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Rhodium/zinc co-catalyzed asymmetric ring opening reactions of oxabenzonorbornadienes with carboxylic acids

Xiaobo He [a], Jingchao Chen [a,*], Xin Xu [a], Fan Yang [a], Cuiping Gu [a], Yongyun Zhou [a], Baomin Fan [a,b,*]

[a] *YMU-HKBU Joint Laboratory of Traditional Natural Medicine, Yunnan Minzu University, Yuehua Street, Kunming 650500, China*
[b] *State Key Laboratory of Elemento-organic Chemistry, Nankai University, Weijing Road, Tianjin 300071, China*

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ABSTRACT

The asymmetric ring opening reactions of oxabenzonorbornadienes with carboxylic acids are described. By using the complex of $[Rh(COD)Cl]_2$ and (*S*,*S*)-BDPP, with ZnI_2 as the co-catalyst, a range of aromatic acids and alkyl acids were utilized as nucleophiles to afford the corresponding chiral hydronaphthalene products with high enantioselectivities (84–94% *ee*). Thus, the present methodology has provides an effective synthetic method for the preparation of enantioenriched hydronaphthalenes.

1. Introduction

Over the past decade, the asymmetric ring opening reactions of benzonorbornadiene derivatives have attracted continuous interest[1] as they provide straightforward access to chiral hydronaphthalenes, which are substructures in many biologically active natural products and pharmaceuticals.[2] Remarkable progress towards this type of reaction has been made by Lautens et al.,[3] Yang et al.,[4] and others.[5] By using transition metal/Lewis acid co-catalyst systems, our group has developed effective asymmetric ring opening reactions of oxa/azabenzonorbornadienes by using terminal alkynes,[6] amines[7] and phenols.[8] Most recently, we turned our attention to carboxylic acid nucleophiles. The ring opening reactions of oxa/azabenzonorbornadienes by carboxylic acids have provided allyl esters as products, which are versatile reaction substrates of Trost-Tsuji reactions.[9] After Lautens et al. have pioneered the asymmetric ring opening reactions with carboxylate nucleophiles,[10] Yang et al. also reported this type of reaction with iridium catalysts, but generally low enantioselectivities were observed.[11] On the basis of the successful applications of the rhodium/BDPP and ZnI_2 co-catalyst system to the asymmetric ring opening reactions of oxabenzonorbornadienes with amines,[7b] we herein propose that this type of co-catalyst system could also be applied to the asymmetric ring opening reactions of oxabenzonorbornadienes by using carboxylic acids as nucleophiles.

2. Results and discussion

The complex of $[Rh(COD)Cl]_2$ and (*R*,*R*)-BDPP has proved to be an effective catalyst in our previous study of asymmetric ring opening reactions of oxabenzonorbornadienes with amines. However, when we began our studies of the asymmetric ring opening reaction of oxabenzonorbornadienes with carboxylic acids under previously established reaction conditions, we only observed the generation of 1-naphthol and none of the desired product was obtained (Table 1, entry 1). When the reaction was carried out at 60 °C, it also failed to give any of the desired product besides 1-naphthol (Table 1, entry 2). We reasoned that the generation of 1-naphthol was caused by the acidic environment and a suitable base was needed to neutralize it,[10] and also increase the nucleophilicity of the carboxylic acid. The addition of 6 equivalents of triethylamine led to a satisfactory 95% yield with 89% enantiomeric excess (Table 1, entry 3). When screening other aprotic solvents, we noticed that DCM, acetonitrile and ethers decreased both the reaction yields and the enantiomeric excess (Table 1, entries 4–8). Thus, DCE was identified as the optimal reaction solvent for present reaction.

Based on our previous study of the ring opening reactions of oxa/azabenzonorbornadienes, Lewis acids were identified as essential co-catalysts, which significantly enhanced the activity of the catalytic systems. Therefore, we studied the effect of various Lewis acids in the present reaction and the experimental results are summarized in Table 2. Although ZnI_2 was very effective, other zinc salts such as $ZnCl_2$, $ZnBr_2$ and $Zn(OTf)_2$ proved to be inferior and lower conversions were observed even when the reaction was carried out for a prolonged reaction time, although the *ee* values remained high (Table 2, entries 2–4). Similar results were obtained with other Lewis acids, such as AgOTf, CuBr, $Cu(OTf)_2$, $Al(OTf)_3$, and $AlCl_3$ (Table 2, entries 5–9). We noticed that the anion of the Lewis acid also played an important role as the use of CuI and FeI_2 had afforded a yield of 59% and 73%, respectively (Table 2, entries 10–11). We next tested Bu_4NI but it only gave a low

* Corresponding authors.

