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Palladium-catalyzed *syn*-stereocontrolled ring-opening of oxabicyclic alkenes with arylsulfonyl hydrazides

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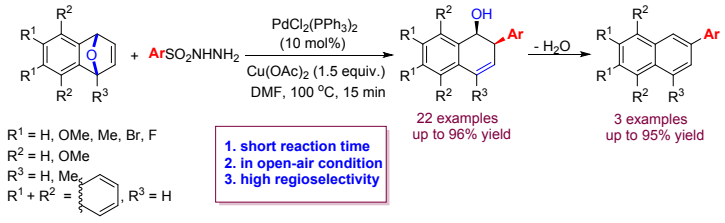
Supporting Information



ABSTRACT: A novel palladium-catalyzed ring-opening of oxabicyclic alkenes with arylsulfonyl hydrazides was first developed. In this work, we provide an efficient one-pot reaction to afford the corresponding *cis*-2-aryl-1,2-dihydronaphthalen-1-ols and 2-aryl-naphthalenes in moderate to excellent yields (up to 95%) under an open-air condition. Various types of functional groups attached to the substrates were tolerated in this method. Among them, the *cis*-1,2-configuration of product **3ag** was confirmed by X-ray crystallographic analysis. In addition, a plausible mechanism for the ring-opening was also proposed.

KEYWORDS: palladium catalyst; ring-opening; oxabicyclic alkenes; arylsulfonyl hydrazides; regioselectivity

INTRODUCTION

Transition metal catalyzed ring-opening of oxabenzonorbornadienes has wide application value in organic chemistry. It is an effective means of constructing multiple stereocenters in organic synthesis[1]. Studies have shown that the corresponding backbone of the ring-opening reaction product naphthalene exists in a wide series of natural materials and bioactive molecules[2]. On this basis, previous workers have developed many ring-opening reactions of oxa(aza)bicyclic alkenes with a range of heteroatom and carboanion nucleophiles in the presence of catalysts including Ir,[3] Pd,[4] Rh,[5] Ni,[6] Cu,[7] Ru,[8] Pt,[9] Fe,[10] etc.[11]

Research shows that various carboanion nucleophiles including organic zincs,[4g,12] organoaluminums,[6e,13] organolithiums,[14] organoboronic acids,[15] Grignard reagents[16] and alkyne reagents,[3d,8e,17] have been widely applied for asymmetric ring-opening of the oxabenzonorbornadienes. Our research group has also been engaged in studying the ring-opening for several years. The

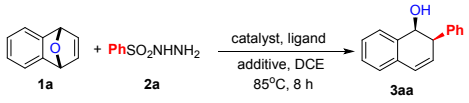
continuous interest in these types of reactions promoted our group to further investigate the ring-opening of oxabenzonorbornadienes with a series of heteroatom nucleophiles. Last few years, our group have reported asymmetric ring-opening reactions of Ir-catalyzed oxa(aza)bicyclic alkenes with various nucleophiles including phenols, alcohols, carboxylic acids and amines, resulting the compounds are excellent yields with high enantioselectivities.[5]

In recent years, studies have found that aryl halides,[12e,18] organometallic reagents[19] and arylboronic acids[3b,20] can be used as aryl donors in ring-opening reactions to form carbon–carbon bond. However, these arylating agents also have some drawbacks. For example, aryl halides normally have low activity to react with oxa(aza)bicyclic alkenes; the organometallic reagents are generally sensitive to air and moisture; arylboronic acids are more expensive, and so forth. Herein, it is very important to search for a split-new carboanion nucleophile as an aryl donor for ring-opening with oxa(aza)bicyclic alkenes. To the best of our knowledge, arylsulfonyl and sulfinic compounds have been widely used in the synthesis of functional structures of various biologically active compounds, and have become a novel and low-cost organic synthesis reagent.[21] These compounds mainly include arylsulfonyl chloride, sodium arylsulfinate, arylsulfonyl hydrazide and arylsulfinic acid, which can be used as arylating agents to form C–C bonds, respectively. Over the past few years, our group have realized the ring-opening of oxabicyclic alkenes with sodium arylsulfinates in the presence of Pd or Pt catalysts.[3h,9d] In our continuing interest in the discovery of new arylating reagents based on sodium arylsulfinates, we envisioned that arylsulfonyl hydrazides could be employed as novel aryl sources to react with oxa(aza)bicyclic alkenes. are generally stable in air. They can be prepared in one step from readily available arylsulfonyl chlorides and hydrazine hydrates. Recently, there has been increasing interest in constructing C–C bond by liberating N_2 and SO_2 of arylsulfonyl hydrazides in situ. However, the reaction of oxabenzonorbornadienes with arylsulfonyl hydrazides has not been explored so far. Herein, we first developed an effective method, which employs arylsulfonyl hydrazides as aryl donors for the ring-opening of oxabicyclic alkenes in the presence of palladium catalyst.

RESULTS AND DISCUSSION

The initial optimization of the conditions was conducted with oxabicyclic alkenes **1a** and phenylsulfonyl hydrazide **2a** in 1,2-dichloroethane (DCE) at 85 °C under an air atmosphere. According to the previously reported literatures,[22] the copper salt can promote the removal of SO_2 from arylsulfonyl hydrazides. Therefore, we tried to use copper acetate as an oxidant. We observed that the reaction can hardly occur in the presence of palladium catalyst or copper acetate. These control experiments indicated that the palladium catalyst and copper salt were essential for the desired reaction (Table 1, entries 1–2). When $Pd(OAc)_2/PPh_3$ and $Cu(OAc)_2$ were simultaneously added into the system, we succeeded in obtaining the target product **3aa**, but the yield was only 36% (Table 1, entry 3). Encouraged by these results, we examined a range of Pd catalysts under the same condition. The results indicated $Pd(PPh_3)_2Cl_2$ is the best catalyst in this reaction (Table 1, entries 3–6). Subsequently, various ligands were screened under the same catalytic conditions. We found that the yield of **3aa** was improved to 54% when the system was conducted without other ligands (Table 1, entries 7–10). We also investigated the effect of two different chiral bisphosphine ligands including (*S*)-BINAP and (*R*)-BINAP on enantioselectivity. Unfortunately, we obtained the corresponding product **3aa** in low yield with poor enantioselectivity (23% and 15% ee, respectively. Table 1, entries 8–9). Moreover, the influence of the catalyst loading was examined, the results showed that reducing the catalyst loading significantly decreased the yield (39%) (Table 1, entry 11). In consideration of the above studies, the catalyst loading of 10 mol% $Pd(PPh_3)_2Cl_2$ was optimally selected to further optimize the reaction.

