Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information for

Photochromic Benzo[*b*]phosphole Oxide with Excellent Thermal Irreversibility and Fatigue Resistance in Thin Film Solid State via Direct Attachment of Dithienyl Units to the Weakly Aromatic Heterocycle

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Experimental Details

Materials and Reagents. *N*,*N*-Dimethylformamide (DMF, Arkonic Scientific, AR) was distilled over calcium hydride, and then degassed before use. 1,2-Bis(2,5-dimethylthiophen-3-yl)ethyne (BDTE) was prepared according to the literature procedure.[1] All other reagents were of analytical grade and were used as received.

Physical Measurements and Instrumentation. ^{1}H NMR spectra were recorded on a Bruker DPX-500 (500 MHz) Fourier transform NMR spectrometer. 2D ^{1}H–^{1}H COSY spectra were recorded on a Bruker DPX-500 (500 MHz) Fourier transform NMR spectrometer. ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AVANCE 400 (162 MHz) Fourier transform NMR spectrometer. The chemical shifts (δ, ppm) of ^{1}H and ^{31}P{^{1}H} NMR were recorded relative to tetramethylsilane (Me_4Si) and 85% phosphoric acid (H_3PO_4), respectively. All measurements were performed at 298 K unless specified otherwise. All electron impact (EI) mass spectra were recorded on a Thermo Scientific DFS High Resolution Magnetic Sector mass spectrometer. Elemental analyses of the new compounds were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences, Beijing.

UV–Vis absorption spectra were recorded using a Varian Cary 50 UV–vis spectrophotometer. Photoirradiation was carried out using a 300 W Oriel Corporation Model 60011 Xe (ozone-free) lamp, and monochromatic light was obtained by passing the light through an Applied Photophysics F 3.4 monochromator. All measurements were conducted at room temperature. The kinetics experiments of the thermal backward reaction of the closed form isomer of dithienylethene were measured by using a Varian Cary 50 UV-Vis spectrophotometer with a single cell peltier thermostat to control the working temperature.

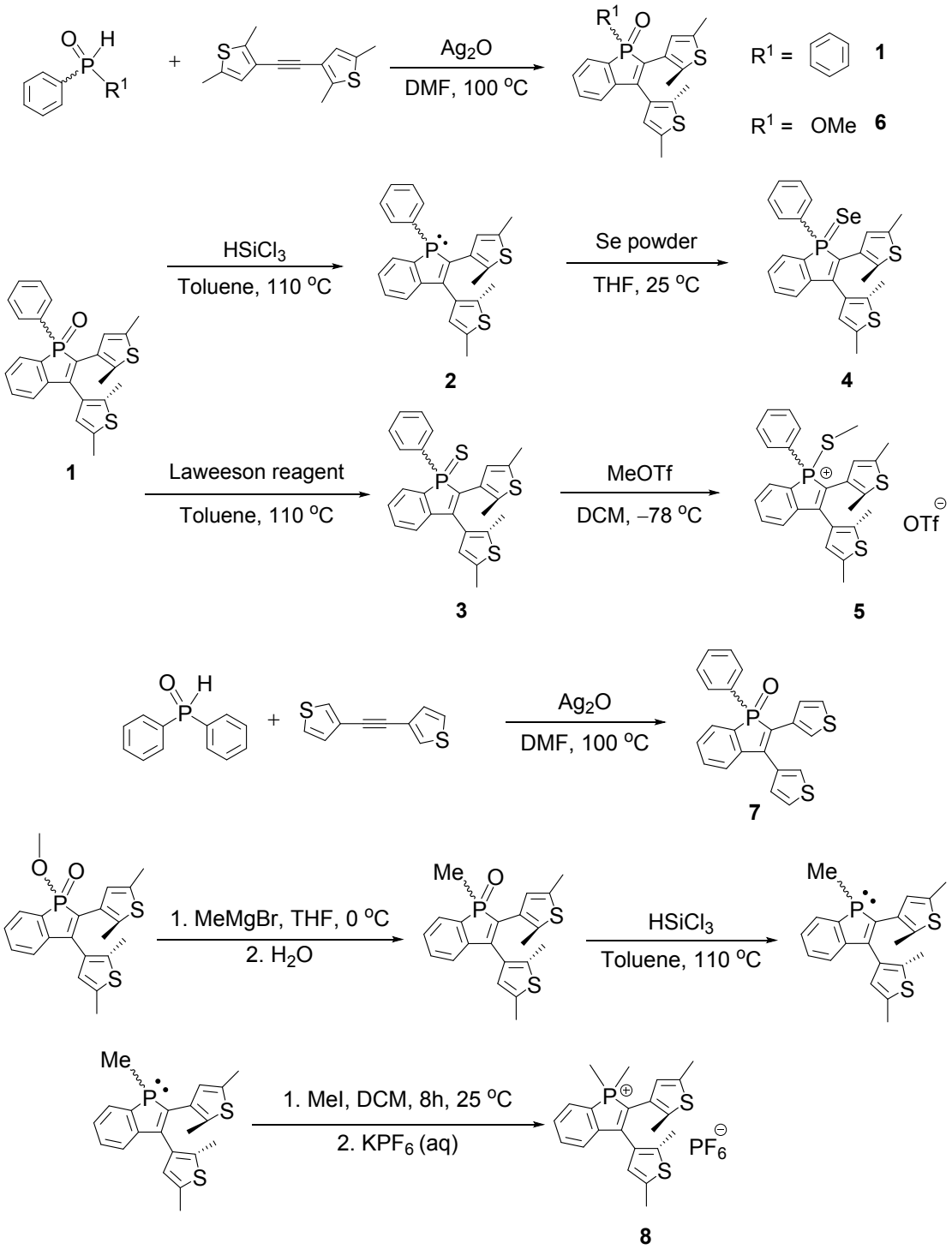
Steady-state emission and excitation spectra at room temperature were recorded on a Spex Fluorolog-3 Model FL3-211 spectrofluorometer equipped with a R2658P PMT detector. For solution emission and excitation spectra, samples were degassed on a high-vacuum line in a degassing cell with a 10-cm^3 Pyrex round-bottomed flask connected by a side-arm to a 1-cm quartz fluorescence cuvette and sealed from the atmosphere by a Rotaflo HP6/6 quick release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze-pump-thaw cycles prior to the measurements. Luminescence quantum yield was measured by the optical dilute method developed by Demas and Crosby.[2–3] A solution of quinine sulphate in 0.5 M sulfuric acid (ϕ_{lum} = 0.546, λ_{ex} = 365 nm)[2,4] at 298 K was used as the standard.

Cyclic voltammetric measurements were performed by using a CH Instrument, Inc. model CHI620 electrochemical analyzer interfaced to a personal computer. The electrolytic cell used was a conventional two-compartment cell. The reference electrode was separated from the working electrode compartment by a vycor glass. Electrochemical measurements were performed in dichloromethane solution with 0.1 mol dm^{-3} $^{n}Bu_4NPF_6$ as supporting electrolyte at room temperature. The reference electrode was a $Ag/AgNO_3$ (0.1 M in acetonitrile) electrode, and the working electrode was a glassy carbon (CH Instrument) electrode with a platinum wire

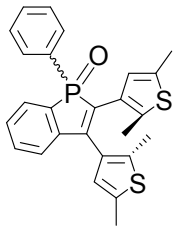
as a counter electrode in a compartment separated from the working electrode by a sintered-glass frit. The ferrocenium/ferrocene couple ($FeCp_2^{+/0}$) was used as the internal reference.[5] All solutions for electrochemical studies were deaerated with prepurified argon gas before measurement.

Chemical actinometry was employed for the photochemical quantum yield determination.[2,6] Incident light intensities were taken from the average values measured just before and after each photolysis experiment using ferrioxalate[2,6] actinometry. In the determination of the photochemical quantum yield, the sample solutions were prepared at concentrations with absorbance slightly greater than 2.0 at the excitation wavelength.[2,6] The quantum yield was determined at a small percentage of conversion by monitoring the initial rate of change of absorbance ($\Delta A/\Delta t$) at the absorption maximum of the closed form in the visible region.

Synthesis and structural characterizations.

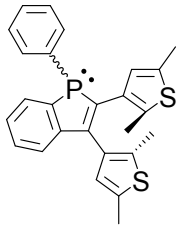


Scheme S1 Synthetic route of photochromic benzo[*b*]phosphole derivatives **1**–**8**.



2,3-Bis(2,5-dimethylthiophen-3-yl)-1-phenylbenzo[*b*]phosphole-1-oxide (1)

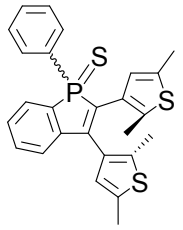
This was prepared according to modification of a literature procedure for the synthesis of benzo[*b*]phosphole oxide derivatives[7] and the reaction was performed under anhydrous condition using standard Schlenk technique. Yield: 95.1 mg, 0.21 mmol; 52% ^{1}H NMR (500 MHz, [D_6]acetone, 298 K): Diastereomeric pair A δ 1.87 (s, 3H, –CH_3), 1.91 (s, 3H, –CH_3), 2.27 (s, 3H, –CH_3), 2.47 (s, 3H, –CH_3), 6.71 (s, 1H, thienyl), 6.87 (s, 1H, thienyl), 7.32–7.37 (m, 2H, phenyl), 7.43–7.50 (m, 3H, phenyl), 7.56–7.60 (m, 3H, phenyl), 7.61–7.64 (m, 1H, phenyl). Diastereomeric pair B δ 1.80 (s, 3H, –CH_3), 2.13 (s, 3H, –CH_3), 2.23 (s, 3H, –CH_3), 2.40 (s, 3H, –CH_3), 6.36 (s, 1H, thienyl), 6.55 (s, 1H, thienyl), 7.40–7.43 (m, 2H, phenyl), 7.48–7.52 (m, 2H, phenyl), 7.65–7.70 (m, 3H, phenyl), 7.72–7.74 (m, 2H, phenyl).^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 298 K): δ 14.07, 14.10, 14.26, 14.72, 15.17, 15.28, 123.91, 124.00, 124.07, 125.17, 125.50, 125.79, 125.80, 126.09, 128.60, 128.68, 128.74, 128.81, 128.82, 128.90, 129.00, 129.06, 129.11, 129.13, 129.20, 129.68, 129.87, 130.31, 130.34, 130.42, 130.52, 130.80, 130.87, 130.98, 131.05, 131.57, 131.59, 131.80, 131.97, 131.98, 132.12, 132.14 132.26, 132.28, 132.43, 132.49, 132. 80, 132. 89, 133.13, 135.13, 135.19, 135.43, 135.85, 135.91, 136.00, 136.04, 136.63, 136.90, 137.07, 143.52, 143.70, 143.79, 143.97, 145.35, 145.47, 145.51, 145.63. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ 35.14, 35.31. Diastereomeric ratio (dr) of A/B = 1.67. Positive EI-MS, *m*/*z*: 446. HRMS (Positive EI) calcd for $C_{26}H_{23}OP^{32}S_2$: *m*/*z* = 446.0928; found: 446.0923 $[M]^+$. Elemental analyses, Found (%): C 69.83, H 5.16; Calcd (%) for $C_{26}H_{23}OPS_2$: C 69.93, H 5.19.



2,3-Bis(2,5-dimethylthiophen-3-yl)-1-phenylbenzo[*b*]phosphole (2)

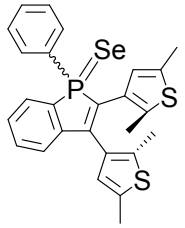
This was prepared according to modification of a literature procedure for the synthesis of phosphole derivatives[8] and the reaction was performed under anhydrous condition using standard Schlenk technique. Yield: 55.9 mg, 0.13 mmol; 59%. ^{1}H NMR (500 MHz, [D_6]acetone, 298 K): Diastereomer A δ 1.86 (s, 3H, –CH_3), 1.96 (s, 3H, –CH_3), 2.28 (s, 3H, –CH_3), 2.48 (s, 3H, –CH_3), 6.54 (s, 1H, thienyl), 6.85 (s, 1H, thienyl), 7.23–7.26 (m, 2H, phenyl), 7.28–7.34 (m, 5H, phenyl), 7.41–7.45 (m, 2H, phenyl). Diastereomer B δ 1.88 (s, 3H, –CH_3), 2.22 (s, 3H, –CH_3), 2.26 (s, 3H, –CH_3), 2.35 (s, 3H, –CH_3), 6.34 (s, 1H, thienyl), 6.41 (s, 1H, thienyl),

7.28–7.34 (m, 4H, phenyl), 7.41–7.45 (m, 2H, phenyl), 7.66–7.70 (m, 3H, phenyl). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 298 K): δ 12.90, 13.18, 13.21, 13.72, 14.12, 14.14, 14.22, 14.32, 122.89, 124.63, 124.68 124.76, 124.81, 125.67, 125.68, 125.88, 126.25, 126.29, 126.79, 126.83, 127.13, 127.16, 127.43, 127.48, 127.54, 127.59, 128.07, 128.20, 128.21, 128.33, 128.35, 131.21, 131.62, 131.75, 131.93, 131.95, 132.07, 132.09, 132.19, 132.22, 132.32, 132.33, 132.43, 132.46, 132.74, 132.85, 133.01, 133.03, 133.72, 133.73, 134.49, 134.76, 139.15, 139.21, 140.46, 140.52, 141.39, 141.73, 141.78, 141.80, 142.12, 142.16, 145.55, 145.58, 146.09, 146.13. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K): δ 3.10, 3.50. Diastereomeric ratio (dr) of A/B = 1.92. Positive EI-MS, *m*/*z*: 430. HRMS (Positive EI) calcd for $C_{26}H_{23}P^{32}S_2$: *m*/*z* = 430.0979; found: 430.0966 $[M]^+$. Elemental analyses, Found (%): C 69.61, H 5.49; Calcd (%) for $C_{26}H_{23}PS_2 \cdot H_2O$: C 69.62, H 5.62.



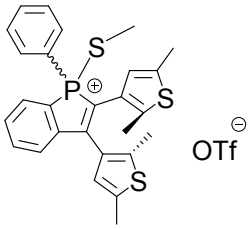
2,3-Bis(2,5-dimethylthiophen-3-yl)-1-phenylbenzo[*b*]phosphole-1-sulfide (3)

This was prepared according to modification of a literature procedure for the synthesis of phosphole sulfide derivatives[8] and the reaction was performed under anhydrous condition using standard Schlenk technique. Yield: 64.0 mg, 0.14 mmol; 63%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): Diastereomer A δ 1.61 (s, 3H, $-CH_3$), 1.96 (s, 3H, $-CH_3$), 2.33 (s, 3H, $-CH_3$), 2.44 (s, 3H, $-CH_3$), 6.64 (s, 1H, thienyl), 7.05 (s, 1H, thienyl), 7.32–7.37 (m, 3H, phenyl), 7.37–7.43 (m, 1H, phenyl), 7.48–7.51 (m, 3H, phenyl), 7.64–7.72 (m, 2H, phenyl). Diastereomer B δ 1.72 (s, 3H, $-CH_3$), 2.03 (s, 3H, $-CH_3$), 2.25 (s, 3H, $-CH_3$), 2.42 (s, 3H, $-CH_3$), 6.22 (s, 1H, thienyl), 6.51 (s, 1H, thienyl), 7.37–7.43 (m, 5H, phenyl), 7.64–7.72 (m, 2H, phenyl), 7.79–7.84 (m, 2H, phenyl). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 298 K): δ 13.90, 13.95, 14.39, 14.70, 15.26, 124.24, 124.31, 124.37, 125.22, 125.65, 125.80, 126.05, 128.26, 128.34, 128.50, 128.58, 128.67, 128.69, 128.73, 128.77, 128.80, 128.87, 128.98, 129.02, 129.05, 129.09, 129.32, 129.34, 129.85, 130.13, 130.23, 130.73, 130.80, 130.83, 130.93, 131.01, 131.78, 131.79, 131.93, 131.95, 132.28, 133.71, 134.23, 134.62, 135.11, 135.14, 135.25, 135.28, 135.31, 135.56, 135.65, 135.70, 135.86, 136.30, 136.36, 136.53, 136.70, 136.80, 143.74, 143.82, 143.90, 143.97, 144.53, 144.63, 144.66, 144.77. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K): δ 47.29, 47.46. Diastereomeric ratio (dr) of A/B = 1.16. Positive EI-MS, *m*/*z*: 462. HRMS (Positive EI) calcd for $C_{26}H_{23}P^{32}S_3$: *m*/*z* = 462.0699; found: 462.0678 $[M]^+$. Elemental analyses, Found (%): C 67.67, H 5.04; Calcd (%) for $C_{26}H_{23}PS_3$: C 67.50, H 5.01.



2,3-Bis(2,5-dimethylthiophen-3-yl)-1-phenylbenzo[*b*]phosphole-1-selenide (4)

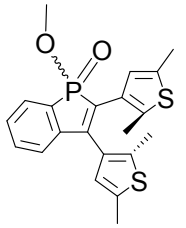
This was prepared according to modification of a literature procedure for the synthesis of phosphole selenide derivatives[9] and the reaction was performed under anhydrous condition using standard Schlenk technique. Yield: 93.5 mg, 0.18 mmol 79%. ^{1}H NMR (500 MHz, [D$_6$]acetone, 298 K): Diastereomer A δ 1.70 (s, 3H, –CH$_3$), 1.97 (s, 3H, –CH$_3$), 2.31 (s, 3H, –CH$_3$), 2.45 (s, 3H, –CH$_3$), 6.86 (s, 1H, thienyl), 7.22 (s, 1H, thienyl), 7.50–7.54 (m, 5H, phenyl), 7.64–7.68 (m, 2H, phenyl), 7.84–7.86 (m, 2H, phenyl). Diastereomer B δ 1.77 (s, 3H, –CH$_3$), 2.09 (s, 3H, –CH$_3$), 2.23 (s, 3H, –CH$_3$), 2.42 (s, 3H, –CH$_3$), 6.28 (s, 1H, thienyl), 6.63 (s, 1H, thienyl), 7.39–7.46 (m, 4H, phenyl), 7.59–7.65 (m, 3H, phenyl), 7.76–7.81 (m, 2H, pheny). ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$, 298 K): δ 13.88, 13.96, 14.42, 14.70, 15.26, 124.48, 124.54, 124.56, 124.62, 125.31, 125.70, 126.02, 126.11, 127.94, 128.09, 128.22, 128.29, 128.39, 128.51, 128.55, 128.59, 128.70, 128.79, 129.04, 129.11, 129.13, 129.26, 129.33, 130.03, 130.12, 130.65, 130.74, 131.20, 131.28, 131.48, 131.56, 131.85, 131.87, 132.02, 132.04, 132.20, 132.98, 133.44, 134.06, 134.52, 134.97, 135.13, 135.33, 135.39, 135.51, 135.54, 135.67, 135.80, 136.46, 136.52, 136.68, 136.90, 143.87, 144.01, 144.42, 144.48, 144.55, 144.61. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]acetone, 298 K): δ 35.29, 36.33. Diastereomeric ratio (dr) of A/B = 1.22. Positive EI-MS, *m*/*z*: 510. HRMS (Positive EI) calcd for $C_{26}H_{23}P^{32}S_2{}^{80}Se$: *m*/*z* = 510.0144; found: 510.0199 [M]$^{+}$. Elemental analyses, Found (%): C 60.22, H 4.55; Calcd (%) for $C_{26}H_{23}PS_2Se \cdot 0.5H_2O$: C 60.23, H 4.67.



