Supporting Information

Access to 4-Methylene-phospholenes through BF_3•Et_2O Catalyzed Isomerization of 3,4-Dimethylphosphole Sulfides

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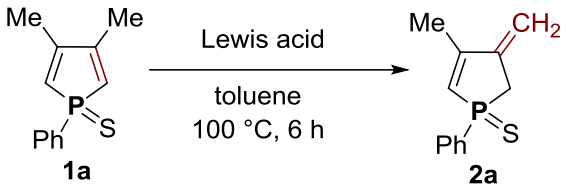
General information

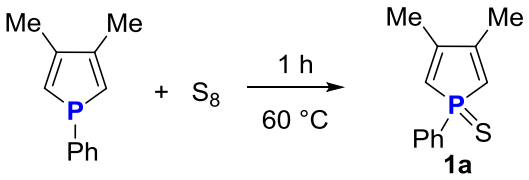
All reactions were performed under nitrogen using solvents dried by standard methods except for special statement. Toluene and THF were dried with Na and distilled before use. NMR spectra were obtained using BrukerAV300 spectrometer. All spectra were recorded in $CDCl_3$. All coupling constants (*J* values) were reported in hertz (Hz). Chemical shifts were expressed in parts per million (ppm) downfield from internal TMS (^1H). ^{13}C and ^{31}P spectra were recorded with proton decoupling. HRMS spectra were obtained by waters UPLC G2-XS Q-tof mass spectrometer. Melting Point: heating rate: 4°C/min, the thermometer was not corrected. Silica gel (200-300 mesh) were used for the chromatographic separations. All commercially available reagents were used without further purification. All new compounds were synthesized in small scale, and were purified by column chromatography or thin layer chromatography. 3,4-dimethyl-1-phenylphosphole was prepared according to the literature method.[1]

Experimental Procedures and Characterization Data

Table S1. Screening of Lewis Acids for the Isomerization of **1a**

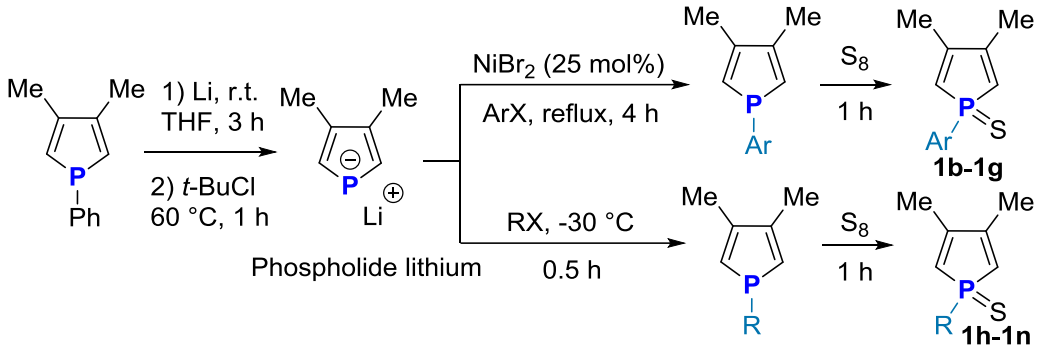


Entry	Lewis acid	Yield
1	$Sc(OTf)_3$ (20 mol%)	No reaction
2	$FeCl_2$ (20 mol%)	No reaction
3	$FeCl_3$ (20 mol%)	No reaction
4	$ZnCl_2$ (20 mol%)	No reaction
5	$AlCl_3$ (20 mol%)	18%
6	$BF_3{\cdot}Et_2O$ (20 mol%)	54%
7	BBr_3 (20 mol%)	27%
8	$BF_3{\cdot}Et_2O$ (30 mol%)	83%



A THF (20 mL) solution of 3,4-dimethyl-1-phenylphosphole (1 mL, 5 mmol) and sulfur powder (192 mg, 6 mmol) was heated at 60 °C for 1 hour. The solution was cooled down to room temperature and the solvent was removed by rotary evaporation. Purification was performed via column chromatography on silica using a 5:1 mixture of petroleum ether and ethyl acetate as the eluent to afford **1a** (1.01 g, 92%) as yellow solid.

Phosphole sulfide **1a** is a known compound.[2] **$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$)** δ 46.3 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.89 – 7.80 (m, 2H), 7.53 – 7.40 (m, 3H), 6.14 (d, J = 30.9 Hz, 2H), 2.13 (s, 6H).

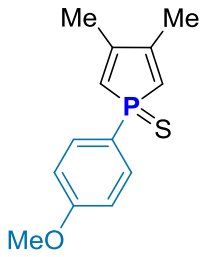


General procedure for the synthesis of phosphole sulfides 1b-1g

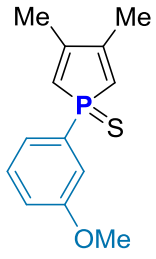
A 50 mL Schlenk tube was charged with nitrogen. Excess lithium wire was then added to a solution of 3,4-dimethyl-1-phenylphosphole (1 mL, 5 mmol) in THF (10 mL) at room temperature. The mixture was stirred at room temperature for 3 hours, yielding phospholide lithium and phenyllithium. After removing the lithium wire, *t*-BuCl (5 mmol) was added to the reaction mixture and heated for 1 hour to quench the phenyllithium. Subsequently, 12 mmol (2.4 eq.) of Ar-X and 1.25 mmol (0.25 eq.) of $NiBr_2$ were added to the reaction mixture, which was then refluxed for 4 hours. Sulfurization was completed by adding sulfur powder and heating the mixture at 60 °C for 1 hour. After cooling to room temperature, the mixture was filtered through a celite pad. The filtrate was evaporated to dryness, and the resulting residue was purified by column chromatography on silica gel using a 5:1 mixture of petroleum ether and ethyl acetate as the eluent, yielding phosphole sulfides **1b-1g**.

General procedure for the synthesis of phosphole sulfides 1h-1n

A 50 mL Schlenk tube was charged with nitrogen. Excess lithium wire was then added to a solution of 3,4-dimethyl-1-phenylphosphole (1 mL, 5 mmol) in THF (10 mL) at room temperature. The mixture was stirred at room temperature for 3 hours, yielding phospholide lithium and phenyllithium. After removing the lithium wire, *t*-BuCl (5 mmol) was added to the reaction mixture and heated for 1 hour to quench the phenyllithium. Subsequently, 6 mmol (1.2 eq.) of R-X was added to the reaction mixture at -30 °C and maintained at this temperature for 0.5 h. Sulfurization was completed by adding sulfur powder and heating the mixture at 60 °C for 1 hour. After cooling to room temperature, the mixture was filtered through a celite pad. The filtrate was evaporated to dryness, and the resulting residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as the eluent, yielding phosphole sulfides **1h-1n**.

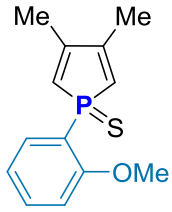


1b: yellow solid, **m.p.** 66.8-70.0 °C. ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 413.1 mg, 33%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 45.7 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 7.76 (dd, J =13.2, 8.7 Hz, 2H), 6.93 (dd, J = 8.4, 1.8 Hz, 2H), 6.10 (d, J = 30.8 Hz, 2H), 3.83 (s, 3H), 2.12 (s, 6H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** 162.74 (d, J_{CP} = 2.9 Hz), 153.2 (d, J_{CP} = 17.7 Hz), 132.4 (d, J_{CP} = 13.4 Hz), 126.0 (d, J_{CP} = 82.9 Hz), 118.2 (d, J_{CP} = 85.3 Hz), 114.3 (d, J_{CP} = 14.0 Hz), 55.4 (s), 17.4 (d, J_{CP} = 17.8 Hz). **HRMS (ESI)** $[M+Na]^+$ Calcd. for $C_{13}H_{15}NaOPS^+$: 273.0474; Found: 273.0468.

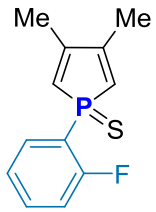


1c: yellow solid, **m.p.** 82.1-84.3 °C. ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 488.3 mg, 39%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 46.4 (s).**^1H NMR (300 MHz, $CDCl_3$)** δ 7.57 – 7.15 (m, 3H), 7.08 – 6.87 (m, 1H), 6.11 (d, J = 31.0 Hz, 2H), 3.83 (s, 3H), 2.12 (s, 6H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 159.8 (d, J_{CP} = 15.8 Hz), 153.8 (d, J_{CP} = 17.7 Hz), 129.9 (d, J_{CP} = 14.7 Hz), 129.3 (d, J_{CP}

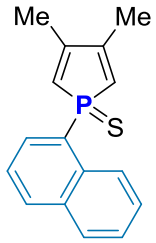
= 78.4 Hz), 125.6 (d, J_{CP} = 82.7 Hz), 122.1 (d, J_{CP} = 11.3 Hz), 117.7 (d, J_{CP} = 2.7 Hz), 116.0 (d, J_{CP} = 13.4 Hz), 55.5 (s), 17.5 (d, J_{CP} = 17.9 Hz). **HRMS (ESI)** $[M+Na]^+$ Calcd. for $C_{13}H_{15}NaOPS^+$: 273.0474; Found: 273.0467.



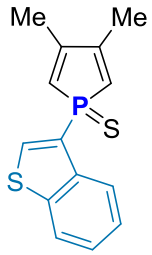
1d: yellow solid, **m.p.** 108.3-112.0 °C. ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 437.6 mg, 35%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 39.9 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 7.76 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.71 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.07 – 6.86 (m, 2H), 6.31 (d, *J* = 29.8 Hz, 2H), 3.90 (s, 3H), 2.07 (s, 6H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 160.9 (d, J_{CP} = 2.7 Hz), 152.4 (d, J_{CP} = 19.2 Hz), 133.7 (d, J_{CP} = 2.2 Hz), 132.9 (d, J_{CP} = 9.0 Hz), 124.2 (d, J_{CP} = 85.8 Hz), 120.9 (d, J_{CP} = 12.4 Hz), 119.7 (d, J_{CP} = 81.9 Hz), 111.6 (d, J_{CP} = 6.3 Hz), 56.0 (s), 17.5 (d, J_{CP} = 18.2 Hz). **HRMS (ESI)** $[M+Na]^+$ Calcd. for $C_{13}H_{15}NaOPS^+$: 274.0507; Found: 274.0499.



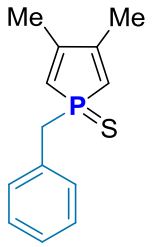
1e: yellow solid, **m.p.** 115.0-118.5 °C. ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 354.8 mg, 30%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 48.9 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 4.3 Hz, 1H), 7.80 (dd, *J* = 13.5, 7.6 Hz, 1H), 7.37 (t, *J* = 7.1 Hz, 1H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 29.8 Hz, 2H), 2.09 (s, 6H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 153.7 (d, *J* = 19.3 Hz), 142.0 (d, *J* = 8.9 Hz), 136.2 (d, *J* = 85.0 Hz), 132.8 (s), 132.8 (d, *J* = 14.4 Hz), 128.0 (d, *J* = 11.2 Hz), 123.1 (d, *J* = 85.6 Hz), 99.2 (d, *J* = 7.8 Hz), 17.7 (d, J_{CP} = 18.0 Hz). **HRMS (ESI)** $[M+Na]^+$ Calcd. for $C_{12}H_{21}FNaPS^+$: 261.0274 ; Found: 261.0266.



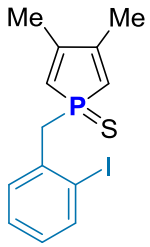
1f: yellow solid, **m.p.** 76.2-79.6 °C. ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 606.4 mg, 45%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 44.8 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 8.81 (d, J = 8.1 Hz, 1H), 8.03 – 7.73 (m, 3H), 7.64 – 7.53 (m, 1H), 7.51 – 7.42 (m, 1H), 7.31 (d, J = 7.5 Hz, 1H), 6.45 (d, J = 30.6 Hz, 2H), 1.96 (s, 6H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 153.1 (d, J_{CP} = 18.4 Hz), 133.8 (d, J_{CP} = 9.0 Hz), 133.3 (s), 133.2 (d, J_{CP} = 3.1 Hz), 130.2 (d, J_{CP} = 10.8 Hz), 129.3 (s), 128.5 (s), 127.5 (s), 127.0 (d, J_{CP} = 56.2 Hz), 126.1 (d, J_{CP} = 7.1 Hz), 124.8 (d, J_{CP} = 14.2 Hz), 124.5 (d, J_{CP} = 83.8 Hz), 17.6 (d, J_{CP} = 17.6 Hz). **HRMS (ESI)** $[M+Na]^+$ Calcd. for $C_{16}H_{15}NaPS^+$: 293.0525 ; Found: 293.0516.



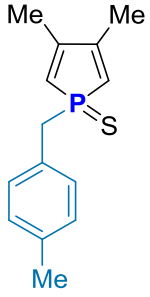
1g: pink solid, **m.p.** 86.7-89.0 °C. ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 323.6 mg, 23%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 35.3 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 8.40 (d, J = 10.9 Hz, 1H), 7.93 – 7.80 (m, 2H), 7.44 – 7.34 (m, 2H), 6.22 (d, J = 31.3 Hz, 2H), 2.16 (s, 6H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 154.0 (d, J_{CP} = 19.0 Hz), 141.7 (d, J_{CP} = 11.9 Hz), 139.1 (d, J_{CP} = 16.0 Hz), 137.2 (d, J_{CP} = 13.5 Hz), 125.1 (s), 125.0 (s), 124.4 (d, J_{CP} = 81.1 Hz), 124.2 (s), 123.1 (s), 123.1 (s), 17.6 (d, J_{CP} = 18.2 Hz). **HRMS (ESI)** $[M+Na]^+$ Calcd. for $C_{14}H_{13}NaPS_2^+$: 299.0089; Found: 299.0087.



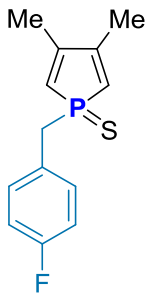
1h: yellow solid, ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 569.7 mg, 49%, known compound.[2] **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 50.7 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 7.17 – 7.03 (m, 5H), 5.84 (d, J = 30.9 Hz, 2H), 3.28 (d, J = 14.4 Hz, 2H), 1.80 (s, 6H).



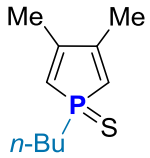
1i: yellow solid, **m.p.** 75.6-82.4 °C. ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 794.6 mg, 44%. **$^{31}P\{^1H\}$ NMR (121 MHz, DMSO-d6)** δ 51.2 (s).**^1H NMR (300 MHz, DMSO-d6)** δ 7.37 (d, *J* = 7.7 Hz, 1H), 6.98 – 6.79 (m, 2H), 6.54 (d, *J* = 5.7 Hz, 1H), 5.70 (d, *J* = 31.6 Hz, 2H), 3.27 (d, *J* = 15.5 Hz, 2H), 1.44 (s, 6H). **$^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d6)** δ 153.70 (d, J_{CP} = 17.1 Hz), 139.47 (d, J_{CP} = 2.7 Hz), 136.08 (d, J_{CP} = 8.9 Hz), 131.18 (d, J_{CP} = 4.8 Hz), 129.24 (d, J_{CP} = 3.5 Hz), 127.97 (d, J_{CP} = 3.6 Hz), 122.69 (d, J_{CP} = 78.4 Hz), 102.45 (d, J_{CP} = 6.8 Hz), 45.03 (d, J_{CP} = 44.3 Hz), 17.10 (d, J_{CP} = 17.4 Hz). **HRMS (ESI)** $[M+H]^+$ Calcd. for $C_{13}H_{15}IPS^+$: 360.9672; Found: 360.9664.



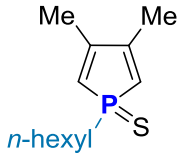
1j: yellow solid, **m.p.** 46.5-52.0 °C. ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 831.5 mg, 67%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 50.9 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 7.07 (s, 4H), 5.96 (d, *J* = 30.8 Hz, 2H), 3.36 (d, *J* = 14.2 Hz, 2H), 2.31 (d, *J* = 2.4 Hz, 3H), 1.96 (s, 6H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 153.4 (d, J_{CP} = 16.8 Hz), 136.8 (d, J_{CP} = 4.2 Hz), 129.6 (d, J_{CP} = 5.5 Hz), 128.9 (d, J_{CP} = 3.2 Hz), 128.8 (s), 123.4 (d, J_{CP} = 79.1 Hz), 39.8 (d, J_{CP} = 46.2 Hz), 21.2 (s), 17.4 (d, J_{CP} = 17.1 Hz). **HRMS (ESI)** $[M+H]^+$ Calcd. for $C_{14}H_{18}PS^+$: 249.0862; Found: 249.0860.



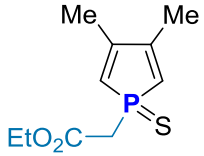
1k: Yellow solid, ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 819.0 mg, 65%. **$^{31}P\{^1H\}$ NMR (121 MHz, CDCl3)** δ 51.9 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 7.14 (bs, 2H), 7.00-6.94 (m, 2H), 5.96 (d, *J* = 30.9 Hz, 2H), 3.37 (d, *J* = 14.2 Hz, 2H), 1.97 (s, 6H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 153.8 (d, *J* = 17.0 Hz), 131.3 (d, *J* = 5.4 Hz), 131.2 (d, *J* = 5.3 Hz), 127.8 (d, *J* = 13.8 Hz), 123.0 (d, *J* = 79.3 Hz), 115.1 (d, *J* = 21.1 Hz), 39.4 (d, *J* = 46.4 Hz), 17.3 (d, *J* = 17.1 Hz). **HRMS (ESI)** $[M+H]^+$ Calcd. for $C_{13}H_{15}FPS^+$: 253.0611; Found: 253.0608



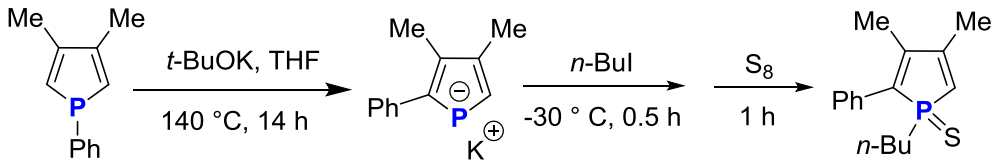
1l: yellow oil, ethyl acetate/petroleum ether = 1:10, R_f = 0.40, 605.2 mg, 60%, known compound.[3] **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 51.9 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 5.77 (d, *J* = 31.5 Hz, 2H), 1.82 (s, 6H), 1.76 – 1.67 (m, 2H), 1.39 – 1.29 (m, 2H), 1.21 – 1.09 (m, 2H), 0.67 (t, *J* = 7.2 Hz, 3H).



1m: yellow oil, ethyl acetate/petroleum ether = 1:10, R_f = 0.40, 622.8 mg, 55%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 51.6 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 6.01 (d, *J* = 31.2 Hz, 2H), 2.07 (s, 6H), 2.03 – 1.90 (m, 2H), 1.70 – 1.54 (m, 2H), 1.42 – 1.22 (m, 6H), 0.88 (t, *J* = 6.7 Hz, 3H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 153.0 (d, J_{CP} = 16.9 Hz), 124.0 (d, J_{CP} = 78.0 Hz), 31.5 (d, J_{CP} = 51.0 Hz), 31.2 (s), 30.2 (d, J_{CP} = 14.8 Hz), 23.6 (d, J_{CP} = 3.7 Hz), 22.4 (s), 17.4 (d, J_{CP} = 16.9 Hz), 14.0 (s). **HRMS (ESI)** $[M+H]^+$ Calcd. for $C_{12}H_{22}PS^+$: 229.1175; Found: 229.1173.



1n: yellow oil, ethyl acetate/petroleum ether = 1:10, R_f = 0.30, 511.2 mg, 44%, known compound.[3] **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 43.7 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 5.95 (d, *J* = 31.5 Hz, 2H), 4.02 (q, *J* = 6.9 Hz, 2H), 2.99 (d, *J* = 14.1 Hz, 2H), 1.94 (s, 6H), 1.11 (t, *J* = 6.9 Hz, 3H).

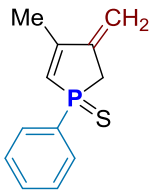


In a 75 mL heavy wall pressure tube, *t*-BuOK (1.2 eq.) was added to a solution of 3,4-dimethyl-1-phenylphosphole (1 mL, 5 mmol) in THF (10 mL). The solution was stirred at 140 °C in an oil bath for 14 h. After cooling to room temperature, open the cap and transfer the 2-phenylphospholide solution to another 50 mL Schlenk flask. *n*-BuI was then added to the reaction mixture at -30 °C and maintained at this temperature for 0.5 h. Sulfurization was completed by adding sulfur powder and heating the mixture at 60 °C for 1 hour. After cooling to room temperature, the mixture was filtered through a celite pad. The filtrate was evaporated to dryness, and the resulting residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as the eluent, yielding phosphole sulfide **1o** as yellow solid.

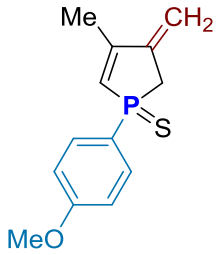
1o: yellow solid, **m.p.** 58.6-60.7 °C. ethyl acetate/petroleum ether = 1:10, R_f = 0.40, 276.4 mg, 39%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 56.7 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 7.7 Hz, 2H), 7.44 – 7.30 (m, 3H), 6.06 (d, *J* = 31.2 Hz, 1H), 2.14 (s, 3H), 2.02 (d, *J* = 2.4 Hz, 3H), 1.97 – 1.79 (m, 2H), 1.58 – 1.18 (m, 4H), 0.83 (t, *J* = 7.1 Hz, 3H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 154.0 (d, J_{CP} = 16.0 Hz), 145.8 (d, J_{CP} = 24.2 Hz), 135.5 (d, J_{CP} = 75.2 Hz), 133.4 (d, J_{CP} = 11.8 Hz), 128.9 (d, J_{CP} = 4.4 Hz), 128.6 (s), 128.1 (d, J_{CP} = 1.2 Hz), 121.5 (d, J_{CP} = 78.0 Hz), 31.2 (d, J_{CP} = 49.6 Hz), 25.0 (d, J_{CP} = 3.9 Hz), 23.6 (d, J_{CP} = 15.4 Hz), 18.1 (d, J_{CP} = 16.2 Hz), 14.4 (d, J_{CP} = 13.3 Hz), 13.6(s). **HRMS (ESI)** $[M+H]^+$ Calcd. for $C_{16}H_{22}PS^+$: 277.1175; Found: 277.1166.

General procedure for the isomerization of phosphole sulfides.

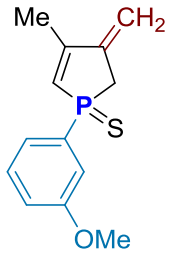
In a 25 mL Schlenk tube, 15 μL (0.12 mmol, 0.3 eq.) $BF_3 \cdot Et_2O$ was added to a solution of phosphole sulfides **1** (0.4 mmol) in toluene (3 mL). The reaction mixture was stirred at 100 °C in an oil bath for 6 h. After cooling to room temperature, the mixture was evaporated to dryness, and the resulting residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as the eluent, yielding isomerization product **2a-2n**.



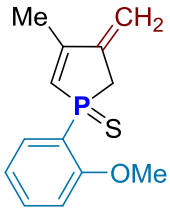
2a, ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 74.6mg 83%, known compound.[4] **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 49.8 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 7.86 – 7.93(m, 2H), 7.53 – 7.42 (m 3H), 6.11 (d, *J* = 24.9 Hz, 1H), 5.37 (d, *J* = 46.5 Hz, 2H), 3.32 – 3.11 (m, 2H), 2.14 (s, 3H).



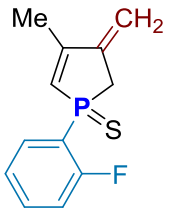
2b: yellow oil, ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 78.8 mg, 78%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 47.9 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 7.74 (dd, *J* = 13.2, 8.5 Hz, 2H), 6.96 (dd, *J* = 8.6, 2.0 Hz, 2H), 6.09 (d, *J* = 24.9 Hz, 1H), 5.35 (d, *J* = 44.6 Hz, 2H), 3.84 (s, 3H), 3.42 – 2.98 (m, 2H), 2.13 (s, 3H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 162.4 (d, J_{CP} = 2.9 Hz), 156.1 (d, J_{CP} = 12.9 Hz), 145.5 (d, J_{CP} = 9.6 Hz), 132.8 (d, J_{CP} = 13.1 Hz), 127.9 (d, J_{CP} = 78.1 Hz), 123.6 (d, J_{CP} = 85.5 Hz), 114.0 (d, J_{CP} = 13.8 Hz), 112.7 (d, J_{CP} = 13.8 Hz), 55.4 (s), 40.5 (d, J_{CP} = 59.6 Hz), 16.4 (d, J_{CP} = 17.3 Hz). **HRMS (ESI)** $[M+Na]^+$ Calcd. for $C_{13}H_{15}NaOPS^+$: 273.0474; Found: 273.0463.



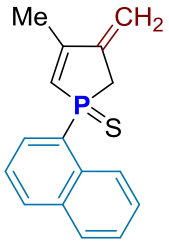
2c: yellow oil, ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 80.1 mg, 80%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 50.1 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 7.52 – 7.25 (m, 3H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.10 (d, *J* = 25.1 Hz, 1H), 5.48 – 5.25 (m, 2H), 3.85 (s, 3H), 3.39 – 3.06 (m, 2H), 2.14 (s, 3H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 159.6 (d, J_{CP} = 15.7 Hz), 156.6 (d, J_{CP} = 12.7 Hz), 145.4 (d, J_{CP} = 9.3 Hz), 134.3 (d, J_{CP} = 78.5 Hz), 129.7 (d, J_{CP} = 14.6 Hz), 127.4 (d, J_{CP} = 78.1 Hz), 122.7 (d, J_{CP} = 11.0 Hz), 117.6 (d, J_{CP} = 2.9 Hz), 116.2 (d, J_{CP} = 13.3 Hz), 112.9 (d, J_{CP} = 13.9 Hz), 55.5 (s), 40.3 (d, J_{CP} = 59.2 Hz), 16.4 (d, J_{CP} = 17.3 Hz). **HRMS (ESI)** $[M+H]^+$ Calcd. for $C_{13}H_{16}OPS^+$: 251.0654; Found: 251.0656.



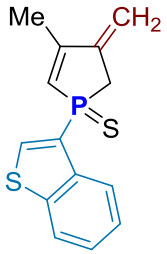
2d: yellow oil, ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 68.7 mg, 74%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 48.2 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 8.16 (ddd, *J* = 16.7, 7.6, 1.5 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.89 (dd, *J* = 8.1, 5.7 Hz, 1H), 6.05 (d, *J* = 25.3 Hz, 1H), 5.49 – 5.15 (m, 2H), 3.78 (s, 3H), 3.54 (dd, *J* = 17.3, 9.2 Hz, 1H), 3.14 – 2.95 (m, 1H), 2.07 (s, 3H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 160.2 (d, J_{CP} = 2.9 Hz), 154.9 (d, J_{CP} = 14.3 Hz), 146.8 (d, J_{CP} = 10.4 Hz), 135.4 (d, J_{CP} = 10.6 Hz), 134.0 (d, J_{CP} = 2.5 Hz), 126.7 (d, J_{CP} = 80.4 Hz), 120.9 (d, J_{CP} = 12.9 Hz), 119.7 (d, J_{CP} = 78.6 Hz), 111.2 (d, J_{CP} = 14.8 Hz), 110.8 (d, J_{CP} = 6.1 Hz), 55.5 (s), 38.5 (d, J_{CP} = 61.8 Hz), 16.3 (d, J_{CP} = 18.0 Hz). **HRMS (ESI)** $[M+Na]^+$ Calcd. for $C_{13}H_{15}NaOPS^+$: 273.0474; Found: 273.0448.



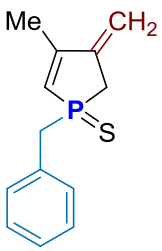
2e: yellow oil, ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 66.1 mg, 71%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 57.1 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 7.99 (dd, *J* = 7.8, 3.7 Hz, 1H), 7.88 – 7.77 (m, 1H), 7.54 – 7.34 (m, 1H), 7.19 – 6.98 (m, 1H), 6.40 (d, *J* = 23.6 Hz, 1H), 5.33 (dd, *J* = 34.8, 1.6 Hz, 2H), 3.19 - 3.74 (dm, 2H), 2.11 (s, 3H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 157.0 (d, *J* = 14.4 Hz), 145.0 (d, *J* = 10.5 Hz), 142.0 (d, *J*= 8.8 Hz), 137.5 (d, J_{CP} = 83.7 Hz), 133.3 (d, *J* = 12.0 Hz), 132.5 (d, *J* = 2.7 Hz), 127.9 (d, *J* = 11.1 Hz), 125.4 (d, *J* = 81.9 Hz), 113.4 (d, *J* = 14.4 Hz), 98.0 (d, J_{CP} = 8.2 Hz), 38.8 (d, J_{CP} = 59.7 Hz), 16.6 (d, J_{CP} = 17.3 Hz). **HRMS (ESI)** $[M+Na]^+$ Calcd. for $C_{12}H_{21}FNaPS^+$: 261.0274; Found: 261.0277.



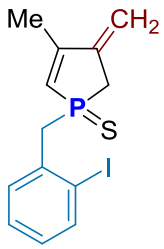
2f: yellow oil, ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 84.4 mg, 81%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 49.1 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 8.59 (d, *J* = 8.3 Hz, 1H), 8.04 – 7.86 (m, 3H), 7.70 – 7.41 (m, 3H), 6.50 (d, *J* = 24.1 Hz, 1H), 5.33 (d, *J* = 49.0 Hz, 2H), 3.29 - 3.64 (dm, 2H), 2.15 (s, 3H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 156.0 (d, J_{CP} = 13.8 Hz), 145.3 (d, J_{CP} = 9.7 Hz), 134.1 (d, J_{CP} = 9.2 Hz), 132.8 (d, J_{CP} = 3.0 Hz), 131.6 (d, J_{CP} = 9.5 Hz), 131.1 (d, J_{CP} = 10.7 Hz), 130.0 (s), 129.6 (d, J_{CP} = 1.2 Hz), 127.00 (s), 126.9 (d, J_{CP} = 60.4 Hz), 125.9 (s), 125.8 (s), 124.6 (d, *J* = 14.1 Hz), 113.4 (d, J_{CP} = 13.8 Hz), 39.5 (d, *J* = 58.3 Hz), 16.6 (d, J_{CP} = 17.3 Hz). **HRMS (ESI)** $[M+Na]^+$ Calcd. for $C_{16}H_{15}NaPS^+$: 293.0525; Found: 293.0531.



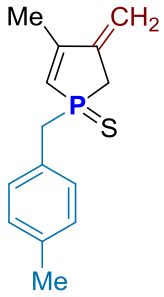
2g: yellow oil, ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 84.2 mg, 78%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 40.1 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 8.42 (d, *J* = 11.1 Hz, 1H), 7.97 – 7.87 (m, 1H), 7.73 – 7.64 (m, 1H), 7.44 – 7.36 (m, 2H), 6.21 (d, *J* = 25.4 Hz, 1H), 5.67 – 5.33 (m, 2H), 3.48 (dd, *J* = 17.9, 8.2 Hz, 1H), 3.18 (t, *J* = 16.2 Hz, 1H), 2.17 (s, 3H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 157.7 (d, J_{CP} = 14.1 Hz), 146.4 (d, J_{CP} = 10.5 Hz), 143.4 (d, J_{CP} = 12.0 Hz), 141.7 (d, J_{CP} = 16.6 Hz), 138.3 (d, J_{CP} = 13.2 Hz), 129.7 (s), 129.0 (s), 128.6 (s), 127.9 (s), 126.2 (d, J_{CP} = 19.3 Hz), 124.3 (d, J_{CP} = 39.2 Hz), 115.0 (d, J_{CP} = 14.3 Hz), 39.3 (d, J_{CP} = 60.7 Hz), 17.7 (d, J_{CP} = 17.6 Hz). **HRMS (ESI)** $[M+Na]^+$ Calcd. for $C_{14}H_{13}NaPS_2^+$: 299.0089; Found: 299.0092



2h: yellow oil, ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 69.5 mg, 74%. **$^{31}P\{^1H\}$ NMR (121 MHz, CDCl3)** δ 55.1 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 7.39 – 7.23 (m, 3H), 7.21 – 7.14 (m, 2H), 5.95 (d, *J* = 25.3 Hz, 1H), 5.10 (dd, *J* = 32.1, 1.2 Hz, 2H), 3.45 (dd, *J* = 14.5, 3.0 Hz, 2H), 3.10 (dd, *J* = 17.4, 7.0 Hz, 1H), 2.83 (dd, *J* = 24.1, 9.9 Hz, 1H), 1.94 (s, 3H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 156.4 (d, J_{CP} = 12.0 Hz), 144.7 (d, J_{CP} = 9.3 Hz), 131.9 (d, J_{CP} = 8.6 Hz), 129.9 (d, J_{CP} = 5.5 Hz), 128.5 (d, J_{CP} = 3.4 Hz), 127.2 (d, J_{CP} = 3.9 Hz), 125.8 (d, J_{CP} = 74.3 Hz), 112.2 (d, J_{CP} = 13.1 Hz), 43.5 (d, J_{CP} = 46.3 Hz), 36.0 (d, J_{CP} = 56.7 Hz), 16.2 (d, J_{CP} = 16.6 Hz). **HRMS (ESI)** $[M+H]^+$ Calcd. for $C_{13}H_{16}PS^+$: 235.0705; Found: 235.0704.

