Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Tandem [5+1]/[8+2] Cycloaddition Reactions Involving Phosphiranes and Tropones: A Facile Access to 6,5,7-Fused Tricyclic Skeleton

Mingyue Cui, Juan Li, Rongqiang Tian,* Zheng Duan*

a College of Chemistry, Green Catalysis Center, International Phosphorus Laboratory, International Joint Research Laboratory for Functional Organophosphorus Materials of Henan Province, Zhengzhou University, Zhengzhou 450001, P. R. China. E-mail: tianrq@zzu.edu.cn. duanzheng@zzu.edu.cn.

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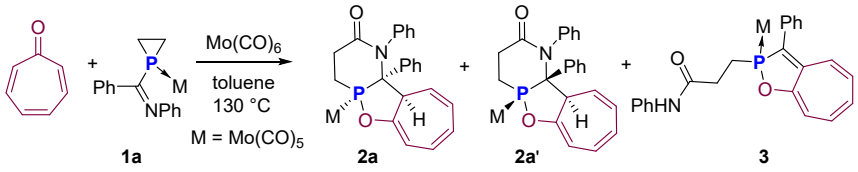
General information

All reactions were performed under nitrogen using solvents dried by standard methods except for special statement. NMR spectra were obtained using BrukerAV300 spectrometer. All spectra were recorded in $CDCl_3$. All coupling constants (*J* values) were reported in hertz (Hz). Chemical shifts were expressed in parts per million (ppm) downfield from internal TMS (^1H). HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-T of HR-MS spectrometer. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. Melting Point: heating rate: 4°C/min, the thermometer was not corrected. Silica gel (200-300 mesh) were used for the chromatographic separations. All commercially available reagents were used without further purification. 2-chloroethylphosphine $W(CO)_5$ complex[1], 1-iminylphosphirane complexes (1a-1e)[2] and 2-methoxytropone[3] and 2- phenyltropone[4] were prepared according to literature method. All new compounds were synthetic in small scale and were purified by thin layer chromatography. The purities of the new compounds are acceptable according to NMR spectra analysis.

Experimental Procedures and Characterization Data



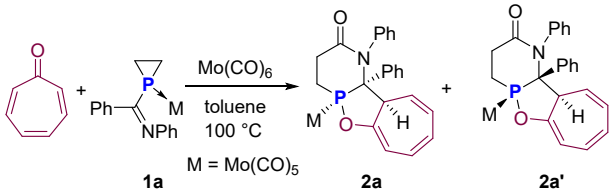
Under the atmosphere of N_2, a solution of **1a** (143.09 mg, 0.30 mmol), $Mo(CO)_6$ (79.20 mg, 0.30 mmol) and tropone (58.35 μL, 0.60 mmol) in toluene (6 mL) were stirred at 130 °C for 4 h in a heavy wall pressure tube (75 mL). The precipitate was filtered off, and the filtrate was concentrated under vacuum. The resulting brown oil was further purified by thin layer chromatography (petroleum ether/dichloromethane = 2:3), yielding **2a** (34.83 mg, 0.06 mmol, 19%, R_f = 0.61) as brown solid, **2a'** (32.99 mg, 0.05 mmol, 18%, R_f = 0.38) as brown solid and **3** (29.33 mg, 0.05 mmol, 16%, R_f = 0.80) as red solid. Single crystals of **2a**, **2a'** and **3** were grown from a mixed solvent of *n*-hexane/dichloromethane (5:1) at room temperature by slow evaporation.

2a: m.p. > 294 °C (dec). **^{31}P NMR (121 MHz, $CDCl_3$)** δ: 164.0 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.17 – 7.01 (m, 10H, CH), 6.78 – 6.64 (m, 2H, CH), 6. 51 – 6. 46 (m, 1H, CH), 6.12 (d, J = 6.0 Hz, 1H, CH), 5.71 (dd, J = 9.6, J = 4.8 Hz, 1H, CH), 3. 48 – 3. 17 (m, 4H, CH_2, CH), 2.25 – 2.19 (m, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.5 (d, J_{CP} = 33.8 Hz, CO *trans*), 203.3 (d, J_{CP} = 7.5 Hz, CO *cis*), 170.1 (d, J_{CP} = 3.8 Hz, CO), 148.9 (d, J_{CP} = 9.8 Hz, C), 139.6 (d, J_{CP} = 3.8 Hz, C), 138.6 (d, J_{CP} = 1.5 Hz, C), 129.7 (s, CH), 128.5 (d, J_{CP} = 3.0 Hz, CH), 128.4 (s, CH, two kinds of carbon signals overlapping), 128.1 (s, CH, two kinds of carbon signals overlapping), 127.4 (s, CH), 127.2 (s, CH), 127.0 (s, CH), 120.7 (s, CH), 103.1 (d, J_{CP} = 3.8 Hz, CH), 75.4 (d, J_{CP} = 9.0 Hz, C), 50.4 (d, J_{CP} = 3.0 Hz, CH), 28.6 (d, J_{CP} = 3.8 Hz, CH_2), 25.9 (d, J_{CP} = 6.0 Hz, CH_2). **HRMS (ESI):** m/z calcd for $C_{28}H_{21}MoNO_7P$ $(M+H)^+$ 612.0104, found 612.0103.

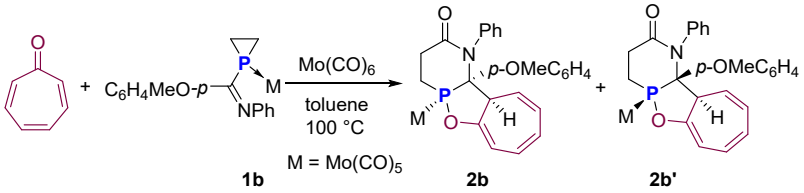
2a': m.p. 164.7 – 165.5 °C. **^{31}P NMR (121 MHz, $CDCl_3$)** δ: 169.5 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.40 – 7.30 (m, 3H, CH), 7.15 – 7.05 (m, 5H, CH), 6.70 – 6.64 (m, 1H, CH), 6.55 – 6.49 (m, 1H, CH), 6.32 (bs, 2H, CH), 6.19 – 6.14 (m, 1H, CH), 6.06 (d, J = 6.0 Hz, 1H, CH), 5.31 (dd, J = 9.0, J = 5.7 Hz, 1H, CH), 3.32 – 2.86 (m, 5H, CH_2, CH). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.7 (d, J_{CP} = 32.3 Hz, CO *trans*), 203.5 (d, J_{CP} = 9.8 Hz, CO *cis*), 168.7 (d, J_{CP} = 5.3 Hz, CO), 143.6 (s, C), 137.8 (s, C), 135.6 (d, J_{CP} = 10.5 Hz, C), 131.3 (d, J_{CP} = 8.3 Hz, CH), 130.8 (s, CH), 129.3 (s, CH), 129.2 (s, CH), 128.7 (s, CH, two kinds of carbon signals overlapping), 128.0 (s, CH), 126.8 (s, CH), 125.1 (s, CH), 118.6 (s, CH), 102.2 (d, J_{CP} = 5.3 Hz, CH), 75.8 (s, C), 49.0 (d, J_{CP} = 7.5 Hz, CH), 31.3 (d, J_{CP} = 11.3 Hz, CH_2), 28.2 (d, J_{CP} = 3.8 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{28}H_{21}MoNO_7P$ $(M+H)^+$ 612.0104, found 612.0104.

3: m.p. 170.9 – 171.5 °C. **^{31}P NMR (121 MHz, $CDCl_3$)** δ: 182.2 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.50 – 7. 25 (m, 9H, CH), 7.13 – 7.08 (m, 1H, CH), 6.55 (d, J = 12.0 Hz, 1H, CH), 6.11 – 6.01 (m, 2H, CH), 5.95 – 5.87 (m, 2H, CH), 2.79 – 2.59 (m, 4H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 209.3 (d, J_{CP} = 29.3 Hz, CO *trans*), 204.1 (d, J_{CP} = 10.5 Hz, CO *cis*), 169.1 (d, J_{CP} = 9.0 Hz, CO), 167.4 (d, J_{CP} = 6.8 Hz, C), 141.6 (d, J_{CP} = 9.0 Hz, C), 137.6 (s, C), 132.8 (s, CH), 132.2 (d, J_{CP} = 15.0 Hz, C), 131.3 (s, CH), 129.4 (s, CH), 129.1 (s, CH), 128.6 (s, CH), 128.3 (d, J_{CP} = 5.3 Hz, CH), 126.8

(d, J_{CP} = 14.2 Hz, CH), 126.6 (d, J_{CP} = 9.8 Hz, CH), 124.6 (s, CH), 123.6 (d, J_{CP} = 27.0 Hz, C), 119.8 (s, CH), 110.2 (d, J_{CP} = 3.5 Hz, CH), 40.1 (d, J_{CP} = 4.7 Hz, CH_2), 30.7 (d, J_{CP} = 4.3 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{28}H_{21}MoNO_7P$ $(M+H)^+$ 612.0104, found 612.0105.



Under the atmosphere of N_2, a solution of **1a** (143.09 mg, 0.30 mmol), $Mo(CO)_6$ (79.20 mg, 0.30 mmol) and tropone (58.35 μL, 0.60 mmol) in toluene (6 mL) were stirred at 100 °C for 4 h in a heavy wall pressure tube (75 mL). The precipitate was filtered off, and the filtrate was concentrated under vacuum. The resulting brown oil was further purified by thin layer chromatography (petroleum ether/dichloromethane = 2:3), yielding **2a** (75.15 mg, 0.12 mmol, 41%, R_f = 0.61) as brown solid and **2a'** (43.99 mg, 0.07 mmol, 24%, R_f = 0.38) as brown solid.

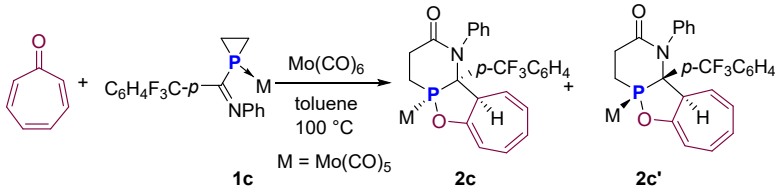


Under the atmosphere of N_2, a solution of **1b** (152.09 mg, 0.30 mmol), $Mo(CO)_6$ (79.20 mg, 0.30 mmol) and tropone (58.35 μL, 0.60 mmol) in toluene (6 mL) were stirred at 100 °C for 4 h in a heavy wall pressure tube (75 mL). The precipitate was filtered off, and the filtrate was concentrated under vacuum. The resulting brown oil was further purified by thin layer chromatography (petroleum ether/dichloromethane = 1:7), yielding **2b** (88.46 mg, 0.14 mmol, 46%, R_f = 0.54) as yellowish solid and **2b'** (65.38 mg, 0.10 mmol, 34%, R_f = 0.35) as yellow solid.

2b: m.p. > 280 °C (dec). **^{31}P NMR (121 MHz, $CDCl_3$)** δ: 164.2 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.17 – 7.12 (m, 3H, CH), 7.05 – 7.03 (m, 4H, CH), 6.75 – 6.61 (m, 4H, CH), 6.48 – 6.43 (m, 1H, CH), 6.10 – 6.08 (m, 1H, CH), 5.70 – 5.66 (m, 1H, CH), 3.62 (s, 3H, OCH_3), 3.37 – 3.13 (m, 4H, CH_2, CH), 2.21 – 2.16 (m, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.7 (d, J_{CP} = 34.5 Hz, CO *trans*), 203.5 (d, J_{CP} = 9.8 Hz,

CO *cis*), 170.2 (d, J_{CP} = 3.8 Hz, CO), 159.5 (d, J_{CP} = 2.3 Hz, C), 149.0 (d, J_{CP} = 9.8 Hz, C), 139.6 (d, J_{CP} = 3.0 Hz, C), 130.4 (d, J_{CP} = 0.8 Hz, C), 129.7 (s, CH), 128.5 (s, CH, two kinds of carbon signals overlapping), 128.2 (s, CH, two kinds of carbon signals overlapping), 127.4 (s, CH), 127.1 (d, J_{CP} = 6.0 Hz, CH), 120.8 (s, CH), 113.8 (s, CH), 103.1 (d, J_{CP} = 4.5 Hz, CH), 74.9 (d, J_{CP} = 10.5 Hz, C), 55.2 (s, OCH_3), 50.5 (d, J_{CP} = 3.8 Hz, CH), 28.6 (d, J_{CP} = 3.8 Hz, CH_2), 25.7 (d, J_{CP} = 6.0 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{29}H_{23}MoNO_8P$ $(M+H)^+$ 642.0210, found 642.0211.

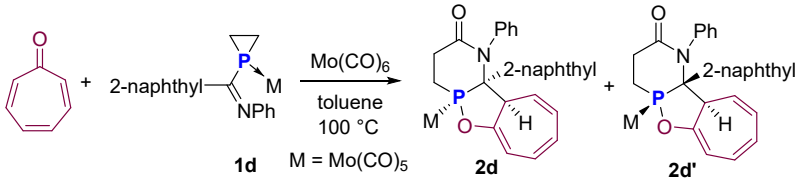
2b': m.p. > 280 °C (dec). **^{31}P NMR (121 MHz, $CDCl_3$)** δ: 171.2 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.16 – 7.10 (m, 3H, CH), 7.05 – 7.02 (m, 2H, CH), 6.87 – 6.84 (m, 2H, CH), 6.70 – 6.65 (m, 1H, CH), 6.54 – 6.49 (m, 1H, CH), 6.34 (bs, 2H, CH), 6.18 – 6.14 (m, 1H, CH), 6.05 (d, *J* = 5.7 Hz, 1H, CH), 5.33 – 5.28 (m, 1H, CH), 3.80 (s, 3H, OCH_3), 3.31 – 2.83 (m, 5H, CH_2, CH). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.8 (d, J_{CP} = 32.3 Hz, CO *trans*), 203.5 (d, J_{CP} = 9.8 Hz, CO *cis*), 168.7 (d, J_{CP} = 5.3 Hz, CO), 160.1 (s, C), 143.6 (s, C), 137.8 (s, C), 132.6 (d, J_{CP} = 7.5 Hz, CH), 130.8 (s, CH), 129.2 (s, CH), 128.7 (s, CH), 128.0 (s, CH), 127.4 (d, J_{CP} = 11.3 Hz, C), 126.7 (s, CH), 125.1 (s, CH), 118.7 (s, CH), 114.0 (s, CH), 102.1 (d, J_{CP} = 5.3 Hz, CH), 75.4 (s, C), 55.5 (s, OCH_3), 49.1 (d, J_{CP} = 6.8 Hz, CH), 31.1 (d, J_{CP} = 11.3 Hz, CH_2), 28.1 (d, J_{CP} = 4.5 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{29}H_{23}MoNO_8P$ $(M+H)^+$ 642.0210, found 642.0213.



Under the atmosphere of N_2, a solution of **1c** (163.49 mg, 0.30 mmol), $Mo(CO)_6$ (79.20 mg, 0.30 mmol) and tropone (58.35 μL, 0.60 mmol) in toluene (6 mL) were stirred at 100 °C for 4 h in a heavy wall pressure tube (75 mL). The precipitate was filtered off, and the filtrate was concentrated under vacuum. The resulting brown oil was further purified by thin layer chromatography (petroleum ether/dichloromethane = 1:4), yielding **2c** (91.66 mg, 0.13 mmol, 45%, R_f = 0.68) as brown oil and **2c'** (36.67 mg, 0.05 mmol, 18%, R_f = 0.45) as brown oil.

2c: ^{31}P NMR (121 MHz, $CDCl_3$) δ: 164.6 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.43 (d, *J* = 7.5 Hz, 3H, CH). 7.16 – 7.06 (m, 6H, CH), 6.77 – 6.64 (m, 2H, CH), 6.51 – 6.47 (m, 1H, CH), 6.14 (d, *J* = 5.7 Hz, 1H, CH), 5.72 – 5.67 (m, 1H, CH), 3.45 – 3.17 (m, 4H, CH_2, CH), 2.23 (d, *J* = 12.6 Hz, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.0 (d, J_{CP} = 33.8 Hz, CO *trans*), 203.2 (d, J_{CP} = 9.8 Hz, CO *cis*), 169.9 (d, J_{CP} = 3.8 Hz, CO), 148.6 (d, J_{CP} = 9.8 Hz, C), 143.1 (s, C), 139.3 (d, J_{CP} = 3.0 Hz, C), 130.6 (qd, J_{CF} = 33.0, J_{CP} = 3.0 Hz, C), 129.7 (s, CH), 128.7 (s, CH), 127.9 (s, CH, two kinds of carbon signals overlapping), 127.7 (s, CH), 127.5 (s, CH), 127.3 (s, CH), 125.6 – 125.2 (m, CH), 123.6 (q, J_{CF} = 270.0 Hz, CF_3), 120.4 (s, CH), 103.5 (d, J_{CP} = 3.8 Hz, CH), 75.6 (d, J_{CP} = 7.5 Hz, C), 50.6 (s, CH), 28.5 (d, J_{CP} = 3.0 Hz, CH_2), 26.0 (d, J_{CP} = 6.0 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{29}H_{20}MoNO_7PF_3$ $(M+H)^+$ 679.9978, found 679.9979.

2c': ^{31}P NMR (121 MHz, $CDCl_3$) δ: 167.5 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.62 (d, *J* = 8.1 Hz, 2H, CH), 7.32 (d, *J* = 8.1 Hz, 2H, CH), 7.23 – 7.09 (m, 3H, CH), 6.71 – 6.65 (m, 1H, CH), 6.57 – 6.51 (m, 1H, CH), 6.38 (d, *J* = 3.9 Hz, 2H, CH), 6.18 (dd, *J* = 9.0, *J* = 5.7 Hz, 1H, CH), 6.09 (d, *J* = 6.0 Hz, 1H, CH), 5.20 – 5.16 (m, 1H, CH), 3.35 – 2.84 (m, 5H, CH_2, CH). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.1 (d, J_{CP} = 32.3 Hz, CO *trans*), 203.3 (d, J_{CP} = 9.8 Hz, CO *cis*), 168.7 (d, J_{CP} = 4.5 Hz, CO), 143.8 (d, J_{CP} = 1.5 Hz, C), 139.8 (d, J_{CP} = 9.8 Hz, C), 137.8 (d, J_{CP} = 0.8 Hz, C), 131.6 (d, J_{CP} = 7.5 Hz, CH), 131.3 (qd, J_{CF} = 33.0 Hz, J_{CP} = 0.8 Hz, C), 130.7 (s, CH), 129.2 (s, CH), 128.9 (s, CH), 128.3 (s, CH), 127.0 (s, CH), 125.6 (s, CH), 125.5 (d, J_{CP} = 3.8 Hz, CH), 123.6 (q, J_{CF} = 270.8 Hz, CF_3), 118.3 (s, CH), 102.6 (d, J_{CP} = 5.3 Hz, CH), 75.5 (s, C), 49.1 (d, J_{CP} = 6.8 Hz, CH), 31.2 (d, J_{CP} = 11.3 Hz, CH_2), 28.1 (d, J_{CP} = 3.0 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{29}H_{20}MoNO_7PF_3$ $(M+H)^+$ 679.9978, found 679.9979.



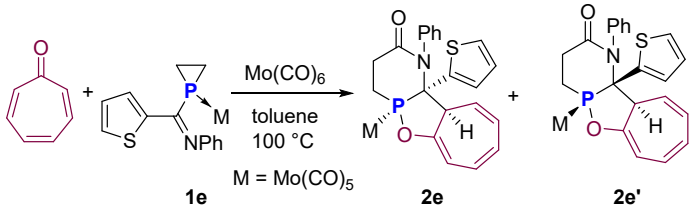
Under the atmosphere of N_2, a solution of **1d** (158.09 mg, 0.30 mmol), $Mo(CO)_6$

(79.20 mg, 0.30 mmol) and tropone (58.35 μL, 0.60 mmol) in toluene (6 mL) were stirred at 100 °C for 4 h in a heavy wall pressure tube (75 mL). The precipitate was filtered off, and the filtrate was concentrated under vacuum. The resulting brown oil was further purified by thin layer chromatography (petroleum ether/dichloromethane = 1:2), yielding **2d** (71.39 mg, 0.11 mmol, 36%, R_f = 0.54) as brown oil and **2d'** (67.42 mg, 0.10 mmol, 34%, R_f = 0.31) as brown oil.

2d: ^{31}P NMR (121 MHz, $CDCl_3$) δ: 160.0 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.66 – 7.63 (m, 4H, CH), 7.39 – 7.37 (m, 3H, CH), 7.14 – 7.06 (m, 4H, CH), 6.96 – 6.94 (m, 1H, CH), 6.82 – 6.76 (m, 1H, CH), 6.71 – 6.66 (m, 1H, CH), 6.52 – 6.47 (m, 1H, CH), 6.17 (d, *J* = 6.0 Hz, 1H, CH), 5.77 – 5.72 (m, 1H, CH), 3.46 – 3.24 (m, 4H, CH_2, CH), 2.22 (d, *J* = 12.9 Hz, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.4 (d, J_{CP} = 34.5 Hz, CO *trans*), 203.3 (d, J_{CP} = 9.8 Hz, CO *cis*), 170.2 (d, J_{CP} = 3.8 Hz, CO), 149.0 (d, J_{CP} = 9.0 Hz, C), 139.7 (d, J_{CP} = 2.3 Hz, C), 136.2 (s, C), 132.91 (s, C), 132.88 (s, C), 129.8 (s, CH), 128.5 (s, CH, three kinds of carbon signals overlapping), 128.1 (s, CH, three kinds of carbon signals overlapping), 127.5 (s, CH), 127.4 (s, CH), 127.2 (s, CH), 127.1 (s, CH), 126.9 (s, CH), 126.5 (s, CH), 120.8 (s, CH), 103.2 (d, J_{CP} = 3.8 Hz, CH), 75.7 (d, J_{CP} = 9.0 Hz, C), 50.6 (d, J_{CP} = 2.3 Hz, CH), 28.6 (d, J_{CP} = 3.8 Hz, CH_2), 25.9 (d, J_{CP} = 6.0 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{32}H_{23}MoNO_7P$ $(M+H)^+$ 662.0261, found 662.0259.

2d': ^{31}P NMR (121 MHz, $CDCl_3$) δ: 170.7 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.84 – 7.82 (m, 2H, CH), 7.76 – 7.70 (m, 2H, CH), 7.56 – 7.48 (m, 2H, CH), 7.17 – 7.03 (m, 4H, CH), 6.71 – 6.65 (m, 1H, CH), 6.57 – 6.51 (m, 1H, CH), 6.38 (bs, 2H, CH), 6.20 – 6.15 (m, 1H, CH), 6.09 (d, *J* = 5.7 Hz, 1H, CH), 5.35 – 5.30 (m, 1H, CH), 3.33 – 2.97 (m, 5H, CH_2, CH). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.6 (d, J_{CP} = 32.3 Hz, CO *trans*), 203.5 (d, J_{CP} = 9.8 Hz, CO *cis*), 169.0 (d, J_{CP} = 5.3 Hz, CO), 143.9 (s, C), 137.9 (s, C), 133.0 (s, C), 132.9 (d, J_{CP} = 9.8 Hz, C), 132.7 (s, C), 131.4 (d, J_{CP} = 9.0 Hz, CH), 130.8 (s, CH), 129.2 (s, CH), 128.8 (s, CH), 128.5 (s, CH), 128.2 (s, CH), 128.1 (s, CH), 127.8 (d, J_{CP} = 6.8 Hz, CH), 127.7 (s, CH), 127.5 (s, CH), 127.0 (s, CH), 126.9 (s, CH), 125.3 (s, CH), 118.8 (s, CH), 102.4 (d, J_{CP} = 5.3 Hz, CH), 76.0 (s, C), 49.2 (d, J_{CP} = 6.0 Hz, CH), 31.4 (d, J_{CP} = 11.3 Hz, CH_2), 28.4 (d, J_{CP} = 4.5 Hz,

CH_2). **HRMS (ESI)**: m/z calcd for $C_{32}H_{22}MoNO_7PNa$ $(M+Na)^+$ 684.0080, found 684.0081.

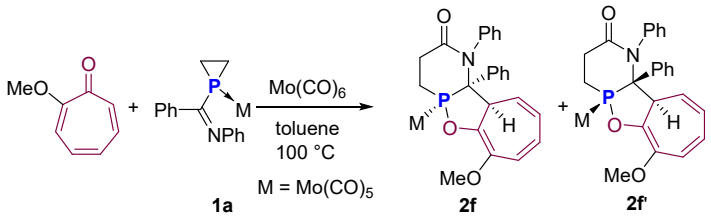


Under the atmosphere of N_2, a solution of **1e** (144.88 mg, 0.30 mmol), $Mo(CO)_6$ (79.20 mg, 0.30 mmol) and tropone (58.35 μL, 0.60 mmol) in toluene (6 mL) were stirred at 100 °C for 4 h in a heavy wall pressure tube (75 mL). The precipitate was filtered off, and the filtrate was concentrated under vacuum. The resulting brown oil was further purified by thin layer chromatography (petroleum ether/dichloromethane = 1:5), yielding **2e** (90.69 mg, 0.15 mmol, 49%, R_f = 0.65) as brown solid and **2e'** (44.42 mg, 0.07 mmol, 24%, R_f = 0.45) as brown solid.

2e: m.p. 123.5 – 124.3 °C. ^{31}P NMR (121 MHz, $CDCl_3$) δ: 164.5 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.21 – 7.06 (m, 6H, CH), 6.81 – 6.59 (m, 4H, CH), 6.46 – 6.41 (m, 1H, CH), 6.14 (d, J = 6.0 Hz, 1H, CH), 5.61 (dd, J = 9.3, J = 4.8 Hz, 1H, CH), 3.43 – 3.12 (m, 4H, CH, CH_2), 2.22 – 2.18 (m, 1H, CH). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.4 (d, J_{CP} = 34.5 Hz, CO *trans*), 203.4 (d, J_{CP} = 9.8 Hz, CO *cis*), 169.6 (d, J_{CP} = 3.8 Hz, CO), 148.3 (d, J_{CP} = 9.8 Hz, C), 142.9 (s, C), 139.6 (d, J_{CP} = 3.8 Hz, C), 129.9 (s, CH), 128.5 (s, CH), 128.4 (d, J_{CP} = 6.0 Hz, CH), 128.3 (s, CH), 127.4 (s, CH), 127.3 (s, CH), 127.1 (s, CH), 126.8 (d, J_{CP} = 2.3 Hz, CH), 126.4 (d, J_{CP} = 3.0 Hz, CH), 120.4 (s, CH), 103.8 (d, J_{CP} = 3.8 Hz, CH), 74.0 (d, J_{CP} = 12.0 Hz, C), 52.9 (d, J_{CP} = 3.8 Hz, CH), 28.6 (d, J_{CP} = 3.0 Hz, CH_2), 25.7 (d, J_{CP} = 6.0 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{26}H_{19}MoNO_7PS$ $(M+H)^+$ 617.9668, found 617.9671.

2e': m.p. > 280 °C (dec). **^{31}P NMR (121 MHz, $CDCl_3$)** δ: 172.2 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.50 (d, J = 4.8 Hz, 1H, CH), 7.22 – 7.13 (m, 3H, CH), 6.98 – 6.95 (m, 1H, CH), 6.81 (d, J = 3.6 Hz, 1H, CH), 6.69 – 6.64 (m, 1H, CH), 6.54 – 6.48 (m, 3H, CH), 6.20 (dd, J = 9.0, J = 5.7 Hz, 1H, CH), 6.06 (d, J = 6.0 Hz, 1H, CH), 5.59 – 5.54 (m, 1H, CH), 3.22 – 2.91 (m, 5H, CH_2, CH). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.5 (d, J_{CP} = 32.3 Hz, CO *trans*), 203.4 (d, J_{CP} = 9.8Hz, CO *cis*), 168.9 (d, J_{CP} = 4.5

Hz, CO), 143.0 (s, C), 137.9 (d, J_{CP} = 13.5 Hz, C), 137.3 (s, C), 132.0 (d, J_{CP} = 6.8 Hz, CH), 130.2 (s, CH), 129.3 (s, CH), 128.8 (s, CH), 128.2 (s, CH), 127.7 (s, CH), 127.0 (s, CH), 126.9 (s, CH), 125.4 (s, CH), 118.0 (s, CH), 102.3 (d, J_{CP} = 6.0 Hz, CH), 72.3 (s, C), 50.2 (d, J_{CP} = 6.0 Hz, CH), 31.0 (d, J_{CP} = 12.0 Hz, CH_2), 28.2 (d, J_{CP} = 4.5 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{26}H_{19}MoNO_7PS$ $(M+H)^+$ 617.9668, found 617.9666.

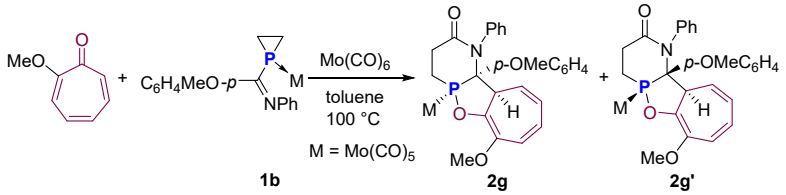


Under the atmosphere of N_2, a solution of **1a** (143.09 mg, 0.30 mmol), $Mo(CO)_6$ (79.20 mg, 0.30 mmol) and 2-methoxytropone (81.63 mg, 0.60 mmol) in toluene (6 mL) were stirred at 100 °C for 4 h in a heavy wall pressure tube (75 mL). The precipitate was filtered off, and the filtrate was concentrated under vacuum. The resulting brown oil was further purified by thin layer chromatography (petroleum ether/ethyl acetate = 2:1), yielding **2f** (44.23 mg, 0.07 mmol, 23%, R_f = 0.71) as yellow oil and **2f'** (28.85 mg, 0.05 mmol, 15%, R_f = 0.30) as yellow oil.

2f: ^{31}P NMR (121 MHz, $CDCl_3$) δ: 164.7 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.19 – 7.11 (m, 7H, CH), 7.05 – 7.01 (m, 3H, CH), 6.75 – 6.61 (m, 2H, CH), 6.42 – 6.37 (m, 1H, CH), 5.83 (dd, J = 9.3, J = 5.1 Hz, 1H, CH), 3.81 (s, 3H, OCH_3), 3.49 – 3.11 (m, 4H, CH_2, CH), 2.28 – 2.23 (m, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.6 (d, J_{CP} = 33.8 Hz, CO *trans*), 203.4 (d, J_{CP} = 10.5 Hz, CO *cis*), 170.1 (d, J_{CP} = 4.5 Hz, CO), 139.5 (d, J_{CP} = 3.0 Hz, C), 138.5 (d, J_{CP} = 1.5 Hz, C), 137.0 (d, J_{CP} = 4.5 Hz, C), 134.4 (d, J_{CP} = 8.3 Hz, C), 128.6 (d, J_{CP} = 2.3 Hz, CH), 128.4 (s, CH, two kinds of carbon signals overlapping), 128.1 (s, CH), 128.07 (s, CH, two kinds of carbon signals overlapping), 128.0 (s, CH), 127.0 (s, CH), 126.1 (s, CH), 123.3 (s, CH), 75.8 (d, J_{CP} = 8.3 Hz, C), 59.8 (s, OCH_3), 48.1 (d, J_{CP} = 3.0 Hz, CH), 28.6 (d, J_{CP} = 3.8 Hz, CH_2), 25.9 (d, J_{CP} = 6.0 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{29}H_{23}MoNO_8P$ $(M+H)^+$ 642.0210, found 642.0213.

2f': ^{31}P NMR (121 MHz, $CDCl_3$) δ: 172.5 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.42 –

7.34 (m, 3H, CH), 7.21 – 7.11 (m, 5H, CH), 6.67 – 6.52 (m, 2H, CH), 6.38 (bs, 2H, CH), 6.12 – 6.08 (m, 1H, CH), 5.46 – 5.41 (m, 1H, CH), 3.67 (s, 3H, OCH_3), 3.32 – 2.91 (m, 5H, CH_2, CH). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.6 (d, J_{CP} = 32.3 Hz, CO *trans*), 203.6 (d, J_{CP} = 9.8 Hz, CO cis), 168.9 (d, J_{CP} = 4.5 Hz, CO), 137.8 (s, C), 136.9 (d, J_{CP} = 6.0 Hz, C), 135.4 (d, J_{CP} = 11.3 Hz, C), 131.2 (d, J_{CP} = 8.3 Hz, CH), 130.7 (s, CH), 129.6 (s, C), 129.3 (s, CH), 128.7 (s, CH), 128.66 (s, CH), 128.3 (s, CH), 128.1 (s, CH), 125.9 (s, CH), 123.9 (s, CH), 120.4 (s, CH), 76.0 (s, C), 60.3 (s, OCH_3), 45.9 (d, J_{CP} = 7.5 Hz, CH), 31.6 (d, J_{CP} = 11.3 Hz, CH_2), 28.4 (d, J_{CP} = 4.5 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{29}H_{23}MoNO_8P$ $(M+H)^+$ 642.0210, found 642.0210.

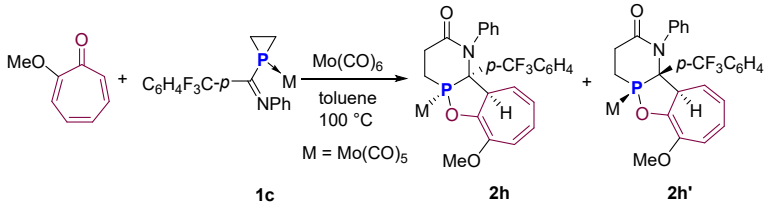


Under the atmosphere of N_2, a solution of **1b** (152.09 mg, 0.30 mmol), $Mo(CO)_6$ (79.20 mg, 0.30 mmol) and 2-methoxytropone (81.63 mg, 0.60 mmol) in toluene (6 mL) were stirred at 100 °C for 4 h in a heavy wall pressure tube (75 mL). The precipitate was filtered off, and the filtrate was concentrated under vacuum. The resulting brown oil was further purified by thin layer chromatography (petroleum ether/dichloromethane = 1:7), yielding **2g** (36.24 mg, 0.05 mmol, 18%, R_f = 0.41) as yellowish solid and **2g'** (24.16 mg, 0.04 mmol, 12%, R_f = 0.32) as yellow solid.

2g: m.p. > 280 °C (dec). **^{31}P NMR (121 MHz, $CDCl_3$)** δ: 164.4 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.18 – 7.13 (m, 3H, CH), 7.07 – 7.00 (m, 4H, CH), 6.74 – 6.61 (m, 4H, CH), 6.42 – 6.37 (m, 1H, CH), 5.85 – 5.81 (m, 1H, CH), 3.80 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.49 – 3.07 (m, 4H, CH_2, CH), 2.26 – 2.21 (m, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.6 (d, J_{CP} = 33.8 Hz, CO *trans*), 203.5 (d, J_{CP} = 9.8 Hz, CO *cis*), 170.2 (d, J_{CP} = 3.8 Hz, CO), 159.5 (d, J_{CP} = 2.3 Hz, C), 139.5 (d, J_{CP} = 3.0 Hz, C), 136.6 (d, J_{CP} = 4.5 Hz, C), 134.6 (d, J_{CP} = 9.8 Hz, C), 130.3 (d, J_{CP} = 0.8 Hz, C), 128.5 (s, CH two kinds of carbon signals overlapping), 128.1 (s, CH, two kinds of carbon signals overlapping), 128.08 (d, J_{CP} = 3.8 Hz, CH), 127.0 (s, CH), 126.1 (s,

CH), 123.7 (s, CH), 113.8 (s, CH), 75.2 (d, J_{CP} = 10.5 Hz, C), 59.8 (s, OCH_3), 55.2 (s, OCH_3), 48.2 (d, J_{CP} = 3.8 Hz, CH), 28.6 (d, J_{CP} = 3.8 Hz, CH_2), 25.7 (d, J_{CP} = 5.3 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{30}H_{25}MoNO_9P$ $(M+H)^+$ 672.0316, found 672.0314.

2g': m.p. > 280 °C (dec). **^{31}P NMR (121 MHz, $CDCl_3$)** δ: 173.2 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.21 – 7.10 (m, 3H, CH), 7.03 – 7.00 (m, 2H, CH), 6.88 – 6.85 (m, 2H, CH), 6.67 – 6.63 (m, 1H, CH), 6.57 – 6.51 (m, 1H, CH), 6.40 (bs, 2H, CH), 6.12 – 6.07 (m, 1H, CH), 5.44 (dd, J = 9.0, J = 6.0 Hz, 1H, CH), 3.82 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.28 – 2.88 (m, 5H, $2CH_2$, CH). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.7 (d, J_{CP} = 32.3 Hz, CO *trans*), 203.6 (d, J_{CP} = 9.8 Hz, CO *cis*), 168.9 (d, J_{CP} = 5.3 Hz, CO), 160.1 (s, C), 137.8 (s, C), 136.8 (d, J_{CP} = 6.0 Hz, C), 132.5 (d, J_{CP} = 7.5 Hz, CH), 130.7 (s, CH), 130.0 (s, C), 128.7 (s, CH), 128.3 (s, CH), 128.0 (s, CH), 127.3 (d, J_{CP} = 11.3 Hz, C), 126.1 (s, CH), 123.9 (s, CH), 120.9 (s, CH), 114.0 (s, CH), 75.6 (s, C), 60.3 (s, OCH_3), 55.5 (s, OCH_3), 46.2 (d, J_{CP} = 6.8 Hz, CH), 31.4 (d, J_{CP} = 11.3 Hz, CH_2), 28.3 (d, J_{CP} = 4.5 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{30}H_{25}MoNO_9P$ $(M+H)^+$ 672.0316, found 672.0319.

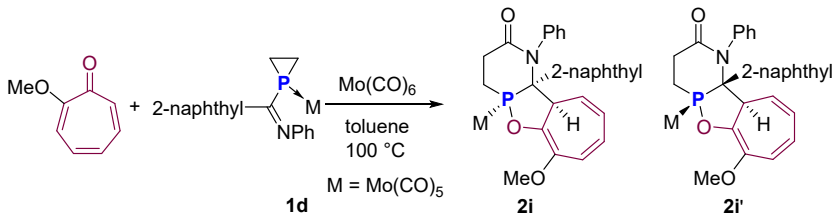


Under the atmosphere of N_2, a solution of **1c** (152.09 mg, 0.30 mmol), $Mo(CO)_6$ (79.20 mg, 0.30 mmol) and 2-methoxytropone (81.63 mg, 0.60 mmol) in toluene (6 mL) were stirred at 100 °C for 4 h in a heavy wall pressure tube (75 mL). The precipitate was filtered off, and the filtrate was concentrated under vacuum. The resulting brown oil was further purified by thin layer chromatography (petroleum ether/ ethyl acetate = 3:1), yielding **2h** (51.05 mg, 0.07 mmol, 24%, R_f = 0.60) as yellow oil and **2h'** (8.51 mg, 0.01 mmol, 4%, R_f = 0.30) as yellow oil.

2h: ^{31}P NMR (121 MHz, $CDCl_3$) δ: 165.1 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.45 – 7.43 (m, 4H, CH), 7.19 – 7.14 (m, 2H, CH), 7.08 – 7.00 (m, 3H, CH), 6.77 – 6.64 (m, 2H, CH), 6.44 – 6.39 (m, 1H, CH), 5.86 – 5.81 (m, 1H, CH), 3.80 (s, 3H, OCH_3), 3.55

– 3.11 (m, 4H, CH_2, CH), 2.28 (d, J = 12.3 Hz, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 206.9 (d, J_{CP} = 34.5 Hz, CO *trans*), 203.2 (d, J_{CP} = 9.8 Hz, CO *cis*), 169.9 (d, J_{CP} = 4.5 Hz, CO), 143.0 (s, C), 139.3 (d, J_{CP} = 3.8 Hz, C), 136.9 (d, J_{CP} = 4.5 Hz, C), 134.2 (d, J_{CP} = 10.5 Hz, C), 130.6 (qd, J_{CF} = 32.3 Hz, J_{CP} = 3.0 Hz, C), 128.7 (s, CH), 128.4 (s, CH), 127.92 (d, J_{CP} = 8.3 Hz, CH), 127.87 (s, CH, two kinds of carbon signals overlapping), 127.3 (s, CH), 126.4 (s, CH), 125.6 – 125.4 (m, CH), 123.5 (q, J_{CF} = 270.8 Hz, CF_3), 123.2 (s, CH), 75.9 (d, J_{CP} = 6.8 Hz, C), 59.8 (s, OCH_3), 48.3 (d, J_{CP} = 3.0 Hz, CH), 28.5 (d, J_{CP} = 3.0 Hz, CH_2), 26.0 (d, J_{CP} = 6.0 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{30}H_{22}MoNO_8PF_3$ $(M+H)^+$ 710.0084, found 710.0087.

2h': ^{31}P NMR (121 MHz, $CDCl_3$) δ: 172.1 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.63 (d, J = 8.1 Hz, 2H, CH), 7.29 (d, J = 8.1 Hz, 2H, CH), 7.21 – 7.12 (m, 3H, CH), 6.66 – 6.53 (m, 2H, CH), 6.41 (d, J = 2.4 Hz, 2H, CH), 6.11 (dd, J = 8.4, J = 5.7 Hz, 1H, CH), 5.26 (dd, J = 9.0, J = 5.7 Hz, 1H, CH), 3.69 (s, 1H, OCH_3), 3.32 – 2.89 (m, 5H, CH_2, CH). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.1 (d, J_{CP} = 32.3 Hz, CO *trans*), 203.4 (d, J_{CP} = 9.0 Hz, CO *cis*), 169.0 (d, J_{CP} = 5.3 Hz, CO), 139.7 (d, J_{CP} = 9.8 Hz, C), 137.6 (d, J_{CP} = 0.8 Hz, C), 137.4 (d, J_{CP} = 6.0 Hz, C), 131.6 (s, CH), 131.5 (s, CH), 131.4 (qd, J_{CF} = 33.0 Hz, J_{CP} = 0.8 Hz, C), 130.6 (s, CH), 129.0 (s, CH), 128.8 (s, C), 128.3 (d, J_{CP} = 2.3 Hz, CH), 125.5 (d, J_{CP} = 3.8 Hz, CH), 125.4 (s, CH), 124.2 (s, CH), 123.5 (q, J_{CF} = 271.5 Hz, CF_3), 118.6 (s, CH), 75.7 (d, J_{CP} = 0.8 Hz, C), 60.2 (s, OCH_3), 45.8 (d, J_{CP} = 6.8 Hz, CH), 31.5 (d, J_{CP} = 11.3 Hz, CH_2), 28.2 (d, J_{CP} = 3.8 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{30}H_{22}MoNO_8PF_3$ $(M+H)^+$ 710.0084, found 710.0083.

