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Enantioselective Cu(II)-catalyzed Henry reactions with chiral cyclohexane-based amidophosphine ligands

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ABSTRACT

Copper-catalyzed asymmetric Henry reactions are described. Using a new chiral amidophosphine ligand, the Henry reaction of nitromethane and various aldehydes proceeded smoothly to provide chiral β-nitroalcohols in reasonable yields (up to 98%) with high enantioselectivity (up to 97% ee).

1. Introduction

The Henry reaction, which is a nucleophilic addition of nitroalkanes to carbonyl compounds, is a useful C–C bond formation reaction. The produced β-nitroalcohols can be easily transformed to a variety of valuable synthetic intermediates such as amino alcohols, carboxylic acids and aldehydes.[1] Since Shibasaki et al.[2] reported the first example of an asymmetric Henry reaction in 1992, impressive progress has been made on the exploration of chiral organometallic and organic catalysts for this asymmetric reaction.[3] Among them, the copper-based catalyst systems have received much attention due to the low toxicity, low cost and good chelating properties. Although nitrogen- and phosphine-containing ligands are attractive in the field of asymmetric catalysis,[4] to our knowledge, there has been only one example of the chiral N,P-ligand-copper catalyzed Henry reaction. In 2007, Shi et al.[5] described a Cu(I)-catalyzed Henry reaction using chiral BINOL-derived phosphine-salen type ligands, achieving up to 80% ee. Therefore, the exploration of new and efficient chiral N,P-ligands for the copper-catalyzed Henry reaction is still in demand.

It is well known that the *trans*-1,2-cyclohexane scaffold is one of the most popular chiral backbones in chiral ligands and chiral organocatalysts. Among the impressive advances in the development of nitrogen- and phosphine-containing ligands based on the *trans*-1,2-cyclohexane fragment, considerable effort has been focused on the derivatization of chiral *trans*-1,2-diaminocyclohexane, in particular the Trost ligands.[6] On the other hand, the chiral cyclohexane-based bidentate or tridentate P,N-ligands have been poorly developed (Fig. 1), and these ligands were used in asymmetric allylic alkylation and hygrogenation.[7] Additionally, Toste et al. have developed a monophosphine gold(I) catalyst based on the chiral cyclohexane backbone for asymmetric three-component reactions.[8] To the best of our knowledge, the use of chiral cyclohexane-based P,N-ligands in the copper-catalyzed reaction or Henry reaction has not been described.

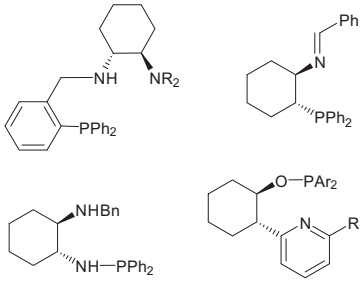

Figure 1. The reported chiral cyclohexane-based bidentate and tridentate P,N-ligands.

In our recent studies on asymmetric organocatalysis, we have found that the chiral cyclohexane-based amide-phosphines are efficient for [4+2] cycloaddition.[9] Our new approach is to develop novel amidophosphine ligands derived from chiral compound **L1** and its enantiomer (Fig. 2). As mentioned above, the copper-catalyzed Henry reaction is selected to evaluate the chiral ligands. Herein, we report our preliminary results on the synthesis of novel amidophosphine ligands and their application to the asymmetric Henry reaction.

2. Results and discussion

2.1. Synthesis of the chiral ligands

Ligand **L1** and its enantiomer were synthesized according to the reported procedure.[7b,10] Amidophosphine **L2** was prepared by the

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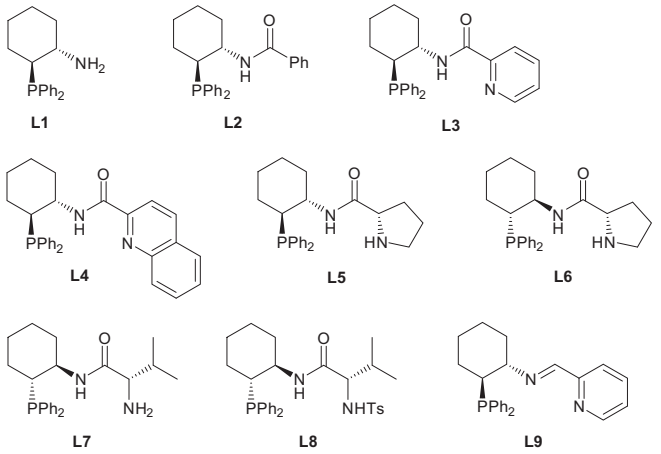
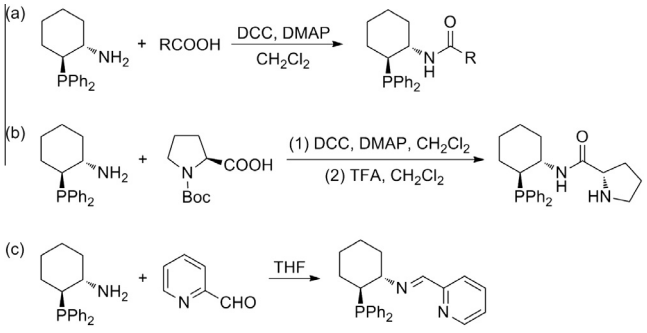


Figure 2. The structures of the chiral phosphine ligands.

condensation reaction between **L1** and benzoyl chloride.[11] Amidophosphine **L3**–**L8** were prepared via the condensation reaction between **L1** or its enantiomer and the corresponding carboxylic acids,[9] and a further deprotecting step was carried out to obtain ligands **L5**–**L7** (Scheme 1). Iminophosphine **L9** was prepared by the condensation of **L1** with picolinaldehyde.

