Supporting Information

Dibenzo[*b*,*e*]phosphindolizine Synthesized by Ring-closing Metathesis of Benzo[*b*]phospholes with Two Vinyl Tethers

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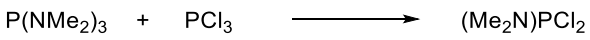
1. Experimental Details

General. All anaerobic and/or moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen atmosphere or with glovebox techniques under argon atmosphere. Analytical thin-layer chromatography (TLC) was performed using Silicagel 70 F_{254} TLC Plate-*Wako*. The developed chromatogram was analyzed by UV lamp (254 nm). The silica gel column chromatography was performed with Wako-gel® 60N (150-425 μm, irregular). Preparative gel permeation chromatography (GPC) was performed with an YMC LC-forte/R instrument equipped with YMC-GPC T2000 and T4000 columns using chloroform as an eluent. The ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{31}P NMR (162 MHz) spectra were measured in $CDCl_3$ with a JEOL JNM-ECS400 spectrometer. Signals due to tetramethylsilane (0.0 ppm) in ^{1}H NMR and $CDCl_3$ (77.16 ppm) in ^{13}C NMR were used as internal references, and chemical shifts are reported in ppm downfield. ^{31}P NMR chemical shifts are externally referenced to 85% H_3PO_4 (0 ppm). Low- and high-resolution mass spectra were recorded on a JEOL JMS-700 spectrometer at EI mode. All melting points were determined on a Yanaco micro melting point apparatus (MP-J3) and were uncorrected. The melting points of **1d** and **7d** were measured under an argon atmosphere in a sealed tube.

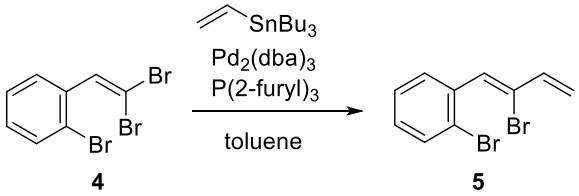
Reagents. Et_2O, THF, toluene, and CH_2Cl_2 (Wako, Super dehydrated grade) were purchased and used as received. Tri(2-furyl)phosphine (TCI), *n*-BuLi (Mitsuwa), oxone (Aldrich), elemental sulfur (Wako), elemental selenium (Wako), Grubbs 2nd (Aldrich), 4-methylmorpholine *N*-oxide (Oakwood), MS 4A (Wako), sodium carbonate (Kishida), potassium *tert*-butoxide (nacalai), ethanol (Wako), and acetonitrile (Wako), and $CDCl_3$ (CIL) were purchased and used as received. Phosphorus trichloride and tris(dimethylamino)phosphine were distilled prior to use. 1-Bromo-2-(2,2-dibromovinyl)benzene (**4**),[S1] tributyl(vinyl)tin,[S2] tris(dibenzylideneacetone)dipalladium(chloroform) ($Pd_2(dba)_3{\cdot}CHCl_3$),[S3] 1-bromo-2-vinylbenzene,[S4] trimethylphosphine,[S5] 1-bromo-2-bromomethyl-4-iodobenzene,[S6] mesitylboronic acid,[S7] tetrakis(triphenylphosphine)palladium,[S8] and methyltriphenylphosphonium iodide[S9] were synthesized according to the reported procedures.

Synthesis of dichloro(dimethylamino)phosphine (S1)



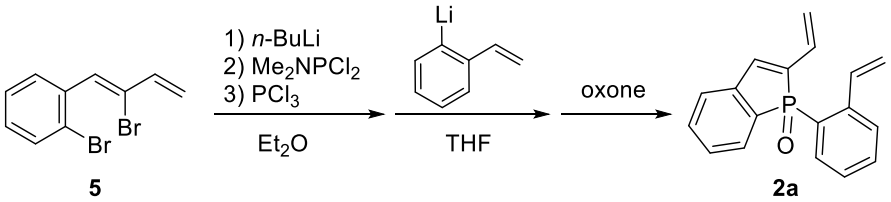
To phosphorus trichloride (6.40 mL, 73.2 mmol) charged into 50 mL flask was added dropwise tris(dimethylamino)phosphine (6.71 mL, 36.6 mmol) at 0 °C. The mixture was stirred at room temperature for 2.5 h, and then distilled under reduced pressure (40-41˚C, 16 mmHg; lit.[S10] 57-59 ˚C, 24 mmHg) to give **S1** as colorless liquid (14.1 g, 96.6 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.86 (d, J = 12.4 Hz, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$). δ = 37.7 (d, J = 21.2 Hz, CH_3). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ = 165.9.

Synthesis of 2-bromo-1-(2-bromophenyl)-1,3-butadiene (5)



This compound was prepared according to the synthetic procedures reported by Shen and co-worker.[S11] To a solution of 1-bromo-2-(2,2-dibromovinyl)benzene (**4**, 5.20 g, 15.3 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (386 mg, 0.373 mmol), and tri(2-furyl)phosphine (522 mg, 2.25 mmol) in toluene (75 mL) was added tributyl(vinyl)tin (4.60 mL, 15.8 mmol) at 0 ˚C. The reaction mixture was stirred at 60 ˚C for 21 h. Water and ethyl acetate were added, and then the organic layer was separated. The aqueous layer was extracted with AcOEt. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered through a pad of Celite®, and then evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane (R_f = 0.48) to give **5** as pale-yellow liquid (3.24 g, 11.3 mmol, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.41 (d, *J* = 10.6 Hz, 1H), 5.78 (d, *J* = 16.1 Hz, 1H), 6.57 (dd, *J* = 16.1, 10.6 Hz, 1H), 7.04 (s, 1H), 7.18 (dd, *J* = 7.8, 7.4 Hz, 1H), 7.34 (dd, *J* = 7.8, 7.4 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 120.3, 124.2, 126.7, 126.9, 129.6, 131.3, 131.8, 132.6, 136.2, 136.5. HRMS (EI, 70 eV) *m/z* found: 285.8987 ([M]$^+$), calcd for $C_{10}H_8{}^{79}Br_2$ 285.8993.

Synthesis of 2-vinyl-1-(2-vinylphenyl)benzophosphole-*P*-oxide (2a)

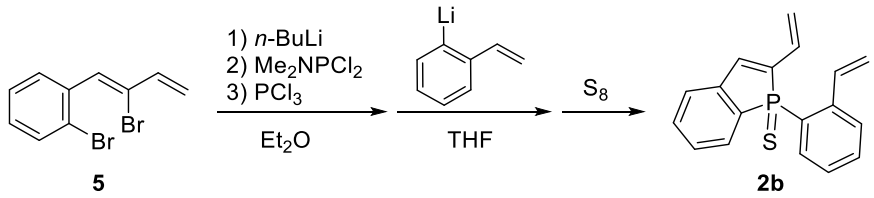


To a solution of **5** (2.59 g, 8.99 mmol) in Et_2O (86 mL) was added *n*-BuLi in hexane (1.56 M; 12.7 mL, 19.8 mmol) at 0 ˚C. After the reaction mixture was stirred at room temperature for 1 h, dichloro(dimethylamino)phosphine (1.40 mL, 12.1 mmol) was added dropwise at 0 ˚C. The reaction mixture was stirred at room temperature for 1 h. Phosphorus trichloride (1.02 mL, 11.7 mmol) was added dropwise at 0 ˚C, and then the reaction mixture was stirred at room temperature for 1 h. After the volatiles were removed under reduced pressure at 0 ˚C, THF (20 mL) was added. To this solution at −78 ˚C was added 1-lithio-2-vinylbenzene, which was prepared from 1-bromo-2-vinylbenzene (2.00 g, 10.9 mmol) and *n*-BuLi in hexane (1.56 M; 7.20 mL, 11.2 mmol) in THF (30 mL) at −78 ˚C for 20 min. After the reaction mixture was stirred at room temperature for 1.5 h, the mixture was quenched with NH_4Cl aq. at −30 ˚C. The organic layer was separated, and then the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered through a pad of Celite, and then evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane/ethyl

acetate = 50/1 (R_f = 0.43) to give benzophosphole as orange oil (511 mg). A suspension of benzophosphole (511 mg, 1.95 mmol) and oxone (1.44 g, 2.34 mmol) in CH_2Cl_2 (50 mL) and MeOH (10 mL) was refluxed for 23 h. Water was added, and then the organic layer was separated. The aqueous layer was extracted with and CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered through a pad of Celite®, and then evaporated under reduced pressure to give **2a** as pale-yellow liquid (500 mg, 1.80 mmol, 20% from **5**).

Mp. 150-151 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.27 (dd, J = 11.1, 1.2 Hz, 1H), 5.37 (d, J = 11.1 Hz, 1H), 5.62 (dd, J = 17.5, 1.2 Hz, 1H), 5.64 (d, J = 17.5 Hz, 1H), 6.66 (ddd, J = 23.0, 17.5, 11.1 Hz, 1H), 7.16 (d, J = 35.4 Hz, 1H), 7.25-7.35 (m, 3H), 7.42-7.53 (m, 3H), 7.59 (dd, J = 7.2, 4.4 Hz, 1H), 7.64 (dd, J = 9.0, 8.1 Hz, 1H), 7.87 (ddd, J = 14.2, 7.8, 1.2 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 118.0 (CH_2), 121.7 (d, J = 5.8 Hz, CH_2), 124.9 (d, J = 9.6 Hz, CH), 127.1 (d, J = 9.6 Hz, CH), 127.4 (d, J = 92.5 Hz), 127.8 (d, J = 12.6 Hz, CH), 129.0 (d, J = 10.6 Hz, CH), 129.2 (d, J = 10.6 Hz, CH), 130.0 (d, J = 9.6 Hz, CH), 132.3 (d, J = 11.5 Hz, CH), 132.7 (d, J = 2.9 Hz, CH), 133.1 (d, J = 1.9 Hz, CH), 133.6 (d, J = 107 Hz), 134.9 (d, J = 5.7 Hz, CH), 138.1 (d, J = 95.3 Hz), 140.0 (d, J = 20.2 Hz, CH), 141.6 (d, J = 27.9 Hz), 142.7 (d, J = 8.6 Hz); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ = 39.7. HRMS (EI, 70 eV) *m/z* found: 278.0860 ([M]$^+$), calcd for $C_{18}H_{15}PO$ 278.0861.

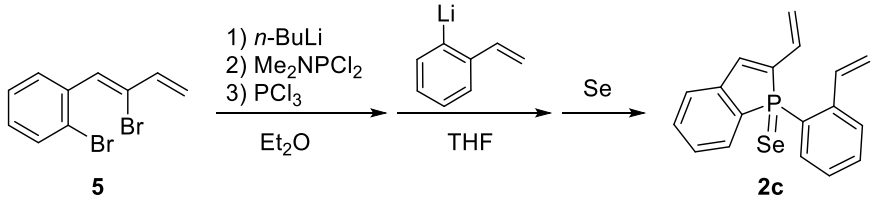
Synthesis 2-vinyl-1-(2-vinylphenyl)benzophosphole-*P*-sulfide (2b)



To a solution of **5** (1.52 g, 5.28 mmol) in Et_2O (50 mL) was added *n*-BuLi in hexane (1.56 M; 7.40 mL, 11.6 mmol) at 0 ˚C dropwise for 5 min. After the reaction mixture was stirred at room temperature for 100 min, dichloro(dimethylamino)phosphine (0.80 mL, 6.9 mmol) was added at 0 ˚C. The reaction mixture was stirred at room temperature for 10 min. Phosphorus trichloride (0.59 mL, 6.7 mmol) was added at 0 ˚C, and then the reaction mixture was stirred at room temperature for 60 min. After the volatiles were removed under reduced pressure, THF (20 mL) was added. 1-lithio-2-vinylbenzene, which was prepared from 1-bromo-2-vinylbenzene (1.26 g, 6.86 mmol) and *n*-BuLi in hexane (1.56 M; 4.6 mL, 7.2 mmol) in THF (20 mL) at −78 ˚C for 30 min, was added at −78 ˚C. After the reaction mixture was stirred at room temperature for 45 min, elemental sulfur (291 mg, 9.08 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 24 h. Aqueous NH_4Cl solution was added, and then the organic layer was separated. The aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered through a pad of Celite, and then evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane/ethyl acetate = 10/1 (R_f = 0.30) to give **2b** as orange oil (482 mg, 1.81 mmol, 34% form **5**). The highly pure compound **2b** tended to give the insoluble material likely due to oligomerization, which prevent the isolation of **2** in highly pure form.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.03 (d, *J* = 11.0 Hz, 1H), 5.31 (d, *J* = 10.6 Hz, 1H), 5.38 (d, *J* = 17.0 Hz, 1H), 5.55 (d, *J* = 17.9 Hz, 1H), 6.60 (ddd, *J* = 23.5, 17.9, 10.6 Hz, 1H), 6.83 (dd, *J* = 17.0,11.0 Hz, 1H), 7.15 (d, *J* = 34.9 Hz, 1H), 7.27-7.33 (m, 1H), 7.38-7.54 (m, 5H), 7.57 (dd, *J* = 10.3, 7.6 Hz, 1H), 8.58 (ddd, *J* = 17.4, 7.4, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 118.0 (CH_2), 121.4 (d, *J* = 6.7 Hz, CH_2), 125.2 (d, *J* = 8.7 Hz, CH), 125.3 (d, *J* = 71.2 Hz), 127.6 (d, *J* = 9.7 Hz, CH), 128.0 (d, *J* = 13.5 Hz, CH), 128.4 (d, *J* = 11.6 Hz, CH), 129.0 (d, *J* = 11.6 Hz, CH), 129.3 (d, *J* = 11.5 Hz, CH), 132.4 (d, *J* = 1.9 Hz, CH), 132.7 (d, *J* = 2.9 Hz, CH), 134.4 (d, *J* = 5.7 Hz, CH), 134.9 (d, *J* = 14.5 Hz, CH), 137.1 (d, *J* = 91.5 Hz), 138.1 (d, *J* = 17.3 Hz, CH), 140.2 (d, *J* = 78.1 Hz), 141.8 (d, *J* = 2.0 Hz), 141.9 (d, *J* = 13.5 Hz); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ = 44.0. HRMS (EI, 70 eV) *m/z* found: 294.0632 ([M]$^+$), calcd for $C_{18}H_{15}PS$ 294.0632.

Synthesis 2-vinyl-1-(2-vinylphenyl)benzophosphole-*P*-selenide (2c)

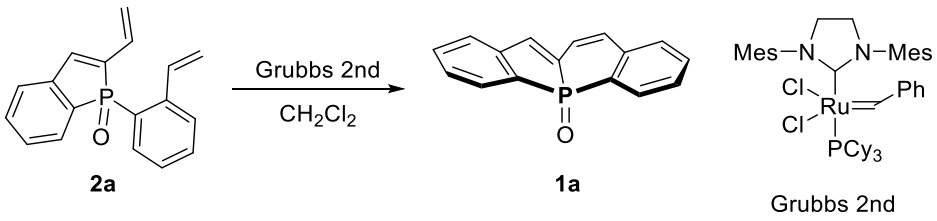


To a solution of **5** (1.51 g, 5.24 mmol) in Et_2O (50 mL) was added *n*-BuLi in hexane (1.56 M; 7.40 mL, 11.6 mmol) at 0 ˚C dropwise for 5 min. After the reaction mixture was stirred at room temperature for 40 min, dichloro(dimethylamino)phosphine (0.79 mL, 6.8 mmol) was added at 0 ˚C. The reaction mixture was stirred at room temperature for 30 min. Phosphorus trichloride (0.60 mL, 6.8 mmol) was added at 0 ˚C, and then the reaction mixture was stirred at room temperature for 60 min. After the volatiles were removed under reduced pressure, THF (20 mL) was added. 1-lithio-2-vinylbenzene, which was prepared from 1-bromo-2-vinylbenzene (1.34 g, 7.33 mmol) and *n*-BuLi in hexane (1.56 M; 4.7 mL, 7.4 mmol) in THF (25 mL) at −78 ˚C for 50 min, was added at −78 ˚C. After the reaction mixture was stirred at room temperature for 60 min, elemental selnium (497 mg, 6.29 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 13 h. Aqueous NH_4Cl solution was added, and then the organic layer was separated. The aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered through a pad of Celite, and then evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane/ethyl acetate = 10/1 (R_f = 0.25) to give **2c** as yellow oil (474 mg, 1.39 mmol, 27% from **5**). The isolation of **2c** in highly pure form was unsuccessful likely due to its low stability under ambient condition.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.00 (d, *J* = 11.0 Hz, 1H), 5.31 (d, *J* = 11.1 Hz, 1H), 5.36 (d, *J* = 17.0 Hz, 1H), 5.54 (d, *J* = 17.5 Hz, 1H), 6.61 (ddd, *J* = 23.4, 17.5, 11.0 Hz, 1H), 6.70 (dd, *J* = 17.0, 11.1 Hz, 1H), 7.14 (d, *J* = 35.0 Hz, 1H), 7.29-7.51 (m, 6H), 7.56 (dd, *J* = 10.6, 7.4 Hz, 1H), 8.66-8.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 118.2 (CH_2), 121.5 (d, *J* = 6.8 Hz, CH_2), 123.2 (d, *J* = 62.6 Hz), 125.3 (d, *J* = 7.7 Hz, CH), 127.6 (d, *J* = 9.7 Hz, CH), 128.2 (d, *J* = 14.4 Hz, CH), 128.7 (d, *J* = 12.5 Hz, CH), 128.9 (d, *J* = 12.5 Hz, CH), 129.3 (d, *J* = 11.5 Hz, CH), 132.7 (d, *J* = 1.9 Hz, CH), 132.9 (d, *J* = 2.8 Hz, CH), 134.7 (d, *J* = 5.8 Hz, CH), 136.83 (d, *J* = 16.4 Hz, CH), 136.85 (d, *J* = 84.8 Hz), 137.3 (d, *J* = 16.4 Hz, CH), 140.0 (d,

J = 71.2 Hz), 141.7 (d, J = 4.8 Hz), 141.9 (d, J = 11.5 Hz); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ = 29.9 (d, $^{1}J_{PSe}$ = 728 Hz) . HRMS (EI, 70 eV) *m/z* found: 342.0073 ([M]$^+$), calcd for $C_{18}H_{15}P^{80}Se$ 342.0077.

Synthesis of dibenzo[*b*,*e*]phosphindolizine-*P*-oxide (1a)

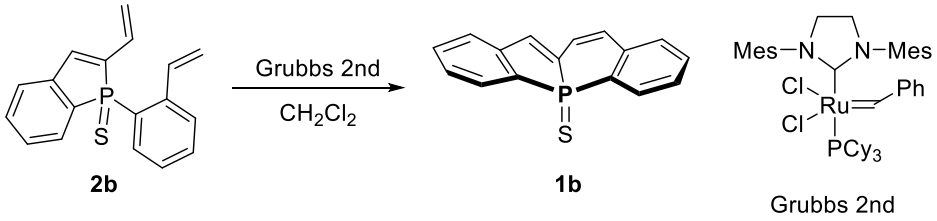


2a **1a** Grubbs 2nd

A solution of **2a** (400 mg, 1.44 mmol) and Grubbs 2nd (97.8 mg, 115 μmol) in CH_2Cl_2 (24 mL) was stirred at reflux for 88 h. The reaction mixture was filtered through a pad of Celite with $CHCl_3$, and then the volatile of the filtrate was evaporated under reduced pressure. The residue was chromatographed on silica gel with ethyl acetate/THF = 5/1 (R_f = 0.25), and then purified by GPC (eluent, $CHCl_3$). The residual solid was washed with hexane to give **1a** as yellow solid (78.5 mg, 0.314 mmol, 22%).

Mp. 210-211 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.53 (dd, J = 10.1, 3.3 Hz, 1H), 6.76 (dd, J = 16.5, 10.1 Hz, 1H), 6.96 (d, J = 35.4 Hz, 1H), 7.25-7.32 (m, 3H), 7.37 (ddd, J = 6.9, 6.9, 4.1 Hz, 1H), 7.42-7.46 (m, 1H), 7.46-7.51 (m, 1H), 7.85 (dd, J = 12.8, 7.3 Hz, 1H), 7.96 (dd, J = 8.2, 8.2 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 124.2 (d, J = 4.8 Hz, CH), 126.1 (d, J = 10.6 Hz, CH), 127.9 (d, J = 11.6 Hz, CH), 129.5 (d, J = 9.6 Hz, CH), 130.0 (d, J = 96.3 Hz), 130.4 (d, J = 9.6 Hz, CH), 131.01 (d, J = 9.7 Hz, CH), 131.03 (d, J = 112 Hz), 131.3 (d, J = 6.8 Hz, CH), 131.6 (d, J = 10.6 Hz, CH), 133.0 (d, J = 1.9 Hz, CH), 133.3 (CH), 135.9 (d, J = 92.5 Hz), 138.9 (d, J = 18.3 Hz, CH), 139.6 (d, J = 6.7 Hz), 143.0 (d, J = 30.8 Hz); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ = 24.5. HRMS (EI, 70 eV) *m/z* found: 250.0547 ([M]$^+$), calcd for $C_{16}H_{11}PO$ 250.0548.

Synthesis of dibenzo[*b*,*e*]phosphindolizine-*P*-sulfide (1b).



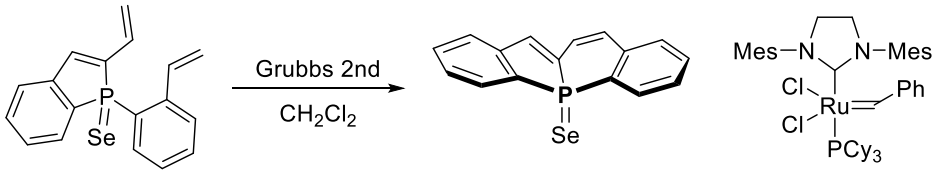
2b **1b** Grubbs 2nd

A solution of **2b** (200 mg, 0.679 mmol) and Grubbs 2nd (46.1 mg, 54.3 μmol) in CH_2Cl_2 (7 mL) was stirred at reflux for 36 h. The reaction mixture was filtered through a pad of Celite with $CHCl_3$, and then the volatile of the filtrate was evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane/ethyl acetate = 5/1 (R_f = 0.30), and then purified by GPC (eluent, $CHCl_3$) to give **1b** as yellow solid (12.7 mg, 47.7 μmol, 7%).

Mp. 180 ˚C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.59 (dd, J = 10.5, 3.7 Hz, 1H), 6.79 (dd, J = 17.0, 10.5 Hz, 1H), 7.00 (d, J = 35.9 Hz, 1H), 7.21-7.30 (m, 2H), 7.36 (dd, J = 7.2, 3.2 Hz, 1H), 7.39-7.50 (m,

3H), 7.76 (dd, *J* = 14.3, 7.3 Hz, 1H), 8.01 (dd, *J* = 10.1, 7.8 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 123.4 (d, *J* = 5.8 Hz, CH), 126.2 (d, *J* = 9.6 Hz, CH), 128.5 (d, *J* = 12.6 Hz, CH), 129.5 (d, *J* = 11.6 Hz, CH), 130.4 (d, *J* = 10.6 Hz, CH), 130.6 (d, *J* = 7.7 Hz, CH), 131.1 (d, *J* = 9.6 Hz, CH), 132.11 (d, *J* = 78.1 Hz), 132.12 (CH), 132.2 (d, *J* = 11.6 Hz, CH), 132.9 (CH), 135.6 (d, *J* = 90.5 Hz), 137.54 (d, *J* = 15.5 Hz, CH), 137.57 (d, *J* = 6.0 Hz), 138.1 (d, *J* = 77.1 Hz), 142.9 (d, *J* = 27.9 Hz); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ = 31.8. HRMS (EI, 70 eV) *m/z* found: 266.0316 ([M]$^+$), calcd for $C_{16}H_{11}PS$ 266.0319.

Synthesis of dibenzo[*b*,*e*]phosphindolizine-*P*-selenide (1c).

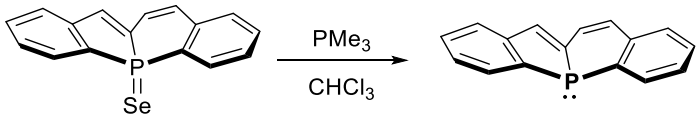


2c **1c** Grubbs 2nd

A solution of **2c** (114 mg, 0.334 mmol) and Grubbs 2nd (22.4 mg, 26.4 μmol) in CH_2Cl_2 (5 mL) was stirred at reflux for 2.5 days. The reaction mixture was filtered through a pad of Celite with $CHCl_3$, and then the volatile of the filtrate was evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane/ethyl acetate = 5/1 (R_f = 0.18) to 3/1, and then purified by GPC (eluent, $CHCl_3$) to give **1c** as yellow solid (13.2 mg, 42.1 μmol, 13%).

Mp. 201-205 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.60 (dd, *J* = 10.5, 3.7 Hz, 1H), 6.80 (dd, *J* = 17.4, 10.5 Hz, 1H), 6.99 (d, *J* = 35.4 Hz, 1H), 7.23 (dd, *J* = 7.4, 5.1 Hz, 1H), 7.26-7.31 (m, 1H), 7.36-7.49 (m, 4H), 7.74 (dd, *J* = 15.1, 6.9 Hz, 1H), 8.01 (dd, *J* = 10.9, 7.2 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 123.2 (d, *J* = 6.8 Hz, CH), 126.3 (d, *J* = 8.7 Hz, CH), 128.5 (d, *J* = 13.5 Hz, CH), 129.5 (d, *J* = 11.5 Hz, CH), 130.64 (d, *J* = 6.8 Hz, CH), 130.72 (d, *J* = 10.6 Hz, CH), 131.1 (d, *J* = 9.6 Hz, CH), 131.5 (d, *J* = 69.4 Hz), 132.1 (d, *J* = 2.8 Hz, CH), 132.2 (d, *J* = 11.6 Hz, CH), 132.8 (d, *J* = 1.9 Hz, CH), 135.8 (d, *J* = 81.0 Hz), 137.0 (d, *J* = 4.8 Hz), 137.36 (d, *J* = 70.3 Hz), 137.41 (d, *J* = 15.4 Hz, CH), 142.8 (d, *J* = 27.0 Hz); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ = 15.1 (d, $^{1}J_{PSe}$ = 719 Hz). HRMS (EI, 70 eV) *m/z* found: 313.9766 ([M]$^+$), calcd for $C_{16}H_{11}P^{80}Se$: 313.9764.

Synthesis of dibenzo[*b*,*e*]phosphindolizine (1d).



1c **1d**

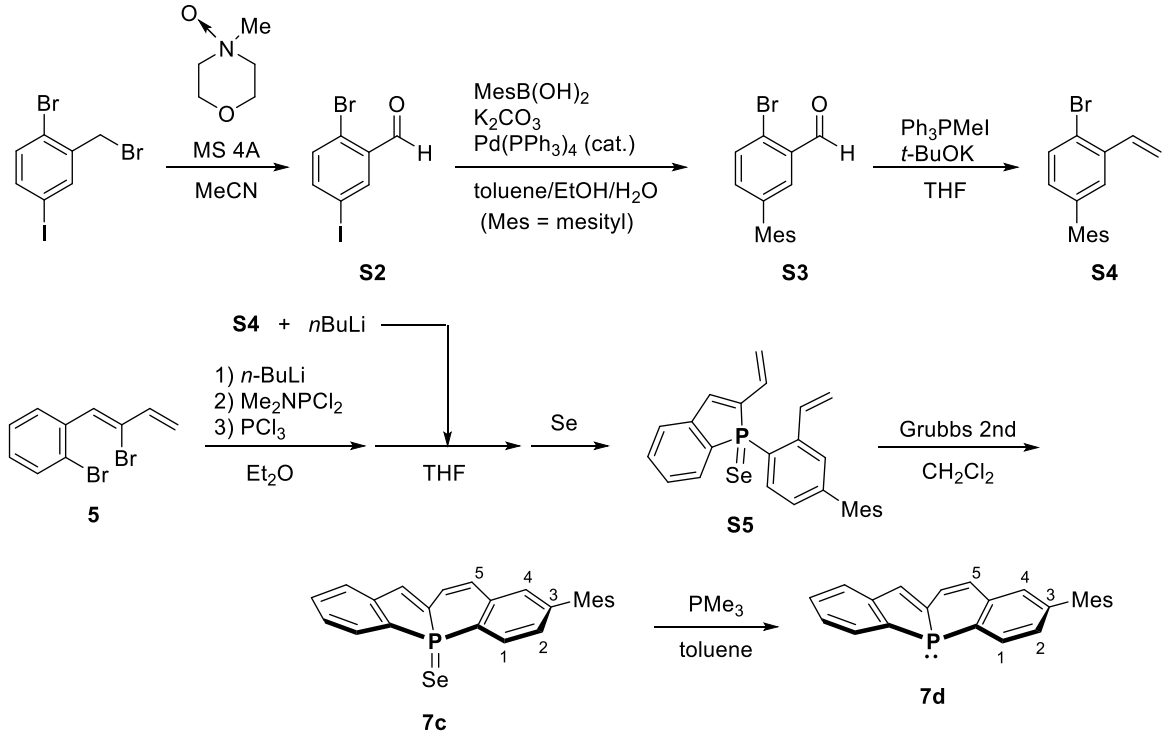
To a solution of **1c** (23.2 mg, 74.1 μmol) in $CHCl_3$ (2.5 mL) was added PMe_3 (22.6 mL, 222 μmol). The volatiles were removed under reduced pressure (~1 mmHg) at 70 ˚C to give **1d** as yellow solid (17.3 mg, 74.1 μmol, 100%).

Mp. 117-118 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.58 (dd, *J* = 10.1, 1.9 Hz, 1H), 6.99 (dd, *J* = 10.1, 10.1 Hz, 1H), 7.01 (d, *J* = 11.0 Hz, 1H), 7.16-7.26 (m, 3H), 7.26-7.32 (m, 1H), 7.43 (ddd, *J* = 7.3, 7.3, 1.4 Hz,

1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.59-7.64 (m, 1H), 8.01 (dd, *J* = 7.4, 5.0 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 124.7 (d, *J* = 2.9 Hz, CH), 125.0 (d, *J* = 9.6 Hz, CH), 125.3 (d, *J* = 15.4 Hz, CH), 127.2 (d, *J* = 5.8 Hz, CH), 127.6 (CH), 128.80 (CH), 128.85 (d, *J* = 15.4 Hz, CH), 130.0 (d, *J* = 18.3 Hz, CH), 130.6 (d, *J* = 2.0 Hz, CH), 131.3 (d, *J* = 15.4 Hz, CH), 132.9 (d, *J* = 3.8 Hz, CH), 134.3 (d, *J* = 21.2 Hz), 135.8 (d, *J* = 7.7 Hz), 139.0 (d, *J* = 12.5 Hz), 146.5 (d, *J* = 7.7 Hz), 147.5 (d, *J* = 2.9 Hz); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ = 3.9. HRMS (EI, 70 eV) *m/z* found: 234.0598 ([M]$^+$), calcd for $C_{16}H_{11}P$: 234.0598.

Synthesis of 3-mestityl-dibenzo[*b*,*e*]phosphindolizine (7d).

Compound **7d** was synthesized by the route shown in Scheme S1.



Scheme S1. Synthesis of 7d.

Synthesis of 2-bromo-5-iodobenzaldehyde (S2)

This compound was prepared according to the synthetic procedures reported by Tovar and co-worker.[S12] To a suspension of 4-methylmorpholine *N*-oxide (9.45 g, 80.7 mmol) and MS 4A (64.6 g) in MeCN (260 mL) was added 1-bromo-2-bromomethyl-4-iodobenzene (9.69 g, 25.8 mmol) at 0 ˚C. The reaction mixture was stirred at 0 ˚C for 4 h, and then was filtered through a pad of Celite. The volatile of the filtrate was evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane/ethyl acetate = 20/1 (R_f = 0.38) to give **S2** as colorless solid (6.34 g, 20.4 mmol, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) 7.39 (d, *J* = 8.3 Hz, 1H), 7.74 (dd, *J* = 8.3, 2.3 Hz, 1H), 8.20 (d, *J* = 2.3 Hz, 1H), 10.25 (s, 1H). The analytical data are agreement with the ones in the literature.[S13]

Synthesis of 4-bromo-2',4',6'-trimethyl[1,1'-biphenyl]-3-carbaldehyde (S3)

A suspension of **S2** (6.34 g, 20.4 mmol), mesitylbononic acid (3.35 g, 20.4 mmol), K_2CO_3 (5.64 g, 40.8 mmol), and $Pd(PPh_3)_4$ (2.36 g, 2.04 mmol) in toluene (140 mL), EtOH (36 mL), and H_2O (18 mL) was stirred at 90 ˚C for 24 h. The organic layer was separated and then the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered through a pad of Celite, and then evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane/AcOEt = 30/1 (R_f = 0.35) to give **S3** as colorless solid (6.40 g, >99%).

Mp. 134-136 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.98 (s, 6H), 2.33 (s, 3H), 6.94 (s, 2H), 7.25 (dd, *J* = 7.9, 2.3 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H) 7.72 (d, *J* = 2.3 Hz, 1H), 10.41 (s, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 20.9, 21.7, 125.4, 128.5, 130.9, 133.6, 134.1, 135.7, 136.5, 136.7, 137.6, 141.4, 192.0. HRMS (EI, 70 eV) *m/z* found: 302.0305 ([M]$^+$), calcd for $C_{16}H_{15}O^{79}Br$: 302.0306.

