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Platinum(II)-Catalyzed Asymmetric Ring-Opening Addition of Arylboronic Acids to Oxabenzonorbornadienes

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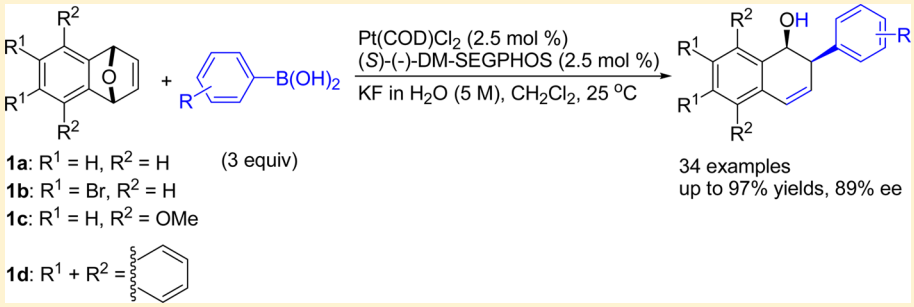
Supporting Information



ABSTRACT: A new platinum(II)-catalyzed asymmetric ring-opening addition of arylboronic acids to oxabenzonorbornadienes was developed, which afforded the corresponding *cis*-2-aryl-1,2-dihydronaphthalen-1-ol products in high yields (up to 97%) with moderate to good enantioselectivities (up to 89% ee) under very mild conditions. The effects of various ligands, catalyst loading, bases, solvents, and temperatures on the yield and enantioselectivity of the reaction were also investigated. The cis configuration of product **2m** was confirmed by X-ray diffraction analysis. A potential mechanism for the present catalytic reaction is proposed.

INTRODUCTION

The transition-metal-catalyzed asymmetric ring-opening (ARO) reactions of oxa- and azabicyclic alkenes undoubtedly provide an efficient synthetic tool for the selective formation of carbon−carbon and carbon−heteroatom bonds.[1] This process is especially valuable as multiple stereocenters can be established rapidly and efficiently in a single step. Many metal catalysts, such as Fe,[2] Ni,[3] Cu,[4] Ru,[5] Rh,[6] Pd,[7] and so forth, have been investigated for ring-opening reactions with heteroatom nucleophiles[8] and carbanion nucleophiles.[9]

Organoboronic acids are ideal carbanion nucleophiles because they are air- and moisture-tolerant.[10] Rhodium- and palladium-catalyzed ARO of oxa- and azabenzonorbornadienes with arylboronic acids have been reported by Lautens et al.,[11] Hou et al.,[12] and Murakami et al.,[13] and the *cis*-2-aryl-1,2-dihydronaphthalen-1-ol products were produced in excellent yields (up to 99%) with good enantioselectivities (up to 83% ee). To the best of our knowledge, similar ARO reactions of oxa- and azabicyclic alkenes with arylboronic acids in the presence of other transition-metal catalysts remain unknown, presenting a challenge to chemists.

Our group has been interested in the ARO of oxa- and azabenzonorbornadienes with various nucleophiles for some time. In our previous work, we successfully demonstrated the iridium-catalyzed ARO of oxa- and azabenzonorbornadienes with various nucleophiles, including amines,[14] phenols,[15] and alcohols,[16] to afford the ring-opening products in high yields with excellent enantioselectivities. The 1,2-trans products were generated via the enantioselective cleavage of a carbon−heteroatom bond followed by an S_N2' nucleophilic displacement. Our continuous interest in developing ARO of oxa- and azabicyclic alkenes prompted us to explore other transition-metal catalysts to expand the scope of the reactions. In this article, we report a novel ARO addition of arylboronic acids to oxabenzonorbornadienes in the presence of platinum complex and KF solution (5 M in H_2O) to afford the corresponding ring-opening products of *cis*-2-aryl-1,2-dihydronaphthalen-1-ols in high yields (up to 97%) with moderate to good enantioselectivities (up to 89% ee). The 1,2-cis products, potential valuable scaffolds for the synthesis of optically active compounds, were generated by transmetalation−enantioselective addition to the C═C bond over the enantioselective C−O bond cleavage. Compared to the results with Rh or Pd, the ring-opening addition reactions catalyzed by Pt showed better reactivity and higher enantioselectivity.

RESULTS AND DISCUSSION

Substrates **1a−d** were readily prepared by Diels−Alder reactions according to literature procedures.[17] We began our studies by searching for the optimal platinum catalyst system. In our initial experiments, oxabenzonorbornadiene **1a** was treated with phenylboronic acid in the presence of $Pt(COD)Cl_2$ and P,P or N,P ligand (Table 1). To explore the ring-opening

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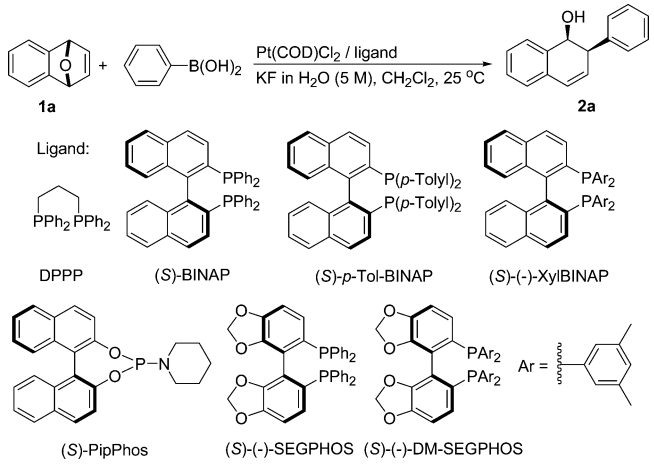
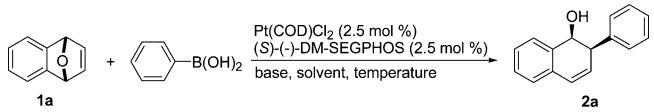
Table 1. Effects of Chiral Ligand and Catalyst Loading[a]



entry	$Pt(COD)Cl_2$ (mol %)	ligand (mol %)	time (h)	yield (%)	ee (%)[b]
1	2.5	DPPP (2.5)	24	80	0
2	2.5	(*S*)-BINAP (2.5)	22	87	80
3	2.5	(*S*)-*p*-Tol-BINAP (2.5)	22	86	64
4	2.5	(*S*)-(−)-XylBINAP (2.5)	48	77	75
5	2.5	(*S*)-PipPhos (2.5)	96	31	20
6	2.5	(*S*)-(−)-SEGPHOS (2.5)	24	89	77
7	2.5	(*S*)-(−)-DM-SEGPHOS (2.5)	20	90	82
8	1.5	(*S*)-(−)-DM-SEGPHOS (1.5)	56	67	78
9	3.0	(*S*)-(−)-DM-SEGPHOS (3.0)	17	85	78
10	4.0	(*S*)-(−)-DM-SEGPHOS (4.0)	17	80	75

[a]The reaction was carried out with **1a** (0.2 mmol), 3.0 equiv of phenylboronic acid (0.6 mmol), and 0.5 equiv of KF (5 M in H_2O) in CH_2Cl_2 (2.0 mL) at 25 °C in the presence of $Pt(COD)Cl_2$ and ligand. [b]Determined by HPLC with a Chiralcel OD-H column.

