Organic & Biomolecular Chemistry

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2014, **12**, 2080

Platinum-catalyzed *anti*-stereocontrolled ring-opening of oxabicyclic alkenes with Grignard reagents†

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Received 6th November 2013,
Accepted 23rd January 2014

DOI: 10.1039/c3ob42199f

www.rsc.org/obc

A new platinum-catalyzed *anti*-stereocontrolled ring-opening of oxabicyclic alkenes with various Grignard reagents was reported, which afforded the corresponding *anti*-2-substituted-1,2-dihydronaphthalen-1-ol products with moderate to good yields in the presence of a catalytic amount of $Pt(PPh_3)_4$ (2.5 mol%) under mild conditions. The effects of catalyst loading, solvent and temperature on the yield were also investigated. Furthermore, the *trans*-configuration of the product **5i** was confirmed by X-ray diffraction analysis.

Introduction

The transition-metal-catalyzed ring-opening reaction of oxa- and azabicyclic alkenes, employing organometallic reagents, is an important method for C–C and C–X bond formation.[1] These ring-opening reactions are very useful to create highly substituted ring systems. In a series of publications, Lautens *et al.* have described the utility of regio- and stereoselective ring-opening reactions of oxabicyclic alkenes for the synthesis of cycloalkenols and natural products.[2] They also 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* ring-opening products.[3] In 1993, Hoveyda and co-workers reported a zirconium-catalyzed asymmetric allylic alkylation with Grignard reagents, yielding products with excellent enantioselectivities.[4] In 2002, an unprecedented copper phosphoramidite catalyzed enantioselective alkylative ring-opening of oxabenzonorbornadiene derivatives with dialkylzinc reagents was reported by Feringa and co-workers.[5] The reaction shows a high level of *anti*-stereoselectivity (up to *anti*/*syn* >99 : 1). In 2003, Carretero and co-workers reported copper-catalyzed *anti*-stereocontrolled ring-opening of oxabicyclic alkenes with Grignard reagents.[6] Nakamura and co-workers also demonstrated the Fe-catalyzed *syn*-stereocontrolled arylative and alkenylative ring opening of [2.2.1]- and [3.2.1]oxabicyclic alkene with Grignard reagents.[7] This transformation was best performed in the presence of a nickel,[8] palladium,[9] rhodium,[10] copper[11] or ruthenium[12] catalyst by using organometallic reagents such as an organoaluminum, organozinc or organoboron reagent as well as amine, phenol or alcohol nucleophiles. Recently, our group reported the iridium-catalyzed *anti*-stereocontrolled ring-opening of benzo- and alkyl-substituted oxa- and azabicyclic alkenes using amines, phenols, alcohols, or carboxylic acids as nucleophiles.[13] However, the application of the Grignard reagent as a carbanion nucleophile has been rarely explored due to the structural variety of the Grignard regent and its selectivity, because the Grignard reagent is very reactive and sensitive to the reaction conditions. Therefore, the development of highly catalytic reactions with the Grignard reagent remains a challenge. To the best of our knowledge, the utility of a platinum catalyst for this type of reaction has not previously been documented. 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 platinum catalyst. Herein we first report the *anti*-stereocontrolled ring-opening of benzo-substituted oxabicyclic alkenes with various Grignard reagents to afford the corresponding *anti*-2-substituted-1,2-dihydronaphthalen-1-ols in good yields in the presence of $Pt(PPh_3)_4$. Furthermore, the effects of catalyst loading, solvent and temperature on the yield were also investigated. The *trans*-configuration of the product **5i** was confirmed by X-ray diffraction analysis.

Results and discussion

We began our studies by searching for the optimal platinum catalyst system. In our initial experiment, treatment of a

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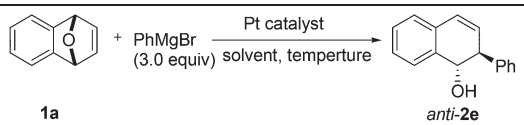
†Electronic supplementary information (ESI) available. CCDC 946820. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ob42199f

toluene solution of oxabenzonorbornadiene **1a** with phenyl magnesium bromide (3 equiv.) provided the corresponding ring-opening product **2e** in the presence of 2.5 mol% of $Pt(COD)Cl_2$ (*anti*/*syn* >98/2, 32%). Encouraged by the above results, the effects of several commercially available platinum salts as catalysts on the reactivity and selectivity in the ring-opening of **1a** with Grignard reagent were also investigated and compared. Oxabenzonorbornadiene **1a** reacted with phenyl magnesium bromide (3 equiv.) affording the corresponding product **2e** in 54% yield for 17 h at room temperature in the presence of 2.5 mol% of $Pt(PPh_3)_4$ (Table 1, entry 2). However, using $[Pt(CH_2{=}CH_2)Cl_2]_2$ or $PtCl_2$ as a catalyst did not improve the yield (Table 1, entries 3 and 4). Therefore, $Pt(PPh_3)_4$ was the best catalyst in terms of yields.

To further optimize the reaction conditions, the impact of catalyst loading and temperature on the reaction was then investigated. First, the yield of **2e** was strongly influenced by catalyst loading. As the amount of catalyst loading gradually increased to 2.5 mol%, the yield of **2e** was increased to 90% (Table 1, entries 2, 5 and 6). Therefore, the optimal catalyst loading of $Pt(PPh_3)_4$ is 2.5 mol%. Second, the effect of temperature on the reactivity was also investigated (as shown in Table 1). By increasing the oil bath temperature to 55 °C, the yield of **2e** was increased to 62% (Table 1, entry 7). However, with further increasing the temperature to 80 °C, we obtained the corresponding ring-opening product **2e** in only 15% yield (Table 2, entry 9). Therefore, the optimized reaction temperature was identified as 55 °C in toluene (Table 1, entry 7). Third, the effect of solvents on reactivity was investigated. A solvent effect study showed that 1,2-dichloroethane (DCE) is the best one among the solvents tested. When the reaction was carried out in CH_3CN, dioxane and tetrahydropyran (THP), respectively, we did not obtain any ring-opening product **2e**. Furthermore, a high yield of product **2e** (up to 90%) was achieved when the reaction proceeded at 55 °C in DCE (Table 1, entry 10). The yield of **2e** slightly decreased to 72% when we reduced the reaction time to 17 h in CH_2Cl_2 (Table 1, entry 11). We also found that using *n*-hexane as a solvent also obtained **2e** in moderate yield (84%) (Table 1, entry 12). Therefore, DCE was chosen as the best solvent.

