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Platinum-Catalyzed Asymmetric Ring-Opening Reactions of Oxabenzonorbornadienes with Phenols

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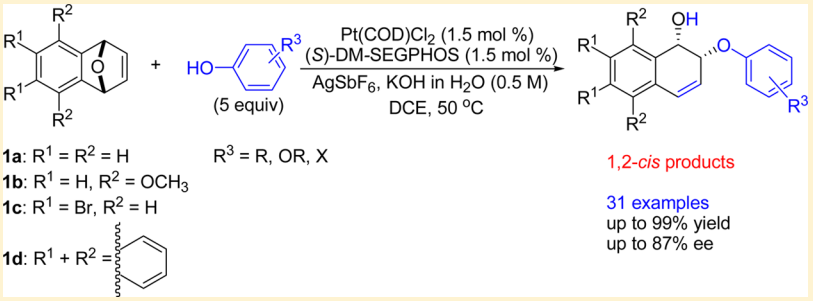
Supporting Information



ABSTRACT: A platinum(II)-catalyzed asymmetric ring opening of oxabenzonorbornadienes with phenols was developed, which afforded the corresponding *cis*-2-(un)substituted phenoxy-1,2-dihydronaphthalen-1-ol products rather than the *trans* ones in excellent yields (up to 99%) with moderate to good enantioselectivities (up to 87% ee) under mild conditions. In addition, the *cis*-configuration of product **2b** was confirmed by X-ray diffraction analysis. Based on the results, a potential mechanism for the present catalytic reaction was proposed.

INTRODUCTION

Transition-metal-catalyzed asymmetric ring-opening (ARO) reactions of oxa- and azabicyclic alkenes are an efficient and enantioselective synthetic strategy for generating a hydronaphthalene skeleton which could be further transformed into optical compounds found in a wide range of pharmacological agents.[1] Transition-metal catalysts were often applied in the carbon−carbon and carbon−heteroatom bond-forming processes to provide more than one stereocenter in a single step.[2] Many metal catalysts, consisting of Rh,[3] Ir,[4] Pd,[5] Ni,[6] Fe,[7] Cu,[8] etc., have been investigated for ring-opening reactions with various carbanion nucleophiles and heteroatom nucleophiles.

Lautens et al.,[3a] Yang et al.,[4f,g] and Fan et al.[9] reported the rhodium- and iridium-catalyzed ARO of oxa- and azabicyclic alkenes with phenol nucleophiles, with C−O or C−N bonds successfully generated. The products were obtained through an S_N2' nucleophilic displacement of the bridgehead leaving group with inversion to give the 1,2-*trans* ring-opening products in high yields with excellent enantioselectivities. However, the formation of *cis*-2-phenoxy-1,2-dihydronaphthalen-1-ol products has not been reported yet. In addition, the rhodium and iridium catalyst systems show less compatibility with electron-rich substrates. Against the above background, this work aimed to develop a Pt-catalyzed system for the ARO of oxabenzonorbornadienes with phenols, one that is complementary to the rhodium,[3a] iridium,[4f,g,9] and platinum[10] catalyst systems.

Our group has studied the transition-metal-catalyzed ARO of oxa- and azabenzonorbornadienes with manifold nucleophiles extensively. We previously reported the iridium-catalyzed ARO of oxa- and azabicyclic alkenes with a variety of nucleophiles, including amines,[4a−e] alcohols,[4i] and phenols,[4f−h] affording the corresponding 1,2-*trans* ring-opening products in high yields with good enantioselectivities. Recently, our group reported the Pt-catalyzed ARO of oxabicyclic alkenes with carbanion nucleophiles, including organoboronic acids,[10a] Grignard reagents,[10b] and terminal alkynes,[10c] producing the corresponding ring-opening products in good to excellent yields with good enantioselectivities. Given the successes with the platinum catalyst system, we sought to expand the scope of the platinum(II)-catalyzed ARO to heteroatom nucleophiles. Although phenolic nucleophiles have been successfully used in rhodium- and iridium-catalyzed ARO reactions, platinum never has been used as a catalyst with this class of nucleophiles, nor could we obtain the *cis*-2-phenoxy-1,2-dihydronaphthalen-1-ol products.

In this study, we report a Pt-catalyzed ARO of oxabenzonorbornadienes with phenols in the presence of $AgSbF_6$ and

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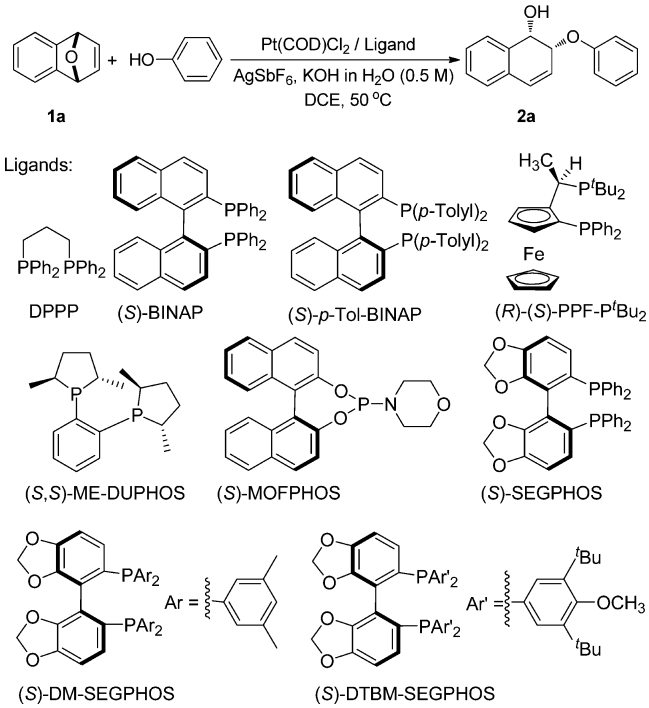
KOH solution (0.5 M in H_2O), producing the corresponding 1,2-*cis* ring-opening products in high yields with moderate to good enantioselectivities. Compared with the iridium catalyst system,[4g,9] the ring-opening reactions of the electron-rich substrates catalyzed by platinum offered much better yields (up to 99%). The *cis*-configuration of product **2b** was confirmed by X-ray diffraction analysis.

RESULTS AND DISCUSSION

Substrates **1a**–**d** were readily prepared by the Diels–Alder reaction of benzynes with furan according to literature procedures.[11] Our initial investigation began by treating oxabenzonorbornadiene **1a** with phenol in the presence of complex Pt(COD)Cl_2 (COD = 1,5-cyclo-octadiene) and bisphosphine ligand, using $AgSbF_6$ as the additive and 1,2-dichloroethane (DCE) as the solvent at 50 °C. We could obtain the desired ring-opening product **2a** in a good yield (89%) after 20 h when an achiral bisphosphine ligand 1,3-bis-(diphenylphosphino)propane (DPPP) was first used to validate the catalytic activity of the platinum complex in the ARO reaction of **1a** with phenol. The inspiring results impelled us to investigate bisphosphine ligands with different chiral backbones using Pt(COD)Cl_2 as the catalyst precursor. When (*S*)-BINAP (Table 1, entry 2) and (*S*)-*p*-Tol-BINAP (Table 1, entry 3) were used as the ligands, they gave similar yields and enantioselectivities. Several other chiral ligands, including (*S*,*S*)-ME-DUPHOS, (*R*)-(*S*)-PPF-P^tBu_2, and (*S*)-MOFPHOS, were then examined, but these ligands gave unsatisfactory results in both yields and enantioselectivities (Table 1, entries 4–6). When SEGPHOS-type ligands were used, (*S*)-DM-SEGPHOS generated **2a** in 86% yield with 70% ee (Table 1, entry 8), whereas (*S*)-SEGPHOS gave lower yield (63%) but slightly better ee value (73%) (Table 1, entry 7). To achieve better yield and enantioselectivity, a bulkier ligand (*S*)-DTBM-SEGPHOS was tried. The enantioselectivity of product **2a** was improved to 80% ee but with moderate yield (Table 1, entry 9). Based on these results, we chose (*S*)-DM-SEGPHOS as the ligand for the reaction. We next explored the effect of catalyst loading on the reaction. The results in Table 1 indicate that the catalyst loading has a significant effect on the product's enantioselectivity. The yields were maintained at good levels with enantiomer excesses increasing from 70 to 89% with decreasing catalyst loadings from 5.0 to 1.0 mol % (Table 1, entries 8 and 10–13). Based on the results, a catalyst loading of 1.5 mol % of Pt(COD)Cl_2 with 1.5 mol % of (*S*)-DM-SEGPHOS (Table 1, entry 8) was chosen as the optimum condition in terms of yield and enantioselectivity.

