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Nickel-Catalyzed Asymmetric Ring Opening of Oxabenzonorbornadienes with Arylboronic Acids

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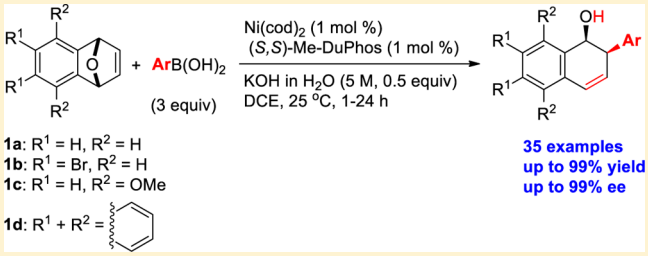
Supporting Information

ABSTRACT: A new, versatile, and highly efficient nickel-catalyzed asymmetric ring-opening (ARO) reaction of oxabenzonorbornadienes with a wide variety of arylboronic acids has been developed, yielding *cis*-2-aryl-1,2-dihydronaphthalen-1-ols in high yields (up to 99%) with good to excellent enantioselectivities (up to 99% ee) under very mild conditions. The effects of various nickel precursors, chiral bidentate ligands, catalyst loadings, bases, solvents, and temperatures on the yield and enantioselectivity of the reaction were also investigated. A plausible mechanism was proposed to account for the formation of the corresponding *cis*-ring-opened products based on the X-ray structure of product **4b**.



INTRODUCTION

Transition-metal-catalyzed asymmetric ring-opening (ARO) reactions of oxa- and azabicyclic alkenes have emerged as an important method for the construction of carbon−carbon and carbon−heteroatom bonds.[1] These transformations are especially valuable because multiple stereocenters can be established in a single step, and the resulting hydronaphthalene scaffolds exist in a wide range of natural products and bioactive molecules.[2] Numerous metal catalysts, including rhodium,[3] palladium,[4] iridium,[5] copper,[6] zirconium,[7] nickel,[8] etc., have been explored for the ARO of heterobicyclic alkenes with hydride reagents as well as heteroatom and carbon nucleophiles.

Among various carbon nucleophiles, arylboronic acids are highly useful due to their commercial availability, structural diversity, stability, and low toxicity. In 2002, Lautens and co-workers reported the rhodium-catalyzed ARO addition of arylboronic acids to [2.2.1]oxabicycle alkenes, in which high yields and excellent enantioselectivities were obtained.[3j] Meanwhile, Murakami et al. also described the rhodium-catalyzed ring opening of oxabenzonorbornadienes with arylboronic acids to obtain the corresponding racemic products.[9] In 2003, Lautens and co-workers successfully extended the substrate scope of oxabenzonorbornadienes to less-reactive aza-counterparts in the presence of a palladium catalyst, affording *cis*-1-amino-2-aryldihydronaphthalenes in excellent yields.[4h] In 2008, a chiral phosphine-containing palladacycle catalyzed enantioselective arylative ring opening of oxabenzonorbornadienes with arylboronic acids was developed by Hou and co-workers.[4i] The reaction showed high catalytic activity (up to 99% yield) and asymmetric induction ability (up to 83% ee). Recently, our group demonstrated a platinum-catalyzed ARO of oxabenzonorbornadienes with arylboronic acids, which generated *cis*-ring-opened products in high yields (up to 97%) with good enantioselectivities (up to 89% ee).[10] However, one common disadvantage for these reported catalysts is that they are expensive, need a high catalyst loading, and suffer poor compatibilities. Therefore, development of a more versatile and efficient chiral catalyst for this type of reaction is of great interest.

Nickel catalysts are particularly attractive by virtue of their low price and high efficiency for the ARO of oxabicyclic alkenes with DIBAL-H (diisobutyl aluminum hydride) and carboxylic acids in excellent enantioselectivities of up to 99.5% ee.[8] In addition, Lautens et al. and Cheng et al. have reported nickel-catalyzed ring-opening reactions of oxabicyclic alkenes using organic halides, alkynes, Grignard reagents, and organozirconium reagents, as important carbon nucleophiles.[11] However, to the best of our knowledge, nickel-catalyzed enantioselective ring opening of oxabicyclic alkenes by arylboronic acids remains in demand. Herein, we report a new, versatile, and highly efficient nickel-catalyzed ARO of oxabenzonorbornadienes with arylboronic acids, which afford *cis*-2-aryl-1,2-dihydronaphthalen-1-ols in high yields (up to 99%) with good to excellent enantioselectivities (up to 99% ee). In particular, compared to the previous rhodium, palladium, and platinum catalysts, this catalyst system features a cheaper catalyst precursor, lower catalyst loading, and higher

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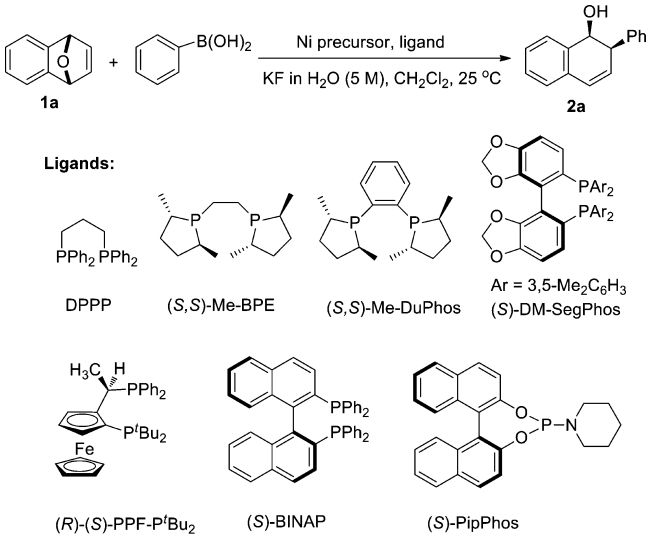
efficiency and enantioselectivity as well as better functional group tolerance.

RESULTS AND DISCUSSION

The substrates **1a**–**d** were readily prepared by Diels–Alder reactions of benzynes with furan according to literature procedures.[3c,12] To understand the nature of the catalytic reaction and optimize the reaction conditions, we began our investigation by treating oxabenzonorbornadiene **1a** with phenylboronic acid in CH_2Cl_2 at 25 °C in the presence of 1 mol % $Ni(cod)_2$/DPPP as the catalyst, using KF as the additive.[10] The desired ring-opened product **2a** was obtained in 25% yield after 7 h (Table 1, entry 1). Thereafter, a series of

Table 1. Effects of Nickel Precursor, Ligand, and Catalyst Loading[a]



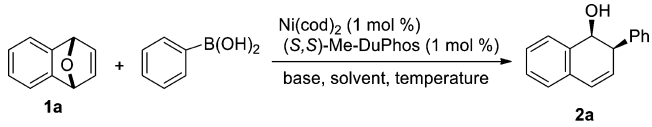
entry	Ni precursor (mol %)	ligand	time (h)	yield (%)	ee (%)[b]
1	$Ni(cod)_2$ (1.0)	DPPP	7	25	–
2	$Ni(cod)_2$ (1.0)	(*S*)-DM-SegPhos	7	60	70
3	$Ni(cod)_2$ (1.0)	(*S*)-BINAP	7	49	79
4	$Ni(cod)_2$ (1.0)	(*R*)-(*S*)-PPF-P^{t}Bu$_2$	24	n.r.	–
5	$Ni(cod)_2$ (1.0)	(*S*)-PipPhos	24	n.r.	–
6	$Ni(cod)_2$ (1.0)	(*S*,*S*)-Me-BPE	24	trace	–
7	$Ni(cod)_2$ (1.0)	(*S*,*S*)-Me-DuPhos	3	95	90
8	$Ni(dppe)Cl_2$ (1.0)	(*S*,*S*)-Me-DuPhos	7	90	84
9	$Ni(PPh_3)_2Cl_2$ (1.0)	(*S*,*S*)-Me-DuPhos	3	89	88
10	$Ni(PPh_3)_2Br_2$ (1.0)	(*S*,*S*)-Me-DuPhos	3	90	87
11	$Ni(cod)_2$ (0.5)	(*S*,*S*)-Me-DuPhos	5	80	89
12	$Ni(cod)_2$ (2.0)	(*S*,*S*)-Me-DuPhos	4	79	89

[a]Reaction conditions (unoptimized): **1a** (0.3 mmol, 1 equiv), $PhB(OH)_2$ (3 equiv), and KF (5 M in H_2O, 0.5 equiv) reacted in CH_2Cl_2 (2 mL) at 25 °C, and the molar ratio of Ni precursor/ligand = 1:1. [b]Determined by HPLC with a Chiralcel OD-H column.

chiral bidentate ligands were examined, among which (*S*,*S*)-Me-DuPhos showed the best performance with regard to reactivity and enantioselectivity (Table 1, entry 7). Other chiral bidentate ligands including (*S*)-DM-SegPhos, (*S*)-BINAP, (*S*,*S*)-Me-BPE, (*R*)-(*S*)-PPF-P^{t}Bu$_2$, and (*S*)-PipPhos gave either inferior results or no reaction (Table 1, entries 2–6). With (*S*,*S*)-Me-DuPhos as the chiral ligand, the impact of several commercially available nickel sources was also evaluated. It was observed that both neutral and cationic Ni(II) salts were effective in catalyzing the reaction (Table 1, entries 7–10). A slightly better result, a 95% yield with 90% ee, was still achieved by $Ni(cod)_2$. The catalyst loading also had a significant effect on the yield of **2a**. At 1 mol % catalyst loading, **2a** was formed cleanly (90% yield), whereas neither an increase nor decrease in catalyst loading improved the yield of the desired product (Table 1, entries 7, 11, and 12).