2,3-Bis(2,5-dimethylthiophen-3-yl)-1-(methylthio)-1-phenyl-1H-benzo[*b*]phosphol-1-ium trifluoromethanesulfonate (5)

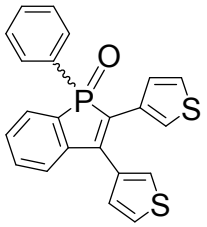
This was prepared according to modification of a literature procedure for the synthesis of phospholium derivatives[10] and the reaction was performed under anhydrous condition using standard Schlenk technique. Yield: 117 mg, 0.19 mmol, 86%. ^{1}H NMR (500 MHz, [D$_6$]acetone, 298 K): Diastereomer A δ 1.75 (s, 3H, –CH$_3$), 2.07 (s, 3H, –CH$_3$), 2.43 (s, 3H, –CH$_3$), 2.47 (s, 3H, –CH$_3$), 2.62 (d, *J* = 16 MHz, 3H, –SMe), 6.95 (s, 1H, thienyl), 7.07 (s, 1H, thienyl), 7.72–7.80 (m, 3H, phenyl), 7.86–7.94 (m, 2H, phenyl), 8.01–8.03 (m, 3H, phenyl), 8.37–8.40 (m, 1H, phenyl). Diastereomer B δ 1.83 (s, 3H, –CH$_3$), 2.11 (s, 3H, –CH$_3$), 2.33 (s, 3H, –CH$_3$), 2.44 (s,

3H, –CH_3), 2.54 (d, *J* = 16 MHz, 3H, –SMe), 6.47 (s, 1H, thienyl), 6.84 (s, 1H, thienyl), 7.72–7.80 (m, 2H, phenyl), 7.82–7.90 (m, 5H, phenyl), 7.99–8.01 (m, 1H, phenyl), 8.28–8.32 (m, 1H, phenyl). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 298 K): δ 11.85, 11.87, 12.50, 12.52, 14.05, 14.17, 15.09, 15.12, 15.23, 15.25, 15.30, 115.56, 115.79, 116.13, 116.34, 117.97, 118.46, 119.16, 119.58, 119.73, 119.88, 120.03, 120.08, 120.60, 122.00, 123.77, 123.90, 124.66, 124.74, 125.05, 125.12, 125.35, 127.34, 127.37, 127.41, 127.45, 128.42, 128.53, 128.58, 128.68, 130.76, 130.86, 131.09, 131.18, 131.98, 132.05, 132.14, 132.22, 132.27, 132.35, 132.41, 132.49, 132.56, 136.26, 136.27, 136.54, 136.56, 136.90, 138.16, 138.23, 138.56, 138.64, 138.67, 138.71, 138.83, 138.96, 139.29, 139.48, 144.75, 144.93, 145.04, 145.22, 153.97, 154.03, 154.13, 154.19. $^{31}P\{^1H\}$ NMR (162 MHz, [D_6]acetone, 298 K): δ 49.43, 49.87. Diastereomeric ratio (dr) of A/B = 1.45. Positive FAB-MS, *m*/*z*: 477.2 $[M]^+$. Elemental analyses, Found (%): C 51.42, H 4.08; Calcd (%) for $C_{28}H_{26}F_3O_4PS_3 \cdot 0.5CH_2Cl_2$: C 51.15, H 4.07.



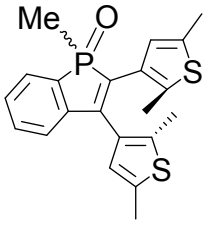
2,3-Bis(2,5-dimethylthiophen-3-yl)-1-methoxybenzo[*b*]phosphole-1-oxide (6)

This was prepared according to modification of a literature procedure for the synthesis of benzo[*b*]phosphole oxide derivatives[7] and the reaction was performed under anhydrous condition using standard Schlenk technique. Yield: 10 mg, 0.025 mml; 6.1%. ^1H NMR (500 MHz, [D_6]acetone, 298 K): Diastereomer A δ 1.88 (s, 3H, –CH_3), 1.97 (s, 3H, –CH_3), 2.37 (s, 3H, –CH_3), 2.46 (s, 3H, –CH_3), 3.60 (d, *J* = 12 Hz, 3H, –OMe), 6.78 (s, 1H, thienyl), 6.81 (s, 1H, thienyl), 7.27–7.29 (m, 1H, phenyl), 7.47–7.51 (m, 1H, phenyl), 7.55–7.59 (m, 1H, phenyl), 7.71–7.75 (m, 1H, phenyl). Diastereomer B δ 1.92 (s, 3H, –CH_3), 2.07 (s, 3H, –CH_3), 2.37 (s, 3H, –CH_3), 2.40 (s, 3H, –CH_3), 3.70 (d, *J* = 12 Hz, 3H, –OMe), 6.54 (s, 1H, thienyl), 6.77 (s, 1H, thienyl), 7.24–7.27 (m, 1H, phenyl), 7.47–7.51 (m, 1H, phenyl), 7.55–7.59 (m, 1H, phenyl), 7.71–7.75 (m, 1H, phenyl). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 298 K): δ14.14, 14.21, 14.32, 14.71, 15.21, 15.24, 15.29, 52.34, 52.38, 123.94, 124.03, 125.47, 125.83, 125.84, 125.95, 126.14, 126.29, 126.70, 126.79, 127.00, 127.17, 127.54, 127.62, 127.70, 127.73, 127.75, 127.79, 128.25, 128.31, 128.71, 128.78, 128.95, 129.01, 129.92, 130.04, 130.66, 130.79, 133.08, 135.26, 135.32, 135.69, 135.93, 135.99, 136.33, 136.39, 136.69, 136.89, 136.97, 141.57, 141.79, 142.00, 142.22, 144.23, 144.43, 144.87, 145.07. $^{31}P\{^1H\}$ NMR (162 MHz, [D_6]acetone, 298 K): δ44.15, 44.26. Diastereomeric ratio (dr) of A/B = 2.15. Positive EI-MS, *m*/*z*: 400. HRMS (Positive EI) calcd for $C_{21}H_{21}O_2P^{32}S_2$: *m*/*z* = 400.0721; found: 400.0718 $[M]^+$. Elemental analyses, Found (%): C 62.66, H 5.37; Calcd (%) for $C_{21}H_{21}O_2PS_2$: C 62.98, H 5.29.



2,3-Bis(thiophen-3-yl)-1-phenylbenzo[*b*]phosphole-1-oxide (7)

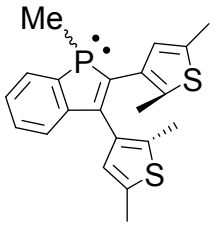
This was prepared according to modification of a literature procedure for the synthesis of benzo[*b*]phosphole oxide derivatives[7] and the reaction was performed under anhydrous condition using standard Schlenk technique. Yield: 35 mg, 0.089 mmol, 21.6%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 6.70–6.71 (d, *J* = 4 Hz, 1H, thienyl), 7.06–7.08 (m, 1H, thienyl), 7.08–7.10 (dd, *J* = 4 , 8Hz, 1H, thienyl), 7.23–7.25 (dd, *J* = 4 , 8Hz, 1H, thienyl), 7.33–7.37 (m, 1H, thienyl), 7.40–7.42 (m, 3H, phenyl), 7.43–7.45 (m, 1H, phenyl), 7.47–7.49 (m, 1H, thienyl), 7.50–7.53 (m, 2H, phenyl), 7.66–7.70 (m, 1H, phenyl), 7.76–7.81 (m, 2H, phenyl). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 298 K): δ 123.62, 123.69, 124.99, 125.20, 125.71, 125.75, 126.97, 127.06, 127.11, 128.04, 128.89, 128.93, 128.98, 129.79, 130.44, 130.90, 130.97, 131.07, 131.78, 132.26, 132.27, 132.97, 133.04, 133.12, 134.49, 134.59, 142.94, 143.09, 143.98, 144.16. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ 38.61. Positive EI-MS, *m*/*z*: 864. HRMS (Positive EI) calcd for $C_{22}H_{15}OP^{32}S_2$: *m*/*z* = 390.0302; found: 390.0283 $[M]^+$. Elemental analyses, Found (%): C 67.53, H 3.67; Calcd (%) for $C_{22}H_{15}OPS_2$: C 67.67, H 3.87.



2,3-Bis(2,5-dimethylthiophen-3-yl)-1-methylbenzo[*b*]phosphole-1-oxide (1-Me)

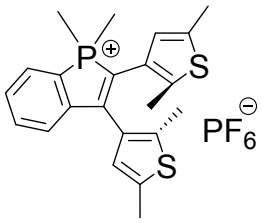
This was prepared according to modification of a literature procedure for the synthesis of phosphine oxide derivatives using Grignard reaction[11] and the reaction was performed under anhydrous condition using standard Schlenk technique. Yield: 60 mg, 0.16 mmol; 63%. ^{1}H NMR (400 MHz, [D_6]acetone, 298 K): Diastereomer A δ 1.54–1.57 (d, *J* = 12 Hz, 3H, –PMe), 1.89 (s, 3H, $-CH_3$), 1.97 (s, 3H, $-CH_3$), 2.38 (s, 3H, $-CH_3$), 2.46 (s, 3H, $-CH_3$), 6.76 (s, 1H, thienyl), 6.80 (s, 1H, thienyl), 7.28–7.31 (m, 1H, phenyl), 7.46–7.51 (m, 1H, phenyl), 7.53–7.57 (m, 1H, phenyl), 7.82–7.86 (m, 1H, phenyl). Diastereomer B δ 1.70–1.74 (d, *J* = 16 Hz, 3H, –PMe), 1.93 (s, 3H, $-CH_3$), 2.14 (s, 3H, $-CH_3$), 2.38 (s, 3H, $-CH_3$), 2.39 (s, 3H, $-CH_3$), 6.43 (s, 1H, thienyl), 6.83 (s, 1H, thienyl), 7.22–7.25 (m, 1H, phenyl), 7.46–7.51 (m, 1H, phenyl), 7.53–7.57 (m, 1H, phenyl), 7.82–7.86 (m, 1H, phenyl). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 298 K): δ 14.07, 14.09, 14.14, 14.27, 14.60, 14.88, 14.92, 15.20, 15.24, 15.28, 15.34, 123.93, 123.95, 124.00, 124.02, 125.33, 125.48, 125.85, 125.86, 126.34, 128.13, 128.19, 128.23, 128.49, 128.56, 128.63, 129.24, 129.30, 130.14 130.24, 131.07, 131.17, 131.37, 131.43, 131.45, 132.04, 132.07

132.10, 132.17, 132.66, 132.80, 134.86, 135.05, 135.10, 135.67, 135.72, 136.39, 136.44, 136.52, 136.95, 137.09, 142.03, 142.20, 142.83, 143.01, 143.61, 143.77, 144.55, 144.70. $^{31}P\{^{1}H\}$ NMR (162 MHz, [D_6]acetone, 298 K): δ 40.59, 40.69. Diastereomeric ratio (dr) of A/B = 1.88. Positive EI-MS, *m*/*z*: 384. HRMS (Positive EI) calcd for $C_{21}H_{21}OP^{32}S_2$: *m*/*z* = 384.0771; found: 384.0762 $[M]^+$.



2,3-Bis(2,5-dimethylthiophen-3-yl)-1-methylbenzo[*b*]phosphole (2-Me)

This was prepared according to modification of a literature procedure for the synthesis of phosphole derivatives[8] and the reaction was performed under anhydrous condition using standard Schlenk technique. Yield: 48 mg, 0.13 mmol; 81.5%. ^{1}H NMR (400 MHz, [D_6]acetone, 298 K): Diastereomer A δ 1.27 (d, *J* = 1.4 Hz, 3H, –PMe), 1.83 (s, 3H, $-CH_3$), 2.03 (s, 3H, $-CH_3$), 2.35 (s, 3H, $-CH_3$), 2.46 (s, 3H, $-CH_3$), 6.52 (s, 1H, thienyl), 6.78 (s, 1H, thienyl), 7.21–7.28 (m, 1H, phenyl), 7.29–7.33 (m, 1H, phenyl), 7.38–7.39 (m, 1H, phenyl), 7.77–7.80 (m, 1H, phenyl). Diastereomer B δ 1.37–1.38 (d, *J* = 1.4 Hz, 3H, –PMe), 1.99 (s, 3H, $-CH_3$), 2.18 (s, 3H, $-CH_3$), 2.33 (s, 3H, $-CH_3$), 2.36 (s, 3H, $-CH_3$), 6.28 (s, 1H, thienyl), 6.59 (s, 1H, thienyl), 7.29–7.33 (m, 1H, phenyl), 7.38–7.39 (m, 2H, phenyl), 7.77–7.80 (m, 1H, phenyl). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, 298 K): δ 10.49, 10.63, 11.12, 11.26, 13.84, 14.01, 14.03, 14.27, 14.31, 14.78, 15.16, 15.20, 15.22, 15.36, 123.88, 123.94, 125.05, 125.10, 125.14, 125.19, 126.57, 126.59, 127.19, 127.45, 127.49, 127.71. 127.76, 127.84, 127.88, 128.40, 128.53, 132.43, 132.68 132.70, 132.86, 132.98, 133.16, 133.25, 133.28, 133.59, 133.61, 134.69, 134.94, 134.98, 135.34, 135.71, 138.68, 138.74, 140.24, 140.29, 144.71, 145.16, 145.21, 145.84, 145.88, 145.95, 145.98, 146.92, 146.95. $^{31}P\{^{1}H\}$ NMR (162 MHz, [D_6]acetone, 298 K): δ –10.94, –10.90. Diastereomeric ratio (dr) of A/B = 2.22. Positive EI-MS, *m*/*z*: 368. HRMS (Positive EI) calcd for $C_{21}H_{21}P^{32}S_2$: *m*/*z* = 368.0822; found: 368.0816 $[M]^+$.



2,3-Bis(2,5-dimethylthiophen-3-yl)-1,1-dimethyl-1H-benzo[*b*]phosphol-1-ium hexafluorophosphate (8)

This was prepared according to modification of a literature procedure for the synthesis of phospholium derivatives[12] and the reaction was performed under anhydrous condition using standard Schlenk technique. Yield: 40 mg, 0.076 mmol, 54%. ^{1}H NMR (400 MHz, $CDCl_3$, 298

K): δ 1.83 (s, 3H, –CH_3), 2.00 (s, 3H, –CH_3), 2.12–2.15 (d, *J* = 12 Hz 3H, PMe), 2.35–2.39 (d, *J* = 12 Hz, 3H, PMe), 2.45 (s, 3H, –CH_3), 2.47 (s, 3H, –CH_3), 6.54 (s, 1H, thienyl), 6.57 (s, 1H, thienyl), 7.52–7.55 (m, 1H, phenyl), 7.65–7.70 (m, 1H, phenyl), 7.73–7.77 (m, 1H, phenyl), 8.34–8.38 (m, 1H, phenyl). $^{19}F\{^1H\}$ NMR (377 MHz, $CDCl_3$, 298 K): δ –71.56 (d, J_{P-F} = 710 Hz, PF_6^-). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 298 K): δ 6.73, 7.07, 7.66, 7.99, 14.05, 14.75, 15.24, 120.98, 121.50, 122.09, 123.61, 124.96, 125.00, 125.03, 126.31, 126.38, 128.46, 128.56, 130.98, 131.05, 131.98, 132.04, 135.53, 135.54, 137.77, 137.83, 138.15, 138.44, 139.62, 145.09, 145.25, 152.70, 152.84. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K): δ –144.08 (m, J_{P-F} = 710 Hz, PF_6^-), 33.15 (s, PMe_2^+). Positive FAB-MS, *m*/*z*: 382.9 $[M]^+$. Elemental analyses, Found (%): C 49.05, H 4.79; Calcd (%) for $C_{22}H_{24}F_6P_2S_2 \cdot 0.5H_2O$: C 49.16, H 4.69.

Table S1 Electrochemical data

Compound	Oxidation[a,b] E_{pa}[c] / V vs SCE	Reduction[a,b] E_{pc}[d] / *V* vs SCE [$E_{1/2}$[e] / *V* vs SCE] (ΔE_p / mV) [f]
1	+1.50	−1.93
2	+1.34, +1.56,	–[g]
3	+1.45	−1.99
4	+1.40	−1.88
5	+1.72	−0.91, [−1.81] (108)
6	+1.46	−1.85

[a] In CH_2Cl_2 with 0.1 M $^nBu_4NPF_6$ as supporting electrolyte.

[b] Working electrode, glassy carbon; scan rate, 100 mVs^{-1}.

[c] E_{pa} is reported for irreversible oxidation wave.

[d] E_{pc} is reported for irreversible reduction wave.

[e] $E_{1/2} = (E_{pa} + E_{pc}) / 2$; E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively.

[f] $\Delta E_p = (E_{pa} - E_{pc})$.

[g] No reduction wave was observed.