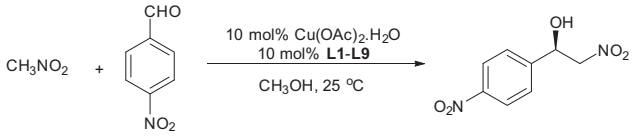


Scheme 1. Representative synthetic pathways for: (a) **L3** and **L4**; (b) **L5**; (c) **L9**.

2.2. Asymmetric Henry reaction

Initially, the enantioselective Henry reaction of nitromethane with 4-nitrobenzaldehyde was selected as the model reaction to test the catalytic performance of the new chiral ligands. The reactions were performed with 10 mol% of $Cu(OAc)_2{\cdot}H_2O$ and 10 mol% of ligands **L1**–**L9** in CH_3OH at 25 °C, and the results were summarized in Table 1. The results indicated that all the ligands gave good yields (81–98%) with different enantioselectivities. While aminophosphine **L1** and amidophosphine **L2** provided racemic products (entries 1 and 2), the iminophosphine **L9** displayed poor stereoselectivity (entry 9). With 2-picolinic acid derivative **L3** as the chiral ligand, the Cu(II)-catalyzed Henry reaction was achieved in 78% ee with 98% yield (entry 3). We observed a chiral match between the cyclohexane backbone and the amino acid scaffold, and ligand **L6** was more efficient than its diastereomer **L5** (entry 6 vs entry 5). According to the results shown in Table 1, ligand **L3** was selected for further experiments, and the related product was assigned the (*R*)-configuration by referring to the specific rotations in literature.[5]

Table 1
Screening of the chiral ligands for the asymmetric Henry reaction[a]

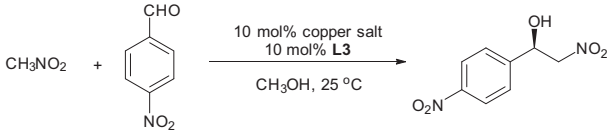


Entry	Ligand	Time (d)	Yield[b] (%)	ee[c] (%)
1	**L1**	2.5	91	0
2	**L2**	2.5	93	1
3	**L3**	1.5	98	78
4	**L4**	2.5	81	49
5	**L5**	1	96	33
6	**L6**	0.5	96	−48
7	**L7**	1.5	98	−29
8	**L8**	1	91	−24
9	**L9**	0.5	95	14

[a] The reactions were carried out with 4-nitrobenzaldehyde (0.2 mmol), nitromethane (0.6 mL), 10 mol% $Cu(OAc)_2{\cdot}H_2O$ and 10 mol% chiral ligand in 0.8 mL CH_3OH at 25 °C.
[b] Isolated yield.
[c] The ee values were determined by HPLC using a Chiralcel OD-H column.

Encouraged by these preliminary results, our attention was then focused on the screening of copper salts (Table 2). The results indicated that $Cu(OAc)_2{\cdot}H_2O$, $Cu(OAc)_2$ and $Cu(HCO_2)_2{\cdot}4H_2O$ were good promoters for the Henry reaction, giving high yields with 78% ee (entries 1–3). Although $Cu(acac)_2$, $Cu(CH_3CN)_4ClO_4$ and $Cu(CH_3CN)_4BF_4$ provided excellent yields, the enantioselectivities were poor (entries 4, 11 and 12). The Henry reaction in the presence of $CuSO_4$ was sluggish, and both the conversion and the enantioselectivity were unfavorable (entry 5). When $Cu(OTf)_2$, $Cu(NO_3)_2{\cdot}3H_2O$, $CuCl_2$ and $Cu(OTf){\cdot}0.5C_6H_6$ were used as the pre-catalyst, the acetal of 4-nitrobenzaldehyde was obtained instead of the corresponding β-nitroalcohol (entries 6–9). These results indicated that the copper salt played an important role in controlling the reaction rate, reaction selectivity and stereoselectivity. In terms of the yield and enantioselectivity, $Cu(OAc)_2{\cdot}H_2O$ was chosen as the copper source for subsequent reactions.

Table 2
Screening of copper salts for the asymmetric Henry reaction[a]

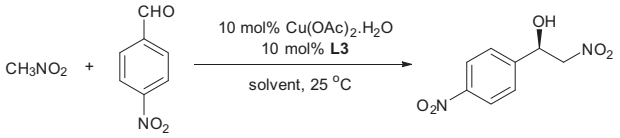


Entry	Copper salt	Time (d)	Yield[b] (%)	ee[c] (%)
1	$Cu(OAc)_2{\cdot}H_2O$	1.5	98	78
2	$Cu(OAc)_2$	2	98	78
3	$Cu(HCO_2)_2{\cdot}4H_2O$	1.5	95	78
4	$Cu(acac)_2$	0.3	99	2
5	$CuSO_4$	3	33	38
6	$Cu(OTf)_2$	1	nd[d]	–
7	$Cu(NO_3)_2{\cdot}3H_2O$	1	nd[d]	–
8	$CuCl_2$	1	nd[d]	–
9	$Cu(OTf){\cdot}0.5C_6H_6$	3	nd[d]	–
10	CuI	2.5	76	37
11	$Cu(CH_3CN)_4ClO_4$	1	99	10
12	$Cu(CH_3CN)_4BF_4$	1.5	91	12

[a] The reactions were carried out with 4-nitrobenzaldehyde (0.2 mmol), nitromethane (0.6 mL), 10 mol% copper salt and 10 mol% **L3** in 0.8 mL CH_3OH at 25 °C.
[b] Isolated yield.
[c] The ee values were determined by HPLC using a Chiralcel OD-H column.
[d] The desired products were not detected, and the acetal of 4-nitrobenzaldehyde was obtained.

