Tetrahedron: *Asymmetry* 19 (2008) 1593–1599

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Kinetic resolution of phosphoryl and sulfonyl esters of 1,1′-bi-2-naphthol via Pd-catalyzed alcoholysis of their vinyl ethers

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ARTICLE INFO

Article history:
Received 2 May 2008
Accepted 24 June 2008
Available online 16 July 2008

ABSTRACT

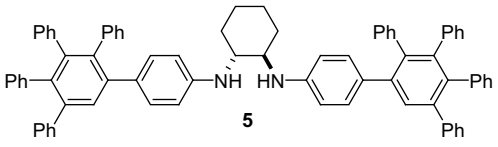
Kinetic resolution of phosphoryl and sulfonyl esters of 1,1′-bi-2-naphthol has been achieved via the Pd-catalyzed alcoholysis of their vinyl ethers. The highest k_{rel} value reached 36.8 with substrate **3c**, and (*R*)-**3c** 99.0% ee was obtained in 43% isolated yield.

1. Introduction

The hydrolysis and alcoholysis of organic molecules are fundamental reactions in organic synthesis. The reactions with biocatalysts in particular play a major role in the asymmetric synthesis of optically active compounds.[1] On the other hand, in the area of homogeneous catalysis, fewer studies with little progress have been made compared to those on enzymatic reactions. In recent years, we and others have carried out research on hydrolysis[2] and alcoholysis[3] reactions with metal–complex catalysts. As well as the Co-catalyzed hydrolytic kinetic resolution of epoxides,[2] we have developed transition metal-catalyzed stereoselective hydrolysis and alcoholysis of alkenyl ethers[3a] and azlactones.[3c] Using the Pd-catalyzed vinyl ether alcoholysis reaction,[3a] an efficient kinetic resolution of mono-vinyl, mono-acyl derivatives of axially chiral diols, such as 2-acyloxy-2′-vinyloxy-1,1′-biaryls, has been achieved.[3b] Enantioselective oxidative coupling of hydroxyaryls is one of the conventional approaches to this class of compounds.[4] However, this method is only applicable for 2-naphthols into 1,1′-bi-2-naphthols, but not for phenols into 1,1′-bi-2-phenols due to the instability of the radical intermediate. Thus, an advantage of our strategy is that the reaction is applicable to 1,1′-bi-2-phenols as well as to 1,1′-bi-2-naphthols. In our alcoholysis reaction system,[3b] the acyl group on the substrates is indispensable for obtaining high selectivity and reactivity. In addition, the bulkiness of the acyl group significantly affected the selectivity and reactivity. The k_{rel} value of the kinetic resolution changed as follows: acetyl (6.1), 1-heptanoyl (14.3), pivaloyl (20.3), and 1-adamantanoyl (28.7). Thus, we have continued further the investigation on the effect of directing group at the 2-position of the 2,2′-dihydroxy-1,1′-biaryls. Herein, we report that phosphoryl (PO) and sulfonyl (SO_2) groups act as efficient directing groups in the catalytic alcoholysis reaction as well as report on the influence of the substituents on them with regard to the selectivity and reactivity.

2. Results and discussion

The vinyl ether substrates bearing a phosphoryl group, **1a–d**, and a sulfonyl group, **3a–e**, were prepared from racemic 1,1′-bi-2-naphthol and the corresponding phosphoryl or sulfonyl chlorides. The catalytic alcoholysis reactions to give **2a–d** or **4a–e** using methanol as reagent were carried out under the similar conditions to those mentioned in the previous report (Scheme 1).[3b] The catalyst consists of 5 mol % $Pd(OAc)_2$ and 6 mol % chiral diamine ligand having tetraphenylphenyl group:[5] (*R*,*R*)-*N*,*N*′-di[4-((2′,3′,4′,5′-tetraphenyl)phenyl)phenyl]-1,2-cyclohexanediamine **7** (Scheme 2).



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Substrate **1a**, which has a dimethoxyphosphoryl group, underwent alcoholysis of the vinyl group to give 73% ee of the product (*S*)-**2a** in 56% yield and 95% ee of unreacted (*R*)-**1a** in 42% yield (Table 1, entry 1). The k_{rel} value of the kinetic resolution was calculated as 22.9, which is slightly better than that of the standard substrate with a pivaloyl group mentioned (k_{rel} = 20.3) in our previous study.[3b] The selection rule for enantiomers is same as

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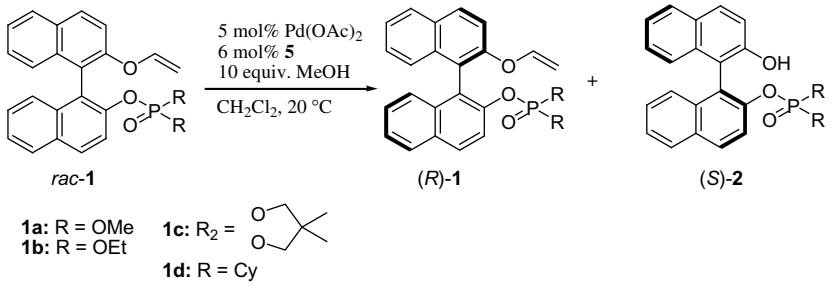
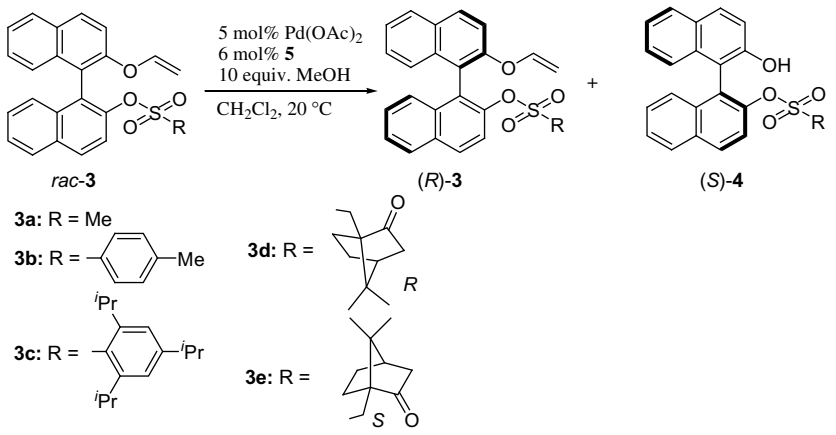
doi:10.1016/j.tetasy.2008.06.034



Scheme 1. Pd-catalyzed methanolysis of vinyl ethers **1**.



Scheme 2. Pd-catalyzed methanolysis of vinyl ethers **3**.

Table 1
Kinetic resolution via palladium-catalyzed methanolysis of **1**[a]

Entry	Substrate	Time (h)	Conversion (%)[b]	ee of (*R*)-**1**[c] (yield (%))[d]	ee of (*S*)-**2**[c] (yield (%))[d]	k_{rel}[e]
1	**1a**	24	56.5	94.8 (42.2)	73.0 (56.0)	22.9
2	**1b**	48	61.1	98.5 (36.7)	62.7 (62.1)	20.0
3	**1c**	24	39.1	41.0 (59.3)	63.8 (39.1)	6.7
4	**1d**	24	33.2	27.4 (65.4)	55.2 (33.1)	4.8

