Supplementary Information

Anti-Markovnikov Hydrophosphoroselenoylation of Alkenes Using Phosphorodiselenoic Acid Esters Leading to the Formation of Phosphonoselenoic Acid Esters.

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**Preparation of the starting materials**

**Synthesis of (Sax)-Binaphthylphosphoroselenoic acid derivatives**

\[
\text{Se} + \text{PhMgBr} \quad \text{THF, 0 ºC, 20 min} \quad \xrightarrow{\text{THF, conditions}} \quad \text{R} \quad \text{O} \quad \text{Se} \quad \text{Cl}
\]

(Sax)-4-Phenylseleno-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (2c)

To a THF suspension (20 mL) of elemental selenium (869 mg, 11 mmol) was added PhMgBr (0.98 THF solution, 11.2 mL, 11 mmol) at 0 ºC, and the mixture was stirred at that temperature for 10 min. This solution was added to a THF solution (30 mL) of (Sax)-4-Chloro-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (4.297 g, 10 mmol) via cannula at -90 ºC (acetone / liq N\(_2\)), and stirred at that temperature for 1 h. The flask was taken into the ice bath, and stirred for 15 min. Then, the reaction was quenched with addition of water, and ether was added to dilute the solution. The organic layer was washed with water three times, and the resulting aqueous phase was extracted with ether three times. The combined organic layer was dried over MgSO\(_4\), filtered, and concentrated. Purification by column chromatography on silica gel (CH\(_2\)Cl\(_2\) : hexane = 1 : 2, Rf = 0.3) gave 2c (4.443 g, 81%) as a white powder. mp: 171-172 ºC; IR (KBr): 1587, 1507, 1438, 1322, 1216, 1193, 1154, 1068, 1019, 999, 976, 949, 841, 771, 749, 694, 648, 607, 576, 561, 541, 518, 484, 464, 448, 418, 403 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.20-7.38 (m, 7H, Ar), 7.45-7.53 (m, 3H, Ar), 7.61-7.67 (m, 3H, Ar), 7.92-7.98 (m, 3H, Ar), 8.03 (d, \(J = 8.8\) Hz, 1H, Ar); \(^13\)C NMR (CDCl\(_3\)): \(\delta\) 121.3, 121.4, 121.7, 122.7, 125.8, 125.9, 126.0, 127.0, 127.2, 128.4, 128.6, 129.5, 129.6, 130.7, 130.9, 131.8, 132.0, 132.4, 132.5, 136.8, 147.0, 147.1, 148.4, 148.6 (Ar); \(^31\)P NMR (CDCl\(_3\)): \(\delta\) 97.5 (\(\text{J}_{P\text{-Se}} = 963.7\text{ Hz}, 524.7\text{ Hz}\)); \(^77\)Se NMR (CDCl\(_3\)): \(\delta\) -36.3 (\(\text{J}_{P\text{-Se}} = 963.7\text{ Hz}\)) 492.3 (\(\text{J}_{P\text{-Se}} = 524.7\text{ Hz}\)), MS (EI) m/z 550 (M\(^+\)); HRMS Calcd for C\(_{216}\)H\(_{179}\)O\(_2\)PSe\(_2\): 551.9291, Found: 551.9289.

(Sax)-2,6-Diphenyl-4-phenylseleno-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (2d)

To a THF suspension (24 mL) of elemental selenium (285 mg, 3.6 mmol) was added PhMgBr (1.1 M THF solution, 3.27 mL, 3.6 mmol) at 0 ºC, and the mixture was stirred at that temperature for 20 min. This solution was added to a THF solution (36 mL) of (Sax)-4-Chloro-2,6-diphenyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (1.404 g, 2.4 mmol) via cannula at -90 ºC (acetone / liq N\(_2\)), and stirred at that temperature for 1 h. The flask was taken into the ice bath, and stirred for 15 min. Then, the reaction was quenched with addition of water, and ether was added to dilute the solution. The organic layer was washed with water three times, and the resulting aqueous phase was extracted with ether three times. The combined organic layer was dried over MgSO\(_4\), filtered, and concentrated. Purification by column chromatography on silica gel (CH\(_2\)Cl\(_2\) : hexane = 1 : 2, Rf = 0.38) gave 2d (1.104 g, 65%) as a white powder. mp: 231-235 ºC; IR (KBr): 3058, 1594,
1577, 1498, 1474, 1452, 1439, 1402, 1243, 1187, 1148, 1132, 1075, 986, 958, 893, 881, 856, 824, 778, 765, 745, 721, 708, 696, 672, 646, 616, 606, 578, 567, 547, 523, 509 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 6.65-6.67 (m, 2H, Ar), 7.01 (t, \(J = 7.8\) Hz, 2H, Ar), 7.18-7.22 (m, 1H, Ar), 7.29-7.57 (m, 12H, Ar), 7.65-7.68 (m, 2H, Ar), 7.82-7.84 (m, 2H, Ar), 7.98 (d, \(J = 8.3\) Hz, 1H, Ar), 8.02 (d, \(J = 8.3\) Hz, 1H, Ar), 8.08 (s, 1H, Ar), 8.13 (s, 1H, Ar); \(^13\)C NMR (CDCl\(_3\)): \(\delta\) 124.0, 124.3, 126.1, 126.2, 126.5, 126.6, 126.9, 127.1, 127.5, 127.8, 128.0, 128.5, 128.8, 129.1, 130.2, 130.4, 131.2, 131.3, 131.7, 131.9, 132.2, 133.9, 134.7, 136.6, 137.4, 144.8, 145.0, 145.8, 146.0 (Ar); \(^31\)P NMR (CDCl\(_3\)): \(\delta\) 96.1 \((\cdot J\_P\_Se = 974.0\) Hz, 512.2 Hz); \(^77\)Se NMR (CDCl\(_3\)): \(\delta\) -33.4 \((\cdot J\_P\_Se = 976.0\) Hz, 512.0 \((\cdot J\_P\_Se = 512.4\) Hz), MS (El) m/z 704 (M\(^+\)); HRMS Calcd for C\(_{38}\)H\(_{32}\)O\(_2\)PSe: 703.9923, Found: 703.9912.

\((S\_ax)\)\(\text{-}4\) Phenylseleno-2,6-bis(trisopropylsilyl)dinaphtho[2,1-\(d\):1',2'-\(f\)]1,3,2\)dioxaphosphepine-4-selenide (2e)

To a THF suspension (30 mL) of elemental selenium (237 mg, 3 mmol) was added PhMgBr (1.1 M THF solution, 2.73 mL, 3 mmol) at 0 \(^\circ\)C, and the mixture was stirred at that temperature for 20 min. This solution was added to a THF solution (20 mL) of \((S\_ax)\)\(\text{-}4\) Chloro-2,6-bis(trisopropylsilyl)naphtho[2,1-\(d\):1',2'-\(f\)]1,3,2\)dioxaphosphepine-4-selenide (1.484 g, 2 mmol) via cannula at -90 \(^\circ\)C (acetone / liq N\(_2\)), and stirred at room temperature for 20 min. After that, the mixture was stirred at 73 \(^\circ\)C for 3 h. The flask was taken into the ice bath, and stirred for 15 min. Then, the reaction was quenched with addition of water, and AcOEt was added to dilute the solution. The organic layer was washed with water three times, and the resulting aqueous phase was extracted with ether three times. The combined organic layer was dried over MgSO\(_4\), filtered, and concentrated. Purification by column chromatography on silica gel (CH\(_2\)Cl\(_2\): hexane = 1 : 2, Rf = 0.63) gave 2e (0.995 g, 58%) as a white powder. mp: 143 \(^\circ\)C; IR (KBr): 3052, 2944, 2888, 2865, 1464, 1440, 1383, 1366, 1253, 1200, 1184, 1174, 1147, 1253, 1200, 1184, 1174, 1088, 1019, 1001, 967, 951, 880, 853, 751, 737, 688, 677, 641, 622, 607, 588, 547, 530 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.18-1.24 (m, 36 H, SiCH\(_3\)_3), 1.77-1.91 (m, 6H, SiCH\(_3\)_3), 6.63 (t, \(J = 7.8\) Hz, 2H, Ar), 6.68 (d, \(J = 8.8\) Hz, 2H, Ar), 6.72 (d, \(J = 8.3\) Hz, 2H, Ar), 6.78-6.82 (m, 1H, Ar), 7.00-7.03 (m, 2H,Ar), 7.09-7.14 (m, 2H, Ar), 7.37 (t, \(J = 7.3\) Hz, 1H, Ar), 7.42 (t, \(J = 7.3\) Hz, 1H, Ar), 7.86 (d, \(J = 8.3\) Hz, 2H, Ar), 8.08 (s, 1H, Ar), 8.11 (s, 1H, Ar); \(^13\)C NMR (CDCl\(_3\)): \(\delta\) 12.4, 12.8, 19.4, 19.6, 121.2, 122.1, 125.2, 125.4, 126.2, 126.6, 126.8, 127.4, 127.5, 127.9, 128.1, 128.2, 128.4, 128.6, 130.7, 131.0, 133.7, 134.0, 135.1, 138.8, 139.2, 151.6 (d, \(J = 15.7\) Hz), 152.8 (d, \(J = 15.7\) Hz); \(^31\)P NMR (CDCl\(_3\)): \(\delta\) 79.9 \((\cdot J\_P\_Se = 953.3\) Hz, 580.2 Hz); \(^77\)Se NMR (CDCl\(_3\)): \(\delta\) 18.8 \((\cdot J\_P\_Se = 951.6\) Hz), 503.4 \((\cdot J\_P\_Se = 579.5\) Hz); MS (El) m/z 864 (M\(^+\)).

\((S\_ax)\)\(\text{-}4\) Phenylseleno-dinaphtho[2,1-\(d\):1',2'-\(f\)]1,3,2\)dioxaphosphepine 4-sulfide (2b)

To a 10 mL two-necked flask were added 2e (1.1 g, 2 mmol), THF (4.0 mL), tri-\(n\)-butylphosphine (0.6 mL, 2.4 mmol) under Ar atmosphere. The reaction mixture stirred for 30 min. After that, sulfur (320 mg, 10 mmol) was added to the mixture, and it was further stirred for 9 h. The mixture was concentrated. Purification by column
chromatography on silica gel (CH$_2$Cl$_2$: hexane = 1:2, Rf = 0.31) gave 2b (695 mg, 69%) as a white solid mp: 170-176 °C; IR (KBr): 3053, 1619, 1587, 1473, 1461, 1438, 1361, 1322, 1216, 1191, 1155, 1068, 976, 950, 841, 812, 739, 681, 652, 583, 566, 553, 526, 463, 423 cm$^{-1}$; $^1$H NMR (CDCl$_3$): δ 7.13-7.31 (m, 7H, Ar), 7.37-7.45 (m, 3H, Ar), 7.53 (dd, $J = 8.8$ Hz, 1.0 Hz, 1H, Ar), 7.58-7.61 (m, 2H, Ar), 7.84-7.96 (m, 4H); $^{13}$C NMR (CDCl$_3$): δ 121.3, 121.6, 122.4, 122.5, 122.5, 124.9, 125.0, 125.8, 125.9, 126.6, 126.7, 127.0, 127.2, 128.4, 128.5, 129.4, 130.7, 130.9, 131.7, 131.9, 132.4, 132.4, 132.4, 132.4, 136.6, 136.8, 146.7, 146.9, 148.0, 148.2; $^{31}$P NMR (CDCl$_3$): δ 98.1 ($^{1}$J$_{P-Se}$ = 524.3 Hz); $^{77}$Se NMR (CDCl$_3$): δ 447.2 ($^{1}$J$_{P-Se}$ = 524.3 Hz); MS (EI) m/z 504 (M$^+$); HRMS Calcd for C$_{26}$H$_{17}$O$_2$PSSe: 503.9852, Found: 503.9858.

