Supporting Information

An approach to 7-aza-1-phosphanorbornane complexes: Strain promoted rearrangement of 1-iminylphosphirane complexes and cycloaddition with olefins

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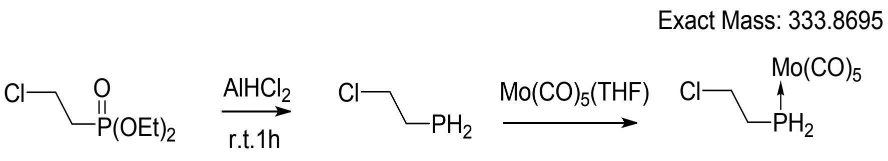
General information

All reactions were performed under nitrogen using solvents dried by standard methods except for special statement. Tetrahydrofuran (THF), toluene and ether were dried with sodium benzophenone 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) and external 85% H_3PO_4 (31P). HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-T of HR-MS spectrometer. Element analyses were performed on a Thermo Flash EA 1112 automatic element analyzer. 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. UV-Visible spectra were recorded at room temperature on a VARIAN Cary 5000 spectrophotometer. Silica gel (200-300 mesh) and aluminum oxide neutral (100-200 mesh) were used for the chromatographic separations. All commercially available reagents were used without further purification. All new compounds were synthetic in small scale, and were purified by column chromatography. The purities of the new compounds are acceptable according to NMR spectra analysis.

Experimental Procedures and Characterization Data

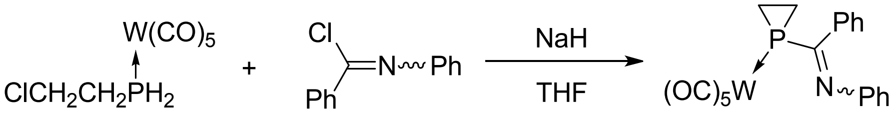


1a

At -78 °C, $AlCl_3$ (12.0 g, 90 mmol) was added to a suspension of $LiAlH_4$ (1.15 g, 30 mmol) in diethyl ether (70 mL) in four portions. The mixture was stirred in an ice bath for 0.5 h. A solution of diethylchloroethylphosphonate (3.00 g, 15 mmol) in diethyl ether (10 mL) was added to the mixture at 0 °C and stirred for 1 h at r.t. All the volatiles were distilled and cooled in liquid nitrogen under vacuum. Diethyl ether

(20 mL) was added to the mixture. All the volatiles were distilled and cooled in liquid nitrogen under vacuum again. This step was repeated until there was no detectable ^{31}P signal of the chloroethylphosphane in the parent mixture. All the cooled volatiles were collected and transferred into a solution of [$Mo(CO)_5(THF)$] (15 mmol) in THF (50 mL). The reaction was complete after stirring for 8 h at r.t. The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, Ether/Ethyl acetate = 15:1, R_f = 0.42) providing 3.00 g of **1a** as white solid (9.0 mmol, 60%).

1a: ^{31}P NMR ($CDCl_3$): δ 87.2. ^1H NMR ($CDCl_3$): δ 2.26 - 2.37(m, 2H), 3.72 - 3.81 (m, 2H), 3.85 (t, J = 6.8 Hz, 1H), 4.93 (t, J = 6.8 Hz, 1H).^{13}C NMR ($CDCl_3$): δ25.12 (d, J_{CP} = 23.4 Hz), 43.12 (d, J_{CP} = 6.6 Hz), 204.43 (d, J_{CP} = 9.3 Hz, CO *cis*), 208.23 (d, J_{CP} = 24.2 Hz, CO *trans*).



1b

2a,b

yield = 86%

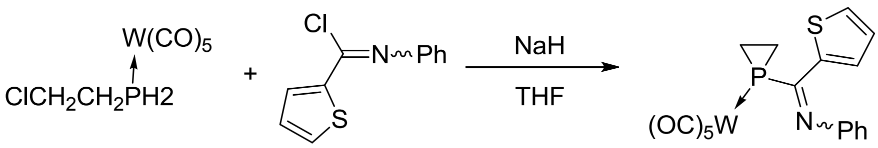
NaH (96 mg, 2.4 mmol) was added to a solution of **1b** (420 mg, 1.0 mmol) in THF (10 mL) at -20 °C. The mixture was stirred vigorously from -20 °C to 0 °C about 10 min, N-phenylbenzimidoyl chloride (258 mg, 1.2 mmol) was added to the mixture at -20 °C and stirred for 0.5 h from -20 °C to 0 °C. The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (aluminum oxide neutral, petroleum ether, R_f = 0.56) providing 484 mg of **2a,b** as yellow solid (0.86 mmol, 86%, **2a**:**2b** = 7:10). The NMR data of **2a** and **2b** was selected from NMR spectra of **2a,b** mixture.

2a: ^{31}P NMR ($CDCl_3$): δ -180.2 (J_{PW} = 260 Hz). ^1H NMR ($CDCl_3$): δ 1.40 – 1.48 (m, 2H, CH_2), 1.70 – 1.86 (m, 2H, CH_2), 6.61 (d, J = 7.7 Hz, 2H, CH), 6.95 (t, J = 7.4 Hz, 1H, CH), 7.05 – 7.50 (m, 7H, CH). ^{13}C NMR ($CDCl_3$): δ 11.44 (d, J_{CP} = 15.5 Hz, CH_2), 120.57 (s, CH), 124.79 (s, CH), 128.84 (s, CH), 129.59(s, CH), 129.68 (s, CH), 131.79 (s, CH), 133.31 (d, J_{CP} = 25.5 Hz, C), 149.60 (d, J_{CP} = 23.4 Hz, C), 172.67 (d,

J_{CP} = 39.9 Hz, C=N), 195.40 (d, J_{CP} = 1.9 Hz, CO *cis*), 197.90 (d, J_{CP} = 33.6 Hz, CO *trans*).

2b: ^{31}P NMR ($CDCl_3$): δ -199.8 (J_{PW} = 260 Hz), ^{1}H NMR ($CDCl_3$): δ 1.30 – 1.40 (m, 2H, CH_2), 1.48 – 1.64 (m, 2H, CH_2), 7.05 – 7.50(m, 8H, CH), 8.14 (d, *J* = 7.3 Hz, 2H, CH). ^{13}C NMR ($CDCl_3$): δ 13.96 (d, J_{CP} = 12.6 Hz, CH_2), 119.78 (s, CH), 125.46 (s, CH), 127.79 (d, J_{CP} = 2.1 Hz, CH), 128.65 (s, CH), 128.72 (s, CH), 128.89 (s, CH), 137.12 (d, J_{CP} = 26.2 Hz, C), 150.33 (d, J_{CP} = 12.3 Hz, C), 164.99 (d, J_{CP} = 14.8 Hz, C=N), 195.35 (d, J_{CP} = 5.5 Hz, CO *cis*), 197.05 (d, J_{CP} = 32.1 Hz, CO trans).

The mixture Elemental Analysis Calcd (%) for $C_{20}H_{14}NO_5PW$: C, 42.66; H, 2.51; N, 2.49. Found: C, 42.33; H, 3.06; N, 2.28. HRMS: m/z calcd for $C_{20}H_{14}NO_5PW$ $(M+H)^+$ 564.0192, found 564.0191. IR (neat) δ 2073.63, 1910.85, 1566.76 cm^{-1}.



1b

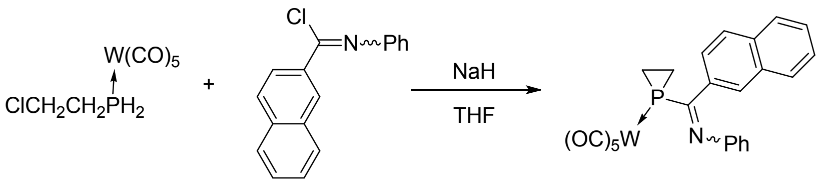
3a,b

yield = 84%

NaH (96.0 mg, 2.4 mmol) was added to a solution of **1b** (420 mg, 1.0 mmol) in THF (10 mL) at -20 °C. The mixture was stirred vigorously from -20 °C to 0 °C about 10 min. N-phenylthiophene-2-carbimidoyl chloride (265 mg, 1.2 mmol) was added to the mixture at -20 °C and stirred for 0.5 h from -20 °C to 0 °C. The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (aluminum oxide neutral, petroleum ether, R_f = 0.56) providing 478 mg of **3a,b** as yellow solid (0.84 mmol, 84%, **3a**:**3b** = 1:12). The NMR data of **3b** was selected from NMR spectra of **3a,b** mixture.

3b: ^{31}P NMR ($CDCl_3$): δ -199.7 (J_{PW} = 253 Hz). ^{1}H NMR ($CDCl_3$): δ 1.26 – 1.31 (m, 2H, CH_2), 1.50 – 1.57 (m, 2H, CH_2), 7.08 (d, *J* = 7.7 Hz, 2H, CH), 7.15 – 7.18 (m, 1H, CH), 7.22 (d, *J* = 7.5 Hz, 1H, CH), 7.43 (t, *J* = 7.7 Hz, 2H, CH), 7.53 (d, *J* = 5.0 Hz, 1H, CH), 7.93 (d, *J* = 3.6 Hz, 1H, CH). ^{13}C NMR ($CDCl_3$): δ 13.42 (d, J_{CP} = 14.1

Hz, CH_2), 120.30 (s, CH), 125.56 (s, CH), 127.94 (s, CH), 129.57 (s, CH), 131.77 (s, CH), 131.84 (d, J_{CP} = 3.7 Hz, CH), 143.57 (d, J_{CP} = 32.6 Hz, C), 149.63 (d, J_{CP} = 11.4 Hz, C), 158.60 (d, J_{CP} = 13.0 Hz, C=N), 195.32 (d, J_{CP} = 7.5 Hz, CO *cis*), 196.84 (d, J_{CP} = 32.5 Hz, CO *trans*). HRMS: m/z calcd for $C_{18}H_{12}NO_5PSW$ $(M+H)^+$ 569.9756, found 569.9757.



1b 4a,b

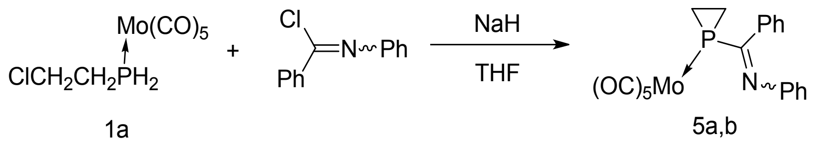
yield = 90%

NaH (96.0 mg, 2.4 mmol) was added to a solution of **1b** (420 mg, 1.0 mmol) in THF (10 mL) at -20 °C. The mixture was stirred vigorously from -20 °C to 0 °C about 10 min, N-phenyl-2-naphthimidoyl chloride (318 mg, 1.2 mmol) was added to the mixture at -20 °C and stirred for 0.5 h from -20 °C to 0 °C. The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (aluminum oxide neutral, petroleum ether, R_f = 0.56) providing 552 mg of **4a,b** as yellow solid (0.90 mmol, 90%, **4a**:**4b** = 1:2.3). The NMR data of **4a** and **4b** was selected from NMR spectra of **4a,b** mixture.

4a: ^{31}P NMR ($CDCl_3$): δ -180.3 (J_{PW} = 260 Hz). ^{1}H NMR ($CDCl_3$): δ 1.36 – 1.46 (m, 2H, CH_2), 1.78 – 1.85 (m, 2H, CH_2), 6.66 (d, J = 7.7 Hz, 2H, CH), 6.90 (t, J = 7.3 Hz, 1H, CH), 7.43 – 7.98 (m, 5H, CH), 8.18 (d, J = 8.7 Hz, 2H, CH), 8.78 (s, 2H, CH). ^{13}C NMR ($CDCl_3$): δ 11.81 (d, J_{CP} = 15.5 Hz, CH_2), 124.57 (d, J_{CP} = 1.6 Hz, CH), 124.94 (s, CH), 127.08 (s, CH), 127.58 (s, CH), 127.94 (s, CH), 128.04 (d, J_{CP} = 2.2 Hz, CH), 128.41 (s, CH), 128.73 (s, CH), 128.94 (s, CH), 130.84 (d, J_{CP} = 26.0 Hz, C), 132.93 (d, J_{CP} = 53.6 Hz, C), 134.48 (d, J_{CP} = 25.9 Hz, C), 149.62 (d, J_{CP} = 23.1 Hz, C), 172.43 (d, J_{CP} = 39.8 Hz, C=N), 195.35 (d, J_{CP} = 7.6 Hz, CO *cis*), 197.90 (d, J_{CP} = 33.3 Hz, CO *trans*).

4b: ^{31}P NMR ($CDCl_3$): δ -201.7 (J_{PW} = 250 Hz). ^{1}H NMR ($CDCl_3$): δ 1.36 – 1.46 (m, 2H, CH_2), 1.54 – 1.61 (m, 2H, CH_2), 6.99 – 7.06 (m, 1H, CH), 7.10 (d, J = 7.6 Hz, 2H, CH), 7.21 (t, J = 7.4 Hz, 1H, CH), 7.43 – 7.98 (m, 8H, CH). ^{13}C NMR ($CDCl_3$): δ 14.19 (d, J_{CP} = 12.6 Hz, CH_2), 119.86 (s, CH), 124.44 (d, J_{CP} = 3.2 Hz, CH), 125.48 (s, CH), 127.02 (s, CH), 127.88 (s, CH), 128.23 (s, CH), 128.77 (s, CH), 129.31 (s, CH), 129.76 (s, CH), 130.89 (d, J_{CP} = 5.5 Hz, C), 132.76 (s, C), 134.91 (s, C), 150.52 (d, J_{CP} = 12.3 Hz, C), 164.54 (d, J_{CP} = 14.3 Hz, C=N), 195.58 (d, J_{CP} = 7.5 Hz, CO *cis*), 197.10 (d, J_{CP} = 32.1 Hz, CO *trans*). IR (neat) δ 2071.63, 1902.95, 1569.65 cm^{-1}.

The mixture HRMS: m/z calcd for $C_{24}H_{16}NO_5PW$ $(M+H)^+$ 614.0348, found 614.0347.



yield = 86%

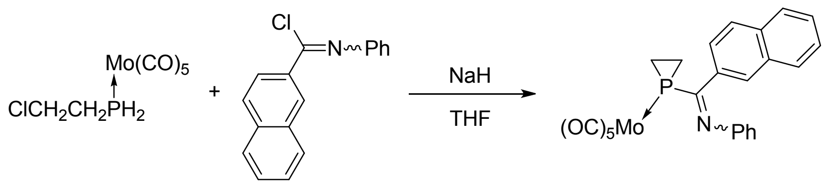
NaH (96.0 mg, 2.4 mmol) was added to a solution of **1a** (334 mg, 1.0 mmol) in THF (10 mL) at -20 °C. The mixture was stirred vigorously from -20 °C to 0 °C about 10 min. N-phenylbenzimidoyl chloride (258 mg, 1.2 mmol) was added to the mixture at -20 °C and stirred for 0.5 h from -20 °C to 0 °C. The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (aluminum oxide neutral, petroleum ether, R_f = 0.61) providing 410 mg of **5a,b** as yellow solid (0.86 mmol, 86%, **5a**:**5b** = 2:3). The NMR data of **5a** and **5b** was selected from NMR spectra of **5a,b** mixture.

5a: ^{31}P NMR ($CDCl_3$): δ -162.4. ^{1}H NMR ($CDCl_3$): δ 1.35 – 1.38 (m, 2H, CH_2), 1.73 – 1.80 (m, 2H, CH_2), 6.63 (d, J = 7.7 Hz, 2H, CH), 6.98 (t, J = 7.4 Hz, 1H, CH), 7.04 – 7.17 (m, 2H, CH), 7.21 – 7.32 (m, 1H, CH), 7.45 – 7.55 (m, 4H, CH). ^{13}C NMR ($CDCl_3$): δ 10.93 (d, J_{CP} = 18.4 Hz, CH_2), 120.50 (s, CH), 124.62 (s, CH), 127.72 (d, J_{CP} = 2.1 Hz, CH), 128.64 (s, CH), 128.75 (s, CH), 129.46 (s, CH), 133.84 (d, J_{CP}= 25.1 Hz, C), 149.82 (d, J_{CP} = 21.9 Hz, C), 173.95 (d, J_{CP} = 30.2 Hz, C=N), 204.55 (d, J_{CP} = 10.4 Hz, CO *cis*), 208.59 (d, J_{CP} = 34.5 Hz, CO *trans*).

5b: ^{31}P NMR ($CDCl_3$): δ -178.3. ^{1}H NMR ($CDCl_3$): δ 1.25 – 1.31(m, 2H, CH_2), 1.48 – 1.56 (m, 2H, CH_2), 7.04 – 7.17 (m, 3H, CH), 7.21 – 7.32 (m, 3H, CH), 7.45 –

7.55 (m, 2H, CH), 8.15 (d, J = 7.6 Hz, 2H, CH). ^{13}C NMR ($CDCl_3$): 13.44 (d, J_{CP} = 15.3 Hz, CH_2), 119.85 (s, CH), 125.31 (s, CH), 128.61 (s, CH), 128.79 (s, CH), 129.58 (s, CH), 131.65 (s, CH), 137.41 (d, J_{CP} = 25.1 Hz, C), 150.37 (d, J_{CP}= 11.6 Hz, C), 166.81 (d, J_{CP} = 21.5 Hz, C=N), 204.13 (d, J_{CP} = 9.9 Hz, CO *cis*), 207.95 (d, J_{CP} = 32.8 Hz, CO *trans*).

The mixture Elemental Analysis Calcd (%) for $C_{20}H_{14}NO_5PMo$: C, 50.54; H, 2.97; N, 2.95. Found: C, 50.22; H, 3.06; N, 2.69. HRMS: m/z calcd for $C_{20}H_{14}NO_5PMo$ $(M+H)^+$ 477.9736, found 477.9736. IR (neat) δ 2074.85, 1909.98, 1566.84 cm^{-1}.



1a

6a,b

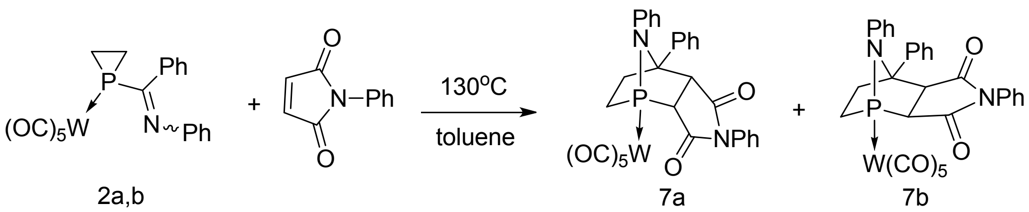
yield = 88%

NaH (96.0 mg, 2.4 mmol) was added to a solution of **1a** (333 mg, 1.0 mmol) in THF (10 mL) at -20 °C. The mixture was stirred vigorously from -20 °C to 0 °C about 10 min. N-phenyl-2-naphthimidoyl chloride (318 mg, 1.2 mmol) was added to the mixture at -20 °C and stirred for 0.5 h from -20 °C to 0 °C. The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (aluminum oxide neutral, petroleum ether, R_f = 0.61) providing 464 mg of **6a,b** as yellow solid (0.88 mmol, 88%, **6a**:**6b** = 1:2.4). The NMR data of **6a** and **6b** was selected from NMR spectra of **6a,b** mixture.

6a: ^{31}P NMR ($CDCl_3$): δ -162.2. ^{1}H NMR ($CDCl_3$): δ 1.30 – 1.39 (m, 2H, CH_2), 1.76 – 1.84 (m, 2H, CH_2), 6.64 – 8.77 (m, 12H, CH). ^{13}C NMR ($CDCl_3$): δ 11.29 (d, J_{CP} = 18.5 Hz, CH_2), 120.65 (s, CH), 124.54 (d, J_{CP} = 1.8 Hz, CH), 124.74 (s, CH), 126.98 (s, CH), 127.45 (s, CH), 127.88 (s, CH), 128.34 (s, CH), 128.60 (s, CH), 130.70 (d, J_{CP} = 5.9 Hz, CH), 132.84 (d, J_{CP} = 51.7 Hz, C), 134.67 (d, J_{CP} = 24.5 Hz, C), 149.77 (d, J_{CP} = 21.2 Hz, C), 151.09 (s, C), 173.67 (d, J_{CP} = 29.7 Hz, C=N), 204.55 (d, J_{CP} = 10.0 Hz, CO *cis*).

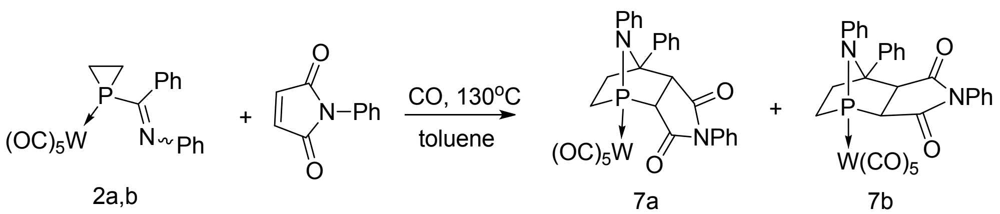
6b: ^{31}P NMR ($CDCl_3$): δ -179.6. ^{1}H NMR ($CDCl_3$): δ 1.30 – 1.39 (m, 2H, CH_2), 1.50 – 1.58 (m, 2H, CH_2), 6.64 – 8.77 (m, 12H, CH). ^{13}C NMR ($CDCl_3$): δ 13.64 (d, J_{CP} = 15.1 Hz, CH_2), 119.89 (s, CH), 124.36 (d, J_{CP} = 3.1 Hz, CH), 125.32 (s, CH), 126.92 (s, CH), 127.81 (s, CH), 128.11 (s, CH), 128.75 (d, J_{CP} = 7.1 Hz, CH), 129.22 (s, CH), 129.63 (s, CH), 132.67 (s, C), 134.81 (s, C), 150.40 (s, C), 150.56 (s, C), 166.48 (d, J_{CP} = 21.0 Hz, C=N), 204.24 (d, J_{CP} = 9.9 Hz, CO *cis*), 207.97 (d, J_{CP} = 32.6 Hz, CO *trans*).

The mixture HRMS: m/z calcd for $C_{24}H_{16}NO_5PMo$ $(M+H)^+$ 527.9893, found 527.9897.



2a,b 7a 7b
yield = 18% yield = 14%

Under the atmosphere of N_2, a solution of **2a,b** (282 mg, 0.5 mmol) and N-phenylmaleimide (173 mg, 1.0 mmol) in toluene (3 mL) was stirred at 130 °C for 12 h in a heavy wall pressure tube (75 mL). The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, dichloromethane/ petroleum ether = 2:1) providing 66 mg of **7a** as yellow solid (0.091 mmol, 18%, R_f = 0.51) and 52 mg of **7b** as yellow solid (0.071 mmol, 14%, R_f = 0.28).

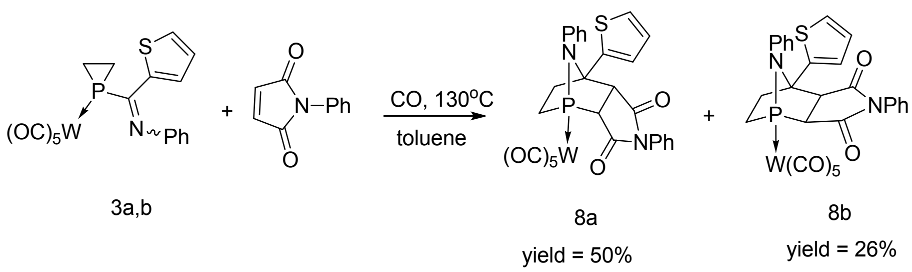


2a,b 7a 7b
yield = 40% yield = 35%

Under the atmosphere of CO, a solution of **2a,b** (282 mg, 0.5 mmol) and N-phenylmaleimide (173 mg, 1.0 mmol) in toluene (3 mL) was stirred at 130 °C for 12 h in a heavy wall pressure tube (75 mL). The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, dichloromethane/ petroleum ether = 2:1) providing 147 mg of **7a** as yellow solid (0.20 mmol, 40%, R_f = 0.51) and 129 mg of **7b** as yellow solid (0.18 mmol, 35%, R_f = 0.28). The single crystal **7a** was grown from DCM and **7b** was grown from a mixture of DCM and hexane.

7a: m.p. 197-198 °C. ^{31}P NMR ($CDCl_3$): δ 79.3 (J_{PW} = 281 Hz). ^{1}H NMR ($CDCl_3$): δ 2.13 – 2.23 (m, 1H, CH_2), 2.35 (t, J = 13.5 Hz, 1H, CH_2), 2.43 – 2.63 (m, 2H, CH_2), 4.05 (q, J = 10.6 Hz, 2H, CH), 6.87 (d, J = 7.4 Hz, 2H, CH), 7.01 – 7.20 (m, 6H, CH), 7.26 (d, J = 7.6 Hz, 2H, CH), 7.36 (d, J = 6.8 Hz, 1H, CH), 7.43 (dd, J = 10.7, 7.9 Hz, 4H, CH). ^{13}C NMR ($CDCl_3$): δ 29.44 (d, J_{CP} = 21.9 Hz, CH_2), 34.88 (d, J_{CP} = 5.0 Hz, CH_2), 53.35 (d, J_{CP} = 15.6 Hz, CH), 56.69 (d, J_{CP} = 1.7 Hz, CH), 79.60 (d, J_{CP} = 7.7 Hz, C), 126.13 (s, CH), 126.85 (d, J_{CP} = 2.1 Hz, CH), 128.19 (s, CH), 128.38 (s, CH), 128.85 (d, J_{CP} = 4.6 Hz, CH), 129.04 (s, CH), 129.26 (d, J_{CP} = 1.5 Hz, CH), 129.37 (s, CH), 131.38 (s, C), 137.30 (d, J_{CP} = 6.4 Hz, C), 139.98 (d, J_{CP} = 2.8 Hz, C), 171.64 (s, C), 173.66 (d, J_{CP} = 1.8 Hz, C), 194.36 (d, J_{CP} = 7.4 Hz, CO *cis*), 197.29 (d, J_{CP} = 29.3 Hz, CO *trans*). HRMS: m/z calcd for $C_{30}H_{21}N_2O_7PW$ $(M+H)^+$ 737.0668, found 737.0674.

7b: m.p. 122-123 °C. ^{31}P NMR ($CDCl_3$): δ 87.1 (J_{PW} = 281 Hz). ^{1}H NMR ($CDCl_3$): δ 2.38 – 2.51 (m, 2H, CH_2), 2.64 – 2.72 (m, 1H, CH_2), 2.83 – 2.89 (m, 1H, CH_2), 3.23 – 3.30 (m, 2H, CH), 6.88 (d, J = 7.4 Hz, 2H, CH), 7.14 – 7.27 (m, 8H, CH), 7.32 (d, J = 7.6 Hz, 2H, CH), 7.39 – 7.44 (m, 1H, CH), 7.48 – 7.53 (m, 2H, CH), ^{13}C NMR ($CDCl_3$): δ 33.12 (d, J_{CP} = 14.9 Hz, CH_2), 38.58 (d, J_{CP} = 3.5 Hz, CH_2), 48.04 (d, J_{CP} = 23.7 Hz, CH), 56.68 (d, J_{CP} = 3.7 Hz, CH), 78.88 (d, J_{CP} = 8.3 Hz, C), 126.50 (s, CH), 126.64 (d, J_{CP} = 2.6 Hz, CH), 127.57 (s, CH), 127.76 (s, CH), 128.38 (d, J_{CP} = 3.2 Hz, CH), 128.97 (s, CH), 129.26 (s, CH), 129.44 (s, CH), 129.57 (d, J_{CP} = 1.6 Hz, CH), 131.95 (s, C), 135.79 (d, J_{CP} = 6.6 Hz, C), 140.78 (d, J_{CP} = 2.4 Hz, C), 172.67 (s, C), 194.62 (d, J_{CP} = 7.4 Hz, CO *cis*), 197.60 (d, J_{CP} = 29.8 Hz, CO *trans*). HRMS: m/z calcd for $C_{30}H_{21}N_2O_7PW$ $(M+H)^+$ 737.0668, found 737.0669.

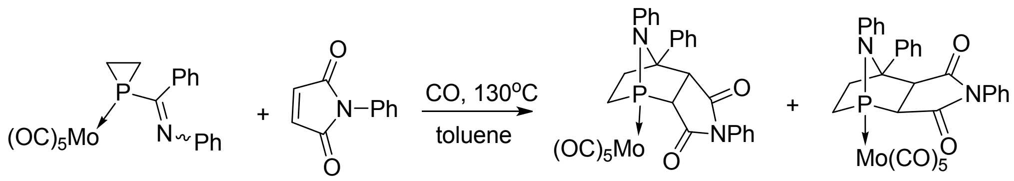


Under the atmosphere of CO, a solution of **3a,b** (285 mg, 0.5 mmol) and N-phenylmaleimide (173 mg, 1.0 mmol) in toluene (3 mL) was stirred at 130 °C for 12 h in a heavy wall pressure tube (75 mL). The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, dichloromethane/ petroleum ether = 2:1) providing 186 mg of **8a** as yellowish solid (0.25 mmol, 50%, $R_f = 0.53$) and 96 mg of **8b** as yellowish solid (0.13 mmol, 26%, $R_f = 0.35$).

8a: m.p. 116-117 °C. ^{31}P NMR ($CDCl_3$): δ 76.3 (J_{PW} = 281 Hz). ^{1}H NMR ($CDCl_3$): δ 2.15 – 2.25 (m, 1H, CH_2), 2.41 – 2.48 (m, 1H, CH_2), 2.61 – 2.63 (m, 2H, CH_2), 4.10 – 4.20 (m, 2H, CH), 6.83 – 6.93 (m, 3H, CH), 7.08 – 7.19 (m, 5H, CH), 7.30 – 7.32 (m, 2H, CH), 7.38 – 7.45 (m, 3H, CH). ^{13}C NMR ($CDCl_3$): δ 29.15 (d, J_{CP} = 22.7 Hz, CH_2), 35.11 (d, J_{CP} = 4.8 Hz, CH_2), 53.41 (d, J_{CP} = 14.9 Hz, CH), 56.58 (d, J_{CP} = 1.6 Hz, CH), 76.53 (s, C), 126.10 (s, CH), 126.77 (d, J_{CP} = 5.3 Hz, CH), 127.41 (d, J_{CP} = 0.7 Hz, CH), 128.05 (s, CH), 129.05 (s, CH), 129.12 (s, CH), 129.37 (s, CH), 129.46 (s, CH), 129.54 (s, CH), 131.35 (s, C), 139.59 (d, J_{CP} = 3.3 Hz, C), 140.03 (d, J_{CP} = 7.4 Hz, C), 171.60(s, C=O), 173.12 (d, J_{CP} = 2.3 Hz, C=O), 194.29 (d, J_{CP} = 7.4 Hz, CO *cis*), 197.22 (d, J_{CP} = 29.4 Hz, CO *trans*). HRMS: m/z calcd for $C_{28}H_{19}N_2O_7PSW$ $(M+H)^+$ 743.0233, found 743.0236. IR (neat) δ 2079.22 1927.56, 1708.93 cm^{-1}.

8b: m.p. 238-239 °C. ^{31}P NMR ($CDCl_3$): δ 86.2 (J_{PW} = 283 Hz). ^{1}H NMR ($CDCl_3$): δ 2.30 – 2.40 (m, 1H, CH_2), 2.46 – 2.57 (m, 1H, CH_2), 2.64 – 2.84 (m, 2H, CH_2), 3.23 (d, *J* = 7.7 Hz, 1H, CH), 3.30 (dd, *J* = 7.7, 4.0 Hz, 1H, CH), 6.59 (d, *J* = 3.5 Hz, 1H, CH), 6.79 – 6.82 (m, 1H, CH), 6.92 (d, *J* = 7.5 Hz, 2H, CH), 7.16 – 7.25 (m, 5H, CH), 7.31 – 7.33 (m, 1H, CH), 7.36 – 7.41 (m, 1H, CH), 7.45 – 7.49 (m, 2H, CH). ^{13}C NMR ($CDCl_3$): δ 33.81 (d, J_{CP} = 14.1 Hz, CH_2), 40.61 (d, J_{CP} = 3.8 Hz,

CH_2), 48.22 (d, J_{CP} = 23.2 Hz, CH), 56.64 (d, J_{CP} = 3.9 Hz, CH), 76.31 (d, J_{CP} = 9.9 Hz, C), 125.36 (s, CH), 126.41 (s, CH), 126.45 (s, CH), 127.33 (d, J_{CP} = 2.5 Hz, CH), 128.52 (s, CH), 128.91 (s, CH), 129.05 (d, J_{CP} = 2.6 Hz, CH), 129.36 (s, CH), 129.54 (d, J_{CP} = 2.0 Hz, CH), 131.75 (s, C), 138.07 (d, J_{CP} = 7.7 Hz, C), 140.35 (d, J_{CP} = 2.8 Hz, C), 172.29 (d, J_{CP} = 6.8 Hz, C), 194.30 (d, J_{CP} = 7.5 Hz, CO *cis*), 197.28 (d, J_{CP} = 30.3 Hz, CO *trans*). HRMS: m/z calcd for $C_{28}H_{19}N_2O_7PSW$ $(M+H)^+$ 743.0233, found 743.0239. IR (neat) δ 2080.21, 1920.87, 1709.07 cm^{-1}.



5a,b

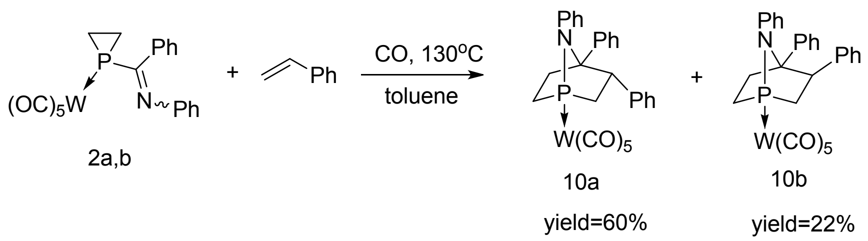
9a

9b

Under the atmosphere of CO, a solution of **5a,b** (239 mg, 0.5 mmol) and N-phenylmaleimide (173 mg, 1.0 mmol) in toluene (3 mL) was stirred at 130 °C for 12 h in a heavy wall pressure tube (75 mL). The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, dichloromethane/ petroleum ether = 2:1) providing 124 mg of **9a** as yellow solid (0.19 mmol, 38%, R_f = 0.59) and 107 mg of **9b** as yellow solid (0.17 mmol, 33%, R_f = 0.38).

9a: m.p. 200-201 °C. ^{31}P NMR ($CDCl_3$): δ 104.6. ^1H NMR ($CDCl_3$): δ 2.23 – 2.40 (m, 2H, CH_2), 2.52 – 2.62 (m, 2H, CH_2), 4.01 (d, J = 10.1 Hz, 1H, CH), 4.14 (d, J = 10.0 Hz, 1H, CH), 6.92 (d, J = 7.1 Hz, 2H, CH), 7.08 (d, J = 6.6 Hz, 1H, CH), 7.12 – 7.24 (m, 5H, CH), 7.32 (d, J = 7.3 Hz, 2H, CH), 7.42 (d, J = 6.9 Hz, 1H, CH), 7.46 – 7.54 (m, 4H, CH). ^{13}C NMR ($CDCl_3$): δ 28.78 (d, J_{CP} = 17.5 Hz, CH_2), 34.63 (d, J_{CP} = 4.5 Hz, CH_2), 53.05 (d, J_{CP} = 10.7 Hz, CH), 56.44 (d, J_{CP} = 1.9 Hz, CH), 79.87 (d, J_{CP} = 5.5 Hz, C), 126.15 (s, CH), 126.68 (d, J_{CP} = 2.2 Hz, CH), 128.14 (s, CH), 128.39 (s, CH), 128.65 (d, J_{CP} = 4.7 Hz, CH), 129.03 (s, CH), 129.20 (d, J_{CP} = 1.4 Hz, CH), 129.38 (s, CH), 131.42 (s, C), 137.51 (d, J_{CP} = 5.9 Hz, C), 140.22 (d, J_{CP} = 3.4 Hz, C), 171.81 (s, C), 173.82 (d, J_{CP} = 1.6 Hz, C), 203.76 (d, J_{CP} = 9.9 Hz, CO *cis*), 207.73 (d, J_{CP} = 30.8 Hz, CO *trans*). HRMS: m/z calcd for $C_{30}H_{21}MoN_2O_7P$ $(M+H)^+$ 651.0213, found 651.0212. IR (neat) δ 2081.53, 1941.12, 1706.59 cm^{-1}.

9b: ^{31}P NMR ($CDCl_3$): δ 110.6. ^1H NMR ($CDCl_3$): δ 2.32 – 2.36 (m, 2H, CH_2), 2.59 – 2.65 (m, 1H, CH_2), 2.74 – 2.86 (m, 1H, CH_2), 3.17 – 3.27 (m, 2H, CH), 6.81 (d, J = 7.5 Hz, 2H, CH), 7.08– 7.19 (m, 8H, CH), 7.27 (d, J = 7.5 Hz, 2H, CH), 7.35 – 7.40 (m, 1H, CH), 7.43 – 7.48 (m, 2H, CH), ^{13}C NMR ($CDCl_3$): δ 32.48 (d, J_{CP} = 9.9 Hz, CH_2), 38.07 (d, J_{CP} = 2.8 Hz, CH_2), 48.15 (d, J_{CP} = 18.9 Hz, CH), 56.60 (d, J_{CP} = 3.1 Hz, CH), 79.13 (d, J_{CP} = 5.8 Hz, C), 126.48 (s, CH), 127.57 (s, CH), 127.73 (s, CH), 128.20 (d, J_{CP} = 3.0 Hz, CH), 128.92 (s, CH), 129.24 (s, CH), 129.41 (s, CH), 129.47 (s, CH), 131.95 (s, C), 135.92 (d, J_{CP} = 6.1 Hz, CH), 140.97 (d, J_{CP} = 3.0 Hz, C), 140.78 (d, J_{CP} = 2.4 Hz, C), 172.86 (s, d, J_{CP} = 13.7 Hz, C), 204.00 (d, J_{CP} = 9.8 Hz, CO *cis*), 208.10 (d, J_{CP} = 30.9 Hz, CO *trans*). HRMS: m/z calcd for $C_{30}H_{21}MoN_2O_7P$ $(M+H)^+$ 651.0213, found 651.0239.

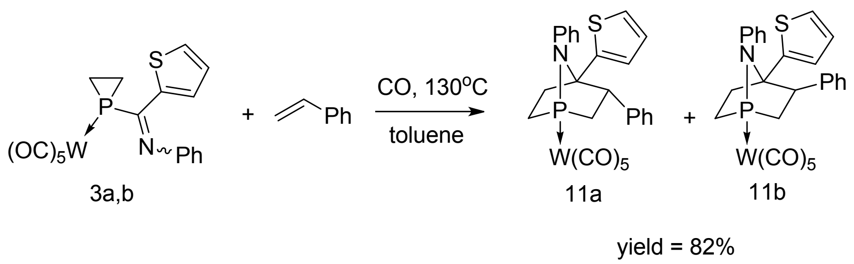


Under the atmosphere of CO, a solution of **2a,b** (282 mg, 0.5 mmol) and styrene (115 μL, 1.0 mmol) in toluene (3 mL) was stirred at 130 °C for 6 h in a heavy wall pressure tube (75 mL). The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, dichloromethane/ petroleum ether = 1:10) providing 200 mg of **10a** as yellowish solid (0.30 mmol, 60%, R_f = 0.38) and 73 mg of **10b** as yellowish solid (0.11 mmol, 22%, R_f = 0.36).

10a: m.p. 160-161 °C. ^{31}P NMR ($CDCl_3$): δ 75.0 (J_{PW} = 260 Hz). ^1H NMR ($CDCl_3$): 2.15 – 2.35 (m, 4H, CH_2), 2.55 – 2.72 (m, 2H, CH_2), 3.65 (dd, J = 11.3, 6.7 Hz, 1H, CH), 6.68 – 6.70 (m, 2H, CH), 6.97 – 7.06 (m, 5H, CH), 7.11 – 7.23 (m, 8H, CH). ^{13}C NMR ($CDCl_3$): δ 28.72 (d, J_{CP} = 4.0 Hz, CH_2), 33.96 (d, J_{CP} = 15.7 Hz, CH_2), 36.00 (d, J_{CP} = 33.3 Hz, CH_2), 58.96 (d, J_{CP} = 5.5 Hz, CH), 80.69 (d, J_{CP} = 11.3 Hz, C), 125.52 (d, J_{CP} = 2.5 Hz, CH), 127.24 (d, J_{CP} = 2.9 Hz, CH), 127.92 (d, J_{CP} =

1.8 Hz, CH), 128.37 (s, CH), 128.43 (s, CH), 128.53 (s, CH), 128.76 (s, CH), 128.90 (d, J_{CP} = 1.8 Hz, CH), 137.17 (d, J_{CP} = 3.1 Hz, C), 139.23 (d, J_{CP} = 7.7 Hz, C), 142.42 (d, J_{CP} = 1.8 Hz, C), 195.32 (d, J_{CP} = 7.4 Hz, CO *cis*), 198.61 (d, J_{CP} = 24.9 Hz, CO *trans*). HRMS: m/z calcd for $C_{28}H_{22}NO_5PW$ $(M+H)^+$ 668.0818, found 668.0821. IR (neat) δ 2073.72, 1913.54 cm^{-1}.

10b: m.p. 75-76 °C. ^{31}P NMR ($CDCl_3$): δ 71.1 (J_{PW} = 260 Hz). ^1H NMR ($CDCl_3$): δ 2.26 (t, J = 7.3 Hz, 2H, CH_2), 2.45 (dd, J = 14.8, 9.8 Hz, 1H, CH_2), 2.64 – 2.85 (m, 3H, CH_2), 3.23 – 3.29 (m, 1H, CH), 6.67 (d, J = 7.4 Hz, 2H, CH), 6.81 (t, J = 7.3 Hz, 2H, CH), 6.85 – 7.16 (m, 11H, CH). ^{13}C NMR ($CDCl_3$): δ 33.09 (d, J_{CP} = 15.0 Hz, CH_2), 37.74 (d, J_{CP} = 3.8 Hz, CH_2), 38.49 (d, J_{CP} = 32.0 Hz, CH_2), 58.76 (d, J_{CP} = 5.5 Hz, CH), 80.38 (d, J_{CP} = 11.5 Hz, C), 125.50 (d, J_{CP} = 2.9 Hz, CH), 126.20 (s, CH), 126.55 (s, CH), 126.90 (s, CH), 127.56 (s, CH), 128.45 (s, CH), 128.77 (s, CH), 129.07 (d, J_{CP} = 2.4 Hz, CH), 138.80 (d, J_{CP} = 7.9 Hz, C), 141.96 (d, J_{CP} = 1.6 Hz, C), 143.40 (s, C), 195.30 (d, J_{CP} = 7.5 Hz, CO *cis*), 198.51 (d, J_{CP} = 25.5 Hz, CO *trans*). HRMS: m/z calcd for $C_{28}H_{22}NO_5PW$ $(M+H)^+$ 668.0818, found 668.0822. IR (neat) δ 2073.72, 1913.54 cm^{-1}.

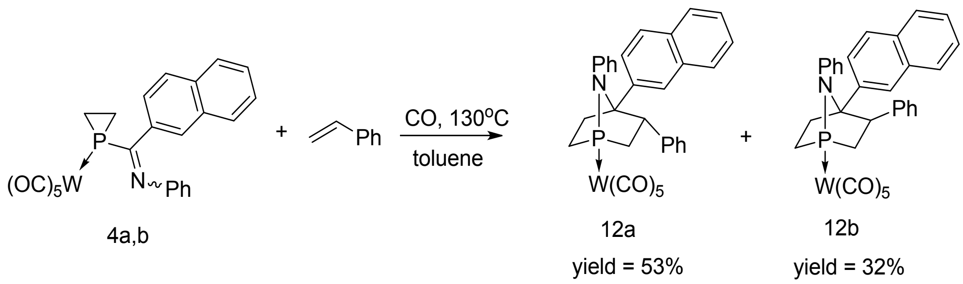


Under the atmosphere of CO, a solution of **3a,b** (284 mg, 0.5 mmol) and styrene (115 μL, 1.0 mmol) in toluene (3 mL) was stirred at 130 °C for 6 h in a heavy wall pressure tube (75 mL). The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, dichloromethane/ petroleum ether = 1:10, R_f = 0.38) providing 276 mg of **11a,b** as yellowish solid (0.41 mmol, 82%, 11a:11b = 4:1). The NMR data of **11a** and **11b** was selected from NMR spectra of **11a,b** mixture.

11a: ^{31}P NMR ($CDCl_3$): δ 72.9 (J_{PW} = 260 Hz). ^1H NMR ($CDCl_3$): δ 2.13 – 2.73

(m, 6H, CH_2), 3.80 (dd, J = 11.4, 6.4 Hz, 1H, CH), 6.54 (d, J = 3.1 Hz, 1H, CH), 6.99 – 6.72 (m, 1H, CH), 6.93 – 7.19 (m, 11H, CH). ^{13}C NMR ($CDCl_3$): δ 30.45 (d, J_{CP} = 4.1 Hz, CH_2), 34.07 (d, J_{CP} = 17.0 Hz, CH_2), 36.75 (d, J_{CP} = 31.4 Hz, CH_2), 57.89 (d, J_{CP} = 5.2 Hz, CH), 78.42 (d, J_{CP} = 12.7 Hz, C), 125.90 (s, CH), 126.18 (s, CH), 126.31 (s, CH), 127.33 (d, J_{CP} = 6.8 Hz, CH), 128.19 (s, CH), 128.55 (s, CH), 128.83 (d, J_{CP} = 0.6 Hz, CH), 129.37 (d, J_{CP} = 5.5 Hz, CH), 137.58 (d, J_{CP} = 3.2 Hz, C), 141.94 (d, J_{CP} = 2.0 Hz, C), 142.47 (d, J_{CP} = 8.9 Hz, C), 195.23 (d, J_{CP} = 7.3 Hz, CO *cis*), 198.53 (d, J_{CP} = 25.3 Hz, CO *trans*).

11b: ^{31}P NMR ($CDCl_3$): δ 68.4 (J_{PW} = 263 Hz). ^{1}H NMR ($CDCl_3$): δ 2.13 – 2.73 (m, 6H, CH_2), 3.22 – 3.28 (m, 1H, CH), 6.11 (d, J = 3.2 Hz, 1H, CH), 6.44 – 6.47 (m, 1H, CH), 6.81 (d, J = 4.9 Hz, 1H, CH), 6.93 – 7.19 (m, 10H, CH). ^{13}C NMR ($CDCl_3$): δ 33.66 (d, J_{CP} = 14.4 Hz, CH_2), 39.28 (d, J_{CP} = 32.0 Hz, CH_2), 39.64 (d, J_{CP} = 3.9 Hz, CH_2), 57.98 (s, CH), 78.35 (d, J_{CP} = 13.2 Hz, C), 124.68 (s, CH), 125.58 (s, CH), 126.34 (s, CH), 127.00 (d, J_{CP} = 3.0 Hz, CH), 127.91 (s, CH), 128.74 (s, CH), 129.09 (s, CH), 141.40 (d, J_{CP} = 9.1 Hz, C), 141.74 (d, J_{CP} = 1.8 Hz, C), 143.90 (s, C), 195.18 (d, J_{CP} = 7.3 Hz, CO *cis*), 198.46 (d, J_{CP} = 25.3 Hz, CO *trans*). The mixture HRMS: m/z calcd for $C_{26}H_{20}NO_5PSW$ $(M+H)^+$ 674.0382, found 674.0379.

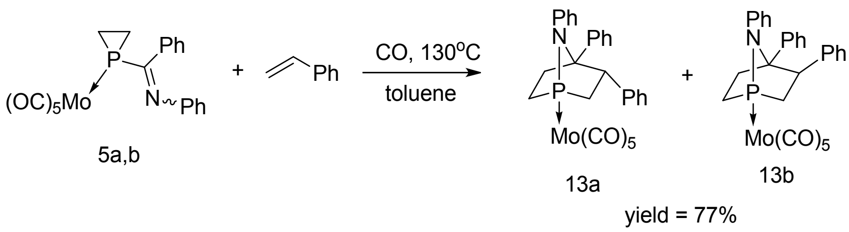


Under the atmosphere of CO, a solution of **4a,b** (307 mg, 0.5 mmol) and styrene (115 µL, 1.0 mmol) in toluene (3 mL) was stirred at 130 °C for 6 h in a heavy wall pressure tube (75 mL). The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, dichloromethane/ petroleum ether = 1:10) providing 190 mg of **12a** as yellowish solid (0.27 mmol, 53%, R_f = 0.35) and 115 mg of **12b** as yellowish solid (0.16 mmol, 32%, R_f = 0.33).

12a: m.p. 210-211 °C. ^{31}P NMR ($CDCl_3$): δ 75.2 (J_{PW} =260 Hz). ^{1}H NMR

(CDCl$_3$): δ 2.24 (dd, J = 14.4, 6.5 Hz, 1H, CH$_2$), 2.28 – 2.39 (m, 3H, CH$_2$), 2.69 – 2.76 (m, 2H, CH$_2$), 3.78 (dd, J = 11.5, 6.5 Hz, 1H, CH), 6.65 (d, J = 7.3 Hz, 2H, CH), 6.93 – 7.15 (m, 8H, CH), 7.24 (s, 1H, CH), 7.33 – 7.41 (m, 2H, CH), 7.46 (d, J = 8.6 Hz, 1H, CH), 7.56 (d, J = 7.2 Hz, 1H, CH), 7.67 (dd, J = 17.7, 8.0 Hz, 2H, CH). ^{13}C NMR (CDCl$_3$): δ 29.00 (d, J_{CP} = 3.8 Hz, CH$_2$), 34.05 (d, J_{CP} = 15.5 Hz, CH$_2$), 36.21 (d, J_{CP} = 33.5 Hz, CH$_2$), 58.31 (d, J_{CP} = 5.6 Hz, CH), 80.96 (d, J_{CP} = 11.3 Hz, C), 125.67 (d, J_{CP} = 2.4 Hz, CH), 126.02 (d, J_{CP} = 9.3 Hz, CH), 126.45 (s, CH), 127.24 (s, CH), 127.53 (s, CH), 127.76 (d, J_{CP} = 6.4 Hz, CH), 127.99 (s, CH), 128.07 (s, CH), 128.49 (d, J_{CP} = 4.5 Hz, CH), 128.72 (s, CH), 128.98 (d, J_{CP} = 1.6 Hz, CH), 132.59 (d, J_{CP} = 21.1 Hz, C), 136.82 (d, J_{CP} = 7.8 Hz, C), 137.16 (d, J_{CP} = 2.9 Hz, C), 142.42 (d, J_{CP} = 1.7 Hz, C), 195.35 (d, J_{CP} = 7.4 Hz, CO *cis*), 198.63 (d, J_{CP} = 25.1 Hz, CO *trans*). HRMS: m/z calcd for $C_{32}H_{24}NO_5PW$ $(M+H)^+$ 718.0974, found 718.0979. IR (neat) δ 2073.53, 1937.99 cm^{-1}.

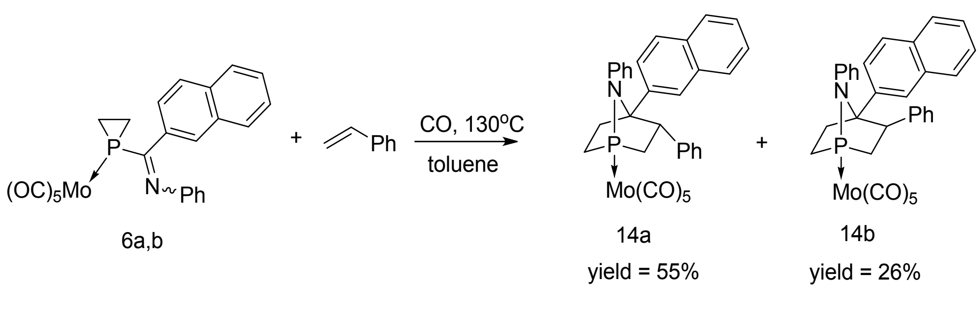
12b: m.p. 181-182 ^{o}C. ^{31}P NMR (CDCl$_3$): δ 71.0 (J_{PW} =261 Hz). ^{1}H NMR (CDCl$_3$): δ 2.31 (t, J = 7.4 Hz, 2H, CH$_2$), 2.49 – 2.54 (1H, CH$_2$), 2.72 (d, J = 14.8 Hz, 1H, CH$_2$), 2.81 – 3.01 (m, 2H, CH$_2$), 3.31 –3.37 (m, 1H, CH), 6.48 (dd, J = 8.7, 1.3 Hz, 1H, CH), 6.93 – 7.13 (m, 11H, CH), 7.30 – 7.37 (m, 2H, CH), 7.52 – 7.59 (m, 3H, CH). ^{13}C NMR (CDCl$_3$): δ 33.22 (d, J_{CP} = 15.2 Hz, CH$_2$), 37.98 (d, J_{CP} = 3.7 Hz, CH$_2$), 38.61 (d, J_{CP} = 32.2 Hz, CH$_2$), 58.84 (d, J_{CP} = 5.4 Hz, CH), 80.49 (d, J_{CP} = 11.6 Hz, C), 125.52 (s, CH), 125.56 (s, CH), 125.72 (d, J_{CP} = 4.6 Hz, CH), 126.65 (s, CH), 127.00 (d, J_{CP} = 3.3 Hz, CH), 127.32 (s, CH), 127.61 (s, CH), 127.77 (s, CH), 128.89 (s, CH), 129.10 (d, J_{CP} = 2.5 Hz, CH), 132.08 (d, J_{CP} = 57.5 Hz, C), 136.97 (d, J_{CP} = 7.9 Hz, C), 141.87 (d, J_{CP} = 1.4 Hz, C), 143.17 (s, C), 195.30 (d, J_{CP} = 7.4 Hz, CO *cis*), 198.50 (d, J_{CP} = 25.5 Hz, CO *trans*). HRMS: m/z calcd for $C_{32}H_{24}NO_5PW$ $(M+H)^+$ 718.0974, found 718.0979.



