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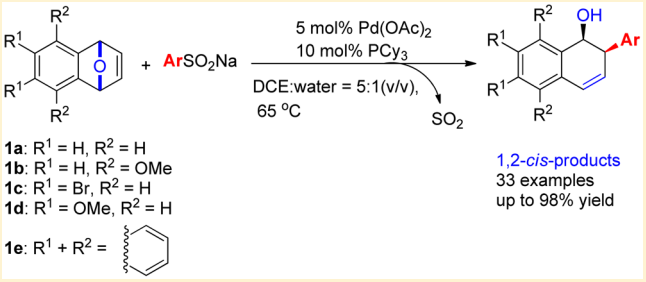
Palladium-Catalyzed *syn*-Stereocontrolled Ring-Opening of Oxabicyclic Alkenes with Sodium Arylsulfinates

Yue Li, Wen Yang, Guo Cheng, and Dingqiao Yang*

Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, People's Republic of China

Supporting Information

ABSTRACT: Palladium-catalyzed *syn*-stereocontrolled ring-opening reactions of oxabenzonorbornadienes with a wide range of sodium arylsulfinates were investigated, affording the desired products in good to excellent yields under an air atmosphere. This protocol provides a low-cost new viable and convenient method toward the synthesis of *cis*-2-aryl-1,2-dihydronaphthalen-1-ol with good functional group tolerance. In addition, the *cis* configuration of **3da** was established by X-ray diffraction analysis, and a plausible mechanism for the ring-opening reaction was proposed.



INTRODUCTION

The transition metal-catalyzed ring-opening reactions of oxa- and azabicyclic alkenes not only play an important role in the carbon−carbon and carbon−heteroatom bond-forming reactions but also provide an effective approach to generate multiple stereocenters in one single step.[1] The corresponding hydronaphthalenes have the potential to be motifs of a wide range of natural products and biologically active molecules.[2] In this regard, a number of commonly used transition metal catalysts, including Pd,[3] Ni,[4] Ir,[5] Cu,[6] Rh,[7] Ru,[8] and so forth,[9] have been investigated for the ring-opening of oxa- and azabicyclic alkenes with various carbanion or heteroatom nucleophiles.

Various aryl donators, such as aryl halides,[10] organometallic reagents,[11] and arylboronic acids,[12] have been applied in this type of reaction. The study referring to the reactions of oxabenzonorbornadiene with aryl halides is relatively rare because of the low activity of aryl halides. On the contrary, highly active organometallic reagents may incur some side effects to give the ring-opening product in low yields. Moreover, organometallic reagents are air- and water-sensitive, and caution is required to handle them. In recent years, arylboronic acids, due to their stability and low toxicity, have been employed as effective carbanion nucleophiles in the ring-opening reactions of oxabicyclic alkenes to afford the corresponding product 2-aryl-1,2-dihydronaphthalen-1-ol in high yields. However, arylboronic acids still have some drawbacks, such as being comparably expensive and having high nucleophile equivalence. Therefore, it is necessary to find a new group of nucleophiles as the aryl source to react with oxabicyclic alkenes.

Arylsulfinate salts are ideal reagents in organic chemistry due to their low cost, remarkable stability, ease of handling, and simple preparation from their corresponding sulfonyl chlorides. Sodium arylsulfinates have been successfully applied as sulfonylation reagents,[13] and increasing attention has recently been paid to the construction of C−C bonds through the extrusion of SO_2.[14] For example, sodium arylsulfinates are generally used as arene donors to react with olefins, alkynes, benzyl chlorides, aryl halides, arylboronic acids, aldehydes, heteroarenes, and so forth.[15] However, there is no literature reported to date in which sodium arylsulfinates are used in the ring-opening reactions of oxabenzonorbornadienes. Hence, it is valuable to develop a new protocol that employs sodium arylsulfinates as nucleophiles in the ring-opening reactions of oxabenzonorbornadienes.

Our group has always and is still interested in the ring-opening reactions of oxa- and azabicyclic alkenes with various carbon and heteroatom nucleophiles. Throughout the years, we have reported iridium-catalyzed asymmetric ring-opening reactions (ARO) of aza- and oxabenzonorbornadienes with various heteroatom nucleophiles, such as amines, phenols, alcohols, and carboxylic acids, to give the corresponding products in high yields with excellent enantioselectivities.[5] Subsequently, we successfully demonstrated the platinum catalyst system could catalyze the ARO of oxabenzonorbornadienes with phenols.[16] Meanwhile, we have also explored carbanion nucleophiles for forming carbon−carbon bonds,[11d,12e,f] for example, platinum- or nickel-catalyzed ARO of oxabicyclic alkenes with arylboronic acids and platinum-catalyzed ARO of oxabenzonorbornadienes with Grignard reagents. In this article, we report a new, efficient and green method of palladium-catalyzed *syn*-stereocontrolled ring-opening reactions of oxabicyclic alkenes with sodium arylsulfinates.

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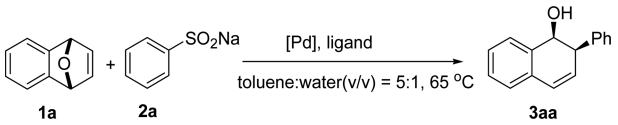
This protocol can afford the corresponding 1,2-*cis* ring-opening products in high yields under an air atmosphere.

RESULTS AND DISCUSSION

Preliminary optimization of the reaction conditions was carried out using oxabenzonorbornadiene **1a** and sodium benzenesulfinate **2a** as model substrates in toluene/water (5:1, v/v) at 65 °C. When **1a** reacted with **2a** in the presence of 5 mol % $PdCl_2$/dppp under nitrogen, desired ring-opened product **3aa** was obtained in 51% yield after 8 h (Table 1, entry 1).

Table 1. Effects of Catalyst Precursors, Ligands, and Catalyst Loadings[a]



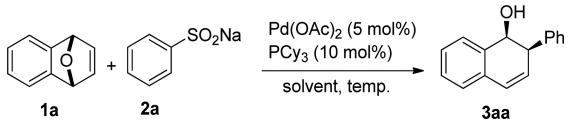
entry	catalyst (mol %)	ligand (mol %)	time (h)	yield (%)
1	$PdCl_2$ (5)	dppp (5)	8	51
2	$Pd(PPh_3)_2Cl_2$ (5)	dppp (5)	10	36
3	$Pd(OOCCF_3)_2$ (5)	dppp (5)	6	71
4	$Pd(OAc)_2$ (5)	dppp (5)	8	73
5	$Pd(OAc)_2$ (5)	PPh_3 (10)	7	66
6	$Pd(OAc)_2$ (5)	dppf (5)	10	45
7	$Pd(OAc)_2$ (5)	Xantphos (5)	6	85
8	$Pd(OAc)_2$ (5)	TFP (10)	10	27
9	$Pd(OAc)_2$ (5)	PCy_3 (10)	6	91
10[b]	$Pd(OAc)_2$ (2.5)	PCy_3 (5)	6	65
11[b]	$Pd(OAc)_2$ (1)	PCy_3 (2)	8	36

[a]Conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), [Pd] (mol %), ligand (mol %), toluene/water = 5:1 (3 mL, v/v), 65 °C (under nitrogen). [b]The conversion of **1a** was 100%.