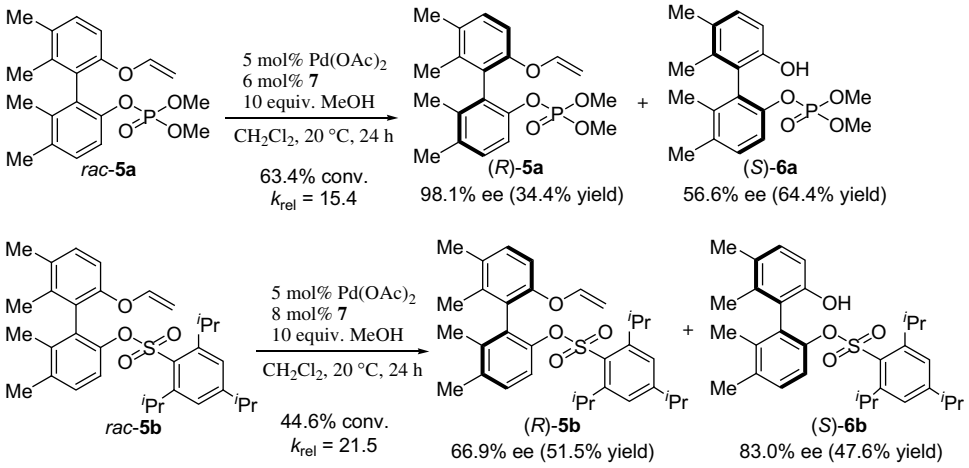
[a] A mixture of $Pd(OAc)_2$ (0.01 mmol) and **7** (0.012 mmol) in CH_2Cl_2 was stirred at 20 °C for 1 h, after which the solvent was removed under reduced pressure. To this were added CH_2Cl_2 (0.125 mL), **1** (0.2 mmol), and MeOH (0.081 mL, 2.0 mmol), and then stirred at 20 °C for 24–48 h.
[b] Calculated with the equation: conv = $ee_{sub}/(ee_{sub} + ee_{pro})$, see Ref. 3c.
[c] Determined by HPLC analysis.
[d] Isolated yield.
[e] Calculated with the equations: $k_{rel} = \ln[(1 - conv)(1 - ee_{sub})]/\ln[(1 - conv)(1 + ee_{sub})] = \ln[1 - conv(1 + ee_{pro})]/\ln[1 - conv(1 - ee_{pro})]$, see Ref. 3c.

the previous reaction in terms of axial chirality.[3b] When the phosphoryl group has a slightly larger substituent, such as a diethoxy group **1b**, a little decrease in k_{rel} value (20.0) was observed (Table 1, entry 2). 2,2-Dimethyl-1,3-propylenedioxyphosphoryl **1c** and dicyclohexylphosphoryl **1d** gave k_{rel} values 6.7 and 4.8, respectively (Table 1, entries 3 and 4). Although a bulkier substituent showed higher selectivity when the acyl group was employed in the previous work,[3b] an opposite tendency was observed when **1** is employed as a substrate. The alcoholysis reaction was found to be applicable to the substrates bearing a sulfonyl group, **3a**–**e** (Table 2). Substrate **3a**, which has a methanesulfonyl group, gave a rather low k_{rel} value (k_{rel} = 4.0, Table 2, entry 1). Slightly better selectivity (k_{rel} = 4.8) was observed when the directing group was changed to 4-toluenesulfonyl group **3b** (Table 2, entry 2). The highest selectivity was observed with **3c**, which has a 2,4,6-triisopropylphenylsulfonyl group as a directing group (Table 2, entry 3). The k_{rel} value reached 36.8. The unreacted substrate (*R*)-**3c** was obtained with 99.0% ee in 43% isolated yield. The alcoholysis product (*S*)-**4c** was obtained with 75.7% ee in 56% isolated yield at the same time. In contrast to substrates **1**, substrates **3** gave higher selectivity when a sterically congested directing group was used. A chiral substituent was introduced on the sulfonyl group. When a (*R*)-camphorsulfonyl group was introduced **3d**, the selectivity factor of 6.7 was observed. On the other hand, when an (*S*)-camphorsulfonyl group was introduced, **3e**, the k_{rel} value increased to 13.5. This result suggests that the chirality on the

Table 2
Kinetic resolution via palladium-catalyzed methanolysis of **3**[a]

Entry	Substrate	Time (h)	Conversion (%)[b]	ee of (*R*)-**3**[c] (yield (%))[d]	ee of (*S*)-**4**[c] (yield (%))[d]	k_{rel}[e]
1	**3a**	24	46.6	40.7 (51.7)	46.7 (48.3)	4.0
2	**3b**	24	47.0	45.6 (51.6)	51.4 (47.8)	4.8
3	**3c**	24	56.7	99.0 (43.3)	75.7 (55.5)	36.8
4	**3d**[f]	24	47.9	54.8[g] (49.6)	59.5[h] (49.7)	6.7
5	**3e**[i]	24	61.7	95.0[j] (41.8)	58.9[k] (57.8)	13.5

[a] A mixture of $Pd(OAc)_2$ (0.01 mmol) and **7** (0.012 mmol) in CH_2Cl_2 were stirred at 20 °C for 1 h, after which the solvent was removed under reduced pressure. To this were added CH_2Cl_2 (0.125 mL), **3** (0.2 mmol), and MeOH (0.081 mL, 2.0 mmol), and then stirred at 20 °C for 24 h.
[b] Calculated with the equation: conv = $ee_{sub}/(ee_{sub} + ee_{pro})$, see Ref. 3c.
[c] Determined by HPLC analysis.
[d] Isolated yield.
[e] Calculated with the equations: $k_{rel} = \ln[(1 - conv)(1 - ee_{sub})]/\ln[(1 - conv)(1 + ee_{sub})] = \ln[1 - conv(1 + ee_{pro})]/\ln[1 - conv(1 - ee_{pro})]$, see Ref. 3c.
[f] A 1:1 mixture of (a*S*,*R*)-**3d** and (a*R*,*R*)-**3d**.
[g] Diastereomeric excess of (a*R*,*R*)-**3d** to (a*S*,*R*)-**3d**.
[h] Diastereomeric excess of (a*S*,*R*)-**4d** to (a*R*,*R*)-**4d**.
[i] A 1:1 mixture of (a*S*,*S*)-**3e** and (a*R*,*S*)-**3e**.
[j] Diastereomeric excess of (a*R*,*S*)-**3e** to (a*S*,*S*)-**3e**.
[k] Diastereomeric excess of (a*S*,*S*)-**4e** to (a*R*,*S*)-**4e**.



Scheme 3. Pd-catalyzed methanolysis of vinyl ethers **5**.

sulfonyl substituent affects the selectivity. However, in both cases, the fast-reacting isomer was determined based on the absolute configuration of the binaphthyl group, therefore (a*R*,*R*)-**3d** and (a*R*,*S*)-**3e** were obtained as an enantioenriched recovered substrate. This result indicates that axial chirality plays more important role in this reaction. In order to examine the applicability to 1,1′-bi-2-phenol derivatives, 5,5′,6,6′-tetramethyl-1,1′-bi-2-phenol[6] derivatives having phosphoryl or sulfonyl groups were tested (Scheme 3). In both cases, good selectivities were observed. When dimethoxyphosphoryl group was introduced, **5a**, the k_{rel} value was found to be 15.4; when a 2,4,6-triisopropylphenylsulfonyl group was introduced, **5b**, the k_{rel} value was 21.4. This result suggests that this reaction is applicable to 1,1′-bi-2-phenol derivatives.

3. Conclusion

In conclusion, the kinetic resolution of the phosphoryl and sulfonyl esters of 1,1′-bi-2-naphthol and 1,1′-bi-2-phenol has been achieved via Pd-catalyzed alcoholysis of their vinyl ethers using chiral diamine **7** as ligand. The highest k_{rel} value reached 36.8 with substrate **3c**, and 99.0% ee of (*R*)-**3c** was obtained in 43% isolated yield. The selectivity changed depending on the structure of the substituent on phosphoryl and sulfonyl groups. Efforts are currently underway to expand this strategy to control the chirality on the phosphoryl and sulfonyl groups.

4. Experimental

4.1. General

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on JEOL JMN AL 400 instruments. ^{13}C NMR (151 MHz) and ^{31}P NMR (243 MHz) spectra were recorded on Bruker DRX-600 instruments. Column chromatography was performed on silica-gel (Kanto Chemicals, Silica Gel 60N, spherical, neutral; particle size 40–100 μm). The enantiomeric excess (ee) was determined by HPLC using DAICEL CHIRALPAK AD-H (**1a**, **2a**, **4a**, and **6a**), CHIRALCEL OD-H (**1b**, **2b**, **2d**, **3a**, **3b**, and **4b**), and CHIRALPAK IA (**1c**, **1d**, **2c**, **4c**, and **6b**). The ee of **1c**, **3c**, **5a**, and **5b** were determined by the analysis of **2c**, **4c**, **6a**, and **6b**, which were obtained by the hydrolysis with $PdCl_2(MeCN)_2$.[3a] The diastereomeric excesses (de) of **3d**, **3e**, **4d**, and **4e** were determined by ^{1}H NMR measurement. Recycling preparative HPLC was performed with Japan Analytical Industry LC-918 equipped with GPC columns JAIGEL-W252.

