Supporting Information

1,1'-Binaphthyl-2,2'-diyl Phosphoroselenoyl Chloride as a Chiral Molecular Tool for the Preparation of Enantiomerically Pure Alcohols and Amines

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General Remarks: The IR spectra were obtained on a JASCO FT-IR spectrophotometer. The ^1H NMR spectra were recorded on a JEOL α -400 (400 MHz) in CDCl_3 . Chemical shifts of protons were reported in δ values referred to tetramethylsilane as an internal standard in CDCl_3 , and the following abbreviations were used: s: singlet, d: doublet, t: triplet, m: multiplet. The ^{13}C NMR spectra were measured on a JEOL α -400 (100 MHz) in CDCl_3 . The ^{31}P NMR spectra (162 MHz) were measured on a JEOL α -400 in CDCl_3 and with 85 % H_3PO_4 as an external standard. ^{77}Se NMR (76 MHz) spectra were measured on a JEOL α -400 in CDCl_3 with Me_2Se as an external standard. All spectra were acquired in the proton-decoupled mode, generally 0.05–0.5 mmol solutions in CDCl_3 (0.4 mL) were used. The mass spectra (MS) and high resolution mass spectra (HRMS) were taken on a JEOL JNM 700 mass spectrometer. Elemental analyses were carried out by Elemental Analysis Center of Kyoto University. Melting points were determined using a Yanagimoto melting point apparatus and are uncorrected. High performance liquid chromatography was performed on a Japan Analytical Industry LC-908 recycling preparative HPLC coupled to RI indicator and UV detector (256 nm) with a Mightysil Si 60 column (250 mm X 20 mm). Optical rotations were measured on a JASCO P-1010 Polarimeter.

Materials: Triethylamine and phosphorus trichloride were distilled from calcium hydride. Diethyl ether (Et_2O) dehydride and tetrahydrofuran (THF) dehydride were purchased from Kanto Chemical Co., Ltd. Piperidine, benzylamine, butyllithium 1.6 M solution in hexane, and selenium (powder) were purchased from Nacalai Tesque Inc. 2-Butanol, 2-heptanol, 2-hexanol, 3-octanol, 4-phenyl-2-butanol, (*R*)-(+)-1,1'-bi-2-naphthol, and 5-undecanol were purchased from Tokyo Chemical Industry Co., Ltd. 1-Cyclohexylethanol and (*R*)-(–)-4-phenyl-2-butanol were purchased from Aldrich Chemical Company, Inc., and used without further purification. 3-Heptanol was prepared by reacting valeraldehyde with EtMgBr . Silica gel used on column chromatography was

run on silica gel 60 of Kanto Chemical Co., Ltd. All manipulations were carried out under argon atmosphere.

(*R*)-4-Chloro-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-selenide ((*R*_{ax})-1)

To a toluene solution (50 mL) of phosphorus trichloride (3 mL, 30 mmol) was added triethylamine (8.4 mL, 60 mmol) at 0 °C with vigorous stirring under Ar atmosphere. To the resulting solution was added (*R*_{ax})-1,1'-bi-2-naphthol (8.58 g, 30 mmol) in toluene (10 mL) at 0 °C, and the reaction mixture was stirred at that temperature for 3 min. After the addition of elemental selenium (2.45 g, 31 mmol), the mixture was warmed to 110 °C and stirred for an additional 6 h. The reaction mixture was concentrated in vacuo. The resulting solid was subjected to column chromatography on silica gel (hexane : CH₂Cl₂ = 3 : 2) to give (*R*_{ax})-1 (12.12 g, 94%, *R*_f = 0.70) as a white solid.: $[\alpha]_D^{20}$ -414 (*c* = 1, CHCl₃); mp: 240–241 °C; IR (KBr): 3006, 1588, 1509, 1460, 1433, 1355, 1214, 1190, 1157, 1142, 1067, 969, 946, 868, 840, 806, 769, 749, 705, 652 cm⁻¹; ¹H NMR (CDCl₃): δ 7.22–8.32 (m, 12H, C₂₀H₁₂); ¹³C NMR (CDCl₃): δ 120.4, 121.1, 122.4, 122.6, 126.3, 126.9, 127.0, 127.1, 127.2, 128.7, 131.3, 131.4, 132.0, 132.2, 132.3, 132.5, 146.5, 146.6, 147.8, 148.0 (Ar); ³¹P NMR (CDCl₃): δ 69.0 (¹*J*_{P-Se} = 1060.9 Hz); ⁷⁷Se NMR (CDCl₃): δ -69.2 (d, ¹*J*_{P-Se} = 1060.9 Hz); MS (EI): *m/z*: 430 [*M*⁺]; Anal. Calcd for C₂₀H₁₂ClO₂PSe: C, 55.90; H, 2.81. Found: C, 55.65; H, 2.78.

Representative procedure for the synthesis of a mixture of diastereomers of 4-alkoxydinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-selenide 3

To THF solutions (3 mL) of the chloride (*R*_{ax})-1 (0.43 g, 1.0 mmol) were added alcohols **2** (1.1 mmol) and Et₃N (0.28 mL, 2.0 mmol) at room temperature. The resulting solutions were stirred at reflux in THF for 3 h and concentrated in vacuo to give residues which were subjected to column chromatography on silica gel with CH₂Cl₂ and hexane as eluent to give the corresponding selenides

3.

