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Binaphthyl-based chiral ligands: design, synthesis and evaluation of their performance in enantioselective addition of diethylzinc to aromatic aldehydes†

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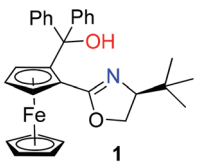
The design strategy and the performance of binaphthyl-based chiral ligands were evaluated with computation and enantioselective addition of diethylzinc to aromatic aldehydes. Under optimized conditions, enantioselective addition of diethylzinc to aromatic aldehydes provided the desired optically active secondary alcohols in high isolated yields (up to 91%) and excellent enantiomeric excesses (up to 98% ee).

1. Introduction

Chiral ligand design has been the focal point of asymmetric synthesis. To this end, significant efforts have been made towards the design of new chiral ligands for asymmetric reactions.[1] Among the variety of chiral ligands developed, binaphthyl-based chiral ligands have played important roles in a variety of asymmetric catalytic reactions. For examples, BINOL,[2] BINAM,[3] BINAP,[4] NOBIN,[5] binaphthyl dicarboxylic acid[6] and other binaphthyl-related structures have all been explored in both academia and industry[1b] (Fig. 1). Among these structures, BINOL can be regarded as a general starting material from which different chiral ligands/organocatalysts could be prepared.[2g,7] We are interested in expanding the structure diversity of binaphthyl-based compounds, and in developing new chiral ligands based on binaphthyl structures. Herein we wish to report our preliminary progress on design and evaluation of catalytic activity of several binaphthyl-based chiral ligands.

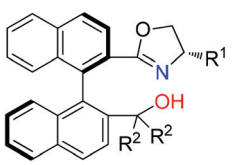
2. Results and discussion

The work was initiated from the structure modification of 1,1′-binaphthyl 2,2′-dicarboxylic acid. This compound was chosen as the starting material due to the fact that the derivatization of the carboxyl group was easy to carry out, and successful transformations would provide diversified functional groups such as different alcohols, amides or oxazolines. Integration of such functional groups in a single chiral molecule has been proved to be effective, and chiral ligand **1** has been successfully used in a variety of asymmetric catalytic reactions.[8]



1

On the basis of literature results and our understanding on the design of chiral ligands, compounds **2** bearing both hydroxyl and oxazoline groups were first proposed.



2

The synthesis of chiral ligands **2** started from racemic 1,1′-binaphthyl-2,2′-dicarboxylic acid **3**. A number of monooxazolines bearing binaphthyl backbone were prepared through a four-step reaction sequence (Scheme 1). Racemic 1,1′-biphenyl-2,2′-dicarboxylic acid was easily transformed into its monoester **4**, which could then react with different amino alcohols to generate amides **5**. At this stage, we were happy to find that, when (*R*)-2-amino-2-phenylethanol (D-phenylglycinol) was used, the diastereomers **5a** and **5b** were easy to separate, thus

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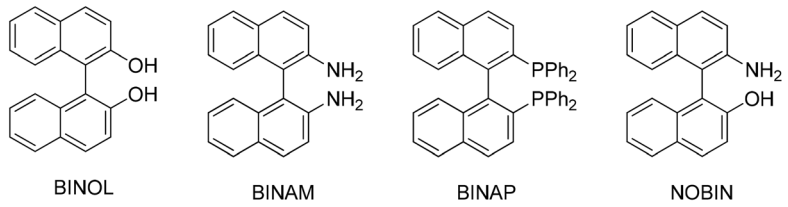
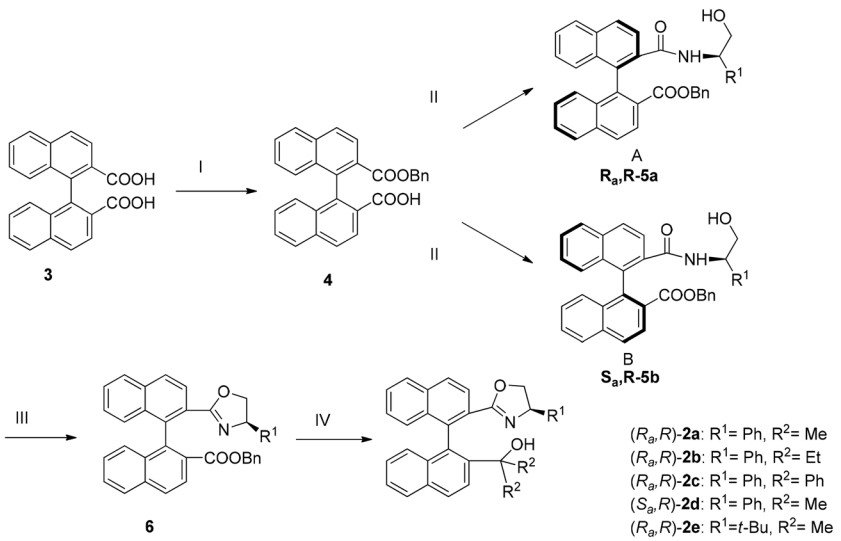


Fig. 1 Examples of successful binaphthyl-based chiral compounds.



Scheme 1 Synthesis of binaphthyl-based monooxazolines. Conditions: (I) K_2CO_3, BnBr, DMF, 60%; (II) (*R*)-phenylglycinol or (*R*)-*tert*-leucinol, EDCI, HOBT, Et_3N; DCM; 80–90%; (III) TsCl; DMAP; Et_3N; DCM; 90–95%; (IV) R^2MgBr, THF, 0 °C, 85–90%.

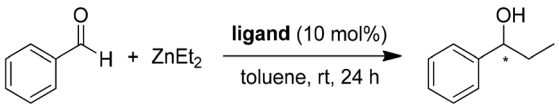
enabling a feasible resolution of 1,1′-biphenyl-2,2′-dicarboxylic acid in an easy-to-carry out manner. This may be due to the steric hindrance of the bulky functional groups in compounds **5**, which rendered the diasteromers **A** and **B** different enough to allow an easy column chromatography separation. The stereochemistry of compound **5** was also confirmed with X-ray diffraction experiment on (R_a,*R*)-**5a**.

In this regard, the diasteromers of both ligands can be prepared in large quantities from easily available racemic starting materials. Subsequently, compounds **5** were converted to oxazoline **6**, and reaction of **6** with the corresponding Grignard reagents furnished the preparation of chiral ligands **2a–2e**.

Next, the performance of compounds **2a–2e** were evaluated in enantioselective addition of diethylzinc to aldehydes. Since the pioneer work by Oguni and Omi in 1984,[9] huge amount of works concerning the enantioselective addition of dialkylzincs to aldehydes have been published, and a plethora of chiral ligands such as amino alcohols (*N,O*-ligands), diols (*O,O*-ligands), diamines (*N,N*-ligands) were developed.[2g,10] Such reactions can be carried out under mild conditions, giving the desired alcohols in good yields and high ee's. The well documented feature of the reaction made it an ideal model for the evaluation of the designing strategy as well as the performance of the newly designed chiral ligands.

In this regard, chiral ligands **2a–2e** were subjected to enantioselective addition of diethylzinc to benzaldehyde. The results are summarized in Table 1. All experiments were carried out in 0.5 mmol scale. Benzaldehyde (0.5 mmol) was added to a mixture of 10 mol% of chiral ligand and 2 equiv. of

Table 1 Enantioselective addition of diethylzinc to benzaldehyde promoted by chiral ligands **2a–2e**[a]



Entry	Ligand	Yield[b] (%)	ee[c] (%)	Config.[d]
1	**2a**	89	46	*R*
2	**2b**	77	40	*R*
3	**2c**	61	28	*R*
4	**2d**	53	25	*S*
5	**2e**	50	30	*R*

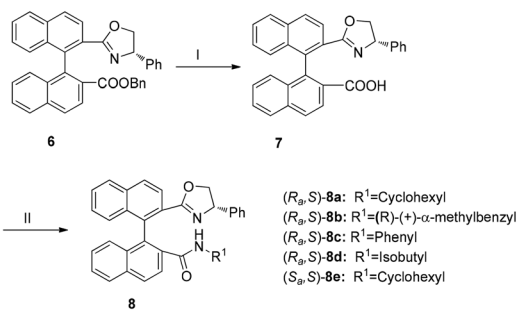
[a] Reaction conditions: Benzaldehyde (0.5 mmol) was added to a solution of the ligand (0.05 mmol) and Et_2Zn (1.0 mmol, 1 mL of 1 M toluene solution) in toluene (2.0 mL). Reaction time: 24 h. [b] Isolated yields. [c] The ee values were determined by HPLC (chiralcel OD-H column). [d] Absolute configuration was assigned by comparing the specific rotation with reported sign and value of the product.[8f]

Et_2Zn (1 M in toluene), and the desired product was isolated after 24 h. Preliminary results showed that ligands **2a** and **2d** provided products in opposite but different enantiomeric excesses, suggesting that binaphyl group was responsible for the enantioselection, and the axial and the central chirality should match with each other to get a meaningful stereoselectivity.

The results in Table 1 suggested that chiral ligands **2a–2e** were not so efficient in inducing enantioselective addition of diethylzinc to benzaldehyde. We reasoned that the low enantioselectivity should be due to the insufficient chirality induction feature of these chiral catalysts. To find new structures which may be more suitable for the asymmetric induction, a new type of chiral ligands **8a–8e** were proposed. We envisioned that replacing the tertiary alcohol with amide would give more diversified structures from which more potential chiral ligands could be expected (Scheme 2). Further, such ligands could be conveniently prepared from intermediate (R_a, *S*)-**6** through saponification and subsequent amide formation. Due to the availability of the chiral aminoalcohols, (*S*)-phenylglycinol was used instead of (*R*)-phenylglycinol in further study. The stereochemistry of the ligands were also established based on single crystal X-ray diffraction experiments on **8c** and **8e** (Fig. 2).

Again, the performance of compounds **8a–8e** were evaluated in enantioselective addition of diethylzinc to benzaldehyde. All experiments were carried out by adding 0.5 mmol of benzaldehyde to a mixture of 10 mol% of chiral ligand and 2 equiv. of Et_2Zn. The results are listed in Table 2.

The results in Table 2 suggested that, after preliminary optimization of the reaction conditions, compound **8a** gave product with highest ee. Addition of DiMPEG 2000 showed little effect on the stereo outcome of the reaction (entry 13).[11] The results from **8a** and **8e** also indicated the binaphyl moiety was responsible for the enantioselection, and the axial and central chirality should match with each other. However, none of the ee's in Tables 1 and 2 exceeded 90%, suggesting that the chiral transfer mediated by these chiral ligands was not so efficient. To get structural insights into the chiral induction, DFT calculation was carried out at M06-2X/SDD level.[12] To validate the method, results from DFT calculation and X-ray diffraction for **8c** were first compared (Fig. 3), and representative



Scheme 2 Synthesis of chiral ligands **8a–8e**. Conditions: (I) K_2CO_3, MeOH, 92%; (II) RNH_2, EDCI, HOBT, Et_3N; DCM; 50–95%.