To further optimize reaction conditions, the impacts of different parameters including solvents, bases, and temperatures on the reactivity and enantioselectivity were subsequently investigated (Table 2). An initial study of common solvents

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



entry	solvent	base	temp (°C)	time (h)	yield (%)	ee (%)[b]
1	CH_3CN	KF	25	24	n.r.	–
2	THF	KF	25	24	trace	–
3	CH_3OH	KF	25	22	20	85
4	toluene	KF	25	3	88	88
5	CH_2Cl_2	KF	25	3	92	90
6	$CHCl_3$	KF	25	3	85	89
7	DCE	KF	25	1	95	89
8	DCE	Cs_2CO_3	25	1	97	88
9	DCE	K_3PO_4	25	1	97	84
10	DCE	KOH	25	1	98	89
11	DCE	Et_3N	25	24	trace	–
12	DCE	–	25	24	trace	–
13	DCE	KOH[c]	25	1	94	90
14	DCE	KOH	0	3	89	91
15	DCE	KOH	60	0.5	94	87
16	DCE	KOH	90	2	36	84

[a]Reaction conditions: $Ni(cod)_2$ (1 mol %), (*S*,*S*)-Me-DuPhos (1 mol %), **1a** (0.3 mmol, 1 equiv), $PhB(OH)_2$ (3 equiv), and base (5 M in H_2O, 0.5 equiv) reacted in the solvent of choice (2 mL) at the stated temperature. [b]Determined by HPLC with a Chiralcel OD-H column. [c]Anhydrous KOH solid (0.5 equiv) was added.

revealed a strong influence of the nature of solvent on reactivity. The polar solvent CH_3CN and ethereal solvent tetrahydrofuran (THF) were totally ineffective (Table 2, entries 1–2). The protic solvent CH_3OH afforded only a 20% yield but satisfactory enantioselectivity (90% ee) (Table 2, entry 3). Importantly, the reaction worked very well in the aromatic solvent toluene and chlorinated solvents such as $CHCl_3$, CH_2Cl_2, and 1,2-dichloroethane (DCE) (Table 2, entries 4–7). Among several solvents examined, DCE turn out to be the best, providing product **2a** in 95% yield with 89% ee. The impact of bases was then surveyed to improve the efficiency of the reaction as the base usually plays an important role in the reaction involving arylboronic acids.[13] KOH proved to be a better base than KF, Cs_2CO_3, and K_3PO_4, providing the ring-opening product in 95% yield and 89% ee after only 1 h (Table 2, entries 7–10). The reaction proceeded barely when the organic weak base Et_3N was used (Table 2, entry 11). As expected, no reaction took place in the absence of any bases (Table 2, entry 12). Interestingly, anhydrous $KOH_{(s)}$ caused no deleterious effects, which suggested that the addition of water is not essential in the present ARO reaction (Table 2, entry 13). Temperature was also found to be crucial in this asymmetric

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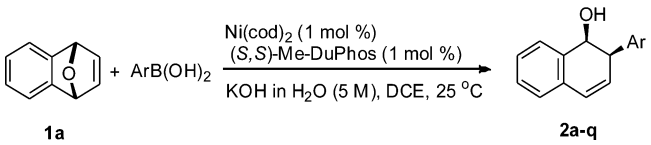
transformation. The proper temperature was found to be 25 °C (Table 2, entry 10). The reaction run at 0 °C gave a diminished yield and slightly improved ee (Table 2, entry 14). Raising the temperature to 60 °C somewhat decreased the yield and ee, whereas a further increase to 90 °C resulted in only a 36% conversion even after a prolonged reaction time (Table 2, entries 15–16). Consequently, the optimum reaction conditions were determined as follows: 1 mol % $Ni(cod)_2$, 1 mol % (*S*,*S*)-Me-DuPhos, 3 equiv of arylboronic acids, and 0.5 equiv of KOH (5 M in H_2O) in DCE at 25 °C.

Under the optimized reaction conditions, a series of mono- and disubstituted arylboronic acids were examined to evaluate their effect on the reactivity and enantioselectivity (Table 3). It

Table 3. Nickel-Catalyzed ARO of Oxabenzonorbornadiene 1a with Various Arylboronic Acids[a]



1a 2a-q

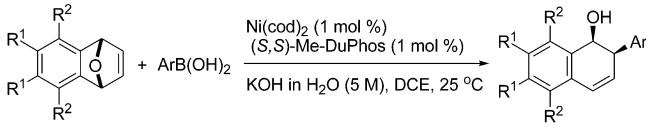
entry	Ar	product	time (h)	yield (%)	ee (%)[b]
1	C_6H_5	**2a**	1	98	89
2	3-FC_6H_4	**2b**	7	90	86
3	4-ClC_6H_4	**2c**	5	56	90
4	3-ClC_6H_4	**2d**	5	99	86
5	2-ClC_6H_4	**2e**	24	40	66
6	4-$F_3CC_6H_4$	**2f**	20	80	90
7	4-$CH_3C_6H_4$	**2g**	5	91	89
8	3-$CH_3C_6H_4$	**2h**	5	63	90
9	2-$CH_3C_6H_4$	**2i**	20	44	90
10	4-$CH_3SC_6H_4$	**2j**	7	84	84
11	2-naphthyl	**2k**	6	56	89
12	2,3-$(CH_3)_2C_6H_3$	**2l**	5	97	74
13	2,4-$(CH_3)_2C_6H_3$	**2m**	5	98	72
14	2,6-$(CH_3)_2C_6H_3$	**2n**	48	n.r.	–
15	3,5-$(CH_3)_2C_6H_3$	**2o**	3	98	89
16	3-Cl-4-$CH_3C_6H_3$	**2p**	5	99	82
17	3,4-$OCH_2OC_6H_3$	**2q**	5	99	92

[a]Reaction conditions: $Ni(cod)_2$ (1 mol %), (*S*,*S*)-Me-DuPhos (1 mol %), **1a–d** (0.3 mmol, 1 equiv), arylboronic acids (3 equiv), and KOH (5 M in H_2O, 0.5 equiv) reacted in DCE (2 mL) at 25 °C. [b]Determined by HPLC with a Chiralcel OD-H column.

appeared that the electronic property of the substituents on the phenyl ring in arylboronic acids had little effect on enantioselectivities. Except for 2-chlorophenylboronic acid, which gave product **2e** in slightly lower enantioselectivity (66% ee), other monosubstituted phenylboronic acids, with electron-donating, electron-withdrawing, or neutral substituents, could react with oxabenzonorbornadiene **1a** smoothly to generate the corresponding ring-opening products in good enantioselectivities (86–90% ee's) (Table 3, entries 1–10). However, the positional property of the substituents had a significant impact on reactivity. In general, *para*- and *meta*-substituted arylboronic acids gave better results than *ortho*-substituent counterparts (Table 3, entries 3–5 and 7–9). Moreover, it should be noteworthy that the treatment of **1a** with 2-methylboronic acid afforded product **2i** in modest yield (44%) but high enantioselectivity (90% ee), which dramatically decreased to no more than 30% ee in analogous palladium- and platinum-catalyzed reactions (Table 3, entry 9).[4i,10] 2-Naphthylboronic acid proved to be a suitable nucleophile, with moderate yield (56%) and good ee (89%) (Table 3, entry 11). Disubstituted arylboronic acids also showed remarkable reactivity and good enantioselectivity (Table 3, entries 12, 13, and 15–17). For instance, the reactions of **1a** with 3,5-dimethylphenyl and 3,4-(methylenedioxy)phenylboronic acids gave products **2o** and **2q** in excellent yields (98% vs 99%) with good ee (89% vs 92%), respectively (Table 3, entries 15 and 17). Unfortunately, owing to steric hindrance, 2,6-dimethylphenylboronic acid failed to furnish the expected product **2n** (Table 3, entry 14).