4.2. Materials

$CDCl_3$, C_6D_6 and acetone-d_6 (Cambridge Isotope Laboratories Inc.) were used as solvent for obtaining NMR spectra. (*R*,*R*)-*N*,*N*′-Di[4-((2′,3′,4′,5′-tetraphenyl)phenyl)phenyl]-1,2-cyclohexanediamine **7** and 5,5′,6,6′-tetramethyl-2,2′-dihydroxy-1,1′-biphenyl were synthesized by a literature method.[3a,6] $Pd(OAc)_2$ (Wako Chemicals), MeOH (Aldrich, anhydrous), and CH_2Cl_2 (Aldrich, anhydrous) were used in the kinetic resolution. Benzene (Wako Chemicals, spectrochemical analysis grade) and $CHCl_3$ (Wako Chemicals, spectrochemical analysis grade) were used for measurement of optical rotation. All other chemical reagents used were of commercial grade.

4.3. Synthesis of 2′-vinyloxy-1,1′-binaphthyl-2-yl phosphates 1

4.3.1. Dimethyl 2′-vinyloxy-1,1′-binaphthyl-2-yl phosphate 1a

A mixture of $Cu(OAc)_2$ (545 mg, 3.0 mmol, 1.2 equiv) and pyridine (2.02 mL, 25 mmol, 10.0 equiv) in CH_2Cl_2 (8 mL) was stirred at rt for 5 min. To this were added **2a** (1.25 g, 2.5 mmol, 1.0 equiv) and vinylboronic anhydride–pyridine complex (421 mg, 1.75 mmol, 0.7 equiv) and the mixture was stirred at rt under an O_2 atmosphere for 40 h. The reaction mixture was concentrated under reduced pressure. The crude product was purified by silica-gel chromatography to give a yellow solid (58%).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.12 (d, 3H, J = 11.2 Hz), 3.41 (d, 3H, J = 11.2 Hz), 4.19 (dd, 1H, J = 1.8, 6.2 Hz), 4.45 (dd, 1H, J = 1.8, 13.8 Hz), 6.49 (dd, 1H, J = 6.2, 13.8 Hz), 7.23–7.45 (m, 7H), 7.73 (d, 1H, J = 8.0 Hz), 7.88 (d, 1H, J = 8.0 Hz), 7.92 (d, 1H, J = 8.2 Hz), 7.97 (d, 1H, J = 9.2 Hz), 7.98 (d, 1H, J = 8.8 Hz); ^{13}C NMR (150 MHz, C_6D_6) δ 54.2 (d, J = 6.0 Hz), 54.5 (d, J = 5.6 Hz), 95.1, 119.0, 120.7, 121.9, 123.4 (d, J = 8.3 Hz), 125.5, 125.9, 126.7, 127.0, 127.5, 127.6, 128.9, 130.0, 130.6, 130.7, 131.2, 132.0, 134.8, 134.9, 147.8 (d, J = 6.4 Hz), 149.7, 153.1; ^{31}P NMR (243 MHz, C_6D_6) δ −3.8; Elemental Anal. Calcd (%) for $C_{24}H_{21}O_5P$: C, 68.57; H, 5.03. Found: C, 68.47; H, 5.03.

4.3.2. Diethyl 2′-vinyloxy-1,1′-binaphthyl-2-yl phosphate 1b

White solid (58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, 3H, J = 7.2 Hz), 1.07 (t, 3H, J = 7.2 Hz), 3.40–3.55 (m, 2H), 3.62–3.85 (m, 2H), 4.18 (dd, 1H, J = 1.0, 6.0 Hz), 4.43 (dd, 1H, J = 1.0, 13.6 Hz), 6.51 (dd, 1H, J = 6.0, 13.6 Hz), 7.20–7.30 (m, 4H), 7.37–7.45 (m, 3H), 7.78 (d, 1H, J = 8.8 Hz), 7.87 (d, 1H, J = 8.0 Hz), 7.91 (d, 1H, J = 8.0 Hz), 7.95–7.99 (m, 2H); ^{13}C NMR (150 MHz, C_6D_6) δ

16.1 (d, J = 6.6 Hz), 16.3 (d, J = 6.0 Hz), 64.3 (d, J = 6.6 Hz), 64.5 (d, J = 6.6 Hz), 95.0, 119.1, 120.6, 122.1, 123.2 (d, J = 7.8 Hz), 125.5, 125.8, 126.7, 127.1, 127.5, 127.6, 128.8, 128.9, 130.5, 130.7, 131.3, 132.0, 134.8, 134.9, 148.0 (d, 1C, J = 5.0 Hz), 149.8, 153.2; ^{31}P NMR (243 MHz, C_6D_6) δ −6.0; Elemental Anal. Calcd (%) for $C_{26}H_{25}O_5P$: C, 69.64; H, 5.62. Found: C, 69.41; H, 5.59.

4.3.3. 2-(5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yloxy)-2′-vinyloxy-1,1′-binaphthalene 1c

White foam (77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 3H), 1.08 (s, 3H), 2.94 (d, 1H, J = 10.8 Hz), 3.16 (d, 1H, J = 10.8 Hz), 3.24 (ddd, 1H, J = 2.8, 10.8, 23.2 Hz), 3.47 (ddd, 1H, J = 2.8, 10.8, 23.2 Hz), 4.20 (dd, 1H, J = 1.6, 6.0 Hz), 4.43 (dd, 1H, J = 1.6, 14.0 Hz), 6.49 (dd, 1H, J = 6.0, 14.0 Hz), 7.23–7.34 (m, 4H), 7.38–7.46 (m, 2H), 7.46 (d, 1H, J = 8.8 Hz), 7.88–8.02 (m, 5H); ^{13}C NMR (150 MHz, C_6D_6) δ 19.4, 21.6, 31.5, 77.8 (d, J = 7.1 Hz), 78.1 (d, J = 7.1 Hz), 95.5, 119.2, 120.5, 121.9 (d, 1C, J = 8.8 Hz), 122.2, 125.7, 125.8, 126.4, 126.9, 127.5, 127.9, 128.8, 129.1, 130.6, 131.2, 131.3, 131.9, 134.5, 134.7, 147.6 (d, J = 5.4 Hz), 149.4, 153.2; ^{31}P NMR (243 MHz, C_6D_6) δ −14.3; Elemental Anal. Calcd (%) for $C_{27}H_{25}O_5P$: C, 70.43; H, 5.47. Found: C, 70.20; H, 5.53.

4.3.4. 2′-Vinyloxy-1,1′-binaphthyl-2-yl dicyclohexylphosphinate 1d

White foam (54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.30–1.80 (m. 22H), 4.19 (dd, 1H, J = 1.8, 6.2 Hz), 4.46 (dd, 1H, J = 1.8, 13.8 Hz), 6.52 (dd, 1H, J = 6.2, 13.8 Hz), 7.20–7.31 (m, 4H), 7.38–7.40 (m, 2H), 7.43 (d, 1H, J = 8.8 Hz), 7.89 (d, 2H, J = 8.0 Hz), 7.90 (d, 1H, J = 8.8 Hz), 7.96 (d, 1H, J = 8.8 Hz), 8.05 (d, 1H, J = 9.2 Hz); ^{13}C NMR (150 MHz, C_6D_6); δ 25.2 (d, J = 3.0 Hz), 25.7 (d, J = 4.3. Hz), 25.9 (d, J = 3.0 Hz), 26.0, 26.2, 26.6 (d, J = 7.6 Hz), 26.6, 26.7 (d, J = 7.6 Hz), 26.9 (d, J = 7.5 Hz), 27.0 (d, J = 62.2 Hz), 37.1 (d, J = 87.3 Hz), 37.3 (d, 1C, J = 87.9 Hz), 94.8, 121.2 (d, J = 6.0 Hz), 121.5, 122.7, 125.2, 125.5, 126.4, 127.1, 127.3, 127.6, 128.8, 128.9, 129.1, 130.3, 130.6, 131.4, 131.5, 134.8, 135.0, 149.6, 150.7 (d, J = 9.0 Hz), 153.0; ^{31}P NMR (243 MHz, C_6D_6) δ 58.43; Elemental Anal. Calcd (%) for $C_{34}H_{37}O_3P$: C, 77.84; H, 7.11. Found: C, 77.42; H, 7.11.

