Salicylaldimine based copper (II) complex: a potential catalyst for the asymmetric Henry reaction

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Abstract

The chiral ligand synthesized from L-diphenylvalinol and salicylaldehyde is found to catalyse the asymmetric Henry reaction with copper(II)acetate monohydrate. Various nitroaldols were formed with 77-95% ee and good yield. The mechanism for the formation of a particular enantiomer is also discussed. The enantioselection in the formation of the chiral nitroaldol is discussed in terms of steric bulkiness of the catalytic system.

Keywords: Asymmetric Henry reactions, diphenylvalinol, valinol, copper(II) acetate, salen ligand

Introduction

Among the C-C bond forming reactions, the nitroaldol (Henry) reaction is one of the classical reactions in organic synthesis.[1] It is well known that the nitroaldol products find increasing applications in pharmaceutical industries, in the synthesis of natural products, polyamino alcohols and polyhydroxylated amides. Generally, the nitroaldol reaction involves the addition of a nitronate ion to a carbonyl compound. The nitronate ion can be generated in situ by the deprotonation of a nitroalkane with an external base. The addition is facilitated either by a Lewis acid catalyst or by a suitable bifunctional catalyst, while the former activates the carbonyl partner, the latter works as a Lewis acid- Bronsted base which activates and bring both reactants together.[2] The current study is to identify a weakly Lewis acidic system bearing moderately basic charged ligands that would facilitate the deprotonation of nitroalkanes for the Henry reaction to proceed. We felt that, divalent metal acetate-chiral ligand combination will meet these requirements because, acetate ion has been employed as a Bronsted base in the enantioselective nitroaldol reaction.[3]

Catalysts for asymmetric Henry reaction reported so far are metal catalysts and organocatalysts. The metal catalysts include rare earth BINOL complexes,[4a] dinuclear zinc catalysts,[4b] Cu-bis(oxazoline) catalysts,[14a] dual Lewis acid/amine chiral amino alcohol ligands,[4c]

tridentate-bis(thiazole) and bis(tetrazole) ligands,[4d] diethylzinc triggered reactions,[4e] ketoamino cobalt complexes,[4f] metal complexes on solid support.[4g] The organocatalysts include guanidine derived bifunctional catalysts, [5a] cinchona alkaloid derived catalysts [5b] and silyl nitronates as activated nitroalkanes.[5c]

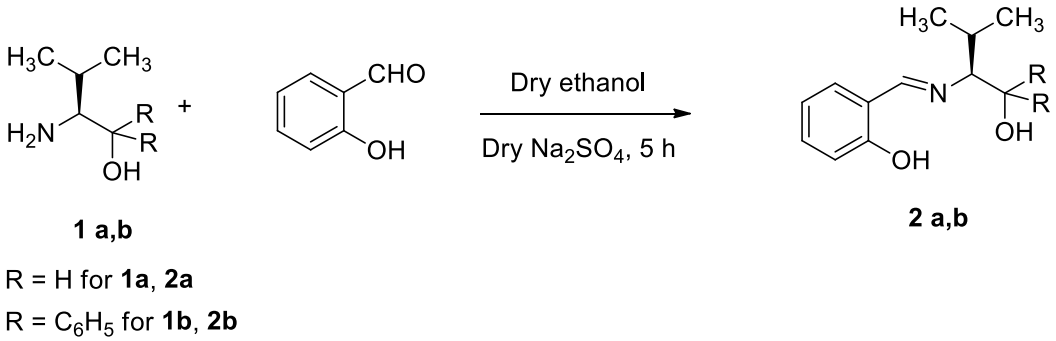
Chiral Schiff bases have been used frequently in catalytic asymmetric synthesis.[6] Schiff base type, particularly chiral salen ligands have attracted much attention because they can coordinate with a variety of transition metal ions to afford the corresponding stable chiral metal complexes. In general, these complexes are quite efficient catalysts for the asymmetric Henry reaction.[7]