The substrate scope of oxabenzonorbornadiene derivatives was further evaluated, and the results were compiled in Table 4.

Table 4. Scope of Nickel-Catalyzed ARO of Oxabenzonorbornadienes 1b–d with Various Arylboronic Acids[a]



1b: R^1 = Br, R^2 = H
1c: R^1 = H, R^2 = OCH_3
1d: $R^1 + R^2$ = 

3a-h
4a-j
5a

entry	substrate	Ar	product	time (h)	yield (%)	ee (%)[b]
1	**1b**	C_6H_5	**3a**	10	93	90
2	**1b**	3-FC_6H_4	**3b**	20	88	92
3	**1b**	3-ClC_6H_4	**3c**	5	94	88
4	**1b**	4-$CH_3C_6H_4$	**3d**	20	90	98
5	**1b**	3-$CH_3C_6H_4$	**3e**	5	97	99
6	**1b**	2,3-$(CH_3)_2C_6H_3$	**3f**	20	89	90
7	**1b**	3,5-$(CH_3)_2C_6H_3$	**3g**	20	85	90
8	**1b**	3-Cl-4-$CH_3C_6H_3$	**3h**	20	97	89
9	**1c**	C_6H_5	**4a**	7	87	84
10	**1c**	4-ClC_6H_4	**4b**	20	60	86
11	**1c**	3-ClC_6H_4	**4c**	6	91	78
12	**1c**	4-$CH_3C_6H_4$	**4d**	5	96	83
13	**1c**	3-$CH_3C_6H_4$	**4e**	5	97	83
14	**1c**	2,3-$(CH_3)_2C_6H_3$	**4f**	5	98	73
15	**1c**	2,4-$(CH_3)_2C_6H_3$	**4g**	5	98	65
16	**1c**	3,5-$(CH_3)_2C_6H_3$	**4h**	6	99	86
17	**1c**	3-Cl-4-$CH_3C_6H_3$	**4i**	5	87	86
18	**1c**	3,4-$OCH_2OC_6H_3$	**4j**	5	97	97
19	**1d**	C_6H_5	**5a**	24	92	85

[a]Reaction conditions: $Ni(cod)_2$ (1 mol %), (*S*,*S*)-Me-DuPhos (1 mol %), **1a–d** (0.3 mmol, 1 equiv), arylboronic acids (3 equiv), and KOH (5 M in H_2O, 0.5 equiv) reacted in DCE (2 mL) at 25 °C. [b]Determined by HPLC with a Chiralcel OD-H or Chiralpak AD-H column.

Besides **1a**, the oxabenzonorbornadienes with different substituents on the phenyl ring all reacted with various arylboronic acids smoothly to generate the anticipated ring-opening products in high yields (up to 99%) with good to excellent enantioselectivities (up to 99%). Furthermore, the nature of disubstituted groups in oxabenzonorbornadienes has a substantial impact on the reactivity and enantioselectivity. Electron-deficient substrate **1b** displayed more reactive and enantioselective than electron-rich substrate **1c** (Table 4,

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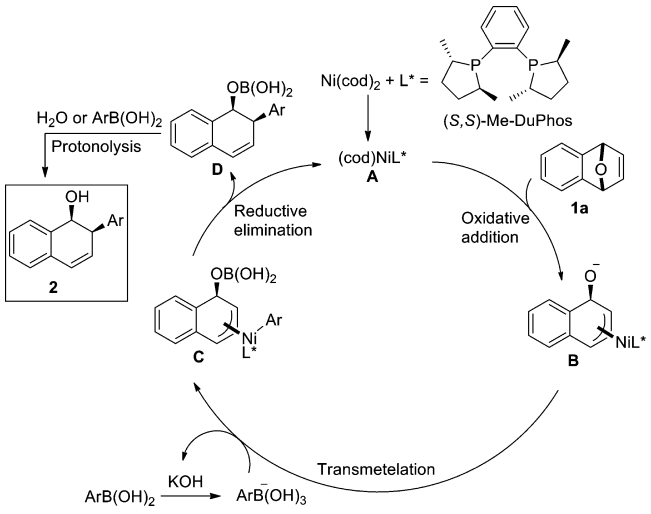
entries 1−8 vs 9−18). For example, 6,7-dibromo-substituted **1b** reacted with phenylboronic acid to provide product **3a** in 93% yield with 90% ee, whereas 5,8-dimethoxy-substituted **1c** with phenylboronic acid afforded **4a** in 87% yield with 84% ee (Table 4, entries 1 and 9). The excellent performance of this catalyst system is highlighted by the reaction of **1b** with 3-methylboronic acid, which furnished product **3e** in excellent yield (97%) with remarkable enantioselectivity (99% ee) (Table 4, entry 5). In addition, bulkier substrate **1d** was also a viable substrate for this reaction, providing the corresponding product **5a** in 92% yield with 85% ee after 24 h (Table 4, entry 19).

The single crystal of ring-opened product **4b** was obtained by solvent evaporation from a mixture of petroleum ether, ethyl acetate, and CH_2Cl_2. Its absolute configuration was assigned as (1*S*,2*R*) and determined as a 1,2-*cis*-configuration by X-ray crystallography, as shown in the Supporting Information.

Based on our observations and the known nickel chemistry, the following key pathways in Scheme 1 were proposed to account for the formation of ring-opened products **2**.[8a,b,11a] The active chiral nickel(0) catalyst **A** was initially formed through replacing one 1,5-cyclooctadiene (cod) ligand of the catalyst precursor Ni(cod)$_2$ by (*S*,*S*)-Me-DuPhos.[14] Oxidative addition of oxabenzonorbornadiene **1a** with nickel(0) catalyst **A** occurs to yield (π-allyl)nickel(II) complex **B**. Chelation of **A** with the carbon−carbon double bond and oxygen atom of **1a** may be responsible for the high *exo* selectivity. This species then undergoes transmetalation with ArB(OH)$_2$ to form (alkenyl)-(π-allyl)-nickel(II) intermediate **C**, which might require a base to activate arylboronic acids and promote the catalytic cycle.[9] Reductive elimination and further protonolysis with water or arylboronic acids afford *cis*-ring-opened product **2** and regenerate the nickel(0) species. It should be noted that, in the present proposed mechanism, the oxidation state of nickel changes from 0 to +2 and finally reduces back to 0.

Scheme 1. Proposed Mechanism for Nickel(0)-Catalyzed ARO of Oxabenzonorbornadiene 1a with Arylboronic Acids



CONCLUSIONS

In conclusion, we have developed a new, versatile, and highly efficient nickel-catalyzed ARO reaction of oxabenzonorbornadienes with arylboronic acids under very mild conditions. It provides a convenient and rapid entry to *cis*-2-aryl-1,2-dihydronaphthalen-1-ols in high yields with good to excellent enantioselectivities. Compared with the previous rhodium-, palladium-, and platinum-catalyzed protocols, this nickel catalyst system features a cheaper catalyst precursor, lower catalyst loading, higher efficiency and enantioselectivity, and better functional group tolerance. More detailed mechanistic studies and the applications of this methodology in the synthesis of bioactive molecules are currently underway in our laboratory.

EXPERIMENTAL SECTION

General Procedure for Nickel-Catalyzed ARO Reactions of Oxabenzonorbornadienes 1a−d with Arylboronic Acids. A 10.0 mL round-bottom flask was flame-dried under a stream of nitrogen and cooled to room temperature. Ni(cod)$_2$ (0.8 mg, 0.003 mmol, 1 mol %) and (*S*,*S*)-Me-DuPhos (0.9 mg, 0.003 mmol, 1 mol %) were simultaneously added and followed by the addition of anhydrous DCE (2 mL). After the mixture was stirred for about 30 min, to the system were added substrates **1a−d** (0.3 mmol), arylboronic acids (0.9 mmol), and KOH solution (5 M in H_2O, 30 μL, 0.5 equiv) sequentially. The reaction mixture was stirred at room temperature until it was completed as judged by thin-layer chromatography. The solvent was removed *in vacuo*, and the crude mixture was purified by column chromatography on 200−300 mesh silica gels to afford target products.

*(1S,2R)-2-Phenyl-1,2-dihydronaphthalen-1-ol (**2a**).* Prepared according to general procedure. Colorless oil (65.3 mg, 98% yield). R_f = 0.21 on silica gel (ethyl acetate/petroleum ether 1:10, 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 7.4 (minor) and 11.3 min (major). $[\alpha]_D^{25}$ = +160.4 (*c* 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3418(br), 3027(m), 2917(w), 1599(w), 1490(m), 1449(m), 1067(m), 765(s), 697(s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.23 (m, 8H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.71 (dd, *J* = 9.6, 1.6 Hz, 1H), 6.13 (dd, *J* = 9.6, 3.9 Hz, 1H), 4.93 (t, *J* = 5.7 Hz, 1H), 3.88 (d, *J* = 5.6 Hz, 1H), 1.50 (d, *J* = 7.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.7, 135.9, 132.7, 129.7, 129.3, 128.7, 128.3, 128.2, 128.0, 127.4, 126.7, 126.4, 71.3, 47.3. HRMS (APCI-ion trap) *m*/*z*: [M − 3H]$^-$ calcd for $C_{16}H_{11}O$, 219.0810; found 219.0809.