Under the atmosphere of CO, a solution of **5a,b** (239 mg, 0.5 mmol) and styrene (115 μL, 1.0 mmol) in toluene (3 mL) was stirred at 130 °C for 6 h in a heavy wall pressure tube (75 mL). The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, dichloromethane/ petroleum ether = 1:10, $R_f = 0.35$) providing 224 mg of **13a,b** as yellowish solid (0.39 mmol, 77%, 13a:13b = 3.2:1). The NMR data of **13a** was selected from NMR spectra of **13a,b** mixture.

13a: ^{31}P NMR ($CDCl_3$): δ 98.8. ^{1}H NMR ($CDCl_3$): 2.12 – 2.29 (m, 4H, CH_2), 2.57 – 2.65 (m, 2H, CH_2), 3.64 (dd, J = 11.4, 6.8 Hz, 1H, CH), 6.68 – 6.71 (m, 2H, CH), 6.96 (d, J = 8.1 Hz, 2H, CH), 6.99 – 7.06 (m, 3H, CH), 7.09 – 7.22 (m, 8H, CH). δ ^{13}C NMR ($CDCl_3$): 28.23 (d, J_{CP} = 4.0 Hz, CH_2), 33.43 (d, J_{CP} = 11.4 Hz, CH_2), 35.53 (d, J_{CP} = 28.9 Hz, CH_2), 58.74 (d, J_{CP} = 5.4 Hz, CH), 80.85 (d, J_{CP} = 9.0 Hz, C), 125.26 (d, J_{CP} = 2.4 Hz, CH), 127.17 (d, J_{CP} = 2.2 Hz, CH), 127.88 (s, CH), 128.10 (s, CH), 128.16 (s, CH), 128.50 (s, CH), 128.78 (s, CH), 137.30 (d, J_{CP} = 2.8 Hz, C), 139.46 (d, J_{CP} = 7.2 Hz, C), 142.66 (d, J_{CP} = 2.1 Hz, C), 204.65 (d, J_{CP} = 9.8 Hz, CO *cis*), 208.91 (d, J_{CP} = 26.8 Hz, CO *trans*).

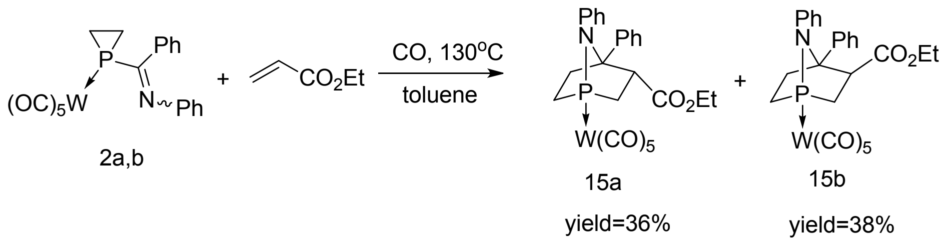
The mixture HRMS: m/z calcd for $C_{28}H_{23}NO_5PMo$ $(M+H)^+$ 582.0364, found 582.0362.



Under the atmosphere of CO, a solution of **6a,b** (264 mg, 0.5 mmol) and styrene (115 μL, 1.0 mmol) in toluene (3 mL) was stirred at 130 °C for 6 h in a heavy wall pressure tube (75 mL). The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, dichloromethane/ petroleum ether = 1:10) providing 174 mg of **14a** as yellowish solid (0.28 mmol, 55%, R_f = 0.37) and 82 mg of **14b** as yellowish solid (0.13 mmol, 26%, R_f = 0.35).

14a: m.p. 197-198 °C. ^{31}P NMR ($CDCl_3$): δ 98.8. ^{1}H NMR ($CDCl_3$): δ 2.22 (dd, J = 14.4, 6.6 Hz, 1H, CH_2), 2.33 – 2.38 (m, 3H, CH_2), 2.61 – 2.73 (m, 2H, CH_2), 3.77 (dd, J = 11.4, 6.5 Hz, 1H, CH), 6.65 (d, J = 7.3 Hz, 2H, CH), 6.92 – 7.16 (m, 8H, CH), 7.25 (s, 1H, CH), 7.34 – 7.42 (m, 2H, CH), 7.46 (d, J = 8.6 Hz, 1H, CH), 7.57 (d, J = 8.1 Hz, 1H, CH), 7.65 (d, J = 8.6 Hz, 1H, CH), 7.71 (d, J = 7.3 Hz, 1H, CH). ^{13}C NMR ($CDCl_3$): δ 28.50 (d, J_{CP} = 4.1 Hz, CH_2), 35.72 (d, J_{CP} = 29.0 Hz, CH_2), 33.50 (d, J_{CP} = 11.3 Hz, CH_2), 58.08 (d, J_{CP} = 5.5 Hz, CH), 81.10 (d, J_{CP} = 9.1 Hz, C), 125.39 (d, J_{CP} = 2.3 Hz, CH), 126.00 (s, CH), 125.89 (s, CH), 126.45 (s, CH), 127.16 (s, CH), 127.49 (s, CH), 127.64 (s, CH), 127.74 (s, CH), 127.92 (s, CH), 128.03 (s, CH), 128.20 (d, J_{CP} = 4.5 Hz, CH), 128.72 (s, CH), 128.85 (d, J_{CP} = 1.7 Hz, CH), 132.41 (s, C), 132.72 (s, C), 137.04 (d, J_{CP} = 7.1 Hz, C), 137.27 (d, J_{CP} = 2.8 Hz, C), 142.63 (s, C), 204.66 (d, J_{CP} = 9.7 Hz, CO *cis*), 208.90 (d, J_{CP} = 26.8 Hz, CO *trans*). HRMS: m/z calcd for $C_{32}H_{24}NO_5PMo$ $(M+H)^+$ 632.0519, found 632.0526.

14b: m.p. 152-153 °C. ^{31}P NMR ($CDCl_3$): δ 94.8. ^{1}H NMR ($CDCl_3$): δ 2.24 – 2.31 (m, 2H, CH_2), 2.46 (dd, J = 14.9, 9.5 Hz, 1H, CH_2), 2.61 – 2.66 (m, 1H, CH_2), 2.81 – 2.95 (m, 2H, CH_2), 3.29 – 3.35 (m, 1H, CH), 6.49 (dd, J = 8.7, 1.6 Hz, 1H, CH), 6.94 – 7.12 (m, 11H, CH), 7.29 – 7.38 (m, 2H, CH), 7.48 – 7.60 (m, 3H, CH). ^{13}C NMR ($CDCl_3$): δ 32.70 (d, J_{CP} = 10.8 Hz, CH_2), 37.48 (d, J_{CP} = 4.0 Hz, CH_2), 38.05 (d, J_{CP} = 27.6 Hz, CH_2), 58.64 (d, J_{CP} = 5.4 Hz, CH), 80.62 (d, J_{CP} = 9.1 Hz, C), 125.32 (s, CH), 125.53 (s, CH), 125.68 (d, J_{CP} = 5.5 Hz, CH), 126.59 (s, CH), 127.00 (d, J_{CP} = 3.4 Hz, CH), 127.32 (s, CH), 127.57 (s, CH), 127.76 (s, CH), 128.89 (s, CH), 128.99 (d, J_{CP} = 2.3 Hz, CH), 131.69 (s, C), 132.47 (s, C), 137.19 (d, J_{CP} = 7.2 Hz, C), 142.13 (d, J_{CP} = 2.2 Hz, C), 143.31 (s, C), 204.67 (d, J_{CP} = 9.6 Hz, CO *cis*), 208.81 (d, J_{CP} = 27.1 Hz, CO *trans*). HRMS: m/z calcd for $C_{32}H_{24}NO_5PMo$ $(M+H)^+$ 632.0519, found 632.0528.

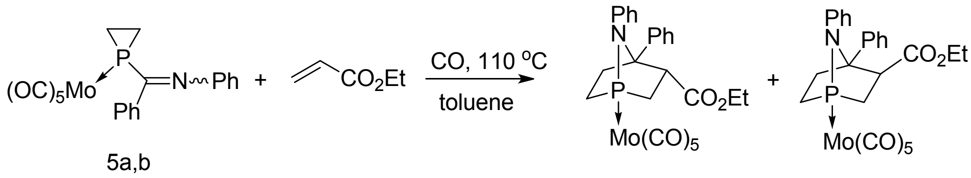


A solution of **2a,b** (282 mg, 0.5 mmol) and ethyl acrylate (110 µL, 1.0 mmol) in toluene (3 mL) was stirred at 130 °C for 6 h in a heavy wall pressure tube (75 mL). All the volatile was removed by rotary evaporator. The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, dichloromethane/ petroleum ether = 1:5) providing 119 mg of **15a** as yellowish solid (0.18 mmol, 36%, R_f = 0.41) and 126 mg of **15b** as yellowish solid (0.19 mmol, 38%, R_f = 0.37). The single crystal of **15a** was grown from a mixture of DCM and hexane.

15a: m.p. 165-166 °C. ^{31}P NMR ($CDCl_3$): δ 73.8 (J_{PW} = 262 Hz). ^{1}H NMR ($CDCl_3$): δ 0.96 (t, J = 7.1 Hz, 3H, CH_3), 2.28 (dd, J = 15.2, 7.3 Hz, 2H, CH_2), 2.36 (d, J = 6.0 Hz, 1H, CH_2), 2.47 (t, J = 12.1 Hz, 2H, CH_2), 2.83 (ddd, J = 15.4, 13.0, 6.3 Hz, 1H, CH_2), 3.38 (dd, J = 11.2, 6.1 Hz, 1H, CH), 3.85 – 4.08 (m, 2H, CH_2), 6.90 (d, J = 7.7 Hz, 2H, CH), 7.02 (d, J = 6.4 Hz, 1H, CH), 7.07 – 7.22 (m, 5H, CH) 7.32 (d, J = 7.1 Hz, 2H, CH). ^{13}C NMR ($CDCl_3$): δ 13.90 (s, CH_3), 30.68 (d, J_{CP} = 4.4 Hz, CH_2), 33.03 (d, J_{CP} = 17.5 Hz, CH_2), 34.59 (d, J_{CP} = 31.5 Hz, CH_2), 56.67 (d, J_{CP} = 5.3 Hz, CH), 60.95 (s, CH_2), 78.80 (d, J_{CP} = 11.3 Hz, C), 125.91 (d, J_{CP} = 2.1 Hz, CH), 127.60 (s, CH), 127.98 (s, CH), 128.16 (s, CH), 128.74 (d, J_{CP} = 5.0 Hz, CH), 128.83 (d, J_{CP} = 1.3 Hz, CH), 138.47 (d, J_{CP} = 7.3 Hz, C), 141.37 (d, J_{CP} = 2.2 Hz, C), 171.98 (d, J_{CP} = 3.9 Hz, C), 195.06 (d, J_{CP} = 7.3 Hz, CO *cis*), 198.37 (d, J_{CP} = 25.7 Hz, CO trans). Elemental Analysis Calcd(%) for $C_{25}H_{22}NO_7PW$: C, 45.27; H, 3.34; N, 2.11. Found: C, 45.20; H, 3.43; N, 1.92. HRMS: m/z calcd for $C_{25}H_{22}NO_7PW$ $(M+H)^+$ 664.0716, found 664.0720.

15b: m.p. 79-80 °C. ^{31}P NMR ($CDCl_3$): δ 70.5 (J_{PW} = 263 Hz). ^{1}H NMR ($CDCl_3$): δ 0.78 (t, J = 7.2 Hz, 3H, CH_3), 2.06 (m, 1H, CH_2), 2.21 – 2.25 (m, 2H, CH_2), 2.62 – 2.79 (m, 3H, CH_2), 2.99 – 3.05 (m, 1H, CH), 3.45 (dq, J = 10.7, 7.2 Hz, 1H, CH_2), 3.77 (dq, J = 10.8, 7.1 Hz, 1H, CH_2), 6.95 – 6.97 (m, 2H, CH), 7.07 (d, J =

6.3 Hz, 1H, CH), δ 7.13 – 7.24 (m, 7H, CH). ^{13}C NMR ($CDCl_3$): δ 13.48 (s, CH_3), 32.50 (d, J_{CP} = 14.9 Hz, CH_2), 34.00 (d, J_{CP} = 32.4 Hz, CH_2), 38.18 (d, J_{CP} = 4.0 Hz, CH_2), 57.08 (d, J_{CP} = 5.9 Hz, CH), 60.78 (s, CH_2), δ 78.95 (d, J_{CP} = 11.5 Hz, C), 125.69 (d, J_{CP} = 2.6 Hz, CH), 127.37 (s, CH), 127.86 (s, CH), 128.35 (s, CH), 129.03 (d, J_{CP} = 2.2 Hz, CH), 137.93 (d, J_{CP} = 7.7 Hz, C), 141.49 (d, J_{CP} = 2.5 Hz, C), 171.90 (s, C), 195.02 (d, J_{CP} = 7.4 Hz, CO *cis*), 198.43 (d, J_{CP} = 25.9 Hz, CO *trans*). HRMS: m/z calcd for $C_{25}H_{22}NO_7PW$ $(M+H)^+$ 664.0716, found 664.0723. IR (neat) δ 2071.74, 1911.91, 1726.74 cm^{-1}.



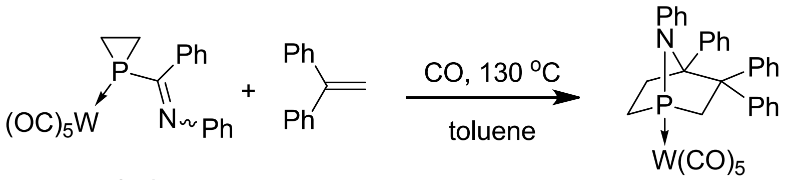
5a,b 16a 16b

yield = 34% yield = 35%

Under the atmosphere of CO, a solution of **5a,b** (239 mg, 0.50 mmol) and ethyl acrylate (110 μL, 1.00 mmol) in toluene (3 mL) was stirred at 110 °C for 6 h in a heavy wall pressure tube (75 mL). All the volatile was removed by rotary evaporator. Purification was performed via column chromatography on silica gel using 10/1 petroleum ether/dichloromethane, to give off yellowish solid **16a** (98 mg, 34%, R_f = 0.44) and yellowish solid **16b** (101 mg, 35%, R_f = 0.42). The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, dichloromethane/ petroleum ether = 1:5) providing 98 mg of **16a** as yellowish solid (0.17 mmol, 34%, R_f = 0.44) and 101mg of **16b** as yellowish solid (0.18 mmol, 35%, R_f = 0.42).

16a: m.p. 138-139 °C. ^{31}P NMR ($CDCl_3$): δ 99.1. ^{1}H NMR ($CDCl_3$): δ 0.97 (t, J = 7.1 Hz, 3H, CH_3), 2.20 – 2.45 (m, 5H, CH_2), 2.76 – 2.88 (m, 1H, CH_2), 3.34 – 3.40 (m, 1H, CH), 3.86 – 4.08 (m, 2H, CH_2), 6.88 – 6.89 (m, 2H, CH), 6.97 – 7.03 (m, 1H, CH), 7.07 – 7.26 (m, 5H, CH), 7.31 – 7.34 (m, 2H, CH). ^{13}C NMR ($CDCl_3$): δ 13.89 (s, CH_3) , 30.23 (d, J_{CP} = 4.3 Hz, CH_2), 32.53 (d, J_{CP} = 13.2 Hz, CH_2), 34.04 (d, J_{CP} = 27.1 Hz, CH_2), 56.40 (d, J_{CP} = 4.9 Hz, CH), 60.88 (s, CH_2), 79.00 (d, J_{CP} = 8.8 Hz, C), 125.68 (d, J_{CP} = 2.1 Hz, CH), 127.53 (s, CH), 127.96 (s, CH), 128.14 (s, CH), 128.50 (d, J_{CP} = 5.0 Hz, CH), 128.72 (d, J_{CP} = 1.5 Hz, CH), 138.68 (d, J_{CP} = 6.7 Hz, C), 141.62 (d, J_{CP}= 2.6 Hz, C), 172.07 (d, J_{CP}= 3.6 Hz, C), 204.41 (d, J_{CP} = 9.8 Hz, CO *cis*), 208.27 (d, J_{CP} = 31.3 Hz, CO *trans*). HRMS: m/z calcd for $C_{25}H_{22}NO_7PMo$ $(M+H)^+$ 578.0261, found 578.0267.

16b: m.p. >300 °C. ^{31}P NMR ($CDCl_3$): δ 93.7. ^1H NMR ($CDCl_3$): δ 0.77 (t, J = 7.2 Hz, 3H, CH_3), 2.01 (dd, J = 14.0, 9.4 Hz, 1H, CH_2), 2.15 – 2.20 (m, 2H, CH_2), 2.54 – 2.75 (m, 3H, CH_2), 2.96 – 3.02 (m, 1H, CH), 3.43 (dq, J = 10.7, 7.2 Hz, 1H, CH_2), 3.75 (dq, J = 10.8, 7.1 Hz, 1H, CH_2), 6.91 (d, J = 7.7 Hz, 2H, CH), 7.00 – 7.05 (m, 1H, CH), 7.11 – 7.23 (m, 7H, CH). ^{13}C NMR ($CDCl_3$): δ 13.45 (s, CH_3), 31.92 (d, J_{CP} = 10.5 Hz, CH_2), 33.37 (d, J_{CP} = 27.7 Hz, CH_2), 37.69 (d, J_{CP} = 4.2 Hz, CH_2), 56.84 (d, J_{CP} = 5.7 Hz, CH), 60.73 (s, CH_2), 79.13 (d, J_{CP} = 9.0 Hz, C), 125.45 (d, J_{CP} = 2.7 Hz, CH), 127.30 (s, CH), 127.81 (s, CH), 128.15 (d, J_{CP} = 3.9 Hz, CH), 128.34 (s, CH), 128.91 (d, J_{CP} = 2.2 Hz, CH), 138.11 (d, J_{CP} = 7.1 Hz, C), 141.72 (d, J_{CP} = 3.0 Hz, C), 172.03 (d, J_{CP} = 1.8 Hz, C), 204.38 (d, J_{CP} = 9.7 Hz, CO *cis*), 208.70 (d, J_{CP} = 27.6 Hz, CO *trans*). HRMS: m/z calcd for $C_{25}H_{22}NO_7PMo$ $(M+H)^+$ 578.0261, found 578.0260.



2a,b

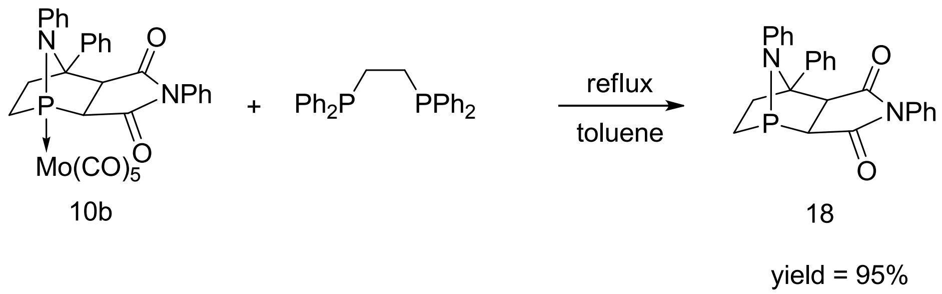
17

yield = 39%

Under the atmosphere of CO, a solution of **2a,b** (263 mg, 0.50 mmol) and 1,1-diphenylethylene (180 µL, 1.0 mmol) in toluene (3 mL) was stirred at 130 °C for 30 h in a heavy wall pressure tube (75 mL). The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, dichloromethane/ petroleum ether = 1:10) providing 145 mg of **17** as yellowish solid (0.20 mmol, 39%, R_f = 0.38) .

17: m.p. >300 °C. ^{31}P NMR ($CDCl_3$): δ 61.8 (J_{PW} = 263 Hz). ^1H NMR ($CDCl_3$):

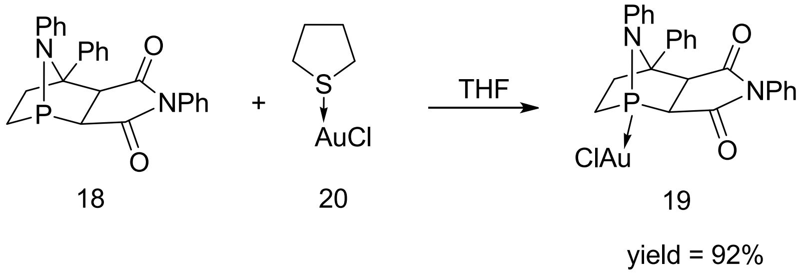
δ 2.06 – 2.22 (m, 2H, CH_2), 2.66 (dd, *J* = 14.6, 4.6 Hz, 1H, CH_2), 2.87 – 2.96 (m, 1H, CH_2), 3.17 – 3.28(m, 1H, CH_2), 3.67 (dd, *J* = 14.7, 2.4 Hz, 1H, CH_2), 6.83 – 6.97 (m, 11H, CH), 7.14 – 7.29 (m, 7H, CH), 7.50 (d, *J* = 7.4 Hz, 2H, CH). ^{13}C NMR ($CDCl_3$): δ 33.27 (d, J_{CP} = 3.7 Hz, CH_2), 34.98 (d, J_{CP} = 16.6 Hz, CH_2), 47.36 (d, J_{CP} = 31.6 Hz, CH_2), 63.15 (s, C), 83.56 (d, J_{CP} = 11.0 Hz, C), 125.68 (d, J_{CP} = 2.7 Hz, CH), 126.33 (d, J_{CP} = 2.4 Hz, CH), 126.57 (s. CH), 126.62 (s, CH), 127.08 (s, CH), 128.01 (s, CH), 128.69 (d, J_{CP} = 1.3 Hz, CH), 129.74 (s, CH), 131.23 (s, CH), 138.05 (d, J_{CP} = 7.5 Hz, C), 141.97 (s, C), 146.42 (s, C), 146.49 (d, J_{CP} = 3.3 Hz, C), 195.16 (d, J_{CP} = 7.4 Hz, CO *cis*), 198.29 (d, J_{CP} = 24.8 Hz, CO *trans*). HRMS: m/z calcd for $C_{34}H_{27}NO_5PW$ $(M+H)^+$ 744.1131, found 744.1137. IR (neat) δ 2073.08, 1919.93 cm^{-1}.



Under the atmosphere of N_2, complex **10b** (195 mg, 0.30 mmol) and dppe (61 mg, 0.15 mmol) were heated in refluxing toluene (3 mL) for 3h. The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, dichloromethane) providing 117 mg of **18** as yellowish solid (0.29 mmol, 95%, R_f = 0.42).

18: ^{31}P NMR ($CDCl_3$): δ 68.54. ^{1}H NMR ($CDCl_3$): δ 1.55 – 1,71 (m, 1H, CH_2), 1.96 (dd, *J* = 26.3, 11.8 Hz, 1H, CH_2), 2.21 – 2.44 (m, 2H, CH_2), 3.12 – 3.17 (m, 1H, CH), 3.35 – 3.37 (m, 1H, CH), 6.70 (d, *J* = 7.7 Hz, 2H, CH), 6.80 (t, *J* = 7.2 Hz, 1H, CH), 6.98 (dd, *J* = 14.9, 7.4 Hz, 4H, CH), 7.22 – 7.37 (m, 8H, CH). ^{13}C NMR ($CDCl_3$): δ 25.24 (d, J_{CP} = 19.8 Hz, CH_2), 38.56 (s, CH_2), 48.87 (d, J_{CP} = 20.6 Hz, CH), 55.29 (s, CH), 80.78 (d, J_{CP} = 9.3 Hz, C), 121.89 (d, J_{CP} = 2.4 Hz, CH), 122.80 (d, J_{CP} = 8.5 Hz, CH), 126.62 (s, CH), 127.50 (s, CH), 127.90 (s, CH), 128.51 (s, CH), 128.64 (s, CH), 128.79 (s, CH), 129.08 (s, CH), 131.98 (s, C), 136.83 (s, C), 143.61

(d, J_{CP} = 8.7 Hz, C), 174.35 (s, C=O), 175.97 (d, J_{CP} = 7.1 Hz, C=O). HRMS: m/z calcd for $C_{25}H_{21}N_2O_2P$ $(M+H)^+$ 413.1413, found 413.1415.



Under the atmosphere of N_2, a solution of **18** (82 mg, 0.20 mmol) and **20** (64 mg, 0.20 mmol) in THF (3 mL) stirred for 0.5 h at r.t. All the volatile was removed by rotary evaporator. Then the crude product was washed for 2 times with 3 mL n-hexane and filtered to give 119 mg of **19 as** yellowish solid (0.18 mmol, 92%). The single crystal of **19** was grown from a mixture of DCM and hexane.

19: ^{31}P NMR ($CDCl_3$): δ 96.95. ^{1}H NMR ($CDCl_3$): δ 2.33 – 2.48 (m, 2H, CH_2), 2.57 – 2.65 (m, 1H, CH_2), 2.87 – 2.96 (m, 1H, CH_2), 3.47 – 3.52 (m, 1H, CH), 4.03 (dd, J = 7.4, 1.6 Hz, 1H, CH), 6.86 (d, J = 7.7 Hz, 2H, CH), 6.95 – 7.00 (m, 1H, CH), 7.05 – 7.18 (m, 9H, CH), 7.35 – 7.38 (m, 3H, CH). ^{13}C NMR ($CDCl_3$): δ 25.65 (d, J_{CP} = 25.1 Hz, CH_2), 35.95 (d, J_{CP} = 3.7 Hz, CH_2), 45.40 (d, J_{CP} = 37.7 Hz, CH), 55.46 (d, J_{CP} = 4.3 Hz, CH), 76.05 (d, J_{CP} = 17.1 Hz, C), 125.03 (s, CH), 125.48 (d, J_{CP} = 4.3 Hz, CH), 126.52 (s, CH), 127.83 (s, CH), 128.04 (s, CH), 128.66 (s, CH), 128.74 (d, J_{CP} = 12.1 Hz, CH), 129.12 (d, J_{CP} = 1.8 Hz, CH), 129.18 (s, CH), 131.64 (s, C), 134.92 (d, J_{CP} = 8.7 Hz, C), 139.91 (s, C), 172.36 (s, C=O), 172.46 (d, J_{CP} = 3.1 Hz, C=O). HRMS: m/z calcd for $C_{25}H_{21}AuClN_2O_2P$ $(M+H)^+$ 645.0767, found 645.0775.

X-ray crystallographic studies of compound 7a

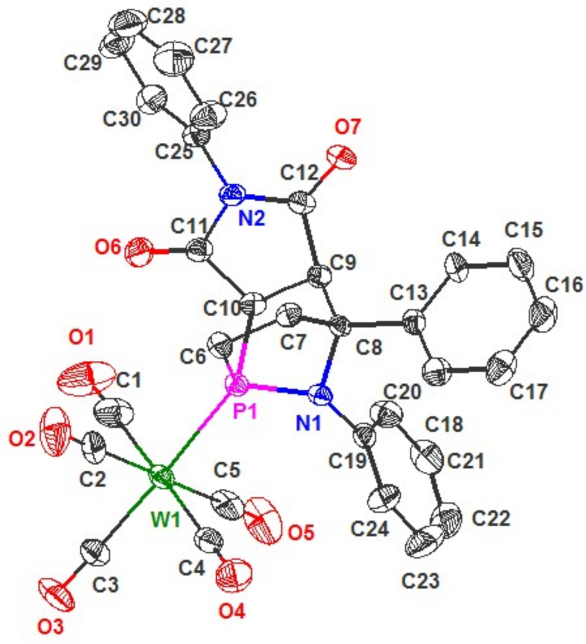


Table 1 Crystal data and structure refinement for 7a.

Identification code	7a
Empirical formula	$C_{30}H_{21}N_2O_7PW$
Formula weight	736.31
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	16.786(3)
b/Å	9.1802(5)
c/Å	19.895(2)
α/°	90
β/°	111.372(19)
γ/°	90
Volume/Å^3	2855.0(8)
Z	4
ρ_{calc}g/cm^3	1.713
μ/mm^{-1}	4.152
F(000)	1440.0
Crystal size/mm^3	0.13 × 0.1 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.846 to 52.724
Index ranges	$-20 \leq h \leq 14, -11 \leq k \leq 10, -23 \leq l \leq 24$
Reflections collected	12646
Independent reflections	5815 [R_{int} = 0.0400, R_{sigma} = 0.0621]
Data/restraints/parameters	5815/0/370
Goodness-of-fit on F^2	1.125

Final R indexes [I>=2σ (I)]	R_1 = 0.0451, wR_2 = 0.0912
Final R indexes [all data]	R_1 = 0.0645, wR_2 = 0.0992
Largest diff. peak/hole / e $Å^{-3}$	1.73/-0.83

Table 2 Bond Lengths for 7a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	O1	1.125(10)	C12	O7	1.213(7)
C1	W1	2.047(10)	C13	C14	1.371(8)
C2	O2	1.156(8)	C13	C18	1.396(9)
C2	W1	2.017(8)	C14	C15	1.389(10)
C3	O3	1.141(8)	C15	C16	1.362(11)
C3	W1	2.019(7)	C16	C17	1.367(11)
C4	O4	1.134(8)	C17	C18	1.391(9)
C4	W1	2.047(8)	C19	C20	1.385(9)
C5	O5	1.158(8)	C19	C24	1.372(9)
C5	W1	2.015(8)	C19	N1	1.455(7)
C6	C7	1.540(8)	C20	C21	1.380(10)
C6	P1	1.841(6)	C21	C22	1.368(12)
C7	C8	1.549(8)	C22	C23	1.371(13)
C8	C9	1.598(8)	C23	C24	1.395(10)
C8	C13	1.526(8)	C25	C26	1.363(9)
C8	N1	1.505(7)	C25	C30	1.367(10)
C9	C10	1.546(8)	C25	N2	1.456(8)
C9	C12	1.519(8)	C26	C27	1.394(11)
C10	C11	1.510(9)	C27	C28	1.362(12)
C10	P1	1.877(6)	C28	C29	1.348(12)
C11	N2	1.405(8)	C29	C30	1.394(10)
C11	O6	1.201(7)	N1	P1	1.700(5)
C12	N2	1.387(8)	P1	W1	2.4550(16)

Table 3 Bond Angles for 7a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	W1	178.5(8)	C21	C22	C23	119.3(8)
O2	C2	W1	179.2(8)	C22	C23	C24	120.1(9)
O3	C3	W1	177.4(7)	C19	C24	C23	120.2(8)
O4	C4	W1	179.2(7)	C26	C25	C30	120.5(7)
O5	C5	W1	177.3(7)	C26	C25	N2	119.0(7)
C7	C6	P1	103.1(4)	C30	C25	N2	120.5(6)
C6	C7	C8	109.4(5)	C25	C26	C27	119.1(8)
C7	C8	C9	109.0(5)	C28	C27	C26	120.8(9)
C13	C8	C7	111.2(5)	C29	C28	C27	119.4(8)
C13	C8	C9	116.2(5)	C28	C29	C30	121.1(9)
N1	C8	C7	101.4(4)	C25	C30	C29	119.1(7)
N1	C8	C9	104.4(4)	C8	N1	P1	102.2(4)
N1	C8	C13	113.3(5)	C19	N1	C8	121.8(5)
C10	C9	C8	106.4(5)	C19	N1	P1	121.3(4)
C12	C9	C8	116.1(5)	C11	N2	C25	123.5(5)
C12	C9	C10	103.5(5)	C12	N2	C11	113.3(5)
C9	C10	P1	104.8(4)	C12	N2	C25	123.2(5)
C11	C10	C9	106.3(5)	C6	P1	C10	96.7(3)
C11	C10	P1	113.0(4)	C6	P1	W1	119.5(2)
N2	C11	C10	107.1(5)	C10	P1	W1	124.0(2)
O6	C11	C10	128.0(6)	N1	P1	C6	91.7(3)
O6	C11	N2	125.0(6)	N1	P1	C10	92.7(3)
N2	C12	C9	108.6(5)	N1	P1	W1	124.14(17)
O7	C12	C9	127.1(6)	C1	W1	C4	179.2(3)
O7	C12	N2	124.3(6)	C1	W1	P1	92.0(2)
C14	C13	C8	123.6(6)	C2	W1	C1	89.1(4)

C14	C13	C18	118.7(6)	C2	W1	C3	87.3(3)
C18	C13	C8	117.4(6)	C2	W1	C4	90.2(3)
C13	C14	C15	119.6(8)	C2	W1	P1	87.5(2)
C16	C15	C14	121.7(8)	C3	W1	C1	90.1(3)
C15	C16	C17	119.7(8)	C3	W1	C4	90.0(3)
C16	C17	C18	119.6(8)	C3	W1	P1	174.3(2)
C17	C18	C13	120.9(7)	C4	W1	P1	87.82(19)
C20	C19	N1	123.4(6)	C5	W1	C1	89.6(4)
C24	C19	C20	119.8(6)	C5	W1	C2	178.6(3)
C24	C19	N1	116.8(6)	C5	W1	C3	92.4(3)
C21	C20	C19	119.1(8)	C5	W1	C4	91.2(3)
C22	C21	C20	121.6(8)	C5	W1	P1	92.89(19)

Table 4 Torsion Angles for 7a.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
C6	C7	C8	C9	71.9(6)	C13	C14	C15	C16	0.6(12)
C6	C7	C8	C13	-158.7(5)	C14	C13	C18	C17	0.5(10)
C6	C7	C8	N1	-37.9(6)	C14	C15	C16	C17	-1.3(13)
C7	C6	P1	C10	-66.7(5)	C15	C16	C17	C18	1.5(12)
C7	C6	P1	N1	26.2(4)	C16	C17	C18	C13	-1.2(11)
C7	C6	P1	W1	157.7(3)	C18	C13	C14	C15	-0.3(10)
C7	C8	C9	C10	-70.1(6)	C19	C20	C21	C22	0.2(12)
C7	C8	C9	C12	44.4(7)	C19	N1	P1	C6	170.5(5)
C7	C8	C13	C14	-107.2(7)	C19	N1	P1	C10	-92.7(5)
C7	C8	C13	C18	66.3(7)	C19	N1	P1	W1	42.5(5)
C7	C8	N1	C19	-163.4(5)	C20	C19	C24	C23	-1.0(11)
C7	C8	N1	P1	57.3(4)	C20	C19	N1	C8	-59.7(8)
C8	C9	C10	C11	115.1(5)	C20	C19	N1	P1	72.1(7)

C8	C9	C10	P1	-4.8(5)	C20	C21	C22	C23	-0.8(14)
C8	C9	C12	N2	-105.0(6)	C21	C22	C23	C24	0.5(15)
C8	C9	C12	O7	76.6(8)	C22	C23	C24	C19	0.4(14)
C8	C13	C14	C15	173.1(6)	C24	C19	C20	C21	0.7(11)
C8	C13	C18	C17	-173.2(6)	C24	C19	N1	C8	121.7(7)
C8	N1	P1	C6	-49.9(4)	C24	C19	N1	P1	-106.5(6)
C8	N1	P1	C10	47.0(4)	C25	C26	C27	C28	1.5(14)
C8	N1	P1	W1	-177.9(3)	C26	C25	C30	C29	-1.4(12)
C9	C8	C13	C14	18.3(8)	C26	C25	N2	C11	127.6(7)
C9	C8	C13	C18	-168.2(5)	C26	C25	N2	C12	-51.8(10)
C9	C8	N1	C19	83.3(6)	C26	C27	C28	C29	-1.4(15)
C9	C8	N1	P1	-56.0(4)	C27	C28	C29	C30	-0.1(14)
C9	C10	C11	N2	1.8(7)	C28	C29	C30	C25	1.5(12)
C9	C10	C11	O6	-177.4(7)	C30	C25	C26	C27	-0.1(12)
C9	C10	P1	C6	67.7(4)	C30	C25	N2	C11	-52.2(9)
C9	C10	P1	N1	-24.4(4)	C30	C25	N2	C12	128.4(7)
C9	C10	P1	W1	-159.6(3)	N1	C8	C9	C10	37.6(5)
C9	C12	N2	C11	-11.0(7)	N1	C8	C9	C12	152.2(5)
C9	C12	N2	C25	168.5(6)	N1	C8	C13	C14	139.3(6)
C10	C9	C12	N2	11.2(6)	N1	C8	C13	C18	-47.3(7)
C10	C9	C12	O7	-167.2(6)	N1	C19	C20	C21	-177.9(6)
C10	C11	N2	C12	5.7(7)	N1	C19	C24	C23	177.7(7)
C10	C11	N2	C25	-173.8(6)	N2	C25	C26	C27	-179.9(7)
C11	C10	P1	C6	-47.6(5)	N2	C25	C30	C29	178.4(7)
C11	C10	P1	N1	-139.7(4)	O6	C11	N2	C12	-175.0(7)
C11	C10	P1	W1	85.1(4)	O6	C11	N2	C25	5.5(11)
C12	C9	C10	C11	-7.7(6)	O7	C12	N2	C11	167.4(6)
C12	C9	C10	P1	-127.6(4)	O7	C12	N2	C25	-13.0(10)

C13	C8	C9	C10	163.2(5)	P1	C6	C7	C8	4.1(6)
C13	C8	C9	C12	-82.2(6)	P1	C10	C11	N2	116.2(5)
C13	C8	N1	C19	-44.1(7)	P1	C10	C11	O6	-63.0(9)
C13	C8	N1	P1	176.6(4)					

X-ray crystallographic studies of compound 7b

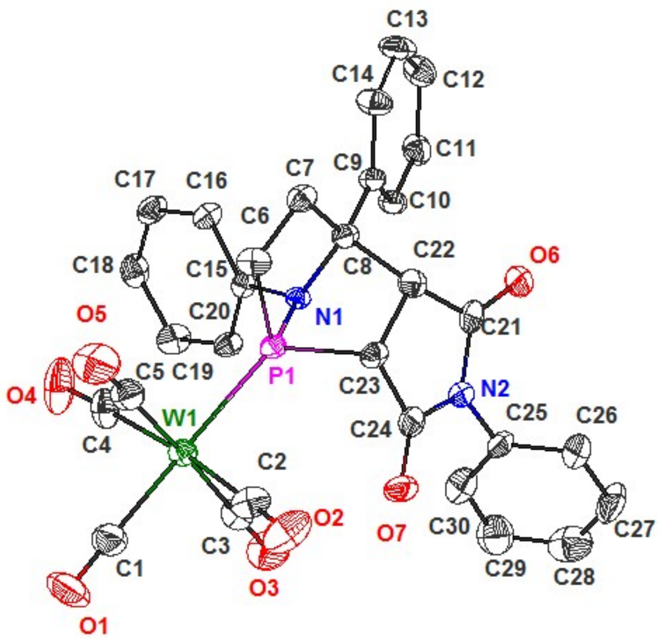


Table 5 Crystal data and structure refinement for 7b.

Identification code	7b
Empirical formula	$C_{30}H_{21}N_2O_7PW$
Formula weight	736.31
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	20.6471(6)
b/Å	11.9030(3)
c/Å	11.9069(4)
α/°	90
β/°	92.994(3)
γ/°	90
Volume/Å^3	2922.29(15)
Z	4
ρ_{calc}g/cm^3	1.674

μ/mm^{-1}	4.056
F(000)	1440.0
Crystal size/mm^3	0.21 × 0.17 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.846 to 50.246
Index ranges	-23 ≤ h ≤ 24, -13 ≤ k ≤ 14, -10 ≤ l ≤ 14
Reflections collected	11559
Independent reflections	5209 [R_{int} = 0.0428, R_{sigma} = 0.0628]
Data/restraints/parameters	5209/0/370
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0357, wR_2 = 0.0520
Final R indexes [all data]	R_1 = 0.0535, wR_2 = 0.0584
Largest diff. peak/hole / e Å^{-3}	0.74/-0.95

Table 6 Bond Lengths for 7b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	O1	1.129(7)	C15	C20	1.370(6)
C1	W1	2.005(7)	C15	N1	1.444(5)
C2	O2	1.132(5)	C16	C17	1.389(6)
C2	W1	2.034(6)	C17	C18	1.376(7)
C3	O3	1.146(6)	C18	C19	1.385(6)
C3	W1	2.033(6)	C19	C20	1.374(6)
C4	O4	1.131(5)	C21	C22	1.517(7)
C4	W1	2.041(6)	C21	N2	1.393(7)
C5	O5	1.141(6)	C21	O6	1.212(6)
C5	W1	2.040(6)	C22	C23	1.559(6)
C6	C7	1.528(6)	C23	C24	1.513(7)
C6	P1	1.829(5)	C23	P1	1.858(5)
C7	C8	1.568(6)	C24	N2	1.401(6)
C8	C9	1.513(6)	C24	O7	1.209(6)
C8	C22	1.575(6)	C25	C26	1.372(7)
C8	N1	1.483(6)	C25	C30	1.362(8)

C9	C10	1.399(6)	C25	N2	1.440(6)
C9	C14	1.385(6)	C26	C27	1.394(8)
C10	C11	1.384(6)	C27	C28	1.363(9)
C11	C12	1.372(7)	C28	C29	1.388(9)
C12	C13	1.373(7)	C29	C30	1.374(8)
C13	C14	1.396(6)	N1	P1	1.731(4)
C15	C16	1.393(6)	P1	W1	2.4531(14)

Table 7 Bond Angles for 7b.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	W1	178.5(6)	N2	C24	C23	108.1(5)
O2	C2	W1	178.7(6)	O7	C24	C23	127.8(5)
O3	C3	W1	178.5(5)	O7	C24	N2	124.1(5)
O4	C4	W1	175.2(5)	C26	C25	N2	120.1(6)
O5	C5	W1	178.4(5)	C30	C25	C26	121.0(6)
C7	C6	P1	105.1(3)	C30	C25	N2	118.8(5)
C6	C7	C8	108.0(4)	C25	C26	C27	118.5(7)
C7	C8	C22	105.0(4)	C28	C27	C26	120.5(7)
C9	C8	C7	113.9(4)	C27	C28	C29	120.4(7)
C9	C8	C22	113.9(4)	C30	C29	C28	118.8(7)
N1	C8	C7	107.7(4)	C25	C30	C29	120.8(6)
N1	C8	C9	114.1(4)	C8	N1	P1	102.0(3)
N1	C8	C22	101.1(4)	C15	N1	C8	123.0(3)
C10	C9	C8	121.9(4)	C15	N1	P1	119.6(3)
C14	C9	C8	120.8(4)	C21	N2	C24	112.5(5)
C14	C9	C10	117.2(4)	C21	N2	C25	125.7(4)
C11	C10	C9	120.6(5)	C24	N2	C25	121.7(4)
C12	C11	C10	121.1(5)	C6	P1	C23	96.1(2)
C11	C12	C13	119.7(5)	C6	P1	W1	118.36(18)
C12	C13	C14	119.5(5)	C23	P1	W1	123.44(16)
C9	C14	C13	122.0(5)	N1	P1	C6	94.3(2)
C16	C15	N1	122.9(4)	N1	P1	C23	88.6(2)
C20	C15	C16	119.3(4)	N1	P1	W1	127.67(14)
C20	C15	N1	117.8(4)	C1	W1	C2	89.1(2)
C17	C16	C15	119.4(5)	C1	W1	C3	87.9(2)
C18	C17	C16	120.4(5)	C1	W1	C4	86.1(2)

C17	C18	C19	119.9(5)	C1	W1	C5	90.6(2)
C20	C19	C18	119.4(5)	C1	W1	P1	178.93(18)
C15	C20	C19	121.5(4)	C2	W1	C4	174.5(2)
N2	C21	C22	109.4(5)	C2	W1	C5	89.6(2)
O6	C21	C22	127.0(6)	C2	W1	P1	90.01(18)
O6	C21	N2	123.6(6)	C3	W1	C2	88.9(2)
C21	C22	C8	115.2(4)	C3	W1	C4	93.5(2)
C21	C22	C23	103.6(4)	C3	W1	C5	177.9(2)
C23	C22	C8	106.9(4)	C3	W1	P1	92.61(16)
C22	C23	P1	104.6(3)	C4	W1	P1	94.76(18)
C24	C23	C22	105.6(4)	C5	W1	C4	87.8(2)
C24	C23	P1	111.5(4)	C5	W1	P1	88.91(17)

Table 8 Torsion Angles for 7b.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C6	C7	C8	C9	159.5(4)	C22	C8	C9	C14	-104.2(5)
C6	C7	C8	C22	-75.2(5)	C22	C8	N1	C15	-161.1(4)
C6	C7	C8	N1	32.0(5)	C22	C8	N1	P1	61.2(3)
C7	C6	P1	C23	64.9(3)	C22	C21	N2	C24	-9.9(6)
C7	C6	P1	N1	-24.1(3)	C22	C21	N2	C25	173.4(4)
C7	C6	P1	W1	-161.7(2)	C22	C23	C24	N2	-3.1(5)
C7	C8	C9	C10	-160.9(4)	C22	C23	C24	O7	177.4(5)
C7	C8	C9	C14	16.2(7)	C22	C23	P1	C6	-65.4(3)
C7	C8	C22	C21	-172.1(5)	C22	C23	P1	N1	28.8(3)
C7	C8	C22	C23	73.5(5)	C22	C23	P1	W1	164.6(2)
C7	C8	N1	C15	89.1(4)	C23	C24	N2	C21	8.2(5)
C7	C8	N1	P1	-48.6(3)	C23	C24	N2	C25	-175.0(4)
C8	C9	C10	C11	179.6(5)	C24	C23	P1	C6	-179.1(4)
C8	C9	C14	C13	-179.2(5)	C24	C23	P1	N1	-84.9(4)
C8	C22	C23	C24	119.7(4)	C24	C23	P1	W1	50.9(4)
C8	C22	C23	P1	1.9(5)	C25	C26	C27	C28	0.2(10)

C8	N1	P1	C6	42.4(3)	C26	C25	C30	C29	-0.8(9)
C8	N1	P1	C23	-53.6(3)	C26	C25	N2	C21	63.4(7)
C8	N1	P1	W1	173.7(2)	C26	C25	N2	C24	-113.0(6)
C9	C8	C22	C21	-46.8(6)	C26	C27	C28	C29	-0.3(11)
C9	C8	C22	C23	-161.2(4)	C27	C28	C29	C30	-0.2(10)
C9	C8	N1	C15	-38.3(6)	C28	C29	C30	C25	0.7(9)
C9	C8	N1	P1	-176.0(3)	C30	C25	C26	C27	0.3(9)
C9	C10	C11	C12	-1.3(8)	C30	C25	N2	C21	-118.3(6)
C10	C9	C14	C13	-1.9(8)	C30	C25	N2	C24	65.3(6)
C10	C11	C12	C13	-0.5(8)	N1	C8	C9	C10	-36.7(6)
C11	C12	C13	C14	1.0(8)	N1	C8	C9	C14	140.4(5)
C12	C13	C14	C9	0.2(9)	N1	C8	C22	C21	76.0(5)
C14	C9	C10	C11	2.4(7)	N1	C8	C22	C23	-38.4(5)
C15	C16	C17	C18	0.5(7)	N1	C15	C16	C17	-178.9(4)
C15	N1	P1	C6	-97.1(4)	N1	C15	C20	C19	177.3(4)
C15	N1	P1	C23	166.9(4)	N2	C21	C22	C8	-109.1(5)
C15	N1	P1	W1	34.2(4)	N2	C21	C22	C23	7.2(5)
C16	C15	C20	C19	-3.6(7)	N2	C25	C26	C27	178.6(5)
C16	C15	N1	C8	-28.5(6)	N2	C25	C30	C29	-179.1(5)
C16	C15	N1	P1	102.4(5)	O6	C21	C22	C8	71.6(7)
C16	C17	C18	C19	-1.7(8)	O6	C21	C22	C23	-172.1(5)
C17	C18	C19	C20	0.2(8)	O6	C21	N2	C24	169.4(5)
C18	C19	C20	C15	2.5(7)	O6	C21	N2	C25	-7.3(8)
C20	C15	C16	C17	2.1(7)	O7	C24	N2	C21	-172.3(5)
C20	C15	N1	C8	150.5(4)	O7	C24	N2	C25	4.5(8)
C20	C15	N1	P1	-78.6(5)	P1	C6	C7	C8	-1.0(4)
C21	C22	C23	C24	-2.4(5)	P1	C23	C24	N2	109.9(4)
C21	C22	C23	P1	-120.2(3)	P1	C23	C24	O7	-69.5(6)

C22 C8 C9 C10 78.7(6)

X-ray crystallographic studies of compound 15a

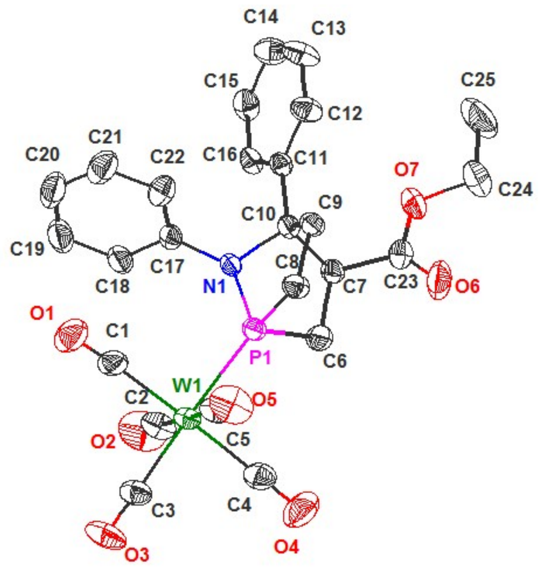


Table 9 Crystal data and structure refinement for 15a.

Identification code	15a
Empirical formula	$C_{25}H_{22}NO_7PW$
Formula weight	663.25
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.9036(3)
b/Å	19.9413(5)
c/Å	12.7372(4)
α/°	90
β/°	107.901(3)
γ/°	90
Volume/Å^3	2635.41(14)
Z	4
ρ_{calc}g/cm^3	1.672
μ/mm^{-1}	4.486
F(000)	1296.0
Crystal size/mm^3	0.18 × 0.15 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.662 to 52.744
Index ranges	-13 ≤ h ≤ 8, -15 ≤ k ≤ 24, -15 ≤ l ≤ 15

Reflections collected	12479
Independent reflections	5385 [R_{int} = 0.0378, R_{sigma} = 0.0553]
Data/restraints/parameters	5385/16/325
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0383, wR_2 = 0.0646
Final R indexes [all data]	R_1 = 0.0617, wR_2 = 0.0735
Largest diff. peak/hole / e Å^{-3}	0.94/-0.58

Table 10 Bond Lengths for 15a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	O1	1.129(6)	C11	C16	1.382(6)
C1	W1	2.054(6)	C12	C13	1.386(7)
C2	O2	1.131(7)	C13	C14	1.355(8)
C2	W1	2.039(7)	C14	C15	1.369(7)
C3	O3	1.149(6)	C15	C16	1.373(7)
C3	W1	1.995(6)	C17	C18	1.373(7)
C4	O4	1.140(7)	C17	C22	1.377(7)
C4	W1	2.026(7)	C17	N1	1.446(5)
C5	O5	1.118(7)	C18	C19	1.396(8)
C5	W1	2.043(6)	C19	C20	1.371(9)
C6	C7	1.550(6)	C20	C21	1.345(9)
C6	P1	1.811(5)	C21	C22	1.383(7)
C7	C10	1.571(6)	C23	O6	1.190(6)
C7	C23	1.510(7)	C23	O7	1.336(6)
C8	C9	1.547(6)	C24	C25	1.504(12)
C8	P1	1.830(5)	C24	O7	1.471(8)
C9	C10	1.560(6)	N1	P1	1.720(4)
C10	C11	1.512(6)	O7	C24A	1.452(18)
C10	N1	1.505(5)	P1	W1	2.4779(12)
C11	C12	1.388(6)	C24A	C25A	1.53(2)

Table 11 Bond Angles for 15a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	W1	174.3(5)	C17	C22	C21	120.3(6)
O2	C2	W1	178.4(6)	O6	C23	C7	126.9(6)
O3	C3	W1	179.5(6)	O6	C23	O7	122.9(5)
O4	C4	W1	177.7(6)	O7	C23	C7	110.2(5)
O5	C5	W1	178.8(6)	O7	C24	C25	105.7(7)
C7	C6	P1	104.4(3)	C10	N1	P1	100.4(3)
C6	C7	C10	107.2(4)	C17	N1	C10	121.4(4)
C23	C7	C6	112.1(4)	C17	N1	P1	120.3(3)
C23	C7	C10	112.0(4)	C23	O7	C24	114.0(6)
C9	C8	P1	103.7(3)	C23	O7	C24A	127(2)
C8	C9	C10	108.1(4)	C6	P1	C8	97.5(2)
C9	C10	C7	108.1(4)	C6	P1	W1	121.77(17)
C11	C10	C7	111.8(4)	C8	P1	W1	119.69(16)
C11	C10	C9	116.3(4)	N1	P1	C6	90.6(2)
N1	C10	C7	99.5(3)	N1	P1	C8	95.3(2)
N1	C10	C9	107.2(3)	N1	P1	W1	124.73(13)
N1	C10	C11	112.7(4)	C1	W1	P1	94.22(15)
C12	C11	C10	121.6(4)	C2	W1	C1	92.7(2)
C16	C11	C10	120.3(4)	C2	W1	C5	179.2(2)
C16	C11	C12	118.0(5)	C2	W1	P1	90.03(16)
C13	C12	C11	120.1(5)	C3	W1	C1	88.1(2)
C14	C13	C12	121.0(6)	C3	W1	C2	90.3(2)
C13	C14	C15	119.3(5)	C3	W1	C4	89.1(2)
C14	C15	C16	120.6(5)	C3	W1	C5	90.4(2)
C15	C16	C11	120.9(5)	C3	W1	P1	177.66(17)
C18	C17	C22	119.6(5)	C4	W1	C1	174.4(2)

C18	C17	N1	116.4(5)	C4	W1	C2	92.1(2)
C22	C17	N1	124.0(5)	C4	W1	C5	88.2(2)
C17	C18	C19	119.4(6)	C4	W1	P1	88.58(17)
C20	C19	C18	119.8(7)	C5	W1	C1	87.0(2)
C21	C20	C19	120.8(7)	C5	W1	P1	89.26(15)
C20	C21	C22	120.0(7)	O7	C24A	C25A	94(2)

Table 12 Torsion Angles for 15a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C6	C7	C10	C9	70.1(5)	C11	C12	C13	C14	-0.8(9)
C6	C7	C10	C11	-160.8(4)	C12	C11	C16	C15	0.1(7)
C6	C7	C10	N1	-41.6(5)	C12	C13	C14	C15	0.7(10)
C6	C7	C23	O6	-14.5(9)	C13	C14	C15	C16	-0.3(9)
C6	C7	C23	O7	164.5(4)	C14	C15	C16	C11	-0.1(8)
C7	C6	P1	C8	-68.2(4)	C16	C11	C12	C13	0.3(8)
C7	C6	P1	N1	27.2(4)	C17	C18	C19	C20	0.8(9)
C7	C6	P1	W1	159.8(3)	C17	N1	P1	C6	170.5(4)
C7	C10	C11	C12	-110.9(5)	C17	N1	P1	C8	-91.9(4)
C7	C10	C11	C16	66.2(5)	C17	N1	P1	W1	40.2(4)
C7	C10	N1	C17	-162.9(4)	C18	C17	C22	C21	-0.1(8)
C7	C10	N1	P1	61.5(3)	C18	C17	N1	C10	144.3(4)
C7	C23	O7	C24	173.3(7)	C18	C17	N1	P1	-88.7(5)
C7	C23	O7	C24A	-160.5(19)	C18	C19	C20	C21	-0.1(11)
C8	C9	C10	C7	-72.4(5)	C19	C20	C21	C22	-0.8(11)
C8	C9	C10	C11	161.0(4)	C20	C21	C22	C17	0.9(9)
C8	C9	C10	N1	34.0(5)	C22	C17	C18	C19	-0.7(8)
C9	C8	P1	C6	66.1(4)	C22	C17	N1	C10	-36.8(6)
C9	C8	P1	N1	-25.2(3)	C22	C17	N1	P1	90.3(5)
C9	C8	P1	W1	-160.6(2)	C23	C7	C10	C9	-53.3(5)

C9	C10	C11	C12	13.8(6)	C23	C7	C10	C11	75.9(5)
C9	C10	C11	C16	-169.1(4)	C23	C7	C10	N1	-164.9(4)
C9	C10	N1	C17	84.7(5)	C23	O7	C24A	C25A	-109(3)
C9	C10	N1	P1	-50.8(4)	C25	C24	O7	C23	-173.1(11)
C10	C7	C23	O6	106.1(7)	N1	C10	C11	C12	138.0(5)
C10	C7	C23	O7	-74.9(6)	N1	C10	C11	C16	-44.9(6)
C10	C11	C12	C13	177.5(5)	N1	C17	C18	C19	178.3(5)
C10	C11	C16	C15	-177.0(4)	N1	C17	C22	C21	-179.1(5)
C10	N1	P1	C6	-53.3(3)	O6	C23	O7	C24	-7.6(10)
C10	N1	P1	C8	44.2(3)	O6	C23	O7	C24A	19(2)
C10	N1	P1	W1	176.3(2)	P1	C6	C7	C10	5.4(5)
C11	C10	N1	C17	-44.4(5)	P1	C6	C7	C23	128.7(4)
C11	C10	N1	P1	-179.9(3)	P1	C8	C9	C10	-1.9(4)

X-ray crystallographic studies of compound 19

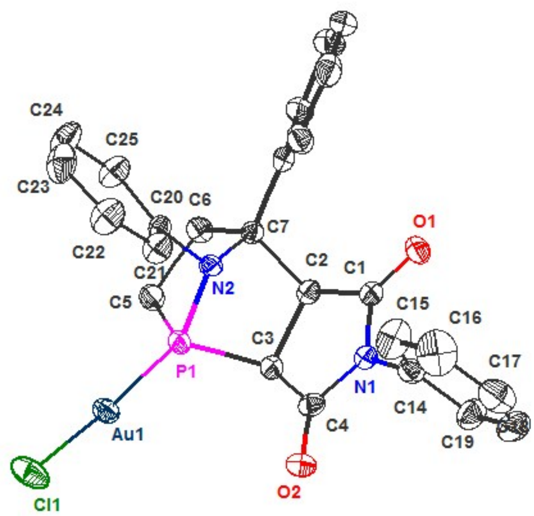


Table 13 Crystal data and structure refinement for 19.