4.4. Synthesis of 2′-hydroxy-1,1′-binaphthyl-2-yl phosphates 2

4.4.1. Dimethyl 2′-hydroxy-1,1′-binaphthyl-2-yl phosphate 2a

To a mixture of 1,1′-bi-2-naphthol (2.86 g, 10.0 mmol, 1 equiv) and dimethyl chlorophosphate (1.45 g, 10.0 mmol, 1 equiv) in CH_2Cl_2 (20 mL) was added Et_3N (2.09 mL, 15.0 mmol, 1.5 equiv) at 0 °C and the mixture was stirred at rt for 20 h. The reaction mixture was quenched by adding HCl (1 N, 40 mL) and extracted with CH_2Cl_2. The resulting extracts were washed with brine, and dried with Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography to give white powder (2.17 g, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.15 (d, 3H, J = 11.4 Hz), 3.59 (d, 3H, J = 11.4 Hz), 6.08 (s, 1H), 7.03 (d, 1H, J = 9.2 Hz), 7.25–7.34 (m, 4H), 7.40 (d, 1H, J = 8.8 Hz), 7.48 (dd, 1H, J = 7.0, 7.0 Hz), 7.59 (d, 1H, J = 8.8 Hz), 7.85 (d, 1H, J = 8.0 Hz), 7.91 (d, 1H, J = 8.8 Hz), 7.95 (d, 1H, J = 8.4 Hz), 8.04 (d, 1H, J = 8.8 Hz); ^{13}C NMR (150 MHz, C_6D_6) δ 54.4 (d, J = 6.0 Hz), 54.9 (d, J = 6.0 Hz), 115.6, 119.5, 119.9, 122.7 (d, J = 5.6 Hz), 123.6, 124.7, 125.8, 126.1, 126.7, 127.6, 128.0, 128.2, 129.1, 130.2, 130.9, 131.7, 133.7, 133.8, 147.1 (d, 1C, J = 7.2 Hz), 152.3; ^{31}P NMR (243 MHz, C_6D_6) δ −2.6; Elemental Anal. Calcd (%) for $C_{22}H_{19}O_5P$: C, 67.00; H, 4.86. Found: C, 67.31; H, 5.26.

4.4.2. Diethyl 2′-hydroxy-1,1′-binaphthyl-2-yl phosphate 2b

White solid (82%); ^{1}H NMR (400 MHz, $CDCl_3$); δ 0.86 (t, 3H, J = 7.2 Hz), 1.20 (t, 3H, J = 7.2 Hz), 3.30–3.36 (m, 1H), 3.50–3.58 (m, 1H), 3.94 (dq, 2H, J = 7.2, 7.2 Hz), 6.23 (s, 1H), 7.02 (d, 1H, J = 6.0 Hz), 7.22–7.26 (m, 2H), 7.30–7.35 (m, 2H), 7.39 (d, 1H, J = 8.8 Hz), 7.47 (dd, 1H, J = 7.4, 8.8 Hz), 7.61 (d, 1H, J = 9.2 Hz), 7.84 (d, 1H, J = 8.0 Hz), 7.90 (d, 1H, J = 8.8 Hz), 7.94 (d, 1H, J = 8.4 Hz), 8.03 (d, 1H, J = 8.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.5 (d, J = 6.9 Hz), 15.9 (d, J = 6.1 Hz), 64.4 (d, J = 6.1 Hz), 64.8 (d, J = 6.0 Hz), 116.0, 119.6, 119.9, 122.7 (d, J = 5.8 Hz), 123.8, 124.7, 125.9, 126.0, 126.6, 127.3, 127.9, 128.2, 129.2, 130.1, 130.8, 131.6, 133.8, 147.3 (d, J = 7.2 Hz), 152.3; ^{31}P NMR (243 MHz, C_6D_6) δ −4.5; Elemental Anal. Calcd (%) for $C_{24}H_{23}O_5P$: C, 68.24; H, 5.49. Found: C, 68.29; H, 5.14.

4.4.3. 2-(5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yloxy)-2′-hydroxy-1,1′-binaphthyl 2c

White solid (94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.26 (s, 3H), 1.08 (s, 3H), 3.06 (d, 1H, J = 10.8 Hz), 3.11 (d, 1H, J = 10.8 Hz), 3.33 (ddd, 1H, J = 3.2, 10.8, 23.2 Hz), 3.46 (ddd, 1H, J = 3.2, 10.8, 23.2 Hz), 5.14 (s, 1H), 7.11 (d, 1H, J = 8.8 Hz), 7.24–7.39 (m, 5H), 7.47–7.54 (m, 1H), 7.86 (d, 1H, J = 6.8 Hz), 7.93 (d, 1H, J = 9.2 Hz), 7.97 (d, 2H, J = 8.4 Hz), 8.06 (d, 1H, J = 9.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.4, 21.6, 31.5 (d, J = 5.8 Hz), 77.9 (d, J = 6.8 Hz), 78.0 (d, J = 6.8 Hz), 114.2, 118.2, 119.8, 119.9 (d, 1C, J = 5.1 Hz), 123.7, 124.9, 125.6, 126.0, 127.0, 127.7, 128.1, 128.5, 129.0, 130.3, 131.3, 131.5, 133.4, 133.6, 147.1 (d, J = 6.0 Hz), 151.9; ^{31}P NMR (243 MHz, C_6D_6); δ −13.8; Elemental Anal. Calcd (%) for $C_{25}H_{23}O_5P$: C, 69.12; H, 5.34. Found: C, 69.03; H, 5.36.

4.4.4. 2′-Hydroxy-1,1′-binaphthyl-2-yl dicyclohexylphosphinate 2d

White powder (80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78–1.25 (m, 11H), 1.25–1.64 (m, 11H), 6.00 (s,1H), 7.05 (d, 1H, J = 8.4 Hz), 7.22–7.50 (m, 6H), 7.83 (d, 1H, J = 7.6 Hz), 7.85 (d, 1H, J = 6.4 Hz), 7.91 (d, 1H, J = 8.8 Hz), 7.92 (d, 1H, J = 8.4 Hz), 7.98 (d, 1H, J = 8.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.9 (d, 1C, J = 3.8 Hz), 25.1 (d, J = 2.5 Hz), 25.2, 25.4 (d, 1C, J = 2.8 Hz), 25.6, 25.7, 26.0 (2C), 26.1 (d, J = 5.6 Hz), 26.2 (d, J = 5.6 Hz), 36.5 (d, J = 86.5 Hz), 37.0 (d, J = 85.2 Hz), 116.1, 119.1, 120.9, 121.0 (d, J = 4.5 Hz), 123.5, 124.8, 125.5, 125.6, 126.6, 127.4, 128.0, 128.2, 129.3, 130.0, 130.6, 131.0, 133.7, 133.8, 149.0 (d, J = 9.9 Hz), 152.2; ^{31}P NMR (243 MHz, C_6D_6) δ 62.3; Elemental Anal. Calcd (%) for $C_{32}H_{35}O_3P$: C, 77.09; H, 7.08. Found: C, 76.71; H, 7.17.

4.5. Synthesis of 2′-vinyloxy-1,1′-binaphthyl-2-yl sulfonates 3

Similar procedures to the synthesis of **1** were used.

4.5.1. 2′-Vinyloxy-1,1′-binaphthyl-2-yl methanesulfonate 3a

White foam (42%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 4.27 (dd, 1H, J = 2.0, 6.4 Hz), 4.51 (dd, 1H, J = 2.0, 14.0 Hz), 6.54 (dd, 1H, J = 6.4, 14.0 Hz), 7.18 (d, 1H, J = 8.4 Hz), 7.20–7.55 (m, 6H), 7.70 (d, 1H, J = 9.2 Hz), 7.91 (d, 1H, J = 8.4 Hz), 7.96 (d, 1H, J = 8.0 Hz), 8.02 (d, 1H, J = 8.8 Hz), 8.03 (d, 1H, J = 9.2 Hz); ^{13}C NMR (150 MHz, C_6D_6) δ 38.2, 95.9, 118.6, 120.9, 122.6, 125.5, 125.6, 126.6, 126.7, 127.1, 127.7, 128.0, 128.9, 129.0, 130.8, 131.0, 131.1, 132.9, 134.4, 134.6, 146.9, 149.2, 153.1; Elemental Anal. Calcd (%) for $C_{23}H_{18}O_4S$: C, 70.75; H, 4.65. Found: C, 70.58; H, 4.76.