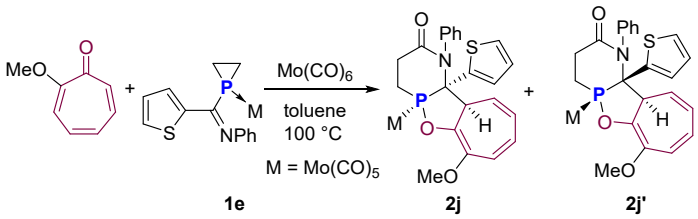


Under the atmosphere of N_2, a solution of **1d** (158.09 mg, 0.30 mmol), $Mo(CO)_6$ (79.20 mg, 0.30 mmol) and 2-methoxytropone (81.63 mg, 0.60 mmol) in toluene (6 mL) were stirred at 100 °C for 4 h in a heavy wall pressure tube (75 mL). The precipitate was filtered off, and the filtrate was concentrated under vacuum. The

resulting brown oil was further purified by thin layer chromatography (petroleum ether/ ethyl acetate = 4:1), yielding **2i** (43.53 mg, 0.06 mmol, 21%, R_f = 0.50) as yellow oil and **2i'** (31.10 mg, 0.05 mmol, 15%, R_f = 0.28) as yellow oil.

2i: ^{31}P NMR (121 MHz, $CDCl_3$) δ: 160.8 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.67 – 7.65 (m, 3H, CH), 7.41 – 7.38 (m, 4H, CH), 7.11 – 7.09 (m, 4H, CH), 6.97 – 6.95 (m, 1H, CH), 6.81 – 6.77 (m, 1H, CH), 6.71 – 6.65 (m, 1H, CH), 6.45 – 6.40 (m, 1H, CH), 5.90 – 5.85 (m, 1H, CH), 3.84 (s, 3H, OCH_3), 3.54 – 3.27 (m, 4H, CH_2, CH), 2.28 (d, J = 13.5 Hz, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.4 (d, J_{CP} = 33.8 Hz, CO *trans*), 203.3 (d, J_{CP} = 9.8 Hz, CO *cis*), 170.2 (d, J_{CP} = 4.5 Hz, CO), 139.6 (d, J_{CP} = 3.8 Hz, C), 136.9 (d, J_{CP} = 3.8 Hz, C), 136.1 (d, J_{CP} = 0.8 Hz, C), 134.5 – 134.3 (m, C), 132.9 (d, J_{CP} = 1.5 Hz, C, two kinds of carbon signals overlapping), 128.5 (s, CH, three kinds of carbon signals overlapping), 128.2 (s, CH), 128.1 (s, CH, four kinds of carbon signals overlapping), 127.4 (s, CH), 127.1 (s, CH), 126.9 (s, CH), 126.6 (s, CH), 126.2 (s, CH), 123.3 – 123.2 (m, CH), 76.0 (d, J_{CP} = 8.3 Hz, C), 59.8 (s, OCH_3), 48.3 (d, J_{CP} = 2.3 Hz, CH), 28.6 (d, J_{CP} = 3.8 Hz, CH_2), 25.9 (d, J_{CP} = 6.0 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{33}H_{25}MoNO_8P$ $(M+H)^+$ 692.0366, found 692.0366.

2i': ^{31}P NMR (121 MHz, $CDCl_3$) δ: 173.0 (s). **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.86 – 7.82 (m, 2H, CH), 7.78 – 7.75 (m, 1H, CH), 7.70 (s, 1H, CH), 7.59 – 7.51 (m, 2H, CH), 7.19 – 7.07 (m, 4H, CH), 6.68 – 6.64 (m, 1H, CH), 6.59 – 6.54 (m, 1H, CH), 6.44 (bs, 2H, CH), 6.10 (dd, J = 9.0, J = 5.4 Hz, 1H, CH), 5.44 (dd, J = 9.0, J = 5.7 Hz, 1H, CH), 3.69 (s, 3H, OCH_3), 3.33 – 3.02 (m, 5H, CH_2, CH). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 207.5 (d, J_{CP} = 32.3 Hz, CO *trans*), 203.6 (d, J_{CP} = 9.8 Hz, CO *cis*), 169.2 (d, J_{CP} = 5.3 Hz, CO), 137.8 (d, J_{CP} = 0.8 Hz, C), 137.0 (d, J_{CP} = 6.0 Hz, C), 132.9 (s, C), 132.8 (d, J_{CP} = 11.3 Hz, C), 132.6 (s, C), 131.4 (s, CH), 131.3 (s, CH), 130.7 (s, CH), 129.8 (s, C), 128.8 (s, CH), 128.5 (s, CH), 128.4 (s, CH), 128.1 (d, J_{CP} = 3.0 Hz, CH), 127.75 (d, J_{CP} = 3.8 Hz, CH), 127.7 (d, J_{CP} = 3.8 Hz, CH), 127.5 (s, CH), 127.1 (s, CH), 125.9 (s, CH), 124.1 (s, CH), 120.6 (s, CH), 76.1 (s, C), 60.2 (s, OCH_3), 46.2 (d, J_{CP} = 6.8 Hz, CH), 31.7 (d, J_{CP} = 12.0 Hz, CH_2), 28.6 (d, J_{CP} = 3.8 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{33}H_{25}MoNO_8P$ $(M+H)^+$ 692.0366, found 692.0367.

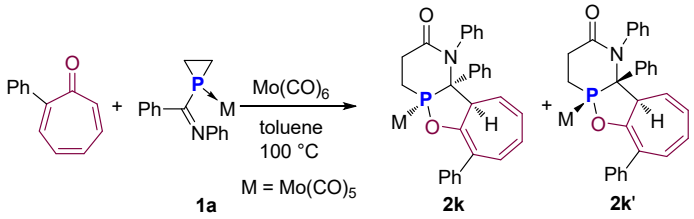


Under the atmosphere of N_2, a solution of **1e** (144.88 mg, 0.30 mmol), $Mo(CO)_6$ (79.20 mg, 0.30 mmol) and 2-methoxytropone (81.63 mg, 0.60 mmol) in toluene (6 mL) were stirred at 100 °C for 4 h in a heavy wall pressure tube (75 mL). The precipitate was filtered off, and the filtrate was concentrated under vacuum. The resulting brown oil was further purified by thin layer chromatography (petroleum ether/ ethyl acetate = 2:1), yielding **2j** (52.40 mg, 0.08 mmol, 27%, R_f = 0.60) as yellow oil and **2j'** (15.53 mg, 0.02 mmol, 8%, R_f = 0.40) as yellow oil.

2j: ^{31}P NMR (121 MHz, $CDCl_3$) δ: 165.1 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.22 – 7.17 (m, 2H, CH), 7.13 – 7.03 (m, 4H, CH), 6.86 – 6.76 (m, 2H, CH), 6.72 – 6.59 (m, 2H, CH), 6.39 – 6.35 (m, 1H, CH), 5.79 – 5.74 (m, 1H, CH), 3.82 (s, 3H, OCH_3), 3.52 – 3.15 (m, 4H, CH_2, CH), 2.27 – 2.23 (m, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.4 (d, J_{CP} = 34.5 Hz, CO *trans*), 203.4 (d, J_{CP} = 9.8 Hz, CO *cis*), 169.6 (d, J_{CP} = 3.8 Hz, CO), 142.7 (s, C), 139.5 (d, J_{CP} = 3.8 Hz, C), 137.0 (d, J_{CP} = 4.5 Hz, C), 133.7 (d, J_{CP} = 9.8 Hz, C), 128.6 (d, J_{CP} = 6.0 Hz, CH), 128.5 (s, CH), 128.4 (s, CH), 128.2 (s, CH), 128.1 (s, CH), 127.3 (s, CH), 126.9 (d, J_{CP} = 2.3 Hz, CH), 126.2 (s, CH), 126.1 (s, CH), 123.4 (s, CH), 74.3 (d, J_{CP} = 12.0 Hz, C), 59.7 (s, OCH_3), 50.8 (d, J_{CP} = 3.8 Hz, CH), 28.6 (d, J_{CP} = 3.0 Hz, CH_2), 25.6 (d, J_{CP} = 6.0 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{27}H_{21}MoNO_8PS$ $(M+H)^+$ 647.9774, found 647.9778.

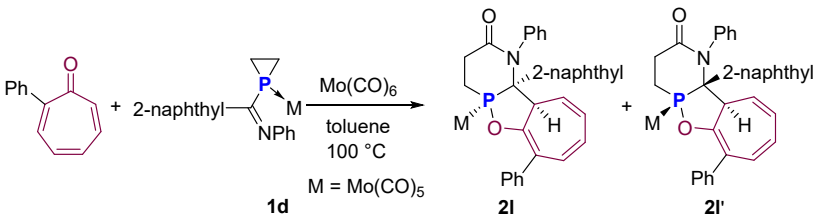
2j': ^{31}P NMR (121 MHz, $CDCl_3$) δ: 174.4 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.50 (dd, J = 5.1, J = 0.9 Hz, 1H, CH), 7.23 – 7.17 (m, 3H, CH), 6.99 – 6.96 (m, 1H, CH), 6.79 – 6.78 (m, 1H, CH), 6.67 – 6.50 (m, 4H, CH), 6.15 – 6.09 (m, 1H, CH), 5.72 (dd, J = 9.3, J = 5.7 Hz, 1H, CH), 3.66 (s, 3H, OCH_3), 3.24 – 2.85 (m, 5H, CH_2, CH). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.5 (d, J_{CP} = 32.3 Hz, CO *trans*), 203.5 (d, J_{CP} = 9.8 Hz, CO *cis*), 169.0 (d, J_{CP} = 4.5 Hz, CO), 137.8 (d, J_{CP} = 13.5 Hz, C), 137.2 (s, C), 136.6 (d, J_{CP} = 6.0 Hz, C), 131.9 (d, J_{CP} = 6.8 Hz, CH), 130.2 (s, C), 130.1 (s, CH), 128.8 (s, CH), 128.6 (s, CH), 128.3 (s, CH), 127.7 (s, CH), 126.9 (s, CH), 126.7 (s, CH), 124.3

(s, CH), 121.6 (s, CH), 72.4 (s, C), 60.3 (s, OCH_3), 47.6 (d, J_{CP} = 6.8 Hz, CH), 31.3 (d, J_{CP} = 12.0 Hz, CH_2), 28.3 (d, J_{CP} = 4.5 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{27}H_{21}MoNO_8PS$ $(M+H)^+$ 647.9774, found 647.9772.



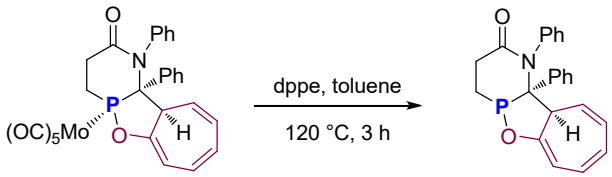
Under the atmosphere of N_2, a solution of **1a** (143.09 mg, 0.30 mmol), $Mo(CO)_6$ (79.20 mg, 0.30 mmol) and 2-phenyltropone (109.24 g, 0.60 mmol) in toluene (6 mL) were stirred at 100 °C for 4 h in a heavy wall pressure tube (75 mL). The precipitate was filtered off, and the filtrate was concentrated under vacuum. The resulting brown oil was further purified by thin layer chromatography (petroleum ether/ethyl acetate = 4:1), yielding **2k** (96.87 mg, 0.14 mmol, 47%, R_f = 0.41) as brown solid and traces of **2k'**.

2k: m.p. 135.9 – 136.5 °C. **^{31}P NMR (121 MHz, $CDCl_3$)** δ: 164.4. **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.49 – 7.29 (m, 6H, CH), 7.21 – 7.13 (m, 5H, CH), 7.08 – 6.94 (m, 5H, CH), 6.86 – 6.81 (m, 1H, CH), 6.58 – 6.54 (m, 1H, CH), 5.93 – 5.88 (m, 1H, CH), 3.44 – 3.21 (m, 4H, CH_2, CH), 2.24 – 2.18 (m, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.6 (d, J_{CP} = 34.5 Hz, CO *trans*), 203.3 (d, J_{CP} = 9.8 Hz, CO *cis*), 170.0 (d, J_{CP} = 4.5 Hz, CO), 144.4 (d, J_{CP} = 10.5 Hz, C), 139.6 (d, J_{CP} = 3.8 Hz, C), 138.7 (d, J_{CP} = 1.5 Hz, C), 136.2 (s, C), 133.4 (s, CH), 129.6 (s, CH, two kinds of carbon signals overlapping), 128.72 (s, CH), 128.68 (s, CH), 128.5 (s, CH), 128.4 (s, CH), 128.2 (s, CH), 128.2 (s, CH), 127.4 (s, CH), 127.1 (s, CH), 127.0 (s, CH), 122.9 (s, CH), 115.3 (d, J_{CP} = 3.8 Hz, CH), 75.5 (d, J_{CP} = 8.3 Hz, C), 50.9 (d, J_{CP} = 3.0 Hz, CH), 28.4 (d, J_{CP} = 3.0 Hz, CH_2), 25.9 (d, J_{CP} = 6.0 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{34}H_{25}MoNO_7P$ $(M+H)^+$ 688.0418, found 688.0503.



Under the atmosphere of N_2, a solution of **1d** (158.09 mg, 0.30 mmol), $Mo(CO)_6$ (79.20 mg, 0.30 mmol) and 2-phenyltropone (109.24 g, 0.60 mmol) in toluene (6 mL) were stirred at 100 °C for 4 h in a heavy wall pressure tube (75 mL). The precipitate was filtered off, and the filtrate was concentrated under vacuum. The resulting brown oil was further purified by thin layer chromatography (petroleum ether/ethyl acetate = 4:1), yielding **2l** (101.72 mg, 0.14 mmol, 46%, R_f = 0.43) as yellow oil and traces of **2l'**.

2l: ^{31}P NMR (121 MHz, $CDCl_3$) δ: 160.7. **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.72 – 7.66 (m, 4H, CH), 7.51 – 7.24 (m, 8H, CH), 7.17 – 6.85 (m, 7H, CH), 6.61 – 6.56 (m, 1H, CH), 5.97 – 5.93 (m, 1H, CH), 3.50 – 3.17 (m, 4H, CH_2, CH), 2.28 – 2.15 (m, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 207.5 (d, J_{CP} = 34.5 Hz, CO *trans*), 203.3 (d, J_{CP} = 9.8 Hz, CO *cis*), 170.1 (d, J_{CP} = 3.8 Hz, CO), 144.4 (d, J_{CP} = 9.8 Hz, C), 139.7 (d, J_{CP} = 2.3 Hz, C), 136.3 (s, C, two kinds of carbon signals overlapping), 133.5 (s, CH), 133.00 (s, C), 132.98 (s, C), 129.6 (s, CH, two kinds of carbon signals overlapping), 128.6 (s, CH, three kinds of carbon signals overlapping), 128.3 (s, CH, three kinds of carbon signals overlapping), 128.2 (s, CH), 127.5 (s, CH), 127.4 (s, CH), 127.2 (s, CH), 127.1 (s, CH), 127.0 (s, CH), 126.7 (s, CH), 123.0 (s, CH), 115.48 (d, J_{CP} = 3.8 Hz, C), 75.8 (d, J_{CP} = 8.3 Hz, C), 51.3 (d, J_{CP} = 3.8 Hz, CH), 28.5 (d, J_{CP} = 3.0 Hz, CH_2), 26.0 (d, J_{CP} = 5.3 Hz, CH_2). **HRMS (ESI)**: m/z calcd for $C_{38}H_{27}MoNO_7P$ $(M+H)^+$ 738.0574, found 738.0586.



2a **4a**, 65%

Under the atmosphere of N_2, a solution of **2a** (61.10 mg, 0.10 mmol) and dppe (39.81 mg, 0.10 mmol) in toluene (2 mL) were stirred at 120 °C for 3 h in a heavy wall pressure tube (75 mL). The resulting brown solution was purified by thin layer chromatography (petroleum ether/ethyl acetate = 1:2), yielding **4a** (24.30 mg, 0.07 mmol, 65%, R_f = 0.50) as yellow oil.

4a: ^{31}P NMR (121 MHz, $CDCl_3$) δ: 118.3 (s). **^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.19 –

6.98 (m, 10H, CH), 6.74 – 6.59 (m, 2H, CH), 6.48 – 6.43 (m, 1H, CH), 5.94 (d, J = 6.0 Hz, 1H, CH), 5.75 (dd, J = 9.0, 5.1 Hz, 1H, CH), 3.24 – 2.89 (m, 4H, CH_2, CH), 1.96 – 1.87 (m, 1H, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 170.6 (s, CO), 151.8 (d, J_{CP} = 11.3 Hz, C), 140.3 (d, J_{CP} = 11.3 Hz, C), 139.8 (s, C), 130.34 (s, CH), 130.33 (s, CH), 128.5 (s, CH), 128.4 (s, CH), 128.3 (s, CH), 127.8 (s, CH), 127.72 (s, CH), 126.99 (s, CH), 126.4 (s, CH), 121.3 (s, CH), 102.1 (s, CH), 74.3 (d, J_{CP} = 21.8 Hz, C), 47.0 (s, CH), 27.1 (d, J_{CP} = 12.0 Hz, CH_2), 18.0 (d, J_{CP} = 30.0 Hz, CH_2). **HRMS (ESI):** m/z calcd for $C_{23}H_{21}NO_2P$ $(M+H)^+$ 374.1305, found 374.1280.

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[3] A. Khrizman, R. D. Slack, R. C. Remsing, S. Little, V. Yardley and G. Moyna, Synthesis and In *Vitro* Protozoocidal Evaluation of Novel Diazabicyclic Tropolone Derivatives, *Arch. Pharm. Chem. Life Sci.,* 2007, **340**, 569–576.

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X-ray crystallographic data of compound 2a

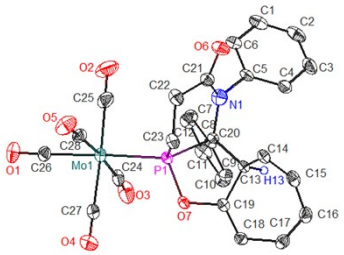


Table 1 Crystal data and structure refinement for 2a (CCDC: 1970636).

Identification code	**2a**
Empirical formula	$C_{28}H_{20}MoNO_7P$
Formula weight	609.36
Temperature/K	300.19
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.9608(12)
b/Å	13.6919(17)
c/Å	21.739(3)
α/°	90
β/°	101.338(4)
γ/°	90
Volume/Å^3	2615.1(6)
Z	0
ρ_{calc}g/cm^3	1.548
μ/mm^{-1}	0.611
F(000)	1232.0
Crystal size/mm^3	0.5 × 0.5 × 0.4
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.654 to 55.174
Index ranges	-11 ≤ h ≤ 11, -17 ≤ k ≤ 17, -27 ≤ l ≤ 28
Reflections collected	32995
Independent reflections	6048 [R_{int} = 0.0666, R_{sigma} = 0.0493]
Data/restraints/parameters	6048/0/415
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0405, wR_2 = 0.0926
Final R indexes [all data]	R_1 = 0.0619, wR_2 = 0.1071
Largest diff. peak/hole / e Å^{-3}	0.61/-0.68

Table 2 Bond Lengths for 2a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mo1	P1	2.4731(8)	C2	C3	1.370(6)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mo1	C24	2.055(4)	C3	C4	1.391(5)
Mo1	C25	2.038(4)	C4	C5	1.372(4)
Mo1	C26	2.028(3)	C5	C6	1.381(4)
Mo1	C27	2.058(4)	C7	C8	1.395(4)
Mo1	C28	2.033(4)	C7	C12	1.380(4)
P1	O7	1.638(2)	C8	C9	1.389(4)
P1	C20	1.888(3)	C8	C20	1.532(4)
P1	C23	1.806(3)	C9	C10	1.382(4)
O1	C26	1.116(4)	C10	C11	1.374(5)
O2	C25	1.134(4)	C11	C12	1.375(5)
O3	C24	1.131(4)	C13	C14	1.503(4)
O4	C27	1.128(4)	C13	C19	1.508(4)
O5	C28	1.134(4)	C13	C20	1.566(3)
O6	C21	1.218(4)	C14	C15	1.338(4)
O7	C19	1.390(3)	C15	C16	1.440(5)
N1	C5	1.450(3)	C16	C17	1.342(5)
N1	C20	1.478(3)	C17	C18	1.446(4)
N1	C21	1.387(4)	C18	C19	1.316(4)
C1	C2	1.367(6)	C21	C22	1.502(4)
C1	C6	1.376(5)	C22	C23	1.523(5)

Table 3 Bond Angles for 2a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C24	Mo1	P1	91.87(8)	C7	C8	C20	120.5(3)
C24	Mo1	C27	86.86(15)	C9	C8	C7	117.4(3)
C25	Mo1	P1	94.81(11)	C9	C8	C20	122.1(2)
C25	Mo1	C24	92.34(15)	C10	C9	C8	121.3(3)
C25	Mo1	C27	177.50(14)	C11	C10	C9	120.3(3)
C26	Mo1	P1	176.02(9)	C10	C11	C12	119.4(3)
C26	Mo1	C24	91.18(12)	C11	C12	C7	120.6(3)
C26	Mo1	C25	87.61(14)	C14	C13	C19	107.4(2)
C26	Mo1	C27	90.04(13)	C14	C13	C20	119.3(2)
C26	Mo1	C28	85.83(12)	C19	C13	C20	106.9(2)
C27	Mo1	P1	87.58(9)	C15	C14	C13	118.7(3)
C28	Mo1	P1	90.98(9)	C14	C15	C16	126.3(3)
C28	Mo1	C24	175.72(13)	C17	C16	C15	126.4(3)
C28	Mo1	C25	90.60(14)	C16	C17	C18	125.8(3)
C28	Mo1	C27	90.07(14)	C19	C18	C17	122.2(3)
O7	P1	Mo1	111.78(7)	O7	C19	C13	113.8(2)
O7	P1	C20	92.80(11)	C18	C19	O7	121.1(2)
O7	P1	C23	104.78(14)	C18	C19	C13	125.0(3)
C20	P1	Mo1	129.50(8)	N1	C20	P1	112.67(18)
C23	P1	Mo1	115.88(11)	N1	C20	C8	111.6(2)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C23	P1	C20	97.86(13)	N1	C20	C13	114.0(2)
C19	O7	P1	114.06(17)	C8	C20	P1	106.20(17)
C5	N1	C20	117.2(2)	C8	C20	C13	110.1(2)
C21	N1	C5	115.7(2)	C13	C20	P1	101.56(16)
C21	N1	C20	126.1(2)	O6	C21	N1	119.6(3)
C2	C1	C6	119.8(4)	O6	C21	C22	119.7(3)
C1	C2	C3	120.4(3)	N1	C21	C22	120.5(3)
C2	C3	C4	120.2(4)	C21	C22	C23	118.0(3)
C5	C4	C3	119.2(3)	C22	C23	P1	108.6(2)
C4	C5	N1	121.3(3)	O3	C24	Mo1	175.8(3)
C4	C5	C6	120.0(3)	O2	C25	Mo1	177.7(3)
C6	C5	N1	118.7(3)	O1	C26	Mo1	177.0(3)
C1	C6	C5	120.3(3)	O4	C27	Mo1	178.0(3)
C12	C7	C8	121.0(3)	O5	C28	Mo1	176.6(3)

X-ray crystallographic data of compound 2a'

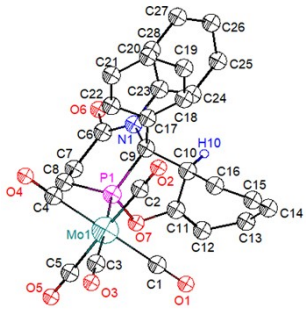


Table 4 Crystal data and structure refinement for 2a' (CCDC: 2122446).

Identification code	**2a'**
Empirical formula	$C_{28}H_{20}MoNO_7P$
Formula weight	609.36
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.1503(6)
b/Å	10.2283(7)
c/Å	17.1133(11)
α/°	95.243(5)
β/°	91.796(6)
γ/°	115.453(7)
Volume/Å^3	1435.70(18)
Z	1
ρ_{calc}g/cm^3	1.508
μ/mm^{-1}	5.516
F(000)	658.0

Crystal size/mm^3	0.16 × 0.12 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.642 to 134.136
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 10, -18 ≤ l ≤ 20
Reflections collected	10148
Independent reflections	5120 [R_{int} = 0.0377, R_{sigma} = 0.0530]
Data/restraints/parameters	5120/1/363
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0423, wR_2 = 0.1009
Final R indexes [all data]	R_1 = 0.0535, wR_2 = 0.1085
Largest diff. peak/hole / e Å^{-3}	0.69/-0.49

Table 5 Bond Lengths for 2a'.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mo1	P1	2.4708(9)	C10	C11	1.500(5)
Mo1	C1	2.056(5)	C10	C16	1.505(5)
Mo1	C2	2.056(4)	C11	C12	1.332(5)
Mo1	C3	2.023(5)	C12	C13	1.435(6)
Mo1	C4	2.026(5)	C13	C14	1.345(7)
Mo1	C5	2.041(5)	C14	C15	1.438(7)
P1	O7	1.666(3)	C15	C16	1.328(6)
P1	C8	1.815(4)	C17	C18	1.387(5)
P1	C9	1.883(3)	C17	C22	1.383(5)
O1	C1	1.126(6)	C18	C19	1.397(6)
O2	C2	1.127(5)	C19	C20	1.360(7)
O3	C3	1.131(6)	C20	C21	1.370(7)
O4	C4	1.140(7)	C21	C22	1.398(6)
O5	C5	1.123(7)	C23	C24	1.386(5)
O6	C6	1.216(5)	C23	C28	1.383(5)
O7	C11	1.383(4)	C24	C25	1.380(6)
N1	C6	1.363(4)	C25	C26	1.360(7)
N1	C9	1.509(4)	C26	C27	1.393(7)
N1	C23	1.453(4)	C27	C28	1.386(6)
C6	C7	1.513(5)	Cl1	C29	1.670(11)
C7	C8	1.519(5)	Cl1	C291	1.844(13)
C9	C10	1.564(5)	C29	Cl11	1.844(13)
C9	C17	1.519(5)			

Table 6 Bond Angles for 2a'.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Mo1	P1	90.63(12)	N1	C9	P1	113.1(2)
C2	Mo1	P1	97.10(12)	N1	C9	C10	107.9(3)
C2	Mo1	C1	89.76(18)	N1	C9	C17	108.4(3)
C3	Mo1	P1	174.73(18)	C10	C9	P1	99.0(2)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	Mo1	C1	89.45(19)	C17	C9	P1	113.0(2)
C3	Mo1	C2	88.2(2)	C17	C9	C10	115.3(3)
C3	Mo1	C4	89.5(2)	C11	C10	C9	106.4(3)
C3	Mo1	C5	89.3(2)	C11	C10	C16	104.8(3)
C4	Mo1	P1	90.55(15)	C16	C10	C9	119.9(3)
C4	Mo1	C1	178.4(2)	O7	C11	C10	113.6(3)
C4	Mo1	C2	89.0(2)	C12	C11	O7	122.8(4)
C4	Mo1	C5	91.0(3)	C12	C11	C10	123.6(4)
C5	Mo1	P1	85.47(16)	C11	C12	C13	121.2(4)
C5	Mo1	C1	90.1(2)	C14	C13	C12	126.1(4)
C5	Mo1	C2	177.4(2)	C13	C14	C15	126.1(4)
O7	P1	Mo1	113.75(10)	C16	C15	C14	125.5(4)
O7	P1	C8	99.40(17)	C15	C16	C10	118.7(4)
O7	P1	C9	92.50(14)	C18	C17	C9	121.9(3)
C8	P1	Mo1	117.11(13)	C22	C17	C9	119.4(3)
C8	P1	C9	103.28(16)	C22	C17	C18	118.4(3)
C9	P1	Mo1	125.48(11)	C17	C18	C19	120.5(4)
C11	O7	P1	112.5(2)	C20	C19	C18	120.1(4)
C6	N1	C9	130.3(3)	C19	C20	C21	120.5(4)
C6	N1	C23	114.6(3)	C20	C21	C22	119.8(5)
C23	N1	C9	115.1(3)	C17	C22	C21	120.7(4)
O1	C1	Mo1	178.9(4)	C24	C23	N1	119.4(3)
O2	C2	Mo1	177.0(4)	C28	C23	N1	120.3(3)
O3	C3	Mo1	179.0(6)	C28	C23	C24	120.2(4)
O4	C4	Mo1	178.5(6)	C25	C24	C23	119.6(4)
O5	C5	Mo1	178.6(7)	C26	C25	C24	120.9(5)
O6	C6	N1	120.0(3)	C25	C26	C27	119.7(4)
O6	C6	C7	119.0(3)	C28	C27	C26	120.2(4)
N1	C6	C7	121.0(3)	C23	C28	C27	119.3(4)
C6	C7	C8	116.4(3)	C29	Cl1	C29[1]	70.9(6)
C7	C8	P1	110.7(3)	Cl1	C29	Cl1[1]	109.1(6)

Table 7 Torsion Angles for 2a'.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Mo1	P1	O7	C11	-105.2(2)	C9	N1	C23	C24	93.7(4)
Mo1	P1	C8	C7	-168.3(2)	C9	N1	C23	C28	-87.6(4)
Mo1	P1	C9	N1	-160.07(17)	C9	C10	C11	O7	-23.5(4)
Mo1	P1	C9	C10	86.0(2)	C9	C10	C11	C12	157.8(4)
Mo1	P1	C9	C17	-36.4(3)	C9	C10	C16	C15	-171.2(4)
P1	O7	C11	C10	-5.3(4)	C9	C17	C18	C19	173.8(4)
P1	O7	C11	C12	173.4(3)	C9	C17	C22	C21	-174.6(4)
P1	C9	C10	C11	36.8(3)	C10	C9	C17	C18	26.1(5)
P1	C9	C10	C16	-81.7(3)	C10	C9	C17	C22	-160.5(3)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
P1	C9	C17	C18	138.9(3)	C10	C11	C12	C13	12.6(6)
P1	C9	C17	C22	-47.7(4)	C11	C10	C16	C15	69.5(4)
O6	C6	C7	C8	-149.5(4)	C11	C12	C13	C14	30.6(8)
O7	P1	C8	C7	-45.4(3)	C12	C13	C14	C15	0.2(9)
O7	P1	C9	N1	78.2(2)	C13	C14	C15	C16	-33.8(8)
O7	P1	C9	C10	-35.8(2)	C14	C15	C16	C10	-8.2(7)
O7	P1	C9	C17	-158.2(2)	C16	C10	C11	O7	104.5(3)
O7	C11	C12	C13	-165.9(4)	C16	C10	C11	C12	-74.2(4)
N1	C6	C7	C8	31.7(5)	C17	C9	C10	C11	157.6(3)
N1	C9	C10	C11	-81.1(3)	C17	C9	C10	C16	39.1(4)
N1	C9	C10	C16	160.3(3)	C17	C18	C19	C20	0.4(7)
N1	C9	C17	C18	-94.9(4)	C18	C17	C22	C21	-1.0(6)
N1	C9	C17	C22	78.5(4)	C18	C19	C20	C21	-0.5(8)
N1	C23	C24	C25	-179.1(4)	C19	C20	C21	C22	-0.2(8)
N1	C23	C28	C27	178.8(4)	C20	C21	C22	C17	0.9(7)
C6	N1	C9	P1	-1.9(5)	C22	C17	C18	C19	0.3(6)
C6	N1	C9	C10	106.6(4)	C23	N1	C6	O6	-2.0(5)
C6	N1	C9	C17	-128.0(4)	C23	N1	C6	C7	176.7(3)
C6	N1	C23	C24	-82.8(4)	C23	N1	C9	P1	-177.7(2)
C6	N1	C23	C28	95.9(4)	C23	N1	C9	C10	-69.2(4)
C6	C7	C8	P1	-57.6(4)	C23	N1	C9	C17	56.2(4)
C8	P1	O7	C11	129.5(2)	C23	C24	C25	C26	0.3(7)
C8	P1	C9	N1	-22.1(3)	C24	C23	C28	C27	-2.5(6)
C8	P1	C9	C10	-136.0(2)	C24	C25	C26	C27	-2.4(8)
C8	P1	C9	C17	101.5(3)	C25	C26	C27	C28	2.0(8)
C9	P1	O7	C11	25.6(2)	C26	C27	C28	C23	0.4(7)
C9	P1	C8	C7	49.5(3)	C28	C23	C24	C25	2.1(6)
C9	N1	C6	O6	-177.9(4)	C29[1]	Cl1	C29	Cl1[1]	-0.001(1)
C9	N1	C6	C7	0.9(6)					

X-ray crystallographic data of compound 3

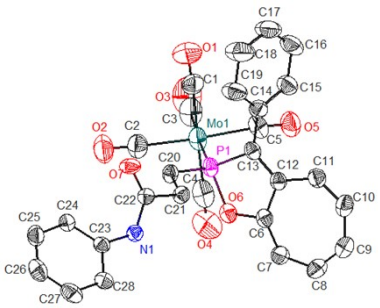


Table 8 Crystal data and structure refinement for 3（CCDC：2122444）.

Identification code	**3**
Empirical formula	$C_{28}H_{20}MoNO_7P$
Formula weight	609.36
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.45862(18)
b/Å	31.4061(4)
c/Å	8.29854(16)
α/°	90
β/°	103.2846(18)
γ/°	90
Volume/Å^3	2906.49(8)
Z	4
ρ_{calc}g/cm^3	1.393
μ/mm^{-1}	4.584
F(000)	1232.0
Crystal size/mm^3	0.293 × 0.067 × 0.056
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.414 to 134.138
Index ranges	$-13 \le h \le 13$, $-37 \le k \le 36$, $-6 \le l \le 9$
Reflections collected	11377
Independent reflections	5178 [R_{int} = 0.0371, R_{sigma} = 0.0478]
Data/restraints/parameters	5178/74/381
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0515, wR_2 = 0.1332
Final R indexes [all data]	R_1 = 0.0682, wR_2 = 0.1502
Largest diff. peak/hole / e Å^{-3}	0.72/-0.28

Table 9 Bond Lengths for 3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	Mo1	2.048(10)	C10	C11	1.334(6)
C1	O1	1.18(2)	C11	C12	1.454(5)
C1A	Mo1A	2.16(4)	C12	C13	1.362(5)
C1A	O1A	1.02(7)	C13	C14	1.476(6)
C2	Mo1	2.048(12)	C13	P1	1.797(4)
C2	O2	1.151(17)	C14	C15	1.377(6)
C2A	Mo1A	2.03(3)	C14	C19	1.386(6)
C2A	O2A	1.12(4)	C15	C16	1.395(7)
C3	Mo1	2.041(10)	C16	C17	1.350(8)
C3	O3	1.135(14)	C17	C18	1.353(9)
C3A	Mo1A	1.93(2)	C18	C19	1.401(8)
C3A	O3A	1.14(4)	C20	C21	1.511(5)
C4	Mo1	2.062(16)	C20	P1	1.828(4)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C4	O4	1.137(16)	C21	C22	1.519(5)
C4A	Mo1A	2.04(3)	C22	N1	1.340(5)
C4A	O4A	1.20(2)	C22	O7	1.214(4)
C5	Mo1	2.09(2)	C23	C24	1.377(5)
C5	O5	1.08(5)	C23	C28	1.396(5)
C5A	Mo1A	2.01(7)	C23	N1	1.417(4)
C5A	O5A	1.25(11)	C24	C25	1.383(6)
C6	C7	1.343(6)	C25	C26	1.356(7)
C6	C12	1.453(5)	C26	C27	1.363(7)
C6	O6	1.373(5)	C27	C28	1.385(6)
C7	C8	1.427(7)	Mo1	P1	2.4149(19)
C8	C9	1.333(7)	Mo1A	P1	2.563(4)
C9	C10	1.424(7)	O6	P1	1.670(3)

Table 10 Bond Angles for 3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	Mo1	175.7(13)	C26	C27	C28	121.1(4)
O1A	C1A	Mo1A	173(5)	C27	C28	C23	119.1(4)
O2	C2	Mo1	177.5(10)	C1	Mo1	C4	178.7(5)
O2A	C2A	Mo1A	178(3)	C1	Mo1	C5	86.6(8)
O3	C3	Mo1	177.3(13)	C1	Mo1	P1	88.5(4)
O3A	C3A	Mo1A	179(3)	C2	Mo1	C1	89.9(5)
O4	C4	Mo1	177.6(13)	C2	Mo1	C4	90.2(6)
O4A	C4A	Mo1A	171(4)	C2	Mo1	C5	175.9(8)
O5	C5	Mo1	173(3)	C2	Mo1	P1	94.7(4)
O5A	C5A	Mo1A	165(6)	C3	Mo1	C1	89.4(5)
C7	C6	C12	132.6(4)	C3	Mo1	C2	89.0(5)
C7	C6	O6	116.7(4)	C3	Mo1	C4	91.9(4)
O6	C6	C12	110.7(3)	C3	Mo1	C5	88.8(7)
C6	C7	C8	127.8(4)	C3	Mo1	P1	175.8(3)
C9	C8	C7	128.6(5)	C4	Mo1	C5	93.4(8)
C8	C9	C10	128.4(5)	C4	Mo1	P1	90.2(3)
C11	C10	C9	130.7(5)	C5	Mo1	P1	87.4(6)
C10	C11	C12	129.7(4)	C1A	Mo1A	P1	91.7(10)
C6	C12	C11	122.0(4)	C2A	Mo1A	C1A	88.3(13)
C13	C12	C6	114.2(3)	C2A	Mo1A	C4	90.6(15)
C13	C12	C11	123.8(4)	C2A	Mo1A	P1	91.2(10)
C12	C13	C14	127.8(4)	C3A	Mo1A	C1A	85.4(13)
C12	C13	P1	108.7(3)	C3A	Mo1A	C2A	92.0(12)
C14	C13	P1	123.2(3)	C3A	Mo1A	C4A	94.6(12)
C15	C14	C13	122.0(4)	C3A	Mo1A	C5A	92.3(19)
C15	C14	C19	117.0(4)	C3A	Mo1A	P1	175.6(8)
C19	C14	C13	121.0(4)	C4A	Mo1A	C1A	178.9(17)

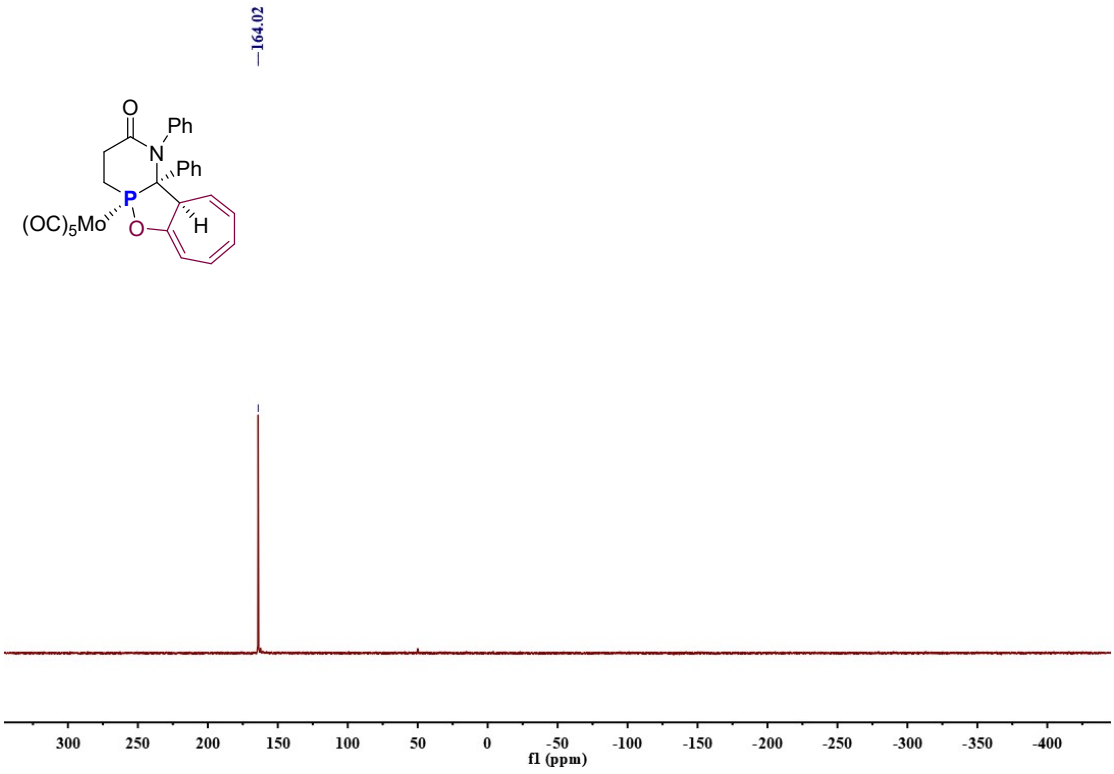
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C14	C15	C16	121.6(5)	C4A	Mo1A	P1	88.3(8)
C17	C16	C15	119.9(5)	C5A	Mo1A	C1A	106.1(17)
C16	C17	C18	120.5(6)	C5A	Mo1A	C2A	165.3(17)
C17	C18	C19	119.9(6)	C5A	Mo1A	C4A	75.0(19)
C14	C19	C18	121.0(5)	C5A	Mo1A	P1	85.4(17)
C21	C20	P1	115.3(3)	C22	N1	C23	128.1(3)
C20	C21	C22	110.6(3)	C6	O6	P1	114.4(2)
N1	C22	C21	114.8(3)	C13	P1	C20	106.44(18)
O7	C22	C21	120.2(3)	C13	P1	Mo1	119.54(14)
O7	C22	N1	125.0(3)	C13	P1	Mo1A	113.96(16)
C24	C23	C28	119.4(4)	C20	P1	Mo1	120.09(14)
C24	C23	N1	122.9(3)	C20	P1	Mo1A	116.78(17)
C28	C23	N1	117.6(3)	O6	P1	C13	92.02(16)
C23	C24	C25	119.6(4)	O6	P1	C20	101.07(17)
C26	C25	C24	121.2(4)	O6	P1	Mo1	112.72(14)
C25	C26	C27	119.6(4)	O6	P1	Mo1A	122.92(16)

Table 11 Torsion Angles for 3.