Table 1. Effects of catalysts, ligands, and catalyst loadings[a,b,c]

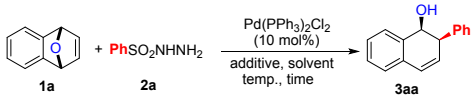


entry	catalyst (10 mol%)	ligand (20 mol%)	additive (1.5 equiv.)	yield[c] (%)	ee (%)
1	none	none	$Cu(OAc)_2$	–	
2	$Pd(OAc)_2$	PPh_3	none	–	
3	$Pd(OAc)_2$	PPh_3	$Cu(OAc)_2$	36	
4	$PdCl_2$	PPh_3	$Cu(OAc)_2$	40	
5	$Pd(PPh_3)_2Cl_2$	PPh_3	$Cu(OAc)_2$	46	
6	$Pd(CH_3CN)_2Cl_2$	PPh_3	$Cu(OAc)_2$	37	
7	**$Pd(PPh_3)_2Cl_2$**	**none**	**$Cu(OAc)_2$**	**54**	
8	$Pd(PPh_3)_2Cl_2$	(*R*)-BINAP	$Cu(OAc)_2$	34	15
9	$Pd(PPh_3)_2Cl_2$	(*S*)-BINAP	$Cu(OAc)_2$	39	23
10	$Pd(PPh_3)_2Cl_2$	DPPE	$Cu(OAc)_2$	35	
11[b]	$Pd(PPh_3)_2Cl_2$	none	$Cu(OAc)_2$	39	

[a]Unless otherwise noted, the reaction was conducted with oxabicyclic alkene **1a** (0.1 mmol, 14.4 mg) and **2a** (0.2 mmol, 34.4 mg) in the presence of 10 mol% catalyst and 20 mol% ligand in 2.0 mL of solvent in 8 h. [b]The catalyst loading is 5 mol%. [c]Isolated yield.

Next, we continued to study the influence of additives, solvents and temperatures on the reaction. To further optimize the reaction, several cupric salts, such as CuO, $(CF_3SO_3)_2Cu$, $CuCl_2$ and $Cu(C_5H_7O_2)_2$ were also tested. Unfortunately, they led to much lower yields (Table 2, entries 1–4). Then, we explored the effect of solvent effect on the reaction. The results indicated the solvent effect has a significant influence on the yield. The reaction only gave low yields in the protic solvent CH_3OH or the non-polar (aprotic) solvent tetrahydrofuran (THF) (Table 2, entries 5–6). Better results were obtained with moderate yields in the polar (aprotic) solvent 1,4-dioxane or CH_3CN (Table 2, entries 7–8). Fortunately, high boiling dipolar (aprotic) solvent dimethyl sulfoxide (DMSO) or dimethyl formamide (DMF) dramatically enhanced the yield up to 79% and 82%, respectively (Table 2, entries 9–10). However, we haven't yet achieved the best conditions. The effect of temperature on this reaction was also examined. Results indicated the temperature had an obvious effect on reaction rate too. When the temperature was 100 °C, the product **3aa** was obtained in an excellent yield (93%) within 15 min (Table 2, entry 12). Therefore, the optimal reaction conditions were established as 10 mol% $Pd(PPh_3)_2Cl_2$, 2.0 equiv of arylsulfonyl hydrazides and 1.5 equiv of $Cu(OAc)_2$ in DMF at 100 °C for 0.25 h under an air atmosphere.

Table 2. Optimization of solvents, temperatures and additives[a,b]



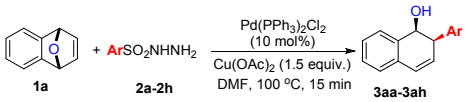
entry	solvent (2 mL)	temp. (°C)	additive (1.5 equiv.)	yield[b] (%)	time (h)
1	DCE	85	CuO	45	8
2	DCE	85	$(CF_3SO_3)_2Cu$	40	8
3	DCE	85	$CuCl_2$	38	8
4	DCE	85	$Cu(C_5H_7O_2)_2$	47	8
5	CH_3OH	85	$Cu(OAc)_2$	50	8
6	THF	85	$Cu(OAc)_2$	56	8
7	CH_3CN	85	$Cu(OAc)_2$	67	4
8	1,4-dioxane	85	$Cu(OAc)_2$	70	4
9	DMF	85	$Cu(OAc)_2$	82	1
10	DMSO	85	$Cu(OAc)_2$	79	1
11	DMF	65	$Cu(OAc)_2$	55	10
12[b]	**DMF**	**100**	**$Cu(OAc)_2$**	**93**	**0.25**

[a]Unless otherwise noted, the reaction was conducted with oxabicyclic alkene **1a** (0.1 mmol, 14.4 mg) and **2a** (0.2 mmol, 34.4 mg) in the presence of 10 mol% catalyst (7.0 mg) in 2.0 mL of solvent. [b]Isolated yield.

With the optimized conditions in hand, we went on to investigate the generality of the reaction with various arylsulfonyl hydrazides, which were listed in Table 3. We could see the structures of arylsulfonyl hydrazides **2** have a significant impact on the reactivity from Table 3. Although mostly arylsulfonyl hydrazides **2** proceeded smoothly with substrate **1a**, it is apparent that the arylsulfonyl hydrazides **2** with an electron donating group on the phenyl ring gave higher yield than those having an electron withdrawing group (Table 3, entries 2–7). Considering the effect of the group position properties of the mono-substituted arylsulfonyl hydrazides on the reactivity, we noted that they had significant effect on the reactivity. For example, when 4-chlorobenzenesulfonyl hydrazide **2e** acted as the nucleophilic reagent, the yield of target product **3ae** was as high as 91% (Table 3, entry 5). In contrast, when 2-chlorobenzenesulfonyl hydrazide **2d** as a nucleophile, the product **3ad** was obtained in only 63% yield (Table 3, entry 4). In addition to these, when 2,4,6-trimethylbenzenesulfonyl hydrazide **2h** was employed in

the reaction, the desired product **3ah** was obtained in 36% yield due to the influence of steric hindrance (Table 3, entry 8).