4.5.2. 2′-Vinyloxy-1,1′-binaphthyl-2-yl 4-toluenesulfonate 3b

White foam (56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (s, 3H), 4.22 (dd, 1H, J = 2.0, 6.2 Hz), 4.44 (dd, 1H, J = 2.0, 13.8 Hz), 6.45 (dd, 1H, J = 6.2, 13.8 Hz), 6.73 (d, 2H, J = 8.0 Hz), 6.83 (d, 1H, J = 8.8 Hz), 7.02 (d, 2H, J = 8.1 Hz), 7.09–7.14 (m, 2H), 7.22–7.26 (m, 1H), 7.30 (d, 1H, J = 8.8 Hz), 7.32–7.38 (m, 1H), 7.40–7.48 (m, 1H), 7.78 (d, 1H, J = 8.8 Hz), 7.80 (d, 1H, J = 8.6 Hz), 7.88 (d, 1H, J = 8.8 Hz), 7.92 (d, 1H, J = 8.0 Hz), 7.99 (d, 1H, J = 8.8 Hz); ^{13}C NMR (150 MHz, C_6D_6) δ 21.6, 95.7, 118.8, 120.7, 122.7, 125.0, 125.8, 126.5, 127.1, 127.4,

127.5, 128.1, 128.4, 128.6, 128.8, 129.0, 129.6, 130.69, 130.71, 130.9, 132.9, 134.4, 134.5, 134.6, 144.2, 147.1, 149.6, 153.3; Elemental Anal. Calcd (%) for $C_{29}H_{22}O_4S$: C, 74.66; H, 4.75. Found: C, 74.52; H, 5.00.

4.5.3. 2′-Vinyloxy-1,1′-binaphthyl-2-yl 2,4,6-triisopropylbenzenesulfonate 3c

White foam (71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (d, 6H, J = 6.6 Hz), 1.03 (d, 6H, J = 6.6 Hz), 1.24 (d, 6H, J = 7.2 Hz), 2.88 (qq, 1H, J = 6.8, 6.8 Hz), 3.78 (qq, 2H, J = 6.8, 7.2 Hz), 4.17 (dd, 1H, J = 1.8, 6.0 Hz), 4.44 (dd, 1H, J = 1.8, 13.8 Hz), 6.49 (dd, 1H, J = 6.0, 13.8 Hz), 7.07 (s, 2H), 7.16–7.46 (m, 8H), 7.85 (d, 1H, J = 8.8 Hz), 7.87–7.94 (m, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 24.0 (2C), 25.0 (2C), 25.2 (2C), 30.6 (2C), 34.9, 95.4, 118.7, 121.1, 121.7, 124.3, 125.3, 126.5, 127.22, 127.25, 127.4, 127.5, 127.6, 128.4, 128.6, 128.8, 128.9, 130.4, 131.0, 131.2, 132.8, 133.4, 134.89, 134.91, 147.2, 149.8, 151.5, 153.4, 154.2; Elemental Anal. Calcd (%) for $C_{37}H_{38}O_4S$: C, 76.78; H, 6.62. Found: C, 76.78; H, 6.64.

4.5.4. (a*S*,*R*)-2′-Vinyloxy-1,1′-binaphthyl-2-yl camphorsulfonate (a*S*,*R*)-3d

White foam (56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.38 (s, 3H), 0.68 (s, 3H), 1.20–1.39 (m, 2H), 1.77–1.88 (m, 2H), 1.91 (dd, 1H, J = 4.3, 4.3 Hz), 2.01–2.09 (m, 1H), 2.05 (d, 1H, J = 14.9 Hz), 2.20 (ddd, 1H, J = 3.9, 4.1, 18,5 Hz), 3.09 (d, 1H, J = 14.9 Hz), 4.26 (dd, 1H, J = 1.8, 6.1 Hz), 4.51 (dd, 1H, J = 1.8, 13.9 Hz), 6.56 (dd, 1H, J = 6.1, 13.9 Hz), 7.19 (d, 1H, J = 6.0 Hz), 7.22–7.35 (m, 3H), 7.31 (ddd, 1H, J = 1.2, 6.8, 6.8 Hz), 7.46–7.53 (m, 2H), 7.71 (d, 1H, J = 9.0 Hz), 7.88 (d, 1H, J = 8.3 Hz), 7.95 (d, 1H, J = 8.0 Hz), 7.99 (d, 1H, J = 9.0 Hz), 8.01 (d, 1H, J = 9.0 Hz); ^{13}C NMR (150 MHz, C_6D_6) δ 19.6, 20.1, 25.6, 27.1, 42.5, 43.3, 47.6, 49.5, 58.2, 96.0, 118.9, 120.8, 122.8, 125.5, 125.7, 126.6, 126.9, 127.1, 127.6, 127.9, 128.6, 128.9, 129.0, 130.7, 131.2, 131.3, 132.9, 134.5, 147.0, 149.4, 153.4, 212.3; Elemental Anal. Calcd (%) for $C_{32}H_{30}O_5S$: C, 72.98; H, 5.74. Found: C, 72.88; H, 5.50.

4.5.5. (a*S*,*S*)-2′-Vinyloxy-1,1′-binaphthyl-2-yl camphorsulfonate (a*S*,*S*)-3e

White foam (72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.53 (s, 3H), 0.81 (s, 3H), 1.19–1.27 (m, 2H), 1.77–1.88 (m, 2H), 1.94 (dd, 1H, J = 4.6, 4.6 Hz), 1.96–2.04 (m, 1H), 2.21 (ddd, 1H, J = 3.9, 4.0, 18.8 Hz), 2.45 (d, 1H, J = 14.9 Hz), 2.91 (d, 1H, J = 14.9 Hz), 4.23 (dd, 1H, J = 1.7, 6.2 Hz), 4.48 (dd, 1H, J = 1.7, 13.9 Hz), 6.54 (dd, 1H, J = 6.2, 13.9 Hz), 7.19 (d, 1H, J = 8.5 Hz), 7.25–7.35 (m, 3H), 7.39 (ddd, 1H, J = 1.4, 6.6, 8.4 Hz), 7.46 (d, 1H, J = 8.8 Hz), 7.48 (ddd, 1H, J = 1.4, 6.6, 8.4 Hz), 7.76 (d, 1H, J = 9.0 Hz), 7.89 (d, 1H, J = 8.0 Hz), 7.97 (d, 1H, J = 8.1 Hz), 8.00 (d, 1H, J = 8.7 Hz), 8.02 (d, 1H, J = 9.0 Hz); ^{13}C NMR (150 MHz, C_6D_6) δ 19.6, 20.1, 25.6, 27.6, 42.5, 43.3, 47.7, 49.5, 58.2, 96.1, 118.8, 120.9, 122.5, 125.5, 125.6, 126.6, 126.9, 127.1, 127.6, 128.0, 128.8, 129.1, 130.8, 131.2, 131.3, 132.9, 134.5, 134.6, 147.1, 149.4, 153.3, 212.2; Elemental Anal. Calcd (%) for $C_{32}H_{30}O_5S$: C, 72.98; H, 5.74. Found: C, 72.70; H, 6.04.

4.6. Synthesis of 2′-Hydroxy-1,1′-binaphthyl-2-yl sulfonates 4

4.6.1. 2′-Hydroxy-1,1′-binaphthyl-2-yl methanesulfonate 4a

White powder (35%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 5.10 (s, 1H), 7.04 (d, 1H, J = 8.4 Hz), 7.28 (ddd, 1H, J = 1.4, 6.8, 8.4 Hz), 7.33–7.42 (m, 4H), 7.55 (ddd, 1H, J = 1.2, 6.4, 8.4 Hz), 7.70 (d, 1H, J = 9.2 Hz), 7.86 (d, 1H, J = 10.0 Hz), 7.95 (d, 1H, J = 8.8 Hz), 7.99 (d, 1H, J = 8.4 Hz), 8.09 (d, 1H, J = 9.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 38.4, 113.7, 118.0, 121.9, 123.6, 123.9, 124.5, 126.0, 126.9, 127.2, 127.9, 128.0, 128.4, 128.9, 130.9, 131.2, 132.6, 133.3, 133.4, 146.3, 151.7; Elemental Anal. Calcd (%) for $C_{21}H_{16}O_4S$: C, 69.21; H, 4.43. Found: C, 69.01; H, 4.26.