A mixture of diastereomers of 4-(1-methylpropoxy)dinaphto[2,1-d:1',2'-f][1,3,2]dioxaphosphopin-4-selenide (3b): ^1H NMR (CDCl_3): δ 0.91 (t, $J = 7.3$ Hz, 3H, CH_3CH_2), 1.05 (t, $J = 7.6$ Hz, 3H, CH_3CH_2), 1.34 (d, $J = 6.4$ Hz, 3H, CH_3CH), 1.52 (d, $J = 6.3$ Hz, 3H, CH_3CH), 1.56-1.90 (m, 2H, CH_3CH_2 , 2H, CH_3CH_2), 4.93-5.05 (m, 1H, CH, 1H, CH), 7.23–7.61 (8H, Ar, 8H, Ar), 7.94–8.06 (4H, Ar, 4H, Ar); ^{13}C NMR (CDCl_3): δ 9.5, 9.6, 20.7 (d, $J = 3.3$ Hz), 21.2 (d, $J = 3.3$ Hz), 29.9 (d, $J = 6.6$ Hz), 30.1 (d, $J = 6.6$ Hz), 81.8 (d, $J = 4.9$ Hz), 82.1 (d, $J = 5.8$ Hz), 120.8, 125.7, 126.5, 126.6, 127.1, 127.2, 128.4, 128.5, 130.7, 131.0, 131.6, 132.0, 132.4, 132.5, 146.3, 146.4, 146.5, 148.1; ^{31}P NMR (CDCl_3): δ 78.03 ($^1J_{\text{P-Se}} = 1010.3$ Hz), 78.18 ($^1J_{\text{P-Se}} = 1010.3$ Hz); ^{77}Se NMR (CDCl_3): δ -325.85 (d, $^1J_{\text{Se-P}} = 1010.3$ Hz), -326.69 (d, $^1J_{\text{Se-P}} = 1010.3$ Hz); MS (EI): m/z : 468 [M^+]; Anal Calcd for $\text{C}_{24}\text{H}_{21}\text{O}_3\text{PSe}$ (467.35): C, 61.68; H, 4.53. Found: C, 61.41; H, 4.70.

A mixture of diastereomers of 4-(1-ethylpentoxy)dinaphto[2,1-d:1',2'-f][1,3,2]dioxaphosphopin-4-selenide (3e): ^1H NMR (CDCl_3): δ 0.82 (t, $J = 6.8$ Hz, 3H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 0.91 (t, $J = 7.6$ Hz, 3H, $\text{CH}_3\text{CH}_2\text{CH}$), 1.00 (t, $J = 7.1$ Hz, 3H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 1.08 (t, $J = 7.3$ Hz, 3H, $\text{CH}_3\text{CH}_2\text{CH}$), 1.21-1.89 (m, 8H, CH_2 , 8H, CH_2), 4.87-4.97 (m, 1H, CH, 1H, CH), 7.29–7.61 (8H, Ar, 8H, Ar), 7.94–8.05 (4H, Ar, 4H, Ar); ^{13}C NMR (CDCl_3): δ 9.40, 9.49, 13.91, 14.13, 22.47, 22.71, 27.03, 27.16, 27.67 (d, $J = 4.4$ Hz), 28.11 (d, $J = 4.4$ Hz), 33.78 (d, $J = 4.9$ Hz), 34.33 (d, $J = 4.9$ Hz), 85.87 (d, $J = 6.8$ Hz), 85.94 (d, $J = 6.8$ Hz), 120.78, 121.55, 122.02, 122.47, 125.71, 126.54, 126.66, 127.13, 127.29, 128.40, 128.56, 130.63, 130.96, 131.62, 131.96, 132.43, 132.48, 146.49, 146.57, 148.08, 148.23; ^{31}P NMR (CDCl_3): δ 79.05 ($^1J_{\text{P-Se}} = 1012$ Hz), 79.09 ($^1J_{\text{P-Se}} = 1012$ Hz); ^{77}Se NMR (CDCl_3): δ -326.22 (d, $^1J_{\text{Se-P}} = 1012$ Hz), -325.25 (d, $^1J_{\text{Se-P}} = 1012$ Hz); MS

(EI): m/z : 509 [M^+] ; Anal Calcd for $C_{27}H_{27}O_3PSe$ (510.09): C, 63.66; H, 5.34. Found: C, 63.47; H, 5.32.

A mixture of diastereomers of 4-(1-butylheptoxy)dinaphto[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-selenide (3f): 1H NMR ($CDCl_3$): δ 0.83 (t, $J = 6.8$ Hz, 3H, $\underline{CH}_3(CH_2)_5$), 0.83 (t, $J = 7.3$ Hz, 3H, $\underline{CH}_3(CH_2)_5$), 0.94 (t, $J = 6.6$ Hz, 3H, $\underline{CH}_3(CH_2)_3CH$), 1.00 (t, $J = 6.8$ Hz, 3H, $\underline{CH}_3(CH_2)_3CH$), 1.17–1.87 (m, 16H, CH_2 , 16H, CH_2), 4.92–5.01 (m, 1H, CH, 1H, CH), 7.26–7.61 (8H, Ar, 8H, Ar), 7.94–8.05 (4H, Ar, 4H, Ar); ^{13}C NMR ($CDCl_3$): δ 13.91, 13.91, 14.14, 14.18, 22.48, 22.54, 22.68, 22.72, 24.84, 24.99, 27.03, 27.16, 29.04, 29.30, 31.63, 31.84, 34.39 (d, $J = 4.9$ Hz), 34.68 (d, $J = 4.9$ Hz), 34.89 (d, $J = 4.4$ Hz), 35.21 (d, $J = 4.4$ Hz), 84.82 (d, $J = 5.6$ Hz), 84.88 (d, $J = 5.6$ Hz), 120.78, 121.53, 122.03, 122.43, 125.70, 126.53, 126.65, 127.12, 127.28, 128.39, 128.55, 130.62, 130.95, 131.61, 131.95, 132.42, 132.48, 146.49, 146.57, 148.07, 148.22; ^{31}P NMR ($CDCl_3$): δ 78.85 ($^1J_{P-Se} = 1012$ Hz), 78.92 ($^1J_{P-Se} = 1012$ Hz); ^{77}Se NMR ($CDCl_3$): δ –324.93 (d, $^1J_{Se-P} = 1012$ Hz), –325.41 (d, $^1J_{Se-P} = 1012$ Hz); MS (EI): m/z : 566 [M^+] ; Anal Calcd for $C_{31}H_{35}O_3PSe$: (566.15): C, 65.84; H, 6.24. Found: C, 65.57; H, 6.18.

