Supporting Information

Phosphonoselenoic Acid Esters from the Reaction between Phosphoroselenoyl Chlorides and Grignard Reagents: Synthetic and Stereochemical Aspects

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General Remarks: The IR spectra were obtained on a JASCO FT/IR 410 spectrometer. The ^{1}H NMR spectra were recorded on a JEOL α-400 (400 MHz) in $CDCl_3$. Chemical shifts of protons were reported in δ values referred to tetramethylsilane as an internal standard in $CDCl_3$, and the following abbreviations were used: s: singlet, d: doublet, t: triplet, m: multiplet. The ^{13}C NMR spectra were measured on a JEOL α-400 (100 MHz) in $CDCl_3$. The ^{19}F NMR spectra were measured on a JEOL α-400 (376 MHz) in $CDCl_3$ and with CF_3COOH as an external standard. The ^{31}P NMR spectra were measured on a JEOL α-400 (162 MHz) in $CDCl_3$ and with 85% H_3PO_4 as an external standard. The 77Se NMR spectra were measured on a JEOL α-400 (76 MHz) in $CDCl_3$ and with Me_2Se as an external standard. All spectra were acquired in the proton-decoupled mode. The mass spectra (MS) and the high-resolution mass spectra (HRMS) were taken on a JMS-700 mass spectrometer. Melting points were determined using a Yanaco seisakusho MP-S2 micro melting point apparatus and are uncorrected.

DFT calculations.

Table S1. Coordinates (Å) of the optimized structure for **1a** calculated at the B3LYP/6-31G (d, p) level of theory

atom	x	v	z
C	-0.08171	-1.08404	-3.42371
C	-0.28892	-1.84507	-2.32473
C	-1.07144	-1.35736	-1.23054
C	-1.65223	-0.07843	-1.31378
C	-1.39459	0.7076	-2.4839
C	-0.6394	0.22403	-3.49758
H	-0.8044	-3.12656	-0.00246
H	0.51492	-1.45359	-4.24812
H	0.13998	-2.83604	-2.2468
C	-1.25079	-2.14092	-0.04588
C	-2.44326	0.41146	-0.20954
H	-1.804	1.70598	-2.54221
H	-0.44775	0.83104	-4.37347
C	-2.5263	-0.351	0.92359
C	-1.93843	-1.65039	1.00723
H	-2.06628	-2.21695	1.92074
C	-3.11927	1.76333	-0.23261
C	-4.10462	2.13589	-1.21824
C	-2.82	2.65185	0.76246
C	-4.57777	1.22549	-2.21848
C	-4.66054	3.42826	-1.17547
C	-3-.38352	3.96243	0.8092
C	-5.51313	1.60472	-3.11999
H	-4.1833	0.21941	-2.23609
C	-5.63834	3.80225	-2.15126
C	-4.26134	4.33958	-0.14565
H	-3.08968	4.62695	1.61179
C	-6.0493	2.92389	-3.09434
H	-5.86677	0.90562	-3.86738
H	-6.04688	4.80398	-2.1101
H	-4.69612	5.33133	-0.13371

H	-6.79288	3.20814	-3.82818
O	-3.27781	0.08406	2.04006
O	-1.8784	2.28894	1.7572
P	-2.588	1.31745	2.94405
Se	-3.91934	2.19427	4.35174
Cl	-0.78696	0.45348	3.64769

Table S2. Coordinates (Å) of the optimized structure for **1b** calculated at the B3LYP/6-31G (d, p) level of theory

atom	x	v	z
C	-0.1172	-1.09217	-3.45728
C	-0.33368	-1.86961	-2.34413
C	-1.08666	-1.3792	-1.24374
C	-1.65671	-0.06352	-1.31042
C	-1.39074	0.71991	-2.46761
C	-0.64205	0.21993	-3.50942
H	-0.83142	-3.15654	-0.03211
H	0.46593	-1.4758	-4.28886
H	0.08125	-2.87194	-2.28112
C	-1.25869	-2.15876	-0.06981
C	-2.42858	0.43064	-0.19929
H	-1.77458	1.73127	-2.5197
H	-0.44726	0.84286	-4.37726
C	-2.48173	-0.35796	0.93952
C	-1.92509	-1.65041	1.01608
H	-2.0426	-2.21296	1.93513
C	-3.11376	1.75381	-0.21909
C	-4.0881	2.12253	-1.21275
C	-2.84996	2.669	0.78608
C	-4.55579	1.21784	-2.2058
C	-4.65652	3.44078	-1.18117
C	-3.41266	3.95912	0.83818
C	-5.49558	1.60452	-3.13488
H	-4.17304	0.20474	-2.21997
C	-5.61145	3.81079	-2.1659
C	-4.28344	4.34349	-0.15009

H	-3.14358	4.61186	1.6603
C	-6.02166	2.91712	-3.12693
H	-5.84085	0.89136	-3.87741
H	-6.02367	4.81571	-2.1343
H	-4.72188	5.33708	-0.13699
H	-6.75738	3.2103	-3.86957
O	-3.16789	0.08838	2.07976
O	-1.95662	2.3149	1.81005
P	-2.57721	1.32695	2.96494
Cl	-0.77382	0.62486	3.68596
S	-3.75838	2.00141	4.16334

Table S3. Coordinates (Å) of the optimized structure for **1c** calculated at the B3LYP/6-31G (d, p) level of theory

atom	x	v	z
C	-0.12516	-1.07903	-3.46341
C	-0.34076	-1.86179	-2.35379
C	-1.09154	-1.37601	-1.24987
C	-1.66081	-0.05969	-1.3092
C	-1.39576	0.72921	-2.4628
C	-0.64875	0.23377	-3.50808
H	-0.83526	-3.15973	-0.04772
H	0.45641	-1.45901	-4.29775
H	0.07335	-2.86478	-2.29623
C	-1.26175	-2.16142	-0.07941
C	-2.43058	0.42944	-0.19377
H	-1.77851	1.74119	-2.5096
H	-0.45443	0.86098	-4.37292
C	-2.48038	-0.3643	0.94081
C	-1.9245	-1.65755	1.01067
H	-2.03992	-2.2237	1.92777
C	-3.11762	1.75157	-0.20955
C	-4.08827	2.11796	-1.20848
C	-2.85769	2.67042	0.79342
C	-4.5595	1.20676	-2.19385
C	-4.64805	3.43982	-1.19149

C	-3.40467	3.96816	0.82493
C	-5.49532	1.59026	-3.1283
H	-4.18363	0.191	-2.19717
C	-5.59876	3.80661	-2.18145
C	-4.26807	4.35068	-0.17039
H	-3.12742	4.63118	1.63616
C	-6.01308	2.90614	-3.13433
H	-5.84404	0.87191	-3.86416
H	-6.0043	4.8145	-2.16041
H	-4.69425	5.34963	-0.1707
H	-6.74568	3.19658	-3.8811
O	-3.15645	0.08055	2.08687
O	-1.97193	2.32485	1.8282
P	-2.56596	1.31483	2.97144
Cl	-0.76105	0.63141	3.68992
O	-3.54205	1.83706	3.99073

NPA charge distribution and energy levels of LUMO+1 and LUMO+2 of **1** are shown in Table S4, and molecular orbitals of **1** are shown in Figure S1. The NPA charge distribution revealed that, even though the differences among **1a**–**1c** are small, the phosphorus atom of **1a** is the most positively charged, while that of **1b** is the least positively charged.

Table S4 NPA charge distribution and energy levels of LUMO+1 and LUMO+2 of **1**

		charge distribution			Energy level (eV)	
	E	E	P	Cl	LUMO+1	LUMO+2
1a	O	-0.47	1.08	-0.18	-1.38	-0.82
1b	S	-0.24	0.80	-0.15	-1.44	-1.04
1c	Se	-0.32	0.90	-0.16	-1.71	-1.11

Molecular orbitals of 1

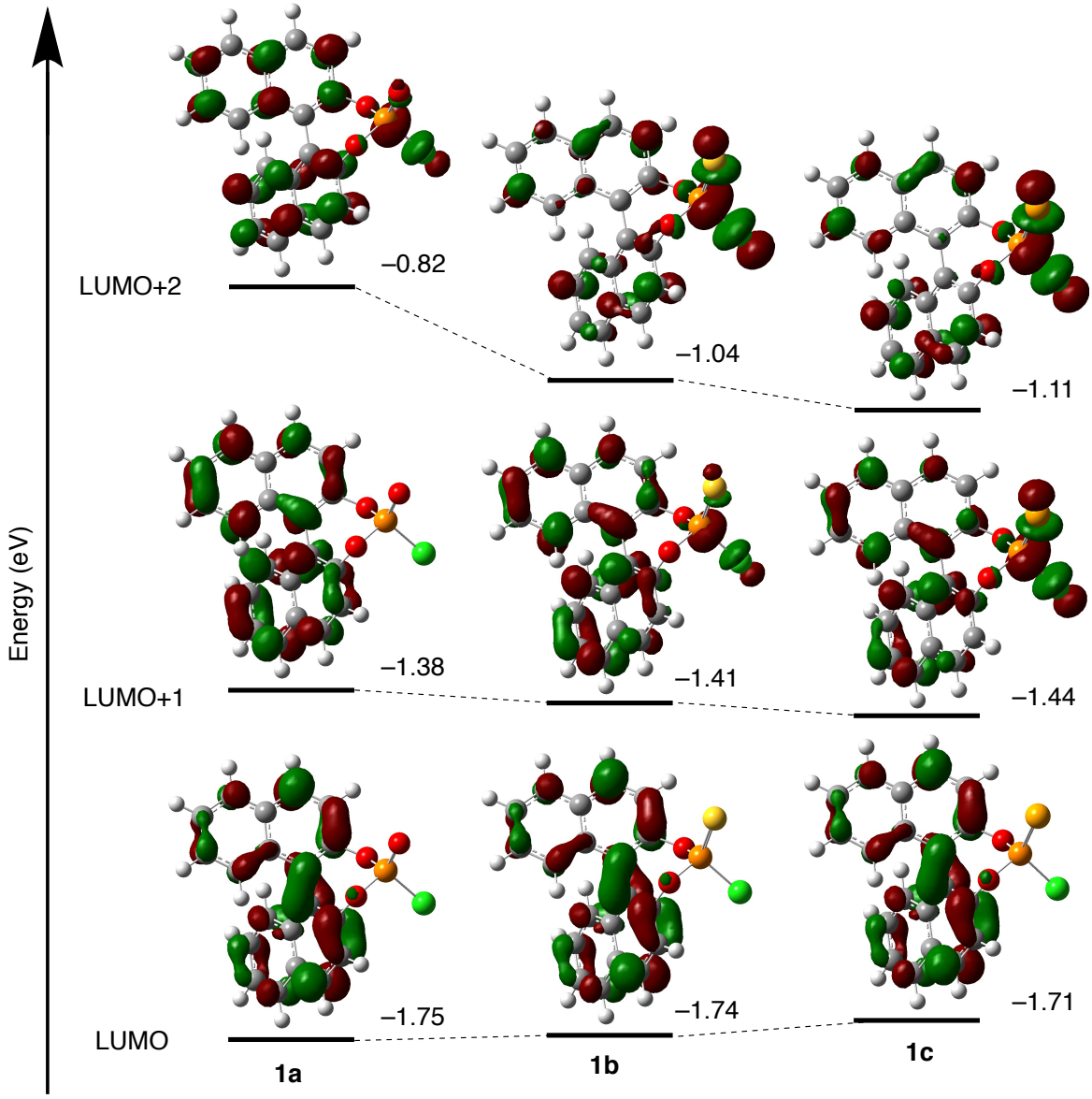


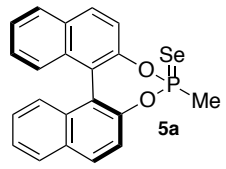
Figure S1. Energy diagrams and the pictorial representations of the selected Kohn–Sham molecular orbitals for the phosphoryl (**1a**), phosphorothionyl (**1b**), phosphoroselenoyl chlorides (**1c**) calculated at the B3LYP/6-31G(d,p) level.

Synthesis of compounds **5**, **7**–**11**

Two synthetic procedures were used for phosphonoselenoic acid esters **5**, **7**–**9**

Typical Procedure A for the preparation of (S_{ax})-4-methylbinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (**5a**): Methylmagnesium bromide (**2a**) (0.68 M Et_2O solution, 0.74 mL, 0.5 mmol) was added to a toluene solution (5 mL) of (S_{ax})-binaphthylphosphoroselenoic acid chloride ((S_{ax})-BISEPCl) (214 mg, 0.5 mmol) via syringe pomp at 40 ºC over 20 minutes, and it was stirred at that temperature for 30 min. After that, saturated NH_4Cl aqueous solution was added to the resulting mixture and water was further added to dilute the solution. The aqueous phase was extracted with ether three times. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.15) to give (S_{ax})-4-methylbinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (**5a**) (156 mg, 76%) as a colorless solid.

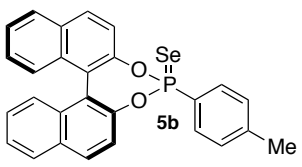
(S_{ax})-4-Methylbinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (5a)



Chemical Formula: $C_{21}H_{15}O_2PSe$
Exact Mass: 410.00
Molecular Weight: 409.28

mp: 214.3-214.9 °C; IR (KBr): 2913, 1618, 1587, 1505, 904, 865, 836, 812, 770, 752 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10 (d, J = 13.5 Hz, 3H, $C\underline{H}_3$), 7.13-7.25 (m, 3H, Ar), 7.29-7.39 (m, 4H, Ar), 7.48 (d, J = 8.5 Hz, 1H, Ar), 7.84 (d, J = 8.1 Hz, 2H, Ar), 7.89-7.94 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 23.0 (δ, $^1J_{C\text{-}P}$ = 86.4 Hz, $\underline{C}H_3$), 120.3, 121.6, 122.7, 125.7, 125.9, 126.6, 126.9, 127.2, 128.4, 128.6, 130.8, 131.1, 131.7, 132.0, 132.5, 132.6, 146.0, 146.2, 148.0, 148.2 (Ar); ^{31}P NMR ($CDCl_3$): δ 115.7 ($^1J_{P\text{-}Se}$ = 921.2 Hz); ^{77}Se NMR ($CDCl_3$): δ −193.9 ($^1J_{P\text{-}Se}$ = 921.2 Hz); MS (EI) m/z 410 (M^+); HRMS Calcd for $C_{21}H_{15}O_2PSe$: 409.9975, Found: 409.9974.

(S_{ax})-4-(p-Tolyl)binaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (5b)



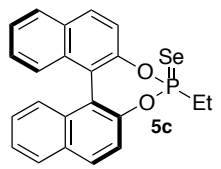
Chemical Formula: $C_{27}H_{19}O_2PSe$
Exact Mass: 486.03
Molecular Weight: 485.37

The compound was synthesized *via* Procedure A, with 4-methylmagnesium bromide (**2b**) (0.5 M Et_2O solution, 5.0 mL, 2.5 mmol), toluene (10 mL), and (S_{ax})-BISEPCl (1.07 g, 2.5 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.18) gave the corresponding ester (**5b**) (1.05 g, 86%) as a colorless solid.

mp: 197.7-198.2 °C; IR (KBr): 2917, 2863, 1618, 1589, 1507, 1462, 1434, 854, 805, 771, 754 cm^{-1};

^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3H, C$\underline{H}_3$), 6.90 (dd, J = 9.0, 0.9 Hz, 1H, Ar), 7.12-7.15 (m, 2H, Ar), 7.24-7.38 (m, 3H, Ar), 7.46-7.50 (m, 3H, Ar), 7.58-7.67 (m, 3H, Ar), 7.78 (d, J = 9.0 Hz, 1H, Ar), 7.89 (d, J = 8.1, 1H, Ar), 7.98 (d, J = 8.1 Hz, 1H, Ar), 8.07 (d, J = 9.0 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 21.6 (C$\underline{H}_3$), 121.1 (d, $J_{P\text{-}C}$ = 1.9 Hz), 121.9 (d, $J_{P\text{-}C}$ = 1.9 Hz), 122.3 (d, $J_{P\text{-}C}$ = 2.8 Hz), 122.8 (d, $J_{P\text{-}C}$ = 2.8 Hz), 125.7, 126.5, 126.6, 127.0, 127.2, 128.4, 128.5, 128.7, 128.9, 130.4, 130.7, 131.5, 131.7, 131.9, 132.0, 132.4, 132.6, 144.2 (d, $J_{P\text{-}C}$ = 2.8 Hz), 145.9, 146.0, 148.3, 148.5 (Ar); ^{31}P NMR ($CDCl_3$): δ 110.0 ($^1J_{P\text{-}Se}$ = 929.1 Hz); ^{77}Se NMR ($CDCl_3$): δ -242.8 ($^1J_{P\text{-}Se}$ = 929.1 Hz); MS (EI) m/z 486 (M^+); HRMS Calcd for $C_{27}H_{19}O_2PSe$: 486.0288, Found: 486.0290.

(S_{ax})-4-Ethylbinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (5c)

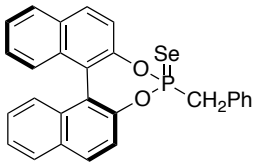


Chemical Formula: $C_{22}H_{17}O_2PSe$
Exact Mass: 424.01
Molecular Weight: 423.30

The compound was synthesized *via* Procedure A, with ethylmagnesium bromide (**2c**) (0.79 M Et_2O solution, 0.63 mL, 0.5 mmol), toluene (5 mL), and (S_{ax})-BISEPCl (215 mg, 0.5 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.18) gave the corresponding ester (**5c**) (153 mg, 72%) as a colorless solid.

mp: 238.6-239.5 °C; IR (KBr): 2981, 2939, 1640, 1618, 1587, 1505, 1460, 1430, 951, 856, 813, 767, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.38 (dt, J = 23.9 Hz, 7.81 Hz, 3H, PCH$_2$C$\underline{H}_3$), d 2.27 (dq, J = 14.6 Hz, 7.32 Hz, 2H, PC$\underline{H}_2$CH$_3$), 7.25-7.34 (m, 3H, Ar), 7.39-7.51 (m, 4H, Ar), 7.58 (d, J = 8.8 Hz, 1H, Ar), 7.96 (d, J = 8.3 Hz, 2H, Ar), 8.02 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 7.30 (d, $^2J_{C\text{-}P}$ = 2.8 Hz, PCH$_2$C$\underline{H}_3$), d 27.8 (d, $^1J_{C\text{-}P}$ = 81.7 Hz, P$\underline{C}$H$_2$CH$_3$), 120.2, 121.7, 122.5, 122.7, 125.6, 125.8, 126.5, 126.9, 127.2, 128.4, 128.5, 130.7, 131.0, 131.6, 131.9, 132.6, 146.1, 146.2, 148.1, 148.3 (Ar); ^{31}P NMR ($CDCl_3$): δ 128.0 ($^1J_{P\text{-}Se}$ = 920.8 Hz); ^{77}Se NMR ($CDCl_3$): δ -251.2 ($^1J_{P\text{-}Se}$ = 920.8 Hz); MS (EI) m/z 424 (M^+); HRMS Calcd for $C_{22}H_{17}O_2PSe$: 424.0131, Found: 424.0146.

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



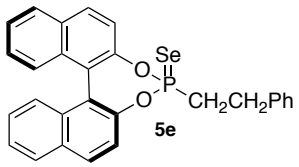
Chemical Formula: $C_{27}H_{19}O_2PSe$
Exact Mass: 486.03
Molecular Weight: 485.37

The compound was synthesized *via* Procedure A, with benzylmagnesium bromide (**2d**) (0.19 M THF solution, 20.6 ml, 4.0 mmol), toluene (20 mL), and (S_{ax})-BISEPCl (1.72 g, 4.0 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.18) gave the corresponding ester (**5d**) (1.62g, 83%) as a colorless solid

mp: 94-100 °C; IR (KBr): 1588, 1462, 1321, 1222, 1067, 951, 856, 750, 695, 600, 563, 508 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.64-3.79 (m, 2H, PC$\underline{H}_2$), 7.23-7.35 (m, 6H), 7.38-7.52 (m, 7H), 7.93 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 8.7 Hz, 1H), 7.99 (d, J = 9.2 Hz, 1H), 8.00 (d, J = 8.7 Hz, 1H, Ar) ^{13}C NMR ($CDCl_3$): δ 42.4 (d, $^1J_{C\text{-}P}$ = 78.2 Hz, P$\underline{C}$H$_2$), 120.7, 122.0, 122.6, 122.9, 125.8, 126.0, 126.7, 127.0, 127.4, 127.8, 128.6, 128.7, 128.8, 130.0 (d, J = 5.7 Hz, Ar), 130.6, 130.7, 130.9, 131.1,

131.7, 132.1, 132.7, 132.8, 146.2 (d, J = 9.5 Hz, Ar), 148.5 (d, J = 13.4 Hz, Ar); ^{31}P NMR ($CDCl_3$): δ 117.8 ($^1J_{P\text{-}Se}$ = 934.3 Hz); ^{77}Se NMR ($CDCl_3$): δ -222.3 ($^1J_{P\text{-}Se}$ = 934.3 Hz); MS (EI) m/z 486 (M^+); HRMS Calcd for $C_{27}H_{19}O_2PSe$: 486.0288, Found:486.0267.

(S_{ax})-4-(2-Phenylethyl)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphophepin-4-selenide (5e) [S1)]



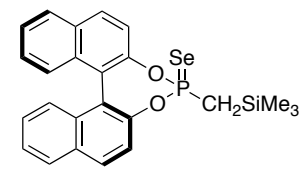
Chemical Formula: $C_{28}H_{21}O_2PSe$
Exact Mass: 500.04
Molecular Weight: 499.40

The following compound was synthesized *via* Procedure A, with phenethylmagnesium bromide (**2e**) (0.68 M THF solution, 11.8 ml, 8.0 mmol), toluene (40 mL), and (S_{ax})-BISEPCl (3.43 g, 8.0 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.28) gave the corresponding ester (**5e**) (2.79 g, 79%) as a colorless solid

^{1}H NMR ($CDCl_3$): δ 2.51-2.61 (m, 2H), 3.06-3.17 (m, 1H), 3.22-3.33 (m, 1H), 7.16 (d, J = 8.7 Hz, 1H), 7.23-7.36 (m, 8H), 7.39 (d, J = 8.2 Hz, 1H), 7.46-7.51 (m, 2H), 7.59 (dd, J = 0.9, 8.7 Hz, 1H), 7.94 (d, J = 9.2 Hz, 1H), 7.96 (d, J = 9.2 Hz, 2H), 8.05 (d, J = 9.2 Hz, 1H, Ar)

Typical procedure B for the preparation of (S_{ax})-4-((trimethylsilyl)methyl)binaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (**5f**): To a two-necked flask were added (S_{ax})-binaphthylphosphoroselenoic acid chloride ((S_{ax})-BISEPCl) (645.0 mg, 1.5 mmol), DMAP (366.1 mg, 3.0 mmol), and toluene (7.5 mL) under Ar atmosphere. The reaction mixture was stirred for 30 min. After that, (trimethylsilyl)methylmagnesium chloride (**2f**) (0.76 M THF solution, 1.97 ml, 1.5 mmol) was added to the suspension via syringe pomp at 40 ºC over 20 min, and it was stirred at that temperature for 30 min. After that, saturated NH_4Cl aqueous solution was added to the resulting mixture, and water was further added to dilute the solution. The aqueous phase was extracted with ether three times. The combined organic layer was dried over Na_2SO_4 or $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.28) to give (S_{ax})-4-((trimethylsilyl)methyl)binaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (**5f**) (474.1 mg, 66%) as a colorless solid.