Encouraged by this result, various palladium catalysts were screened for the ring-opening reaction of **1a** with **2a**, and the results indicate that $Pd(OAc)_2$ is the best catalyst for this reaction compared with $PdCl_2$, $Pd(PPh_3)_2Cl_2$, and $Pd(OOCCF_3)_2$ (Table 1, entries 2−4). Then, a series of phosphine ligands were tested for this reaction under similar conditions. Among them, PCy_3 (tricyclohexyl phosphine) gave corresponding product **3aa** in 91% yield and other ligands only moderate yields (Table 1, entries 5−9). Meanwhile, the catalyst loading also had a significant impact on the yield; the yield of **3aa** decreased as the amount of catalyst loading gradually decreased to 1 mol % (Table 1, entries 10−11). On the basis of these results, a catalyst loading of 5 mol % of $Pd(OAc)_2$ with 10 mol % of PCy_3 was chosen for further optimizing the reaction conditions in terms of yield.

For a better yield to be obtained, the effects of solvent and temperature on the reaction were subsequently investigated. Various types of solvents were initially tested (Table 2, entries 1−8). These results show that solvents play an important role in the reaction. A mixture of water and polar solvent CH_3CN or protic solvent *i*-PrOH gave moderate yields (Table 2, entries 1−2). A worse result was obtained in the dipolar aprotic solvent dimethylformamide (DMF) with water (Table 2, entry 3). Fortunately, when the reaction was carried out in a mixed solvent of water with toluene and 1,2-dichloroethane (DCE), desired product **3aa** was obtained in 91 and 98% yield, respectively (Table 2, entries 4 and 5). On the basis of these findings, we speculated that water-immiscible organic solvent may increase the yield. Thus, chloroform ($CHCl_3$) was chosen

Table 2. Optimization of Solvents and Temperatures[a]



entry	solvent (v/v)	temp (°C)	time (h)	yield (%)
1	CH_3CN/water = 5:1	65	6	42
2	*i*-PrOH/water = 5:1	65	7	47
3	DMF/water = 5:1	65	7	27
4	toluene/water = 5:1	65	6	91
5	DCE/water = 5:1	65	2	98
6	$CHCl_3$/water = 5:1	65	5	88
7	DCE	65	10	57
8	water	65	24	n.r.
9	DCE/water = 5:1	rt	12	73
10	DCE/water = 5:1	45	5	76
11	DCE/water = 5:1	85	2	82
12[b]	**DCE/water = 5:1**	**65**	**2**	**97**

[a]Conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), $Pd(OAc)_2$ (5 mol %), PCy_3 (10 mol %), solvent (3 mL), temperature (under a nitrogen atmosphere). [b]Carried out in air.

to prove this viewpoint; the reaction can proceed smoothly in a mixture of $CHCl_3$ and water, and the corresponding product was obtained in a high yield (Table 2, entry 6). The best mixed solvent (DCE/water = 5:1, v/v) has been identified; then, organic solvent (DCE) and water were used for this reaction, respectively (Table 2, entry 7 and 8). However, satisfactory results have not been achieved. Next, the impact of reaction temperature was investigated. The optimum product yields were obtained (Table 2, entries 9−12). Similar yields were obtained whether in a nitrogen or air atmosphere (Table 2, entries 5 and 12). Therefore, the optimal reaction conditions were: 5 mol % $Pd(OAc)_2$, 10 mol % PCy_3, and 1.5 equiv of sodium arylsulfinates in DCE at 65 °C for 2 h in the presence of air.

With the optimized reaction conditions identified, the scope of sodium arylsulfinates was explored for this reaction. The results suggested that the reactivity of sodium arylsulfinates is structure related (Table 3). Although a series of sodium arylsulfinates reacted smoothly with **1a**, it is clear that sodium arylsulfinates with electron-donating substituents on the phenyl rings achieved higher yields than those with electron-withdrawing groups (Table 3, entries 2−11), possibly because the nucleophilic ability of electron-rich sodium arylsulfinates are stronger than those of electron-deficient ones. For example, when sodium 4-methoxybenzenesulfinate acted as the nucleophile, the yield of expected product **3ad** reached 96% (Table 3, entry 4). On the contrary, when sodium arylsulfinates bearing a strong electron-withdrawing substituent, such as a nitro or trifluoromethyl group reacted with **1a**, the yields of the corresponding product **3aj** and **3ak** were obtained in only 60 and 73%, respectively (Table 3, entries 10 and 11). It is remarkable that the position property of monosubstituted sodium arylsulfinates had no effect on the reactivity (Table 3, entries 6, 8, and 9). Notably, the reaction of biphenyl-4-sulfinic acid sodium with **1a** gave desired product **3an** in a low yield (Table 3, entry 14). In addition, disubstituted arylsulfinic acid sodium salts were tested for this reaction. Sodium 2,5-dimethylbenzenesulfinate was shown to be an effective nucleophile with an excellent yield of 92%, whereas the most hindered 2,4,6-trimethylbenzenesulfinic acid sodium salt

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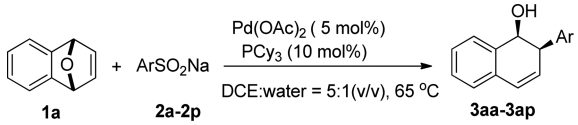
Table 3. Palladium-Catalyzed ARO of Oxabenzonorbornadiene 1a with Various Sodium Arylsulfinates[a]



entry	Ar	product	yield (%)
1	C_6H_5	**3aa**	97
2	4-$H_3CC_6H_4$	**3ab**	92
3	4-*t*-BuC_6H_4	**3ac**	85
4	4-$CH_3OC_6H_4$	**3ad**	96
5	4-FC_6H_4	**3ae**	75
6	4-ClC_6H_4	**3af**	96
7	4-BrC_6H_4	**3ag**	69
8	3-ClC_6H_4	**3ah**	98
9	2-ClC_6H_4	**3ai**	93
10	4-$O_2NC_6H_4$	**3aj**	60
11	4-$F_3CC_6H_4$	**3ak**	73
12	2,5-$(CH_3)_2C_6H_4$	**3al**	92
13	2,4,6-$(CH_3)_3C_6H_4$	**3am**	39
14	4-Ph−C_6H_4	**3an**	44
15	1-naphthyl	**3ao**	86
16	2-naphthyl	**3ap**	85

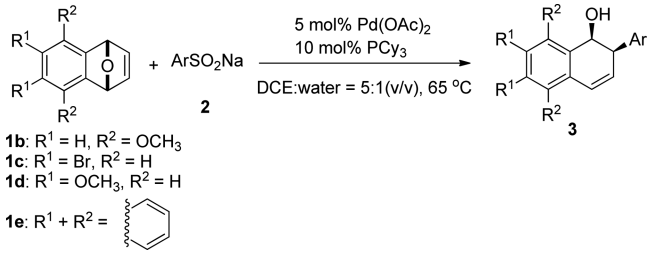
[a]Conditions: **1a** (0.3 mmol), **2** (0.45 mmol), $Pd(OAc)_2$ (5 mol %), PCy_3 (10 mol %), DCE/water = 5:1 (3 mL, v/v), 65 °C, under air.

afforded target product **3am** in poor yield (Table 3, entries 12−13). Sodium naphthylsulfinates showed high activity for this reaction, whether it was 1-naphthyl or 2-naphthyl sulfinic acid sodium salts (Table 3, entries 15−16).