A mixture of diastereomers of 4-(1-cyclohexylethoxy)dinaphto[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-selenide (3h): 1H NMR ($CDCl_3$): δ 1.51(d, $J = 6.3$ Hz, 3H, $\underline{CH}_3CH$), 1.53 (d, $J = 6.3$ Hz, 3H, $\underline{CH}_3CH$), 0.93–1.89 (m, 11H, $\underline{CH}(CH_2)_5$, 11H, $\underline{CH}(CH_2)_5$), 4.79–4.93 (m, 1H, CH, 1H, CH), 7.25–7.62 (8H, Ar, 8H, Ar), 7.94–8.05 (4H, Ar, 4H, Ar); ^{13}C NMR ($CDCl_3$): δ 18.18, 18.92, 25.82, 25.90, 26.02, 26.06, 26.18, 26.47, 28.20, 28.24, 28.28, 28.41, 43.38 (d, $J = 6.8$ Hz), 43.51 (d, $J = 6.3$ Hz), 84.56 (d, $J = 6.33$ Hz), 84.86 (d, $J = 6.33$ Hz), 120.84, 121.53, 122.08, 122.47, 125.71, 126.55, 126.66, 127.15, 127.30, 128.41, 128.56, 130.57, 130.62, 130.97, 131.63, 131.98, 132.46, 132.52, 146.36, 146.44, 146.57, 146.66, 148.03, 148.14, 148.29; ^{31}P NMR ($CDCl_3$):

δ 78.47 ($^1J_{\text{P-Se}} = 1012$ Hz), 79.02 ($^1J_{\text{P-Se}} = 1012$ Hz); ^{77}Se NMR (CDCl_3): δ -327.97 (d, $^1J_{\text{Se-P}} = 1012$ Hz), -325.29 (d, $^1J_{\text{Se-P}} = 1012$ Hz); MS (EI): m/z : 521 [M^+]; HRMS Calcd for $\text{C}_{28}\text{H}_{27}\text{O}_3\text{PSe}$: 522.0863. Found: 522.0867.

Separation of a mixture of diastereomers 4-(1-methylhexoxy)dinaphto[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-selenide (3a)

A mixture of diastereomers **3a** (4.0 g) as light yellow oils was left under argon at room temperature for 4 d. The solid precipitate was collected and washed with hexane to give (R_{ax},S)-**3a** (1.19 g, 46%, 86%de) as a light yellow solid. The sticky oil obtained after hexane washing was collected and subjected to column chromatography on silica gel to give (R_{ax},R)-**3a** (1.36 g, 53%, 72%de).

(R_{ax},S)-**3a**: mp: 176–180 °C; ^1H NMR (CDCl_3): δ 0.95 (t, $J = 7.3$ Hz, 3H, CH_3CH_2), 1.34 (d, $J = 5.8$ Hz, 3H, CH_3CH), 1.34–1.54 (m, 6H, CH_2), 1.60–1.69 (m, 1H, CHCH_2), 1.77–1.86 (m, 1H, CHCH_2), 4.99–5.09 (m, 1H, CH), 7.26–7.60 (8H, Ar), 7.94–8.05 (4H, Ar); ^{13}C NMR (CDCl_3): δ 14.10, 21.25, 22.63, 24.87, 31.64, 37.10 (d, $J = 6.6$ Hz), 81.08 (d, $J = 5.79$ Hz), 120.79, 121.47, 121.98, 122.46, 125.73, 126.56, 126.68, 127.13, 127.29, 128.40, 128.56, 130.67, 130.99, 131.63, 131.97, 132.43, 132.49, 146.42, 146.51, 148.03, 148.19; ^{31}P NMR (CDCl_3): δ 78.10 ($^1J_{\text{P-Se}} = 1012$ Hz); ^{77}Se NMR (CDCl_3): δ -326.78 (d, $^1J_{\text{Se-P}} = 1012$ Hz); MS (EI): m/z : 510 [M^+]; Anal Calcd for $\text{C}_{27}\text{H}_{27}\text{O}_3\text{PSe}$ (509.44): C, 63.66; H, 5.34. Found: C, 63.68; H, 5.38.

