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# Iridium-catalyzed highly enantioselective ring opening reaction of oxabenzonorbornadienes with amines

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ABSTRACT

The complex of $[Ir(COD)Cl]_2$ and (*R*)-xylyl-phanephos was used as an effective catalyst for the asymmetric ring opening reaction of oxabenzonorbornadienes with various amines. Under the optimized reaction conditions, high enantioselectivities with moderate to good yields could be obtained from a wild scope of oxabenzonorbornadienes and amines.



## 1. Introduction

As an efficient method for the construction of chiral dihydronaphthalenes, which are important building blocks in the synthesis of natural products or bioactive molecules, the transitional metal catalyzed asymmetric ring opening reactions of oxa/azabenzonorbornadienes with various nucleophiles have been extensively studied. Notable successes have been achieved for the asymmetric ring opening reactions with carbo-nucleophiles in the past few decades. For instance, many efficient chiral catalysts had been developed based on Pd,[1] Rh,[2] Cu,[3] Pt[4] and Ni[5] for the same or different carbo-nucleophiles. However, only rhodium catalysts bearing chiral ferrocenyl diphosphine ligands, which were developed by Lautens et al. were found efficient for asymmetric ring opening reactions with hetero-nucleophiles over a relatively long period of time.[6] Changes have appeared in the last few years. In addition to new rhodium catalysts with chiral monophosphine ligands, which were established by Luo et al.[7] some chiral iridium complexes have been employed as catalysts in this type of reactions. For example, the iridium catalysts possessing Binap family ligands were reported by Yang et al. to promote the asymmetric ring opening reactions of oxa/azabenzonorbornadienes with several hetero-nucleophiles smoothly.[8] The complexes of $[Ir(COD)Cl]_2$ with some monophosphine ligands were also found to be suitable catalysts for these reactions by Tang et al.[9] and by our own group.[10] Recently, by using Lewis acid as co-catalyst, a new iridium catalytic system was also established for the asymmetric ring opening reaction of azabenzonorbornadienes with amines.[11] However, these iridium catalysts encountered unstable catalytic activity to the reaction enantioselectivities or yields, and one of them lacked the tolerance of a wide scope of amines. Thus, further development of new chiral iridium catalysts, especially those with high enantioselective-control ability and a wider reaction scope, is still interesting and necessary.

Recently, our group has been attracted by the transitional metal catalyzed asymmetric reactions of norbornadiene derivatives. We have developed several efficient chiral catalysts or catalytic systems for asymmetric [2+2] cycloaddition reactions,[12] hydroalkynylation reactions[13] and alkynylative ring opening reactions[14] of norbornadiene derivatives with terminal alkynes. During the course of our investigation on the $[Ir(COD)Cl]_2$/(*R*)-xylyl-phanephos complex catalyzed asymmetric [2+2] cycloaddition reactions of oxabenzonorbornadienes, we found that this complex could also promote some asymmetric ring opening reactions with hetero-nucleophiles. Herein, we report the results of the application of this iridium catalyst in the asymmetric ring opening reaction of oxabenzonorbornadienes with amines.

## 2. Results and discussion

Initially, under the former optimized reaction conditions for the [2+2] cycloaddition reaction,[12] the complex of $[Ir(COD)Cl]_2$ and (*R*)-xylyl-phanephos[15] was tested in the asymmetric ring opening reaction of oxabenzonorbornadiene **1a** with *N*-methylaniline **2a**. After stirring at 70 °C for 22 hours, the aimed ring opening product **3aa** was obtained in 68% yield and with 92% ee (Table 1, entry 1). With this encouraging result in hand, the reaction conditions were further optimized. Besides THF (tetrahydrofuran), DMAc (*N*,*N*-dimethylacetamide), DMF (*N*,*N*-dimethylformamide), DME (dimethoxyethane), THP (tetrahydropyran) and toluene all provided the expected product in moderate yields with good ees (Table 1, entries 2–6). DCE (1,2-dichloroethane) was proved inferior here (Table 1, entry 7). In all the solvents screened, dioxane gave the highest enantioselectivity with a good yield (Table 1, entry 8). The temperature effect was then studied using dioxane