The scope of this ring-opening reaction was further expanded to various types of oxabenzonorbornadienes **1b−e**. As evident from Table 4, the derivatives of **1a** containing electron-withdrawing or -donating groups on the aryl rings could be tolerated in the optimized protocol. The electron-deficient substrates reacted better with a variety of sodium arylsulfinates than with electron-rich substrates (Table 4); electron-withdrawing groups could make the C−O bond of oxabenzonorbornadiene easier to cleave. Moreover, the position of the substituent on oxabenzonorbornadienes also affected this reaction (Table 4, entries 1, 4, 15, and 16). Furthermore, the influence of different sodium arylsulfinates on the reaction for each substrate is similar to **1a**. For example, an alkyl substituent on the aromatic ring of arylsulfinic acid sodium salts showed higher reactivity than that of a halogen substituent (Table 4, entries 1−10 and 12−13). The ring-opening reactions seem to be insensitive to the position of the substituent on sodium benzenesulfinate, as the reaction of chlorine-substituted benzenesulfinic acid sodium salts with **1b** proceeded smoothly and generated the expected products in high yield regardless of the substituted position of chlorine (Table 4, entries 4, 6, and 7). Moreover, the bulkier substrate **1e** was also tolerated under the same conditions, affording desired product **3ea** in excellent yield (Table 4, entry 17).

The single crystal of ring-opening product **3da** was cultivated by solvent evaporation from a mixed solvent of ethyl acetate and petroleum ether. The configuration of **3da** was characterized by single-crystal X-ray diffraction; the data indicated that the structure can be assigned as (1*S*, 2*R*) and confirmed as 1,2-*syn*-configuration (shown in Supporting Information).

Table 4. Palladium-Catalyzed ARO of Oxabenzonorbornadiene 1b−e with Various Sodium Arylsulfinates[a]

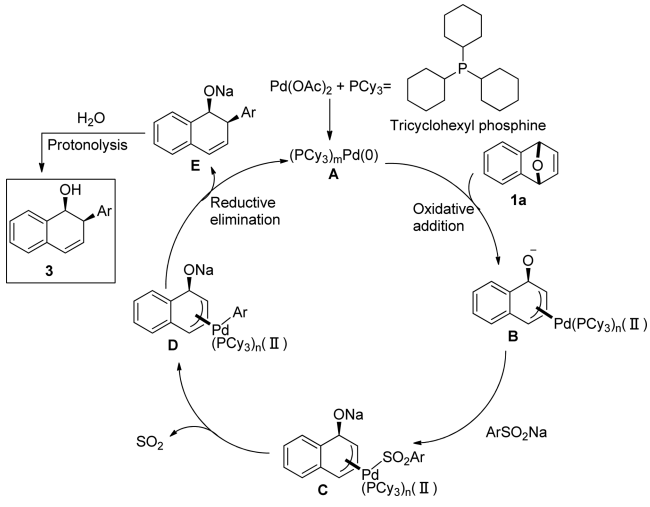


entry	substrate	Ar	product	yield (%)
1	**1b**	C_6H_5	**3ba**	91
2	**1b**	4-$H_3CC_6H_4$	**3bb**	93
3	**1b**	4-FC_6H_4	**3be**	93
4	**1b**	4-ClC_6H_4	**3bf**	88
5	**1b**	4-BrC_6H_4	**3bg**	57
6	**1b**	3-ClC_6H_4	**3bh**	98
7	**1b**	2-ClC_6H_4	**3bi**	92
8	**1b**	2,5-$(CH_3)_2C_6H_4$	**3bl**	91
9	**1c**	C_6H_5	**3ca**	96
10	**1c**	4-*t*-BuC_6H_4	**3cc**	88
11	**1c**	4-$CH_3OC_6H_4$	**3cd**	88
12	**1c**	4-ClC_6H_4	**3cf**	93
13	**1c**	4-BrC_6H_4	**3cg**	75
14	**1c**	4-$O_2NC_6H_4$	**3cj**	72
15	**1d**	C_6H_5	**3da**	74
16	**1d**	4-ClC_6H_4	**3df**	72
17	**1e**	C_6H_5	**3ea**	92

[a]Conditions: **1** (0.3 mmol), **2** (0.45 mmol), $Pd(OAc)_2$ (5 mol %), PCy_3 (10 mol %), DCE/water = 5:1 (3 mL, v/v), 65 °C, under air.

By combination of the above results with the general mechanism of desulfitative reactions, a possible mechanism for this palladium-catalyzed ring-opening reaction was proposed, as shown in Scheme 1. Palladium catalyst **A** is initially generated from catalyst precursor $Pd(OAc)_2$ through homocoupling of sodium arylsulfinates. Oxidative addition of palladium(0) catalyst **A** to oxabenzonorbornadiene **1a** produces (π-allyl)-

Scheme 1. Plausible Mechanism for Palladium-Catalyzed Ring-Opening Reaction of Oxabenzonorbornadiene 1a with Sodium Arylsulfinate



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palladium(II) complex **B**, followed by an exchange reaction of intermediate **B** with sodium arylsulfinates to give intermediate **C**. Then, **C** undergoes desulfonylation to afford (aryl)(π-allyl)-palladium(II) intermediate **D**. Furthermore, a reductive elimination of **D** affords desired product **3** and regenerates Pd(0) species **A** for the next catalytic cycle.

CONCLUSIONS

In summary, we have successfully developed a new, versatile, and efficient palladium-catalyzed *syn*-stereocontrolled ring-opening reaction of oxabicyclic alkene with sodium arylsulfinate as the aryl source. Arylsulfinic acid sodium salt was first used as a carbanion nucleophile for the ring-opening reaction by releasing SO_2. The low cost, remarkable stability, and ease of handling of the reagents made the reaction proceed smoothly under an air atmosphere. This protocol provided a convenient approach to *cis*-2-phenyl-1,2-dihydronaphthalen-1-ol derivatives in high yield with good functional group tolerance.

EXPERIMENTAL SECTION

General Procedure for Palladium-Catalyzed *syn*-Stereocontrolled Ring-Opening Reactions of Oxabenzonorbornadienes 1a−e with Sodium Arylsulfinates. All experiments were carried out under air. $Pd(OAc)_2$ (3.4 mg, 5 mol %) and PCy_3 (8.4 mg, 10 mol %) were simultaneously added to a 10.0 mL round-bottomed flask, followed by the addition of DCE (2.5 mL). After the mixture was stirred for approximately 30 min, oxabenzonorbornadienes **1a−e** (0.3 mmol), sodium arylsulfinate (1.5 equiv, 0.45 mmol), and water (0.5 mL) were put into the reaction system. The mixed solution was stirred at 65 °C for 2 h. After cooling to room temperature, the reaction mixture was treated through vacuum evaporation, concentrated, and then purified by column chromatography (200−300 mesh silica gels) to obtain the desired products.