Synthesis of 4-bromo-2',4',6'-trimethyl-3-vinyl-1,1'-biphenyl (S4)

To a suspension of Ph_3PMeI (10.98 g, 27.2 mmol) in THF (170 mL) was added *t*-BuOK (3.52 g, 31.4 mmol). To this suspension, a solution of **S3** (6.34 g, 20.2 mmol) in THF (10 mL). After the reaction mixture was stirred at room temperature for 75 min, hexane (100 mL) was added. The mixture was filtered through a pad of Celite and silica gel. The solvent of the filtrate was removed under reduced pressure. The residue was chromatographed on silica gel with hexane (R_f = 0.40) to give **S4** as colorless solid (4.00 g, 13.3 mmol, 65% from **S2**).

Mp. 100-102 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.01 (s, 6H), 2.33 (s, 3H), 5.35 (dd, *J* = 11.0, 0.9 Hz, 1H), 5.66 (dd, *J* = 17.5, 0.9 Hz, 1H), 6.91 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.95 (s, 2H), 7.09 (dd, *J* = 17.5, 11.0 Hz, 1H), 7.34 (d, *J* = 1.8 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 20.9, 21.2, 116.8, 122.0, 127.8, 128.3, 130.4, 133.1, 135.9, 136.0, 137.2, 137.5, 137.8, 140.6. HRMS (EI, 70 eV) *m/z* found: 300.0513 ([M]$^+$), calcd for $C_{17}H_{17}{}^{79}Br$: 300.0514.

Synthesis of 1-(2',4',6'-trimethyl-3-vinyl[1,1'-biphenyl]-4-yl)-2-vinyl-benzo[*b*]phosphole-*P*-selenide (S5).

This compound was synthesized according to the method for the synthesis of **2c** by using **S4** instead of 1-bromo-2-vinylbenzene. 4-Lithio-2',4',6'-trimethyl-3-vinyl-1,1'-biphenyl was prepared from **S4** (1.74 g, 5.76 mmol) and *n*-BuLi in hexane (1.56 M; 3.9 mL, 6.1 mmol) in THF (25 mL) at −78 ˚C for 60 min. The crude mixture was purified by column chromatography on silica gel with hexane/ethyl acetate = 10/1 (R_f = 0.30). Yield of **S5**. 807 mg (1.76 mmol, 34%) from 1.51 g (5.24 mmol) of **5** and 1.74 g (5.76 mmol) of **S4**.

Mp. 59-60 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.96 (s, 3H), 2.01 (s, 3H), 2.33 (s, 3H), 5.00 (d, *J* = 11.0, 1H), 5.34 (d, *J* = 17.0 Hz, 1H), 5.36 (d, *J* = 11.1 Hz, 1H), 5.61 (d, *J* = 17.4 Hz, 1H), 6.64 (ddd, *J* = 23.4, 17.4, 11.0 Hz, 1H), 6.77 (dd, *J* = 17.0, 11.1 Hz, 1H), 6.95 (s, 2H), 7.16 (d, *J* = 34.4 Hz, 1H), 7.21 (d, *J* = 3.7 Hz, 1H), 7.26-7.29 (m, 1H), 7.33-7.38 (m, 1H), 7.44-7.50 (m, 2H), 7.67 (dd, *J* = 10.5, 7.4 Hz, 1H), 8,69 (dd, *J* = 18.4, 8.2 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 20.8 (CH_3), 20.9 (CH_3), 21.2 (CH_3), 118.0 (CH_2), 121.4 (d, *J* = 63.5 Hz), 121.5 (d, *J* = 6.7 Hz, CH_2), 125.4 (d, *J* = 8.6 Hz, CH), 128.4 (CH), 128.5 (d, *J* = 9.6 Hz, CH), 128.9 (d, *J* = 8.7 Hz, CH), 129.0 (d, *J* = 8.7 Hz, CH), 129.3 (d, *J* = 2.9 Hz, CH),

129.4 (CH), 132.4 (CH), 134.3 (d, J = 4.8 Hz, CH), 135.7 (d, J = 4.8 Hz), 136.9 (d, J = 50.1 Hz), 137.1 (d, J = 18.3 Hz, CH), 137.2 (d, J = 16.4 Hz, CH), 137.4, 137.5 (d, J = 4.8 Hz), 140.1 (d, J = 72.1 Hz), 141.7 (d, J = 2.9 Hz), 141.9 (d, J = 19.3 Hz), 146.2 (d, J = 2.9 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ = 29.7 (d, $^{1}J_{PSe}$ = 724 Hz). HRMS (EI, 70 eV) *m/z* found: 460.0865 ([M]$^+$), calcd for $C_{27}H_{25}P^{80}Se$: 460.0859.

Synthesis of 3-mesityl-dibenzo[*b*,*e*]phosphindolizine-*P*-selenide (7c).

A solution of **S5** (37.9 mg, 82.5 μmol) and Grubbs 2nd (5.6 mg, 6.6 μmol) in THF (1.8 mL) was stirred at 50 ˚C for 61 h. The reaction mixture was filtered through a pad of Celite with $CHCl_3$ and then the volatile of the filtrate was evaporated under reduced pressure. The residue was separated by preparative TLC (silica gel) with hexane/ethyl acetate = 5/1 (R_f = 0.25), and then purified by GPC (eluent, $CHCl_3$), followed by washing with hexane to give **7c** as yellow solid (5.3 mg, 12 μmol, 15%).

Mp. 222-223 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.90 (s, 3H), 2.05 (s, 3H), 2.32 (s, 3H), 6.58 (dd, J = 10.1, 3.7 Hz, 1H), 6.83 (dd, J = 17.5, 10.5 Hz, 1H), 6.90 (s, 1H), 6.95 (s, 1H), 7.025 (d, J = 35.8 Hz, 1H), 7.028 (d, J = 4.6 Hz, 1H), 7.08-7.11 (m, 1H), 7.39-7.52 (m, 3H), 7.80 (dd, J = 14.5, 7.5 Hz, 1H), 8.05 (dd, J = 10.3, 7.1 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 20.8 (CH_3), 21.0 (CH_3), 21.2 (CH_3), 123.4 (d, J = 5.8 Hz, CH), 126.4 (d, J = 8.7 Hz, CH), 128.3 (CH), 128.5 (CH), 129.3 (d, J = 68.4 Hz), 129.5 (d, J = 10.6 Hz, CH), 129.6 (d, J = 12.5 Hz, CH), 130.7 (d, J = 10.6 Hz, CH), 130.9 (d, J = 7.7 Hz, CH), 132.1 (d, J = 9.7 Hz, CH), 132.3 (d, J = 11.6 Hz, CH), 132.8 (CH), 135.7, 135.9, 136.1 (d, J = 82.8 Hz), 137.2 (d, J = 5.8 Hz), 137.3, 137.44 (d, J = 14.5 Hz, CH), 137.49, 137.58 (d, J = 72.2 Hz), 142.8 (d, J = 26.9 Hz), 145.5 (d, J = 2.9 Hz); ; ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ = 15.1 (d, $^{1}J_{PSe}$ = 719 Hz). HRMS (EI, 70 eV) *m/z* found: 432.0542 ([M+H]$^+$), calcd for $C_{25}H_{21}P^{80}Se$: 432.0546.

Synthesis of 3-mesityl-dibenzo[*b*,*e*]phosphindolizine (7d).

To a solution of **7c** (16.9 mg, 39.2 μmol) in $CHCl_3$ (2.5 mL) was added PMe_3 (12.0 μL, 118 μmol). The volatiles were removed under reduced pressure (~1 mmHg) at 90 ˚C to give **7d** as yellow solid (13.4 mg, 38.0 μmol, 97%).

Mp. 70-71 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.89 (s, 3H), 2.07 (s, 3H), 2.32 (s, 3H), 6.58 (d, J = 10.1 Hz, 1H), 6.91 (br s, 1H), 6.95 (br s, 1H), 6.98-7.07 (m, 4H), 7.31 (dd, J = 6.9, 6.4 Hz, 1H), 7.45 (dd, J = 7.8, 7.8 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.68 (dd, J = 7.8, 7.8 Hz, 1H), 8.05 (dd, J = 6.0, 6.0 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 124.8 (d, J = 1.9 Hz, CH), 125.0 (d, J = 9.7 Hz, CH), 125.4 (d, J = 15.4 Hz, CH), 128.26 (CH), 128.31 (d, J = 8.7 Hz, CH), 128.8 (CH), 129.0 (d, J = 15.4 Hz, CH), 130.0 (d, J = 18.3 Hz, CH), 131.2 (d, J = 16.4 Hz, CH), 131.5 (d, J = 1.9 Hz, CH), 132.2 (d, J = 21.2 Hz), 133.1 (d, J = 2.9 Hz, CH), 135.9 (d, J = 7.7 Hz), 136.1 (br), 136.2 (br), 137.0, 138.3, 139.2 (d, J = 13.5 Hz), 140.8, 146.5 (d, J = 8.7 Hz), 147.7 (d, J = 2.0 Hz); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ = 4.1. HRMS (EI, 70 eV) *m/z* found: 352.1377 ([M]$^+$), calcd for $C_{25}H_{21}P$: 352.1381.

2. Spectral Data

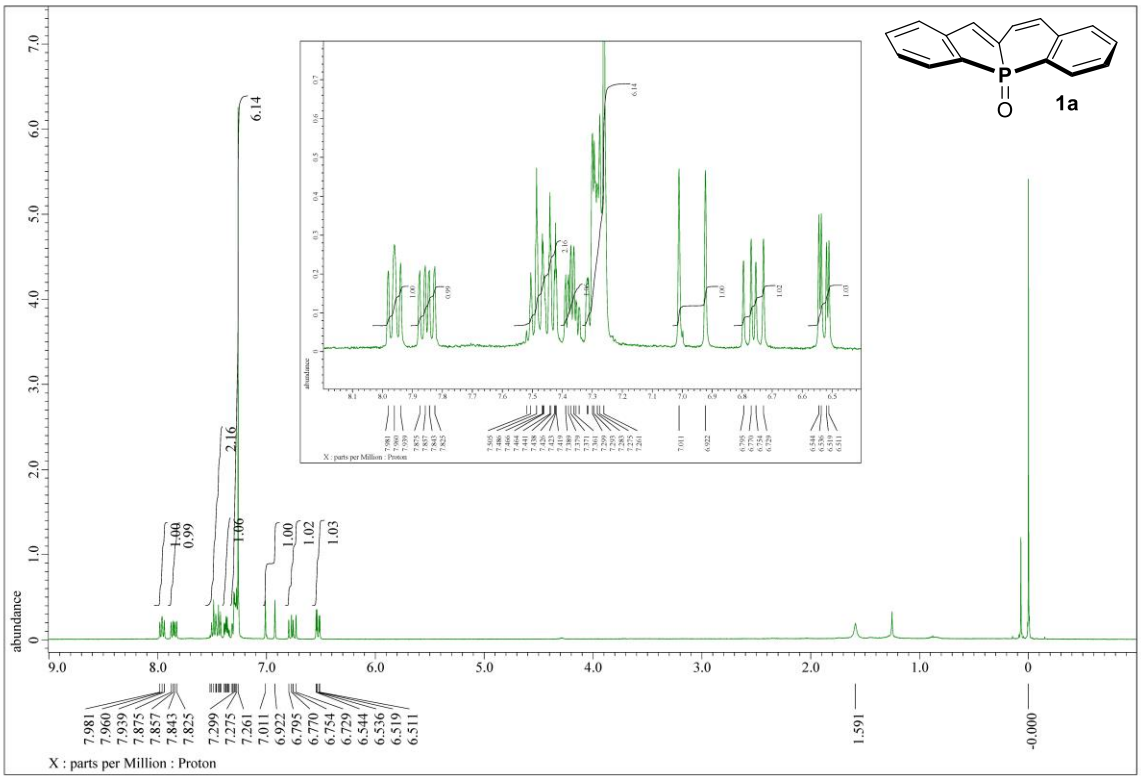


Figure S1. ^{1}H NMR Spectrum of 1a.

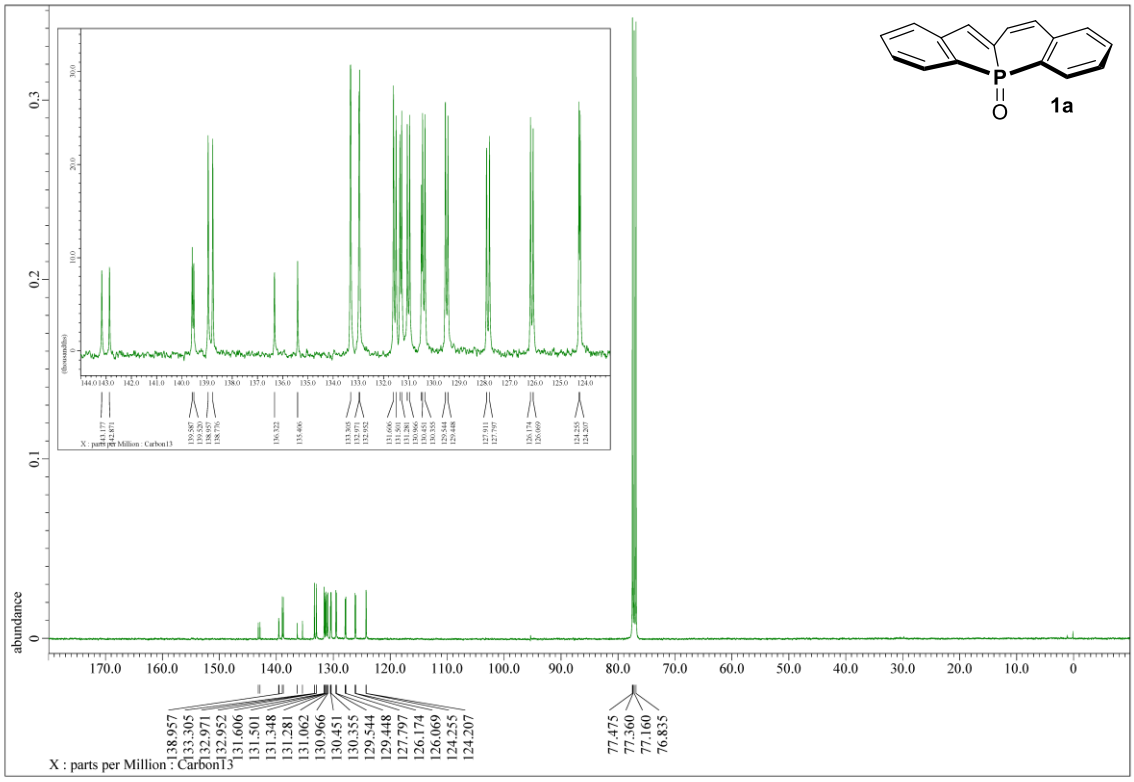


Figure S2. ^{13}C NMR Spectrum of 1a.

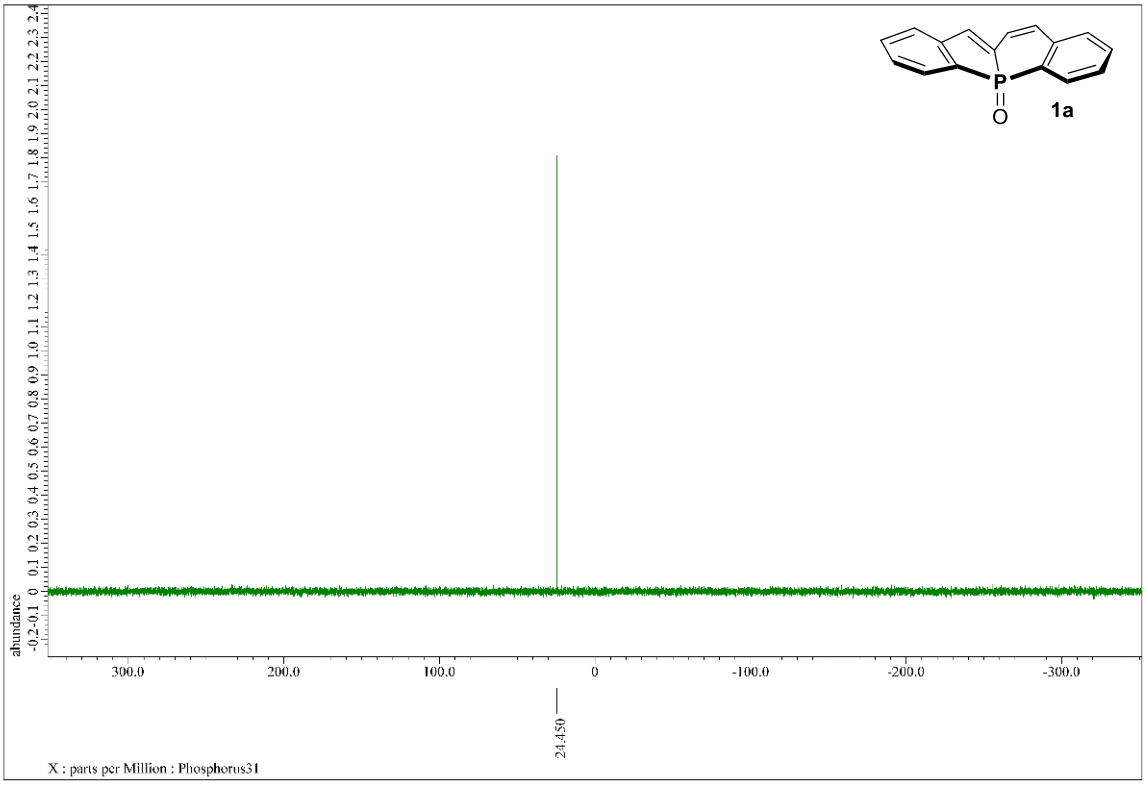


Figure S3. ^{31}P NMR Spectrum of 1a.

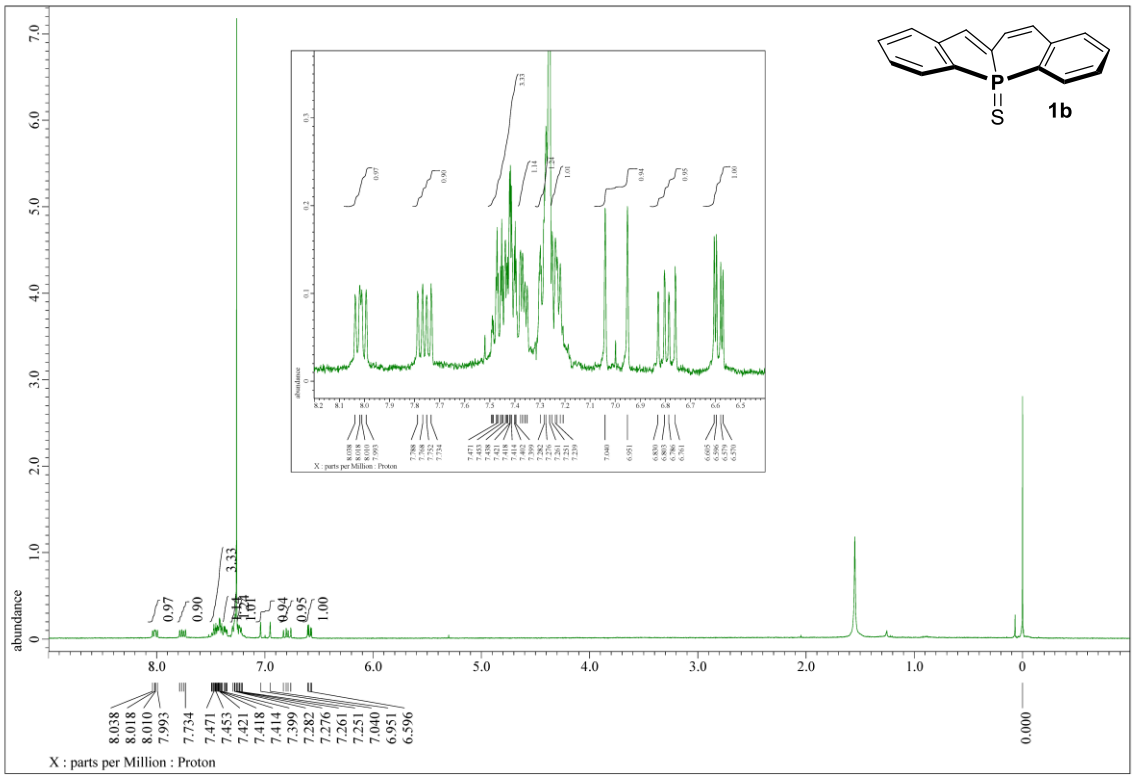


Figure S4. ^{1}H NMR Spectrum of 1b.

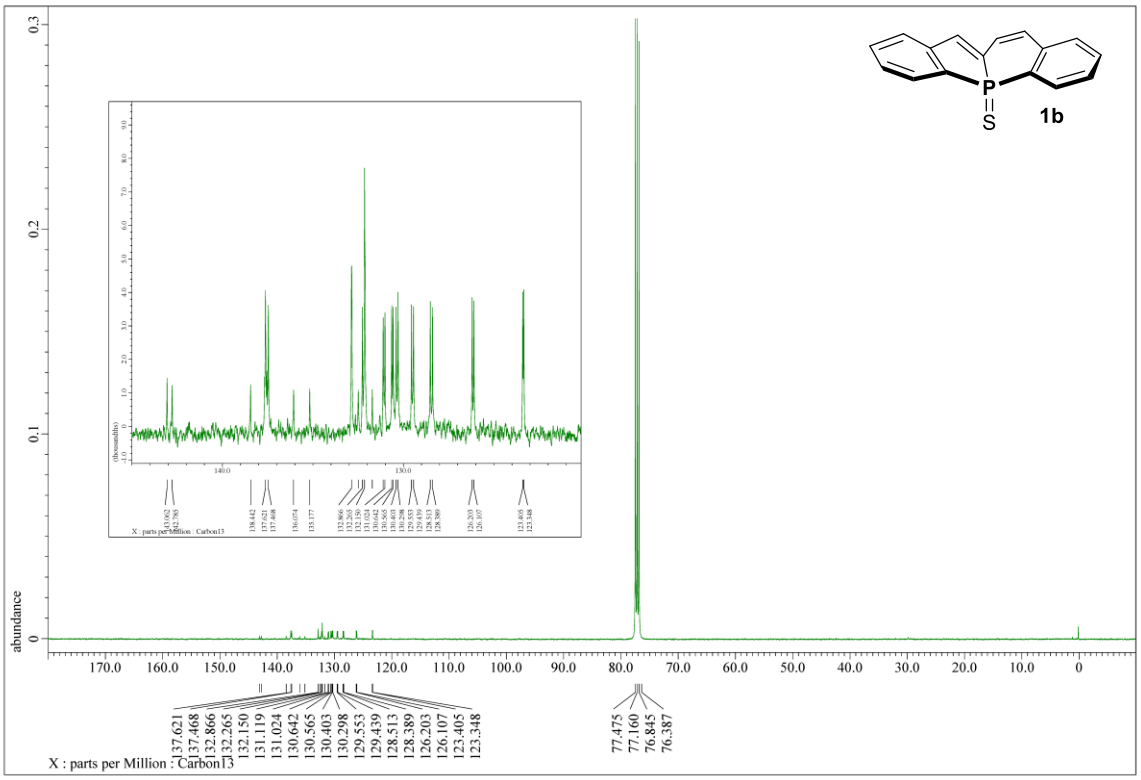


Figure S5. ^{13}C NMR Spectrum of 1b.

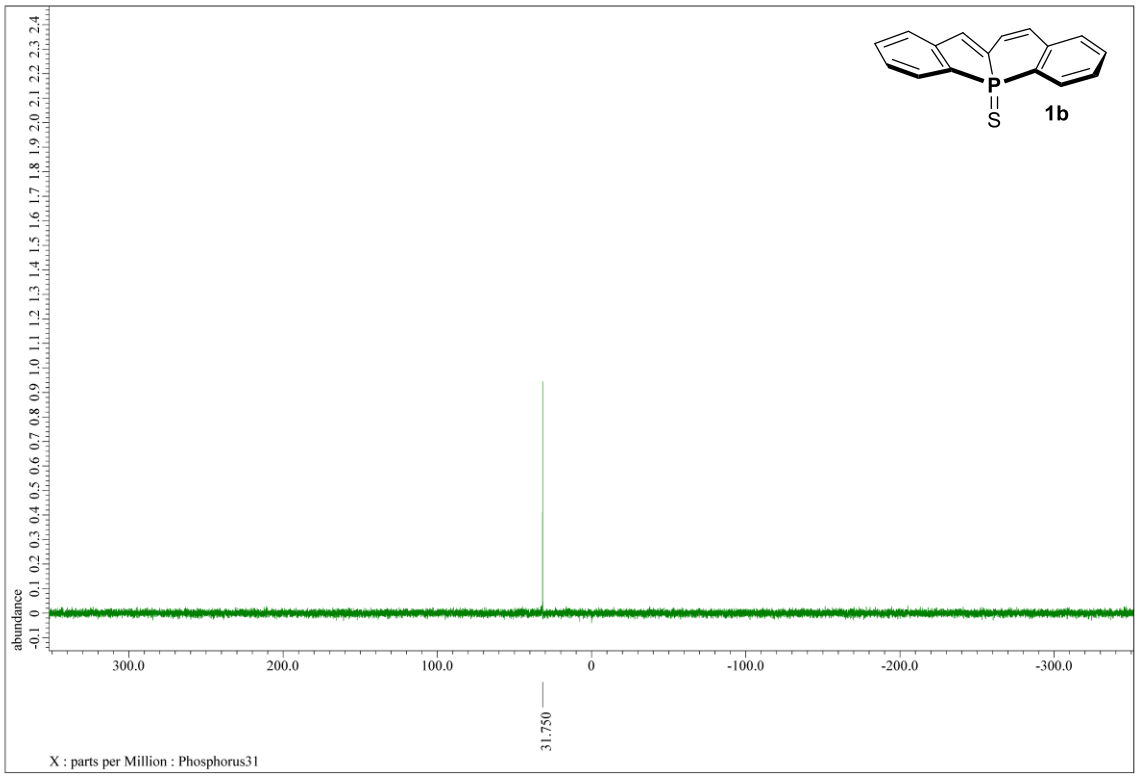


Figure S6. ^{31}P NMR Spectrum of 1b.

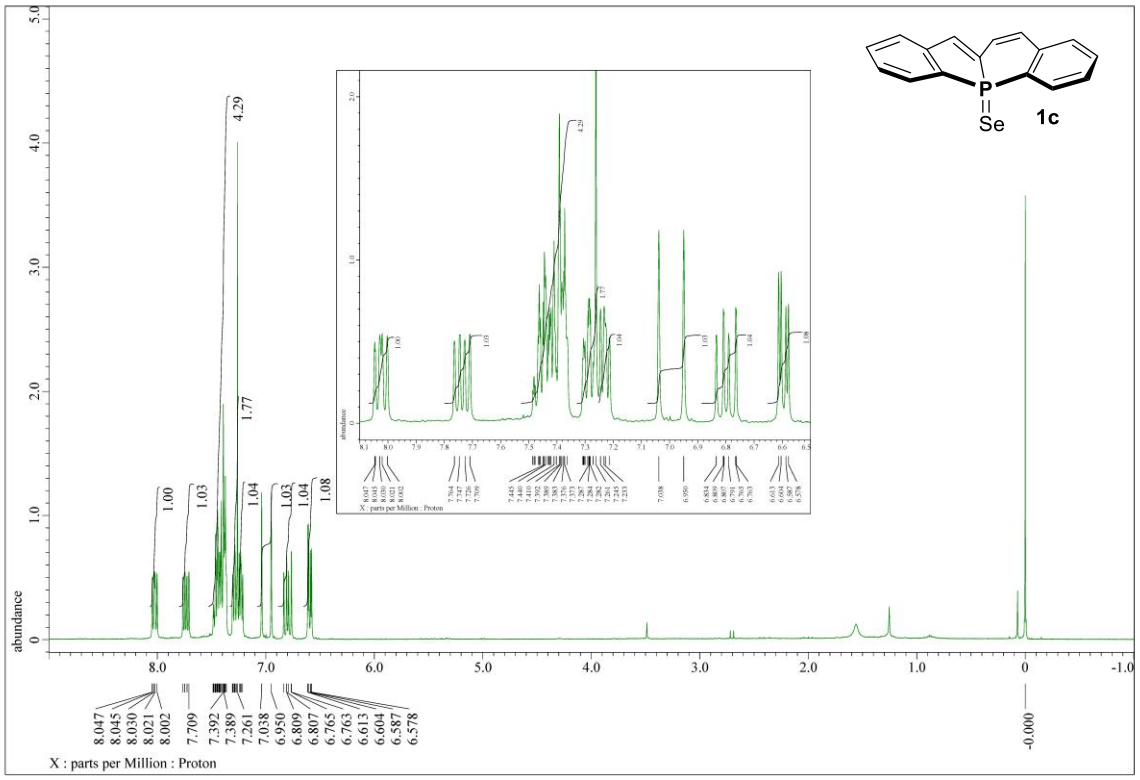


Figure S7. ^{1}H NMR Spectrum of 1c.

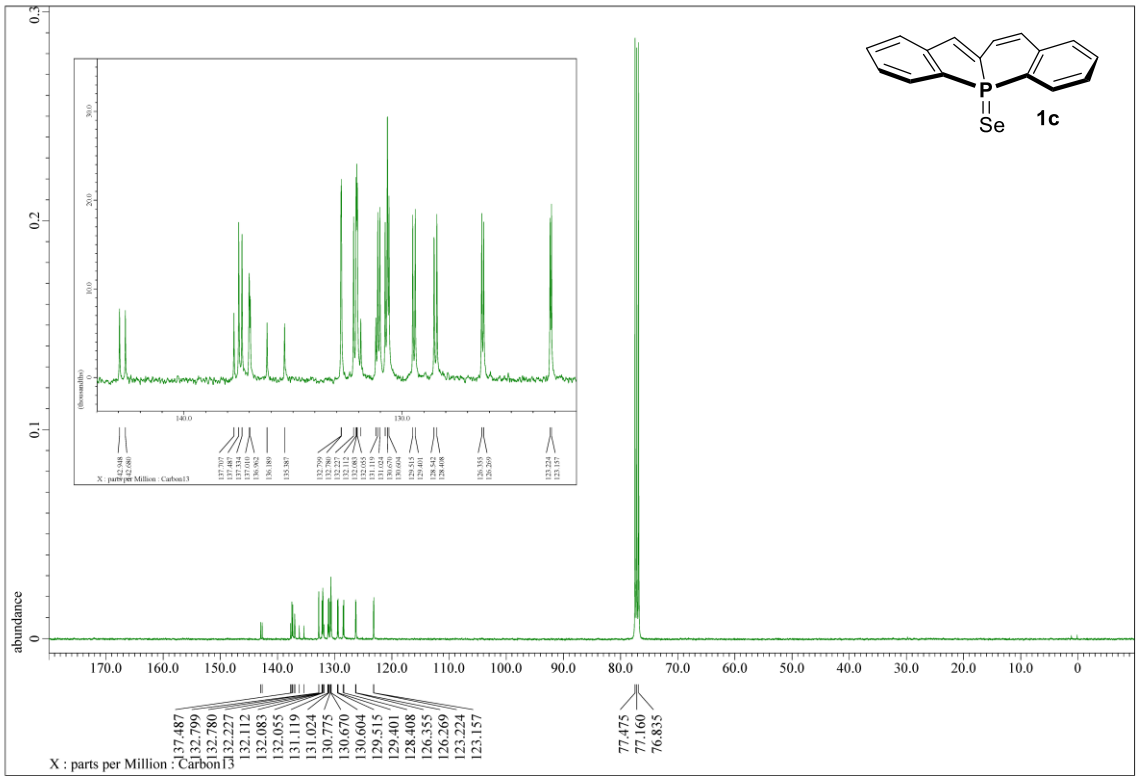


Figure S8. ^{13}C NMR Spectrum of 1c.

