Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2020

Supporting Information

Nonbenzenoid Aromaticity of 1-Phosphafulvenes: Synthesis of Phosphacymantrene

Yanjie Liu, Rongqiang Tian,* Zheng Duan,* François Mathey

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 (R. Tian).
*E-mail:duanzheng@zzu.edu.cn (Z. Duan).

Table of Contents

General information.....s3

Experimental Procedures and Characterization Data.....s3

X-ray crystallographic studies of compound **5a**.....s9

X-ray crystallographic studies of compound **5b**.....s13

X-ray crystallographic studies of compound **7b**.....s17

X-ray crystallographic studies of compound **8a**.....s21

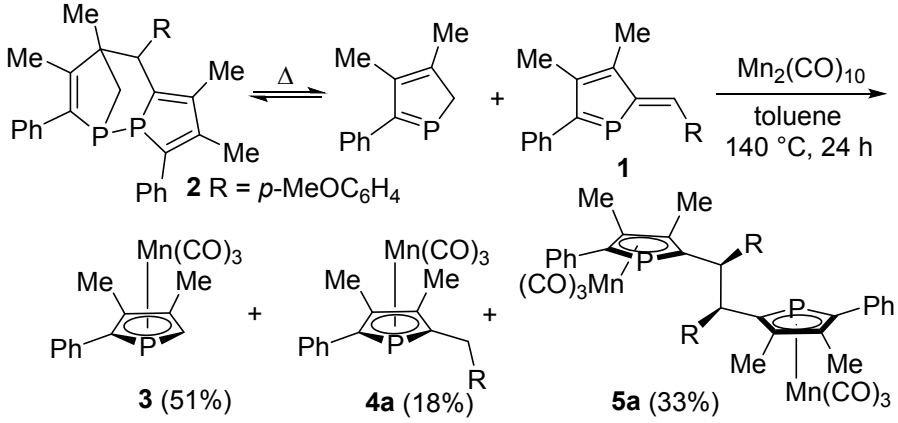
X-ray crystallographic studies of compound **9**.....s25

NMR spectrums.....s30

General information

All reactions were performed under nitrogen using solvents dried by standard methods. NMR spectra were obtained using Bruker AV300 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-Tof HRMS spectrometer. UV-Visible spectra were recorded at room temperature on a VARIAN Cary 5000 spectrophotometer. 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) was 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. Compound **2** and **6a** (Hu, Z.; Li, Z.; Zhao, K.; Tian, R.; Duan, Z.; Mathey, F. *Org. Lett.* **2015**, *17*, 3518.) and **6b** (Y. Liu, K. Zhang, R. Tian, Z. Duan, F. Mathey, *Org. Lett*. **2020**, *22*, 6972) were prepared according to literature method. The purities of the new compounds are acceptable according to NMR spectra analysis.

Experimental Procedures and Characterization Data



A solution of **2** (247 mg, 0.5 mmol) and $Mn_2(CO)_{10}$ (198 mg, 0.5 mmol) in toluene (5 mL) was stirred at 140 °C in oil bath for 24 h in a pressure tube (filled with nitrogen). The resulting solution was evaporated to dryness and the crude product was

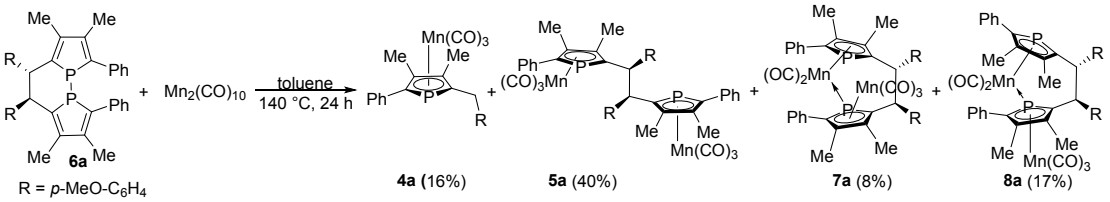
purified by column chromatography (silica gel, Petroleum ether/Ethyl acetate = 20:1) providing 84 mg of **3** (Mercier, F.; Holand, S.; Mathey, F. Synthesis and some reactions of a 2,2'-biphospholyl. *J. Organomet. Chem*. **1986**, *316*, 271-279.) as yellow solid (0.26 mmol, 51%, R_f = 0.65), 40 mg of **4a** as colourless oil (0.09 mmol, 18%, R_f = 0.50) and 72 mg of **5a** as yellow solid (0.08 mmol, 33%, R_f = 0.35). The single crystal of **5a** was grown from a mixture of DCM and MeOH.

3: ^{31}P NMR ($CDCl_3$, 121 MHz): δ -35.8. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.14 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 4.37-4.59 (m, 1H, CH), 7.18-7.27 (m, 5H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 13.4 (s, CH_3), 16.1 (s, CH_3), 95.3 (d, J_{CP} = 63.0 Hz, CH-P), 110.1 (d, J_{CP} = 7.5 Hz, C-Me), 111.8 (d, J_{CP} = 3.8 Hz, C-Me), 120.0 (d, J_{CP} = 57.8 Hz, C-P), 127.9 (s, Ph CH), 128.3 (s, Ph CH), 130.3 (d, J_{CP} = 6.7 Hz, Ph CH), 135.0 (d, J_{CP} = 17.3 Hz, Ph C), 224.1 (s, CO).

4a: colourless oil. ^{31}P NMR ($CDCl_3$, 121 MHz): δ -29.5. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.14 (s, 6H, CH_3), 3.40-3.49 (m, 2H, CH_2), 3.79 (s, 3H, OCH_3), 6.85-6.88 (m, 2H, CH), 7.16-7.25 (m, 7H, CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 13.5 (s, CH_3), 14.0 (s, CH_3), 34.4 (d, J_{CP} = 18.0 Hz, CH_2), 55.3 (s, OCH_3), 107.1 (d, J_{CP} = 6.0 Hz, C-Me), 112.5 (d, J_{CP} = 4.5 Hz, C-Me), 114.0 (s, Ph CH), 115.7 (d, J_{CP} = 57.0 Hz, C-P), 119.4 (d, J_{CP} = 60.8 Hz, C-P), 127.8 (s, Ph CH), 128.2 (s, Ph CH), 129.7 (d, J_{CP} = 2.2 Hz, Ph CH), 130.5 (d, J_{CP} = 6.0 Hz, Ph CH), 131.9 (d, J_{CP} = 2.3 Hz, Ph C), 134.6 (d, J_{CP} = 17.3 Hz, Ph C), 158.4 (s, Ph C), 224.3 (s, CO). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}MnO_4P$ 447.0552; Found 447.0557. IR (neat) δ 2009.98, 1930.91 cm^{-1}.

5a: yellow solid, m.p. >250 °C. ^{31}P NMR ($CDCl_3$, 121 MHz): δ -25.0. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.03 (s, 6H, CH_3), 2.05 (s, 6H, CH_3), 3.79 (s, 6H, OCH_3), 4.04 (d, *J* = 12.9 Hz, 2H, CH), 6.74-6.76 (m, 4H, CH), 7.09-7.12 (m, 5H, CH), 7.24-7.26 (m, 9H, CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 13.9 (s, CH_3), 14.1 (s, CH_3), 50.8 (d, J_{CP} = 9.0 Hz, CH), 55.2 (s, OCH_3), 108.8 (d, J_{CP} = 3.8 Hz, C-Me), 112.4 (s, Ph CH), 113.2 (d, J_{CP} = 6.0 Hz, C-Me), 116.3 (d, J_{CP} = 59.3 Hz, C-P), 120.4 (d, J_{CP} = 71.3 Hz, C-P), 127.5 (s, Ph CH), 128.1 (s, Ph CH), 130.3 (s, Ph CH), 130.35 (s, Ph CH), 134.40 (s, Ph C), 134.9 (d, J_{CP} = 18.0 Hz, Ph C), 158.6 (s, Ph C), 224.5 (s, CO).

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{46}H_{39}Mn_2O_8P_2$ 891.0876; Found 891.0876. IR (neat) δ 2012.39, 1930.91 cm^{-1}.

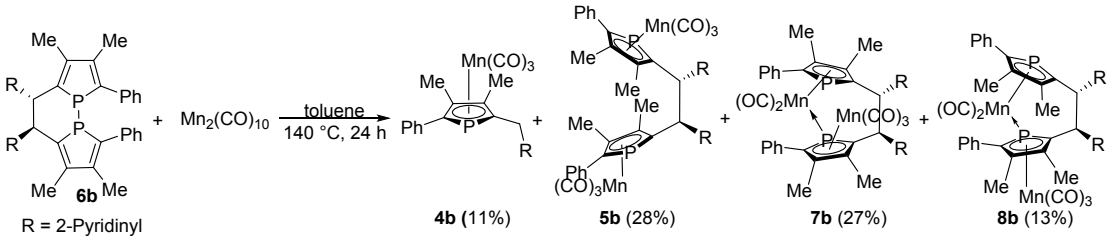


A solution of biphosphole **6a** (153 mg, 0.25 mmol) and $Mn_2(CO)_{10}$ (98 mg, 0.25 mmol) in toluene (5 mL) was stirred at 140 °C in oil bath for 24 h in a pressure tube (filled with nitrogen). The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, Petroleum ether/Dichloromethane = 10:1) providing 36 mg of **4a** as yellow oil (0.081 mmol, 16%, R_f = 0.55), 89 mg of **5a** as yellow solid (0.10 mmol, 40%, R_f = 0.40), 17 mg of **7a** as yellow solid (0.020 mmol, 8%, R_f = 0.38) and 37 mg of **8a** as yellow solid (0.043 mmol, 17%, R_f = 0.35). The single crystal of **8a** was grown from a mixture of acetone and Et_2O.

7a: yellow solid, m.p. >250 °C. ^{31}P NMR ($CDCl_3$, 121 MHz): δ -70.6, 132.4. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.42 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.42 (*pseudo*-t, J_{CP} = 11.1 Hz, 1H, CH), 3.67 (s, 3H, OMe), 3.70 (s, 3H, OMe), 4.15 (d, J_{CP} = 11.1 Hz, 1H, CH), 6.45-6.48 (m, 1H, CH), 6.58-6.60 (m, 3H, CH), 6.76-6.78 (m, 1H, CH), 6.99 (s, 2H, CH), 7.18-7.32 (m, 11H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 13.4 (s, CH_3), 13.8 (s, CH_3), 14.2 (s, CH_3), 14.6 (s, CH_3), 49.0 (*pseudo*-t, J_{CP} = 9.0 Hz, CH), 50.1 (*pseudo*-t, J_{CP} = 10.5 Hz, CH), 55.0 (s, OMe), 55.1 (s, OMe), 99.27 (d, J_{CP} = 86.3 Hz, C-P), 99.31 (d, J_{CP} = 78.8 Hz, C-P), 106.5 (d, J_{CP} = 2.3 Hz, C-Me), 106.7 (d, J_{CP} = 4.5 Hz, C-Me), 108.7 (s, C-Me), 110.4 (d, J_{CP} = 4.5 Hz, C-Me), 111.5 (d, J_{CP} = 60.8 Hz, C-P), 112.9 (s, Ph CH), 113.4 (s, Ph CH), 113.6 (s, Ph CH), 118.2 (d, J_{CP} = 58.5 Hz, C-P), 127.7 (d, J_{CP} = 5.3 Hz, Ph CH), 127.8 (s, Ph CH), 128.2 (s, Ph CH), 128.8 (s, Ph CH), 130.5 (d, J_{CP} = 7.5 Hz, Ph CH), 131.0 (d, J_{CP} = 4.5 Hz, Ph CH), 131.8 (d, J_{CP} = 8.3 Hz, Ph C), 132.4 (d, J_{CP} = 12.8 Hz, Ph C), 133.2 (s, Ph CH), 133.9 (s, Ph C), 135.1 (d, J_{CP} = 17.3 Hz, Ph C), 157.6 (s, Ph C), 158.2 (s, Ph C), 224.1 (s, CO), 224.6 (d, J_{CP} = 22.5 Hz, CO), 227.5 (d, J_{CP} = 29.3 Hz,

CO). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{45}H_{39}Mn_2O_7P_2$ 863.0927; Found 863.0906. IR (neat) δ 2008.53, 1963.69, 1927.53 cm^{-1}.

8a: yellow solid, m.p. >250 °C. ^{31}P NMR ($CDCl_3$, 121 MHz): δ -46.3, 138.9. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.29 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 3.46 (*pseudo*-t, *J* = 11.1 Hz, 1H, CH), 3.67 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 4.08 (d, *J* = 11.1 Hz, 1H, CH), 6.54-6.61 (m, 3H, CH), 6.72-6.76 (m, 2H, CH), 6.92-6.95 (m, 2H, CH), 7.11-7.14 (m, 1H, CH), 7.26-7.31 (m, 10H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 13.6 (s, CH_3), 14.0 (d, J_{CP} = 3.0 Hz, CH_3), 14.4 (s, CH_3), 16.1 (s, CH_3), 50.3 (*pseudo*-t, J_{CP} = 9.0 Hz, CH), 52.6 (*pseudo*-t, J_{CP} = 11.3 Hz, CH), 55.06 (s, OCH_3), 55.14 (s, OCH_3), 100.8 (d, J_{CP} = 5.3 Hz, C-Me), 103.8 (d, J_{CP} = 6.0 Hz, C-Me), 106.0 (d, J_{CP} = 85.5 Hz, C-P), 106.1 (d, J_{CP} = 80.3 Hz, C-P), 107.0 (d, J_{CP} = 3.8 Hz, C-Me), 108.3 (d, J_{CP} = 8.3 Hz, C-Me), 111.9 (d, J_{CP} = 60.0 Hz, C-P), 112.7 (s, Ph CH), 113.6 (s, Ph CH), 114.7 (s, Ph CH), 120.0 (d, J_{CP} = 59.3 Hz, C-P), 127.7 (d, J_{CP} = 9.0 Hz, Ph CH), 128.0 (s, Ph CH), 128.2 (s, Ph CH), 129.5 (d, J_{CP} = 15.1 Hz, Ph CH), 130.3 (d, J_{CP} = 6.8 Hz, Ph CH), 132.1 (d, J_{CP} = 4.5 Hz, Ph CH), 132.3 (d, J_{CP} = 7.5 Hz, Ph C), 132.4 (s, Ph CH), 132.8 (d, J_{CP} = 6.0 Hz, Ph C), 135.0 (s, Ph C), 135.4 (d, J_{CP} = 18.0 Hz, Ph C), 157.6 (s, Ph C), 158.3 (s, Ph C), 224.2 (s, CO), 226.0 (d, J_{CP} = 24.0 Hz, CO), 227.2 (d, J_{CP} = 23.3 Hz, CO). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{45}H_{39}Mn_2O_7P_2$ 863.0927; Found 863.0918. IR (neat) δ 2003.23, 1960.80, 1929.95, 1915.48, 1903.43 cm^{-1}.



A solution of biphosphole **6b** (139 mg, 0.25 mmol) and $Mn_2(CO)_{10}$ (98 mg, 0.25 mmol) in toluene (4 mL) was stirred at 140 °C in oil bath for 24 h in a pressure tube (filled with nitrogen). The resulting solution was evaporated to dryness and the crude product was purified by column chromatography (silica gel, Petroleum ether/Ethyl

acetate = 10:1) providing 23 mg of **4b** as yellow oil (0.055 mmol, 11%, R_f = 0.40), 58 mg of **5b** as yellow solid (0.070 mmol, 28%, R_f = 0.45), 54 mg of **7b** as yellow solid (0.067 mmol, 27%, R_f = 0.35) and 27 mg of **8b** as yellow solid (0.034 mmol, 13%, R_f = 0.33). The single crystal of **7b** was grown from a mixture of DCM and EA.

4b: yellow oil. ^{31}P NMR ($CDCl_3$, 121 MHz): δ -28.8. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.16 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 3.56-3.73 (m, 2H, CH_2), 7.15-7.25 (m, 7H, CH), 7.65 (t, J = 7.8 Hz, 1H, CH), 8.58 (s, 1H, CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 13.5 (s, CH_3), 14.0 (s, CH_3), 37.9 (d, J_{CP} = 17.9 Hz, CH_2), 108.2 (d, J_{CP} = 6.8 Hz, C-Me), 112.0 (d, J_{CP} = 3.8 Hz, C-Me), 116.1 (d, J_{CP} = 61.5 Hz, C-P), 116.3 (d, J_{CP} = 57.8 Hz, C-P), 121.9 (s, CH), 122.9 (s, CH), 127.8 (s, CH), 128.1 (s, CH), 130.5 (d, J_{CP} = 6.0 Hz, CH), 134.6 (d, J_{CP} = 17.3 Hz, C), 136.8 (s, CH), 149.6 (s, CH), 159.4 (s, C), 224.2 (s, CO). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{18}MnNO_3P$ 418.0399; Found 418.0403. IR (neat) δ 2012.87, 1934.28 cm^{-1}.

