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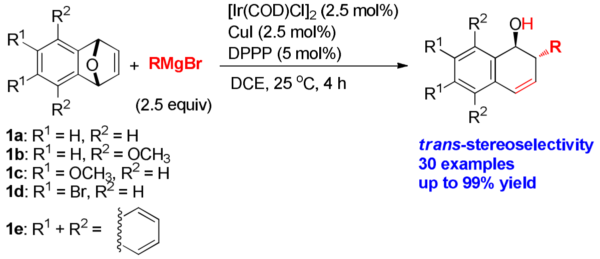
Iridium/Copper Co-Catalyzed *anti*-Stereoselective Ring-Opening of Oxabenzonorbornadienes with Grignard Reagents

Guo Cheng, Wen Yang, Yue Li, 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

*E-mail: yangdq@scnu.edu.cn (D.Y.). Phone: +86 20 31040403; Fax: +86 20 31040403.



ABSTRACT: Cooperative catalysis has been widely considered as one of the most powerful strategy to improve the synthetic efficiency. A new iridium/copper co-catalyst was developed for the ring-opening reaction of oxabenzonorbornadienes with a wide variety of Grignard reagents, which afforded the corresponding *anti*-2-substituted-1,2-dihydronaphthalen-1-ols in high yields (up to 99% yield) under mild conditions. The effects of catalyst loading, Lewis acid, Grignard reagent loading and reaction temperature on the yield were investigated. To the best of our knowledge, it represents the first example in ring-opening reactions of oxabicyclic alkenes with Grignard reagent nucleophiles in a *trans*-stereoselective manner.

KEYWORDS: Iridium/copper co-catalyst; Oxabenzonorbornadienes; Grignard reagents; Ring-opening reaction; *trans*-Stereoselective

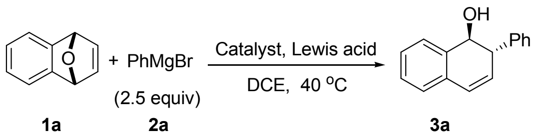
INTRODUCTION

Development of new methods and efficient strategies for carbon–carbon bond-forming processes that can create multiple stereocenters is one of the challenges in synthetic organic chemistry. The transition metal-catalyzed ring-opening reaction of oxa- and azabicyclic alkenes have provided an important method to construct C–C and C–X bond formation.[1] This process may afford valuable hydronaphthalene scaffolds of a wide range of natural products and bioactive molecules.[2] In the past several decades, a large variety of carbanion nucleophiles have been used to perform this transformation. Initially, organolithium reagents[3], organozincs[4], and organocuprates[5] showed limited success in affording *syn*-addition ring-opening products in moderate to good yields. In sharp contrast, Grignard reagent, which is the most accessible organometallic reagent, has limited applications in catalytic reactions. The main limitations of Grignard reagent are its high reactivity, which results in a rapid, and its sensitivity to reaction conditions.[6] Prior to 1996, Lautens *et al.* reported the nickel-catalyzed ring-opening of [2.2.1]oxabicyclic alkenes, in which a large excess of Grignard reagents was used to generate mainly *syn*-stereoselective ring-opening products.[7] Later on, copper-catalyzed *anti*-stereoselective ring-opening of oxabicyclic alkenes with Grignard reagents was gradually reported in succession by Carretero's group[8], Zhou's group[9], and Alexakis's group[10], respectively. In addition, Nakamura's group has also described that iron-catalyzed *syn*-stereoselective ring opening of [2.2.1] and [3.2.1]oxabicyclic alkenes with Grignard reagents.[11] More recently, our group has reported a new platinum-catalyzed *anti*-stereoselective ring-opening of oxabicyclic alkenes with various Grignard reagents, which affords the corresponding *anti*-2-substituted-1,2-dihydronaphthalen-1-ols with moderate to good yields.[12] Furthermore, our group has been committed to the iridium-catalyzed *anti*-stereoselective ring-opening of benzo- and alkyl-substituted oxa- and azabicyclic alkenes, using amines[13], phenols[14], alcohols[15], or carboxylic acids[16] as nucleophiles. While this mono-catalysis strategy has successfully delivered vast numbers of new reactions over many decades, multi-catalysis concepts have recently began to emerge, which can allow access to many difficult or unattainable transformations. In particular, synergistic catalysis, wherein two catalysts and two catalytic cycles work in concert to create a single new bond, has emerged as a powerful new mechanistic approach to reaction engineering. Therefore, cooperative catalysis has been widely considered as one of the most powerful strategy to improve the synthetic efficiency, in many cases enabling chemical reactions that are impossible or inefficient using traditional single catalyst method.[17] On the other hand, the cooperative effect of multicatalyst might be expected to improve the reactivity and selectivity. The use of multiple catalyst systems can enlarge the substrate and reaction scope for the reaction design, improve the reactivity, and benefit the control of selectivity.[18] Recently, Fan's group has reported a transition metal/Lewis acid cooperative catalysis for asymmetric ring-opening reaction of oxa- and azabenzonorbornadienes with terminal alkynes[19a], phenols[19b] or amines[19c, 19d]. To the best of our knowledge, however, iridium/copper co-catalyzed ring opening of oxabicyclic alkenes with Grignard reagents remains in demand. So our continuous interest in developing ring-opening of oxa- and azabicyclic alkenes prompted us to further explore and expand the scope of this type of reaction in the presence of a new iridium/copper co-catalyst. Against the above background, we report $[Ir(COD)Cl]_2$ and Lewis acid CuI co-catalyst for ring opening of oxabenzonorbornadienes with Grignard reagents, we have afforded the biologically corresponding 2-substituted-1,2-dihydronaphthalen-1-ols in high yields (up to 99% yield). According to our laboratory previous work of iridium catalytic system, we have obtained *trans*-configuration of the product rather than *cis* by X-ray diffraction analysis.[13-16] Furthermore, the effects of catalyst loading, Lewis acid, Grignard reagent and temperature on the yield were investigated. It represents the first example in ring-opening reactions of oxabicyclic alkenes with Grignard reagent nucleophiles in a *trans*-stereoselective manner.