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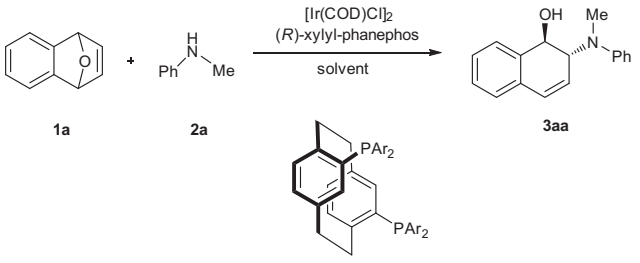
0957-4166/

**Table 1**
Screening reaction conditions[a]



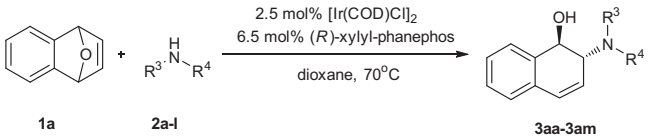

| Entry | Solvent | Temp (°C) | Time (h) | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|---|---|
| 1 | THF | 70 | 22 | 68 | 92 |
| 2 | DMAc | 70 | 3 | 71 | 90 |
| 3 | DMF | 70 | 9 | 72 | 92 |
| 4 | DME | 70 | 21 | 67 | 88 |
| 5 | THP | 70 | 21 | 55 | 91 |
| 6 | Toluene | 70 | 17 | 49 | 85 |
| 7 | DCE | 70 | 78 | Trace | / |
| 8 | Dioxane | 70 | 21 | 62 | 96 |
| 9 | Dioxane | 90 | 5.5 | 58 | 95 |
| 10[d] | Dioxane | 50 | 125 | 38 | 95 |
| 11[e] | Dioxane | 70 | 51 | 40 | 87 |
| 12[f] | Dioxane | 70 | 22 | 75 | 96 |

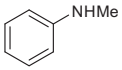
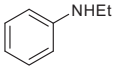
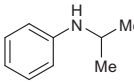
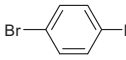
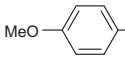
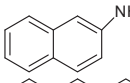
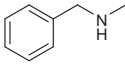
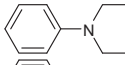
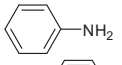
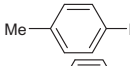
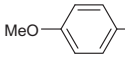
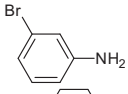
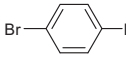
[a] The reaction was carried out with oxabenzonorbornadiene **1a** (0.3 mmol) and 3.0 equiv of *N*-methylaniline (0.9 mmol) in solvent (2.0 mL) at 70 °C (oil bath temperature) in the presence of $[Ir(COD)Cl]_2$ (1.5 mol %) and (*R*)-xylyl-phanephos (3.9 mol %).
[b] Isolated yield after neutral alumina column chromatography.
[c] Determined by HPLC with a Chiralcel OD-H column.
[d] The reaction was not completed.
[e] (*R*)-Phanephos was used as the chiral ligand.
[f] 2.5 mol % $[Ir(COD)Cl]_2$ and 6.5 mol % (*R*)-xylyl-phanephos was added.

as the solvent. Increasing the reaction temperature from 70 °C to 90 °C led to a slightly lower yield and a similar ee for the reaction (Table 1, entry 9). Lowering the reaction temperature to 50 °C did not improve the ee, but resulted in a great decrease in the reaction speed. Even after 5 days of heating and stirring, a lot of **1a** still remained in the reaction solution and **3aa** could only be separated out in 38% yield (Table 1, entry 10). When (*R*)-phanephos was used instead of (*R*)-xylyl-phanephos as the chiral ligand in the reaction, both the yield and the enantioselectivity of the reaction decreased (Table 1, entry 11). It was also found that increasing the catalyst loading improved the reaction results, and a 75% yield with 96% ee could be obtained when 5% catalyst was used (Table 1, entry 12).

With the optimal reaction conditions in hand, a series of amines were tested as nucleophiles in the ring opening reaction of **1a** (Table 2). It could be seen that the steric properties of the alkyl groups on the nitrogen atom in the *N*-alkyl substituted anilines had little effect on the enantioselectivities but a great effect on the yields of the reactions (Table 2, entries 1–3). Both of the *N*-methyl arylamines with electron-withdrawing group (Table 2, entry 4) or with an electron-donating group (Table 2, entry 5) were suitable nucleophiles, although a relatively long reaction time was needed for the latter. When *N*-methyl naphthylamine **2f** was employed as the nucleophile in the reaction, a high enantioselectivity with a good yield could be obtained (Table 2, entry 6). Under the promotion of this iridium catalyst, the dialkyl amines **2g** and **2h** also reacted with **1a**, but the asymmetric ring opening products were obtained in low yields and decreased enantioselectivities (Table 2, entries 7 and 8). Two additional amines *tert*-butylamine and cyclohexanamine only give the desired product in trace amounts but generated naphthalen-1-ol as a by-product. Besides secondary amines, primary aryl amines were also found to be