Table 1 Ring-opening of oxabenzonorbornadiene **1a** with PhMgBr catalyzed by various platinum catalysts in different solvents[a]

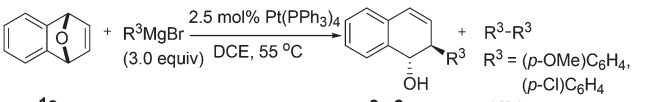


1a *anti*-**2e**

Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Time (h)	Yield[b] (%)
1	$Pt(COD)Cl_2$ (2.5)	Toluene	25	17	32
2	$Pt(PPh_3)_4$ (2.5)	Toluene	25	17	54
3	$[Pt(CH_2{=}CH_2)Cl_2]_2$ (2.5)	Toluene	25	23	38
4	$PtCl_2$ (2.5)	Toluene	25	18	5
5	$Pt(PPh_3)_4$ (1)	Toluene	25	17	10
6	$Pt(PPh_3)_4$ (2)	Toluene	25	17	43
7	$Pt(PPh_3)_4$ (2.5)	Toluene	55	17	62
8	$Pt(PPh_3)_4$ (3)	Toluene	55	17	51
9	$Pt(PPh_3)_4$ (2.5)	Toluene	80	17	15
10	$Pt(PPh_3)_4$ (2.5)	DCE	55	17	90
11	$Pt(PPh_3)_4$ (2.5)	CH_2Cl_2	55	17	72
12	$Pt(PPh_3)_4$ (2.5)	*n*-Hexane	55	17	84

[a] The reaction was carried out with **1a** (0.2 mmol) and 3.0 equiv. of PhMgBr (0.6 mmol) in solvent (1.0 mL) at different temperatures. [b] Isolated yield after silica gel column chromatography. *Anti*-stereoselectivity was determined by HPLC with a Chiralpak AD-H column.

Table 2 Platinum-catalyzed anti-stereocontrolled ring-opening of oxabenzonorbornadiene **1a** with various Grignard reagents[a]



1a **2a-2g** **2ff-2gg**

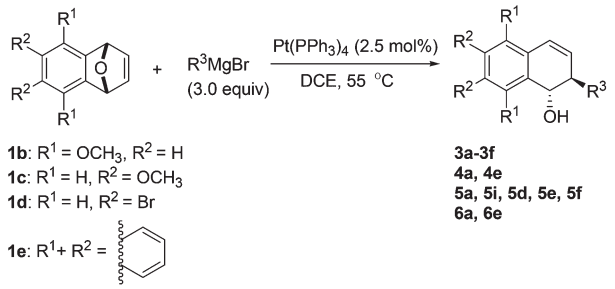
Entry	R^3	Product	Time (h)	Yield[e] (%)
1	CH_3	**2a**	14	71
2	$(CH_2)_4CH_3$	**2b**	1.3	54
3		**2c**	0.7	57
4	$CH_2CH{=}CH_2$	**2d**	2	74
5	Ph	**2e**	17	90
6[b]	$(p\text{-OMe})C_6H_4$	**2f**	10	—
7[b,c]	$(p\text{-OMe})C_6H_4$	**2f**	10	47
8[d]	$(p\text{-Cl})C_6H_4$	**2g**	5	31

[a] The reaction was carried out with **1a** (0.2 mmol) and 3.0 equiv. of Grignard reagent (0.6 mmol) in DCE (1.0 mL) in the presence of $Pt(PPh_3)_4$ (2.5 mol%). [b] **2ff** (4,4′-Dimethoxybiphenyl) (67% yield) was detected. [c] The reaction was carried out in *n*-hexane. [d] **2gg** (4,4′-Dichlorobiphenyl) (70% yield) was found. [e] Isolated yield after silica gel column chromatography.

On the basis of these studies, the *anti*-stereoselective ring-opening of **1a** with various Grignard reagents was explored under the optimized reaction conditions: 2.5 mol% of $Pt(PPh_3)_4$ at 55 °C in DCE. To evaluate the scope of the reaction, we further examined ring-opening of **1a** with various Grignard reagents under the optimal reaction conditions, and the results are summarized in Table 2. From Table 2, it can be seen that the stereostructure of the Grignard reagent significantly influenced the yields of the reaction (Table 2, entries 2–5). The Grignard reagent with a small Me group gave the ring-opening product in better yield (Table 2, entry 1). Furthermore, the reactivity of alkyl Grignard reagents was better than the aryl Grignard reagents in terms of yields, due to the coupling reaction of aryl Grignard reagents among themselves (Table 2, entries 6 and 8). Fortunately, the ring-opening of **1a** with aryl Grignard reagents could proceed in *n*-hexane, obtaining better yields than in DCE (Table 2, entry 7). It appeared that solvents may play a crucial role to balance the competitive reactions between the ring-opening reaction and the coupling reaction.