Table 2. Combined Effects of Solvent, Base, and Temperature[a]



entry	solvent	base	temperature (°C)[b]	time (h)	yield (%)	ee (%)[c]
1	MeOH	KF	25	20	28	96
2	*i*PrOH	KF	70	48	21	84
3	THF	KF	70	48	46	79
4	toluene	KF	80	30	38	55
5	DCE	KF	25	15	61	86
6	$CHCl_3$	KF	25	48	89	78
7	CH_2Cl_2	KF	25	20	90	82
8	CH_2Cl_2		25	48	n.r.	
9	CH_2Cl_2	KCl	25	72	65	69
10	CH_2Cl_2	KBr	25	72	21	66
11	CH_2Cl_2	KI	25	72	16	71
12	CH_2Cl_2	CsF	25	38	85	75
13	CH_2Cl_2	Cs_2CO_3	25	44	60	87
14	CH_2Cl_2	K_3PO_4	25	38	75	81
15	CH_2Cl_2	K_2CO_3	25	48	56	85
16	CH_2Cl_2	KF	0	48	51	84
17	CH_2Cl_2	KF	50	10	55	76

[a]The reaction was carried out with **1a** (0.2 mmol), 3.0 equiv of phenylboronic acid (0.6 mmol), and 0.5 equiv of base (5 M in H_2O) in the solvent (2.0 mL) of choice at the corresponding temperature in the presence of $Pt(COD)Cl_2$ (2.5 mol %) and (*S*)-(−)-DM-SEGPHOS (2.5 mol %). [b]Oil bath temperature. [c]Determined by HPLC with a Chiralcel OD-H column.

reaction, an achiral bisphosphine ligand DPPP was first chosen to validate the catalytic activity of platinum complex in ARO of **1a** with phenylboronic acid. Ring-opening product **2a** was obtained in an encouraging yield of 80% after 24 h (Table 1, entry 1). Inspired by this result, we then attempted several chiral ligands, including (*S*)-BINAP, (*S*)-*p*-Tol-BINAP, (*S*)-

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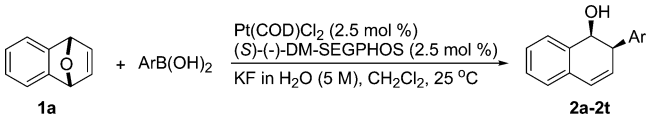
(−)-XylBINAP, (*S*)-PipPhos, (*S*)-(−)-SEGPHOS, and (*S*)-(−)-DM-SEGPHOS, to optimize the reaction. Among the ligands screened, (*S*)-(−)-DM-SEGPHOS was the most effective and afforded **2a** in 90% yield with 82% ee (Table 1, entry 7). We next investigated the effect of catalyst loading on the reaction. The results indicated that 2.5 mol % of $Pt(COD)Cl_2$ with 2.5 mol % of (*S*)-(−)-DM-SEGPHOS would be a more suitable catalyst loading in terms of the yield and enantioselectivity, whereas increasing or decreasing the amount of catalyst loading improved neither the yield nor ee value of **2a** (Table 1, entries 8−10). Therefore, we decided to choose 2.5 mol % of $Pt(COD)Cl_2$/(*S*)-(−)-DM-SEGPHOS as the best catalyst system to optimize the reaction further.

With the optimal chiral ligand and catalyst loading in hand, we next screened the effects of different parameters, including solvents, bases, and temperatures, on the reactivity and enantioselectivity for the reaction (Table 2). Some common solvents were initially tested (Table 2, entries 1−7). It was observed that the reaction in protic solvents MeOH and *i*PrOH gave excellent enantioselectivities (up to 96% ee) but poor conversion (Table 2, entries 1 and 2). When the reaction was carried out in THF, expected product **2a** was afforded in only 46% yield with 79% ee (Table 2, entry 3), whereas the employment of toluene gave a worse result (38% yield, 55% ee) (Table 2, entry 4). Moderate to good yields and enantioselectivities were obtained when DCE, $CHCl_3$, and CH_2Cl_2 were respectively employed as the solvents (Table 2, entries 5−7). The study on solvent effect indicated that CH_2Cl_2 showed the best combination of reactivity and enantioselectivity among all solvents tested (90% yield, 82% ee). With CH_2Cl_2 as the solvent, the reaction also required the addition of an inorganic base and water to achieve good activity. It was observed that no reaction occurred at all in the absence of a base (Table 2, entry 8). The impact of the base was further investigated to improve the efficiency of the reaction (Table 2, entries 7, 9−15). When the base was changed from KF to KCl, KBr, and KI, poor yields and ee values of **2a** were obtained (Table 2, entries 9−11). Control experiments also revealed that strong bases, such as KF, CsF, Cs_2CO_3, K_3PO_4, and K_2CO_3, could make the reaction proceed smoothly, but they gave either unsatisfactory yields (Table 2, entries 13−15) or undesirable ee values (Table 2, entry 12) with the exception of KF, which exhibited positive influence on the yield and enantioselectivity of **2a** (Table 2, entry 7). Temperature also play a crucial role in the ring-opening reaction. By examining the effect of temperature, we observed that the best result was obtained at 25 °C (90% yield, 82% ee) (Table 2, entry 7). When the reaction was carried out at 0 °C, ring-opening product **2a** was formed in 51% yield with 84% ee (Table 2, entry 16). Unexpectedly, the reaction at 50 °C required only 10 h to achieve complete conversion and afforded **2a** in 55% yield with 76% ee (Table 2, entry 17). Therefore, the optimal reaction conditions were identified as follows: 2.5 mol % of $Pt(COD)Cl_2$/(*S*)-(−)-DM-SEGPHOS, 3.0 equiv of arylboronic acid, and 0.5 equiv of KF (5 M in H_2O) in CH_2Cl_2 at 25 °C.

Under the optimized conditions, the scope of arylboronic acids was evaluated. The results of ARO of oxabenzonorbornadiene **1a** with various arylboronic acids were summarized in Table 3. The results indicated that the structures of arylboronic acids had a significant impact on the reactivity and enantioselectivity. In general, arylboronic acids with electron-withdrawing substituents led to relatively higher yields and lower enantioselectivities (Table 3, entries 2−7), whereas

Table 3. Platinum(II)-Catalyzed ARO Addition of Various Arylboronic Acids to Oxabenzonorbornadiene 1a[a]



1a **2a-2t**

entry	Ar	product	time (h)	yield (%)	ee (%)[b]
1	phenyl	**2a**	20	90	82
2	4-bromophenyl	**2b**	72	78	68
3	3-bromophenyl	**2c**	44	79	46
4	4-chlorophenyl	**2d**	20	86	68
5	3-chlorophenyl	**2e**	44	90	44
6	2-chlorophenyl	**2f**	42	48	49
7	4-fluorophenyl	**2g**	21	84	75
8	4-acetylphenyl	**2h**	62	trace	
9	4-methylphenyl	**2i**	19	84	82
10	3-methylphenyl	**2j**	19	90	80
11	2-methylphenyl	**2k**	90	20	11
12	4-ethylphenyl	**2l**	46	61	85
13	4-*tert*-butylphenyl	**2m**	42	70	82
14	4-methoxyphenyl	**2n**	39	51	87
15	3-methoxyphenyl	**2o**	42	61	81
16	4-ethoxyphenyl	**2p**	62	62	89
17	3,5-dimethylphenyl	**2q**	48	76	81
18	2-naphthyl	**2r**	42	54	77
19	3-thienyl	**2s**	96	22	75
20	4-pyridinyl	**2t**	96	n.r.	

[a]The reaction was carried out with **1a** (0.2 mmol), 3.0 equiv of arylboronic acid (0.6 mmol), and 0.5 equiv of KF (5 M in H_2O) in CH_2Cl_2 (2.0 mL) at 25 °C in the presence of $Pt(COD)Cl_2$ (2.5 mol %) and (*S*)-(−)-DM-SEGPHOS (2.5 mol %). [b]Determined by HPLC with a Chiralcel OD-H column.

electron-donating systems were less reactive and more selective (Table 3, entries 9−17). The ring-opening of **1a** with para-substituted phenylboronic acids offerd better enantioselectivities than those with meta- and ortho-substituted phenylboronic acids (Table 3, entries 2−6, 9−11 and 14−15). However, ARO appeared to be intolerant of substituents on the phenyl ring ortho to boron. For example, 2-chlorophenylboronic acid and 2-methylphenylboronic acid gave products **2f** and **2k** in poor yields with low ee values, respectively (Table 3, entries 6 and 11). When 4-acetylphenylboronic acid was used as the nucleophile, no ring-opening product **2h** was found because of the highly electron-withdrawing acetyl group that reduced the reactivity of the 4-acetylphenyl carbanion (Table 3, entry 8). It is noteworthy that the addition of methoxy- or ethoxy-substituted phenylboronic acids to **1a** was found to give better enantioselectivities than that of methyl- and ethyl-substituted phenylboronic acids (Table 3, entries 9, 10, 12, and 14−16). The ARO of **1a** with 3,5-dimethylphenylboronic acid also showed high reactivity and enantioselectivity (76% yield, 81% ee) (Table 3, entry 17), whereas the reaction of **1a** with 2-naphthylboronic acid gave product **2r** in only 54% yield with 77% ee (Table 3, entry 18). Additionally, two arylboronic acids containing heterocycle were employed in the ring-opening of **1a**, but the results were unsatisfactory (Table 3, entries 19 and 20). For example, thiophene-3-boronic acid reacted with **1a** and obtained **2s** in poor yield (22% yield) with modest enantioselectivity (75% ee), whereas the ring-opening reaction of **1a** with pyridine-4-boronic acid failed to afford expected

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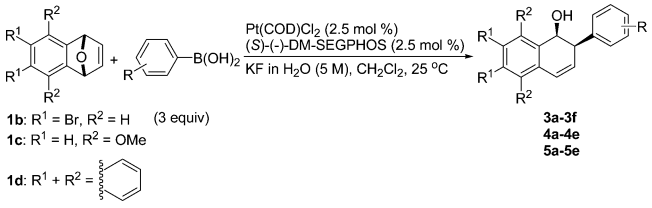
product **2t** even after a prolonged reaction time (Table 3, entry 20).