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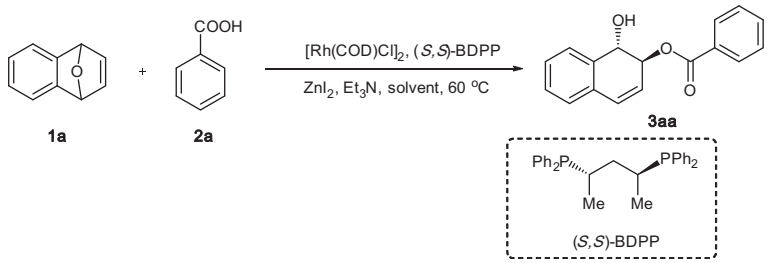
0957-4166/

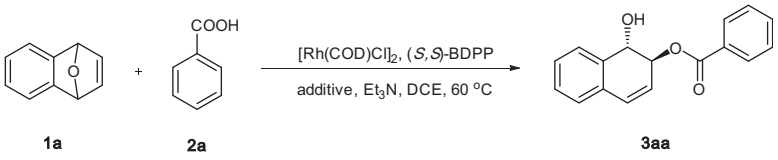
Table 1
Screening of reaction solvent[a]



Entry	Solvent	Time (h)	Yield (%)[b]	Ee (%)[c]
1[d,e]	DCE	16 h	0	—
2[d]	DCE	12 h	0	—
3	DCE	1.5	95	89
4	DCM	1.5	82	88
5	CH_3CN	3	49	86
6	THF	1.5	89	80
7	Diethyl ether	4	63	80
8	1,4-Dioxane	1.5	67	76

[a] The reaction was carried out with **1a** (0.20 mmol), 5.0 equiv of benzoic acid **2a** (1.0 mmol), 0.1 equiv of ZnI_2 (0.02 mmol) and 6.0 equiv of Et_3N (1.20 mmol) in solvent (2.0 mL) at 60 °C in the presence of $[Rh(COD)Cl]_2$ (2.5 mol %) and (*S*,*S*)-BDPP (6.5 mol %).
[b] Isolated yield after silica gel column chromatography.
[c] Determined by HPLC with a Chiralcel OD-H column.
[d] No Et_3N was used.
[e] The reaction was carried out at room temperature.

Table 2
Study of the effect of Lewis acid and reaction temperature[a]



Entry	Additive	Time (h)	Yield (%)[b]	Ee (%)[c]
1	ZnI_2	1.5	95	89
2	$ZnCl_2$	72	38	88
3	$ZnBr_2$	72	52	87
4	$Zn(OTf)_2$	48	25	89
5	AgOTf	48	16	88
6	CuBr	72	36	88
7	$Cu(OTf)_2$	48	33	90
8	$Al(OTf)_3$	48	26	89
9	$AlCl_3$	48	52	89
10	CuI	72	59	90
11	FeI_2	24	73	87
12	$^nBu_4NI$	48	39	89
13[d]	ZnI_2	1.5	95	91
14[e]	ZnI_2	72	85	91
15	—	72	20	86

[a] The reaction was carried out with **1a** (0.20 mmol), 5.0 equiv of benzoic acid **2a** (1.0 mmol), 0.1 equiv of Lewis acid (0.02 mmol) and 6.0 equiv of Et_3N (1.20 mmol) in DCE (2.0 mL) at 60 °C in the presence of $[Rh(COD)Cl]_2$ (2.5 mol %) and (*S*,*S*)-BDPP (6.5 mol %).
[b] Isolated yield after silica gel column chromatography.
[c] Determined by HPLC with a Chiralcel OD-H column.
[d] The reaction was carried out at 40 °C.
[e] The reaction was carried out at ambient temperature.

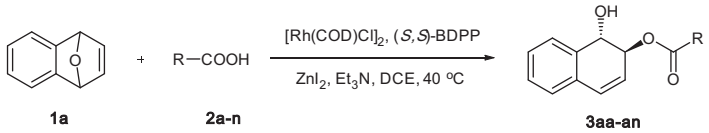
reaction yield (Table 2, entry 12). The following temperature experiments were carried out by employing ZnI_2 as the Lewis acid and a lower temperature of 40 °C proved to be beneficial to achieve a high *ee* (Table 2, entry 13). When the reaction was carried out at ambient temperature, it retained the enantioselectivity but lowered yield (Table 2, entry 14). It is obvious that the Lewis acid was indispensable in present protocol, because the control experiment that without any Lewis acid only gave a low reaction yield (Table 2, entry 15).