(S_{ax})-4-((Trimethylsilyl)methyl)binaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (5f)

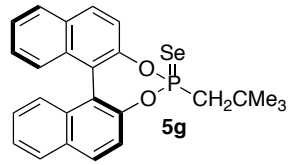


Chemical Formula: $C_{24}H_{23}O_2PSeSi$
Exact Mass: 482.04
Molecular Weight: 481.46

mp: 92-97 °C; IR (KBr): 3055, 2952, 2924, 1620, 1588, 1508, 1462, 1432, 1360, 1322, 1251, 1223, 11200, 1155, 1096, 1070, 979, 952, 852, 832, 814, 749, 709, 696, 672, 654, 605, 563 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.29 (s, 9H, Si($C\underline{H}_3$)$_3$), 1.87 (dd, J = 13.2, 16.6 Hz, 1H), 1.98 (dd, J = 13.2, 22.3 Hz, 1H), 7.27-7.36 (m, 3H), 7.42-7.52 (m, 4H), 7.55 (dd, J =

1.2, 9.2 Hz, 1H), 7.95 (d, J = 7.5 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 8.6 Hz, 1H), 8.03 (d, J = 8.6 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 0.04 (d, $^3J_{C\text{-}P}$ = 3.6 Hz Si($\underline{C}H_3)_3$), 25.3 (d, $^1J_{C\text{-}P}$ = 64.8 Hz, P$\underline{C}H_2$), 122.9, 122.1, 123.0 (d, J = 2.4 Hz, Ar), 123.1 (d, J = 2.4 Hz, Ar), 125.7, 125.8, 126.5, 126.9, 127.1, 127.4, 128.5, 128.7, 130.7, 130.9, 131.7, 132.0, 132.7, 132.8, 146.6 (d, J = 10.8 Hz, Ar), 148.2 (d, J = 14.4 Hz, Ar); ^{31}P NMR ($CDCl_3$): δ 119.2 ($^1J_{P\text{-}Se}$ = 907.6 Hz); ^{77}Se NMR ($CDCl_3$): δ -173.0 ($^1J_{P\text{-}Se}$ = 907.6 Hz); MS (EI) m/z 482 (M^+); HRMS Calcd for $C_{24}H_{23}O_2PSeSi$: 482.0370, Found:482.0368.

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

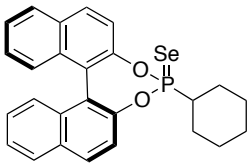


Chemical Formula: $C_{25}H_{23}O_2PSe$
Exact Mass: 466.06
Molecular Weight: 465.38

The following compound was synthesized *via* Procedure B, with neopentylmagnesium bromide (**2g**) (0.31 M THF solution, 9.7 ml, 3.0 mmol), toluene (18 mL), DMAP (0.74 g, 6.0 mmol) and (S_{ax})-BISEPCl (1.29 g, 3.0 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.28) gave the corresponding ester (**5g**) (0.92 g, 66%) as a colorless solid.

mp: 194-195 °C; IR (KBr): 2959, 1587, 1508, 1462, 1363, 1324, 1220, 1156, 1070, 1028, 977, 951, 836, 816, 751, 694, 595, 570 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.27 (s, 9H, C($C\underline{H}_3)_3$), 2.37 (d, J = 15 Hz, 2H, P$C\underline{H}_2$), 7.25-7.33 (m, 3H), 7.39-7.49 (m, 4H), 7.56 (dd, J = 1.4, 8.7 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 8.02 (d, J = 9.2 Hz, 1H), 8.03 (d, J = 8.7 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 30.8, 31.1, 31.2, 46.9 ($^1J_{C\text{-}P}$ = 74.4 Hz, P$\underline{C}H_2$), 120.8, 122.3, 122.7, 123.0, 123.0, 125.7, 125.9, 126.6, 126.9, 127.1, 127.5, 128.5, 128.7, 130.6, 131.0, 131.6, 132.0, 132.7, 132.8, 146.2 (d, J = 11.4 Hz, Ar), 148.5 (d, J = 15.3 Hz, Ar); ^{31}P NMR ($CDCl_3$): δ 118.8 ($^1J_{P\text{-}Se}$ = 924.3 Hz); ^{77}Se NMR ($CDCl_3$): δ -173.6 ($^1J_{P\text{-}Se}$ = 924.3 Hz); MS (EI) m/z 466 (M^+); HRMS Calcd for $C_{25}H_{23}O_2PSe$: 466.0601, Found:466.0604.

(S_{ax})-4-Cyclohexylbinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (5h)



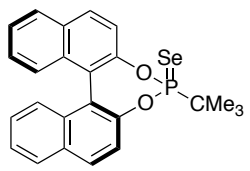
Chemical Formula: $C_{26}H_{23}O_2PSe$
Exact Mass: 478.06
Molecular Weight: 477.39

The following compound was synthesized *via* Procedure A, with cyclohexylmagnesium bromide (**2h**) (1.09 M THF solution, 5.5 mL, 5.0 mmol), toluene (24 mL), and (S_{ax})-BISEPCl (2.15 g, 5.0 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.13) gave the corresponding ester (**5h**) (1.66 g, 69%) as a colorless solid.

mp: 237.1-238.0 °C; IR (KBr): 3054, 2929, 2854, 1587, 1508, 1227, 1069, 953, 860, 694, 566 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.13-1.21 (m, 1H, P$C\underline{H}C_5H_{10}$), 1.24-1.34 (m, 2H), 1.62-1.80 (m, 4H), 1.92-2.03 (m, 2H), 2.12-2.21 (m, 2H), 7.23-7.31 (m, 3H, Ar), 7.38-7.49 (m, 4H, Ar), 7.56 (d, J = 8.59 Hz, 1H, Ar), 7.92 (d, J = 4.58 Hz, 1H, Ar), 7.94 (d, J = 4.58 Hz, 1H, Ar), 8.00 (d, J = 9.16 Hz, 1H, Ar), 8.02

(d, J = 9.16 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 25.1, 25.2, 25.2, 25.4, (d, $J_{C\text{-}P}$ = 6.0 Hz, PCHCH$_2$<u>C</u>H$_2$) 26.1 (d, $J_{C\text{-}P}$ = 12.0 Hz, PCH<u>C</u>H$_2$CH$_2$), 41.7 (d, $J_{C\text{-}P}$ = 78.0 Hz, P<u>C</u>HC$_5$H$_{10}$), 120.12, 121.9, 122.4, 122.7, 125.5, 125.7, 126.4, 126.7, 126.8, 127.2, 128.3, 128.5, 130.6, 130.9, 131.4, 131.8, 132.5, 132.7, 146.1, 146.2, 148.4, 148.5; ^{31}P NMR ($CDCl_3$): δ 132.6 ($^1J_{P\text{-}Se}$ = 921.5 Hz); ^{77}Se NMR ($CDCl_3$): δ -285.2 (d, $^1J_{P\text{-}Se}$ = 921.5 Hz); MS (EI) m/z 478 (M^+); HRMS Calcd for $C_{26}H_{23}O_2PSe$: 478.0601, Found: 478.0589.

(S_{ax})-4-(*tert*-Butyl)binaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (5i)

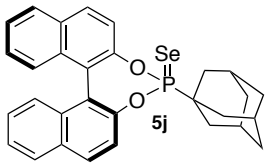


Chemical Formula: $C_{24}H_{21}O_2PSe$
Exact Mass: 452.04
Molecular Weight: 451.36

The following compound was synthesized *via* Procedure A, with *tert*-butylmagnesium chloride (**2i**) (0.79 M THF solution, 5.10 ml, 4.0 mmol), toluene (40 mL), and (S_{ax})-BISEPCl (1.73 g, 4.0 mmol). Purification by column chromatography on silica gel (EtOAc : hexane = 1 : 10, Rf = 0.40) gave the corresponding ester (**5i**) (1.59 g, 87%) as a colorless solid.

mp: 267-268 °C; IR (KBr): 3061, 2970, 1590, 1506, 1462, 1321, 1225, 1071, 953, 839, 756, 650 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.32 (d, J = 19.3 Hz, 9H, C(C<u>H</u>$_3$)$_3$), 7.18-7.24 (m, 4H, Ar), 7.32-7.40 (m, 3H), 7.47 (dd, J = 1.4 Hz, 9.0 Hz, 1H), 7.82-7.88 (m, 3H), 7.95 (d, J = 9.0 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 26.1 (C(<u>C</u>H$_3$)$_3$), 42.0 (d, $^1J_{P\text{-}C}$ = 72.0 Hz, <u>C</u>(CH$_3$)$_3$), 120.9, 121.0, 122.4, 122.9, 125.7, 126.5, 126.8, 127.1, 127.5, 128.4, 128.7, 130.6, 130.7, 131.3, 132.1, 132.9, 146.8, 146.9, 150.9, 151.0 (Ar); ^{31}P NMR ($CDCl_3$): δ 139.5 ($^1J_{P\text{-}Se}$ = 917.0 Hz); ^{77}Se NMR ($CDCl_3$): δ -283.4 ($^1J_{P\text{-}Se}$ = 917.0 Hz); MS (EI) m/z 452 (M^+); HRMS Calcd for $C_{24}H_{21}O_2PSe$: 452.0444, Found: 452.0421.

(S_{ax})-4-(Adamantan-2-yl)binaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (5j)



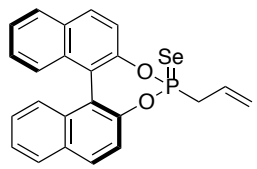
Chemical Formula: $C_{30}H_{27}O_2PSe$
Exact Mass: 530.09
Molecular Weight: 529.47

The following compound was synthesized *via* Procedure A, with 2-adamanthylmagnesium bromide (**2j**) (0.41 M THF solution, 8.50 ml, 3.5 mmol), toluene solution (35 mL), and (S_{ax})-BISEPCl (1.52 g, 3.5 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 5, Rf = 0.23) gave the corresponding ester (**5j**) (1.15 g, 63%) as a colorless solid.

mp: 282-283 °C; IR (KBr): 3064, 2909, 2849, 1590, 1507, 1462, 1323, 1223, 1071, 951, 831 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.70-1.75 (m, 6H, Adm), 2.00 (m, 6H Adm), 2.10-2.14 (m, 3H, Adm), 7.15 (d, J = 8.5 Hz, 1H), 7.19-7.23 (m, 1H, Ar), 7.27-7.31 (m, 2H, Ar), 7.42-7.48 (m, 2H, Ar), 7.50-7.52 (m, 2H, Ar), 7.91-7.93 (m, 2H, Ar), 7.96 (d, J = 9.0 Hz, 1H), 8.02 (d, J = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 27.4 ($^3J_{C\text{-}P}$ = 12.2 Hz), 36.1, 36.2, 44.6 ($^1J_{C\text{-}P}$ = 71.4 Hz) (Adm), 120.7, 121.0, 122.3, 122.7, 125.5, 126.2, 126.5, 126.9, 127.3, 128.2, 128.5, 130.4, 131.0, 131.9, 132.6, 146.5, 146.6, 150.8, 151.0 (Ar); ^{31}P NMR ($CDCl_3$): δ 136.9 ($^1J_{P\text{-}Se}$ = 913.4 Hz); ^{77}Se NMR ($CDCl_3$): δ -300.0

($^1J_{P\text{-}Se}$ = 913.4 Hz); MS (EI) m/z 530 (M^+); HRMS Calcd for $C_{30}H_{27}O_2PSe$: 530.0914, Found: 530.0926.

(S_{ax})-4-Allylbinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (5k)

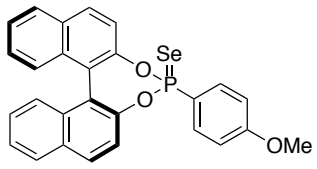


Chemical Formula: $C_{23}H_{17}O_2PSe$
Exact Mass: 436.01
Molecular Weight: 435.31

The following compound was synthesized *via* Procedure A, with allylmagnesium bromide (**2k**) (0.93 M Et_2O solution, 0.54 mL, 0.5 mmol), toluene (5 mL), and (S_{ax})-BISEPCl (215 mg, 0.5 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.20) gave the corresponding ester (**5k**) (85 mg, 39%) as a colorless solid.

mp: 187.1-187.5 °C; IR (KBr): 1507, 1225, 1068, 954, 856, 751, 597, 567 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.13-3.19 (m, 2H, $PC\underline{H_2}CHCH_2$), 5.33-5.42 (m, 2H, $PCH_2CHC\underline{H_2}$), 5.92-6.04 (m, 1H, $PCH_2C\underline{H}CH_2$), 7.25-7.34 (m, 3H, Ar), 7.39-7.52 (m, 4H, Ar), 7.57 (dd, J = 1.4, 8.7 Hz, 1H, Ar), 7.96 (d, J = 8.2 Hz, 2H, Ar), 8.02 (d, J = 8.2 Hz, 1H, Ar), 8.04 (d, J = 7.8 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 40.4 (d, $J_{P\text{-}C}$ = 80.8 Hz, $P\underline{C}H_2CHCH_2$), 120.5, 121.8, 121.9, 122.6, 122.7, 125.7, 125.9, 126.3, 126.4, 126.6, 126.9, 127.3, 128.4, 128.6, 130.8, 130.9, 131.6, 132.0, 132.6, 132.7, 146.0, 146.1, 148.1, 148.2 (Ar) ; ^{31}P NMR ($CDCl_3$): δ 117.0 ($^1J_{P\text{-}Se}$ = 930.4 Hz); ^{77}Se NMR ($CDCl_3$): δ -228.5 ($^1J_{P\text{-}Se}$ = 930.4 Hz); MS (EI) m/z 436 (M^+); HRMS Calcd for $C_{23}H_{17}O_2PSe$: 436.0131, Found: 436.0165.

(S_{ax})-4-(4-Methoxyphenyl)binaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (5l)



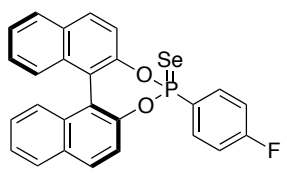
Chemical Formula: $C_{27}H_{19}O_3PSe$
Exact Mass: 502.02
Molecular Weight: 501.37

The following compound was synthesized *via* Procedure B, with 4-methoxyphenylmagnesium bromide (**2l**) (0.45 M THF solution, 1.10 mL, 0.5 mmol), toluene (5 mL), DMAP (122 mg, 1.0 mmol) and (S_{ax})-BISEPCl (215 mg, 0.5 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : AcOEt : hexane = 1 : 1 : 50, Rf = 0.09) gave the corresponding ester (**5l**) (162 mg, 65%) as a colorless solid.

mp: 112.8-122.4 °C (dec); IR (KBr): 1594, 1500, 1461, 1260, 1221, 1117, 1068, 949, 835, 750, 663, 607, 564, 519 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80 (s, 3H, $OC\underline{H_3}$), 6.80-6.82 (m, 2H, Ar), 6.91 (d, J = 8.7 Hz, 1H, Ar), 7.27-7.39 (m, 3H, Ar), 7.47-7.50 (m, 3H, Ar), 7.62-7.67 (m, 3H, Ar), 7.80 (d, J = 8.7 Hz, 1H, Ar), 7.91 (d, J = 8.2, 1H, Ar), 7.98 (d, J = 8.2 Hz, 1H, Ar), 8.08 (d, J = 8.7 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 55.4 (s, $O\underline{C}H_3$), 113.5, 113.6, 121.2, 121.9, 122.0, 122.5, 122.9, 123.2, 125.7, 125.8, 126.6, 126.7, 127.1, 127.3, 128.5, 128.6, 130.5, 130.8, 131.6, 132.0, 132.5, 132.7, 134.1, 134.2, 146.1, 146.2, 148.4, 148.6, 163.7, 163.8 (Ar); ^{31}P NMR ($CDCl_3$): δ 109.7 ($^1J_{P\text{-}Se}$ = 938.4 Hz); ^{77}Se NMR ($CDCl_3$): δ -246.4 (d, $^1J_{P\text{-}Se}$ = 938.4 Hz); MS (EI) m/z 502 (M^+); HRMS Calcd for

$C_{27}H_{19}O_3PSe$: 502.0237, Found: 502.0247.

(S_{ax})-4-(4-Fluorophenyl)binaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (5m)

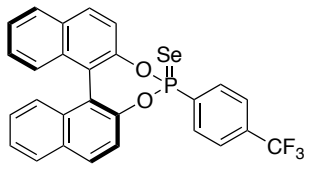


Chemical Formula: $C_{26}H_{16}FO_2PSe$
Exact Mass: 490.00
Molecular Weight: 489.34

The following compound was synthesized *via* Procedure B, with 4-fluorophenylmagnesium bromide (**2m**) (1.92 M Et_2O solution, 1.56 mL, 3.0 mmol), toluene (30 mL), DMAP (733 mg, 6.0 mmol) and (S_{ax})-BISEPCl (1.29 g, 3.0 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.15) gave the corresponding ester (**5m**) (1.01 g, 69%) as a colorless solid.

mp: 228.5-229.7 °C; IR (KBr): 3056, 1908, 1590, 1496, 1221, 1114, 951, 836, 662, 607, 512 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.88-6.89 (d, *J* = 8.59 Hz, 1H, Ar), 7.03-7.06 (m, 2H, Ar), 7.14-7.29 (m, 3H, Ar), 7.37-7.41 (m, 3H, Ar), 7.49-7.59 (m, 3H, Ar), 7.69 (d, *J* = 8.78 Hz, 1H, Ar), 7.80 (d, *J* = 8.78, 1H, Ar), 7.86 (d, *J* = 8.29 Hz, 1H, Ar), 7.99 (d, *J* = 9.27 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 115.3, 115.5, 115.5, 115.6, 120.9, 121.8, 122.5, 122.8, 125.8, 125.9, 126.7, 126.8, 127.0, 127.2, 1 28.5, 128.6, 130.6, 130.9, 131.6, 132.1, 132.4, 132.6, 134.5, 134.6, 134.6, 134.7, 145.8, 145.9, 148. 2, 148.3, 164.9, 167.0 (Ar); ^{19}F NMR ($CDCl_3$): δ -103.9; ^{31}P NMR ($CDCl_3$): δ 106.8 ($^1J_{P\text{-}Se}$ = 938.7 Hz); ^{77}Se NMR ($CDCl_3$): δ -242.0 (d, $^1J_{P\text{-}Se}$ = 938.7 Hz); MS (EI) m/z 490 (M^+); HRMS Calcd for $C_{26}H_{16}FO_2PSe$: 490.0037, Found: 490.0024.

(S_{ax})-4-(4-(Trifluoromethyl)phenyl)binaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (5n)

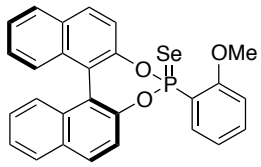


Chemical Formula: $C_{27}H_{16}F_3O_2PSe$
Exact Mass: 540.00
Molecular Weight: 539.34

The following compound was synthesized *via* Procedure A, with (4-trifluoromethyl)phenylmagnesium bromide (**2n**) (0.79 M THF solution, 2.40 ml, 2.0 mmol), toluene (20 mL), and (S_{ax})-BISEPCl (863.6 mg, 2.0 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 5, Rf = 0.18) gave the corresponding ester (**5n**) (900.2 mg, 83%) as a colorless solid.

mp: 144-145 °C; IR (KBr): 3050, 1589, 1461, 1397, 1324, 1220, 1063, 950, 838, 750 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.88 (dd, *J* = 0.9 Hz, *J* = 9.0 Hz, 1H), 7.29-7.38 (m, 3H, Ar), 7.46 (d, *J* = 8.5 Hz, 1H), 7.49-7.53 (m, 2H, Ar), 7.61 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.66 (dd, *J* = 1.4 Hz, *J* = 9.0 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.85-7.93 (m, 3H, Ar), 8.00 (d, *J* = 8.1 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 120.7, 121.9, 122.1, 122.5, 122.9, 125.1, 125.2, 126.1, 126.9, 127.0, 127.1, 127.3, 128.7, 128.8, 130.9, 131.2, 131.8, 132.3, 132.4, 132.6, 132.7, 134.7, 135.0, 145.7, 145.8, 148.2, 148.4 (Ar); ^{19}F NMR ($CDCl_3$): δ -63.1; ^{31}P NMR ($CDCl_3$): δ 104.7 ($^1J_{P\text{-}Se}$ = 946.5 Hz); ^{77}Se NMR ($CDCl_3$): δ -231.7 ($^1J_{P\text{-}Se}$ = 946.5 Hz); MS (EI) m/z 540 (M^+); HRMS Calcd for $C_{27}H_{16}F_3O_2PSe$: 540.0005, Found: 540.0071.

(S_{ax})-4-(2-Methoxyphenyl)binaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (5o)

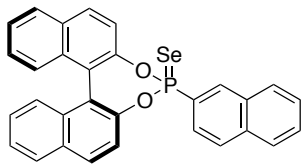


Chemical Formula: $C_{27}H_{19}O_3PSe$
Exact Mass: 502.02
Molecular Weight: 501.37

The following compound was synthesized *via* Procedure B, with 2-methoxyphenylmagnesium bromide (**2o**) (0.90 M Et_2O solution, 0.56 mL, 0.5 mmol), toluene (5 mL), DMAP (122 mg, 1.0 mmol) and (S_{ax})-BISEPCl (215 mg, 0.5 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : AcOEt : hexane = 1 : 2 : 30, Rf = 0.13) gave the corresponding ester (**5o**) (113 mg, 45%) as a colorless solid.

mp: 222.5-223.2 °C; IR (KBr): 1588, 1476, 1322, 1223, 1068, 1018, 953, 854, 751, 614, 564, 518, 412 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.60 (d, J = 1.37 Hz, 3H, OCH_3), 6.75-6.83 (m, 2H, Ar), 7.07 (d, J = 8.70 Hz, 1H, Ar), 7.12-7.16 (m, 2H, Ar), 7.23-7.37 (m, 5H, Ar), 7.58-7.66 (m, 2H, Ar), 7.69-7.74 (m, 2H, Ar), 7.85 (d, J = 8.24 Hz, 1H, Ar), 7.95 (d, J = 8.70 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 55.8 (OCH_3), 111.7, 111.8, 119.9, 120.3, 120.4, 120.5, 120.9, 122.3, 122.4, 123.0, 125.5, 125.6, 126.3, 126.4, 127.1, 127.2, 128.2, 128.6, 130.3, 130.6, 131.5, 132.0, 132.5, 132.7, 134.0, 134.1, 134.8, 146.2, 146.3, 149.3, 149.4, 160.5 (Ar); ^{31}P NMR ($CDCl_3$): δ 102.4 ($^1J_{P\text{-}Se}$ = 928.2 Hz); ^{77}Se NMR ($CDCl_3$): δ −175.4 (d, $^1J_{P\text{-}Se}$ = 928.2 Hz); MS (EI) m/z 502 (M^+); HRMS Calcd for $C_{27}H_{19}O_3PSe$: 502.0237, Found:502.0263.