Table S2 Crystal and structure determination data of **1**

empirical formula	$C_{26}H_{23}OPS_2$
formula weight	446.53
temp, K	296 (2)
wavelength, Å	0.71073
crystal system	Triclinic
space group	$P\bar{1}$
a, Å	8.4616(4)
b, Å	11.5086(5)
c, Å	12.4957(6)
α, deg	83.4270(10)
β, deg	77.3210(10)
γ, deg	83.7100(10)
Volume, Å^3	1174.89 (9)
Z	2
Density (calcd), gcm^{-3}	1.262
Crystal size	0.50 mm x 0.40 mm x 0.30 mm
Index ranges	$-10 \le h \le 10$, $-13 \le k \le 13$, $-14 \le l \le 14$
reflections collected	16694
Independent reflection	4226 [*R*(int) = 0.0284]
GOF on F^2	1.025
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0443, wR_2 = 0.1143
Largest diff. peak and hole, eÅ^{-3}	0.400 and −0.428

Table S3 Selected bond lengths [Å] and angles [deg] for **1** with estimated standard deviations (esds) given in parentheses

Bond Lengths / Å		Bond Angles / deg	
P(1)-O(1)	1.4830(15)	O(1)-P(1)-C(21)	113.36(10)
P(1)-C(21)	1.799(2)	O(1)-P(1)-C(20)	118.27(10)
P(1)-C(20)	1.803(2)	C(21)-P(1)-C(20)	107.94(10)
P(1)-C(14)	1.819(2)	O(1)-P(1)-C(14)	116.24(10)
C(13)-C(14)	1.359(3)	C(20)-P(1)-C(14)	92.37(10)
C(13)-C(15)	1.493(3)	C(21)-P(1)-C(14)	106.33(10)
C(15)-C(20)	1.403(3)		

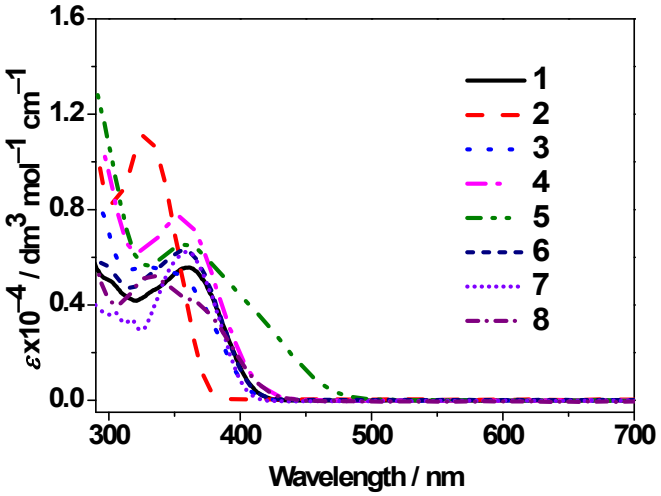


Fig. S1 Electronic absorption spectra of the open forms of **1**–**8** in benzene solution at 298 K.

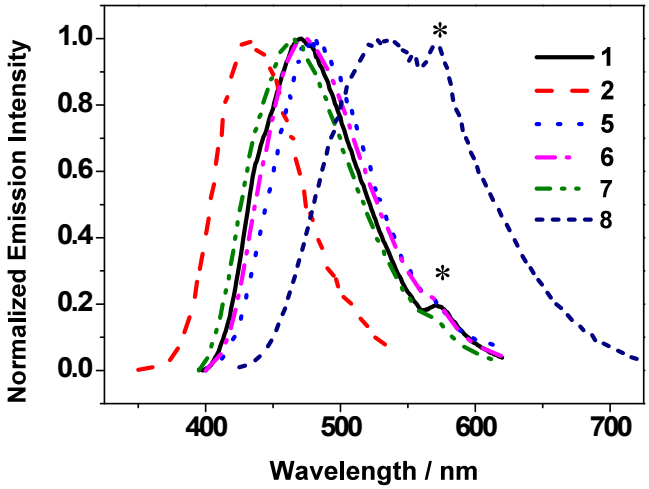


Fig. S2 Normalized emission spectra of the degassed benzene solution of the open forms of **1**–**2** and **5**–**8** at 298 K; asterisk represents an instrumental artifact.

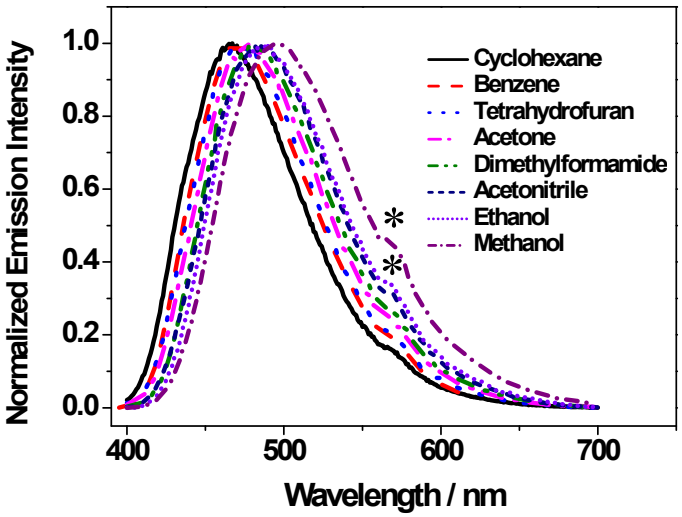


Fig. S3 Normalized emission spectra of the open form of **1** in various solvents at 298 K; asterisk represents an instrumental artifact.

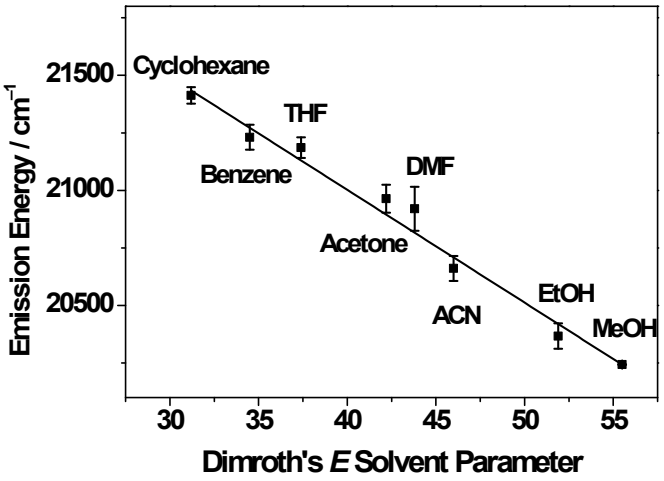


Fig. S4 A plot of emission energy of the open form of **1** in different solvents versus the Dimroth's *E* solvent parameter and its linear least-squares fit (–).

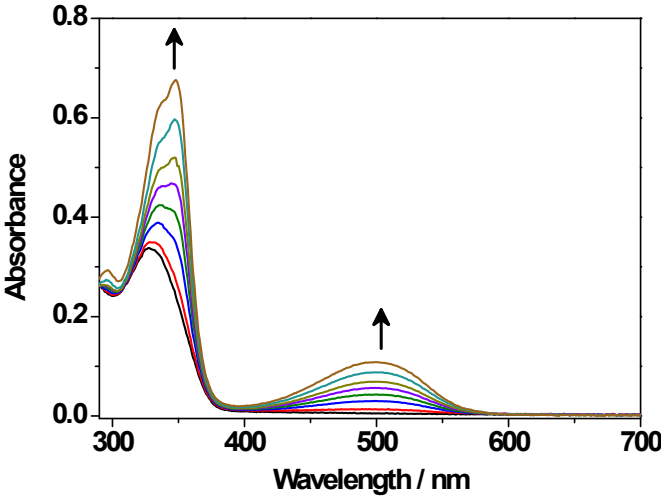


Fig. S5 UV–Vis absorption spectral changes of **2** in degassed benzene solution upon UV excitation at 360 nm.

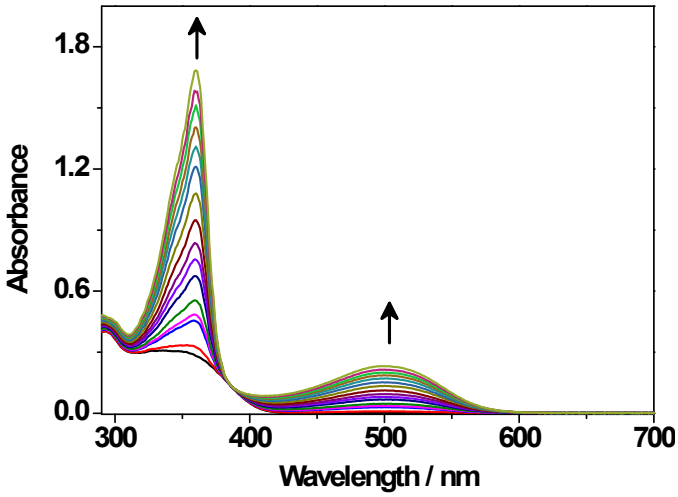


Fig. S6 UV–Vis absorption spectral changes of **3** in degassed benzene solution upon UV excitation at 360 nm.

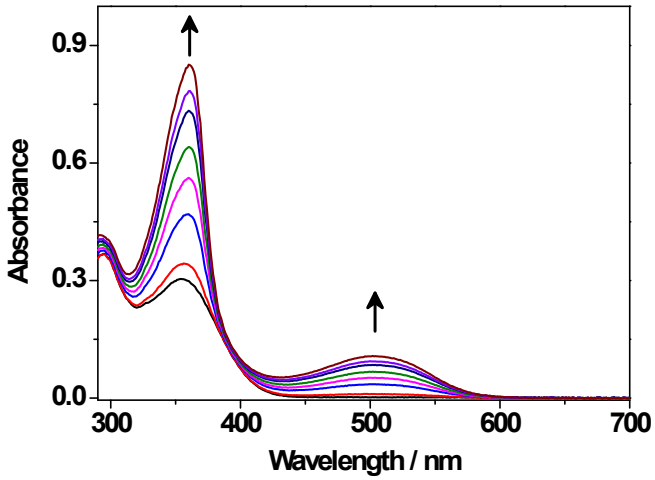


Fig. S7 UV–Vis absorption spectral changes of **4** in degassed benzene solution upon UV excitation at 360 nm.

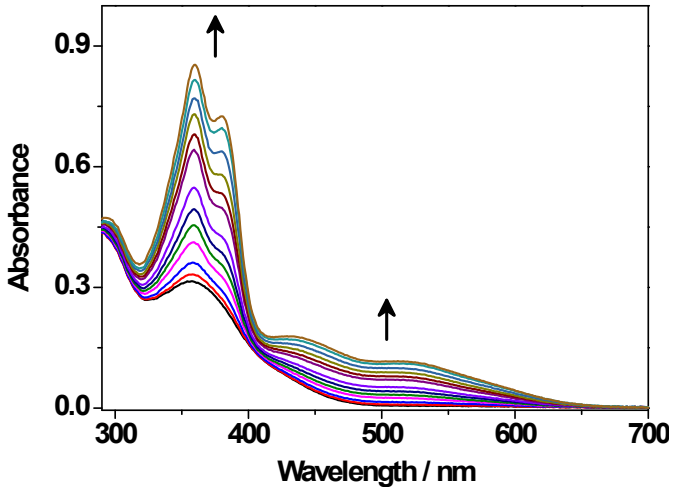


Fig. S8 UV–Vis absorption spectral changes of **5** in degassed benzene solution upon UV excitation at 360 nm.

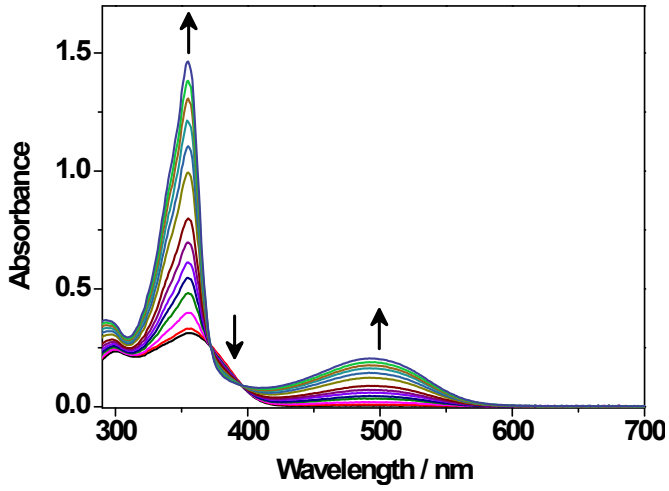


Fig. S9 UV–Vis absorption spectral changes of **6** in degassed benzene solution upon UV excitation at 360 nm.

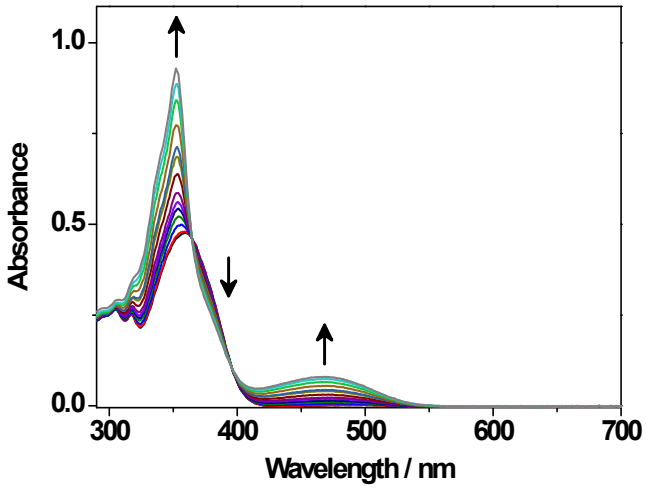


Fig. S10 UV–Vis absorption spectral changes of **7** in degassed benzene solution upon UV excitation at 360 nm.

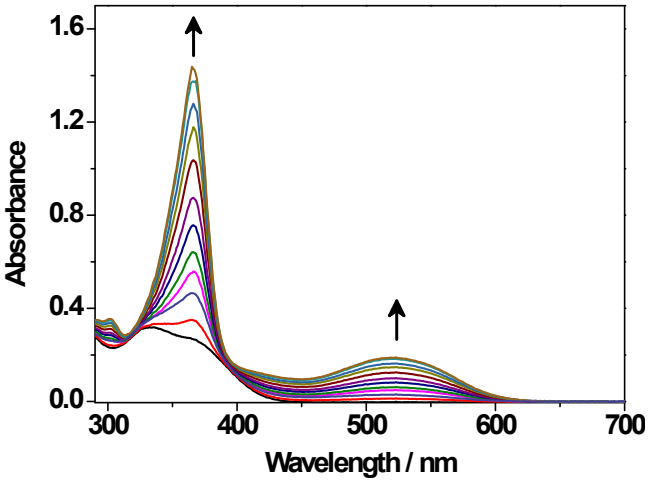


Fig. S11 UV–Vis absorption spectral changes of **8** in degassed benzene solution upon UV excitation at 360 nm.

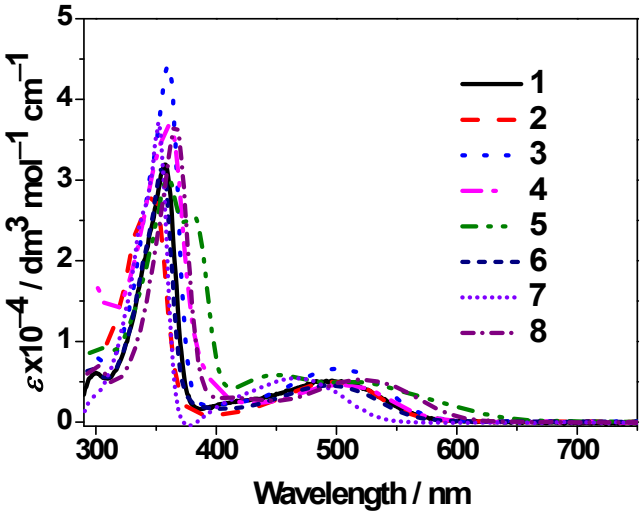


Fig. S12 Electronic absorption spectra of the closed forms of **1**–**8** in degassed benzene solution at 298 K.

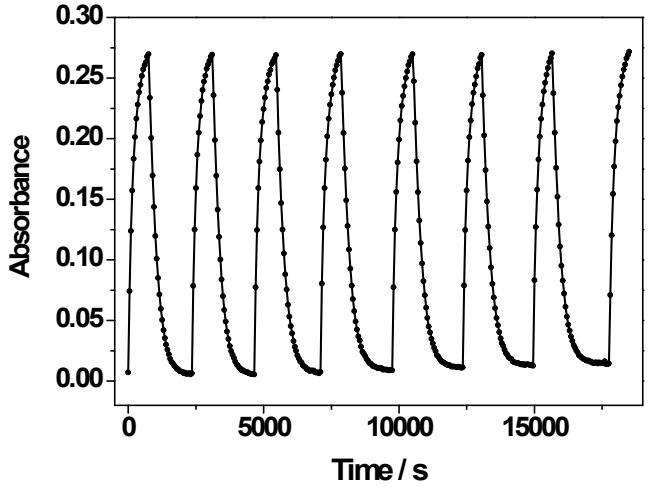


Fig. S13 UV–Vis absorbance changes of **1** at 500 nm on alternate excitation at 360 nm and 500 nm over seven cycles in degassed benzene solution at 298 K.

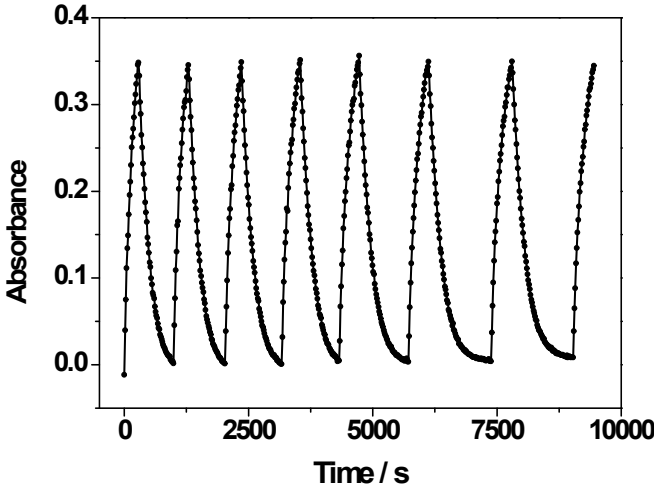


Fig. S14 UV–Vis absorbance changes of **2** at 500 nm on alternate excitation at 360 nm and 500 nm over seven cycles in degassed benzene solution at 298 K.