*(1S,2R)-2-(3-Fluorophenyl)-1,2-dihydronaphthalen-1-ol (**2b**).* Prepared according to general procedure. Colorless oil (64.9 mg, 90% yield). R_f = 0.22 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). The ee was determined to be 86% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 7.7 (minor) and 11.0 min (major). $[\alpha]_D^{25}$ = +155.0 (*c* 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3424(br), 3048(w), 2924(s), 2866(w), 1663(w), 1595(s), 1489(s), 1450(s), 1238(m), 785(s), 708(w); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33−7.23 (m, 4H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.98−6.93 (m, 2H), 6.70 (d, *J* = 9.6 Hz, 1H), 6.08 (dd, *J* = 9.6, 3.9 Hz, 1H), 4.90 (t, *J* = 5.3 Hz, 1H), 3.84 (s, 1H), 1.53 (d, *J* = 7.1 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 163.0 (d, $^1J_{C-F}$ = 243.8 Hz), 140.7 (d, $^3J_{C-F}$ = 7.5 Hz), 136.0, 132.4, 130.0 (d, $^3J_{C-F}$ = 7.5 Hz), 129.0, 128.6, 128.5, 128.2, 126.7, 126.6, 125.0 (d, $^4J_{C-F}$ = 2.5 Hz), 116.2 (d, $^2J_{C-F}$ = 21.3 Hz), 114.3 (d, $^2J_{C-F}$ = 21.3 Hz), 71.3, 47.1. ^{19}F NMR (470 MHz, $CDCl_3$): δ −112.7 − −112.8 (m). HMRS (ESI-ion trap) *m*/*z*: [M + Na]$^+$ calcd for $C_{16}H_{13}OFNa$, 263.0848; found 263.0832.

*(1S,2R)-2-(4-Chlorophenyl)-1,2-dihydronaphthalen-1-ol (**2c**).* Prepared according to general procedure. A white solid (43.1 mg, 56% yield). Mp 59−60 °C. R_f = 0.22 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). The ee was determined to be 90% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 6.8 (minor) and 10.2 min (major). $[\alpha]_D^{25}$ = +127.1 (*c* 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3418(br), 3027(w), 2923(m), 2852(w), 1663(w), 1487(s), 1407(m), 1089(m), 840(m), 801(s), 765(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.16 (m, 8H), 6.70 (d, *J* = 9.6 Hz, 1H), 6.06 (dd, *J* = 9.5, 3.9 Hz, 1H), 4.89 (d, *J* = 5.1 Hz, 1H), 3.81 (s, 1H), 1.53 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 136.3, 135.9, 133.2, 132.4, 130.7, 129.2,

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128.7, 128.5, 128.4, 128.2, 126.6, 126.5, 71.2, 46.7. 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 (**2d**). Prepared according to general procedure. Pale yellow oil (76.2 mg, 99% yield). R_f = 0.26 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). The ee was determined to be 86% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 6.8 (minor) and 9.2 min (major). $[\alpha]_D^{25}$ = +108.7 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3412(br), 3033(w), 2923(w), 2853(w), 1663(m), 1594(m), 1569(m), 1473(m), 1072(m), 782(s), 700(m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.32−7.13 (m, 8H), 6.70 (d, J = 9.6 Hz, 1H), 6.05 (dd, J = 9.6, 3.6 Hz, 1H), 4.85 (d, J = 3.7 Hz, 1H), 3.80 (s, 1H), 1.59 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.3, 135.8, 134.4, 132.3, 129.8, 129.5, 128.9, 128.6, 128.6, 128.2, 127.5, 127.4, 126.8, 126.6, 71.2, 47.1. HRMS (ESI-ion trap) m/z: $[M + Cl]^-$ calcd for $C_{16}H_{13}OCl_2$, 291.0344; found 291.0344.

(1S,2R)-2-(2-Chlorophenyl)-1,2-dihydronaphthalen-1-ol (**2e**). Prepared according to a general procedure. A white solid (30.8 mg, 40% yield). Mp 130−131 °C. R_f = 0.23 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). The ee was determined to be 66% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 7.2 (minor) and 12.1 min (major). $[\alpha]_D^{25}$ = +24.3 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3302(br), 3044(w), 2918(w), 2852(w), 1591(m), 1427(m), 1353(s), 1119(m), 1012(m), 818(m), 755(m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.44−7.19 (m, 8H), 6.74 (dd, J = 9.6 Hz, 2.4 Hz, 1H), 6.04 (dd, J = 9.6, 1.8 Hz, 1H), 4.89 (d, J = 3.7 Hz, 1H), 4.50−4.47 (m, 1H), 1.57 (s, 1H). $^{13}C\{^1H\}$ 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, 128.1, 128.0, 127.0, 126.7, 69.2, 44.0. 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-Trifluoromethylphenyl)-1,2-dihydronaphthalen-1-ol (**2f**). Prepared according to general procedure. A white solid (69.7 mg, 80% yield). Mp 72−73 °C. R_f = 0.26 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). The ee was determined to be 90% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 6.5 (minor) and 10.3 min (major). $[\alpha]_D^{25}$ = +120.3 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3363(br), 3037(w), 2923 (w), 2852(w), 1619(w), 1416(w), 1325 (s), 1163(m), 1122(m), 1067(m), 807(m), 768(w). ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 7.7 Hz, 2H), 7.38−7.17 (m, 6H), 6.73 (d, J = 9.6 Hz, 1H), 6.08 (dd, J = 9.5, 4.0 Hz, 1H), 4.89 (s, 1H), 3.89 (s, 1H), 1.59 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 142.5, 135.8, 132.4, 129.7, 129.5 (q, $^2J_{C-F}$ = 24.0 Hz), 128.8, 128.7, 128.6, 128.3, 126.7, 126.6, 124.2 (q, $^1J_{C-F}$ = 270.3 Hz), 125.4 (q, $^3J_{C-F}$ = 3.7 Hz), 71.3, 47.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ − 62.5. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{17}H_{13}OF_3Na$, 313.0816; found 313.0807.

(1S,2R)-2-(4-Methylphenyl)-1,2-dihydronaphthalen-1-ol (**2g**). Prepared according to general procedure. Colorless oil (64.5 mg, 91% yield). R_f = 0.33 on silica gel (ethyl acetate/petroleum ether 1:10, 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 5.8 (minor) and 8.1 min (major). $[\alpha]_D^{25}$ = +170.5 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3429(br), 3027(m), 2918(m), 2858(w), 1663(w), 1512(m), 1451(m), 1070(m), 790(s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.34−7.22 (m, 3H), 7.17−7.10 (m, 5H), 6.68 (dd, J = 9.6, 1.8 Hz, 1H), 6.11 (dd, J = 9.6, 4.1 Hz, 1H), 4.91 (d, J = 5.2 Hz, 1H), 3.84−3.81 (m, 1H), 2.31 (s, 3H), 1.53 (s, 1H). $^{13}C\{^1H\}$ 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. 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 (**2h**). Prepared according to general procedure. Colorless oil (44.7 mg, 63% yield). R_f = 0.34 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). The ee was determined to be 90% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 5.8 (minor) and 7.6 min (major). $[\alpha]_D^{25}$ = +140.9 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3434(br), 3027(m), 2918(m), 2854(w), 1665(w), 1604(m), 1480(m), 1451(m), 1070(m), 774(s), 708(m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.35−7.16 (m, 5H), 7.10−7.05 (m, 3H), 6.70 (dd, J = 9.6, 2.0 Hz, 1H), 6.11 (dd, J = 9.6, 3.9 Hz, 1H), 4.89 (t, J = 4.9 Hz, 1H), 3.85−3.82 (m, 1H), 2.33 (s, 3H), 1.53 (d, J = 6.6 Hz, 1H). $^{13}C\{^1H\}$ 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. 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 (**2i**). Prepared according to general procedure. Colorless oil (31.2 mg, 44% yield). R_f = 0.29 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). The ee was determined to be 90% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 5.9 (minor) and 8.9 min (major). $[\alpha]_D^{25}$ = +65.2 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3412(br), 3027(m), 2923(m), 2852(w), 1665(w), 1599(w), 1484(m), 1454(m), 1070(m), 763(s), 744(s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.34−7.15 (m, 8H), 6.70 (dd, J = 9.6, 2.4 Hz, 1H), 6.06 (dd, J = 9.6, 3.2 Hz, 1H), 4.80 (t, J = 5.8 Hz, 1H), 4.19−4.16 (m, 1H), 2.42 (s, 3H), 1.54 (d, J = 6.3 Hz, 1H). $^{13}C\{^1H\}$ 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. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{17}H_{16}ONa$, 259.1099; found: 259.1090.