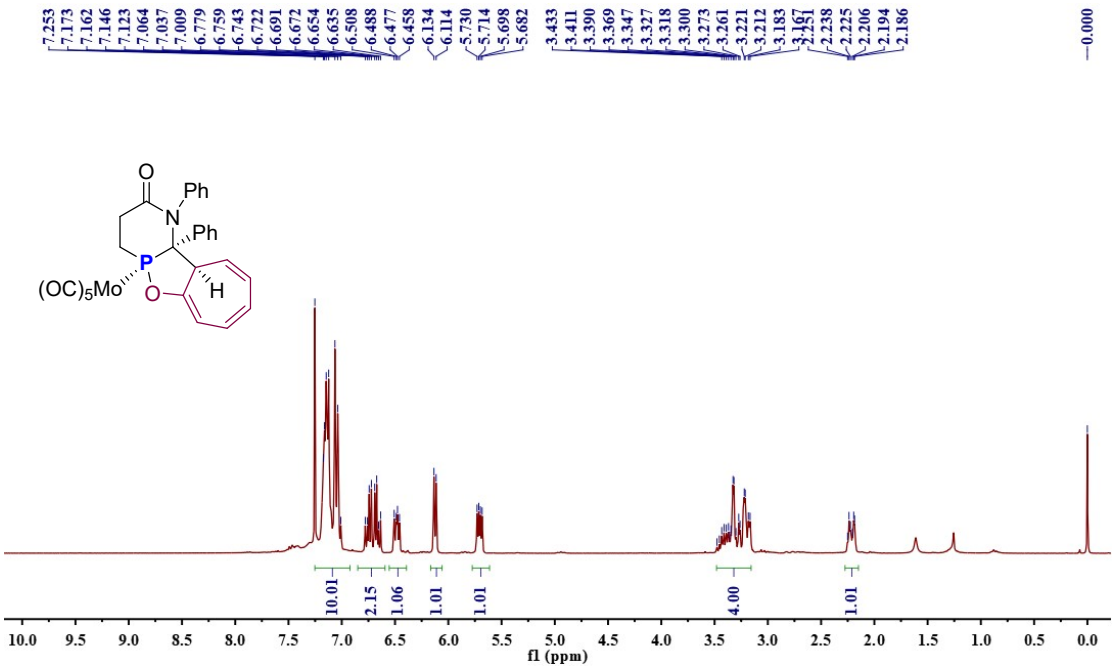
A	B	C	D	Angle/°	A	B	C	D	Angle/°
C6	C7	C8	C9	-2.6(9)	C14	C15	C16	C17	2.0(9)
C6	C12	C13	C14	-176.5(4)	C15	C14	C19	C18	-0.5(10)
C6	C12	C13	P1	-1.8(4)	C15	C16	C17	C18	-0.5(12)
C6	O6	P1	C13	-1.0(3)	C16	C17	C18	C19	-1.3(14)
C6	O6	P1	C20	-108.2(3)	C17	C18	C19	C14	1.8(13)
C6	O6	P1	Mo1	122.3(2)	C19	C14	C15	C16	-1.4(8)
C6	O6	P1	Mo1A	119.4(3)	C20	C21	C22	N1	122.1(4)
C7	C6	C12	C11	4.0(7)	C20	C21	C22	O7	-57.9(5)
C7	C6	C12	C13	-178.2(4)	C21	C20	P1	C13	-45.2(4)
C7	C6	O6	P1	179.6(3)	C21	C20	P1	Mo1	174.9(3)
C7	C8	C9	C10	0.1(11)	C21	C20	P1	Mo1A	-173.7(3)
C8	C9	C10	C11	3.1(11)	C21	C20	P1	O6	50.3(3)
C9	C10	C11	C12	-1.0(10)	C21	C22	N1	C23	-175.2(3)
C10	C11	C12	C6	-3.4(7)	C23	C24	C25	C26	-1.9(7)
C10	C11	C12	C13	179.0(5)	C24	C23	C28	C27	-1.0(6)
C11	C12	C13	C14	1.3(6)	C24	C23	N1	C22	28.3(6)
C11	C12	C13	P1	176.0(3)	C24	C25	C26	C27	-0.7(8)
C12	C6	C7	C8	-0.1(8)	C25	C26	C27	C28	2.5(8)
C12	C6	O6	P1	0.2(4)	C26	C27	C28	C23	-1.7(7)
C12	C13	C14	C15	65.3(6)	C28	C23	C24	C25	2.7(6)
C12	C13	C14	C19	-115.4(6)	C28	C23	N1	C22	-154.5(4)
C12	C13	P1	C20	103.8(3)	N1	C23	C24	C25	179.9(4)
C12	C13	P1	Mo1	-116.1(3)	N1	C23	C28	C27	-178.3(4)
C12	C13	P1	Mo1A	-126.0(3)	O6	C6	C7	C8	-179.4(4)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C12	C13	P1	O6	1.6(3)	O6	C6	C12	C11	-176.7(3)
C13	C14	C15	C16	177.9(5)	O6	C6	C12	C13	1.1(4)
C13	C14	C19	C18	-179.8(7)	O7	C22	N1	C23	4.9(6)
C14	C13	P1	C20	-81.2(3)	P1	C13	C14	C15	-108.7(5)
C14	C13	P1	Mo1	58.9(4)	P1	C13	C14	C19	70.6(6)
C14	C13	P1	Mo1A	49.0(4)	P1	C20	C21	C22	176.8(3)
C14	C13	P1	O6	176.6(3)					

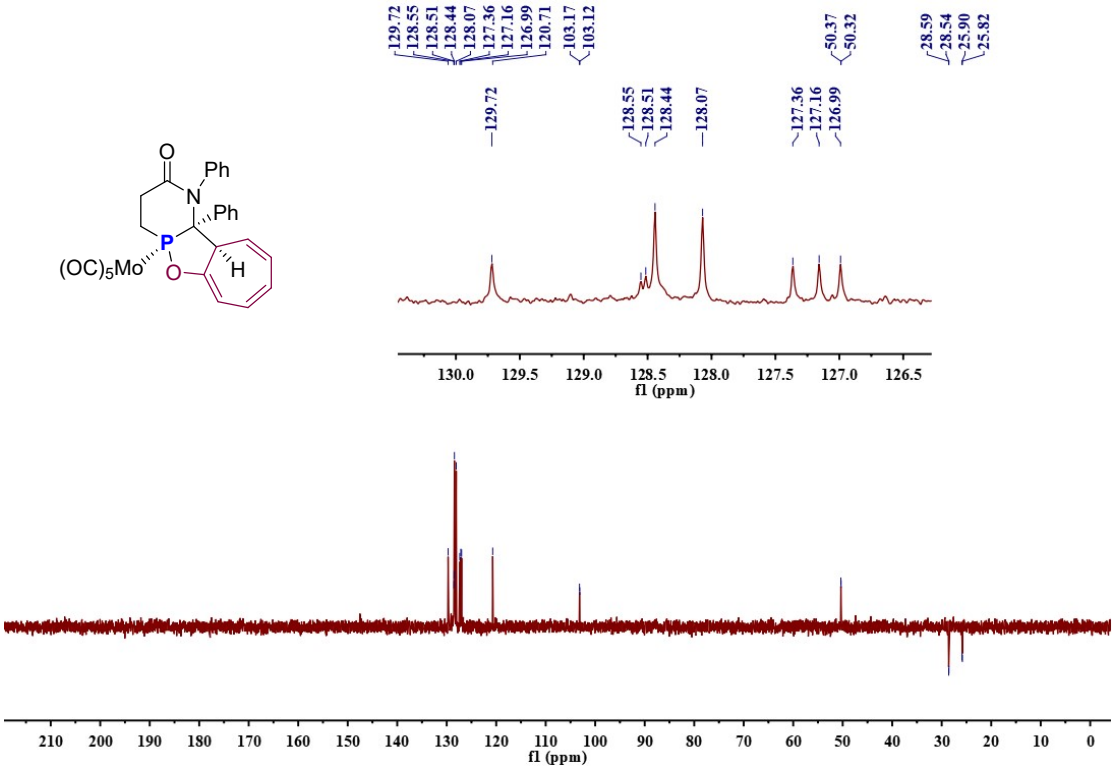
NMR spectra



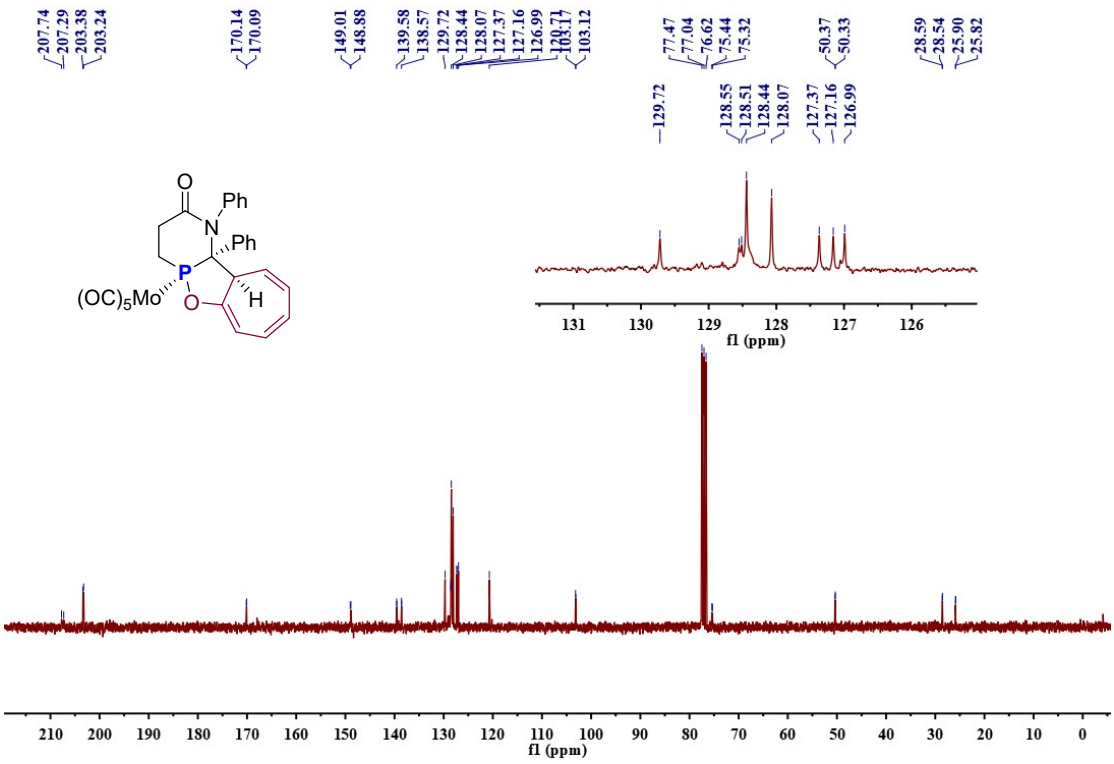
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2a



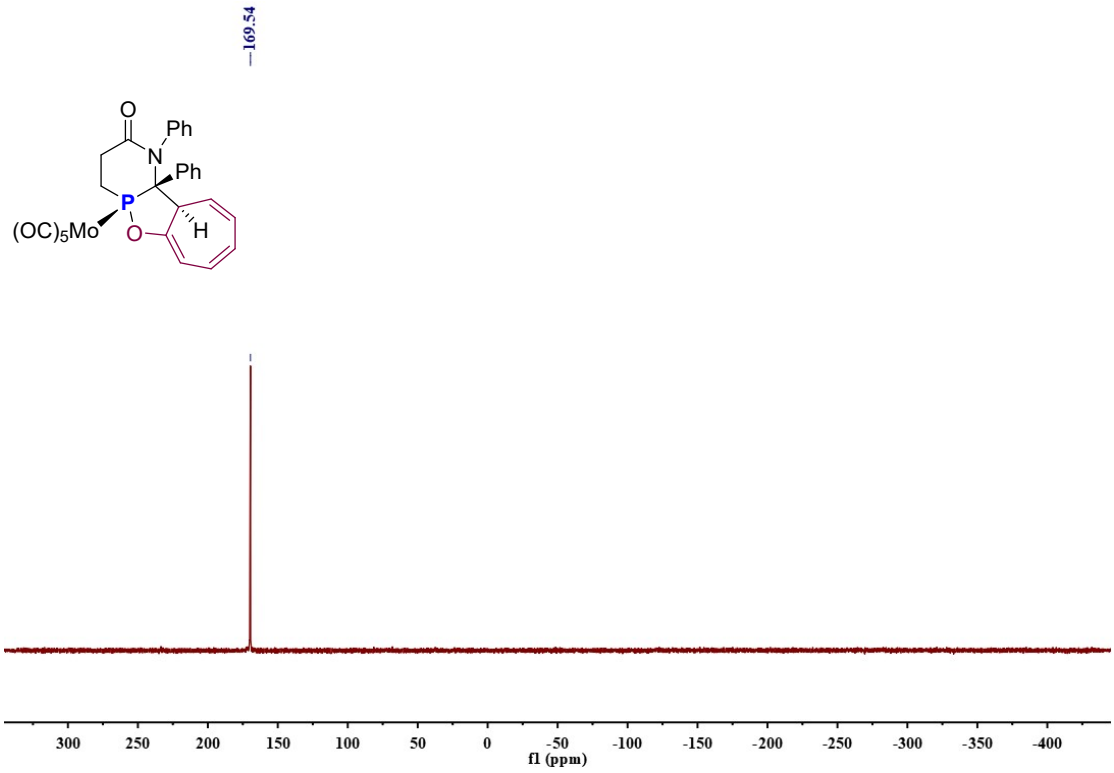
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2a



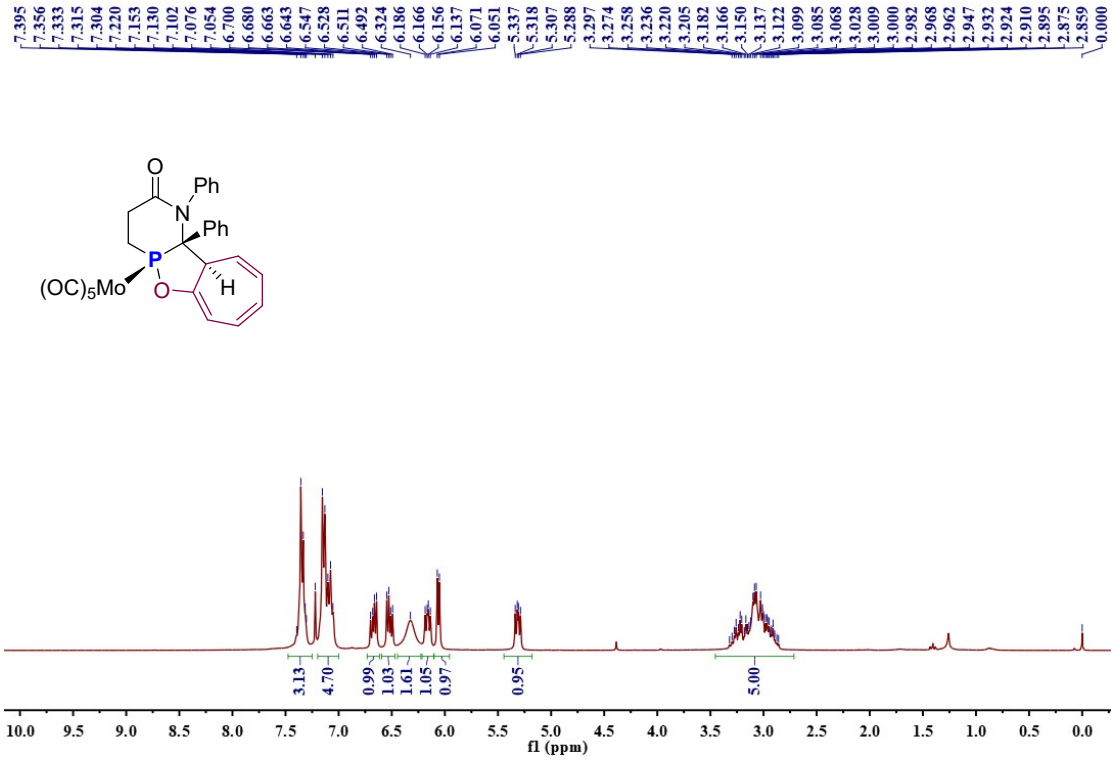
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 2a



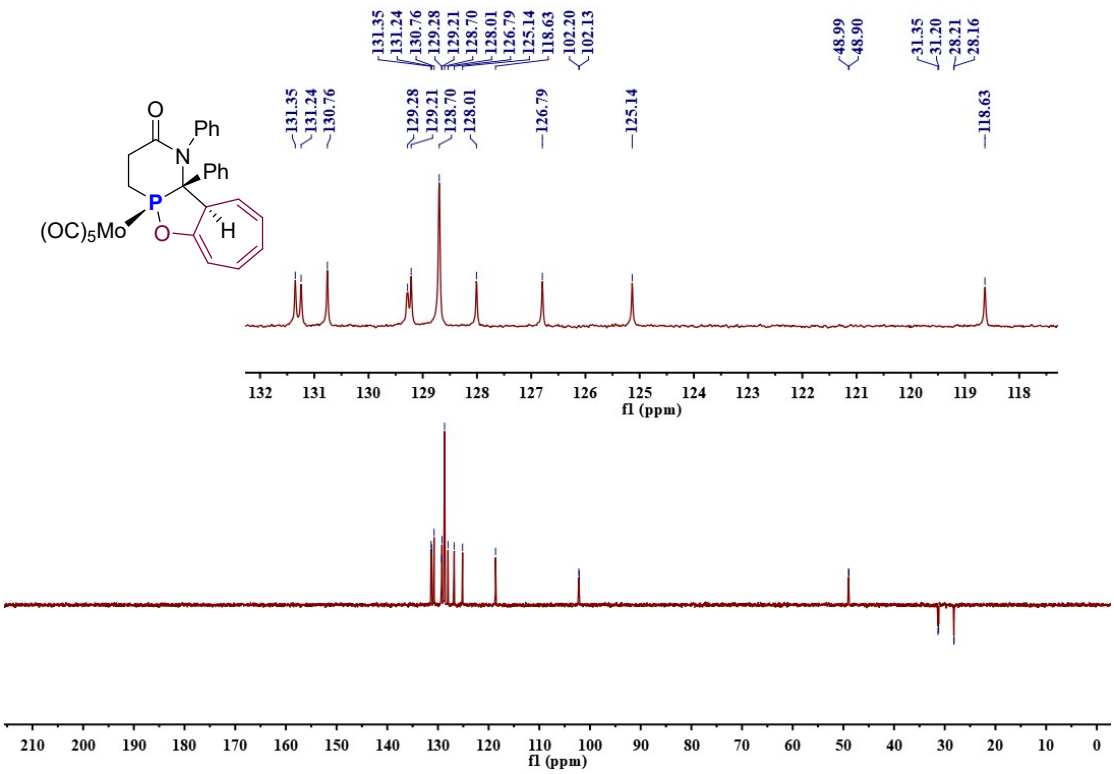
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2a



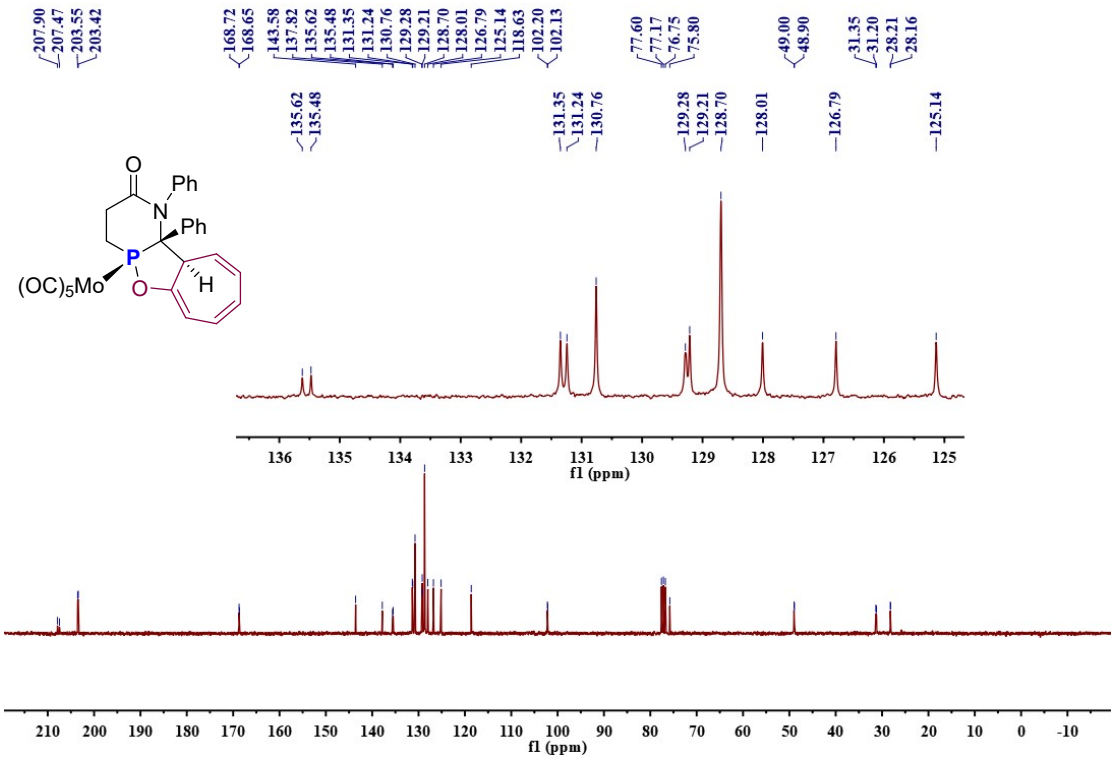
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2a'



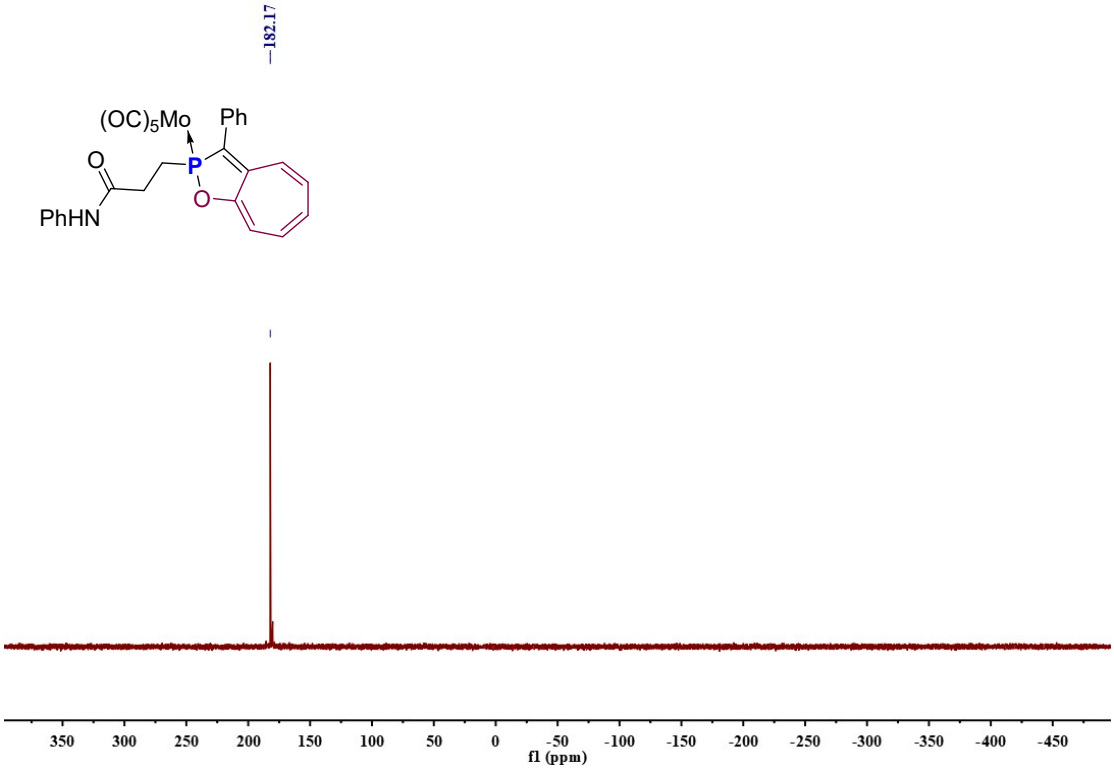
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2a'



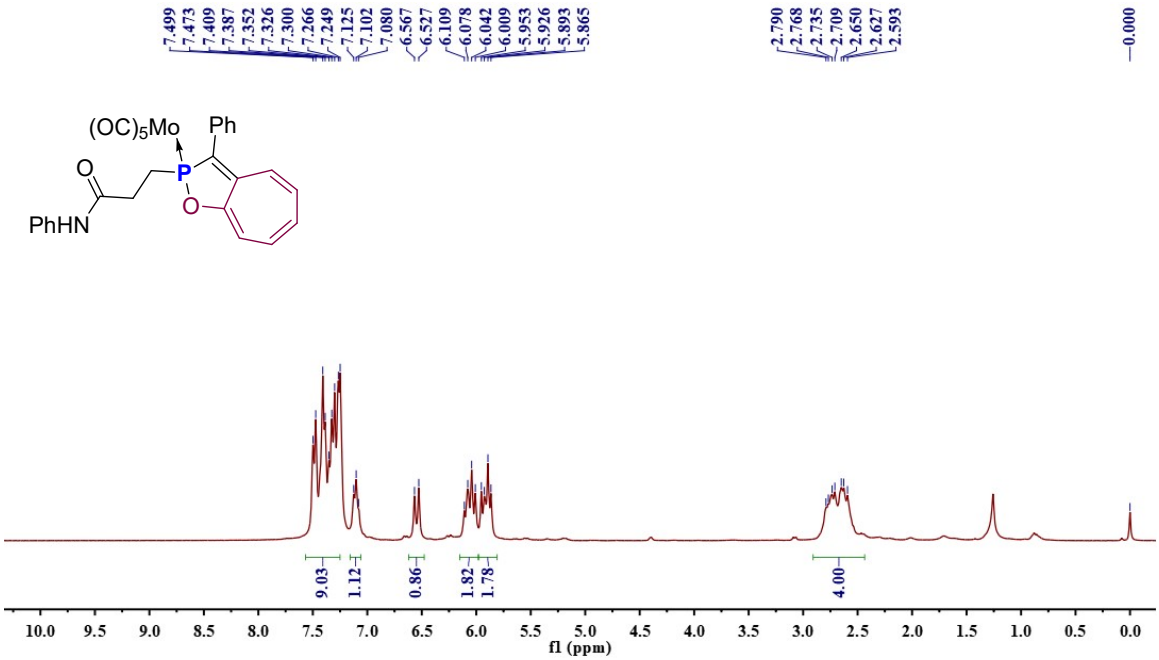
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 2a'



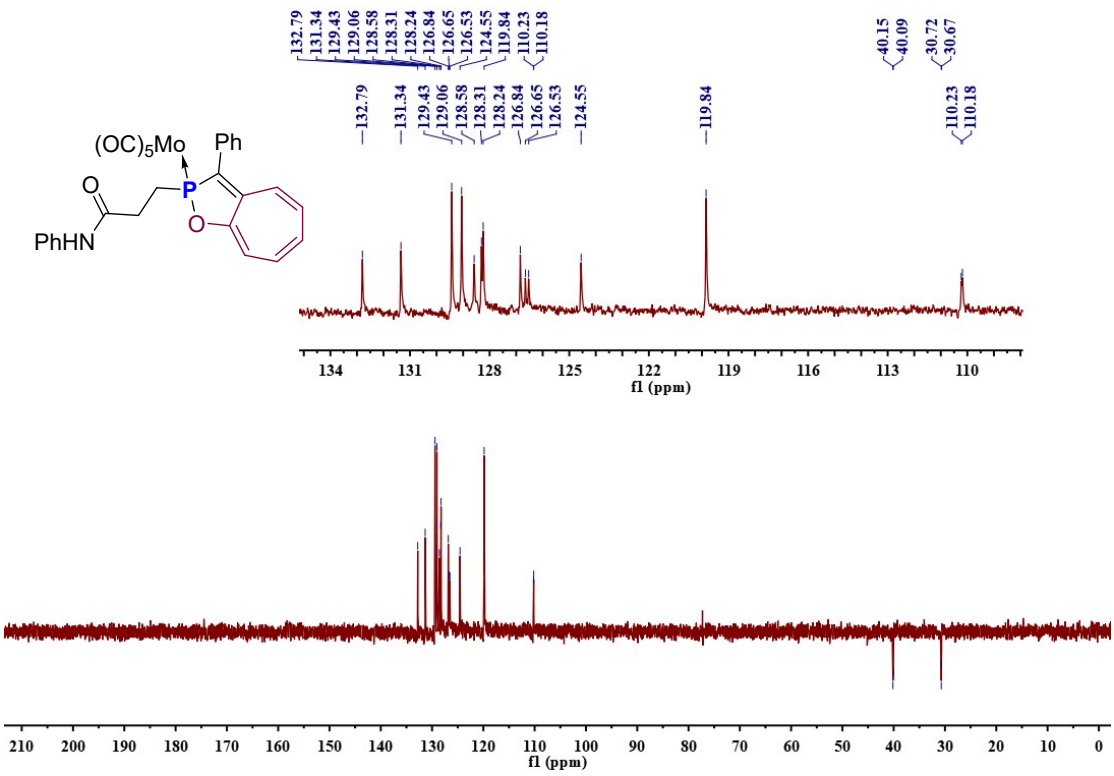
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2a'



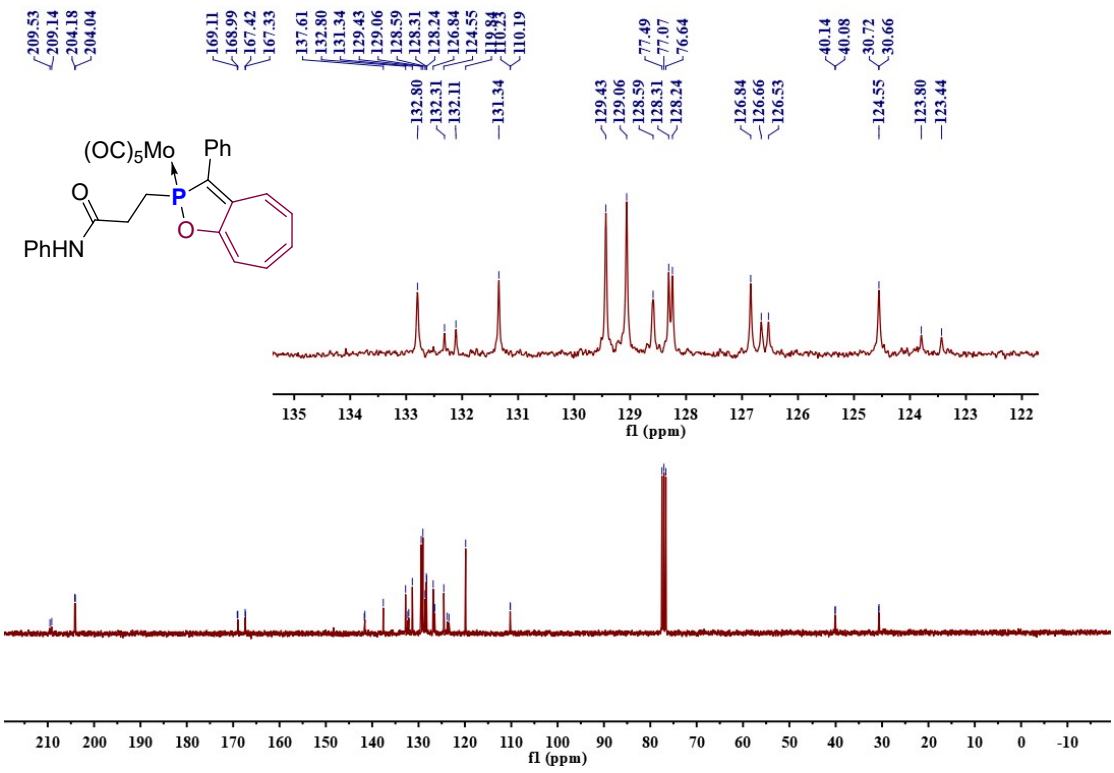
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 3



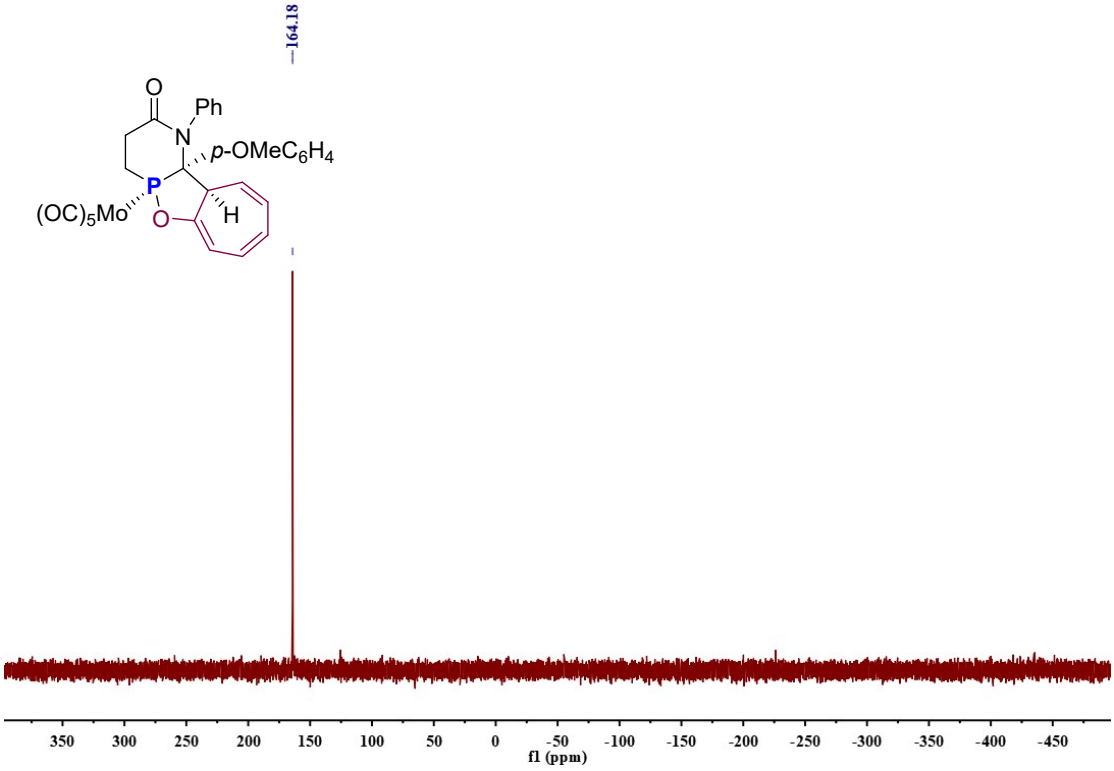
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 3



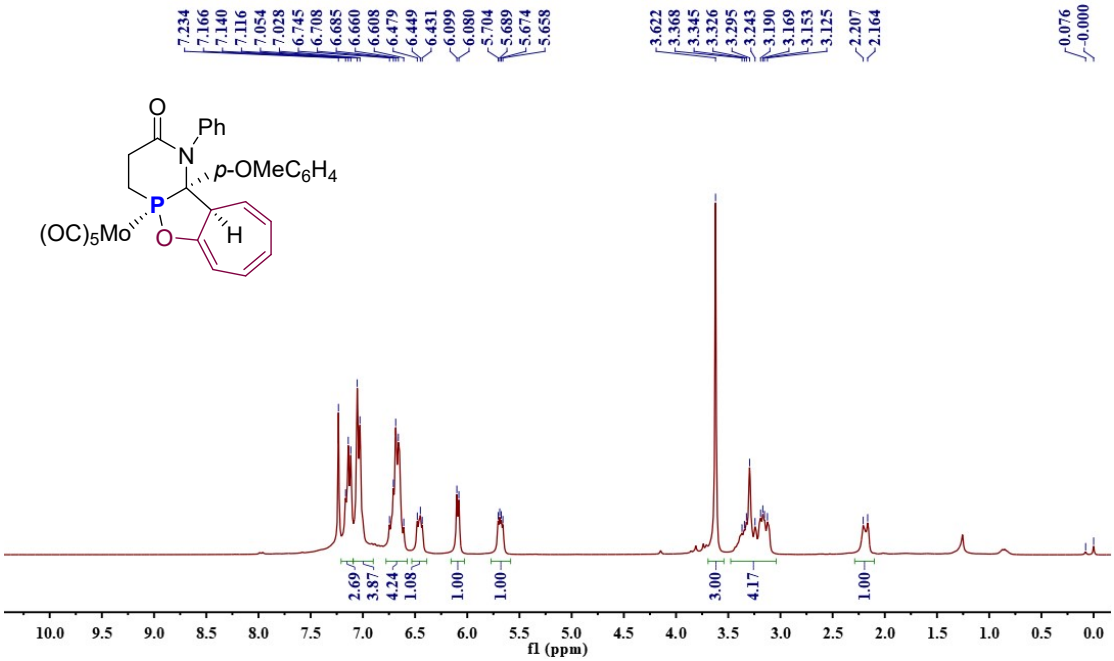
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 3



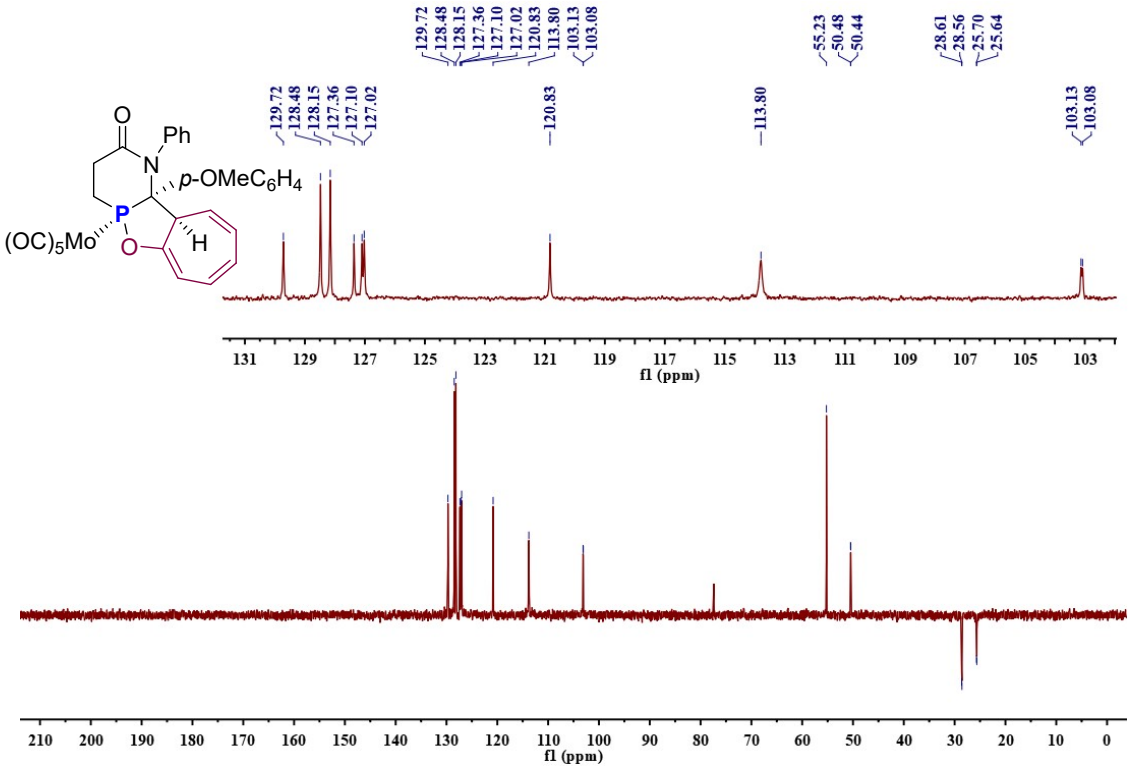
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 3



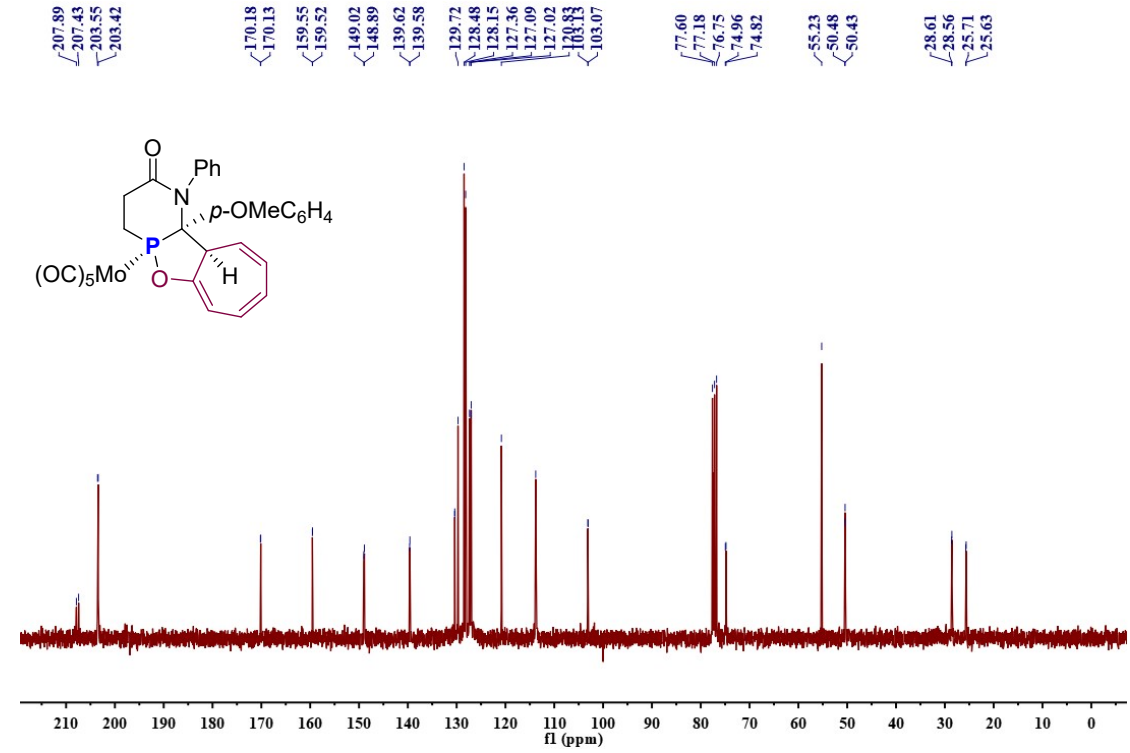
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2b



