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Supporting Information

Annulation of Phosphole Sulfides via [3+2] Cycloaddition with Nitrones

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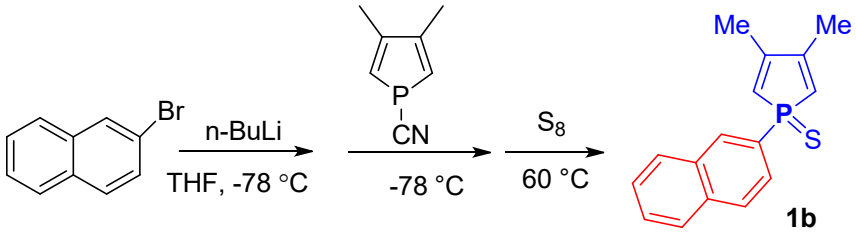
General information

All reactions were performed under nitrogen using solvents dried by standard methods except for special statement. 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). HRMS spectra were obtained on a waters UPLC G2-ZS Q-tof of HRMS spectrometer. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. 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. Phosphole Sulfides (1a-1e)[1], nitrones complexes (2a-2m)[2] and 3,4-dimethyl-1-cyanophosphole[3] were prepared according to literature method. All new compounds were synthetic in small scale, and were purified by thin layer chromatography. The purities of the new compounds are acceptable according to NMR spectra analysis.

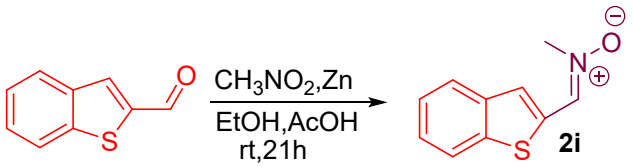
Experimental Procedures and Characterization Data



1b

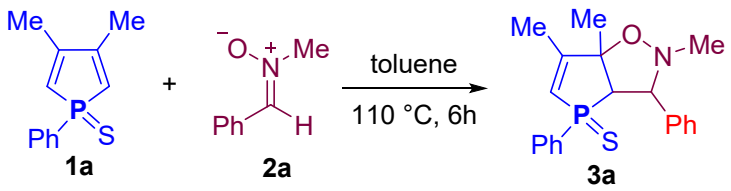
A solution of *n*-butyllithium (2 mL, 2.5 mol/L, 5 mmol) in n-hexane was added dropwise into a solution of 2-bromonaphthalene (1.04 g, 5 mmol) at -78 °C and the solution was warmed to room temperature slowly. 3,4-Dimethyl-1-cyanophosphole (755 mg, 5 mmol) was then added to the dark solution at -78 °C and the solution was warmed to room temperature slowly again. The solution was treated with sulfur powder (0.34 g, 10.6 mmol) at 60 °C for 6 h. H_2O (30 mL) was added to the solution, and then the mixture was extracted with EtOAc (30 mL x 3). The combined organic layer was washed with H_2O (30 mL) and brine (30 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using a 5:1 petroleum ether: ethyl acetate mixture, providing bright yellow solid **1b** (0.9 g, 67%).

1b: **m.p.** 82.6-83.3°C,**^{31}P NMR (121 MHz, $CDCl_3$)** δ 45.57 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.6 (d, *J* = 16.7 Hz, 1H), 8.05 – 7.44 (m, 6H), 6.2 (d, *J* = 30.9 Hz, 2H), 2.2 (d, *J* = 0.8 Hz, 6H, CH_3).**^{13}C NMR (75 MHz, $CDCl_3$)** δ 154.0 (d, *J* = 17.5 Hz, C), 134.8 (s, C), 133.5 (d, *J* = 11.8 Hz, CH), 133.0 (d, *J* = 14.3 Hz, C), 128.7 (s, CH), 128.4 (d, *J* = 12.3 Hz, CH), 128.1 (s, CH), 127.3 (d, *J* = 64.9 Hz, CH), 126.4 (s, CH), 125.3 (s, CH), 124.7 (d, *J* = 12.2 Hz, CH), 124.2 (m, C), 17.5 (d, *J* = 17.8 Hz, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{16}H_{16}PS^+$ 271.0710, found 271.0716.



To an ice cooled suspension of benzo[b]thiophene-2-carboxaldehyde (810 mg, 5 mmol), nitromethane (1.07 mL,20 mmol) and zinc powder (1.95 g, 30 mmol) in 95% ethanol (50 mL), glacial acetic acid (2 mL, 35 mmol) was dropwised over a period of 1 h. After completion of addition, the mixture was allowed to stir for 20 h at rt. The reaction mixture was filtered with celite. The filtrate concentrated under vacuum and the crude product was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: methanol mixture, providing pale yellow solid nitrone **2i** (0.539 g, 56 % yield).

2i：**m.p.** 162.4-163.2°C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.9 (s, 2H, CH), 7.8 (d, *J* = 16.8 Hz, 1H, CH), 7.7 (s, 1H, CH), 7.4 (d, *J* = 6.8 Hz, 2H, CH), 3.9 (s, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 140.8 (s, C), 137.8 (s, C), 132.7 (s, CH), 131.4 (s, C), 125.9 (s, CH), 125.7 (s, CH), 124.6 (s, CH), 123.7 (s, CH), 122.6 (s, CH), 52.3 (s, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{10}H_{10}NOS^+$ 192.0483, found 192.0478.

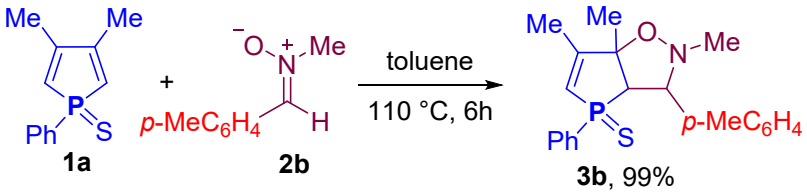


In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1a** (44 mg, 0.2 mmol) and nitrone **2a** (81 mg, 0.6 mmol) in toluene (2 mL) was stirred at 110 °C for 6 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether : ethyl acetate mixture, providing **3a** (66.7mg, 94%) as a white solid. Single crystals

for X-ray analysis were obtained by slowing evaporation of **3a** in a mixture of *n*-hexane and ethyl acetate.

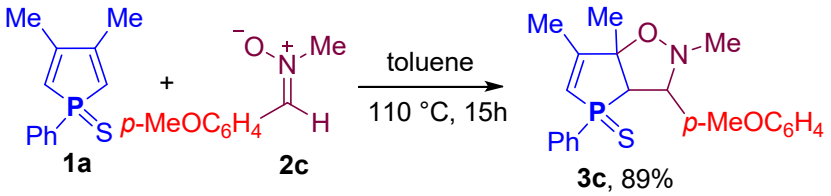
This reaction was repeated with 220 mg phosphole sulfide **1a** (1 mmol) and 203 mg nitrone **2a** (1.5 mmol) in toluene (5mL), providing 349 mg **3a** in 98% yield.

3a: **m.p.** 115.2-116.0 °C. **^{31}P NMR (121 MHz, $CDCl_3$)** δ 58.04 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.74 – 7.67 (m, 2H, CH), 7.5 (t, *J* = 8.9 Hz, 2H, CH), 7.47 – 7.35 (m, 3H, CH), 7.35 – 7.16 (m, 3H, CH), 5.8 (d, *J* = 26.0 Hz, 1H, CH), 4.5 (brs, 1H, CH), 2.9 (d, *J* = 7.6 Hz, 1H, CH), 2.6 (s, 3H, CH_3), 2.1 (s, 3H, CH_3), 1.7 (s, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 138.4 (d, *J* = 3.4 Hz, C), 134.1 (s, C), 133.0 (s, C), 131.7 (d, *J* = 3.1 Hz, CH), 130.5 (d, *J* = 11.4 Hz, CH), 128.8 (s, CH), 128.7 (s, CH), 128.3 (s, CH), 127.9 (s, CH), 121.6 (d, *J* = 80.5 Hz, CH), 92.9 (d, *J* = 12.7 Hz, C), 75.4 (s, CH), 62.4 (d, *J* = 55.4 Hz, CH), 42.7 (s, NCH_3), 24.3 (s, CH_3), 16.3 (d, *J* = 18.1 Hz, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{20}H_{23}NOPS^+$ 356.1238, found 356.1244.



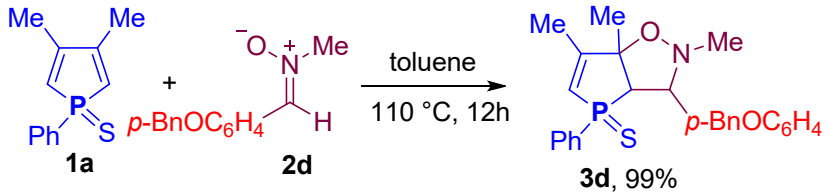
In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1a** (44 mg, 0.2 mmol) and nitrone **2b** (60 mg, 0.4 mmol) in toluene (2 mL) was stirred at 110 °C for 6 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture, providing **3b** (74 mg, 99%) as a pale yellow solid.

3b: **m.p.** 111.4-112.0 °C. **31P NMR (121 MHz, $CDCl_3$)** δ 57.88 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.74 – 7.67 (m, 2H, CH), 7.4 (t, *J* = 15.9 Hz, 5H, CH), 7.3 (s, 1H), 7.1 (d, *J* = 7.8 Hz, 1H, CH), 5.9 (d, *J* = 25.56 Hz, 1H, CH), 4.5 (s, 1H, CH), 2.8 (d, *J* = 7.62 Hz, 1H, CH), 2.6 (s, 3H, CH_3), 2.3 (s, 3H, CH_3), 2.1 (s, 3H, CH_3), 1.7 (s, 3H, CH_3).**^{13}C NMR (75 MHz, $CDCl_3$)** δ137.57 (s, C), 135.19 (d, *J* = 3.2 Hz, C), 134.09 (s, C), 133.01 (s, C), 131.7 (d, *J* = 3.1 Hz, CH), 130.5 (d, *J* = 11.4 Hz, CH), 129.3 (s, CH), 128.7 (d, *J* = 9.4 Hz, CH), 128.3 (s, CH), 121.6 (d, *J* = 79.9 Hz, CH), 92.4 (m, C), 76.7 (s, CH), 62.7 (d, *J* = 55.5Hz, CH), 42.6 (s, NCH_3), 24.1 (brs, CH_3), 21.2 (s, CH_3), 16.30 (d, *J*= 18.1 Hz, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{21}H_{25}NOPS^+$ 370.1394, found 370.1396.



In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1a** (44 mg, 0.2 mmol) and nitrone **2c** (66 mg, 0.4 mmol) in toluene (2 mL) was stirred at 110 °C for 15 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture, providing **3c** (68.5 mg, 89%) as a pale yellow solid.

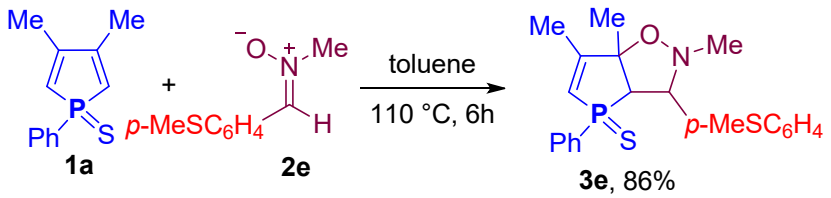
3c: **m.p.** 113.2-114.1 °C. **^{31}P NMR (121 MHz, $CDCl_3$)** δ 57.72 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.92 – 7.56 (m, 2H, CH), 7.45 – 7.35 (m, 5H, CH), 6.9 (d, J = 17.3 Hz, 2H), 5.8 (d, J = 26.0 Hz, 1H), 4.5 (s, 1H), 3.8 (s, 3H, CH_3), 2.8 (d, J = 7.8 Hz, 1H, CH), 2.6 (s, 3H, CH_3), 2.1 (s, 3H, CH_3), 1.7 (d, J = 10.9 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 159.2 (s, C), 134.1 (s, C), 133.0 (s, C), 131.7 (d, J = 3.1 Hz, CH), 130.5(d, J = 11.4 Hz, CH), 129.9 (s, C), 129.6 (s, CH), 128.8 (d, J = 12.6 Hz, CH), 121.6 (d, J = 81.25 Hz, CH), 114.0 (s, CH), 92.6 (d, J = 12.6 Hz, C),75.2 (m, CH), 62.2 (d, J = 55.6 Hz, CH), 55.2 (s, OCH_3), 42.5 (s, NCH_3), 24.4 (s, CH_3), 16.3 (d, J = 18.1 Hz, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{21}H_{25}NO_2PS^+$ 386.1344, found 386.1341.



In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1a** (44 mg, 0.2 mmol) and nitrone **2d** (96 mg, 0.4 mmol) in toluene (2 mL) was stirred at 110 °C for 12 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture, providing **3d** (99.5 mg, 99%) as a white solid.

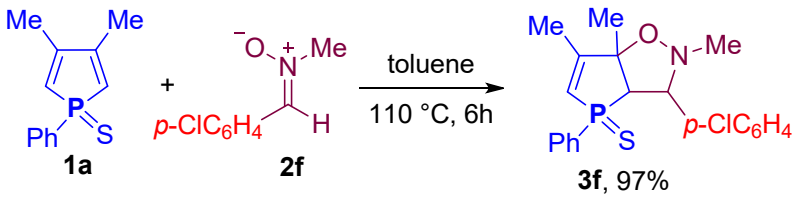
3d: m.p. 96.7-97.5 °C, **^{31}P NMR (121 MHz, $CDCl_3$)** δ 57.06 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.88 – 7.64 (m, 2H, CH), 7.61 – 7.21 (m, 10H, CH), 7.0 (d, J = 8.6 Hz, 2H, CH), 5.8 (d, J = 26.0 Hz, 1H, CH), 5.0 (s, 2H, CH_2), 4.5 (s, 1H, CH), 2.9 (d, J = 7.8 Hz, 1H, CH), 2.6 (s, 3H, CH_3), 2.1 (s, 3H, CH_3), 1.7 (s, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.1 (m, C), 158.5 (s, C), 137.0 (s, C), 133.6 (d, J = 81.9 Hz, C), 131.8 (s, CH), 130.5 (d, J = 11.4 Hz, CH), 130.3 (s, C), 129.7 (s, CH), 128.8 (d, J = 12.6 Hz, CH), 128.6 (s, CH), 128.0 (s, CH), 127.6 (s, CH), 121.6 (d, J = 80.6 Hz, CH),

114.9 (s, CH), 92.4 (d, J = 14.3 Hz, C), 70.0 (s, CH), 62.2 (d, J = 55.5 Hz, CH), 60.4 (s, CH_2), 42.8 (s, NCH_3), 21.1 (s, CH_3), 16.3 (d, J = 18.1 Hz, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{27}H_{29}NO_2PS^+$ 462.1657, found 462.1658.



In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1a** (44 mg, 0.2 mmol) and nitrone **2e** (72 mg, 0.4 mmol) in toluene (2 mL) was stirred at 110 °C for 6 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture, providing **3e** (69 mg, 86%) as a white solid.

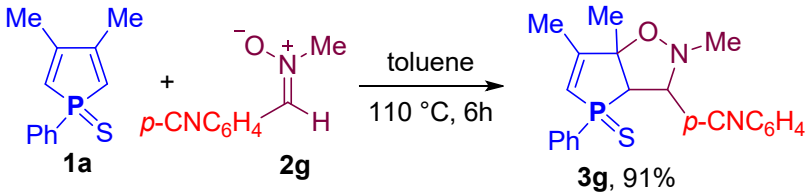
3e: m.p. 114.7-115.2°C. **^{31}P NMR (121 MHz, $CDCl_3$)** δ 57.41 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.88 – 7.67 (m, 2H, CH), 7.46 – 7.40 (m, 5H, CH), 7.2 (d, J = 8.1 Hz, 2H, CH), 5.8 (d, J = 26.1 Hz, 1H, CH), 4.5 (brs, 1H, CH), 2.8 (d, J = 7.7 Hz, 1H, CH), 2.6 (s, 3H, CH_3), 2.4 (s, 3H, CH_3), 2.1 (s, 3H, CH_3), 1.7 (s, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 138.1 (s, C), 135.0 (s, C), 134.1 (s, C), 132.9 (s, C), 131.7 (s, CH), 130.5 (d, J = 11.5 Hz, CH), 128.9 (s, CH), 128.7 (s, CH), 126.5 (s, CH), 121.1 (s, CH), 92.7 (s, C), 74.9 (s, CH), 62.3 (d, J = 55.7 Hz, CH), 42.3 (s, NCH_3), 24.3(s, CH_3), 16.3 (d, J = 18.0 Hz, CH_3), 15.6 (s, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{21}H_{25}NOPS_2^+$ 402.1115, found 402.1119.



In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1a** (44 mg, 0.2 mmol) and nitrone **2f** (68 mg, 0.4 mmol) in toluene (2 mL) was stirred at 110 °C for 6 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture, providing **3f** (76 mg, 97%) as a white solid.

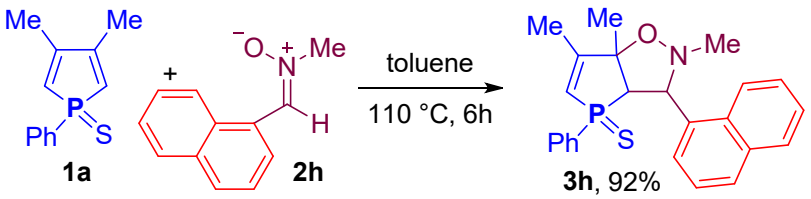
3f: m.p. 116.5-117.2°C. **^{31}P NMR (121 MHz, $CDCl_3$)** δ 57.76 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.81 – 7.63 (m, 2H, CH), 7.50 – 7.40 (m, 5H, CH), 7.32 – 7.21 (m, 2H, CH), 5.8 (d, J = 26.1 Hz, 1H, CH), 4.5 (d, J = 11.3 Hz, 1H, CH), 2.8 (s, 1H, CH), 2.6 (s, 3H, CH_3), 2.1 (s, 3H, CH_3), 1.70 (s,

3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 161.1 (m, C), 136.9 (d, *J* = 3.1 Hz, C), 133.6 (s, C), 133.3 (s, *J* = 81.8 Hz, C), 131.9 (d, *J* = 3.0 Hz, CH), 130.5 (d, *J* = 11.5 Hz, CH), 129.7 (s, CH), 128.8 (s, CH), 128.8 (d, *J* = 80.3 Hz, CH), 121.5 (s, CH), 92.86 (d, *J* = 12.4 Hz, C), 74.73 (s, CH), 62.5 (d, *J* = 55.4 Hz, CH), 42.7 (s, NCH_3), 24.4 (s, CH_3), 16.3 (d, *J* = 18.1 Hz, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{20}H_{22}ClNOPS^+$ 390.0848, found 390.0850.



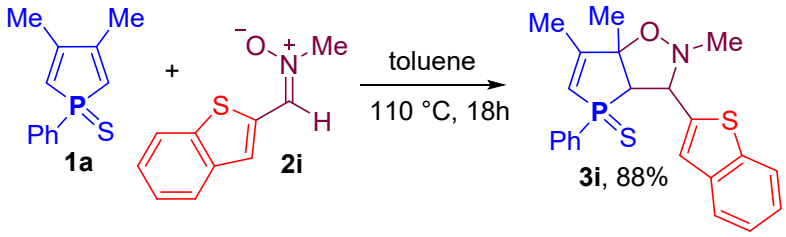
In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1a** (44 mg, 0.2 mmol) and nitrone **2g** (38 mg, 0.24 mmol) in toluene (2 mL) was stirred at 110 °C for 6 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture, providing **3g** (69 mg, 91%) as a white solid.

3g: m.p. 115.6-116.4°C. **^{31}P NMR (121 MHz, $CDCl_3$)** δ 57.67 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.84 – 7.64 (m, 4H, CH), 7.64 – 7.53 (m, 2H, CH), 7.54 – 7.34 (m, 3H, CH), 5.8 (d, *J* = 26.2 Hz, 1H, CH), 4.6 (brs, 1H, CH), 2.8 (d, *J* = 7.7 Hz, 1H, CH), 2.6 (s, 3H, CH_3), 2.1 (s, 3H, CH_3), 1.7 (s, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 161.4 (m, C), 144.3 (d, *J* = 3.3 Hz, C), 133.0 (d, *J* = 3.1 Hz, C) 132.5 (s, CH), 132.0 (d, *J* = 3.1 Hz, CH), 130.4 (d, *J* = 11.5 Hz, CH), 129.0 (s, CH), 128.8 (s, CH), 121.5 (d, *J* = 80.7 Hz, CH), 118.7 (s, C), 111.7 (s, C), 93.2 (d, *J* = 12.3 Hz, C), 74.7 (s, CH), 62.8 (d, *J* = 54.9 Hz, CH), 42.9 (s, NCH_3), 24.4 (s, CH_3), 16.3 (d, *J* = 18.1 Hz, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{21}H_{22}N_2OPS^+$ 381.1190, found 381.1200.



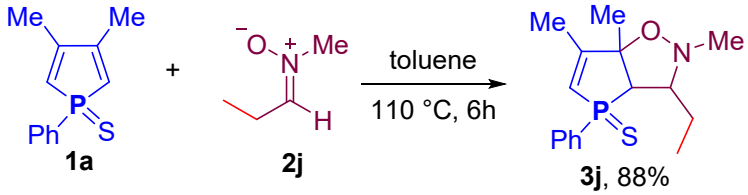
In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1a** (44 mg, 0.2 mmol) and nitrone **2h** (56 mg, 0.3 mmol) in toluene (2 mL) was stirred at 110 °C for 6 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture, providing **3h** (75 mg, 92%) as a white solid.

3h: m.p. 148.6-149.4°C. **^{31}P NMR (121 MHz, $CDCl_3$)** δ 60.29 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.5 (d, *J* = 8.5 Hz, 1H, CH), 7.97 – 7.94 (m, 1H, CH), 7.90 – 7.66 (m, 4H, CH), 7.65 – 7.33 (m, 6H, CH), 5.9 (d, *J* = 25.8 Hz, 1H, CH), 5.73 – 5.66 (m, 1H, CH), 3.0 (d, *J* = 6.9 Hz, 1H, CH), 3.0 (s, 3H, CH_3), 2.3 (s, 3H, CH_3), 1.6 (s, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 164.6 (d, *J* = 15.4 Hz, C), 136.9 (d, *J* = 8.1 Hz, C), 134.0 (s, C), 133.8 (s, C), 132.7 (s, C), 131.9 (d, *J* = 2.9 Hz, CH), 130.4 (s, CH), 130.4 (d, *J* = 11.3 Hz, CH), 128.8 (s, CH), 128.8 (d, *J* = 12.8 Hz, CH), 128.0 (s, CH), 126.2 (s, CH), 125.6 (d, *J* = 4.0 Hz, CH), 124.76 (s, CH), 124.13 (s, CH), 120.25 (d, *J* = 79.9 Hz, CH), 95.30 (d, *J* = 13.3 Hz, C), 70.72 (s, CH), 62.69 (d, *J* = 52.1 Hz, CH), 44.81 (s, NCH_3), 25.07 (d, *J* = 5.8 Hz, CH_3), 16.25 (d, *J* = 18.5 Hz, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{24}H_{25}NOPS^+$ 406.1394, found 406.1395.



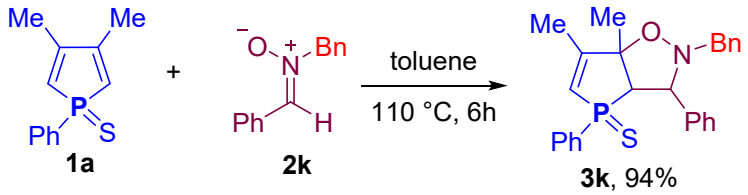
In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1a** (41.2 mg, 0.19 mmol) and nitrone **2i** (60 mg, 0.32 mmol) in toluene (2 mL) was stirred at 110 °C for 12 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture, providing **3i** (69 mg, 88%) as a white solid.

3i: m.p. 115.2-116.0°C. **^{31}P NMR (121 MHz, $CDCl_3$)** δ 54.93 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.00 – 7.65 (m, 4H, CH), 7.60 – 7.23 (m, 6H, CH), 5.9 (d, *J* = 26.1 Hz, 1H, CH), 5.1 (s, 1H, CH), 3.0 (d, *J* = 5.6 Hz, 1H, CH), 2.7 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 1.8 (s, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 141.9 (m, C), 140.2 (s, C), 139.3 (s, C), 133.7 (s, C), 132.6 (s, C), 131.9 (d, *J* = 3.0 Hz, CH), 130.6 (d, *J* = 11.5 Hz, CH), 128.9 (d, *J* = 12.7 Hz, CH), 124.4 (s, CH), 123.7 (s, CH), 122.4 (s, CH), 121.8 (d, *J* = 86.6 Hz, CH), 92.4 (m, C), 71.0 (m, CH), 62.1 (d, *J* = 55.1 Hz, CH), 41.9 (m, NCH_3), 23.5 (m, CH_3), 16.2 (d, *J* = 19.2 Hz, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{22}H_{23}NOPS_2^+$ 412.0959, found 412.0962.



In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1a** (31 mg, 0.14 mmol) and nitrone **2j** (24 mg, 0.28 mmol) in toluene (2 mL) was stirred at 110 °C for 6 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture, providing **3j** (37.6 mg, 88%) as a white solid.

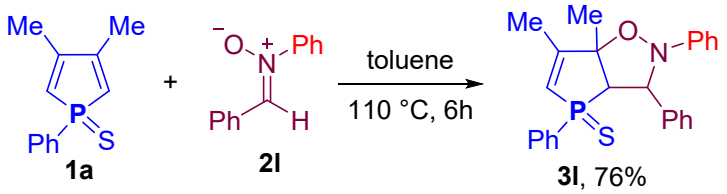
3j: m.p. 114.7-115.2°C. **^{31}P NMR (121 MHz, CDCl$_3$)** δ 59.56 (s). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.85 – 7.18 (m, 2H, CH), 7.61 – 7.42 (m, 3H, CH), 5.8 (d, *J* = 25.7 Hz, 1H, CH), 3.5 (d, *J* = 13.2 Hz, 1H, CH), 2.7 (s, 3H, CH_3), 2.5 (d, *J* = 6.3 Hz, 1H, CH), 2.1 (d, *J* = 14.9 Hz, 3H, CH_3), 1.79 – 1.56 (, 2H, CH_2), 1.3 (m, 3H, CH_3), 0.9 (t, *J* = 7.4 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, CDCl$_3$)** δ 162.6 (m, C), 133.8 (m, C), 131.8 (d, *J* = 3.0 Hz, CH), 130.5 (d, *J* = 11.4 Hz, CH), 128.8 (d, *J* = 12.5 Hz, CH), 121.0 (d, *J* = 80.5 Hz, CH), 92.9 (m, C), 72.4 (m, CH), 58.9 (m, CH), 43.7 (m, NCH_3), 29.7 (m, CH_2), 24.5 (d, *J* = 6.5 Hz, CH_3), 16.2 (d, *J* = 18.4 Hz, CH_3), 10.7 (s, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{16}H_{23}NOPS^+$ 308.1238, found 308.1243.



In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1a** (24.3 mg, 0.11 mmol) and nitrone **2k** (34.8 mg, 0.16 mmol) in toluene (2 mL) was stirred at 110 °C for 6 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture, providing **3k** (44.7 mg, 94%) as a white solid.

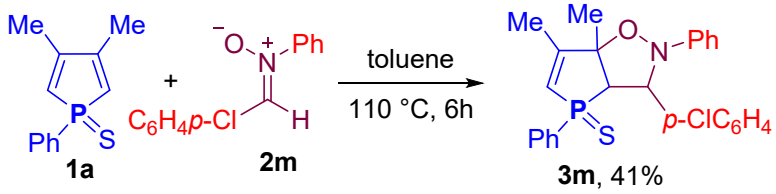
3k: m.p. 115.6-116.2°C. **^{31}P NMR (121 MHz, CDCl$_3$)** δ 58.47 (s). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.76 – 7.69 (m, 2H, CH), 7.57 (d, *J* = 7.2 Hz, 2H, CH), 7.50 – 7.36 (m, 3H, CH), 7.36 – 7.11 (m, 8H, CH), 5.8 (d, *J* = 25.9 Hz, 1H, CH), 4.9 (brs, 1H, CH), 3.93 – 3.85 (m, 2H, CH_2), 2.9 (d, *J* = 6.7 Hz, 1H, CH), 2.0 (s, 3H, CH_3), 1.7 (s, 3H, CH_3). **^{13}C NMR (75 MHz, CDCl$_3$)** δ 139.4 (d, *J* = 4.2 Hz, C), 138.2 (s, C), 134.2 (s, C), 133.1 (s, C), 131.8 (d, *J* = 2.9 Hz, CH), 130.5 (d, *J* = 11.5 Hz, CH), 128.9 (s, CH), 128.7 (s, CH), 128.3 (s, CH), 128.2 (s, CH), 128.1 (s, CH), 127.3 (d, *J* = 67.0

Hz), 121.5 (d, J = 80.5 Hz), 93.3 (d, J = 12.7 Hz, C), 73.0 (s, CH), 62.3 (d, J = 54.8 Hz, CH), 59.0 (s, CH_2), 24.2 (s, CH_3), 16.4 (d, J = 18.2 Hz, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{26}H_{27}NOPS^+$ 432.1551, found 432.1554.



In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1a** (23.4 mg, 0.11 mmol) and nitrone **2l** (34.8 mg, 0.16 mmol) in toluene (2 mL) was stirred at 110 °C for 6 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture, providing **3l** (35,1 mg, 76%) as a yellow solid.

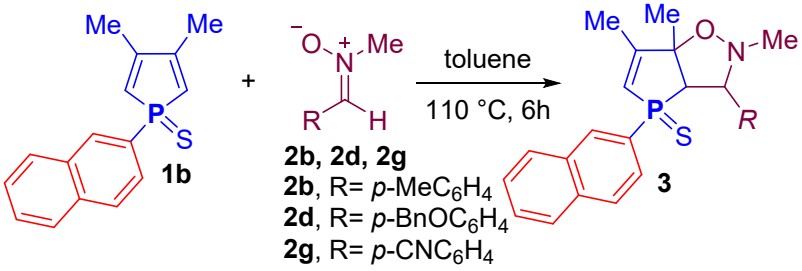
3l: m.p. 115.2-116.0°C. **^{31}P NMR (121 MHz, $CDCl_3$)** δ 58.56 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.81 – 7.74 (m, 2H, CH), 7.53 – 7.35 (m, 5H, CH), 7.2 (t, J = 7.4 Hz, 2H, CH), 7.17 – 7.10 (m, 3H, CH), 6.9 (d, J = 7.8 Hz, 2H, CH), 6.8 (t, J = 7.3 Hz, 1H, CH), 6.04 – 5.77 (m, 2H, CH), 3.0 (d, J = 3.6 Hz, 1H, CH), 2.1 (d, J = 11.2 Hz, 3H, CH_3), 1.7 (s, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 162.6 (d, J = 14.7 Hz, C), 147.6 (s, C), 140.8 (d, J = 7.4 Hz, C), 133.6 (d, J = 81.6 Hz, C), 131.8 (d, J = 3.0 Hz, CH), 130.5 (d, J = 11.4 Hz, CH), 128.9 (s, CH), 128.7 (d, J = 1.7 Hz, CH), 128.4 (s, CH), 127.6 (s, CH), 127.32 (s, CH), 122.4 (s, CH), 121.5 (s, CH), 116.0 (s, CH), 92.8 (d, J = 13.3 Hz, C), 69.2 (s, CH), 63.1 (d, J = 53.7 Hz, CH), 23.2 (d, J = 4.6 Hz, CH_3), 16.1 (d, J = 18.3 Hz, CH_3). **HRMS** (m/z) $[M + Na]^+$ Calcd for $C_{25}H_{24}NNaOPS^+$ 440.1214, found 440.1217.



In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1a** (23.2 mg, 0.11 mmol) and nitrone **2l** (38.2 mg, 0.17 mmol) in toluene (2 mL) was stirred at 110 °C for 6 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture, providing **3l** (20 mg, 41%) as a yellow solid.

3m: m.p. 109.2-110.0°C, **^{31}P NMR (121 MHz, $CDCl_3$)** δ 58.35 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.86 – 7.64 (m, 2H, CH), 7.55 – 7.35 (m, 5H, CH), 7.29 – 7.09 (m, 4H, CH), 6.99 – 6.80 (m, 3H,

CH), 5.9 (d, J = 24.6 Hz, 1H, CH), 5.8 (d, J = 3.6 Hz, 1H), 2.9 (d, J = 3.9 Hz, 1H), 2.2 (s, 3H, CH_3), 1.7 (s, 3H, CH_3). **^{13}C NMR (75 MHz, CDCl$_3$)** δ 162.5 (d, J = 14.6 Hz, C), 147.3 (s, C), 139.2 (d, J = 7.4 Hz, C), 133.9 (s, C), 133.0 (d, J = 21.6 Hz, C), 131.9 (d, J = 3.0 Hz, CH), 130.5 (d, J = 11.5 Hz, CH), 129.0 (s, CH), 128.9 (s, CH), 128.9 (s, J = 12.6 Hz,CH), 128.5 (s, CH), 121.8 (s, CH), 121.4 (s, J = 4.65 Hz, CH), 116.19 (s, CH), 92.76 (d, J = 13.3 Hz, C), 68.80 (s, CH), 63.08 (d, J = 53.7 Hz, CH), 23.2 (d, J = 4.5 Hz, CH_3), 16.1 (d, J = 18.3 Hz, CH_3). **HRMS** (m/z) $[M + Na]^+$ Calcd for $C_{25}H_{23}ClNONaPS^+$ 474.0824, found 474.0828.



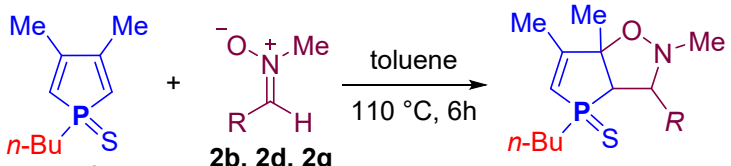
In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1b** (0.10 mmol) and nitrone **2** (0.15 mmol) in toluene (2 mL) was stirred at 110 °C for 6 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture.

3bb: 40.4 mg, 98% yield; white solid. **m.p.** 158.6-159.2°C, **^{31}P NMR (121 MHz, CDCl$_3$)** δ 57.07 (s). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.4 (d, J = 16.2 Hz, 1H, CH), 7.96 – 7.80 (m, 3H, CH), 7.65 – 7.50 (m, 3H, CH), 7.4 (d, J = 8.0 Hz, 2H, CH), 7.1 (d, J = 7.9 Hz, 2H, CH), 6.0 (t, J = 29.2 Hz, 1H, CH), 4.5 (d, J = 13.1 Hz, 1H, CH), 3.0 (d, J = 7.7 Hz, 1H, CH), 2.6 (s, 3H, CH_3), 2.3 (s, 3H, CH_3), 2.2 (s, 3H, CH_3), 1.7 (d, 3H, CH_3). **^{13}C NMR (75 MHz, CDCl$_3$)** δ 137.6 (s, C), 135.1 (s, C), 134.5 (s, C), 132.9 (s, CH), 132.5 (m, C), 131.0 (m, C), 129.9 (s, C), 129.4 (s, CH), 128.9 (s, CH), 128.7 (d, J = 12.3 Hz, CH), 128.2 (s, CH), 127.7 (s, CH), 127.1 (s, CH), 125.1 (s, CH), 125.0 (s, CH), 121.8(m, CH), 92.7 (m, C), 75.270 (m, CH), 62.7 (s, CH), 42.63 (m, CH_3), 24.4 (m, CH_3), 21.1 (s, CH_3), 16.4 (m, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{25}H_{27}NOPS^+$ 420.1551, found 420.1554.

3bd: 45.3 mg, 88% yield; pale yellow solid. **m.p.** 114.2-115.0°C, **^{31}P NMR (121 MHz, CDCl$_3$)** δ 56.15 (s). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.4 (d, J = 16.2 Hz, 1H, CH), 7.99 – 7.78 (m, 3H, CH), 7.73 – 7.54 (m, 3H, CH), 7.53 – 7.22 (m, 7H, CH), 6.9 (d, J = 8.7 Hz, 2H, CH), 5.9 (d, J = 26.0 Hz, 1H, CH), 5.0 (s, 2H, CH_2), 3.0 (d, J = 7.8 Hz, 1H, CH), 2.6 (s, 3H, CH_3), 2.2 (s, 3H, CH_3), 2.1 (s,

1H, CH), 1.8 (s, 3H, CH_3).**^{13}C NMR (75 MHz, $CDCl_3$)** δ 158.5 (s, C), 136.9 (s, C), 134.6 (s, C), 132.8 (d, *J* = 11.3 Hz, CH), 132.5 (d, *J* = 14.0 Hz, C), 131.0 (s, C), 130.3 (s, C), 129.9 (s, C), 129.6 (s, CH), 129.0 (s, CH), 128.78 (s, CH), 128.6 (s, CH), 128.3 (s, CH), 128.0 (s, CH), 127.8 (s, CH), 127.5 (s, CH), 127.1 (s, CH), 125.1 (s, CH), 125.0 (s, CH), 121.7 (m, CH), 114.9 (s, CH), 92.7 (m, C), 70.0 (s, CH2), 62.2 (d, *J* = 55.8 Hz, CH), 42.5 (m, CH_3), 21.4 (m, CH_3), 16.2 (s, CH_3), 14.2 (s, CH). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{31}H_{31}NO_2PS^+$ 512.1813, found 512.1817.

3bg: 41.7 mg, 92% yield; white solid. **m.p.** 116.7-117.4°C, **^{31}P NMR (121 MHz, $CDCl_3$)** δ 55.18 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.4 (d, J = 16.4 Hz, 1H, CH), 7.9 (dt, J = 14.0, 7.1 Hz, 5H, CH), 7.74 – 7.48 (m, 4H, CH), 7.4 (t, J = 7.6 Hz, 1H, CH), 5.9 (d, J = 26.3 Hz, 1H, CH), 4.6 (dd, J = 18.2, 7.4 Hz, 1H, CH), 2.9 (d, J = 7.6 Hz, 1H, CH), 2.7 (s, 3H, CH_3), 2.2 (s, 3H, CH_3), 1.8 (s, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.1 (s, C), 140.4 (s, C), 134.6 (s, C), 133.1 (s, CH), 132.9 (d, *J* = 11.7 Hz, CH), 132.5 (m, C), 131.6 (s, C), 129.8 (d, *J* = 81.8 Hz, C), 129.5 (s, CH), 128.9 (s, CH), 128.8 (s, CH), 128.4 (s, CH), 127.5 (d, *J* = 41.2 Hz, CH), 124.8 (d, *J* = 12.0 Hz, CH), 121.7 (d, *J* = 80.5 Hz, CH), 118.6 (s, C), 112.9 (s, C), 93.17 (m, C), 75.5 (m, CH), 62.7 (d, *J* = 55.3 Hz, CH), 42.7 (m, CH_3), 24.4 (m, CH_3), 16.4 (d, *J* = 18.0 Hz, CH_3). **HRMS** (m/z) $[M + Na]^+$ Calcd for $C_{25}H_{23}N_2NaOPS^+$ 453.1166, found 453.1171.