(1S,2R)-2-[4-(Methylthio)phenyl]-1,2-dihydronaphthalen-1-ol (**2j**). Prepared according to general procedure. Colorless oil (67.6 mg, 84% yield). R_f = 0.18 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). 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 9.8 (minor) and 16.0 min (major). $[\alpha]_D^{25}$ = +328.5 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3360(br), 3196(w), 2918(s), 2853(m), 1742(m), 1634(m), 1462(m), 1414(m), 1240(s), 1051(m), 883(w), 801(w). ^1H NMR (500 MHz, $CDCl_3$): δ 7.33 (d, J = 7.2 Hz, 1H), 7.30−7.23 (m, 2H), 7.20−7.15 (m, 5H), 6.69 (d, J = 9.6 Hz, 1H), 6.09 (dd, J = 9.5, 3.9 Hz, 1H), 4.92 (t, J = 6.4 Hz, 1H), 3.81 (s, 1H), 2.45 (s, 3H), 1.48 (d, J = 7.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 137.5, 136.2, 134.4, 132.6, 129.8, 129.6, 128.3, 128.1, 126.9, 126.6, 126.4, 71.3, 46.8, 15.9. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{17}H_{16}OSNa$, 291.0820; found 291.0802.

(1S,2R)-1,2-Dihydro-[2,2′-binaphthalen]-1-ol (**2k**). Prepared according to general procedure. Colorless oil (43.6 mg, 56% yield). R_f = 0.27 on silica gel (ethyl acetate/petroleum ether 1:10, 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 10.3 (minor) and 12.8 min (major). $[\alpha]_D^{25}$ = +152.4 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3407(br), 3049(m), 2918(m), 2852(w), 1660(m), 1597(m), 1506(w), 1377(w), 1077(m), 807(s), 746(s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.80−7.34 (m, 4H), 7.47−7.42 (m, 2H), 7.34−7.18 (m, 5H), 6.75 (dd, J = 9.6, 1.9 Hz, 1H), 6.20 (dd, J = 9.6, 4.0 Hz, 1H), 4.98 (s, 1H), 4.02−3.99 (m, 1H), 1.55 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 136.2, 135.4, 133.5, 132.8, 132.7, 129.6, 128.5, 128.4, 128.3, 128.1, 127.8, 127.6, 127.3, 126.8, 126.5, 126.2, 125.9, 71.3, 47.5. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{20}H_{16}ONa$, 295.1099; found 295.1089.

(1S,2R)-2-(2,3-Dimethylphenyl)-1,2-dihydronaphthalen-1-ol (**2l**). Prepared according to general procedure. Colorless oil (72.8 mg, 97% yield). R_f = 0.22 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). The ee was determined to be 74% 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 9.3 min (major). $[\alpha]_D^{25}$ = +67.2 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3431(br), 3026(m), 2928(m), 2866(w), 1661(w), 1589(w), 1464(m), 1379(m), 1069(m), 827(m), 775(s). ^1H NMR (500 MHz, $CDCl_3$): δ 7.35−7.23 (m, 3H), 7.19−7.16 (m, 2H), 7.11−7.06 (m, 2H), 6.71 (dd, J = 9.6, 2.5 Hz, 1H), 6.07 (dd, J = 9.6, 2.9 Hz, 1H), 4.78 (t, J = 5.0 Hz, 1H), 4.28 (dt, J = 5.4, 2.8 Hz, 1H), 2.33 (d, J = 4.8 Hz, 6H), 1.50 (d, J = 5.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 137.3, 136.6, 135.4, 135.2, 132.5, 130.8, 129.1, 128.7, 127.9, 127.8, 127.7, 127.2, 126.6, 125.8, 69.8, 43.5, 21.1,

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15.2. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{18}H_{18}ONa$, 273.1255; found 273.1240.

(1S,2R)-2-(2,4-Dimethylphenyl)-1,2-dihydronaphthalen-1-ol ***(2m)***. Prepared according to general procedure. Colorless oil (73.6 mg, 98% yield). R_f = 0.24 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). The ee was determined to be 72% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 6.0 (minor) and 9.4 min (major). $[\alpha]_D^{25}$ = +108.2 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3422(br), 3030(m), 2922(s), 2853(w), 1668(w), 1503(m), 1452(m), 1377(m), 1074(m), 800(s), 764(m). ^1H NMR (500 MHz, $CDCl_3$): δ 7.36−7.24 (m, 3H), 7.17 (dd, J = 14.1, 7.6 Hz, 2H), 7.06 (s, 1H), 6.98 (d, J = 7.8 Hz, 1H), 6.71 (d, J = 9.6 Hz, 1H), 6.07 (dd, J = 9.6, 2.9 Hz, 1H), 4.82 (t, J = 4.9 Hz, 1H), 4.17 (d, J = 2.4 Hz, 1H), 2.41 (s, 3H), 2.31 (s, 3H), 1.55 (d, J = 5.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 136.9, 136.5, 135.6, 133.5, 132.6, 131.6, 130.7, 129.2, 128.6, 127.9, 127.8, 127.6, 127.1, 126.5, 69.8, 42.9, 21.0, 19.8. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{18}H_{18}ONa$, 273.1255; found 273.1241.

(1S,2R)-2-(3,5-Dimethylphenyl)-1,2-dihydronaphthalen-1-ol ***(2o)***. Prepared according to general procedure. Colorless oil (73.6 mg, 98% yield). R_f = 0.37 on silica gel (ethyl acetate/petroleum ether 1:10, 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 5.0 (minor) and 6.3 min (major). $[\alpha]_D^{25}$ = +139.7 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3434(br), 3022(m), 2918(s), 2857(w), 1663(w), 1602(s), 1482(m), 1454(m), 1377(m), 1075(m), 851(m), 806(s), 787(s), 760(m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.24−7.21 (m, 3H), 7.16 (d, J = 7.2 Hz, 1H), 6.90 (s, 3H), 6.68 (d, J = 9.6 Hz, 1H), 6.10 (dd, J = 9.4, 2.8 Hz, 1H), 4.84 (s, 1H), 3.80 (d, J = 1.3 Hz, 1H), 2.28 (s, 6H), 1.55 (s, 1H). $^{13}C\{^1H\}$ 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. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{18}H_{18}ONa$, 273.1255; found 273.1239.

(1S,2R)-2-(3-Chloro-4-methylphenyl)-1,2-dihydronaphthalen-1-ol ***(2p)***. Prepared according to a general procedure. Colorless oil (80.4 mg, 99% yield). R_f = 0.30 on silica gel (ethyl acetate/petroleum ether 1:10, 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 7.0 (minor) and 9.7 min (major). $[\alpha]_D^{25}$ = +253.5 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3424(br), 3028(m), 2905(s), 2847(w), 1730(m), 1663(w), 1566(w), 1483(s), 1441(m), 1248(m), 1055(s), 997(m), 795 (s), 760(m). ^1H NMR (500 MHz, $CDCl_3$): δ 7.33−7.23 (m, 4H), 7.17−7.14 (m, 2H), 7.04 (d, J = 7.8 Hz, 1H), 6.70 (d, J = 9.6 Hz, 1H), 6.06 (dd, J = 9.6, 3.9 Hz, 1H), 4.88 (t, J = 6.4 Hz, 1H), 3.79 (s, 1H), 2.33 (s, 3H), 1.50 (d, J = 7.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 137.3, 136.0, 135.1, 134.5, 132.5, 131.1, 129.8, 129.1, 128.5, 128.2, 127.4, 126.7, 126.5, 71.3, 46.7, 19.7. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{17}H_{15}OClNa$, 293.0709; found 293.0691.

(1S,2R)-2-(Benzo[d][1,3]dioxol-5-yl)-1,2-dihydronaphthalen-1-ol ***(2q)***. Prepared according to general procedure. Pale yellow oil (79.1 mg, 99% yield). R_f = 0.14 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). The ee was determined to be 92% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 12.1 (minor) and 16.3 min (major). $[\alpha]_D^{25}$ = +247.5 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3366(br), 3028(w), 2905(m), 2837(w), 1743(m), 1634(w), 1483(s), 1445(m), 1248(s), 1045(s), 939(m), 795 (s), 760(m). ^1H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, J = 7.1 Hz, 1H), 7.29−7.22 (m, 2H), 7.15−7.14 (m, 1H), 6.75−6.72 (m, 2H), 6.70 (s, 1H), 6.66 (dd, J = 9.6, 1.7 Hz, 1H), 6.07 (dd, J = 9.6, 4.3 Hz, 1H), 5.90−5.89 (m, 2H), 4.90 (t, J = 6.7 Hz, 1H), 3.77 (ddd, J = 6.2, 4.3, 1.9 Hz, 1H), 1.57 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 147.9, 147.0, 136.2, 132.6, 131.1, 129.8, 128.3, 128.2, 128.1, 126.5, 126.4, 122.5, 109.6, 108.4, 101.0, 71.3, 46.9. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{17}H_{14}O_3Na$, 289.0841; found 289.0820.

