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Iridium-Catalyzed Asymmetric Ring-Opening of Oxabenzonorbornadienes with Phenols

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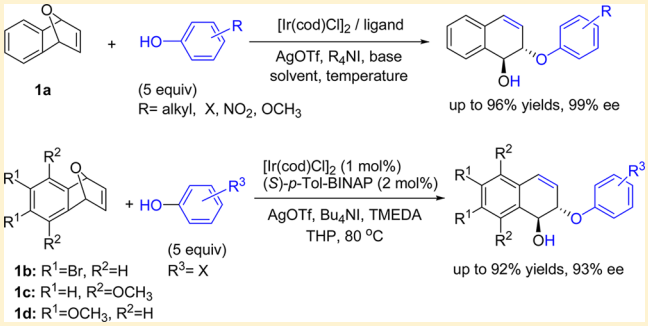
Supporting Information

ABSTRACT: A novel iridium-catalyzed asymmetric ring-opening (ARO) reaction of oxabenzonorbornadienes with a variety of phenols was reported, which afforded the corresponding *trans*-2-phenoxy-1,2-dihydronaphthalen-1-ol products in high yields with moderate to excellent enantioselectivities (up to 98% ee) under mild conditions. The trans products are formed via the enantioselective cleavage of a bridgehead carbon−oxygen bond in **1** followed by S_N2 nucleophilic attack by phenols. The effects of various bisphosphine ligands, Ag (I) salts, ammonium halides, bases, and solvents on the yield and enantioselectivity of the reaction were also investigated. The trans-configuration of the product **2a** was confirmed by X-ray crystal structure analysis. A possible mechanism for the present catalytic reaction was proposed.



INTRODUCTION

Transition-metal-catalyzed asymmetric ring-opening (ARO) reactions of oxa- and azabicyclic alkenes have been demonstrated to be useful methods for the synthesis of chiral building blocks.[1] Metal-catalyzed transformations that can establish the absolute configuration with more than one stereocenter are particularly attractive to synthetic chemists. The ARO reactions of oxa- and azabicyclic alkenes with various carbon- and heteroatom nucleophiles represent a type of organic reaction for the efficient formation of asymmetric carbon−carbon and carbon-heteroatom bonds, affording a variety of the ring-opened products.[2] This area has received increasing attention and has been extensively investigated. Many parameters have been examined for these reactions, including a variety of metal catalysts such as Fe,[3] Ni,[4] Cu,[5] Ru,[6] Rh,[7] Pd,[8] etc., and nucleophiles such as alcohols,[9] phenols,[7c,10] thiophenols,[11] amines,[7d,g,h,12] Grignard reagents,[3,13] organozinc reagents,[8a,c−e,j,14] organoboronic acids,[8l,n,15] organic halides,[4a,8f,i] alkynes,[4b,6b,16] and others.[5b,d,17] Recently, Lautens and co-workers reported the Rh-catalyzed ARO of oxabicyclic alkenes with water.[18] Those reactions provided potential promising methods to form carbon−oxygen bonds through the addition of oxygen-based nucleophiles to the oxabicyclic alkenes, offering facile and efficient synthetic routes to optically active compounds bearing multiple stereocenters. In addition, oxabicyclic alkenes are valuable synthetic intermediates, as they can serve as a general template to create highly substituted ring systems.

Very recently, we have reported the iridium-catalyzed ARO reaction of oxa- and azabicyclic alkenes with amines and phenols.[19,20] However, the ARO reactions of oxabicyclic alkenes with phenols have rarely been investigated. Our interest in generating carbon−oxygen bonds has prompted us to expand the scope of the reaction to include phenol-induced ring-openings of oxabicyclic alkenes for an efficient access to *trans*-2-phenoxy-1,2-dihydronaphthalen-1-ols with regio-, diastereo-, and enantioselectivities. Ring-opening carbon−oxygen bond formation with oxabenzonorbornadiene **1** is a valuable synthetic methodology to create highly functionalized ring systems. These methods offer potentially useful routes to the synthesis of enantioenriched *trans*-2-phenoxy-1,2-dihydronaphthalen-1-ols, which are the scaffolds for total synthesis of bioactive compounds.[21] Herein we report the full details of the catalytic ARO reaction of oxabenzonorbornadienes with phenols in the presence of iridium catalysts. The reactions afford the corresponding *trans*-2-phenoxy-1,2-dihydronaphthalen-1-ols in moderate to good yields with excellent enantioselectivities (up to 98% ee) under relatively mild conditions.

RESULTS AND DISCUSSION

The substrates **1a−d** were readily prepared by the Diels−Alder reactions of benzynes with furan according to literature procedures.[7e,22] To explore the ring-opening reactions, an achiral ligand 1,1′-bis(diphenylphosphino)ferrocene (DPPF) was first chosen to validate the catalytic activity of the iridium complex in the ring-opening reactions of oxabenzonorbornadiene **1a** with 4-chlorophenol in tetrahydrofuran (THF) at 80 °C (not shown in Table 1); unfortunately, we did not obtain

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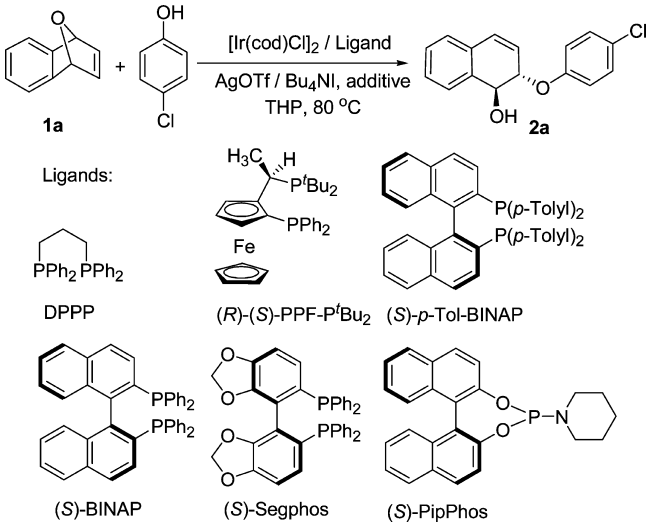
Table 1. Effect of Ligands and Additives[a]



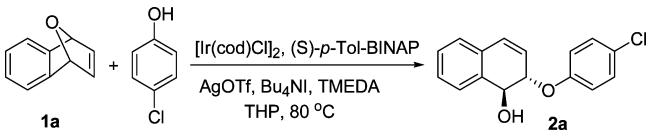
entry	ligand	additive	time (h)	yield (%)	ee[b] (%)
1[c]	DPPP		72	10	0
2[c]	(*S*)-*p*-Tol-BINAP		48	15	30
3	(*S*)-*p*-Tol-BINAP		12	30	69
4	(*S*)-BINAP		12	20	51
5	(*R*)-(*S*)-PPF-P^{t}Bu$_2$		48	17	32
6	(*S*)-Segphos		12	18	22
7	(*S*)-PipPhos		48	n.r.	
8	(*S*)-*p*-Tol-BINAP	NH_4I[d]	48	trace	
9	(*S*)-*p*-Tol-BINAP	Bu_4NI[d]	12	31	79
10	(*S*)-*p*-Tol-BINAP	Cs_2CO_3[e]	48	trace	
11	(*S*)-*p*-Tol-BINAP	Cs_2CO_3[f]	48	31	71
12	(*S*)-*p*-Tol-BINAP	Et_3N[e]	12	25	41
13[g]	(*S*)-*p*-Tol-BINAP	Bu_4NI/Et_3N	2	50	81
14[g]	(*S*)-*p*-Tol-BINAP	Bu_4NI/TMEDA[h]	2	60	94
15[g]	(*S*)-*p*-Tol-BINAP	Bu_4NI/PMP[i]	2	61	92

[a]Conditions: $[Ir(cod)Cl]_2$ (2.5 mol %), ligand (5 mol %), AgOTf (10 mol %), Bu_4NI (20 mol %), **1a** (0.2 mmol), and 4-chlorophenol (1 mmol) reacted in THP at 80 °C (oil bath temperature). [b]Determined by HPLC with a Chiralcel AD-H column. [c]Without addition of AgOTf and Bu_4NI. [d]Ammonium halide (1 equiv) was added. [e]Base (5 equiv) was added. [f]Cs_2CO_3 (5 equiv, 5 M in H_2O) was added. [g]Tetrabutylammonium iodide (1 equiv) and a base (5 equiv) were added. [h]*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA). [i]1,2,2,6,6-Pentamethylpiperidine (PMP).