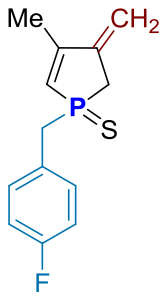


2i: yellow oil, ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 101.3 mg, 66%. **$^{31}P\{^1H\}$ NMR (121 MHz, CDCl3)** δ 55.59 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.32 – 7.24 (m, 1H), 7.01 – 6.85 (m, 1H), 6.02 (d, *J* = 25.6 Hz, 1H), 5.19 – 5.01 (m, 2H), 3.73 (dd, *J* = 14.9, 3.5 Hz, 2H), 3.25 (dd, *J* = 17.4, 7.0 Hz, 1H), 2.86 (t, *J* = 15.9 Hz, 1H), 1.93 (s, 3H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 156.4 (d, J_{CP} = 12.1 Hz), 144.6 (d, J_{CP} = 9.2 Hz), 139.9 (d, J_{CP} = 3.2 Hz), 135.6 (d, J_{CP} = 8.7 Hz), 131.1 (d, J_{CP} = 4.8 Hz), 128.9 (d, J_{CP} = 3.8 Hz), 128.3 (d, J_{CP} = 3.4 Hz), 125.7 (d, J_{CP} = 74.1 Hz), 112.0 (d, J_{CP} = 13.4 Hz), 101.4 (d, J_{CP} = 7.0 Hz), 47.7 (d, J_{CP} = 45.1 Hz), 36.8 (d, J_{CP} = 56.2 Hz), 16.3 (d, J_{CP} = 16.7 Hz). **HRMS (ESI)** $[M+Na]^+$ Calcd. for $C_{13}H_{14}INaPS^+$: 382.9491; Found: 382.9510.

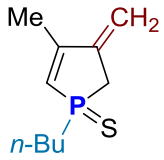


2j (0.2mmol): The reaction was set up with 0.2 mmol **1j**. Yellow oil, ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 21.7 mg, 45%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 54.7 (s). **^1H NMR (300 MHz,**

$CDCl_3$) δ 7.16 – 6.94 (m, 4H), 5.95 (d, J = 25.3 Hz, 1H), 5.12 (d, J = 31.2 Hz, 2H), 3.41 (dd, J = 14.3, 2.2 Hz, 2H), 3.09 (dd, J = 17.4, 7.0 Hz, 1H), 2.90 – 2.70 (m, 1H), 2.31 (d, J = 2.3 Hz, 3H), 1.95 (s, 3H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 156.2 (d, J_{CP} = 11.8 Hz), 144.8 (d, J_{CP} = 9.0 Hz), 136.9 (d, J_{CP} = 4.0 Hz), 129.7 (d, J_{CP} = 5.4 Hz), 129.2 (d, J_{CP} = 3.3 Hz), 128.7 (d, J_{CP} = 8.7 Hz), 126.0 (d, J_{CP} = 74.1 Hz), 112.2 (d, J_{CP} = 13.1 Hz), 43.0 (d, J_{CP} = 46.8 Hz), 35.9 (d, J_{CP} = 56.6 Hz), 21.1 (s), 16.3 (d, J_{CP} = 16.5 Hz). **HRMS (ESI)** $[M+H]^+$ Calcd. for $C_{14}H_{18}PS^+$: 249.0862; Found: 249.0872.

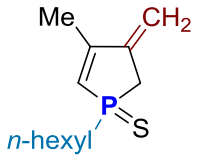


2k: yellow oil, ethyl acetate/petroleum ether = 1:5, R_f = 0.40, 73.9 mg, 71%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 55.0 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 7.20 – 7.11 (m, 2H), 6.99 (t, J = 8.6 Hz, 2H), 5.94 (d, J = 25.3 Hz, 1H), 5.25 – 5.05 (m, 2H), 3.41 (d, J = 14.2 Hz, 2H), 3.08 (dd, J = 17.5, 6.9 Hz, 1H), 2.91 – 2.75 (m, 1H), 1.97 (s, 3H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 156.6 (d, J = 12.0 Hz), 144.6 (d, J = 9.2 Hz), 131.4 (d, J = 13.5 Hz), 131.4 (d, J = 2.6 Hz), 125.6 (d, J = 75.3 Hz), 115.6 (d, J = 3.2 Hz), 115.3 (d, J = 3.3 Hz), 112.4 (d, J = 13.1 Hz), 42.6 (d, J_{CP} = 46.6 Hz), 36.0 (d, J_{CP} = 56.6 Hz), 16.3 (d, J_{CP} = 16.5 Hz). **HRMS (ESI)** $[M+H]^+$ Calcd. for $C_{13}H_{15}FPS^+$: 253.0611; Found: 253.0622.

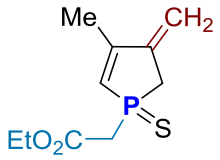


2l: yellow oil, ethyl acetate/petroleum ether = 1:10, R_f = 0.40, 60.8 mg, 75%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 56.0 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 6.03 (d, J = 25.4 Hz, 1H), 5.28 (d, J = 31.7 Hz, 2H), 3.11 (dd, J = 17.3, 6.6 Hz, 1H), 2.90 (t, J = 15.9 Hz, 1H), 2.03 (t, J = 7.5 Hz, 5H), 1.70 – 1.51 (m, 2H), 1.41 - 1.61 (dm, 4H), 0.93 (t, J = 7.2 Hz, 3H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 155.6 (d, J_{CP} = 12.0 Hz), 145.1 (d, J_{CP} = 9.0 Hz), 126.7 (d, J_{CP} = 73.3 Hz), 112.4 (d, J_{CP} = 13.1 Hz), 36.8 (d, J_{CP} = 55.7 Hz), 35.1 (d, J_{CP} = 52.2 Hz), 25.2 (d, J_{CP} = 3.9 Hz), 23.7 (d, J_{CP} = 15.7 Hz),

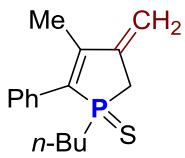
16.3 (d, J_{CP} = 16.4 Hz), 13.7 (s). **HRMS (ESI)** $[M+H]^+$ Calcd. for $C_{10}H_{18}PS^+$: 201.0862; Found: 201.0860.



2m: yellow oil, ethyl acetate/petroleum ether = 1:10, R_f = 0.40, 66.8 mg, 69%. **$^{31}P\{^1H\}$ NMR (121 MHz, CDCl3)** δ 54.8 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 6.03 (d, J = 25.5 Hz, 1H), 5.28 (d, J = 31 Hz, 2H), 3.10 (dd, J = 17.4, 6.6 Hz, 1H), 2.90 (t, J = 15.9 Hz, 1H), 2.09 – 1.94 (m, 5H), 1.68 – 1.54 (m, 2H), 1.38 (dd, J = 9.5, 4.4 Hz, 2H), 1.29 (dd, J = 8.3, 5.3 Hz, 4H), 0.88 (t, J = 6.6 Hz, 3H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 155.5 (d, J_{CP} = 12.1 Hz), 145.2 (d, J_{CP} = 9.0 Hz), 126.8 (d, J_{CP} = 73.2 Hz), 112.4 (d, J_{CP} = 13.0 Hz), 36.9 (d, J_{CP} = 55.7 Hz), 35.3 (d, J_{CP} = 51.9 Hz), 31.3 (s), 30.2 (d, J_{CP} = 15.3 Hz), 23.1 (d, J_{CP} = 3.9 Hz), 22.4 (s), 16.3 (d, J_{CP} = 16.4 Hz), 14.0 (s). **HRMS (ESI)** $[M+Na]^+$ Calcd. for $C_{12}H_{21}NaPS^+$: 251.0994; Found: 251.1006.



2n: yellow oil, ethyl acetate/petroleum ether = 1:5, R_f = 0.30, 66.6 mg, 72%. **$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$)** δ 49.7 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 6.02 (d, J = 25.7 Hz, 1H), 5.25 (d, J = 31.1 Hz, 2H), 4.14 – 3.99 (m, 2H), 3.42 (dd, J = 17.6, 8.4 Hz, 1H), 3.19 (d, J = 2.6 Hz, 1H), 3.14 (d, J = 2.2 Hz, 1H), 2.89 (t, J = 16.1 Hz, 1H), 1.97 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H). **$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$)** δ 165.9 (d, J_{CP} = 6.2 Hz), 156.8 (d, J_{CP} = 13.7 Hz), 144.5 (d, J_{CP} = 10.3 Hz), 125.7 (d, J_{CP} = 76.2 Hz), 113.0 (d, J_{CP} = 14.4 Hz), 61.7 (s), 43.3 (d, J_{CP} = 42.0 Hz), 36.7 (d, J_{CP} = 58.2 Hz), 16.3 (d, J_{CP} = 17.6 Hz), 14.1 (s). **HRMS (ESI)** $[M+Na]^+$ Calcd. for $C_{10}H_{15}NaO_2PS^+$: 253.0423; Found: 253.0419.



2o (0.2mmol): yellow oil, ethyl acetate/petroleum ether = 1:10, R_f = 0.40, 40.0 mg, 70%. **$^{31}P\{^1H\}$ NMR (121 MHz, CDCl3)** δ 60.9 (s). **^1H NMR (300 MHz, $CDCl_3$)** δ 7.43 – 7.36 (m, 2H), 7.32 –

7.20 (m, 3H), 5.36 – 5.09 (m, 2H), 3.13 (dd, J = 17.3, 6.6 Hz, 1H), 2.95 – 2.78 (m, 1H), 1.88 – 1.75 (m, 5H), 1.43 – 1.28 (m, 2H), 1.18 - 1.24 (m, 2H), 0.72 (t, J = 7.2 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)** δ 149.2 (d, J_{CP} = 19.1 Hz), 144.4 (d, J_{CP} = 8.3 Hz), 137.9 (d, J_{CP} = 69.9 Hz), 133.7 (d, J_{CP} = 9.4 Hz), 128.9 (d, J_{CP} = 4.4 Hz), 128.3 (s), 128.0 (d, J_{CP} = 1.4 Hz), 112.2 (d, J_{CP} = 12.2 Hz), 36.0 (d, J_{CP} = 55.6 Hz), 33.8 (d, J_{CP} = 50.3 Hz), 25.0 (d, J_{CP} = 3.9 Hz), 23.5 (d, J_{CP} = 15.9 Hz), 13.8 (d, J_{CP} = 12.6 Hz), 13.6 (s). **HRMS (ESI)** $[M+Na]^+$ Calcd. for $C_{16}H_{21}NaPS^+$: 299.0994; Found: 299.1013.

References:

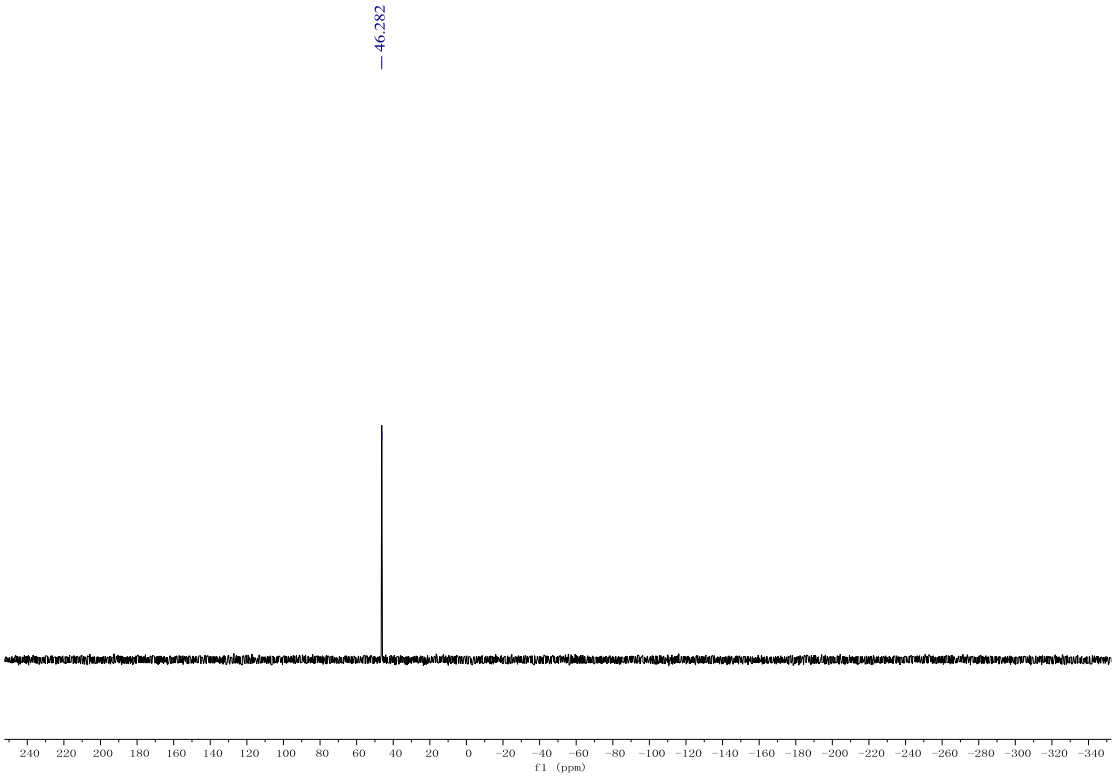
[1] A. Breque, F. Mathey, P. Savignac, *Synthesis*, 1981, **1981**, 983.

[2] T. Moller, P. Wonneberger, N. Kretzschmar and E. Hey-Hawkins, *Chem. Commun.*, 2014, **50**, 5826.

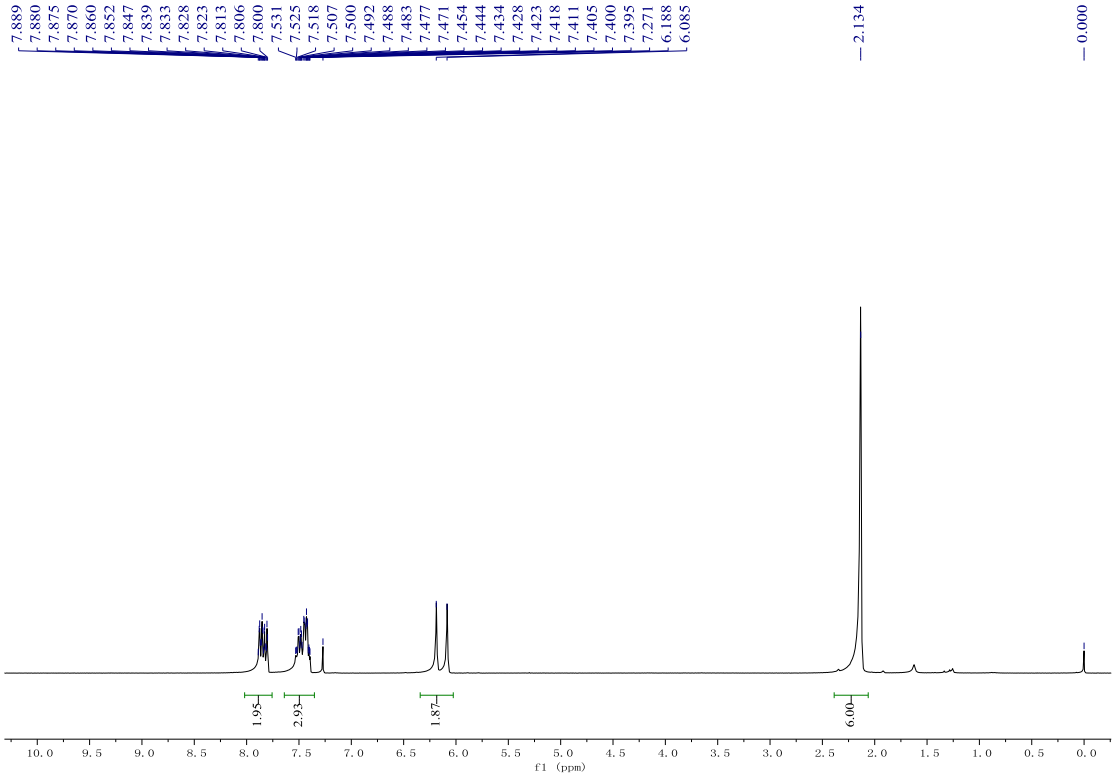
[3] Y. Hou, M. Cui, K. Zhang, L. Chen, R.Tian, *Org. Chem. Front.*, 2022, **9**, 6606.

[4] W. Luo, A. Ciric, R. Tian, F. Mathey, *Organometallics*, 2010, **29**, 1862–1864.

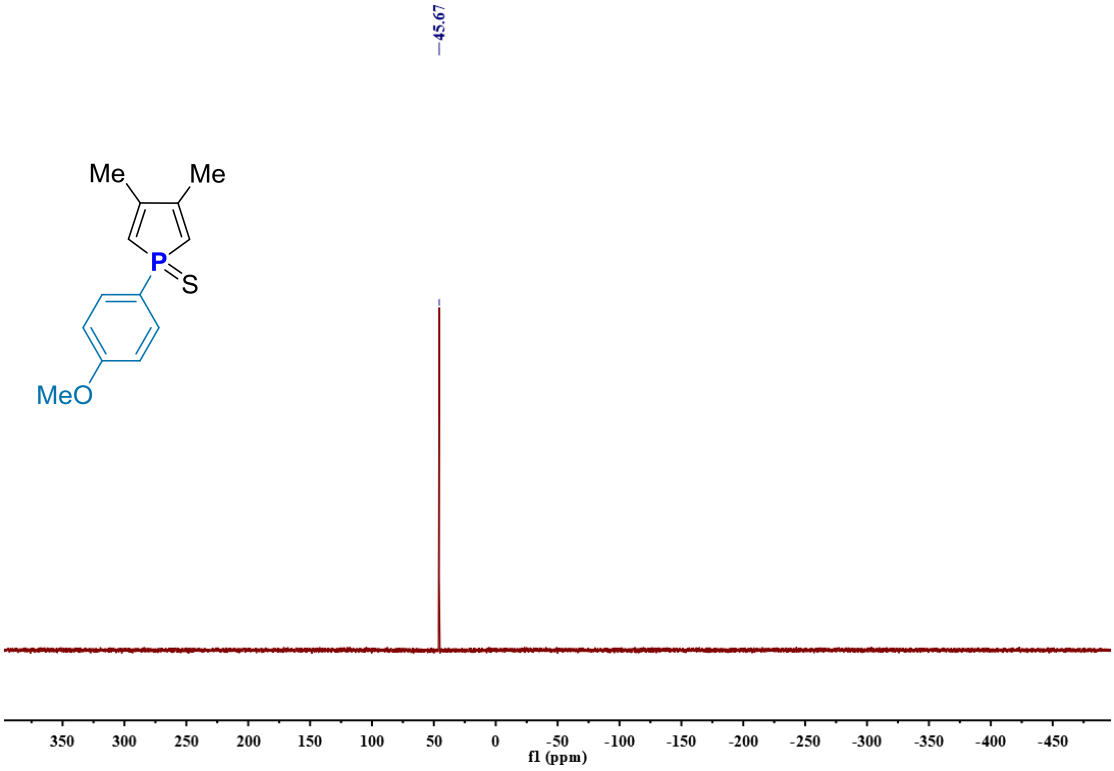
NMR Spectrums



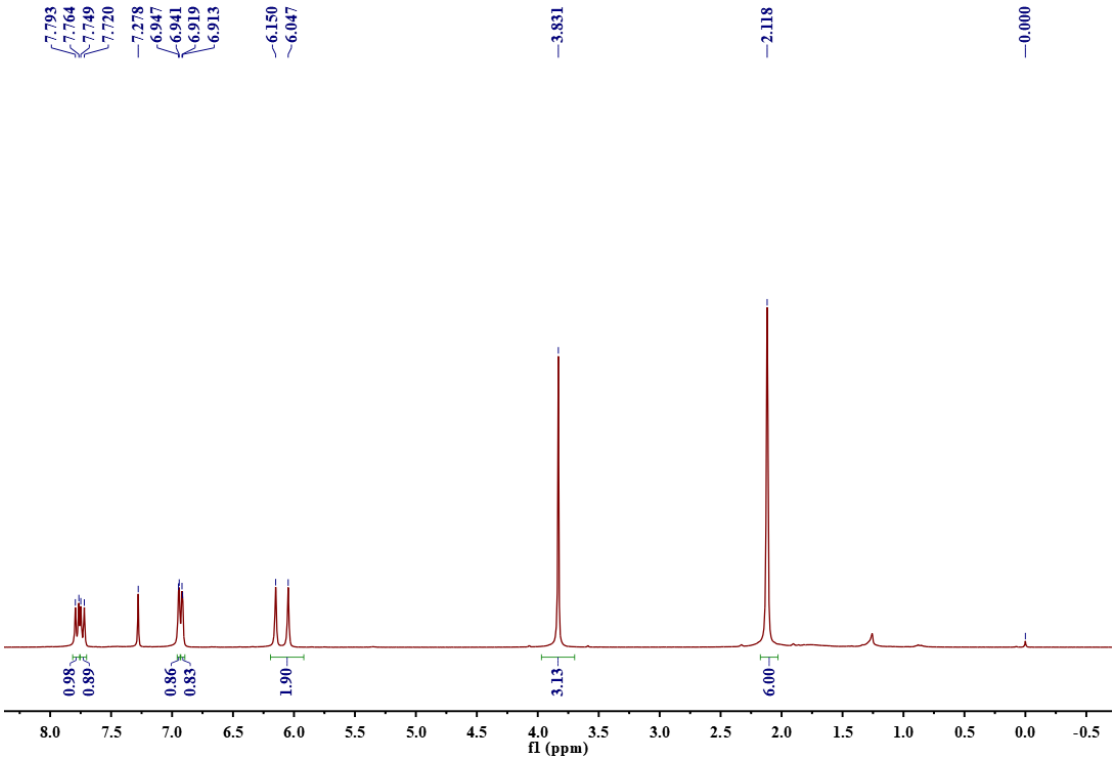
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 1a



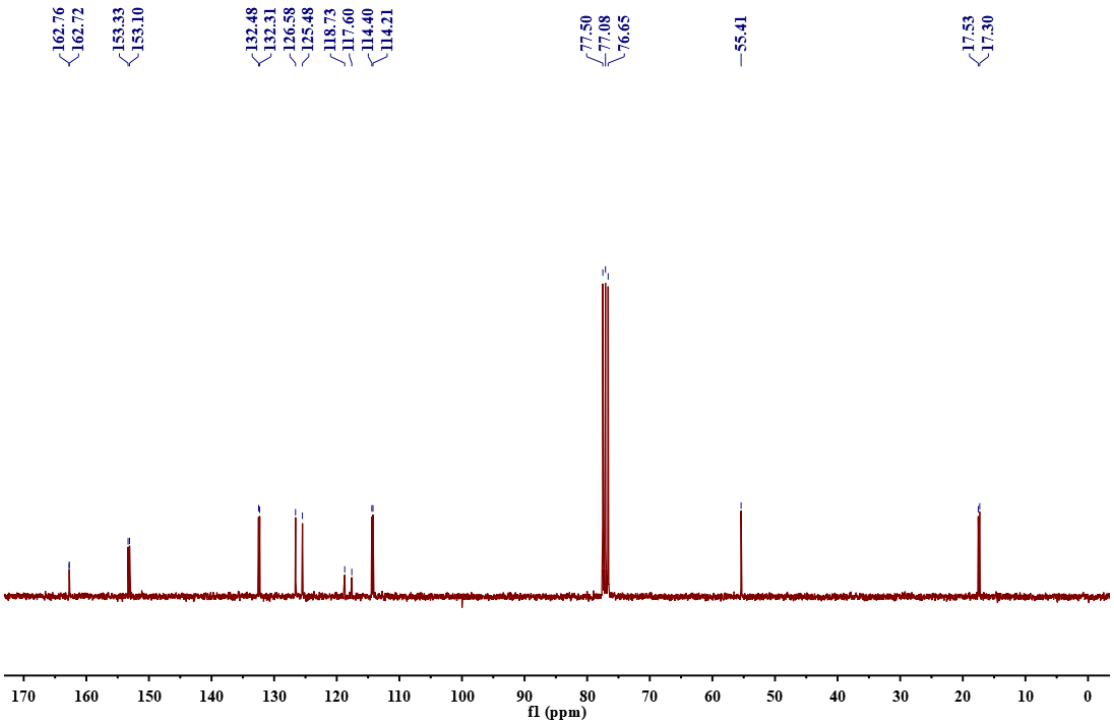
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 1a



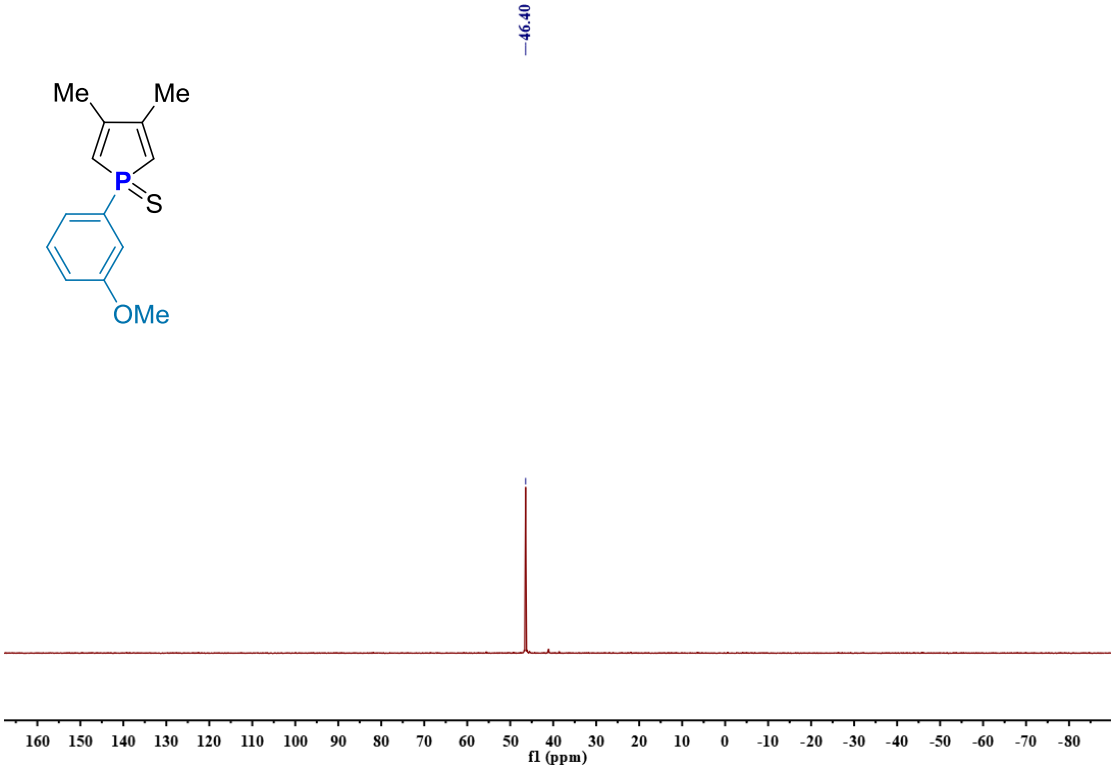
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 1b



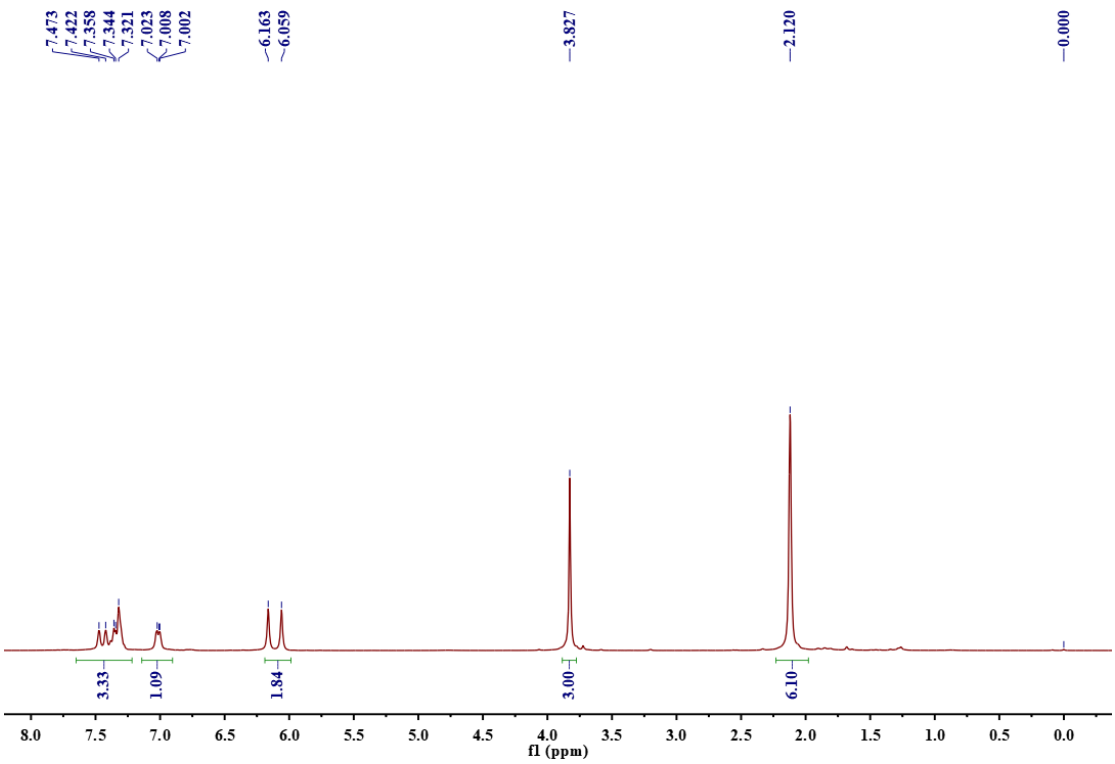
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 1b



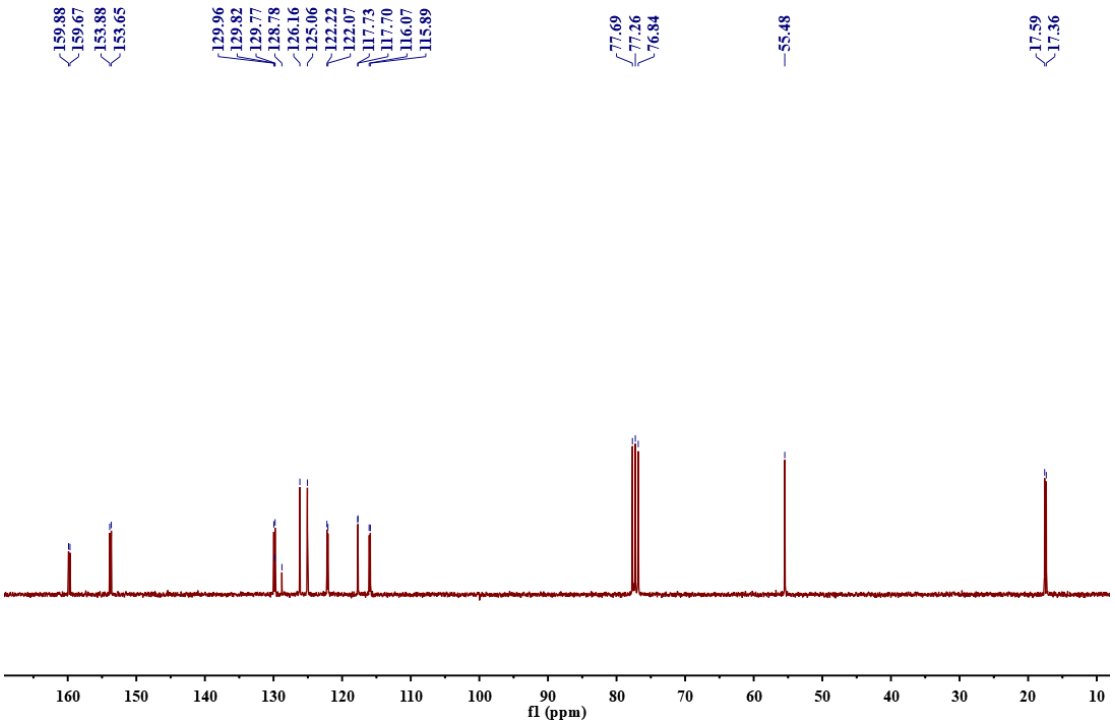
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 1b



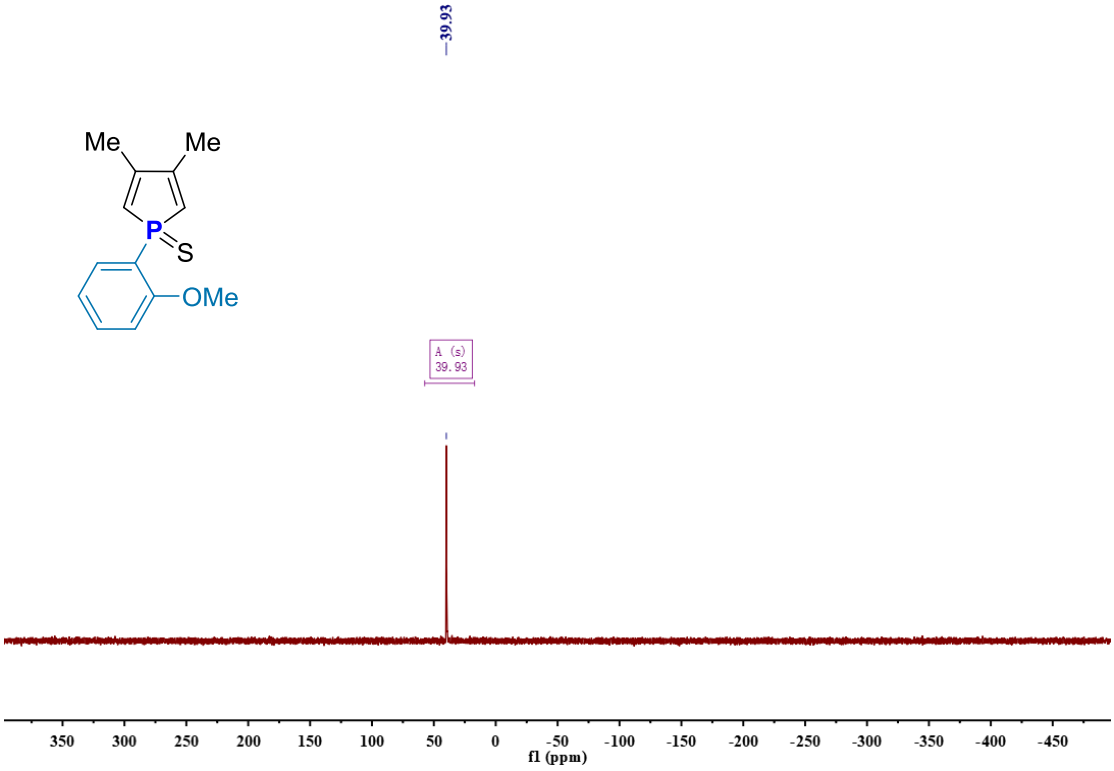
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 1c