Next, the reaction solvent was surveyed (Table 3). In all the solvents screened except toluene and $CHCl_3$, good yields were achieved (86–99% ee, entries 2 and 4–15). The lower yields in toluene and $CHCl_3$ were a result of the lower conversion. The Henry reaction in DMSO and CH_3CN resulted in poor enantioselectivities (entries 9 and 10). Among all the solvents in Table 3, *t*-BuOH provided the highest enantioselectivity. Therefore, *t*-BuOH was chosen as the solvent to carry out additional experiments.

Table 3
Screening of solvents in the asymmetric Henry reaction[a]

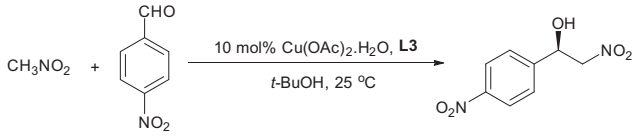


Entry	Solvent	Time (d)	Yield[b] (%)	ee[c] (%)
1	Toluene	3	51	75
2	CH_2Cl_2	3	87	77
3	$CHCl_3$	3	46	78
4	Et_2O	2.5	95	73
5	THF	2	95	75
6	EtOAc	3	92	77
7	Acetone	2.5	98	74
8	CH_3NO_2	3	86	72
9	DMSO	0.5	98	10
10	CH_3CN	3	96	48
11	CH_3OH	1.5	98	78
12	EtOH	1.5	99	75
13	*i*-PrOH	1.5	99	81
14	*i*-BuOH	1.5	99	78
15	*t*-BuOH	1.5	99	83

[a] The reactions were carried out with 4-nitrobenzaldehyde (0.2 mmol), nitromethane (0.6 mL), 10 mol% $Cu(OAc)_2{\cdot}H_2O$ and 10 mol% **L3** in 0.8 mL solvent at 25 °C.
[b] Isolated yield.
[c] The ee values were determined by HPLC using a Chiralcel OD-H column.

With *t*-BuOH as solvent, the reaction conditions including the substrate concentration, the catalyst loading and the reaction temperature were investigated (Table 4). The results indicated that similar yields were produced within a substrate concentration range of 0.05–0.35 M (regarding the volume of *t*-BuOH), while an obvious decrease of the enantioselectivity was observed with 0.35 M (entries 2–4 vs 1). Subsequently, the ratio of ligand **L3** to $Cu(OAc)_2{\cdot}H_2O$ was examined, and the amount of $Cu(OAc)_2{\cdot}H_2O$ was kept consistent at 10 mol%. When the loading of ligand **L3** was reduced to 5 mol%, a long reaction time was needed to complete the Henry reaction (entry 5 vs entry 2). When the ratio of **L3** to $Cu(OAc)_2{\cdot}H_2O$ was changed to 1.5:1 or 2:1, the reaction rate was improved, but the enantioselectivity decreased remarkably (entries 6 and 7). These results are in agreement with Yudin's observation on Pd-catalyzed allylic substitution using cyclohexane-based iminophosphine ligands.[7c] When the catalyst loading was reduced to 5 mol% (1:1 **L3** to copper), similar results were obtained with a longer reaction time (entry 8 vs entry 2). Increasing the temperature to 40 °C accelerated the Henry reaction rate, while the enantioselectivity was notably decreased (entry 10 vs entry 2). Because of the melting point of *t*-BuOH, the reaction at 0 °C was performed in *i*-PrOH. Although a slightly higher enantioselectivity was exhibited, the Henry reaction became sluggish at 0 °C (entry 9 vs entry 13 in Table 3).

Table 4
Further optimization of the reaction conditions[a]

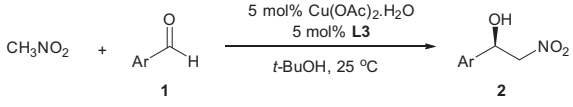


Entry	**L3** (mol%)	Concn (M)	Time (d)	Yield[b] (%)	ee[c] (%)
1	10	0.35	1.5	98	73
2	10	0.25	1.5	98	83
3	10	0.15	2.5	96	84
4	10	0.05	4.5	98	84
5	5	0.25	3	87	83
6	15	0.25	1.1	99	22
7	20	0.25	0.8	99	13
8[d]	5	0.25	3	98	85
9[e]	10	0.25	3.5	38	87
10[f]	10	0.25	1	99	58
11[g]	10	0.25	1	99	53

[a] Unless stated otherwise, the reactions were carried out with 4-nitrobenzaldehyde (0.2 mmol), nitromethane (0.6 mL), 10 mol% $Cu(OAc)_2{\cdot}H_2O$ in *t*-BuOH at 25 °C.
[b] Isolated yield.
[c] The ee values were determined by HPLC using a Chiralcel OD-H column.
[d] The amount of $(CuOAc)_2{\cdot}H_2O$ was 5 mol%.
[e] The reaction was performed at 0 °C in *i*-PrOH.
[f] The reaction was performed at 40 °C.
[g] The reaction was performed at 40 °C in *i*-PrOH.

