= 7.2 Hz, 1H), 2.98 (dd, J= 14.8, 8.4 Hz, 1H), 2.94 (bs, 1H, -OH), 2.88 (dd, J= 14.8, 1.6 Hz, 1H), 1.73 (bs, 1H, -OH). ^{13}C-NMR (400 MHz, $CDCl_3$) δ (ppm): 159.1, 146.8, 146.4, 144.2, 144.1, 137.2, 134.1, 129.0, 128.6, 128.5, 128.4, 128.2, 126.3, 126.19, 126.17, 124.9, 122.5, 118.3, 106.7, 81.4, 77.7, 68.2, 42.5. Anal. Calcd. for $C_{39}H_{33}O_3N$ (%): C 83.10, H 5.90, N 2.48; Found: C 82.65, H 5.89, N 2.38. $[\alpha]_D^{28}$ = +6.00 (c 1.00, CH_2Cl_2).

General procedure for Henry reaction

The dark green solution of $Cu(OAc)_2.nH_2O$ (0.06 mmol) and Schiff base ligand (**L**) (0.05 mmol) was allowed to stir in 2 mL of solvent at room temperature for 2 h. At the end of 2 h, the appropriate aldehyde (0.5 mmol) and nitromethane (2.5 mmol) were added. The reaction mixture was stirred at room temperature until most of the aldehyde had been consumed. The solvent was evaporated in vacuo and the crude product was purified with column chromatography.

(1S)-1-(2-Chlorophenyl)-2-nitroethanol (3a)

Colorless oil, 95% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.56 (dd, J= 7.6, 2 Hz, 1H, Ar-H), 7.40-7.24 (m, 3H, Ar-H), 5.88-5.84 (m, 1H), 4.57 (dd, J= 13.6, 2.4 Hz, 1H), 4.36 (dd, J= 13.6, 9.6 Hz, 1H). HPLC conditions: 93:7 hexane:$i-$PrOH, 0.8 mL/min, 267 nm, t_{minor} = 14.4 min (R), t_{major} = 15.3 min (S), 90% ee, $[\alpha]_D^{28}$ = +44.0 (c 0.55, CH_2Cl_2).

(1S)-1-(2-Nitrophenyl)-2-nitroethanol (3b)

Brown crystals, 81% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.06 (dd, J= 8, 1.2 Hz, 1H, Ar-H), 7.95 (d, J= 8 Hz, 1H, Ar-H), 7.75 (td, J= 7.6, 0.8 Hz, 1H, Ar-H), 7.55 (td, J= 8.4, 1.6 Hz, 1H, Ar-H), 6.03 (d, J= 8 Hz, 1H), 4.85 (dd, J= 14, 2.4 Hz, 1H), 4.56 (dd, J= 13.6, 9.2 Hz, 1H), 3.35 (bs, 1H, -OH). HPLC conditions: 90:10 hexane:$i-$PrOH, 1 mL/min, 267 nm, t_{minor} = 15.9 min (R), t_{major} = 18.3 min (S), 88% ee, $[\alpha]_D^{28}$ = +235 (c 0.89, CH_2Cl_2).

(1S)-1-(3-Nitrophenyl)-2-nitroethanol (3c)

Yellow oil, 90% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31-8.30 (m, 1H, Ar-H), 8.21-8.19 (m, 1H, Ar-H), 7.79-7.77 (m, 1H, Ar-H), 7.61 (t, J= 7.6 Hz, 1H, Ar-H), 5.61 (dd, J= 7.6, 4.4 Hz, 1H), 4.64-4.62 (m, 2H), 3.51 (bs, 1H, -OH). HPLC conditions: 90:10 hexane:$i-$PrOH, 1 mL/min, 267 nm, t_{minor} = 25.9 min (R), t_{major} = 28.6 min (S), 70% ee, $[\alpha]_D^{28}$ = +28.8 (c 1.04, CH_2Cl_2).

(1S)-1-(4-Nitrophenyl)-2-nitroethanol (3d)

White crystals, 71% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.28-8.26 (m, 2H, Ar-H), 7.64-7.62 (m, 2H, Ar-H), 5.59-5.63 (m, 1H), 4.60 (d, J= 6 Hz, 1H), 4.58 (d, J= 2 Hz, 1H), 3.17 (bs, 1H, -OH). HPLC conditions: 90:10 hexane:$i-$PrOH, 1 mL/min, 267 nm, t_{minor} = 28.7 min (R), t_{major} = 35.40 min (S), 76% ee, $[\alpha]_D^{28}$ = +29.3 (c 0.75, CH_2Cl_2).

(1S)-1-Phenyl-2-nitroethanol (3e)

Yellow oil, 96% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.39-7.34 (m, 5H, Ar-H), 5.43 (dd, J= 9.6, 2.8 Hz, 1H), 4.59 (dd, J= 13.6, 9.6 Hz, 1H), 4.49 (dd, J= 13.2, 2.8 Hz, 1H), 3.08 (bs, 1H, -OH). HPLC conditions: 90:10 hexane:$i-$PrOH, 1 mL/min, 267 nm, t_{minor} = 13.8 min (R), t_{major} = 15.0 min (S), 78% ee, $[\alpha]_D^{28}$ = +35.3 (c 1.36, CH_2Cl_2).