Results and discussion

To explore the ring-opening reactions and optimize the reaction conditions, an achiral ligand 1,3-bis(diphenylphosphino)propane (DPPP) was first chosen to validate the catalytic activity of the iridium complex in the ring-opening reactions of oxabenzonorbornadiene **1a** with phenyl magnesium bromide **2a** (2.5 equiv) as benchmark substrates in 1,2-dichloroethane (DCE) at 40 °C. The desired ring-opening product **3a** was achieved in poor yield (*anti/syn* > 99/1, 15%) (Table 1, entry 1), implying that $[Ir(COD)Cl]_2$ may be used the catalyst precursor. Further optimization of the reaction conditions, many Lewis acids were added, such as $ZnCl_2$, ZnI_2 and $AgSbF_6$ as additives in this reaction, and the yields of this reaction were only slightly improved (Table 1, entries 2-5). When silver(I) triflate (AgOTf) was employed in the presence of $[Ir(COD)Cl]_2$ with DPPP, the yield was increased to 65% (Table 1, entry 5). On the other hand, we have tried $CuCl_2$ and $Cu(OAc)_2$ as Lewis catalysts, which still afforded excellent yields (Table 1, entry 6-7). Fortunately, when $[Ir(COD)Cl]_2$ and CuI were used as co-catalyst, the yield of this reaction can be significantly improved, reaching 94% (Table 1, entry 8). However, when the reaction was carried out with only CuI as catalyst in the absence of $[Ir(COD)Cl]_2$, merely 50% yield were obtained in 10 h (Table 1, entry 9). Meanwhile, the amount of catalyst loading also had a significant impact on the yield (Table 1, entries 10−12).

Table 1. Optimization of Reaction Conditions[a]



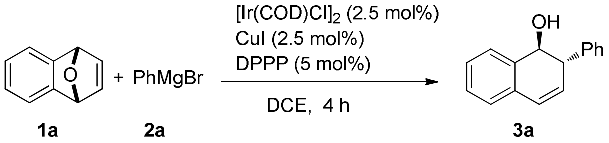
entry	catalyst (mol%)	Lewis acid (mol%)	time (h)	yield (%)
1	$[Ir(COD)CI]_2$ (2.5)/DPPP (5.0)	-	24	15
2	$[Ir(COD)CI]_2$ (2.5)/DPPP (5.0)	$ZnCl_2$ (10.0)	10	35
3	$[Ir(COD)CI]_2$ (2.5)/DPPP (5.0)	ZnI_2 (10.0)	16	30
4	$[Ir(COD)CI]_2$ (2.5)/DPPP (5.0)	$AgSbF_6$ (10.0)	16	28
5	$[Ir(COD)CI]_2$ (2.5)/DPPP (5.0)	AgOTf (10.0)	10	65

6	$[Ir(COD)CI]_2$ (2.5)/DPPP (5.0)	$CuCl_2$ (5.0)	4	89
7	$[Ir(COD)CI]_2$ (2.5)/DPPP (5.0)	$Cu(OAc)_2$ (5.0)	4	80
8	$[Ir(COD)CI]_2$ (2.5)/DPPP (5.0)	CuI (5.0)	4	94
9	DPPP (5.0)	CuI (5.0)	10	50
10	$[Ir(COD)CI]_2$ (1.0)/DPPP (2.0)	CuI (1.0)	4	81
11	**$[Ir(COD)CI]_2$ (2.5)/DPPP (5.0)**	**CuI (2.5)**	**4**	**95**
12	$[Ir(COD)CI]_2$ (2.5)/DPPP (5.0)	CuI (1.0)	4	72

[a] Reaction conditions: $[Ir(COD)Cl]_2$, CuI and DPPP in DCE (2 mL) was stirred for 30 min under N_2 atm. Then, **1a** (28.8 mg, 0.2 mmol) with **2a** (2.5 equiv) were added, and the reaction mixture was stirred at room temperature for indicating period of time.

To further optimize reaction conditions, we then investigated the impact on temperature and Grignard reagent loading for the reaction (Table 2). By examining the effect of temperature, we observed that the best result was at 25 °C (99% yield) (Table 2, entries 1−3). Furthermore, the effect of an amount of Grignard reagent loading on the reactivity was also investigated (Table 2, entries 1, 4 and 5). When the loading of Grignard reagent was decreased to 1.5 equiv, the yield of **3a** was decreased to 82% (Table 2, entry 4). Consequently, the optimum reaction conditions were determined as follows: 2.5 mol% $[Ir(COD)Cl]_2$, 5.0 mol% DPPP, and 2.5 mol% CuI was stirred for 30 min in DCE under N_2 atmosphere; then, **1a** with 2.5 equivalent of Grignard reagent **2a** were added, and the reaction mixture was stirred for 4 h at 25 ^{o}C.

Table 2. Effect of Temperature and Grignard Reagent Loading[a]

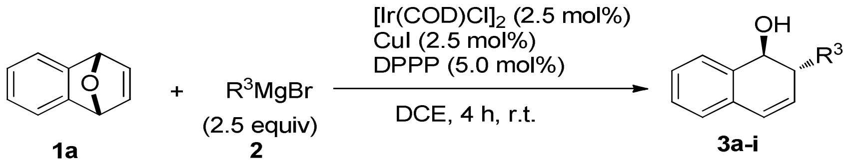


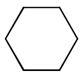
entry	temp (^oC)	**2a** (equiv.)	**3a** yield (%)
1	**25**	**2.5**	**99**
2	40	2.5	95
3	55	2.5	98
4	25	1.5	82
5	25	2.0	97

[a]Reaction conditions: $[Ir(COD)Cl]_2$ (2.5 mol%), CuI (2.5 mol%) and DPPP (5 mol%) in DCE (2 mL) was stirred for 30 min under N_2 atm. **1a** (28.8 mg, 0.2 mmol) with **2a** were added, and the reaction mixture was stirred for 4 h.

With the optimized reaction conditions in hand, we further examined ring-opening of **1a** with various Grignard reagents **2**, and the results are listed in Table 3. It is obvious that the reactivity of aryl Grignard reagents was better than the alkyl Grignard reagents in terms of yields, because the carbanion nucleophilic of aryl group is greater than that of alkyl group (Table 3, entries 1−7 and entries 8−9). Furthermore, the results indicated that the positional property of the methyl on the phenyl ring in aryl Grignard reagents had little effect on reactivity; whatever the substituents in *ortho*-, *meta*- or *para*-positions, high yields were obtained (Table 3, entries 2−4) (up to 98% yield). When the ring-opening of **1a** reacted with aryl Grignard reagents which have electron-withdrawing substituents in *para*-position, the reaction still offered high yields (Table 3, entry 5). However, the ring-opening addition of 4-methoxyphenyl to **1a** lowered the yield to 80% (Table 3, entry 6). Meanwhile, 3-fluorophenyl magnesium bromide as nucleophile for the ring-opening was found to give moderate yield (Table 3, entry 7). Unsuccessfully, 2,4,6-trimethylphenyl magnesium bromide failed to provide the expected product **3j** due to steric hindrance (Table 3, entry 10).

