



# Enantioselective and aerobic oxidative coupling of 2-naphthol derivatives using chiral dinuclear vanadium(V) complex in water



Makoto Sako, Shinobu Takizawa\*, Yasushi Yoshida, Hiroaki Sasai\*

The Institute of Scientific and Industrial Research (ISIR), Osaka University, Mihogaoka, Ibaraki, Osaka 567-0047, Japan

## ARTICLE INFO

### Article history:

Received 11 March 2015

Accepted 28 April 2015

Available online 19 May 2015

## ABSTRACT

The enantioselective oxidative coupling of 2-naphthols in water was established using dinuclear vanadium(V/IV) catalysis with O<sub>2</sub> as the sole co-oxidant. In the vanadium-catalyzed reaction, the corresponding coupling products were obtained in good to excellent yields with up to 94% enantiomeric excess. In water, racemization of the coupling product was suppressed even at high temperature (70 °C).

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Water is a much safer reaction solvent compared to toxic and/or flammable organic solvents, making aqueous processes environmentally benign methodologies. To date, a number of efficient, metal-catalyzed reactions and organocatalyzed reactions in water have been reported.<sup>1</sup> The preparation of enantiomerically pure 1,1'-bi-2-naphthol (BINOL) and its derivatives are of great importance due to their wide utility in asymmetric synthesis.<sup>2</sup> Among the synthetic methods used to access enantiomerically pure BINOLs, asymmetric and catalytic oxidative coupling of 2-naphthols is one of the most straightforward processes.<sup>3,4</sup> We previously developed the dinuclear vanadium(V) complex (*R<sub>a</sub>,S,S*)-**1** (Fig. 1), which can catalyze the oxidative coupling of 2-naphthols through a dual activation mechanism.<sup>4m-p</sup> (*R<sub>a</sub>,S,S*)-**1** can be easily prepared in a one-pot, single operation reaction from a chiral binaphthyl derivative, amino acids, and vanadium salts in MeOH under an O<sub>2</sub> atmosphere and reflux conditions. The vanadium complex is stable in hydrophilic, polar solvents such as MeOH and EtOH in air. Thus we envisioned that in water, the chiral dinuclear vanadium(V) complex could promote the oxidative coupling of 2-naphthols to give BINOLs in high yields and with high enantioselectivities. To date, several procedures for the oxidative coupling of 2-naphthols in water have been developed using Ru(OH)<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>,<sup>5</sup> biopolymer-supported copper,<sup>6</sup> or ferric hydrogen-sulfate.<sup>7</sup> These protocols produced BINOL, but only in racemic form. In 2015, Adão and Pessoa et al. reported the enantioselective oxidative coupling of 2-naphthol using amino acid-derived Cu(II) catalysts in EtOH/H<sub>2</sub>O to provide BINOL (up to 33% yield, 44% ee).<sup>8</sup> However, the yield and enantiomeric excess of BINOL remain

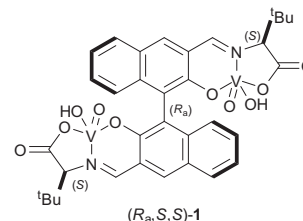


Figure 1. Dinuclear vanadium(V) complex (*R<sub>a</sub>,S,S*)-**1**.

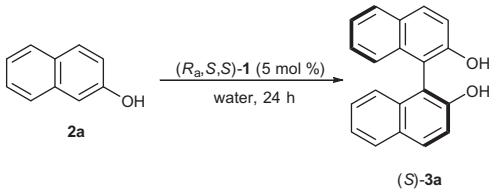
unsatisfactory. Therefore, the development of an efficient oxidative coupling of 2-naphthols in water with high enantiocontrol has been a challenge. Herein, we report the highly enantioselective oxidative coupling of 2-naphthols in water. Under O<sub>2</sub> in water, the dinuclear vanadium(V) complex (*R<sub>a</sub>,S,S*)-**1** promotes oxidative coupling of 2-naphthols, to afford the corresponding coupling products in good yields with high enantioselectivities.

## 2. Results and discussion

Initially, the optimization of the reaction conditions for the oxidative coupling of 2-naphthol **2a** was performed with (*R<sub>a</sub>,S,S*)-**1** (5 mol %) in water (Table 1). We previously reported that the oxidative coupling of **2a** in the presence of 5 mol % (*R<sub>a</sub>,S,S*)-**1** in CH<sub>2</sub>Cl<sub>2</sub> under air at 30 °C afforded (*S*)-BINOL **3a** in quantitative yield with 90% ee (entry 9).<sup>4n</sup> In contrast, either no reaction or low conversion was observed in aqueous media, most likely due to the low solubility of 2-naphthol in water (entries 1 and 2). To improve the solubility, a catalytic amount of surfactant, such as anionic surfactant sodium dodecyl sulfate (SDS), cationic surfactant tetrabutylammonium bromide (TBAB), or neutral surfactant

\* Corresponding authors. Tel.: +81 6 6879 8466; fax: +81 6 6879 8469.