5b: yellow solid, m.p. >250 °C. ^{31}P NMR ($CDCl_3$, 121 MHz): δ -9.9. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.15 (s, 6H, CH_3), δ 2.23 (s, 6H, CH_3), 4.37-4.41 (m, 2H, CH), 6.78 (d, J = 7.8 Hz, 2H, CH), 6.92-6.96 (m, 2H, CH), 7.13-7.15 (m, 4H, CH), 7.26-7.30 (m, 8H, CH), 8.49 (d, J = 4.5 Hz, 2H, CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 14.1 (s, 2CH_3), 16.5 (s, CH_3), 16.6 (s, CH_3), 56.6 (d, J_{CP} = 9.8 Hz, CH), 110.1 (d, J_{CP} = 4.5 Hz, C-Me), 111.9 (d, J_{CP} = 7.5 Hz, C-Me), 114.1 (d, J_{CP} = 69.8 Hz, C-P), 117.6 (d, J_{CP} = 60.8 Hz, C-P), 121.8 (s, CH), 123.5 (s, CH), 127.6 (s, CH), 128.2 (s, CH), 130.2 (d, J_{CP} = 5.3 Hz, CH), 135.2 (d, J_{CP} = 17.3 Hz, C), 136.0 (s, CH), 148.3 (s, CH), 162.5 (s, C), 223.5 (s, CO). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{42}H_{33}Mn_2N_2O_6P_2$ 833.0569; Found 833.0557. IR (neat) δ 2015.28, 2005.64, 1946.34, 1938.62, 1928.98, 1911.14 cm^{-1}.

7b: yellow solid, m.p. >250 °C. ^{31}P NMR ($CDCl_3$, 121 MHz): δ -66.9, 131.8. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.35 (s, 3H, CH_3), 2.12-2.27 (m, 9H, 3CH_3), 3.88 (t, J = 11.1 Hz, 1H, CH), 4.63 (s, 1H, CH), 6.86-7.31 (m, 16H, CH), 8.46 (s, 2H, CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 13.3 (s, CH_3), 13.6 (d, J_{CP} = 3.0 Hz, CH_3), 14.1 (s, CH_3), 14.6 (d, J_{CP} = 3.0 Hz, CH_3), 49.3 (s, CH), 51.4 (s, CH), 98.0 (s, C-Me), 99.2 (d,

J_{CP} = 7.5 Hz, C-Me), 106.0 (s, C-Me), 107.3 (d, J_{CP} = 66.8 Hz, 2C-P), 109.0 (s, C-Me), 109.7 (d, J_{CP} = 60.8 Hz, C-P), 119.5 (d, J_{CP} = 59.3 Hz, C-P), 121.2 (s, CH), 121.6 (s, CH), 124.0 (s, CH), 127.5 (s, CH), 127.6 (s, CH), 127.8 (s, CH), 128.2 (s, CH), 130.5 (s, CH), 130.6 (s, CH), 131.1 (s, CH), 131.2 (s, CH), 132.6 (d, J_{CP} = 12.8 Hz, C), 135.4 (d, J_{CP} = 16.5 Hz, C), 135.7 (s, CH), 149.0 (s, CH), 149.6 (s, CH), 159.5 (d, J_{CP} = 9.0 Hz, C), 160.3 (s, C), 224.1 (s, CO), 224.9 (d, J_{CP} = 24.8 Hz, CO), 227.7 (d, J_{CP} = 29.3 Hz, CO). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{41}H_{33}Mn_2N_2O_5P_2$ 805.0620; Found 805.0622. IR (neat) δ 2008.53, 1963.73, 1938.62, 1916.45, 1899.09 cm^{-1}.

8b: yellow solid, m.p. >250 °C. ^{31}P NMR ($CDCl_3$, 121 MHz): δ -44.5, 145.3. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.22 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 3.98 (*pseudo*-t, *J* = 11.1 Hz, 1H, CH), 4.53 (d, *J* = 10.8 Hz, 1H, CH), 6.71-6.73 (m, 1H, CH), 6.84 (m, 1H, CH), 6.96 (m, 2H, CH), 7.26-7.33 (m, 12H, CH), 8.51 (d, *J* = 13.5 Hz, 2H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 13.2 (s, CH_3), 14.1 (s, CH_3), 14.3 (s, CH_3), 15.3 (s, CH_3), 50.9 (t, J_{CP} = 7.5 Hz, CH), 53.7 (t, J_{CP} = 11.3 Hz, CH), 100.25 (s, C-Me), 100.33 (s, C-Me), 105.5 (d, J_{CP} = 67.5 Hz, C-P), 105.54 (d, J_{CP} = 63.8 Hz, C-P), 107.3 (d, J_{CP} = 4.5 Hz, C-Me), 108.3 (d, J_{CP} = 7.5 Hz, C-Me), 109.5 (d, J_{CP} = 60.0 Hz, C-P), 121.1 (s, CH), 121.4 (d, J_{CP} = 60.8 Hz, C-P), 122.0 (s, CH), 123.9 (s, CH), 126.5 (s, CH), 127.7 (d, J_{CP} = 6.8 Hz, CH), 127.9 (s, CH), 128.2 (s, CH), 130.3 (d, J_{CP} = 7.6 Hz, CH), 132.18 (s, CH), 132.23 (s, CH), 132.3 (s, C), 135.5 (d, J_{CP} = 17.3 Hz, C), 135.6 (s, CH), 136.4 (s, CH), 149.5 (s, CH), 150.0 (s, CH), 160.5 (d, J_{CP} = 6.0 Hz, C), 160.94 (s, C), 224.0 (s, CO), 226.2 (d, J_{CP} = 23.3 Hz, CO), 226.8 (d, J_{CP} = 24.0 Hz, CO). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{41}H_{33}Mn_2N_2O_5P_2$ 805.0620; Found 805.0624. IR (neat) δ 2009.01, 1963.69, 1934.77, 1911.14, 1901.98 cm^{-1}.

X-ray crystallographic studies of compound 5a

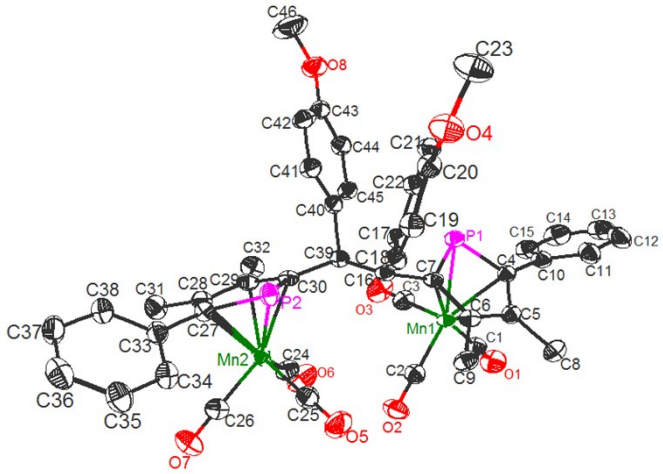


Table 1 Crystal data and structure refinement for 5a.

Identification code	**5a**
Empirical formula	$C_{46}H_{38}Mn_2O_8P_2$
Formula weight	890.58
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.3750(5)
b/Å	15.3397(4)
c/Å	23.4824(8)
α/°	90
β/°	102.276(4)
γ/°	90
Volume/Å^3	4355.7(3)
Z	4
ρ_{calc}g/cm^3	1.358
μ/mm^{-1}	5.836
F(000)	1832.0
Crystal size/mm^3	0.3 × 0.13 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.31 to 134.15
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 11, -28 ≤ l ≤ 27
Reflections collected	19772
Independent reflections	7715 [R_{int} = 0.0402, R_{sigma} = 0.0484]
Data/restraints/parameters	7715/0/529
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0453, wR_2 = 0.1063

Final R indexes [all data]	$R_1 = 0.0655$, $wR_2 = 0.1152$
Largest diff. peak/hole / e $Å^{-3}$	0.41/-0.26

Table 2 Bond Lengths for 5a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	Mn1	1.800(4)	C24	O6	1.146(4)
C1	O1	1.135(4)	C25	Mn2	1.786(4)
C2	Mn1	1.805(4)	C25	O5	1.144(4)
C2	O2	1.138(4)	C26	Mn2	1.795(4)
C3	Mn1	1.794(4)	C26	O7	1.142(4)
C3	O3	1.141(4)	C27	C28	1.422(4)
C4	C5	1.424(4)	C27	C33	1.491(4)
C4	C10	1.488(4)	C27	P2	1.775(3)
C4	P1	1.771(3)	C27	Mn2	2.170(3)
C4	Mn1	2.178(3)	C28	C29	1.426(4)
C5	C6	1.416(4)	C28	C31	1.509(5)
C5	C8	1.520(4)	C28	Mn2	2.163(3)
C5	Mn1	2.158(3)	C29	C30	1.423(4)
C6	C7	1.424(4)	C29	C32	1.521(4)
C6	C9	1.509(4)	C29	Mn2	2.172(3)
C6	Mn1	2.182(3)	C30	C39	1.529(4)
C7	C16	1.528(4)	C30	P2	1.779(3)
C7	P1	1.786(3)	C30	Mn2	2.188(3)
C7	Mn1	2.189(3)	C33	C34	1.391(5)
C10	C11	1.386(5)	C33	C38	1.393(5)
C10	C15	1.385(5)	C34	C35	1.386(5)
C11	C12	1.389(6)	C35	C36	1.368(6)
C12	C13	1.366(7)	C36	C37	1.368(6)
C13	C14	1.367(7)	C37	C38	1.389(5)
C14	C15	1.389(5)	C39	C40	1.530(4)
C16	C17	1.521(4)	C40	C41	1.376(4)
C16	C39	1.571(4)	C40	C45	1.400(4)
C17	C18	1.403(4)	C41	C42	1.384(5)
C17	C22	1.388(4)	C42	C43	1.391(5)
C18	C19	1.374(4)	C43	C44	1.370(5)
C19	C20	1.385(4)	C43	O8	1.367(4)
C20	C21	1.391(4)	C44	C45	1.377(4)
C20	O4	1.367(4)	C46	O8	1.396(6)
C21	C22	1.377(4)	P1	Mn1	2.3898(9)
C23	O4	1.410(5)	P2	Mn2	2.3835(10)

C24	Mn2	1.792(4)

Table 3 Bond Angles for 5a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	Mn1	178.6(3)	C37	C36	C35	119.7(4)
O2	C2	Mn1	178.1(4)	C36	C37	C38	121.1(4)
O3	C3	Mn1	178.3(4)	C37	C38	C33	119.9(4)
C5	C4	C10	125.9(3)	C30	C39	C16	112.0(2)
C5	C4	P1	112.7(2)	C30	C39	C40	108.4(2)
C5	C4	Mn1	70.06(17)	C40	C39	C16	117.5(2)
C10	C4	P1	121.2(2)	C41	C40	C39	122.2(3)
C10	C4	Mn1	128.7(2)	C41	C40	C45	117.4(3)
P1	C4	Mn1	73.67(11)	C45	C40	C39	120.2(3)
C4	C5	C8	124.1(3)	C40	C41	C42	121.9(3)
C4	C5	Mn1	71.58(18)	C41	C42	C43	119.8(3)
C6	C5	C4	112.1(3)	C44	C43	C42	118.8(3)
C6	C5	C8	123.8(3)	O8	C43	C42	124.7(4)
C6	C5	Mn1	71.86(17)	O8	C43	C44	116.5(3)
C8	C5	Mn1	125.7(2)	C43	C44	C45	121.2(3)
C5	C6	C7	113.5(3)	C44	C45	C40	120.8(3)
C5	C6	C9	122.8(3)	C4	P1	C7	90.20(15)
C5	C6	Mn1	70.05(17)	C4	P1	Mn1	61.00(10)
C7	C6	C9	123.7(3)	C7	P1	Mn1	61.23(9)
C7	C6	Mn1	71.27(16)	C27	P2	C30	90.23(15)
C9	C6	Mn1	129.2(2)	C27	P2	Mn2	60.85(10)
C6	C7	C16	122.5(3)	C30	P2	Mn2	61.41(9)
C6	C7	P1	111.3(2)	C1	Mn1	C2	91.28(16)
C6	C7	Mn1	70.70(16)	C1	Mn1	C4	91.50(14)
C16	C7	P1	125.4(2)	C1	Mn1	C5	93.44(15)
C16	C7	Mn1	131.2(2)	C1	Mn1	C6	125.56(15)
P1	C7	Mn1	73.11(10)	C1	Mn1	C7	159.35(15)
C11	C10	C4	119.8(3)	C1	Mn1	P1	126.48(12)
C15	C10	C4	121.5(3)	C2	Mn1	C4	147.53(14)
C15	C10	C11	118.5(3)	C2	Mn1	C5	109.18(14)
C10	C11	C12	120.7(4)	C2	Mn1	C6	86.94(14)
C13	C12	C11	119.9(5)	C2	Mn1	C7	98.64(13)
C12	C13	C14	120.4(4)	C2	Mn1	P1	142.23(11)
C13	C14	C15	120.2(5)	C3	Mn1	C1	90.29(17)
C10	C15	C14	120.4(4)	C3	Mn1	C2	93.79(17)
C7	C16	C39	114.5(2)	C3	Mn1	C4	118.54(15)

C17	C16	C7	107.9(2)	C3	Mn1	C5	156.62(15)
C17	C16	C39	116.9(2)	C3	Mn1	C6	144.15(15)
C18	C17	C16	120.4(3)	C3	Mn1	C7	106.95(14)
C22	C17	C16	122.7(3)	C3	Mn1	P1	87.69(12)
C22	C17	C18	116.8(3)	C4	Mn1	C6	65.43(12)
C19	C18	C17	121.7(3)	C4	Mn1	C7	70.48(11)
C18	C19	C20	120.3(3)	C4	Mn1	P1	45.33(8)
C19	C20	C21	119.2(3)	C5	Mn1	C4	38.35(11)
O4	C20	C19	115.8(3)	C5	Mn1	C6	38.09(11)
O4	C20	C21	125.0(3)	C5	Mn1	C7	66.23(11)
C22	C21	C20	119.8(3)	C5	Mn1	P1	71.59(9)
C21	C22	C17	122.2(3)	C6	Mn1	C7	38.03(11)
O6	C24	Mn2	179.3(4)	C6	Mn1	P1	70.97(8)
O5	C25	Mn2	179.7(4)	C7	Mn1	P1	45.66(7)
O7	C26	Mn2	179.3(4)	C24	Mn2	C26	89.97(19)
C28	C27	C33	127.4(3)	C24	Mn2	C27	150.08(15)
C28	C27	P2	113.0(2)	C24	Mn2	C28	111.78(15)
C28	C27	Mn2	70.55(19)	C24	Mn2	C29	88.86(15)
C33	C27	P2	119.5(2)	C24	Mn2	C30	99.37(15)
C33	C27	Mn2	127.2(2)	C24	Mn2	P2	141.98(13)
P2	C27	Mn2	73.55(12)	C25	Mn2	C24	92.84(17)
C27	C28	C29	111.4(3)	C25	Mn2	C26	91.92(18)
C27	C28	C31	124.9(3)	C25	Mn2	C27	116.91(15)
C27	C28	Mn2	71.15(18)	C25	Mn2	C28	154.94(16)
C29	C28	C31	123.7(3)	C25	Mn2	C29	143.63(15)
C29	C28	Mn2	71.13(19)	C25	Mn2	C30	106.14(15)
C31	C28	Mn2	126.4(2)	C25	Mn2	P2	86.02(13)
C28	C29	C32	122.9(3)	C26	Mn2	C27	92.06(16)
C28	C29	Mn2	70.45(18)	C26	Mn2	C28	92.66(16)
C30	C29	C28	113.8(3)	C26	Mn2	C29	124.43(16)
C30	C29	C32	123.3(3)	C26	Mn2	C30	159.09(16)
C30	C29	Mn2	71.57(17)	C26	Mn2	P2	128.04(14)
C32	C29	Mn2	128.8(2)	C27	Mn2	C29	65.60(12)
C29	C30	C39	122.4(3)	C27	Mn2	C30	70.59(12)
C29	C30	P2	111.4(2)	C27	Mn2	P2	45.59(8)
C29	C30	Mn2	70.33(17)	C28	Mn2	C27	38.30(12)
C39	C30	P2	126.0(2)	C28	Mn2	C29	38.42(12)
C39	C30	Mn2	128.2(2)	C28	Mn2	C30	66.53(12)
P2	C30	Mn2	73.04(11)	C28	Mn2	P2	71.84(9)
C34	C33	C27	120.3(3)	C29	Mn2	C30	38.10(11)

C34	C33	C38	118.0(3)	C29	Mn2	P2	71.08(9)
C38	C33	C27	121.6(3)	C30	Mn2	P2	45.55(8)
C35	C34	C33	121.3(3)	C20	O4	C23	118.2(3)
C36	C35	C34	120.0(4)	C43	O8	C46	118.2(4)

X-ray crystallographic studies of compound 5b

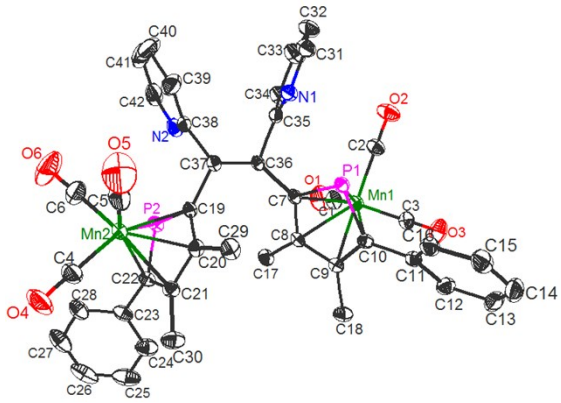


Table 4 Crystal data and structure refinement for 5b.

