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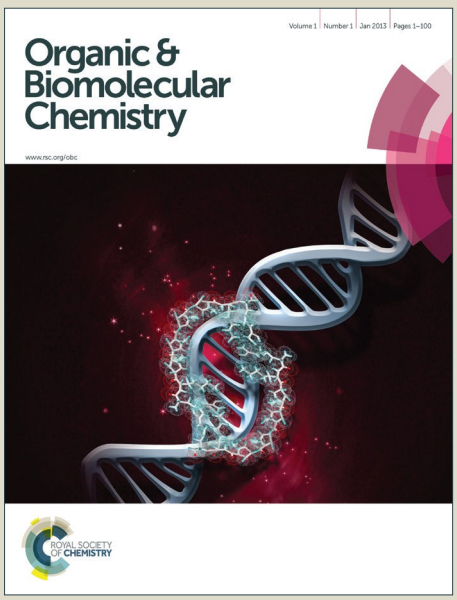

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Journal Name

ARTICLE

Rhodium-Catalyzed Asymmetric Ring Opening Reaction of Oxabenzonorbornadienes with Amines Using ZnI_2 as Activator

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The complex of $[Rh(COD)Cl]_2$ and (*R*,*R*)-BDPP was used as an effective catalyst for the asymmetric ring opening reaction of oxabenzonorbornadienes with various amines by employing ZnI_2 as activator. Under the optimized reaction conditions, high enantioselectivities with good yields could be obtained from a wide scope of oxabenzonorbornadienes and amines.

Introduction

The desymmetric additional ring opening reaction of oxa/azabenzonorbornadienes with heteroatom nucleophiles is an effective method for the construction of hydronaphthalenes bearing multiple functional groups.[1] Caused by the broad existence of chiral hydronaphthalene structures in natural products and bioactive molecules,[2] the asymmetric version of this type of reactions has attracted continuous interest and investigation.[3] The development of simple and efficient chiral catalysts for such reactions is undoubtedly an important and continuing topic for related researchers. Using Josiphos type ligands, some chiral rhodium catalysts had been developed by Lautens group and achieved great success. These rhodium catalysts could promote phenols,[4] alcohols,[5] amines,[6] thiols,[7] carboxylic acids,[8] water[9] or some other heteroatom compounds,[10] to react with oxa/azabenzonorbornadienes and generate the corresponding ring opening products. Some iridium catalysts comprising diphosphine or monophosphine ligands had also been applied in the ring opening reactions of oxa/azabenzonorbornadienes with some heteroatom nucleophiles by Yang group,[11] Tang group[12] and our own group.[13] Recently, inspired by the successful application of Lewis acids as additives in the transition metal-catalyzed asymmetric ring opening (ARO) reactions of oxa/azabenzonorbornadienes with carbo-nucleophiles,[14] we had proved that the combination of chiral palladium complexes with Lewis acids was very effective on the ARO reactions of oxa/azabenzonorbornadienes with heteroatom nucleophiles.[15] This methodology was also found useful in increasing the chiral iridium complexes' efficiency in the ARO reaction of azabenzonorbornadienes with amines.[16] In order to further investigate the effect of Lewis acids, we have studied the rhodium catalyzed ARO reaction of oxabenzonorbornadienes by using ZnI_2 as activator. Herein, we describe the $[Rh(COD)Cl]_2/ZnI_2$ co-catalyzed asymmetric ring opening reactions of oxabenzonorbornadienes with amines.

Results and discussion

Our initial trials were carried out with the reaction of aniline and oxabenzonorbornadiene **1a** using a cooperative catalytic system comprising $[Rh(COD)Cl]_2$ and CuI. As it was shown in table 1, the bis(oxazoline) ligand (*R*,*R*)-Ph-pybox, monophosphine ligands such as (*S*)-NMDPP and (*R*)-Monophos were proved not suitable for the present reaction (Table 1, entries 1-3). By employing diphosphine ligand, (*R*)-BINAP gave a promising result and the desired chiral hydronaphthalene product was obtained in low yield and ee (Table 1, entry 4). Encouraged by this result, further evaluation of other diphosphine ligands suggested that good yields were obtained by using (*R*)-SEGPHOS and (*R*)-Difluorphos (Table 1, entries 5-6). By switching to bidentate phosphines bearing point chirality ultimately led to the discovery that (*R*,*R*)-BDPP gave excellent yield and good enantioselectivity (Table 1, entry 8). Notably, we observed a decreasing of enantioselectivity in the absence of CuI, this result indicated that Lewis acid played a unique role in the present reaction (Table 1, entry 9).