E-mail address: [taki@sanken.osaka-u.ac.jp](mailto:taki@sanken.osaka-u.ac.jp) (S. Takizawa).

**Table 1**Optimization of reaction conditions for the oxidative coupling of 2-naphthol **2a** in water


| Entry          | Air or O <sub>2</sub> | Temp. (°C) | Additive (5 mol %) | % yield <sup>a</sup> | % ee <sup>b</sup> |
|----------------|-----------------------|------------|--------------------|----------------------|-------------------|
| 1              | Air                   | 30         | None               | NR                   | —                 |
| 2              | O <sub>2</sub>        | 30         | None               | 11                   | Rac.              |
| 3              | O <sub>2</sub>        | 30         | SDS                | 9                    | Rac.              |
| 4              | O <sub>2</sub>        | 30         | TBAB               | 5                    | 17                |
| 5              | O <sub>2</sub>        | 30         | Triton X-100       | 26                   | 25                |
| 6              | O <sub>2</sub>        | 50         | None               | 92 (91) <sup>c</sup> | 80                |
| 7              | O <sub>2</sub>        | 90         | None               | >99                  | 66                |
| 8 <sup>d</sup> | O <sub>2</sub>        | 50         | None               | NR                   | —                 |
| 9 <sup>e</sup> | Air                   | 30         | None               | Quant                | 90                |

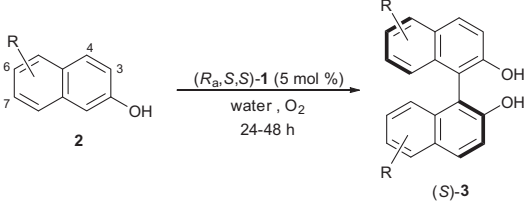
<sup>a</sup> <sup>1</sup>H NMR yield, 1,3,5-trimethoxybenzene was used as an internal standard.<sup>b</sup> Determined by HPLC.<sup>c</sup> Yield of isolated product.<sup>d</sup> Without (R<sub>a</sub>,S,S)-1.<sup>e</sup> Result when the reaction was carried out in CH<sub>2</sub>Cl<sub>2</sub>.<sup>4n</sup>

polyoxyethylene *p*-*t*-octylphenyl ether (Triton X-100) was added (entries 3–5), although almost no improvement in either the chemical yield or enantioselectivity was observed. However, when the temperature was raised to 50 °C, **3a** was isolated in 91% yield with 80% ee (entry 6). When the temperature was increased to over 90 °C, the product's ee drastically decreased due to decomposition of the complex (entry 7). Without (R<sub>a</sub>,S,S)-1, no reaction was observed under the optimized reaction conditions (entry 8). Based on these results, efficient dual activation of 2-naphthol using (R<sub>a</sub>,S,S)-1 in water requires a temperature of at least 50 °C to promote a single electron transfer from 2-naphthol to the catalyst.<sup>4m–p</sup>

To elucidate the applicability of the oxidative coupling using the vanadium complex in water, various 2-naphthol derivatives were

**Table 2**

Oxidative coupling of 2-naphthol derivatives catalyzed by dinuclear vanadium complex in water



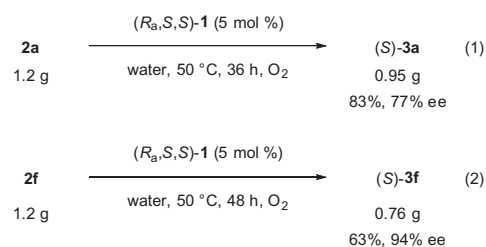
| Entry | Substrate, R                                     | Temp. (°C) | Yield <sup>a</sup> (%) | ee <sup>b</sup> (%) |
|-------|--------------------------------------------------|------------|------------------------|---------------------|
| 1     | <b>2a</b> , H                                    | 50         | <b>3a</b> , 91         | 80                  |
| 2     | <b>2b</b> , 7-OMOM                               | 50         | <b>3b</b> , 78         | 83                  |
| 3     | <b>2c</b> , 7-OMEM                               | 50         | <b>3c</b> , 65         | 63                  |
| 4     | <b>2d</b> , 7-OCH <sub>2</sub> CHCH <sub>2</sub> | 50         | <b>3d</b> , 78         | 85                  |
| 5     | <b>2e</b> , 7-Br                                 | 70         | <b>3e</b> , 85         | 73                  |
| 6     | <b>2f</b> , 7-OMe                                | 50         | <b>3f</b> , 87         | 94                  |
| 7     | <b>2g</b> , 6-OMe                                | 70         | <b>3g</b> , 95         | 63                  |
| 8     | <b>2h</b> , 6-Me                                 | 70         | <b>3h</b> , 89         | 77                  |
| 9     | <b>2i</b> , 4-Ph                                 | 70         | <b>3i</b> , 82         | 85                  |
| 10    | <b>2j</b> , 3-OMe                                | 70         | <b>3j</b> , 69         | 44                  |