(S$_{ax}$)-4-Phenylseleno-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide (2a)

To a 20 mL two-necked flask were added 2c (550 mg, 1 mmol), CH$_2$Cl$_2$ (2 mL) and hydrogen peroxide (30% aqueous solution, 0.31 mL, 3 mmol), and the mixture was stirred at room temperature for 6 h. After that, the mixture was concentrated. Purification by column chromatography on silica gel (CH$_2$Cl$_2$: MeOH = 10:1, Rf = 0.78). The resulting red orange residue was recrystallized from CH$_2$Cl$_2$ (0.5 mL) and hexane (5 mL) to give a yellow crystalline solid. The solid was purified by column chromatography on silica gel (CH$_2$Cl$_2$: hexane:EtOAc = 5:5:1, Rf = 0.35) to give 2a (131 mg, 27%) as a yellow solid. mp: 204-210 °C; IR (KBr): 3053, 1619, 1590, 1508, 1465, 1436, 1360, 1235, 1270, 1212, 1072, 1019, 982, 945, 822, 772, 755, 708, 694, 653, 600, 573, 526, 507, 463, 445, 418 cm$^{-1}$; $^1$H NMR (CDCl$_3$): δ 7.18-7.36 (m, 7H, Ar), 7.45-7.52 (m, 3H, Ar), 7.59-7.67 (m, 1H, Ar), 7.67-7.69 (m, 2H, Ar), 7.93-8.03 (m, 4H, Ar); $^{13}$C NMR (CDCl$_3$): δ 20.9, 120.9, 121.0, 121.0, 121.5, 121.6, 121.6, 121.9, 122.0, 125.8, 125.9, 126.7, 127.1, 127.7, 128.4, 128.5, 129.2, 129.5, 129.5, 131.0, 131.4, 131.6, 131.7, 131.8, 132.2, 132.3, 136.0, 136.1, 146.6, 146.7, 146.8, 146.9; $^{31}$P NMR (CDCl$_3$): δ 26.9 ($^{1}$J$_{P-Se}$ = 552.9 Hz); $^{77}$Se NMR (CDCl$_3$): δ 295.4 ($^{1}$J$_{P-Se}$ = 552.9 Hz); MS (EI) m/z 488 (M$^+$); HRMS Calcd for C$_{26}$H$_{17}$O$_3$PS$_2$: 488.0081, Found: 488.0066.

• General procedure for Hydrophosphoroselenoylation of alkenes

Procedure A:

To a two-necked flask were added (S$_{ax}$)-binaphthylphosphorodiselenoic acid phenyl ester (1.0 equiv), AIBN (0.125 equiv), toluene, and alkene (1.2 – 20 equiv) under Ar atmosphere. The mixture was warmed up to 80 °C, and tri-n-butyltin hydride (1.5 equiv) in toluene was added slowly over 20 min via syringe pomp. The reaction mixture was stirred for 3 h. After that, the mixture was cooled to room temperature, and concentrated. The crude product was purified by column chromatography on silica gel to give desired products.

Procedure B:

To a two-necked flask were added (S$_{ax}$)-binaphthylphosphorodiselenoic acid phenyl ester (1.0 equiv), AIBN
(0.125 equiv), toluene, and alkene (1.2 ~ 5.0 equiv) under Ar atmosphere. The mixture was warmed up to 80 °C, and tri-n-butyltin hydride (1.5 equiv) in toluene was added slowly over 20 min via syringe pomp. The reaction mixture was stirred for 1 h. After that, AIBN was added to the mixture, and it was further stirred for 3 h in twice. The mixture was cooled to room temperature, and concentrated. The crude product was purified by column chromatography on silica gel to give desired products.

\((S,S)-4-(2-Phenylethyl)-dinaphtho[2,1-d:1’,2’-f][1,3,2]dioxaphophen-4-selenide (5cb)\)

The following compound was synthesized via Procedure A, with 2c (8.25 g, 15 mmol), styrene (4b) (2.07 mL, 18 mmol). Purification by column chromatography on silica gel (CH\(_2\)Cl\(_2\) : hexane = 4 : 7, Rf = 0.30) gave 5cb (6.14 g, 82%) as a white solid.

\([\alpha]_D^{28} = +350.5 (c = 1.003, \text{CHCl}_3); \text{mp: } 71-77 ^\circ\text{C}; \text{IR (KBr): } 3058, 3024, 2903, 2860, 1588, 1506, 1461, 1432, 1390, 1361, 1319, 1224, 1191, 1156, 1142, 1069, 979, 952, 865, 840, 816, 750, 720, 697, 599, 568 \text{ cm}^{-1}; ^1\text{H} \text{NMR (CDCl}_3\text{): } \delta 2.55 (m, 2H, PCH}_2\text{CH}_2), 3.12 (m, 1H, PCH}_2\text{H}, 7.49 (m, 2H, Ar), 7.59 (dd, J = 8.3 Hz, 1H, Ar), 7.95 (dd, J = 8.3 Hz, 2H, Ar); ^13\text{C} \text{NMR (CDCl}_3\text{): } \delta 29.4 (PCH}_2\text{CH}_2), 36.2 (d, J_{C-P} = 77.7 \text{ Hz, PCH}_2\text{CH}_2), 120.2, 120.3, 121.8, 122.5, 122.7, 122.8, 125.7, 125.9, 126.6, 126.7, 126.9, 127.3, 128.5, 128.6, 128.7, 130.8, 131.0, 131.1, 132.0, 132.6, 132.7, 139.7, 139.9, 146.0, 146.1, 148.1, 148.2, (Ar); ^31\text{P} \text{NMR (CDCl}_3\text{): } \delta 123.5 (J_{P,S} = 923.0 \text{ Hz}); ^7\text{Se} \text{ NMR (CDCl}_3\text{): } \delta -238.9 (J_{P,S} = 923.0 \text{ Hz}); MS (EI) m/z 500 (M\(^+\)); HRMS Caled for C\(_{28}\)H\(_21\)O\(_2\)PSe: 500.0444, Found: 500.0443; Anal. Caled for C\(_{28}\)H\(_21\)O\(_2\)PSe (499.3989): C, 67.34; H, 4.24, Found: C, 67.12; H, 4.41.

\((S,S)-4-(2-Ethoxycarbonylthethyl)-dinaphtho[2,1-d:1’,2’-f][1,3,2]dioxaphophen-4-selenide (5cc)\)

The following compound was synthesized via Procedure B, with 2c (276.9 mg, 0.5 mmol), ethyl acrylate (4c) (0.27 mL, 2.5 mmol). Purification by column chromatography on silica gel (CH\(_2\)Cl\(_2\) : hexane = 1 : 2, Rf = 0.20) gave a white solid. Further purification was performed by GPC to give 5cc (58 mg, 24%) as a white solid.

\([\alpha]_D^{27} = +380 (c = 0.475, \text{CHCl}_3); \text{mp: } 71-77 ^\circ\text{C}; \text{IR (KBr): } 3051, 2976, 2928, 1734, 1588, 1507, 1462, 1372, 1322, 1221, 1068, 979, cm\(^{-1}\); ^1\text{H} \text{NMR (CDCl}_3\text{): } \delta 1.18 (m, 3H, CH\(_2\)CH\(_3\)), 2.52 (m, 2H, PCH\(_2\)CH\(_2\)), 2.69-2.92 (m, 2H, PCH\(_2\)CH\(_2\)), 4.08 (m, 2H, CH\(_2\)CH\(_3\)), 7.17-7.32 (m, 4H, Ar), 7.38-7.49 (m, 4H, Ar), 7.87 (d, J = 8.3 Hz, 2H, Ar), 7.95 (dd, J = 8.8 Hz, 3.4 Hz, 2H, Ar); ^13\text{C} \text{NMR (CDCl}_3\text{): } \delta 14.2 (\text{CH}_2\text{CH}_3), 28.4 (PCH}_2\text{CH}_2), 29.6 (d, J_{C-P} = 85.2 \text{ Hz, PCH}_2\text{CH}_2), 61.2 (\text{CH}_2\text{CH}_3), 120.3, 121.7, 122.4, 122.7, 125.8, 125.9, 126.6, 127.0, 127.2, 128.5, 128.6, 130.8, 131.3, 131.7, 132.0, 132.6, 145.9, 146.0, 148.0, 148.1, 171.2, 171.4 (Ar); ^31\text{P} \text{NMR (CDCl}_3\text{): } \delta 122.3 (J_{P,S} = 926.9 \text{ Hz}); ^7\text{Se} \text{ NMR (CDCl}_3\text{): } \delta -239.8 (J_{P,S} = 926.9 \text{ Hz}); MS (EI) m/z 496 (M\(^+\)); HRMS Caled for C\(_{28}\)H\(_21\)O\(_2\)PSe: 496.0337, Found: 496.0334.
The following compound was synthesized via Procedure A, with 2c (550 mg, 1 mmol), butyl vinyl ether (4d) (0.16 mL, 1.2 mmol). Purification by column chromatography on silica gel (CH2Cl2: hexane = 4:5, RF = 0.30) gave 5cd (273 mg, <55%) containing small amounts of unidentified products (13P NMR δ 120.9, 118.8, 118.2, 115.6, 114.8, 114.3 ppm, total 4%) as a pale yellow solid. 

[α]D27 = +378 (c = 1.27, CHCl3); mp: 55-62 °C; IR (KBr): 3058, 3023, 3002, 2962, 2925, 2869, 1619, 1588, 1507, 1462, 1432, 1361, 1322, 1222, 1192, 1155, 1111, 1068, 978, 945, 837, 813, 739, 696, 651, 603, 569 cm⁻¹; 1H NMR (CDCl3): δ 0.87 (t, J = 7.3 Hz, 3H, OCH2CH2CH2CH3), 1.35 (m, 2H, OCH2CH2CH2CH3), 1.50-1.57 (m, 2H, OCH2CH2CH2CH3), 2.37 (m, 1H, PCH2CH2), 2.55 (m, 1H, PCH2CH2), 3.44 (m, 2H, OCH2CH2CH2CH3), 3.84 (dd, J1P,CH = 24.4 Hz, 1H, PCH2CH2), 3.93 (m, 1H, PCH2CH2), 7.18-7.34 (m, 4H, Ar), 7.38-7.50 (m, 4H, Ar), 7.88 (d, J = 8.3 Hz, 2H, Ar), 7.94 (d, J = 8.8 Hz, 1H, Ar), 7.96 (d, J = 8.8 Hz, 1H, Ar); 13C NMR (CDCl3): δ 13.9 (OCH2CH2CH2CH3), 19.3 (OCH2CH2CH2CH3), 31.7 (OCH2CH2CH2CH3), 34.8 (d, J1C-P = 810.0 Hz, PCH2CH2), 64.8 (OCH2CH2CH2CH3), 71.3 (PCH2CH2), 120.9, 121.8, 122.6, 122.8, 125.7, 125.8, 126.6, 126.8, 127.0, 127.2, 128.4, 128.6, 130.7, 131.0, 131.7, 131.9, 132.6, 146.0, 146.1, 148.2, 148.4 (Ar); 31P NMR (CDCl3): δ +121.2 (J1P,Se = 922.6 Hz); 77Se NMR (CDCl3): δ -237.6 (J1P,Se = 922.6 Hz); MS (EI) m/z 496 (M⁺); HRMS Calc'd for C26H25O3PSe: 496.0707, Found: 496.0707.

The following compound was synthesized via Procedure A, with 2d (550 mg, 1 mmol), α-methylstyrene (4a) (0.16 mL, 1.2 mmol). Purification by column chromatography on silica gel (CH2Cl2: hexane = 1:2, RF = 0.23) gave 5ca (400 mg, 78%, dr = 50:50) as a white powder. Separation of a mixture of diastereomers was performed on a recycling preparative HPLC equipped with mightysil using CH2Cl2:CHCl3:hexane = 1:1 as eluent.

(Sax,R)-18a (dr: >99 : 1, The first fraction on HPLC): [α]D27 = +354 (c = 0.811, CHCl3); mp: 230-232 °C; IR (KBr): 3058, 3023, 3002, 2962, 2925, 2900, 1618, 1587, 1505, 1461, 1431, 1392, 1359, 1320, 1222, 1192, 1154, 1068, 978, 952, 913, 856, 842, 814, 773, 752, 700, 598, 564 cm⁻¹; 1H NMR (CDCl3): δ 1.40 (d, J = 7.3 Hz, 3H, CH3), 2.35 (dt, J = 14.9 Hz, 6.8 Hz, 1H, CH2), 2.49 (dt, J = 15.1 Hz, 6.8 Hz, 1H, CH2), 3.66 (m, 1H, CH), 6.42 (d, J = 8.8 Hz, 1H, Ar), 7.15-7.41 (m, 11H, Ar), 7.49 (d, J = 8.8 Hz 1H, Ar), 7.73 (d, J = 8.8 Hz, 1H, Ar), 7.82 (d, J = 8.3 Hz, 1H, Ar), 7.87 (d, J = 8.3 Hz 1H, Ar), 7.96 (d, J = 8.8 Hz 1H, Ar); 13C NMR (CDCl3): δ 22.7 (d, J1C-P = 10.8 Hz, CH3), 55.3 (CH), 43.1 (d, J1C-P = 76.1 Hz, CH2), 120.6, 121.9, 122.3, 122.4, 122.8, 125.7, 125.8, 126.5, 126.7, 126.9, 127.0, 127.3, 127.4, 128.3, 128.6, 128.8, 130.7, 131.6, 132.0, 132.6, 145.7, 145.8, 146.1, 146.2, 148.1, 148.2 (Ar); 31P NMR (CDCl3): δ 125.0 (J1P,Se = 921.6 Hz); 77Se NMR (CDCl3): δ -233.8 (J1P,Se = 921.6 Hz); MS (EI) m/z 514 (M⁺); HRMS Calc'd for C26H23O3PSe: 514.0595, Found: 514.0574.