Among them, the copper catalysed asymmetric Henry reaction performed at room temperature has captured much focus in recent years.[8] Chiral copper complexes derived from –ONO type tridentate chiral ligands are of much interest and in most of the cases they afforded nitroaldols with impressive enantioselectivities.[9] Among the chiral Schiff bases, the amino acid derived ligands can catalyse the enantioselective Henry reaction under mild conditions. However, still there is scope for developing a cheap and efficient catalytic system which can work under mild reaction conditions with excellent enantioselectivity. The chiral Schiff base derived from L-phenylalaninol was found to catalyse the enantioselective Henry reaction in combination with copper(II) acetate.[10] The salen ligands synthesized from L-valinol and L-diphenylvalinol were reported to catalyse the enantioselective trimethylsilylcyanation of aldehydes by N. Oguni *et al.* in 1993.[11,12]

To the best of our knowledge there is no report for these salen ligands to catalyse the asymmetric Henry reaction. Hence in this paper, we report the synthesis of chiral Schiff bases from salicylaldehyde and L-valinol and L-diphenylvalinol and their potential with $Cu(OAc)_2$. H_2O to catalyse the asymmetric nitroaldol reaction. The mechanism of the catalytic cycle is also discussed in detail.

Results and Discussion

Ligands **2a,b** were prepared by condensation of L-valinol **1a** and L-1,1-diphenylvalinol **1b**, respectively, with salicylaldehyde in more than 90% yield (Scheme 1).



1 a,b

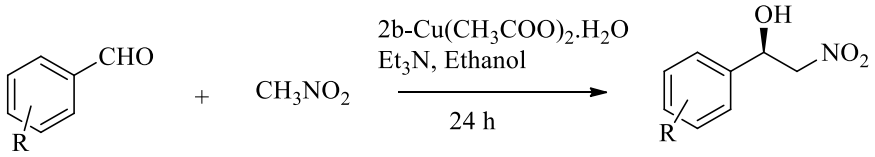
R = H for **1a**, **2a**

R = C_6H_5 for **1b**, **2b**

2 a,b

Scheme 1. Synthesis of imines **2a** and **2b**.

In order to test the ability of these ligands to induce enantioselectivity in the copper catalysed asymmetric Henry reaction (Scheme 2), nitromethane and benzaldehyde were made to react with 5 mol% of ligand **2a** and the metal salt copper(II) acetate mono hydrate in an ethanolic medium at room temperature. No conversion, however, was observed under these conditions. This may be due to the poor Lewis acidity of the catalytic system, which is insufficient for the formation of nitronate anion. Then the Lewis acidity of the catalytic system was increased by adding additives. Triethylamine, which is a Lewis base, was tried as an additive. This resulted in the product (R)-(-)-2-nitro-1-phenylethanol in 60% yield with 40% enantiomeric excess. The enantioselectivity of the catalytic system was increased as expected. It is found that 1 mol% of triethylamine is sufficient for increasing the conversion of the reaction. The optimization of reaction conditions are given in table 1.



Scheme 2. Asymmetric nitroaldol reaction catalysed by **2b**-$Cu(OAc)_2$ complex.

In order to increase the enantiomeric excess of the product, the temperature was decreased from room temperature to 0 °C. As a result of this, the yield of the product was decreased to 6% but the enantiomeric excess remained the same (Table 1, entry 3). This indicates that, 0 °C is not providing the sufficient activation energy required for the substrates to react. Then the temperature was increased. The reaction was carried out under reflux conditions. But this condition resulted in the loss of enantioselectivity. The racemic nitroaldol product was formed in 60% yield (Table 1, entry 4.) The effect of temperature on the catalytic reaction clearly shows that, room temperature alone will provide the necessary stereo control for the ligand system which makes the process more selective.