Under the standard reaction conditions, a series of carboxylic acids including aromatic acids and alkyl acids were subjected to the process to investigate the reaction scope. (Table 3) In general, all of the carboxylic acids were suitable for the present reaction and gave good enantioselectivities (88–91%). However, the reaction yields were affected by the substrates. For instance, with OCH_3, Cl, and Br on the phenyl ring of benzoic acid, the reaction yields were suppressed by electronic characteristics (Table 3, entries 2–4). It should be noted that the steric effect had little

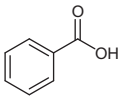
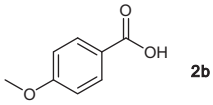
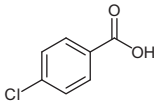
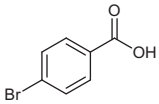
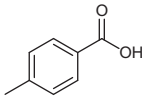
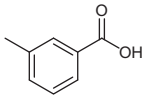
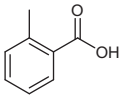
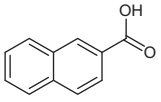
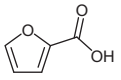
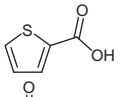
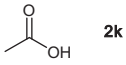
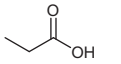
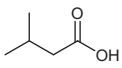
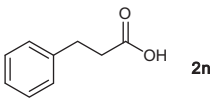
impact on the activity of benzoic acid (Table 3, entries 5–7). Other aryl acids, including 2-naphthoic acid, 2-furoic acid and 2-thiophenecarboxylic acid were also suitable nucleophiles for present transformations (Table 3, entries 8–10). Furthermore, we found that a range of alkyl acids showed good reaction activities as well, and afforded the desired products with good enantioselectivities (Table 3, entries 11–14).

To further extend the reaction scope, a series of oxabenzonorbornadienes were reacted with benzoic acid and the corresponding products were obtained in good to excellent *ee*s (84–94%). It should

Table 3
Substrate scope of carboxylic acids[a]



1a 2a-n 3aa-an

Entry	Carboxylic acid	Time (h)	Yield (%)[b]	Ee (%)[c]
1	 2a	1.5	95	91
2[d]	 2b	16	68	89
3	 2c	6	70	90
4	 2d	6	68	89
5[d]	 2e	4	90	90
6[d]	 2f	4.5	90	90
7[d]	 2g	5	88	90
8	 2h	4	82	89
9	 2i	2	70	90
10	 2j	6	76	90
11	 2k	6	70	88
12	 2l	6	78	94
13	 2m	6	78	90
14	 2n	6	73	90

[a] The reaction was carried out with **1a** (0.20 mmol), 5.0 equiv of benzoic acid **2** (1.0 mmol), 0.1 equiv of ZnI_2 (0.02 mmol) and 6.0 equiv of Et_3N (1.20 mmol) in DCE (2.0 mL) at 40 °C in the presence of $[Rh(COD)Cl]_2$ (2.5 mol %) and (*S*,*S*)-BDPP (6.5 mol %).
[b] Isolated yield after silica gel column chromatography.
[c] Determined by HPLC with a Chiralcel OD-H column.
[d] *N*,*N*-Diisopropylethylamine was used instead of triethylamine to improve the reaction yield.

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be noted that the reaction of dimethyl-substituted oxabenzonorbornadiene **1b** proceeded smoothly to afford the corresponding ring-opening products in good yields and with excellent enantioselectivities (Table 4, entry 2). However, the reactions were sluggish when using oxabenzonorbornadienes **1c**–**e** and gave 51–68% yields with starting materials recovered (Table 4, entries 3–5). Conversely, oxabenzonorbornadiene **1f** was found to be very active in the presence of ZnI_2 and led to the generation of 6,7-dimethoxynaphthalen-1-ol as a by-product with a lower yield of the desired product (Table 4, entry 6). The bromo groups on the phenyl ring of oxabenzonorbornadiene were tolerated under present reaction conditions (Table 4, entry 7), which allows for further potential functionalizations by traditional cross-coupling reactions. However, the reactions of **1h** and **1i** did not give the corresponding ring-opening products under the standard conditions.

3. Conclusion

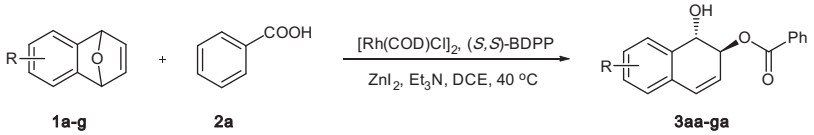
In conclusion, the asymmetric ring opening reactions of oxabenzonorbornadienes were accomplished by using the rhodium/zinc as the co-catalyst. This co-catalytic system exhibits wide substrate compatibility and good functional group tolerance. A wide range of carboxylic acids were found to be suitable to give the corresponding chiral hydronaphthalene products with high enantioselectivities.