**Table 2**
Asymmetric ring opening reactions of **1a** with different amines[a,b]



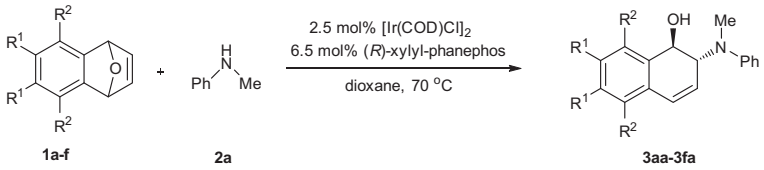

| Entry | Amine **2** | Time (h) | Yield[c] (%) | ee[d] (%) |
|---|---|---|---|---|
| 1 |  **2a** | 22 | 75 | 96 |
| 2 |  **2b** | 23 | 56 | 97 |
| 3 |  **2c** | 24 | 30 | 96 |
| 4 |  **2d** | 21 | 50 | 95 |
| 5 |  **2e** | 75 | 49 | 97 |
| 6 |  **2f** | 23 | 56 | 97 |
| 7 |  **2g** | 46 | 36 | 88 |
| 8 |  **2h** | 45 | 30 | 84 |
| 9 |  **2i** | 42 | 52 | 92 |
| 10 |  **2j** | 51 | 62 | 90 |
| 11 |  **2k** | 73 | 47 | 89 |
| 12 |  **2l** | 25 | 51 | 94 |
| 13 |  **2m** | 29 | 58 | 96 |

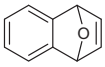
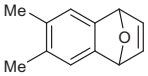
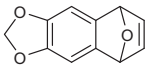
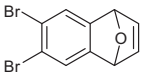
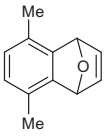
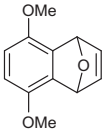
[a] The reaction was carried out with oxabenzonorbornadiene **1a** (0.3 mmol) and 3.0 equiv of amine **2** (0.9 mmol) in dioxane (2.0 mL) at 70 °C (oil bath temperature) in the presence of $[Ir(COD)Cl]_2$ (2.5 mol %) and (*R*)-xylyl-phanephos (6.5 mol %).
[b] 1-Naphthol was generated as a by-product in most cases.
[c] Isolated yield after neutral alumina column chromatography.
[d] Determined by HPLC with a Chiralcel OD-H or AD-H column.

applicable nucleophiles in this iridium-catalyzed asymmetric ring opening reaction. The aryl amines with or without substituents on the phenyl ring could all react with **1a** smoothly and generate the ring opening products with high enantioselectivities (Table 2, entries 9–13). It should be noted that the electron-withdrawing groups on the phenyl ring of aryl amines resulted in higher enantioselectivities than the electron-donating ones for the corresponding reactions.

Using *N*-methylaniline **2a** as the nucleophile, oxabenzonorbornadienes with different substituents were also applied as substrates in this iridium-catalyzed asymmetric ring opening reaction (Table 3). Compared with those of the amine counterparts, the electronic properties of the substituents on the phenyl ring of the oxabenzonorbornadienes had an opposite effect on the enantioselectivities of the reactions. The electron-donating groups resulted in higher enantioselectivities than the electron-withdrawing ones (Table 3, entries 3, 6–4). On the other hand, the positions of the electron-donating groups on the phenyl ring of the oxabenzonorbornadienes could also affect the yields of the reactions greatly. It was found that under the catalysis of this

**Table 3**
Asymmetric ring opening reactions of different oxabenzonorbornadienes with *N*-methylaniline **2a**[a]




| Entry | Oxabenzonorbornadienes **1** | | Time (h) | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|---|---|
| 1 |  | **1a** | 22 | 75 | 96 |
| 2 |  | **1b** | 10 | 56 (20)[d] | 97 |
| 3 |  | **1c** | 8 | 48 (21)[d] | 98 |
| 4 |  | **1d** | 12 | 40 (14)[d] | 86 |
| 5 |  | **1e** | 90 | 79 | 98 |
| 6 |  | **1f** | 72 | 81 | 97 |