<sup>a</sup> Isolated product yield.<sup>b</sup> Determined by HPLC.

examined (Table 2). 2-Naphthols bearing electron-donating or withdrawing groups such as MOM-O, MEM-O, CH<sub>2</sub>=CHCH<sub>2</sub>O, Br, MeO, Me, or Ph, at the C7, C6, or C4 position underwent the coupling reaction to produce the corresponding BINOL derivatives **3b–3i** in good yields with high enantioselectivities (entries 2–9). 3-MeO-2-naphthol **2j** was also converted into coupling product **3j** in good yield with moderate enantioselectivity (entry 10). The reactions of **2e** and **2g–j** had to be carried out at higher temperature (70 °C) and longer reaction time (48 h) due to the low solubility of **2e** and **2g–j** in water.

In an effort to clarify whether racemization of the products occurs, optically active 7,7'-dimethoxy-substituted BINOL **3f** [94% ee (S)] or 6,6'-dimethoxy-substituted BINOL **3g** [81% ee (S)] was stirred in water at 70 °C under the coupling conditions [100 mol % 2-naphthol **2a** and 5 mol % dinuclear vanadium(V) complex (R<sub>a</sub>,S,S)-1]. After 24 h, the dimethoxy-substituted BINOLs were recovered with 93% ee for (S)-**3f** and 77% ee for (S)-**3g**.<sup>9</sup> Under the optimal reaction conditions in water, the ee of **3f** and **3g** decreased slightly. However, using ClCH<sub>2</sub>CH<sub>2</sub>Cl as the reaction solvent instead of water resulted in decreasing ee; **3f**: from 94% ee (S) to 74% ee (S); **3g**: from 81% ee (S) to 11% ee (R).<sup>10</sup> It should be noted that in water, racemization of BINOLs is significantly suppressed as compared to an organic solvent.<sup>11</sup>

To prove the utility of the present methodology, the oxidative coupling of **2** on a gram scale was examined (Scheme 1). The reaction using 1.2 g of **2a** or **2f** in the presence of 5 mol % (R<sub>a</sub>,S,S)-1 allowed the formation of (S)-**3a** in 83% yield with 77% ee and (S)-**3f** in 63% yield with 94% ee, respectively (Eqs. 1 and 2).

**Scheme 1.** Oxidative coupling of 2-naphthols catalyzed by dinuclear vanadium complex in water on a gram scale.

### 3. Conclusion

In conclusion, we have developed the first example of a highly efficient and enantioselective oxidative coupling of 2-naphthols **2** in water catalyzed by a chiral dinuclear vanadium(V) complex. In water, (R<sub>a</sub>,S,S)-1 maintained high catalytic activity for the coupling reaction to produce BINOLs **3** in high yields with up to 94% ee. In water, almost no racemization of BINOLs was observed at 70 °C. Furthermore, a gram scale synthesis of BINOLs in aqueous media was achieved with good yields and high enantioselectivities.

### 4. Experimental

#### 4.1. General

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with JEOL JMN ECS400 FT NMR, JNM ECA600 FT NMR or Bruker AVANCE II (<sup>1</sup>H NMR 400, 600 or 700 MHz, <sup>13</sup>C NMR 100, 150 or 175 MHz). <sup>1</sup>H NMR spectra are reported as follows: chemical shift in ppm relative to the chemical shift of TMS at 0 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet), and coupling constants (Hz). <sup>13</sup>C NMR spectra are reported in ppm relative to