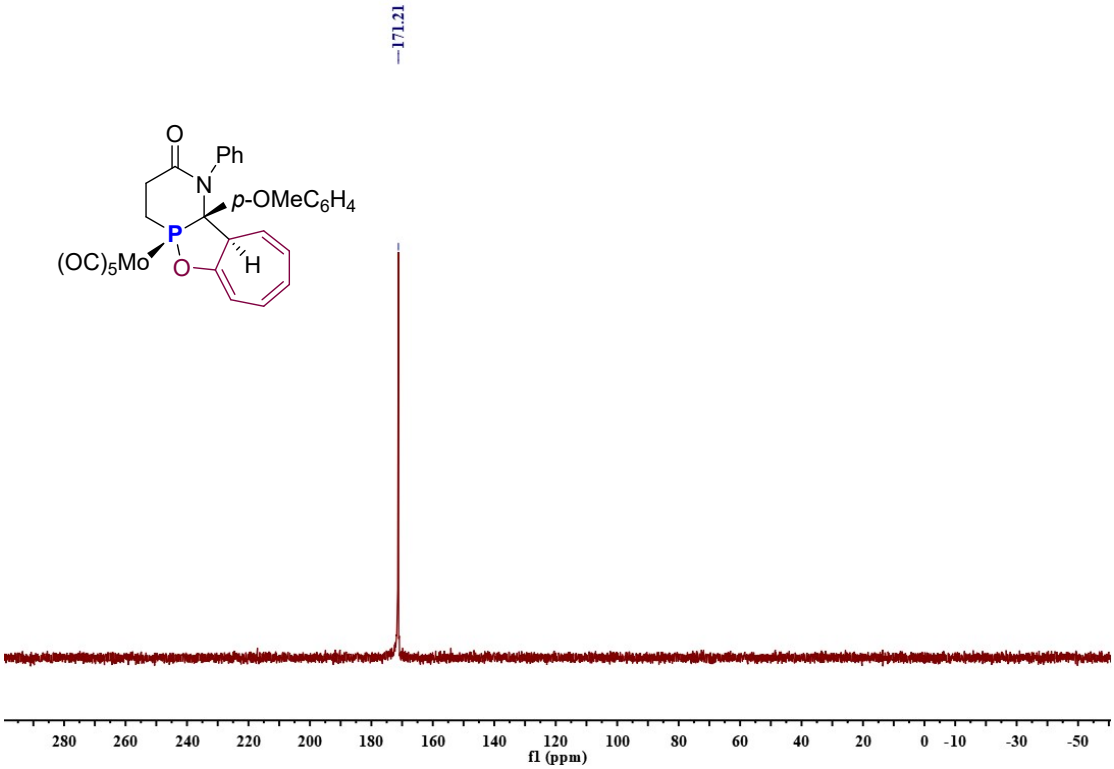
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2b



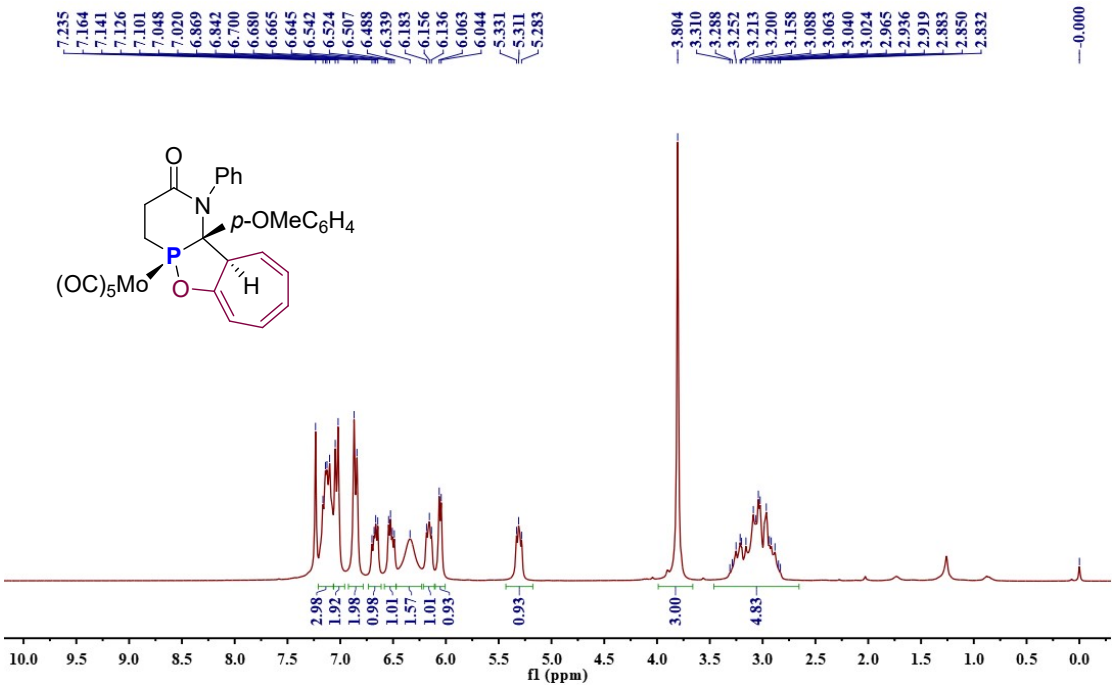
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 2b



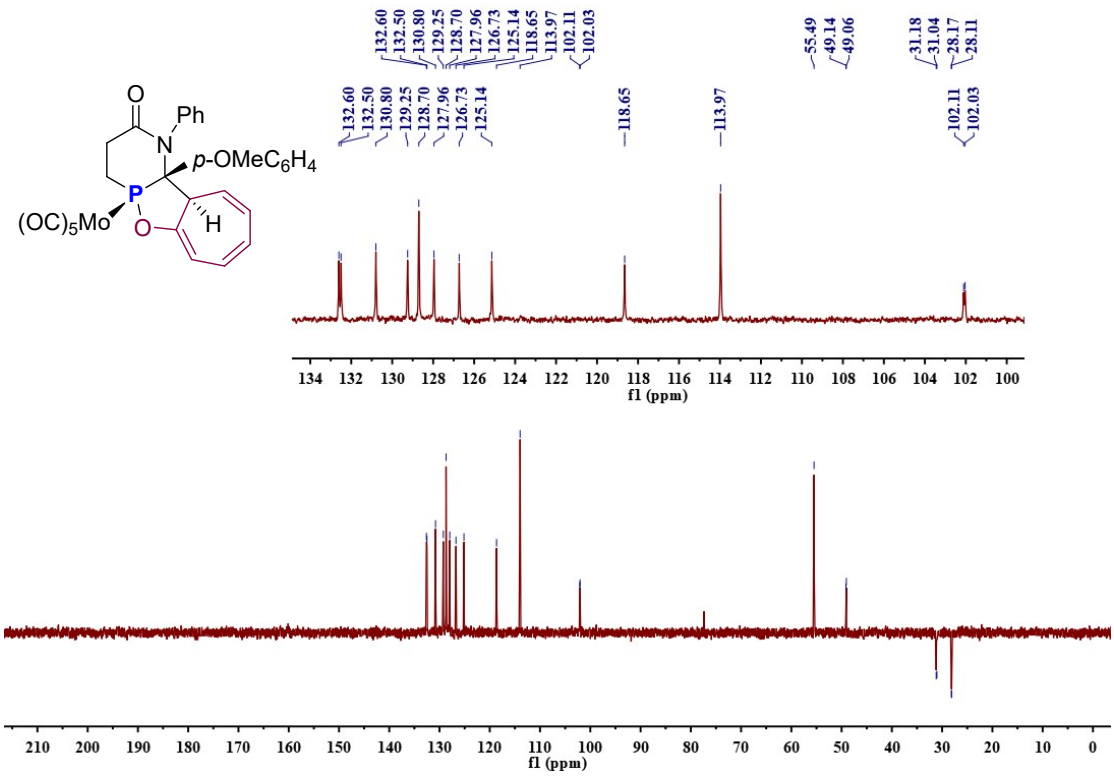
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2b



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



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



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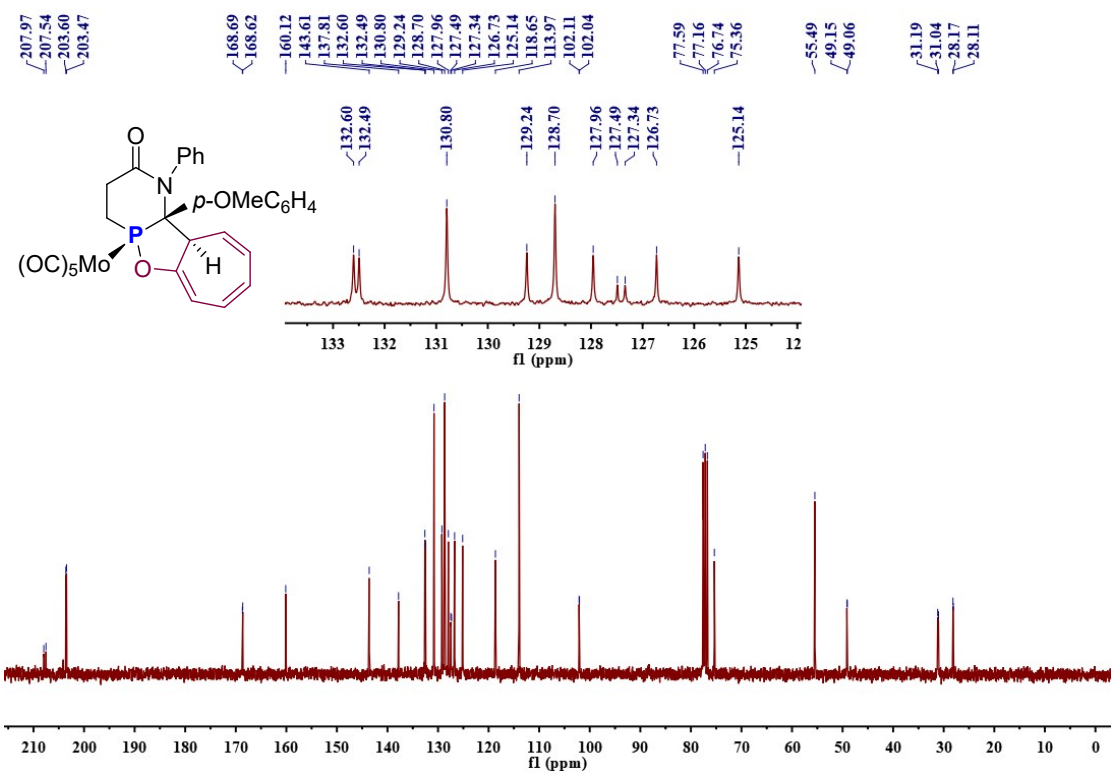
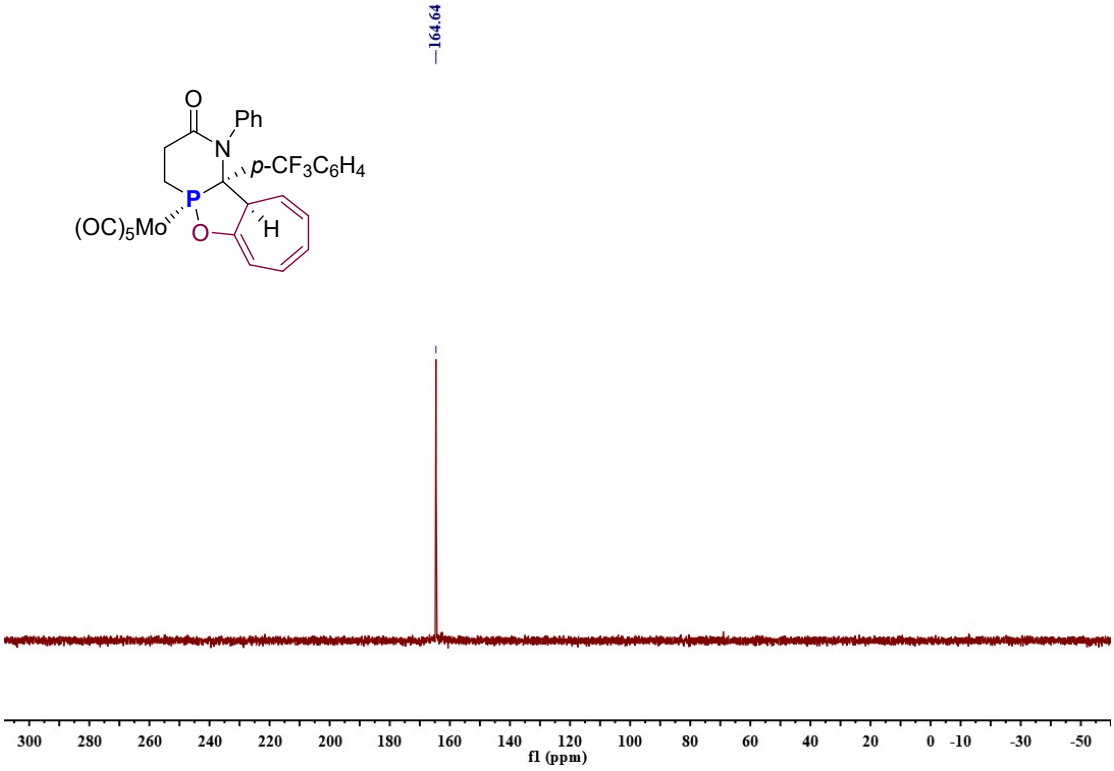
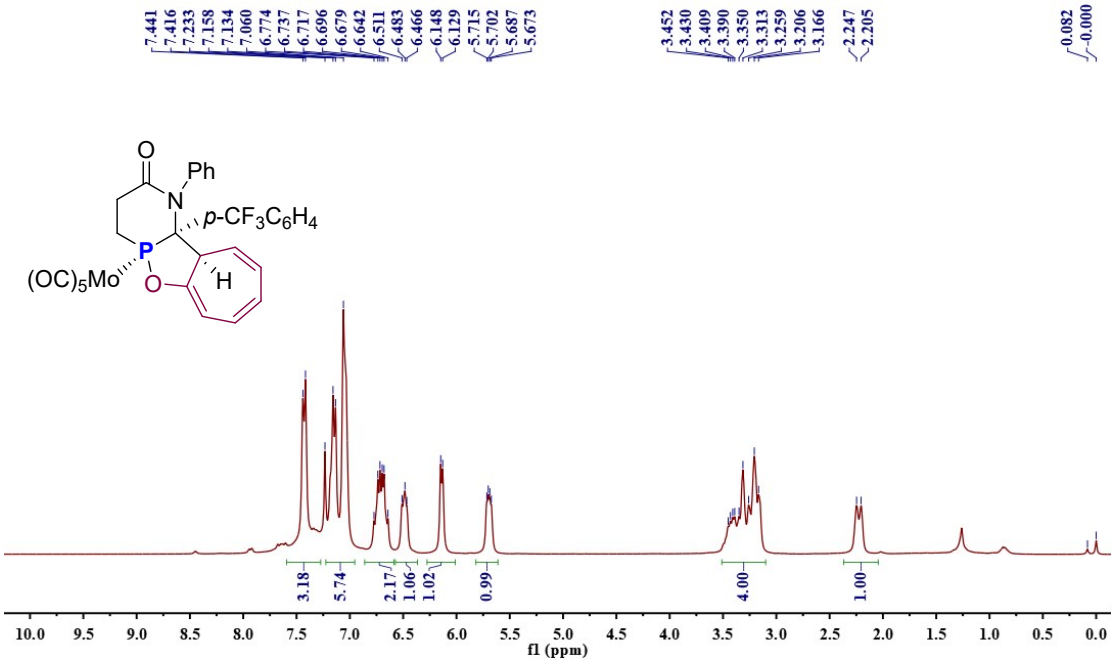


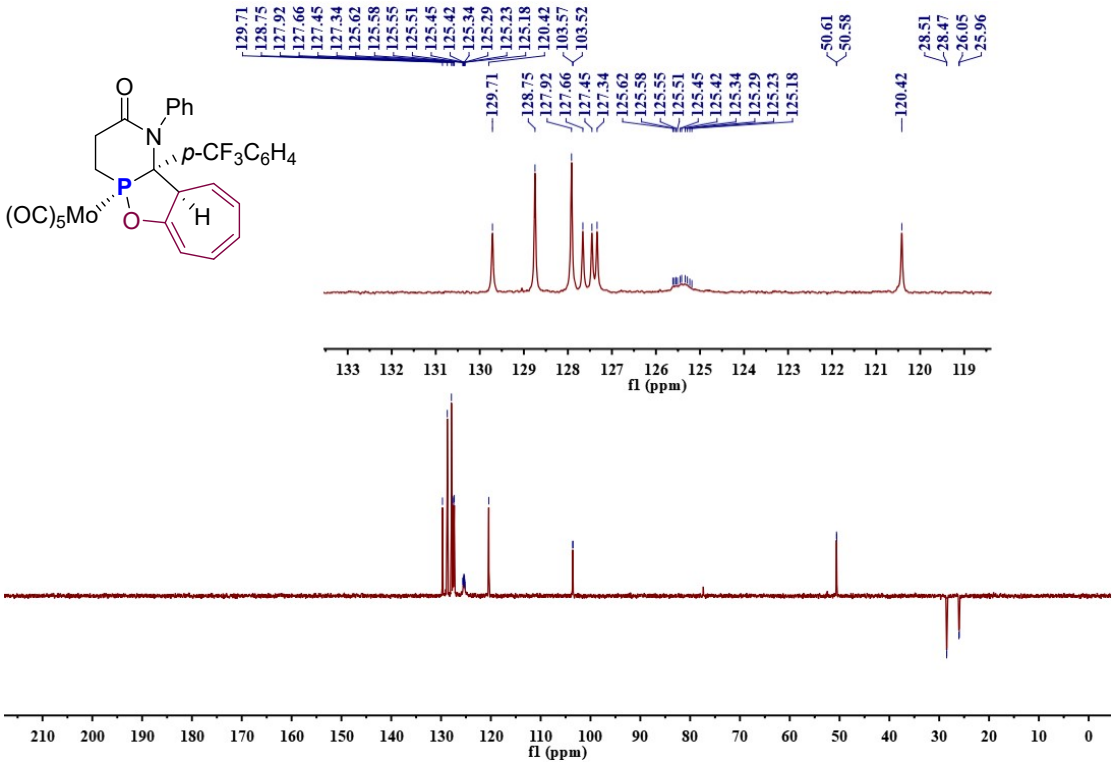
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2b'



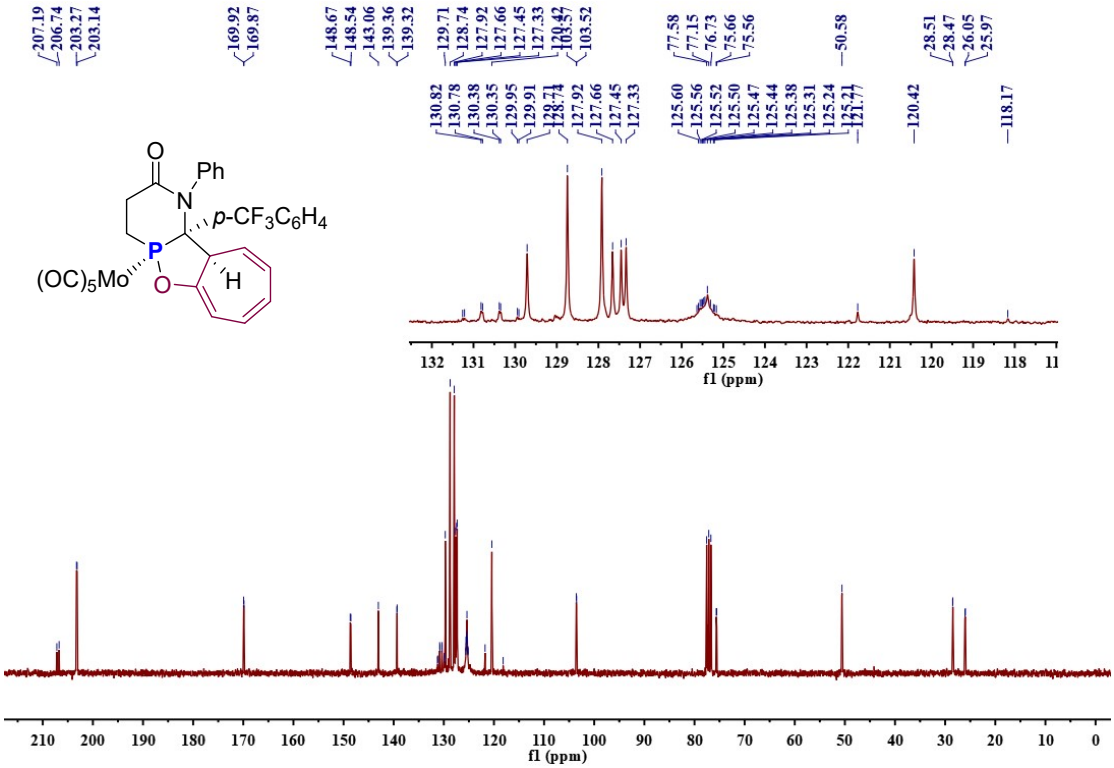
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2c



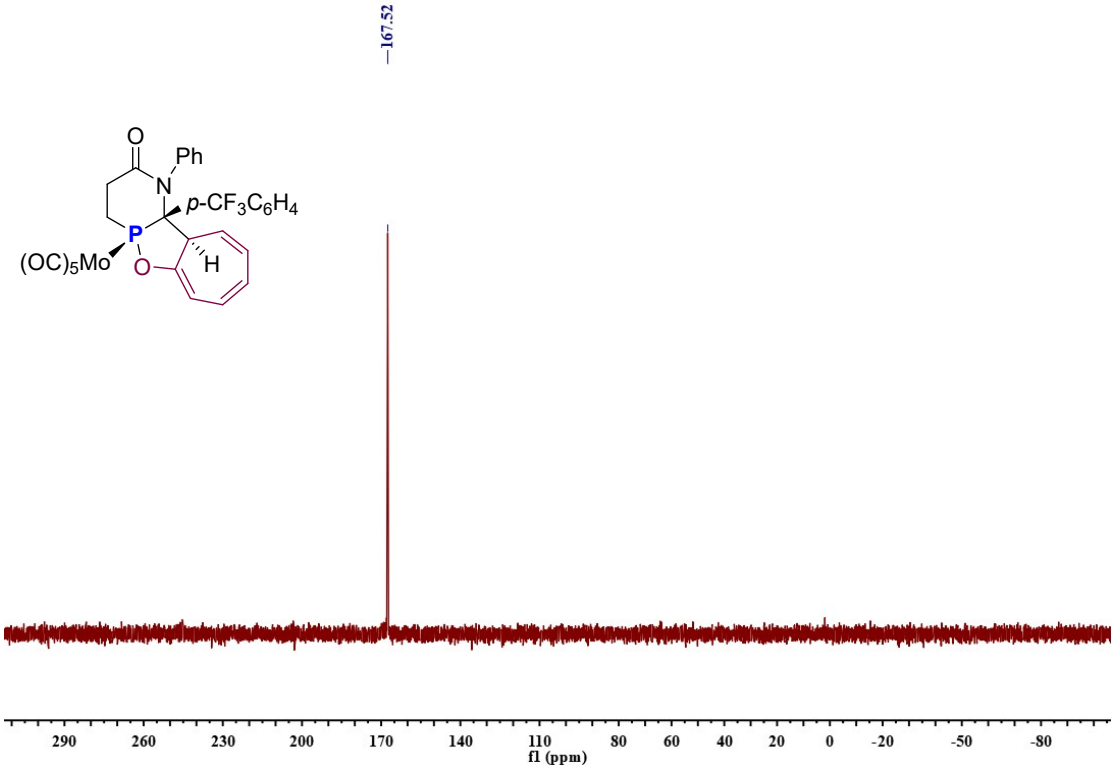
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2c



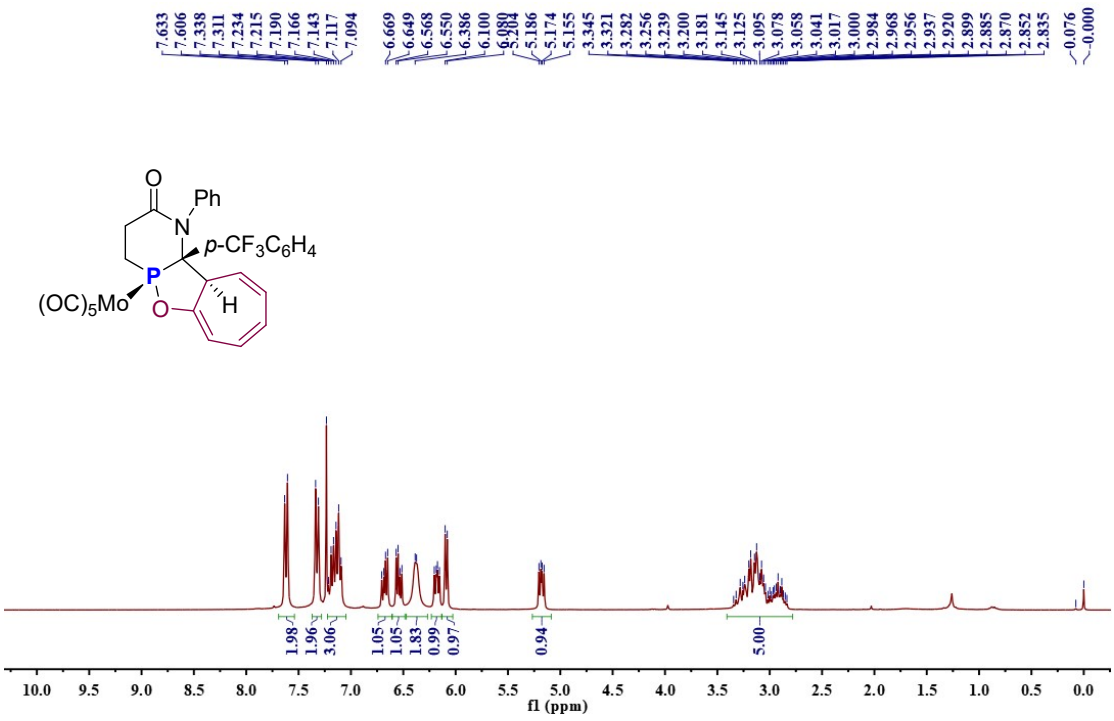
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 2c



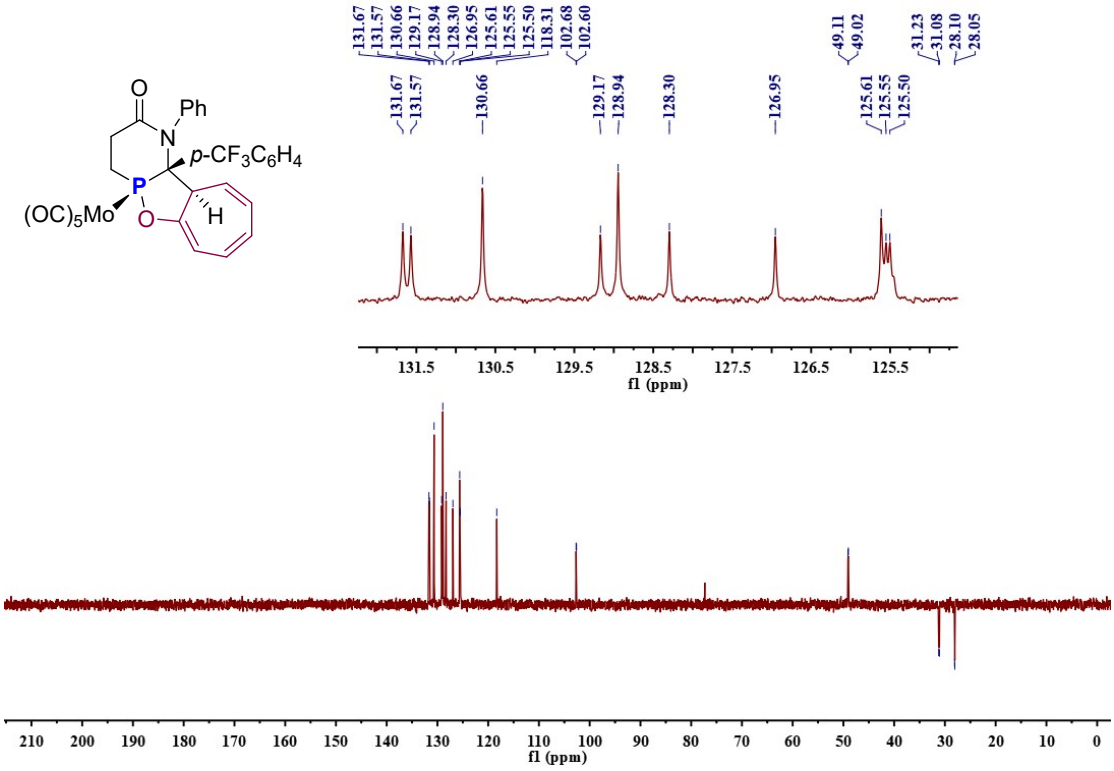
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2c



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



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



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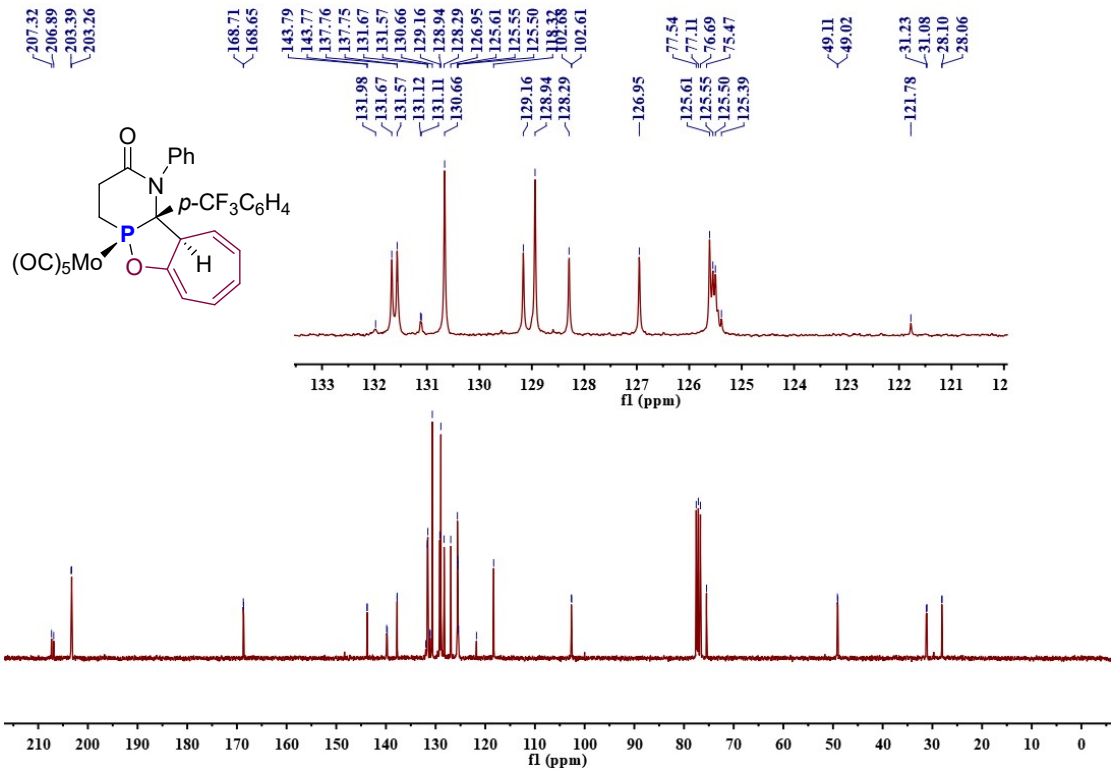
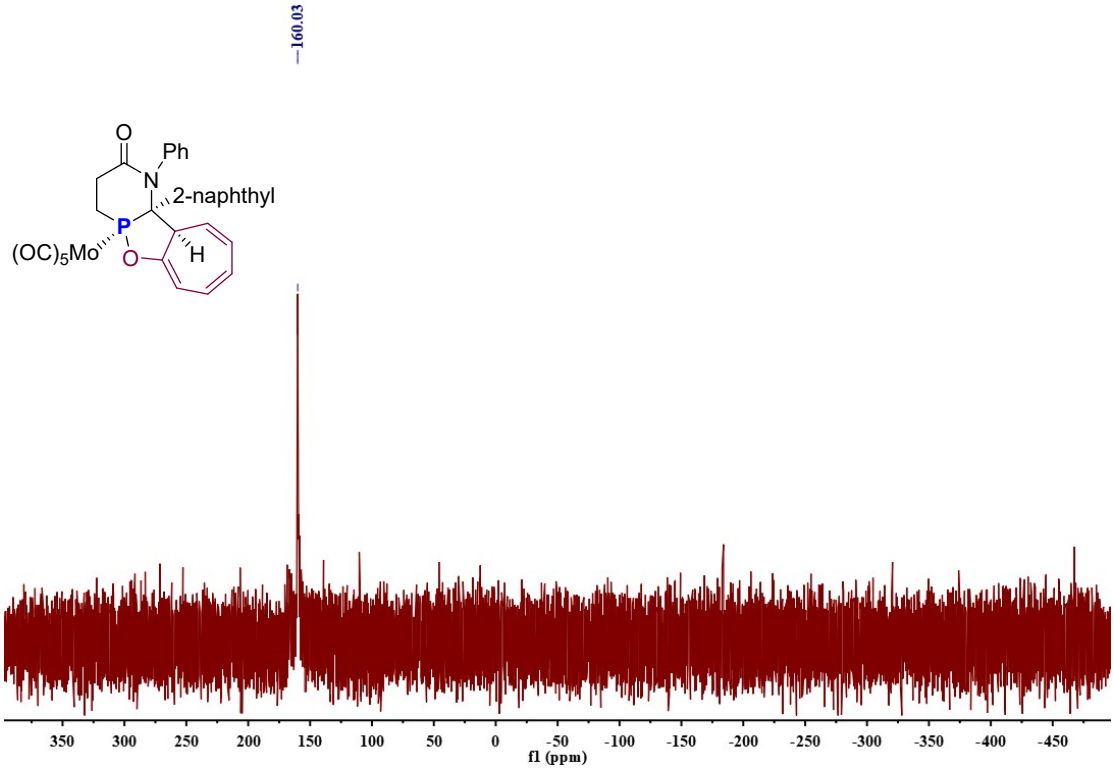
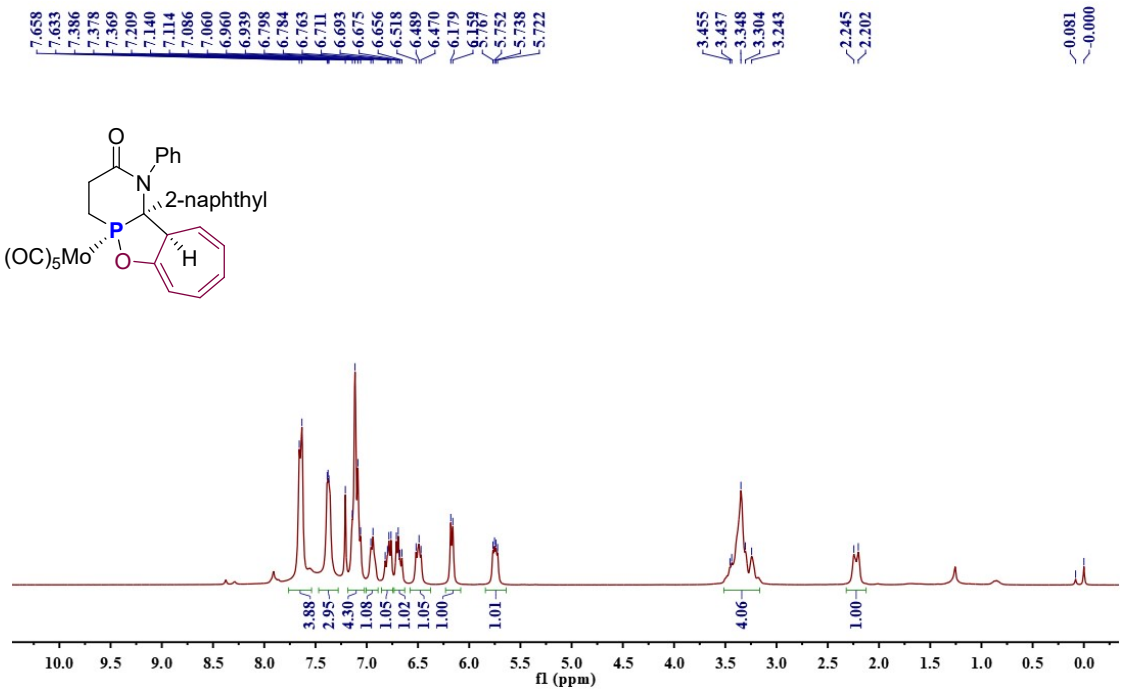


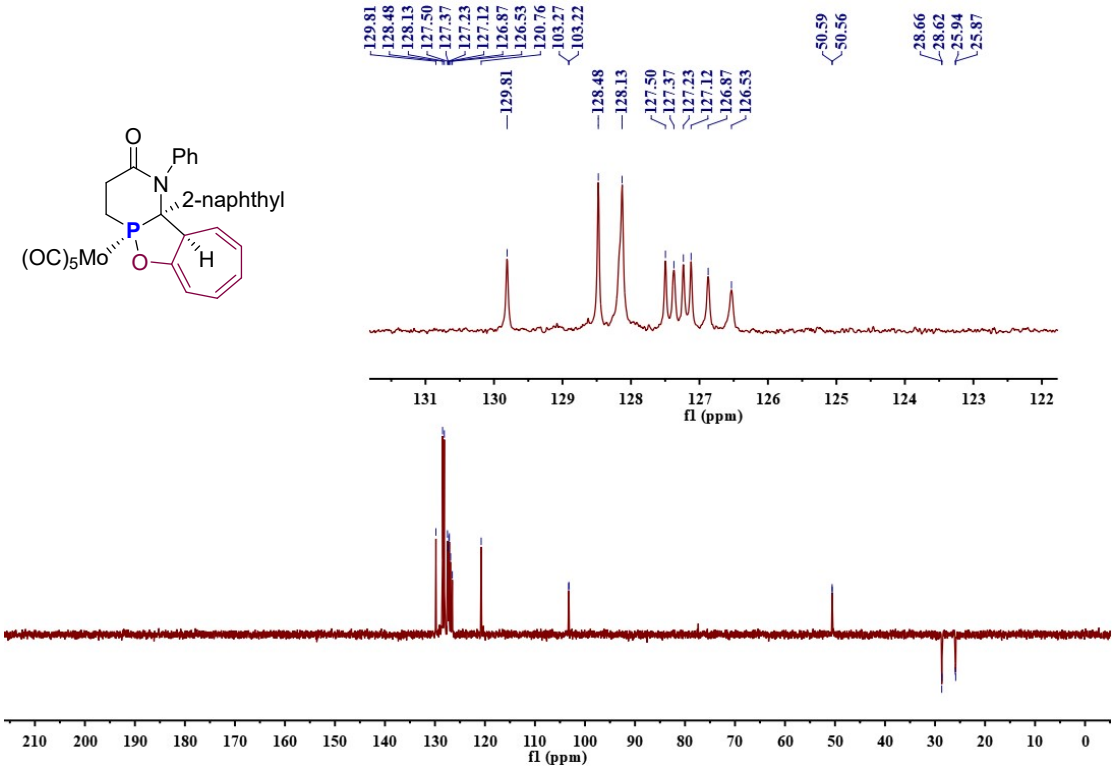
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2c'