[a] The reaction was carried out with oxabenzonorbornadiene **1** (0.3 mmol) and 3.0 equiv of **2a** (0.9 mmol) in dioxane (2.0 mL) at 70 °C (oil bath temperature) in the presence of $[Ir(COD)Cl]_2$ (2.5 mol %) and (*R*)-xylyl-phanephos (6.5 mol %).
[b] Isolated yield after neutral alumina column chromatography.
[c] Determined by HPLC with a Chiralcel OD-H or AD-H column.
[d] Isolated yield of the corresponding substituted 1-naphthol as the by-product.

iridium catalyst, the *ortho*-disubstituted oxabenzonorbornadienes were easier to convert into the isomerized by-product, substituted 1-naphthols. This competitive consumption of oxabenzonorbornadienes could greatly decrease the yields of the asymmetric ring opening reactions (Table 3, entries 2–4). Better yields were obtained for the asymmetric ring opening reactions of *para*-disubstituted oxabenzonorbornadienes, although longer reaction times were needed (Table 3, entries 5 and 6).

## 3. Conclusions

In conclusion, we have found that the complex of $[Ir(COD)Cl]_2$ and (*R*)-xylyl-phanephos was an efficient catalyst for the asymmetric ring opening reactions of oxabenzonorbornadienes with amines. Under the promotion of this iridium catalyst, both primary amines and secondary amines could react with oxabenzonorbornadiene **1a** smoothly to generally generate the ring opening products with high enantioselectivities and moderate to good yields. Furthermore, the substituent effects of oxabenzonorbornadienes on this iridium-catalyzed ring opening reaction have also been investigated. A mechanism study on the catalytic procedure and further improvement of this iridium catalyst are currently in progress.

## 4. Experimental

### 4.1. General

The reactions were carried out under argon atmosphere by using a Drybox (Mikrouna, Supper 1220/750). Oxabenzonorbornadienes were synthesized according to the published procedures.[1] Amines were purchased from reagent companies and distilled before use, while other commercial reagents were used as received without further purification. Anhydrous dioxane was distilled from sodium benzophenone ketyl prior to use. $^1H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker-Avance 400 spectrometer. Chemical shifts ($\delta$) are reported in ppm with tetramethylsilane as internal standard, and *J* values are given in Hz. The ee values were determined by Agilent 1260 Series HPLC using Daicel AD-H or OD-H, chiral columns with a mixture of *i*-propyl alcohol and *n*-hexane as eluent. The absolute configurations were assigned by comparison of the chiral HPLC data reported in the literature.[6a] Melting points were measured on an X-4 melting point apparatus and are 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.

### 4.2. Typical procedure for the Ir-catalyzed asymmetric ring opening reactions

At first, $[Ir(COD)Cl]_2$ (5.1 mg, 0.0075 mmol), (*R*)-xylyl-phanephos (13.5 mg, 0.0195 mmol) and 1.0 mL of dioxane were added to a Schlenk tube in an argon atmosphere. The resulting solution was stirred at room temperature for 30 min, then a solution of oxobenzonorbornadiene **1a** (43.2 mg, 0.3 mmol) in dioxane (1.0 mL) was added, and the mixture was stirred for an additional 20 min. After the addition of *N*-methylaniline **2a** (97.0 μl, 0.9 mmol), the mixture was stirred at 70 °C under an argon

atmosphere with TLC monitoring until the complete consumption of **1a**. After removing the solvent under reduced pressure, the residue of the reaction solution was then purified by chromatography on a neutral alumina column to afford the desired product **3aa** (56.1 mg, 75% yield). The enantiomeric excess of the product was determined to be 96% by HPLC with a Daicel Chiralcel OD-H column.

### 4.3. (1*R*,2*R*)-2-(Methyl(phenyl)amino)-1,2-dihydronaphthalen-1-ol 3aa

White solid, 75% yield, 96% ee. $[\alpha]_D^{22}$ = +31.5 (*c* 0.34, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.56–7.54 (m, 1H), 7.29–7.26 (m, 3H), 7.25–7.24 (m, 1H), 7.13–7.10 (m, 1H), 6.98–6.96 (d, *J* = 8.6 Hz, 2H), 6.82–6.78 (t, *J* = 7.3 Hz, 1H), 6.61–5.58 (dd, *J* = 9.8, 2.4 Hz, 1H), 5.95–5.92 (dd, *J* = 9.8 Hz, 3.0 Hz, 1H), 5.13–5.10 (dd, *J* = 9.8 Hz, 3.2 Hz, 1H), 4.76–4.72 (dt, *J* = 9.9 Hz, 2.7 Hz, 1H), 2.85 (s, 3H), 2.31–2.30 (d, *J* = 3.4 Hz, 1H). The ee of **3aa** 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; $t_{major}$ = 11.0 min, $t_{minor}$ = 13.2 min.