(Sax, S)-18a (dr: 2 : 98, The second fraction on HPLC): [α]D27 = +375 (c = 0.567, CHCl3); mp: 100-103 °C; IR
The product **5ca** was also synthesized via Procedure A, with **1c** (430 mg, 1 mmol), α-methylstyrene (0.16 mL, 1.2 mmol), xylene (7 mL). Purification by column chromatography on silica gel gave **5ca** (390 mg, 76%) as a white powder.

(S<sub>ax</sub>)-(2-Phenylpropyl)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphophepin-4-oxide (5aa)

The following compound was synthesized via Procedure A, with **2a** (243 mg, 0.5 mmol), toluene (3.5 mL), α-methylstyrene (**4a**) (0.078 mL, 0.6 mmol) Purification by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub> : hexane : EtOAc = 5 : 5 : 1, Rf = 0.46) gave **5aa** (105 mg, <47%, dr: 54 : 46) containing small amounts of unidentified products (**1H NMR** δ 0.90 ~ 1.37) as a white solid. IR (KBr): 3060, 3028, 2965, 1620, 1590, 1508, 1464, 1433, 1402, 1361, 1326, 1281, 1226, 1156, 1071, 984, 962, 872, 844, 815, 748, 699, 656, 605, 569, 554, 530, 475; **1H NMR** (**CDCl<sub>3**): δ 1.51 (d, **J** = 7.3 Hz, 1H, CH<sub>3</sub>), 1.63 (d, **J** = 7.3 Hz, 1.5H, CH<sub>2</sub>), 2.16-2.36 (m, 2H, CH<sub>2</sub>), 3.46 (m, 0.5H, CH), 3.58 (m, 0.5H, CH), 6.74 (d, **J** = 8.8 Hz, 0.5H, Ar), 7.17-7.39 (m, 9.5H, Ar), 7.43-7.49 (m, 2H, Ar), 7.51 (dd, **J** = 8.8 Hz, 1.0 Hz, 0.5H, Ar), 7.58 (dd, **J** = 8.8 Hz, 1.0 Hz, 0.5H, Ar), 7.87 (d, **J** = 8.8 Hz, 0.5H, Ar), 7.90 (d, **J** = 8.3 Hz, 0.5H, Ar), 7.94 (d, **J** = 8.3 Hz, 1H, Ar), 7.95 (d, **J** = 8.3 Hz, 0.5H, Ar), 8.01 (d, **J** = 8.8 Hz, 1H, Ar), 8.02 (d, **J** = 8.8 Hz, 0.5H, Ar); **13C NMR** (**CDCl<sub>3**): δ 22.9 (d, **J** = 3.3 Hz, CH<sub>3</sub>), 23.0 (CH<sub>3</sub>), 32.0 (d, **J** = 70.3 Hz, CH<sub>2</sub>), 33.2 (d, **J** = 71.1 Hz, CH<sub>2</sub>), 34.1 (d, **J** = 2.5 Hz, CH), 34.4 (d, **J** = 2.5 Hz, CH), 120.0, 120.1, 121.1, 121.7, 121.8, 121.8, 121.8, 121.9, 125.6, 125.7, 125.8, 126.6, 126.6, 126.7, 126.7, 126.8, 126.9, 127.2, 127.2, 128.3, 128.4, 128.5, 128.6, 128.7, 130.9, 131.0, 131.0, 131.4, 131.4, 131.4, 131.5, 131.8, 132.3, 132.4, 132.5, 145.6, 145.7, 145.8, 145.9, 147.2, 147.3, 147.3, 147.3, 147.4; **31P NMR** (**CDCl<sub>3**): δ 41.3, 41.7; MS (EI) m/z 514 (M<sup>+</sup>); HRMS Calcd for C<sub>20</sub>H<sub>22</sub>O<sub>3</sub>P: 514.1538, Found: 514.1412.

(S<sub>ax</sub>)-(2-Phenylethyl)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphophepin-4-sulfide (5ba)

The following compound was synthesized via Procedure A, with **2b** (503 mg, 1 mmol), toluene (7 mL), α-methylstyrene (**4a**) (0.16 mL, 1.2 mmol) Purification by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub> : hexane = 1 : 3, Rf = 0.28) **5ba** (179 mg, 38%, dr = 59 : 41) containing small amounts of unidentified products (**1H NMR** δ...
0.84 ~ 1.37) as a white solid.

IR (KBr): 3058, 3023, 2965, 1619, 1588, 1507, 1461, 1396, 1361, 1322, 1220, 1155, 1069, 980, 959, 915, 862, 748, 698, 644, 567, 544, 526, 419 cm$^{-1}$; $^1$H NMR (CDCl$_3$): $\delta$ 1.48 (d, $J = 6.8$ Hz, 1.5H, CH$_3$), 1.63 (d, $J = 6.8$ Hz, 1.5H, CH$_3$), 2.30-2.54 (m, 2H, CH$_2$), 3.58 (m, 0.5H, CH), 3.67 (m, 0.5H, CH), 6.54 (d, $J = 8.3$ Hz, 0.5H, Ar), 7.16-7.40 (m, 9H, Ar), 7.40-7.51 (m, 3H, Ar), 7.56 (dd, $J = 8.8$ Hz, 1.0 Hz, 0.5H, Ar), 7.81 (d, $J = 8.8$ Hz, 0.5H, Ar), 7.89-8.05 (m, 3.5H, Ar); $^{13}$C NMR (CDCl$_3$): $\delta$ 22.8 (d, $J_{C,P} = 10.8$ Hz, CH$_2$), 23.0 (d, $J_{C,P} = 5.8$ Hz, CH$_3$), 35.0 (CH), 35.3 (CH), 38.7 (d, $J_{P,C} = 92.6$ Hz, CH$_2$), 40.5 (d, $J_{P,C} = 92.6$ Hz, CH$_2$), 120.4, 120.5, 121.8, 122.2, 122.4, 122.5, 122.5, 122.5, 122.6, 125.6, 125.7, 125.8, 126.5, 126.6, 126.7, 126.8, 126.8, 126.9, 126.9, 127.2, 127.3, 128.3, 128.4, 128.5, 128.7, 130.7, 131.0, 131.5, 131.9, 131.9, 132.5, 132.5, 132.5, 132.6, 145.6, 145.7, 145.8, 145.9, 146.0, 148.0, 148.1, 148.2; $^{31}$P NMR (CDCl$_3$): $\delta$ 117.1, 116.5; MS (EI) m/z 466 (M$^+$); HRMS Caled for C$_{26}$H$_{32}$O$_2$PSe: 514.0615, Found: 514.0588.

The product 5ba was also synthesized via Procedure A, with 1b (382 mg, 1 mmol), xylene (7 mL), $\alpha$-methylstyrene (4a) (0.16 mL, 1.2 mmol) at reflux temperature for 69 h. Purification by column chromatography on silica gel 5ba (179 mg, 46%, $\text{dr} = 50 : 50$) as a white powder. Separation of a mixture of diastereomers was performed on a recycling preparative HPLC equipped with mightysil using CH$_2$Cl$_2$ : hexane = 2 : 3 as eluent.

(d: 1 : 99, The first fraction on HPLC): $[\alpha]_D^{27} = +215$ (C = 0.094, CHCl$_3$); mp: 231-236 °C; IR (KBr): 3337, 3070, 3020, 2924, 2854, 1726, 1619, 1587, 1508, 1462, 1432, 1379, 1362, 1321, 1281, 1261, 1222, 1189, 1160, 1097, 1067, 1029, 1008, 977, 949, 898, 872, 851, 836, 823, 814, 773, 757, 735, 695, 653, 631, 602, 585, 568, 528, 509 cm$^{-1}$; $^1$H NMR (CDCl$_3$): $\delta$ 1.22 (dd, $J = 7.3$ Hz, 20.8 Hz, 3H, CH$_3$), 2.36-2.49 (m, 1H, CH), 2.67 (q, $J = 9.3$ Hz, 1H, CH$_2$), 3.22 (ddd, $J = 3.4$ Hz, 8.8 Hz, 13.7 Hz, 1H, CH$_2$), 7.04-7.06 (m, 2H, Ar), 7.10-7.36 (m, 8H, Ar), 7.39-7.46 (m, 2H, Ar), 7.51-7.54 (m, 1H, Ar), 7.88-7.92 (m, 3H, Ar), 7.98-8.00 (d, $J = 8.8$ Hz, 1H, Ar); $^{13}$C NMR (CDCl$_3$): $\delta$ 12.9 (CH$_3$), 36.5 (CH$_2$), 38.8 (d, $J_{C,P} = 76.0$ Hz, CH), 120.0, 120.0, 121.9, 122.3, 122.3, 122.8, 122.8, 125.7, 125.8, 126.5, 126.6, 126.8, 127.0, 127.4, 128.4, 128.6, 129.4, 130.7, 131.0, 131.5, 131.9, 132.6, 132.7, 137.6, 137.7, 146.2, 146.3, 148.4, 148.5 (Ar); $^{31}$P NMR (CDCl$_3$): $\delta$ 133.8 ($J_{P,Se} = 924.4$ Hz); $^{77}$Se NMR (CDCl$_3$): $\delta$ 299.6 ($J_{P,Se} = 927.7$ Hz); MS (EI) m/z 514 (M$^+$); HRMS Caled for C$_{26}$H$_{32}$O$_2$PSe: 514.0601, Found: 514.0588.

(d: 99 : 1, The second fraction on HPLC): $[\alpha]_D^{27} = +301$ (C = 0.115, CHCl$_3$); mp: 245-248°C; IR (KBr): 3430,
The product 5ce was also synthesized via Procedure B, with 2e (552.8 mg, 1 mmol), trans-β-methylstyrene (4e') (0.35 μL, 3 mmol). Purification by column chromatography on silica gel gave 5ce (46.9 mg, 51%, dr = 56 : 44) as a white powder.

4-(2-Methyl-3-(trimethylsilyl)propyl)dinaphth[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-selenide (5cf)

The following compound was synthesized via Procedure A, with 2e (164.8 mg, 0.3 mmol), (2-methylpropenyl)trimethylsilane (4f) (63 μL, 0.36 mmol). Purification by column chromatography on silica gel (CH₂Cl₂ : hexane = 1 : 3, Rf = 0.38) gave 5cf (85.6 mg, 55%, dr = 47 : 53) as a colorless solid. IR (KBr): 2925, 2893, 1588, 1507, 1462, 1322, 1248, 1222, 1198, 1155, 1070, 1011, 978, 952, 835, 814, 772, 749, 696, 651, 597, 566, 530, 503, 486, 436, 423, 407 cm⁻¹; ¹H NMR (CDCl₃): δ 0.02 (s, Si(CH₃)₃), 4.5H), 0.10 (s, Si(CH₃)₃), 4.5H), 0.89 (dd, J = 14.6 Hz, 4.9 Hz, 1H, CH₂SiMe₃), 1.08 (dd, J = 14.6 Hz, 4.4 Hz, 1H, CH₂SiMe₃), 1.13 (d, J = 6.8 Hz, 1H, CH₂SiMe₃), 1.31 (d, J = 6.8 Hz, 1H, CH₂SiMe₃), 2.16-2.38 (m, 2H), 2.49-2.57 (m, 1H), 7.28-7.36 (m, 3H, Ar), 7.41-7.54 (m, 4H, Ar), 7.57-7.61 (m, 1H, Ar), 7.98 (d, J = 8.3 Hz, 1H, Ar), 8.04 (d, J = 8.8 Hz, 1H, Ar), 8.06 (d, J = 8.8 Hz, 1H, Ar), 13C NMR (CDCl₃): δ 0.0 (Si(CH₂)₃), 0.1 (Si(CH₂)₃), 24.3 (d, J₁C-P = 10.8 Hz, CH₂CH), 24.9 (d, J₁C-P = 10.8 Hz, CH₂CH), 27.2, 27.3, 27.4, 27.5, 44.5 (d, J₁C-P = 74.4 Hz, CH₂CH), 45.3 (d, J₁C-P = 75.2 Hz, CH₂CH), 121.2, 121.3, 122.6, 123.3, 123.4, 126.2, 126.3, 126.4, 127.1, 127.4, 127.6, 127.9, 129.0, 129.2, 131.2, 131.3, 131.5, 132.2, 132.5, 133.2, 133.3, 146.7, 146.8, 146.9, 148.8, 149.0 (Ar); ³¹P NMR (CDCl₃): δ 125.6 (¹P,Se = 920.7 Hz), 125.7 (¹P,Se = 920.7 Hz); ⁷³Se NMR (CDCl₃): δ -229.6 (¹P,Se = 915.0 Hz), -227.7 (¹P,Se = 921.1 Hz); MS (EI) m/z 514 (M⁺); HRMS Calcd for C₂₃H₂₃O₂PSe: 514.0601; Found: 514.0588.