To optimize the reaction conditions, the effects of additives, solvents, bases, and temperature on the reactivity and enantioselectivity were subsequently investigated (Table 2). We initially used $AgSbF_6$ as the additive in the platinum-catalyzed ARO reaction. The yields increased by 30% in contrast to those without $AgSbF_6$ (Table 2, entries 1 and 9). To obtain better results, several other AgX (X = BF_4, OTf, PF_6, ClO_4) salts were then tested (Table 2, entries 2–5), but no better yields and enatioselectivities were achieved. In addition, other additives of Lewis acids, such as $KSbF_6$ and $ZnCl_2$, were investigated (Table 2, entries 6 and 7). The results showed that $AgSbF_6$ was the best one. Thereafter, the effect of molar ratio of Pt(COD)Cl_2/AgX was also investigated. The best result was obtained when the molar ratio of Pt(COD)Cl_2/$AgSbF_6$ was 1:2 (Table 2, entry 1). Control experiments revealed that the yields

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



entry	Pt(COD)Cl_2 (mol %)	ligand (mol %)	time (h)	yield (%)	ee[b] (%)
1	5.0	DPPP (5.0)	20	89	
2	5.0	(*S*)-BINAP (5.0)	20	81	64
3	5.0	(*S*)-*p*-Tol-BINAP (5.0)	20	79	66
4	5.0	(*S*,*S*)-ME-DUPHOS (5.0)	36	39	28
5	5.0	(*R*,*S*)-PPF^tBu_2 (5.0)	72	trace	
6	5.0	(*S*)-MOFPHOS (5.0)	72	trace	
7	5.0	(*S*)-SEGPHOS (5.0)	20	63	73
8	5.0	(*S*)-DM-SEGPHOS (5.0)	20	86	70
9	5.0	(*S*)-DTBM-SEGPHOS (5.0)	24	60	80
10	3.5	(*S*)-DM-SEGPHOS (3.5)	15	80	72
11	2.5	(*S*)-DM-SEGPHOS (2.5)	16	83	74
12	1.5	(*S*)-DM-SEGPHOS (1.5)	24	85	80
13	1.0	(*S*)-DM-SEGPHOS (1.0)	40	71	89

[a]The reaction was carried out with **1a** (0.2 mmol), 5.0 equiv of phenol (1 mmol), 0.05 equiv of KOH (0.5 M in H_2O), and $AgSbF_6$ (2 equiv to Pt) in DCE (2.0 mL) at 50 °C in the presence of Pt(COD)Cl_2 and ligand under N_2. [b]Determined by HPLC with a Chiralcel OD-H column.

decreased when the molar ratio of Pt(COD)Cl_2/$AgSbF_6$ was 1:1 or in the absence of $AgSbF_6$ (Table 2, entries 8 and 9).

The effect of solvents was then examined (Table 2, entries 10–15). The selection of solvents proved to have a dramatic influence on the yield. To our surprise, no expected product was achieved after 72 h (Table 2, entry 10) when the reaction was carried out in tetrahydrofuran (THF), which is a good solvent for the Rh- and Ir-catalyzed ARO reactions.[3a,4g] In addition, reactions in the solvents of CH_3OH, CH_3CN, and toluene gave poor yields but good enantioselectivities (Table 2, entries 11–13). Although the desired product was formed with

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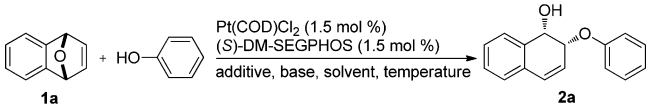
Table 2. Effects of Additive, Solvent, Base, and Temperature[a]



entry	additive	solvent	base	temp[b] (°C)	time (h)	yield (%)	ee[c] (%)
1	$AgSbF_6$	DCE	KOH	50	24	85	80
2	$AgBF_4$	DCE	KOH	50	24	62	69
3	AgOTf	DCE	KOH	50	24	48	75
4	$AgPF_6$	DCE	KOH	50	24	69	76
5	$AgClO_4$	DCE	KOH	50	72	trace	
6	$KSbF_6$	DCE	KOH	50	24	52	62
7	$ZnCl_2$	DCE	KOH	50	48	47	68
8[d]	$AgSbF_6$	DCE	KOH	50	24	63	74
9[e]		DCE	KOH	50	24	55	74
10	$AgSbF_6$	THF	KOH	50	72	nr	
11	$AgSbF_6$	CH_3OH	KOH	50	72	25	78
12	$AgSbF_6$	CH_3CN	KOH	50	72	25	78
13	$AgSbF_6$	toluene	KOH	50	72	14	76
14	$AgSbF_6$	$CHCl_3$	KOH	50	72	39	82
15	$AgSbF_6$	CH_2Cl_2	KOH	50	20	88	76
16	$AgSbF_6$	DCE	CsF	50	36	63	72
17	$AgSbF_6$	DCE	K_3PO_4	50	28	73	72
18	$AgSbF_6$	DCE	K_2CO_3	50	24	75	72
19	$AgSbF_6$	DCE	^{t}BuOK[f]	50	28	58	73
21	$AgSbF_6$	DCE	KOH	25	36	58	74
22	$AgSbF_6$	DCE	KOH	75	36	52	71

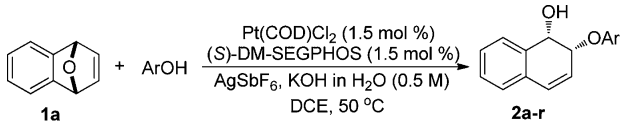
[a]The reaction was carried out with $Pt(COD)Cl_2$ (1.5 mol %), (*S*)-DM-SEGPHOS (1.5 mol %), additive (3 mol %), **1a** (0.2 mmol), 5.0 equiv of phenol (1 mmol), and 0.05 equiv of base (0.5 M in H_2O) in the solvent (2.0 mL) at the corresponding temperature under N_2. [b]Oil bath temperature. [c]Determined by HPLC with a Chiralcel OD-H column. [d]$AgSbF_6$ (1.5 mol %) was used. [e]Without additive. [f]Base (0.05 equiv) was added.

good ee value (82% ee) in $CHCl_3$, only 39% yield was obtained (Table 2, entry 14). The reaction in CH_2Cl_2 proceeded relatively faster with slightly lower enantioselectivity than in DCE (Table 2, entry 15). The results indicate that DCE shows the best combination of reactivity and enantioselectivity among all the solvents tested (85% yield, 80% ee) (Table 2, entry 1).

After exploring the effect of solvents, we turned our attentions to the choice of the bases. No reaction took place without bases present (not shown in Table 2). Moderate yields and enantioselectivities were obtained when CsF, K_3PO_4, and K_2CO_3 aqueous solution were used (Table 2, entries 16−18). As we added organic base ^{t}BuOK, the reaction also proceeded to give the desired product **2a** in 58% yield with 73% ee (Table 2, entry 19). We also tried potassium phenolate as the nucleophile instead of phenol and KOH solution, and no reaction took place. The results indicated that KOH was the best base for this reaction system (Table 2, entry 1). Furthermore, the reaction temperature optimization indicated that 50 °C was the optimum reaction temperature in terms of yield and enantioselectivity (Table 2, entries 20 and 21). Based on the above results, the standard reaction conditions for the reaction were identified as follows: 1.5 mol % of $Pt(COD)Cl_2$/(*S*)-DM-SEGPHOS, 5.0 equiv of phenols, 3.0 mol % of $AgSbF_6$, and 0.05 equiv of KOH (0.5 M in H_2O) in DCE at 50 °C.

With the $Pt(COD)Cl_2$ and (*S*)-DM-SEGPHOS catalyst system in hand, we evaluated the effectiveness of this catalyst system and examined the scope of the reaction with respect to the nucleophile. The results were summarized in Table 3. From

Table 3. Scope of the Pt-Catalyzed ARO of Oxabenzonorbornadiene 1a with Various Phenols[a]



entry	Ar	product	time (h)	yield (%)	ee[b] (%)
1	C_6H_5	**2a**	24	85	80
2	4-$CH_3C_6H_4$	**2b**	24	67	80
3	3-$CH_3C_6H_4$	**2c**	24	80	71
4	2-$CH_3C_6H_4$	**2d**	24	72	84
5	4-$CH_3OC_6H_4$	**2e**	24	91	47
6	3-$CH_3OC_6H_4$	**2f**	30	80	65
7	4-ClC_6H_4	**2g**	24	72	23
8	3-ClC_6H_4	**2h**	12	82	17
9	2-ClC_6H_4	**2i**	36	68	75
10	3-BrC_6H_4	**2j**	30	71	35
11	4-$CH_3COC_6H_4$	**2k**	36	54	72
12	4-biphenyl	**2l**	36	84	87
13	2-naphthyl	**2m**	60	40	23
14	2,4-$(CH_3)_2C_6H_3$	**2n**	24	67	86
15	2,4-$(Cl)_2C_6H_3$	**2o**	30	42	60
16	3,5-$(CH_3)_2C_6H_3$	**2p**	20	81	69
17	4-Cl-3-$CH_3C_6H_3$	**2q**	30	83	29
18	2,6-(*tert*-butyl)$_2C_6H_3$	**2r**	72	nr	
19	4-$CH_3OC_6H_4$	**2e**	30	45	36
	4-ClC_6H_4	**2g**	30	28	14

[a]The reaction was carried out with $Pt(COD)Cl_2$ (1.5 mol %), (*S*)-DM-SEGPHOS (1.5 mol %), $AgSbF_6$ (3 mol %), **1a** (0.2 mmol), 5.0 equiv of phenol (1 mmol), and 0.05 equiv of KOH (0.5 M in H_2O) in DCE (2.0 mL) at 50 °C under N_2. [b]Determined by HPLC with a Chiralcel OD-H column or Chiralpak AD-H column.