(S_{ax})-4-(Naphtalen-2-yl)binaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (5p)

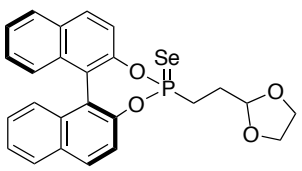


Chemical Formula: $C_{30}H_{19}O_2PSe$
Exact Mass: 522.03
Molecular Weight: 521.40

The following compound was synthesized *via* Procedure A, with 2-naphthylmagnesium bromide (**2p**) (0.29 M THF solution, 3.45 ml, 1.0 mmol), toluene (10 mL), and (S_{ax})-BISEPCl (426.5 mg, 1.0 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 5, Rf = 0.49) gave the corresponding ester (**5p**) (422.4 mg, 82%) as a colorless solid.

mp: 218-219 °C; IR (KBr): 3049, 1587, 1507, 1460, 1221, 1089, 954, 834, 747, 710, 655 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.87 (dd, J = 0.9 Hz, 9.0 Hz, 1H), 7.29-7.38 (m, 2H, Ar), 7.40 (d, J = 8.1 Hz, 1H), 7.48-7.63 (m, 6H, Ar), 7.69-7.76 (m, 3H, Ar), 7.82 (d, J = 8.1 Hz, 1H), 7.82-7.89 (m, 2H, Ar), 8.00 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 9.0 Hz, 1H), 8.45 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 121.2, 122.1, 122.5, 123.0, 125.9, 126.7, 126.8, 127.2, 127.4, 127.9, 128.0, 128.6, 128.7, 129.0, 129.5, 130.6, 131.0, 131.7, 132.0, 132.1, 132.2, 132.6, 132.8, 134.8, 134.9, 135.4, 146.1, 146.2, 148.6, 148.7 (Ar); ^{31}P NMR ($CDCl_3$): δ 109.1 ($^1J_{P\text{-}Se}$ = 934.3 Hz); ^{77}Se NMR ($CDCl_3$): δ -234.7 ($^1J_{P\text{-}Se}$ = 934.3 Hz); MS (EI) m/z 522 (M^+); HRMS Calcd for $C_{30}H_{19}O_2PSe$: 522.0288, Found: 522.0309.

(S_{ax})-4-(2-(1,3-Dioxolan-2-yl)ethyl)binaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-selenide (5q)

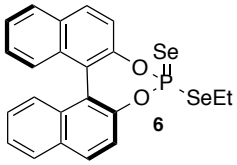


Chemical Formula: $C_{25}H_{21}O_4PSe$
Exact Mass: 496.03
Molecular Weight: 495.37

The following compound was synthesized *via* Procedure A, with (2-(1,3-dioxolan-2-yl)ethyl)magnesium bromide (**2q**) (0.43 M THF solution, 7.0 ml, 3.0 mmol), toluene (10 mL), and (S_{ax})-BISEPCl (1.29 g, 3.0 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 2 : 1, Rf = 0.25) gave the corresponding ester (**5q**) (0.95 g, 64%) as a colorless solid.

mp: 100-110 °C; IR (KBr): 2924, 1588, 1508, 1463, 1322, 1222, 1191, 1155, 1140, 1069, 1045, 976, 951, 857, 838, 813, 750, 696, 598, 567 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.18-2.45 (m, 4H), 3.84-3.96 (m, 4H), 5.03 (t, J = 4.0 Hz, 1H), 7.26-7.35 (m, 3H, Ar), 7.39 (d, J = 8.5 Hz, 1H, Ar), 7.45-7.52 (m, 3H, Ar), 7.57 (dd, J = 0.9, 8.5 Hz, 1H), 7.96 (d, J = 8.1 Hz, 2H), 8.02 (d, J = 9.0 Hz, 1H), 8.04 (d, J = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 27.7, 28.4 (d, $^2J_{C\text{-}P}$ = 84.6 Hz), 65.3, 102.7 (d, $^3J_{C\text{-}P}$ = 20.7 Hz), 120.5, 121.9, 122.6, 122.9, 125.8, 126.0, 126.7, 127.0, 127.1, 127.4, 128.6, 128.7, 130.9, 131.2, 131.8, 132.1, 132.7, 146.2 (d, J = 10.3 Hz), 148.3 (d, J = 14.1 Hz) (Ar); ^{31}P NMR ($CDCl_3$): δ 124.6 ($^1J_{P\text{-}Se}$ = 924.4 Hz); ^{77}Se NMR ($CDCl_3$): δ -236.0 ($^1J_{P\text{-}Se}$ = 924.4 Hz); MS (EI) m/z 496 (M^+); HRMS Calcd for $C_{25}H_{21}O_4PSe$: 496.0343, Found: 493.0359.

(S_{ax})-4-(Ethylselanyl)binaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (6)

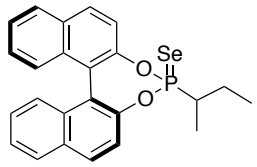


Chemical Formula: $C_{22}H_{17}O_2PSe_2$
Exact Mass: 503.93
Molecular Weight: 502.26

The following compound was synthesized *via* Procedure A, with ethylmagnesium bromide (**2c**) (2.5 M Et_2O solution, 0.4 mL, 1.0 mmol), toluene (4 mL), and (S_{ax})-BISEPCl (431 mg, 1.0 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.38) gave the corresponding ester (**6**) (26 mg, 5%) as a colorless solid.

mp: 180.6-182.9 °C; IR (KBr): 2921, 2853, 1586, 1508, 1460, 1320, 1215, 1198, 1157, 1065, 975, 941, 845, 832, 810, 772, 755, 706, 696, 651, 606, 581, 563, 546, 522, 410 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.62 (d, J = 7.3 Hz, 3H, $CH_2C\underline{H_3}$), 3.04-3.27 (m, 2H, $C\underline{H_2}$), 7.27-7.33 (m, 2H), 7.38 (d, J = 8.7 Hz, 1H), 7.43 (d, J = 8.7 Hz, 1H), 7.47-7.52 (m, 3H), 7.61 (dd, J = 1.4, 9.2 Hz, 1H), 7.96 (d, J = 8.2 Hz, 2H), 8.02 (d, J = 8.2 Hz, 1H), 8.04 (d, J = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 16.6 (d, J = 5.6 Hz), 28.1, 121.4, 121.7, 122.7 (d, J = 2.8 Hz), 122.9 (d, J = 3.8 Hz, 1H), 125.8, 125.9, 126.6, 126.7, 127.0, 127.2, 128.5, 128.6, 130.5, 130.8, 131.8, 132.0, 132.5, 147.0 (d, J = 13.2 Hz), 148.2 (d, J = 16.0 Hz, Ar); ^{31}P NMR ($CDCl_3$): δ 104.5 ($^1J_{P\text{-}Se}$ = 517.1, 952.2 Hz); ^{77}Se NMR ($CDCl_3$): δ –60.8 ($^1J_{P\text{-}Se}$ = 952.2 Hz), 375.5 ($^1J_{P\text{-}Se}$ = 517.1 Hz); MS (EI) m/z 504 (M^+); HRMS Calcd for $C_{22}H_{17}O_2PSe_2$: 503.9297, Found: 503.9315.

(S_{ax})-4-(*sec*-Butyl)binaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (7)



Chemical Formula: $C_{24}H_{21}O_2PSe$
Exact Mass: 452.04
Molecular Weight: 451.36

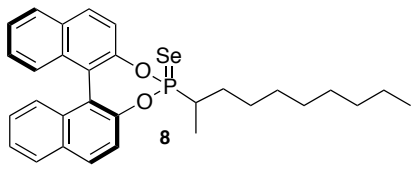
The following compound was synthesized *via* Procedure B, with *sec*-Butylmagnesium bromide (**2r**) (0.56 M THF solution, 18 mL, 10 mmol), toluene (100 mL), DMAP (2.44 g, 20 mmol) and (S_{ax})-BISEPCl (4.29 g, 10 mmol). Purification by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.28) gave the corresponding ester (**7**) (3.22 g, 71%, dr = 50 : 50) as a colorless solid. The diastereoisomers were separated by recrystallization from CH_2Cl_2 and AcOEt.

(dr = 83 : 17): IR (KBr): 2970, 1588, 1506, 1461, 1320, 1218, 1069, 950, 913, 734, 600, 503 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.97 (t, J = 7.6 Hz, 0.5H, $CH_2C\underline{H_3}$), 1.10 (t, J = 7.6 Hz, 2.5H, $CH_2C\underline{H_3}$), 1.26 (dd, J = 22.9, 6.7 Hz, 2.5H, $PCHC\underline{H_3}$), 1.40 (dd, J = 22.9, 6.7 Hz, 0.5 H, $PCHC\underline{H_3}$), 1.54-1.67 (m, 1H), 1.90-2.00 (m, 0.2H), 2.08-2.20 (m, 1.8H), 7.21-7.30 (m, 3H, Ar), 7.37-7.48 (m, 4H, Ar), 7.57 (m, 1H, Ar), 7.92 (d, J = 8.5 Hz, 2H, Ar), 7.97-8.03 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 11.2 (d, $^2J_{C\text{-}P}$ = 16.0 Hz), 11.5 (d, $^2J_{C\text{-}P}$ = 16.9 Hz), 13.0, 13.1, 23.6, 38.3 (d, $^1J_{C\text{-}P}$ = 77.1 Hz, P$\underline{C}$H), 38.4 (d, $^1J_{C\text{-}P}$ = 77.1 Hz, P$\underline{C}$H(CH_3)CH_2CH_3)), 120.0, 120.1 (d, $J_{C\text{-}P}$ = 2.8 Hz), 122.0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 122.3, 122.4 (d, $J_{C\text{-}P}$ = 2.8 Hz), 122.6 (d, $J_{C\text{-}P}$ = 2.8 Hz), 125.5, 125.7, 126.4, 126.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 127.2, 128.3, 128.5, 130.6, 130.8, 131.4, 131.8, 132.5, 132.6, 146.1 (d, $J_{C\text{-}P}$ = 10.3 Hz), 146.3, 148.3 (d, $J_{C\text{-}P}$ = 14.1 Hz) (Ar); ^{31}P NMR ($CDCl_3$): δ 135.1 ($^1J_{P\text{-}Se}$ = 920.3 Hz), 135.6 ($^1J_{P\text{-}Se}$ = 920.3 Hz); ^{77}Se NMR ($CDCl_3$): δ -297.5 ($^1J_{P\text{-}Se}$ = 920.3 Hz), -299.2 ($^1J_{P\text{-}Se}$ = 920.3 Hz); MS (EI) m/z 452 (M^+); HRMS Calcd for $C_{24}H_{21}O_2PSe$: 452.0444, Found: 452.0442.

(S_{ax},*S*)-4-(*sec*-Butyl)binaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (7a)

(dr = >99 : 1): mp: 202.0-202.6 °C; IR (KBr): 2925, 1588, 1462, 1320, 1226, 1071, 950, 836, 742, 560, 503 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.11 (t, J = 7.3 Hz, 3H, $CH_2C\underline{H_3}$), 1.26 (dd, J = 22.0, 6.9 Hz, 3H, $PCHC\underline{H_3}$), 1.59-1.67 (m, 1H, P$\underline{C}$HCH_3), 2.09-2.21 (m, 2H, $C\underline{H_2}CH_3$), 7.23-7.31 (m, 3H, Ar), 7.37-7.49 (m, 4H, Ar), 7.57 (dd, J = 8.7, 1.4 Hz, 1H, Ar), 7.94 (d, J = 8.2 Hz, 2H, Ar), 8.01 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 11.5 (d, $^2J_{C\text{-}P}$ = 17.3 Hz, PCH($\underline{C}H_3$)), 13.1, 23.7, 38.4 (d, $^1J_{C\text{-}P}$ = 76.7 Hz, P$\underline{C}$H), 120.2, 122.0, 122.5, 122.7, 125.6, 125.8, 126.5, 126.8, 126.9, 127.2, 128.3, 128.5, 130.6, 130.8, 131.5, 131.9, 132.6, 132.7, 146.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 148.4 (d, $J_{C\text{-}P}$ = 13.4 Hz) (Ar); ^{31}P NMR ($CDCl_3$): δ 135.1 ($^1J_{P\text{-}Se}$ = 922.9 Hz); ^{77}Se NMR ($CDCl_3$): δ -299.1 ($^1J_{P\text{-}Se}$ = 922.9 Hz); MS (EI) m/z 452 (M^+); HRMS Calcd for $C_{24}H_{21}O_2PSe$: 452.0444, Found: 452.0442.

(S_{ax})-4-(Decan-2-yl)binaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (8)



Chemical Formula: $C_{30}H_{33}O_2PSe$
Exact Mass: 536.14
Molecular Weight: 535.52

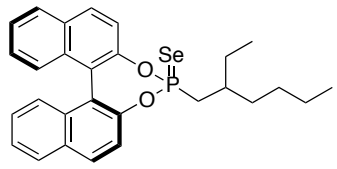
The following compound was synthesized *via* Procedure A, with methylmagnesium bromide (**2s**) (0.09 M THF solution, 5.8 mL, 0.5 mmol), toluene solution (5 mL), and (S_{ax})-BISEPCl (215 mg, 0.5 mmol). Purification by column chromatography on silica gel (AcOEt : hexane = 1 : 25, Rf = 0.48) gave three fractions (first:

28%, (dr = 0: 100), second: 7% (dr = 30: 70), third: 24% (dr = 100: 0)) the corresponding ester (**8**) as a colorless solid.

(8a) (dr = 0: 100): mp: 143.6-144.5 °C; IR (KBr): 3055, 2928, 2851, 1588, 1224, 1198, 840, 812, 601, 565 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, *J* = 6.3 Hz, 3H, $PCH(CH_3)(CH_2)_7C\underline{H}_3$), 1.26 (dd, *J* = 6.9, 22.3 Hz, 3H, $PCH(C\underline{H}_3)(CH_2)_7CH_3$), 1.31-1.37 (m, 11H), 1.56-1.64 (m, 2H), 2.01-2.07 (m, 1H), 2.20-2.27 (m, 1H, P$C\underline{H}$), 7.27-7.32 (m, 3H, Ar), 7.38-7.41 (m, 2H, Ar), 7.45-7.50 (m, 2H, Ar), 7.57 (d, *J* = 8.6 Hz, 1H, Ar), 7.95 (d, *J* = 8.0 Hz, 2H, Ar), 7.99-8.02 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 13.8 (d, *J* = 90.0 Hz), 22.7, 26.6, 26.7, 29.3, 29.5, 29.6, 30.2, 31.9, 36.8 (d, *J* = 76.8 Hz), 120.3, 122.0, 122.5, 122.7, 125.6, 125.8, 126.5, 126.8, 126.9, 127.3, 128.3, 128.6, 130.6, 130.7, 131.5, 131.9, 132.6, 132.7, 146.3 (d, *J* = 10.8 Hz), 148.5 (d, *J* = 14.4 Hz) (Ar); ^{31}P NMR ($CDCl_3$): δ 135.5 ($^1J_{P\text{-}Se}$ = 920.3 Hz); ^{77}Se NMR ($CDCl_3$): δ -299.9 (d, $^1J_{P\text{-}Se}$ = 920.3 Hz); MS (EI) m/z 536 (M^+); HRMS Calcd for $C_{30}H_{33}O_2PSe$: 536.1383, Found: 536.1383.

(8b) (dr = 100: 0): mp: 44.4-53.0 °C; IR (KBr): 3055, 2927, 2852, 1588, 1225, 1198, 841, 812, 601, 565 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, *J* = 6.9 Hz, 3H, $PCH(CH_3)(CH_2)_7C\underline{H}_3$), 1.2-1.28 (m, 11H), 1.40 (dd, *J* = 6.9, 23.5 Hz, 3H, $PCH(C\underline{H}_3)$), 1.46-1.58 (m, 2H), 1.83-1.90 (m, 1H), 2.19-2.26 (m, 1H, P$C\underline{H}$), 7.27-7.33 (m, 3H, Ar), 7.40 (d, *J* = 8.6 Hz, 1H, Ar), 7.42 (d, *J* = 8.6 Hz, 1H, Ar), 7.45-7.51 (m, 2H, Ar), 7.58 (dd, *J* = 1.2, 8.6 Hz, 1H, Ar), 7.95 (d, *J* = 8.0 Hz, 2H, Ar), 7.99-8.05 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 13.7 (d, *J* = 78.0 Hz), 22.6, 26.7, 26.8, 29.1, 29.3, 29.5, 30.4, 31.8, 37.0 (d, *J* = 76.8 Hz), 120.1, 122, 122.4, 122.8, 125.6, 125.8, 126.5, 126.8, 126.9, 127.3, 128.4, 128.6, 130.6, 130.9, 131.5, 131.9, 132.6, 132.7, 146.4 (d, *J* = 10.8 Hz), 148.5 (d, *J* = 13.2 Hz); ^{31}P NMR ($CDCl_3$): δ 135.8 ($^1J_{P\text{-}Se}$ = 920.3 Hz); ^{77}Se NMR ($CDCl_3$): δ -298.4 (d, $^1J_{P\text{-}Se}$ = 920.3 Hz); MS (EI) m/z 536 (M^+); HRMS Calcd for $C_{30}H_{33}O_2PSe$: 536.1383, Found: 536.1363.

(S_{ax})-4-(2-Ethylhexyl)binaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-selenide (9)



Chemical Formula: $C_{28}H_{29}O_2PSe$
Exact Mass: 508.11
Molecular Weight: 507.46

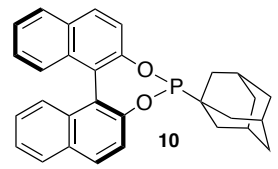
The following compound was synthesized *via* Procedure B. with 2-ethylhexylmagnesium bromide (**2t**) (0.92 M Et_2O solution, 0.55 mL, 0.5 mmol), toluene (5.0 mL), DMAP (122 mg, 2 mmol), (S_{ax})-BISEPCl (215 mg, 0.5 mmol). Purification by column chromatography on silica gel (DCM : hexane = 1 : 3) gave the corresponding ester (183 mg, 72%, dr = 50 : 50) as a colorless solid. The diastereoisomers were separated by recrystallization from CH_2Cl_2 and isopropyl alcohol.

(dr = 56 : 44): IR (KBr): 2927, 1588, 1508, 1462, 1322, 1223, 1070, 954, 839, 696, 600, 565 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.84 (t, *J* = 7.3 Hz, 1.5H), 0.85 (t, *J* = 6.9 Hz, 1.5H), 0.93 (t, *J* = 6.9 Hz, 1.5H), 0.96 (t, *J* = 7.3 Hz, 1.5H), 1.17-1.39 (m, 4H), 1.43-1.74 (m, 4H), 2.14-2.27 (m, 3H), 7.27-7.34 (m, 3H, Ar), 7.39-7.52 (m, 4H, Ar), 7.55-7.58 (m, 1H, Ar), 7.96 (d, *J* = 8.2 Hz, 2H, Ar), 8.01 (d, *J* = 8.2 Hz, 1H, Ar), 8.04 (d, *J* = 8.2 Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 10.2, 10.8, 14.0, 14.1, 22.7, 22.8,

26.1 (d, J = 11.5 Hz), 26.7 (d, J = 11.5 Hz), 28.1, 28.6, 32.7 (d, J = 11.5 Hz), 33.3 (d, J = 9.6 Hz), 35.0, 35.2, 38.2 (d, J = 76.7 Hz), 120.6, 122.0, 122.6, 122.8, 125.6, 125.8, 126.5, 126.8, 126.9, 127.3, 128.4, 128.6, 130.6, 130.8, 131.6, 131.9, 132.6, 132.7, 146.2, 146.3, 148.2, 148.3 (Ar); ^{31}P NMR ($CDCl_3$): δ 127.6 ($^1J_{P\text{-}Se}$ = 920.3 Hz), 127.7 ($^1J_{P\text{-}Se}$ = 920.3 Hz); ^{77}Se NMR ($CDCl_3$): δ -225.2 (d, $^1J_{P\text{-}Se}$ = 920.3 Hz) Only one signal was observed for two diastereoisomers; MS (EI) m/z 508 (M^+); HRMS Calcd for $C_{24}H_{21}O_2PSe$: 508.1070, Found: 508.1066.

(dr = 92 : 8): mp: 138.0-138.8 °C; IR (KBr): 2926, 1587, 1507, 1462, 1322, 1224, 1070, 953, 813, 696, 599, 565 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.83 (t, J = 7.3 Hz, 3H, $CH_2C\underline{H_3}$), 0.93 (t, J = 6.9 Hz, 3H, $CH_2C\underline{H_3}$), 1.27-1.40 (m, 4H), 1.41-1.67 (m, 4H), 2.16-2.27 (m, 3H), 7.24-7.33 (m, 3H, Ar), 7.39-7.51 (m, 4H, Ar), 7.57 (dd, J = 1.4, 8.7 Hz, 1H, Ar), 7.96 (d, J = 8.2 Hz, 2H), 8.01 (d, J = 7.8 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 10.2, 14.1, 22.8, 26.1 (d, $J_{C\text{-}P}$ = 9.6 Hz), 28.6, 33.3 (d, $J_{C\text{-}P}$ = 11.5 Hz), 35.0, 38.2 (d, $^1J_{C\text{-}P}$ = 76.7 Hz, P$\underline{C}H_2$), 120.6, 122.0, 122.6, 122.8, 125.6, 125.8, 126.5, 126.8, 126.9, 127.3, 128.4, 128.5, 130.6, 130.8, 131.5, 131.9, 132.6, 146.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 148.2 (d, $J_{C\text{-}P}$ = 13.4 Hz) (Ar); ^{31}P NMR ($CDCl_3$): δ 127.6 ($^1J_{P\text{-}Se}$ = 919.2 Hz); ^{77}Se NMR ($CDCl_3$): δ -226.0 (d, $^1J_{P\text{-}Se}$ = 919.2 Hz); MS (EI) m/z 508 (M^+); HRMS Calcd for $C_{24}H_{21}O_2PSe$: 508.1070, Found: 508.1066.