(Sₐ)-4-(3-Tetrahydropyran-1-yl)-dinaphth[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-selenide (5cg)

The following compound was synthesized via Procedure A, with 2c (550 mg, 1 mmol), 3,4-dihydro-2H-pyrene (4g) (1.81 mL, 20 mmol). Purification by column chromatography on silica gel (CH₂Cl₂ : hexane = 1 : 1, Rf = 0.39 for (Sₐ)₅cg, 0.31
for \((S_{\text{ex}}, S)-5\text{cg}\) gave \(5\text{cg}\) (294 mg, 61\%, \(d_r = 38 : 62\)) as a white powder. Separation of a mixture of diastereomers was performed on a recycling preparative HPLC equipped with mightysil using \(\text{CH}_2\text{Cl}_2\) as eluent.

\((S_{\text{ex}}, R)-5\text{cg}\) (\(d_r > 99 : 1\), The first fraction on HPLC): \([\alpha]_D^{26} = +367\) \((c = 1.03, \text{CHCl}_3)\); mp: 225-229 °C; IR (KBr): 3056, 2966, 2860, 1619, 1589, 1507, 1463, 1434, 1362, 1321, 1275, 1222, 1156, 1135, 1096, 1070, 1027, 978, 953, 888, 854, 819, 792, 754, 697, 655, 603, 580, 566 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.74 (m, 2H, \(\text{CHCH}_2\)\)), 2.10 (m, 1H, \(\text{CHCH}_2\text{CH}_2\)), 2.30 (br s, 1H, \(\text{CH}\)), 2.57 (m, 1H, \(\text{CHCH}_3\text{CH}_2\)), 3.44 (dt, \(J = 3.1\) Hz, 11.4 Hz, 1H, \(\text{CHCH}_2\text{OCH}_3\)), 3.67 (dt, \(J = 2.6\) Hz, 11.1 Hz, 1H, \(\text{CHCH}_2\text{OCH}_3\)), 3.92 (br d, \(J = 11.7\) Hz, 1H, \(\text{CHCH}_2\text{OCH}_3\)), 4.10 (br d, \(J = 11.2\) Hz, 1H, \(\text{CHCH}_2\text{OCH}_3\)), 7.26-7.56 (m, 8H, Ar), 7.96 (dd, \(J = 8.3\) Hz, 3.9 Hz, 2H, Ar), 8.03 (dd, \(J = 8.8\) Hz, 3.4 Hz, 2H, Ar); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 23.9 (\(\text{CHCH}_2\text{CH}_2\)), 25.0 (d, \(^{2}J_{\text{C-P}} = 14.9\) Hz, \(\text{CHCH}_2\text{CH}_2\)), 40.8 (d, \(^{1}J_{\text{C-P}} = 77.6\) Hz, \(\text{CH}\)), 67.1 (d, \(^{2}J_{\text{C-P}} = 5.8\) Hz, \(\text{CHCH}_2\text{OCH}_3\)), 68.0 (\(\text{CHCH}_2\text{OCH}_3\)), 119.9, 119.9, 121.8, 122.3, 122.4, 122.6, 122.7, 125.8, 126.0, 126.6, 126.9, 127.0, 127.3, 128.4, 128.6, 130.8, 131.2, 131.6, 132.0, 132.6, 132.7, 145.9, 146.0, 148.1, 148.3 (Ar); \(^{31}\)P NMR (CDCl\(_3\)): \(\delta\) 123.4 (\(^{1}J_{\text{P-Se}} = 926.8\) Hz); \(^{77}\)Se NMR (CDCl\(_3\)): \(\delta\) -262.6 (\(^{1}J_{\text{P-Se}} = 926.8\) Hz); MS (EI) m/z 480 (M\(^+\)); HRMS Calcd for C\(_{33}\)H\(_{27}\)O\(_3\)PSe: 480.0394, Found: 480.0395.

\((S_{\text{ex}}, S)-5\text{cg}\) (\(d_r > 1 : 99\), The second fraction on HPLC) \([\alpha]_D^{27} = +377\) \((c = 0.668, \text{CHCl}_3)\); mp: 125-133 °C; IR (KBr): 3056, 2955, 2851, 1619, 1589, 1508, 1463, 1433, 1362, 1322, 1272, 1222, 1156, 1132, 1099, 1069, 1028, 977, 948, 839, 813, 790, 749, 696, 653, 603, 580, 565 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.54-1.65 (m, 2H, \(\text{CHCH}_2\text{CH}_2\)), 1.92-2.05 (m, 1H, \(\text{CHCH}_2\text{CH}_2\)), 2.08 (br s, 1H, \(\text{CH}\)), 2.56 (m, 1H, \(\text{CHCH}_2\text{CH}_2\)), 3.47 (dt, \(J = 3.4\) Hz, 11.2 Hz, 1H, \(\text{CHCH}_2\text{OCH}_3\)), 3.78 (dt, \(J = 2.4\) Hz, 11.2 Hz, 1H, \(\text{CHCH}_2\text{OCH}_3\)), 3.94 (br d, \(J = 11.7\) Hz, 1H, \(\text{CHCH}_2\text{OCH}_3\)), 4.38 (br d, \(J = 11.2\) Hz, 1H, \(\text{CHCH}_2\text{OCH}_3\)), 7.26-7.55 (m, 8H, Ar), 7.97 (dd, \(J = 7.8\) Hz, 7.3 Hz, 2H, Ar), 8.03 (d, \(J = 8.8\) Hz, 2H, Ar); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 23.7 (d, \(^{3}J_{\text{C-P}} = 3.3\) Hz, \(\text{CHCH}_2\text{CH}_2\)), 24.9 (d, \(^{2}J_{\text{C-P}} = 13.2\) Hz, \(\text{CHCH}_2\text{CH}_2\)), 40.5 (d, \(^{1}J_{\text{C-P}} = 75.5\) Hz, \(\text{CH}\)), 67.2 (d, \(^{2}J_{\text{C-P}} = 9.9\) Hz, \(\text{CHCH}_2\text{OCH}_3\)), 68.1 (\(\text{CHCH}_2\text{OCH}_3\)), 120.2, 120.2, 121.9, 121.9, 122.2, 122.3, 122.7, 122.8, 125.8, 125.9, 126.6, 126.9, 127.3, 128.5, 128.6, 130.7, 131.3, 131.6, 132.0, 132.6, 145.5, 145.6, 148.2, 148.4 (Ar); \(^{31}\)P NMR (CDCl\(_3\)): \(\delta\) 121.9 (\(^{1}J_{\text{P-Se}} = 926.8\) Hz); \(^{77}\)Se NMR (CDCl\(_3\)): \(\delta\) -263.6 (\(^{1}J_{\text{P-Se}} = 926.8\) Hz); MS (EI) m/z 480 (M\(^+\)); HRMS Calcd for C\(_{33}\)H\(_{27}\)O\(_3\)PSe: 480.0394, Found: 480.0395.

\((S_{\text{ex}})-4-(1,2,3,4-Tetrahydroxynaphthalen-2-yl)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide\)

(5\text{ch})

The following compound was synthesized via Procedure B, with \(2\text{e}\) (429.7 mg, 0.77 mmol), 1,2-dihydronaphthalene (\(4\text{h}\)) (0.39 mL, 3 mmol). Purification by column chromatography on silica gel (\(\text{CH}_2\text{Cl}_2\) : hexane = 1 : 2, \(R_f = 0.43\)) gave \(5\text{ci}\) (250.6 mg, 62\%, \(d_r = 54 : 46\)) as a white powder. Separation of a mixture of diastereomers was performed on a recycling preparative HPLC equipped with mightysil using \(\text{CH}_2\text{Cl}_2\) : hexane = 2 : 3 as eluent.

\((d_r = 99 : 1, The first fraction on HPLC): \([\alpha]_D^{27} = +135\) \((C = 0.052, \text{CHCl}_3)\); mp: 219-221°C; IR (KBr): 3431,
2940, 1589, 1506, 1461, 1433, 1321, 1222, 1200, 1067, 1045, 978, 953, 925, 853, 840, 822, 811, 787, 743, 696, 654, 607, 565 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.93 (m, 1H, CH), 2.21 (m, 1H, CHCH\(_2\)CH\(_2\)), 2.50 (m, 1H, CHCH\(_2\)CH\(_2\)), 2.66 (m, 1H, CHCH\(_2\)CH\(_2\)), 2.83 (m, 1H, CHCH\(_2\)CH\(_2\)), 3.14 (m, 1H, CHCH\(_3\)), 3.35 (m, 1H, CHCH\(_3\)), 6.99 (d, \(J = 7.3\) Hz, 1H, Ar), 7.04-7.42 (m, 10H, Ar), 7.53 (d, \(J = 8.8\) Hz, 1H, Ar), 7.84-7.90 (m, 3H Ar), 7.98 (d, \(J = 8.8\) Hz, 1H, Ar); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 23.3 (CH\(_2\)CH\(_2\)CH\(_2\)), 28.0 (d, \(^2\)J\(_{C-P}\) = 15.7 Hz, CHCH\(_2\)C), 29.1 (CHCH\(_2\)CH\(_2\)), 38.3 (d, \(^1\)J\(_{C-P}\) = 81.9 Hz, CH), 120.1, 121.9, 122.4, 122.8, 125.7, 125.8, 126.1, 126.2, 126.6, 126.9, 126.9, 127.2, 128.4, 128.6, 129.0, 129.1, 130.8, 131.1, 131.5, 132.0, 132.6, 132.7, 133.5, 133.7, 135.3, 146.1, 146.2, 148.3, 148.4 (Ar); \(^{31}\)P NMR (CDCl\(_3\)): \(\delta\) 131.8 (\(^{1}\)J\(_{P-Se}\) = 923.6 Hz), \(^{77}\)Se NMR (CDCl\(_3\)): \(\delta\) -295.8 (\(^{1}\)J\(_{P-Se}\) = 927.7 Hz); MS (EI) m/z 526 (M\(^+\)); HRMS Calcd for C\(_{30}\)H\(_{29}\)O\(_2\)PSe: 526.0601, Found: 526.0588.

\((\text{S}_{\text{en}})\)-4-(2-Phenylcyclohexyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-selenide (5ei)

The following compound was synthesized via Procedure B, with 2c (550 mg, 1 mmol), 1-phenyl-1-cyclohexene (4i) (0.48 mL, 3 mmol). Purification by column chromatography on silica gel (AcOEt : hexane = 1 : 30, Rf = 0.25, 0.15) gave diastereomers of 5ei (89.9 mg, 17%, dr = 85 : 0 : 0 : 15, The first fraction on TLC), (229.3 mg, 41%, dr = 0 : 95 : 5 : 0, The second fraction on TLC) as a white powder. Separation of the first fraction on TLC was performed by GPC.

(dr = > 99 : 0 : 0 : 1): [\(\alpha\)]\(_D\)
\(^{20}\) = +336 (c = 0.4960, CHCl\(_3\)); mp: 98-100 °C; IR (KBr): 2926, 2853, 1589, 1507, 1462, 1322, 1223, 1198, 1156, 1322, 1227, 1198, 1156, 1070, 979, 951, 834, 812, 772, 750, 723, 696, 614, 600, 589, 565, 521 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.53-1.61 (m, 2H), 1.73-1.81 (m, 1H), 1.97-2.09 (m, 2H), 2.33-2.59 (m, 3H), 2.85 (ddt, \(J = 19.7, 8.1, 4.9\) Hz, 1H), 3.40 (ddt, \(J = 18.9, 6.7, 4.9\) Hz, 1H), 7.17-7.33 (m, 9H, Ar), 7.40-7.53 (m, 4H, Ar), 7.88-7.96 (m, 4H, Ar); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 22.6, 23.6 (d, \(^2\)J\(_{C-P}\) = 9.4 Hz), 24.6, 29.5 (d, \(^2\)J\(_{C-P}\) = 7.5 Hz), 41.8, 46.2 (d, \(^1\)J\(_{C-P}\) = 74.2 Hz, CH), 120.3, 120.4, 122.0, 122.2, 122.6, 125.4, 125.6, 126.3, 126.6, 126.8, 126.9, 127.4, 127.8, 128.3, 128.5, 129.9, 130.3, 130.6, 131.4, 131.8, 132.5, 132.6, 132.7, 142.5, 146.1, 146.2, 148.8, S11
148.9 (Ar); $^{31}$P NMR (CDCl$_3$): $\delta$ 120.4 ($^{1}J_{P,Se}$ = 917.7 Hz); $^{77}$Se NMR (CDCl$_3$): $\delta$ -273.1 ($^{1}J_{P,Se}$ = 915.0 Hz); MS (EI) m/z 554 (M$^+$); HRMS Calcd for C$_{32}$H$_{25}$O$_2$PSe: 554.0914, Found: 554.0909.