Under the optimized conditions, the substrate scope of this transformation was evaluated. The results are summarized in Table 3. The results indicated that the structures of oxabicyclic alkenes had a significant impact on the reactivity. The electronic properties of substrates have no obvious effect on the

Table 3 Anti-stereocontrolled ring-opening of oxabenzonorbornadienes **1b–e** with various Grignard reagents[a]



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

3a-3f
4a, 4e
5a, 5i, 5d, 5e, 5f
6a, 6e

Entry	Substrate	R^3	Product	Time (h)	Yield[f] (%)
1	**1b**	CH_3	**3a**	5.5	62
2	**1b**	$(CH_2)_4CH_3$	**3b**	1	46
3	**1b**		**3c**	0.7	54
4	**1b**	$CH_2CH{=}CH_2$	**3d**	1.7	62
5	**1b**	Ph	**3e**	3	75
6[b]	**1b**	$(p\text{-OMe})C_6H_4$	**3f**	14	41
7[c]	**1c**	CH_3	**4a**	6	24
8[d]	**1c**	Ph	**4e**	3.5	27
9	**1d**	CH_3	**5a**	5.5	56
10	**1d**	$CH(CH_3)_2$	**5i**	6	37
11	**1d**	$CH_2CH{=}CH_2$	**5d**	2.5	45
12	**1d**	Ph	**5e**	4	72
13[e]	**1d**	$(p\text{-OMe})C_6H_4$	**5f**	3	62
14	**1e**	CH_3	**6a**	5.5	39
15	**1e**	Ph	**6e**	5.5	41

[a] The reaction was carried out with substrate **1b–e** (0.2 mmol) and 3.0 equiv. of Grignard reagents (0.6 mmol) in DCE (1.0 mL) in the presence of $Pt(PPh_3)_4$ (2.5 mol%). [b] The reaction occurred in *n*-hexane at room temperature. [c] 2,3-Dimethoxy-6-methylnaphthalene (64% yield) was collected. [d] 2,3-Dimethoxy-6-phenylnaphthalene (59% yield) was collected. [e] The reaction occurred in *n*-hexane. [f] Isolated yield after silica gel column chromatography.

ring-opening reaction. All ring-opening of oxabicyclic alkenes with various Grignard reagents proceeded smoothly to give the expected products in moderate yields. The electron-rich substrate **1b** with Grignard reagents containing 3,6-dimethoxy on the phenyl ring and electron-deficient **1d** with 4,5-dibromo on the phenyl ring afforded moderate yields (Table 3, entries 1–6 and 9–13). It is noteworthy that substrate **1c** dehydrated to form by-products, substituting naphthalene with higher yields (Table 3, entries 7–8). Furthermore, substrate **1e** with Grignard reagents showed low reactivity due to the steric hindrance (Table 3, entries 14 and 15).

The single crystal of the ring-opened product **5i** was obtained by solvent evaporation from a solution consisting of dichloromethane, petroleum ether and chloroform. Its configuration was assigned as (1*S*,2*R*) and was confirmed as *anti*-1,2-configuration by X-ray diffraction analysis as shown in Fig. 1.

Conclusions

In summary, we have developed an efficient platinum-catalyzed *anti*-stereocontrolled ring-opening of oxabicyclic alkenes

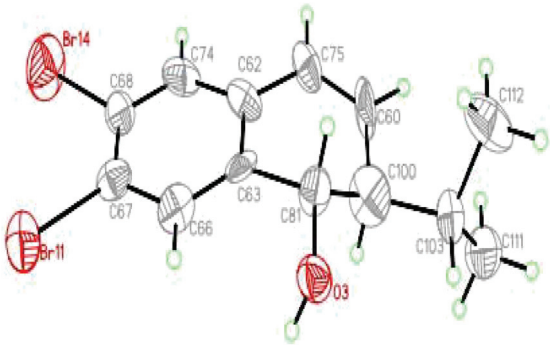


Fig. 1 ORTEP plot for **5i**. Crystal data. $C_{13}H_{14}Br_2O$, M = 346.04. Monoclinic a = 12.698(9), b = 15.704(11), c = 15.785(19), *alpha* = 108.667(14), *beta* = 96.252(14), *gamma* = 111.779(10), T = 293 K, crystal system, triclinic, space group, $P\bar{1}$, Z = 8, final R indices [$I > 2\text{sigma}(I)$], R_1 = 0.0789, wR_2 = 0.1502, R indices (all data), R_1 = 0.2821, wR_2 = 0.2223. CCDC 946820.

with various Grignard reagents. Ring-opening of oxabicyclic alkenes with various Grignard reagents was achieved in the presence of $Pt(PPh_3)_4$ under mild conditions, for a wide range of Grignard reagents and oxabicyclic alkenes. It provides an efficient and practical approach for the synthesis of *anti*-2-substituted-1,2-dihydronaphthalen-1-ol derivatives. A study on further expansion of the synthetic utility of the platinum-catalyzed ring-opening to other types of substrates is being pursued in our laboratory.

Experiment

General procedures

All flasks were flame-dried under a stream of nitrogen and cooled to room temperature before use. Solvents and solutions were transferred with syringes and cannulae using standard inert atmosphere techniques. All ^1H and ^{13}C NMR spectra were recorded at 400 and 100 M NMR, respectively, using $CDCl_3$ as a solvent. The chemical shifts of all ^1H and ^{13}C NMR spectra are referenced to the residual signal of $CDCl_3$ (δ 7.26 ppm) for the ^1H NMR spectra and (δ 77.16 ppm) for the ^{13}C NMR spectra. Spectral features are tabulated in the following order: chemical shift (δ, ppm); multiplicity (s-singlet, d-doublet, t-triplet, m-multiplet); coupling constants (J, Hz); number of protons. IR spectra were obtained using CH_2Cl_2 liquid film. MS were recorded using EI at 70 eV. High resolution mass spectra (HRMS) (ion trap) were obtained from a mass spectrometer (APCI or ESI). The melting points are uncorrected. Single crystal structure was determined by an X-ray diffraction apparatus.