the central line of triplet for  $\text{CDCl}_3$  at 77 ppm. Optical rotations were measured with JASCO P-1030 polarimeter. HPLC analyses were performed on a JASCO HPLC system (JASCO PU 980 pump and UV-975 UV/Vis detector) using a mixture of hexane and 2-propanol as eluents. Column chromatography on  $\text{SiO}_2$  was performed with Kishida Silica Gel (63–200  $\mu\text{m}$ ). Commercially available organic and inorganic compounds were used without further purification. ( $R_a,S,S$ )-**1**, **2b**, **2d**, **2h**, **2i**, and **2j** were prepared following the reported procedures.<sup>40,12</sup> Products **3a**, **3b**, **3d**, **3e**, **3f**, **3g**, **3h**, **3i**, and **3j** were identical in all respects with the data reported in the literature.<sup>4n,13</sup> Absolute configurations were assigned by comparison of the specific rotation reported in the literature.<sup>4n,13</sup>

#### 4.2. Preparation of 7-((2-methoxyethoxy)methoxy)-2-naphthol **2c**

To a solution of 2,7-dihydroxynaphthalene (961 mg, 6.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) were added  $^i\text{Pr}_2\text{NEt}$  (1.15 mL, 6.6 mmol) and MEMCl (0.75 mL, 6.6 mmol) at 0 °C. The mixture was warmed to rt and then stirred for 24 h. After the reaction was completed, water was added to the reaction mixture and the solution was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and evaporated in vacuo. After the purification via  $\text{SiO}_2$  column chromatography (hexane/acetone = 3:1), the desired product was obtained as a yellow oil (675 mg, 45%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.67 (d,  $J$  = 8.7 Hz, 2H), 7.27 (d,  $J$  = 2.3 Hz, 1H), 7.05 (dd,  $J$  = 8.7, 2.3 Hz, 1H), 7.04 (d,  $J$  = 2.3 Hz, 1H), 6.96 (dd,  $J$  = 8.7, 2.3 Hz, 1H), 5.37 (s, 2H), 5.01 (s, 1H), 3.88–3.86 (m, 2H), 3.60–3.57 (m, 2H), 3.39 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.2 (C), 154.4 (C), 135.6 (C), 129.1 (CH), 129.1 (CH), 124.4 (C), 116.0 (CH), 115.9 (CH), 108.7 (CH), 108.4 (CH), 93.1 ( $\text{CH}_2$ ), 71.3 ( $\text{CH}_2$ ), 67.3 ( $\text{CH}_2$ ), 58.6 ( $\text{CH}_3$ ); HRMS (ESI) calcd for  $\text{C}_{14}\text{H}_{16}\text{NaO}_4$ ,  $m/z$  = 271.0946 [( $\text{M}+\text{Na}$ ) $^+$ ], found  $m/z$  = 271.0938; IR (KBr):  $\nu$  3360, 3062, 2931, 1635, 1515, 1448, 1200, 1159, 1007, 833  $\text{cm}^{-1}$ .

#### 4.3. General procedure for coupling reactions of 2-naphthols **2** using ( $R_a,S,S$ )-**1** in water

A test tube was charged with a water (1 mL) heterogeneous solution of coupling substrate **2** (0.2 mmol) under  $\text{O}_2$  (1 atm) atmosphere. Vanadium catalyst ( $R_a,S,S$ )-**1** (0.01 mmol, 5 mol %) was added to the solution. The reaction mixture was stirred at 50 °C for **2a**, **2b**, **2c**, **2d**, and **2f** or 70 °C for **2e**, **2g**, **2h**, **2i**, and **2j** until the reaction had reached completion by monitoring with TLC analysis. The reaction mixture was then directly purified by silica gel column chromatography eluting with ethyl acetate/hexane to give the coupling product.

#### 4.4. ( $S$ )-1,1'-Bi-2-naphthol **3a**<sup>4n</sup>

Reaction time: 24 h; reaction temperature: 50 °C; 91% yield;  $[\alpha]_D^{22}$  = –26.9 (c 1.0, THF, 80% ee);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.98 (d,  $J$  = 8.7 Hz, 2H), 7.89 (d,  $J$  = 7.8 Hz, 2H), 7.43–7.34 (m, 4H), 7.31 (td,  $J$  = 7.8, 1.6 Hz, 2H), 7.15 (d,  $J$  = 8.2 Hz, 2H), 5.04 (s, 2H). The enantiomeric excess was determined by HPLC with a Daicel Chiralpak AS-H column (hexane/2-propanol = 7:1,  $\lambda$  = 229 nm, flow rate = 1.0 mL/min);  $t_R$  (major enantiomer) = 9.8 min,  $t_R$  (minor enantiomer) = 15.1 min, 80% ee.

