Supplementary Information

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

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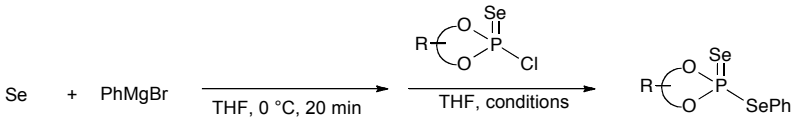
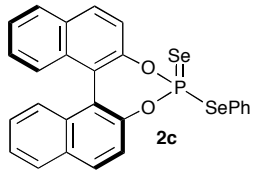
• Preparation of the starting materials

Synthesis of (S_{ax})-Binaphthylphosphoroselenoic acid derivatives

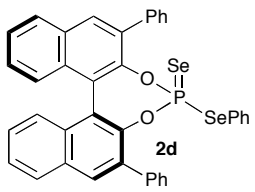


(S_{ax})-4-Phenylseleno-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (2c)



To a THF suspension (20 mL) of elemental selenium (869 mg, 11mmol) 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 (S_{ax})-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_2Cl_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, 1460, 1438, 1322, 1216, 1193, 1154, 1068, 1019, 999, 976, 949, 841, 815, 771, 749, 694, 648, 607, 576, 561, 541, 518, 484, 464, 448, 418, 403 cm^{-1}; ^1H NMR ($CDCl_3$): δ 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 ($CDCl_3$): δ 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 ($CDCl_3$): δ 97.5 ($^1J_{P\text{-}Se}$ = 963.7 Hz, 524.7 Hz); ^{77}Se NMR ($CDCl_3$): δ -36.3 ($^1J_{P\text{-}Se}$ = 963.7 Hz) 492.3 ($^1J_{P\text{-}Se}$ = 524.7 Hz), MS (EI) m/z 550 (M^+); HRMS Calcd for $C_{26}H_{17}O_2PSe_2$: 551.9291, Found: 551.9289.

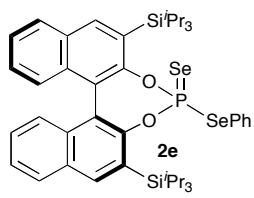
(S_{ax})-2,6-Diphenyl-4-phenylseleno-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (2d)



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 (S_{ax})-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_2Cl_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,

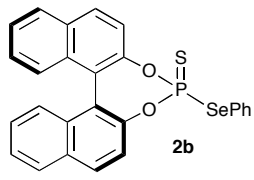
1577, 1498, 1474, 1452, 1439, 1402, 1243, 1187, 1148, 1132, 1075, 986, 958, 893, 881, 856, 824, 778, 765, 745, 721, 708, 696, 672, 646, 616, 606, 578, 567, 547, 523, 509 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.65-6.67 (m, 2H, Ar), 7.01 (t, *J* = 7.8 Hz, 2H, Ar), 7.18-7.22 (m, 1H, Ar), 7.29-7.57 (m, 12H, Ar), 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 ($CDCl_3$): δ 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 ($CDCl_3$): δ 96.1 ($^{1}J_{P\text{-}Se}$ = 974.0 Hz, 512.2 Hz); ^{77}Se NMR ($CDCl_3$): δ -33.4 ($^{1}J_{P\text{-}Se}$ = 976.0 Hz) 512.0 ($^{1}J_{P\text{-}Se}$ = 512.4 Hz), MS (EI) m/z 704 (M^+); HRMS Calcd for $C_{38}H_{25}O_2PSe_2$: 703.9923, Found: 703.9912.

(S_{ax})-4-Phenylseleno-2,6-bis(triisopropylsilyl)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 ºC, and the mixture was stirred at that temperature for 20 min. This solution was added to a THF solution (20 mL) of (S_{ax})-4-Chloro-2,6-bis(triisopropylsilyl)naphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (1.484 g, 2 mmol) via cannula at -90 ºC (acetone / liq N_2), and stirred at room temperature for 20 min. After that, the mixture was stirred at 73 ºC 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_2Cl_2 : hexane = 1 : 2, Rf = 0.63) gave **2e** (0.995 g, 58%) as a white powder. mp: 143 ºC; IR (KBr): 3052, 2944, 2888, 2865, 1464, 1440, 1383, 1366, 1253, 1200, 1184, 1174, 1147, 1253, 1200, 1184, 1174, 1147, 1088, 1019, 1001, 967, 951, 880, 853, 751, 737, 688, 677, 641, 622, 607, 588, 547, 530 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.18-1.24 (m, 36 H, SiCHC$\underline{H}_3$), 1.77-1.91 (m, 6H, SiC$\underline{H}$CH$_3$), 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 ($CDCl_3$): δ 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 ($CDCl_3$): δ 79.9 ($^{1}J_{P\text{-}Se}$ = 953.3 Hz, 580.2 Hz); ^{77}Se NMR ($CDCl_3$): δ 18.8 ($^{1}J_{P\text{-}Se}$ = 951.6 Hz), 503.4 ($^{1}J_{P\text{-}Se}$ = 579.5 Hz); MS (EI) m/z 864 (M^+).

(S_{ax})-4-Phenylseleno-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-sulfide (2b)

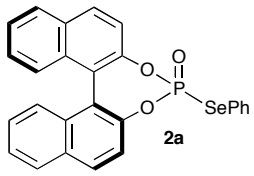


To a 10 mL two-necked flask were added **2c** (1.1 g, 2 mmol), THF (4.0 mL), tri-*n*-butylphosphine (0.6 mL, 2.4 mmol) under Ar atmosphere. The reaction mixture stirred for 30 min. After that, sulfur (320 mg, 10 mmol) was added to the mixture, and it was further stirred for 9 h. The mixture was concentrated. Purification by column

chromatography on silica gel (CH_2Cl_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, 1508, 1473, 1461, 1438, 1361, 1322, 1216, 1191, 1155, 1068, 976, 950, 841, 812, 739, 681, 652, 583, 566, 553, 526, 463, 423 cm^{-1}; ^1H 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, 121.3, 121.6, 122.4, 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, 130.9, 131.7, 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 ($^1J_{P\text{-}Se}$ = 524.3 Hz); ^{77}Se NMR ($CDCl_3$): δ 447.2 ($^1J_{P\text{-}Se}$ = 524.3 Hz); MS (EI) m/z 504 (M^+); HRMS Calcd for $C_{26}H_{17}O_2PSSe$: 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_2Cl_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_2Cl_2 : MeOH = 10 : 1, Rf = 0.78). The resulting red orange residue was recrystallized from CH_2Cl_2 (0.5 mL) and hexane (5 mL) to give a yellow crystalline solid. The solid was purifies by column chromatography on silica gel (CH_2Cl_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, 1325, 1270, 1212, 1072, 1019, 982, 945, 822, 772, 755, 708, 694, 653, 600, 573, 526, 507, 463, 445, 418 cm^{-1}; ^1H 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, 1292.2, 129.5, 129.5, 131.0, 31.3, 131.4, 131.6, 131.7, 131.8, 132.2, 132.3, 132.3, 136.0, 136.1, 146.6, 146.7, 146.8, 146.9; ^{31}P NMR ($CDCl_3$): δ 26.9 ($^1J_{P\text{-}Se}$ = 552.9 Hz); ^{77}Se NMR ($CDCl_3$): δ 295.4 ($^1J_{P\text{-}Se}$ = 552.9 Hz); MS (EI) m/z 488 (M^+); HRMS Calcd for $C_{26}H_{17}O_3PSe$: 488.0081, Found: 488.0066.



2a

• 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 ºC, 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.

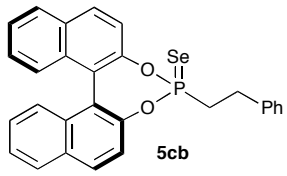
Procedure B:

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 ºC, 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_{ax})-4-(2-Phenylethyl)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphophepin-4-selenide (5cb)

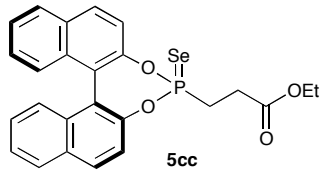
The following compound was synthesized via Procedure A, with **2c** (8.25 g, 15 mmol), styrene (**4b**) (2.07 mL, 18 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 4 : 7, Rf = 0.30) gave **5cb** (6.14 g , 82%) as a white powder.



5cb

$[\alpha]_D^{28}$ = +350.5 (c = 1.003, $CHCl_3$); mp: 150-151 ºC; 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 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.55 (m, 2H, $PCH_2\underline{C}H_2$), 3.12 (m, 1H, $PCH_2\underline{C}H_2$), 3.27 (m, 1H, $PCH_2\underline{C}H_2$), 7.16 (d, *J* = 8.8 Hz, 1H, Ar), 7.22-7.33 (m, 8H, Ar), 7.39 (d, *J* = 8.3 Hz, 1H, Ar), 7.46-7.50 (m, 2H, Ar), 7.59 (dd, *J* =8.8 Hz, 1.5 Hz, 1H, Ar), 7.94 (d, J = 9.3 Hz, 1H, Ar), 7.96 (d, J = 8.8 Hz, 2H, Ar), 8.05 (d, J = 9.3 Hz, 1H, Ar) ; ^{13}C NMR ($CDCl_3$): δ 29.4 ($PCH_2\underline{C}H_2$), 36.2 (d, $^1J_{C\text{-}P}$ = 77.7 Hz, $PCH_2\underline{C}H_2$), 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, 131.6, 132.0, 132.6, 132.7, 139.7, 139.9, 146.0, 146.1, 148.1, 148.2, (Ar); ^{31}P NMR ($CDCl_3$): δ 123.5 ($^1J_{P\text{-}Se}$ = 923.0 Hz); ^{77}Se NMR ($CDCl_3$): δ -238.9 ($^1J_{P\text{-}Se}$ = 923.0 Hz); MS (EI) m/z 500 (M^+); HRMS Calcd for $C_{28}H_{21}O_2PSe$: 500.0444, Found: 500.0443; Anal. Calcd for $C_{28}H_{21}O_2PSe$ (499.3989): C, 67.34; H, 4.24, Found: C, 67.12; H, 4.41.

(S_{ax})-4-(2-Ethoxycarbonylethyl)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphophepin-4-selenide (5cc)



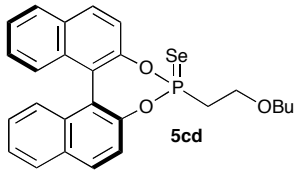
5cc

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_2Cl_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, $CHCl_3$); mp: 71-77 °C; IR (KBr): 3051, 2976, 2928, 1734, 1588, 1507, 1462, 1372, 1322, 1221, 1068, 979, cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.18 (m, 3H, $CH_2C\underline{H}_3$), 2.52 (m, 2H, PCH_2CH_2), 2.69-2.92 (m, 2H, PCH_2CH_2), 4.08 (m, 2H, $C\underline{H}_2CH_3$), 7.17-7.7.32 (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}C NMR ($CDCl_3$): δ 14.2 ($CH_2\underline{C}H_3$), 28.4 ($PCH_2\underline{C}H_2$), 29.6 (d, $^1J_{C\text{-}P}$ = 85.2 Hz, $P\underline{C}H_2CH_2$), 61.2 ($\underline{C}H_2CH_3$), 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}P NMR ($CDCl_3$): δ 122.3 ($^1J_{P\text{-}Se}$ = 926.9 Hz); ^{77}Se NMR ($CDCl_3$): δ -239.8 ($^1J_{P\text{-}Se}$ = 926.9 Hz); MS (EI) m/z 496 (M^+); HRMS Calcd for $C_{25}H_{21}O_4PSe$: 496.0337, Found: 496.0334.

(S_{ax})-4-(2-*n*-Butoxyethyl)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphophepin-4-selenide (5cd)

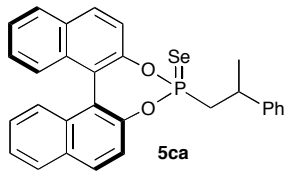
The following compound was synthesized via Procedure A, with **2c** (550 mg, 1 mmol), butyl vinyl ether (**4d**) (0.16 mL, 1.2 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 4 : 5, Rf = 0.30) gave **5cd** (273 mg, <55%) containing small amounts of unidentified products (^{31}P NMR d 120.9, 118.8, 118.2, 115.6, 114.8, 114.3 ppm, total 4%) as a pale yellow solid.



5cd

$[\alpha]_D^{27}$ = +378 (c = 1.27, $CHCl_3$); mp: 55-62 °C; IR (KBr): 3056, 2957, 2930, 2869, 1619, 1588, 1507, 1462, 1432, 1361, 1322, 1222, 1192, 1155, 1111, 1068, 978, 945, 837, 813, 739, 696, 651, 603, 569 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.87 (t, *J* = 7.3 Hz 3H, $OCH_2CH_2CH_2C\underline{H}_3$), 1.35 (m, 2H, $OCH_2CH_2C\underline{H}_2CH_3$), 1.50-1.57 (m, 2H, $OCH_2C\underline{H}_2CH_2CH_3$), 2.37 (m, 1H, $PC\underline{H}_2CH_2$), 2.55 (m, 1H, $PC\underline{H}_2CH_2$), 3.44 (m, 2H, $OC\underline{H}_2CH_2CH_2CH_3$), 3.84 (dm, $^3J_{P\text{-}H}$ = 24.4 Hz, 1H, $PCH_2C\underline{H}_2$), 3.93 (m, 1H, $PCH_2C\underline{H}_2$), 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); ^{13}C NMR ($CDCl_3$): δ 13.9 ($OCH_2CH_2CH_2\underline{C}H_3$), 19.3 ($OCH_2CH_2\underline{C}H_2CH_3$), 31.7 ($OCH_2\underline{C}H_2CH_2CH_3$), 34.8 (d, $^1J_{C\text{-}P}$ = 81.0 Hz, $P\underline{C}H_2CH_2$), 64.8 ($O\underline{C}H_2CH_2CH_2CH_3$), 71.3 ($PCH_2\underline{C}H_2$), 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); ^{31}P NMR ($CDCl_3$): δ 121.2 ($^1J_{P\text{-}Se}$ = 922.6 Hz); ^{77}Se NMR ($CDCl_3$): δ -237.6 ($^1J_{P\text{-}Se}$ = 922.6 Hz); MS (EI) m/z 496 (M^+); HRMS Calcd for $C_{26}H_{25}O_3PSe$: 496.0707, Found: 496.0707.

(S_{ax})-4-(2-Phenylpropyl)-dinaphtho[2,1-d:1',2'-f][1,3,2] dioxaphophepin-4-selenide (5ca)



5ca

The following compound was synthesized via Procedure A, with **2c** (550 mg, 1 mmol), α-methylstyrene (**4a**) (0.16 mL, 1.2 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : 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 CH_2Cl_2 : hexane = 2 : 3 or 1:1 as eluent.

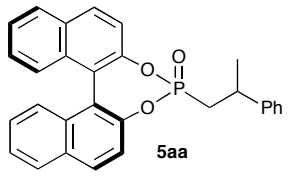
***(S_{ax}, R)*-18a** (dr: >99 : 1, The first fraction on HPLC): $[\alpha]_D^{27}$ = +354 (c = 0.811, $CHCl_3$); mp: 230-232 °C; IR (KBr): 3058, 3023, 3002, 2962, 2925, 2900, 1618, 1587, 1505, 1461, 1431, 1392, 1359, 1320, 1222, 1192, 1154, 1068, 978, 952, 913, 856, 842, 814, 773, 752, 700, 598, 564 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.40 (d, *J* = 7.3 Hz, 3H, CH_3), 2.35 (dt, *J* = 14.9 Hz, 6.8 Hz, 1H, CH_2), 2.49 (dt, *J* = 15.1 Hz, 6.8 Hz, 1H, CH_2), 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); ^{13}C NMR ($CDCl_3$): δ 22.7 (d, $^3J_{C\text{-}P}$ = 10.8 Hz, CH_3), 35.3 (CH), 43.1 (d, $^1J_{C\text{-}P}$ = 76.1 Hz, CH_2), 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); ^{31}P NMR ($CDCl_3$): δ 125.0 ($^1J_{P\text{-}Se}$ = 921.6 Hz); ^{77}Se NMR ($CDCl_3$): δ -233.8 ($^1J_{P\text{-}Se}$ = 921.6 Hz); MS (EI) m/z 514 (M^+); HRMS Calcd for $C_{29}H_{23}O_2PSe$: 514.0595, Found: 514.0574.

***(S_{ax}, S)*-18a** (dr: 2 : 98, The second fraction on HPLC): $[\alpha]_D^{27}$ = +375 (c = 0.567, $CHCl_3$); mp: 100-103 °C; IR

(KBr): 3056, 3025, 2962, 1620, 1588, 1507, 1461, 1432, 1361, 1321, 1222, 1155, 1069, 1028, 977, 952, 838, 745, 697, 651, 619, 600, 569, 527 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.63 (d, J = 6.8 Hz, 3H, CH_3), 2.51 (dt, J = 10.0 Hz, 4.9 Hz, 1H, CH_2), 2.49 (dt, J = 9.5 Hz, 5.4 Hz, 1H, CH_2), 3.62 (m, 1H, CH), 7.16-7.38 (m, 9H, Ar), 7.46-7.52 (m, 4H, Ar), 7.94-8.05 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$): δ 23.0 (d, $^3J_{C\text{-}P}$ = 5.8 Hz, CH_3), 35.7 (CH), 41.6 (d, $^1J_{C\text{-}P}$ = 75.3 Hz, CH_2), 120.6, 121.9, 122.7, 125.7, 125.9, 126.5, 126.7, 126.9, 127.3, 128.4, 128.6, 130.7, 131.0, 131.6, 131.9, 132.6, 132.7, 145.5, 145.6, 146.0, 146.1, 148.1, 148.3 (Ar); ^{31}P NMR ($CDCl_3$): δ 124.2 ($^1J_{P\text{-}Se}$ = 920.9 Hz); ^{77}Se NMR ($CDCl_3$): δ -229.1 ($^1J_{P\text{-}Se}$ = 920.9 Hz); MS (EI) m/z 514 (M^+); HRMS Calcd for $C_{29}H_{23}O_2PSe$: 514.0595, Found: 514.0574.

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

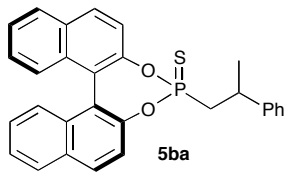
(S_{ax})-4-(2-Phenylpropyl)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphophepin-4-oxide (5aa)



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_2Cl_2 : hexane : EtOAc = 5 : 5 : 1, Rf = 0.35) 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 ($CDCl_3$): δ 1.51 (d, J = 7.3 Hz, 1.5H, CH_3), 1.63 (d, J = 7.3 Hz, 1.5H, CH_3), 2.16-2.36 (m, 2H, CH_2), 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); ^{13}C NMR ($CDCl_3$): δ 22.9 (d, $^3J_{C\text{-}P}$ = 3.3 Hz, CH_3), 23.0 (CH_3), 32.0 (d, $^1J_{C\text{-}P}$ = 70.3 Hz, CH_2), 33.2 (d, $^1J_{C\text{-}P}$ = 71.1 Hz, CH_2), 34.1 (d, $^2J_{C\text{-}P}$ = 2.5 Hz, CH), 34.4 (d, $^2J_{C\text{-}P}$ = 2.5 Hz, CH), 120.0, 120.1, 121.1, 121.7, 121.8, 121.8, 121.8, 121.9, 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, 131.2, 131.4, 131.5, 131.8, 132.3, 132.4, 132.5, 145.6, 145.7, 145.8, 145.8, 145.9, 147.2, 147.3, 147.3, 147.3, 147.4; ^{31}P NMR ($CDCl_3$): δ 41.3, 41.7; MS (EI) m/z 450 (M^+); HRMS Calcd for $C_{29}H_{23}O_3P$: 450.1358, Found: 450.1412.

(S_{ax})-4-(2-Phenyethyl)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphophepin-4-sulfide (5ba)



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_2Cl_2 : hexane = 1 : 3, Rf = 0.28) **5ba** (179 mg, 38%, dr = 59 : 41) containing small amounts of unidentified products (^1H NMR δ

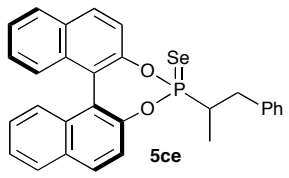
0.84 ~ 1.37) as a white solid.

IR (KBr): 3058, 3023, 2965, 1619, 1588, 1507, 1461, 1432, 1396, 1361, 1322, 1220, 1155, 1069, 980, 959, 915, 862, 748, 698, 644, 567, 544, 526, 419 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 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, 0.5 Hz, Ar), 7.89-8.05 (m, 3.5H, Ar); ^{13}C NMR ($CDCl_3$): δ 22.8 (d, $^{3}J_{C\text{-}P}$ = 10.8 Hz, CH_3), 23.0 (d, $^{3}J_{C\text{-}P}$ = 5.8 Hz, CH_3), 35.0 (CH), 35.3 (CH), 38.7 (d, $^{1}J_{C\text{-}P}$ = 92.6 Hz, CH_2), 40.5 (d, $^{1}J_{C\text{-}P}$ = 92.6 Hz, CH_2), 120.4, 120.5, 121.8, 122.2, 122.2, 122.4, 122.5, 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, 131.5, 131.8, 131.8, 131.9, 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 ($CDCl_3$): δ 117.1, 116.5; MS (EI) m/z 466 (M^+); HRMS Calcd for $C_{29}H_{23}O_2PS$: 466.1156, Found: 466.1137.

The product **5ba** was also synthesized via Procedure A, with **1b** (382 mg, 1 mmol), xylene (7 mL), α-methylstyrene (**4a**) (0.16 mL, 1.2 mmol) at reflux temperature for 69 h. Purification by column chromatography on silica gel **5ba** (179 mg, 40%, dr = 55 : 45).

(S_{ax})-4-(1-Phenyl-2-propyl)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-selenide (5ce)

The following compound was synthesized via Procedure B, with **2c** (110.1 mg, 0.2 mmol), *cis*-β-methylstyrene (**4e**) (78 μL, 0.6 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 2、Rf = 0.33) gave **5ce** (46.9 mg, 46%, 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_2Cl_2 : hexane = 2 : 3 as eluent.



5ce

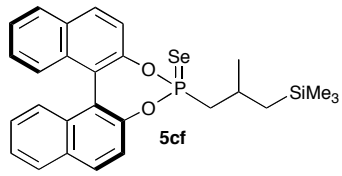
(dr: 1 : 99, The first fraction on HPLC): $[\alpha]_D^{27}$ = +215 (C = 0.094, $CHCl_3$); mp: 231-236 °C; IR (KBr): 3337, 3070, 3020, 2924, 2854, 1726, 1619, 1587, 1508, 1462, 1432, 1379, 1362, 1321, 1281, 1261, 1222, 1189, 1160, 1097, 1067, 1029, 1008, 977, 949, 898, 872, 851, 836, 823, 814, 773, 757, 735, 695, 653, 631, 602, 585, 568, 528, 509 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 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 ($CDCl_3$): δ 12.9 (CH_3), 36.5 (CH_2), 38.8 (d, $^{1}J_{C\text{-}P}$ = 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 ($CDCl_3$): δ 133.8 ($J_{P\text{-}Se}$ = 924.4 Hz); ^{77}Se NMR ($CDCl_3$): δ 299.6 ($J_{P\text{-}Se}$ = 927.7 Hz); MS (EI) m/z 514 (M^+); HRMS Calcd for $C_{29}H_{23}O_2PSe$: 514.0601, Found: 514.0588.

(dr: 99 : 1, The second fraction on HPLC): $[\alpha]_D^{27}$ = +301 (C = 0.115, $CHCl_3$); mp: 245-248°C; IR (KBr): 3430,

3061, 3025, 2925, 2852, 1619, 1589, 1504, 1460, 1400, 1373, 1317, 1257, 1224, 1193, 1156, 1144, 1099, 1070, 1028, 1011, 979, 956, 861, 841, 818, 772, 749, 719, 695, 650, 602, 587, 567, 524, 508 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.11 (dd, J = 6.8 Hz, 21.5 Hz, 3H, CH_3), 2.45-2.55 (m, 1H, CH), 2.67 (dt, J = 10.2 Hz, 13.7 Hz, 1H, CH_2), 3.44 (ddd, J = 3.9 Hz, 10.7 Hz, 13.9 Hz, 1H, CH_2), 7.09 (d, J = 7.8 Hz, 1H, Ar), 7.17-7.33 (m, 9H, Ar), 7.38-7.45 (m, 2H, Ar), 7.50-7.53 (m, 1H, Ar), 7.87-7.91 (m, 2H, Ar), 7.96 (d, J = 9.3 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 13.6 (CH_3), 36.6 (CH_2), 38.8 (d, $^1J_{C\text{-}P}$ = 76.1 Hz, CH), 120.2, 120.2, 121.9, 121.9, 122.4, 122.5, 122.7, 122.7, 125.6, 125.9, 126.5, 126.8, 126.9, 127.3, 128.4, 128.6, 128.6, 129.4, 130.7, 130.8, 131.5, 131.9, 132.6, 132.7, 137.8, 137.9, 146.1, 146.2, 148.3, 148.4 (Ar); ^{31}P NMR ($CDCl_3$): δ 134.0 ($J_{P\text{-}Se}$ = 921.5 Hz); ^{77}Se NMR ($CDCl_3$): δ 299.3 ($J_{P\text{-}Se}$ = 921.6 Hz); MS (EI) m/z 514 (M^+); HRMS Calcd for $C_{29}H_{23}O_2PSe$: 514.0601, Found: 514.0588.

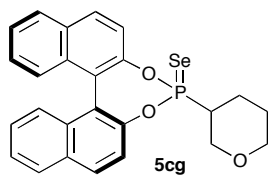
The product **5ce** was also synthesized via Procedure B, with **2c** (552.8 mg, 1 mmol), *trans*-β-methylstyrene (**4e'**) (0.35 μL, 3 mmol). Purification by column chromatography on silica gel gave **5ce** (46.9 mg, 51%, dr = 56 : 44) as a white powder.

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



The following compound was synthesized via Procedure A, with **2c** (164.8 mg, 0.3 mmol), (2-methylpropenyl)trimethylsilane (**4f**) (63 μL, 0.36 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.38) gave **5cf** (85.6 mg, 55%, dr = 47 : 53) as a colorless solid. IR (KBr): 2952, 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 ($CDCl_3$): δ 0.02 (s, $Si(C\underline{H}_3)_3$, 4.5H), 0.10 (s, $Si(C\underline{H}_3)_3$, 4.5H), 0.89 (dd, J = 14.6 Hz, 4.9 Hz, 1H, $C\underline{H}_2SiMe_3$), 1.08 (dd, J = 14.6 Hz, 4.4 Hz, 1H, $C\underline{H}_2SiMe_3$), 1.13 (d, J = 6.8 Hz, 1.5H, $CHC\underline{H}_3$), 1.31 (d, J = 6.8 Hz, 1.5H, $CHC\underline{H}_3$), 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, 1.5H, Ar), 8.04 (d, J = 8.8 Hz, 1H, Ar), 8.06 (d, J = 8.8 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 0.0 ($Si(\underline{C}H_3)_3$), 0.1 ($Si(\underline{C}H_3)_3$), 24.3 (d, $^2J_{C\text{-}P}$ = 10.8 Hz, $CH_2\underline{C}H$), 24.9 (d, $^2J_{C\text{-}P}$ = 9.1 Hz, $CH_2\underline{C}H$), 27.2, 27.3, 27.4, 27.5, 44.5 (d, $^1J_{C\text{-}P}$ = 74.4 Hz, $\underline{C}H_2CH$), 45.3 (d, $^1J_{C\text{-}P}$ = 75.2 Hz, $\underline{C}H_2CH$), 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, 148.9, 149.0 (Ar); ^{31}P NMR ($CDCl_3$): δ 125.6 ($^1J_{P\text{-}Se}$ = 920.7 Hz), 125.7 ($^1J_{P\text{-}Se}$ = 920.7 Hz); ^{77}Se NMR ($CDCl_3$): δ -229.6 ($^1J_{P\text{-}Se}$ = 915.0 Hz), -227.7 ($^1J_{P\text{-}Se}$ = 921.1 Hz); MS (EI) m/z 524 (M^+); HRMS Calcd for $C_{27}H_{29}O_2PSeSi$: 524.0840, Found: 524.0854.

(S_{ax})-4-(3-Tetrahydropyran-1-yl)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphophepin-4-selenide (5cg)



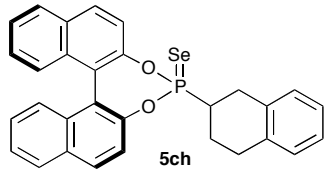
The following compound was synthesized via Procedure A, with **2c** (550 mg, 1 mmol), 3,4-dihydro-2*H*-pyrane (**4g**) (1.81 mL, 20 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 1, Rf = 0.39 for ***(S_{ax}, R)*-5cg**, 0.31

for ***(S_{ax}, S)*-5cg**) gave **5cg** (294 mg, 61%, dr = 38 : 62) as a white powder. Separation of a mixture of diastereomers was performed on a recycling preparative HPLC equipped with mightysil using CH_2Cl_2 as eluent.