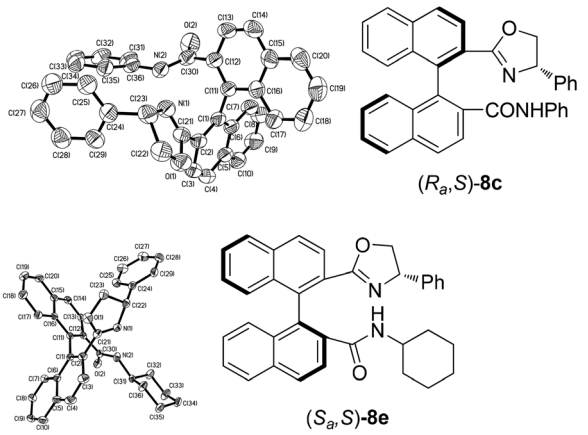
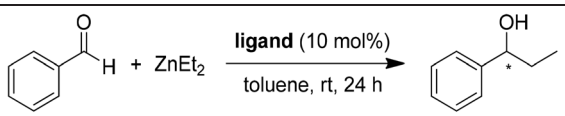


Fig. 2 ORTEP Drawings of compounds **8c** and **8e** at 30% displacement ellipsoid probability (the hydrogen atoms were omitted for clarity).

Table 2 Enantioselective addition of diethylzinc to benzaldehyde promoted by **8a–8e**[a]



Entry	Ligand	Yield[b] (%)	ee[c] (%)	Config.[d]
1	**8a**	87	68	*R*
2	**8b**	88	29	*R*
3	**8c**	26	24	*R*
4	**8d**	73	23	*R*
5	**8e**	76	45	*S*
6[e]	**8a**	85	80	*R*
7[f]	**8a**	73	60	*R*
8[e,g]	**8a**	89	82	*R*
9[e,h]	**8a**	75	73	*R*
10[e,i]	**8a**	50	23	*R*
11[e,j]	**8a**	80	67	*R*
12[g]	**8a**	86	82	*R*
13[g,k]	**8a**	88	83	*R*
14	7	78	0	—

[a] Reaction conditions: Benzaldehyde (0.5 mmol) was added to a solution of the ligand (0.05 mmol) and Et_2Zn (1.0 mmol, 1 mL of 1 M toluene solution) in toluene (2.0 mL). Reaction time: 24 h. [b] Isolated yields. [c] The ee values were determined by HPLC (chiralcel OD-H column). [d] Absolute configuration assigned by comparison to the literature.[8f,e] 5 mol% **8a** was used. [f] 2 mol% **8a** was used. [g] Reaction temperature = 0 °C. [h] Reaction temperature = −10 °C. [i] Solvent = *n*-hexane. [j] Solvent = DCM. [k] In the presence of DiMPEG 2000 (10 mol%).

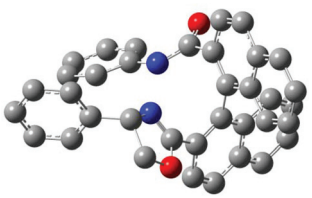


Fig. 3 Computer model of **8c** at M06-2X/SDD level.

Table 3 Comparison of calculated and X-ray diffraction results of **8c**

Parameters	Calculated	Found
Dihedral angle		
C(2)–C(1)–C(11)–C(12)	−101.33239	−101.22942
C(11)–C(12)–C(30)–O(2)	−119.97215	−119.39080
C(11)–C(12)–C(30)–N(2)	63.21263	65.73975
Hydrogen bond		
N···H	2.06454	2.08207
Bond angle		
O(1)–C(21)–N(1)	116.03199	118.31333

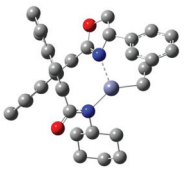


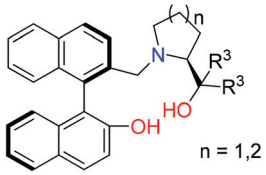
Fig. 4 Computer model of **8a**-Zn at M06-2X/SDD level.

data in Table 3 suggested that the calculated structure was very close to X-ray diffraction structure in respect to the torsion of the binaphyl structure, the torsion of the amide bond, the structure of the oxazoline as well as the hydrogen bond between the amide hydrogen and the nitrogen atom in the oxazoline (Table 3).

After the establishment of the computation method, active species formed in the reaction between chiral ligand **8a** and diethylzinc was proposed and optimized (Fig. 4), and the structure was examined to get structural insights.

Preliminary computer model suggested that the central metal Zn in active species **8a**-Zn possessed a three-coordination distorted seesaw structure, the phenyl group of the oxazoline chiral elements was far away from the reaction center, thus diminishing the effect of oxazoline moiety on the stereoselectivity of the reaction. Carefully examining the model suggested that the chirality transfer was not effective in the current catalyst system.

The preliminary computer model suggested that the binaphthyl moiety should bear appropriate dihedral angle to get sufficient chirality transfer during the reaction. In this regard, another type of chiral ligands **9** which combined the potential of both binaphthyl group and proline were proposed. Such structures were proposed based on the results that proline and related structures were important starting materials for the preparation of different chiral ligands/catalysts,[13] and based on our experience in the design of prolinol-containing new chiral ligands for asymmetric organic reactions.[14] In our previous study, we found that the chemical space of a chiral ligand can be effectively expanded using isosteric approach. Encouraged by these preliminary results,[15] we decided to prepare new chiral ligands incorporating the advantages of both binaphthyl skeleton and amino alcohols.

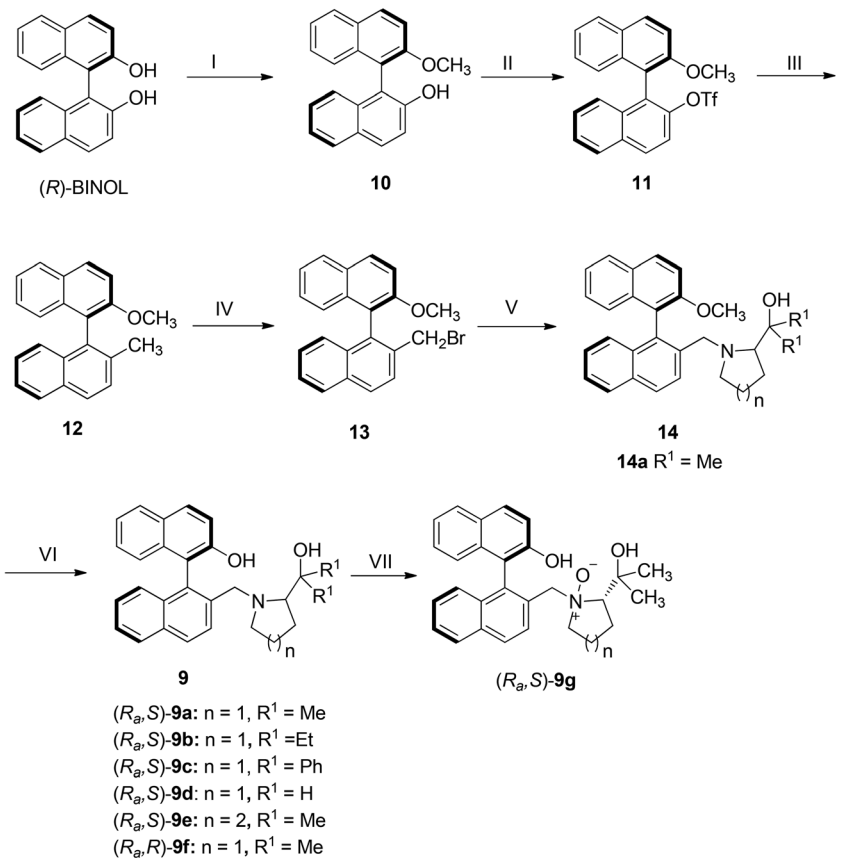


9

The preparation of chiral ligands **9** started from commercially available (*R*)-BINOL (Scheme 3). Monoprotection of hydroxyl group was realized using CH_3I as the methylation agent in the presence of an appropriate base, and the desired mono-methoxylated compound **10** could be obtained in high yield. Triflation of the remaining hydroxyl group in **10** furnished compound **11**, and Ni(II)-catalyzed methylation of **11** gave compound **12** which could be converted **13** *via* free radical bromination. Using AIBN as the free radical initiator and NBS as the bromine source, bromination of **12** proceeded readily, yielding the desired **13** in satisfactory yield. Nucleophilic substitution of **13** with different amino alcohols gave compounds **14** which could be converted to the desired chiral ligands **9** *via* BBr_3-promoted demethylation. For the purpose of comparison, *N*-oxide **9g** was also prepared *via* oxidation of **9a** with *m*-CPBA.

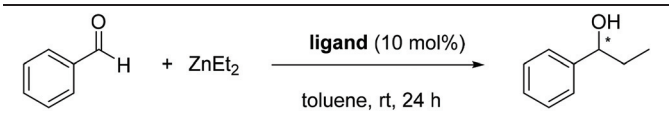
Next, ligand **9a–9g** were evaluated in enantioselective addition of diethylzinc to benzaldehyde. The results are shown in Table 4. Compound **9a** gave the best result, and the product could be obtained in 81% yield and 80% ee (Table 4, entry 1). Increasing or decreasing the bulkiness of the substituents on the hydroxylmethyl group resulted in the decrease of the enantioselectivity of the reaction (Table 4, entries 3, 5 and 7). Lower ee also observed when the five-membered ring was replaced with six-membered ring (Table 4, entries 1 *vs.* 8), possibly due to the different conformation of the two ring systems. It was noteworthy that ligand (R_a,*R*)-**9f** afforded the opposite enantiomer with lower ee, suggesting that the enantioselection came from the prolinol moiety, and the axial chirality and the central chirality of the amino alcohol should match with each other (Table 4, entries 1 *vs.* 10). Lower ee's were observed in reactions using *N*-oxide ligand **9g** or *O*-methyl ligand **14a–14c** or **14e** as chiral ligands, suggesting that both the tertiary amine and the phenolic hydroxyl group were necessary for the asymmetric reactions (Table 4, entries 1 *vs.* 2, 3 *vs.* 4, 5 *vs.* 6 and 8 *vs.* 9).

Next, the reaction conditions were further optimized using **9a** as chiral ligand. The results are summarized in Table 5. As shown in Table 5, less polar solvents such as benzene, *n*-hexane, cyclohexane or toluene were suitable for the reaction, and best result was observed when the reaction was carried out in toluene (81% yield, 86% ee). Reaction carried out in *n*-hexane or dichloroethane afforded product with good ee's but relatively low yield, possibly due to the poor solubility of chiral ligand in these solvents. Almost no reaction was observed when the reactions were carried out in tetrahydrofuran or 1,4-dioxane, possibly due to the coordination nature of the solvents. When the catalyst was exposed to such sol-



Scheme 3 Synthesis of chiral ligands **9a–9g**: (I) CH_3I, K_2CO_3, acetone, 92%; (II) Tf_2O, pyridine, DCM, 99%; (III) $(NiCl_2)$dppp, CH_3MgBr, THF, 96%; (IV) NBS, AIBN, DCE, 81%; (V) amino alcohols, K_2CO_3, NaI, CH_3CN, 65–88%; (VI) BBr_3, DCM, 74–93%; (VII) *m*-CPBA, DCM, 80%.