Table 3. Ring-Opening of Oxabenzonorbornadienes with Various Grignard Reagents[a]



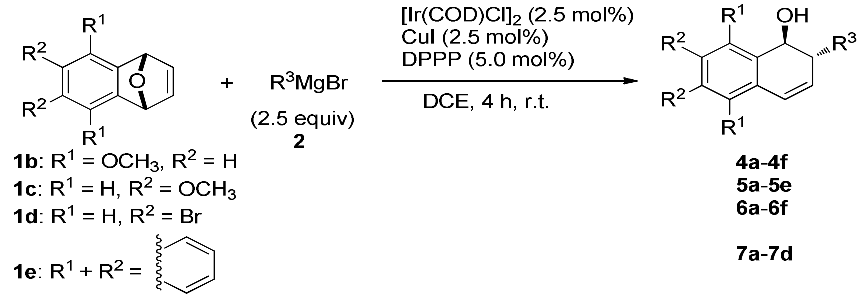
entry	R^3	product	yield (%)
1	C_6H_5	**3a**	99
2	2-$CH_3C_6H_4$	**3b**	98
3	3-$CH_3C_6H_4$	**3c**	96
4	4-$CH_3C_6H_4$	**3d**	97
5	4-ClC_6H_4	**3e**	91
6	4-$CH_3OC_6H_4$	**3f**	80
7	3-FC_6H_4	**3g**	71
8	CH_3	**3h**	22
9		**3i**	35
10	2,4,6-$(CH_3)_3C_6H_2$	**3j**	-

[a]Reaction conditions: [Ir(COD)Cl]$_2$ (2.5 mol%), CuI (2.5 mol%) and DPPP (5 mol%) in DCE (2 mL) was stirred for 30

min under N_2 atm. **1a** (28.8 mg, 0.2 mmol) with **2a** (2.5 equiv) were added, and the reaction mixture was stirred for 4 h.

To extend the scope of this reaction, several types of oxabenzonorbornadienes **1b–e** with various Grignard reagents were also investigated under the standard reaction conditions and the results were summarized in Table 4. The electron-rich substrate **1b** containing 3,6-dimethoxy on the phenyl ring with aryl Grignard reagents afforded high yields (Table 4, entries 1–6). The substrate **1b** with 2-methylphenyl magnesium bromide, owing to its steric hindrance, gave product **4b** in slightly lower yield (67%). On the other hand, electron-rich substrate **1c** containing 4,5-dimethoxy with any aryl Grignard reagents afforded high yields (Table 4, entries 7–11). When compared with electron-deficient **1d** (Table 4, entries 12–17), electron-rich substrate **1c** displayed more reactive than electron-deficient substrate **1d**, and 3-fluorophenyl magnesium bromide for the ring-opening were found to give low yield (45 %) (Table 4, entry 17). Furthermore, substrate **1e** with Grignard reagents showed slightly lower reactivity due to steric hindrance (Table 4, entries 18-21).

Table 4. Ring-Opening of Oxabenzonorbornadienes 1b-e with Various Grignard Reagents[a]



entry	substrate	R^3	product	yield (%)
1	**1b**	C_6H_5	**4a**	96
2	**1b**	$2\text{-}CH_3C_6H_4$	**4b**	67
3	**1b**	$3\text{-}CH_3C_6H_4$	**4c**	97
4	**1b**	$4\text{-}CH_3C_6H_4$	**4d**	97
5	**1b**	$4\text{-}ClC_6H_4$	**4e**	80
6	**1b**	$3\text{-}FC_6H_4$	**4f**	95
7	**1c**	C_6H_5	**5a**	95
8	**1c**	$2\text{-}CH_3C_6H_4$	**5b**	90
9	**1c**	$3\text{-}CH_3C_6H_4$	**5c**	94
10	**1c**	$4\text{-}CH_3C_6H_4$	**5d**	95
11	**1c**	$4\text{-}ClC_6H_4$	**5e**	91
12	**1d**	C_6H_5	**6a**	88
13	**1d**	$2\text{-}CH_3C_6H_4$	**6b**	78
14	**1d**	$3\text{-}CH_3C_6H_4$	**6c**	75
15	**1d**	$4\text{-}CH_3C_6H_4$	**6d**	78
16	**1d**	$4\text{-}ClC_6H_4$	**6e**	75
17	**1d**	$3\text{-}FC_6H_4$	**6f**	45
18	**1e**	C_6H_5	**7a**	85
19	**1e**	$2\text{-}CH_3C_6H_4$	**7b**	88
20	**1e**	$3\text{-}CH_3C_6H_4$	**7c**	80
21	**1e**	$4\text{-}ClC_6H_4$	**7d**	89

[a] Reaction conditions: $[Ir(COD)Cl]_2$ (2.5 mol%), CuI (2.5 mol%) and DPPP (5 mol%) in DCE (2 mL) was stirred for 30 min under N_2 atm. Oxabenzonorbornadiene **1** (0.2 mmol) with **2** (2.5 equiv) were added, and the reaction mixture was stirred for 4 h.

CONCLUSIONS

In summary, we have developed a simple, facile, and straightforward access to an extensive array of *anti*-stereoselective ring-opening of oxabicyclic alkenes with various Grignard reagents in the presence of iridium/copper co-catalyst, which can afford the corresponding *anti*-2-substituted-1,2-dihydronaphthalen-1-ols with good to excellent yields (up to 99% yield). The reaction is wide in scope for both the Grignard reagent and the oxabicyclic alkene. This protocol has the characteristic of mild reaction conditions and excellent yields. To the best of our knowledge, it represents the first example in ring-opening reaction of oxabenzonorbornadienes with carbanion-based nucleophiles giving exclusive *trans*-ring opening product. Further investigations are underway to clarify the mechanism of this transformation and to explore the scope of the co-catalyst system in asymmetric ring opening (ARO) reactions.