The molecular configuration of **2m** was unambiguously confirmed by X-ray diffraction analysis. The single crystal was obtained by solvent evaporation from a mixture of $CHCl_3$, hexane, and ethyl acetate. The configuration of **2m** was assigned as (1S,2R) and confirmed as the 1,2-cis configuration, as shown in the Supporting Information.

The substrate scope of the oxabicyclic alkenes was also evaluated, and the results are listed in Table 4. From Table 4, we can see that the ARO addition of arylboronic acids to oxabenzonorbornadienes **1b–d** proceeded smoothly to give the expected products in high yields (up to 97%) with moderate to good enantioselectivities (up to 89% ee). The ARO of **1b** with arylboronic acids bearing an electron-rich Me group showed better results than those bearing electron-deficient Br and Cl groups (Table 4, entries 2–5), furnishing **3d** and **3e** in excellent yields (89 and 92%, respectively) and high ee values (84 and 81% ee, respectively). However, in the case of 4-methoxyphenylboronic acid as the nucleophile for the reaction of **1b**, the yield was decreased to 61% (Table 4, entry 6). Furthermore, the ARO of **1c** are preferred for arylboronic acids involving electron-deficient substituents, obtaining the corresponding products in better yields and ee values (Table 4, entries 7–11). For example, 4-bromophenylboronic acid and 4-chlorophenylboronic acid for the ring-opening of **1c** gave ring-opening products **4b** and **4c** in 80% yield with 78% ee and 92% yield with 84% ee, respectively (Table 4, entries 8 and 9), whereas 4-methylphenylboronic acid and 3-methylphenylboronic acid afforded **4d** and **4e** in 81% yield with 73% ee and 71% yield with 83% ee, respectively (Table 4, entries 10 and 11). 1,4-Epoxy-1,4-dihydrotriphenylene **1d** also showed high reactivity and excellent enantioselectivity in the ARO with arylboronic acids under the same conditions (Table 4, entries 12–16). Ring-opening products **5a–e** were formed with almost complete conversion and satisfactory enantioselectivities. The ARO of **1d** with arylboronic acid bearing the electron-donating group Me on the phenyl ring para to boron offered better enantioselectivity (89% ee) than the one bearing the electron-withdrawing group Cl (81% ee) (Table 4, entries 13 and 14). It is also noteworthy that 4-methylphenylboronic acid performing the ARO reaction of **1d** showed the best yield and ee value (96% yield, 89% ee) compared with phenylboronic acid (95% yield, 85% ee), 3-methylphenylboronic acid (92% yield, 79% ee), and 4-ethylphenylboronic acid (90% yield, 87% ee) (Table 4, entries 12 and 14–16).

On the basis of these results, a proposed mechanism for the platinum(II)-catalyzed ARO addition of phenylboronic acid to oxabenzonorbornadiene **1a** is summarized in Scheme 1. The active catalyst of chiral platinum complex **A** was first formed through replacing the ligand COD of the precatalyst $Pt(COD)Cl_2$ by (*S*)-(−)-DM-SEGPHOS.[18] Then, platinum complex **B** was generated by transmetalation of phenyl from boron to platinum.[11,19] This process might require a base to activate the boron species and promote the reaction.[20] Next followed the addition of the phenyl–platinum linkage across a carbon–carbon double bond of **1a** from the exo side to give **C**.[13] *β*-Elimination of oxygen to open the furyl ring and to give the ring-opened intermediate **D** occurs followed by the hydrolysis to liberate ring-opened product **2a**. Meanwhile, the platinum(II) species **A** that is regenerated promotes the next catalytic cycle.

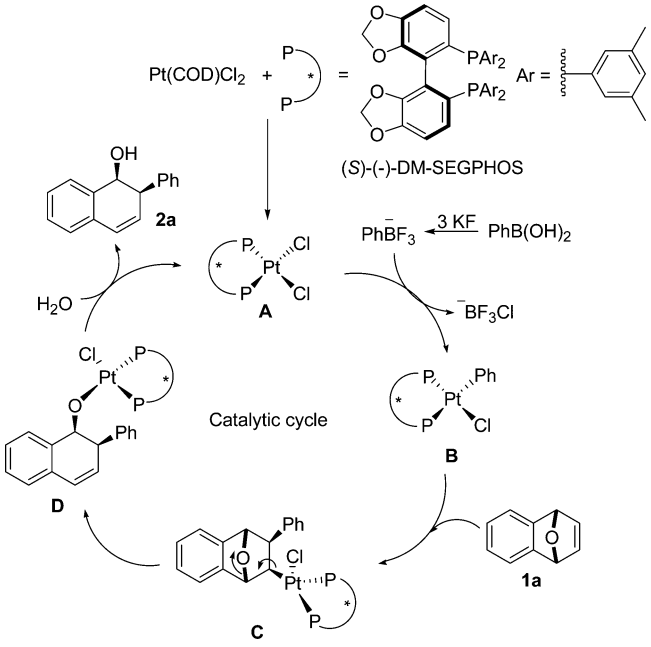
Table 4. Scope of Platinum(II)-Catalyzed ARO Addition of Various Arylboronic Acids to Oxabenzonorbornadienes 1b–d[a]



entry	substrate	R	product	time (h)	yield (%)	ee (%)[b]
1	**1b**	H	**3a**	29	80	71
2	**1b**	4-bromo	**3b**	96	77	62
3	**1b**	4-chloro	**3c**	78	92	76
4	**1b**	4-methyl	**3d**	96	89	84
5	**1b**	3-methyl	**3e**	37	92	81
6	**1b**	4-methoxy	**3f**	48	61	78
7	**1c**	H	**4a**	48	92	58
8	**1c**	4-bromo	**4b**	47	80	78
9	**1c**	4-chloro	**4c**	47	92	84
10	**1c**	4-methyl	**4d**	18	81	73
11	**1c**	3-methyl	**4e**	18	71	83
12	**1d**	H	**5a**	9	95	85
13	**1d**	4-chloro	**5b**	9	97	81
14	**1d**	4-methyl	**5c**	9	96	89
15	**1d**	3-methyl	**5d**	12	92	79
16	**1d**	4-ethyl	**5e**	24	90	87

[a]The reaction was carried out with oxabenzonorbornadiene (0.2 mmol), 3.0 equiv of arylboronic acid (0.6 mmol), and 0.5 equiv of KF (5 M in H_2O) in CH_2Cl_2 (2.0 mL) at 25 °C in the presence of $Pt(COD)Cl_2$ (2.5 mol %) and (*S*)-(−)-DM-SEGPHOS (2.5 mol %). [b]Determined by HPLC with a Chiralcel OD-H or Chiralpak AD-H column.

Scheme 1. Working Hypothesis for the Platinum(II)-Catalyzed ARO Addition of Phenylboronic Acid to Oxabenzonorbornadiene 1a



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CONCLUSIONS

We have successfully developed a new platinum(II)-catalyzed ARO of oxabenzonorbornadienes with the addition of arylboronic acids. $Pt(COD)Cl_2$ and (*S*)-(−)-DM-SEGPHOS were used as the catalyst system in ARO for the first time. The ARO addition can proceed smoothly in the presence of platinum catalyst. It provides a practical and efficient approach to synthesize the optically active *cis*-2-aryl-1,2-dihydronaphthalen-1-ol derivatives in high yields with good enantioselectivities under very mild conditions. It is also noteworthy that the addition of chiral ligands and KF have a significant impact on the reactivity and enantioselectivity of ARO. Further investigations on the applications of platinum catalysts in asymmetric reactions are in progress in our laboratory and will be reported in due course.