Different additives were then screened and the experimental results were summarized in table 2. The results proved that the selection of additives was crucial for higher yield and enantioselectivity. For example, the addition of trifluoromethanesulfonic salts, such as CuOTf, AgOTf, $Zn(OTf)_2$, $Fe(OTf)_2$, and $Al(OTf)_3$ gave no product even though some of them have been successfully employed in the ring opening reactions of oxabenzonorbornadienes (Table 2, entries 3, 4, 8, 11, and 13). Some halides, including CuI, CuBr, $ZnCl_2$, $ZnBr_2$, ZnI_2, $FeCl_2$, FeI_2, and $AlBr_3$ were further screened. It was found that $ZnCl_2$ and $FeCl_2$ improved the reaction enantioselectivities

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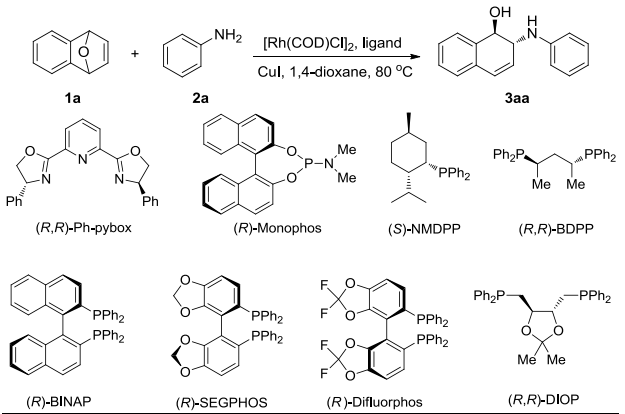
slightly by slowing down the reaction rate (Table 2, entries 5 and 9 compared with entry 9 in table 1).

Table 1. Screening of chiral ligands[a]

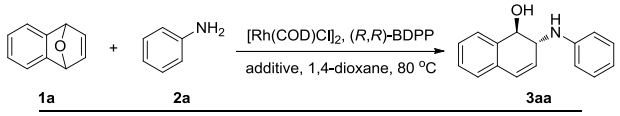


entry	ligand	time (h)	yield[b] (%)	ee[c] (%)
1	(*R*,*R*)-Ph-pybox	13	trace	/
2	(*S*)-NMDPP	13	trace	/
3	(*R*)-Monophos	14	Trace	5
4	(*R*)-BINAP	14	20	26
5	(*R*)-SEGPHOS	14	83	10
6	(*R*)-Difluorphos	13	86	5
7	(*R*,*R*)-DIOP	14	92	54
8	(*R*,*R*)-BDPP	0.2	95	71
9[d]	(*R*,*R*)-BDPP	0.5	95	57

[a]The reaction was carried out with **1a** (0.30 mmol), 5.0 equiv of aniline **2a** (1.5 mmol) and 0.1 equiv of CuI in 1,4-dioxane (2.0 mL) at 80 °C in the presence of $[Rh(COD)Cl]_2$ (2.5 mol %) and bidentate ligand (6.5 mol %) or monodentate ligand (11.0 mol %). [b]Isolated yield after neutral alumina column chromatography. [c]Determined by HPLC with a Chiralcel AD-H column. [d]No CuI was added.

And the bromide salts including CuBr, $ZnBr_2$ and $AlBr_3$ further improved the reaction enantioselectivities (Table 2, entries 2, 6 and 12). Among these halides, iodine salts promoted both the reaction rate and enantioselectivities (Table 2, entries 1, 7 and 10). Beside Lewis acids, organic halide additives such as $^nBu_4NCl$, $^nBu_4NBr$ and $^nBu_4NI$ were also tested and the results indicated that they also accelerated the reaction but only give moderate enantioselectivities (Table 2, entries 14-16). Therefore, ZnI_2 was found to be optimal in terms of yield and enantioselectivity.

Table 2. Screening of additives[a]

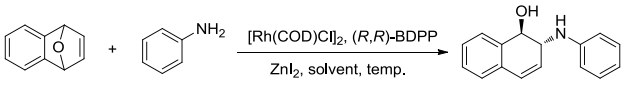


entry	additive	time (h)	yield[b] (%)	ee[c] (%)
1	CuI	0.2	95	71
2	CuBr	1	71	73
3	CuOTf	14	trace	/
4	AgOTf	14	NR	/
5	$ZnCl_2$	15	30	60
6	$ZnBr_2$	1	85	78
7	ZnI_2	0.1	94	82
8	$Zn(OTf)_2$	14	NR	/
9	$FeCl_2$	5	86	69
10	FeI_2	1.5	84	73
11	$Fe(OTf)_2$	39	NR	/
12	$AlBr_3$	15	66	73
13	$Al(OTf)_3$	39	NR	/
14	$^nBu_4NCl$	0.2	93	60
15	$^nBu_4NBr$	0.2	92	64
16	$^nBu_4NI$	0.1	93	74

[a]The reaction was carried out with **1a** (0.30 mmol), 5.0 equiv of aniline **2a** (1.5 mmol) and 0.1 equiv of additive in 1,4-dioxane (2.0 mL) at 80 °C in the presence of $[Rh(COD)Cl]_2$ (2.5 mol %) and (*R*,*R*)-BDPP (6.5 mol %). [b]Isolated yield after neutral alumina column chromatography. [c]Determined by HPLC with a Chiralcel AD-H column.