the desired ring-opened product **2a**. Another achiral ligand 1,3-bis(diphenylphosphino)propane (DPPP) was tested without additives and resulted in poor yield (10%) (Table 1, entry 1) after 72 h. The results encouraged us to optimize the catalytic reaction conditions, the desired ring-opened product **2a** was obtained in a 15% yield with 30% ee in the presence of 2.5 mol % $[Ir(cod)Cl]_2$ and 5 mol % (*S*)-*p*-Tol-BINAP (Table 1, entry 2). The yield was increased to 31% (Table 1, entry 9) when silver(I) triflate (AgOTf) and ammonium halides as additives were employed in the presence of $[Ir(cod)Cl]_2$. Silver chloride was first precipitated by the addition of AgOTf, which was followed by the addition of the (*S*)-*p*-Tol-BINAP ligand and then the addition of tetrabutylammonium iodide (Bu_4NI). In this way, by a halide-exchange protocol, cationic iridium complexes $[Ir((S)$-*p*-Tol-BINAP$)I]_2$ are formed. Considering the halide effect on the ring-opening reactions,[7a,e,12] Bu_4NI was added as additive to the reaction mixture, and the corresponding ring-opened product **2a** was obtained in 31% yield with 79% ee (Table 1, entry 9). Several bases were added to the reaction mixture, but the results were not satisfactory (Table 1, entries 10−12). The reaction seemed to proceed smoothly when 1 equiv of Bu_4NI and 5 equiv of a base were added to the mixture (Table 1, entries 13−15). It was further discovered that when using Bu_4NI and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) as additives, the reaction provided the expected ring-opened product **2a** in moderate yield with excellent enantioselectivity (94% ee) (Table 1, entry 14). These results showed that Bu_4NI and TMEDA as additives were highly effective for promoting the ring-opening of **2a**. On the other hand, the choice of ligand was very important. To determine if there was a more suitable ligand for the asymmetric reaction, a variety of achiral and chiral ligands were evaluated (Table 1). Several chiral ligands such as (*S*)-BINAP, (*S*)-*p*-Tol-BINAP, (*R*)-(*S*)-PPF-P^{t}Bu$_2$, (*S*)-Segphos, and (*S*)-PipPhos were then examined. Indeed, not all ligands showed the same type or level of reactivity. Table 1 presents the excellent performance of (*S*)-*p*-Tol-BINAP with regard to catalytic activity and stereoselectivity when the molar ratio of (*S*)-*p*-Tol-BINAP to iridium was 2:1 (Table 1, entries 11−15). Other ligands such as (*S*)-BINAP, (*R*)-(*S*)-PPF-P^{t}Bu$_2$, (*S*)-Segphos, and (*S*)-PipPhos gave either unsatisfactory results (Table 1, entries 4−6) or no reaction (Table 1, entry 7). Therefore, we decided to choose (*S*)-*p*-Tol-BINAP as the ligand for the reactions.

To obtain better yield and enantioselectivity, we then investigated the impact of catalyst loading on the reaction (Table 2, entries 1−5). The yield and enantioselectivity of **2a**

Table 2. Effect of the Catalyst Loading[a]



entry	$[Ir(cod)Cl]_2$ (mol %)	time (h)	yield (%)	ee[b] (%)
1	0.5	72	47	92
2	1	1	83	98
3	1.5	1	82	95
4	2.0	1	68	96
5	2.5	2	60	94

[a]Conditions: the reaction was carried out with **1a** (0.2 mmol) and 4-chlorophenol (1 mmol) in the presence of halide additive Bu_4NI (0.2 mmol) and TMEDA (1 mmol) in THP at 80 °C (oil bath temperature), and the ratio of $[Ir(cod)Cl]_2$/(S)-p-Tol-BINAP/AgOTf/Bu_4NI = 1:2:4:8. [b]Determined by HPLC with a Chiralcel AD-H column.

were strongly influenced by the catalyst loading. By allowing the reaction to run for three days, the catalyst loading could be lowered to 0.25 mol % (Table 2, entry 1). It would be a more suitable catalyst loading in terms of the yield and ee when the molar ratio of $[Ir(cod)Cl]_2$ to (*S*)-*p*-Tol-BINAP was 1:2 (Table 2, entry 2). However, a further increase in catalyst loading for the reaction did not improve the yield and ee (Table 2, entries 3−5).

To optimize the present reaction conditions, the effects of different reaction parameters including the selection of solvents and the reaction temperatures on reactivity and enantioselec-

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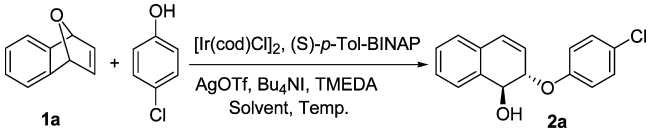
tivity were next investigated (as shown in Table 3). First of all the effect of the solvent was investigated. It proved to have a

Table 3. Optimization of the Solvent and Temperature[a]



entry	solvent	temperature (°C)	time (h)	yield (%)	ee[b] (%)
1	CH_3CN	80	72	n.r.	
2	DCE	80	72	trace	
3	toluene	80	72	18	87
4	DME	80	2	57	99
5	1,4-dioxane	80	2	65	95
6	THF	80	2	63	94
7	THP	100	0.5	54	93
8	THP	80	1	83	98
9	THP	60	3	82	93
10	THP	20	72	n.r.	

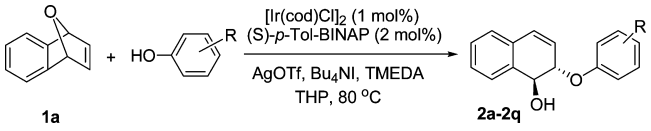
[a]Conditions (unoptimized): $[Ir(cod)Cl]_2$ (1 mol %), ligand (2 mol %), AgOTf (4 mol %), Bu_4NI (8 mol %), **1a** (0.2 mmol), halide additive Bu_4NI (0.2 mmol), TMEDA (1 mmol), and 4-chlorophenol (1 mmol) reacted in the solvent of choice at the corresponding temperature. [b]Determined by HPLC with a Chiralcel AD-H column.

dramatic effect on the enantioselectivity of the reaction. When the reaction was carried out in CH_3CN and 1,2-dichloroethane (DCE), respectively, we did not obtain any product **2a** (Table 3, entries 1 and 2), while the employment of toluene resulted in only 18% conversion after 72 h (Table 3, entry 3). The use of 1,2-dimethoxyethane (DME) resulted in moderate yield (57%) with excellent ee (up to 99% ee) (Table 3, entry 4). Similar results were obtained with 1,4-dioxane and THF (Table 3, entries 5 and 6). The solvent was then changed from THF to tetrahedropyran (THP), and a dramatic effect was observed on the enantioselectivity, as it increased to 98% ee (Table 3, entry 8). Solvent effect study showed that THP was the best one among the solvents tested. The effects of the temperature were then investigated in the ring-opening reaction. By increasing the oil bath temperature to 80 °C and running the reaction in THP, the yield of **2a** was increased to 83% with 98% ee (Table 3, entry 8). Further increase of the temperature to 100 °C resulted in 54% yield with 93% ee (Table 3, entry 7), although only 0.5 h was required for full conversion. Unexpectedly, lowering the temperature to 20 °C resulted in no reaction (Table 3, entry 10). Therefore, optimum reaction temperature was identified as 80 °C in THP, giving the desired product **2a** in good yield (83%) with excellent enantioselectivity (98% ee) (Table 3, entry 8).

The single crystal of the product **2a** was obtained by solvent evaporation from a solution consisting of petroleum ether, ethanol, and ethyl acetate. Its absolute configuration was assigned as (1*S*,2*S*) and confirmed as 1,2-trans-configuration by X-ray crystal structure analysis, as shown in the Supporting Information.

With the optimized reaction conditions in hand (1 mol % of $[Ir(cod)Cl]_2$, 2 mol % of (*S*)-*p*-Tol-BINAP, 4 mol % AgOTf, 8 mol % Bu_4NI, and 5 equiv of TMEDA in THP at 80 °C), we attempted to expand the scope of the iridium-catalyzed ARO reaction of oxabenzonorbornadiene **1a** with various phenols. The results were summarized in Table 4, from which it could be seen that the structures of phenols had a very significant

Table 4. Ir-Catalyzed ARO of Oxabenzonorbornadiene 1a with Various Phenols[a]



entry	R	product	time (h)	yield (%)	ee[b] (%)
1	4-Cl	**2a**	1	83	98
2	3-Cl	**2b**	1	85	76
3	2-Cl	**2c**	1	75	95
4	4-NO_2	**2d**	1.5	70	46
5	H	**2e**	2	74	93
6	4-CH_3	**2f**	2	77	77
7	3-CH_3	**2g**	2	75	66
8	2-CH_3	**2h**	2	65	75
9	4-OCH_3	**2i**	2	60	94
10	2,3-dichloro	**2j**	1	80	98
11	2,4-dichloro	**2k**	1	96	90
12	2,5-dichloro	**2l**	1	86	77
13	2,6-dichloro	**2m**	48	21	43
14	4-chloro-3-methyl	**2n**	1	90	60
15	2-bromo-4-chloro	**2o**	1	84	73
16	4-bromo-2-chloro	**2p**	1	86	94
17	2,4-dibromo	**2q**	1	80	75
18	2,6-di-*tert*-butyl	**2r**	72	n.r.	

[a]Conditions: $[Ir(cod)Cl]_2$ (1 mol %), (*S*)-*p*-Tol-BINAP (2 mol %), AgOTf (4 mol %), Bu_4NI (8 mol %), substrate **1a** (0.2 mmol), halide additive Bu_4NI (0.2 mmol), TMEDA (1 mmol), and substituted phenol (1 mmol) reacted in THP (2.0 mL) at 80 °C (oil bath temperature). [b]Determined by HPLC (Chiralcel AD-H or Chiralcel OD-H column).

impact on reactivity and enantioselectivity. In general, the reaction of **1a** with para-substituted phenol offered better results than those with ortho- and meta-substituted phenol (Table 4, entries 1−3 and 6−8). Additionally, we observed significant difference in the relative rates of reaction, with the more acidic phenols adding faster. The reaction afforded better yield and enantioselectivity when **1a** reacted with monosubstituted phenols having electron-withdrawing groups than those with electron-donating groups (Table 4, entries 1−3 and 6−8). It was also noteworthy that phenol and 4-methoxyphenol for the ring-opening were found to give moderate yield (74% and 60%, respectively) and high ee (93% and 94%, respectively) (Table 4, entries 5 and 9), whereas the reaction of **1a** with 4-nitrophenol gave the corresponding product **2d** in 70% yield with 46% ee (Table 4, entry 4). Phenols having multisubstituted groups also showed high reactivity and moderate to good enantioselectivity (Table 4, entries 10−12 and 14−17). For instance, the reactions of **1a** with 2,3-dichlorophenol and 2,4-dichlorophenol gave the corresponding products **2j** and **2k** in high yields (80% vs 96%) with excellent ee (98% vs 90%), respectively (Table 4, entries 10 and 11). The reactions of **1a** with phenols having electron-withdrawing multisubstituted groups gave the corresponding products **2l−q** in moderate yields with good ee (Table 4, entries 12−17). Due to the steric bulkiness of the *tert*-butyl group, the ring-opening reaction by 2,6-di-*tert*-butyl phenol did not afford any desired product **2r** (Table 4, entry 18).