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



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



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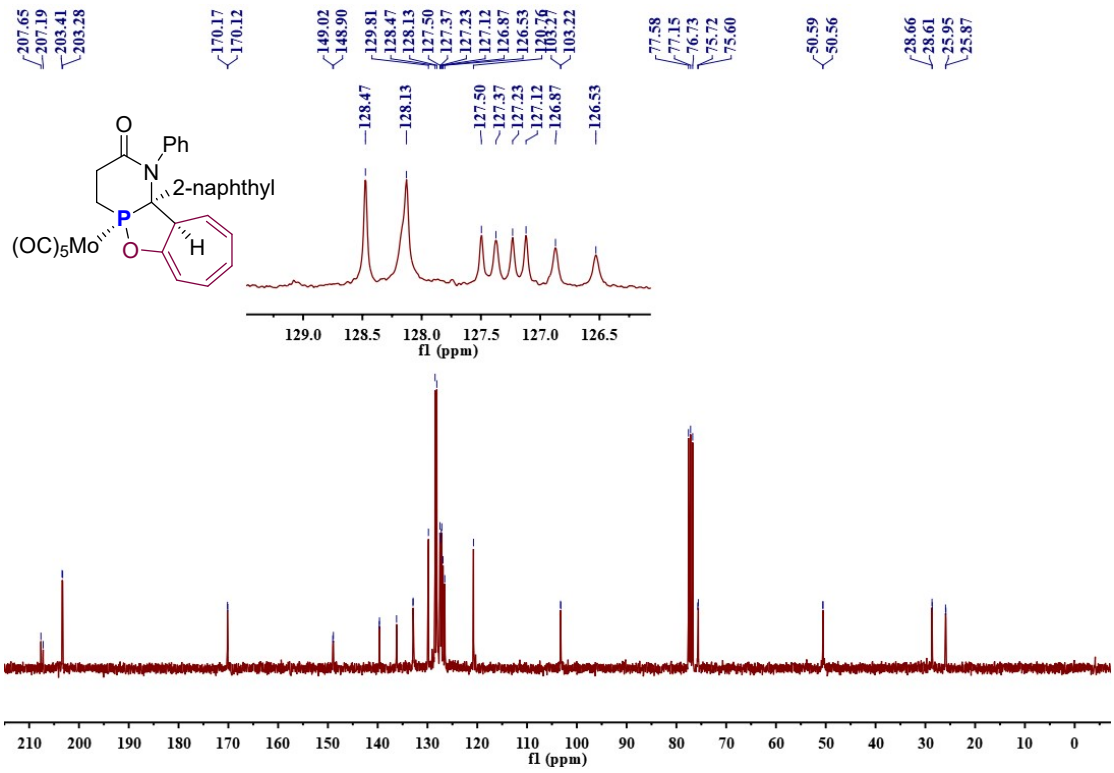
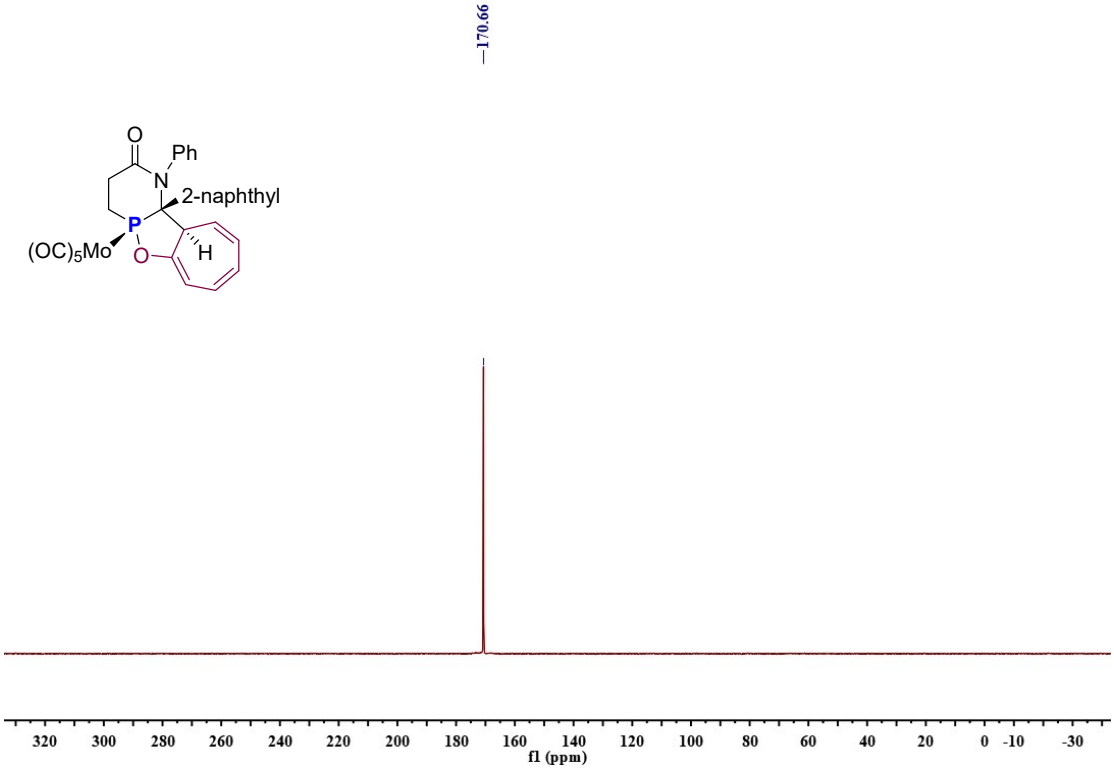


$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2d



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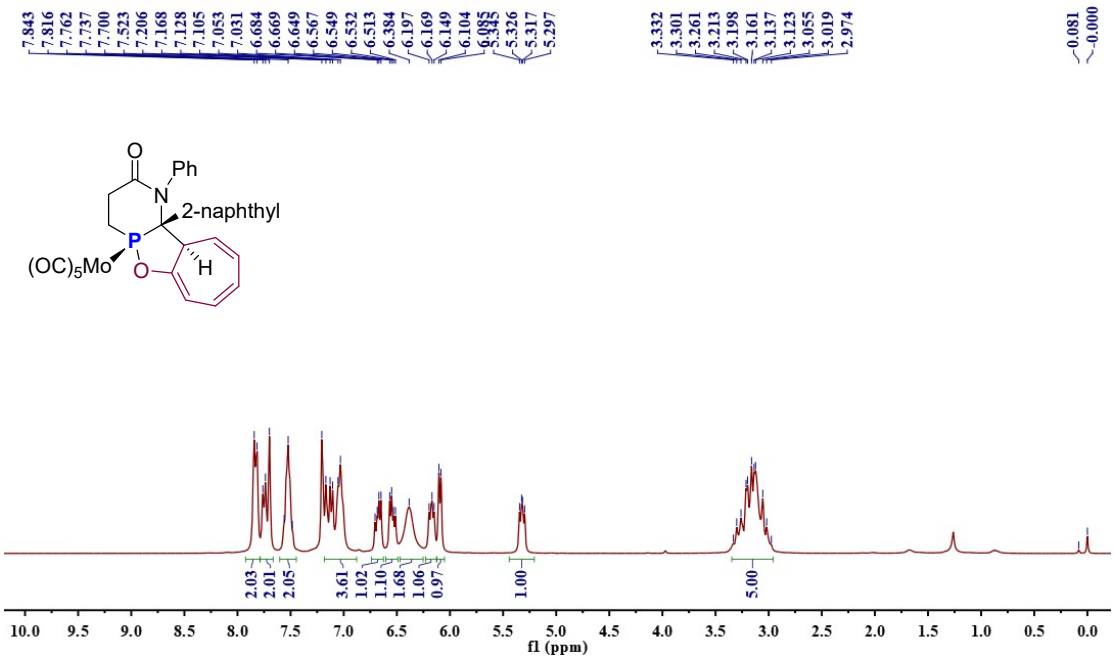
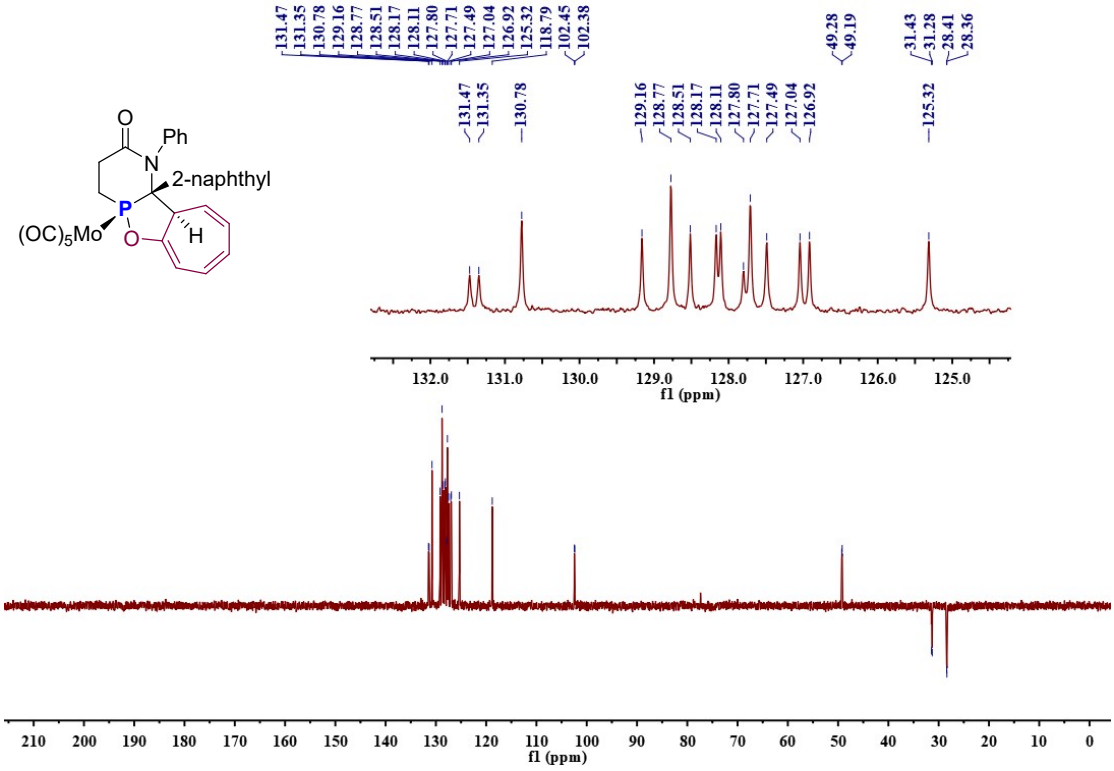


^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2d'



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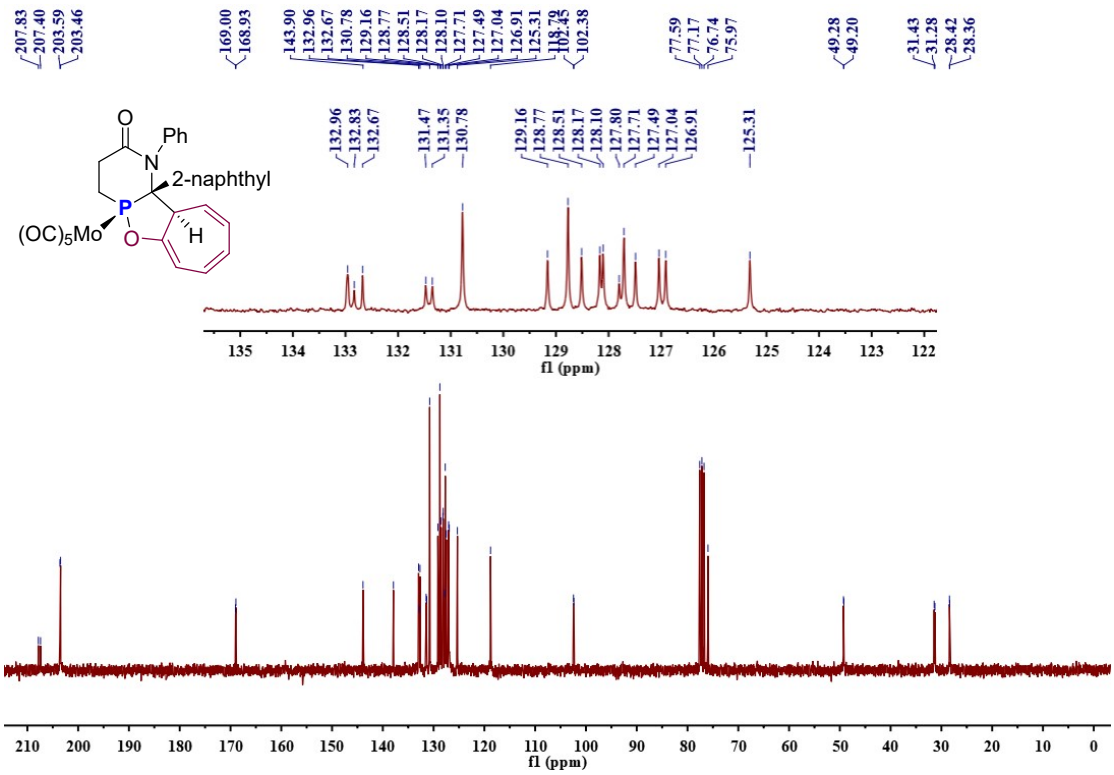
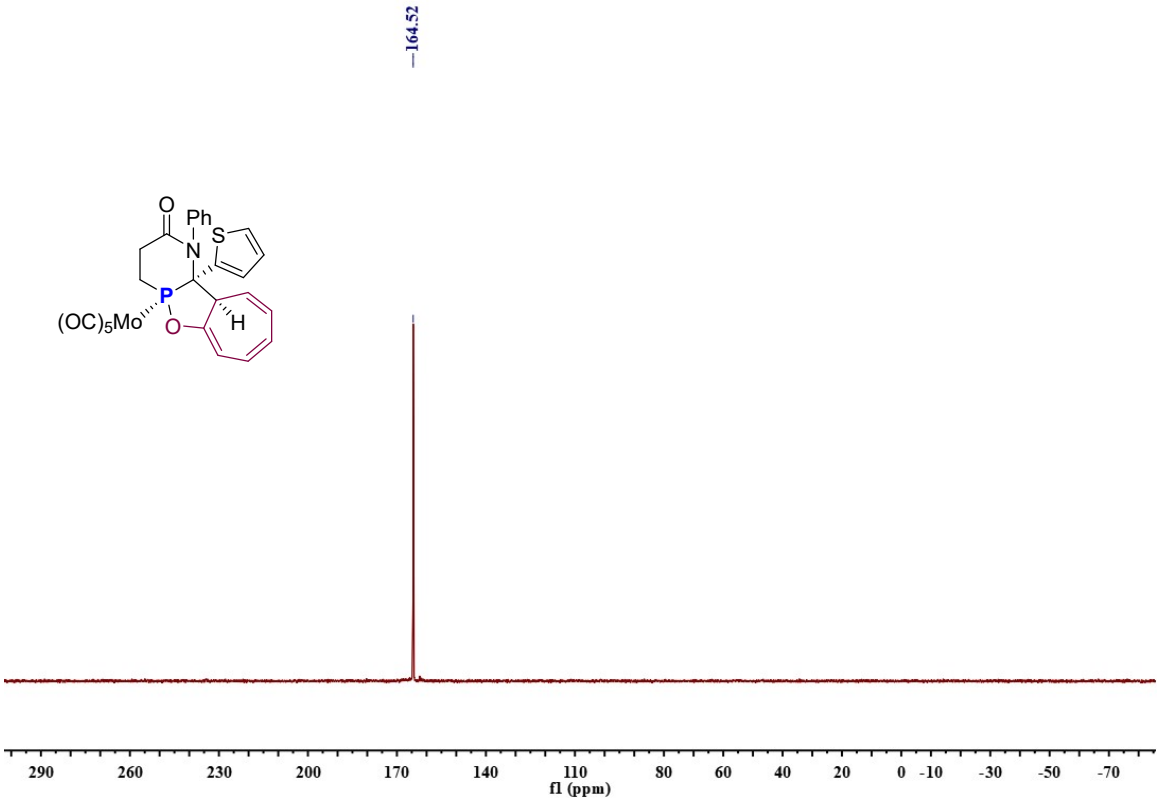
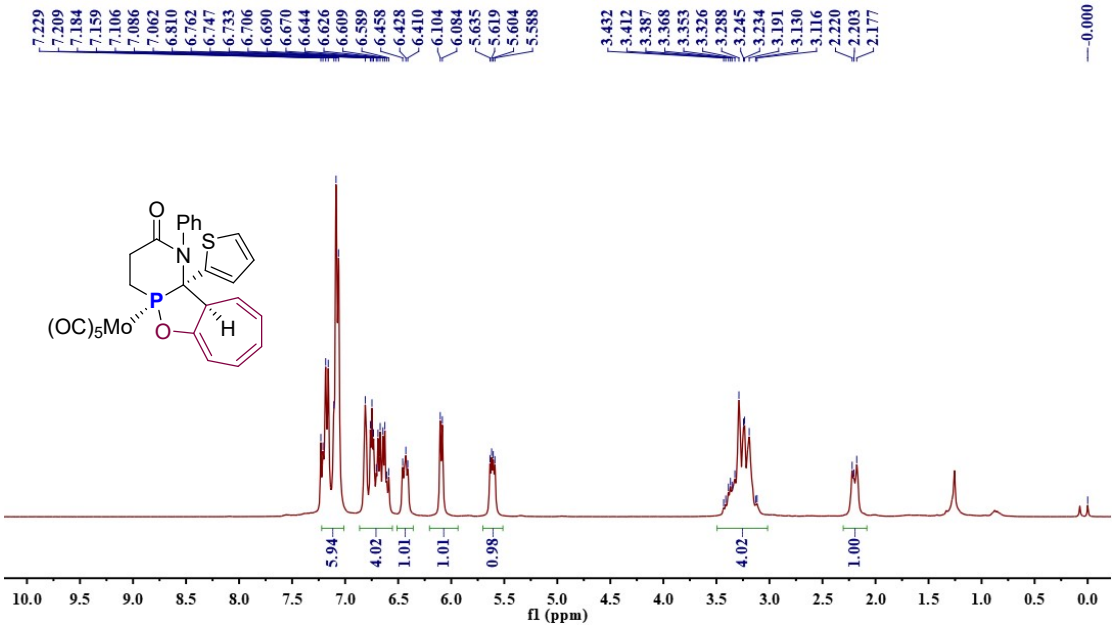


$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2d'



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



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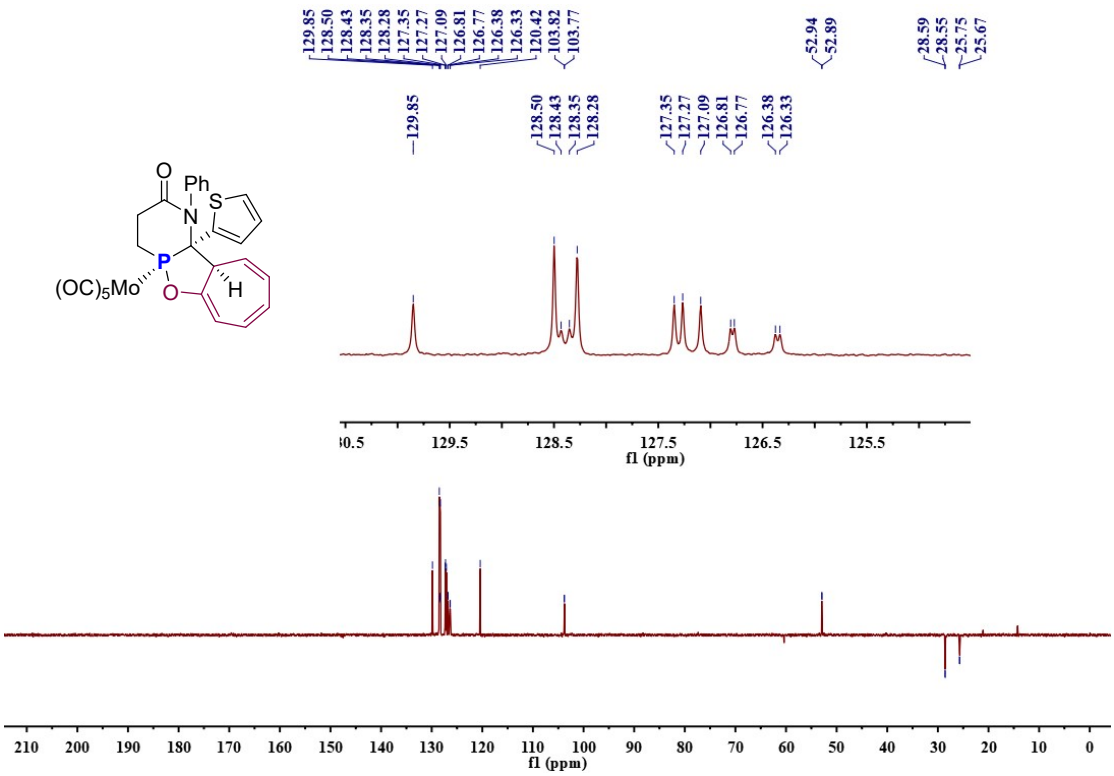

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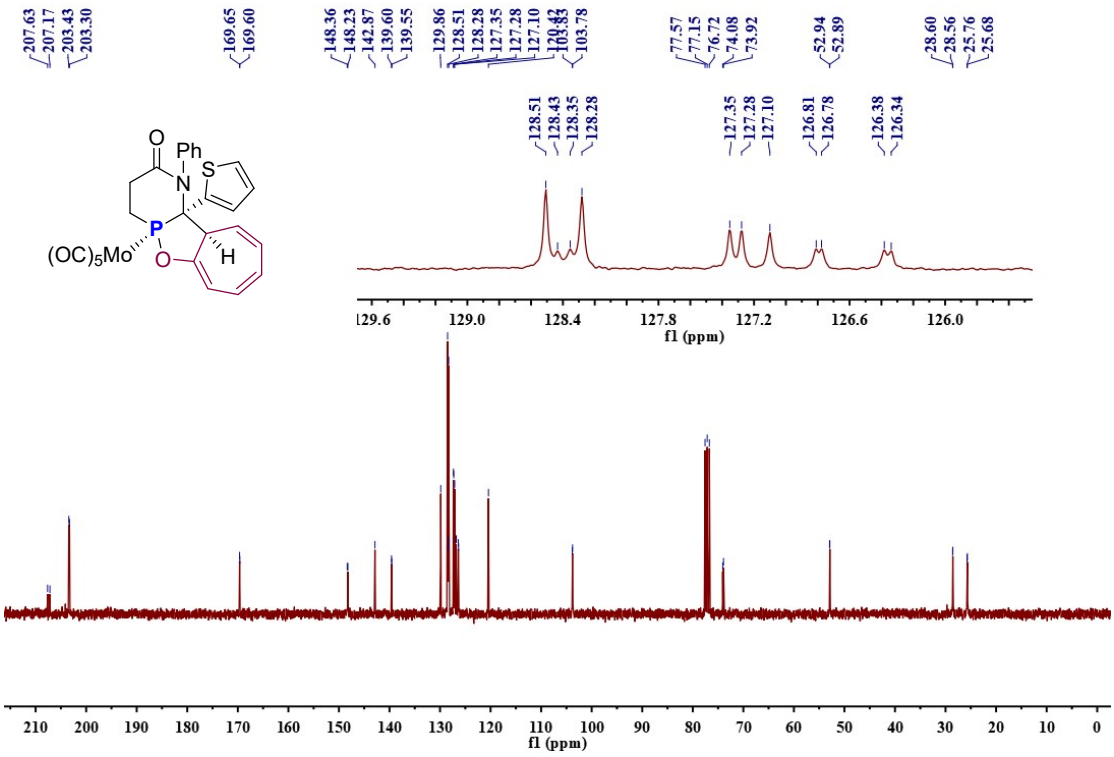
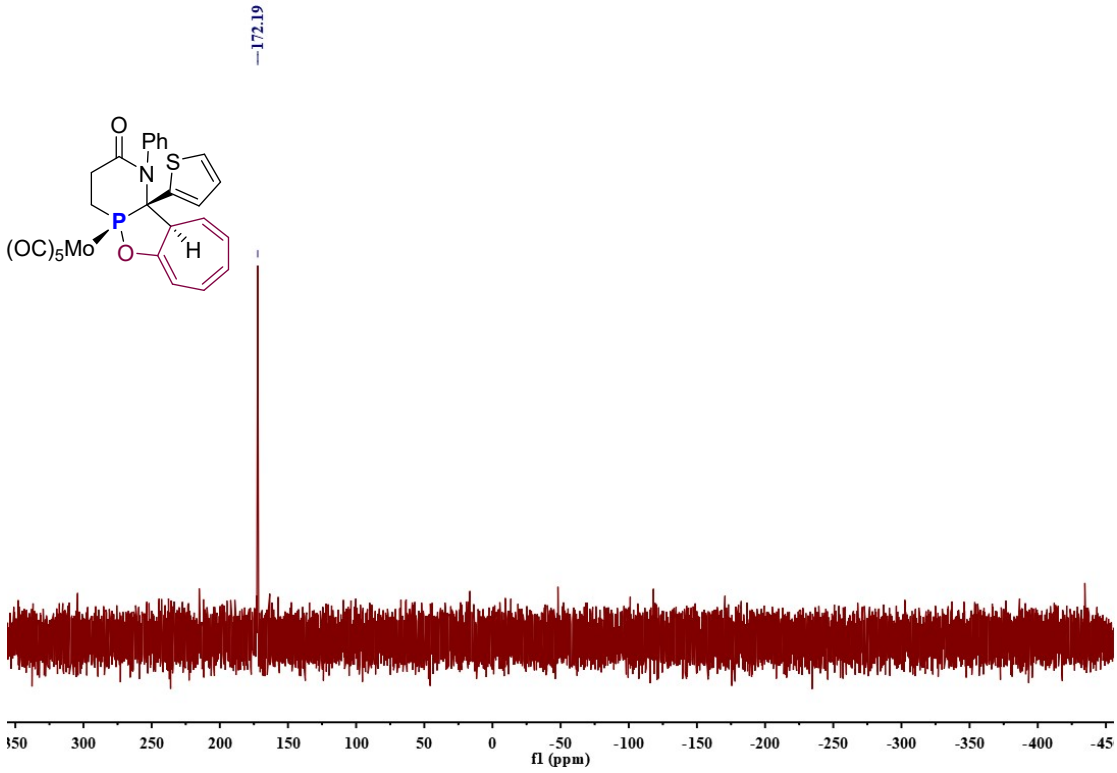


$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2e



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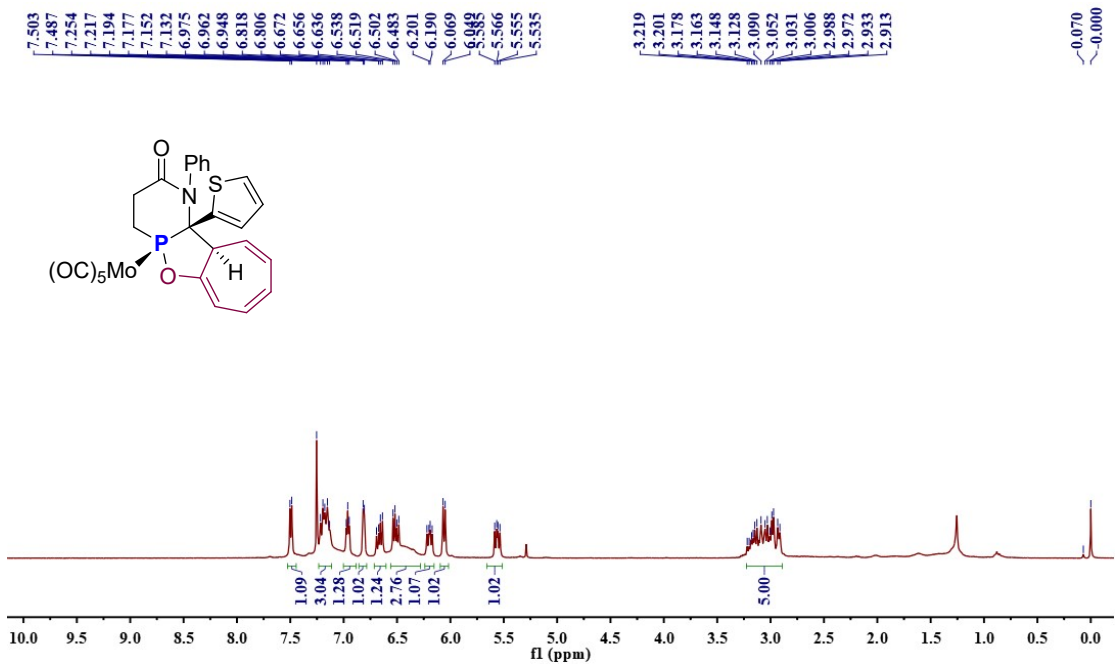

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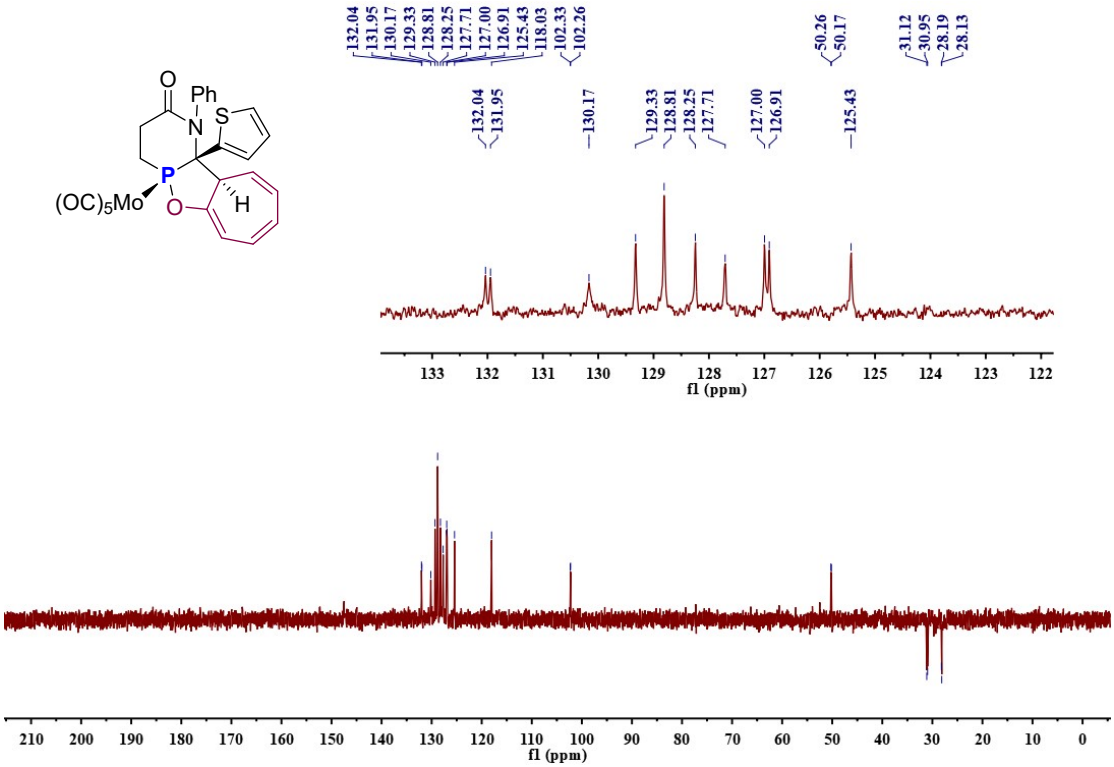
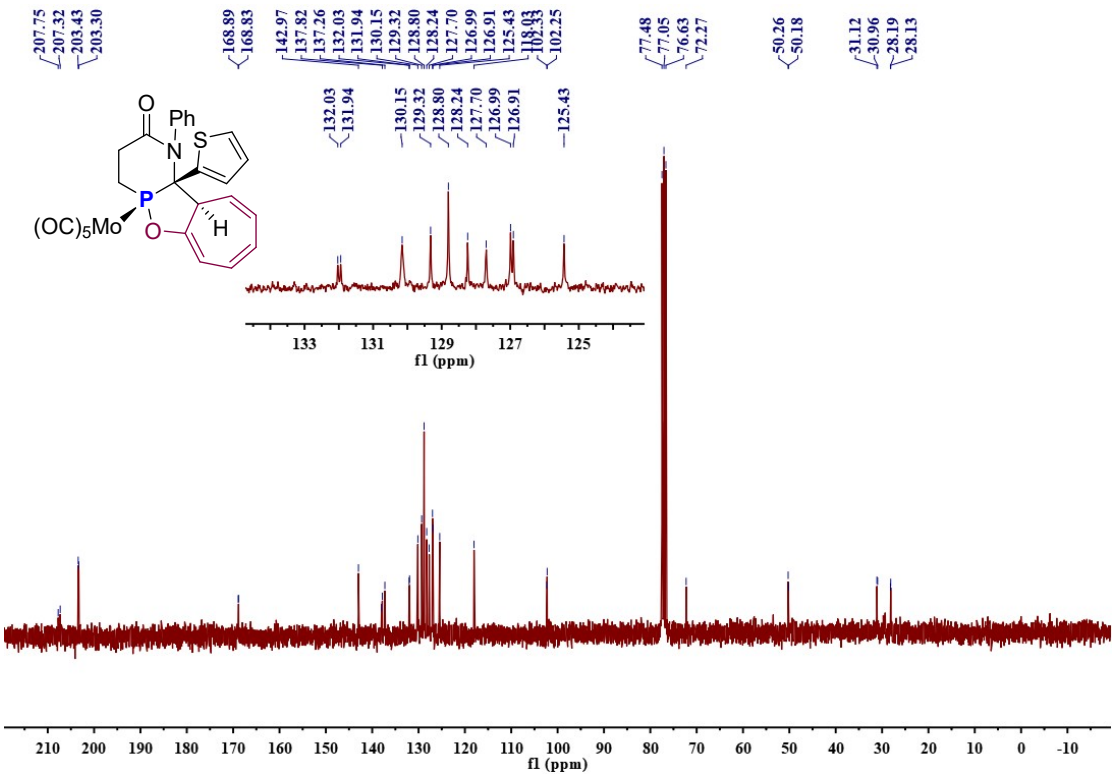
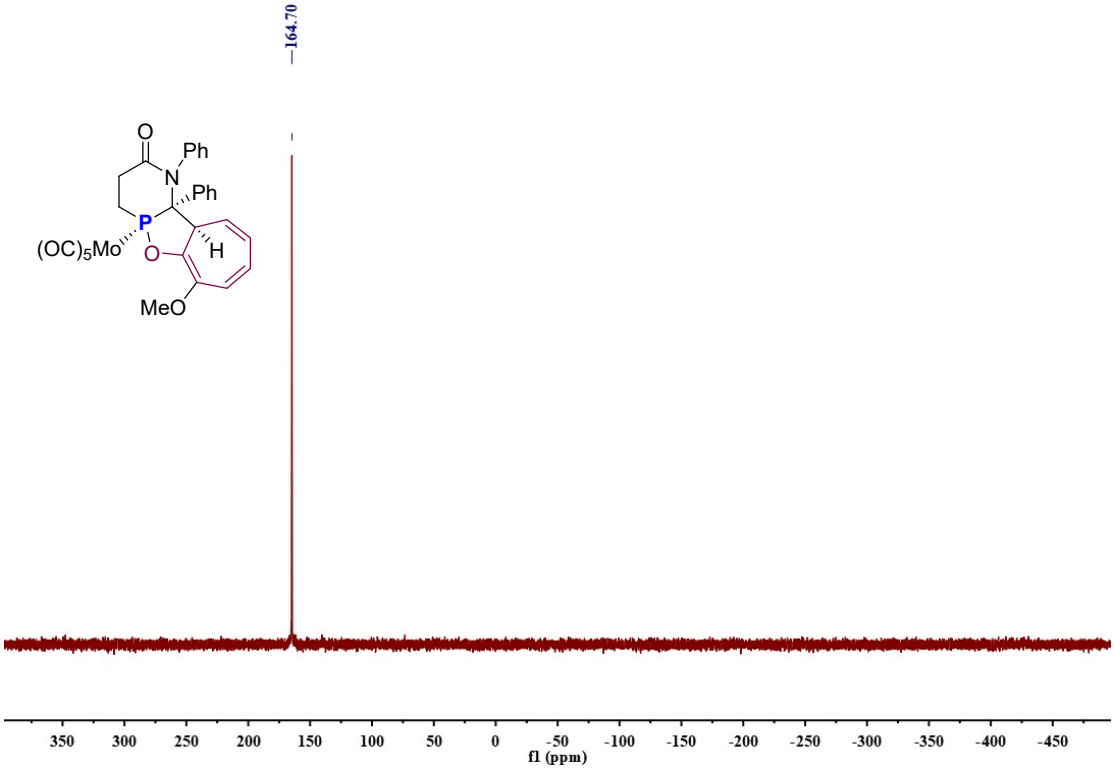


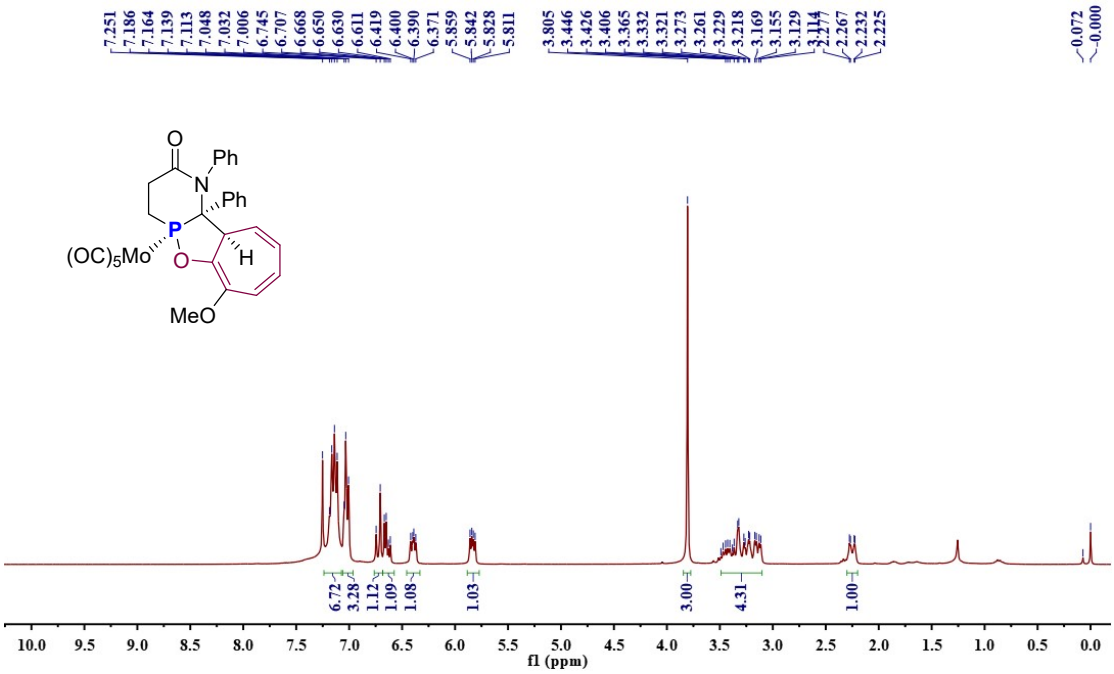
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 2e'



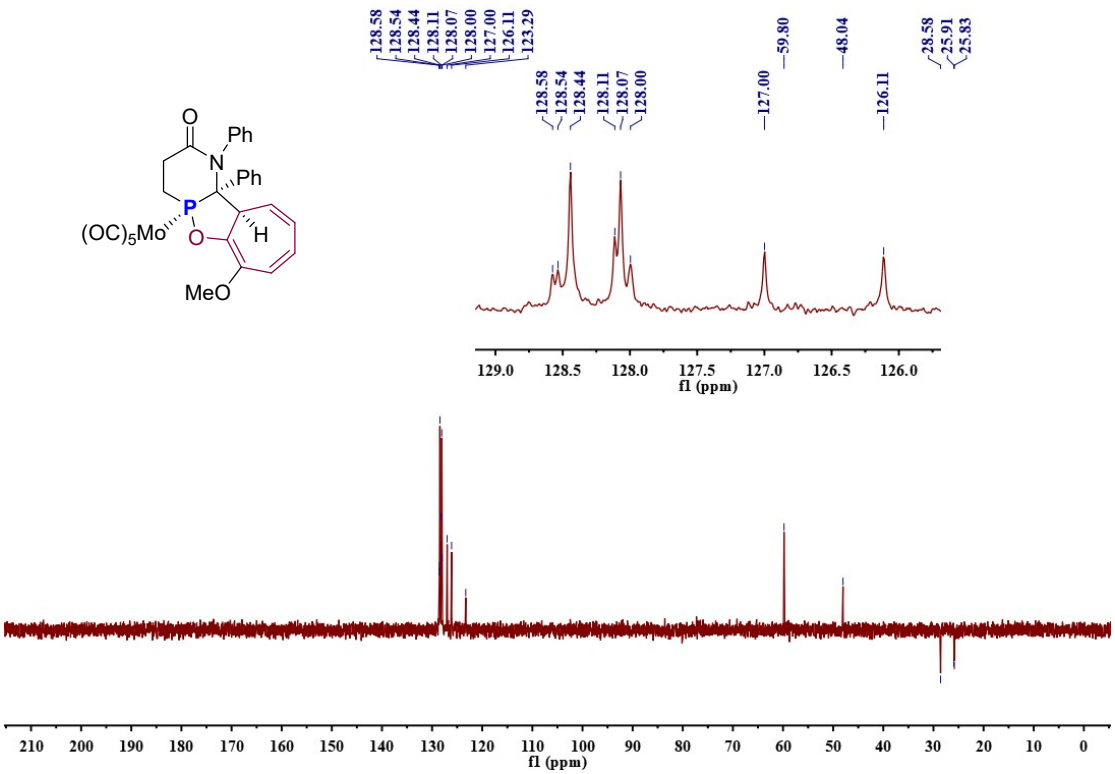
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2e'