4.6.2. 2′-Hydroxy-1,1′-binaphthyl-2-yl 4-toluenesulfonate 4b

White powder (56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 5.01 (s, 1H), 6.83 (d, 1H, J = 8.0 Hz), 6.91 (d, 2H, J = 8.0 Hz), 7.13 (ddd, 1H, J = 1.2, 6.8, 8.4 Hz), 7.18 (d, 2H, J = 8.4 Hz), 7.24–7.29 (m, 3H), 7.34 (ddd, 1H, J = 1.2, 6.8, 8.0 Hz), 7.52 (ddd, 1H, J = 1.2, 6.8, 8.4 Hz), 7.73 (d, 1H, J = 9.2 Hz), 7.78 (d, 1H, J = 8.0 Hz), 7.85 (d, 1H, J = 9.2 Hz), 7.97 (d, 1H, J = 8.4 Hz), 8.07 (d, 1H, J = 9.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.7, 113.8, 118.1, 121.8, 123.4, 123.9, 124.7, 125.9, 126.3, 126.7, 126.8, 127.6, 127.7, 127.9, 128.4, 129.0, 129.4, 130.5, 131.1, 132.6, 132.8, 133.5 (2C), 144.8, 146.4, 151.7; Elemental Anal. Calcd (%) for $C_{27}H_{20}O_4S$: C, 73.62; H, 4.58. Found: C, 73.31; H, 4.93.

4.6.3. 2′-Hydroxy-1,1′-binaphthyl-2-yl 2,4,6-triisopropylbenzenesulfonate 4c

White powder (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (d, 6H, J = 6.8 Hz), 1.06 (d, 6H, J = 6.4 Hz), 1.24 (d, 6H, J = 7.2 Hz), 2.88 (qq, 1H, J = 6.8, 6.8 Hz), 3.81 (qq, 2H, J = 6.8, 6.8 Hz), 5.28 (s, 1H), 6.92 (d, 1H, J = 8.0 Hz), 7.07 (s, 2H), 7.18 (ddd, 1H, J = 1.2, 6.8, 8.0 Hz), 7.22–7.30 (m, 3H), 7.33 (ddd, 1H, J = 1.2, 6.8, 8.4 Hz), 7.38 (d, 1H, J = 9.2 Hz), 7.50 (ddd, 1H, J = 1.2, 6.8, 8.0 Hz), 7.80 (d, 1H, J = 8.0 Hz), 7.83 (d, 1H, J = 8.8 Hz), 7.94 (d, 1H, J = 8.0 Hz), 7.98 (d, 1H, J = 8.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.6 (2C), 24.4 (2C), 24.5 (2C), 29.8 (2C), 34.3, 114.6, 118.6, 121.4, 123.5, 123.6, 124.5, 125.0, 125.9, 126.2, 126.4, 126.6, 126.7, 127.7, 128.0, 128.4, 129.2, 130.4, 130.7, 130.9, 132.4, 133.7, 133.8, 146.7, 150.5, 151.9, 154.0; Elemental Anal. Calcd (%) for $C_{35}H_{36}O_4S$: C, 76.06; H, 6.56. Found: C, 75.85; H, 6.13.

4.6.4. (a*S*,*R*)-2′-Hydroxy-1,1′-binaphthyl-2-yl camphorsulfonate (a*S*,*R*)-4d

White foam (72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.51 (s, 3H), 0.67 (s, 3H), 1.24 (ddd, 1H, J = 3.6, 9.2, 12.8 Hz), 1.36 (ddd, 1H, J = 4.4, 9.2, 13.6 Hz), 1.74–1.85 (m, 2H), 1.94 (dd, 1H, J = 3.6, 3.6 Hz), 1.98–2.08 (m, 1H), 2.24 (ddd, 1H, J = 3.6, 3.6, 16.0 Hz), 2.32 (d, 1H, J = 15.0 Hz), 3.23 (d, 1H, J = 15.0 Hz), 5.18 (s, 1H), 7.03 (d, 1H, J = 7.6 Hz), 7.26–7.41 (m, 5H), 7.54 (ddd, 1H, J = 1.4, 6.6, 8.3 Hz), 7.73 (d, 1H, J = 7.6 Hz), 7.84 (d, 1H, J = 7.6 Hz), 7.92 (d, 1H, J = 9.2 Hz), 7.98 (d, 1H, J = 8.0 Hz), 8.08 (d, 1H, J = 9.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.2, 19.3, 24.7, 26.8, 42.3, 42.7, 47.6, 48.7, 57.8, 114.3, 118.5, 122.2, 123.9, 124.0, 124.7, 126.1, 126.8, 127.1, 127.7, 128.2, 128.4, 129.2, 130.8, 131.1, 132.6, 133.5, 133.6, 146.3, 151.8, 214.0; Elemental Anal. Calcd (%) for $C_{30}H_{28}O_5S$: C, 71.98; H, 5.64. Found: C, 71.61; H, 5.62.

4.6.5. (a*S*,*S*)-2′-Hydroxy-1,1′-binaphthyl-2-yl camphorsulfonate (a*S*,*S*)-4e

White foam (86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.61 (s, 3H), 0.85 (s, 3H), 1.23–1.38 (m, 2H), 1.80–1.89 (m, 2H), 1.98 (dd, 1H, J = 4.4, 4.8 Hz), 1.98–2.07 (m, 1H), 2.25 (ddd, 1H, J = 3.6, 4.0, 18.8 Hz), 2.42 (d, 1H, J = 14.8 Hz), 3.11 (d, 1H, J = 14.8 Hz), 5.20 (s, 1H), 7.05 (d, 1H, J = 8.0 Hz), 7.26–7.38 (m, 5H), 7.54 (ddd, 1H, J = 1.2, 6.8, 8.4 Hz), 7.73 (d, 1H, J = 8.8 Hz), 7.85 (d, 1H, J = 7.6 Hz), 7.93 (d, 1H, J = 8.8 Hz), 7.99 (d, 1H, J = 8.4 Hz), 8.09 (d, 1H, J = 9.2 Hz); ^{13}C NMR (150 MHz, C_6D_6) δ 19.4, 19.5, 24.8, 26.8, 42.3, 42.8, 47.8, 48.7, 57.7, 114.2, 118.3, 122.1, 123.8, 123.9, 124.6, 126.1, 126.9, 127.2, 127.8, 128.1, 128.5, 129.1, 130.8, 131.1, 132.6, 133.4, 133.5, 146.3, 151.8, 213.7; Elemental Anal. Calcd (%) for $C_{30}H_{28}O_5S$: C, 71.98; H, 5.64. Found: C, 71.81; H, 5.84.

4.7. Synthesis of 2′-vinyloxy-(5,5′,6,6′-tetramethyl-1,1′-biphenyl)-2-yl phosphate and sulfonate 5

Similar procedures to the synthesis of **1** were used.

4.7.1. Dimethyl 2′-vinyloxy-(5,5′,6,6′-tetramethyl-1,1′-biphenyl)-2-yl phosphate 5a

Colorless oil (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90 (s, 3H), 1.91 (s, 3H), 2.27 (s, 3H), 2.29 (s, 3H), 3.35 (d, 3H, J = 11.2 Hz), 3.53 (d, 3H, J = 11.2 Hz), 4.20 (dd, 1H, J = 1.6, 6.0 Hz), 4.49 (dd, 1H, J = 1.6, 14.0 Hz), 6.43 (dd, 1H, J = 6.0, 14.0 Hz), 6.81 (d, 1H, J = 8.0 Hz), 7.10 (d, 1H, J = 8.0 Hz), 7.14 (d, 1H, J = 8.0 Hz), 7.16 (d, 1H, J = 8.0 Hz); ^{13}C NMR (150 MHz, acetone-d_6) δ 16.7, 16.7, 19.9, 19.9, 54.4 (d, J = 6.8 Hz), 54.7 (d, J = 6.8 Hz), 94.2, 114.5, 117.1, 127.9, 129.5 (d, J = 7.2 Hz), 130.2, 130.4, 132.3, 133.7, 137.7, 137.9, 147.4 (d, J = 6.0 Hz), 150.0, 153.6; ^{31}P NMR (243 MHz, acetone-d_6) δ −3.5; Elemental Anal. calcd (%) for $C_{20}H_{25}O_5P$: C, 63.82; H, 6.69. Found: C, 63.75; H, 6.68.