Table 4 Enantioselective addition of diethylzinc to benzaldehyde using **9a–9g** as the chiral ligands[a]



Entry	Ligand	Yield[b] (%)	ee[c] (%)	Config.[d]
1	**9a**	81	80	*R*
2	**14a**	54	61	*R*
3	**9b**	46	22	*R*
4	**14b**	18	12	*R*
5	**9c**	87	41	*R*
6	**14c**	52	30	*R*
7	**9d**	64	30	*R*
8	**9e**	71	69	*R*
9	**14e**	43	41	*R*
10	**9f**	62	67	*S*
11	**9g**	70	65	*R*

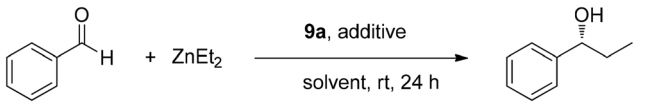
[a] Reaction conditions: Benzaldehyde (0.5 mmol) was added to a solution of the ligand (0.05 mmol) and Et_2Zn (1.0 mmol, 1 mL of 1 M toluene solution) in toluene (2.0 mL). Reaction time: 24 h. [b] Isolated yields. [c] The ee values were determined by HPLC (Chiralcel OD-H column). [d] Absolute configuration was assigned by comparison to reported value and sign of specific rotation of the product.[8f]

vents, all the coordination site of the central metal would be occupied due to solvent coordination, and the catalyst would be deactivated as a result. Therefore, toluene was finally chosen as the reaction medium for further optimization of the reaction condition.

When 10 mol% of DiMPEG 2000 was used as additive,[11] the performance of the chiral ligand was significantly enhanced, and the product could be obtained in 89% isolated yield with 92% ee. Temperature also played a role in the reaction, and product with 96% ee could be obtained when the reaction was carried out at 0 °C (Table 5, entry 13). Further lowering the reaction temperature led to a drop in both yield and enantioselectivity (Table 5, entry 16). Catalyst loading was proved to be crucial as well, and 5 mol% of **9a** was sufficient to obtain high enantioselectivity with a gratifying yield. Further reducing the amount of **9a** to 2 mol% led to a drop of enantioselectivity (Table 5, entries 14 and 15). Finally, the optimum conditions were fixed as follows: benzaldehyde (0.5 mmol) was added to a solution of the ligand **9a** (0.025 mmol), DiMPEG 2000 (0.05 mmol), and Et_2Zn (1.0 mmol, 1 mL of 1 M toluene solution) in toluene (2.0 mL). The reaction was carried out at 0 °C for 24 h.

With the optimum reaction conditions in hand, different aldehydes were subjected to the same reaction to further study

Table 5 Optimization of the reaction conditions for **9a**-promoted enantioselective addition of diethylzinc to benzaldehyde[a]



Entry	**9a** (mol%)	Solvent	Temp. (°C)	Yield[b] (%)	ee[c] (%)
1	10	Toluene	25	81	86
2	10	Chlorobenzene	25	61	71
3	10	Benzene	25	58	75
4	10	Xylene	25	62	59
5	10	$CHCl_3$	25	68	61
6	10	DCM	25	66	79
7	10	DCE	25	47	81
8	10	THF	25	Trace	—
9	10	Dioxane	25	Trace	—
10	10	Cyclohexane	25	66	81
11	10	Hexane	25	71	86
12[d]	10	Toluene	25	89	92
13[d]	10	Toluene	0	89	96
14[d]	5	Toluene	0	86	96
15	2	Toluene	0	81	88
16	10	Toluene	−10	66	84

[a] Reaction conditions: Benzaldehyde (0.5 mmol) was added to a solution of the ligand **9a** (0.05 mmol) and Et_2Zn (1.0 mmol, 1 mL of 1 M toluene solution) in toluene (2.0 mL). Reaction time: 24 h. [b] Isolated yields. [c] The ee values were determined by HPLC using chiral column Chiralcel OD-H. [d] In the presence of DiMPEG 2000 (10 mol%).

the scope of the reaction. The results are summarized in Table 6. Ligand **9a** exhibited excellent catalytic activity for different aromatic aldehydes. *Re*-face addition could be deduced based on the absolute configuration of the products which could be assigned by comparison of the specific rotations with literature results. The substituents on the aromatic rings showed some impact on the reaction, and substrates bearing halogen atoms generally gave higher isolated yields as compared with those bearing electron-donating substituents (Table 6, entries 2–8 and entries 9–13). Naphthaldehydes also gave desired results in satisfactory yields irrespective of the large steric hindrance of the substrates (Table 6, entries 15 and 16). Cinnamaldehyde also gave product with good yield and satisfactory ee.

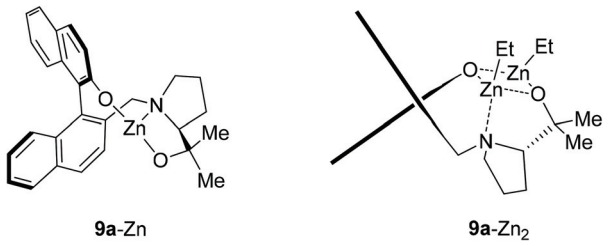
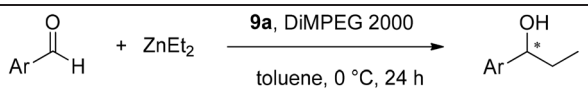


Fig. 5 Possible species in the reaction mixture.

To get structural insights into the reaction, DFT calculation was carried out to study the possible species in the reaction. When chiral ligand **9a** was exposed to excess amount of diethylzinc, two different species, namely, mono-zinc form **9a**-Zn or di-zinc form **9a**-Zn_2 might be formed. A computation at M06-2X/SDD level suggested that the di-zinc form **9a**-Zn_2 was more favored comparing with monozinc moiety **9a**-Zn (Fig. 5).

Table 6 Enantioselective addition of diethylzinc to different aldehydes[a]



Entry	Aldehydes	Product	Yield[b] (%)	ee[c] (%)	Config.[d]
1	Benzaldehyde	**15a**	86	96	*R*
2	2-Methylbenzaldehyde	**15b**	81	96	*R*
3	3-Methylbenzaldehyde	**15c**	79	91	*R*
4	4-Methylbenzaldehyde	**15d**	79	94	*R*
5	3,4-Dimethylbenzaldehyde	**15e**	78	87	*R*
6	2-Methoxybenzaldehyde	**15f**	84	88	*R*
7	3-Methoxybenzaldehyde	**15g**	88	96	*R*
8	4-Methoxybenzaldehyde	**15h**	83	95	*R*
9	3-Fluorobenzaldehyde	**15i**	86	95	*R*
10	2-Chlorobenzaldehyde	**15j**	88	97	*R*
11	3-Chlorobenzaldehyde	**15k**	91	95	*R*
12	2-Bromobenzaldehyde	**15l**	89	98	*R*
13	4-Bromobenzaldehyde	**15m**	86	96	*R*
14	4-Formylbenzonitrile	**15n**	88	94	*R*
15	1-Naphthaldehyde	**15o**	86	90	*R*
16	2-Naphthaldehyde	**15p**	89	95	*R*
17	Cinnamaldehyde	**15q**	88	83	*R*

[a] Reaction conditions: Aldehyde (0.5 mmol) was added to a solution of the ligand **9a** (0.025 mmol), DiMPEG 2000 (0.05 mmol) and Et_2Zn (1.0 mmol, 1 mL of 1 M toluene solution) in toluene (2.0 mL) at 0 °C for 24 h. [b] Isolated yields. [c] The ee values were determined by HPLC using chiral columns: Chiralcel OD-H or OB-H or Chiralpak AD-H, respectively. In all cases, the product chromatograms were compared against a known racemic mixture. [d] Absolute configuration assigned by comparison to the literature.[8f,10m,15h,16]

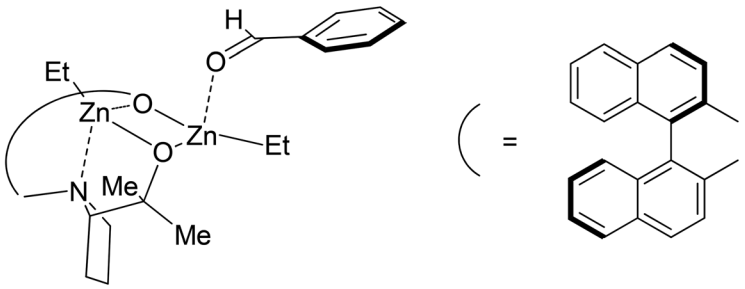


Fig. 6 Plausible transition state in enantioselective addition of diethyl zinc to aldehydes using **9a** as chiral ligand.

Based on the literature reports[17] and the preliminary computation result, possible reaction intermediate was depicted as shown in Fig. 6. After reaction of **9a** with excess amount of diethylzinc, a dimetal **9a**-Zn_2 species was formed as the predominant form of the catalyst. In this model, one of the zinc possessed a distorted tetrahedral four-coordination structure, and the other zinc atom possessed a planar three-coordination structure. Orientation of the aldehyde from a less hindered direction, with *Re*-face of the carbonyl group more feasible for nucleophilic attack.

3. Conclusions

In summary, different types of chiral ligands containing both axial and central chirality were designed, synthesized and evaluated using enantioselective addition of diethylzinc to aromatic aldehydes as models. The results showed that the chiral elements should be close to the central metal, and the axial chirality and the central chirality should match with each other. All chiral ligands can be used in enantioselective addition of diethylzinc to aromatic aldehydes, and chiral ligand **9a** derived from BINOL and L-proline exhibited the best performance among the chiral ligands prepared. Using compound **9a** as chiral ligand, the desired chiral alcohols could be obtained in excellent yields with up to 98% ee at low catalyst loadings. Further, efficient chemical resolution was realized when 1,1′-naphthyl-2,2′-dicarboxylic acid was converted to suitable diastereomers. This would allow the derivatization of 1,1′-naphthyl-2,2′-dicarboxylic acid in an easy-to-carry out manner. Further optimization of these chiral ligands was in good progress, and the results will be reported in due time.

4. Experimental section

4.1. General experimental information

Unless otherwise indicated, commercial reagents were used as received without further purification. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 400 MHz spectrometer at 298 K, using tetramethylsilane (TMS) as an internal standard. Column chromatography separations were performed employing 200–300 mesh silica gel. Melting points were measured on a digital melting point apparatus without correction of the thermometer. Infrared spectra were reported in wave number. HRMS spectra were obtained on a Varian FTICR-MS 7.0T mass spectrometer. HPLC analyses were carried out using Chiralcel OD-H, AD-H or OB-H.