4. Experimental section

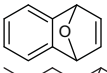
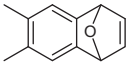
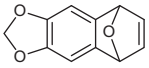
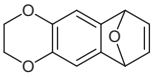
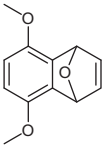
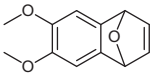
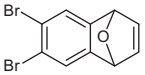
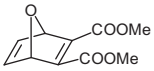
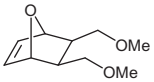
4.1. General

Oxabenzonorbornadienes **1a**–**i** were prepared according to the literature procedures.[12] The reactions and manipulations were performed under an atmosphere of argon by using standard Schlenk techniques and Drybox (Mikrouna, Supper 1220/750). Anhydrous THF (Tetrahydrofuran), diethyl ether and 1,4-dioxane were distilled from sodium benzophenone ketyl prior to use. Anhydrous DCE (Dichloroethane) and CH_3CN (acetonitrile) were distilled from calcium hydride and stored under argon. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker-Avance 400 MHz spectrometer. $CDCl_3$ was used as solvent. Chemical shifts (δ) are reported in ppm with tetramethylsilane as internal standard, and J values are given in Hz. Enantiomeric excesses were determined by Agilent 1260 Series HPLC using Daicel OD-H, OJ-H or AS-H chiral columns eluted with a mixture of isopropyl alcohol and hexane. Melting

Table 4
Substrate scope of oxabenzonorbornadienes[a]



1a-g **2a** **3aa-ga**

Entry	Oxabenzonorbornadiene	Time (h)	Yield (%)[b]	Ee (%)[c]
1	 **1a**	1.5	95	91
2	 **1b**	2	96	90
3	 **1c**	48	52	91
4	 **1d**	48	51	94
5[d]	 **1e**	18	68	86
6	 **1f**	1.5	40	93
7	 **1g**	6	74	84
8	 **1h**	72	0	–
9	 **1i**	16	0	–

[a] The reaction was carried out with **1** (0.20 mmol), 5.0 equiv of benzoic acid **2a** (1.0 mmol), 0.1 equiv of ZnI_2 (0.02 mmol) and 6.0 equiv of Et_3N (1.20 mmol) in DCE (2.0 mL) at 40 °C in the presence of $[Rh(COD)Cl]_2$ (2.5 mol %) and (*S*,*S*)-BDPP (6.5 mol %).
[b] Isolated yield after silica gel column chromatography.
[c] Determined by HPLC with a Chiralcel OD-H, OJ-H or AS-H column.
[d] The reaction was carried out with **1e** (0.20 mmol), 0.2 equiv of ZnI_2 (0.02 mmol) and 6.0 equiv of Et_3N (1.20 mmol) in DCE (2.0 mL) at 40 °C in the presence of $[Rh(COD)Cl]_2$ (5.0 mol %) and (*S*,*S*)-BDPP (13 mol %) with 5.0 equiv of benzoic acid **2a** (1.0 mmol) added dropwise during 0.5 h.

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points were measured on X-4 melting point apparatus and are uncorrected. High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer. Column chromatography was performed with silica gel (200–300 mesh) with petroleum ether and ethyl acetate as eluents. The absolute configurations were assigned by comparison of the chiral HPLC data of **3ak** with that reported in the literature.[10]

4.2. General procedure for the asymmetric ring opening reactions

At first, $[Rh(COD)Cl]_2$ (2.4 mg, 0.0049 mmol), (*S*,*S*)-BDPP (5.7 mg, 0.013 mmol) and 1.0 mL DCE were added to a Schlenk tube under an argon atmosphere. Then ZnI_2 (6.4 mg, 0.02 mmol) was added and the mixtures were stirred for 10 min. After the addition of Et_3N (166 μL, 1.2 mmol) and oxabenzonorbornadiene (0.2 mmol), the mixtures were stirred for an additional 10 min. Then, a solution of carboxylic acid (1.0 mmol) in DCE (1.0 mL) was added, and the mixtures were stirred at 40 °C under argon atmosphere with TLC monitoring until the complete consumption of oxabenzonorbornadiene. The reaction mixture was concentrated, and the residue was purified by chromatography on a silica gel column to afford the desired ring opening product. The enantiomeric excess value of the product was determined by HPLC on a chiral stationary phase.