Identification code	19
Empirical formula	$C_{26}H_{23}AuCl_3N_2O_2P$
Formula weight	729.75
Temperature/K	293(2)

Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.98190(18)
b/Å	10.06167(17)
c/Å	22.0504(4)
α/°	90
β/°	92.6420(15)
γ/°	90
Volume/Å^3	2655.53(8)
Z	4
ρ_{calc}g/cm^3	1.825
μ/mm^{-1}	13.979
F(000)	1416.0
Crystal size/mm^3	0.3373 × 0.1794 × 0.1599
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.028 to 134.126
Index ranges	$-14 \leq h \leq 10$, $-10 \leq k \leq 12$, $-26 \leq l \leq 26$
Reflections collected	10631
Independent reflections	4731 [R_{int} = 0.0401, R_{sigma} = 0.0497]
Data/restraints/parameters	4731/0/316
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0383, wR_2 = 0.0950
Final R indexes [all data]	R_1 = 0.0476, wR_2 = 0.1032
Largest diff. peak/hole / e Å^{-3}	0.56/-1.55

Table 14 Bond Lengths for 19.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	Cl1	2.2946(16)	C11	C12	1.346(12)
Au1	P1	2.2136(14)	C12	C13	1.382(10)
C1	C2	1.521(7)	C14	C15	1.361(10)
C1	N1	1.391(7)	C14	C19	1.367(9)
C1	O1	1.191(7)	C14	N1	1.439(7)
C2	C3	1.554(7)	C15	C16	1.385(12)
C2	C7	1.572(7)	C16	C17	1.355(14)
C3	C4	1.519(8)	C17	C18	1.328(13)
C3	P1	1.829(6)	C18	C19	1.402(10)

C4	N1	1.390(8)	C20	C21	1.375(8)
C4	O2	1.199(7)	C20	C25	1.388(8)
C5	C6	1.535(8)	C20	N2	1.442(7)
C5	P1	1.821(6)	C21	C22	1.383(9)
C6	C7	1.570(7)	C22	C23	1.364(12)
C7	C8	1.508(7)	C23	C24	1.376(12)
C7	N2	1.493(6)	C24	C25	1.377(10)
C8	C9	1.383(9)	N2	P1	1.712(4)
C8	C13	1.374(8)	C26	Cl2	1.759(14)
C9	C10	1.388(10)	C26	Cl3	1.715(14)
C10	C11	1.361(13)			

Table 15 Bond Angles for 19.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
P1	Au1	Cl1	174.37(6)	C15	C14	C19	119.9(7)
N1	C1	C2	108.3(5)	C15	C14	N1	119.3(6)
O1	C1	C2	126.9(5)	C19	C14	N1	120.7(6)
O1	C1	N1	124.8(5)	C14	C15	C16	119.2(9)
C1	C2	C3	104.3(4)	C17	C16	C15	121.4(9)
C1	C2	C7	112.8(4)	C18	C17	C16	119.1(8)
C3	C2	C7	108.0(4)	C17	C18	C19	121.5(8)
C2	C3	P1	102.7(4)	C14	C19	C18	118.8(7)
C4	C3	C2	105.3(4)	C21	C20	C25	118.8(5)
C4	C3	P1	111.7(4)	C21	C20	N2	116.5(5)
N1	C4	C3	107.9(5)	C25	C20	N2	124.7(5)
O2	C4	C3	126.8(6)	C20	C21	C22	120.3(6)
O2	C4	N1	125.3(6)	C23	C22	C21	120.2(7)
C6	C5	P1	103.7(4)	C22	C23	C24	120.3(7)
C5	C6	C7	107.7(4)	C23	C24	C25	119.5(7)

C6	C7	C2	105.9(4)	C24	C25	C20	120.8(7)
C8	C7	C2	114.5(4)	C1	N1	C14	122.1(5)
C8	C7	C6	113.9(4)	C4	N1	C1	113.8(5)
N2	C7	C2	101.3(4)	C4	N1	C14	124.0(5)
N2	C7	C6	107.2(4)	C7	N2	P1	100.0(3)
N2	C7	C8	113.0(4)	C20	N2	C7	124.5(4)
C9	C8	C7	123.2(5)	C20	N2	P1	116.5(4)
C13	C8	C7	119.2(5)	C3	P1	Au1	124.89(18)
C13	C8	C9	117.7(6)	C5	P1	Au1	123.9(2)
C8	C9	C10	120.9(7)	C5	P1	C3	98.2(3)
C11	C10	C9	119.7(7)	N2	P1	Au1	114.99(16)
C12	C11	C10	120.2(7)	N2	P1	C3	91.0(2)
C11	C12	C13	120.6(7)	N2	P1	C5	96.0(3)
C8	C13	C12	120.8(7)	Cl3	C26	Cl2	110.8(7)

Table 16 Torsion Angles for 19.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C1	C2	C3	C4	2.9(6)	C9	C10	C11	C12	1.7(12)
C1	C2	C3	P1	120.0(4)	C10	C11	C12	C13	0.2(13)
C1	C2	C7	C6	170.9(4)	C11	C12	C13	C8	0.0(12)
C1	C2	C7	C8	44.5(6)	C13	C8	C9	C10	4.1(9)
C1	C2	C7	N2	-77.4(5)	C14	C15	C16	C17	1.4(16)
C2	C1	N1	C4	6.6(6)	C15	C14	C19	C18	1.3(11)
C2	C1	N1	C14	-171.8(5)	C15	C14	N1	C1	79.9(9)
C2	C3	C4	N1	0.7(6)	C15	C14	N1	C4	-98.4(8)
C2	C3	C4	O2	-177.9(6)	C15	C16	C17	C18	-1.0(15)
C2	C3	P1	Au1	-152.7(3)	C16	C17	C18	C19	0.8(14)
C2	C3	P1	C5	65.4(4)	C17	C18	C19	C14	-0.9(13)

C2	C3	P1	N2	-30.9(4)
C2	C7	C8	C9	-90.1(7)
C2	C7	C8	C13	87.7(6)
C2	C7	N2	C20	168.1(5)
C2	C7	N2	P1	-59.8(4)
C3	C2	C7	C6	-74.4(5)
C3	C2	C7	C8	159.3(4)
C3	C2	C7	N2	37.3(5)
C3	C4	N1	C1	-4.6(6)
C3	C4	N1	C14	173.8(5)
C4	C3	P1	Au1	-40.3(5)
C4	C3	P1	C5	177.7(4)
C4	C3	P1	N2	81.5(4)
C5	C6	C7	C2	72.6(6)
C5	C6	C7	C8	-160.7(5)
C5	C6	C7	N2	-35.0(6)
C6	C5	P1	Au1	150.0(3)
C6	C5	P1	C3	-67.5(4)
C6	C5	P1	N2	24.4(4)
C6	C7	C8	C9	147.9(6)
C6	C7	C8	C13	-34.4(7)
C6	C7	N2	C20	-81.2(6)
C6	C7	N2	P1	50.9(4)
C7	C2	C3	C4	-117.3(5)
C7	C2	C3	P1	-0.2(5)
C7	C8	C9	C10	-178.1(6)
C7	C8	C13	C12	180.0(6)
C7	N2	P1	Au1	-175.8(2)
C19	C14	C15	C16	-1.6(13)
C19	C14	N1	C1	-99.6(7)
C19	C14	N1	C4	82.2(8)
C20	C21	C22	C23	-2.2(12)
C20	N2	P1	Au1	-38.9(4)
C20	N2	P1	C3	-168.7(4)
C20	N2	P1	C5	92.9(4)
C21	C20	C25	C24	-3.2(11)
C21	C20	N2	C7	-144.3(5)
C21	C20	N2	P1	90.3(6)
C21	C22	C23	C24	-1.5(14)
C22	C23	C24	C25	2.8(14)
C23	C24	C25	C20	-0.5(13)
C25	C20	C21	C22	4.5(10)
C25	C20	N2	C7	34.3(9)
C25	C20	N2	P1	-91.0(6)
N1	C1	C2	C3	-5.6(6)
N1	C1	C2	C7	111.3(5)
N1	C14	C15	C16	179.0(8)
N1	C14	C19	C18	-179.3(6)
N2	C7	C8	C9	25.2(7)
N2	C7	C8	C13	-157.0(5)
N2	C20	C21	C22	-176.8(6)
N2	C20	C25	C24	178.2(7)
O1	C1	C2	C3	174.0(6)
O1	C1	C2	C7	-69.0(8)
O1	C1	N1	C4	-173.1(6)
O1	C1	N1	C14	8.5(9)

C7	N2	P1	C3	54.4(3)	O2	C4	N1	C1	174.0(6)
C7	N2	P1	C5	-44.0(4)	O2	C4	N1	C14	-7.6(9)
C8	C7	N2	C20	45.1(7)	P1	C3	C4	N1	-110.1(4)
C8	C7	N2	P1	177.2(4)	P1	C3	C4	O2	71.3(7)
C8	C9	C10	C11	-3.9(11)	P1	C5	C6	C7	2.9(6)
C9	C8	C13	C12	-2.1(10)					

DFT calculations

Computational Methods

All of the calculations were carried out by using Gaussian09.[1] The optimized structures were illustrated using CYLView.[2] The density functional theory (DFT) calculations were performed with the B3LYP[3, 4] functional using the integral equation formalism polarizable continuum model IEF-PCM[5] in toluene solvent, and basis set 6-31G(d) was employed for H, C, N, O, and P atoms, while LANL2DZ for W was used.[6] Then, frequency calculations at the same level of theory were carried out to identify all of the stationary points as minima (zero imaginary frequency) or transition state (only one frequency), and to provide corrections for free energies. On the basis of the optimized structures at the above level, the single-point energies were further refined at TPSSTPSS[7]/6-311++G(d, p)//LanL2TZ level with the same solvent effects. The free energy in the discussion is the single-point energy at the TPSSTPSS[7]/6-311++G(d, p)//LanL2TZ level plus the correction at the B3LYP/6-31G(d)//LanL2DZ level.

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Geometrical Coordinates of the Listed Complexes

2a

0 1

C	0.10334400	-3.06098200	0.11447200
C	0.17059000	-2.68566800	-1.34168500
H	-0.80942800	-3.52679100	0.47885900
H	1.01044400	-3.43148300	0.58216800
H	-0.68337600	-2.90992600	-1.97593800
H	1.13360900	-2.77726300	-1.83757200
P	-0.05034000	-1.23878100	-0.19431500
C	1.64458600	-0.47088600	-0.04791800
C	2.87097100	-1.32698300	-0.01235300
C	3.72388700	-1.36078100	-1.12712400
C	3.18598600	-2.10009900	1.11659900
C	4.87126600	-2.15451400	-1.11029800
H	3.48909000	-0.76043600	-2.00144400
C	4.34132300	-2.88327700	1.13318200
H	2.53787500	-2.07082600	1.98860600
C	5.18319200	-2.91530700	0.01897300
H	5.52346900	-2.17452600	-1.97879200
H	4.58233300	-3.46756400	2.01670600
H	6.07897000	-3.52963100	0.03121200
N	1.58597400	0.80617000	-0.08318900
C	2.69263800	1.67966100	-0.00009800
C	3.71809700	1.55444400	0.95211700
C	2.68783700	2.78556800	-0.86684300
C	4.73139600	2.51089500	1.01236000
H	3.70878000	0.72720500	1.65314900
C	3.72217400	3.71772600	-0.82055100
H	1.86731900	2.89318700	-1.56963900
C	4.74717600	3.58624600	0.12078000
H	5.51378400	2.41202200	1.76003400
H	3.71681500	4.55926100	-1.50786600
H	5.54336900	4.32373300	0.16866500
W	-2.18202600	0.15064600	0.05192700
C	-1.39120400	1.55992800	-1.22869900
O	-0.97165400	2.35624600	-1.95214000
C	-2.98247200	-0.85801700	-1.54351800

O	-3.42161400	-1.43619200	-2.44446600
C	-1.32768400	1.14773900	1.64124400
O	-0.86017800	1.70676700	2.53654200
C	-2.93000800	-1.26608500	1.33364500
O	-3.34590400	-2.07085300	2.05316100
C	-3.86439800	1.23701400	0.24085000
O	-4.83590600	1.86203400	0.34883600

TS1

0 1

C	0.06838600	-2.68491800	-1.31180800
C	0.86015900	-1.59902800	-1.93541400
H	-0.89565600	-2.89513500	-1.77115500
H	0.62022200	-3.59175100	-1.06657800
H	0.33363500	-0.86179800	-2.53278900
H	1.85296100	-1.84259000	-2.30464500
P	-0.07263100	-1.42032200	0.06667800
C	1.63077100	-0.64236500	-0.43232600
C	2.88241800	-1.39427300	-0.04637900
C	4.02901000	-1.25015500	-0.84755000
C	2.93994800	-2.24179000	1.06805400
C	5.20097100	-1.93740700	-0.53983100
H	3.99899400	-0.59100000	-1.71116400
C	4.11826900	-2.92530300	1.38002500
H	2.06379100	-2.35584500	1.69922200
C	5.24944100	-2.77767400	0.57713300
H	6.07710400	-1.81737000	-1.17092600
H	4.14805800	-3.57279600	2.25195600
H	6.16387100	-3.31264500	0.81770300
N	1.55178700	0.64460500	-0.65734600
C	2.47838600	1.61287700	-0.27836700
C	3.29296200	1.55812700	0.87467900
C	2.51917800	2.77725200	-1.07661500
C	4.13254500	2.62317600	1.19111400
H	3.24593600	0.69551200	1.52938900
C	3.38344500	3.82250900	-0.76858300
H	1.86273800	2.82806300	-1.94012400
C	4.19536900	3.75199300	0.36829500
H	4.74247900	2.57162000	2.08920800
H	3.41240000	4.70237800	-1.40566000
H	4.85802400	4.57519100	0.61997600
W	-2.11737700	0.06257000	0.11923000
C	-1.52462400	1.04793900	-1.59374100
O	-1.21008200	1.59478000	-2.56035400

C	-3.11690300	-1.33071000	-0.99677300
O	-3.65549200	-2.13538200	-1.63196600
C	-1.03564000	1.41601400	1.24014600
O	-0.44254900	2.17118600	1.88051100
C	-2.69948000	-0.90006200	1.84212300
O	-3.03942600	-1.43236800	2.81044800
C	-3.77438500	1.22559300	0.21907500
O	-4.72158800	1.89175900	0.26065000

Int1

0 1

C	0.35381200	-1.98971900	2.02225600
C	1.38218500	-2.32521700	0.93805700
H	-0.48944400	-2.68232700	2.00911200
H	0.81927700	-2.04011900	3.01407500
H	0.87961400	-2.64245600	0.01062700
H	2.06229700	-3.12946000	1.23220800
P	-0.20204800	-0.21224500	1.70436900
C	2.14390100	-1.05525300	0.62833800
C	3.52694000	-1.09550200	0.13070800
C	3.91305400	-2.16017000	-0.70747400
C	4.49618300	-0.14961700	0.51878600
C	5.22237000	-2.25534600	-1.17217900
H	3.18129000	-2.90130300	-1.01321400
C	5.80884800	-0.26492200	0.07025100
H	4.22745900	0.66021100	1.18722600
C	6.17464000	-1.31039300	-0.78255600
H	5.49975600	-3.07116700	-1.83299200
H	6.54888300	0.46316600	0.38900000
H	7.19852700	-1.39143300	-1.13587200
N	1.43568800	0.02464400	0.86608300
C	1.80144400	1.36183300	0.47279600
C	2.06521100	1.64531800	-0.87169900
C	1.82490700	2.37368000	1.43730700
C	2.37688600	2.95190200	-1.24402000
H	2.01287900	0.85461200	-1.61203400
C	2.14309200	3.67689800	1.05181300
H	1.60188500	2.13604800	2.47189400
C	2.42034800	3.96791700	-0.28540800
H	2.57581600	3.17621700	-2.28768000
H	2.16848800	4.46385500	1.79958100
H	2.66077100	4.98457500	-0.58201300
W	-2.06128400	-0.12444000	-0.18296600
C	-0.68320700	-0.68037600	-1.57899200

O	0.13594400	-1.00357100	-2.33772900
C	-2.48811200	-2.09108300	0.17992200
O	-2.71545100	-3.20769700	0.39536300
C	-1.61891200	1.86121700	-0.49738300
O	-1.40206100	2.98282300	-0.68056200
C	-3.34432600	0.43011400	1.32770600
O	-4.05926500	0.74121000	2.18231600
C	-3.53324400	-0.03234000	-1.54659200
O	-4.37762900	0.01044100	-2.34543300

R2

0 1

C	-2.97829500	0.33544700	0.00000300
H	-4.00542400	-0.01676700	0.00000100
H	-2.84108900	1.41362600	0.00001000
C	-1.95555200	-0.53003700	-0.00000400
H	-2.18701000	-1.59542800	-0.00001000
C	-0.51541700	-0.22077700	-0.00000200
C	0.40669800	-1.28245000	0.00000200
C	-0.00932000	1.09308100	-0.00000300
C	1.78178200	-1.04668400	0.00000100
H	0.03548600	-2.30497500	0.00000200
C	1.36257000	1.33055400	0.00000100
H	-0.69426100	1.93611000	-0.00000700
C	2.26626000	0.26226200	0.00000200
H	2.47312300	-1.88527800	0.00000200
H	1.73050400	2.35330400	0.00000000
H	3.33631900	0.45104000	0.00000200

TS2

0 1

C	-0.74212400	-1.55575200	1.19948500
C	-2.00238900	-0.73960100	1.57268200
H	-0.10907200	-1.73433000	2.07017300
H	-1.00630200	-2.52587700	0.77344800
H	-1.96899400	-0.45046400	2.63417800
H	-2.91230100	-1.32878300	1.43323000
P	0.19805600	-0.56471400	-0.07636900
C	-2.04968900	0.51573100	0.72935000
C	-3.24565700	1.35340400	0.68505700
C	-4.23686600	1.17509700	1.67744000
C	-3.50921900	2.29182000	-0.34191800
C	-5.41761300	1.91508300	1.65949100
H	-4.07847500	0.46294600	2.47965300

C	-4.69289500	3.02009500	-0.35808100
H	-2.79509000	2.43425200	-1.14357000
C	-5.65325100	2.84335200	0.64471500
H	-6.15525100	1.76151700	2.44220700
H	-4.87161000	3.72615700	-1.16426900
H	-6.57560300	3.41671800	0.62743000
N	-0.83609200	0.83219500	0.22271200
C	-0.46025300	2.13583800	-0.25352600
C	-0.51782000	3.22050900	0.62976600
C	0.00551800	2.31517200	-1.55998400
C	-0.12290500	4.48435700	0.19707100
H	-0.86440400	3.06669000	1.64643300
C	0.40674500	3.58476700	-1.98193700
H	0.04812700	1.47511600	-2.24456400
C	0.34082800	4.67119000	-1.10843000
H	-0.16644200	5.32255700	0.88625400
H	0.76889800	3.71898600	-2.99692000
H	0.65370600	5.65688300	-1.43981800
W	2.76982300	-0.45385300	0.13298600
C	2.79862600	1.53111500	0.68290900
O	2.86264200	2.63732500	1.00855100
C	2.58031300	-0.97521500	2.10780100
O	2.45413700	-1.26846300	3.22024000
C	2.86707900	0.09357200	-1.84581200
O	2.91597400	0.40611000	-2.95873900
C	2.78756100	-2.43683400	-0.40124100
O	2.81546100	-3.55408500	-0.70224800
C	4.77693200	-0.49321500	0.27736800
O	5.93347300	-0.51654500	0.37575100
C	-1.21053400	-1.34395100	-1.90515300
H	-0.74133400	-0.68565100	-2.62961100
H	-0.79684100	-2.35064300	-1.90320500
C	-2.54433200	-1.12909200	-1.58064900
H	-2.98168000	-0.17388700	-1.85843000
C	-3.48521700	-2.10834800	-1.04959900
C	-4.81800300	-1.71432300	-0.78776600
C	-3.15239600	-3.46030100	-0.79952500
C	-5.76239800	-2.61711600	-0.30288400
H	-5.10729100	-0.68341500	-0.97528900
C	-4.09679100	-4.35906500	-0.31155200
H	-2.14744600	-3.81750000	-1.00714800
C	-5.40969900	-3.94678400	-0.05833300
H	-6.77897600	-2.27977400	-0.11646400
H	-3.80864500	-5.39244300	-0.13523600

H	-6.14491500	-4.65238000	0.31819600

10a

0 1

C	-0.50013600	-0.79588600	1.93768900
C	-1.96336900	-0.30589700	1.78079400
H	0.05120200	-0.21130500	2.67965700
H	-0.42344300	-1.84967600	2.22457200
H	-2.15454700	0.52696900	2.46144200
H	-2.67706100	-1.09291300	2.03491100
P	0.24638200	-0.51643800	0.24539600
C	-2.16376300	0.16175300	0.30232600
C	-3.35879300	1.07040600	0.06736800
C	-4.41219100	1.15212200	0.98753700
C	-3.46142600	1.80353900	-1.12681700
C	-5.53084600	1.94914400	0.72866300
H	-4.37540200	0.58749800	1.91320100
C	-4.57455000	2.60174400	-1.38506400
H	-2.65583200	1.75802600	-1.85304300
C	-5.61602600	2.67883800	-0.45630900
H	-6.33514600	1.99491300	1.45799900
H	-4.62643000	3.16698100	-2.31177800
H	-6.48386200	3.30135100	-0.65628800
N	-0.86280700	0.76920100	-0.14683200
C	-0.52595000	2.14928000	0.04608100
C	-0.85832200	2.88235300	1.19592300
C	0.16333200	2.79848200	-0.99042600
C	-0.50287300	4.22830000	1.30225100
H	-1.40141000	2.41275500	2.00757800
C	0.53617000	4.13706800	-0.87055900
H	0.39274900	2.24374200	-1.89412700
C	0.20220100	4.86000400	0.27648900
H	-0.77388000	4.78074800	2.19798700
H	1.07482300	4.61765200	-1.68277600
H	0.48319300	5.90530000	0.36784400
W	2.76246800	-0.47563000	-0.07894000
C	2.91798900	1.41960700	0.72242000
O	3.05558600	2.46603400	1.18855500
C	2.97026100	-1.25922300	1.80944600
O	3.08532000	-1.70082500	2.87166900
C	2.51944300	0.30318400	-1.96418500
O	2.38792700	0.73035600	-3.03056900
C	2.63919500	-2.37082500	-0.85808000
O	2.57689900	-3.43923100	-1.29610800

C	4.76803800	-0.51741000	-0.32870200
O	5.91740300	-0.54223700	-0.47414300
C	-0.81022300	-1.74619600	-0.65531800
H	-0.44106600	-1.89622200	-1.67309300
H	-0.76161400	-2.71080600	-0.14441300
C	-2.23274500	-1.10992100	-0.65649400
H	-2.38834500	-0.68031800	-1.64924600
C	-3.38245000	-2.07114500	-0.39932300
C	-4.57769100	-1.90549300	-1.11740300
C	-3.31595600	-3.12363700	0.52738700
C	-5.66766700	-2.75306200	-0.91600300
H	-4.65248700	-1.10004600	-1.84313000
C	-4.40478500	-3.97343600	0.73439600
H	-2.40559600	-3.29911200	1.09433400
C	-5.58610700	-3.79164100	0.01350600
H	-6.57852800	-2.60326200	-1.48952200
H	-4.32441700	-4.78220400	1.45588400
H	-6.43129100	-4.45638000	0.16968100

2a’

0 1

C	-3.61535300	-0.98776900	-0.33636200
C	-3.21547200	-1.47658500	1.01045900
H	-4.48250500	-1.44373100	-0.80970300
H	-3.50134300	0.07072900	-0.54901900
H	-3.80658200	-2.25577700	1.48578800
H	-2.79280400	-0.75428500	1.70425600
P	-2.08507400	-2.08614600	-0.37828200
C	-0.64544500	-0.89589400	-0.21405900
C	-0.81325400	0.57935600	-0.02286700
C	-0.44317500	1.17134300	1.19551900
C	-1.34985400	1.38902500	-1.03707900
C	-0.60586700	2.54307700	1.39313900
H	-0.02134700	0.55463600	1.98397100
C	-1.49658200	2.76324300	-0.84210600
H	-1.63661800	0.94242100	-1.98556200
C	-1.12995900	3.34281200	0.37501600
H	-0.31763300	2.98732000	2.34190500
H	-1.90002000	3.37985400	-1.64065900
H	-1.25176000	4.41139700	0.52867500
N	0.46884200	-1.53392000	-0.22825900
C	1.74073800	-0.92317100	-0.16833600
C	2.15031400	0.08253300	-1.05991500
C	2.66714000	-1.43579400	0.75528200

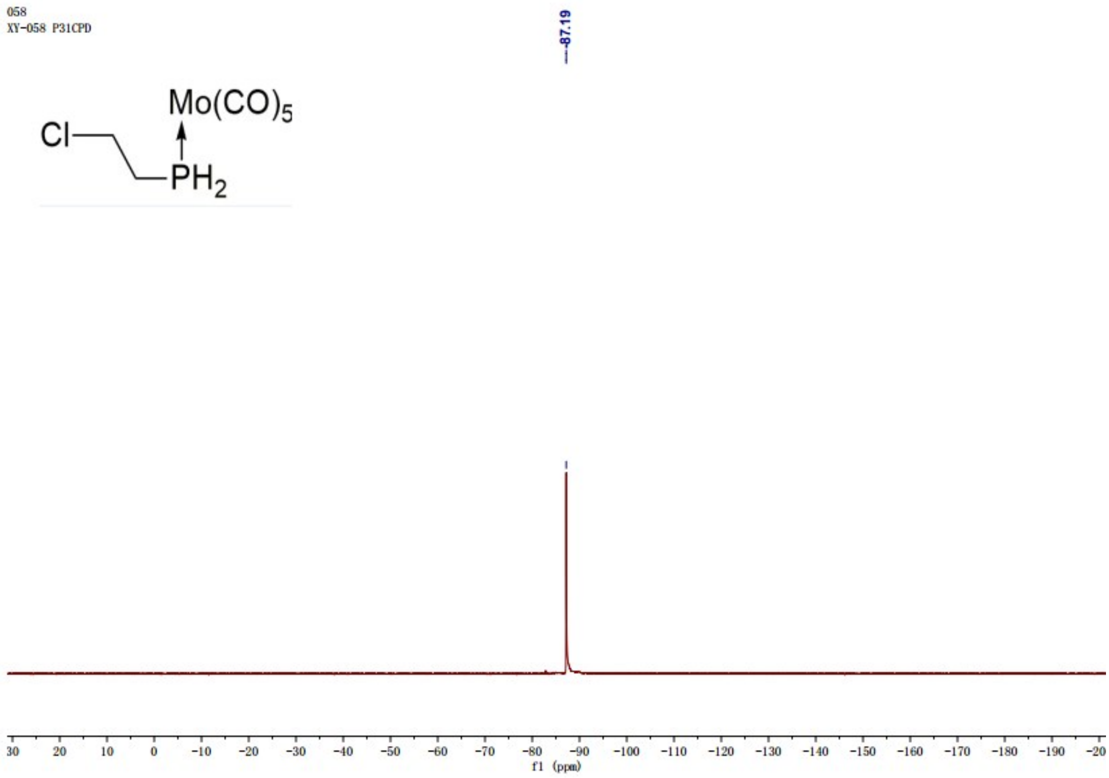
C	3.45401900	0.57624000	-1.00768900
H	1.45124200	0.46166600	-1.79806600
C	3.95932500	-0.91795900	0.81877100
H	2.35411800	-2.23686100	1.41858900
C	4.36117200	0.08891300	-0.06395700
H	3.75957400	1.34888700	-1.70855900
H	4.65966400	-1.31340600	1.54989300
H	5.37374400	0.48056200	-0.02435500

TS1’

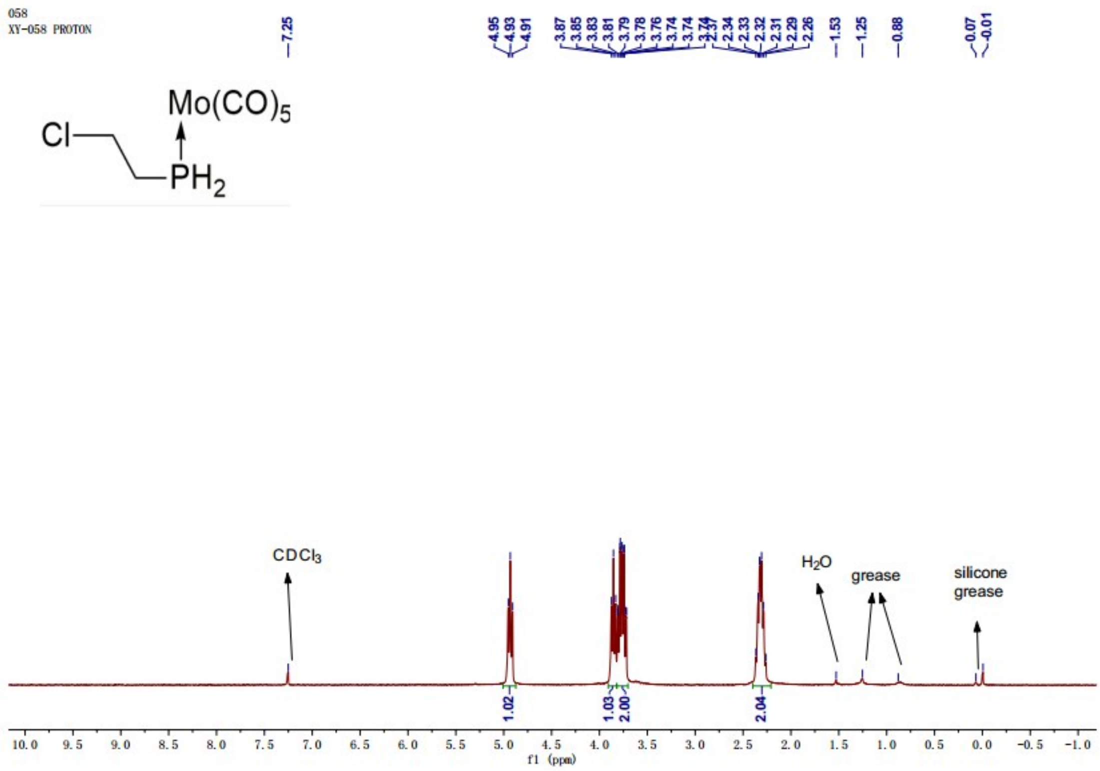
0 1

C	-3.10184600	-1.98426400	0.23448300
C	-1.91934500	-1.77422200	1.14294000
H	-3.65074100	-2.91167300	0.39777800
H	-3.76654400	-1.12366100	0.14526600
H	-1.47144000	-2.64761400	1.60968300
H	-1.98439300	-0.93081600	1.82942600
P	-1.68206700	-2.16234300	-0.95189300
C	-0.70988500	-0.89516400	0.06027100
C	-1.05242200	0.57803400	0.08232400
C	-0.61005000	1.36303700	1.16080500
C	-1.82778000	1.18138400	-0.91541700
C	-0.93092400	2.71691500	1.23434700
H	-0.00726100	0.90502500	1.94075800
C	-2.14797500	2.53985200	-0.84442200
H	-2.16855200	0.58246900	-1.75538200
C	-1.70184800	3.31071400	0.22975600
H	-0.58087800	3.30943800	2.07531700
H	-2.74478800	2.99369300	-1.63109900
H	-1.95198900	4.36662100	0.28622600
N	0.50469200	-1.39276300	0.29937100
C	1.69105700	-0.71420700	0.05614800
C	1.87808900	0.28679700	-0.92656300
C	2.82030500	-1.13692400	0.79625500
C	3.13498200	0.85159800	-1.13033300
H	1.04148900	0.60048900	-1.54096200
C	4.06555500	-0.55000200	0.60294200
H	2.68130000	-1.92797300	1.52732800
C	4.23214500	0.44949200	-0.36283100
H	3.25923500	1.61212000	-1.89726500
H	4.91433000	-0.88062800	1.19618300
H	5.20804300	0.89875200	-0.52469900

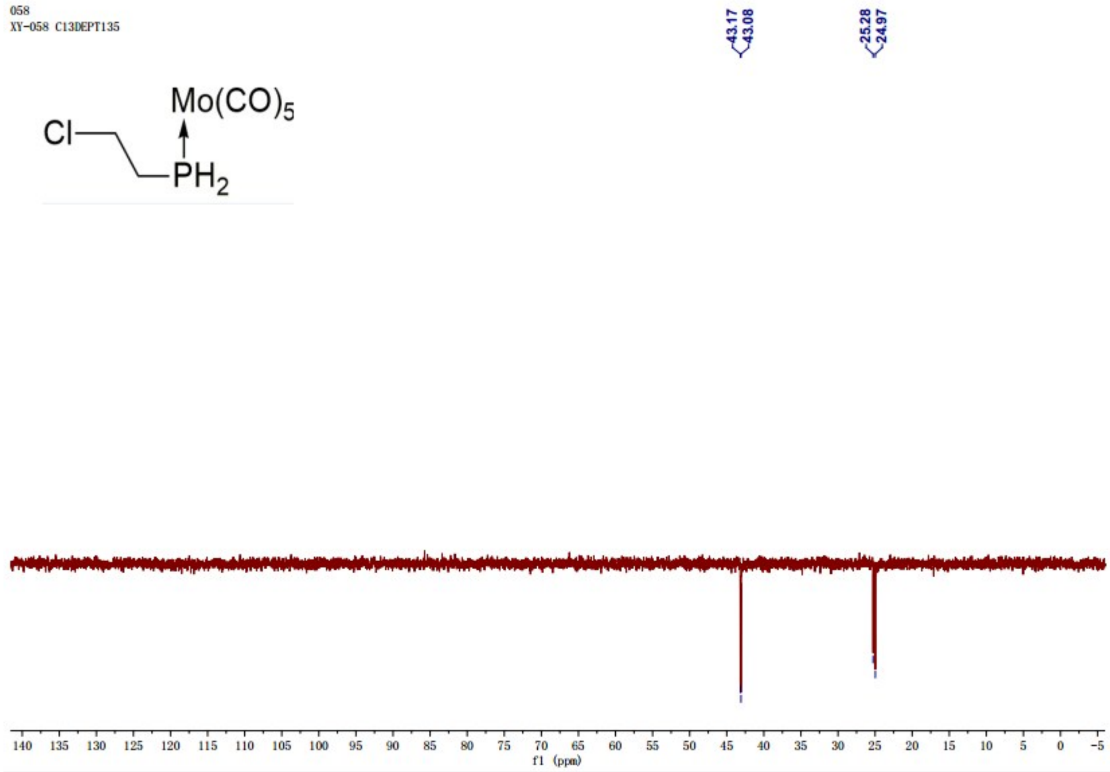
NMR spectrums



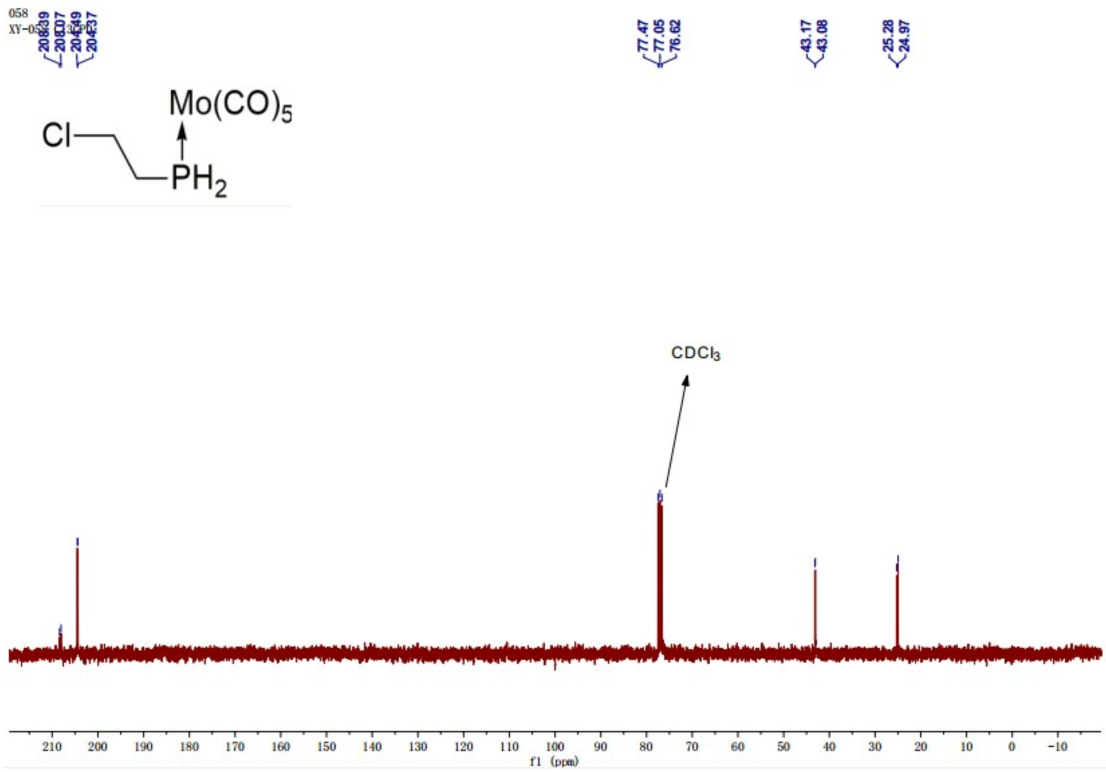
$^{31}P\{^1H\}$ NMR of Compound 1a



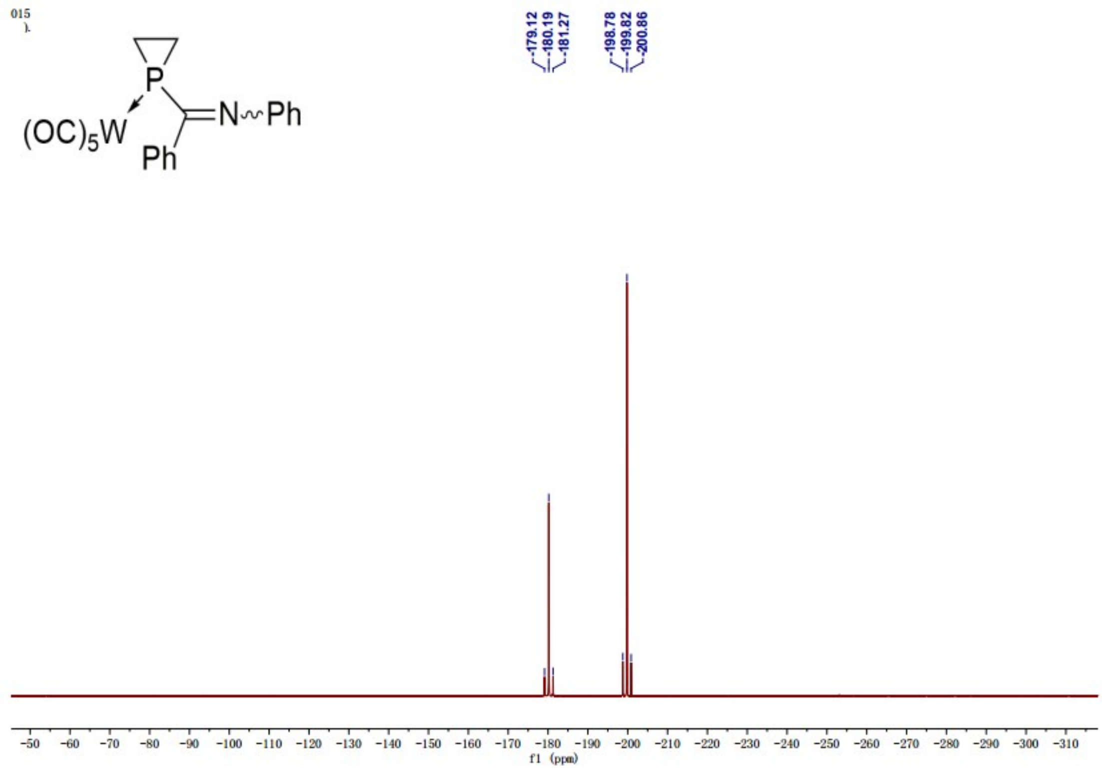
^{1}H NMR of Compound 1a



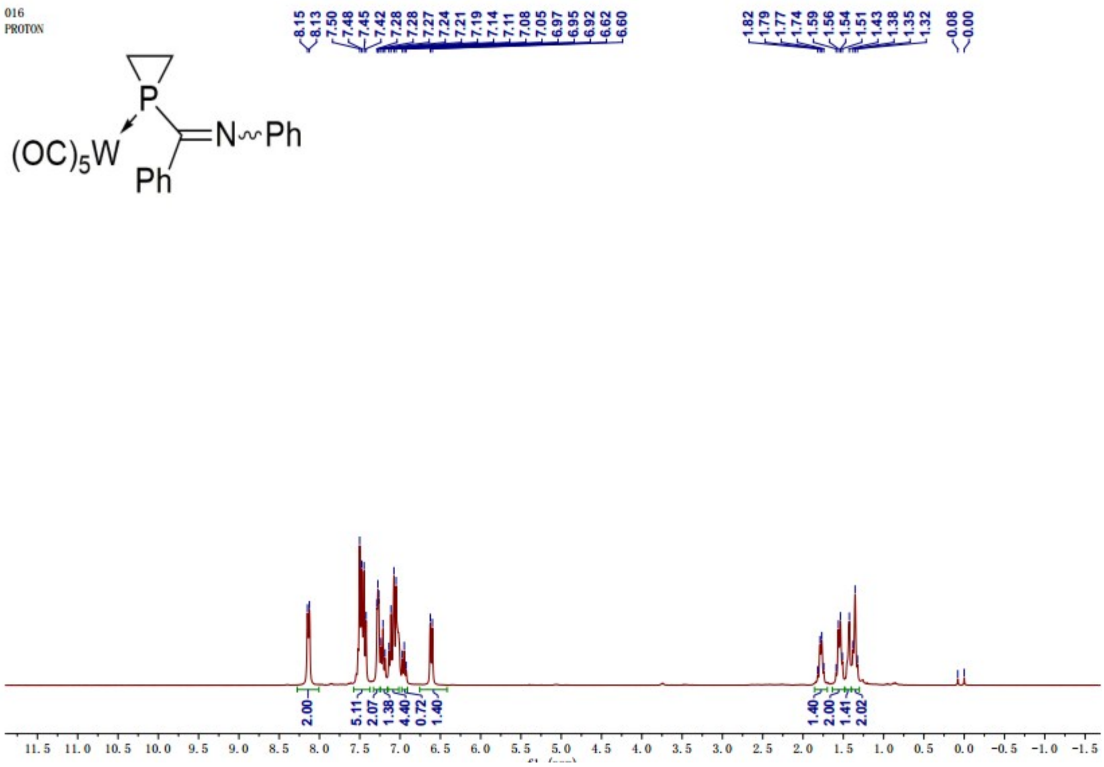
Dept135 NMR of Compound 1a



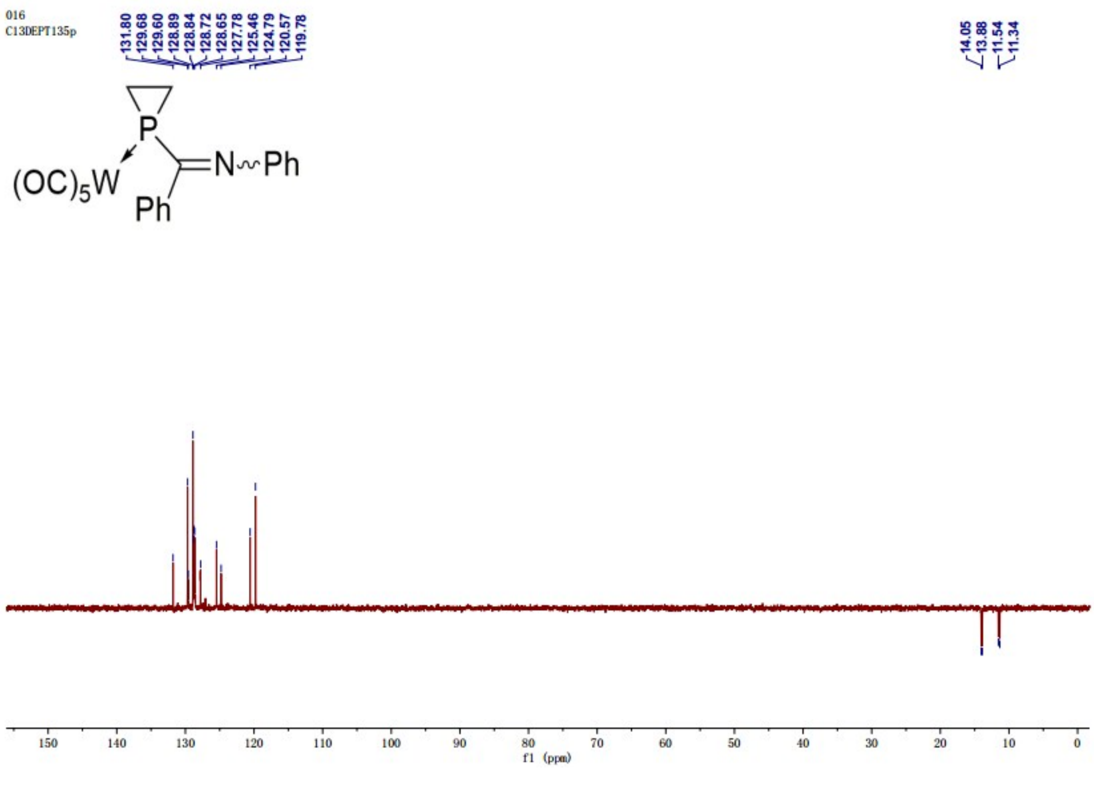
$^{13}C\{^1H\}$ NMR of Compound 1a



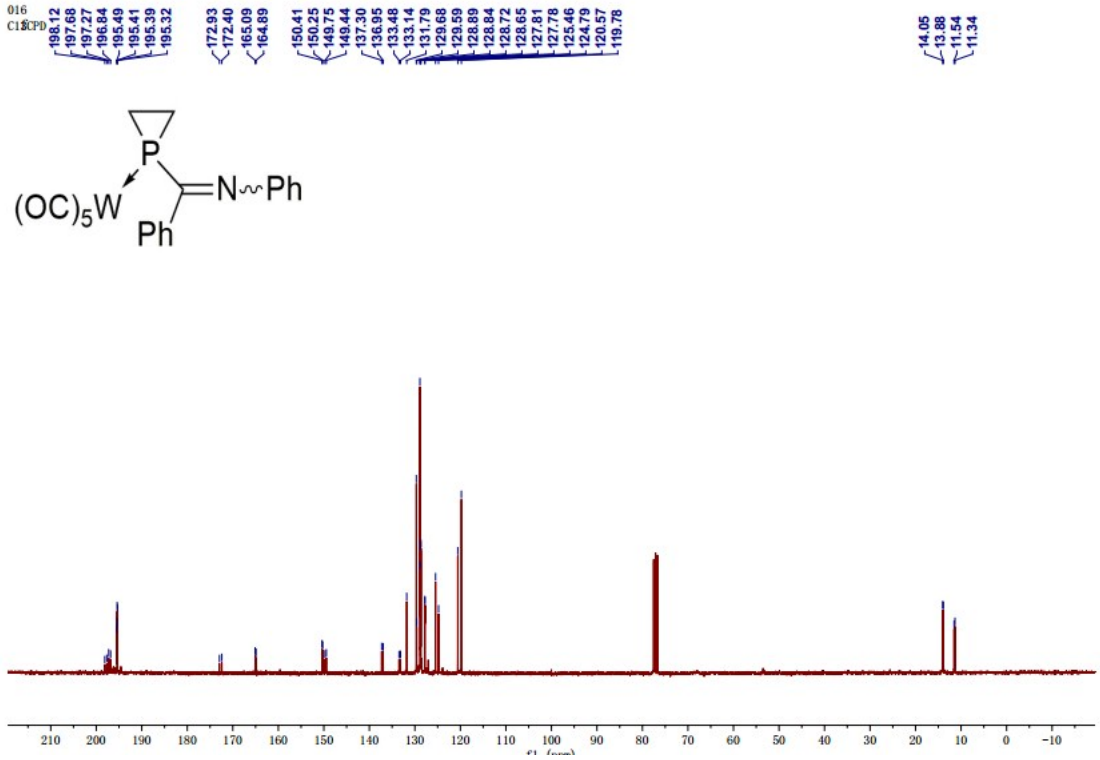
$^{31}P\{^1H\}$ NMR of Compound 2a,b



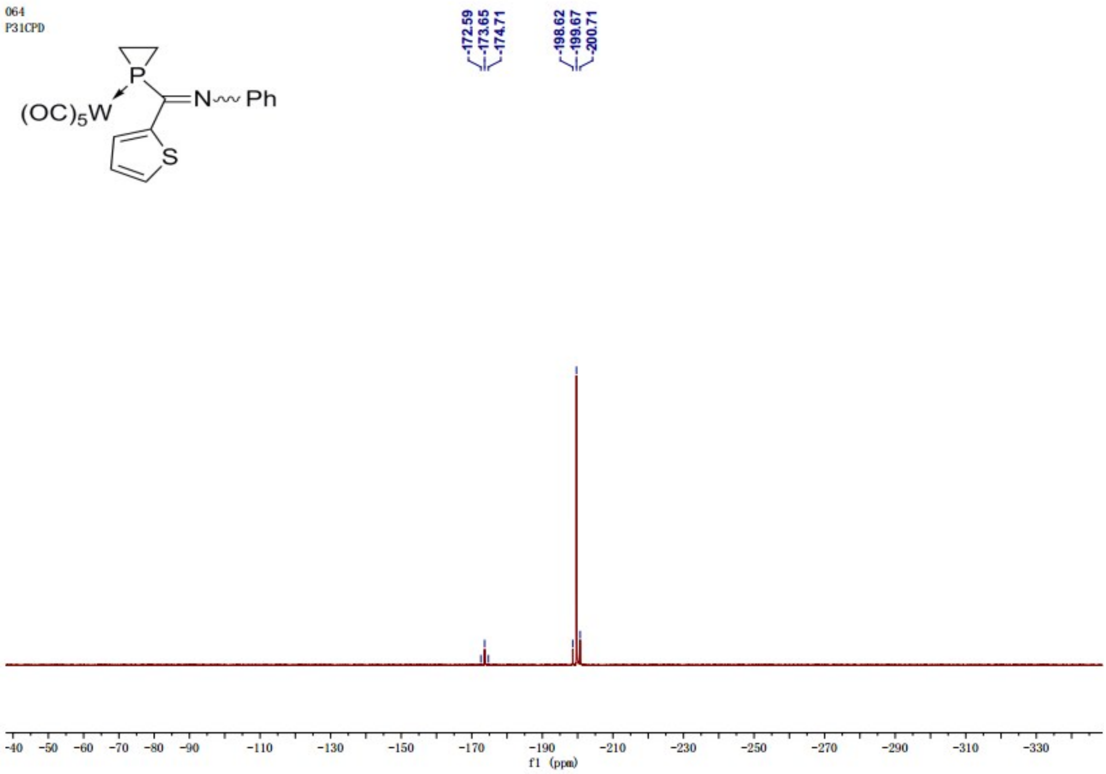
^{1}H NMR of Compound 2a,b



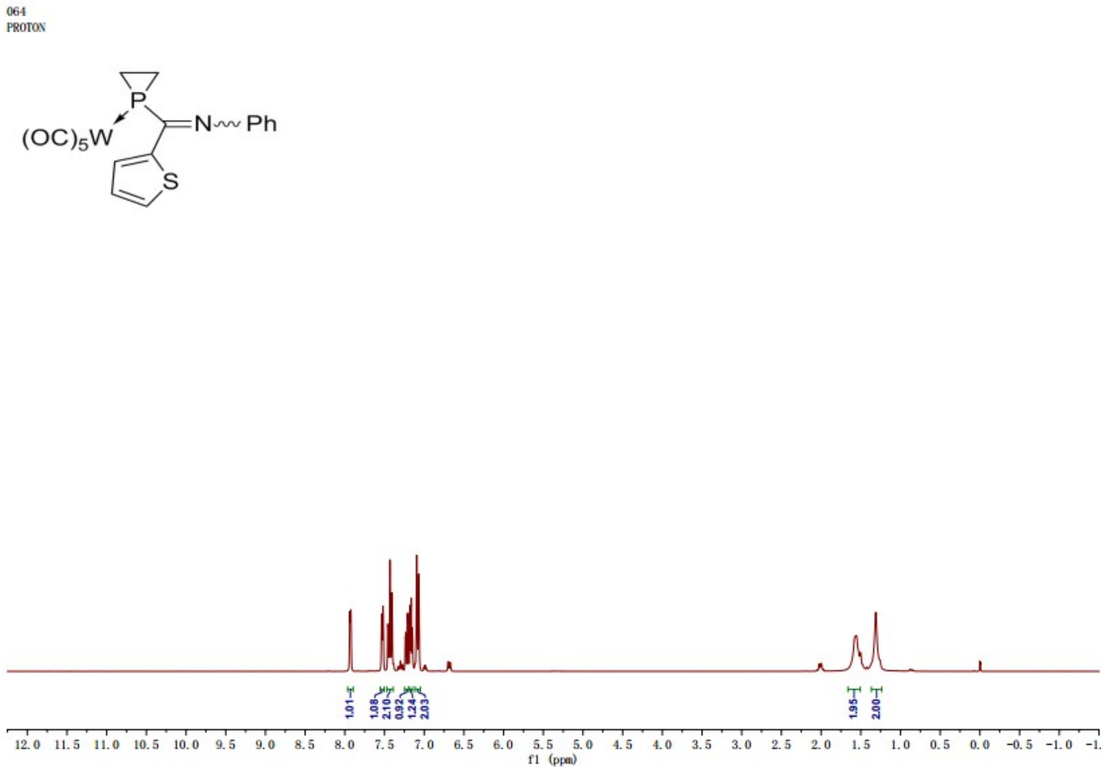
Dept135 NMR of Compound 2a,b



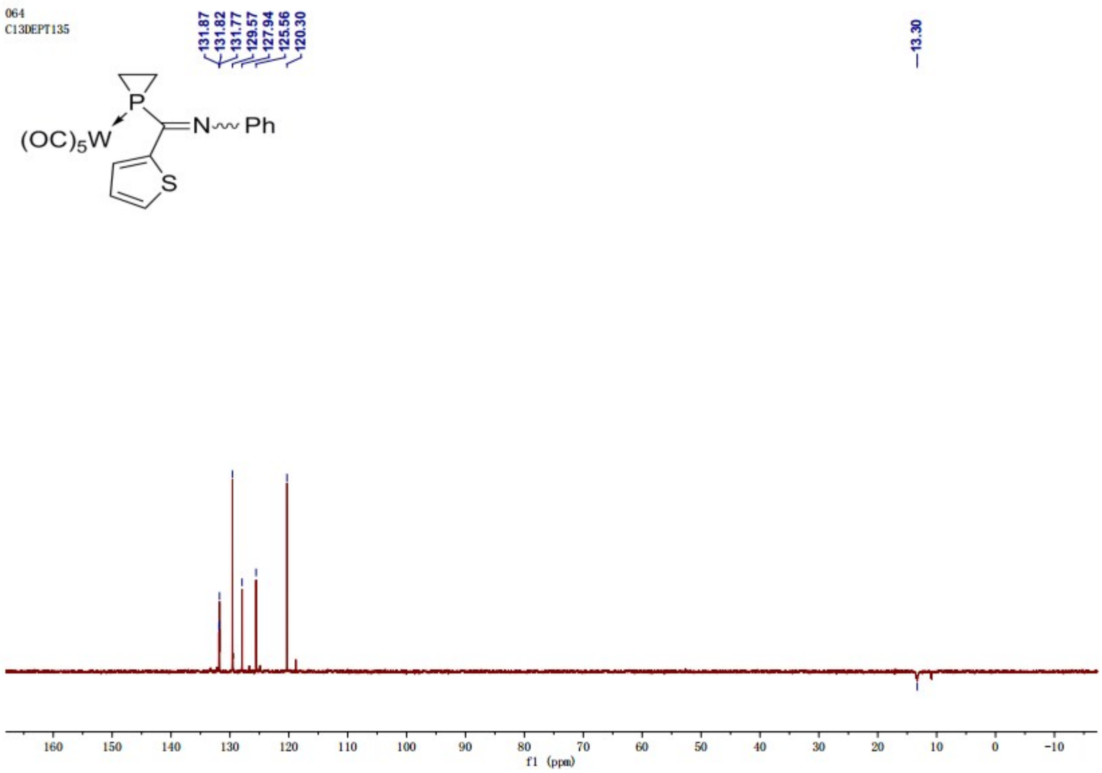
$^{13}C\{^{1}H\}$ **NMR of Compound 2a,b**