***(S_{ax}, R)*-5cg** (dr > 99 : 1, The first fraction on HPLC): $[\alpha]_D^{26}$ = +367 (c = 1.03, $CHCl_3$); 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}; ^1H NMR ($CDCl_3$): δ 1.74 (m, 2H, $CHCH_2C\underline{H}_2$), 2.10 (m, 1H, $CHC\underline{H}_2CH_2$), 2.30 (br s, 1H, C<u>H</u>), 2.57 (m, 1H, $CHC\underline{H}_2CH_2$), 3.44 (dt, *J* = 3.1 Hz, 11.4 Hz, 1H, $CHCH_2OC\underline{H}_2$), 3.67 (dt, *J* = 2.6 Hz, 11.1 Hz, 1H, $CHCH_2OC\underline{H}_2$), 3.92 (br d, *J* = 11.7 Hz, 1H, $CHC\underline{H}_2OCH_2$), 4.10 (br d, *J* = 11.2 Hz, 1H, $CHC\underline{H}_2OCH_2$), 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 ($CDCl_3$): δ 23.9 ($CHCH_2\underline{C}H_2$), 25.0 (d, $^2J_{C\text{-}P}$ = 14.9 Hz, $CH\underline{C}H_2CH_2$), 40.8 (d, $^1J_{C\text{-}P}$ = 77.6 Hz, <u>C</u>H), 67.1 (d, $^2J_{C\text{-}P}$ = 5.8 Hz, $CH\underline{C}H_2OCH_2$), 68.0 ($CHCH_2O\underline{C}H_2$), 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 ($CDCl_3$): δ 123.4 ($^1J_{P\text{-}Se}$ = 926.8 Hz); ^{77}Se NMR ($CDCl_3$): δ -262.6 ($^1J_{P\text{-}Se}$ = 926.8 Hz); MS (EI) m/z 480 (M^+); HRMS Calcd for $C_{25}H_{21}O_3PSe$: 480.0394, Found: 480.0395.

***(S_{ax}, S)*-5cg** (dr > 1 : 99, The second fraction on HPLC) $[\alpha]_D^{27}$ = +377 (c = 0.668, $CHCl_3$); 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}; ^1H NMR ($CDCl_3$): δ 1.54-1.65 (m, 2H, $CHCH_2C\underline{H}_2$), 1.92-2.05 (m, 1H, $CHC\underline{H}_2CH_2$), 2.08 (br s, 1H, C<u>H</u>), 2.56 (m, 1H, $CHC\underline{H}_2CH_2$), 3.47 (dt, *J* = 3.4 Hz, 11.2 Hz, 1H, $CHCH_2OC\underline{H}_2$), 3.78 (dt, *J* = 2.4 Hz, 11.2 Hz, 1H, $CHCH_2OC\underline{H}_2$), 3.94 (br d, *J* = 11.7 Hz, 1H, $CHC\underline{H}_2OCH_2$), 4.38 (br d, *J* = 11.2 Hz, 1H, $CHC\underline{H}_2OCH_2$), 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 ($CDCl_3$): δ 23.7 (d, $^3J_{C\text{-}P}$ = 3.3 Hz, $CHCH_2\underline{C}H_2$), 24.9 (d, $^2J_{C\text{-}P}$ = 13.2 Hz, $CH\underline{C}H_2CH_2$), 40.5 (d, $^1J_{C\text{-}P}$ = 78.5 Hz, <u>C</u>H), 67.2 (d, $^2J_{C\text{-}P}$ = 9.9 Hz, $CH\underline{C}H_2OCH_2$), 68.1 ($CHCH_2O\underline{C}H_2$), 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, 132.7, 145.5, 145.6, 148.2, 148.4 (Ar); ^{31}P NMR ($CDCl_3$): δ 121.9 ($^1J_{P\text{-}Se}$ = 926.8 Hz); ^{77}Se NMR ($CDCl_3$): δ -263.6 ($^1J_{P\text{-}Se}$ = 926.8 Hz); MS (EI) m/z 480 (M^+); HRMS Calcd for $C_{25}H_{21}O_3PSe$: 480.0394, Found: 480.0395.

(*S*_{ax})-4-(1,2,3,4-Tetrahydronaphthalen-2-yl)-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (5ch)



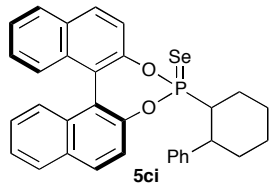
The following compound was synthesized via Procedure B, with **2c** (429.7 mg, 0.77 mmol), 1,2-dihydronaphtalene (**4h**) (0.39 mL, 3 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 2, Rf = 0.43) gave **5ci** (250.6 mg, 62%, dr = 54 : 46) as a white powder. Separation of a mixture of diastereomers was performed on a recycling preparative HPLC equipped with mightysil using CH_2Cl_2 : hexane = 2 : 3 as eluent.

(dr = 99 : 1, The first fraction on HPLC): $[\alpha]_D^{27}$ = +135 (C = 0.052, $CHCl_3$); 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 ($CDCl_3$): δ 1.93 (m, 1H, CH), 2.21 (m, 1H, $CHC\underline{H_2}CH_2$), 2.50 (m, 1H, $CHC\underline{H_2}CH_2$), 2.66 (m, 1H, $CHCH_2C\underline{H_2}$), 2.83 (m, 1H, $CHCH_2C\underline{H_2}$), 3.14 (m, 1H, $CHC\underline{H_2}$), 3.35 (m, 1H, $CHC\underline{H_2}$), 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 ($CDCl_3$): δ 23.3 ($CH\underline{C}H_2CH_2C$), 28.0 (d, $^{2}J_{C\text{-}P}$ = 15.7 Hz, $CH\underline{C}H_2C$), 29.1 ($CHCH_2\underline{C}H_2C$), 38.3 (d, $^{1}J_{C\text{-}P}$ = 81.9 Hz, <u>C</u>H), 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 ($CDCl_3$): δ 131.8 ($^{1}J_{P\text{-}Se}$ = 923.6 Hz), ^{77}Se NMR ($CDCl_3$): δ -295.8 ($^{1}J_{P\text{-}Se}$ = 927.7 Hz); MS (EI) m/z 526 (M^+); HRMS Calcd for $C_{30}H_{23}O_2PSe$: 526.0601, Found: 526.0588.

(dr: 2 : 98, The second fraction on HPLC): $[\alpha]_D^{27}$ = +225 (C = 0.063, $CHCl_3$); mp: 143-146 °C; IR (KBr): 3424, 2928, 1588, 1507, 1461, 1433, 1321, 1221, 1191, 1155, 1069, 977, 952, 852, 837, 812, 791, 745, 696, 653, 606, 565 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.03 (m, 1H, CH), 2.37 (m, 1H, $CHC\underline{H_2}CH_2$), 2.48 (m, 1H, $CHC\underline{H_2}CH_2$), 2.78 (m, 1H, $CHCH_2C\underline{H_2}$), 2.94 (d, *J* = 17.5 Hz, 2H, $CHC\underline{H_2}$), 3.17 (m, 1H, $CHCH_2C\underline{H_2}$), 6.96-7.04 (m, 4H, Ar), 7.19-7.56 (m, 8H, Ar), 7.84-7.92 (m, 3H Ar), 7.99 (d, *J* = 8.8 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 23.4 ($CH\underline{C}H_2CH_2C$), 28.1 (d, $^{2}J_{C\text{-}P}$ = 16.5 Hz, $CH\underline{C}H_2C$), 29.1 ($CHCH_2\underline{C}H_2C$), 38.5 (d, $^{1}J_{C\text{-}P}$ = 82.7 Hz, <u>C</u>H), 120.0, 121.9, 122.4, 122.7, 125.7, 125.9, 126.0, 126.1, 126.6, 126.9, 126.9, 127.2, 128.4, 128.6, 128.8, 128.9, 130.8, 131.0, 131.5, 132.6, 132.7, 133.8, 134.0, 135.2, 146.1, 146.2, 148.3, 148.4 (Ar); ^{31}P NMR ($CDCl_3$): δ 130.7 ($^{1}J_{P\text{-}Se}$ = 923.6 Hz), ^{77}Se NMR ($CDCl_3$): δ -297.3 ($^{1}J_{P\text{-}Se}$ = 927.7 Hz); MS (EI) m/z 526 (M^+); HRMS Calcd for $C_{30}H_{23}O_2PSe$: 526.0601, Found: 526.0588.

(S_{ax})-4-(2-Phenylcyclohexyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-selenide (5ci)



5ci

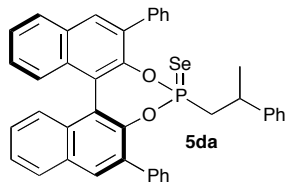
The following compound was synthesized via Procedure B, with **2c** (550 mg, 1 mmol), 1-phenyl-1-cyclohexene (**4i**) (0.48 mL, 3 mmol). Purification by column chromatography on silica gel (AcOEt : hexane = 1 : 30, Rf = 0.25, 0.15) gave diastereomers of **5ci** (89.9 mg, 17%, dr = 85 : 0 : 0 : 15, The 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): $[\alpha]_D^{29}$ = +336 (c = 0.4960, $CHCl_3$); mp: 98-100 ºC; 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 ($CDCl_3$): δ 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 ($CDCl_3$): δ 22.6, 23.6 (d, $^{2}J_{C\text{-}P}$ = 9.4 Hz), 24.6, 29.5 (d, $^{2}J_{C\text{-}P}$ = 7.5 Hz), 41.8, 46.2 (d, $^{1}J_{C\text{-}P}$ = 74.2 Hz, <u>C</u>H), 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,

148.9 (Ar); ^{31}P NMR ($CDCl_3$): δ 120.4 ($^1J_{P\text{-}Se}$ = 917.7 Hz): ^{77}Se NMR ($CDCl_3$: δ -273.1 ($J_{P\text{-}Se}$ = 915.0 Hz), ; MS (EI) m/z 554 (M^+); HRMS Calcd for $C_{32}H_{27}O_2PSe$: 554.0914, Found: 554.0909.

(dr = 0 : 95 : 5 : 0): $[\alpha]_D^{30}$ = +289 (c = 0.3820, $CHCl_3$); mp: 158-160 ºC; IR (KBr): 2929, 2857, 1589, 1508, 1463, 1449, 1323, 1224, 1193, 1156, 1069, 979, 951, 833, 815, 751, 721, 696, 652, 610, 603, 588, 564, 537, 526, 457 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.46-1.61 (m, 2H), 1.70-1.87 (m, 2H), 2.01-2.05 (m, 1H), 2.45-2.60 (m, 2H), 2.90-2.95 (m, 1H), 3.18-3.31 (m, 2H), 5.91 (d, *J* = 9.0 Hz, 1H, Ar), 7.15-7.47 (m, 10H, Ar), 7.71-7.74 (m, 3H, Ar), 7.84 (d, *J* = 8.1 Hz, 1H, Ar), 7.88 (d, *J* = 8.1 Hz, 1H, Ar), 7.96 (d, *J* = 8.5 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 21.6 (d, $^2J_{C\text{-}P}$ = 2.8 Hz), 25.7, 27.8 (d, $^2J_{C\text{-}P}$ = 1.9 Hz), 28.2, 45.3 (d, $^1J_{C\text{-}P}$ = 71.4 Hz, CH), 120.8, 121.9, 122.0, 122.5, 122.8, 122.9, 125.4, 125.5, 126.2, 126.4, 126.8, 127.2, 128.1, 128.2, 128.4, 130.1, 130.2, 131.2, 131.7, 132.4, 132.5, 143.4, 145.6, 145.7, 148.6, 148.7 (Ar); ^{31}P NMR ($CDCl_3$): δ 123.6 ($^1J_{P\text{-}Se}$ = 923.6 Hz), ^{77}Se NMR ($CDCl_3$): δ 189.7 (dm); MS (EI) m/z 554 (M^+); HRMS Calcd for $C_{32}H_{27}O_2PSe$: 554.0914, Found: 554.0931.

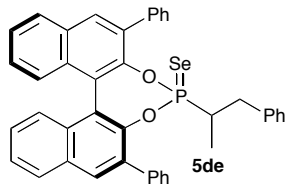
(S_{ax})-2,6-Diphenyl-4-(2-phenylpropyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (5da)



5da

The following compound was synthesized via Procedure B, with **2c** (211 mg, 0.3 mmol), α-methylstyrene (**4a**) (49 mg, 0.4 mmol). Purification by column chromatography on silica gel (CH_2Cl_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 ($CDCl_3$): δ 0.88 (d, *J* = 6.8 Hz, 1.5H, CH_3), 1.01 (d, *J* = 6.8 Hz, 1.5H, CH_3), 1.43 (ddd, *J* = 22.3 Hz, *J* = 11.2 Hz, *J* = 3.5 Hz, 0.5H), 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 ($CDCl_3$): δ 21.7 ($^3J_{C\text{-}P}$ = 4.1 Hz, CH_3), 23.4 ($^3J_{C\text{-}P}$ = 6.6 Hz, CH_3), 35.1 (CH), 35.3 (CH), 41.3 ($^1J_{C\text{-}P}$ = 75.2 Hz, CH_2), 43.1 ($^1J_{C\text{-}P}$ = 73.5 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 ($CDCl_3$): δ 118.7 ($^1J_{P\text{-}Se}$ = 929.6 Hz), 121.2 ($^1J_{P\text{-}Se}$ = 929.6 Hz), ^{77}Se NMR ($CDCl_3$): δ 235.9 ($^1J_{P\text{-}Se}$ = 933.3 Hz), 205.2 ($^1J_{P\text{-}Se}$ = 933.3 Hz); MS (EI) m/z 666 (M^+); HRMS Calcd for $C_{41}H_{31}O_2PSe$: 666.1227, Found: 666.1210.

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



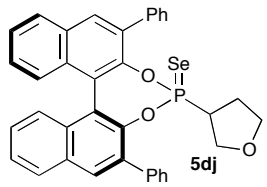
5de

The following compound was synthesized via Procedure B, with **2c** (140.3 mg, 0.2 mmol), *cis*-β-methylstyrene (**4e'**) (130 μL, 1 mmol). Purification by column chromatography on silica gel (CH_2Cl_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,

1602, 1496, 1453, 1406, 1377, 1362, 1333, 1305, 1264, 1245, 1192, 1176, 1149, 1132, 1076, 1030, 1004, 989, 961, 884, 861, 830, 765, 751, 725, 697, 677, 661, 614, 606, 583, 571, 558, 513 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.64 (d, J = 6.8 Hz, 1.5H, CH_2), 0.70 (d, J = 6.4 Hz, 1.5H, CH_2), 1.90-2.19 (m, 2.5H, CH), 2.22-2.29 (m, 0.5H, CH), 6.71 (d, J = 6.8 Hz, 1H, Ar), 6.90 (d, 6.4 Hz, 1H, Ar), 7.09-7.21 (m, 4H, Ar), 7.30-7.42 (m, 9H, Ar), 7.49-7.55 (m, 2H, Ar), 7.64-7.68 (m, 3H, Ar), 7.80 (d, J = 7.8 Hz, 1H, Ar), 8.01 (d, J = 8.3 Hz, 2H, Ar), 8.05 (s, 0.5H, Ar), 8.12 (s, 1H, Ar), 8.13 (s, 0.5H, Ar); ^{13}C NMR ($CDCl_3$): δ 11.6, 12.7, 34.9, 35.7, 37.9 (d, $^{1}J_{C\text{-}P}$ = 76.0 Hz, CH), 38.8 (d, $^{1}J_{C\text{-}P}$ = 75.1 Hz, CH), 123.5, 124.0, 124.1, 126.0, 126.1, 126.2, 126.3, 126.5, 126.7, 126.9, 127.1, 127.2, 127.5, 127.6, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 128.9, 129.0, 129.1, 129.3, 129.9, 130.0, 130.2, 130.5, 130.9, 131.1, 131.2, 131.5, 132.0, 132.3, 132.4, 133.8, 135.1, 136.5, 136.7, 136.8, 137.4, 137.6, 137.7, 137.9, 143.9, 144.0, 146.2, 146.4 (Ar); ^{31}P NMR ($CDCl_3$): δ 131.1 ($^{1}J_{P\text{-}Se}$ = 929.6 Hz), 131.4 ($^{1}J_{P\text{-}Se}$ = 929.6 Hz); ^{77}Se NMR ($CDCl_3$): δ -291.3 ($^{1}J_{P\text{-}Se}$ = 927.2 Hz), -285.9 ($^{1}J_{P\text{-}Se}$ = 927.2 Hz); MS (EI) m/z 666 (M^+); HRMS Calcd for $C_{41}H_{31}O_2PSe$: 666.1227, Found: 666.1229.

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.

(S_{ax})-2,6-Diphenyl-4-(tetrahydrofuran-3-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (5dj)



5dj

The following compound was synthesized via Procedure B, with **2c** (351.3 mg, 0.5 mmol), 2,5-dihydrofuran (**4j'**) (1.5 mL, 40 equiv). Purification by column chromatography on silica gel (CH_2Cl_2 : 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 CH_2Cl_2 : hexane = 1 : 3 as eluent.

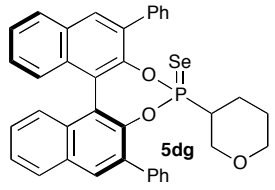
(dr = > 1 : 99, The first fraction on TLC): $[\alpha]_D^{30}$ = +296 (c = 1.000, $CHCl_3$); mp: 129-144 ºC; IR (KBr): 3055, 2997, 2947, 2865, 1498, 1462, 1453, 1406, 1246, 1229, 1190, 1150, 1077, 988, 962, 917, 896, 884, 862, 831, 781, 767, 752, 724, 699, 678, 616, 512 cm^{-1}; ^{1}H NMR ($CDCl_3$): 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); ^{13}C NMR ($CDCl_3$): δ 26.9 (d, J = 2.5 Hz, $CHCH_2CH_2$), 40.9 (d, $^{1}J_{C\text{-}P}$ = 83.4 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, 131.9, 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); ^{31}P NMR ($CDCl_3$): δ 27.1 ($^{1}J_{P\text{-}Se}$ = 941.4 Hz); ^{77}Se NMR ($CDCl_3$): δ -300.9 ($^{1}J_{P\text{-}Se}$ = 939.4 Hz); MS (EI) m/z 618 (M^+); HRMS Calcd for $C_{36}H_{27}O_3PSe$: 618.0863, Found: 618.0844.

(dr = > 99 : 1, The second fraction on TLC): $[\alpha]_D^{29}$ = +292 (c = 0.474, $CHCl_3$); mp: 173-183 ºC; IR (KBr): 3055, 2925, 2867, 2360, 1498, 1452, 1406, 1246, 1192, 1150, 1078, 988, 962, 884, 862, 831, 766, 751, 723, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$): 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

(m,1H), 7.31-7.45 (m, 8H, Ar), 7.49-7.55 (m, 4H, Ar), 7.63-7.66 (m, 2H, Ar), 7.73-7.75 (m, 2H, Ar), 8.01 (d, J = 8.4 Hz, 2H, Ar), 8.12 (s, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 28.4, 41.1 (d, $^1J_{C\text{-}P}$ = 83.4 Hz, CH), 67.5 (d, J = 9.1 Hz), 67.9 (d, J = 9.1 Hz), 123.7, 124.1, 126.1, 126.2, 126.6, 126.8, 127.0, 127.1, 127.6, 127.9, 128.5, 128.6, 128.7, 128.9, 130.0, 130.1, 130.4, 131.0, 131.1, 131.7, 132.0, 132.2, 132.3, 133.3, 136.3, 137.5 (Ar); ^{31}P NMR ($CDCl_3$): δ 125.3 ($^1J_{P\text{-}Se}$ = 938.4 Hz); ^{77}Se NMR ($CDCl_3$): δ -295.9 ($^1J_{P\text{-}Se}$ = 939.4 Hz); MS (EI) m/z 618 (M^+); HRMS Calcd for $C_{36}H_{27}O_3PSe$: 618.0863, Found: 618.0857.

The product **5dj** was synthesized via Procedure B, with **2c** (702.5 mg, 1.0 mmol), 2,3-dihydrofuran (**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_{ax})-2,6-Diphenyl-4-(3-Tetrahydropyran-1-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (5dg)



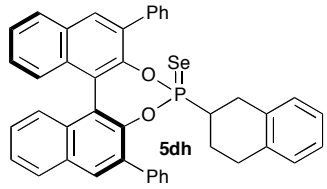
The following compound was synthesized via Procedure B, with **2c** (351.6 mg, 0.5 mmol), 3,4-dihydro-2*H*-pyrane (**4g**) (0.91 mL, 10 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf =0.25, 0.15) gave each diastereomers **5dg** (147.1 mg, 47%, dr = > 1 : 99 The first fraction on TLC), (31.6 mg, 10%, dr = > 99 : 1, The second fraction on TLC) as white powders.

(dr = > 1 : 99): $[\alpha]_D^{29}$ = +275 (c = 0.3160, $CHCl_3$); mp: 155-162 ºC; IR (KBr): 3055, 2923, 2850, 1595, 1498, 1466, 1452, 1406, 1362, 1333, 1307, 1270, 1245, 1235, 1192, 1175, 1149, 1133, 1098, 1075, 1026, 989, 961, 884, 862, 829, 792, 781, 766, 751, 723, 709, 698, 676, 647, 615, 605, 578, 555, 514, 503 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.18 (br, 1H), 1.12-1.16 (m, 2H), 1.22-1.35 (m, 1H), 2.02-2.12 (m, 1H), 3.03-3.14 (m, 2H), 3.70 (d, J = 10.7 Hz, 1H, CHC$\underline{H_2}$O), δ 3.87 (d, J = 10.2 Hz, 1H, CHC$\underline{H_2}$O), 7.31-7.44 (m, 8H, Ar), 7.46-7.56 (m, 4H, Ar), 7.60-7.62 (m, 2H, Ar), 7.71 (d, J = 8.3 Hz, 2H, Ar),8.01 (d, J = 8.3 Hz, 2H, Ar), 8.09 (s, 1H, Ar), 8.10 (s, 1H, Ar), ^{13}C NMR ($CDCl_3$): δ 23.1 ($CHCH_2\underline{C}H_2$), 25.0 (d, $^2J_{C\text{-}P}$ = 15.7 Hz, $CH\underline{C}H_2CH_2$), 40.4 (d, $^1J_{C\text{-}P}$ = 75.2 Hz, $\underline{C}H$), 66.5 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, $CH\underline{C}H_2OCH_2$), 67.8 ($CHCH_2O\underline{C}H_2$), 123.6, 124.0, 126.1, 126.5, 126.8, 126.9, 127.1, 127.6, 127.9, 128.0, 128.4, 128.6, 128.7, 130.0, 130.4, 130.9, 131.1, 131.6, 131.9, 132.2, 133.6, 135.0, 136.8, 137.5, 143.5, 143.6, 145.7, 145.9, ^{31}P NMR ($CDCl_3$): δ 121.4 ($^1J_{P\text{-}Se}$ = 932.5 Hz), ^{77}Se NMR ($CDCl_3$): δ -261.0 ($J_{P\text{-}Se}$ = 933.2 Hz); MS (EI) m/z 632 (M^+); HRMS Calcd for $C_{37}H_{29}O_3PSe$: 632.1020, Found: 632.1032.

(dr = > 99 : 1): $[\alpha]_D^{29}$ = +241 (c = 0.2630, $CHCl_3$), mp: 167-174 ºC; IR (KBr): 3055, 2954, 2852, 1498, 1452, 1406, 1245, 1192, 1175, 1149, 1131, 1098, 1075, 1029, 989, 961, 884, 863, 829, 781, 766, 751, 724, 709, 698, 615, 577, 514 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.26-1.37 (m, 1H), 1.40-1.48 (m, 2H), 1.80-1.83 (m, 1H), 1.98-2.10 (m, 1H), 2.32 (br d, J = 9.8 Hz, 1H), 3.00 (dt, J = 11.2 Hz, J = 2.4 Hz, 1H), 3.09 (dt, J = 10.7 Hz, J = 3.4 Hz, 1H), 3.71 (br d, 11.7 Hz, 1H), 7.32-7.47 (m, 8H, Ar), 7.51-7.57 (m, 4H, Ar), 7.62-7.64 (m, 2H, Ar), 7.72-7.74 (m, 2H, Ar), 8.00-8.04 (m, 2H, Ar), 8.11 (s, 1H, Ar), 8.12 (s, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 23.3 ($CHCH_2\underline{C}H_2$), 24.8 (d, $^2J_{C\text{-}P}$ = 13.2 Hz, $CH\underline{C}H_2CH_2$), 40.2 (d, $^1J_{C\text{-}P}$ = 76.0 Hz, $\underline{C}H$), 66.7 (d, $^2J_{C\text{-}P}$ = 11.6 Hz, $CH\underline{C}H_2OCH_2$), 68.0

($CHCH_2O\underline{C}H_2$), 123.5, 124.0, 126.1, 126.5, 126.7, 127.0, 127.2, 127.5, 127.9, 128.2, 128.5, 128.6, 128.8, 130.0, 130.5, 131.6, 131.9, 132.0, 132.2, 132.3, 133.8, 135.1, 136.4, 137.5 (Ar), 143.3 (d, J = 9.9 Hz, Ar), 146.0 (d, J = 14.9 Hz, Ar); ^{31}P NMR ($CDCl_3$): δ 118.7 ($^1J_{P\text{-}Se}$ = 932.5 Hz), ^{77}Se NMR ($CDCl_3$): δ -260.8 ($^1J_{P\text{-}Se}$ = 933.3 Hz). MS (EI) m/z 632 (M^+); HRMS Calcd for $C_{37}H_{29}O_3PSe$: 632.1020, Found: 632.1034.

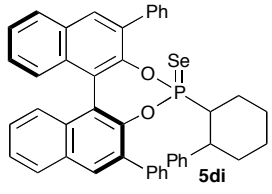
(S_{ax})-2,6-Diphenyl-4-(1,2,3,4-tetrahydronaphthalen-2-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (5dh)



The following compound was synthesized via Procedure B, with **2c** (140.8 mg, 0.2 mmol), 1,2-dihydronaphthalene (**4h**) (127.8 mg, 1 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : 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, 1333, 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}; ^{1}H NMR ($CDCl_3$): δ 0.53 (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); ^{13}C NMR: δ 22.7, 23.0, 27.8, 28.09 (d, J = 18.2 Hz), 28.8, 37.9 (d, $^1J_{C\text{-}P}$ = 80.2 Hz), 38.4 (d, $^1J_{C\text{-}P}$ = 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, 127.9, 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); ^{31}P NMR ($CDCl_3$): δ 129.1 ($^1J_{P\text{-}Se}$ = 932.5 Hz), The signal clue to the minor product was not obtained.; ^{77}Se NMR ($CDCl_3$): δ -299.2 ($^1J_{P\text{-}Se}$ = 927.2 Hz), 286.0 ($^1J_{P\text{-}Se}$ = 927.2 Hz); MS (EI) m/z 678 (M^+); HRMS Calcd for $C_{41}H_{31}O_2PSe$: 678.1227, Found: 678.1232.

(S_{ax})-2,6-Diphenyl-4-(2-phenylcyclohexyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-selenide (5di)



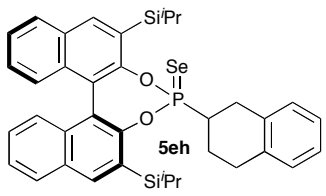
The following compound was synthesized via Procedure B, with **2c** (351.6 mg, 0.5 mmol), 1-phenyl-cyclohexene (**4i**) (0.91 mL, 10 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane : AcOEt)= 1 : 60 : 1, Rf = 0.23, 0.20) gave each diastereomers **5di** (178 mg, 51%, dr = 96 : 4) as white powders. Separation of a mixture of diastereomers was performed on silica gel column chromatography using CH_2Cl_2 : hexane = 1 : 3 as eluent. (dr = > 99 : 1, The first fraction on TLC): $[\alpha]_D^{29}$ = +272 (c = 0.416, $CHCl_3$); mp: 151-154 ºC; 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}; ^{1}H NMR ($CDCl_3$): 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 ($CDCl_3$): δ 20.9, 24.2, 24.5 (d, J = 14.0 Hz), 33.1 (d, J = 7.4 Hz), 41.2, 46.0 (d, $^1J_{C\text{-}P}$ = 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 ($CDCl_3$): δ 124.8 ($^1J_{P\text{-}Se}$ = 932.5 Hz); ^{77}Se NMR ($CDCl_3$): δ 207.3 ($^1J_{P\text{-}Se}$ = 932.5 Hz); MS (EI) m/z 706 (M^+); HRMS Calcd for $C_{44}H_{35}O_2PSe$:, Found:706.1538.

(dr = 3 : 97, The second fraction on TLC): $[\alpha]_D^{29}$ = +177 (c = 0.1680, $CHCl_3$), mp: 146-147 ºC; IR (KBr): 2925, 1497, 1451, 1406, 1192, 1175, 1149, 960, 884, 856, 826, 778, 766, 752, 724, 698, 682 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.12-1.35 (m, 3H), 1.38-1.49 (m, 3H), 1.67-1.70 (m, 1H), 1.77-1.88 (m, 1H), 2.29 (ddt, J = 20.0 Hz, 12.2 Hz, 3.9 Hz, 1H), 2.44-2.48 (m, 1H), 6.84 (d, J = 6.8 Hz, 2H, Ar), 7.0-7.04 (m, 3H, Ar), 7.25-7.43 (m, 7H, Ar), 7.45-7.59 (m, 7H, Ar), 7.83 (d, J = 7.3 Hz, 2H, Ar), 7.93 (d, J = 8.3 Hz, 1H, Ar), 7.98 (s, 1H, Ar), 8.00 (d, J = 8.3 Hz, 1H, Ar), 8.09 (s, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 20.0, 23.2, 25.3 (d, $^2J_{C\text{-}P}$ = 13.2 Hz), 33.9 (d, $^2J_{C\text{-}P}$ = 14.9 Hz), 39.5, 47.6 (d, $^1J_{C\text{-}P}$ = 74.4 Hz), 123.5, 124.1, 125.7, 125.8, 125.9, 126.3, 126.6, 126.9, 127.2, 127.3, 127.4, 127.9, 128.3, 128.4, 128.5, 128.9, 130.1, 130.3, 131.1, 131.7, 132.3, 132.5, 133.7, 135.5, 137.4, 137.8, 141.8, 143.9 (d, J = 10.8 Hz), 146.7 (d, J = 14.9 Hz); ^{31}P NMR ($CDCl_3$): δ 121.7 ($^1J_{P\text{-}Se}$ = 944.4 Hz); ^{77}Se NMR ($CDCl_3$): δ -214.9 (dm); MS (EI) m/z 706 (M^+); HRMS Calcd for $C_{44}H_{35}O_2PSe$:, Found:706.1544.