Identification code	**5b**
Empirical formula	$C_{42}H_{34}Mn_2N_2O_7P_2$
Formula weight	850.53
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.7464(3)
b/Å	13.8241(2)
c/Å	15.3780(2)
α/°	90
β/°	97.0866(14)
γ/°	90
Volume/Å^3	3954.81(11)
Z	4
ρ_{calc}g/cm^3	1.428
μ/mm^{-1}	6.395
F(000)	1744.0
Crystal size/mm^3	0.2 × 0.17 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.968 to 134.16
Index ranges	-21 ≤ h ≤ 22, -15 ≤ k ≤ 16, -12 ≤ l ≤ 18
Reflections collected	17079

Independent reflections	7061 [R_{int} = 0.0335, R_{sigma} = 0.0407]
Data/restraints/parameters	7061/0/503
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0410, wR_2 = 0.1006
Final R indexes [all data]	R_1 = 0.0534, wR_2 = 0.1083
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.43

Table 5 Bond Lengths for 5b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	Mn1	1.802(3)	C19	P2	1.780(3)
C1	O1	1.139(4)	C20	C21	1.418(4)
C2	Mn1	1.803(3)	C20	C29	1.519(4)
C2	O2	1.137(4)	C20	Mn2	2.166(3)
C3	Mn1	1.785(3)	C21	C22	1.421(4)
C3	O3	1.141(4)	C21	C30	1.507(4)
C4	Mn2	1.793(3)	C21	Mn2	2.174(3)
C4	O4	1.136(4)	C22	C23	1.487(4)
C5	Mn2	1.781(4)	C22	Mn2	2.186(3)
C5	O5	1.127(5)	C22	P2	1.776(3)
C6	Mn2	1.789(4)	C23	C24	1.383(5)
C6	O6	1.138(5)	C23	C28	1.381(5)
C7	C8	1.424(4)	C24	C25	1.387(5)
C7	C36	1.516(4)	C25	C26	1.360(7)
C7	Mn1	2.171(3)	C26	C27	1.365(7)
C7	P1	1.786(3)	C27	C28	1.389(5)
C8	C9	1.422(4)	C31	C32	1.366(5)
C8	C17	1.504(4)	C31	N1	1.338(4)
C8	Mn1	2.167(3)	C32	C33	1.371(5)
C9	C10	1.418(4)	C33	C34	1.378(5)
C9	C18	1.519(4)	C34	C35	1.378(4)
C9	Mn1	2.197(3)	C35	C36	1.521(4)
C10	C11	1.486(4)	C35	N1	1.337(4)
C10	Mn1	2.208(3)	C36	C37	1.575(4)
C10	P1	1.776(3)	C37	C38	1.517(4)
C11	C12	1.395(4)	C38	C39	1.382(5)
C11	C16	1.396(4)	C38	N2	1.335(4)
C12	C13	1.384(5)	C39	C40	1.394(6)
C13	C14	1.366(6)	C40	C41	1.355(8)
C14	C15	1.364(6)	C41	C42	1.366(7)
C15	C16	1.375(5)	C42	N2	1.333(5)

C19	C20	1.422(4)	Mn1	P1	2.3723(8)
C19	C37	1.520(4)	Mn2	P2	2.3752(8)
C19	Mn2	2.183(3)			

Table 6 Bond Angles for 5b

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	Mn1	179.4(3)	C7	C36	C35	111.6(2)
O2	C2	Mn1	178.1(3)	C7	C36	C37	114.0(2)
O3	C3	Mn1	178.6(3)	C35	C36	C37	108.1(2)
O4	C4	Mn2	179.5(5)	C19	C37	C36	111.9(2)
O5	C5	Mn2	179.5(6)	C38	C37	C19	113.0(2)
O6	C6	Mn2	179.1(4)	C38	C37	C36	107.5(2)
C8	C7	C36	124.5(2)	C39	C38	C37	120.6(3)
C8	C7	Mn1	70.69(15)	N2	C38	C37	116.5(3)
C8	C7	P1	112.0(2)	N2	C38	C39	122.7(3)
C36	C7	Mn1	124.53(17)	C38	C39	C40	117.9(5)
C36	C7	P1	123.50(19)	C41	C40	C39	119.7(5)
P1	C7	Mn1	72.95(9)	C40	C41	C42	118.3(4)
C7	C8	C17	125.2(3)	N2	C42	C41	124.0(5)
C7	C8	Mn1	70.99(14)	C1	Mn1	C2	90.98(15)
C9	C8	C7	112.9(2)	C1	Mn1	C7	99.87(13)
C9	C8	C17	121.9(3)	C1	Mn1	C8	88.42(13)
C9	C8	Mn1	72.14(15)	C1	Mn1	C9	111.44(13)
C17	C8	Mn1	126.55(19)	C1	Mn1	C10	149.01(13)
C8	C9	C18	122.7(2)	C1	Mn1	P1	143.13(12)
C8	C9	Mn1	69.84(14)	C2	Mn1	C7	103.43(13)
C10	C9	C8	112.4(2)	C2	Mn1	C8	140.54(14)
C10	C9	C18	124.5(3)	C2	Mn1	C9	156.09(12)
C10	C9	Mn1	71.62(14)	C2	Mn1	C10	119.63(12)
C18	C9	Mn1	132.7(2)	C2	Mn1	P1	85.80(10)
C9	C10	C11	127.0(2)	C3	Mn1	C1	90.97(15)
C9	C10	Mn1	70.81(15)	C3	Mn1	C2	89.25(15)
C9	C10	P1	112.8(2)	C3	Mn1	C7	163.06(12)
C11	C10	Mn1	126.75(19)	C3	Mn1	C8	130.20(13)
C11	C10	P1	120.2(2)	C3	Mn1	C9	98.22(13)
P1	C10	Mn1	72.17(9)	C3	Mn1	C10	93.94(12)
C12	C11	C10	123.4(3)	C3	Mn1	P1	125.63(10)
C12	C11	C16	117.5(3)	C7	Mn1	C9	65.75(10)
C16	C11	C10	119.1(3)	C7	Mn1	C10	70.12(10)

C13	C12	C11	120.4(3)	C7	Mn1	P1	46.03(7)
C14	C13	C12	120.6(4)	C8	Mn1	C7	38.32(10)
C15	C14	C13	119.9(3)	C8	Mn1	C9	38.02(10)
C14	C15	C16	120.5(4)	C8	Mn1	C10	65.29(10)
C15	C16	C11	121.0(3)	C8	Mn1	P1	71.86(7)
C20	C19	C37	123.4(2)	C9	Mn1	C10	37.57(10)
C20	C19	Mn2	70.30(16)	C9	Mn1	P1	71.35(7)
C20	C19	P2	112.7(2)	C10	Mn1	P1	45.47(7)
C37	C19	Mn2	127.8(2)	C4	Mn2	C19	156.71(15)
C37	C19	P2	123.8(2)	C4	Mn2	C20	119.76(16)
P2	C19	Mn2	72.85(10)	C4	Mn2	C21	91.60(15)
C19	C20	C29	125.4(3)	C4	Mn2	C22	95.38(14)
C19	C20	Mn2	71.54(16)	C4	Mn2	P2	133.75(12)
C21	C20	C19	112.4(2)	C5	Mn2	C4	90.16(18)
C21	C20	C29	122.2(3)	C5	Mn2	C6	90.5(2)
C21	C20	Mn2	71.22(17)	C5	Mn2	C19	96.12(15)
C29	C20	Mn2	127.1(2)	C5	Mn2	C20	90.21(16)
C20	C21	C22	112.5(2)	C5	Mn2	C21	117.41(18)
C20	C21	C30	124.0(3)	C5	Mn2	C22	154.78(17)
C20	C21	Mn2	70.63(17)	C5	Mn2	P2	135.98(14)
C22	C21	C30	123.4(3)	C6	Mn2	C4	92.3(2)
C22	C21	Mn2	71.42(17)	C6	Mn2	C19	110.02(15)
C30	C21	Mn2	128.7(2)	C6	Mn2	C20	147.97(16)
C21	C22	C23	123.9(3)	C6	Mn2	C21	151.83(17)
C21	C22	Mn2	70.53(17)	C6	Mn2	C22	113.79(17)
C21	C22	P2	112.8(2)	C6	Mn2	P2	85.66(13)
C23	C22	Mn2	129.5(2)	C19	Mn2	C22	69.96(10)
C23	C22	P2	123.0(2)	C19	Mn2	P2	45.74(7)
P2	C22	Mn2	72.85(10)	C20	Mn2	C19	38.16(10)
C24	C23	C22	118.6(3)	C20	Mn2	C21	38.15(11)
C28	C23	C22	122.8(3)	C20	Mn2	C22	65.71(11)
C28	C23	C24	118.6(3)	C20	Mn2	P2	71.93(8)
C23	C24	C25	120.6(4)	C21	Mn2	C19	65.60(10)
C26	C25	C24	120.1(5)	C21	Mn2	C22	38.05(11)
C25	C26	C27	120.1(4)	C21	Mn2	P2	71.72(8)
C26	C27	C28	120.4(4)	C22	Mn2	P2	45.59(7)
C23	C28	C27	120.1(4)	C35	N1	C31	117.8(3)
N1	C31	C32	123.5(3)	C42	N2	C38	117.3(4)
C31	C32	C33	118.6(3)	C7	P1	Mn1	61.03(9)
C32	C33	C34	118.9(3)	C10	P1	C7	89.84(13)

C33	C34	C35	119.4(3)	C10	P1	Mn1	62.36(8)
C34	C35	C36	121.8(3)	C19	P2	Mn2	61.41(9)
N1	C35	C34	121.9(3)	C22	P2	C19	89.54(13)
N1	C35	C36	116.4(2)	C22	P2	Mn2	61.56(10)

X-ray crystallographic studies of compound 7b

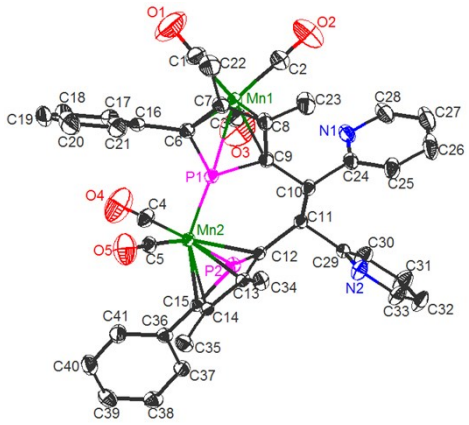


Table 7 Crystal data and structure refinement for 7b.

Identification code	**7b**
Empirical formula	$C_{41}H_{32}Mn_2N_2O_5P_2$
Formula weight	804.50
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.6738(3)
b/Å	9.62622(18)
c/Å	24.7524(5)
α/°	90
β/°	90.0503(17)
γ/°	90
Volume/Å^3	3734.62(12)
Z	4
ρ_{calc}g/cm^3	1.431
μ/mm^{-1}	0.809
F(000)	1648.0
Crystal size/mm^3	0.18 × 0.16 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.704 to 52.744
Index ranges	$-19 \le h \le 17$, $-10 \le k \le 12$, $-27 \le l \le 30$

Reflections collected	18551
Independent reflections	7605 [R_{int} = 0.0363, R_{sigma} = 0.0518]
Data/restraints/parameters	7605/0/473
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0428, wR_2 = 0.0918
Final R indexes [all data]	R_1 = 0.0634, wR_2 = 0.1011
Largest diff. peak/hole / e $Å^{-3}$	0.31/-0.30

Table 8 Bond Lengths for 7b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	Mn1	1.778(4)	C14	C15	1.414(3)
C1	O1	1.159(4)	C14	C35	1.515(3)
C2	Mn1	1.797(3)	C14	Mn2	2.149(2)
C2	O2	1.154(4)	C15	C36	1.499(3)
C3	Mn1	1.798(4)	C15	Mn2	2.178(2)
C3	O3	1.153(4)	C15	P2	1.783(2)
C4	Mn2	1.795(3)	C16	C17	1.383(5)
C4	O4	1.140(3)	C16	C21	1.387(4)
C5	Mn2	1.787(3)	C17	C18	1.378(5)
C5	O5	1.154(3)	C18	C19	1.350(7)
C6	C7	1.428(4)	C19	C20	1.360(7)
C6	C16	1.482(4)	C20	C21	1.404(5)
C6	Mn1	2.188(3)	C24	C25	1.388(4)
C6	P1	1.754(2)	C24	N1	1.338(4)
C7	C8	1.424(4)	C25	C26	1.386(5)
C7	C22	1.510(4)	C26	C27	1.372(6)
C7	Mn1	2.154(3)	C27	C28	1.367(5)
C8	C9	1.429(3)	C28	N1	1.339(3)
C8	C23	1.511(4)	C29	C30	1.372(4)
C8	Mn1	2.181(3)	C29	N2	1.334(3)
C9	C10	1.522(3)	C30	C31	1.384(4)
C9	Mn1	2.224(3)	C31	C32	1.362(5)
C9	P1	1.761(3)	C32	C33	1.361(4)
C10	C11	1.559(3)	C33	N2	1.344(4)
C10	C24	1.530(3)	C36	C37	1.387(3)
C11	C12	1.529(3)	C36	C41	1.385(4)
C11	C29	1.528(3)	C37	C38	1.393(4)
C12	C13	1.430(3)	C38	C39	1.370(4)
C12	Mn2	2.174(2)	C39	C40	1.375(4)
C12	P2	1.779(2)	C40	C41	1.386(4)

C13	C14	1.437(3)	Mn1	P1	2.3989(8)
C13	C34	1.503(3)	Mn2	P1	2.1499(7)
C13	Mn2	2.173(2)	Mn2	P2	2.3746(7)