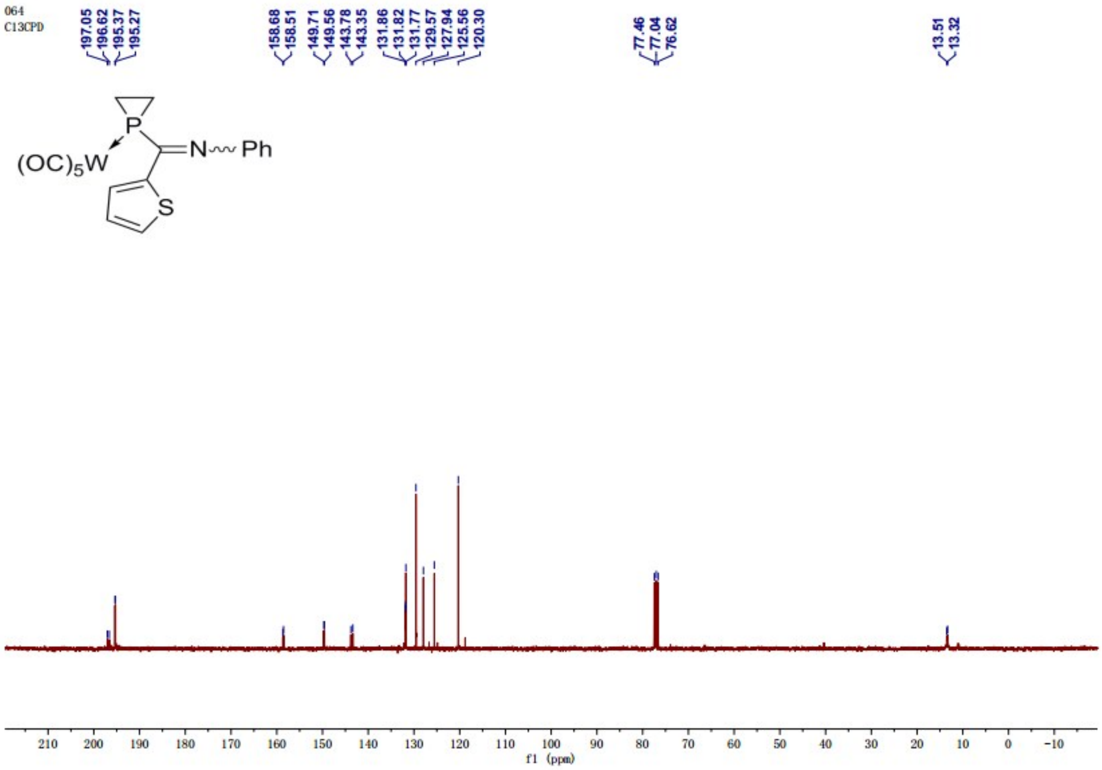
$^{31}P\{^{1}H\}$ **NMR of Compound 3a,b**



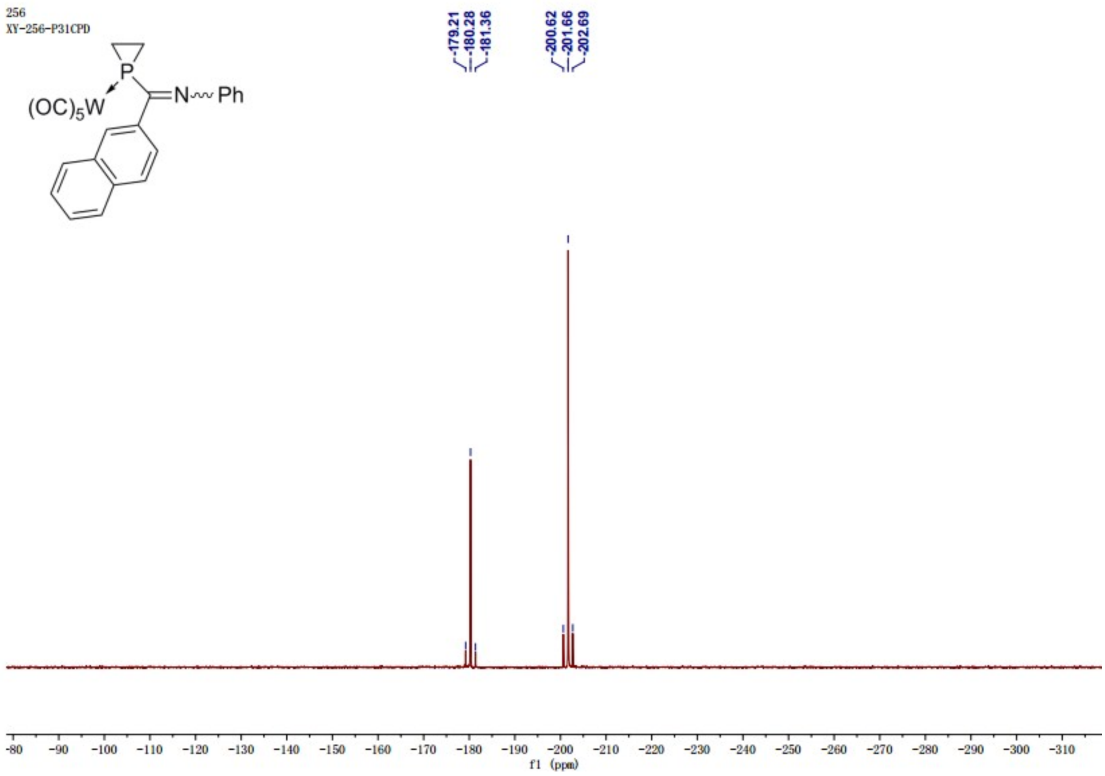
^{1}H NMR of Compound 3a,b



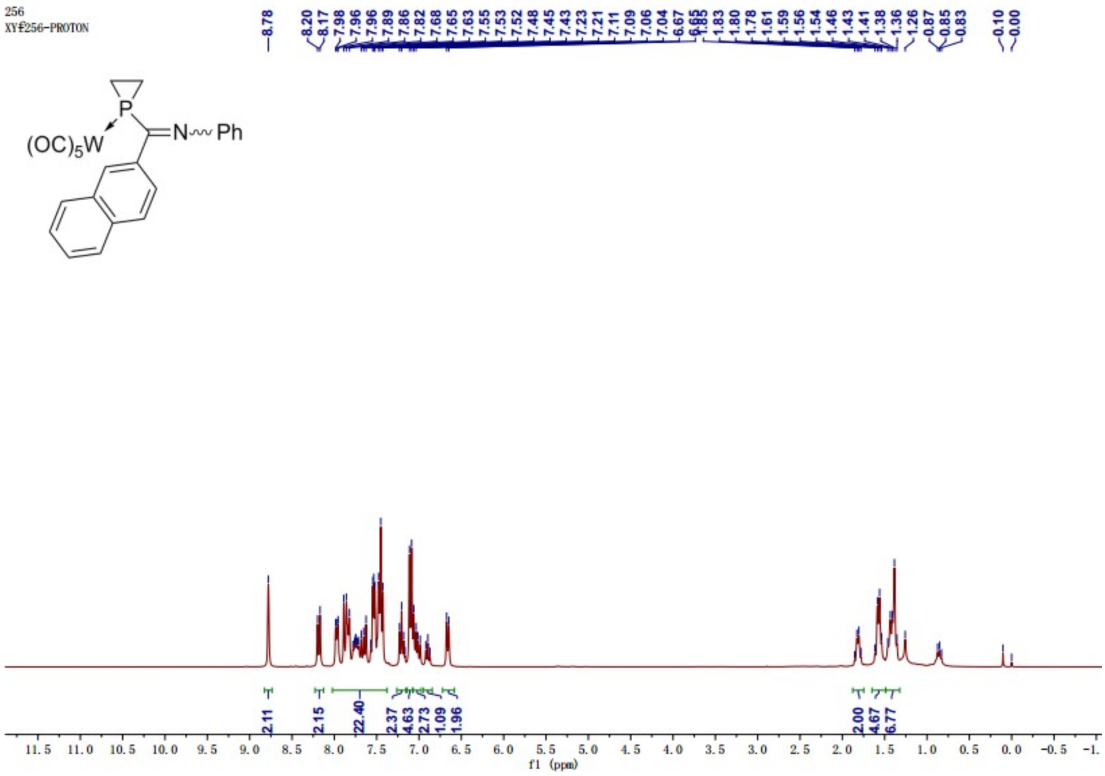
Dept135 NMR of Compound 3a,b



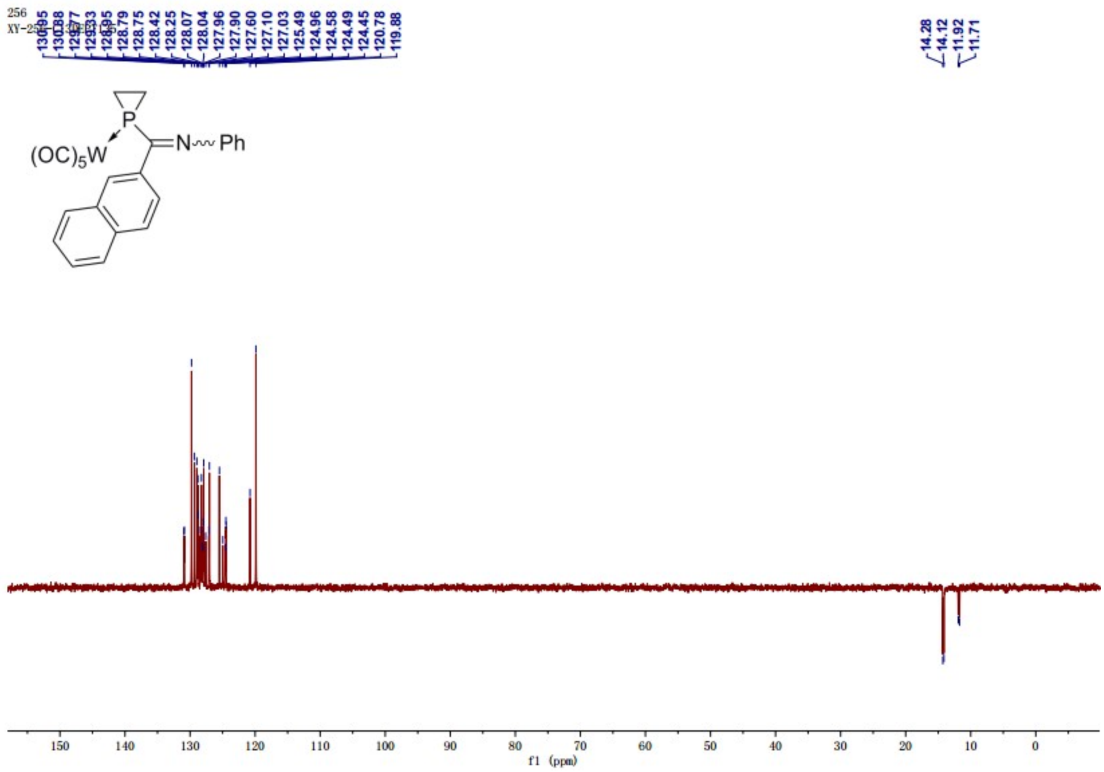
$^{13}C\{^1H\}$ NMR of Compound 3a,b



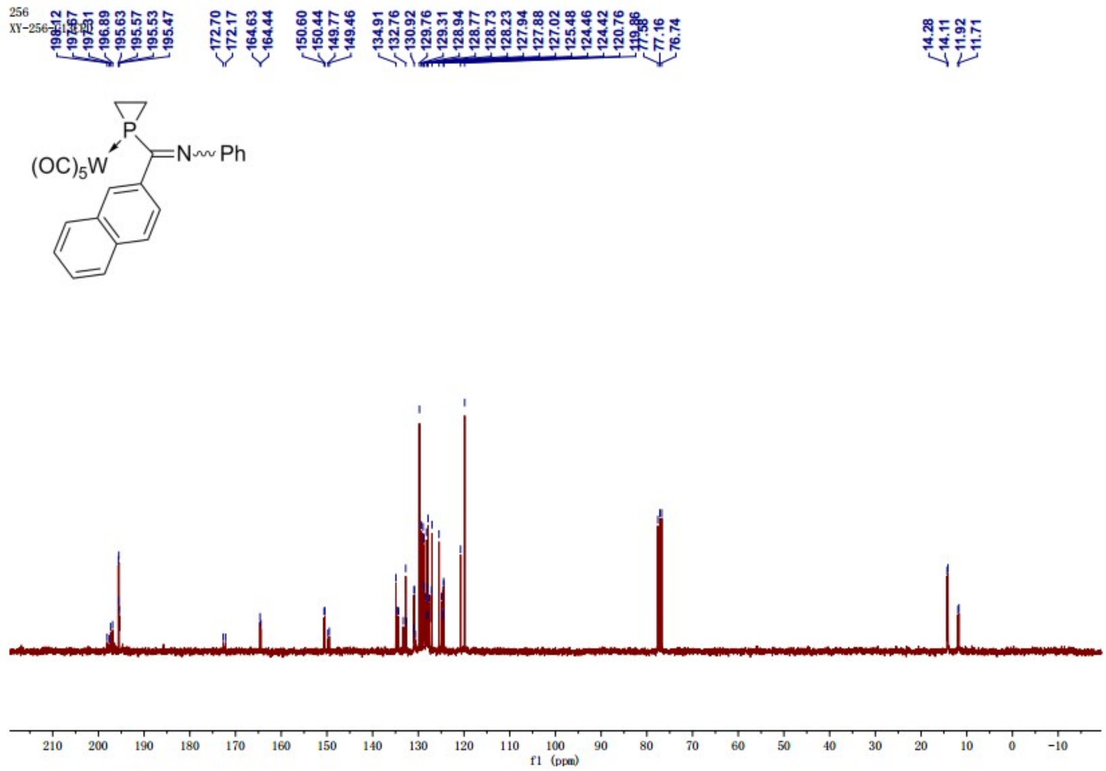
$^{31}P\{^1H\}$ NMR of Compound 4a,b



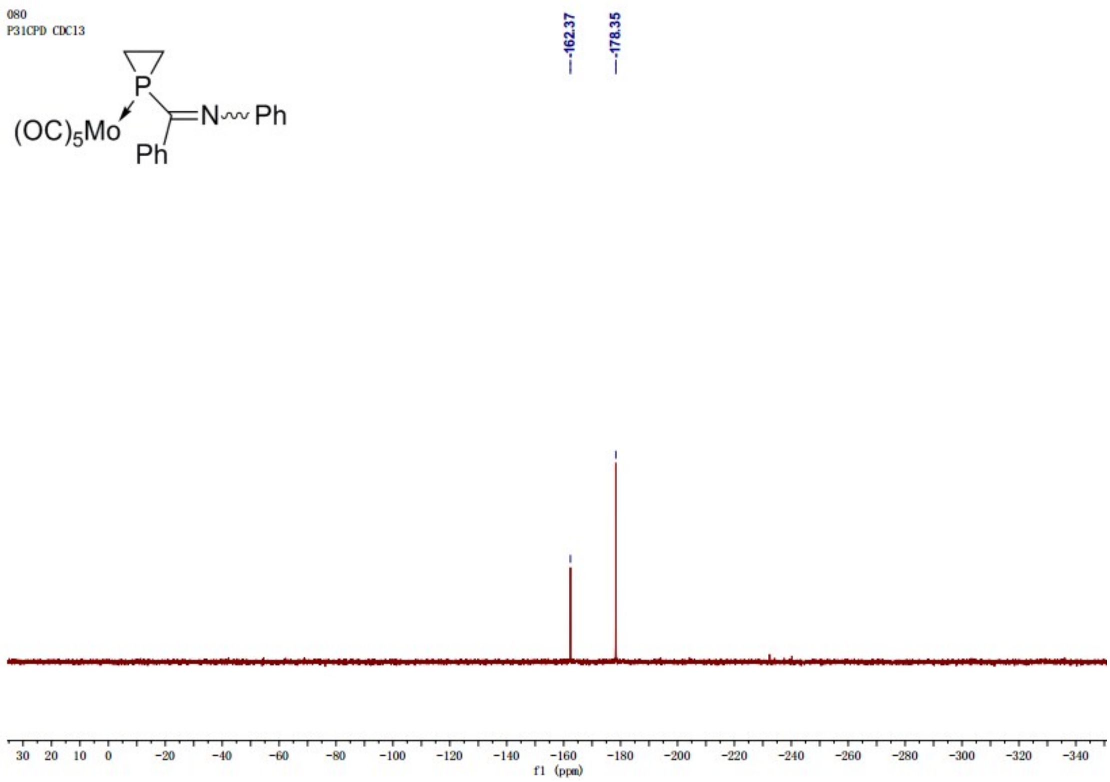
^{1}H NMR of Compound 4a,b



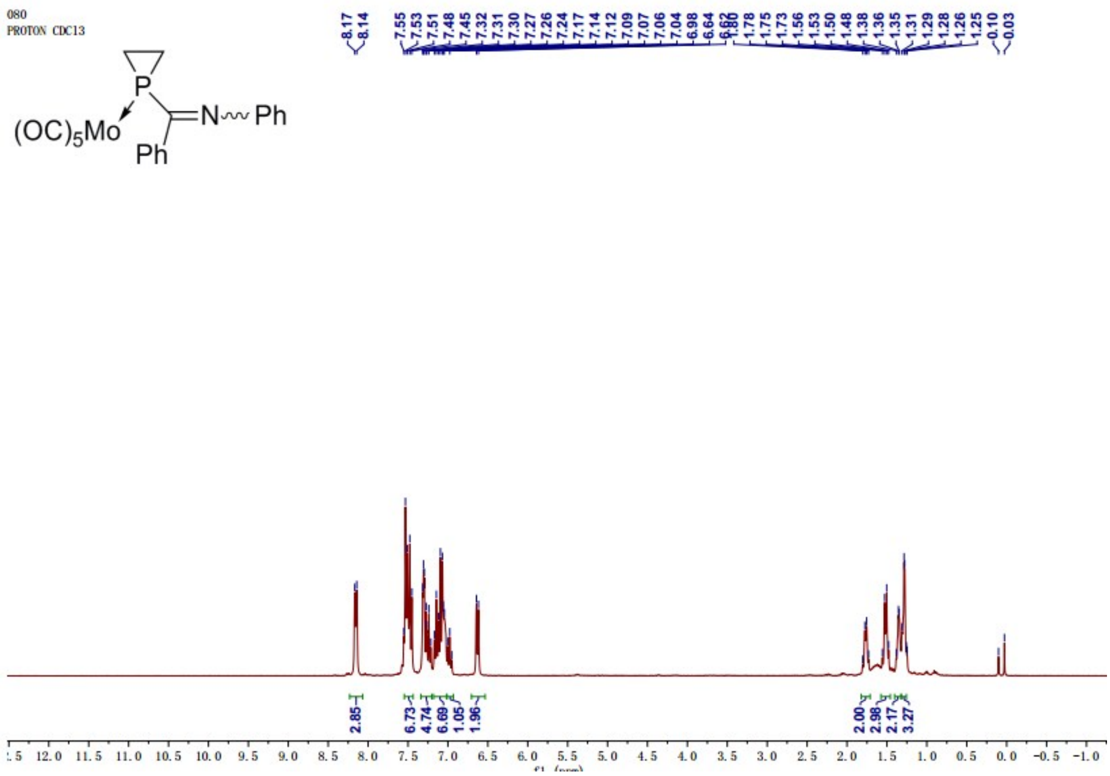
Dept135 NMR of Compound 4a,b



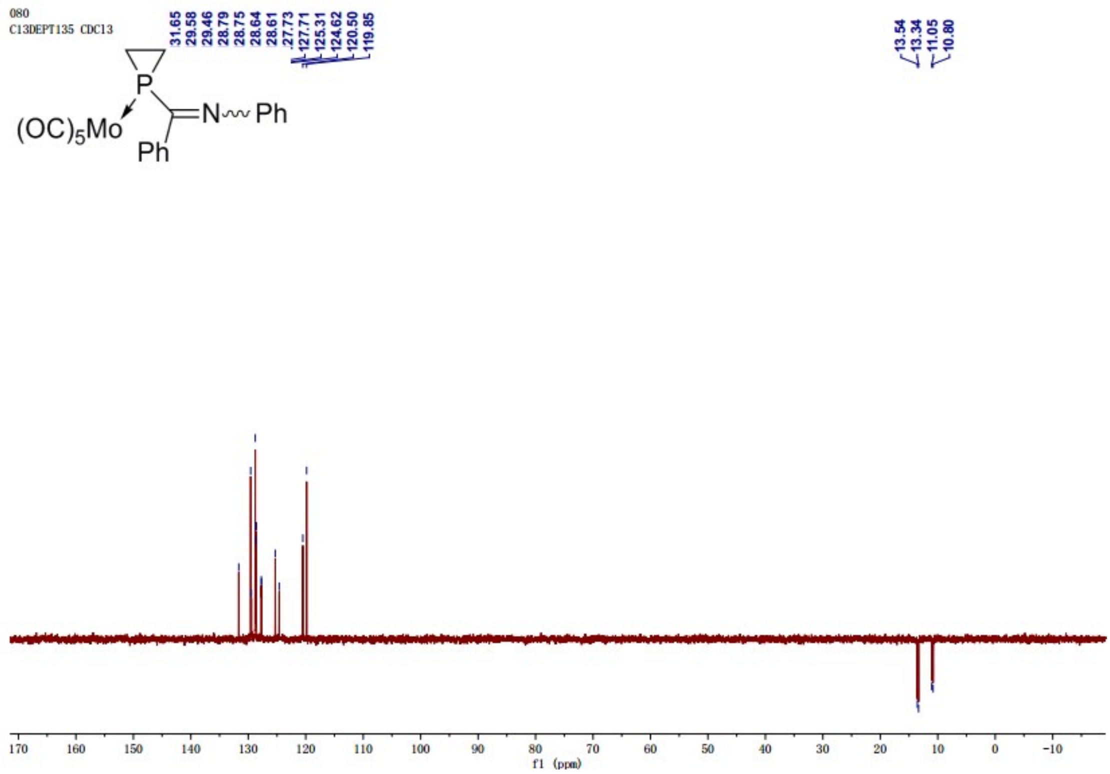
$^{13}C\{^{1}H\}$ NMR of Compound 4a,b



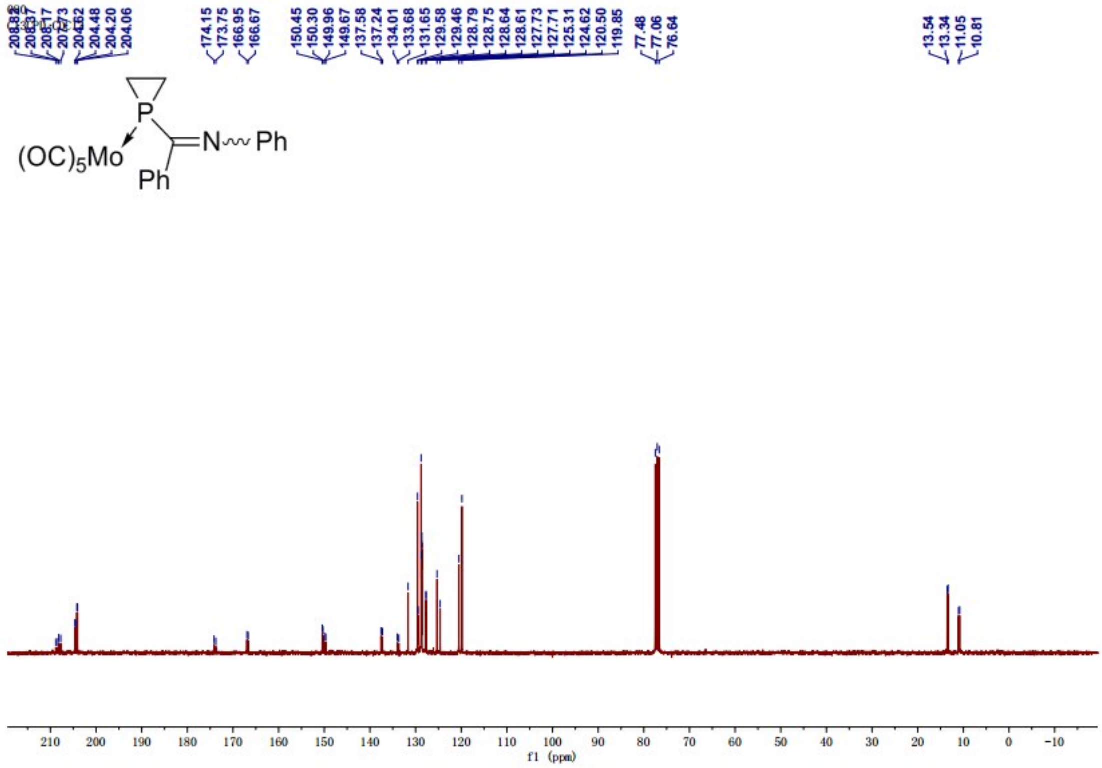
$^{31}P\{^{1}H\}$ NMR of Compound 5a,b



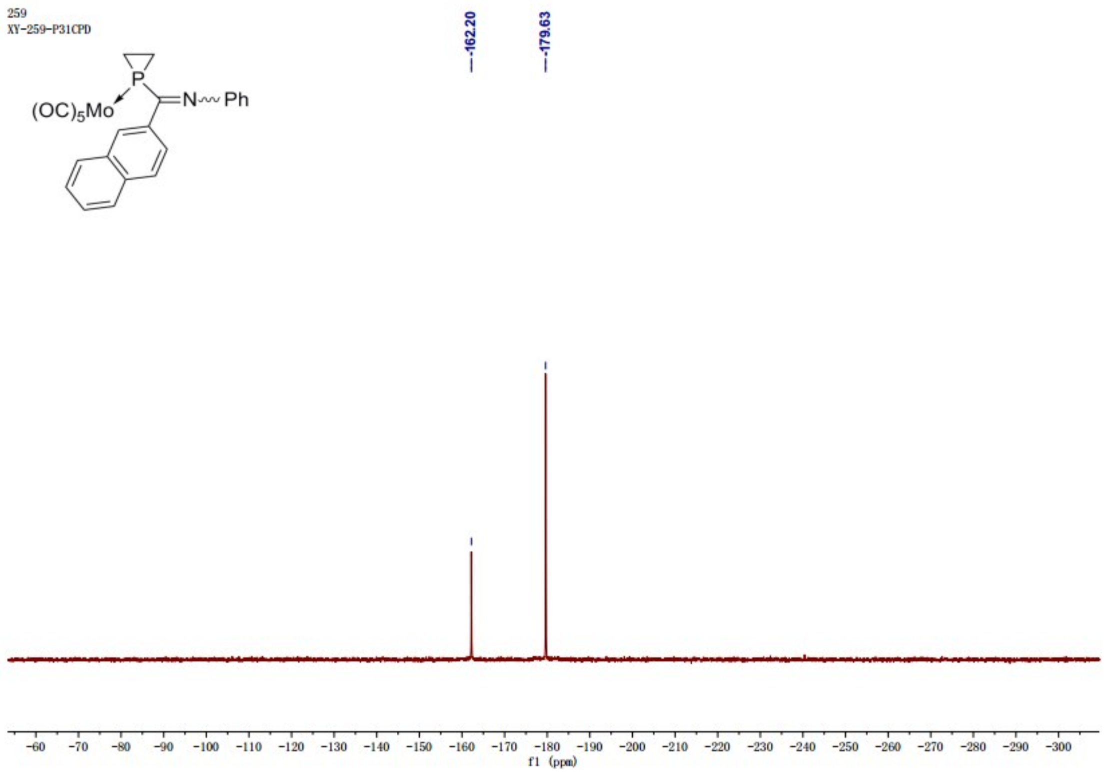
^{1}H NMR of Compound 5a,b



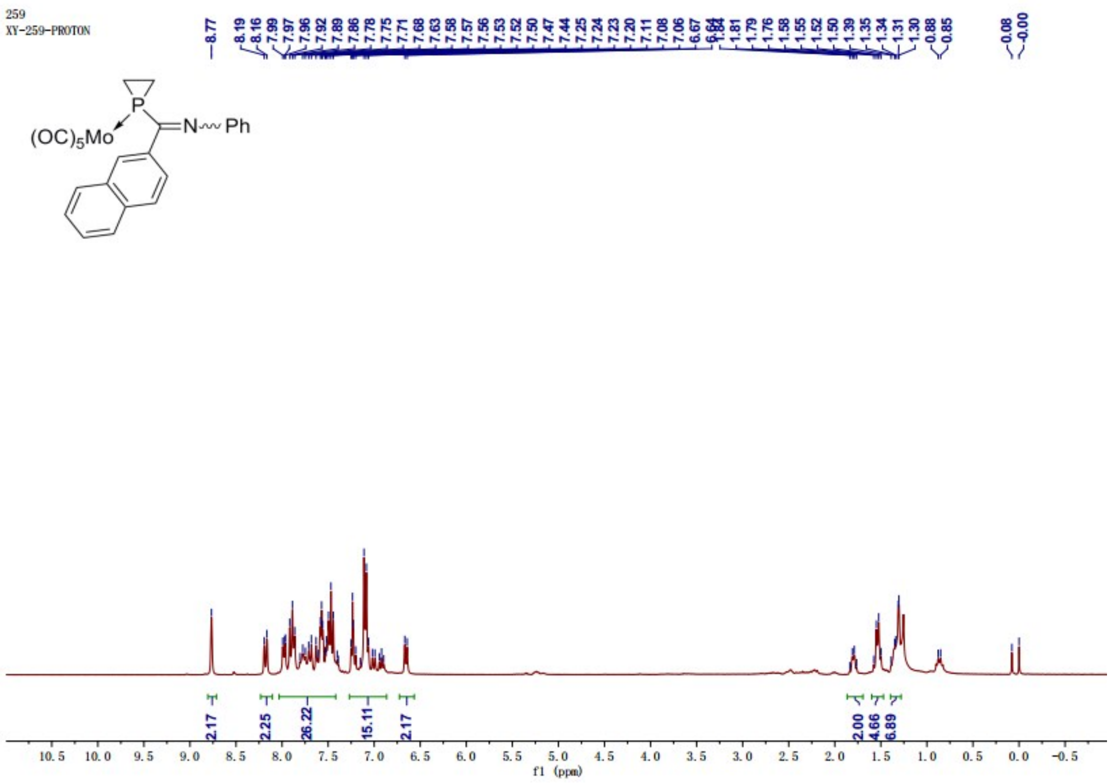
Dept135 NMR of Compound 5a,b



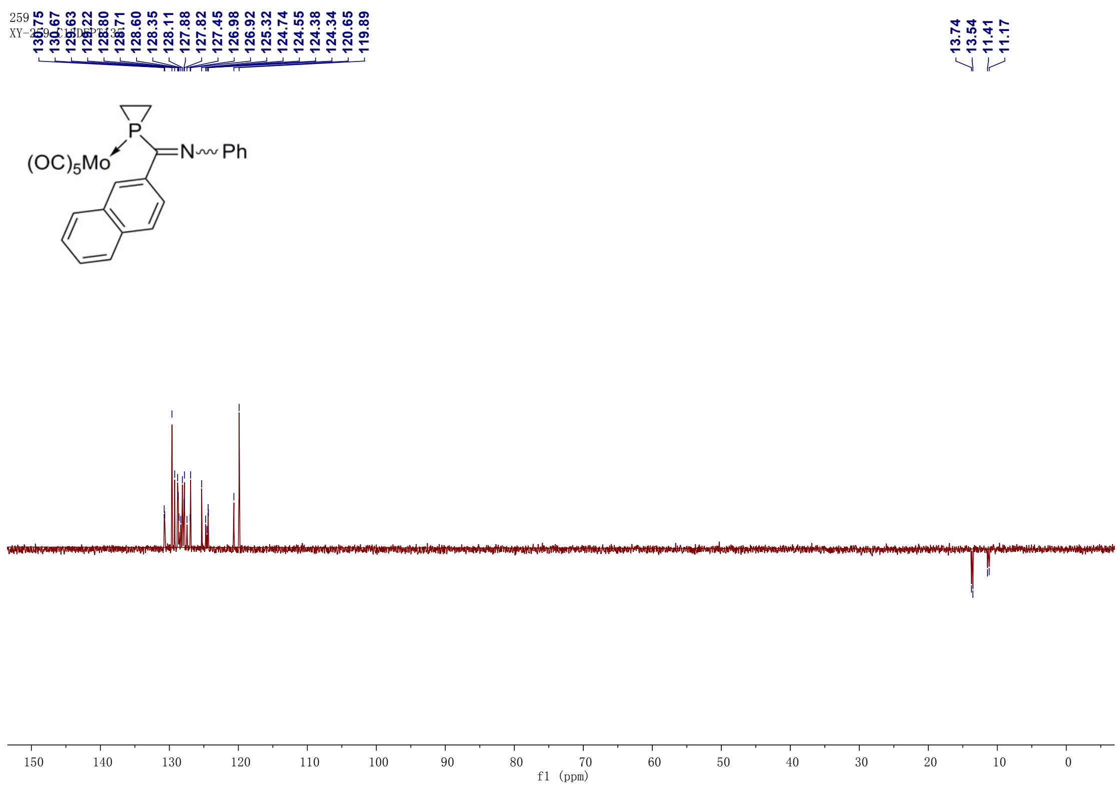
[13]C{[1]H} NMR of Compound 5a,b



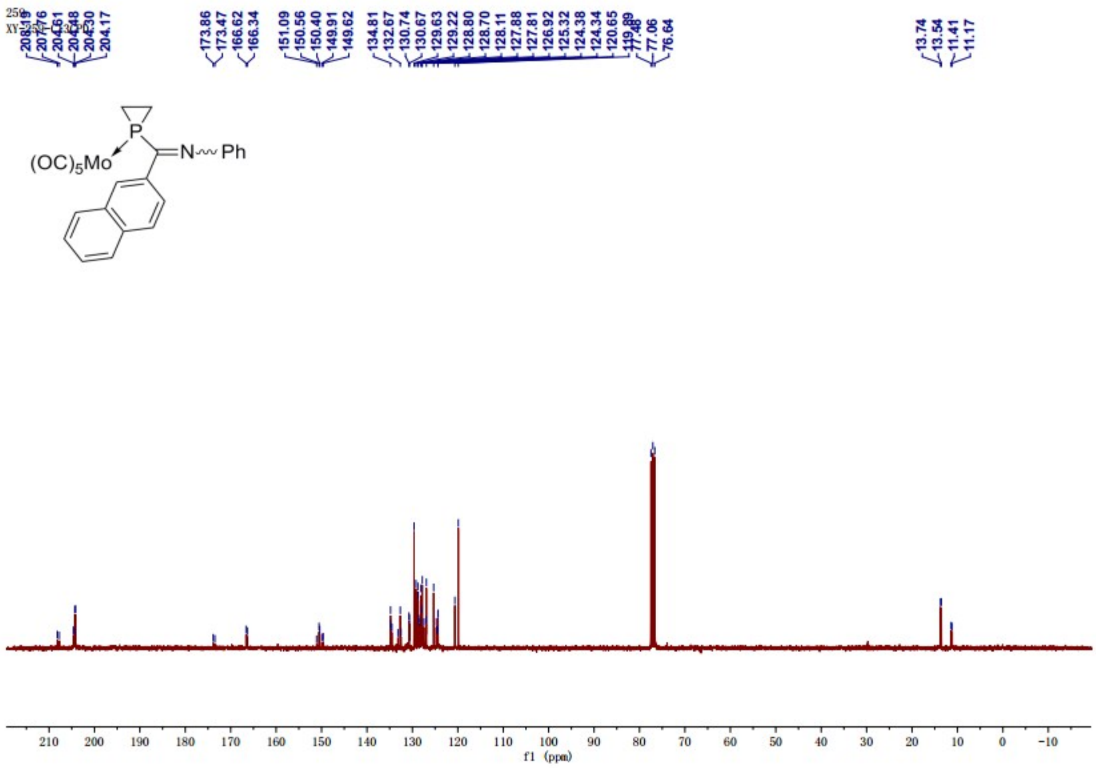
[31]P{[1]H} NMR of Compound 6a,b



^{1}H NMR of Compound 6a,b



Dept135 NMR of Compound 6a,b



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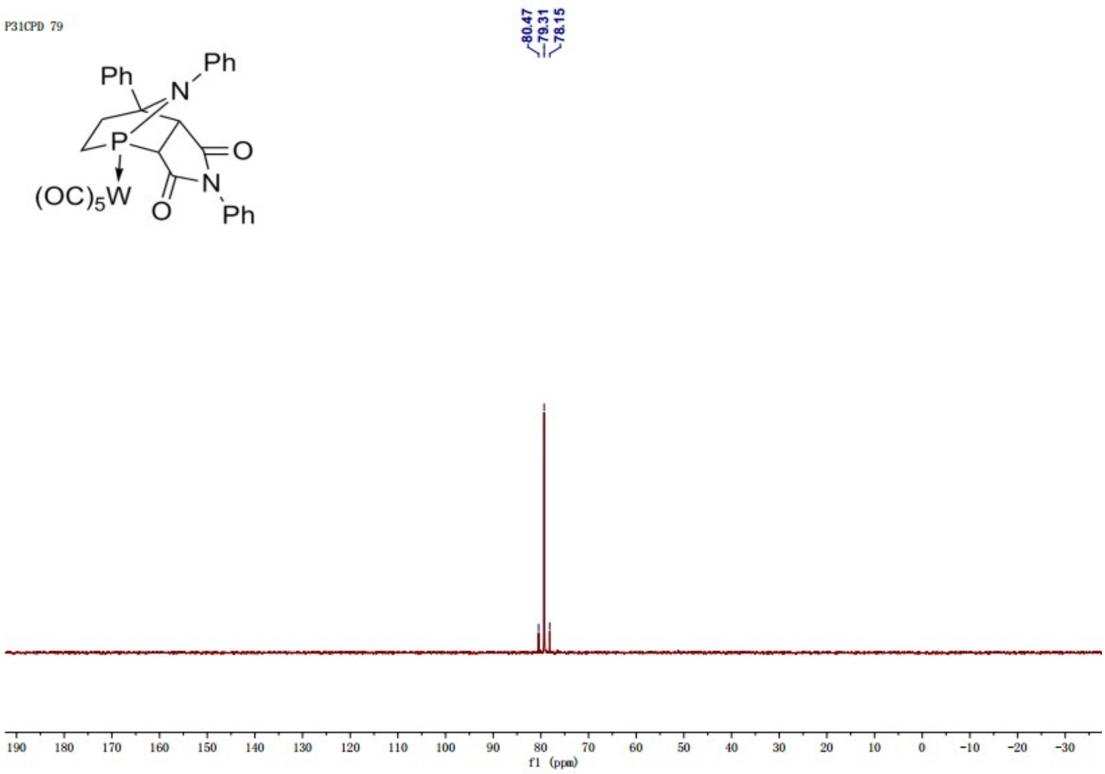
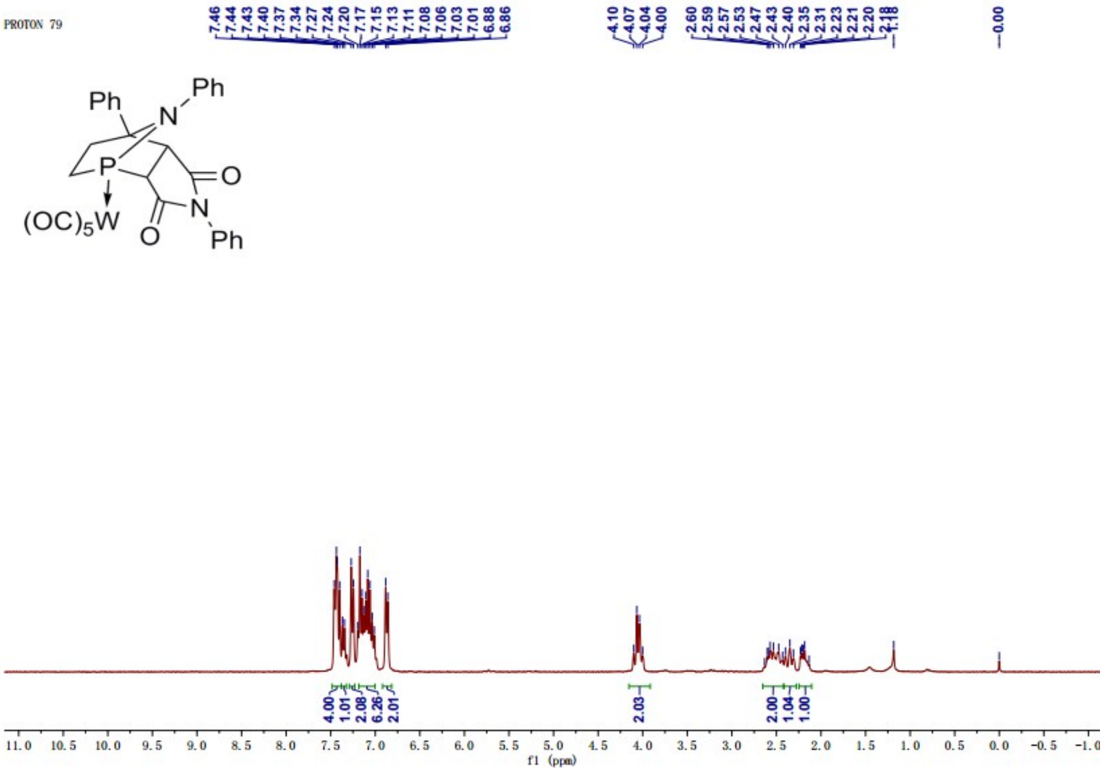
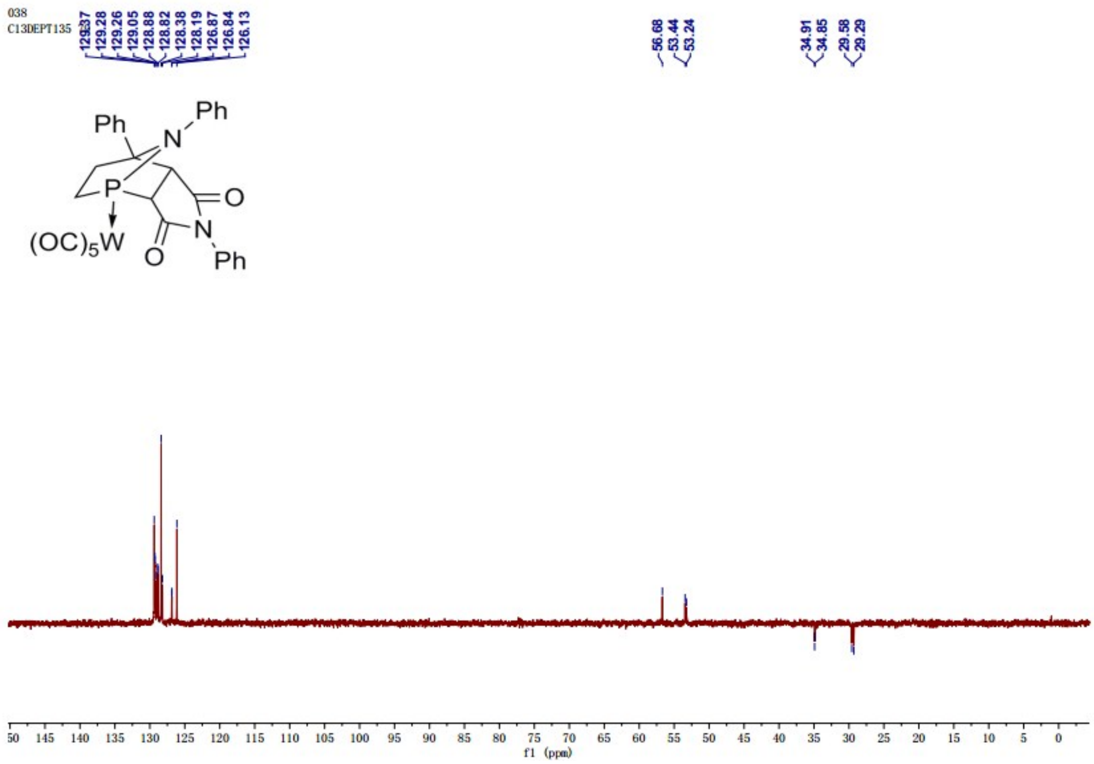


$^{31}P\{^{1}H\}$ NMR of Compound 7a



^{1}H NMR of Compound 7a



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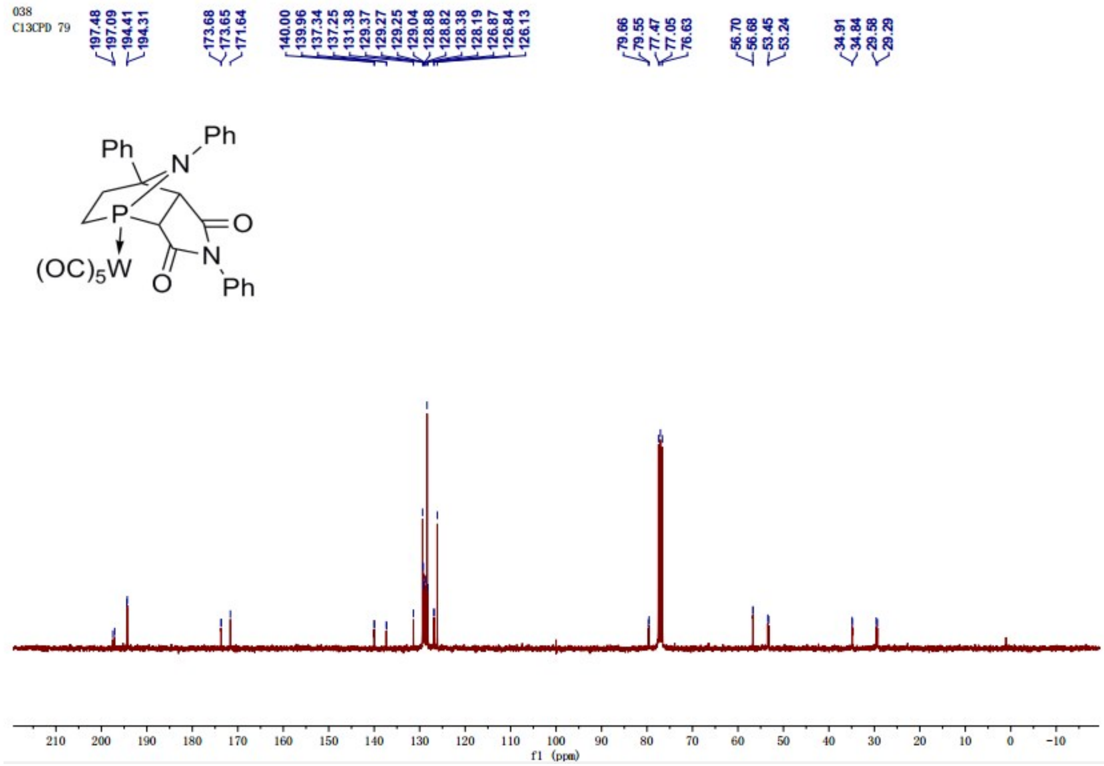
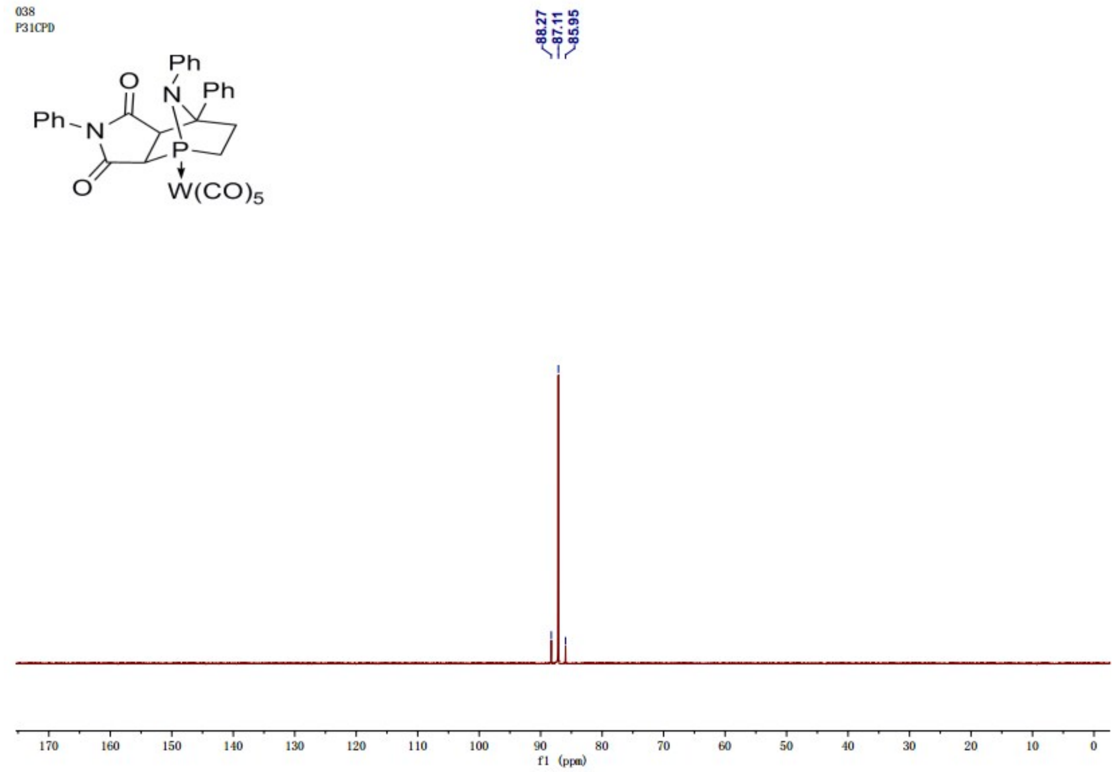
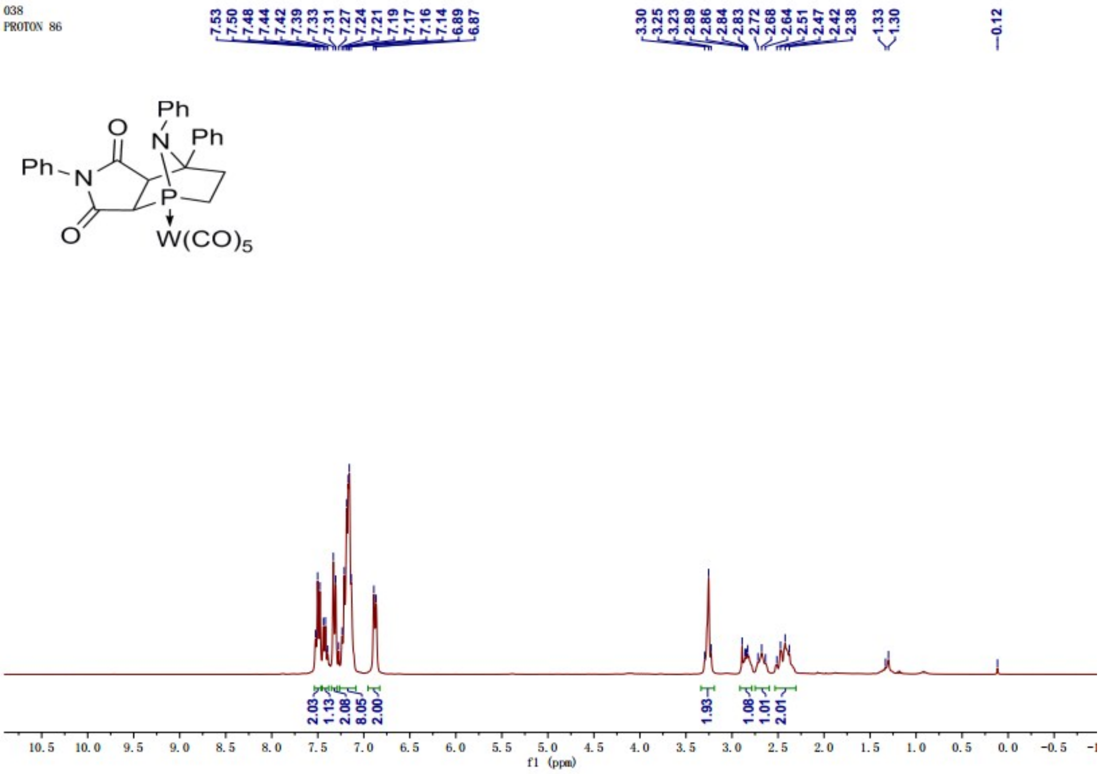