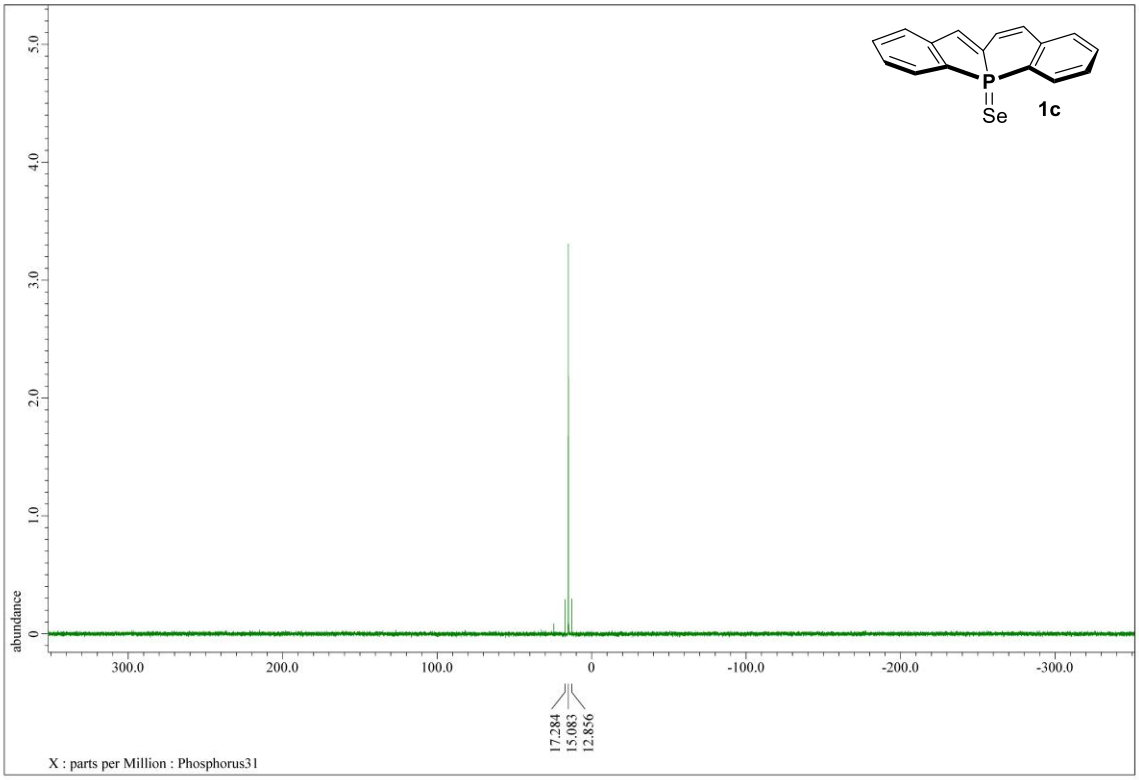


Figure S9. ^{31}P NMR Spectrum of 1c.

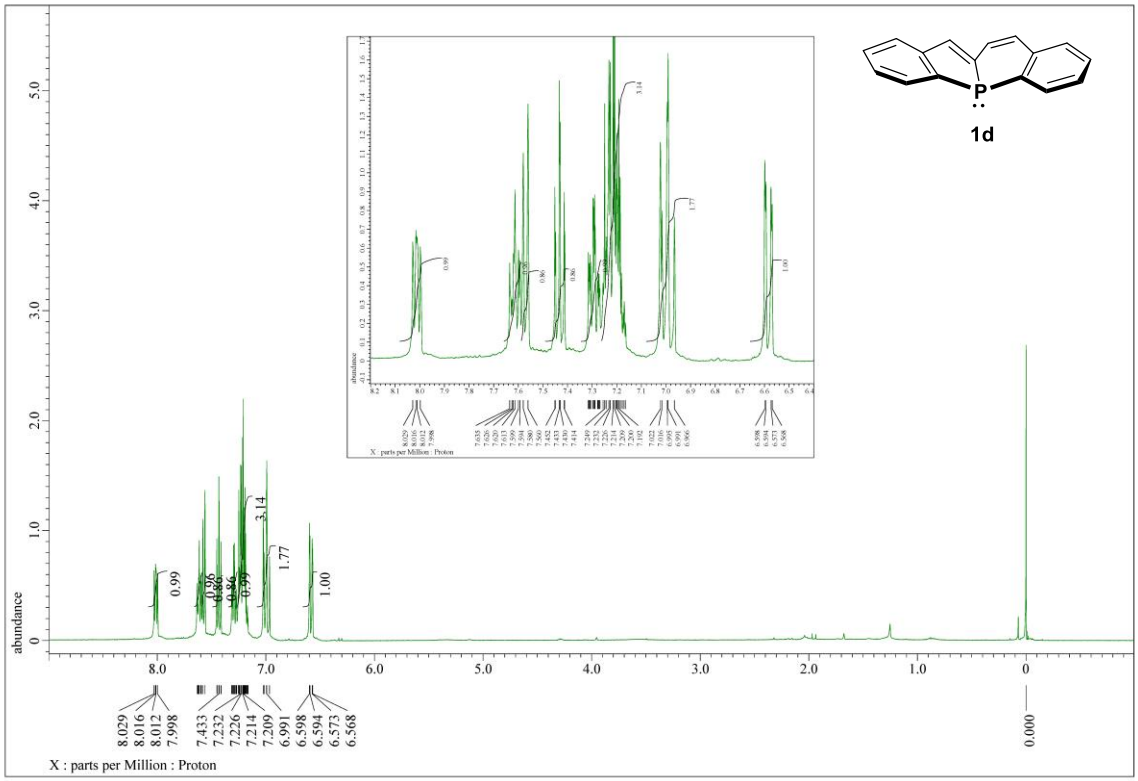


Figure S10. ^{1}H NMR Spectrum of 1d.

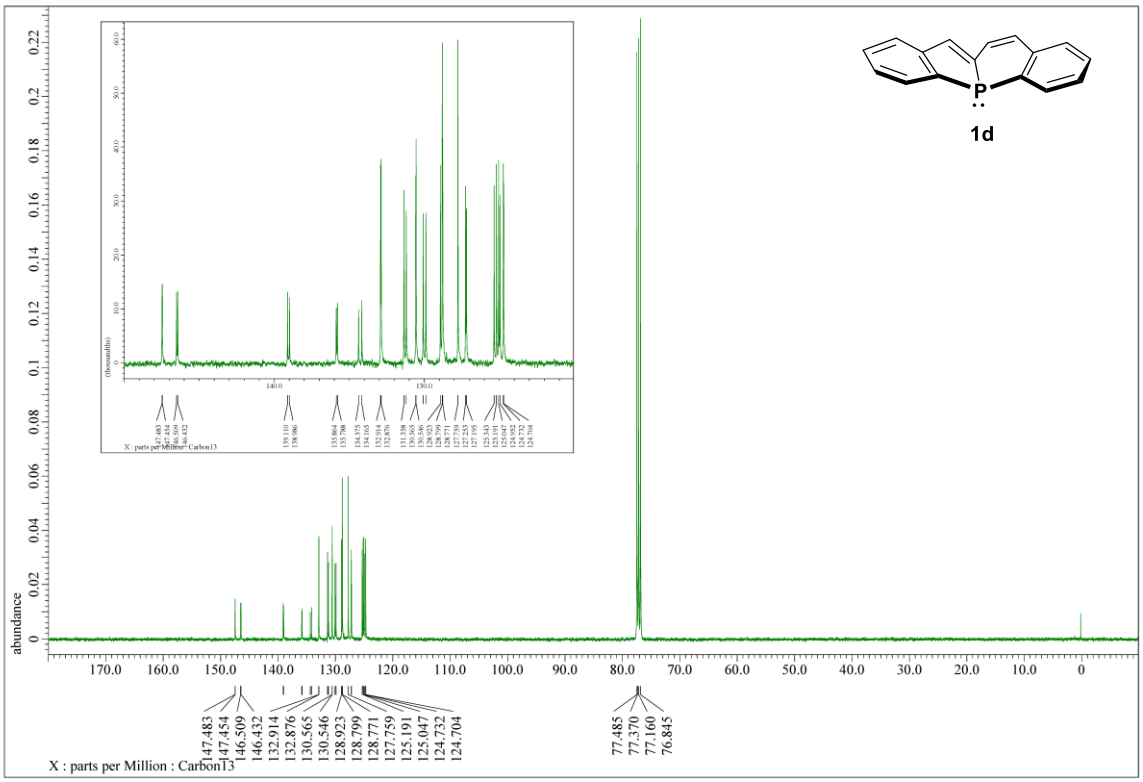


Figure S11. ^{13}C NMR Spectrum of 1d.

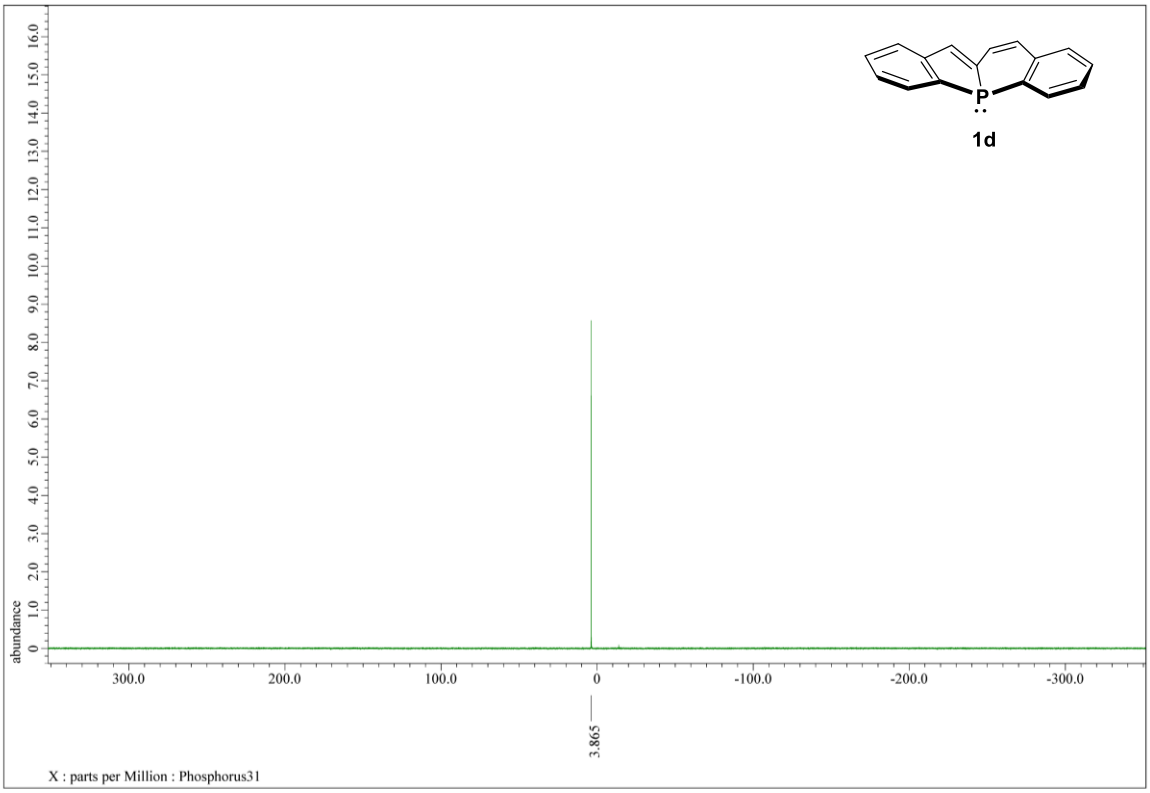


Figure S12. ^{31}P NMR Spectrum of 1d.

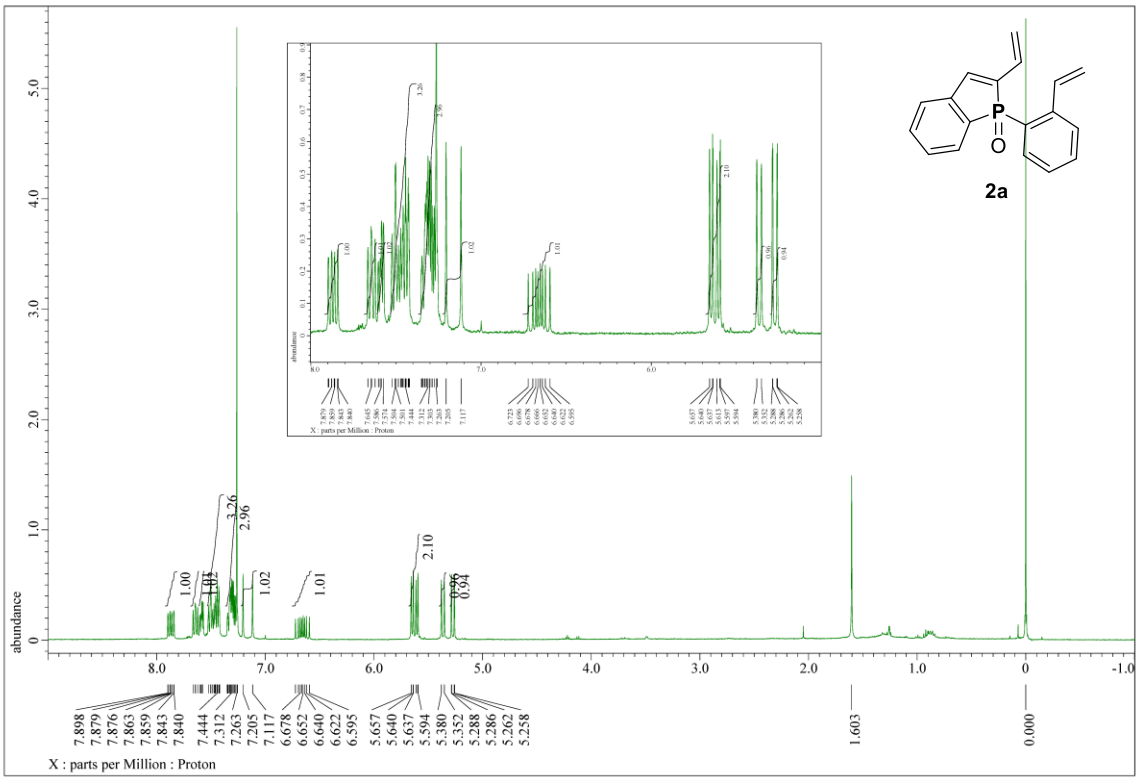


Figure S13. ^{1}H NMR Spectrum of 2a.

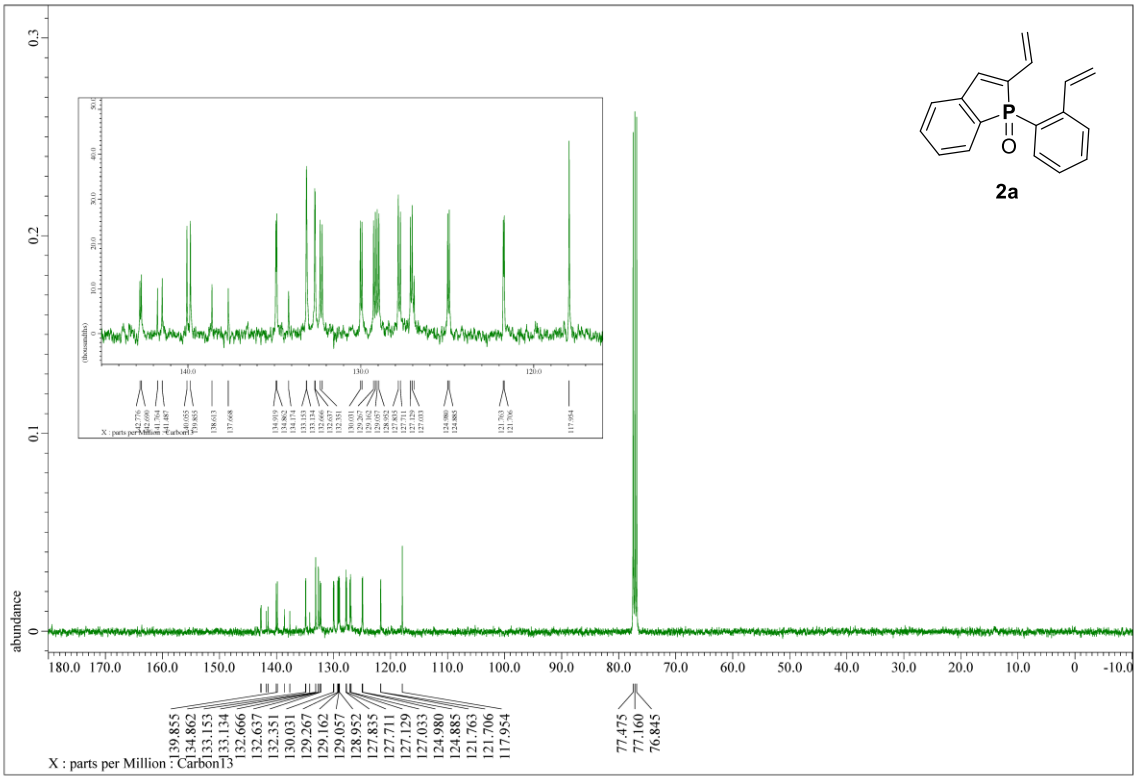


Figure S14. ^{13}C NMR Spectrum of 2a.

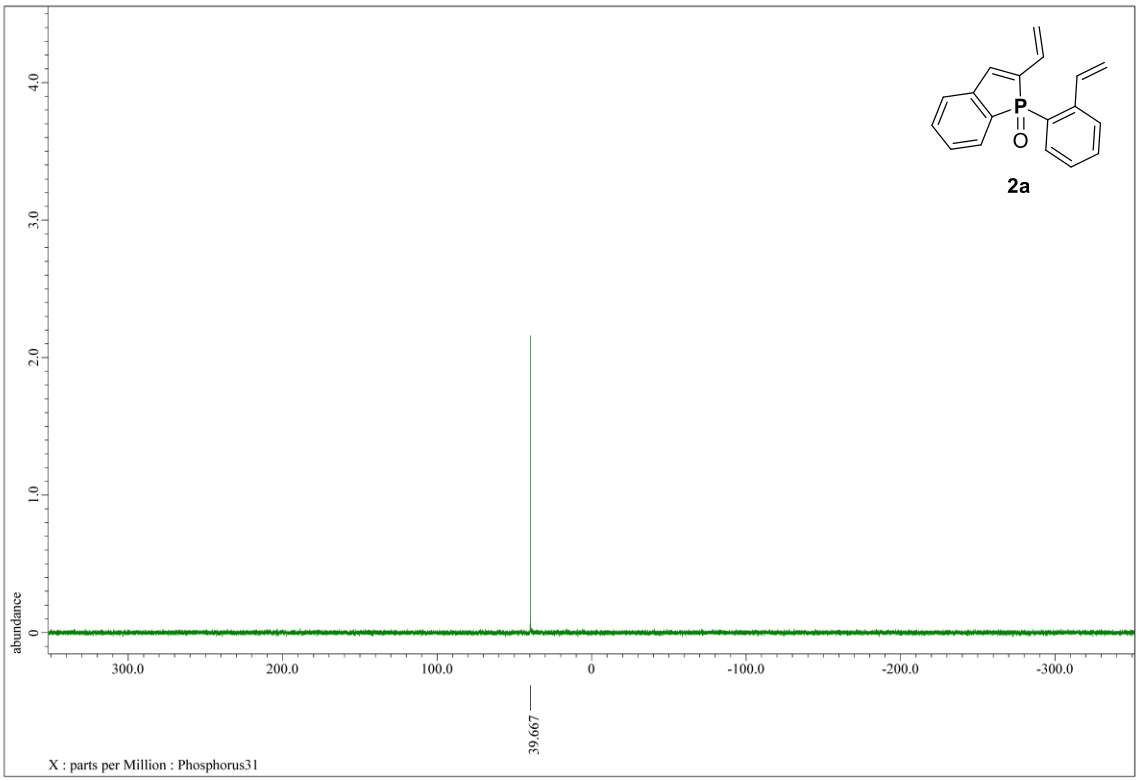


Figure S15. ^{31}P NMR Spectrum of 2a.

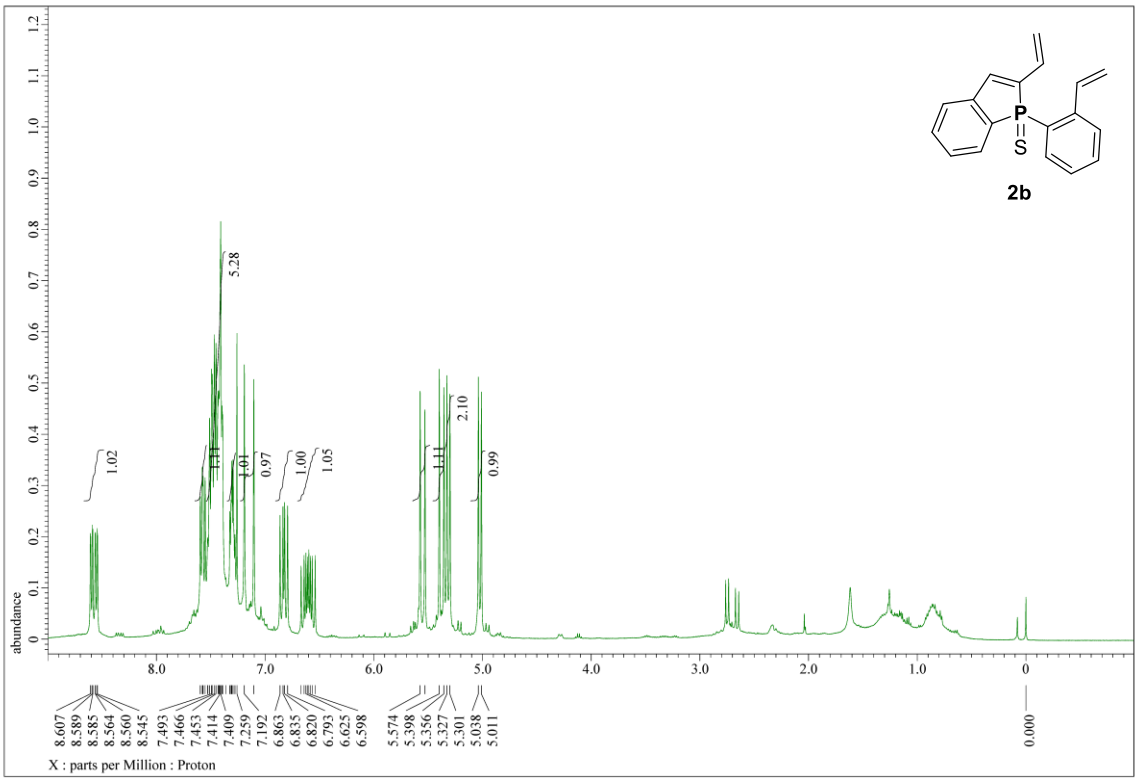


Figure S16. ^{1}H NMR Spectrum of 2b.

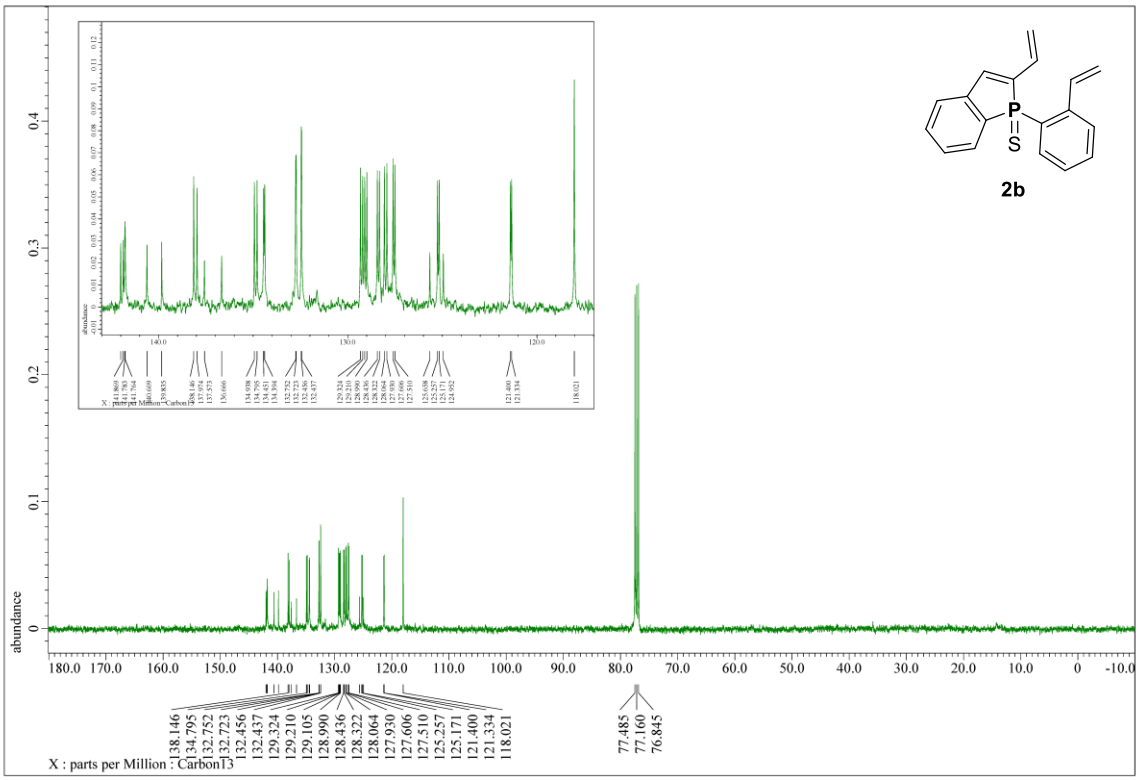


Figure S17. ^{13}C NMR Spectrum of 2b.

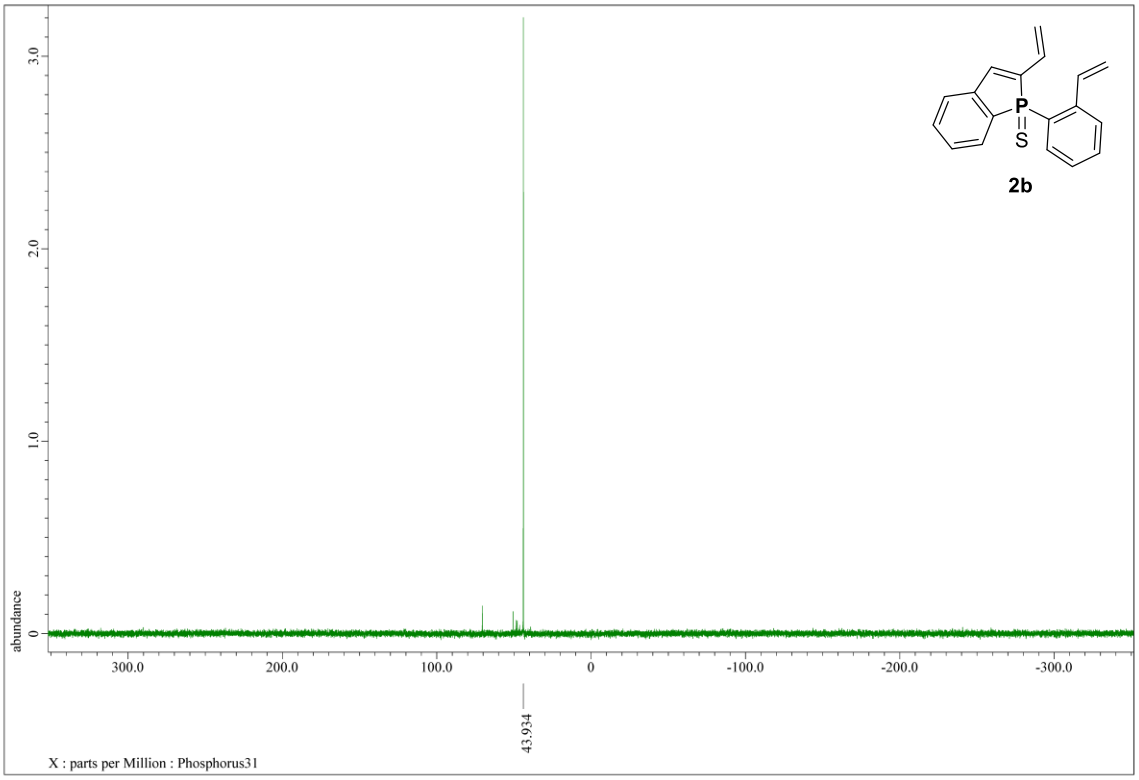


Figure S18. ^{31}P NMR Spectrum of 2b.

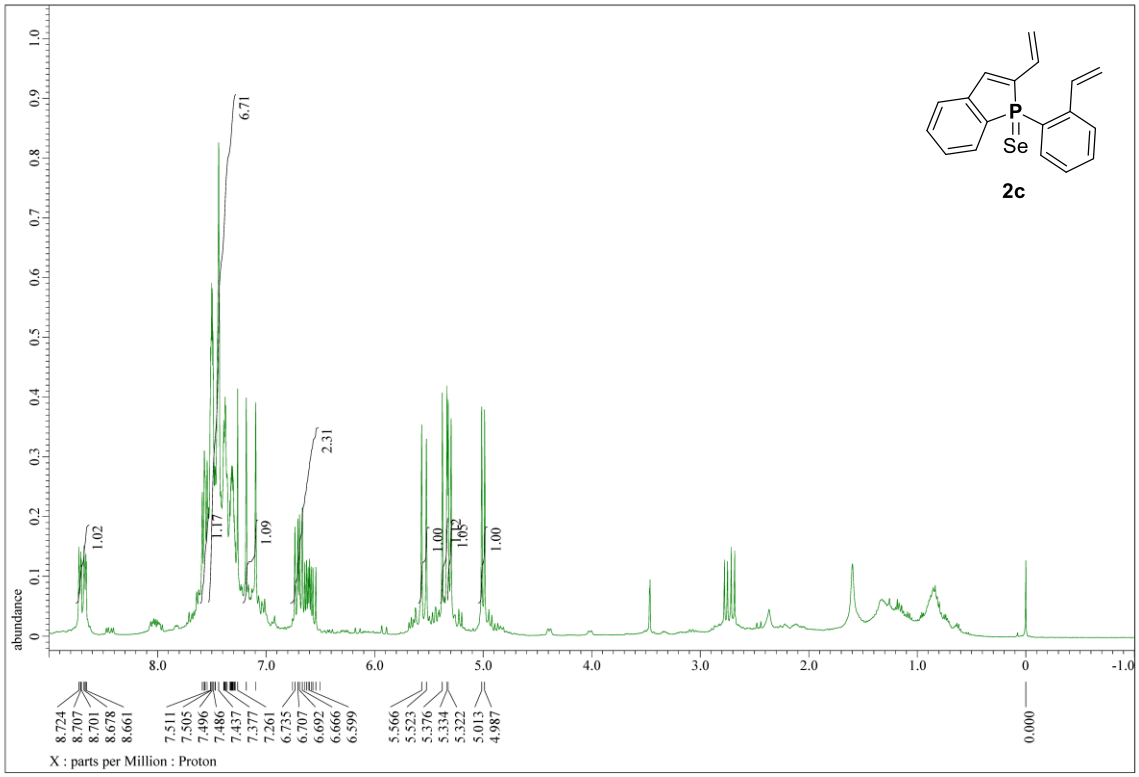


Figure S19. ^{1}H NMR Spectrum of 2c.

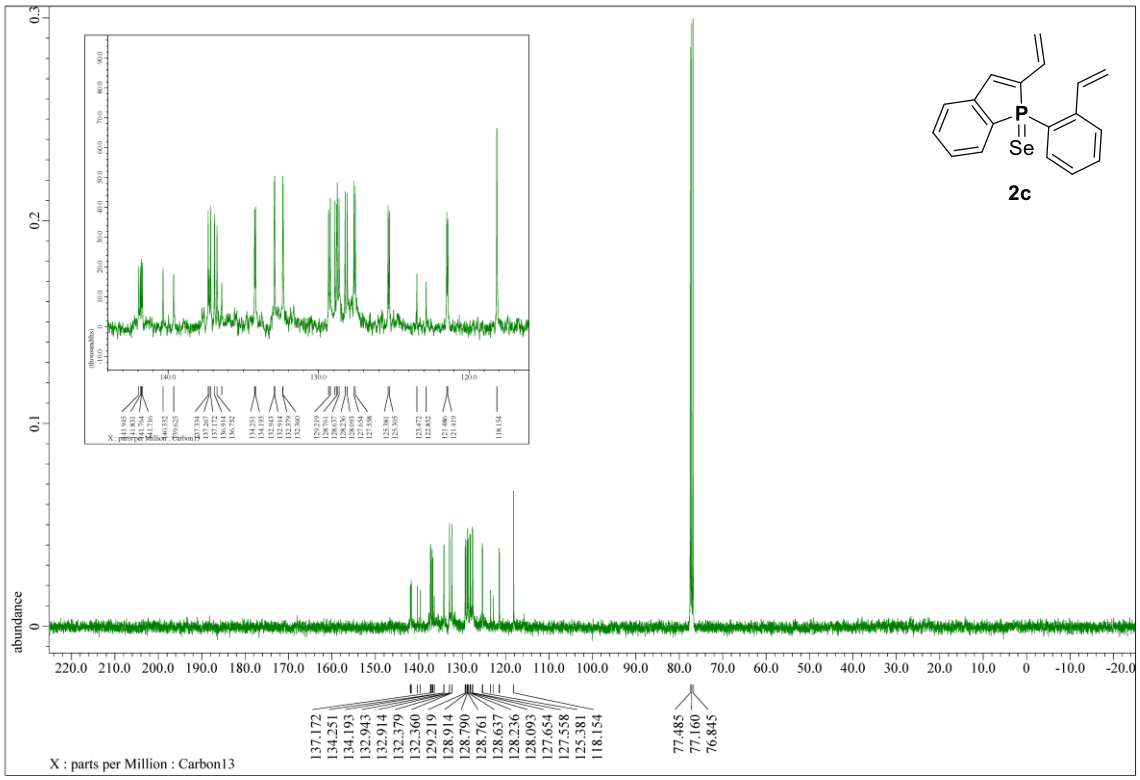


Figure S20. ^{13}C NMR Spectrum of 2c.