In an attempt to improve the reaction enantioselectivity, different reaction parameters including solvents and the reaction temperature were also investigated (Table 3). It was proved that solvent selection had little impact on the reaction yield but appeared significant on enantioselectivity, and the using of MeCN and DCE gave high ees (Table 3, entries 2 and 5). Temperature experiments showed that the temperatures from 0 °C to 80 °C had little effect to the reaction outcomes and all gave satisfactory results (Table 3, entries 5-7). However, when the ZnI_2 loading was decreased to 5 mol%, the yield of hydronaphthalene decreased sharply to 63% (Table 3, entry 8). Notably, reducing the loadings of $[Rh(COD)Cl]_2$ to 1.25 mol % and (*R*,*R*)-BDPP to 3.25 mol % also afforded the product in high yield with good enantioselectivity as well (Table 3, entry 9). Although the reaction time was prolonged to 4h, in consideration of reaction economy, it was identified as the optimum reaction condition.

Table 3. Optimization of reaction conditions[a]



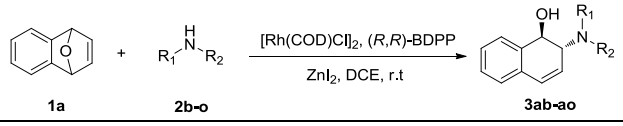
entry	solvent	time(h)	yield[b] (%)	ee[c] (%)
1	THF	15	85	75
2	CH_3CN	3	92	93
3	toluene	3	92	79
4	DMF	3	93	79
5	DCE	0.1	95	94
6[d]	DCE	24	90	94
7[e]	DCE	3	94	94
8[f]	DCE	7	63	90
9[e,g]	DCE	4	94	94

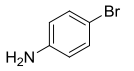
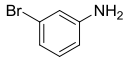
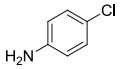
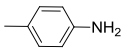
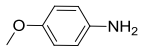
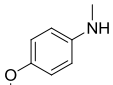
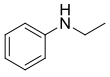
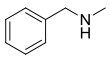
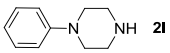
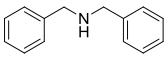
[a]The reaction was carried out with **1a** (0.30 mmol), 5.0 equiv of aniline **2a** (1.5 mmol) and 0.1 equiv of ZnI_2 in solvent (2.0 mL) at 80 °C in the presence of $[Rh(COD)Cl]_2$ (2.5 mol %) and (*R*,*R*)-BDPP (6.5 mol %). [b]Isolated yield after neutral alumina column chromatography. [c]Determined by HPLC with a Chiralcel AD-H column. [d]React at 0 °C. [e]React at room temperature. [f]5% ZnI_2

was used. [g]1.25 mol % $[Rh(COD)Cl]_2$ and 3.25 mol % (*R*,*R*)-BDPP were used.

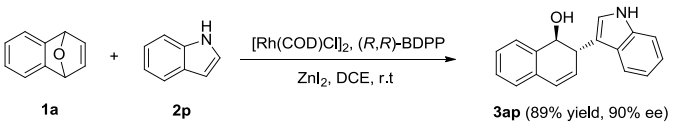
With the optimum reaction conditions in hand, various amines were employed in the present asymmetric ring opening reaction to extend its scope (Table 4). In general, amines including aryl amines and alkyl amines were suitable for this progress and excellent enantioselectivities were obtained by using primary amines whereas secondary amines gave good enantioselectivities with faster reaction rate. The amines bearing halogen substituents on the *para*-, *meta*-, and *ortho*-position, were suitable to afford the corresponding products (Table 4, entries 1-4). Other substituted anilines including *N*-alkyl anilines also reacted smoothly to generate the products (Table 4, entries 5-9). To our delight, alkyl amines such as *N*-methylbenzylamine, *N*-phenylpiperazine, dibenzylamine, *tert*-butylamine and piperidine were also suitable for this protocol (Table 4, entries 10-14). The absolute configuration of the product **3al** was assigned as 1*R*, 2*R* by an X-ray crystallographic analysis (Figure 1, for details, see the Supporting Information).[17] As same as the ring opening product reported by Lautens,[6c] by using indole as nucleophile, **3ap** was obtained (Scheme 1).

Table 4. Scope of amines[a]



entry	amine	time	yield[b] (%)	ee[c] (%)
1	 **2b**	14	93	99
2	 **2c**	23	56	98
3	 **2d**	23	81	99
4	 **2e**	14	94	99
5	 **2f**	14	83	95
6	 **2g**	14	83	96
7[d]	 **2h**	1	86	90
8[d]	 **2i**	1	95	88
9[d]	 **2j**	1	75	89
10[d]	 **2k**	5	89	81
11[d]	 **2l**	3	93	99
12[d]	 **2m**	4	87	87
13	 **2n**	20	87	98
14[d]	 **2o**	4	88	94

[a]The reaction was carried out with **1a** (0.30 mmol), 5.0 equiv of amine **2b-o** (1.5 mmol) and 0.1 equiv of ZnI_2 in DCE (2.0 mL) at room temperature in the presence of $[Rh(COD)Cl]_2$ (1.25 mol %) and (*R*,*R*)-BDPP (3.25 mol %). [b]Isolated yield after neutral alumina column chromatography. [c]Determined by HPLC with a Chiralcel AD-H, OD-H or OJ-H column. [d]DCM (dichloromethane) was used as solvent.