(1S,2R)-6,7-Dibromo-2-phenyl-1,2-dihydronaphthalen-1-ol ***(3a)***. Prepared according to general procedure. Colorless oil (106.0 mg, 93% yield). R_f = 0.19 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). The ee was determined to be 90% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 95:5, 1.0 mL/min, λ = 254 nm). Retention times were 12.3 (minor) and 16.4 min (major). $[\alpha]_D^{25}$ = +142.7 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3374(br), 3033(w), 2918(m), 2852(w), 1660(w), 1580(w), 1468(m), 1380(w), 1070(m), 1013(w), 886(m), 760(m), 700(s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.40 (s, 1H), 7.29 (s, 3H), 7.17 (d, J = 5.5 Hz, 2H), 6.59 (d, J = 9.6 Hz, 1H), 6.20 (dd, J = 9.2, 4.4 Hz, 1H), 4.96 (d, J = 5.5 Hz, 1H), 3.82 (s, 1H), 1.57 (s, 1H). $^{13}C\{^1H\}$ 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. 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-(3-fluorophenyl)-1,2-dihydronaphthalen-1-ol ***(3b)***. Prepared according to general procedure. Colorless oil (105.1 mg, 88% yield). R_f = 0.14 on silica gel (ethyl acetate/petroleum ether 1:15, v/v). The ee was determined to be 92% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 95:5, 1.0 mL/min, λ = 254 nm). Retention times were 12.5 (minor) and 15.4 min (major). $[\alpha]_D^{25}$ = +203.8 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3412(br), 3046(w), 2928(s), 2847(w), 1665(w), 1584(m), 1483(s), 1449(m), 1242(m), 1080(s), 891(s), 783(s), 702(m). ^1H NMR (500 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.41 (s, 1H), 7.28−7.25 (m, 1H), 6.99−6.95 (m, 2H), 6.90−6.87 (m, 1H), 6.61 (dd, J = 9.6, 1.6 Hz, 1H), 6.17 (dd, J = 9.7, 4.7 Hz, 1H), 4.94 (s, 1H), 3.81 (ddd, J = 6.4, 4.7, 1.6 Hz, 1H), 1.57 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 163.0 (d, $^1J_{C-F}$ = 246.3 Hz), 138.7 (d, $^3J_{C-F}$ = 6.3 Hz), 136.8, 133.2, 131.5, 131.1, 131.0, 130.3 (d, $^3J_{C-F}$ = 7.5 Hz), 126.8, 125.0 (d, $^4J_{C-F}$ = 2.5 Hz), 124.3, 123.9, 116.2 (d, $^2J_{C-F}$ = 21.3 Hz), 114.8 (d, $^2J_{C-F}$ = 20 Hz), 70.2, 46.5. ^{19}F NMR (470 MHz, $CDCl_3$): δ −112.1 − −112.2 (m). HRMS (ESI-ion trap) m/z: $[M - H]^-$ calcd for $C_{16}H_{10}OFBr_2$, 394.9082; found 394.9082.

(1S,2R)-6,7-Dibromo-2-(3-chlorophenyl)-1,2-dihydronaphthalen-1-ol ***(3c)***. Prepared according to general procedure. Colorless oil (116.9 mg, 94% yield). R_f = 0.26 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). The ee was determined to be 88% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 95:5, 1.0 mL/min, λ = 254 nm). Retention times were 13.5 (minor) and 15.6 min (major). $[\alpha]_D^{25}$ = +235.8 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3408(br), 3030(w), 2922(s), 2857(w), 1665(w), 1595(m), 1476(s), 1430(m), 1250(m), 1072(s), 885(s), 785(s), 700(m). ^1H NMR (500 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.41 (s, 1H), 7.25−7.20 (m, 3H), 7.06 (d, J = 7.3 Hz, 1H), 6.61 (d, J = 9.6 Hz, 1H), 6.15 (dd, J = 9.6, 4.4 Hz, 1H), 4.92 (t, J = 7.0 Hz, 1H), 3.79 (t, J = 5.2 Hz, 1H), 1.58 (d, J = 6.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 138.4, 136.7, 134.6, 133.2, 131.6, 131.1, 130.9, 130.0, 129.5, 128.0, 127.4, 126.8, 124.4, 123.8, 70.2, 46.5. HRMS (ESI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{16}H_8OClBr_2$, 410.8610; found 410.8611.

(1S,2R)-6,7-Dibromo-2-(4-methylphenyl)-1,2-dihydronaphthalen-1-ol ***(3d)***. Prepared according to general procedure. Pale yellow oil (106.4 mg, 90% yield). R_f = 0.19 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). The ee was determined to be 98% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 95:5, 1.0 mL/min, λ = 254 nm). Retention times were 9.3 (minor) and 11.1 min (major). $[\alpha]_D^{25}$ = +119.3 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3412(br), 3016(m), 2918(s), 2851(w), 1665(w), 1575(w), 1509 (s), 1465(s), 1377(m), 1276(m), 1108(s), 1075(s), 1018(m), 889(s), 848(s), 779(m), 683(w). ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.39 (s, 1H), 7.07 (dd, J = 23.9, 7.7 Hz, 4H), 6.57 (d, J = 9.6 Hz, 1H), 6.18 (dd, J = 9.5, 4.8 Hz, 1H), 4.95 (d, J = 2.3 Hz, 1H), 3.78 (t, J = 5.6 Hz, 1H), 2.30 (s, 3H), 1.55 (s, 1H). $^{13}C\{^1H\}$ 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, 123.5, 70.2, 46.3, 21.0. 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. Colorless oil (114.7 mg, 97% yield). R_f = 0.33 on silica gel (ethyl acetate/petroleum ether 1:15, v/v). The ee was determined to be 99% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm). Retention times were 5.1 (minor) and 6.9 min (major). $[\alpha]_D^{25}$ = +133.1 (c 1.00, $CHCl_3$). IR (neat film,

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cm^{-1}): 3407(br), 3033(m), 2918(m), 2852(w), 1602(w), 1465(m), 1377 (w), 1108(m), 1072(m), 1020(w), 886(s), 776(s), 705(m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.39 (s, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 7.4 Hz, 1H), 7.00 (s, 1H), 6.95 (d, J = 7.5 Hz, 1H), 6.58 (d, J = 9.6 Hz, 1H), 6.18 (dd, J = 9.6, 4.6 Hz, 1H), 4.91 (d, J = 5.7 Hz, 1H), 3.78 (t, J = 5.0 Hz, 1H), 2.31 (s, 3H), 1.58 (s, 1H). $^{13}C\{^1H\}$ 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. 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-(2,3-dimethylphenyl)-1,2-dihydronaphthalen-1-ol (**3f**).* Prepared according to general procedure. Colorless oil (109.0 mg, 89% yield). R_f = 0.22 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). The ee was determined to be 90% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 99:1, 1.0 mL/min, λ = 254 nm). Retention times were 18.2 (minor) and 19.7 min (major). $[\alpha]_D^{25}$ = +168.2 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3431(br), 3036(w), 2922(s), 2857(w), 1601(m), 1464(s), 1375(m), 1246(m), 1074(m), 887(m), 779(m), 710(m). ^1H NMR (500 MHz, $CDCl_3$): δ 7.60 (s, 1H), 7.43 (s, 1H), 7.11 (d, J = 5.1 Hz, 1H), 7.07−7.00 (m, 2H), 6.60 (d, J = 9.6 Hz, 1H), 6.15 (dd, J = 9.6, 3.7 Hz, 1H), 4.84 (t, J = 6.1 Hz, 1H), 4.27 (dd, J = 5.5, 2.4 Hz, 1H), 2.33 (d, J = 5.5 Hz, 6H), 1.55 (d, J = 6.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 137.6, 136.4, 135.4, 134.8, 133.4, 132.8, 132.5, 131.0, 129.5, 126.9, 126.0, 125.9, 124.4, 123.3, 69.0, 42.7, 21.2, 15.4. HRMS (ESI-ion trap) m/z: $[M - H]^-$ calcd for $C_{18}H_{15}OBr_2$, 404.9490; found 404.9489.