To extend the scope of this reaction to other substrates, we used substituted oxabenzonorbornadienes **1b**, **1c**, and **1d** with phenols to perform the reaction, and these results are

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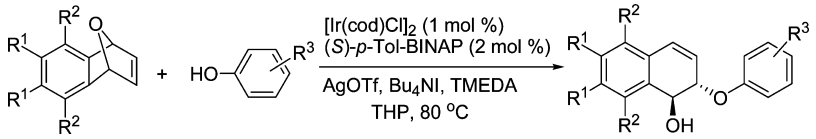
Table 5. Scope of Ir-Catalyzed ARO of Oxabenzonorbornadienes 1b−d with Various Phenols[a]



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

3a-3h
4a-4d
5a-5b

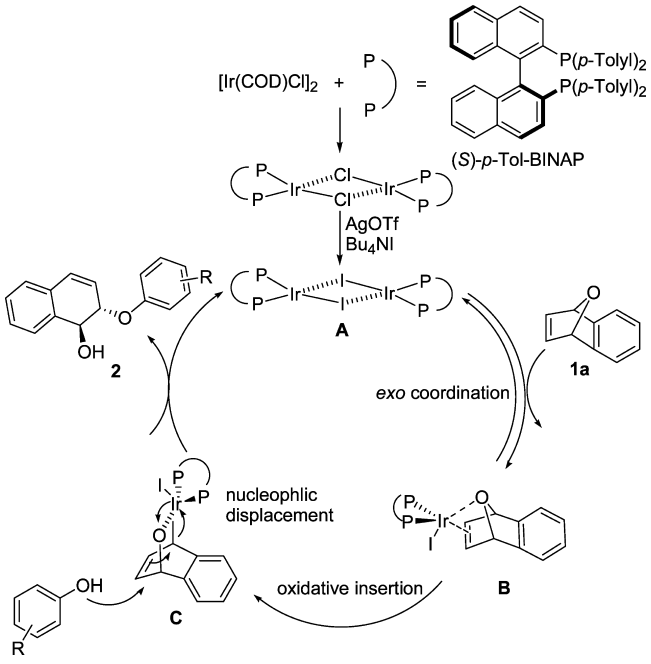
entry	substrate	R^3	product	time (h)	yield (%)	ee[b](%)
1	**1b**	4-Cl	**3a**	4	87	82
2	**1b**	3-Cl	**3b**	4	87	66
3	**1b**	2-Cl	**3c**	4	83	55
4	**1b**	2,3-dichloro	**3d**	3	75	75
5	**1b**	2,4-dichloro	**3e**	3	71	79
6	**1b**	2,5-dichloro	**3f**	3	87	75
7	**1b**	2-bromo-4-chloro	**3g**	3	92	70
8	**1b**	4-bromo-2-chloro	**3h**	3	82	93
9	**1c**	4-Cl	**4a**	8	74	60
10	**1c**	2,4-dichloro	**4b**	8	45	50
11	**1c**	4-bromo-2-chloro	**4c**	8	47	50
12	**1c**	4-chloro-3-methyl	**4d**	5	42	48
13	**1d**	4-Cl	**5a**	6	45	84
14	**1d**	3-Cl	**5b**	6	46	51

[a]Conditions: $[Ir(cod)Cl]_2$ (1 mol %), ligand (2 mol %), AgOTf (4 mol %), Bu_4NI (8 mol %), substrate **1** (0.2 mmol), halide additive Bu_4NI (0.2 mmol), TMEDA (1 mmol), and phenol (1 mmol) reacted in THP at 80 °C (oil bath temperature). [b]Determined by HPLC (Chiralcel AD-H or Chiralcel OD-H column).

summarized in Table 5. Table 5 shows that all reactions of substrates of oxabicyclic alkenes with various phenols proceeded smoothly to give the expected products in high yields with moderate to excellent enantioselectivities. Except for the reaction of **1b** with 2-chlorophenol which showed slightly lower enantioselectivity (Table 5, entry 3), other reactions of **1b** treated with other phenols gave the corresponding products in considerable yields with moderate to good ee (up to 93% ee) (Table 5, entries 1, 2, and 4−8). Furthermore, the structure of the disubstituted groups of the oxabenzonorbornadienes has substantial effect on the reaction. The reactions of electron-rich **1c** and **1d** with phenols, respectively, required a longer reaction time and gave lower yields with inferior ee, when compared with electron-deficient **1b** (Table 5, entries 9−12 and 14), whereas there was an exception that the product **5a** was obtained in moderate yield (45%) with 84% ee (Table 5, entry 13). It is also noteworthy that the reaction of 4-bromo-2-chlorophenol with **1b** affords the expected product **3h** in good yield (82%) with high ee (93%).

Based on our findings and observations, a plausible mechanism has been proposed for the formation of the ring-opened products **2** as shown in Scheme 1. The active catalyst of chiral dimeric iridium complex **A**, $[Ir((S)\text{-}p\text{-Tol-BINAP})I]_2$, is first formed through treatment of the precatalyst, $[Ir(cod)Cl]_2$, with AgOTf to remove the chloride and followed by the addition of the (*S*)-*p*-Tol-BINAP ligand, which replaces the 1.5-cyclooctadiene (cod) ligand, and then the addition of Bu_4NI. The oxygen atom and the double bond of oxabenzonorbornadiene **1a** are then reversibly coordinated to the iridium center of the active catalyst to give the intermediate **B**, followed by the oxidative insertion of iridium catalyst into the C−O bond forms **C**. Then phenol nucleophile attack with configuration inversion is proposed to occur in an S_N2 displacement of the iridium catalyst. Consequently, the product **2** is subsequently released and the iridium complex **A** is regenerated.

Scheme 1. Working Hypothesis for the ARO Reaction of Oxabenzonorbornadiene 1a with Phenols



CONCLUSIONS

In summary, we have developed that a highly regio- and stereoselective iridium-catalyzed ring-opening of oxabenzonorbornadienes with phenols. It provides an efficient and practical approach to the synthesis of optically active *trans*-2-substituted-

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1,2-dihydronaphthalen-1-ol derivatives in moderate to good yields and excellent enantioselectivities under mild conditions. Use of both Bu_4NI and TMEDA improve the reaction rate and yield in the present reaction. Additionally, the presence of electron-withdrawing groups on the oxabenzonorbornadienes and phenols are found to have positive impact on the reactivity and enantioselectivity. Our results further reveal that the nature of the chiral ligand has a significant impact on this ring-opening reaction. Studies on further expansion of the scope and synthetic utility of the Ir-catalyzed ARO reactions are also being pursued in our laboratory. As the ring-opened products, cyclic alcohols with two chiral centers, are biologically important compounds, future study will be focused on evaluating the biological and pharmaceutical activities of these compounds.

EXPERIMENTAL SECTION

Only representative procedures and characterization of the products are described here. Full details are presented in the Supporting Information.

General Procedure I for the ARO Reactions of Oxabenzonorbornadienes 1a−1d with Phenols. A 5.0 mL round-bottom flask fitted with a reflux condenser was flame-dried under a stream of nitrogen and cooled to room temperature. $[Ir(cod)Cl]_2$ (1.3 mg, 1.0 mol %) and (S)-*p*-Tol-BINAP (2.7 mg, 2.0 mol %) were simultaneously added and followed by the addition of anhydrous THP (2.0 mL). After the mixture was stirred for about 20 min, silver trifluoromethanesulfonate (2.0 mg, 4.0 mol %) was added. After another 10 min, Bu_4NI (5.9 mg, 8 mol %) was added and the mixture was stirred for 10 min. To this mixture, substrate **1** (0.2 mmol) was added, and then the mixture was heated. When the temperature of the oil bath climbed to 80 °C, Bu_4NI (73.8 mg, 1 equiv) and TMEDA (116.1 mg, 5 equiv) were added and followed by the phenol (5 equiv). The reaction temperature was maintained at 80 °C until completion as judged by thin-layer chromatography. The solvent was removed in vacuum, and the crude mixture was then poured into dichloromethane and washed three times with 5% aqueous NaOH. The aqueous layers were combined and back-extracted three times with dichloromethane. The organic layers were combined, dried over anhydrous Na_2SO_4, and then filtered. The filtrate was concentrated in vacuo, and the resulting residue was purified by column chromatography on silica gel (silica gel: 200−300 mesh) to give the target product.