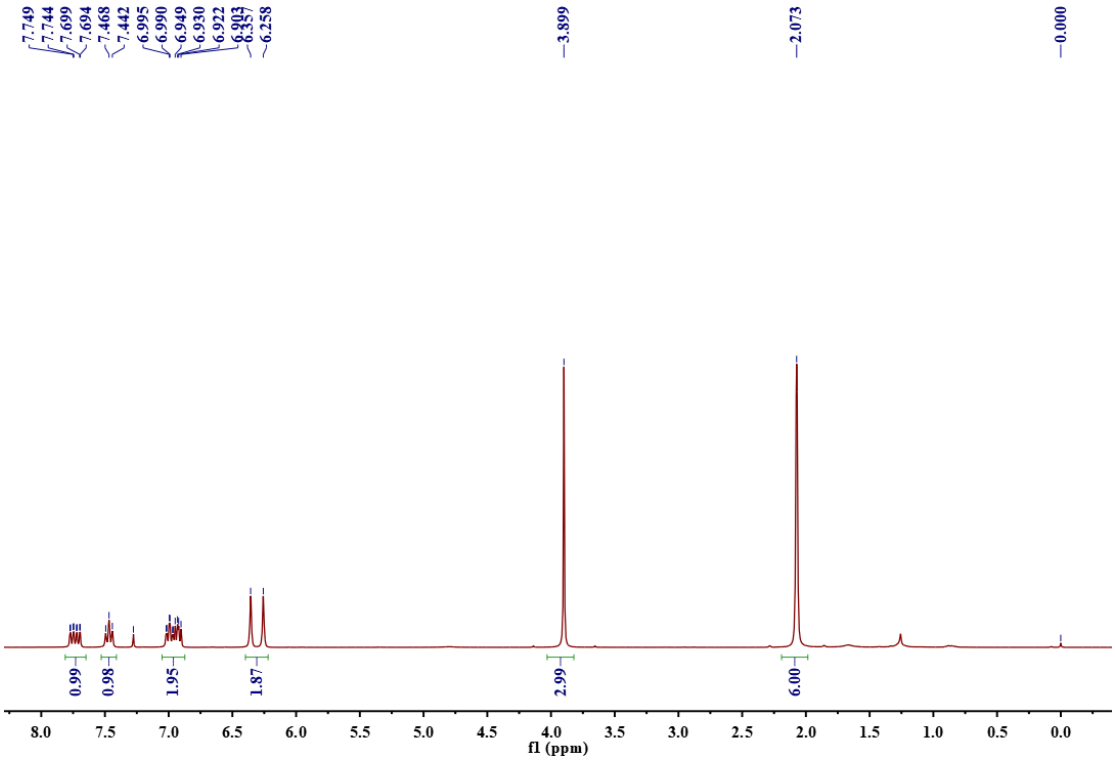
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 1c



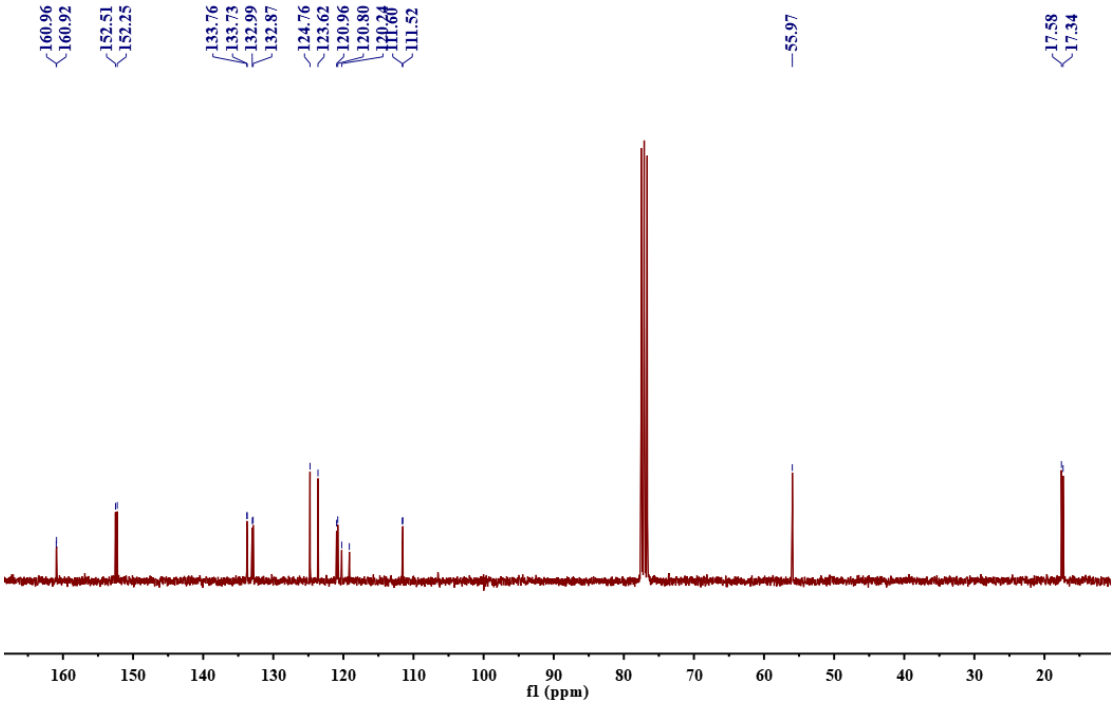
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of Compound 1c



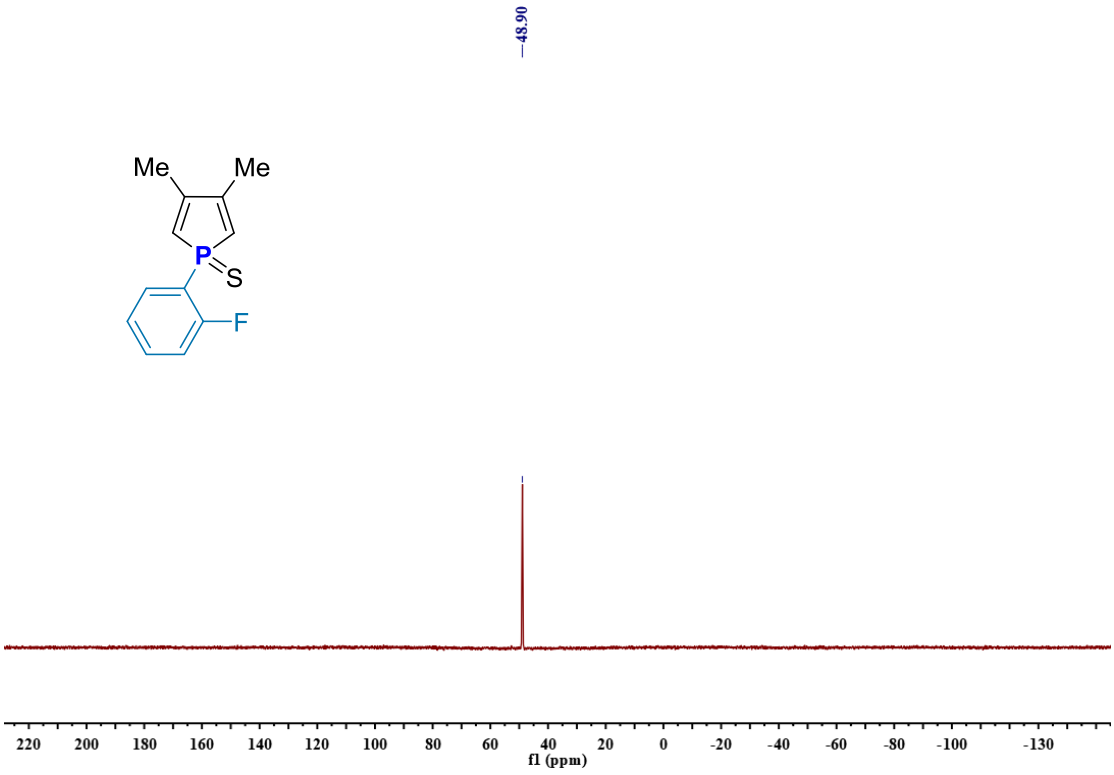
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 1d



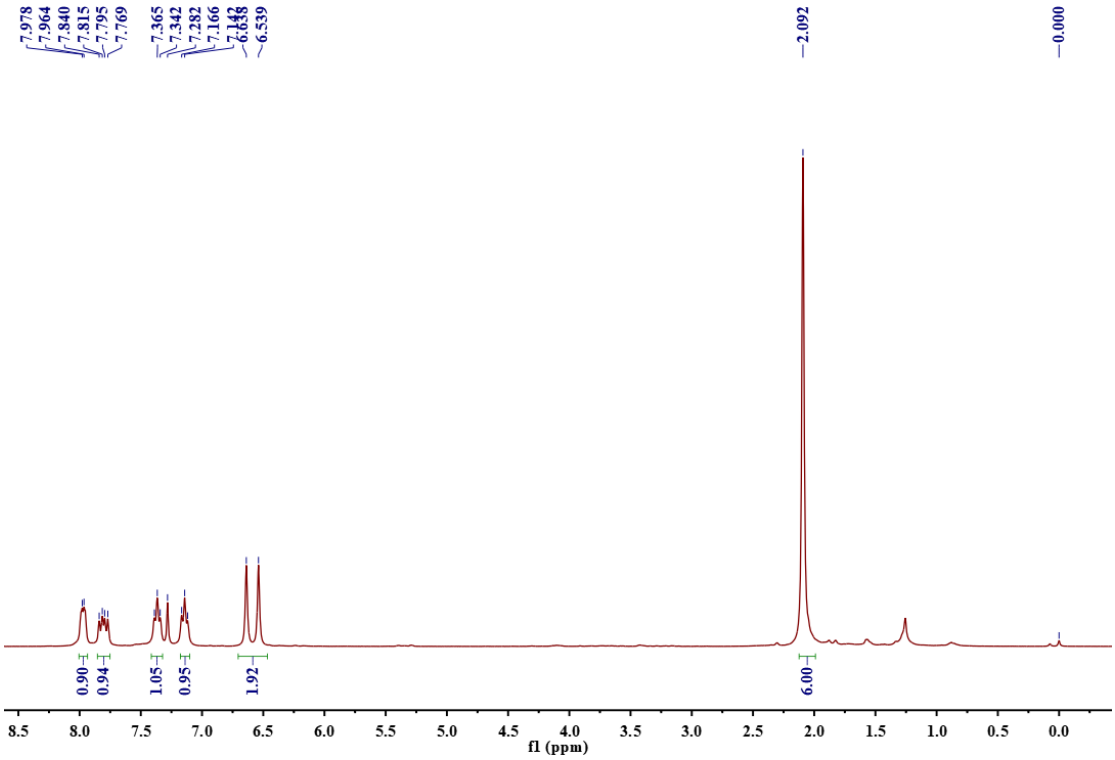
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 1d



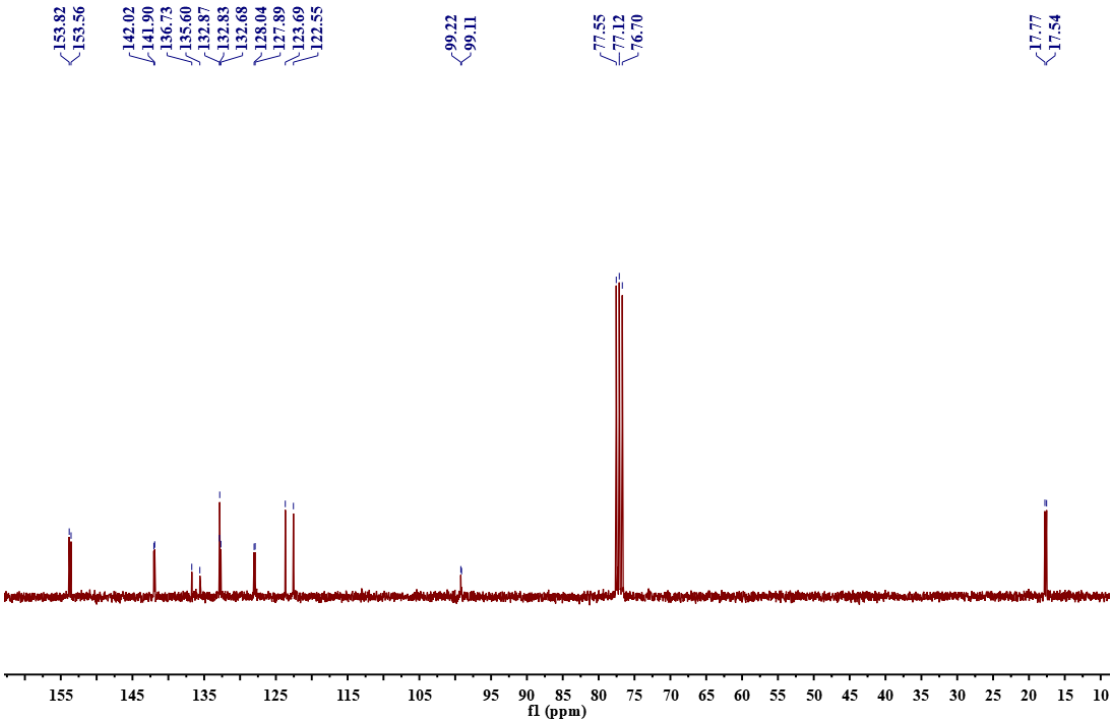
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 1d



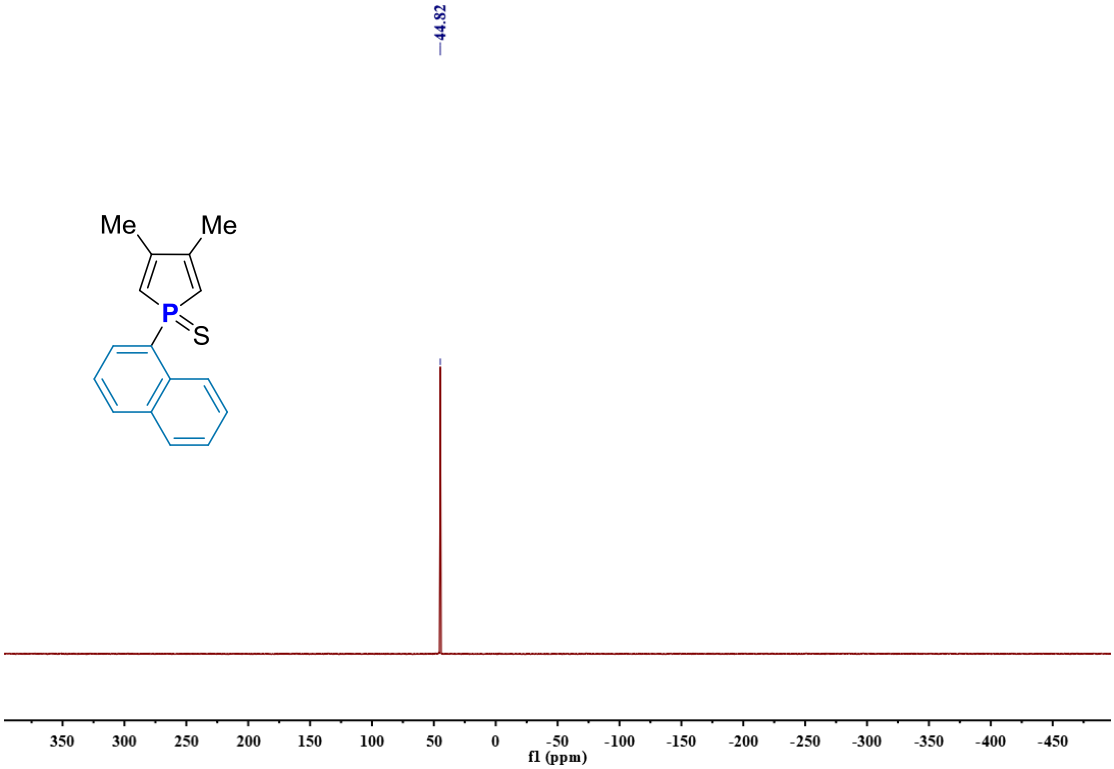
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 1e



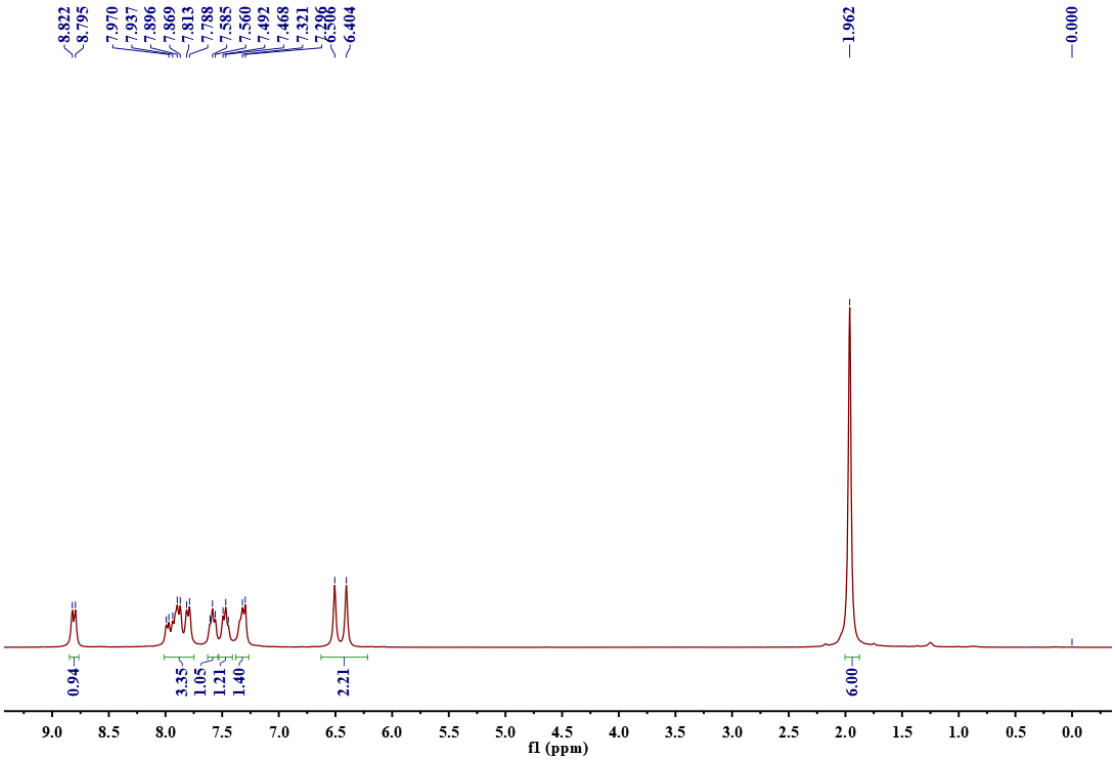
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 1e



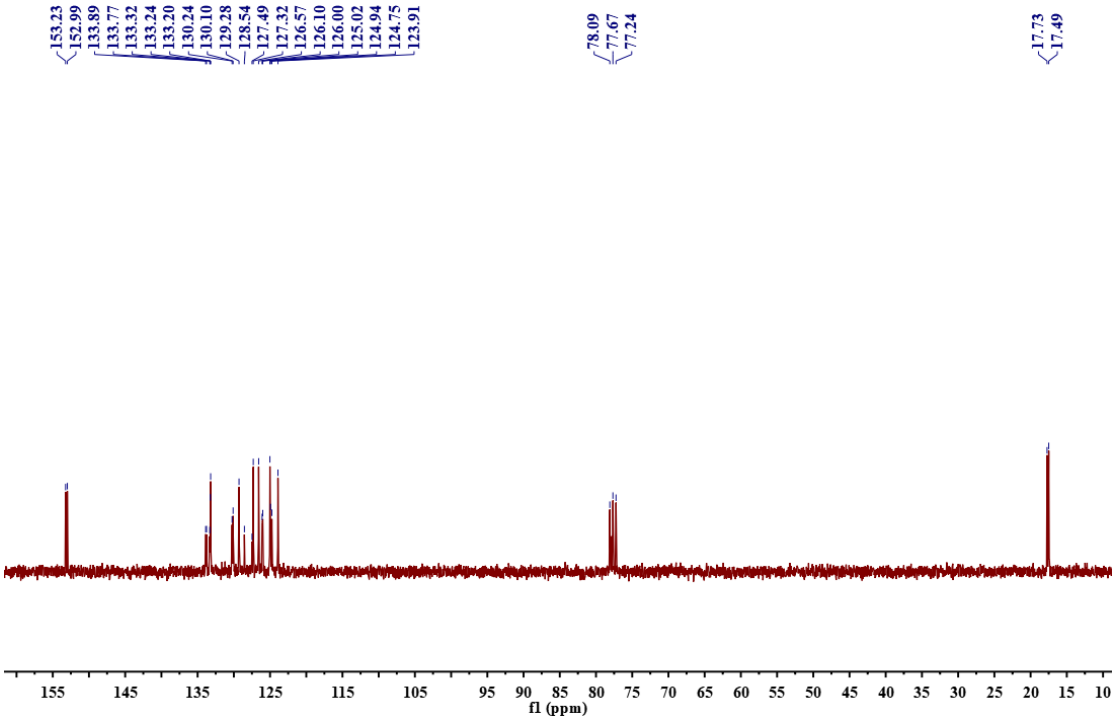
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of Compound 1e



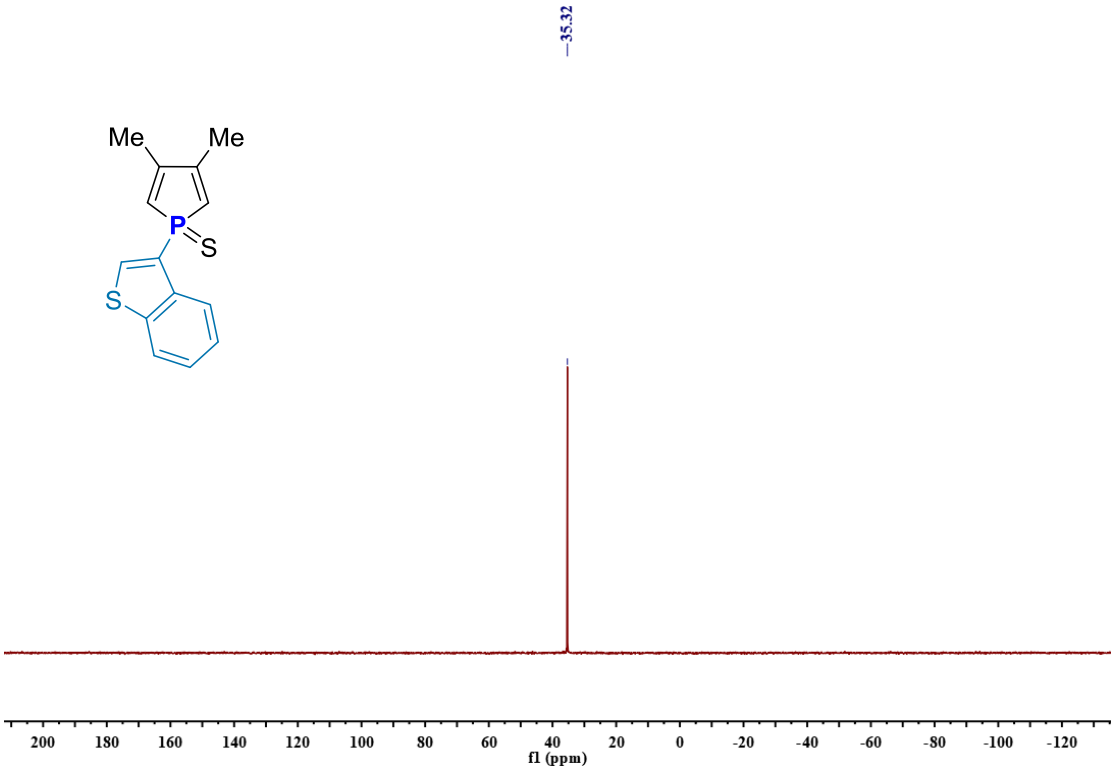
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 1f



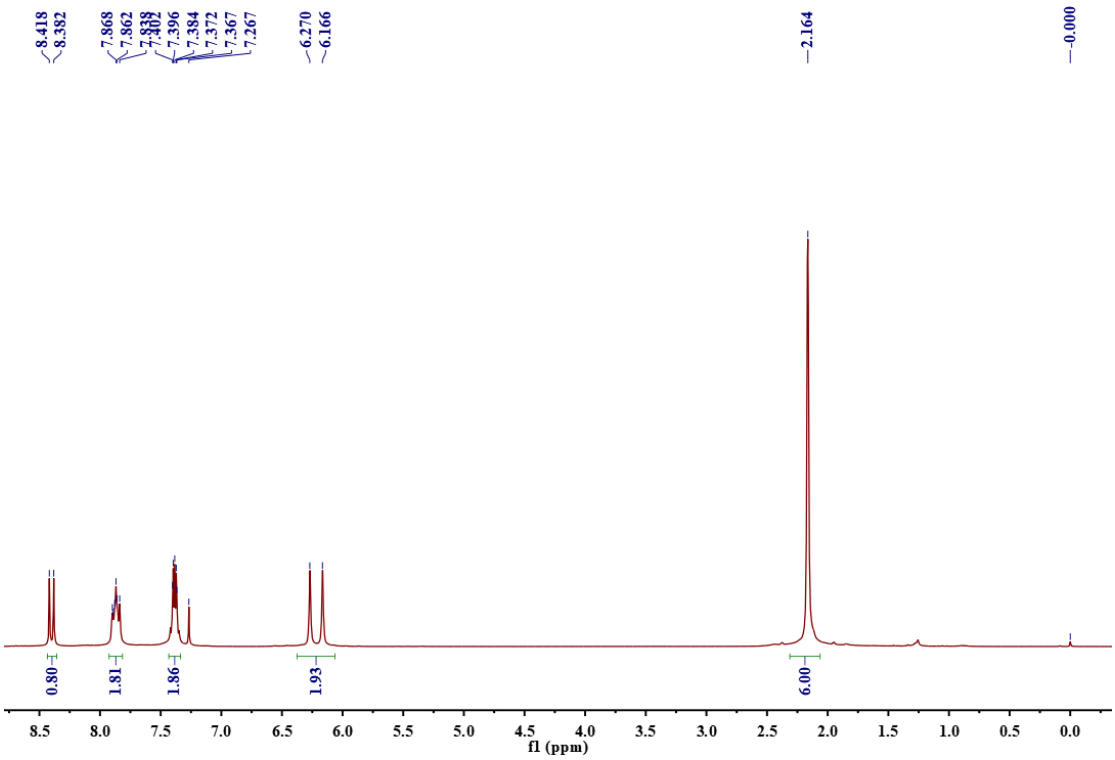
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 1f



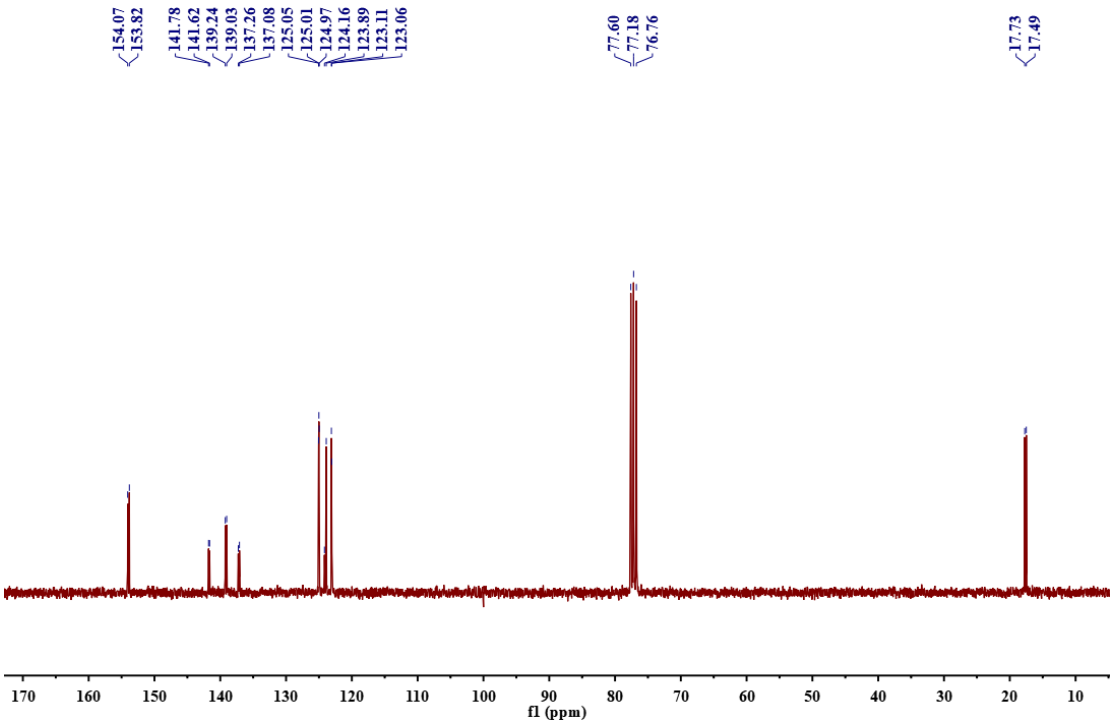
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 1f



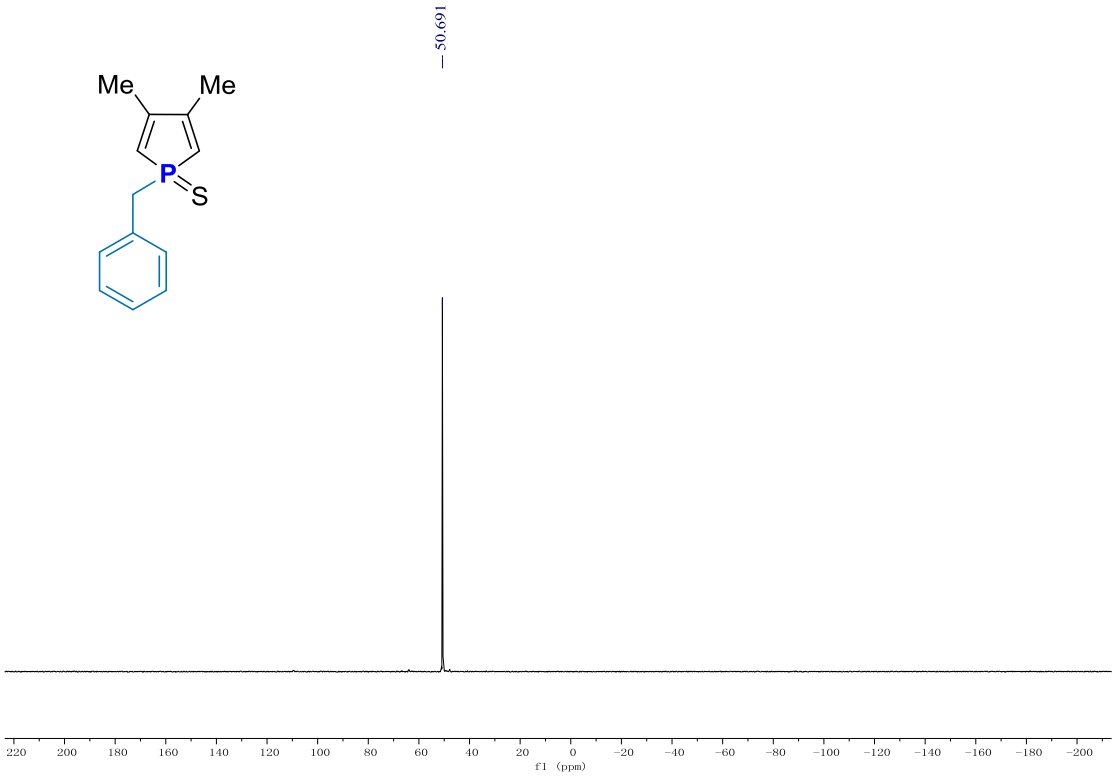
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 1g



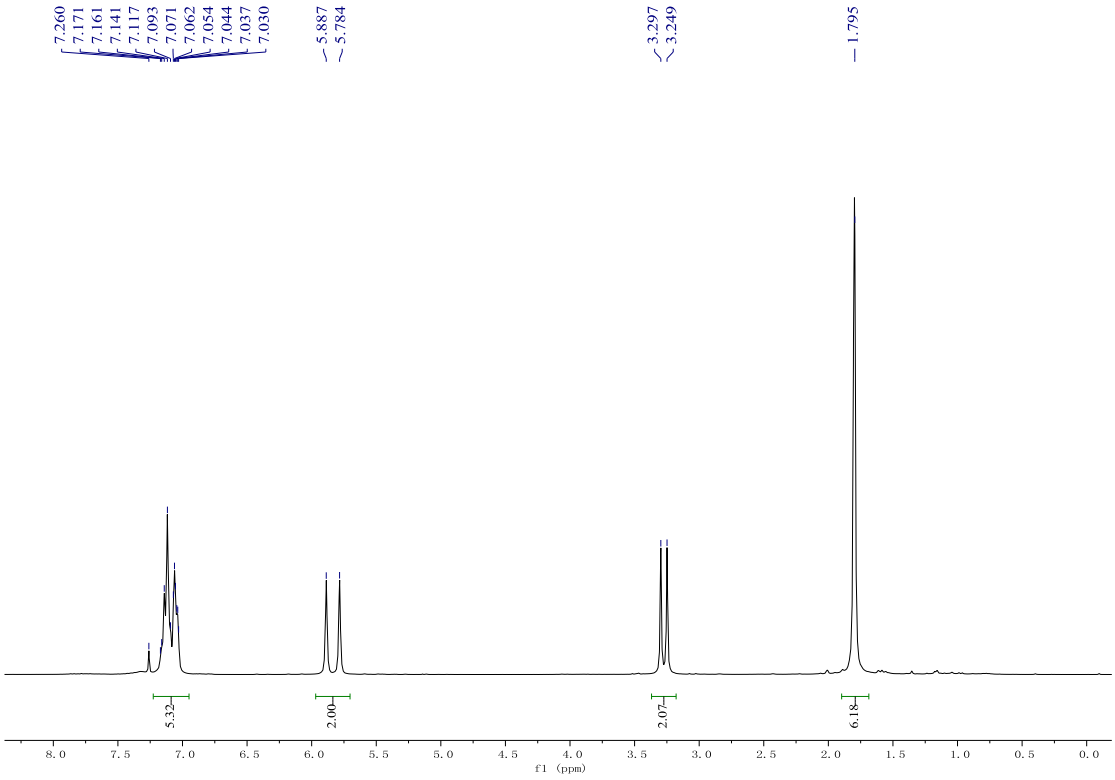
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 1g