### 4.4. (1*R*,2*R*)-2-(Ethyl(phenyl)amino)-1,2-dihydronaphthalen-1-ol 3ab

Colorness oil, 56% yield, 97% ee. $[\alpha]_D^{22}$ = −16.7 (*c* 0.502, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.53–7.51 (m, 1H), 7.28–7.23 (m, 4H), 7.13–7.11 (m, 1H), 6.96–6.94 (d, *J* = 8.3 Hz, 2H), 6.79–6.75 (t, *J* = 7.2 Hz, 1H), 6.61–6.58 (dd, *J* = 9.8, 1.9 Hz, 1H), 5.97–5.94 (dd, *J* = 9.8, 3.0 Hz, 1H), 5.11–5.09 (d, *J* = 9.3 Hz, 1H), 4.68–4.66 (d, *J* = 9.3 Hz, 1H), 3.37–3.32 (q, *J* = 7.0 Hz, 2H), 2.37 (s, 1H), 1.16–1.13 (t, *J* = 7.0 Hz, 3H). The ee of **3ab** 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; $t_{major}$ = 8.3 min, $t_{minor}$ = 9.8 min.

### 4.5. (1*R*,2*R*)-2-(Isopropyl(phenyl)amino)-1,2-dihydronaphthalen-1-ol 3ac

Yellow oil, 30% yield, 96% ee. $[\alpha]_D^{22}$ = −66.3 (*c* 0.228, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$)$\delta$ 7.32–7.22 (m, 6H), 7.15–7.13 (m, 1H), 6.64–6.57 (m, 3H), 6.08–6.04 (dd, *J* = 9.48 Hz, 4.32 Hz, 1H), 5.01–4.98 (m, 1H), 4.72–4.70 (m, 1H), 4.24 (s, 1H), 3.88 (s, 1H), 1.46 (s, 6H). The ee of **3ac** 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; $t_{major}$ = 4.9 min, $t_{minor}$ = 5.6 min.

### 4.6. (1*R*,2*R*)-2-((4-Bromophenyl)(methyl)amino)-1,2-dihydronaphthalen-1-ol 3ad

Colorness oil, 50% yield, 95% ee. $[\alpha]_D^{22}$ = +75.4 (*c* 0.130, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.55–7.52 (m, 1H), 7.35–7.28 (m, 4H), 7.14–7.12 (m, 1H), 6.85–6.81 (m, 2H), 6.63–6.60 (dd, *J* = 9.7 Hz, 2.4 Hz, 1H), 5.91–5.88 (dd, *J* = 9.8 Hz, 3.1 Hz, 1H), 5.09–5.06 (dd, *J* = 9.4 Hz, 2.1 Hz, 1H), 4.70–4.66 (dt, *J* = 9.5 Hz, 2.7 Hz, 1H), 2.81 (s, 3H), 2.23–2.22 (m, 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; $t_{major}$ = 8.6 min, $t_{minor}$ = 9.9 min.

### 4.7. (1*R*,2*R*)-2-((4-Methoxyphenyl)(methyl)amino)-1,2-dihydronaphthalen-1-ol 3ae

Brown oil, 49% yield, 97% ee. $[\alpha]_D^{22}$ = +21.5 (*c* 0.0744, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.59–7.57 (m, 1H), 7.31–7.24 (m, 2H), 7.11–7.09 (m, 1H), 6.98–6.96 (m, 2H), 6.87–6.83 (m, 2H), 6.58–6.55 (dd, *J* = 9.8 Hz, 2.5 Hz, 1H), 5.97–5.94 (dd, *J* = 9.8 Hz, 2.8 Hz, 1H), 5.12–5.09 (d, *J* = 10.5 Hz, 1H), 4.56–4.52 (dt, *J* = 10.4 Hz, 2.6 Hz, 1H), 3.78 (s, 3H), 2.81 (s, 3H), 2.64 (s, 1H). The ee of **3ae** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm; $t_{minor}$ = 17.2 min, $t_{major}$ = 20.4 min.