4.2. Preparation of chiral ligands

4.2.1. 2′-((Benzyloxy)carbonyl)-[1,1′-binaphthalene]-2-carboxylic acid (4). To a solution of (1,1′-binaphthalene)-2,2′-dicarboxylic acid (20.00 g, 58 mmol) in 200 mL of DMF was added anhydrous potassium carbonate (3.60 g, 26 mmol) in batches at room temperature. The reaction mixture was stirred for 1 h. Benzyl bromide (7.0 mL, 58 mmol) was added slowly to the reaction mixture and the reaction was continued for another 15 h at room temperature. After completion of the reaction, the solvent was removed *in vacuo*, and the residue was dissolved in 6 M HCl (aq) (50 mL). The aqueous solution was extracted with DCM (100 mL × 3), and the organic layer was dried over anhydrous $MgSO_4$. The organic layer was concentrated *in vacuo*, and the residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 5 : 1) to yield **4** (13.20 g, 60% yield) as a white solid, m.p. = 170–171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.7 Hz, 1H), 8.03–7.78 (m, 5H), 7.50–7.46 (m, 2H), 7.22–7.04 (m, 5H), 7.01–6.95 (m, 2H), 6.87–6.70 (m, 2H), 4.96–4.76 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 166.9, 140.5, 139.4, 134.9, 134.9, 134.7, 132.6, 128.0, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.1, 127.0, 127.0, 126.5, 126.2, 125.8, 125.8, 66.6.

4.2.2. Benzyl-2′-(((*R*)-2-hydroxy-1-phenylethyl)carbamoyl)-[1,1′-binaphthalene]-2-carboxylate (5a,5b). To a solution of **4** (6.00 g, 14 mmol), Et_3N (20 mL, 0.14 mol) and Hobt (3.80 g, 28 mmol) in dry DCM (100 mL) was added dropwise a solution of EDCI (5.90 g, 31 mmol) in dry DCM (20 mL) with stirring at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and D-phenylglycinol (2.10 g, 15 mmol) was added. The suspension was allowed to warm to room temperature and stirred overnight. TLC analysis (petroleum ether : ethyl acetate = 1 : 1) indicated that the reaction was completed and the reaction was quenched by addition of 1 M HCl (aq) (40 mL). The organic layer was washed twice with 1 M HCl (aq). The combined organic layers were washed with saturated aqueous NaCl (100 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (petroleum ether : ethyl acetate = 3 : 1) to give

product **5a** (3.00 g, 40% yield) as white solid and **5b** (3.00 g, 40% yield) as colorless oil. For **5a**: m.p. = 143–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–7.85 (m, 5H), 7.75 (d, J = 8.2 Hz, 1H), 7.58–7.47 (m, 2H), 7.39–7.03 (m, 10H), 6.91–6.72 (m, 4H), 4.97–4.78 (m, 2H), 4.76–4.71 (m, 1H), 3.07–3.02 (m, 1H), 2.93–2.88 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 168.9, 138.5, 137.4, 135.0, 134.7, 134.7, 134.1, 133.0, 132.6, 132.1, 129.5, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 127.4, 127.2, 127.0, 126.7, 126.2, 124.9, 124.9, 124.7, 67.7, 66.4, 55.9.

Crystal data for **5a**: $C_{37}H_{29}NO_4$, M = 551.61, a = 10.77140(10) Å, b = 11.31850(10) Å, c = 13.33430(10) Å, α = 66.4290(10)°, β = 80.6470(10)°, γ = 75.0790(10)°, V = 1436.53(2) Å^3, T = 100.00(13) K, space group $P1$, Z = 2, μ(CuKα) = 0.659 mm^{-1}, 54 918 reflections measured, 11 105 independent reflections (R_{int} = 0.0267). The final R_1 values were 0.0261 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.0655 ($I > 2\sigma(I)$). The final R_1 values were 0.0266 (all data). The final w$R(F^2)$ values were 0.0658 (all data). The goodness of fit on F^2 was 1.059. Flack parameter = −0.01(3). CCDC 2039075.†

For **5b**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.81 (m, 5H), 7.75 (d, J = 8.6 Hz, 1H), 7.54–7.44 (m, 2H), 7.35–7.13 (m, 6H), 7.13–6.85 (m, 6H), 6.43–6.25 (m, 2H), 4.89 (q, J = 12.1 Hz, 2H), 4.67–4.55 (m, 1H), 3.59–3.41 (m, 1H), 2.56–2.53 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 168.6, 138.1, 137.2, 135.1, 134.9, 134.3, 134.2, 133.2, 132.6, 132.1, 129.3, 128.8, 128.8, 128.6, 128.4, 128.4, 128.3, 128.0, 127.8, 127.4, 127.3, 127.1, 127.0, 126.3, 126.2, 125.2, 124.9, 67.5, 66.6, 56.5.

4.2.3. Benzyl-2′-((*S*)-4-phenyl-4,5-dihydrooxazol-2-yl)-[1,1′-binaphthalene]-2-carboxylate (6). To a solution of **5** (3.00 g, 5.44 mmol), Et_3N (8.0 mL, 54 mmol) and DMAP (0.06 g, 0.54 mmol) in dry DCM (80 mL) was added dropwise a solution of TsCl (2.07 g, 10.88 mmol) in dry DCM (20 mL) with stirring at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. TLC analysis (petroleum ether : ethyl acetate = 4 : 1) indicated that the reaction was complete and the reaction was quenched by addition of 1 M HCl aq (40 mL), and then organic layer was washed with 1 M HCl (aq) (twice), the combined organic layers were washed with saturated NaCl solution (80 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluted with petroleum ether : ethyl acetate = 3 : 1) to give product **6** (2.60 g, 90% yield) as white solid, m.p. = 163–164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18–8.09 (m, 1H), 8.01 (d, J = 1.3 Hz, 1H), 7.93–7.77 (m, 4H), 7.50–7.36 (m, 2H), 7.21–7.01 (m, 10H), 6.82–6.72 (m, 2H), 6.68–6.56 (m, 2H), 5.05–4.76 (m, 4H), 4.19–4.06 (m, 1H), 3.68–3.57 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 165.0, 142.5, 139.9, 138.4, 135.5, 135.1, 134.3, 133.1, 128.4, 128.4, 128.3, 128.1, 128.1, 127.9, 127.9, 127.8, 127.7, 127.6, 127.1, 126.8, 126.7, 126.4, 126.3, 126.2, 124.7, 74.5, 69.8, 66.6.

4.2.4. (R_a,*R*)-2-(2′-(4-Phenyl-4,5-dihydrooxazol-2-yl)-[1,1′-binaphthalen]-2-yl)propan-2-ol (2a). To a solution of **6** (800 mg, 1.5 mmol) in dry THF (30 mL), was added dropwise 1 M CH_3MgBr (6.0 mL, 6 mmol) in THF at 0 °C under argon atmosphere. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction was monitored with TLC (petroleum ether : ethyl acetate = 10 : 1). After completion of the reaction, the reaction mixture was poured into ice water, and was extracted with EtOAc (30 mL × 2). The organic layer was combined and was washed with saturated aqueous NaCl (80 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (petroleum ether : ethyl acetate = 8 : 1) to give product **2a** (610 mg, 88% yield) as white solid. $[\alpha]_D^{20}$ = 15.0 (c = 1.0, $CHCl_3$); m.p. = 208–210 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.70 (m, 4H), 7.47 (d, J = 8.8 Hz, 1H), 7.33–7.20 (m, 2H), 7.13–6.88 (m, 4H), 6.79 (t, J = 7.7 Hz, 2H), 6.71–6.60 (m, 1H), 6.05–5.89 (m, 2H), 5.12–4.96 (m, 1H), 4.45–4.40 (m, 1H), 3.69–3.65 (m, 1H), 1.42 (s, 3H), 1.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 146.4, 141.8, 141.2, 134.5, 133.6, 133.1, 132.2, 131.2, 128.3, 128.2, 128.1, 127.9, 127.4, 127.1, 127.0, 126.3, 125.9, 125.9, 125.4, 125.4, 124.6, 75.0, 73.6, 69.4, 32.8, 30.9. IR (KBr): ν = 3250, 2970, 1644, 1447 cm^{-1}. HRMS (ESI, M + H$^+$) calcd for $C_{32}H_{28}NO_2$ 458.2120, found 458.2118.

4.2.5. (R_a,*R*)-3-(2′-(4-Phenyl-4,5-dihydrooxazol-2-yl)-[1,1′-binaphthalen]-2-yl)pentan-3-ol (2b). Compound **2b** was prepared according to the general procedure of **2a** and was isolated as white solid (610 mg, 85% yield) after flash chromatography (petroleum ether : ethyl acetate = 4 : 1), m.p. = 79–80 °C; $[\alpha]_D^{20}$ = +7.0 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 8.5, 0.7 Hz, 1H), 7.83–7.74 (m, 4H), 7.38–7.23 (m, 3H), 7.13–7.03 (m, 1H), 7.01–6.97 (m, 1H), 6.92 (dd, J = 8.7, 1.3 Hz, 2H), 6.81–6.71 (m, 2H), 6.65 (dd, J = 8.7, 1.0 Hz, 1H), 6.23 (s, 1H), 5.99–5.87 (m, 2H), 5.04 (dd, J = 10.3, 7.1 Hz, 1H), 4.47 (dd, J = 10.4, 8.4 Hz, 1H), 3.73 (dd, J = 8.4, 7.1 Hz, 1H), 2.08–1.99 (m, 1H), 1.61–1.52 (m, 1H), 1.44–1.29 (m, 2H), 0.61 (t, J = 7.6 Hz, 3H), 0.49 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 143.6, 141.9, 141.2, 134.6, 134.2, 133.6, 133.2, 132.2, 128.3, 128.2, 128.1, 127.4, 127.3, 127.1, 126.9, 126.9, 126.9, 126.8, 126.2, 125.9, 125.8, 125.5, 124.9, 124.6, 78.4, 75.2, 69.4, 33.5, 32.5, 9.0, 7.7. IR (KBr): ν = 3310, 2950, 1649, 1412 cm^{-1}. HRMS (ESI, M + H$^+$) calcd for $C_{34}H_{32}NO_2$ 486.2433, found 486.2430.