#### 4.5. ( $S$ )-7,7'-Bis(methoxymethoxy)-1,1'-bi-2-naphthol **3b**<sup>4n</sup>

Reaction time: 48 h; reaction temperature: 50 °C; 78% yield;  $[\alpha]_D^{13}$  = +127.6 (c 1.1,  $\text{CHCl}_3$ , 83% ee);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.87 (d,  $J$  = 8.7 Hz, 2H), 7.79 (d,  $J$  = 8.7 Hz, 2H), 7.21 (d,  $J$  = 8.7 Hz, 2H), 7.14 (dd,  $J$  = 8.7, 2.3 Hz, 2H), 6.65 (d,  $J$  = 2.3 Hz, 2H), 5.08 (s,

2H), 4.99 (s, 4H), 3.31 (s, 6H). The enantiomeric excess was determined by HPLC with a Daicel Chiralpak AS-H column (hexane/2-propanol = 7:1,  $\lambda$  = 235 nm, flow rate = 1.0 mL/min);  $t_R$  (major enantiomer) = 16.5 min,  $t_R$  (minor enantiomer) = 27.9 min, 83% ee.

#### 4.6. ( $S$ )-7,7'-Bis((2-methoxyethoxy)methoxy)-1,1'-bi-2-naphthol **3c**

Reaction time: 48 h; reaction temperature: 50 °C; 65% yield, yellow oil;  $[\alpha]_D^{22}$  = +61.9 (c 0.7,  $\text{CHCl}_3$ , 63% ee);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d,  $J$  = 9.2 Hz, 2H), 7.80 (d,  $J$  = 8.7 Hz, 2H), 7.26 (s, 2H), 7.23 (d,  $J$  = 9.2 Hz, 2H), 7.16 (dd,  $J$  = 8.7, 2.3 Hz, 2H), 6.71 (d,  $J$  = 2.3 Hz, 2H), 5.15 (s, 2H), 5.10 (s, 4H), 3.70–3.62 (m, 4H), 3.45–3.34 (m, 4H), 3.28 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.4 (C), 153.3 (C), 134.6 (C), 131.1 (CH), 130.0 (CH), 125.4 (C), 116.0 (CH), 115.8 (CH), 110.2 (C), 107.9 (CH), 93.4 ( $\text{CH}_2$ ), 71.4 ( $\text{CH}_2$ ), 67.5 ( $\text{CH}_2$ ), 59.0 ( $\text{CH}_3$ ); HRMS (ESI) calcd for  $\text{C}_{28}\text{H}_{30}\text{NaO}_8$ ,  $m/z$  = 517.1838 ( $\text{M}+\text{Na}$ ) $^+$ , found  $m/z$  = 517.1826; IR (KBr):  $\nu$  3390, 3058, 2931, 1621, 1512, 1203, 1159, 1019, 982, 834  $\text{cm}^{-1}$ . The enantiomeric excess was determined by HPLC with a Daicel Chiralpak AS-H column (hexane/2-propanol = 4:1,  $\lambda$  = 220 nm, flow rate = 1.0 mL/min);  $t_R$  (major enantiomer) = 22.0 min,  $t_R$  (minor enantiomer) = 30.1 min, 63% ee.

#### 4.7. ( $S$ )-7,7'-Bis(allyloxy)-1,1'-bi-2-naphthol **3d**<sup>4n</sup>

Reaction time: 48 h; reaction temperature: 50 °C; 78% yield;  $[\alpha]_D^{22}$  = +177.6 (c 1.5,  $\text{CHCl}_3$ , 85% ee);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.85 (d,  $J$  = 8.7 Hz, 2H), 7.77 (d,  $J$  = 8.7 Hz, 2H), 7.20 (d,  $J$  = 8.7 Hz, 2H), 7.04 (dd,  $J$  = 8.7, 2.4 Hz, 2H), 6.47 (d,  $J$  = 2.4 Hz, 2H), 5.90–5.80 (m, 2H), 5.15–5.09 (m, 4H), 5.06 (s, 2H), 4.32–4.21 (m, 4H). The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IA column (hexane/2-propanol = 7:1,  $\lambda$  = 235 nm, flow rate = 1.0 mL/min);  $t_R$  (major enantiomer) = 12.2 min,  $t_R$  (minor enantiomer) = 22.7 min, 85% ee.