### 4.8. (1*R*,2*R*)-2-(Methyl(naphthalen-2-yl)amino)-1,2-dihydronaphthalen-1-ol 3af

Yellow liquid, 56% yield, 97% ee. $[\alpha]_D^{22}$ = +48.5 (*c* 0.109, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.59–7.54 (m, 3H), 7.45–7.43 (m, 1H), 7.30–7.10 (m, 6H), 7.02–6.99 (m, 2H), 6.49–6.46 (dd, *J* = 9.8 Hz, 2.4 Hz, 1H), 5.85–5.81 (dd, *J* = 9.8 Hz, 2.9 Hz, 1H), 5.04–5.01 (d, *J* = 10.0 Hz, 1H), 4.76–4.73 (dt, *J* = 10.0 Hz, 2.6 Hz, 1H), 2.80 (s, 3H). The ee of **3af** 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; $t_{minor}$ = 18.5 min, $t_{major}$ = 28.6 min.

### 4.9. (1*R*,2*R*)-2-(Dibenzylamino)-1,2-dihydronaphthalen-1-ol 3ag

Colorness oil, 36% yield, 88% ee. $[\alpha]_D^{22}$ = −68.8 (*c* 0.247, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.52–7.50 (d, *J* = 6.9 Hz 1H), 7.33–7.32 (d, *J* = 4.3 Hz, 8H), 7.26–7.17 (m, 4H), 7.05–7.04 (d, *J* = 6.6 Hz, 1H), 6.57–6.54 (dd, *J* = 9.9 Hz, 2.3 Hz, 1H), 6.16–6.13 (dd, *J* = 9.9 Hz, 2.0 Hz, 1H), 5.04–5.01 (d, *J* = 11.7 Hz, 1H), 3.99–3.96 (d, *J* = 13.6 Hz, 2H), 3.69–3.66 (d, *J* = 11.7 Hz, 1H), 3.62–3.58 (d, *J* = 13.6 Hz, 2H), 3.07 (s, 1H). The ee of **3ag** 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; $t_{major}$ = 7.5 min, $t_{minor}$ = 8.9 min.

### 4.10. (1*R*,2*R*)-2-(4-Phenylpiperazin-1-yl)-1,2-dihydronaphthalen-1-ol 3ah

White solid, 30% yield, 84% ee. $[\alpha]_D^{22}$ = −107.6 (*c* 0.341, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.59–7.57 (d, *J* = 7.2 Hz, 1H), 7.28–7.21 (m, 4H), 7.09–7.07 (d, *J* = 7.2 Hz, 1H), 6.94–6.85 (m, 3H), 6.56–6.53 (dd, *J* = 9.6 Hz, 1.6 Hz, 1H), 6.16–6.13 (dd, *J* = 9.6 Hz, 2.0 Hz, 1H), 4.93–4.90 (d, *J* = 11.2 Hz, 1H), 3.52–3.49 (d, *J* = 11.6 Hz, 1H), 3.35–3.16 (m, 5H), 2.97–2.93 (m, 2H), 2.71–2.68 (m, 2H). 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 = 95/5, 1.0 mL/min, 254 nm; $t_{minor}$ = 16.0 min, $t_{major}$ = 17.4 min.

### 4.11. (1*R*,2*R*)-2-(Phenylamino)-1,2-dihydronaphthalen-1-ol 3ai

Silvery white solid, 52% yield, 92% ee. $[\alpha]_D^{22}$ = −68.8 (*c* 0.032, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.46–7.44 (m, 1H), 7.29–7.24 (m, 2H), 7.20–7.15 (m, 2H), 7.13–7.10 (m, 1H), 6.76–6.68 (m, 1H), 6.55–6.52 (dd, *J* = 9.6 Hz, 1.5 Hz, 1H), 6.01–5.98 (dd, *J* = 9.7 Hz, 3.6 Hz, 1H), 4.83–4.81 (d, *J* = 7.8 Hz, 1H), 4.32–4.28 (m, 1H). The ee of **3ah** 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; $t_{minor}$ = 9.3 min, $t_{major}$ = 11.8 min.