(R_{ax},R)-**3a**: mp: 112–114 °C; ^1H NMR (CDCl_3): δ 0.81 (t, $J = 7.1$ Hz, 3H, CH_3CH_2), 1.52 (d, $J = 6.4$ Hz, 3H, CH_3CH), 1.12–1.40 (m, 6H, CH_2), 1.48–1.57 (m, 1H, CHCH_2), 1.64–1.73 (m, 1H, CHCH_2), 4.98–5.08 (m, 1H, CH), 7.25–7.61 (8H, Ar), 7.93–8.05 (4H, Ar); ^{13}C NMR (CDCl_3): δ 14.00, 21.77 (d, $J = 3.4$ Hz), 22.43, 24.69, 31.44, 36.95 (d, $J = 6.3$ Hz), 80.75 (d, $J = 5.4$ Hz), 120.77, 121.50, 122.07, 122.46, 125.73, 126.55, 126.67, 127.11, 127.27, 128.40, 128.56, 130.68, 130.98, 131.63, 131.97, 132.46, 146.32, 146.41, 147.99, 148.15; ^{31}P NMR (CDCl_3): δ 77.90 ($^1J_{\text{P-Se}} = 1013$ Hz); ^{77}Se

NMR (CDCl₃): δ -324.45 (d, $^1J_{\text{Se-P}} = 1013$ Hz); MS (EI): m/z : 510 [M^+]; Anal Calcd for C₂₇H₂₇O₃PSe (509.44): C, 63.66; H, 5.34. Found: C, 63.68; H, 5.38.

Separation of a mixture of diastereomers of 4-(1-methylpentoxy)dinaphto[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-selenide (3c)

A mixture of diastereomers **3c** (4.0 g) as a light yellow oil was left under argon at room temperature for 5 d. The solid precipitate was collected and washed with hexane to give (*R*_{ax},*S*)-**3c** (0.79 g, 32%, 86%de) as a light yellow solid. The sticky oil after hexane washing was collected and subjected to column chromatography on silica gel to give (*R*_{ax},*R*)-**3c** (1.38 g, 56%, 50%de).

(*R*_{ax},*S*)-**3c**: mp: 169–171 °C; ^1H NMR (CDCl₃): δ 0.98 (t, $J = 6.8$ Hz, 3H, CH₃CH₂), 1.27 (d, $J = 6.34$ Hz, 3H, CH₃CH), 1.26-1.55 (m, 4H, CH₂) 1.61-1.68 (m, 1H, CH₂CH), 1.78-1.87 (m, 1H, CH₂CH), 4.99-5.09 (m, 1H, CH), 7.25–7.60 (8H, Ar), 7.93–8.05 (4H, Ar); ^{13}C NMR (CDCl₃): δ 14.09, 21.24 (d, $J = 3.4$ Hz), 22.56, 27.32, 36.82 (d, $J = 6.3$ Hz), 81.03 (d, $J = 5.37$ Hz), 120.76, 120.78, 121.47, 121.49, 121.99, 122.01, 122.44, 122.46, 125.73, 126.55, 126.67, 127.12, 127.28, 128.40, 128.56, 130.66, 130.98, 131.63, 131.97, 132.42, 132.48, 146.43, 146.52, 148.04, 148.20; ^{31}P NMR (CDCl₃): δ 78.12 ($^1J_{\text{P-Se}} = 1010$ Hz); ^{77}Se NMR (CDCl₃): δ -326.57 (d, $^1J_{\text{Se-P}} = 1010$ Hz); MS (EI): m/z : 495 [M^+]; HRMS Calcd for C₂₆H₂₅O₃PSe: 496.0707. Found: 496.0676.

(*R*_{ax},*R*)-**3c**: mp: 69–73 °C; ^1H NMR (CDCl₃): δ 0.81 (t, $J = 6.8$ Hz, 3H, CH₃CH₂), 1.20-1.35 (m, 4H, CH₂), 1.52 (d, $J = 6.3$ Hz, 3H, CH₃CH) 1.50-1.57 (m, 1H, CH₂CH), 1.65-1.73 (m, 1H, CH₂CH), 4.98-5.09 (m, 1H, CH), 7.23–7.62 (8H, Ar), 7.91–8.04 (4H, Ar); ^{13}C NMR (CDCl₃): δ 13.87, 21.77 (d, $J = 2.9$ Hz), 22.34, 27.13, 36.66 (d, $J = 6.8$ Hz), 80.72 (d, $J = 4.8$ Hz), 120.71, 120.73, 121.45, 121.48, 121.99, 122.01, 122.41, 122.43, 125.70, 126.52, 126.64, 127.05, 127.20, 128.36, 128.51, 130.66, 130.95, 131.58, 131.91, 132.40, 132.41, 146.26, 146.34, 147.93, 148.09; ^{31}P NMR (CDCl₃): δ 77.99 ($^1J_{\text{P-Se}} = 1013$ Hz); ^{77}Se NMR (CDCl₃): δ -324.85 (d, $^1J_{\text{Se-P}} = 1013$ Hz); MS (EI):

m/z: 495 [M⁺] ; HRMS Calcd for C₂₆H₂₅O₃PSe: 496.0707. Found: 496.0676.

Separation of a mixture of diastereomers of 4-(1-ethylhexoxy)dinaphto[2,1-d:1',2'-f][1,3,2]dioxaphosphopin-4-selenide (3d)

To a mixture of the diastereomers **3d** (2.0 g) was added hot hexane (20 mL), and stirred on the hot plate until complete dissolution. Then, the mixture was left until cooling to room temperature and stored in the refrigerator for 2 d. The solution was filtered and the filtrate was concentrated to give (*R*_{ax},*S*)-**3d** (0.40 g, 86%de) as a colorless solid. The precipitate (1.6 g, 47%de) was recrystallized from CH₂Cl₂/*i*-PrOH (1 : 1) to give (*R*_{ax},*R*)-**3d** (0.50 g, 80%de) as a colorless solid.