(1*S*,2*S*)-2-(4-Chlorophenoxy)-1,2-dihydronaphthalen-1-ol (2a). Following general procedure I, **2a** was obtained as a white crystalline solid (45.2 mg, 83%). The ee was determined to be 98% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 16.5 min (major) and 23.4 min (minor); R_f = 0.24 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 125−126 °C. $[\alpha]^{25}_D$ = +97.5 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3298(br), 2928(w), 2851(w), 1590(m), 1485(s), 1233(s), 1032(m), 980(m), 839(m), 779(m), 743(m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 6.8 Hz, 1H), 7.32−7.23 (m, 4H), 7.12 (d, J = 6.4 Hz, 1H), 6.87 (d, J = 8.4 Hz, 2H), 6.52 (d, J = 9.6 Hz, 1H), 5.96 (d, J = 9.6 Hz, 1H), 5.16 (dd, J = 3.6, 10.0 Hz, 1H), 5.05 (d, J = 10.0 Hz, 1H), 2.65 (d, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 135.3, 131.8, 129.6, 129.3, 128.3, 128.1, 126.6, 126.4, 125.5, 125.3, 117.1, 79.4, 72.3; MS (EI, 70 eV) m/z (%): 254.05 ($[M - H_2O]^+$, 10), 145.08 (23), 144.20 (92), 128.04 (100), 127.44 (44), 116.03 (68), 115.13 (86), 114.58 (45); Anal. Calcd for $C_{16}H_{13}ClO_2$: C, 70.46; H, 4.80. Found: C, 70.38; H, 4.81.

(1*S*,2*S*)-2-(3-Chlorophenoxy)-1,2-dihydronaphthalen-1-ol (2b). Following general procedure I, **2b** was obtained as a white crystalline solid (46.2 mg, 85%). The ee was determined to be 76% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm); Retention times were 11.5 min (major) and 18.0 min (minor). R_f = 0.27 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 85−86 °C. $[\alpha]^{25}_D$ = +107.5 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3220(br), 3038(w), 2923(w), 2844(w), 1596(s), 1253(s), 1044(s), 905(m), 776(s), 743(s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 6.0 Hz, 1H), 7.29−7.11 (m, 4H), 6.96 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 1H), 6.52 (d, J = 9.6 Hz, 1H), 5.96 (d, J = 10.0 Hz, 1H), 5.16 (d, J = 10.0 Hz, 1H), 5.06 (d, J = 10.0 Hz, 1H), 2.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 135.3, 135.1, 131.8, 130.5, 129.4, 128.3, 128.2, 126.6, 125.4, 125.3, 121.7, 116.3, 114.1, 79.4, 72.2; MS (EI, 70 eV) m/z (%): 254.03 ($[M - H_2O]^+$, 2), 148.97 (31), 145.04 (43), 143.98 (95), 129.95 (25), 127.95 (100), 116.02 (35), 114.99 (66), 64.95 (29); Anal. Calcd for $C_{16}H_{13}ClO_2$: C, 70.46; H, 4.80. Found: C, 70.31; H, 4.83.

(1*S*,2*S*)-2-(2-Chlorophenoxy)-1,2-dihydronaphthalen-1-ol (2c). Following general procedure I, **2c** was obtained as a white crystalline solid (40.8 mg, 75%). The ee was determined to be 95% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 95/5, 1.0 mL/min, λ = 254 nm). Retention times were 21.0 min (major) and 24.6 min (minor); R_f = 0.29 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 128−129 °C. $[\alpha]^{25}_D$ = +32.1 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3341(br), 2919(m), 2851(w), 1634(m), 1583(m), 1480(s), 1278(s), 1041(s), 892(m), 767(m), 691(m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 6.8 Hz, 1H), 7.42−7.12 (m, 5H), 6.99−6.94 (m, 2H), 6.52 (d, J = 10.0 Hz, 1H), 6.05 (d, J = 10.0 Hz, 1H), 5.30 (d, J = 9.6 Hz, 1H), 5.11 (d, J = 10.2 Hz, 1H), 2.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 135.4, 131.8, 130.6, 129.2, 128.3, 128.0, 127.8, 126.5, 125.9, 125.1, 124.1, 122.5, 115.9, 82.0, 72.5; MS (EI, 70 eV) m/z (%): 254.06 ($[M - H_2O]^+$, 3), 145.06 (80), 143.68 (90), 128.19 (40), 127.55 (60), 116.08 (43), 114.96 (100); Anal. Calcd for $C_{16}H_{13}ClO_2$: C, 70.46; H, 4.80. Found: C, 70.18; H, 4.84.

(1*S*,2*S*)-2-(4-Nitrophenoxy)-1,2-dihydronaphthalen-1-ol (2d). Following general procedure I, **2d** was obtained as a white crystalline solid (39.6 mg, 70%). The ee was determined to be 46% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.5 mL/min, λ = 254 nm). Retention times were 25.7 min (major) and 48.3 min (minor); R_f = 0.25 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). mp 120−122 °C. $[\alpha]^{25}_D$ = +76.7 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3489(br), 3078(w), 2922(m), 2844(w), 1591(s), 1508(s), 1341(s), 1248(s), 1113(s), 983(s), 745(m), 750(s); ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, J = 2.3, 9.2 Hz, 2H), 7.63−7.61 (m, 1H), 7.33−7.31 (m, 2H), 7.16−7.15 (m, 1H), 7.01 (dd, J = 1.6, 9.2 Hz, 2H), 6.59 (d, J = 9.6 Hz, 1H), 5.95 (d, J = 9.6 Hz, 1H), 5.21 (s, 2H), 2.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 141.8, 135.1, 131.5, 130.2, 128.6, 128.4, 126.8, 126.1, 125.5, 124.2, 115.5, 79.6, 72.0; MS (EI, 70 eV) m/z (%): 265.04 ($[M - H_2O]^+$, 2), 144.15 (70), 143.55 (42), 127.82 (29), 116.04 (40), 114.94 (100), 109.05(21); Anal. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.94. Found: C, 67.68; H, 4.65; N, 5.01.

(1*S*,2*S*)-2-Phenoxy-1,2-dihydronaphthalen-1-ol (2e). Following general procedure I, **2e** was obtained as a white crystalline solid (35.2 mg, 74%). The ee was determined to be 93% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 12.8 min (major) and 19.7 min (minor); R_f = 0.22 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 108−109 °C. $[\alpha]^{25}_D$ = +142.8 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3251(br), 3029(w), 2853(w), 1599(s), 1494(s), 1247(s), 1060(s), 980(m), 745(s), 695(s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 6.4 Hz, 1H), 7.32−7.25 (m, 4H), 7.12 (d, J = 6.8 Hz, 1H), 7.01−6.95 (m, 3H), 6.52 (d, J = 9.6 Hz, 1H), 6.03 (d, J = 10.0 Hz, 1H), 5.15 (dd, J = 10.0, 20.0 Hz, 2H), 2.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 135.5, 131.9, 129.7, 129.0, 128.2, 128.0, 126.5, 126.1, 125.2, 121.5, 115.8, 79.0, 72.4; MS (EI, 70 eV) m/z (%): 220.02 ($[M - H_2O]^+$, 5), 145.02 (62), 144.27 (54), 143.75 (100), 128.01 (15), 126.87 (49), 117.02 (23), 116.02 (45), 114.93 (88), 93.90 (43); Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.42; H, 5.98.

(1*S*,2*S*)-2-(*p*-Tolyloxy)-1,2-dihydronaphthalen-1-ol (2f). Following general procedure I, **2f** was obtained as a white crystalline solid (38.8 mg, 77%). The ee was determined to be 77% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 15.6 min (major) and 25.4 min (minor); R_f = 0.26 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 79−80 °C. $[\alpha]^{25}_D$ = +130.8 (c = 1.00, $CHCl_3$).

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IR (KBr, cm^{-1}) 3201(br), 3029(w), 2920(w), 2851(w), 1612(w), 1507(s), 1227(s), 1032(s), 980(m), 824(m), 778(m), 743(m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.2 Hz, 1H), 7.29−7.20 (m, 2H), 7.10−7.07 (m, 3H), 6.85 (d, J = 8.4 Hz, 2H), 6.48 (d, J = 10.0 Hz, 1H), 6.00 (dd, J = 1.9, 10.0 Hz, 1H), 5.15 (d, J = 10.2 Hz, 1H), 5.05 (d, J = 10.2 Hz, 1H), 2.72 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 135.6, 131.9, 130.8, 130.2, 128.8, 128.1, 128.0, 126.4, 126.3, 125.2, 115.9, 79.3, 72.4, 20.5; MS (EI, 70 eV) m/z (%): 233.81 ([M − H_2O]$^+$, 3), 145.06 (23), 143.95 (100), 126.95 (24), 114.95 (50) 108.00 (52), 106.78 (21); Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.81; H, 6.44.

(1*S*,2*S*)-2-(*m*-Tolyloxy)-1,2-dihydronaphthalen-1-ol (2g). Following general procedure I, **2g** was obtained as a white crystalline solid (37.8 mg, 75%). The ee was determined to be 66% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 10.6 min (major) and 19.4 min (minor); R_f = 0.26 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 62−63 °C. $[\alpha]^{25}_D$ = +113.5 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3292(br), 3038(w), 2912(w), 2851(w), 1590(m), 1485(s), 1255(s), 1151 (m), 1047(s), 980(m), 779(s), 743(s), 691(m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 6.8 Hz, 1H), 7.30−7.23 (m, 2H), 7.17 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 6.81−6.74 (m, 3H), 6.49 (d, J = 10.0 Hz, 1H), 6.01 (d, J = 10.0 Hz, 1H), 5.17 (d, J = 10.0 Hz, 1H), 5.09 (dd, J = 1.4, 10.2 Hz, 1H), 2.72 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 139.8, 135.6, 131.9, 129.4, 128.9, 128.2, 128.0, 126.4, 126.3, 125.2, 122.3, 116.7, 112.7, 79.1, 72.4, 21.5; MS (EI, 70 eV) m/z (%): 233.98 ([M − H_2O]$^+$, 3), 145.04 (24), 143.95 (100), 126.87 (20), 114.93 (53) 107.99 (45), 106.96 (32); Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: 80.75; H, 6.46.