(S_{ax})-4-(1,2,3,4-Tetrahydronaphthalen-2-yl)-2,6-bis(triisopropylsilyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (5eh)

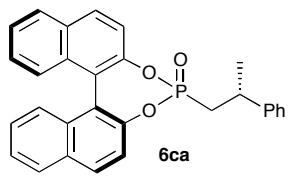
The following compound was synthesized via Procedure B, with **2c** (258.8 mg, 0.3 mmol), 1,2-dihydronaphtalene (196 μL, 1.5 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 2, Rf = 0.53) gave **5eh** (168 mg, 67%, dr = 8 : 92) as a white powder.



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: δ 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), 7.94 (d, J = 8.3 Hz, 1H, Ar), 8.13 (s, 1H, Ar), 8.14 (s, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 12.5, 13.0, 19.1, 19.3, 19.5, 26.0, 29.2 (d, $^2J_{C\text{-}P}$ = 18.2 Hz, CH$\underline{C}$H$_2$CH$_2$), 30.5 (d, $^2J_{C\text{-}P}$ = 5.8 Hz, CH$\underline{C}$H$_2$C), 44.1 (d, $^1J_{C\text{-}P}$ = 80.2 Hz), 120.5, 121.9, 125.2, 125.3, 125.7, 126.0, 126.1, 126.4, 126.8, 126.9, 127.2, 128.2, 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 ($CDCl_3$): δ 117.0 ($^1J_{P\text{-}Se}$ = 923.6 Hz), δ 118.6 ($^1J_{P\text{-}Se}$ = 923.6 Hz); ^{77}Se NMR ($CDCl_3$): δ -213.2 ($^1J_{P\text{-}Se}$ = 921.1 Hz), The signal due to the minor product was not observed.

• Deselenation-oxidation of phosphonoselenoic acid esters **5**

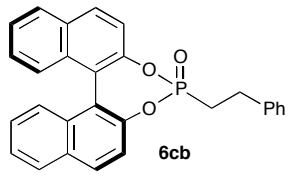
(S_{ax})-4-(2-Phenylpropyl)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphophepin-4-oxide (6ca)



6ca

To a 10 mL two-necked flask were added selenophosphonate **6ca** (154 mg, 0.3 mmol), CH_2Cl_2 (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_2Cl_2 : hexane : AcOEt = 5 : 5 : 1) gave **6ca** (117 mg, 86%) as a white solid. $[a]_D^{28}$ = +320 (C = 0.555, $CHCl_3$); 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, 656, 605, 570, 554, 529 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.37 (d, J = 7.3 Hz, 3H, CH_3), 2.09 (m, 1H, CH_2), 2.13 (m, 1H, CH_2), 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): ^{13}C NMR ($CDCl_3$): δ 22.8 (d, $^3J_{C\text{-}P}$ = 10.8 Hz, CH_3), 32.8 (d, $^1J_{C\text{-}P}$ = 129.0 Hz, CH_2), 34.0 (d, $^2J_{C\text{-}P}$ = 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); ^{31}P NMR ($CDCl_3$): δ 41.7; MS (EI) m/z 450 (M^+); HRMS Calcd for $C_{29}H_{23}O_3P$: 450.1385, Found: 450.1385.

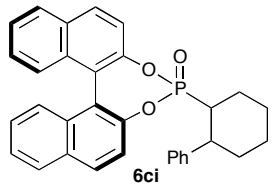
(S_{ax})-4-(2-Phenylethyl)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphophepin-4-oxide (6cb)



6cb

To a 30 mL round-bottom flask were added selenophosphate **6cb** (249.5 mg, 0.5 mmol), CH_2Cl_2 (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_2Cl_2, 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; $[\alpha]_D^{29}$ = +372 (c = 1.000, $CHCl_3$) mp: 218-221 ºC 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^{-1}; ^1H NMR ($CDCl_3$): 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); ^{13}C NMR ($CDCl_3$): δ 25.8 (d, $^2J_{C\text{-}P}$ = 130.7 Hz), 28.1 (d, $^1J_{C\text{-}P}$ = 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); ^{31}P NMR ($CDCl_3$): δ 41.7 (s); MS (EI) m/z 436 (M^+); HRMS Calcd for $C_{28}H_{21}O_3P$:436.1228, Found:436.1224.

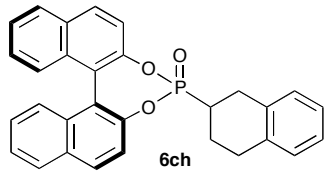
(S_{ax})-4-(2-Phenylcyclohexyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-oxide (6ci)



6ci

To a 30 mL round-bottom flask were added selenophosphate **5ci** (166 mg, 0.3 mmol, dr = 95 : 5), CH_2Cl_2 (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 CH_2Cl_2, 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, ^{31}P NMR δ 43.3, The first fraction on TLC) containing unidentified products (^{31}P 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), $[\alpha]_D^{29}$ = +294 (c = 0.287, $CHCl_3$); mp: 135-136 ºC 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}; ^{1}H NMR ($CDCl_3$): 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); ^{13}C NMR ($CDCl_3$): δ 22.9 (d, $^2J_{C\text{-}P}$ = 4.1 Hz), 25.5, 26.8, 27.6 (d, $^2J_{C\text{-}P}$ = 3.3 Hz), 39.1 (d, $^1J_{C\text{-}P}$ = 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); ^{31}P NMR ($CDCl_3$): δ 42.8 (s); MS (EI) m/z 490 (M^+); HRMS Calcd for $C_{32}H_{27}O_3P$:490.1698, Found: 490.1705.

(S_{ax})-4-(1,2,3,4-tetrahydronaphthalen-2-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-oxide (6ch)

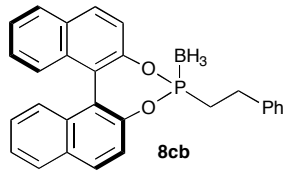


6ch

To a 10 mL two-necked flask were added selenophosphonate **5ch** (74 mg, 0.33 mmol, dr = 50 : 50), CH_2Cl_2 (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 (CH_2Cl_2 : 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}; ^{1}H NMR ($CDCl_3$): δ 1.96 (m, 1H, CH), 2.27 (m, 1.5H, CHC$\underline{H}_2$CH_2C), 2.38 (m, 0.5H, CHC$\underline{H}_2$CH_2C), 2.59-2.88 (m, 2H, CHCH_2C$\underline{H}_2$C), 2.97 (m, 0.5H, CHC$\underline{H}_2$C), 3.09-3.26 (m, 1.5H, CHC$\underline{H}_2$C), 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); ^{13}C NMR ($CDCl_3$): δ 22.6 (m, CH$\underline{C}$H$_2$CH$_2$C), 28.4 (m, CH$\underline{C}$H$_2$C, CHCH$_2\underline{C}$H$_2$C), 30.3 (d, $^1J_{C\text{-}P}$ = 20.7 Hz, $\underline{C}$H), 31.7 (d, $^1J_{C\text{-}P}$ = 20.7 Hz, $\underline{C}$H), 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, 128.9, 129.1, 131.1, 131.2, 131.8, 132.4, 132.5, 133.6, 133.9, 134.0, 135.2, 135.3, 145.7, 145.7, 145.8, 147.7, 147.8 (Ar); ^{31}P NMR ($CDCl_3$): δ 43.3, 43.5; MS (EI) m/z 462 (M^+); HRMS Calcd for $C_{30}H_{23}O_3P$: 462.1385, Found: 462.1396.

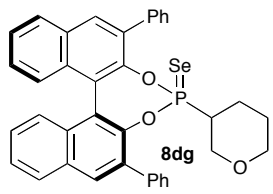
• Deselenation - boration of phosphonoselenoic acid esters **5**

(S_{ax})- 4-(2-Phenylethyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepineborane (8cb)



To a 20 mL two-necked flask were added selenophophonate (**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, BH_3-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 CH_2Cl_2, 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. $[\alpha]_D^{33}$ = +415 (c = 0.542, $CHCl_3$), mp: 147-149 ºC; 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 ($CDCl_3$): δ 2.26 (dd, *J* = 17.5 Hz, 9.0 Hz, 2H, $CH_2C\underline{H}_2Ph$), 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); ^{13}C NMR ($CDCl_3$): δ 27.8 (d, $^2J_{C\text{-}P}$ = 2.8 Hz, $CH_2\underline{C}H_2Ph$), 30.5 (d, $^1J_{C\text{-}P}$ = 32.9 Hz, $\underline{C}H_2CH_2Ph$), 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; ^{31}P NMR ($CDCl_3$): δ 177.8 (m); MS (EI) m/z 434 (M^+); HRMS Calcd for $C_{28}H_{24}BO_2P$: 434.1607, Found: 434.1606.

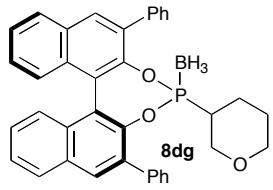
(S_{ax})-2,6-Diphenyl-4-(3-Tetrahydropyran-1-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepineborane (8dg)



To a 10 mL two-necked flask were added selenophosphonate (**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, BH_3-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. $[\alpha]_D^{32}$ = +285 (c = 0.2930, $CHCl_3$); mp: 245-247 ºC; IR (KBr): 3056, 3031, 2974, 2950, 2850, 2405, 2380, 2343, 1595, 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 ($CDCl_3$): 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); ^{13}C NMR ($CDCl_3$): δ 21.5 (d, $^3J_{C\text{-}P}$ = 5.6 Hz, $CHCH_2\underline{C}H_2$), 25.3 (d, $^2J_{C\text{-}P}$ = 12.2 Hz, $CH\underline{C}H_2CH_2$), 36.5 (d, $^1J_{C\text{-}P}$ = 32.9 Hz, $\underline{C}HCH_2O$), 66.0 (d, $^2J_{C\text{-}P}$ = 7.5 Hz, $CH\underline{C}H_2O$), 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); ^{31}P NMR ($CDCl_3$):

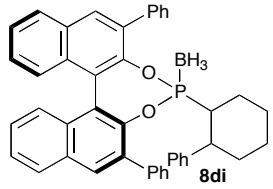
δ 176.9 (m); MS (EI) m/z 566 (M^+); HRMS Calcd for $C_{37}H_{32}BO_3P$:566.2182, Found:566.2199.

(S_{ax})-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, BH_3-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. $[\alpha]_D^{31}$ = +385 (c = 0.416, $CHCl_3$); mp: 154-156 ºC ;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 ($CDCl_3$): 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) ; ^{13}C NMR ($CDCl_3$): 26.8 (d, $^3J_{C\text{-}P}$ = 2.5 Hz, $CHCH_2\underline{C}H_2$), 37.0 (d, $^1J_{C\text{-}P}$ = 36.4 Hz, $\underline{C}H$), 65.8 (d, $^2J_{C\text{-}P}$ = 13.2 Hz, $CH\underline{C}H_2CH_2$), 67.8 (d, $^2J_{C\text{-}P}$ = 6.6 Hz, $CH\underline{C}H_2O$), 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) ; ^{31}P NMR ($CDCl_3$): δ 177.4 (m); MS (EI) m/z 552 (M^+); HRMS Calcd for $C_{36}H_{30}O_3PB$: 552.2026, Found: 552.2021.

(S_{ax})-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, BH_3-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. $[\alpha]_D^{32}$ = +317 (c = 0.596, $CHCl_3$); mp: 155-157 ºC ;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 ($CDCl_3$): δ -0.50 - 0.50 (br, 3H, $B\underline{H}_3$), 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); ^{13}C NMR ($CDCl_3$): 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); ^{31}P NMR ($CDCl_3$): δ 184.8 (m); MS (EI) m/z 640 (M^+); HRMS Calcd for $C_{44}H_{38}O_2PB$: 640.2702, Found: 640.2718.

• X-ray structure analysis

The measurement of (S_{ax}, *R*)-4-(2-phenylpropyl)-dinaphtho[2,1-d:1',2'-f][1,3,2] dioxaphophepin-4-selenide ((S_{ax}, *R*)-**5ca**) (MM366) was carried out on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 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_2Cl_2 solution (0.5 mL) of (S_{ax}, *R*)-**5ca** (127 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_{ax}, *R*)-4-(3-Tetrahydropyran-1-yl)-dinaphtho[2,1-d:1',2'-f][1,3,2] dioxaphophepin-4-selenide ((S_{ax}, *R*)-**5cg**) (MM393) was carried out on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 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_2Cl_2 solution (0.4 mL) of (S_{ax}, *R*)-**5cg** (100 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 **5ca** and **5cg** are shown in Figures 1 and 2, and crystallographic data are listed in Table S1.

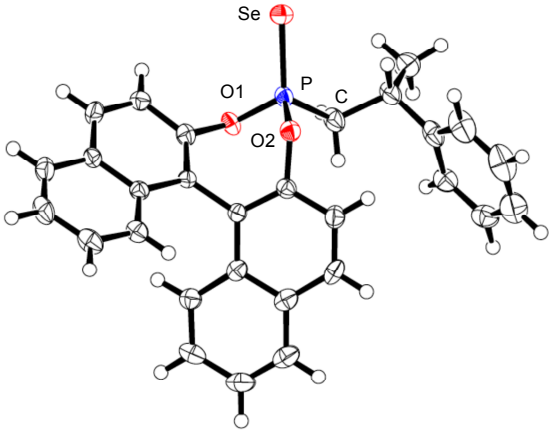


Fig. 1 ORTEP drawing of (S_{ax}, *R*)-**5ca** with 50% thermal ellipsoids. Selected bond lenghs [Å]: P-Se 2.0634, P-O(1) 1.615(2), P-O(2) 1.6102, P-C 1.793(4).

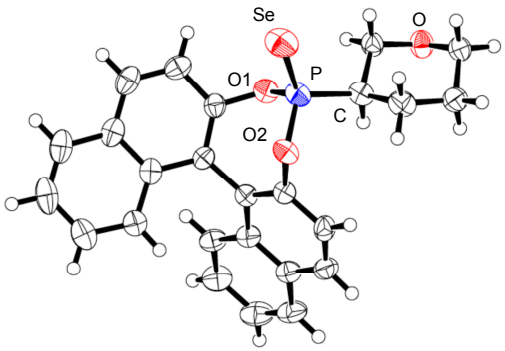


Fig. 2 ORTEP drawing of (S_{ax}, *R*)-**5cg** with 50% thermal ellipsoids. Selected bond lenghs [Å]: P-Se 2.0612(15), P-O(1) 1.608(4), P-O(2) 1.605(3), P-C 1.805(5).

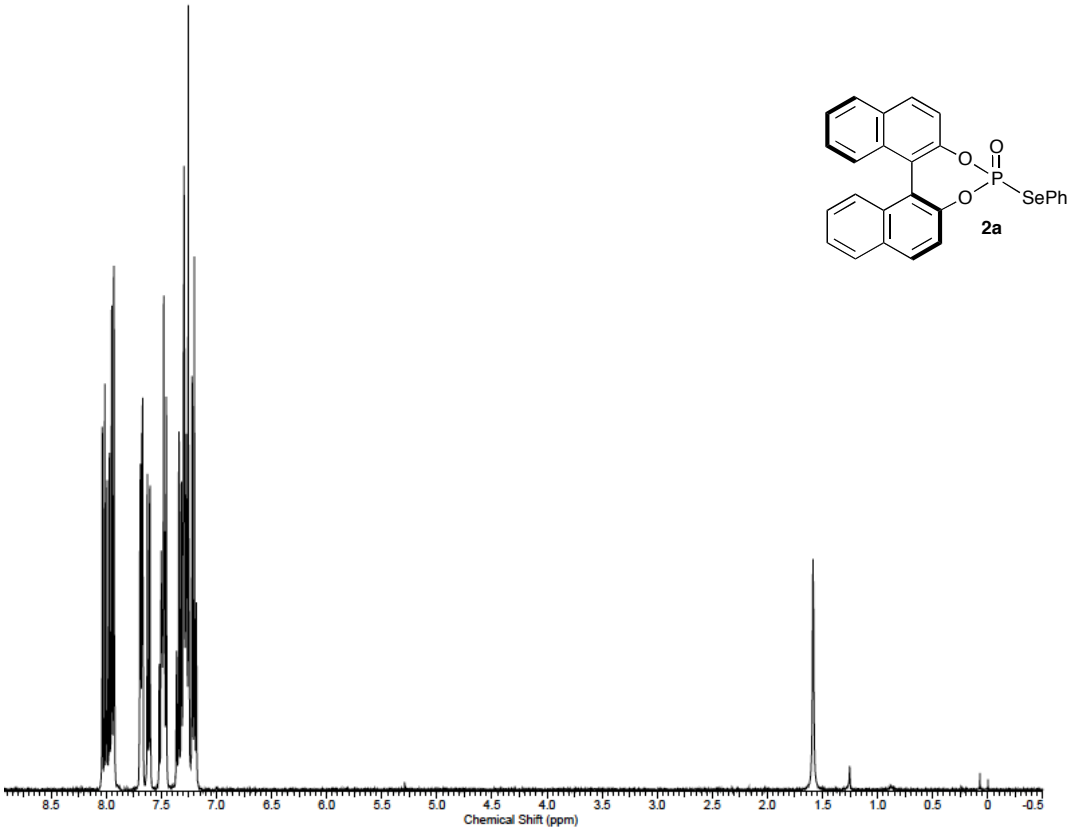
Table S1. Crystal data and structure refinement for (S_{ax}, *R*)-**5ca** and (S_{ax},*R*)-**5cg**.

	(S_{ax}, *R*)-**5ca**		(S_{ax}, *R*)-**5cg**	
Identification code	MM366		MM393	
Empirical formula	$C_{29}H_{23}O_2PSe$		$C_{25}H_{21}O_3PSe$	
Formula weight	513.40		479.35	
Temperature	193(2) K		193(2) K	
Wavelength	71.070 pm		71.070 pm	
Crystal system	Orthorhombic		Orthorhombic	
Space group	$P2_12_12_1$		$P2_12_12_1$	
Unit cell dimensions	a = 1315.1(8) pm b = 2305.6(13) pm c = 780.6(5) pm	a = 90° b = 90° c = 90°	a = 1747.9(8) pm b = 1023.1(5) pm c = 1245.9 (6) pm	a = 90° b = 90° c = 90°
Volume	2.37(1) nm^3		2.2279(19) nm^3	
Z	4		4	
Density (calculated)	1.441 Mg/m^3		1.429 Mg/m^3	
Absorption coefficient	1.679 mm^{-1}		1.781 mm^{-1}	
F(000)	1048		976	
Crystal size	0.29 X 0.17 X 0.17 mm^3		0.25 X 0.23 X 0.17 mm^3	
Theta range for data collection	3.03 to 27.48°		3.27 to 27.48°	
Index ranges	-16<=h<=17, -28<=k<=29, -10<=l<=7		-22<=h<=17, -12<=k<=13, -11<=l<=16	
Reflections collected	19181		17803	
Independent reflections	5357 [R(int) = 0.0579]		5079 [R(int) = 0.0525]	
Completeness to theta = 27.48°	98.9%		99.3%	
Absorption correction	Integration		Integration	
Max. and min. transmission	0.774 and 0.0579		0.732 and 0.522	
Refinement method	Full-matrix least-squares on F^2		Full-matrix least-squares on F^2	
Data / restraints / parameters	5357 / 0 / 299		5079 / 0 / 272	
Goodness-of-fit on F^2	1.121		1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.0932		R1 = 0.0633, wR2 = 0.1647	
R indices (all data)	R1 = 0.0520, wR2 = 0.0949		R1 = 0.0713, wR2 = 0.1711	
Absolute structure parameter	0.008(10)		0.007(14)	
Extinction coefficient	–		0.002(2)	
Largest diff. peak and hole	0.580 and -0.482 e.$Å^{-3}$		0.477 and -0.617 e.$Å^{-3}$	

References

S1) T. Higashi, NUMABS, Numerical Absorption Correction. In Rigaku Corporation, Tokyo, Japan, 1999.

S2) G. M. Sheldrick, SHELXL-97, A Program for the Refinement of Crystal Structures. In University of Gottingen: Gottingen, Germany, 1997.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O
P
O
SePh
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7.0
6.5
6.0
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3.0
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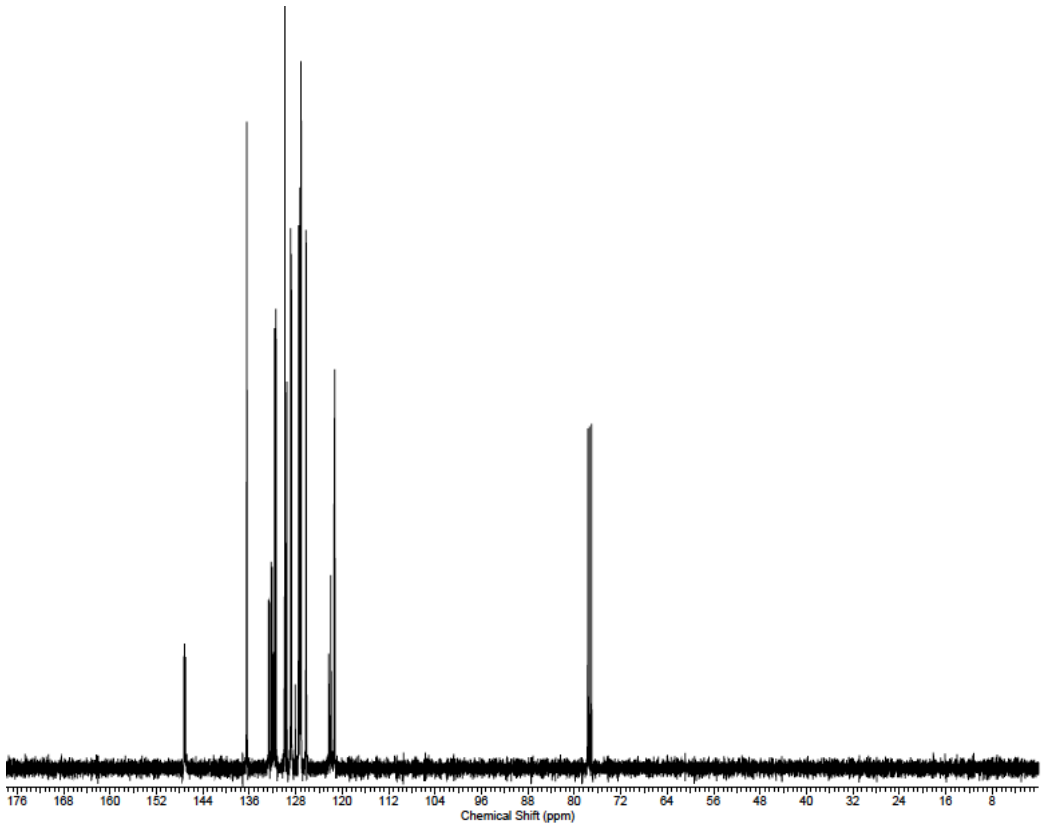
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)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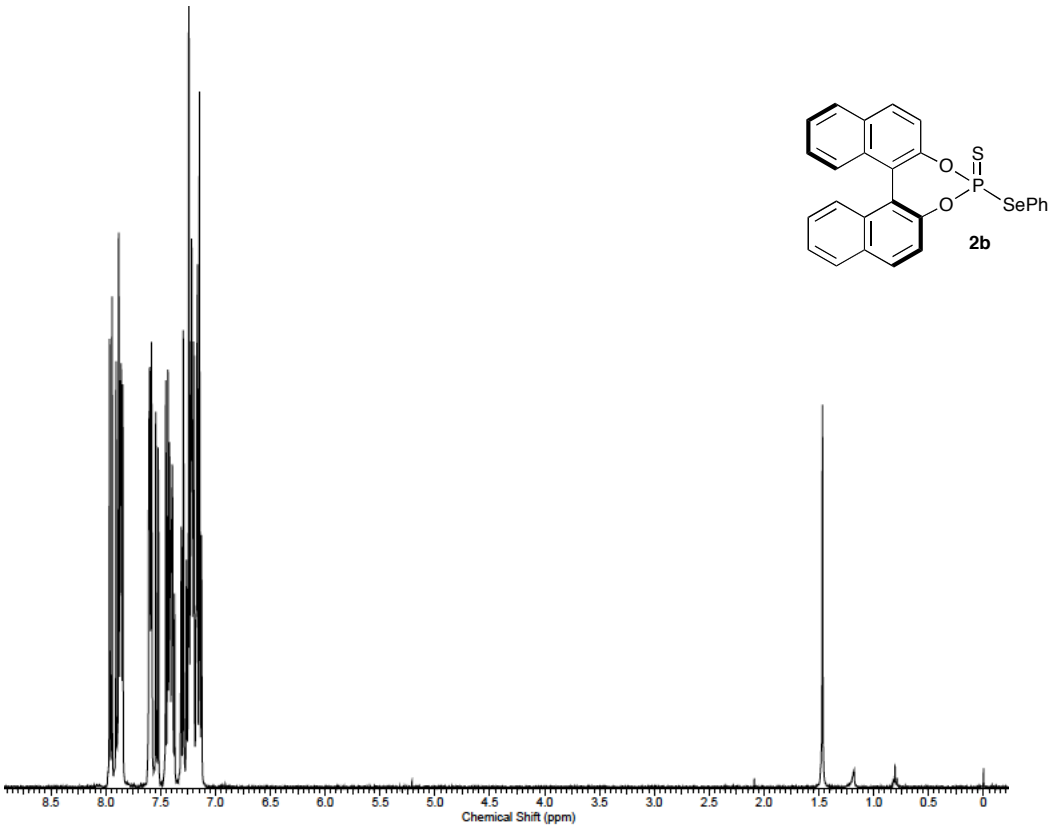
8
Chemical Shift (ppm)