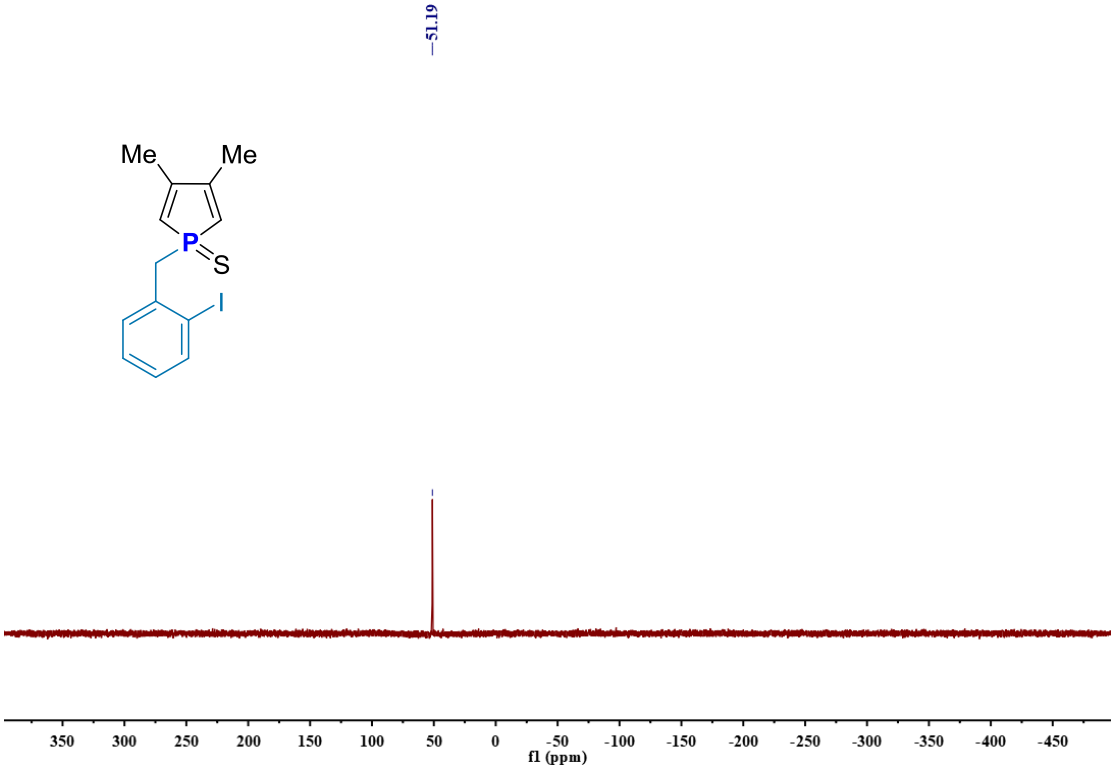
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of Compound 1g



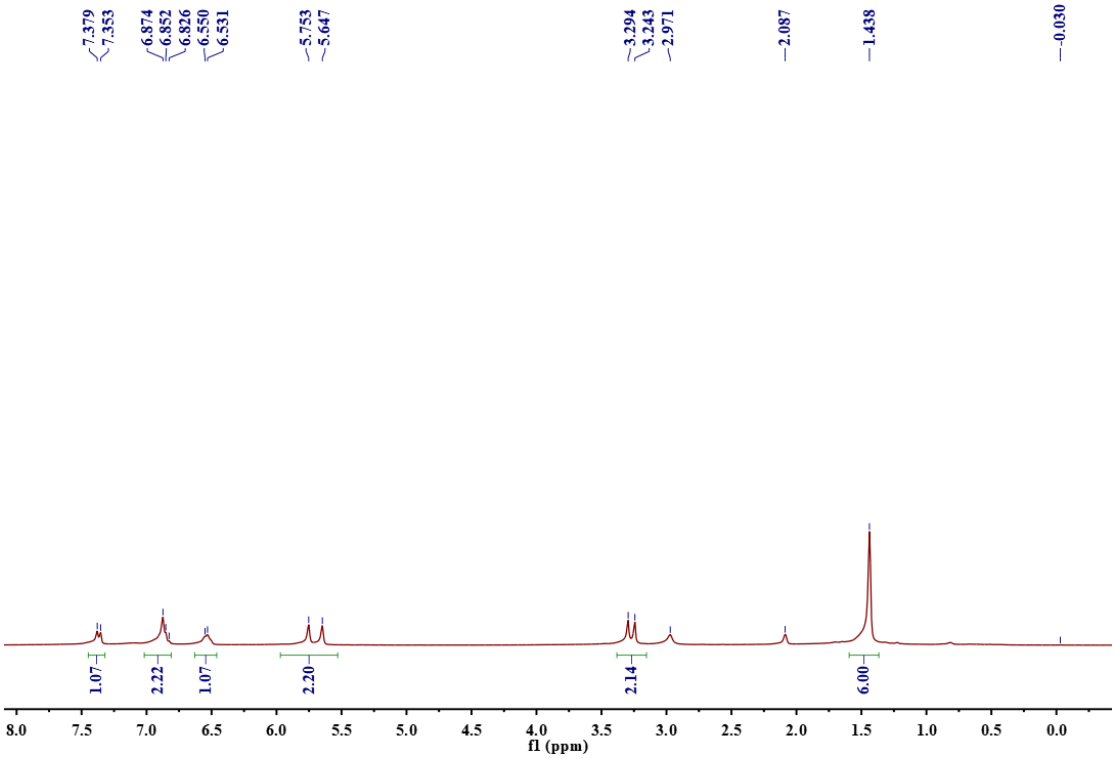
$^{31}P\{^{1}H\}$ NMR (121 MHz, DMSO) of Compound 1h



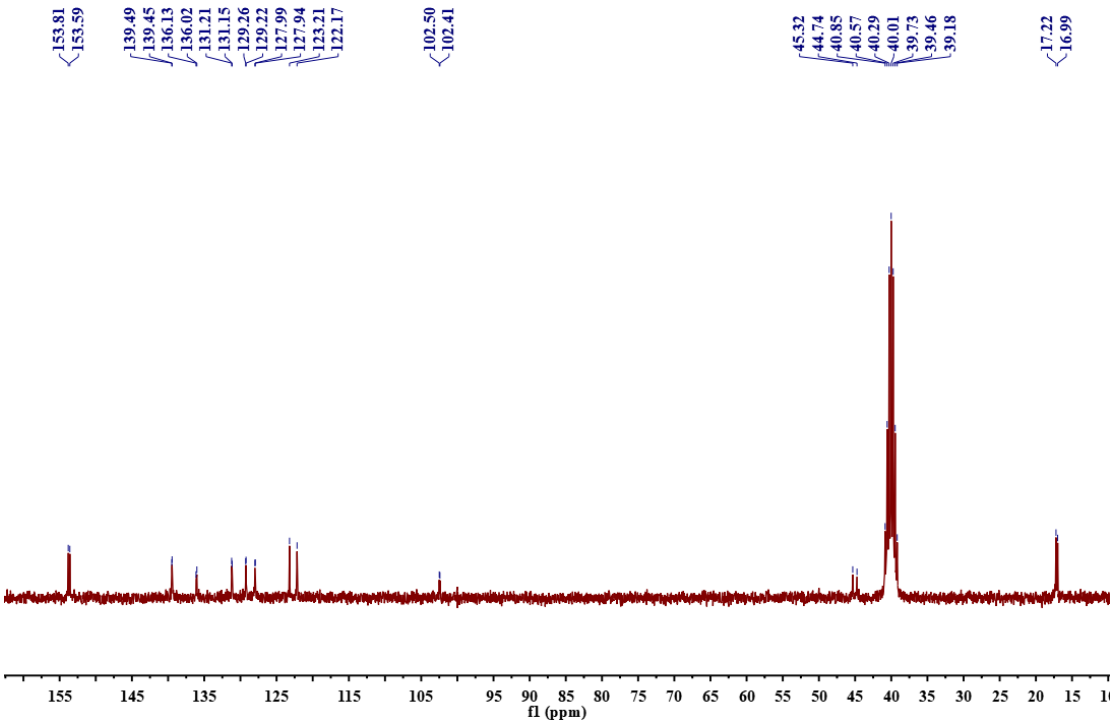
^{1}H NMR (300 MHz, DMSO) of Compound 1h



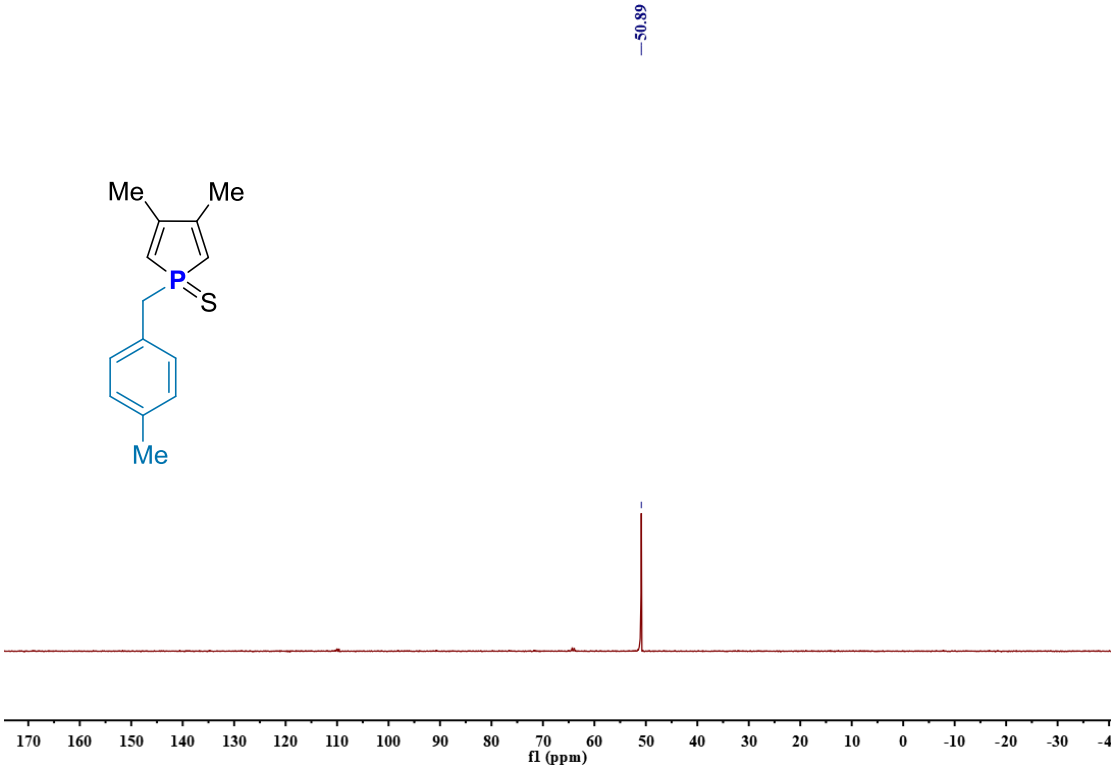
$^{31}P\{^{1}H\}$ NMR (121 MHz, DMSO) of Compound 1i



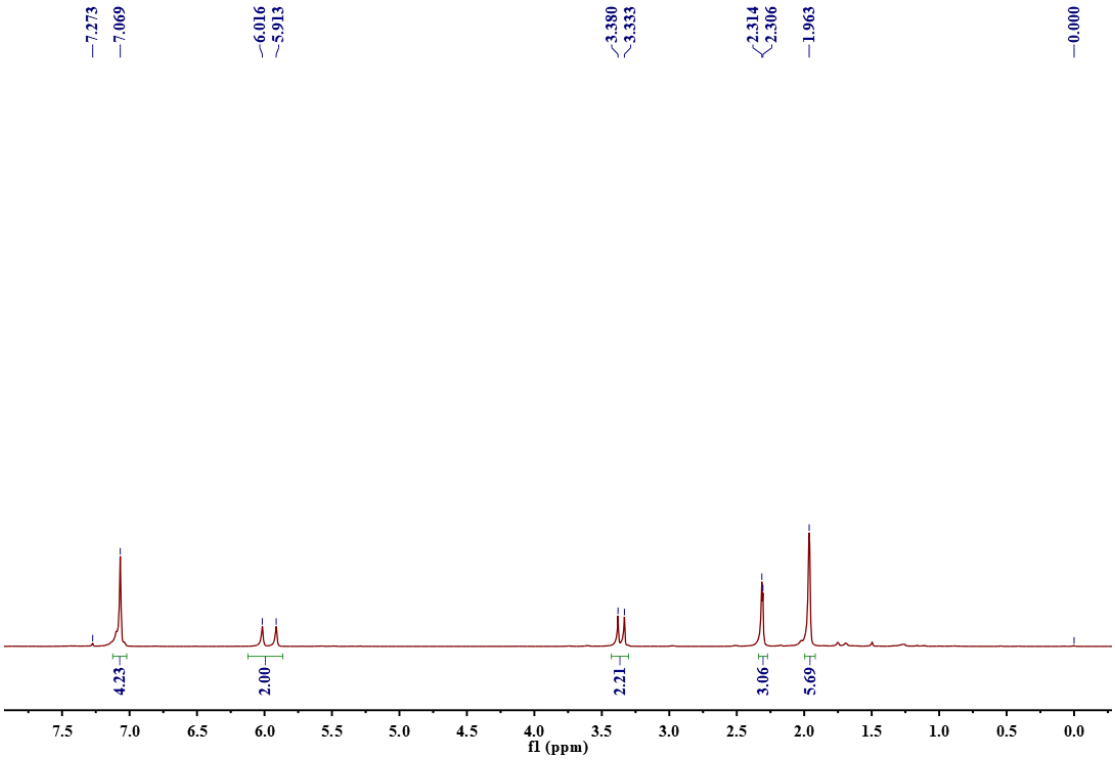
^{1}H NMR (300 MHz, DMSO) of Compound 1i



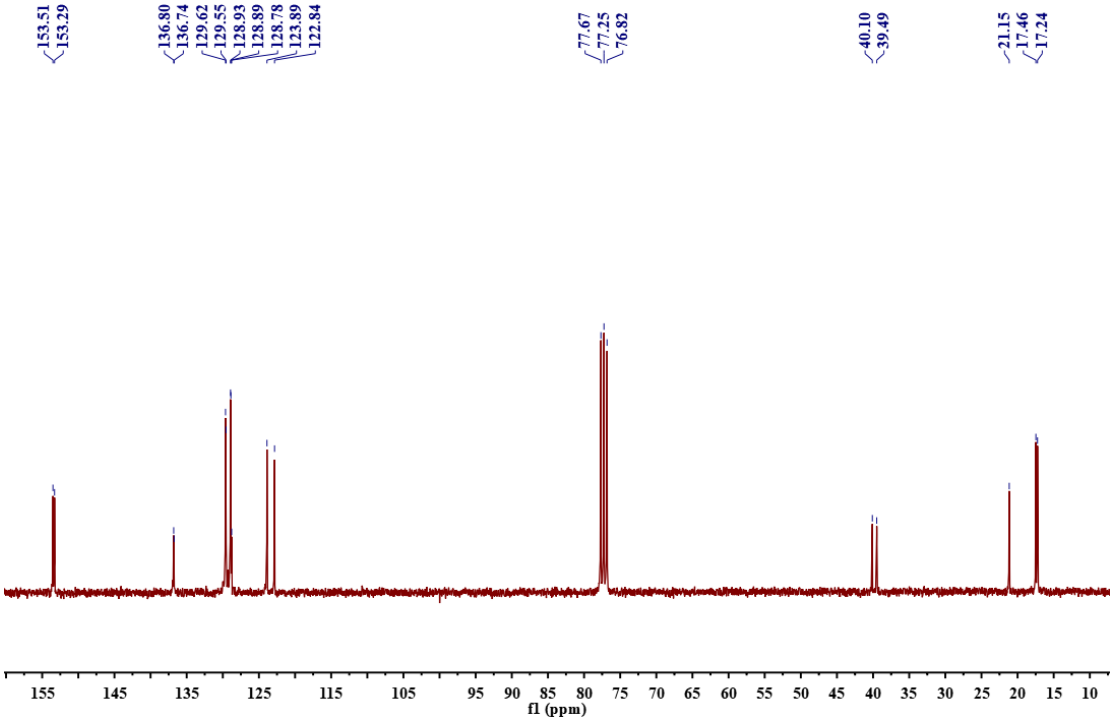
$^{13}C\{^{1}H\}$ NMR (75 MHz, DMSO) of Compound 1i



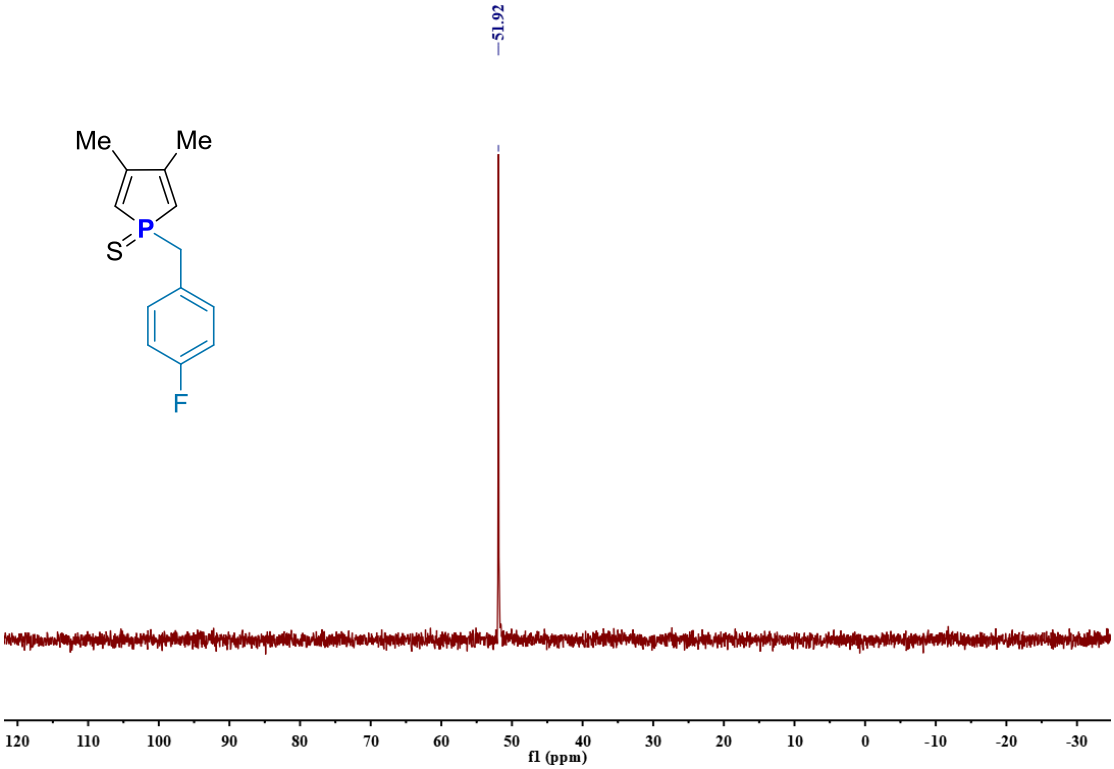
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 1j



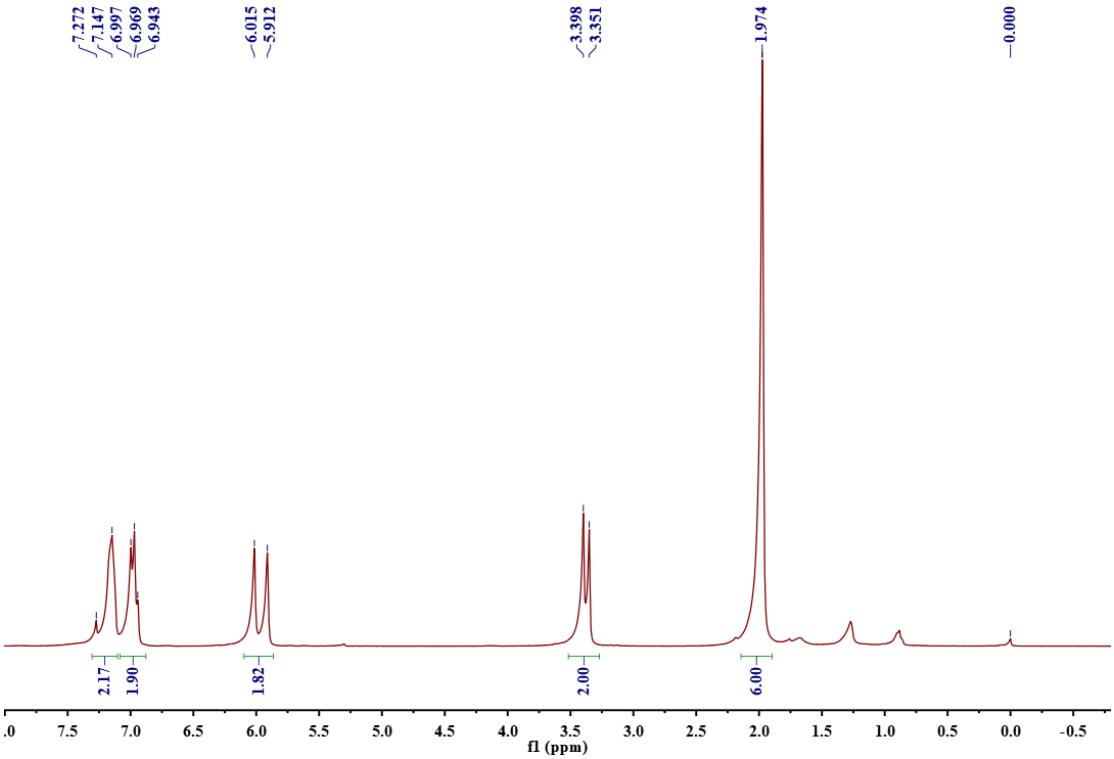
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 1j



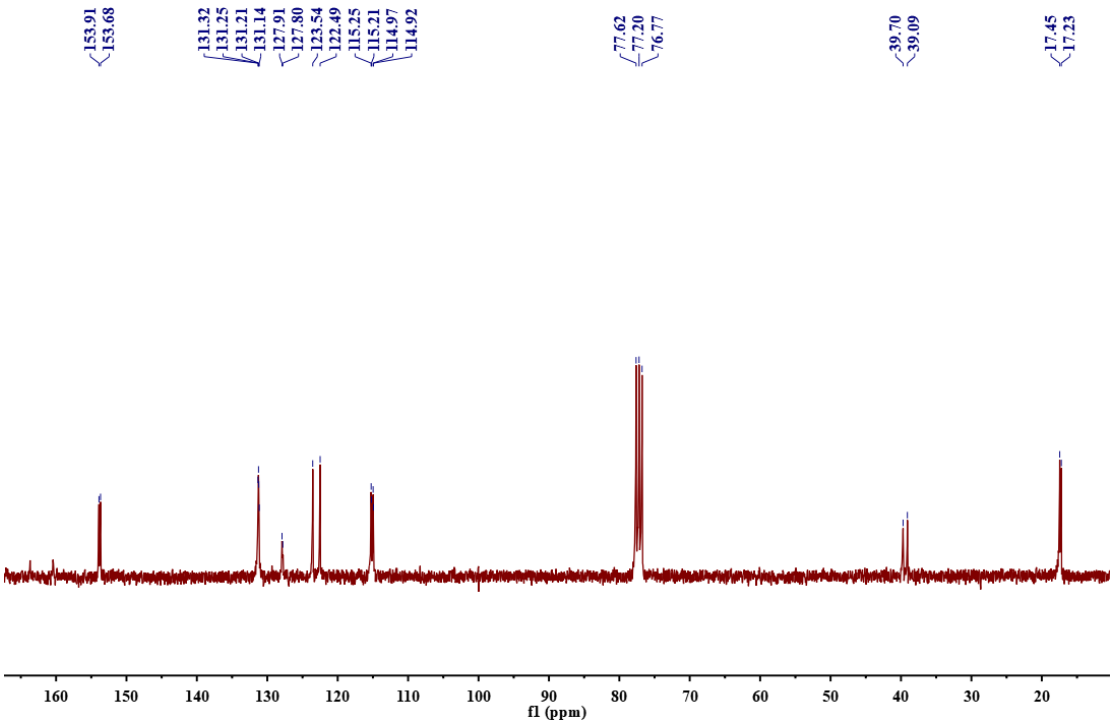
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of Compound 1j



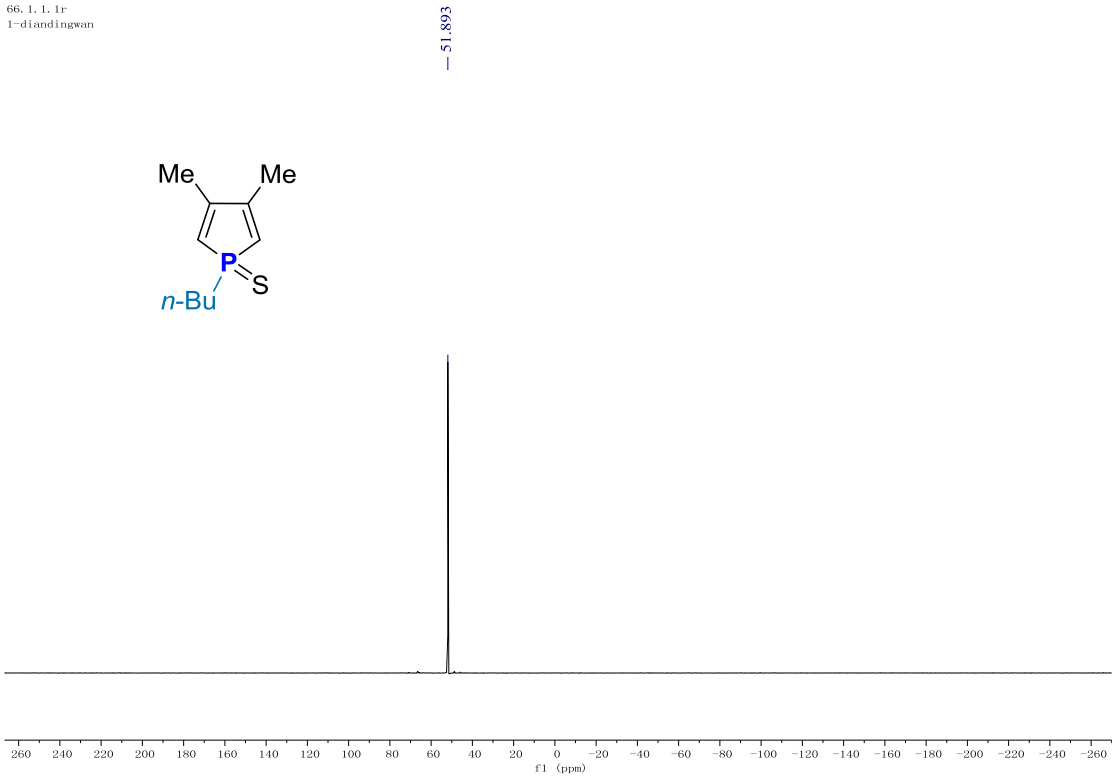
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 1k



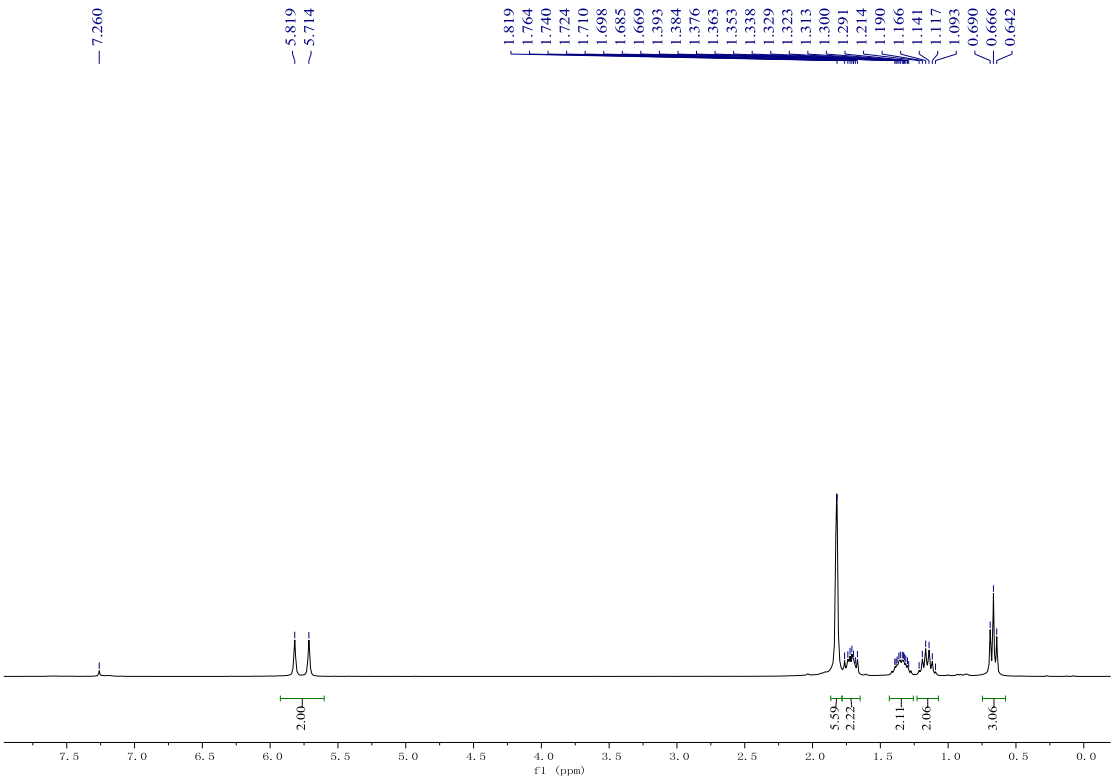
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 1k



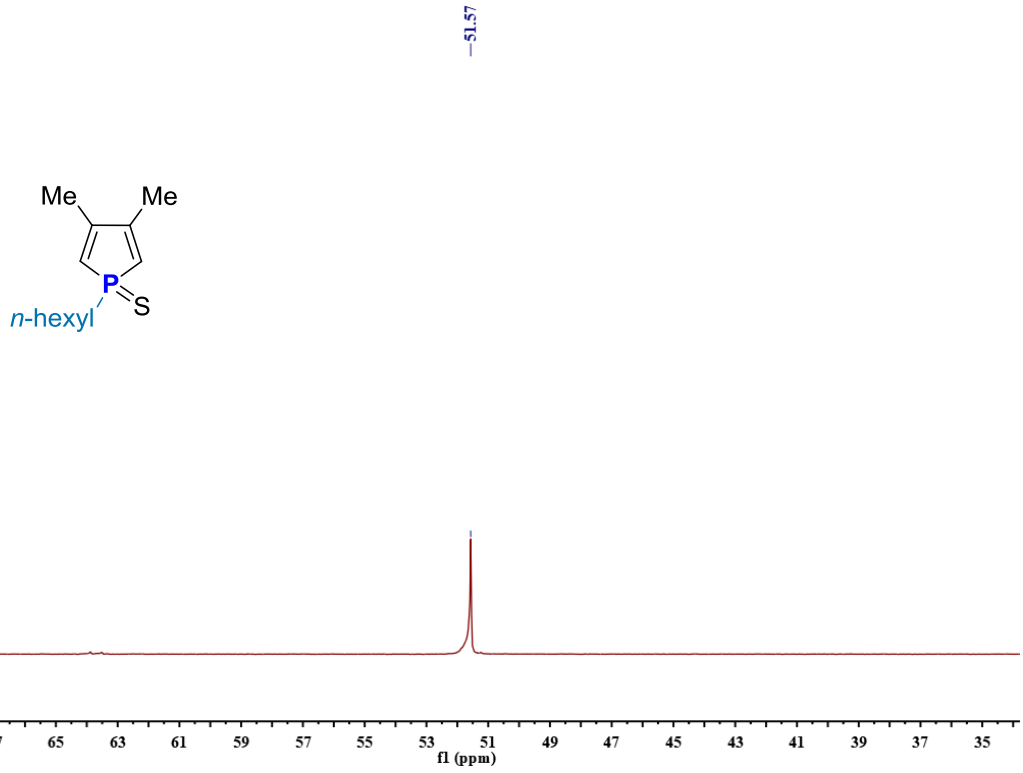
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 1k