4.2.1. (1*S*,2*S*)-1-Hydroxy-1,2-dihydronaphthalen-2-yl benzoate 3aa

White solid; 95% yield; 94% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 7.6 Hz, 2H), 7.60–7.56 (m, 2H), 7.45 (t, J = 15.1 Hz, 2H), 7.34–7.28 (m, 2H), 7.15 (d, J = 6.0 Hz, 1H), 6.58 (d, J = 9.6 Hz, 1H), 5.99 (d, J = 9.6 Hz, 1H), 5.89 (d, J = 9.0 Hz, 1H), 5.14 (d, J = 8.8 Hz, 1H), 2.52 (s, 1H). The *ee* of **3aa** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 9.7 min, t_{major} = 12.3 min.

4.2.2. (1*S*,2*S*)-1-Hydroxy-1,2-dihydronaphthalen-2-yl 4-methoxybenzoate 3ab

White solid; 54% yield; 89% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.7 Hz, 2H), 7.60 (t, J = 7.8 Hz, 1H), 7.29 (t, J = 7.0 Hz, 2H), 7.13 (t, J = 8.2 Hz, 1H), 6.91 (d, J = 8.7 Hz, 2H), 6.55 (d, J = 9.8 Hz, 1H), 5.97 (dd, J = 9.6, 2.4 Hz, 1H), 5.85 (d, J = 9.1 Hz, 1H), 5.13–5.10 (m, 1H), 3.86 (s, 3H), 2.77 (d, J = 4.9 Hz, 1H). The *ee* of **3ab** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 13.8 min, t_{major} = 24.7 min.

4.2.3. (1*S*,2*S*)-1-Hydroxy-1,2-dihydronaphthalen-2-yl 4-chlorobenzoate 3ac

White solid; 70% yield; 90% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 7.64 Hz, 2H), 7.59 (t, J = 8.0 Hz, 1H), 7.42 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.15 (d, J = 7.9 Hz, 1H), 6.59(d, J = 9.8 Hz, 1H), 5.97 (dd, J = 10.0, 2.8 Hz, 1H), 5.87 (d, J = 8.9 Hz, 1H), 5.11 (d, J = 8.9 Hz, 1H). The *ee* of **3ac** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 8.8 min, t_{major} = 14.5 min.

4.2.4. (1*S*,2*S*)-1-Hydroxy-1,2-dihydronaphthalen-2-yl 4-bromobenzoate 3ad

White solid; 68% yield; 89% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.2 Hz, 3H), 7.30 (t, J = 8.5 Hz, 2H), 7.14 (t, J = 8.5 Hz, 1H), 6.57 (d, J = 9.9 Hz, 1H), 5.96(dd, J = 9.6, 2.8 Hz, 1H), 5.86 (d, J = 8.0 Hz, 1H), 5.10 (t, J = 14 Hz, 1H), 2.59 (d, J = 6.0 Hz, 1H). The *ee* of **3ad** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 9.4 min, t_{major} = 16.2 min.

4.2.5. (1*S*,2*S*)-1-Hydroxy-1,2-dihydronaphthalen-2-yl 4-methylbenzoate 3ae

White solid; 84% yield; 90% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 7.7 Hz, 2H), 7.61 (d, J = 6.7 Hz, 1H), 7.31 (t, J = 7.8 Hz, 3H), 7.24 (s, 1H), 7.14 (d, J = 6.1 Hz, 1H), 6.57 (d, J = 9.8 Hz, 1H), 5.98 (dd, J = 10.0, 2.8 Hz, 1H), 5.87 (d, J = 9.3 Hz, 1H), 5.13 (d, J = 9.2 Hz, 1H), 2.43 (s, 1H), 2.42 (s, 3H). The *ee* of **3ae** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 8.6 min, t_{major} = 13.2 min.

4.2.6. (1*S*,2*S*)-1-Hydroxy-1,2-dihydronaphthalen-2-yl 3-methylbenzoate 3af

White solid; 90% yield; 90% *ee*; mp 107–108 °C; $[\alpha]_D^{21}$ = +315 (c = 0.316, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 9.0 Hz, 2H), 7.61 (d, J = 6.2 Hz, 1H), 7.39 (d, J = 7.4 Hz, 1H), 7.35–7.29 (m, 3H), 7.14 (d, J = 6.7 Hz, 1H), 6.57 (d, J = 9.8 Hz, 1H), 5.99 (d, J = 10.0 Hz, 1H), 5.88 (d, J = 9.2 Hz, 1H), 5.14 (d, J = 8.7 Hz, 1H), 2.56 (s, 1H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.06, 138.28, 135.40, 134.10, 131.62, 130.33, 129.75, 129.60, 128.40, 128.34, 126.99, 126.77, 125.98, 125.56, 76.26, 72.13, 21.27; MS (ESI) calcd for $C_{18}H_{16}O_3$ (M^+): 280.1099; Found: 280.1099 (M^+). The *ee* of **3af** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 8.8 min, t_{major} = 11.8 min.