4.7.2. 2′-Vinyloxy-(5,5′,6,6′-tetramethyl-1,1′-biphenyl)-2-yl 2,4,6-triisopropylbenzenesulfonate 5b

White foam (86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (d, 6H, J = 6.8 Hz), 1.14 (d, 6H, J = 6.8 Hz), 1.25 (d, 6H, J = 6.8 Hz), 1.91 (s, 3H), 1.93 (s, 3H), 2.26 (s, 3H), 2.28 (s, 3H), 2,90 (h, 1H, J = 6.8 Hz), 3.91 (h, 2H, J = 6.8 Hz), 4.15 (dd, 1H, J = 1.6, 6.0 Hz), 4.45 (dd, 1H, J = 1.6, 14.0 Hz), 6.40 (dd, 1H, J = 6.0, 14.0 Hz), 6.67 (d, 1H, J = 8.2 Hz), 6.75 (d, 1H, J = 8.2 Hz), 7.02 (d, 1H, J = 8.2 Hz), 7.09 (d, 1H, J = 8.2 Hz), 7.13 (s, 2H); ^{13}C NMR (100 MHz, acetone-d_6) δ 16.8, 17.0, 20.1, 20.2, 23.7 (2C), 24.9 (2C), 24.8 (2C), 30.4 (2C), 34.8, 94.3, 114.7, 119.3, 124.8, 127.5 (2C), 130.2, 130.8, 132.2, 132.6, 136.1, 138.1, 138.6, 147.1, 150.3, 151.5, 153.8, 155.1; Elemental Anal. Calcd (%) for $C_{33}H_{42}O_4S$: C, 74.12; H, 7.92. Found: C, 74.05; H, 7.91.

4.8. Synthesis of 2′-hydroxy-(5,5′,6,6′-tetramethyl-1,1′-biphenyl)-2-yl phosphate and sulfonate 6

4.8.1. Synthesis of dimethyl 2′-hydroxy-(5,5′,6,6′-tetramethyl-1,1′-biphenyl)-2-yl phosphate 6a

To a mixture of 5,5′,6,6′-tetramethyl-2,2′-dihydroxy-1,1′-biphenyl (0.48 g, 2.0 mmol, 1 equiv) and dimethyl chlorophosphate (0.29 g, 2.0 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was added Et_3N (0.25 mL, 2.0 mmol, 1 equiv) at 0 °C and the mixture was stirred at rt for 20 h. The reaction mixture was quenched by adding HCl (1 N, 10 mL) and extracted with CH_2Cl_2. The resulting extracts were washed with brine, and dried with Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography to give colorless oil (37%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.84 (s, 3H), 1.91 (s, 3H), 2.24 (s, 3H), 2.31 (s, 3H), 3.26 (d, 3H, J = 11.6 Hz), 3.66 (d, 3H, J = 11.6 Hz), 5.50 (s, 1H), 6.83 (d, 1H, J = 8.0 Hz), 7.04 (d, 1H, J = 8.0 Hz), 7.07 (d, 1H, J = 8.0 Hz), 7.19 (d, 1H, J = 8.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.3, 16.4, 19.8, 20.1, 54.1 (d, J = 6.5 Hz), 54.7 (d, J = 6.5 Hz), 114.8, 117.3, 125.1, 128.6 (d, J = 5.6 Hz), 128.8, 130.0, 130.4, 134.6, 135.9, 138.4, 146.6 (d, J = 6.9 Hz), 151.6; ^{31}P NMR (243 MHz, $CDCl_3$) δ −2.2; Elemental Anal. Calcd (%) for $C_{18}H_{23}O_5P$: C, 61.71; H, 6.61. Found: C, 61.83; H, 6.62.

4.8.2. 2′-Hydroxy-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2-yl 2,4,6-triisopropylbenzenesulfonate 6b

White foam (75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (d, 6H, J = 6.8 Hz), 1.16 (d, 6H, J = 6.8 Hz), 1.26 (d, 6H, J = 6.8 Hz), 1.78 (s, 3H), 1.90 (s, 3H), 2.20 (s, 3H), 2.30 (s, 3H), 2,91 (h, 1H, J = 6.8 Hz), 3.90 (h, 2H, J = 6.8 Hz), 4.67 (s, 1H), 6.73 (d, 1H, J = 8.2 Hz), 6.74 (d, 1H, J = 8.2 Hz), 7.02 (d, 1H, J = 8.2 Hz), 7.11 (d, 1H, J = 8.2 Hz), 7.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6, 16.7, 20.0, 20.5, 23.7 (2C), 24.5 (2C), 24.7 (2C), 29.8 (2C), 34.3, 113.5, 119.1, 123.5 (2C), 123.7, 128.4, 130.1, 130.1, 130.2, 130.9, 135.4, 136.0, 138.8, 146.1, 150.3, 150.8, 153.6; Elemental Anal. Calcd (%) for $C_{31}H_{40}O_4S$: C, 73.19; H, 7.93. Found: C, 73.07; H, 7.86.

4.9. Kinetic resolution

4.9.1. Typical procedure (Table 1, entry 1): dimethyl 2′-(vinyloxy)-1,1′-binaphthyl-2-yl phosphate 1a

A mixture of $Pd(OAc)_2$ (2.2 mg, 10 μmol, 5 mol %) and (*R*,*R*)-*N*,*N*′-di[4-((2′,3′,4′,5′-tetraphenyl)phenyl)phenyl]-1,2-cyclohexanediamine (**7**) (12.3 mg, 12 μmol, 6 mol %) in CH_2Cl_2 was stirred at rt under N_2 atmosphere for 1 h. The mixture was concentrated under reduced pressure and dried in vacuo. After 2 h, to this was added **1a** (104.9 mg, 0.2 mmol, 1 equiv) and MeOH (81.0 μL, 2.0 mmol, 10 equiv) in CH_2Cl_2 (125 μL) and the mixture was stirred at 20 °C under ambient atmosphere for 24 h. Silica-gel column chromatography was carried out to give (*R*)-**1a** (42.2%, 94.8% ee) and (*S*)-**2a** (56.0%, 73.0% ee); (*R*)-**1a**: $[\alpha]_D^{23} = +29.5$ (*c* 1.00, C_6H_6), (*S*)-**2a**: $[\alpha]_D^{24} = -25.2$ (*c* 1.00, $CHCl_3$); HPLC analysis: Chiralpak AD-H, hexane/2-propanol = 10:1, flow rate = 1.0 mL/min, retention time; 12.8 min (*S*)-**1a**, 18.6 min (*R*)-**1a**; Chiralpak AD-H, hexane/2-propanol = 10:1, flow rate = 1.0 mL/min, retention time; 16.9 min (*S*)-**2a**, 23.8 min (*R*)-**2a**.

4.9.2. Diethyl 2′-vinyloxy-1,1′-binaphthyl-2-yl phosphate 1b (Table 1, entry 2)

(*R*)-**1b** (36.7%, 98.5% ee): $[\alpha]_D^{28} = +39.6$ (*c* 1.00, C_6H_6), (*S*)-**2b** (62.1%, 62.7% ee): $[\alpha]_D^{25} = -32.2$ (*c* 1.00, $CHCl_3$); HPLC analysis: Chiralcel OD-H, hexane/2-propanol = 20:1, flow rate = 1.0 mL/min, retention time; 10.3 min (*R*)-**1b**, 12.1 min (*S*)-**1b**; Chiralcel OD-H, hexane/2-propanol = 20:1, flow rate = 1.0 mL/min, retention time; 13.7 min (*R*)-**2b**, 16.6 min (*S*)-**2b**.

4.9.3. 2-(5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yloxy)-2′-vinyloxy-1,1′-binaphthalen 1c (Table 1, entry 3)

(*R*)-**1c** (59.3%, 41.0% ee): $[\alpha]_D^{28} = +2.7$ (*c* 1.00, C_6H_6), (*S*)-**2c** (39.1%, 63.8% ee): $[\alpha]_D^{25} = -8.5$ (*c* 1.00, $CHCl_3$); HPLC analysis: Chiralpak IA, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, retention time; 43.4 min (*S*)-**2c**, 67.5 min (*R*)-**2c**.

4.9.4. 2′-Vinyloxy-1,1′-binaphthyl-2-yl dicyclohexylphosphinate 1d (Table 1, entry 4)

(*R*)-**1d** (65.4%, 27.4% ee): $[\alpha]_D^{28} = -0.6$ (*c* 1.00, C_6H_6), (*S*)-**2d** (33.1%, 55.2% ee): $[\alpha]_D^{25} = -26.9$ (*c* 1.00, $CHCl_3$). HPLC analysis: Chiralpak IA, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, retention time; 8.5 min (*S*)-**1d**, 11.9 min (*R*)-**1d**; Chiralcel OD-H, hexane/2-propanol = 20:1, flow rate = 1.0 mL/min, retention time; 9.0 min (*R*)-**2d**, 10.7 min (*S*)-**2d**.