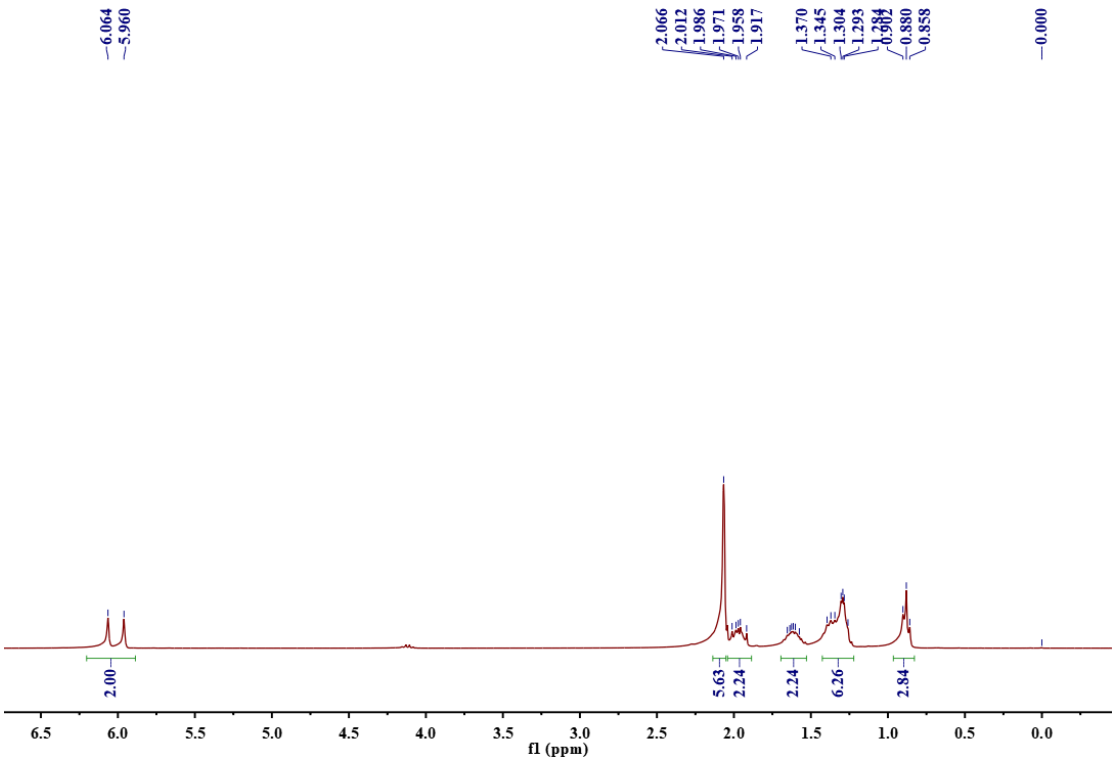
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 1l



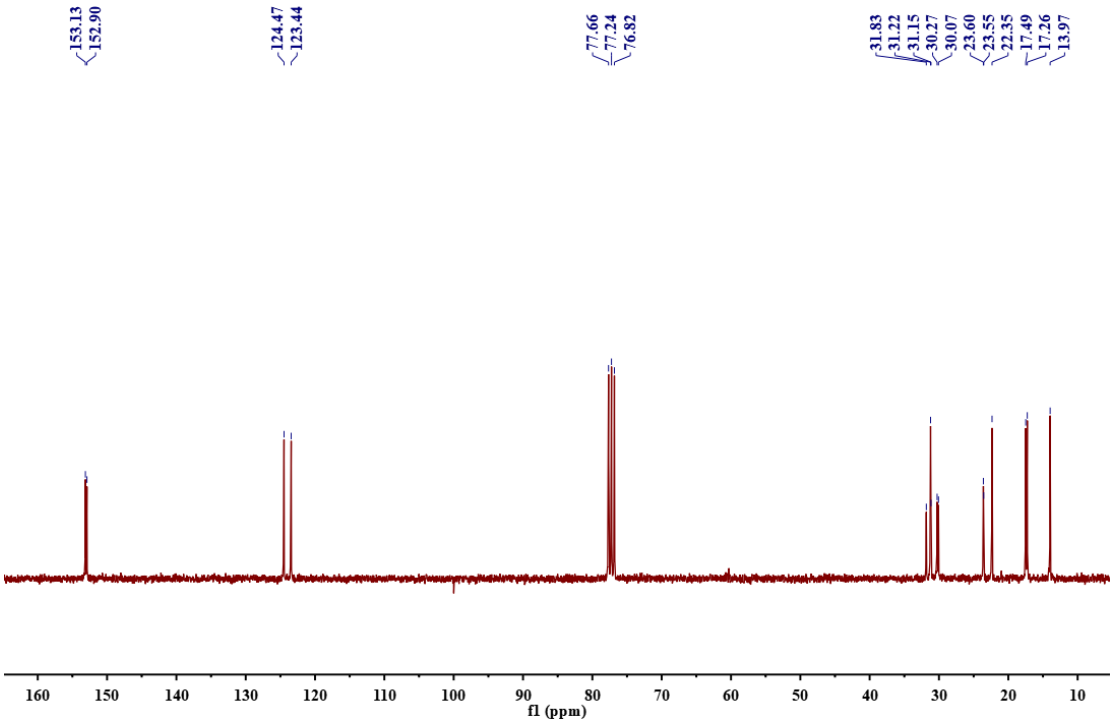
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 1l



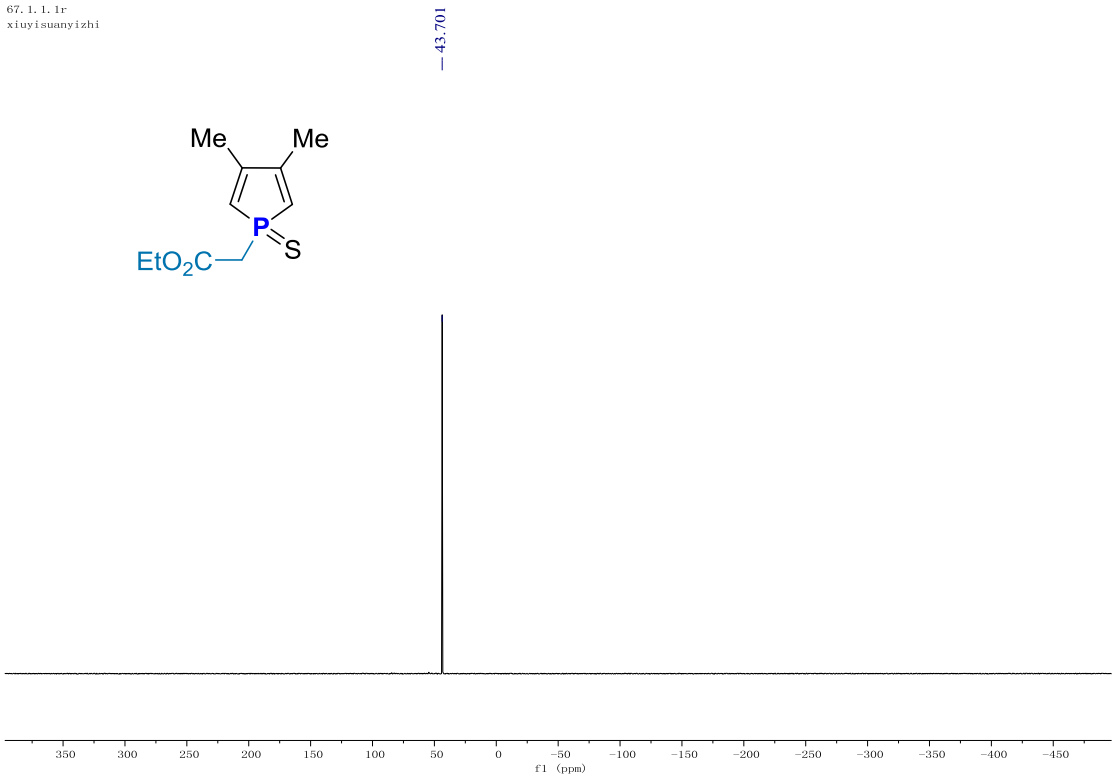
^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) of Compound 1m



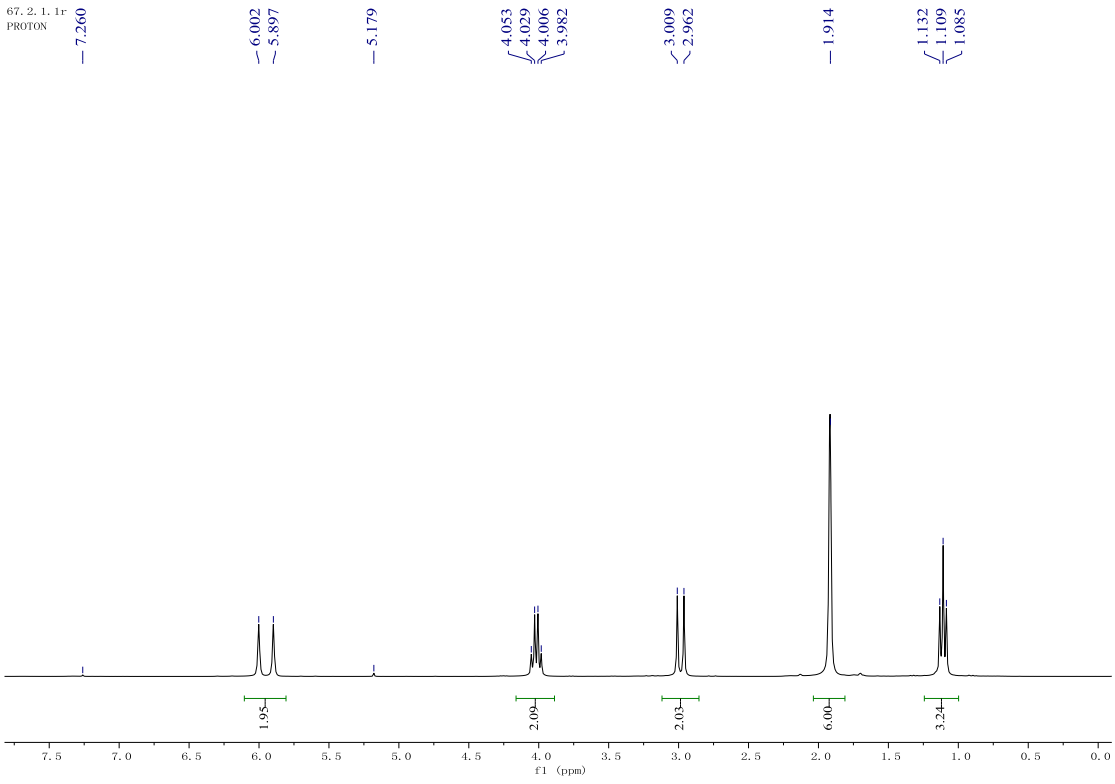
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 1m



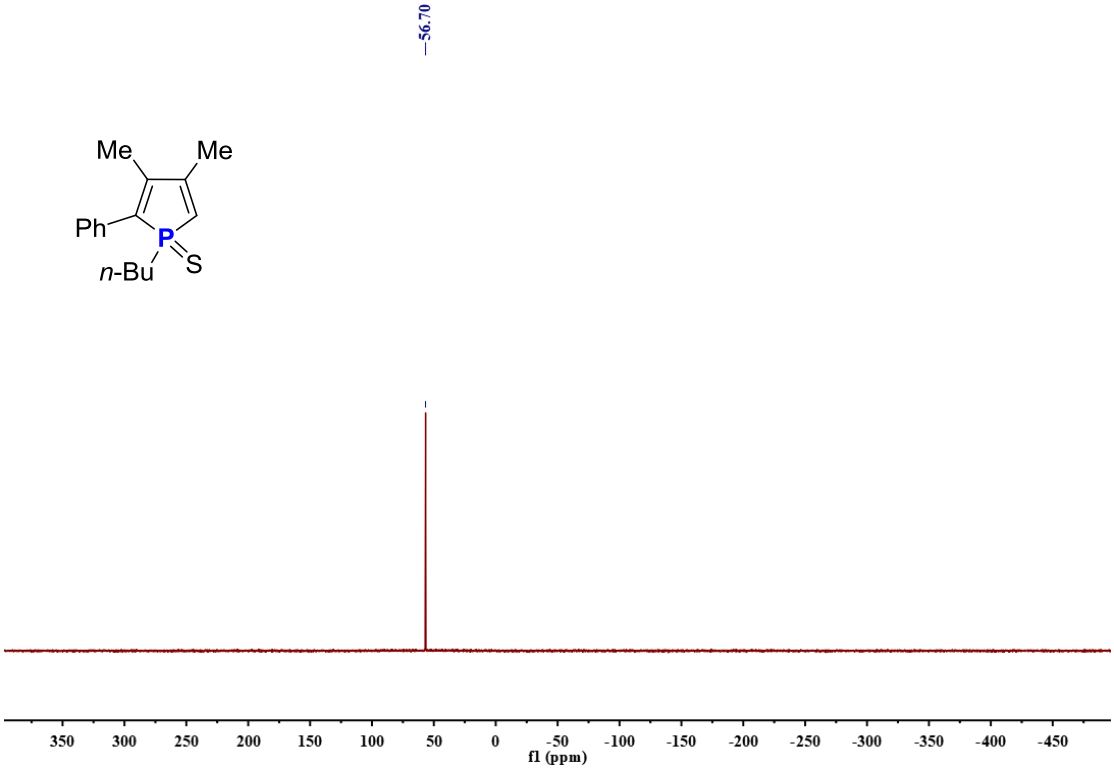
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of Compound 1m



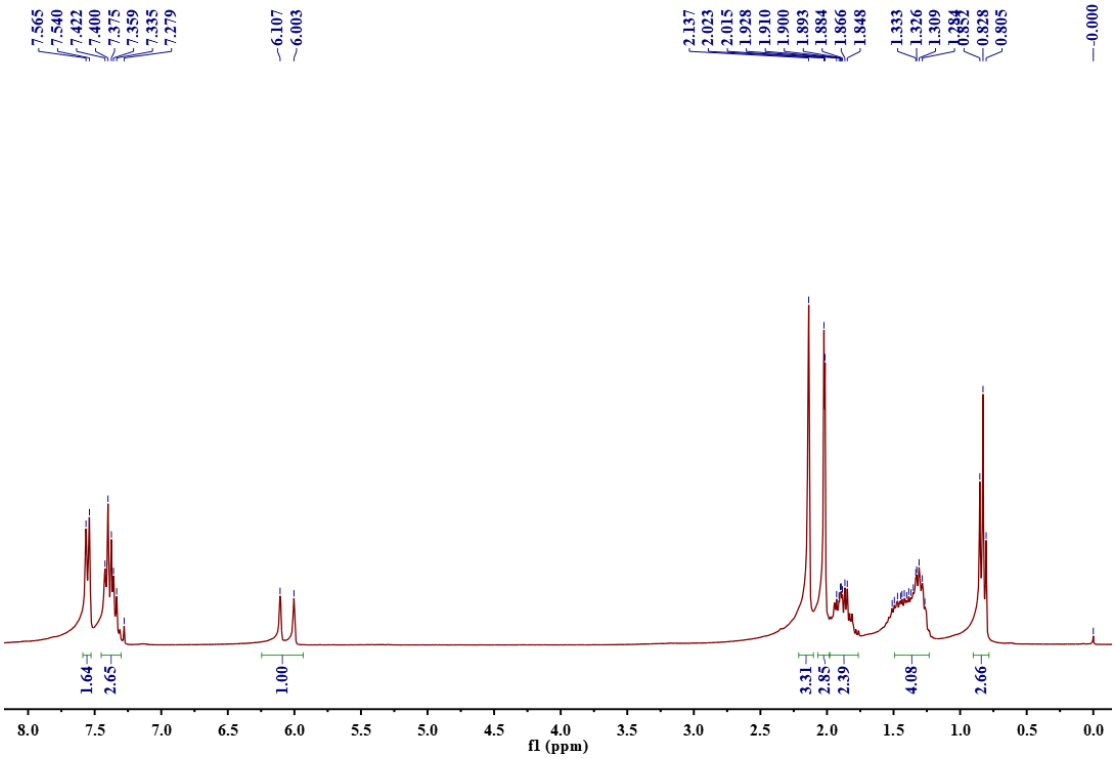
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 1n



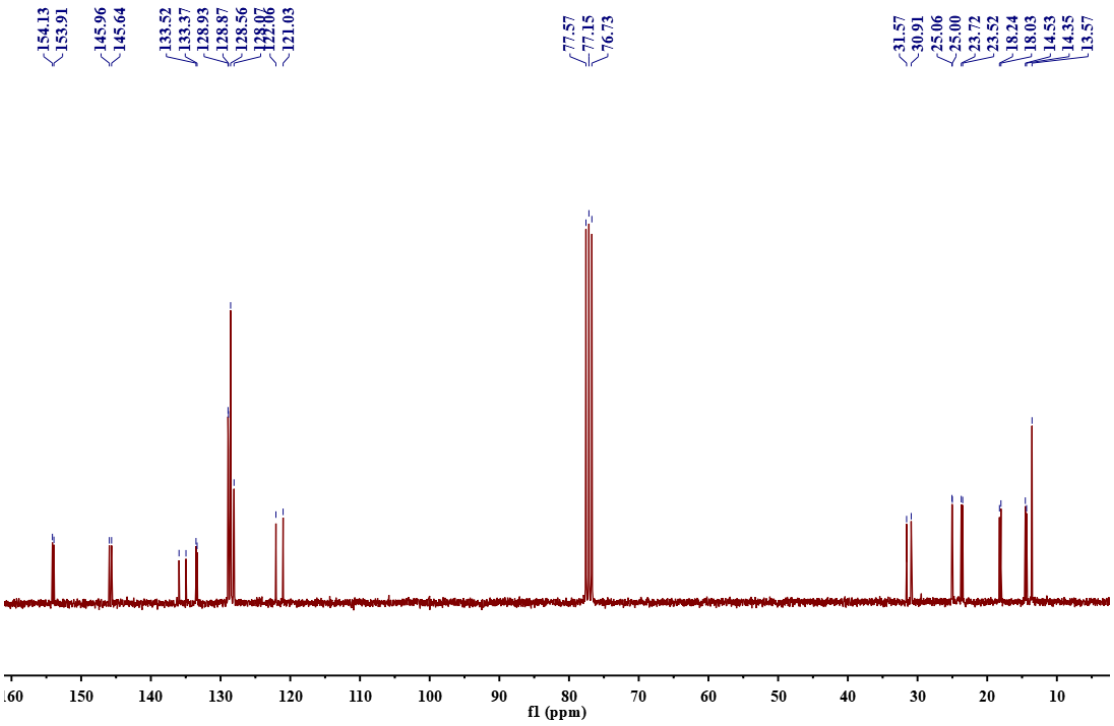
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 1n



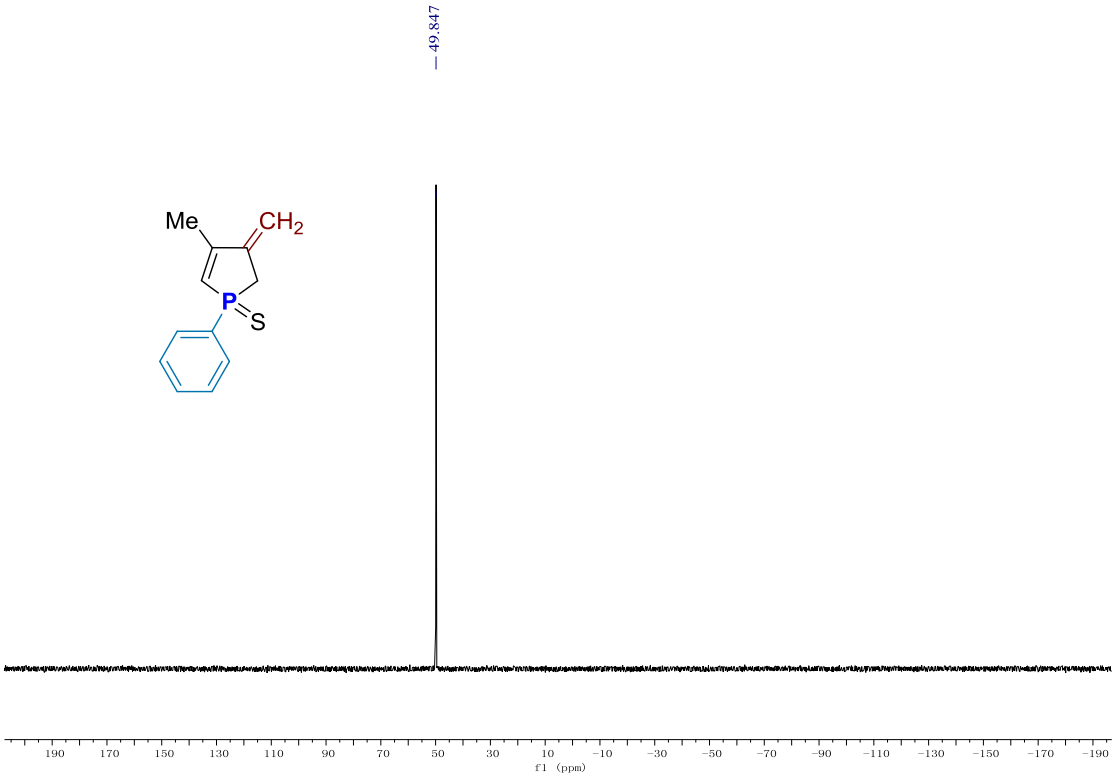
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 1o



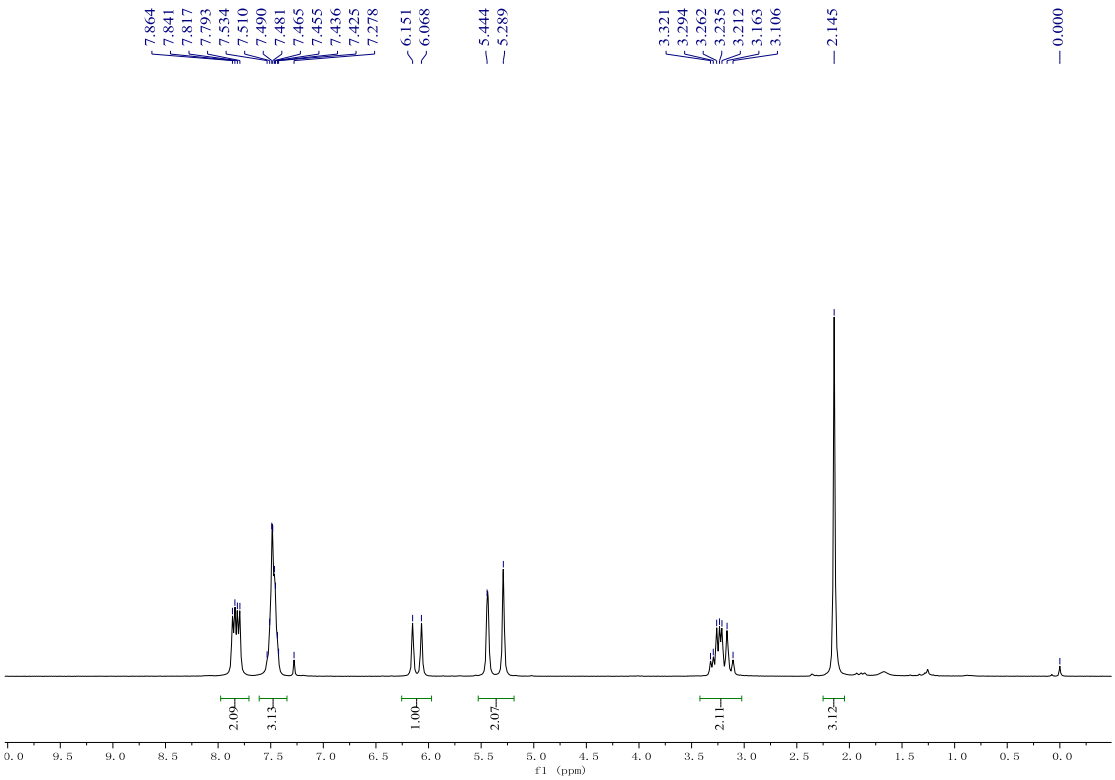
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 1o



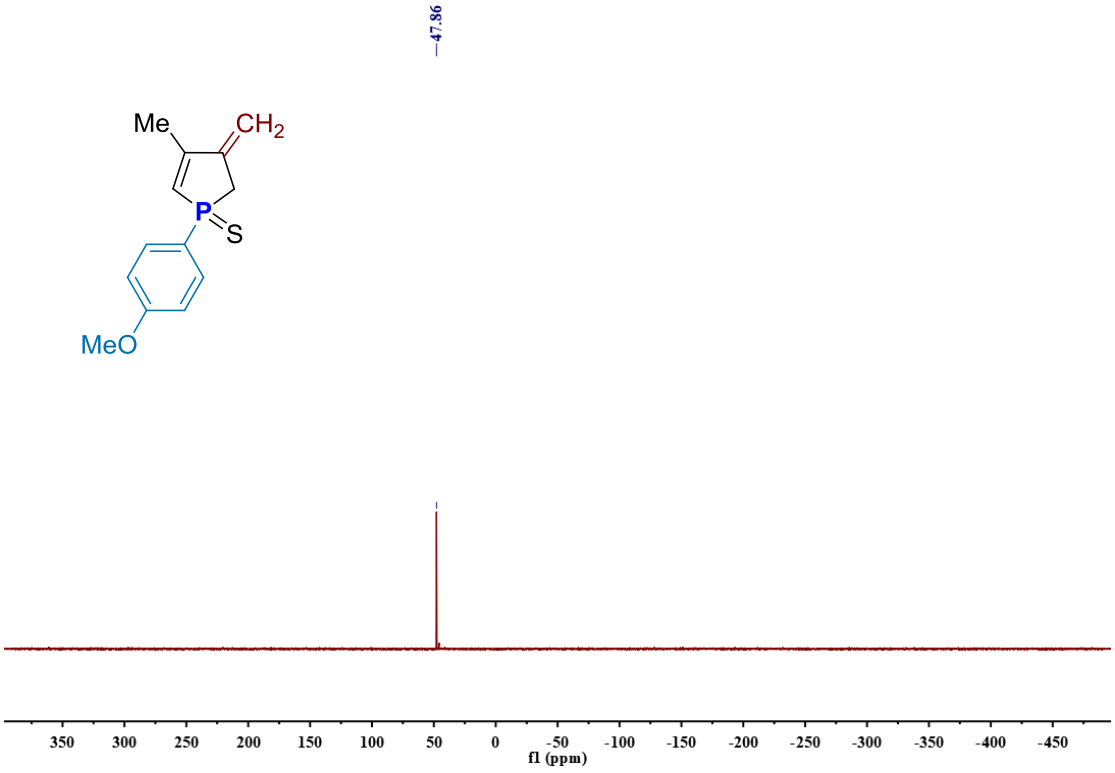
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 1o



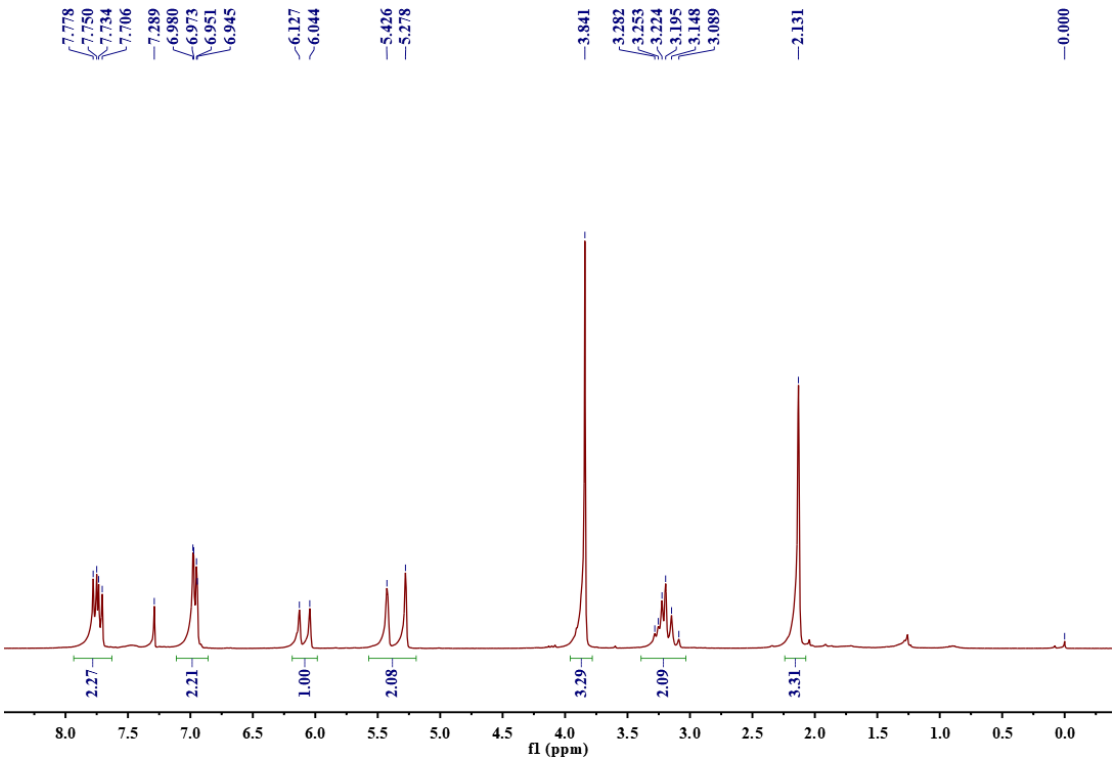
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2a



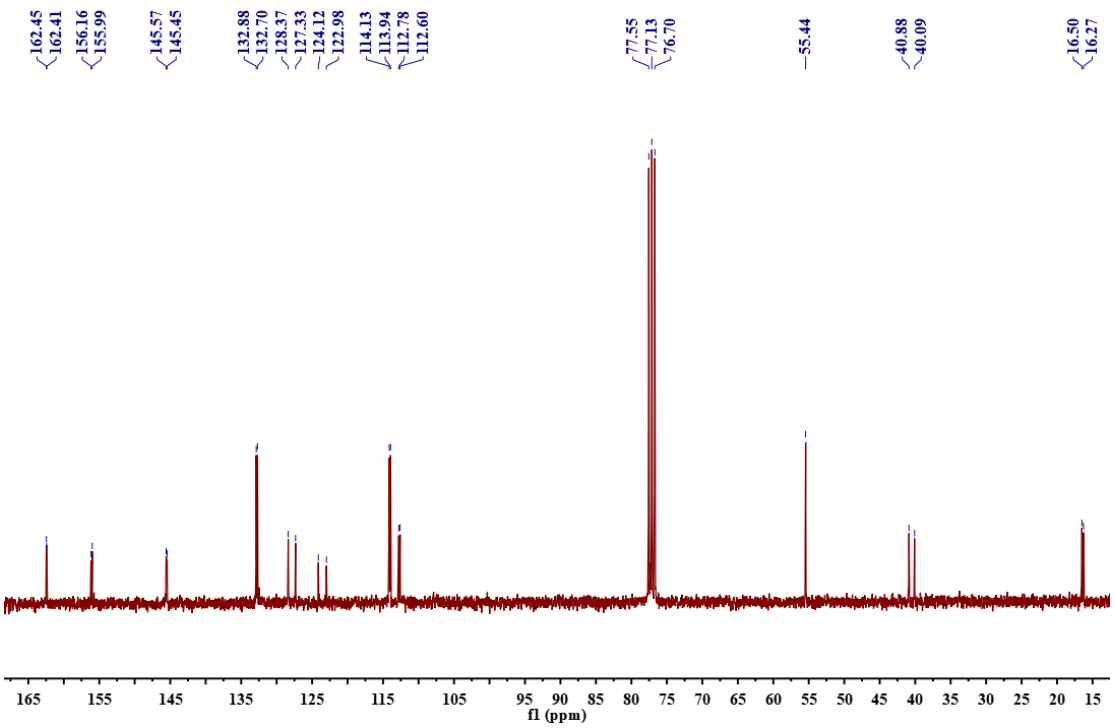
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2a



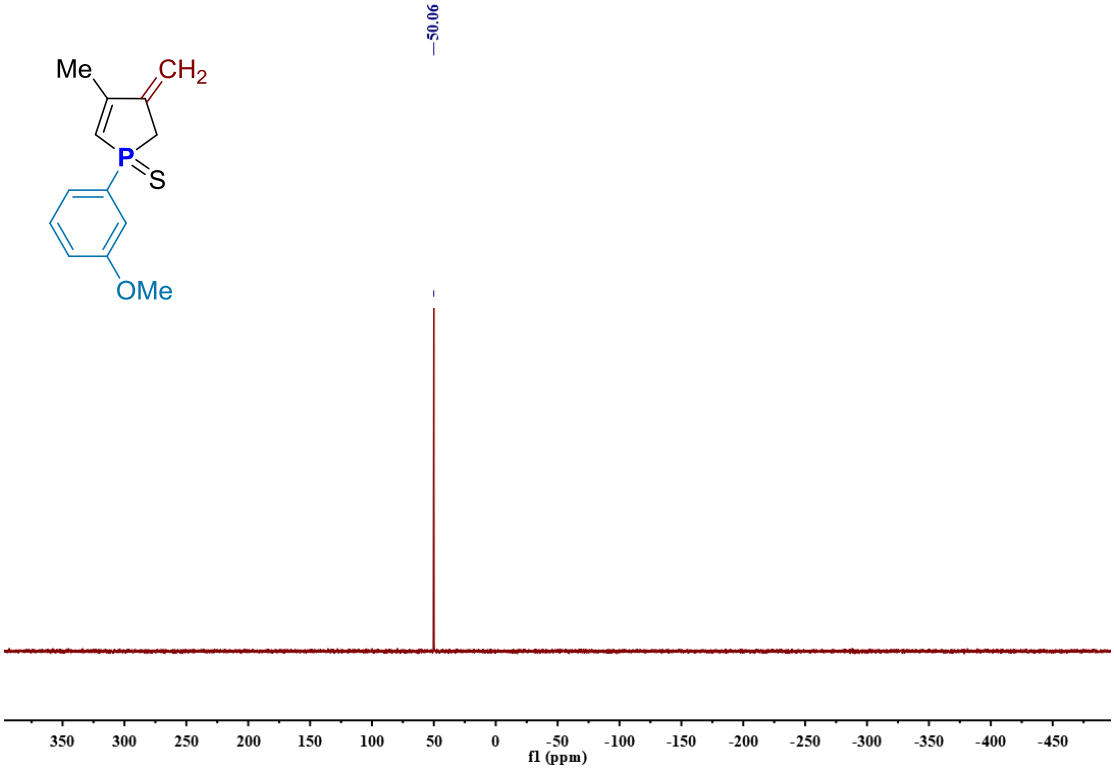
^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) of Compound 2b