2b, 2d, 2g
2b, R= *p*-MeC_6H_4
2d, R= *p*-$BnOC_6H_4$
2g, R= *p*-CNC_6H_4

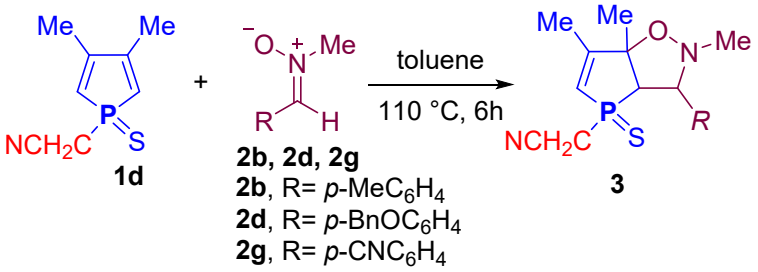
In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1c** (0.11-0.13 mmol) and nitrone **2** (1.5eq) in toluene (2 mL) was stirred at 110 °C for 6 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture, providing **3.**

1c: 21.3 mg, 0.13 mmol, **3cb:**35.9 mg, 79% yield; white solid. **m.p.** 78.2-79.0°C, **^{31}P NMR (121 MHz, $CDCl_3$)** δ 60.57 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.4 (d, *J* = 7.8 Hz, 2H, CH), 7.2 (d, *J* = 7.8 Hz, 2H, CH), 5.7 (d, *J* = 26.5 Hz, 1H, CH), 4.3 (brs, 1H, CH), 2.7 (d, *J* = 7.1 Hz, 1H, CH), 2.6 (s, 3H, CH_3), 2.3 (s, 3H, CH_3), 2.0 (d, *J* = 15.3 Hz, 3H, CH_3), 1.93 – 1.79 (m, 2H, CH_2), 1.6 (s, 3H,

CH_3), 1.56 – 1.39 (m, 2H, CH_2), 1.3 (m, 2H, CH_2), 0.8 (t, J = 7.2 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 159.8 (m, C), 137.7 (s, C), 135.1 (s, C), 129.4 (s, CH), 128.3 (s, CH), 121.9 (d, J = 75.1 Hz, CH), 92.2 (s, C), 75.2(m, CH), 59.8 (d, J = 53.1 Hz, CH), 42.5(m, CH_3), 35.9 (d, J = 54.4 Hz, CH_2), 24.9 (d, J = 3.9 Hz, CH_2), 24.6 (m, CH_3), 23.5 (d, J = 15.5 Hz, CH_2), 21.2 (s, CH_3), 16.0 (d, J = 17.3 Hz, CH_3), 13.6 (s, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{19}H_{29}NOPS^+$ 350.1707, found 350.1708.

1c: 19.5 mg, 0.11 mmol, **3cd:** 38.8 mg, 80% yield; pale yellow solid. **m.p.** 103.4-104.1°C, **^{31}P NMR (121 MHz, $CDCl_3$)** δ 60.49 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.59 – 7.25 (m, 7H, CH), 7.0 (d, J = 8.6 Hz, 2H, CH), 5.7 (t, J = 21.6 Hz, 1H, CH), 5.1 (s, 2H, CH_2), 4.2 (dd, J = 22.9, 15.6 Hz, 1H, CH), 2.8 (t, J = 10.6 Hz, 1H, CH), 2.6 (s, 3H, CH_3), 2.0 (s, 3H, CH_3), 1.94 – 1.79 (m, 2H, CH_2), 1.6 (d, J = 17.6 Hz, 3H, CH_3), 1.59 – 1.42 (m, 2H, CH_2), 1.39 – 1.23 (m, 2H, CH_2), 0.9 (t, J = 7.2 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 158.6 (s, C), 137.0 (s, C), 130.2 (s, C), 130.2 (s, C), 129.6 (s, CH), 128.6 (s, CH), 128.0 (s, CH), 127.5 (s, CH), 121.9 (d, J = 75.2 Hz, CH), 115.0 (s, CH), 92.3 (s, C), 70.0 (s, CH_2), 59.7 (d, J = 53.3 Hz, CH), 42.6 (m, CH_3), 35.8 (d, J = 54.4 Hz, CH_2), 29.7 (m, CH_3), 24.9 (d, J = 3.9 Hz, CH_2), 24.6 (m, CH_3), 23.5 (d, J = 15.4 Hz, CH_2), 16.0 (d, J = 17.2 Hz, CH_3), 13.6 (s, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{25}H_{33}NO_2PS^+$ 442.1970, found 442.1973.

1c: 22.2 mg, 0.13 mmol, **3cg:** 40.8 mg, 87% yield; white sticky, **^{31}P NMR (121 MHz, $CDCl_3$)** δ 61.88 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.95 – 7.78 (m, 2H, CH), 7.66 – 7.36 (m, 2H, CH), 5.7 (t, J = 22.3 Hz, 1H, CH), 4.4 (dd, J = 17.0, 7.9 Hz, 1H, CH), 2.7 (t, J = 7.6 Hz, 1H, CH), 2.6 (s, 3H, CH_3), 2.0 (m, 3H, CH_3), 1.9 (m, 2H, CH_2), 1.7 (d, J = 14.5 Hz, 3H, CH_3), 1.5 (m, 2H, CH_2), 1.3 (m, 2H, CH_2), 0.8 (t, J = 7.2 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 159.6 (m, C), 140.2 (s, C), 131.6 (s, CH), 131.5 (d, J = 143.3 Hz, CH), 121.8 (d, J = 75.3 Hz, CH), 118.6 (s, C), 112.9 (s, C), 92.8 (d, J = 12.0 Hz, C), 74.5 (m, CH), 60.0 (d, J = 52.6 Hz, CH), 42.7 (s, CH_3), 35.7 (d, J = 54.6 Hz, CH_2), 24.9 (d, J = 3.9 Hz, CH_2), 24.6 (m, CH_3), 23.5 (d, J = 15.5 Hz, CH_2), 16.0 (d, J = 17.1 Hz, CH_3), 13.5 (s, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{19}H_{26}N_2OPS^+$ 361.1503, found 361.1496.



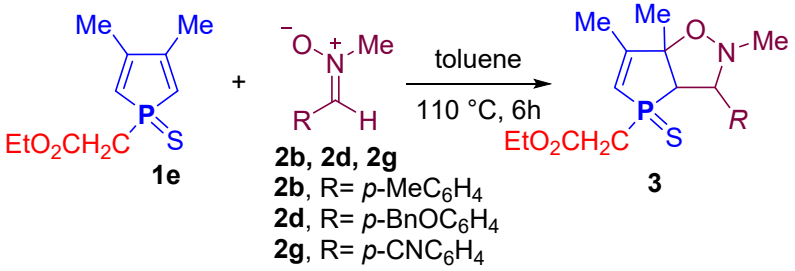
In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1d** (0.09 – 0.1 mmol) and nitrone **2** (0.1 mmol, 1.5eq) in toluene (2 mL) was stirred at 110 °C for 6 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture, providing **3.**

3db: 24.6 mg, 82% yield (with 16.7 mg **1d** , 0.09 mmol); pale yellow solid. **m.p.** 151.6-152.4°C, **^{31}P NMR (121 MHz, $CDCl_3$)** δ 55.90 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.4 (d, *J* = 7.9 Hz, 2H, CH), 7.2 (d, *J* = 7.8 Hz, 2H, CH), 5.8 (d, *J* = 28.3 Hz, 1H, CH), 4.2 (d, *J* = 30.5 Hz, 1H, CH), 3.2 (dd, *J* = 17.2, 14.7 Hz, 1H, CH), 3.10 – 2.92 (m, 2H, CH_2), 2.6 (s, 3H, CH_3), 2.4 (s, 3H, CH_3), 2.1 (d, *J* = 8.6 Hz, 3H, CH_3), 1.8 (s, 3H, CH_3).**^{13}C NMR (75 MHz, $CDCl_3$)** δ 138.2 (s, C), 134.2 (s, C), 129.6 (s, CH), 128.4 (s, CH), 119.3 (d, *J* = 79.3 Hz, CH), 113.5 (d, *J* = 9.1 Hz, C), 92.7 (s, C), 75.11 (m, CH), 58.9 (d, *J* = 55.9 Hz, CH), 42.4 (m, CH_3), 26.3 (d, *J* = 44.2 Hz, NCH_2), 23.3(m, CH_3), 21.2 (s, CH_3), 16.4 (d, *J* = 18.8 Hz, CH_3). **HRMS** (m/z) $[M + Na]^+$ Calcd for $C_{17}H_{21}N_2ONaPS^+$ 355.1010, found 355.1001.

3dd: 32.7 mg, 77% yield (with 18 mg **1d** , 0.1 mmol); white solid. **m.p.** 115.4-116.0°C, **^{31}P NMR (121 MHz, $CDCl_3$)** δ 56.71 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.65 – 7.30 (m, 7H, CH), 7.0 (d, *J* = 8.6 Hz, 2H, CH), 5.8 (d, *J* = 28.3 Hz, 1H, CH), 5.1 (s, 2H, CH_2), 4.35 – 4.08 (m, 1H, CH), 3.1 (m, 2H, CH_2), 3.0 (d, *J* = 7.7 Hz, 1H, CH), 2.6 (s, 3H, CH_3), 2.1 (d, *J* = 7.7 Hz, 3H, CH_3), 1.8 (s, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 164.3 (m, C), 158.9 (s, C), 136.9 (s, C), 129.8 (s), 129.3 (s, C), 128.7 (s, CH), 128.1 (s, CH), 127.6 (s, CH), 119.31= (d, *J* = 79.2 Hz, CH), 115.2 (s, CH), 113.6 (d, *J* = 9.0 Hz, C), 92.6 (s, C), 75.2 (m, CH), 70.0 (s, CH_2), 58.7 (d, *J* = 56.0 Hz, CH), 42.1 (m, CH_3), 26.2 (d, *J* = 44.4 Hz, CH_2), 23.3 (s, CH_3), 16.5 (d, *J* = 19.1 Hz, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{23}H_{26}N_2O_2PS^+$ 425.1453, found 425.1457 .

3dg: 26.7 mg, 84% yield (with 16.6 mg **1d** , 0.09 mmol); pale yellow solid. **m.p.** 147.2-148.1°C, **^{31}P NMR (121 MHz, $CDCl_3$)** δ 55.21 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.4 (t, *J* = 10.3 Hz, 2H, CH), 7.2 (d, *J* = 7.9 Hz, 2H, CH), 5.8 (d, *J* = 28.3 Hz, 1H, CH), 4.2 (s, 1H, CH), 3.1 (m, 2H, CH_2),

3.03 – 2.93 (m, 1H, CH), 2.6 (s, 3H, CH_3), 2.07 (dd, J = 7.4, 6.0 Hz, 3H, CH_3), 1.83 (s, 3H, CH_3).**^{13}C NMR (75 MHz, $CDCl_3$)** δ 164.1 (m, C), 139.2 (s, C), 132.6 (d, J = 93 Hz, CH), 131.6 (d, J = 168.8 Hz, CH), 119.2 (d, J = 79.4 Hz, CH), 118.5 (s, C), 113.4 (s, C), 113.1 (s, C), 93.0 (d, J = 13.7 Hz, C), 74.3 (m, CH), 59.1 (d, J = 55.6 Hz, CH), 42.5 (s, CH_3), 26.3 (d, J = 44.9 Hz, CH_2), 23.24 (s, CH_3), 16.5 (d, J = 18.9 Hz, CH_3). **HRMS** (m/z) $[M + Na]^+$ Calcd for $C_{17}H_{18}N_3ONaPS^+$ 366.0806, found 366.0805.



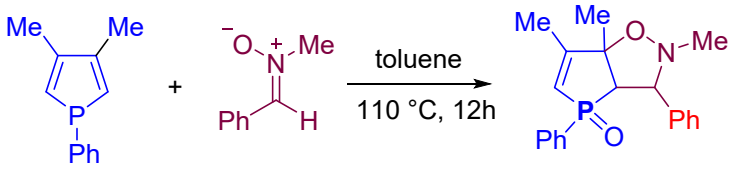
In a Schlenk tube (filled with nitrogen), a solution of phosphole sulfide **1e** (46.0 mg, 0.2 mmol) and nitrone **2** (1.5eq) in toluene (2 mL) was stirred at 110 °C for 6 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 5:1 petroleum ether: ethyl acetate mixture, providing **3.**

3eb: 66.0 mg, 83% yield; white solid. **m.p.** 78.2-79.1°C, **^{31}P NMR (121 MHz, $CDCl_3$)** δ 55.77 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.4 (d, J = 7.9 Hz, 2H, CH), 7.2 (d, J = 7.9 Hz, 2H, CH), 5.8 (d, J = 26.8 Hz, 1H, CH), 4.2 (brs, 1H, CH), 4.07 – 3.90 (m, 2H, CH_2), 3.1 (s, 1H, CH), 3.10 (dd, J = 14.6, 3.4 Hz, 2H, CH_2), 2.5 (s, 3H, CH_3), 2.33(s, 3H, CH_3), 2.0 (s, 3H, CH_3), 1.7 (s, 3H, CH_3), 1.1 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.6 (d, J = 6.2 Hz, C), 160.7 (m, C), 137.7 (s, C), 134.7 (d, J = 3.0 Hz, C), 129.4 (s, CH), 128.4 (s, CH), 121.4 (d, J = 78.1 Hz, CH), 92.3 (d, J = 13.3 Hz, C), 75.2 (m, CH), 61.6 (s, CH), 58.9 (d, J = 55.3 Hz, CH2), 43.9 (d, J = 44.3 Hz, CH_2), 42.40 (s, CH_3), 24.0 (s, CH_3), 21.1 (s, CH_3), 16.1 (d, J = 18.6 Hz, CH_3), 14.0 (s, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{19}H_{27}NO_3PS^+$ 380.1449, found 380.1452.

3ed: 80.3 mg, 86% yield; pale yellow solid. **m.p.** 89.4-90.1°C, **^{31}P NMR (121 MHz, $CDCl_3$)** δ 55.70 (s).**^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.62 – 7.24 (m, 7H, CH),7.0 (d, J = 8.6 Hz, 2H, CH), 5.8 (d, J = 26.8 Hz, 1H, CH), 5.1 (s, 2H, CH_2), 4.2 (brs, 1H, CH), 4.0 (q, J = 7.0 Hz, 2H, CH_2), 3.19 – 3.04 (m, 2H, CH_2), 2.55 (s, 3H, CH_3), 2.09 – 2.01 (m, 1H, CH), 2.0 (d, J = 24.2 Hz, 3H, CH_3), 1.7 (s, 3H, CH_3), 1.1 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.6 (d, J = 6.1 Hz, C),

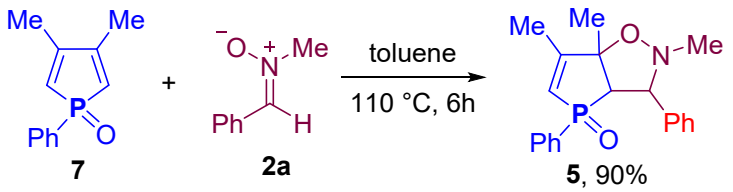
160.7 (m, C),158.7 (s, C), 137.0 (s, C), 129.9 (s, C), 129.8 (s, CH), 128.6 (s, CH), 128.0 (s, CH), 127.5 (s, CH), 121.4 (d, J = 78.3 Hz, CH), 115.0 (s, CH), 92.2 (d, J = 13.7 Hz, C), 74.9 (m, CH), 70.0 (s, CH_2), 61.6 (s, CH), 58.7 (d, J = 55.3 Hz, CH_2), 43.8 (d, J = 44.3 Hz, CH_2), 42.2 (m, CH_3), 25.6 (s, CH_3), 16.1 (d, J = 18.6 Hz, CH_3), 14.1(s, CH_3). **HRMS** (m/z) $[M + Na]^+$ Calcd for $C_{25}H_{30}NNaO_4PS^+$ 494.1531, found 494.1540.

3eg: 70.7 mg, 90% yield; white solid. **m.p.** 147.2-148.1°C, **^{31}P NMR (121 MHz, $CDCl_3$)** δ 53.35 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.94 – 7.69 (m, 2H, CH), 7.67 – 7.38 (m, 2H, CH), 5.91 – 5.64 (m, 1H, CH), 4.35 (dd, J = 18.8, 7.9 Hz, 1H, CH), 4.16 – 3.87 (m, 2H, CH_2), 3.13 (s, 1H, CH), 3.1 (d, J = 6.0 Hz, 2H, CH_2), 2.6 (s, 3H, CH_3), 2.0 (d, J = 9.7 Hz, 3H, CH_3), 1.6 (s, 3H, CH_3), 1.1 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 165.5 (d, J = 6.0 Hz, C), 160.8 (d, J = 15.2 Hz, C), 140.0 (d, J = 3.2 Hz, C), 132.5 (s, J = 106.5 Hz,CH),130.6(d, J = 160.5 Hz,CH), 121.2 (d, J = 78.3 Hz, CH), 118.6 (s, C), 112.9 (s, C), 92.8 (d, J = 13.2 Hz, C), 74.3 (s,CH), 61.8 (s, CH), 59.0 (d, J = 54.8 Hz, CH_2), 43.6 (d, J = 45.2 Hz, CH_2), 42.7 (s, NCH_3), 24.1 (d, J = 6.5 Hz, CH_3), 16.1 (d, J = 18.5 Hz, CH_3), 14.1 (s, CH_3). **HRMS** (m/z) $[M + Na]^+$ Calcd for $C_{19}H_{23}N_2NaO_3PS^+$ 413.1065, found 413.1069.



4 **2a** **5**, 65%

In a Schlenk tube (filled with nitrogen), a solution of phosphole **4** (102 mg, 0.5 mmol) and nitrone **2a** (135 mg, 1 mmol) in toluene (2 mL) was stirred at 110 °C for 12 h. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel using 3:1 petroleum ether : ethyl acetate mixture, providing **5** (110.5 mg, 65%) as a white solid.



7 **2a** **5**, 90%

In a Schlenk tube (filled with nitrogen), a solution of phosphole oxide **7** (61 mg, 0.3 mmol) and nitrone **2a** (81 mg, 0.6 mmol) in toluene (2 mL) was stirred at 110 °C for 6 h. After evaporation

of the solvent, the residue was purified by thin layer chromatography on silica gel using 3:1 petroleum ether : ethyl acetate mixture, providing **5** (91.6 mg, 90%) as a white solid.

5: m.p. 117.4-118.1°C, **^{31}P NMR (121 MHz, $CDCl_3$)** δ 46.66 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.5 (m, 4H, CH), 7.46 – 7.32 (m, 3H, CH), 7.34 – 7.17 (m, 3H, CH), 5.9 (d, *J* = 21.9 Hz, H, CH), 4.3 (s, H, CH), 2.8 (t, *J* = 13.5 Hz, H, CH), 2.6 (s, 3H, CH_3), 2.1 (d, *J* = 1.4 Hz, 3H, CH_3), 1.7 (s, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 138.3 (d, *J* = 2.5 Hz, C), 133.8 (s, C), 132.5 (s, C), 131.9 (d, *J* = 2.8 Hz, CH), 130.3 (d, *J* = 10.5 Hz, CH), 128.9 (s, CH), 128.7 (d, *J* = 2.1 Hz, CH), 127.8 (s, CH), 121.4 (s, CH), 120.1 (s, CH), 90.3 (d, *J* = 15.0 Hz, C), 61.6 (s, CH), 60.7 (s, CH), 42.6 (s, CH_3), 24.1 (s, CH_3), 16.3 (d, *J* = 18.4 Hz, CH_3). **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{20}H_{23}NO_2P^+$ 340.1466, found 340.1464.

References

[1] (a) K. S. Chan, M. L. Yeung, W.-K. Chan, R.-J. Wang, T. C. W. Mak, Chromium and Tungsten Pentacarbonyl Groups as Reactivity and Selectivity Auxiliaries in [3 + 2] Cycloaddition of Alkynyl Fischer Carbene Complexes with N-Alkyl Nitrones. *J. Org. Chem.*, 1995, **60**, 1741–1747; (b) S. Pagoti, D. Dutta, J. Dash, A Magnetoclick Imidazolidinone Nanocatalyst for Asymmetric 1,3-Dipolar Cycloadditions. *Adv. Synth. Catal*., 2013, **355**, 3532–3538; (c) J. Gracia-Vitoria, I. Osante, C. Cativiela, T. Tejero, P. Merino, Experimental and Computational Studies on the 1,3-Dipolar Cycloaddition between Enantiomerically Pure 2,3- Dihydrothiazoles and Nitrones. *Eur. J. Org. Chem*., 2019, 4426–4435.

[2] (a) S. Holand, F. Mathey, New Method for Building Carbon-Phosphorus Heterocycles, *J. Org. Chem.*, 1981, **46**, 4386–4389; (b) F. Mathey, Product class 14: phospholes, *Sci. Synth.*, 2002, **9**, 553-600.

[3] S. Hol, F. Mathey, Introducing new phosphorus substituents in terminal phosphinidene complexes. An illustration with [(ethoxycarbonyl)phosphinidene] - , (tert-butoxyphosphinidene) - , and (fluorenylphosphinidene) pentacarbonyltungsten complexes. *Organometallics*, 1988, **7**, 1796–1801.

X-ray crystallographic studies of compound 3a

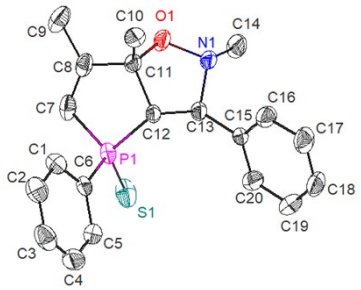


Table 1 Crystal data and structure refinement for 3a

Identification code	exp_11095
Empirical formula	$C_{20}H_{23}NOPS$
Formula weight	356.42
Temperature/K	199.99(10)
Crystal system	monoclinic
Space group	P21/n
a/Å	11.43300(10)
b/Å	11.85120(10)
c/Å	14.09910(10)
α/°	90
β/°	92.0950(10)
γ/°	90
Volume/Å^3	1909.08(3)
Z	4
ρcalcg/cm^3	1.240
μ/mm^{-1}	2.334
F(000)	756.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.752 to 147.126
Index ranges	-11 ≤ h ≤ 14, -8 ≤ k ≤ 14, -17 ≤ l ≤ 16
Reflections collected	9165
Independent reflections	3760 [R_{int} = 0.0212, R_{sigma} = 0.0261]
Data/restraints/parameters	3760/0/220
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0342, wR_2 = 0.0925
Final R indexes [all data]	R_1 = 0.0367, wR_2 = 0.0945
Largest diff. peak/hole / e Å^{-3}	0.23/-0.35

Table 2 Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	P1	1.9485(5)	C7	C8	1.327(2)
P1	C6	1.8127(14)	C8	C9	1.503(2)
P1	C7	1.7828(15)	C8	C11	1.5194(19)
P1	C12	1.8425(13)	C10	C11	1.517(2)
O1	N1	1.4644(14)	C11	C12	1.5552(17)
O1	C11	1.4446(15)	C12	C13	1.5395(17)
N1	C13	1.4824(16)	C13	C15	1.5130(18)
N1	C14	1.4523(19)	C15	C16	1.381(2)
C1	C2	1.392(2)	C15	C20	1.3860(19)
C1	C6	1.392(2)	C16	C17	1.388(2)
C2	C3	1.380(3)	C17	C18	1.372(3)
C3	C4	1.377(3)	C18	C19	1.375(3)
C4	C5	1.385(2)	C19	C20	1.389(2)
C5	C6	1.389(2)			

Table 3 Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	P1	S1	113.13(5)	C9	C8	C11	118.65(14)
C6	P1	C12	107.65(6)	O1	C11	C8	104.99(11)
C7	P1	S1	116.05(5)	O1	C11	C10	110.93(12)
C7	P1	C6	107.22(7)	O1	C11	C12	104.01(10)
C7	P1	C12	93.77(7)	C8	C11	C12	109.94(11)
C12	P1	S1	117.07(4)	C10	C11	C8	114.23(12)
C11	O1	N1	103.52(9)	C10	C11	C12	112.03(11)
O1	N1	C13	102.08(10)	C11	C12	P1	106.42(9)
C14	N1	O1	104.89(11)	C13	C12	P1	115.78(9)
C14	N1	C13	111.99(12)	C13	C12	C11	103.99(10)
C2	C1	C6	119.75(14)	N1	C13	C12	102.01(10)
C3	C2	C1	120.12(16)	N1	C13	C15	109.46(11)
C4	C3	C2	120.23(15)	C15	C13	C12	114.91(11)
C3	C4	C5	120.20(15)	C16	C15	C13	121.40(12)
C4	C5	C6	120.13(15)	C16	C15	C20	118.37(13)
C1	C6	P1	120.54(10)	C20	C15	C13	120.23(13)
C5	C6	P1	119.86(11)	C15	C16	C17	120.79(15)
C5	C6	C1	119.57(13)	C18	C17	C16	120.29(16)
C8	C7	P1	113.78(11)	C17	C18	C19	119.66(15)
C7	C8	C9	125.26(15)	C18	C19	C20	120.11(15)
C7	C8	C11	116.05(12)	C15	C20	C19	120.76(15)