With the optimal reaction conditions in hand [5 mol% $Cu(OAc)_2{\cdot}H_2O$ and 5 mol% **L3** in 0.8 mL *t*-BuOH (0.2 mmol scale) at 25 °C], the scope of substrates was examined (Table 5). A variety of aromatic aldehydes were employed as electrophiles to react with nitromethane, giving the corresponding β-nitroalcohols in moderate-to-excellent yields and good enantioselectivities (81–97% ee). Benzaldehydes containing electron-withdrawing groups have been proven to be more reactive than benzaldehyde

Table 5
Substrate scope of the enantioselective Henry reaction[a]



Entry	Ar	Time (d)	Yield[b] (%)	ee[c] (%)
1	4-$NO_2C_6H_4$	3	98 **2a**	85
2	3-$NO_2C_6H_4$	4	94 **2b**	81
3	2-$NO_2C_6H_4$	4	93 **2c**	84
4	4-$CF_3C_6H_4$	4	85 **2d**	88
5	4-CNC_6H_4	4	68 **2e**	87
6	4-BrC_6H_4	5	53 **2f**	86
7	4-ClC_6H_4	4	71 **2g**	89
8	4-FC_6H_4	4	62 **2h**	91
9	C_6H_5	4	27 **2i**	88
10[d]	C_6H_5	5	66 **2i**	88
11[d]	4-MeC_6H_4	5	54 **2j**	89
12[d]	3-MeC_6H_4	5	52 **2k**	89
13[d]	2-MeC_6H_4	5	60 **2l**	89
14[d]	4-PhC_6H_4	6	82 **2m**	85
15	Naphthalen-1-yl	6	77 **2n**	84
16	Naphthalen-2-yl	6	73 **2o**	85
17	2,3-$Cl_2C_6H_3$	5	97 **2p**	88
18	2,6-$Cl_2C_6H_3$	5	89 **2q**	97
19	(*E*)-C_6H_5CH = CH	6	64 **2r**	69

[a] Unless stated otherwise, the reactions were carried out with aldehyde (0.2 mmol), nitromethane (0.6 mL), 5 mol% $Cu(OAc)_2{\cdot}H_2O$ and 5 mol% **L3** in 0.8 mL *t*-BuOH at 25 °C.
[b] Isolated yield.
[c] The ee values were determined by HPLC using a Daicel Chiralcel OD-H.
[d] 10 mol% $(CuOAc)_2{\cdot}H_2O$ and 10 mol% **L3** were used.

and 4-methyl benzaldehyde, and better yields were obtained (entries 1–8 vs 9–13). Notably, 2-nitrobenzaldehyde could provide excellent yield and good enantioselectivity (entry 3). With 10 mol% of $(CuOAc)_2{\cdot}H_2O$ and **L3**, the Henry reaction between nitromethane and 4-phenylbenzaldehyde provided 82% yield and 85% ee (entry 14). 1-Naphthaldehyde and 2-naphthaldehyde proceeded well to afford the desired products in moderate yields and good enantioselectivities (entries 15 and 16). In addition, dichloro-substituted benzaldehydes gave high yields and stereoselectivities (entries 17 and 18). Moreover, the α,β-unsaturated aldehyde such as cinnamaldehyde gave the corresponding product in 64% yield with 69% ee (entry 19). Furthermore, different nitroalkanes were tested with 4-nitrobenzaldehyde as the electrophile under the typical reaction conditions (Fig. 3). Unfortunately, both the diastereoselectivity and the enantioselectivity were unsatisfactory. More efficient catalytic system should thus be explored for these nitroalkanes.

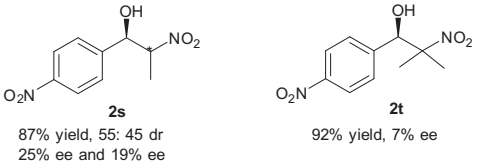


Figure 3. The Henry reaction of nitroalkanes.

We have tried but failed to get a single crystal of the Cu(II)–**L3** complex, so the real active species is not yet fully understood in this catalytic asymmetric Henry reaction. According to the literature concerning Cu(II)-catalyzed enantioselective Henry reactions,[12] a plausible transition state was proposed as shown in Figure 4. The ligand **L3** might be tridentate. The benzaldehyde should be positioned in one of the Lewis acidic equatorial sites for maximal activation. The Henry reaction does not need an external base, suggesting that a weakly Lewis acidic metal complex facilitates the deprotonation of nitroalkane. In the depicted transition state, the nitronate would attack the activated aldehyde from the *Si*-face to form the Henry adduct with an (*R*)-configuration.

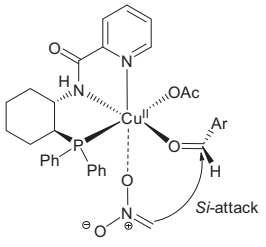


Figure 4. A plausible transition state of the asymmetric Henry reaction.

3. Conclusion

In conclusion, seven new phosphine- and nitrogen-containing ligands **L3**–**L9** were successfully synthesized and employed in the asymmetric Henry reaction. In the presence of the copper(II) complex with chiral ligand **L3**, the Henry reaction was achieved in moderate to excellent yields (up to 98%) and good to excellent enantioselectivities (up to 97% ee) under mild conditions. X-ray crystallographic analysis of the copper complexes and the extension of these chiral ligands to other asymmetric reactions are currently underway in our laboratory.