(1S,2R*)-2-Phenyl-1,2-dihydronaphthalen-1-ol* (**3aa**).[12e] Prepared according to the general procedure. Colorless oil (64.6 mg, 97% yield). R_f = 0.25 on silica gel (ethyl acetate/petroleum ether = 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42−7.27 (m, 6H), 7.24 (dt, J = 7.2, 4.9 Hz, 2H), 7.16 (d, J = 7.3 Hz, 1H), 6.70 (dd, J = 9.6, 1.7 Hz, 1H), 6.12 (dd, J = 9.6, 4.0 Hz, 1H), 4.92 (d, J = 5.8 Hz, 1H), 3.92−3.83 (m, 1H), 1.52 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.8, 136.1, 132.7, 129.7, 129.3, 128.7, 128.4, 128.3, 128.1, 127.5, 126.8, 126.4, 71.4, 47.4. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{16}H_{11}O$, 219.08; found 219.04.

(1S,2R*)-2-(4-Methylphenyl)-1,2-dihydronaphthalen-1-ol* (**3ab**).[12e] Prepared according to the general procedure. Colorless oil (65.2 mg, 92% yield). R_f = 0.18 on silica gel (ethyl acetate/petroleum ether = 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (d, J = 7.3 Hz, 1H), 7.28−7.21 (m, 2H), 7.16−7.08 (m, 5H), 6.67 (dd, J = 9.6, 1.9 Hz, 1H), 6.10 (dd, J = 9.6, 4.1 Hz, 1H), 4.90 (t, J = 6.4 Hz, 1H), 3.81 (ddd, J = 6.1, 4.1, 2.0 Hz, 1H), 2.31 (s, 3H), 1.52 (d, J = 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.3, 136.4, 134.5, 132.9, 130.1, 129.6, 129.3, 128.4, 128.3, 128.1, 126.8, 126.5, 71.5, 47.1, 21.2. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{17}H_{13}O$, 233.10; found 233.29.

(1S,2R*)-2-(4-tert-Butylphenyl)-1,2-dihydronaphthalen-1-ol* (**3ac**).[12e] Prepared according to the general procedure. White solid (70.9 mg, 85% yield). Mp 122−124 °C. R_f = 0.19 on silica gel (ethyl acetate/petroleum ether = 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (t, J = 8.1 Hz, 3H), 7.29−7.22 (m, 2H), 7.17 (dd, J = 15.4, 7.8 Hz, 3H), 6.68 (dd, J = 9.6, 1.9 Hz, 1H), 6.11 (dd, J = 9.6, 4.1 Hz, 1H), 4.91 (t, J = 6.0 Hz, 1H), 3.83 (ddd, J = 6.0, 4.2, 2.0 Hz, 1H), 1.54 (d, J = 6.3 Hz, 1H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 150.4, 136.4, 134.7, 132.9, 130.1, 129.1, 128.4, 128.2, 128.1, 126.9, 126.5, 125.8, 71.5, 47.0, 34.7, 31.5. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{20}H_{19}O$, 275.14; found 275.03.

(1S,2R*)-2-(4-Methoxyphenyl)-1,2-dihydronaphthalen-1-ol* (**3ad**).[12e] Prepared according to the general procedure. Colorless oil (72.6 mg, 96% yield). R_f = 0.13 on silica gel (ethyl acetate/petroleum ether = 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, J = 7.2 Hz, 1H), 7.29−7.23 (m, 2H), 7.17−7.14 (m, 3H), 6.85−6.81 (m, 2H), 6.67 (dt, J = 9.1, 4.5 Hz, 1H), 6.10 (dd, J = 9.6, 4.3 Hz, 1H), 4.92 (d, J = 6.1 Hz, 1H), 3.81 (ddd, J = 6.2, 4.3, 1.9 Hz, 1H), 3.77 (s, 3H), 1.52 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.0, 135.8, 132.8, 130.4, 129.6, 128.4, 128.2, 127.6, 126.7, 126.6, 114.4, 74.7, 55.5, 49.4. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{17}H_{13}O_2$, 249.09; found 249.69.

(1S,2R*)-2-(4-Fluorophenyl)-1,2-dihydronaphthalen-1-ol* (**3ae**).[12e] Prepared according to the general procedure. A white solid (54.0 mg, 75% yield). Mp 100−101 °C. R_f = 0.13 on silica gel (ethyl acetate/petroleum ether = 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35−7.16 (m, 6H), 7.05−6.93 (m, 2H), 6.70 (dd, J = 9.6, 1.8 Hz, 1H), 6.09 (dd, J = 9.6, 4.1 Hz, 1H), 4.91 (dd, J = 7.7, 6.4 Hz, 1H), 3.96−3.63 (m, 1H), 1.47 (d, J = 8.3 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 162.4 (d, $^1J_{C-F}$ = 243.8 Hz), 136.2, 133.5 (d, $^4J_{C-F}$ = 2.5 Hz), 132.7, 131.0 (d, $^3J_{C-F}$ = 7.5 Hz), 129.8, 128.6, 128.5, 128.4, 126.7, 126.6, 115.6 (d, $^2J_{C-F}$ = 20.0 Hz), 71.5, 46.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.4. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{16}H_{10}FO$, 237.07; found 237.23.

(1S,2R*)-2-(4-Chlorophenyl)-1,2-dihydronaphthalen-1-ol* (**3af**).[12e] Prepared according to the general procedure. A white solid (73.7 mg, 96% yield). Mp 113−114 °C. R_f = 0.13 on silica gel (ethyl acetate/petroleum ether = 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35−7.24 (m, 5H), 7.18 (t, J = 7.5 Hz, 3H), 6.71 (dd, J = 9.6, 1.9 Hz, 1H), 6.08 (dd, J = 9.6, 4.1 Hz, 1H), 4.91 (d, J = 5.9 Hz, 1H), 3.89−3.72 (m, 1H), 1.51 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 136.5, 136.1, 133.4, 132.6, 130.9, 129.4, 128.9, 128.7, 128.6, 128.4, 126.8, 126.7, 71.4, 46.9. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{16}H_{10}ClO$, 253.04; found 253.17.

(1S,2R*)-2-(4-Bromophenyl)-1,2-dihydronaphthalen-1-ol* (**3ag**).[12e] Prepared according to the general procedure. Colorless oil (62.1 mg, 69% yield). R_f = 0.13 on silica gel (ethyl acetate/petroleum ether = 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46−7.38 (m, 2H), 7.33−7.24 (m, 3H), 7.19−7.15 (m, 1H), 7.15−7.08 (m, 2H), 6.71 (dd, J = 9.6, 1.9 Hz, 1H), 6.07 (dd, J = 9.6, 4.1 Hz, 1H), 4.91 (dd, J = 7.8, 6.2 Hz, 1H), 3.81 (ddd, J = 6.0, 4.1, 2.0 Hz, 1H), 1.44 (t, J = 7.1 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.0, 136.1, 132.6, 131.9, 131.2, 129.3, 128.7, 128.6, 128.4, 126.8, 126.7, 121.5, 71.4, 47.0. HRMS (ESI-ion trap) m/z: $[M + Cl]^-$ calcd for $C_{16}H_{13}BrClO$, 334.9838; found 334.9833.