(S_{ax})-4-(Adamantan-2-yl)binaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine (10)



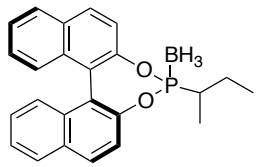
Chemical Formula: $C_{30}H_{27}O_2P$
Exact Mass: 450.17
Molecular Weight: 450.51

To the solution of **5j** (161.9 mg, 0.3 mmol) in THF (1.0 mL) was added tri(*n*-butyl)phosphine (0.15 mL, 0.6 mmol), and the resulting solution was stirred at room temperature for 1 h. The precipitate was filtered and washed with hexane (4 × 5 mL). The corresponding phosphonite (**10**) (92.5 mg, 70%) was isolated as a colorless solid after drying under reduced pressure.

mp: 275-278 °C; IR (KBr): 3059, 2901, 2845, 1590, 1504, 1463, 1230, 1071, 953, 818, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.71 (m, 8H, Adm), 1.85-1.88 (m, 4H, Adm), 1.95 (m, 3H, Adm), 7.20 (m, 3H, Ar), 7.27-7.29 (m, 1H, Ar), 7.38-7.42 (m, 2H, Ar), 7.47-7.59 (m, 2H, Ar), 7.89-7.92 (m, 3H, Ar), 7.97-7.99 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ 27.7 ($^3J_{C\text{-}P}$ = 8.5 Hz), 35.1 ($^2J_{C\text{-}P}$ = 14.1 Hz) 40.9 ($^1J_{C\text{-}P}$ = 35.7 Hz) (Adm), 121.7, 122.8, 124.7, 125.0, 126.2, 126.3, 127.1, 127.3, 128.3, 128.5, 129.6, 130.7, 130.9, 131.6, 133.1, 133.2, 151.1, 151.1, 151.6, 151.7 (Ar); ^{31}P NMR ($CDCl_3$): δ 203.6; MS (EI) m/z 450 (M^+); HRMS Calcd for $C_{30}H_{27}O_2P$: 450.1749, Found: 450.1720.

(S_{ax})-4-(*sec*-Butyl)binaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepineborane (11)

To a 20 mL two-necked flask were added selenophophonate (**7**) (451 mg, 1.0 mmol, dr = 59 : 41), THF (5.0 mL), tri(*n*-butyl)phosphine (0.26 mL, 1.5 mmol) under Ar atmosphere. The reaction mixture was stirred for 22.5 h. After that, BH_3•THF (1M, 2.0 mL) was added to the mixture, and it

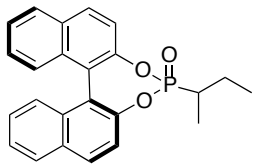


Chemical Formula: $C_{24}H_{24}BO_2P$
Exact Mass: 386.16
Molecular Weight: 386.23

was further stirred for 2.3 h. The resulting solution was concentrated. Purification by silica gel column chromatography (acetone : hexane = 4 : 5, Rf = 0.25) gave (**11**) (200 mg, 52%) containing selenophophonate and tri(*n*-butyl)phosphine selenide as a white solid. The solid was purified by GPC. The resulting solid (188 mg, 0.49 mmol) was dissolved in CH_2Cl_2 (2.0 mL). To this solution was added hydrogen peroxide (35% aqueous solution, 36 μL, 1.46 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 (acetone : hexane = 1 : 30, Rf = 0.15) to give the corresponding ester (91 mg, 48%, dr = 59 : 41) as a colorless solid.

(dr = 59 : 41): IR (KBr): 2969, 2387, 1589, 1507, 1462, 1322, 1230, 1072, 954, 861, 562, 526, 464, 417 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.14-0.87 (br, 3H, $B\underline{H}_3$), 0.97 (t, J = 7.5 Hz, 1.9H, $CH_2C\underline{H}_3$), 1.08 (t, J = 7.5 Hz, 1.1H, $CH_2C\underline{H}_3$), 1.26 (dd, J = 7.5, 17.2 Hz, 1.1H, $PCHC\underline{H}_3$), 1.36 (dd, J = 7.5, 18.3 Hz, 1.9H, $PCHC\underline{H}_3$), 1.51-1.63 (m, 1H, $PC\underline{H}CH_3$), 1.84-1.96 (m, 1.6H), 2.01-2.11 (m, 0.4H), 7.24-7.26 (m, 2H, Ar), 7.28-7.31 (m, 1H, Ar), 7.35 (d, J = 8.6 Hz, 1H, Ar), 7.39-7.49 (m, 3H, Ar), 7.53 (d, J = 8.6 Hz, 1H), 7.94 (d, J = 8.6 Hz, 2H, Ar), 7.98-8.03 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 11.7, 11.8, 11.8, 11.9, 12.0, 22.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 22.5 (d, $J_{C\text{-}P}$ = 3.6 Hz), 34.2 (d, $J_{C\text{-}P}$ = 33.6 Hz), 34.3 (d, $J_{C\text{-}P}$ = 33.6 Hz), 120.4, 121.7, 122.3, 122.7, 122.8, 125.5, 125.7, 126.9, 127.2, 128.4, 128.5, 130.7, 130.8, 131.5, 131.9, 132.5, 132.7, 147.3, 147.4, 147.5 (Ar); ^{31}P NMR ($CDCl_3$): δ 183.6 (br), 184.1 (br) ; MS (EI) m/z 386 (M^+); HRMS Calcd for $C_{24}H_{24}BO_2P$: 386.1607, Found: 386.1584.

(S_{ax})-4-(*sec*-Butyl)binaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-oxide



Chemical Formula: $C_{24}H_{21}O_3P$
Exact Mass: 388.12
Molecular Weight: 388.40

(dr = 47 : 53): IR (KBr): 2970, 1590, 1507, 1464, 1229, 1072, 964, 873, 751, 656, 566, 480 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.03 (t, J = 7.3 Hz, 1.5H, $CH_2C\underline{H}_3$), 1.12 (t, J = 7.3 Hz, 1.5H, $CH_2C\underline{H}_3$), 1.31 (dd, J = 19.7, 7.3 Hz, 1.5H, $PCHC\underline{H}_3$), 1.42 (dd, J = 19.7, 7.3 Hz, 1.5H, $PCHC\underline{H}_3$), 1.61-1.72 (m, 1H, $PC\underline{H}CH_3$), 1.90-2.17 (m, 2H), 7.25-7.33 (m, 3H, Ar), 7.37-7.39 (m, 1H, Ar), 7.43-7.51 (m, 3H), 7.57 (m, 1H, Ar), 7.94-7.97 (m, 2H, Ar), 8.0-8.04 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$): δ 11.6 (d, $^2J_{C\text{-}P}$ = 14.4 Hz, $PCH(\underline{C}H_3)$), 12.0 (d, $^2J_{C\text{-}P}$ = 14.4 Hz, $PCH(\underline{C}H_3)$), 12.3 (d, $^2J_{C\text{-}P}$ = 4.8 Hz), 12.6 (d, $^2J_{C\text{-}P}$ = 4.8 Hz), 22.9 (d, $^2J_{C\text{-}P}$ = 4.8 Hz), 23.1 (d, $^2J_{C\text{-}P}$ = 2.4 Hz), 30.3 (d, $^1J_{C\text{-}P}$ =38.4 Hz, $P\underline{C}H$), 31.3 (d, $^1J_{C\text{-}P}$ = 38.4 Hz, $P\underline{C}H$), 119.9, 120.0, 120.1, 120.1, 121.3, 121.7, 121.7, 121.8 125.6, 125.7, 126.6, 126.8, 126.9, 127.3, 128.3, 128.5, 130.9, 131.0, 131.2, 131.4, 131.8, 132.4, 132.6, 145.9 (d, J = 6.0 Hz), 146.0 (d, J = 4.8 Hz), 147.9 (d, J = 9.6 Hz), 148.0 (d, J = 10.8 Hz, Ar); ^{31}P NMR ($CDCl_3$): δ 46.6, 46.7; MS (EI) m/z 388 (M^+); HRMS Calcd for $C_{24}H_{21}O_3P$: 388.1228, Found: 388.1210.

X-ray structure analysis

Crystal samples were cut from the grown crystals and mounted on a glass fiber. The crystals were coated with an epoxy resin because they were air sensitive. Measurements were carried out on a Rigaku/MSC Mercury CCD using a graphite-monochromator with Mo Kα radiation (λ = 0.71069 Å). The structure was solved by direct methods (SIR97)[S2)] and refined by full-matrix least-squares procedures (SHELXL-97)[S3)] using the Yadokari-XG 2009.[S4)] The crystal data are shown in Tables S5.

Table S5. Crystal Data and Structure Refinement for S_{ax},*S*-**7a**

Empirical formula	$C_{24}H_{21}O_2PSe$
Formula weight	451.34
Temperature	0(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 7.4584(3) Å
	b = 8.9425(4) Å
	c = 31.2167(13) Å
Volume	2082.05(15) $Å^3$
Z	4
Density (calculated)	1.440 g/cm^{-3}
Crystal size	0.20 x 0.20 x 0.10 mm^3
Reflections collected	58681
Independent reflections	4756
Flack parameter	0.100(7)
Goodness-of-fit on F^2	1.136
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0248, wR_2 = 0.0661
R indices (all data)	R_1 = 0.0255, wR_2 = 0.0664

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S2 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.*, **1999**, *32*, 115.

S3 G. M. Sheldrick, SHELXL-97, *A Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, **1997**.

S4 (*a*) K. Wakita, Yadokari-XG, *Software for Crystal Structure Analyses*, **2001**. (*b*) C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *J. Cryst. Soc. Jpn.*, **2009**, *51*, 218.

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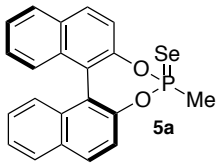

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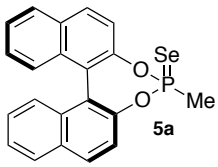

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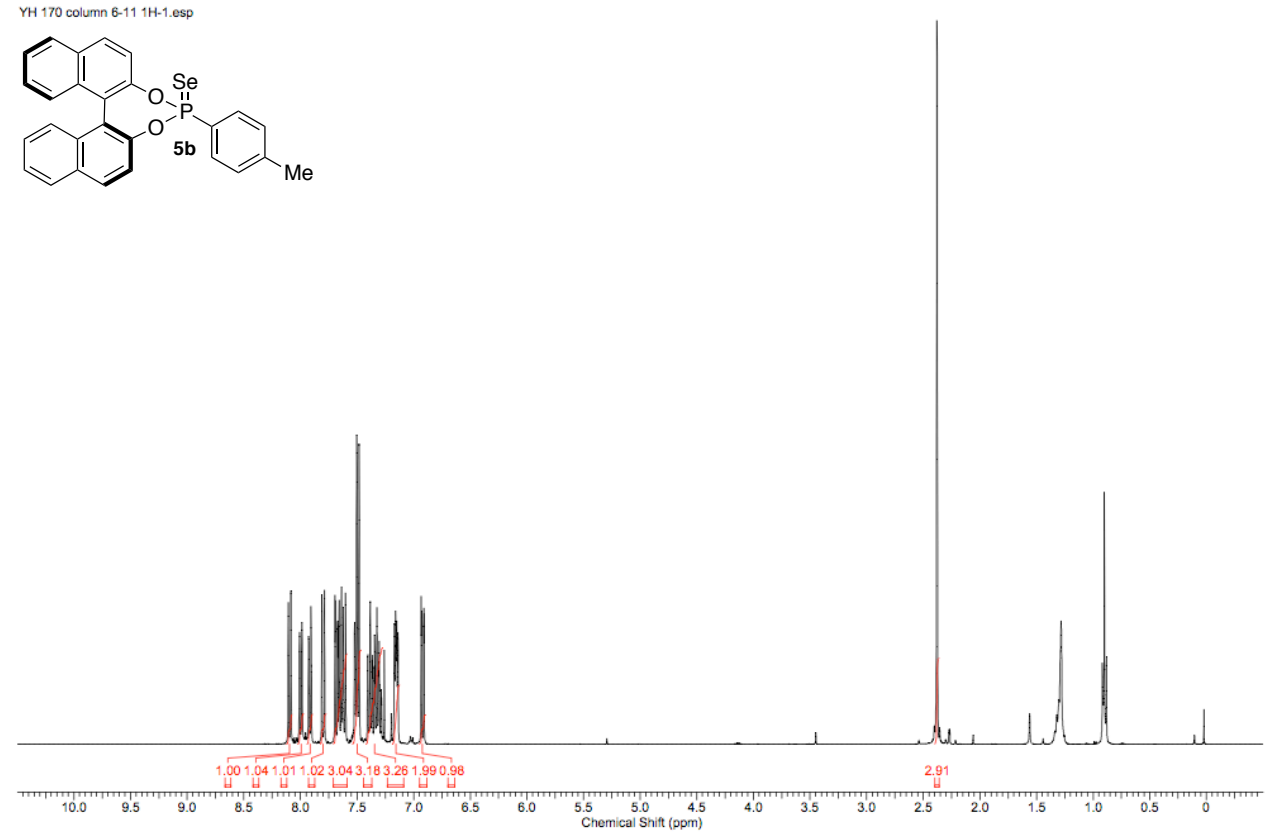
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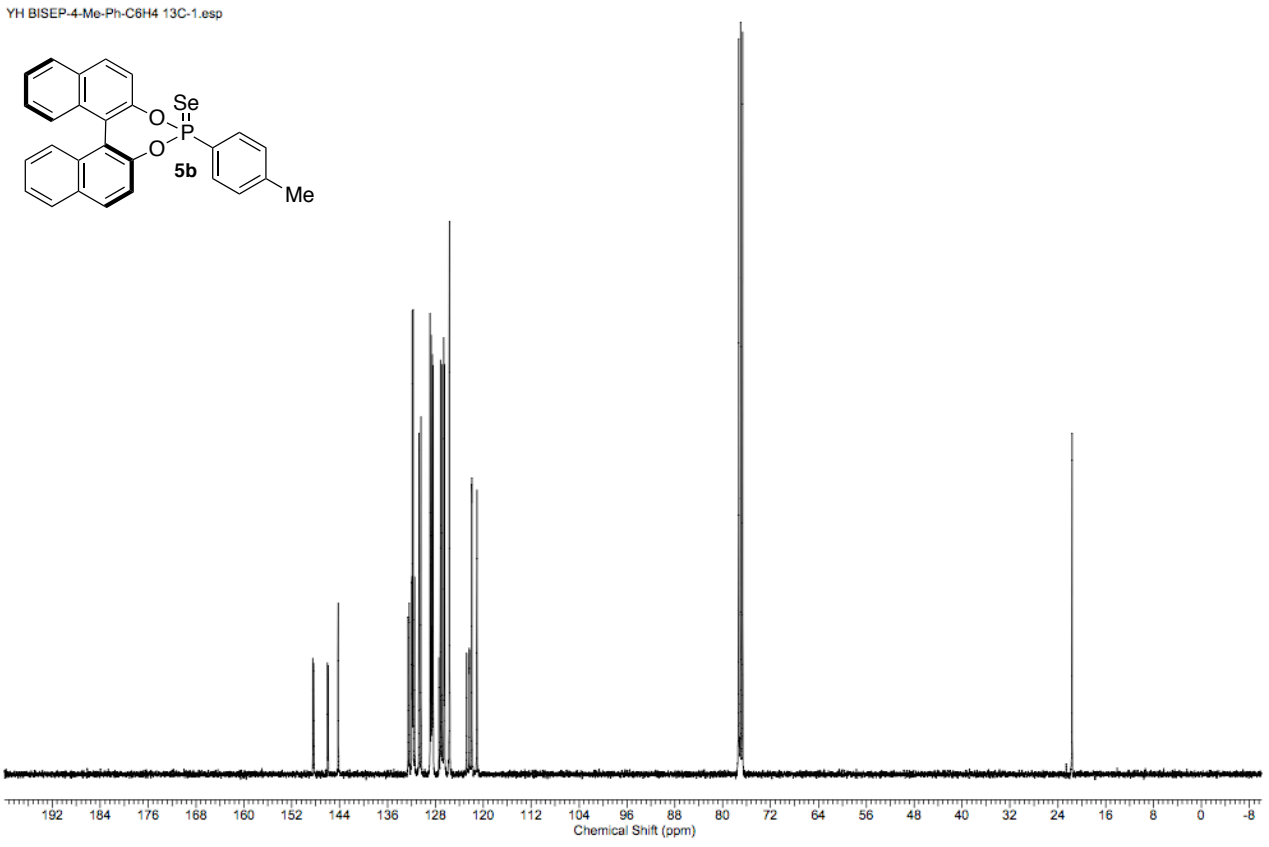
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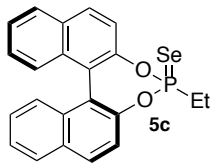

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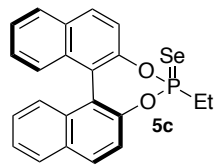