EXPERIMENTAL SECTION

General Procedure I for Platinum-Catalyzed ARO Addition of Arylboronic Acids to Oxabenzonorbornadienes. A 10 mL round-bottomed flask fitted with a reflux condenser was flame-dried under a stream of nitrogen and cooled to room temperature. $Pt(COD)Cl_2$ (1.9 mg, 2.5 mol %) and (*S*)-(−)-DM-SEGPHOS (3.6 mg, 2.5 mol %) were simultaneously added followed by the addition of CH_2Cl_2 (2.0 mL). The mixture was stirred for about 30 min before oxabenzonorbornadiene **1** (0.2 mmol) and arylboronic acid (3 equiv) were added. Finally, KF solution (5 M in H_2O, 20 μL, 0.5 equiv) was added. The resulting mixture was stirred at 25 °C until completion, as monitored by thin-layer chromatography. The solvent was removed in vacuo, and the crude mixture was then purified by column chromatography on silica gel (silica gel, 200−300 mesh) to afford the target product.

(1S,2R)-2-Phenyl-1,2-dihydronaphthalen-1-ol ***(2a)***. Prepared according to general procedure I. Colorless oil (40 mg, 90%). R_f = 0.21 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 82% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 8.0 (minor) and 12.2 min (major). $[\alpha]_D^{25}$ = +385.7 (*c* 1.00, $CHCl_3$). IR (neat): 3546, 3423 (br), 3030, 2920, 1601, 1493, 1451, 1379, 1071, 767 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34−7.22 (m, 8H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.70 (dd, *J* = 1.6, 9.6 Hz, 1H), 6.12 (dd, *J* = 4.0, 9.6 Hz, 1H), 4.92 (d, *J* = 5.6 Hz, 1H), 3.88−3.85 (m, 1H), 1.53 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 136.1, 132.6, 129.7, 129.3, 128.7, 128.3, 128.2, 128.0, 127.4, 126.7, 126.4, 71.3, 47.4 ppm. HRMS (APCI-ion trap) *m*/*z*: $[M - 3H]^-$ calcd for $C_{16}H_{11}O$, 219.0810; found, 219.0809.

(1S,2R)-2-(4-Bromophenyl)-1,2-dihydronaphthalen-1-ol ***(2b)***. Prepared according to general procedure I. Colorless oil (47 mg, 78%). R_f = 0.17 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 68% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 7.4 (minor) and 10.8 min (major). $[\alpha]_D^{25}$ = +410.7 (*c* 1.00, $CHCl_3$). IR (neat): 3444 (br), 3043, 2925, 1661, 1488, 1073, 1004, 803 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.33−7.23 (m, 3H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.70 (dd, *J* = 2.0, 9.6 Hz, 1H), 6.06 (dd, *J* = 4.0, 9.6 Hz, 1H), 4.89 (d, *J* = 6.0 Hz, 1H), 3.81−3.78 (m, 1H), 1.55 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.9, 135.9, 132.4, 131.6, 131.0, 129.1, 128.5, 128.4, 128.2, 126.6, 126.5, 121.3, 71.2, 46.8 ppm. (APCI-ion trap) *m*/*z*: $[M - 3H]^-$ calcd for $C_{16}H_{10}OBr$, 296.9915, 298.9894; found, 296.9924, 298.9905.

(1S,2R)-2-(3-Bromophenyl)-1,2-dihydronaphthalen-1-ol ***(2c)***. Prepared according to general procedure I. Colorless oil (48 mg, 79%). R_f = 0.19 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 46% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 7.8 (minor) and 10.6 min (major). $[\alpha]_D^{25}$ = +48.8 (*c* 1.00, $CHCl_3$). IR (neat): 3047 (br), 3069, 2926, 1665, 1594, 1567, 1473, 1068, 774 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44−7.15 (m, 8H), 6.71 (dd, *J* = 1.6, 9.6 Hz, 1H), 6.06 (dd, *J* = 3.6, 9.6 Hz, 1H), 4.86 (s, 1H), 3.82−3.80 (m, 1H), 1.57 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 135.7, 132.4, 132.3, 130.4, 130.1, 128.8, 128.6, 128.5, 128.2, 127.8, 126.8, 126.6, 122.6, 71.2, 47.1 ppm. HRMS (ESI-ion trap) *m*/*z*: $[M - 3H]^-$ calcd for $C_{16}H_{10}OBr$, 296.9915, 298.9894; found, 296.9915, 298.9894.

(1S,2R)-2-(4-Chlorophenyl)-1,2-dihydronaphthalen-1-ol ***(2d)***. Prepared according to general procedure I. White solid (44 mg, 86%). R_f = 0.16 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). mp 58−60 °C. The ee was determined to be 68% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 7.8 (minor) and 11.8 min (major). $[\alpha]_D^{25}$ = +46.3 (*c* 1.00, $CHCl_3$). IR (neat): 3547, 3430 (br), 3029, 2920, 1608, 1486, 1451, 1376, 1073, 778 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.33−7.16 (m, 8H), 6.70 (d, *J* = 9.6 Hz, 1H), 6.06 (dd, *J* = 3.6, 9.2 Hz, 1H), 4.89 (d, *J* = 5.6 Hz, 1H), 3.82−3.80 (m, 1H), 1.53 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.3, 135.9, 133.2, 132.4, 130.7, 129.2, 128.7, 128.5, 128.4, 128.2, 126.6, 126.5, 71.2, 46.7 ppm. HRMS (ESI-ion trap) *m*/*z*: $[M + Cl]^-$ calcd for $C_{16}H_{13}OCl_2$, 291.0344; found, 291.0345.

(1S,2R)-2-(3-Chlorophenyl)-1,2-dihydronaphthalen-1-ol ***(2e)***. Prepared according to general procedure I. Colorless oil (46 mg, 90%). R_f = 0.19 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 44% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 8.0 (minor) and 11.1 min (major). $[\alpha]_D^{25}$ = +140.0 (*c* 1.00, $CHCl_3$). IR (neat): 3416 (br), 3073, 2926, 1661, 1594, 1567, 1474, 1073, 783 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.32−7.11 (m, 8H), 6.70 (d, *J* = 9.6 Hz, 1H), 6.06 (dd, *J* = 4.0, 9.6 Hz, 1H), 4.85 (d, *J* = 4.4 Hz, 1H), 3.82−3.79 (m, 1H), 1.59 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 135.8, 134.4, 132.3, 129.8, 129.5, 128.9, 128.6, 128.5, 128.2, 127.5, 127.4, 126.8, 126.6, 71.2, 47.1 ppm. HRMS (ESI-ion trap) *m*/*z*: $[M + Cl]^-$ calcd for $C_{16}H_{13}OCl_2$, 291.0344; found, 291.0344.

(1R,2S)-2-(2-Chlorophenyl)-1,2-dihydronaphthalen-1-ol ***(2f)***. Prepared according to general procedure I. Colorless oil (25 mg, 48%). R_f = 0.16 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 49% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 8.2 (major) and 16.7 min (minor). $[\alpha]_D^{25}$ = +33.0 (*c* 1.00, $CHCl_3$). IR (neat): 3565, 3383 (br), 3035, 2924, 1473, 1434, 1371, 1307, 1036, 753 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44−7.19 (m, 8H), 6.74 (dd, *J* = 2.4, 9.6 Hz, 1H), 6.04 (dd, *J* = 1.6, 9.6 Hz, 1H), 4.89 (d, *J* = 3.2 Hz, 1H), 4.50−4.47 (m, 1H), 1.57 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.9, 135.1, 134.2, 132.1, 131.0, 129.6, 129.1, 128.8, 128.5, 128.3,

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128.1, 128.0, 127.0, 126.7, 69.2, 44.0 ppm. HRMS (ESI-ion trap) m/z: $[M + Cl]^-$ calcd for $C_{16}H_{13}OCl_2$, 291.0344; found, 291.0345.