In general, increase in the concentration of a catalytic system will increase the enantioselectivity of that particular asymmetric transformation. Hence, the catalytic amount of the ligand **2a**-$Cu(OAc)_2.H_2O$ was increased from 5 mol% to 10 mol%. With 10 mol% of the ligand **2a**-$Cu(OAc)_2.H_2O$ at room temperature, the enantiomeric excess of the nitroaldol was increased to 54% with full conversion (Table 1, entry 5). Hence, it was decided that 10 mol% of the ligand **2a** with $Cu(OAc)_2.H_2O$ is sufficient to carry out the asymmetric Henry reactions. In order to induce more enantioselectivity in the asymmetric Henry reaction, the effect of solvent on the enantioselectivity was studied by performing the reaction with different solvents. In the methanolic medium the conversion was 98%. The product (R)-(-)-2-nitro-1-phenylethanol was formed with 12% enantiomeric excess (Table 1, entry 6). With all other solvents like THF, acetonitrile, dichloromethane, chloroform, diethyl ether and toluene there is no conversion to the product nitroaldol. Then the reaction was done by taking nitromethane, which is one of the

substrates as solvent (Table 1, entry 7). This led to decrease in the yield and enantioselectivity of the nitroaldol product.

Hence with ligand **2a**, the maximum enantioselectivity that could be obtained was 54% under various reaction conditions. This may be due to the presence of primary alcohol moiety in ligand **2a** which is not bulky enough to induce more enantioselectivity. The increase in the bulkiness of the ligand system may increase the enantioselectivity. Because, the ligand system may differentiate the two enantiotopic faces of the prochiral aldehyde, if there is a restricted rotation, which can be achieved with a bulky group in the place of methylene group in the amino alcohol part of the ligand **2a**. Hence, the methylene group in the ligand **2a** was replaced with diphenyl group, by synthesising L-diphenylvalinol **1b** and the corresponding Schiff base **2b** by condensing with salicylaldehyde.

Then, the ligand **2b**-$Cu(OAc)_2.H_2O$ was screened for the enantioselective Henry reaction. With 10 mol% of the ligand **2b**-$Cu(OAc)_2.H_2O$ the product (R)-(-)-2-nitro-1-phenylethanol was formed in 99% yield with 70% enantiomeric excess in ethanol medium at room temperature (Table 1, entry 8). Then the reaction was carried out under reflux conditions. The product nitroaldol was formed in 99% yield without any enantiomeric excess (Table 1, entry 9).

Table 1. Asymmetric Henry reaction using benzaldehyde and nitromethane[a]

S. No	Ligand	Cat. Amount	Solvent	Temp (°C)	Yield (%)[b]	ee (%)[c]	Abs. config.[d]
1[e]	**2a**	5 mol%	Ethanol	Rt	0	0	-
2	**2a**	5 mol%	Ethanol	Rt	60	40	R
3	**2a**	5 mol%	Ethanol	0	6	40	R
4	**2a**	5 mol%	Ethanol	78	60	0	-
5	**2a**	10 mol%	Ethanol	Rt	99	54	R
6	**2a**	10 mol%	Methanol	Rt	98	12	R
7	**2a**	10 mol%	Nitromethane	Rt	6	0	-
8	**2b**	10 mol%	Ethanol	Rt	99	70	R
9	**2b**	10 mol%	Ethanol	78	99	0	-

[a]The ratio of ligand **2a** / **2b**-Cu(OAc)2.H2O: nitromethane: triethylamine: benzaldehyde was 0.1 mmol: 1 mmol: 0.01 mmol: 1 mmol.
[b]Isolated yield after column chromatography.
[c]The enantiomeric excess was determined by HPLC analysis using chiralcel OD-H column.
[d]The absolute configuration was assigned to the major enantiomer by comparison with the sign of the specific rotation given in the literature data.[14a]
[e]The reaction was carried out without adding triethylamine.

The possible mechanism for the asymmetric Henry reaction catalysed by ligand **2b**-$Cu(OAc)_2$. H_2O can be explained by taking the mechanistic pathway proposed by J.R. Pedro *et al.*[13] for their catalyst, which has almost similar structural environment as that of ligand **2b** (Figure 1).