(*R*_{ax},*S*)-**3d**: mp: 140–141 °C; ¹H NMR (CDCl₃): δ 0.91 (t, *J* = 7.6 Hz, 3H, CH₃CH₂CH₂), 0.96 (t, *J* = 7.1 Hz, 3H, CH₃CH₂CH), 1.21–1.86 (m, 10H, CH₂), 4.87–4.96 (m, 1H, CH), 7.26–7.60 (8H, Ar), 7.94–8.05 (4H, Ar); ¹³C NMR (CDCl₃): δ 9.40, 14.13, 22.67, 24.72, 27.67 (d, *J* = 4.4 Hz), 31.81, 34.62 (d, *J* = 4.9 Hz), 85.97 (d, *J* = 6.3 Hz), 120.80, 121.57, 122.07, 122.48, 125.71, 126.54, 126.66, 127.15, 127.31, 128.41, 128.57, 130.63, 130.96, 131.63, 131.98, 132.46, 132.51, 146.52, 146.60, 148.11, 148.27; ³¹P NMR (CDCl₃): δ 78.95 (¹*J*_{P-Se} = 1010 Hz); ⁷⁷Se NMR (CDCl₃): δ –325.85 (d, ¹*J*_{Se-P} = 1010 Hz); MS (EI): m/z: 524 [M⁺] ; HRMS Calcd for C₂₈H₂₉O₃PSe: 524.1020. Found: 524.1019.

(*R*_{ax},*R*)-**3d**: mp: 156–157 °C; ¹H NMR (CDCl₃): δ 0.81 (t, *J* = 7.1 Hz, 3H, CH₃CH₂CH₂), 1.08 (t, *J* = 7.3 Hz, 3H, CH₃CH₂CH), 1.19–1.44 (m, 6H, CH₂), 1.53–1.74, 1.78–1.89 (m, 4H, CH₂), 4.87–4.96 (m, 1H, CH), 7.27–7.61 (8H, Ar), 7.94–8.06 (4H, Ar); ¹³C NMR (CDCl₃): δ 9.46 (d, *J* = 9.7 Hz), 13.98, 22.46, 24.55, 28.12 (d, *J* = 4.4 Hz), 31.55, 34.06 (d, *J* = 4.9 Hz), 85.86 (d, *J* = 6.3 Hz), 120.82, 121.58, 125.72, 126.55, 126.66, 127.16, 127.32, 128.41, 128.57, 130.66, 130.96, 131.65, 131.98, 132.46, 146.53, 146.61, 148.12; ³¹P NMR (CDCl₃): δ 78.85 (¹*J*_{P-Se} = 1012 Hz); ⁷⁷Se NMR (CDCl₃): δ –324.53 (d, ¹*J*_{Se-P} = 1012 Hz); MS (EI): m/z: 524 [M⁺] ; HRMS Calcd for C₂₈H₂₉O₃PSe:

524.1020. Found: 524.1019.

Separation of a mixture of diastereomers of 4-(1-methyl-3-phenylpropoxy)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-selenide (3g**)**

Separation of a mixture of diastereomers **3g** was performed on a recycling preparative HPLC, equipped with mighty (GPC) using CH₂Cl₂ and hexane (1 : 1) as eluent.

(*R*_{ax},*S*)-**3g**: mp: 130–133 °C; ¹H NMR (CDCl₃): δ 1.34 (d, *J* = 6.3 Hz, 3H, CH₃CH), 1.91–2.01 (m, 1H, CH₂CH), 2.08–2.17 (m, 1H, CH₂CH), 2.73–2.90 (m, 2H, CH₂CH₂CH), 5.03–5.14 (m, 1H, CH), 7.21–7.60 (12H, Ar), 7.93–8.05 (4H, Ar); ¹³C NMR (CDCl₃): δ 21.33 (d, *J* = 2.9 Hz), 31.58, 38.83 (d, *J* = 7.32 Hz), 80.36 (d, *J* = 5.36 Hz), 120.72, 120.74, 121.4, 121.5, 121.9, 122.0, 122.4, 122.5, 125.8, 126.2, 126.6, 126.7, 127.1, 127.3, 128.4, 128.5, 130.7, 131.0, 131.6, 132.0, 132.4, 132.5, 141.2, 146.4, 146.5, 148.0, 148.2; ³¹P NMR (CDCl₃): δ 77.99 (¹*J*_{P-Se} = 1013 Hz); ⁷⁷Se NMR (CDCl₃): δ –324.53 (d, ¹*J*_{Se-P} = 1013 Hz); MS (EI): *m/z*: 544 [*M*⁺]; HRMS Calcd for C₃₀H₂₅O₃PSe: 544.0707. Found: 544.0714.

(*R*_{ax},*R*)-**3g**: mp: 80–85 °C; ¹H NMR (CDCl₃): δ 1.56 (d, *J* = 6.4 Hz, 3H, CH₃CH), 1.81–1.91 (m, 1H, CH₂CH), 1.96–2.06 (m, 1H, CH₂CH), 2.56–2.71 (m, 2H, CH₂CH₂CH), 5.03–5.13 (m, 1H, CH), 7.07–7.63 (12H, Ar), 7.94–8.06 (4H, Ar); ¹³C NMR (CDCl₃): δ 21.86 (d, *J* = 2.9 Hz), 31.38, 38.75 (d, *J* = 6.83 Hz), 79.96 (d, *J* = 5.36 Hz), 120.8, 121.47, 121.49, 122.1, 122.5, 125.6, 125.9, 126.6, 126.7, 127.3, 128.4, 128.44, 128.6, 130.7, 131.0, 131.7, 132.0, 132.5, 141.2, 146.3, 146.4, 147.9, 148.1; ³¹P NMR (CDCl₃): δ 77.81 (¹*J*_{P-Se} = 1013 Hz); ⁷⁷Se NMR (CDCl₃): δ –322.65 (d, ¹*J*_{Se-P} = 1013 Hz); MS (EI): *m/z*: 544 [*M*⁺]; HRMS Calcd for C₃₀H₂₅O₃PSe: 544.0707. Found: 544.0714.