Table 9 Bond Angles for 7b.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	Mn1	179.2(4)	C32	C31	C30	118.9(3)
O2	C2	Mn1	177.1(3)	C33	C32	C31	118.5(3)
O3	C3	Mn1	179.3(3)	N2	C33	C32	123.8(3)
O4	C4	Mn2	178.7(3)	C37	C36	C15	118.5(2)
O5	C5	Mn2	177.2(2)	C41	C36	C15	123.3(2)
C7	C6	C16	126.0(2)	C41	C36	C37	118.1(2)
C7	C6	Mn1	69.51(15)	C36	C37	C38	120.9(3)
C7	C6	P1	110.90(19)	C39	C38	C37	119.7(3)
C16	C6	Mn1	129.5(2)	C38	C39	C40	120.4(3)
C16	C6	P1	122.72(19)	C39	C40	C41	119.8(3)
P1	C6	Mn1	74.04(9)	C40	C41	C36	121.1(3)
C6	C7	C22	123.3(3)	C1	Mn1	C2	88.99(16)
C6	C7	Mn1	72.11(16)	C1	Mn1	C3	91.85(17)
C8	C7	C6	112.5(2)	C1	Mn1	C6	91.04(13)
C8	C7	C22	124.1(3)	C1	Mn1	C7	97.19(15)
C8	C7	Mn1	71.86(16)	C1	Mn1	C8	131.19(15)
C22	C7	Mn1	125.9(2)	C1	Mn1	C9	161.11(13)
C7	C8	C9	113.7(2)	C1	Mn1	P1	123.19(11)
C7	C8	C23	122.5(2)	C2	Mn1	C3	93.26(16)
C7	C8	Mn1	69.78(17)	C2	Mn1	C6	144.87(15)
C9	C8	C23	123.6(2)	C2	Mn1	C7	106.86(15)
C9	C8	Mn1	72.69(16)	C2	Mn1	C8	88.32(14)
C23	C8	Mn1	130.0(2)	C2	Mn1	C9	103.90(13)
C8	C9	C10	125.9(2)	C2	Mn1	P1	147.76(12)
C8	C9	Mn1	69.47(16)	C3	Mn1	C6	121.84(13)
C8	C9	P1	109.95(18)	C3	Mn1	C7	158.01(13)
C10	C9	Mn1	132.43(18)	C3	Mn1	C8	136.97(12)
C10	C9	P1	123.30(17)	C3	Mn1	C9	100.98(12)
P1	C9	Mn1	72.98(9)	C3	Mn1	P1	88.01(10)
C9	C10	C11	113.6(2)	C6	Mn1	C9	70.45(9)
C9	C10	C24	116.4(2)	C6	Mn1	P1	44.68(7)
C24	C10	C11	105.17(19)	C7	Mn1	C6	38.38(10)
C12	C11	C10	120.23(19)	C7	Mn1	C8	38.36(10)

C29	C11	C10	109.41(19)	C7	Mn1	C9	66.11(10)
C29	C11	C12	107.79(18)	C7	Mn1	P1	70.26(7)
C11	C12	Mn2	131.28(15)	C8	Mn1	C6	65.75(10)
C11	C12	P2	117.24(17)	C8	Mn1	C9	37.84(9)
C13	C12	C11	128.5(2)	C8	Mn1	P1	69.58(7)
C13	C12	Mn2	70.77(13)	C9	Mn1	P1	44.60(6)
C13	C12	P2	113.78(17)	C4	Mn2	C12	132.31(11)
P2	C12	Mn2	73.07(8)	C4	Mn2	C13	162.02(11)
C12	C13	C14	110.7(2)	C4	Mn2	C14	128.81(11)
C12	C13	C34	126.4(2)	C4	Mn2	C15	96.56(11)
C12	C13	Mn2	70.81(13)	C4	Mn2	P1	97.58(9)
C14	C13	C34	122.9(2)	C4	Mn2	P2	91.62(9)
C14	C13	Mn2	69.67(13)	C5	Mn2	C4	92.82(12)
C34	C13	Mn2	128.73(17)	C5	Mn2	C12	134.87(11)
C13	C14	C35	123.0(2)	C5	Mn2	C13	98.49(11)
C13	C14	Mn2	71.49(13)	C5	Mn2	C14	87.08(11)
C15	C14	C13	113.4(2)	C5	Mn2	C15	110.56(10)
C15	C14	C35	123.4(2)	C5	Mn2	P1	90.56(8)
C15	C14	Mn2	72.04(13)	C5	Mn2	P2	156.40(9)
C35	C14	Mn2	128.85(17)	C12	Mn2	C15	70.25(9)
C14	C15	C36	123.0(2)	C12	Mn2	P2	45.79(6)
C14	C15	Mn2	69.82(13)	C13	Mn2	C12	38.42(9)
C14	C15	P2	112.81(17)	C13	Mn2	C15	66.40(9)
C36	C15	Mn2	131.89(17)	C13	Mn2	P2	72.53(7)
C36	C15	P2	123.65(18)	C14	Mn2	C12	66.14(9)
P2	C15	Mn2	72.89(8)	C14	Mn2	C13	38.84(9)
C17	C16	C6	122.2(3)	C14	Mn2	C15	38.14(9)
C17	C16	C21	118.2(3)	C14	Mn2	P1	133.61(7)
C21	C16	C6	119.5(3)	C14	Mn2	P2	72.19(7)
C18	C17	C16	121.4(4)	C15	Mn2	P2	45.87(7)
C19	C18	C17	119.8(5)	P1	Mn2	C12	84.03(6)
C18	C19	C20	120.9(4)	P1	Mn2	C13	96.25(7)
C19	C20	C21	120.1(5)	P1	Mn2	C15	153.89(7)
C16	C21	C20	119.6(4)	P1	Mn2	P2	111.80(3)
C25	C24	C10	121.2(3)	C24	N1	C28	117.3(3)
N1	C24	C10	116.1(2)	C29	N2	C33	117.2(3)
N1	C24	C25	122.4(3)	C6	P1	C9	92.75(12)
C26	C25	C24	118.8(3)	C6	P1	Mn1	61.29(9)
C27	C26	C25	119.0(3)	C6	P1	Mn2	135.76(9)
C28	C27	C26	118.5(3)	C9	P1	Mn1	62.43(9)

N1	C28	C27	124.0(4)	C9	P1	Mn2	128.79(9)
C30	C29	C11	121.5(2)	Mn2	P1	Mn1	145.86(4)
N2	C29	C11	116.3(2)	C12	P2	C15	89.31(11)
N2	C29	C30	122.2(2)	C12	P2	Mn2	61.14(7)
C29	C30	C31	119.2(3)	C15	P2	Mn2	61.24(8)

X-ray crystallographic studies of compound 8a

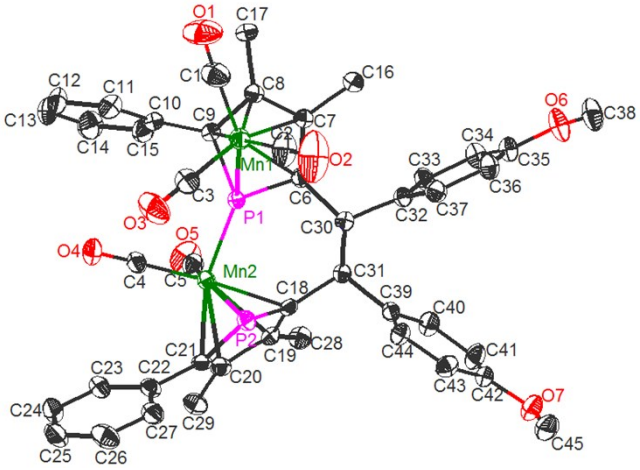


Table 10 Crystal data and structure refinement for 8a.

Identification code	**8a**
Empirical formula	$C_{45}H_{38}Mn_2O_7P_2$
Formula weight	862.57
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.67365(18)
b/Å	14.2261(3)
c/Å	26.7140(5)
α/°	90
β/°	93.5276(15)
γ/°	90
Volume/Å^3	4048.67(13)
Z	4
ρ_{calc}g/cm^3	1.415
μ/mm^{-1}	6.240
F(000)	1776.0
Crystal size/mm^3	0.17 × 0.07 × 0.06
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/°	6.63 to 134.15
Index ranges	$-9 \leq h \leq 12$, $-16 \leq k \leq 16$, $-31 \leq l \leq 28$
Reflections collected	16980
Independent reflections	7210 [R_{int} = 0.0450, R_{sigma} = 0.0827]
Data/restraints/parameters	7210/0/511
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0536, wR_2 = 0.1114
Final R indexes [all data]	R_1 = 0.0891, wR_2 = 0.1232
Largest diff. peak/hole / e $Å^{-3}$	0.50/-0.29

Table 11 Bond Lengths for 8a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	Mn1	1.793(6)	C19	Mn2	2.151(4)
C1	O1	1.156(6)	C20	C21	1.407(6)
C2	Mn1	1.786(6)	C20	C29	1.515(5)
C2	O2	1.133(6)	C20	Mn2	2.148(4)
C3	Mn1	1.798(5)	C21	C22	1.487(5)
C3	O3	1.136(5)	C21	Mn2	2.184(4)
C4	Mn2	1.802(5)	C21	P2	1.800(4)
C4	O4	1.143(5)	C22	C23	1.394(6)
C5	Mn2	1.785(5)	C22	C27	1.379(6)
C5	O5	1.144(5)	C23	C24	1.375(6)
C6	C7	1.431(5)	C24	C25	1.389(7)
C6	C30	1.549(5)	C25	C26	1.358(7)
C6	Mn1	2.197(4)	C26	C27	1.392(6)
C6	P1	1.747(4)	C30	C31	1.571(5)
C7	C8	1.430(6)	C30	C32	1.520(5)
C7	C16	1.519(5)	C31	C39	1.526(5)
C7	Mn1	2.132(4)	C32	C33	1.390(6)
C8	C9	1.421(5)	C32	C37	1.372(6)
C8	C17	1.508(5)	C33	C34	1.381(6)
C8	Mn1	2.150(4)	C34	C35	1.370(6)
C9	C10	1.499(5)	C35	C36	1.373(7)
C9	Mn1	2.181(4)	C35	O6	1.371(5)
C9	P1	1.744(4)	C36	C37	1.410(6)
C10	C11	1.378(6)	C38	O6	1.410(6)
C10	C15	1.374(7)	C39	C40	1.381(6)
C11	C12	1.392(7)	C39	C44	1.377(6)
C12	C13	1.365(8)	C40	C41	1.381(6)

C13	C14	1.358(8)	C41	C42	1.380(6)
C14	C15	1.380(6)	C42	C43	1.372(6)
C18	C19	1.412(5)	C42	O7	1.374(5)
C18	C31	1.522(5)	C43	C44	1.396(5)
C18	Mn2	2.168(4)	C45	O7	1.402(6)
C18	P2	1.796(4)	Mn1	P1	2.4025(13)
C19	C20	1.442(5)	Mn2	P1	2.1326(12)
C19	C28	1.505(6)	Mn2	P2	2.3773(13)

Table 12 Bond Angles for 8a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	Mn1	176.5(5)	C34	C35	O6	115.4(5)
O2	C2	Mn1	178.6(6)	O6	C35	C36	124.7(5)
O3	C3	Mn1	179.8(6)	C35	C36	C37	119.7(4)
O4	C4	Mn2	179.3(5)	C32	C37	C36	121.0(5)
O5	C5	Mn2	176.1(5)	C40	C39	C31	120.1(4)
C7	C6	C30	130.1(3)	C44	C39	C31	122.7(4)
C7	C6	Mn1	68.3(2)	C44	C39	C40	117.2(4)
C7	C6	P1	110.2(3)	C41	C40	C39	121.8(5)
C30	C6	Mn1	127.0(3)	C42	C41	C40	119.9(5)
C30	C6	P1	119.6(3)	C43	C42	C41	119.9(4)
P1	C6	Mn1	74.07(14)	C43	C42	O7	125.0(4)
C6	C7	C16	127.7(4)	O7	C42	C41	115.0(4)
C6	C7	Mn1	73.2(2)	C42	C43	C44	119.0(4)
C8	C7	C6	112.5(3)	C39	C44	C43	122.2(4)
C8	C7	C16	119.8(4)	C1	Mn1	C3	95.5(2)
C8	C7	Mn1	71.1(2)	C1	Mn1	C6	145.3(2)
C16	C7	Mn1	124.8(3)	C1	Mn1	C7	106.9(2)
C7	C8	C17	124.7(4)	C1	Mn1	C8	87.0(2)
C7	C8	Mn1	69.8(3)	C1	Mn1	C9	102.1(2)
C9	C8	C7	113.4(4)	C1	Mn1	P1	145.8(2)
C9	C8	C17	121.8(4)	C2	Mn1	C1	90.9(3)
C9	C8	Mn1	72.0(2)	C2	Mn1	C3	90.8(3)
C17	C8	Mn1	129.3(3)	C2	Mn1	C6	89.9(2)
C8	C9	C10	128.0(4)	C2	Mn1	C7	95.1(2)
C8	C9	Mn1	69.7(2)	C2	Mn1	C8	129.6(2)
C8	C9	P1	110.1(3)	C2	Mn1	C9	160.3(2)
C10	C9	Mn1	129.5(3)	C2	Mn1	P1	123.1(2)
C10	C9	P1	121.3(3)	C3	Mn1	C6	119.12(19)

P1	C9	Mn1	74.55(15)	C3	Mn1	C7	156.64(19)
C11	C10	C9	122.3(5)	C3	Mn1	C8	139.6(2)
C15	C10	C9	118.9(4)	C3	Mn1	C9	102.6(2)
C15	C10	C11	118.7(5)	C3	Mn1	P1	87.80(16)
C10	C11	C12	119.8(6)	C6	Mn1	P1	44.36(10)
C13	C12	C11	120.8(6)	C7	Mn1	C6	38.55(14)
C14	C13	C12	119.3(5)	C7	Mn1	C8	39.01(15)
C13	C14	C15	120.6(6)	C7	Mn1	C9	67.03(16)
C10	C15	C14	120.8(6)	C7	Mn1	P1	70.05(11)
C19	C18	C31	121.3(4)	C8	Mn1	C6	66.33(16)
C19	C18	Mn2	70.3(2)	C8	Mn1	C9	38.29(14)
C19	C18	P2	112.1(3)	C8	Mn1	P1	69.43(11)
C31	C18	Mn2	128.1(3)	C9	Mn1	C6	70.95(15)
C31	C18	P2	126.4(3)	C9	Mn1	P1	44.41(10)
P2	C18	Mn2	73.01(14)	C4	Mn2	C18	150.22(19)
C18	C19	C20	113.2(4)	C4	Mn2	C19	154.56(17)
C18	C19	C28	124.9(4)	C4	Mn2	C20	115.38(18)
C18	C19	Mn2	71.6(2)	C4	Mn2	C21	92.93(18)
C20	C19	C28	121.9(4)	C4	Mn2	P1	92.35(14)
C20	C19	Mn2	70.3(2)	C4	Mn2	P2	104.59(16)
C28	C19	Mn2	128.5(3)	C5	Mn2	C4	92.4(2)
C19	C20	C29	122.0(4)	C5	Mn2	C18	117.35(19)
C19	C20	Mn2	70.5(2)	C5	Mn2	C19	88.87(19)
C21	C20	C19	112.3(4)	C5	Mn2	C20	92.70(19)
C21	C20	C29	125.3(4)	C5	Mn2	C21	125.65(18)
C21	C20	Mn2	72.5(2)	C5	Mn2	P1	94.03(15)
C29	C20	Mn2	130.0(3)	C5	Mn2	P2	160.94(16)
C20	C21	C22	126.3(4)	C18	Mn2	C21	71.17(14)
C20	C21	Mn2	69.6(2)	C18	Mn2	P2	46.27(11)
C20	C21	P2	112.7(3)	C19	Mn2	C18	38.15(14)
C22	C21	Mn2	125.2(3)	C19	Mn2	C21	66.17(16)
C22	C21	P2	121.0(3)	C19	Mn2	P2	72.07(12)
P2	C21	Mn2	72.54(13)	C20	Mn2	C18	67.00(14)
C23	C22	C21	123.0(4)	C20	Mn2	C19	39.20(15)
C27	C22	C21	119.4(4)	C20	Mn2	C21	37.89(16)
C27	C22	C23	117.6(4)	C20	Mn2	P2	72.39(12)
C24	C23	C22	121.2(5)	C21	Mn2	P2	46.24(11)
C23	C24	C25	119.9(5)	P1	Mn2	C18	85.04(10)
C26	C25	C24	119.7(5)	P1	Mn2	C19	112.91(11)
C25	C26	C27	120.2(5)	P1	Mn2	C20	151.13(12)

C22	C27	C26	121.3(5)	P1	Mn2	C21	139.64(11)
C6	C30	C31	112.0(3)	P1	Mn2	P2	93.84(4)
C32	C30	C6	111.7(3)	C35	O6	C38	117.8(4)
C32	C30	C31	109.0(3)	C42	O7	C45	119.5(4)
C18	C31	C30	117.5(3)	C6	P1	Mn1	61.57(14)
C18	C31	C39	109.1(3)	C6	P1	Mn2	130.57(14)
C39	C31	C30	110.2(3)	C9	P1	C6	93.42(19)
C33	C32	C30	119.9(4)	C9	P1	Mn1	61.04(14)
C37	C32	C30	122.3(4)	C9	P1	Mn2	135.86(14)
C37	C32	C33	117.7(4)	Mn2	P1	Mn1	137.43(6)
C34	C33	C32	121.7(4)	C18	P2	C21	89.54(19)
C35	C34	C33	120.0(5)	C18	P2	Mn2	60.72(12)
C34	C35	C36	119.9(4)	C21	P2	Mn2	61.22(13)

X-ray crystallographic studies of compound 9

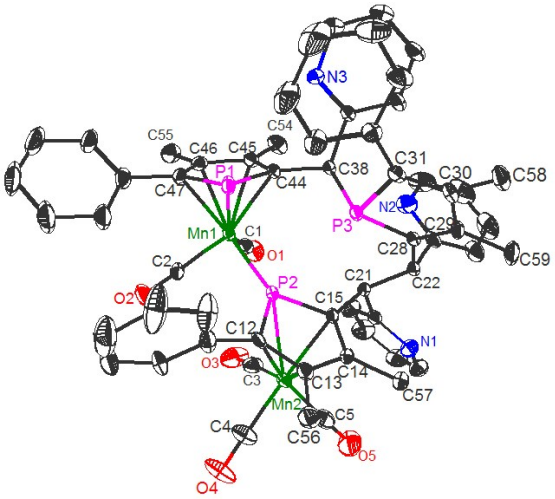


Table 13 Crystal data and structure refinement for 9.