(1S,2R)-2-(4-Fluorophenyl)-1,2-dihydronaphthalen-1-ol ***(2g)***. Prepared according to general procedure I. White solid (40 mg, 84%). R_f = 0.19 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). mp 59−60 °C. The ee was determined to be 75% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 7.1 (minor) and 11.4 min (major). $[\alpha]_D^{25}$ = +149.5 (c 1.00, $CHCl_3$). IR (neat): 3560, 3396 (br), 3033, 2923, 1657, 1602, 1508, 1451, 1222, 806 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.32−7.15 (m, 6H), 6.97 (t, J = 8.4 Hz, 2H), 6.69 (d, J = 9.6 Hz, 1H), 6.07 (dd, J = 4.0, 9.6 Hz, 1H), 4.88 (t, J = 6.4 Hz, 1H), 3.81 (s, 1H), 1.55 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 (d, $^1J_{CF}$ = 244.1 Hz), 136.0, 133.3 (d, $^4J_{CF}$ = 3.1 Hz), 132.5, 130.8 (d, $^3J_{CF}$ = 7.9 Hz), 129.6, 128.4, 128.3, 128.2, 126.6, 126.5, 115.4 (d, $^2J_{CF}$ = 21.1 Hz), 71.3, 46.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.33, −115.41 (m) ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{16}H_{13}OFNa$, 263.0848; found, 263.0842.

(1S,2R)-2-(4-Methylphenyl)-1,2-dihydronaphthalen-1-ol ***(2i)***. Prepared according to general procedure I. Colorless oil (40 mg, 84%). R_f = 0.20 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 82% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 6.4 (minor) and 9.3 min (major). $[\alpha]_D^{25}$ = +183.3 (c 1.00, $CHCl_3$). IR (neat): 3546, 3435 (br), 3030, 2919, 1510, 1485, 1452, 1375, 1071, 790 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34−7.10 (m, 8H), 6.68 (dd, J = 1.2, 9.6 Hz, 1H), 6.11 (dd, J = 4.0, 9.6 Hz, 1H), 4.91 (d, J = 4.8 Hz, 1H), 3.84−3.81 (m, 1H), 2.31 (s, 3H), 1.53 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 136.2, 134.4, 132.7, 129.9, 129.4, 129.1, 128.2, 128.1, 128.0, 126.7, 126.3, 71.3, 46.9, 21.1 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{17}H_{16}ONa$, 259.1099; found, 259.1090.

(1S,2R)-2-(3-Methylphenyl)-1,2-dihydronaphthalen-1-ol ***(2j)***. Prepared according to general procedure I. Colorless oil (42 mg, 90%). R_f = 0.20 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 80% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 6.7 (minor) and 8.8 min (major). $[\alpha]_D^{25}$ = +170.9 (c 1.00, $CHCl_3$). IR (neat): 3547, 3425 (br), 3031, 2920, 1606, 1488, 1452, 1378, 1072, 777 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35−7.16 (m, 5H), 7.10−7.05 (m, 3H), 6.70 (dd, J = 2.4, 10.0 Hz, 1H), 6.11 (dd, J = 3.6, 9.6 Hz, 1H), 4.89 (t, J = 4.8 Hz, 1H), 3.85−3.82 (m, 1H), 2.33 (s, 3H), 1.53 (d, J = 6.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 137.8, 136.0, 132.6, 130.0, 129.7, 128.6, 128.4, 128.2, 128.1, 128.0, 126.9, 126.4, 126.1, 71.3, 47.3, 21.5 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{17}H_{16}ONa$, 259.1099; found, 259.1091.

(1S,2R)-2-(2-Methylphenyl)-1,2-dihydronaphthalen-1-ol ***(2k)***. Prepared according to general procedure I. Colorless oil (9 mg, 20%). R_f = 0.16 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 11% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 7.5 (minor) and 12.5 min (major). $[\alpha]_D^{25}$ = +443.5 (c 1.00, $CHCl_3$). IR (neat): 3533, 3405 (br), 3029, 2926, 1668, 1481, 1463, 1378, 1072, 765 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34−7.15 (m, 8H), 6.70 (dd, J = 2.4, 9.6 Hz, 1H), 6.06 (dd, J = 3.2, 9.6 Hz, 1H), 4.80 (t, J = 5.6 Hz, 1H), 4.19−4.17 (m, 1H), 2.42 (s, 3H), 1.54 (d, J = 6.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 136.6, 135.4, 132.5, 130.7, 130.5, 129.3, 128.7, 128.0, 127.9, 127.7, 127.3, 126.6, 126.4, 69.6, 43.2, 19.9 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{17}H_{16}ONa$, 259.1099; found, 259.1090.

(1S,2R)-2-(4-Ethylphenyl)-1,2-dihydronaphthalen-1-ol ***(2l)***. Prepared according to general procedure I. Colorless oil (31 mg, 61%). R_f = 0.25 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 85% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 5.7 (minor) and 9.0 min (major). $[\alpha]_D^{25}$ = +248.4 (c 1.00, $CHCl_3$). IR (neat): 3558, 3429 (br), 3026, 2962, 2926, 1665, 1512, 1451, 1378, 1072, 839, 809 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34−7.12 (m, 8H), 6.68 (d, J = 9.6 Hz, 1H), 6.11 (dd, J = 3.2, 9.6 Hz, 1H), 4.91 (d, J = 5.2 Hz, 1H), 3.83 (s, 1H), 2.61 (q, J = 7.6 Hz, 2H), 1.54 (s, 1H), 1.21 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 136.2, 134.7, 132.7, 130.0, 129.2, 128.3, 128.2, 128.1, 128.0, 126.7, 126.3, 71.3, 47.0, 28.5, 15.5 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{18}H_{18}ONa$, 273.1255; found, 273.1246.

(1S,2R)-2-(4-tert-Butylphenyl)-1,2-dihydronaphthalen-1-ol ***(2m)***. Prepared according to general procedure I. White solid (39 mg, 70%). R_f = 0.31 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). mp 122−124 °C. The ee was determined to be 82% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 5.2 (minor) and 10.5 min (major). $[\alpha]_D^{25}$ = +217.0 (c 1.00, $CHCl_3$). IR (neat): 3558, 3421 (br), 3028, 2957, 2922, 1668, 1480, 1367, 1269, 1073, 810, 765 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.36−7.15 (m, 8H), 6.68 (d, J = 9.6 Hz, 1H), 6.12 (dd, J = 4.0, 9.6 Hz, 1H), 4.92 (s, 1H), 3.85−3.83 (m, 1H), 1.55 (s, 1H), 1.30 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 136.2, 134.5, 132.7, 130.0, 128.9, 128.3, 128.0, 127.9, 126.7, 126.4, 125.7, 71.3, 46.9, 34.5, 31.4 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{20}H_{22}ONa$, 301.1568; found, 301.1559.

(1S,2R)-2-(4-Methoxyphenyl)-1,2-dihydronaphthalen-1-ol ***(2n)***. Prepared according to general procedure I. Colorless oil (26 mg, 51%). R_f = 0.10 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 87% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 9.6 (minor) and 15.4 min (major). $[\alpha]_D^{25}$ = +324.0 (c 1.00, $CHCl_3$). IR (neat): 3552, 3458 (br), 3032, 2926, 1613, 1510, 1411, 1249, 1179, 1030, 805 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 6.8 Hz, 1H), 7.30−7.22 (m, 2H), 7.16 (d, J = 7.6 Hz, 3H), 6.84 (d, J = 8.0 Hz, 2H), 6.68 (d, J = 9.6 Hz, 1H), 6.10 (dd, J = 4.0, 9.6 Hz, 1H), 4.93 (s, 1H), 3.81 (s, 1H), 3.77 (s, 3H), 1.51 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 136.3, 132.7, 130.3, 130.1, 129.1, 128.2, 128.1, 128.0, 126.5, 126.3, 114.1, 71.3, 55.3, 46.4 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{17}H_{16}O_2Na$, 275.1048; found, 275.1038.

(1S,2R)-2-(3-Methoxyphenyl)-1,2-dihydronaphthalen-1-ol ***(2o)***. Prepared according to general procedure I. Colorless oil (31 mg, 61%). R_f = 0.10 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 81% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 10.4 (minor) and 14.9 min (major). $[\alpha]_D^{25}$ = +233.6 (c 1.00, $CHCl_3$). IR (neat): 3439 (br), 3354, 3032, 2917, 1660,

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1595, 1483, 1455, 1253, 1044, 772 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 7.2 Hz, 1H), 7.30−7.21 (m, 3H), 7.16 (d, J = 7.2 Hz, 1H), 6.86 (d, J = 7.6 Hz, 1H), 6.81−6.80 (m, 2H), 6.69 (dd, J = 1.6, 9.6 Hz, 1H), 6.11 (dd, J = 4.0, 9.6 Hz, 1H), 4.92 (d, J = 5.6 Hz, 1H), 3.85−3.82 (m, 1H), 3.73 (s, 3H), 1.57 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 139.3, 136.1, 132.6, 129.6, 129.5, 128.3, 128.2, 128.0, 126.7, 126.4, 121.5, 114.8, 112.9, 71.3, 55.1, 47.4 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{17}H_{16}O_2Na$, 275.1048; found, 275.1038.