Scheme 1. The reaction of oxabenzonorbornadiene and indole

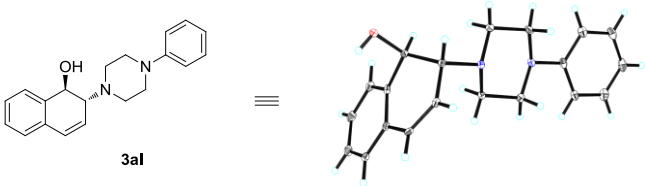
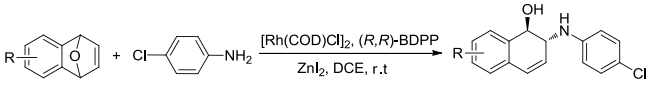
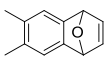
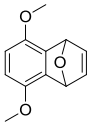
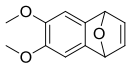


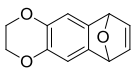
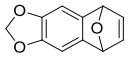
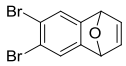
Figure 1. X-ray structure of **3al**.

Using 4-chloroaniline **2e** as nucleophile, a range of oxabenzonorbornadienes were also examined in this asymmetric ring opening reaction. As it was shown in table 5, all of the tested oxabenzonorbornadienes could react with 4-chloroaniline efficiently to give the corresponding hydronaphthalenes with excellent enantioselectivities (95%-99% ee), whereas the oxabenzonorbornadiene with relatively bulky groups afforded a moderate yield (Table 5, entry 2).

Table 5. Scope of oxabenzonorbornadiene derivatives[a]



entry	oxabenzonorbornadiene	time	yield[b] (%)	ee[c] (%)
1	 **1b**	4	95	98
2	 **1c**	11	64	95
3	 **1d**	11	93	99

4		**1e**	5	75	99
5		**1f**	3	89	98
6		**1g**	10	81	95

[a]The reaction was carried out with **1b-g** (0.30 mmol), 5.0 equiv of 4-chloroaniline **2e** (1.5 mmol) and 0.1 equiv of ZnI_2 in DCE (2.0 mL) at room temperature in the presence of $[Rh(COD)Cl]_2$ (1.25 mol %) and (*R*,*R*)-BDPP (3.25 mol %). [b]Isolated yield after neutral alumina column chromatography. [c]Determined by HPLC with a Chiralcel AD-H column or AS-H column.

A general mechanism for this type of reactions has been proposed by the groups of Lautens[6d, 18], Tang[12] and Yang[11b]. However, in consideration of the effect of Lewis acid on the reaction and the variation of the enantioselectivities with different amines as nucleophiles, another reaction pathway was hypothesized here for this chiral rhodium complex/ZnI_2 co-catalyzed asymmetric ring opening reaction of oxabenzonorbornadienes with amines (Figure 2). The catalytic cycle is initiated by the coordination of $[Rh(cod)Cl]_2$ with (*R*,*R*)-BDPP to generate the chiral rhodium complex **A**. The following coordination of **A** with **1a**, zinc ion, and aniline leads to the intermediate **B**. Subsequently, the intermediate **B** undergoes addition reaction and affords intermediate **C**, which then gives the ring-opened species **D** by β-elimination and rearragement. Next, intermediate **D** can be transformed into **E** via reductive elimination. Finally, product **3aa** was formed by cation dissociation.

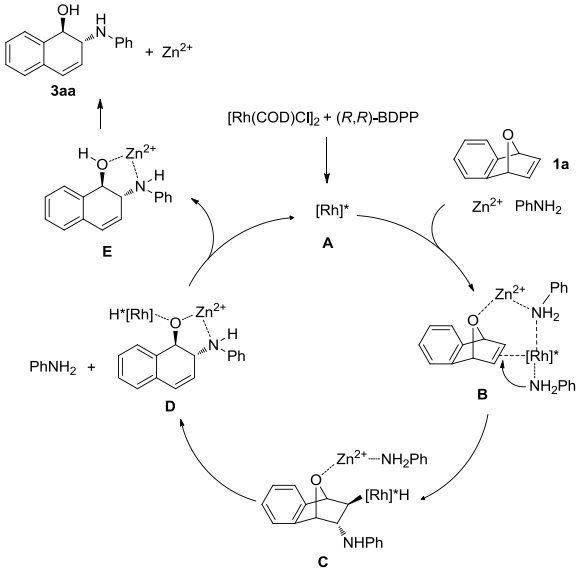


Figure 2. Proposed mechanism for $[Rh(COD)Cl]_2/ZnI_2$-cocatalyzed ARO reaction of oxabenzonorbornadiene **1a** and amine **2a**.

Conclusions

In summary, by using ZnI_2 as activator, the rhodium complex of $[Rh(COD)Cl]_2$ and (*R*,*R*)-BDPP was found an efficient catalyst for the asymmetric ring opening reactions of oxabenzonorbornadienes with amines. Promoted by this rhodium/ZnI_2 co-catalytic system, various amines, including aryl amines and alkyl amines could serve as suitable nucleophiles to react smoothly with oxabenzonorbornadienes **1a**. The corresponding ring opening products could be generated in good yields with generally excellent enantioselectivities. Also, oxabenzonorbornadienes with different substituents were also tested in this co-catalytic system. Further mechanistic studies toward the particular effect of Lewis acid and synthetic application are ongoing in our laboratory.