4.2.6. (R_a,*R*)-Diphenyl-(2′-(4-phenyl-4,5-dihydrooxazol-2-yl)-[1,1′-binaphthalen]-2-yl)methanol (2c). Compound **2c** was prepared according to the general procedure of **2a** and was isolated as white solid (780 mg, 90% yield) after flash chromatography (petroleum ether : ethyl acetate = 8 : 1), m.p. = 198–200 °C; $[\alpha]_D^{20}$ = +1.9 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 2.8 Hz, 2H), 7.86–7.69 (m, 3H), 7.40–7.28 (m, 2H), 7.27–7.19 (m, 4H), 7.16–7.07 (m, 6H), 7.06–6.99 (m, 4H), 6.93–6.74 (m, 4H), 6.58–6.54 (m, 1H), 6.24 (dd, J = 8.6, 4.0 Hz, 1H), 4.97 (t, J = 9.9 Hz, 1H), 4.51 (dd, J = 10.1, 8.4 Hz, 1H), 4.10–3.95 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 150.7, 144.8, 143.7, 141.5, 140.6, 134.5, 134.4, 134.0, 132.5, 132.3, 129.2, 129.1, 128.6, 128.3, 128.0, 128.0, 127.9, 127.8, 127.7, 127.5, 127.3, 127.1, 127.1, 126.9, 126.7, 126.5, 126.3, 126.1, 125.8, 124.9, 124.7, 83.0, 75.5, 70.3. IR (KBr): ν = 3165, 2969, 1647, 1380 cm^{-1}. HRMS-ESI (m/z): [M + H]$^+$ calcd for $C_{42}H_{32}NO_2$, 582.2433, found 582.2430.

4.2.7. (S_a,*R*)-2-((*S*)-2′-(4-Phenyl-4,5-dihydrooxazol-2-yl)-[1,1′-binaphthalen]-2-yl)propan-2-ol (2d). Compound **2d** was prepared according to the general procedure of **2a** and was isolated as white solid (500 mg, 85% yield) after flash chromatography (petroleum ether : ethyl acetate = 3 : 1), m.p. = 83–86 °C; $[\alpha]_D^{20}$ = +1.6 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–7.80 (m, 5H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.48–7.36 (m, 2H), 7.27–7.10 (m, 6H), 6.89–6.71 (m, 3H), 4.99–4.95 (m, 1H), 4.42–4.38 (m, 1H), 3.74 (t, *J* = 8.5 Hz, 1H), 1.60 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 145.6, 141.7, 140.9, 134.4, 133.6, 133.1, 132.0, 130.8, 128.6, 128.1, 128.0, 127.9, 127.5, 127.4, 127.3, 127.1, 126.4, 126.3, 126.3, 125.4, 125.3, 125.2, 124.8, 74.9, 74.3, 69.7, 32.9, 31.2. IR (KBr): ν = 3165, 2921, 1647, 1380 cm^{-1}. HRMS (ESI, M + H$^+$) calcd for $C_{32}H_{28}NO_2$ 458.2120, found 458.2118.

4.2.8. (R_a,*R*)-2-(2′-(4-(*tert*-Butyl)-4,5-dihydrooxazol-2-yl)-[1,1′-binaphthalen]-2-yl)propan-2-ol (2e). Compound **2e** was prepared according to the general procedure of **2a** and was isolated as white solid (440 mg, 86% yield) after flash chromatography (petroleum ether : ethyl acetate = 1 : 1), m.p. = 173–175 °C; $[\alpha]_D^{20}$ = +37.8 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.66 (m, 4H), 7.64–7.55 (m, 2H), 7.29–7.25 (m, 1H), 7.16–7.08 (m, 1H), 7.04–7.00 (m, 1H), 6.90–6.86 (m, 2H), 6.49–6.47 (dt, 1H), 5.96 (s, 1H), 3.99 (dd, *J* = 10.0, 8.5 Hz, 2H), 3.82–3.60 (m, 3H), 1.60 (s, 3H), 1.01 (s, 3H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 145.5, 140.7, 134.3, 133.3, 133.0, 132.1, 128.2, 127.8, 127.7, 127.3, 127.1, 126.8, 126.0, 125.9, 125.6, 125.0, 124.9, 124.8, 124.6, 75.90, 73.0, 68.4, 33.2, 33.0, 30.6, 24.7. IR (KBr): ν = 3162, 2937, 1648, 1333 cm^{-1}. HRMS (ESI, M + H$^+$) calcd for $C_{30}H_{32}NO_2$ 438.2433, found 438.2430.

4.2.9. 2′-((*S*)-4-Phenyl-4,5-dihydrooxazol-2-yl)-[1,1′-binaphthalene]-2-carboxylic acid (7). A mixture of **6** (6.00 g, 11.24 mmol) and NaOH (1.26 g, 22.48 mmol) in MeOH (80 mL) was refluxed for 16 h. The reaction mixture was concentrated *in vacuo* to remove MeOH. The residue was partitioned between ethyl acetate (100 mL) and 1 N aq. HCl (50 mL). The separated organic layer was washed with water, dried over $MgSO_4$ and evaporated to dryness. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 1 : 1) to afford compound **7** (4.60 g, 92% yield), m.p. = 148–149 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.6 Hz, 1H), 8.04–7.90 (m, 3H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.57–7.47 (m, 2H), 7.37–7.20 (m, 3H), 7.14 (d, *J* = 8.6 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.86 (t, *J* = 8.0 Hz, 3H), 6.00 (d, *J* = 7.5 Hz, 2H), 5.21 (m, 1H), 4.77 (m, 1H), 4.03 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 168.5, 140.5, 136.48, 135.4, 134.9, 134.1, 133.3, 132.4, 131.8, 129.4, 129.0, 128.6, 128.6, 128.3, 128.2, 128.2, 128.0, 127.6, 127.6, 127.4, 127.2, 126.2, 125.6, 124.3, 124.3, 123.8, 76.4, 68.1.

4.2.10. (R_a,*S*)-*N*-Cyclohexyl-2′-(4-phenyl-4,5-dihydrooxazol-2-yl)-[1,1′-binaphthalene]-2-carboxamide (8a). To a solution of **7** (800 mg, 1.80 mmol), Et_3N (2.6 mL, 18 mmol) and Hobt (565 mg, 3.73 mmol) in dry DCM (30 mL) was added dropwise a solution of EDCI (760 mg, 3.96 mmol) in dry DCM (10 mL) with stirring at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and then cyclohexylamine (196 mg, 1.98 mmol) was added. The suspension was allowed to warm to room temperature and stirred overnight. The reaction was monitored with TLC (petroleum ether : ethyl acetate = 1 : 1) and was quenched by addition of 1 M aqueous HCl (40 mL). The organic layer was washed twice with 1 M HCl, and saturated aqueous NaCl (100 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (petroleum ether : ethyl acetate = 3 : 1) to give product **8a** (849 mg, 90% yield), m.p. = 259–261 °C; $[\alpha]_D^{20}$ = +22.3 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.5 Hz, 1H), 8.06–7.86 (m, 5H), 7.75 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.55–7.45 (m, 2H), 7.34 (q, *J* = 1.9 Hz, 2H), 7.09 (dd, *J* = 32.4, 8.0 Hz, 2H), 6.91 (t, *J* = 7.5 Hz, 2H), 6.01 (d, *J* = 7.5 Hz, 2H), 5.16 (t, *J* = 9.3 Hz, 1H), 4.65 (t, *J* = 9.4 Hz, 1H), 3.78 (td, *J* = 8.2, 1.7 Hz, 1H), 3.55–3.40 (m, 1H), 1.71–1.63 (m, 1H), 1.50 (d, *J* = 13.5 Hz, 1H), 1.43–1.35 (m, 1H), 1.25–1.12 (m, 2H), 1.0–0.86 (m, 3H), 0.73 (d, *J* = 13.0 Hz, 1H), 0.28–0.15 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 166.3, 141.7, 137.2, 137.0, 134.6, 134.0, 132.8, 132.3, 132.2, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.6, 127.5, 127.1, 126.9, 126.6, 125.9, 125.8, 125.7, 125.0, 124.1, 75.1, 69.6, 47.5, 32.4, 32.0, 25.5, 24.6, 24.4. IR (KBr): ν = 3354, 2932, 1649, 1445, 737, 624 cm^{-1}. IR (KBr): ν = 3431, 3057, 2926, 1649 cm^{-1}. HRMS-ESI (*m*/*z*): [M + H]$^+$ calcd for $C_{36}H_{33}N_2O_2$, 525.2542, found 525.2538.

4.2.11. (R_a,*S*)-2′-(4-Phenyl-4,5-dihydrooxazol-2-yl)-*N*-((*R*)-1-phenylethyl)-[1,1′-binaphthalene]-2-carboxamide (8b). Compound **8b** was prepared according to the general procedure of **8a** and was isolated as white solid (790 mg, 80% yield) after flash chromatography (petroleum ether : ethyl acetate = 4 : 1), m.p. = 231–233 °C; $[\alpha]_D^{20}$ = +8.9 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.6 Hz, 1H), 8.01–7.88 (m, 4H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.57–7.45 (m, 2H), 7.40–7.35 (m, 2H), 7.32–7.25 (m, 1H), 7.21–7.12 (m, 3H), 7.10–7.03 (m, 3H), 6.89 (t, *J* = 7.7 Hz, 2H), 6.11–5.96 (m, 2H), 5.23–4.48 (m, 3H), 3.79 (t, *J* = 8.2 Hz, 1H), 0.53 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 166.3, 143.4, 141.6, 137.1, 137.0, 134.7, 134.2, 133.0, 132.5, 132.3, 128.7, 128.5, 128.4, 128.4, 128.2, 128.0, 127.9, 127.7, 127.7, 127.2, 127.1, 126.9, 126.8, 126.2, 126.0, 125.9, 125.8, 125.0, 124.1, 75.2, 69.6, 48.6, 21.9. IR (KBr): ν = 3445, 2921, 1641, 648 cm^{-1}. HRMS-ESI (*m*/*z*): [M + H]$^+$ calcd for $C_{38}H_{31}N_2O_2$, 547.2386, found 547.2385.

4.2.12. (R_a,*S*)-*N*-Phenyl-2′-(4-phenyl-4,5-dihydrooxazol-2-yl)-[1,1′-binaphthalene]-2-carboxamide (8c). Compound **8c** was prepared according to the general procedure of **8a** and was isolated as white solid (350 mg, 50% yield) after flash chromatography (petroleum ether : ethyl acetate = 3 : 1), m.p. = 175–177 °C; $[\alpha]_D^{20}$ = +48.6 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$ δ 10.45 (s, 1H), 8.25–6.65 (m, 23H), 5.09–3.68 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 165.9, 141.0, 138.2, 136.4, 136.0, 134.4, 133.8, 132.5, 132.0, 131.8, 128.8, 128.6, 128.5, 128.2, 128.0, 127.8, 127.6, 127.4, 127.0, 126.8, 126.6, 126.6, 125.9, 125.6, 124.7, 123.9, 123.3, 119.7, 74.7, 69.8. IR (KBr): ν = 3429, 2966, 1652, 698 cm^{-1}. HRMS-ESI (*m*/*z*): [M + H]$^+$ calcd for $C_{36}H_{27}N_2O_2$, 519.2073, found 519.2070.