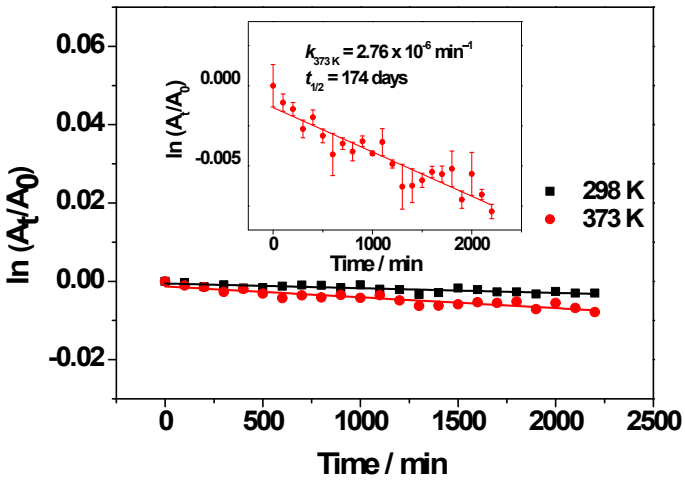


Fig. S15 A plot of $\ln(A_t/A_0)$ versus time for the absorbance decay at 500 nm of the closed form isomer of **1** at 25 and 100 °C in nitrogen-flushed 1,2-dichlorobenzene solution. A_0 and A_t denote initial absorbance and absorbance at time t, respectively; solid lines represent theoretical linear fits. Inset shows the expanded thermal decay plot at 100 °C.

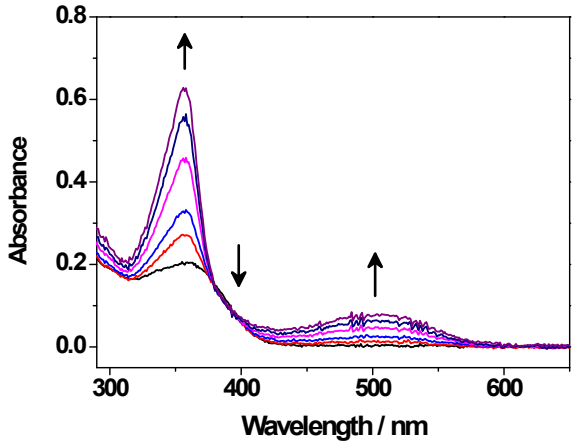


Fig. S16 UV–Vis absorption spectral changes of **1** on PMMA thin film upon UV excitation at 360 nm.

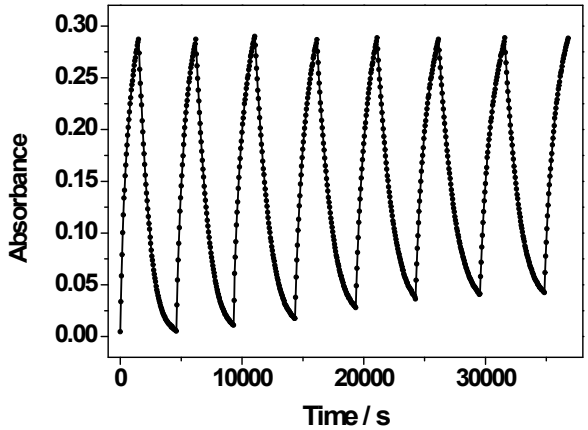


Fig. S17 UV–Vis absorbance changes of **1** at 500 nm on alternate excitation at 360 nm and 500 nm over seven cycles in non-degassed benzene solution at 298 K.

NMR Spectra of 1–8

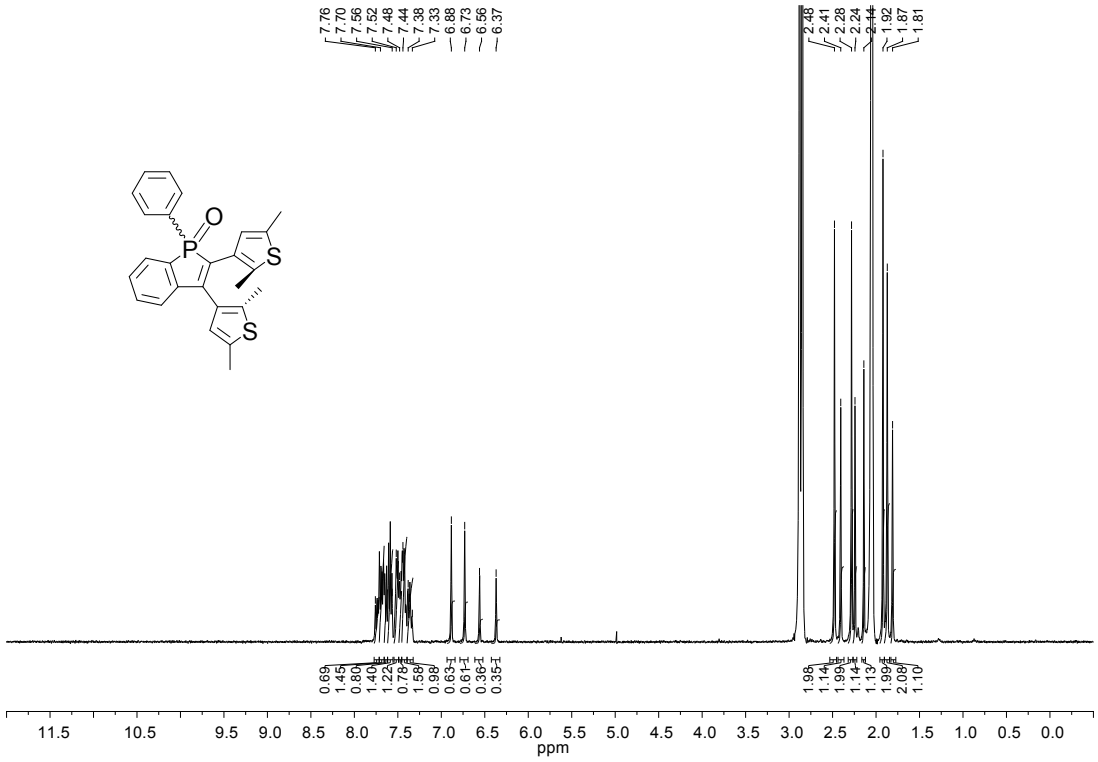


Fig. S18 ^{1}H NMR spectrum of **1** in $[D_6]$acetone.

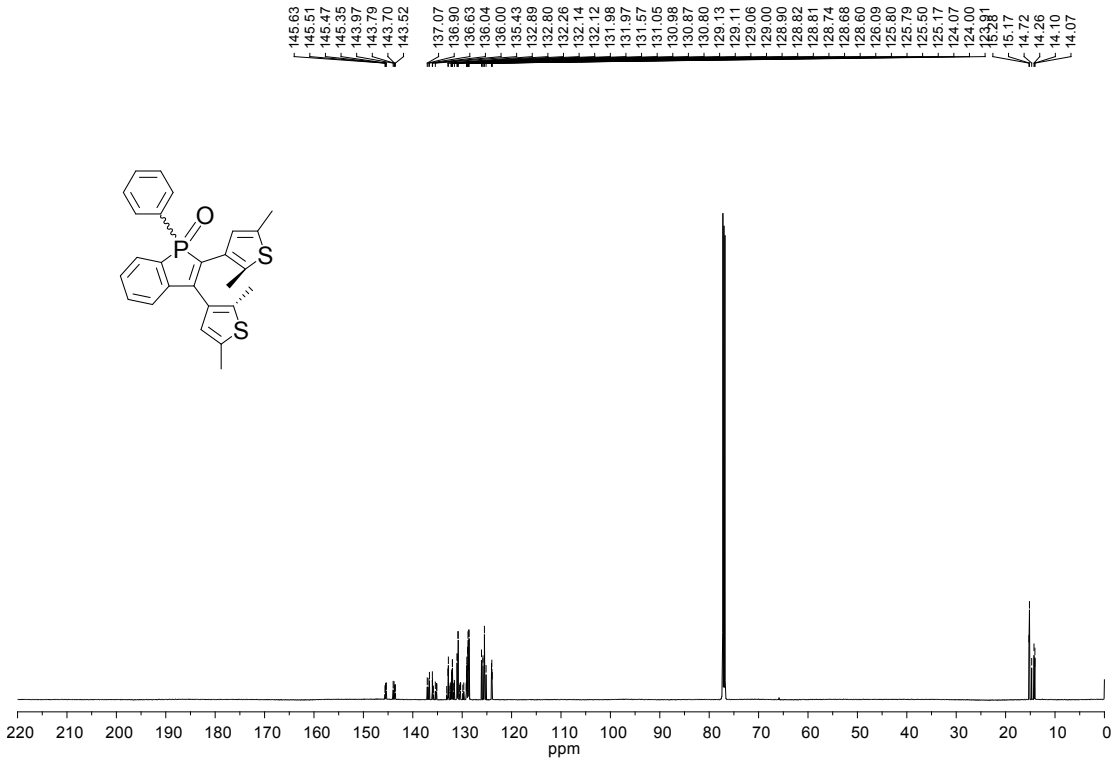


Fig. S19 $^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$.

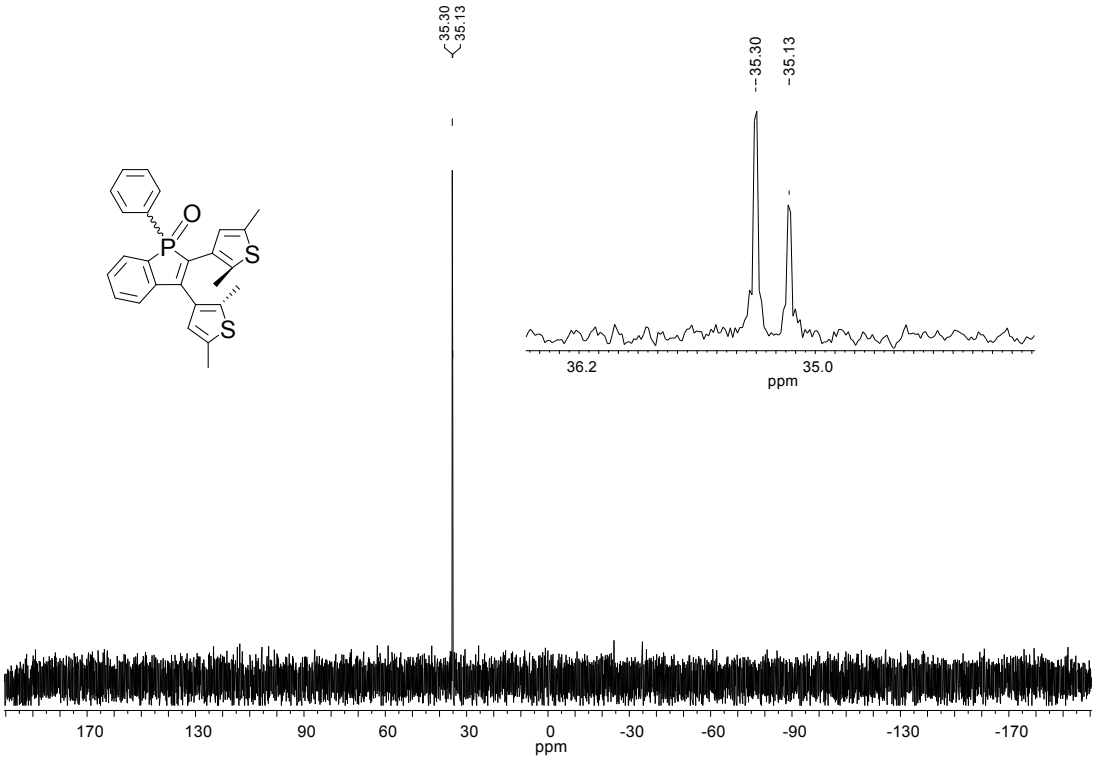


Fig. S20 $^{31}P\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$.

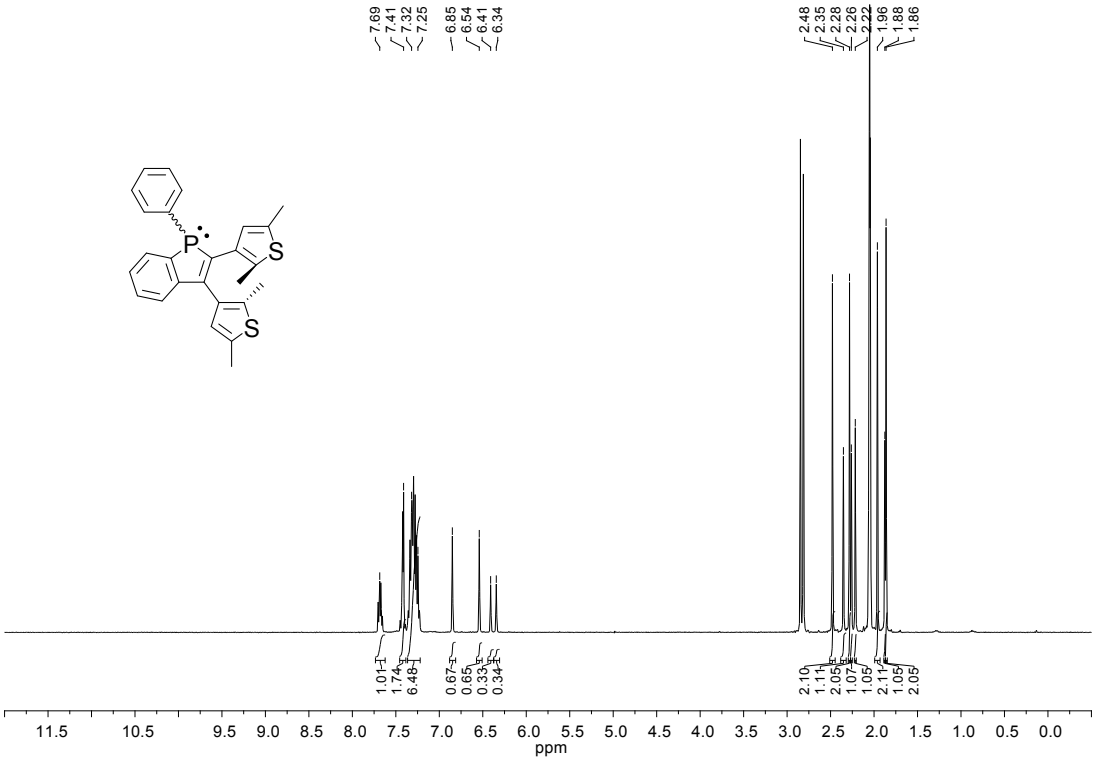


Fig. S21 ^{1}H NMR spectrum of **2** in $[D_6]$acetone.

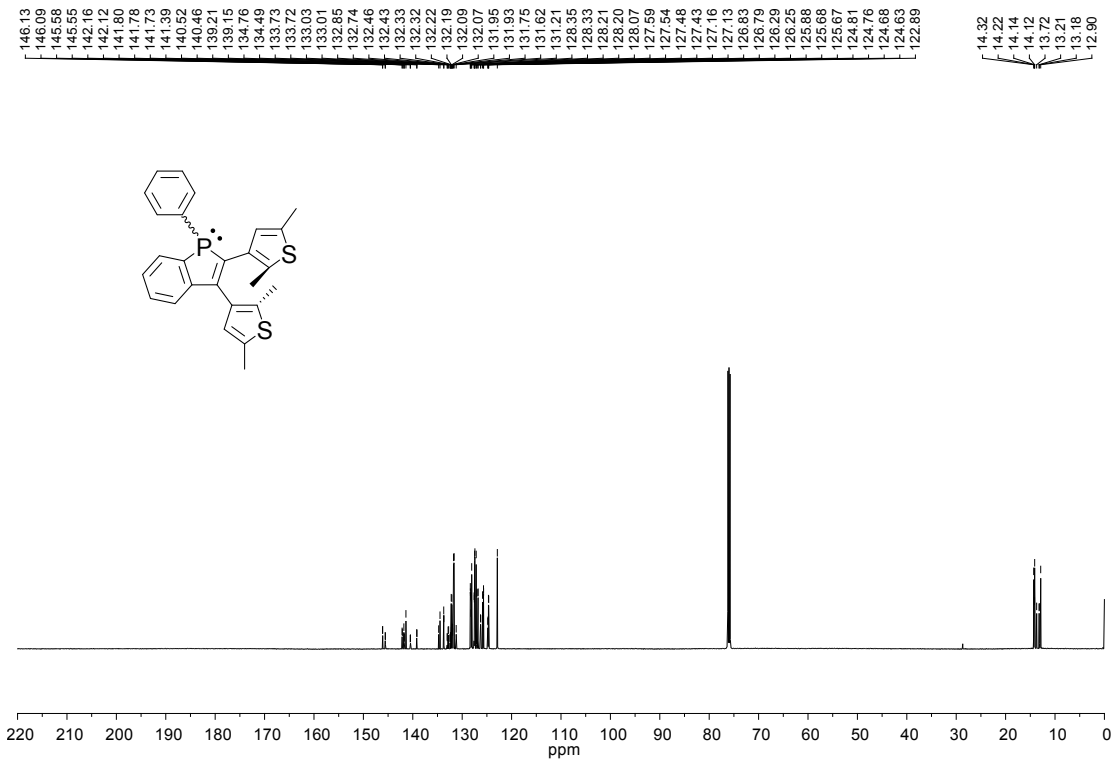


Fig. S22 $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$.