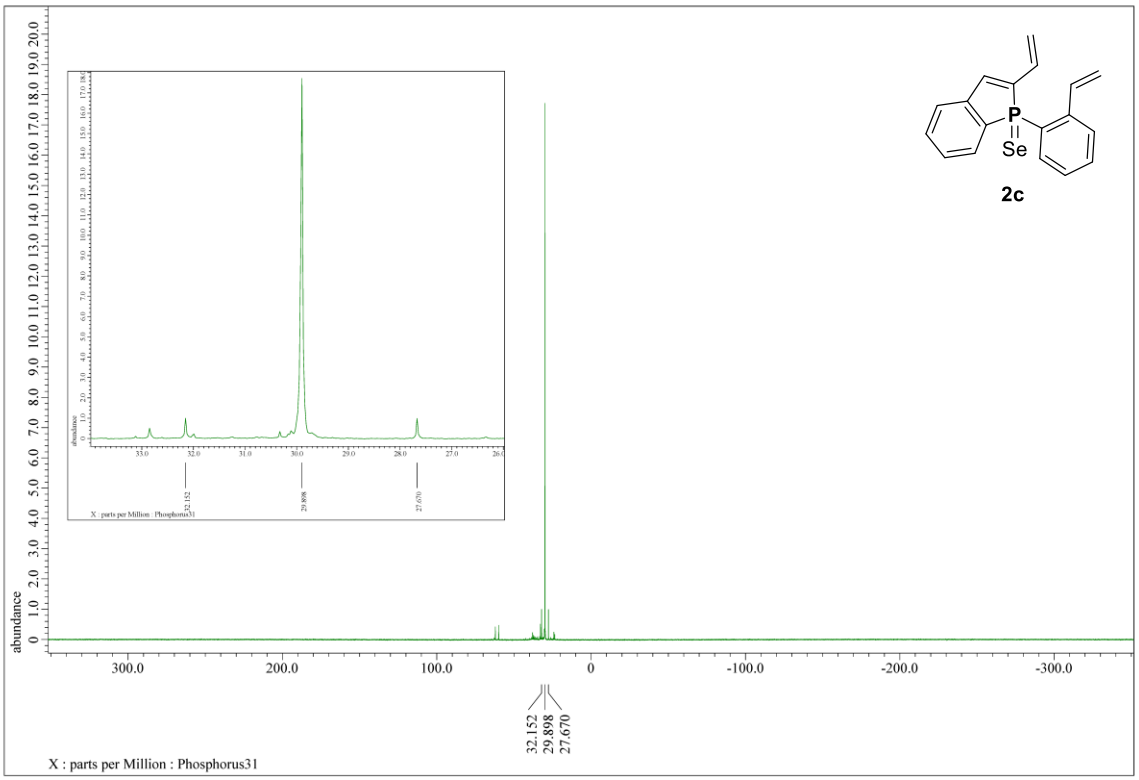


Figure S21. ^{31}P NMR Spectrum of 2c.

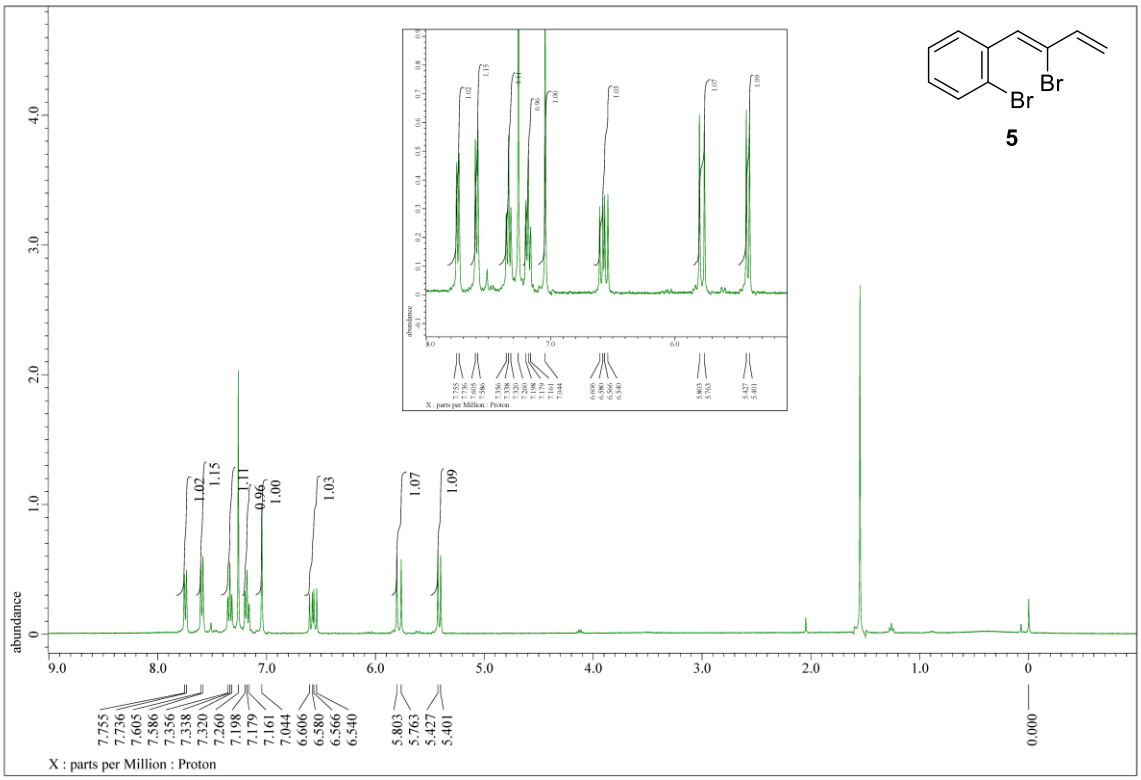


Figure S22. ^{1}H NMR Spectrum of 5.

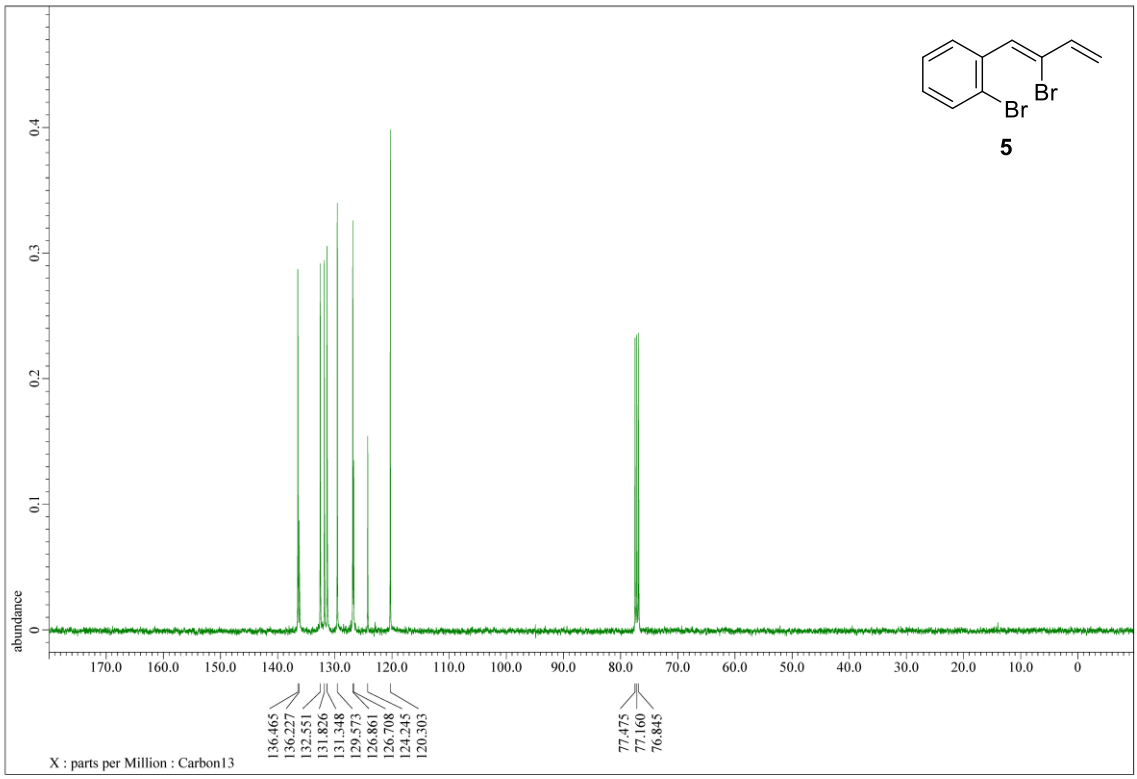


Figure S23. ^{13}C NMR Spectrum of 5.

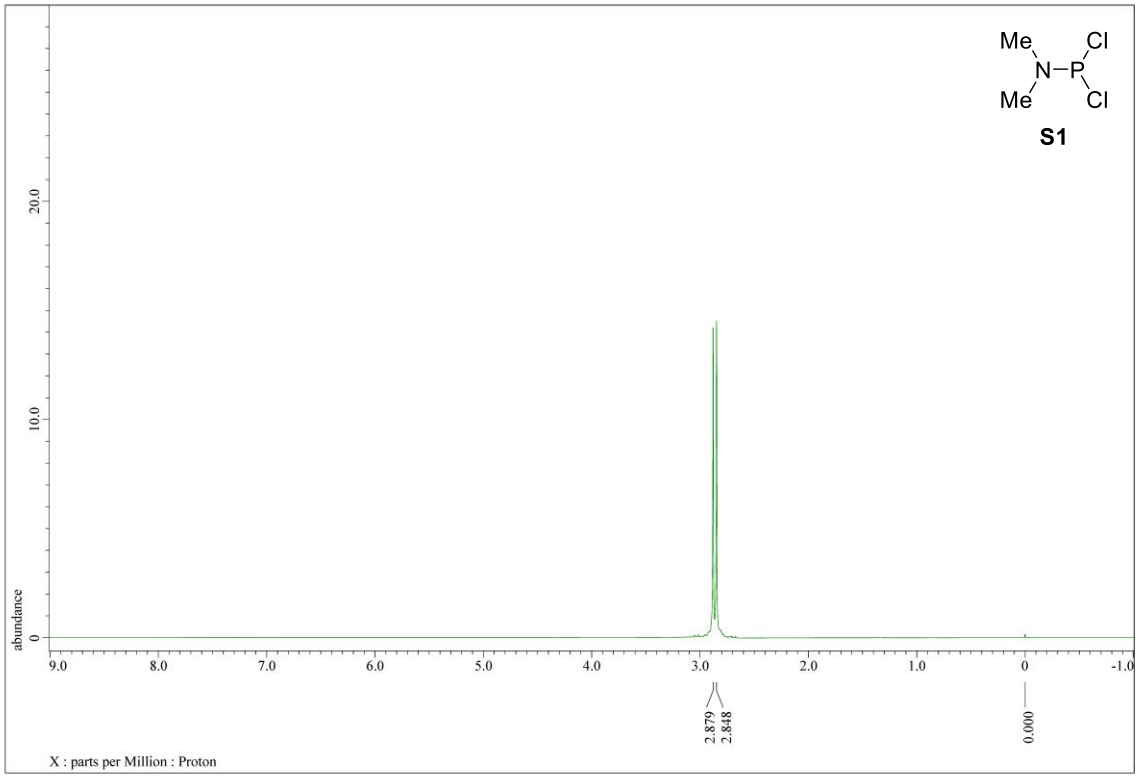


Figure S24. ^{1}H NMR Spectrum of S1.

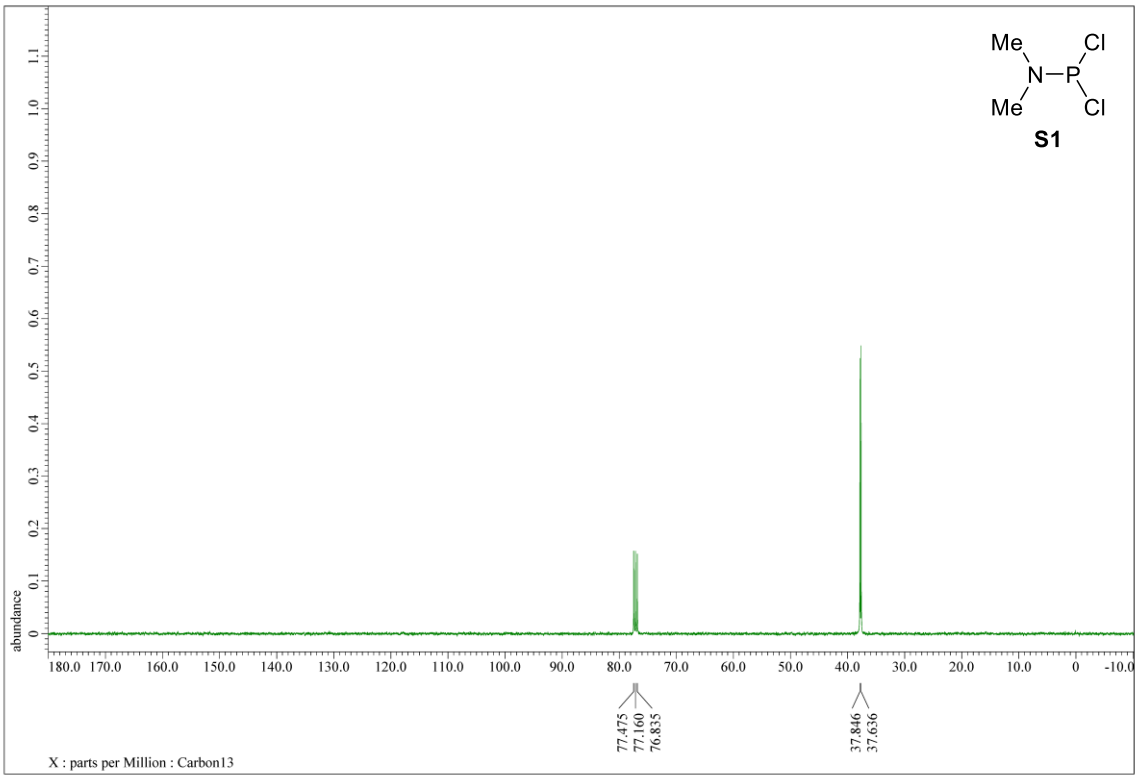


Figure S25. ^{13}C NMR Spectrum of S1.

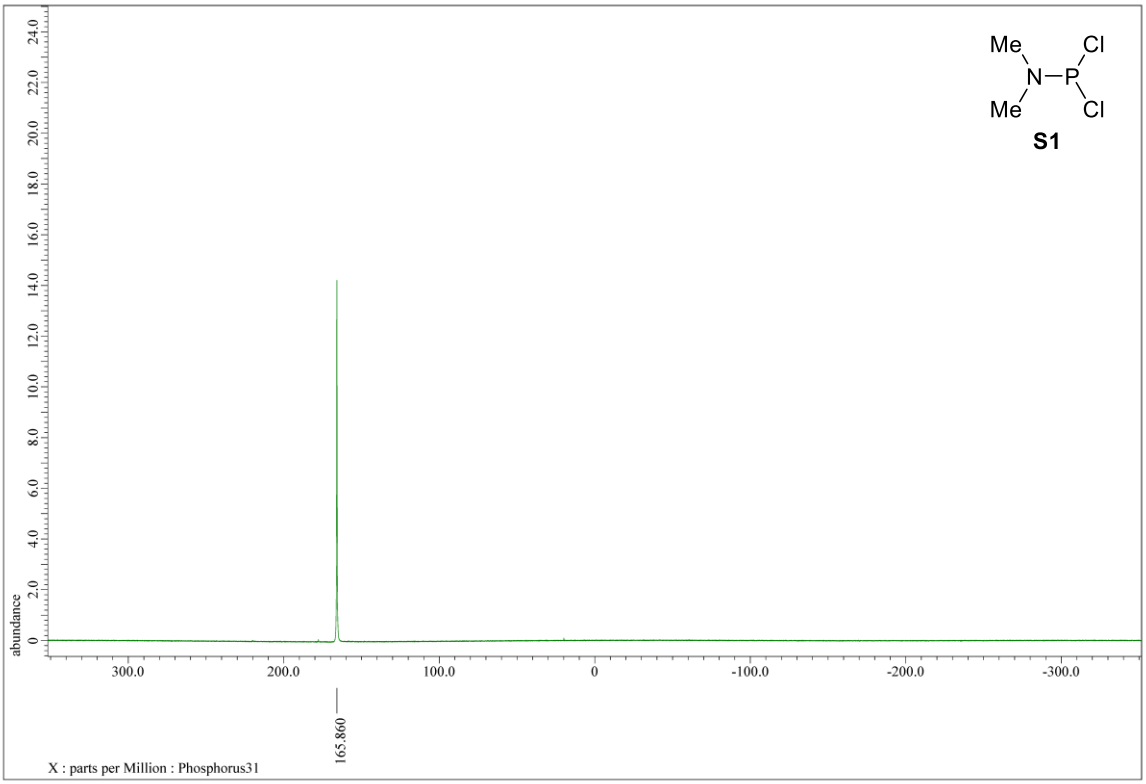


Figure S26. ^{31}P NMR Spectrum of S1.

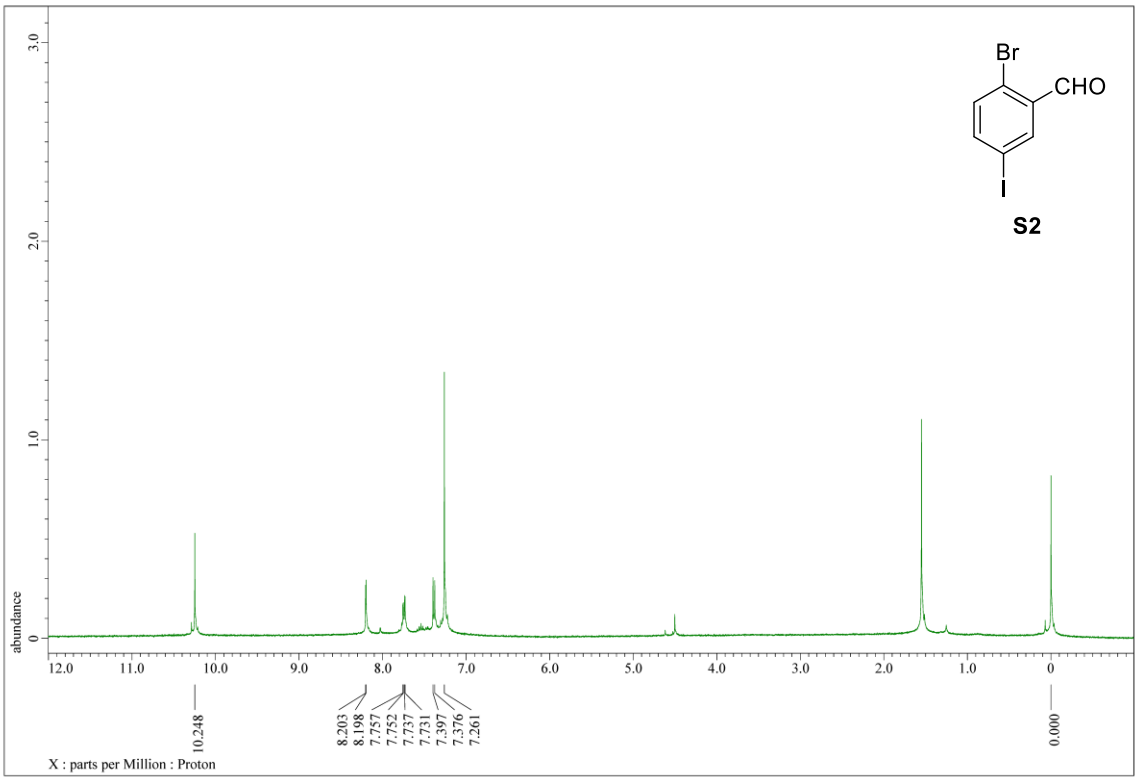


Figure S27. ^{1}H NMR Spectrum of S2.

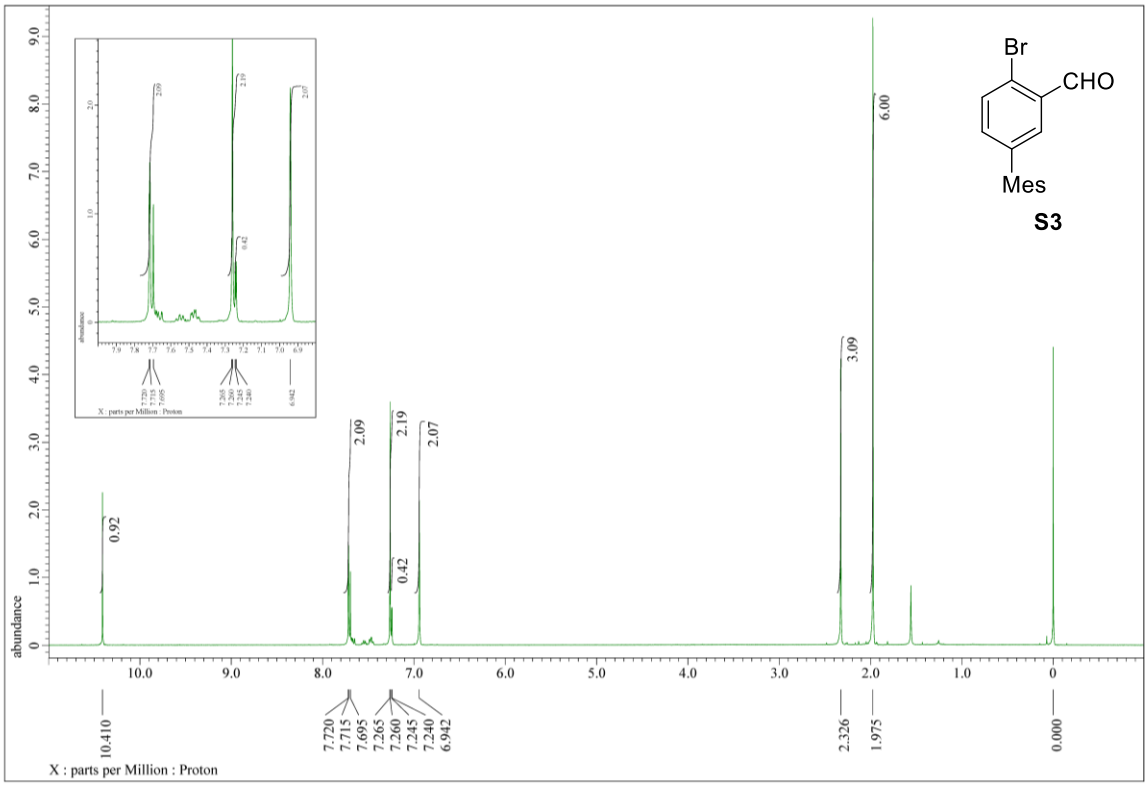


Figure S28. ^{1}H NMR Spectrum of S3.

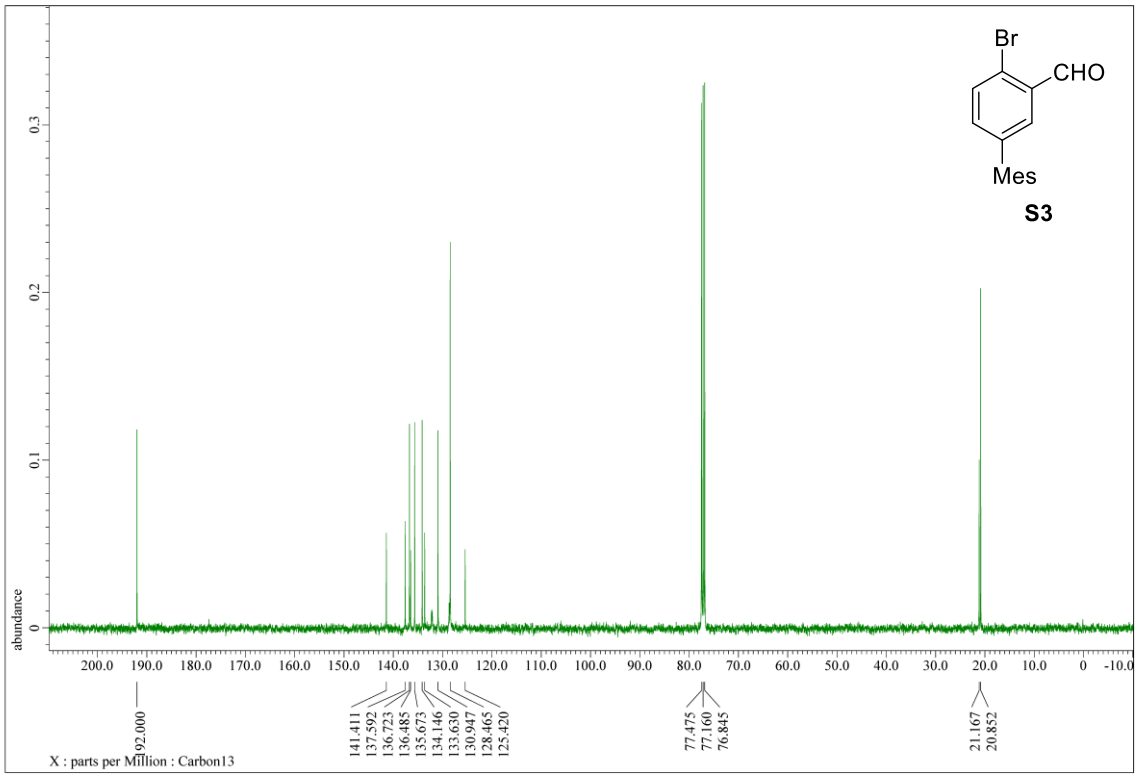


Figure S29. ^{13}C NMR Spectrum of S3.

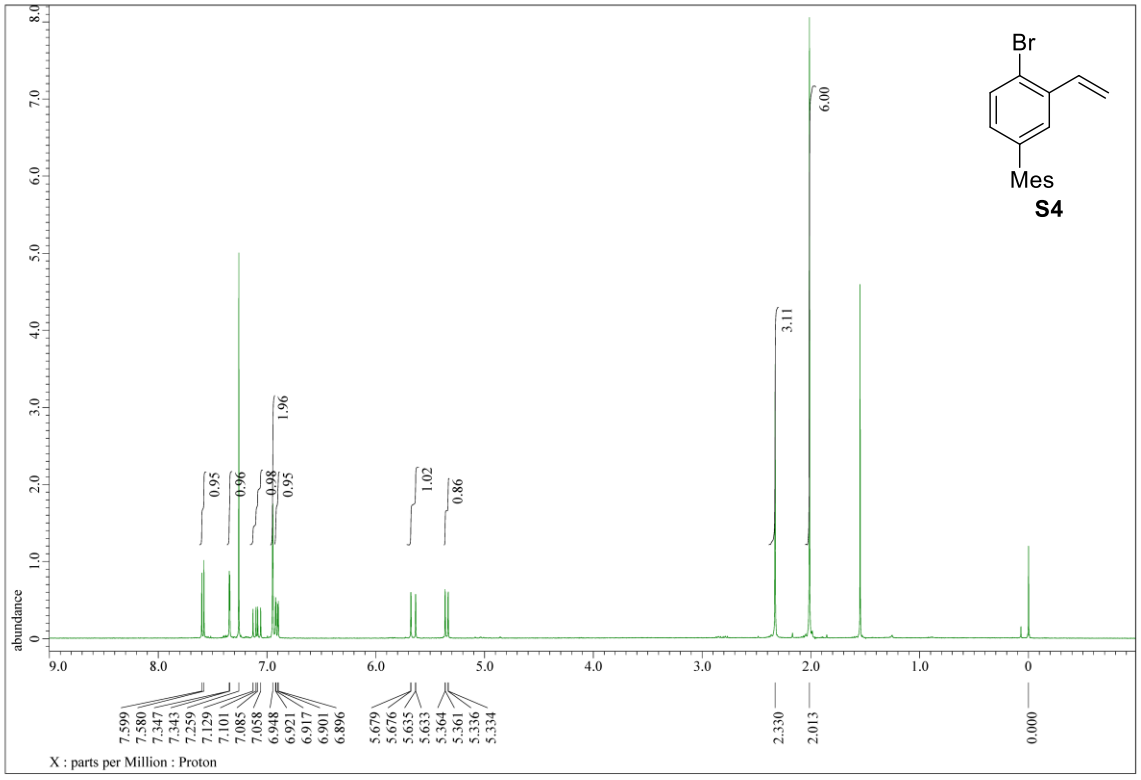


Figure S30. ^{1}H NMR Spectrum of S4.

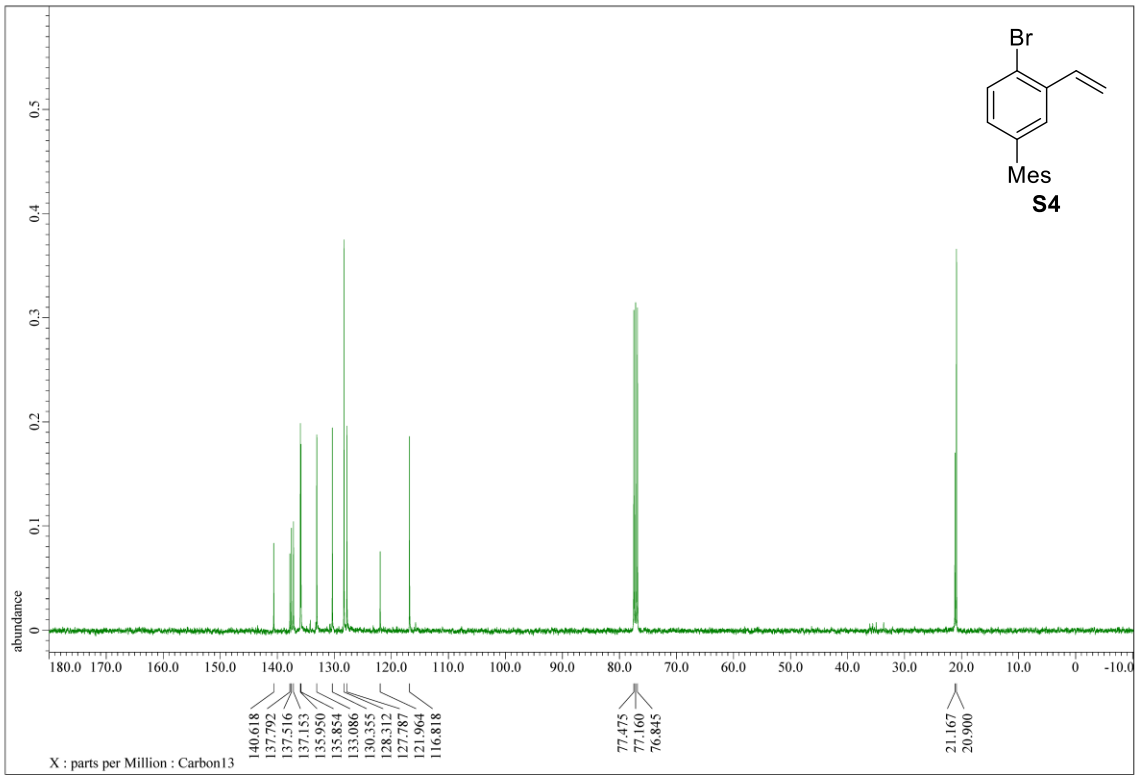


Figure S31. ^{13}C NMR Spectrum of S4.

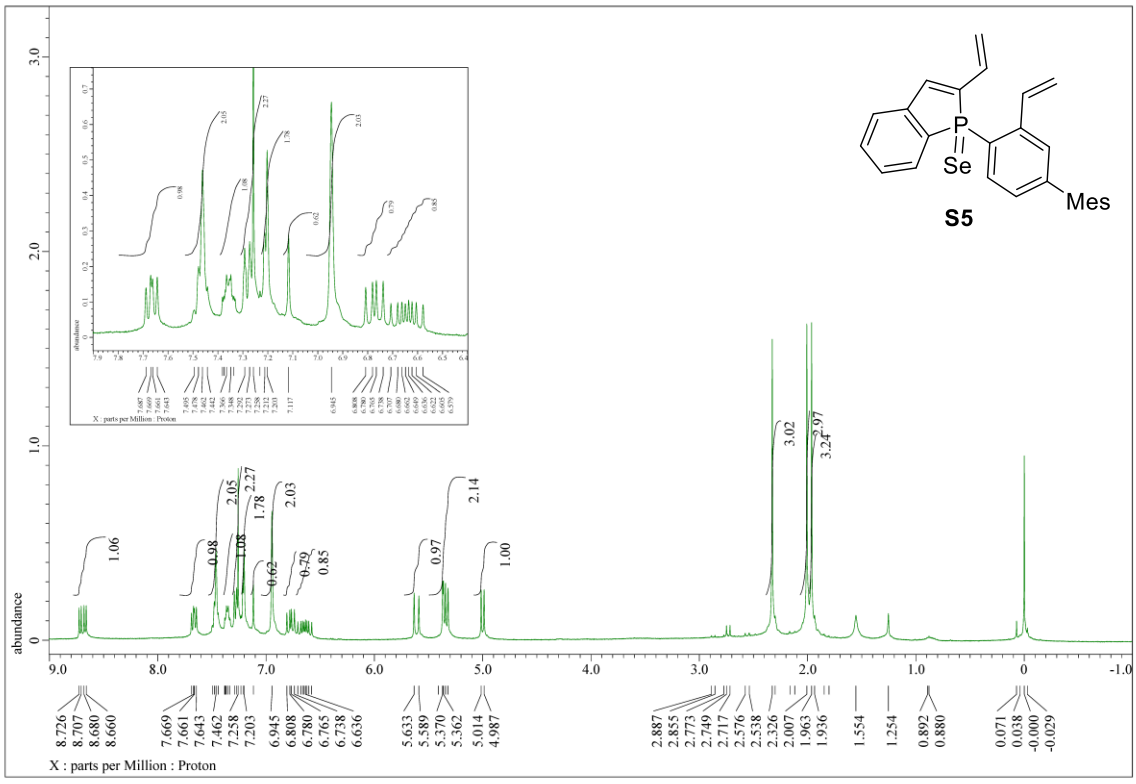


Figure S32. ^{1}H NMR Spectrum of S5.