(1*S*,2*S*)-2-(*o*-Tolyloxy)-1,2-dihydronaphthalen-1-ol (2h). Following general procedure I, **2h** was obtained as a white crystalline solid (32.8 mg, 65%). The ee was determined to be 75% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm). Retention times were 25.8 min (major) and 28.1 min (minor); R_f = 0.26 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 113−114 °C. $[\alpha]^{25}_D$ = +170.2 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3290(br), 2926(w), 2850(m), 1596(w), 1486(s), 1233(s), 1032(m), 980(m), 840(m), 779(m), 743(m), 655(m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.64−7.62 (m, 1H), 7.31−7.24 (m, 2H), 7.18−7.10 (m, 3H), 6.92−6.84 (m, 2H), 6.49 (dd, J = 1.6, 10.0 Hz, 1H), 6.03−5.97 (m, 1H), 5.21 (d, J = 10.4 Hz, 1H), 5.11 (d, J = 10.0 Hz, 1H), 2.62 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 135.6, 131.9, 131.2, 128.8, 128.2, 128.0, 127.8, 126.9, 126.5, 126.4, 125.2, 121.2, 113.0, 79.4, 72.6, 16.5; MS (EI, 70 eV) m/z (%): 234.05 ([M − H_2O]$^+$, 2), 145.02 (30), 143.95 (100), 128.01 (21), 126.99 (22), 116.03 (31), 114.94 (58) 107.99 (49), 106.78 (22); Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.72; H, 6.46.

(1*S*,2*S*)-2-(4-Methoxyphenoxy)-1,2-dihydronaphthalen-1-ol (2i). Following general procedure I, **2i** was obtained as a white crystalline solid (32.2 mg, 60%). The ee was determined to be 94% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 2.0 mL/min, λ = 254 nm). Retention times were 12.5 min (major) and 20.7 min (minor); R_f = 0.14 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 92−93 °C. $[\alpha]^{25}_D$ = +109.2 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3221(br), 2914(w), 2828(w), 1612(w), 1508(s), 1470(m), 1221(s), 1033(m), 772(m), 749(s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 6.4 Hz, 1H), 7.31−7.25 (m, 2H), 7.11 (d, J = 6.8 Hz, 1H), 6.87 (dd, J = 8.6, 27.4 Hz, 4H), 6.49 (d, J = 9.6 Hz, 1H), 6.01 (d, J = 9.6 Hz, 1H), 5.15 (d, J = 10.0 Hz, 1H), 5.00 (d, J = 10.0 Hz, 1H), 3.77 (s, 3H), 2.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 151.3, 135.5, 131.9, 128.8, 128.1, 128.0, 126.4, 126.3, 125.2, 117.2, 114.8, 80.0, 72.4, 55.7; MS (EI, 70 eV) m/z (%): 250.02 ([M − H_2O]$^+$, 3), 145.03 (10), 143.95 (63), 126.95 (15), 123.91 (100), 116.03 (22), 114.93 (45) 108.90 (45); Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.29; H, 5.98.

(1*S*,2*S*)-2-(2,3-Dichlorophenoxy)-1,2-dihydronaphthalen-1-ol (2j). Following general procedure I, **2j** was obtained as a white crystalline solid (50.0 mg, 80%). The ee was determined to be 98% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 2.0 mL/min, λ = 254 nm). Retention times were 6.7 min (major) and 8.0 min (minor); R_f = 0.18 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 166−167 °C. $[\alpha]^{25}_D$ = +127.8 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3219(br), 2921(w), 2851(w), 1578(m), 1454(s), 1287(s), 1041(m), 989(m), 777(s), 736(m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 6.8 Hz, 1H), 7.32−7.26 (m, 2H), 7.14 (d, J = 3.2 Hz, 3H), 6.93−6.85 (m, 1H), 6.54 (d, J = 10.0 Hz, 1H), 6.01 (d, J = 10.0 Hz, 1H), 5.30 (d, J = 10.0 Hz, 1H), 5.11 (d, J = 10.4 Hz, 1H), 2.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 135.3, 134.2, 131.7, 129.5, 128.4, 128.1, 127.4, 126.5, 125.4, 125.1, 123.3, 113.4, 82.1, 72.4; MS (EI, 70 eV) m/z (%): 288.03 ([M − H_2O]$^+$, 16), 207.02 (24), 163.96 (38), 161.91 (66), 145.12 (29), 144.19 (100), 126.09 (34), 116.00 (81), 114.72 (88); Anal. Calcd for $C_{16}H_{12}Cl_2O_2$: C, 62.56; H, 3.94. Found: C, 62.41; H, 3.96.

(1*S*,2*S*)-2-(2,4-Dichlorophenoxy)-1,2-dihydronaphthalen-1-ol (2k). Following general procedure I, **2k** was obtained as a white crystalline solid (58.8 mg, 96%). The ee was determined to be 90% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 2.0 mL/min, λ = 254 nm). Retention times were 8.3 min (major) and 9.9 min (minor); R_f = 0.24 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 127−128 °C. $[\alpha]^{25}_D$ = +102.0 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3394(br), 2932(w), 1643(s), 1477(s), 1263(m), 1099(m), 980(m), 779(s), 746(s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 6.8 Hz, 1H), 7.39 (d, J = 1.6 Hz, 1H), 7.32−7.25 (m, 2H), 7.17−7.11 (m, 2H), 6.89 (d, J = 8.8 Hz, 1H), 6.51 (d, J = 10.0 Hz, 1H), 5.97 (d, J = 10.0 Hz, 1H), 5.26 (d, J = 10.4 Hz, 1H), 5.05 (d, J = 10.0 Hz, 1H), 2.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 135.3, 131.7, 130.3, 129.5, 128.4, 128.1, 127.8, 126.8, 126.6, 125.3, 125.1, 124.9, 116.6, 82.1, 72.4; MS (EI, 70 eV) m/z (%): 288.01 ([M − H_2O]$^+$, 7), 207.03 (21), 163.90 (54), 161.85 (88), 145.05 (20), 144.17 (100), 143.64 (70), 125.98 (21), 116.02 (63), 115.18 (77), 114.66 (56); Anal. Calcd for $C_{16}H_{12}Cl_2O_2$: C, 62.56; H, 3.94. Found: C, 62.30; H, 3.99.

(1*S*,2*S*)-2-(2,5-Dichlorophenoxy)-1,2-dihydronaphthalen-1-ol (2l). Following general procedure I, **2l** was obtained as a white crystalline solid (52.6 mg, 86%). The ee was determined to be 77% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 2.0 mL/min, λ = 254 nm). Retention times were 5.7 min (minor) and 7.5 min (major); R_f = 0.31 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 109−110 °C. $[\alpha]^{25}_D$ = +68.5 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3288(br), 2926(w), 1582(m), 1473(s), 1229(m), 1047(m), 984(s), 778(s), 749(m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 6.8 Hz, 1H), 7.32−7.25 (m, 3H), 7.13 (d, J = 6.4 Hz, 1H), 6.97−6.93 (m, 2H), 6.54 (d, J = 10.0 Hz, 1H), 6.00 (d, J = 9.6 Hz, 1H), 5.28 (d, J = 10.0 Hz, 1H), 5.08 (d, J = 10.4 Hz, 1H), 2.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 135.2, 133.1, 131.7, 131.1, 129.6, 128.4, 128.1, 126.6, 125.1, 125.1, 122.5, 122.4, 116.1, 82.1, 72.3; MS (EI, 70 eV) m/z (%): 287.95 ([M − H_2O]$^+$, 6), 163.84 (40), 161.84 (60), 148.93 (33), 145.02 (100), 144.28 (59), 143.74 (95), 128.02 (23), 126.92 (53), 117.03 (26), 116.03 (47), 114.93 (98), 62.85 (19); Anal. Calcd for $C_{16}H_{12}Cl_2O_2$: C, 62.56; H, 3.94. Found: C, 62.33; H, 3.98.

(1*S*,2*S*)-2-(2,6-Dichlorophenoxy)-1,2-dihydronaphthalen-1-ol (2m). Following general procedure I, **2m** was obtained as a white crystalline solid (12.8 mg, 21%). The ee was determined to be 43% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 12.0 min (major) and 16.2 min (minor); R_f = 0.30 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 74−75 °C. $[\alpha]^{25}_D$ = +69.0 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3464(br), 2926(m), 2850(w), 2359(w), 1568(w), 1445(s), 1244(s), 1041(m), 962(m), 779(m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 6.8 Hz, 1H), 7.34−7.26 (m, 4H), 7.13−7.11 (m, 1H), 7.02 (td, J = 1.6, 8.1 Hz, 1H), 6.52 (d, J = 9.6 Hz, 1H), 6.10 (dd, J = 1.8, 9.8 Hz, 1H), 5.33−5.22 (m, 2H), 2.77 (d, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 135.3, 131.7, 129.3, 129.3, 129.0, 128.3, 128.2, 126.6, 125.9, 125.8, 125.1, 84.5, 72.9; MS (EI, 70 eV) m/z (%): 306.00 ([M]$^+$, 5), 287.94 (24), 163.61 (42), 161.84 (83), 145.02 (80), 144.20 (98), 143.64 (90), 130.76 (36), 128.04 (27), 127.04 (35), 125.94 (34), 117.99 (76), 116.04 (69),

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115.32 (44.13), 114.80 (100); Anal. Calcd for $C_{16}H_{12}Cl_2O_2$: C, 62.56; H, 3.94. Found: C, 62.34; H, 3.97.