(1S)-1-(4-Methylphenyl)-2-nitroethanol (3f)

Yellow crystals, 88% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.29-7.20 (m, 4H, Ar-H), 5.42 (d, J= 9.2 Hz, 1H), 4.60 (dd, J= 13.6, 10.4 Hz, 1H), 4.48 (dd, J= 13.2, 2.8 Hz, 1H), 2.74 (bs, 1H, -OH), 2.36 (s, 3H, CH_3). HPLC conditions: 85:15 hexane:$i-$PrOH, 0.5 mL/min, 267 nm, t_{minor} = 19.8 min (R), t_{major} = 24.5 min (S), 74% ee, $[\alpha]_D^{28}$ = +17.3 (c 0.81, CH_2Cl_2).

(+)-1-(4-Ethylphenyl)-2-nitroethanol (3g)

Yellow oil, 60% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31-7.29 (m, 2H, Ar-H), 7.23-7.21 (m, 2H, Ar-H), 5.43-5.39 (m, 1H), 4.50 (dd, J= 13.2, 9.6 Hz, 1H), 4.48 (dd, J= 13.2, 3.2 Hz, 1H), 2.86 (d, J= 3.6 Hz, 1H), 2.65 (q, J= 7.6 Hz, 2H, -CH_2), 1.23 (t, J= 7.6 Hz, 3H, CH_3). HPLC conditions: 90:10 hexane:$i-$PrOH, 1 mL/min, 267 nm, t_{minor} = 12.2 min (R), t_{major} = 15.7 min (S), 76% ee, $[\alpha]_D^{28}$ = +32.0 (c 0.75, CH_2Cl_2).

(1S)-1-(4-Methoxyphenyl)-2-nitroethanol (3h)

Yellow oil, 68% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.30 (d, J= 8.8 Hz, 2H, Ar-H), 6.91 (d, J= 8.8 Hz, 2H, Ar-H), 5.40-5.38 (m, 1H), 4.59 (dd, J= 13.2, 9.6 Hz, 1H), 4.46 (dd, J= 12.8, 2.8 Hz, 1H), 3.81 (s, 3H, -OCH_3), 2.84 (bs, 1H, -OH). HPLC conditions: 90:10 hexane:$i-$PrOH, 1 mL/min, 267 nm, t_{minor} = 20.4 min (R), t_{major} = 25.5 min (S), 70% ee, $[\alpha]_D^{28}$= +28.0 (c 0.50, CH_2Cl_2).

Results and discussion

The desired amino alcohol (**2**) derived from the chiral L-(+)-aspartic acid dimethyl ester was obtained using a Grignard reaction and used in the condensation reaction with 2-hydroxy-1-naphthaldehyde to synthesize the Schiff base ligand (**L**) (Figure 2).

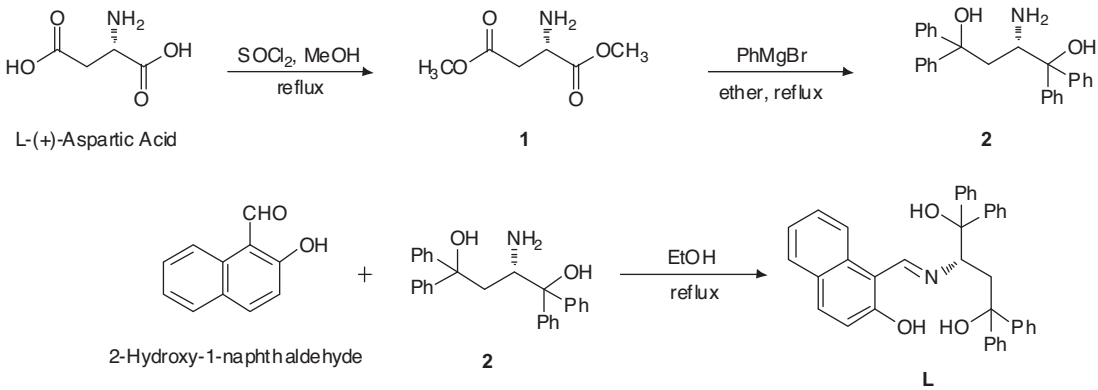


Figure 2. Synthesis of the chiral amino alcohol derivative (**2**) and the Schiff base ligand.

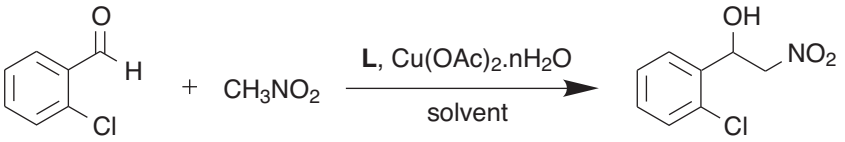
Initial studies of this ligand were focused on the reaction of nitromethane with 2-chlorobenzaldehyde, as shown in Table 1.