Crystal data for **8c**: $C_{36}H_{26}N_2O_2$, M = 518.59, a = 12.96320 (10) Å, b = 12.96320(10) Å, c = 16.2424(2) Å, α = 90°, β = 90°, γ = 120°, V = 2363.77(5) Å^3, T = 294 K, space group $P31$, Z = 3, μ(CuKα) = 0.534 mm^{-1}, 21 690 reflections measured, 6231 independent reflections (R_{int} = 0.0170). The final R_1 values were 0.0329 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.0963 ($I > 2\sigma(I)$). The final R_1 values were 0.0347 (all data). The final w$R(F^2)$ values were 0.0987 (all data). The goodness of fit on F^2 was 1.100. Flack parameter = 0.11(8). CCDC 2039078.†

4.2.13. (R_a,*S*)-*N*-Isobutyl-2′-(4-phenyl-4,5-dihydrooxazol-2-yl)-[1,1′-binaphthalene]-2-carboxamide (8d). Compound **8d** was prepared according to the general procedure of **8a** and was isolated as colorless oil (790 mg, 88% yield) after flash chromatography (petroleum ether : ethyl acetate = 2 : 1); $[\alpha]_D^{20}$ = +33.1 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82–8.79 (m, 1H), 8.19–7.66 (m, 6H), 7.59–7.18 (m, 5H), 7.14–6.82 (m, 4H), 6.15–5.91 (m, 2H), 5.17–5.13 (m, 1H), 4.67–4.62 (m, 1H), 3.77 (t, J = 8.3 Hz, 1H), 2.97–2.90 (m, 1H), 2.70–2.64 (m, 1H), 1.29–1.09 (m, 1H), 0.47–0.38 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 166.3, 141.7, 137.2, 137.0, 134.7, 134.1, 132.9, 132.3, 132.1, 128.7, 128.5, 128.4, 128.2, 127.9, 127.9, 127.6, 127.6, 127.2, 127.0, 126.7, 126.0, 126.0, 125.8, 125.2, 124.2, 75.2, 69.8, 53.5, 47.0, 28.4, 20.0. HRMS-ESI (m/z): $[M + H]^+$ calcd for $C_{34}H_{31}N_2O_2$, 499.2386, found 499.2385.

4.2.14. (S_a,*S*)-*N*-Cyclohexyl-2′-(4-phenyl-4,5-dihydrooxazol-2-yl)-[1,1′-binaphthalene]-2-carboxamide (8e). Compound **8e** was prepared according to the general procedure of **8a** and was isolated as white solid (630 mg, 89% yield) after flash chromatography (petroleum ether : ethyl acetate = 2 : 1), m.p. = 93–95 °C; $[\alpha]_D^{20}$ = +2.3 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–7.78 (m, 7H), 7.53–7.46 (m, 2H), 7.35–7.31 (m, 2H), 7.25–7.13 (m, 4H), 6.94–6.88 (m, 2H), 4.82 (dd, J = 10.1, 8.5 Hz, 1H), 4.38 (dd, J = 10.1, 8.5 Hz, 1H), 3.91 (t, J = 8.5 Hz, 1H), 3.49–3.39 (m, 1H), 1.56–1.45 (m, 1H), 1.41–1.31 (m, 2H), 1.23–1.14 (m, 1H), 1.07 (ddd, J = 11.6, 3.6, 1.8 Hz, 1H), 0.97–0.79 (m, 3H), 0.66–0.50 (m, 2H), 0.21–0.07 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 166.0, 141.8, 137.2, 136.9, 135.0, 134.3, 133.1, 132.7, 132.4, 129.0, 129.0, 128.9, 128.6, 128.2, 128.2, 128.1, 127.9, 127.8, 127.2, 127.1, 126.9, 126.7, 126.5, 125.4, 124.9, 75.2, 70.5, 47.9, 32.7, 32.4, 25.7, 25.1, 24.9. IR (KBr): ν = 3429, 2966, 1652, 698 cm^{-1}. HRMS-ESI (m/z): $[M + H]^+$ calcd for $C_{36}H_{33}N_2O_2$, 525.2542, found 525.2539.

Crystal data for **8e**: $C_{36}H_{32}N_2O_2$, M = 524.63, a = 9.3208(3) Å, b = 15.9714(5) Å, c = 19.0521(6) Å, α = 90°, β = 90°, γ = 90°, V = 2836.21(16) Å^3, T = 133.15 K, space group $P212121$, Z = 4, μ(MoKα) = 0.076 mm^{-1}, 38 259 reflections measured, 7943 independent reflections (R_{int} = 0.0416). The final R_1 values were 0.0426 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.0930 ($I > 2\sigma(I)$). The final R_1 values were 0.0537 (all data). The final w$R(F^2)$ values were 0.0993 (all data). The goodness of fit on F^2 was 1.042. Flack parameter = 0.1(5). CCDC 2039077.†

4.2.15. (*R*)-2′-Methoxy-[1,1′-binaphthalen]-2-ol (10). To a solution of (*R*)-BINOL (10.20 g, 40 mmol) and potassium carbonate (7.24 g, 52 mmol) in DMF (150 mL) was added dropwise CH_3I (2.7 mL, 44 mmol) at room temperature, and the resulting mixture was stirred at 50 °C for 16 h. The reaction was monitored with TLC. After the completion of the reaction, the residue was washed with DCM (100 mL × 3). The combined organic layer was washed with saturated aqueous NaCl (100 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (petroleum ether : ethyl acetate = 10 : 1) to give product **10** as colorless oil (11.00 g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 9.1 Hz, 1H), 7.91–7.79 (m, 3H), 7.42 (d, J = 9.1 Hz, 1H), 7.37–7.31 (m, 2H), 7.31–7.22 (m, 2H), 7.21–7.15 (m, 2H), 7.03 (d, J = 8.4 Hz, 1H), 4.94 (s, 1H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 151.4, 134.2, 133.9, 131.1, 129.9, 129.5, 129.3, 128.3, 127.4, 126.5, 125.0, 124.9, 124.3, 123.3, 117.6, 115.5, 115.1, 113.9, 56.8.

4.2.16. (*R*)-2′-Methoxy-[1,1′-binaphthalen]-2-yl trifluoromethanesulfonate (11). To a solution of **10** (10.00 g, 33 mmol) in CH_2Cl_2 (200 mL) were added pyridine (5.3 mL, 66 mmol,) and subsequently trifluoromethanesulfonic anhydride dropwise (11.20 g, 39.6 mmol) at 0 °C. After the completion of the addition, the cooling bath was removed, the mixture was allowed to warm to room temperature, and was stirred for 16 h. After the completion of the reaction, the mixture was washed with hydrochloric acid (1 M, 80 mL), saturated aqueous $NaHCO_3$ (80 mL), and saturated aqueous NaCl (80 mL). The organic phase was dried over $MgSO_4$, and concentrated *in vacuo*. The product was purified by flash column chromatography (petroleum ether : ethyl acetate = 10 : 1) to afford **11** (14.00 g, 99% yield) as a white solid, m.p. = 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–7.98 (m, 2H), 7.95 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.60–7.47 (m, 2H), 7.44 (d, J = 9.1 Hz, 1H), 7.40–7.27 (m, 3H), 7.28–7.18 (m, 1H), 7.00 (d, J = 8.4 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 145.8, 133.8, 133.7, 132.7, 131.2, 130.3, 128.9, 128.4, 128.2, 127.5, 127.4, 127.0, 127.0, 124.9, 123.8, 120.0, 119.7, 116.8, 115.2, 113.0, 56.3.

4.2.17. (*R*)-2-Methoxy-2′-methyl-1,1′-binaphthalene (12). All flasks used in the reaction were heated under vacuum for 30 minutes and purged with argon for 10 minutes. 1,3-Bis (diphenylphosphino)propane nickel(II) chloride (850 mg, 1.7 mmol) was placed in a 500 mL three-necked round bottom flask and a solution of triflate **11** (7.00 g, 16.5 mmol) in THF (60 mL) was added. The mixture was cooled to 0 °C, and CH_3MgBr (3.0 M in THF, 20 mL, 75 mmol) was added dropwise. The reaction suspension was allowed to warm to room temperature during 2 h and refluxed for 12 h. After the completion of the reaction, the reaction mixture was poured into ice water, the aqueous phase was extracted with ethyl acetate (100 mL × 3). The combined organic layer was washed with water (100 mL), and saturated aqueous NaCl (100 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (petroleum ether) to provide **12** (4.70 g, 96% yield) as a white solid, m.p. = 66–68 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 9.0 Hz, 1H), 7.90–7.80 (m, 3H), 7.48 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 9.1 Hz, 1H), 7.37–7.26 (m, 2H), 7.20–7.11 (m, 3H), 6.99 (d, J = 8.4 Hz, 1H), 3.70 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 135.1, 133.8, 133.3, 132.5, 132.3, 129.5, 129.3,

128.8, 128.1, 128.0, 127.6, 126.7, 126.0, 125.2, 124.8, 123.7, 122.1, 114.0, 56.7, 20.4.

4.2.18. (*R*)-2-(Bromomethyl)-2′-methoxy-1,1′-binaphthalene (13). To a solution of **12** (2.93 g, 10 mmol) and AIBN (165 mg, 1 mmol) in DCE (50 mL) was added NBS (1.87 g, 10.5 mmol) in portions in a period of 1 h at room temperature, and the resulting mixture was refluxed for 6 h. The reaction mixture was cooled to room temperature and was concentrated *in vacuo*. The residue was washed with DCM (50 × 3 mL), the combined organic layer was washed with saturated aqueous NaCl (50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (petroleum ether) to give product **13** as a white solid (3.20 g, 81% yield), m.p. = 86–88 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 9.1 Hz, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.77 (dd, J = 8.1, 3.3 Hz, 2H), 7.62 (d, J = 8.5 Hz, 1H), 7.35–7.31 (m, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.10 (ddd, J = 23.8, 11.9, 8.4 Hz, 3H), 6.88 (d, J = 8.5 Hz, 1H), 4.21 (dd, J = 27.0, 10.0 Hz, 2H), 3.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 134.1, 134.0, 133.9, 133.4, 133.1, 130.3, 129.0, 128.7, 128.2, 128.1, 127.8, 126.8, 126.7, 126.6, 126.4, 125.3, 123.9, 119.6, 113.5, 56.4, 32.9.