(1*S*,2*S*)-2-(4-Chloro-3-methylphenoxy)-1,2-dihydronaphthalen-1-ol (2n). Following general procedure I, **2n** was obtained as a white crystalline solid (51.5 mg, 90%). The ee was determined to be 60% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 12.3 min (major) and 19.0 min (minor); R_f = 0.24 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 126−127 °C. $[\alpha]^{25}_D$ = +103.7 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3260(br), 2920(w), 2851(w), 2359(m), 1597(w), 1477(s), 1232(m), 1169(m), 1048(m), 986(m), 859(m), 779(s)745(m), 669(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 6.4 Hz, 1H), 7.29−7.21 (m, 3H), 7.11 (d, J = 6.8 Hz, 1H), 6.82 (s, 1H), 6.71 (d, J = 8.4 Hz, 1H), 6.51 (d, J = 10.0 Hz, 1H), 5.97 (d, J = 10.0 Hz, 1H), 5.15 (d, J = 10.4 Hz, 1H), 5.04 (d, J = 10.0 Hz, 1H), 2.72 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 137.4, 135.4, 131.8, 129.8, 129.2, 128.3, 128.1, 126.5, 125.7, 125.2, 118.4, 114.4, 79.3, 72.3, 20.4; MS (EI, 70 eV) m/z (%): 268.08 ([M − H_2O]$^+$, 8), 207.02 (16), 144.19 (76), 143.67 (75), 142.00 (70), 116.02 (53), 114.97 (100), 106.95 (74); Anal. Calcd for $C_{17}H_{15}ClO_2$: C, 71.20; H, 5.27. Found: C, 71.05; H, 5.31.

(1*S*,2*S*)-2-(2-Bromo-4-chlorophenoxy)-1,2-dihydronaphthalen-1-ol (2o). Following general procedure I, **2o** was obtained as a white crystalline solid (58.7 mg, 84%). The ee was determined to be 73% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 2.0 mL/min, λ = 254 nm). Retention times were 8.6 min (major) and 9.5 min (minor); R_f = 0.22 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 126−128 °C. $[\alpha]^{25}_D$ = +44.4 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3296(br), 2922(m), 2851(w), 2361(m), 1577(w), 1470(s), 1261(m), 1044(s), 985(m), 777(m), 746(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65−7.56 (m, 2H), 7.32−7.11 (m, 4H), 6.87 (d, J = 8.8 Hz, 1H), 6.52 (d, J = 9.6 Hz, 1H), 5.99 (d, J = 10.0 Hz, 1H), 5.28 (d, J = 10.4 Hz, 1H), 5.05 (d, J = 10.4 Hz, 1H), 2.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 135.3, 133.1, 131.7, 129.5, 128.5, 128.4, 128.1, 127.1, 126.5, 125.4, 125.1, 116.2, 113.9, 82.4, 72.4; MS (EI, 70 eV) m/z (%): 331.97 ([M − H_2O]$^+$, 3), 207.88 (41), 207.00 (27), 205.85 (41), 148.94 (36), 145.03 (20), 143.99 (100), 116.01 (50), 115.00 (80); Anal. Calcd for $C_{16}H_{12}BrClO_2$: C, 54.65; H, 3.44. Found: C, 54.84; H, 3.40.

(1*S*,2*S*)-2-(4-Bromo-2-chlorophenoxy)-1,2-dihydronaphthalen-1-ol (2p). Following general procedure I, **2p** was obtained as a white crystalline solid (60.2 mg, 86%). The ee was determined to be 94% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 2.0 mL/min, λ = 254 nm). Retention times were 9.4 min (major) and 12.4 min (minor); R_f = 0.20 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 128−129 °C. $[\alpha]^{25}_D$ = +92.7 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3302(br), 2924(m), 2852(w), 2363(m), 1657(m), 1565(w), 1475(s), 1257(m), 1047(m), 978-(m),823(m),774(m), 690(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65−7.54 (m, 2H), 7.29 (t, J = 6.2 Hz, 3H), 7.12 (d, J = 6.4 Hz, 1H), 6.85 (d, J = 8.8 Hz, 1H), 6.52 (d, J = 10.0 Hz, 1H), 5.98 (d, J = 9.6 Hz, 1H), 5.27 (d, J = 10.0 Hz, 1H), 5.06 (d, J = 10.0 Hz, 1H), 2.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 135.2, 133.0, 131.7, 130.7, 129.5, 128.4, 128.1, 126.5, 125.3, 125.2, 125.1, 117.0, 113.8, 82.1, 72.4; MS (EI, 70 eV) m/z (%): 331.94 ([M − H_2O]$^+$, 3), 207.90 (54), 207.09 (27), 205.90 (52), 145.06 (34), 144.24 (74), 143.73 (100), 127.79 (10), 127.02 (20), 126.12 (10), 116.11 (47), 115.24 (85), 114.65 (52); Anal. Calcd for $C_{16}H_{12}BrClO_2$: C, 54.65; H, 3.44. Found: C, 54.87; H, 3.40.

(1*S*,2*S*)-2-(2,4-Dibromophenoxy)-1,2-dihydronaphthalen-1-ol (2q). Following general procedure I, **2q** was obtained as a white crystalline solid (63.0 mg, 80%). The ee was determined to be 75% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 2.0 mL/min, λ = 254 nm). Retention times were 9.3 min (major) and 11.2 min (minor); R_f = 0.47 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). mp 128−129 °C. $[\alpha]^{25}_D$ = +100.8 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3305(br), 2925(w), 1646(w), 1471(s), 1262(s), 1044(s), 989(m), 779(s), 743(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 23.6 Hz, 2H), 7.34−7.11 (m, 4H), 6.80 (d, J = 8.0 Hz, 1H), 6.51 (d, J = 9.2 Hz, 1H), 5.97 (d, J = 9.2 Hz, 1H), 5.27 (d, J = 10.0 Hz, 1H), 5.05 (d, J = 10.0 Hz, 1H), 2.90 (d, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 135.8, 135.2, 131.7, 131.4, 129.5, 128.4, 128.1, 126.5, 125.3, 125.1, 116.7, 114.3, 114.1, 82.3, 72.4; MS (EI, 70 eV) m/z (%): 377.86 ([M − H_2O + 2]$^+$, 3), 251.86 (26), 249.83 (15), 143.96 (100), 144.97 (16), 116.01 (37), 114.97 (79); Anal. Calcd for $C_{16}H_{12}Br_2O_2$: C, 48.52; H, 3.05. Found: C, 48.69; H, 3.08.

(1*S*,2*S*)-6,7-Dibromo-2-(4-chlorophenoxy)-1,2-dihydronaphthalen-1-ol (3a). Following general procedure I, **3a** was obtained as a white solid (74.1 mg, 87%). The ee was determined to be 82% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 18.3 min (major) and 30.2 min (minor); R_f = 0.26 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 161−163 °C. $[\alpha]^{25}_D$ = +85.7 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3356(br), 2919(w), 2851(w), 2361(m), 1605(m), 1492(s), 1283(s), 1239(s), 1050(m), 892(m), 824(m), 772(m), 691(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.36−7.25 (m, 3H), 6.87 (d, J = 8.4 Hz, 2H), 6.41 (d, J = 10.0 Hz, 1H), 6.04 (d, J = 10.0 Hz, 1H), 5.12−5.01 (m, 2H), 2.76 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.8, 139.1, 133.6, 131.6, 131.4, 129.8, 129.2, 127.3, 125.1, 123.4, 123.0, 117.9, 78.2, 70.1; MS (EI, 70 eV) m/z (%): 411.89 ([M − H_2O + 2]$^+$, 5), 303.89 (39), 301.86 (76), 299.91 (35), 194.94 (66), 192.89 (88), 130.00 (35), 129.23 (26), 128.08 (100), 127.48 (65), 114.03 (74), 113.10 (58); Anal. Calcd for $C_{16}H_{11}Br_2ClO_2$: C, 44.64; H, 2.58. Found: C, 44.48; H, 2.60.

(1*S*,2*S*)-6,7-Dibromo-2-(3-chlorophenoxy)-1,2-dihydronaphthalen-1-ol (3b). Following general procedure I, **3b** was obtained as a white solid (74.8 mg, 87%). The ee was determined to be 66% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 12.8 min (major) and 28.3 min (minor); R_f = 0.28 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 148−150 °C. $[\alpha]^{25}_D$ = +72.5 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3350(br), 2920(w), 2844(w), 2361(w), 1593(s), 1475(s), 1246(s), 1054(m), 985(s), 879(m), 775(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.36 (s, 1H), 7.23 (t, J = 8.0 Hz, 1H), 7.00 − 6.94 (m, 2H), 6.82 (d, J = 8.4 Hz, 1H), 6.41 (d, J = 10.0 Hz, 1H), 6.04 (d, J = 10.0 Hz, 1H), 5.07 (dd, J = 24.2, 10.6 Hz, 2H), 2.78 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.9, 139.1, 134.2, 133.6, 131.6, 131.4, 129.1, 127.4, 123.4, 123.0, 121.4, 116.3, 115.1, 78.2, 70.1; MS (EI, 70 eV) m/z (%): 411.88 ([M − H_2O + 2]$^+$, 5), 303.81 (48), 301.80 (100), 299.81 (48), 224.02 (25), 221.90 (27), 194.86 (77), 192.86 (94), 128.06 (96), 127.55 (79), 114.02 (72); Anal. Calcd for $C_{16}H_{11}Br_2ClO_2$: C, 44.64; H, 2.58. Found: C, 44.48; H, 2.60.