NMR spectra

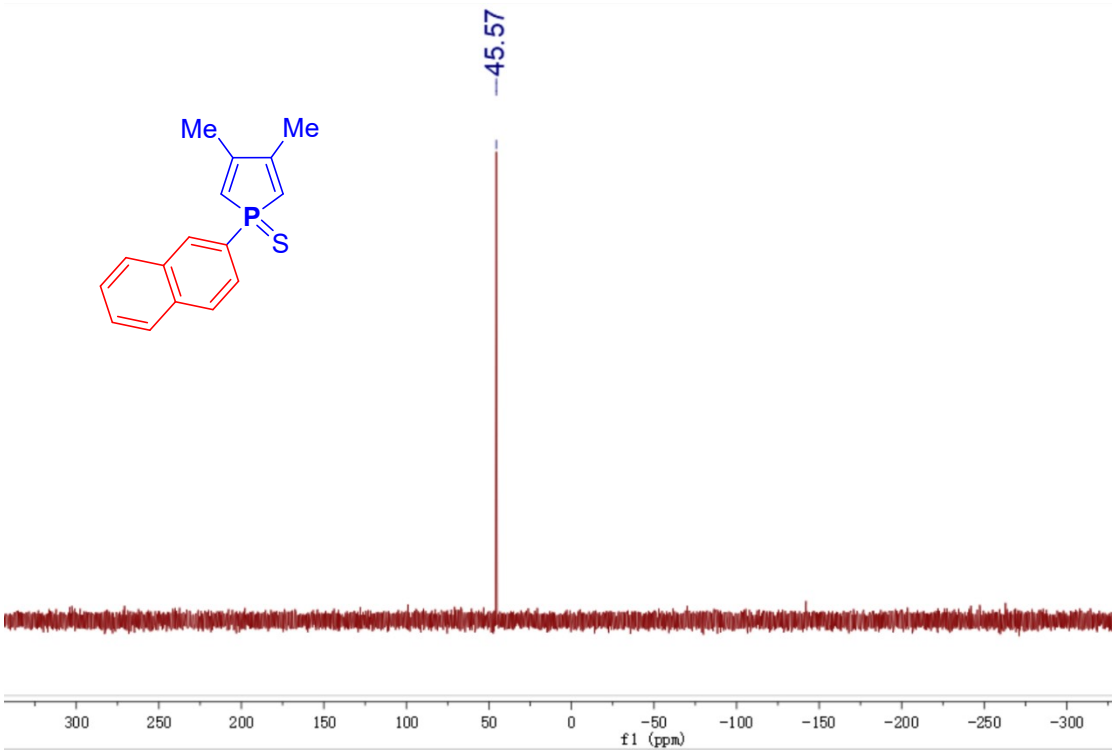


Figure S1. ^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of Compound 1b

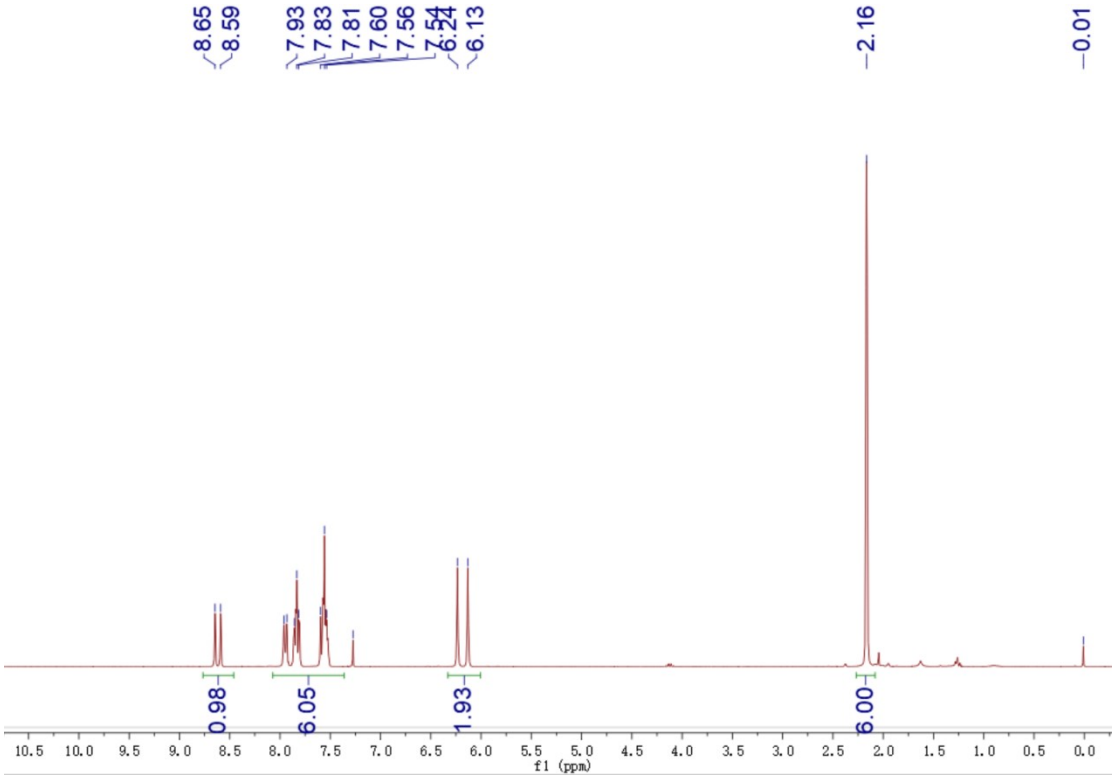


Figure S2. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 1b

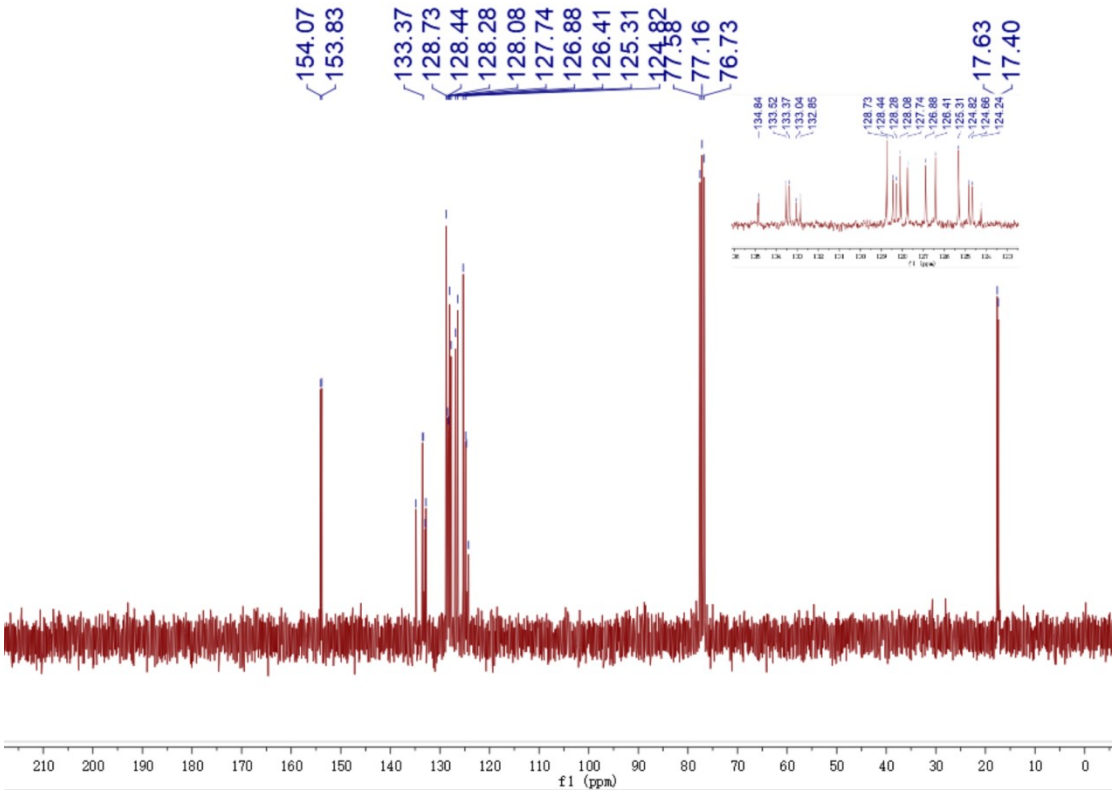


Figure S3. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 1b

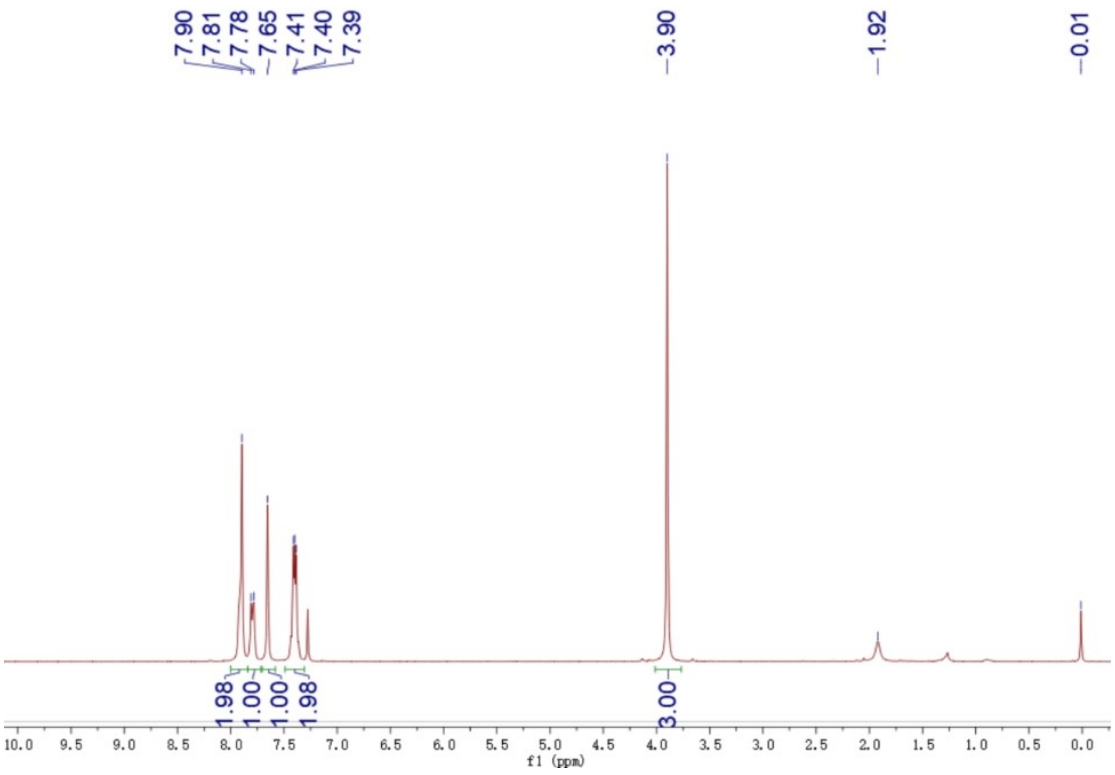


Figure S4. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2i

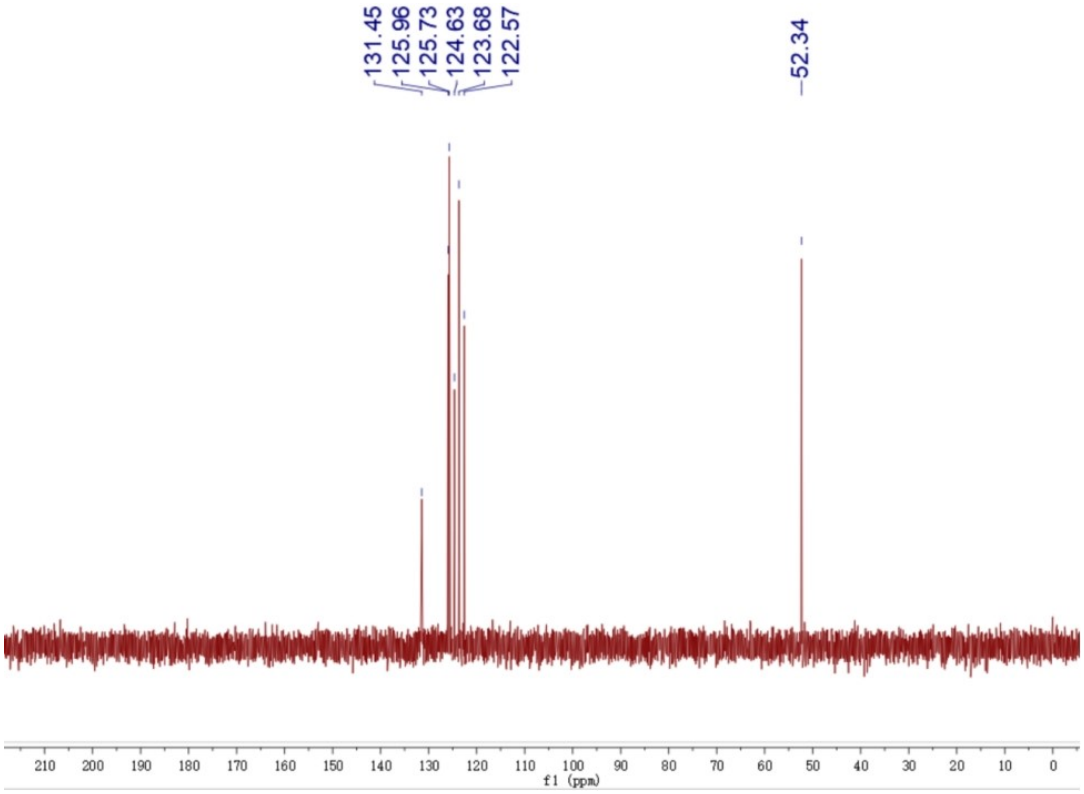


Figure S5. ^{135}Dept NMR (75 MHz, $CDCl_3$) of Compound 2i

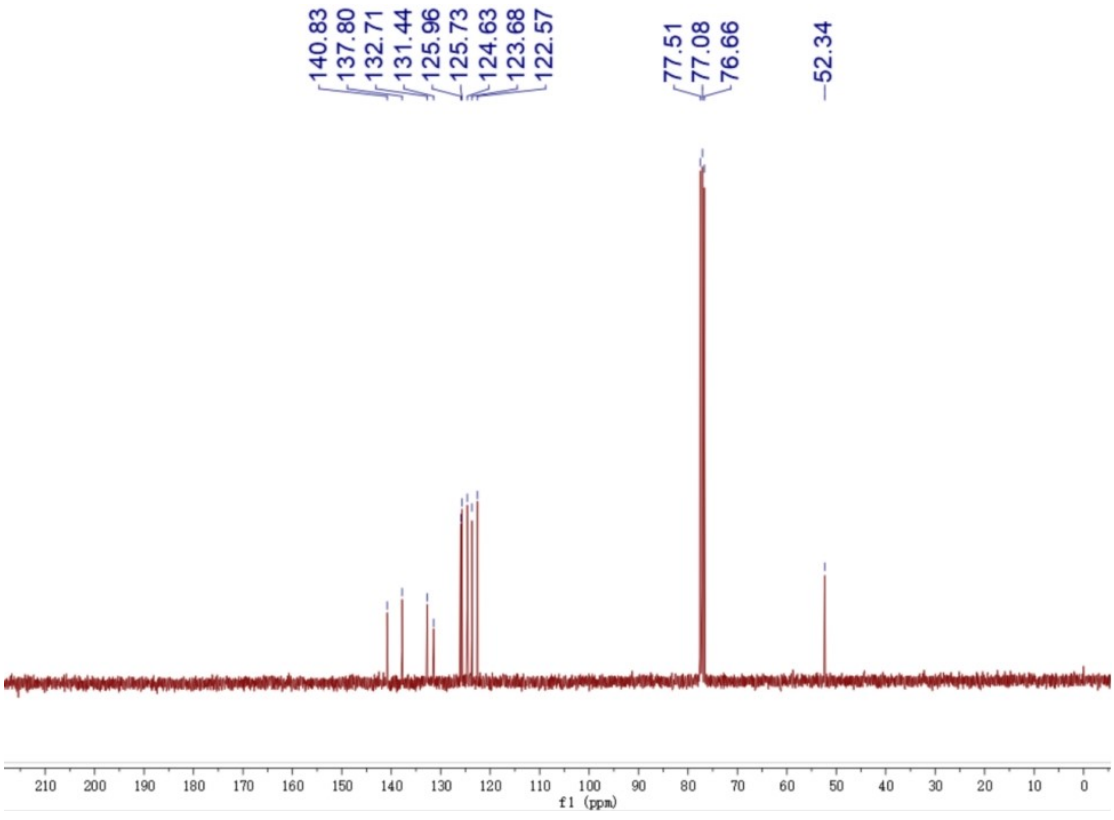


Figure S6. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2i

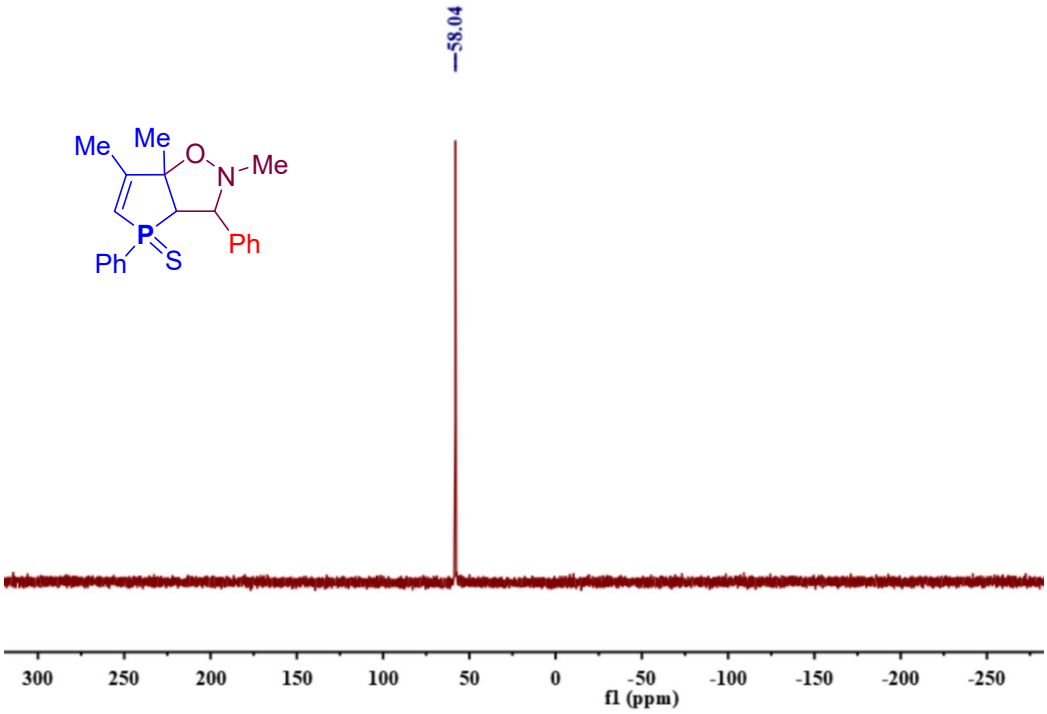


Figure S7. ^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of Compound 3a

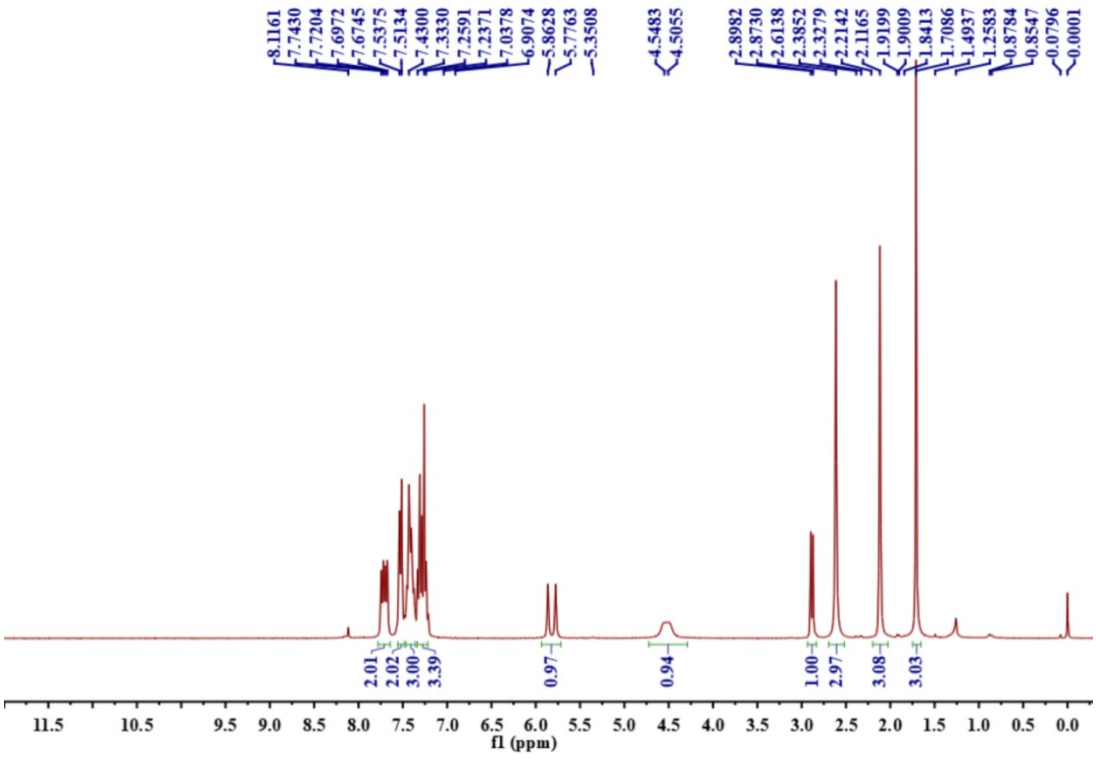


Figure S8. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3a

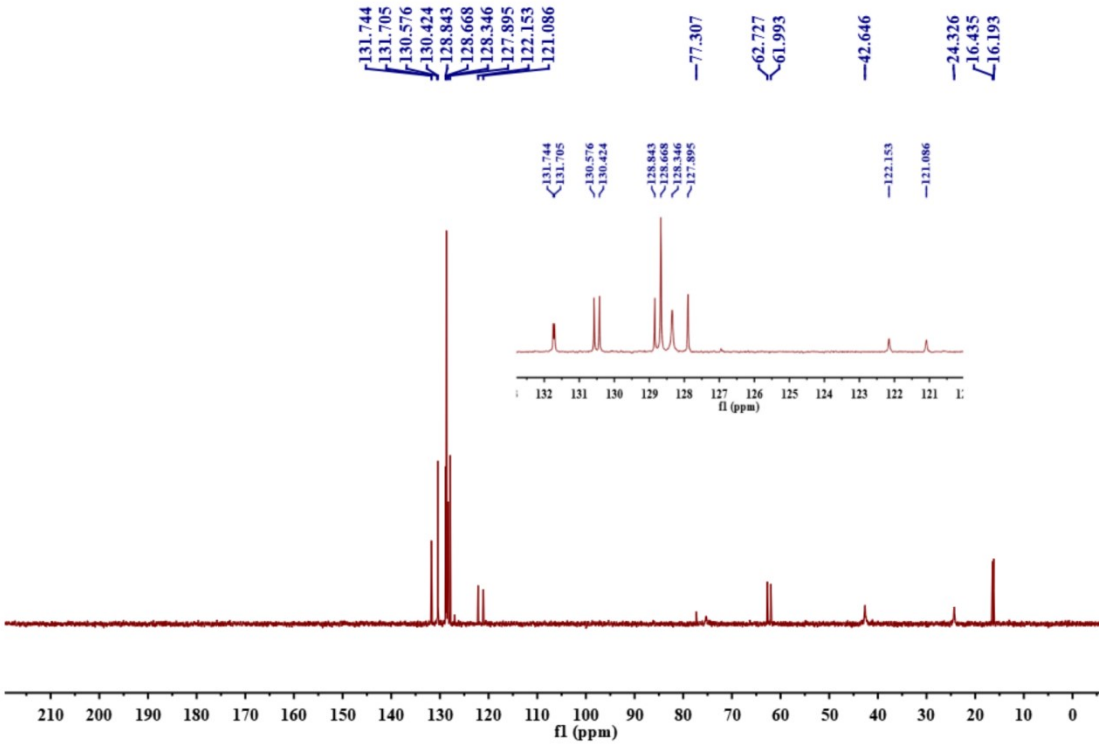


Figure S9. ^{135}Dept NMR (75 MHz, $CDCl_3$) of Compound 3a

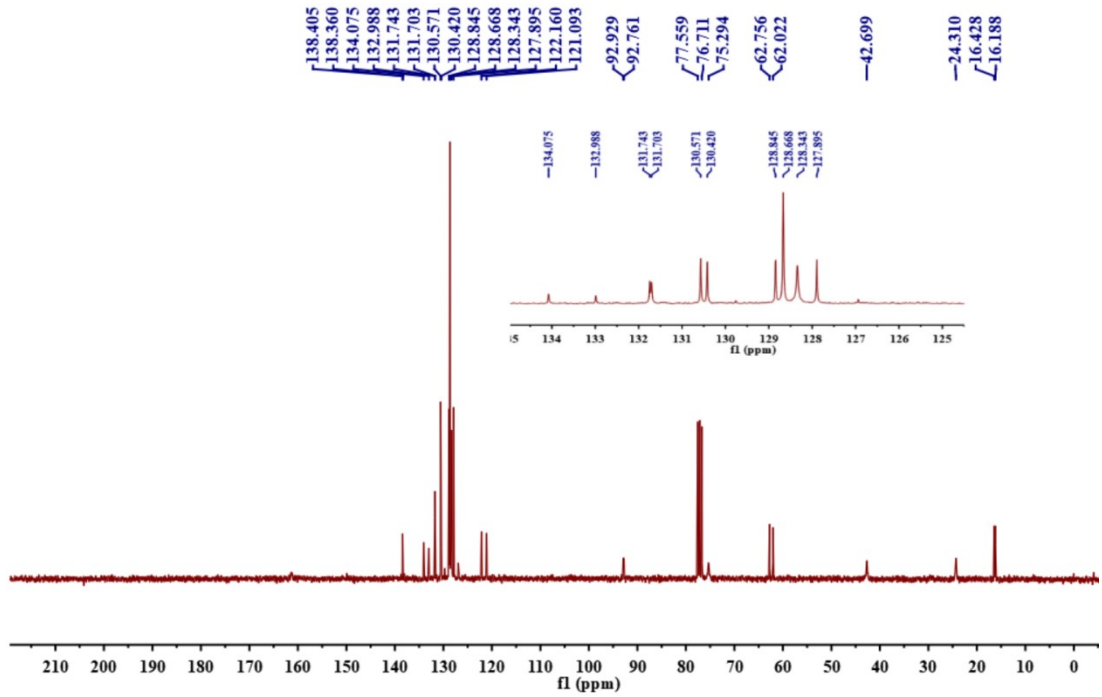


Figure S10. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3a

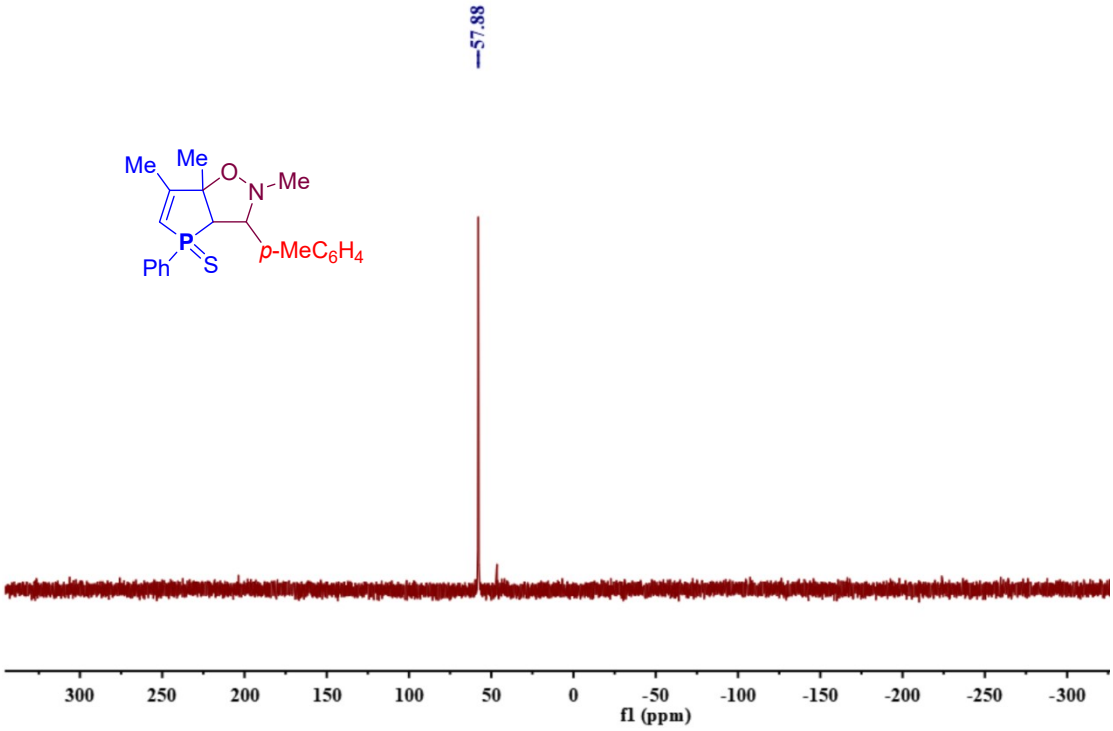


Figure S11. ^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of Compound 3b

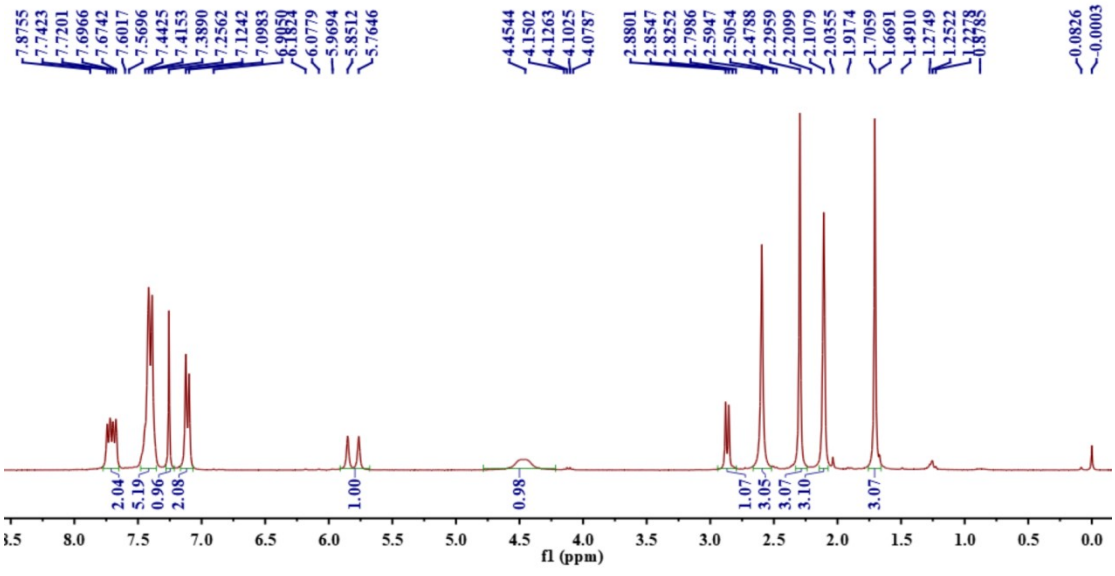


Figure S12. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3b

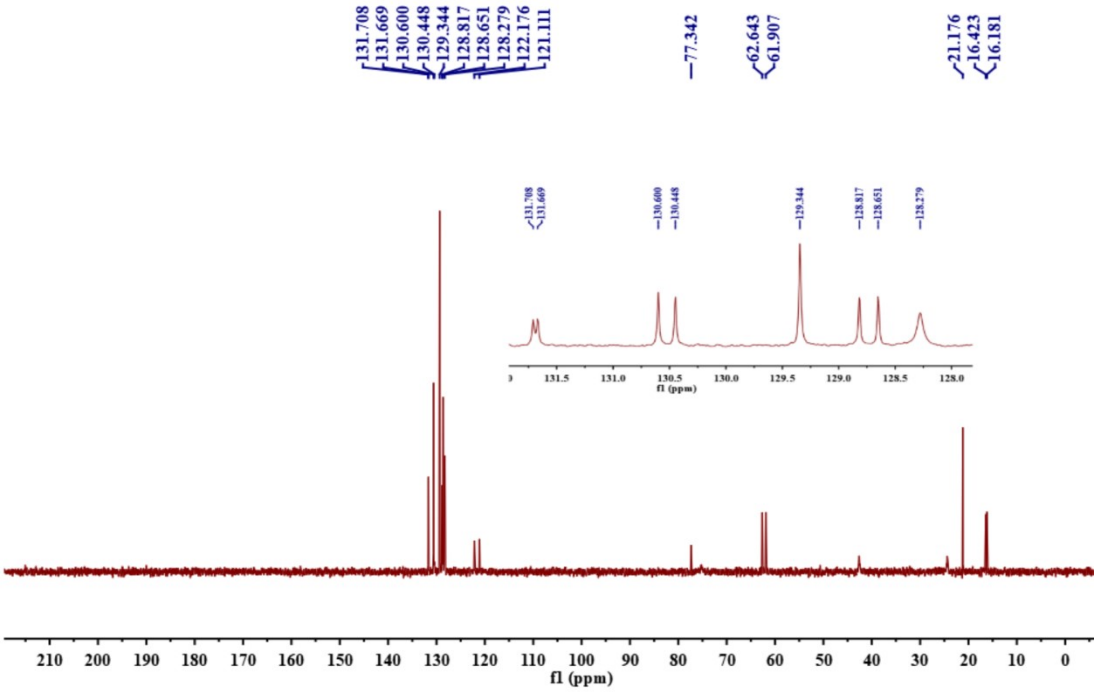


Figure S13. ^{135}Dept NMR (75 MHz, $CDCl_3$) of Compound 3b