S
O
P
O
SePh
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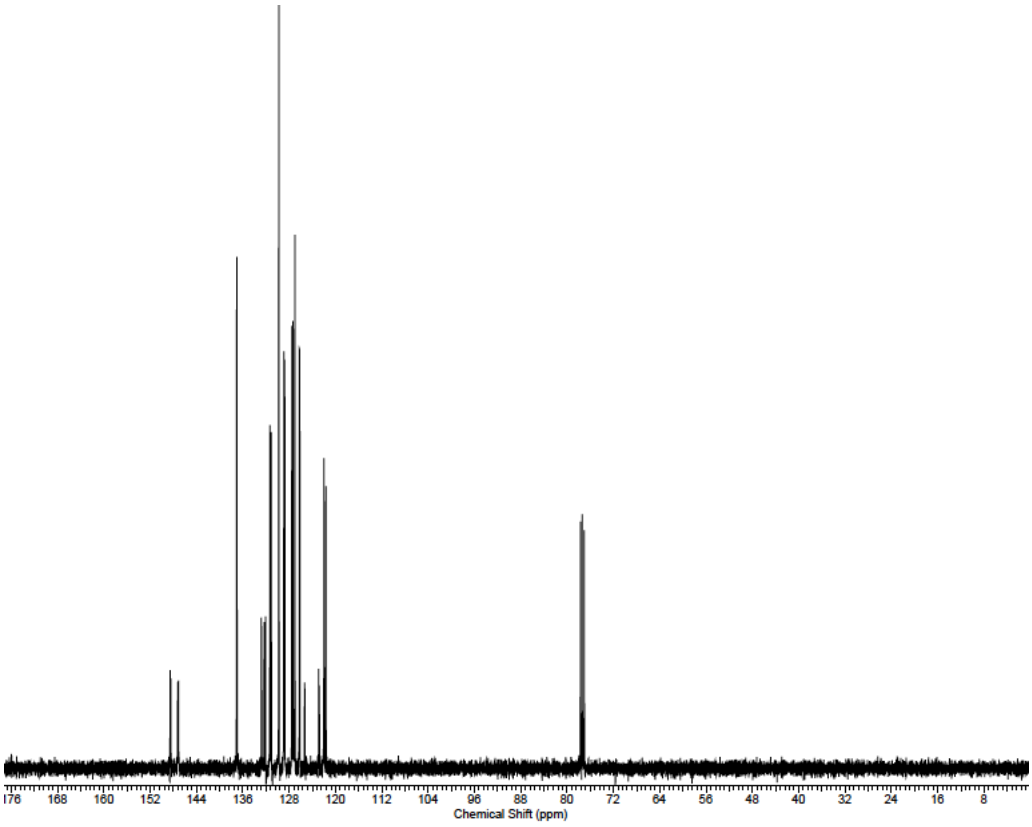
Chemical Shift (ppm)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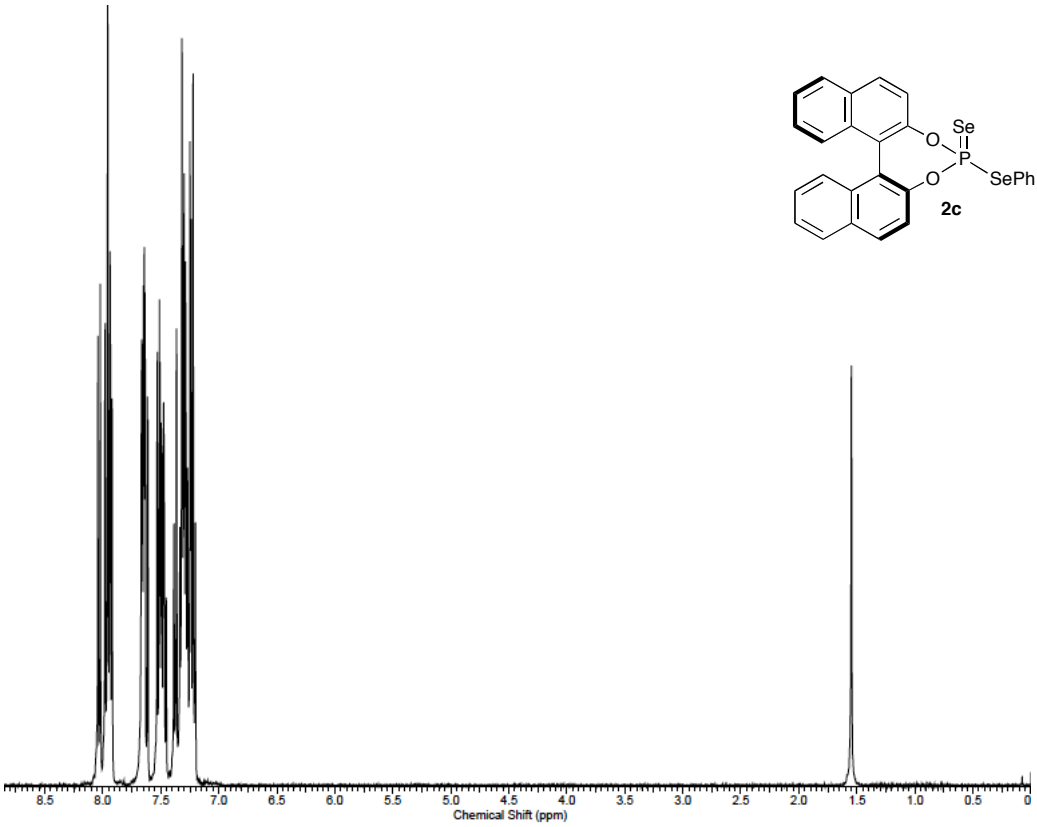
8
Chemical Shift (ppm)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O
P
O
SePh
2c
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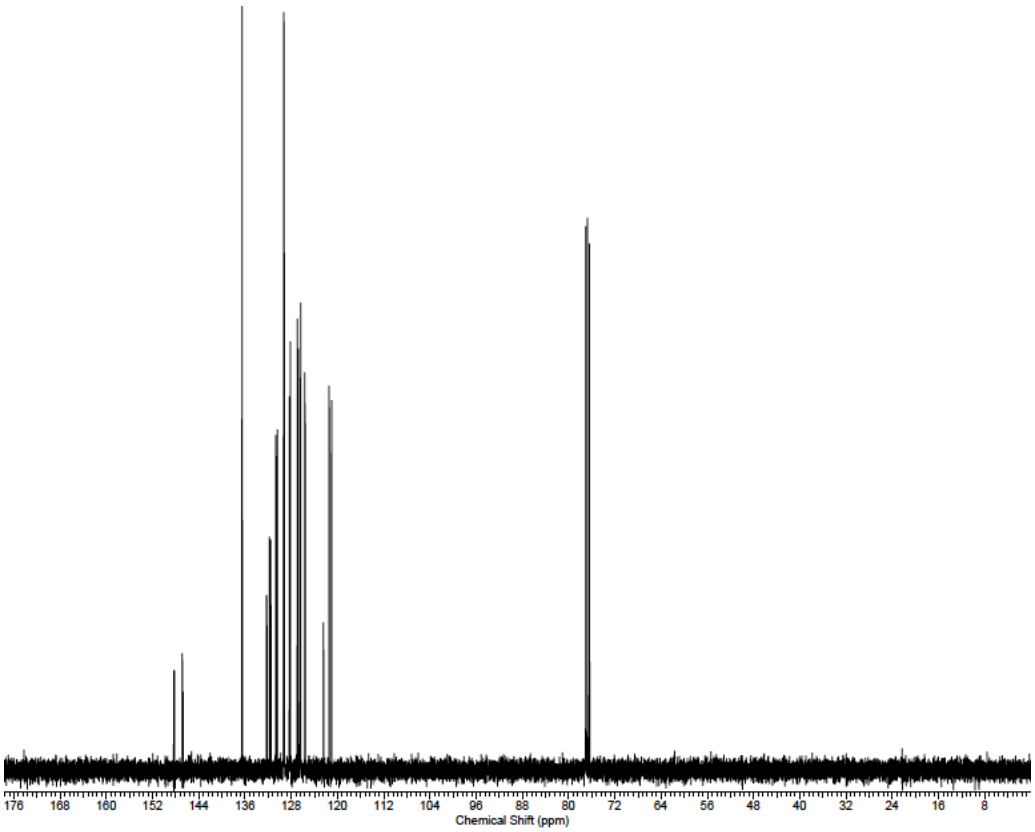
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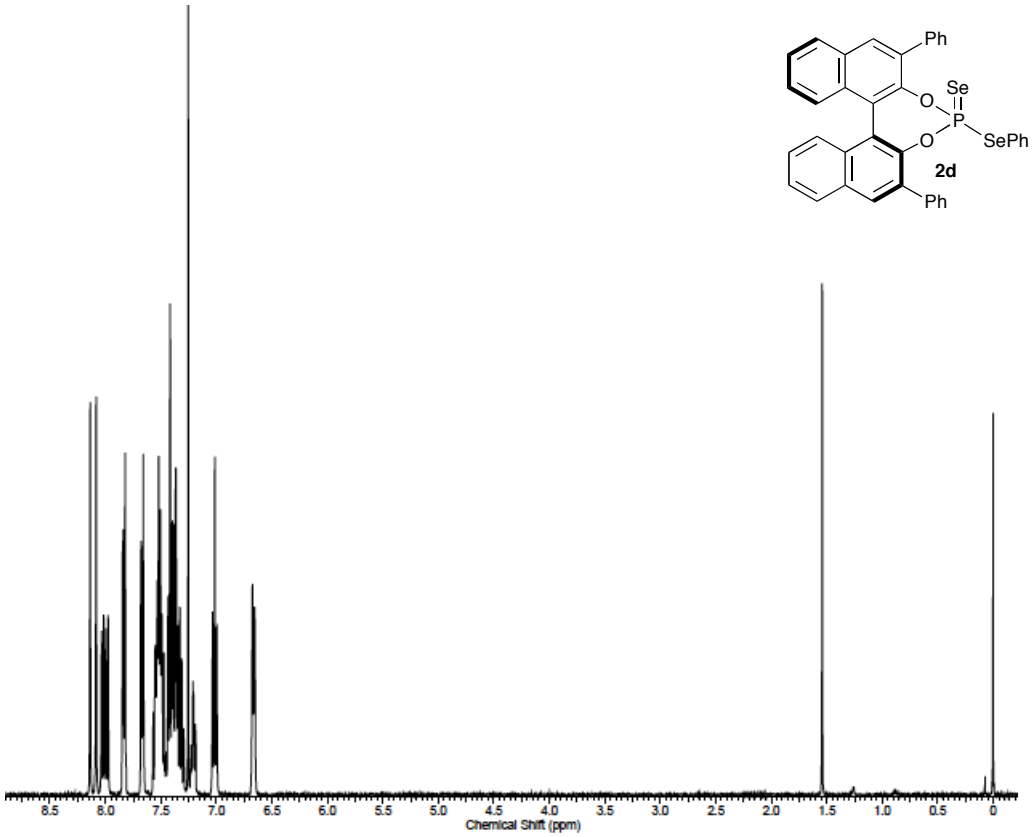
16
8
Chemical Shift (ppm)


Ph
Se
O
P
O
SePh
2d
Ph
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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1.0
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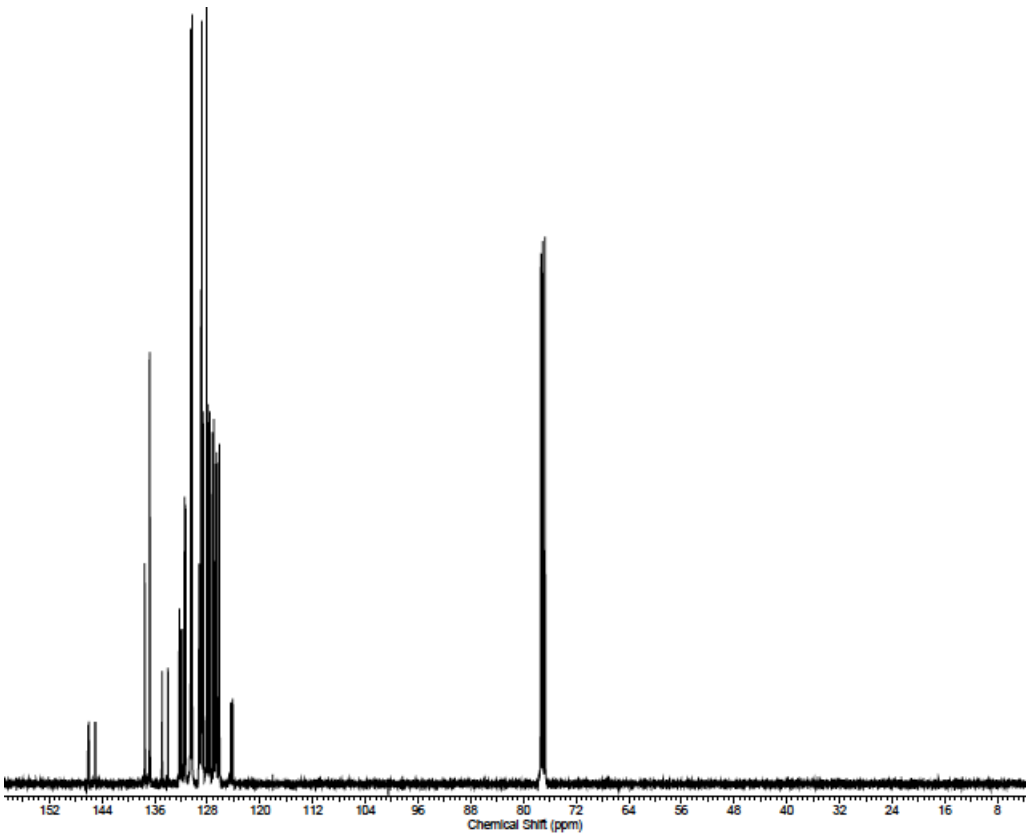
0
Chemical Shift (ppm)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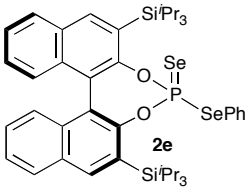
32
24
16
8
Chemical Shift (ppm)


Si^{i}Pr$_3$
Se
O
P
O
SePh
Si^{i}Pr$_3$

2e

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7.5
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6.5
6.0
5.5
5.0
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3.0
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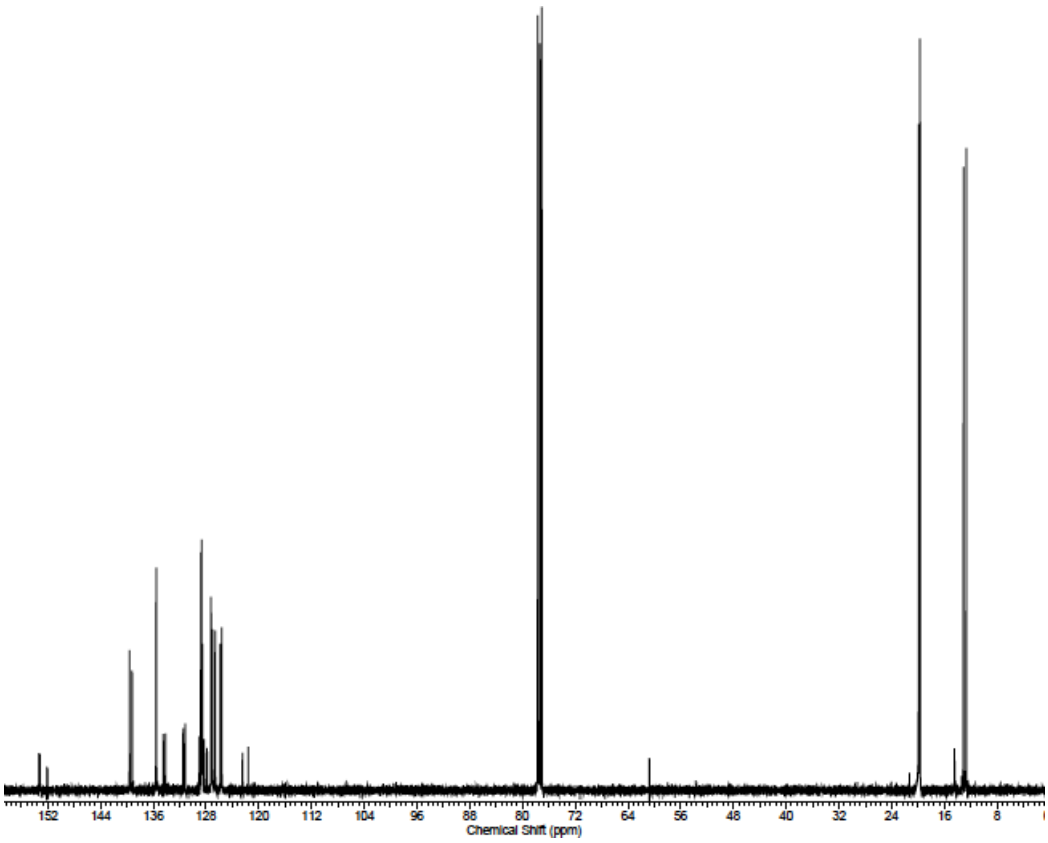
0.5
0
-0.5
Chemical Shift (ppm)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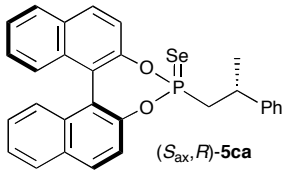
Se
O
P
O
Ph

(S_{ax},*R*)-**5ca**

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5.5
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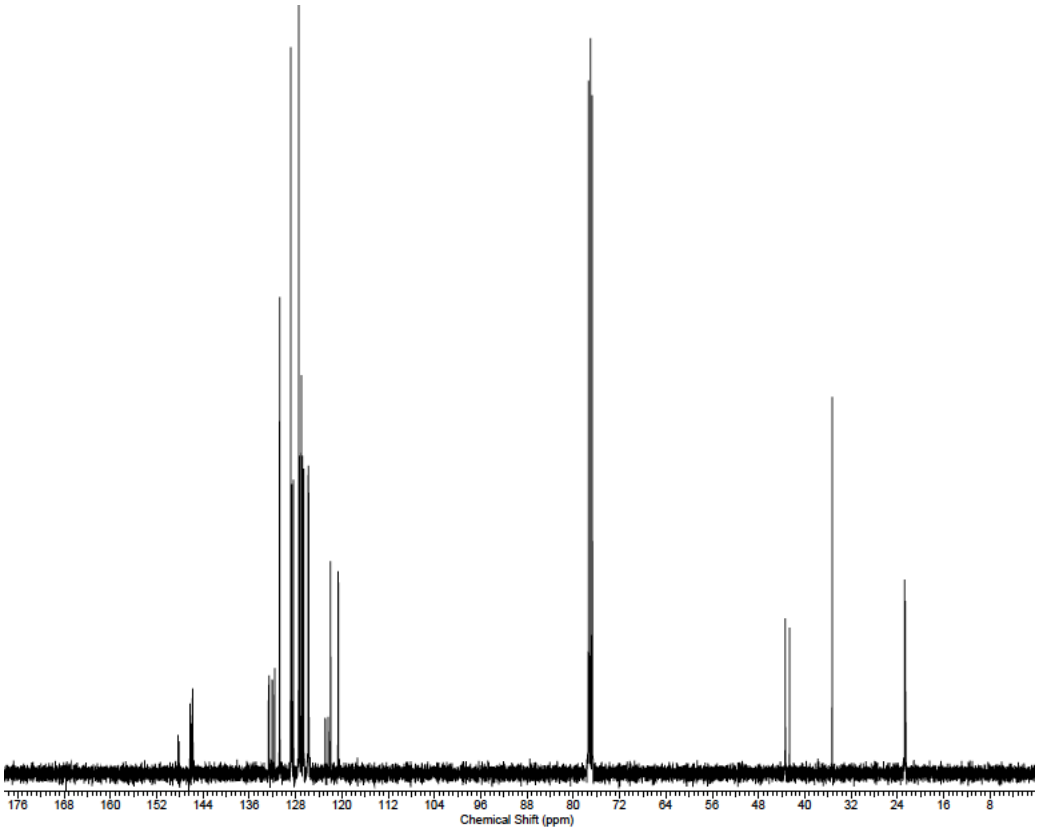
0
Chemical Shift (ppm)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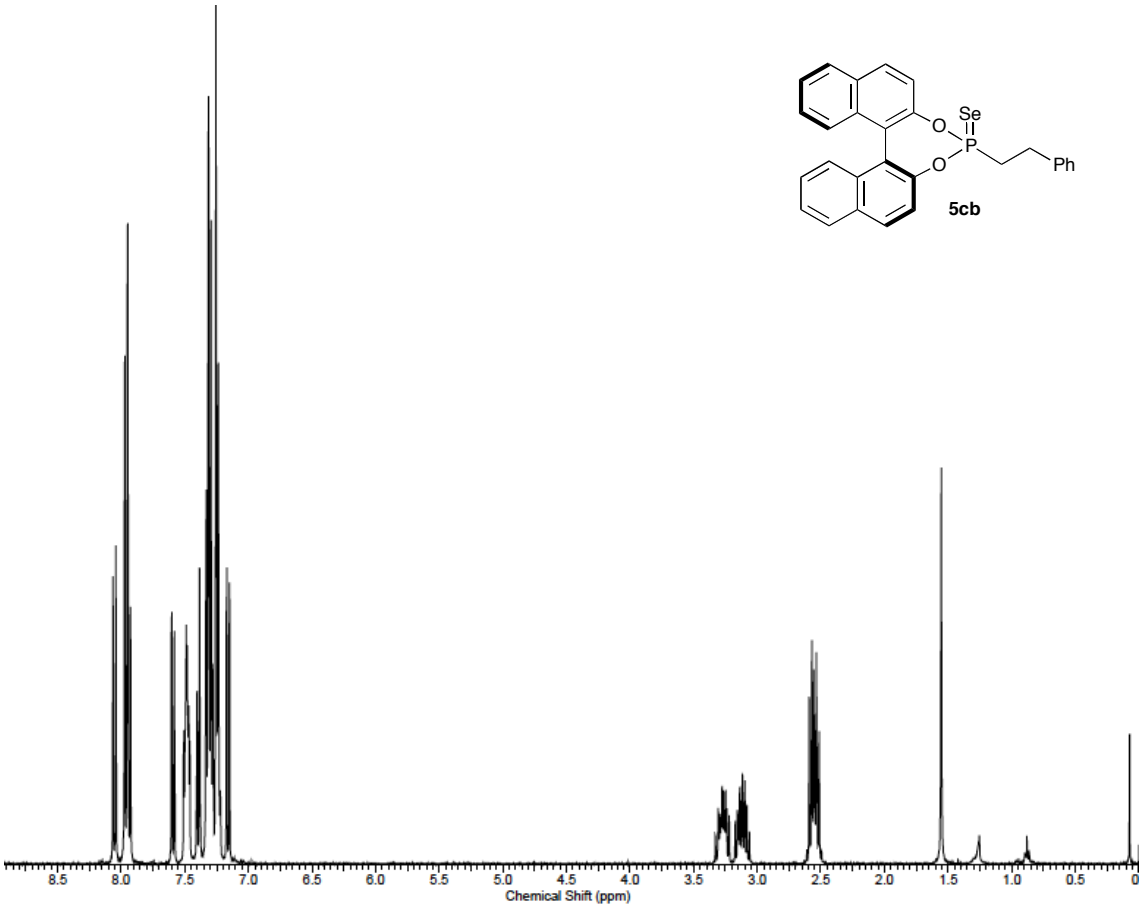
Chemical Shift (ppm)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O
P
O
Ph
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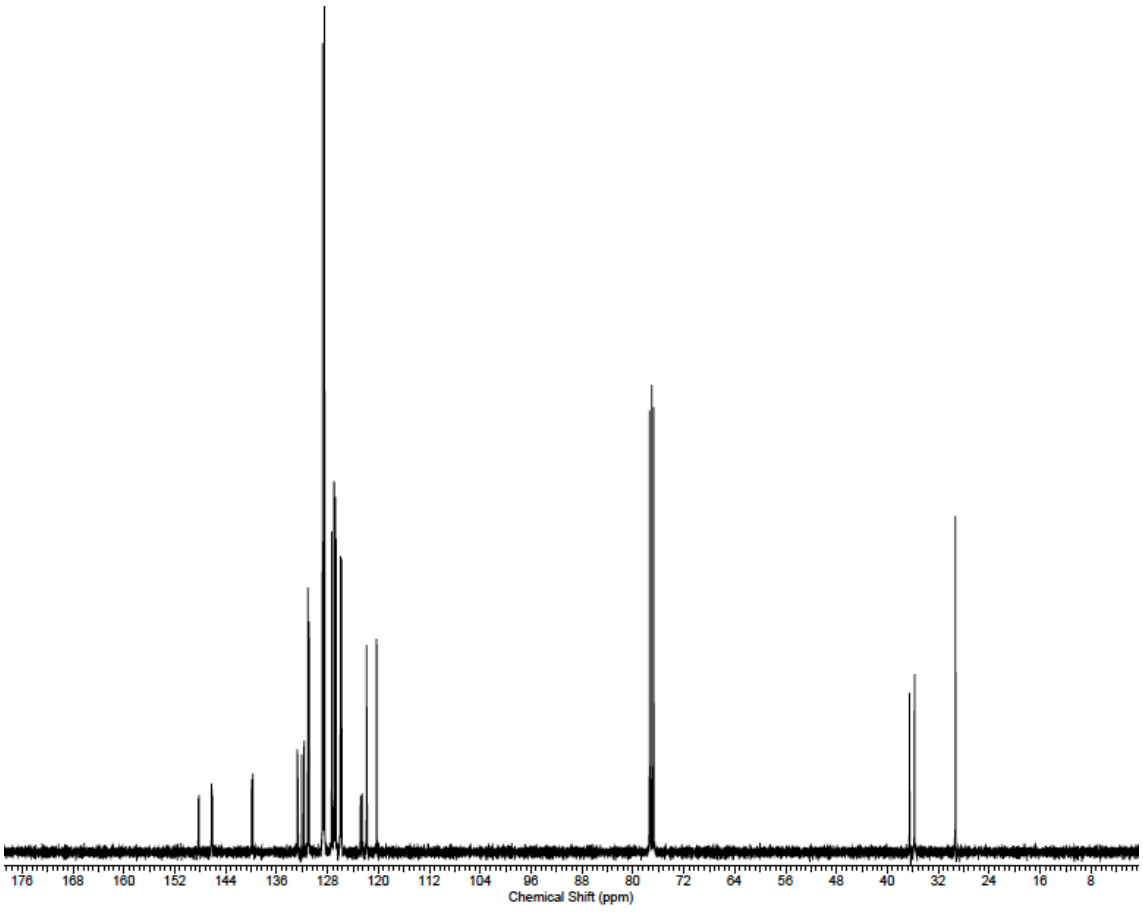
Chemical Shift (ppm)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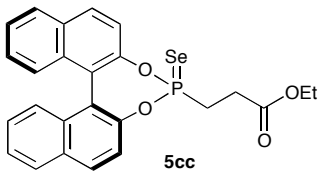
Chemical Shift (ppm)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O
OEt
O

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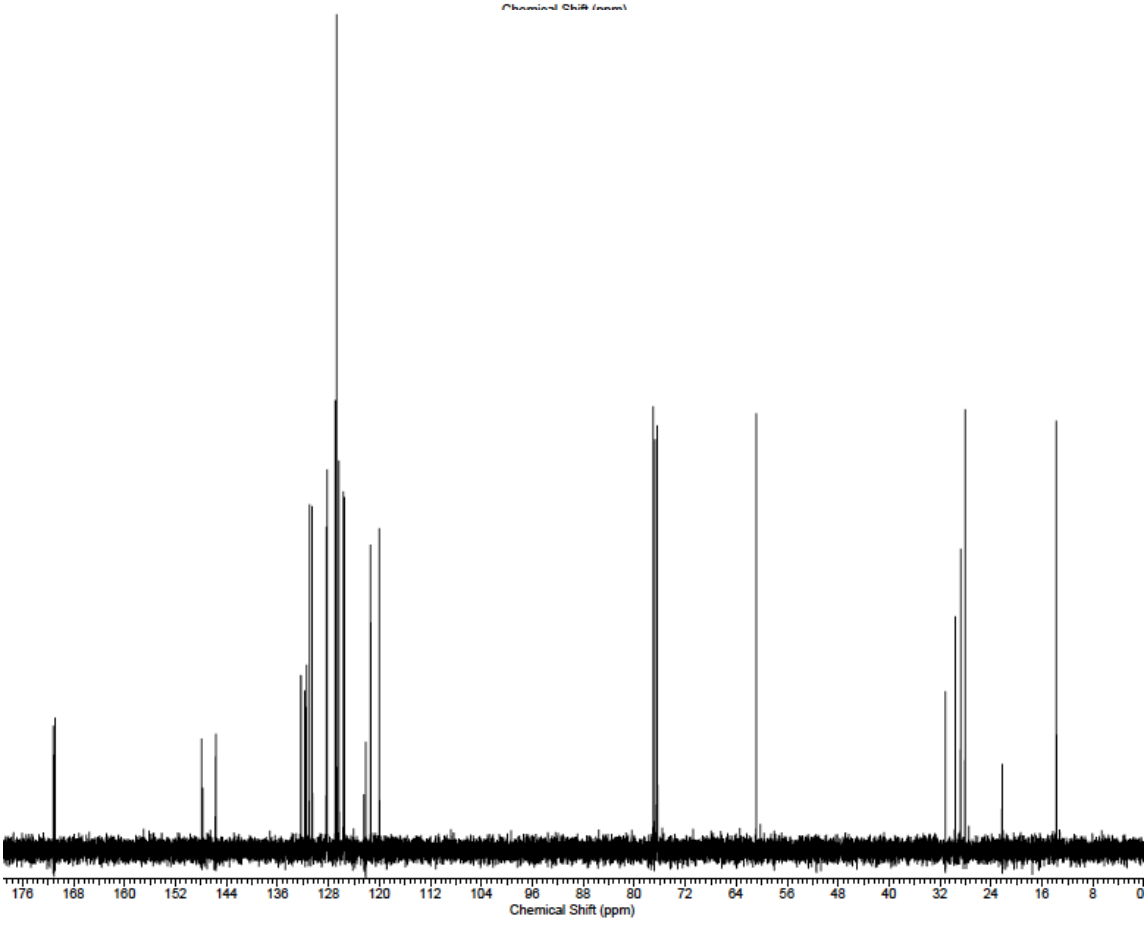
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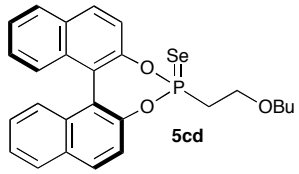
Chemical Shift (ppm)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P
O
OBu

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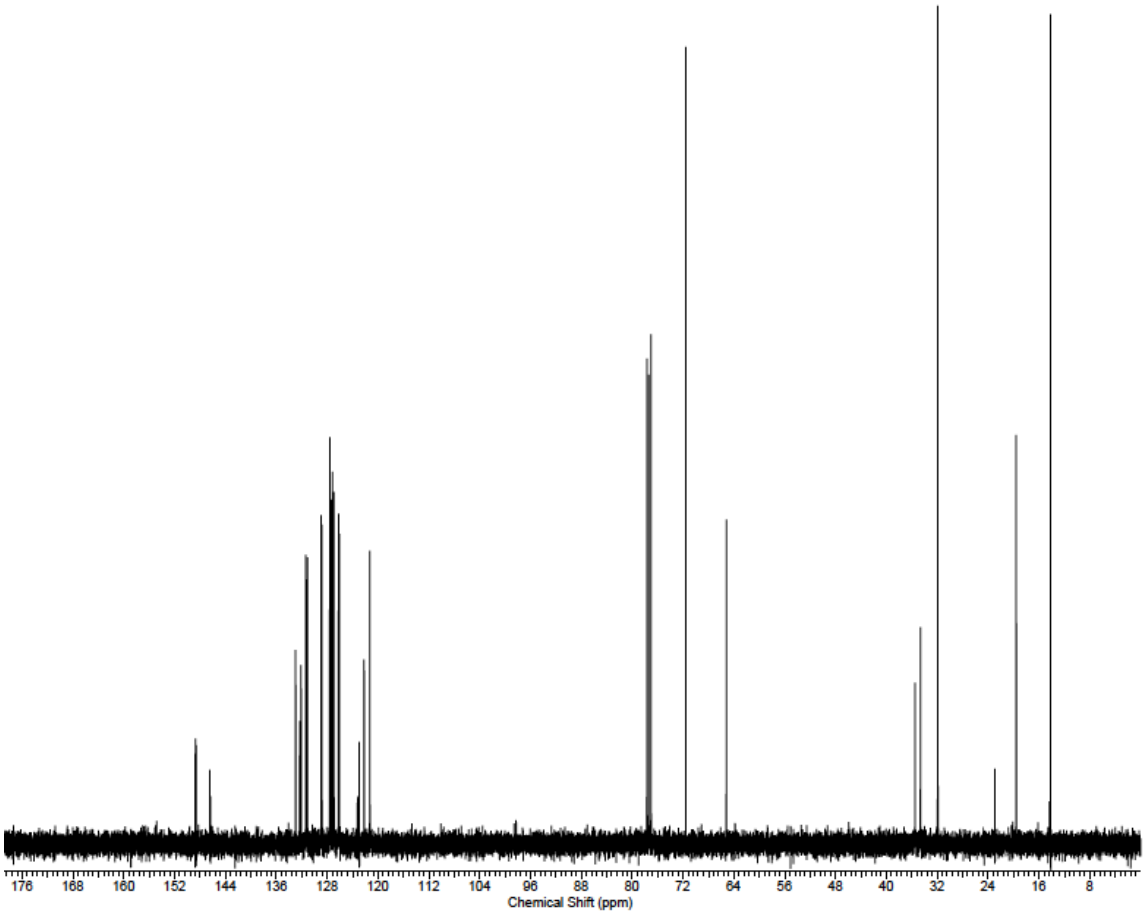
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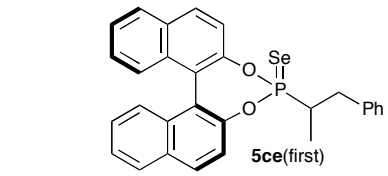
8
Chemical Shift (ppm)