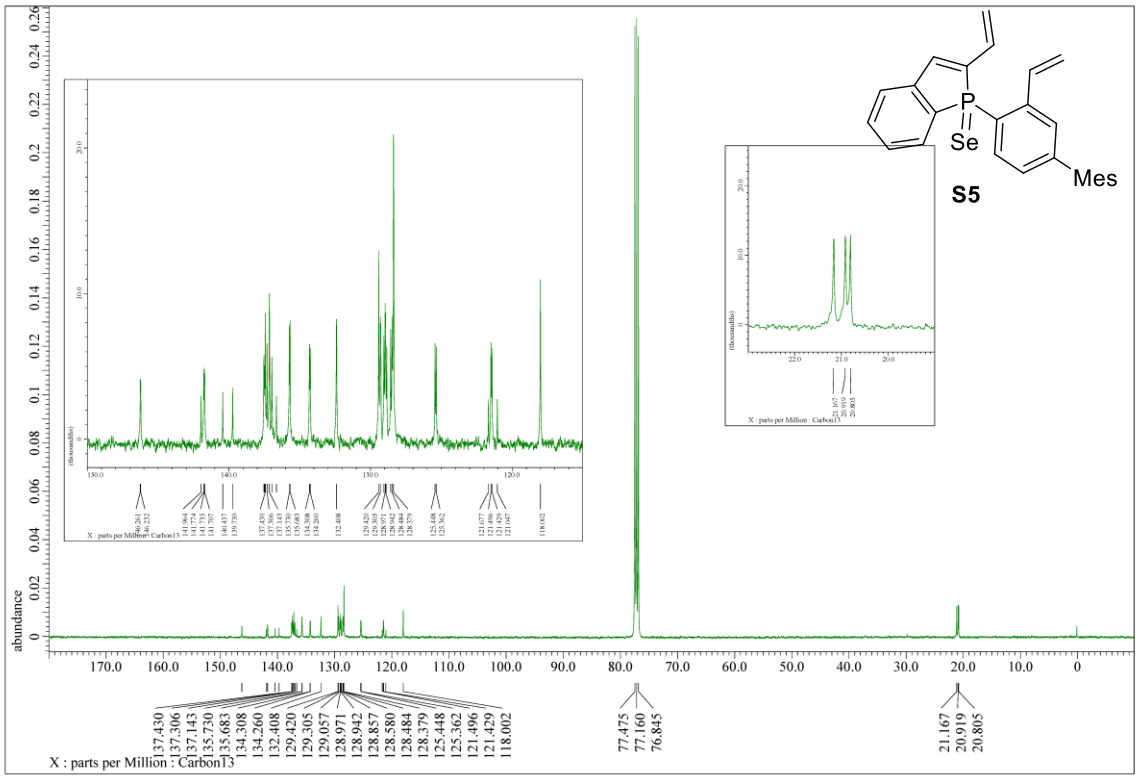


Figure S33. ^{13}C NMR Spectrum of S5.

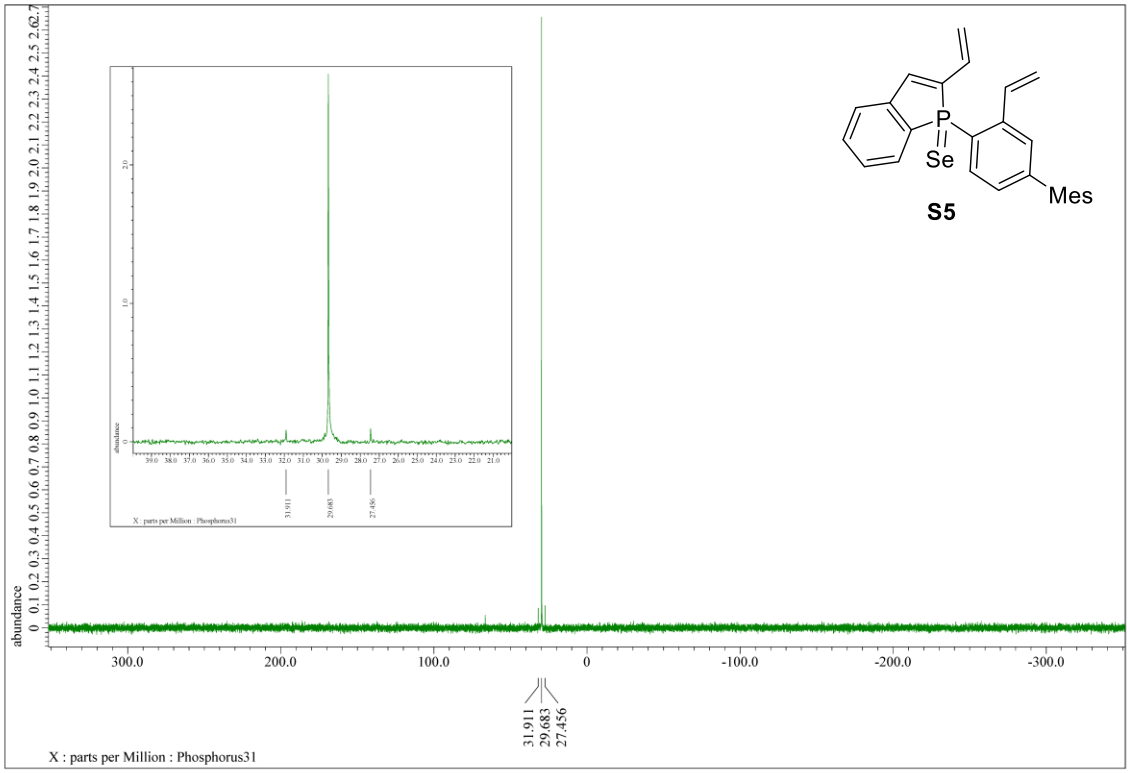


Figure S34. ^{31}P NMR Spectrum of S5.

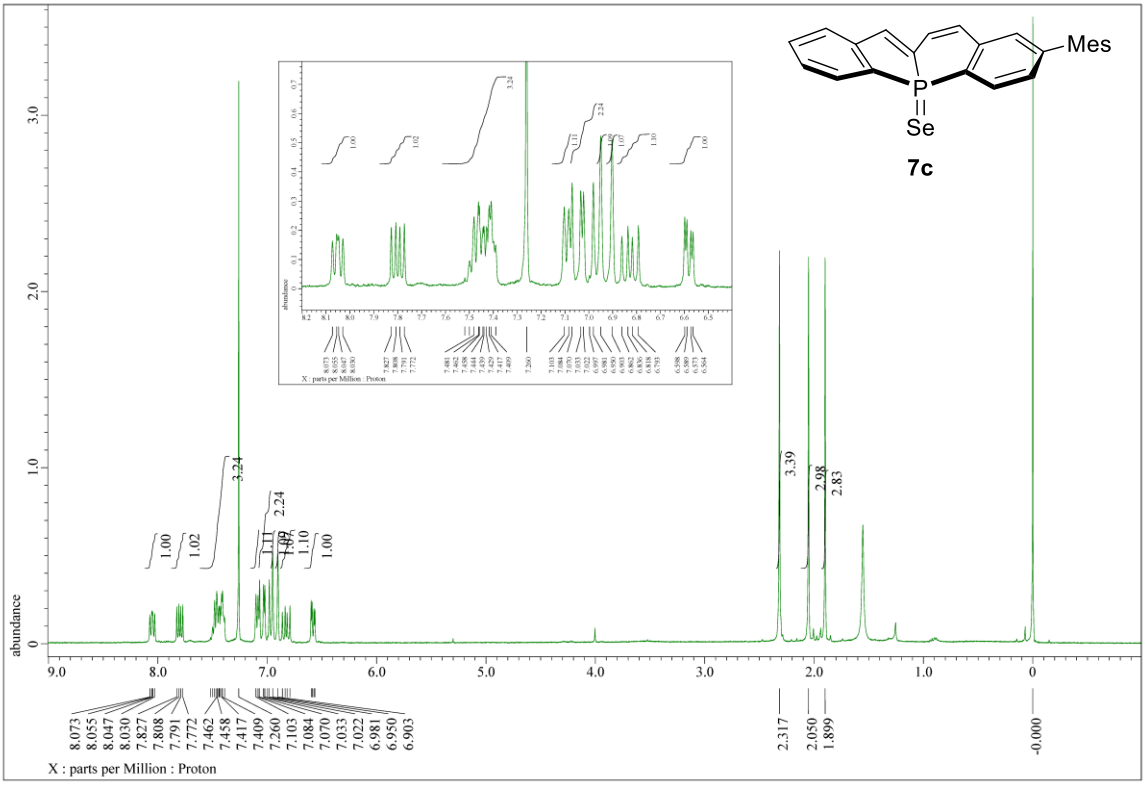


Figure S35. ^{1}H NMR Spectrum of 7c.

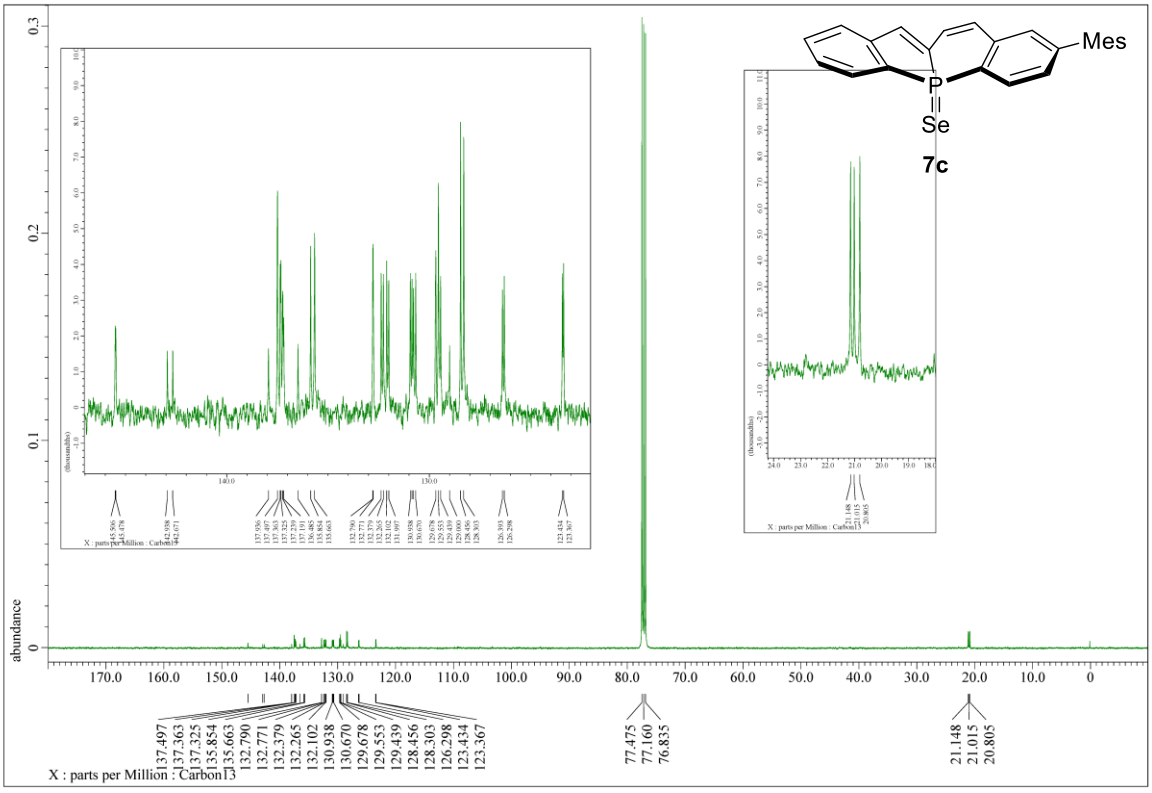


Figure S36. ^{13}C NMR Spectrum of 7c.

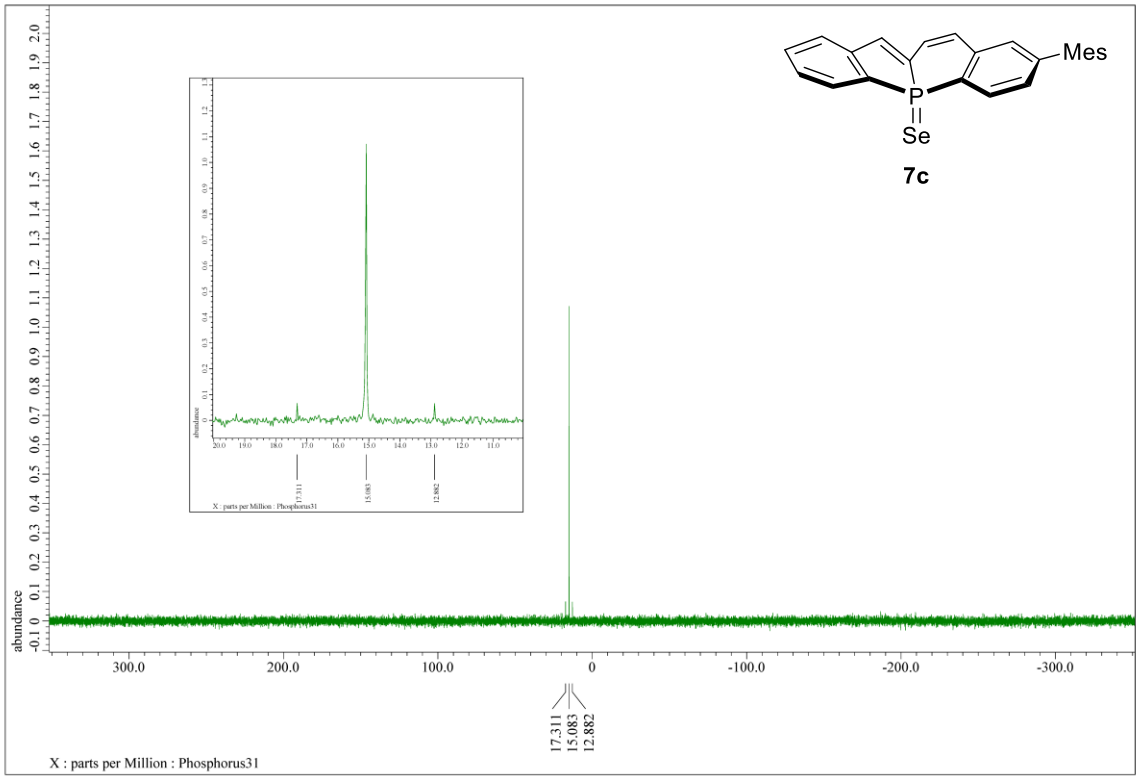


Figure S37. ^{31}P NMR Spectrum of 7c.

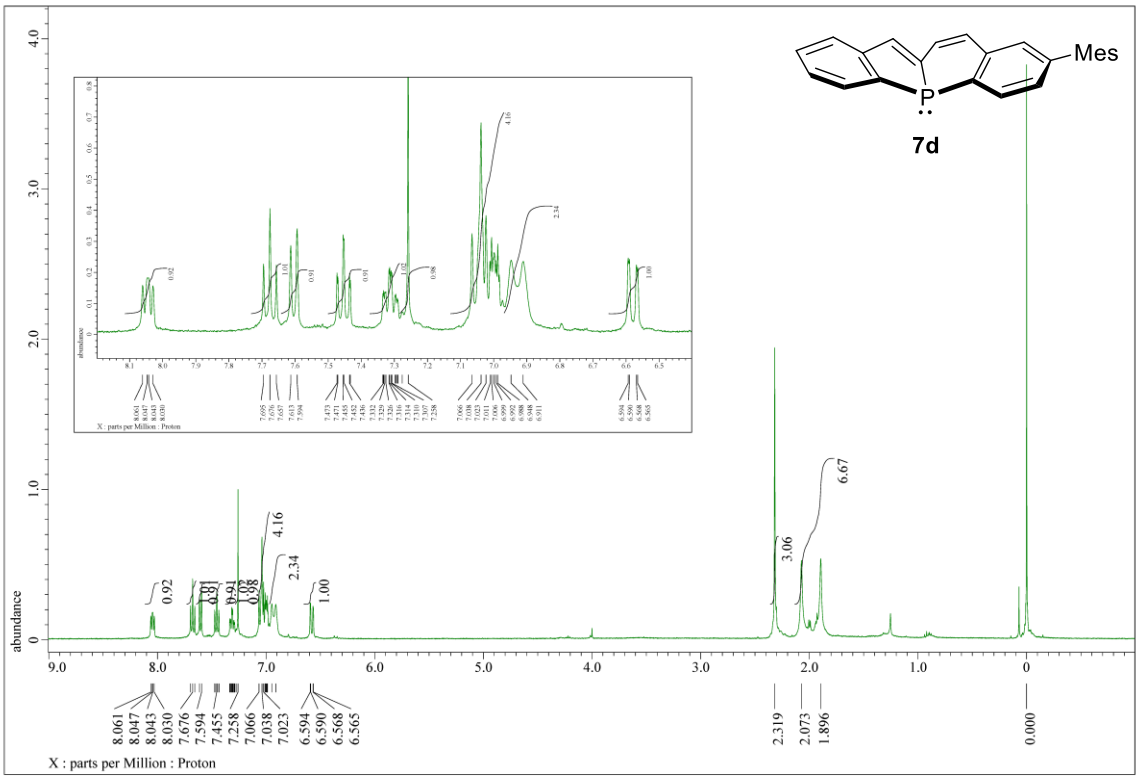


Figure S38. ^{1}H NMR Spectrum of 7d.

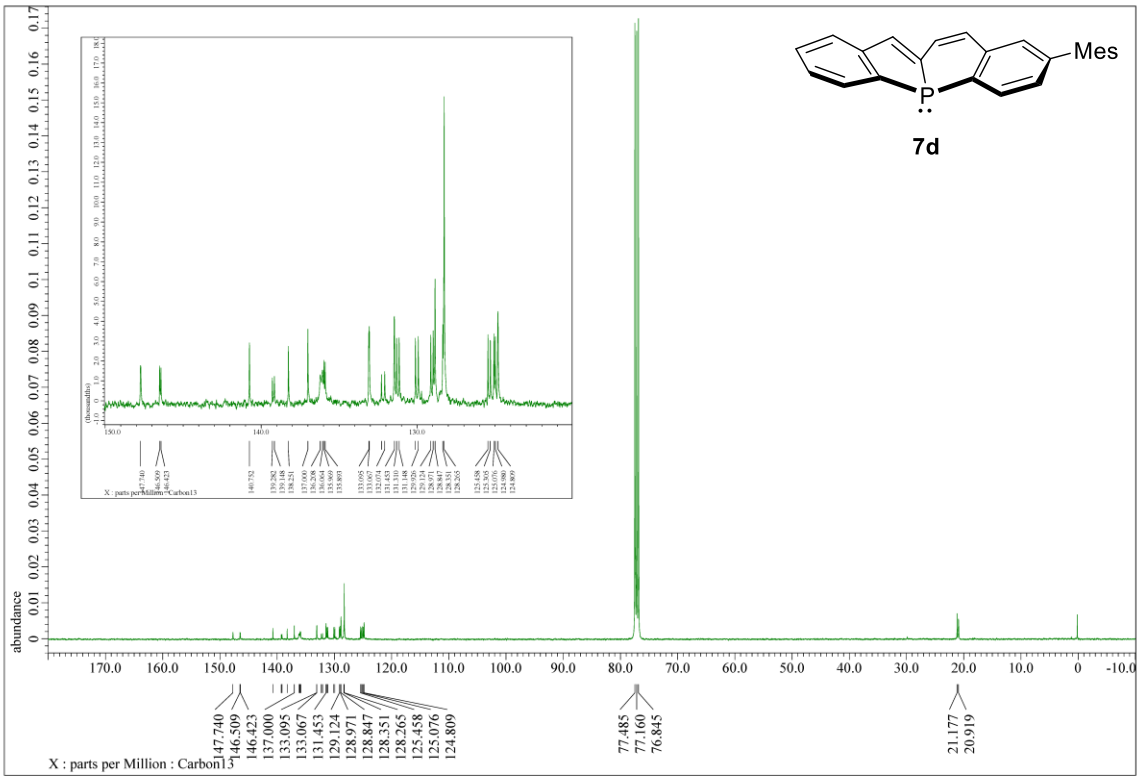


Figure S39. ^{13}C NMR Spectrum of 7d.

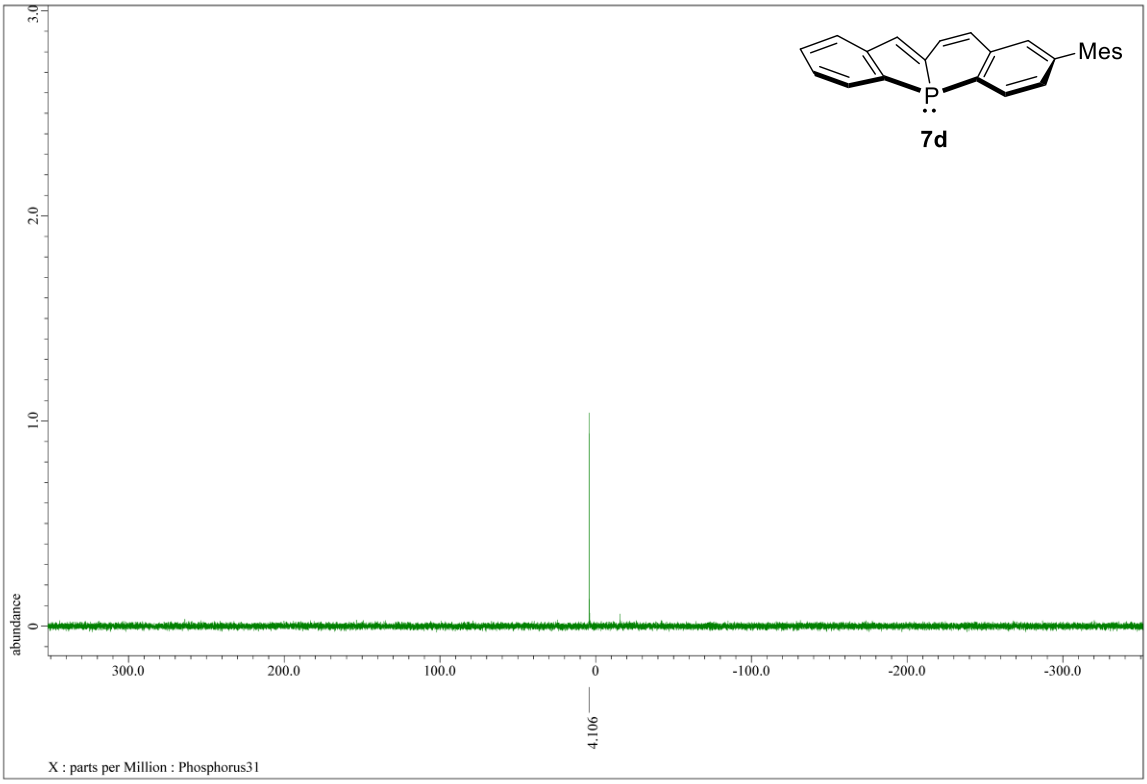


Figure S40. ^{31}P NMR Spectrum of 7d.

3. X-ray Crystallographic Analysis

Single crystals of **1a**–**c** were grown by recrystallization from a toluene/hexane solution at −20 ºC (for **1a** and **1c**) and from a dichloromethane/hexane solution at 5 ºC (for **1b**). Single crystals of **1d** were grown by slow evaporation of a toluene/hexane solution at room temperature under argon atmosphere. X-ray data were collected on a Rigaku Saturn diffractometer with VariMax multi-layer mirror monochromated Mo-Kα radiation (λ = 0.71073 Å) at −170 ºC. The data were corrected for Lorentz and polarization effects. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the REQABS program in CrystalClear software. The structures were solved by direct methods (SIR2014[S14] for **1a**–**1c** or SHELXS-2013[S15] for **1d**) and refined by full-matrix least squares against F^2 using all data. Non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were generated by AFIX instructions. All calculations were performed using Yadokari-XG 2009[S16] software package except for refinement, which was performed using SHELXL-2013.[S17] CCDC-1886029 (**1a**), CCDC-1886030 (**1b**), CCDC-1886031 (**1c**), and CCDC-1886032 (**1d**) contain the supplementary crystallographic data for this paper.

Table S1. Crystal Data for **1a**–**d**.

	1a	**1b**	**1c**	**1d**
Formula	$C_{16}H_{11}PO$	$C_{16}H_{11}PS$	$C_{16}H_{11}PSe$	$C_{16}H_{11}P$
Formula weight	250.22	266.30	313.18	234.22
Crystal Size/mm	0.22 × 0.16 × 0.08	0.19 × 0.16 × 0.12	0.23 × 0.08 × 0.07	0.12 × 0.10 × 0.06
Temperature/ °C	−170	−170	−170	−170
Crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	$P2_1/c$ (#14)	*P*bca (#61)	*P*bca (#61)	$P2_1$ (#4)
Lattice parameters				
a/Å	11.341(4)	7.099(2)	7.0608(4)	7.174(3)
b/Å	9.571(3)	12.750(4)	12.8843(8)	7.276(2)
c/Å	11.845(4)	27.638(9)	27.9209(18)	11.608(4)
α/°	90	90	90	90
β/°	112.200(5)	90	90	106.916(5)
γ/°	90	90	90	90
V/Å^3	1190.4(7)	2501.6(14)	2540.1(3)	579.7(3)
Z	4	8	8	2
D_{calc} /g cm^{-3}	1.396	1.414	1.638	1.342
μ (cm^{-1})	0.213	0.362	3.058	0.207
$2\theta_{max}$/°	55.0	55.0	55.0	55.0
No. of reflections	14228	23615	23815	4756
Independent reflections	2720	2849	2892	2573
No. of parameters	163	163	163	154
R_{int}	0.0269	0.0320	0.0310	0.0193
Completeness to θ (%)	99.7	99.4	99.4	98.8
R_1 [$I>2\sigma(I)$]	0.0368	0.0347	0.0283	0.0337
wR_2 (all data)	0.0939	0.0899	0.0714	0.0864
Largest diff. peak (e.Å^{-3})	0.505	0.442	0.794	0.477
Largest diff. hole (e.Å^{-3})	−0.339	−0.403	−0.362	-0.173
Goodness-of-fit	1.065	1.037	1.083	1.061
Absolute Structural Parameter	–	–	–	0.05(3)

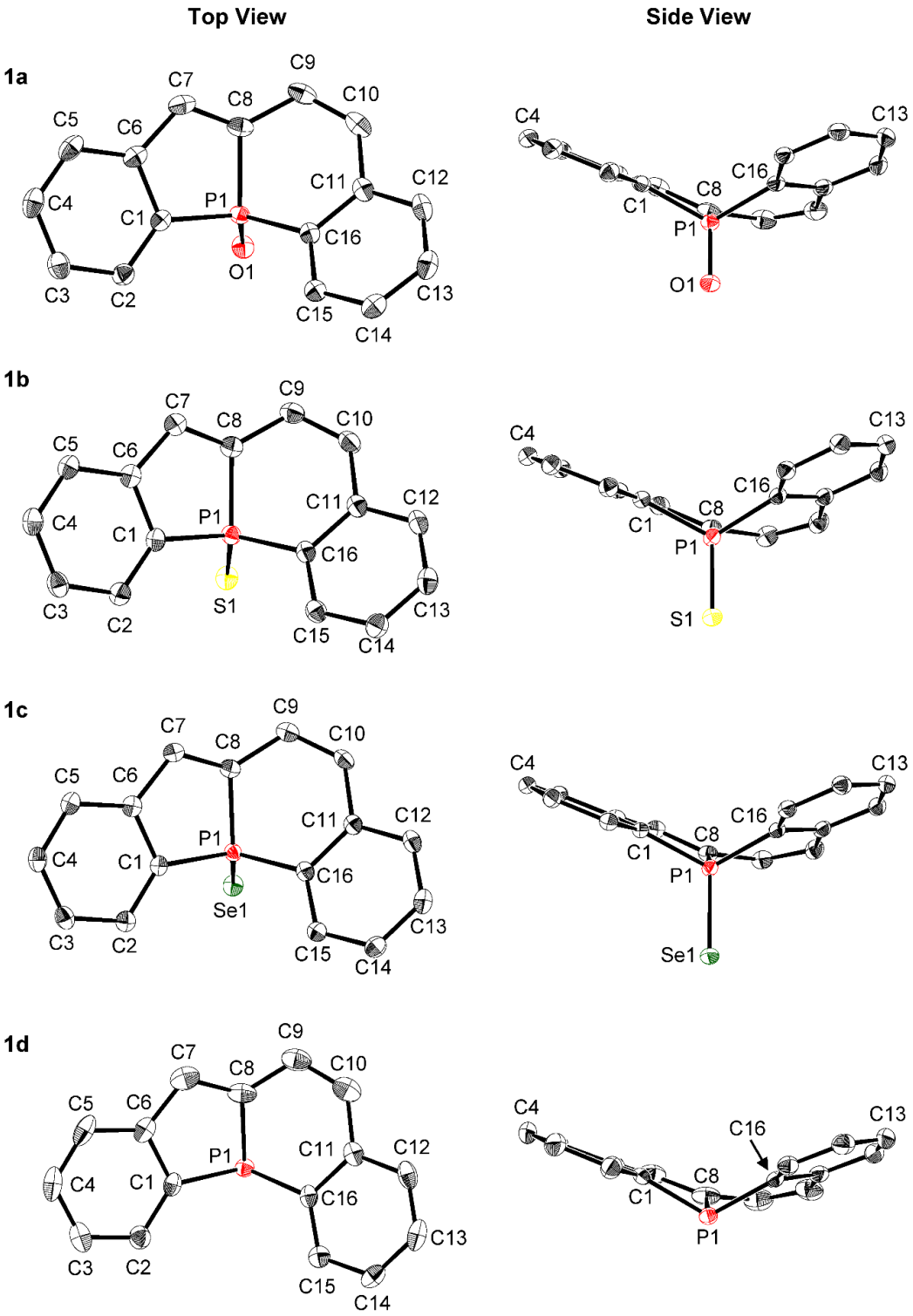
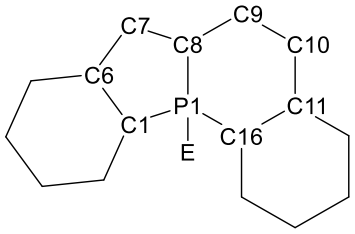


Figure S41. Molecular Structures of **1a**–**d**.

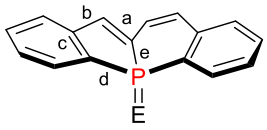
Table S2. Selected structural parameters of dibenzo[*b*,*e*]phosphindolizine **1a**–**d**.



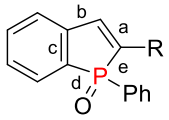
structural parameter	**1a** (E = O)	**1b** (E = S)	**1c** (E = Se)	**1d** (E = lp)
d(P1=E) /Å	1.4880(11)	1.9559(8)	2.1097(5)	–
d(P1−C1) /Å	1.8005(15)	1.8098(15)	1.8104(18)	1.806(3)
d(P1−C8) /Å	1.7960(16)	1.8016(16)	1.8006(19)	1.794(3)
d(P1−C16) /Å	1.7859(15)	1.7969(15)	1.8001(19)	1.811(3)
d(C1−C6) /Å	1.411(2)	1.409(2)	1.407(3)	1.420(4)
d(C6−C7) /Å	1.471(2)	1.469(2)	1.470(3)	1.459(4)
d(C7−C8) /Å	1.351(2)	1.351(2)	1.353(3)	1.379(4)
d(C8−C9) /Å	1.449(2)	1.450(2)	1.452(3)	1.430(4)
d(C9−C10) /Å	1.348(2)	1.345(2)	1.348(3)	1.331(4)
d(C10−C11) /Å	1.473(2)	1.470(2)	1.475(3)	1.461(4)
d(C11−C16) /Å	1.417(2)	1.4149(19)	1.416(3)	1.421(3)
deg(C1−P1−C8) /º	92.56(7)	92.18(7)	92.53(9)	90.83(13)
deg(C1−P1−C16) /º	117.21(7)	117.27(7)	118.33(8)	115.92(11)
deg(C8−P1−C16) /º	100.35(7)	99.80(7)	99.89(9)	99.90(12)
ΣP/º [a]	310.1(2)	309.3(2)	310.8(3)	306.7(4)
d(C_4P)[b]	0.18	0.18	0.18	0.34
d(C_5P)[c]	0.70	0.68	0.67	0.66

a) Sum of the three bond C−P−C bond angles. b) Deviation of the phosphorus atom from the C4 plane of C_4P five-membered ring. c) Deviation of the phosphorus atom from the least square plane including the five carbon atoms of C_5P six-membered ring.