Materials

Reagents were obtained from commercial vendors and used without further purification. CH_3CN, 1,2-dichloroethane (DCE), CH_2Cl_2, and diethyl ether were distilled from calcium hydride. Toluene, DME, dioxane, THF, and tetrahydropyran (THP) were distilled from sodium benzophenone ketyl

immediately prior to use. Oxabenzonorbornadienes **1a–e** were prepared according to the literature procedures.[14]

General procedure I for the platinum-catalyzed ring-opening 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. $Pt(PPh_3)_4$ (6.2 mg, 2.5 mol%) were simultaneously added followed by the addition of anhydrous DCE (2.0 mL). After the mixture was stirred for about 20 min, substrate **1a** (28.8 mg, 0.2 mmol) was added, and then the mixture was heated. When the temperature of the oil bath climbed to 55 °C, the Grignard reagent (0.6 mmol) was added gradually and dropped by a syringe pump. The reaction temperature was maintained at 55 °C until completion 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 with ether (10 mL × 3), dried over $MgSO_4$, filtered, and concentrated to give a crude product which was subjected to column chromatography to give the target product.

(1*S,2*R**)-2-Methyl-1,2-dihydronaphthalen-1-ol (2a).** Prepared according to general procedure I. A white solid (22.7 mg, 71%). R_f = 0.17 on silica gel (ethyl acetate–petroleum ether = 1 : 20, v/v). m.p. 63–64 °C. IR (film, cm^{-1}) 3398(br), 2922(s), 2852(s), 1668(m), 1460(s), 1371(m), 1188(m), 974(m), 788(m). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 7.2 Hz, 1H), 7.29–7.22 (m, 2H), 7.12 (d, J = 7.2 Hz, 1H), 6.51 (dd, J = 2.4, 9.6 Hz, 1H), 5.80 (dd, J = 2.8, 9.2 Hz, 1H), 4.57 (d, J = 4.8 Hz, 1H), 2.67–2.61 (m, 1H), 1.65(s, 1H), 1.25 (d, J = 2.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 132.4, 132.3, 128.4, 127.6, 127.3, 126.6, 126.4, 71.7, 35.2, 14.1. HRMS (EI^+) calcd for $C_{11}H_{12}O$ [M^+]: 160.0888. Found: 160.0889.

(1*S,2*R**)-2-Pentyl-1,2-dihydronaphthalen-1-ol (2b).** Prepared according to general procedure I. A colorless oil liquid (23.3 mg, 54%). R_f = 0.17 on silica gel (ethyl acetate–petroleum ether = 1 : 20, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 6.4 Hz, 1H), 7.31–7.21 (m, 2H), 7.12 (d, J = 16.4 Hz, 1H), 6.54 (dd, J = 2.0, 9.2 Hz, 1H), 5.93 (dd, J = 2.4, 10.4 Hz, 1H), 4.59 (d, J = 4.4 Hz, 1H), 2.50–2.43 (m, 1H), 1.84–1.77 (m, 1H), 1.55–1.48 (m, 3H), 1.38–1.32 (m, 4H), 0.94–0.87 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 132.7, 131.3, 128.5, 127.6, 127.6, 126.7, 126.4, 70.3, 40.4, 32.0, 29.1, 26.9, 22.6, 14.1. HRMS (EI^+) calcd for $C_{15}H_{20}O$ [M]$^+$: 216.1514. Found: 216.1516.

(1*S,2*R**)-2-Cyclohexyl-1,2-dihydronaphthalen-1-ol (2c).** Prepared according to general procedure I. A white solid (26.0 mg, 57%). R_f = 0.16 on silica gel (ethyl acetate–petroleum ether = 1 : 20, v/v). m.p. 81–82 °C. IR (film, cm^{-1}) 3518(br), 3045(s), 2920(s), 2846(s), 1448(s), 1303(m), 1082(m), 960(m), 891(m), 806(m), 758(m), 663(m), 528(m). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.21 (m, 3H), 7.13 (d, J = 6.0 Hz, 1H), 6.60 (d, J = 8.8 Hz, 1H), 5.99 (d, J = 8.4 Hz, 1H), 4.71 (s, 1H), 2.04–2.20 (m, 4H), 1.63–1.80 (m, 8H), 1.00–1.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 132.7, 129.2, 128.6, 127.7, 127.6, 127.1, 126.4, 105.0, 68.9, 46.0, 36.4, 30.9, 26.6, 26.4(2C). HRMS (EI^+) calcd for $C_{16}H_{20}O$ [M^+]: 228.1514. Found: 228.1517.

(1*S,2*R**)-2-Allyl-1,2-dihydronaphthalen-1-ol (2d).** Prepared according to general procedure I. A colorless oil liquid (29.6 mg, 74%). R_f = 0.18 on silica gel (ethyl acetate–petroleum ether = 1 : 20, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.20 (m, 3H), 7.13 (d, J = 6.8 Hz, 1H), 6.56 (d, J = 9.2 Hz, 1H), 6.01–5.89 (m, 1H), 5.84 (d, J = 9.2, 1H), 5.19 (d, J = 17.2, 1H), 5.12 (d, J = 10.0, 1H), 4.60 (s, 1H), 2.62–2.52 (m, 2H), 2.40–2.33 (m, 1H), 1.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 136.5, 132.6, 130.2, 128.6, 127.7, 127.6, 127.0, 126.6, 116.9, 70.2, 40.2, 33.6. HRMS (EI^+) calcd for $C_{13}H_{14}O$ [M^+]: 186.1045. Found: 186.1037.