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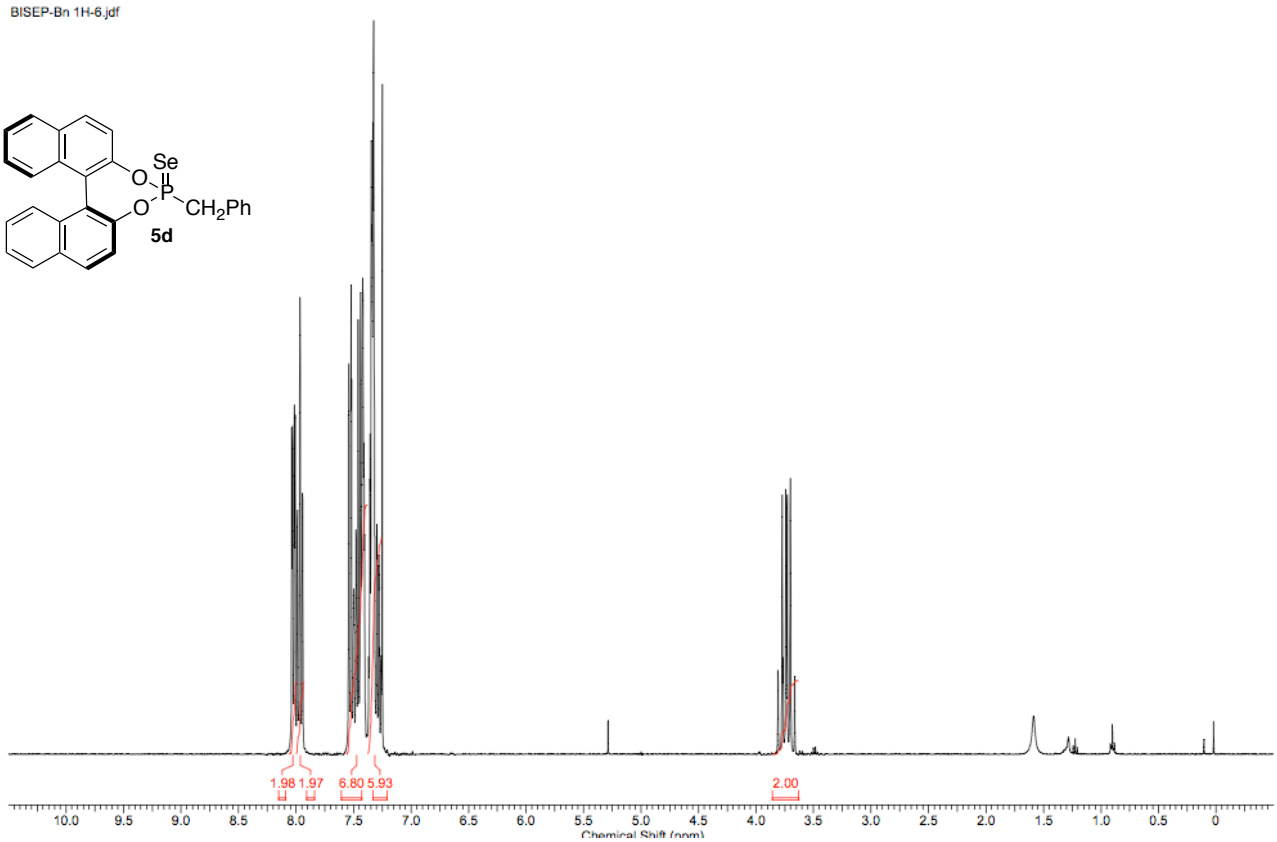
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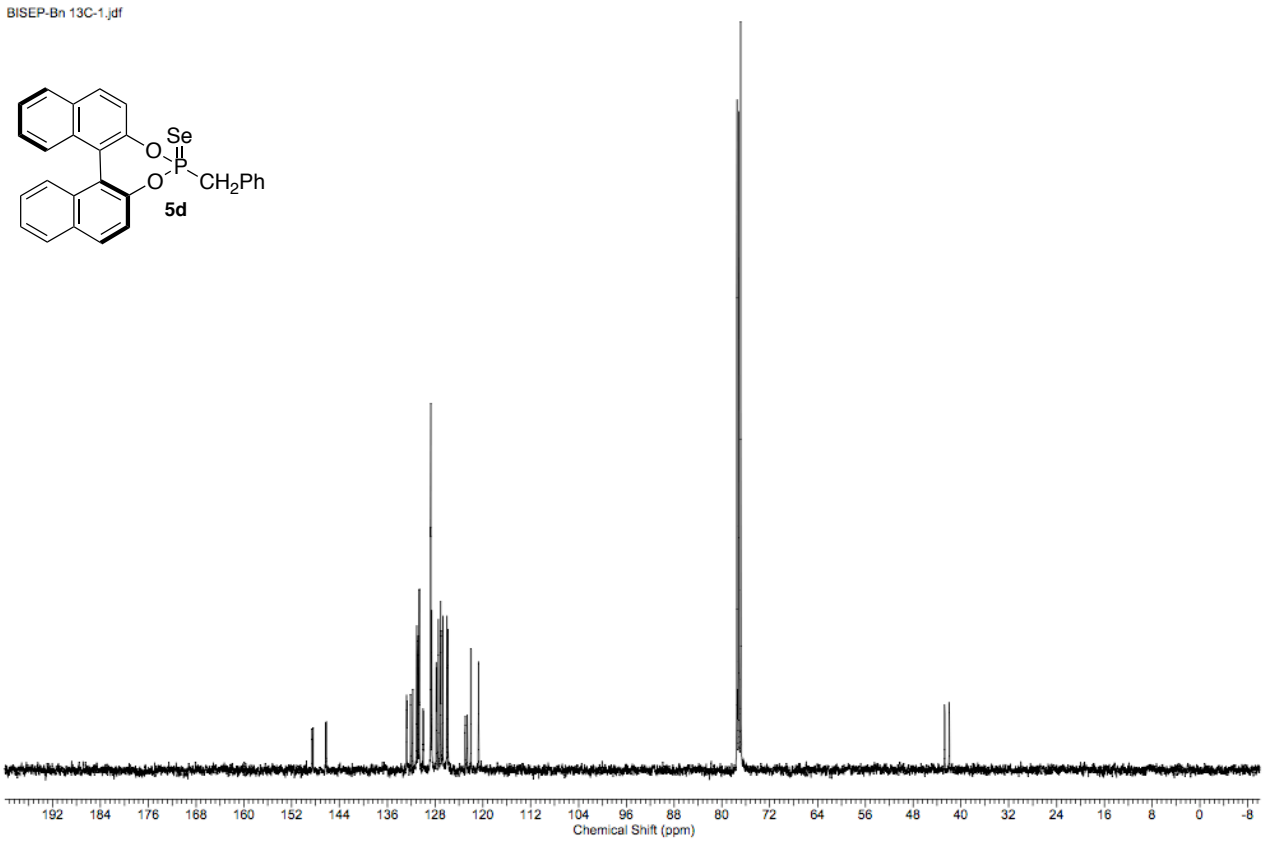
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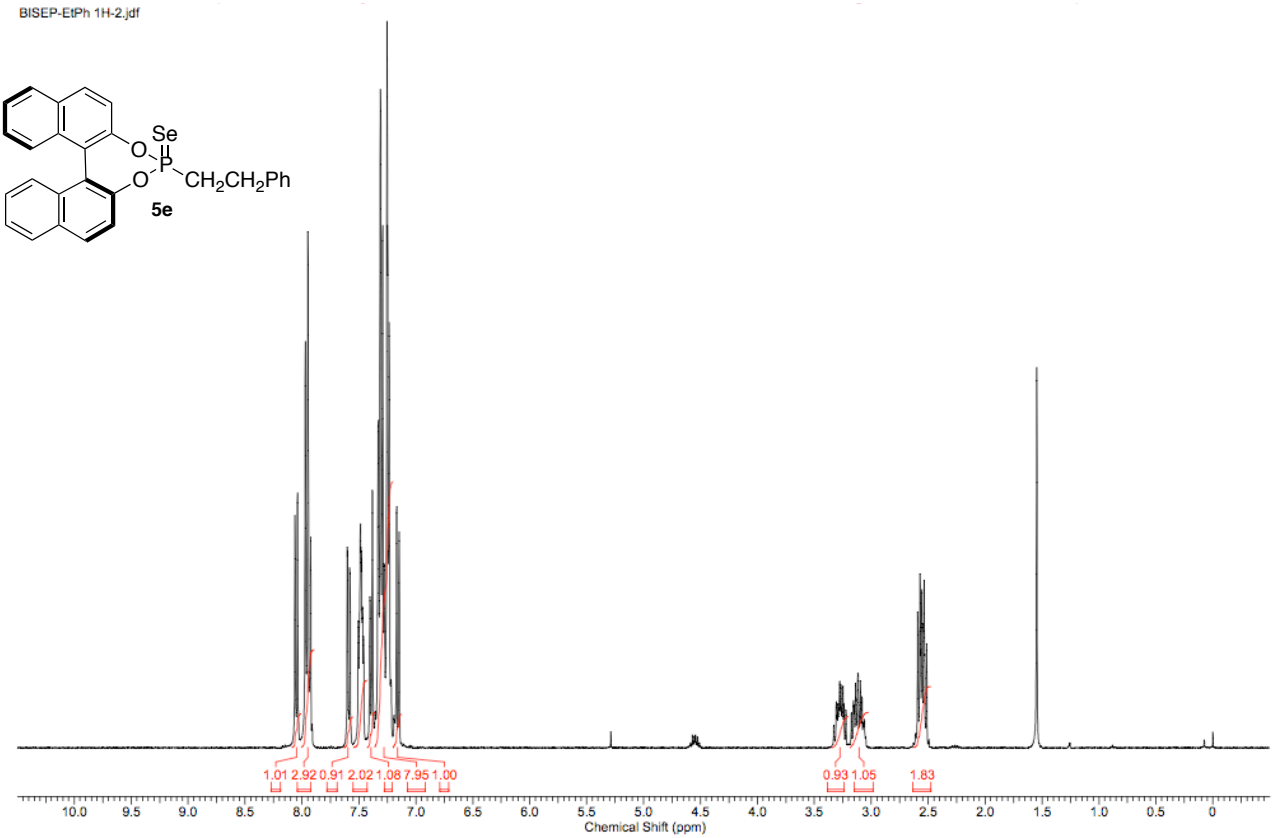
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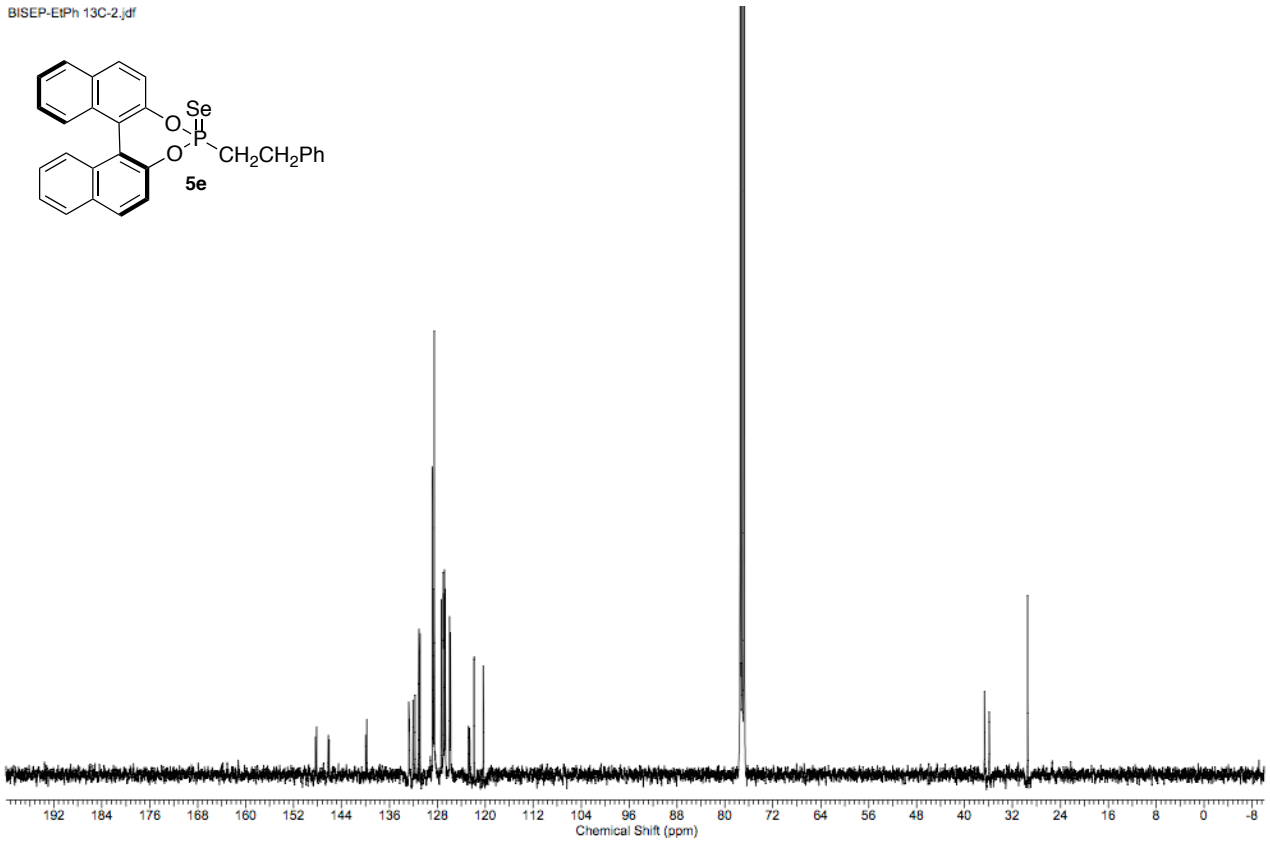
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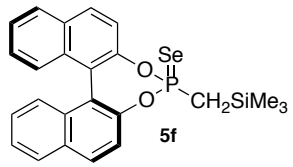

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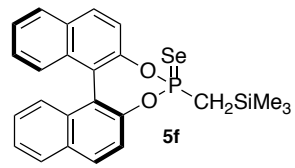

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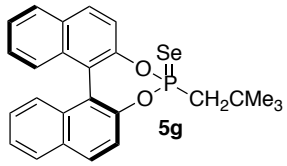

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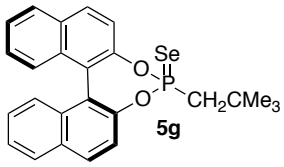
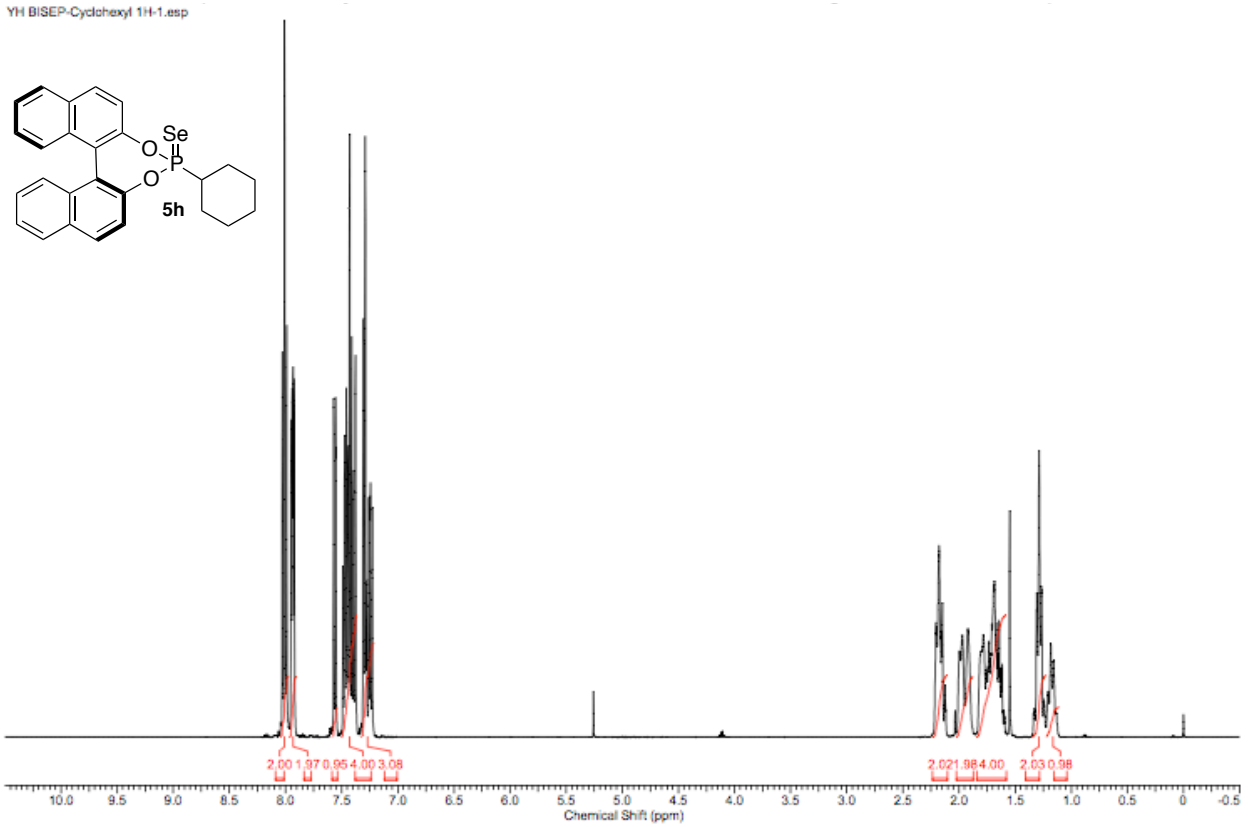
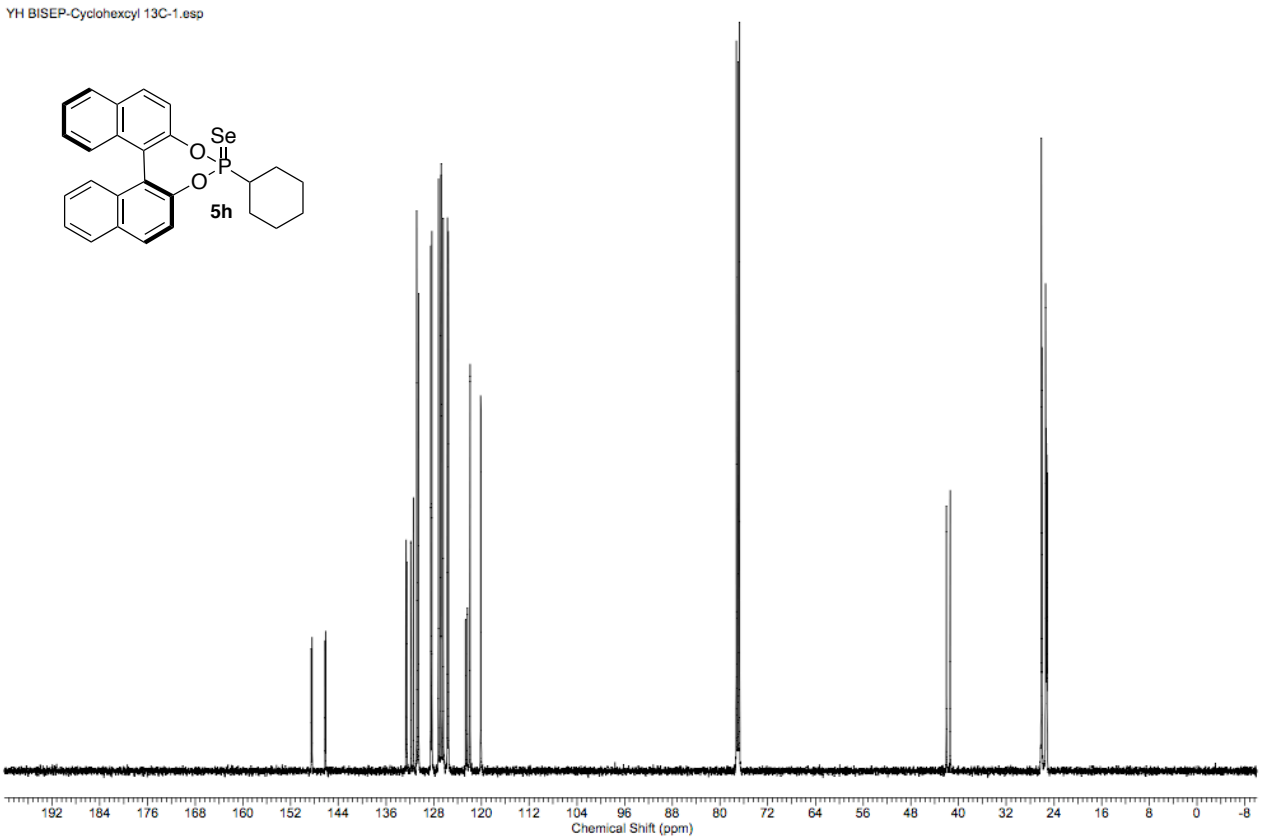
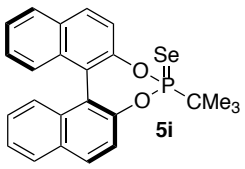


5g


YH BISEP-Cyclohexyl 1H-1.esp
Se
O
P
O
5h
2.00 1.97 0.95 4.00 3.08
2.02 1.98 4.00 2.03 0.98
10.0 9.5 9.0 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)

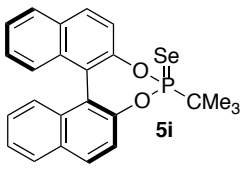

YH BISEP-Cyclohexcyl 13C-1.esp
Se
O
P
O
5h
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)