Table 3, we can see that a number of phenols and naphthols reacted smoothly with **1a** and generated the corresponding 1,2-*cis* ring-opening products with moderate to good enantioselectivities. The results also revealed that the electronic property of the substituents on the aromatic rings has a crucial influence on the enantioselectivity. Phenols with electron-donating substituents gave yields relatively higher and better enantioselectivities (Table 3, entries 2−6) than those with electron-withdrawing substituents (Table 3, entries 7−11). In general, the higher the pK_a value of the phenol, the higher the yield and the enantioselectivity. For example, phenol (pK_a ≈ 9.9) offered 85% yield and 80% ee, while 4-chlorophenol (pK_a ≈ 8.5) gave 72% yield and 23% ee (Table 3, entries 1 and 7). When it came to the positional property of the substituents on the aromatic ring for the nucleophile reagents, we noted that the asymmetric ring opening of **1a** with the *meta*-substituted phenols offered better yields but lower enantioselectivities than those with *para*- and *ortho*-substituted phenols (Table 3, entries 2−4 and 7−9). Although the *ortho*-substituted phenols led to relatively inferior yields, surprisingly good enantioselectivities were obtained. For instance, 2-chlorophenol and 2-methylphenol gave products **2d** and **2i** in moderate yields with good ee values (84 and 75% ee, respectively) (Table 3, entries 4 and 9). The reaction proceeded smoothly even when 3-bromophenol was used as

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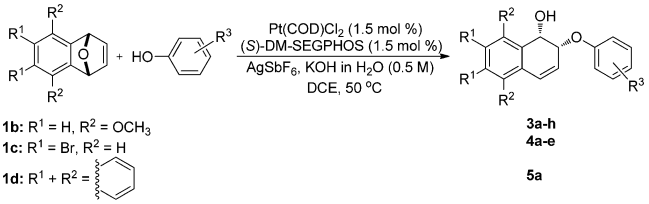
the nucleophile, achieving 71% yield with only 35% ee (Table 3, entry 10). As the phenol with the strong electron-withdrawing acetyl group was used as the nucleophile, the corresponding product **2k** was obtained in 54% yield with 72% ee (Table 3, entry 11). For biphenyl-4-ol and 2-naphthol, ring-opening products **2l** and **2m** were produced in dramatically different yields (84 and 40%, respectively) and ee values (87 and 23% ee, respectively) (Table 3, entries 12 and 13). Phenols having disubstituted groups also showed good reactivity with moderate to good enantioselectivity (Table 3, entries 14−17). The reactions of **1a** with phenols containing electron-donating multisubstituted groups gave the corresponding products **2n** and **2p** in good yields with moderate to good ee values (Table 3, entries 14 and 16), while 2,4-dichlorophenol gave 42% yield and 60% ee (Table 3, entry 15). Due to the steric bulkiness of the *tert*-butyl groups, the ring-opening reaction of **1a** with 2,6-di-*tert*-butylphenol did not afford any desired product (Table 3, entry 18). In one competition experiment, 5 equiv of 4-methoxylphenol and 4-chlorophenol was used as the nucleophiles, and the ring-opening reaction proceed at 73% conversion with a greater than 2:1 ratio of **2e** to **2g** (Table 3, entry 19), indicating that the less acidic phenol reacted preferentially. Inspired by the good results of phenols as the nucleophiles, we turned our attention to the nitrogen nucleophiles, such as aniline and *N*-methylaniline, but no ring-opening reaction occurred (not shown in Table 3).

To broaden the scope of this reaction, various types of oxabenzonorbornadienes **1b−d** with various phenols under the standard reaction conditions were also investigated, and the results are listed in Table 4. From Table 4, we can see that the ARO reactions of oxabenzonorbornadienes **1b−d** with various phenols proceeded smoothly to give the expected products in high yields (up to 99%) with moderate to good enantioselectivities (up to 84% ee). Compared with results from a previous study,[4g] electron-rich substrate **1b** gave much more favorable results than electron-deficient substrate **1c** in the platinum catalyst system (Table 4, entries 1−13), while the electron-rich substrate gave ring-opening products in moderate yields and the electron-deficient substrate offered good results in the Ir catalyst system. The ARO of **1b** with phenols bearing the electron-donating methyl and methoxy groups showed higher ee values than those bearing the electron-withdrawing Cl group (Table 4, entries 1−5). Moreover, the *meta*-substituted phenols, such as 3-methylphenol and 3-chlorophenol, afforded the corresponding products **3b** and **3e** in better yields (99 and 96%, respectively) but slightly lower enantioselectivities (76 and 45% ee, respectively) than those with *para*- and *ortho*-substituents (Table 4, entries 2−4 and 7−9). Phenols involving disubstituted groups also showed good reactivity and moderate to good enantioselectivity (Table 4, entries 6−8). It was noteworthy that the 2,4-dimethylphenol gave good ee value (84%) (Table 4, entry 6) compared to those that are bulky and less sterically demanding (Table 4, entries 7 and 8). The reactions of electron-poor **1c** with phenols required much longer reaction time and gave lower yields with inferior ee values when compared with electron-rich **1b** (Table 4, entries 9−13), whereas there was an exception where product **4a** was obtained in moderate yield (54%) with 78% ee (Table 4, entry 9). As 4-chloro-3-methylphenol was used as the nucleophile, the reaction afforded the corresponding product **4e** in moderate yield with very low ee value (Table 4, entry 13). Besides, bulkier substrate **1d** achieved the ring-opening product **5a** in 91% yield with only 28% ee (Table 4, entry 14).

Table 4. Scope of the Pt-Catalyzed ARO of Oxabenzonorbornadienes 1b−d with Various Phenols[a]



entry	substrate	R^3	product	time (h)	yield (%)	ee[b] (%)
1	**1b**	4-CH_3	**3a**	24	89	79
2	**1b**	3-CH_3	**3b**	36	99	76
3	**1b**	4-OCH_3	**3c**	24	91	78
4	**1b**	4-Cl	**3d**	30	89	72
5	**1b**	3-Cl	**3e**	36	96	45
6	**1b**	2,4-$(CH_3)_2$	**3f**	30	85	84
7	**1b**	3,5-$(CH_3)_2$	**3g**	36	95	72
8	**1b**	4-Cl-3-CH_3	**3h**	24	98	65
9	**1c**	4-CH_3	**4a**	72	54	78
10	**1c**	3-CH_3	**4b**	72	55	44
11	**1c**	4-Cl	**4c**	72	42	25
12	**1c**	3-Cl	**4d**	72	50	49
13	**1c**	4-Cl-3-CH_3	**4e**	72	65	14
14	**1d**	3-CH_3	**5a**	60	91	28

[a]The reaction was carried out with Pt(COD)Cl_2 (1.5 mol %), (*S*)-DM-SEGPHOS (1.5 mol %), $AgSbF_6$ (3 mol %), **1b−d** (0.2 mmol), 5.0 equiv of phenol (1 mmol), and 0.05 equiv of KOH (0.5 M in H_2O) in DCE (2.0 mL) at 50 °C under N_2. [b]Determined by HPLC with a Chiralcel OD-H column or Chiralpak AD-H column.

The stereochemistry of 1,2-*cis* ring-opened product **2b** was unambiguously confirmed by X-ray crystallography. The single-crystal analysis of **2b** was achieved by solvent evaporation from a mixture of hexane, ethyl acetate, and $CHCl_3$. Its absolute configuration was assigned as (1*S*,2*R*) and confirmed as 1,2-*cis*-configuration, as revealed in the Supporting Information. Furthermore, compared with the NMR spectroscopy of 1,2-*trans*-configuration ring-opened products, there were some chemical shift changes in both ^1H and $^{13}C\{^1H\}$ NMR spectroscopy of 1,2-*cis* ring-opened products. The chemical shifts of the H1, H2 or C1, C2 in 1,2-*cis* ring-opened products generally decreased from left to right. To be specific, the δ value ranges for 1,2-dihydrogen (H1, H2) of 1,2-*trans* ring-opened products are 5.33−5.07 and 5.22−4.98 ppm, respectively, and those for H1, H2 of 1,2-*cis* ring-opened products are 5.26−4.84 and 5.12−4.82 ppm, respectively. Besides, changes in $^{13}C\{^1H\}$ NMR spectroscopy are observed in chemical shifts, as well. The C1 and C2 of NMR spectroscopy (69.8−56.2 and 76.7−61.6 ppm, respectively) of 1,2-*cis* ring-opened products occurred at lower field ranges than the C1, C2 (72.9−64.9 and 84.5−74.1 ppm, respectively) of 1,2-*trans* ring-opened products.[4g] That would be another way to distinguish the 1,2-*cis* from 1,2-*trans* ring-opened products.