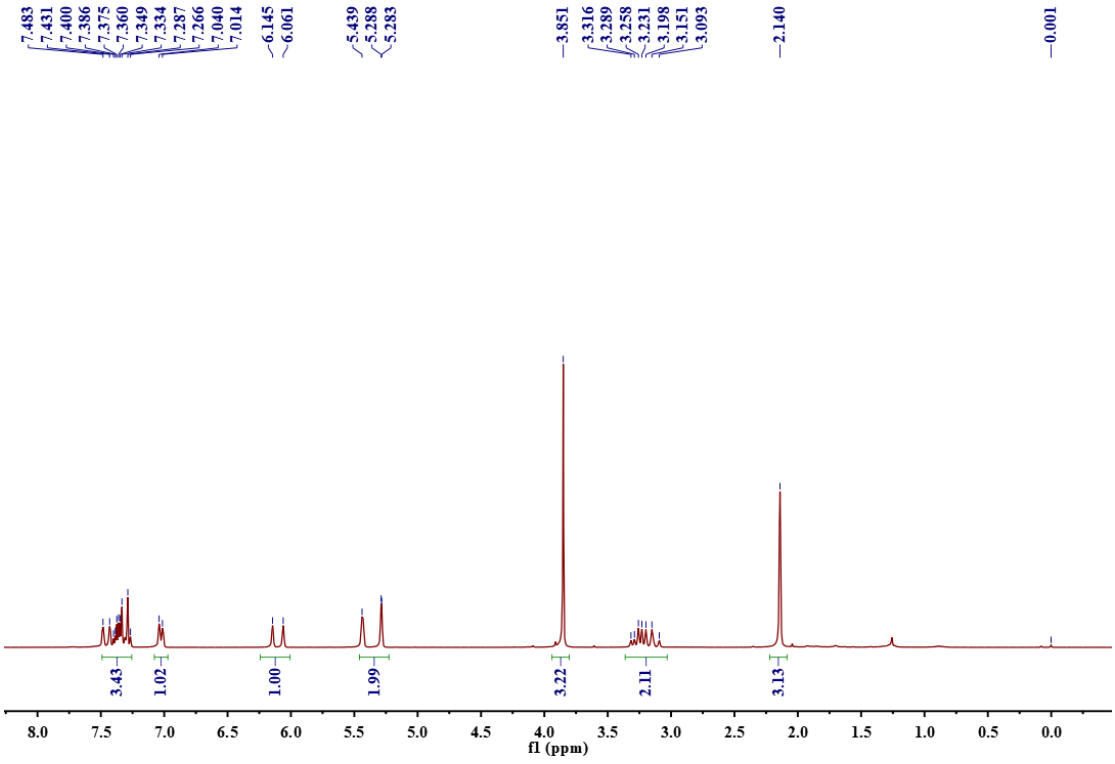
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2b



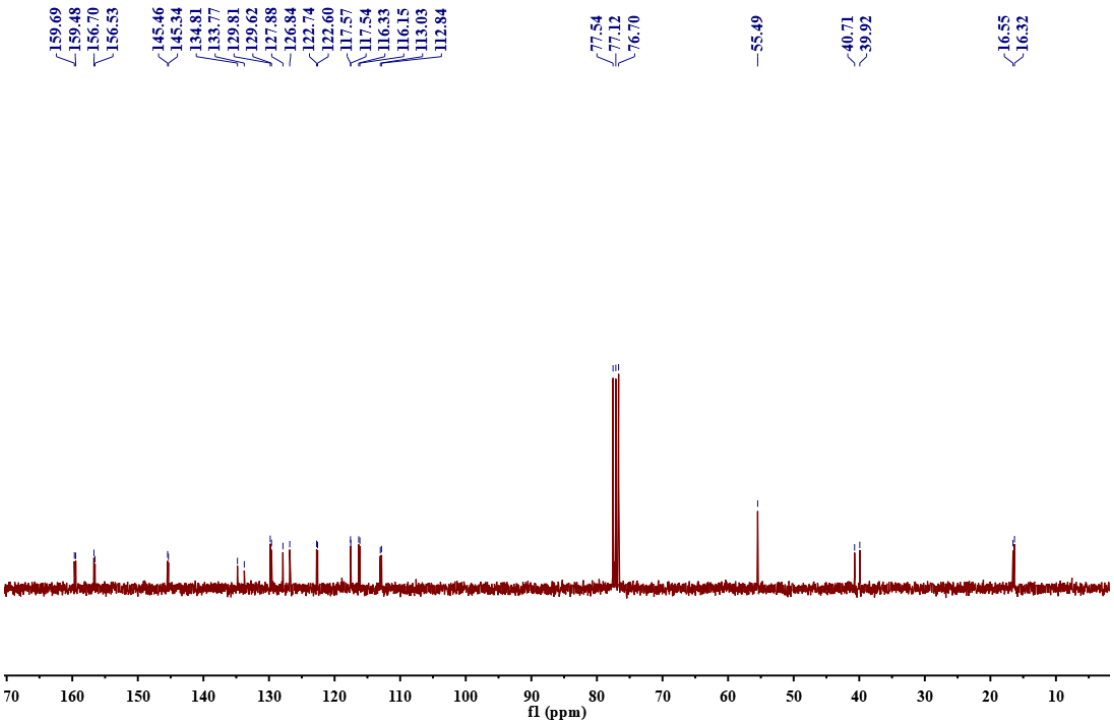
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of Compound 2b



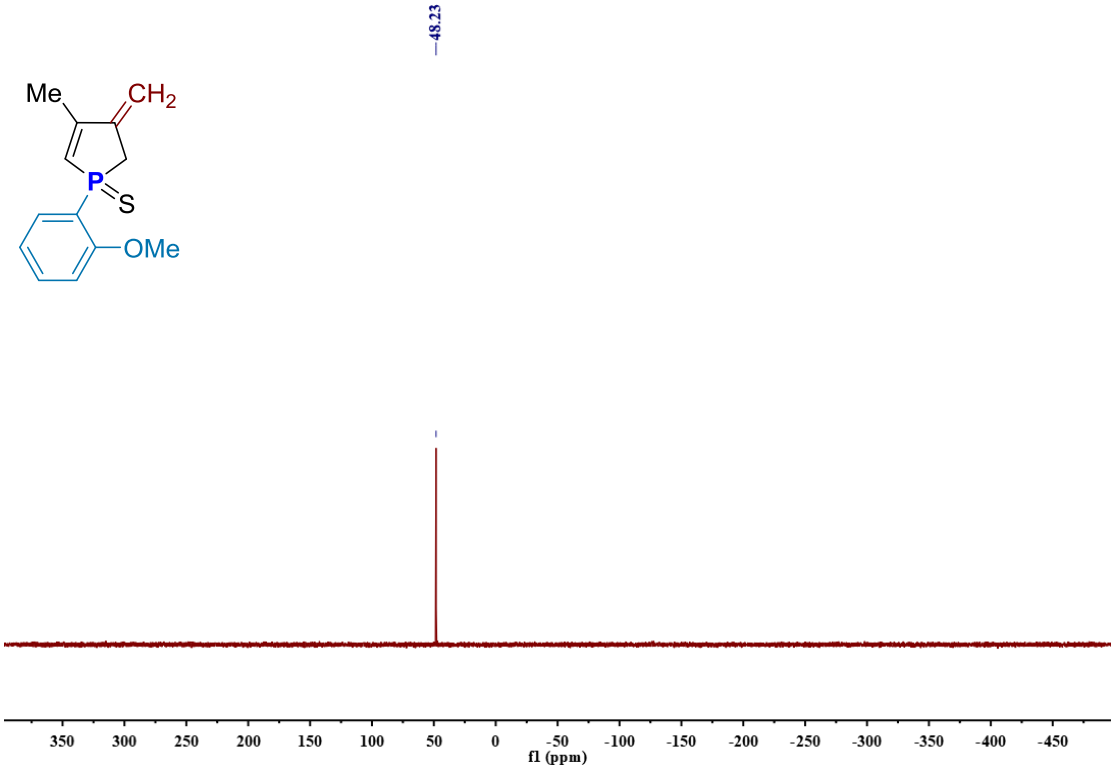
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2c



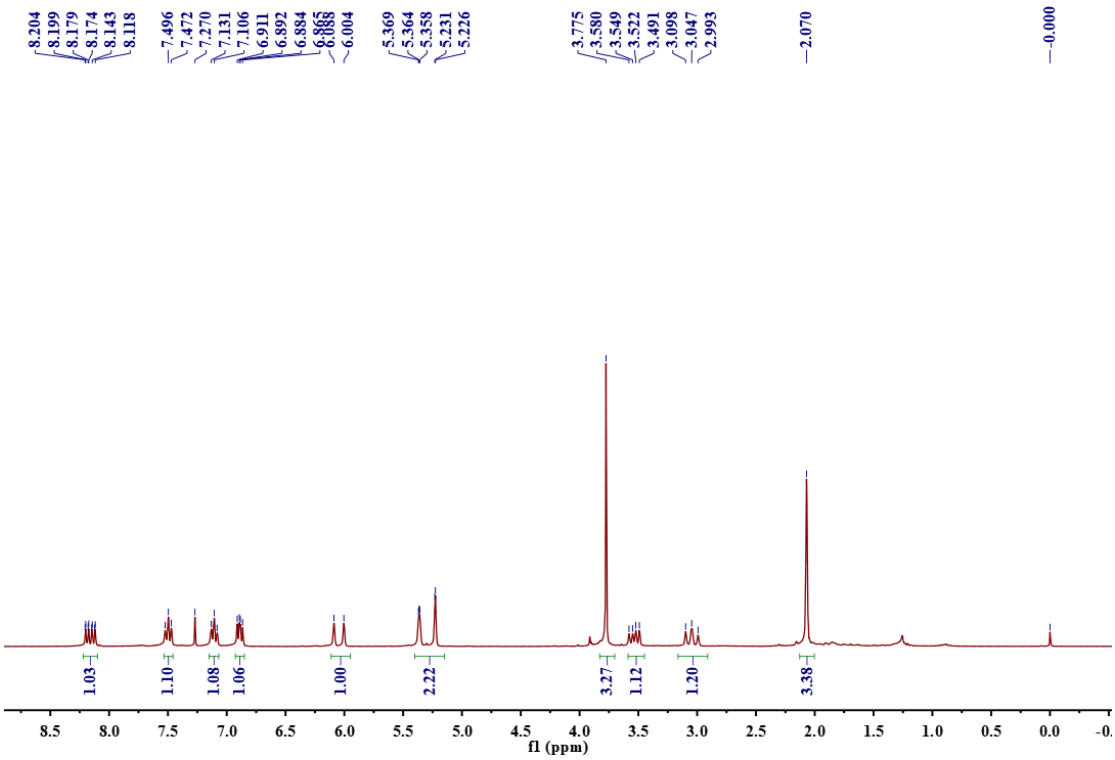
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2c



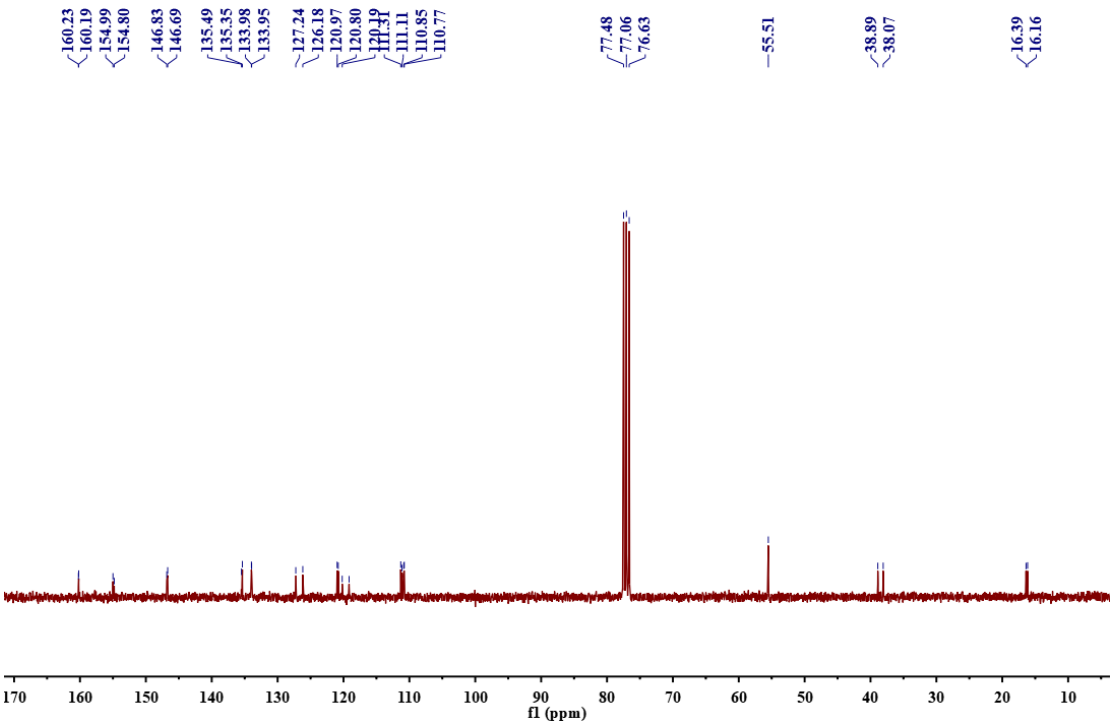
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2c



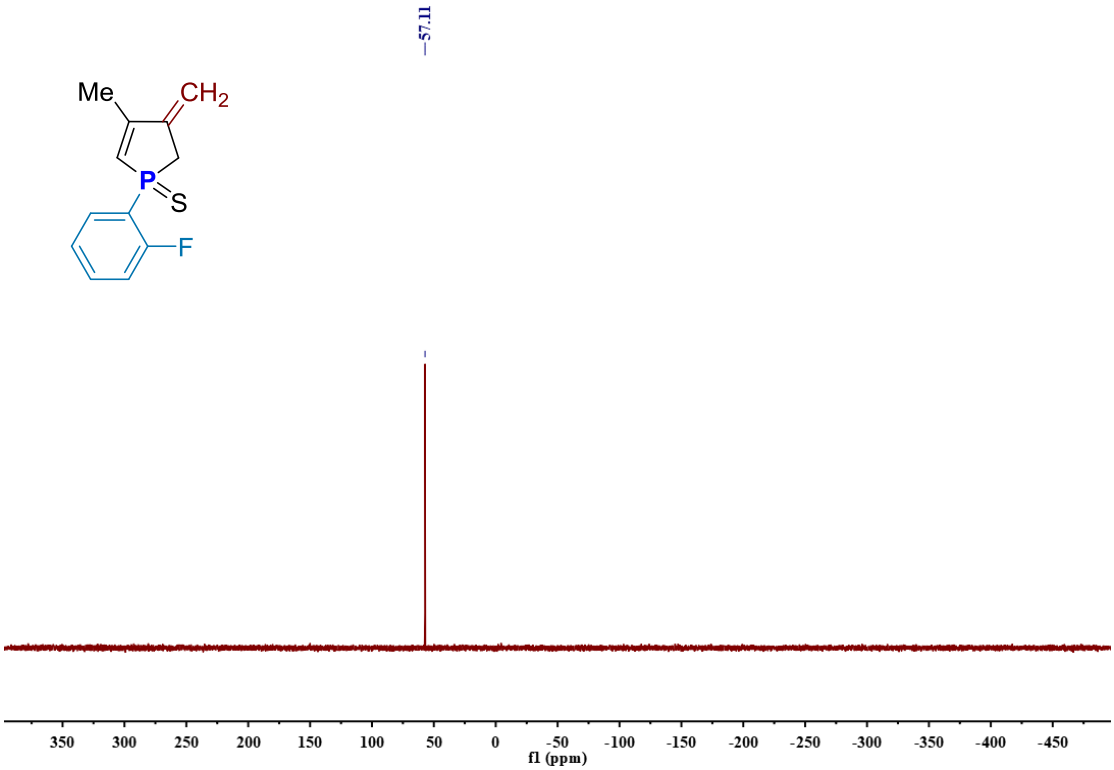
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2d



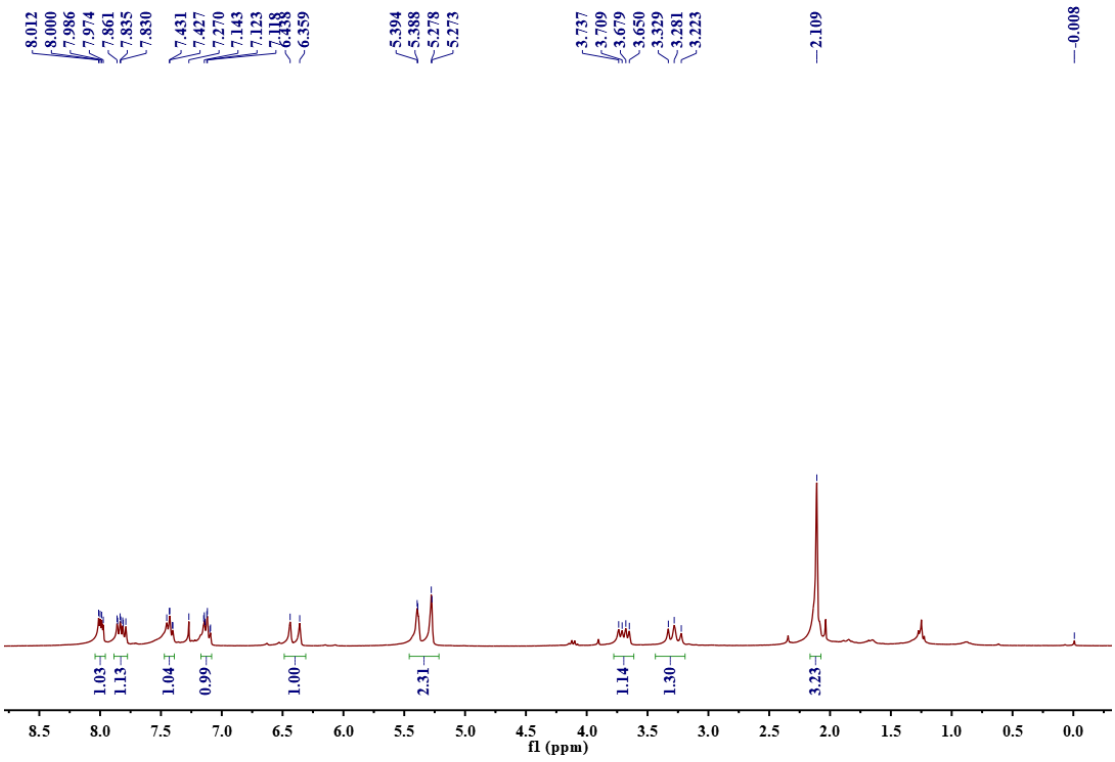
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2d



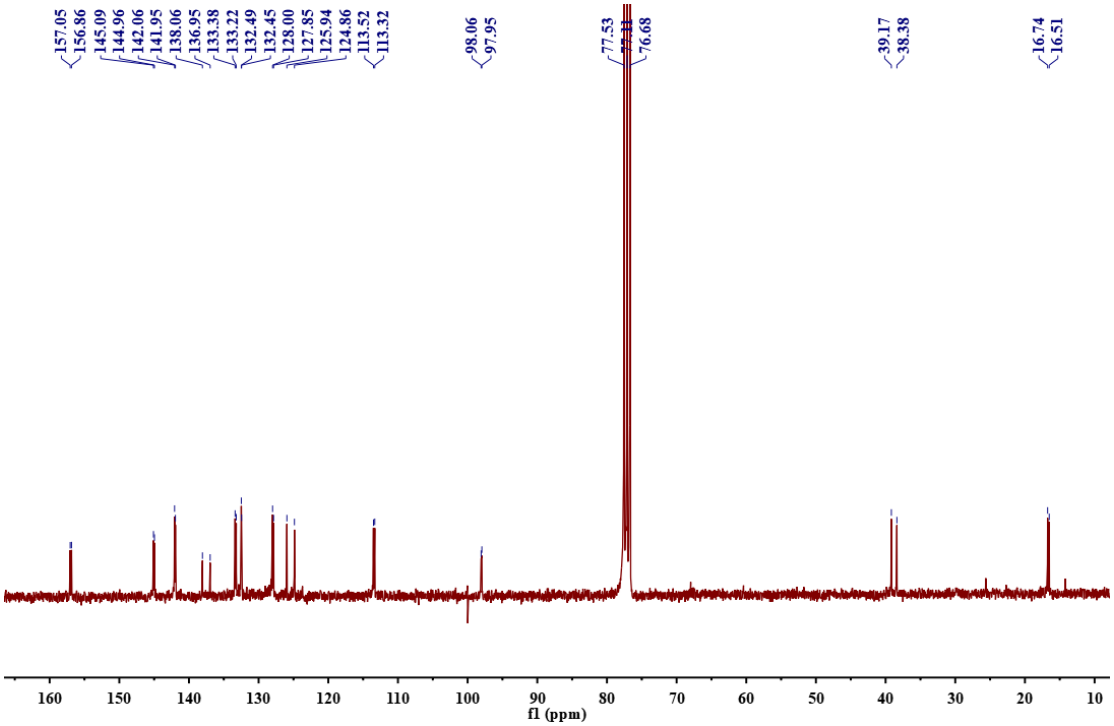
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of Compound 2d



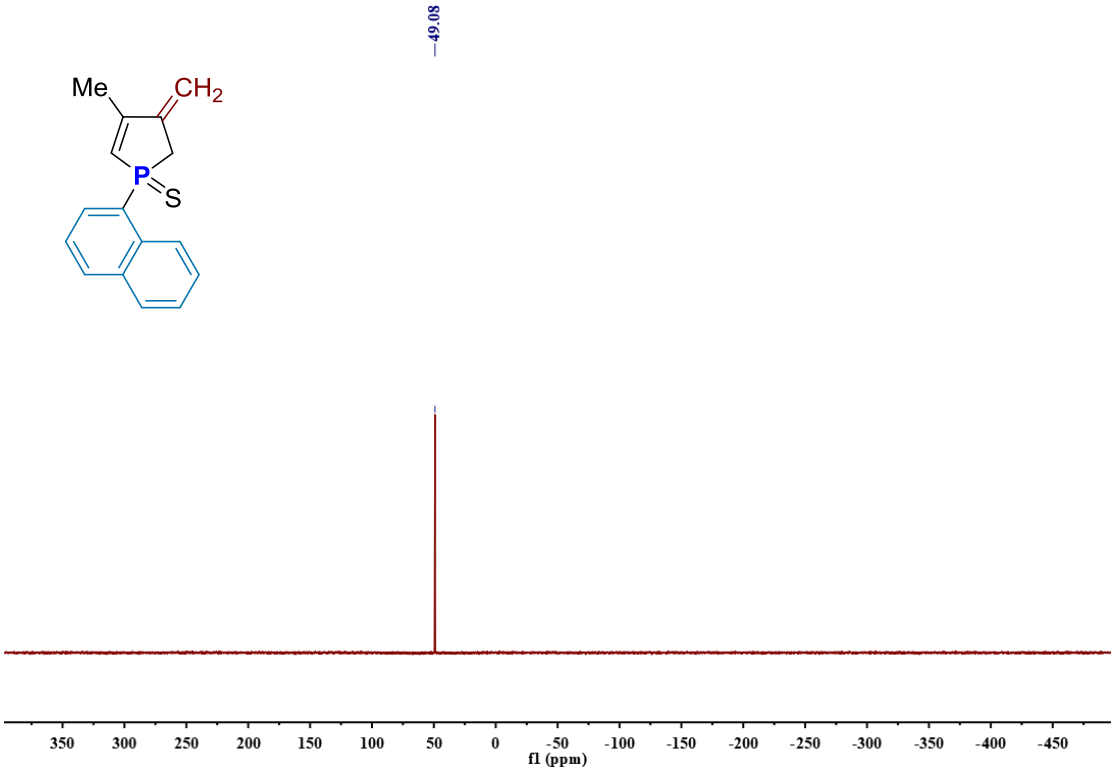
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2e



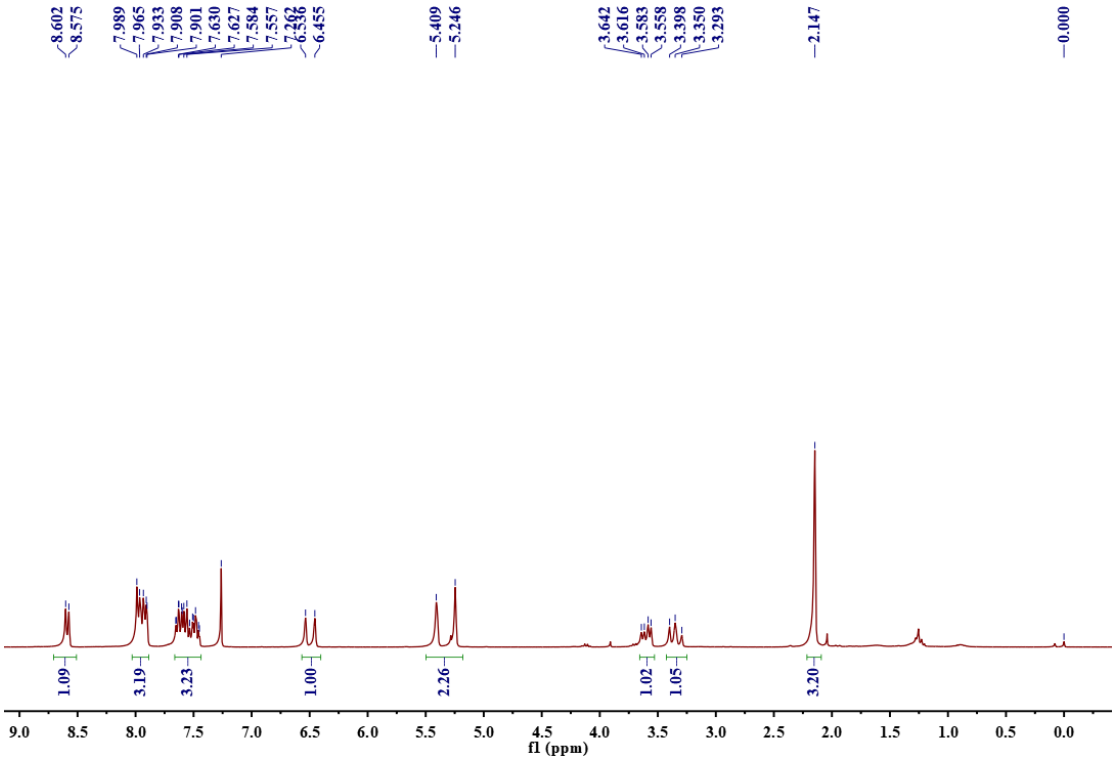
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2e



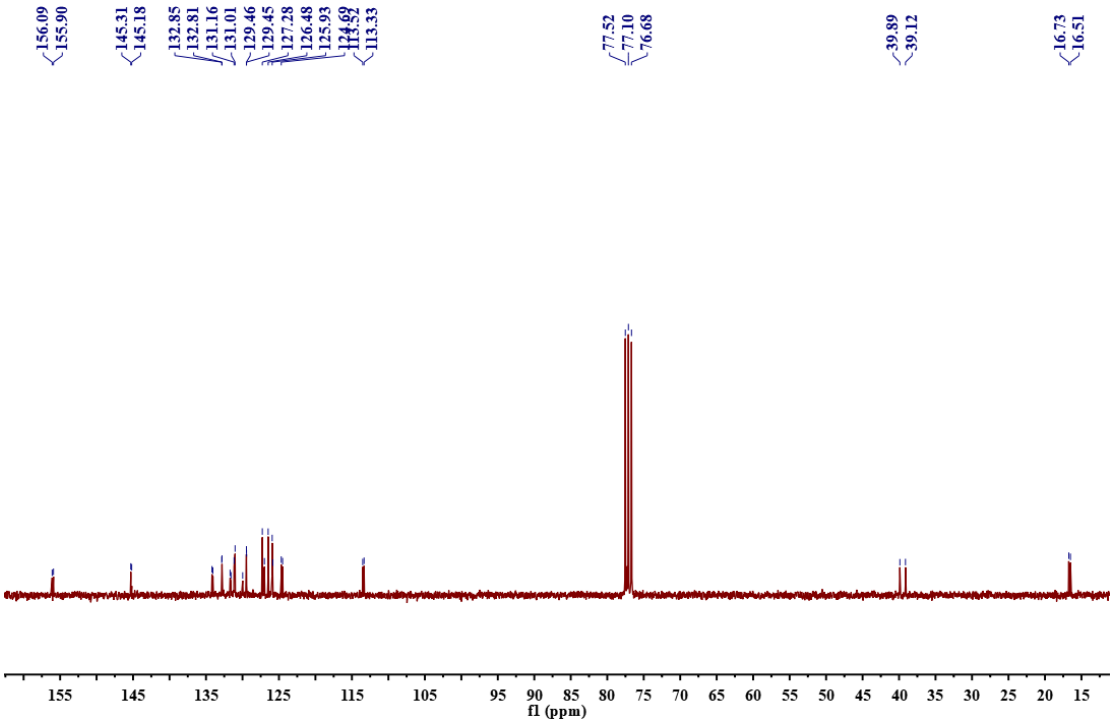
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2e



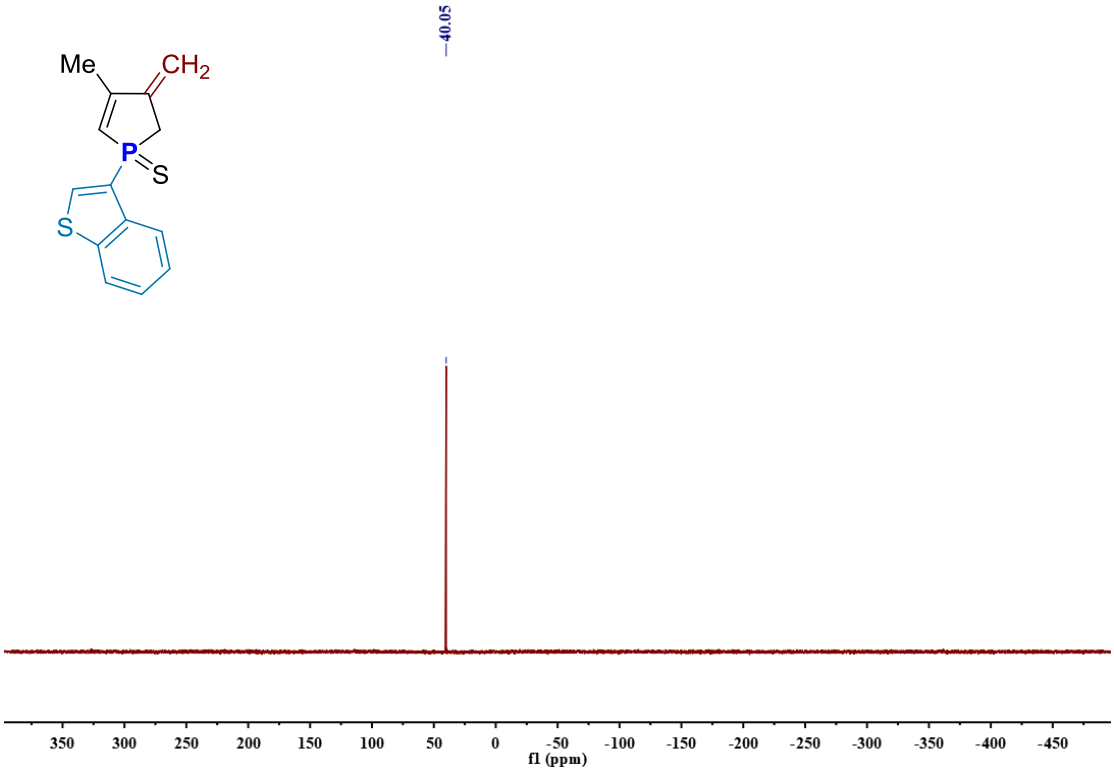
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2f



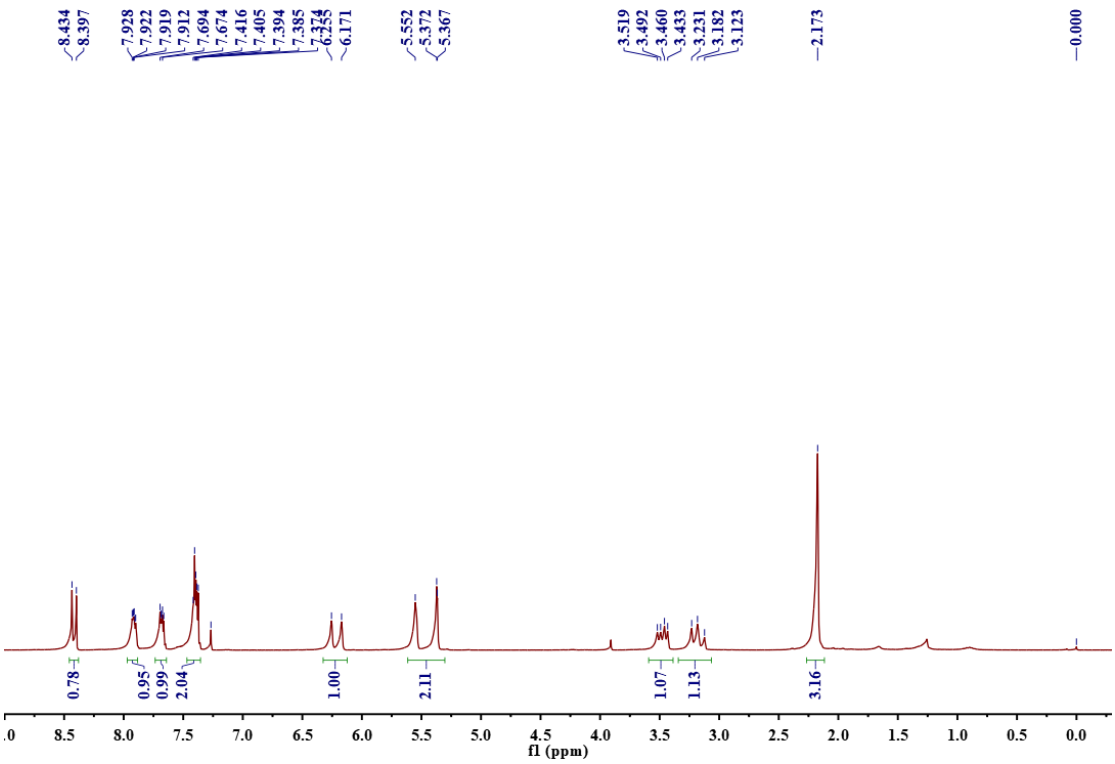
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2f