### 4.12. (1*R*,2*R*)-2-(*p*-Tolylamino)-1,2-dihydronaphthalen-1-ol 3aj

Light yellow solid, 62% yield, 90% ee. $[\alpha]_D^{22}$ = −100.4 (*c* 0.243, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.51–7.49 (m, 1H), 7.29–7.27 (t, *J* = 4.0 Hz, 2H), 7.14–7.12 (m, 1H), 7.04–7.02 (d, *J* = 8.1 Hz, 2H), 6.74–6.72 (d, *J* = 8.3 Hz, 2H), 6.56–6.53 (dd, *J* = 9.7 Hz, 1.4 Hz, 1H), 6.02–6.00 (dd, *J* = 9.6, 3.3 Hz, 1H), 4.90–4.88 (d, *J* = 8.4 Hz,

1H), 4.32–4.29 (m, 1H), 2.85 (s, 1H), 2.26 (s, 3H). The ee of **3ai** 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; $t_{minor}$ = 9.9 min, $t_{major}$ = 12.5 min.

### 4.13. (1*R*,2*R*)-2-((4-Methoxyphenyl)amino)-1,2-dihydronaphthalen-1-ol 3ak

White solid, 47% yield, 89% ee. $[\alpha]_D^{22}$ = −80.3 (*c* 0.0648, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.53–7.51 (m, 1H), 7.30–7.28 (m, 2H), 7.27 (s, 2H), 7.14–7.12 (m, 1H), 6.83–6.76 (m, 4H), 6.55–6.53 (dd, *J* = 9.6 Hz, 1.8 Hz, 1H), 6.03–6.00 (dd, *J* = 9.7 Hz, 3.3 Hz, 1H), 4.89–4.87 (d, *J* = 8.7 Hz, 1H), 3.77 (s, 3H). The ee of **3aj** 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; $t_{minor}$ = 14.2 min, $t_{major}$ = 18.7 min.

### 4.14. (1*R*,2*R*)-2-((3-Bromophenyl)amino)-1,2-dihydronaphthalen-1-ol 3al

Yellow oil, 51% yield, 94% ee. $[\alpha]_D^{22}$ = −75.5 (*c* 0.11, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.48–7.46 (m, 1H), 7.35–7.28 (m, 2H), 7.18–7.16 (m, 1H), 7.07–7.03 (t, *J* = 8.3 Hz, 1H), 6.89–6.87 (m, 2H), 6.65–6.59 (m, 2H), 6.02–5.99 (dd, *J* = 9.6 Hz, 3.8 Hz, 1H), 4.85–4.83 (d, *J* = 7.3 Hz, 1H), 4.31–4.28 (m, 1H), 2.47 (s, 1H). The ee of **3ak** 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; $t_{minor}$ = 8.3 min, $t_{major}$ = 11.1 min.

### 4.15. (1*R*,2*R*)-2-((4-Bromophenyl)amino)-1,2-dihydronaphthalen-1-ol 3am

Light yellow solid, 58% yield, 96% ee. $[\alpha]_D^{22}$ = −70.5 (*c* 0.095, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.49–7.46 (m, 1H), 7.33–7.26 (m, 4H), 7.16–7.14 (m, 1H), 6.66–6.62 (m, 2H), 6.60–6.57 (dd, *J* = 9.6 Hz, 1.4 Hz, 1H), 6.01–5.98 (dd, *J* = 9.6 Hz, 3.7 Hz, 1H), 4.86–4.84 (d, *J* = 7.5 Hz, 1H), 4.30–4.27 (qd, *J* = 3.7 Hz, 1.7 Hz, 1H), 2.41 (s, 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 = 80/20, 1.0 mL/min, 254 nm; $t_{minor}$ = 11.8 min, $t_{major}$ = 13.0 min.

### 4.16. (1*R*,2*R*)-6,7-Dimethyl-2-(methyl(phenyl)amino)-1,2-dihydronaphthalen-1-ol 3ba

Yellowish-white solid, 56% yield, 97% ee. $[\alpha]_D^{22}$ = +18.3 (*c* 0.278, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.30–7.24 (m, 3H), 6.97–6.95 (d, *J* = 8.1 Hz, 2H), 6.91 (s, 1H), 6.81–6.78 (t, *J* = 7.3 Hz, 1H), 6.57–6.54(dd, *J* = 9.8 Hz, 2.3 Hz, 1H), 5.87–5.84(dd, *J* = 9.7 Hz, 3.2 Hz, 1H), 5.03–5.01(d, *J* = 9.1 Hz, 1H), 4.71–4.68 (dt, *J* = 9.1 Hz, 2.8 Hz, 1H), 2.81 (s, 3H), 2.28–2.26 (d, *J* = 8.7 Hz, 7H). The ee of **3ba** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm; $t_{major}$ = 12.0 min, $t_{minor}$ = 15.6 min.