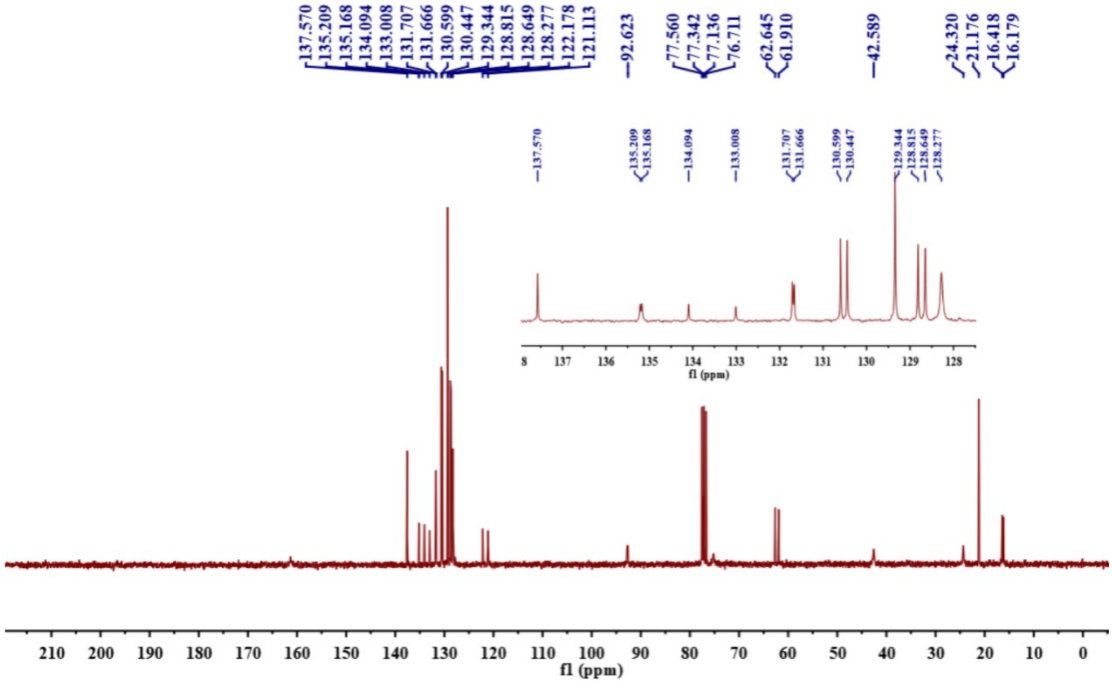


Figure S14. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3b

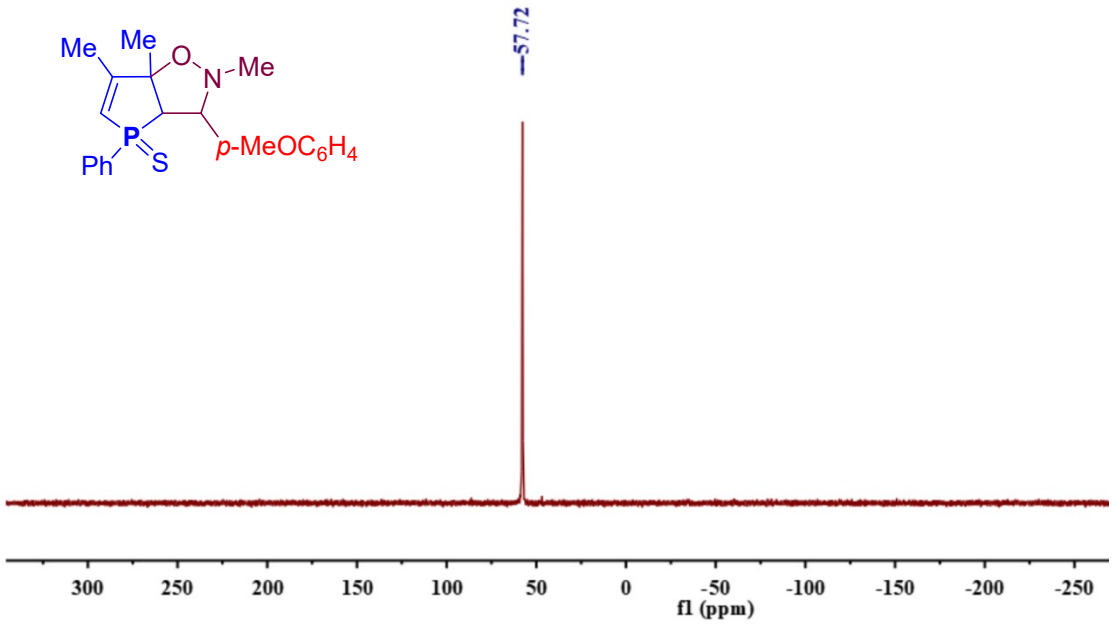


Figure S15. ^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of Compound 3c

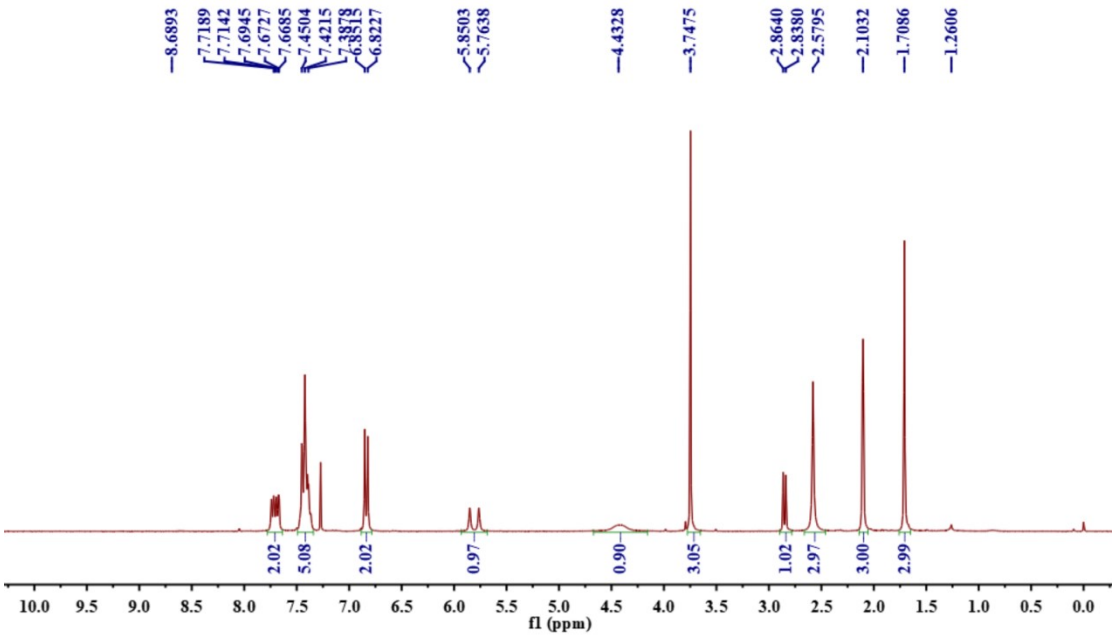


Figure S16. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3c

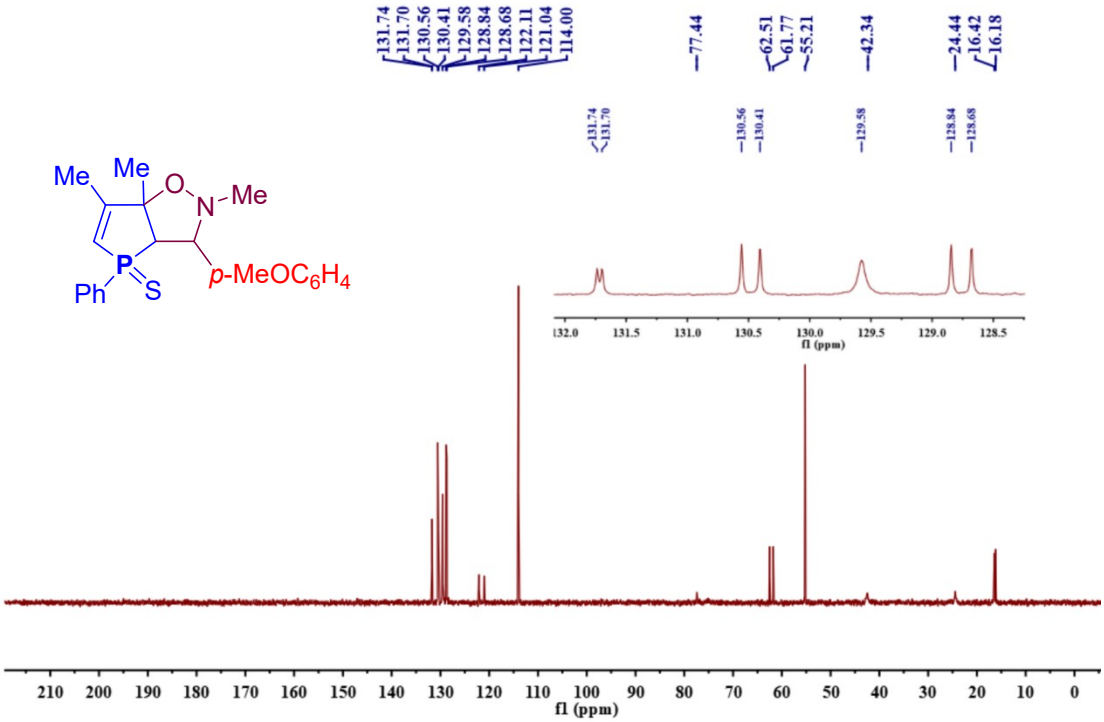


Figure S17. ^{135}Dept NMR (75 MHz, $CDCl_3$) of Compound 3c

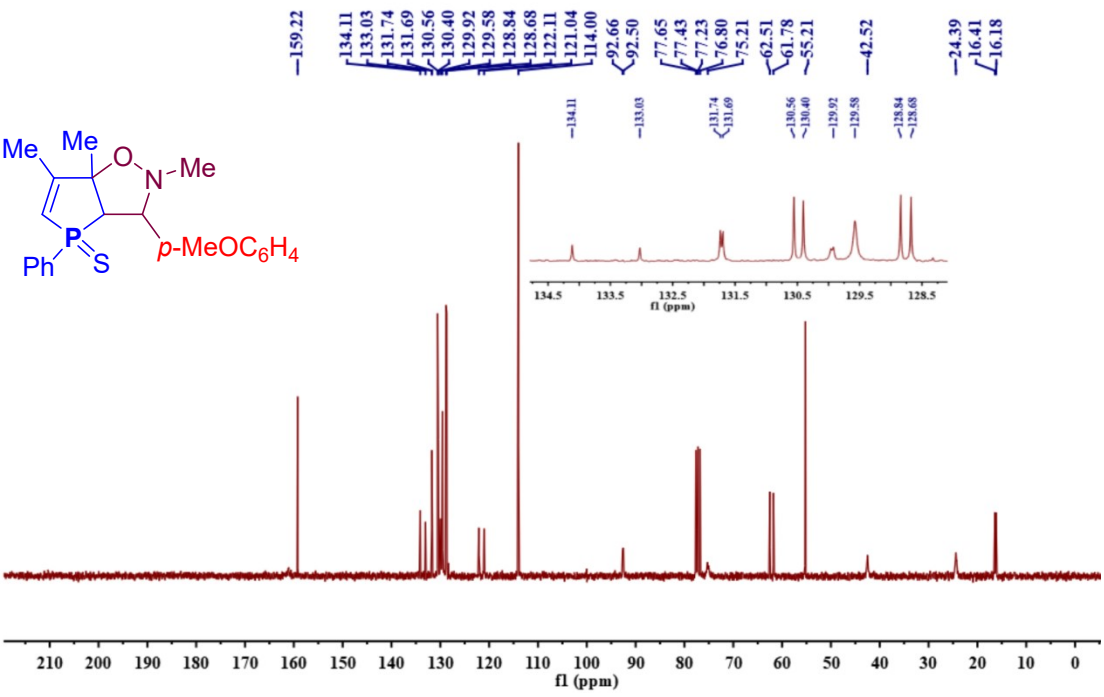


Figure S18. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3c

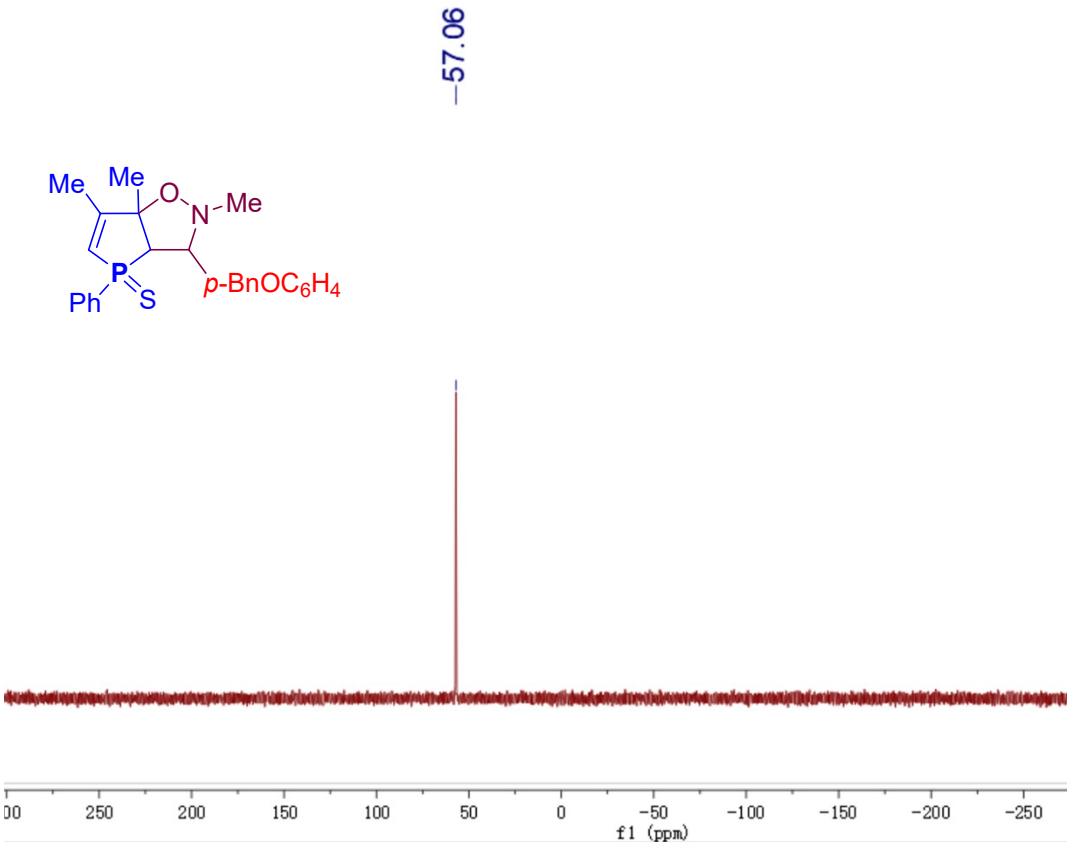


Figure S19. ^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of Compound 3d

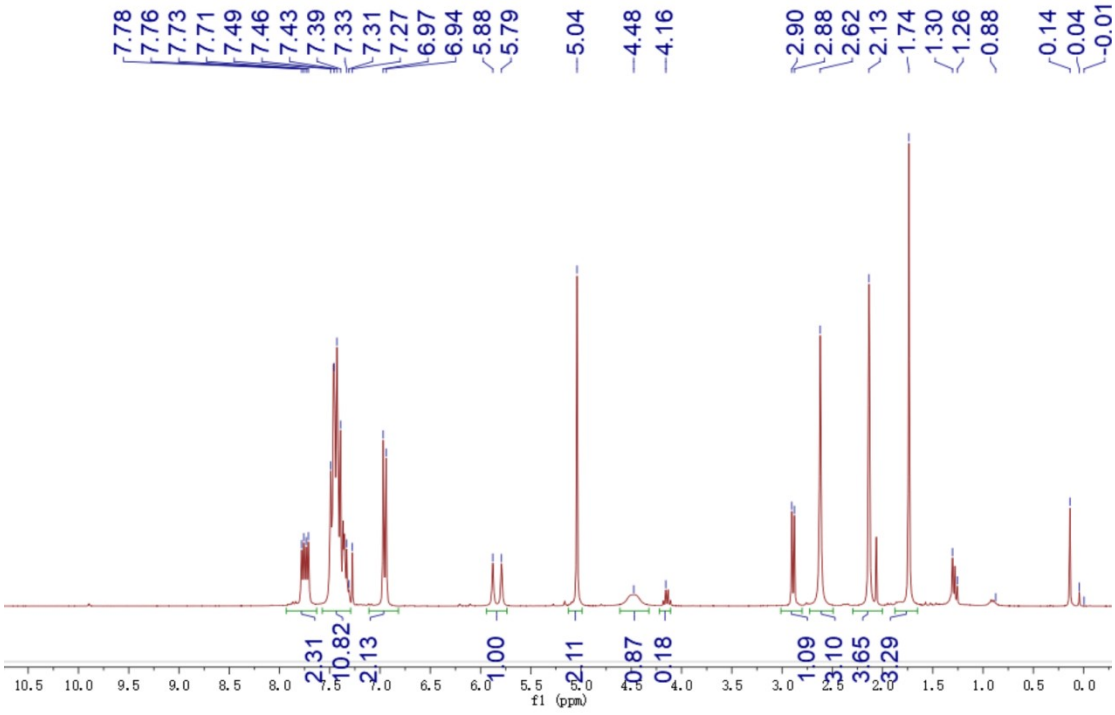


Figure S20. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3d

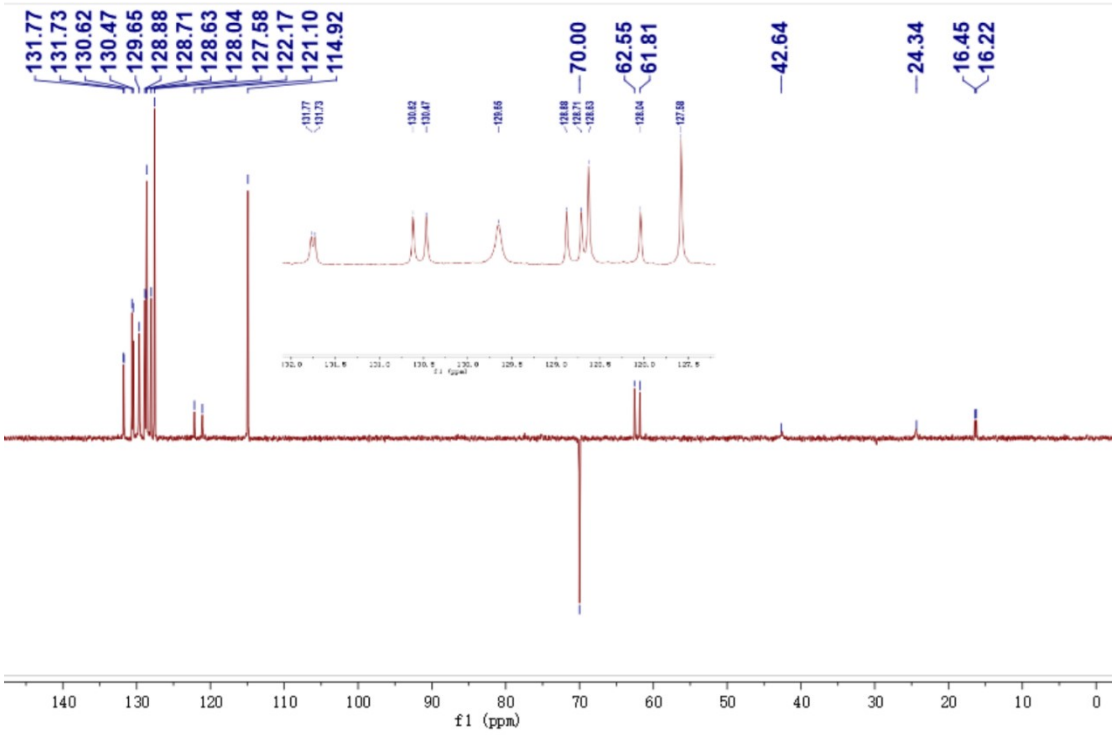


Figure S21. ^{135}Dept NMR (75 MHz, $CDCl_3$) of Compound 3d

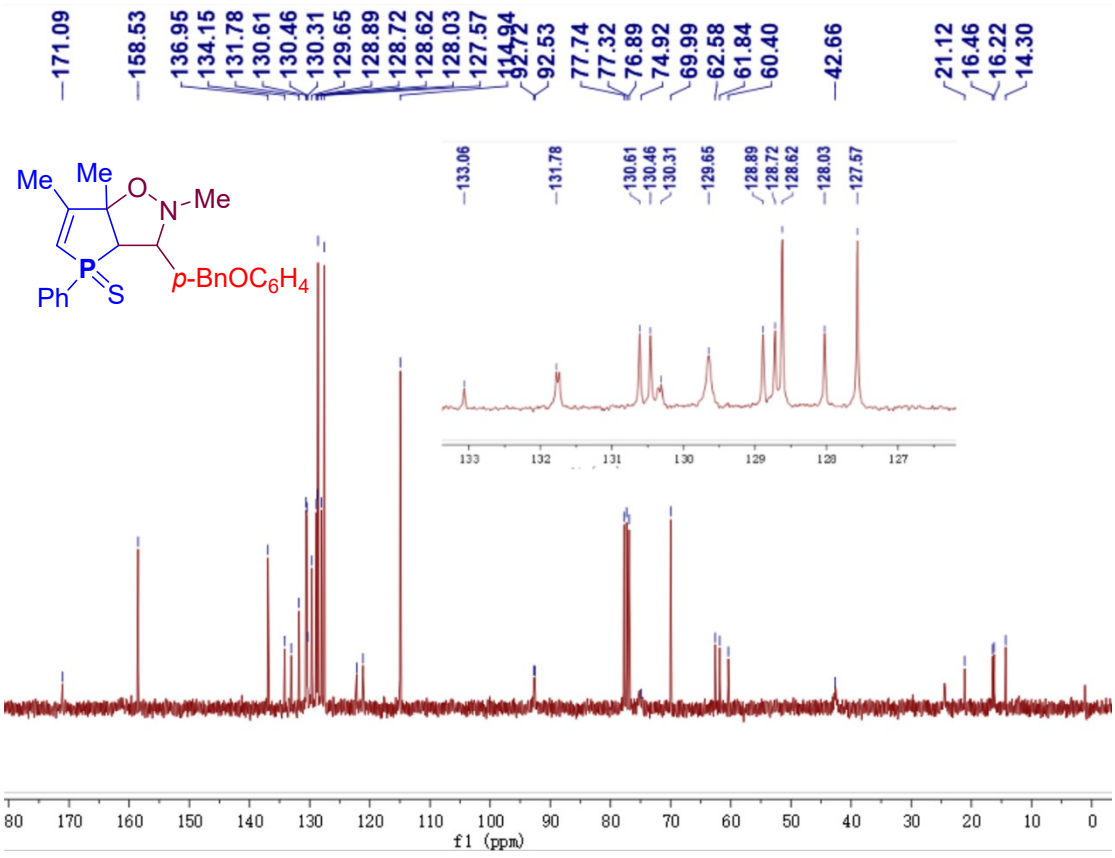


Figure S22. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3d

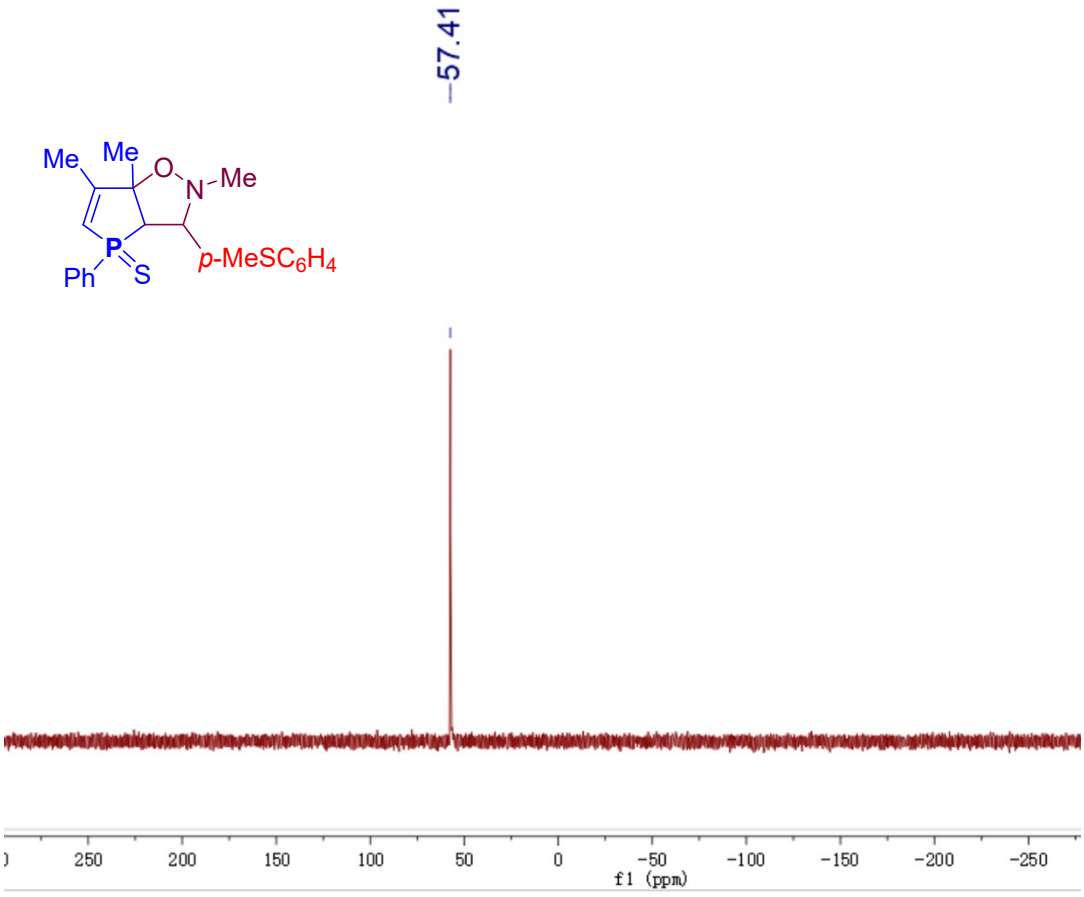


Figure S23. ^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of Compound 3e

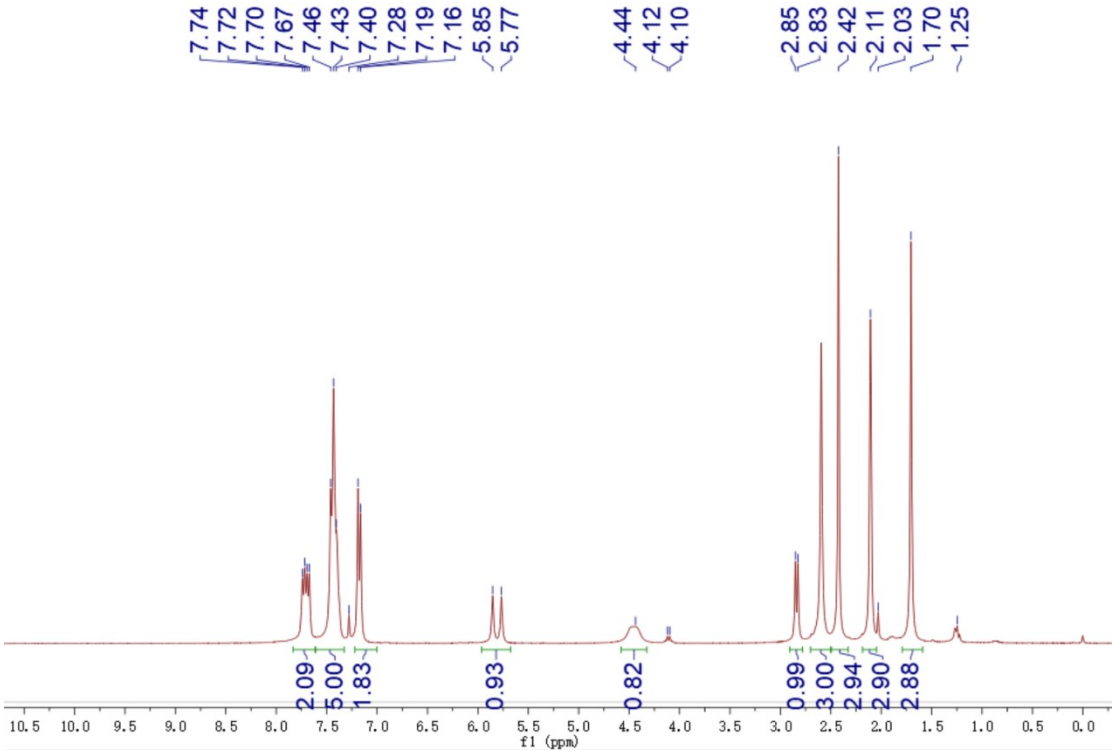


Figure S24. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3e

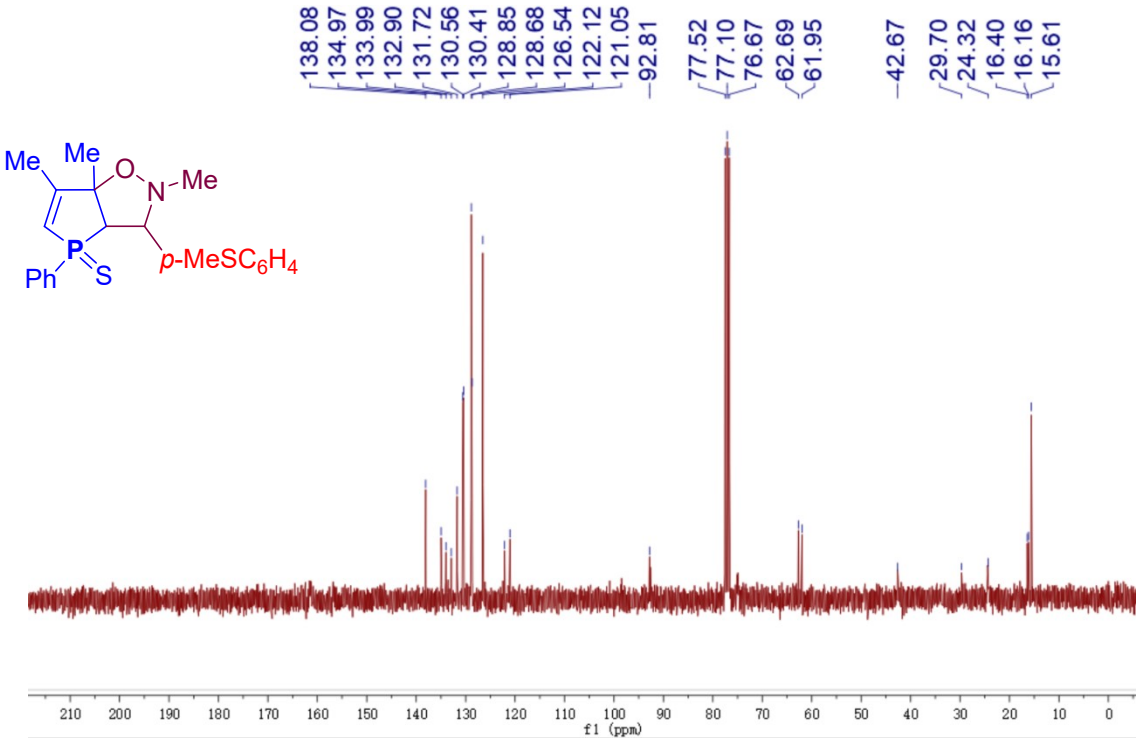


Figure S25. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3e

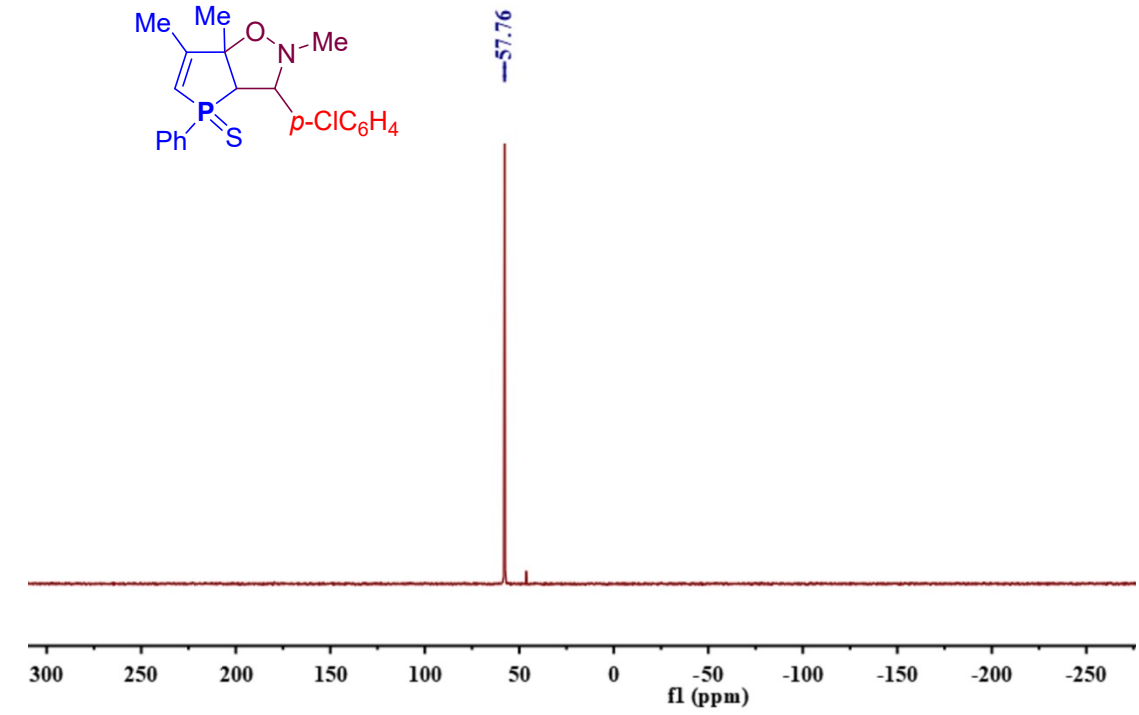


Figure S26. $^{31}P\ \{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) of Compound 3f