Se
O
P
O
Ph

5ce(first)

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6.5
6.0
5.5
5.0
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3.5
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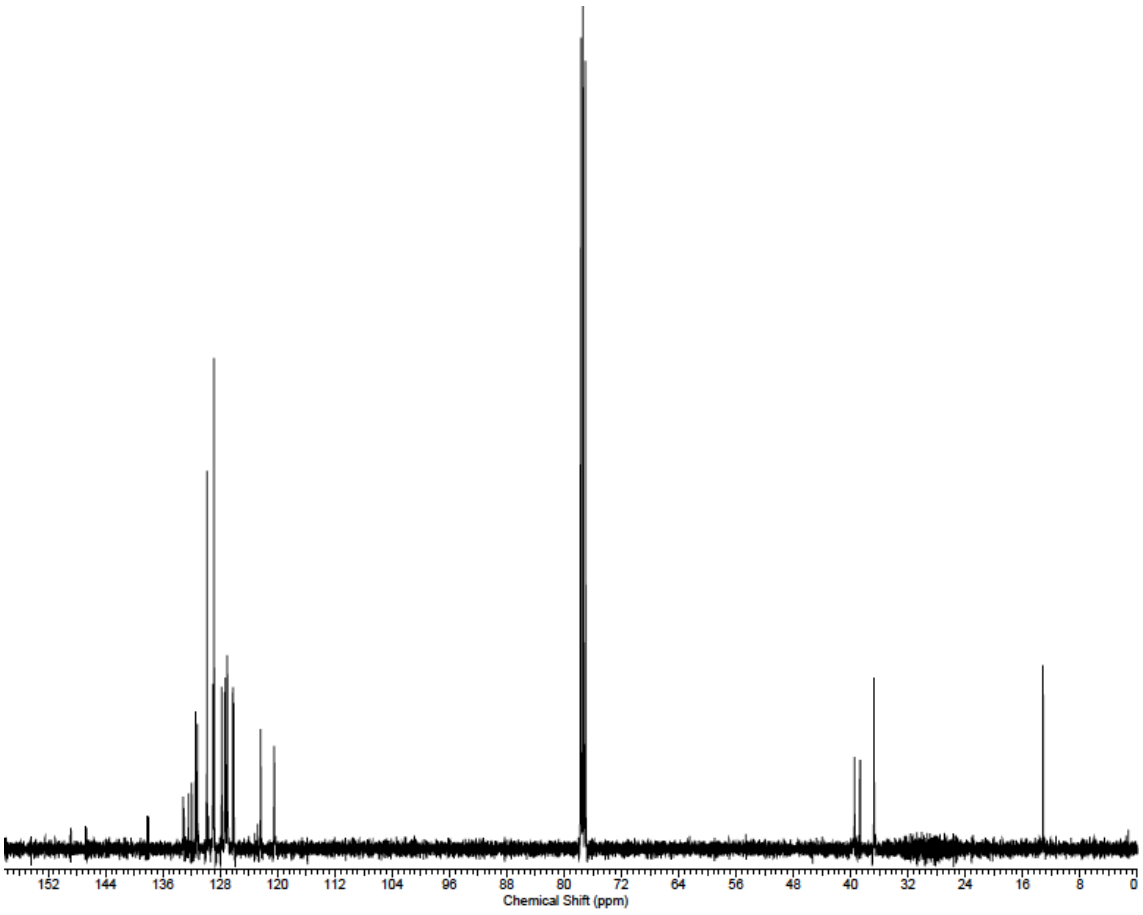
0.5
0
Chemical Shift (ppm)


152
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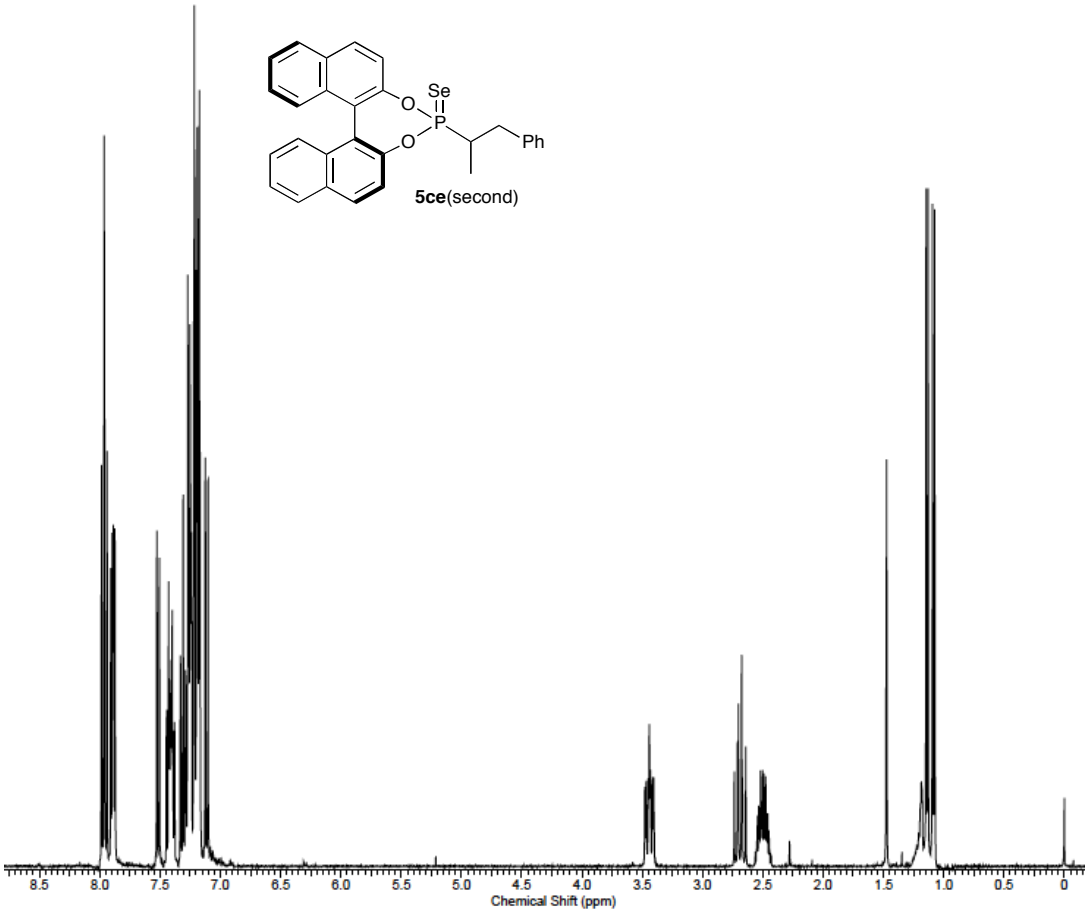
16
8
0
Chemical Shift (ppm)


Se
O
P
O
Ph
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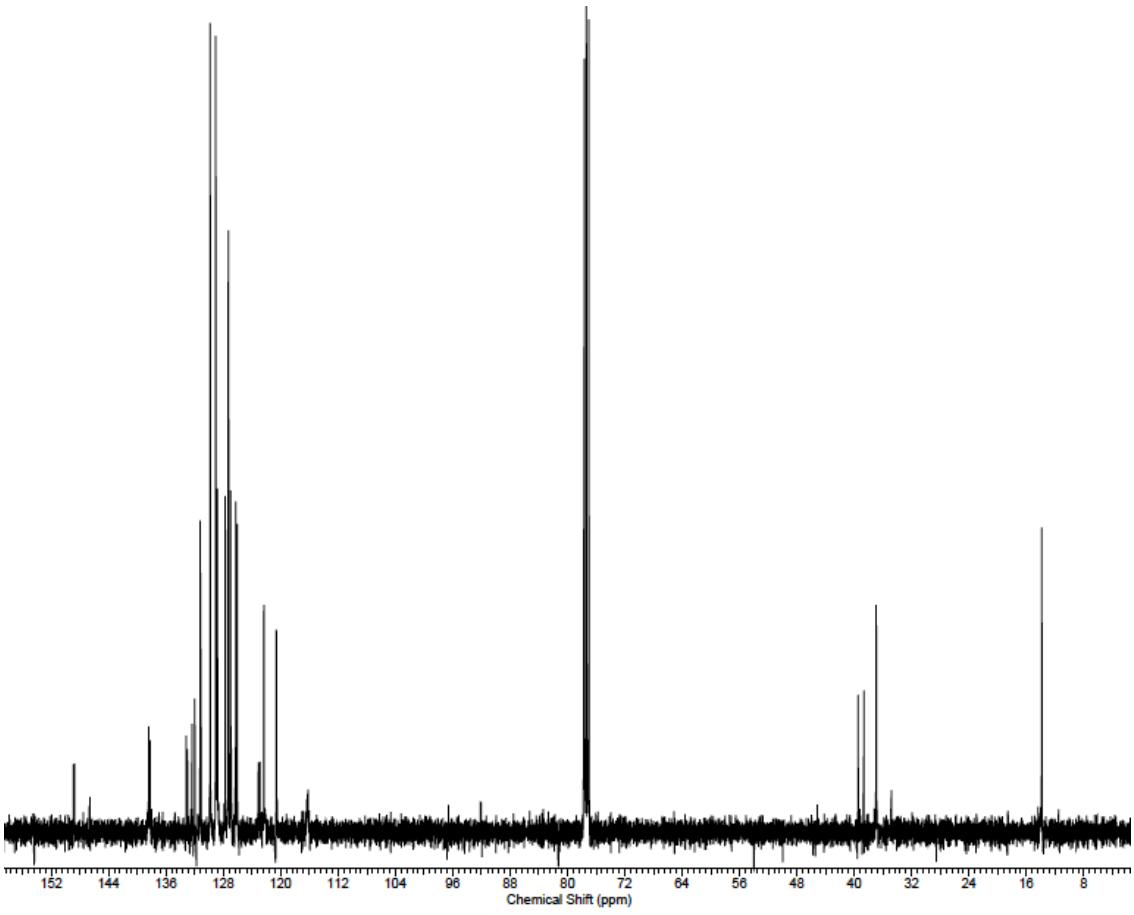
0.5
0
Chemical Shift (ppm)

5ce(second)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40
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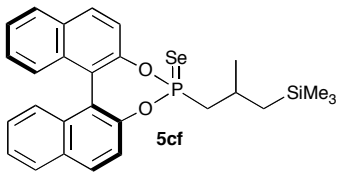
24
16
8
Chemical Shift (ppm)


Se
O
P
O
SiMe3

5cf

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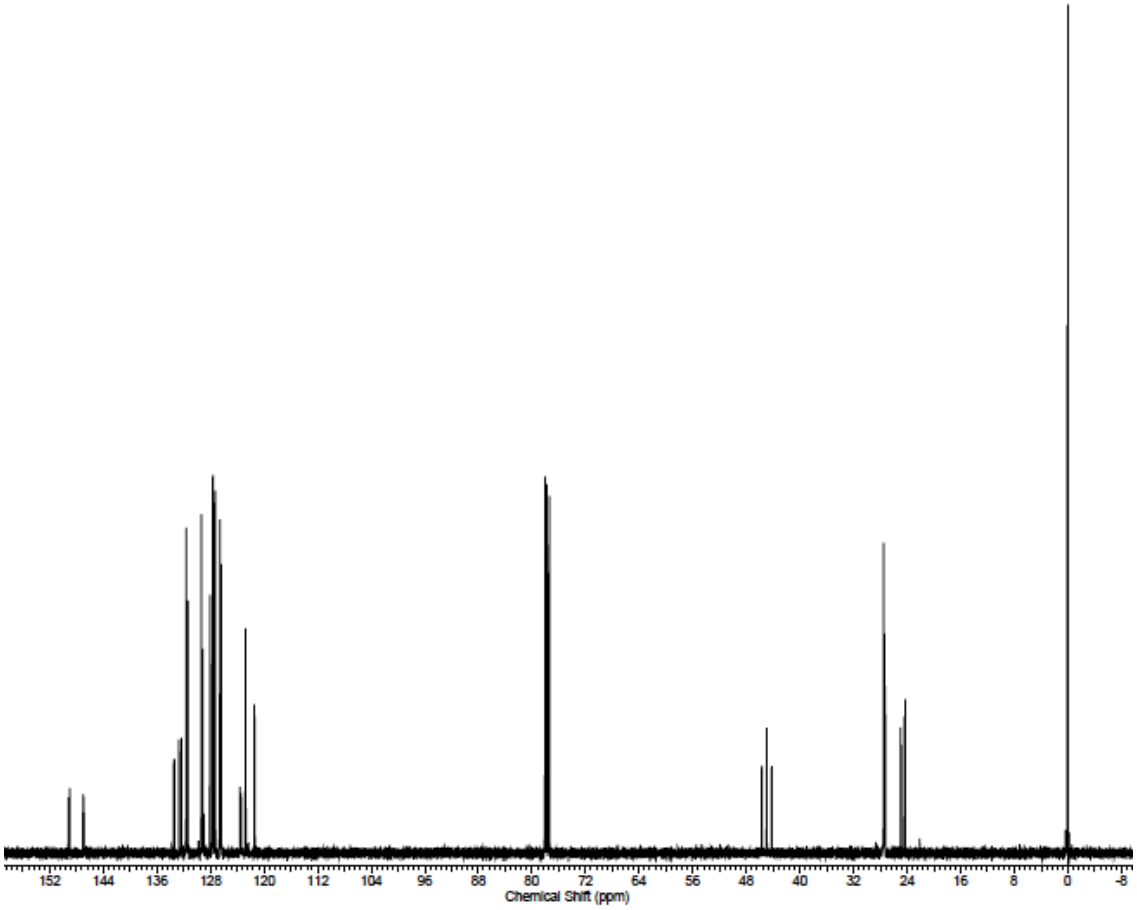
0
-0.5
Chemical Shift (ppm)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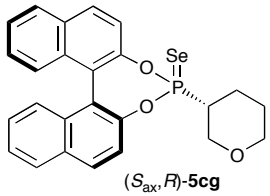
-8
Chemical Shift (ppm)


Se
O
P
O
O

(S_{ax},*R*)-**5cg**

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.0
1.5
1.0
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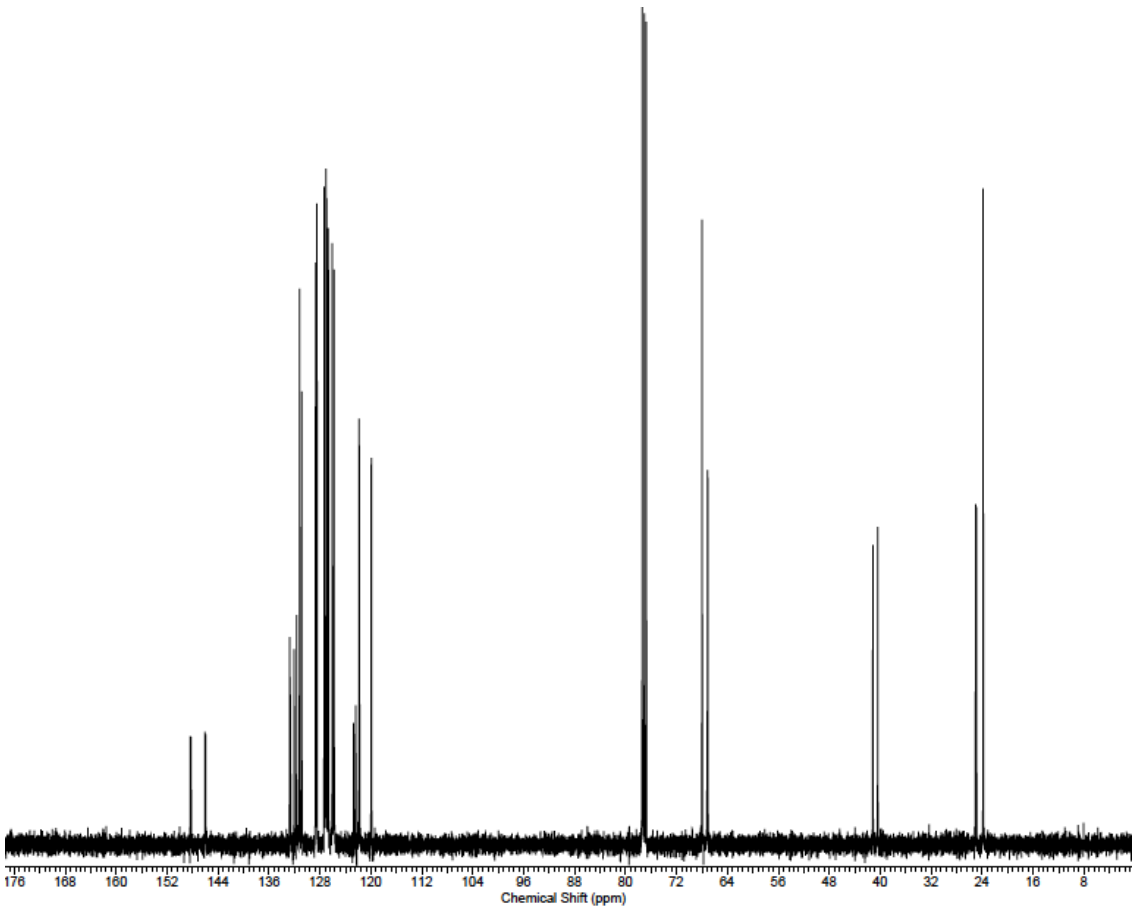
Chemical Shift (ppm)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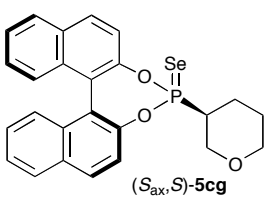
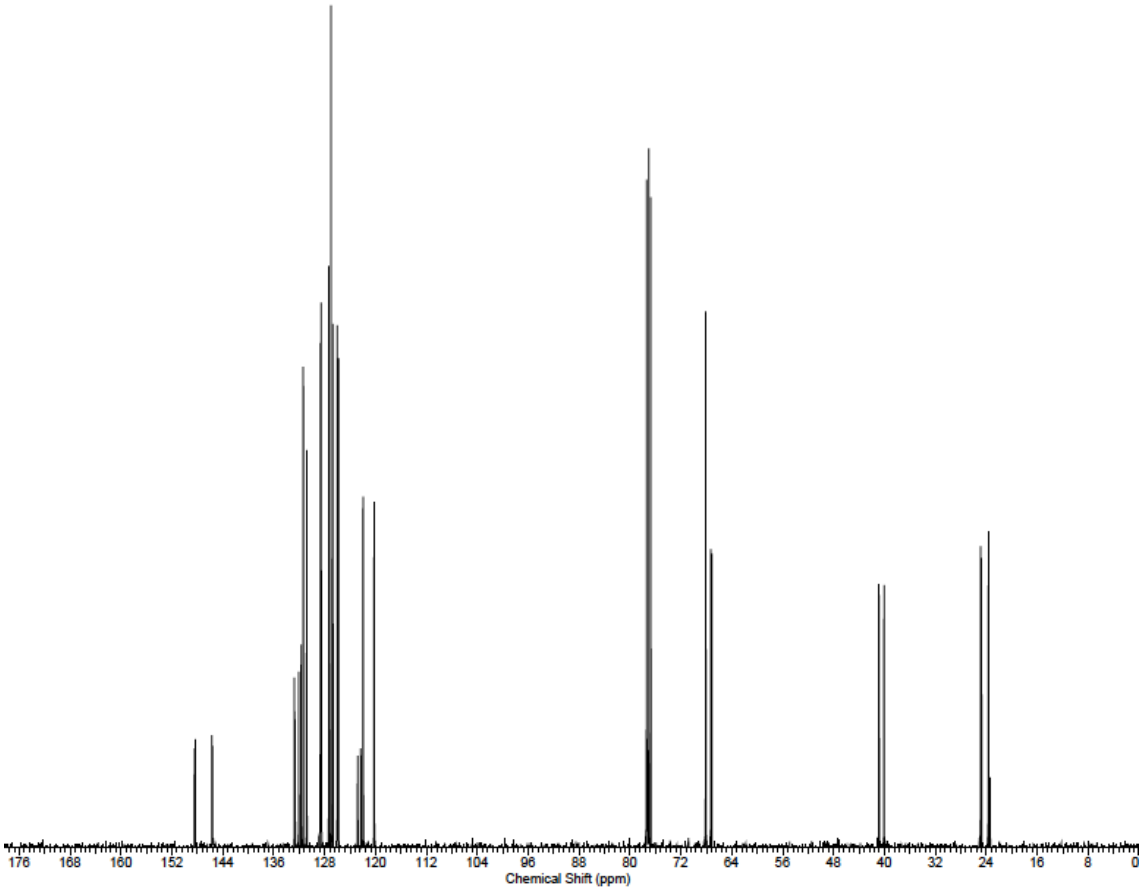
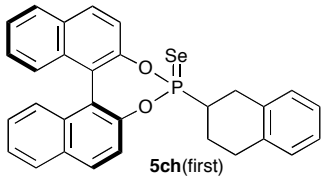
8
Chemical Shift (ppm)


Se
O
P
O
O

(S_{ax},S)-**5cg**

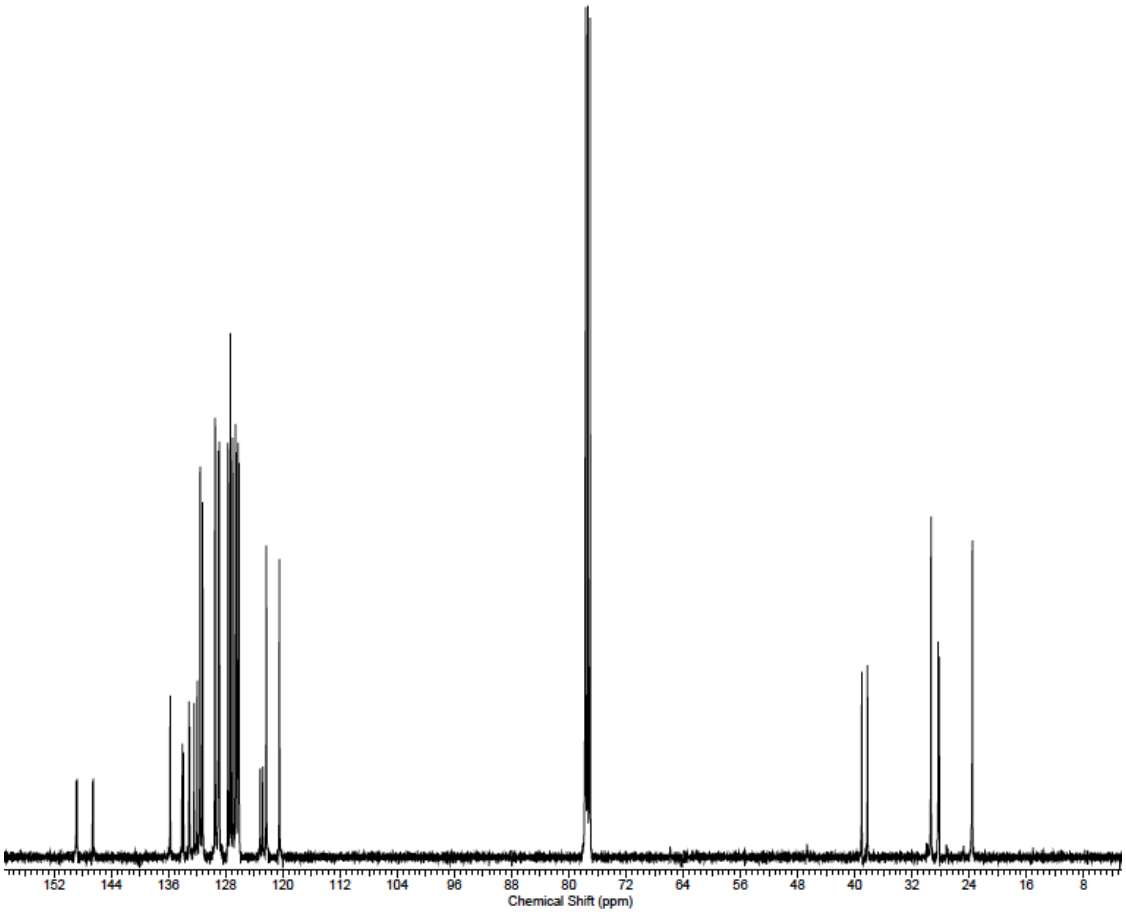
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

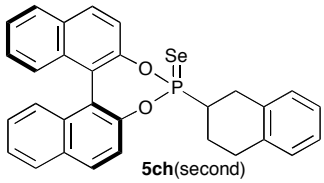

176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


Se
O
P
O

5ch(first)

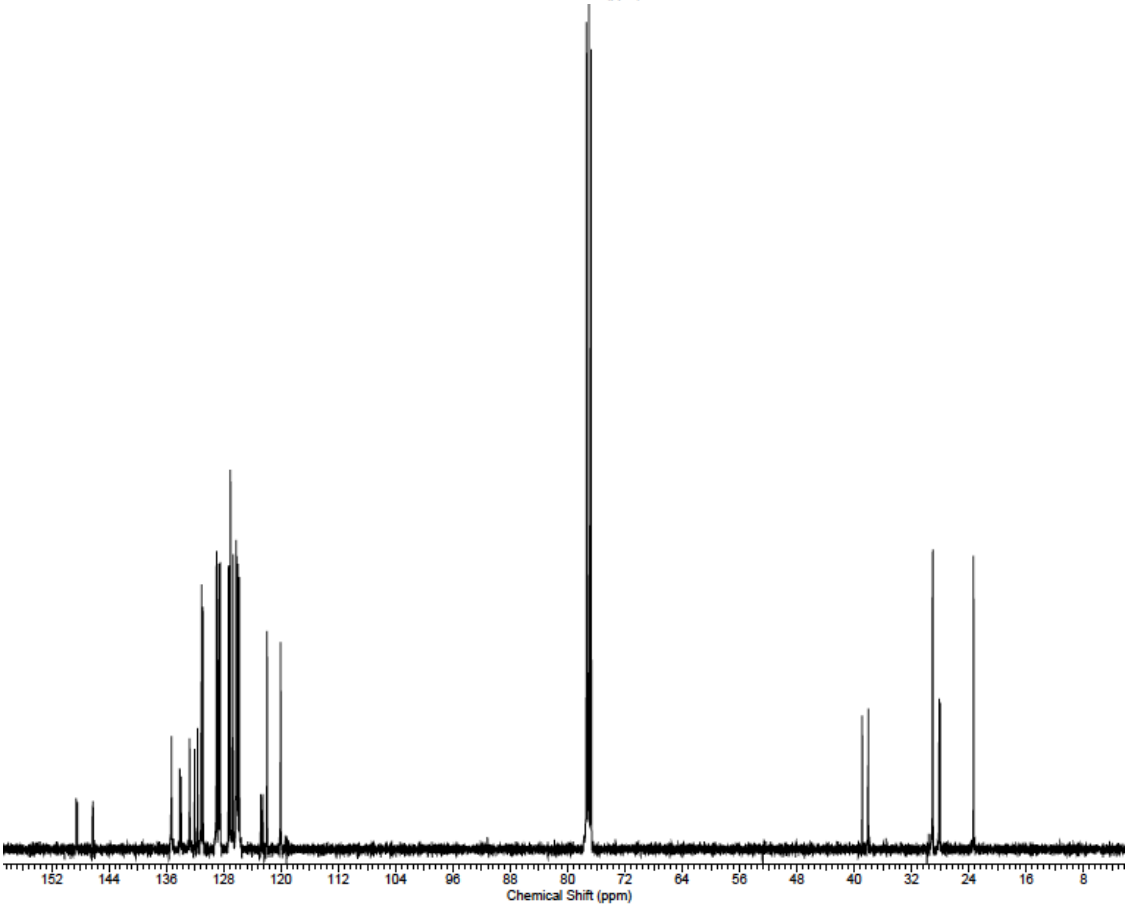
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

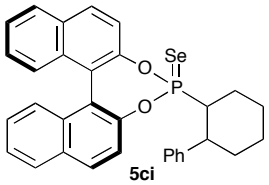

152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


Se
O
P
O

5ch(second)