(1S,2R*)-2-(3-Chlorophenyl)-1,2-dihydronaphthalen-1-ol* (**3ah**).[12e] Prepared according to the general procedure. Colorless oil (75.3 mg, 98% yield). R_f = 0.21 on silica gel (ethyl acetate/petroleum ether = 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35−7.24 (m, 6H), 7.20−7.14 (m, 2H), 6.72 (dd, J = 9.6, 2.1 Hz, 1H), 6.08 (dd, J = 9.6, 3.8 Hz, 1H), 4.94−4.82 (m, 1H), 3.84 (ddd, J = 5.9, 3.8, 2.2 Hz, 1H), 1.46 (d, J = 9.7 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.5, 136.0, 134.6, 132.5, 130.0, 129.7, 129.1, 128.8, 128.7, 128.4, 127.7, 127.6, 127.0, 126.8, 71.4, 47.3. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{16}H_{10}ClO$, 253.04; found 253.04.

(1S,2R*)-2-(2-Chlorophenyl)-1,2-dihydronaphthalen-1-ol* (**3ai**).[12e] Prepared according to the general procedure. Colorless oil (71.4 mg, 93% yield). R_f = 0.19 on silica gel (ethyl acetate/petroleum ether = 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (dt, J = 6.3, 2.9 Hz, 1H), 7.40−7.31 (m, 3H), 7.29−7.18 (m, 4H), 6.73 (dd, J = 9.6, 2.7 Hz, 1H), 6.04 (ddd, J = 9.6, 2.9, 0.8 Hz, 1H), 4.88 (t, J = 5.2 Hz, 1H), 4.48 (dt, J = 5.3, 2.9 Hz, 1H), 1.54 (d, J = 5.8 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.1, 135.4, 134.4, 132.3, 131.2, 129.8, 129.2, 129.0, 128.6, 128.5, 128.3, 128.2, 127.2, 126.9, 69.4, 44.2. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{16}H_{10}ClO$, 253.04; found 253.70.

(1S,2R*)-2-(4-Nitrophenyl)-1,2-dihydronaphthalen-1-ol* (**3aj**). Prepared according to the general procedure. A pale yellow solid (48.1 mg, 60% yield). Mp 122−123 °C. R_f = 0.3 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, J = 7.2 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 7.31 (qd, J = 8.6, 1.9 Hz, 3H), 7.21 (d, J = 7.3 Hz, 1H), 6.77 (dd, J = 9.6, 2.0 Hz, 1H), 6.08 (dd, J = 9.6, 3.8 Hz, 1H), 4.94 (t, J = 6.6 Hz, 1H), 3.96 (ddd, J = 5.7, 3.8, 2.3 Hz, 1H), 1.58−1.54 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 147.4, 146.7, 135.7, 132.3, 130.4, 129.2, 129.0, 128.7, 128.3,

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127.0, 126.9, 123.8, 71.4, 47.5. HRMS (ESI-ion trap) m/z: $[M - H]^-$ calcd for $C_{16}H_{12}NO_3$, 266.0823; found 266.0815.

(1S,2R*)-2-(4-Trifluoromethylphenyl)-1,2-dihydronaphthalen-1-ol* (**3ak**).[12f] Prepared according to the general procedure. White solid (63.5 mg, 73% yield). Mp 112−114 °C. R_f = 0.11 on silica gel (ethyl acetate/petroleum ether = 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, J = 8.1 Hz, 2H), 7.40−7.24 (m, 5H), 7.19 (d, J = 7.4 Hz, 1H), 6.74 (dd, J = 9.6, 1.9 Hz, 1H), 6.09 (dd, J = 9.6, 3.9 Hz, 1H), 5.03−4.78 (m, 1H), 3.92 (t, J = 5.5 Hz, 1H), 1.47 (d, J = 8.1 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 142.6, 136.0, 132.5, 129.9, 129.6 (q, $^2J_{C-F}$ = 30.0 Hz), 129.0, 128.9, 128.8, 128.6, 126.9, 126.8, 124.8 (q, $^1J_{C-F}$ = 271.3 Hz), 125.6 (q, $^3J_{C-F}$ = 3.7 Hz), 71.5, 47.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.46. HRMS (ESI-ion trap) m/z: $[M - H]^-$ calcd for $C_{17}H_{12}F_3O$, 289.0846; found 289.0834.

(1S,2R*)-2-(2,5-Dimethylphenyl)-1,2-dihydronaphthalen-1-ol* (**3al**).[2h] Prepared according to the general procedure. Colorless oil (69.0 mg, 92% yield). R_f = 0.27 on silica gel (ethyl acetate/petroleum ether = 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (dt, J = 7.5, 4.1 Hz, 2H), 7.27−7.22 (m, 1H), 7.21−7.16 (m, 1H), 7.11 (d, J = 7.1 Hz, 2H), 7.01 (t, J = 8.7 Hz, 1H), 6.71 (dd, J = 9.6, 2.7 Hz, 1H), 6.06 (dd, J = 9.6, 2.4 Hz, 1H), 4.74 (t, J = 5.1 Hz, 1H), 4.16 (dt, J = 5.4, 2.9 Hz, 1H), 2.37 (s, 3H), 2.27 (s, 3H), 1.54 (d, J = 5.6 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 136.9, 136.0, 135.4, 133.5, 132.7, 130.8, 130.7, 130.2, 128.9, 128.2, 128.1, 128.03, 128.01, 126.8, 69.6, 43.5, 21.3, 19.4. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{18}H_{15}O$, 247.11; found 247.21.

(1S,2R*)-2-(2,4,6-Trimethylphenyl)-1,2-dihydronaphthalen-1-ol* (**3am**). Prepared according to the general procedure. Colorless oil (30.9 mg, 39% yield). R_f = 0.27 on silica gel (ethyl acetate/petroleum ether = 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (dd, J = 12.3, 4.6 Hz, 2H), 7.29−7.19 (m, 2H), 6.92 (s, 2H), 6.60 (dd, J = 9.6, 3.3 Hz, 1H), 6.18 (d, J = 9.6 Hz, 1H), 4.74 (t, J = 4.1 Hz, 1H), 4.21 (dt, J = 5.2, 2.8 Hz, 1H), 2.50 (s, 3H), 2.35 (s, 3H), 2.28 (s, 3H), 1.54 (d, J = 4.4 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 139.2, 137.2, 136.5, 135.3, 133.0, 132.8, 132.4, 131.2, 129.6, 129.3, 129.2, 127.5, 127.0, 124.2, 70.2, 43.4, 21.7, 21.3, 20.9. HRMS (ESI-ion trap) m/z: $[M - CH_3]^+$ calcd for $C_{18}H_{17}O$, 249.1274; found 249.1273.