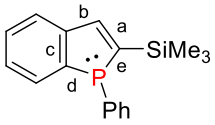
Table S3. Selected structural parameters of **1a**, **1d**, and the related benzo[*b*]phospholes.



1a: E = O
1d: E = lone-pair



S6a: R = $SiMe_3$
S6b: R = 4-CNC_6H_4
S6c: R = -CH=CHPh



S6d

structural parameter	observed		reported			
	1a	**1d**	**S6a**[d]	**S6b**[e]	**S6c**[f]	**S6d**[d]
d(P=O) /Å	1.4880(11)	–	1.4859(8)	1.477(2)	1.4859(10)	–
a /Å	1.351(2)	1.379(4)	1.3483(15)	1.335(4)	1.3510(19)	1.326(4)
b /Å	1.471(2)	1.459(4)	1.4821(14)	1.466(3)	1.462(2)	1.471(4)
c /Å	1.411(2)	1.420(4)	1.3984(15)	1.392(4)	1.400(2)	1.403(3)
d /Å	1.8005(15)	1.806(3)	1.8032(11)	1.799(3)	1.8017(15)	1.821(2)
e /Å	1.7960(16)	1.794(3)	1.8056(11)	1.808(2)	1.8139(13)	1.815(3)
ΣP/°[a]	310.1(2)	306.7(4)	308.8(2)	305.3(4)	307.1(2)	296.3(3)
d(C_4P)[b]	0.18	0.34	–[c]	0.06	0.02	–[c]

a) Sum of the three bond C–P–C bond angles. b) Deviation of the phosphorus atom from the C4 plane of C_4P five-membered ring. c) Not reported. The authors mentioned that phosphole skeleton is planar. d) Ref S18. e) Ref S19. f) Ref S20.

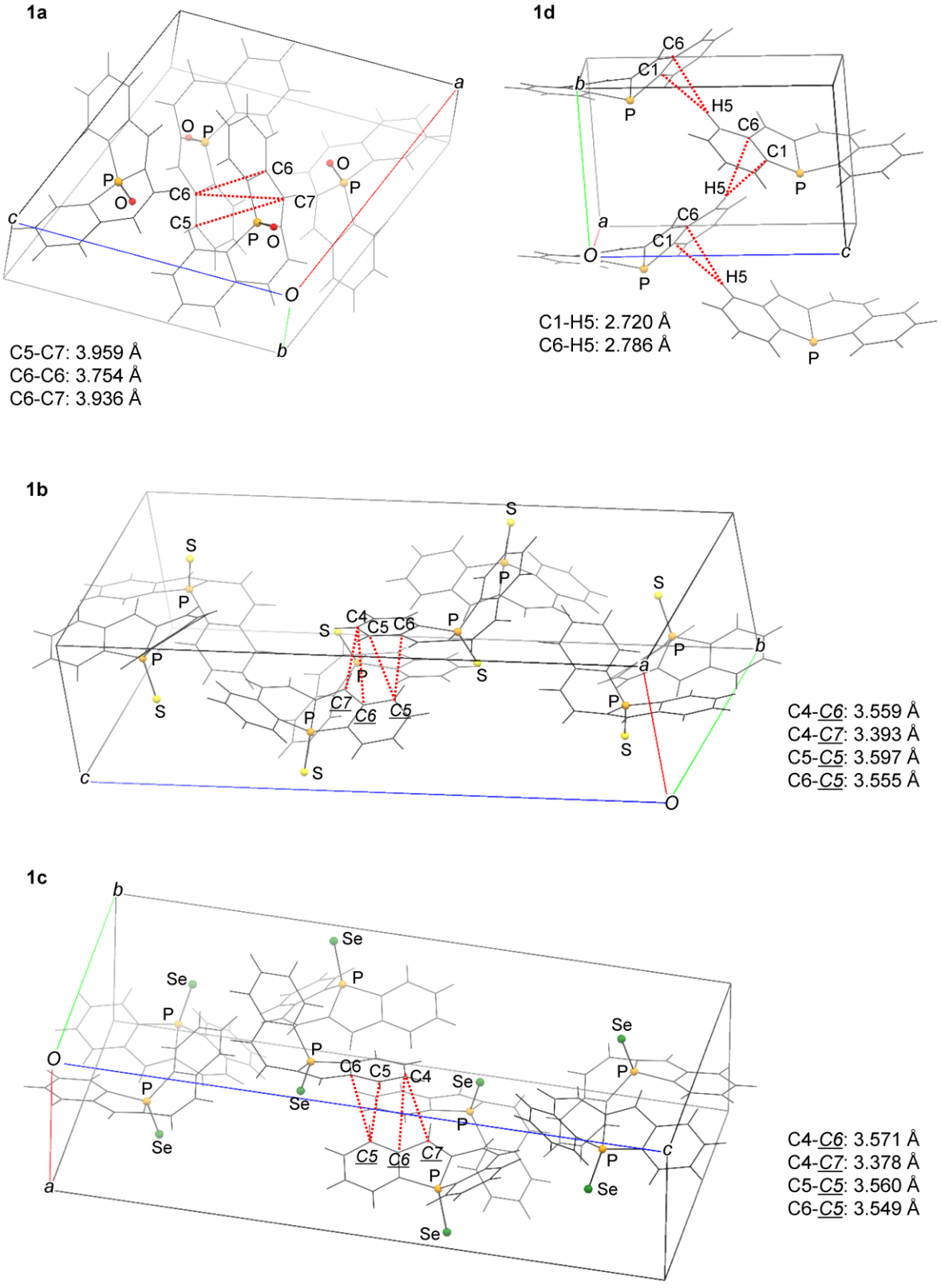


Figure S42. Packing Structures of **1a**–**d**.

4. UV-vis Absorption Spectra

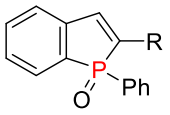
UV-vis spectra of **1a**–**d** were measured on a JASCO V-670 spectrophotometer with a dichloromethane solution (ca. 5×10^{-4} M) in a 1 mm quarts cell. The solution of **1d** was prepared under argon atmosphere. The results are shown in Figure 3a and Table S4.

Table S4. UV-vis spectral parameter of **1a-d** in CH_2Cl_2.

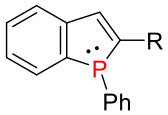
	1a	**1b**	**1c**	**1d**
λ_a / nm (ε)	397 (3410)	362 (3800)	377 (4760)	374 (5380)
	308[a] (3730)	299 (5370)	311[a] (4980)	294[a] (7790)
	261 (28500)	253 (24500)	257 (28400)	267 (22670)

a) observed as a shoulder.

Table S5. Physical properties of the reported benzo[*b*]phospholes.



S6c: R = -CH=CHPh
S6e: R = vinyl
S6f: R = Ph



13: R = H
S6h: R = Ph

	S6c[a]	**S6e**[a]	**S6f**[b]	**13**[c]	**S6h**[b]
λ_a / nm (ε)	367 (20000)[d]	339 (6170)[d]	347 (8800)[e]	316 (3630)[f]	321 (13800)[e]
E_{ox}/V (*vs.* Fc/Fc$^+$)[d]	+1.04	n.d.[g]	–[h]	–[h]	–[h]
E_{red}/V (*vs.* Fc/Fc$^+$)[d]	−2.07	−2.23	–[h]	–[h]	–[h]

a) Ref. S20. b) Ref. S21. c) Ref. S22. d) In CH_2Cl_2. e) In THF. f) In ethanol. g) n.d. = Not determined. h) Not reported.

5. Cyclic and Differential Pulse Voltammetry

Cyclic voltammetry (CV) experiments were carried out with an ALS 612B electrochemical analyzer (BAS Inc.) using a Pt wire counter working electrode, a Pt wire counter electrode, and Ag/AgCl reference electrode. The differential pulse voltammetry (DPV) measurements were performed in the same electrochemical system. The measurements of **1a**–**d** were carried out in the degassed 1 mM CH_2Cl_2 solution for oxidation or 1 mM THF solution containing 0.1 M tetrabutylammonium hexafluorophosphate ($n$$Bu_4NPF_6$: recrystallized from methanol three times) as a supporting electrolyte with scan rates of 100-500 mVs^{-1} at room temperature. CH_2Cl_2 (spectral grade, nacalai) and THF (spectral grade, nacalai) were dried over calcium hydride and potassium, respectively, degassed by freeze-pump-thaw cycles, distilled in a vacuum line, and stored in a glovebox. Ferrocene (Wako) was added as an internal reference at the end of the experiments. Cyclic voltammograms with the scan rate of 100 mVs^{-1} and differential pulse voltammograms are shown in Figure S43. The results are summarized in Table S6.

Table S6. Summary of CV measurement.

Compd.	E_{ox}/V[a]	E_{red}/V[a]	E_{HOMO}/eV[b]	E_{LUMO}/eV[b]	$E_{HOMO\text{-}calc}$/eV[c]	$E_{LUMO\text{-}calc}$/eV[c]
1a	+1.18 (+1.64)	−1.84 (−1.20)	−6.28	−3.26	−5.78	−2.24
1b	+1.13 (+1.61)	−1.87 (−1.24)	−6.23	−3.23	−5.64	−2.26
1c	+0.32 (+0.79)	−1.87 (−1.24)	−5.42	−3.23	−5.28	−2.24
1d	+0.59 (+1.05)	−2.51 (−1.89)	−5.69	−2.59	−5.29	−1.60

a) Potentials *vs.* Fc/Fc^+. Potentials *vs.* Ag/Ag^+ were described in the parentheses. b) Estimated by the formal potential of the redox couple of ferrocene/ferrocenium (Fc/Fc^+) of −5.10 eV.[S23] c) Calculated at B3LYP/6-31G(d) level.

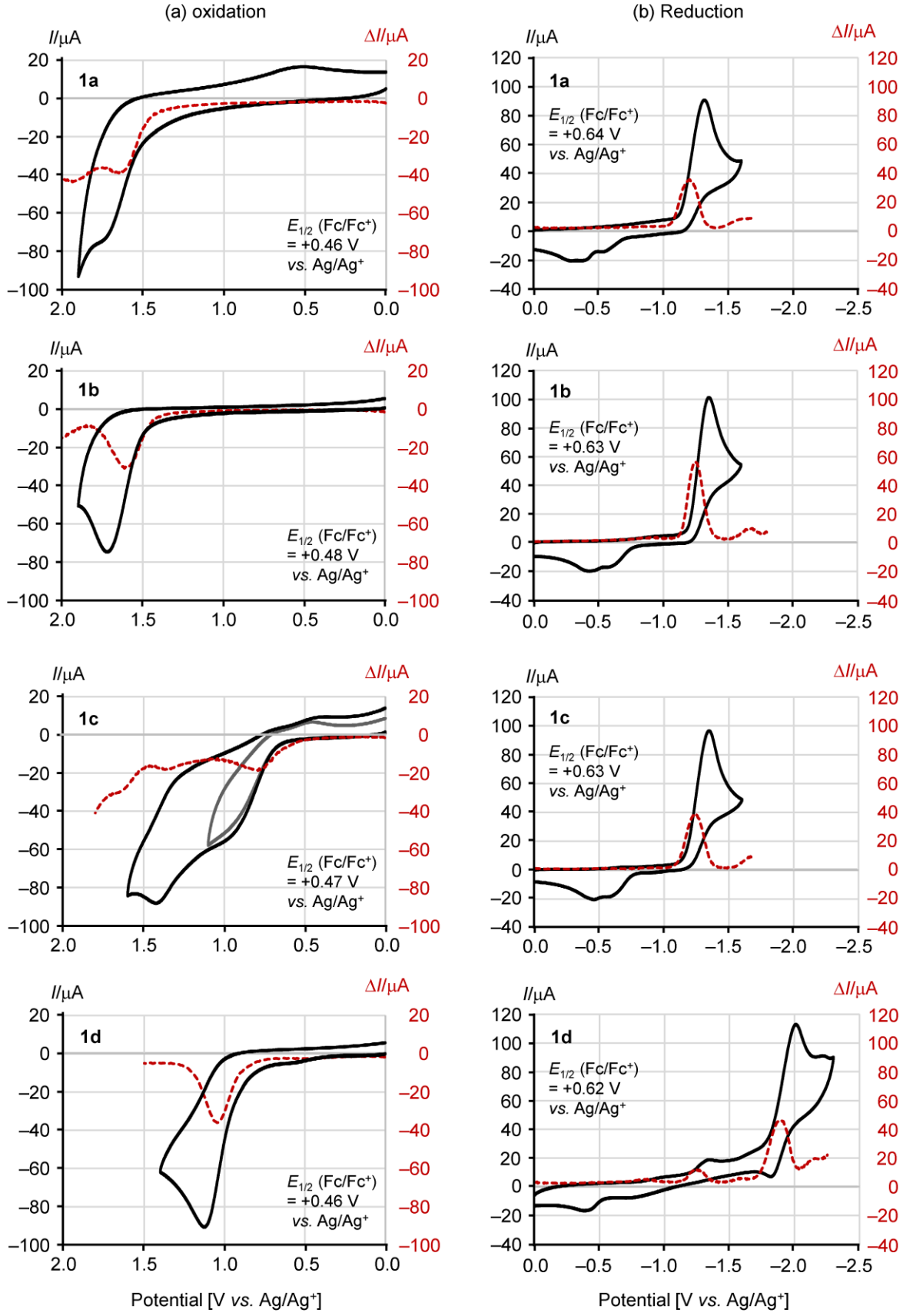


Figure S43. Cyclic voltammogram and differential pulse voltammograms of **1a**–**1d**.

6. Temperature Dependent ^{1}H NMR Spectra.

Temperature dependent ^{1}H NMR spectra (500 MHz) of **7d** were measured in $CDCl_3$ with a JEOL JNM-ECZ500R spectrometer. The solution was prepared in an argon glovebox and charged in an NMR tube with J-young valve. The spectra were measured every 5 °C from to 50 °C and every 1 °C from 52 °C to 58 °C. The observed NMR spectra are shown in Figures 5, S44, and S45.

For the determination of the inversion barriers of the phosphorus atom ($\Delta G^{\ddagger}$), the rate constants (k_{Tc}) at the coalescence temperatures (T_c) were calculated by using the Gutowski–Holm method (eq. 1),[S24] where $\Delta\nu$ is the difference in chemical shifts of the two *ortho*-methyl signals of mesityl group in **7d**.

$$k_{Tc} = \pi\Delta\nu / \sqrt{2} \qquad (1)$$

Inserting the resulting rate constants (k_{Tc}) into the Eyring equation (eq. 2) provided the value of $\Delta G^{\ddagger}$, where R is the Gas constant, h the Planck constant, and k_B the Boltzmann constant.

$$\Delta G^{\ddagger} = -RT_c \ln (k_{Tc}h / k_B T_c) \qquad (2)$$

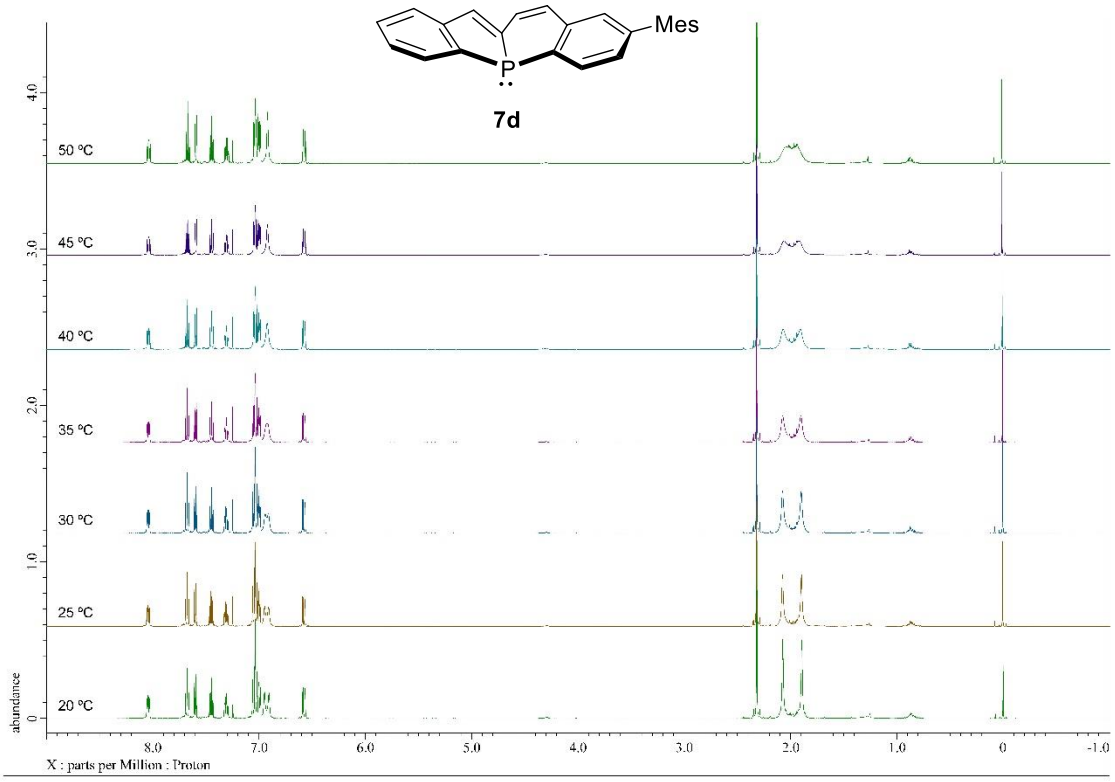


Figure S44. Temperature dependent ^{1}H NMR spectra (20 ºC-50 ºC) of **7d** in $CDCl_3$.

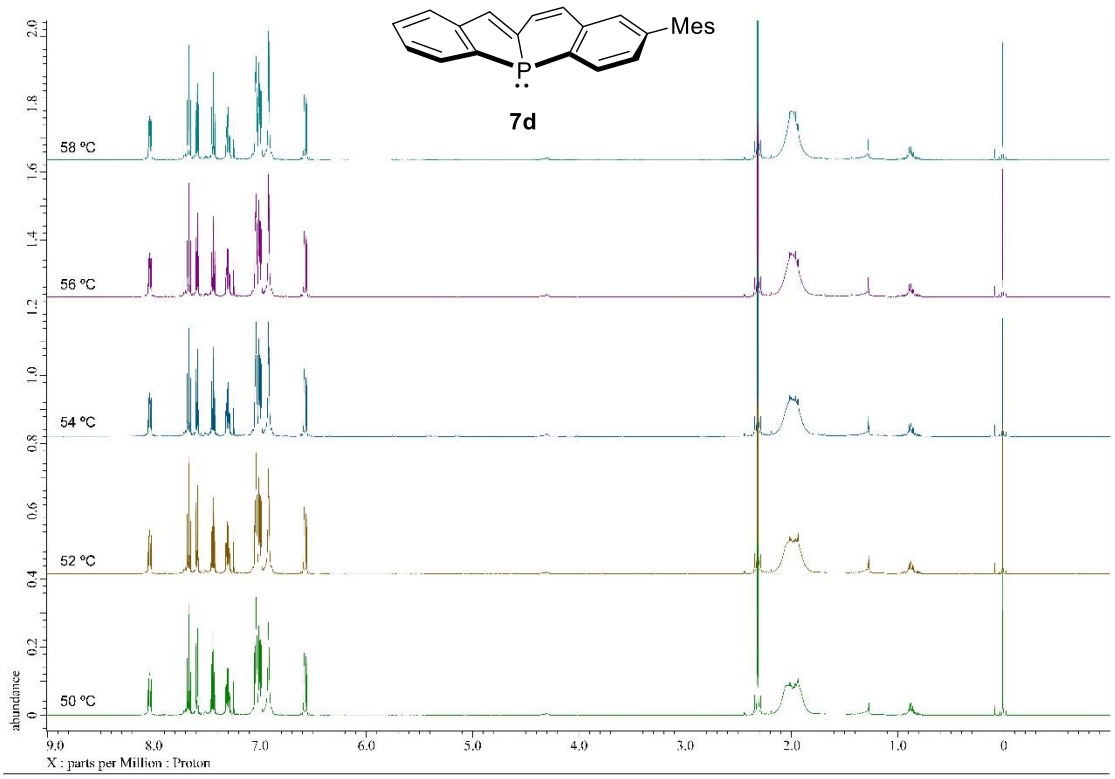
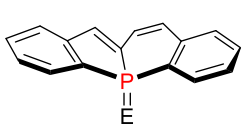


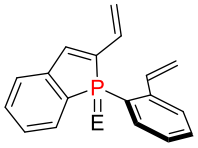
Figure S45. Temperature dependent ^{1}H NMR spectra (50–58 °C) of **7d** in $CDCl_3$.

7. Theoretical Calculations

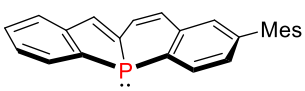
All theoretical calculations were performed using the Gaussian 09[S25] and GRRM14[S26] programs on a Fujitsu PRIMERGY RX300 system of the Research Center for Computational Science, Japan. All structures were optimized without any symmetry assumptions. Zero-point energy, enthalpy, and Gibbs free energy at 298.15 K and 1 atm were estimated from the gas-phase studies. The structures of **1a**–**d**, **2a**–**d**, **7d** **8-H$_2$**, **9**–**13**, and **S7a**–**c** were optimized at B3LYP/6-31G(d) level.[S27] Transition states of the inversion of pyramidal phosphorus atom of **1d**, **7d**, **8-H$_2$**, and **9**–**13** (**1d-TS, 7d-TS**, **8-H$_2$-TS**, **9-TS**, **10-TS**, **11-TS**, **12-TS**, and **13-TS**, respectively) were optimized at B3LYP/6-31G(d) level. Harmonic vibration frequency calculations at the same level were performed to verify all stationary points as local minima (with no imaginary frequency) or transition states (with one imaginary). The TDDFT calculations of **1a-d** were performed at B3LYP/6-311+G(2d,p) level in conjunction with PCM model (dichloromethane)[S28] to evaluate solvation effects. The GIAO calculations of the ground and transition states of **1d**, **7d**, **8-H$_2$**, and **9-13** were carried out at B3LYP/6-311+G(d,p) level.



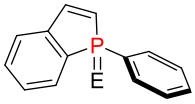
1a: E = O
1b: E = S
1c: E = Se
1d: E = lp



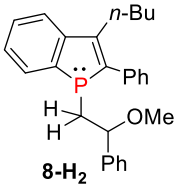
2a: E = O
2b: E = S
2c: E = Se
2d: E = lp



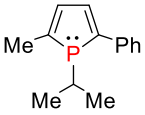
7d



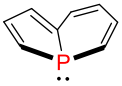
S7a: E = O
S7b: E = S
S7c: E = Se
13: E = lp



8-H$_2$



9



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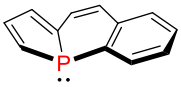

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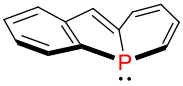

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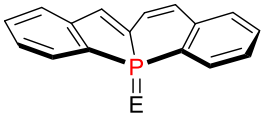
Table S7. Uncorrected and thermal-corrected (298 K) energies of stationary points (Hartree).[a]

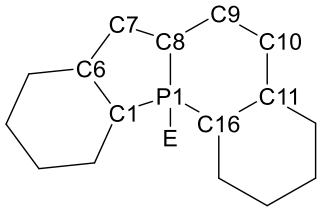
Local minimum	*E*	*E* + *ZPE*	*H*	G	
1a	-1032.90036527	-1032.677560	-1032.663288	-1032.717452	
1b	-1355.87022602	-1355.649363	-1355.634612	-1355.690184	
1c	-3357.06160330	-3356.841535	-3356.826418	-3356.883705	
1d	-957.66193530	-957.443766	-957.430495	-957.482520	
2a	-1111.49521771	-1111.218892	-1111.200438	-1111.264646	
2b	-1434.45873743	-1434.184391	-1434.165466	-1434.230848	
2c	-3435.65504508	-3435.381198	-3435.362029	-3435.428693	
2d	-1036.25465086	-1035.983032	-1035.965529	-1036.027842	
7d	-1306.66701326	-1306.285125	-1306.261610	-1306.338651	
8-H$_2$	-1462.91927754	-1462.428791	-1462.400373	-1462.489827	
9	-885.06706027	-884.796135	-884.779924	-884.838735	
10	-650.35096625	-650.227533	-650.219507	-650.259024	
11	-804.00576682	-803.834933	-803.824325	-803.870061	
12	-804.00461316	-803.833827	-803.823165	-803.868972	
13	-881.45525061	-881.249768	-881.237022	-881.289382	
S7a	-956.69755475	-956.487449	-956.473768	-956.527680	
S7b	-1279.66700049	-1279.458854	-1279.444693	-1279.500345	
S7c	-3280.86185204	-3280.654238	-3280.639831	-3280.696195	
Transition State	*E*	*E* + *ZPE*	*H*	G	ΔG^b
1d-TS	-957.63512842	-957.417621	-957.404944	-957.455447	17.0
7d-TS	-1306.64000790	-1306.258920	-1306.235920	-1306.311879	16.8
8-H$_2$-TS	-1462.87780346	-1462.388176	-1462.360195	-1462.448692	25.8
9-TS	-885.03649548	-884.766380	-884.750566	-884.809279	18.5
10-TS	-650.34353259	-650.220504	-650.213134	-650.251288	4.9
11-TS	-803.99050584	-803.820198	-803.810217	-803.854509	9.8
12-TS	-803.98574129	-803.815556	-803.805537	-803.849909	12.0
13-TS	-881.41875489	-881.214198	-881.201971	-881.252773	23.0

a) *E*: electronic energy; *ZPE*: zero-point energy; *H* (= $E + ZPE + E_{vib} + E_{rot} + E_{trans} + RT$): sum of electronic and thermal enthalpies; *G* (= $H - TS$): sum of electronic and thermal free energies. b) The relative energy (kcal mol^{-1}) compared to that of the local minimum.

Table S8. Selected structural parameters of dibenzo[*b*,*e*]phosphindolizine **1a**–**d**.



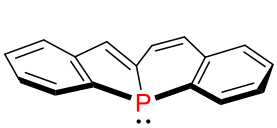
1a: E = O
1b: E = S
1c: E = Se
1d: E = lp



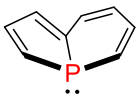
structural parameter	**1a** (calcd.)	**1b** (calcd.)	**1c** (calcd.)	**1d** (calcd.)
d(P1=E) /Å	1.503	1.971	2.111	–
d(P1−C1) /Å	1.828	1.830	1.828	1.826
d(P1−C8) /Å	1.825	1.829	1.830	1.814
d(P1−C16) /Å	1.818	1.825	1.827	1.834
d(C1−C6) /Å	1.416	1.416	1.415	1.426
d(C6−C7) /Å	1.474	1.470	1.468	1.455
d(C7−C8) /Å	1.354	1.354	1.354	1.363
d(C8−C9) /Å	1.451	1.450	1.450	1.446
d(C9−C10) /Å	1.354	1.354	1.353	1.357
d(C10−C11) /Å	1.471	1.470	1.469	1.467
d(C11−C16) /Å	1.423	1.422	1.422	1.424
deg(C1−P1−C8) /º	91.77	91.52	91.42	90.50
deg(C1−P1−C16) /º	116.09	116.16	116.46	116.21
deg(C8−P1−C16) /º	98.68	98.38	98.15	98.91
ΣP/º [a]	306.5	306.1	306.0	305.6

a) Sum of the three bond C−P−C bond angles.

Table S9. Selected structural parameters of phosphindolizines **1d**, **10**–**12**, and benzo[*b*]phosphole **13**.



1d



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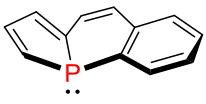

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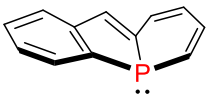

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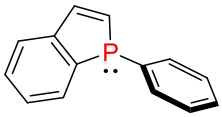
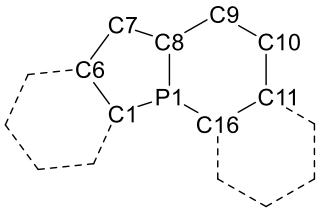
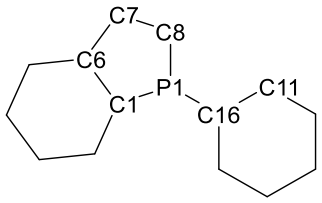


13





structural parameter	**1d** (calcd.)	**10**	**11**	**12**	**13**
d(P1−C1) /Å	1.826	1.778	1.796	1.820	1.838
d(P1−C8) /Å	1.814	1.790	1.795	1.814	1.827
d(P1−C16) /Å	1.834	1.784	1.821	1.808	1.854
d(C1−C6) /Å	1.426	1.383	1.373	1.428	1.417
d(C6−C7) /Å	1.455	1.431	1.443	1.450	1.463
d(C7−C8) /Å	1.363	1.384	1.374	1.368	1.351
d(C8−C9) /Å	1.446	1.429	1.440	1.441	–
d(C9−C10) /Å	1.357	1.371	1.360	1.363	–
d(C10−C11) /Å	1.467	1.442	1.462	1.455	–
d(C11−C16) /Å	1.424	1.367	1.426	1.359	1.403[b]
deg(C1−P1−C8) /º	90.50	93.31	92.09	90.94	89.37
deg(C1−P1−C16) /º	116.21	128.36	121.49	120.36	104.58
deg(C8−P1−C16) /º	98.91	102.92	101.24	99.62	104.36
ΣP/º [a]	305.6	324.6	314.8	310.9	298.3

a) Sum of the three bond C−P−C bond angles. b) average of the two C−C bond lengths.

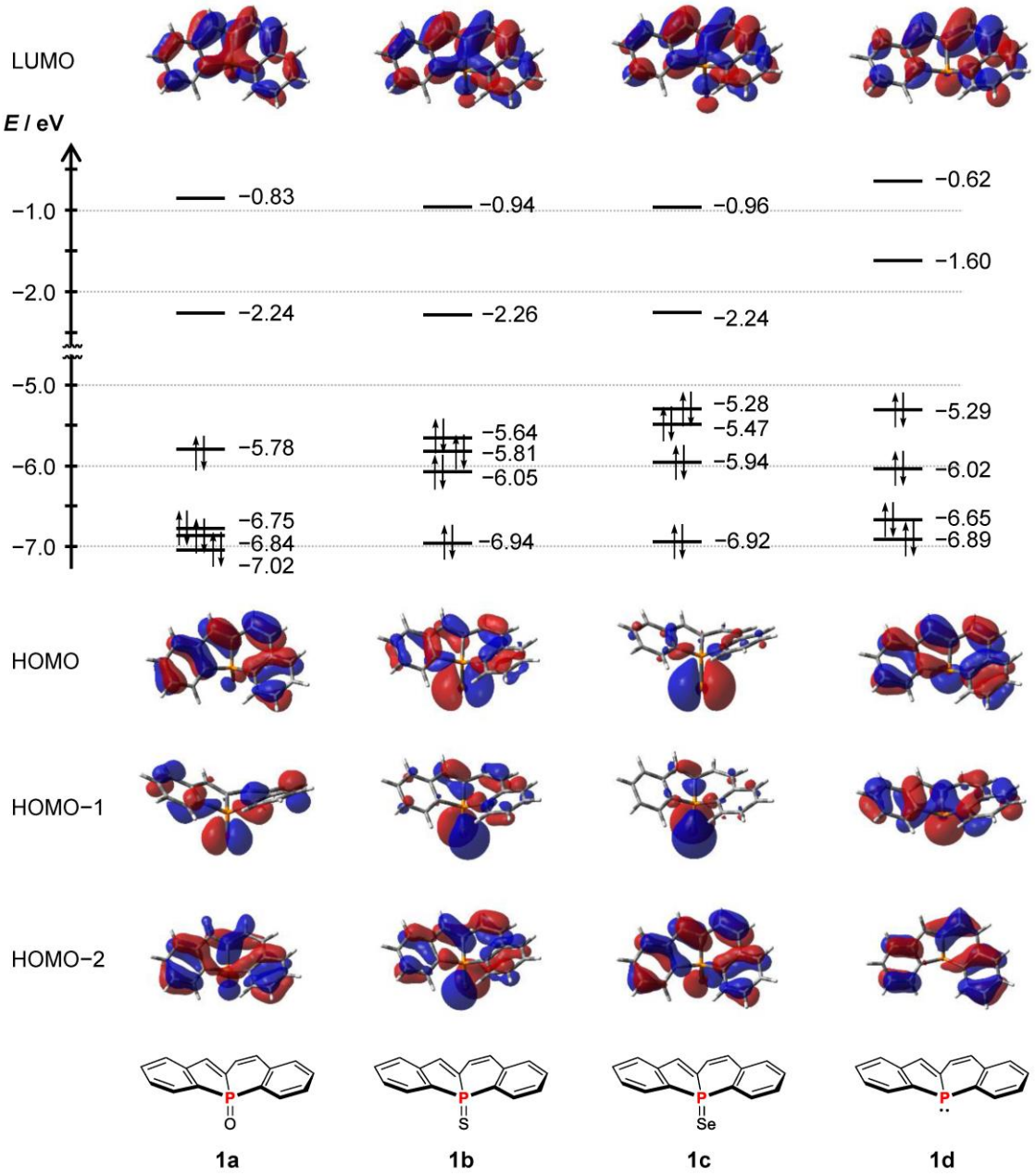


Figure S46. Energy diagram and the selected molecular orbitals of **1a**–**d** (isovalue = 0.03).