Identification code	**9**
Empirical formula	$C_{59}H_{48}N_3O_5P_3Mn_2$
Formula weight	1081.79
Temperature/K	273.15

Crystal system	triclinic
Space group	P-1
a/Å	12.0038(6)
b/Å	13.6029(7)
c/Å	18.5921(10)
α/°	102.356(3)
β/°	97.645(3)
γ/°	113.816(3)
Volume/Å^3	2629.9(2)
Z	2
ρ_{calc}g/cm^3	1.366
μ/mm^{-1}	0.624
F(000)	1116.0
Crystal size/mm^3	0.5 × 0.4 × 0.3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.44 to 55.42
Index ranges	-15 ≤ h ≤ 15, -17 ≤ k ≤ 17, -24 ≤ l ≤ 24
Reflections collected	47201
Independent reflections	12195 [R_{int} = 0.0848, R_{sigma} = 0.1035]
Data/restraints/parameters	12195/0/656
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0746, wR_2 = 0.1637
Final R indexes [all data]	R_1 = 0.1343, wR_2 = 0.1823
Largest diff. peak/hole / e Å^{-3}	0.96/-0.65

Table 14 Bond Lengths for 9.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	P2	2.1809(11)	C30	C31	1.363(6)
Mn1	P1	2.3886(14)	C30	C58	1.510(6)
Mn1	C2	1.780(4)	C23	C22	1.520(6)
Mn1	C47	2.188(4)	C23	N2	1.331(6)
Mn1	C45	2.186(4)	C23	C24	1.389(7)
Mn1	C44	2.204(4)	C45	C44	1.395(6)
Mn1	C46	2.157(4)	C45	C46	1.444(6)
Mn1	C1	1.778(6)	C45	C54	1.512(6)
Mn2	P2	2.4099(12)	C46	C55	1.497(6)
Mn2	C13	2.149(5)	C20	N1	1.337(5)
Mn2	C14	2.160(4)	C20	C19	1.375(7)
Mn2	C15	2.200(4)	C1	O1	1.151(6)
Mn2	C4	1.788(5)	C48	C49	1.384(7)

Mn2	C12	2.195(5)	C48	C53	1.378(8)
Mn2	C3	1.785(6)	C4	O4	1.132(6)
Mn2	C5	1.811(6)	C16	C17	1.362(8)
P3	C28	1.804(4)	C16	N1	1.335(7)
P3	C38	1.885(4)	C37	C36	1.375(8)
P3	C31	1.800(4)	C12	C11	1.489(6)
P2	C15	1.765(4)	C3	O3	1.145(6)
P2	C12	1.759(4)	C11	C10	1.377(7)
P1	C47	1.786(4)	C11	C6	1.385(8)
P1	C44	1.781(4)	C17	C18	1.358(8)
C21	C15	1.519(6)	C5	O5	1.151(7)
C21	C20	1.521(6)	C49	C50	1.392(9)
C21	C22	1.563(5)	C43	C42	1.335(7)
C2	O2	1.152(5)	C43	N3	1.345(6)
C47	C46	1.407(7)	C53	C52	1.391(8)
C47	C48	1.492(6)	C51	C50	1.338(11)
C13	C14	1.421(6)	C51	C52	1.351(11)
C13	C12	1.425(6)	C41	C42	1.352(8)
C13	C56	1.511(6)	C41	C40	1.378(7)
C32	C31	1.471(6)	C36	C35	1.398(10)
C32	C37	1.400(7)	C10	C9	1.406(10)
C32	C33	1.400(7)	C27	C26	1.365(10)
C28	C29	1.348(6)	C27	N2	1.340(7)
C28	C22	1.515(6)	C9	C8	1.332(12)
C14	C15	1.435(6)	C33	C34	1.372(9)
C14	C57	1.510(6)	C34	C35	1.372(10)
C38	C39	1.512(5)	C26	C25	1.376(10)
C38	C44	1.516(5)	C6	C7	1.387(8)
C39	N3	1.316(5)	C25	C24	1.369(8)
C39	C40	1.397(6)	C8	C7	1.383(12)
C29	C30	1.456(6)	C18	C19	1.381(8)
C29	C59	1.517(6)			

Table 15 Bond Angles for 9.

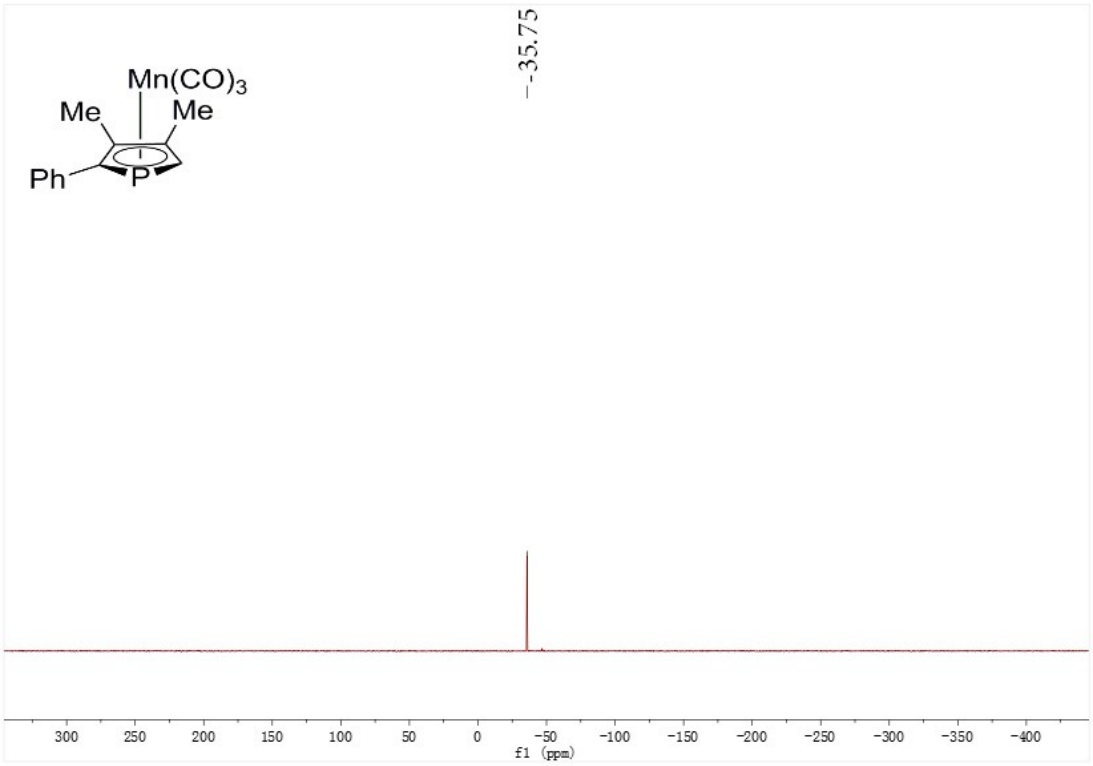
Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
P2	Mn1	P1	90.58(5)	C57	C14	Mn2	128.4(3)
P2	Mn1	C47	131.22(13)	C39	C38	P3	112.6(3)
P2	Mn1	C45	128.46(11)	C39	C38	C44	112.7(3)
P2	Mn1	C44	96.48(10)	C44	C38	P3	111.2(3)

C2	Mn1	P2	91.84(14)	N3	C39	C38	118.4(3)
C2	Mn1	P1	113.66(15)	N3	C39	C40	121.7(4)
C2	Mn1	C47	89.26(17)	C40	C39	C38	119.9(4)
C2	Mn1	C45	139.70(17)	C28	C29	C30	115.2(4)
C2	Mn1	C44	157.28(19)	C28	C29	C59	124.0(4)
C2	Mn1	C46	102.25(18)	C30	C29	C59	120.8(4)
C47	Mn1	P1	45.68(12)	C29	C30	C58	121.4(4)
C47	Mn1	C44	69.39(15)	C31	C30	C29	114.2(4)
C45	Mn1	P1	70.93(12)	C31	C30	C58	124.3(4)
C45	Mn1	C47	65.10(17)	N2	C23	C22	116.7(4)
C45	Mn1	C44	37.07(15)	N2	C23	C24	122.5(5)
C44	Mn1	P1	45.40(12)	C24	C23	C22	120.8(4)
C46	Mn1	P2	160.86(12)	C44	C45	Mn1	72.2(2)
C46	Mn1	P1	72.00(13)	C44	C45	C46	113.0(4)
C46	Mn1	C47	37.78(18)	C44	C45	C54	123.6(4)
C46	Mn1	C45	38.84(16)	C46	C45	Mn1	69.5(2)
C46	Mn1	C44	65.76(15)	C46	C45	C54	123.4(4)
C1	Mn1	P2	96.30(14)	C54	C45	Mn1	128.8(3)
C1	Mn1	P1	155.66(14)	C32	C31	P3	122.7(3)
C1	Mn1	C2	89.5(2)	C30	C31	P3	108.6(3)
C1	Mn1	C47	132.48(19)	C30	C31	C32	128.2(4)
C1	Mn1	C45	86.68(19)	P1	C44	Mn1	72.79(13)
C1	Mn1	C44	110.44(18)	C38	C44	Mn1	129.5(3)
C1	Mn1	C46	96.7(2)	C38	C44	P1	124.5(3)
C13	Mn2	P2	70.17(12)	C45	C44	Mn1	70.8(2)
C13	Mn2	C14	38.51(16)	C45	C44	P1	113.2(3)
C13	Mn2	C15	66.06(16)	C45	C44	C38	122.1(4)
C13	Mn2	C12	38.28(16)	P2	C15	Mn2	73.94(13)
C14	Mn2	P2	70.49(11)	C21	C15	Mn2	131.5(3)
C14	Mn2	C15	38.42(15)	C21	C15	P2	119.9(3)
C14	Mn2	C12	66.30(15)	C14	C15	Mn2	69.3(2)
C15	Mn2	P2	44.74(10)	C14	C15	P2	111.1(3)
C4	Mn2	P2	129.3(2)	C14	C15	C21	128.3(3)
C4	Mn2	C13	94.1(2)	C47	C46	Mn1	72.3(2)
C4	Mn2	C14	124.9(2)	C47	C46	C45	111.2(4)
C4	Mn2	C15	160.1(2)	C47	C46	C55	125.4(4)
C4	Mn2	C12	93.4(2)	C45	C46	Mn1	71.6(2)
C4	Mn2	C5	88.7(3)	C45	C46	C55	123.2(5)
C12	Mn2	P2	44.61(11)	C55	C46	Mn1	125.8(3)
C12	Mn2	C15	70.44(15)	N1	C20	C21	117.2(4)

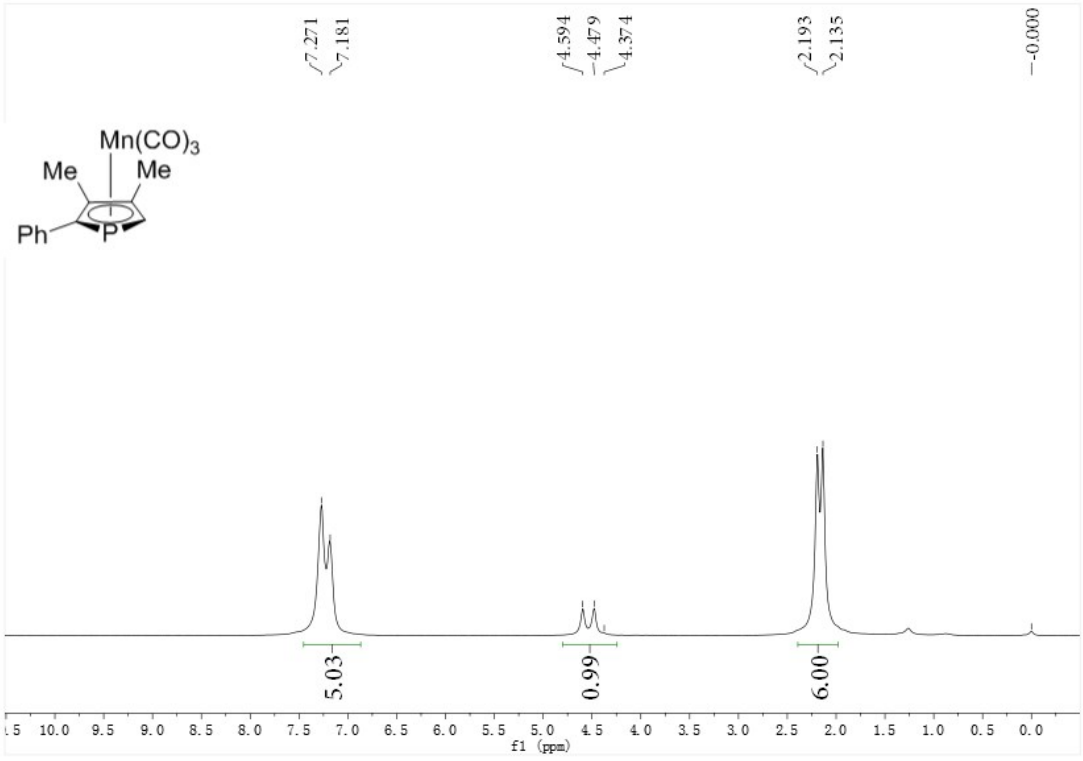
C3	Mn2	P2	87.00(16)	N1	C20	C19	122.0(4)
C3	Mn2	C13	154.7(2)	C19	C20	C21	120.7(4)
C3	Mn2	C14	143.1(2)	C28	C22	C21	116.7(3)
C3	Mn2	C15	105.47(19)	C28	C22	C23	111.1(3)
C3	Mn2	C4	92.0(3)	C23	C22	C21	107.1(3)
C3	Mn2	C12	116.8(2)	O1	C1	Mn1	175.1(4)
C3	Mn2	C5	92.4(3)	C49	C48	C47	121.2(5)
C5	Mn2	P2	141.97(17)	C53	C48	C47	120.4(4)
C5	Mn2	C13	112.2(2)	C53	C48	C49	118.1(5)
C5	Mn2	C14	88.5(2)	O4	C4	Mn2	177.5(6)
C5	Mn2	C15	99.67(19)	N1	C16	C17	123.9(5)
C5	Mn2	C12	150.5(2)	C36	C37	C32	121.0(5)
C28	P3	C38	105.62(19)	P2	C12	Mn2	74.18(17)
C31	P3	C28	91.8(2)	C13	C12	Mn2	69.1(3)
C31	P3	C38	109.46(18)	C13	C12	P2	110.9(3)
Mn1	P2	Mn2	137.18(5)	C13	C12	C11	124.9(4)
C15	P2	Mn1	135.95(14)	C11	C12	Mn2	133.8(3)
C15	P2	Mn2	61.32(13)	C11	C12	P2	123.0(3)
C12	P2	Mn1	131.86(15)	O3	C3	Mn2	178.3(4)
C12	P2	Mn2	61.22(15)	C10	C11	C12	124.7(6)
C12	P2	C15	91.99(19)	C10	C11	C6	119.1(5)
C47	P1	Mn1	61.23(15)	C6	C11	C12	116.0(5)
C44	P1	Mn1	61.80(13)	C18	C17	C16	118.2(6)
C44	P1	C47	89.0(2)	O5	C5	Mn2	178.6(6)
C15	C21	C20	115.5(3)	C48	C49	C50	120.4(7)
C15	C21	C22	113.8(3)	C42	C43	N3	123.7(5)
C20	C21	C22	108.4(3)	C48	C53	C52	120.1(6)
O2	C2	Mn1	177.4(4)	C50	C51	C52	120.4(6)
P1	C47	Mn1	73.09(14)	C42	C41	C40	118.7(5)
C46	C47	Mn1	69.9(2)	C37	C36	C35	120.3(6)
C46	C47	P1	113.5(3)	C43	C42	C41	119.6(5)
C46	C47	C48	126.6(4)	C11	C10	C9	118.7(7)
C48	C47	Mn1	129.4(3)	N2	C27	C26	123.6(6)
C48	C47	P1	119.7(4)	C8	C9	C10	121.3(7)
C14	C13	Mn2	71.1(3)	C34	C33	C32	121.5(6)
C14	C13	C12	113.6(4)	C33	C34	C35	120.6(6)
C14	C13	C56	123.4(4)	C27	C26	C25	118.5(6)
C12	C13	Mn2	72.6(3)	C34	C35	C36	119.2(6)
C12	C13	C56	122.9(4)	C11	C6	C7	121.4(7)
C56	C13	Mn2	127.0(3)	C24	C25	C26	119.2(6)