A potential mechanism was proposed for the formation of the 1,2-*cis* ring-opening products, as outlined in Scheme 1. The active catalyst of chiral platinum complex **A** was initially formed by replacing the ligand COD of the precatalyst Pt(COD)Cl_2 with addition of (*S*)-DM-SEGPHOS and following $AgSbF_6$ to remove the chlorides.[12] The oxygen atom and the double bond of oxabenzonorbornadiene **1a** were then coordinated to the platinum center of the active catalyst to give the intermediate

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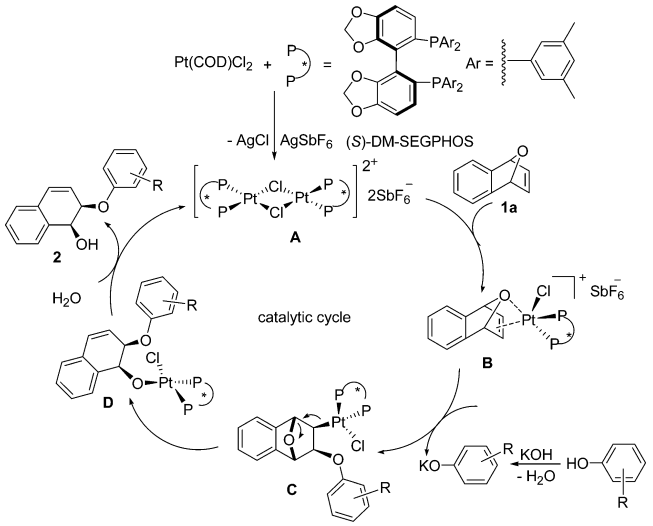
Scheme 1. Proposed Mechanism for the Platinum(II)-Catalyzed ARO of Oxabenzonorbornadiene 1a with Phenols



B,[13] of which the addition of the phenolate to a carbon−carbon double bond would give intermediate **C**.[14] *β*-Elimination of oxygen to open the furan ring and to give the ring-opened intermediate **D** occurs thereafter, followed by the hydrolysis to release 1,2-*cis* ring-opened product **2**. Meanwhile, the generating platinum complex **A** promoted the next catalytic cycle.

CONCLUSIONS

In summary, we have successfully demonstrated a platinum(II)-catalyzed ARO of oxabenzonorbornadienes with a variety of phenols to prepare 1,2-*cis* ring-opening products in good to excellent yields with moderate to good enantioselectivities. In addition, we have also successfully optimized suitable reaction conditions for the ARO reaction of oxabicyclic alkenes with phenols. In contrast to rhodium- and iridium-catalyzed protocols, this platinum catalyst system displayed higher catalytic activity toward electron-rich substrates with yields up to 99%. Most noteworthy, instead of generating 1,2-*trans* products generally observed in the Rh- and Ir-catalyzed ARO reactions, we could obtain the *cis*-2-(un)substituted phenoxy-1,2-dihydronaphthalen-1-ol products via the platinum(II)-catalyzed ARO of oxabenzonorbornadienes with phenols, which would be an excellent complement to the Rh-, Ir-, and Pt-catalyzed ARO chemistry. Studies on further expansion of the scopes and synthetic utilities of the Pt-catalyzed ring-opening reaction are being pursued and will be reported in due course.

EXPERIMENTAL SECTION

General Procedure for the Platinum(II)-Catalyzed ARO Reactions of Oxabenzonorbornadienes 1a−d with Phenols. A 10 mL round-bottom flask fitted with a reflux condenser was flame-dried under a stream of nitrogen and cooled to room temperature. $Pt(COD)Cl_2$ (1.1 mg, 1.5 mol %) and (*S*)-DM-SEGPHOS (2.2 mg, 1.5 mol %) were simultaneously added followed by the addition of DCE (2.0 mL). After the mixture was stirred for about 20 min, $AgSbF_6$ (2.1 mg, 3.0 mol %) was added. After another 10 min, oxabenzonorbornadienes (0.2 mmol) and phenols (1.0 mmol) were added and followed by KOH solution (0.5 M in H_2O, 20 μL). The reaction was stirred at 50 °C until completion as monitored by thin layer chromatography. After the reaction mixture was cooled to room temperature, the solvent was removed in vacuo. The crude mixture was then poured into 10 mL of dichloromethane and washed three times (3 × 10 mL) with 5% aqueous NaOH. The aqueous layers were combined and back-extracted three times (3 × 10 mL) with CH_2Cl_2. The organic layers were combined, dried over anhydrous Na_2SO_4, and then filtered. The filtrate was concentrated in vacuum, and the resulting residue was purified on a silica gel column (silica gel: 200−300 mesh) using ethyl acetate/petroleum ether as eluent to afford the desired products.

*(1S,2R)-2-Phenoxy-1,2-dihydronaphthalen-1-ol (**2a**).* Prepared according to general procedure, **2a** was obtained as a white crystalline solid (40.5 mg, 85% yield): mp 86−87 °C; R_f = 0.20 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 80% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 9.9 (minor) and 13.4 min (major); $[\alpha]_D^{25}$ = −156.9 (*c* 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3350 (br), 3042, 2921, 2847, 2372, 1595, 1491, 1242, 1087, 889, 752, 692; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57−7.53 (m, 1H), 7.32−7.25 (m, 4H), 7.16−7.12 (m, 1H), 7.00−6.94 (m, 3H), 6.62 (d, *J* = 9.8 Hz, 1H), 6.12 (dd, *J* = 9.7, 3.8 Hz, 1H), 5.00 (dd, *J* = 6.2, 2.2 Hz, 1H), 4.91−4.88 (m, 1H), 2.64 (d, *J* = 7.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.4, 135.6, 131.9, 130.5, 129.6, 128.5, 128.4, 127.1, 127.0, 124.8, 121.7, 116.2, 73.9, 69.5; HRMS (ESI-ion trap) *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{14}O_2Na$, 261.0892; found 261.0880.

*(1S,2R)-2-(4-Methylphenoxy)-1,2-dihydronaphthalen-1-ol (**2b**).* Prepared according to general procedure, **2b** was obtained as a white crystalline solid (33.8 mg, 67% yield): mp 88−89 °C; R_f = 0.21 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 80% using HPLC analysis on a chiralcel AD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm); retention times were 15.2 (major) and 17.8 min (minor); $[\alpha]_D^{25}$ = −289.6 (*c* 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3347 (br), 3280, 3036, 2927, 2853, 2376, 1617, 1510, 1242, 1007, 782, 746, 660; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55−7.53 (m, 1H), 7.31−7.27 (m, 2H), 7.15−7.12 (m, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.88−6.84 (m, 2H), 6.60 (d, *J* = 9.7 Hz, 1H), 6.10 (dd, *J* = 9.7, 3.7 Hz, 1H), 4.95 (t, *J* = 4.2 Hz, 1H), 4.88 (s, 1H), 2.66 (d, *J* = 0.9 Hz, 1H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.3, 135.6, 131.9, 131.1, 130.3, 130.0, 128.5, 128.4, 127.1, 127.0, 125.1, 116.3, 74.3, 69.5, 20.5; HRMS (ESI-ion trap) *m*/*z* $[M + Na]^+$ calcd for $C_{17}H_{16}O_2Na$, 275.1048; found 275.1036.

*(1S,2R)-2-(3-Methylphenoxy)-1,2-dihydronaphthalen-1-ol (**2c**).* Prepared according to general procedure, **2c** was obtained as a white crystalline solid (40.3 mg, 80% yield): mp 73−74 °C; R_f = 0.21 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 71% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm); retention times were 15.1 (minor) and 22.7 min (major); $[\alpha]_D^{25}$ = −285.4 (*c* 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3392 (br), 2918, 2851, 1645, 1485, 1258, 1153, 1034, 782, 690; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 5.6, 3.1 Hz, 1H), 7.33−7.28 (m, 2H), 7.19−7.14 (m, 2H), 6.79 (dd, *J* = 11.0, 8.4 Hz, 3H), 6.62 (d, *J* = 9.8 Hz, 1H), 6.12 (dd, *J* = 9.7, 3.7 Hz, 1H), 5.01 (dd, *J* = 6.2, 2.2 Hz, 1H), 4.90 (d, *J* = 3.6 Hz, 1H), 2.62 (d, *J* = 2.6 Hz, 1H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.4, 139.8, 135.6, 131.9, 130.4, 129.3, 128.5, 128.4, 127.1, 127.0, 125.0, 122.6, 117.2, 113.1, 74.0, 69.6, 21.5; HRMS (ESI-ion trap) *m*/*z* $[M + Na]^+$ calcd for $C_{17}H_{16}O_2Na$, 275.1048; found 275.1036.

*(1S,2R)-2-(2-Methylphenoxy)-1,2-dihydronaphthalen-1-ol (**2d**).* Prepared according to general procedure, **2d** was obtained as colorless oil (36.3 mg, 72% yield); R_f = 0.25 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); 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 11.8 (major) and 15.1 min (minor); $[\alpha]_D^{25}$ = −233.7 (*c* 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3396 (br), 2914, 2847, 1650, 1493, 1236, 1117, 752; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57−7.53 (m, 1H), 7.32−7.28 (m, 2H), 7.15 (dd, *J* = 9.0, 6.1 Hz, 3H), 6.95−6.88 (m, 2H), 6.61 (d, *J* = 9.8 Hz, 1H), 6.09 (dd, *J* = 9.7, 3.7 Hz, 1H), 5.00 (t, *J* = 4.1 Hz, 1H), 4.91 (t, *J* = 5.2 Hz, 1H), 2.66 (d, *J* = 7.0 Hz, 1H), 2.13 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz,

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$CDCl_3$) δ 155.4, 135.6, 131.9, 131.1, 130.4, 128.5, 128.4, 128.2, 127.1, 127.0, 126.8, 125.2, 121.6, 114.0, 74.3, 69.8, 16.2; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}O_2Na$, 275.1048; found 275.1037.