EXPERIMENT SECTION

General Procedure for Iridium/Copper Co-Catalyzed *anti*-Stereoselective Ring-Opening Reactions of Oxabenzonorbornadienes 1a–e with Grignard Reagents. A 10.0 mL two-neck round-bottom flask was flame-dried under a stream of nitrogen and cooled to room temperature. $[Ir(COD)Cl]_2$ (3.4 mg, 2.5 mol%), DPPP (4.1 mg, 5 mol%) and CuI (1.0 mg, 2.5 mol%) were simultaneously added followed by the addition of anhydrous DCE (2.0 mL). After the mixture was stirred for about 30 min at room temperature, oxabenzonorbornadiene **1a** (28.8 mg, 0.2 mmol) was added and then the Grignard reagent (0.5 mmol) was added gradually and dropped by a syringe pump. The mixed solution was stirred at room temperature for 4 h until it was completed as judged by thin-layer chromatography. The reaction was quenched by addition of aqueous 1 M NH_4Cl (2.0 mL). The mixture was extracted three times with CH_2Cl_2 (3 × 10 mL). The organic layers were combined, dried over anhydrous $MgSO_4$, filtered. After vacuum evaporation of the solvent and then concentrated to give a crude product which was purified by column chromatography (200–300 mesh silica gels) to give the target product.

(1S,2S*)-2-Phenyl-1,2-dihydronaphthalen-1-ol* ***(3a)***.[12] Prepared according to general procedure. A white solid (44.0 mg, 99% yield). m.p. 86–87 °C. R_f = 0.21 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.1 Hz, 1H), 7.29–7.22 (m, 7H), 7.17–7.14 (m, 1H), 6.64 (dd, *J* = 9.6, 1.8 Hz, 1H), 6.01 (dd, *J* = 9.6, 3.8 Hz, 1H), 4.81 (d, *J* = 7.9 Hz, 1H), 3.78 (ddd, *J* = 7.8, 3.6, 2.2 Hz, 1H), 1.97 (d, *J* = 7.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 140.9, 135.6, 132.6, 129.9, 129.3, 128.7, 128.7, 128.4, 128.2, 128.2, 127.7, 127.2, 126.4, 126.4, 74.4, 50.1. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{16}H_{11}O$, 219.10; found, 219.04.

(1S,2S*)-2-(2-Methylphenyl)-1,2-dihydronaphthalen-1-ol* ***(3b)***. Prepared according to general procedure. Colorless oil (46.3 mg, 98% yield). R_f = 0.25 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.3 Hz, 1H), 7.30–7.07 (m, 7H), 6.68 (dd, *J* = 9.6, 1.8 Hz, 1H), 5.98 (dd, *J* = 9.6, 4.0 Hz, 1H), 4.90–4.78 (m, 1H), 4.18–4.07 (m, 1H), 2.47 (s, 3H), 1.58 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.5, 136.8, 135.6, 132.6, 130.7, 130.1, 128.3, 128.1,

127.6, 127.6, 127.0, 126.7, 126.4, 126.4, 73.8, 45.6, 20.0. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{17}H_{13}O$, 233.0966; found, 233.0966.

(1S,2S*)-2-(3-Methylphenyl)-1,2-dihydronaphthalen-1-ol (**3c**).* Prepared according to general procedure. A white solid (45.3 mg, 96% yield). m.p. 69–70 °C. $R_f = 0.19$ on silica gel (ethyl acetate/petroleum ether 1:20, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, $J = 8.2, 6.4$ Hz, 1H), 7.26 (ddd, $J = 7.6, 5.3, 1.7$ Hz, 2H), 7.21–7.13 (m, 2H), 7.10–7.02 (m, 3H), 6.63 (dd, $J = 9.6, 2.1$ Hz, 1H), 6.00 (dd, $J = 9.6, 3.6$ Hz, 1H), 4.83 (d, $J = 8.4$ Hz, 1H), 3.74 (ddd, $J = 8.4, 3.3, 2.4$ Hz, 1H), 2.32 (s, 3H), 2.05–1.76 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.0, 138.4, 135.8, 132.6, 130.0, 129.2, 128.7, 128.3, 128.0, 127.9, 127.6, 126.3, 126.1, 125.4, 74.4, 50.2, 21.5. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{17}H_{13}O$, 233.0966; found, 233.0966.

(1S,2S*)-2-(4-Methylphenyl)-1,2-dihydronaphthalen-1-ol (**3d**).* Prepared according to general procedure. A white solid (45.8 mg, 97% yield). m.p. 105–106 °C. $R_f = 0.21$ on silica gel (ethyl acetate/petroleum ether 1:20, v/v). ^1H NMR (500 MHz, $CDCl_3$) δ 7.47–7.42 (m, 1H), 7.34–7.28 (m, 2H), 7.22–7.14 (m, 5H), 6.68 (dd, $J = 9.6, 2.1$ Hz, 1H), 6.06 (dd, $J = 9.6, 3.8$ Hz, 1H), 4.84 (dd, $J = 7.8, 5.0$ Hz, 1H), 3.79 (ddd, $J = 7.9, 3.7, 2.1$ Hz, 1H), 2.36 (s, 3H), 2.03 (d, $J = 3.6$ Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 137.8, 136.9, 135.7, 132.7, 130.1, 129.5, 128.4, 128.2, 128.0, 127.5, 126.4, 126.4, 74.4, 49.7, 21.1. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{17}H_{13}O$, 233.0966; found, 233.0966.

(1S,2S*)-2-(4-Chlorophenyl)-1,2-dihydronaphthalen-1-ol (**3e**).*[12] Prepared according to general procedure. A white solid (46.6 mg, 91% yield). m.p. 134–135 °C.

R$_f$ = 0.25 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40–7.34 (m, 1H), 7.26 (ddt, *J* = 7.3, 4.4, 1.9 Hz, 4H), 7.20–7.12 (m, 3H), 6.67 (dd, *J* = 9.6, 1.8 Hz, 1H), 5.99 (dd, *J* = 9.6, 4.0 Hz, 1H), 4.75 (t, *J* = 6.4 Hz, 1H), 3.82–3.75 (m, 1H), 1.97 (d, *J* = 5.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 139.2, 135.2, 133.0, 132.4, 129.7, 129.1, 128.9, 128.5, 128.3, 127.9, 126.6, 126.6, 74.2, 49.4. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{16}H_{10}ClO$, 253.0420; found, 253.0421.