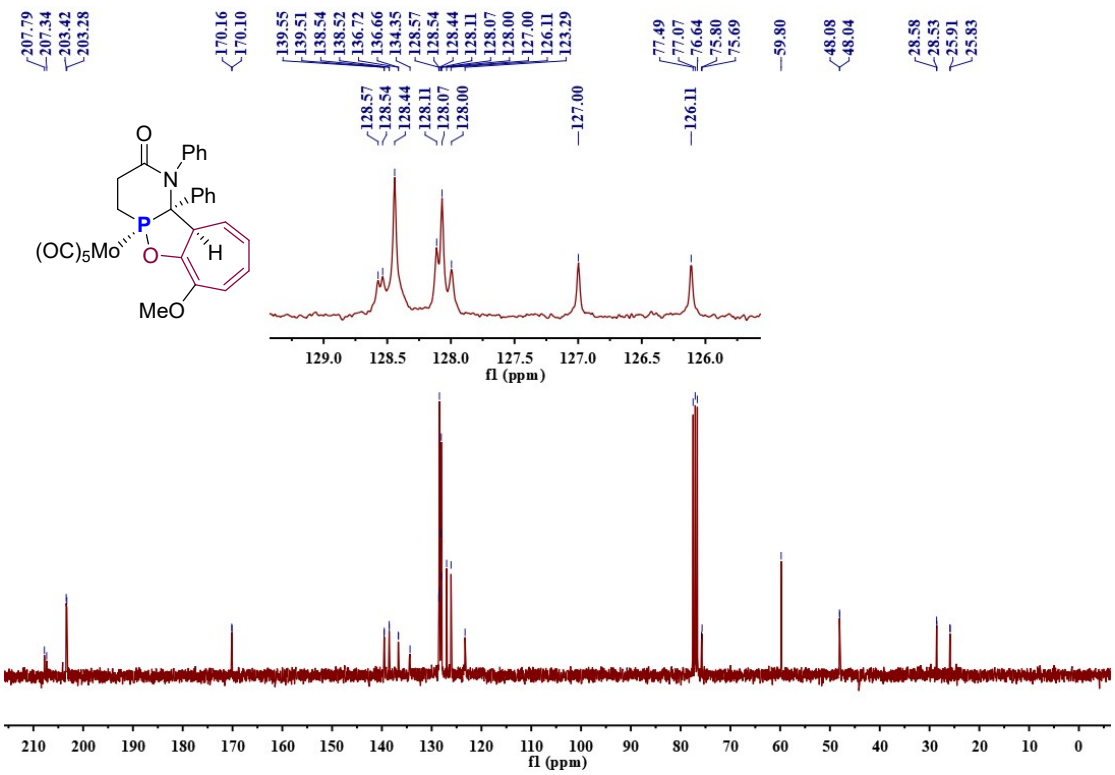
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2f



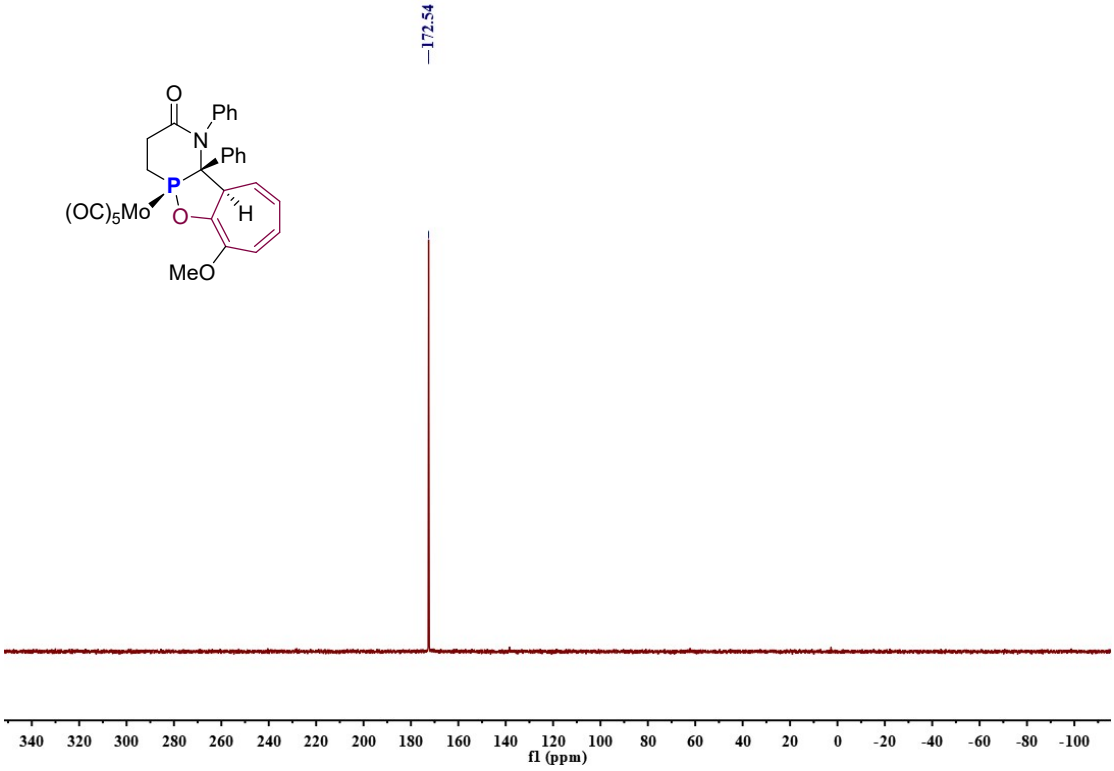
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2f



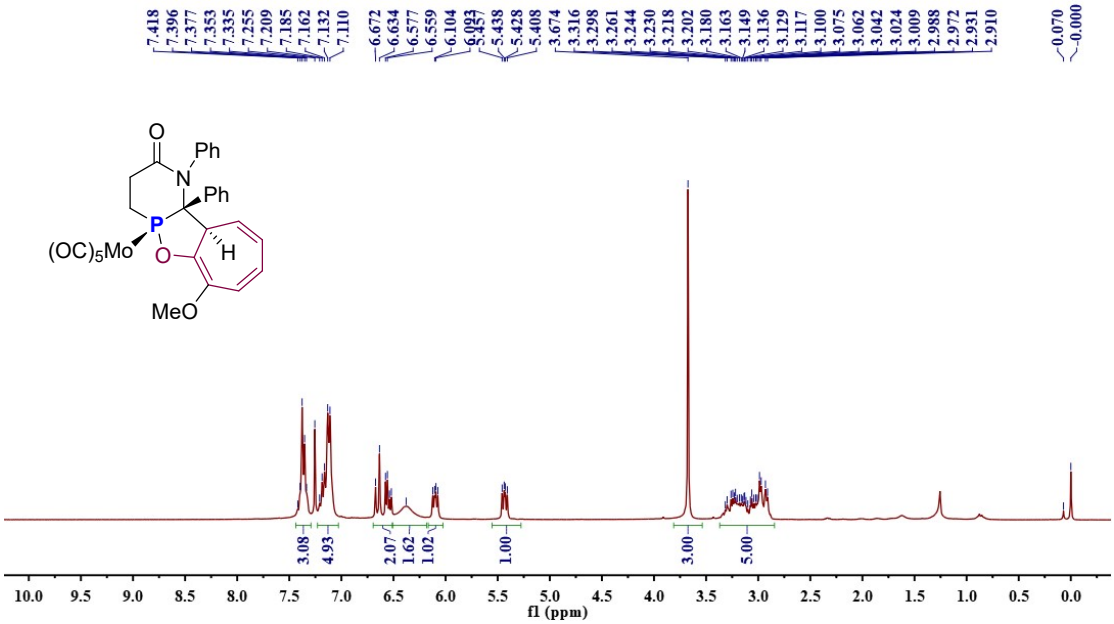
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 2f



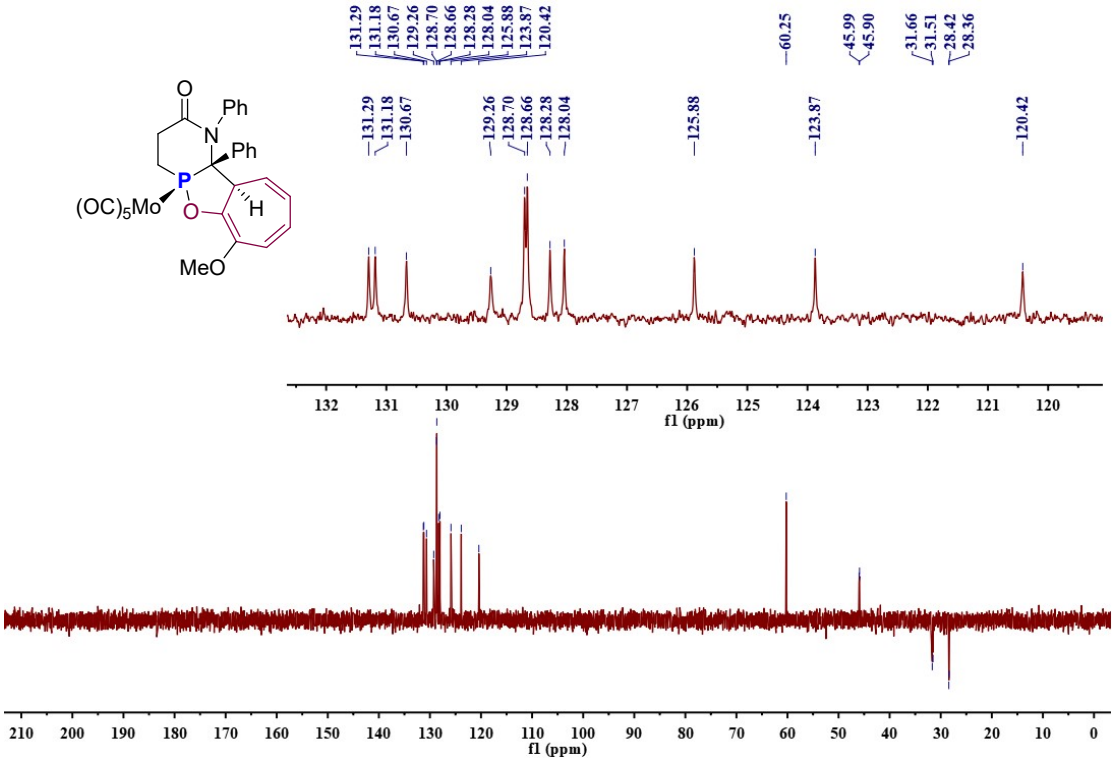
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2f



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



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



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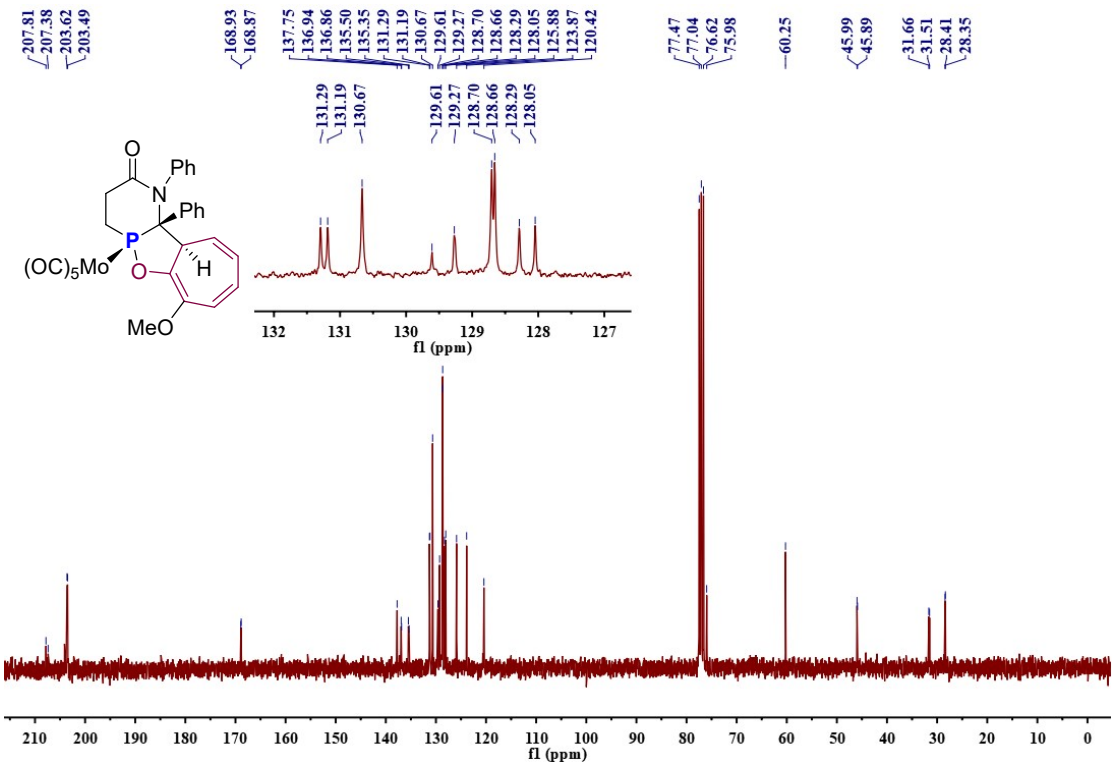
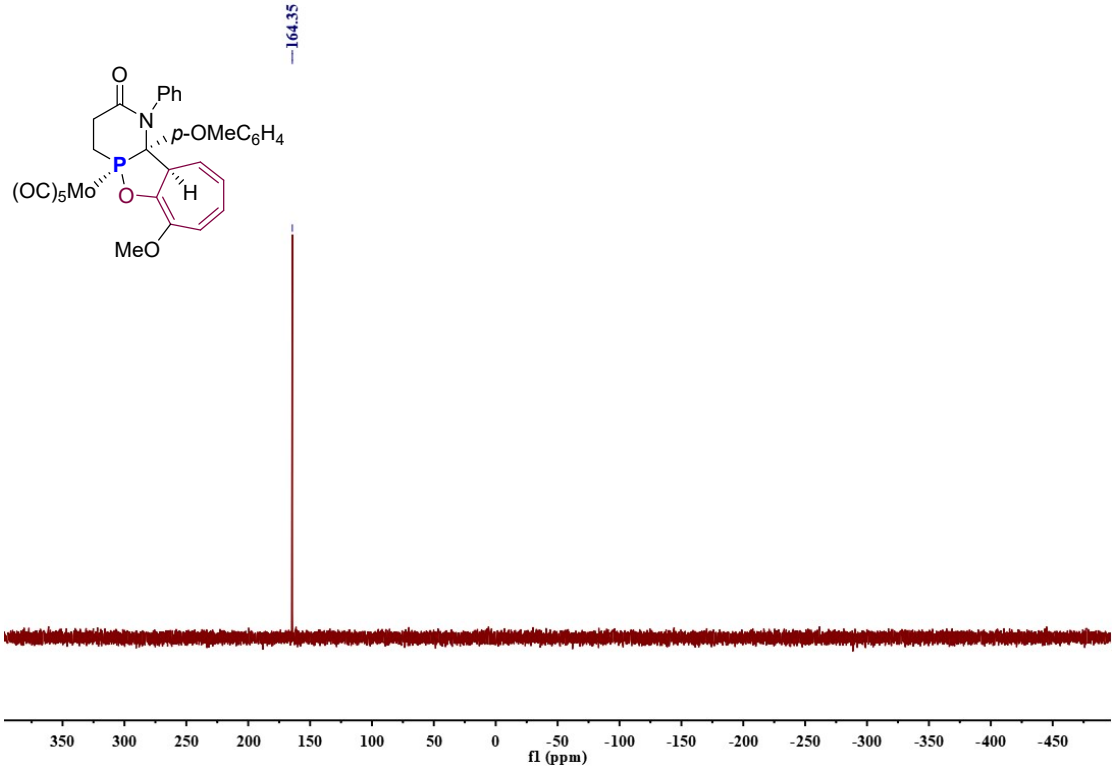
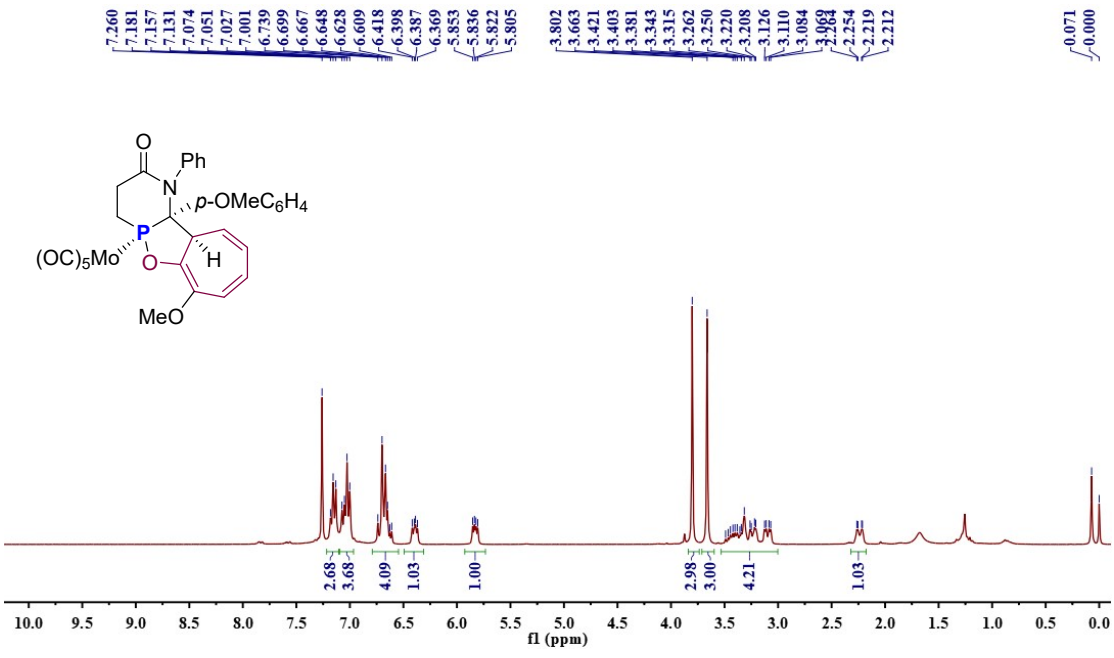


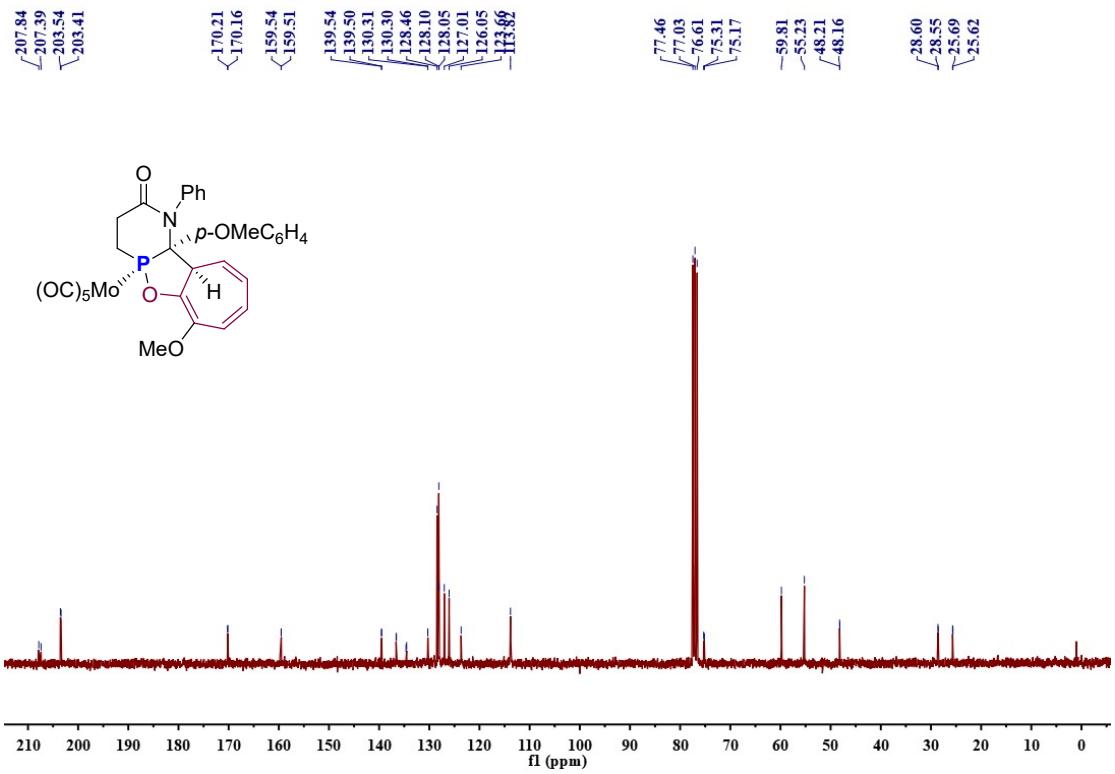
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2f'



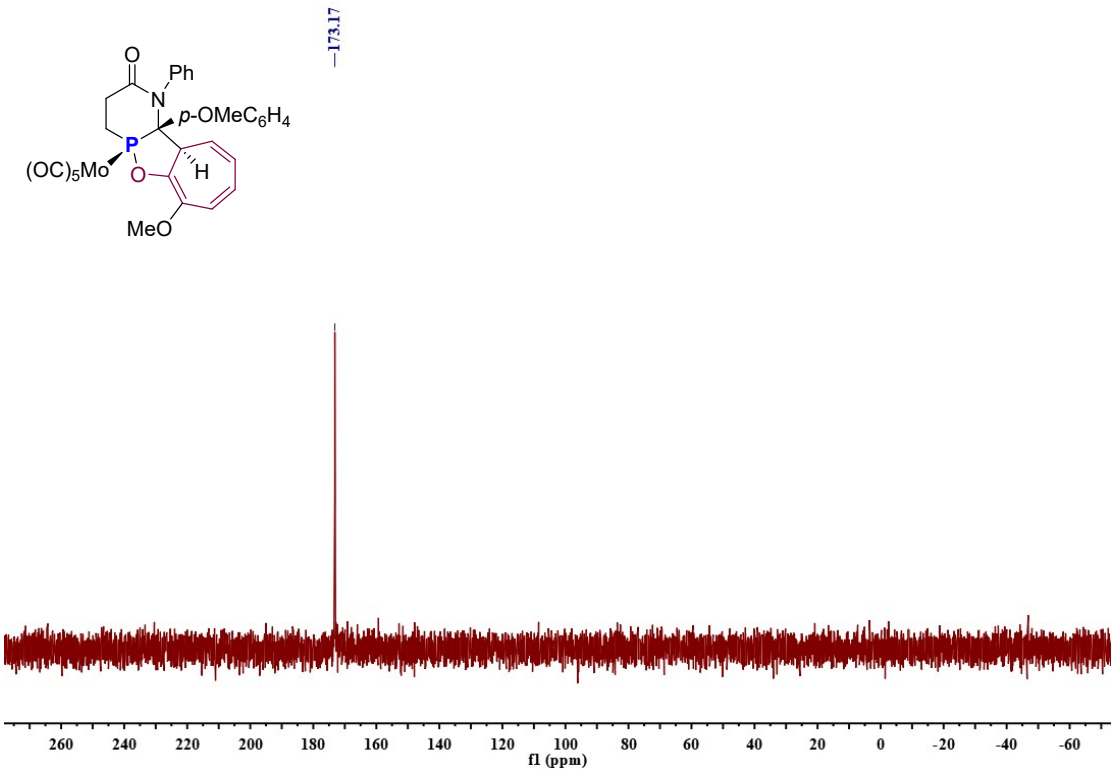
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2g



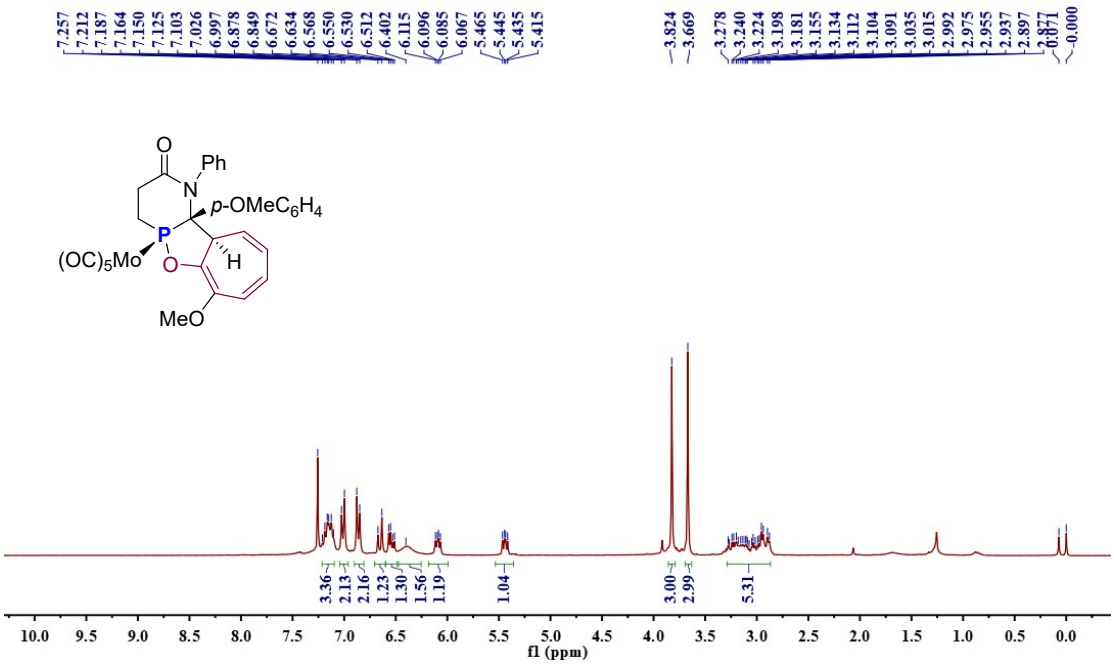
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2g



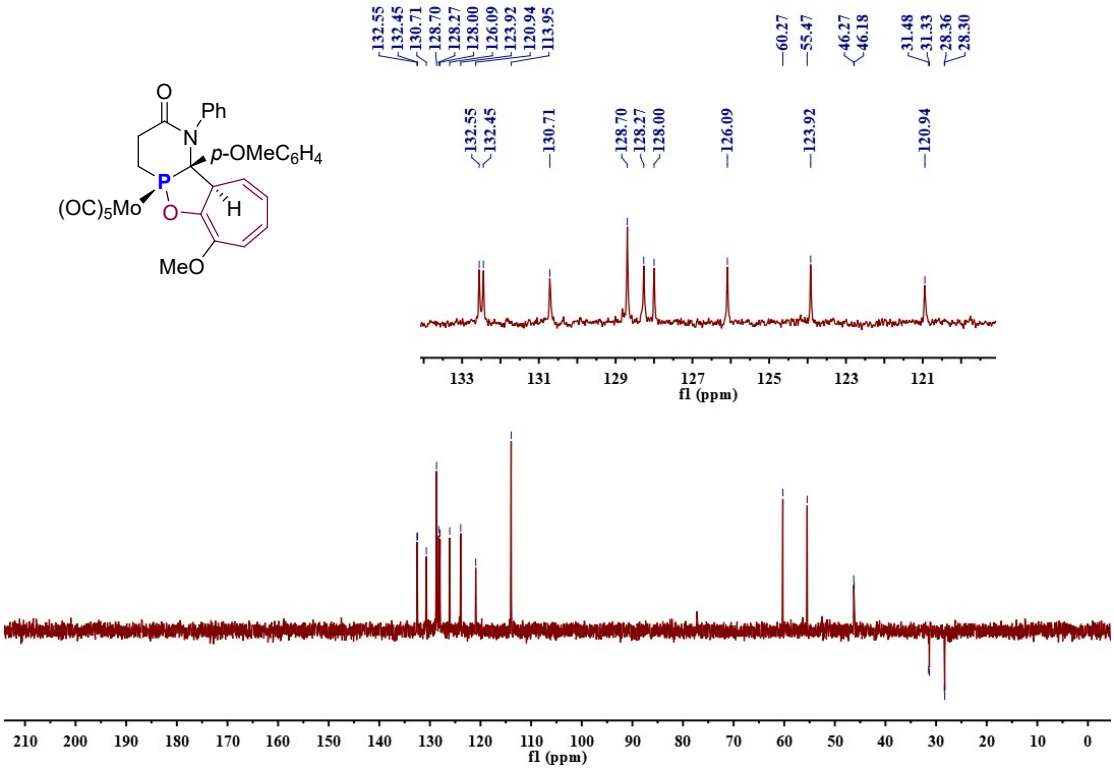
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2g



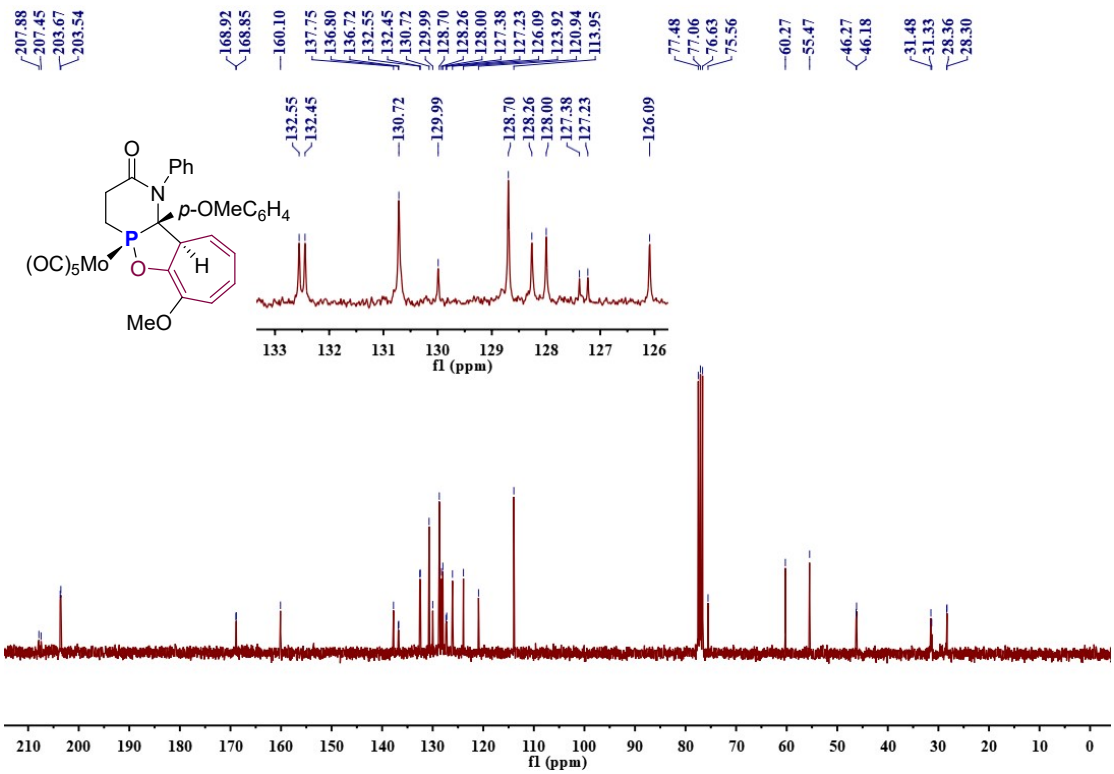
$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2g'



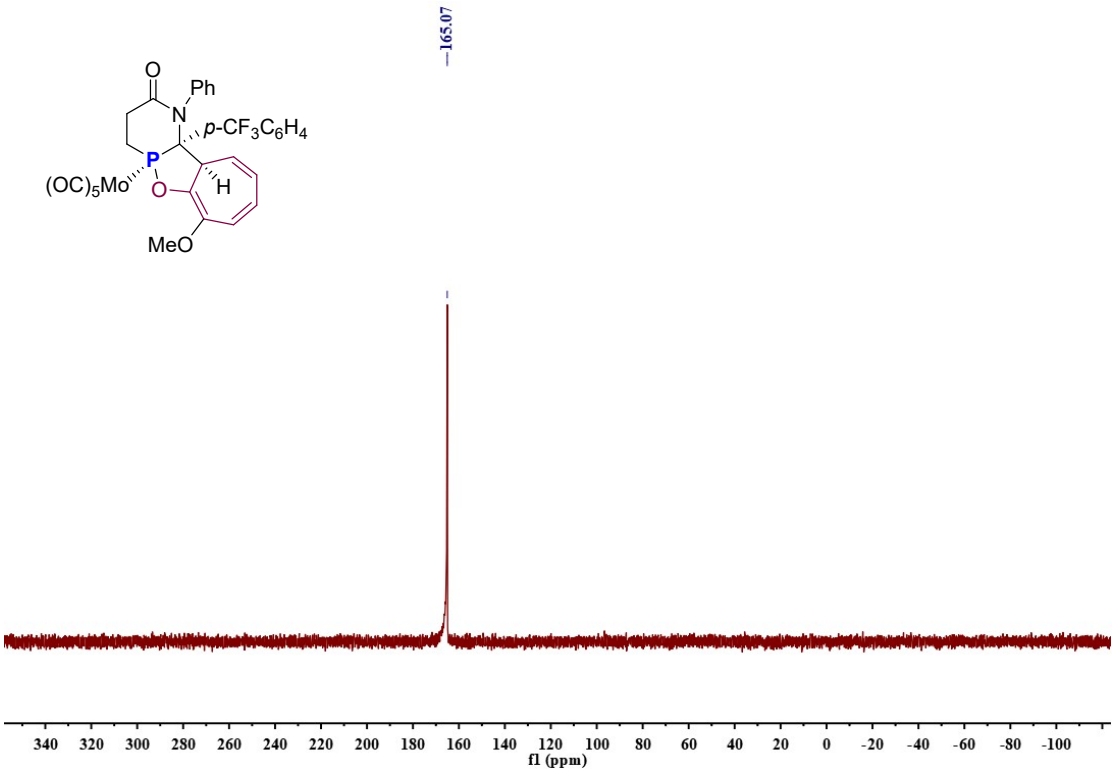
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2g'



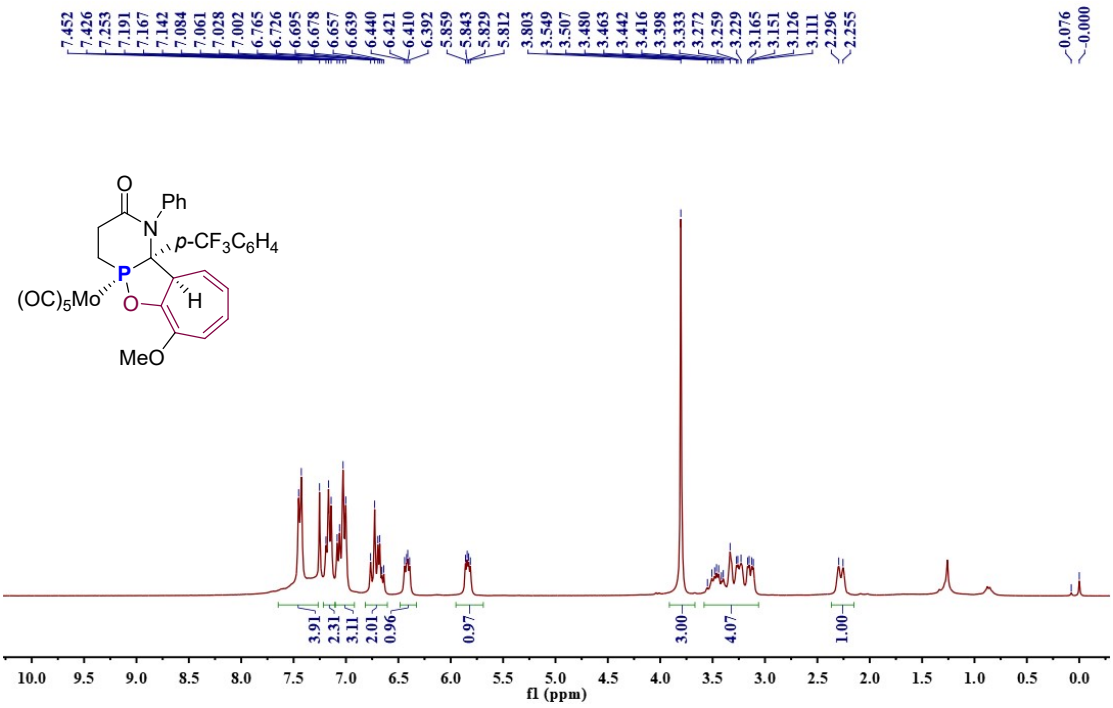
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 2g'



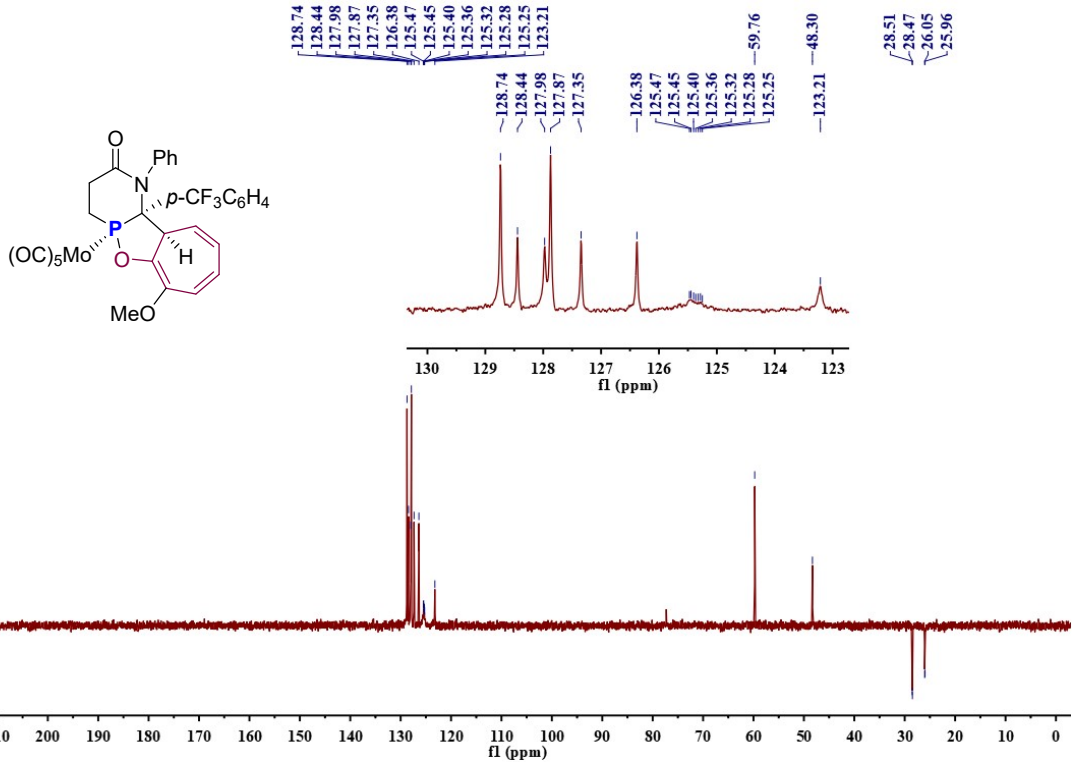
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2g'



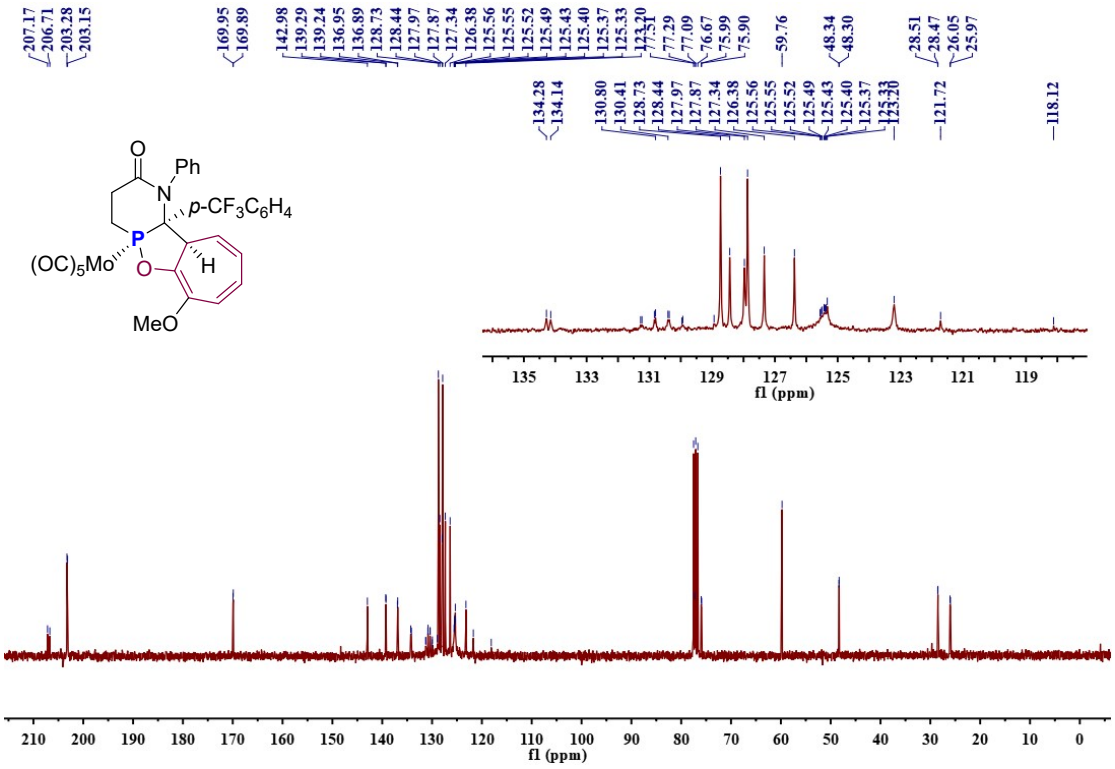
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2h