#### 4.8. ( $S$ )-7,7'-Dibromo-1,1'-bi-2-naphthol **3e**<sup>13a</sup>

Reaction time: 48 h; reaction temperature: 70 °C; 85% yield;  $[\alpha]_D^{21}$  = +129.1 (c 1.8,  $\text{CHCl}_3$ , 73% ee);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.94 (d,  $J$  = 9.2 Hz, 2H), 7.76 (d,  $J$  = 8.7 Hz, 2H), 7.47 (dd,  $J$  = 8.7, 1.8 Hz, 2H), 7.38 (d,  $J$  = 9.2 Hz, 2H), 7.23 (d,  $J$  = 1.8 Hz, 2H), 5.05 (s, 2H). The enantiomeric excess was determined by HPLC with a Daicel Chiralcel OD-H column (hexane/2-propanol = 9:1,  $\lambda$  = 235 nm, flow rate = 1.0 mL/min);  $t_R$  (major enantiomer) = 15.9 min,  $t_R$  (minor enantiomer) = 33.4 min, 73% ee.

#### 4.9. ( $S$ )-7,7'-Dimethoxy-1,1'-bi-2-naphthol **3f**<sup>4n</sup>

Reaction time: 48 h; reaction temperature: 50 °C; 87% yield;  $[\alpha]_D^{22}$  = +122.3 (c 1.0,  $\text{CHCl}_3$ , 94% ee);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86 (d,  $J$  = 8.7 Hz, 2H), 7.77 (d,  $J$  = 8.7 Hz, 2H), 7.21 (d,  $J$  = 8.7 Hz, 2H), 7.02 (dd,  $J$  = 8.7, 2.7 Hz, 2H), 6.47 (d,  $J$  = 2.7 Hz, 2H), 5.04 (s, 2H), 3.56 (s, 6H). The enantiomeric excess was determined by HPLC with a Daicel Chiralpak AS-H column (hexane/2-propanol = 9:1,  $\lambda$  = 235 nm, flow rate = 1.0 mL/min);  $t_R$  (major enantiomer) = 18.8 min,  $t_R$  (minor enantiomer) = 28.0 min, 94% ee.

#### 4.10. ( $S$ )-6,6'-Dimethoxy-1,1'-bi-2-naphthol **3g**<sup>4n</sup>

Reaction time: 48 h; reaction temperature: 70 °C; 95% yield;  $[\alpha]_D^{20}$  = +25.6 (c 1.6,  $\text{CHCl}_3$ , 63% ee);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.83 (dd,  $J$  = 9.2, 1.8 Hz, 2H), 7.33 (dd,  $J$  = 9.2, 1.8 Hz, 2H), 7.19 (s, 2H), 7.05 (d,  $J$  = 9.2 Hz, 2H), 6.97 (dd,  $J$  = 9.2, 1.8 Hz, 2H), 4.94 (s, 2H), 3.89 (s, 6H). The enantiomeric excess was determined by HPLC with a Daicel Chiralpak AS column (hexane/2-propanol = 4:1,

$\lambda = 260$  nm, flow rate = 1.0 mL/min);  $t_R$  (major enantiomer) = 12.1 min,  $t_R$  (minor enantiomer) = 21.8 min, 63% ee.

#### 4.11. (S)-6,6'-Dimethyl-1,1'-bi-2-naphthol 3h<sup>4n</sup>

Reaction time: 48 h; reaction temperature: 70 °C; 89% yield;  $[\alpha]_D^{17} = +51.9$  (c 0.7, CHCl<sub>3</sub>, 77% ee); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.88 (d,  $J = 9.2$  Hz, 2H), 7.66 (s, 2H), 7.34 (d,  $J = 9.2$  Hz, 2H), 7.14 (d,  $J = 8.2$  Hz, 2H), 7.05 (d,  $J = 8.2$  Hz, 2H), 4.96 (s, 2H), 2.47 (s, 6H). The enantiomeric excess was determined by HPLC with a Daicel Chiralpak AS-H column (hexane/2-propanol = 7:1,  $\lambda = 229$  nm, flow rate = 1.0 mL/min);  $t_R$  (major enantiomer) = 8.2 min,  $t_R$  (minor enantiomer) = 12.9 min, 77% ee.

#### 4.12. (S)-4,4'-Diphenyl-1,1'-bi-2-naphthol 3i<sup>13b</sup>

Reaction time: 48 h; reaction temperature: 70 °C; 82% yield;  $[\alpha]_D^{22} = -22.1$  (c 1.0, CHCl<sub>3</sub>, 85% ee); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.97–7.94 (m, 2H), 7.64–7.48 (m, 10H), 7.38 (s, 2H), 7.36–7.31 (m, 6H), 5.16 (s, 2H). The enantiomeric excess was determined by HPLC with a Daicel Chiralcel OD-H column (hexane/2-propanol = 4:1,  $\lambda = 220$  nm, flow rate = 1.0 mL/min);  $t_R$  (minor enantiomer) = 8.4 min,  $t_R$  (major enantiomer) = 13.3 min, 85% ee.