(1S,2R)-2-(4-Methoxyphenoxy)-1,2-dihydronaphthalen-1-ol ***(2e)***. Prepared according to general procedure, **2e** was obtained as a white crystalline solid (48.8 mg, 91% yield): mp 92−93 °C; R_f = 0.15 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 47% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 15.1 (minor) and 18.5 min (major); $[\alpha]_D^{25}$ = −135 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3384 (br), 2923, 2845, 1508, 1225, 1040, 829, 782; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56−7.53 (m, 1H), 7.32−7.27 (m, 2H), 7.16−7.13 (m, 1H), 6.93−6.90 (m, 2H), 6.84−6.81 (m, 2H), 6.62 (d, J = 9.7 Hz, 1H), 6.10−6.07 (m, 1H), 4.89−4.87 (m, 2H), 3.77 (s, 3H), 2.68 (d, J = 5.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.7, 151.4, 135.6, 131.9, 130.3, 128.5, 128.4, 127.1, 127.0, 125.1, 118.0, 114.7, 75.2, 69.5, 55.7; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}O_3Na$, 291.0997; found 291.0985.

(1S,2R)-2-(3-Methoxyphenoxy)-1,2-dihydronaphthalen-1-ol ***(2f)***. Prepared according to general procedure, **2f** was obtained as a white crystalline solid (42.9 mg, 80% yield): mp 66−67 °C; R_f = 0.10 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 65% using HPLC analysis on a chiralcel AD-H column (hexane/2-propanol 85:15, 1.0 mL/min, λ = 254 nm); retention times were 14.0 (major) and 18.7 min (minor); $[\alpha]_D^{25}$ = −257.1 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3459 (br), 2923, 2856, 2361, 1646, 1597, 1491, 1285, 1201, 1148, 1042, 885, 748, 580; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56−7.54 (m, 1H), 7.33−7.28 (m, 2H), 7.20−7.14 (m, 2H), 6.62 (d, J = 9.7 Hz, 1H), 6.57−6.51 (m, 3H), 6.13 (dd, J = 9.7, 3.8 Hz, 1H), 5.00 (t, J = 4.2 Hz, 1H), 4.90 (s, 1H), 3.76 (s, 3H), 2.62 (d, J = 6.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 160.9, 158.6, 135.6, 131.8, 130.5, 130.0, 128.5, 128.4, 127.1, 124.8, 108.0, 107.3, 102.6, 73.9, 69.5, 55.3, 29.7; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{17}H_{16}O_3Na$, 291.0997; found 291.0985.

(1S,2R)-2-(4-Chlorophenoxy)-1,2-dihydronaphthalen-1-ol ***(2g)***. Prepared according to general procedure, **2g** was obtained as a white crystalline solid (39.2 mg, 72% yield): mp 111−112 °C; R_f = 0.16 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 23% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 95:5, 1.0 mL/min, λ = 254 nm); retention times were 20.4 (major) and 22.7 min (minor); $[\alpha]_D^{25}$ = −78.9 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3347 (br), 2927, 2857, 1598, 1491, 1245, 1096, 1005, 785, 698; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57−7.54 (m, 1H), 7.33−7.28 (m, 2H), 7.24−7.22 (m, 2H), 7.15 (dt, J = 4.0, 3.1 Hz, 1H), 6.90−6.86 (m, 2H), 6.63 (d, J = 9.8 Hz, 1H), 6.08 (dd, J = 9.7, 3.8 Hz, 1H), 4.92 (dd, J = 10.5, 6.5 Hz, 2H), 2.60−2.59 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.1, 135.6, 131.8, 131.0, 129.6, 128.6, 127.2, 126.9, 126.7, 124.2, 117.7, 74.4, 69.6; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{16}H_{13}ClO_2Na$, 295.0502; found 295.0489.

(1S,2R)-2-(3-Chlorophenoxy)-1,2-dihydronaphthalen-1-ol ***(2h)***. Prepared according to general procedure, **2h** was obtained as a white crystalline solid (39.2 mg, 72% yield): mp 75−76 °C; R_f = 0.16 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 17% using HPLC analysis on a chiralcel AD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm); retention times were 11.6 (minor) and 13.8 min (major); $[\alpha]_D^{25}$ = +81.5 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3353 (br), 2927, 2853, 1595, 1482, 1245, 1093, 920, 782, 697; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, J = 5.9, 2.5 Hz, 1H), 7.34−7.29 (m, 2H), 7.21−7.15 (m, 2H), 6.97−6.96 (m, 2H), 6.84 (ddd, J = 8.4, 2.3, 0.8 Hz, 1H), 6.65 (d, J = 9.7 Hz, 1H), 6.11 (dd, J = 9.7, 3.9 Hz, 1H), 4.97 (t, J = 4.3 Hz, 1H), 4.91 (t, J = 5.4 Hz, 1H), 2.56−2.53 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.1, 135.5, 135.0, 131.7, 131.1, 130.4, 128.6, 128.5, 127.2, 126.8, 124.0, 121.9, 116.7, 114.5, 74.1, 69.6; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{16}H_{13}ClO_2Na$, 295.0502; found 295.0490.

(1S,2R)-2-(2-Chlorophenoxy)-1,2-dihydronaphthalen-1-ol ***(2i)***. Prepared according to general procedure, **2i** was obtained as colorless oil (37.1 mg, 68% yield); R_f = 0.17 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 75% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 10.0 (minor) and 13.4 min (major); $[\alpha]_D^{25}$ = −172.9 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3366 (br), 2921, 2853, 1723, 1595, 1492, 1242, 1092, 889, 752, 694; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, J = 8.6, 3.6 Hz, 1H), 7.32−7.23 (m, 4H), 7.17−7.14 (m, 1H), 7.01−6.96 (m, 2H), 6.64 (dd, J = 9.7, 5.3 Hz, 1H), 6.11 (ddd, J = 20.2, 9.7, 3.8 Hz, 1H), 5.03−4.91 (m, 2H), 2.59 (d, J = 40.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 157.4, 135.5, 131.9, 131.0, 130.5, 129.6, 129.5, 128.6, 128.4, 127.1, 124.8, 121.7, 117.6, 116.2, 73.9, 69.6; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{16}H_{13}ClO_2Na$, 295.0502; found 295.0489.

(1S,2R)-2-(3-Bromophenoxy)-1,2-dihydronaphthalen-1-ol ***(2j)***. Prepared according to general procedure, **2j** was obtained as a white solid (44.9 mg, 71% yield): mp 80−81 °C; R_f = 0.19 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 35% using HPLC analysis on a chiralcel AD-H column (hexane/2-propanol 85:15, 1.0 mL/min, λ = 254 nm); retention times were 9.6 (minor) and 11.4 min (major); $[\alpha]_D^{25}$ = +91.7 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3392 (br), 2928, 2846, 2361, 1645, 1472, 1238, 1004, 906, 780; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, J = 6.0, 2.4 Hz, 1H), 7.34−7.29 (m, 2H), 7.17−7.10 (m, 4H), 6.90−6.87 (m, 1H), 6.65 (d, J = 9.7 Hz, 1H), 6.10 (dd, J = 9.7, 3.9 Hz, 1H), 4.95 (dd, J = 17.2, 12.9 Hz, 2H), 2.55 (d, J = 1.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.2, 135.5, 131.7, 131.1, 130.7, 128.6, 128.5, 127.1, 126.8, 124.8, 124.0, 122.9, 119.6, 115.0, 74.1, 69.6; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{16}H_{13}BrO_2Na$, 338.9997; found 338.9975.

(1S,2R)-1-[4-(1-Hydroxy-1,2-dihydronaphthalen-2-yloxy)phenyl]-ethanone ***(2k)***. Prepared according to general procedure, **2k** was obtained as a white solid (30.2 mg, 54% yield): mp 113−114 °C; R_f = 0.23 on silica gel (ethyl acetate/petroleum ether 1:5, v/v); ee was determined to be 72% using HPLC analysis on a chiralcel AD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 22.3 (major) and 26.1 min (minor); $[\alpha]_D^{25}$ = +357.1 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3382 (br), 2923, 2851, 2356, 1645, 1128, 770, 690; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93−7.90 (m, 2H), 7.57 (dd, J = 6.1, 2.5 Hz, 1H), 7.35−7.30 (m, 2H), 7.16 (dd, J = 5.4, 3.3 Hz, 1H), 7.00−6.96 (m, 2H), 6.66 (d, J = 9.7 Hz, 1H), 6.13 (dd, J = 9.7, 3.9 Hz, 1H), 5.09 (t, J = 4.3 Hz, 1H), 4.95 (d, J = 3.6 Hz, 1H), 2.63 (s, 1H), 2.54 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.7, 161.4, 135.5, 131.6, 131.3, 130.9, 130.6, 128.7, 128.6, 127.2, 126.8, 123.7, 115.4, 73.7, 69.6, 26.3; HRMS (ESI-ion trap) m/z $[M + H]^+$ calcd for $C_{18}H_{17}O_3$, 281.1178; found 281.1158.