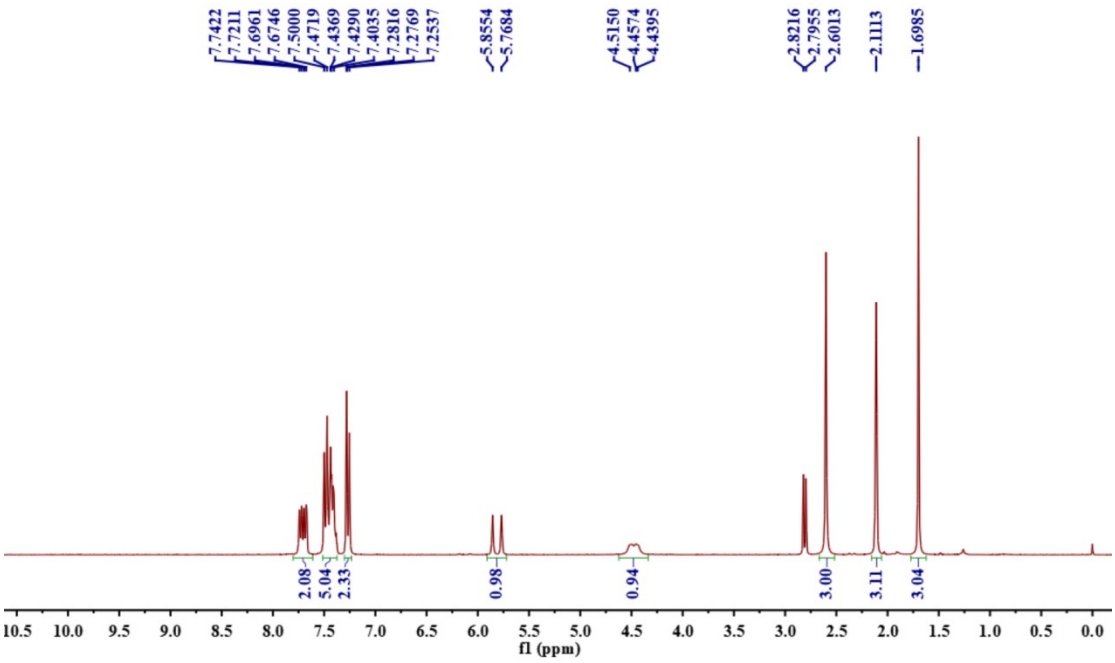


Figure S27. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3f

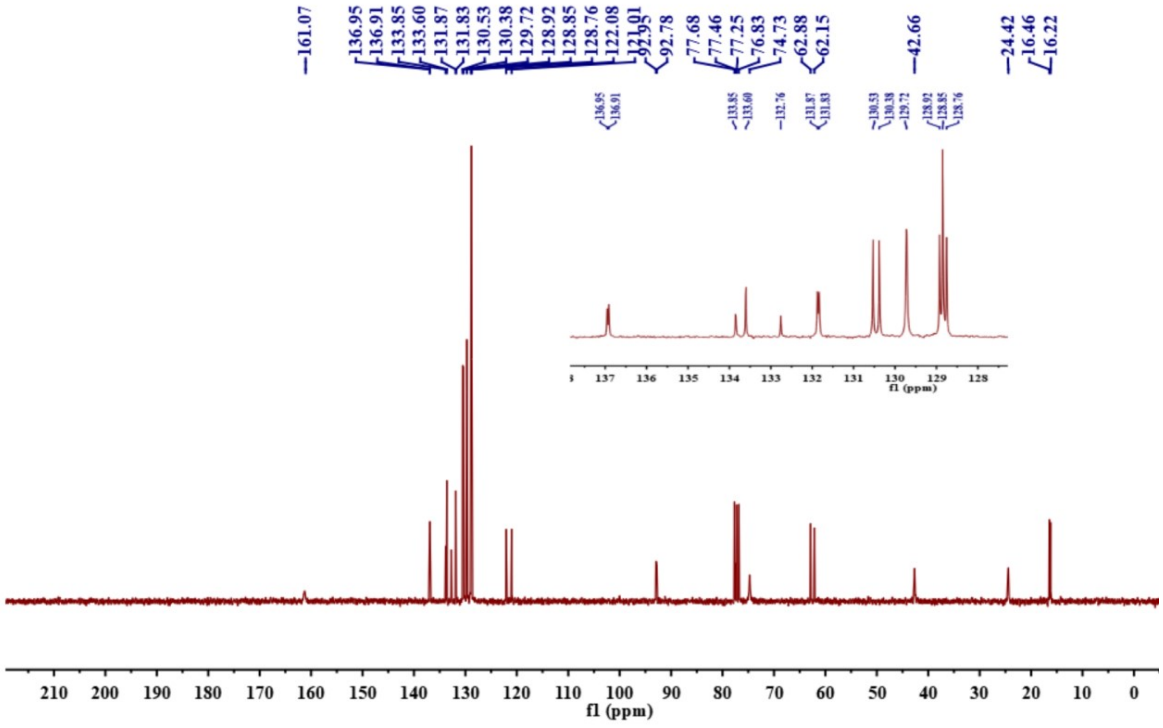


Figure S28. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of Compound 3f

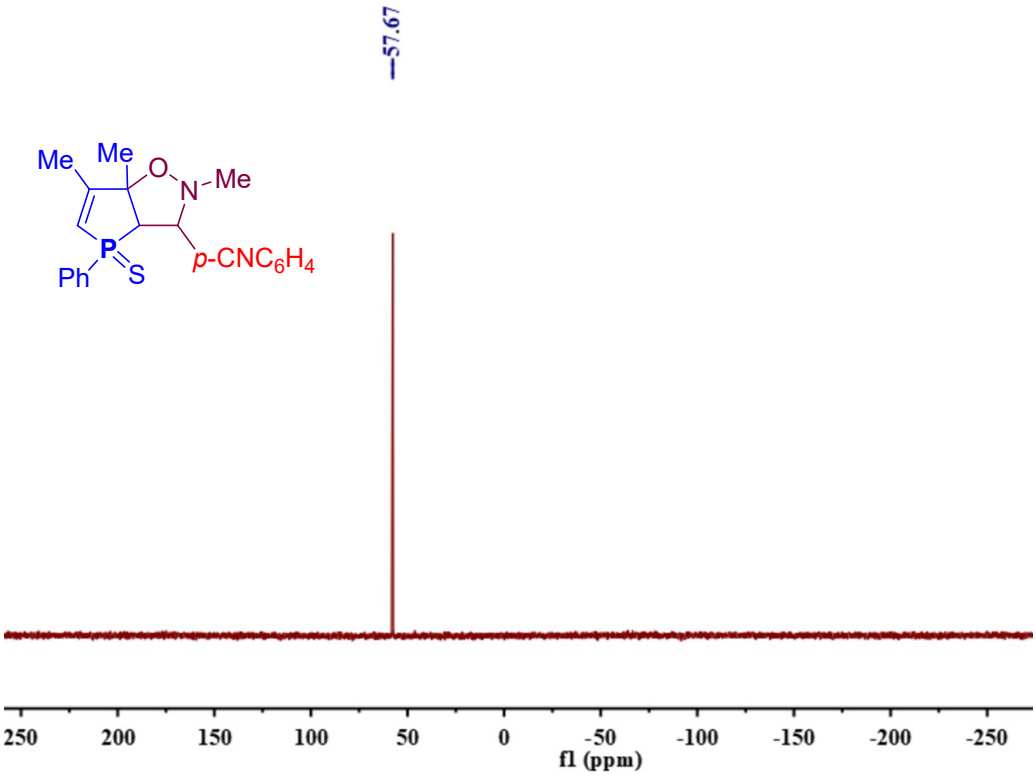


Figure S29. ^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of Compound 3g

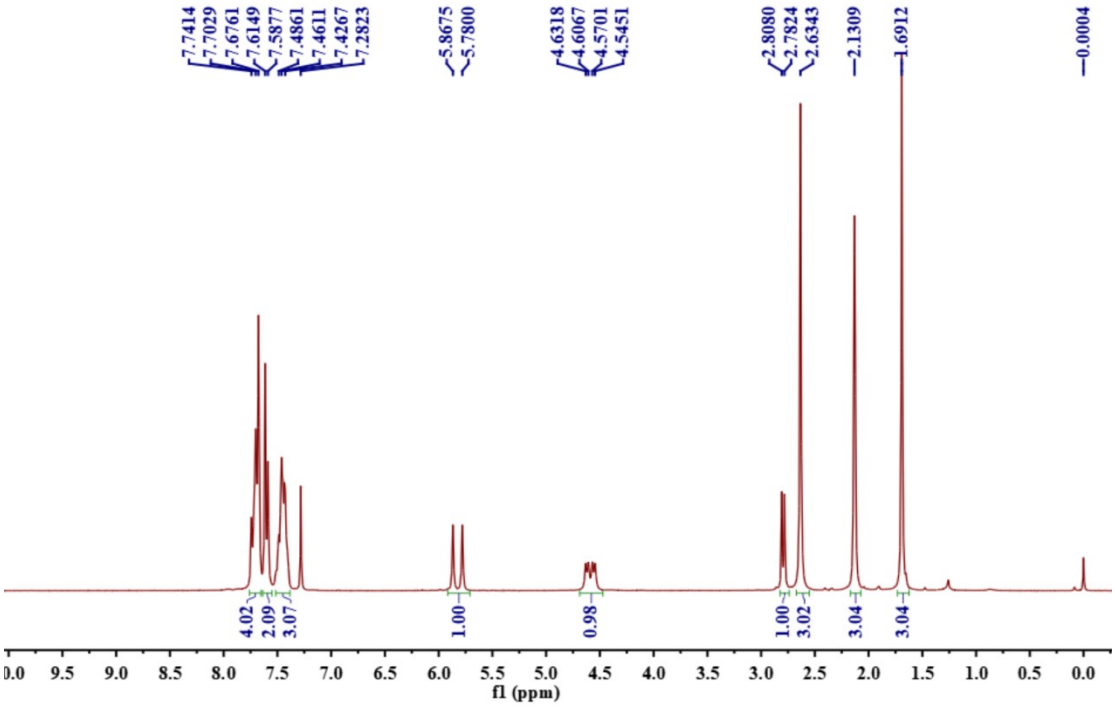


Figure S30. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3g

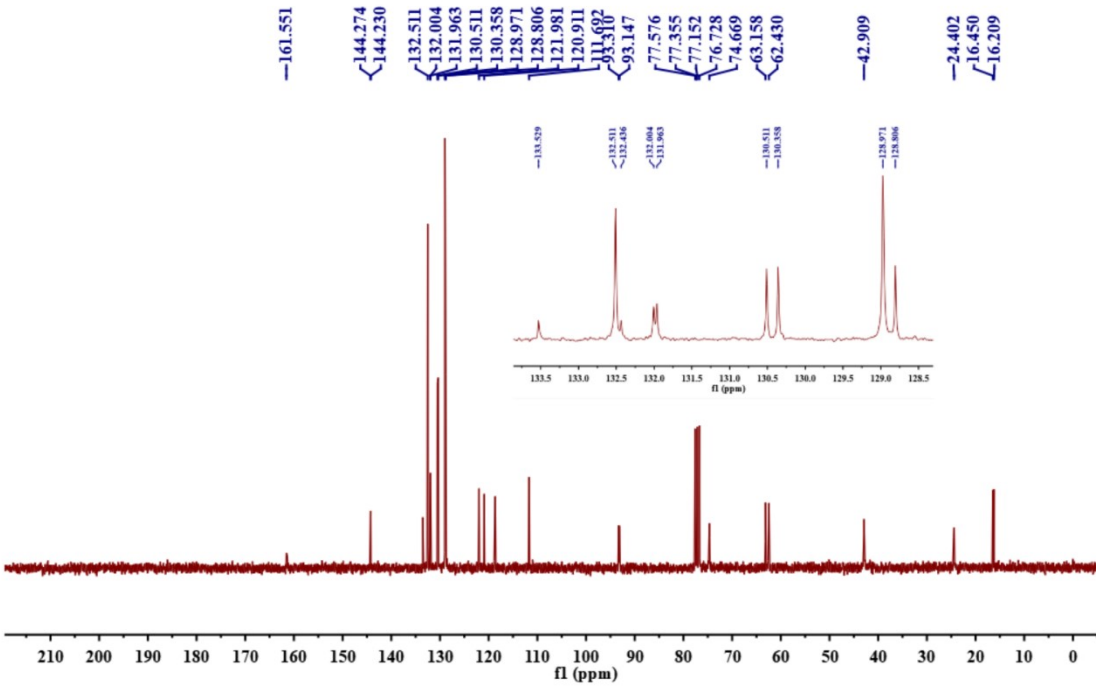


Figure S31. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3g

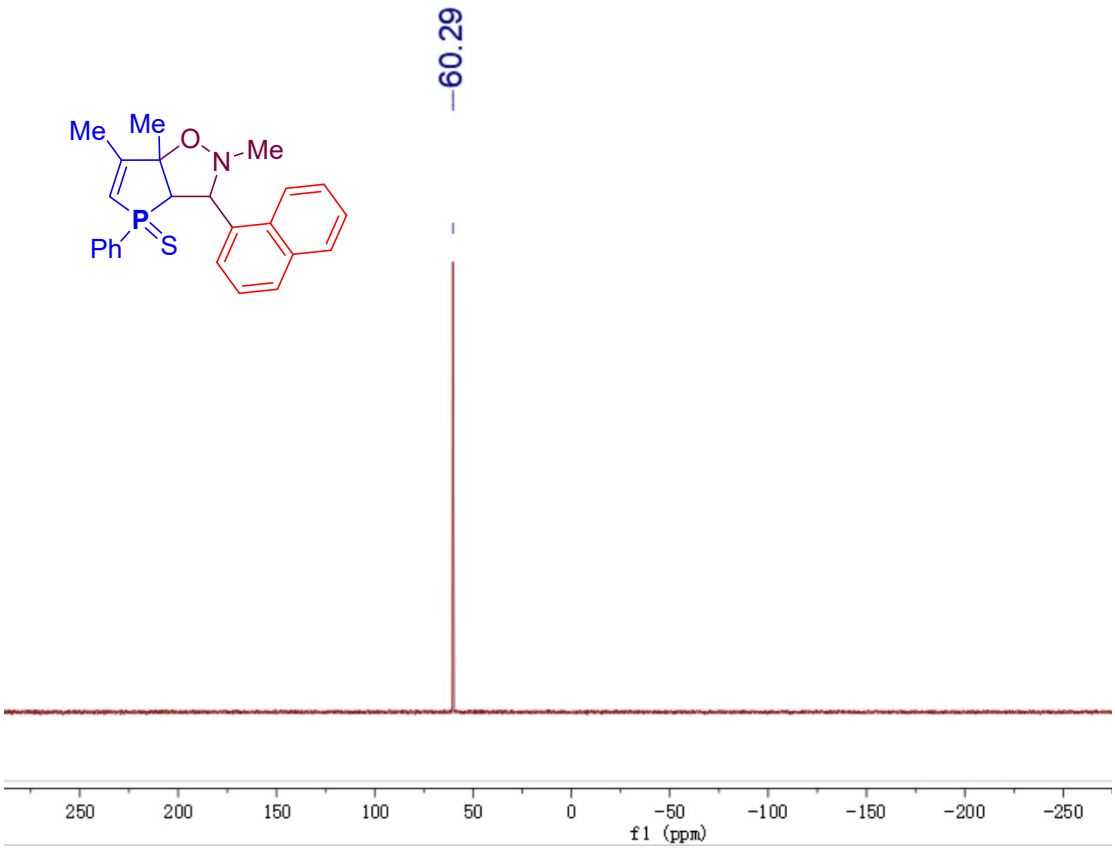


Figure S32. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) of Compound 3h

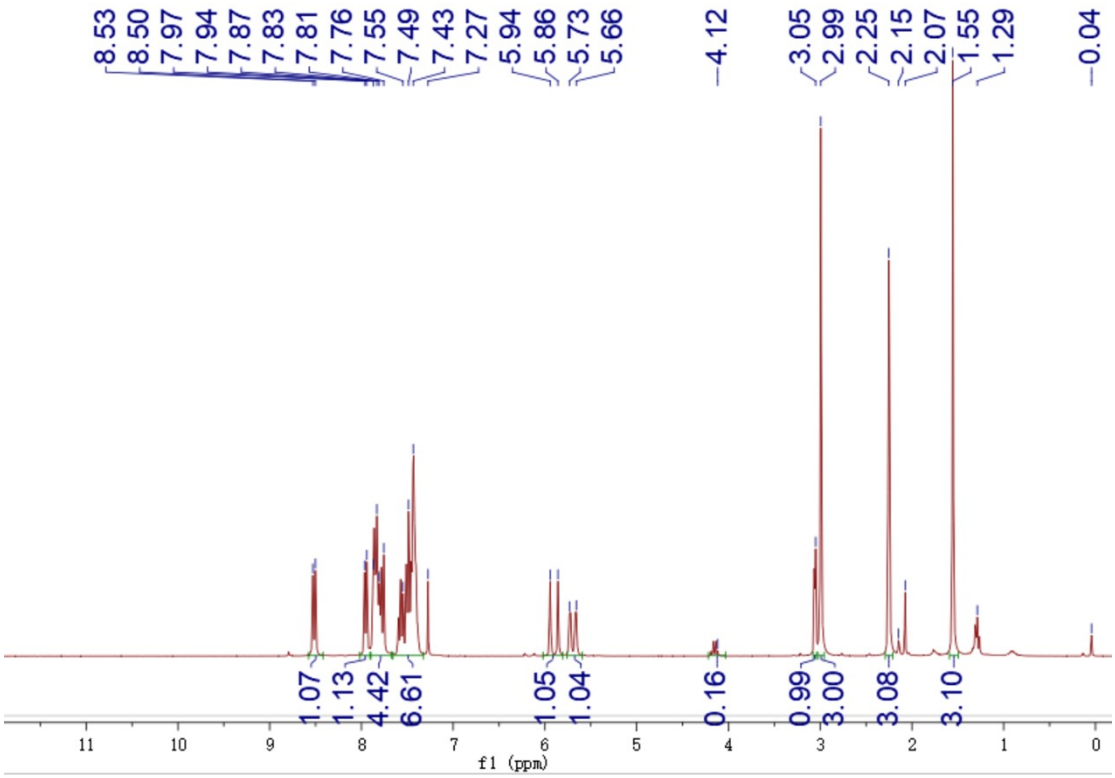


Figure S33. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3h

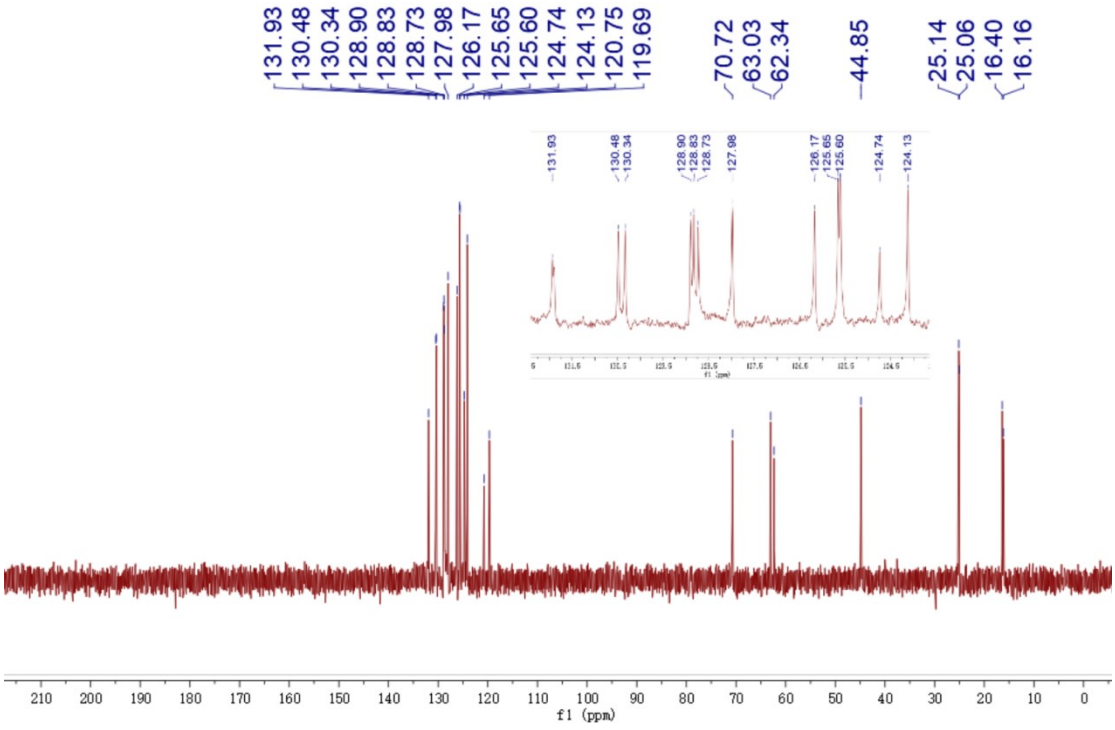


Figure S34. ^{135}Dept NMR (75 MHz, $CDCl_3$) of Compound 3h

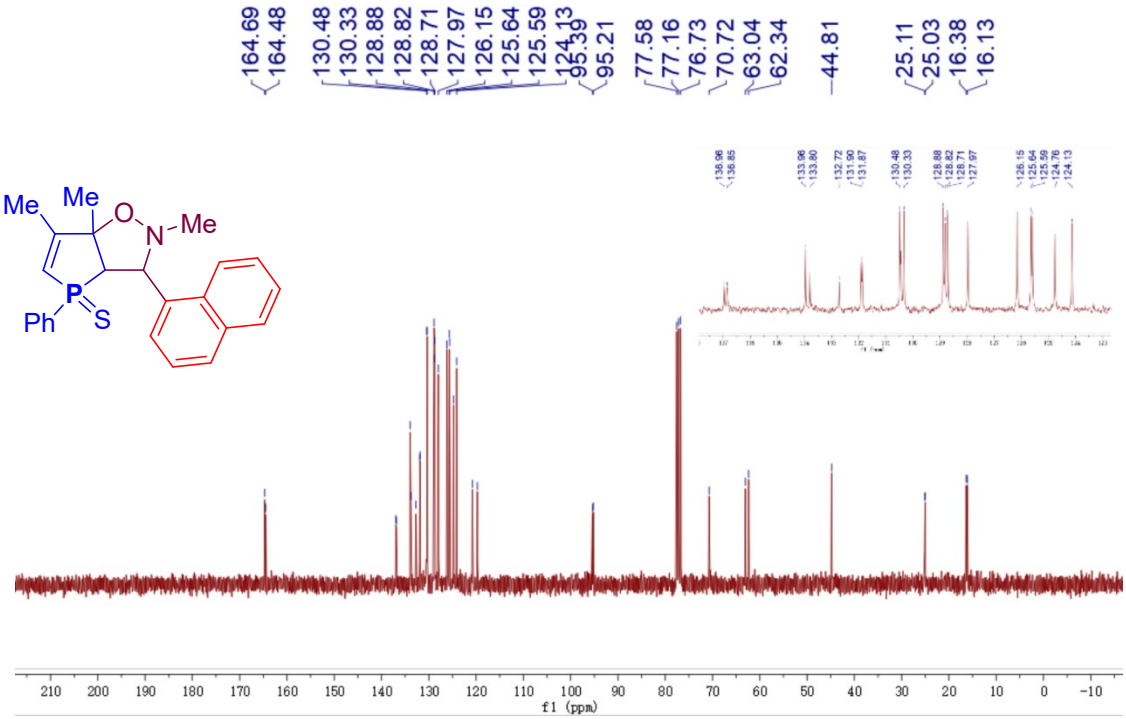


Figure S35. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3h

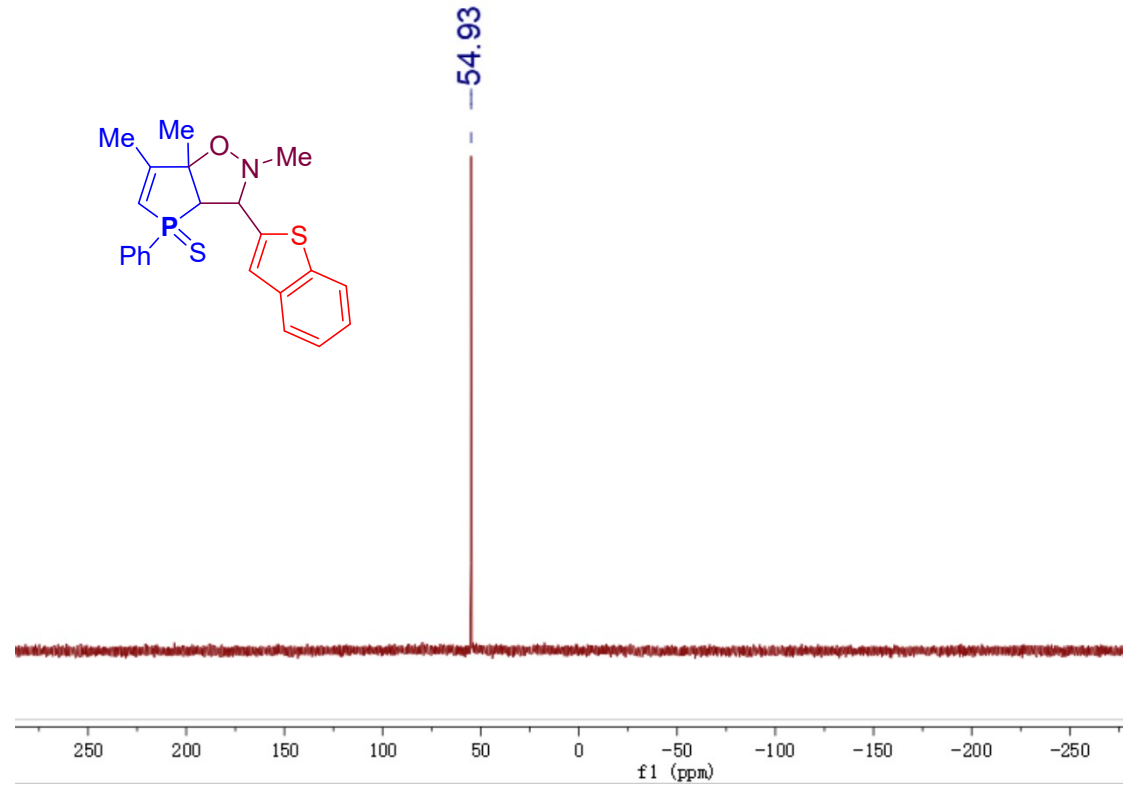


Figure S36. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) of Compound 3i

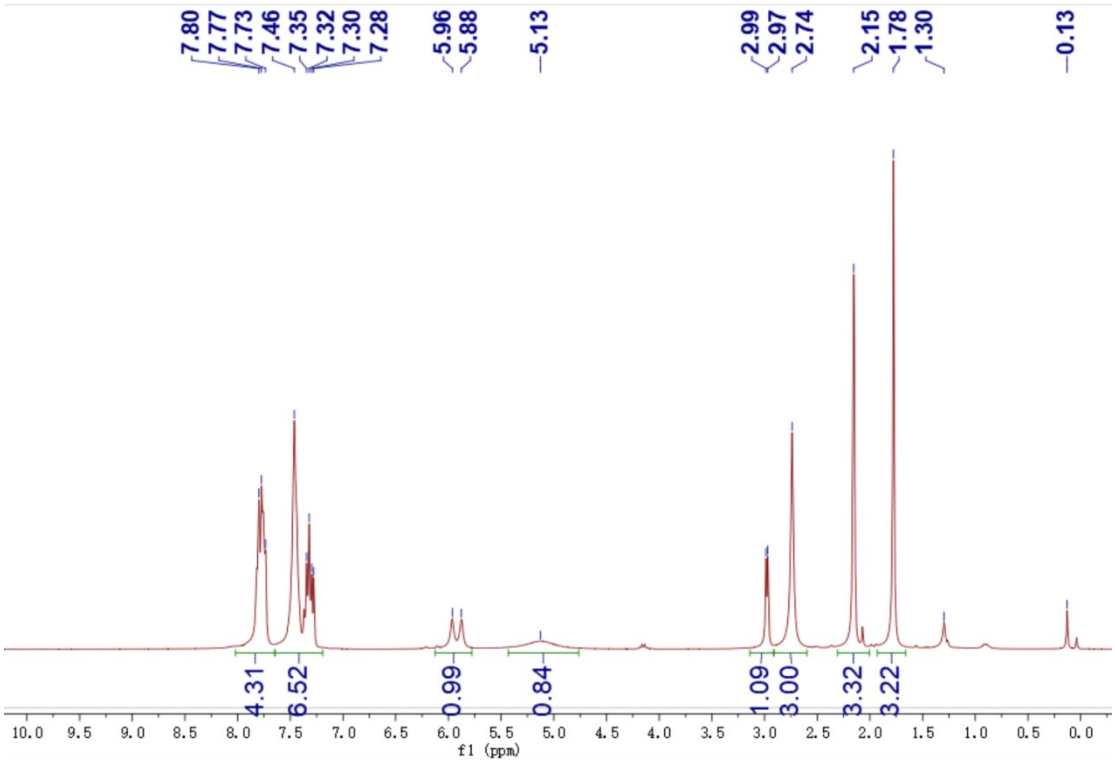


Figure S37. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3i

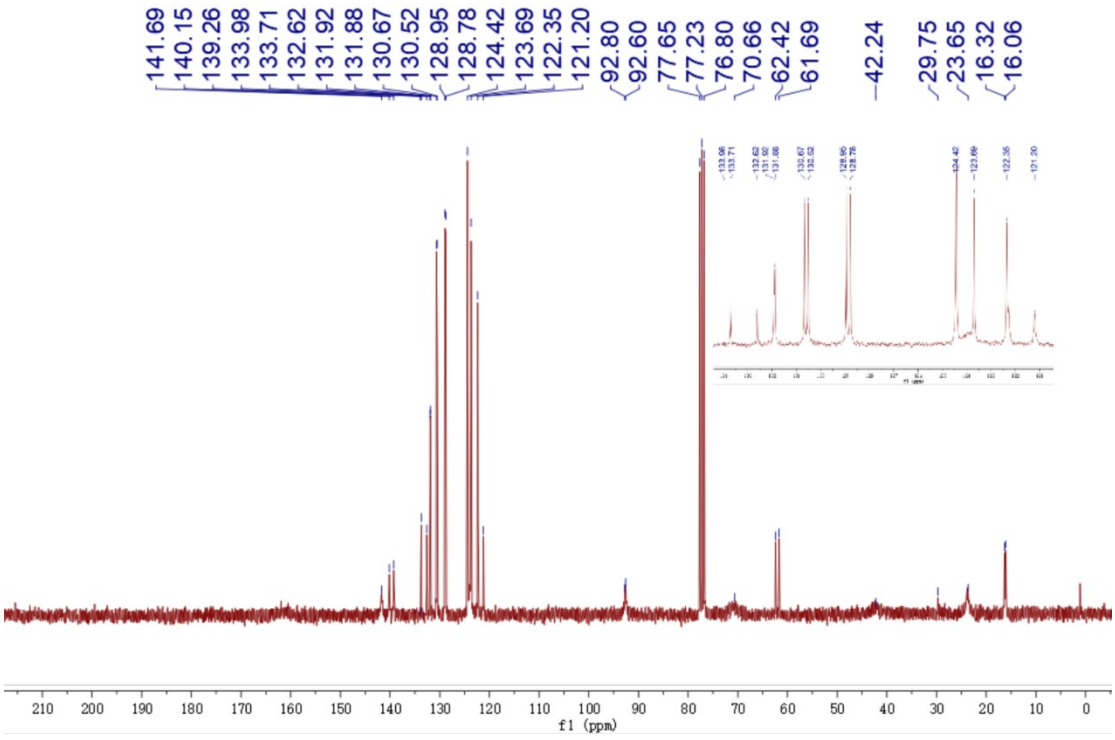


Figure S38. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of Compound 3i

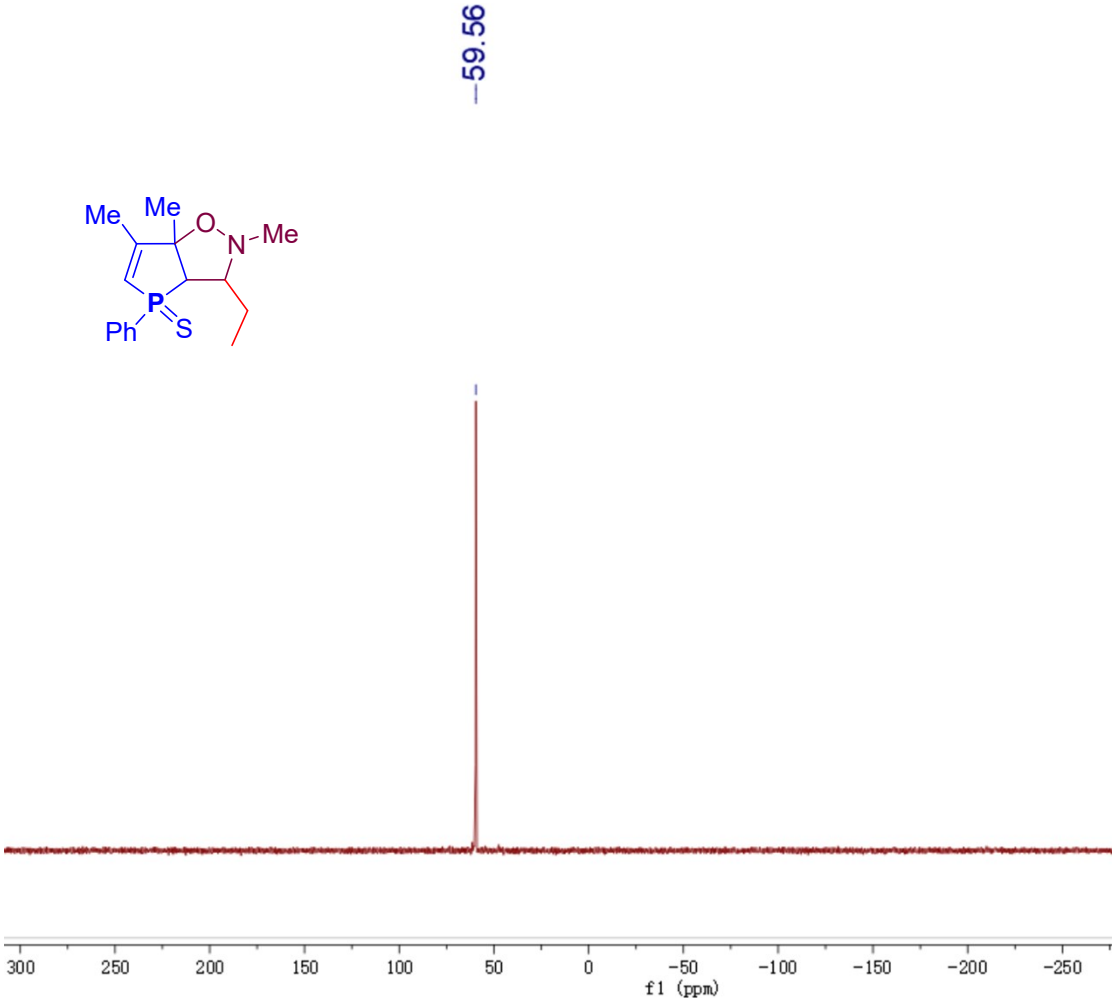


Figure S39. ^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of Compound 3j

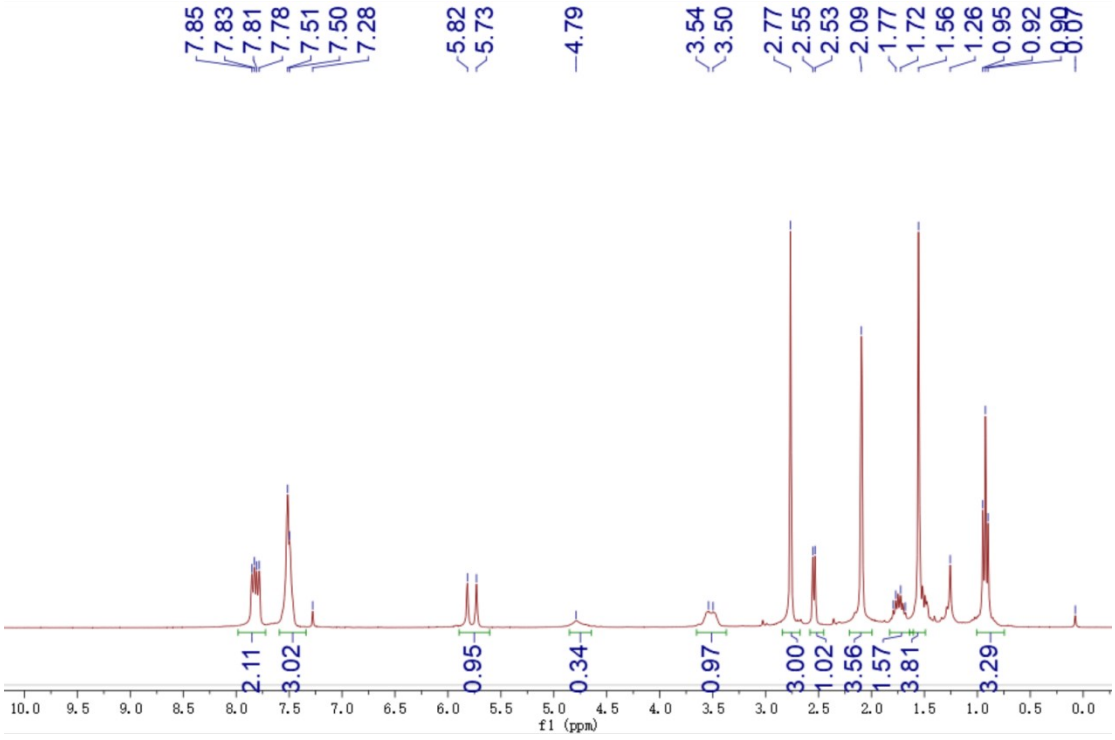


Figure S40. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3j

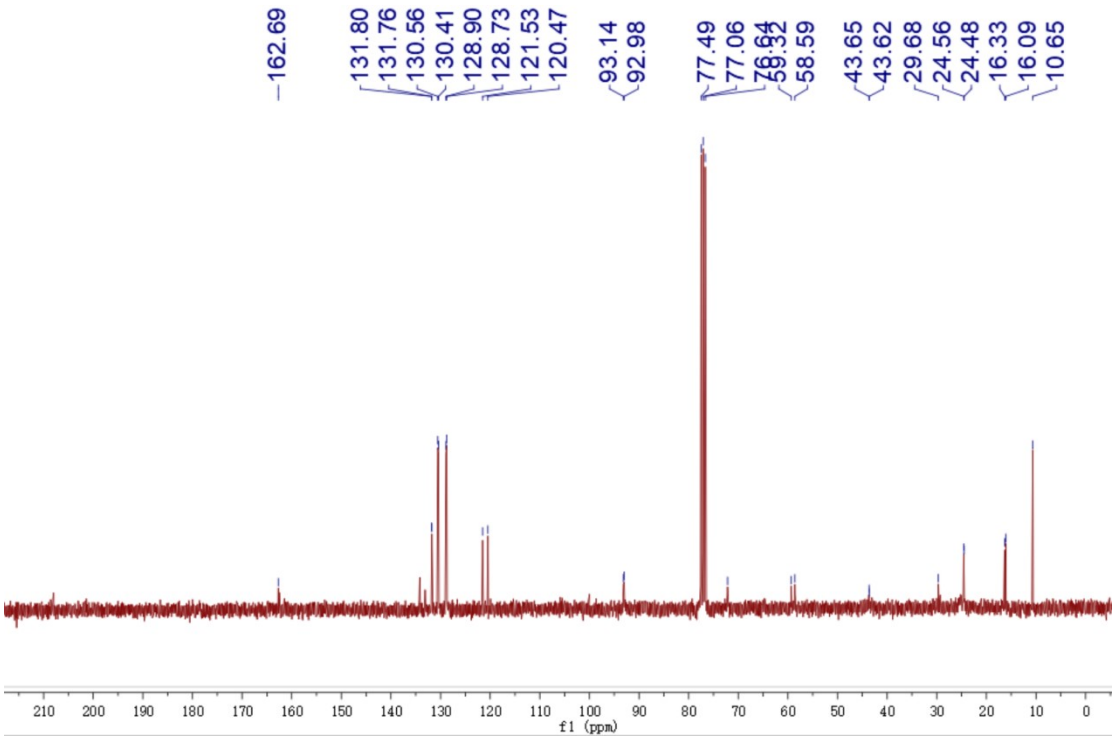


Figure S41. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3j

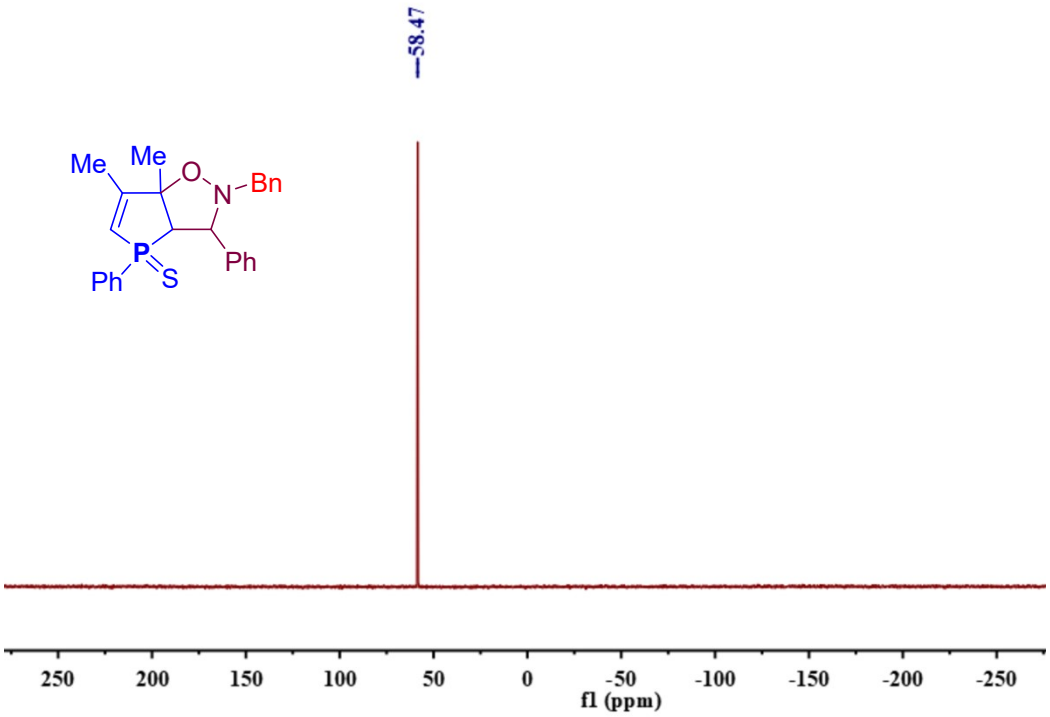


Figure S42. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) of Compound 3k

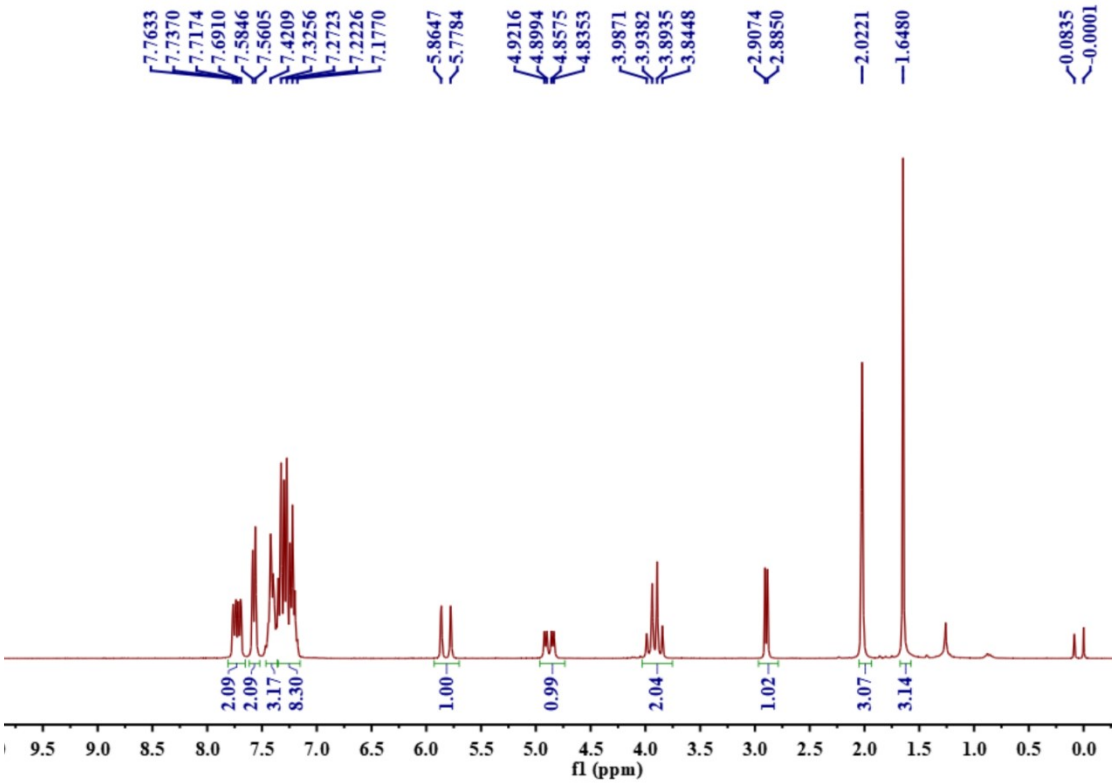


Figure S43. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3k

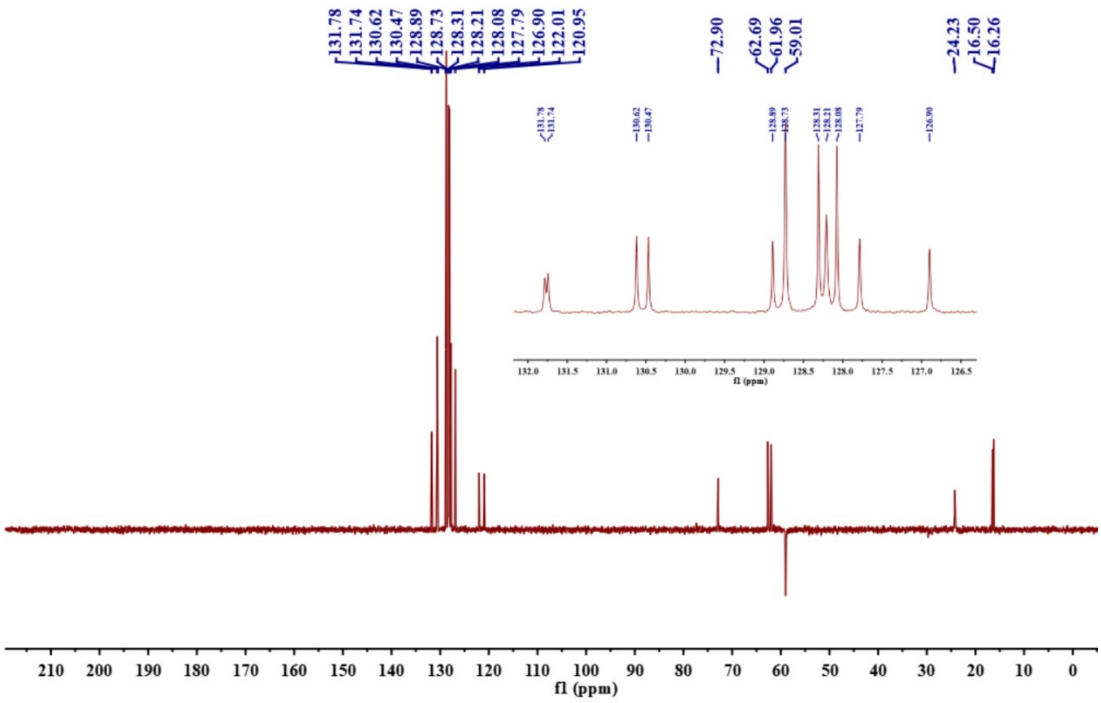


Figure S44. ^{135}Dept NMR (75 MHz, $CDCl_3$) of Compound 3k

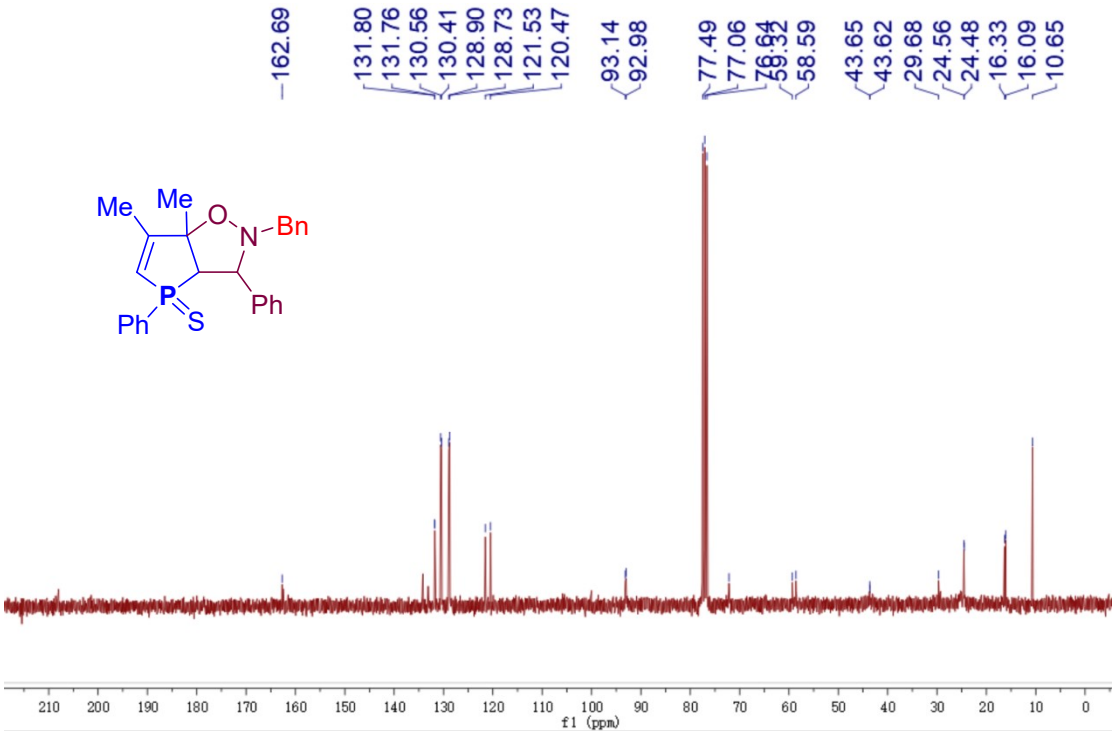