(1*S,2*S**)-2-Phenyl-1,2-dihydronaphthalen-1-ol (2e).** Prepared according to general procedure I. A white solid (40.0 mg, 90%). R_f = 0.16 on silica gel (ethyl acetate–petroleum ether = 1 : 20, v/v). m.p. 86–87 °C. IR (film, cm^{-1}) 3379(br), 3028(s), 2924(s), 2852(s), 1600(s), 1489(s), 1450(s), 1072(s), 1033(s), 779(s), 752(s), 698(s). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.2 Hz, 1H), 7.36–7.21 (m, 7H), 7.18 (dd, J = 1.6, 6.8 Hz, 1H), 6.67 (dd, J = 1.6, 9.2 Hz, 1H), 6.04 (dd, J = 3.6, 9.6 Hz, 1H), 4.84 (d, J = 8.0 Hz, 1H), 3.84–3.76 (m, 1H), 2.02 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 135.5, 132.6, 129.8(2C), 128.8(2C), 128.4, 128.2, 128.1, 127.6, 127.2(2C), 126.4, 74.3, 50.1. HRMS (EI^+) calcd for $C_{16}H_{14}O$ [M^+]: 222.1045. Found: 222.1039.

(1*S,2*S**)-2-(4-Chlorophenyl)-1,2-dihydronaphthalen-1-ol (2g).** Prepared according to general procedure I. A white solid (15.9 mg, 31%). R_f = 0.21 on silica gel (ethyl acetate–petroleum ether = 1 : 20, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.21 (m, 5H), 7.21–7.13 (m, 3H), 6.70 (d, J = 9.6, 1H), 6.06 (dd, J = 4.0, 9.6 Hz, 1H), 4.89 (d, J = 5.2 Hz, 1H), 3.81 (s, 1H), 1.53 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 135.1, 132.9, 132.4, 129.7 (2C), 129.1, 128.8(2C), 128.5, 128.2, 127.9, 126.7, 126.6, 74.3, 49.3. HRMS (APCI) calcd for [$C_{16}H_{13}ClO$ + Cl]$^+$: 291.0344. Found: 291.0345.

4,4′-Dichlorobiphenyl (2gg). Compound **2gg** was the couple-product of 4-chlorophenylmagnesium bromide; it was obtained as a white solid. R_f = 0.8 on silica gel (ethyl acetate–petroleum ether = 1 : 20, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 4H), 7.41 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4(2C), 133.7(2C), 129.0(4C), 128.2(4C). HRMS (EI^+) calcd for $C_{12}H_8Cl_2$ [M^+]: 222.0003. Found: 222.0005.

(1*S,2*S**)-2-(4-Methoxyphenyl)-1,2-dihydronaphthalen-1-ol (2f).** Prepared according to general procedure I. A white solid (23.7 mg, 47%). R_f = 0.20 on silica gel (ethyl acetate–petroleum ether = 1 : 20, v/v). m.p. 73–74 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 6.4, 1H), 7.32–7.23 (m, 2H), 7.17 (d, J = 7.6, 3H), 6.85 (d, J = 8.0, 2H), 6.69 (d, J = 9.6, 1H), 6.12 (dd, J = 3.6, 9.2 Hz, 1H), 4.94 (s, 1H), 3.82 (s, 1H), 3.78 (s, 3H), 1.62 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 135.3, 132.6, 132.5, 130.1, 129.4(2C), 128.3(2C), 128.0, 127.4, 126.6, 126.4, 114.2, 74.5, 55.3, 49.1. HRMS (APCI) calcd for [$C_{17}H_{16}O_2$ + Na]$^+$: 275.1048. Found: 275.1038.

4,4′-Dimethoxybiphenyl (2ff). Compound **2ff** was the couple-product of 4-methoxyphenylmagnesium bromide; it was obtained as a white solid. R_f = 0.41 on silica gel (ethyl acetate–petroleum ether = 1 : 20, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.0, 4H), 6.97 (d, J = 8.0, 4H), 3.85 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7(2C), 133.5(2C), 127.7(4C), 114.1(4C), 55.6(2C). HRMS (EI^+) calcd for $C_{14}H_{14}O_2$ [M^+]: 214.0994. Found: 214.0997.

(1*S,2*R**)-5,8-Dimethoxy-2-methyl-1,2-dihydronaphthalen-1-ol (3a).** Prepared according to general procedure I. A colorless oil liquid (27.3 mg, 62%). R_f = 0.20 on silica gel (ethyl acetate–petroleum ether = 1 : 10, v/v). IR (film, cm^{-1}) 3466(br), 3034(s), 2954(s), 2929(s), 2835(s), 1596(s), 1481(s), 1367(m), 1307(m), 1257(s), 1116(s), 1087(s), 958(s), 910(s), 798(s), 765(s), 717(s). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (dd, J = 9.7, 2.8 Hz, 1H), 6.80–6.73 (m, 2H), 5.74 (d, J = 9.7 Hz, 1H), 4.89 (d, J = 4.4 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.54 (m, 1H), 1.69 (d, J = 8.8 Hz, 1H), 1.35 (d, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 149.5, 132.0, 125.7, 122.4, 120.5, 111.1, 110.4, 64.3, 56.1(2C), 34.6, 15.2; HRMS (APCI) calcd for $[C_{13}H_{16}O_3 + Na]^+$: 243.0997. Found: 243.0992.

(1*S,2*R**)-5,8-Dimethoxy-2-pentyl-1,2-dihydronaphthalen-1-ol (3b).** Prepared according to general procedure I. A colorless oil liquid (25.4 mg, 46%). R_f = 0.20 on silica gel (ethyl acetate–petroleum ether = 1 : 10, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, J = 10.0 Hz, 1H), 6.82–6.73 (m, 2H), 5.81 (d, J = 9.6 Hz, 1H), 4.99 (s, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 2.35 (s, 1H), 1.90–1.81 (m, 1H), 1.63–1.56 (m, 3H), 1.40–1.33 (m, 4H), 0.96–0.84 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 149.5, 130.8, 125.7, 122.8, 120.6, 111.1, 110.4, 62.6, 56.2, 56.1, 39.8, 32.0, 29.6, 26.9, 22.7, 14.1. HRMS (EI^+) calcd for $C_{17}H_{24}O_3$ [M^+]: 276.1725. Found: 276.1717.