### 4.17. (5*R*,6*R*)-6-(Methyl(phenyl)amino)-5,6-dihydronaphtho[2,3-d][1,3]dioxol-5-ol 3ca

Brown oil, 48% yield, 98% ee. $[\alpha]_D^{22}$ = +11.6 (*c* 0.0865, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.30–7.26 (m, 2H), 7.07 (s, 1H), 6.99–6.97 (d, *J* = 8.2 Hz, 2H), 6.84–6.80 (t, *J* = 7.3 Hz, 1H), 6.64 (s, 1H), 6.50–6.47 (dd, *J* = 9.8 Hz, 2.4 Hz, 1H), 5.98–5.97 (m, 2H), 5.86–5.83 (dd, *J* = 9.8 Hz, 3.2 Hz, 1H), 5.00–4.98 (d, *J* = 9.4 Hz, 1H), 4.70–4.66 (dt, *J* = 9.5 Hz, 2.8 Hz, 1H), 2.84 (s, 3H), 2.30 (s, 1H). The ee of **3ca** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 254 nm; $t_{major}$ = 50.9 min, $t_{minor}$ = 54.9 min.

### 4.18. (1*R*,2*R*)-6,7-Dibromo-2-(methyl(phenyl)amino)-1,2-dihydronaphthalen-1-ol 3da

Yellow solid, 40% yield, 86% ee. $[\alpha]_D^{22}$ = +50.7 (*c* 0.412, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.82 (s, 1H), 7.29–7.25 (m, 2H), 6.96–6.94 (d, *J* = 8.1 Hz, 2H), 6.85–6.81 (t, *J* = 7.3 Hz, 1H), 6.47–6.44 (dd, *J* = 9.9 Hz, 2.7 Hz, 1H), 6.02–5.99 (dd, *J* = 9.8 Hz, 2.6 Hz, 1H), 5.08–5.05 (d, *J* = 11.1 Hz, 1H), 4.72–4.68 (dt, *J* = 11.1 Hz, 2.6 Hz, 1H), 2.89 (s, 3H), 2.56 (s, 1H). The ee of **3da** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm; $t_{major}$ = 18.5 min, $t_{minor}$ = 21.4 min.

### 4.19. (1*R*,2*R*)-5,8-Dimethyl-2-(methyl(phenyl)amino)-1,2-dihydronaphthalen-1-ol 3ea

Colorness oil, 79% yield, 98% ee. $[\alpha]_D^{22}$ = −334 (*c* 0.628, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.22–7.18 (m, 2H), 6.98–6.91 (m, 3H), 6.88–6.86 (d, *J* = 8.1 Hz, 2H), 6.72–6.68 (m, 1H), 5.91–5.87 (qd, *J* = 5.7 Hz, 1.3 Hz, 1H), 4.80 (s, 1H), 4.57–4.56 (d, *J* = 5.7 Hz, 1H), 2.31–2.30 (m, 6H), 2.24 (s, 3H), 1.60 (s, 1H). The ee of **3ea** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 97/3, 0.5 mL/min, 254 nm; $t_{minor}$ = 39.1 min, $t_{major}$ = 41.4 min.

### 4.20. (1*R*,2*R*)-5,8-Dimethoxy-2-(methyl(phenyl)amino)-1,2-dihydronaphthalen-1-ol 3fa

Brownish-yellow solid, 81% yield, 97% ee. $[\alpha]_D^{22}$ = −156.5 (*c* 0.20 $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.30–7.24 (m, 2H), 7.19–7.16 (dd, *J* = 10.0 Hz, 1.7 Hz, 1H), 6.98–6.96 (d, *J* = 8.0 Hz, 2H), 6.82–6.74 (m, 3H), 5.97–5.93 (td, *J* = 5.2 Hz, 0.8 Hz, 1H), 5.16–5.15 (d, *J* = 1.3 Hz, 1H), 4.70–4.68 (m, 1H), 3.82(s, 3H), 3.78 (s, 3H), 2.54 (s, 3H). The ee of **3fa** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, 254 nm; $t_{minor}$ = 44.3 min, $t_{major}$ = 49.8 min.

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