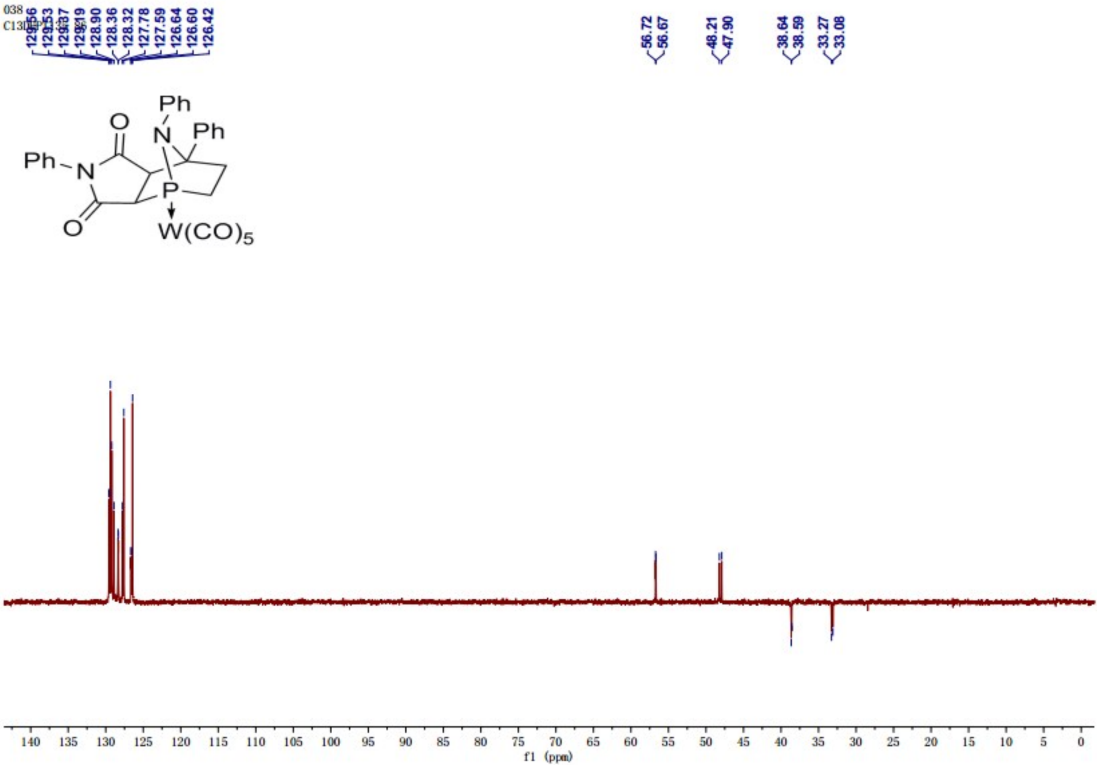
$^{13}C\{^{1}H\}$ **NMR of Compound 7a**



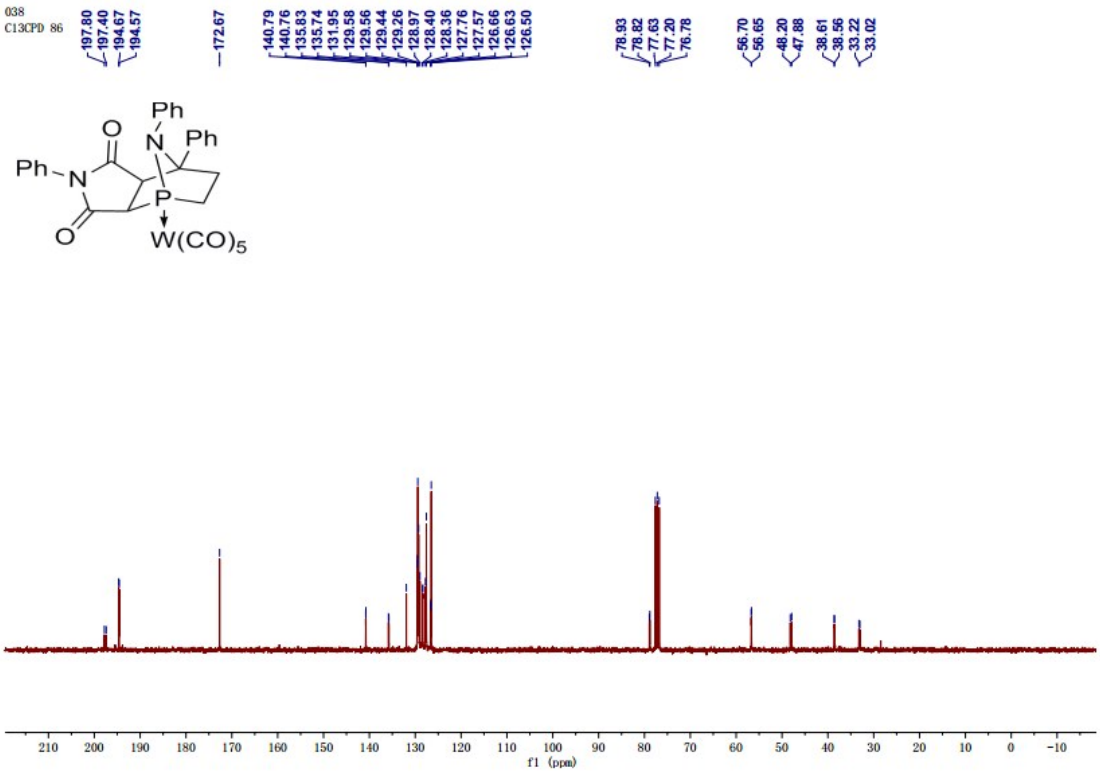
$^{31}P\{^{1}H\}$ **NMR of Compound 7b**



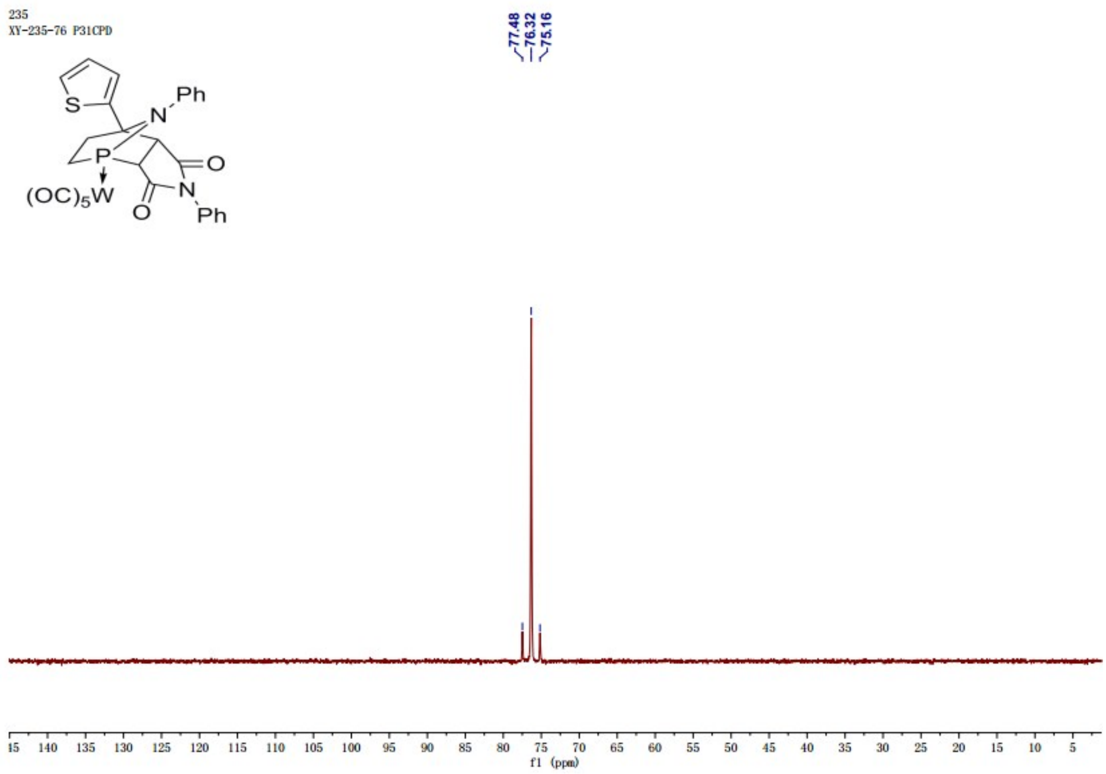
^{1}H NMR of Compound 7b



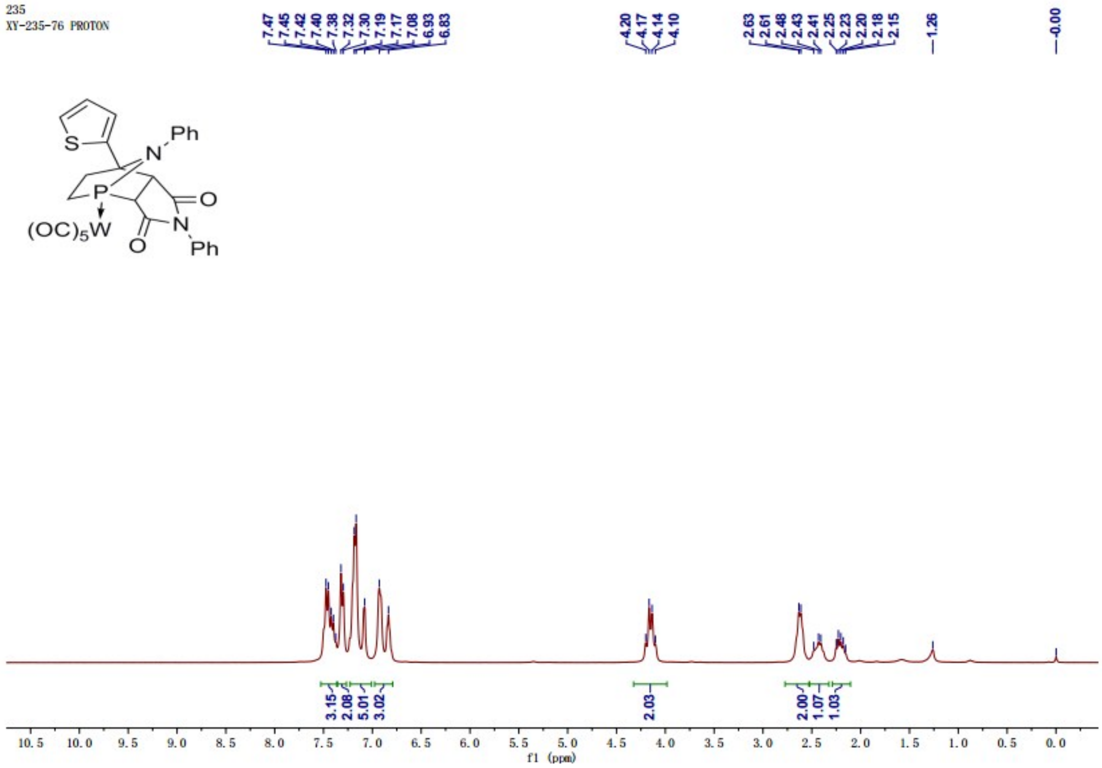
Dept135 NMR of Compound 7b



$^{13}C\{^{1}H\}$ NMR of Compound 7b



$^{31}P\{^{1}H\}$ NMR of Compound 8a



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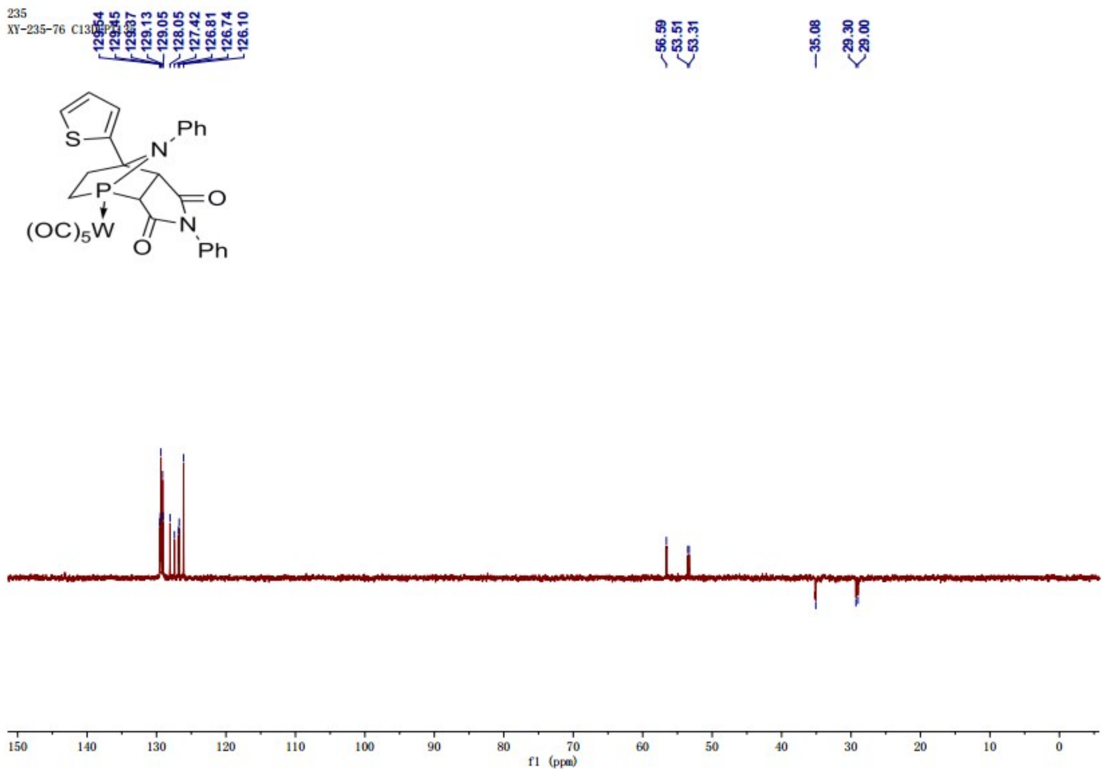

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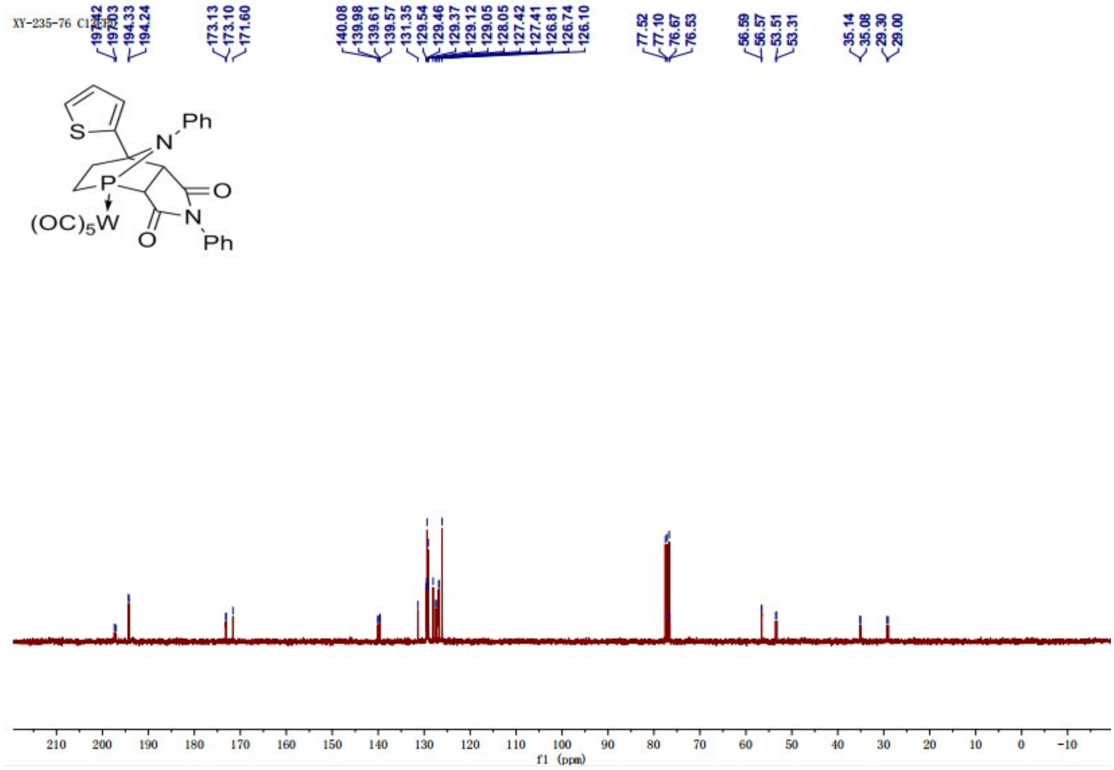
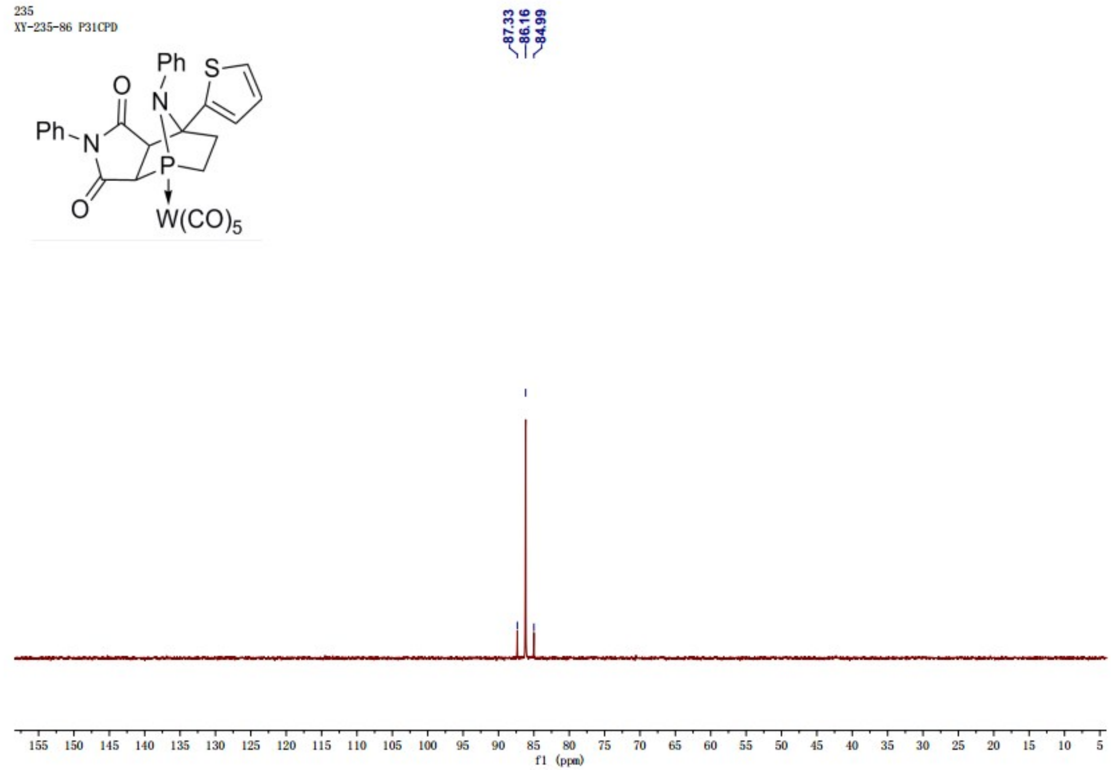
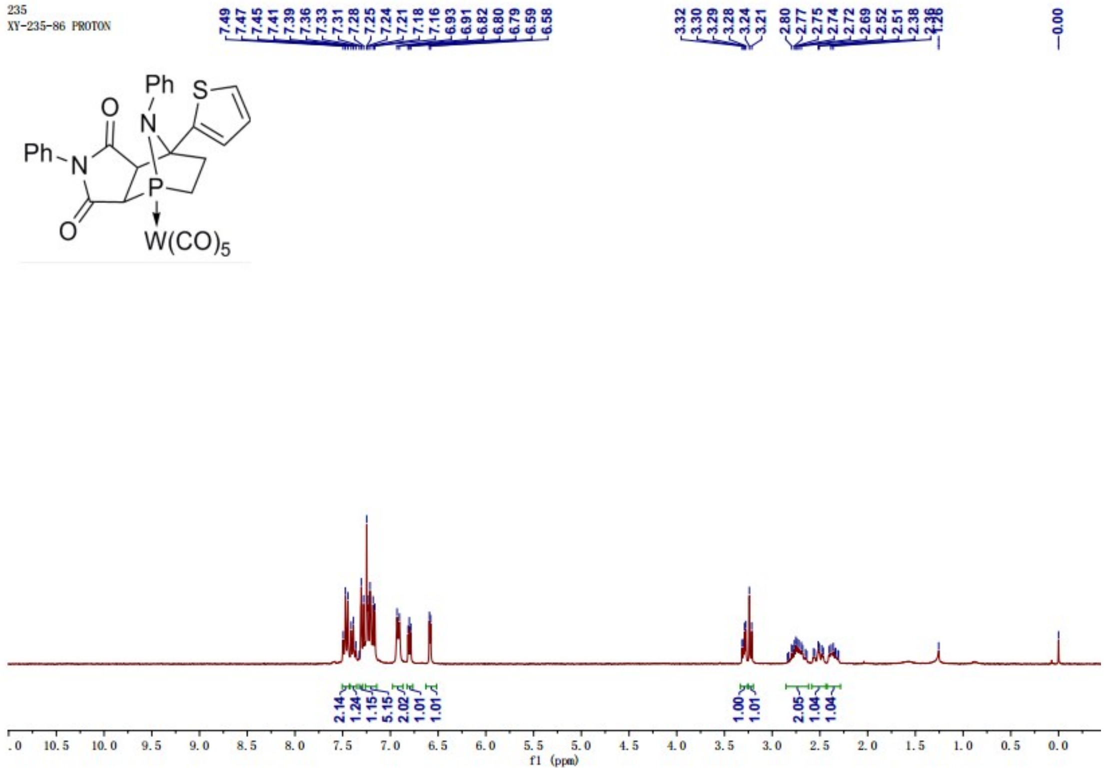


$^{13}C\{^{1}H\}$ NMR of Compound 8a



$^{31}P\{^{1}H\}$ NMR of Compound 8b



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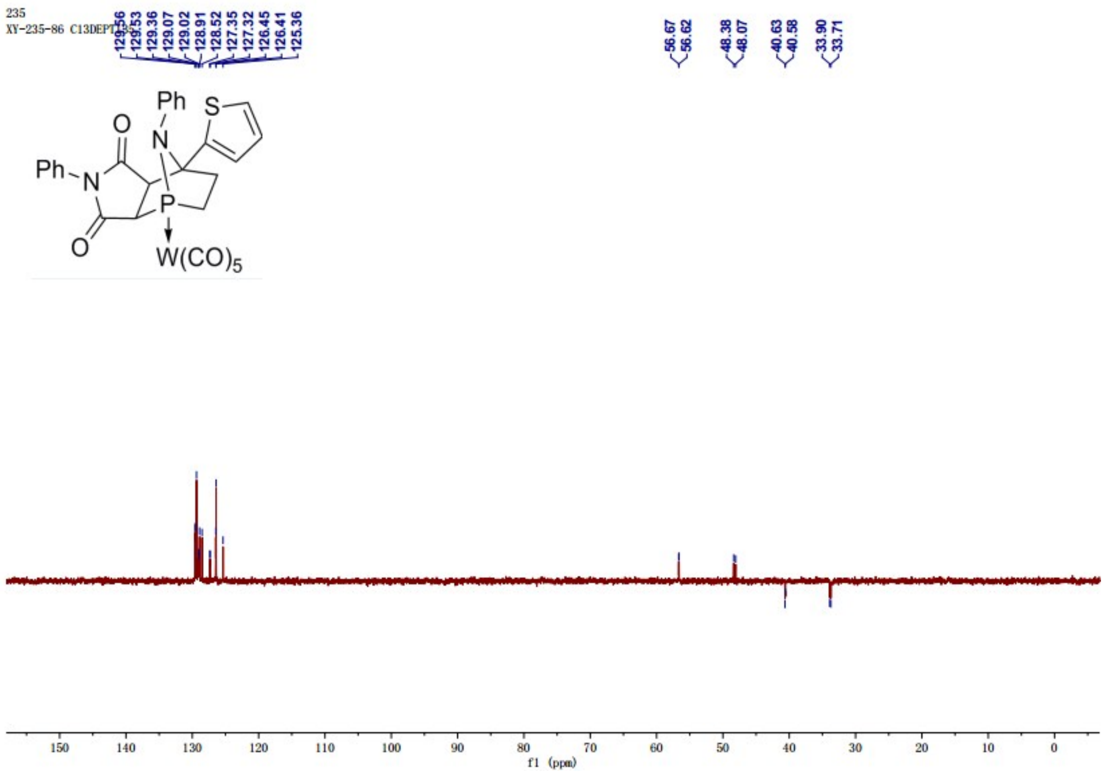

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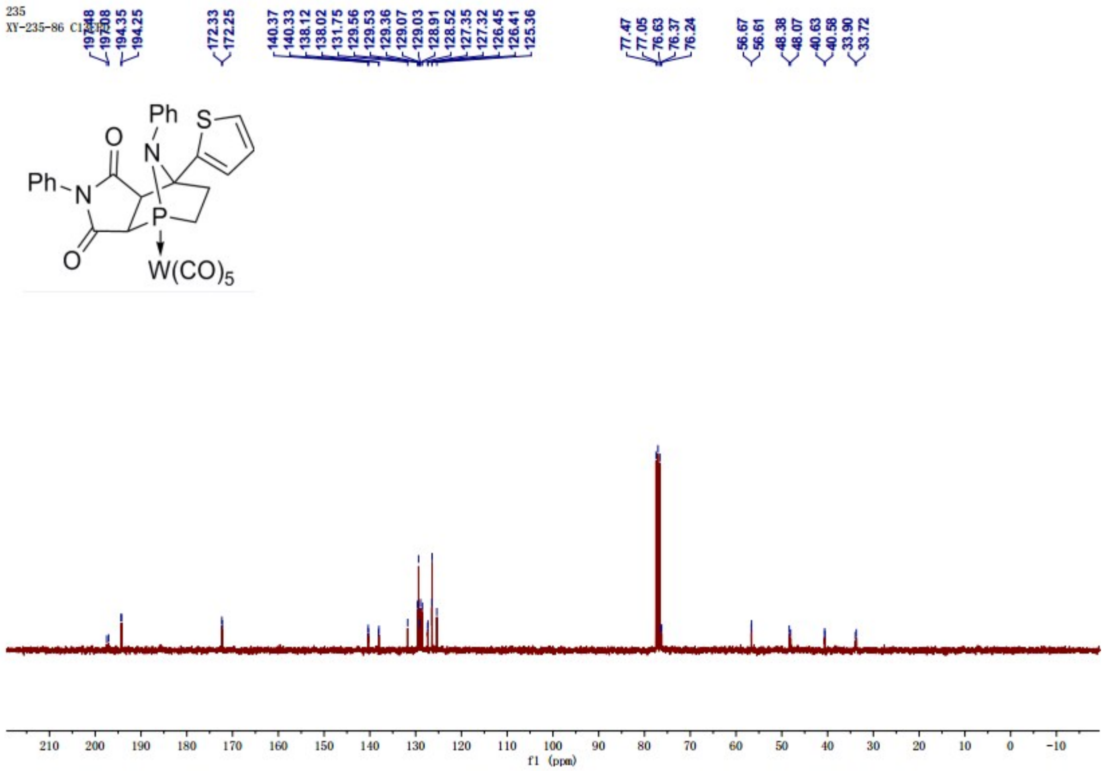

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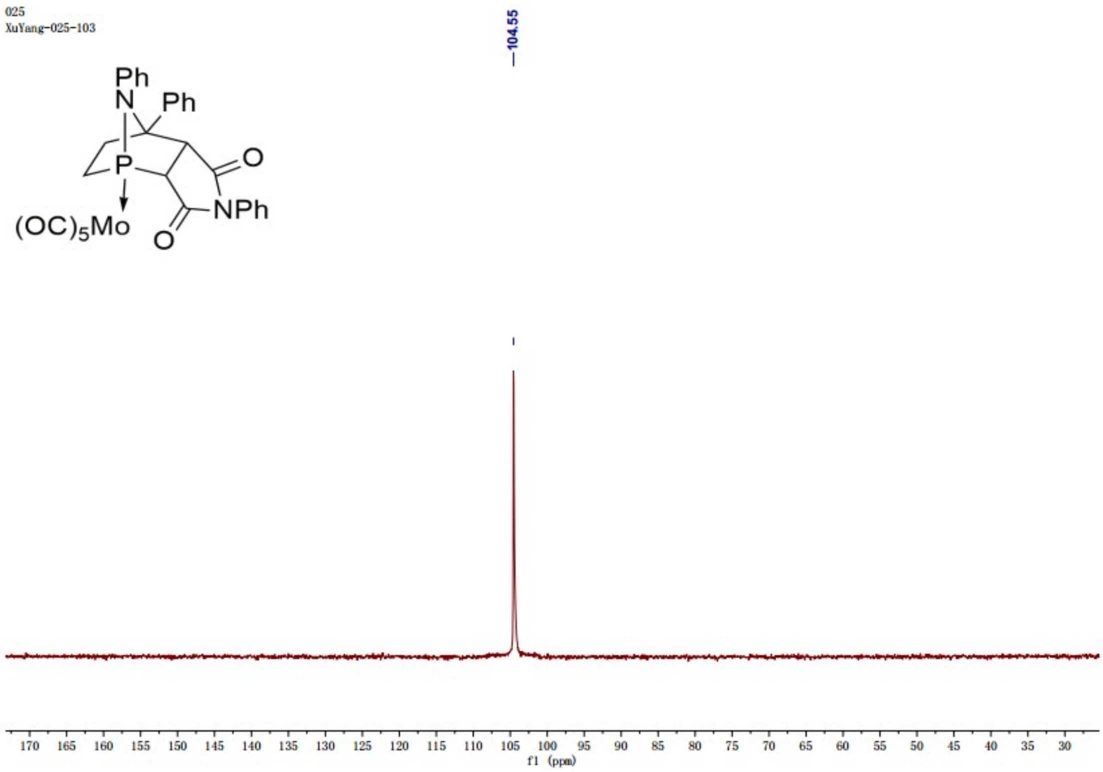

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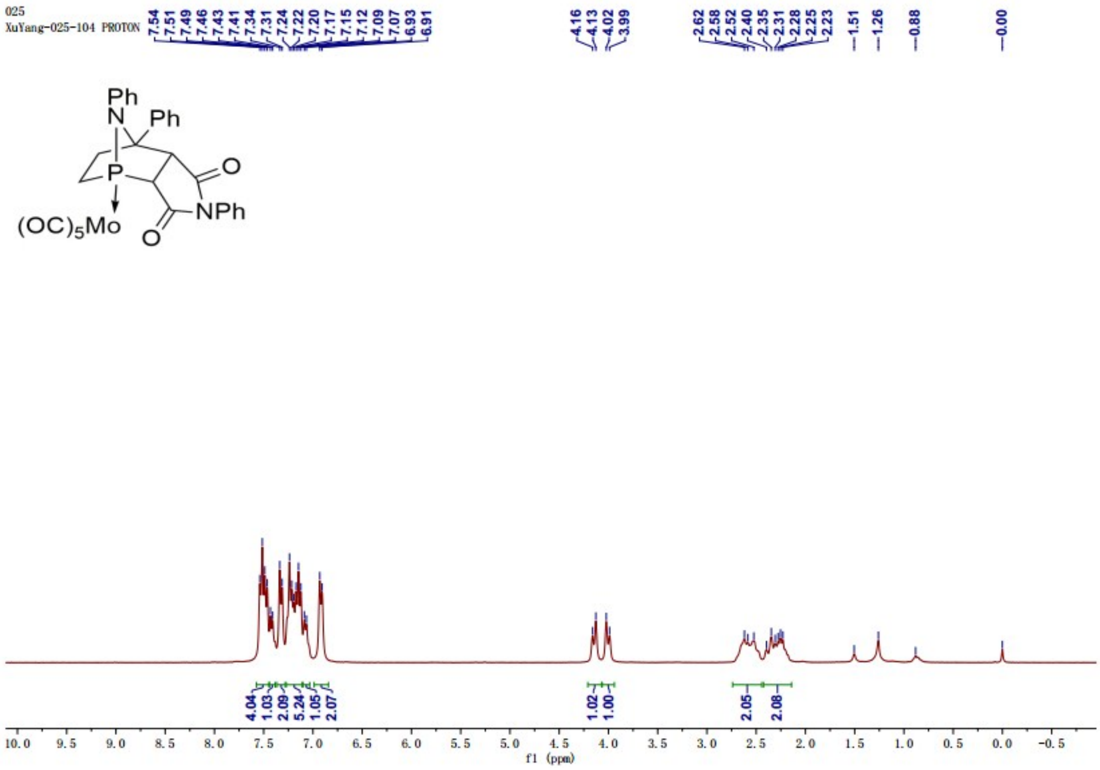

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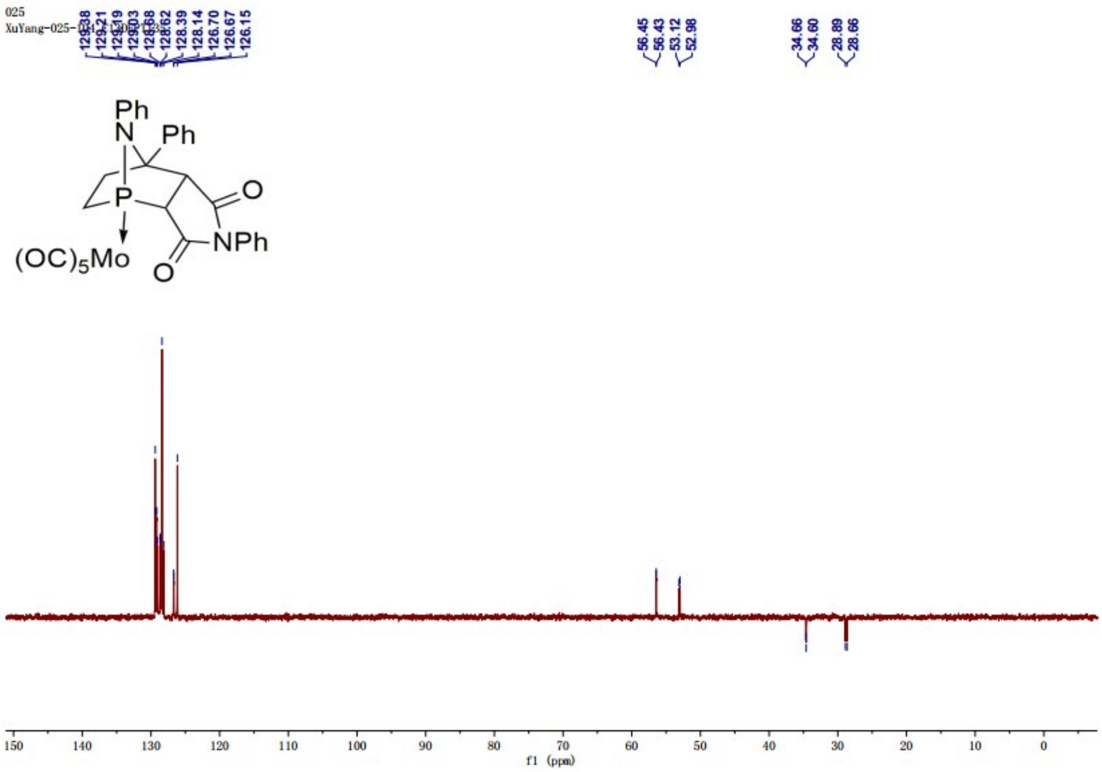

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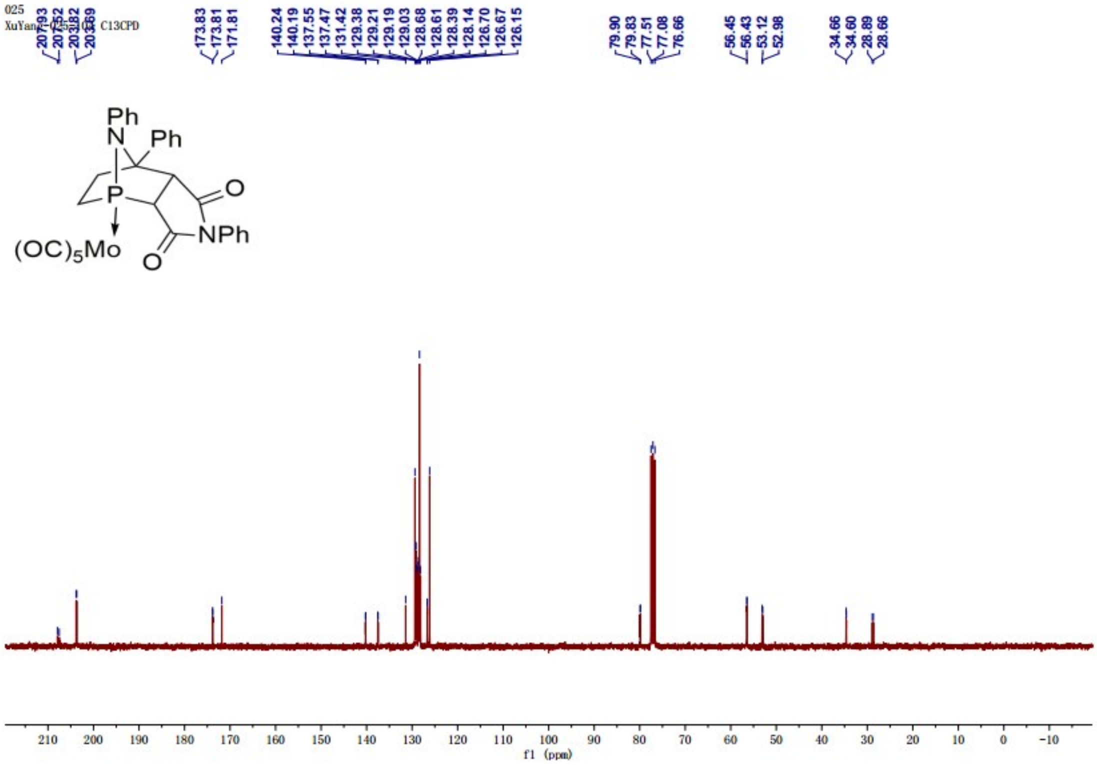

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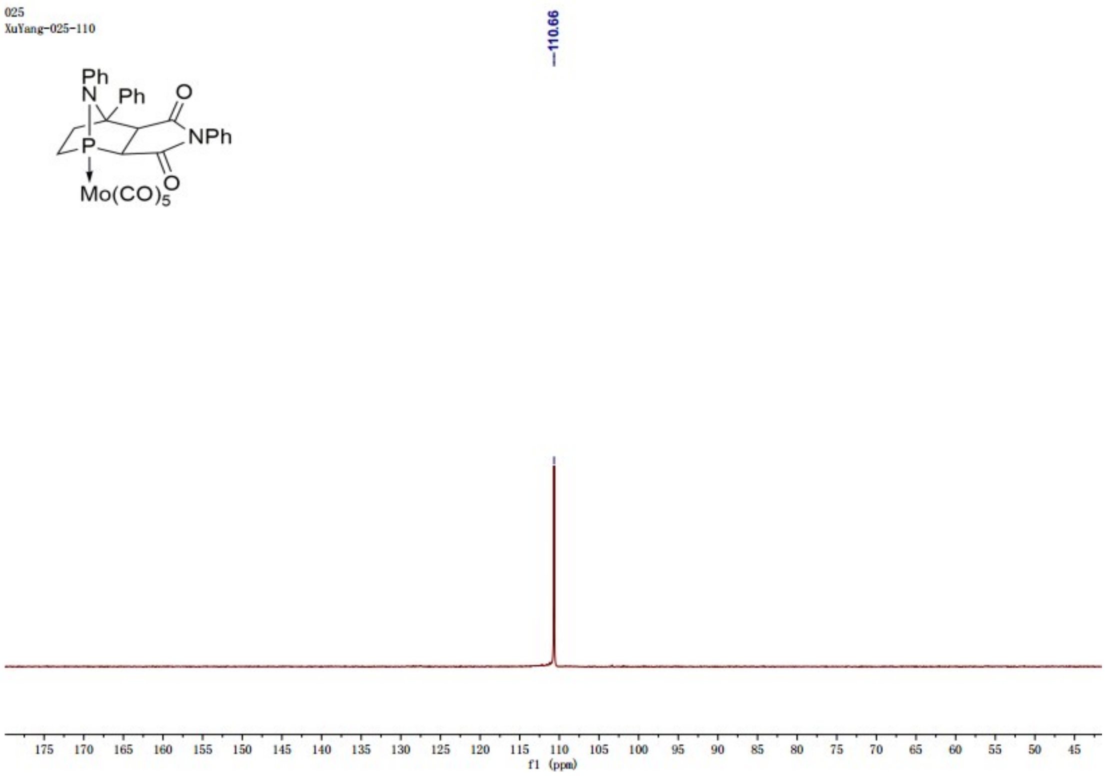

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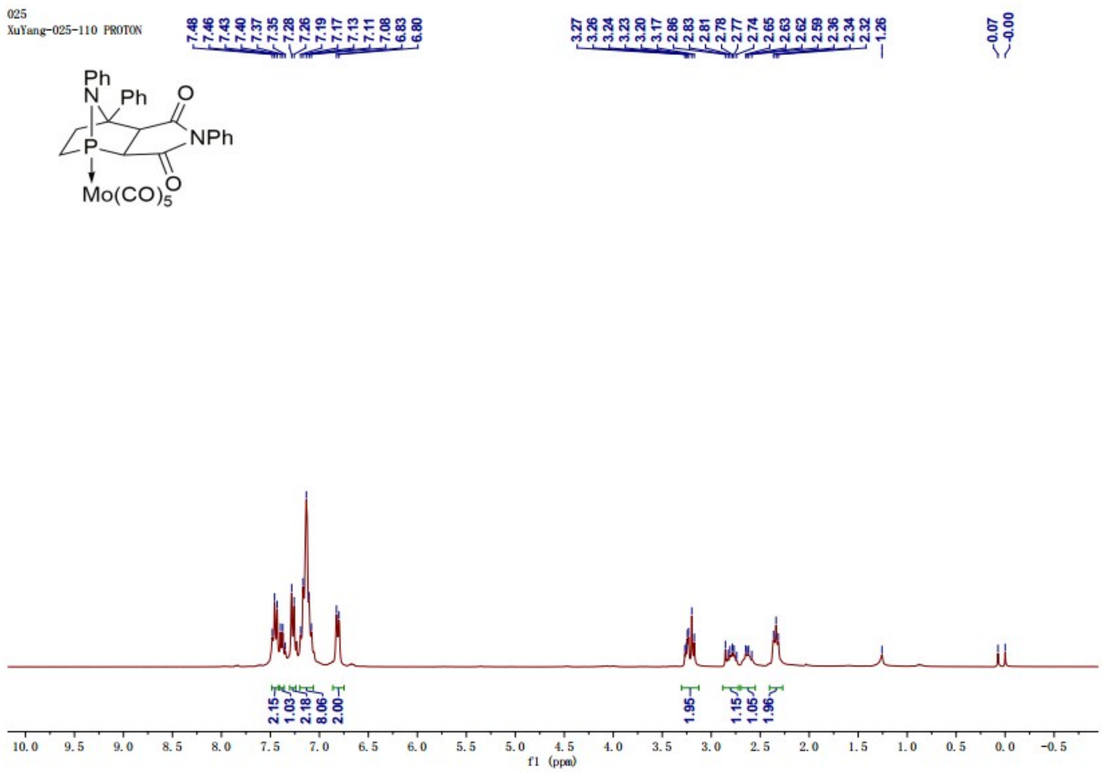

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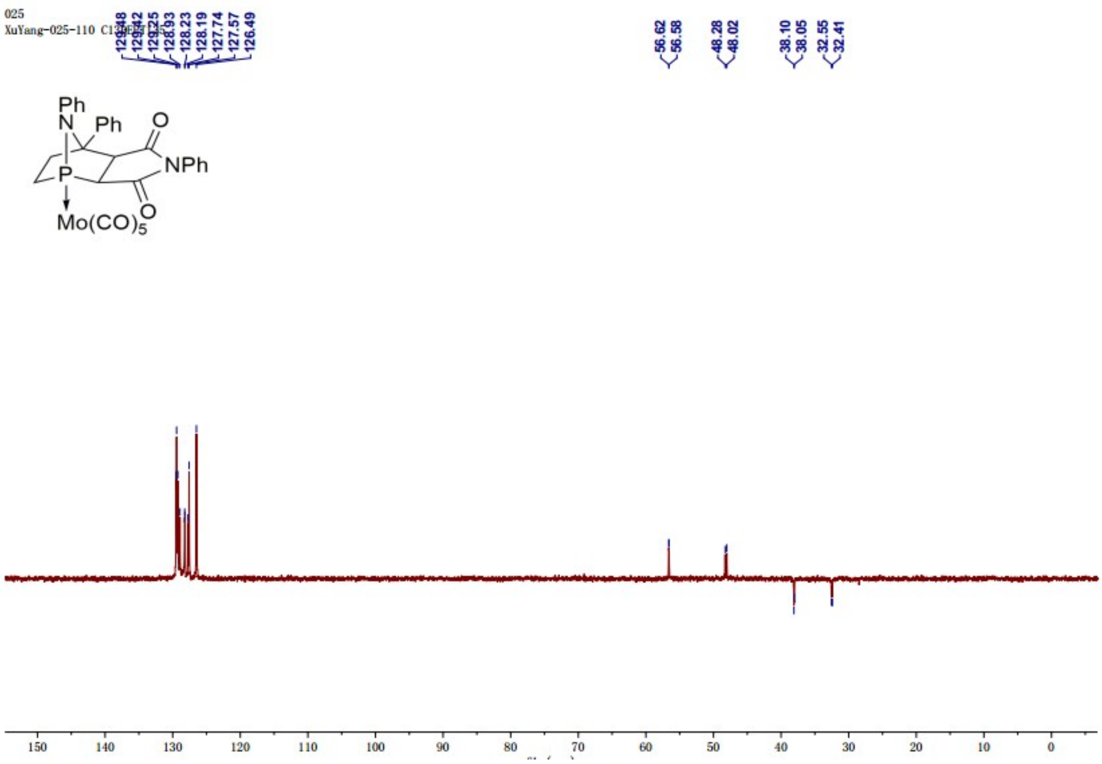

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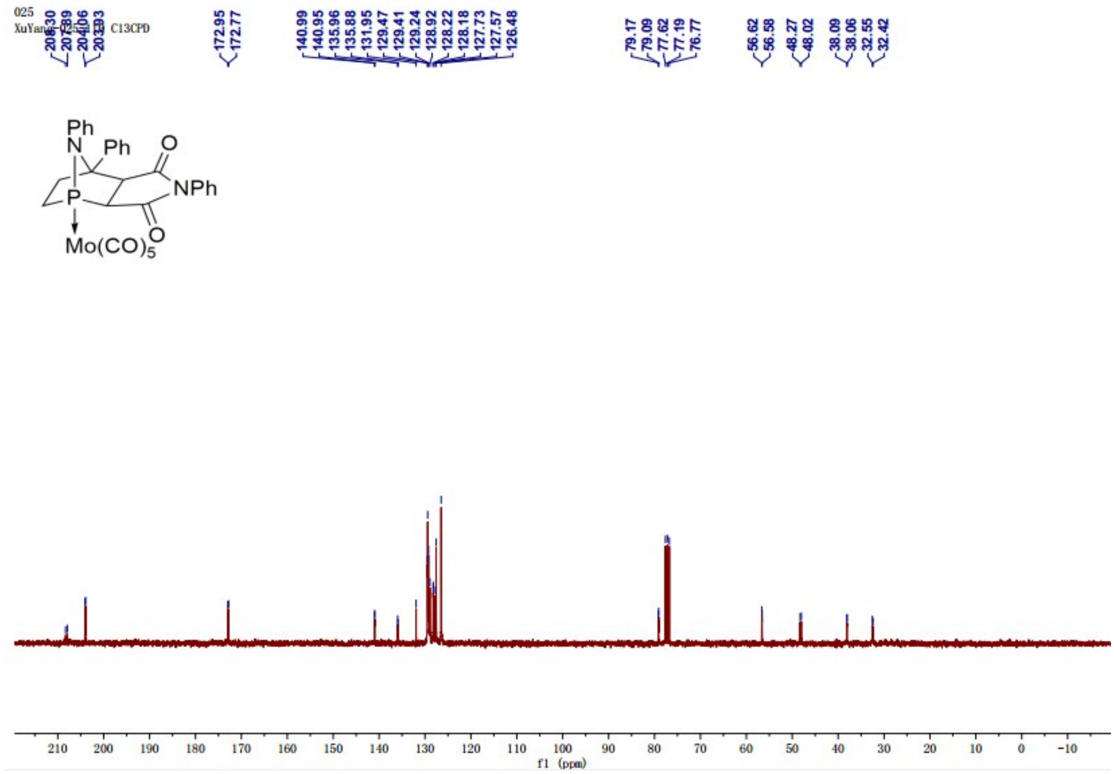