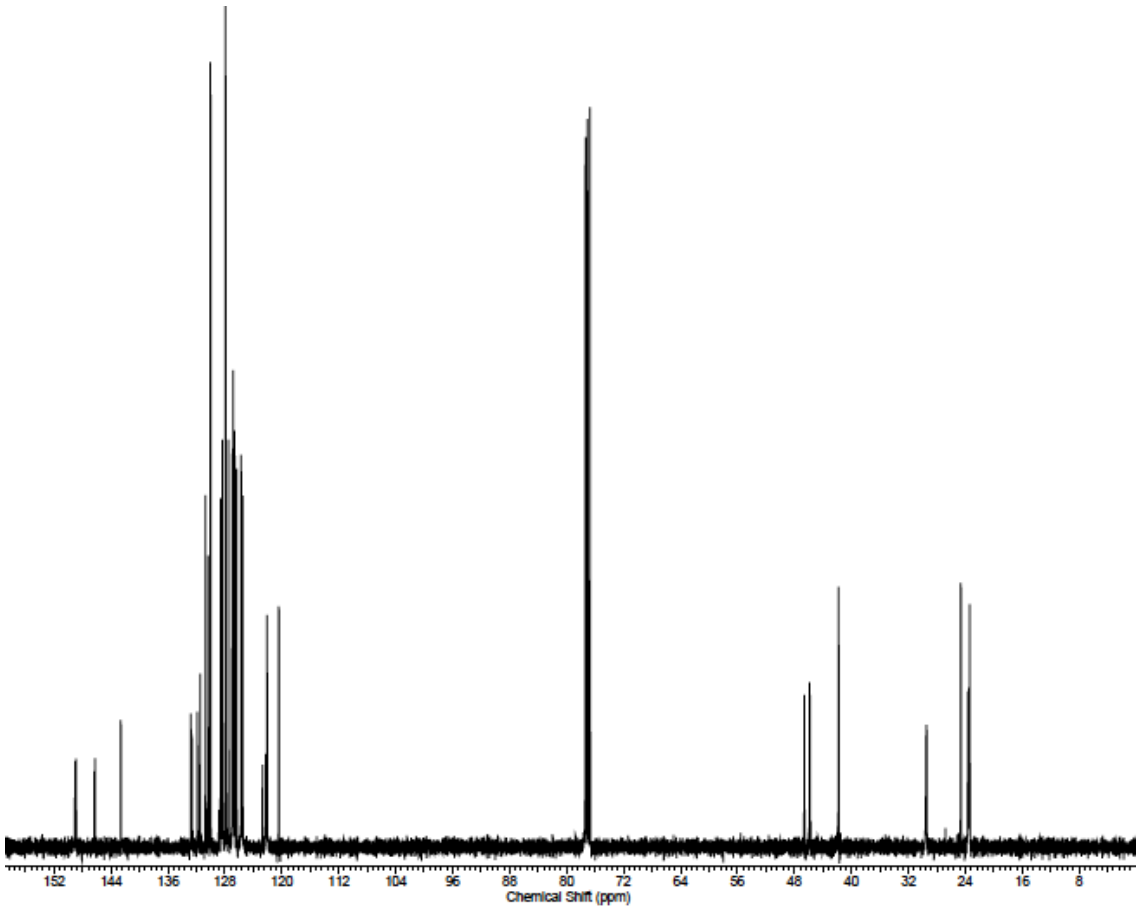
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

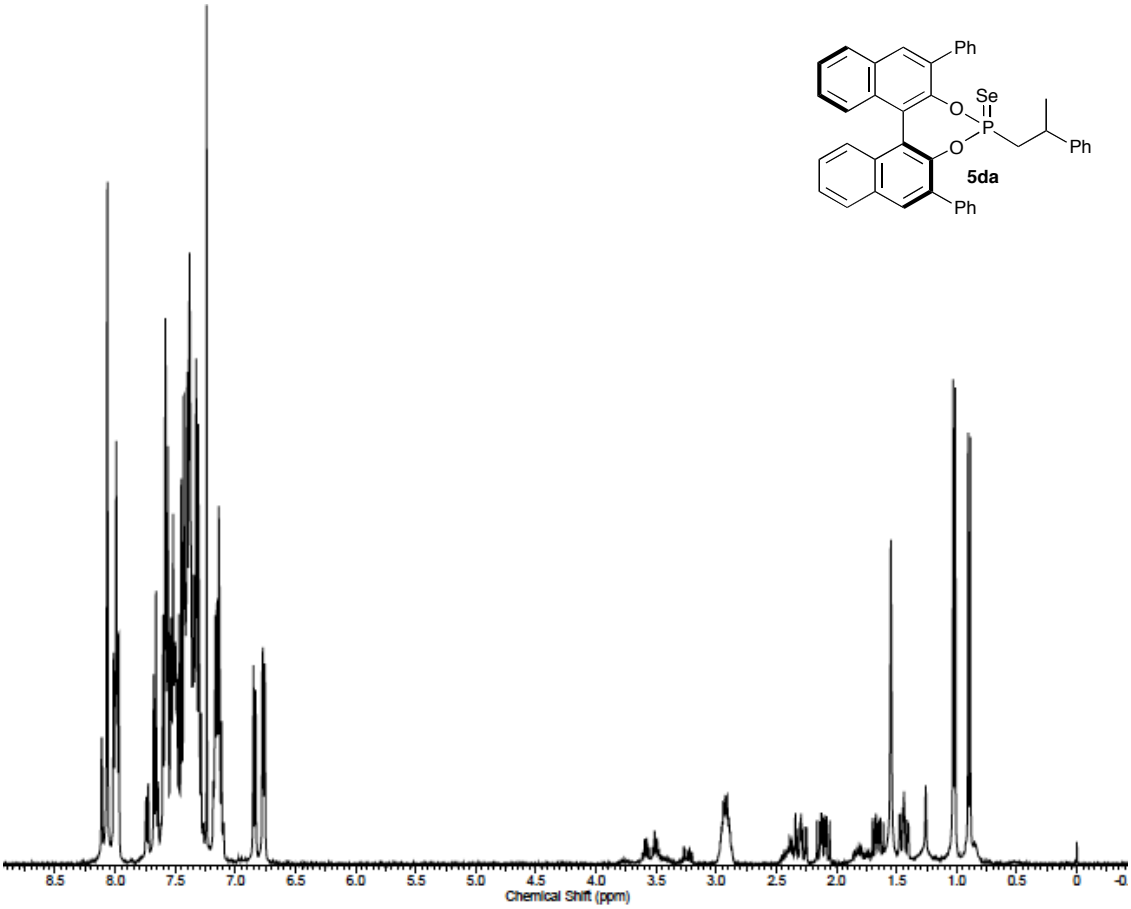

152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

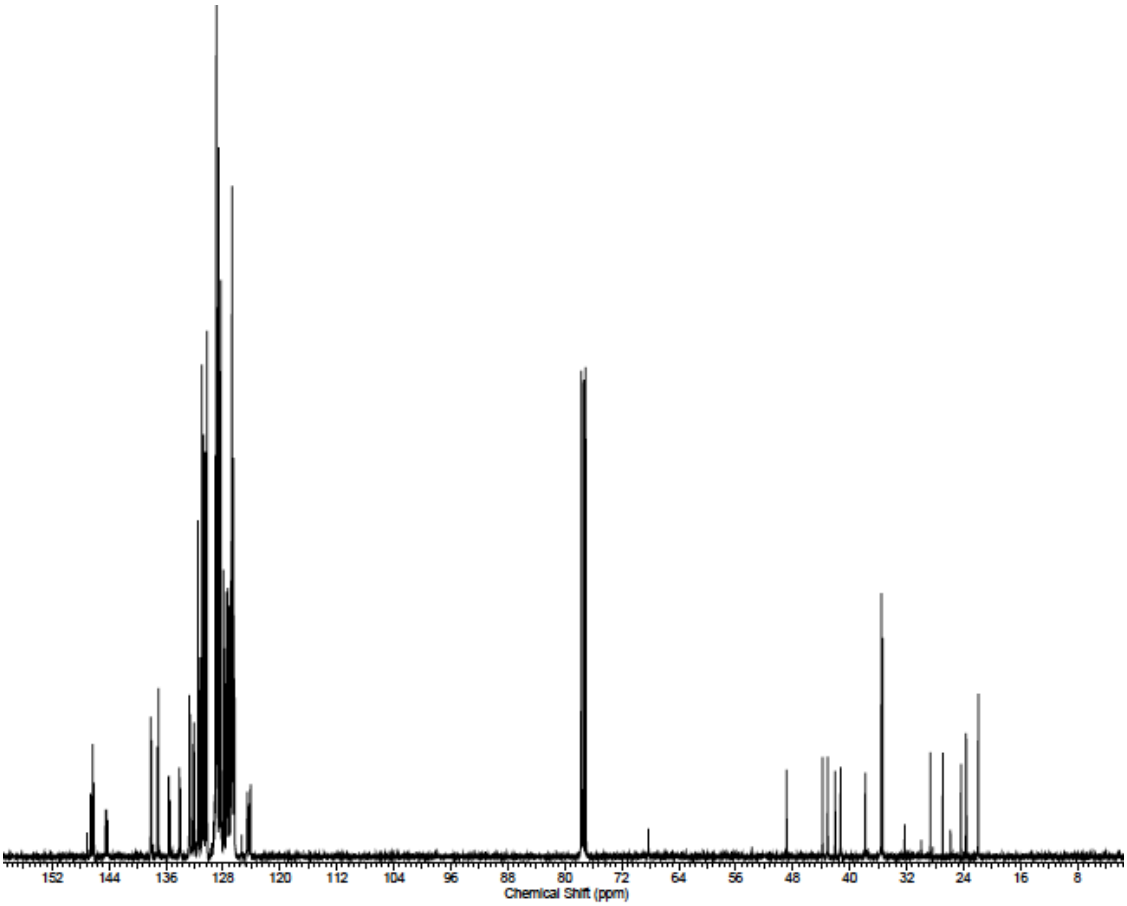

Se
O
P
O
Ph

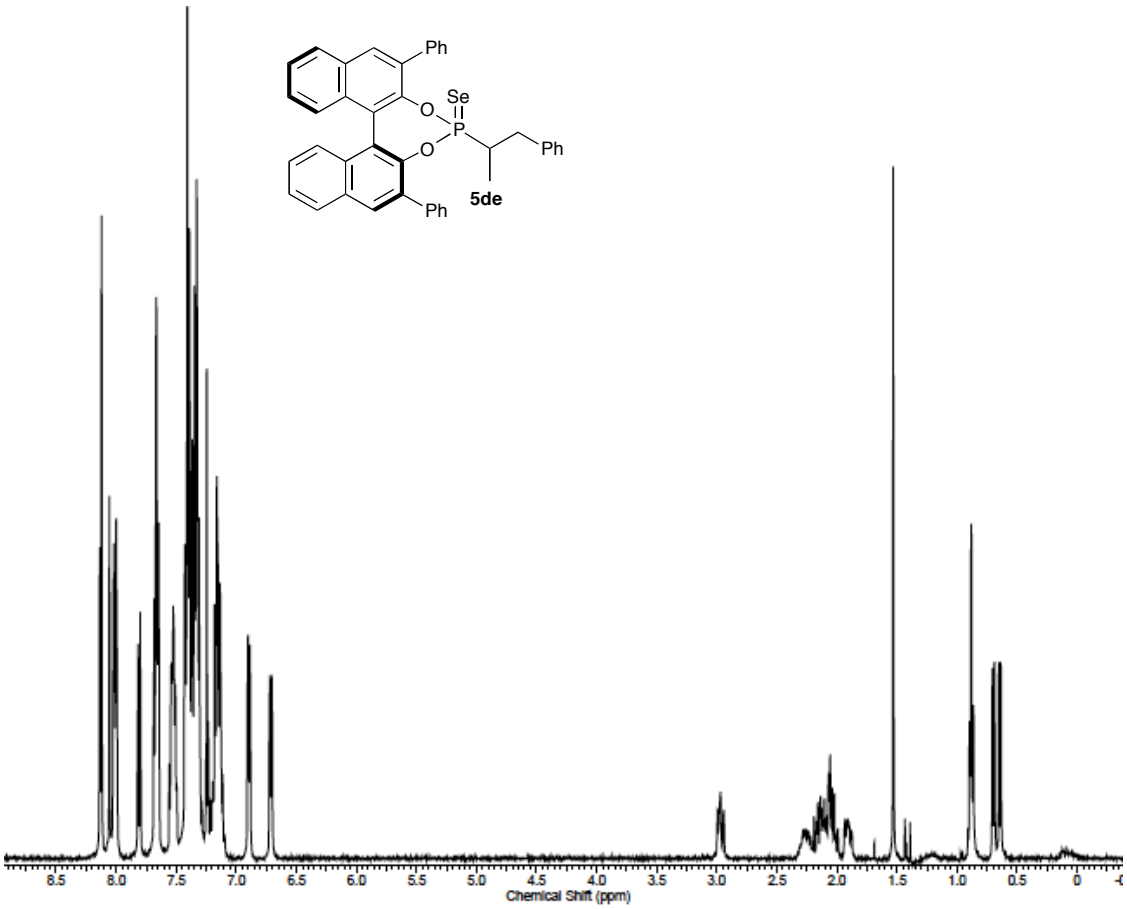
5ci

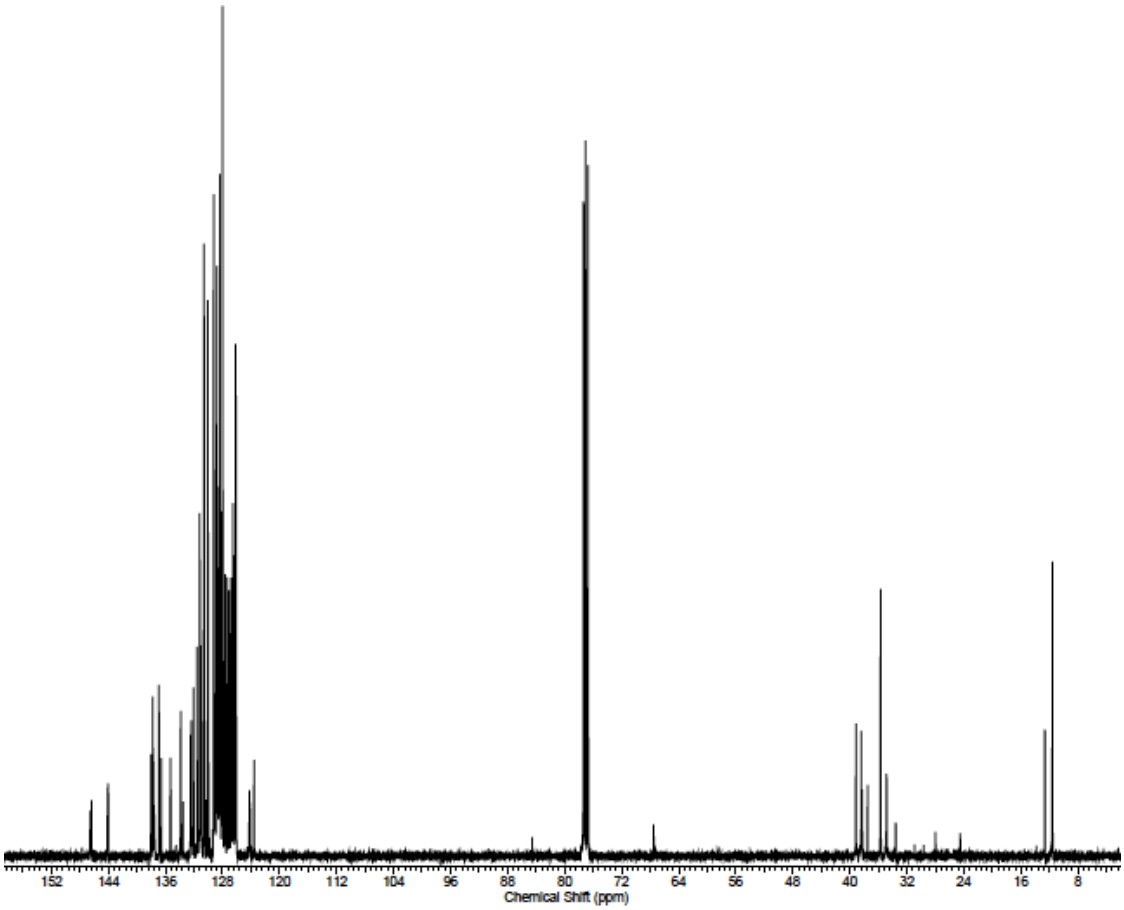
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)