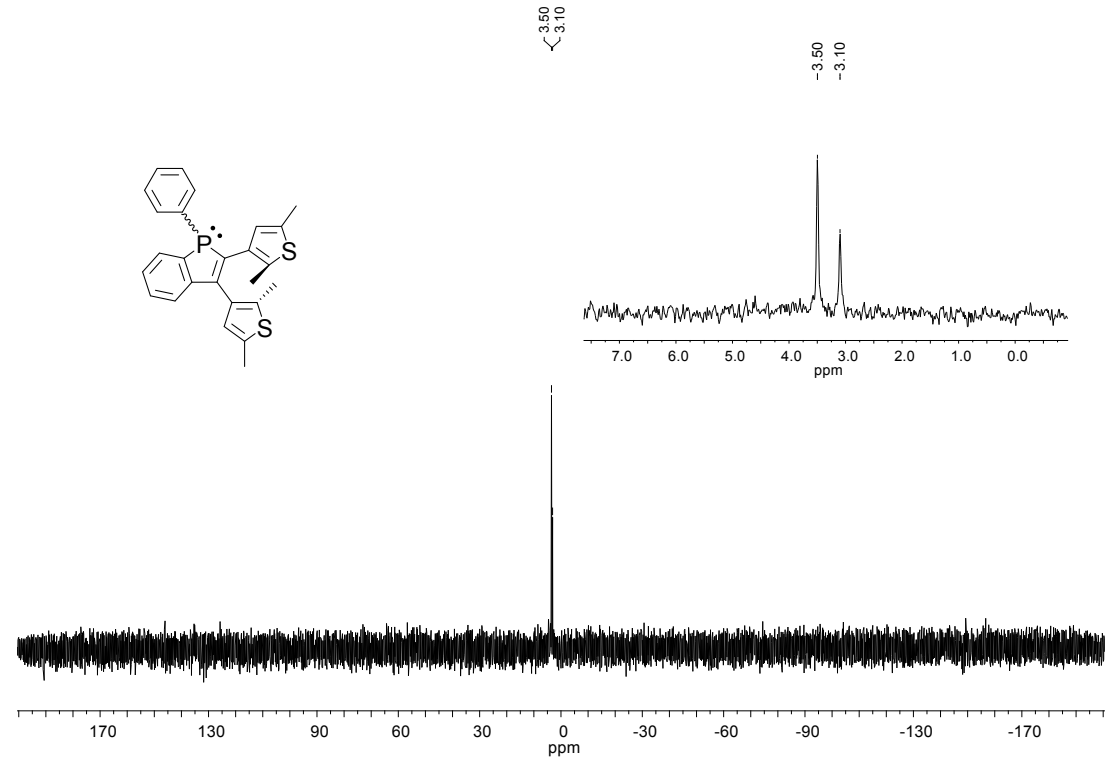


Fig. S23 $^{31}P\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$.

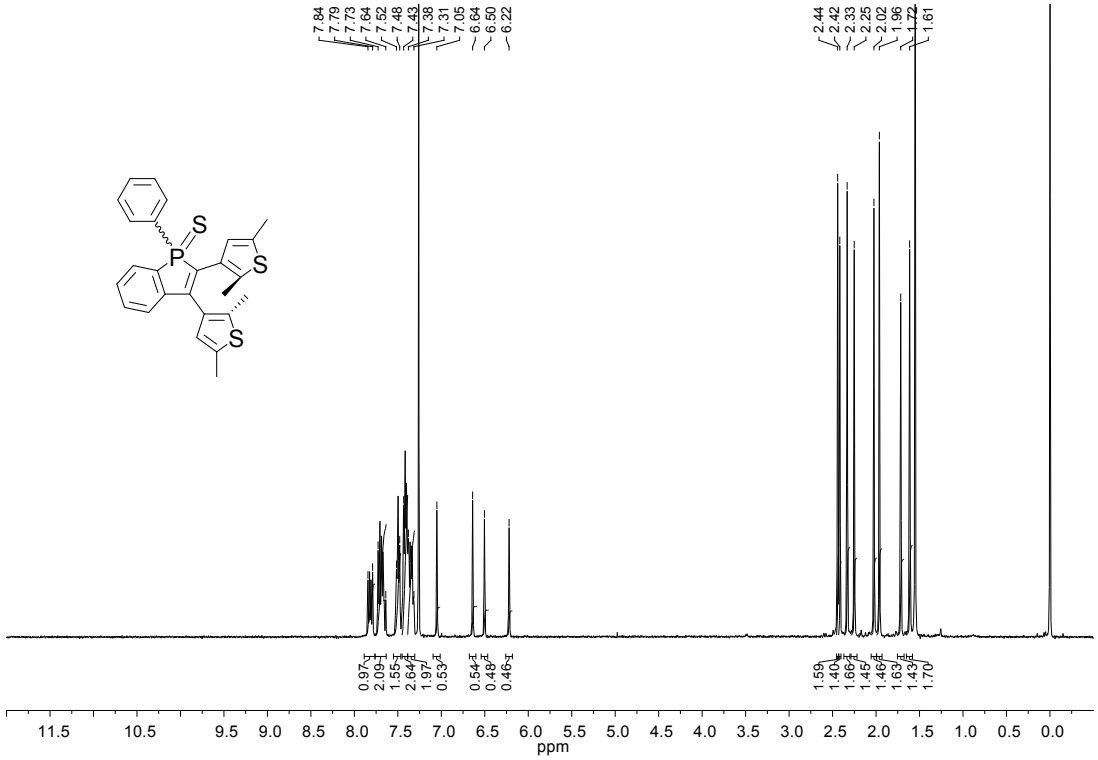


Fig. S24 ^{1}H NMR spectrum of **3** in $CDCl_3$.

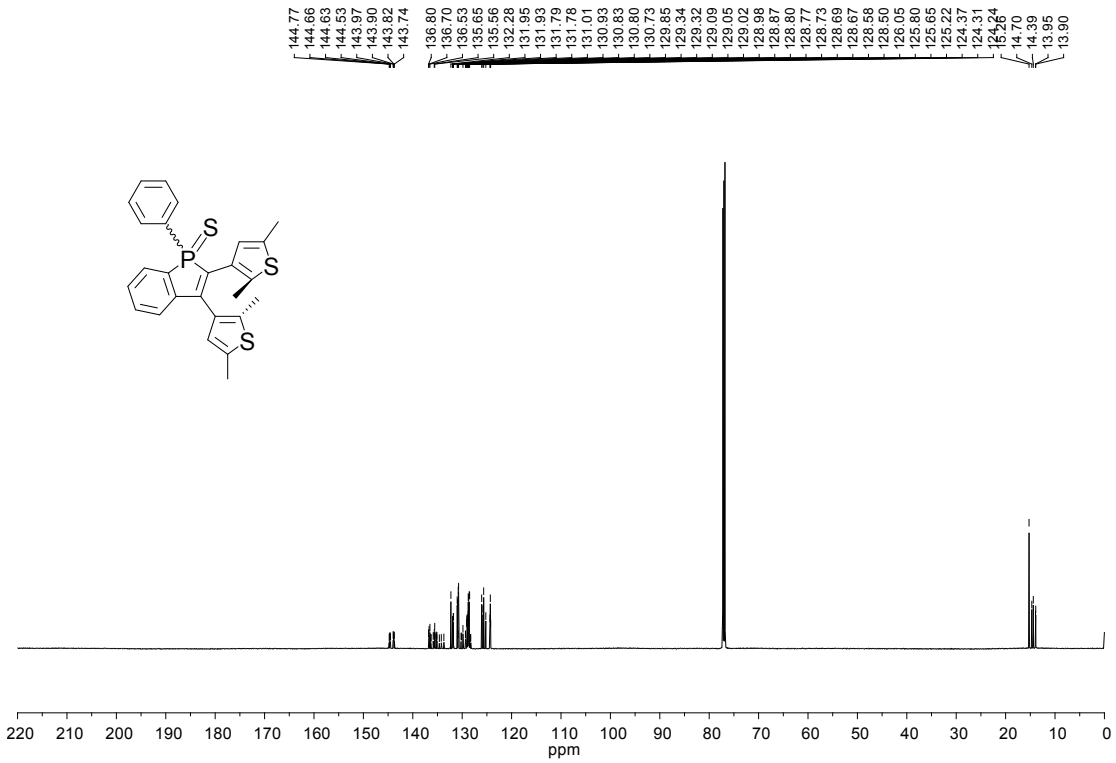


Fig. S25 $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

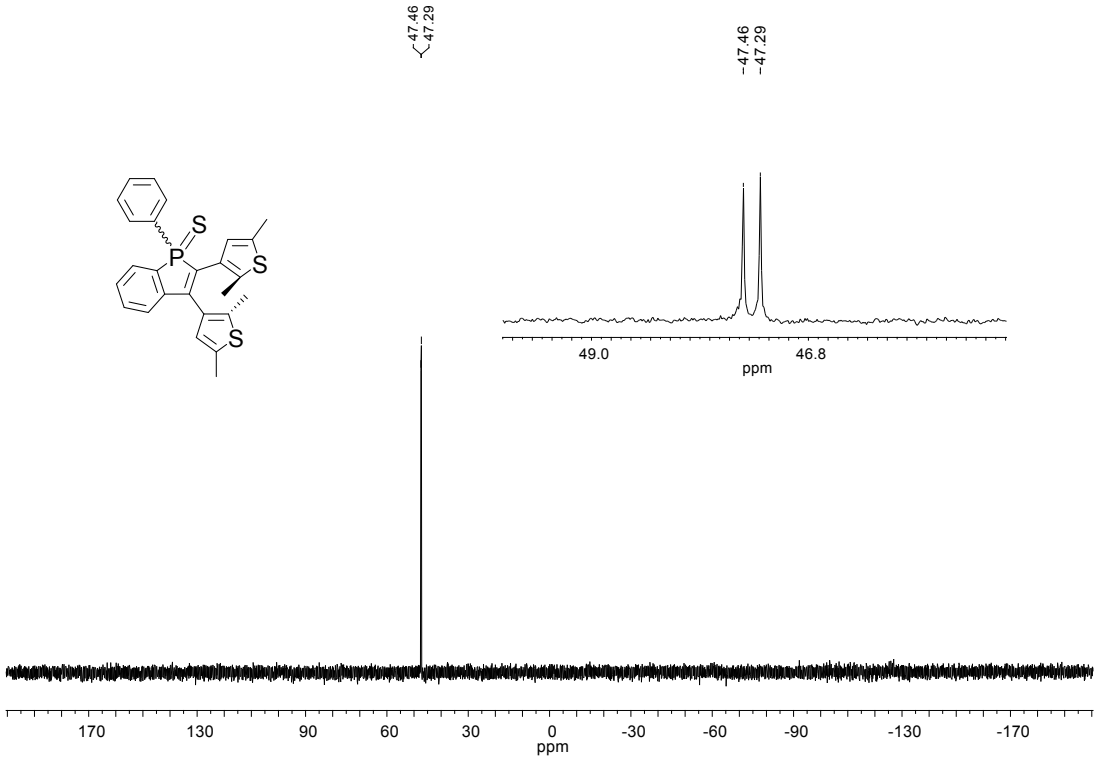


Fig. S26 $^{31}P\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

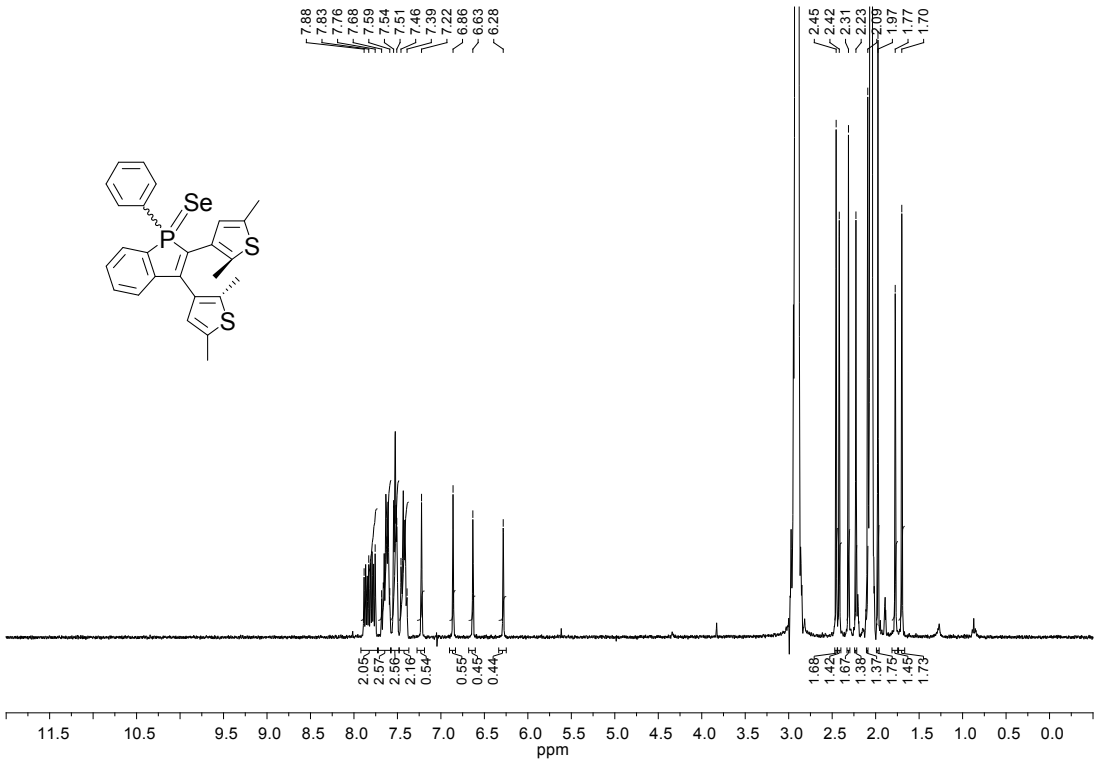


Fig. S27 ^{1}H NMR spectrum of **4** in $[D_6]$acetone.

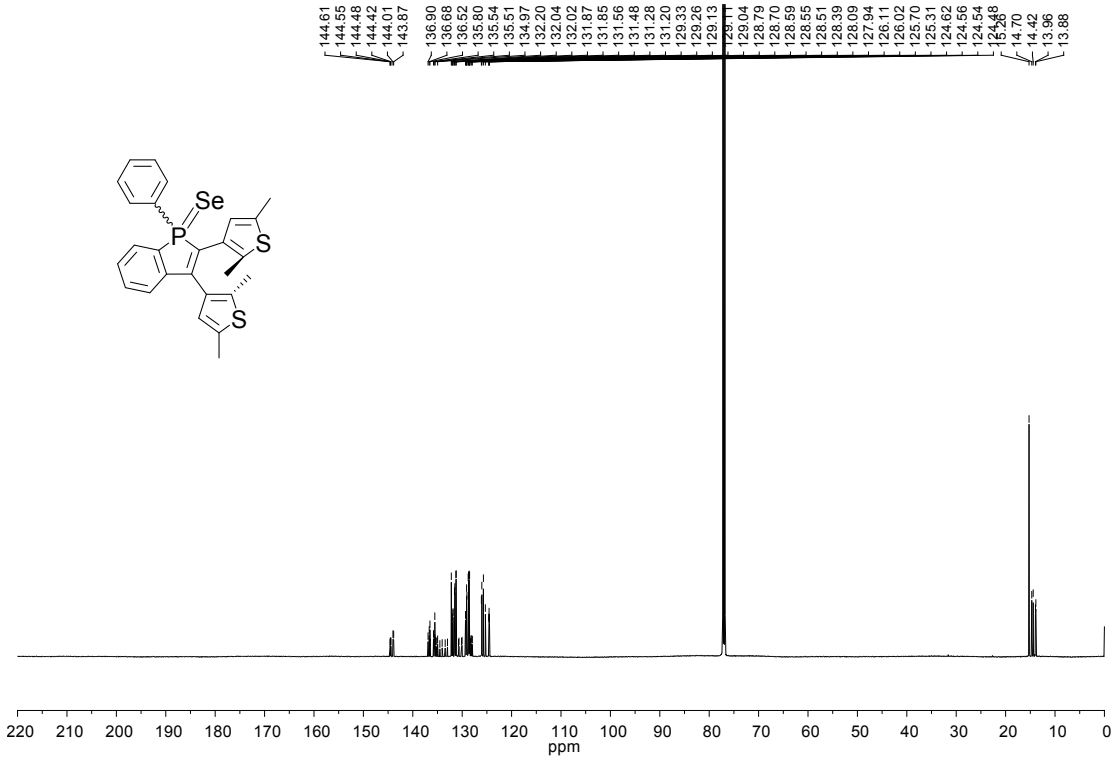


Fig. S28 $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$.

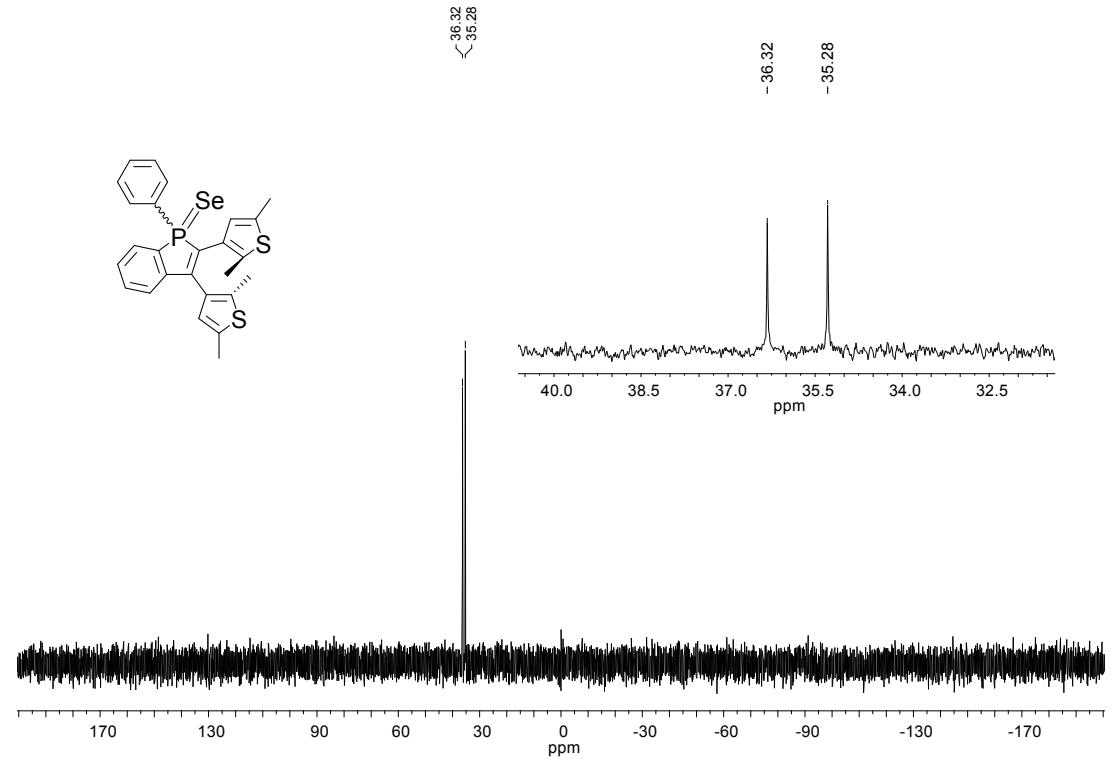


Fig. S29 $^{31}P\{^{1}H\}$ NMR spectrum of **4** in $[D_6]$acetone.