C37	C32	C31	120.7(4)	C9	C8	C7	121.2(8)
C33	C32	C31	121.7(4)	C17	C18	C19	119.4(6)
C33	C32	C37	117.4(5)	C8	C7	C6	118.1(8)
C29	C28	P3	108.5(3)	C51	C50	C49	120.4(7)
C29	C28	C22	124.2(4)	C51	C52	C53	120.5(8)
C22	C28	P3	127.1(3)	C16	N1	C20	117.4(4)
C13	C14	Mn2	70.3(2)	C39	N3	C43	117.6(4)
C13	C14	C15	112.2(3)	C23	N2	C27	117.4(5)
C13	C14	C57	122.7(4)	C41	C40	C39	118.6(5)
C15	C14	Mn2	72.3(2)	C20	C19	C18	118.9(5)
C15	C14	C57	124.9(4)	C25	C24	C23	118.8(6)

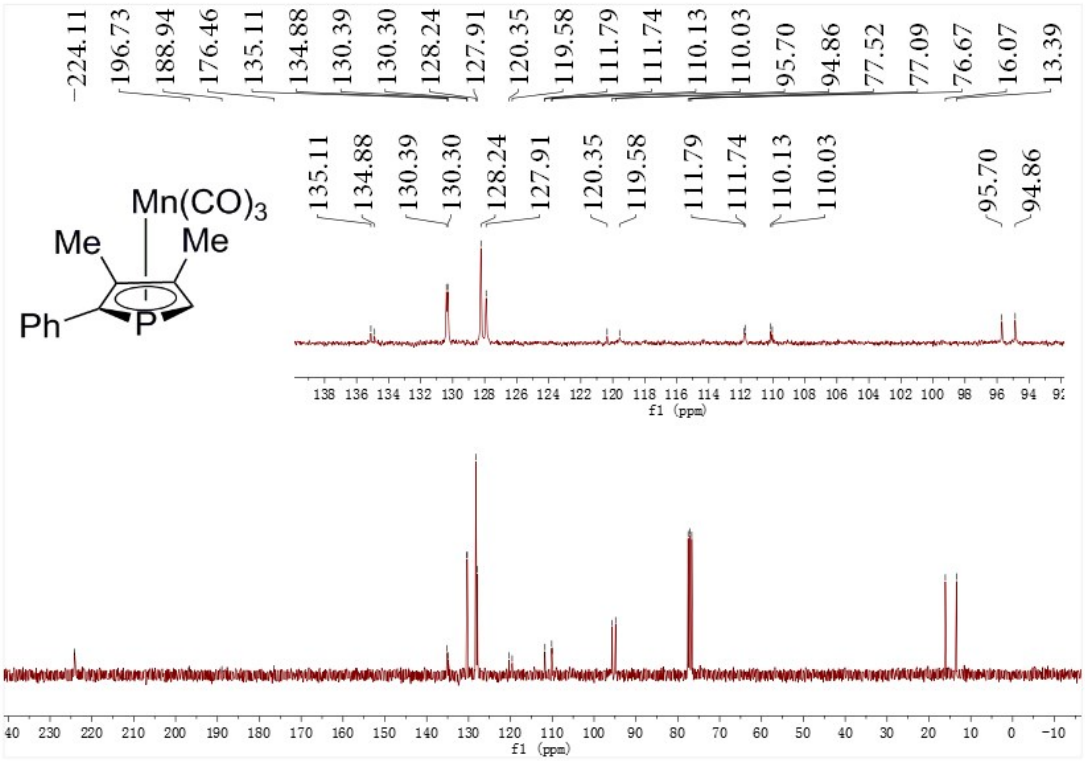
NMR spectrums



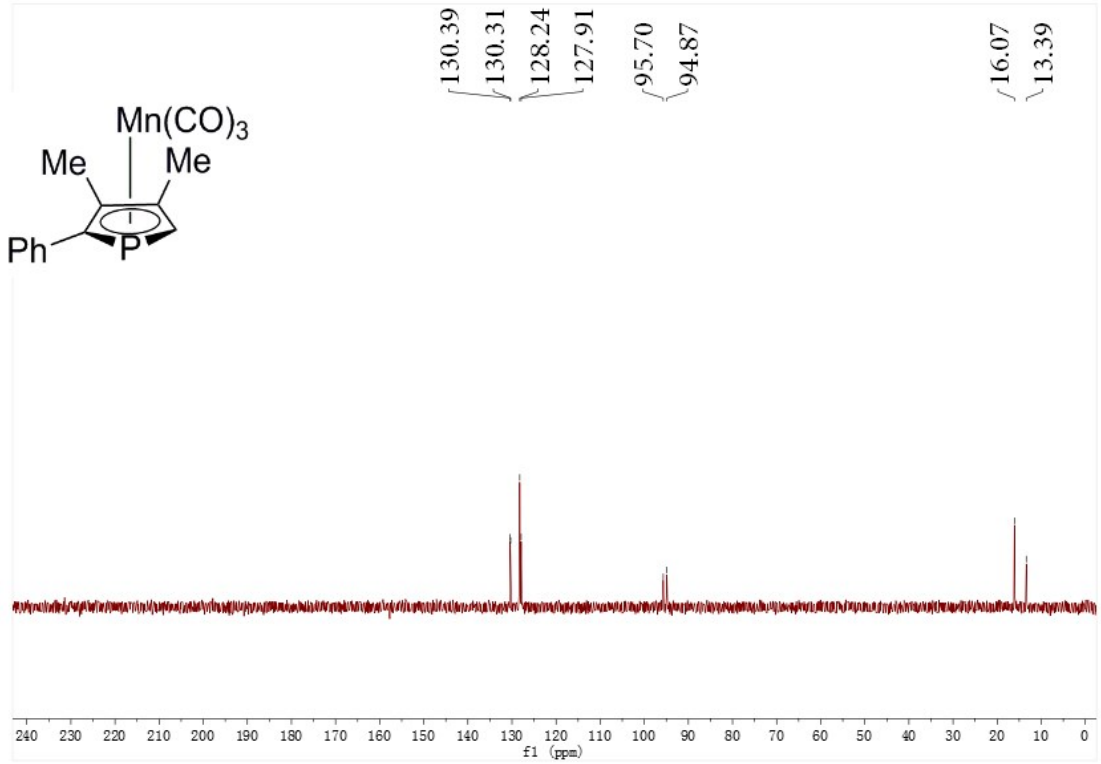
$^{31}P\{^{1}H\}$ ($CDCl_3$, 121 MHz) NMR of **3**



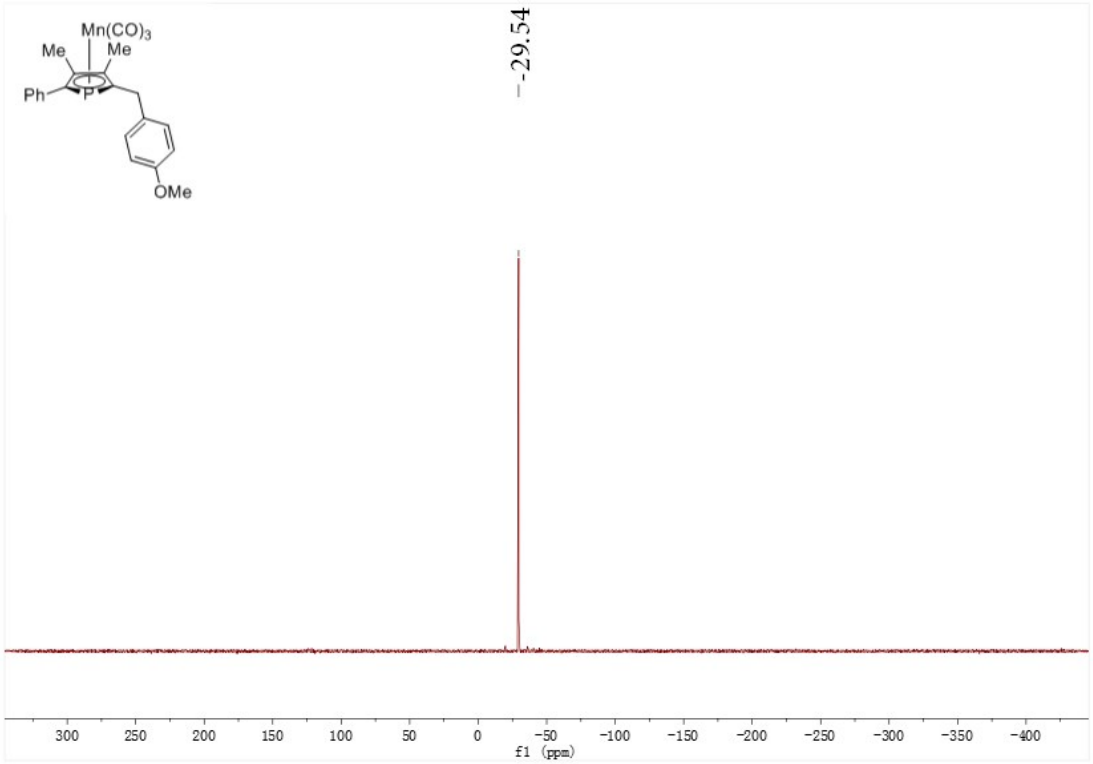
^{1}H ($CDCl_3$, 300 MHz) NMR of **3**



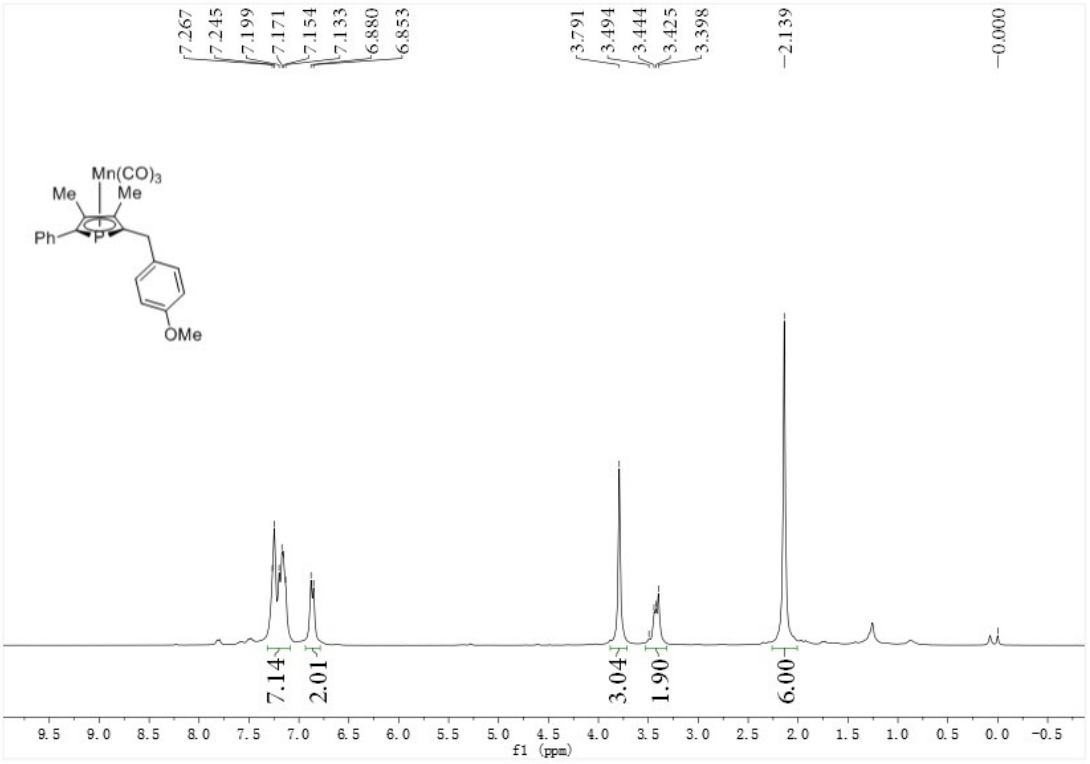
$^{13}C\{^{1}H\}$ ($CDCl_3$, 75 MHz) NMR of **3**



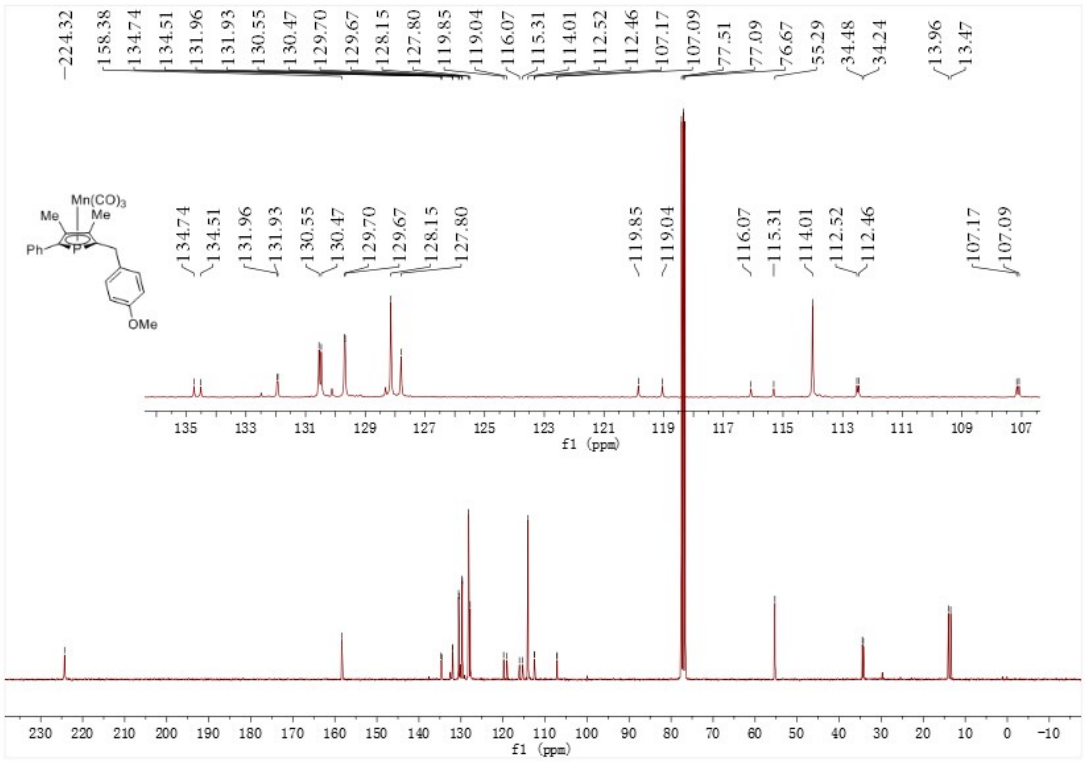
Dept135 ($CDCl_3$, 75 MHz) NMR of Complex **3**