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Experimental section

General

The reactions and manipulations were performed under an atmosphere of argon by using standard Schlenk techniques and Drybox (Mikrouna, Supper 1220/750). Anhydrous toluene and THF (tetrahydrofuran) were distilled from sodium benzophenone ketyl prior to use. Anhydrous DCE (dichloroethane), DMF (*N*,*N*-dimethylformamide) and CH_3CN (acetonitrile) were distilled from calcium hydride and stored under argon. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker-Avance 400 MHz spectrometer. $CDCl_3$ was used as solvent. Chemical shifts (δ) were reported in ppm with tetramethylsilane as internal standard, and *J* values were given in Hz. The enantioselective excesses were determined by Agilent 1260 Series HPLC using Daicel AD-H、AS-H、OD-H、OJ-H chiral columns eluted with a mixture of isopropyl alcohol and hexane. Melting points were measured on X-4 melting point apparatus and uncorrected. High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer. Column chromatography was performed with neutral alumina with petroleum ether and ethyl acetate as eluents.

Typical procedure for rhodium/ZnI_2-cocatalyzed asymmetric ring opening reaction of oxabenzonorbornadienes with amines.

$[Rh(COD)Cl]_2$ (1.8 mg, 0.0037 mmol), (*R*,*R*)-BDPP (4.3 mg, 0.0097 mmol) and 1.0 mL DCE were added to a Schlenk tube under an argon atmosphere. The resulting solution was stirred at room temperature for 30 min, then ZnI_2 (9.6 mg, 0.03 mmol) was added and stirred for additional 10 min, then oxabenzonorbornadiene **1a** (43.2 mg, 0.3 mmol) was added, and the mixture was stirred for an additional 10 min. After the addition of aniline **2a** (139.5 mg, 1.5 mmol) and DCE (1.0 mL), the mixture was stirred at room temperature under argon atmosphere with TLC monitoring until the complete consumption of **1a**. The reaction mixture was concentrated. The residue was purified by chromatography on a neutral alumina column to afford the desired product **3aa** (66.9 mg, 94% yield). The enantioselective excess value of the product was determined by HPLC on a chiral stationary phase (94% ee).

(1*R*,2*R*)-2-(phenylamino)-1,2-dihydronaphthalen-1-ol (3aa)
White solid, 94% yield, 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 6.3 Hz, 1H), 7.32 – 7.13 (m, 5H), 6.75 (dd, *J* = 22.9, 7.5 Hz, 3H), 6.56 (d, *J* = 9.6 Hz, 1H), 6.02 (d, *J* = 9.4 Hz, 1H), 4.84 (d, *J* = 7.5 Hz, 1H), 4.33 (d, *J* = 5.4 Hz, 1H). The *ee* of **3aa** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm; t_{minor} = 8.28 min, t_{major} = 10.20 min.

(1*R*,2*R*)-2-((4-bromophenyl)amino)-1,2-dihydronaphthalen-1-ol (3ab)
White solid, 93% yield, 99% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.1 Hz, 1H), 7.23 – 7.11 (m, 4H), 7.10 – 7.01 (m, 1H), 6.49 – 6.41 (m, 3H), 5.86 (dd, *J* = 9.6, 3.7 Hz, 1H), 4.68 (d, *J* = 7.4 Hz, 1H), 4.16 – 4.09 (m, 1H), 3.55 (s, 1H). The *ee* of **3ab** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm; t_{minor} = 10.34 min, t_{major} = 11.32 min.

(1*R*,2*R*)-2-((2-bromophenyl)amino)-1,2-dihydronaphthalen-1-ol (3ac)
White solid, 56% yield, 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.33 – 7.15 (m, 4H) , 6.88 (d, *J* = 8.2 Hz, 1H), 6.69 – 6.55 (m, 2H), 5.99 (d, *J* = 9.6 Hz, 1H), 4.91 (d, *J* = 7.1 Hz, 1H), 4.36 (s, 2H), 2.42 (s, 1H). The *ee* of **3ac** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor}= 10.57 min, t_{major} = 11.61 min.

(1*R*,2*R*)-2-((3-bromophenyl)amino)-1,2-dihydronaphthalen-1-ol (3ad)
White solid, 81% yield, 99% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 6.9 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.06 (d, *J* = 6.9 Hz, 1H), 6.94 (t, *J* = 7.9 Hz, 1H), 6.78 – 6.75 (m, 2H), 6.50 (t, *J* = 8.9 Hz, 2H), 5.89 (dd, *J* = 9.6, 3.4 Hz, 1H), 4.72 (d, *J* = 7.2 Hz, 1H), 4.18 (s, 1H). The *ee* of **3ad** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm; t_{minor} = 7.20 min, t_{major} = 9.58 min.