(1*S,2*R**)-2-Cyclohexyl-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (3c).** Prepared according to general procedure I. A faint yellow solid (31.1 mg, 54%). R_f = 0.19 on silica gel (ethyl acetate–petroleum ether = 1 : 10, v/v). IR (film, cm^{-1}) 3535(br), 3045(m), 2995(m), 2926(s), 2846(s), 1597(s), 1487(s), 1444(s), 1261(s), 1076(s), 964(m), 887(m), 806(s), 711(s). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, J = 9.9 Hz, 1H), 6.81–6.69 (m, 2H), 6.00 (d, J = 9.8 Hz, 1H), 5.16 (d, J = 3.6 Hz, 1H), 3.95 (m, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 2.21 (d, J = 12.0 Hz, 1H), 2.14 (d, J = 11.7 Hz, 1H), 2.04 (d, J = 8.9 Hz, 1H), 1.75 (m, 6H), 1.36–1.30 (m, 2H), 1.06–0.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 149.5, 128.8, 125.9, 122.8, 121.0, 111.0, 110.4, 61.0, 56.1, 56.0, 45.4, 36.5, 31.2, 31.1, 26.7, 26.4(2C). HRMS (EI^+) calcd for $C_{18}H_{24}O_3$ [M^+]: 288.1726. Found: 288.1724.

(1*S,2*R**)-2-Allyl-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (3d).** Prepared according to general procedure I. A white solid (32.2 mg, 62%). R_f = 0.19 on silica gel (ethyl acetate–petroleum ether = 1 : 10, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, J = 9.6 Hz, 1H), 6.82–6.74 (m, 2H), 6.03–5.95 (m, 1H), 5.82 (d, J = 9.6 Hz, 1H), 5.22 (d, J = 17.2 Hz, 1H), 5.14 (d, J = 10.0 Hz, 1H), 5.00 (s, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 2.64–2.59 (m, 1H), 2.49–2.41 (m, 2H), 2.05–1.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 149.5, 136.8, 129.6, 125.5, 122.7, 120.9, 116.8, 111.2, 110.5, 62.6, 56.2, 56.0, 39.7, 34.1. HRMS (APCI) calcd for $[C_{15}H_{18}O_3 - H_2O + H]^+$: 229.1229. Found: 229.1236.

(1*S,2*S**)-5,8-Dimethoxy-2-phenyl-1,2-dihydronaphthalen-1-ol (3e).** Prepared according to general procedure I. A colorless oil liquid (42.3 mg, 75%). R_f = 0.20 on silica gel (ethyl acetate–petroleum ether = 1 : 10, v/v). IR (film, cm^{-1}) 3442(br), 3024(s), 2997(s), 2935(s), 2835(s), 1595(s), 1485(s), 1456(s), 1440(s), 1348(s), 1305(s), 1257(s), 1099(s), 1002(s), 896(s), 856(s), 738(s), 702(s). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.13 (m, 5H), 7.11 (d, J = 10.0 Hz, 1H), 6.81 (d, J = 8.8 Hz, 1H), 6.73 (d, J = 9.2 Hz, 1H), 6.12 (dd, J = 5.6, 10.0 Hz, 1H), 5.17 (bs, 1H), 3.91 (d, J = 5.2 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 2.44 (s 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 149.5, 140.0, 128.5(2C), 128.2, 128.0 (2C), 126.8, 123.2, 122.4, 120.4, 111.3, 110.6, 67.4, 56.2, 55.9, 48.1. HRMS (EI^+) calcd for $C_{18}H_{18}O_3$ [M^+]: 282.1256. Found: 282.1252.

(1*S,2*S**)-5,8-Dimethoxy-2-(4-methoxyphenyl)-1,2-dihydronaphthalen-1-ol (3f).** Prepared according to general procedure I. A colorless oil liquid (25.6 mg, 41%). R_f = 0.18 on silica gel (ethyl acetate–petroleum ether = 1 : 10, v/v). IR (film, cm^{-1}) 3460(br), 2997(m), 2927(s), 2852(s), 1722(m), 1668(m), 1604(s), 1483(s), 1460(s), 1365(w), 1255(s), 1180(s), 1095(s), 958(m), 864(m), 829(s), 800(s), 721(s), 540(m). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13–7.02 (m, 3H), 6.83–6.67 (m, 4H), 6.11 (dd, J = 9.6, 5.6 Hz, 1H), 5.12 (s, 1H), 3.98 (s, 1H), 3.84 (s, 3H), 3.75 (s, 6H), 1.63(s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 151.3, 149.5, 131.8, 129.0, 128.5, 123.2, 122.4, 120.2, 113.9, 111.3, 110.5, 67.6, 56.2, 55.9, 55.2, 47.3. HRMS (EI^+) calcd for $C_{19}H_{20}O_4$ [M^+]: 312.1362. Found: 312.1359.

(1*S,2*R**)-6,7-Dimethoxy-2-methyl-1,2-dihydronaphthalen-1-ol (4a).** Prepared according to general procedure I. A white solid (10.6 mg, 24%). R_f = 0.19 on silica gel (ethyl acetate–petroleum ether = 1 : 5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.73 (s, 1H), 6.59 (d, J = 9.0 Hz, 1H), 5.96 (dd, J = 3.2, 7.6 Hz, 1H), 4.75 (d, J = 7.2 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 3.78 (s, 1H), 2.01 (s, 1H). 1.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 148.5, 128.7, 128.4, 127.7, 127.2, 110.2, 109.8, 74.4, 56.0, 55.9, 14.2. HRMS (EI^+) calcd for $C_{13}H_{16}O_3$ [M^+]: 220.1099. Found: 220.1098.