4. Experimental

4.1. General

All reactions were carried out under N_2 atmosphere using standard Schlenk techniques with magnetic stirring. Anhydrous solvents were distilled from CaH_2 (dichloromethane, chloroform, ethyl acetate, acetonitrile), sodium (CH_3OH, EtOH, *i*-PrOH, *t*-BuOH), or sodium-benzophenone (toluene, ether, THF). Anhydrous DMSO was dried over CaH_2 and distilled under reduced pressure. All aldehydes and nitroalkanes were commercially available and purified by standard methods. Thin-layer chromatography (TLC) was performed on Silicycle 10–40 μm silica gel plates. Column chromatography was performed using silica gel (300–400 mesh) eluting with petroleum ether and ethyl acetate.

Melting points were taken without correction. Optical rotations were measured on a WZZ-2A digital polarimeter at the wavelength of the sodium D-line (589 nm). IR spectra were recorded on Nicolet Magna-I 550 spectrometer. The NMR spectra were recorded on Bruker 400 spectrometer. The chemical shifts of ^{1}H NMR spectra were referenced to tetramethylsilane (δ 0.00) using $CDCl_3$ as solvent. The chemical shifts of ^{31}P NMR spectra were referenced to 85% H_3PO_4 (0.0 ppm). High Resolution Mass spectra (HRMS) were recorded on Micromass GCT with Electron Spray Ionization (ESI) resource. HPLC analysis was performed on Waters equipment using Daicel Chiralcel OD-H or Chiralpak IC-H column.

Ligands **L1**[7b,10] and **L2**[11] were prepared according to literature procedures.

4.2. Synthesis of chiral ligands L3–L8

To a solution of **L1** or its enantiomer (0.35 mmol) in dry CH_2Cl_2 (6 mL), dicyclohexylcarbodiimide (0.39 mmol), carboxylic acid or *N*-protected amino acid (0.44 mmol) and DMAP (0.11 mmol) were added, respectively. Then the reaction mixture was stirred at 25 °C under N_2 atmosphere for 2–6 h (monitoring by TLC). After the reaction was completed, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel to afford the amidophosphine compounds.

For preparing ligands **L5**–**L7**, a mixture of 1:1 CH_2Cl_2/TFA (12 mL) was added to the *N*-Boc amidophosphine, and the solution was stirred at 25 °C for 3 h under N_2 atmosphere. Then the reaction mixture was neutralized with aqueous $NaHCO_3$ to pH ca. 9, and it was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by a flash column chromatography on silica gel to afford the deprotected products.

4.2.1. *N*-((1*S*,2*S*)-2-(Diphenylphosphino)cyclohexyl)picolinamide L3

White solid, 91% yield, mp 52.9–53.7 °C, $[\alpha]_D^{25}$ = + 89.1 (*c* 0.74, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.35 (d, 1H, *J* = 4.4 Hz), 8.14 (d, 1H, *J* = 8.0 Hz), 8.05 (d, 1H, *J* = 8.8 Hz), 7.73 (t, 1H, *J* = 7.6 Hz), 7.56–7.48 (m, 4H), 7.31–7.26 (m, 4H), 7.23–7.19 (m, 2H), 7.15–7.12 (m, 1H), 4.11–4.03 (m, 1H), 2.55–2.51 (m, 1H), 2.21–2.18 (m, 1H), 1.82–1.74 (m, 3H), 1.51–1.26 (m, 3H), 1.16–1.08 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 162.9, 149.8, 147.7, 137.0, 136.8 (d, *J* = 13.2 Hz), 135.9 (d, *J* = 16.1 Hz), 134.3 (d, *J* = 20.7 Hz), 132.8 (d, *J* = 18.7 Hz), 128.7, 128.2 (d, *J* = 6.4 Hz), 128.1 (d, *J* = 7.5 Hz), 127.9, 125.7, 122.0, 50.2 (d, *J* = 16.6 Hz), 40.1 (d, *J* = 15.3 Hz), 33.3 (d, *J* = 7.0 Hz), 27.3 (d, *J* = 5.5 Hz), 25.3 (d, *J* = 5.5 Hz), 24.4; ^{31}P NMR ($CDCl_3$, 122 MHz, 85% H_3PO_4): −8.94; IR (KBr, cm^{-1}): *ν* 2933, 2859, 1677, 1519, 1430, 749, 697, 659, 614, 510; HRMS (ESI) calcd for $C_{24}H_{26}N_2OP$ ($[M+H]^+$): 389.1777, found: 389.1788.

4.2.2. *N*-((1*S*,2*S*)-2-(Diphenylphosphino)cyclohexyl)quinoline-2-carboxamide L4