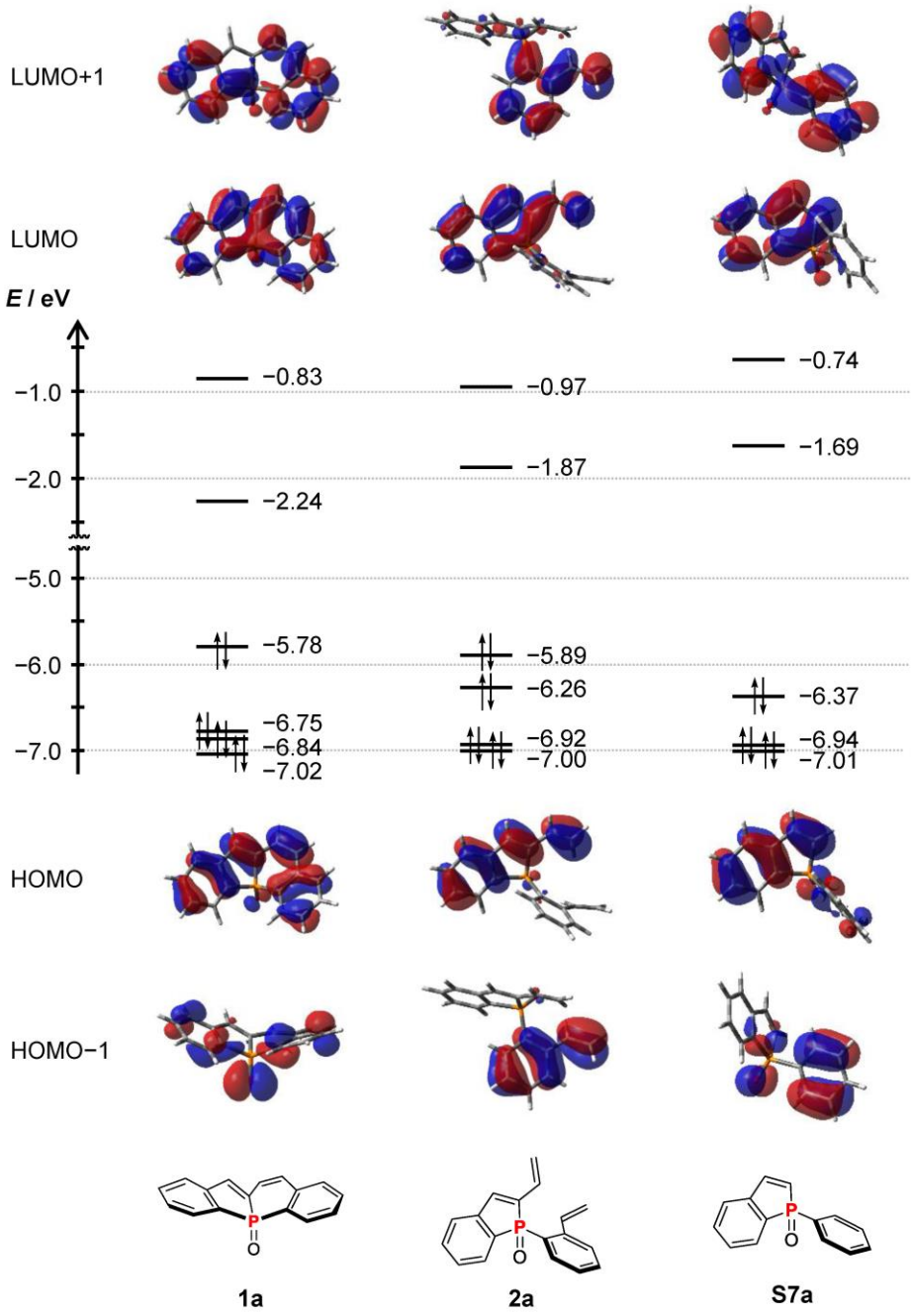


Figure S47. Energy diagram and the selected molecular orbitals of **1a**, **2a**, and **S7a** (isovalue = 0.03).

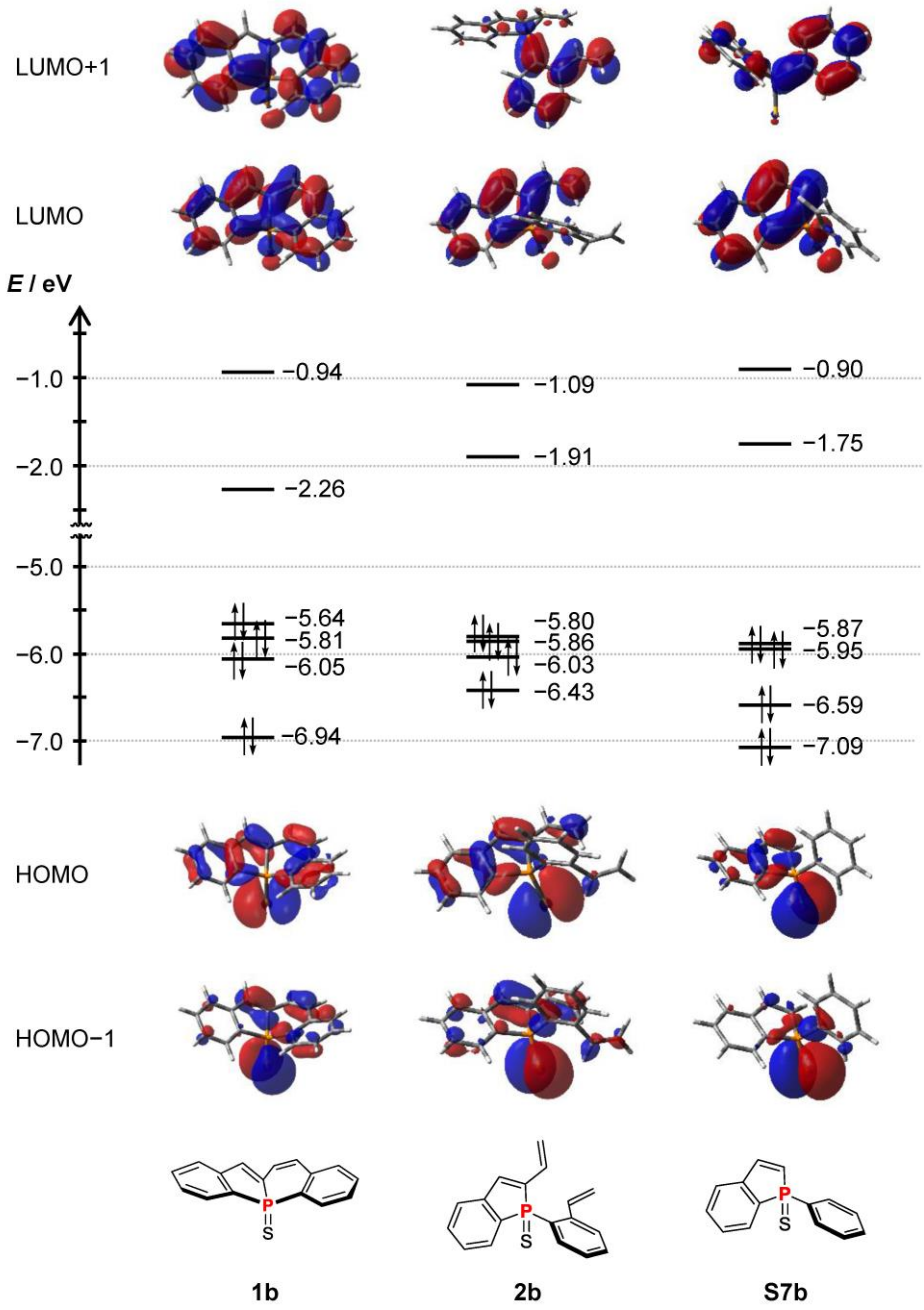


Figure S48. Energy diagram and the selected molecular orbitals of **1b**, **2b**, and **S7b** (isovalue = 0.03).

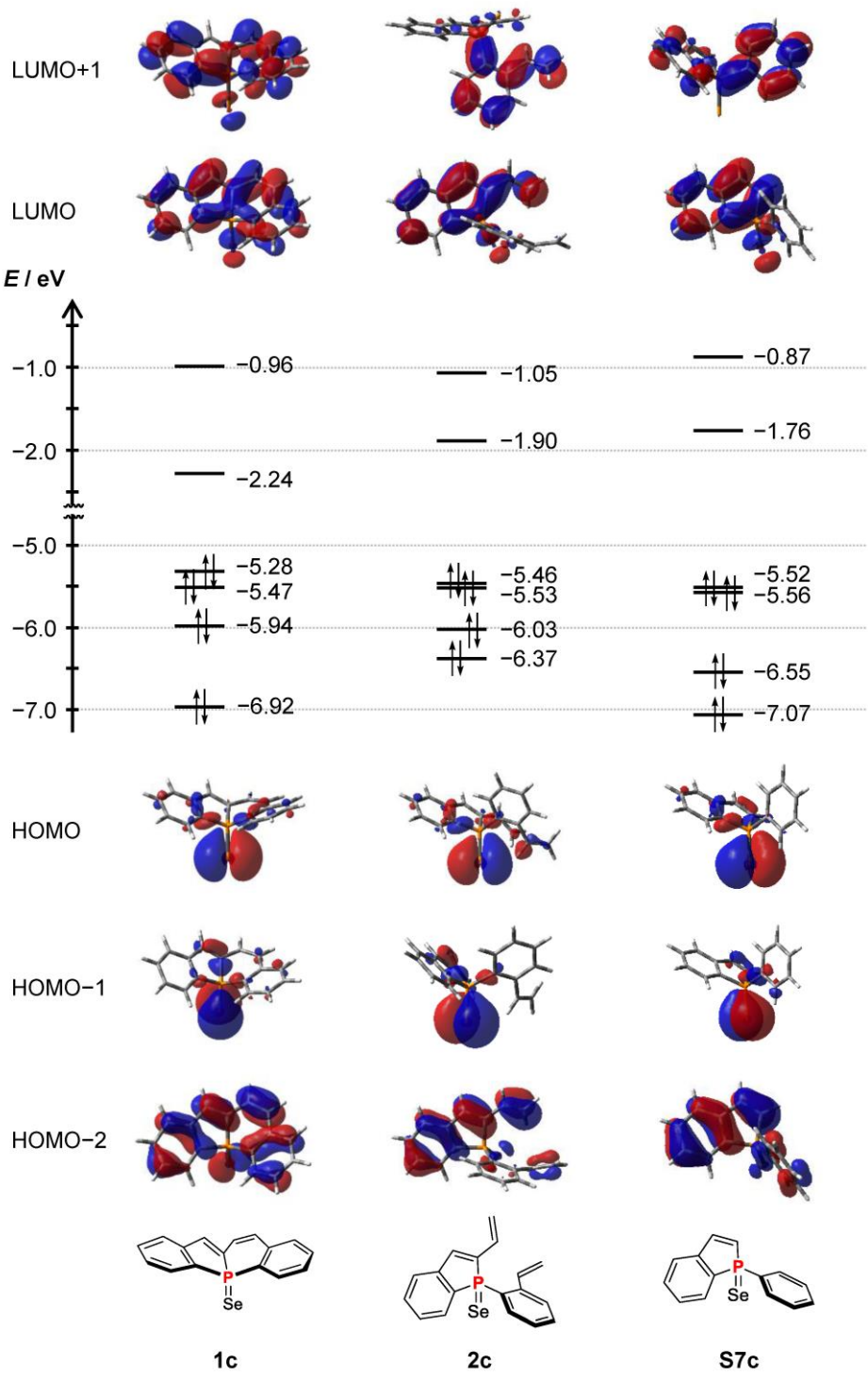


Figure S49. Energy diagram and the selected molecular orbitals of **1c**, **2c**, and **S7c** (isovalue = 0.03).

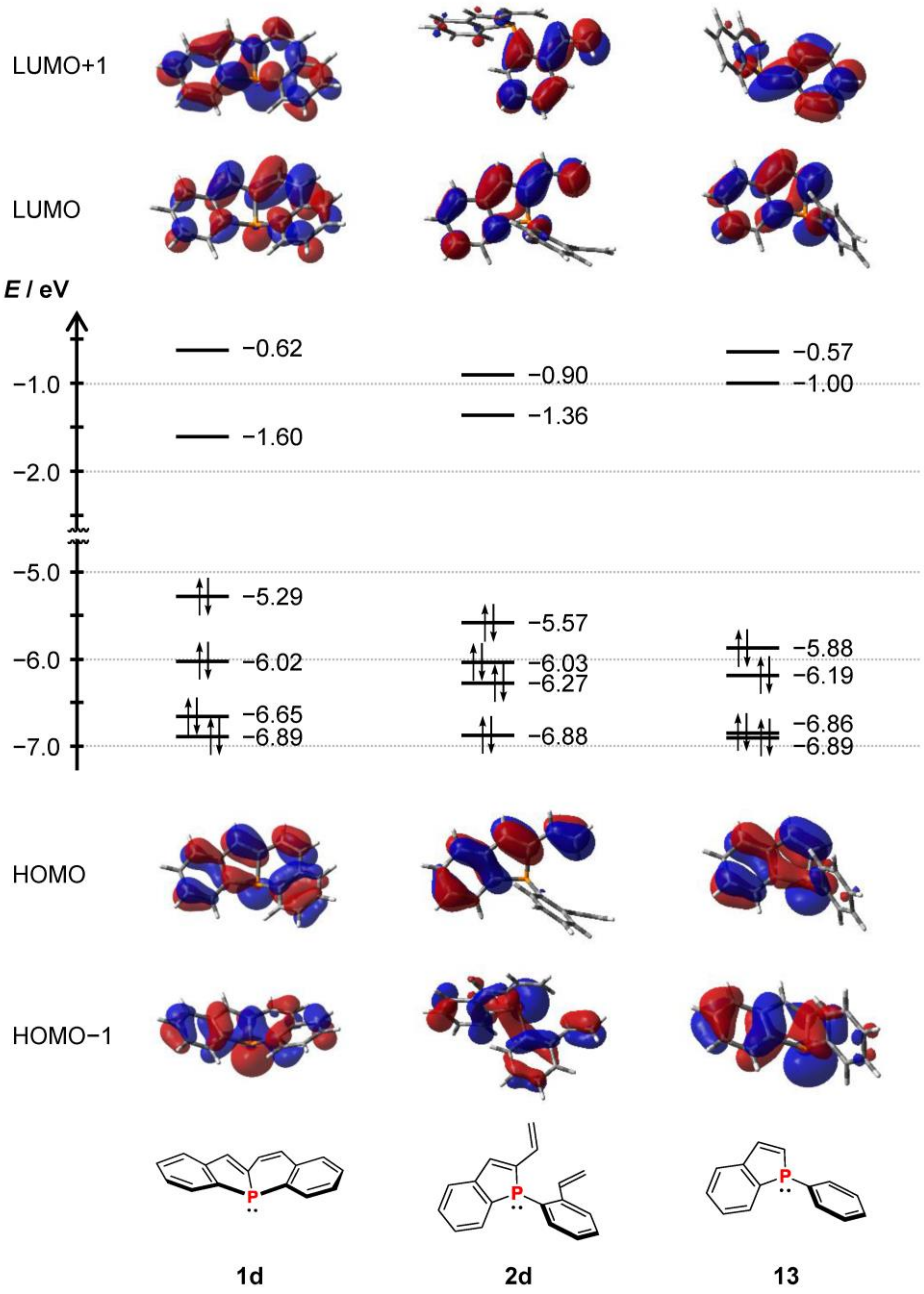


Figure S50. Energy diagram and the selected molecular orbitals of **1d**, **2d**, and **13** (isovalue = 0.03).

Table S10. Transition energies, wavelengths, and oscillator strengths (*f*) of the transitions of **1a**–**d** longer than 250 nm (9 states for **1a**, 14 states for **1b**, 15 states for **1c**, and 10 states for **1d**).

1a: The 65th orbital is the HOMO, and the 66th orbital is the LUMO.

Excited State 1: Singlet-A
2.8309 eV 437.97 nm f=0.1381
65 -> 66 0.70069
Excited State 2: Singlet-A
3.8207 eV 324.50 nm f=0.0965
64 -> 66 0.66179
65 -> 68 -0.11646
Excited State 3: Singlet-A
3.8999 eV 317.92 nm f=0.0219
61 -> 66 0.12015
63 -> 66 0.62836
65 -> 67 -0.28402
Excited State 4: Singlet-A
4.1566 eV 298.28 nm f=0.0280
60 -> 66 -0.11053
61 -> 66 0.29252
62 -> 66 0.57085
64 -> 66 0.15375
65 -> 67 0.16066
65 -> 68 -0.10235
Excited State 5: Singlet-A
4.2385 eV 292.52 nm f=0.2536
60 -> 66 0.37799
62 -> 66 -0.14780
63 -> 66 0.20309
65 -> 67 0.52033
Excited State 6: Singlet-A
4.3348 eV 286.02 nm f=0.0382
61 -> 66 0.56578
62 -> 66 -0.19626
63 -> 66 -0.12789
64 -> 67 0.11148
65 -> 68 0.10632
65 -> 69 0.28510
Excited State 7: Singlet-A
4.4280 eV 280.00 nm f=0.1970
60 -> 66 0.55617
62 -> 66 0.13707
63 -> 66 -0.17560
65 -> 67 -0.30477
65 -> 69 -0.17662
Excited State 8: Singlet-A
4.5755 eV 270.97 nm f=0.1268
61 -> 66 -0.13544
62 -> 66 0.18896
65 -> 68 0.61898
65 -> 69 0.14315
Excited State 9: Singlet-A
4.7889 eV 258.90 nm f=0.1773
60 -> 66 0.12664
61 -> 66 -0.15065
62 -> 66 0.17388
64 -> 66 -0.11680
64 -> 67 -0.13981
65 -> 68 -0.20564
65 -> 69 0.57132

1b: The 69th orbital is the HOMO, and the 70th orbital is the LUMO.

Excited State 1: Singlet-A
2.8214 eV 439.44 nm f=0.0758
68 -> 70 -0.14825
69 -> 70 0.68473
Excited State 2: Singlet-A
3.1317 eV 395.90 nm f=0.0664
67 -> 70 -0.18819
68 -> 70 0.66341
69 -> 70 0.11979
Excited State 3: Singlet-A
3.2717 eV 378.96 nm f=0.0549
67 -> 70 0.67483
68 -> 70 0.16661
Excited State 4: Singlet-A
3.9204 eV 316.25 nm f=0.0623
65 -> 70 0.10404
66 -> 70 0.66147
69 -> 72 -0.12364
69 -> 73 0.13418
Excited State 5: Singlet-A
4.0042 eV 309.64 nm f=0.0697
64 -> 70 0.11403
65 -> 70 0.30020
66 -> 70 -0.11876
69 -> 71 0.60552
Excited State 6: Singlet-A
4.2170 eV 294.01 nm f=0.0533
64 -> 70 -0.27516
65 -> 70 0.41724
68 -> 71 -0.11156
69 -> 71 -0.14993
69 -> 72 -0.37853
69 -> 73 -0.19268
Excited State 7: Singlet-A
4.3120 eV 287.54 nm f=0.1204
64 -> 70 0.40006
65 -> 70 0.34673
67 -> 71 0.17443
68 -> 71 0.24729
69 -> 71 -0.23300
69 -> 73 0.22261
Excited State 8: Singlet-A
4.3831 eV 282.87 nm f=0.0119
64 -> 70 -0.31327
65 -> 70 0.10977
68 -> 71 0.56569
69 -> 72 0.18050
69 -> 73 -0.10851
Excited State 9: Singlet-A
4.4457 eV 278.88 nm f=0.2484

65 -> 70 0.26986
67 -> 71 -0.21795
68 -> 71 -0.27567
69 -> 71 -0.16081
69 -> 72 0.48715
Excited State 10: Singlet-A
4.5761 eV 270.94 nm f=0.0409
64 -> 70 -0.21287
67 -> 71 0.60840
68 -> 72 0.11922
69 -> 72 0.20010
Excited State 11: Singlet-A
4.6589 eV 266.12 nm f=0.1042
64 -> 70 -0.23517
66 -> 70 -0.10015
67 -> 71 -0.15703
67 -> 73 -0.11406
68 -> 72 0.37007
69 -> 73 0.48491
Excited State 12: Singlet-A
4.7634 eV 260.29 nm f=0.1104
64 -> 70 0.12332
66 -> 71 -0.13917
67 -> 72 -0.24092
68 -> 72 0.53135
69 -> 73 -0.30303
Excited State 13: Singlet-A
4.8538 eV 255.44 nm f=0.0421
66 -> 71 -0.12110
67 -> 72 0.57717
68 -> 72 0.16323
68 -> 73 -0.27829
69 -> 73 -0.15569
Excited State 14: Singlet-A
4.8907 eV 253.51 nm f=0.0186
67 -> 72 0.29227
68 -> 73 0.62701

1c: The 78th orbital is the HOMO, and the 79th orbital is the LUMO.

Excited State 1: Singlet-A
2.6549 eV 466.99 nm f=0.0081
77 -> 79 -0.14640
78 -> 79 0.68578
Excited State 2: Singlet-A
2.8542 eV 434.39 nm f=0.0424
76 -> 79 0.27855
77 -> 79 0.63680
78 -> 79 0.10615
Excited State 3: Singlet-A
3.0657 eV 404.43 nm f=0.1306
76 -> 79 0.64157
77 -> 79 -0.25429
78 -> 79 -0.11994
Excited State 4: Singlet-A
3.8459 eV 322.38 nm f=0.0443
74 -> 79 0.15456
75 -> 79 -0.12193
78 -> 80 0.65830
Excited State 5: Singlet-A
3.9171 eV 316.52 nm f=0.0761
75 -> 79 0.65347
78 -> 80 0.13530
78 -> 81 0.11283
78 -> 82 0.13400
Excited State 6: Singlet-A
4.0537 eV 305.86 nm f=0.0212
77 -> 80 0.61513
78 -> 81 0.29588
Excited State 7: Singlet-A
4.1369 eV 299.70 nm f=0.0077
74 -> 79 0.45943
76 -> 80 -0.36838
77 -> 80 0.17955
78 -> 81 -0.30778
Excited State 8: Singlet-A
4.2039 eV 294.93 nm f=0.0084
73 -> 79 0.41205
74 -> 79 -0.13782
76 -> 80 -0.35770
77 -> 80 -0.16702
78 -> 81 0.22688
78 -> 82 -0.26320
Excited State 9: Singlet-A
4.3317 eV 286.22 nm f=0.1701
73 -> 79 -0.17343
74 -> 79 0.30279
75 -> 79 -0.10118
76 -> 80 -0.15515
76 -> 81 0.17140
77 -> 80 -0.13855
77 -> 81 -0.11240
78 -> 81 0.46621
78 -> 82 0.20122
Excited State 10: Singlet-A
4.3447 eV 285.37 nm f=0.1600
73 -> 79 0.18799
74 -> 79 0.31967
76 -> 80 0.36093
76 -> 81 0.11634
77 -> 81 0.37687
78 -> 80 -0.14190
78 -> 82 -0.14816
Excited State 11: Singlet-A
4.3910 eV 282.36 nm f=0.0767
73 -> 79 -0.31038
74 -> 79 -0.12836
76 -> 80 -0.23690
76 -> 81 0.15283
77 -> 81 0.52587
Excited State 12: Singlet-A
4.4880 eV 276.26 nm f=0.0498
73 -> 79 0.28041
76 -> 81 0.20957
77 -> 82 -0.33684
78 -> 82 0.47294
Excited State 13: Singlet-A
4.5822 eV 270.58 nm f=0.1229
76 -> 81 0.59423
76 -> 82 -0.13557
77 -> 81 -0.17583

78 -> 82 -0.22018

Excited State 14: Singlet-A
4.6216 eV 268.27 nm f=0.0569
73 -> 79 0.17650
76 -> 82 0.20406
77 -> 82 0.59098
78 -> 82 0.19339

Excited State 15: Singlet-A
4.8495 eV 255.66 nm f=0.1099
73 -> 79 -0.10758
75 -> 80 -0.15788
76 -> 82 0.63255
77 -> 82 -0.11995
78 -> 82 -0.14182

1d: The 61th orbital is the HOMO, and the 62th orbital is the LUMO.

Excited State 1: Singlet-A
3.0949 eV 400.60 nm f=0.2421
61 -> 62 0.69806

Excited State 2: Singlet-A
3.6436 eV 340.28 nm f=0.0260
60 -> 62 0.60889
61 -> 63 -0.31749
61 -> 64 0.14579

Excited State 3: Singlet-A
3.8209 eV 324.49 nm f=0.0584
60 -> 62 0.28184
61 -> 63 0.60756
61 -> 64 0.16381

Excited State 4: Singlet-A
4.1451 eV 299.11 nm f=0.1254
58 -> 62 -0.17594
60 -> 62 -0.19217
61 -> 64 0.62639

Excited State 5: Singlet-A
4.2268 eV 293.33 nm f=0.0211
58 -> 62 -0.11606
59 -> 62 0.48281
61 -> 64 -0.13950
61 -> 65 -0.45962

Excited State 6: Singlet-A
4.4546 eV 278.33 nm f=0.0636
58 -> 62 0.43366
59 -> 62 0.36313
60 -> 63 0.21110
61 -> 65 0.28727
61 -> 66 0.11064

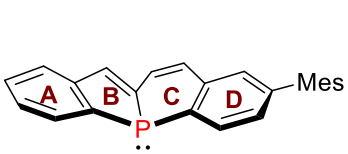
Excited State 7: Singlet-A
4.4923 eV 275.99 nm f=0.0737
58 -> 62 -0.39615
59 -> 62 0.26479
60 -> 63 -0.25318
60 -> 65 0.13434
61 -> 65 0.40044

Excited State 8: Singlet-A
4.6403 eV 267.19 nm f=0.5213
58 -> 62 -0.24668
59 -> 64 0.11398
60 -> 63 0.58286
61 -> 64 -0.13493
61 -> 65 0.10426
61 -> 66 -0.12939

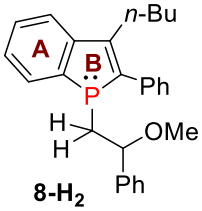
Excited State 9: Singlet-A
4.8400 eV 256.17 nm f=0.0896
60 -> 64 0.66990
61 -> 66 0.13789

Excited State 10: Singlet-A
4.9393 eV 251.01 nm f=0.0942
58 -> 62 0.16076
59 -> 63 -0.10708
60 -> 64 0.10517
60 -> 65 0.44649
61 -> 66 -0.44048
61 -> 67 -0.16912

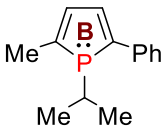
Table S11. The calculated inversion barriers ΔG_{298} (kcal mol^{-1}) and NICS(0) values of dibenzo[*b*,*e*]phosphindolizine **7d**, benzo[*b*]phosphole **8-H$_2$**, and phosphole **9**.



7d



8-H$_2$



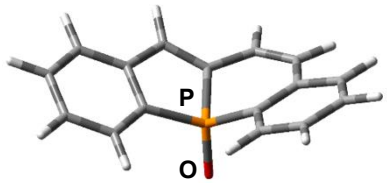
9

	7d	**8-H$_2$**	**9**
ΔG_{298} /kcal mol^{-1}	16.8	25.8	18.5
NICS(0)[a]			
ring **A**	−7.86	−7.67	–
	(−9.27)	(−7.89)	
ring **B**	−2.54	−1.93	−4.51
	(−17.21)	(−13.87)	(−14.03)
ring **C**	+2.46	–	–
	(−6.23)		
ring **D**	−6.77	–	–
	(−8.06)		

a) The NICS values of the transition state (planar geometry) are described in parentheses.

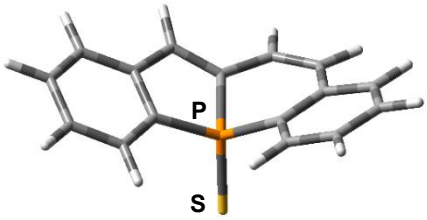
Table S12. Atomic coordinates of the optimized structures.

1a



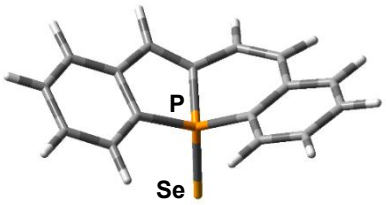
C	0.19861800	1.77812800	0.09846900
C	1.40459200	1.90009200	-0.50418700
C	2.26290700	0.70407700	-0.43620400
C	1.65625300	-0.39912000	0.21142100
H	1.70829600	2.76644100	-1.08971000
C	-1.43533700	-0.45033700	0.10107400
C	-1.70677700	-1.81367100	-0.03827000
C	-2.43028000	0.51462800	-0.22286900
C	-2.94681400	-2.25259300	-0.50512400
H	-0.94365500	-2.54182900	0.22462600
C	-3.68034400	0.04608700	-0.66209900
C	-3.93610200	-1.31602700	-0.80748600
H	-3.14074600	-3.31489300	-0.62243900
H	-4.45696700	0.76795000	-0.90342000
H	-4.91014300	-1.64589800	-1.15851100
C	-1.00433000	2.57680900	-0.03942600
H	-0.93355500	3.65984500	-0.11969200
C	-2.20780500	1.96766800	-0.15975600
H	-3.09192900	2.58296500	-0.31049900
C	2.34143000	-1.59520800	0.36618200
C	3.63145400	-1.72077800	-0.17257500
H	4.16966500	-2.65902900	-0.07217700
C	4.22443300	-0.64437900	-0.83235700
H	5.22497800	-0.74862400	-1.24321900
C	3.54791800	0.57455600	-0.96346000
H	4.02082000	1.41288200	-1.46911100
H	1.89068600	-2.42833300	0.89883700
P	0.06731000	0.15678400	0.92506600
O	-0.00824900	0.07214500	2.42366600

1b



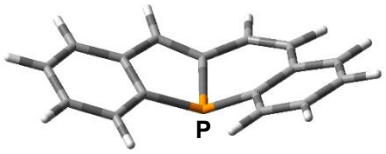
C	0.19826500	1.77297300	-0.13064800
C	1.40470300	1.88473200	-0.73425700
C	2.26110900	0.69373500	-0.64654400
C	1.66132600	-0.39570300	0.02999400
H	1.70620300	2.74528300	-1.32866700
C	-1.43875200	-0.45542600	-0.07736300
C	-1.70302700	-1.82144700	-0.19349000
C	-2.42804800	0.50370100	-0.42944800
C	-2.93621600	-2.26934900	-0.66920900
H	-0.94358900	-2.54226200	0.09741500
C	-3.67226500	0.02420800	-0.87387200
C	-3.92405100	-1.34037500	-0.99920500
H	-3.12651500	-3.33395600	-0.76985300
H	-4.44701400	0.74093200	-1.13539400
H	-4.89365500	-1.67825600	-1.35451700
C	-1.00582300	2.56749800	-0.27669100
H	-0.93321600	3.64887100	-0.37293200
C	-2.20869900	1.95673200	-0.38728000
H	-3.09339300	2.56898300	-0.54563900
C	2.34246900	-1.59099500	0.20781200
C	3.62521600	-1.73088500	-0.34077500
H	4.16151300	-2.66849400	-0.22608300
C	4.21695500	-0.66857800	-1.02657300
H	5.21462100	-0.78418200	-1.44120100
C	3.54470500	0.54905800	-1.17663400
H	4.01784600	1.37682200	-1.69891400
H	1.89496200	-2.40587600	0.77009300
P	0.07078000	0.16852200	0.73725800
S	-0.01541700	0.10781500	2.70574500

1c



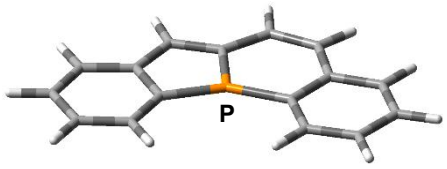
C	-0.19360300	-0.57781200	1.74124600	C	1.00977200	-0.76771700	2.52803900
C	-1.39238700	-1.20343600	1.81340600	H	0.93453500	-0.92666900	3.60181000
C	-2.25168400	-1.04904300	0.63298700	C	2.21317900	-0.84398700	1.91388200
C	-1.65981600	-0.29691500	-0.40945600	H	3.09717600	-1.03823100	2.51674800
H	-1.68370500	-1.85469800	2.63541100	C	-2.35123200	-0.02670700	-1.58139000
C	1.44523300	-0.38608800	-0.47439600	C	-3.63076400	-0.57138900	-1.75497200
C	1.71353500	-0.41259800	-1.84443600	H	-4.17425900	-0.38872000	-2.67755800
C	2.43314300	-0.79812300	0.46168100	C	-4.21310500	-1.33783100	-0.74289600
C	2.94672200	-0.86032900	-2.31941100	H	-5.20980000	-1.74702800	-0.88358600
H	0.95674200	-0.07307100	-2.54641900	C	-3.53504400	-1.57160500	0.45777100
C	3.67857300	-1.21109300	-0.04288100	H	-4.00370300	-2.15036100	1.24973600
C	3.93295100	-1.25010400	-1.41183300	H	-1.91170800	0.60386900	-2.34927100
H	3.13881900	-0.89230400	-3.38797200	P	-0.07258700	0.38370300	0.18944300
H	4.45206300	-1.51642300	0.65771400	Se	-0.00832900	2.49413000	0.18551900
H	4.90299300	-1.58368300	-1.76997000				