#### 4.13. (S)-3,3'-Dimethoxy-1,1'-bi-2-naphthol 3j<sup>4n</sup>

Reaction time: 48 h; reaction temperature: 70 °C; 69% yield;  $[\alpha]_D^{23} = -6.2$  (c 1.2, CHCl<sub>3</sub>, 44% ee); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.78 (d,  $J = 8.2$  Hz, 2H), 7.34–7.29 (m, 4H), 7.18–7.12 (m, 4H), 5.88 (s, 2H), 4.09 (s, 6H). The enantiomeric excess was determined by HPLC with a Daicel Chiralpak AS column (hexane/2-propanol = 1:1,  $\lambda = 236$  nm, flow rate = 1.0 mL/min);  $t_R$  (major enantiomer) = 19.2 min,  $t_R$  (minor enantiomer) = 46.4 min, 44% ee.

#### Acknowledgements

This work was supported by JST Core Research for Evolutionary Science and Technology (CREST), a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. We would like to thank the technical staff of the ISIR Comprehensive Analysis Centre at Osaka University for their assistance.

#### References

- (a) Li, C.-J. *Chem. Rev.* **2005**, *105*, 3095; (b) Raj, M.; Singh, V. K. *Chem. Commun.* **2009**, 6687; (c) Butler, R. N.; Coyne, A. G. *Chem. Rev.* **2010**, *110*, 6302; (d)