(1*R*,2*R*)-2-((4-chlorophenyl)amino)-1,2-dihydronaphthalen-1-ol (3ae)
White solid, 94% yield, > 99% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.8 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.14 – 7.10 (m, 3H), 6.57 (dd, *J* = 15.0, 9.3 Hz, 3H), 5.96 (dd, *J* = 9.6, 3.7 Hz, 1H), 4.78 (d, *J* = 7.5 Hz, 1H), 4.26 – 4.19 (m, 1H). The *ee* of **3ae** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{minor} = 12.22 min, t_{major} = 13.25 min.

(1*R*,2*R*)-2-(*p*-tolylamino)-1,2-dihydronaphthalen-1-ol (3af)
White solid, 83% yield, 95% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 1H), 7.29 – 7.21 (m, 2H), 7.11 – 7.09 (m, 1H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 2H), 6.50 (dd, *J* = 9.7, 1.4 Hz, 1H), 5.97 (dd, *J* = 9.6, 3.5 Hz, 1H), 4.79 (d, *J* = 8.1 Hz, 1H), 4.23 (ddd, *J* = 8.1, 3.3, 1.8 Hz, 1H), 2.24 (s, 3H). The *ee* of **3af** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm; t_{minor} = 8.70 min, t_{major} = 10.93 min.

(1*R*,2*R*)-2-((4-methoxyphenyl)amino)-1,2-dihydronaphthalen-1-ol (3ag)
White solid, 83% yield, 96% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.49 (m, 1H), 7.30 – 7.27 (m, 2H), 7.15 – 7.12 (m, 1H), 6.82 – 6.78 (m, 2H), 6.70 – 6.69 (m, 2H), 6.53 (dd, *J* = 9.7, 1.4 Hz, 1H), 6.00 (dd, *J* = 9.6, 3.3 Hz, 1H), 4.82 (d, *J* = 8.4 Hz, 1H), 4.21 (ddd, *J* = 8.4, 3.1, 1.9 Hz, 1H), 3.76 (s, 3H), 3.00 (s, 1H). The *ee* of **3ag** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm; t_{minor} = 12.32 min, t_{major} = 15.73 min.

(1*R*,2*R*)-2-(methyl(phenyl)amino)-1,2-dihydronaphthalen-1-ol (3ah)
Colorness oil, 86% yield, 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 4.3 Hz, 1H), 7.26 – 7.18 (m, 4H), 7.06 (d, *J* = 4.2 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 9.8 Hz, 1H), 5.81 (d, *J* = 9.8 Hz, 1H), 4.99 (d, *J* = 9.4 Hz, 1H), 4.60 (d, *J* = 9.4 Hz, 1H), 2.73 (s, 3H), 2.14 (s, 1H). The *ee* of **3ah** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 14.01 min, t_{major} = 10.86 min.

(1*R*,2*R*)-2-((4-methoxyphenyl)(methyl)amino)-1,2-dihydronaphthalen-1-ol (3ai)
Colorness oil, 98% yield, 88% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 5.4 Hz, 1H), 7.15 – 7.12 (m, 2H), 6.98 (d, *J* = 5.7 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 8.3 Hz, 2H), 6.44 (d, *J* = 9.7 Hz, 1H), 5.83 (d, *J* = 9.6 Hz, 1H), 4.96 (d, *J* = 10.3 Hz, 1H), 4.41 (d, *J* = 10.0 Hz, 1H), 3.64 (s, 2H), 2.65 (s, 3H). The *ee* of **3ai** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 12.85 min, t_{major} = 15.27 min.

(1*R*,2*R*)-2-(ethyl(phenyl)amino)-1,2-dihydronaphthalen-1-ol (3aj)
Colorness oil, 75% yield, 89% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 1H), 7.20 – 7.12 (m, 3H), 7.05 (d, *J* = 3.8 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 9.7 Hz, 1H), 5.89 – 5.86 (m, 1H), 5.02 (d, *J* = 9.3 Hz, 1H), 4.59 (d, *J* = 9.2 Hz, 1H), 3.27 (q, *J* = 7.0 Hz, 2H), 2.29 (s, 1H), 1.07 (t, *J* = 7.0 Hz, 3H). The *ee* of **3aj** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 9.53 min, t_{major} = 7.99 min.

(1*R*,2*R*)-2-(benzyl(methyl)amino)-1,2-dihydronaphthalen-1-ol (3ak)
Colorness oil, 89% yield, 81% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 4.2 Hz, 4H), 7.17 – 7.09 (m, 4H), 6.96 (d, *J* = 7.2 Hz, 1H), 6.45 (d, *J* = 9.9 Hz, 1H), 6.02 (d, *J* =

9.9 Hz, 1H), 4.85 (d, *J* = 12.0 Hz, 1H), 3.75 (d, *J* = 13.3 Hz, 1H), 3.50 (d, *J* = 13.1 Hz, 2H), 2.24 (s, 3H). The *ee* of **3ak** was determined by HPLC analysis using Daicel Chiralcel OJ-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, 254 nm; t_{minor} = 18.51 min, t_{major} = 15.97 min.