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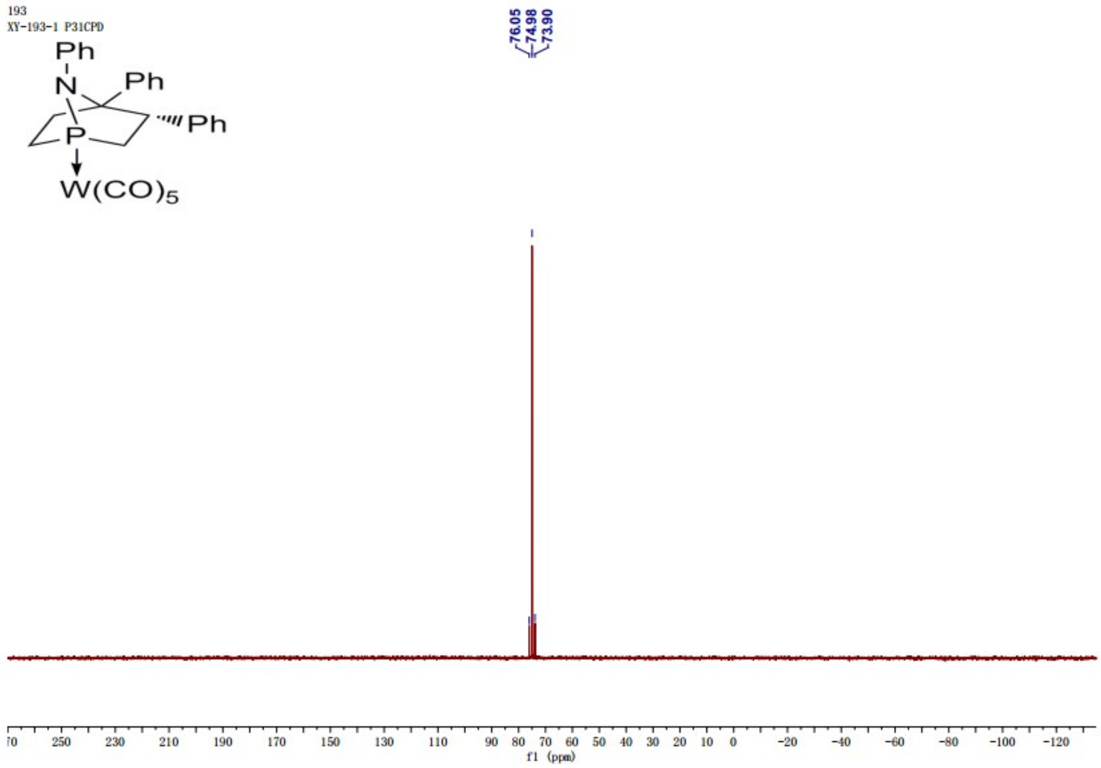
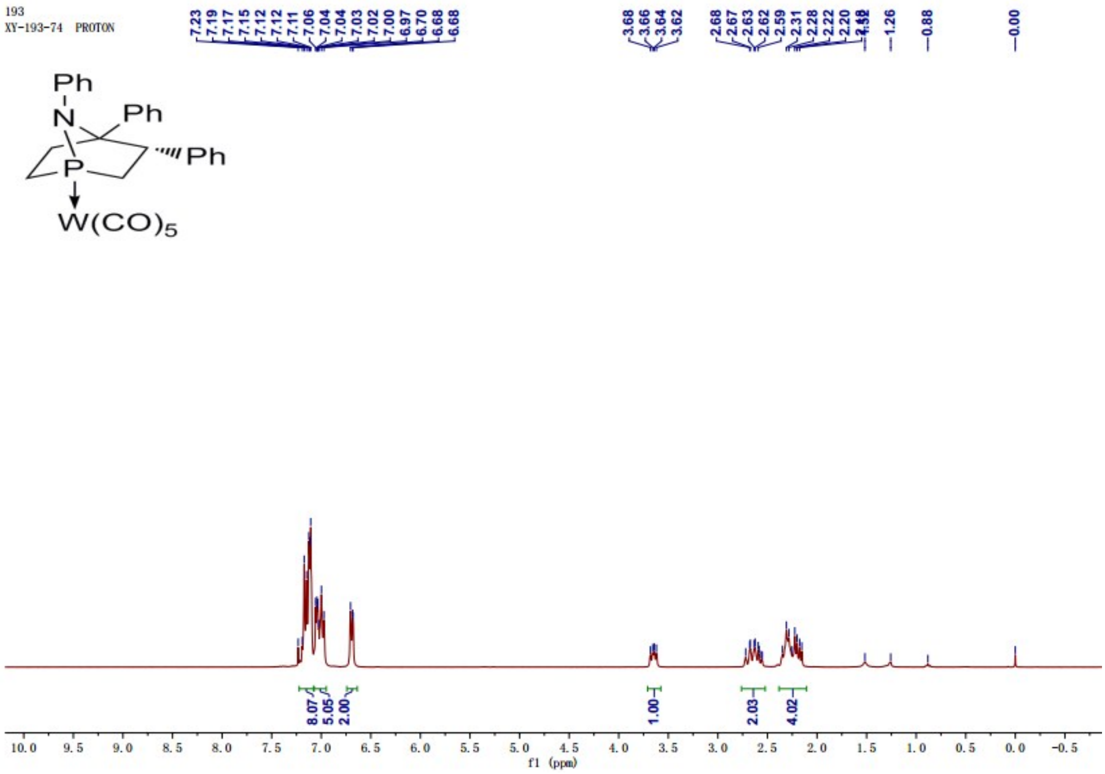


$^{31}P\{^{1}H\}$ NMR of Compound 10a



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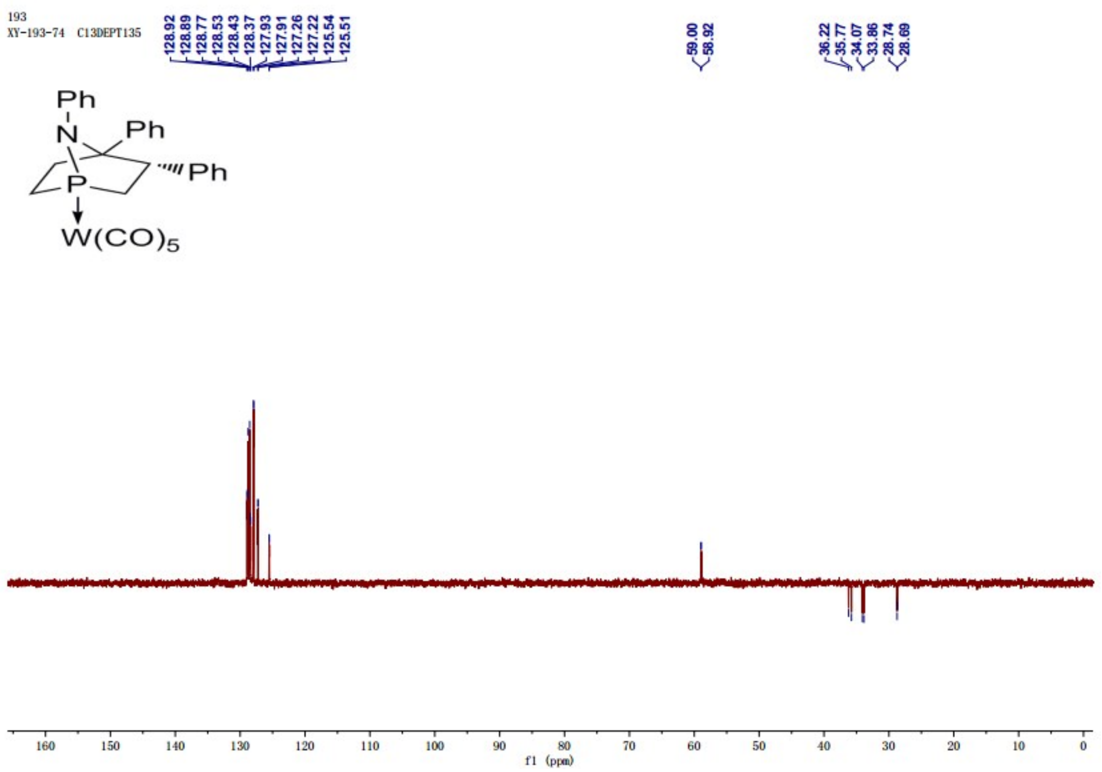

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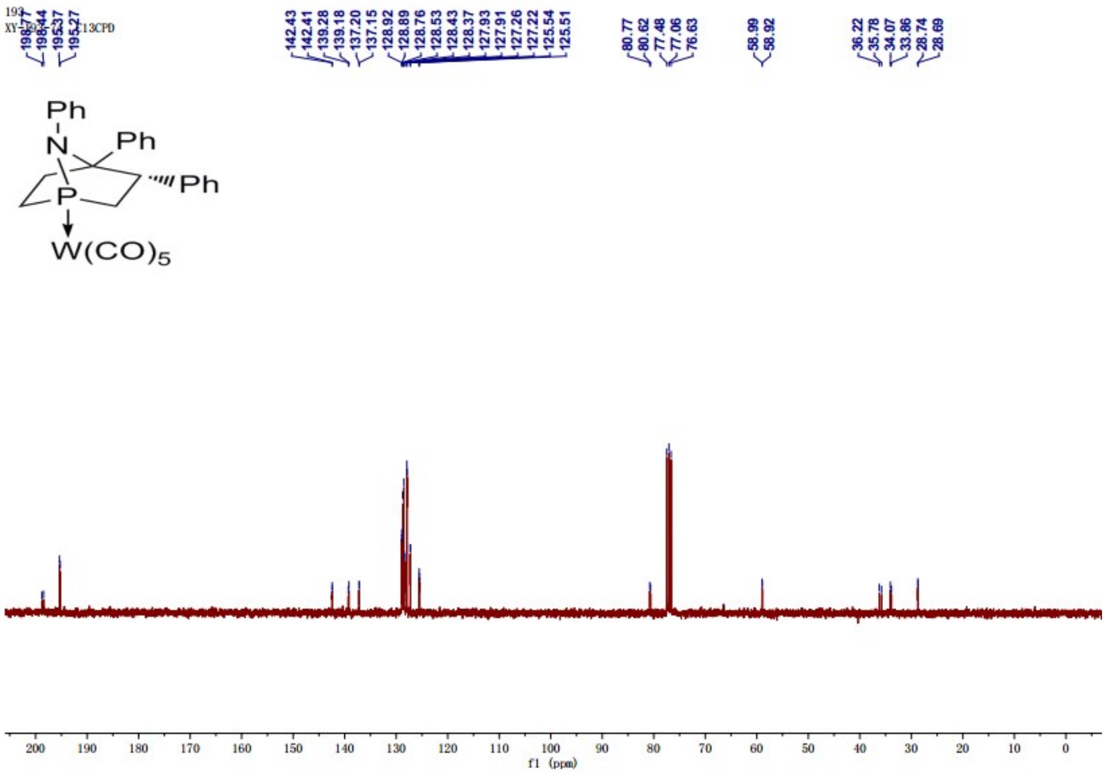

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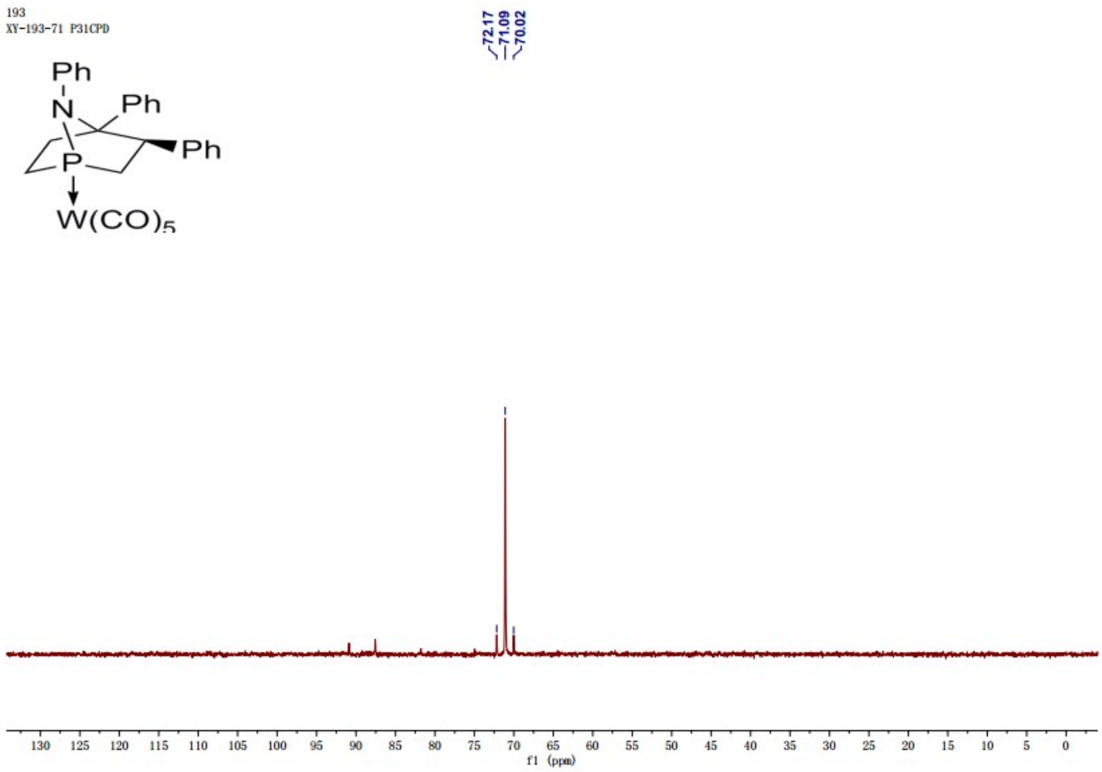

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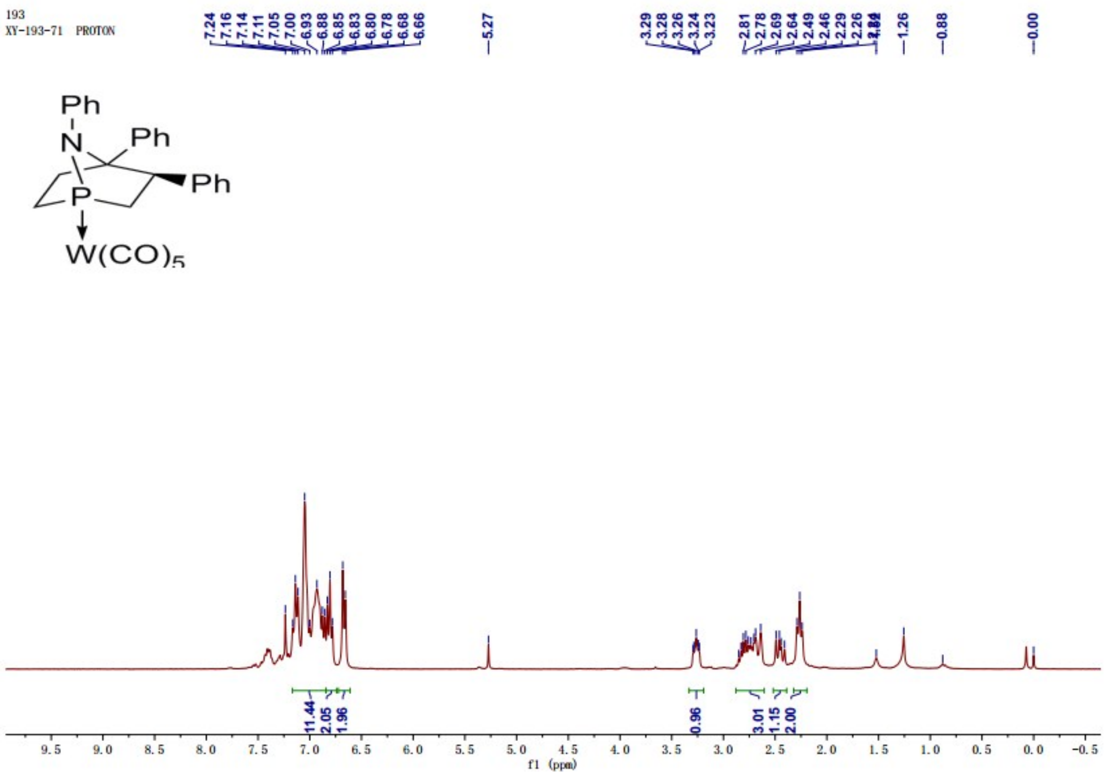

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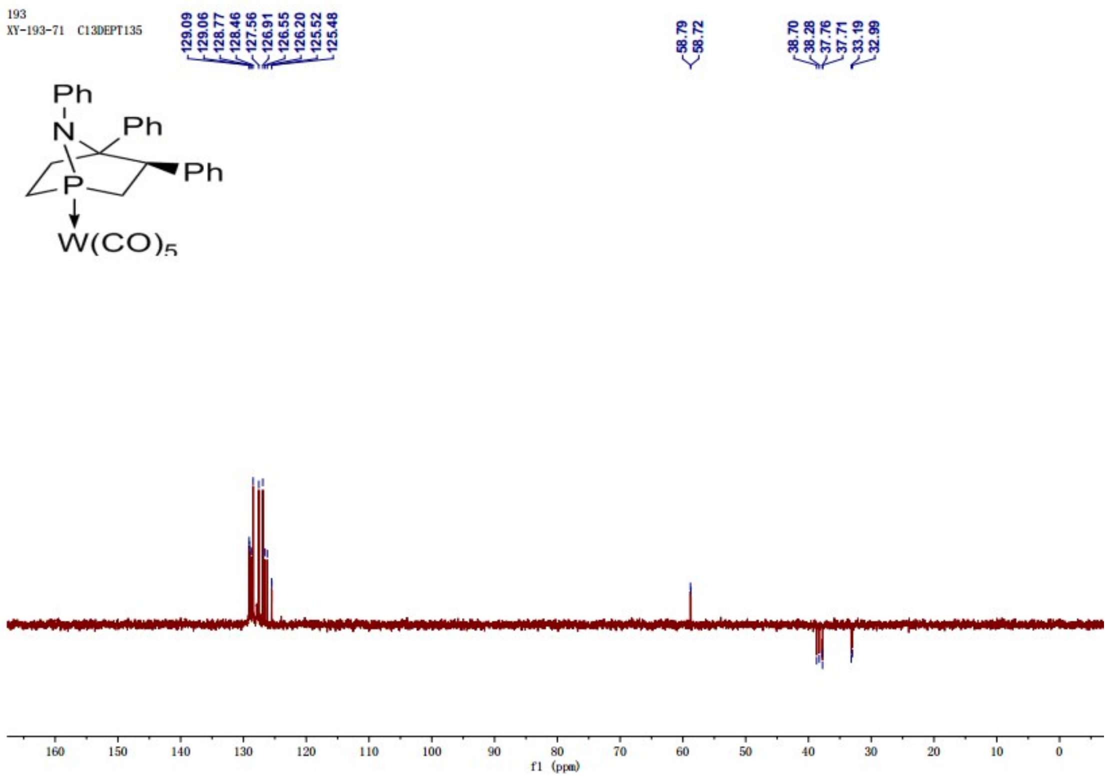

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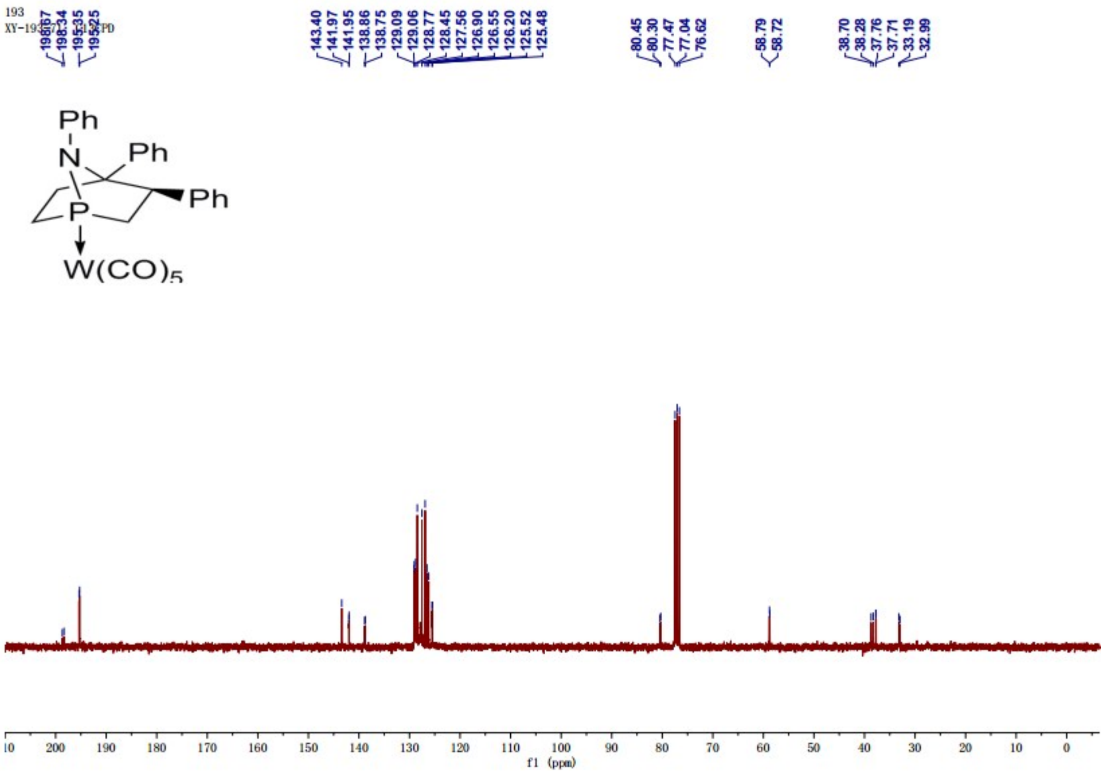

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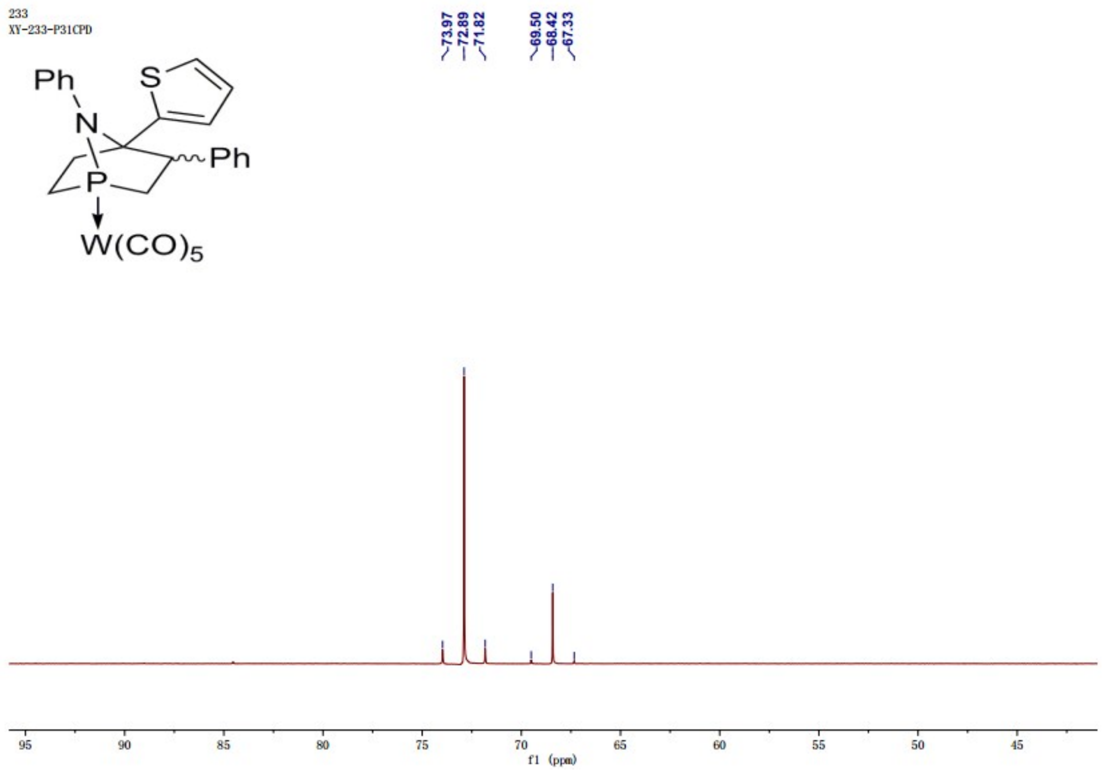
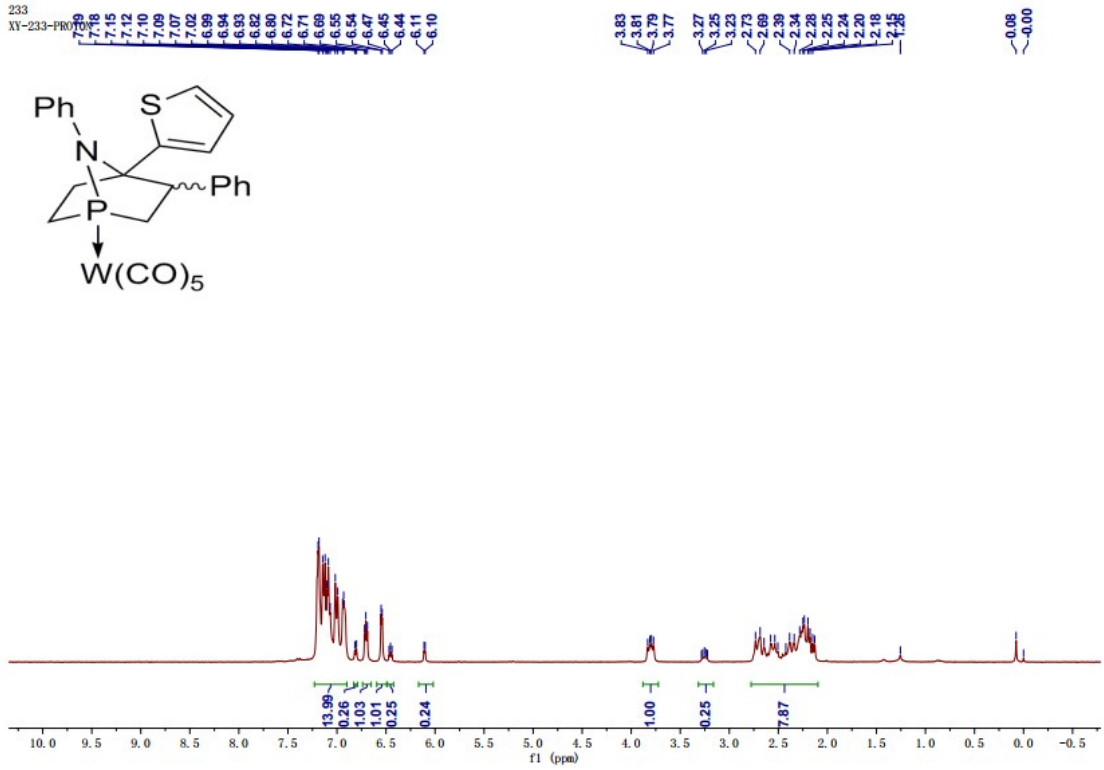


$^{31}P\{^{1}H\}$ NMR of Compound 11a,b



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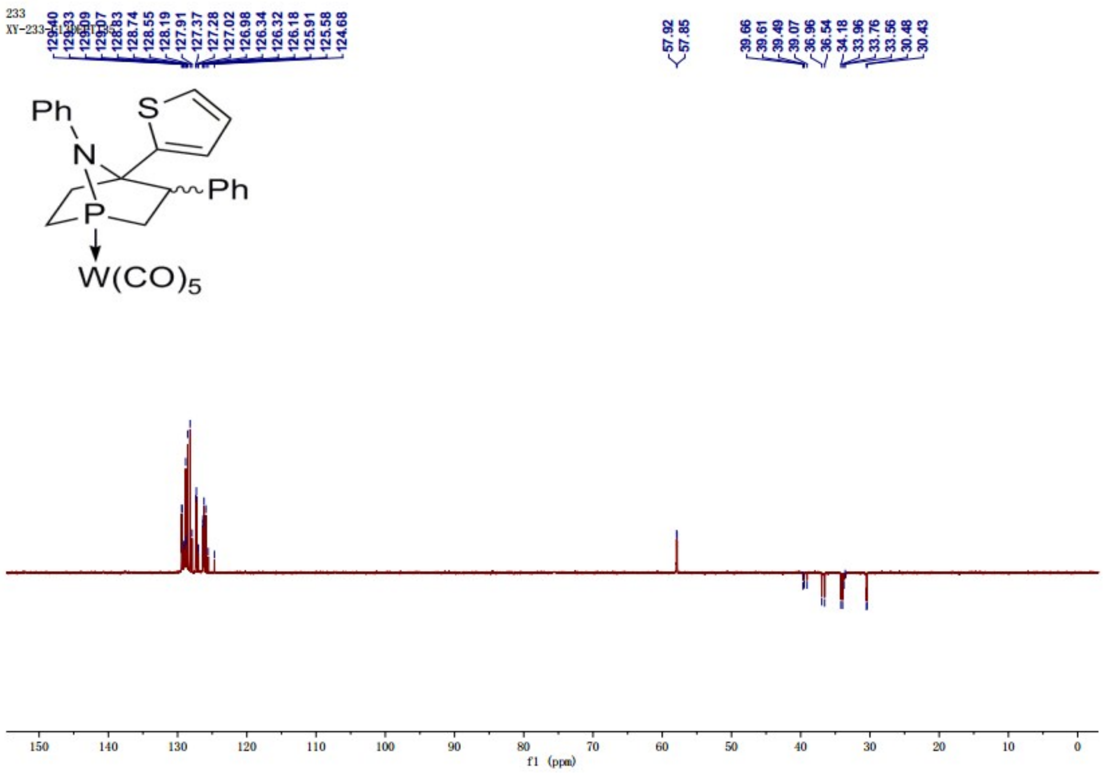
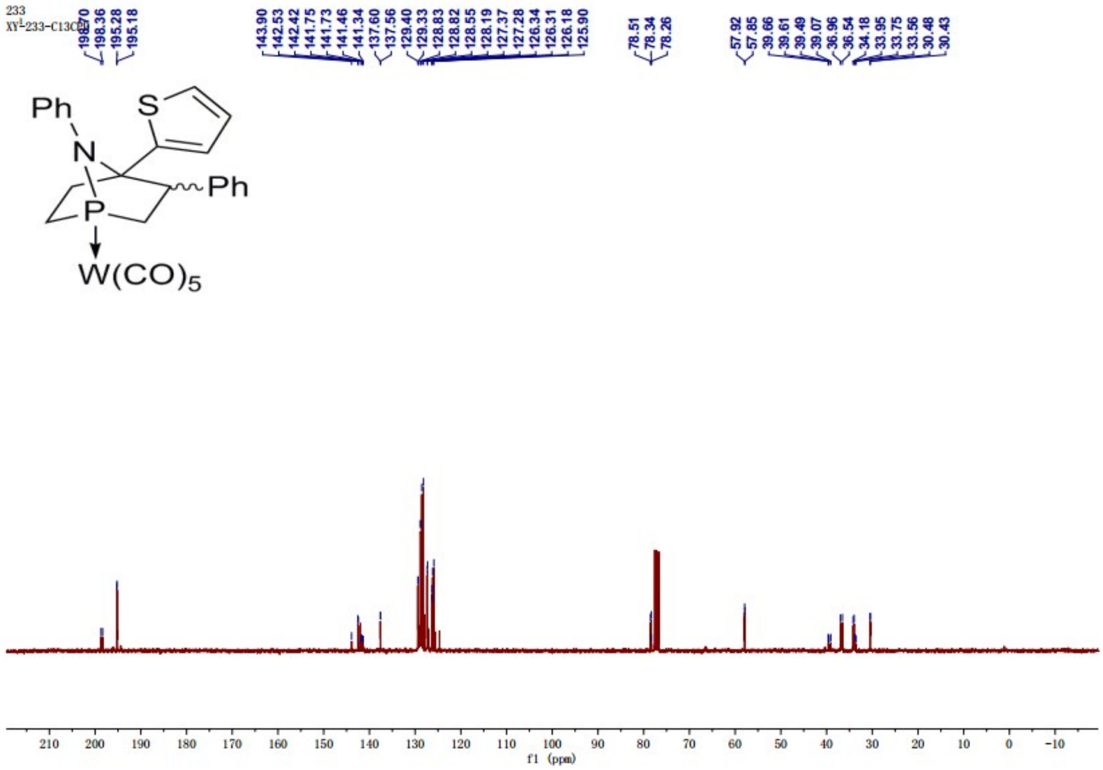
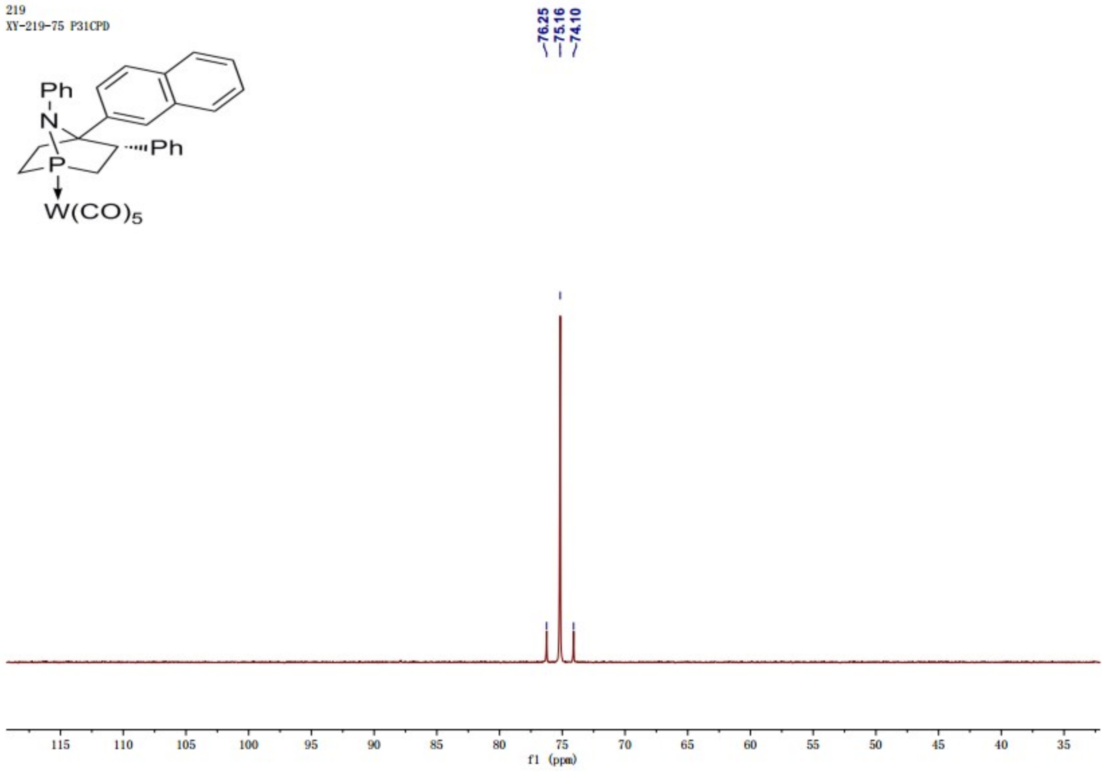


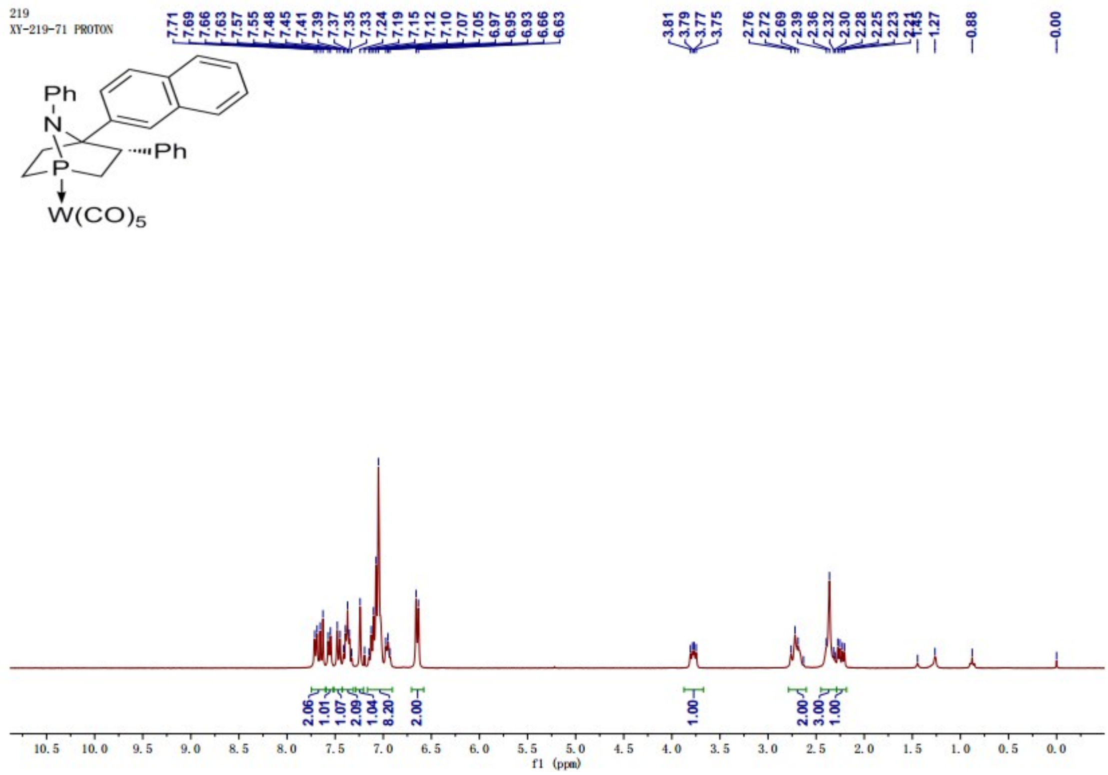
Dept135 NMR of Compound 11a,b



$^{13}C\{^{1}H\}$ NMR of Compound 11a,b



$^{31}P\{^{1}H\}$ NMR of Compound 12a



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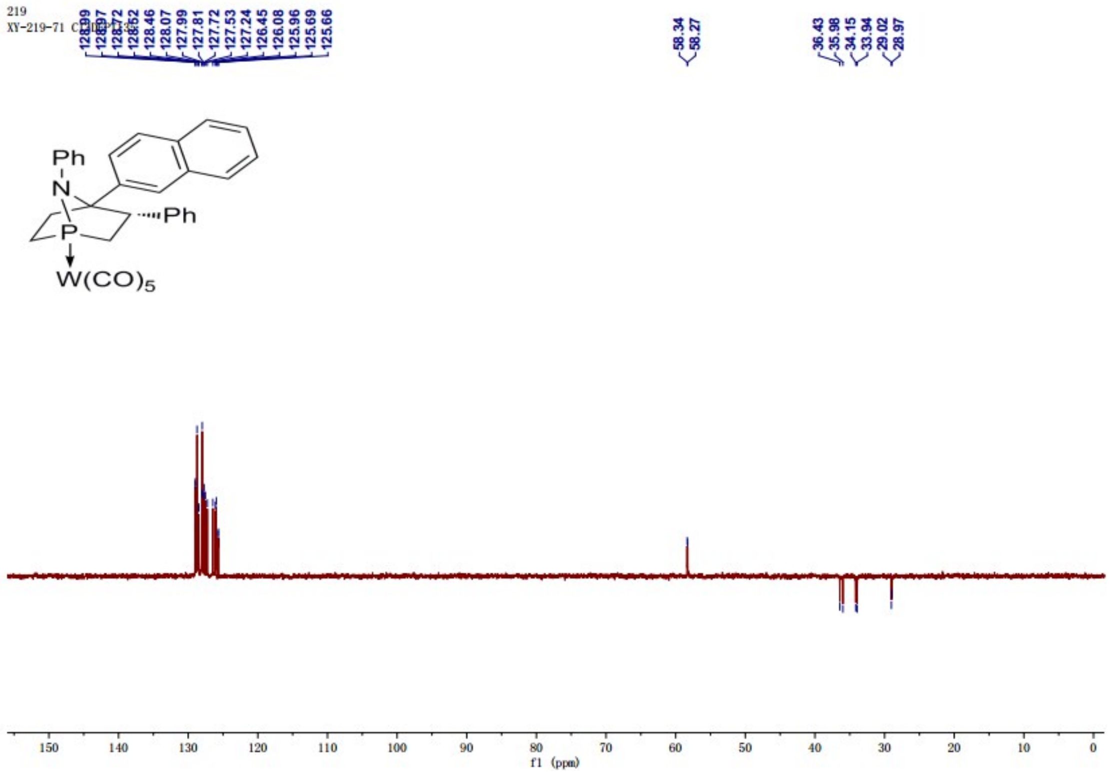

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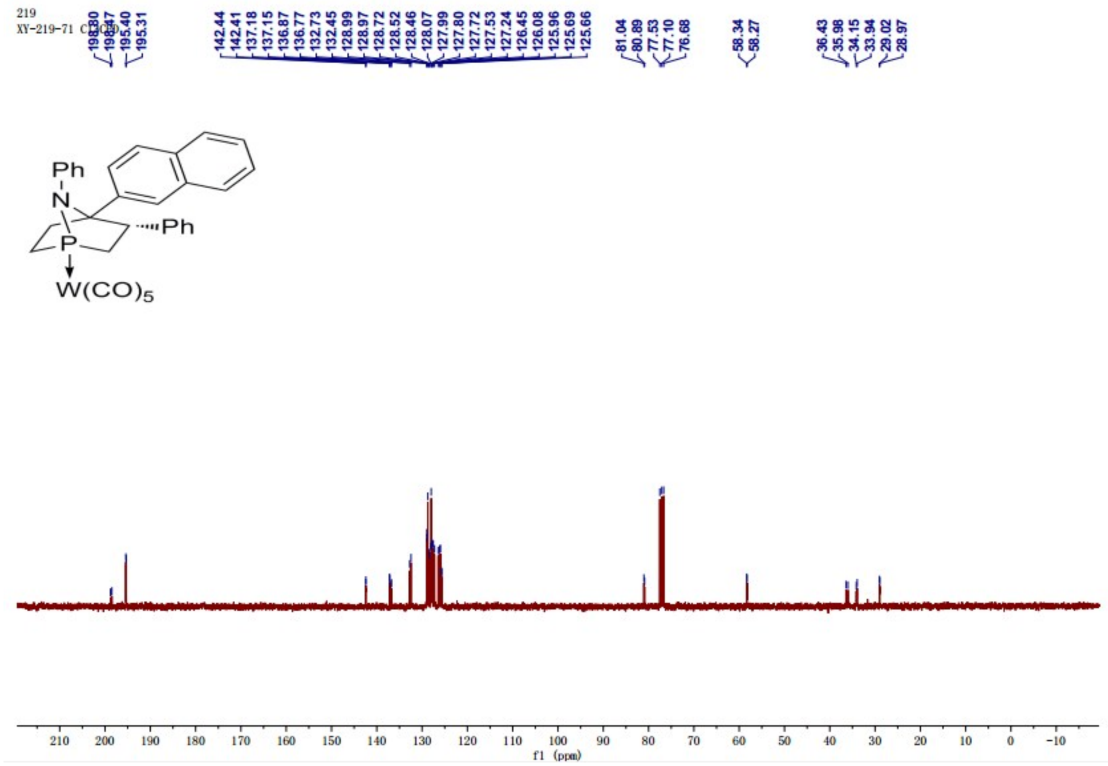

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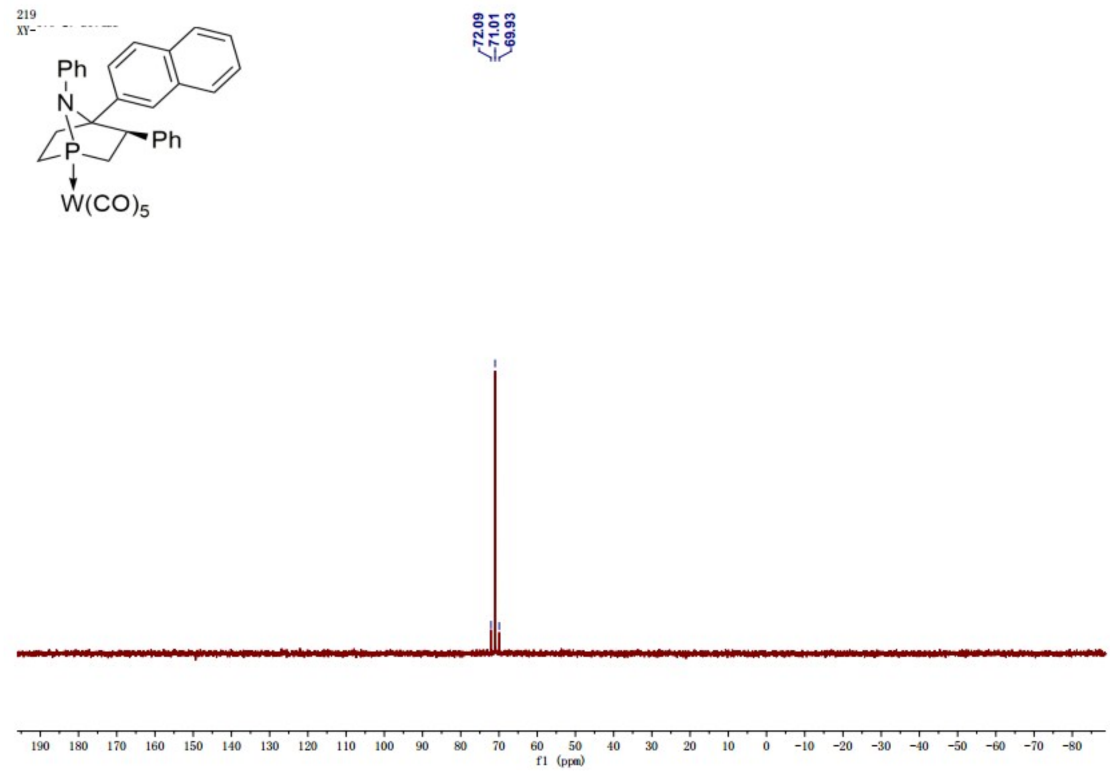

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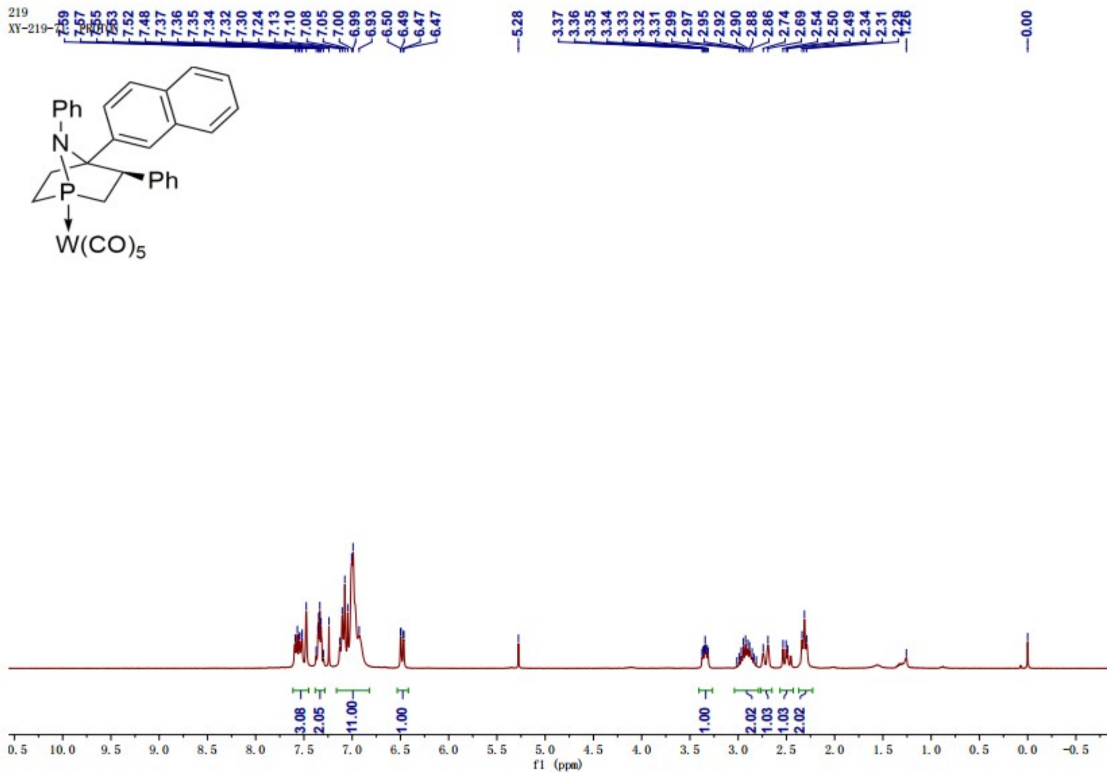

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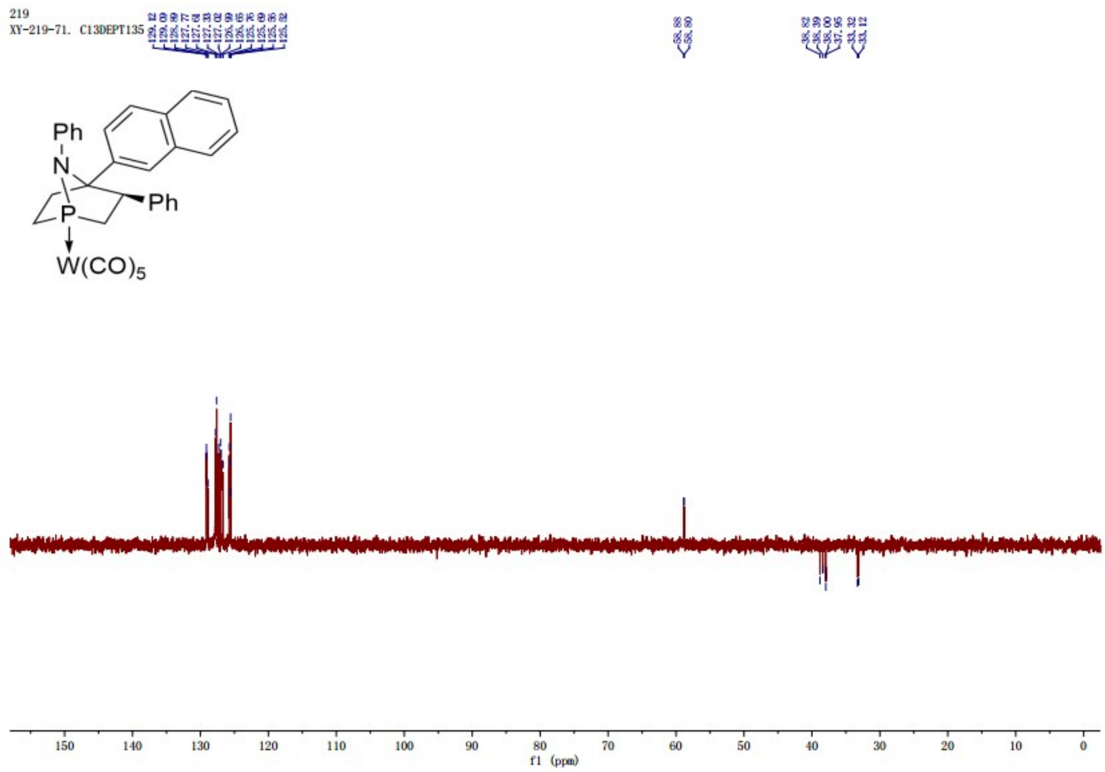

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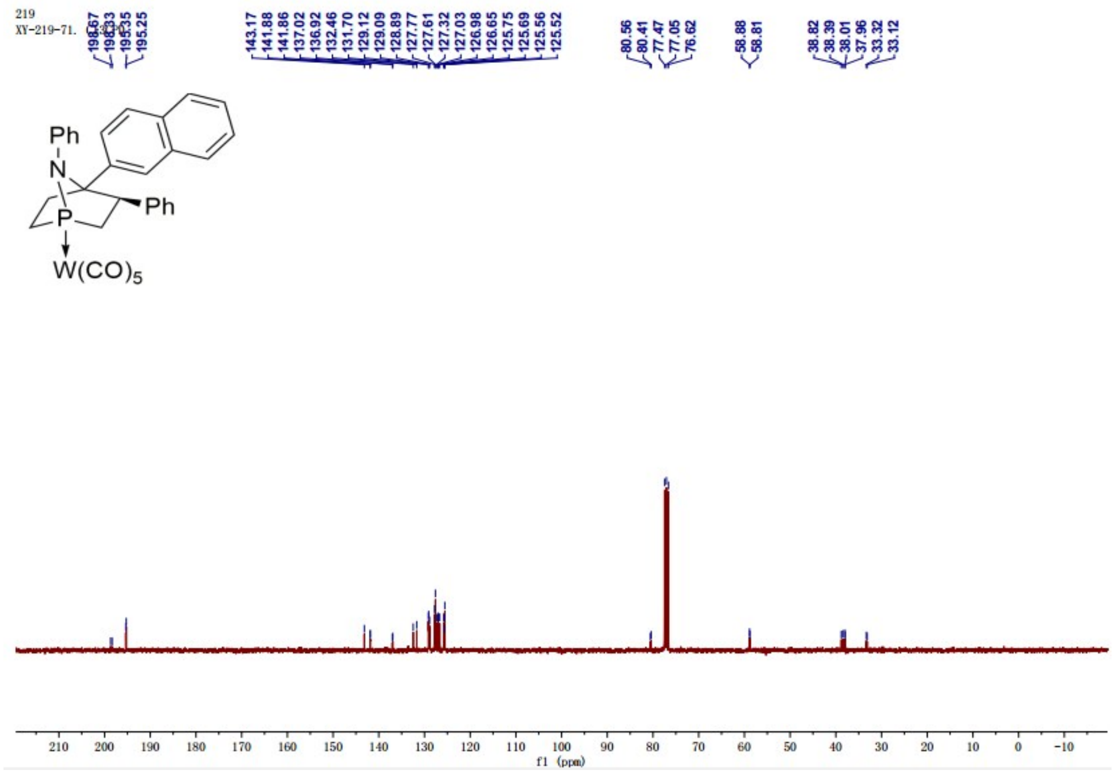