White solid, 94% yield, mp 64.1–65.2 °C, $[\alpha]_D^{25}$ = +204.4 (*c* 0.77, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 8.26 (d, 1H, *J* = 8.4 Hz), 8.23 (d, 1H, *J* = 8.4 Hz), 8.17 (d, 1H, *J* = 8.8 Hz), 7.98 (d, 1H, *J* = 8.4 Hz), 7.83 (d, 1H, *J* = 8.0 Hz), 7.72 (t, 1H, *J* = 7.6 Hz), 7.60–7.50 (m, 5H), 7.33–7.25 (m, 3H), 7.12 (t, 1H, *J* = 7.6 Hz), 6.94–6.90 (m, 1H), 4.20–4.11 (m, 1H), 2.64–2.59 (m, 1H), 2.28–2.17 (m, 1H), 1.84–1.79 (m, 3H), 1.61–1.32 (m, 3H), 1.21–1.13 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ*: 163.0, 149.5, 146.1, 137.0, 136.8 (d, *J* = 13.1 Hz), 136.0 (d, *J* = 15.8 Hz), 134.2 (d, *J* = 20.6 Hz), 132.8 (d, *J* = 19.1 Hz), 129.7 (d, *J* = 14.5 Hz), 129.0, 128.7, 128.2 (×2), 128.1, 128.1, 127.9, 127.5, 118.7, 50.7 (d, *J* = 17.0 Hz), 40.3 (d, *J* = 15.5 Hz), 33.5 (d, *J* = 6.9 Hz), 27.6 (d, *J* = 5.7 Hz), 25.4 (d, *J* = 5.5 Hz), 24.6; ^{31}P NMR ($CDCl_3$, 122 MHz, 85% H_3PO_4): −8.80; IR (KBr, cm^{-1}): *ν* 2933, 2851, 1669, 1527, 1505, 1430, 1273, 847, 741, 697; HRMS (ESI) calcd for $C_{28}H_{28}N_2OP$ ($[M+H]^+$): 439.1934, found: 439.1944.

4.2.3. (*S*)-*N*-((1*S*,2*S*)-2-(Diphenylphosphino)cyclohexyl)pyrrolidine-2-carboxamide L5

White solid, 83% total yield, mp 166.2–167.1 °C, $[\alpha]_D^{25}$ = −10.4 (*c* 0.70, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.78 (d, 1H, *J* = 9.2 Hz), 7.52 (t, 2H, *J* = 6.8 Hz), 7.42–7.33 (m, 4H), 7.31–7.25 (m, 4H), 3.73–3.67 (m, 1H), 3.63 (dd, 1H, J_1 = 9.2 Hz, J_2 = 5.6 Hz), 2.89–2.84 (m, 1H), 2.74–2.68 (m, 1H), 2.34–2.30 (m, 1H), 2.12–2.03 (m, 2H), 1.94–1.86 (m, 2H), 1.70–1.52 (m, 5H), 1.38–1.23 (m, 3H), 1.00–0.91 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 173.9, 137.1 (d, *J* = 13.6 Hz), 135.5 (d, *J* = 17.6 Hz), 134.6 (d, *J* = 20.7 Hz), 132.2 (d, *J* = 17.3 Hz), 128.6, 128.2 (d, *J* = 5.6 Hz), 127.9 (d, *J* = 7.6 Hz), 127.7, 60.6, 49.3 (d, *J* = 16.6 Hz), 47.0, 39.8 (d, *J* = 15.6 Hz), 33.5 (d, *J* = 6.8 Hz), 30.5, 27.1, 26.0, 25.4 (d, *J* = 3.3 Hz), 24.4; ^{31}P NMR ($CDCl_3$, 162 MHz, 85% H_3PO_4): −8.32; IR (KBr, cm^{-1}): *ν* 3307, 2941, 2851, 1669, 1430, 1101, 749, 697, 487; HRMS (ESI) calcd for $C_{23}H_{30}N_2OP$ ($[M+H]^+$): 381.2090, found: 381.2101.

4.2.4. (*S*)-*N*-((1*R*,2*R*)-2-(Diphenylphosphino)cyclohexyl)pyrrolidine-2-carboxamide L6

White solid, 89% total yield, mp 164.8–165.3 °C, $[\alpha]_D^{25}$ = −78.2 (*c* 0.75, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.76 (d, 1H, *J* = 8.8 Hz), 7.52 (t, 2H, *J* = 6.8 Hz), 7.43–7.34 (m, 4H), 7.32–7.27 (m, 4H), 3.74–3.67 (m, 1H), 3.64 (dd, 1H, J_1 = 9.2 Hz, J_2 = 5.6 Hz), 2.91–2.86 (m, 1H), 2.75–2.69 (m, 1H), 2.32 (t, 1H, *J* = 10.0 Hz), 2.14–2.05 (m, 2H), 1.94–1.86 (m, 2H), 1.71–1.54 (m, 5H), 1.39–1.24 (m, 3H), 1.00–0.91 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 174.0, 137.2 (d, *J* = 13.5 Hz), 135.6 (d, *J* = 17.6 Hz), 134.6 (d, *J* = 20.6 Hz), 132.3 (d, *J* = 17.4 Hz), 128.7, 128.3 (d, *J* = 5.6 Hz), 128.0 (d, *J* = 7.5 Hz), 127.8, 60.7, 49.4 (d, *J* = 16.7 Hz), 47.1, 39.9 (d, *J* = 15.6 Hz), 33.6 (d, *J* = 7.0 Hz), 30.6, 27.2, 26.1 (d, *J* = 1.4 Hz), 25.5 (d, *J* = 3.8 Hz), 24.5; ^{31}P NMR ($CDCl_3$, 162 MHz, 85% H_3PO_4): −7.71; IR (KBr, cm^{-1}): *ν* 3309, 2935, 2851, 1669, 1430, 1101, 751, 697, 487; HRMS (ESI) calcd for $C_{23}H_{30}N_2OP$ ($[M+H]^+$): 381.2090, found: 381.2096.