(1S,2S*)-2-(4-Methoxyphenyl)-1,2-dihydronaphthalen-1-ol* ***(3f)***.[12] Prepared according to general procedure. A white solid (40.3 mg, 80% yield). m.p. 84–85 °C. R$_f$ = 0.24 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, *J* = 7.2 Hz, 1H), 7.26 (ddd, *J* = 8.8, 5.7, 1.2 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 3H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.64 (dd, *J* = 9.6, 1.7 Hz, 1H), 6.01 (dd, *J* = 9.6, 3.9 Hz, 1H), 4.78 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.77 (s, 3H), 3.74 (dd, *J* = 5.4, 3.8 Hz, 1H), 1.61 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 158.8, 135.6, 132.6, 130.2, 129.4, 128.1, 128.1, 127.4, 126.4, 126.4, 116.0, 114.8, 114.2, 74.5, 55.3, 49.2. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{17}H_{13}O_2$, 249.0916; found, 249.0917.

(1S,2S*)-2-(3-Fluorophenyl)-1,2-dihydronaphthalen-1-ol* ***(3g)***. Prepared according to general procedure. A white solid (34.1 mg, 71% yield). m.p. 100–101 °C. R$_f$ = 0.20 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 (d, *J* = 7.1 Hz, 1H), 7.26 (ddd, *J* = 14.4, 10.1, 8.2 Hz, 3H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.99–6.87 (m, 2H), 6.73–6.62 (m, 1H), 5.99 (dd, *J* = 9.6, 3.9 Hz, 1H), 4.78 (d, *J* = 7.4 Hz, 1H), 3.79 (dd, *J* = 4.6, 2.3 Hz, 1H), 1.99 (s,

1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 164.2 (d, $^{1}J_{C\text{-}F}$ = 243.8 Hz), 143.4 (d, $^{3}J_{C\text{-}F}$ = 6.9 Hz), 135.3, 132.4, 130.2 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 128.9, 128.5, 128.3, 128.0, 126.6, 126.6, 124.1 (d, $^{4}J_{C\text{-}F}$ = 2.7 Hz), 115.3 (d, $^{2}J_{C\text{-}F}$ = 21.3 Hz), 114.2 (d, $^{2}J_{C\text{-}F}$ = 21.3 Hz), 74.1, 49.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.6. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{16}H_{10}FO$, 237.0716; found, 237.0716.

(1S,2R*)-2-Methyl-1,2-dihydronaphthalen-1-ol* ***(3h)****.*[12] Prepared according to general procedure. A white solid (7.1 mg, 22% yield). m.p. 63–64 °C. R_f = 0.18 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.38 (m, 1H), 7.31–7.21 (m, 3H), 7.13–7.09 (m, 1H), 6.46 (d, J = 9.5 Hz, 1H), 5.93 (dd, J = 9.6, 4.4 Hz, 1H), 4.47 (d, J = 5.9 Hz, 1H), 2.64 (ddd, J = 11.7, 5.9, 1.3 Hz, 1H), 1.07 (d, J = 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 136.6, 132.5, 128.4, 127.6, 127.6, 127.3, 126.5, 126.5, 71.7, 35.3, 14.1. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{11}H_9O$, 157.09; found, 157.08.

(1S,2R*)-2-Cyclohexyl-1,2-dihydronaphthalen-1-ol* ***(3i)****.*[12] Prepared according to general procedure. A white solid (16.0 mg, 35% yield). m.p. 81–82 °C. R_f = 0.22 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.21 (m, 3H), 7.13 (t, J = 9.0 Hz, 1H), 6.58 (dd, J = 9.7, 2.8 Hz, 1H), 5.98 (d, J = 9.7 Hz, 1H), 4.78–4.64 (m, 1H), 2.20–2.01 (m, 3H), 1.82–1.68 (m, 4H), 1.38–1.14 (m, 5H), 1.05–0.96 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 137.0, 132.8, 129.2, 128.6, 127.6, 127.6, 127.1, 126.5, 68.9, 46.1, 36.5, 31.0, 31.0, 26.6, 26.4. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{16}H_{17}O$, 225.15; found, 225.14.

(1S,2S*)-5,8-Dimethoxy-2-phenyl-1,2-dihydronaphthalen-1-ol* ***(4a)***.[12] Prepared according to general procedure. Colorless oil (54.2 mg, 96% yield). R_f = 0.22 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.13 (m, 5H), 7.11 (dd, *J* = 9.9, 1.2 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 1H), 6.72 (d, *J* = 9.0 Hz, 1H), 6.11 (ddd, *J* = 9.9, 5.5, 1.0 Hz, 1H), 5.16 (s, 1H), 3.90 (d, *J* = 5.5 Hz, 1H), 3.83 (s, 3H), 3.72 (s, 3H), 2.43 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.3, 149.6, 140.1, 128.5, 128.2, 128.0, 126.8, 123.3, 122.4, 120.5, 111.3, 110.6, 67.5, 56.2, 55.9, 48.2. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{18}H_{15}O_3$, 279.13; found, 279.12.

(1S,2S*)-5,8-Dimethoxy-2-(2-methylphenyl)-1,2-dihydronaphthalen-1-ol* ***(4b)***. Prepared according to general procedure. Colorless oil (39.7 mg, 67% yield). R_f = 0.23 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.11 (m, 2H), 7.07 (td, *J* = 7.4, 1.1 Hz, 1H), 6.99–6.86 (m, 2H), 6.82–6.70 (m, 2H), 6.06 (dd, *J* = 9.8, 5.5 Hz, 1H), 5.10 (s, 1H), 4.14 (d, *J* = 5.4 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 2.54 (s, 3H), 1.63 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.3, 149.6, 137.8, 136.3, 130.6, 128.2, 127.1, 126.7, 126.0, 123.2, 122.4, 120.7, 111.3, 110.4, 66.3, 56.2, 55.8, 44.0, 19.8. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{19}H_{17}O_3$, 293.1178; found, 293.1175.

(1S,2S*)-5,8-Dimethoxy-2-(3-methylphenyl)-1,2-dihydronaphthalen-1-ol* ***(4c)***. Prepared according to general procedure. Colorless oil (57.5 mg, 97% yield). R_f = 0.19 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 13.8, 9.3 Hz, 2H), 7.04–6.86 (m, 3H), 6.82–6.70 (m, 2H), 6.08 (dt, *J* = 12.0, 6.0 Hz, 1H), 5.16 (d, *J* = 8.8 Hz, 1H), 3.85 (s, 1H), 3.83 (s, 3H), 3.73 (s, 3H),

2.45 (s, 1H), 2.27 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.4, 149.6, 140.2, 138.1, 128.9, 128.4, 128.4, 127.6, 124.9, 123.4, 122.5, 120.3, 111.4, 110.6, 67.7, 56.3, 55.9, 48.2, 21.5. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{19}H_{17}O_3$, 293.1178; found, 293.1178.