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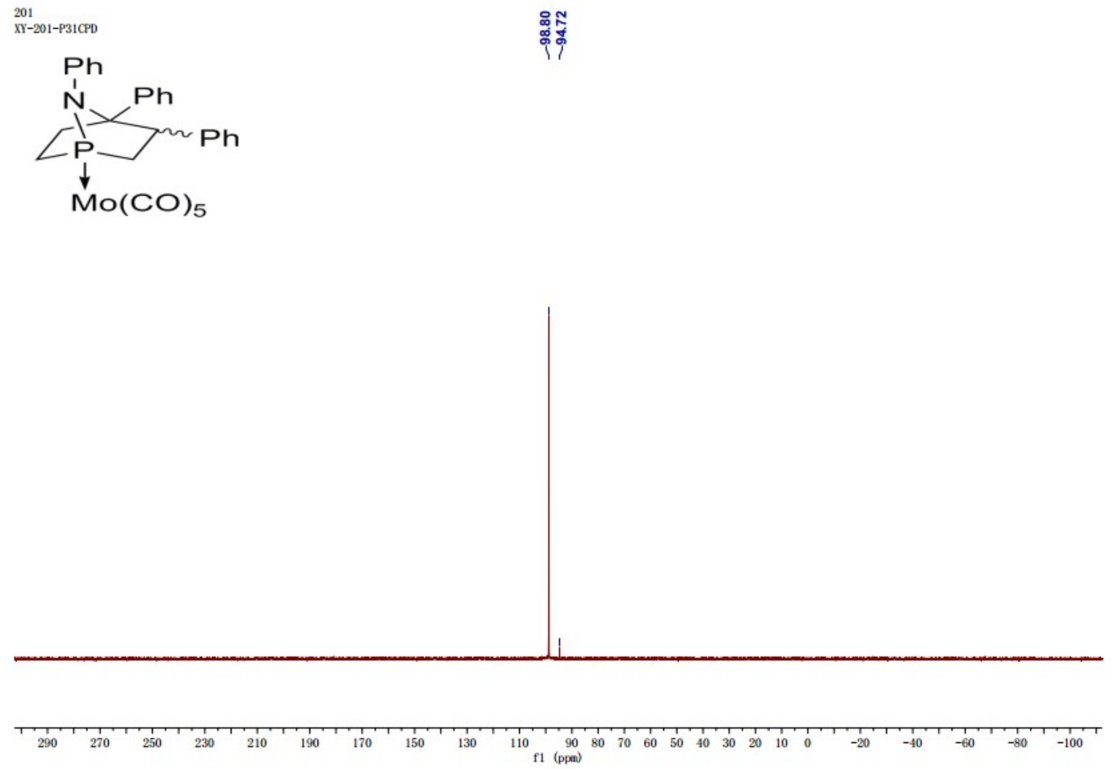

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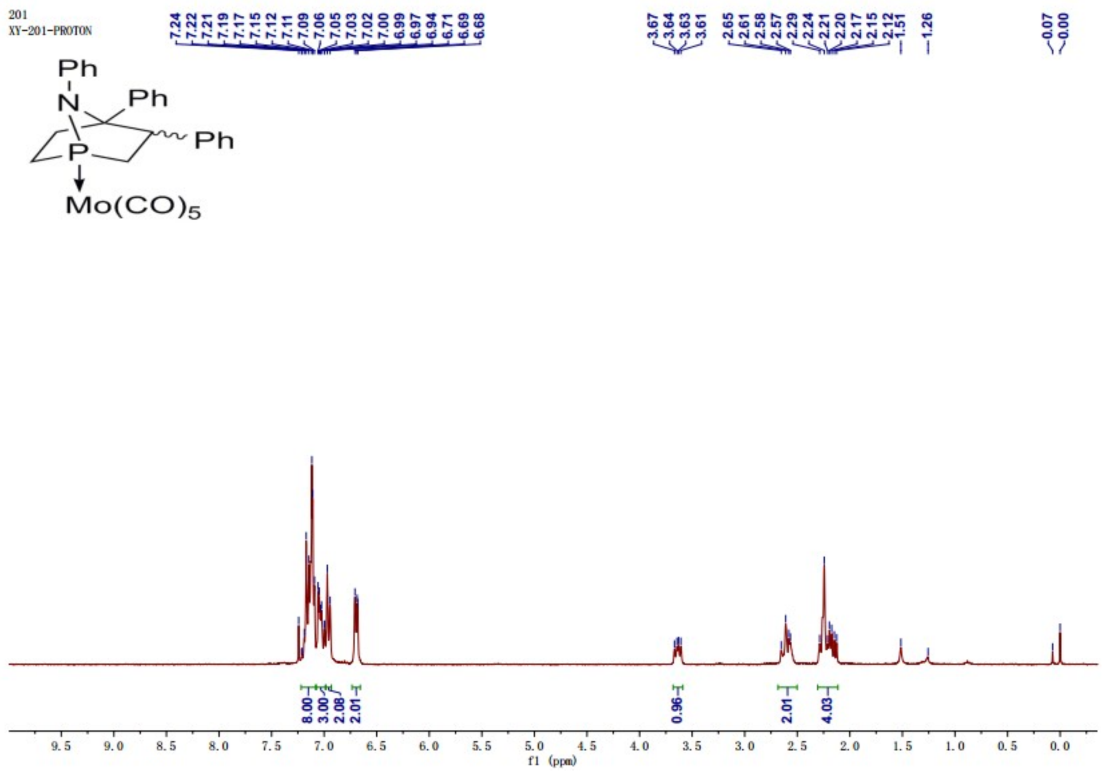
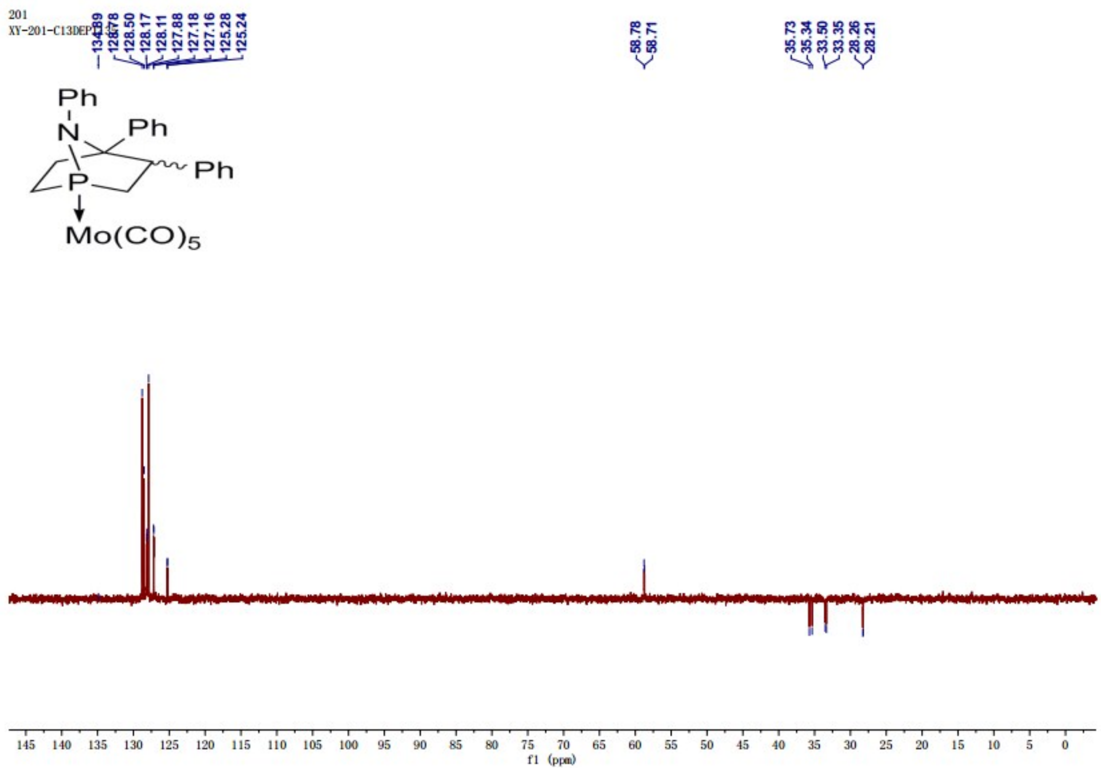


^{1}H NMR of Compound 13a,b



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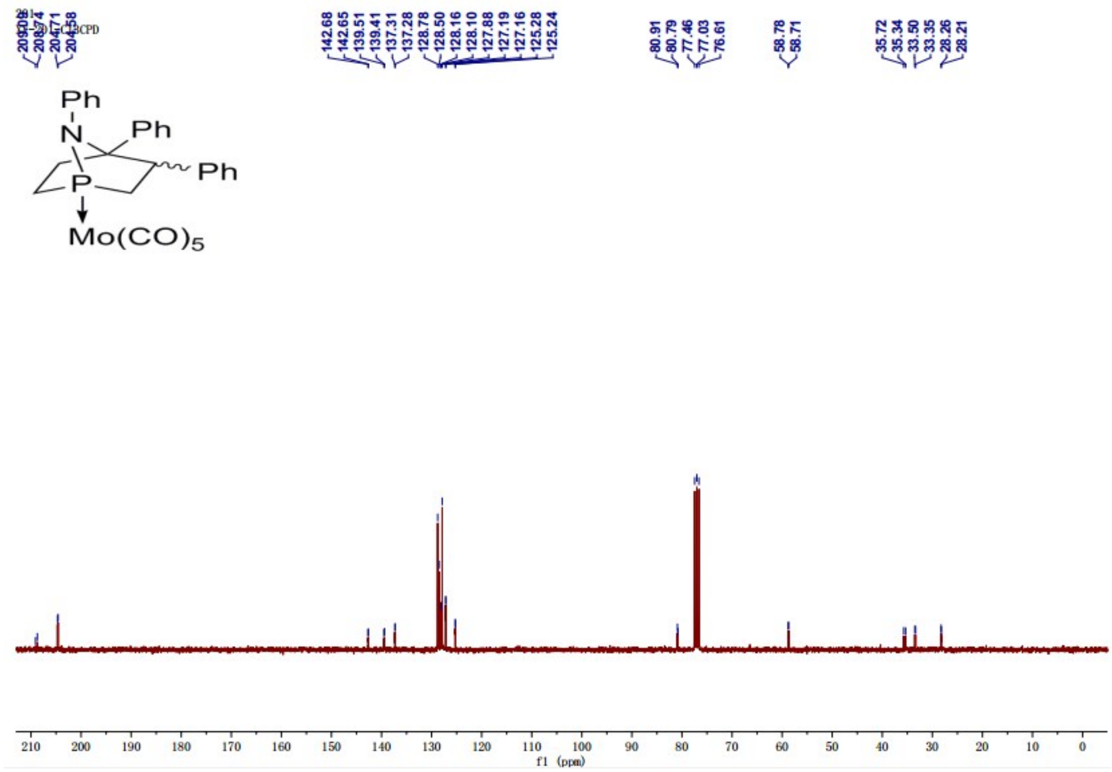

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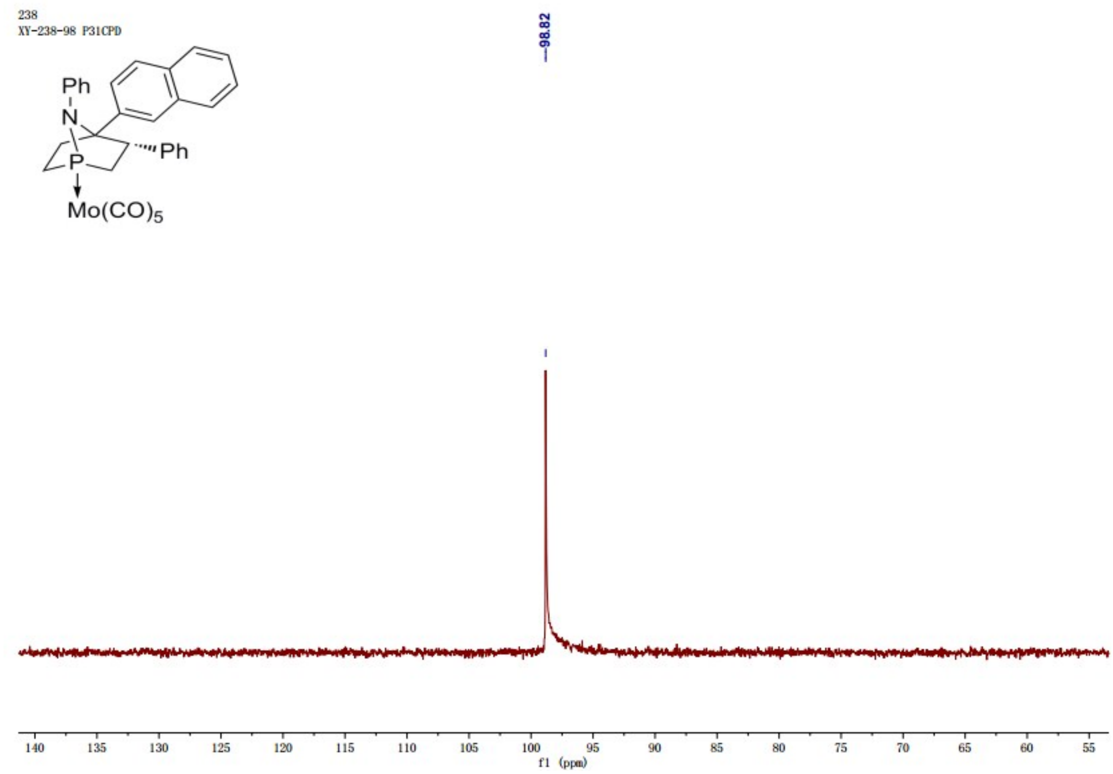
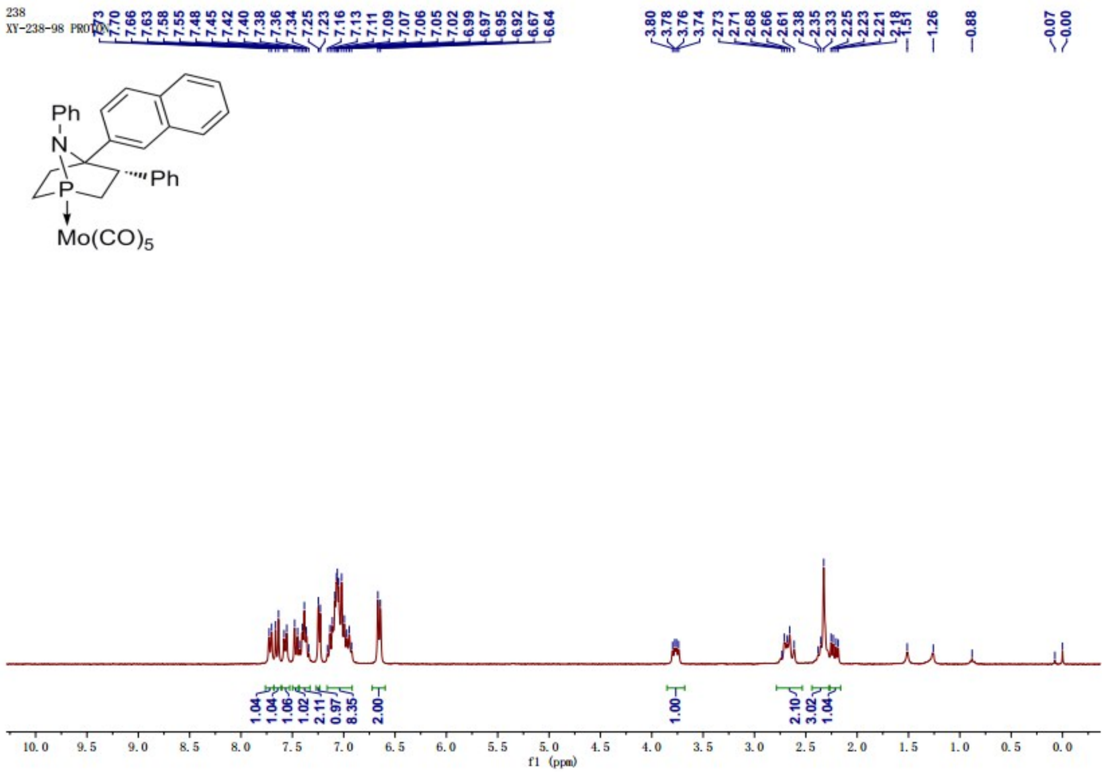


$^{31}P\{^{1}H\}$ NMR of Compound 14a



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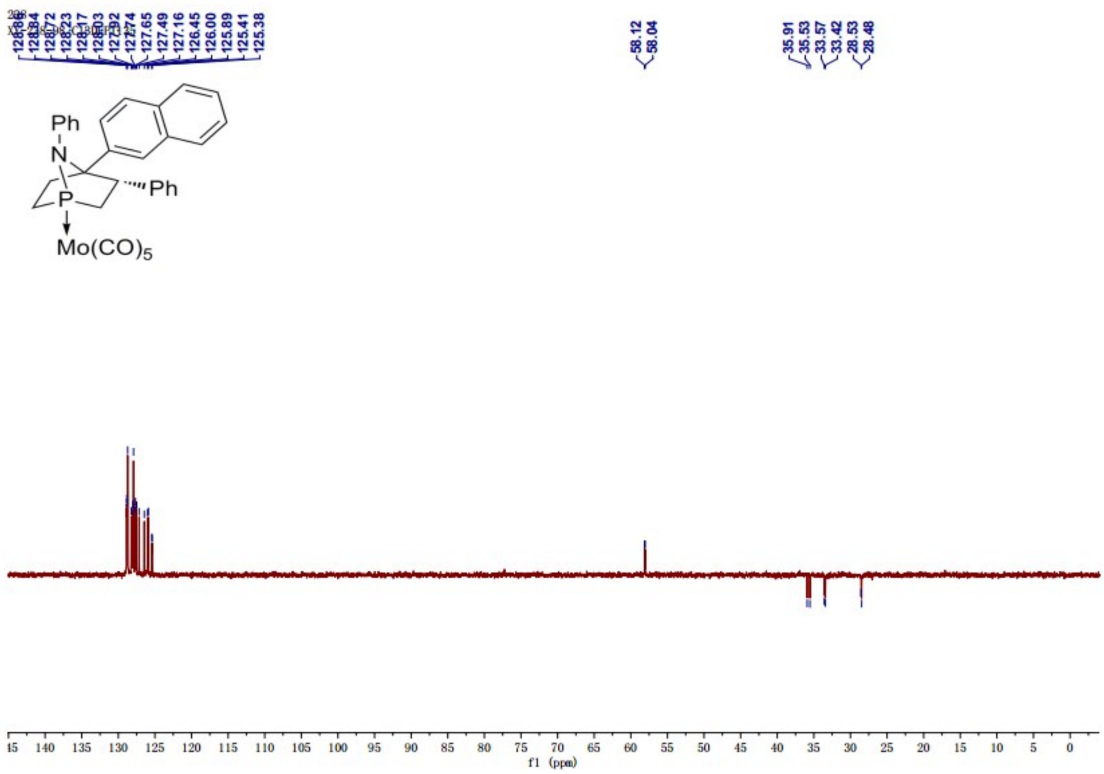

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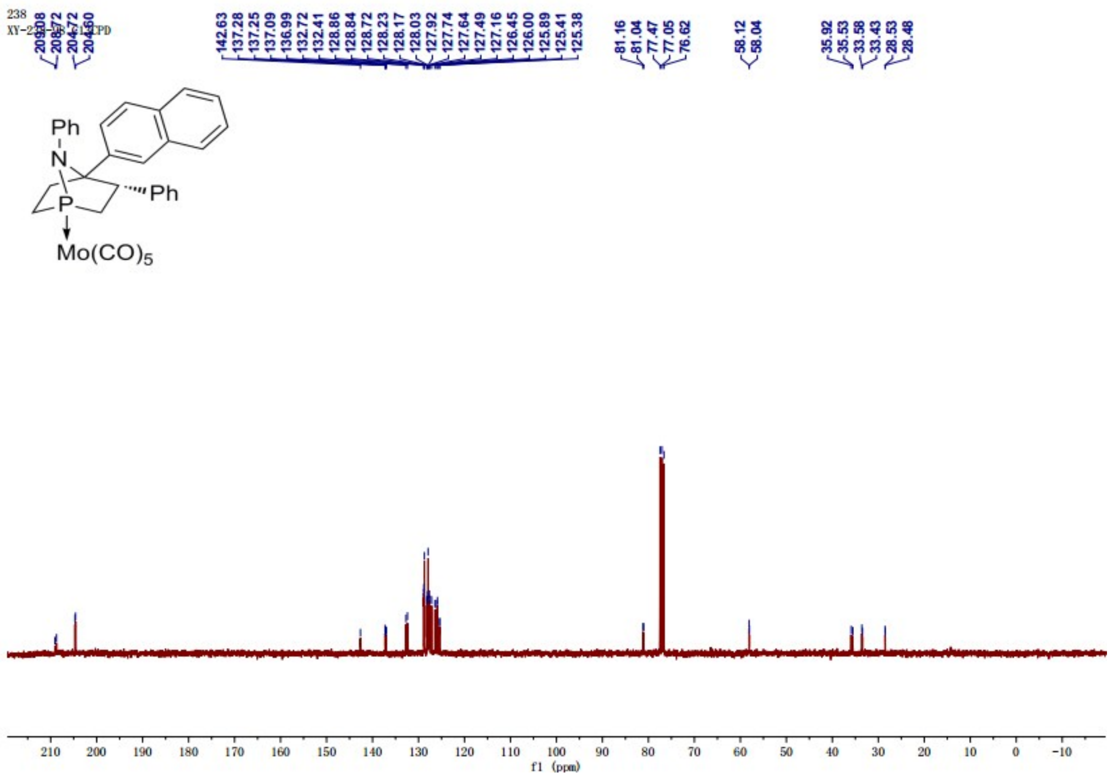
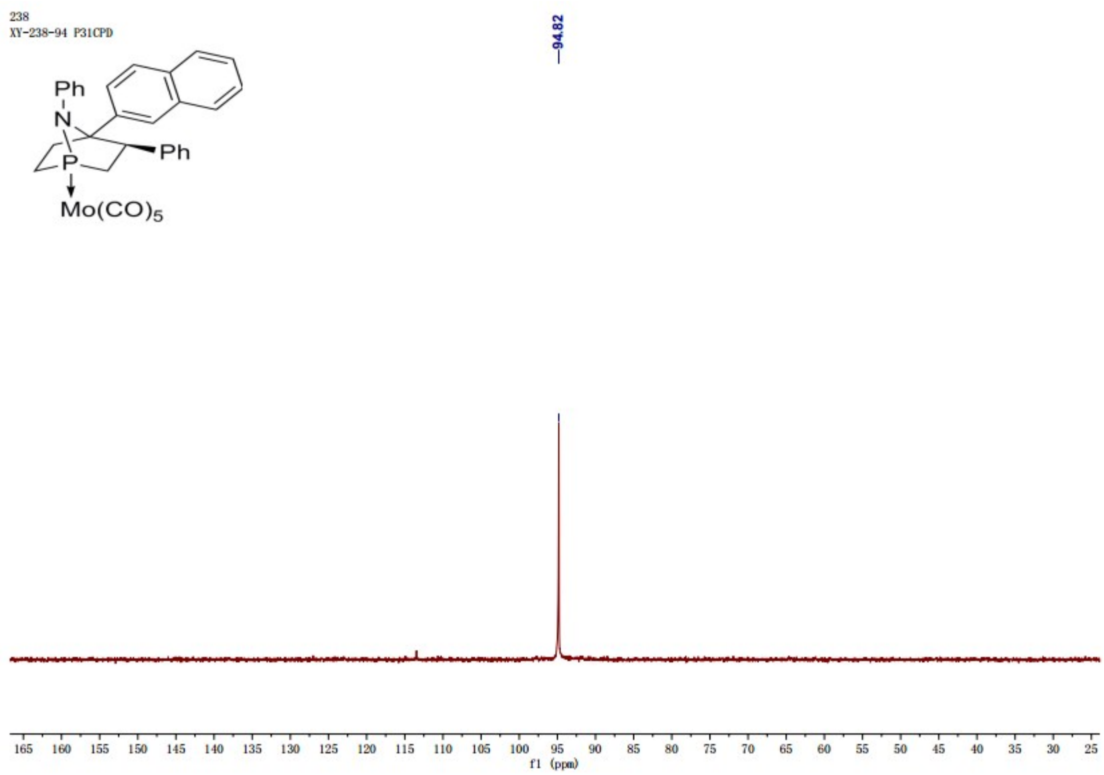
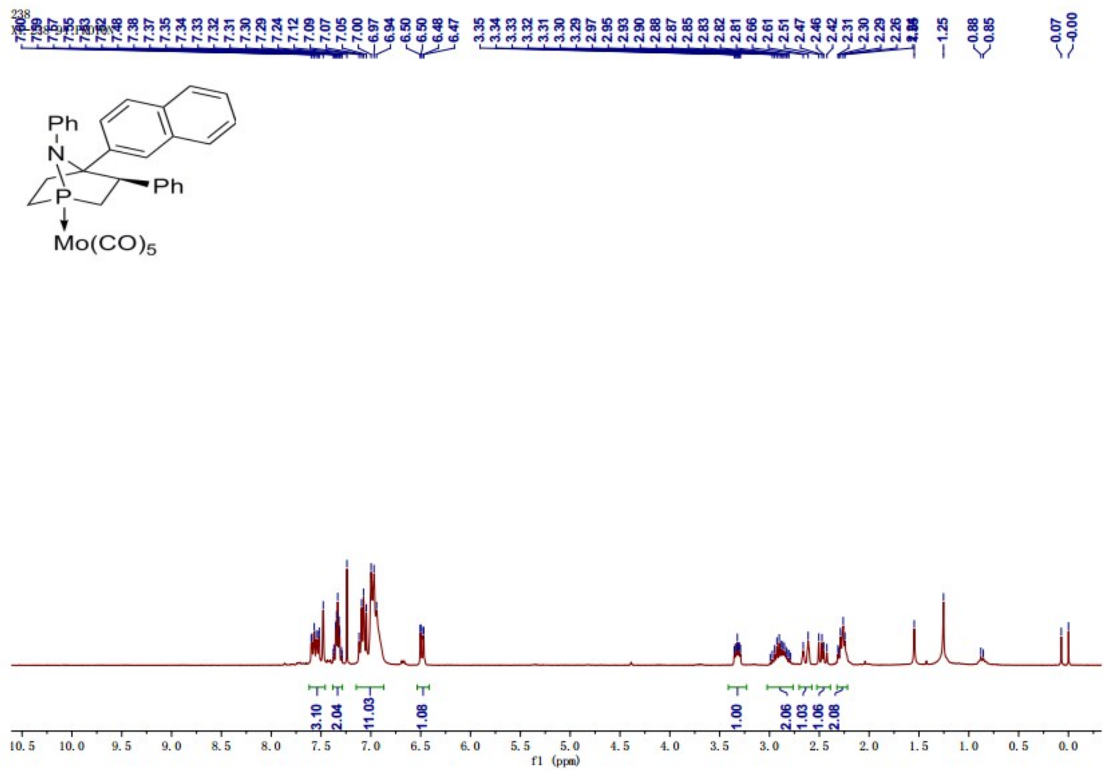