4.2.5. (*S*)-2-Amino-*N*-((1*R*,2*R*)-2-(diphenylphosphino)cyclohexyl)-3-methylbutanamide L7

White solid, 79% total yield, mp 51.2–51.9 °C, $[\alpha]_D^{25}$ = −38.9 (*c* 0.90, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) *δ*: 7.60 (t, 2H, *J* = 6.9 Hz), 7.52–7.42 (m, 2H), 7.39–7.26 (m, 6H), 7.19 (d, 1H, *J* = 9.0 Hz), 4.01–3.88 (m, 1H), 3.00 (d, 1H, *J* = 3.0 Hz), 2.37–2.27 (m, 1H), 2.27–2.17 (m 1H), 2.05–2.00 (m, 1H), 1.71–1.64 (m, 3H), 1.43–1.00 (m, 7H), 0.92 (d, 3H, *J* = 6.9 Hz), 0.75 (d, 3H, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 172.6, 137.8 (d, *J* = 13.9 Hz), 135.9 (d, *J* = 15.8 Hz), 134.2 (d, *J* = 20.6 Hz), 133.0 (d, *J* = 19.1 Hz), 128.7, 128.3 (d, *J* = 6.5 Hz), 128.1 (d, *J* = 7.6 Hz), 59.6, 50.1 (d, *J* = 16.8 Hz), 40.4 (d, *J* = 15.3 Hz), 34.5 (d, *J* = 7.6 Hz), 30.6, 27.9 (d, *J* = 5.8 Hz), 25.6 (d, *J* = 5.7 Hz), 24.7, 19.6, 15.7; ^{31}P NMR ($CDCl_3$, 122 MHz, 85% H_3PO_4): −7.64; IR (KBr, cm^{-1}): *ν* 3323, 2941, 2859, 1662, 1512, 1437, 1079, 741, 697, 502; HRMS (ESI) calcd for $C_{23}H_{32}N_2OP$ ($[M+H]^+$): 383.2247, found: 383.2249.

4.2.6. (*S*)-*N*-((1*R*,2*R*)-2-(Diphenylphosphino)cyclohexyl)-3-methyl-2-(4-methylphenylsulfonamido)butan-amide L8

White solid, 92% yield, mp 96.1–98.3 °C, $[\alpha]_D^{25}$ = −19.1 (*c* 0.98, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.74 (d, 2H, *J* = 8.0 Hz), 7.46 (t, 2H, *J* = 6.8 Hz), 7.39–7.27 (m, 8H), 7.22 (d, 2H, *J* = 8.4 Hz), 6.16 (d, 1H, *J* = 8.4 Hz), 5.29 (d, 1H, *J* = 7.6 Hz), 3.72–3.64 (m, 1H), 3.47 (dd, 1H, J_1 = 7.6 Hz, J_2 = 4.4 Hz), 2.26 (s, 3H), 2.20 (td, 1H, J_1 = 10.4 Hz, J_2 = 2.4 Hz,), 2.04–1.98 (m, 2H), 1.70–1.55 (m, 3H), 1.26–1.14 (m, 3H), 0.94–0.85 (m, 1H), 0.79 (d, 3H, *J* = 6.8 Hz), 0.72 (d, 3H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 169.0, 143.4, 136.8 (d, *J* = 13.7 Hz), 136.6, 135.4 (d, *J* = 17.0 Hz), 134.2 (d, *J* = 20.5 Hz), 132.5 (d, *J* = 18.1 Hz), 129.6, 128.8, 128.6 (d, *J* = 5.9 Hz), 128.2, 128.0 (d, *J* = 7.4 Hz), 127.1, 61.7, 51.0 (d, *J* = 16.8 Hz), 39.1 (d, *J* = 16.1 Hz), 33.0 (d, *J* = 6.1 Hz), 31.2, 27.1, 25.2, 24.1, 21.3, 19.0, 16.8; ^{31}P NMR ($CDCl_3$, 122 MHz, 85% H_3PO_4): −8.61; IR (KBr, cm^{-1}): *ν* 3277, 2933, 1662, 1535, 1445, 1333, 1153, 1093, 741, 697, 659, 555; HRMS (ESI) calcd for $C_{30}H_{38}N_2O_3PS$ ($[M+H]^+$): 537.2335, found: 537.2342.

4.3. Synthesis of chiral ligand L9

To a solution of **L1** (0.35 mmol) in 3 mL dry THF, the picolinaldehyde (0.39 mmol) was added dropwise. Then the reaction mixture was stirred at 25 °C under N_2 atmosphere for 2 h (monitoring by TLC). After the reaction was completed, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on alumina to afford compound **L9**.

Yellow oil, 89% yield, $[\alpha]_D^{25}$ = +189.5 (*c* 1.08, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 8.43 (d, 1H, *J* = 4.4 Hz), 8.19 (s, 1H), 7.42–7.35 (m, 5H), 7.30 (d, 1H, *J* = 7.6 Hz), 7.17 (br s, 3H), 7.10–6.99 (m, 4H), 3.30–3.23 (m, 1H), 2.66–2.61 (m, 1H), 1.73–1.55 (m, 5H), 1.28–1.17 (m, 2H), 1.10–1.01 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 160.3, 154.3, 148.7, 137.5 (d, *J* = 12.4 Hz), 136.4 (d, *J* = 14.7 Hz), 135.9, 134.5 (d, *J* = 20.8 Hz), 133.0 (d, *J* = 18.8 Hz), 128.6, 127.9 (d, *J* = 7.7 Hz), 127.7 (d, *J* = 6.6 Hz), 127.5, 124.2, 121.1, 73.1 (d, *J* = 15.6 Hz), 39.9 (d, *J* = 13.2 Hz), 34.8 (d, *J* = 8.4 Hz), 27.2 (d, *J* = 7.0 Hz), 25.8 (d, *J* = 6.5 Hz), 24.3; ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): −5.01; IR (KBr, cm^{-1}): *ν* 3052, 2930, 2853, 1644, 1586, 1467, 1434, 740, 690, 511; HRMS (ESI) calcd for $C_{24}H_{26}N_2P$ ($[M+H]^+$): 373.1828, found: 373.1821.