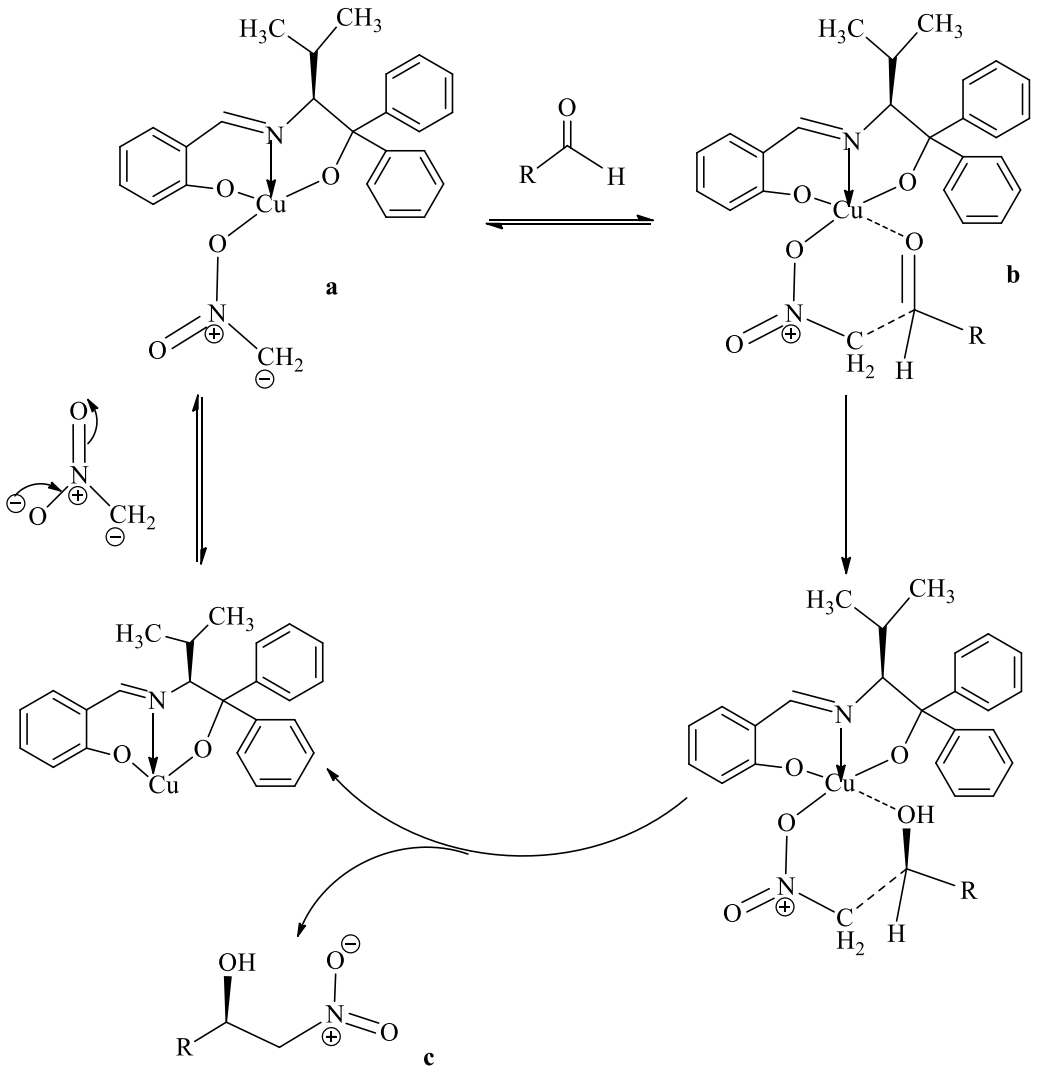


Figure 1. Possible mechanism for ligand **2b**-$Cu(OAc)_2.H_2O$ catalysed asymmetric Henry reaction between nitromethane and benzaldehyde.

First, the coordination of nitronate anion with copper takes place through the oxygen of the nitronate anion near salicylaldimine part (**a)**. Benzaldehyde occupies the fourth equatorial position forming the distorted square planar intermediate (**b)**. The attack of the nitronate anion on the carbonyl group of benzaldehyde takes place at the *si* face, via a stable six membered transition state. The product (R)-(-)-2-nitro-1-phenylethanol (**c)** was formed after work up (Figure 1).