$(S_{a})$-2,6-Diphenyl-4-(2-phenylpropyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (5da)

The following compound was synthesized via Procedure B, with 2e (211 mg, 0.3 mmol), $\alpha$-methylstyrene (4a) (49 mg, 0.4 mmol). Purification by column chromatography on silica gel (CH$_2$Cl$_2$ : hexane = 1 : 2, Rf = 0.18) gave 5da (119 mg, 60%, dr = 56 : 44) as a white powder. IR (KBr): 3056, 3028, 2966, 2926, 1602, 1496, 1452, 1405, 1376, 1361, 1333, 1305, 1266, 1245, 1192, 1175, 1149, 1132, 1076, 1030, 1002, 988, 961, 895, 884, 862, 833, 820, 766, 750, 723, 698, 668, 646, 614, 605, 572, 560, 542, 513, 502 cm$^{-1}$; $^1$H NMR (CDCl$_3$): $\delta$ 1.63-1.69 (m, 0.5H), 2.11 (ddd, $J$ = 17.6 Hz, $J$ = 14.6 Hz, $J$ = 10.8 Hz, 0.5H), 2.29 (m, 0.5H), 2.87-2.97 (m, 1H), 6.76 (d, $J$ = 7.1 Hz, 1H, Ar), 6.83 (d, $J$ = 7.3 Hz, 1H, Ar), 7.11-7.18 (m, 3H, Ar), 7.28-7.60 (m, 15H, Ar), 7.66 (d, $J$ = 7.3 Hz, 1H, Ar), 7.97-8.01 (m, 2H, Ar), 8.06 (br s, 2H, Ar); $^{13}$C NMR (CDCl$_3$): $\delta$ 21.7 ($^{1}J_{C,P}$ = 4.1 Hz, CH$_3$), 23.4 ($^{1}J_{C,P}$ = 6.6 Hz, CH$_3$), 35.1 (CH), 35.3 (CH), 41.3 ($^{1}J_{C,P}$ = 75.2 Hz, CH$_2$), 43.1 ($^{1}J_{C,P}$ = 75.3 Hz, CH$_2$), 123.7, 123.8, 123.9, 124.1, 126.0, 126.1, 126.2, 126.3 126.4, 126.6, 126.7, 126.9, 127.0, 127.1, 127.4, 127.5, 127.8, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 128.6, 128.7, 128.9, 130.0, 130.2, 130.3, 130.4, 130.5, 130.8, 131.0, 131.1, 131.2, 131.6, 131.7, 131.8, 132.2, 133.5, 133.7, 135.0, 135.2, 136.6, 136.8, 137.6, 137.7, 143.7, 143.8, 143.9, 144.1, 145.7, 145.8, 146.6, 146.2 (Ar), $^{31}$P NMR (CDCl$_3$): $\delta$ 111.7 ($^{1}J_{P,Se}$ = 892.6 Hz), 121.2 ($^{1}J_{P,Se}$ = 929.6 Hz), $^{77}$Se NMR (CDCl$_3$): $\delta$ 235.9 ($^{1}J_{P,Se}$ = 933.3 Hz), 205.2 ($^{1}J_{P,Se}$ = 933.3 Hz); MS (EI) m/z 666 (M$^+$); HRMS Calcd for C$_{41}$H$_{31}$O$_2$PSe: 666.1227, Found: 666.1210.

$(S_{a})$-2,6-Diphenyl-4-(1-phenylp-2-propyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (5de)

The following compound was synthesized via Procedure B, with 2e (140.3 mg, 0.2 mmol), $cis$-$\beta$-methylstyrene (4e$^*$) (130 $\mu$L, 1 mmol). Purification by column chromatography on silica gel (CH$_2$Cl$_2$ : hexane = 1 : 2, Rf = 0.25) gave 5de (71.2 mg, 53%, dr = 66 : 34) as a white powder. IR (KBr): 3438, 3055, 3028, 2928, 2360, 2341,
The product 5de was also synthesized via Procedure B, with 2c (140.3 mg, 0.2 mmol), trans-β-methylstyrene (4e) (130 µL, 1 mmol). Purification by column chromatography on silica gel gave 5de (71.2 mg, 53%, dr = 66 : 34) as a white powder.

(Sα)-2,6-Diphenyl-4-(tetrahydrofuran-3-yl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (5dj)

The following compound was synthesized via Procedure B, with 2c (351.3 mg, 0.5 mmol), 2,5-dihydrofuran (4f') (1.5 mL, 40 equiv). Purification by column chromatography on silica gel (CH2Cl2 : hexane = 1 : 2, Rf = 0.25, 0.18) gave 5dj 152.7 mg, 49%, dr = 14 : 86) as a white powder. Separation of a mixture of diastereomers was performed on silica gel column chromatography using CH2Cl2 : hexane = 1 : 3 as eluent.

(dr = > 1 : 99, The first fraction on TLC): [α]D30 = +296 (c = 1.000, CHCl3); mp: 129-144 °C; IR (KBr): 3055, 2997, 2947, 2865, 1498, 1462, 1453, 1406, 1246, 1229, 1190, 1150, 1077, 988, 962, 917, 896, 884, 862, 831, 781, 767, 752, 724, 699, 678, 616, 512 cm⁻¹; ¹H NMR (CDCl3): δ 0.44-0.56 (m, 1H), 1.46-1.61 (m, 1H), 2.36-2.48 (m, 1H), 3.35-3.52 (m, 3H), 3.75-3.82 (m, 1H), 7.32-7.44 (m, 8H, Ar), 7.46 (m, 4H, Ar), 7.60-7.62 (m, 2H, Ar), 7.73-7.75 (m, 2H, Ar), 8.01 (d, J = 8.3 Hz, 2H, Ar), 8.11 (s, 2H, Ar); ¹³C NMR (CDCl3): δ 26.9 (d, J = 2.5 Hz, CHCH₂CH₂), 40.9 (d, J = 38.4 Hz, CH), 68.3 (d, J = 5.0 Hz), 68.5 (d, J = 9.9 Hz), 123.7, 124.9, 126.1, 126.2, 126.5, 126.8, 126.9, 127.1, 127.3, 127.4, 127.5, 127.7, 127.9, 128.2, 128.5, 128.6, 128.7, 130.1, 130.3, 130.9, 131.1, 131.7, 132.2, 132.3, 133.3, 134.9, 136.6, 137.3 (Ar), 143.6 (d, J = 9.9 Hz, Ar), 145.7 (d, J = 14.9 Hz, Ar); ³¹P NMR (CDCl3): δ 27.1 (Jp,se = 941.4 Hz); ⁷⁷Se NMR (CDCl3): δ -300.9 (Jp,se = 939.4 Hz); MS (EI) m/z 618 (M⁺); HRMS Calcd for C₃₁H₂₁O₃PSe: 618.0863, Found: 618.0844.

(dr => 99 : 1, The second fraction on TLC): [α]D29 = +292 (c = 0.474, CHCl3); mp: 173-183 °C; IR (KBr): 3055, 2925, 2867, 2360, 1498, 1452, 1406, 1246, 1192, 1150, 1078, 988, 962, 884, 862, 831, 766, 751, 723, 698 cm⁻¹; ¹H NMR (CDCl3): δ 1.68-1.88 (m, 2H), 2.31-2.47 (m, 2H), 3.19-3.28 (m, 1H), 3.48-3.53 (m, 1H), 3.56-3.62
The product 5dj was synthesized via Procedure B, with 2c (702.5 mg, 1.0 mmol), 2,3-dihydropyran (4j) (1.5 mL, 20 equiv). Purification by column chromatography on silica gel gave 5dj (411.5 mg, 67%, dr = 83 : 17) as a white powder.

\[(S,\alpha)-2,6-Diphenyl-4-(3-Tetrahydropyran-1-yl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (5dg)\]

The following compound was synthesized via Procedure B, with 2c (351.6 mg, 0.5 mmol), 3,4-dihydropyran (4d) (0.91 mL, 10 mmol). Purification by column chromatography on silica gel (CH\(_2\)Cl\(_2\) : hexane = 1 : 3, Rf =0.25, 0.15) gave each diastereomers 5dg (147.1 mg, 47%, dr = > 1 : 99 The first fraction on TLC), (31.6 mg, 10%, dr = > 99 : 1, The second fraction on TLC) as white powders.

\[(\alpha\)\(\beta\)\(\gamma\)\(\delta\)\(\epsilon\)\(\zeta\)\(\eta\)\(\theta\)\(\iota\)\(\kappa\)\(\lambda\)\(\mu\)\(\nu\)\(\xi\)\(\omicron\)\(\pi\)\(\rho\)\(\sigma\)\(\tau\)\(\upsilon\)\(\phi\)\(\chi\)\(\psi\)\(\omega\)\(\alpha\)\(\beta\)\(\gamma\)\(\delta\)\(\epsilon\)\(\zeta\)\(\eta\)\(\theta\)\(\iota\)\(\kappa\)\(\lambda\)\(\mu\)\(\nu\)\(\xi\)\(\omicron\)\(\pi\)\(\rho\)\(\sigma\)\(\tau\)\(\upsilon\)\(\phi\)\(\chi\)\(\psi\)\(\omega\)\(\alpha\)\(\beta\)\(\gamma\)\(\delta\)\(\epsilon\)\(\zeta\)\(\eta\)\(\theta\)\(\iota\)\(\kappa\)\(\lambda\)\(\mu\)\(\nu\)\(\xi\)\(\omicron\)\(\pi\)\(\rho\)\(\sigma\)\(\tau\)\(\upsilon\)\(\phi\)\(\chi\)\(\psi\)\(\omega\)\(\alpha\)\(\beta\)\(\gamma\)\(\delta\)\(\epsilon\)\(\zeta\)\(\eta\)\(\theta\)\(\iota\)\(\kappa\)\(\lambda\)\(\mu\)\(\nu\)\(\xi\)\(\omicron\)\(\pi\)\(\rho\)\(\sigma\)\(\tau\)\(\upsilon\)\(\phi\)\(\chi\)\(\psi\)\(\omega\)\(\alpha\)\(\beta\)\(\gamma\)\(\delta\)\(\epsilon\)\(\zeta\)\(\eta\)\(\theta\)\(\iota\)\(\kappa\)\(\lambda\)\(\mu\)\(\nu\)\(\xi\)\(\omicron\)\(\pi\)\(\rho\)\(\sigma\)\(\tau\)\(\upsilon\)\(\phi\)\(\chi\)\(\psi\)\(\omega\)\(\alpha\)\(\beta\)\(\gamma\)\(\delta\)\(\epsilon\)\(\zeta\)\(\eta\)\(\theta\)\(\iota\)\(\kappa\)\(\lambda\)\(\mu\)\(\nu\)\(\xi\)\(\omicron\)\(\pi\)\(\rho\)\(\sigma\)\(\tau\)\(\upsilon\)\(\phi\)\(\chi\)\(\psi\)\(\omega\)\(\alpha\)\(\beta\)\(\gamma\)\(\delta\)\(\epsilon\)\(\zeta\)\(\eta\)\(\theta\)\(\iota\)\(\kappa\)\(\lambda\)\(\mu\)\(\nu\)\(\xi\)\(\omicron\)\(\pi\)\(\rho\)\(\sigma\)\(\tau\)\(\upsilon\)\(\phi\)\(\chi\)\(\psi\)\(\omega\)\(\alpha\)\(\beta\)\(\gamma\)\(\delta\)\(\epsilon\)\(\zeta\)\(\eta\)\(\theta\)\(\iota\)\(\kappa\)\(\lambda\)\(\mu\)\(\nu\)\(\xi\)\(\omicron\)\(\pi\)\(\rho\)\(\sigma\)\(\tau\)\(\upsilon\)\(\phi\)\(\chi\)\(\psi\)\(\omega\)\(\alpha\)\(\beta\)\(\gamma\)\(\delta\)\(\epsilon\)\(\zeta\)\(\eta\)\(\theta\)\(\iota\)\(\kappa\)\(\lambda\)\(\mu\)\(\nu\)\(\xi\)\(\omicron\)\(\pi\)\(\rho\)\(\sigma\)\(\tau\)\(\upsilon\)\(\phi\)\(\chi\)\(\psi\)\(\omega\)\(\alpha\)\(\beta\)\(\gamma\)\(\delta\)\(\epsilon\)\(\zeta\)\(\eta\)\(\theta\)\(\iota\)\(\kappa\)\(\lambda\)\(\mu\)\(\nu\)\(\xi\)\(\omicron\)\(\pi\)\(\rho\)\(\sigma\)\(\tau\)\(\upsilon\)\(\phi\)\(\chi\)\(\psi\)\(\omega\)\(\alpha\)\(\beta\)\(\gamma\)\(\delta\)\(\epsilon\)\(\zeta\)\(\eta\)\(\theta\)\(\iota\)\(\kappa\)\(\lambda\)\(\mu\)\(\nu\)\(\xi\)\(\omicron\)\(\pi\)\(\rho\)\(\sigma\)\(\tau\)\(\upsilon\)\(\phi\)\(\chi\)\(\psi\)\(\omega\)\(\alpha\)\(\beta\)\(\gamma\)\(\delta\)\(\epsilon\)\(\zeta\)\(\eta\)\(\theta\)\(\iota\)\(\kappa\)\(\lambda\)\(\mu\)\(\nu\)\(\xi\)\(\omicron\)\(\pi\)\(\rho\)\(\sigma\)\(\tau\)\(\upsilon\)\(\phi\)\(\chi\)\(\psi\)\(\omega\)\(\alpha\)\(\beta\)\(\gamma\)\(\delta\)\(\epsilon\)\(\zeta\)\(\eta\)\(\theta\)\(\iota\)\(\kappa\)\(\lambda\)\(\mu\)\(\nu\)\(\xi\)\(\omicron\)\(\pi\)\(\rho\)\(\sigma\)\(\tau\)\(\upsilon\)\(\phi\)\(\chi\)\(\psi\)\(\omega\)
(Sα)-2,6-Diphenyl-4-(1,2,3,4-tetrahydronaphthalen-2-yl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (5dh)

The following compound was synthesized via Procedure B, with 2c (140.8 mg, 0.2 mmol), 1,2-dihydropyranophthalene (4h) (127.8 mg, 1 mmol). Purification by column chromatography on silica gel (CH₂Cl₂ × hexane = 1 : 2, Rf = 0.23) gave 5di (97.7 mg, 72%, dr = 82 : 18) as a white powder.