(1S,2R)-2-([1,1′-Biphenyl]-4-yloxy)-1,2-dihydronaphthalen-1-ol ***(2l)***. Prepared according to general procedure, **2l** was obtained as a white solid (52.8 mg, 84% yield): mp 90−91 °C; R_f = 0.18 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 87% using HPLC analysis on a chiralcel AD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 14.8 (major) and 19.4 min (minor); $[\alpha]_D^{25}$ = −117.8 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3397 (br), 2923, 2856, 2355, 1652, 1524, 1248, 762, 690; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.47−7.45 (m, 2H), 7.42−7.39 (m, 3H), 7.32−7.30 (m, 2H), 7.16 (dd, J = 5.4, 3.3 Hz, 1H), 7.05−7.01 (m, 2H), 6.90−6.86 (m, 2H), 6.65 (d, J = 9.8 Hz, 1H), 6.16 (dd, J = 9.7, 3.8 Hz, 1H), 5.06 (t, J = 3.9 Hz, 1H), 4.95 (d, J = 3.0 Hz, 1H), 2.70 (d, J = 2.1 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.2, 140.6, 135.4, 134.9, 131.9, 128.7, 128.6, 128.5, 128.3, 127.1, 126.9, 126.8, 126.7, 126.6, 124.7, 116.5, 74.1, 69.6; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{22}H_{18}O_2Na$, 337.1205; found 337.1193.

(1S,2R)-2-(Naphthalen-2-yloxy)-1,2-dihydronaphthalen-1-ol ***(2m)***. Prepared according to general procedure, **2m** was obtained as a white solid (23.4 mg, 40% yield): mp 110−111 °C; R_f = 0.23 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 23% using HPLC analysis on a chiralcel AD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ = 254 nm); retention times were 19.9 (major) and 28.9 min (minor); $[\alpha]_D^{25}$ = −194.3 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3361 (br), 2922, 2851, 2376, 1726, 1633, 1465, 1256, 836, 740; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 6.5 Hz,

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2H), 7.65 (d, J = 8.2 Hz, 1H), 7.57 (dd, J = 5.1, 3.6 Hz, 1H), 7.33−7.32 (m, 2H), 7.19−7.07 (m, 5H), 6.66 (d, J = 9.8 Hz, 1H), 6.21 (dd, J = 9.7, 3.7 Hz, 1H), 5.18 (t, J = 3.9 Hz, 1H), 4.98 (d, J = 4.5 Hz, 1H), 2.71 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.2, 135.4, 134.4, 131.9, 130.6, 129.8, 129.4, 128.7, 128.5, 127.7, 126.8, 126.5, 126.3, 124.8, 124.1, 123.5, 119.4, 109.5, 74.1, 69.6; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{20}H_{16}O_2Na$, 311.1048; found 311.1035.

(1S,2R)-2-(2,4-Dimethylphenoxy)-1,2-dihydronaphthalen-1-ol ***(2n)***. Prepared according to general procedure, **2n** was obtained as colorless oil (35.6 mg, 67% yield); R_f = 0.32 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); 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 7.3 (major) and 28.9 min (minor); $[\alpha]_D^{25}$ = −264 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3438 (br), 2918, 2856, 1503, 1251, 1220, 1125, 778; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 1.2 Hz, 1H), 7.30−7.29 (m, 2H), 7.14−7.13 (m, 1H), 6.94 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.2 Hz, 1H), 6.59 (d, J = 9.7 Hz, 1H), 6.08 (d, J = 9.7 Hz, 1H), 4.91 (d, J = 16.9 Hz, 2H), 2.69 (d, J = 4.6 Hz, 1H), 2.18 (d, J = 60.4 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.2, 135.7, 132.0, 131.9, 131.1, 130.2, 128.4, 128.3, 128.1, 127.1, 127.0, 126.9, 125.4, 114.5, 74.7, 69.7, 20.5, 16.2; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{18}H_{18}O_2Na$, 289.1205; found 289.1192.

(1S,2R)-2-(2,4-Dichlorophenoxy)-1,2-dihydronaphthalen-1-ol ***(2o)***. Prepared according to general procedure, **2o** was obtained as colorless oil (25.6 mg, 42% yield); R_f = 0.28 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 60% using HPLC analysis on a chiralcel AD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 8.5 (minor) and 9.6 min (major); $[\alpha]_D^{25}$ = +85 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3299 (br), 2923, 2856, 1476, 1256, 1098, 753; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59−7.57 (m, 1H), 7.36−7.30 (m, 3H), 7.18−7.15 (m, 2H), 6.96 (d, J = 8.8 Hz, 1H), 6.66 (dd, J = 9.7, 5.9 Hz, 1H), 6.10−6.06 (m, 1H), 4.89 (s, 2H), 2.81 (d, J = 6.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.1, 135.5, 131.6, 130.8, 130.2, 128.7, 128.5, 127.7, 127.2, 126.8, 123.5, 118.4, 76.7, 69.7; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{16}H_{12}Cl_2O_2Na$, 329.0112; found 329.0097.

(1S,2R)-2-(3,5-Dimethylphenoxy)-1,2-dihydronaphthalen-1-ol ***(2p)***. Prepared according to general procedure, **2p** was obtained as a white crystalline solid (43.1 mg, 81% yield): mp 83−84 °C; R_f = 0.28 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 69% using HPLC analysis on a chiralcel AD-H column (hexane/2-propanol 90:10, 1.0 mL/min, λ= 254 nm); retention times were 8.9 (major) and 11.4 min (minor); $[\alpha]_D^{25}$ = −252.9 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3371 (br), 2917, 2381, 1594, 1469, 1292, 1151, 1040, 829, 781, 699; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56−7.52 (m, 1H), 7.32−7.27 (m, 2H), 7.16−7.12 (m, 1H), 6.63−6.60 (m, 4H), 6.12 (dd, J = 9.7, 3.7 Hz, 1H), 4.99 (dd, J = 6.2, 2.2 Hz, 1H), 4.88 (s, 1H), 2.64 (d, J = 1.7 Hz, 1H), 2.27 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.4, 139.4, 135.6, 131.9, 130.3, 128.5, 128.4, 127.2, 127.0, 125.2, 123.5, 114.0, 73.9, 69.5, 21.4; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{18}H_{18}O_2Na$, 289.1205; found 289.1193.

(1S,2R)-2-(4-Chloro-3-methylphenoxy)-1,2-dihydronaphthalen-1-ol ***(2q)***. Prepared according to general procedure, **2q** was obtained as a white crystalline solid (47.5 mg, 83% yield): mp 115−116 °C; R_f = 0.18 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 29% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 85:15, 1.0 mL/min, λ = 254 nm); retention times were 10.5 (major) and 13.7 min (minor); $[\alpha]_D^{25}$ = −111.9 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3278 (br), 2922, 2845, 2299, 1481, 1282, 1166, 1042, 781; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57−7.53 (m, 1H), 7.33−7.28 (m, 2H), 7.22 (d, J = 8.7 Hz, 1H), 7.16−7.14 (m, 1H), 6.84 (d, J = 2.9 Hz, 1H), 6.74 (dd, J = 8.7, 3.0 Hz, 1H), 6.63 (d, J = 9.8 Hz, 1H), 6.09 (dd, J = 9.7, 3.8 Hz, 1H), 4.95−4.87 (m, 2H), 2.56 (d, J = 7.7 Hz, 1H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.9, 137.3, 135.6, 131.8, 130.8, 129.8, 128.5, 127.1, 127.0, 124.4, 119.0, 114.9, 74.3, 69.6, 20.3; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{17}H_{15}ClO_2Na$, 309.0658; found 309.0644.

(1S,2R)-5,8-Dimethoxy-2-(4-methylphenoxy)-1,2-dihydronaphthalen-1-ol ***(3a)***. Prepared according to general procedure, **3a** was obtained as colorless oil (55.5 mg, 89% yield); R_f = 0.23 on silica gel (ethyl acetate/petroleum ether 1:5, v/v); ee was determined to be 79% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 12.0 (major) and 21.6 min (minor); $[\alpha]_D^{25}$ = −43.9 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3500 (br), 2938, 2840, 1608, 1510, 1484, 1262, 1090, 814, 721; ^1H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, J = 8.2 Hz, 2H), 6.93−6.90 (m, 3H), 6.80 (dd, J = 21.9, 9.0 Hz, 2H), 5.99 (dt, J = 10.0, 1.8 Hz, 1H), 5.25 (dd, J = 4.5, 1.5 Hz, 1H), 5.09−5.08 (m, 1H), 3.81 (d, J = 10.9 Hz, 6H), 2.49 (s, 1H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.9, 151.3, 149.8, 130.9, 130.1, 126.5, 122.8, 122.4, 122.1, 116.1, 112.3, 111.5, 76.4, 61.7, 56.2, 56.1, 20.5; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{19}H_{20}O_4Na$, 335.1259; found 335.1245.