(1S,2R)-2-(4-Ethoxyphenyl)-1,2-dihydronaphthalen-1-ol ***(2p)***. Prepared according to general procedure I. Colorless oil (33 mg, 62%). R_f = 0.12 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 89% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 7.9 (minor) and 11.9 min (major). $[\alpha]_D^{25}$ = +298.6 (c 1.00, $CHCl_3$). IR (neat): 3551, 3438 (br), 3033, 2977, 2923, 1610, 1513, 1480, 1396, 1248, 1177, 1049, 808 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 6.8 Hz, 1H), 7.30−7.21 (m, 2H), 7.16−7.13 (m, 3H), 6.82 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 9.6 Hz, 1H), 6.10 (dd, J = 4.0, 9.2 Hz, 1H), 4.91 (s, 1H), 3.99 (q, J = 6.8 Hz, 2H), 3.81−3.79 (m, 1H), 1.52 (s, 1H), 1.38 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 136.3, 132.7, 130.3, 130.1, 128.9, 128.2, 128.0, 127.9, 126.5, 126.3, 114.7, 71.3, 63.4, 46.4, 14.9 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{18}H_{18}O_2Na$, 289.1205; found, 289.1194.

(1S,2R)-2-(3,5-Dimethylphenyl)-1,2-dihydronaphthalen-1-ol ***(2q)***. Prepared according to general procedure I. Colorless oil (38 mg, 76%). R_f = 0.26 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 81% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 5.6 (minor) and 7.6 min (major). $[\alpha]_D^{25}$ = +126.7 (c 1.00, $CHCl_3$). IR (neat): 3542, 3429 (br), 3029, 2922, 1599, 1452, 1376, 1258, 1073, 810 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34−7.22 (m, 3H), 7.16 (d, J = 7.2 Hz, 1H), 6.90 (s, 3H), 6.69 (d, J = 9.6 Hz, 1H), 6.10 (dd, J = 2.8, 8.8 Hz, 1H), 4.84 (s, 1H), 3.82−3.79 (m, 1H), 2.28 (s, 6H), 1.55 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 137.9, 136.0, 132.7, 129.8, 129.1, 128.4, 128.1, 127.9, 127.1, 126.9, 126.4, 71.3, 47.3, 21.4 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{18}H_{18}ONa$, 273.1255; found, 273.1239.

(1S,2R)-2-Naphthyl-1,2-dihydronaphthalen-1-ol ***(2r)***. Prepared according to general procedure I. Colorless oil (29 mg, 54%). R_f = 0.19 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 77% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 12.4 (minor) and 15.1 min (major). $[\alpha]_D^{25}$ = +186.6 (c 1.00, $CHCl_3$). IR (neat): 3549, 3432 (br), 3053, 2923, 1599, 1507, 1451, 1377, 1072, 791 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.76−7.71 (m, 4H), 7.45−7.40 (m, 2H), 7.31−7.16 (m, 5H), 6.72 (d, J = 9.6 Hz, 1H), 6.17 (dd, J = 3.6, 9.6 Hz, 1 H), 4.94 (s, 1H), 3.97−3.95 (m, 1H), 1.58 (d, J = 6.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.1, 135.4, 133.5, 132.8, 132.7, 129.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.4, 126.8, 126.5, 126.2, 125.9, 71.3, 47.5 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{20}H_{16}ONa$, 295.1099; found, 295.1089.

(1S,2R)-2-(Thiophen-3-yl)-1,2-dihydronaphthalen-1-ol ***(2s)***. Prepared according to general procedure I. Colorless oil (10 mg, 22%). R_f = 0.22 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 75% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 95:5, 1.0 mL/min, λ = 254 nm). Retention times were 14.3 (minor) and 21.9 min (major). $[\alpha]_D^{25}$ = +416.0 (c 1.00, $CHCl_3$). IR (neat): 3546, 3410 (br), 3034, 2923, 1663, 1506, 1396, 1295, 1077, 788 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 6.8 Hz, 1H), 7.31−7.23 (m, 3H), 7.15 (d, J = 6.8 Hz, 2H), 6.90 (d, J = 4.8 Hz, 1H), 6.65 (d, J = 9.6 Hz, 1H), 6.12 (dd, J = 4.4, 9.6 Hz, 1H), 4.97 (t, J = 6.4 Hz, 1H), 3.97 (t, J = 4.4 Hz, 1H), 1.62 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 136.4, 132.6, 129.5, 128.2, 128.1, 127.9, 126.3, 126.2, 126.1, 123.1, 70.9, 42.7 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{14}H_{12}OSNa$, 251.0507; found, 251.0496.

(1S,2R)-6,7-Dibromo-2-phenyl-1,2-dihydronaphthalen-1-ol ***(3a)***. Prepared according to general procedure I. Colorless oil (61 mg, 80%). R_f = 0.18 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 71% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 8.8 (minor) and 11.1 min (major). $[\alpha]_D^{25}$ = −104.2 (c 1.00, $CHCl_3$). IR (neat): 3517, 3338 (br), 3026, 2919, 1664, 1490, 1465, 1383, 887, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.40 (s, 1H), 7.29 (s, 3H), 7.18 (s, 2H), 6.60 (d, J = 9.6 Hz, 1H), 6.20 (dd, J = 4.4, 9.2 Hz, 1H), 4.96 (d, J = 5.6 Hz, 1H), 3.82 (s, 1H), 1.58 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 135.6, 133.5, 131.8, 131.5, 130.8, 129.3, 128.9, 127.9, 126.4, 124.0, 123.6, 70.3, 46.7 ppm. HRMS (ESI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{16}H_9OBr_2$, 376.9000; found, 376.9013.

(1S,2R)-6,7-Dibromo-2-(4-bromophenyl)-1,2-dihydronaphthalen-1-ol ***(3b)***. Prepared according to general procedure I. Colorless oil (71 mg, 77%). R_f = 0.17 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 62% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 95:5, 1.0 mL/min, λ = 254 nm). Retention times were 10.7 (minor) and 12.4 min (major). $[\alpha]_D^{25}$ = +28.6 (c 1.00, $CHCl_3$). IR (neat): 3372 (br), 2928, 2852, 1666, 1486, 1466, 1392, 1074, 1010 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.44−7.41 (m, 3H), 7.05 (d, J = 8.0 Hz, 2H), 6.61 (d, J = 9.6 Hz, 1H), 6.17 (dd, J = 4.8, 9.6 Hz, 1H), 4.97 (t, J = 7.2 Hz, 1H), 3.79 (t, J = 5.2 Hz, 1H), 1.48 (d, J = 8.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 134.8, 133.3, 131.9, 131.4, 131.2, 131.0, 130.9, 126.7, 124.2, 123.8, 121.9, 70.1, 46.1 ppm. HRMS (ESI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{16}H_8OBr_3$, 454.8105, 456.8084; found, 454.8100, 456.8079.

(1S,2R)-6,7-Dibromo-2-(4-chlorophenyl)-1,2-dihydronaphthalen-1-ol ***(3c)***. Prepared according to general procedure I. Colorless oil (76 mg, 92%). R_f = 0.17 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 76% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 95:5, 1.0 mL/min, λ = 254 nm). Retention times were 9.9 (minor) and 11.8 min (major). $[\alpha]_D^{25}$ = +167.7 (c 1.00, $CHCl_3$). IR (neat): 3545, 3376 (br), 3041, 2922, 1665, 1590, 1487, 1465, 1269, 1086, 1015, 886 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 1H), 7.39 (s, 1H), 7.25 (d, J = 7.6 Hz, 2H), 7.08 (d, J = 7.6 Hz, 2H), 6.59 (d, J = 9.6 Hz, 1H), 6.15 (dd, J = 4.8, 9.6 Hz, 1H), 4.91 (d, J = 5.6 Hz, 1H), 3.77 (t, J = 5.6 Hz, 1H), 1.62 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 134.3, 133.7, 133.3, 131.4, 131.3, 130.9, 130.7, 128.9, 126.7, 124.2, 123.8, 70.2, 46.1 ppm. HRMS (ESI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{16}H_8OBr_2Cl$, 410.8610; found, 410.8605.