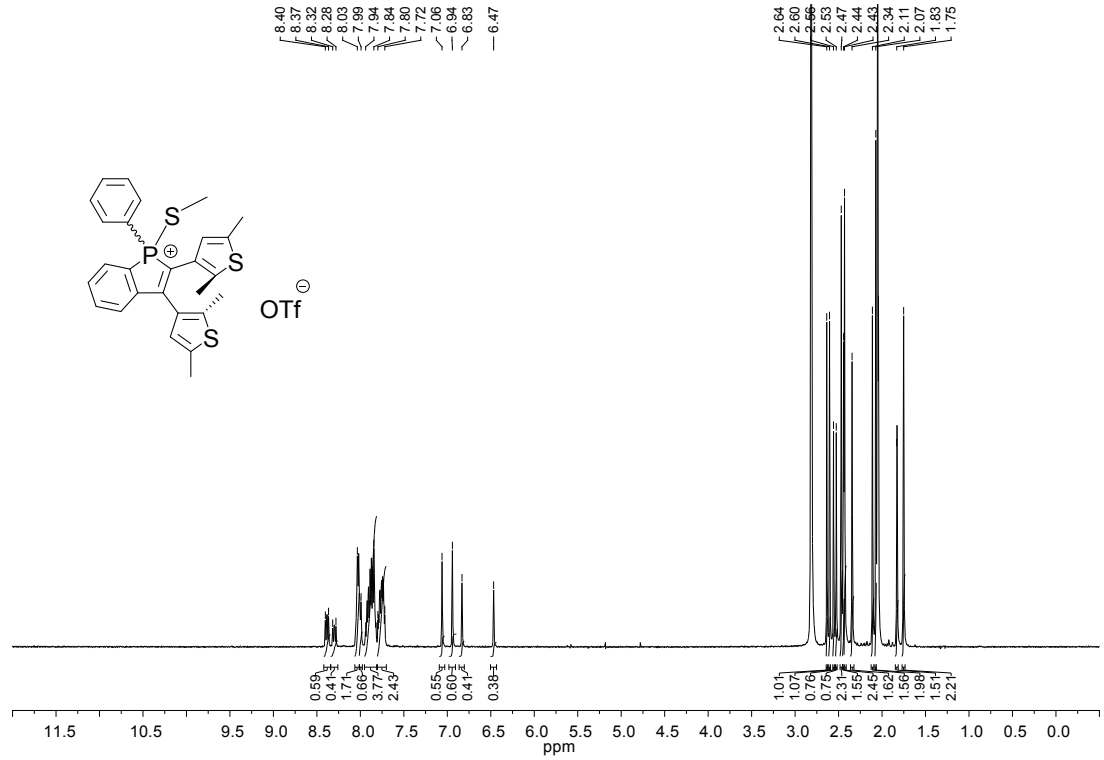


Fig. S30 ^{1}H NMR spectrum of **5** in [D_6]acetone.

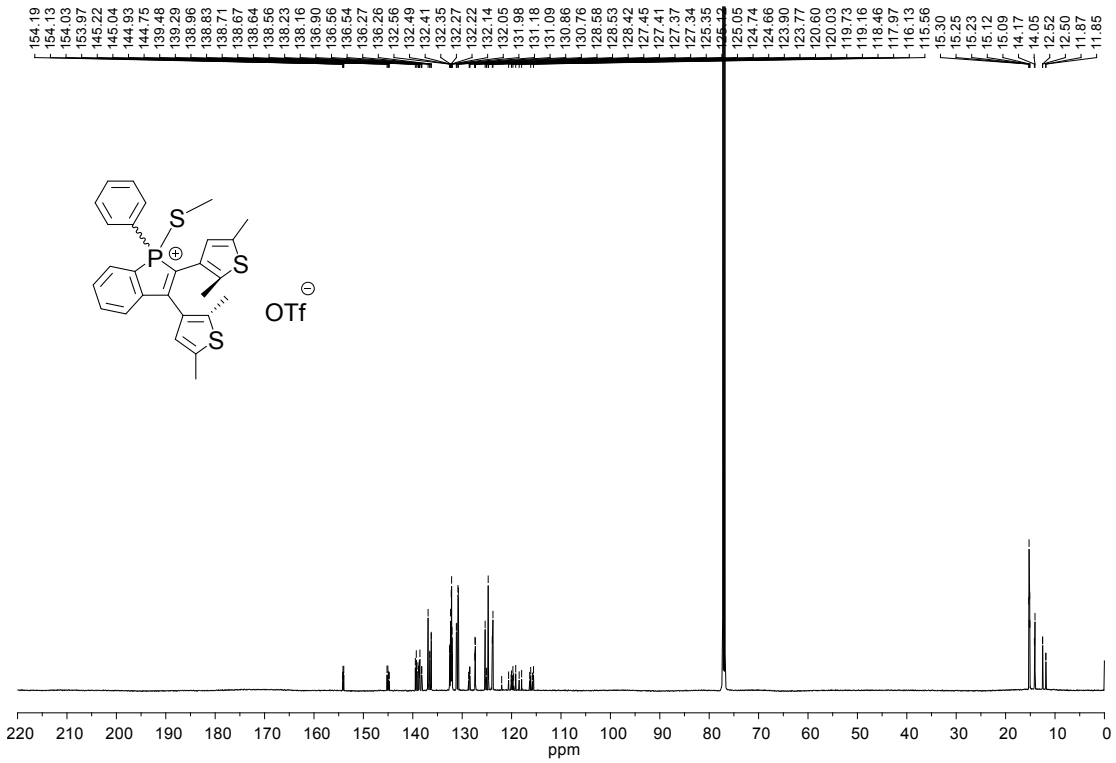


Fig. S31 $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

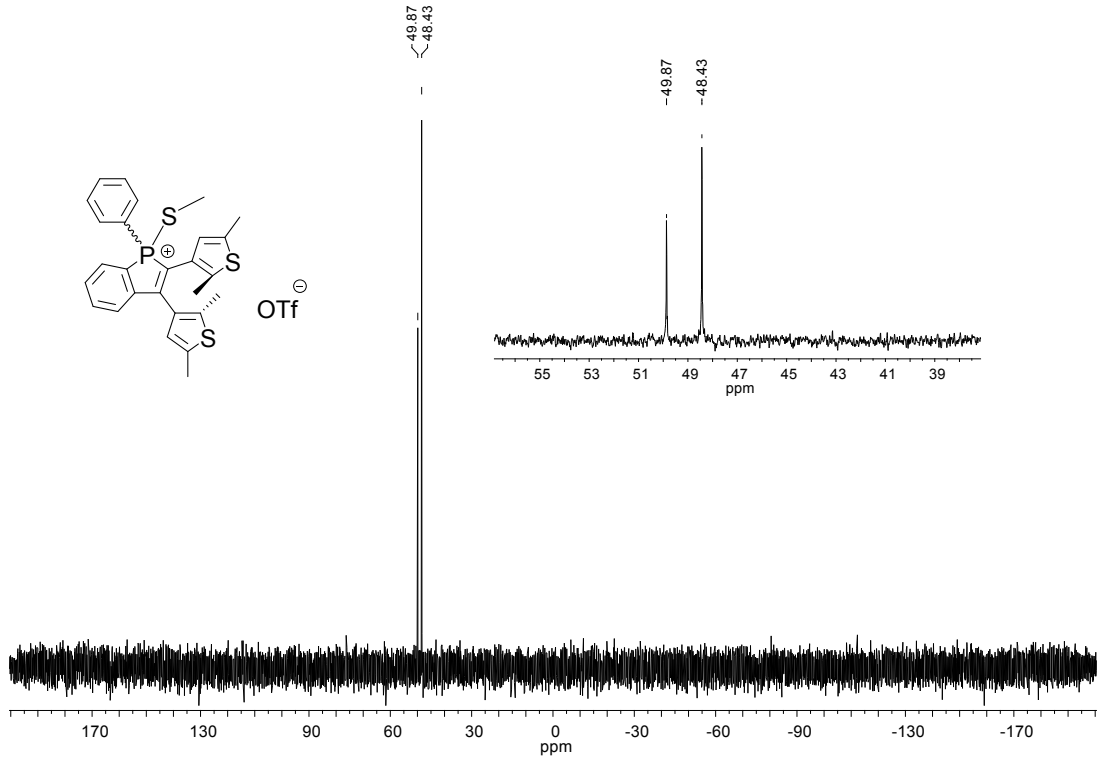


Fig. S32 $^{31}P\{^{1}H\}$ NMR spectrum of **5** in $[D_6]$acetone.

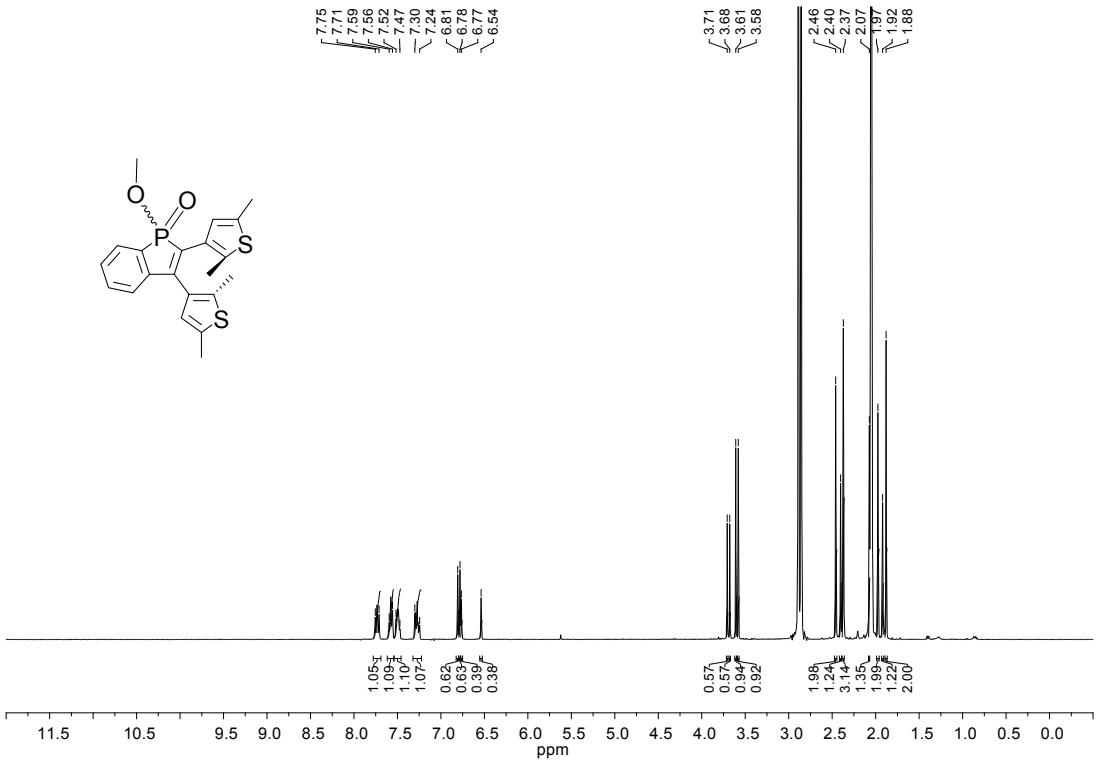


Fig. S33 ^{1}H NMR spectrum of **6** in $[D_6]$acetone.

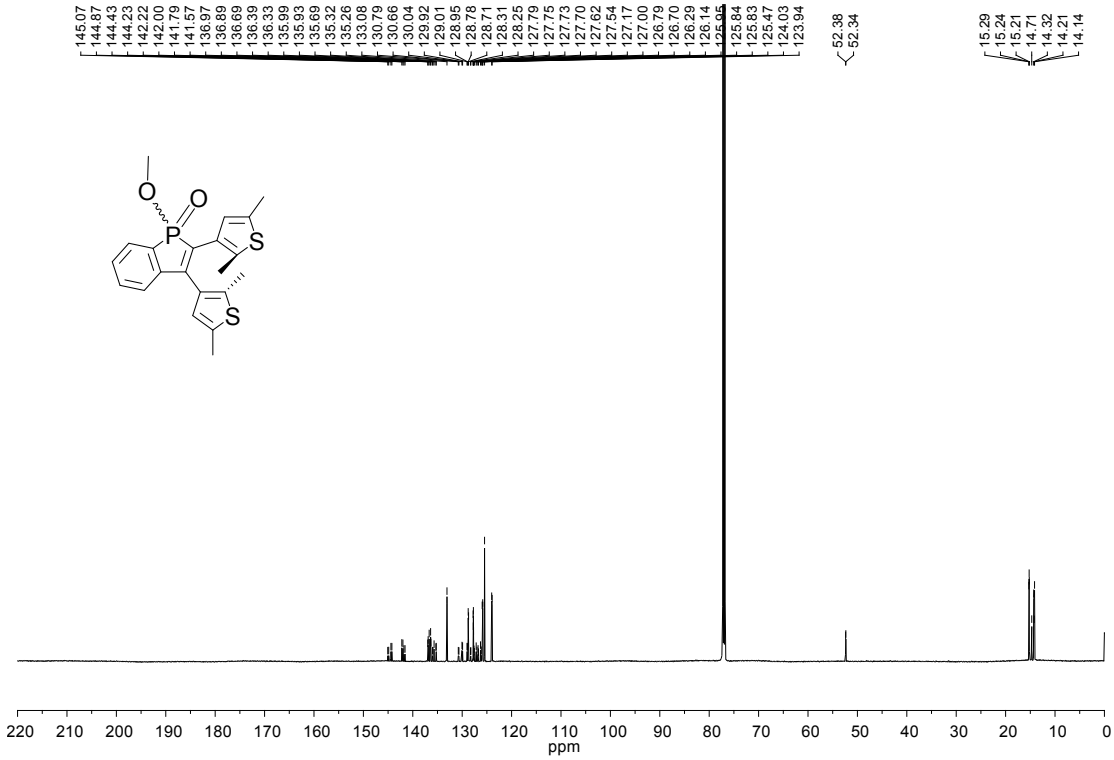


Fig. S34 $^{13}C\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$.

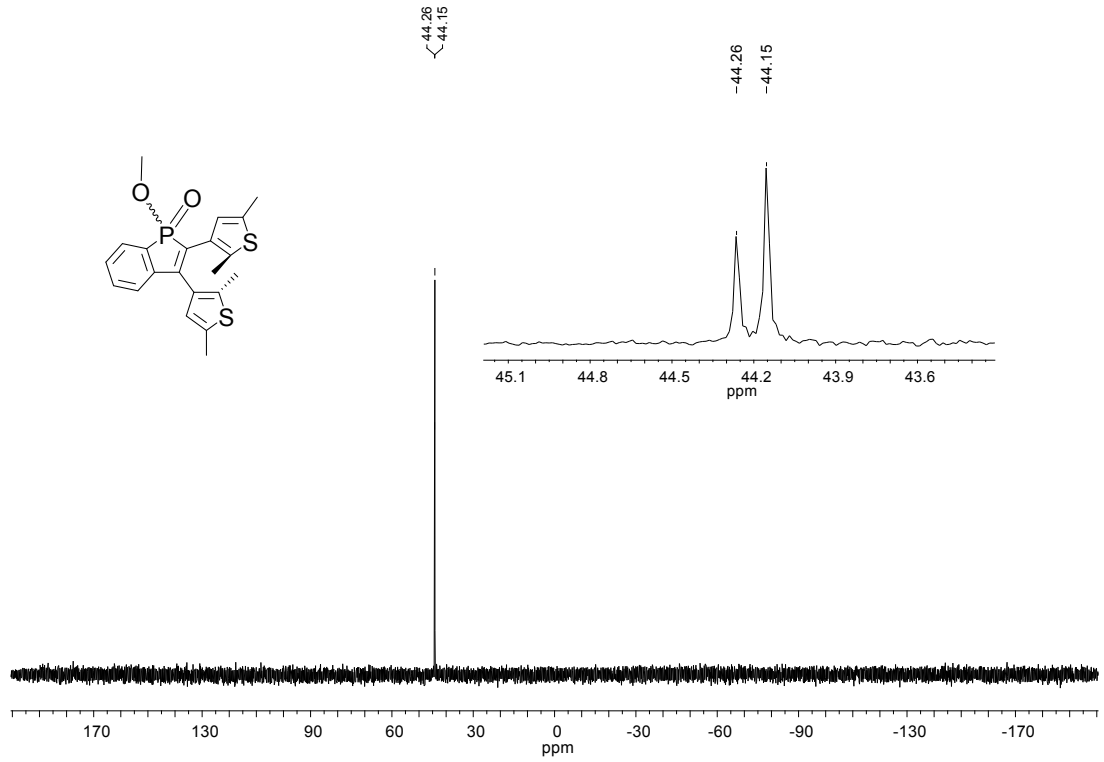


Fig. S35 $^{31}P\{^{1}H\}$ NMR spectrum of **6** in $[D_6]$acetone.