Table 3. Palladium-catalyzed ring-opening of oxabenzonorbornadiene **1a** with various arylsulfonyl hydrazides **2** [a,b]

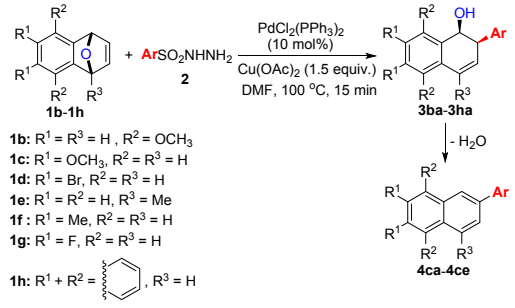


entry	Ar	product	yield[b] (%)
1	C_6H_5	**3aa**	93
2	4-$CH_3C_6H_4$	**3ab**	94
3	4-$CH_3OC_6H_4$	**3ac**	90
4	2-ClC_6H_4	**3ad**	63
5	4-ClC_6H_4	**3ae**	91
6	4-FC_6H_4	**3af**	89
7	4-$O_2NC_6H_4$	**3ag**	85
8	2,4,6-$(CH_3)_3C_6H_2$	**3ah**	36

[a]Unless otherwise noted, the reaction was conducted with oxabicyclic alkene **1a** (0.1 mmol, 14.4 mg) and **2a**–**2h** (0.2 mmol) in the presence of 10 mol% catalyst (7.0 mg) in 2.0 mL of solvent. [b]Isolated yield.

Furthermore, the range of the ring-opening was further surveyed by various oxabenzonorbornadienes **1b**–**1h**, which were summarized in Table 4. As shown in Table 4, apart from substrate **1h**, the ring-opening of other oxabicyclic alkenes with phenylsulfonyl hydrazide **2a** proceeded smoothly to give the desired products in moderate to excellent yields under the optimized condition. Compared with electron-defect substrates, electron-rich substrates reacted better with various arylsulfonyl hydrazides. Interestingly, we could obtain the corresponding further dehydrated products 2-aryl-naphthalenes **4ca**–**4ce** in high yields, but could not obtain the expected ring-opening products **3** when we employed methoxy substituted oxabenzonorbornadiene **1c** to react with arylsulfonyl hydrazides **2** (Table 4, entries 4–6). It's worth noting that the asymmetric substrate **1e** bearing a methyl substituent at the position of oxo-bridge carbon reacted well with arylsulfonyl hydrazides **2**, affording the target products **3** in moderate yield with high regioselectivity (Table 4, entries 10–12). Moreover, substrate **1h** with arylsulfonyl hydrazides **2** showed low reactivity due to the influence of steric hindrance (Table 4, entry 17).

Table 4. Palladium-catalyzed ring-opening of oxabenzonorbornadiene **1b**–**1h** with various arylsulfonyl hydrazides **2**[a,b]

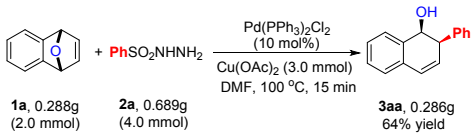


entry	Ar	substrate	prod. **3**	yield[b] (%)	prod. **4**	yield[b] (%)
1	C_6H_5	**1b**	**3ba**	96		
2	4-$CH_3C_6H_4$	**1b**	**3bb**	91		
3	4-ClC_6H_4	**1b**	**3be**	70		
4	C_6H_5	**1c**			**4ca**	95
5	4-$CH_3C_6H_4$	**1c**			**4cb**	94
6	4-ClC_6H_4	**1c**			**4ce**	62
7	C_6H_5	**1d**	**3da**	75		
8	4-$CH_3C_6H_4$	**1d**	**3db**	71		
9	4-ClC_6H_4	**1d**	**3de**	65		
10	C_6H_5	**1e**	**3ea**	83		
11	4-$CH_3C_6H_4$	**1e**	**3eb**	70		
12	4-ClC_6H_4	**1e**	**3ee**	67		
13	C_6H_5	**1f**	**3fa**	88		
14	4-$CH_3C_6H_4$	**1f**	**3fb**	81		
15	4-ClC_6H_4	**1f**	**3fe**	71		
16	C_6H_5	**1g**	**3ga**	91		
17	C_6H_5	**1h**	**3ha**	57		

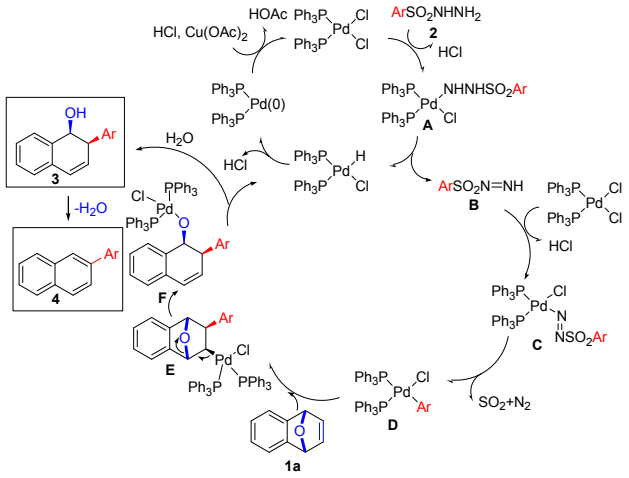
[a]Unless otherwise noted, the reaction was conducted with oxabicyclic alkene **1b-1h** (0.1 mmol) and **2a-2e** (0.2 mmol) in the presence of 10 mol% catalyst (7.0 mg) in 2.0 mL of solvent. [b]Isolated yield.