4.9.5. 2′-Vinyloxy-1,1′-binaphthyl-2-yl methanesulfonate 3a (Table 2, entry 1)

(*R*)-**3a** (51.7%, 40.7% ee): $[\alpha]_D^{28} = -4.4$ (*c* 1.00, C_6H_6), (*S*)-**4a** (48.3%, 46.7% ee): $[\alpha]_D^{24} = -13.7$ (*c* 1.00, $CHCl_3$); HPLC analysis: Chiralcel OD-H, hexane/2-propanol = 20:1, flow rate = 1.0 mL/min, retention time; 15.3 min (*R*)-**3a**, 17.6 min (*S*)-**3a**; Chiralpak AD-H, hexane/2-propanol = 10:1, flow rate = 1.0 mL/min, retention time; 31.5 min (*S*)-**4a**, 35.7 min (*R*)-**4a**.

4.9.6. 2′-Vinyloxy-1,1′-binaphthyl-2-yl 4-toluenesulfonate 3b (Table 2, entry 2)

(*R*)-**3b** (51.6%, 45.6% ee): $[\alpha]_D^{28} = +4.26$ (*c* 1.00, C_6H_6), (*S*)-**4b** (47.8%, 51.4% ee): $[\alpha]_D^{25} = -25.9$ (*c* 1.00, $CHCl_3$); HPLC analysis: Chiralcel OD-H, hexane/2-propanol = 20/1, flow rate = 1.0 mL/min, retention time; 10.7 min (*S*)-**3b**, 12.1 min (*R*)-**3b**; Chiralcel OD-H,

hexane/2-propanol = 20:1, flow rate = 1.0 mL/min, retention time; 24.7 min (*R*)-**4b**, 32.1 min (*S*)-**4b**.

4.9.7. 2′-Vinyloxy-1,1′-binaphthyl-2-yl 2,4,6-triisopropylbenzenesulfonate 3c (Table 2, entry 3)

(*R*)-**3c** (44.3%, 99.0% ee): $[\alpha]_D^{23} = +28.0$ (*c* 1.00, C_6H_6), (*S*)-**4c** (55.5%, 75.7% ee): $[\alpha]_D^{23} = -54.6$ (*c* 1.00, $CHCl_3$); HPLC analysis: Chiralpak IA, hexane/2-propanol = 1000:1, flow rate = 0.5 mL/min, retention time; 15.3 min (*R*)-**4c**, 18.7 min (*S*)-**4c**.

4.9.8. (a*S*,*R*)-2′-Vinyloxy-1,1′-binaphthyl-2-yl camphorsulfonate 3d (Table 2, entry 4)

(a*R*,*R*)-**3d** (49.6%, 54.8% de to (a*S*,*R*)-**3d**): $[\alpha]_D^{23} = -11.8$ (*c* 1.00, C_6H_6), (a*S*,*R*)-**4d** (49.7%, 59.5% de to (a*R*,*R*)-**4d**): $[\alpha]_D^{23} = -22.1$ (*c* 1.00, $CHCl_3$).

4.9.9. (a*S*,*S*)-2′-Vinyloxy-1,1′-binaphthyl-2-yl camphorsulfonate 3e (Table 2, entry 5)

(a*R*,*S*)-**3e** (41.8%, 95.0% de to (a*S*,*S*)-**3e**): $[\alpha]_D^{23} = -2.9$ (*c* 1.00, C_6H_6), (a*S*,*S*)-**4e** (57.8%, 58.9% de to (a*R*,*S*)-**4e**): $[\alpha]_D^{23} = -36.0$ (*c* 1.00, $CHCl_3$).

4.9.10. Dimethyl 2′-vinyloxy-(5,5′,6,6′-tetramethyl-1,1′-biphenyl)-2-yl phosphate 5a (Scheme 3)

(*R*)-**5a** (34.4%, 98.1% ee): $[\alpha]_D^{24} = +21.6$ (*c* 2.30, C_6H_6), (*S*)-**6a** (64.4%, 56.6% ee): $[\alpha]_D^{25} = -18.4$ (*c* 1.00, $CHCl_3$); HPLC analysis: Chiralpak AD-H, hexane/2-propanol = 20:1, flow rate = 1.0 mL/min, retention time; 10.8 min (*R*)-**6a**, 12.1 min (*S*)-**6a**.

4.9.11. 2′-Vinyloxy-(5,5′,6,6′-tetramethyl-1,1′-biphenyl)-2-yl 2,4,6-triisopropylbenzenesulfonate 5b (Scheme 3)

(*R*)-**5b** (51.5%, 66.9% ee): $[\alpha]_D^{24} = -28.7$ (*c* 1.00, C_6H_6), (*S*)-**6b** (47.6%, 83.0% ee): $[\alpha]_D^{24} = -48.3$ (*c* 1.00, $CHCl_3$); HPLC analysis: Chiralpak IA, hexane/2-propanol = 1000:1, flow rate = 0.5 mL/min, retention time; 16.2 min (*R*)-**6b**, 19.6 min (*S*)-**6b**.

4.10. Determination of the absolute configuration

4.10.1. Determination of the absolute configurations of 1d, 2a, 2b, 2c, 2d, 4a, 4b, and 4c

Determination of absolute configuration was performed by the comparison of retention time of HPLC (**1d**, **2a**, **2b**, **2c**, **2d**, **4a**, **4b**, and **4c**) and specific rotation (**1d**, **2a**, **2c**, **4b**, and **4c**) with those of authentic samples derived from enantiomerically pure (*S*)-1,1′-bi-2-naphthol. Specific rotation values were as follows: (*S*)-**1d**: $[\alpha]_D^{23} = +4.10$ (*c* 1.00, C_6H_6), (*S*)-**2a**: $[\alpha]_D^{24} = -42.0$ (*c* 1.00, $CHCl_3$), (*S*)-**2c**: $[\alpha]_D^{25} = -13.6$ (*c* 1.00, $CHCl_3$), (*S*)-**4b**: $[\alpha]_D^{23} = -39.4$ (*c* 1.00, $CHCl_3$), (*S*)-**4c**: $[\alpha]_D^{23} = -80.7$ (*c* 1.00, $CHCl_3$). Absolute configurations of **1a**, **1b**, **1c**, **3a**, **3b**, and **3c** were estimated based on the principle of kinetic resolution.

4.10.2. Determination of the relative and absolute configuration of 3d, 3e, 4d, and 4e

Determination of the relative configuration was performed by ^{1}H NMR measurement of authentic samples: (a*S*,*R*)-**3d**, (a*S*,*S*)-**3e**, (a*S*,*R*)-**4d**, and (a*S*,*S*)-**4e**, which were derived from enantiomerically pure (*S*)-1,1′-bi-2-naphthol. (a*S*,*R*)-**3d**: $[\alpha]_D^{19} = +5.4$ (*c* 1.00, C_6H_6); (a*S*,*S*)-**3e**: $[\alpha]_D^{19} = +19.0$ (*c* 1.00, C_6H_6); (a*S*,*R*)-**4d**: $[\alpha]_D^{19} = -38.2$ (*c* 1.00, $CHCl_3$); (a*S*,*S*)-**4e**: $[\alpha]_D^{19} = -66.3$ (*c* 1.00, $CHCl_3$).

4.10.3. Determination of the absolute configurations of 5a, 5b, 6a and 6b

Determination of the absolute configuration was performed by the comparison of retention time of HPLC (**6a**and**6b**) with that of optically active samples derived from (*R*)-5,5′,6,6′-tetramethyl-2,2′-dihydroxy-1,1′-biphenyl (86.7% ee), which were synthesized by hydrolysis of (*R*)-5,5′,6,6′-tetramethyl-2-vinyloxy-2′-pivaloyloxy-1,1′-biphenyl (86.7% ee).[3a,b]

Acknowledgments

The present work is supported by Grant-in-Aid for Global-COE program, 'Science for Future Molecular Systems' from the Ministry of Education, Culture, Science, Sports and Technology of Japan. We appreciate Professor Katsuki and his research group for permitting the use of NMR equipment.

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