(1S,2S*)-5,8-Dimethoxy-2-(4-methylphenyl)-1,2-dihydronaphthalen-1-ol* ***(4d)****.* Prepared according to general procedure. Colorless oil (57.5 mg, 97% yield). R_f = 0.23 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). ^1H NMR (500 MHz, $CDCl_3$) δ 7.15–7.04 (m, 5H), 6.85–6.81 (m, 1H), 6.77–6.74 (m, 1H), 6.14 (ddd, *J* = 9.8, 5.5, 1.0 Hz, 1H), 5.19 (s, 1H), 3.93–3.90 (m, 1H), 3.87 (s, 3H), 3.76 (s, 3H), 2.45 (d, *J* = 6.1 Hz, 1H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 151.4, 149.5, 137.0, 136.4, 129.2, 128.5, 127.9, 123.3, 122.5, 120.3, 111.3, 110.5, 67.5, 56.2, 55.9, 47.8, 21.0. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{19}H_{17}O_3$, 293.1178; found, 293.1179.

(1S,2S*)-5,8-Dimethoxy-2-(4-chlorophenyl)-1,2-dihydronaphthalen-1-ol* ***(4e)****.* Prepared according to general procedure. A white solid (50.6 mg, 80% yield). m.p. 97–98 °C. R_f = 0.21 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (ddd, *J* = 17.4, 16.4, 8.4 Hz, 5H), 6.81 (d, *J* = 9.0 Hz, 1H), 6.74 (d, *J* = 9.0 Hz, 1H), 6.08 (dd, *J* = 9.8, 5.5 Hz, 1H), 5.10 (s, 1H), 3.87 (d, *J* = 4.6 Hz, 1H), 3.84 (s, 3H), 3.73 (s, 3H), 2.41 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.3, 149.6, 138.4, 132.5, 129.4, 128.6, 127.6, 122.9, 122.2, 120.9, 111.4, 110.8, 67.4, 56.2, 55.9, 47.4. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{18}H_{14}ClO_3$, 313.0631; found, 313.0635.

(1S,2S*)-5,8-Dimethoxy-2-(3-fluorophenyl)-1,2-dihydronaphthalen-1-ol* ***(4f)***. Prepared according to general procedure. Colorless oil (57.0 mg, 95% yield). R_f = 0.25 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.35 (m, 1H), 7.14 (ddd, J = 10.9, 8.7, 3.6 Hz, 2H), 6.97 (d, J = 7.7 Hz, 1H), 6.84–6.78 (m, 2H), 6.72 (s, 1H), 6.12–6.04 (m, 1H), 5.14 (d, J = 1.2 Hz, 1H), 3.90 (d, J = 4.6 Hz, 1H), 3.83 (s, 3H), 3.73 (s, 3H), 1.68 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.1 (d, $^1J_{C\text{-}F}$ = 243.8 Hz), 151.3, 149.6, 142.7 (d, $^4J_{C\text{-}F}$ = 7.0 Hz), 129.9 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 127.4, 125.0, 123.8, 123.8, 121.0 (d, $^2J_{C\text{-}F}$ = 16.6 Hz), 114.9, 114.7, 111.5, 110.8, 67.3, 56.2, 56.0, 47.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.2 (d, J = 17.1 Hz). HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{18}H_{14}FO_3$, 297.0927; found, 297.0927.

(1S,2S*)-6,7-Dimethoxy-2-phenyl-1,2-dihydronaphthalen-1-ol* ***(5a)***.[12] Prepared according to general procedure. Colorless oil (53.6 mg, 95% yield). R_f = 0.23 on silica gel (ethyl acetate/petroleum ether 1:3, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.22 (m, 5H), 6.96 (s, 1H), 6.72 (s, 1H), 6.58 (dd, J = 9.6, 1.7 Hz, 1H), 5.94 (dd, J = 9.6, 4.0 Hz, 1H), 4.74 (d, J = 6.5 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.79–3.73 (m, 1H), 1.97 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.7, 148.7, 140.9, 128.7, 128.4, 128.1, 127.8, 127.1, 127.1, 125.6, 110.4, 110.0, 74.4, 56.0, 56.0, 50.2. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{18}H_{15}O_3$, 279.1021; found, 279.1023.

(1S,2S*)-6,7-Dimethoxy-2-(2-methylphenyl)-1,2-dihydronaphthalen-1-ol* ***(5b)***. Prepared according to general procedure. A white solid (53.3 mg, 90% yield). m. p. 100–101 °C. R_f = 0.22 on silica gel (ethyl acetate/petroleum ether 1:3, v/v). ^{1}H NMR

(500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.4 Hz, 1H), 7.15–7.03 (m, 3H), 6.91 (s, 1H), 6.72 (s, 1H), 6.60 (dd, *J* = 9.6, 1.8 Hz, 1H), 5.88 (dd, *J* = 9.5, 4.2 Hz, 1H), 4.74 (d, *J* = 3.8 Hz, 1H), 4.08 (ddd, *J* = 6.3, 4.2, 1.9 Hz, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 2.48 (s, 3H), 2.01 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 148.6, 148.6, 138.5, 136.8, 130.7, 128.0, 128.0, 127.5, 127.1, 126.9, 126.3, 125.5, 110.6, 109.9, 73.7, 56.0, 56.0, 45.6, 20.0. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{19}H_{17}O_3$, 293.1178; found, 293.1179.

(1S,2S*)-6,7-Dimethoxy-2-(3-methylphenyl)-1,2-dihydronaphthalen-1-ol* ***(5c)****.* Prepared according to general procedure. Yellow oil (55.7 mg, 94% yield). R_f = 0.22 on silica gel (ethyl acetate/petroleum ether 1:3, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.24–6.99 (m, 5H), 6.71 (s, 1H), 6.55 (dd, *J* = 9.6, 1.9 Hz, 1H), 5.91 (dt, *J* = 14.2, 7.1 Hz, 1H), 4.76 (d, *J* = 7.8 Hz, 1H), 4.01 (s, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 2.32 (s, 3H), 1.62 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.6, 148.6, 141.0, 138.4, 129.2, 128.6, 128.4, 128.0, 128.0, 127.0, 125.6, 125.4, 110.2, 110.0, 74.4, 56.0, 56.0, 50.3, 21.5. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{19}H_{17}O_3$, 293.1178; found, 293.1179.