(1*S*,2*S*)-6,7-Dibromo-2-(2-chlorophenoxy)-1,2-dihydronaphthalen-1-ol (3c). Following general procedure I, **3c** was obtained as a white solid (71.0 mg, 83%). The ee was determined to be 55% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 17.4 min (major) and 19.0 min (minor); R_f = 0.30 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 109−110 °C. $[\alpha]^{25}_D$ = +110.9 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3418(br), 2924(m), 2851(w), 2355(w), 1587(m), 1481(s), 1242(s), 1060(s), 893(m), 748(s), 694(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.41−7.31 (m, 2H), 7.21 (t, J = 7.8 Hz, 1H), 6.96 (dd, J = 12.0, 8.0 Hz, 2H), 6.39 (d, J = 9.6 Hz, 1H), 6.10 (d, J = 9.2 Hz, 1H), 5.21 (dd, J = 10.8, 2.8 Hz, 1H), 5.06 (d, J = 10.8 Hz, 1H), 3.08 (d, J = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.5, 139.1, 133.5, 131.8, 131.5, 130.6, 129.0, 128.7, 127.4, 123.4, 123.0, 123.0, 122.6, 116.5, 79.2, 70.1; MS (EI, 70 eV) m/z (%): 411.87 ([M − H_2O + 2]$^+$, 6), 303.80 (48), 301.86 (81), 299.81 (54), 194.96 (79), 192.93 (100), 129.95 (44), 128.13 (81), 127.61 (84), 114.98 (45), 113.96 (76), 112.94 (61); Anal. Calcd for $C_{16}H_{11}Br_2ClO_2$: C, 44.64; H, 2.58. Found: C, 44.49; H, 2.60.

(1*S*,2*S*)-6,7-Dibromo-2-(2,3-dichlorophenoxy)-1,2-dihydronaphthalen-1-ol (3d). Following general procedure I, **3d** was obtained as a white solid (69.0 mg, 75%). The ee was determined to be 75% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 14.7 min (major) and 17.0 min (minor); R_f = 0.23 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 128−130 °C. $[\alpha]^{25}_D$ = +169.8 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3385(br), 2915(w),

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2845(w), 1655(m), 1580(m), 1454(s), 1265(m), 1047(m), 988(m), 884(m), 764(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.37 (s, 1H), 7.15 (d, J = 4.8 Hz, 2H), 6.86 (t, J = 8.8 Hz, 1H), 6.42 (dd, J = 10.0, 1.6 Hz, 1H), 6.07 (d, J = 10.0 Hz, 1H), 5.23 (d, J = 10.8 Hz, 1H), 5.07 (d, J = 10.8 Hz, 1H), 2.94 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.0, 139.0, 133.5, 132.9, 131.8, 131.5, 128.9, 128.6, 127.7, 123.5, 123.1, 123.0, 121.6, 114.7, 79.6, 70.1; MS (EI, 70 eV) m/z (%): 445.81 ([M − H_2O + 2]$^+$, 14), 316.06 (16), 303.80 (48), 301.80 (100), 299.76 (49), 194.97 (77), 193.08 (66), 192.51 (49), 163.54 (52), 162.10 (51), 161.56 (62), 125.98 (73); Anal. Calcd for $C_{16}H_{10}Br_2Cl_2O_2$: C, 41.33; H, 2.17. Found: C, 41.16; H, 2.19.

(1*S*,2*S*)-6,7-Dibromo-2-(2,4-dichlorophenoxy)-1,2-dihydronaphthalen-1-ol (3e). Following general procedure I, **3e** was obtained as a white solid (65.7 mg, 71%). The ee was determined to be 79% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 24.0 min (major) and 25.7 min (minor); R_f = 0.28 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 128−130 °C. $[\alpha]^{25}_D$ = +121.4 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3360(br), 2920(w), 2843(w), 1575(m), 1470(s), 1261(m), 1100(m), 984(m), 883(m), 756(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.39 (d, J = 23.6 Hz, 2H), 7.19 (d, J = 7.2 Hz, 1H), 6.89 (d, J = 8.8 Hz, 1H), 6.42 (d, J = 10.0 Hz, 1H), 6.05 (d, J = 9.6 Hz, 1H), 5.20 (d, J = 8.8 Hz, 1H), 5.02 (d, J = 10.8 Hz, 1H), 2.96 (d, J = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.7, 139.0, 133.5, 131.7, 131.5, 129.9, 128.8, 128.5, 127.6, 125.5, 124.0, 123.4, 123.1, 117.7, 79.7, 70.2; MS (EI, 70 eV) m/z (%): 445.82 ([M − H_2O + 2]$^+$, 5), 303.85 (40), 301.81 (85), 299.76 (41), 194.63 (45), 192.89 (85), 163.92 (67), 162.02 (100), 161.47 (45), 114.57 (46), 113.85 (57); Anal. Calcd for $C_{16}H_{10}Br_2Cl_2O_2$: C, 41.33; H, 2.17. Found: C, 41.13; H, 2.20.

(1*S*,2*S*)-6,7-Dibromo-2-(2,5-dichlorophenoxy)-1,2-dihydronaphthalen-1-ol (3f). Following general procedure I, **3f** was obtained as a white solid (80.4 mg, 87%). The ee was determined to be 75% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 12.5 min (minor) and 23.4 min (major); R_f = 0.30 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 162−164 °C. $[\alpha]^{25}_D$ = +60.8 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3370(br), 2919(w), 2851(w), 2362(m), 1582(w), 1478(s), 1262(m), 1055(m), 980(m), 831(m), 779(m), 691(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.37−732 (m, 2H), 6.96 (d, J = 10.8 Hz, 2H), 6.44 (d, J = 10.0 Hz, 1H), 6.07 (d, J = 9.6 Hz, 1H), 5.22 (d, J = 10.4 Hz, 1H), 5.05 (d, J = 10.8 Hz, 1H), 2.88 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.3, 139.0, 133.5, 132.8, 131.7, 131.5, 131.5, 128.9, 127.5, 123.4, 123.1, 122.4, 121.8, 116.6, 79.8, 70.3; MS (EI, 70 eV) m/z (%): 445.83 ([M − H_2O + 2]$^+$, 6), 303.87 (30), 301.85 (74), 299.85 (39), 194.89 (81), 192.60 (64), 163.90 (47), 161.88 (100), 114.04 (73), 97.06 (90); Anal. Calcd for $C_{16}H_{10}Br_2Cl_2O_2$: C, 41.33; H, 2.17. Found: C, 41.13; H, 2.20.

(1*S*,2*S*)-6,7-Dibromo-2-(2-bromo-4-chlorophenoxy)-1,2-dihydronaphthalen-1-ol (3g). Following general procedure I, **3g** was obtained as a white solid (93.1 mg, 92%). The ee was determined to be 70% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 0.3 mL/min, λ = 254 nm). Retention times were 82.0 min (major) and 85.6 min (minor); R_f = 0.30 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 146−148 °C. $[\alpha]^{25}_D$ = +90.8 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3372(br), 2918(w), 2851(w), 2359(m), 1560(w), 1471(m), 1288(m), 1051(m), 980(m), 869(m), 743(m), 669(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.59 (d, J = 2.4 Hz, 1H), 7.37 (s, 1H), 7.26 −7.23 (m, 1H), 6.86 (d, J = 8.8 Hz, 1H), 6.42 (dd, J = 10.0, 2.0 Hz, 1H), 6.07 (dd, J = 1.6, 10.0 Hz, 1H), 5.22 (d, J = 10.8 Hz, 1H), 5.02 (d, J = 11.2 Hz, 1H), 2.89 (d, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.7, 139.0, 133.5, 132.7, 131.8, 131.5, 129.1, 128.8, 127.5, 125.9, 123.4, 123.1, 117.6, 113.5, 79.8, 70.2; MS (EI, 70 eV) m/z (%): 489.79 ([M − H_2O + 2]$^+$, 7), 303.84 (45), 301.79 (100), 299.83 (38), 209.93 (32), 208.12 (40), 207.58 (87), 205.94 (58), 194.92 (94), 192.89 (99), 113.83 (76), 112.90 (93); Anal. Calcd for $C_{16}H_{10}Br_3ClO_2$: C, 37.72; H, 1.98. Found: C, 37.59; H, 2.00.