4.4. General procedure for the asymmetric Henry reaction

A flame-dried Schlenk tube was charged with **L3** (0.01 mmol) in dry *t*-BuOH (0.8 mL), $Cu(OAc)_2{\cdot}H_2O$ (0.01 mmol) was added and the mixture was stirred at 25 °C under N_2 atmosphere for 30 min. To the resulting solution was added nitromethane (0.6 mL) by a syringe. Then the reaction mixture was stirred for an additional 10 min, and the aldehyde (0.2 mmol) was added. The reaction mixture was stirred at 25 °C (monitoring by TLC). After the reaction was completed, the reaction mixture was filtered through silica gel pad and rinsed with EtOAc. After concentrating under reduced pressure, the residue was purified by column chromatography on silica gel to afford the β-nitroalcohols. The ee values were determined by HPLC analysis with a chiral column.

4.4.1. (*R*)-2-Nitro-1-(4-nitrophenyl)ethanol 2a

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 85/15, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 19.77 min (major), 24.70 min (minor), 85% ee.

4.4.2. (*R*)-2-Nitro-1-(3-nitrophenyl)ethanol 2b

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 85/15, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 21.35 min (major), 24.56 min (minor), 81% ee.

4.4.3. (*R*)-2-Nitro-1-(2-nitrophenyl)ethanol 2c

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 85/15, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 12.83 min (major), 14.16 min (minor), 84% ee.

4.4.4. (*R*)-2-Nitro-1-(4-(trifluoromethyl)phenyl)ethanol 2d

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 14.35 min (major), 18.47 min (minor), 88% ee.

4.4.5. (*R*)-4-(1-Hydroxy-2-nitroethyl)benzonitrile 2e

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 85/15, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 23.36 min (major), 27.77 min (minor), 87% ee.

4.4.6. (*R*)-1-(4-Bromophenyl)-2-nitroethanol 2f

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 22.67 min (major), 30.69 min (minor), 86% ee.

4.4.7. (*R*)-1-(4-Chlorophenyl)-2-nitroethanol 2g

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 18.77 min (major), 23.85 min (minor), 89% ee.

4.4.8. (*R*)-1-(4-Fluorophenyl)-2-nitroethanol 2h

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 15.71 min (major), 18.99 min (minor), 91% ee.

4.4.9. (*R*)-2-Nitro-1-phenylethanol 2i

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 21.01 min (major), 26.38 min (minor), 88% ee.

4.4.10. (*R*)-2-Nitro-1-(*p*-tolyl)ethanol 2j

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 85/15, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 12.27 min (major), 15.43 min (minor), 89% ee.

4.4.11. (*R*)-2-Nitro-1-(*m*-tolyl)ethanol 2k

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 85/15, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 11.45 min (major), 13.22 min (minor), 89% ee.

4.4.12. (*R*)-2-Nitro-1-(*o*-tolyl)ethanol 2l

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 85/15, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 11.24 min (major), 17.54 min (minor), 89% ee.

4.4.13. (*R*)-1-([1,1′-Biphenyl]-4-yl)-2-nitroethanol 2m

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 85/15, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 16.63 min (major), 20.10 min (minor), 85% ee.

4.4.14. (*R*)-1-(Naphthalen-1-yl)-2-nitroethanol 2n

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 85/15, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 14.43 min (major), 17.55 min (minor), 84% ee.

4.4.15. (*R*)-1-(Naphthalen-2-yl)-2-nitroethanol 2o

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 85/15, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 26.19 min (major), 36.23 min (minor), 85% ee.

4.4.16. (*R*)-1-(2,3-Dichlorophenyl)-2-nitroethanol 2p

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 14.76 min (major), 20.14 min (minor), 88% ee.

4.4.17. (*R*)-1-(2,6-Dichlorophenyl)-2-nitroethanol 2q

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 12.44 min (major), 14.24 min (minor), 97% ee.

4.4.18. (*R*,*E*)-1-Nitro-4-phenylbut-3-en-2-ol 2r

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 85/15, flow = 0.6 mL/min, and detected at a UV wave length of 215 nm. Retention times: 46.07 min (minor), 48.76 min (major), 69% ee.

4.4.19. (1*R*)-2-Nitro-1-(4-nitrophenyl)propan-1-ol 2s

The enantiomeric excess was determined on a Daicel Chiralpak IC–H column with hexane/2-propanol = 90/10, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 12.20 min (major), 14.34 min (minor) for one diastereoisomer, 19% ee; 19.72 min (minor), 21.58 min (major) for other diastereoisomer, 25% ee.

4.4.20. (*R*)-2-Methyl-2-nitro-1-phenylpropan-1-ol 2t

The enantiomeric excess was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 0.9 mL/min, and detected at a UV wave length of 220 nm. Retention times: 18.10 min (major), 22.28 min (minor), 7% ee.

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Supplementary data

Supplementary data (the copies of NMR spectra of chiral ligands **L3**–**L9** and HPLC spectra of the Henry products) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetasy.2016.07.015.

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