Figure S45. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3k

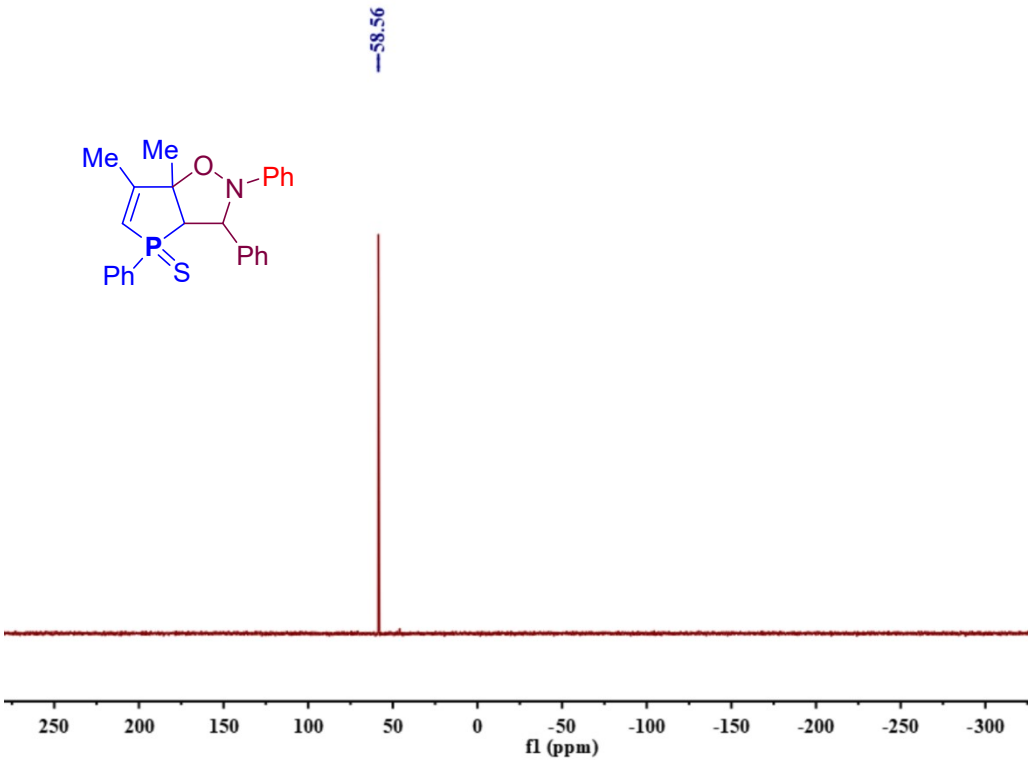


Figure S46. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) of Compound 3l

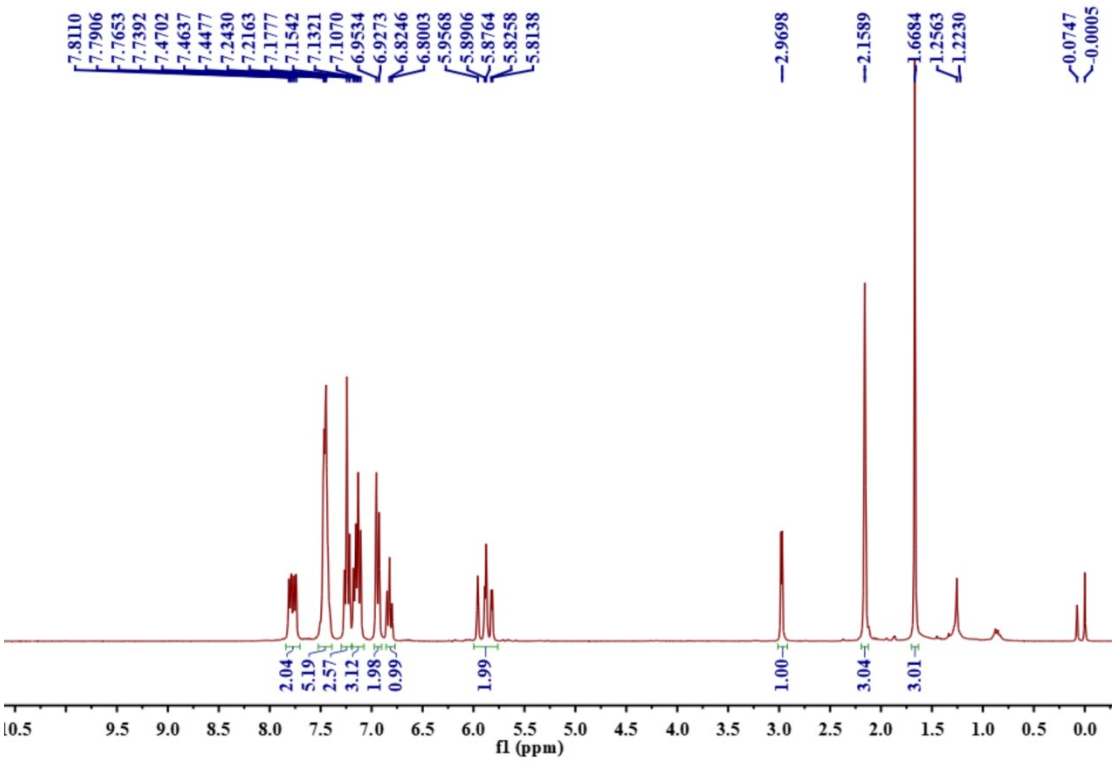


Figure S47. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3l

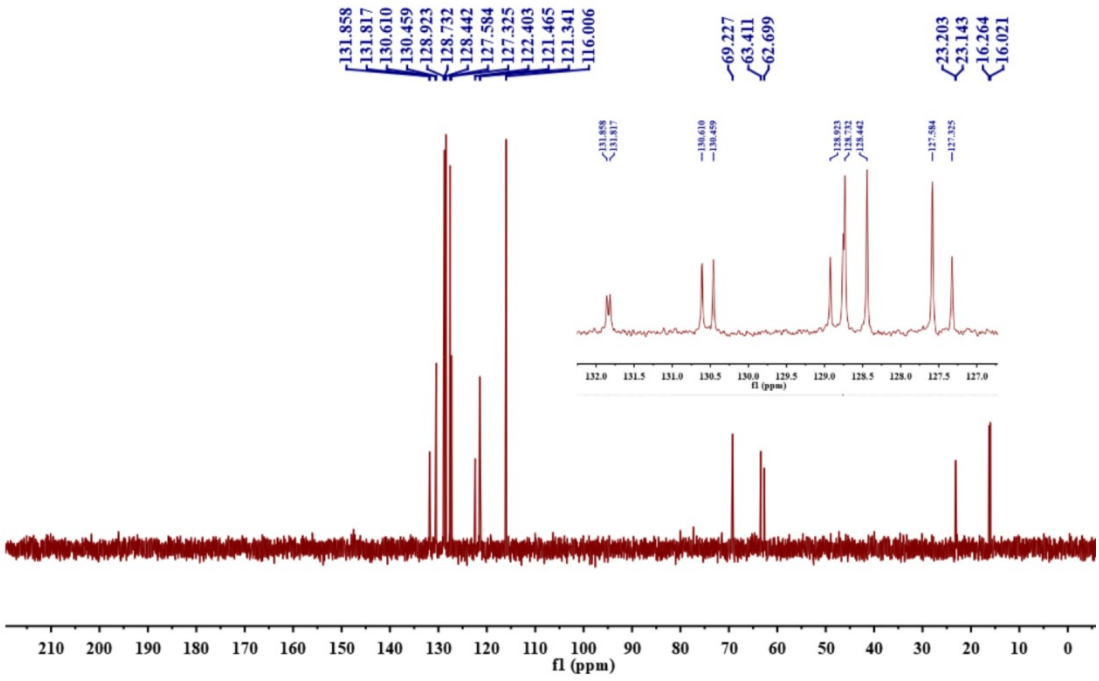


Figure S48. ^{135}Dept NMR (75 MHz, $CDCl_3$) of Compound 3l

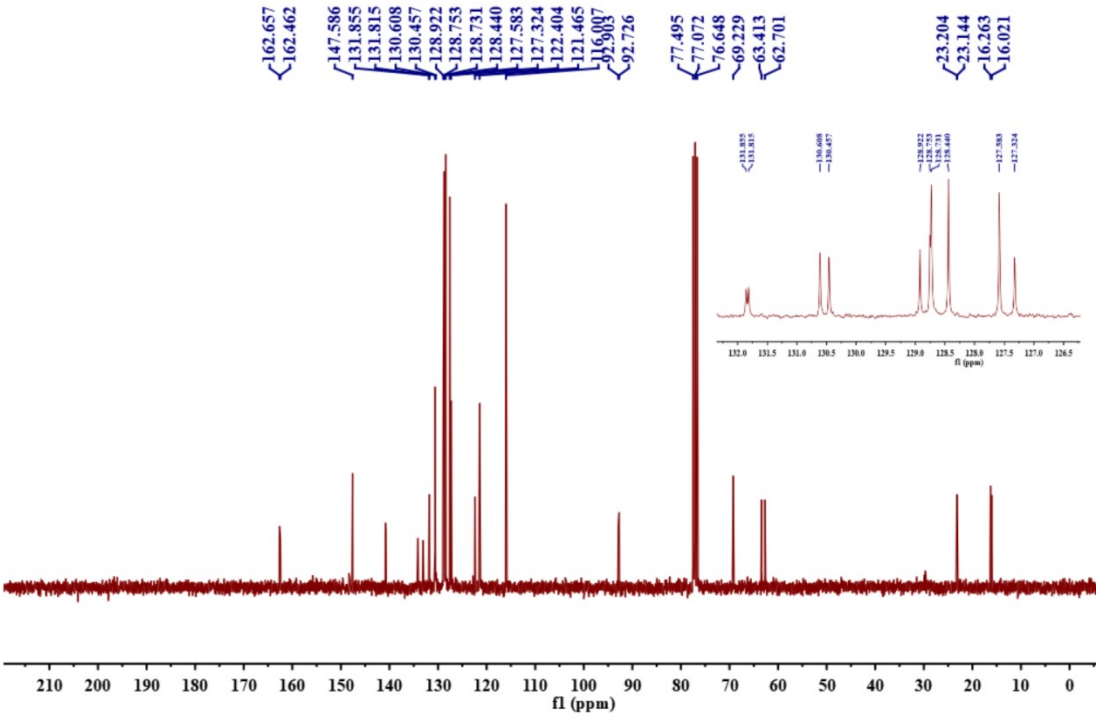


Figure S49. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3l

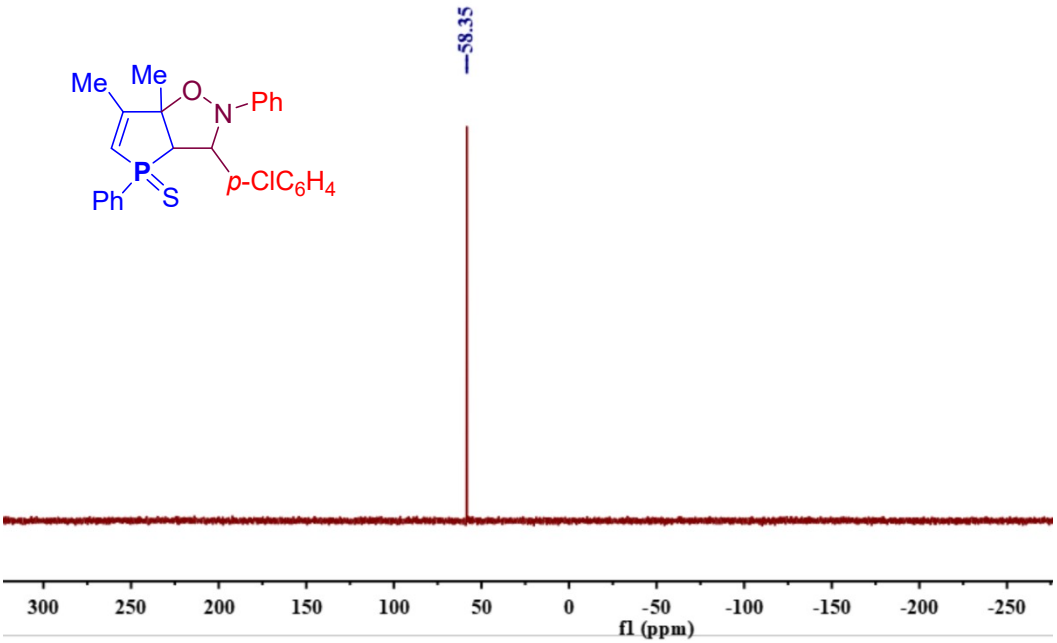


Figure S50. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) of Compound 3m

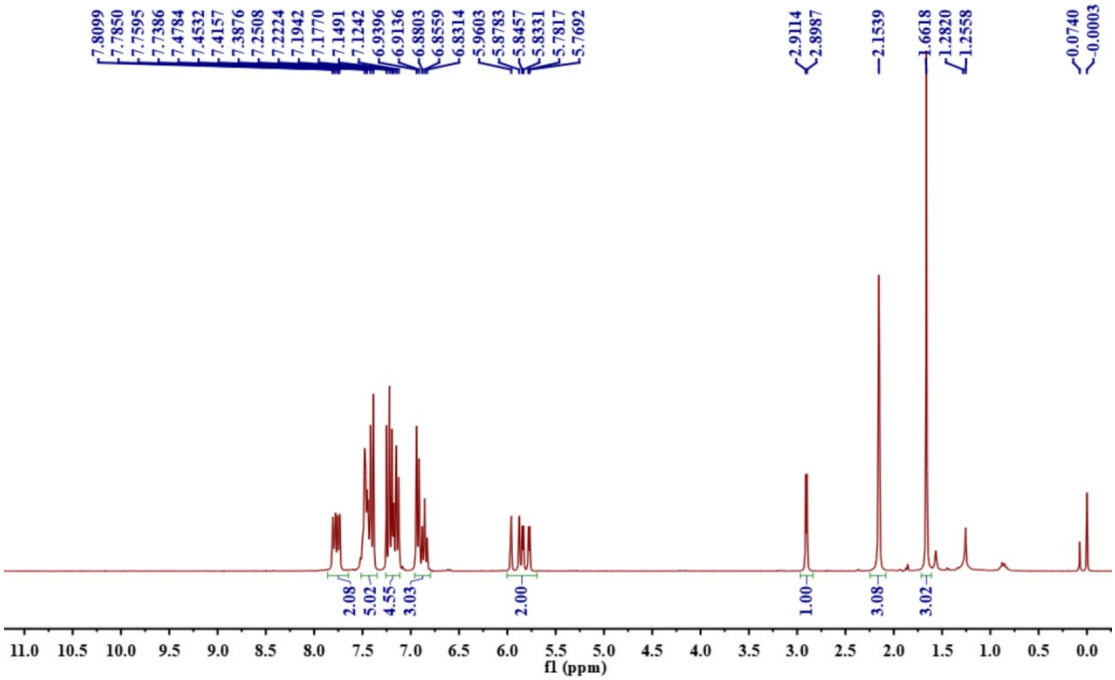


Figure S51. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3m

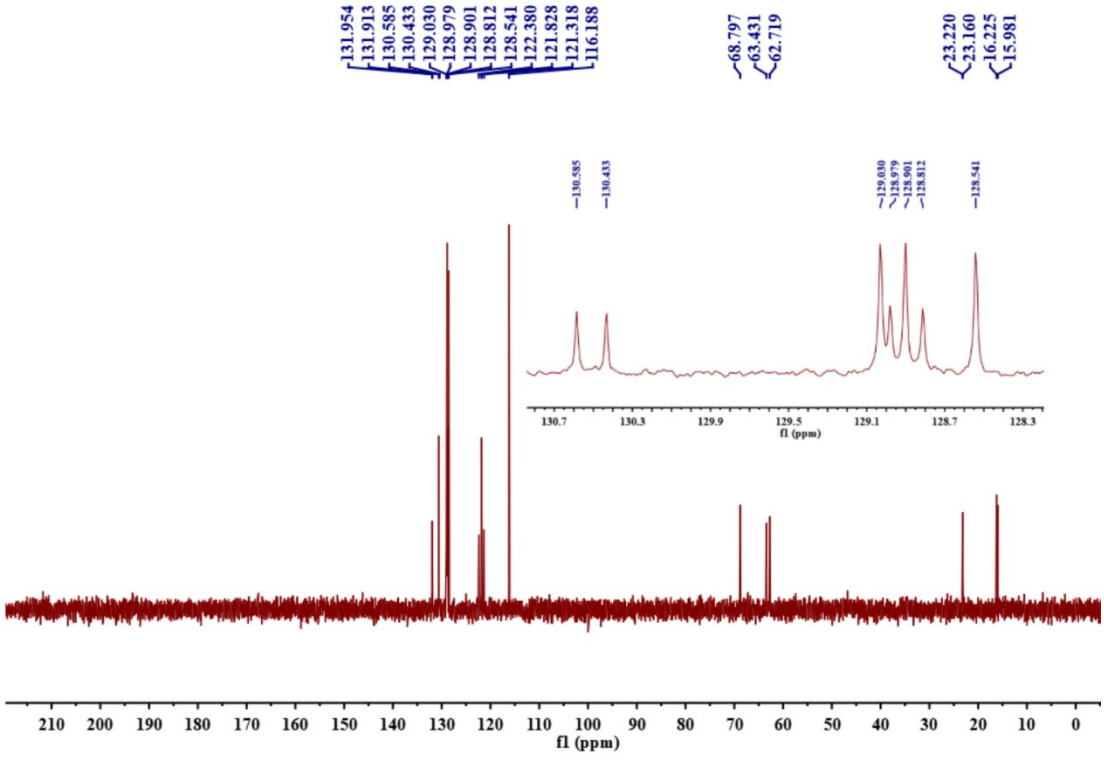


Figure S52. ^{135}Dept NMR (75 MHz, $CDCl_3$) of Compound 3m

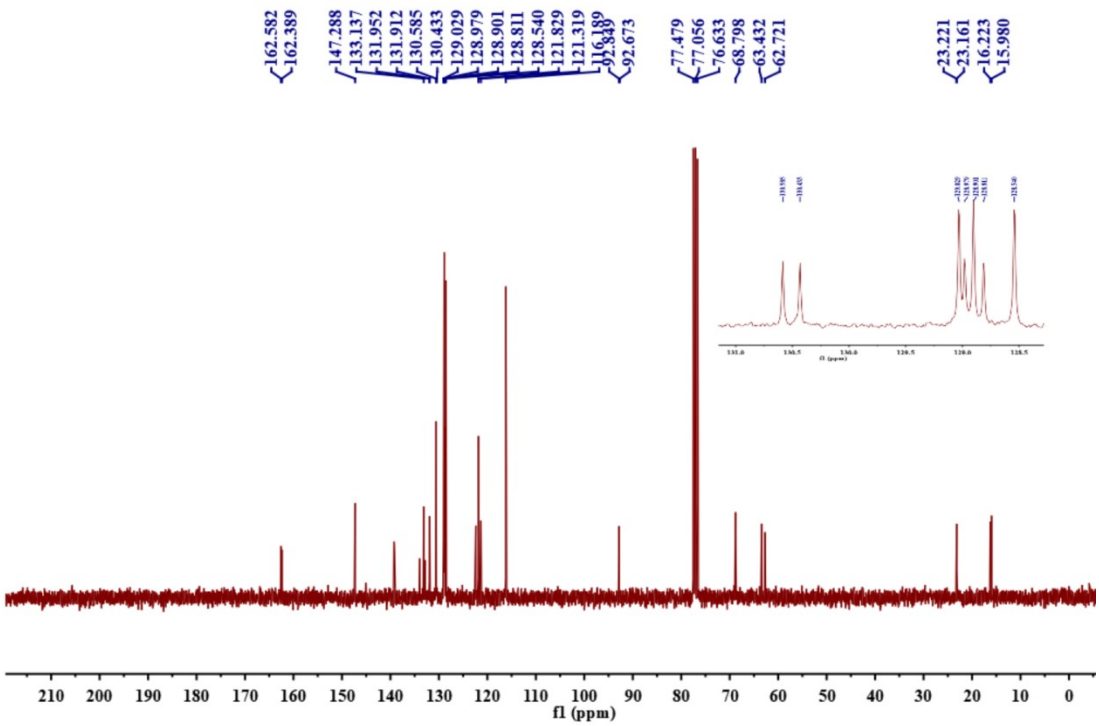


Figure S53. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3m

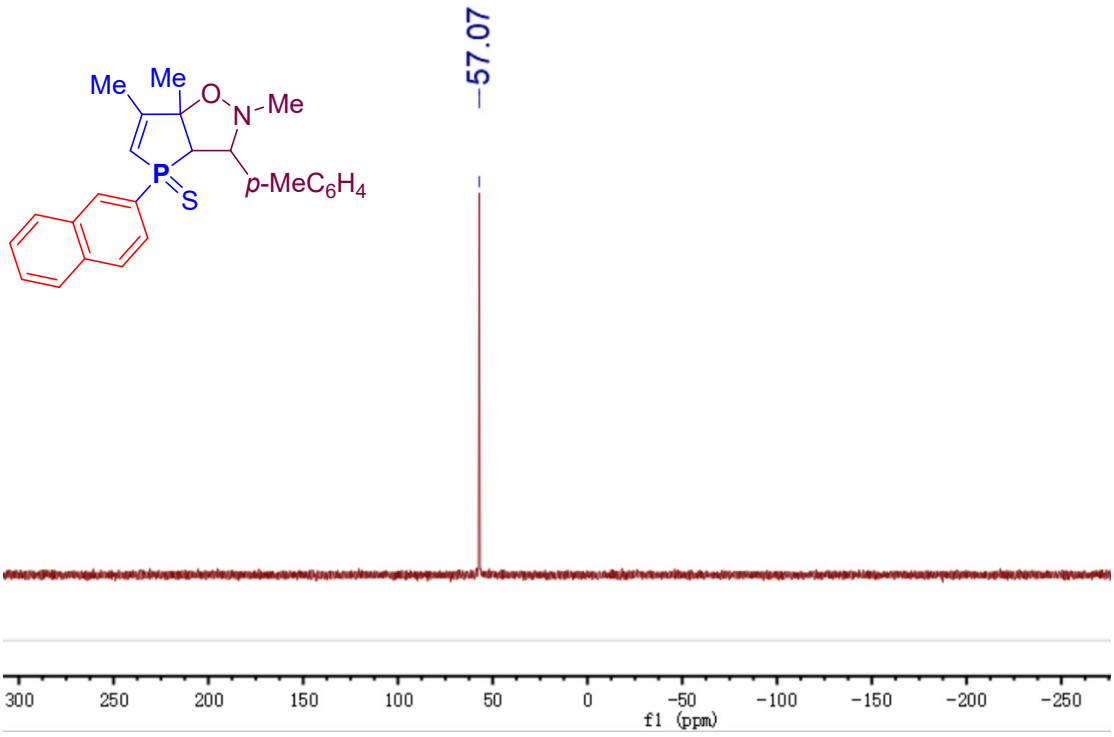


Figure S54. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) of Compound 3bb

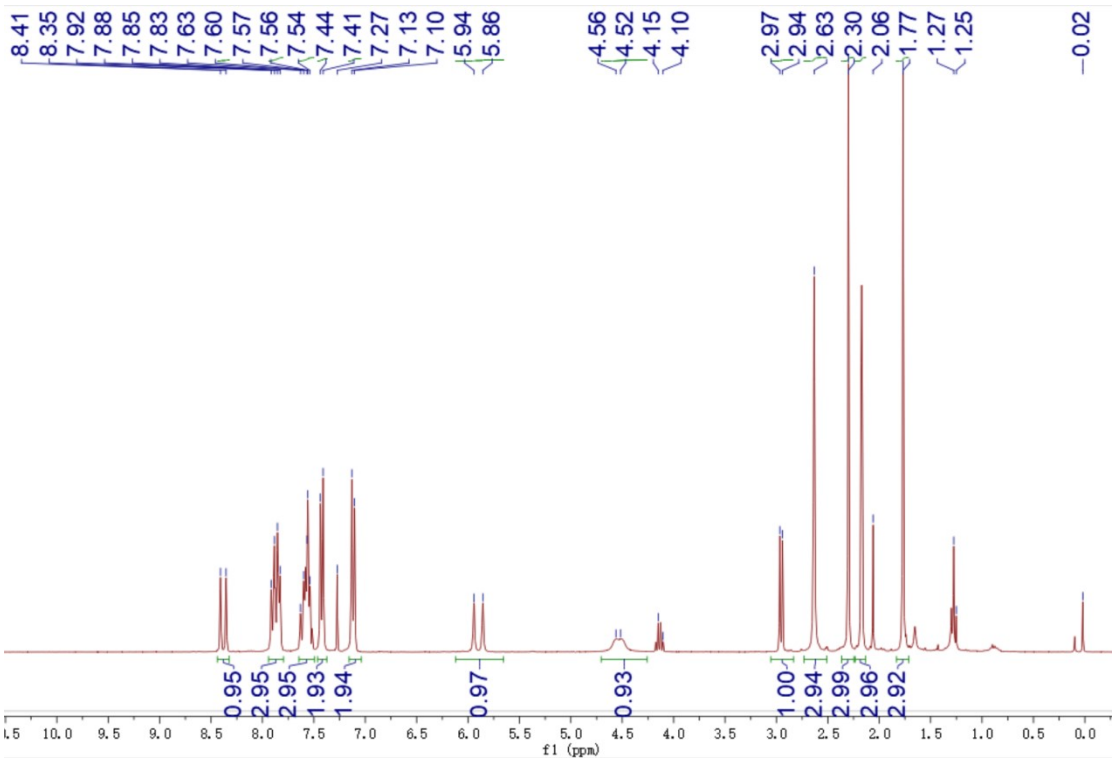


Figure S55. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3bb

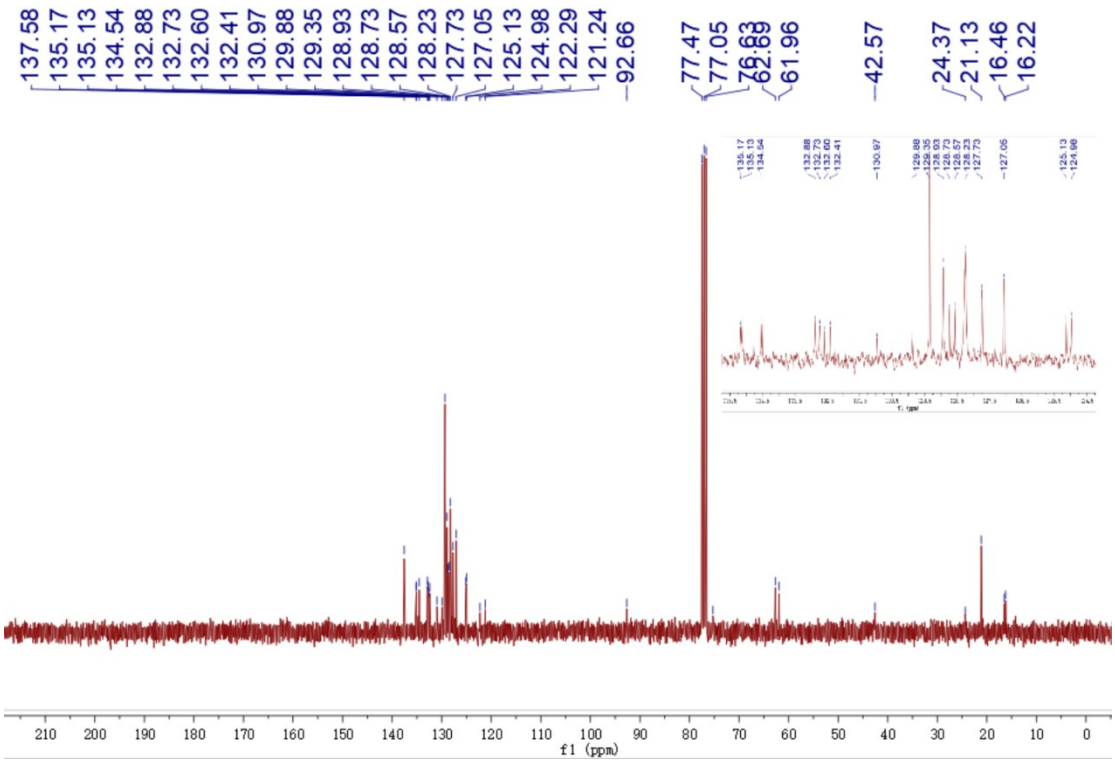


Figure S56. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of Compound 3bb

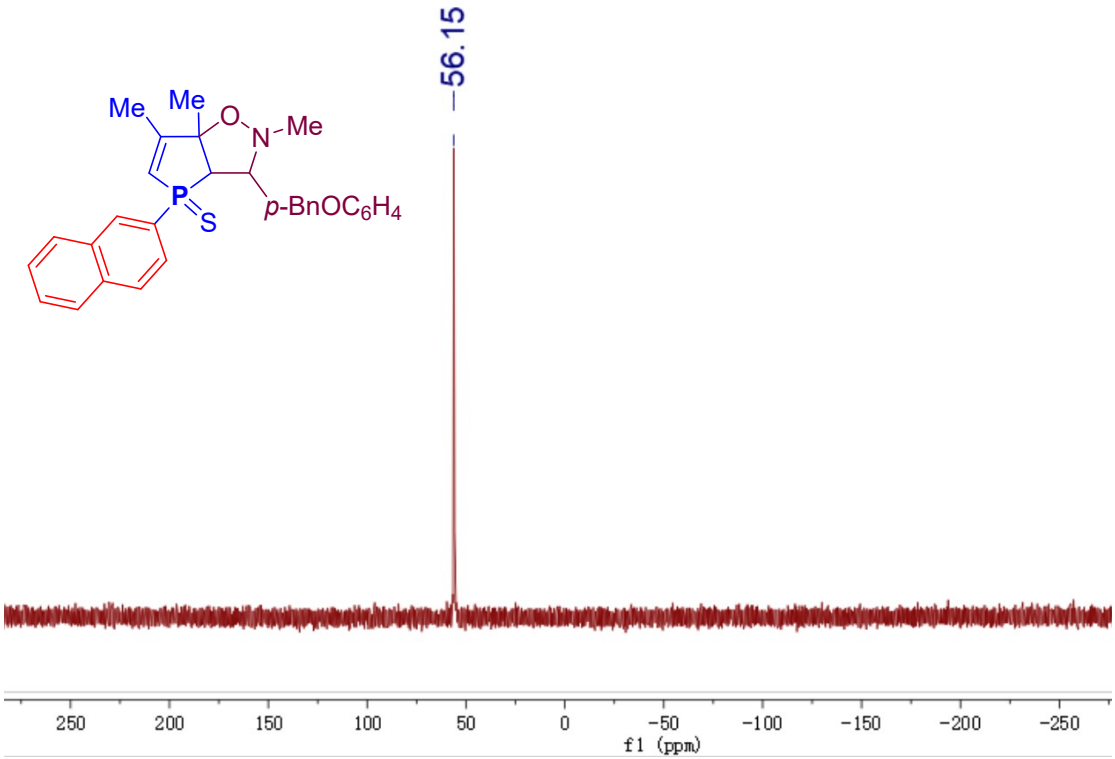


Figure S57. $^{31}P\ \{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) of Compound 3bd

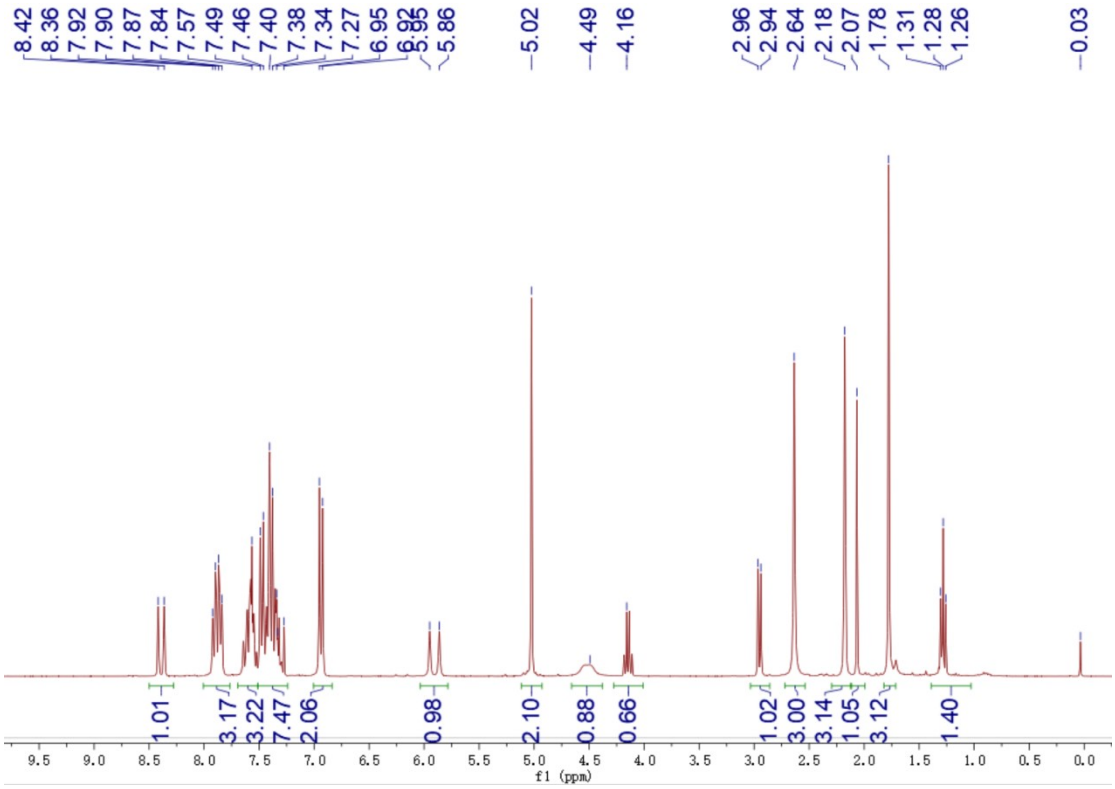


Figure S58. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3bd

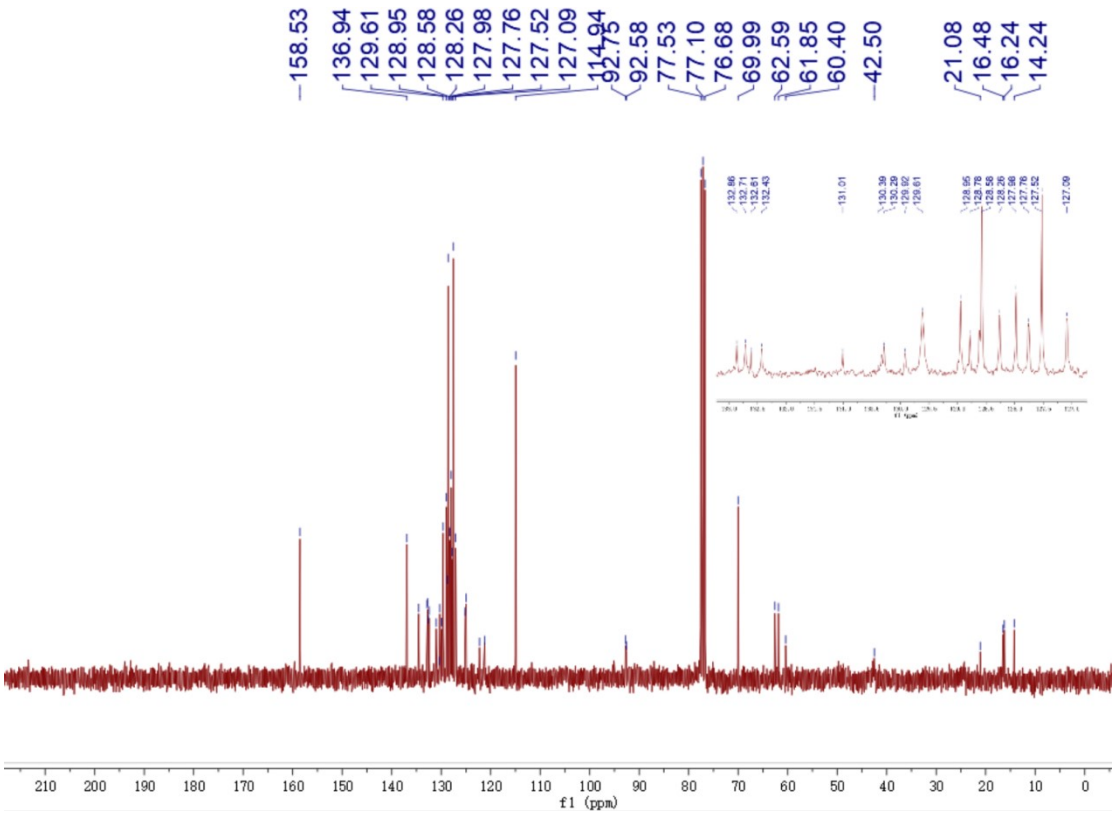


Figure S59. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3bd

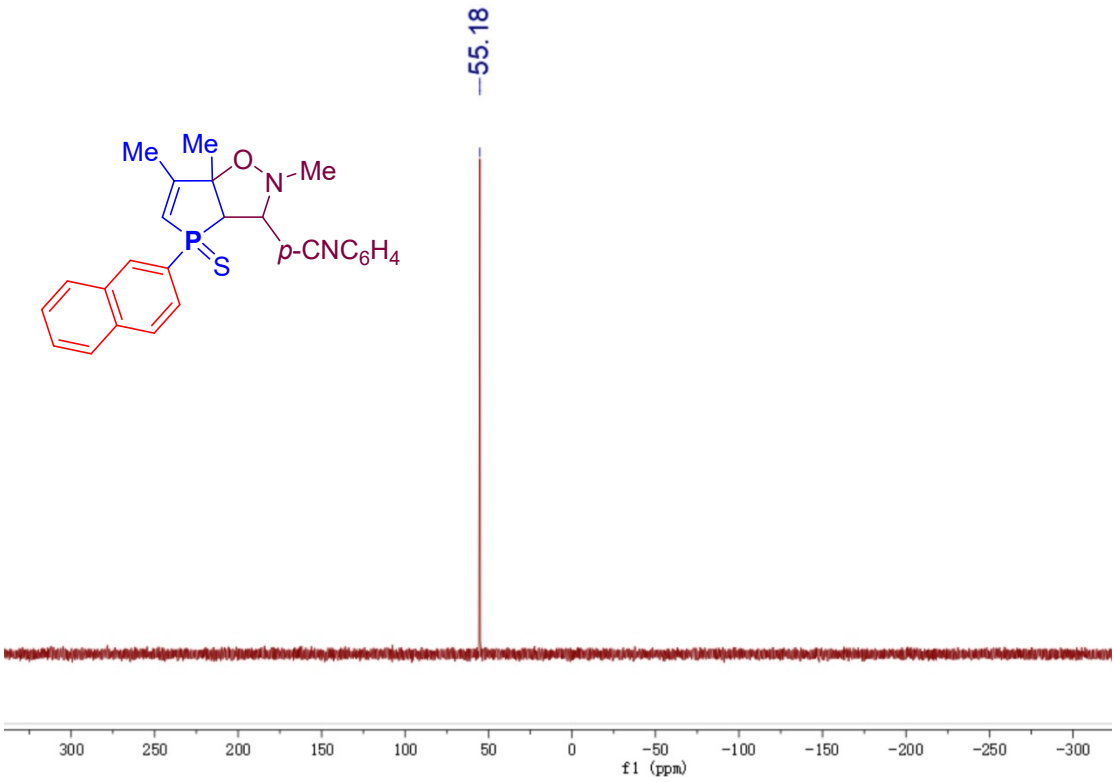


Figure S60. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) of Compound 3bg

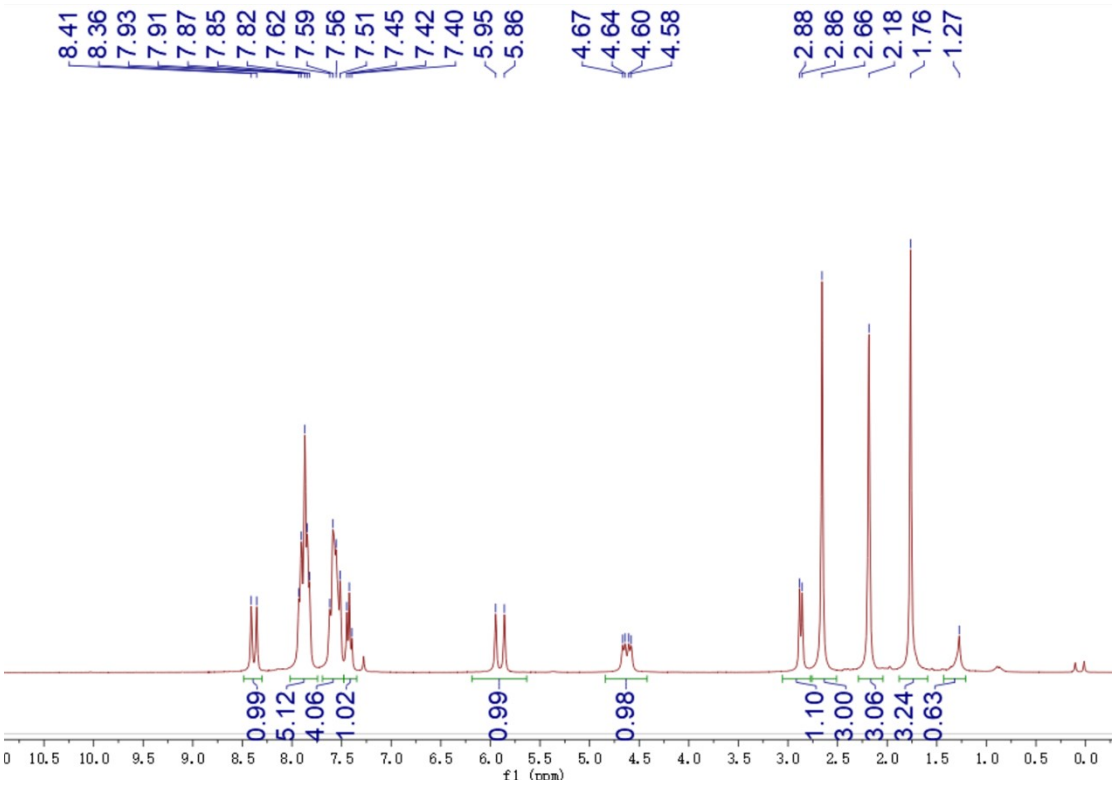


Figure S61. ^{135}Dept NMR (75 MHz, $CDCl_3$) of Compound 3bg

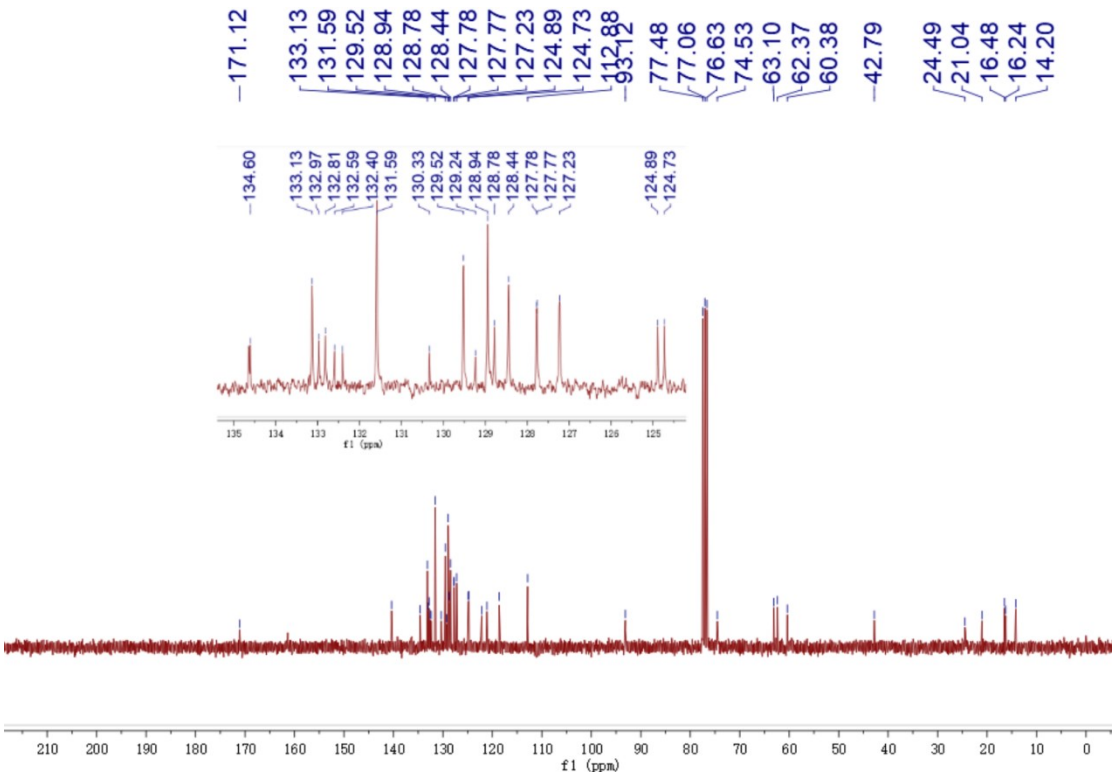


Figure S62. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3bg

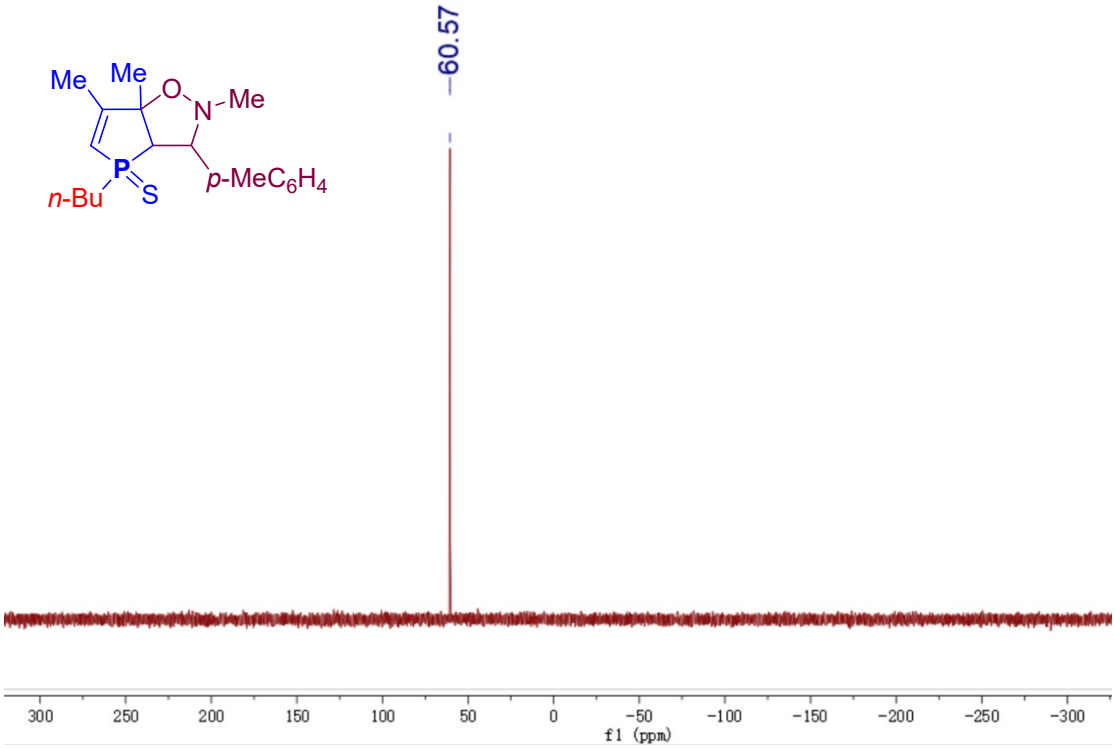


Figure S63. ^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of Compound 3cb