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*(1S,2R)-6,7-Dibromo-2-(4-methylphenyl)-1,2-dihydronaphthalen-1-ol (**3d**).* Prepared according to general procedure I. Colorless oil (70 mg, 89%). R_f = 0.26 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 84% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 95:5, 1.0 mL/min, λ = 254 nm). Retention times were 8.4 (minor) and 9.4 min (major). $[\alpha]_D^{25}$ = +155.1 (*c* 1.00, $CHCl_3$). IR (neat): 3545, 3385 (br), 2922, 2855, 1665, 1509, 1465, 1376, 1077, 886 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.39 (s, 1H), 7.07 (q, *J* = 7.6 Hz, 4H), 6.57 (d, *J* = 9.6 Hz, 1H), 6.18 (dd, *J* = 4.8, 9.6 Hz, 1H), 4.95 (d, *J* = 2.8 Hz, 1H), 3.78 (t, *J* = 5.2 Hz, 1H), 2.30 (s, 3H), 1.55 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 137.3, 133.6, 132.2, 132.0, 131.4, 130.7, 129.6, 129.2, 126.2, 123.9, 123.6, 70.2, 46.3, 21.0 ppm. HRMS (ESI-ion trap) *m/z*: $[M - 3H]^-$ calcd for $C_{17}H_{11}OBr_2$, 390.9156; found, 390.9151.

*(1S,2R)-6,7-Dibromo-2-(3-methylphenyl)-1,2-dihydronaphthalen-1-ol (**3e**).* Prepared according to general procedure I. Colorless oil (73 mg, 92%). R_f = 0.26 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 81% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 5.2 (minor) and 7.2 min (major). $[\alpha]_D^{25}$ = +139.6 (*c* 1.00, $CHCl_3$). IR (neat): 3542, 3425 (br), 3033, 2922, 1603, 1574, 1465, 1376, 1073, 886, 774 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.39 (s, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.00 (s, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 9.6 Hz, 1H), 6.18 (dd, *J* = 4.4, 9.6 Hz, 1H), 4.91 (d, *J* = 6.0 Hz, 1H), 3.78 (t, *J* = 4.8 Hz, 1H), 2.31 (s, 3H), 1.58 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 137.1, 135.7, 133.5, 131.8, 131.6, 130.8, 130.1, 128.8, 128.7, 126.3, 126.1, 124.0, 123.5, 70.2, 46.7, 21.5 ppm. HRMS (ESI-ion trap) *m/z*: $[M - 3H]^-$ calcd for $C_{17}H_{11}OBr_2$, 390.9156; found, 390.9148.

*(1S,2R)-6,7-Dibromo-2-(4-methoxyphenyl)-1,2-dihydronaphthalen-1-ol (**3f**).* Prepared according to general procedure I. Colorless oil (50 mg, 61%). R_f = 0.09 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 78% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 95:5, 1.0 mL/min, λ = 254 nm). Retention times were 13.8 (minor) and 15.0 min (major). $[\alpha]_D^{25}$ = +119.3 (*c* 1.00, $CHCl_3$). IR (neat): 3419 (br), 2925, 1668, 1608, 1510, 1464, 1250, 1178, 1034 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.39 (s, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 9.6 Hz, 1H), 6.18 (dd, *J* = 4.8, 9.6 Hz, 1H), 4.95 (d, *J* = 6.4 Hz, 1H), 3.78 (s, 1H), 3.76 (s, 3H), 1.57 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 137.3, 133.6, 132.2, 131.3, 130.7, 130.4, 126.9, 126.1, 123.9, 123.6, 114.3, 70.2, 55.3, 45.7 ppm. HRMS (ESI-ion trap) *m/z*: $[M - 3H]^-$ calcd for $C_{17}H_{11}O_2Br_2$, 406.9105; found, 406.9106.

*(1S,2R)-5,8-Dimethoxy-2-phenyl-1,2-dihydronaphthalen-1-ol (**4a**).* Prepared according to general procedure I. Colorless oil (52 mg, 92%). R_f = 0.13 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 58% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 15.5 (minor) and 24.9 min (major). $[\alpha]_D^{25}$ = −93.5 (*c* 1.00, $CHCl_3$). IR (neat): 3567, 3472 (br), 2936, 1597, 1483, 1453, 1259, 1091 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.43−7.37 (m, 4H), 7.30 (t, *J* = 6.8 Hz, 1H), 7.09 (dd, *J* = 2.8, 10.0 Hz, 1H), 6.80 (q, *J* = 8.8 Hz, 2H), 6.14 (d, *J* = 9.6 Hz, 1H), 5.08 (d, *J* = 3.2 Hz, 1H), 3.81 (d, *J* = 5.6 Hz, 6H), 3.79 (s, 1H), 1.63 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 149.6, 140.4, 129.1, 128.9, 128.6, 127.0, 124.2, 122.5, 122.1, 111.4, 110.9, 64.3, 56.2, 56.1, 47.3 ppm. HRMS (ESI-ion trap) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{18}O_3Na$, 305.1154; found, 305.1144.

*(1S,2R)-5,8-Dimethoxy-2-(4-bromophenyl)-1,2-dihydronaphthalen-1-ol (**4b**).* Prepared according to general procedure I. White solid (58 mg, 80%). R_f = 0.11 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). mp 112−114 °C. The ee was determined to be 78% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 20.2 (minor) and 30.5 min (major). $[\alpha]_D^{25}$ = +20.7 (*c* 1.00, $CHCl_3$). IR (neat): 3573, 3463 (br), 2935, 1597, 1488, 1462, 1259, 1086, 801 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 9.6 Hz, 1H), 6.80 (q, *J* = 9.2 Hz, 2H), 6.05 (d, *J* = 9.6 Hz, 1H), 5.05 (s, 1H), 3.81 (d, *J* = 6.8 Hz, 6H), 3.72 (s, 1H), 1.65 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 149.6, 139.6, 131.5, 130.9, 128.3, 124.2, 122.3, 122.2, 120.8, 111.4, 111.0, 64.2, 56.2, 56.1, 46.7 ppm. HRMS (ESI-ion trap) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{17}O_3BrNa$, 383.0259, 385.0238; found, 383.0252, 385.0230.

*(1S,2R)-5,8-Dimethoxy-2-(4-chlorophenyl)-1,2-dihydronaphthalen-1-ol (**4c**).* Prepared according to general procedure I. White solid (58 mg, 92%). R_f = 0.11 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). mp 96−98 °C. The ee was determined to be 84% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 19.0 (minor) and 29.6 min (major). $[\alpha]_D^{25}$ = −30.4 (*c* 1.00, $CHCl_3$). IR (neat): 3467 (br), 2935, 1599, 1483, 1462, 1259, 1088, 804 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 4H), 7.08 (dd, *J* = 2.8, 10.0 Hz, 1H), 6.80 (q, *J* = 9.2 Hz, 2H), 6.05 (d, *J* = 10.0 Hz, 1H), 5.05 (s, 1H), 3.81 (d, *J* = 7.6 Hz, 6H), 3.73 (s, 1H), 1.66 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 149.6, 139.1, 132.7, 130.6, 128.6, 128.4, 124.2, 122.3, 122.2, 111.4, 111.0, 64.3, 56.2, 56.1, 46.6 ppm. HRMS (ESI-ion trap) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{17}O_3ClNa$, 339.0764; found, 339.0752.

*(1S,2R)-5,8-Dimethoxy-2-(4-methylphenyl)-1,2-dihydronaphthalen-1-ol (**4d**).* Prepared according to general procedure I. Colorless oil (48 mg, 81%). R_f = 0.12 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 73% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 13.0 (minor) and 20.7 min (major). $[\alpha]_D^{25}$ = −69.2 (*c* 1.00, $CHCl_3$). IR (neat): 3487 (br), 2929, 1600, 1514, 1483, 1462, 1259, 1088, 801 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.08 (dd, *J* = 3.2, 10.0 Hz, 1H), 6.80 (q, *J* = 8.8 Hz, 2H), 6.12 (d, *J* = 10.0 Hz, 1H), 5.06 (s, 1H), 3.81 (d, *J* = 4.4 Hz, 6H), 3.77−3.74 (m, 1H), 2.36 (s, 3H), 1.61 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 149.6, 137.2, 136.6, 129.3, 129.2, 129.0, 124.3, 122.6, 122.0, 111.4, 110.9, 64.4, 56.2, 56.1, 46.8, 21.1 ppm. HRMS (ESI-ion trap) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{20}O_3Na$, 319.1310; found, 319.1300.