(1S,2R*)-2-([1,1′-Biphenyl]-4-yl)-1,2-dihydronaphthalen-1-ol* (**3an**). Prepared according to the general procedure. A white solid (39.4 mg, 44% yield). Mp 132−133 °C. R_f = 0.2 on silica gel (ethyl acetate/petroleum ether = 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58−7.51 (m, 4H), 7.42 (t, J = 7.6 Hz, 2H), 7.38−7.24 (m, 6H), 7.20−7.16 (m, 1H), 6.72 (dd, J = 9.6, 1.9 Hz, 1H), 6.15 (dd, J = 9.6, 4.1 Hz, 1H), 4.97 (d, J = 5.9 Hz, 1H), 3.91 (ddd, J = 6.0, 4.1, 2.0 Hz, 1H), 1.57 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.9, 140.5, 136.9, 136.3, 132.8, 129.9, 129.8, 129.0, 128.6, 128.5, 128.3, 127.6, 127.5, 127.2, 126.9, 126.6, 71.6, 47.2. HRMS (ESI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{22}H_{15}O$, 295.1123; found 295.1122.

(1S,2R*)-1,2-Dihydro-[1′,2-binaphthalen]-1-ol* (**3ao**).[3b] Prepared according to the general procedure. Colorless oil (70.2 mg, 86% yield). R_f = 0.22 on silica gel (ethyl acetate/petroleum ether = 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, J = 8.4 Hz, 1H), 7.88−7.82 (m, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.52−7.38 (m, 4H), 7.28 (dd, J = 11.1, 4.3 Hz, 2H), 7.23−7.19 (m, 1H), 7.18 (d, J = 1.4 Hz, 1H), 6.74 (dt, J = 11.2, 5.6 Hz, 1H), 6.14 (ddd, J = 9.6, 2.9, 0.9 Hz, 1H), 4.87 (t, J = 5.2 Hz, 1H), 4.81−4.65 (m, 1H), 1.38 (d, J = 5.8 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 135.2, 134.7, 134.1, 132.6, 131.9, 130.3, 129.2, 128.9, 128.3, 128.2, 128.1, 128.0, 127.0, 126.8, 126.4, 125.8, 125.6, 123.1, 70.3, 42.8. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{20}H_{13}O$, 269.10; found 269.00.

(1S,2R*)-1,2-Dihydro-[2,2′-binaphthalen]-1-ol* (**3ap**).[12e] Prepared according to the general procedure. Colorless oil (69.4 mg, 85% yield). R_f = 0.22 on silica gel (ethyl acetate/petroleum ether = 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73−7.66 (m, 4H), 7.40−7.34 (m, 2H), 7.27−7.19 (m, 3H), 7.15 (ddd, J = 17.6, 11.7, 4.4 Hz, 2H), 6.68 (dd, J = 9.6, 2.0 Hz, 1H), 6.12 (dd, J = 9.6, 4.0 Hz, 1H), 4.91 (t, J = 6.5 Hz, 1H), 3.94 (ddd, J = 6.0, 4.0, 2.1 Hz, 1H), 1.44 (d, J = 7.3 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 136.3, 135.5, 133.6, 133.0, 132.9, 129.8, 128.7, 128.6, 128.5, 128.3, 128.0, 127.8, 127.5, 127.0, 126.7, 126.3, 126.0, 71.5, 47.6. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{20}H_{13}O$, 269.10; found 268.88.

(1S,2R*)-5,8-Dimethoxy-2-phenyl-1,2-dihydronaphthalen-1-ol* (**3ba**).[12e] Prepared according to the general procedure. Colorless oil (77.0 mg, 91% yield). R_f = 0.27 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51−7.38 (m, 4H), 7.35−7.28 (m, 1H), 7.09 (dd, J = 9.8, 3.0 Hz, 1H), 6.81 (dd, J = 19.0, 8.8 Hz, 2H), 6.30−6.04 (m, 1H), 5.09 (s, 1H), 3.91−3.76 (m, 7H), 1.60 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.5, 149.7, 140.2, 128.7, 128.4, 128.2, 127.0, 123.4, 122.6, 120.6, 111.5, 110.8, 67.6, 56.4, 56.1, 48.4. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{18}H_{15}O_3$, 279.10; found 278.65.

(1S,2R*)-5,8-Dimethoxy-2-(p-tolyl)-1,2-dihydronaphthalen-1-ol* (**3bb**).[12e] Prepared according to the general procedure. White solid (82.6 mg, 93% yield). Mp 101−102 °C. R_f = 0.31 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 7.00 (dd, J = 9.8, 3.2 Hz, 1H), 6.78−6.68 (m, 2H), 6.10−6.01 (m, 1H), 4.99 (td, J = 4.8, 1.4 Hz, 1H), 3.74 (d, J = 5.2 Hz, 6H), 3.71−3.66 (m, 1H), 2.29 (s, 3H), 1.52−1.49 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 151.0, 150.0, 137.4, 136.8, 129.5, 129.4, 129.1, 124.5, 122.8, 122.2, 111.6, 111.1, 64.5, 56.5, 56.4, 47.0, 21.3. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{19}H_{17}O_3$, 293.11; found 292.84.

(1S,2R*)-2-(4-Fluorophenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol* (**3be**). Prepared according to the general procedure. White solid (83.7 mg, 93% yield). Mp 117−118 °C. R_f = 0.25 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47−7.36 (m, 2H), 7.10 (dq, J = 5.0, 3.2 Hz, 3H), 6.85 (q, J = 9.0 Hz, 2H), 6.13−6.06 (m, 1H), 5.12−5.03 (m, 1H), 3.86 (d, J = 6.5 Hz, 6H), 3.82−3.78 (m, 1H), 1.62 (d, J = 5.4 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 162.1 (d, $^1J_{C-F}$ = 243.8 Hz), 150.8, 149.9, 136.4 (d, $^4J_{C-F}$ = 3.2 Hz), 130.8 (d, $^3J_{C-F}$ = 7.9 Hz), 129.0, 124.4, 122.4 (d, $^2J_{C-F}$ = 16.6 Hz), 115.6, 115.4, 111.6, 111.2, 64.5, 56.4, 56.3, 46.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −116.1. HRMS (ESI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{18}H_{14}FO_3$, 297.0927; found 297.0928.

(1S,2R*)-2-(4-Chlorophenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol* (**3bf**).[12e] Prepared according to the general procedure. White solid (83.4 mg, 88% yield). Mp 114−116 °C. R_f = 0.3 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (s, 4H), 7.09 (dd, J = 9.8, 3.2 Hz, 1H), 6.82 (q, J = 9.0 Hz, 2H), 6.09−6.01 (m, 1H), 5.06 (t, J = 4.5 Hz, 1H), 3.82 (d, J = 6.8 Hz, 6H), 3.77−3.73 (m, 1H), 1.60 (d, J = 5.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.8, 149.9, 139.3, 132.9, 130.7, 128.8, 128.6, 124.4, 122.5, 122.4, 111.7, 111.2, 64.5, 56.4, 56.3, 46.8. HRMS (ESI-ion trap) m/z: $[M - OCH_3]^-$ calcd for $C_{17}H_{14}ClO_2$, 285.0677; found 285.0678.