4.2.7. (1*S*,2*S*)-1-Hydroxy-1,2-dihydronaphthalen-2-yl 2-methylbenzoate 3ag

White solid; 88% yield; 90% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 4.7 Hz, 1H), 7.41 (t, J = 14.9 Hz, 1H), 7.30 (t, J = 7.4 Hz, 2H), 7.24 (t, J = 14.1 Hz, 2H), 7.14 (d, J = 4.4 Hz, 1H), 6.58 (d, J = 9.8 Hz, 1H), 6.01 (d, J = 9.8 Hz, 1H), 5.85 (d, J = 8.8 Hz, 1H), 5.10 (d, J = 8.8 Hz, 1H), 2.59 (s, 3H), 2.55 (s, 1H). The *ee* of **3ag** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 9.5 min, t_{major} = 12.3 min.

4.2.8. (1*S*,2*S*)-1-Hydroxy-1,2-dihydronaphthalen-2-yl 2-naphthoate 3ah

White solid; 70% yield; 89% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1H), 8.08 (d, J = 8.6 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.64–7.53 (m, 3H), 7.35–7.29 (m, 2H), 7.16 (t, J = 8.2 Hz, 1H), 6.60 (d, J = 9.8 Hz, 1H), 6.05 (dd, J = 9.6, 2.8 Hz, 1H), 5.96 (d, J = 9.1 Hz, 1H), 5.21 (d, J = 9.1 Hz, 1H), 2.65 (s, 1H). The *ee* of **3ah** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 15.2 min, t_{major} = 23.6 min.

4.2.9. (1*S*,2*S*)-1-Hydroxy-1,2-dihydronaphthalen-2-yl furan-2-carboxylate 3ai

White solid; 70% yield; 90% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.59 (m, 2H), 7.33–7.28 (m, 2H), 7.24 (dd, J = 0.5, 0.5 Hz, 1H), 7.14–7.12 (m, 1H), 6.56 (dd, J = 9.6, 1.6 Hz, 1H), 6.53–6.52 (m, 1H), 5.96 (dd, J = 9.6, 1.6 Hz, 1H), 5.85 (dt, J = 13.2, 2.0 Hz, 1H), 5.12 (d, J = 9.2 Hz, 1H), 2.54 (s, 1H). The *ee* of **3ai** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 7.3 min, t_{major} = 9.2 min.

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4.2.10. (1*S*,2*S*)-1-Hydroxy-1,2-dihydronaphthalen-2-yl thiophene-2-carboxylate 3aj

White solid; 76% yield; 90% *ee*; mp 115–116 °C; $[\alpha]_D^{22}$ = +296.3 (*c* 0.824, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 1.2, 1.2 Hz, 1H), 7.61–7.58 (m, 2H), 7.33–7.26 (m, 2H), 7.14–7.10 (m, 2H), 6.56 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.97 (dd, *J* = 9.6, 2.8 Hz, 1H), 5.84 (dt, *J* = 12.4, 2.8 Hz, 1H), 5.12 (dd, *J* = 8.8, 3.6 Hz, 1H), 2.60 (d, *J* = 5.0 Hz, 1H), ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.48, 135.32, 134.08, 133.31, 133.03, 131.58, 129.67, 128.42, 128.34, 127.89, 126.77, 125.91, 125.36, 76.72, 72.04; MS (ESI) calcd for $C_{15}H_{12}O_3S$ (M^+): 272.0507; Found: 272.0511 (M^+). The *ee* of **3aj** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 7.0 min, t_{major} = 8.6 min.

4.2.11. (1*S*,2*S*)-1-Hydroxy-1,2-dihydronaphthalen-2-yl acetate 3ak

White solid; 82% yield; 88% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 5.8 Hz, 1H), 7.24–7.21 (m, 2H), 7.05 (d, *J* = 4.6 Hz, 1H), 6.46 (d, *J* = 9.8 Hz, 1H), 5.81 (d, *J* = 9.7 Hz, 1H), 5.54 (d, *J* = 9.0 Hz, 1H), 4.88 (d, *J* = 8.8 Hz, 1H), 2.28 (s, 1H), 2.07 (s, 3H). The *ee* of **3ak** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 8.9 min, t_{major} = 12.8 min.