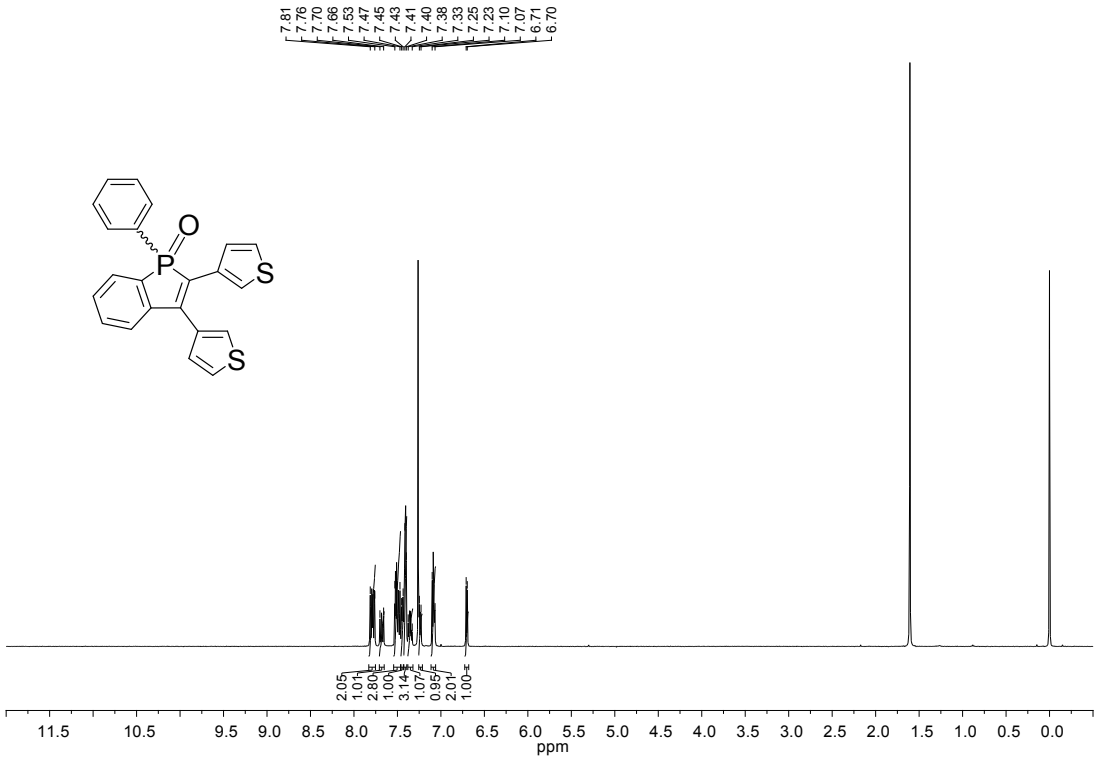


Fig. S36 ^{1}H NMR spectrum of **7** in $CDCl_3$.

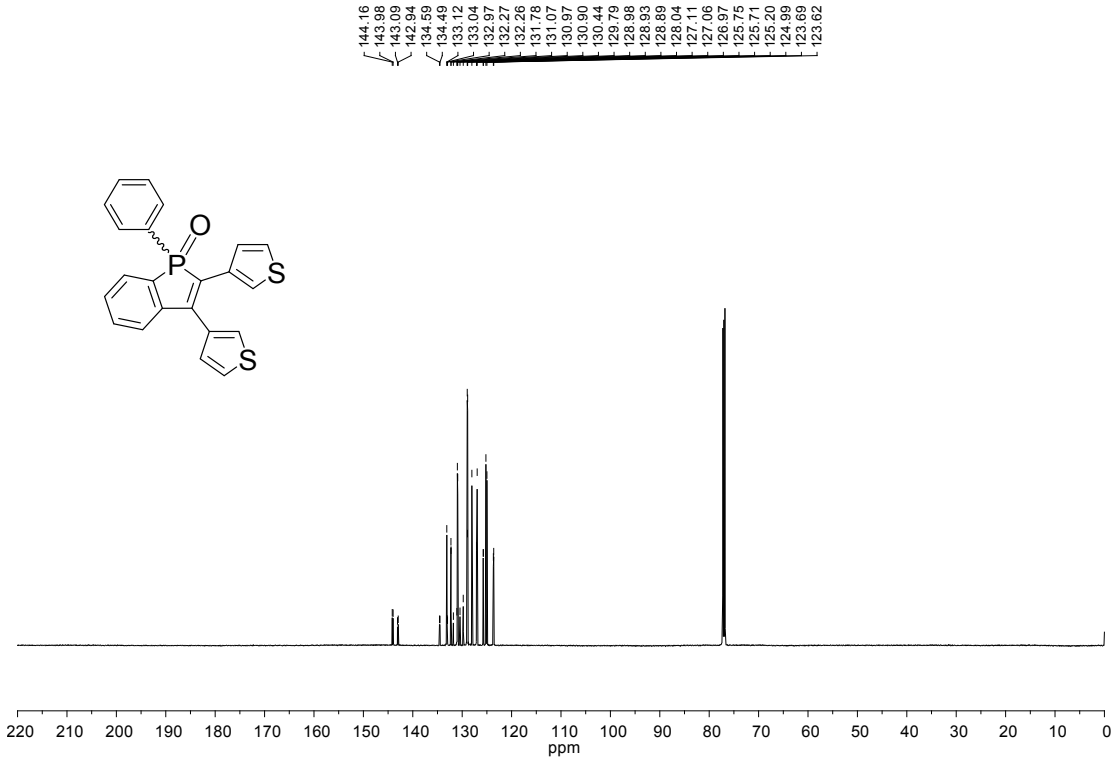


Fig. S37 $^{13}C\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$.

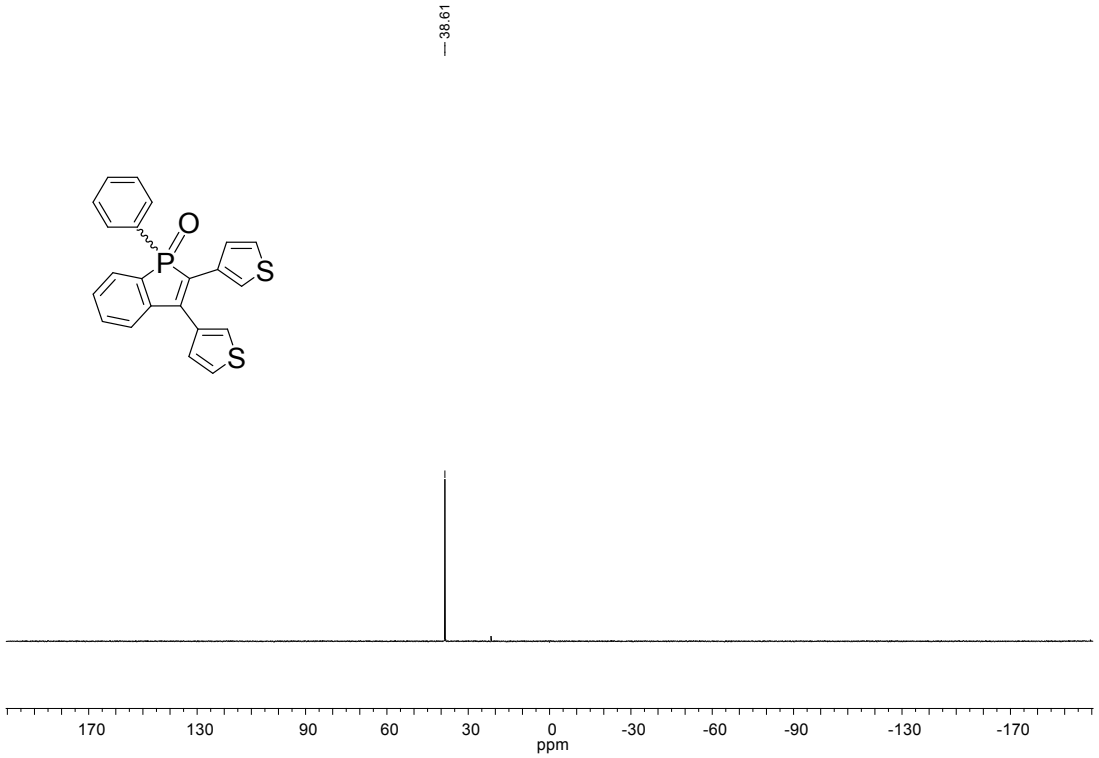


Fig. S38 $^{31}P\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$.

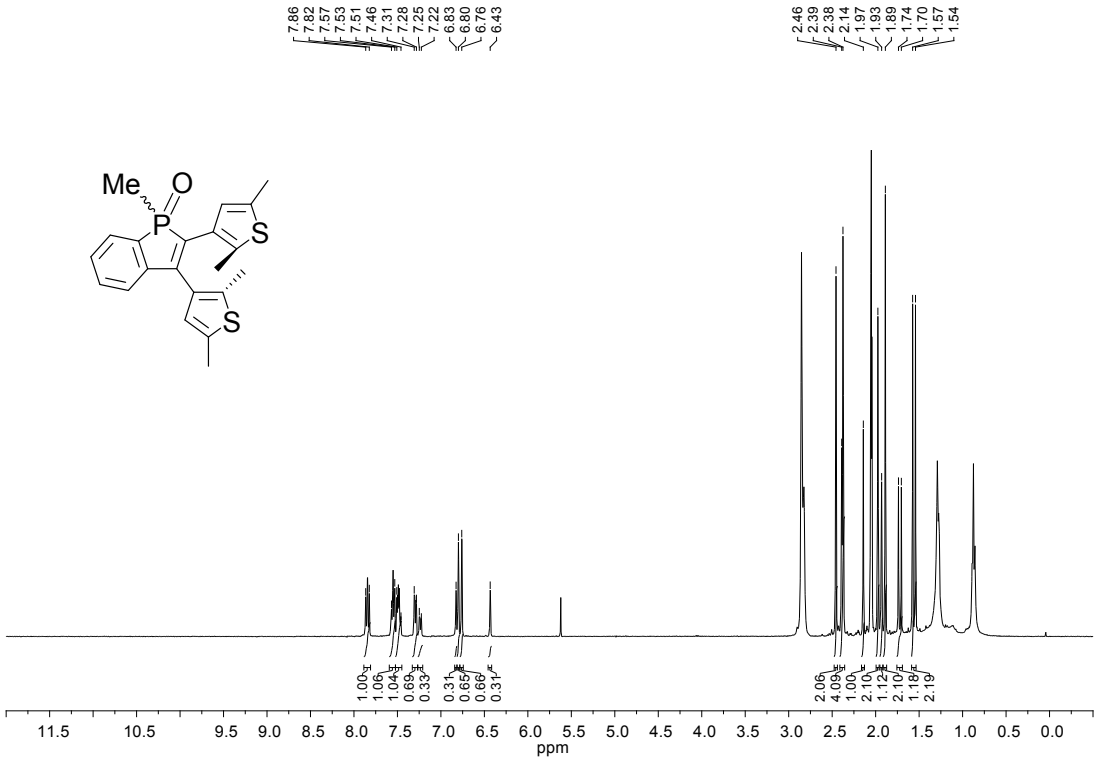


Fig. S39 ^{1}H NMR spectrum of **1-Me** in $[D_6]$acetone.

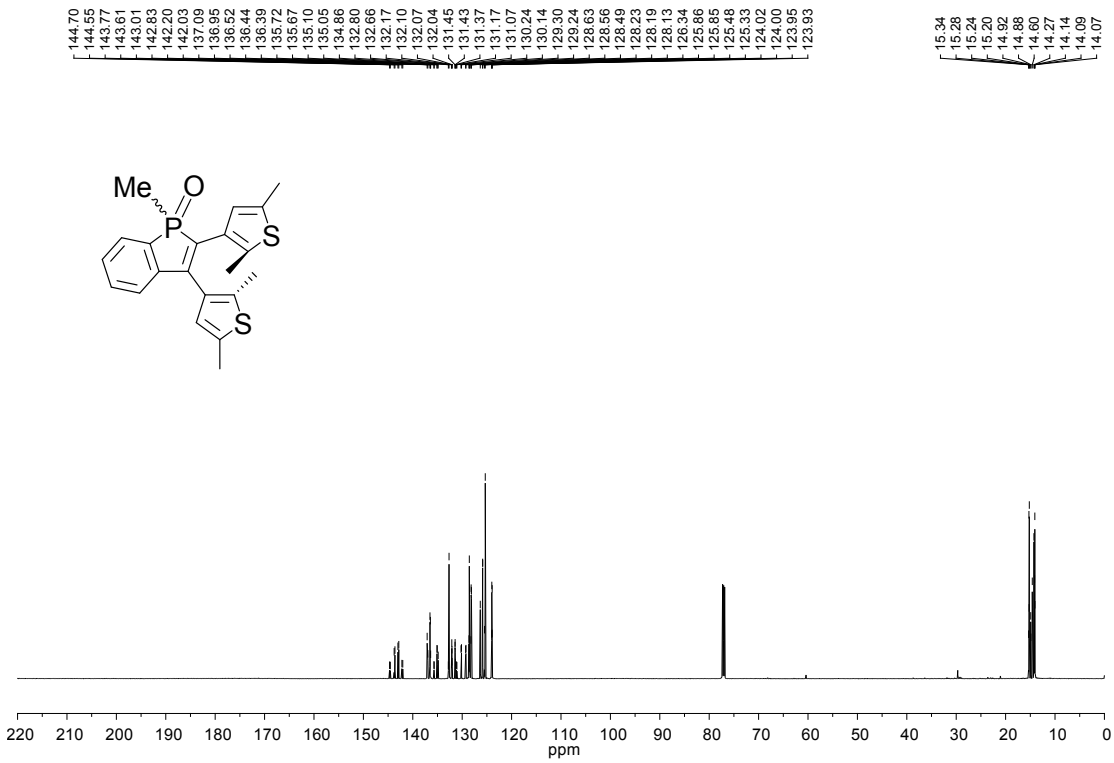


Fig. S40 $^{13}C\{^{1}H\}$ NMR spectrum of **1-Me** in $CDCl_3$.

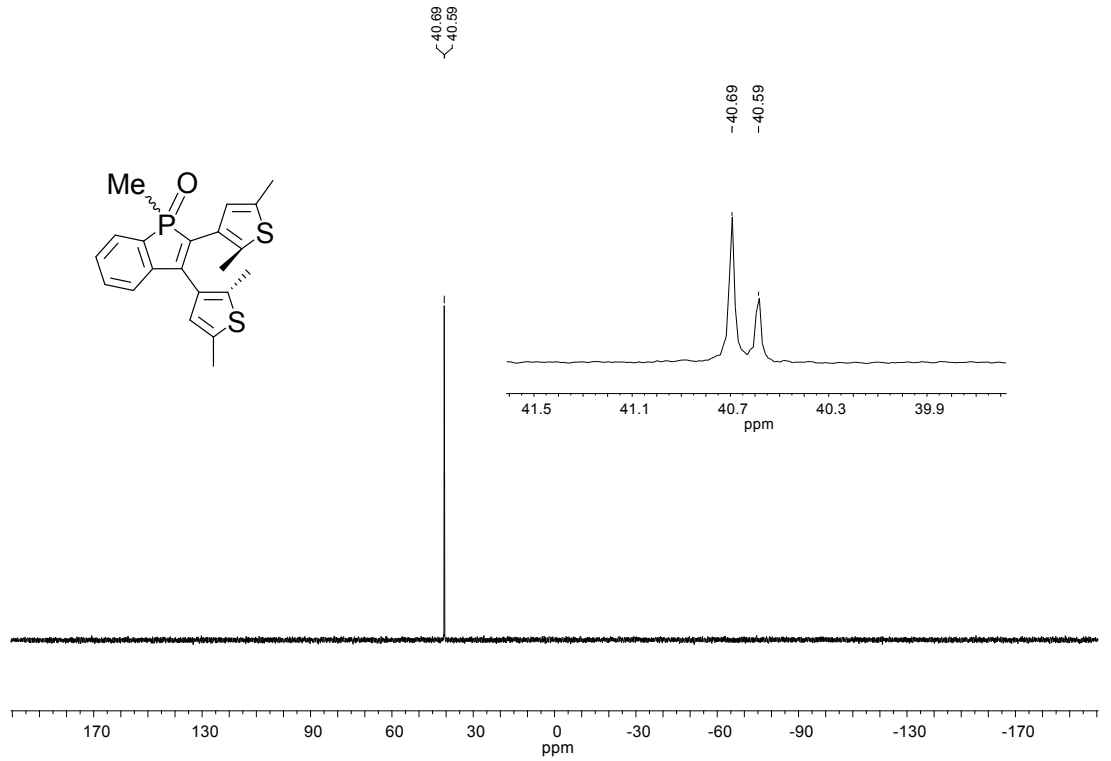


Fig. S41 $^{31}P\{^{1}H\}$ NMR spectrum of **1-Me** in $[D_6]$acetone.

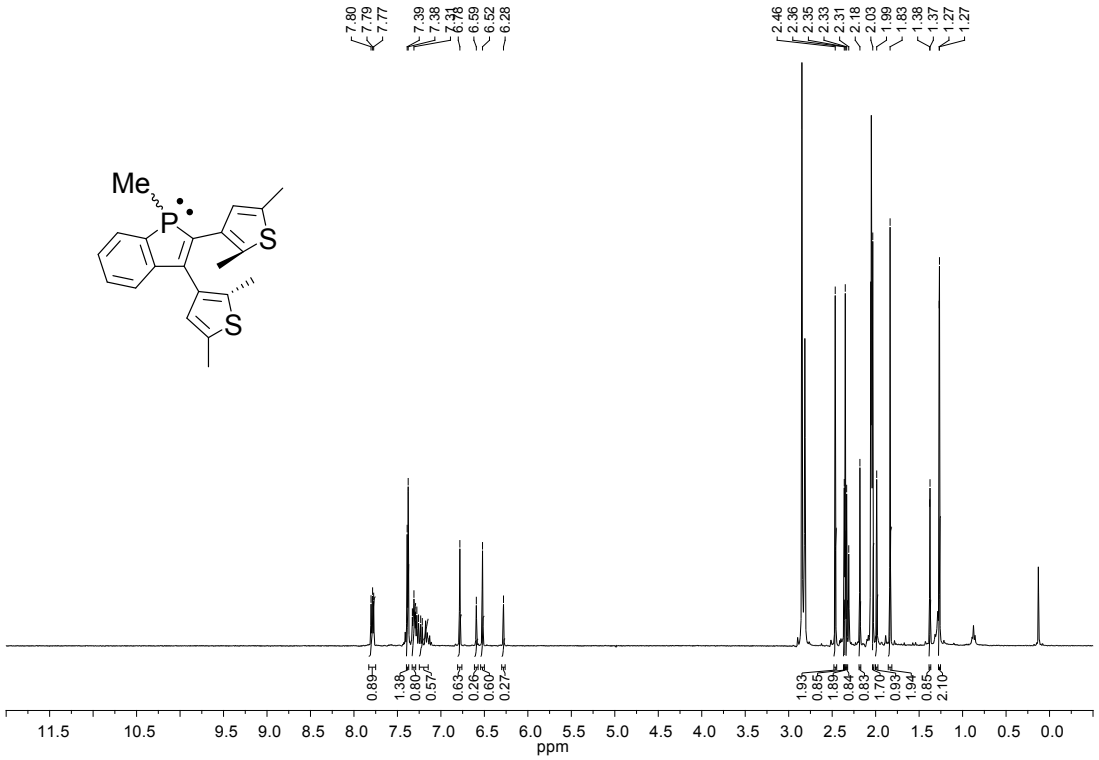


Fig. S42 ^{1}H NMR spectrum of **2-Me** in [D_6]acetone.