IR (KBr): 3436, 3056, 2953, 2925, 2868, 1595, 1496, 1452, 1435, 1405, 1361, 1304, 1267, 1245, 1192, 1175, 1149, 1110, 1076, 1046, 1030, 1002, 989, 962, 927, 884, 861, 831, 791, 781, 766, 747, 723, 698, 676, 647, 615, 605, 584, 571, 558, 533, 514 cm⁻¹; ¹H NMR (CDCl₃): δ 0.93 (br s, 0.5H), 1.23-1.32 (m, 1H), 1.35-1.50 (m, 0.5H), 1.94 (br s, 0.5H), 2.04-2.21 (m, 1.5H), 2.34-2.74 (m, 3H), 6.51 (br s, 0.5H), 6.89-6.91 (m, 1.5H, Ar), 6.99-7.01 (m, 2H, Ar), 7.27-7.32 (m, 2H, Ar), 7.38-7.52 (m, 10H, Ar), 7.61-7.62 (m, 1H, Ar), 7.69-7.70 (m, 1H, Ar), 7.70-7.73 (m, 2H, Ar), 7.92-7.94 (m, 1H, Ar), 7.99-8.00 (m, 1.5H, Ar), 8.04 (s, 0.5H, Ar), 8.11 (s, 0.5H, Ar), 8.12 (s, 0.5H, Ar); ³¹C NMR δ 22.7, 23.0, 27.8, 28.09 (d, J = 18.2 Hz), 28.8, 37.9 (d, J₁/C₃P = 80.2 Hz), 38.4 (d, J₁/C₃P = 80.1 Hz), 123.5, 123.6, 124.0, 125.3, 125.6, 125.8, 126.0, 126.1, 126.5, 126.7, 126.9, 127.0, 127.1, 127.5, 127.6, 127.8, 128.0, 128.1, 128.3, 128.4, 128.6, 128.7, 128.8, 129.0, 129.4, 129.8, 129.9, 130.4, 130.6, 130.8, 131.0, 131.4, 131.5, 131.9, 132.2, 133.5, 133.6, 133.7, 133.9, 134.6, 135.0, 135.1, 135.3, 136.7, 137.5, 137.6, (Ar), 143.7 (d, J = 9.9 Hz, Ar), 143.9 (Ar), 146.0 (d, J = 14.9 Hz, Ar); ³¹P NMR (CDCl₃): δ 129.1 (J₁/P₃Se = 932.5 Hz), The signal clue to the minor product was not obtained.; ⁷⁷Se NMR (CDCl₃): δ -299.2 (J₁/P₃Se = 927.2 Hz), 286.0 (J₁/P₃Se = 927.2 Hz); MS (EI) m/z 678 (M⁺); HRMS Calcd for C₄₆H₈₆O₃PSe: 678.1227, Found: 678.1232.

(Sα)-2,6-Diphenyl-4-(2-phenylcyclohexyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-selenide (5di)

The following compound was synthesized via Procedure B, with 2c (351.6 mg, 0.5 mmol), 1-phenyl-cyclohexene (4i) (0.91 mL, 10 mmol). Purification by column chromatography on silica gel (CH₂Cl₂ × hexane : AcOEt) = 1 : 60 : 1, Rf = 0.23, 0.20 gave each diastereomers 5di (178 mg, 51%, dr = 96 : 4) as white powders. Separation of a mixture of diastereomers was performed on silica gel column chromatography using CH₂Cl₂ × hexane = 1 : 3 as eluent. (dr = > 99 : 1, The first fraction on TLC): [α]D²⁹ = +272 (c = 0.416, CHCl₃); mp: 151-154 °C; IR (KBr): 3053, 3026, 2927, 2852, 1496, 1450, 1405, 1245, 1206, 1192, 1175, 1149, 1075, 989, 960, 884, 858, 826, 778, 765, 748, 724, 697, 676, 615, 571, 511 cm⁻¹; ¹H NMR (CDCl₃): δ 0.90-1.04 (m, 2H), 1.17 (br, 1H), 1.40-1.69 (m, 4H), 1.76-178 (m, 1H), 2.3-2.37 (m, 1H), 2.97-3.01 (m, 1H), 6.70-6.88 (m,
5H, Ar), 7.21-7.57 (m, 14H, Ar), 7.82 (d, J = 7.31 Hz, 2H, Ar), 7.89 (d, J = 8.3 Hz, 1H, Ar), 7.91 (s, 1H, Ar), 8.04 (d, J = 7.8 Hz, 1H, Ar), 8.15 (s, 1H, Ar); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 20.9, 24.2, 24.5 (d, J = 14.0 Hz), 33.1 (d, J = 7.4 Hz), 41.2, 46.0 (d, \(^1J_{C,P} = 71.1\) Hz), 123.7, 123.8, 123.9, 124.0, 125.5, 125.8, 126.0, 126.2, 126.6, 126.8, 127.1, 127.2, 127.3, 127.7, 128.1, 128.3, 128.8, 130.0, 130.2, 130.7, 131.2, 131.6, 132.2, 132.7, 133.7, 135.2, 136.6, 137.5, 142.2, 143.8 (d, J = 11.6 Hz), 146.0 (d, J = 15.7 Hz); \(^{31}\)P NMR (CDCl\(_3\)): \(\delta\) 124.8 (\(^1J_{P,Se} = 93.5\) Hz); \(^{77}\)Se NMR (CDCl\(_3\)): \(\delta\) 207.3 (\(^1J_{P,Se} = 93.25\) Hz); MS (EI) \(m/z\) 706 (M\(^+\)); HRMS Calcd for \(C_{44}H_{35}O_2PSe_2\); Found: 706.1538.

\((S_\alpha)-4(1,2,3,4-Tetrahydronaphthalen-2-yl)-2,6-bis(triisopropylsilyl)dinaphtho[2,1-d:1'2':f][1,3,2]dioxaphophene-4-selenide (5eh)\)

The following compound was synthesized via Procedure B, with 2e (258.8 mg, 0.3 mmol), 1,2-dihydronaphthalene (196 \(\mu\)L, 1.5 mmol). Purification by column chromatography on silica gel (CH\(_2Cl_2\) : hexane = 1 : 2, Rf = 0.53) gave 5eh (168 mg, 67\%, \(dr = 8 : 92\)) as a white powder.

IR (KBr): 3448, 3064, 3020, 2944, 2889, 2865, 2725, 1710, 1617, 1579, 1563, 1495, 1464, 1440, 1383, 1368, 1300, 1273, 1252, 1208, 1192, 1174, 1148, 1091, 1049, 1018, 972, 953, 922, 882, 851, 825, 776, 751, 677, 661, 641, 630, 607, 584, 548, 526, 505 cm\(^{-1}\); \(^1\)H NMR: \(\delta\) 1.03 (d, \(J = 7.6\) Hz, 9H), 1.08-1.33 (m, 27H), 1.58 (sep, \(J = 7.3\) Hz, 3H), 1.81 (sep, \(J = 7.3\) Hz, 4H), 2.25 (br d, 15.1 Hz, 1H), 2.43-2.52 (m, 1H), 2.59-2.96 (m, 4H), 6.46 (d, \(J = 7.6\) Hz, 1H), 6.77 (d, \(J = 8.6\) Hz, 1H), 6.88 (d, \(J = 8.6\) Hz, 1H), 6.91-6.95 (m, 1H, Ar), 7.01-7.03 (m, 2H, Ar), 7.15 (ddd, \(J = 8.6\) Hz, 6.9 Hz, 1.2 Hz, 1H, Ar), 7.22 (ddd, \(J = 8.4\) Hz, 6.9 Hz, 1.2 Hz, 1H, Ar), 7.38-7.46 (m, 2H, Ar), 7.90 (d, \(J = 8.1\) Hz, 1H, Ar), 7.79 (d, \(J = 8.3\) Hz, 1H, Ar), 8.13 (s, 1H, Ar), 8.14 (s, 1H, Ar); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 125.5, 126.0, 126.4, 126.6, 126.9, 127.2, 127.5, 128.3, 128.7, 128.8, 130.6, 130.9, 134.0, 134.1, 134.2, 135.3, 139.0, 139.1, 150.5 (d, \(J = 10.8\) Hz), 153.7 (d, \(J = 14.9\) Hz); \(^{31}\)P NMR (CDCl\(_3\)): \(\delta\) 117.0 (\(^1J_{P,Se} = 923.6\) Hz), 118.6 (\(^1J_{P,Se} = 923.6\) Hz); \(^{77}\)Se NMR (CDCl\(_3\)): \(\delta -213.2\) (\(^1J_{P,Se} = 921.1\) Hz), The signal due to the minor product was not observed.

S16
Deselenation-oxidation of phosphonoselenoic acid esters 5

(S<sub>α</sub>)-4-(2-Phenylpropyl)-dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphopine-4-oxide (6ca)

To a 10 mL two-necked flask were added selenophosphonate 6ca (154 mg, 0.3 mmol), CH<sub>2</sub>Cl<sub>2</sub> (0.6 mL) and hydrogen peroxide (30% aqueous solution, 0.09 mL, 0.9 mmol), and the mixture was stirred at room temperature for 24 h. After that, the mixture was concentrated. Purification by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub> : hexane : AcOEt = 5 : 5 : 1) gave 6ca (117 mg, 86%) as a white solid. [α]<sub>D</sub><sup>28</sup> = +320 (C = 0.555, CHCl<sub>3</sub>); mp: 99-102 °C; IR (KBr): 3440, 3059, 2964, 1620, 1590, 1508, 1464, 1433, 1401, 1361, 1326, 1282, 1226, 1156, 1071, 984, 961, 909, 873, 844, 816, 750, 700, 665, 605, 570, 554, 529 cm<sup>-1</sup>; ¹H NMR (CDCl<sub>3</sub>): δ 1.37 (d, J = 7.3 Hz, 3H, CH<sub>3</sub>), 2.09 (m, 1H, CH<sub>2</sub>), 2.13 (m, 1H, CH<sub>2</sub>), 3.46 (m, 1H, CH), 6.60 (d, J = 8.8 Hz, 1H, Ar), 7.06-7.32 (m, 11H, Ar), 7.46 (d, J = 8.8 Hz, 1H, Ar), 7.71-7.78 (m, 3H, Ar), 7.87 (d, J = 8.8 Hz, 1H, Ar): ¹³C NMR (CDCl<sub>3</sub>): δ 22.8 (d, J<sub>C-P</sub> = 10.8 Hz, CH<sub>3</sub>), 32.8 (d, J<sub>C-P</sub> = 129.0 Hz, CH<sub>2</sub>), 34.0 (d, J<sub>C-P</sub> = 2.5 Hz, CH), 119.9, 120.0, 121.0, 121.6, 121.7, 121.7, 125.5, 125.6, 126.5, 126.6, 126.7, 126.8, 127.0, 128.2, 128.4, 128.6, 130.8, 131.1, 131.3, 131.6, 132.2, 132.3, 145.6, 145.7, 147.1, 147.2 (Ar); ³¹P NMR (CDCl<sub>3</sub>): δ 41.7; MS (EI) m/z 450 (M<sup>+</sup>); HRMS Calcd for C<sub>29</sub>H<sub>31</sub>O<sub>4</sub>P: 450.1385, Found: 450.1385.