(1S,2S*)-6,7-Dimethoxy-2-(4-methylphenyl)-1,2-dihydronaphthalen-1-ol* ***(5d)****.* Prepared according to general procedure. Colorless oil (56.3 mg, 95% yield). R_f = 0.23 on silica gel (ethyl acetate/petroleum ether 1:3, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.14–7.10 (m, 4H), 6.95 (s, 1H), 6.71 (s, 1H), 6.56 (d, *J* = 9.6 Hz, 1H), 5.93 (dd, *J* = 9.5, 4.0 Hz, 1H), 4.72 (d, *J* = 7.3 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.75–3.70 (m, 1H), 2.31 (s, 3H), 1.66 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.5, 148.5,

138.5, 137.7, 129.5, 128.3, 127.1, 125.6, 124.1, 123.8, 110.3, 109.8, 74.4, 56.0, 56.0, 49.8, 21.1. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{19}H_{17}O_3$, 293.1178; found, 293.1179.

(1S,2R*)-6,7-Dimethoxy-2-(4-chlorophenyl)-1,2-dihydronaphthalen-1-ol* ***(5e)****.* Prepared according to general procedure. Yellow oil (57.5 mg, 91% yield). $R_f = 0.25$ on silica gel (ethyl acetate/petroleum ether 1:3, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.23 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 6.5 Hz, 1H), 6.72 (s, 1H), 6.59 (dd, *J* = 9.6, 1.5 Hz, 1H), 5.90 (dd, *J* = 9.6, 4.2 Hz, 1H), 4.67 (d, *J* = 6.3 Hz, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 3.74 (ddd, *J* = 8.7, 5.2, 3.1 Hz, 1H), 1.99 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.8, 148.8, 139.2, 132.9, 129.7, 128.8, 127.7, 127.4, 127.1, 125.4, 110.6, 110.1, 74.2, 56.0, 56.0, 49.4. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{18}H_{14}ClO_3$, 313.0631; found, 313.0632.

(1S,2S*)-6,7-Dibromo-2-phenyl-1,2-dihydrotriphenylen-1-ol* ***(6a)****.*[12] Prepared according to general procedure. Colorless oil (66.5 mg, 88% yield). $R_f = 0.23$ on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.40 (s, 1H), 7.32 (ddd, *J* = 10.5, 5.3, 3.4 Hz, 3H), 7.28 – 7.25 (m, 2H), 6.59 – 6.49 (m, 1H), 6.07 (ddd, *J* = 12.7, 8.6, 3.8 Hz, 1H), 4.82 – 4.72 (m, 1H), 3.74 (ddd, *J* = 9.3, 6.0, 3.3 Hz, 1H), 2.05 (d, *J* = 3.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.3, 136.6, 133.4, 132.1, 131.2, 130.9, 129.0, 128.5, 127.6, 126.0, 124.0, 123.6, 73.6, 50.0. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{16}H_9Br_2O$, 376.93; found, 376.90.

(1S,2R*)-6,7-Dibromo-2-(2-methylphenyl)-1,2-dihydrotriphenylen-1-ol* ***(6b)****.* Prepared according to general procedure. Colorless oil (61.1 mg, 78% yield). R_f =

0.22 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.47–7.41 (m, 1H), 7.26–7.14 (m, 4H), 6.64–6.53 (m, 1H), 6.12–6.01 (m, 1H), 4.89–4.78 (m, 1H), 4.13–4.08 (m, 1H), 2.48 (d, *J* = 5.1 Hz, 3H), 2.15–2.05 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 138.1, 137.0, 136.6, 133.5, 132.6, 131.4, 130.9, 130.9, 127.5, 127.3, 126.6, 126.0, 124.1, 123.5, 73.3, 45.4, 20.0. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{17}H_{11}Br_2O$, 390.9157; found, 390.9154.

(1S,2R*)-6,7-Dibromo-2-(3-methylphenyl)-1,2-dihydrotriphenylen-1-ol* ***(6c)***. Prepared according to general procedure. Colorless oil (58.8 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 7.74 (s, 1H), 7.42 (s, 1H), 7.29–7.26 (m, 1H), 7.15–7.07 (m, 3H), 6.57 (ddd, *J* = 12.0, 9.0, 2.3 Hz, 1H), 6.09 (td, *J* = 9.6, 3.1 Hz, 1H), 4.83–4.77 (m, 1H), 3.71 (dt, *J* = 9.7, 2.8 Hz, 1H), 2.38 (s, 3H), 2.08–2.01 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 140.3, 138.8, 136.7, 133.4, 132.3, 131.0, 130.8, 129.2, 128.9, 128.4, 126.0, 125.5, 124.0, 123.6, 73.6, 50.0, 21.5. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{17}H_{11}Br_2O$, 390.9157; found, 390.9155.

(1S,2S*)-6,7-Dibromo-2-(4-methylphenyl)-1,2-dihydrotriphenylen-1-ol* ***(6d)***. Prepared according to general procedure. A white solid (61.1 mg, 78% yield). m.p. 108–109 °C. R_f = 0.24 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 4.5 Hz, 1H), 7.45–7.39 (m, 1H), 7.16 (dd, *J* = 7.7, 1.8 Hz, 4H), 6.60–6.51 (m, 1H), 6.09 (td, *J* = 9.4, 3.3 Hz, 1H), 4.79–4.73 (m, 1H), 3.75–3.68 (m, 1H), 2.37 (s, 3H), 2.06 (t, *J* = 9.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz,

$CDCl_3$) δ 137.3, 137.1, 136.6, 133.4, 132.4, 131.2, 130.8, 129.7, 128.3, 125.9, 124.0, 123.5, 73.6, 49.5, 21.1. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{17}H_{11}Br_2O$, 390.9157; found, 390.9156.

(1S,2R*)-6,7-Dibromo-2-(4-chlorophenyl)-1,2-dihydrotriphenylen-1-ol* ***(6e)***. Prepared according to general procedure. Colorless oil (61.8 mg, 75% yield). R_f = 0.23 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.47–7.39 (m, 1H), 7.32 (t, *J* = 6.5 Hz, 2H), 7.23–7.18 (m, 2H), 6.64–6.54 (m, 1H), 6.05 (ddd, *J* = 17.9, 9.6, 3.6 Hz, 1H), 4.85–4.61 (m, 1H), 3.80–3.71 (m, 1H), 2.20–2.02 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.6, 136.2, 133.4, 133.2, 131.4, 131.0, 129.8, 129.1, 126.3, 124.3, 123.8, 116.7, 73.5, 49.3. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{16}H_8Br_2ClO$, 410.8609; found, 410.8604.