*(1S,2R)-5,8-Dimethoxy-2-(3-methylphenyl)-1,2-dihydronaphthalen-1-ol (**4e**).* Prepared according to general procedure I. Colorless oil (42 mg, 71%). R_f = 0.14 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 83% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 12.8 (minor) and 18.4 min (major). $[\alpha]_D^{25}$ = +37.0 (*c* 1.00, $CHCl_3$). IR (neat): 3546, 3457 (br), 2919, 1596, 1482, 1457, 1258, 1086 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.31−7.23 (m, 3H), 7.13 (d, *J* = 7.2 Hz, 1H),

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7.09 (dd, J = 3.2, 9.6 Hz, 1H), 6.82 (q, J = 9.2 Hz, 2H), 6.15 (dd, J = 1.6, 10.0 Hz, 1H), 5.08 (s, 1H), 3.83 (d, J = 2.8 Hz, 6H), 3.78−3.76 (m, 1H), 2.39 (s, 3H), 1.58 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 149.6, 140.2, 138.2, 129.8, 129.0, 128.5, 127.8, 126.1, 124.2, 122.6, 122.0, 111.4, 110.8, 64.3, 56.2, 56.1, 47.2, 21.5 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{19}H_{20}O_3Na$, 319.1310; found, 319.1295.

(1S,2R)-2-Phenyl-1,2-dihydrotriphenylen-1-ol (**5a**). Prepared according to general procedure I. Colorless oil (61 mg, 95%). R_f = 0.23 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 85% using HPLC analysis on a Chiralpak AD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 58.1 (minor) and 62.6 min (major). $[\alpha]_D^{25}$ = −155.3 (c 1.00, $CHCl_3$). IR (neat): 3548, 3407 (br), 3022, 2923, 1668, 1495, 1449, 1397, 1072, 751 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (t, J = 7.2 Hz, 2H), 8.31−8.23 (m, 2H), 7.68−7.44 (m, 9H), 7.38 (d, J = 6.4 Hz, 1H), 6.46 (d, J = 9.6 Hz, 1H), 5.41 (s, 1H), 4.01 (s, 1H), 1.68 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 130.8, 130.7, 130.6, 129.9, 129.2, 128.8, 128.7, 128.6, 127.3, 127.2, 126.9, 126.8, 126.6, 126.4, 124.1, 123.9, 123.8, 123.1, 123.0, 67.6, 48.0 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{24}H_{18}ONa$, 345.1255; found, 345.1242.

(1S,2R)-2-(4-Chlorophenyl)-1,2-dihydrotriphenylen-1-ol (**5b**). Prepared according to general procedure I. Colorless oil (69 mg, 97%). R_f = 0.28 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 81% using HPLC analysis on a Chiralpak AD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm). Retention times were 29.1 (minor) and 60.9 min (major). $[\alpha]_D^{25}$ = −103.5 (c 1.00, $CHCl_3$). IR (neat): 3368 (br), 3064, 2923, 1660, 1490, 1446, 1399, 1090, 759 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (t, J = 7.6 Hz, 2H), 8.30−8.22 (m, 2H), 7.73−7.61 (m, 4H), 7.56 (dd, J = 3.2, 9.6 Hz, 1H), 7.43 (s, 4H), 6.38 (dd, J = 1.2, 10.0 Hz, 1H), 5.38 (s, 1H), 3.98−3.95 (m, 1H), 1.66 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 133.1, 130.7, 130.6, 130.5, 130.3, 129.6, 128.8, 128.6, 127.3, 127.0, 126.5, 126.4, 124.1, 124.0, 123.7, 123.2, 123.1, 67.5, 47.4 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{24}H_{17}OClNa$, 379.0866; found, 379.0852.

(1S,2R)-2-(4-Methylphenyl)-1,2-dihydrotriphenylen-1-ol (**5c**). Prepared according to general procedure I. Colorless oil (65 mg, 96%). R_f = 0.26 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 89% using HPLC analysis on a Chiralpak AD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 44.5 (minor) and 52.6 min (major). $[\alpha]_D^{25}$ = +142.5 (c 1.00, $CHCl_3$). IR (neat): 3546, 3429 (br), 3030, 2922, 1665, 1514, 1450, 1377, 1073, 996, 758 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (t, J = 7.6 Hz, 2H), 8.27−8.21 (m, 2H), 7.63 (d, J = 24.0 Hz, 4H), 7.50 (d, J = 9.6 Hz, 1H), 7.36 (d, J = 6.0 Hz, 2H), 7.24 (d, J = 7.2 Hz, 2H), 6.40 (d, J = 10.0 Hz, 1H), 5.35 (s, 1H), 3.93 (s, 1H), 2.39 (s, 3H), 1.68 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0, 136.9, 131.1, 130.7, 130.6, 130.0, 129.5, 129.1, 128.7, 128.6, 127.3, 126.9, 126.8, 126.6, 126.4, 124.1, 123.9, 123.1, 67.6, 47.6, 21.2 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{25}H_{20}ONa$, 359.1412; found, 359.1399.

(1S,2R)-2-(3-Methylphenyl)-1,2-dihydrotriphenylen-1-ol (**5d**). Prepared according to general procedure I. Colorless oil (62 mg, 92%). R_f = 0.22 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 79% using HPLC analysis on a Chiralpak AD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 24.5 (minor) and 41.1 min (major). $[\alpha]_D^{25}$ = +153.7 (c 1.00, $CHCl_3$). IR (neat): 3463 (br), 3362, 3055, 2921, 1663, 1602, 1448, 1375, 758, 725 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (t, J = 9.6 Hz, 2H), 8.25−8.18 (m, 2H), 7.67−7.55 (m, 4H), 7.47 (dd, J = 3.2, 10.0 Hz, 1H), 7.33−7.24 (m, 3H), 7.15 (d, J = 7.6 Hz, 1H), 6.39 (d, J = 10.0 Hz, 1H), 5.34 (d, J = 4.4 Hz, 1H), 3.91−3.89 (m, 1H), 2.40 (s, 3H), 1.68 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 138.4, 130.9, 130.7, 130.6, 130.0, 128.7, 128.6, 128.1, 127.3, 126.9, 126.8, 126.6, 126.4, 126.2, 124.1, 123.9, 123.8, 123.1, 67.6, 47.9, 21.6 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{25}H_{20}ONa$, 359.1412; found, 359.1391.

(1R,2S)-2-(4-Ethylphenyl)-1,2-dihydrotriphenylen-1-ol (**5e**). Prepared according to general procedure I. Colorless oil (63 mg, 90%). R_f = 0.29 on silica gel (petroleum ether/ethyl acetate 10:1, v/v). The ee was determined to be 87% using HPLC analysis on a Chiralpak AD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 40.1 (major) and 41.9 min (minor). $[\alpha]_D^{25}$ = +99.5 (c 1.00, $CHCl_3$). IR (neat): 3379 (br), 3064, 2931, 1664, 1605, 1509, 1449, 996, 758, 724 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (t, J = 8.4 Hz, 2H), 8.27−8.20 (m, 2H), 7.68−7.58 (m, 4H), 7.49 (dd, J = 3.2, 10.0 Hz, 1H), 7.38 (d, J = 7.6 Hz, 2H), 7.27 (d, J = 7.6 Hz, 2H), 6.41 (d, J = 9.6 Hz, 1H), 5.36 (s, 1H), 3.95−3.93 (m, 1H), 2.69 (q, J = 7.6 Hz, 2H), 1.70 (s, 1H), 1.28 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 137.2, 131.1, 130.7, 130.6, 130.0, 129.1, 128.7, 128.6, 128.3, 127.2, 126.9, 126.8, 126.6, 126.3, 124.1, 123.9, 123.8, 123.1, 67.6, 47.6, 28.6, 15.7 ppm. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{26}H_{22}ONa$, 373.1568; found, 373.1547.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental methods; ^{1}H and ^{13}C NMR spectra of compounds **2a−g**, **2i−s**, **3a−f**, **4a−e**, and **5a−e**; ^{19}F NMR spectra of **2g**; HPLC conditions and spectra of compounds **2a**, **2i**, **2l−p**, **3e**, **4e**, and **5a**; and X-ray structure data for compound **2m** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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