Reaction of (*R*_{ax},*R*)-4-(1-ethylhexoxy)binaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-selenide (3d**) with butyllithium leading to (*R*)-3-octanol ((*R*)-**2d**)**

To a THF solution (2 mL) of 4-(1-ethylhexoxy)binaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-selenide (**3d**) (0.59 g, 1.1 mmol) was added butyllithium (2.75 mL, 4.4 mmol) at 0 °C, and the reaction mixture was stirred at 0 °C – room temperature for 1 h, was poured into water, and extracted with Et₂O. The organic layer was dried over MgSO₄ and concentrated. The residue was subjected to column chromatography on silica gel with ethyl acetate and hexane (1 : 4) as eluent to give (*R*)-3-octanol ((*R*)-**2d**) (0.14 g, 98%) as a colorless oil.

Reaction of 4-(1-methyl-3-phenylpropoxy)binaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-selenide (3g**) with benzylamine**

To a THF solution (1 mL) of (*R*_{ax},*S*)-4-(1-methyl-3-phenylpropoxy)binaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-selenide (**3g**) (0.85 g, 1.5 mmol) was added benzylamine (0.655 mL, 6.0 mmol), and the mixture was stirred under reflux for 15 h. To the reaction mixture was added 15% aqueous NaOH solution at room temperature, and stirred under reflux for 1 h. The reaction mixture was poured onto water, and extracted with Et₂O. The organic layer was washed with 1 *N* hydrochloric acid. The aqueous layer was neutralized with 15% aqueous NaOH solution, and extracted with Et₂O. The organic layer was dried over MgSO₄, filtered, and concentrated to give a light yellow oil which was subjected to column chromatography on silica gel to give *N*-benzyl 4-(*R*)-phenyl-2-butylamine ((*R*)-**4**) {0.25 g, 70%, [α]_D²⁰ = +8.3 (*c* = 0.88, methanol)}. For (*S*)-**4** obtained from (*R*_{ax},*R*)-**3g**, [α]_D²⁰ = -8.2 (*c* = 1.0, methanol). *Ee* was measured by chiral HPLC of **4** with a chiralcel AD-H column (hexane : IPA = 400 : 1, flow rate 1 mL/min) *R*_T: (*R*) 6.93 (*S*), 7.75 min.

3-MAR-2006 18:17:04.64
 EXMOD: SINGL
 IRMOD: BCM
 OBNUC: 31P
 OBFRQ: 161.70 MHz
 OBSST: 135320.00 Hz
 PW1: 10.40 usec
 POINT: 32768
 SAMPO: 32768
 TIMES: 128
 SCANS: 100
 DUMMY: 2
 FREQU: 97087.38 Hz
 FILTR: 48550 Hz
 ACQTM: 0.3375 sec
 DEADT: 10.00 usec
 DELAY: 4.12 usec
 PD: 2.6625 sec
 ADBIT: 16
 RGAIN: 23
 IRNUC: 1H
 IRFRQ: 399.65 MHz
 IRSST: 134500.00 Hz
 IRRPW: 46.0 usec
 IRATN: 511
 IRANS: 0
 IRBP1: 26
 IRBP2: 6
 BF: 2.00 Hz
 T1: 0.00 %
 T2: 0.00 %
 T3: 90.00 %
 T4: 100.00 %
 XE: 1143.67 Hz
 XS: -12174.44 Hz
 REFVL: -1219.00 ppm
 OFILE: ALPHA
 MENUF: A31P
 SHMFL: TH5AT
 LKSET: 61679.1 Hz
 LKLEV: 220
 LGAIN: 22
 LKPHS: 60.47 deg
 LKSTG: 128
 CTEMP: 20.8 c
 CSPED: 14 Hz
 FIELD: 1975

3-MAR-2006 18:17:25.50
 EXMOD: SINGL
 IRMOD: BCM
 OBNUC: 31P
 OBFRQ: 161.70 MHz
 OBSST: 135320.00 Hz
 PW1: 10.40 usec
 POINT: 32768
 SAMPO: 32768
 TIMES: 128
 SCANS: 100
 DUMMY: 2
 FREQU: 97087.38 Hz
 FILTR: 48550 Hz
 ACQTM: 0.3375 sec
 DEADT: 10.00 usec
 DELAY: 4.12 usec
 PD: 2.6625 sec
 ADBIT: 16
 RGAIN: 23
 IRNUC: 1H
 IRFRQ: 399.65 MHz
 IRSST: 134500.00 Hz
 IRRPW: 46.0 usec
 IRATN: 511
 IRANS: 0
 IRBP1: 26
 IRBP2: 6
 BF: 2.00 Hz
 T1: 0.00 %
 T2: 0.00 %
 T3: 90.00 %
 T4: 100.00 %
 XE: 177.77 Hz
 XS: -12183.33 Hz
 REFVL: 0.00 ppm
 OFILE: ALPHA
 MENUF: A31P
 SHMFL: TH5AT
 LKSET: 61679.1 Hz
 LKLEV: 220
 LGAIN: 22
 LKPHS: 60.47 deg
 LKSTG: 128
 CTEMP: 20.8 c
 CSPED: 14 Hz
 FIELD: 1975