(1S,2S*)-6,7-Dibromo-2-(3-fluorophenyl)-1,2-dihydrotriphenylen-1-ol* ***(6f)***. Prepared according to general procedure. Colorless oil (35.6 mg, 45% yield). R_f = 0.25 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.34 (d, *J* = 6.3 Hz, 1H), 7.23 (tt, *J* = 11.5, 5.7 Hz, 1H), 6.92 (dddd, *J* = 11.5, 9.9, 7.6, 3.3 Hz, 3H), 6.51 (ddd, *J* = 11.9, 7.5, 2.7 Hz, 1H), 6.05–5.94 (m, 1H), 4.75–4.61 (m, 1H), 3.71–3.65 (m, 1H), 2.00–1.92 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 164.0 (d, $^1J_{C-F}$ = 246.3 Hz), 142.8 (d, $^3J_{C-F}$ = 6.9 Hz), 136.2, 133.1, 131.2, 131.2, 131.0, 130.5 (d, $^3J_{C-F}$ = 8.3 Hz), 126.4, 124.4 (d, $^4J_{C-F}$ = 2.5 Hz), 124.0, 123.8, 115.4 (d, $^2J_{C-F}$ = 21.3 Hz), 114.6 (d, $^2J_{C-F}$ = 20 Hz), 73.4, 49.6. ^{19}F

NMR (376 MHz, $CDCl_3$) δ -112.0. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{16}H_8Br_2FO$, 394.8906; found, 394.8909.

(1S,2S*)-2-Phenyl-1,2-dihydrotriphenylen-1-ol (7**a**).*[12] Prepared according to general procedure. A white solid (54.8 mg, 85% yield). m.p. 80–81 °C. $R_f = 0.23$ on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^1H NMR (500 MHz, $CDCl_3$) δ 8.76–8.67 (m, 2H), 8.43–8.37 (m, 1H), 8.24–8.18 (m, 1H), 7.72–7.56 (m, 5H), 7.19–7.08 (m, 5H), 6.48 (ddd, J = 9.8, 5.9, 1.1 Hz, 1H), 5.56 (d, J = 7.4 Hz, 1H), 4.13 (t, J = 8.6 Hz, 1H), 2.15 (d, J = 7.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 138.7, 130.8, 130.6, 130.2, 129.9, 128.7, 128.7, 127.8, 127.4, 127.4, 127.2, 127.0, 126.9, 126.5, 126.5, 123.9, 123.7, 123.1, 123.1, 122.4, 69.5, 48.8. MS (EI) m/z: $[M - 3H]^-$ calcd for $C_{24}H_{15}O$, 319.14; found, 319.11.

(1S,2S*)-2-(2-Methylphenyl)-1,2-dihydrotriphenylen-1-ol (7**b**).* Prepared according to general procedure. A white solid (59.2 mg, 88% yield). m.p. 71–72 °C. R_f= 0.22 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^1H NMR (500 MHz, $CDCl_3$) δ 8.73–8.65 (m, 2H), 8.41–8.34 (m, 1H), 8.22–8.18 (m, 1H), 7.71–7.56 (m, 5H), 7.17 (d, J = 7.5 Hz, 1H), 7.00 (td, J = 7.3, 1.6 Hz, 1H), 6.84–6.73 (m, 2H), 6.41 (ddd, J = 9.8, 5.9, 1.0 Hz, 1H), 5.49 (s, 1H), 4.36 (d, J = 5.9 Hz, 1H), 2.62 (d, J = 6.6 Hz, 3H), 2.28–2.10 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 136.6, 136.0, 131.0, 130.8, 130.6, 130.2, 129.8, 128.7, 127.4, 127.4, 127.1, 127.4, 126.7, 126.5, 126.5, 126.3, 123.9, 123.6, 123.2, 123.2, 122.5, 68.2, 44.7, 19.9. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{25}H_{17}O$, 333.1279, found, 333.1278.

(1S,2R*)-2-(3-Methylphenyl)-1,2-dihydrotriphenylen-1-ol* *(**7c**)*. Prepared according to general procedure. A white solid (53.8 mg, 80% yield). m.p. 99–100 °C. R_f = 0.25 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77–8.69 (m, 2H), 8.44–8.38 (m, 1H), 8.27–8.21 (m, 1H), 7.73–7.59 (m, 5H), 7.25 (s, 1H), 7.02 (d, *J* = 4.0 Hz, 1H), 6.95–6.91 (m, 2H), 6.48 (ddd, *J* = 9.8, 5.9, 0.9 Hz, 1H), 5.57 (s, 1H), 4.13 (d, *J* = 4.6 Hz, 1H), 2.20 (s, 3H), 1.56 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 138.7, 138.3, 130.8, 130.6, 130.2, 130.0, 128.7, 128.7, 127.9, 127.4, 127.4, 127.0, 127.0, 126.4, 126.4, 124.7, 123.9, 123.7, 123.1, 123.1, 122.2, 69.5, 48.9, 21.4. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{25}H_{17}O$, 333.1279, found, 333.1277.

(1S,2R*)-2-(4-Chlorophenyl)-1,2-dihydrotriphenylen-1-ol* *(**7d**)*. Prepared according to general procedure. A white solid (63.4 mg, 89% yield). m.p. 123–124 °C R_f = 0.20 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (ddd, *J* = 17.6, 6.9, 4.8 Hz, 2H), 8.38 (dd, *J* = 5.5, 4.0 Hz, 1H), 8.23–8.14 (m, 1H), 7.74–7.57 (m, 5H), 7.07 (s, 4H), 6.56–6.34 (m, 1H), 5.48 (d, *J* = 7.4 Hz, 1H), 4.10 (d, *J* = 5.8 Hz, 1H), 2.16 (d, *J* = 7.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 137.0, 132.8, 130.8, 130.7, 130.0, 129.4, 129.2, 128.8, 128.5, 127.5, 127.2, 127.2, 127.1, 126.6, 126.4, 123.9, 123.5, 123.2, 123.2, 122.8, 69.4, 48.1. HRMS (APCI-ion trap) m/z: $[M - 3H]^-$ calcd for $C_{24}H_{14}ClO$, 353.0733, found, 353.0732.

AUTHOR INFORMATION

Corresponding Authors

*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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ASSOCIATED CONTENT

Supporting Information

General experimental remarks; copies of ^{1}H and ^{13}C{^{1}H} spectra for compounds **3a−i**, **4a−f**, **5a−e**, **6a−f** and **7a−d**, and ^{19}F NMR for compounds **3g**, **4f** and **6f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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