*(1S,2R)-6,7-Dibromo-2-(3,5-dimethylphenyl)-1,2-dihydronaphthalen-1-ol (**3g**).* Prepared according to general procedure. Colorless oil (104.1 mg, 85% yield). R_f = 0.23 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). The ee was determined to be 90% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 98:2, 1.0 mL/min, λ = 254 nm). Retention times were 14.4 (minor) and 17.2 min (major). $[\alpha]_D^{25}$ = +198.6 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3408(br), 3040(w), 2928(s), 2857(w), 1668(m), 1582(w), 1446(s), 1385(m), 1246(m), 1080(m), 887(s), 777(s). ^1H NMR (500 MHz, $CDCl_3$): δ 7.59 (s, 1H), 7.40 (s, 1H), 6.92 (s, 1H), 6.80 (s, 2H), 6.58 (d, J = 9.7 Hz, 1H), 6.17 (dd, J = 9.6, 4.4 Hz, 1H), 4.89 (t, J = 7.2 Hz, 1H), 3.76 (t, J = 5.3 Hz, 1H), 2.27 (s, 6H), 1.55 (d, J = 7.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 138.6, 137.1, 135.7, 133.5, 131.8, 131.7, 130.9, 129.6, 127.0, 126.2, 124.1, 123.4, 70.2, 46.7, 21.4. HRMS (ESI-ion trap) m/z: $[M - H]^-$ calcd for $C_{18}H_{15}OBr_2$, 404.9490; found 404.9489.

*(1S,2R)-6,7-Dibromo-2-(3-chloro-4-methylphenyl)-1,2-dihydronaphthalen-1-ol (**3h**).* Prepared according to general procedure. Pale yellow oil (124.7 mg, 97% yield). R_f = 0.28 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). The ee was determined to be 89% 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 11.9 min (major). $[\alpha]_D^{25}$ = +197.9 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3393(br), 3036(w), 2928(s), 2847(m), 1665(m), 1489(m), 1466(m), 1393(m), 1209(m), 1080(m), 891(s), 799(m), 708(m). ^1H NMR (500 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.40 (s, 1H), 7.17 (s, 1H), 7.13 (d, J = 7.7 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.59 (d, J = 9.7 Hz, 1H), 6.14 (dd, J = 9.6, 4.6 Hz, 1H), 4.90 (t, J = 7.1 Hz, 1H), 3.75 (t, J = 5.4 Hz, 1H), 2.32 (s, 3H), 1.60 (d, J = 8.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 136.9, 135.6, 135.2, 134.7, 133.3, 131.5, 131.3, 131.2, 131.0, 129.9, 127.4, 126.7, 124.2, 123.8, 70.2, 46.1, 19.7. HRMS (ESI-ion trap) m/z: $[M - H]^-$ calcd for $C_{17}H_{12}OClBr_2$, 424.8943; found 424.8940.

*(1S,2R)-5,8-Dimethoxy-2-phenyl-1,2-dihydronaphthalen-1-ol (**4a**).* Prepared according to general procedure. Colorless oil (73.7 mg, 87% yield). R_f = 0.23 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). The ee was determined to be 84% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 85:15, 1.0 mL/min, λ = 254 nm). Retention times were 11.1 (minor) and 16.7 min (major). $[\alpha]_D^{25}$ = −46.9 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3421(br), 3030(w), 2941(m), 2833(m), 1601(m), 1483(s), 1441(s), 1344(s), 1258(s), 1090(s), 957(m), 799(m), 758(m), 698(s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.43−7.37 (m, 4H), 7.30 (t, J = 6.3 Hz, 1H), 7.11−7.08 (m, 1H), 6.80 (q, J = 8.9 Hz, 2H), 6.14 (d, J = 9.8 Hz, 1H), 5.09 (s, 1H), 3.81−3.80 (m, 7H), 1.63 (s, 1H). $^{13}C\{^1H\}$ 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. 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-chlorophenyl)-1,2-dihydronaphthalen-1-ol (**4b**).* Prepared according to general procedure. A white solid (57.0 mg, 60% yield). Mp 97−98 °C. R_f = 0.18 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). The ee was determined to be 86% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 85:15, 1.0 mL/min, λ = 254 nm). Retention times were 12.7 (minor) and 18.8 min (major). $[\alpha]_D^{25}$ = −33.2 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3462(br), 3040(w), 2928(m), 2843(m), 1589(w), 1481(s), 1260(s), 1084(s), 799(s), 718(m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 4H), 7.08 (d, J = 9.7 Hz, 1H), 6.80 (q, J = 9.0 Hz, 2H), 6.05 (d, J = 9.7 Hz, 1H), 5.05 (s, 1H), 3.81 (d, J = 7.6 Hz, 6H), 3.73 (s, 1H), 1.66 (s, 1H). $^{13}C\{^1H\}$ 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. 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-(3-chlorophenyl)-1,2-dihydronaphthalen-1-ol (**4c**).* Prepared according to general procedure. Colorless oil (86.5 mg, 91% yield). R_f = 0.24 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). The ee was determined to be 78% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 85:15, 1.0 mL/min, λ = 254 nm). Retention times were 12.2 (minor) and 17.7 min (major). $[\alpha]_D^{25}$ = +192.8 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3426(br), 3055(w), 2932(m), 2837(w), 1593(m), 1485(s), 1258(s), 1090(s), 957(m), 783(m), 731(m). ^1H NMR (500 MHz, $CDCl_3$): δ 7.36−7.18 (m, 5H), 7.09 (dd, J = 9.8, 2.6 Hz, 1H), 6.84−6.79 (m, 1H), 6.07 (d, J = 9.8 Hz, 1H), 5.08 (d, J = 3.7 Hz, 1H), 3.82 (d, J = 5.9 Hz, 6H), 3.75 (s, 1H), 1.62 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 150.6, 149.7, 142.8, 134.1, 129.7, 129.4, 128.8, 128.1, 127.6, 127.4, 127.1, 122.4, 111.6, 111.1, 64.3, 56.3, 56.2, 47.1. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{18}H_{17}O_3ClNa$, 339.0764; found 339.0743.

*(1S,2R)-5,8-Dimethoxy-2-(4-methylphenyl)-1,2-dihydronaphthalen-1-ol (**4d**).* Prepared according to general procedure. Colorless oil (85.4 mg, 96% yield). R_f = 0.21 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). The ee was determined to be 83% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 85:15, 1.0 mL/min, λ = 254 nm). Retention times were 14.5 (minor) and 23.7 min (major). $[\alpha]_D^{25}$ = −20.2 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3549(br), 3049(w), 2932(m), 2843(m), 1599(m), 1514(m), 1483(s), 1258(s), 1086(s), 959(m), 793(s), 714(m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 7.7 Hz, 2H), 7.20 (d, J = 7.7 Hz, 2H), 7.08 (dd, J = 9.8, 3.0 Hz, 1H), 6.80 (q, J = 8.9 Hz, 2H), 6.12 (d, J = 9.8 Hz, 1H), 5.06 (s, 1H), 3.81 (d, J = 4.4 Hz, 6H), 3.75 (s, 1H), 2.36 (s, 3H), 1.61 (s, 1H). $^{13}C\{^1H\}$ 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. 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. Colorless oil (86.2 mg, 97% yield). R_f = 0.28 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). The ee was determined to be 83% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 85:15, 1.0 mL/min, λ = 254 nm). Retention times were 9.9 (minor) and 13.6 min (major). $[\alpha]_D^{25}$ = −41.7 (c 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3449(br), 3003(w), 2938(m), 2837(w), 1601(m), 1483(s), 1331(m), 1257(s), 1008(s), 959(m), 775(m), 712(m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.31−7.23 (m, 3H), 7.14−7.08 (m, 2H), 6.82 (q, J = 8.9 Hz, 2H), 6.15 (d, J = 9.8 Hz, 1H), 5.08 (s, 1H), 3.83 (d, J = 2.9 Hz, 6H), 3.77 (s, 1H), 2.39 (s, 3H), 1.58 (s, 1H). $^{13}C\{^1H\}$ 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, 56.3, 56.2, 47.2, 21.5. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ calcd for $C_{19}H_{20}O_3Na$, 319.1310; found 319.1295.

*(1S,2R)-5,8-Dimethoxy-2-(2,3-dimethylphenyl)-1,2-dihydronaphthalen-1-ol (**4f**).* Prepared according to general procedure. Colorless

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oil (91.3 mg, 98% yield). R_f = 0.25 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). The ee was determined to be 73% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 85:15, 1.0 mL/min, λ = 254 nm). Retention times were 10.8 (minor) and 14.3 min (major). $[\alpha]_D^{25}$ = −33.3 (*c* 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3366(br), 3046(w), 2922(m), 2853(w), 1633(w), 1481(s), 1375(m), 1258(s), 1086(m), 957(w), 777(m), 714(m). ^1H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, *J* = 7.4 Hz, 1H), 7.15−7.07 (m, 3H), 6.84−6.78 (m, 2H), 6.11 (d, *J* = 11.3 Hz, 1H), 5.09 (s, 1H), 4.12 (dd, *J* = 5.7, 3.9 Hz, 1H), 3.82 (d, *J* = 7.1 Hz, 6H), 2.33 (s, 3H), 2.31 (s, 3H), 1.51 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 151.0, 149.7, 138.0, 137.2, 134.8, 130.5, 128.9, 127.6, 125.6, 124.1, 122.7, 121.5, 111.5, 110.9, 62.1, 56.4, 56.3, 43.6, 21.1, 15.1. HRMS (ESI-ion trap) *m*/*z*: $[M + Na]^+$ calcd for $C_{20}H_{22}O_3Na$, 333.1467; found 333.1444.