To further evaluate the reaction efficiency at the preparative scale, a scaled-up reaction was then carried out. The desired product **3aa** was obtained in 64% (0.286 g) yields under the standard conditions, implying its possible applications of this method in synthetic chemistry (Scheme 1).

Scheme 1. Scaled-up experiment of **3aa**



Scheme 2. Plausible Mechanism



According to our experimental results and the general mechanism of desulfurization cross-coupling reactions, we proposed the following plausible mechanism for the Pd-catalyzed ring-opening of oxabicyclic alkene **1a** with arylsulfonyl hydrazides **2** (Scheme 2). Displacement of $Pd(PPh_3)_2Cl_2$ catalyst by arylsulfonyl hydrazide **2** results in the formation of complex **A** which undergoes *β*-hydride elimination to give sulfonyl diazene **B** and meanwhile release $HPd(PPh_3)_2Cl$. Reductive elimination of $HPd(PPh_3)_2Cl$ followed by oxidation with $Cu(OAc)_2$/HCl regenerates Pd(II) catalyst. Displacement of $Pd(PPh_3)_2Cl_2$ with sulfonyl diazene **B** gives complex **C**. Successive extrusion of nitrogen and sulfur dioxide from complex **C** leads to the formation of arylpalladium **D**, which undergoes *exo*-1,2-addition with substrate **1a** to form intermediate **E**, then eliminated the *β*-oxygen atom to afford a new Pd intermediate **F**. Protonation of the last species **F** by water affords *cis*-2-aryl-1,2-dihydronaphthalen-1-ol product **3** and a $HPd(PPh_3)_2Cl$. Further dehydration of ring-opened product **3** gives the 2-aryl-naphthalene **4**.

CONCLUSIONS

In conclusion, we have demonstrated an unprecedented Pd-catalyzed ring-opening reaction of oxabenzonorbornadienes with readily available arylsulfonyl hydrazides as aryl sources under mild conditions. Arylsulfonyl hydrazides were first used as carboanion nucleophiles in the ring-opening by liberating N_2 and SO_2 in situ. This protocol offers a facile means for synthesizing *cis*-2-aryl-1,2-dihydronaphthalen-1-ols **3** and 2-arylnaphthalenes **4** with moderate to excellent yields. Our laboratory is further investigating the applications of palladium catalysts in other ring-opening reactions.

EXPERIMENTAL SECTION

General Methods. Unless otherwise indicated, all reagents and solvents were purchased from commercial sources and used without further purification. Oxabicyclic alkenes (**1a**–**1h**) were prepared according to literature procedures, and the corresponding spectral and physical data were consistent with the literature data.[23] Flash column chromatography was performed using the indicated solvent system on Qingdao-Haiyang silica gel (200−300 mesh). The products were separated by Anhui-Liangchen thin-layer chromatography silica gel. All of the compounds were determined and characterized by ^1H, ^{13}C and ^{19}F NMR. Peaks recorded are relative to the internal standards: TMS (δ = 0.00) for ^1H NMR and $CDCl_3$ (δ = 77.00) for $^{13}C\{^1H\}$ NMR spectra. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 600 MHz and 150 MHz at 25 °C in $CDCl_3$, respectively. ^{19}F NMR spectra were recorded at 565 MHz at 25 °C in $CDCl_3$. Spectral data are reported as follows: chemical shift (δ, ppm); multiplicity (s-singlet, d-doublet, t-triplet, q-quadruplet, and m-multiplet); coupling constants (*J*, Hz) and number of protons. HRMS (ion trap) spectra were obtained using a mass spectrometer (ESI) and MS spectra were recorded using EI at 70 eV. Enantiomeric excesses were determined with a Chiralcel AD-H column eluted with a mixture of hexane and *i*-propanol (hexane/*i*-propanol 92:8 (v/v), 1.0 mL/min, λ = 254 nm) Melting points were uncorrected. The crystal structure determination was carried out by X-ray diffraction apparatus.

General Procedure. All experiments were carried out under an open-air condition. Oxabicyclic alkenes **1** (0.1 mmol), arylsulfonyl hydrazides **2** (2.0 equiv., 0.2 mmol),

$Cu(OAc)_2$ (27.2mg, 1.5 equiv., 0.15 mmol), $Pd(PPh_3)_2Cl_2$ (10 mol%, 7.0mg) and DMF (2.0 mL) were simultaneously added into a 10.0 mL round-bottomed flask. The mixed solution was stirred at 100 °C in oil bath for 15 min. After cooling to room temperature, the reaction mixture was added 20 mL water and then extracted by ethyl acetate (10 mL×3), The organic layers were combined, dried with anhydrous Na_2SO_4, and then filtered. The filtrate was concentrated under vacuum, and the resulting residue was purified by column chromatography on silica gel (200–300 mesh) using ethyl acetate/petroleum ether as eluent to afford the desired product **3** and **4**.

(1S,2R*)-2-Phenyl-1,2-dihydronaphthalen-1-ol* ***(3aa)***. Following the general procedure, **3aa** was obtained as a colorless oil (20.7 mg, 93%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.20 (m, 6H), 7.19 – 7.16 (m, 2H), 7.10 (dd, *J* = 7.4, 1.0 Hz, 1H), 6.64 (dd, *J* = 9.6, 2.1 Hz, 1H), 6.06 (dd, *J* = 9.6, 4.0 Hz, 1H), 4.86 (d, *J* = 5.1 Hz, 1H), 3.80 (ddd, *J* = 6.0, 4.0, 2.1 Hz, 1H), 1.49 (s, 1H). ^{13}C{^{1}H} NMR (150MHz, $CDCl_3$) δ 137.7, 136.1, 132.6, 129.7, 129.3, 128.7, 128.3, 128.2, 128.0, 127.42, 126.7, 126.4, 71.3, 47.3. HRMS *m/z* (ESI-ion trap) [M - H_2 - H]$^-$ calcd for $C_{16}H_{11}O$: 219.0811, found: 219.0814.