4.2.12. (1*S*,2*S*)-1-Hydroxy-1,2-dihydronaphthalen-2-yl propionate 3al

White solid; 78% yield; 94% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (t, *J* = 8.1 Hz 1H), 7.27 (t, *J* = 8.6 Hz, 2H), 7.10 (t, *J* = 8.4 Hz, 1H), 6.51 (d, *J* = 9.8 Hz, 1H), 5.86 (dd, *J* = 9.6, 2.8 Hz, 1H), 5.61 (d, *J* = 9.0 Hz, 2H), 4.94 (d, *J* = 9.0 Hz, 1H), 2.62 (s, 1H), 2.43–2.38 (m, 2H), 1.17 (t, *J* = 15.1 Hz, 3H). The *ee* of **3al** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 7.2 min, t_{major} = 12.3 min.

4.2.13. (1*S*,2*S*)-1-Hydroxy-1,2-dihydronaphthalen-2-yl 3-methylbutanoate 3am

White solid; 78% yield; 90% *ee*; mp 112–113 °C; $[\alpha]_D^{22}$ = +168 (*c* 0.208, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (t, *J* = 8.2 Hz, 1H), 7.28–7.26 (m, 2H), 7.10 (t, *J* = 8.4 Hz, 1H), 6.51 (d, *J* = 9.8 Hz, 1H), 5.86 (dd, *J* = 10.0, 2.8 Hz, 1H), 5.63 (d, *J* = 9.1 Hz, 1H), 4.94 (d, *J* = 9.0 Hz, 1H), 2.47 (s, 1H), 2.26 (d, *J* = 7.4 Hz, 2H), 2.17–2.10 (m, 1H), 0.98 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.52, 135.41, 131.61, 129.45, 128.34, 128.32, 126.73, 125.97, 125.63, 75.23, 72.01, 43.51, 25.85, 22.38; MS (ESI) calcd for $C_{15}H_{18}O_3$ (M^+): 246.1256; Found: 246.1260 (M^+). The *ee* of **3am** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 6.1 min, t_{major} = 10.0 min.

4.2.14. (1*S*,2*S*)-1-Hydroxy-1,2-dihydronaphthalen-2-yl 3-phenylpropanoate 3an

White solid; 73% yield; 90% *ee*; mp 61–62 °C; $[\alpha]_D^{22}$ = +146.6 (*c* 0.56, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 4.4 Hz, 1H), 7.30–7.24 (m, 4H), 7.21 (t, *J* = 14.0 Hz, 3H), 7.09 (d, *J* = 4.9 Hz, 1H), 6.48 (d, *J* = 9.8 Hz, 1H), 5.78 (d, *J* = 9.8 Hz, 1H), 5.58 (d, *J* = 8.9 Hz, 1H), 4.87 (d, *J* = 9.0 Hz, 1H), 2.97 (t, *J* = 15.2 Hz, 2H), 2.71 (t, *J* = 15.2 Hz, 2H), 2.15 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.11, 140.23, 135.22, 131.56, 129.47, 128.56, 126.72, 126.42, 125.91, 125.45, 75.62, 71.83, 35.97, 30.98; MS (ESI) calcd for $C_{19}H_{18}O_3$ (M^+): 294.1256; Found: 294.1255 (M^+). The *ee* of **3an** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 13.7 min, t_{major} = 23.0 min.

4.2.15. (1*S*,2*S*)-1-Hydroxy-6,7-dimethyl-1,2-dihydronaphthalen-2-yl benzoate 3ba

White solid; 96% yield; 90% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (t, *J* = 8.4 Hz, 2H), 7.59–7.55 (m, 1H), 7.44 (t, *J* = 15.4 Hz, 2H), 7.34 (s, 1H), 6.93 (s, 1H), 6.54 (dd, *J* = 11.0, 1.4 Hz, 1H), 5.93 (dd, *J* = 9.6, 3.2 Hz, 1H), 5.84–5.80 (m, 1H), 5.07–5.04 (m, 1H), 2.28 (d, *J* = 12.8 Hz, 6H), 2.44 (s, 1H). The *ee* of **3ba** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 9.8 min, t_{major} = 12.5 min.