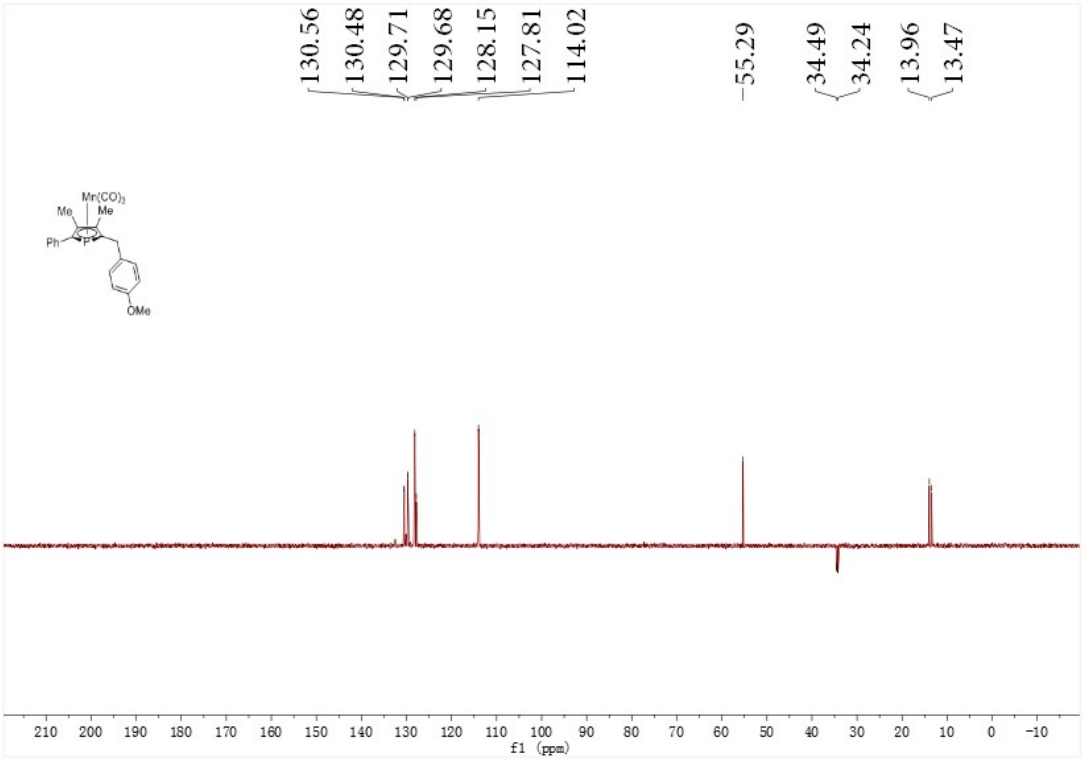
^{31}P {^{1}H} ($CDCl_3$, 121 MHz) NMR of **4a**



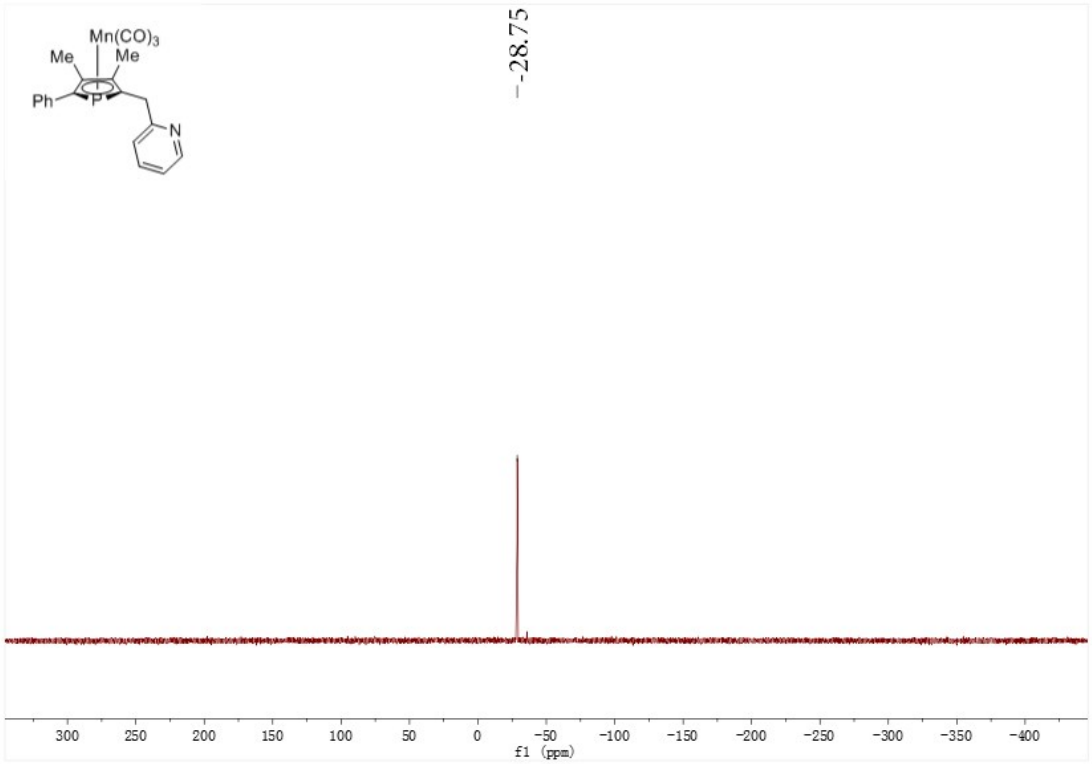
^{1}H ($CDCl_3$, 300 MHz) NMR of **4a**



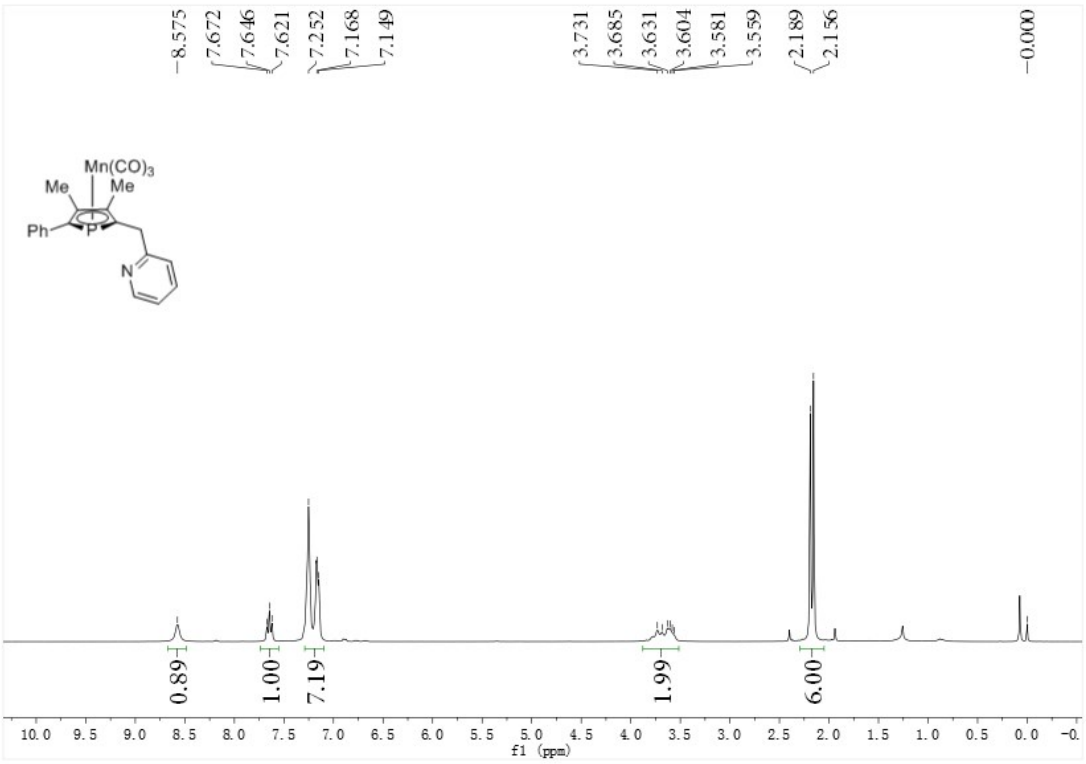
$^{13}C\{^{1}H\}$ ($CDCl_3$, 75 MHz) NMR of **4a**



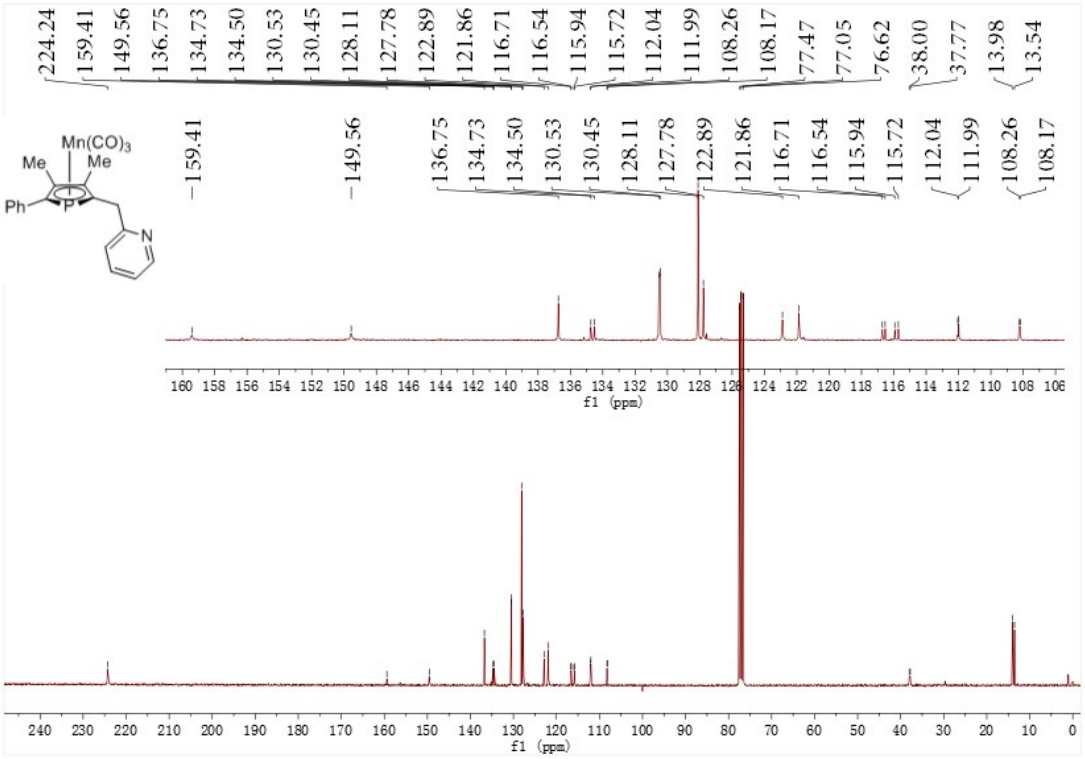
Dept135 ($CDCl_3$, 75 MHz) NMR of **4a**



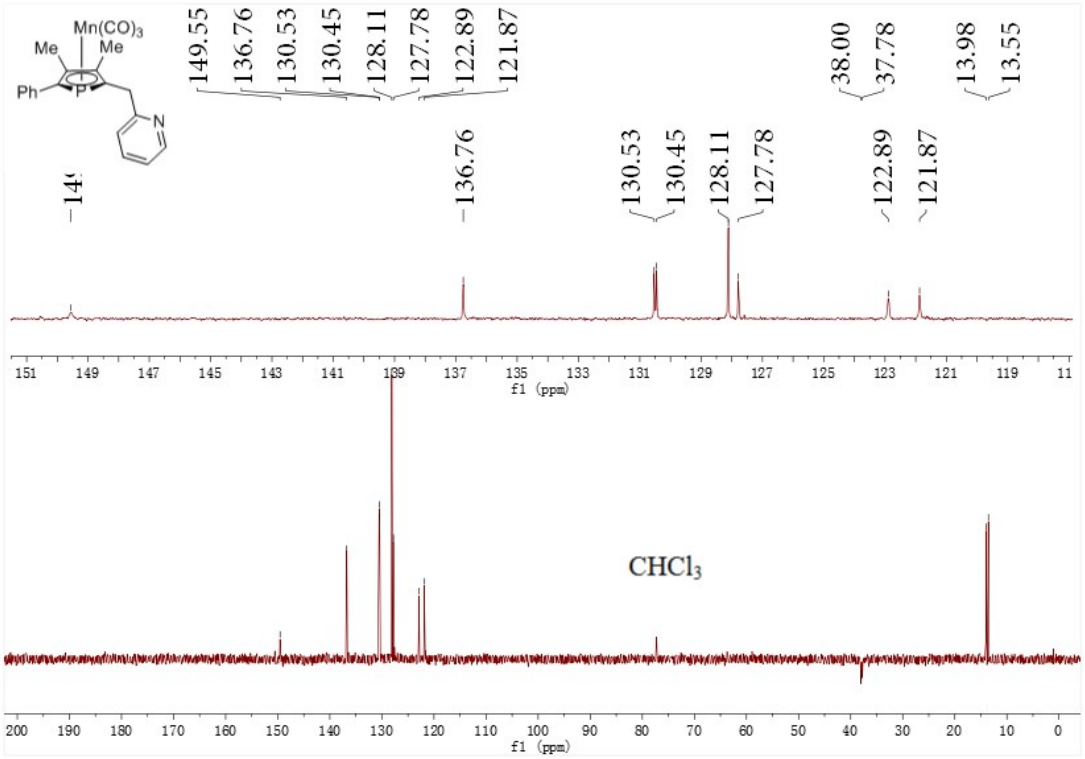
^{31}P {^{1}H} ($CDCl_3$, 121 MHz) NMR of **4b**