(1S,2R*)-2-(p-Tolyl)-1,2-dihydronaphthalen-1-ol* ***(3ab)***. Following the general procedure, **3ab** was obtained as a colorless oil (22.2mg, 94%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 7.3, 0.6 Hz, 1H), 7.21 (td, *J* = 7.4, 1.3 Hz, 1H), 7.16 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.12 – 7.02 (m, 5H), 6.62 (dd, *J* = 9.6, 2.0 Hz, 1H), 6.04 (dd, *J* = 9.6, 4.1 Hz, 1H), 4.85 (d, *J* = 5.7 Hz, 1H), 3.76 (ddd, *J* = 6.1, 4.1, 2.0 Hz, 1H), 2.25 (s, 3H), 1.48 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 137.1, 136.2, 134.4, 132.7, 129.9, 129.4, 129.1, 128.2, 128.1, 128.0, 126.6, 126.3, 71.3, 46.9, 21.0. HRMS *m/z* (ESI-ion trap) [M - H_2 - H]$^-$ calcd for $C_{17}H_{13}O$: 233.0967, found: 233.0971.

(1S,2R*)-2-(4-Methoxyphenyl)-1,2-dihydronaphthalen-1-ol* ***(3ac)***. Following the general procedure, **3ac** was obtained as a colorless oil (22.7mg, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.3 Hz, 1H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.21 – 7.09 (m, 3H), 6.90 – 6.79 (m, 2H), 6.68 (dd, *J* = 9.6, 1.6 Hz, 1H), 6.10 (dd, *J* = 9.6, 4.3 Hz, 1H), 4.93 (d, *J* = 6.1 Hz, 1H), 3.83 – 3.80 (m, 1H), 3.76 (d, *J* = 12.6 Hz, 3H), 1.57 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 159.0, 136.3, 132.7, 130.3, 130.0, 129.1, 128.2, 128.0, 128.0, 126.5, 126.3, 114.1, 71.3, 55.2, 46.4. HRMS *m/z* (ESI-ion trap) [M - H_2 - H]$^-$ calcd for $C_{17}H_{13}O_2$: 249.0916, found: 249.0916.

(1S,2R*)-2-(2-Chlorophenyl)-1,2-dihydronaphthalen-1-ol* ***(3ad)***. Following the general procedure, **3ad** was obtained as a colorless oil (16.1 mg, 63%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 1H), 7.34 – 7.25 (m, 3H), 7.23 – 7.15 (m, 4H), 6.68 (dd, *J* = 9.6, 2.7 Hz, 1H), 5.98 (ddd, *J* = 9.6, 2.9, 0.9 Hz, 1H), 4.83 (s, 1H), 4.42 (dt, *J* = 5.3, 2.9 Hz, 1H), 1.46 (s, 1H). ^{13}C{^{1}H} NMR (150MHz, $CDCl_3$) δ 136.9, 135.2, 134.2, 132.1, 131.0, 129.6, 129.0, 128.8, 128.5, 128.3, 128.1, 128.0, 127.0, 126.7, 69.2, 44.0. HRMS *m/z* (ESI-ion trap) [M - H]$^-$ calcd for $C_{16}H_{12}ClO$: 255.0577, found: 255.0587.

(1S,2R*)-2-(4-Chlorophenyl)-1,2-dihydronaphthalen-1-ol* ***(3ae)***. Following the general procedure, **3ae** was obtained as a white solid (23.3 mg, 91%). m.p. 113.0–114.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.28 – 7.24 (m, 3H), 7.21 – 7.15 (m, 3H), 6.71 (dd, *J* = 9.6, 2.0 Hz, 1H), 6.08 (dd, *J* = 9.6, 4.1 Hz, 1H), 4.92 (d, *J* = 5.9 Hz, 1H), 3.83 (ddd, *J* = 6.0, 4.1, 2.0 Hz, 1H), 1.47 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 136.3, 135.9, 133.2, 132.4, 130.6, 129.2, 128.7, 128.5, 128.4, 128.2, 126.5, 126.5, 71.2, 46.7. HRMS *m/z* (ESI-ion trap) [M - H_2 - H]$^-$ calcd for $C_{16}H_{10}ClO$: 253.0421, found: 253.0423.

(1S,2R*)-2-(4-Fluorophenyl)-1,2-dihydronaphthalen-1-ol* ***(3af)***. Following the general procedure, **3af** was obtained as a white solid (21.4mg, 89%). m.p. 100.0–101.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.31 (m), 7.30 – 7.28 (m), 7.27 – 7.22 (m), 7.20 (d, *J* = 7.4 Hz), 7.13 – 6.93 (m), 6.73 (dd, *J* = 9.6, 1.8 Hz), 6.12 (dd, *J* = 9.6, 4.1 Hz), 4.95 (d, *J* = 5.9 Hz), 3.95 – 3.76 (m), 1.50 (s). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 163.0, 161.3, 136.0, 133.3 (d, *J* = 3.2 Hz), 132.5, 130.8 (d, *J* = 7.8 Hz), 129.6, 128.3 (d, *J* = 9.0 Hz), 128.1, 126.5 (d, *J* = 15.1 Hz), 115.5, 115.3, 71.2, 46.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.4 (s). HRMS *m/z* (ESI-ion trap) [M - H]$^-$ calcd for $C_{16}H_{12}FO$: 239.0871, found: 239.0873.

(1S,2R*)-2-(4-Nitrophenyl)-1,2-dihydronaphthalen-1-ol* ***(3ag)***. Following the general procedure, **3ag** was obtained as a pale-yellow solid (22.7 mg, 85%). m.p. 122.3–123.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.7 Hz), 7.44 (d, *J* = 8.6 Hz), 7.35 – 7.27 (m), 7.21 (d, *J* = 7.3 Hz), 6.77 (dd, *J* = 9.6, 2.0 Hz), 6.08 (dd, *J* = 9.6, 3.8 Hz), 4.93 (s), 3.95 (t, *J* = 5.7 Hz), 1.60 (s). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 147.2, 146.4, 135.5, 132.1, 130.2, 129.0, 128.8, 128.4, 128.1, 126.8, 126.6, 123.5, 71.1, 47.2. HRMS *m/z* (ESI-ion trap) [M - H]$^-$ calcd for $C_{16}H_{12}NO_3$: 266.0816, found: 266.0813.