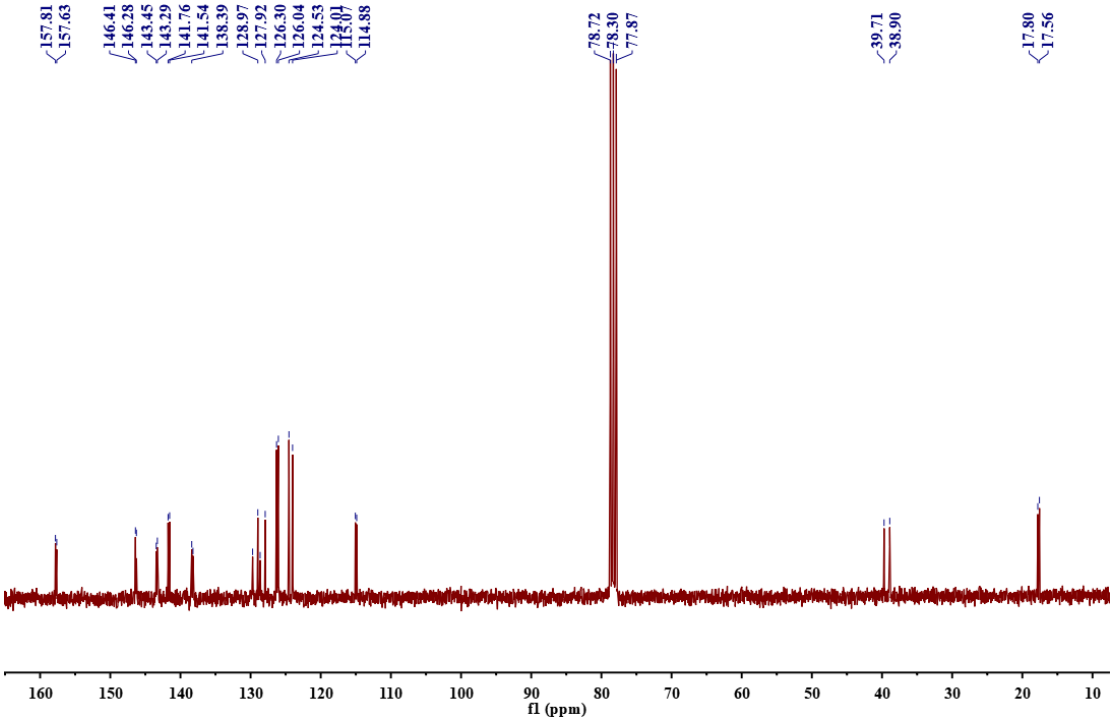
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2f



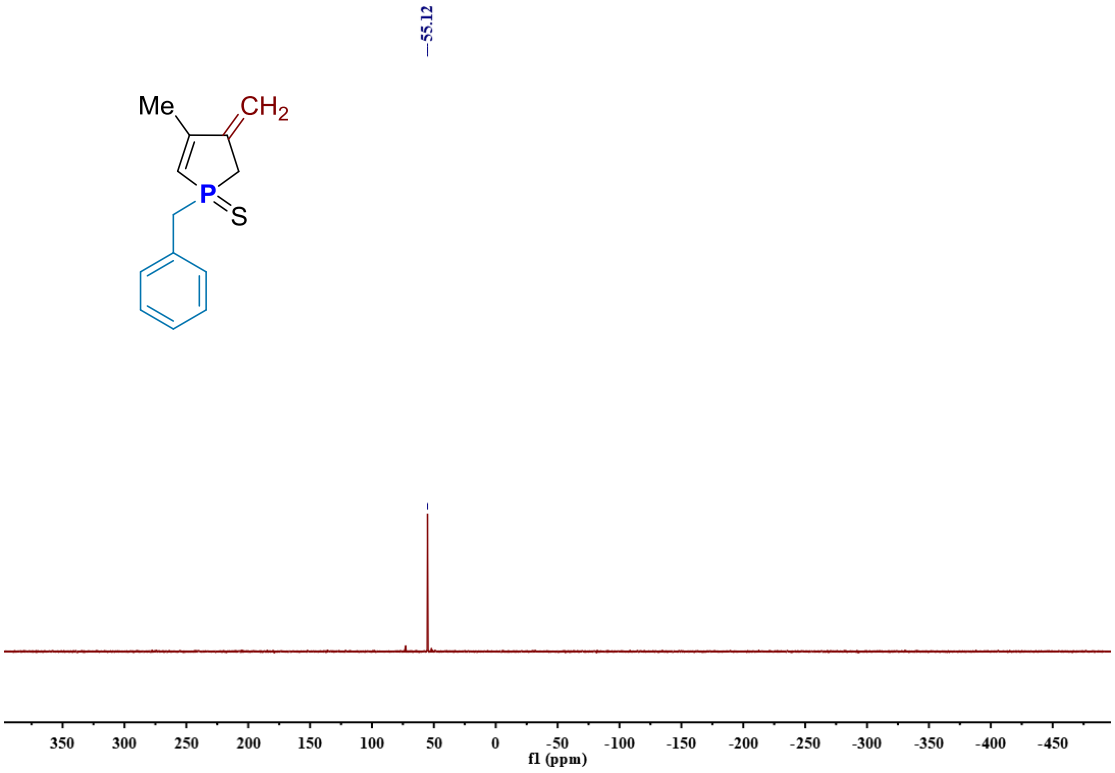
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2g



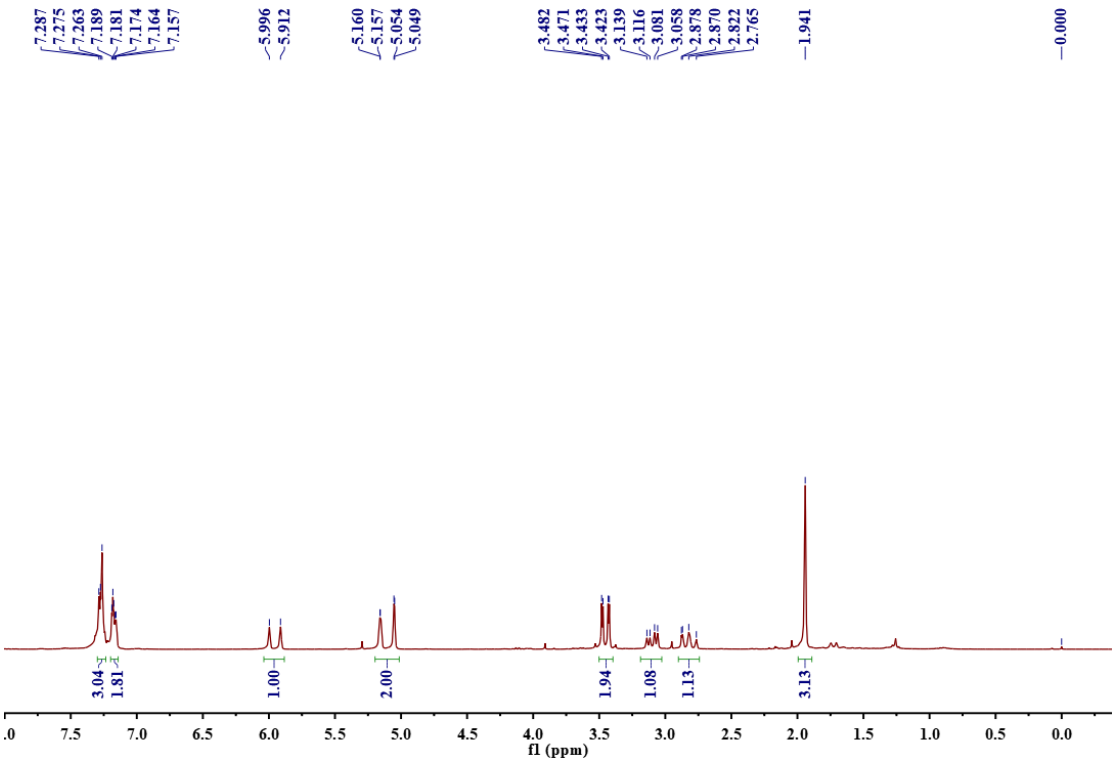
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2g



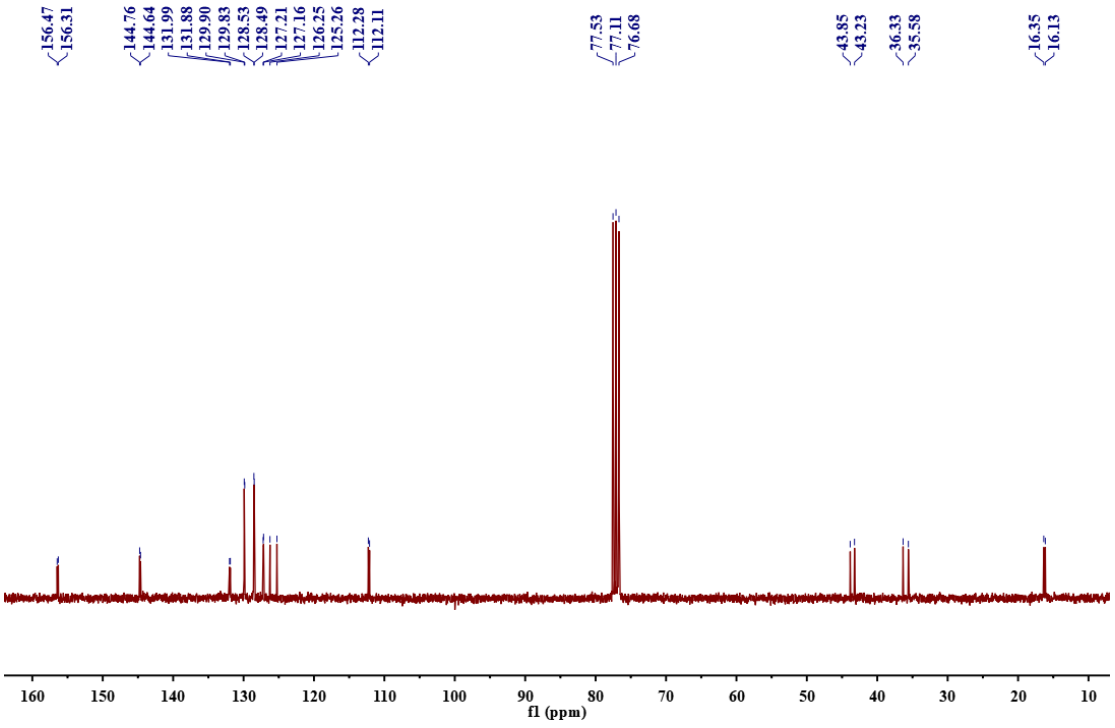
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of Compound 2g



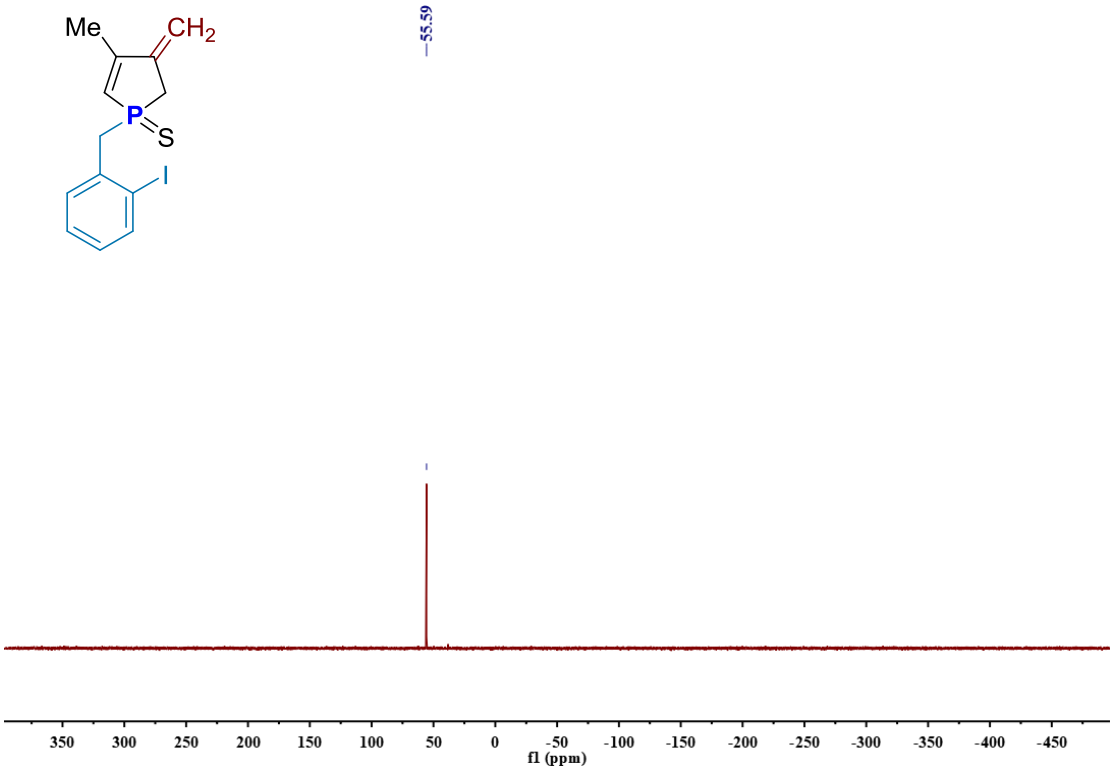
^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) of Compound 2h



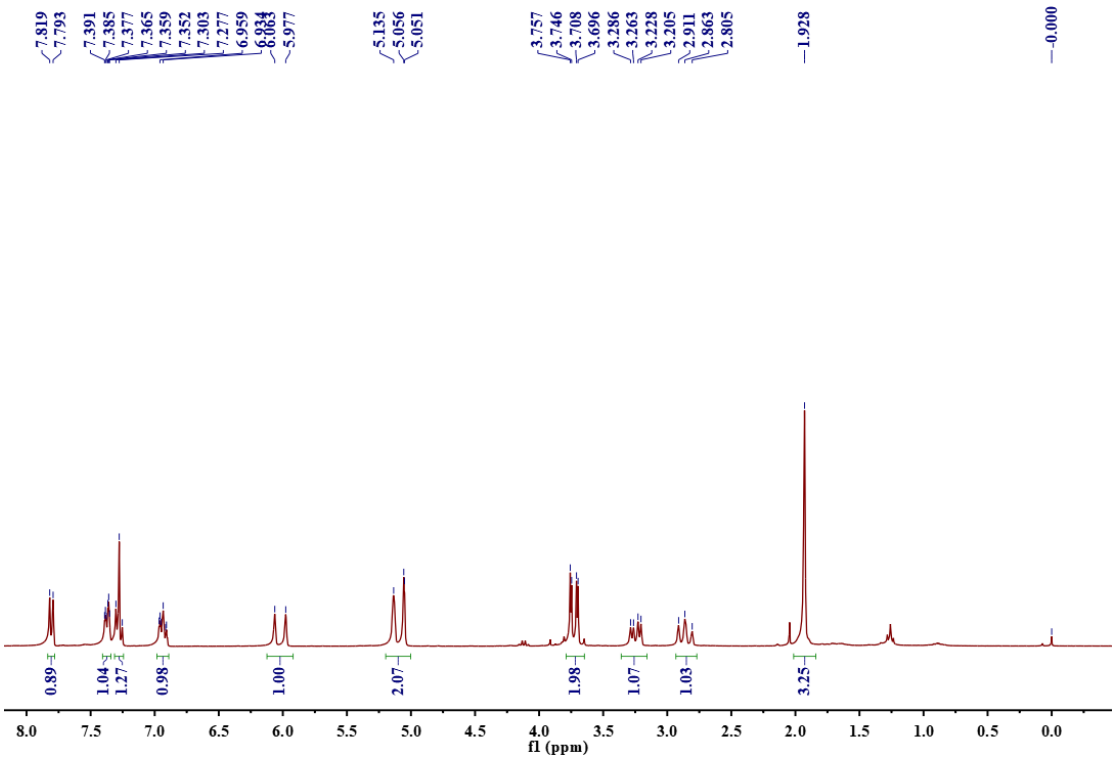
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2h



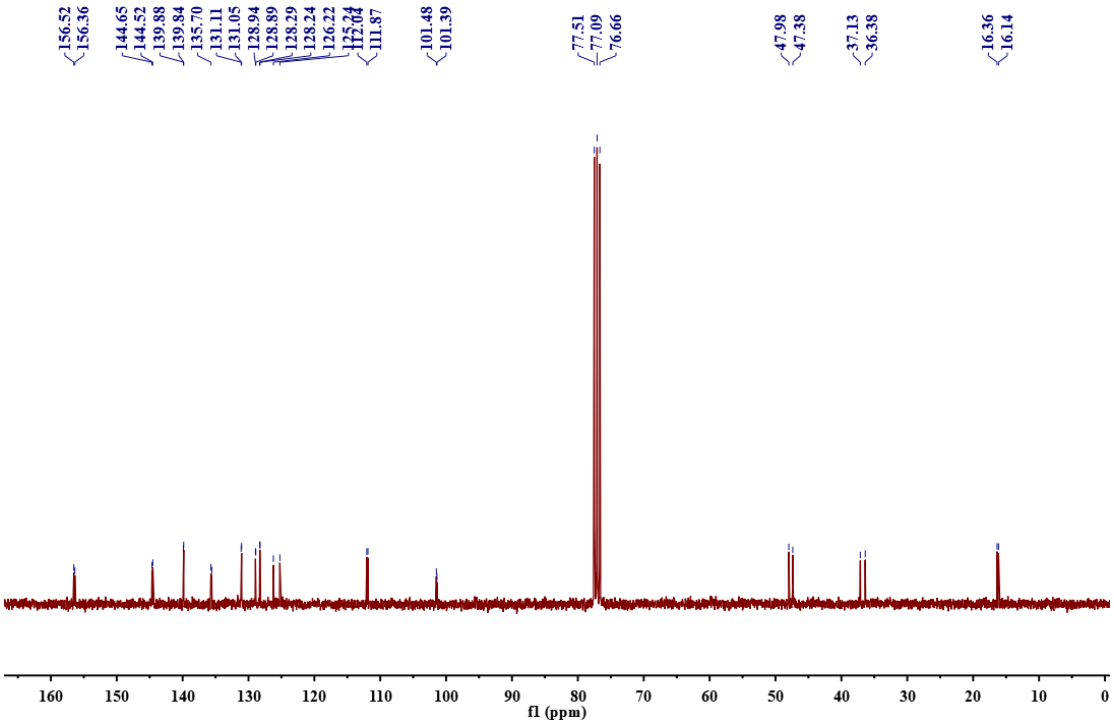
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2h



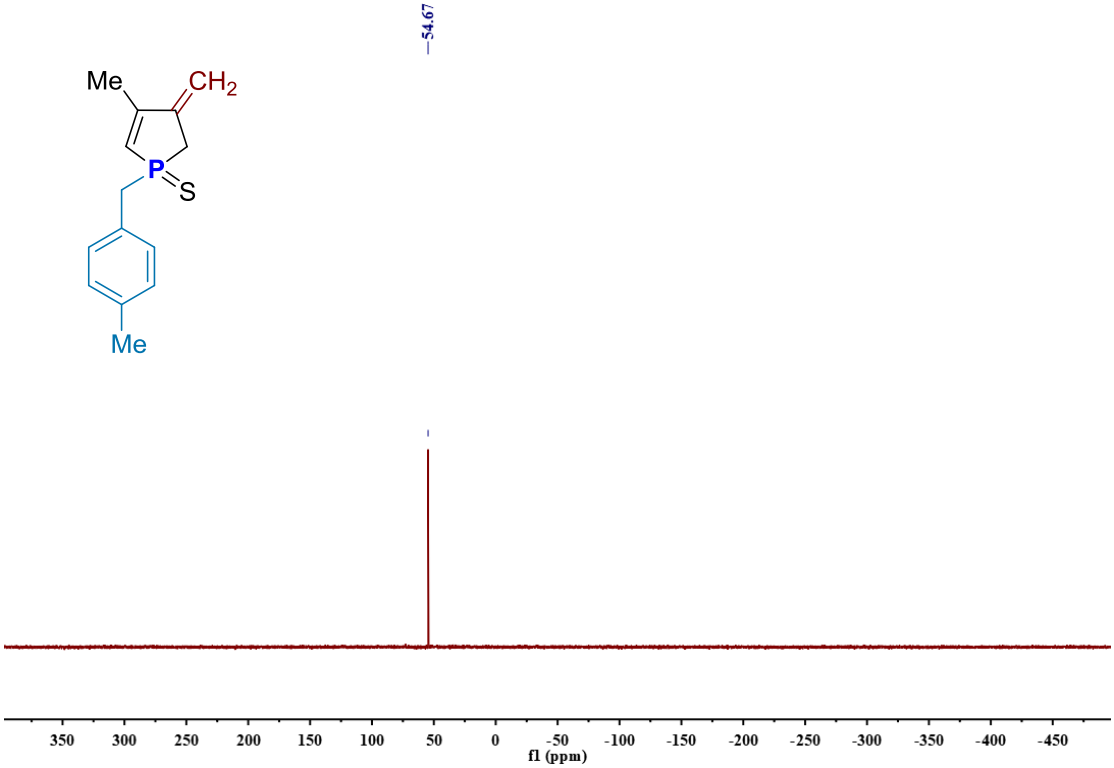
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2i



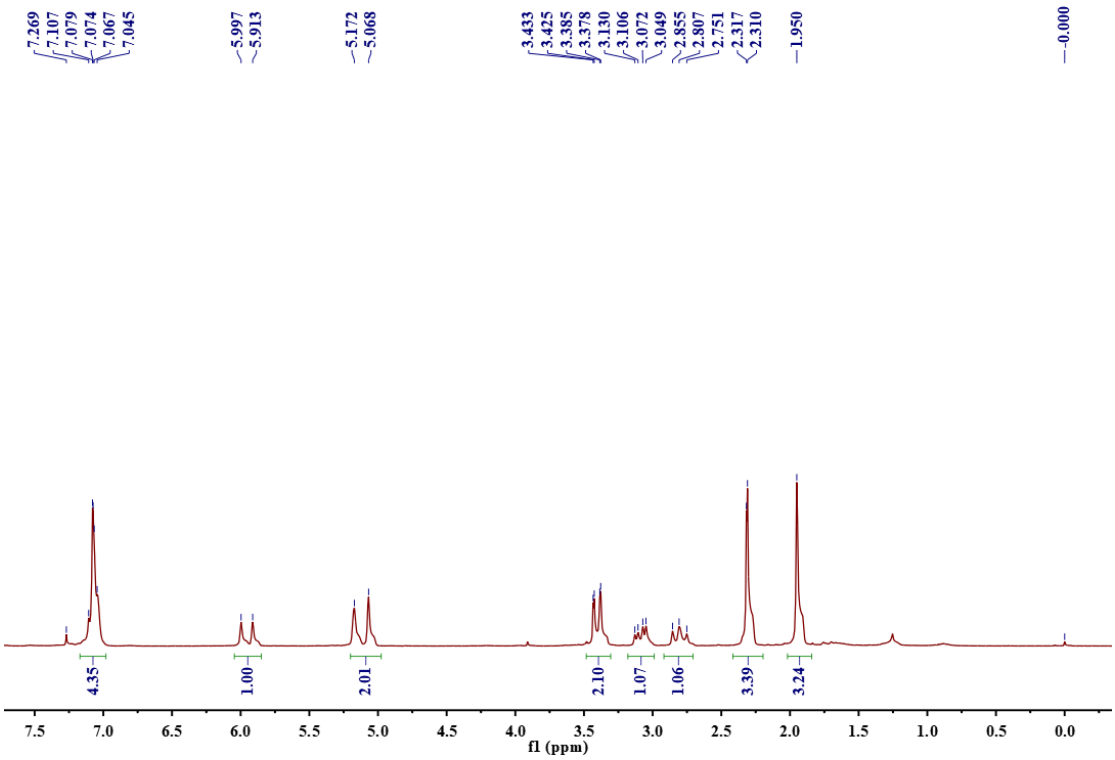
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2i



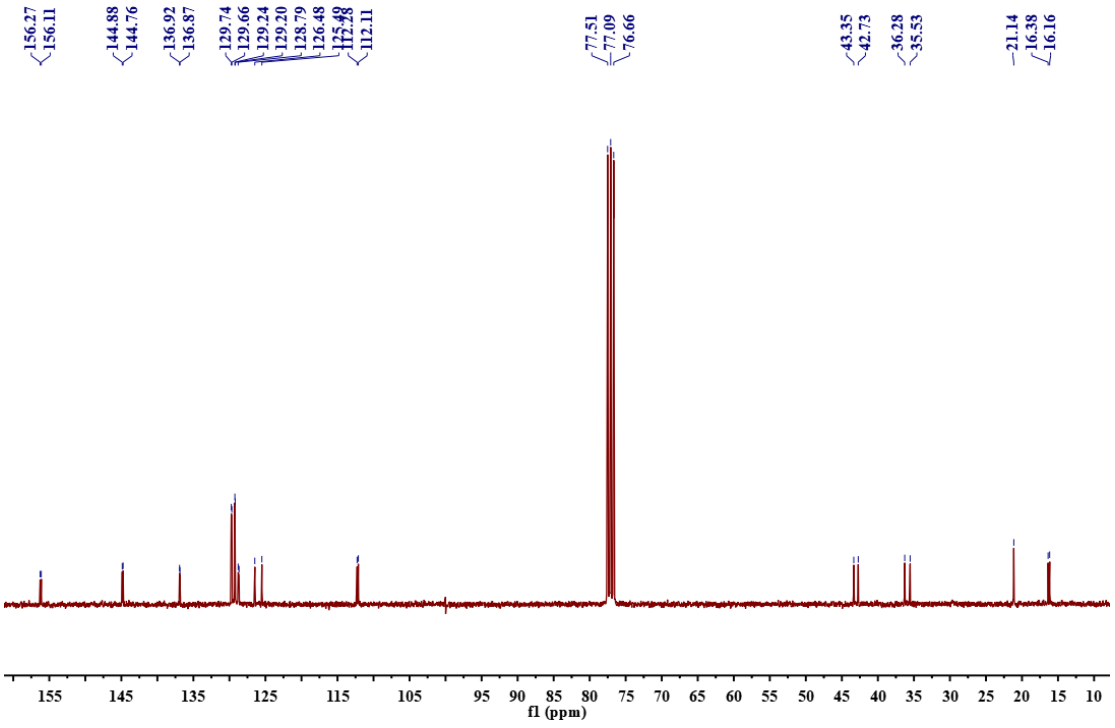
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2i



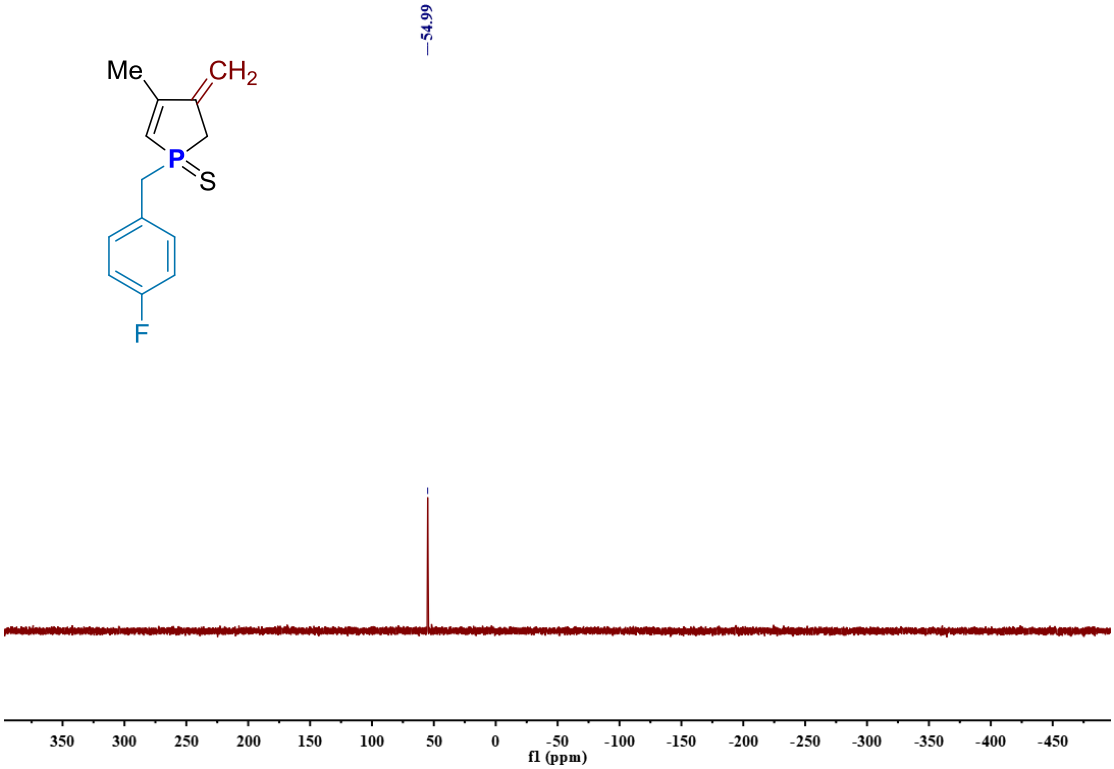
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2j



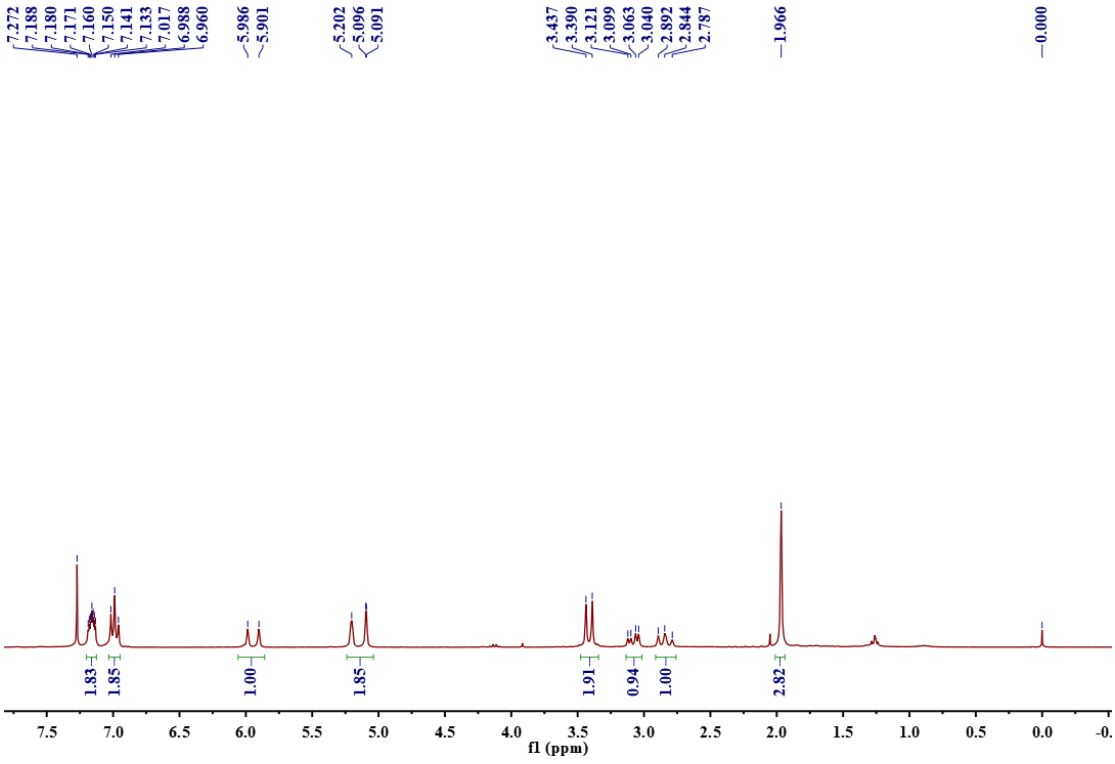
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2j