With the optimised reaction conditions in hand, the scope of the reaction was explored by screening the catalytic system for the asymmetric Henry reaction of various substituted aldehydes and nitromethane (Table 2). The yield of all the nitroaldols was quantitative. High enantiomeric excess (77-95%) was observed for aldehydes bearing either electron withdrawing or electron donating groups.[14] The results are shown in Table 2. All the nitroaldol products formed are in R- configuration

Table 2. Asymmetric Henry reaction between substituted benzaldehydes and nitromethane using 10 mol% **2b**-$Cu(OAc)_2.H_2O$ as catalyst[a]

Entry	Aldehyde	Yield(%)[b]	ee (%)[c]	Abs. configuration[d]
1	Benzaldehyde	99	70	R
2	o-Nitro benzaldehyde	99	95	R
3	m-Nitro benzaldehyde	99	90	R
4	p-Nitro benzaldehyde	99	87	R
5	p-Chloro benzaldehyde	99	80	R
6	p-Methyl benzaldehyde	99	60	R
7	p-Methoxy benzaldehyde	99	88	R
8	o-Chloro benzaldehyde	99	77	R

[a]The ratio of **2b**-$Cu(OAc)_2.H_2O$: nitromethane: triethylamine: benzaldehyde was 0.1 mmol: 1 mmol: 0.01 mmol: 1 mmol.

[b]Isolated yield after column chromatography.

[c]The enantiomeric excess was determined by HPLC analysis using chiralcel OD-H column.

[d]The absolute configuration was assigned to the major enantiomer by comparison with the sign of the specific rotation given in the literature data.[14a]

Conclusions

In conclusion, a new catalytic system for the copper(II) catalysed enantioselective Henry reaction between nitromethane and aromatic aldehydes has been developed. This system can be easily prepared because the chiral source L-valine is readily available. The salen ligand derived from L-diphenylvalinol and $Cu(OAc)_2$. H_2O system has been proven to be a good catalytic system for the asymmetric Henry reaction, by providing the corresponding nitroalkanols with

good yield and high enantiomeric excess. Finally, the reaction can be carried out without the need of air and moisture exclusion which makes the catalyst more attractive.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ with a BRUKER AMX-400 MHz instrument using TMS as an internal standard. Commercial Precoated Silica Gel (Merck 60F-254) plates were used for TLC. 60-120 mesh silica gel was used for column chromatography. Specific rotations were recorded with a Rudolph autopol IV polarimeter. Enantiomeric excess was determined with a Shimadzu 2010A HPLC instrument (Chiral column: Chiralcel OD-H, Mobile phase: 85:15 hexane/i-PrOH, flow rate: 0.8ml/min, UV detector λ = 215nm. FTIR spectra were recorded with a Perkin Elmer-DXB spectrometer. Melting points were determined with a Kherea digital melting point apparatus and are uncorrected. All the chemicals were purchased from Merck. All the solvents used were purchased from Merck and used after purification.

L-Valine methylester hydrochloride. L-valine (2 g, 17.1 mmol) was dissolved in 20 ml of methanol. To this thionyl chloride (2 ml, 17.1 mmol) was added drop wise under an ice cold condition. Then the reaction mixture was stirred overnight. Then the excess thionyl chloride was removed which results L-valine methyl ester (2.8 g) in quantitative yield. Melting point: 171-173 °C, $[\alpha]^{589}_{25}$ +26.6° (C=5 in water); FTIR (cm^{-1}) 3340, 2900, 1736, 1235 cm^{-1}. ^{1}H NMR δ 0.9 (m, ^{3}J = 7.6 Hz, 6H, $-CH_3$), 2.1 (s, 1H, -CH), 2.5 (s, 3H, $-OCH_3$), 3.7 (d, ^{3}J = 12.4 Hz, 1H,-CH), 8.4 (s, 2H, $-NH_2$). ^{13}C NMR δ 17.68, 18.28, 28.97, 38.80- 40.06, 57.23, 170.06.