(1S,2R)-5,8-Dimethoxy-2-(3-methylphenoxy)-1,2-dihydronaphthalen-1-ol ***(3b)***. Prepared according to general procedure, **3b** was obtained as colorless oil (61.8 mg, 99% yield); R_f = 0.16 on silica gel (ethyl acetate/petroleum ether 1:5, v/v); ee was determined to be 76% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 18.9 (major) and 26.5 min (minor); $[\alpha]_D^{25}$ = −45.6 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3423 (br), 2923, 2851, 2361, 1645, 1485, 1261, 1089, 955, 775; ^1H NMR (500 MHz, $CDCl_3$) δ 7.18 (t, J = 7.8 Hz, 1H), 6.92 (dd, J = 10.0, 2.7 Hz, 1H), 6.82 (ddd, J = 21.4, 9.7, 5.0 Hz, 5H), 5.99 (dt, J = 10.0, 1.7 Hz, 1H), 5.25 (d, J = 4.2 Hz, 1H), 5.12 (dt, J = 4.5, 2.3 Hz, 1H), 3.81 (d, J = 11.8 Hz, 6H), 2.50 (s, 1H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 157.0, 151.3, 149.7, 139.7, 129.3, 126.4, 122.7, 122.3, 122.1, 116.9, 112.9, 112.3, 111.5, 76.1, 61.8, 56.2, 56.2, 21.5; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{19}H_{20}O_4Na$, 335.1259; found 335.1246.

(1S,2R)-5,8-Dimethoxy-2-(4-methoxyphenoxy)-1,2-dihydronaphthalen-1-ol ***(3c)***. Prepared according to general procedure, **3c** was obtained as colorless oil (59.7 mg, 91% yield); R_f = 0.12 on silica gel (ethyl acetate/petroleum ether 1:5, v/v); ee was determined to be 78% using HPLC analysis on a chiralcel AD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 40.6 (minor) and 45.7 min (major); $[\alpha]_D^{25}$ = −31 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3464 (br), 2923, 2851, 2361, 1645, 1506, 1483, 1261, 1223, 1086, 1043, 824, 724; ^1H NMR (500 MHz, $CDCl_3$) δ 6.99−6.96 (m, 2H), 6.91 (dd, J = 10.0, 2.7 Hz, 1H), 6.86−6.77 (m, 4H), 5.99 (dt, J = 10.0, 1.8 Hz, 1H), 5.23 (dd, J = 4.5, 1.6 Hz, 1H), 5.02−5.01 (m, 1H), 3.82−3.78 (m, 9H), 2.50 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.5, 151.3, 151.0, 149.8, 126.5, 122.8, 122.4, 122.1, 117.6, 114.8, 112.3, 111.4, 77.4, 61.6, 56.2, 55.7; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{19}H_{20}O_5Na$, 351.1208; found 351.1194.

(1S,2R)-2-(4-Chlorophenoxy)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol ***(3d)***. Prepared according to general procedure, **3d** was obtained as colorless oil (59.1 mg, 89% yield); R_f = 0.16 on silica gel (ethyl acetate/petroleum ether 1:5, v/v); ee was determined to be 72% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 12.9 (major) and 28.8 min (minor); $[\alpha]_D^{25}$ = −42.3 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3469 (br), 2938, 2840, 1590, 1489, 1260, 1090, 956, 806, 729; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28−7.24 (m, 2H), 6.94 (dq, J = 7.3, 3.1 Hz, 3H), 6.81 (q, J = 9.0 Hz, 2H), 5.94 (dt, J = 10.0, 1.8 Hz, 1H), 5.24 (dd, J = 4.4, 1.4 Hz, 1H), 5.07 (dt, J = 4.5, 2.3 Hz, 1H), 3.81 (d, J = 8.9 Hz, 6H), 2.43 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.7, 151.2, 149.8, 129.5, 126.4, 125.7, 122.7, 122.6, 122.2, 117.4, 112.4, 111.7, 76.7, 61.8, 56.2, 56.1; HRMS (ESI-ion trap) m/z $[M + Na]^+$ calcd for $C_{18}H_{17}ClO_4Na$, 355.0713; found 355.0698.

(1S,2R)-2-(3-Chlorophenoxy)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol ***(3e)***. Prepared according to general procedure, **3e** was obtained as colorless oil (63.7 mg, 96% yield); R_f = 0.14 on silica gel (ethyl acetate/petroleum ether 1:5, v/v); ee was determined to be 45% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 12.5(major) and 19.9 min (minor); $[\alpha]_D^{25}$ = −26.7 (c 1.00, $CHCl_3$); IR (neat film,

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cm^{-1}) ν 3433 (br), 2923, 2851, 2361, 1591, 1483, 1261, 1089, 955, 888; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, J = 8.1 Hz, 1H), 7.02−6.89 (m, 4H), 6.81 (q, J = 9.0 Hz, 2H), 5.95 (dt, J = 10.0, 1.7 Hz, 1H), 5.25 (dd, J = 4.5, 1.7 Hz, 1H), 5.10 (dt, J = 4.4, 2.2 Hz, 1H), 3.81 (d, J = 12.5 Hz, 6H), 2.45 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.9, 151.1, 149.8, 135.0, 130.4, 125.5, 122.6, 122.1, 121.7, 116.5, 114.4, 112.4, 111.6, 76.5, 61.8, 56.2, 56.1; HRMS (ESI-ion trap) m/z [M + Na]$^+$ calcd for $C_{18}H_{17}ClO_4Na$, 355.0713; found 355.0699.

*(1S,2R)-2-(2,4-Dimethylphenoxy)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (**3f**).* Prepared according to general procedure, **3f** was obtained as colorless oil (55.4 mg, 85% yield); R_f = 0.19 on silica gel (ethyl acetate/petroleum ether 1:5, v/v); ee was determined to be 84% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 10.7 (major) and 12.1 min (minor); $[\alpha]_D^{25}$ = −50 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3413 (br), 2923, 2851, 2356, 1484, 1259, 1220, 1086, 952, 804, 724; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (s, 1H), 6.96−6.90 (m, 2H), 6.84−6.78 (m, 3H), 6.00 (dt, J = 10.1, 1.8 Hz, 1H), 5.26 (dd, J = 4.4, 1.3 Hz, 1H), 5.06 (dt, J = 4.5, 2.2 Hz, 1H), 3.82 (d, J = 14.3 Hz, 6H), 2.54 (s, 1H), 2.28 (d, J = 6.7 Hz, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 153.0, 151.4, 149.8, 132.0, 130.7, 127.8, 127.1, 126.7, 122.7, 122.5, 122.0, 113.6, 112.4, 111.5, 61.9, 56.2, 20.5, 16.4; HRMS (ESI-ion trap) m/z [M + Na]$^+$ calcd for $C_{20}H_{22}O_4Na$, 349.1416; found 349.1401.

*(1S,2R)-2-(3,5-Dimethylphenoxy)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (**3g**).* Prepared according to general procedure, **3g** was obtained as colorless oil (61.9 mg, 95% yield); R_f = 0.16 on silica gel (ethyl acetate/petroleum ether 1:5, v/v); ee was determined to be 72% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 10.7 (major) and 20.3 min (minor); $[\alpha]_D^{25}$ = −52.1 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3510 (br), 2928, 2835, 2386, 1593 1484, 1257, 1152, 1091, 827, 729; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 (dd, J = 10.0, 2.7 Hz, 1H), 6.80 (dd, J = 21.3, 9.0 Hz, 2H), 6.64 (s, 3H), 5.98 (dt, J = 10.0, 1.7 Hz, 1H), 5.24 (dd, J = 4.5, 1.5 Hz, 1H), 5.11 (dt, J = 4.5, 2.3 Hz, 1H), 3.80 (d, J = 12.4 Hz, 6H), 2.52 (s, 1H), 2.28 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.0, 151.3, 149.7, 139.4, 126.6, 123.3, 122.8, 122.3, 122.0, 113.8, 112.3, 111.5, 76.1, 61.8, 56.2, 56.1, 21.4; HRMS (ESI-ion trap) m/z [M + Na]$^+$ calcd for $C_{20}H_{22}O_4Na$, 349.1416; found 349.1401.

*(1S,2R)-2-(4-Chloro-3-methylphenoxy)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (**3h**).* Prepared according to general procedure, **3h** was obtained as colorless oil (67.8 mg, 98% yield); R_f = 0.11 on silica gel (ethyl acetate/petroleum ether 1:5, v/v); ee was determined to be 65% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 12.0 (major) and 30.8 min (minor); $[\alpha]_D^{25}$ = −17.2 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3505 (br), 2943, 2835, 1595, 1484, 1261, 1170, 1090, 953, 801, 724; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 8.8 Hz, 1H), 6.94−6.90 (m, 2H), 6.80 (dt, J = 8.7, 6.6 Hz, 3H), 5.95 (dt, J = 10.0, 1.8 Hz, 1H), 5.23 (d, J = 3.1 Hz, 1H), 5.07 (dt, J = 4.5, 2.3 Hz, 1H), 3.81 (d, J = 11.2 Hz, 6H), 2.44 (s, 1H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.6, 151.2, 149.8, 137.3, 129.8, 126.7, 125.9, 122.7, 122.4, 122.2, 118.8, 114.7, 112.4, 111.6, 76.6, 61.8, 56.2, 56.1, 20.3; HRMS (ESI-ion trap) m/z [M + Na]$^+$ calcd for $C_{19}H_{19}ClO_4Na$, 369.0870; found 369.0851.