(1S,2R)-5,8-Dimethoxy-2-(2,4-dimethylphenyl)-1,2-dihydronaphthalen-1-ol (**4g**). Prepared according to general procedure. Colorless oil (91.3 mg, 98% yield). R_f = 0.25 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). The ee was determined to be 65% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 85:15, 1.0 mL/min, λ = 254 nm). Retention times were 9.2 (minor) and 14.2 min (major). $[\alpha]_D^{25}$ = −25.9 (*c* 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3445(br), 3003(w), 2932(s), 2837(w), 1607(m), 1485(s), 1335(m), 1258(s), 1088(s), 957(m), 800(s), 714(m). ^1H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, *J* = 7.6 Hz, 1H), 7.10−7.05 (m, 3H), 6.82−6.77 (m, 2H), 6.08 (d, *J* = 10.0 Hz, 1H), 5.07 (s, 1H), 4.00 (d, *J* = 1.6 Hz, 1H), 3.81 (d, *J* = 6.9 Hz, 6H), 2.36 (s, 3H), 2.32 (s, 3H), 1.55 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 151.0, 149.7, 137.5, 136.6, 135.1, 131.4, 130.4, 129.7, 126.9, 124.2, 122.7, 121.7, 111.5, 111.0, 61.9, 56.33, 56.31, 43.0, 21.0, 19.6. HRMS (ESI-ion trap) *m*/*z*: $[M + Na]^+$ calcd for $C_{20}H_{22}O_3Na$, 333.1467; found 333.1446.

(1S,2R)-5,8-Dimethoxy-2-(3,5-dimethylphenyl)-1,2-dihydronaphthalen-1-ol (**4h**). Prepared according to general procedure. Pale yellow oil (92.2 mg, 99% yield). R_f = 0.24 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). The ee was determined to be 86% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 85:15, 1.0 mL/min, λ = 254 nm). Retention times were 9.6 (minor) and 12.0 min (major). $[\alpha]_D^{25}$ = +18.7 (*c* 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3455(br), 3007(w), 2928(m), 2847(w), 1661(w), 1603(m), 1481(s), 1337(w), 1258(s), 1088(s), 858(w), 808(m), 714(m). ^1H NMR (500 MHz, $CDCl_3$): δ 7.09−7.05 (m, 3H), 6.94 (s, 1H), 6.81−6.78 (m, 2H), 6.14 (d, *J* = 9.8 Hz, 1H), 5.07 (s, 1H), 3.81 (s, 6H), 3.73 (s, 1H), 2.34 (s, 6H), 1.57 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 150.9, 149.7, 140.2, 138.2, 129.1, 128.8, 127.5, 126.9, 122.7, 122.0, 111.5, 111.0, 64.3, 56.3, 56.2, 47.1, 21.4. HRMS (ESI-ion trap) *m*/*z*: $[M + Na]^+$ calcd for $C_{20}H_{22}O_3Na$, 333.1467; found 333.1448.

(1S,2R)-5,8-Dimethoxy-2-(3-chloro-4-methylphenyl)-1,2-dihydronaphthalen-1-ol (**4i**). Prepared according to general procedure. Colorless oil (86.3 mg, 87% yield). R_f = 0.17 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). The ee was determined to be 86% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 85:15, 1.0 mL/min, λ = 254 nm). Retention times were 10.8 (minor) and 17.1 min (major). $[\alpha]_D^{25}$ = +44.3 (*c* 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3360(br), 3003(w), 2918(m), 2847(w), 1659(w), 1596(w), 1485(s), 1260(s), 1088(s), 957(m), 808(m), 712(m). ^1H NMR (500 MHz, $CDCl_3$): δ 7.41 (s, 1H), 7.25−7.22 (m, 2H), 7.08 (dd, *J* = 9.8, 3.1 Hz, 1H), 6.83−6.78 (m, 2H), 6.07 (d, *J* = 9.8 Hz, 1H), 5.06 (s, 1H), 3.82 (d, *J* = 5.1 Hz, 6H), 3.72 (dd, *J* = 5.8, 3.6 Hz, 1H), 2.38 (s, 3H), 1.60 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 150.7, 149.7, 139.9, 134.6, 134.4, 130.9, 129.7, 128.4, 127.4, 124.4, 122.4, 122.3, 111.5, 111.1, 64.3, 56.3, 56.2, 46.6, 19.7. HRMS (ESI-ion trap) *m*/*z*: $[M + Na]^+$ calcd for $C_{19}H_{19}O_3ClNa$, 353.0920; found 353.0900.

(1S,2R)-5,8-Dimethoxy-2-(benzo[d][1,3]dioxol-5-yl)-1,2-dihydronaphthalen-1-ol (**4j**). Prepared according to general procedure. Pale yellow oil (95.0 mg, 97% yield). R_f = 0.27 on silica gel (ethyl acetate/petroleum ether 1:3, v/v). The ee was determined to be 97% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 85:15, 1.0 mL/min, λ = 254 nm). Retention times were 17.2 (minor) and 23.7 min (major). $[\alpha]_D^{25}$ = +110.8 (*c* 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3366(br), 3007(w), 2922 (m), 2843(w), 1599(w), 1483(s), 1443(m), 1256(s), 1086(m), 1038(m), 934(w), 800(m), 719(w). ^1H NMR (500 MHz, $CDCl_3$): δ 7.06 (dd, *J* = 9.8, 3.2 Hz, 1H), 6.92 (d, *J* = 1.7 Hz, 1H), 6.88 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.83−6.81 (m, 2H), 6.78 (d, *J* = 9.0 Hz, 1H), 6.07−6.04 (m, 1H), 5.95−5.94 (m, 2H), 5.03 (s, 1H), 3.81 (d, *J* = 3.0 Hz, 6H), 3.71−3.69 (m, 1H), 1.64 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 150.8, 149.7, 147.8, 146.6, 134.3, 129.1, 124.4, 122.5, 122.1, 122.0, 111.5, 111.0, 109.7, 108.3, 101.0, 64.5, 56.3, 56.2, 47.0. HRMS (ESI-ion trap) *m*/*z*: $[M + Na]^+$ calcd for $C_{19}H_{18}O_5Na$, 349.1052; found 349.1028.

(1S,2R)-2-Phenyl-1,2-dihydrotriphenylen-1-ol (**5a**). Prepared according to general procedure. A yellow solid (88.9 mg, 92% yield). Mp 129−130 °C. R_f = 0.19 on silica gel (ethyl acetate/petroleum ether 1:10, 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 49.2 (minor) and 53.3 min (major). $[\alpha]_D^{25}$ = −150.2 (*c* 1.00, $CHCl_3$). IR (neat film, cm^{-1}): 3407(br), 3022(w), 2923(m), 2856(w), 1645(w), 1495(m), 1449(m), 1397(w), 1072(m), 751 (s), 740(s). ^1H NMR (400 MHz, $CDCl_3$): δ 8.73 (t, *J* = 7.6 Hz, 2H), 8.27 (dd, *J* = 23.9, 5.3 Hz, 2H), 7.68−7.44 (m, 9H), 7.38 (d, *J* = 6.5 Hz, 1H), 6.46 (d, *J* = 9.7 Hz, 1H), 5.41 (s, 1H), 4.01 (s, 1H), 1.68 (s, 1H). $^{13}C\{^1H\}$ 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, 126.5, 126.4, 124.1, 123.9, 123.8, 123.1, 123.0, 67.6, 48.0. HRMS (ESI-ion trap) *m*/*z*: $[M + Na]^+$ calcd for $C_{24}H_{18}ONa$, 345.1255; found 345.1242.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures; copies of ^1H and $^{13}C\{^1H\}$ NMR spectra of compounds **2a**−**m**, **2o**−**q**, **3a**−**h**, **4a**−**j**, and **5a**; ^{19}F NMR spectra of compounds **2b**, **2f**, and **3b**; HPLC conditions and spectra of compounds **2a**−**d**, **2f**−**k**, **2o**−**q**, **3b**−**f**, **3h**, **4a**, **4d**−**e**, **4h**−**j**, and **5a**; and X-ray crystal data for compound **4b** 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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