(S)-2-Amino-3-methylbutan-1-ol (1a). 3.8 g (43 mmol) of sodiumborohydride was taken in dry THF and dissolved under nitrogen atmosphere at room temperature. To this 5 g of L-valine was added and dissolved. About 10.8 g of iodine dissolved in dry THF was added slowly using an additional funnel in an ice cold condition. After the addition was over, the reaction mixture was refluxed for 18 hours. Then the reaction mixture was cooled to room temperature and methanol was added cautiously until the solution become clear. Then 20% KOH was added and stirred for 4 hours. Then the product was extracted with methylene dichloride. Then the solvent was evaporated to yield 4.1 g of L-valinol as a colourless viscous liquid. The yield was 92%, $[\alpha]_D^{25}$ = +17.4° (c = 1, Ethanol). ^{1}H NMR δ 0.85 (dd, ^{3}J = 6.8 Hz, 6H, $-(CH_3)_2$), 1.35 (m, ^{3}J = 2.0 Hz, 1H, -CH), 1.5 (m, ^{3}J = 2.0 Hz, 1H, -CH), 1.83 (d, ^{3}J = 7.8 Hz, 2H $-NH_2$), 3.25 (dd, ^{3}J = 1.6 Hz, 1H, -CH), 3.59 (dd, ^{3}J = 2.4 Hz, 1H, -CH), 4.57 (s, 1H, -OH). ^{13}C NMR δ 17.81, 31.88, 57.83, 65.77.

(S)-2-Amino-3-methyl-1,1-diphenylbutanol-1-ol (1b). Magnesium turnings (3.52 g, 143.16 mmol) were taken in dry THF. To this, iodine was added under nitrogen atmosphere and warmed. Bromobenzene (10.1 ml, 95.44 mmol) was added dropwise at 0 °C. Then L-valine methylester hydrochloride (2 g, 11.93 mmol) was added portionwise and stirred for 6 hours. Then the reaction mass was quenched with saturated ammonium chloride and filtered. Then the

solvent was evaporated from the filtrate. The yield was 87%. $[\alpha]_D^{25}$ = -119.8° (c = 0.6, CH_2Cl_2) [Lit[15] $[\alpha]_D^{25}$ = -127.8° (c = 0.639, $CHCl_3$). ^{1}H NMR δ 0.68 (dd, ^3J = 6.8 Hz, 6H, -$(CH_3)_2$), 1.5 (m, ^3J = 2.0 Hz, 1H, -CH), 1.87 (d, ^3J = 5.1 Hz, 2H, -NH_2), 3.62 (d, ^3J = 2.0 Hz, 1H, -CH), 4.23 (s, 1H,-OH), 6.96 (m, ^3J = 8.4 Hz, 2H, phenyl), 7.07 (m, ^3J = 6.4 Hz, 5H, phenyl), 7.28 (t, ^3J = 7.6 Hz, 2H, phenyl), 7.40 (d, ^3J = 1.2 Hz, 1H, phenyl). ^{13}C NMR δ 17.96, 27.20, 72.87, 87.86, 125.71, 127.82, 128.74, 144.87.

(S)1-*N*-(1-Hydroxy-3-methylbut-2-yl)-2-hydroxybenzaldimine (2a). To an ethanolic solution of **1a** (1 g, 9.69 mmol), salicylaldehdye (1.15 ml, 9.69 mmol) was added followed by anhydrous sodium sulphate and stirred at room temperature for 5 hours. Then the reaction mixture was filtered and the solvent was evaporated to yield a yellow crystalline imine with 90% yield. Melting point: 99-102°C, $[\alpha]_D^{25}$ = -24.1° (c = 1, CH_3OH) [Lit.[11] $[\alpha]_D^{24}$ = -26.2° (c = 1, CH_3OH)]. ^{1}H NMR δ 0.88 (dd, ^3J = 1.2 Hz, 6H, -$(CH_3)_2$), 1.87 (m, ^3J = 6.4 Hz, 1H, -CH), 2.99 (m, ^3J = 2.8 Hz, 1H, -CH), 3.69 (dd, ^3J = 2.4 Hz, 1H, -CH), 3.76 (dd, ^3J = 3.6 Hz, 1H, -CH), 5.04 (s, 1H, OH), 6.82 (t, ^3J = 6.4 Hz, 1H, -CH), 6.88 (d, ^3J = 8.4 Hz, 1H, -CH), 7.19 (t, ^3J = 7.6 Hz, 1H, -CH), 7.25 (d, ^3J = 7.2 Hz, 1H, -CH), 8.29 (s, 1H, -C=N), 7.8 (s,1H, -OH). ^{13}C NMR δ 17.85, 32.15, 62.1, 79.81, 117.3, 120.5, 123.7, 130.1, 133.6, 151.4, 161.53.