(S<sub>α</sub>)-4-(2-Phenylethyl)-dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphopine-4-oxide (6cb)

To a 30 mL round-bottom flask were added selenophosphate 6cb (249.5 mg, 0.5 mmol), CH<sub>2</sub>Cl<sub>2</sub> (1 mL) and hydrogen peroxide (30% aqueous solution, 0.15 mL, 1.5 mmol), and the mixture was stirred at room temperature for 4.5 h. After that, the mixture was filtered, washed with CH<sub>2</sub>Cl<sub>2</sub>, and the filtrate was concentrated. The resulting solid was passed through column chromatography on silica gel (EtOAc : Hexane = 1 : 2. Rf = 0.50) to give phosphate 6cb (173.8 mg, 80%) as a white solid; [α]<sub>D</sub><sup>29</sup> = +372 (c = 1.000, CHCl<sub>3</sub>) mp: 218-221 °C IR (KBr): 3111, 3083, 3062, 3026, 3005, 2956, 2913, 1589, 1506, 1463, 1404, 1323, 1284, 1222, 1195, 1154, 1143, 1070, 976, 960, 946, 876, 861, 845, 834, 818, 795, 775, 760, 747, 700, 657, 599, 577, 567, 548, 530, 504, 494 cm<sup>-1</sup>; ¹H NMR (CDCl<sub>3</sub>): δ 2.22-2.31 (m, 2H), 3.02-3.26 (m, 2H), 7.22-7.34 (m, 9H, Ar), 7.38 (d, J = 8.3 Hz, 1H, Ar), 7.45-7.51 (m, 2H, Ar), 7.60 (d, J = 9.3 Hz, 1H, Ar), 7.93-7.97 (m, 2H, Ar), 7.98 (d, J = 8.8 Hz, 1H, Ar), 8.04 (d, J = 8.8 Hz, 1H, Ar); ¹³C NMR (CDCl<sub>3</sub>): δ 25.8 (d, J<sub>C-P</sub> = 130.7 Hz), 28.1 (d, J<sub>C-P</sub> = 4.1 Hz), 119.9, 121.1, 121.8, 121.9, 125.7, 125.8, 126.8, 126.9, 127.2, 128.2, 128.3, 128.4, 128.7, 131.2, 131.3, 131.5, 131.8, 132.4, 132.5, 140.1, 140.2, 145.8 (d, J = 9.9 Hz), 147.3 (d, J = 9.9 Hz); ³¹P NMR (CDCl<sub>3</sub>): δ 41.7 (s); MS (EI) m/z 436 (M<sup>+</sup>); HRMS Calcd for C<sub>29</sub>H<sub>31</sub>O<sub>4</sub>P: 436.1228, Found: 436.1224.

(S<sub>α</sub>)-4-(2-Phenylcyclohexyl)dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphopine-4-oxide (6ci)
To a 30 mL round-bottom flask were added selenophosphinate 5ci (166 mg, 0.3 mmol, dr = 95 : 5), CH₂Cl₂ (1 mL) and hydrogen peroxide (30% aqueous solution, 0.06 mL, 0.9 mmol), and the mixture was stirred at rt for 2.5 h. After that, the mixture was filtered, washed with CH₂Cl₂, and the filtrate was concentrated. The resulting solid was passed through column chromatography on silica gel (EtOAc : Hexane = 1 : 1. Rf = 0.70, 0.55) to give phpsphate 6ci (7 mg, <5%, dr = 1 : 99), 31P NMR δ 43.3. The first fraction on TLC containing unidentified products (31P NMR δ 21.6, 39.4, 40.1 ppm, total 27%), (91 mg, 62%, dr = 99 : 1, The second fraction on TLC) as a white solid;
(dr = 99 : 1), [α]D²⁹ = +294 (c = 0.287, CHCl₃); mp: 135-136 °C IR (KBr): 3057, 3028, 2929, 2856, 1590, 1507, 1464, 1448, 1325, 1278, 1226, 1203, 1156, 1072, 984, 960, 945, 900, 864, 839, 814, 772, 750, 724, 697, 655, 629, 566, 547, 530, 445, 404 cm⁻¹; ¹H NMR (CDCl₃): δ 1.43-2.11 (m, 6H), 2.54-2.72 (m, 3H), 3.07-3.22 (m, 1H), 7.04 (d, J = 8.8 Hz, 1H, Ar), 7.18-7.31 (m, 7H, Ar), 7.38-7.49 (m, 5H, Ar), 7.87 (d, J = 8.8 Hz, 2H, Ar), 7.92 (d, J = 7.8 Hz, 1H, Ar), 7.96 (d, J = 9.3 Hz, 1H, Ar); ¹³C NMR (CDCl₃): δ 22.9 (d, J⁻¹CP = 4.1 Hz), 25.5, 26.8, 27.6 (d, J⁻¹CP = 3.3 Hz), 39.1 (d, ¹JC = 125.7 Hz), 43.6 (d, J = 2.5 Hz), 119.9, 121.1, 121.6, 121.7, 125.3, 125.5, 126.3, 126.5, 126.6, 126.8, 127.4, 127.9, 128.0, 128.2, 128.4, 128.6, 130.7, 130.8, 131.2, 131.6, 132.3, 132.6, 143.3, 145.8 (d, J = 10.8 Hz), 148.1 (d, J = 10.8 Hz); ³¹P NMR (CDCl₃): δ 42.8 (s); MS (EI) m/z 490 (M⁺); HRMS Calcd for C₃₀H₂₇O₅P: 490.1698, Found: 490.1705.

(S₅₄)-4-(1,2,3,4-tetraydroxynaphthalen-2-yl)dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepine-4-oxide (6ch)

To a 10 mL two-necked flask were added selenophosphonate 5ch (74 mg, 0.33 mmol, dr = 50 : 50), CH₂Cl₂ (0.7 mL) and hydrogen peroxide (30% aqueous solution, 1.0 mL, 1.0 mmol), and the mixture was stirred at room temperature for 5 h. After that, the mixture was concentrated. Purification by column chromatography on silica gel (CH₂Cl₂ : hexane : AcOEt = 10 : 10 : 1) gave 6ch (127 mg, 83%, dr = 50 : 50) as a white solid. IR (KBr): 3453, 3060, 2931, 1620, 1590, 1508, 1464, 1434, 1360, 1326, 1281, 1225, 1156, 1072, 1050, 962, 869, 842, 815, 747, 711, 696, 656, 615, 561, 530 cm⁻¹; ¹H NMR (CDCl₃): δ 1.96 (m, 1H, CH), 2.27 (m, 1.5H, CHCH₂CH₂C), 2.38 (m, 0.5H, CHCH₂CH₂C), 2.59-2.88 (m, 2H, CHCH₂CH₂C), 2.97 (m, 0.5H, CHCH₂C), 3.09-3.26 (m, 1.5H, CHCH₂C), 6.91-7.07 (m, 4H, Ar), 7.15-7.23 (m, 3H, Ar), 7.29 (m, 1H, Ar), 7.37 (m, 3H, Ar), 7.54 (m, 1H, Ar), 7.82-7.90 (m, 3H, Ar), 7.95 (d, J = 8.8 Hz, 1H, Ar); ¹³C NMR (CDCl₃): δ 22.6 (m, CHCH₂CH₂C), 28.4 (m, CHCH₂CH₂C), 30.3 (d, ¹JC = 20.7 Hz, CH), 31.7 (d, ¹JC = 20.7 Hz, CH), 119.8, 121.1, 121.5, 121.7, 125.6, 125.8, 126.0, 126.0, 126.2, 126.2, 126.6, 126.8, 126.9, 127.2, 128.3, 128.4, 128.5, 128.8, 129.1, 131.1, 131.2, 131.8, 132.4, 132.5, 133.6, 133.9, 134.0, 135.2, 135.3, 145.7, 145.8, 147.7, 147.8 (Ar); ³¹P NMR (CDCl₃): δ 43.3, 43.5; MS (EI) m/z 462 (M⁺); HRMS Calcd for C₃₀H₂₇O₅P: 462.1385, Found: 462.1396.

* Deselenation - boration of phosphonoselenoic acid esters 5
(Sα)- 4-(2-Phenylethyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepineborane (8cb)

To a 20 mL two-necked flask were added selenophosphate (5cb) (1.50 g, 3.0 mmol), THF (6.0 mL), tri-n-butylphosphine (0.82 mL, 3.3 mmol) under Ar atmosphere. The reaction mixture stirred for 20.5 h. After that, BH₃·THF (1M, 4.5 mL) was added to the mixture, and it was further stirred for 15 min. The mixture was concentrated. Purification by silica gel column chromatography (Acetone : hexane = 1 : 25, Rf = 0.10) gave 8cb (962 mg, 74%) containing 5cb (12%) as a white solid. The solid was dissolved by THF. To this solution was added hydrogen proxide (30% aqueous solution, 71 µL, 0.83 mmol), and stirred for 3 h. After that, the mixture was filtered, washed with CH₂Cl₂, and the filtrate was concentrated. The resulting solid was passed through column chromatography on silica gel (EtOAc : Hexane = 1 : 6, Rf = 0.53) to give 8cb (705 mg, 54%) as a white powder. [α]D 33° = +415 (c = 0.542, CHCl₃), mp: 147-149 °C; IR (KBr): 3061, 3026, 2900, 2403, 2381, 2337, 1588, 1505, 1462, 1454, 1431, 1390, 1361, 1319, 1227, 1200, 1191, 1157, 1144, 1128, 1073, 1060, 1029, 981, 960, 905, 864, 843, 817, 792, 779, 756, 715, 696, 665, 647, 617, 562 cm⁻¹; ¹H NMR (CDCl₃): δ 2.26 (dd, J = 17.5 Hz, 9.0 Hz, 2H, CH₂CH₂Ph), 2.95-3.19 (m, 2H), 7.19-7.38 (m, 10H, Ar), 7.45-7.51 (m, 2H, Ar), 7.56 (dd, J = 9.0 Hz, 0.9 Hz, 1H, Ar), 7.94-7.98 (m, 3H, Ar), 8.04 (d, J = 9.0 Hz, 1H, Ar); ¹³C NMR (CDCl₃): δ 27.8 (d, JCP = 2.8 Hz, CH₂CH₂Ph), 30.5 (d, JCP = 32.9 Hz, CH₂CH₂Ph), 120.3, 121.4, 122.4, 122.8, 125.7, 125.8, 126.7, 126.9, 127.1, 128.2, 128.4, 128.6, 128.7, 130.9, 131.0, 131.6, 131.9, 132.5, 132.7, 140.1, 140.2, 146.9, 147.0, 147.1; ³¹P NMR (CDCl₃): δ 177.8 (m); MS (EI) m/z 434 (M⁺, 0.25 (m, 4H), 1.04 (m, 3H), 1.82-1.92 (m, 1H), 3.06-3.15 (m, 2H), 3.72 (d, J = 10.8 Hz, 1H), 3.81 (d, J = 10.8 Hz, 1H), 7.32-7.57 (m, 12H, Ar), 7.61 (d, J = 7.3 Hz, 2H, Ar), 7.71 (d, J = 7.3 Hz, 2H, Ar), 8.02 (d, J = 8.1 Hz, 1H, Ar), 8.03 (d, J = 8.1 Hz, 1H, Ar), 8.12 (s, 2H, Ar); ¹³C NMR (CDCl₃): δ 21.5 (d, JCP = 5.6 Hz, CHCH₂CH₂), 25.3 (d, JCP = 12.2 Hz, CHCH₂CH₂), 36.5 (d, JCP = 32.9 Hz, CHCH₂O), 66.0 (d, JCP = 7.5 Hz, CHCH₂O), 67.8, 123.5, 123.9, 126.0, 126.2, 126.6, 126.8, 126.9, 127.7, 127.9, 128.0, 128.5, 128.6, 130.0, 130.2, 130.4, 130.9, 131.6, 131.9, 132.1, 132.3, 133.8, 134.7, 136.7, 136.8, 144.4, 144.5, 144.6 (Ar); ³¹P NMR (CDCl₃):

(Sα)-2,6-Diphenyl-4-(3-Tetrahydropyran-1-yl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepineborane (8dg)

To a 10 mL two-necked flask were added selenophosphate (5dg, dr = >1 : 99) (159 mg, 0.25 mmol), THF (2.5 mL), tri-n-butylphosphine (69 µL, 0.28 mmol) under Ar atmosphere. The reaction mixture stirred for 4 h. After that, BH₃·THF (1M, 0.38 mL) was added to the mixture, and it was further stirred for 15 min. The mixture was concentrated. Purification by silica gel column chromatography (Acetone : hexane = 1 : 30, Rf = 0.13) gave phosphonite-borane complex 8dg (98.6 mg, 77%) containing 5dh (6%) as a white solid. [α]D 32° = +285 (c = 0.2930, CHCl₃), mp: 245-247 °C; IR (KBr): 3061, 3026, 2900, 2403, 2381, 2337, 1588, 1505, 1495, 1498, 1467, 1452, 1407, 1362, 1334, 1273, 1237, 1193, 1173, 1150, 1133, 1097, 1075, 1027, 989, 964, 885, 867, 833, 796, 784, 767, 751, 731, 719, 697, 680, 647, 622, 612, 588, 577, 568, 550, 513 cm⁻¹; ¹H NMR (CDCl₃): δ -0.25-0.25 (m, 4H), 1.04-1.19 (m, 3H), 1.82-1.92 (m, 1H), 3.06-3.15 (m, 2H), 3.72 (d, J = 10.8 Hz, 1H), 3.81 (d, J = 10.8 Hz, 1H), 7.32-7.57 (m, 12H, Ar), 7.61 (d, J = 7.3 Hz, 2H, Ar), 7.71 (d, J = 7.3 Hz, 2H, Ar), 8.02 (d, J = 8.1 Hz, 1H, Ar), 8.03 (d, J = 8.1 Hz, 1H, Ar), 8.12 (s, 2H, Ar); ¹³C NMR (CDCl₃): δ 21.5 (d, JCP = 5.6 Hz, CHCH₂CH₂), 25.3 (d, JCP = 12.2 Hz, CHCH₂CH₂), 36.5 (d, JCP = 32.9 Hz, CHCH₂O), 66.0 (d, JCP = 7.5 Hz, CHCH₂O), 67.8, 123.5, 123.9, 126.0, 126.2, 126.6, 126.8, 126.9, 127.7, 127.9, 128.0, 128.5, 128.6, 130.0, 130.2, 130.4, 130.9, 131.6, 131.9, 132.1, 132.3, 133.8, 134.7, 136.7, 136.8, 144.4, 144.5, 144.6 (Ar); ³¹P NMR (CDCl₃):
δ 176.9 (m); MS (EI) m/z 566 (M⁺); HRMS Calcd for C₃₁H₂₂BO₃P:566.2182, Found:566.2199.