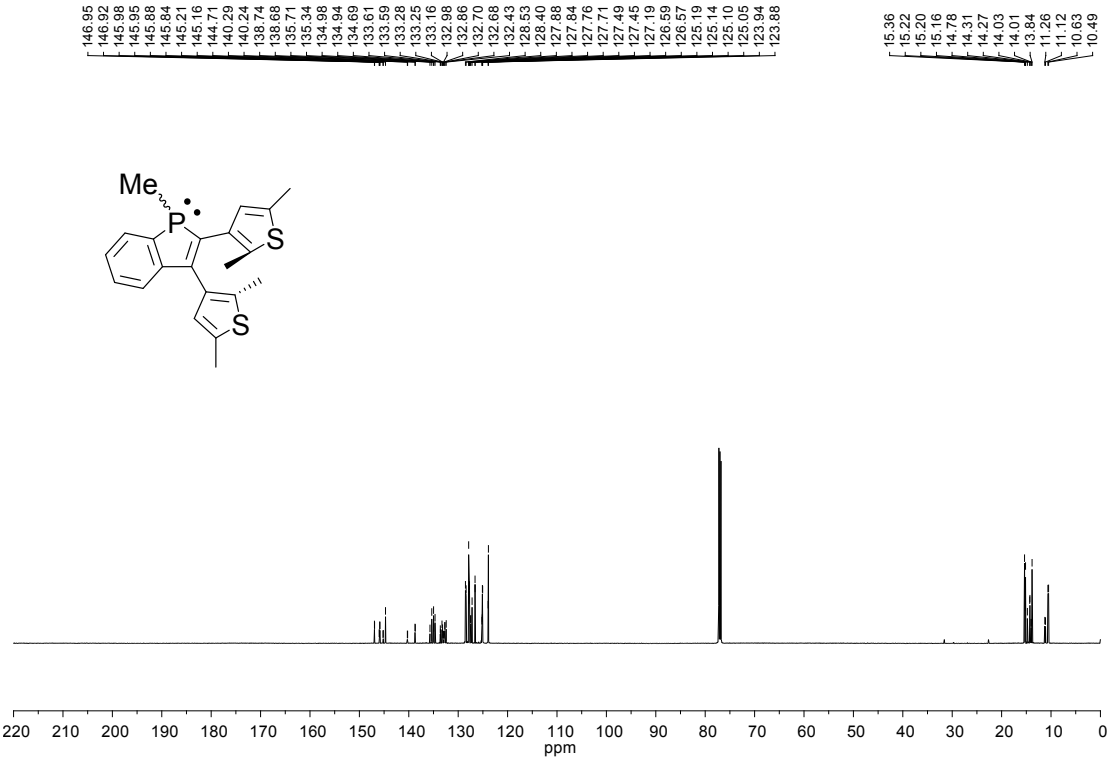


Fig. S43 $^{13}C\{^{1}H\}$ NMR spectrum of **2-Me** in $CDCl_3$.

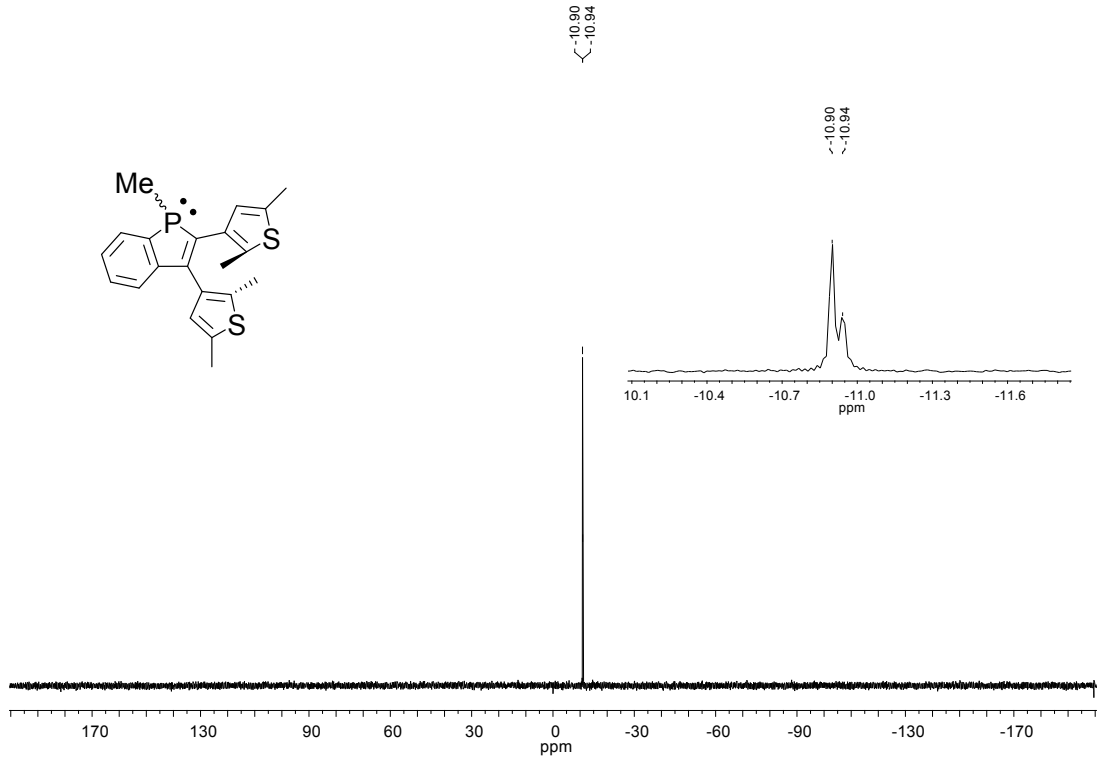


Fig. S44 $^{31}P\{^{1}H\}$ NMR spectrum of **2-Me** in $[D_6]$acetone.

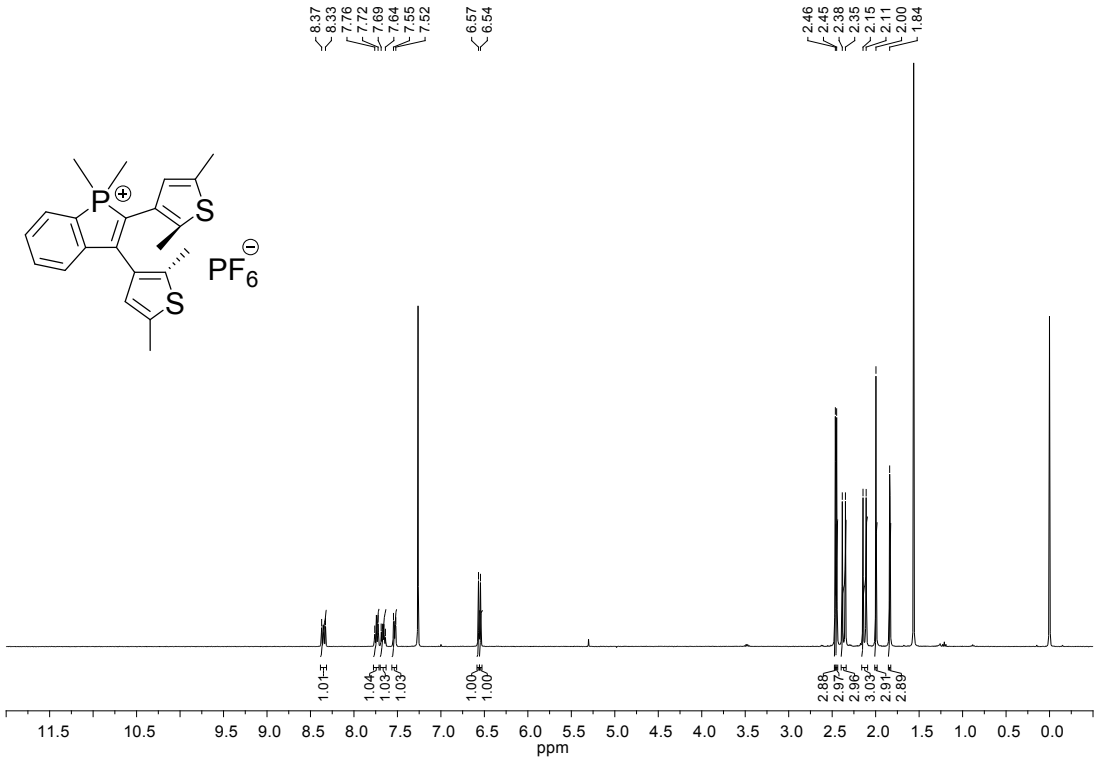


Fig. S45 ^{1}H NMR spectrum of **8** in $CDCl_3$.

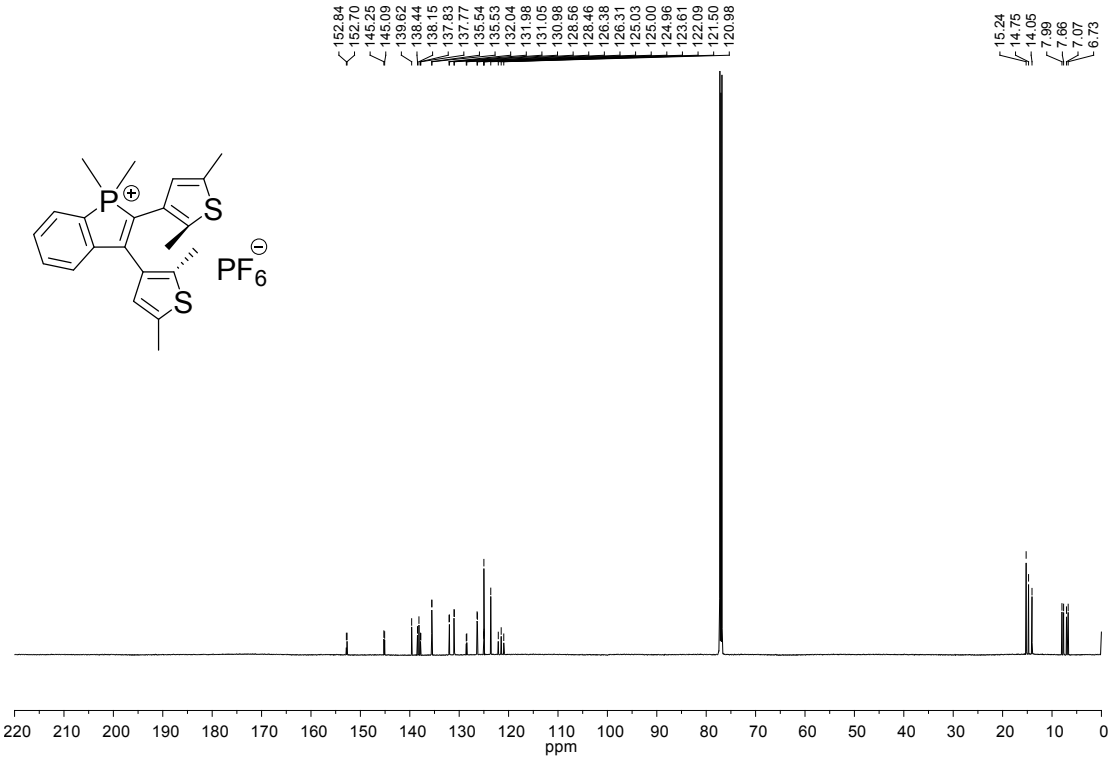


Fig. S46 $^{13}C\{^{1}H\}$ NMR spectrum of **8** in $CDCl_3$.

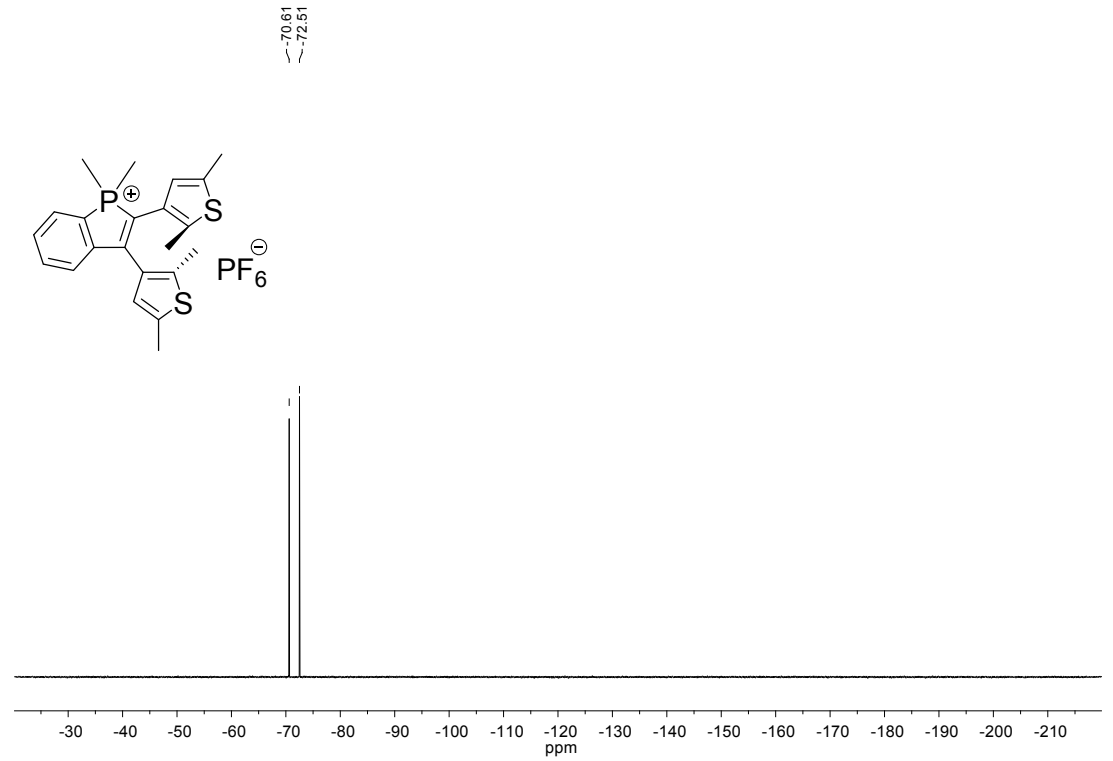


Fig. S47 $^{19}F\{^{1}H\}$ NMR spectrum of **8** in $CDCl_3$.

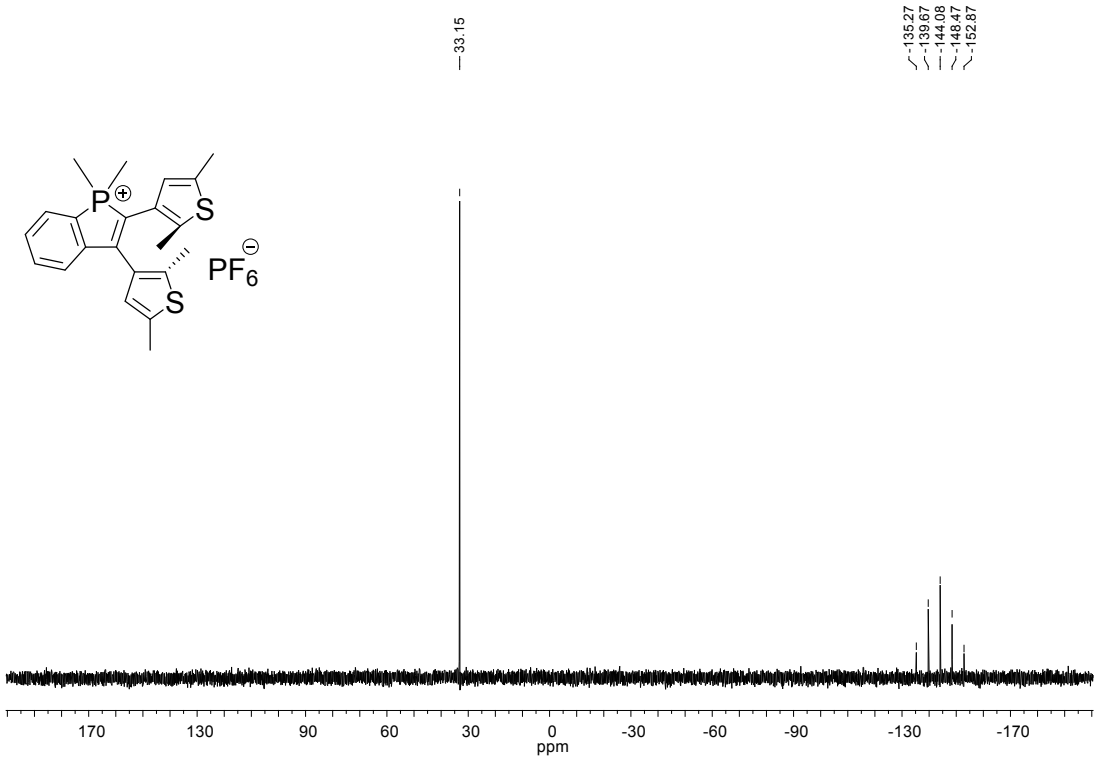


Fig. S48 $^{31}P\{^{1}H\}$ NMR spectrum of **8** in $CDCl_3$.

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