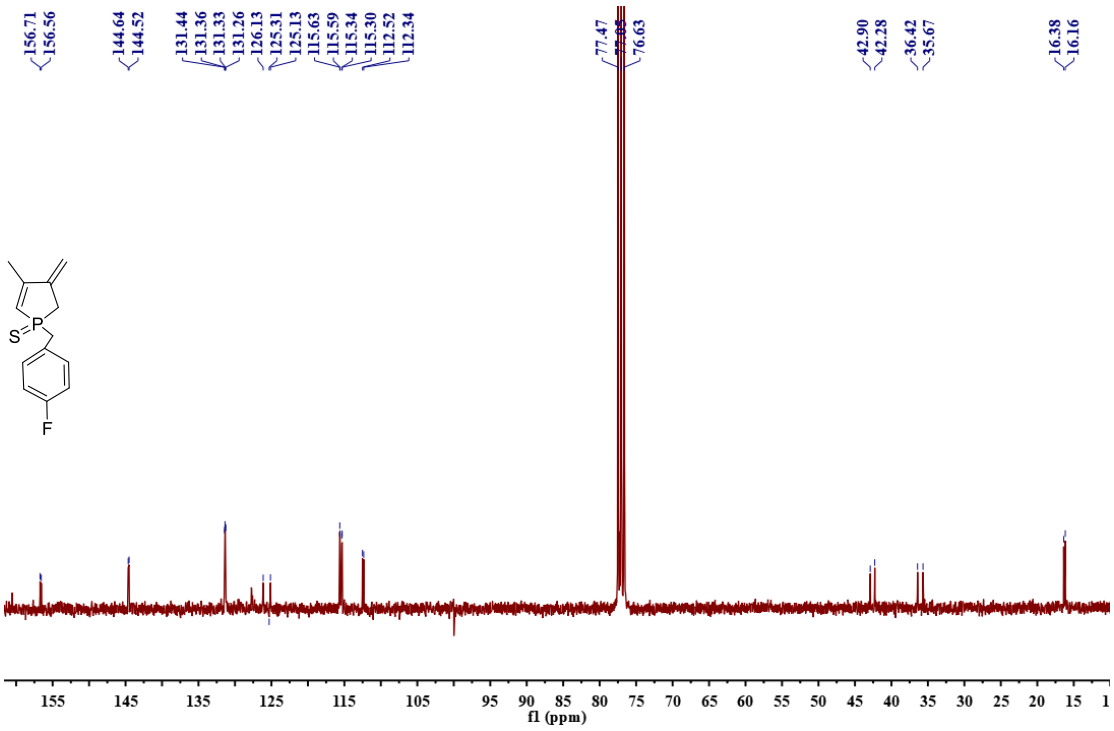
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of Compound 2j



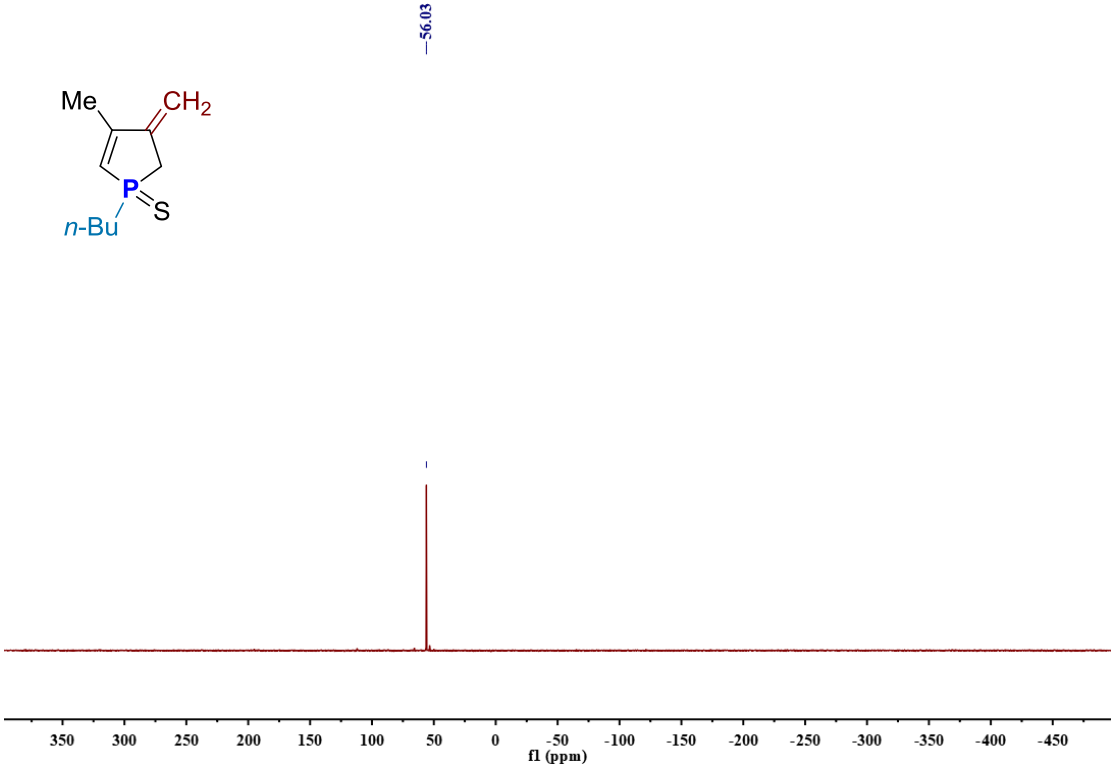
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2k



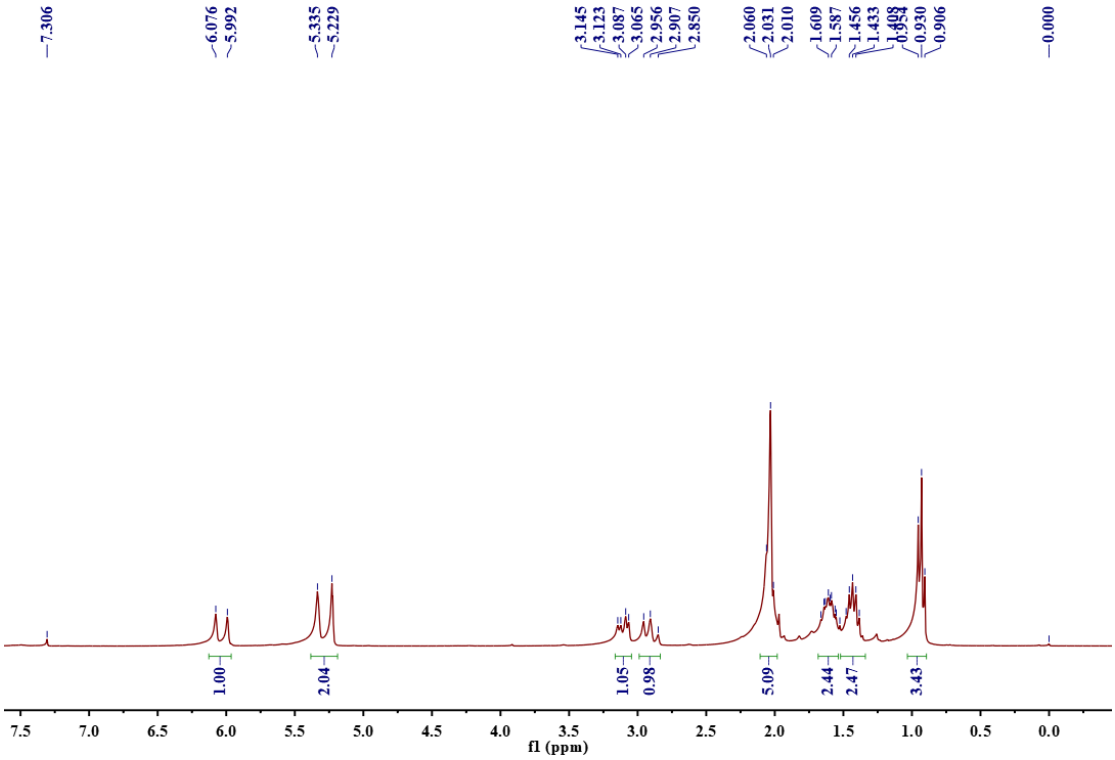
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2k



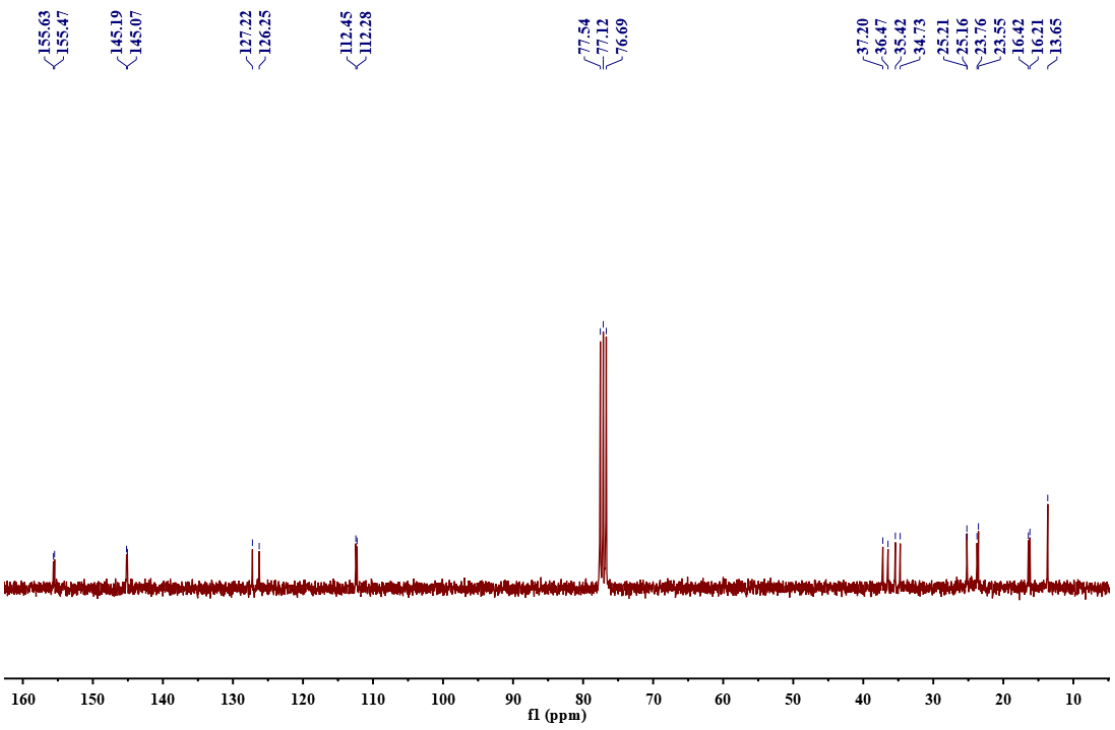
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2k



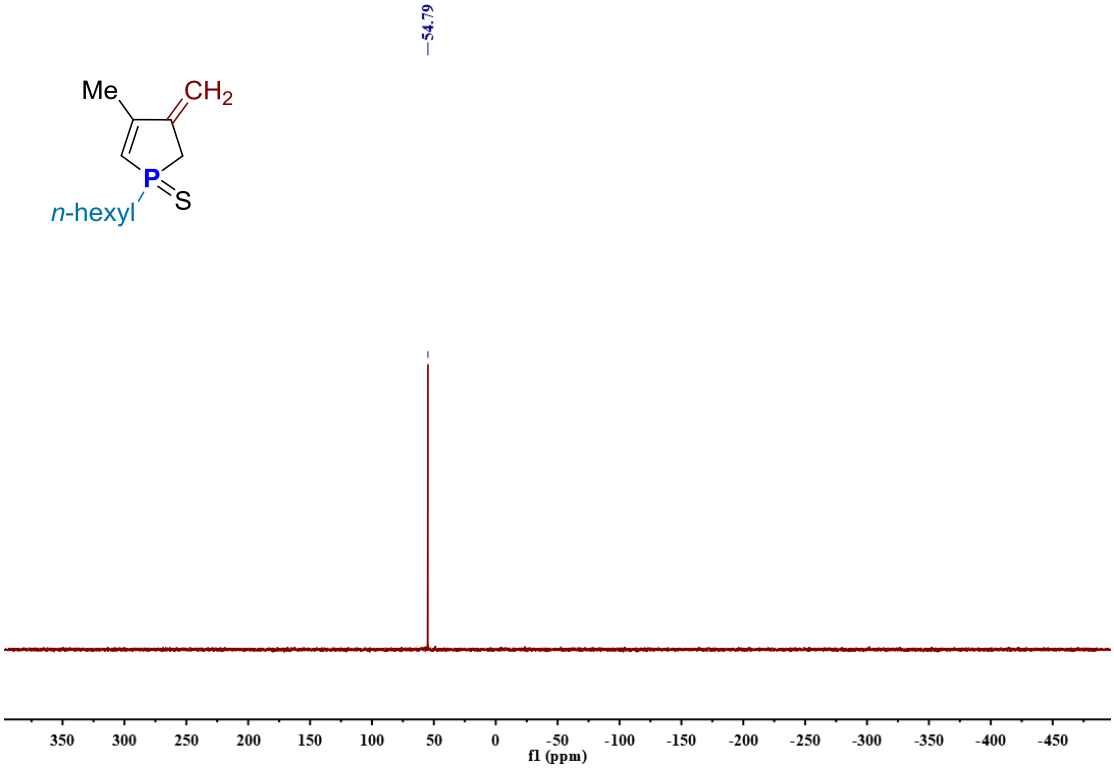
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2l



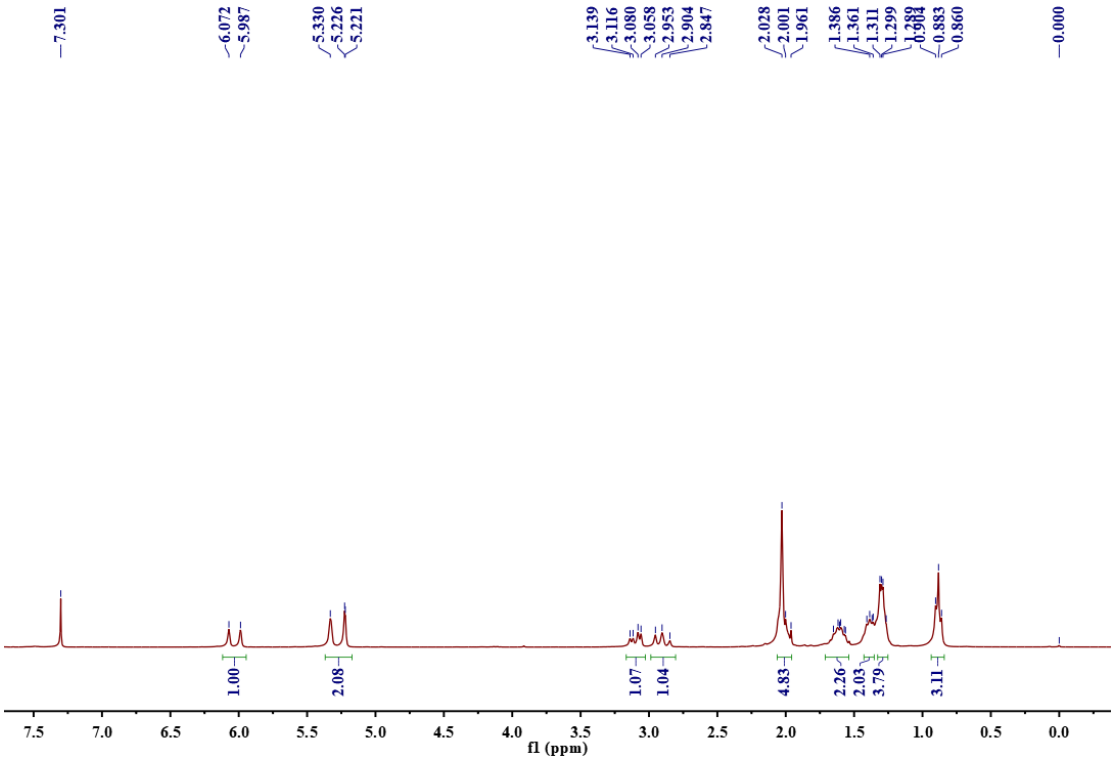
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2l



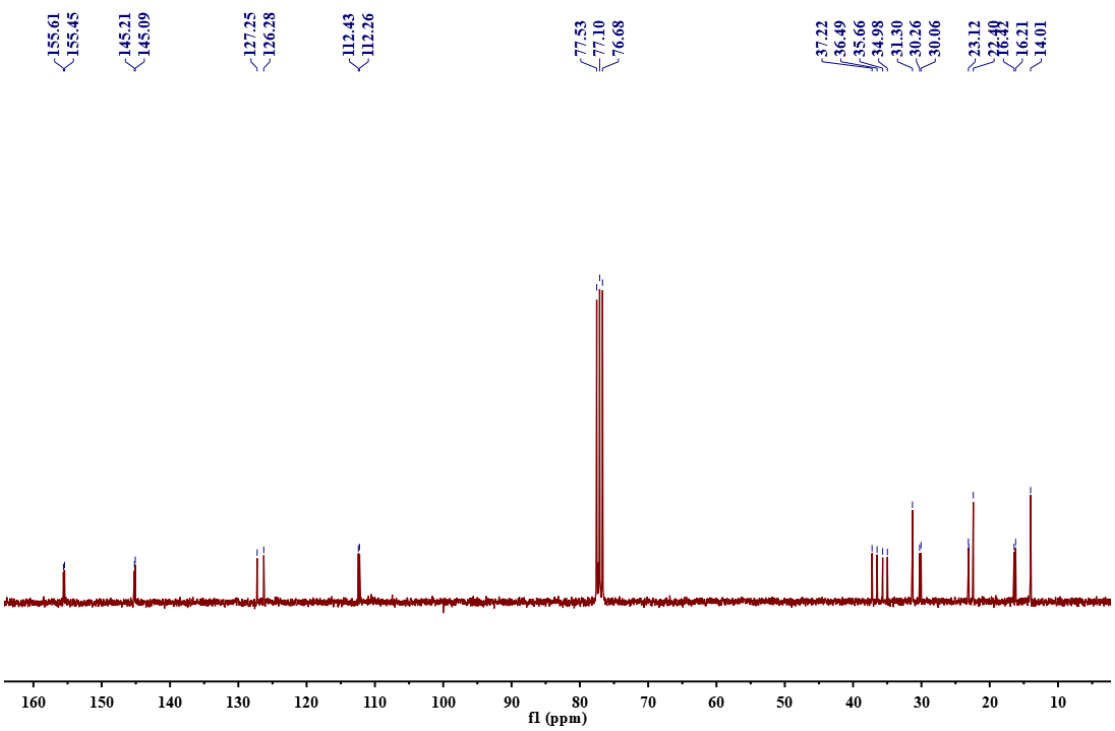
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of Compound 2l



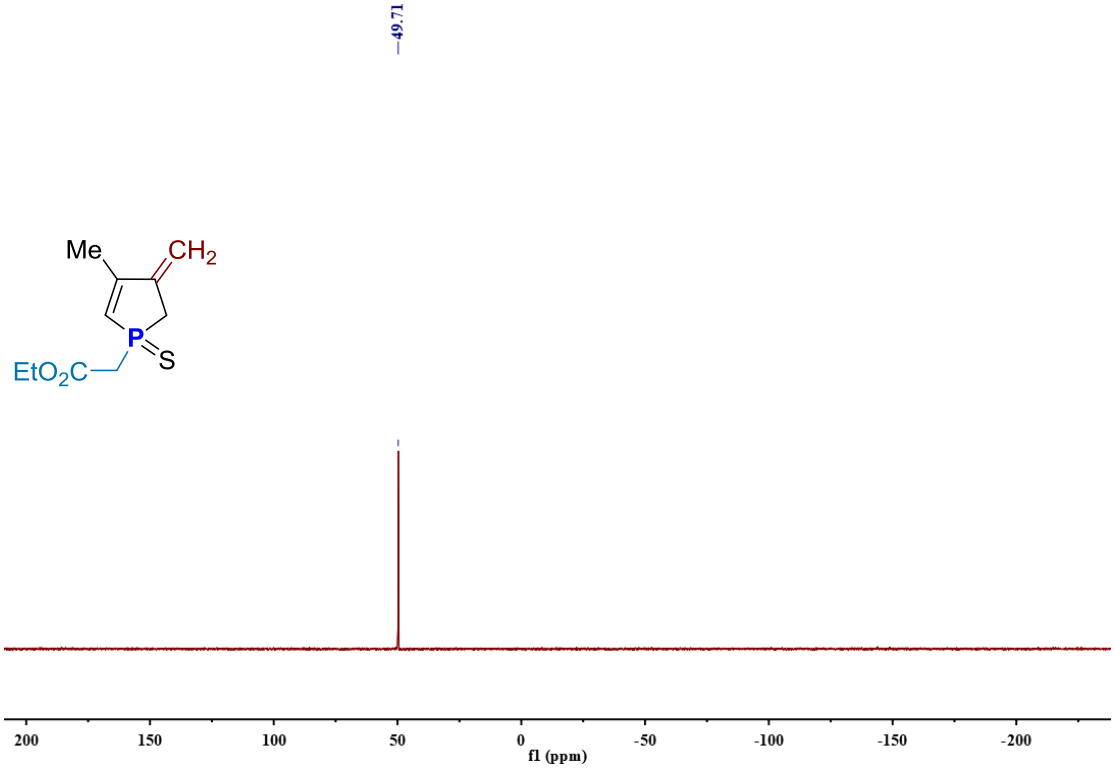
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2m



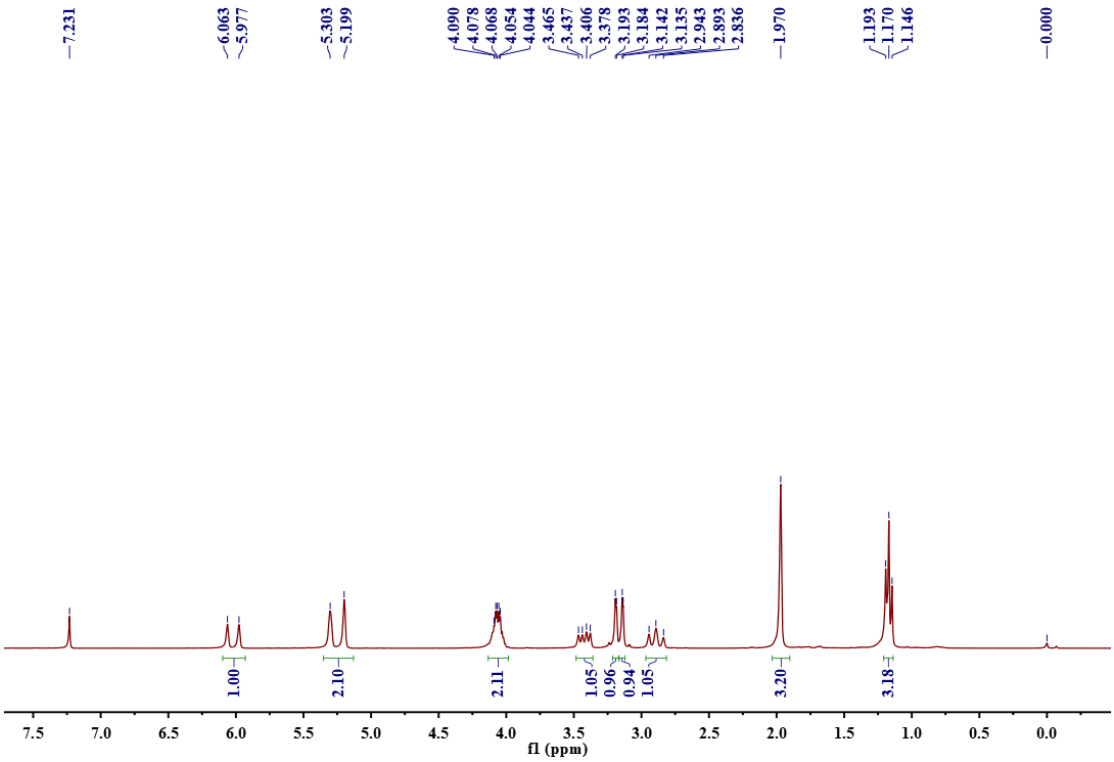
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2m



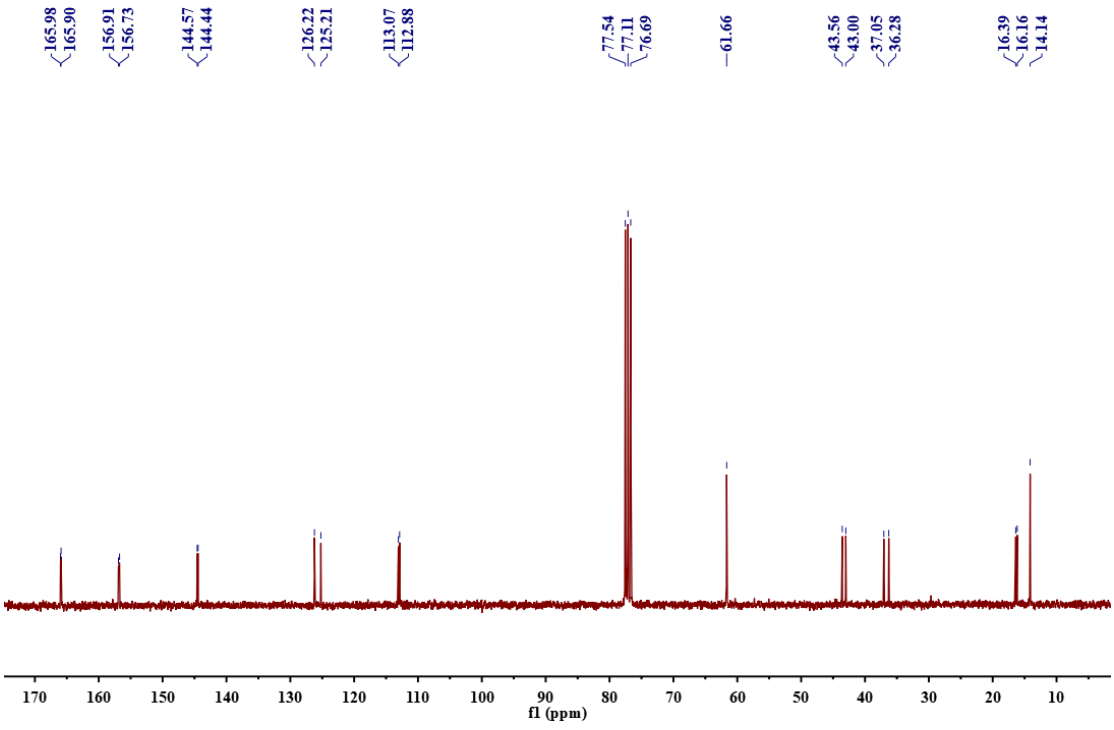
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2m



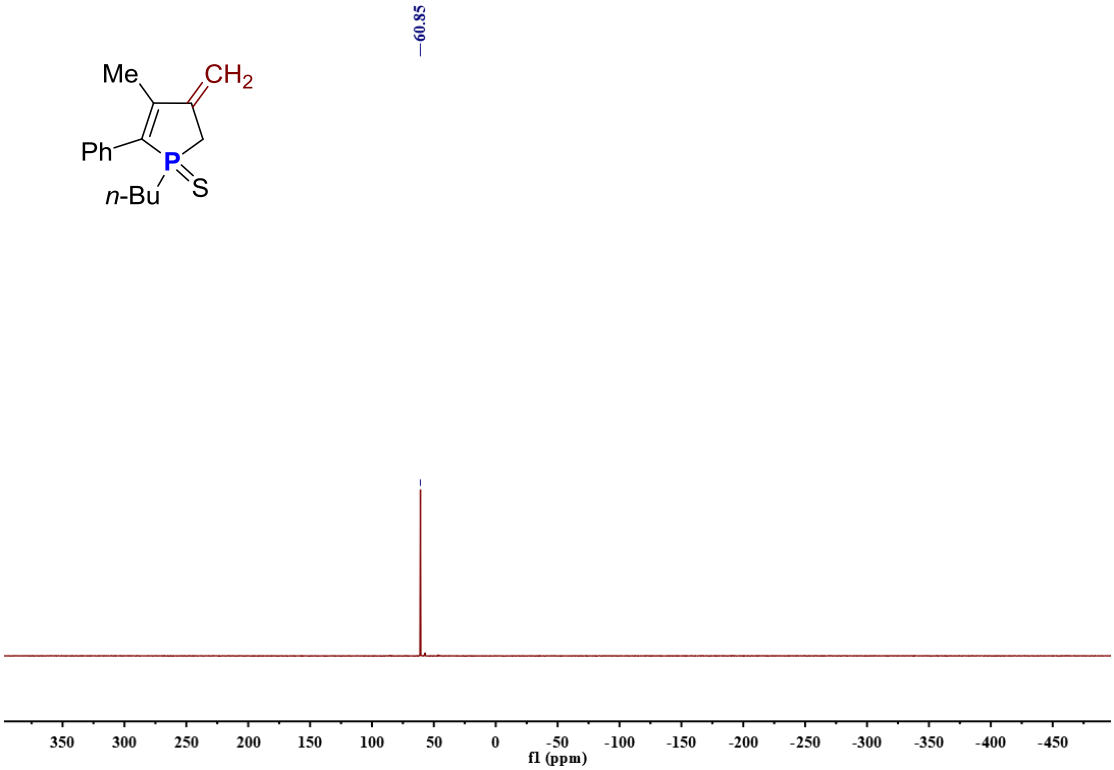
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2n



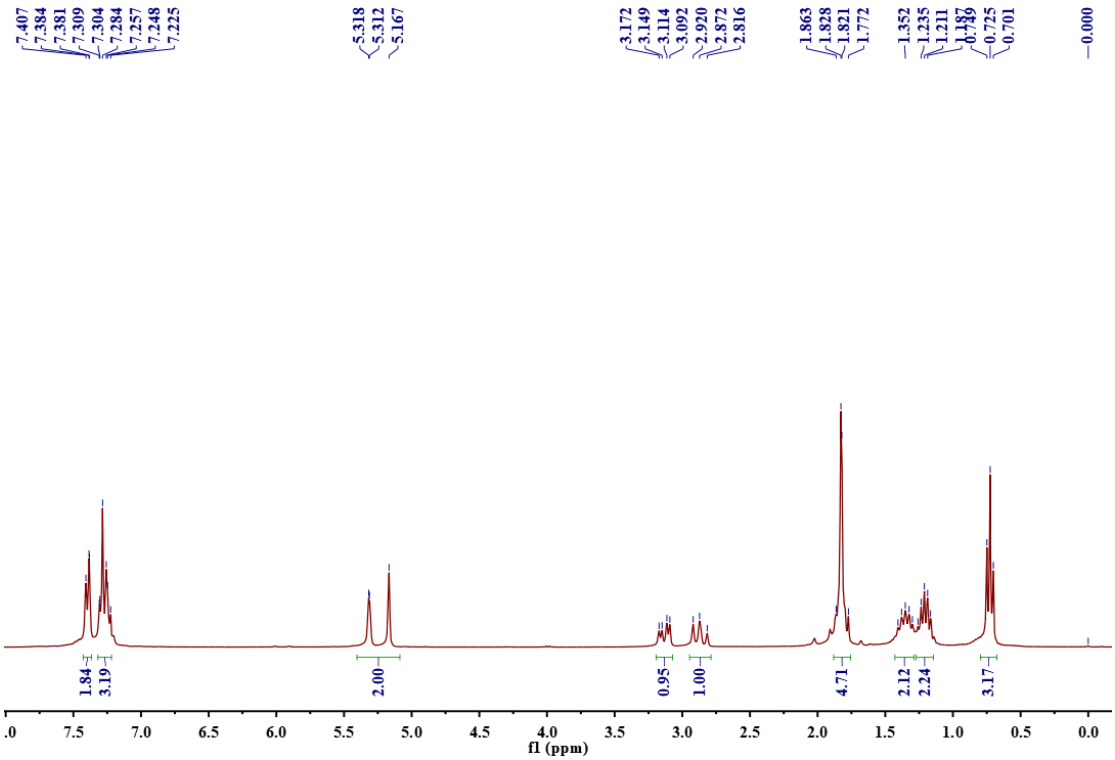
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2n



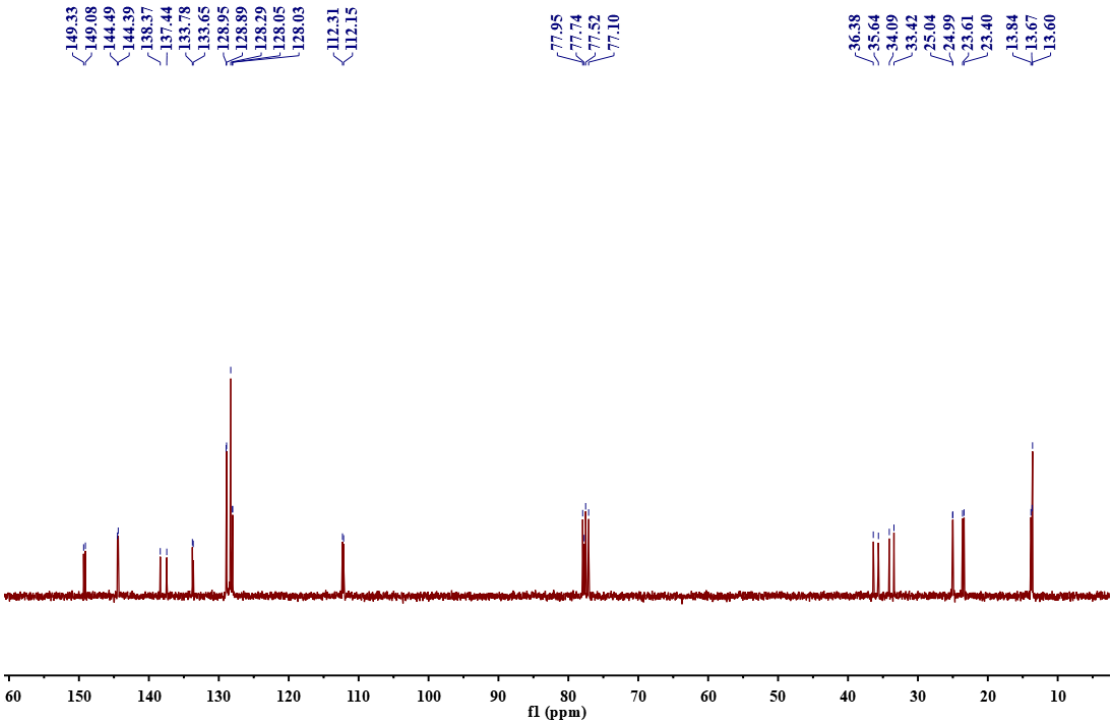
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of Compound 2n



$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2o



^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2o



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2o