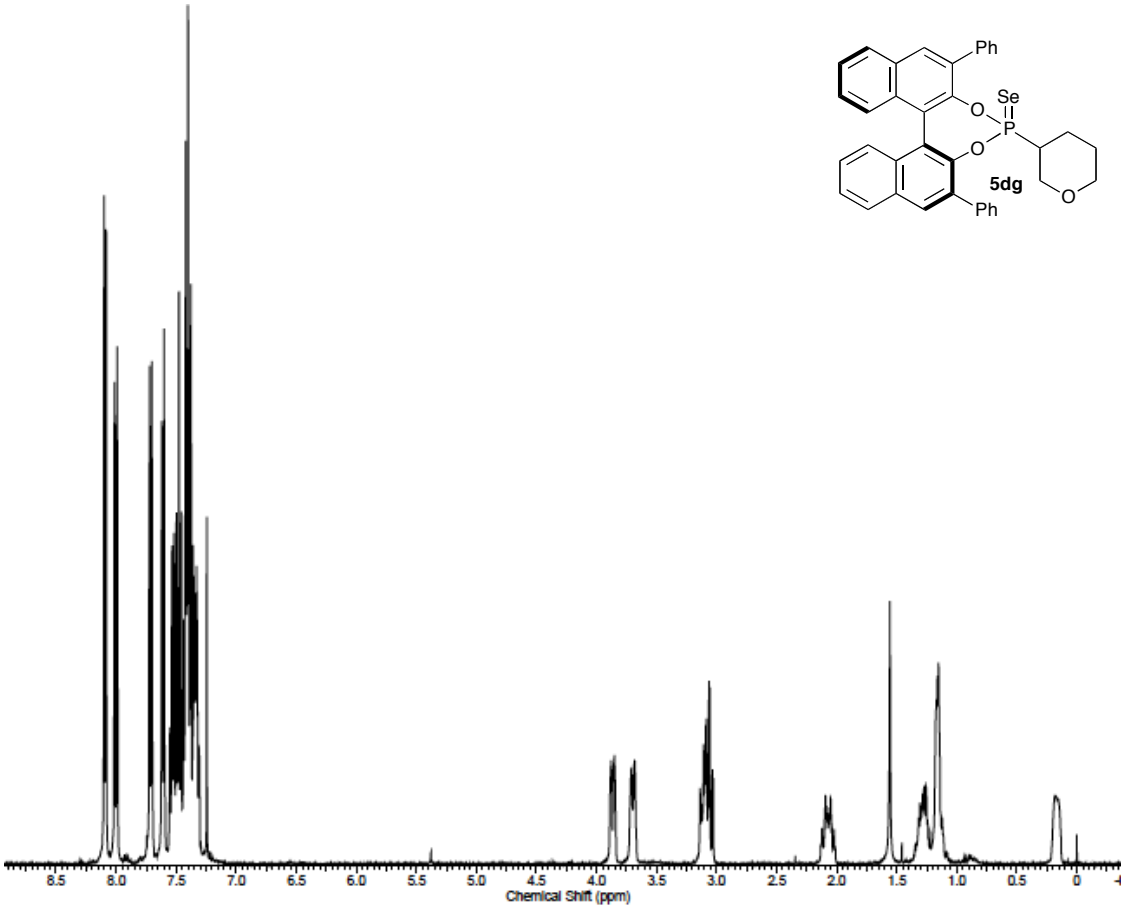

152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

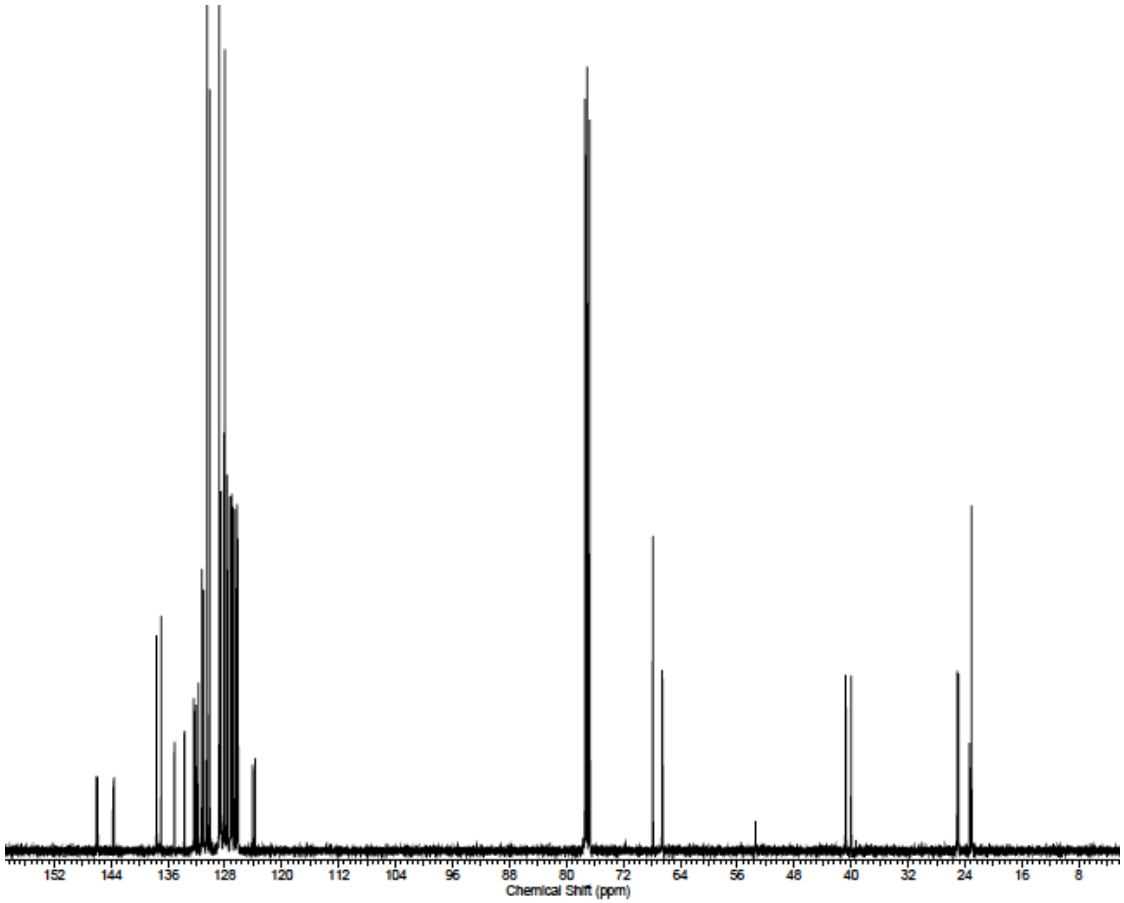

Ph
Se
O
P
O
Ph
5da
Ph
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

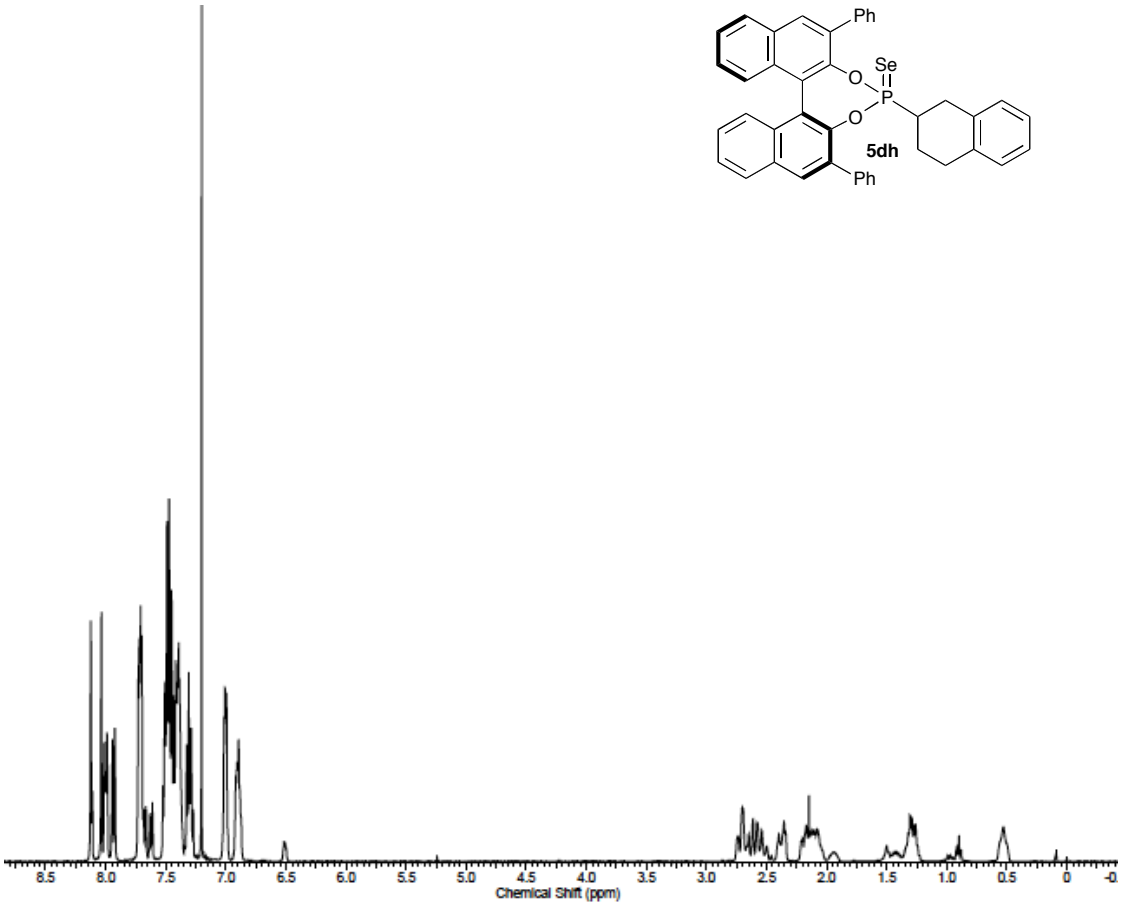

152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


Ph
Se
O
P
O
Ph
Ph
5de
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

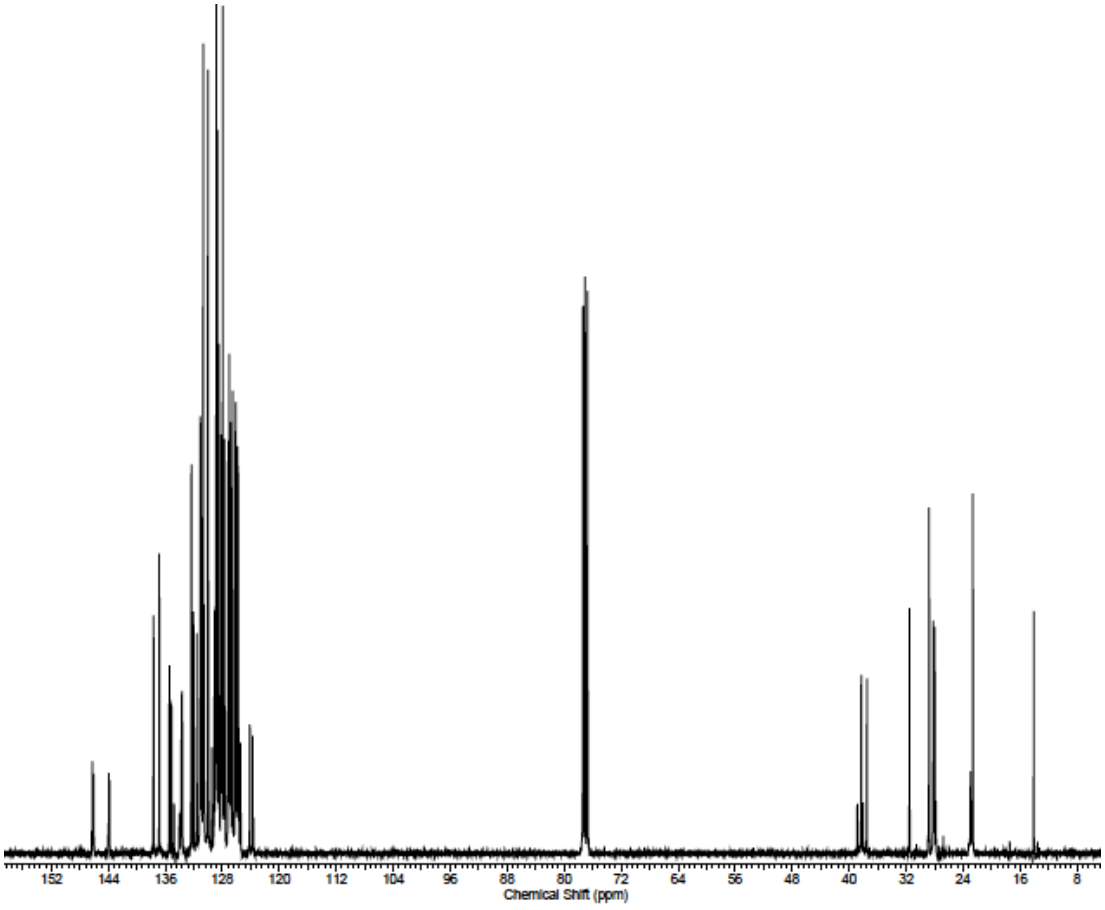

152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

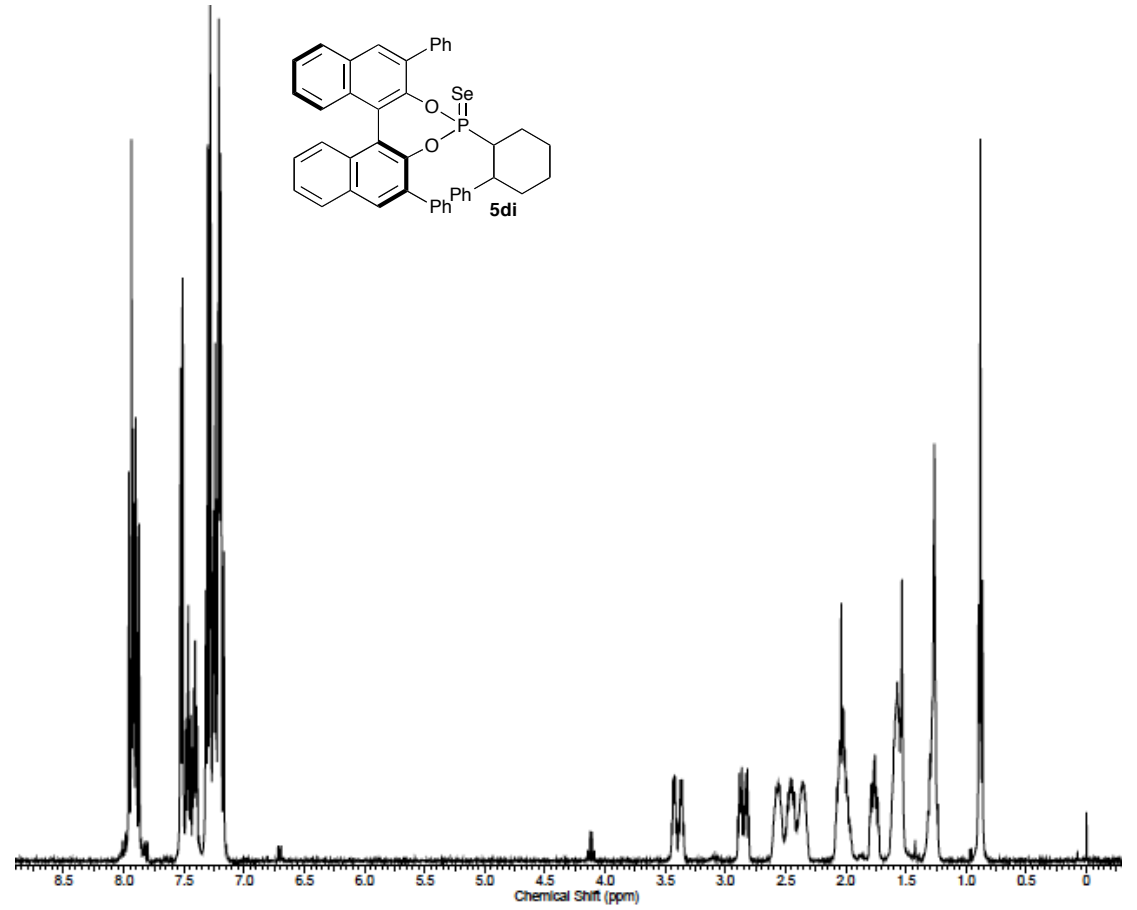

Ph
Se
O
P
O
5dg
O
Ph
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

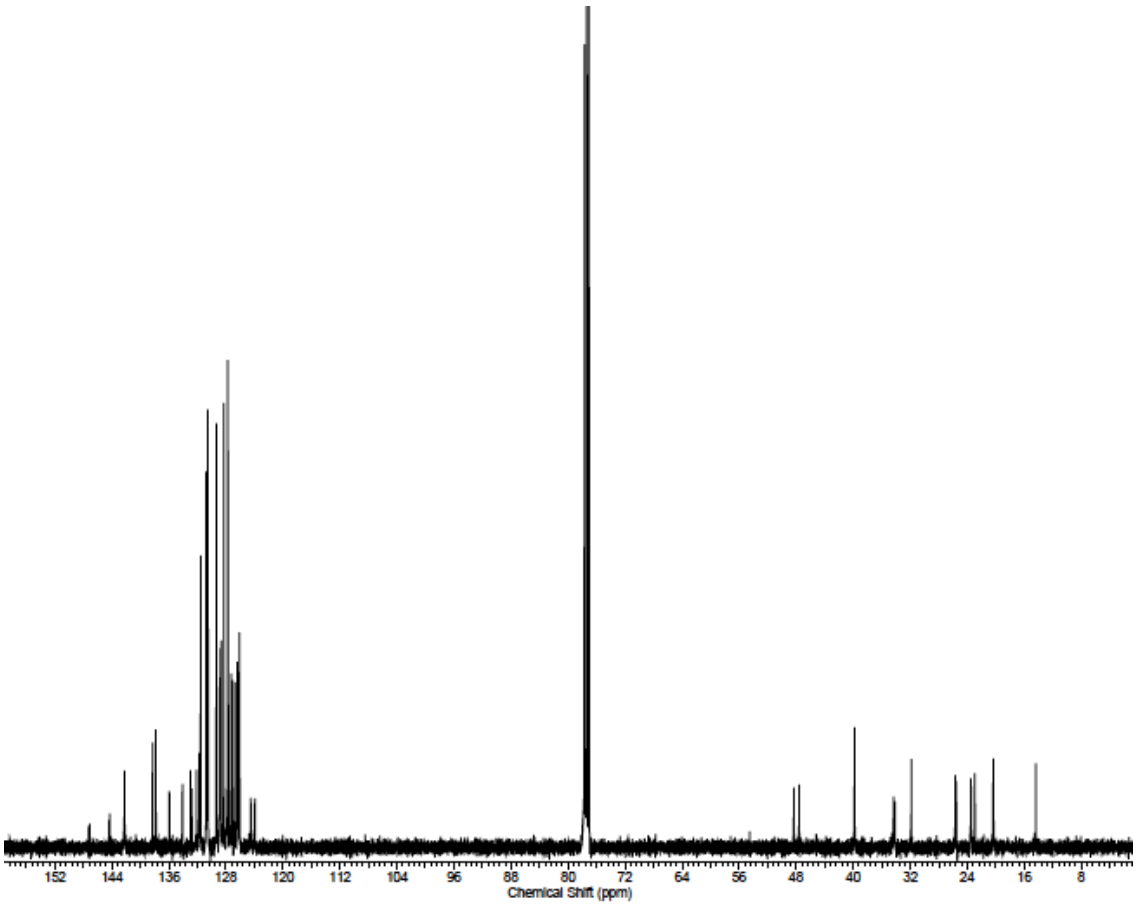

152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

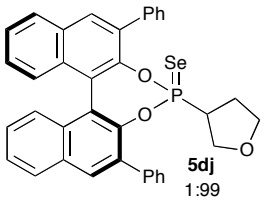

Ph
Se
O
P
O
Ph
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0
Chemical Shift (ppm)

5dh


152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

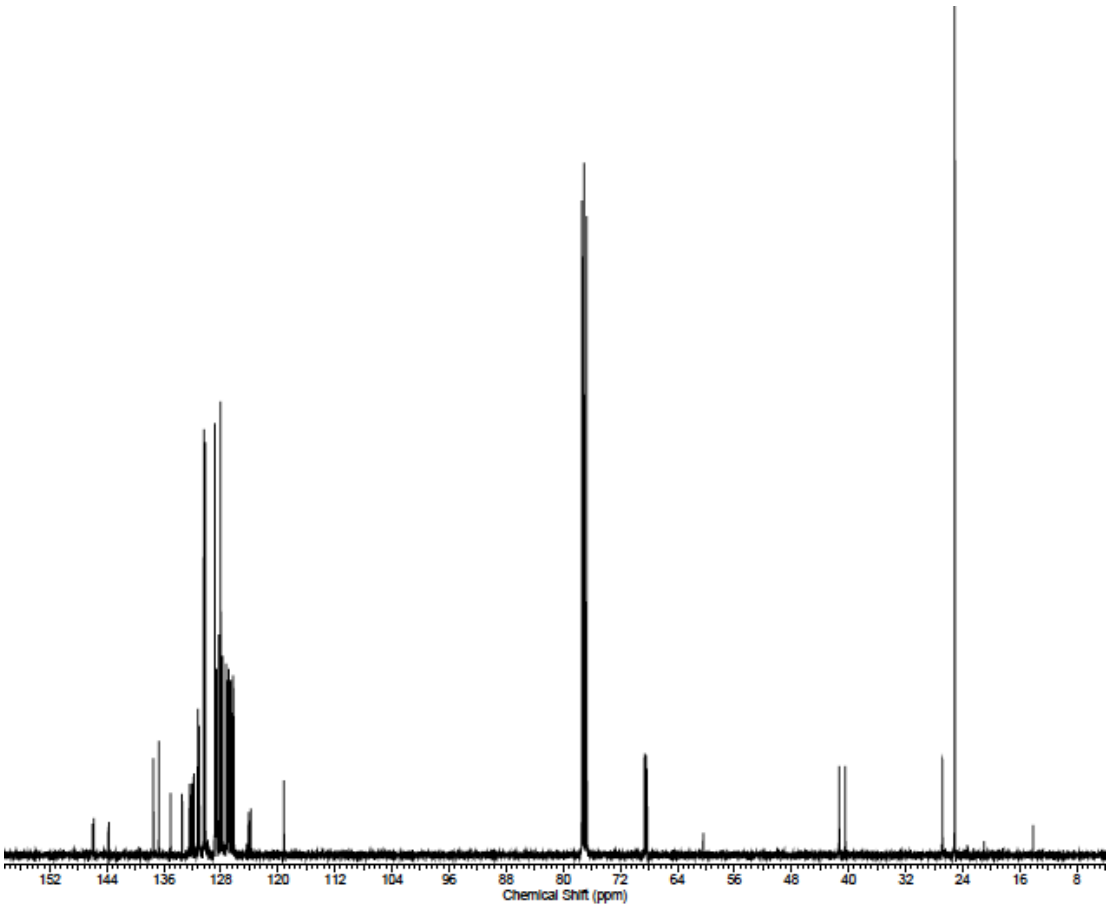

Ph
Se
O
P
O
Ph
Ph
5di
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

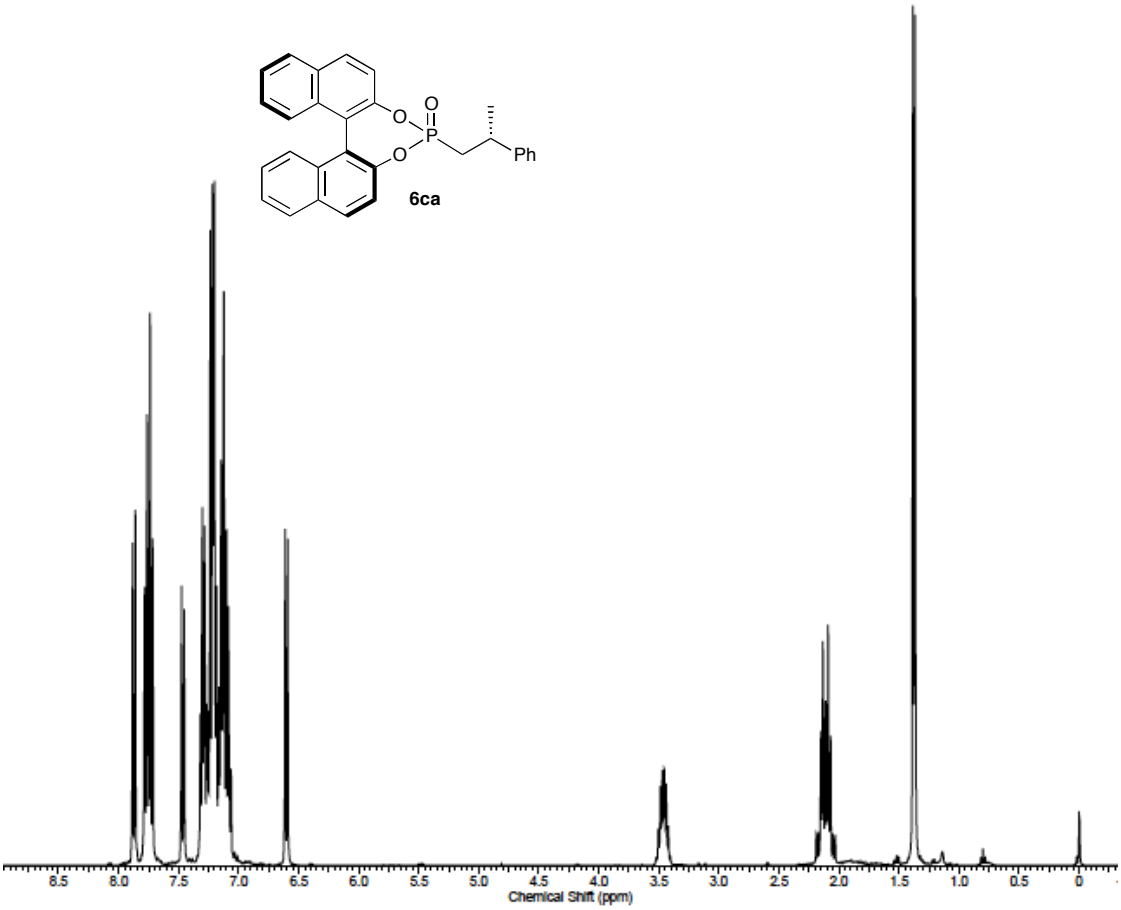

152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

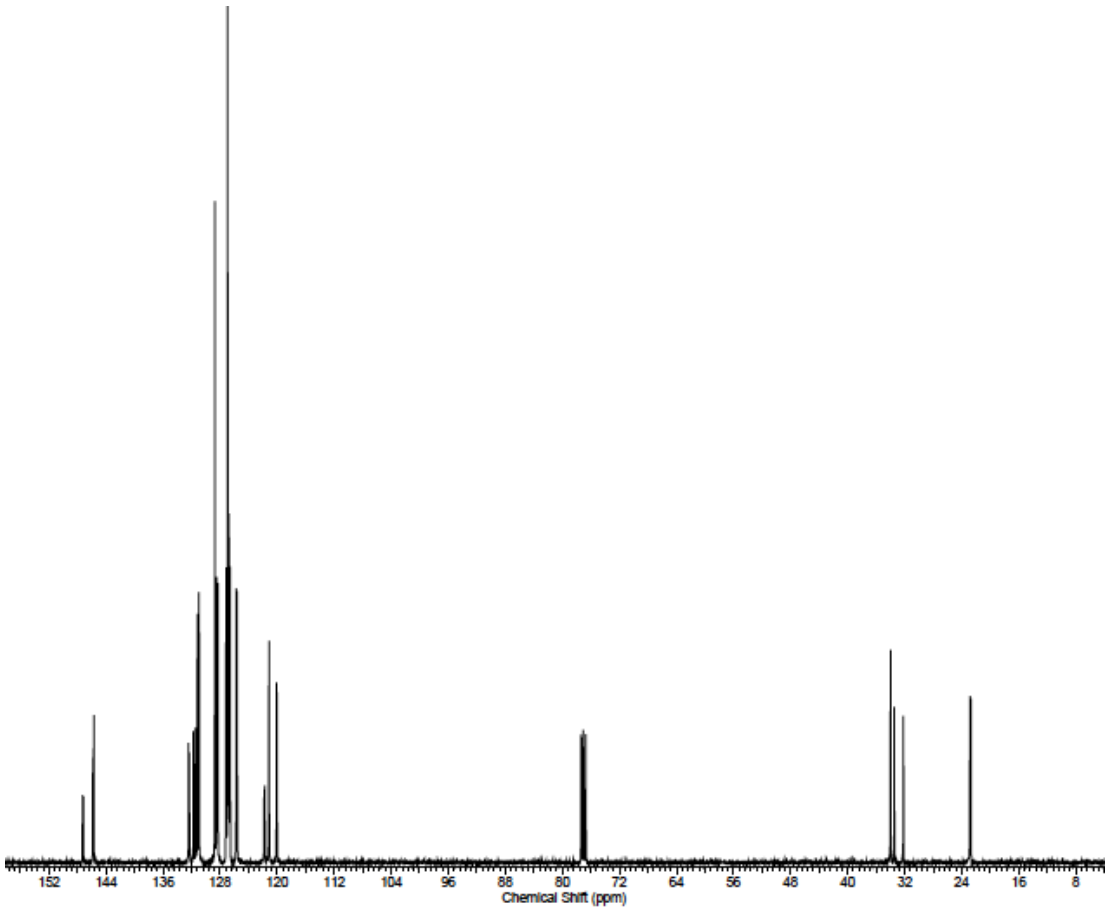

Ph
Se
O
P
O
O
Ph

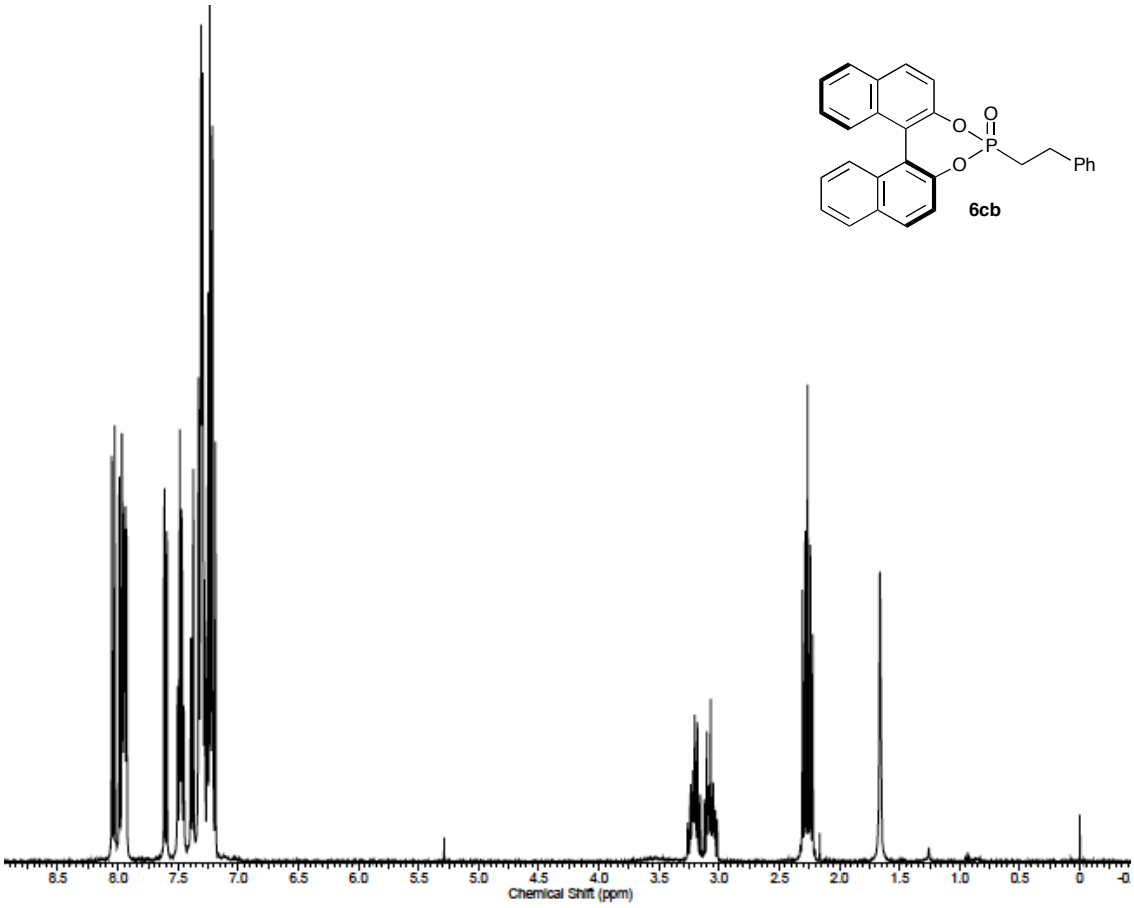
5dj
1:99

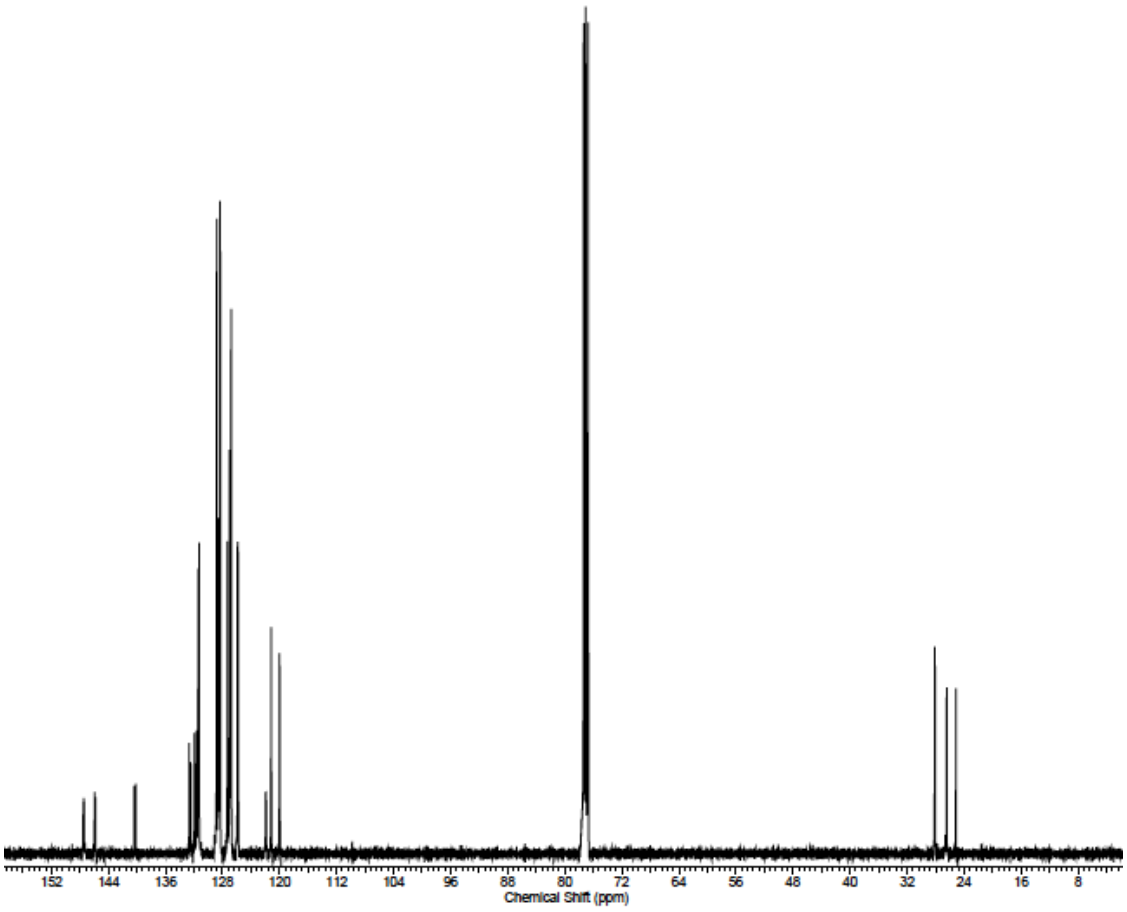
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