(1S,2R*)-2-Mesityl-1,2-dihydronaphthalen-1-ol* ***(3ah)***. Following the general procedure, **3ah** was obtained as a white solid (9.5mg, 36%). m.p. 122.0–124.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (ddd, *J* = 8.8, 6.8, 3.0 Hz), 7.27 (dd, *J* = 7.4, 1.2 Hz), 7.21 (d, *J* = 7.5 Hz), 6.92 (s), 6.60 (dd, *J* = 9.6, 3.3 Hz), 6.25 – 6.11 (m), 4.74 (d, *J* = 4.9 Hz), 4.21 (dt, *J* = 5.3, 2.8 Hz), 2.50 (s), 2.35 (s), 2.28 (s), 1.56 (s). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 139.0, 137.0, 136.3, 135.1, 132.8, 132.6, 132.2, 131.0, 129.3, 129.1, 129.0, 127.3, 126.8, 124.0, 70.0, 43.2, 21.5, 21.0, 20.7. HRMS *m/z* (ESI-ion trap) [M - H_2 - H]$^-$ calcd for $C_{19}H_{17}O$: 261.1280, found: 261.1277.

(1S,2R*)-5,8-Dimethoxy-2-phenyl-1,2-dihydronaphthalen-1-ol* ***(3ba)***. Following the general procedure, **3ba** was obtained as a colorless oil (27.1 mg, 96%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (dt, *J* = 13.3, 7.5 Hz, 4H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.09 (dd, *J* = 9.8, 3.2 Hz, 1H), 6.82 (q, *J* = 9.0 Hz, 2H), 6.24 – 6.07 (m, 1H), 5.09 (dd, *J* = 4.6, 1.2 Hz, 1H), 3.83 (d, *J* = 6.7 Hz, 6H), 3.81 – 3.79 (m, 1H), 1.59 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.7, 149.7, 140.4, 129.1, 128.9, 128.6, 127.0, 124.3, 122.5, 122.1, 111.5, 110.9, 64.3, 56.2, 56.2, 47.3. HRMS *m/z* (ESI-ion trap) [M - H_2 - H]$^-$ calcd for $C_{18}H_{15}O_3$: 279.1022, found: 279.1026.

(1S,2R*)-5,8-Dimethoxy-2-(p-tolyl)-1,2-dihydronaphthalen-1-ol* ***(3bb)***. Following the general procedure, **3bb** was obtained as a white solid (26.9mg, 91%). m.p. 101.0–102.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.08 (dd, *J* = 9.8, 3.2 Hz, 1H), 6.81 (q, *J* = 8.9 Hz, 2H), 6.28 – 6.00 (m, 1H), 5.06 (d, *J* = 4.1 Hz, 1H), 3.83 (t, *J* = 14.7 Hz, 6H), 3.78 – 3.75 (m, 1H), 2.36 (s, 3H), 1.59 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.8, 149.7, 137.2, 136.6, 129.3, 129.1, 128.9, 124.3, 122.6, 122.0, 111.4, 110.9, 64.3, 56.2, 56.2, 46.8, 21.1. HRMS *m/z* (ESI-ion trap) [M - H_2 - H]$^-$ calcd for $C_{19}H_{17}O3$: 293.1178, found: 293.1177.

(1S,2R*)-2-(4-Chlorophenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol* ***(3be)***. Following the general procedure, **3be** was obtained as a white solid (22.1mg, 70%). m.p. 114.0–116.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 4H), 7.08 (dd, *J* = 9.8, 3.2 Hz, 1H), 6.81 (q, *J* = 9.0 Hz, 2H), 6.06 (ddd, *J* = 9.8, 2.3, 1.5 Hz, 1H), 5.06 (s, 1H), 3.82 (d, *J* = 8.6 Hz, 6H), 3.76 – 3.73 (m, 1H), 1.62 (d, *J* = 14.7 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.6, 149.7, 139.1, 132.7, 130.5, 128.5, 128.4, 124.2, 122.3, 111.5, 111.0, 64.3, 56.2, 56.1, 46.6. HRMS *m/z* (ESI-ion trap) [M - H_2 - H]$^-$ calcd for $C_{18}H_{14}ClO_3$: 313.0632, found: 313.0624.

2,3-Dimethoxy-6-phenylnaphthalene ***(4ca)***. Following the general procedure, **4ca** was obtained as a white solid (25.1mg, 95%). m.p. 121.0–122.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.71 – 7.67 (m, 2H), 7.60 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 23.6 Hz, 2H), 4.00 (d, *J* = 1.7 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.8, 149.6, 141.3, 137.0, 129.4, 128.8, 128.4, 127.2, 127.0, 126.8, 124.3, 123.8, 106.6, 106.0, 55.8. HRMS *m/z* (ESI-ion trap) [M + H]$^+$ calcd for $C_{18}H_{17}O_2$: 265.1228, found: 265.1225.

2,3-Dimethoxy-6-(p-tolyl)naphthalene ***(4cb)***. Following the general procedure , **4cb** was obtained as a white solid (26.1mg, 94%). m.p. 136.2–137.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.63 – 7.52 (m, 3H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.16 (s, 1H), 7.13 (s, 1H), 4.00 (d, *J* = 2.3 Hz, 6H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (150

MHz, $CDCl_3$) δ 149.7, 149.4, 138.4, 136.9, 136.7, 129.5, 129.4, 128.2, 127.0, 126.7, 124.0, 123.8, 106.5, 106.1, 55.8, 21.1. HRMS *m/z* (ESI-ion trap) $[M + H]^+$ calcd for $C_{19}H_{19}O_2$: 279.1385, found: 279.1383.

*6-(4-Chlorophenyl)-2,3-dimethoxynaphthalene (**4ce**)*. Following the general procedure, **4ce** was obtained as a white solid (18.5mg, 94%). m.p. 139.0–140.0 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 1.5 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.52 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.13 (d, *J* = 19.5 Hz, 2H), 4.00 (s, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 149.9, 149.7, 139.8, 135.6, 133.0, 129.3, 128.9, 128.5, 128.4, 126.9, 124.2, 123.4, 106.5, 106.0, 55.8. HRMS *m/z* (ESI-ion trap) $[M + H]^+$ calcd for $C_{18}H_{16}ClO_2$: 299.0839, found: 299.0835.