3-MAR-2006 20:03:50.50
 EXMOD : SINGL
 IRMOD : BCM
 OBNUC : 31P
 DBFRQ : 161.70 MHz
 DBSET : 147648.51 Hz
 PW1 : 10.40 usec
 POINT : 32768
 SAMPO : 32768
 TIMES : 128
 SCANS : 65
 DUMMY : 2
 FREQU : 1108.16 Hz
 FILTR : 550 Hz
 ACQTM : 29.5698 sec
 DEADT : 540.25 usec
 DELAY : 363.64 usec
 PD : 2.6625 sec
 ADBIT : 16
 RGAIN : 23
 IRNUC : 1H
 IRFRQ : 399.65 MHz
 IRSET : 134500.00 Hz
 IRRPW : 46.0 usec
 IRATN : 511
 IRRNS : 0
 IRBP1 : 26
 IRBP2 : 6
 BF : 2.00 Hz
 T1 : 0.00 %
 T2 : 0.00 %
 T3 : 90.00 %
 T4 : 100.00 %
 XE : 1108.16 Hz
 XS : 0.00 Hz
 REFVL : 78.85 ppm
 DFILE : ALPHA
 MENUF : A31P
 SHMFL : TH5AT
 LKSET : 61679.1 Hz
 LKLEV : 220
 LGAIN : 22
 LKPHS : 60.47 deg
 LKSG : 666
 CTEMP : 21.0 c
 CSPED : 14 Hz
 FIELD : 1968

3-MAR-2006 20:04:07.75
 EXMOD : SINGL
 IRMOD : BCM
 OBNUC : 31P
 DBFRQ : 161.70 MHz
 DBSET : 147648.51 Hz
 PW1 : 10.40 usec
 POINT : 32768
 SAMPO : 32768
 TIMES : 128
 SCANS : 65
 DUMMY : 2
 FREQU : 1108.16 Hz
 FILTR : 550 Hz
 ACQTM : 29.5698 sec
 DEADT : 540.25 usec
 DELAY : 363.64 usec
 PD : 2.6625 sec
 ADBIT : 16
 RGAIN : 23
 IRNUC : 1H
 IRFRQ : 399.65 MHz
 IRSET : 134500.00 Hz
 IRRPW : 46.0 usec
 IRATN : 511
 IRRNS : 0
 IRBP1 : 26
 IRBP2 : 6
 BF : 2.00 Hz
 T1 : 0.00 %
 T2 : 0.00 %
 T3 : 90.00 %
 T4 : 100.00 %
 XE : 90.40 Hz
 XS : 2.99 Hz
 REFVL : 78.85 ppm
 DFILE : ALPHA
 MENUF : A31P
 SHMFL : TH5AT
 LKSET : 61679.1 Hz
 LKLEV : 220
 LGAIN : 22
 LKPHS : 60.47 deg
 LKSG : 666
 CTEMP : 21.0 c
 CSPED : 14 Hz
 FIELD : 1968

2-JUL-2004 15:55:44.48
 EXMOD: SINGL
 IRMOD: BCM
 OBNUC: 31P
 OBFRQ: 161.70 MHz
 OBSET: 147642.58 Hz
 PW1: 10.40 usec
 POINT: 32768
 SAMPO: 32768
 TIMES: 128
 SCANS: 10
 DUMMY: 2
 FREQU: 1134.82 Hz
 FILTR: 550 Hz
 ACQTM: 28.8752 sec
 DEADT: 540.25 usec
 DELAY: 363.64 usec
 PD: 2.6625 sec
 ADBIT: 16
 RGAIN: 23
 IRNUC: 1H
 IRFRQ: 399.65 MHz
 IRSET: 134500.00 Hz
 IRRPW: 46.0 usec
 IRATN: 511
 IRRNS: 0
 IRBP1: 26
 IRBP2: 6
 BF: 2.00 Hz
 T1: 0.00 %
 T2: 0.00 %
 T3: 90.00 %
 T4: 100.00 %
 XE: 1134.82 Hz
 XS: 0.00 Hz
 REFVL: 78.85 ppm
 DFILE: ALPHA
 MENUF: A31P
 SHMFL: TH5AT
 LKSET: 61679.1 Hz
 LKLEV: 220
 LGAIN: 21
 LKPHS: 60.47 deg
 LKSG: 666
 CTEMP: 22.0 c
 CSPED: 13 Hz
 FIELD: 721

2-JUL-2004 15:55:57.70
 EXMOD: SINGL
 IRMOD: BCM
 OBNUC: 31P
 OBFRQ: 161.70 MHz
 OBSET: 147642.58 Hz
 PW1: 10.40 usec
 POINT: 32768
 SAMPO: 32768
 TIMES: 128
 SCANS: 10
 DUMMY: 2
 FREQU: 1134.82 Hz
 FILTR: 550 Hz
 ACQTM: 28.8752 sec
 DEADT: 540.25 usec
 DELAY: 363.64 usec
 PD: 2.6625 sec
 ADBIT: 16
 RGAIN: 23
 IRNUC: 1H
 IRFRQ: 399.65 MHz
 IRSET: 134500.00 Hz
 IRRPW: 46.0 usec
 IRATN: 511
 IRRNS: 0
 IRBP1: 26
 IRBP2: 6
 BF: 2.00 Hz
 T1: 0.00 %
 T2: 0.00 %
 T3: 90.00 %
 T4: 100.00 %
 XE: 40.14 Hz
 XS: 0.50 Hz
 REFVL: 78.85 ppm
 DFILE: ALPHA
 MENUF: A31P
 SHMFL: TH5AT
 LKSET: 61679.1 Hz
 LKLEV: 220
 LGAIN: 21
 LKPHS: 60.47 deg
 LKSG: 666
 CTEMP: 22.0 c
 CSPED: 13 Hz
 FIELD: 721