KK t-Bu 1H.jdf

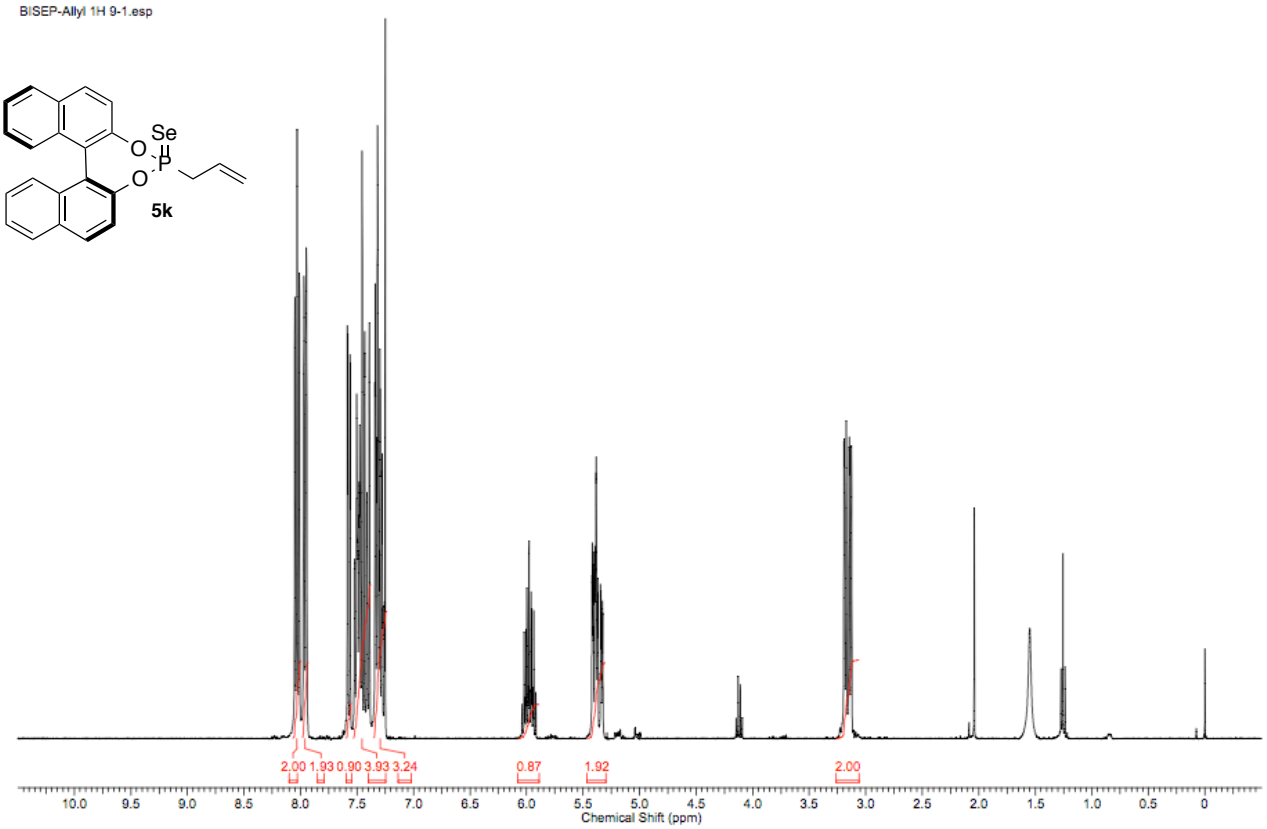


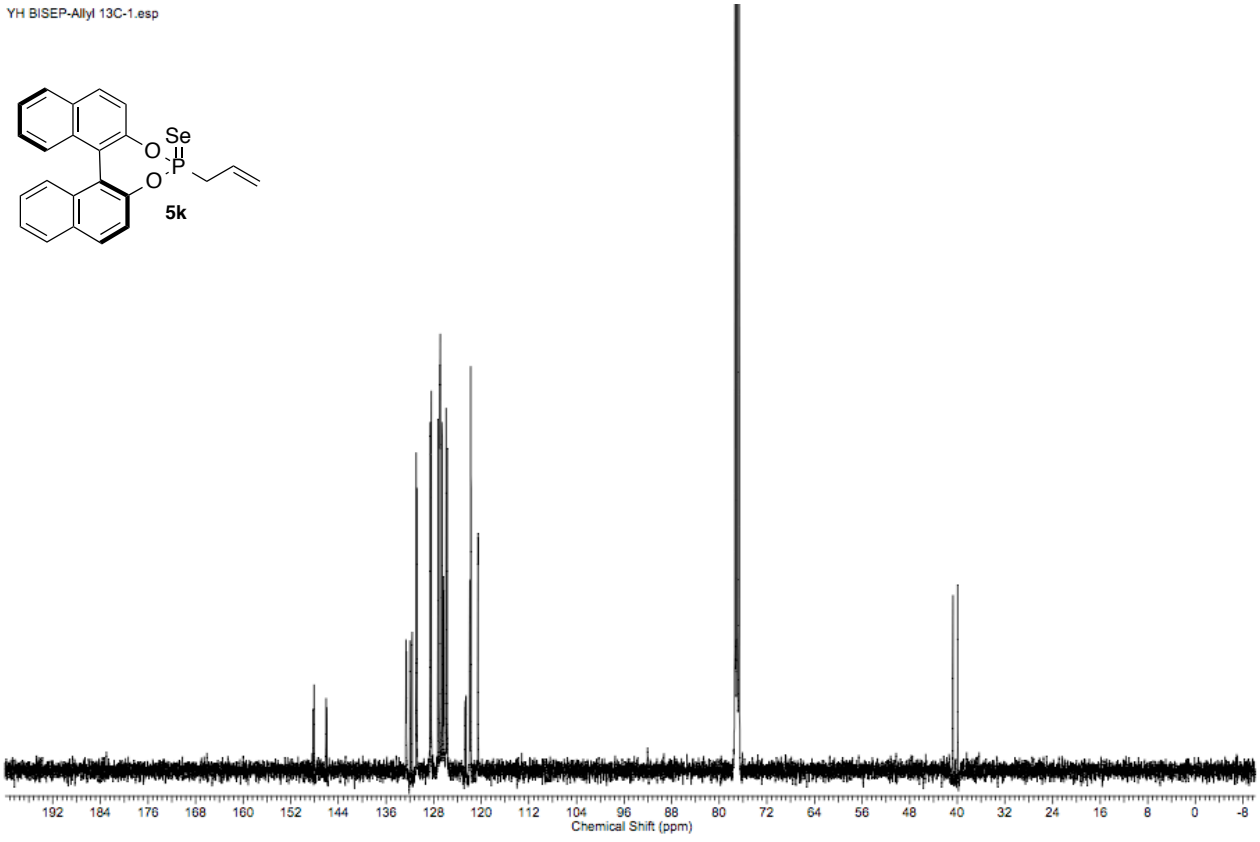
5i

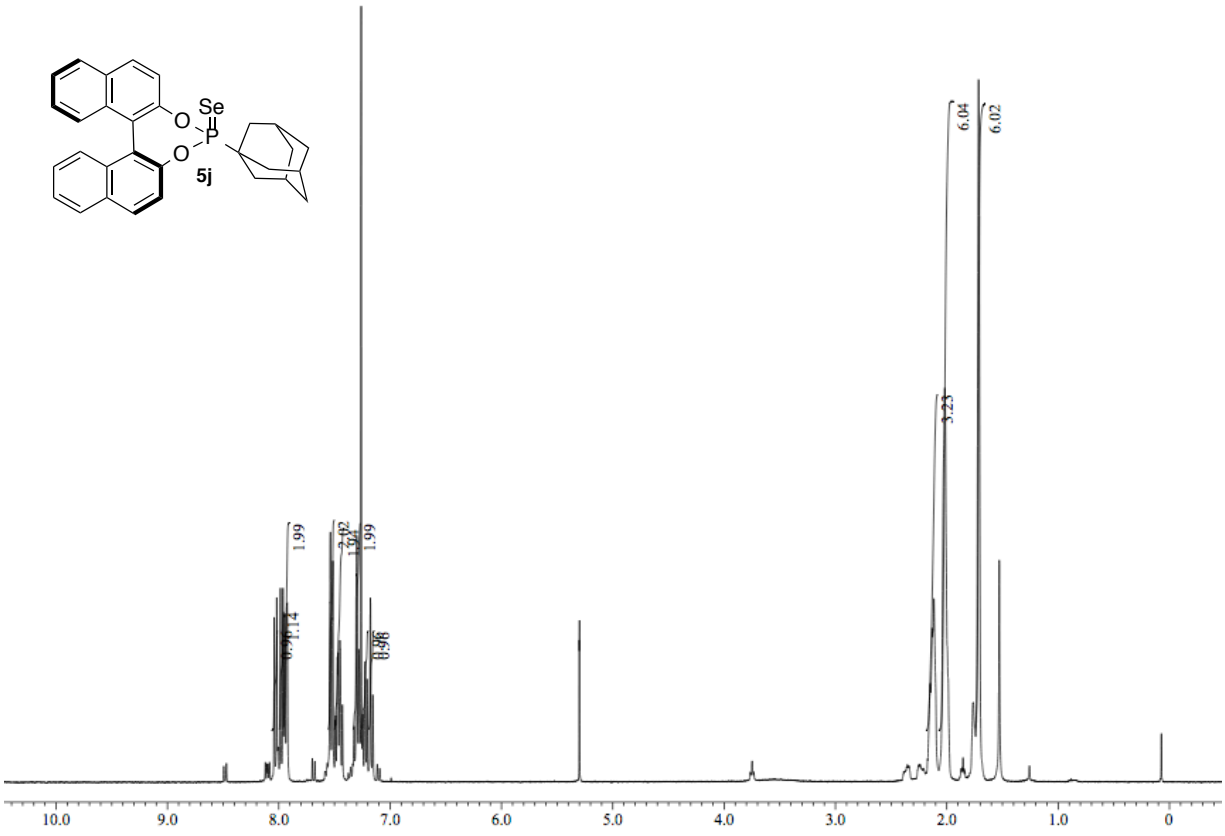
KK t-Bu 13C.jdf

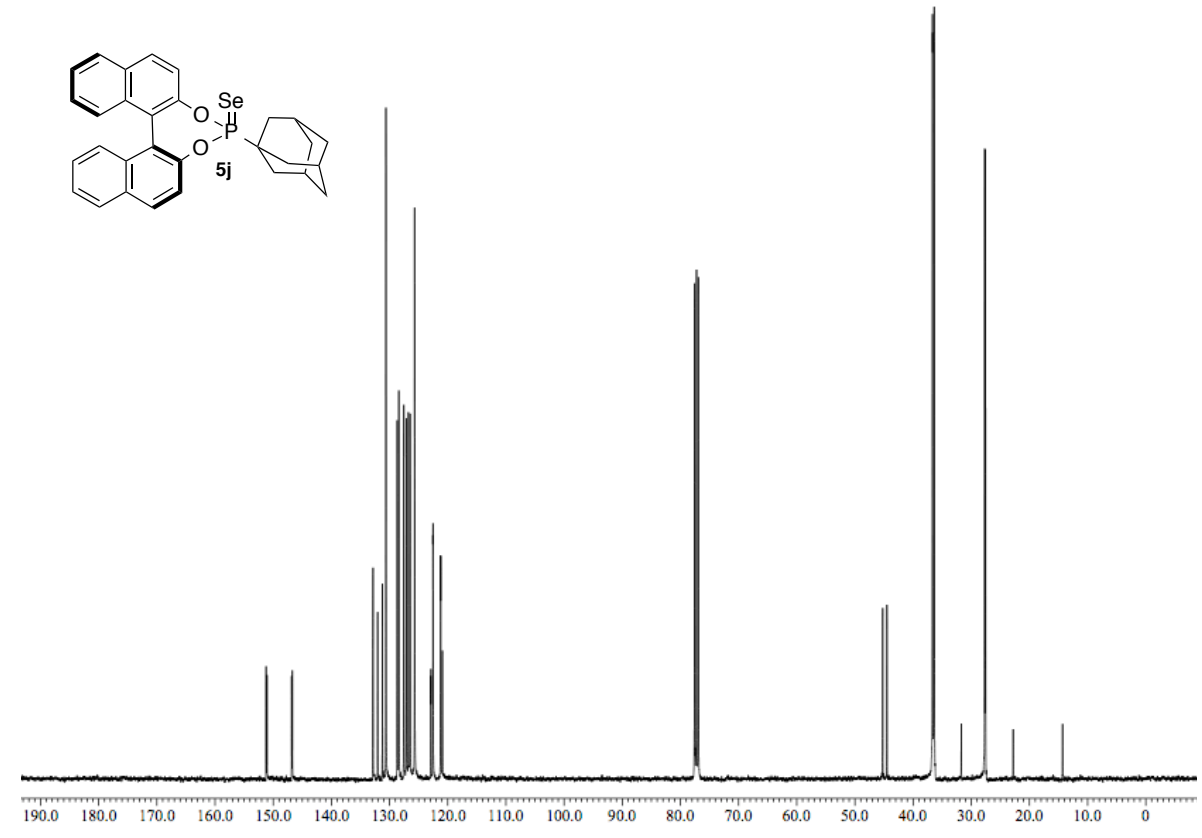


5i

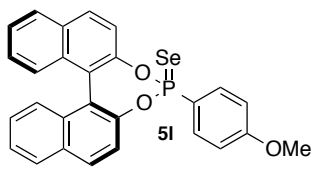

BISEP-Allyl 1H 9-1.esp
Se
O
P
O
5k
2.00 1.93 0.90 3.93 3.24
0.87
1.92
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


YH BISEP-Allyl 13C-1.esp
Se
O
P
O
5k
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)


Se
O
P
O
5j
1.99
1.99
6.04
6.02
3.23
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

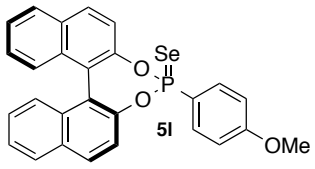

Se
O
P
O
5j
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0

YH 185 column 10-20 1H.esp

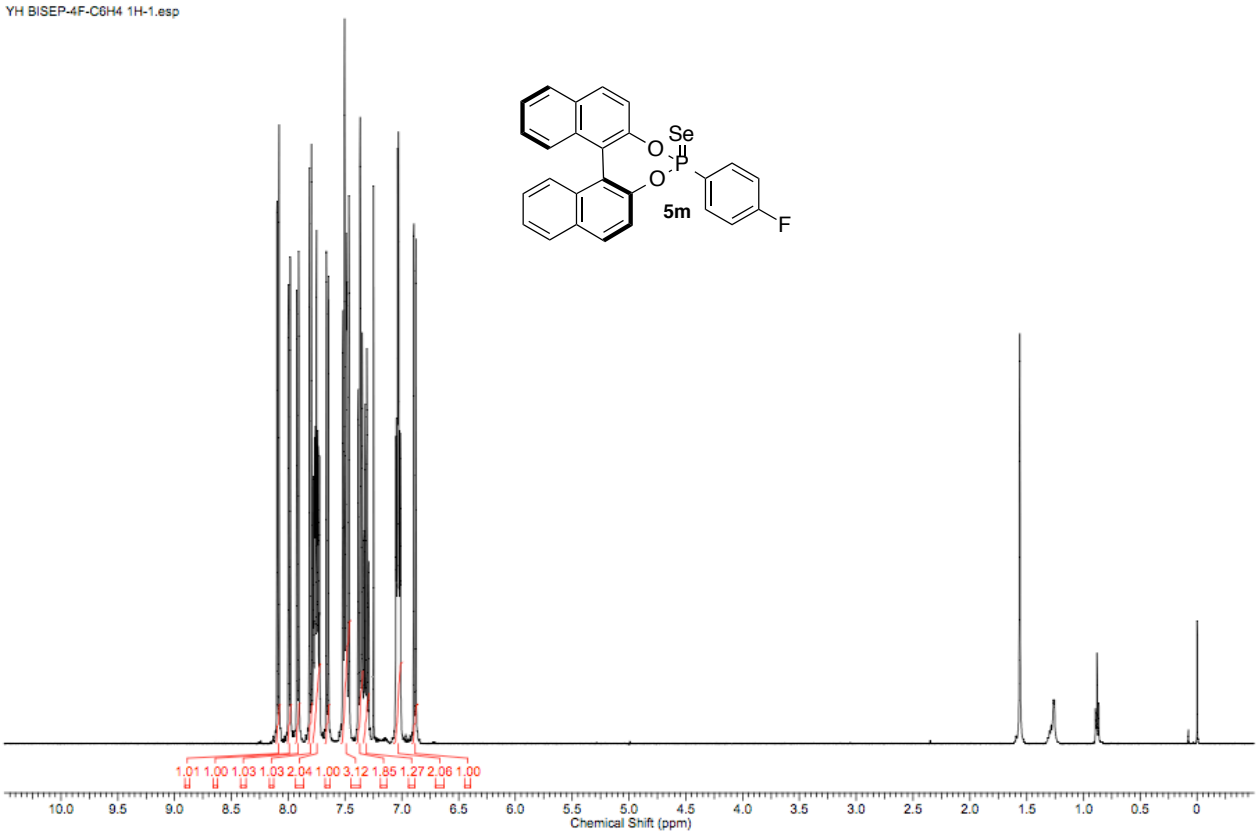


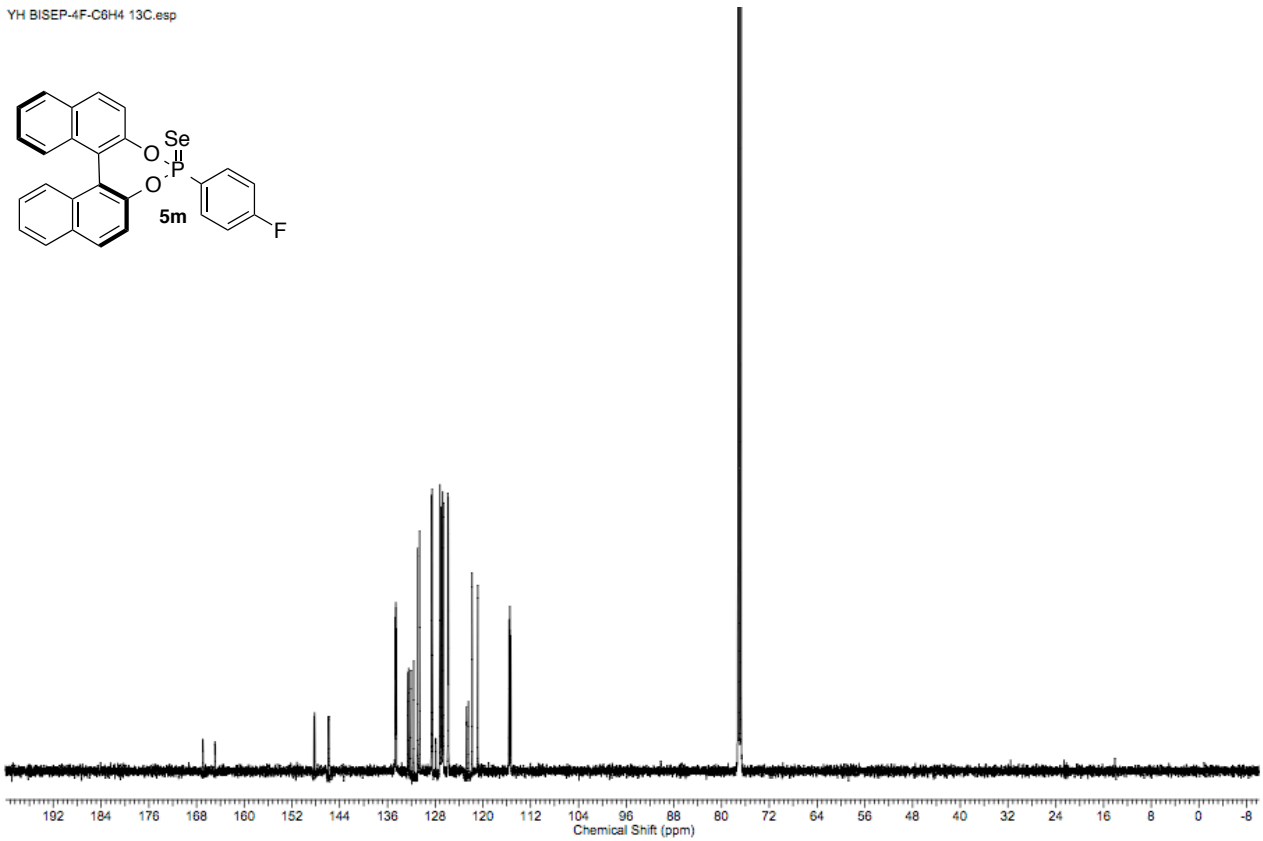
5l

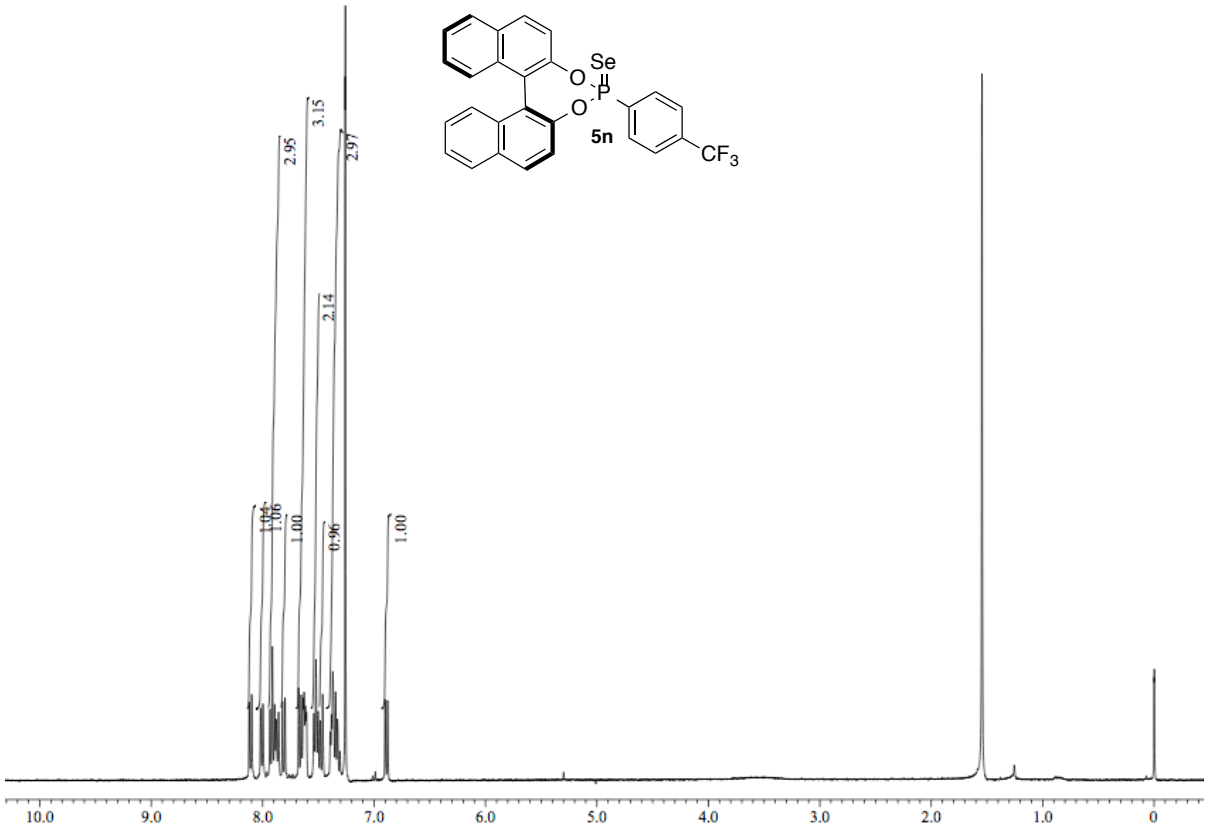
BISEP-ome 13C.esp

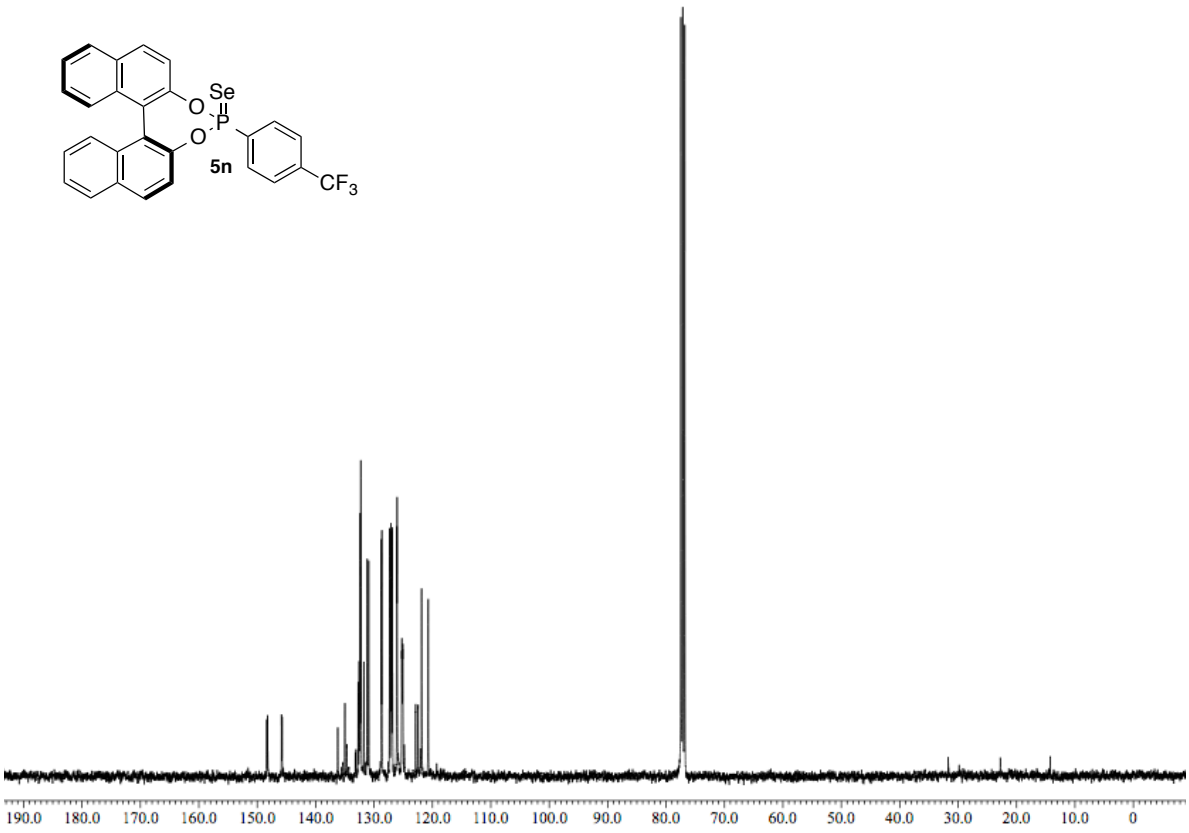


5l

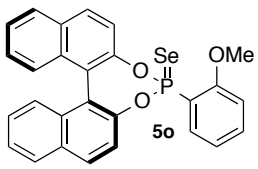

YH BISEP-4F-C6H4 1H-1.esp
Se
O
P
O
F
5m
1.01 1.00 1.03 1.03 2.04 1.00 3.12 1.85 1.27 2.06 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


YH BISEP-4F-C6H4 13C.esp
Se
O
P
O
F
5m
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)


Se
O
P
O
5n
CF3
2.95
3.15
2.97
2.14
1.04
1.06
1.00
0.96
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