(1S,2R*)-2-(4-Bromophenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol* (**3bg**).[12e] Prepared according to the general procedure. White solid (61.6 mg, 57% yield). Mp 106−107 °C. R_f = 0.29 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 7.01 (dd, J = 9.8, 3.1 Hz, 1H), 6.74 (q, J = 9.0 Hz, 2H), 5.98 (dd, J = 9.8, 1.3 Hz, 1H), 4.98 (t, J = 4.1 Hz, 1H), 3.74 (d, J = 7.3 Hz, 6H), 3.66 (d, J = 1.9 Hz, 1H), 1.54 (d, J = 5.3 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 150.8, 149.9, 139.8, 131.7, 131.1, 128.5, 124.4, 122.5, 122.4, 121.0, 111.7, 111.2, 64.4, 56.4, 56.3, 46.9. MS (EI) m/z: $[M - H]^-$ calcd for $C_{18}H_{16}BrO_3$, 359.02; found 358.81.

(1S,2R*)-2-(3-Chlorophenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol* (**3bh**).[12f] Prepared according to the general procedure. Colorless oil (92.9 mg, 98% yield). R_f = 0.24 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, J = 7.0 Hz, 1H), 7.26−7.23 (m, 2H), 7.21 (ddd, J = 6.6, 4.2, 1.8 Hz, 1H), 7.02 (dd, J = 9.8, 3.2 Hz, 1H), 6.75 (q, J = 9.0 Hz, 2H), 6.07−5.91 (m, 1H), 5.01 (t, J = 4.1 Hz, 1H), 3.75 (d, J = 5.3 Hz, 6H), 3.70−3.66 (m, 1H), 1.54−1.51 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 150.8, 149.9, 142.9, 134.5, 129.9, 129.5, 128.2, 127.6, 127.3, 124.4, 122.6, 122.4, 111.7, 111.2, 64.4, 56.4, 56.3, 47.2. MS (EI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{17}ClO_3Na$, 339.08; found 338.84.

(1S,2R*)-2-(2-Chlorophenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol* (**3bi**).[10b] Prepared according to the general procedure. White solid (87.2 mg, 92% yield). Mp 98−99 °C. R_f = 0.3 on silica gel

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(ethyl acetate/petroleum ether = 1:5, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (dd, J = 7.6, 1.6 Hz, 1H), 7.46 (dd, J = 7.9, 1.3 Hz, 1H), 7.34 (td, J = 7.5, 1.3 Hz, 1H), 7.28 (dd, J = 7.5, 1.9 Hz, 1H), 7.15 (dd, J = 9.8, 3.2 Hz, 1H), 6.86 (q, J = 9.0 Hz, 2H), 6.12−6.03 (m, 1H), 5.26 (t, J = 4.6 Hz, 1H), 4.42−4.34 (m, 1H), 3.86 (d, J = 3.9 Hz, 6H), 1.54 (d, J = 5.6 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 150.8, 149.7, 137.9, 134.1, 131.5, 129.4, 128.6, 128.3, 126.8, 124.1, 122.2, 122.1, 111.5, 111.0, 61.6, 56.3, 56.2, 43.9. HRMS (ESI-ion trap) m/z: [M − H]$^-$ calcd for $C_{18}H_{16}ClO_3$, 315.0793; found 315.0788.

(1S,2R*)-2-(2,5-Dimethylphenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol* (**3bl**). Prepared according to the general procedure. Colorless oil (84.7 mg, 91% yield). R_f = 0.11 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 (s, 1H), 7.09−6.99 (m, 2H), 6.95 (dd, J = 7.7, 1.3 Hz, 1H), 6.75 (q, J = 9.0 Hz, 2H), 6.07−5.99 (m, 1H), 5.01 (t, J = 3.2 Hz, 1H), 3.96−3.92 (m, 1H), 3.75 (d, J = 7.8 Hz, 6H), 2.28 (d, J = 8.5 Hz, 6H), 1.45 (d, J = 4.2 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 151.1, 149.8, 138.1, 135.8, 133.2, 130.6, 130.5, 130.4, 128.0, 124.2, 122.8, 121.9, 111.7, 111.1, 61.9, 56.5, 56.4, 43.5, 21.3, 19.3. HRMS (ESI-ion trap) m/z: [M − 3H]$^-$ calcd for $C_{20}H_{19}O_3$, 307.1334; found 307.1334.

(1S,2R*)-6,7-Dibromo-2-phenyl-1,2-dihydronaphthalen-1-ol* (**3ca**).[12e] Prepared according to the general procedure. Colorless oil (108.8 mg, 96% yield). R_f = 0.29 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (s, 1H), 7.33 (s, 1H), 7.23−7.18 (m, 3H), 7.09 (dt, J = 4.3, 2.4 Hz, 2H), 6.52 (dd, J = 9.7, 1.5 Hz, 1H), 6.13 (dd, J = 9.6, 4.8 Hz, 1H), 4.88 (t, J = 7.3 Hz, 1H), 3.75 (ddd, J = 6.5, 4.8, 1.6 Hz, 1H), 1.45 (d, J = 8.7 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.3, 135.8, 133.7, 132.0, 131.6, 131.0, 129.5, 129.1, 128.1, 126.6, 124.2, 123.8, 70.5, 46.9. MS (EI) m/z: [M − 3H]$^-$ calcd for $C_{16}H_9Br_2O$, 376.93; found 377.42.

(1S,2R*)-6,7-Dibromo-2-(4-tert-butylphenyl)-1,2-dihydronaphthalen-1-ol* (**3cc**). Prepared according to the general procedure. Colorless oil (114.6 mg, 88% yield). R_f = 0.38 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (s, 1H), 7.39 (s, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 6.58 (t, J = 7.9 Hz, 1H), 6.19 (dd, J = 9.6, 4.8 Hz, 1H), 4.95 (t, J = 10.4 Hz, 1H), 3.80 (t, J = 5.6 Hz, 1H), 1.56 (s, 1H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 151.1, 150.4, 142.9, 137.5, 133.8, 132.3, 131.6, 130.9, 129.2, 126.4, 126.1, 125.7, 70.5, 46.4, 34.7, 31.5. HRMS (ESI-ion trap) m/z: [M − 3H]$^-$ calcd for $C_{20}H_{17}Br_2O$, 432.9627; found 432.9631.