3-MAR-2006 12:16:21.37
 EXMOD: SINGL
 IRMOD: BCM
 OBNUC: 31P
 OBFRO: 161.70 MHz
 OBSET: 135320.00 Hz
 PW1: 10.40 usec
 POINT: 32768
 SAMPO: 32768
 TIMES: 128
 SCANS: 100
 DUMMY: 2
 FREQU: 97087.38 Hz
 FILTR: 48550 Hz
 ACQTM: 0.3375 sec
 DEADT: 10.00 usec
 DELAY: 4.12 usec
 PD: 2.6625 sec
 ADBIT: 16
 RGAIN: 23
 IRNUC: 1H
 IRFRO: 399.65 MHz
 IRSET: 134500.00 Hz
 IRRPW: 46.0 usec
 IRATN: 511
 IRRNS: 0
 IRBP1: 26
 IRBP2: 6
 BF: 2.00 Hz
 T1: 0.00 %
 T2: 0.00 %
 T3: 90.00 %
 T4: 100.00 %
 XE: 1158.48 Hz
 XS: -12152.22 Hz
 REFVL: 0.00 ppm
 DFILE: ALPHA
 MENUP: A31P
 SHWFL: TH5AT
 LKSET: 61679.1 Hz
 LKLEV: 220
 LGAIN: 23
 LKPHS: 60.47 deg
 LKSIG: 666
 CTEMP: 21.3 c
 CSPED: 9 Hz
 FIELD: 1964

3-MAR-2006 12:16:55.37
 EXMOD: SINGL
 IRMOD: BCM
 OBNUC: 31P
 OBFRO: 161.70 MHz
 OBSET: 135320.00 Hz
 PW1: 10.40 usec
 POINT: 32768
 SAMPO: 32768
 TIMES: 128
 SCANS: 100
 DUMMY: 2
 FREQU: 97087.38 Hz
 FILTR: 48550 Hz
 ACQTM: 0.3375 sec
 DEADT: 10.00 usec
 DELAY: 4.12 usec
 PD: 2.6625 sec
 ADBIT: 16
 RGAIN: 23
 IRNUC: 1H
 IRFRO: 399.65 MHz
 IRSET: 134500.00 Hz
 IRRPW: 46.0 usec
 IRATN: 511
 IRRNS: 0
 IRBP1: 26
 IRBP2: 6
 BF: 2.00 Hz
 T1: 0.00 %
 T2: 0.00 %
 T3: 90.00 %
 T4: 100.00 %
 XE: 168.88 Hz
 XS: -12167.03 Hz
 REFVL: 0.00 ppm
 DFILE: ALPHA
 MENUP: A31P
 SHWFL: TH5AT
 LKSET: 61679.1 Hz
 LKLEV: 220
 LGAIN: 23
 LKPHS: 60.47 deg
 LKSIG: 666
 CTEMP: 21.3 c
 CSPED: 9 Hz
 FIELD: 1964

3-MAR-2006 18:27:32.78
 EXMOD: SINGL
 IRMOD: BCM
 OBNUC: 31P
 OBFHQ: 161.70 MHz
 OBSET: 135320.00 Hz
 PW1: 10.40 usec
 POINT: 32768
 SAMPO: 32768
 TIMES: 128
 SCANS: 100
 DUMMY: 2
 FREQ: 97087.38 Hz
 FILTR: 48550 Hz
 ACQTM: 0.3375 sec
 DEADT: 10.00 usec
 DELAY: 4.12 usec
 PD: 2.6625 sec
 ADBIT: 16
 RGAIN: 23
 IRNUC: 1H
 IRFRQ: 399.65 MHz
 IRSET: 134500.00 Hz
 IRRPW: 46.0 usec
 IRATN: 511
 IRRNS: 0
 IRBP1: 26
 IRBP2: 6
 BF: 2.00 Hz
 T1: 0.00 %
 T2: 0.00 %
 T3: 90.00 %
 T4: 100.00 %
 XE: 1158.46 Hz
 XS: -12294.44 Hz
 REFVL: 0.00 ppm
 DFILE: ALPHA
 MENUF: A31P
 SHMFL: TH5AT
 LKSET: 61679.1 Hz
 LKLEV: 220
 LGAIN: 22
 LKPHS: 60.47 deg
 LKSIG: 128
 CTEMP: 20.8 c
 CSPED: 14 Hz
 FIELD: 1975

3-MAR-2006 18:27:45.95
 EXMOD: SINGL
 IRMOD: BCM
 OBNUC: 31P
 OBFHQ: 161.70 MHz
 OBSET: 135320.00 Hz
 PW1: 10.40 usec
 POINT: 32768
 SAMPO: 32768
 TIMES: 128
 SCANS: 100
 DUMMY: 2
 FREQ: 97087.38 Hz
 FILTR: 48550 Hz
 ACQTM: 0.3375 sec
 DEADT: 10.00 usec
 DELAY: 4.12 usec
 PD: 2.6625 sec
 ADBIT: 16
 RGAIN: 23
 IRNUC: 1H
 IRFRQ: 399.65 MHz
 IRSET: 134500.00 Hz
 IRRPW: 46.0 usec
 IRATN: 511
 IRRNS: 0
 IRBP1: 26
 IRBP2: 6
 BF: 2.00 Hz
 T1: 0.00 %
 T2: 0.00 %
 T3: 90.00 %
 T4: 100.00 %
 XE: 174.81 Hz
 XS: -12306.29 Hz
 REFVL: 0.00 ppm
 DFILE: ALPHA
 MENUF: A31P
 SHMFL: TH5AT
 LKSET: 61679.1 Hz
 LKLEV: 220
 LGAIN: 22
 LKPHS: 60.47 deg
 LKSIG: 128
 CTEMP: 20.8 c
 CSPED: 14 Hz
 FIELD: 1975