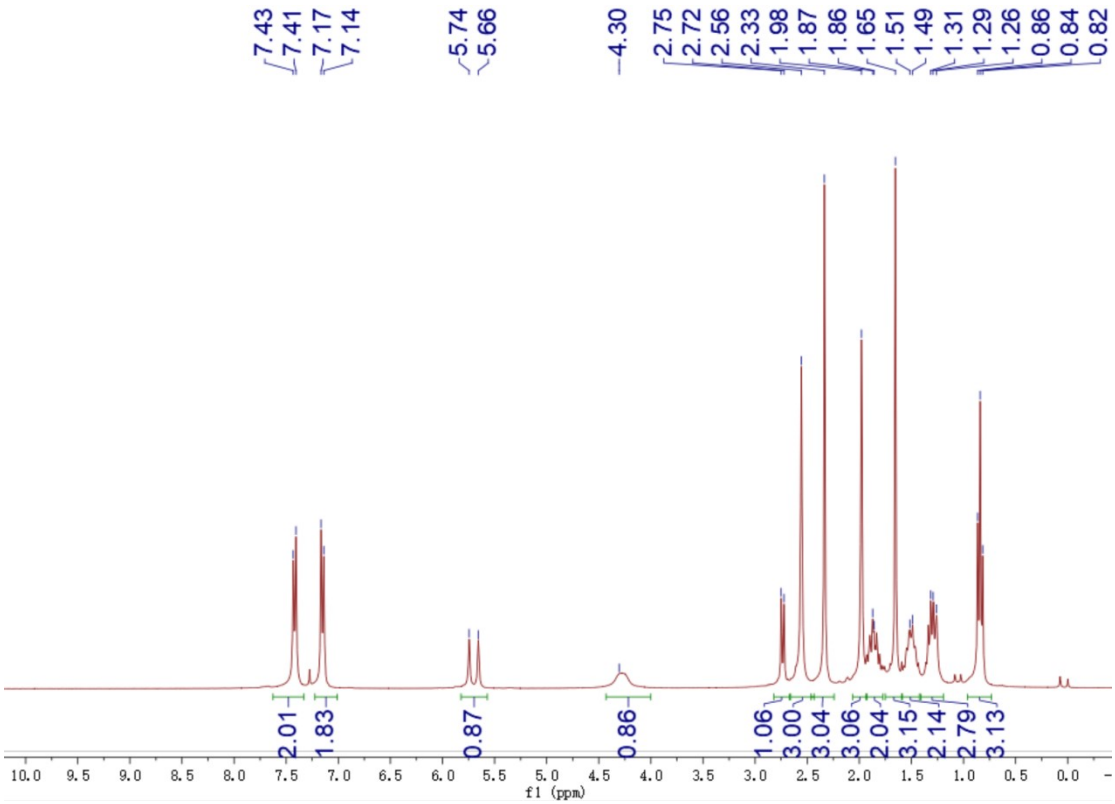


Figure S64. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3cb

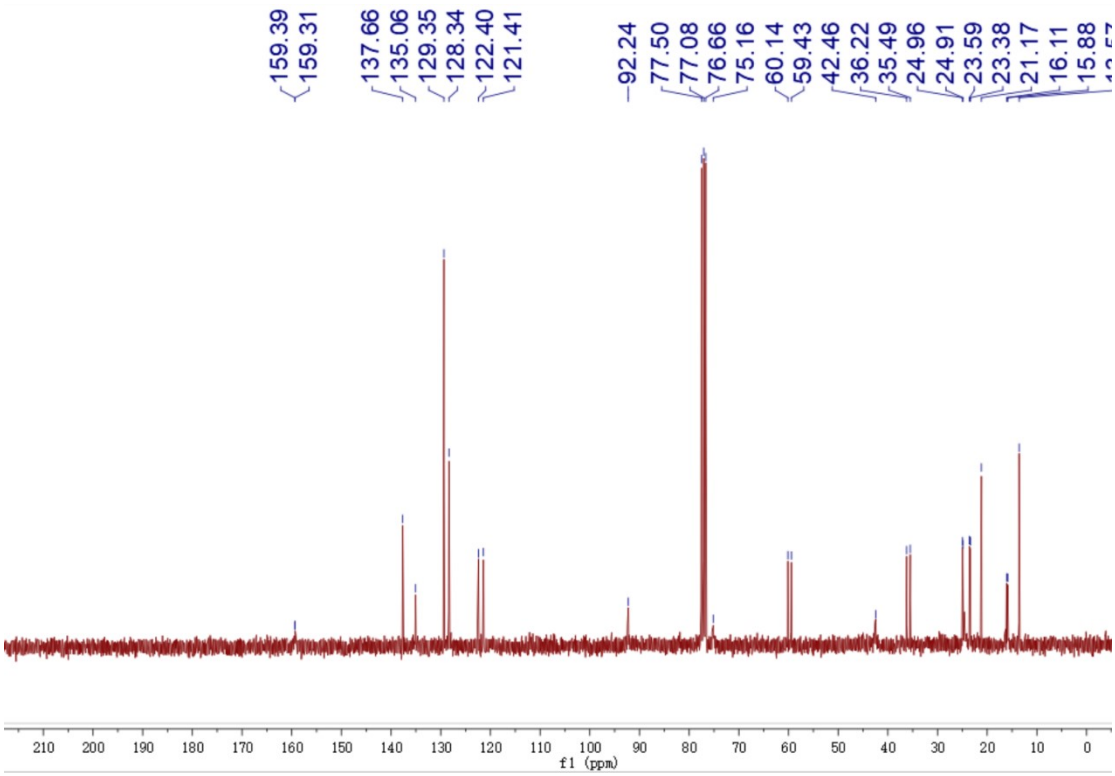


Figure S65. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3cb

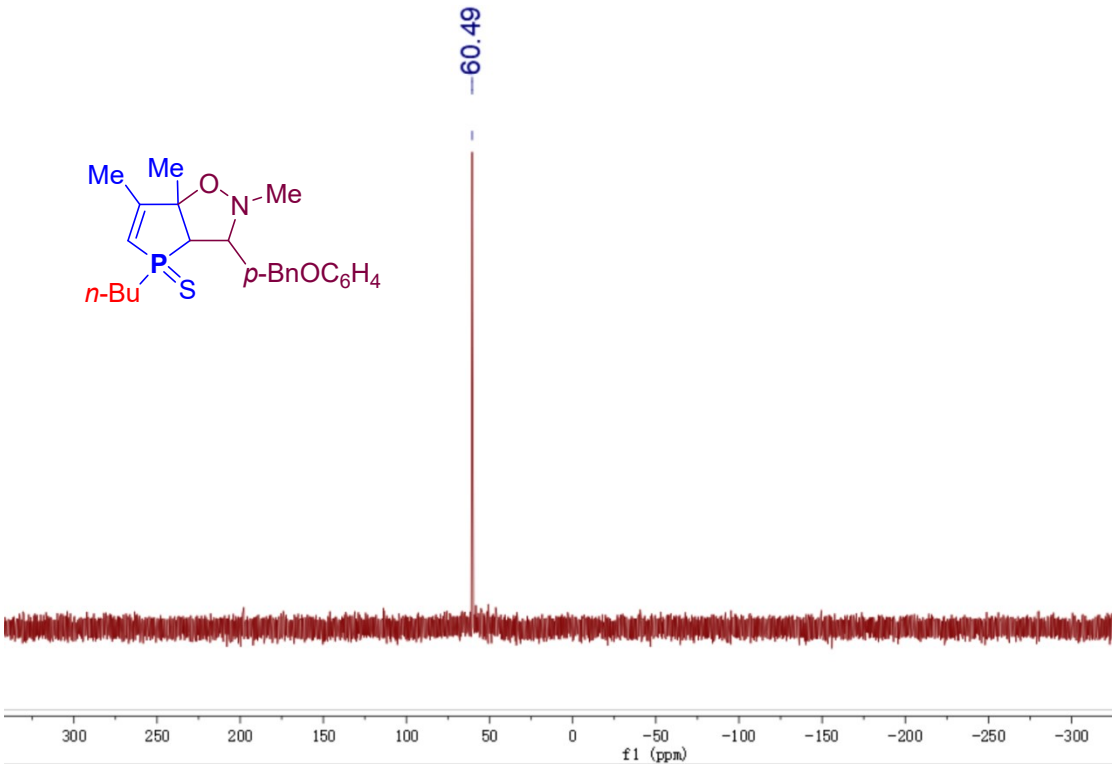


Figure S66. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) of Compound 3cd

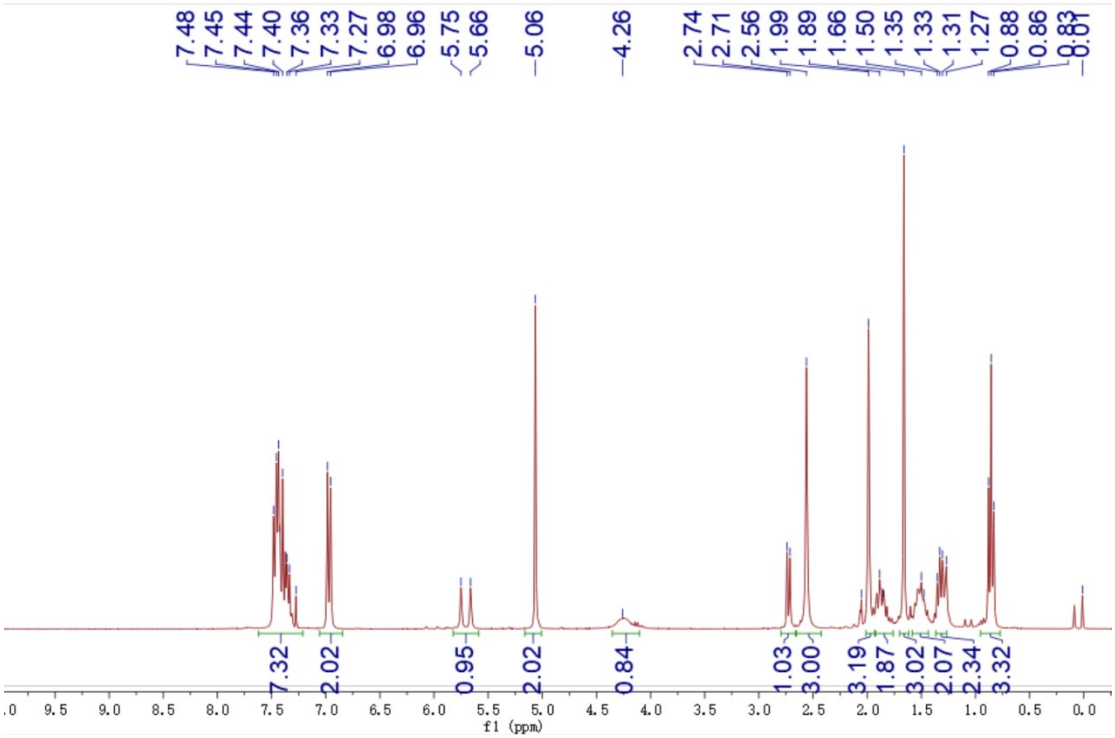


Figure S67. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3cd

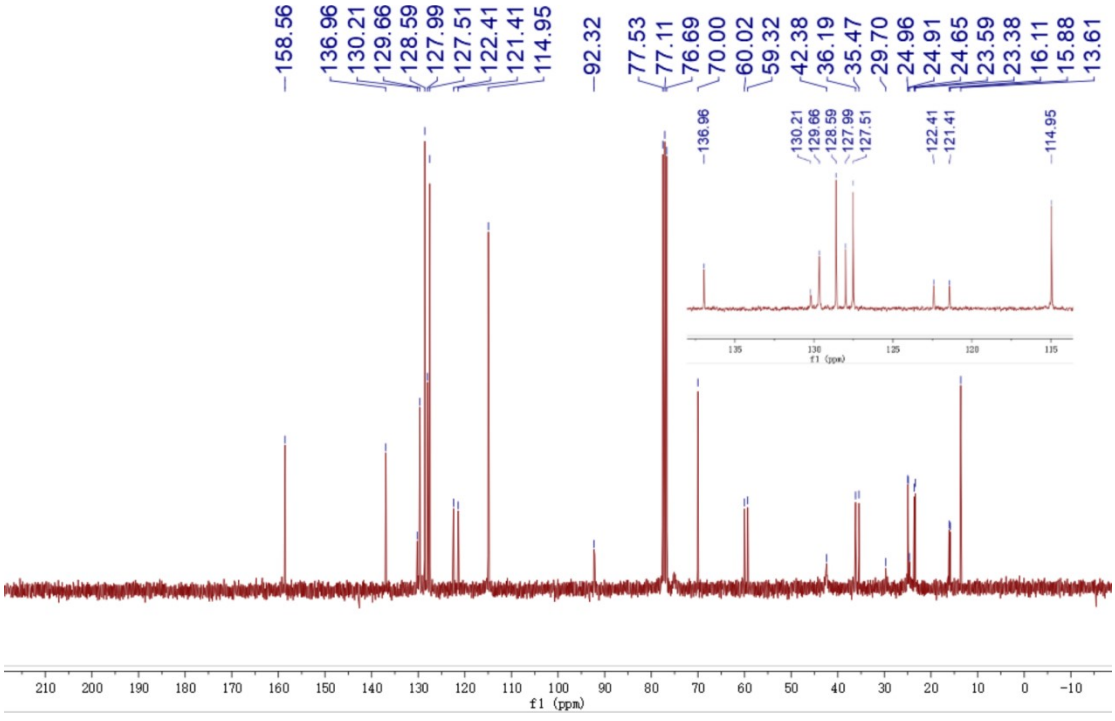


Figure S68. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3cd

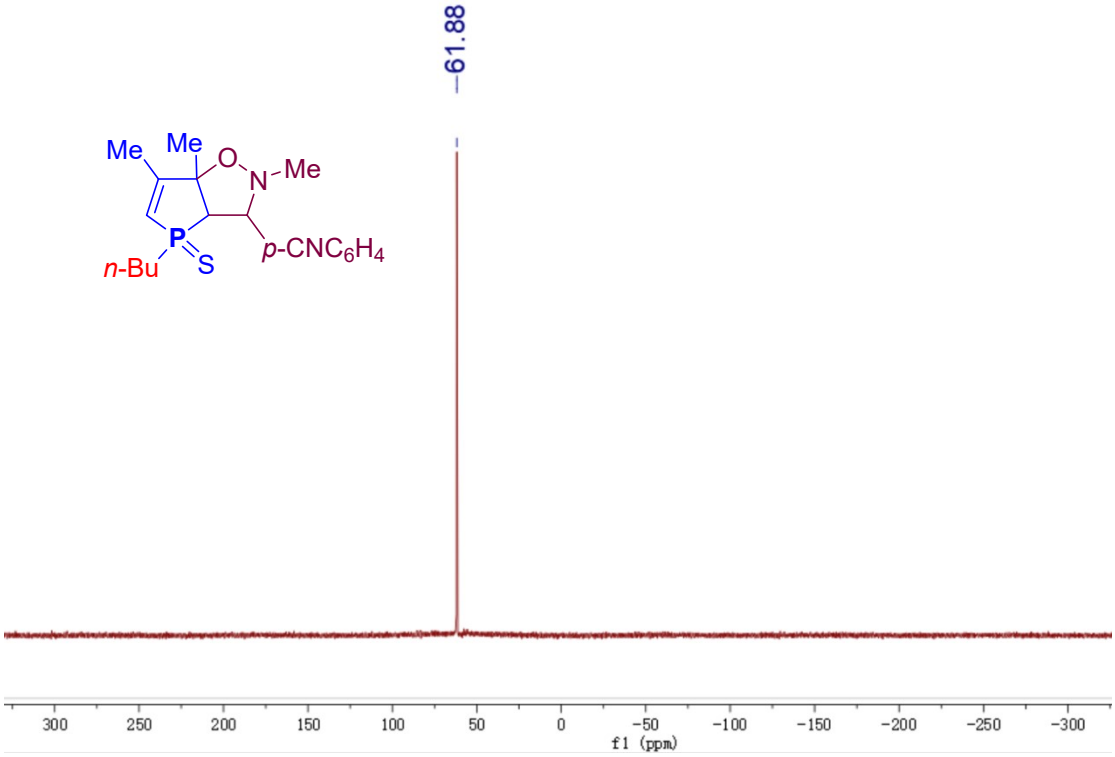


Figure S69. ^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of Compound 3cg

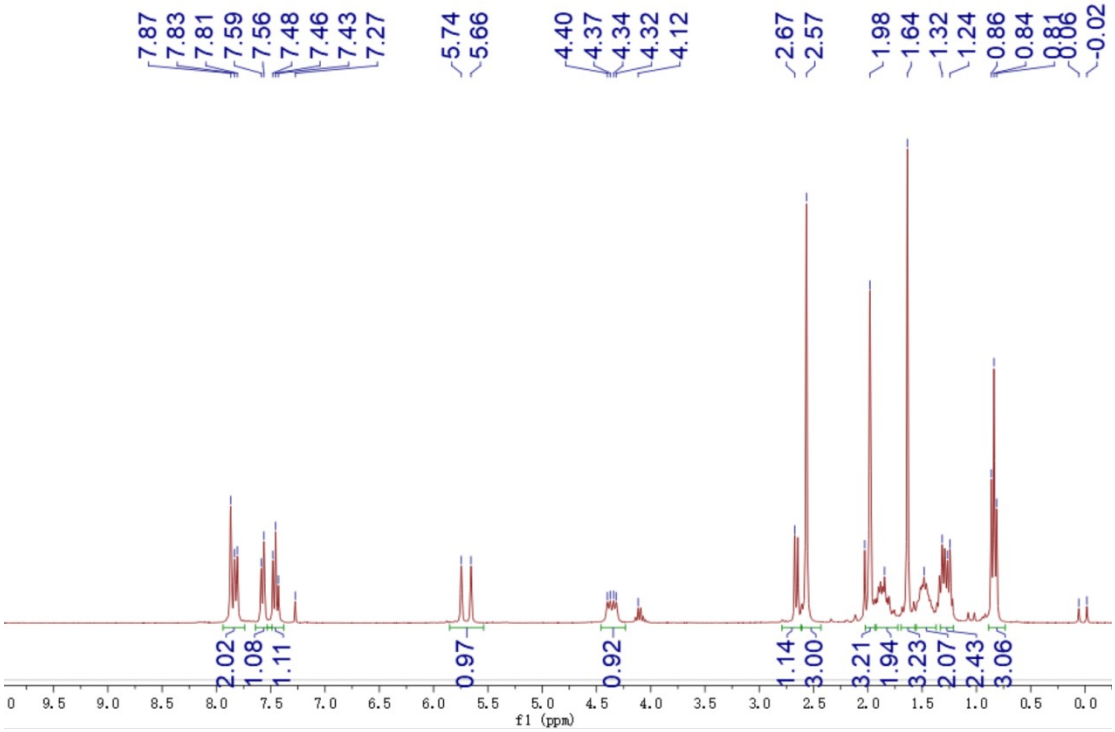


Figure S70. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3cg

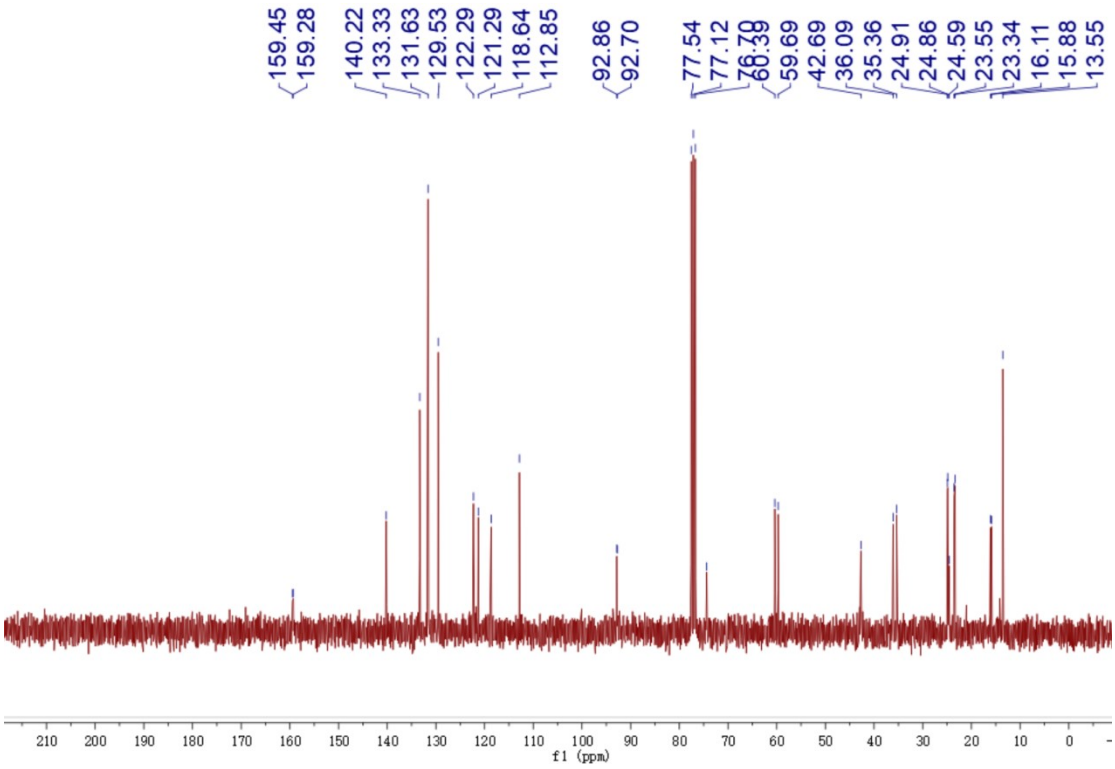


Figure S71. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3cg

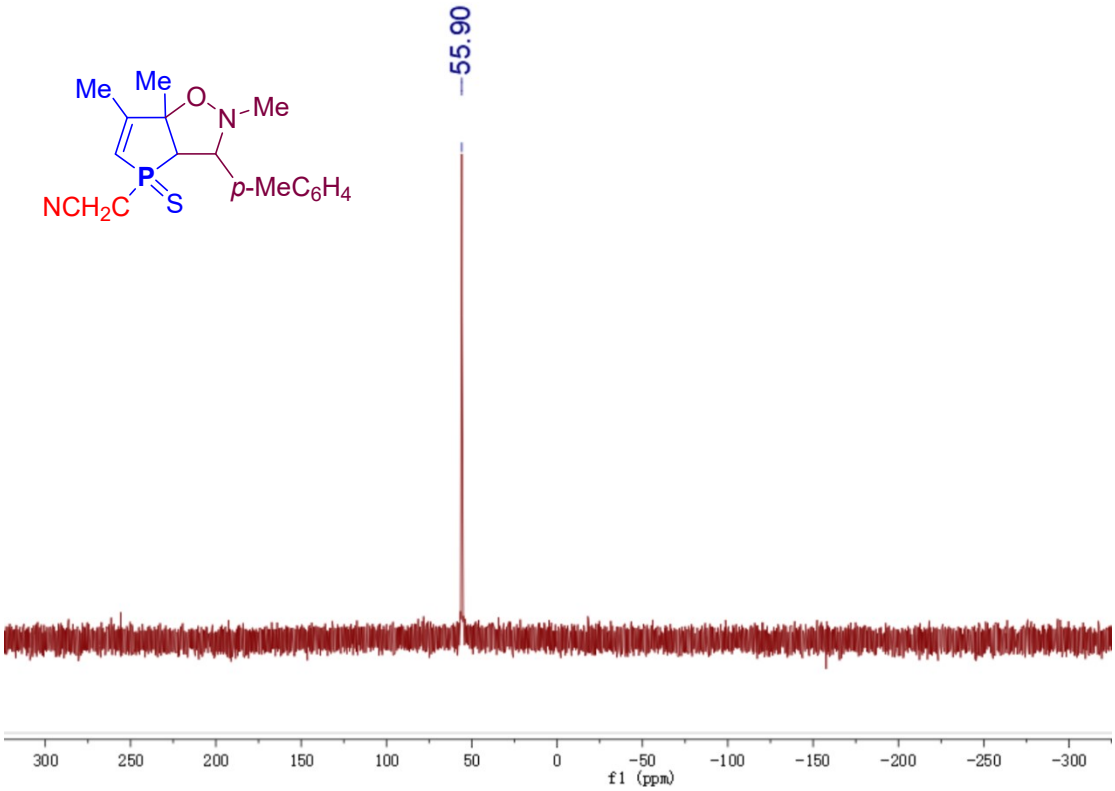


Figure S72. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) of Compound 3db

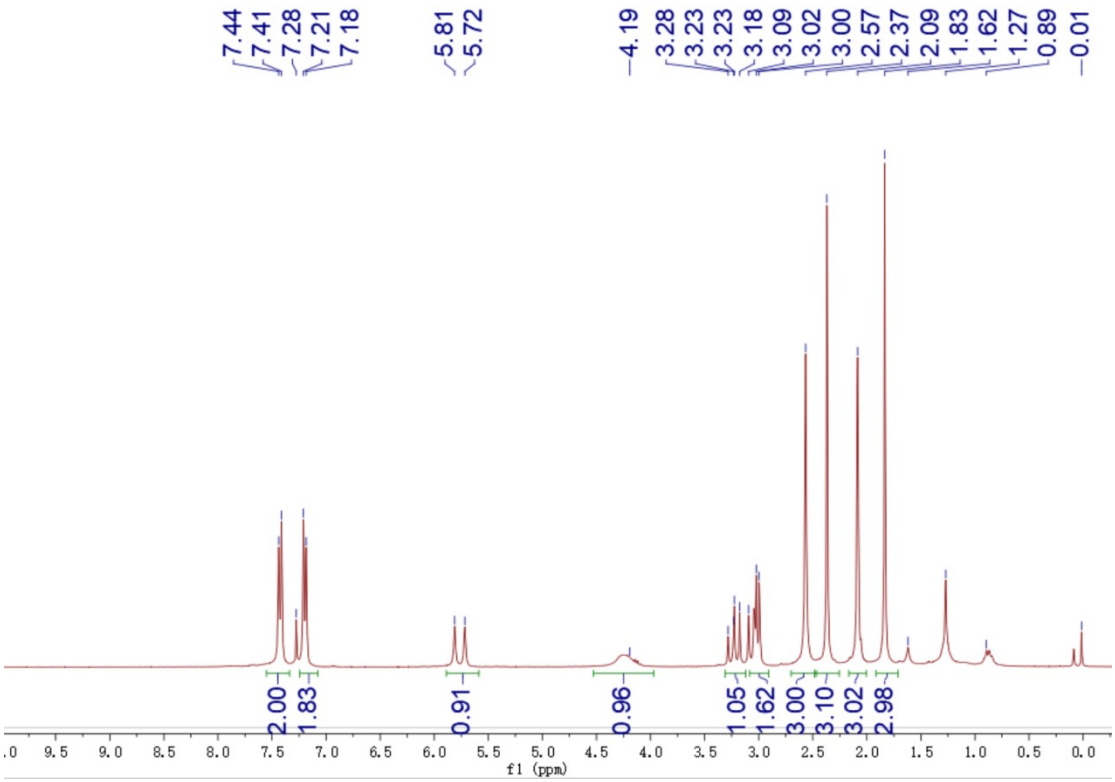


Figure S73. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3db

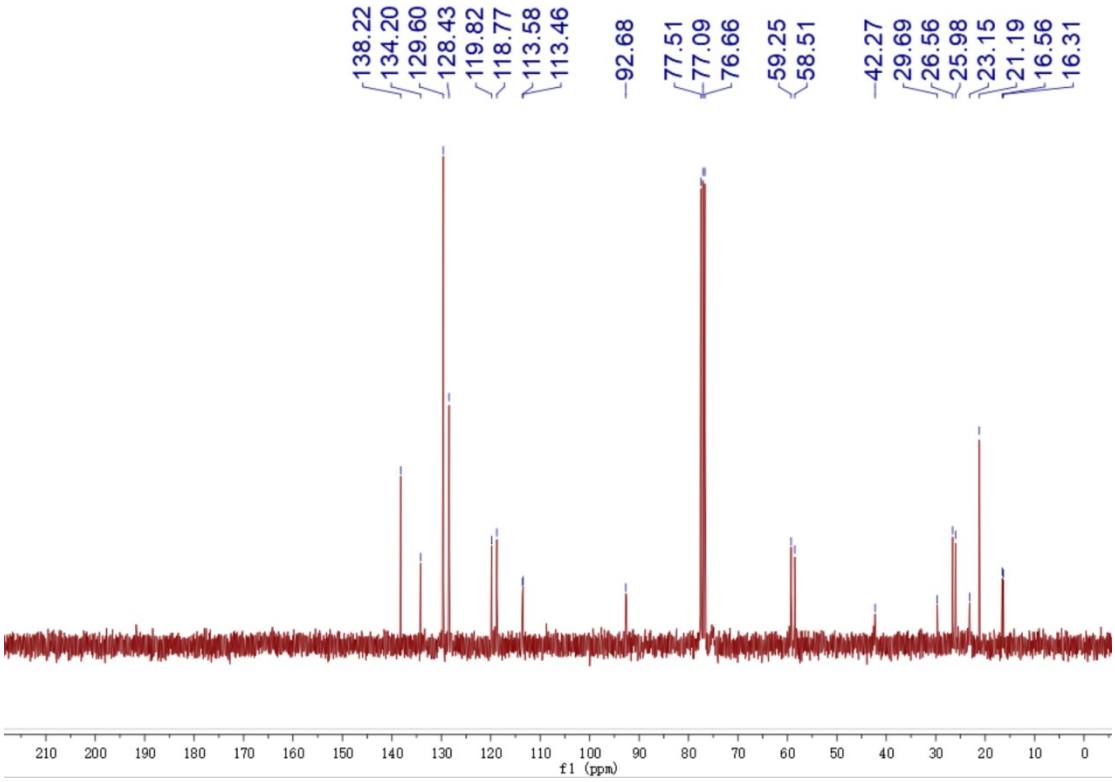


Figure S74. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3d

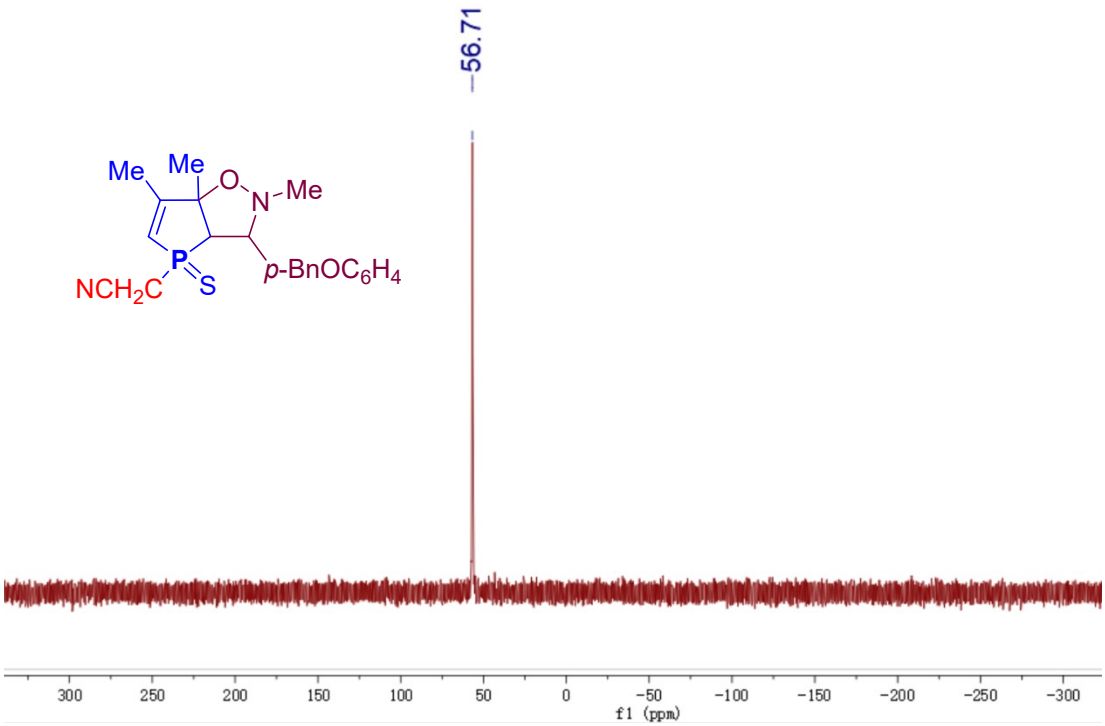


Figure S75. ^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of Compound 3dd

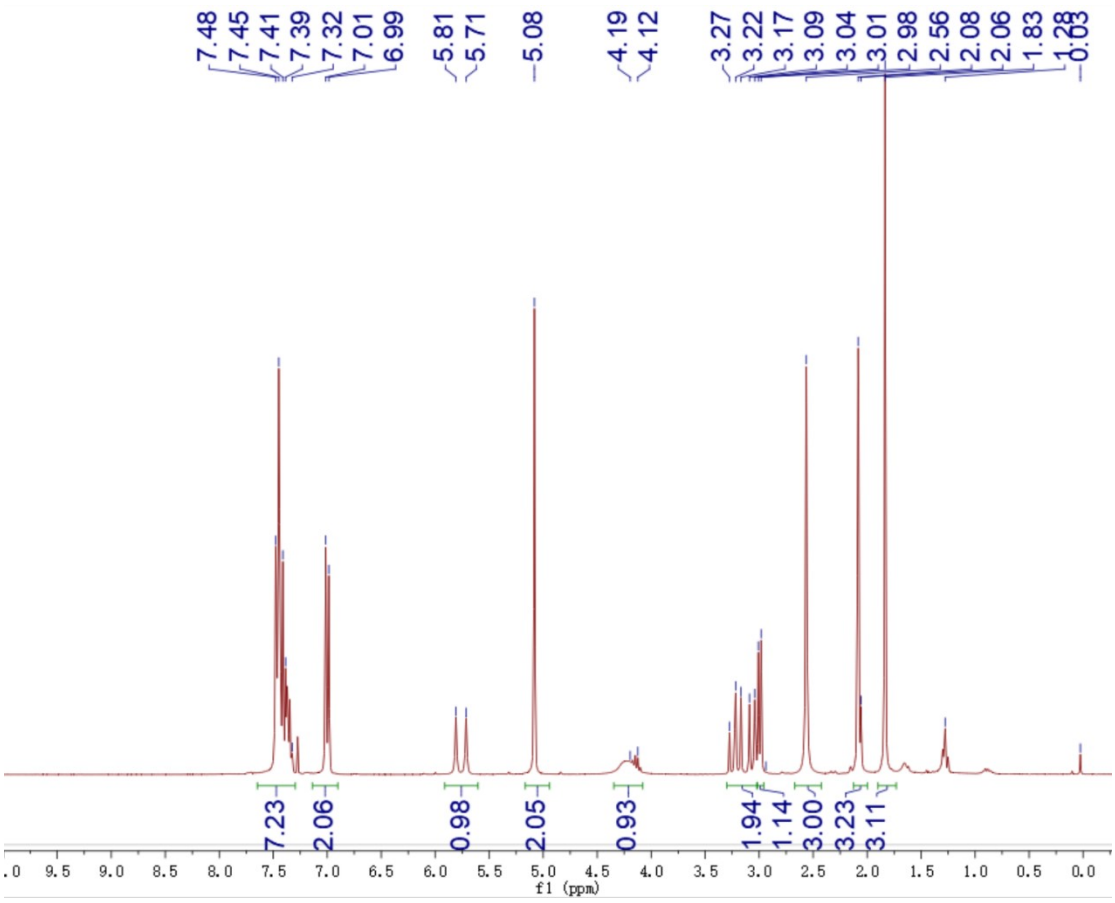


Figure S76. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3dd

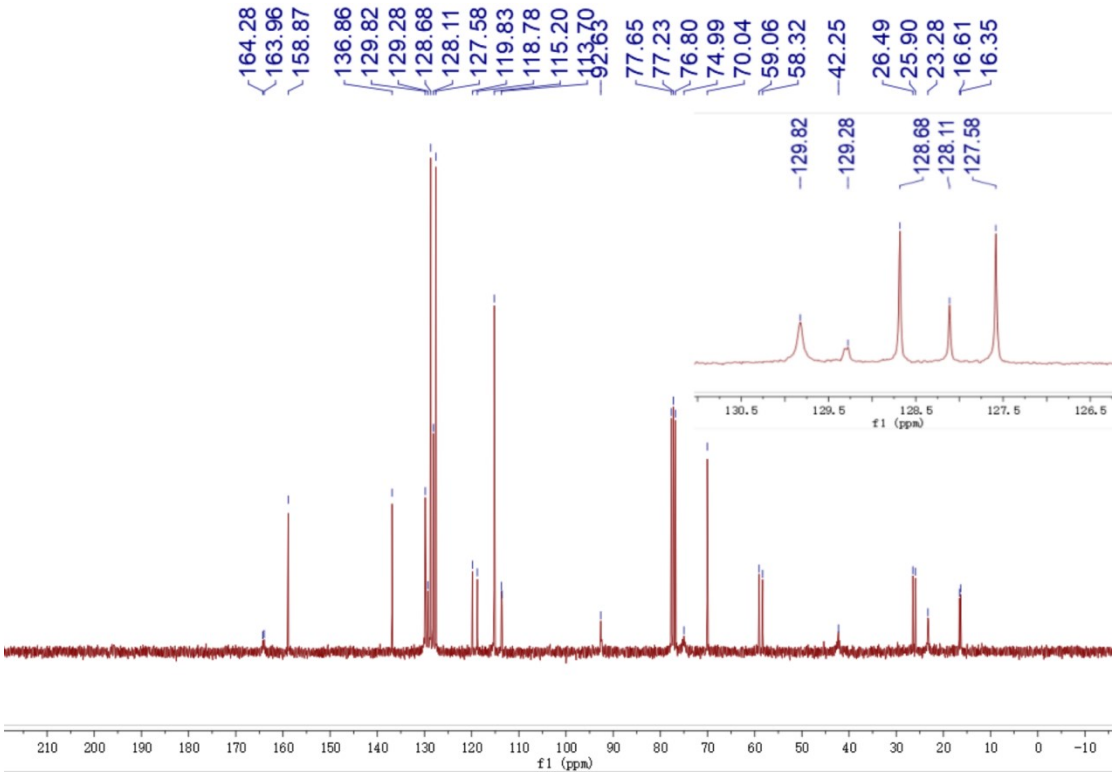


Figure S77. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3dd

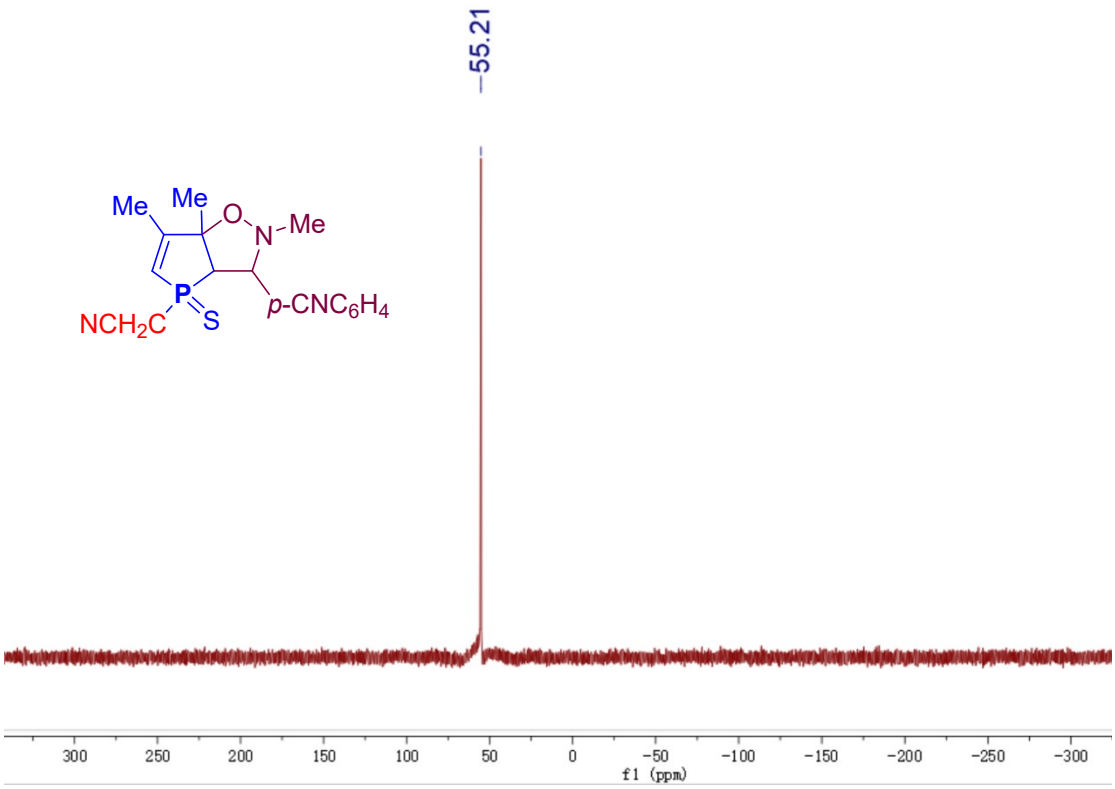


Figure S78. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) of Compound 3dg