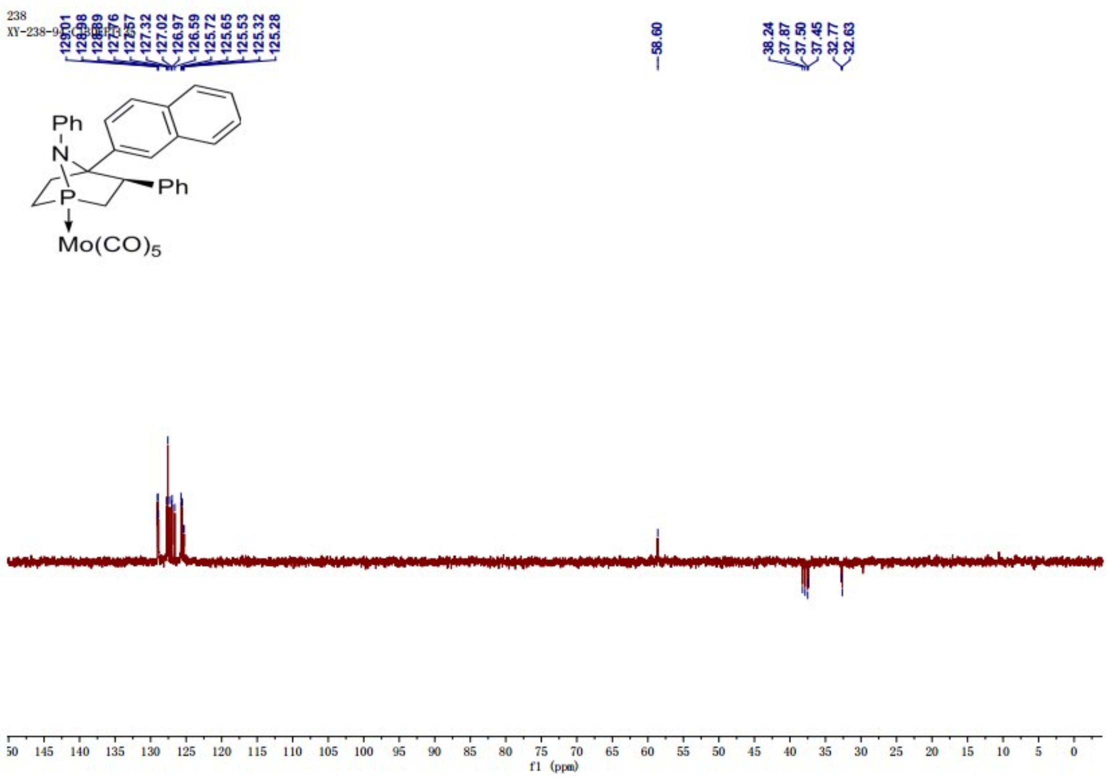
$^{13}C\{^{1}H\}$ NMR of Compound 14a



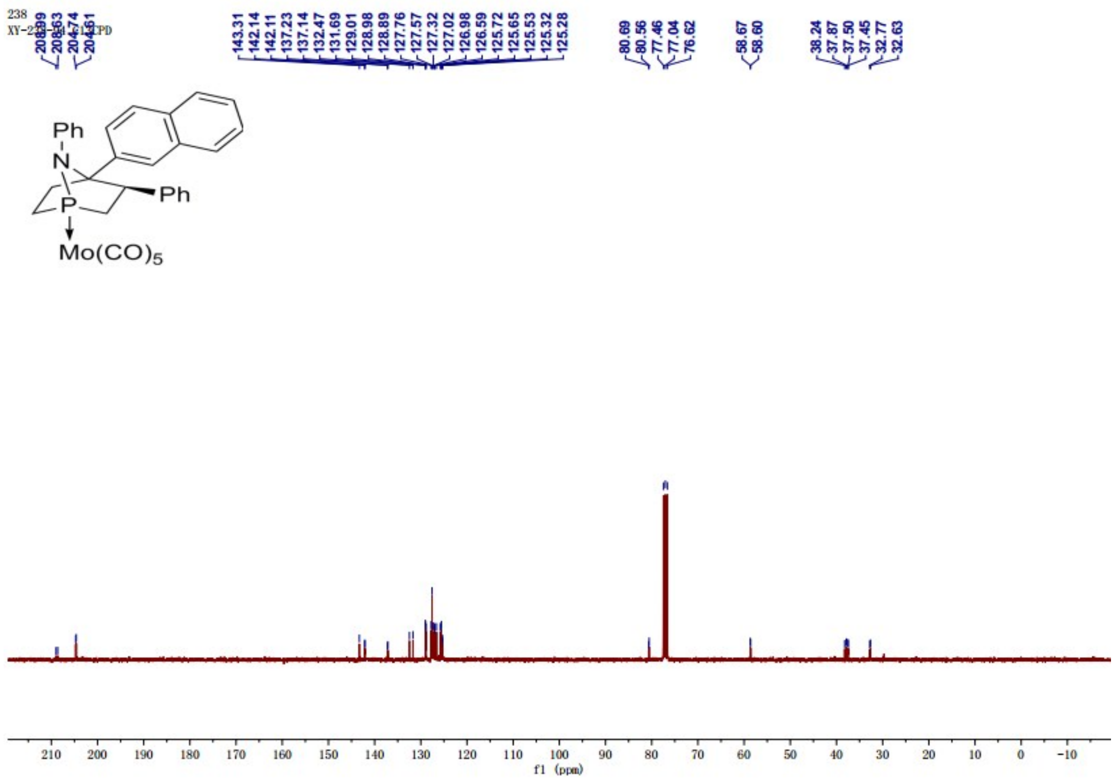
$^{31}P\{^{1}H\}$ NMR of Compound 14b



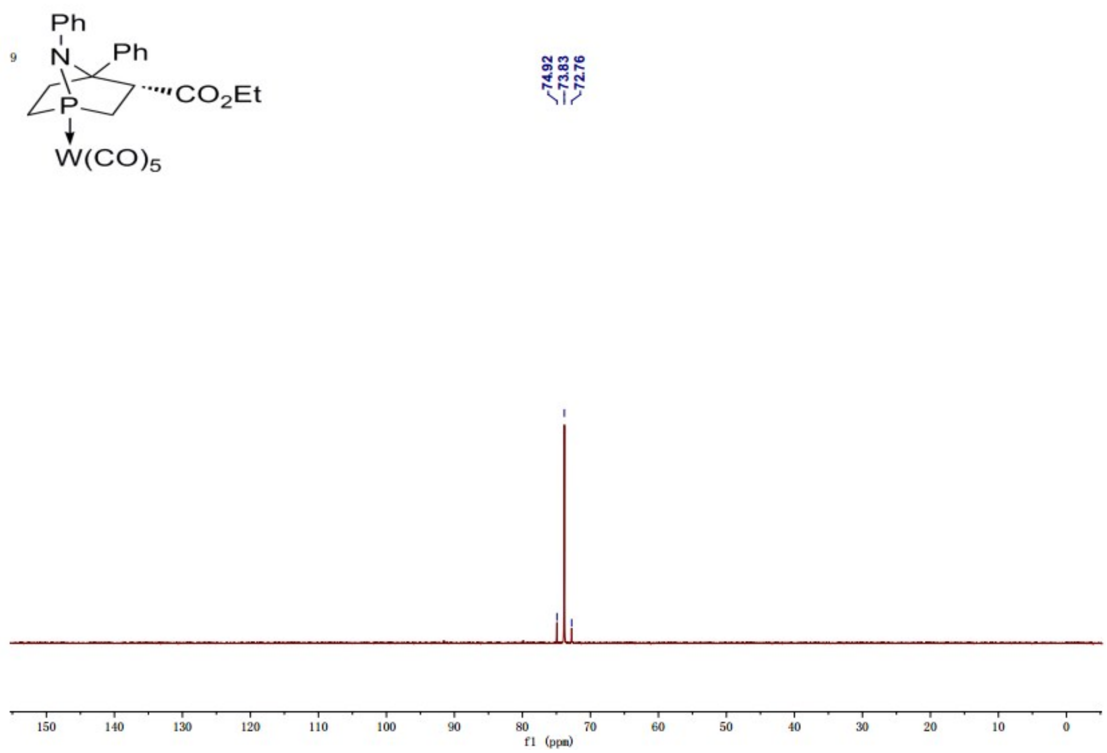
^{1}H NMR of Compound 14b



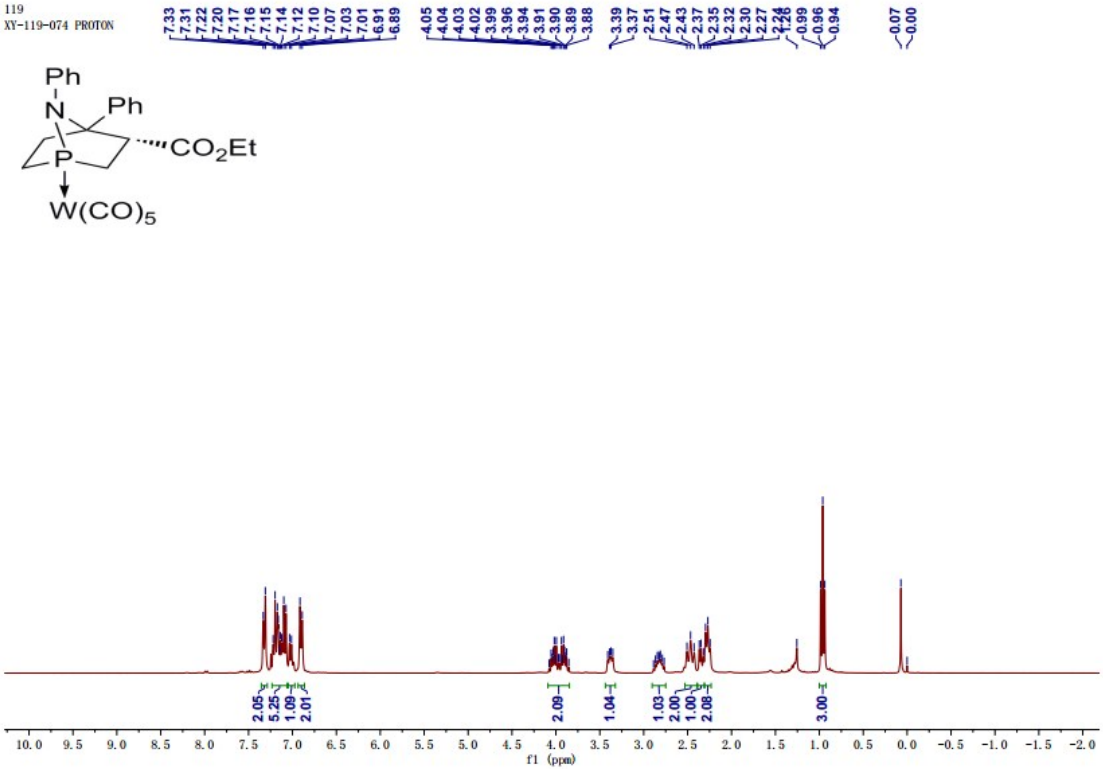
Dept135 NMR of Compound 14b



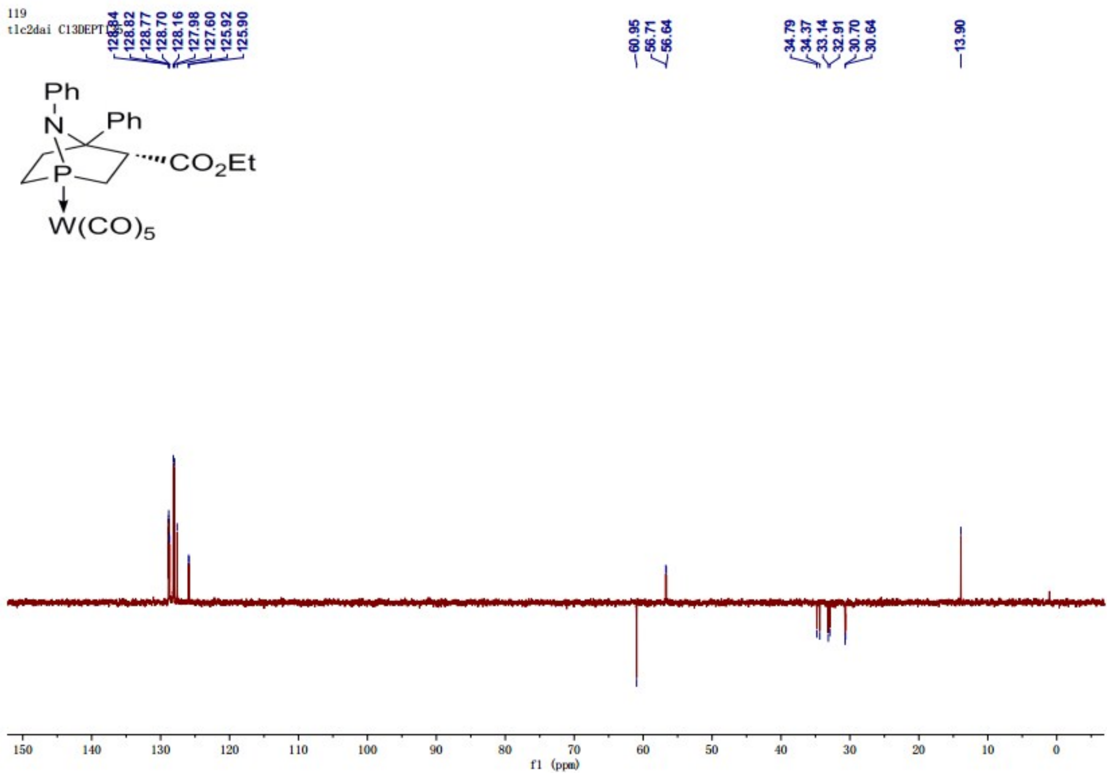
$^{13}C\{^1H\}$ NMR of Compound 14b



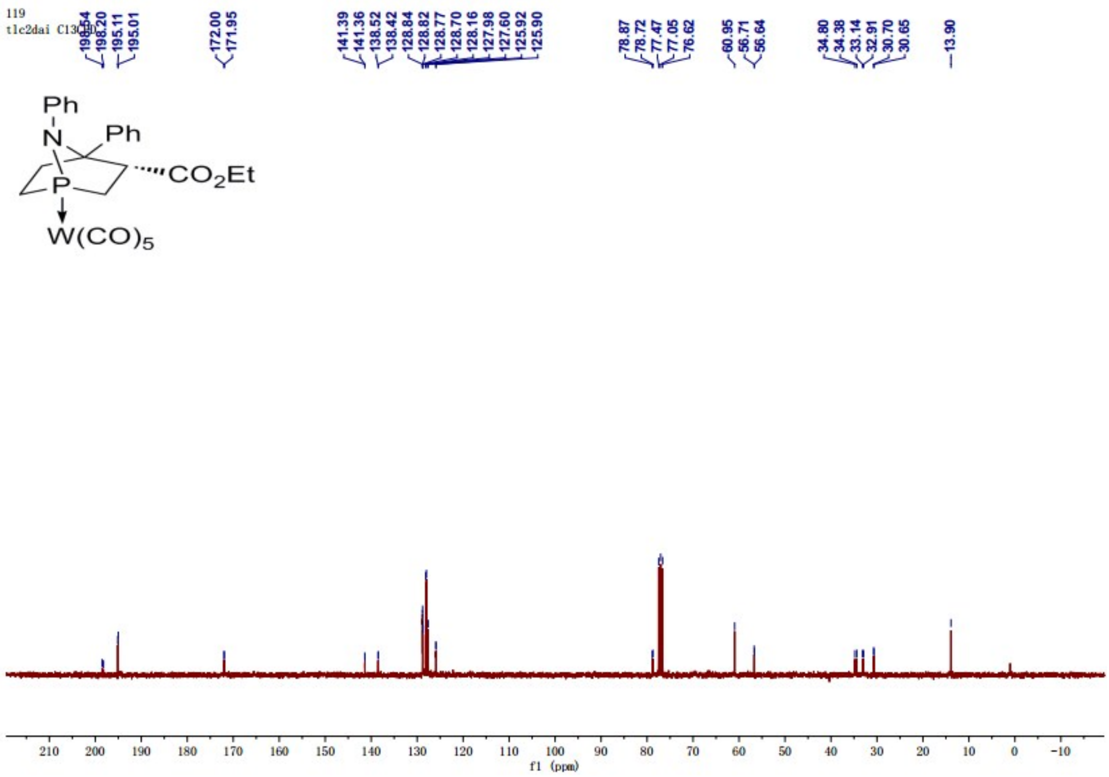
$^{31}P\{^1H\}$ NMR of Compound 15a



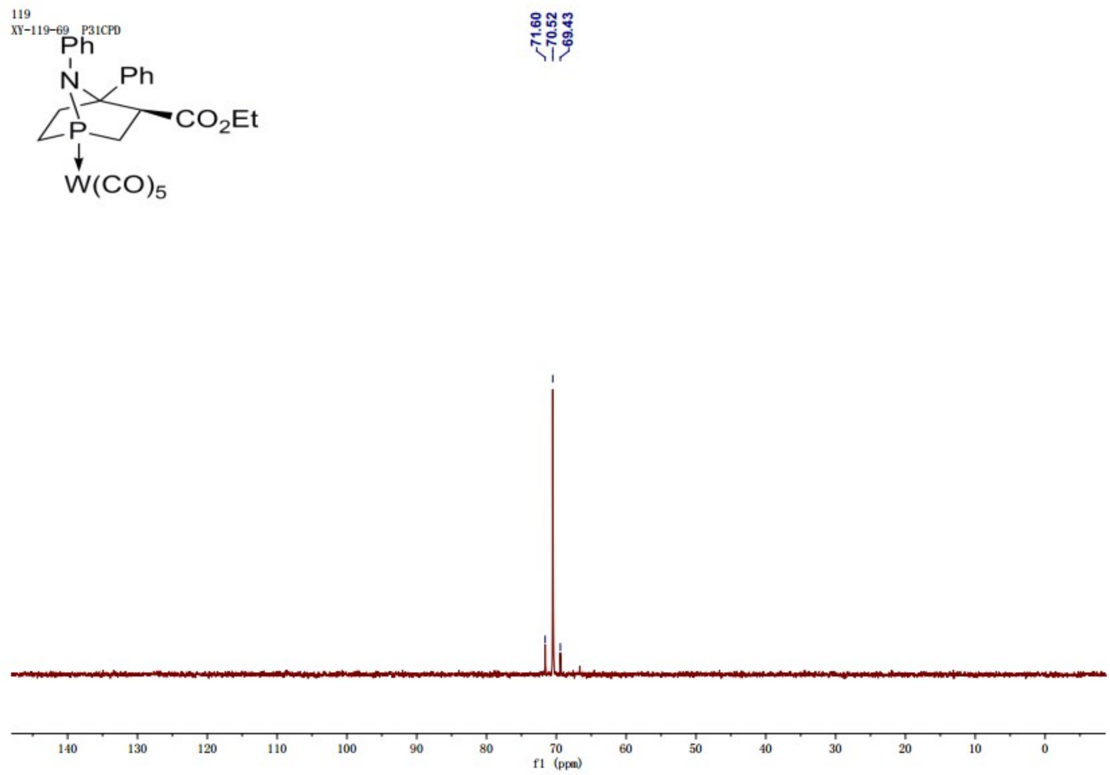
^{1}H NMR of Compound 15a



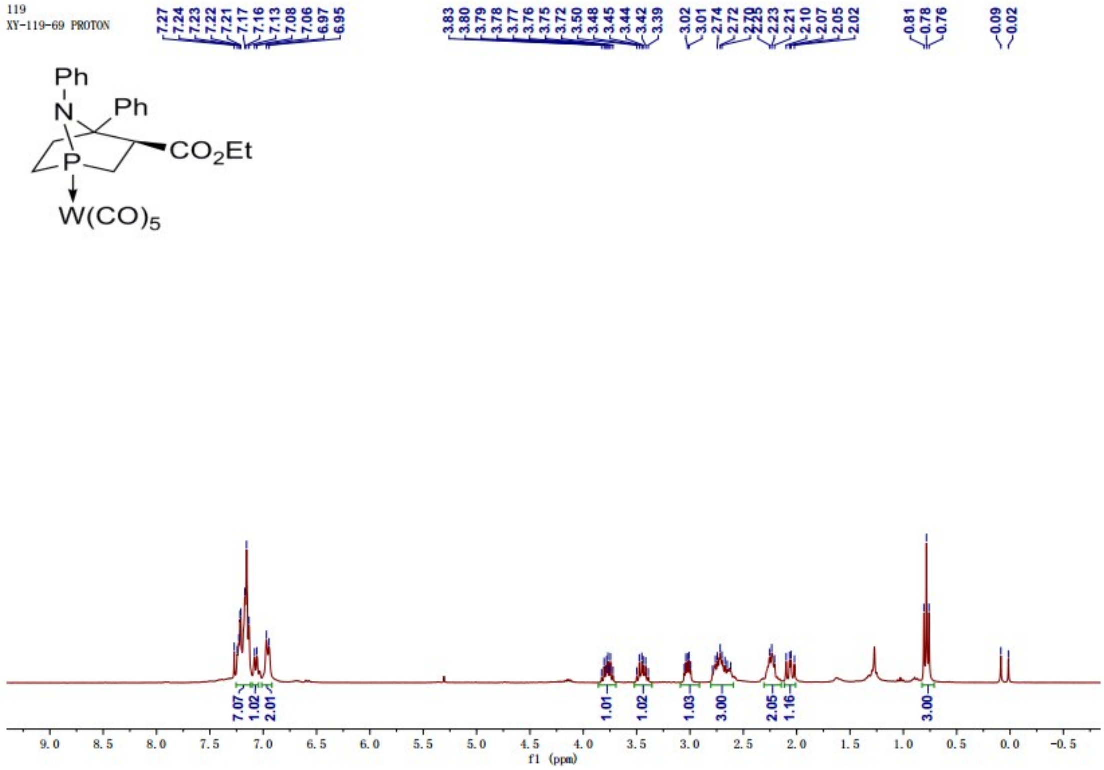
Dept135 NMR of Compound 15a



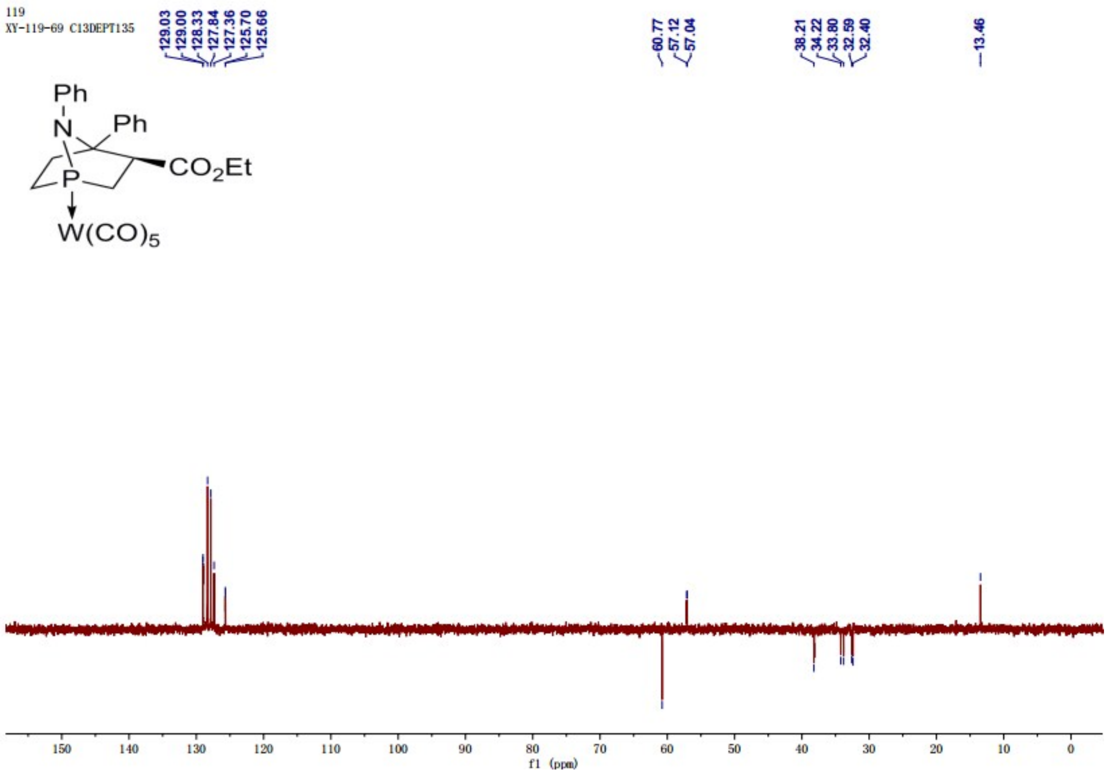
$^{13}C\{^1H\}$ NMR of Compound 15a



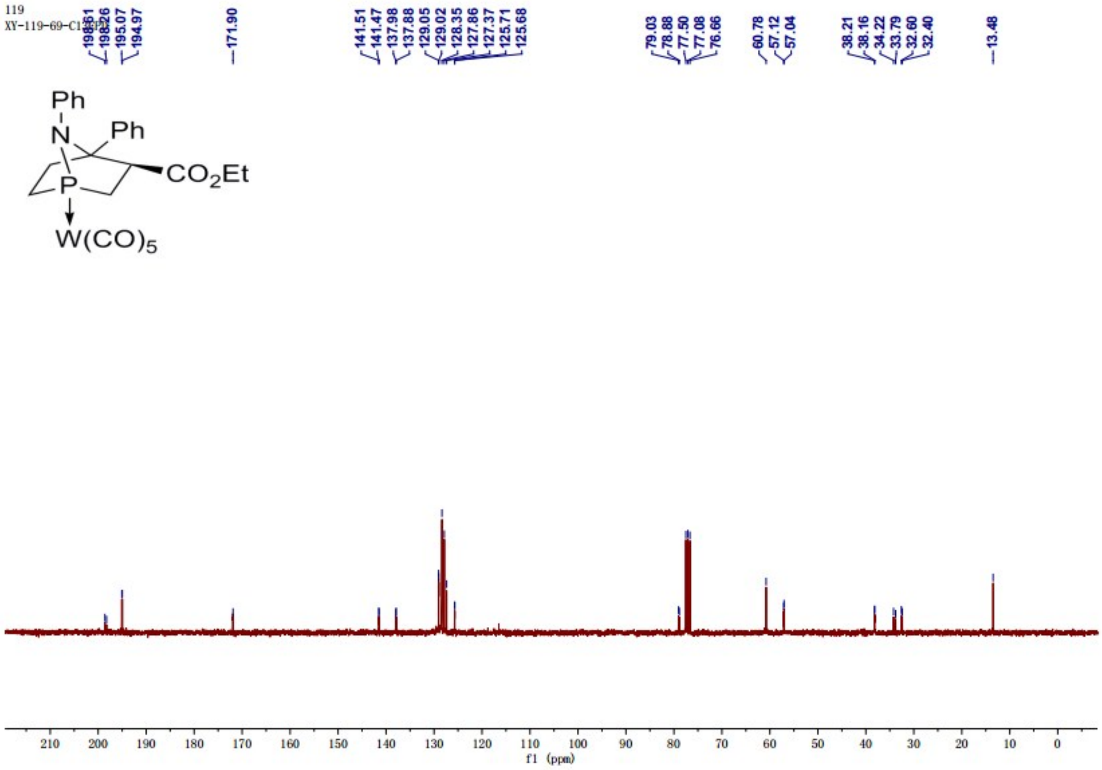
$^{31}P\{^1H\}$ NMR of Compound 15b



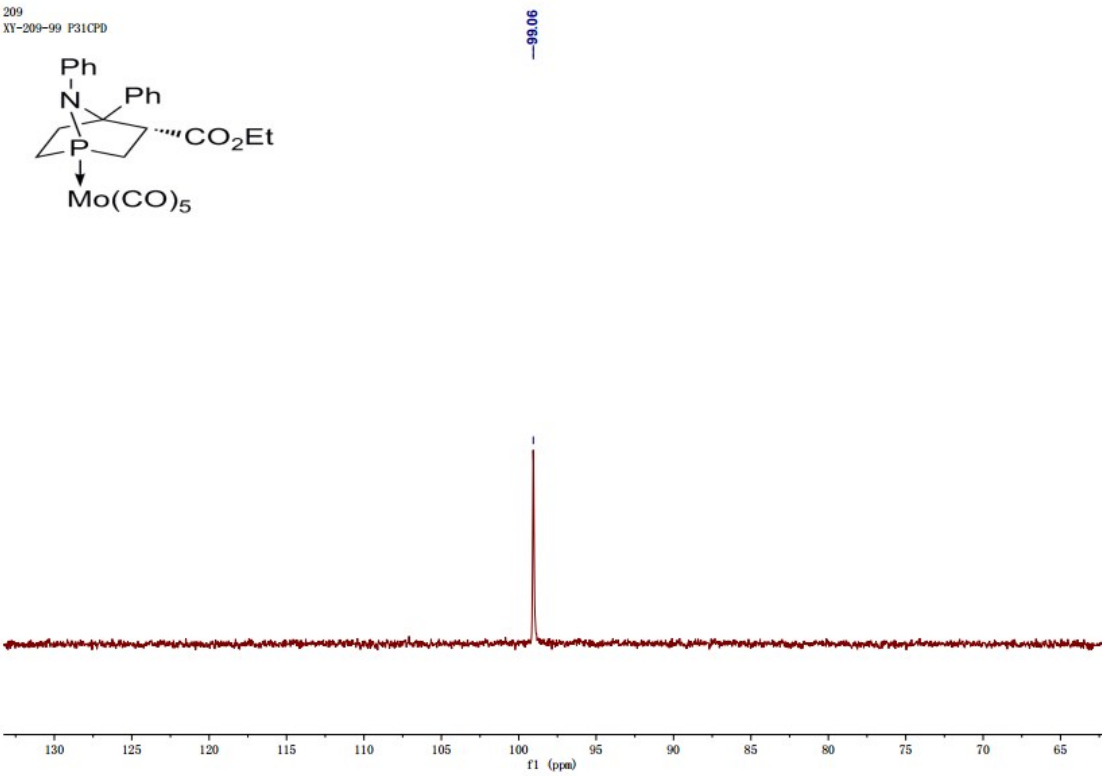
[1]H NMR of Compound 15b



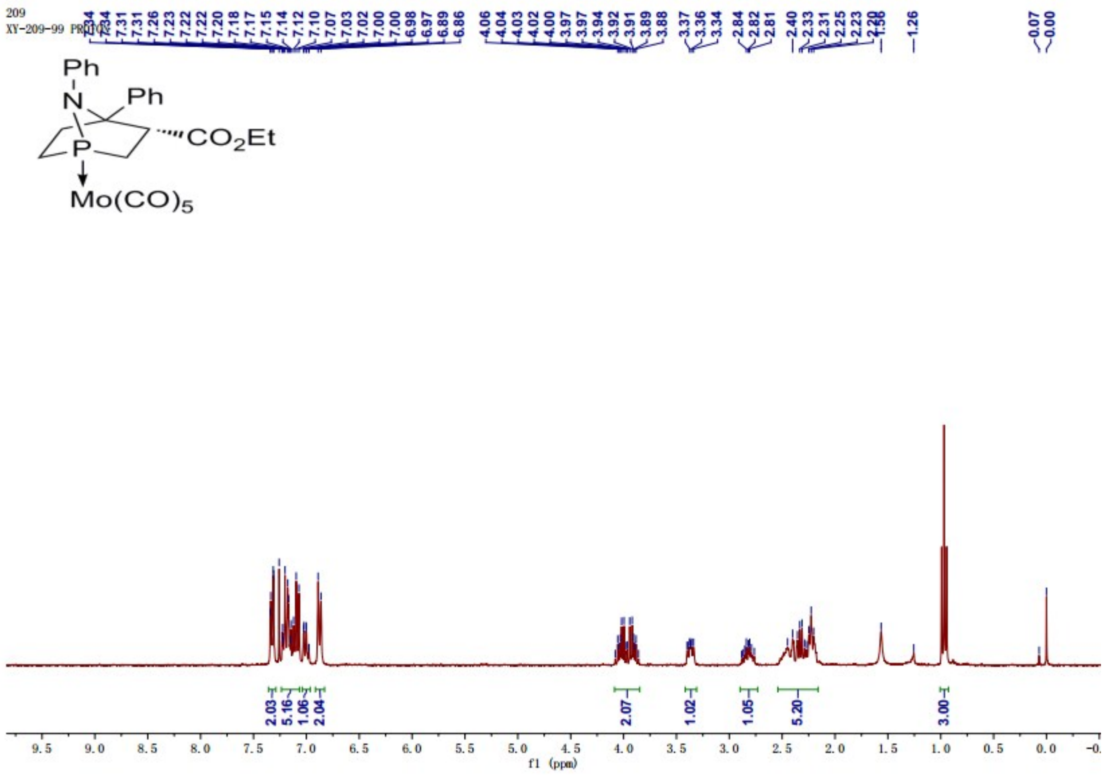
Dept135 NMR of Compound 15b



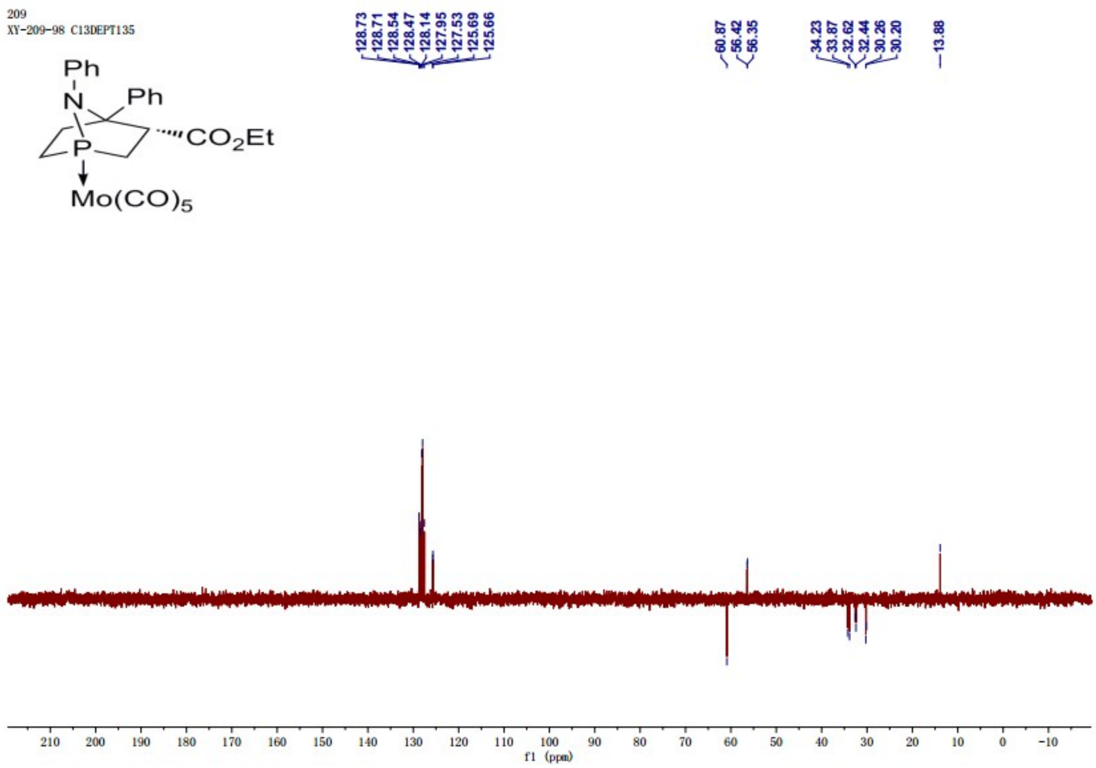
$^{13}C\{^1H\}$ NMR of Compound 15b



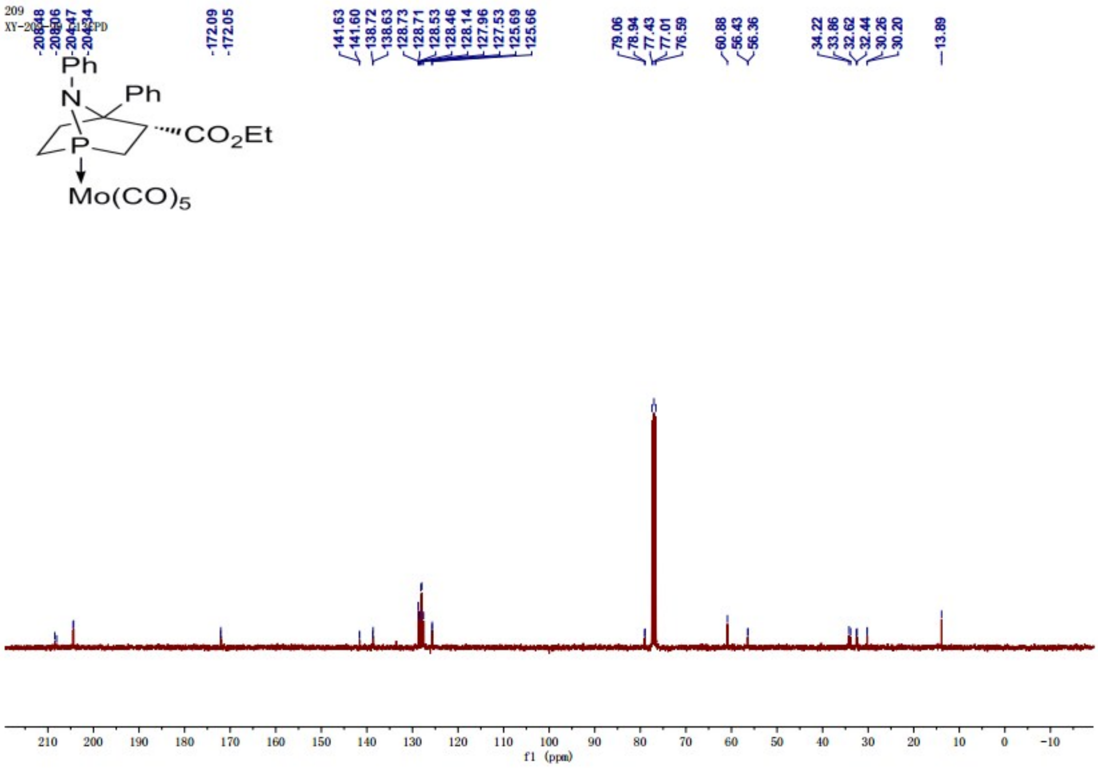
$^{31}P\{^1H\}$ NMR of Compound 16a



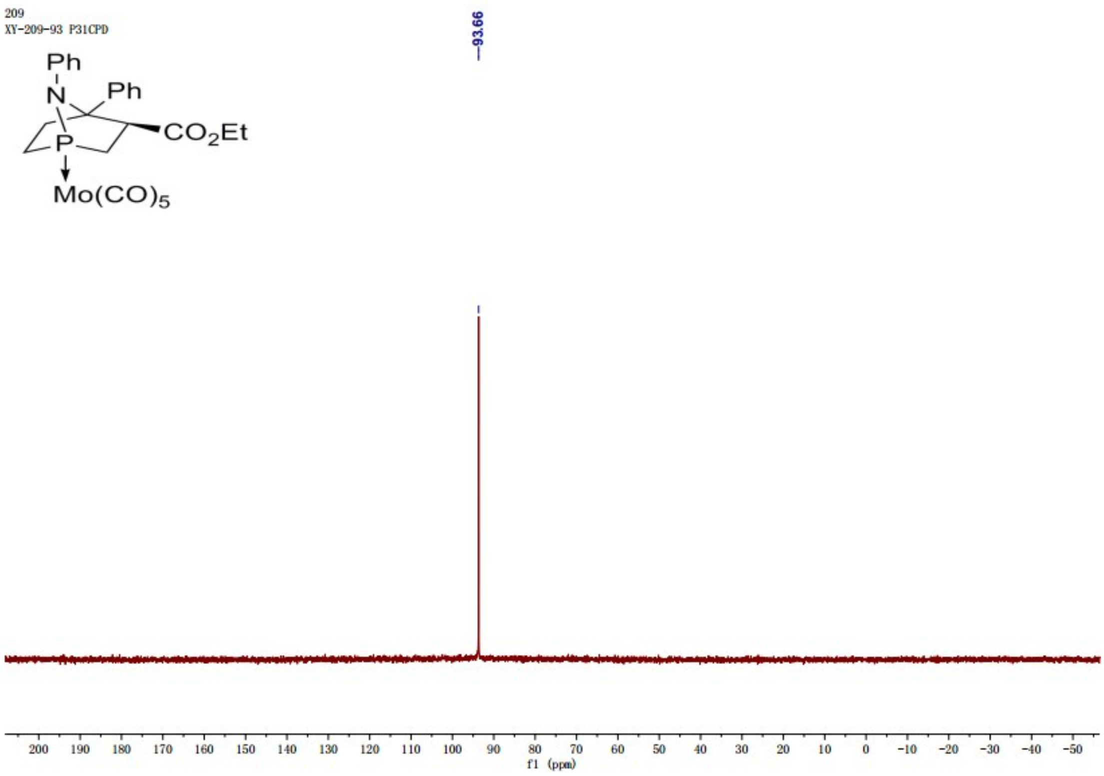
^{1}H NMR of Compound 16a



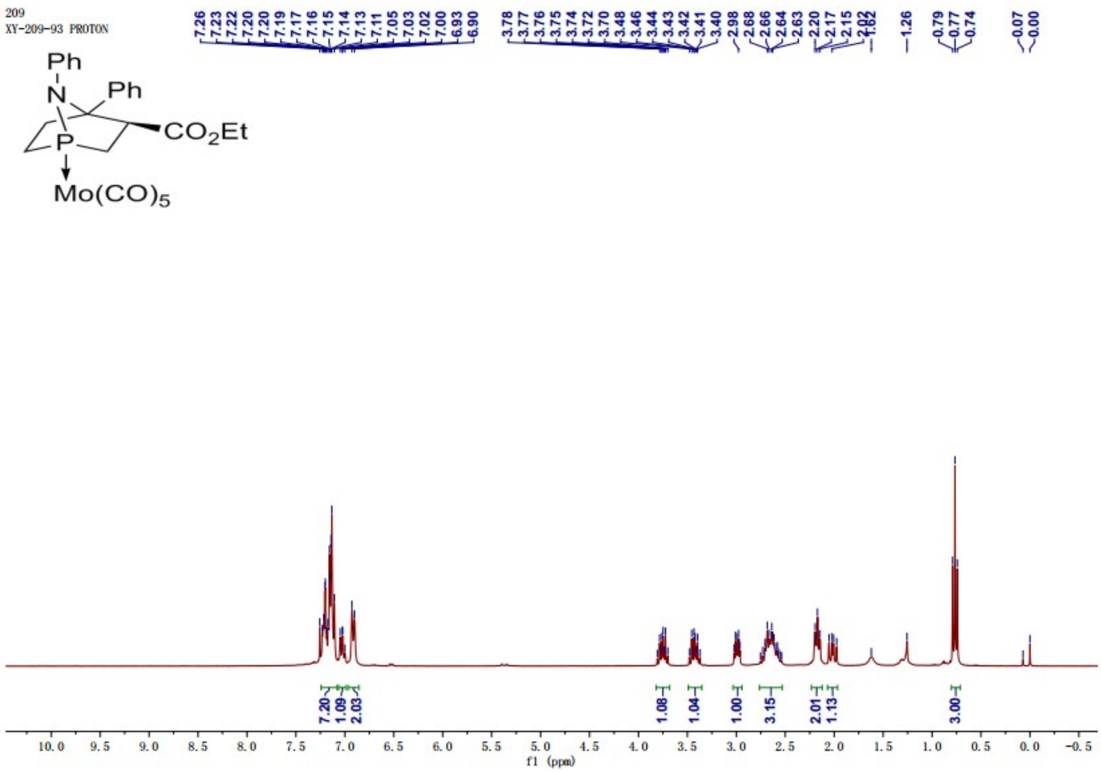
Dept135 NMR of Compound 16a



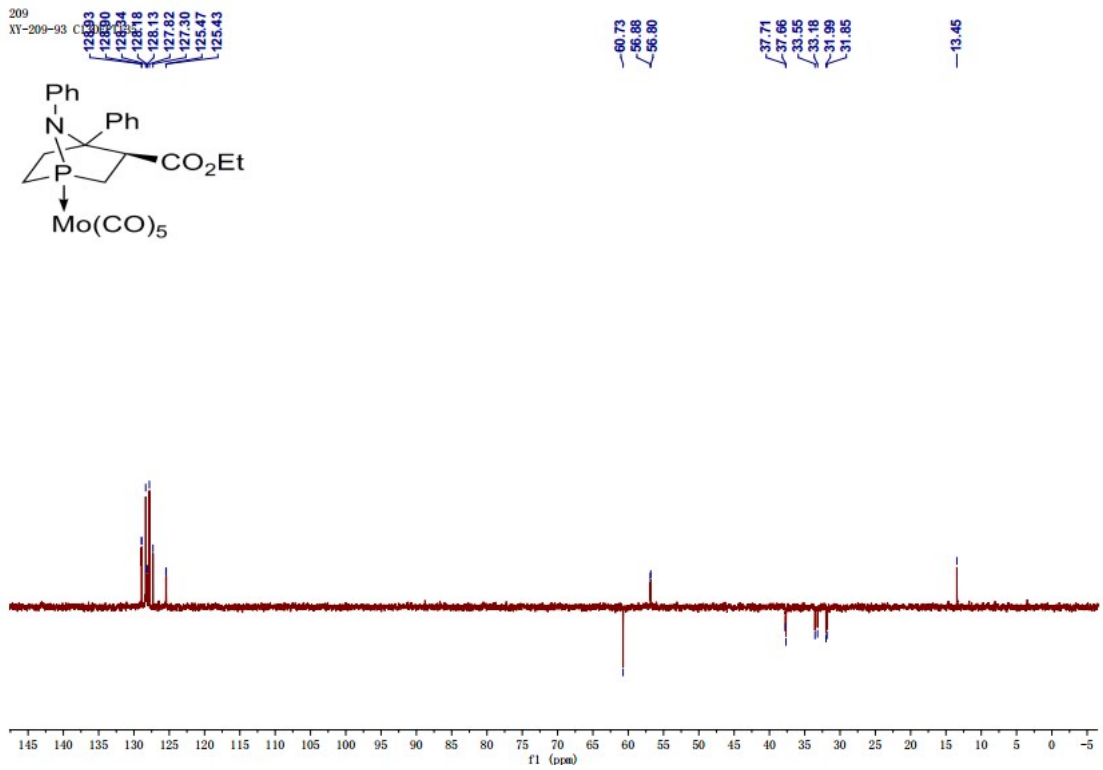
$^{13}C\{^{1}H\}$ NMR of Compound 16a



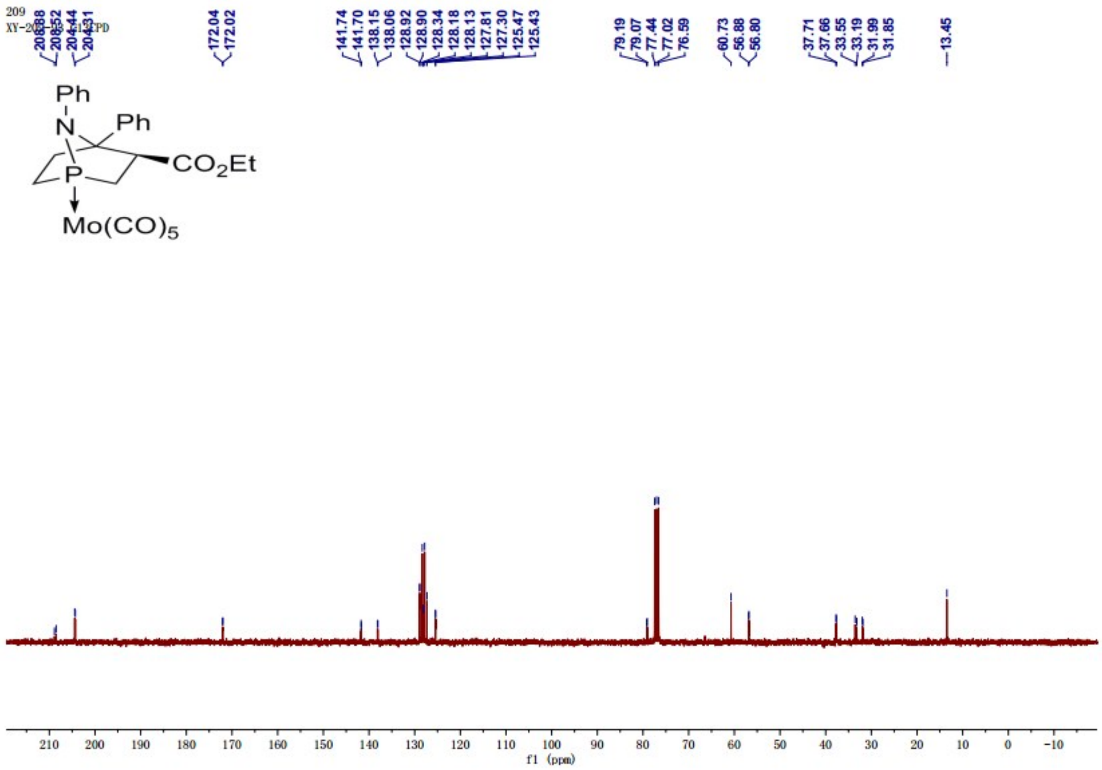
$^{31}P\{^{1}H\}$ NMR of Compound 16b



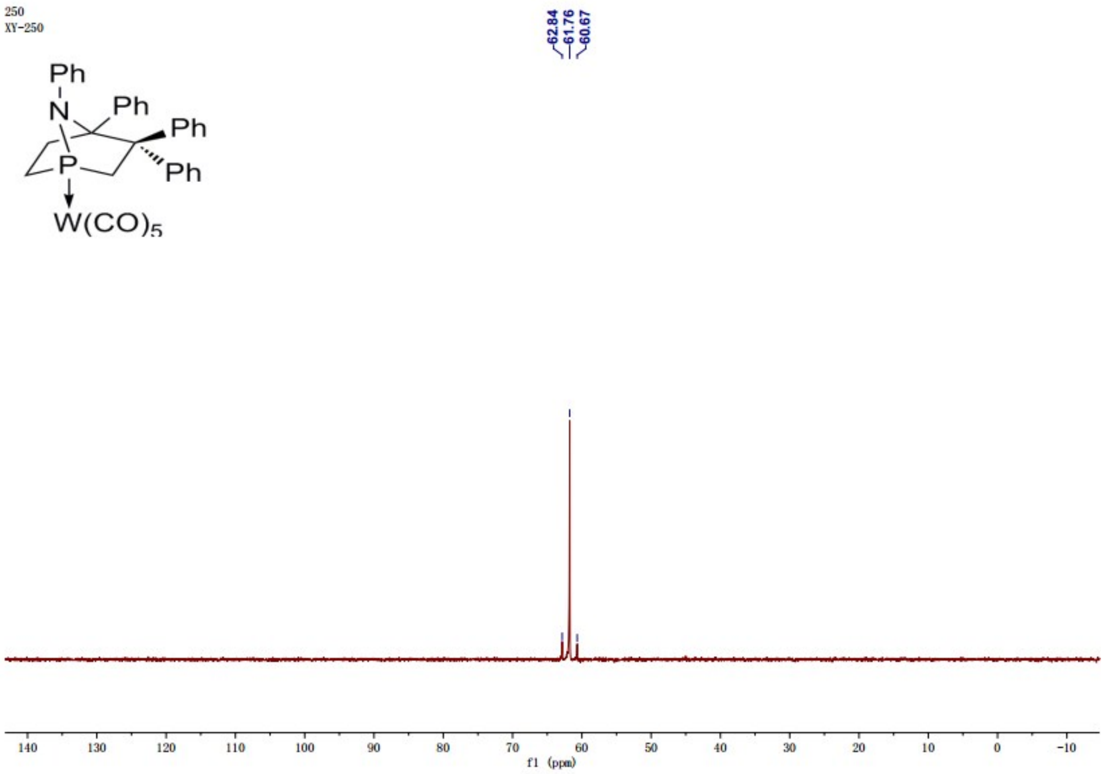
^{1}H NMR of Compound 16b



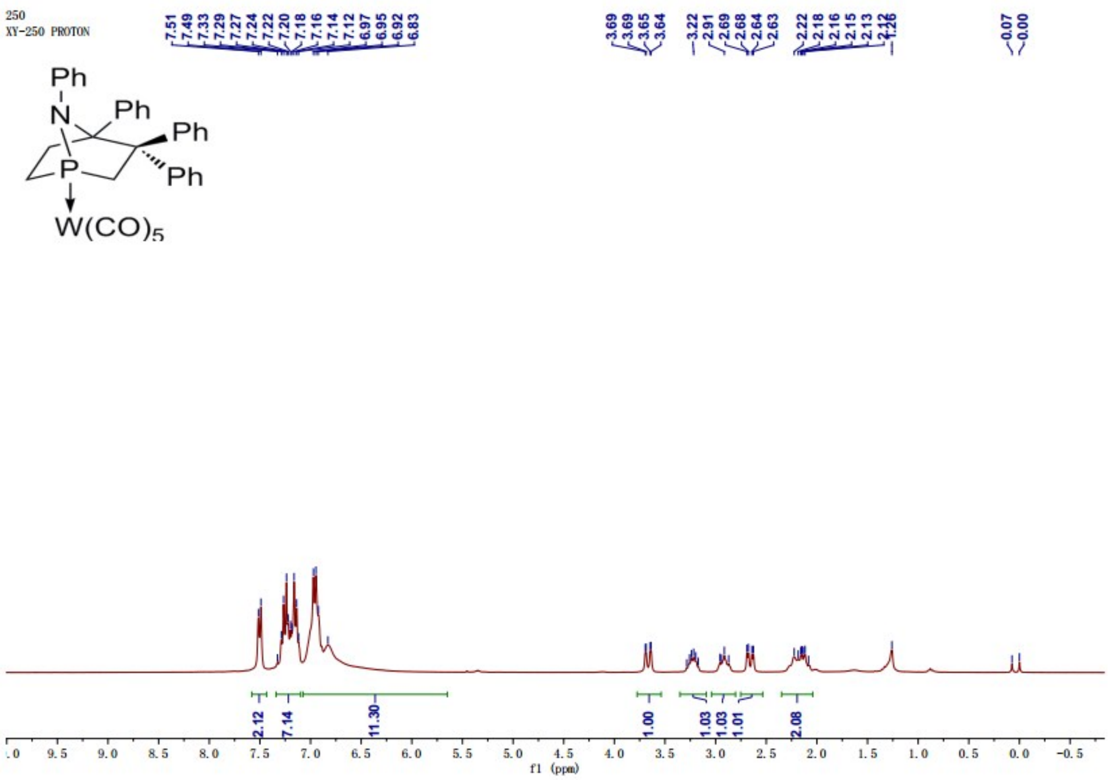
Dept135 NMR of Compound 16b



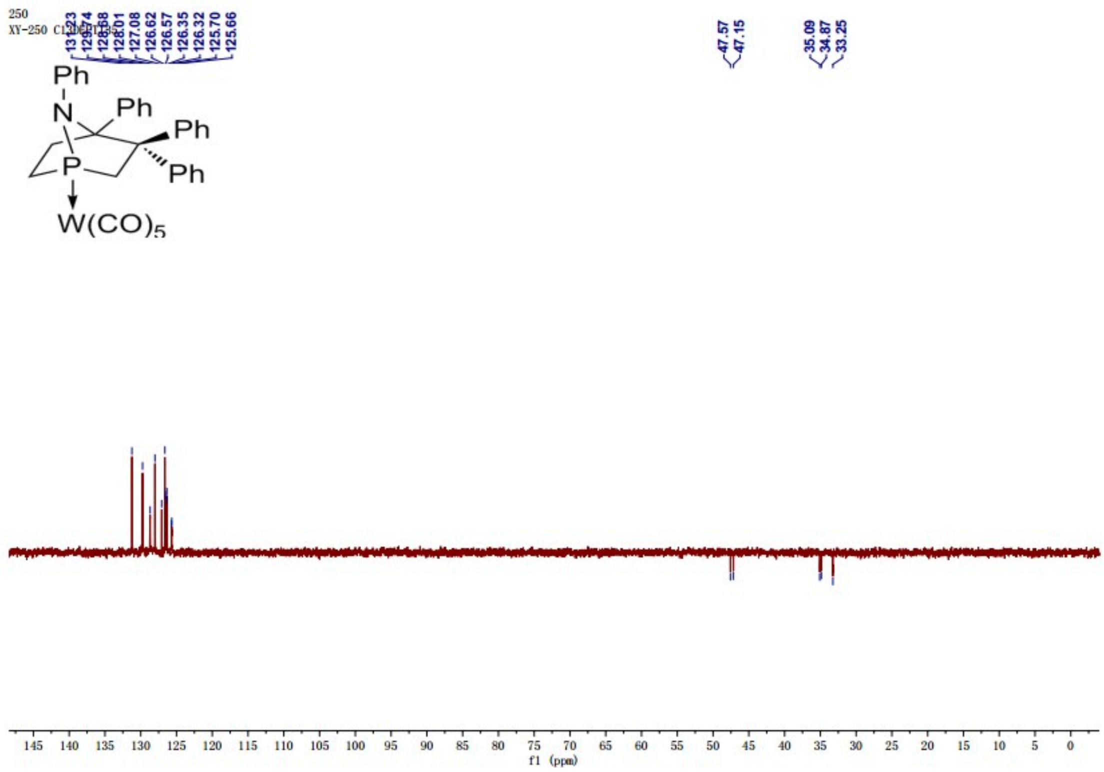
$^{13}C\{^1H\}$ NMR of Compound 16b



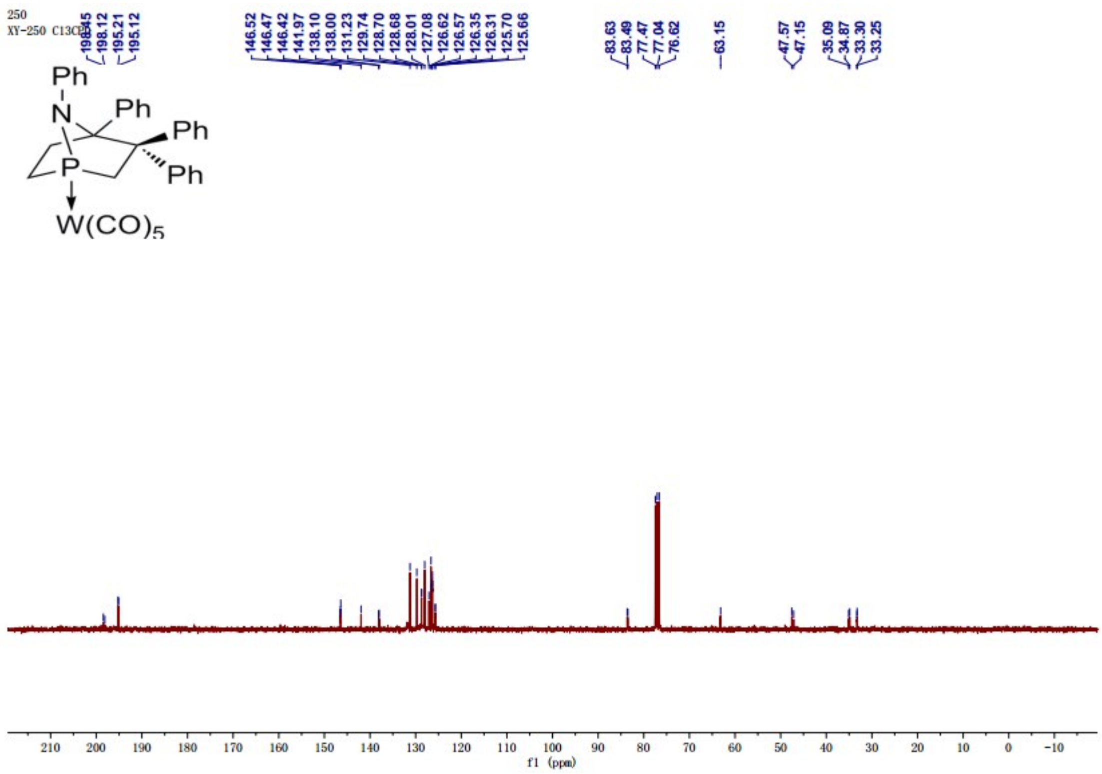
$^{31}P\{^1H\}$ NMR of Compound 17



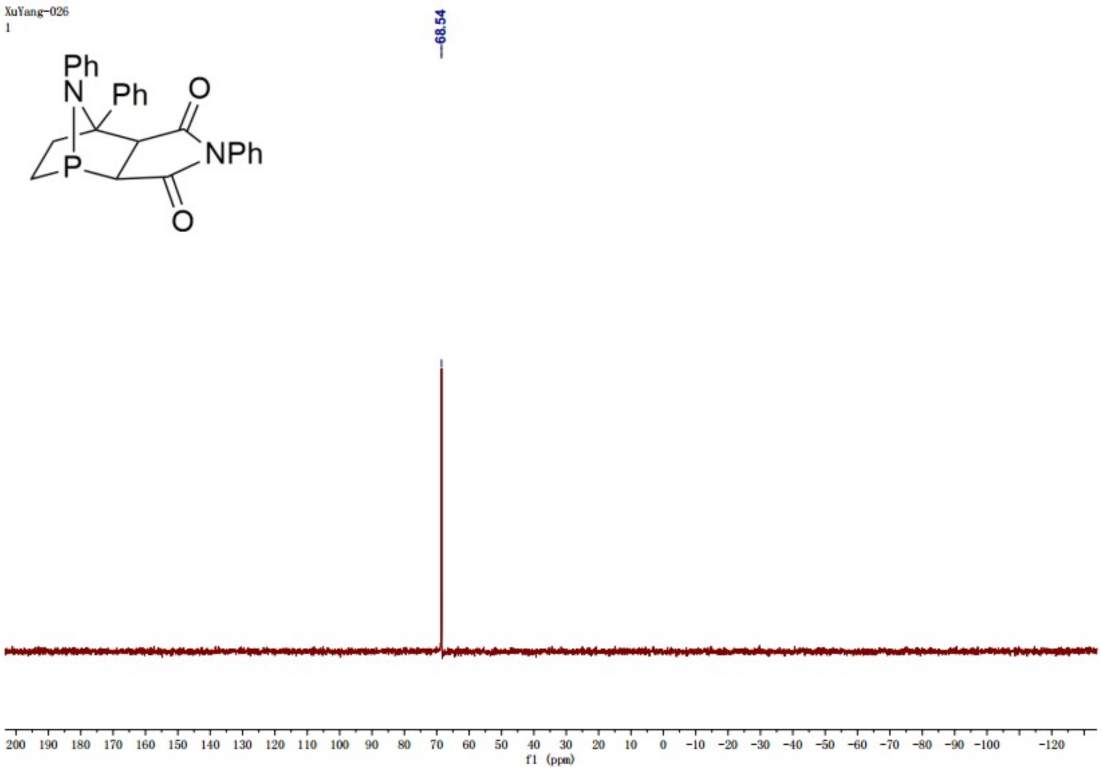
^{1}H NMR of Compound 17



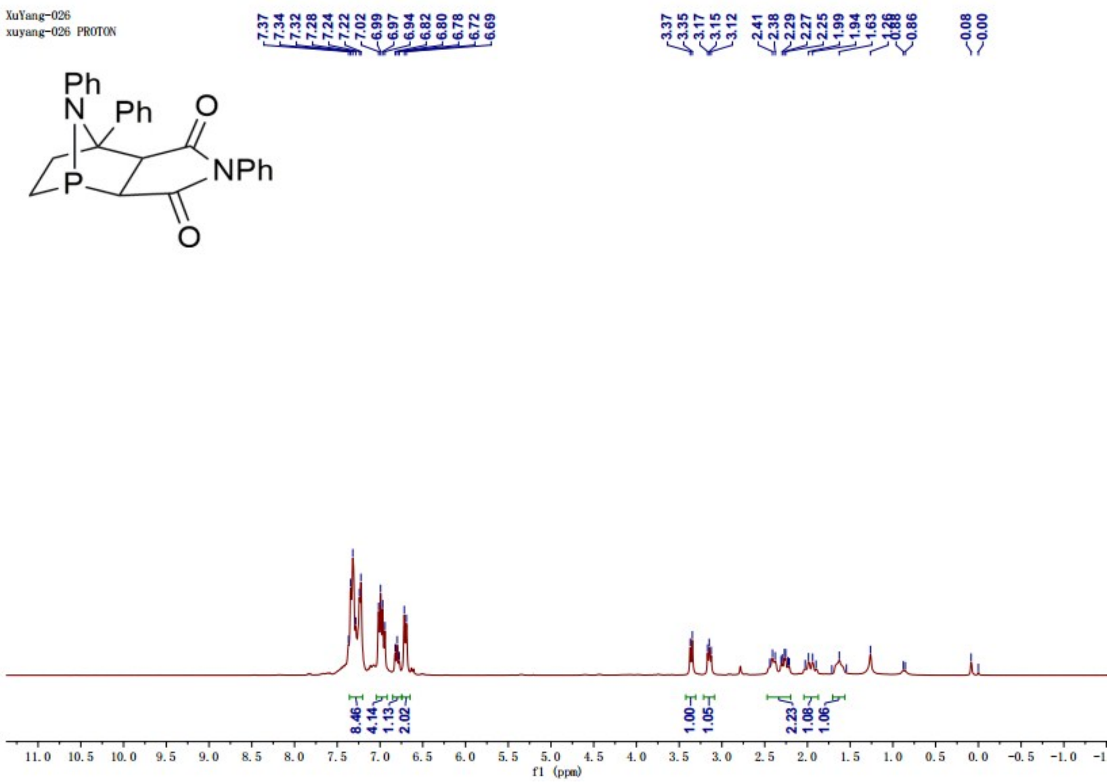
Dept135 NMR of Compound 17



$^{13}C\{^{1}H\}$ NMR of Compound 17



$^{31}P\{^{1}H\}$ NMR of Compound 18



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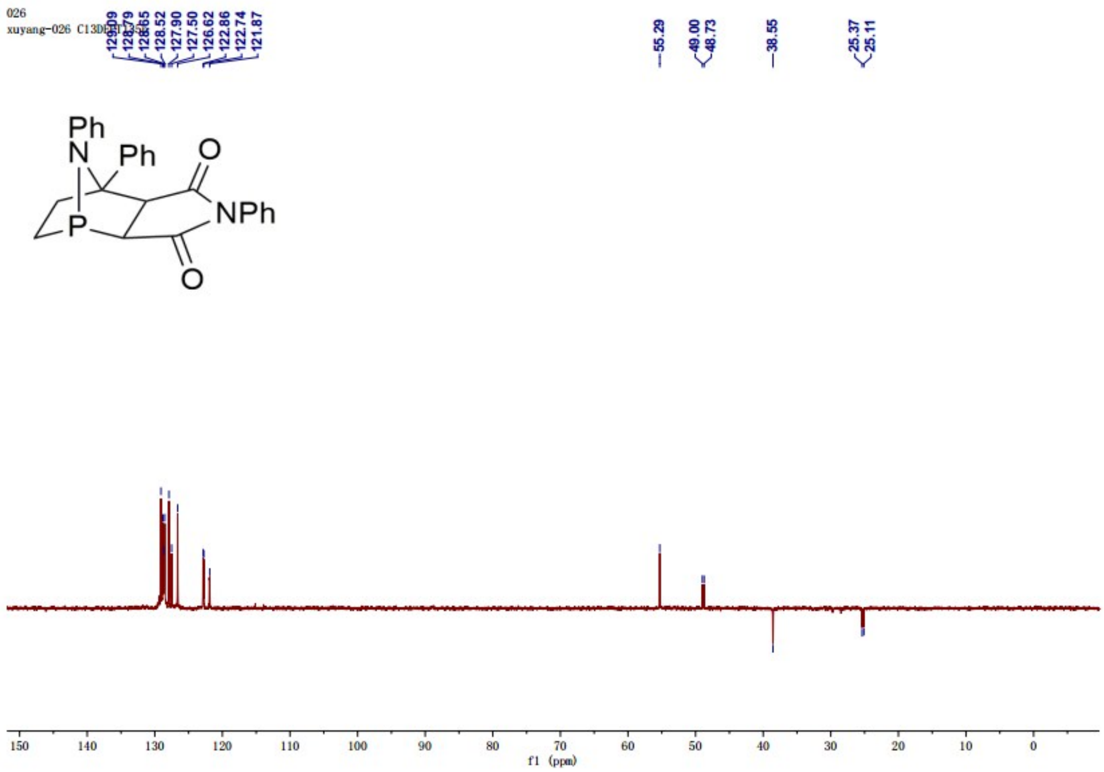
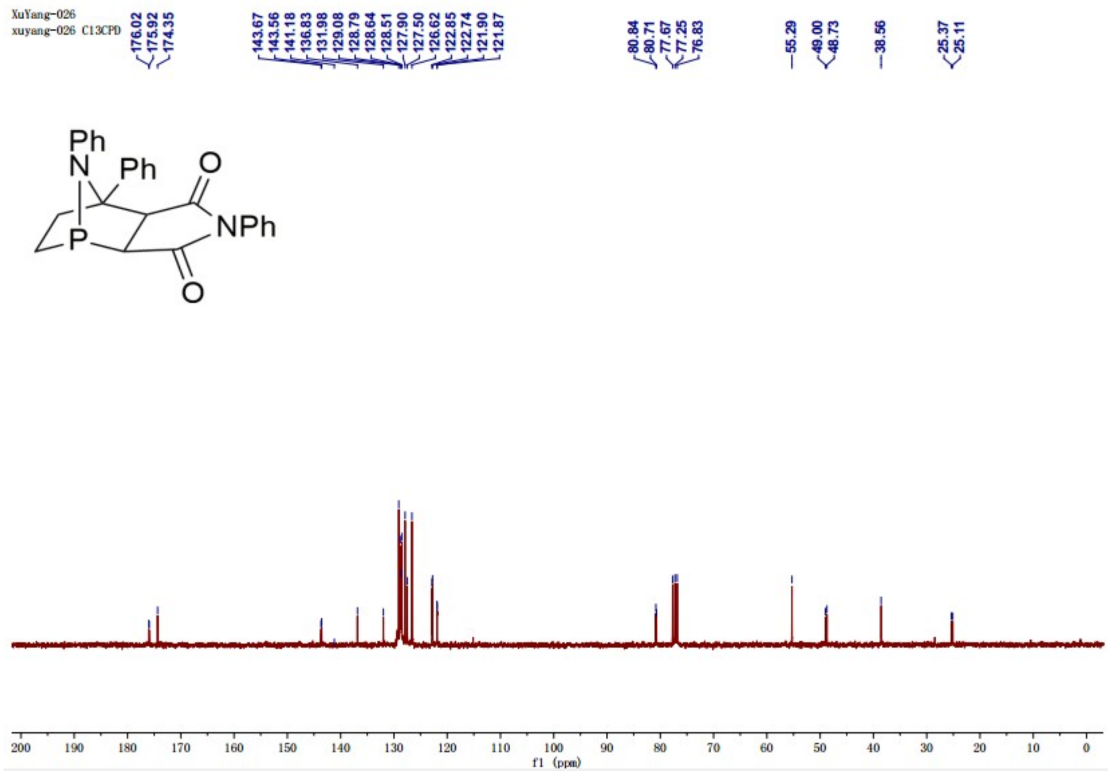
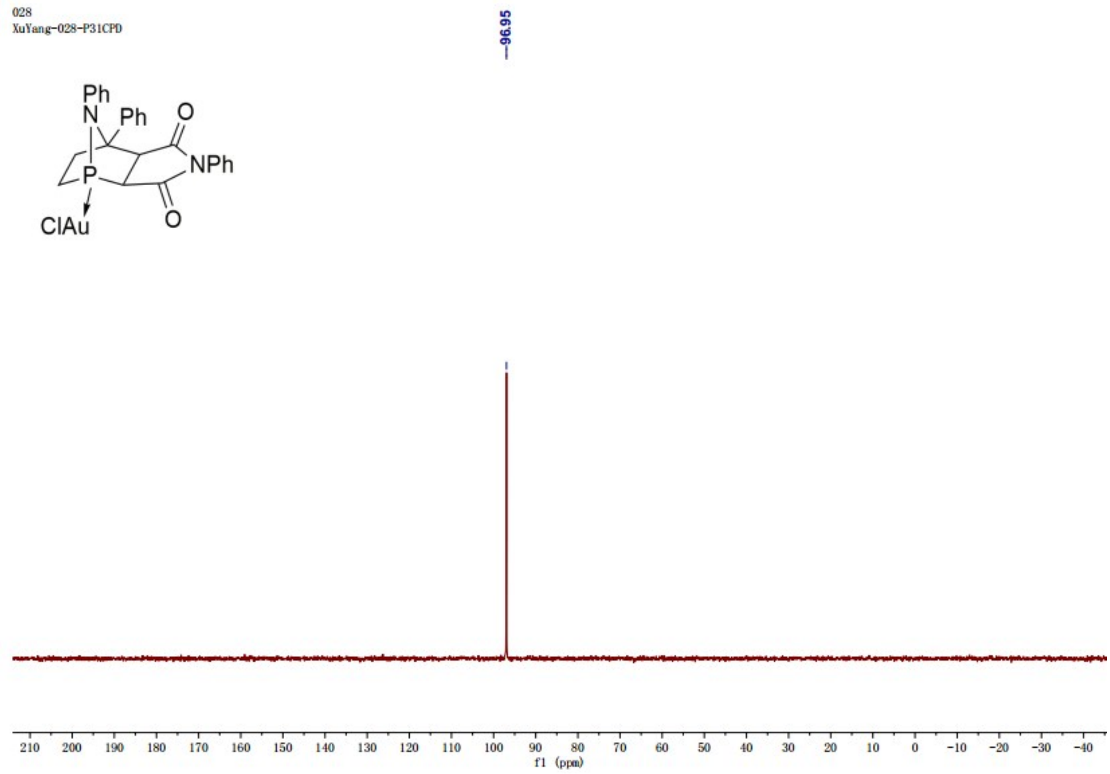


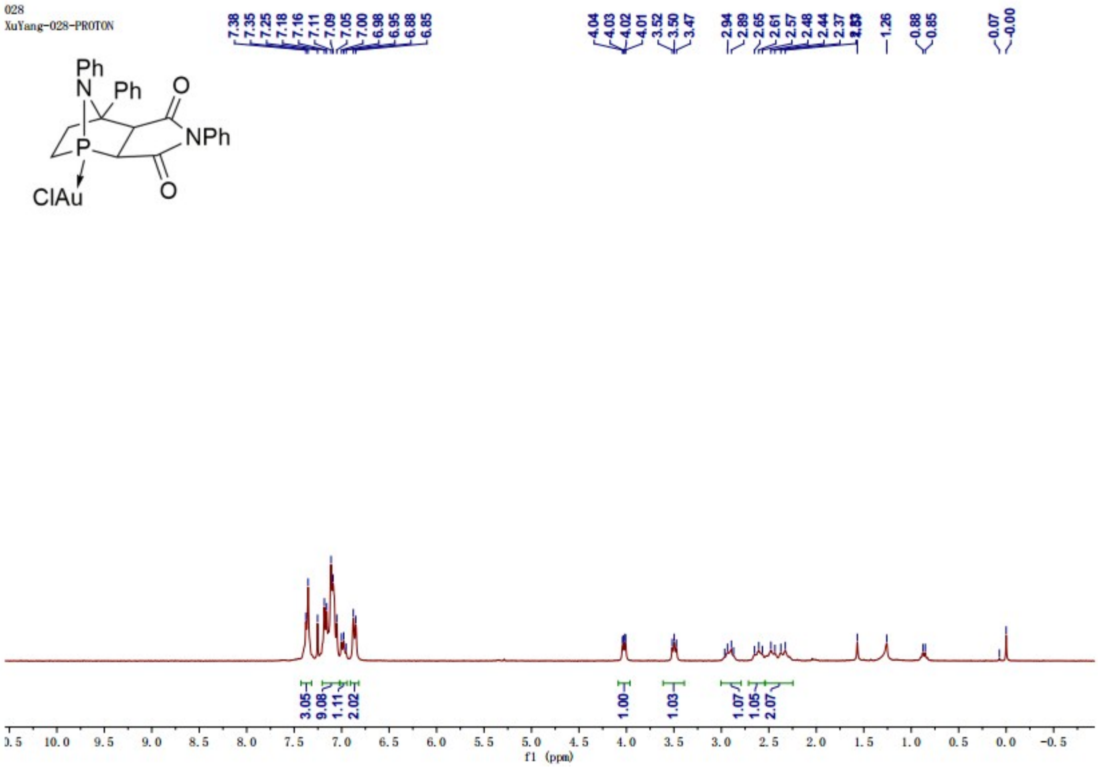
Dept135 NMR of Compound 18



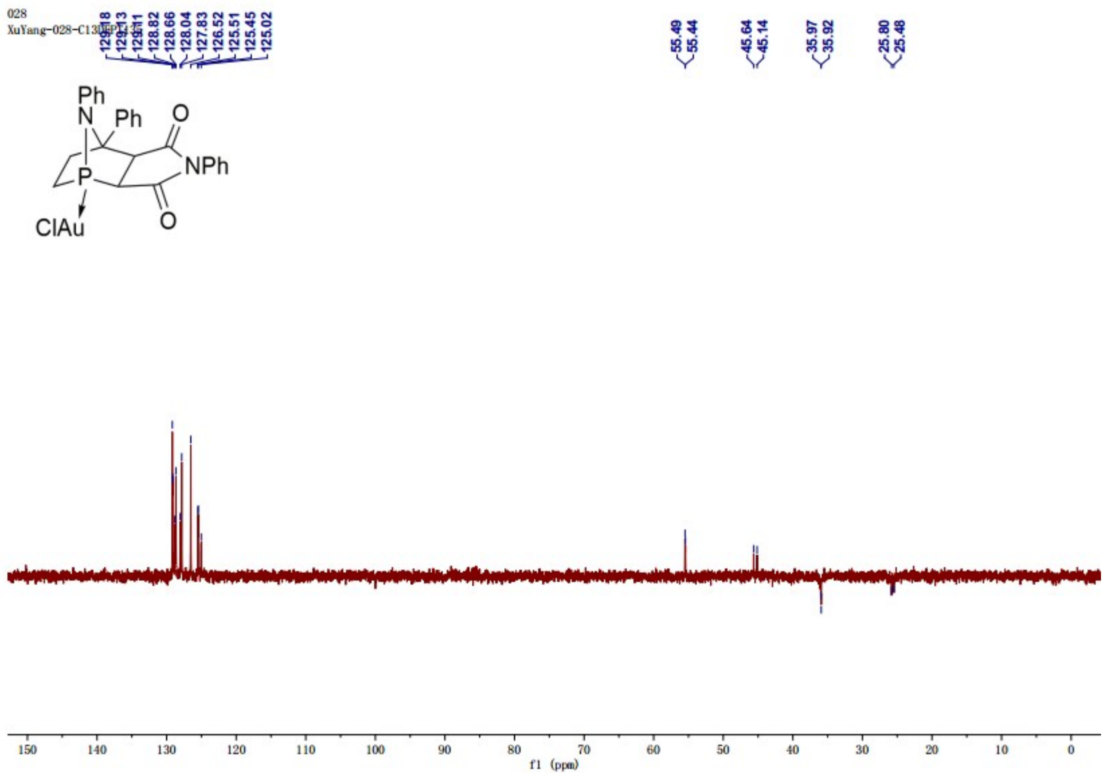
$^{13}C\{^1H\}$ NMR of Compound 18



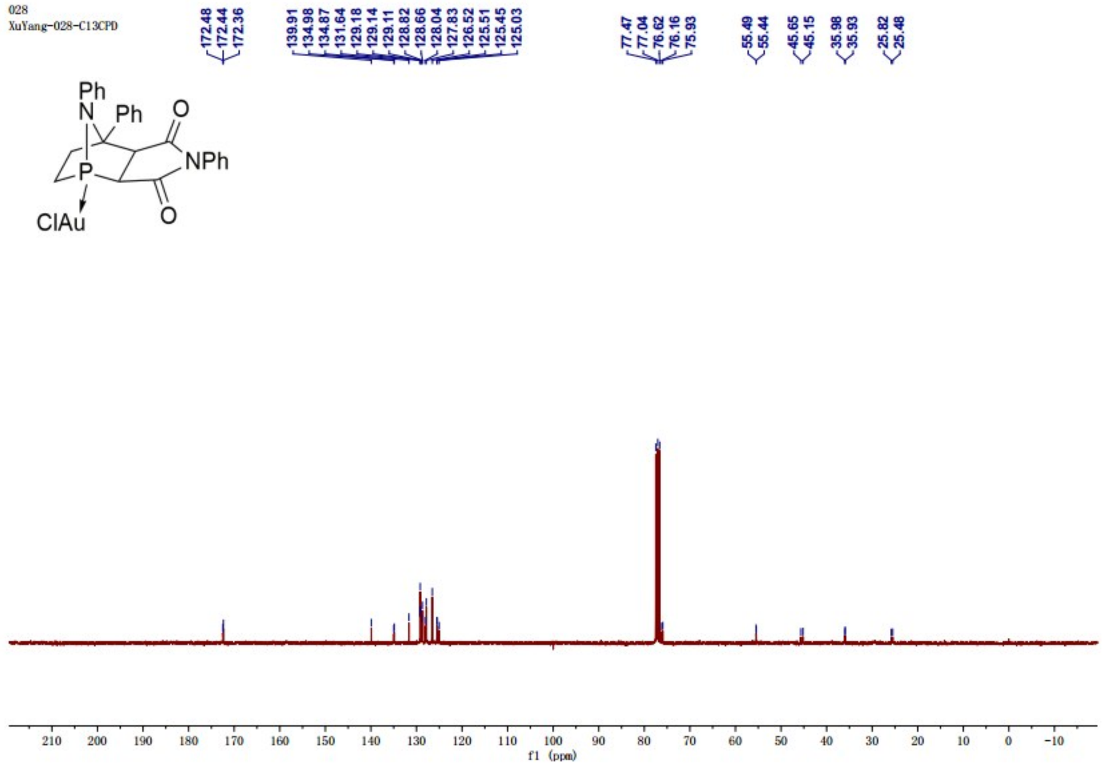
$^{31}P\{^1H\}$ NMR of Compound 19



^{1}H NMR of Compound 19



Dept135 NMR of Compound 19



$^{13}C\{^1H\}$ NMR of Compound 19