*(1R,2R)-6,7-Dibromo-2-(4-methylphenoxy)-1,2-dihydronaphthalen-1-ol (**4a**).* Prepared according to general procedure, **4a** was obtained as a white solid (44.1 mg, 54% yield): mp 76−77 °C; R_f = 0.23 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 78% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 12.3 (minor) and 23.9 min (major); $[\alpha]_D^{25}$ = −215.5 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3355 (br), 2922, 2392, 1508, 1241, 1109, 881, 746; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.38 (s, 1H), 7.08 (d, J = 8.2 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 6.53 (d, J = 9.7 Hz, 1H), 6.23−6.20 (m, 1H), 4.84 (d, J = 2.4 Hz, 2H), 2.69 (s, 1H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.0, 136.8, 132.5, 131.9, 131.6, 131.5, 130.1, 129.1, 126.5, 124.3, 124.2, 116.4, 72.8, 68.9, 20.5; HRMS (ESI-ion trap) m/z [M − H]$^-$ calcd for $C_{17}H_{13}Br_2O_2$, 406.9282; found 406.9260.

*(1S,2R)-6,7-Dibromo-2-(3-methylphenoxy)-1,2-dihydronaphthalen-1-ol (**4b**).* Prepared according to general procedure, **4b** was obtained as a white solid (44.9 mg, 55% yield): mp 77−78 °C; R_f = 0.25 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 44% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 8.8 (major) and 10.2 min (minor); $[\alpha]_D^{25}$ = −129.4 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3423 (br), 2923, 2856, 1651, 1489, 1256, 1156, 1040, 771, 691; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.36 (s, 1H), 7.15 (t, J = 7.7 Hz, 1H), 6.81 (d, J = 7.4 Hz, 1H), 6.76−6.71 (m, 2H), 6.52 (d, J = 9.8 Hz, 1H), 6.22 (dd, J = 9.7, 4.3 Hz, 1H), 4.87 (dd, J = 11.8, 7.3 Hz, 2H), 2.74 (d, J = 0.6 Hz, 1H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.1, 139.8, 136.8, 132.4, 131.8, 131.5, 129.4, 129.1, 126.5, 124.3, 124.2, 122.9, 117.2, 113.0, 72.4, 68.9, 21.4; HRMS (ESI-ion trap) m/z [M − H]$^-$ calcd for $C_{17}H_{13}Br_2O_2$, 406.9282; found 406.9266.

*(1S,2R)-6,7-Dibromo-2-(4-chlorophenoxy)-1,2-dihydronaphthalen-1-ol (**4c**).* Prepared according to general procedure, **4c** was obtained as a white solid (36.1 mg, 42% yield): mp 113−114 °C; R_f = 0.17 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 25% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 10.5 (major) and 12.3 min (minor); $[\alpha]_D^{25}$ = −126.9 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3407 (br), 2923, 2381, 1491, 1236, 1094, 1004, 824; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.40 (s, 1H), 7.25−7.23 (m, 2H), 6.88−6.85 (m, 2H), 6.56 (d, J = 9.7 Hz, 1H), 6.21 (dd, J = 9.7, 4.3 Hz, 1H), 4.85 (dd, J = 11.3, 6.8 Hz, 2H), 2.62−2.60 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.8, 136.7, 132.2, 131.7, 131.6, 129.8, 129.6, 127.1, 125.7, 124.6, 124.4, 117.7, 72.8, 69.0; HRMS (ESI-ion trap) m/z [M − H]$^-$ calcd for $C_{16}H_{10}Br_2ClO_2$, 426.8736; found 426.8723.

*(1S,2R)-6,7-Dibromo-2-(3-chlorophenoxy)-1,2-dihydronaphthalen-1-ol (**4d**).* Prepared according to general procedure, **4d** was obtained as a white solid (42.8 mg, 50% yield): mp 103−104 °C; R_f = 0.18 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 49% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 9.8 (major) and 11.3 min (minor); $[\alpha]_D^{25}$ = +123.4 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3382 (br), 2928, 2851, 1592, 1478, 1228, 1093, 1006, 773, 681; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.40 (s, 1H), 7.20 (t, J = 8.1 Hz, 1H), 7.00−6.93 (m, 2H), 6.82 (ddd, J = 8.3, 2.4, 0.8 Hz, 1H), 6.57 (d, J = 9.7 Hz, 1H), 6.25−6.21 (m, 1H), 4.88 (d, J = 3.1 Hz, 2H), 2.57 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.9, 136.6, 135.0, 132.2, 131.6, 130.4, 129.8, 125.5, 124.5, 124.3, 122.2, 116.7, 114.5, 72.6, 68.9; HRMS (ESI-ion trap) m/z [M − H]$^-$ calcd for $C_{16}H_{10}Br_2ClO_2$, 426.8736; found 426.8716.

*(1S,2R)-6,7-Dibromo-2-(4-chloro-3-methylphenoxy)-1,2-dihydronaphthalen-1-ol (**4e**).* Prepared according to general procedure, **4e** was obtained as a white solid (57.5 mg, 65% yield): mp 112−113 °C; R_f = 0.19 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 14% using HPLC analysis on a chiralcel OD-H column (hexane/2-propanol 80:20, 1.0 mL/min, λ = 254 nm); retention times were 11.5 (major) and 14.8 min (minor); $[\alpha]_D^{25}$ = −136.5 (c 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3381 (br), 2923, 2382, 1582, 1479, 1280, 1240, 1165, 1039, 804, 688; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.39 (s, 1H), 7.22 (d, J = 8.7 Hz, 1H), 6.80 (d, J = 2.9 Hz, 1H), 6.71 (dd, J = 8.7, 3.0 Hz, 1H), 6.55 (d, J = 9.7 Hz, 1H), 6.20 (dd, J = 9.7, 4.2 Hz, 1H), 4.86−4.82 (m, 2H), 2.62 (s, 1H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.7, 137.5, 136.8, 132.3, 131.8, 131.6, 129.8, 129.6, 127.3, 125.9, 124.5, 124.4, 119.1, 114.9, 72.8, 69.0, 20.3; HRMS (ESI-ion trap) m/z [M − H]$^-$ calcd for $C_{17}H_{12}Br_2ClO_2$, 440.8893; found 440.8868.

*(1S,2R)-2-(3-Methylphenoxy)-1,2-dihydrotriphenylen-1-ol (**5a**).* Prepared according to general procedure, **5a** was obtained as colorless oil (64.1 mg, 91% yield); R_f = 0.21 on silica gel (ethyl acetate/petroleum ether 1:10, v/v); ee was determined to be 28% using HPLC analysis on a chiralcel AD-H column (hexane/2-propanol 80:20, 1.0

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mL/min, λ = 254 nm); retention times were 28.3 (major) and 32.4 min (minor); $[\alpha]_D^{25}$ = −65.2 (*c* 1.00, $CHCl_3$); IR (neat film, cm^{-1}) ν 3392 (br), 2923, 2851, 2356, 1641, 1551, 1256, 1156, 763, 725; ^1H NMR (500 MHz, $CDCl_3$) δ 8.76−8.72 (m, 2H), 8.32−8.30 (m, 1H), 8.24−8.23 (m, 1H), 7.73−7.64 (m, 4H), 7.41 (dd, *J* = 10.1, 2.8 Hz, 1H), 7.25 (dd, *J* = 9.8, 5.9 Hz, 1H), 6.94−6.87 (m, 3H), 6.38 (dt, *J* = 10.1, 1.8 Hz, 1H), 5.62 (dd, *J* = 4.8, 1.2 Hz, 1H), 5.40−5.38 (m, 1H), 2.69 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9, 140.0, 130.9, 130.6, 129.9, 129.5, 128.5, 127.7, 127.4, 127.1, 127.0, 126.9, 126.7, 124.2, 123.9, 123.8, 123.1, 123.0, 122.6, 116.9, 112.9, 76.5, 65.0, 21.6; HRMS (ESI-ion trap) *m*/*z* $[M + Na]^+$ calcd for $C_{25}H_{20}O_2Na$, 375.1361; found 375.1343.

■ ASSOCIATED CONTENT

Supporting Information

General experimental methods; copies of ^1H and $^{13}C\{^1H\}$ NMR spectra of compounds **2a−q**, **3a−h**, **4a−e**, and **5a**; HPLC conditions and spectra of compounds **2a−d**, **2f**, **2i**, **2k−l**, **2n**, **3a−c**, **3f−g**, **4a**, and **5a**; and X-ray crystal data for compound **2b** 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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