- Bhowmick, S.; Bhowmick, K. C. *Tetrahedron: Asymmetry* **2011**, *22*, 1945; (e) Simon, M.-O.; Li, C.-J. *Chem. Soc. Rev.* **2012**, *41*, 1415; (f) *Science of Synthesis Water in Organic Synthesis*; Kobayashi, S., Ed., Workbench Edition; Thieme, 2014.
- (a) Pu, L. *Chem. Rev.* **1998**, *98*, 2405; (b) Brunel, J. M. *Chem. Rev.* **2007**, *107*, PR1; (c) In *Privileged Chiral Ligands and Catalysts*; Zhou, Q.-L., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA, 2011; (d) Allen, S. E.; Walvoord, R. R.; Padilla-Salinas, R.; Kozłowski, M. C. *Chem. Rev.* **2013**, *113*, 6234.
- (a) Punniyamurthy, T.; Rout, L. *Coord. Chem. Rev.* **2008**, *252*, 134; (b) Takizawa, S.; Katayama, T.; Sasai, H. *Chem. Commun.* **2008**, 4113; (c) Kozłowski, M. C.; Morgan, B. J.; Linton, E. C. *Chem. Soc. Rev.* **2009**, *38*, 3193; (d) Takizawa, S. *Chem. Pharm. Bull.* **2009**, *57*, 1179; (e) Wang, H. *Chirality* **2010**, *22*, 827; (f) O'Brien, E. M.; Morgan, B. J.; Mulrooney, C. A.; Carroll, P. J.; Kozłowski, M. C. *J. Org. Chem.* **2010**, *75*, 57; (g) Egami, H.; Matsumoto, K.; Oguma, T.; Kunisu, T.; Katsuki, T. *J. Am. Chem. Soc.* **2010**, *132*, 13633; (h) Podlesny, E. E.; Kozłowski, M. C. *Org. Lett.* **2012**, *14*, 1408; (i) Podlesny, E. E.; Kozłowski, M. C. *J. Org. Chem.* **2013**, *78*, 466.
- (a) Hon, S.-W.; Li, C.-H.; Kuo, J.-H.; Barhate, N. B.; Liu, Y.-H.; Wang, Y.; Chen, C.-T. *Org. Lett.* **2001**, *3*, 869; (b) Chu, C.-Y.; Hwang, D.-R.; Wang, S.-K.; Uang, B.-J. *Chem. Commun.* **2001**, 980; (c) Barhate, N. B.; Chen, C.-T. *Org. Lett.* **2002**, *4*, 2529; (d) Luo, Z.; Liu, Q.; Gong, L.; Cui, X.; Mi, A.; Jiang, Y. *Chem. Commun.* **2002**, 914; (e) Luo, Z.; Liu, Q.; Gong, L.; Cui, X.; Mi, A.; Jiang, Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 4532; (f) Chu, C.-Y.; Uang, B.-J. *Tetrahedron: Asymmetry* **2003**, *14*, 53; (g) Somei, H.; Asano, Y.; Yoshida, T.; Takizawa, S.; Yamataka, H.; Sasai, H. *Tetrahedron Lett.* **2004**, *45*, 1841; (h) Tada, M.; Taniike, T.; Kantam, L. M.; Iwasawa, Y. *Chem. Commun.* **2004**, 2542; (i) Tada, M.; Kojima, N.; Izumi, Y.; Taniike, T.; Iwasawa, Y. *J. Phys. Chem. B* **2005**, *109*, 9905; (j) Habaue, S.; Murakami, S.; Higashimura, H. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 5872; (k) Tada, M.; Iwasawa, Y. *Chem. Commun.* **2006**, 2833; (l) Guo, Q.-X.; Wu, Z.-J.; Luo, Z.-B.; Liu, Q.-Z.; Ye, J.-L.; Luo, S.-W.; Cun, L.-F.; Gong, L.-Z. *J. Am. Chem. Soc.* **2007**, *129*, 13927; (m) Takizawa, S.; Katayama, T.; Kameyama, C.; Onitsuka, K.; Suzuki, T.; Yanagida, T.; Kawai, T.; Sasai, H. *Chem. Commun.* **2008**, 1810; (n) Takizawa, S.; Katayama, T.; Somei, H.; Asano, Y.; Yoshida, T.; Kameyama, C.; Rajesh, D.; Onitsuka, K.; Suzuki, T.; Mikami, M.; Yamataka, H.; Jayaprakash, D.; Sasai, H. *Tetrahedron* **2008**, *64*, 3361; (o) Takizawa, S.; Rajesh, D.; Katayama, T.; Sasai, H. *Synlett* **2009**, 1667; (p) Takizawa, S.; Koderia, J.; Yoshida, Y.; Sako, M.; Breukers, S.; Enders, D.; Sasai, H. *Tetrahedron* **2014**, *70*, 1786.
- Reddy, K. R.; Rajgopal, K.; Kantam, M. L. *Catal. Lett.* **2007**, *114*, 36.
- Eshghi, H.; Bakavoli, M.; Moradi, H. *Chin. Chem. Lett.* **2009**, *20*, 663.
- Matsushita, M.; Kamata, K.; Yamaguchi, K.; Mizuno, N. *J. Am. Chem. Soc.* **2005**, *127*, 6632.
- Adão, P.; Barroso, S.; Carvalho, M. F. N. N.; Teixeira, C. M.; Kuznetsov, M. L.; Pessoa, J. C. *Dalton Trans.* **2015**, *44*, 1612.
- After the reaction in water, (S)-**3a** was obtained quantitatively with 82% ee (recovering with **3f**) and 78% ee (recovering with **3g**), respectively.
- After the reaction in ClCH<sub>2</sub>CH<sub>2</sub>Cl at 70 °C, (S)-**3a** was obtained quantitatively with 13% ee (recovering with **3f**) and 23% ee (recovering with **3g**), respectively.
- (a) Kyba, E. B.; Koga, K.; Sousa, L. R.; Siegel, M. G.; Cram, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 2692; (b) Kyba, E. P.; Gokel, G. W.; Jong, F. D.; Koga, K.; Sousa, L. R.; Siegel, M. G.; Kaplan, L.; Sogah, G. D. Y.; Cram, D. J. *J. Org. Chem.* **1977**, *42*, 4173.
- (a) Marsilje, T. H.; Milkiewicz, K. L.; Hangauer, D. G. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 477; (b) Sugimura, T.; Matsushita, N.; Minokami, K.; Kurita, S. *Tetrahedron* **2007**, *63*, 1762; (c) Verga, D.; Percivalle, C.; Doria, F.; Porta, A.; Freccero, M. *J. Org. Chem.* **2011**, *76*, 2319; (d) Zhang, J.; Liu, Q.; Liu, X.; Zhang, S.; Jiang, P.; Wang, Y.; Luo, S.; Li, Y.; Wang, Q. *Chem. Commun.* **2015**, 1297; (e) Sivapackiam, J.; Harpstrite, S. E.; Prior, J. L.; Gu, H.; Rath, N. P.; Sharma, V. *Dalton Trans.* **2010**, 39, 5842.
- (a) Lustenberger, P.; Diederich, F. *Helv. Chim. Acta* **2000**, *83*, 2865; (b) Wieting, J. M.; Fisher, T. J.; Schafer, A. G.; Visco, M. D.; Gallucci, J. C.; Mattson, A. E. *Eur. J. Org. Chem.* **2015**, 525.