2,3-Dimethoxy-6-methylnaphthalene (4aa). Compound **4aa** was the by-product of substrate **1c** with methylmagnesium bromide, **4aa** was obtained as a white solid. R_f = 0.65 on silica gel (ethyl acetate–petroleum ether = 1 : 5, v/v). m.p. 57–58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.2 Hz, 1H), 7.47 (s, 1H), 7.18 (d, J = 8.1 Hz, 1H), 7.09 (s, 1H), 7.05 (s, 1H), 3.99 (s, 6H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 148.8, 133.7, 129.3, 127.1, 126.3, 126.1, 125.5, 106.1, 105.8, 55.8(2C), 21.6. MS (ESI) calcd for $[C_{13}H_{14}O_2 + H]^+$: 203.11. Found: 203.18. HRMS (EI^+) calcd for $C_{13}H_{14}O_2$ [M^+]: 202.0994. Found: 202.0991.

(1*S,2*S**)-6,7-Dimethoxy-2-phenyl-1,2-dihydronaphthalen-1-ol (4e).** Prepared according to general procedure I. A white solid (15.2 mg, 27%). R_f = 0.20 on silica gel (ethyl acetate–petroleum ether = 1 : 5, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.21 (m, 5H), 6.96 (s, 1H), 6.73 (s, 1H), 6.59 (d, J = 9.3 Hz, 1H), 5.95 (d, J = 8.9 Hz, 1H), 4.75 (d, J = 4.9 Hz, 1H), 4.01 (s, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 1.98 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 143.4, 140.8, 128.7(2C), 128.4(2C), 128.0, 127.7, 127.2, 127.1, 125.0, 110.2, 109.8, 82.6, 74.3, 56.0, 50.2. HRMS (EI^+) calcd for $C_{18}H_{18}O_3$ [M^+]: 282.1256. Found: 282.1253.

2,3-Dimethoxy-6-phenylnaphthalene (4ee). Compound **4ee** was the by-product of substrate **1c** with methylmagnesium bromide; **4ee** was obtained as a white solid. R_f = 0.62 on silica gel (ethyl acetate–petroleum ether = 1 : 5, v/v). m.p. 117–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.76 (dd,

J = 8.2, 3.4 Hz, 1H), 7.73–7.68 (m, 2H), 7.63–7.59 (m, 1H), 7.47 (d, J = 3.5 Hz, 2H), 7.36 (s, 1H), 7.18 (d, J = 3.2 Hz, 1H), 7.15 (d, J = 3.2 Hz, 1H), 4.02 (d, J = 3.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.5, 141.4, 137.0, 129.4, 128.8(2C), 128.4, 127.3(2C), 127.0, 126.8, 124.4, 123.8, 106.5, 106.0, 55.9(2C). MS (ESI) calcd for $[C_{18}H_{16}O_2 + H]^+$: 265.12. Found: 264.89. HRMS (EI^+) calcd for $C_{18}H_{16}O_2$ [M^+]: 264.1150. Found: 264.1153.

(1*S,2*R**)-6,7-Dibromo-2-methyl-1,2-dihydronaphthalen-1-ol (5a).** Prepared according to general procedure I. A white solid (35.6 mg, 56%). R_f = 0.17 on silica gel (ethyl acetate–petroleum ether = 1 : 10, v/v). IR (film, cm^{-1}) 3329(br), 3034(s), 2962(s), 2924(s), 2854(s), 1670(m), 1620(m), 1575(s), 1462(s), 1371(s), 1107(s), 1049(s), 883(s), 798(s), 752(m). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.33 (s, 1H), 6.37 (d, J = 9.6 Hz, 1H), 5.93 (dd, J = 9.5, 3.6 Hz, 1H), 4.61 (d, J = 4.9 Hz, 1H), 2.59 (dd, J = 3.7, 1.7 Hz, 1H), 1.76 (s, 1H), 1.15 (d, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 134.5, 133.1, 131.9, 130.9, 124.7, 124.0, 122.9, 70.5, 35.0, 13.1. HRMS (EI^+) calcd for $C_{11}H_{10}Br_2O$ [M^+]: 315.9098. Found: 315.9096.

(1*S,2*R**)-2-Allyl-6,7-dibromo-1,2-dihydronaphthalen-1-ol (5d).** Prepared according to general procedure I. A colorless oil liquid (32.2 mg, 45%). R_f = 0.18 on silica gel (ethyl acetate–petroleum ether = 1 : 10, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.37(s, 1H), 6.45 (d, J = 9.6 Hz, 1H), 5.95 (d, J = 5.2 Hz, 1H), 5.91–5.85 (m, 1H), 5.12 (d, J = 10.4 Hz, 2H), 4.63 (s, 1H), 2.57–2.49 (m, 2H), 2.31–2.26 (m, 1H), 1.74 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 136.1, 133.3, 132.4, 132.2, 131.1, 125.2, 124.3, 122.9, 117.3, 69.4, 39.9, 33.0. MS (EI, 70ev) m/z (%): 326.67 ([M − H_2O + 2], 6), 282.81 (12), 264.80 (6), 251.22 (15), 185.44 (28), 184.51 (16), 144.91 (76), 143.92 (39), 115.88 (10), 115.13 (31), 114.44 (17). HRMS (EI^+) calcd for $C_{13}H_{12}Br_2O$ [M^+]: 341.9255. Found: 341.9254.