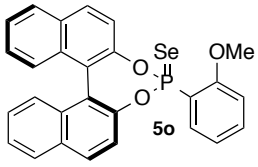

Se
O
P
O
5n
CF3
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0

YH BISEP-o-OMe 1H-1.esp

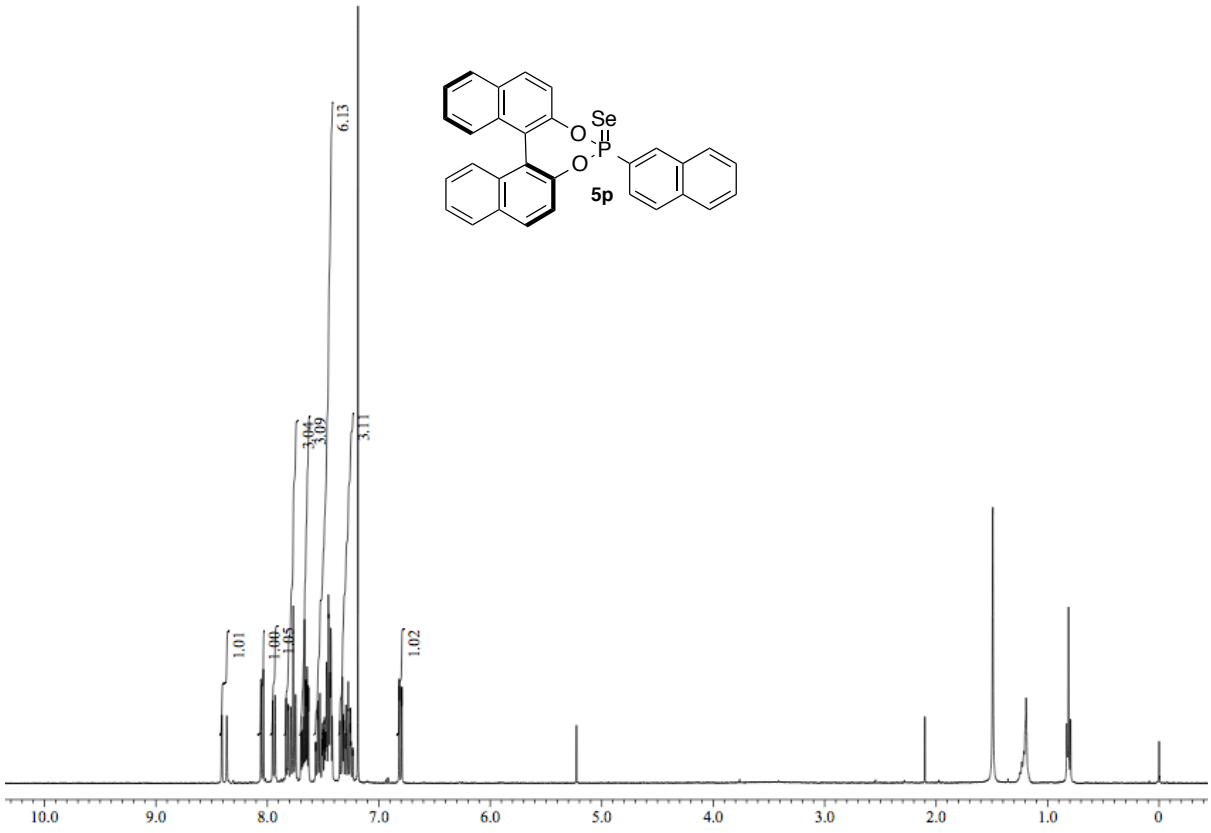


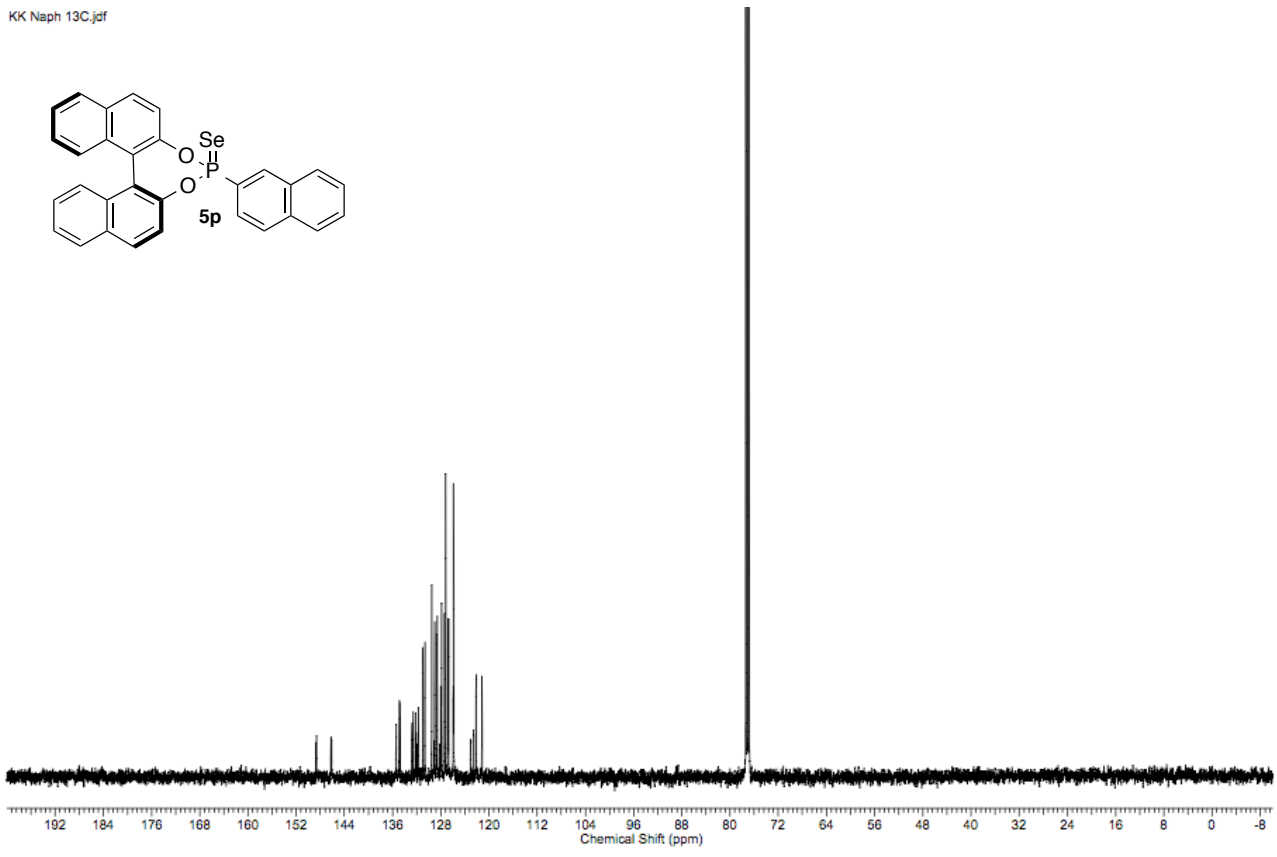
5o

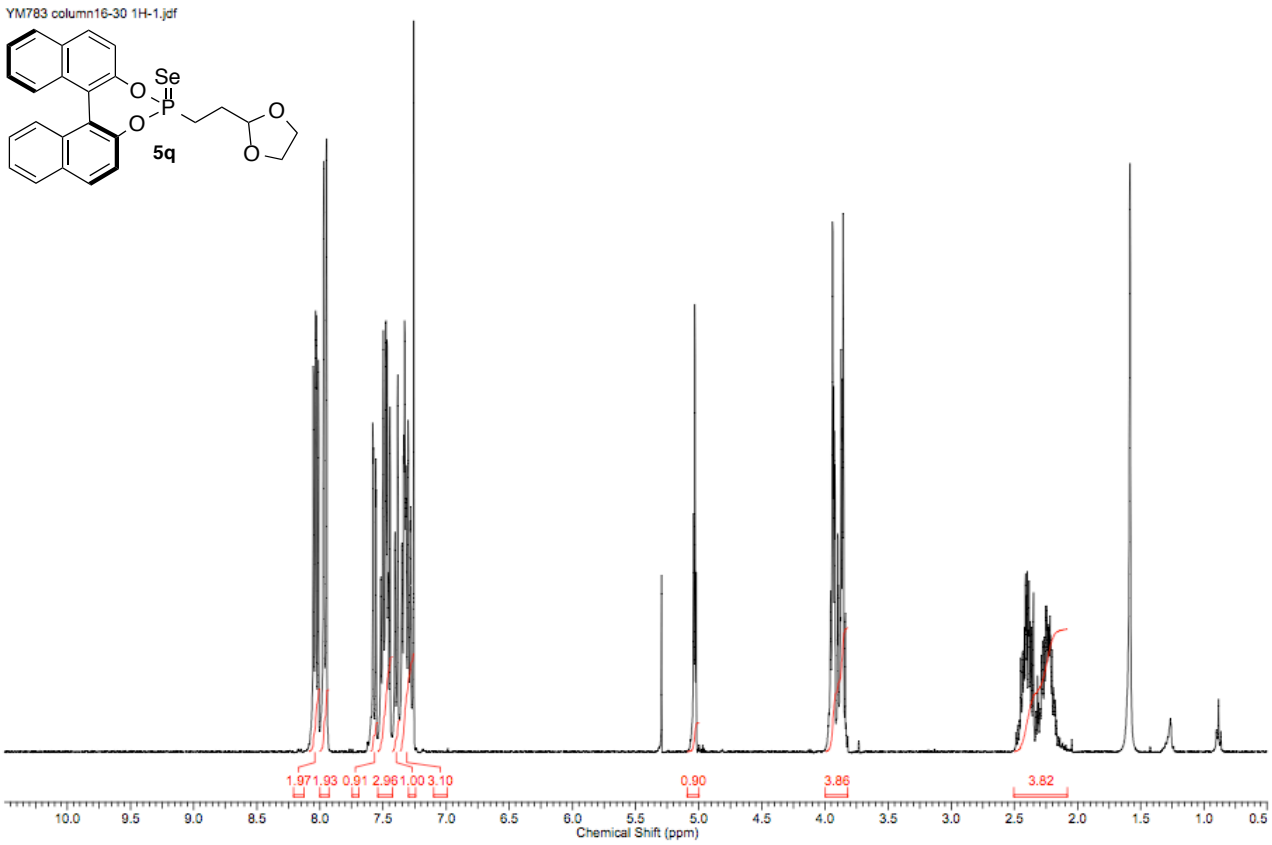
BISEP-ome 13C.esp

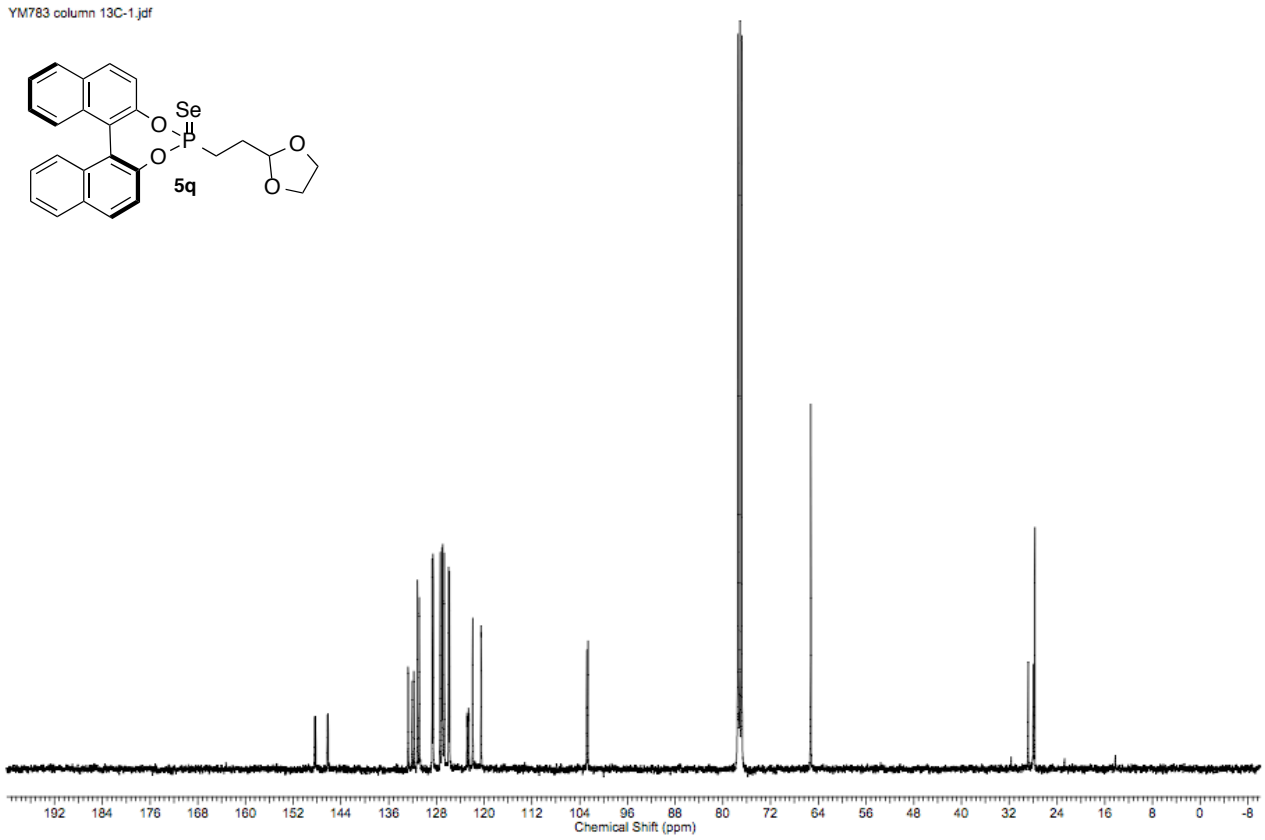


5o

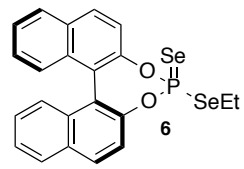

Se
O
P
O
5p
6.13
3.11
3.04
3.09
1.01
1.00
1.05
1.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


KK Naph 13C.jdf
Se
O
P
O
5p
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
-8
Chemical Shift (ppm)


YM783 column16-30 1H-1.jdf
Se
O
P
O
O
O
5q
1.97 1.93 0.91 2.96 1.00 3.10
0.90
3.86
3.82
10.0 9.5 9.0 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)

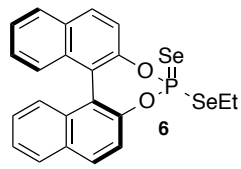

YM783 column 13C-1.jdf
Se
O
P
O
O
O
5q
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)

BISEPSeEt 1H-5.jdf

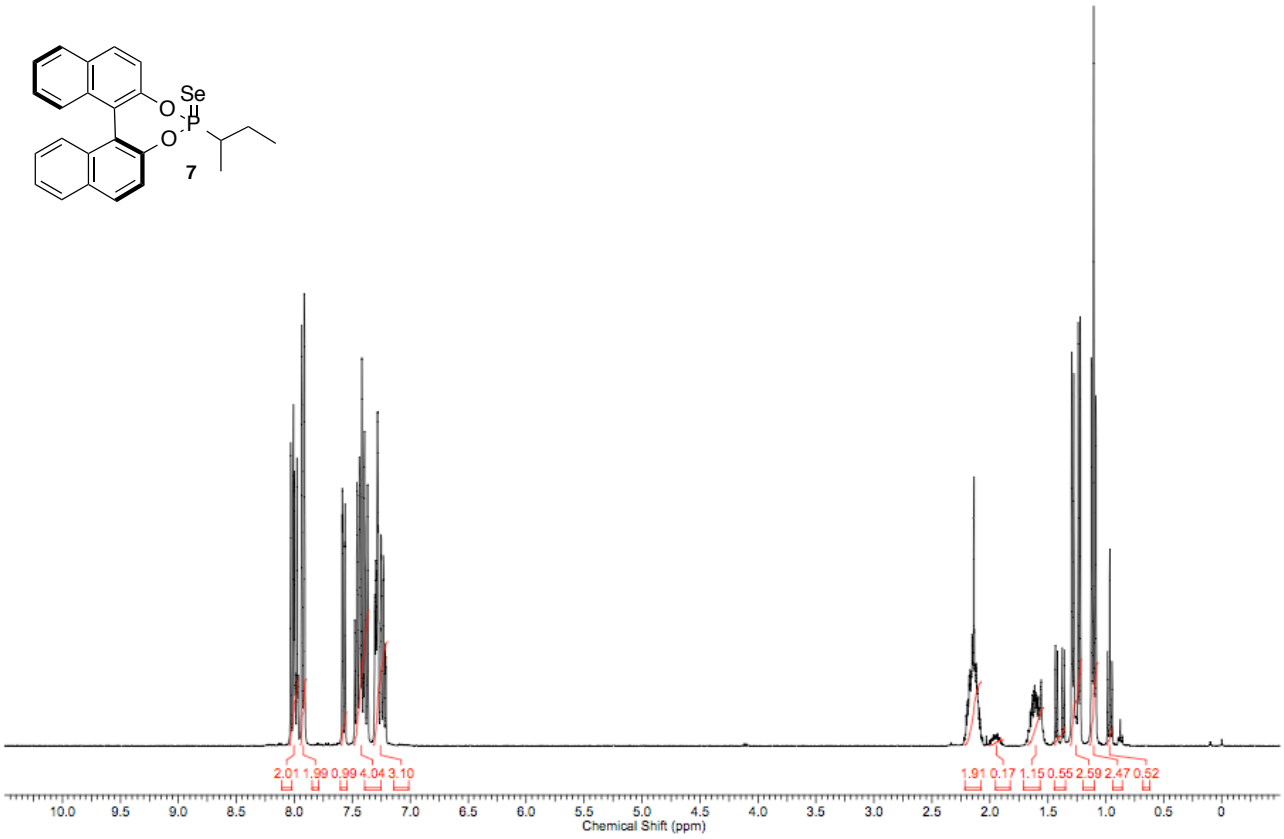


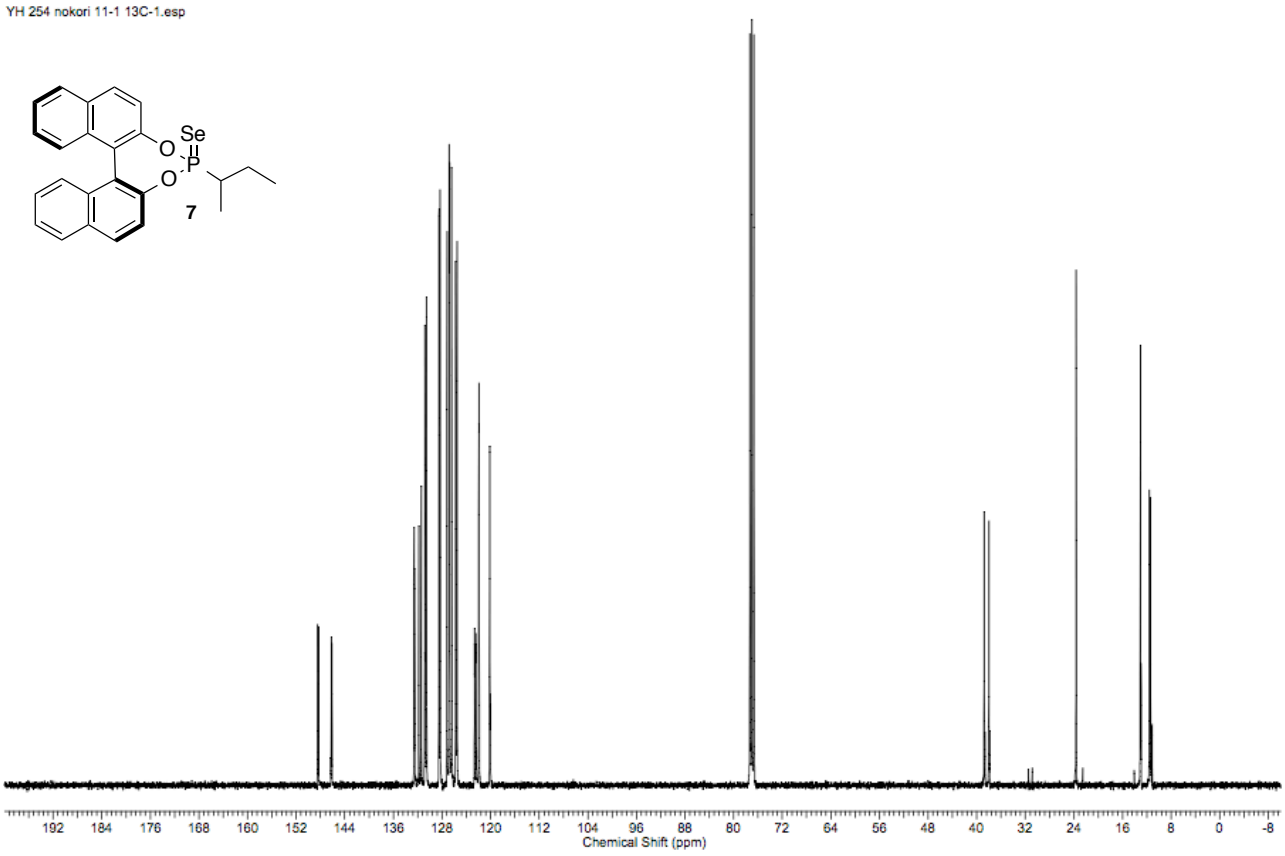
6

BISEPSeEt 13C-1.jdf

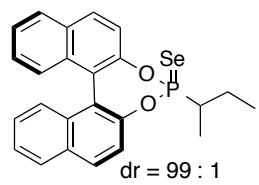


6


Se
O
P
O
7
2.01 1.99 0.99 4.04 3.10
1.91 0.17 1.15 0.55 2.59 2.47 0.52
10.0 9.5 9.0 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)

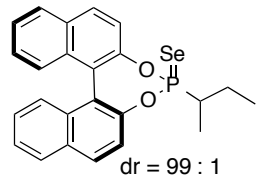

YH 254 nokori 11-1 13C-1.esp
Se
O
P
O
7
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)