(1*R*,2*R*)-2-(4-phenylpiperazin-1-yl)-1,2-dihydronaphthalen-1-ol (3al)

White solid, 93% yield, >99.9% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.1 Hz, 1H), 7.28 – 7.21 (m, 4H), 7.07 (d, *J* = 7.1 Hz, 1H), 6.93 – 6.85 (m, 3H), 6.54 (d, *J* = 9.9 Hz, 1H), 6.11 (d, *J* = 9.9 Hz, 1H), 4.91 (d, *J* = 11.5 Hz, 1H), 3.50 (d, *J* = 11.5 Hz, 1H), 3.21 (m, 4H), 2.95 (d, *J* = 7.6 Hz, 2H), 2.69 (d, *J* = 5.9 Hz, 2H). The *ee* of **3al** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5 with 0.1% tert-Butylamine, 1.0 mL/min, 254 nm, t_{minor} = 15.60 min, t_{major} = 17.37 min.

(1*R*,2*R*)-2-(dibenzylamino)-1,2-dihydronaphthalen-1-ol (3am)

Colorness oil, 87% yield, 87% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.9 Hz, 1H), 7.24 (d, *J* = 4.1 Hz, 8H), 7.16 – 7.10 (m, 4H), 6.96 (d, *J* = 6.9 Hz, 1H), 6.47 (d, *J* = 9.9 Hz, 1H), 6.06 (d, *J* = 9.9 Hz, 1H), 4.94 (d, *J* = 11.7 Hz, 1H), 3.89 (d, *J* = 13.6 Hz, 2H), 3.59 (d, *J* = 11.7 Hz, 1H), 3.51 (d, *J* = 13.6 Hz, 2H), 2.98 (s, 1H). The *ee* of **3am** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm, t_{minor} = 6.92 min, t_{major} = 5.82 min.

(1*R*,2*R*)-2-(tert-butylamino)-1,2-dihydronaphthalen-1-ol (3an)

White solid, 87% yield, 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz, 1H), 7.21 – 7.13 (m, 2H), 6.99 – 6.97 (m, 1H), 6.31 (dd, *J* = 9.7, 2.4 Hz, 1H), 5.88 (dd, *J* = 9.7, 2.3 Hz, 1H), 4.43 (d, *J* = 11.6 Hz, 1H), 3.41 (dt, *J* = 11.6, 2.3 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.80, 132.13, 130.65, 128.21, 128.01, 127.62, 126.12, 124.84, 72.15, 56.47, 53.60, 29.37. MS (ESI) calcd for $C_{14}H_{19}NO$ (M^+): 217.1467; Found: 217.1470. The *ee* of **3an** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20 with 0.1% tert-Butylamine, 1.0 mL/min, 254 nm; t_{minor} = 3.91 min, t_{major} = 4.36 min.

(1*R*,2*R*)-2-(piperidin-1-yl)-1,2-dihydronaphthalen-1-ol (3ao)

Colorness oil, 88% yield, 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.2 Hz, 1H), 7.27 – 7.18 (m, 2H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 9.8 Hz, 1H), 6.11 (d, *J* = 9.9 Hz, 1H), 4.86 (d, *J* = 12.1 Hz, 1H), 3.38 (d, *J* = 12.1 Hz, 1H), 2.76 – 2.74 (m, 2H), 2.47 – 2.45 (m, 2H), 1.63 – 1.57 (m, 4H), 1.49 – 1.46 (m, 2H). The *ee* of **3ao** was determined by HPLC analysis using Daicel Chiralcel OJ-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, 254 nm; t_{minor} = 12.07 min, t_{major} = 9.83 min.

(1*S*,2*S*)-2-(1*H*-indol-3-yl)-1,2-dihydronaphthalen-1-ol (3ap)

White solid, 89% yield, 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.24 – 7.02 (m, 6H), 6.81 (s, 1H), 6.56 (d, *J* = 9.5 Hz, 1H), 6.07 (dd, *J* = 9.5, 3.6 Hz, 1H), 4.92 (d, *J* = 8.0 Hz, 1H), 3.99 – 3.97 (m, 1H). The *ee* of **3ap** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm, t_{minor} = 14.60 min, t_{major} = 17.75 min.

(1*R*,2*R*)-2-((4-chlorophenyl)amino)-6,7-dimethyl-1,2-dihydronaphthalen-1-ol (3be)

White solid, 95% yield, 98% *ee*. mp 146 – 148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 7.14 – 7.12 (m, 2H), 6.95 (s, 1H), 6.63 – 6.59 (m, 2H), 6.54 (d, *J* = 9.7 Hz, 1H), 5.94 (dd, *J* = 9.6, 4.1 Hz, 1H), 4.75 (d, *J* = 6.3 Hz, 1H), 4.24 – 4.21 (m, 1H), 2.26 (s, 6H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.52, 137.35, 137.23, 132.79, 129.55, 129.30, 129.03, 128.65, 126.22, 122.97, 115.16, 71.02, 55.43, 20.01, 19.84. MS (ESI) calcd for $C_{18}H_{18}ClNO$ (M^+): 299.1064; Found: 299.1077. The *ee* of **3be** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm, t_{minor} = 17.70 min, t_{major} = 21.78 min.