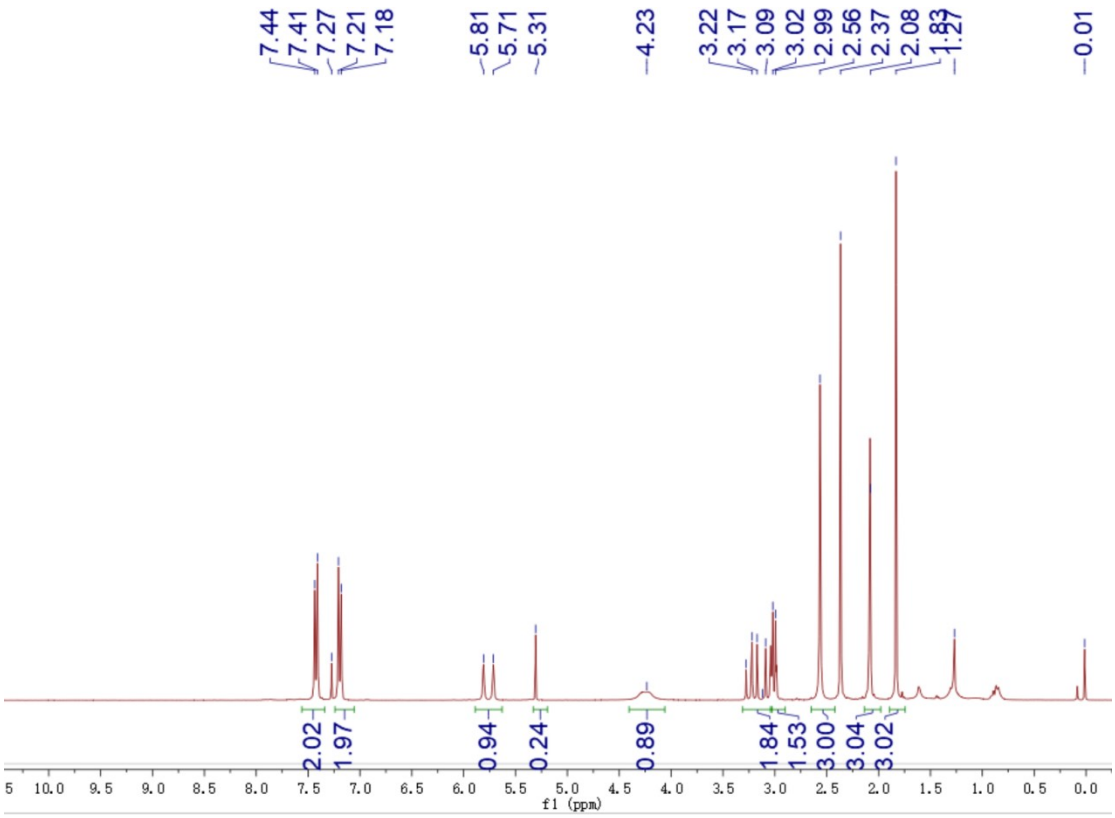


Figure S79. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3dg

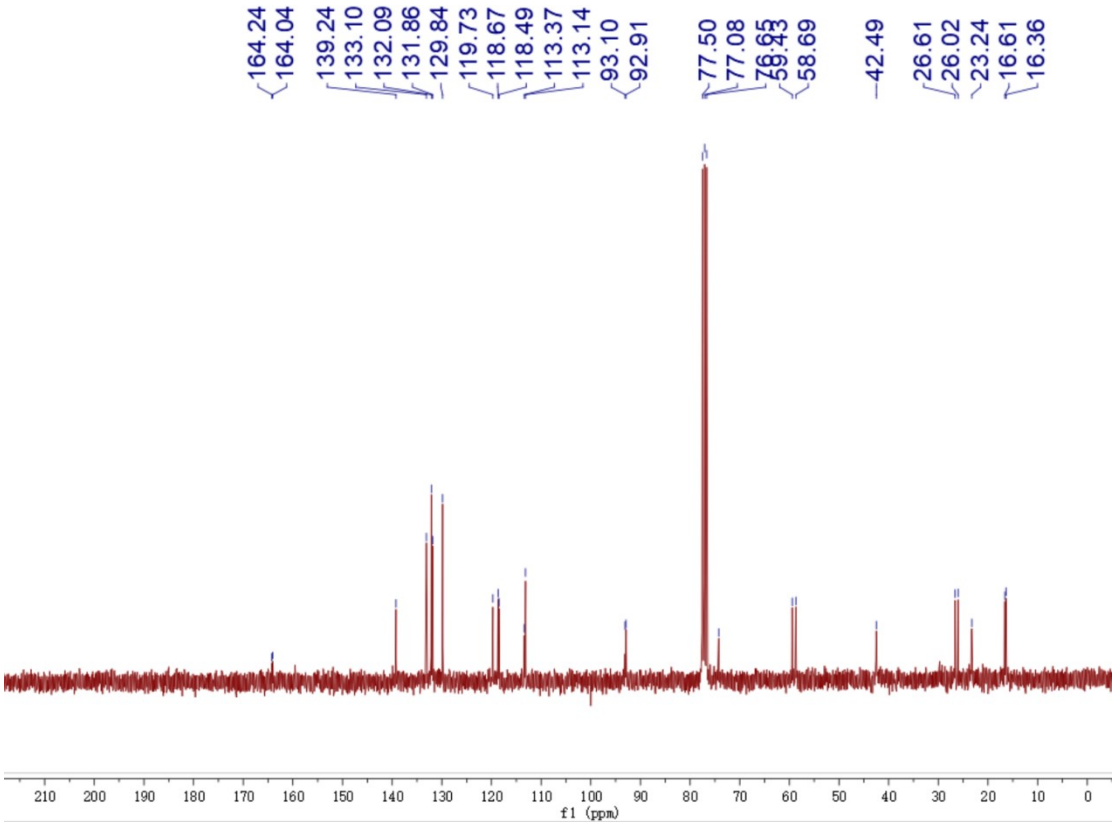


Figure S80. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3dg

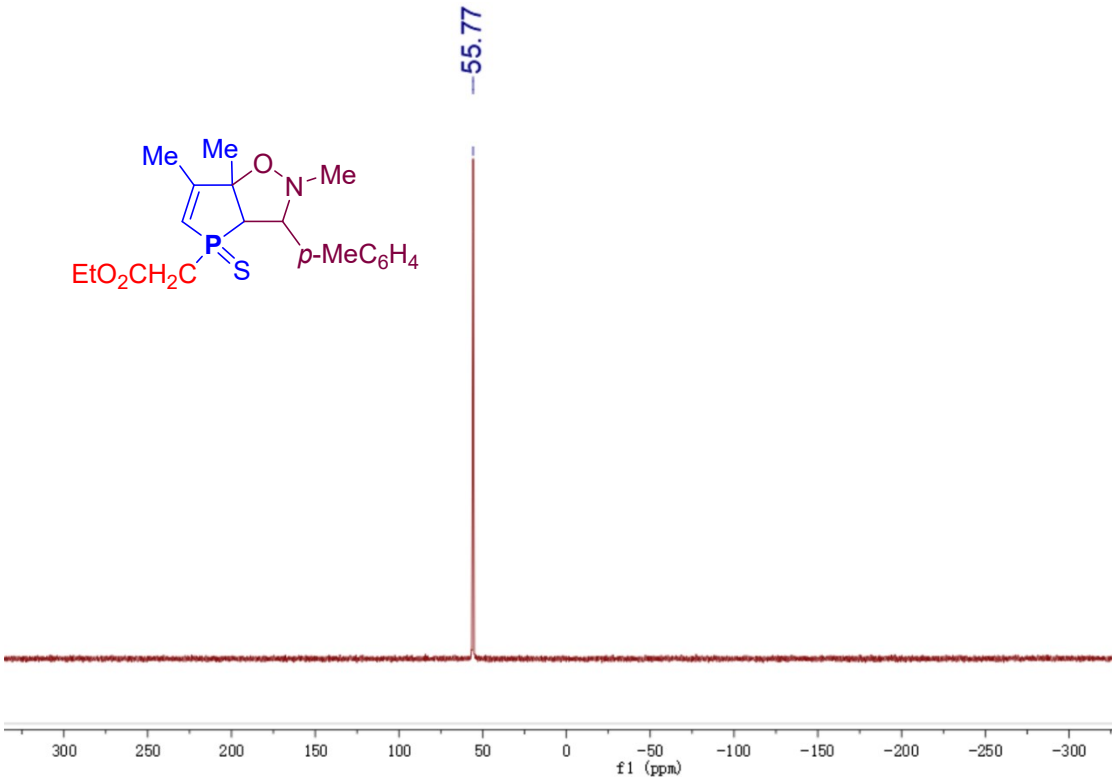


Figure S81. ^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of Compound 3eb

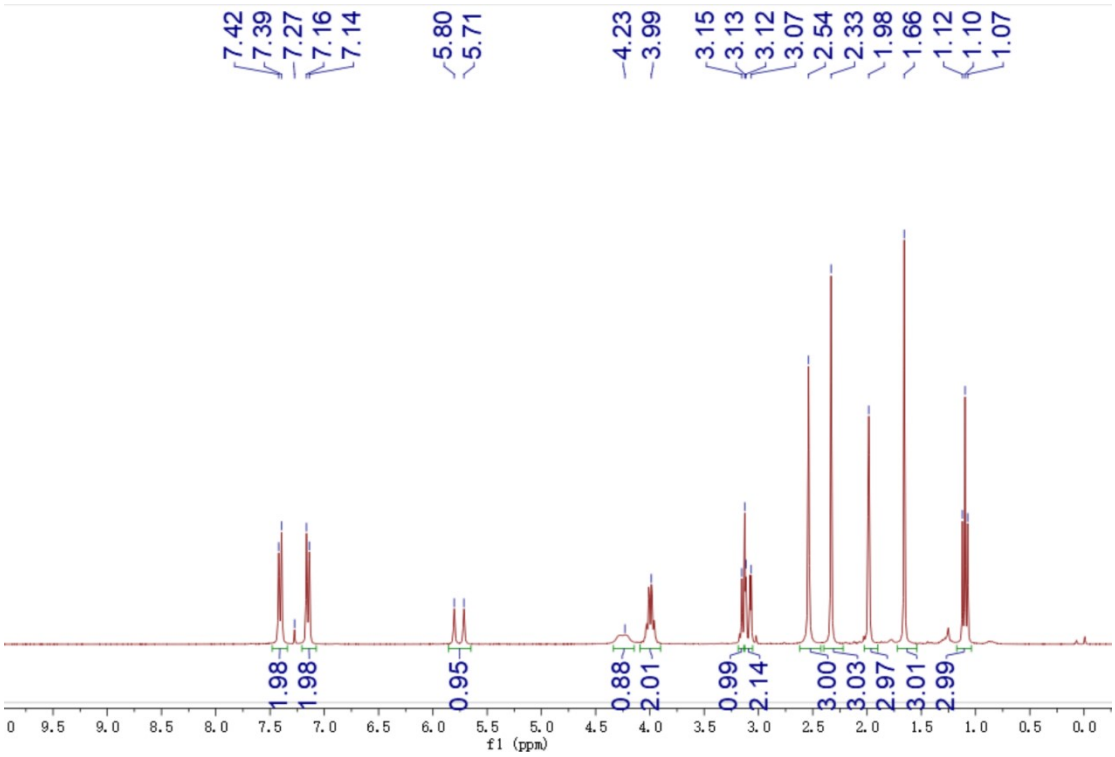


Figure S82. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3eb

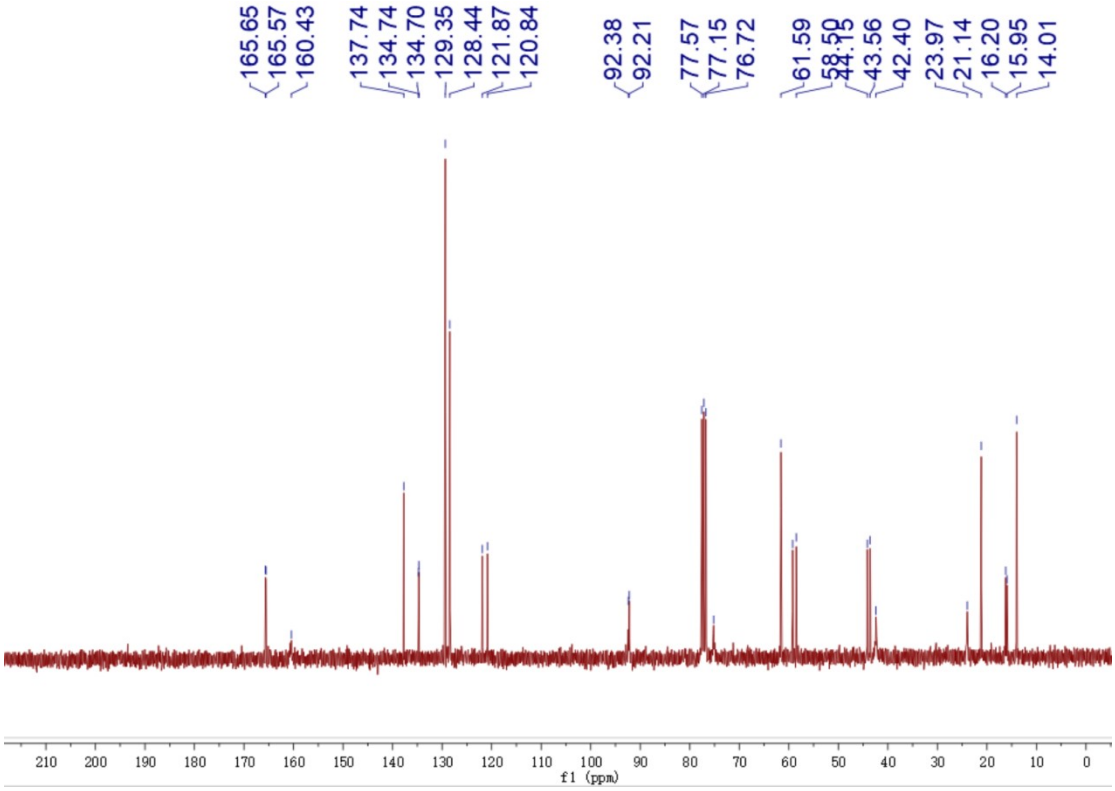


Figure S83. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3eb

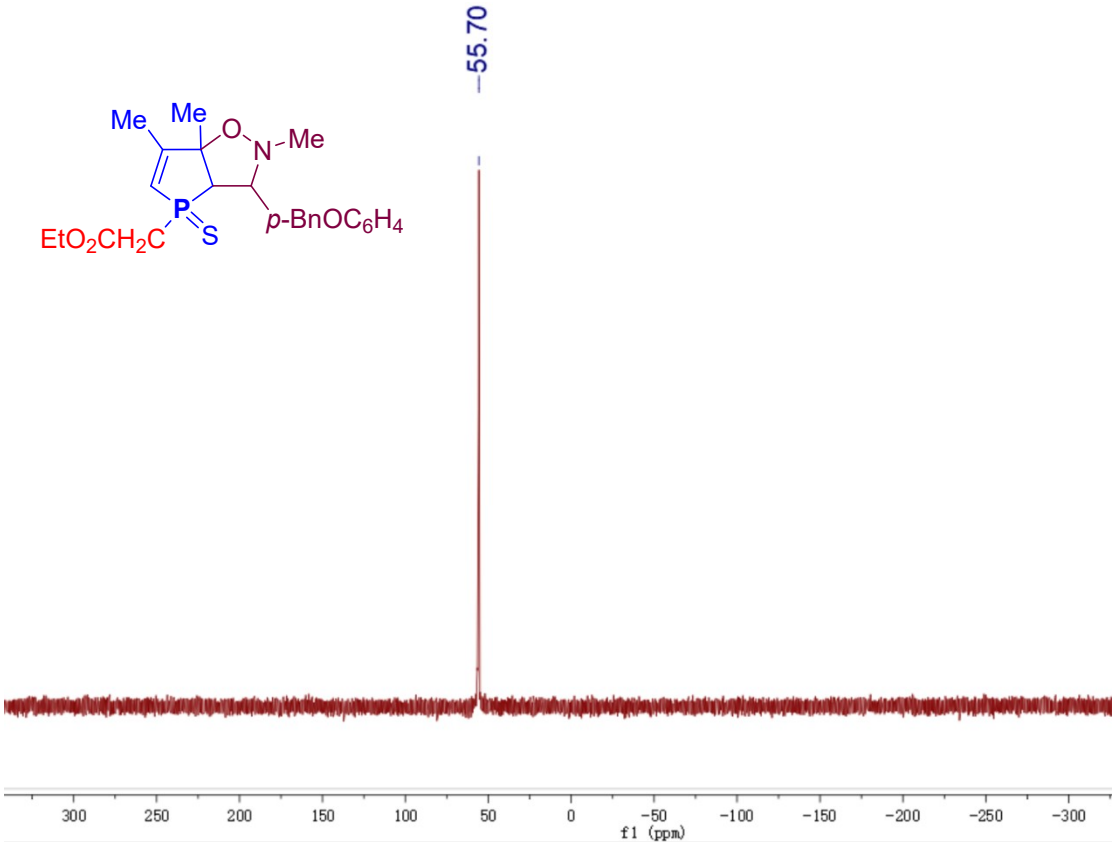


Figure S84. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) of Compound 3ed

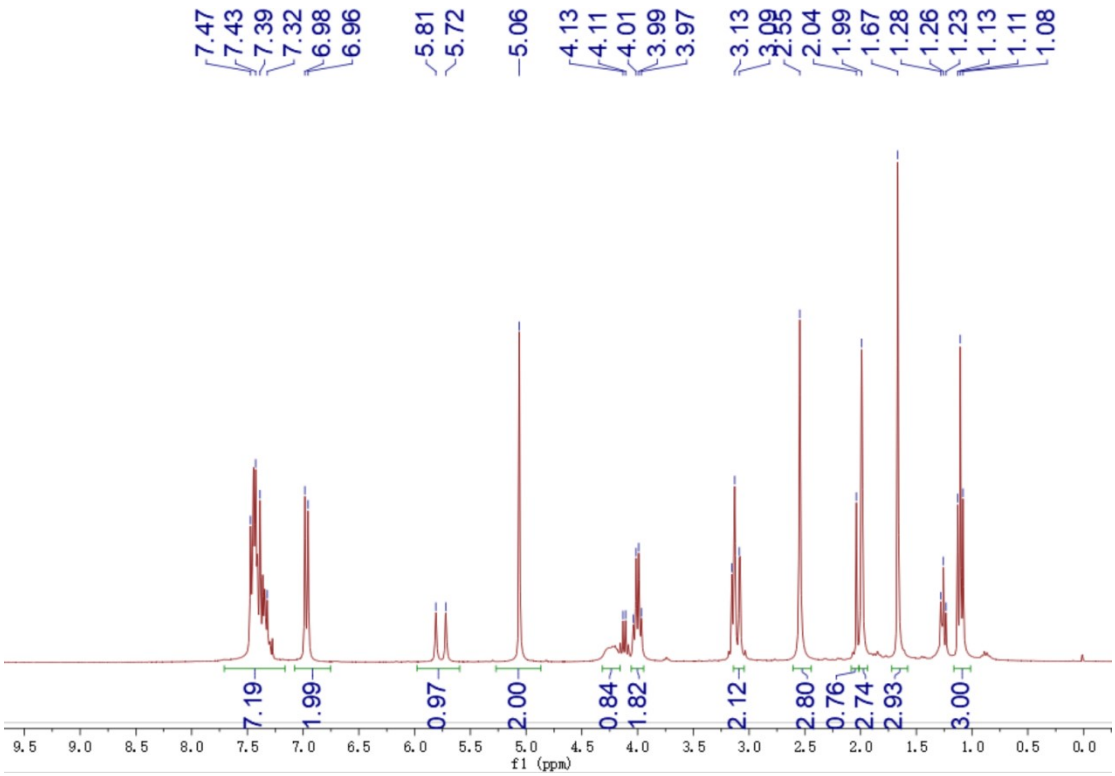


Figure S85. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3ed

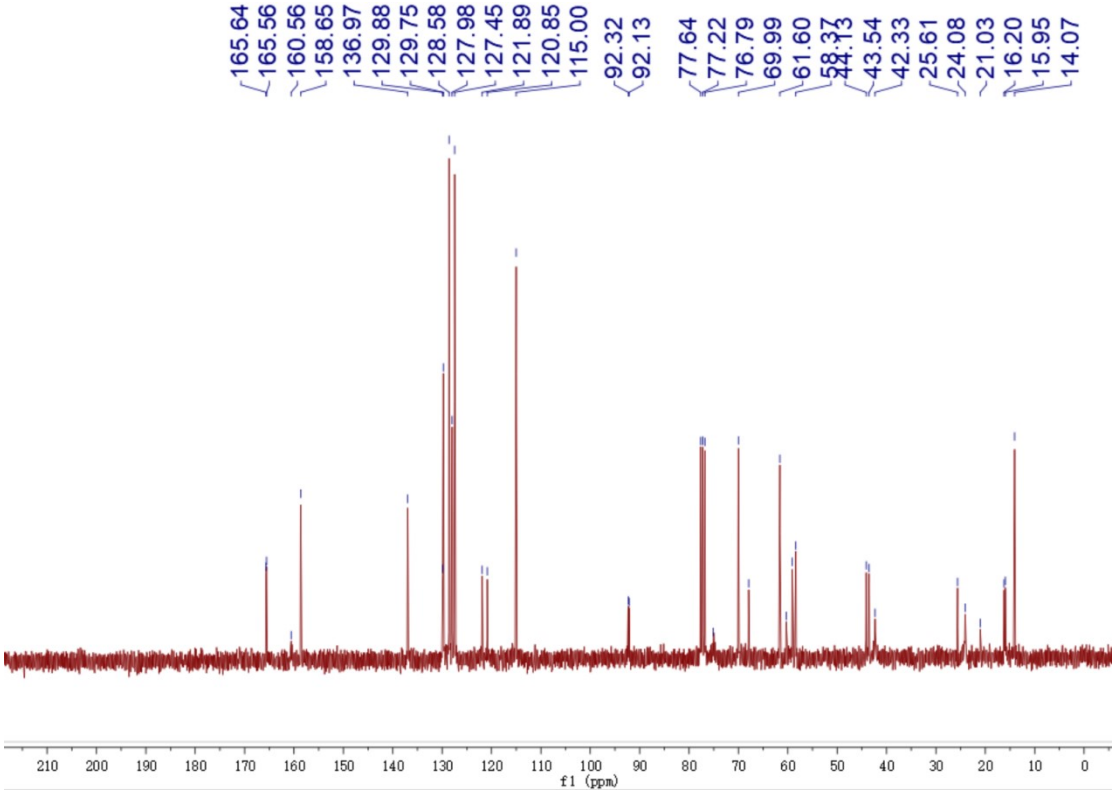


Figure S86. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3ed

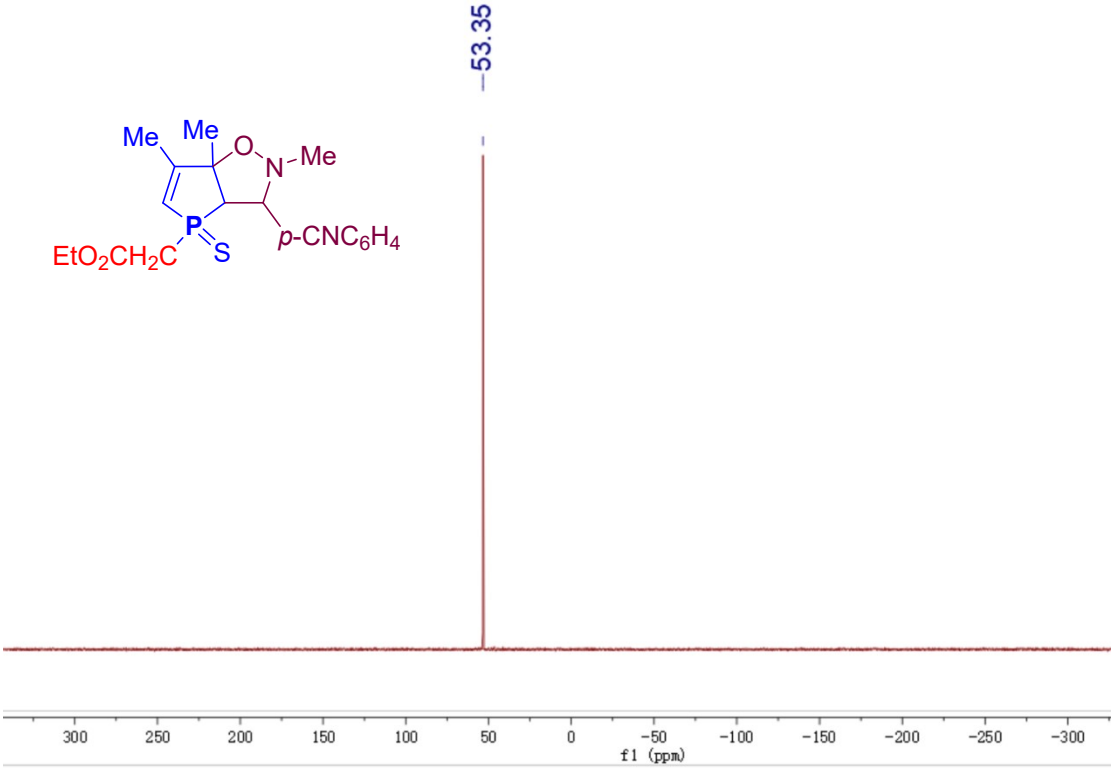


Figure S87. ^{31}P {^{1}H} NMR ($CDCl_3$, 121 MHz) of Compound 3eg

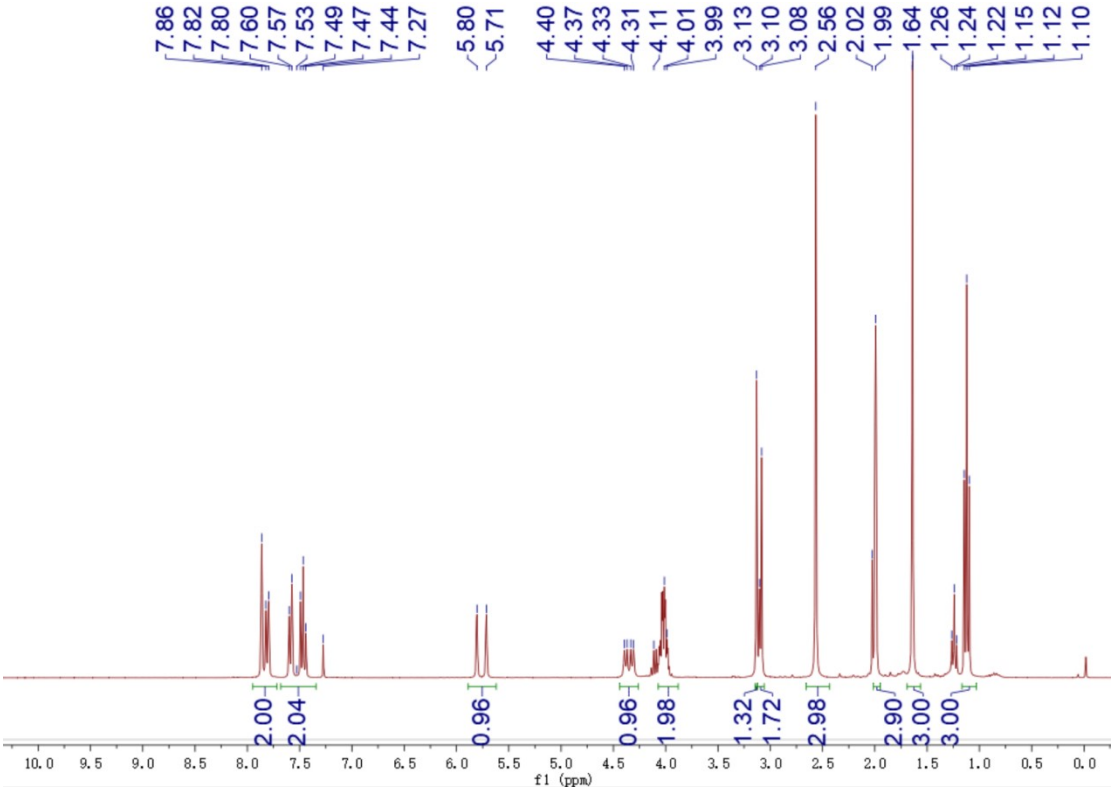


Figure S88. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3eg

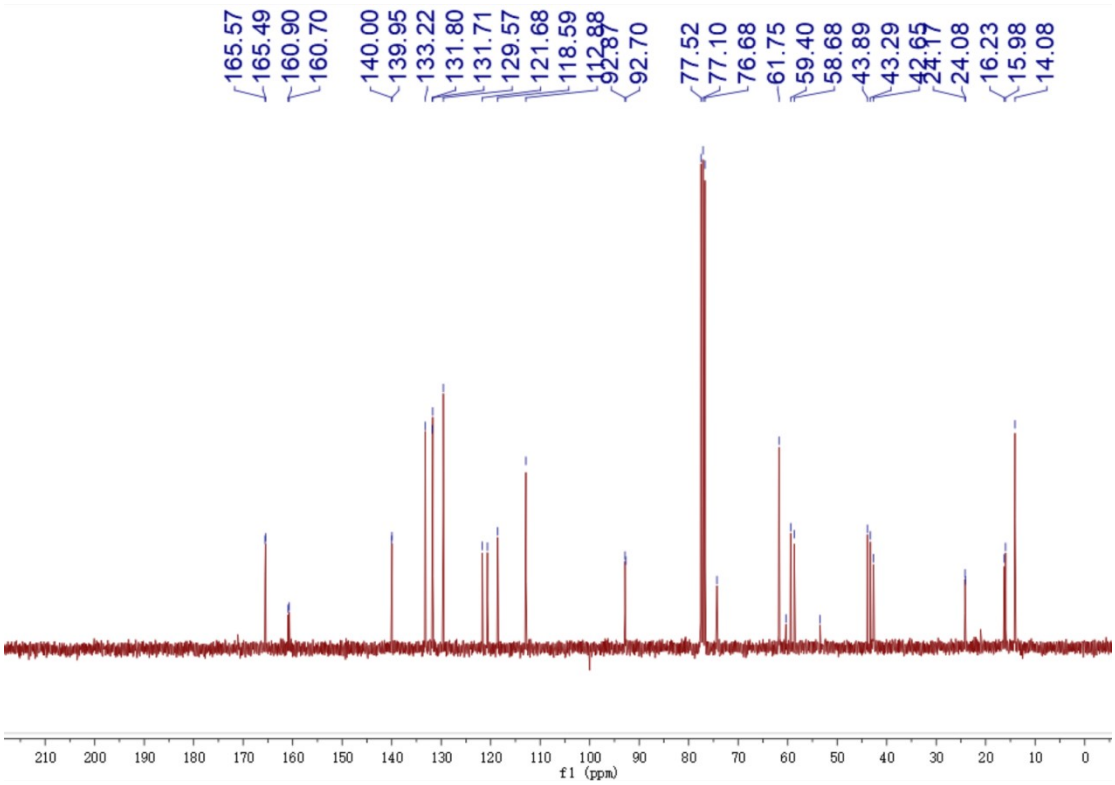


Figure S89. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3eg

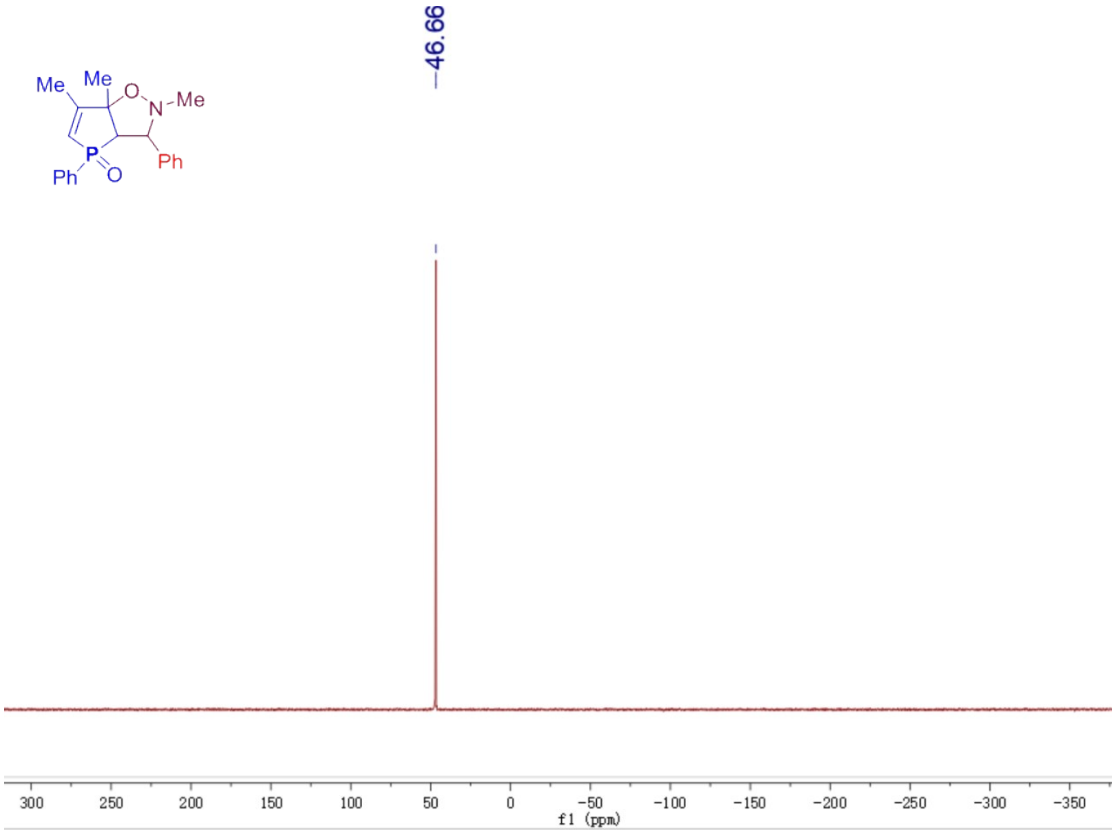


Figure S90. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) of Compound 5

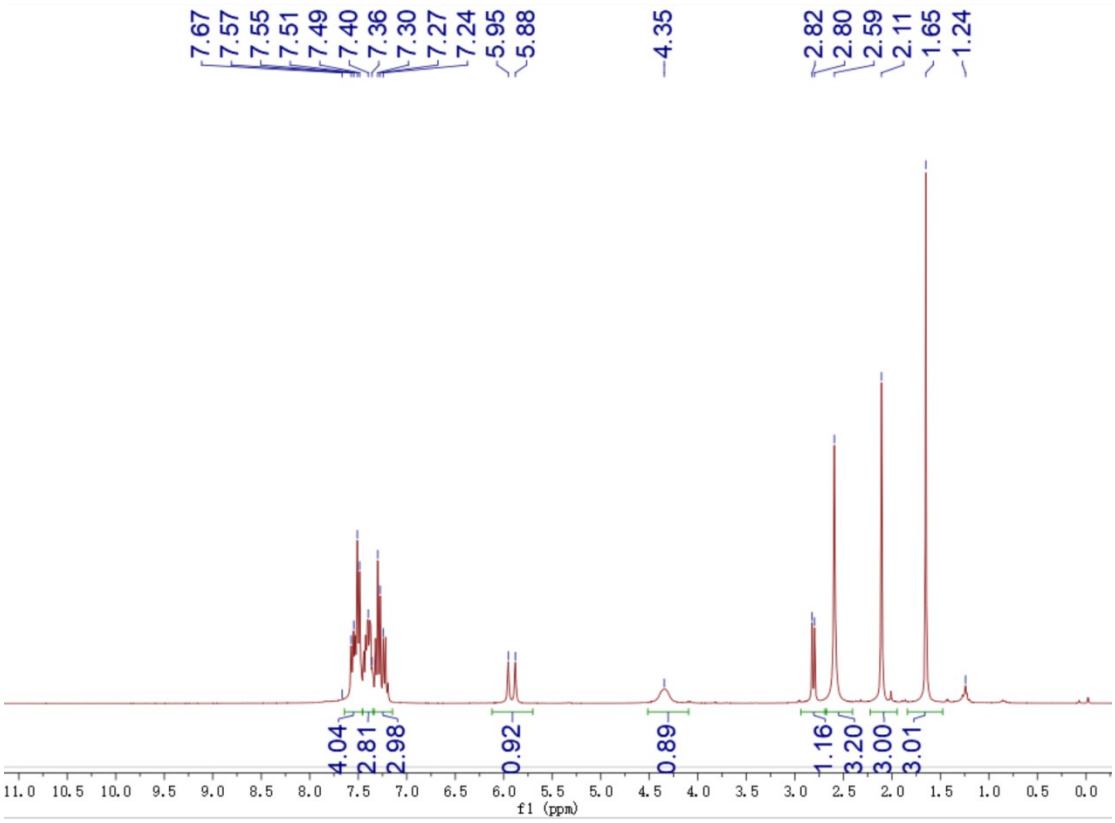


Figure S91. ^{1}H NMR (300 MHz, $CDCl_3$) of Compound 5

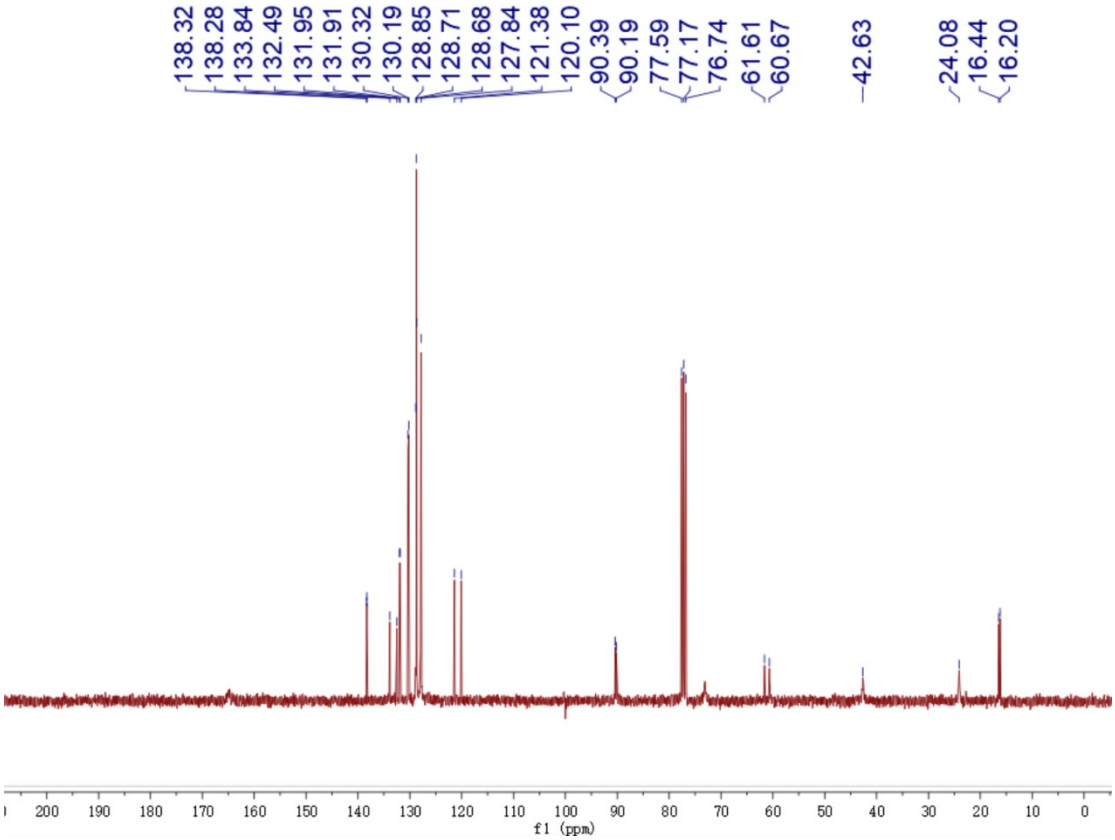


Figure S92. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 5