(1S,2R*)-6,7-Dibromo-2-phenyl-1,2-dihydronaphthalen-1-ol (**3da**)*. Following the general procedure, **3da** was obtained as a colorless oil (28.3mg, 75%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.40 (s, 1H), 7.30 – 7.25 (m, 3H), 7.21 – 7.12 (m, 2H), 6.59 (dd, *J* = 9.6, 1.3 Hz, 1H), 6.20 (dd, *J* = 9.6, 4.8 Hz, 1H), 4.95 (s, 1H), 3.93 – 3.73 (m, 1H), 1.55 (s, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 137.1, 135.6, 133.5, 131.8, 131.4, 130.8, 129.3, 128.9, 127.9, 126.4, 124.0, 123.6, 70.2, 46.7. HRMS *m/z* (ESI-ion trap) $[M - H_2 - H]^-$ calcd for $C_{16}H_9Br_2O$: 374.9021, found: 374.9022.

(1S,2R*)-6,7-Dibromo-2-(p-tolyl)-1,2-dihydronaphthalen-1-ol (**3db**)*. Following the general procedure, **3db** was obtained as a colorless oil (27.8mg, 71%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.39 (s, 1H), 7.08 (dd, *J* = 35.4, 8.0 Hz, 4H), 6.58 (dd, *J* = 9.7, 1.4 Hz, 1H), 6.19 (dd, *J* = 9.6, 4.9 Hz, 1H), 4.96 (d, *J* = 6.2 Hz, 1H), 3.91 – 3.56 (m, 1H), 2.31 (s, 3H), 1.51 (s, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 137.7, 137.3, 133.6, 132.2, 132.0, 131.4, 130.7, 129.6, 129.1, 126.2, 123.9, 123.6, 70.2, 46.2, 21.0. HRMS *m/z* (ESI-ion trap) $[M - H_2 - H]^-$ calcd for $C_{17}H_{11}Br_2O$: 388.9177, found: 388.9179.

(1S,2R*)-6,7-Dibromo-2-(4-chlorophenyl)-1,2-dihydronaphthalen-1-ol (**3de**)*. Following the general procedure, **3de** was obtained as a colorless oil (22.7mg, 65%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.40 (s, 1H), 7.27 – 7.25 (m, 2H), 7.15 – 7.08 (m, 2H), 6.60 (dd, J = 9.7, 1.4 Hz, 1H), 6.16 (dd, J = 9.6, 4.8 Hz, 1H), 4.95 (t, J = 7.3 Hz, 1H), 3.82 – 3.76 (m, 1H), 1.58 (s, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 136.8, 134.2, 133.8, 133.3, 131.4, 131.3, 130.9, 130.6, 128.9, 126.7, 124.2, 123.8, 70.2, 46.1. HRMS *m/z* (ESI-ion trap) $[M - H_2 - H]^-$ calcd for $C_{16}H_8Br_2ClO$: 408.8631, found: 408.8634.

(1S,2R*)-4-Methyl-2-phenyl-1,2-dihydronaphthalen-1-ol (**3ea**)*. Following the general procedure, **3ea** was obtained as a pale-yellow oil (19.6mg, 83%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.33 (m), 7.31 – 7.28 (m), 7.28 – 7.23 (m), 5.94 (dd, *J* = 3.9, 1.2 Hz), 4.89 (d, *J* = 5.7 Hz), 3.83 (ddd, *J* = 5.9, 4.1, 1.9 Hz), 2.19 (t, *J* = 1.6 Hz), 1.53 (s). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 138.2, 136.5, 134.2, 132.9, 129.2, 128.6, 128.2, 127.8, 127.3, 126.5, 126.3, 123.3, 71.5, 47.2, 19.2. HRMS *m/z* (ESI-ion trap) $[M - H_2 - H]^-$ calcd for $C_{17}H_{13}O$: 233.0967, found: 233.0970.

(1S,2R*)-4-Methyl-2-(p-tolyl)-1,2-dihydronaphthalen-1-ol (**3eb**)*. Following the general procedure, **3eb** was obtained as a pale-yellow oil (17.5mg, 70%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 3H), 7.26 (dd, *J* = 6.8, 2.1 Hz, 1H), 7.17 – 7.02 (m, 4H), 5.93 (d, *J* = 3.1 Hz, 1H), 4.88 (d, *J* = 5.4 Hz, 1H), 3.98 – 3.68 (m, 1H), 2.31 (s, 3H), 2.18 (s, 3H), 1.56 (s, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 136.9, 136.7, 134.9, 134.3, 132.7, 129.3, 129.1, 128.1, 127.7, 126.6, 126.5, 123.2, 71.5, 46.8, 21.0, 19.2. HRMS *m/z* (ESI-ion trap) $[M - H_2 - H]^-$ calcd for $C_{18}H_{16}O$: 247.1124, found: 247.1121.

(1S,2R*)-2-(4-Chlorophenyl)-4-methyl-1,2-dihydronaphthalen-1-ol (**3ee**)*. Following the general procedure, **3ee** was obtained as a pale-yellow oil (18.1mg, 67%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 3H), 7.29 – 7.26 (m, 1H), 7.26 (d, *J* = 2.7 Hz, 1H), 7.25 – 7.24 (m, 1H), 7.19 – 7.11 (m, 2H), 5.89 (dd, *J* = 4.1, 1.4 Hz, 1H), 4.87 (s, 1H), 3.79 (ddd, *J* = 5.9, 4.1, 1.9 Hz, 1H), 2.18 (t, *J* = 1.6 Hz, 3H), 1.57 (s, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 136.8, 136.4, 134.0, 133.3, 133.0, 130.6, 128.6, 128.3, 128.0, 126.4, 125.8, 123.4, 71.5, 46.6, 19.2. HRMS *m/z* (ESI-ion trap) $[M - H_2 - H]^-$ calcd for $C_{17}H_{12}ClO$: 267.0577, found: 267.0574.