(1*S*,2*S*)-6,7-Dibromo-2-(4-bromo-2-chlorophenoxy)-1,2-dihydronaphthalen-1-ol (3h). Following general procedure I, **3h** was obtained as a white solid (83.0 mg, 82%). The ee was determined to be 93% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 25.2 min (major) and 30.2 min (minor); R_f = 0.28 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). mp 159−161 °C. $[\alpha]^{25}_D$ = +79.3 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3352(br), 2922(m), 2851(m), 2359(m), 1582 (m), 1476(s), 1244(m), 1059(m), 980(m), 887(m), 752(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.55 (d, J = 2.4 Hz, 1H), 7.36−7.31 (m, 2H), 6.83 (d, J = 8.8 Hz, 1H), 6.42 (dd, J = 2.0, 10.0 Hz, 1H), 6.05 (dd, J = 1.6, 10.0 Hz, 1H), 5.20 (d, J = 10.4 Hz, 1H), 5.02 (d, J = 10.8 Hz, 1H), 2.90 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.0, 138.8, 133.4, 132.5, 131.7, 131.5, 131.4, 128.5, 127.7, 124.3, 123.5, 123.1, 118.2, 112.9, 79.4, 70.1; MS (EI, 70 eV) m/z (%): 489.72 ([M − H_2O + 2]$^+$, 5), 303.89 (39), 301.86 (92), 299.78 (58), 208.08 (74), 206.93 (43), 206.04 (62), 195.16 (57), 194.60 (54), 193.04 (88), 113.99 (100), 112.95 (82); Anal. Calcd for $C_{16}H_{10}Br_3ClO_2$: C, 37.72; H, 1.98. Found: C, 37.53; H, 2.00

(1*S*,2*S*)-2-(4-Chlorophenoxy)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (4a). Following general procedure I, **4a** was obtained as pale yellow oil (49.1 mg, 74%). The ee was determined to be 60% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 23.5 min (major) and 29.3 min (minor); R_f = 0.15 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). $[\alpha]^{25}_D$ = +101.2 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3445(br), 2936(m), 2838(w), 2359(w), 1605(m), 1487(s), 1261(s), 1090(s), 993(s), 823(m), 750(m), 668(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 10.0 Hz, 1H), 6.93 (d, J = 8.4 Hz, 2H), 6.79 (s, 2H), 6.08 (dd, J = 4.8, 10.0 Hz, 1H), 5.25 (s, 1H), 4.98 (s, 1H), 3.79 (s, 6H), 2.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 151.5, 150.0, 129.4, 125.9, 124.4, 123.3, 122.4, 121.0, 117.2, 111.6, 111.3, 74.3, 64.9, 56.2, 55.9; MS (EI, 70 eV) m/z (%): 314.08 ([M − H_2O]$^+$, 19), 205.05 (53), 204.29 (41), 203.78 (63), 188.80 (100), 173.94 (39), 129.93 (34), 127.87 (99); Anal. Calcd for $C_{18}H_{17}ClO_4$: C, 64.97; H, 5.15. Found: C, 64.77; H, 5.19.

(1*S*,2*S*)-2-(2,4-Dichlorophenoxy)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (4b). Following general procedure I, **4b** was obtained as pale yellow oil (32.9 mg, 45%). The ee was determined to be 50% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 26.2 min (major) and 33.7 min (minor); R_f = 0.17 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). $[\alpha]^{25}_D$ = +94.0 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3395(br), 2934(m), 2844(w), 1582(w), 1481(s), 1260(s), 1061(m), 980(m), 802(m), 759(m), 714(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.20−7.11 (m, 3H), 6.80 (s, 2H), 6.06 (dd, J = 4.6, 9.8 Hz, 1H), 5.30 (s, 1H), 5.00 (s, 1H), 3.81 (d, J = 9.2 Hz, 6H), 2.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 151.5, 150.0, 130.1, 127.6, 126.6, 125.3, 124.7, 123.3, 122.1, 121.0, 117.7, 111.6, 111.4, 77.0, 65.7, 56.2, 56.0; MS (EI, 70 eV) m/z (%): 347.97 ([M − H_2O]$^+$, 41), 221.02 (48), 205.03 (60), 204.04 (66), 188.68 (49), 163.93 (86), 162.13 (88), 161.57 (100), 97.87 (53); Anal. Calcd for $C_{18}H_{16}Cl_2O_4$: C, 58.87; H, 4.39. Found: C, 58.67; H, 4.43.

(1*S*,2*S*)-2-(4-Bromo-2-chlorophenoxy)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (4c). Following general procedure I, **4c** was obtained as pale yellow oil (38.5 mg, 47%). The ee was determined to be 50% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 27.8 min (major) and 36.6 min (minor); R_f = 0.19 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). $[\alpha]^{25}_D$ = +61.6 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3441(br), 2926(m), 2851(w), 1605(m), 1493(s), 1256(s), 1210(s), 1150(m), 989(m), 853(m), 808(m), 736(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.30 (d, J = 8.8 Hz, 1H), 7.09 (dd, J = 17.2, 9.2 Hz, 2H), 6.78 (s, 2H), 6.05 (dd, J = 9.8, 4.6 Hz, 1H), 5.29 (s, 1H), 4.99 (s, 1H), 3.79 (d, J = 6.4 Hz, 6H), 3.21 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 151.4, 150.0, 132.8, 130.5, 125.5, 124.7, 123.3, 122.0, 120.9, 118.0, 113.5, 111.6, 111.4, 76.8, 65.5, 56.2, 56.0; MS (EI, 70 eV) m/z (%): 411.99 ([M + 2]$^+$, 3), 205.08 (11), 203.94 (100), 161.00 (26), 130.91 (16); Anal. Calcd for $C_{18}H_{16}BrClO_4$: C, 52.52; H, 3.92. Found: C, 52.26; H, 3.96.

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(1*S*,2*S*)-2-(4-Chloro-3-methylphenoxy)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (4d). Following general procedure I, **4d** was obtained as pale yellow oil (29.1 mg, 42%). The ee was determined to be 48% 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 min (major) and 25.4 min (minor); R_f = 0.17 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). $[\alpha]^{25}_D$ = +111.6 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3395(br), 2934(m), 2835(w), 1586(w), 1481(s), 1260(s), 1061(m), 983(m), 802(m), 758(m), 714(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.4 Hz, 1H), 7.11 (d, J = 10.0 Hz, 1H), 6.87−6.78 (m, 4H), 6.08 (dd, J = 9.4, 4.6 Hz, 1H), 5.25 (s, 1H), 4.97 (s, 1H), 3.78 (s, 6H), 2.82 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 151.5, 150.0, 137.1, 129.7, 126.2, 124.4, 123.4, 122.5, 121.0, 118.5, 114.5, 111.6, 111.3, 74.1, 64.9, 56.2, 55.9, 20.4; MS (EI, 70 eV) m/z (%): 328.04 ($[M - H_2O]^+$, 18), 313.01 (22), 205.03 (76), 204.14 (100), 203.61 (46), 189.19 (88), 188.67 (93), 142.12 (58), 141.55 (41), 106.93 (98); Anal. Calcd for $C_{19}H_{19}ClO_4$: C, 65.80; H, 5.52. Found: C, 65.53; H, 5.56.

(1*S*,2*S*)-2-(4-Chlorophenoxy)-6,7-dimethoxy-1,2-dihydronaphthalen-1-ol (5a). Following general procedure I, **5a** was obtained as pale yellow oil (32.1 mg, 48%). The ee was determined to be 84% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 19.8 min (minor) and 36.5 min (major); R_f = 0.17 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). $[\alpha]^{25}_D$ = +103.1 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3443(br), 2928(m), 2851(w), 2359(w), 1605(m), 1515(s), 1472(s), 1258(m), 1155(m), 1061(m), 980(m), 863(m), 808(m), 743(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.18 (m, 3H), 6.88 (dd, J = 8.8, 3.2 Hz, 2H), 6.68 (d, J = 2.8 Hz, 1H), 6.44 (d, J = 9.6 Hz, 1H), 5.89 (d, J = 9.6 Hz, 1H), 5.05 (dd, J = 31.8, 9.8 Hz, 2H), 3.91 (dd, J = 18.2, 3.4 Hz, 6H), 2.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 148.8, 148.4, 129.6, 129.0, 128.1, 126.3, 124.6, 123.4, 117.1, 110.1, 109.1, 79.4, 72.1, 56.1, 56.1; MS (EI, 70 eV) m/z (%): 314.01 ($[M - H_2O]^+$, 64), 204.28 (88), 203.68 (100), 161.01 (40), 143.99 (31), 128.12 (55), 127.51 (46); Anal. Calcd for $C_{18}H_{17}ClO_4$: C, 64.97; H, 5.15. Found: C, 64.71; H, 5.19.

(1*S*,2*S*)-2-(3-Chlorophenoxy)-6,7-dimethoxy-1,2-dihydronaphthalen-1-ol (5b). Following general procedure I, **5b** was obtained as pale yellow oil (30.6 mg, 46%). The ee was determined to be 51% using HPLC analysis on a Chiralcel AD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm). Retention times were 20.8 min (major) and 24.7 min (minor); R_f = 0.15 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). $[\alpha]^{25}_D$ = +102.0 (c = 1.00, $CHCl_3$). IR (KBr, cm^{-1}) 3463(br), 2929(m), 2850(w), 2360(m), 1582(s), 1467(m), 1280(m), 1120(m), 990(m), 854(m), 775(m), 682(m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.18 (m, 2H), 6.96 (d, J = 5.2 Hz, 2H), 6.83 (d, J = 8.4 Hz, 1H), 6.67 (s, 1H), 6.45 (d, J = 9.6 Hz, 1H), 5.89 (d, J = 10.0 Hz, 1H), 5.07 (dd, J = 24.4, 9.6 Hz, 2H), 3.90 (d, J = 16.4 Hz, 6H), 2.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 148.8, 148.4, 135.1, 130.5, 129.1, 128.1, 124.6, 123.3, 121.6, 116.3, 114.0, 110.1, 109.1, 79.3, 72.1, 56.1, 56.1; MS (EI, 70 eV) m/z (%): 313.96 ($[M - H_2O]^+$, 13), 204.16 (100), 203.64 (62), 160.97 (46), 143.96 (23), 127.99 (66), 114.97 (33); Anal. Calcd for $C_{18}H_{17}ClO_4$: C, 64.97; H, 5.15. Found: C, 64.70; H, 5.20.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General section, copies of ^{1}H and ^{13}C NMR spectra of compounds **2a−q**, **3a−h**, **4a−d**, and **5a**,**b**, HPLC conditions and spectra of compounds **2a**, **2c**, **2e**, **2i**, **2j**, **2k**, **2p**, and **3h**, and X-ray structure data for compound **2a**. 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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