(1*R*,2*R*)-2-((4-chlorophenyl)amino)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (3ce)

White solid, 64% yield, 95% *ee*. mp 70 – 72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 9.8 Hz, 1H), 6.80 (q, *J* = 9.0 Hz, 2H), 6.60 (d, *J* = 8.6 Hz, 2H), 6.09 (dd, *J* = 9.7, 5.6 Hz, 1H), 5.15 (s, 1H), 4.26 (d, *J* = 3.6 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 2.35 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.99, 149.84, 145.09, 129.19, 125.05, 123.38, 122.42, 122.10, 121.28, 114.35, 111.64, 111.07, 63.55, 56.19, 55.91, 52.56. MS (ESI) calcd for $C_{18}H_{18}ClNO_3$ (M^+): 331.0975; Found: 331.0984. The *ee* of **3ce** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm, t_{minor} = 15.30 min, t_{major} = 19.20 min.

(1*R*,2*R*)-2-((4-chlorophenyl)amino)-6,7-dimethoxy-1,2-dihydronaphthalen-1-ol (3de)

White solid, 93% yield, 99% *ee*. mp 179 – 180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.8 Hz, 2H), 6.93 (s, 1H), 6.61 – 6.54 (m, 3H), 6.42 (d, *J* = 9.6 Hz, 1H), 5.83 (dd, *J* = 9.6, 3.9 Hz, 1H), 4.66 (d, *J* = 6.9 Hz, 1H), 4.17 – 4.15 (m, 2H), 3.82 (d, *J* = 1.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.90, 148.86, 145.28, 129.28, 128.44, 127.98, 125.22, 124.59, 122.85, 114.99, 110.92, 110.33, 71.14, 56.08, 55.51. MS (ESI) calcd for $C_{18}H_{18}ClNO_3$ (M^+): 331.0975; Found: 331.0969. The *ee* of **3de** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm, t_{minor} = 14.98 min, t_{major} = 27.46 min.

(6*R*,7*R*)-7-((4-chlorophenyl)amino)-2,3,6,7-tetrahydronaphtho[2,3-*b*][1,4]dioxin-6-ol (3ee)

White solid, 75% yield, 99% *ee*. mp 185 – 187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.6 Hz, 2H), 6.96 (s, 1H), 6.68 (s, 1H), 6.61 (d, *J* = 8.6 Hz, 2H), 6.45 (d, *J* = 9.6 Hz, 1H), 5.89 (dd, *J* = 9.6, 3.9 Hz, 1H), 4.68 (d, *J* = 6.6 Hz, 1H), 4.25 (s, 4H), 4.20 – 4.18 (m, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.43, 143.59, 143.48,

129.39, 129.01, 128.29, 125.61, 125.54, 122.92, 117.07, 116.02, 115.07, 70.84, 64.59, 64.55, 55.36. MS (ESI) calcd for $C_{18}H_{16}ClNO_3$ (M^+): 329.0819; Found: 329.0806. The *ee* of **3ee** was determined by HPLC analysis using Daicel Chiralcel AS-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, 254 nm, t_{minor} = 14.65 min, t_{major} = 21.33 min.

(5*R*,6*R*)-6-((4-chlorophenyl)amino)-5,6-dihydronaphtho[2,3-*d*][1,3]dioxol-5-ol (3fe)

White solid, 89% yield, 98% *ee*. mp 131 – 133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.4 Hz, 2H), 6.95 (s, 1H), 6.66 – 6.58 (m, 3H), 6.44 (d, *J* = 9.6 Hz, 1H), 5.95 (s, 2H), 5.89 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.68 (d, *J* = 7.1 Hz, 1H), 4.20 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.59, 147.36, 145.26, 129.64, 129.28, 128.50, 126.00, 125.38, 122.90, 115.02, 108.39, 107.47, 101.23, 71.31, 55.44. MS (ESI) calcd for $C_{17}H_{14}ClNO_3$ (M^+): 315.0662; Found: 315.0674. The *ee* of **3fe** was determined by HPLC analysis using Daicel Chiralcel AS-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm, t_{minor} = 18.09 min, t_{major} = 22.99 min.

(1*R*,2*R*)-6,7-dibromo-2-((4-chlorophenyl)amino)-1,2-dihydronaphthalen-1-ol (3ge)

White solid, 81% yield, 95% *ee*. mp 172 – 176 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (s, 1H), 7.60 (s, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.66 (d, *J* = 8.5 Hz, 2H), 6.56 (d, *J* = 9.7 Hz, 1H), 6.03 (dd, *J* = 9.6, 2.8 Hz, 1H), 5.84 (d, *J* = 7.5 Hz, 1H), 5.67 (d, *J* = 5.5 Hz, 1H), 4.64 (t, *J* = 6.6 Hz, 1H), 4.10 (s, 1H), 2.50 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.63, 138.83, 133.62, 132.05, 131.28, 130.74, 128.56, 125.56, 122.71, 121.94, 119.15, 114.04, 68.99, 54.29. MS (ESI) calcd for $C_{16}H_{12}Br_2ClNO$ (M^+): 426.8974; Found: 426.8966. The *ee* of **3ge** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm, t_{minor} = 8.51 min, t_{major} = 10.25 min.

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Notes and references

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