(S₄₈) -2,6-Diphenyl-4-(tetrahydrofuran-3-yl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepineborane (7dj)

To a 10 mL two-necked flask were added selenophosphonate (5dj, dr = >1 : 99) (123 mg, 0.20 mmol), THF (2.0 mL), tri- n-butylphosphine (55 µL, 0.22 mmol) under Ar atmosphere. The reaction mixture stirred for 4 h. After that, BH₃·THF (1M, 0.30 mL) was added to the mixture, and it was further stirred for 15 min. The mixture was concentrated. Purification by silica gel column chromatography (Acetone : hexane = 1 : 10, Rf = 0.25) gave phosphonite-borane complex 7dj (82.7 mg, 75%) containing 5dk (1%) as a white solid. [α]D 31 = +385 (c = 0.416, CHCl₃); mp: 154-156 °C; IR (KBr): 3054, 2977, 2867, 2404, 2351, 1497, 1452, 1407, 1333, 1246, 1193, 1177, 1150, 1131, 1078, 1048, 1031, 990, 965, 918, 887, 868, 834, 785, 767, 751, 728, 698, 653, 628, 612, 569, 512 cm⁻¹; ¹H NMR (CDCl₃): δ 0-0.50 (m, 3H), 1.63-1.89 (m, 2H), 2.13-2.25 (m, 1H), 2.47-2.54 (m, 1H), 3.16 (ddd, J = 13.7 Hz, 9.3 Hz, 8.3 Hz, 1H), 3.49-3.57 (m, 2H), 7.33-7.58 (m, 12H, Ar), 7.65-7.67 (m, 2H, Ar), 7.73-7.75 (m, 2H, Ar), 8.03 (d, J= 7.8 Hz, 2H, Ar), 8.13 (s, 1H, Ar), 8.14 (s, 1H, Ar); ¹³C NMR (CDCl₃): 26.8 (d, J= 3.8 Hz, CH₂), 37.0 (d, J= 12.3 Hz, CH₂), 67.8 (d, J= 6.6 Hz, CH₂), 123.6, 123.9, 126.0, 126.1, 126.6, 126.8, 127.0, 127.7, 127.9, 128.4, 128.5, 128.6, 128.8, 129.9, 130.3, 130.9, 131.0, 131.6, 132.0, 132.1, 132.3, 133.4, 134.8, 136.3, 136.7, 144.4, 144.5, 144.6 (Ar); ³¹P NMR (CDCl₃): δ 177.4 (m); MS (EI) m/z 552 (M⁺); HRMS Calcd for C₃₀H₂₆O₃PB: 552.2026, Found: 552.2021.

(S₄₈) -2,6-Diphenyl-4-(2-phenylcyclohexyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepineborane (8di)

To a 10 mL two-necked flask were added selenophosphonate (5di, dr = >1 : 99) (180 mg, 0.25 mmol), THF (2.5 mL), tri-n-butylphosphine (68 µL, 0.28 mmol) under Ar atmosphere. The reaction mixture stirred for 8 h. After that, BH₃·THF (1M, 0.38 mL) was added to the mixture, and it was further stirred for 10 min. The mixture was concentrated. Purification by silica gel column chromatography (Acetone : hexane = 1 : 30, Rf = 0.13) gave phosphonite-borane complex 8di (144 mg, 88%) as a white solid. [α]D 32 = +317 (c = 0.596, CHCl₃); mp: 155-157 °C; IR (KBr): 3055, 3027, 2927, 2853, 2397, 2351, 1497, 1451, 1409, 1245, 1207, 1194, 1176, 1150, 991, 965, 886, 866, 833, 777, 749, 729, 695, 655, 611, 729, 695, 655, 631, 611, 512 cm⁻¹; ¹H NMR (CDCl₃): δ 0.87-1.03 (m, 2H), 1.16-1.19 (m, 1H), 1.36-1.64 (m, 5H), 2.23-2.28 (m, 1H), 2.79-2.84 (m, 1H), 6.57-6.63 (m, 4H), 6.74 (t, J = 6.8 Hz, 1H, Ar), 7.18-7.57 (m, 14H, Ar), 7.78 (d, J = 8.3 Hz, 2H, Ar), 7.88 (d, J = 8.8 Hz, 2H, Ar), 8.05 (d, J = 8.3 Hz, 1H, Ar), 8.16 (s, 1H, Ar); ¹³C NMR (CDCl₃): 22.6, 23.4, 23.7, 29.6, 30.5, 41.4 (J = 23.9 Hz), 123.0, 124.5, 125.5, 125.7, 126.0, 126.3, 126.5, 126.7, 127.2, 127.3, 127.4, 127.7, 128.1, 128.3, 128.7, 130.0, 130.2, 130.3, 130.5, 131.5, 131.6, 132.1, 132.8, 134.1, 134.9, 135.0, 136.7, 136.9, 142.5, 144.5, 144.6, 144.7 (Ar); ³¹P NMR (CDCl₃): δ 184.8 (m); MS (EI) m/z 640 (M⁺); HRMS Calcd for C₄₄H₃₈O₃PB: 640.2702, Found: 640.2718.
X-ray structure analysis

The measurement of \((S_{\text{ax}}, R)-4-(2\text{-phenylpropyl})\text{-dinaphtho[2,1-d:1’,2’-f][1,3,2]}\) dioxaphophepin-4-selenide \((S_{\text{ax}}, R)-5\text{ca}) (MM366) was carried out on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo-K\(\alpha\) radiation \((\lambda = 0.71069 \text{ Å})\). Reflection data were collected at 193 K using a Rigaku XR-TCS-2-050 temperature controller. X-ray absorption was corrected by numerical methods based on the crystal shape.\(^{S1}\) The structure was solved and refined using the Yadokari-XG crystallographic software package of Molecular Structure Corporation. The X-ray quality crystal was obtained by slow diffusion of hexane (2 mL) into CH\(_2\)Cl\(_2\) solution (0.5 mL) of \((S_{\text{ax}}, R)-5\text{ca} (127 \text{ mg})\) at rt under air. The crystal was cut from the grown crystals and was mounted on a glass fiber. The structures were solved by direct method using SHELXL-97.\(^{S2}\) The full-matrix least-squares cycle included nonhydrogen atoms with anisotropic thermal parameters. Hydrogen atoms on C were placed in idealized positions and treated as riding atoms with C-H distances in the range 95-100 pm. Crystallographic data are listed in Table S1.

The measurement of \((S_{\text{ax}}, R)-4-(3\text{-tetrahydropyran-1-yl})\text{-dinaphtho[2,1-d:1’,2’-f][1,3,2]}\) dioxaphophepin-4-selenide \((S_{\text{ax}}, R)-5\text{eg}) (MM393) was carried out on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo-K\(\alpha\) radiation \((\lambda = 0.71069 \text{ Å})\). Reflection data were collected at 193 K using a Rigaku XR-TCS-2-050 temperature controller. X-ray absorption was corrected by numerical methods based on the crystal shape.\(^{S1}\) The structure was solved and refined using the Yadokari-XG crystallographic software package of Molecular Structure Corporation. The X-ray quality crystal was obtained by slow diffusion of hexane (2 mL) into CH\(_2\)Cl\(_2\) solution (0.4 mL) of \((S_{\text{ax}}, R)-5\text{eg} (100 \text{ mg})\) at rt under air. The crystal was cut from the grown crystals and was mounted on a glass fiber. The structures were solved by direct method using SHELXL-97.\(^{S2}\) The full-matrix least-squares cycle included nonhydrogen atoms with anisotropic thermal parameters. Hydrogen atoms on C were placed in idealized positions and treated as riding atoms with C-H distances in the range 95-99 pm. ORTEP drawings of 5\text{ca} and 5\text{eg} are shown in Figures 1 and 2, and crystallographic data are listed in Table S1.
Fig. 1 ORTEP drawing of $\langle S_{\text{cis}}, R \rangle$-5ca with 50% thermal ellipsoids. Selected bond lengths [Å]: P-Se 2.0634, P-O(1) 1.615(2), P-O(2) 1.6102, P-C 1.793(4).

Fig. 2 CICIP drawing of $\langle S_{\text{cis}}, R \rangle$-5ca with 50% thermal ellipsoids. Selected bond lengths [Å]: P-Se 2.0612(15), P-O(1) 1.608(4), P-O(2) 1.605(3), P-C 1.805(5).
Table S1. Crystal data and structure refinement for \( (S_{ax}, R) \)-5ca and \( (S_{ax}, R) \)-5cg.

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<td></td>
</tr>
<tr>
<td>( a = 1315.1(8) ) pm</td>
<td>( a = 90^\circ )</td>
<td>( a = 1747.9(8) ) pm</td>
</tr>
<tr>
<td>( b = 2305.6(13) ) pm</td>
<td>( b = 90^\circ )</td>
<td>( b = 1023.1(5) ) pm</td>
</tr>
<tr>
<td>( c = 780.6(5) ) pm</td>
<td>( c = 90^\circ )</td>
<td>( c = 1245.9(6) ) pm</td>
</tr>
<tr>
<td>Volume</td>
<td>2.371(1) nm(^3)</td>
<td>2.2279(19) nm(^3)</td>
</tr>
<tr>
<td>( Z )</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.441 \text{ Mg/m}^3</td>
<td>1.429 \text{ Mg/m}^3</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.679 mm(^{-1})</td>
<td>1.781 mm(^{-1})</td>
</tr>
<tr>
<td>( F(000) )</td>
<td>1048</td>
<td>976</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.29 X 0.17 X 0.17 mm(^3)</td>
<td>0.25 X 0.23 X 0.17 mm(^3)</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.03 to 27.48(^\circ)</td>
<td>3.27 to 27.48(^\circ)</td>
</tr>
<tr>
<td>Index ranges</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( -16 &lt; h &lt; 17, -28 &lt; k &lt; 29, -10 &lt; l &lt; 17 )</td>
<td>( -22 &lt; h &lt; 17, -12 &lt; k &lt; 13, -11 &lt; l &lt; 16 )</td>
<td></td>
</tr>
<tr>
<td>Reflections collected</td>
<td>19181</td>
<td>17803</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>5357 ( [R(int) = 0.0579] )</td>
<td>5079 ( [R(int) = 0.0525] )</td>
</tr>
<tr>
<td>Completeness to theta = 27.48(^\circ)</td>
<td>98.9%</td>
<td>99.3%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Integration</td>
<td>Integration</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.774 and 0.0579</td>
<td>0.732 and 0.522</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on ( F^2 )</td>
<td>Full-matrix least-squares on ( F^2 )</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5357 / 0 / 299</td>
<td>5079 / 0 / 272</td>
</tr>
<tr>
<td>Goodness-of-fit on ( F^2 )</td>
<td>1.121</td>
<td>1.000</td>
</tr>
<tr>
<td>Final R indices ([&gt;2\sigma(l)])</td>
<td>( R_1 = 0.0477, ) ( wR_2 = 0.0932 )</td>
<td>( R_1 = 0.0633, ) ( wR_2 = 0.1647 )</td>
</tr>
<tr>
<td>( R ) indices (all data)</td>
<td>( R_1 = 0.0520, ) ( wR_2 = 0.0949 )</td>
<td>( R_1 = 0.0713, ) ( wR_2 = 0.1711 )</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>0.008(10)</td>
<td>0.007(14)</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>–</td>
<td>0.002(2)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.580 and -0.482 e.Å(^{-3})</td>
<td>0.477 and -0.617 e.Å(^{-3})</td>
</tr>
</tbody>
</table>

References

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