4.2.19. (R_a,*S*)-2-(1-((2′-Methoxy-[1,1′-binaphthalen]-2-yl) methyl)pyrrolidin-2-yl)propan-2-ol (14a). (*S*)-2-(Pyrrolidin-2-yl) propan-2-ol (4.50 g, 12 mmol), potassium carbonate (2.70 g, 20 mmol) and NaI (150 mg, 1 mmol) were added into a solution of **13** (3.80 g, 10 mol) in acetonitrile (80 mL). The resulting mixture was stirred at room temperature for 16 h. The mixture was washed with ethyl acetate (50 mL × 3). The organic layer was washed with saturated aqueous NaCl (50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (petroleum ether : ethyl acetate = 1 : 1) to give product **14a** (3.70 g, 87% yield) as a white solid, m.p. = 95–96 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 9.0 Hz, 1H), 7.97 (d, J = 8.5 Hz, 1H), 7.94–7.87 (m, 3H), 7.47 (d, J = 9.1 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.4 Hz, 1H), 7.20 (q, J = 7.6 Hz, 2H), 7.11 (d, J = 8.5 Hz, 1H), 6.98 (d, J = 8.5 Hz, 1H), 3.86 (d, J = 13.5 Hz, 1H), 3.76 (s, 3H), 3.40 (d, J = 13.5 Hz, 1H), 2.81–2.70 (m, 1H), 2.54–2.37 (m, 2H), 1.69 (dt, J = 19.5, 7.4 Hz, 1H), 1.62–1.43 (m, 3H), 0.96 (s, 3H), 0.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 137.6, 135.0, 133.7, 133.4, 133.3, 130.2, 129.5, 128.5, 128.2, 127.9, 127.0, 126.6, 126.4, 125.9, 125.8, 124.2, 121.8, 113.9, 73.7, 73.0, 61.7, 56.7, 55.4, 28.7, 28.3, 25.5, 25.1.

4.2.20. (R_a,*S*)-3-(1-((2′-Methoxy-[1,1′-binaphthalen]-2-yl)methyl) pyrrolidin-2-yl)pentan-3-ol (14b). Compound **14b** was prepared according to the procedure of **14a** and was isolated as yellow solid (2.40 g, 84% yield) after flash chromatography (petroleum ether : ethyl acetate = 1 : 1), m.p. = 107–108 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 (d, J = 9.1 Hz, 1H), 8.06–7.90 (m, 4H), 7.63 (d, J = 9.1 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.19 (dd, J = 15.3, 7.8 Hz, 2H), 6.91 (d, J = 8.5 Hz, 1H), 6.75 (d, J = 8.5 Hz, 1H), 3.79 (d, J = 13.8 Hz, 1H), 3.72 (s, 3H), 3.18 (s, 1H), 3.07 (t, J = 12.4 Hz, 1H), 2.75–2.62 (m, 1H), 2.39 (t, J = 7.3 Hz, 1H), 2.25–2.10 (m, 1H), 1.64–1.49 (m, 2H), 1.48–1.32 (m, 3H), 1.31–1.12 (m, 3H), 0.68 (q, J = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.5, 137.6, 133.7, 132.5, 132.3, 131.6, 129.7, 128.5, 128.1, 127.9, 127.3, 126.5, 125.9, 125.4, 125.1, 124.2, 123.4, 119.9, 113.6, 75.5, 69.3, 59.4, 55.8, 54.3, 28.3, 26.6, 26.5, 23.9, 7.8, 7.7.

4.2.21. (R_a,*S*)-2-(1-((2′-Methoxy-[1,1′-binaphthalen]-2-yl)methyl) pyrrolidin-2-yl)diphenylmethanol (14c). Compound **14c** was prepared according to the procedure of **14a** and was isolated as white solid (1.90 g, 80% yield) after flash chromatography (petroleum ether : ethyl acetate = 2 : 1), m.p. = 111–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 9.1 Hz, 1H), 7.95–7.80 (m, 3H), 7.63 (d, J = 8.5 Hz, 1H), 7.54–7.30 (m, 7H), 7.29–7.14 (m, 3H), 7.15–7.06 (m, 4H), 7.02 (t, J = 7.5 Hz, 2H), 6.62 (d, J = 8.5 Hz, 1H), 3.67 (s, 3H), 3.11–2.71 (m, 3H), 2.29–2.08 (m, 1H), 1.80–1.71 (m, 1H), 1.67–1.42 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 147.8, 146.7, 136.5, 134.3, 133.0, 132.7, 132.2, 129.6, 128.9, 128.1, 128.0, 127.9, 127.7, 126.8, 126.7, 126.3, 126.2, 126.0, 125.6, 125.4, 125.1, 123.7, 120.9, 113.3, 77.9, 70.9, 58.4, 56.1, 55.5, 29.7, 24.3.

4.2.22. (R_a,*S*)-2-(1-((2′-Methoxy-[1,1′-binaphthalen]-2-yl)methyl) pyrrolidin-2-yl)methanol (14d). Compound **14d** was prepared according to the procedure of **14a** and was isolated as white solid (2.20 g, 88% yield) after flash chromatography (petroleum ether : ethyl acetate = 1 : 1), m.p. = 86–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 9.0 Hz, 1H), 7.99–7.84 (m, 3H), 7.77 (d, J = 8.3 Hz, 1H), 7.55–7.37 (m, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.20 (dd, J = 15.7, 7.8 Hz, 2H), 7.11 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 8.5 Hz, 1H), 3.78 (d, J = 13.2 Hz, 1H), 3.75 (s, 3H), δ 3.33–3.06 (m, 3H)., 2.97–2.67 (m, 1H), 2.55–2.31 (m, 1H), 2.16 (d, J = 7.4 Hz, 1H), 1.77–1.56 (m, 2H), 1.56–1.38 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 134.3, 133.4, 133.2, 133.1, 129.9, 129.1, 128.1, 128.0, 127.7, 126.7, 126.3, 126.1, 125.6, 125.2, 123.9, 121.1, 113.3, 65.3, 61.7, 57.0, 56.4, 54.6, 27.4, 23.8.

4.2.23. (R_a,*S*)-2-(1-((2′-Methoxy-[1,1′-binaphthalen]-2-yl)methyl) piperidin-2-yl)propan-2-ol (14e). Compound **14e** was prepared according to the procedure of **14a** and was isolated as white solid (1.40 g, 65% yield) after flash chromatography (petroleum ether : ethyl acetate = 1 : 1), m.p. = 90–91 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.00 (m, 1H), 7.97 (d, J = 8.6 Hz, 1H), 7.94–7.87 (m, 3H), 7.48–7.39 (m, 2H), 7.33 (ddd, J = 8.1, 6.7, 1.2 Hz, 1H), 7.21 (dtd, J = 8.2, 6.6, 1.3 Hz, 2H), 7.14 (dd, J = 8.5, 1.2 Hz, 1H), 7.01 (dd, J = 8.5, 1.0 Hz, 1H), 3.91 (s, 1H), 3.78–3.71 (m, 1H), 3.63 (d, J = 13.7 Hz, 1H), 2.80–2.73 (m, 1H), 2.59–2.53 (m, 1H), 2.34 (t, J = 5.8 Hz, 1H), 1.60–1.50 (m, 1H), 1.43–1.16 (m, 5H), 1.12 (s, 3H), 1.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 136.9, 134.3, 133.1, 133.0, 132.9, 129.8, 129.0, 128.1, 128.0, 127.1, 126.7, 126.3, 126.0, 125.4, 125.4, 123.7, 121.0, 113.1, 72.2, 67.4, 56.8, 56.2, 46.0, 29.2, 26.7, 20.7, 20.3, 18.7.

4.2.24. (R_a,*R*)-2-(1-((2′-Methoxy-[1,1′-binaphthalen]-2-yl)methyl) pyrrolidin-2-yl)propan-2-ol (14f). Compound **14f** was prepared according to the procedure of **14a** and was isolated as white solid (1.90 g, 75% yield) after flash chromatography (petroleum ether : ethyl acetate = 1 : 1), m.p. = 104–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.91 (m, 3H), 7.87 (t, J = 7.3 Hz, 2H), 7.44–7.34 (m, 2H), 7.32–7.26 (m, 1H), 7.17 (dd, J = 8.3, 6.9 Hz, 2H), 7.08 (d, J = 8.4 Hz, 1H), 6.99 (d, J = 8.5 Hz, 1H), 3.95 (d, J =

14.5 Hz, 1H), 3.69 (d, J = 6.0 Hz, 3H), 3.32 (d, J = 14.5 Hz, 1H), 2.88 (dt, J = 10.7, 5.5 Hz, 1H), 2.57 (s, 1H), 2.49–2.37 (m, 1H), 2.10 (dt, J = 10.0, 7.1 Hz, 1H), 1.65–1.49 (m, 3H), 1.35 (dd, J = 11.9, 5.7 Hz, 1H), 1.05 (d, J = 10.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 137.3, 133.5, 133.1, 132.8, 132.0, 129.7, 129.1, 128.0, 127.8, 126.6, 126.2, 126.0, 125.3, 125.2, 123.7, 121.0, 113.4, 72.9, 72.7, 60.8, 56.4, 55.6, 28.5, 27.7, 25.3, 25.1.

4.2.25. (R_a,S)-2′-((2-(2-Hydroxypropan-2-yl)pyrrolidin-1-yl)methyl)-[1,1′-binaphthalen]-2-ol (9a). To a solution of **14a** (425 mg, 1 mmol) in 30 mL DCM was added BBr_3 (5 mL, 5 mmol, 1 M in DCM) over a period of 1 h at 0 °C under argon. The reaction was monitored with TLC (petroleum ether : ethyl acetate = 1 : 1). After the completion of the reaction, the mixture was poured into ice water, extracted with DCM (20 mL × 3). The combined organic layer was washed with saturated aqueous NaCl (50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (ethyl acetate) to give product **9a** (310 mg, 76% yield) as a white solid, m.p. = 91–92 °C; $[\alpha]_D^{20}$ = +18.9 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.86 (m, 5H), 7.52–7.45 (m, 2H), 7.36–7.15 (m, 4H), 6.88 (d, J = 8.4 Hz, 1H), 3.93 (d, J = 13.4 Hz, 1H), 3.61 (d, J = 13.4 Hz, 1H), 2.92 (dt, J = 10.5, 6.7 Hz, 1H), 2.73 (t, J = 6.9 Hz, 1H), 2.61–2.38 (m, 1H), 1.70–1.57 (m, 3H), 1.55–1.42 (m, 1H), 0.96 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 135.5, 134.2, 133.4, 133.2, 132.8, 130.1, 128.8, 128.7, 128.2, 128.1, 127.8, 126.7, 126.6, 126.5, 126.3, 124.7, 123.2, 119.0, 117.6, 73.8, 72.0, 61.3, 55.9, 28.1, 27.2, 25.2, 24.6. IR (KBr): ν = 3697, 2967, 1434, 816 cm^{-1}. HRMS-ESI (m/z): $[M + H]^+$ calcd for $C_{28}H_{30}NO_2$, 412.2277, found 412.2275.