(1S,2R*)-6,7-Dimethyl-2-phenyl-1,2-dihydronaphthalen-1-ol (**3fa**)*. Following the general procedure, **3fa** was obtained as a pale-yellow oil (22.0mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.22 – 7.18 (m, 3H), 7.04 (s, 1H), 6.88 (s, 1H), 6.58 (dd, *J* = 9.6, 2.1 Hz, 1H), 5.97 (dd, *J* = 9.6, 3.8 Hz, 1H), 4.77 (s, 1H), 3.81 – 3.73 (m, 1H), 2.18 (d, *J* = 8.5 Hz, 6H), 1.50 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 138.4, 136.5, 136.3, 133.5, 130.2, 129.3, 128.6, 128.5, 128.3, 128.0, 127.9, 127.3, 71.3, 47.6, 19.6, 19.5. HRMS *m/z* (ESI-ion trap) [M - H_2 - H]$^-$ calcd for $C_{18}H_{15}O$: 247.1124, found: 247.1124.

(1S,2R*)-6,7-Dimethyl-2-(p-tolyl)-1,2-dihydronaphthalen-1-ol (**3fb**)*. Following the general procedure, **3fb** was obtained as a pale-yellow oil (21.4mg, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.1 Hz, 2H), 7.15 – 7.09 (m, 3H), 6.95 (s, 1H), 6.63 (dd, *J* = 9.6, 2.1 Hz, 1H), 6.03 (dd, *J* = 9.6, 3.8 Hz, 1H), 4.83 (d, *J* = 5.7 Hz, 1H), 3.80 (ddd, *J* = 5.9, 3.7, 2.4 Hz, 1H), 2.32 (s, 3H), 2.25 (d, *J* = 8.7 Hz, 6H), 1.56 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 136.9, 136.4, 136.3, 135.1, 133.6, 130.3, 129.3, 129.1, 128.8, 128.3, 127.9, 127.8, 71.2, 47.2, 21.0, 19.6, 19.5. HRMS *m/z* (ESI-ion trap) [M - H_2 - H]$^-$ calcd for $C_{19}H_{17}O$: 261.1280, found: 261.1278.

(1S,2R*)-2-(4-Chlorophenyl)-6,7-dimethyl-1,2-dihydronaphthalen-1-ol (**3fe**)*. Following the general procedure, **3fe** was obtained as a colorless oil (20.2mg, 71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.22 – 7.18 (m, 2H), 7.09 (s, 1H), 6.95 (s, 1H), 6.64 (dd, *J* = 9.6, 2.1 Hz, 1H), 5.99 (dd, *J* = 9.6, 3.9 Hz, 1H), 4.82 (t, *J* = 6.1 Hz, 1H), 3.78 (ddd, *J* = 5.9, 3.8, 2.2 Hz, 1H), 2.25 (d, *J* = 8.7 Hz, 6H), 1.42 (d, *J* = 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 136.9, 136.6, 136.5, 133.3, 133.0, 130.6, 130.0, 128.6, 128.3, 128.1, 127.9, 71.1, 47.0, 19.6, 19.5. HRMS *m/z* (ESI-ion trap) [M - H_2 - H]$^-$ calcd for $C_{18}H_{14}ClO$: 281.0734, found: 281.0732.

(1S,2R*)-6,7-Difluoro-2-phenyl-1,2-dihydronaphthalen-1-ol (**3ga**)*. Following the general procedure, **3ga** was obtained as a yellow oil (23.5mg, 91%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.25 (m), 7.22 – 7.12 (m), 6.97 (dd, *J* = 10.5, 7.6 Hz), 6.59 (dd, *J* = 9.7, 1.7 Hz), 6.15 (dd, *J* = 9.6, 4.5 Hz), 4.92 (t, *J* = 6.9 Hz), 3.82 (dd, *J* = 7.7, 3.0 Hz), 1.56 (d, *J* = 5.6 Hz). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.6 (dd, *J* = 27.6, 13.1 Hz), 149.0 (dd, *J* = 29.7, 12.8 Hz), 136.2, 133.3 – 133.0 (m), 130.4 (d, *J* = 2.6 Hz), 129.5 (dd, *J* = 6.3, 4.0 Hz), 129.2, 128.8, 127.8, 126.5, 115.9 (d, *J* = 18.5 Hz), 115.0 (d, *J* = 18.1 Hz), 70.3, 46.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ -138.3 (d, *J* = 20.9 Hz), -139.7 (d, *J* = 21.5 Hz). HRMS *m/z* (ESI-ion trap) [M - H_2 - H]$^-$ calcd for $C_{16}H_9F_2O$: 255.0622, found: 255.0625.

(1S,2R*)-2-Phenyl-1,2-dihydrotriphenylen-1-ol (**3ha**)*. Following the general procedure, **3ha** was obtained as a white solid (18.4mg, 57%). m.p. 156.0–158.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 – 8.70 (m, 2H), 8.35 – 8.23 (m, 2H), 7.73 – 7.66 (m, 2H), 7.66 – 7.57 (m, 3H), 7.54 (dd, *J* = 8.0, 0.9 Hz, 2H), 7.47 (dt, *J* = 7.8, 3.4 Hz, 2H), 7.41 – 7.35 (m, 1H), 6.48 (ddd, *J* = 9.8, 2.3, 1.5 Hz, 1H), 5.43 (s, 1H), 4.16 – 3.93 (m, 1H), 1.55 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 140.1, 130.8, 130.7, 130.6, 129.9, 129.2, 128.8, 128.7, 128.6, 127.3, 127.2, 126.9, 126.9 , 126.5, 126.4, 124.1, 123.9, 123.8, 123.1, 123.1, 67.6, 48.0. HRMS *m/z* (ESI-ion trap) [M - H_2 - H]$^-$ calcd for $C_{24}H_{15}O$: 319.1124, found: 319.1122.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Copies of ^{1}H, ^{19}F and ^{13}C{^{1}H} NMR spectra for all compounds and X-ray crystal data of **3ag** (PDF).

Accession Codes

CCDC 1910703 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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