First, the effect of changing the solvent was investigated for reactions carried out in the presence of 10 mol% catalyst at room temperature (Table 1, Entries 1-15). When ethanol was used as the solvent, the nitroalcohol product was obtained in a high yield and high ee (Table 1, Entry 1). The reaction solvent was found to have a very significant influence on the reaction. For example, when the reaction solvent was changed from ethanol to THF or toluene, the reaction yield and ee were reduced considerably (Table 1, Entries 6 and 9) despite these solvents being commonly used for Henry reactions.[23,24] Since the catalyst is also stable in water, we attempted to carry out this asymmetric reaction in aqueous media. However, the addition of water disfavored the reaction, resulting in a decrease in both ee and yield (Table 1, Entry 4). Thus, all the experimental data demonstrated that ethanol is a superior solvent in terms of yield and enantiomeric excess.

Under the optimized reaction conditions, different aldehydes were tested in order to extend the substrate scope, as shown in Table 2.

The L-(+)-aspartic acid-derived Schiff base catalyst worked well for various aromatic aldehydes, regardless of the presence of electron-withdrawing or electron-donating substituents on the benzaldehyde ring. It appears that aromatic aldehydes with ortho-substituted groups (Table 2, Entries 1 and 2) increase the stereoselectivity.

Table 1. Effects of solvent, temperature, and catalyst loading on the Henry reaction of 2-chlorobenzaldehyde and nitromethane under the catalysis of **L**.

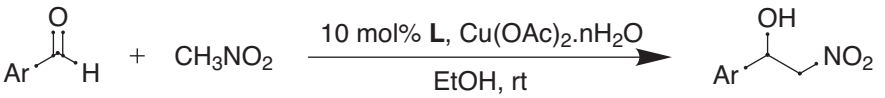


Entry	Solvent	Temp. ($^\circ$C)	Time (h)	Yield[a] (%)	ee[b] (%)	Config.[c]
1	Ethanol	RT	48	95	90	S
2	*t*-Butanol	RT	48	87	90	S
3	*i*-Propanol	RT	48	86	86	S
4	Ethanol:Water (10:1)	RT	48	78	84	S
5	Methanol	RT	48	81	72	S
6	Tetrahydrofuran	RT	48	47	70	S
7	Diethyl ether	RT	48	57	68	S
8	Hexane	RT	48	59	60	S
9	Toluene	RT	48	39	58	S
10	Ethyl acetate	RT	48	12	52	S
11	Acetone	RT	48	16	48	S
12	Dimethylformamide	RT	48	21	38	S
13	Acetonitrile	RT	48	42	38	S
14	Dichloromethane	RT	48	43	28	S
15	*n*-Propanol	RT	48	79	14	S
16	Ethanol	0	120	69	92	S
17[d]	Ethanol	RT	72	82	88	S
18[e]	Ethanol	RT	72	84	88	S

[a]Isolated yields after column chromatography.
[b]Determined by HPLC analysis using a Chiralcel OD-H column.
[c]The absolute configuration of the major product was assigned by comparison with the literature values.[22]
[d]With 5 mol% catalyst loading.
[e]With 20 mol% catalyst loading.

It is likely that the mechanism involves initial coordination of the aromatic aldehyde to a copper atom, followed by nucleophilic attack of $-CH_2NO_2$ onto the less sterically hindered face of the carbonyl group, affording products with high enantioselectivity.[26]

Table 2. Henry reaction of nitromethane with various aldehydes.



Entry	Product	ArCHO	Time (h)	Yield (%)[a]	ee (%)[b]	Config.[c]
1	**3a**	2-Chlorobenzaldehyde	48	95	90	S
2	**3b**	2-Nitrobenzaldehyde	24	81	88	S
3	**3c**	3-Nitrobenzaldehyde	24	90	70	S
4	**3d**	4-Nitrobenzaldehyde	24	71	76	S
5	**3e**	Benzaldehyde	96	96	78	S
6	**3f**	4-Methylbenzaldehyde	96	88	74	S
7	**3g**	4-Ethylbenzaldehyde	96	60	76	n.d.
8	**3h**	4-Methoxybenzaldehyde	96	68	70	S

[a]Isolated yields after column chromatography.
[b]Determined by HPLC analysis using a Chiralcel OD-H column.
[c]The absolute configuration of the major product was assigned by comparison with the literature values.[13,23,25]
n.d.: Not determined.

Conclusion

The enantioselective Henry reaction was performed at room temperature by the employment of a novel L-(+)-aspartic acid-derived Schiff base ligand, yielding β-nitroalkanols with good yields and ee values. The L-(+)-aspartic acid-derived Schiff base ligand is an advantageous catalyst for the Henry reaction as it can be prepared from cheap and easily accessible starting materials in an easy 3-step procedure. The novel catalyst described here and analog compounds with readily tunable sterics and hydrogen-bonding attributes are likely to further expand the scope of various other asymmetric reactions.

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