4.2.26. (R_a,S)-2′-((2-(3-Hydroxypentan-3-yl)pyrrolidin-1-yl)methyl)-[1,1′-binaphthalen]-2-ol (9b). Compound **9b** was prepared according to the procedure of **9a** and was isolated as yellow solid (600 mg, 74% yield) after flash chromatography (petroleum ether : ethyl acetate = 1 : 1), m.p. = 88–89 °C; $[\alpha]_D^{20}$ = +47.2 (c = 1.0, DMSO); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.49 (s, 1H), 8.07–7.79 (m, 5H), 7.41 (t, J = 7.4 Hz, 1H), 7.35 (d, J = 8.8 Hz, 1H), 7.23 (dd, J = 10.9, 7.1 Hz, 2H), 7.14 (t, J = 7.5 Hz, 1H), 6.99 (d, J = 8.5 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H), 3.82 (d, J = 13.8 Hz, 1H), 3.17 (d, J = 13.4 Hz, 1H), 2.80–2.62 (m, 1H), 2.47–2.35 (m, 1H), 2.33–2.15 (m, 1H), 1.66–1.51 (m, 2H), 1.50–1.33 (m, 3H), 1.33–1.11 (m, 3H), 0.68 (q, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.0, 134.3, 132.6, 132.5, 129.2, 128.1, 127.9, 127.9, 127.3, 127.2, 126.2, 125.7, 125.1, 123.9, 122.5, 118.3, 116.9, 75.5, 69.5, 59.5, 54.5, 28.3, 26.5, 24.0, 21.3, 7.8. IR (KBr): ν = 3649, 2968, 1621, 1346 cm^{-1}. HRMS-ESI (m/z): $[M + H]^+$ calcd for $C_{30}H_{34}NO_2$, 440.2590, found 440.2588.

4.2.27. (R_a,S)-2′-((2-(Hydroxydiphenylmethyl)pyrrolidin-1-yl)methyl)-[1,1′-binaphthalen]-2-ol (9c). Compound **9c** was prepared according to the procedure of **9a** and was isolated as yellow solid (900 mg, 78% yield) after flash chromatography (petroleum ether : ethyl acetate = 1 : 1), m.p. = 108–110 °C; $[\alpha]_D^{20}$ = +63.1 (c = 1.0, $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.78 (m, 4H).7.69 (d, J = 8.6 Hz, 1H), 7.43 (dt, J = 17.1, 8.5 Hz, 5H), 7.34–7.26 (m, 2H), 7.25–7.15 (m, 3H), 7.15–7.02 (m, 5H), 7.02–6.93 (m, 1H), 6.51 (d, J = 8.5 Hz, 1H), 4.64 (s, 1H), 3.65 (dd, J = 9.1, 4.2 Hz, 1H), 3.08–2.77 (m, 3H), 2.18–2.02 (m, 1H), 1.88–1.38 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 147.6, 146.4, 138.9, 134.0, 133.1, 132.6, 130.2, 130.0, 129.1, 129.0, 129.0, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 127.0, 127.0, 126.6, 126.4, 126.3, 126.2, 125.6, 125.6, 125.5, 125.4, 124.5, 123.6, 117.5, 116.8, 78.1, 71.0, 58.3, 55.7, 29.4, 24.3. IR (KBr): ν = 3649, 2965, 1618, 661 cm^{-1}. HRMS-ESI (m/z): $[M + H]^+$ calcd for $C_{38}H_{34}NO_2$, 536.2590, found 536.2588.

4.2.28. (R_a,S)-2′-((2-(Hydroxymethyl)pyrrolidin-1-yl)methyl)-[1,1′-binaphthalen]-2-ol (9d). Compound **9d** was prepared according to the procedure of **9a** and was isolated as white solid (1.40 g, 93% yield) after flash chromatography (petroleum ether : ethyl acetate = 6 : 1), m.p. = 98–99 °C; $[\alpha]_D^{20}$ = +6.8 (c = 1.0, DMSO); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.63 (s, 1H), 8.04–7.75 (m, 5H), 7.42 (t, J = 7.2 Hz, 1H), 7.35 (d, J = 8.8 Hz, 1H), 7.22 (dd, J = 20.1, 4.2 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 8.4 Hz, 1H), 6.71 (d, J = 8.5 Hz, 1H), 4.17 (s, 1H), 3.79 (d, J = 13.2 Hz, 1H), 3.11 (dd, J = 25.4, 11.5 Hz, 2H), 3.00–2.87 (m, 1H), 2.87–2.69 (m, 1H), 2.33–2.17 (m, 1H), 2.00 (d, J = 6.9 Hz, 1H), 1.67 (dd, J = 17.1, 8.2 Hz, 1H), 1.54–1.37 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.2, 134.3, 132.6, 132.5, 132.4, 129.1, 128.0, 127.9, 127.9, 127.4, 127.1, 126.2, 125.8, 125.2, 124.0, 122.5, 118.6, 117.2, 65.2, 63.9, 56.8, 54.3, 28.0, 22.6. IR (KBr): ν = 3578, 3053, 2956, 1733, 818 cm^{-1}. HRMS-ESI (m/z): $[M + H]^+$ calcd for $C_{26}H_{26}NO_2$, 384.1964, found 384.1961.

4.2.29. (R_a,S)-2′-((2-(2-Hydroxypropan-2-yl)piperidin-1-yl)methyl)-[1,1′-binaphthalen]-2-ol (9e). Compound **9e** was prepared according to the procedure of **9a** and was isolated as white solid (300 mg, 83% yield) after flash chromatography (petroleum ether : ethyl acetate = 1 : 1), m.p. = 96–97 °C; $[\alpha]_D^{20}$ = +33.1 (c = 1.0, $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.80 (m, 5H), 7.67 (d, J = 8.8 Hz, 1H), 7.47 (ddd, J = 8.0, 4.8, 3.0 Hz, 1H), 7.35–7.24 (m, 2H), 7.24–7.17 (m, 2H), 7.16–7.09 (m, 1H), 6.76 (d, J = 8.5 Hz, 1H), 4.43 (d, J = 12.8 Hz, 1H), 4.08 (d, J = 12.9 Hz, 1H), 3.48–3.27 (m, 1H), 3.02 (dt, J = 14.4, 4.4 Hz, 1H), 2.85 (t, J = 12.3 Hz, 1H), 1.54–1.37 (m, 3H), 1.17 (s, 3H), 1.09 (d, J = 11.6 Hz, 1H), 1.00 (s, 3H), 0.94–0.77 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 135.7, 133.8, 133.8, 133.2, 130.4, 129.2, 128.8, 128.4, 128.2, 127.2, 127.1, 126.9, 126.7, 124.3, 123.3, 119.2, 116.3, 70.9, 69.2, 60.4, 49.4, 30.7, 25.4, 20.9, 17.8, 14.2. IR (KBr): ν = 3689, 2975, 1608, 691 cm^{-1}. HRMS-ESI (m/z): $[M + H]^+$ calcd for $C_{29}H_{32}NO_2$, 426.2433, found 426.2431.

4.2.30. (R_a,R)-2′-((2-(2-Hydroxypropan-2-yl)pyrrolidin-1-yl)methyl)-[1,1′-binaphthalen]-2-ol (9f). Compound **9f** was prepared according to the procedure of **9a** and was isolated as white solid (450 mg, 83% yield) after flash chromatography (petroleum ether : ethyl acetate = 1 : 8), m.p. = 106–107 °C. IR (KBr): ν = 3691, 2987, 1418, 868 cm^{-1}. HRMS-ESI (m/z): $[M + H]^+$ calcd for $C_{28}H_{30}NO_2$, 412.2277, found 412.2278. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.65 (m, 5H), 7.51 (d, J = 8.9 Hz, 1H), 7.38 (t, J = 7.7 Hz, 1H), 7.26–7.00 (m, 4H), 6.68 (d, J = 8.5 Hz, 1H), 4.04 (d, J = 12.8 Hz, 1H), 3.81 (d, J = 12.9 Hz, 1H), 2.98 (d, J = 28.6 Hz, 1H), 2.95–2.73 (m, 2H), 1.82–1.55 (m, 3H), 1.46–1.31 (m, 1H), 0.89 (s, 3H), 0.81 (s, 3H). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 153.0, 135.3, 134.2, 133.9, 133.3, 130.5, 128.9, 128.7, 128.4, 128.2, 127.2, 127.0, 127.0, 126.9, 124.5, 123.5, 120.0, 117.2, 75.9, 71.2, 60.2, 55.0, 28.0, 27.2, 25.9, 23.8.

4.2.31. (R_a,*S*)-1-((2′-Hydroxy-[1,1′-binaphthalen]-2-yl)methyl)-2-(2-hydroxypropan-2-yl)pyrrolidine 1-oxide (9g). To a solution of **14a** (430 mg, 1 mmol) in dry DCM (20 mL) was added *m*-chloroperoxybenzoic acid (350 mg, 2 mmol) at 0 °C. The mixture was allowed to warm to room temperature and was stirred for 12 h. The solvent was removed *in vacuo* to give the crude product. Compound **9g** was obtained as a white solid (330 mg, 80% yield) after flash chromatography (petroleum ether : ethyl acetate = 1 : 8), m.p. = 185–187 °C; $[\alpha]_D^{20}$ = +13.1 (*c* = 1.0, $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.9 Hz, 1H), δ 7.90–7.70 (m, 3H), 7.62 (d, *J* = 23.3 Hz, 1H), 7.45 (d, *J* = 5.8 Hz, 1H), 7.38–7.10 (m, 6H), 6.77 (d, *J* = 7.8 Hz, 1H), 4.62 (d, *J* = 12.3 Hz, 1H), 4.15 (d, *J* = 12.4 Hz, 1H), 3.40–2.80 (m, 3H), 2.21–1.94 (m, 1H), 1.87–1.50 (m, 2H), 1.21 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 136.7, 134.0, 133.7, 132.5, 130.1, 129.5, 128.5, 128.2, 128.0, 127.8, 127.6, 126.9, 126.7, 126.5, 126.3, 123.8, 122.8, 119.3, 116.6, 80.2, 71.4, 69.5, 29.2, 26.7, 25.0, 20.8. IR (KBr): ν = 3689, 2952, 1623, 757 cm^{-1}. HRMS-ESI (*m*/*z*): $[M + H]^+$ calcd for $C_{28}H_{30}NO_3$, 428.2226, found 428.2225.

4.3. General procedure for enantioselective addition of Et_2Zn to aldehydes

To a solution of Et_2Zn (1.0 M in toluene, 1 mL, 2 equiv.), were added slowly a solution of chiral ligand **9a** (11 mg, 5 mol%) and DiMPEG 2000 (50 mg, 10 mol%) in dry toluene at 0 °C under a dry argon atmosphere. After the mixture was stirred for 1 h at 0 °C, freshly distilled aldehyde (0.5 mmol, 1 equiv.) was added, and the reaction mixture was stirred for 24 h at 0 °C. After the reaction was completed, the reaction mixture was quenched with 1 M aqueous HCl and was extracted with ethyl acetate (3 × 5 mL). The combined organic layer was washed with brine, dried with anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) to give the corresponding product. The ee values of the secondary alcohols were determined by chiral HPLC analysis The absolute configurations of the products were assigned by comparing the specific rotation with the literature values.

Conflicts of interest

The authors declare no competing financial interest.

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