4.2.16. (5*S*,6*S*)-5-Hydroxy-5,6-dihydronaphtho[2,3-d][1,3]dioxol-6-yl benzoate 3ca

White solid; 52% yield; 91% *ee*; mp 134–135 °C; $[\alpha]_D^{22}$ = +195.3 (*c* 0.344, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 14.7 Hz, 1H), 7.44 (t, *J* = 15.2 Hz, 2H), 7.11 (s, 1H), 6.65 (s, 1H), 6.46 (d, *J* = 9.8 Hz, 1H), 5.97 (s, 2H), 5.91 (dd, *J* = 10.0, 2.8 Hz, 1H), 5.81 (d, *J* = 8.6 Hz, 1H), 5.01 (d, *J* = 8.2 Hz, 1H), 2.51 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.81, 147.57, 147.44, 133.30, 129.82, 129.79, 129.51, 128.43, 125.81, 123.40, 107.53, 107.48, 101.25, 75.91, 72.06; MS (ESI) calcd for $C_{18}H_{14}O_5$ (M^+): 310.0841; Found: 310.0851 (M^+). The *ee* of **3ca** was determined by HPLC analysis using Daicel Chiralcel OJ-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 40.7 min, t_{major} = 47.8 min.

4.2.17. (6*S*,7*S*)-6-Hydroxy-2,3,6,7-tetrahydronaphtho[2,3-b][1,4]dioxin-7-yl benzoate 3da

White solid; 51% yield; 94% *ee*; mp 153–154 °C; $[\alpha]_D^{21}$ = +211.2 (*c* 0.224, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 14.8 Hz, 1H), 7.44 (t, *J* = 14.5 Hz, 2H), 7.10 (s, 1H), 6.67 (s, 1H), 6.46 (dd, *J* = 9.6, 0.8 Hz, 1H), 5.89 (dd, *J* = 9.6, 3.2 Hz, 1H), 5.78 (m, 1H), 4.99 (d, *J* = 8.2 Hz, 1H), 4.26 (s, 4H), 2.52 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.78, 143.46, 143.22, 133.26, 129.90, 129.23, 129.22, 128.97, 128.41, 125.39, 123.54, 115.93, 75.69, 71.55, 64.49, 64.41; MS (ESI) calcd for $C_{19}H_{16}O_5$ (M^+): 324.0998; Found: 324.0999 (M^+). The *ee* of **3da** was determined by HPLC analysis using Daicel Chiralcel OJ-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 85/15, 0.5 mL/min, 254 nm; t_{minor} = 88.1 min, t_{major} = 92.5 min.

4.2.18. (1*S*,2*S*)-1-Hydroxy-5,8-dimethoxy-1,2-dihydronaphthalen-2-yl benzoate 3ea

White solid; 42% yield; 86% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 14.6 Hz, 1H), 7.37 (t, *J* = 15.2 Hz, 2H), 7.15 (d, *J* = 9.8 Hz, 1H), 6.84 (s, 2H), 6.16 (dd, *J* = 5.0, 5.1 Hz, 1H), 5.76 (s, 1H), 5.28 (s, 1H), 3.84 (d, *J* = 11.9 Hz, 6H), 2.53 (s, 1H). The *ee* of **3ea** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 25.0 min, t_{major} = 20.2 min.

4.2.19. (1*S*,2*S*)-1-Hydroxy-6,7-dimethoxy-1,2-dihydronaphthalen-2-yl benzoate 3fa

White solid; 40% yield; 93% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–8.06 (m, 2H), 7.60–7.56 (m, 1H), 7.47–7.44 (m, 2H), 7.16 (s, 1H), 6.69 (s, 1H), 6.51 (dd, *J* = 9.6, 1.6 Hz, 1H), 5.91 (dd, *J* = 9.6, 3.2 Hz, 1H), 5.85–5.82 (m, 1H), 5.06 (d, *J* = 8.6 Hz, 1H), 3.92 (d, *J* = 16.2 Hz, 6H), 2.55 (s, 1H). The *ee* of **3fa** was determined by HPLC analysis using Daicel Chiralpak AS-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm; t_{minor} = 31.5 min, t_{major} = 20.1 min.

4.2.20. (1*S*,2*S*)-6,7-Dibromo-1-hydroxy-1,2-dihydronaphthalen-2-yl benzoate 3ga

White solid; 74% yield; 84% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 7.5 Hz, 2H), 7.87 (s, 1H), 7.61 (t, J = 15.1 Hz, 1H), 7.47 (t, J = 15.2 Hz, 2H), 7.38 (s, 1H), 6.46 (d, J = 9.7 Hz, 1H), 6.05 (d, J = 9.8 Hz, 1H), 5.86 (d, J = 9.8 Hz, 1H), 5.08 (d, J = 9.8 Hz, 1H), 2.72 (s, 1H). The *ee* of **3ga** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, 254 nm; t_{minor} = 37.4 min, t_{major} = 33.9 min.

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A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetasy.2016.11.004.

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