(S)1-*N*-(1-Hydroxy-1,1-diphenyl-3-methylbut-2-yl)-2-hydroxybenzaldimine (2b). To an ethanolic solution of **1b** (1 g, 3.92 mmol), salicylaldehdye (0.48 ml, 3.92 mmol) was added followed by the addition of anhydrous sodium sulphate. Then the reaction mixture was stirred for 5 hours at room temperature. The reaction mixture was filtered and the solvent was evaporated to yield a yellow crystalline imine with 95% yield. Melting point: 170-172 °C. $[\alpha]_D^{25}$ +77.8 (c= 1, $CHCl_3$) [Lit.[11] $[\alpha]_D^{24}$ +80.7 (c= 1, $CHCl_3$)]. FTIR (cm^{-1}) 3060, 2960, 2874, 1629, 1541, 1446. ^{1}H NMR δ 0.81 (d, ^3J = 6.8 Hz, 3H, -CH3), 0.91 (d, ^3J = 6.8 Hz, 3H, -CH_3), 2.08 (m, ^3J = 2.0 Hz, 1H, -CH), 3.89 (s, 1H, -OH), 4.01(d, ^3J = 2.0 Hz, 1H, -CH), 5.22 (s, 1H, -OH), 6.78 (m, ^3J = 7.2 Hz, 1H, phenyl), 6.84 (d, ^3J = 8.4 Hz, 1H, phenyl), 7.08 (t, ^3J = 1.2 Hz, 1H, phenyl), 7.10 (t, ^3J = 6.4 Hz, 1H, phenyl), 7.13 (m, ^3J = 8.0 Hz, 3H, phenyl), 7.21 (t, ^3J = 13.6 Hz, 1H, aromatic proton), 7.26 (t, ^3J = 8.0 Hz, 2H, aromatic proton), 7.38 (d, ^3J = 7.6 Hz, 2H, aromatic proton), 7.50 (d, ^3J = 7.2 Hz, 2H, aromatic proton), 8.11 (s, 1H,-CH=N). ^{13}C NMR δ 17.93, 22.57, 28.95, 80.4, 116.97, 118.54, 118.69, 125.79, 125.92, 126.75, 126.81, 128.23, 128.27, 131.68, 132.61, 144.31, 146.14, 160.91, 166.77.

General procedure for asymmetric Henry reaction

To an ethanolic solution of **2b** (0.036 g, 0.1 mmol), $Cu(OAc)_2.H_2O$ (0.012 g, 0.1 mmol) was added and stirred for 1 hr. To this nitromethane (0.154 g, 1 mmol) was added followed by the addition of triethylamine (0.01 ml, 1 mol%). Then benzaldehyde (0.212 ml, 1 mmol) was added drop wise and the reaction mixture was stirred for 24 hours at room temperature. After 24 hours, 1M HCl was added to the reaction mixture, and the solvent was evaporated. The aqueous layer was extracted with ethyl acetate. The resulted organic layer was dried over anhydrous sodium sulphate. The product nitroaldol was purified by column chromatography using silica gel as an adsorbent and 95:5 hexane:ethylacetate as an eluant. $[\alpha]_D^{25}$ = -13.9 (c = 1, Ethanol) [Lit.[14a] $[\alpha]_D^{20}$

= -20.2 (c = 1, Ethanol)]. ^{1}H NMR δ 4.14 (t, ^{3}J = 6.0 Hz, 1H, -CH), 4.38 (d, ^{3}J = 2.4 Hz, 1H, -CH), 4.89 (d, ^{3}J = 2.8 Hz, 1H, -CH), 7.02 (d, ^{3}J = 3.2 Hz, 2H, aromatic proton), 7.23 (t, ^{3}J = 3.3 Hz, 1H, aromatic proton), 7.27 (t, ^{3}J = 8.0 Hz, 2H, aromatic proton). ^{13}C NMR δ 69.1, 126.7, 127.1, 128.9, 129.5, 141.3.

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