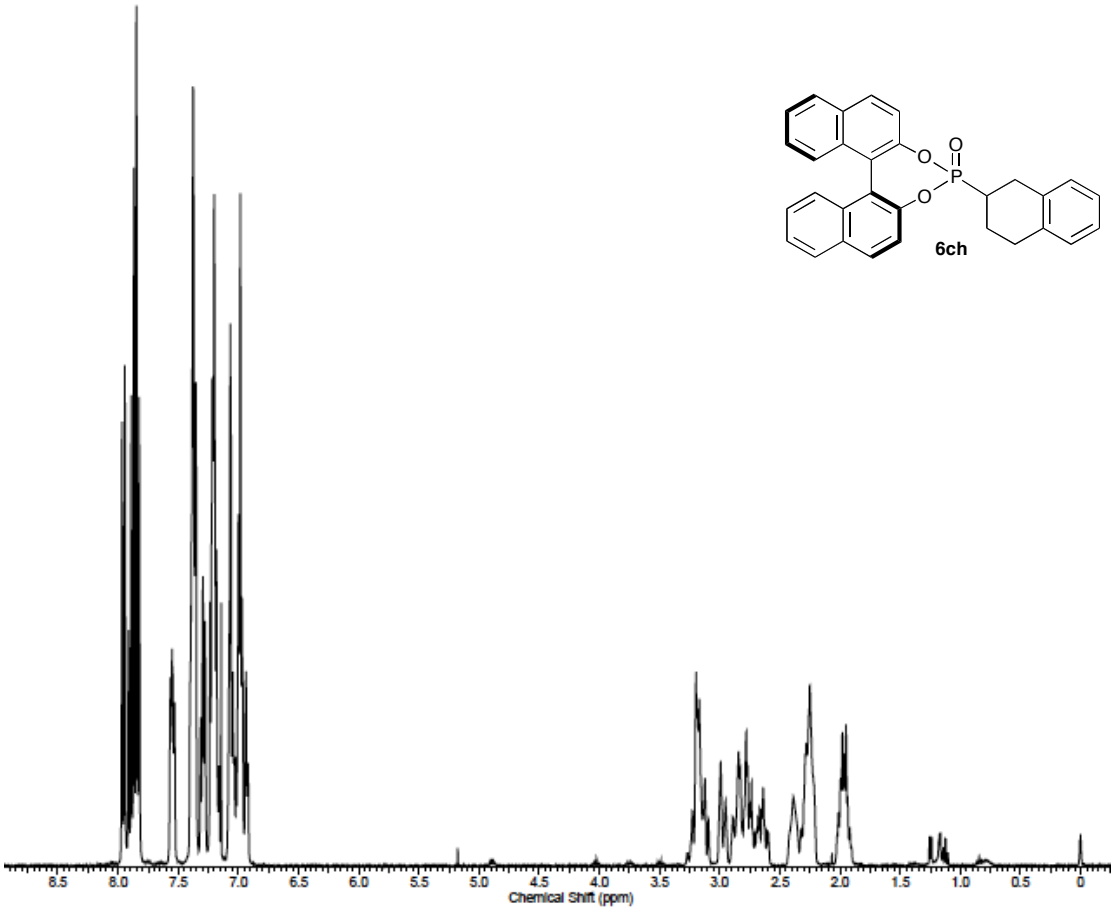

152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

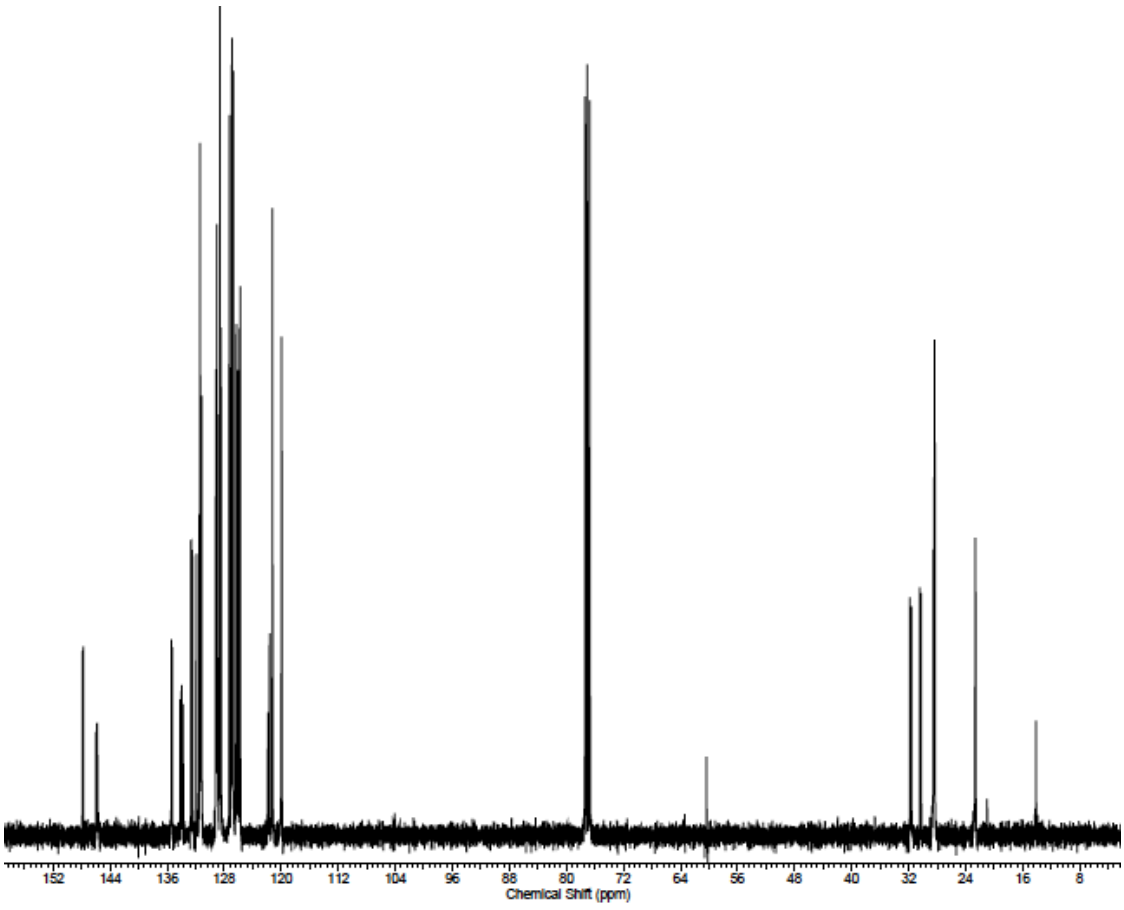

O
O
P
O
Ph
6ca
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

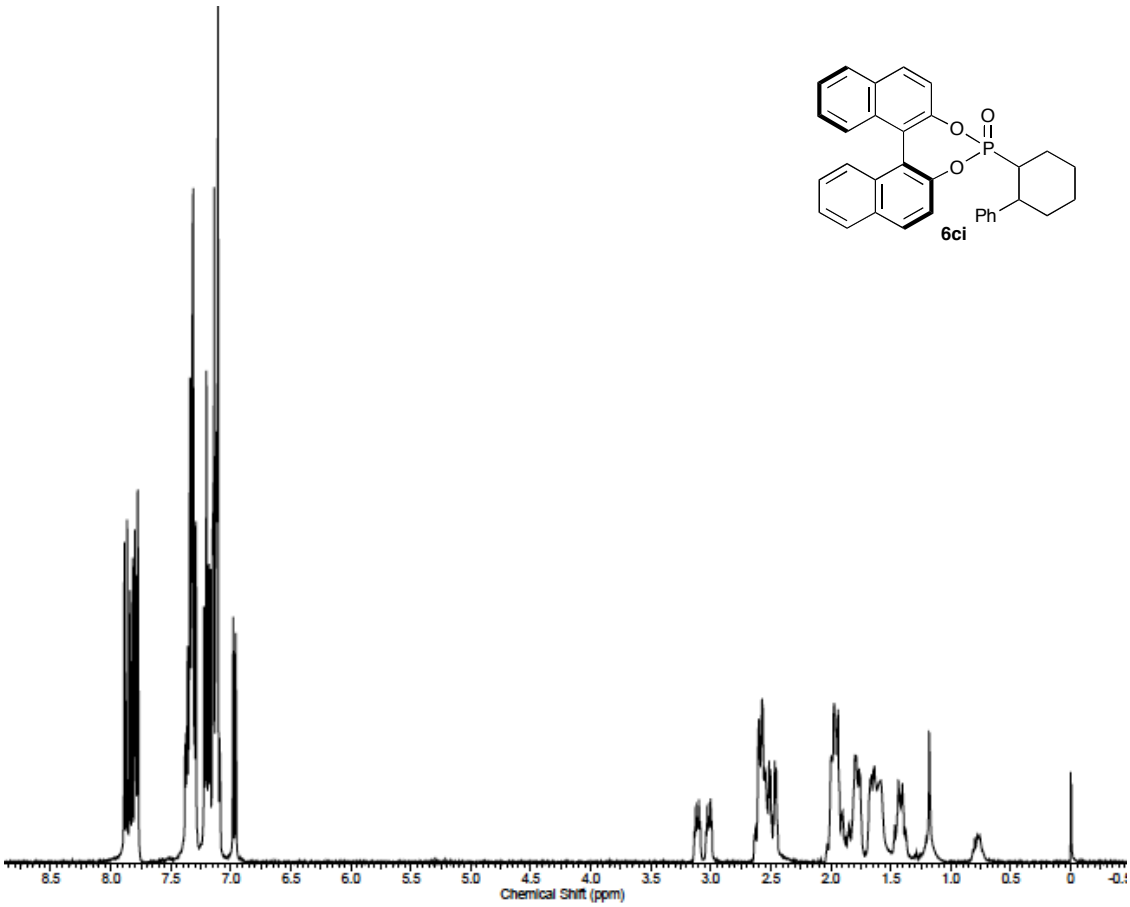

152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

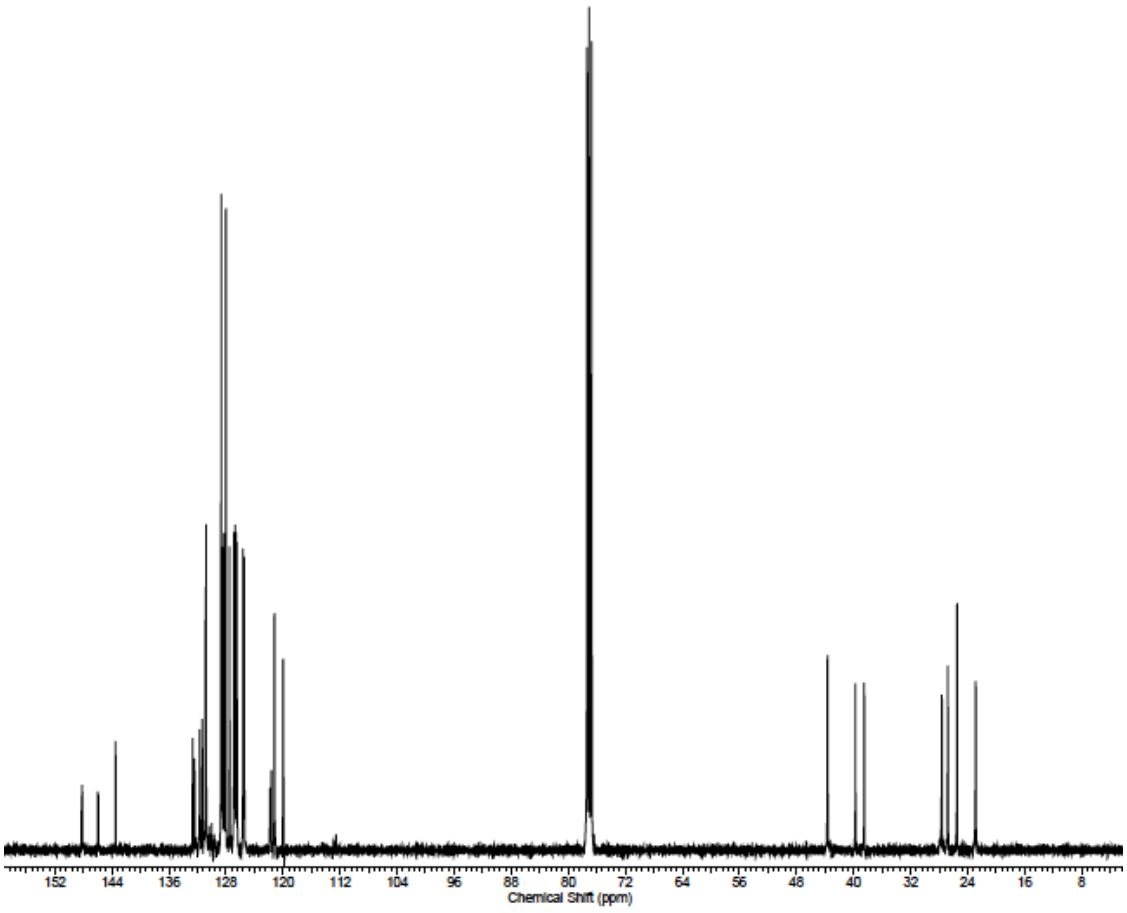

O
O
P
O
Ph
6cb
Chemical Shift (ppm)

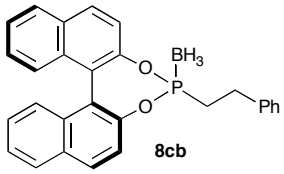

Chemical Shift (ppm)


O
O
P
O
6ch
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

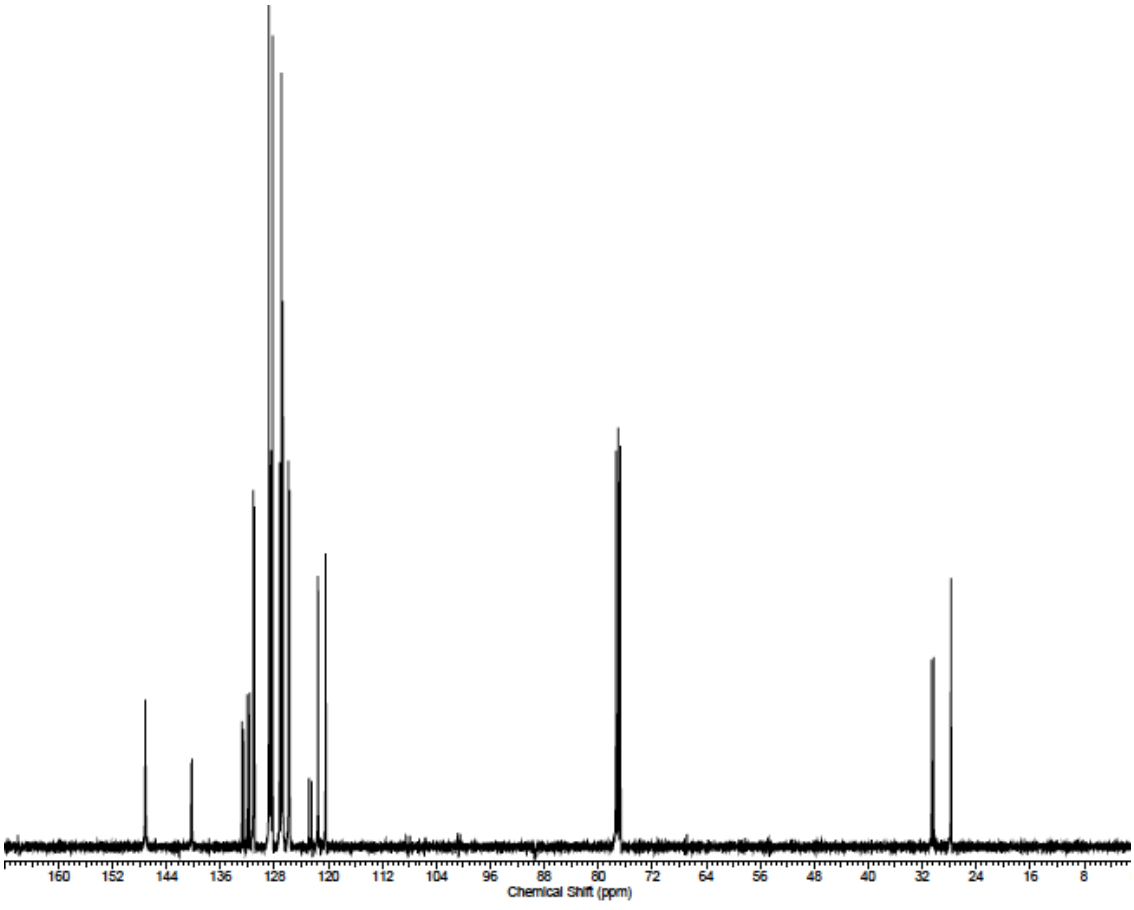

O
O
P
O
Ph
6ci
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

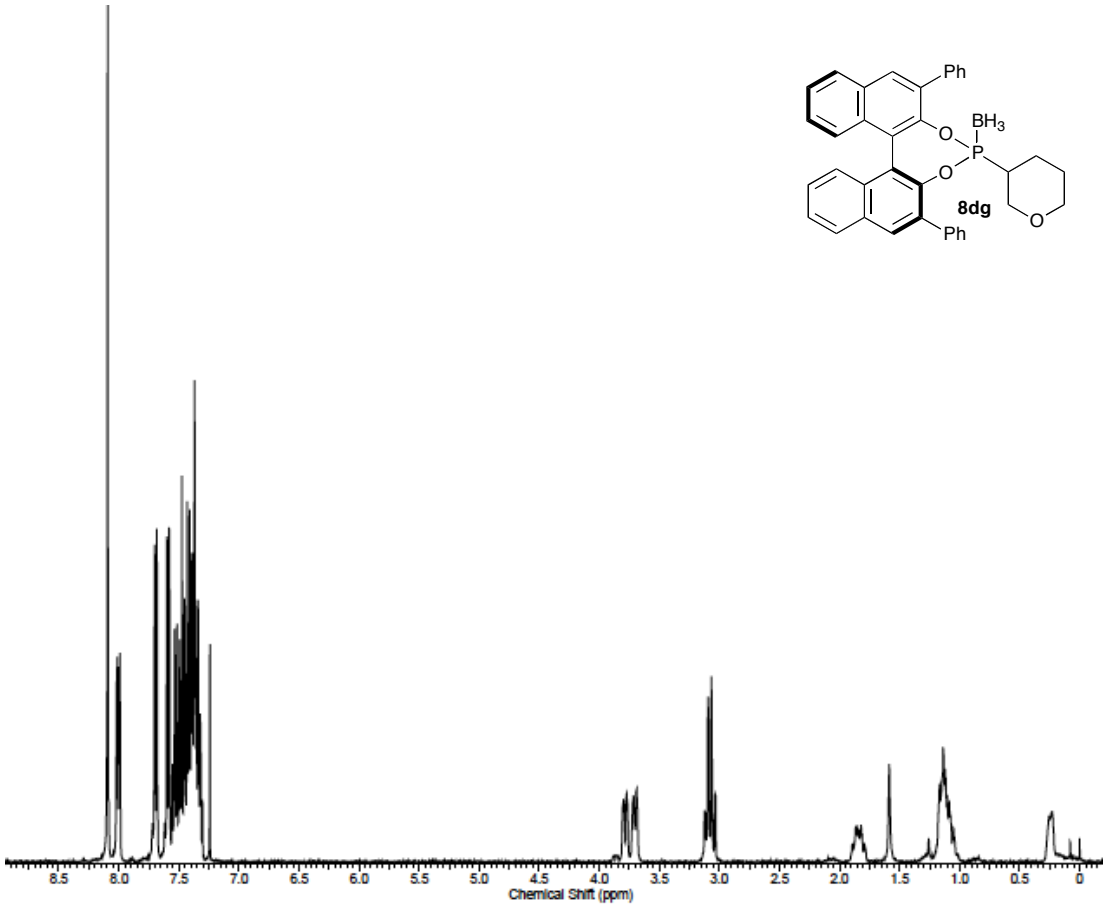

152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

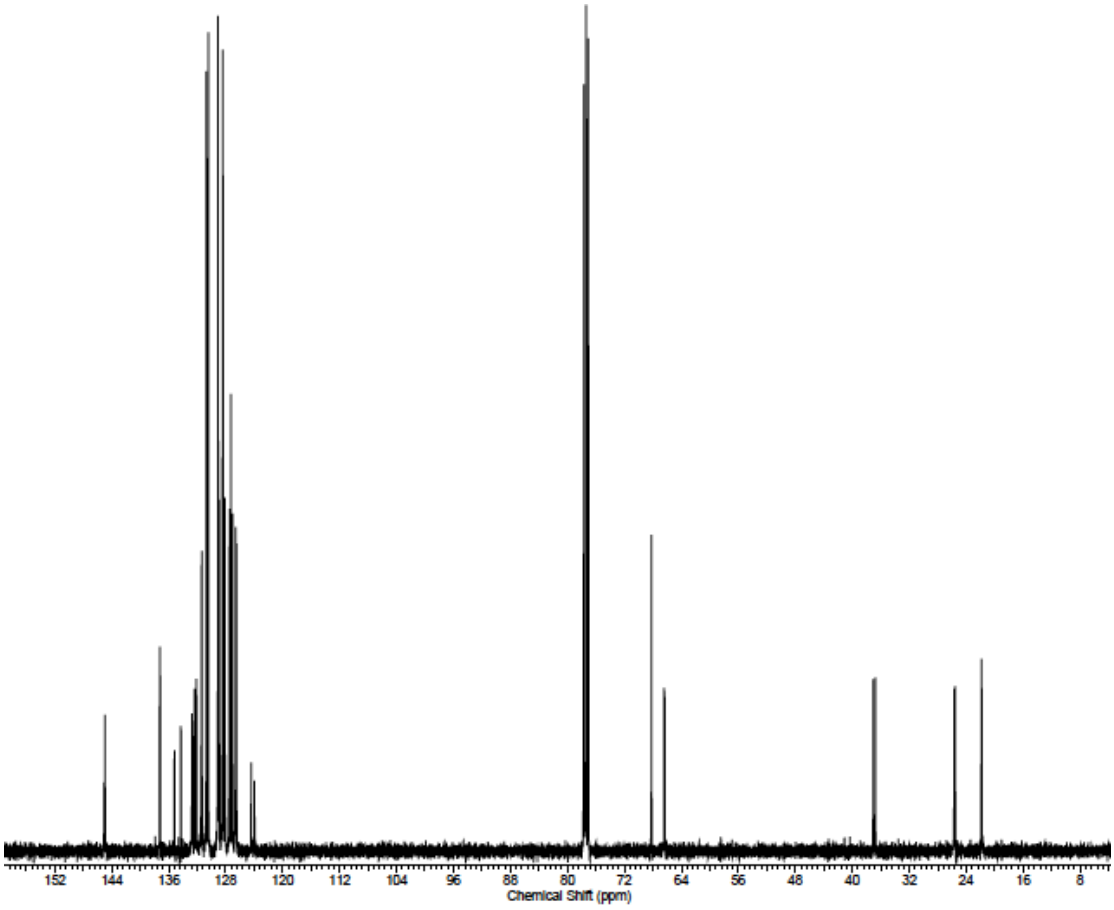

BH3
O
P
O
Ph

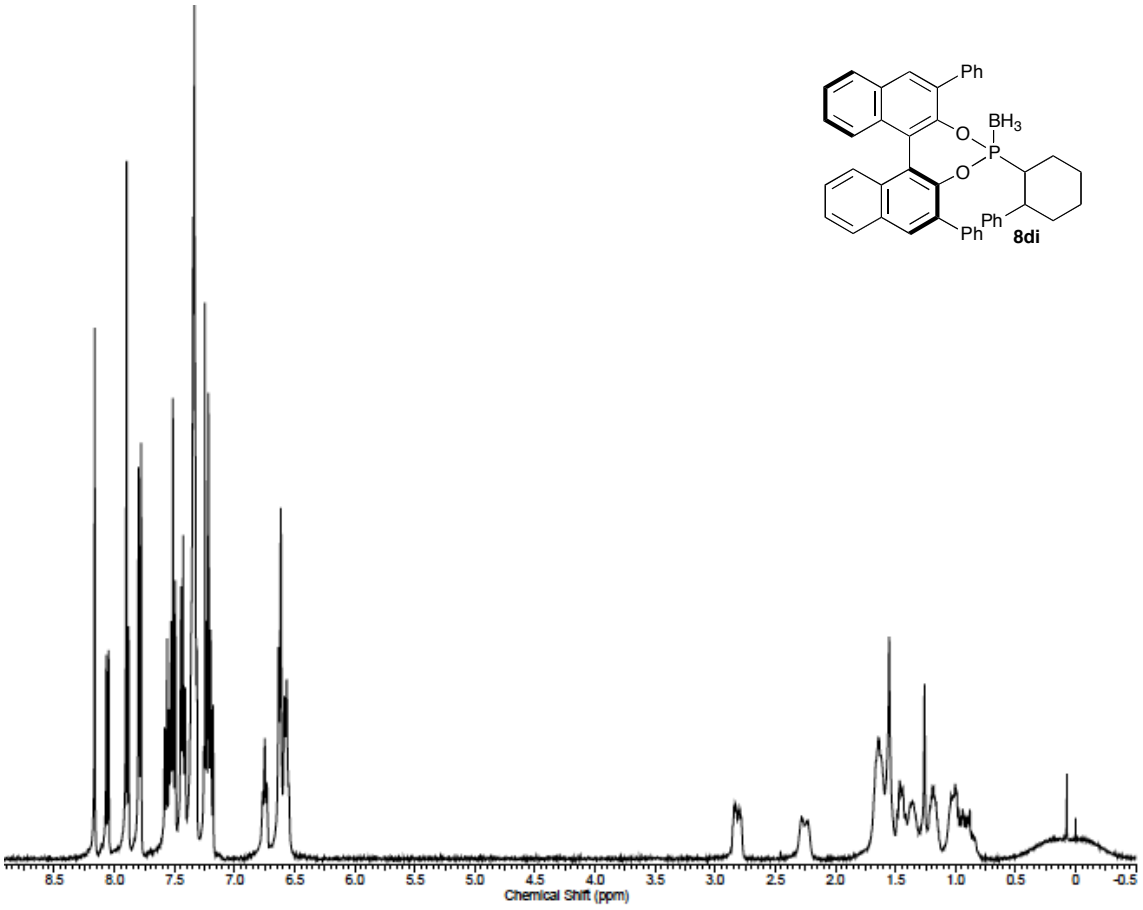
8cb

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

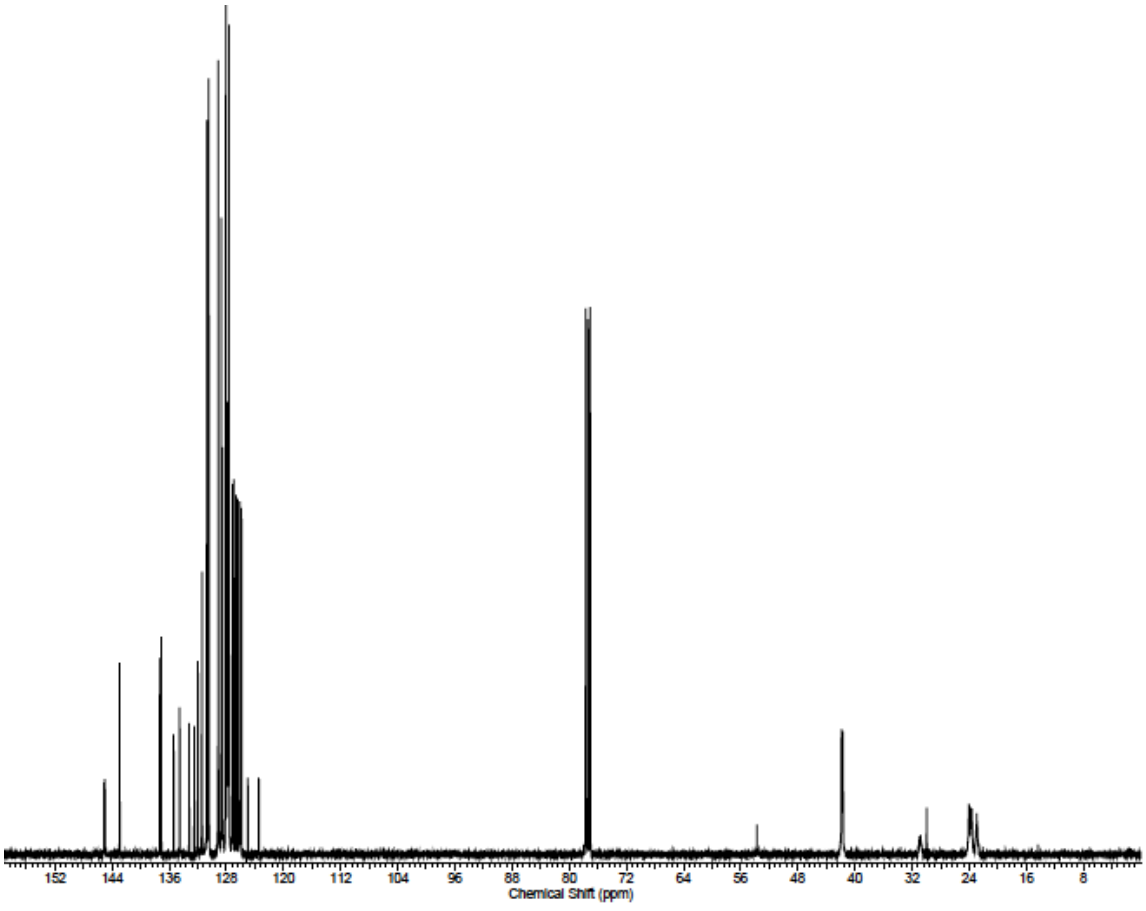

160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

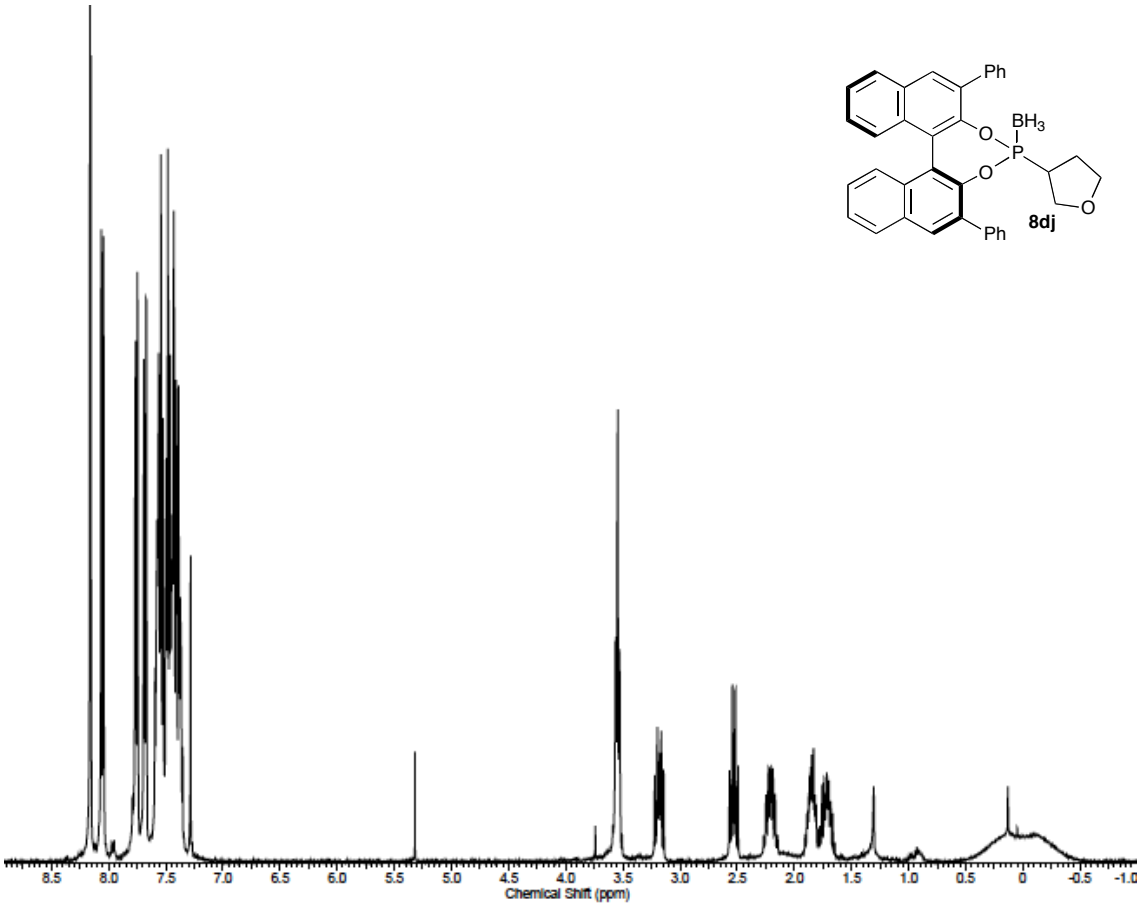

Ph
BH3
O
P
O
8dg
O
Ph
Chemical Shift (ppm)

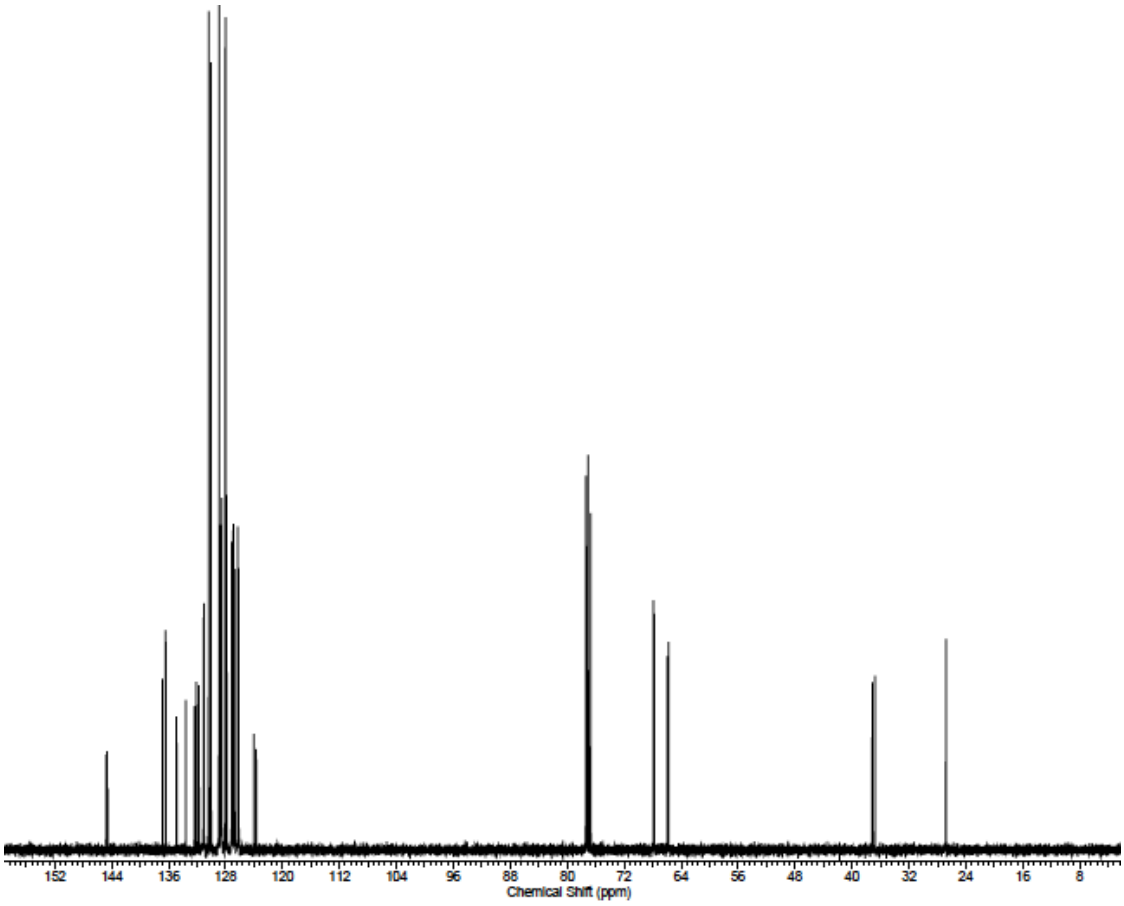

Chemical Shift (ppm)


Ph
BH3
O
P
O
Ph
Ph
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)

8di


152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


Ph
BH3
O
P
O
O
Ph
8dj
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)


152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)