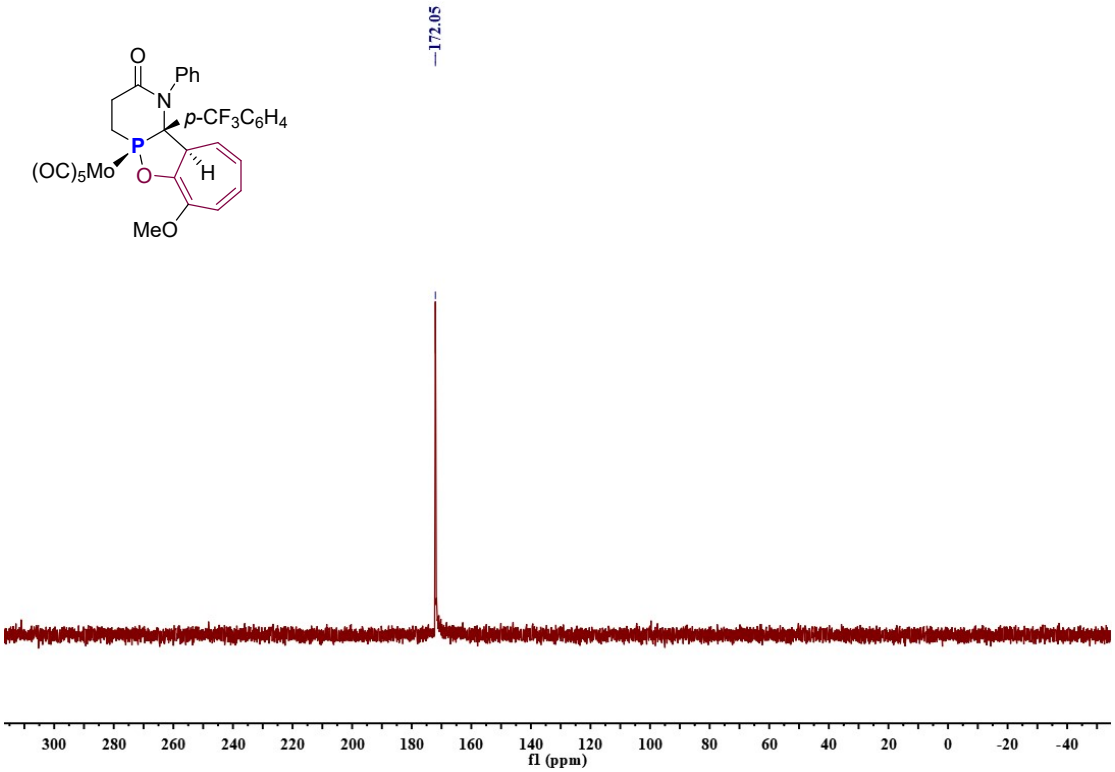
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2h



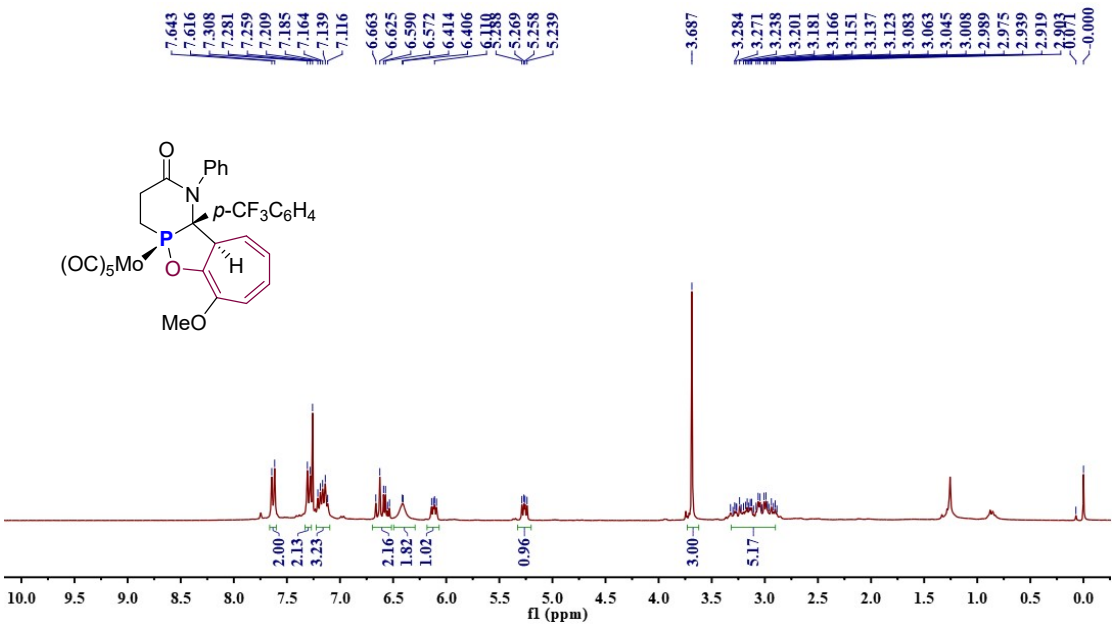
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 2h



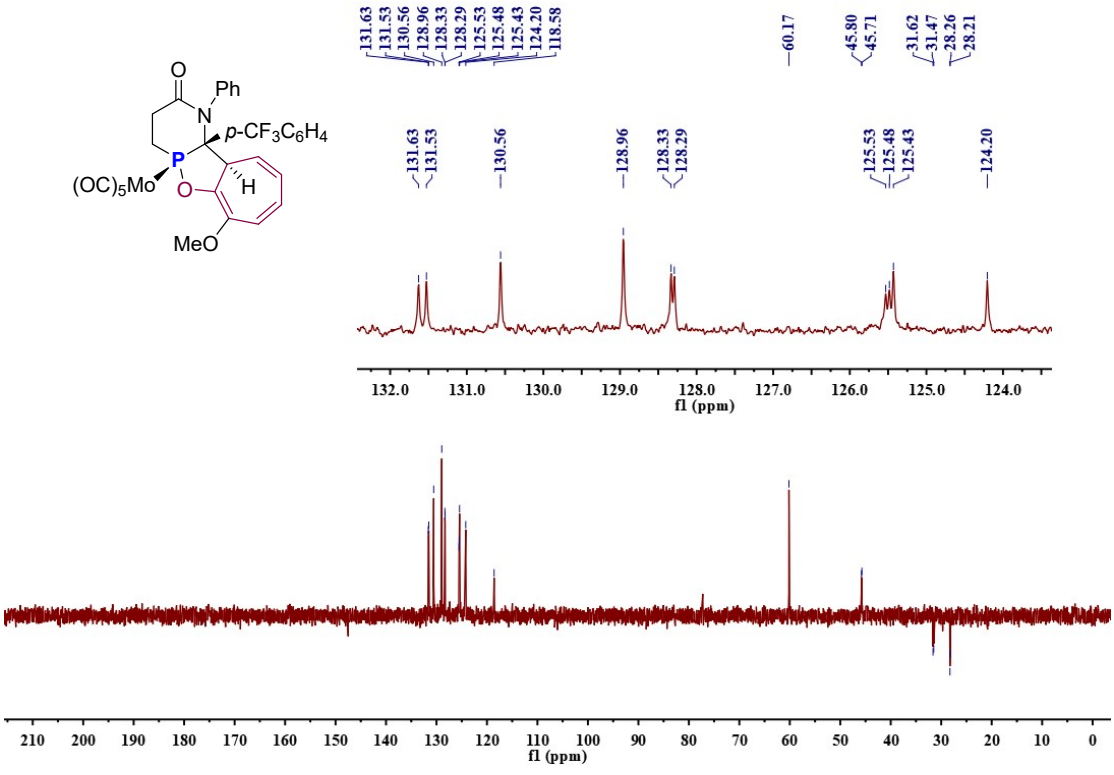
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2h



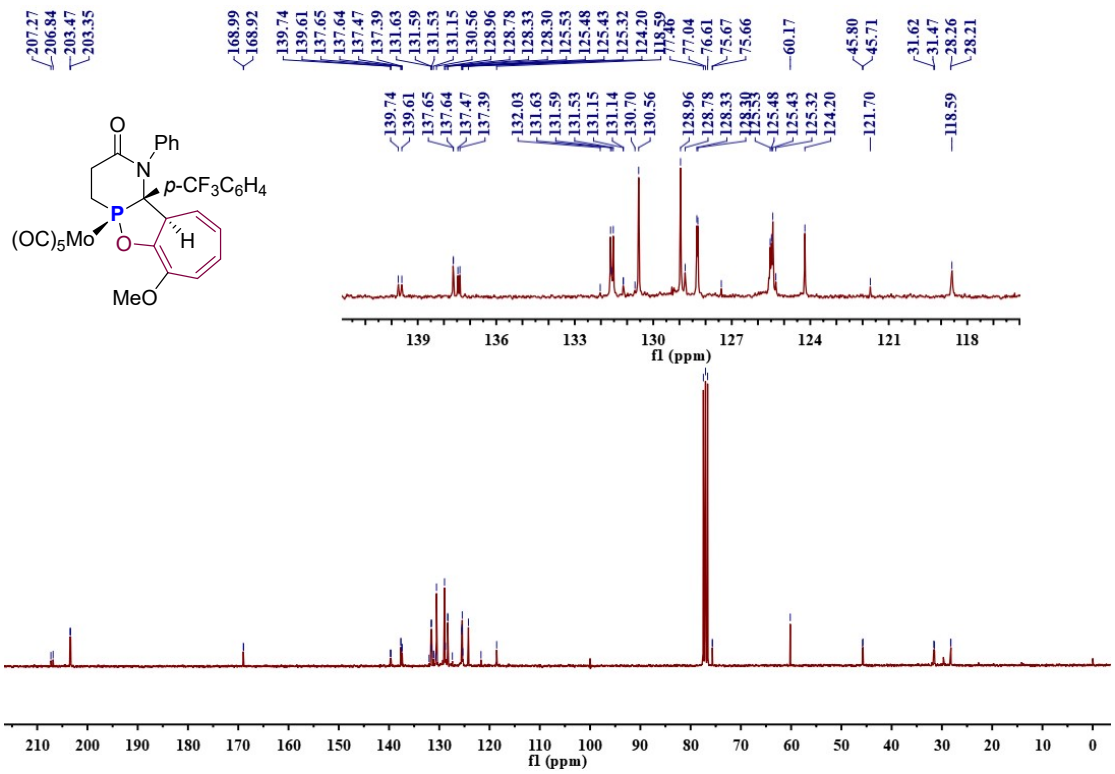
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2h'



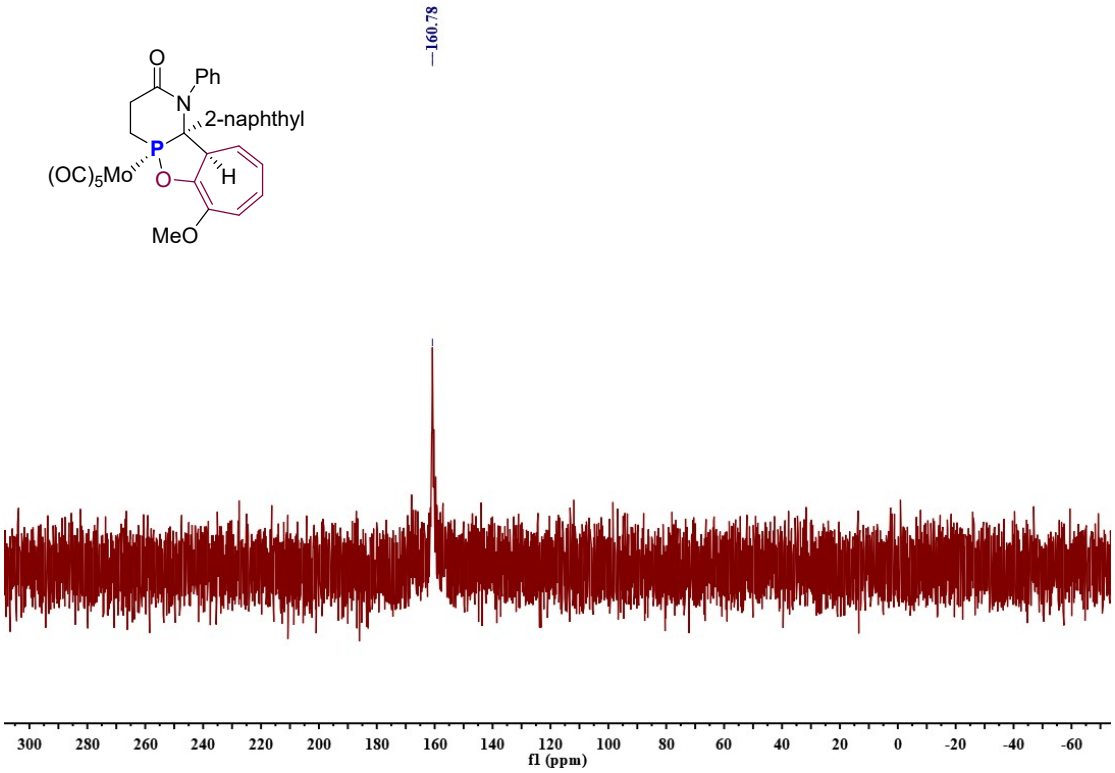
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2h'



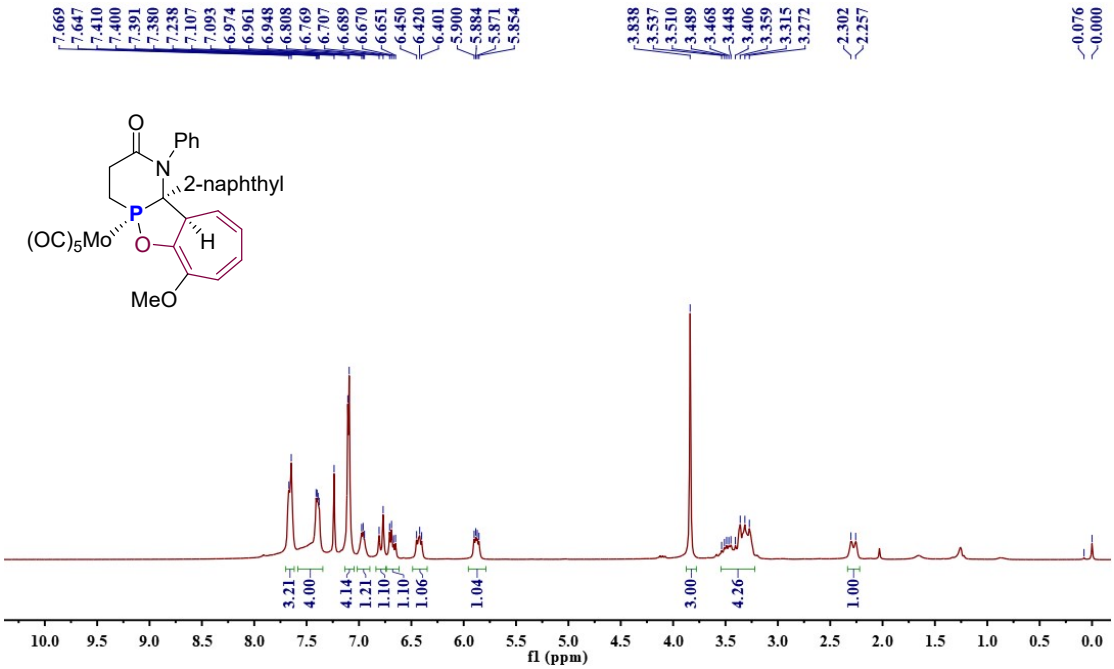
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 2h'



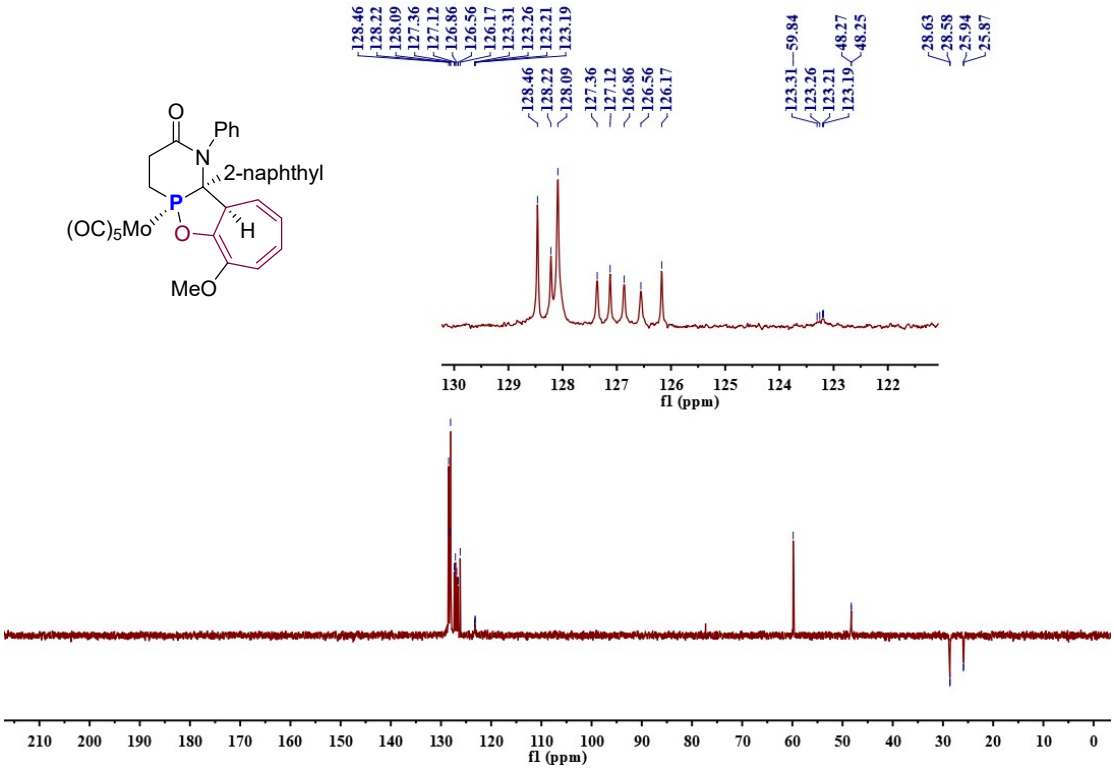
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2h'



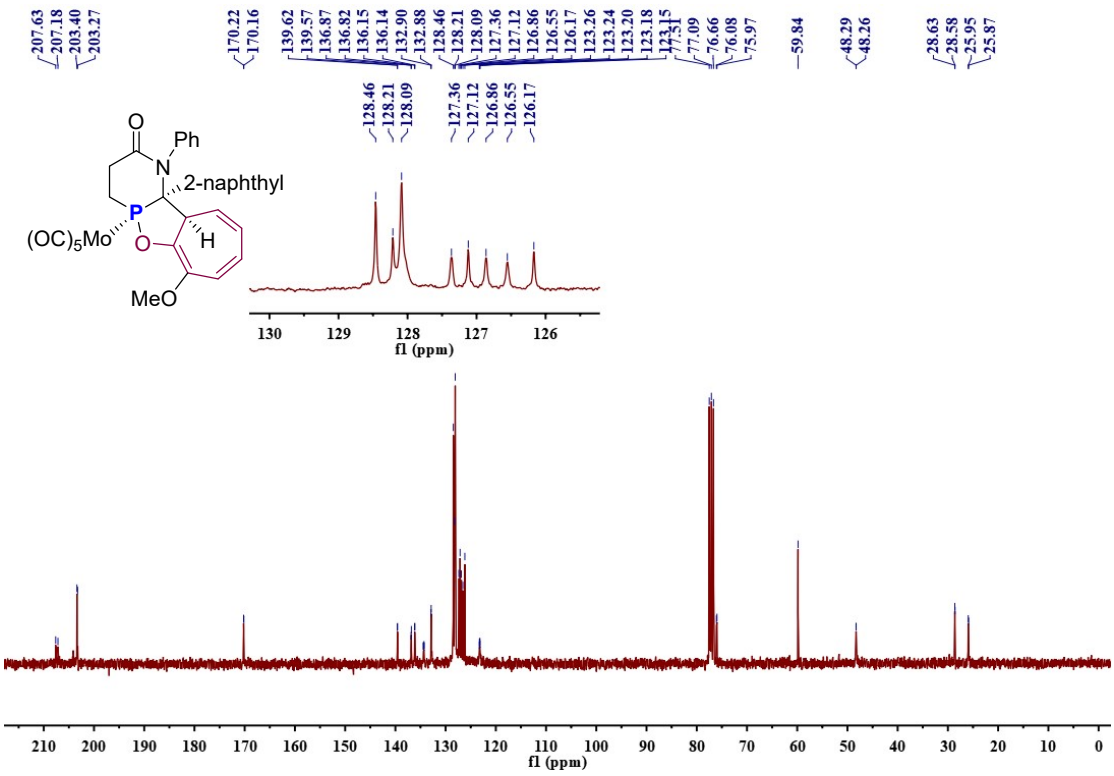
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2i



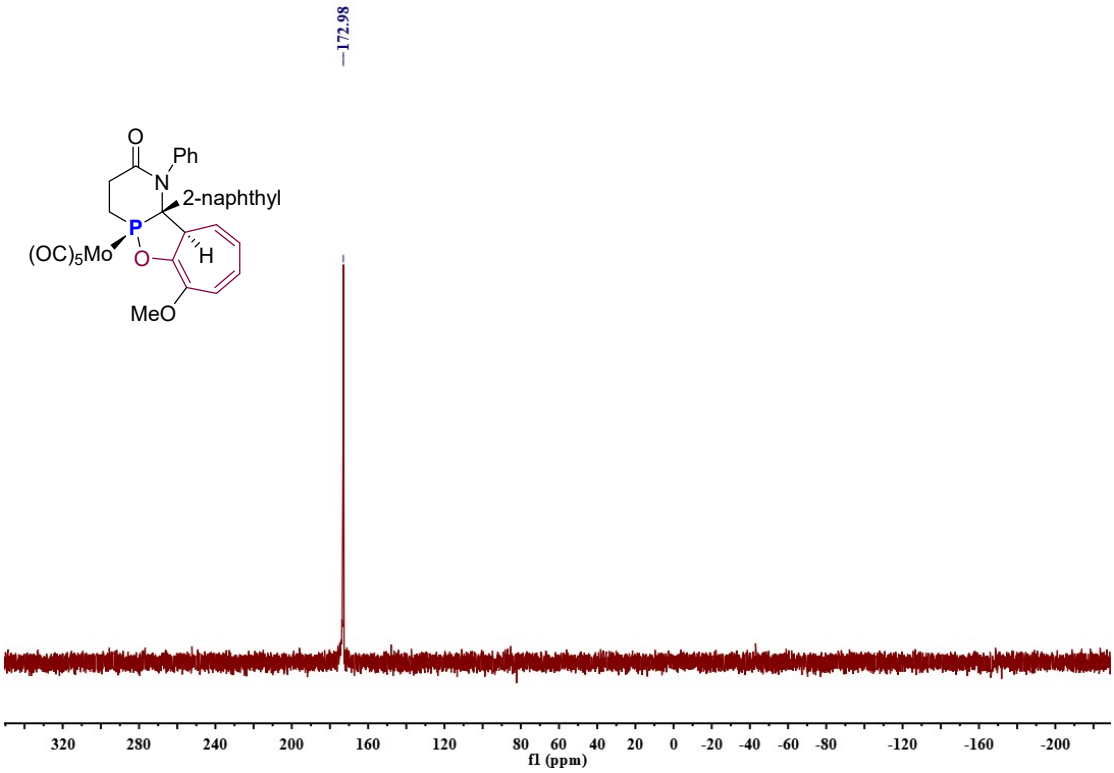
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2i



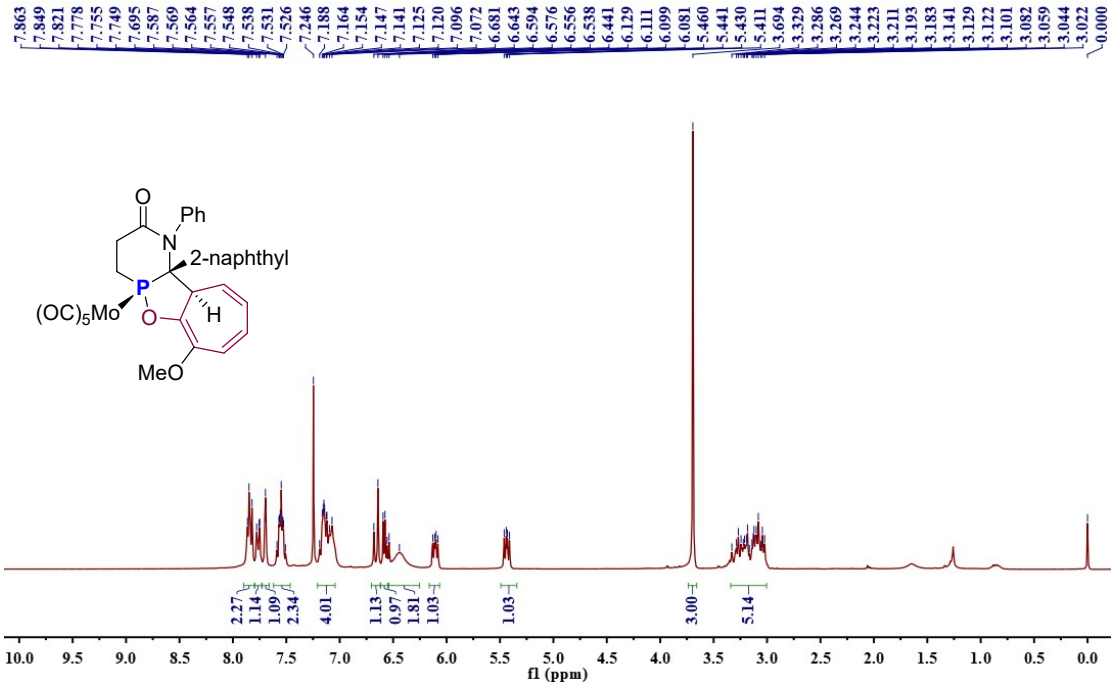
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 2i



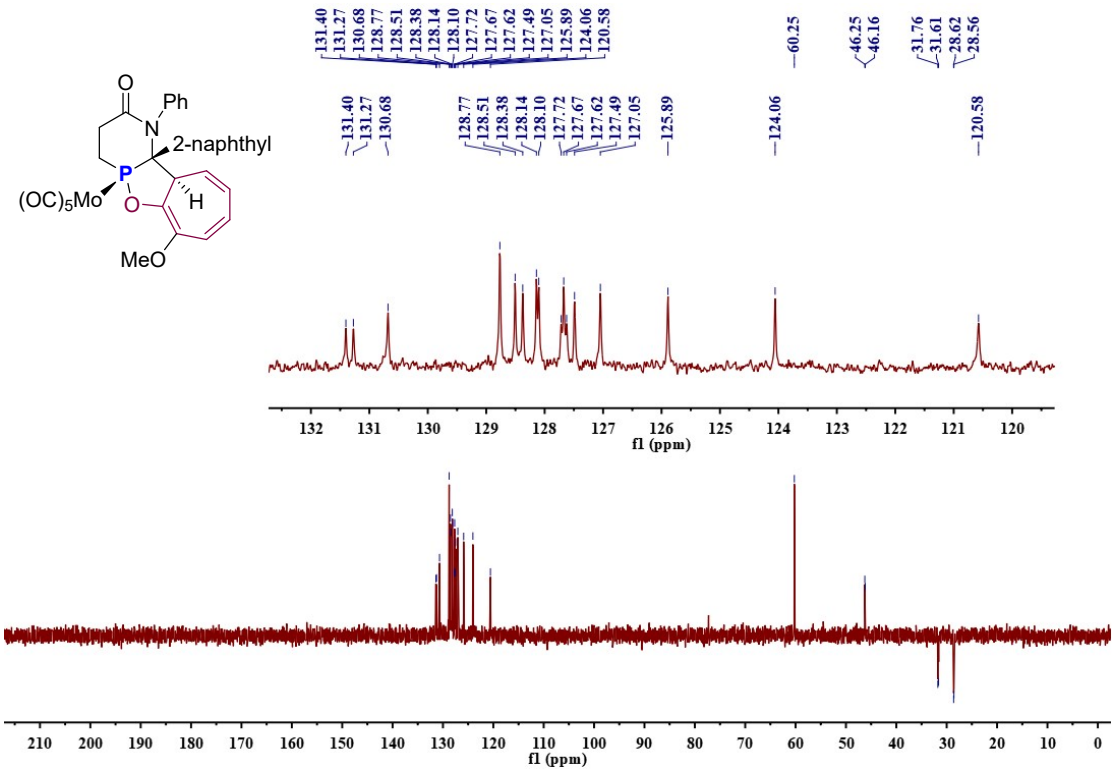
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2i



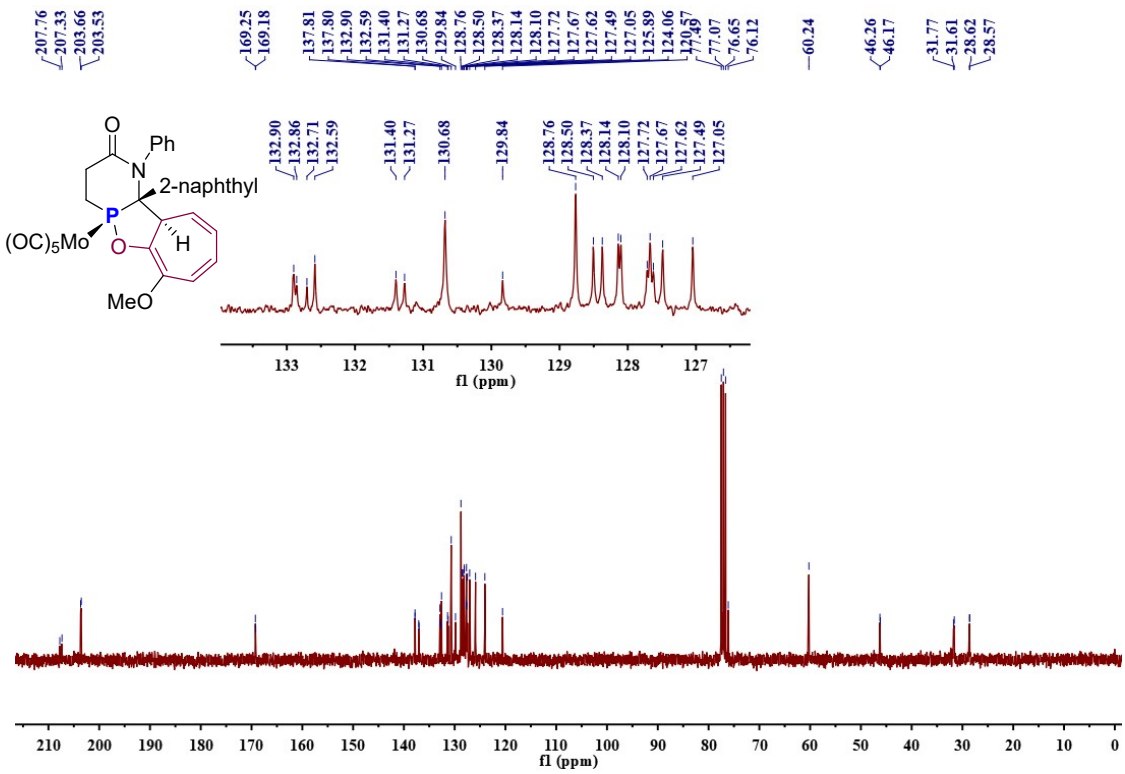
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2i'



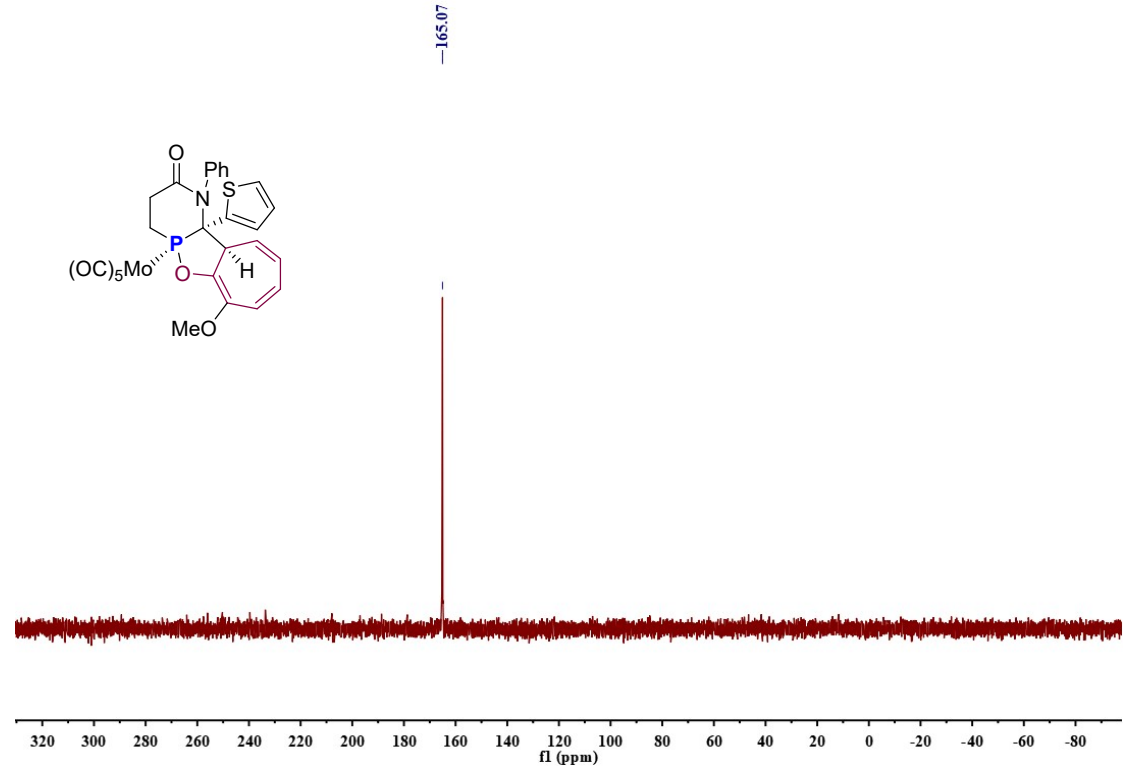
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2i'



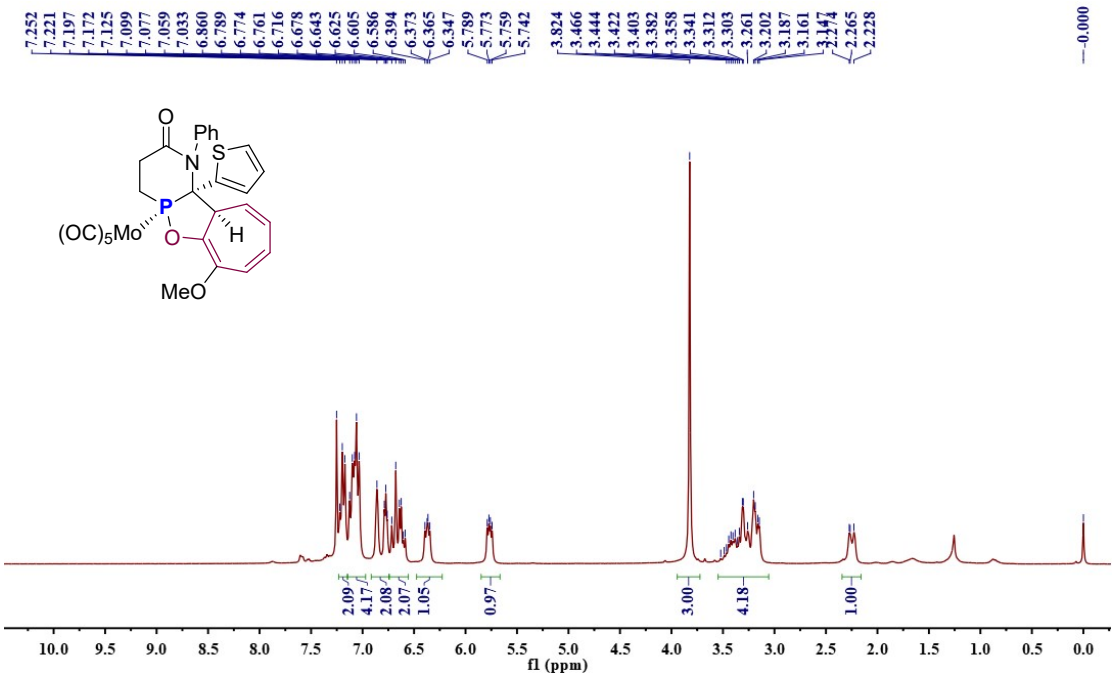
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 2i'



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



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



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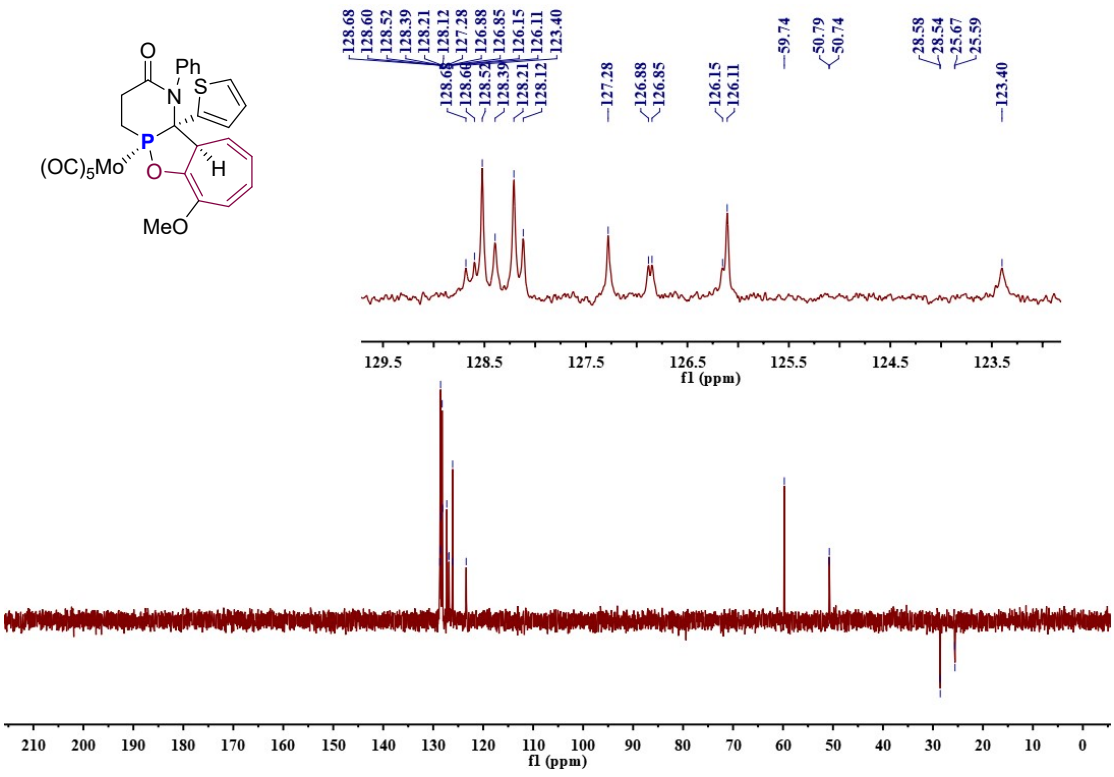
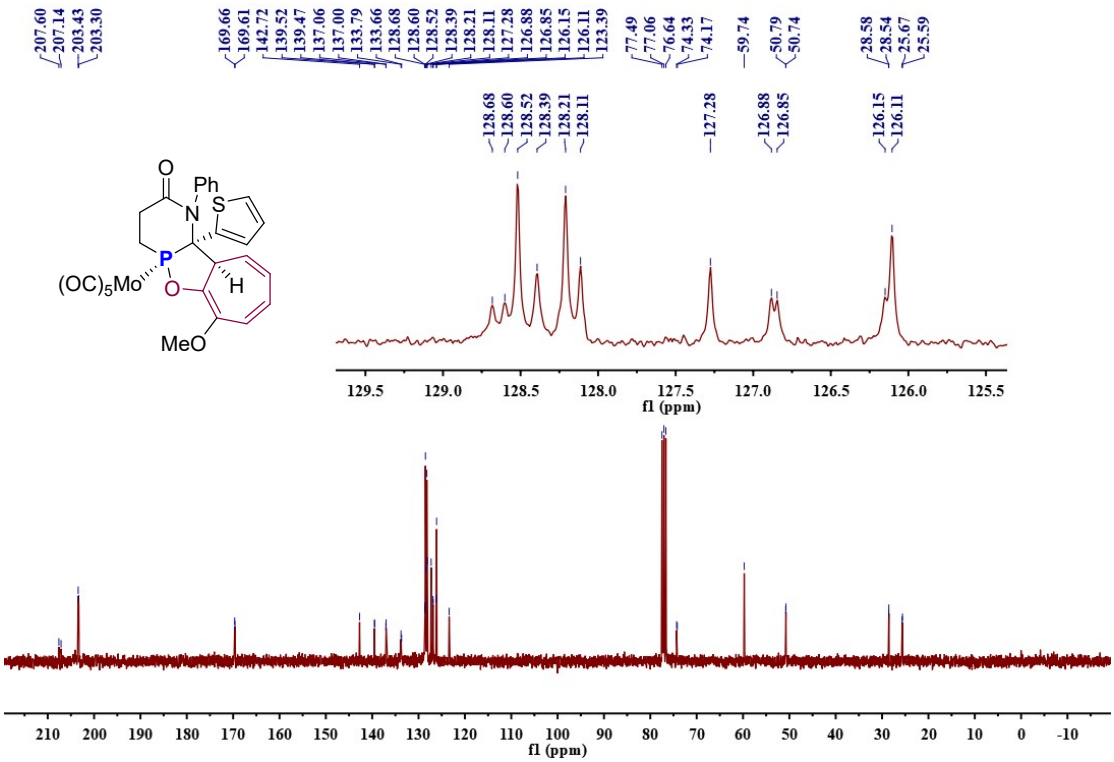
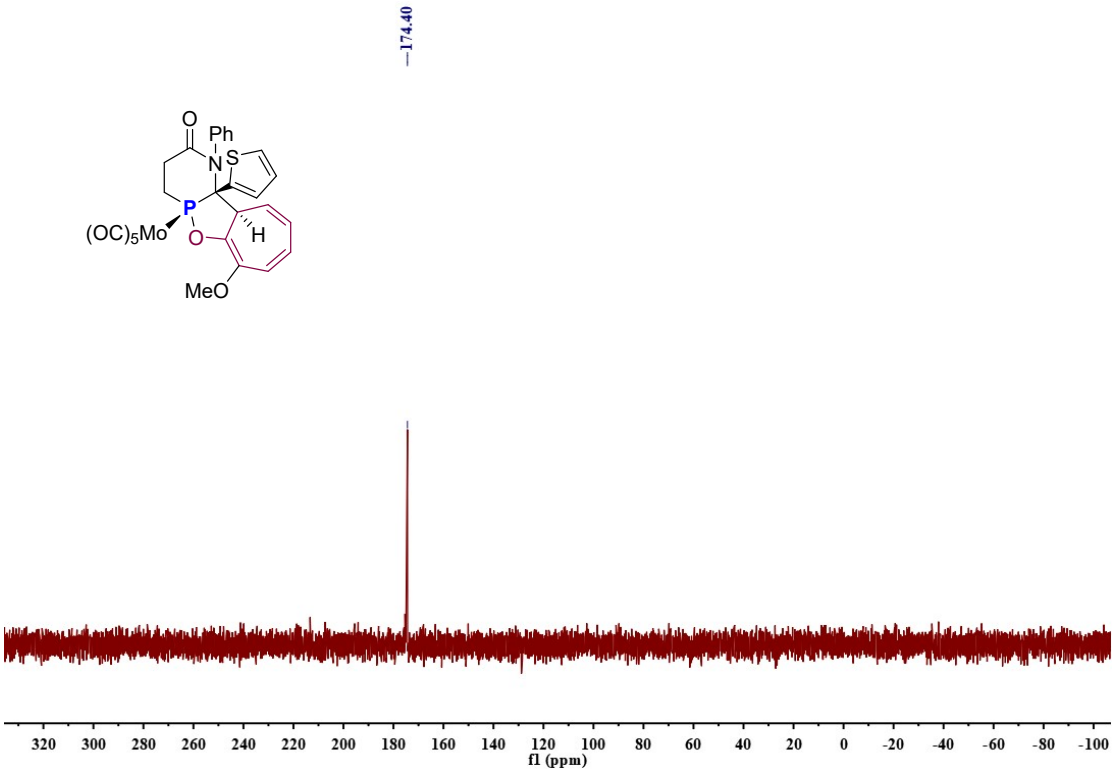