(1*S,2*R**)-6,7-Dibromo-2-isopropyl-1,2-dihydronaphthalen-1-ol (5i).** Prepared according to general procedure I. A white solid (25.6 mg, 37%). R_f = 0.19 on silica gel (ethyl acetate–petroleum ether = 1 : 10, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.36 (s, 1H), 6.46 (d, J = 10.0 Hz, 1H), 6.05 (dd, J = 4.4, 9.6 Hz, 1H), 4.61 (d, J = 5.2 Hz, 1H), 2.43 (d, J = 4.8 Hz, 1H), 1.84–1.79 (m, 1H), 1.63 (s, 1H), 0.95 (d, J = 6.0 Hz, 3H), 0.87 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 133.3, 132.3, 131.0, 130.8, 125.2, 124.6, 123.8, 69.7, 48.8, 29.7, 20.6, 19.0. MS (EI, 70 ev) m/z (%): 328.06 ([M − H_2O + 2], 12), 298.64 (16), 284.89 (10), 273.45 (7), 143.05 (13), 116.03 (29), 115.00 (100), 113.99 (24). HRMS (EI^+) calcd for $C_{13}H_{14}Br_2O$ [M^+]: 343.9411. Found: 343.9410.

(1*S,2*S**)-6,7-Dibromo-2-phenyl-1,2-dihydronaphthalen-1-ol (5e).** Prepared according to general procedure I. A colorless oil liquid (54.7 mg, 72%). R_f = 0.18 on silica gel (ethyl acetate–petroleum ether = 1 : 10, v/v). IR (film, cm^{-1}) 3543(s), 3415(br), 3030(s), 2924(s), 2852(s), 1668(s), 1600(s), 1490(s), 1463(s), 1388(s), 1111(s), 1074(s), 1037(s), 889(s), 763(s), 698(s), 582(s), 536(s). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.39 (s, 1H), 7.37–7.22 (m, 5H), 6.53 (d, J = 9.6 Hz, 1H), 6.08 (dd, J = 9.6, 3.3 Hz, 1H), 4.76 (d, J = 9.3 Hz, 1H), 3.72 (d, J = 9.0 Hz, 1H), 2.12 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 136.5, 133.4, 132.1, 131.1, 130.8, 129.0(2C), 128.4(2C), 127.6, 126.0, 124.0, 123.5, 73.5, 49.9. HRMS (EI^+) calcd for $C_{16}H_{12}Br_2O$ [M^+]: 377.9255. Found: 377.9253.

(1*S,2*S**)-6,7-Dibromo-2-(4-methoxyphenyl)-1,2-dihydronaphthalen-1-ol (5f).** Prepared according to general procedure I. A colorless oil liquid (50.8 mg, 62%). R_f = 0.21 on silica gel (ethyl acetate–petroleum ether = 1 : 10, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.40(s, 1H), 7.15 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 6.52 (d, J = 9.6 Hz, 1H), 6.07 (dd, J = 2.8, 9.6 Hz, 1H), 4.71 (d, J = 8.8 Hz, 1H), 3.75 (s, 3H), 3.68 (d, J = 8.8 Hz, 1H), 2.18 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 149.5, 136.4, 133.4, 132.4, 131.9, 131.3, 130.8, 129.4(2C), 125.8, 124.0, 114.8, 114.3, 73.7, 55.8, 49.0. HRMS (EI^+) calcd for $C_{17}H_{14}Br_2O_2$ [M^+]: 407.9361. Found: 407.9360.

(1*S,2*R**)-2-Methyl-1,2-dihydrotriphenylen-1-ol (6a).** Prepared according to general procedure I. A white solid (9.9 mg, 39%). R_f = 0.18 on silica gel (ethyl acetate–petroleum ether = 1 : 10, v/v). m.p. 61–62 °C. IR (film, cm^{-1}) 3360(br), 3076(s), 2956(s), 2924(s), 2852(s), 1666(m), 1608(s), 1496(s), 1450(s), 1409(s), 1259(s), 1080(s), 1010(s), 981(m), 850(m), 738(s), 615(s). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 3.3 Hz, 2H), 8.34 (d, J = 18.8 Hz, 2H), 7.68 (s, 4H), 7.00 (d, J = 21.7 Hz, 1H), 6.44 (d, J = 5.5 Hz, 1H), 5.31 (s, 1H), 2.98 (d, J = 6.1 Hz, 1H), 2.02(s, 1H), 1.01(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 133.4, 130.7, 130.6, 127.3, 127.1, 126.9, 126.8, 126.3, 125.0, 124.0, 123.5, 123.1(2C), 120.5, 120.3, 69.0, 37.0, 16.7. HRMS (EI^+) calcd for $C_{19}H_{16}O$ [M^+]: 260.1201. Found: 260.1200.

(1*S,2*S**)-2-Phenyl-1,2-dihydrotriphenylen-1-ol (6e).** Prepared according to general procedure I. A white solid (13.5 mg, 41%). R_f = 0.20 on silica gel (ethyl acetate–petroleum ether = 1 : 10, v/v). m.p. 80–81 °C. IR (film, cm^{-1}) 3236(br), 3024(s), 2924(s), 2854(s), 2854(s), 1668(m), 1600(m), 1492(s), 1448(s), 1278(s), 1012(s), 852(m), 883(s), 736(s), 704(s), 603(m). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (dd, J = 18.5, 4.7 Hz, 2H), 8.44–8.38 (m, 1H), 8.24–8.20 (m, 1H), 7.66 (ddd, J = 22.2, 7.4, 4.3 Hz, 6H), 7.17–7.10 (m, 4H), 6.50 (dd, J = 9.5, 6.1 Hz, 1H), 5.57 (s, 1H), 4.16 (d, J = 5.7 Hz, 1H), 2.22–2.12 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 136.8, 130.8, 130.6, 130.1, 129.9, 128.7, 128.6, 127.8, 127.3, 127.1, 127.0(2C), 126.5, 126.4, 125.0, 123.9, 123.6, 123.1(2C), 122.3, 120.3, 69.5, 48.8. HRMS (EI^+) calcd for $C_{24}H_{18}O$ [M^+]: 322.1358. Found: 322.1359.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (21372090 and 21172081), the Natural Science Foundation of Guangdong Province (S2013020013091), and Produce, Learning and Research Project Program of Education Department of Guangdong Province (2011A090200039) for financial support.

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