1d



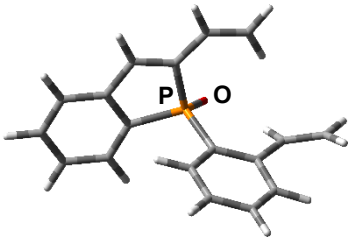
C	0.23869900	1.74526900	0.23015100	H	-5.00975200	-1.54161400	-0.93432500
C	1.49738400	1.91701100	-0.26362500	C	-0.94575400	2.56121200	0.07838900
C	2.31600600	0.71525000	-0.22430000	H	-0.84276600	3.63639100	-0.05989400
C	1.64002100	-0.42557800	0.30124500	C	-2.17184900	1.98957600	-0.02532200
H	1.85166200	2.83639700	-0.72492400	H	-3.03259600	2.63300500	-0.19465200
C	-1.46673300	-0.44036200	0.24594200	C	2.29438600	-1.65376300	0.39166300
C	-1.78695200	-1.79581400	0.12371100	C	3.59731600	-1.77788800	-0.09649300
C	-2.44364800	0.54883400	-0.06118700	H	4.09576600	-2.74289900	-0.06716200
C	-3.04737300	-2.19800400	-0.31879200	C	4.26620100	-0.66171800	-0.61557500
H	-1.04239700	-2.54824600	0.37253500	H	5.28676800	-0.76563400	-0.97456400
C	-3.71826100	0.11412100	-0.47072700	C	3.64109900	0.58189000	-0.66754100
C	-4.01960600	-1.23758100	-0.60623500	H	4.17309600	1.44774800	-1.05429700
H	-3.27127100	-3.25566200	-0.42785900	H	1.79443200	-2.51658500	0.82497000
H	-4.47491600	0.86077100	-0.70113600	P	0.07509000	0.13744000	1.05423300

1d-TS



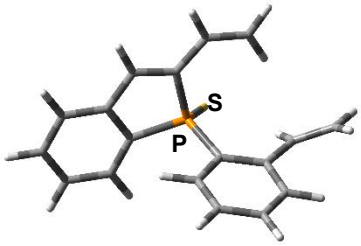
C	0.32264400	1.68313100	-0.00000100	H	-5.44537300	-1.17989300	0.00000100
C	1.69424800	1.90895800	-0.00000100	C	-0.84451500	2.51400700	0.00000000
C	2.47655000	0.71211000	0.00000000	H	-0.71164200	3.59423700	0.00000000
C	1.74439600	-0.54164100	0.00000000	C	-2.11640400	2.01017700	0.00000100
H	2.14652000	2.89556200	-0.00000100	H	-2.93788500	2.72256700	0.00000100
C	-1.61796700	-0.50107100	0.00000000	C	2.41051400	-1.78189400	0.00000000
C	-2.10607600	-1.82243600	-0.00000100	C	3.79273100	-1.80327400	0.00000100
C	-2.52322500	0.61629700	0.00000100	H	4.31587900	-2.75537300	0.00000100
C	-3.47044700	-2.06380400	-0.00000100	C	4.53108600	-0.59617000	0.00000000
H	-1.40788500	-2.65454700	-0.00000200	H	5.61700300	-0.63566000	0.00000100
C	-3.90422500	0.31172600	0.00000100	C	3.89133500	0.62722100	0.00000000
C	-4.37595300	-0.99056100	0.00000000	H	4.46810700	1.54928300	0.00000000
H	-3.83548200	-3.08696900	-0.00000100	H	1.84671500	-2.71038100	0.00000100
H	-4.60821200	1.14052600	0.00000200	P	0.07494100	-0.03840000	0.00000000

2a



C	-0.57071600	1.75452900	0.75865700	H	-4.13040400	-2.33682600	-1.74416900
C	-1.84670000	1.52388300	1.15730800	C	-4.44919300	-0.93734100	-0.13673300
C	-2.57935900	0.47091000	0.44385800	H	-5.47942100	-1.24435400	0.02246900
C	-1.81278800	-0.16567000	-0.55604800	C	-3.90211500	0.07722200	0.65663500
H	-2.32635600	2.08905200	1.95509600	H	-4.50144100	0.55633700	1.42695100
C	1.02075500	-0.64441100	0.06463300	H	-1.76596300	-1.64622700	-2.12108500
C	0.51935200	-1.54041400	1.02387500	P	-0.15199900	0.59788300	-0.62472000
C	1.33468800	-2.49490900	1.62435400	O	0.25664700	1.20552000	-1.93732300
H	-0.52871000	-1.49395700	1.30371300	C	2.39239400	-0.70391700	-0.29755000
C	3.18920700	-1.69496300	0.30803800	C	1.54795400	3.05550800	0.89788400
C	2.67875000	-2.57299800	1.25684600	H	2.01766100	2.54565800	0.06214800
H	0.92094900	-3.17912000	2.35979200	H	2.12975100	3.83488300	1.38085200
H	4.22618800	-1.78526200	-0.00022800	C	3.00467500	0.21288600	-1.28475000
H	3.32541000	-3.32674500	1.69837000	H	2.33990700	0.60707100	-2.04683300
C	0.30732400	2.76468400	1.32049300	C	4.28767200	0.59920100	-1.26880600
H	-0.11035900	3.32767500	2.15662600	H	4.98840300	0.29053000	-0.49653600
C	-2.35831200	-1.16812000	-1.34549400	H	4.67645600	1.26389100	-2.03490200
C	-3.68946600	-1.55525100	-1.13201100				

2b



C	-0.49780300	-1.48396100	-1.17160200	H	-4.26925200	1.96666800	1.91488900
C	-1.76444600	-1.20313200	-1.57141800	C	-4.48699100	0.89897700	0.05473800
C	-2.55323000	-0.32445200	-0.70842500	H	-5.52009100	1.20600000	-0.08375900
C	-1.84654200	0.12561700	0.42617100	C	-3.88190100	0.06863000	-0.89311900
H	-2.19242300	-1.61883200	-2.48210000	H	-4.43921100	-0.27293600	-1.76178600
C	0.99466300	0.78389000	0.02775800	H	-1.90523700	1.25615000	2.25962600
C	0.41722700	1.88073600	-0.63715200	P	-0.16862800	-0.60761000	0.43370500
C	1.17854300	2.96941400	-1.05256600	C	2.39369100	0.78539500	0.27723100
H	-0.64854600	1.88714400	-0.83626700	C	1.66327000	-2.68545100	-1.53169600
C	3.13425700	1.91012500	-0.13592600	H	2.12976800	-2.32422900	-0.62124500
C	2.54834700	2.98392100	-0.79556000	H	2.25734200	-3.35078900	-2.15105700
H	0.69953800	3.80192400	-1.56009700	C	3.11802700	-0.30772000	0.96119900
H	4.19364600	1.93852100	0.09860600	H	2.58544900	-0.82311300	1.75348100
H	3.15648500	3.83395700	-1.09313700	C	4.36445600	-0.69280900	0.65669600
C	0.41469500	-2.35247500	-1.89243100	H	4.93016200	-0.25607000	-0.16311100
H	0.00855900	-2.76422400	-2.81768700	H	4.85465300	-1.48366000	1.21723100
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C	-3.78225700	1.32973700	1.18203600				

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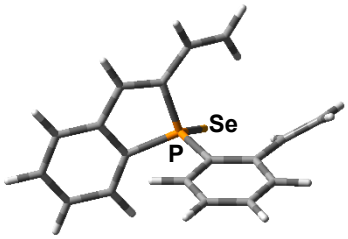

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C	-0.90823800	1.04815000	-0.15238400	C	3.88708000	0.89021800	-1.38087100
C	-0.25399100	2.27844100	0.03743800	H	4.42132900	1.16695000	-2.28522800
C	-0.95152400	3.48282700	0.05792500	C	4.53887200	0.93208500	-0.14528300
H	0.82134900	2.30067100	0.17037300	H	5.57814900	1.24556700	-0.09603500
C	-2.99512400	2.26900400	-0.31124100	C	3.87465400	0.56282100	1.02825900
C	-2.33367600	3.47631300	-0.12087300	H	4.39323300	0.58252600	1.98350900
H	-0.41412700	4.41596600	0.20157600	H	2.04120900	0.42819400	-2.41864800

P	0.17458700	-0.46412200	-0.07439200
C	-2.32002400	1.03273100	-0.31803700
C	-1.58661400	-2.02998100	2.33397100
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H	-2.25475500	-2.42235100	3.09469700
C	-3.12184400	-0.19370100	-0.51519700
H	-2.65416900	-0.99136500	-1.08347900
C	-4.35770100	-0.37235700	-0.03201000
H	-4.85546300	0.36351700	0.59527900
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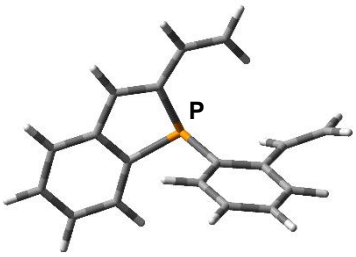

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C	1.04853600	-0.52654400	0.07667600
C	0.63127300	-1.24507800	1.20810500
C	1.50610300	-2.07921200	1.89784400
H	-0.39388200	-1.14494600	1.55182100
C	3.25276300	-1.50719700	0.33589900
C	2.82470500	-2.21101300	1.45474300
H	1.16083600	-2.62769900	2.77016400
H	4.26882000	-1.63853100	-0.02424400
H	3.51395300	-2.87187200	1.97390700
C	0.24055900	2.92596600	0.93576600
H	-0.21733300	3.57284800	1.68604600
C	-2.25632500	-1.36670900	-1.23327900
C	-3.57961700	-1.75806200	-1.00732000
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C	-3.93298100	0.16048300	0.43725500
H	-4.58411800	0.75413500	1.07448100
H	-1.61966700	-1.95631900	-1.88841900
P	-0.13882100	0.59538600	-0.81748600
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H	2.01923700	2.58323700	-0.19336400
H	2.05603900	4.01260300	0.97576200
C	2.88919900	0.09399800	-1.54505700
H	2.14738700	0.35044700	-2.29827500
C	4.15546700	0.48460200	-1.74102700
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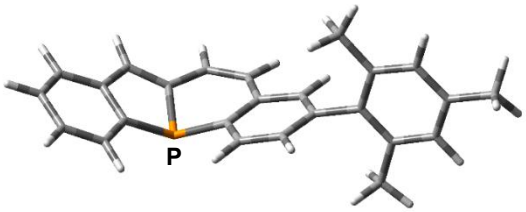
7d



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C	1.01542700	-1.06756700	-0.75830100
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C	-4.34913400	-1.83397500	-0.88197400
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H	-7.21279000	-2.29852400	0.90488300
C	-6.00377600	-0.52356400	0.98289700
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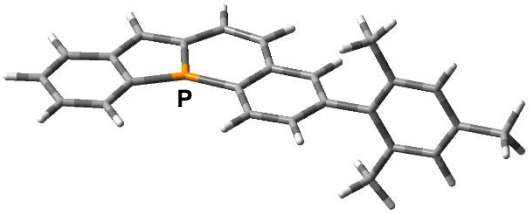
7d-TS



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C	1.18397000	-1.35777700	0.08121100
H	-0.75097800	-2.27733600	0.13505500
C	1.22785000	1.04310800	-0.05919500
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C	-6.51839300	0.10949800	-0.00753700
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C	3.39535300	-0.44260900	-2.52116400
H	2.73877100	-1.32059200	-2.54447400
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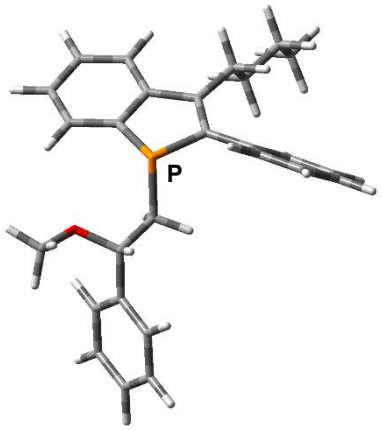
8-H_2



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H	3.59322500	-2.94568200	0.11621100	H	5.55262700	-1.09355000	3.66138000
H	0.12636700	-5.37680600	-0.62716000	H	6.82720300	0.12511100	3.49860300
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C	2.28797500	-0.47821700	-0.45548200	H	-1.27761500	1.18236200	0.08348300
C	1.34186300	0.42712800	-0.84840900	H	-1.23989600	-0.42668500	0.81850500
C	-0.14160200	-3.26287700	-0.95317200	C	-2.87916700	-0.10168700	-0.56933600
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C	2.08352600	4.03851400	0.06978700	H	-4.11504400	-2.84047600	-1.92508400
H	2.27461700	2.14114100	1.06148700	H	-5.07539600	-1.58429200	-1.09599400
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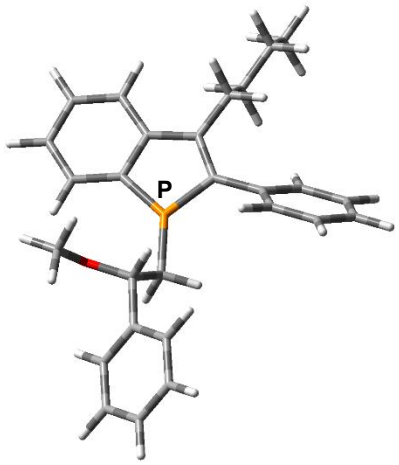

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C	1.13342800	-4.41799200	0.09952700	H	6.96746100	1.05373600	1.93959000
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H	3.16378700	-4.97823700	-0.40367300	C	-1.82577700	-0.00143700	0.69228300
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C	2.15026300	2.78141500	0.52436800	C	-4.75216300	1.22956500	-0.56343700
C	0.18458200	4.00297700	-1.02866300	C	-6.27940100	-0.08231700	1.36264800
H	-0.44147000	2.00356400	-1.52675000	H	-4.66098900	-1.50863900	1.44164100
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H	-0.58137500	4.47199000	-1.64115600	H	-6.87480800	-0.60044200	2.10988400
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C	4.80252800	0.04103700	0.42535000	H	-2.95875500	-2.14577800	-2.40429000
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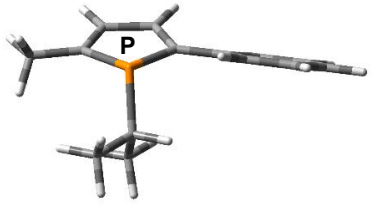

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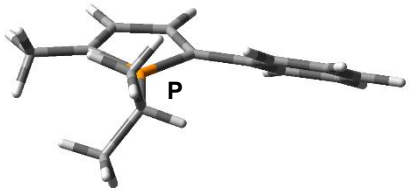
C	-1.71722100	-2.18015600	0.08266100	C	-3.87326600	-0.94773900	-0.49133300
C	-0.27594700	-2.04794500	0.16752300	H	-4.36972600	-1.89259100	-0.24231300
C	0.21352100	-0.81841100	-0.17129000	H	-4.30477400	-0.16793700	0.15151500
H	-2.21680000	-3.12255200	0.30303000	H	-4.14117000	-0.68850100	-1.52335200
H	0.35715400	-2.88834100	0.44430200	C	1.61716200	-0.39280500	-0.14152300
P	-1.16764800	0.20480000	-0.80122600	C	2.10317000	0.59857100	-1.01656000
C	-1.30185800	1.62054000	0.45397800	C	2.52219100	-0.95345200	0.78261800
H	-0.32610300	2.11700500	0.35831300	C	3.43613900	1.00411400	-0.97566000
C	-1.48264000	1.17337700	1.90925800	H	1.43199500	1.03184300	-1.75360300
H	-0.70009600	0.47283700	2.21499200	C	3.85501800	-0.55285900	0.81655200
H	-1.44363600	2.04225700	2.57974700	H	2.16427900	-1.69449700	1.49194100
H	-2.45038400	0.68117000	2.05612300	C	4.32067500	0.42939500	-0.06173300
C	-2.38907700	2.61439800	0.01657500	H	3.78593600	1.76649300	-1.66709200
H	-3.38729800	2.16210500	0.05644000	H	4.53156700	-1.00100500	1.53994100
H	-2.39874900	3.48381200	0.68602000	H	5.35999100	0.74490800	-0.03054800

9-TS



C	-2.30118100	-1.34073600	-0.12565200	H	-1.20597500	2.36165500	-1.83453700
C	-1.48289800	-2.46176400	-0.27294000	C	-3.80398700	-1.33337500	-0.10491100
C	-0.08797400	-2.22986100	-0.26195400	H	-4.18085400	-2.35651500	-0.21111200
C	0.31008900	-0.89681000	-0.11368600	H	-4.20891900	-0.93199200	0.83314100
H	-1.90663700	-3.45471200	-0.39903100	H	-4.23247100	-0.74070200	-0.92371600
H	0.63648700	-3.02720000	-0.39660100	C	1.68229700	-0.37974900	-0.05609400
P	-1.19078200	-0.01120300	0.03459600	C	2.02212100	0.88310100	-0.57694200
C	-1.48975600	1.80721000	0.26704500	C	2.71085800	-1.14679700	0.52457600
H	-0.49572300	2.17373500	0.55456100	C	3.32899400	1.36366000	-0.51160100
C	-2.46680100	2.07153700	1.42595600	H	1.25672200	1.47857700	-1.06874600
H	-2.11040800	1.63140400	2.36127500	C	4.01957900	-0.67232700	0.57596800
H	-2.58263800	3.15267200	1.57192300	H	2.46847000	-2.11412300	0.95496100
H	-3.45954600	1.66025100	1.21171900	C	4.33696500	0.58782900	0.06326400
C	-1.92879300	2.51296500	-1.02754600	H	3.56260500	2.34176200	-0.92488100
H	-2.89908000	2.13820600	-1.37173300	H	4.79386800	-1.28529900	1.03066600
H	-2.02821000	3.59167000	-0.85019100	H	5.35697000	0.95937100	0.11045900

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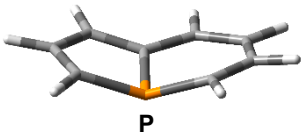

C	0.23163200	0.90154500	0.16592000	H	-1.07092600	2.64297900	0.11573000
C	1.51405900	1.34684000	-0.10499300	C	-2.20239400	0.85091600	-0.05629600
C	2.45235600	0.27985600	-0.27615800	H	-3.13588600	1.40390400	-0.12067900
C	1.94772600	-1.00672600	-0.21408100	P	0.30830900	-0.86236500	0.45822900
H	1.78833900	2.39302200	-0.20786000	H	3.51153000	0.47383800	-0.43018600
C	-1.22766600	-1.44854300	-0.23418400	H	2.55306900	-1.90452800	-0.21602400
C	-2.27942400	-0.57520400	-0.25853100	H	-1.38992000	-2.51112000	-0.38999900
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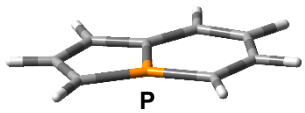

C	-0.26088600	0.92015900	0.00000100	H	1.01366000	2.66183400	-0.00000100
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C	-2.50581900	0.22389300	-0.00000100	H	3.11299400	1.47038000	-0.00000200
C	-1.96246300	-1.08502000	-0.00000100	P	-0.27180500	-0.82372800	0.00000300
H	-1.94732500	2.34458700	-0.00000100	H	-3.58377500	0.36018100	-0.00000100
C	1.32778200	-1.47023300	-0.00000100	H	-2.51245800	-2.01307900	-0.00000100
C	2.34705600	-0.52715600	-0.00000200	H	1.53170100	-2.53434200	-0.00000200
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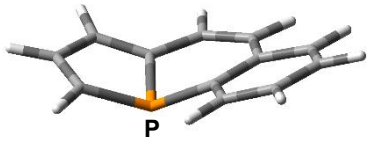

C	1.71173300	0.87546200	0.08910800	C	-3.48062500	-0.08988300	-0.31015300
C	2.94301900	0.58522700	-0.44726400	H	-3.60453000	-2.24733100	-0.34993300
C	3.19412400	-0.83188100	-0.55278200	H	-3.05114900	2.01284600	-0.23217200
C	2.16571900	-1.65603000	-0.16734300	H	-4.54203400	0.05966300	-0.48773300
H	3.64579500	1.33196900	-0.80792900	C	0.93625700	2.08851500	0.09531300
C	-0.73915400	-0.46642500	0.15336700	H	1.44552100	3.04538900	-0.01037400
C	-1.59872900	-1.56455900	0.02521400	C	-0.42313400	2.05861100	0.10488800
C	-1.25577400	0.85843700	0.05146900	H	-0.96162500	3.00284900	0.06313000
C	-2.95648000	-1.38393100	-0.22705300	P	0.98279000	-0.63811100	0.72056800
H	-1.19914200	-2.57154700	0.11729500	H	4.14963300	-1.21494200	-0.90476900
C	-2.64124400	1.00767400	-0.16476300	H	2.24140300	-2.73453200	-0.09604100

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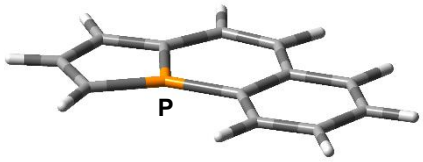

C	-1.73948400	0.88424800	0.00000000	C	3.56824700	-0.04267300	0.00000000
C	-3.11703700	0.59987000	0.00000000	H	3.76617600	-2.20118300	0.00000000
C	-3.40465000	-0.78026500	0.00000000	H	3.07683300	2.04161000	-0.00000100
C	-2.31655300	-1.67742600	0.00000100	H	4.63952600	0.13724600	-0.00000100
H	-3.88795100	1.36330500	0.00000000	C	-0.93461700	2.06059900	0.00000000
C	0.80907400	-0.50725500	0.00000000	H	-1.42898500	3.03060500	-0.00000100
C	1.71323800	-1.58998700	0.00000000	C	0.43722100	2.02441900	-0.00000100
C	1.28315000	0.85151700	0.00000000	H	0.96761700	2.97333500	-0.00000100
C	3.07727400	-1.36134500	0.00000000	P	-0.93836000	-0.64965900	0.00000000
H	1.33224800	-2.60744900	0.00000100	H	-4.42296900	-1.15828100	0.00000100
C	2.69068000	1.02513900	-0.00000100	H	-2.36635100	-2.75535300	0.00000100

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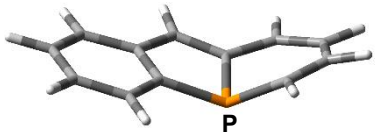
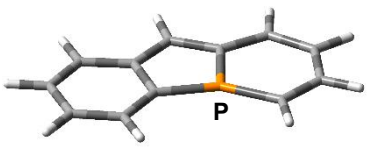


C	-1.09905300	1.00235600	0.28158300	C	2.03405100	-1.44604700	0.06959200
C	0.05515100	1.70399000	0.06772500	C	3.32937400	-0.99786000	-0.18943300
C	1.24202800	0.87410200	-0.00518700	H	4.14042700	-1.71440100	-0.28573500
C	0.98693600	-0.52496500	0.12847300	C	3.58977500	0.37465700	-0.32035800
H	0.09288600	2.77695500	-0.10649200	H	4.60703000	0.71308000	-0.49912200
C	-1.94992600	-1.55722200	-0.33345500	C	2.56371900	1.30730100	-0.21335900
C	-3.13311100	-0.92752900	-0.55775600	H	2.77750200	2.37047900	-0.29252600
C	-2.47312600	1.39045400	0.08467000	H	1.84291400	-2.50798000	0.20323000
H	-2.73523300	2.44729800	0.11087700	P	-0.72780800	-0.72180700	0.70423000
C	-3.41104300	0.47491300	-0.29018900	H	-1.84355500	-2.61714200	-0.54958800
H	-4.42354800	0.81781800	-0.48777900	H	-3.94994400	-1.50390800	-0.99015500

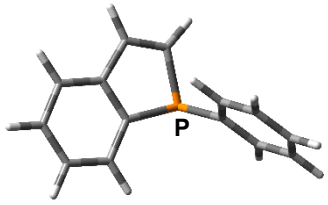
12-TS



C	-1.07134300	1.05737400	0.00000000	C	1.28215300	0.87329000	0.00000000
C	0.14835900	1.73572300	0.00000000	C	1.02132000	-0.55805500	0.00000000

H	0.24168700	2.81677200	-0.00000100	H	4.18937300	-1.77607000	0.00000000
C	-2.14342100	-1.62375700	0.00000000	C	3.65897200	0.33109500	0.00000000
C	-3.33426500	-0.91916000	0.00000000	H	4.69471700	0.66036000	0.00000000
C	-2.44625300	1.42662200	0.00000000	C	2.64763100	1.26727600	0.00000000
H	-2.69868100	2.48563700	0.00000000	H	2.88158400	2.32932700	0.00000000
C	-3.47369500	0.50172300	0.00000000	H	1.84744300	-2.56656200	0.00000000
H	-4.49105400	0.88382700	0.00000000	P	-0.71269900	-0.65370000	0.00000000
C	2.06802800	-1.50281400	0.00000000	H	-2.11496200	-2.70704600	0.00000000
C	3.37415400	-1.05829600	0.00000000	H	-4.24946000	-1.50687400	0.00000000

13



C	-3.34120900	0.02920300	0.81095600	H	-0.97271700	-1.98586200	-1.54844300
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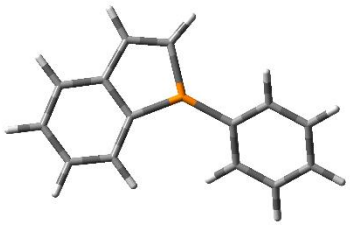
C	-1.30026400	-0.11801800	-0.51460800	C	1.66423600	-0.06096500	1.08332000
C	-2.79319800	-2.00739600	-0.38981100	C	2.70445600	-0.03348200	-1.09841300
C	-3.64859900	-1.28216300	0.44738800	C	2.82661500	-0.60164600	1.62930600
H	-4.01117100	0.59173100	1.45708300	H	0.80753200	0.13922200	1.72076400
H	-3.04224100	-3.02945200	-0.66255100	C	3.87023800	-0.57632000	-0.55088700
H	-4.56115000	-1.74345000	0.81568600	H	2.65869800	0.18953800	-2.16144100
C	-1.65235700	1.95402500	0.63853700	C	3.93213800	-0.86045800	0.81264100
C	-0.46776000	2.25167200	0.06003400	H	2.87257600	-0.82218100	2.69278100
H	0.04603200	3.20103700	0.16863600	H	4.72658500	-0.77476500	-1.19009500
H	-2.20658300	2.63909000	1.27705300	H	4.83783500	-1.28176400	1.24110700
C	-1.62381800	-1.42210300	-0.88479400	P	0.08205200	0.94582000	-1.09265900

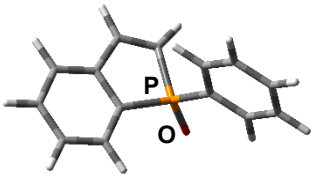
13-TS



C	-0.64060400	2.23722000	-0.25191800	C	4.46455700	-0.68495600	0.04214400
C	-2.00752200	2.07248200	-0.22700100	H	3.74501800	-2.54276000	-0.78627100
C	-2.46238500	0.71818700	-0.07005500	H	4.86904600	1.27003100	0.86071200
C	-1.41311600	-0.25889900	0.03751000	H	5.50270900	-1.00298800	0.07033800
H	-2.70043300	2.90230100	-0.32641300	C	-1.71236000	-1.62293200	0.21026200
C	1.78109400	0.13705800	-0.02858200	C	-3.03810100	-2.02027800	0.26752800
C	2.14641400	-1.14192600	-0.49089900	H	-3.27720200	-3.07190800	0.40130700
C	3.47706000	-1.55004900	-0.43475600	C	-4.08128500	-1.07546500	0.15606100
H	1.39387700	-1.80650300	-0.90476900	H	-5.11407700	-1.40992200	0.20208800
C	4.10852500	0.59198900	0.48288800	C	-3.79909400	0.26949900	-0.00751000

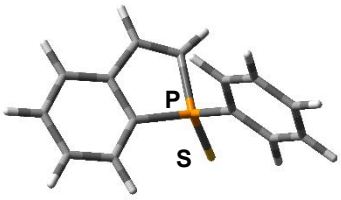
H	-4.60519500	0.99550800	-0.08780600	H	-0.11202500	3.17272400	-0.37494200
H	-0.91569600	-2.35586000	0.30397000	C	2.77672500	0.99937200	0.46871700
P	0.07388500	0.65617200	-0.07575200	H	2.50625200	1.97898700	0.85172900

S7a



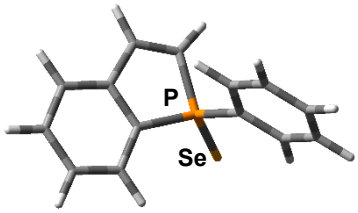
C	-3.32424100	-0.52566400	0.86234700	C	1.57289400	0.14165000	-0.02021000
C	-2.15294100	0.21478000	0.71266800	C	1.61189500	-0.85038000	0.97082700
C	-1.35018900	0.04054200	-0.43433100	C	2.70575100	0.38026100	-0.80808000
C	-2.90008700	-1.59420100	-1.27810200	C	2.77291600	-1.59575900	1.16808400
C	-3.69249800	-1.43034300	-0.14133800	H	0.73753700	-1.04114100	1.58790900
H	-3.94640900	-0.40115200	1.74540200	C	3.86744900	-0.36817000	-0.60704500
H	-3.20115800	-2.29508900	-2.05164900	H	2.66206200	1.15182400	-1.57111900
H	-4.60665700	-2.00781300	-0.03358300	C	3.90163400	-1.35481500	0.37905200
C	-1.61435300	1.22246100	1.65108900	H	2.79899000	-2.36402600	1.93630300
C	-0.46417400	1.80927400	1.27582600	H	4.74426200	-0.17976700	-1.22078300
H	0.06121300	2.57232900	1.83876000	H	4.80609500	-1.93699700	0.53496900
H	-2.14359400	1.45322500	2.57358800	P	0.09311200	1.16730900	-0.34131200
C	-1.71683100	-0.85554700	-1.42849600	O	0.31119600	2.13945400	-1.46477300
H	-1.10194600	-0.98119800	-2.31569000				

S7b



C	-3.33296300	-1.02647600	0.60506300	C	1.56167100	-0.07757600	0.08325600
C	-2.16107100	-0.29038500	0.78092600	C	1.54358100	-1.37090000	0.62810200
C	-1.35859500	0.02467000	-0.33607700	C	2.71017100	0.38708000	-0.56488600
C	-2.89717500	-1.11821300	-1.78367200	C	2.66687300	-2.18849000	0.52081000
C	-3.69371700	-1.43893800	-0.68256000	H	0.65571100	-1.73870600	1.13501700
H	-3.96009000	-1.27452000	1.45788000	C	3.83362500	-0.43580700	-0.66935200
H	-3.19374300	-1.43914000	-2.77822100	H	2.71411300	1.39053400	-0.98091900
H	-4.60640100	-2.01073600	-0.82624000	C	3.81347400	-1.72138400	-0.12814600
C	-1.62673300	0.24017800	2.04884700	H	2.64856800	-3.18929500	0.94379400
C	-0.47109000	0.92147000	1.95106500	H	4.72354800	-0.06927900	-1.17369600
H	0.05737600	1.39892700	2.76765500	H	4.68879200	-2.36031500	-0.20978700
H	-2.16149000	0.08597000	2.98368100	P	0.08528300	1.01418800	0.21402900
C	-1.71853500	-0.37867300	-1.61401200	S	0.31510900	2.80943600	-0.56841400
H	-1.10446500	-0.11657200	-2.47117000				

S7c



C	-3.46525700	-1.25632400	0.49605100	C	1.46829600	-0.58388300	0.11269700
C	-2.24888200	-0.63095600	0.77254200	C	1.33764300	-1.93453400	0.46919300
C	-1.42468300	-0.20621200	-0.29069900	C	2.66091600	-0.12422400	-0.45319200
C	-3.02871200	-1.01698300	-1.88275500	C	2.39642100	-2.81534000	0.25674300
C	-3.84633800	-1.44968800	-0.83623300	H	0.41346800	-2.29702700	0.91046300
H	-4.11052400	-1.58711100	1.30619300	C	3.71907100	-1.01066700	-0.66313700
H	-3.34327600	-1.16467900	-2.91197600	H	2.74454000	0.92561200	-0.72262500
H	-4.79291200	-1.93500600	-1.05774500	C	3.58840300	-2.35387000	-0.30942300
C	-1.68842400	-0.32020100	2.09959700	H	2.29270400	-3.86121200	0.53305500
C	-0.49429800	0.29985300	2.09315000	H	4.64453900	-0.64901700	-1.10293500
H	0.06021900	0.62299100	2.96607400	H	4.41302600	-3.04260700	-0.47310400
H	-2.23313200	-0.57419600	3.00645600	P	0.07883300	0.59513400	0.38445600
C	-1.80749600	-0.38502100	-1.61231000	Se	0.49724300	2.57037600	-0.21503400
H	-1.17738800	-0.02925000	-2.42289900				

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