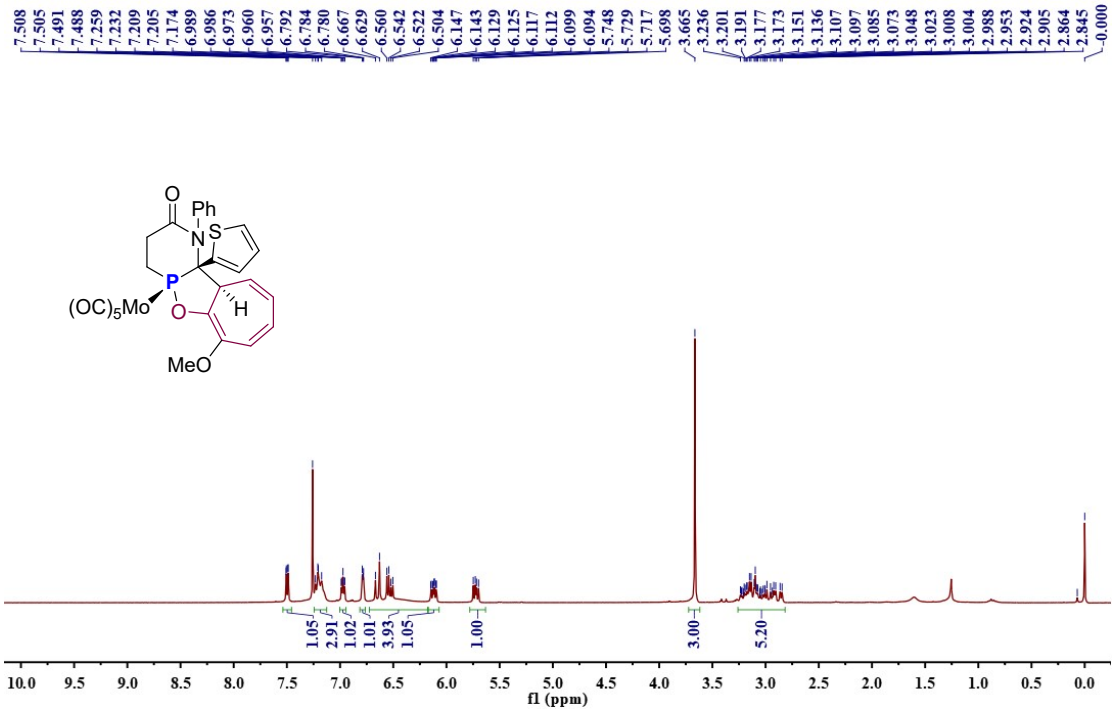
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 2j



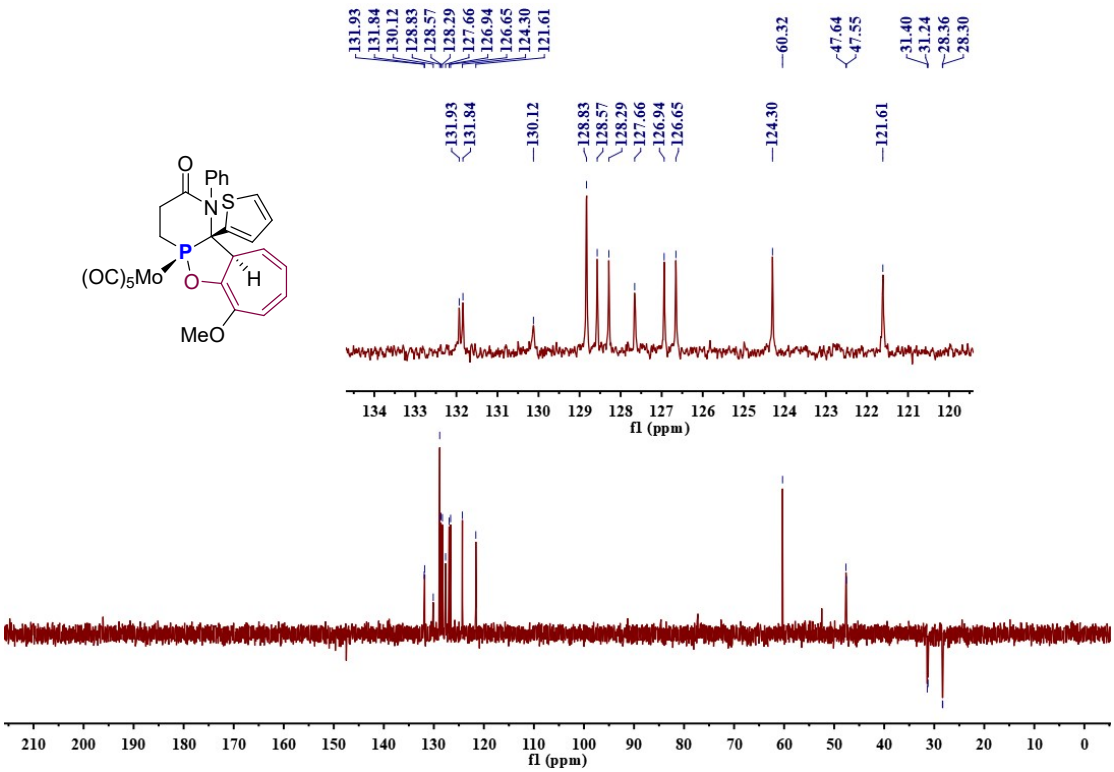
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2j



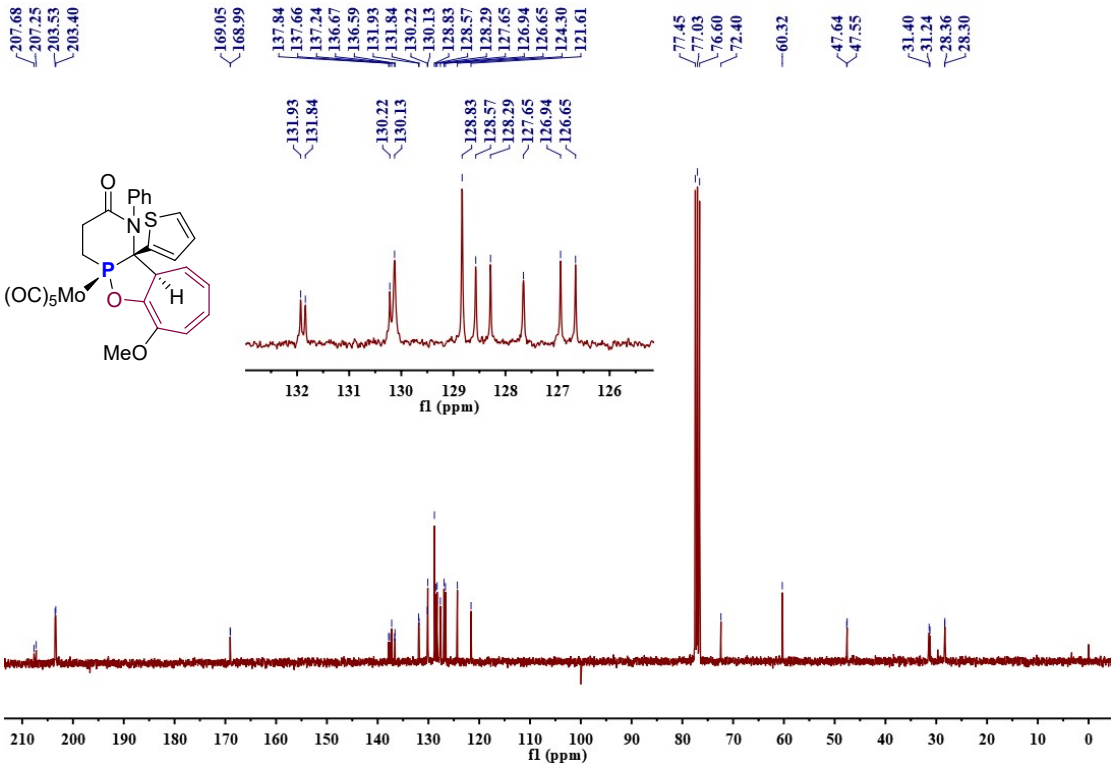
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2j'



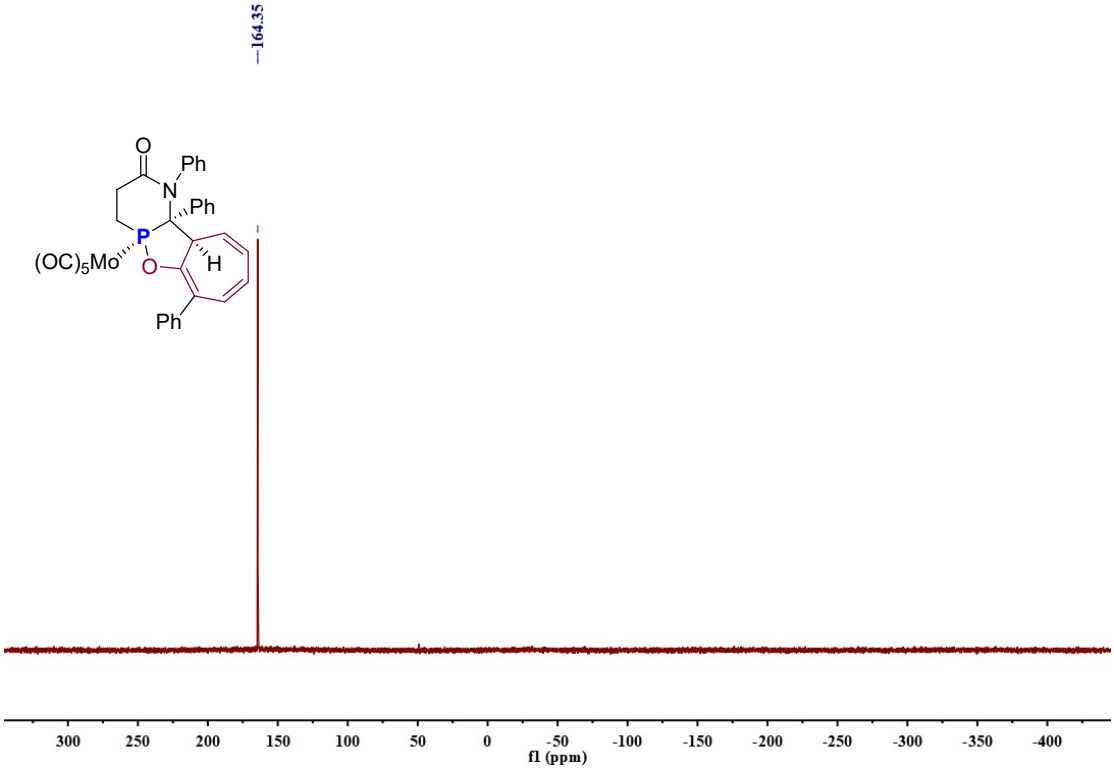
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2j'



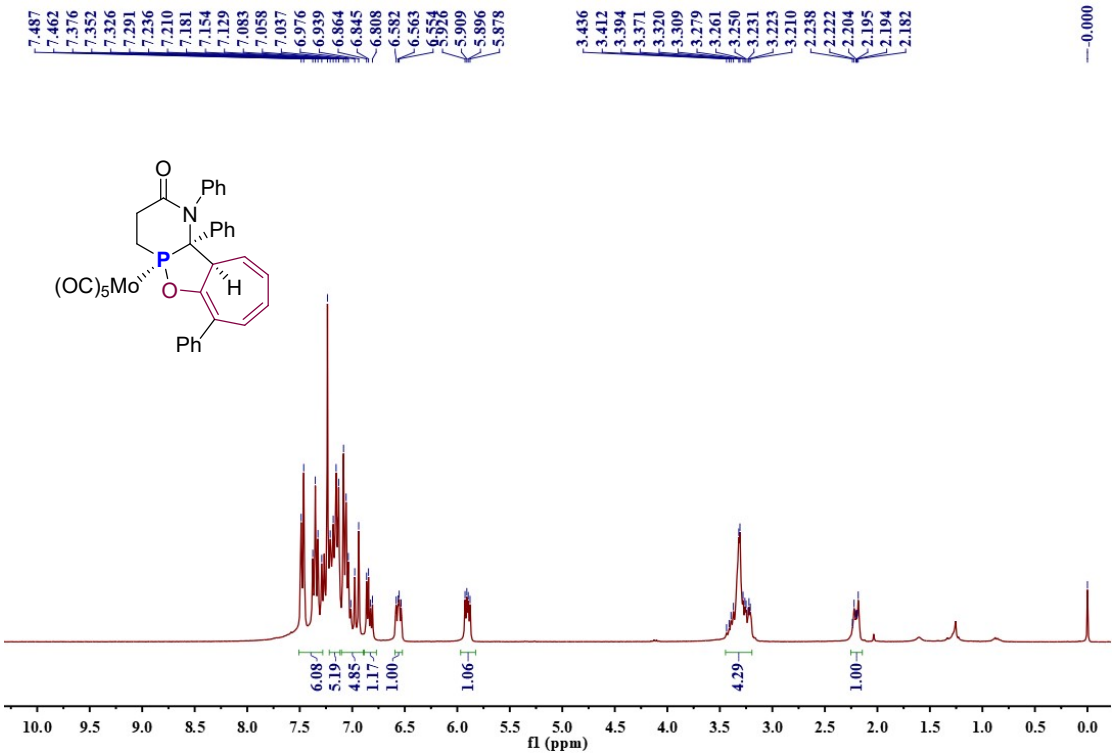
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 2j'



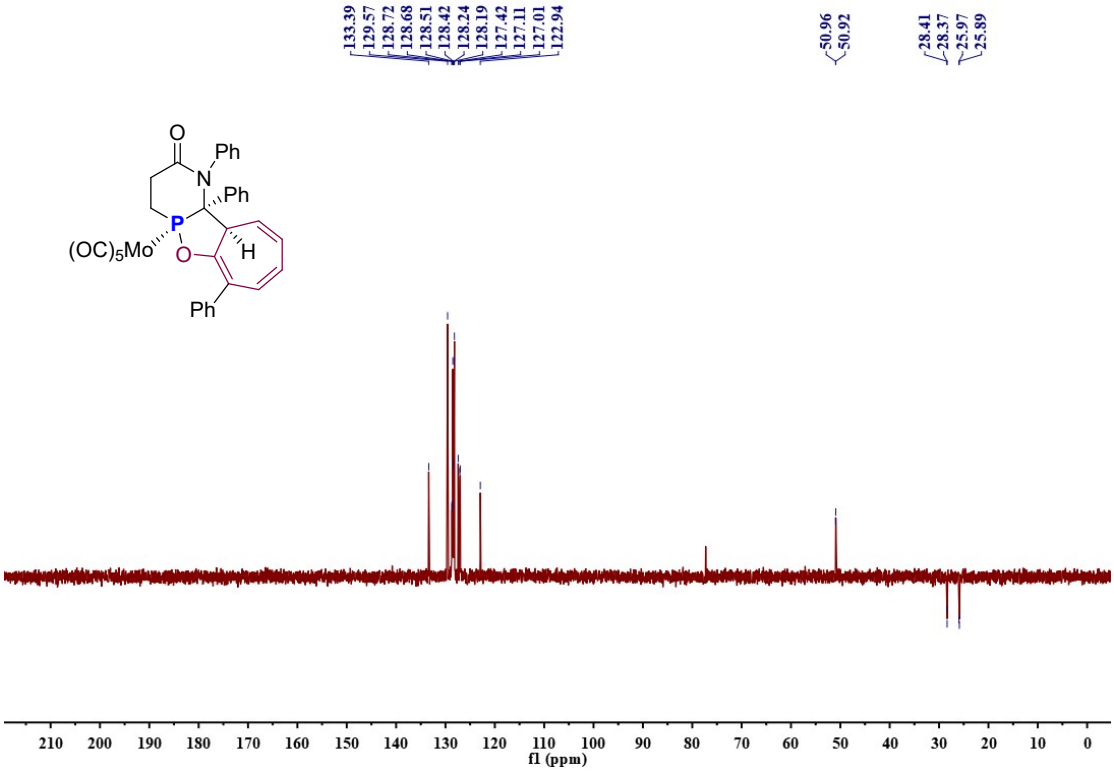
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2j'



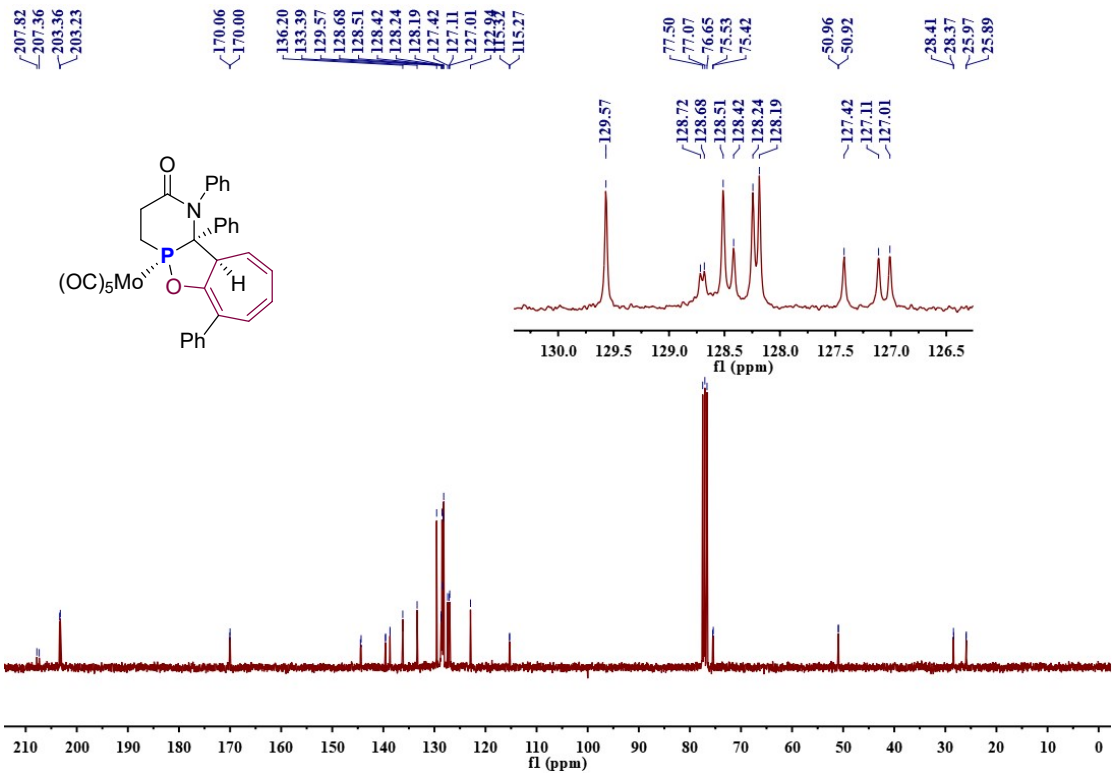
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2k



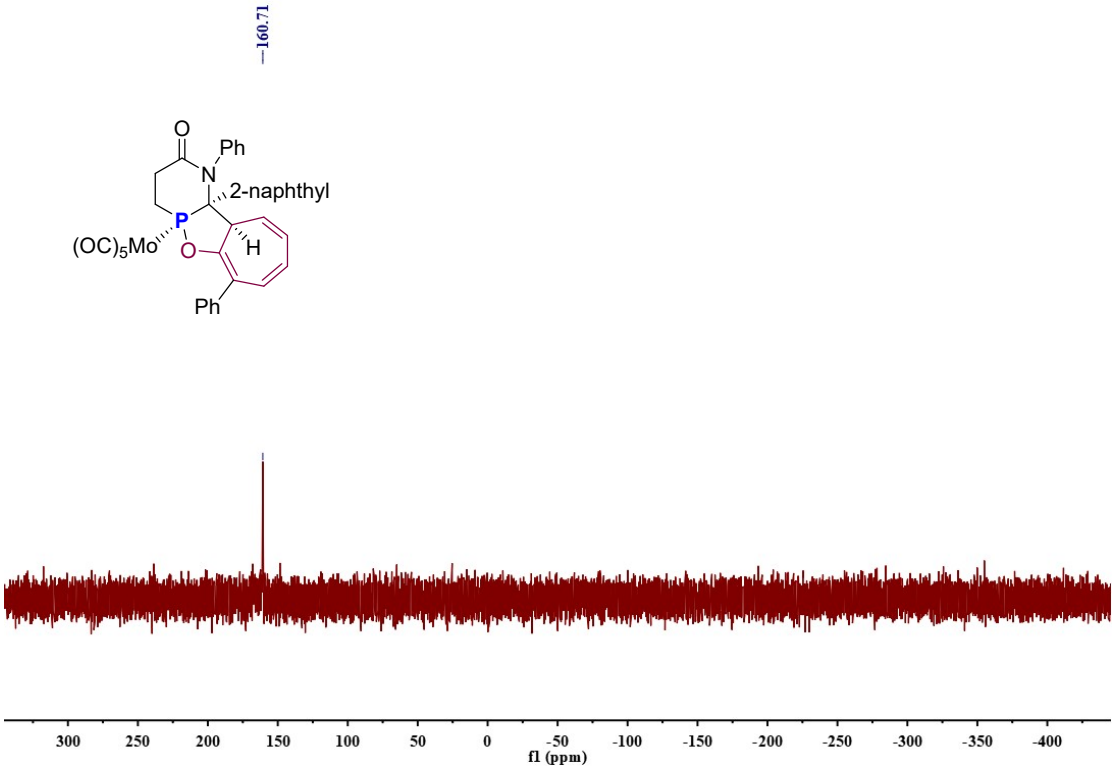
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2k



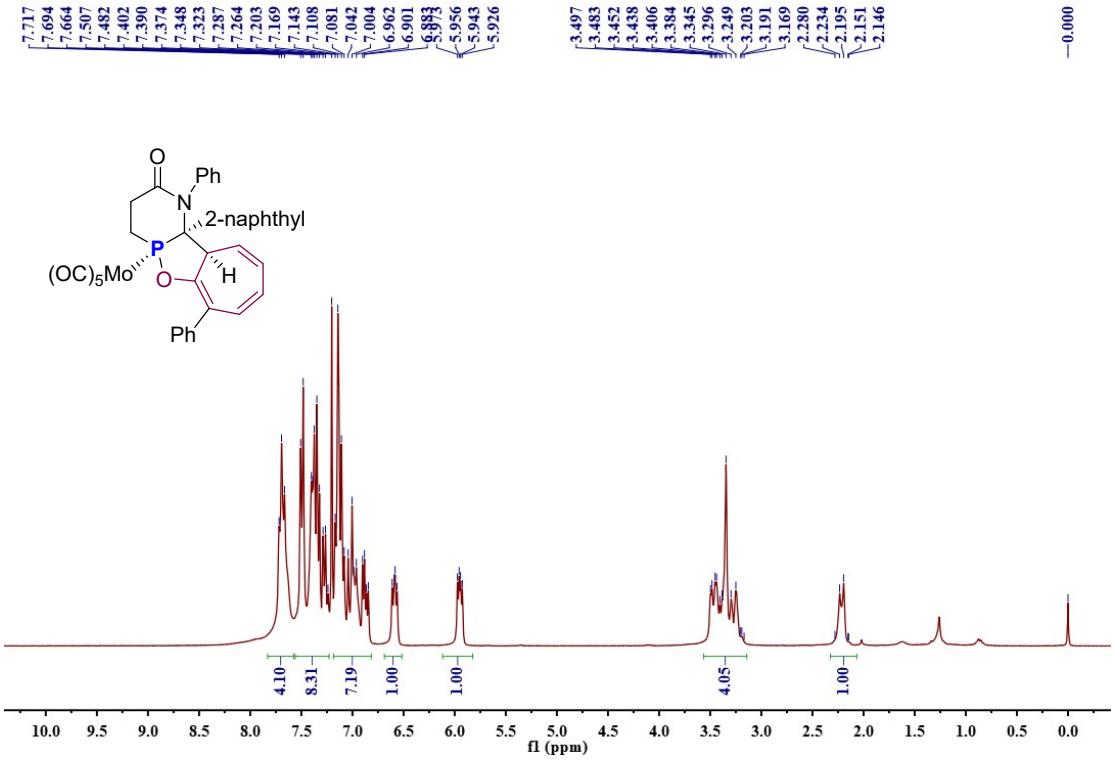
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 2k



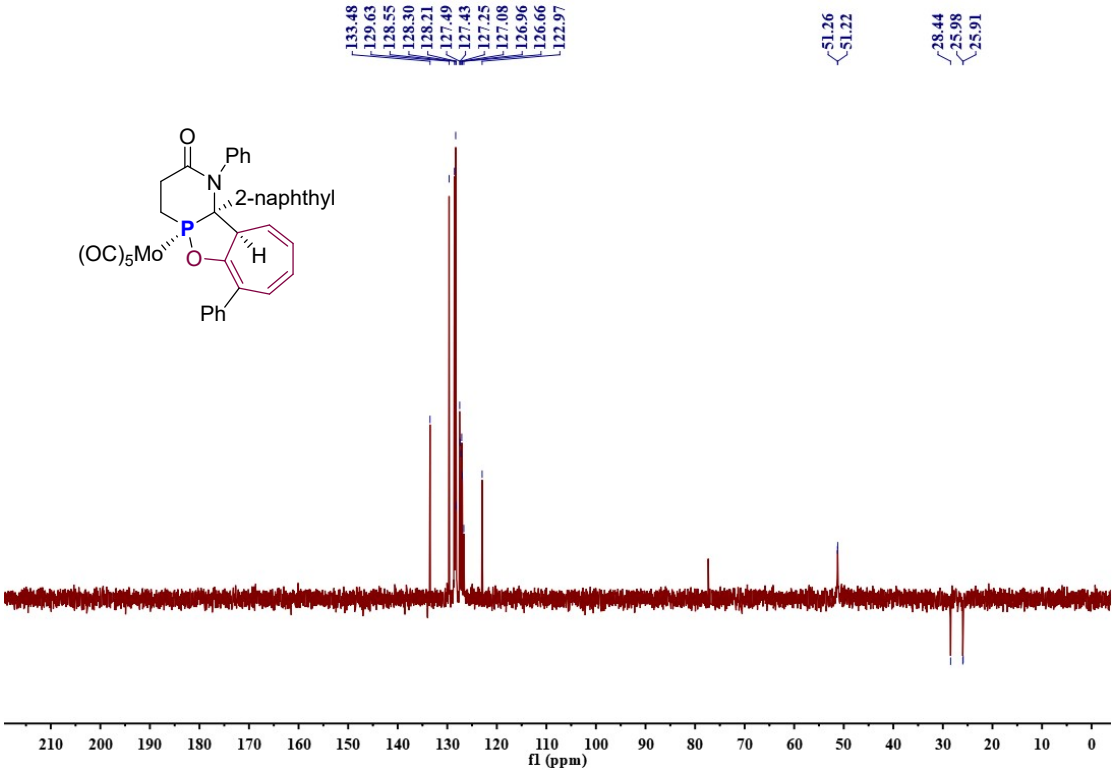
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2k



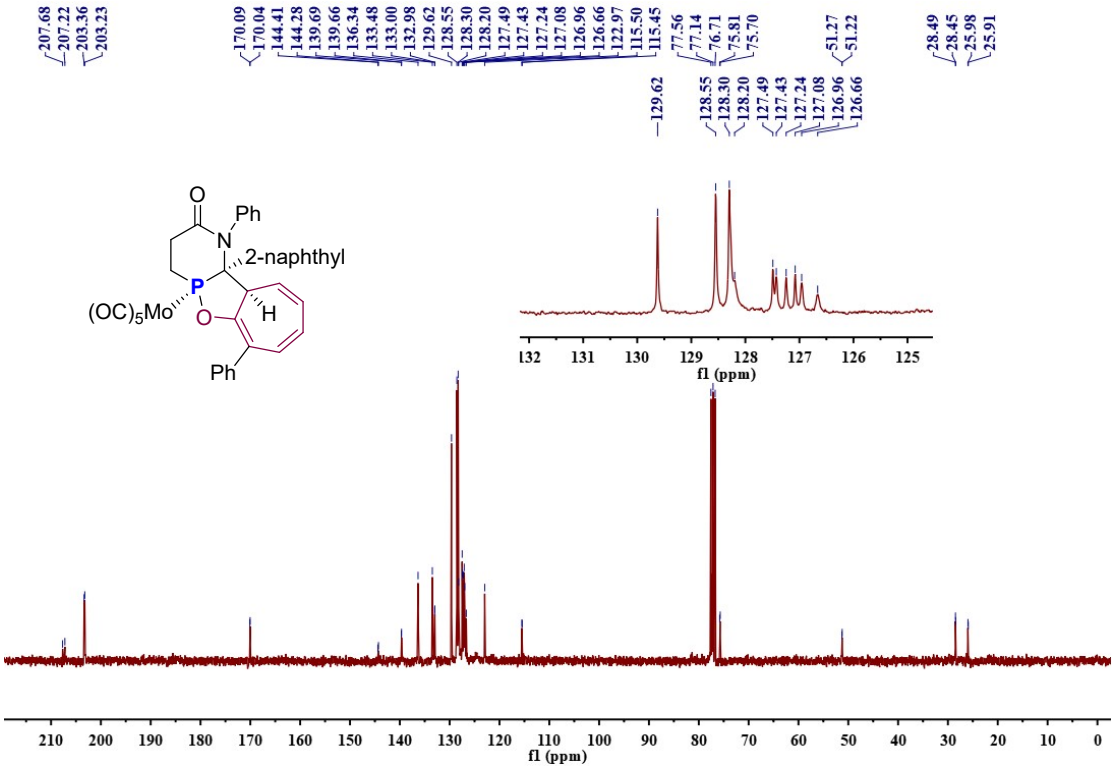
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 2l



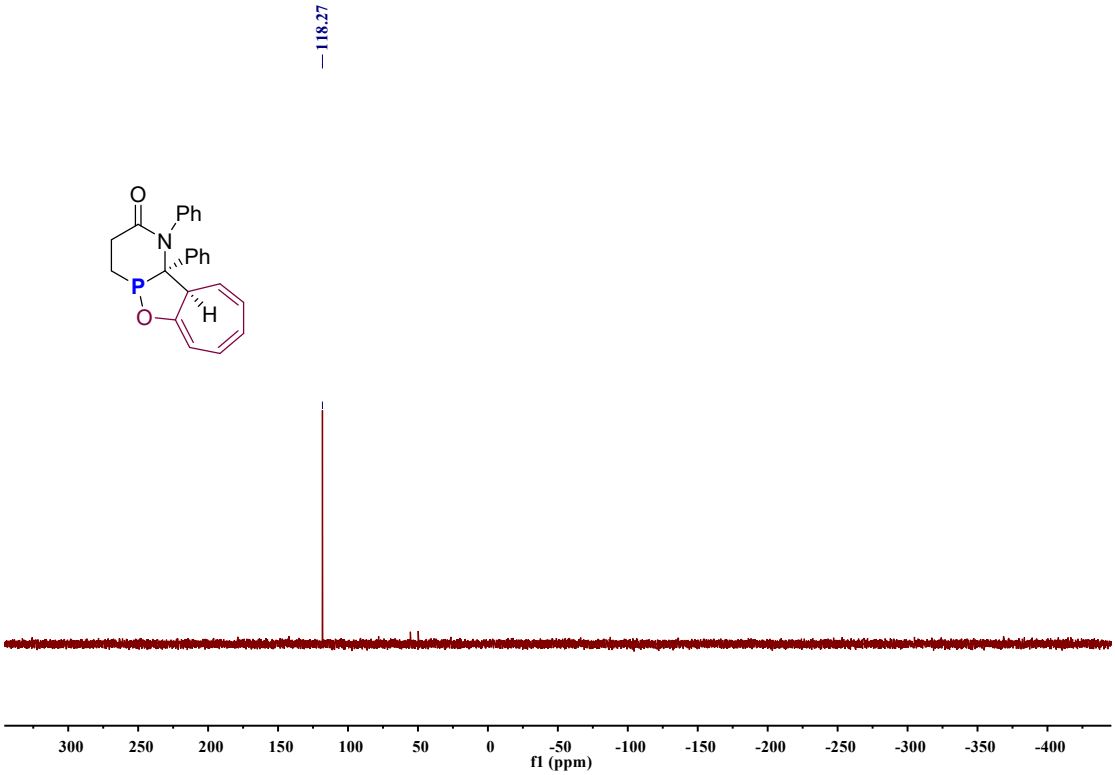
^{1}H NMR (300 MHz, $CDCl_3$) of Compound 2l



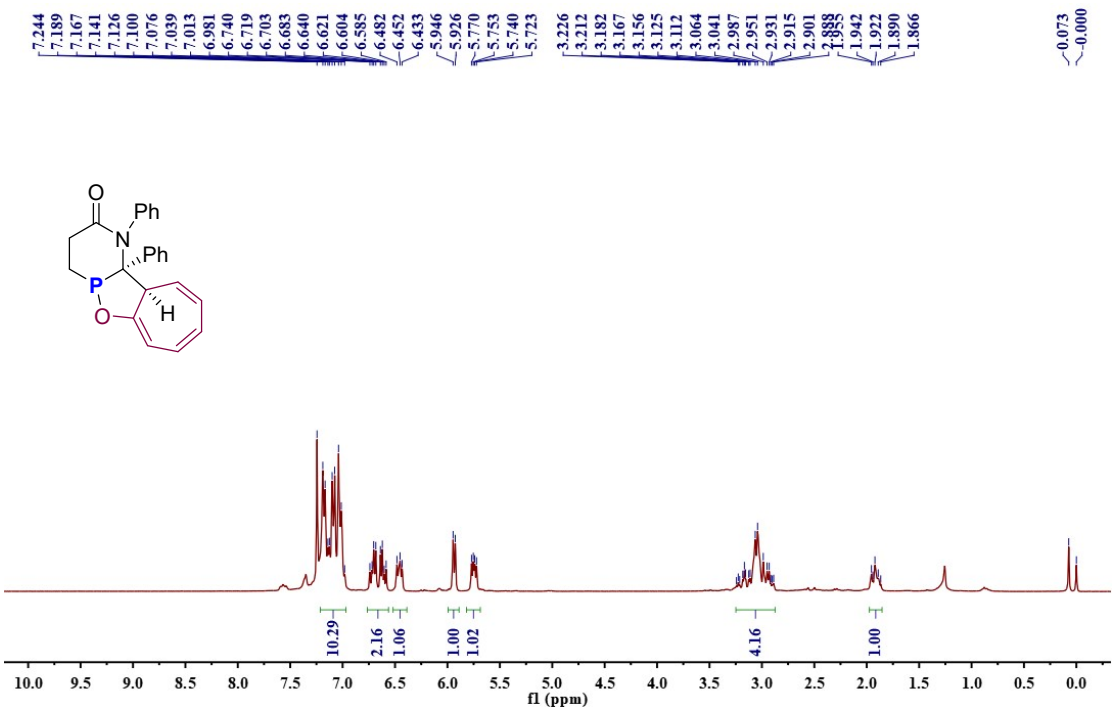
Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 2l



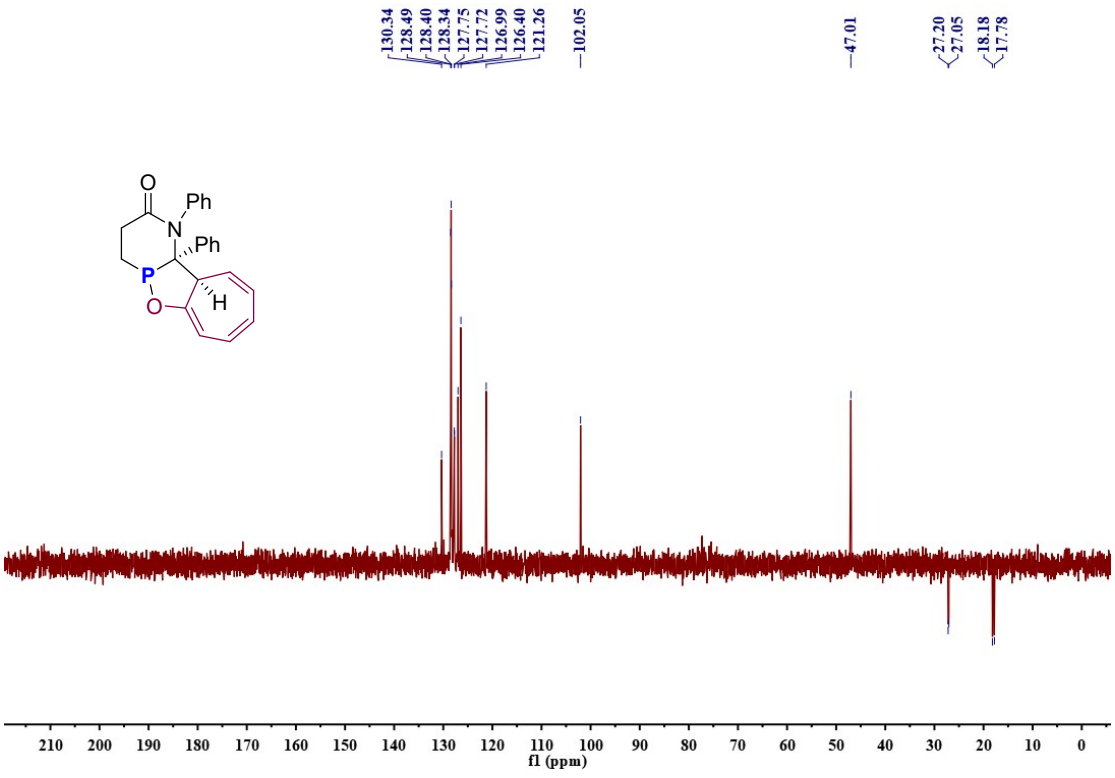
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 2l



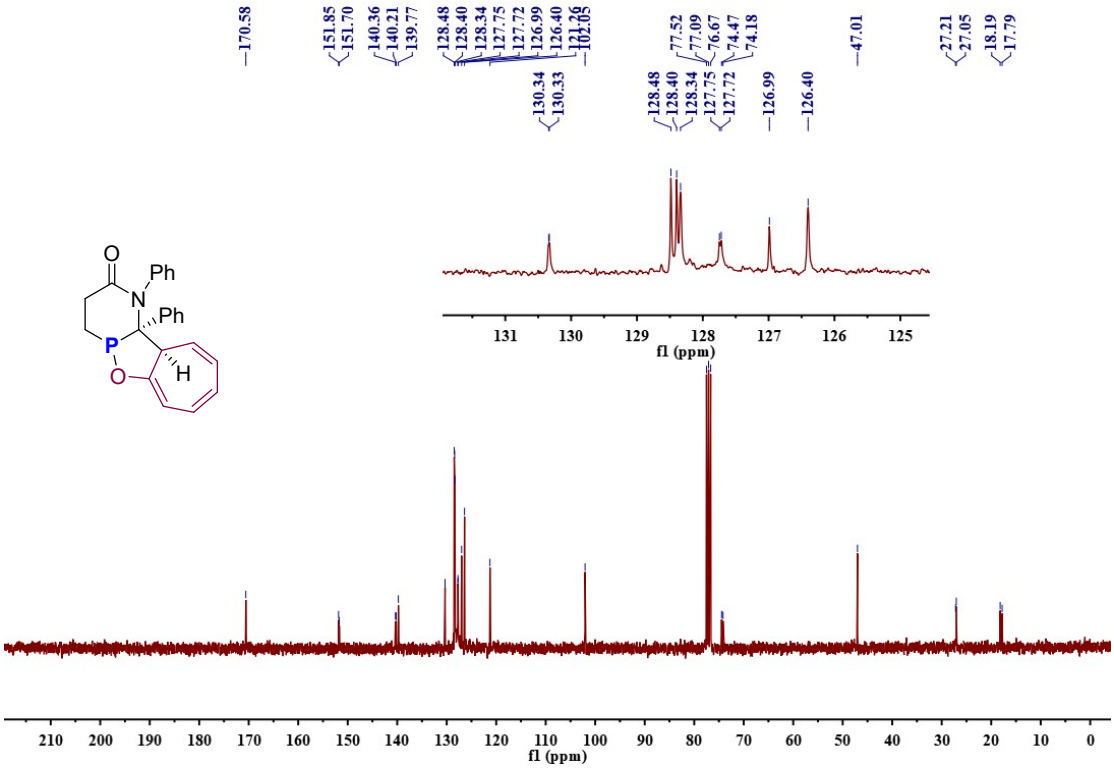
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of Compound 4a



^{1}H NMR (300 MHz, $CDCl_3$) of Compound 4a



Dept 135 NMR (75 MHz, $CDCl_3$) of Compound 4a



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of Compound 4a