YH 254 recrystal 15 1H-1.esp



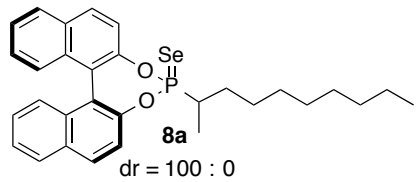
dr = 99 : 1

YH 254 recrystal 15 13C-1.esp



dr = 99 : 1

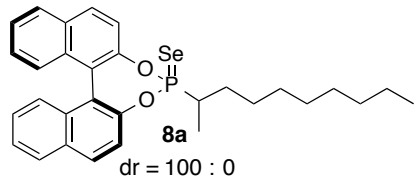
YH 290 GPC 44-51 1H-1.esp



8a

dr = 100 : 0

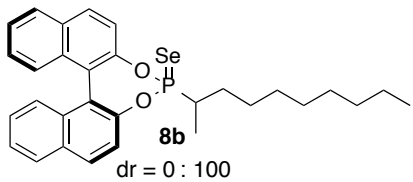
YH 290 GPC 44-51 13C-1.esp



8a

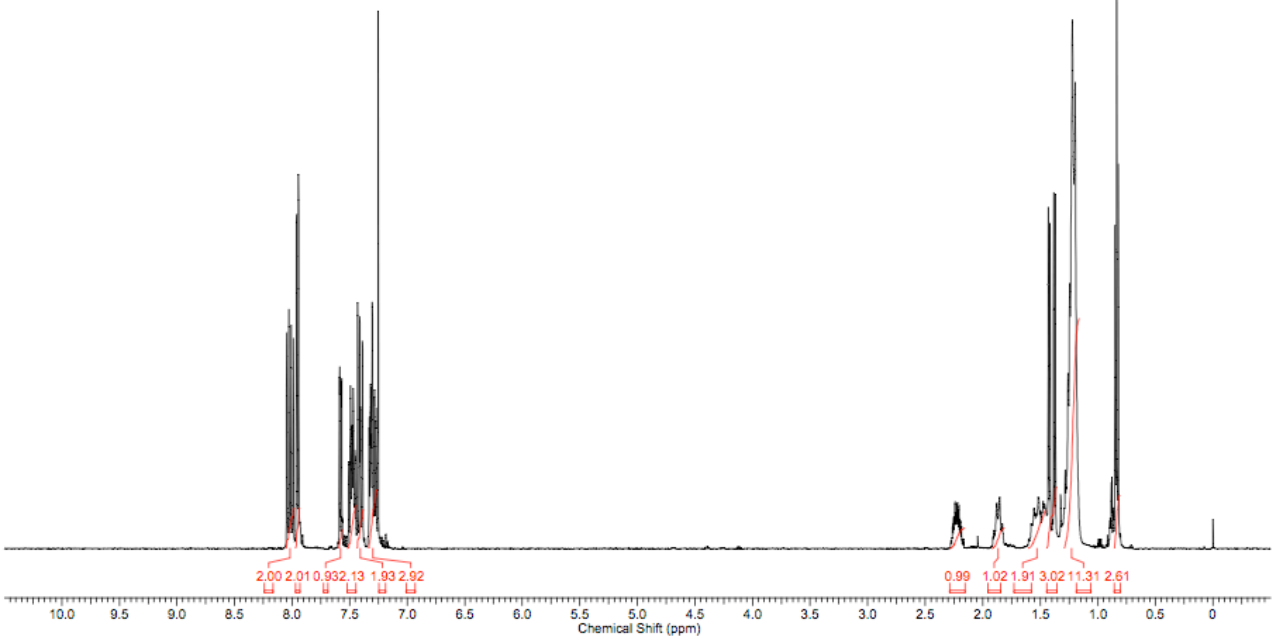
dr = 100 : 0

YH 290 GPC 55-69 1H-1.esp

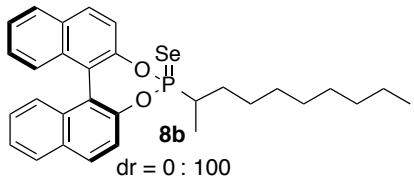


8b

dr = 0 : 100



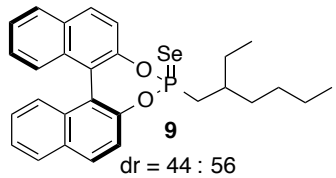
YH 290 GPC 55-69 13C-1.esp



8b

dr = 0 : 100

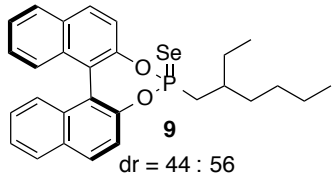
YH 256 nokori 3-2 1H-1.esp



9

dr = 44 : 56

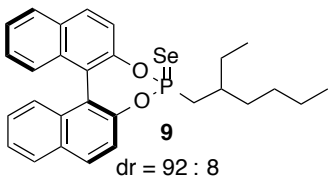
YH 256 nokori 3-2 13C-1.esp



9

dr = 44 : 56

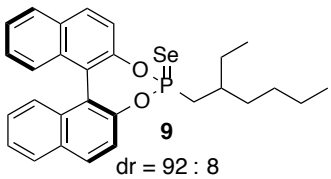
BISEP-2-ethyl-hezane 1H-1.esp



9

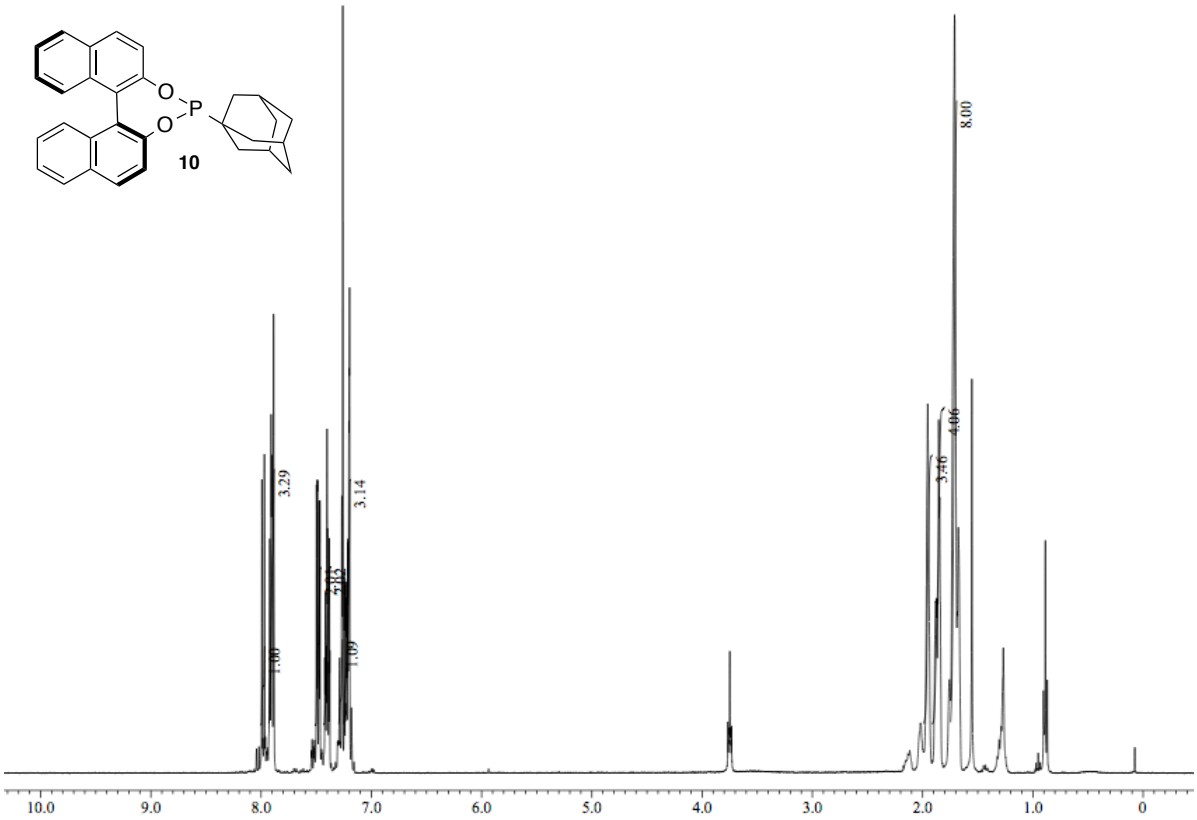
dr = 92 : 8

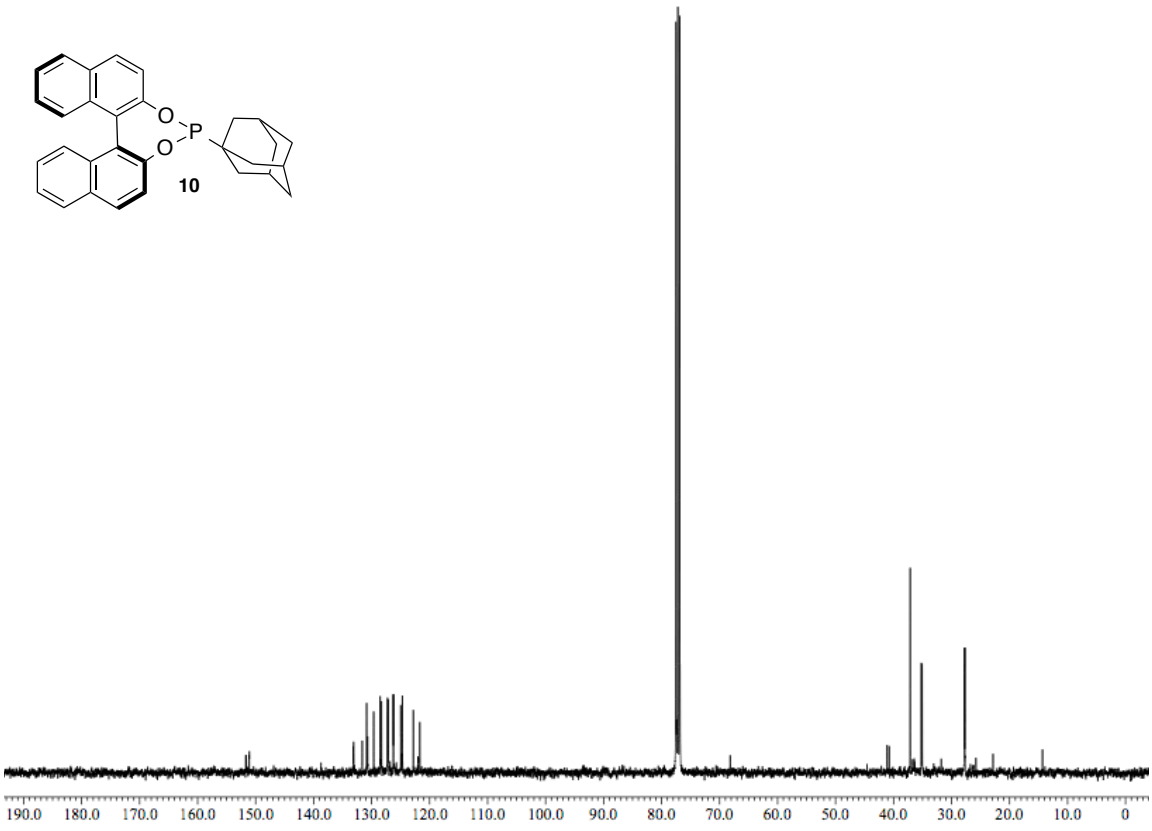
YH BISEP-2-ethyl-hexane R 13C-1.esp



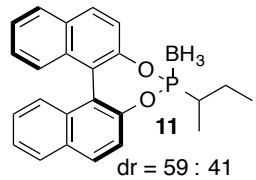
9

dr = 92 : 8


10
3.29
3.14
8.00
4.06
3.46
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


10
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0

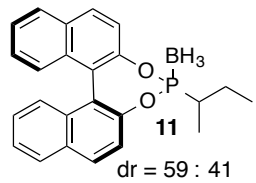
YH 273 column 7-19 2 1H-1.esp



11

dr = 59 : 41

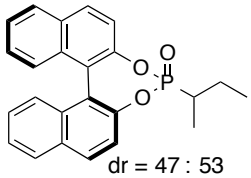
YH 273 column 7-19 13C-1.esp



11

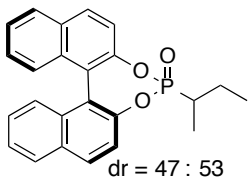
dr = 59 : 41

YH 264 column 10-15 -3 1H-1.esp

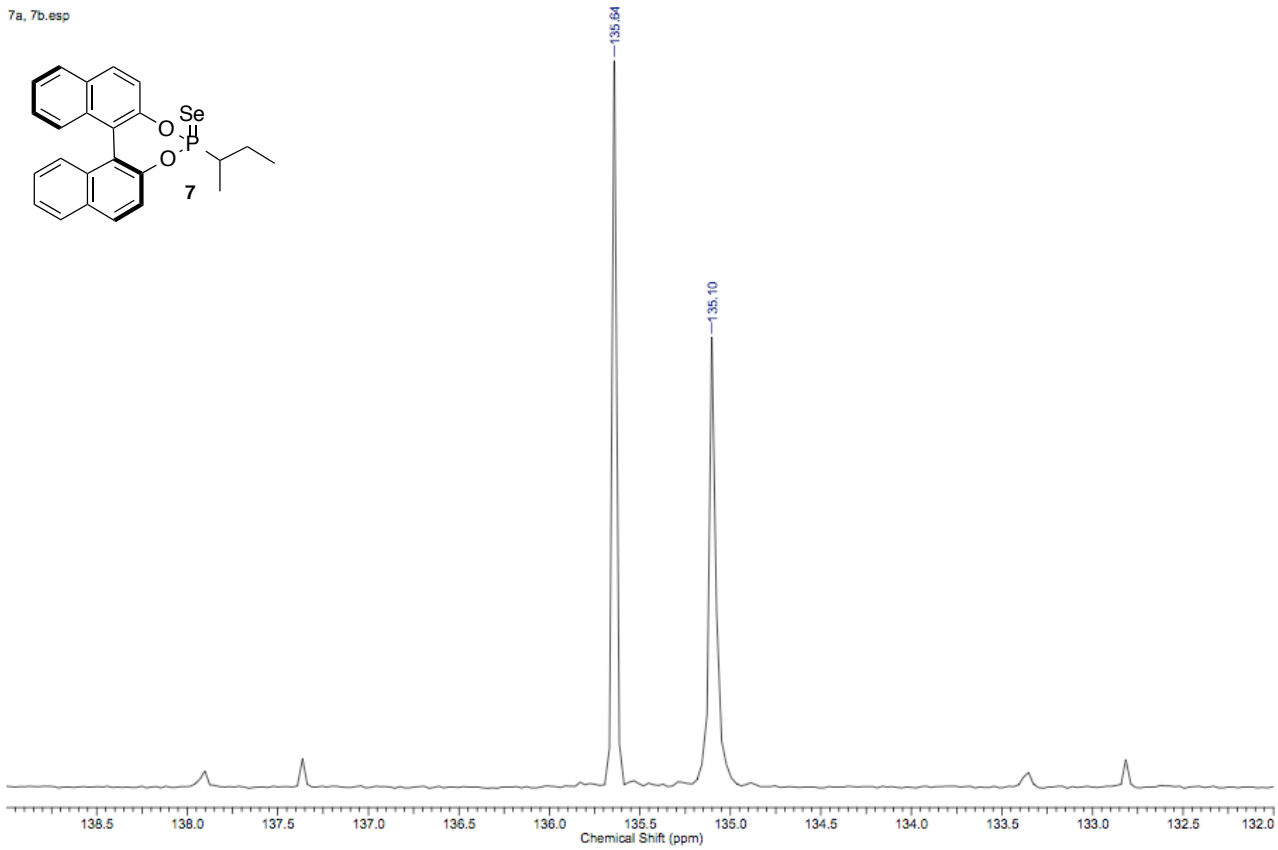


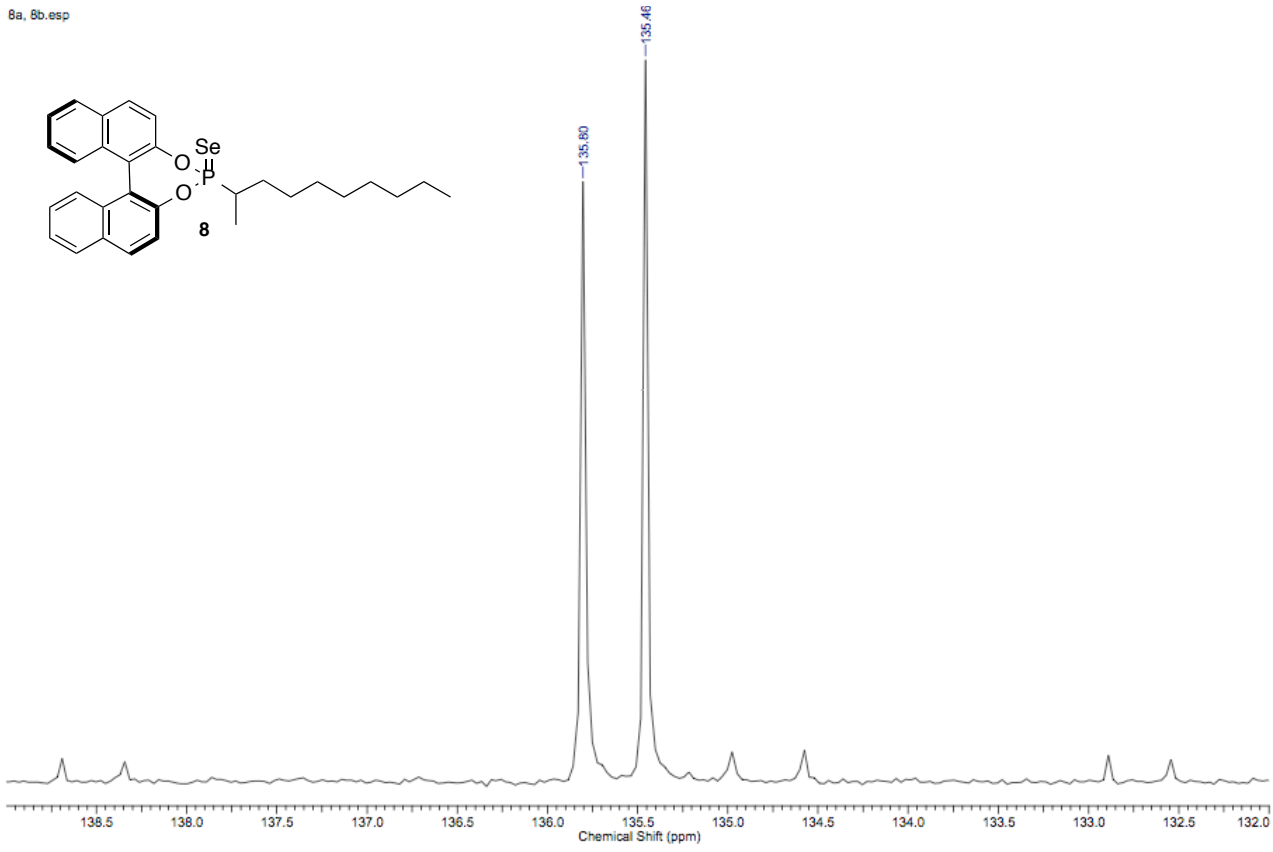
dr = 47 : 53

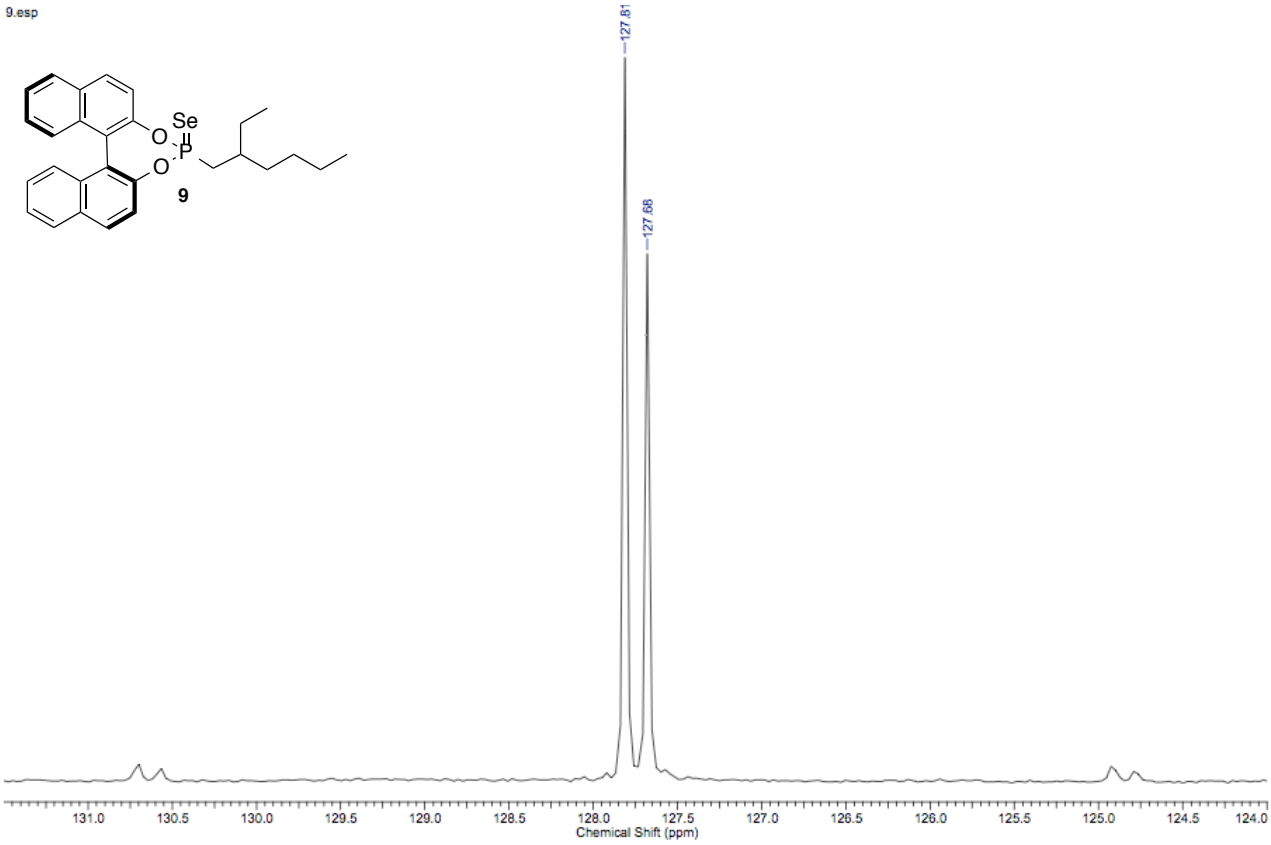
YH 264 column 10-15 13C -1.esp

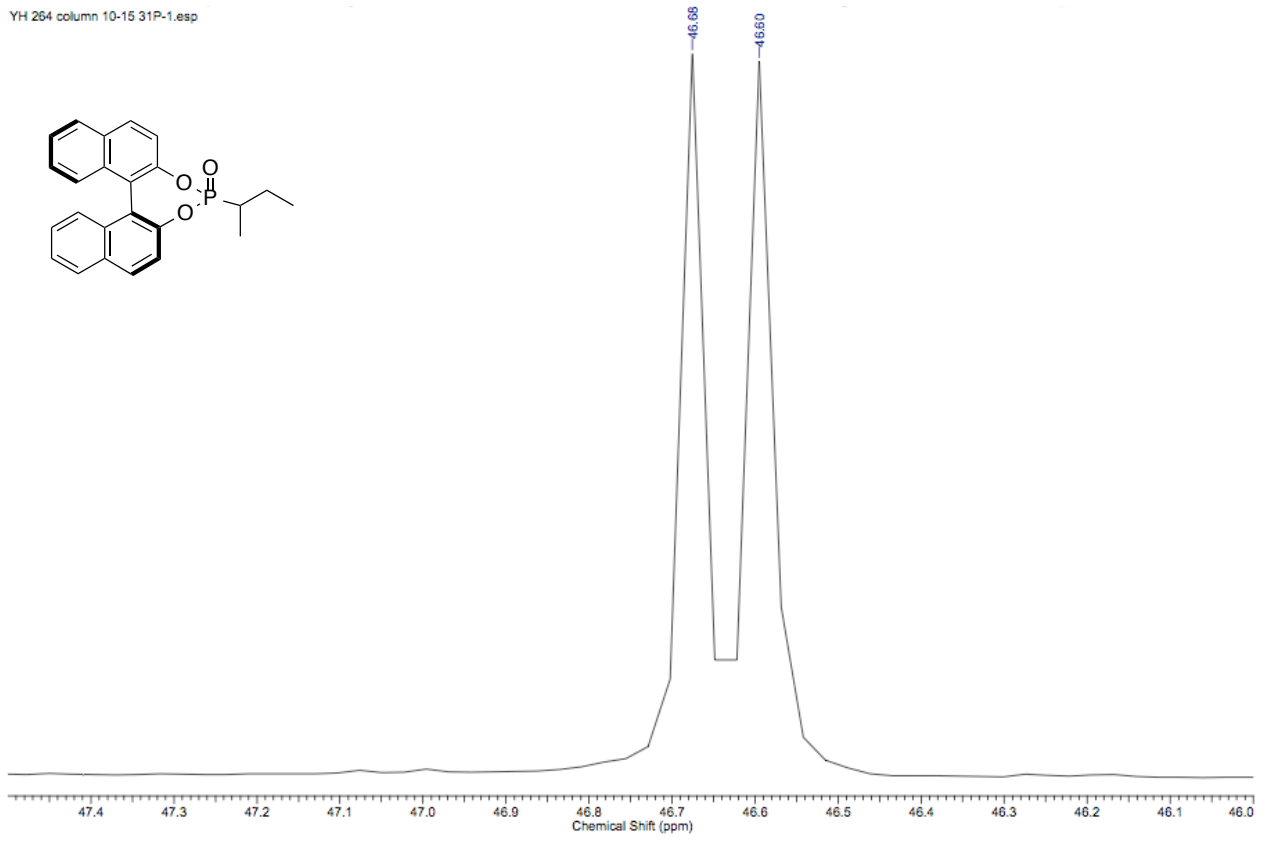


dr = 47 : 53


7a, 7b.esp
Se
O
P
O
7
135.64
135.10
138.5
138.0
137.5
137.0
136.5
136.0
135.5
135.0
134.5
134.0
133.5
133.0
132.5
132.0
Chemical Shift (ppm)


8a, 8b.esp
Se
O
P
O
8
135.80
135.46
138.5
138.0
137.5
137.0
136.5
136.0
135.5
135.0
134.5
134.0
133.5
133.0
132.5
132.0
Chemical Shift (ppm)


9.esp
Se
O
P
O
9
127.81
127.68
131.0
130.5
130.0
129.5
129.0
128.5
128.0
127.5
127.0
126.5
126.0
125.5
125.0
124.5
124.0
Chemical Shift (ppm)


YH 264 column 10-15 31P-1.esp
O
O
P
O
46.66
46.60
47.4
47.3
47.2
47.1
47.0
46.9
46.8
46.7
46.6
46.5
46.4
46.3
46.2
46.1
46.0
Chemical Shift (ppm)