(1S,2R*)-6,7-Dibromo-2-(4-methoxyphenyl)-1,2-dihydronaphthalen-1-ol* (**3cd**).[12e] Prepared according to the general procedure. Colorless oil (107.7 mg, 88% yield). R_f = 0.17 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (s, 1H), 7.31 (s, 1H), 7.00−6.97 (m, 2H), 6.76−6.73 (m, 2H), 6.49 (dd, J = 9.6, 1.3 Hz, 1H), 6.11 (dd, J = 9.6, 5.0 Hz, 1H), 4.90−4.86 (m, 1H), 3.69 (d, J = 4.3 Hz, 4H), 1.45 (d, J = 9.1 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 159.5, 137.6, 133.8, 132.4, 131.5, 130.9, 130.6, 127.1, 126.3, 124.1, 123.8, 114.5, 70.4, 55.5, 46.0. MS (EI) m/z: [M − 3H]$^-$ calcd for $C_{17}H_{11}Br_2O_2$, 406.91; found 406.86.

(1S,2R*)-6,7-Dibromo-2-(4-chlorophenyl)-1,2-dihydronaphthalen-1-ol* (**3cf**).[12e] Prepared according to the general procedure. Colorless oil (114.9 mg, 93% yield). R_f = 0.3 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (s, 1H), 7.34 (s, 1H), 7.21−7.20 (m, 1H), 7.19 (s, 1H), 7.05−7.00 (m, 2H), 6.55−6.51 (m, 1H), 6.09 (dd, J = 9.6, 4.8 Hz, 1H), 4.89 (t, J = 7.4 Hz, 1H), 3.72 (ddd, J = 6.4, 4.9, 1.5 Hz, 1H), 1.41 (d, J = 8.7 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.1, 134.4, 134.0, 133.5, 131.6, 131.5, 131.1, 130.9, 129.2, 126.9, 124.4, 124.1, 70.4, 46.3. MS (EI) m/z: [M − 3H]$^-$ calcd for $C_{16}H_8Br_2ClO$, 410.86; found 410.81.

(1S,2R*)-6,7-Dibromo-2-(4-bromophenyl)-1,2-dihydronaphthalen-1-ol* (**3cg**).[12e] Prepared according to the general procedure. Colorless oil (102.6 mg, 75% yield). R_f = 0.25 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (s, 1H), 7.36−7.33 (m, 3H), 7.00−6.94 (m, 2H), 6.56−6.51 (m, 1H), 6.09 (dd, J = 9.6, 4.8 Hz, 1H), 4.89 (t, J = 7.3 Hz, 1H), 3.73−3.68 (m, 1H), 1.50 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 137.0, 135.0, 133.5, 132.1, 131.6, 131.4, 131.2, 131.1, 126.9, 124.4, 124.1, 122.1, 70.3, 46.3. MS (EI) m/z: [M − 3H]$^-$ calcd for $C_{16}H_8Br_3O$, 454.81; found 454.92.

(1S,2R*)-6,7-Dibromo-2-(4-nitrophenyl)-1,2-dihydronaphthalen-1-ol* (**3cj**). Prepared according to the general procedure. Pale yellow solid (91.3 mg, 72% yield). R_f = 0.21 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11−8.08 (m, 2H), 7.51 (s, 1H), 7.38−7.29 (m, 3H), 6.61 (dd, J = 9.7, 1.6 Hz, 1H), 6.11 (dd, J = 9.6, 4.5 Hz, 1H), 4.93 (t, J = 7.0 Hz, 1H), 3.87 (ddd, J = 6.2, 4.6, 2.4 Hz, 1H), 1.50 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 147.4, 144.4, 136.3, 132.9, 131.5, 131.2, 130.3, 130.2, 127.3, 124.6, 124.1, 123.7, 70.2, 46.6. HRMS (ESI-ion trap) m/z: [M − 3H]$^-$ calcd for $C_{16}H_8Br_2NO_3$, 421.8851; found 421.8852.

(1S,2R*)-6,7-Dimethoxy-2-phenyl-1,2-dihydronaphthalen-1-ol* (**3da**). Prepared according to the general procedure. White solid (62.6 mg, 74% yield). Mp 121−122 °C. R_f = 0.24 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (qt, J = 10.7, 5.4 Hz, 5H), 6.92 (s, 1H), 6.72 (s, 1H), 6.62 (dd, J = 9.6, 2.0 Hz, 1H), 6.03 (dd, J = 9.6, 3.9 Hz, 1H), 4.89−4.81 (m, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.84 (ddd, J = 5.9, 3.9, 2.2 Hz, 1H), 1.46 (d, J = 7.9 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 148.8, 148.7, 138.2 129.5, 129.0, 128.9, 128.0, 127.9, 127.6, 125.7, 110.7, 110.1, 71.5, 56.2, 56.1, 47.6. HRMS (ESI-ion trap) m/z: [M + Cl]$^-$ calcd for $C_{18}H_{18}ClO_3$, 317.0939; found 317.0940.

(1S,2R*)-2-(4-Chlorophenyl)-6,7-dimethoxy-1,2-dihydronaphthalen-1-ol* (**3df**). Prepared according to the general procedure. White solid (68.3 mg, 72% yield). Mp 133−135 °C. R_f = 0.23 on silica gel (ethyl acetate/petroleum ether = 1:5, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27−7.24 (m, 2H), 7.18−7.10 (m, 2H), 6.91 (s, 1H), 6.72 (s, 1H), 6.60 (dd, J = 9.6, 1.6 Hz, 1H), 5.91 (dd, J = 9.5, 4.2 Hz, 1H), 4.67 (t, J = 6.0 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.76 (ddd, J = 6.2, 4.2, 1.7 Hz, 1H), 1.92 (d, J = 6.0 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 149.0, 148.9, 139.3, 133.1, 129.9, 129.0, 127.8, 127.6, 127.3, 125.5, 110.7, 110.2, 74.4, 56.2, 56.1, 49.6. HRMS (ESI-ion trap) m/z: [M − OH]$^-$ calcd for $C_{18}H_{16}ClO_2$, 299.0833; found 299.0845.

(1S,2R*)-2-Phenyl-1,2-dihydrotriphenylen-1-ol* (**3ea**).[12e] Prepared according to the general procedure. White solid (88.9 mg, 92% yield). Mp 156−158 °C. R_f = 0.23 on silica gel (ethyl acetate/petroleum ether = 1:10, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70−8.64 (m, 2H), 8.27−8.22 (m, 1H), 8.21−8.14 (m, 1H), 7.64−7.50 (m, 5H), 7.48−7.45 (m, 2H), 7.42−7.37 (m, 2H), 7.34−7.28 (m, 1H), 6.41 (ddd, J = 9.8, 2.3, 1.5 Hz, 1H), 5.36 (t, J = 4.7 Hz, 1H), 3.98−3.89 (m, 1H), 1.60 (d, J = 5.7 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.3, 131.1, 131.0, 130.8, 130.1, 129.4, 129.0, 128.9, 128.8, 127.6, 127.5, 127.2, 127.1, 126.8, 126.6, 124.3, 124.2, 124.0, 123.3, 123.2, 67.8, 48.2. HRMS (ESI-ion trap) m/z: [M − H]$^-$ calcd for $C_{24}H_{17}O$, 321.1285; found 321.1273.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00667.

X-ray crystal characterization data for compound **3da** (CIF)

Experimental procedures and copies of ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yangdq@scnu.edu.cn. Phone: +86 20 39310068. Fax: +86 20 31040403.

Notes

The authors declare no competing financial interest.

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