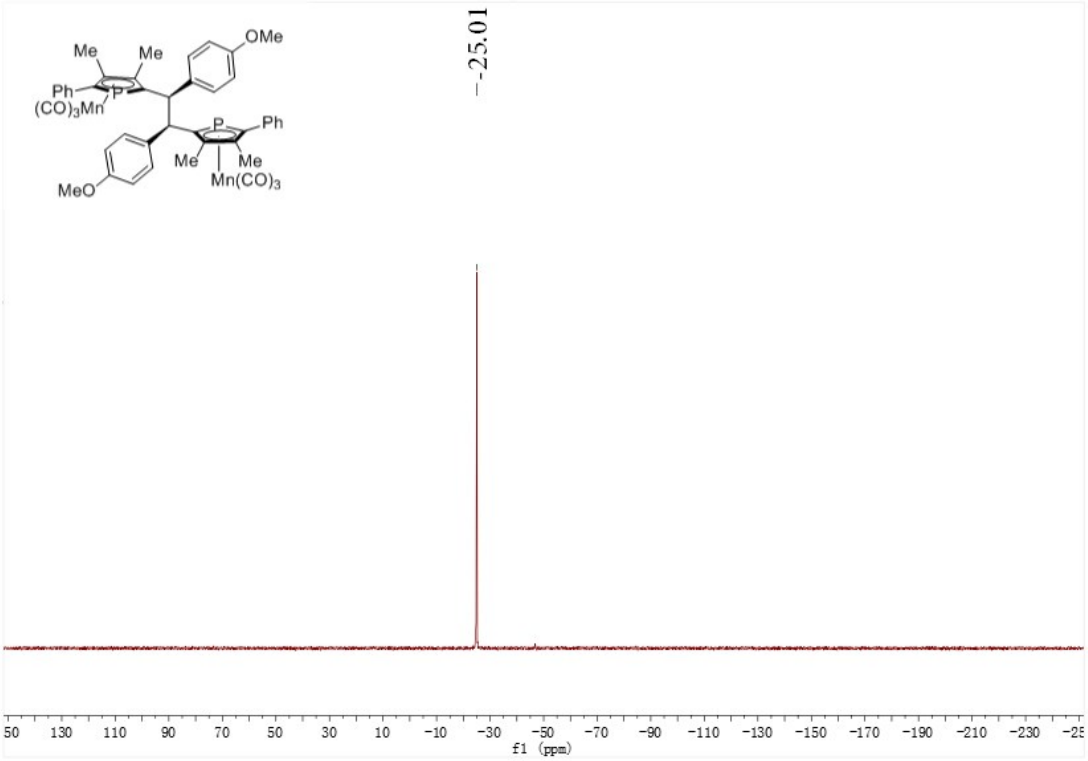
^{1}H ($CDCl_3$, 300 MHz) NMR of **4b**



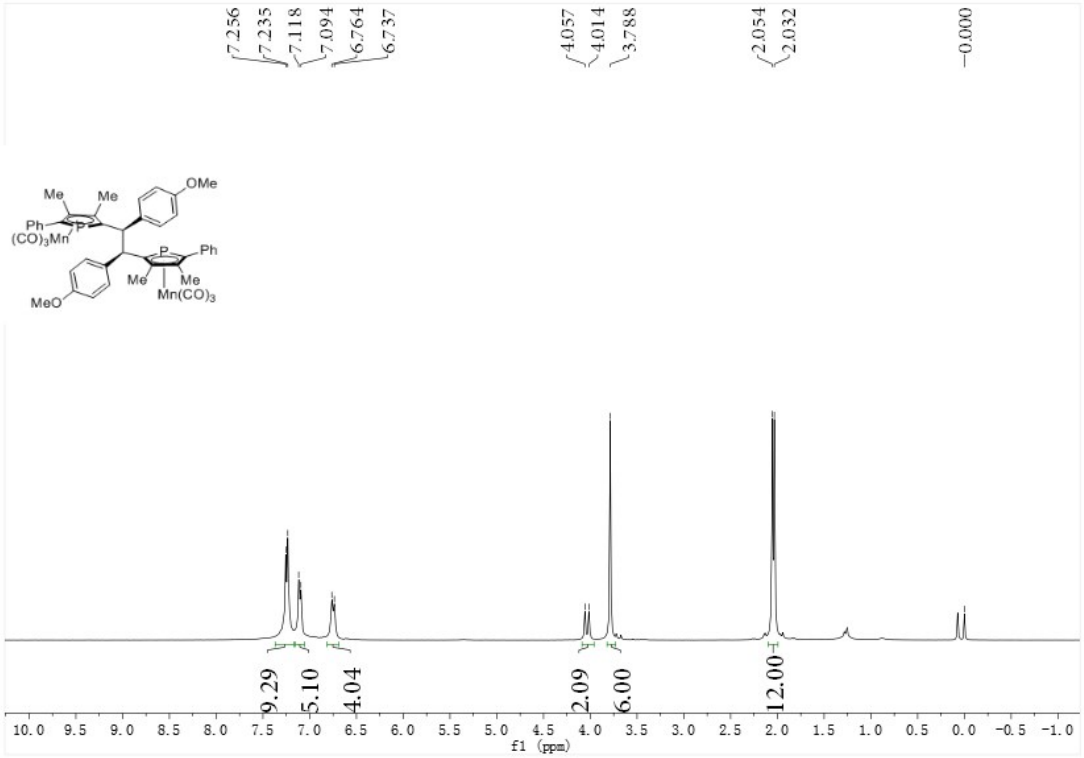
$^{13}C\{^{1}H\}$ ($CDCl_3$, 75 MHz) NMR of **4b**



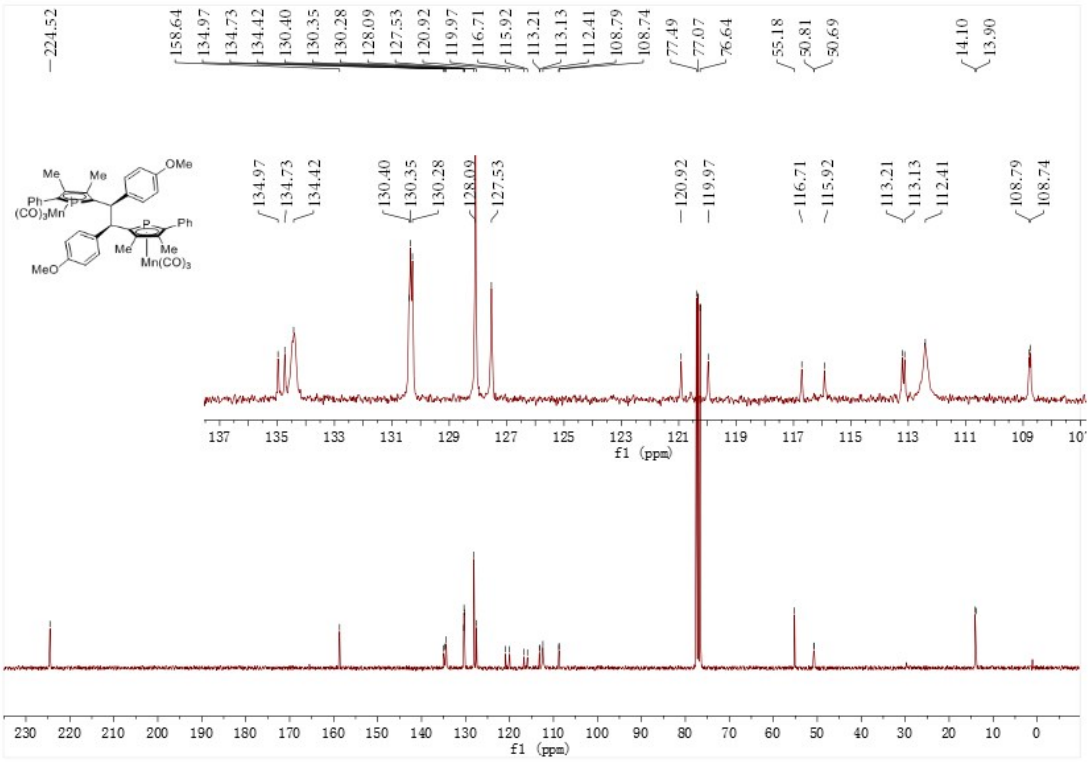
Dept135 ($CDCl_3$, 75 MHz) NMR of **4b**



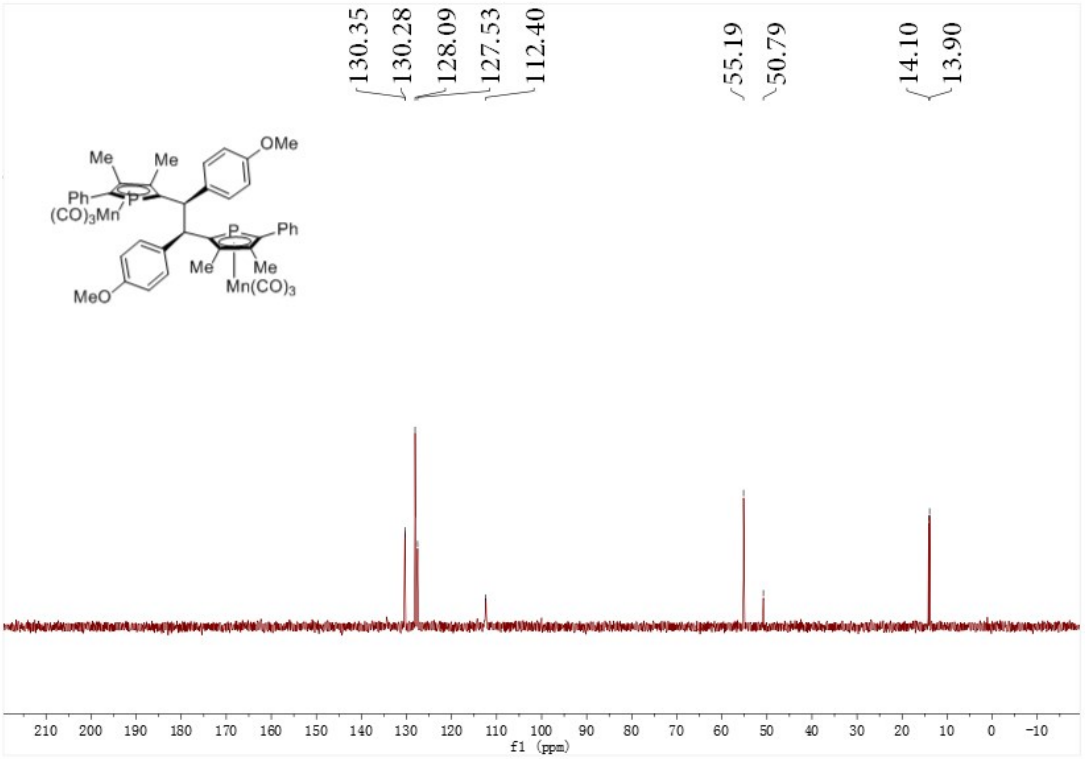
^{31}P {^{1}H} ($CDCl_3$, 121 MHz) NMR of **5a**



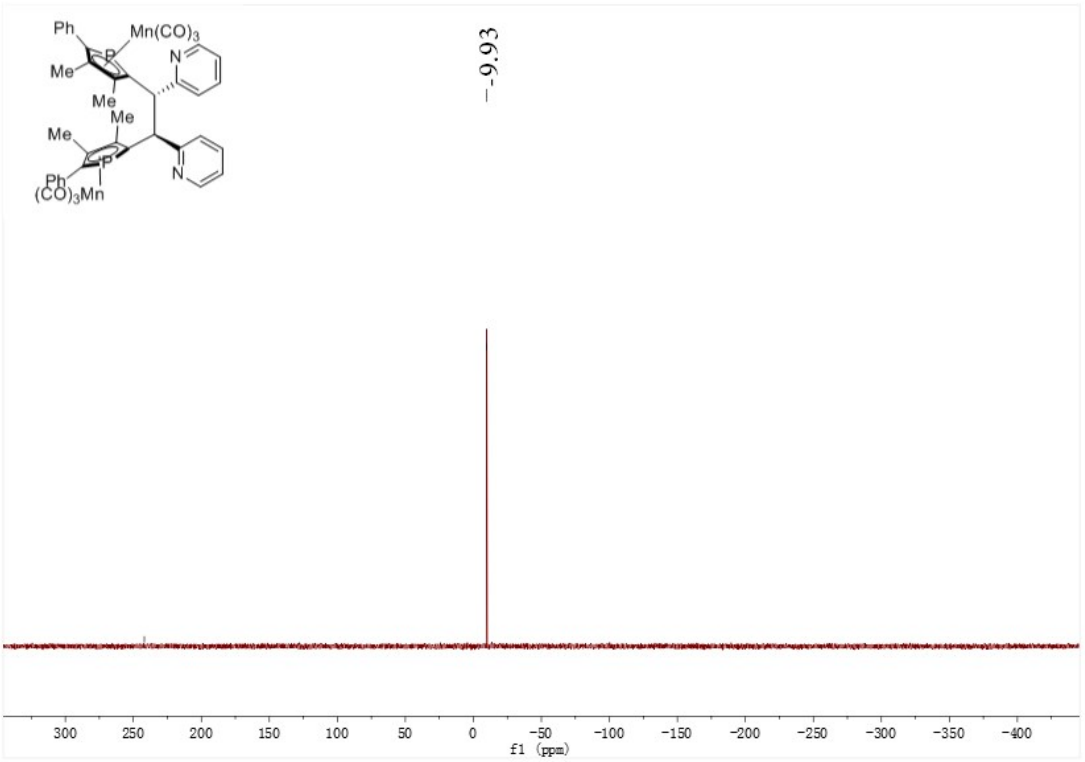
^{1}H ($CDCl_3$, 300 MHz) NMR of **5a**



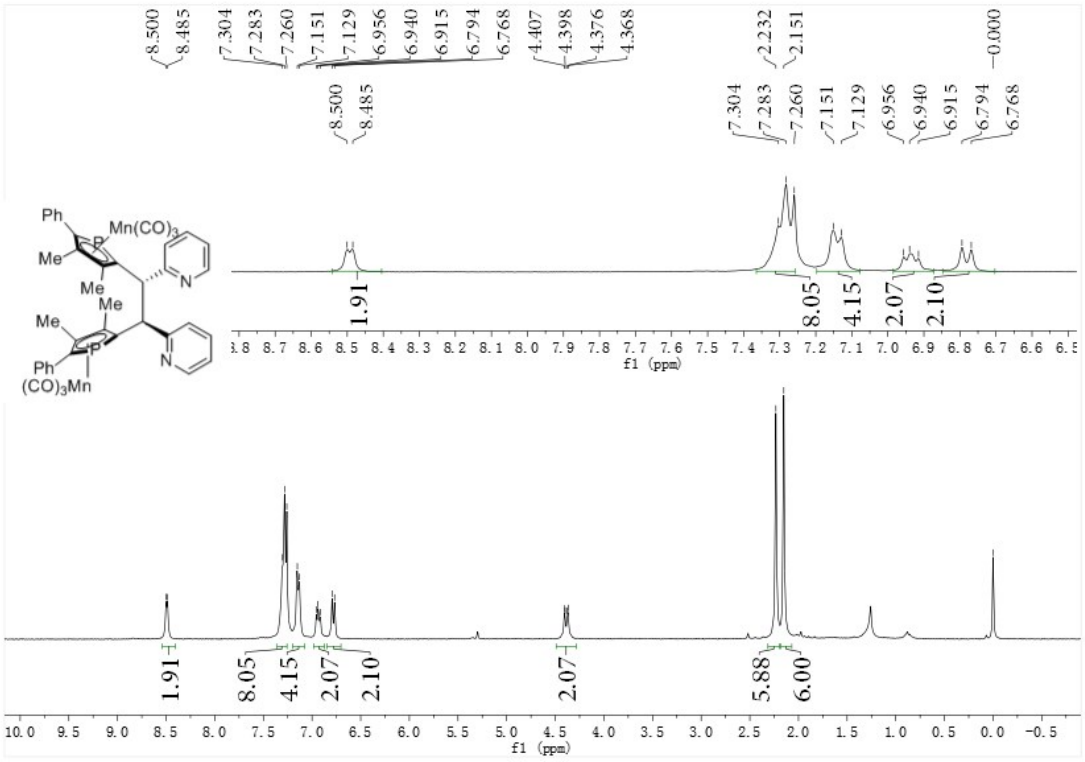
$^{13}C\{^{1}H\}$ ($CDCl_3$, 75 MHz) NMR of **5a**



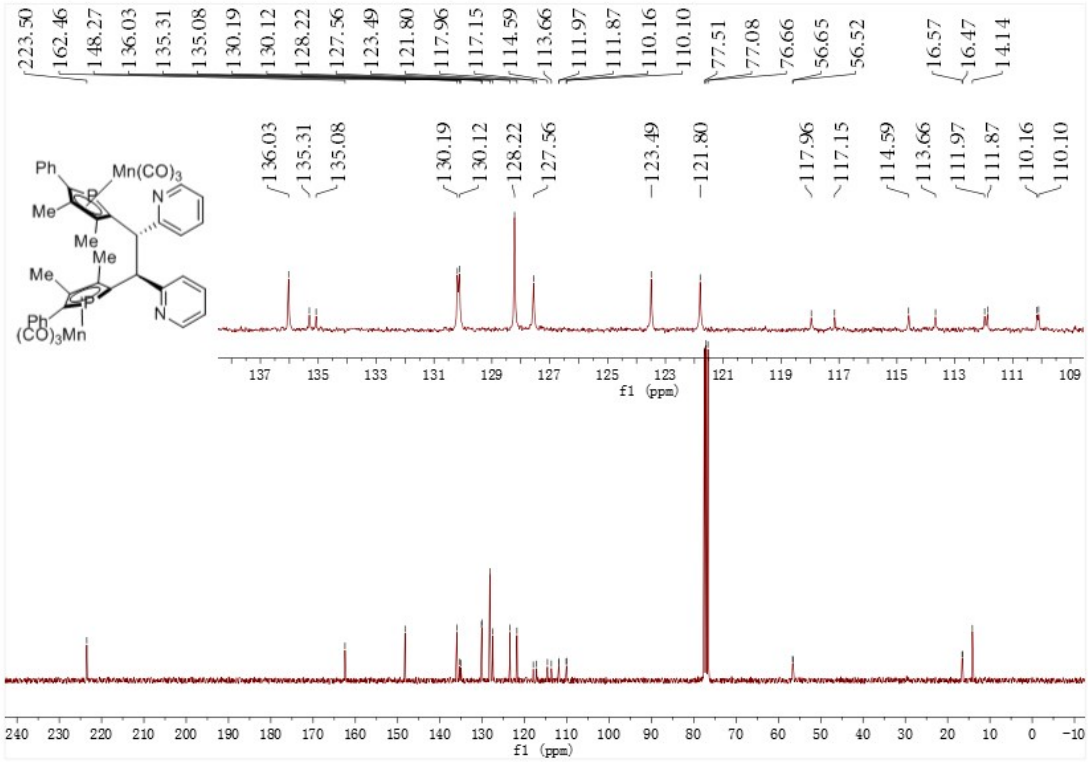
Dept135 ($CDCl_3$, 75 MHz) NMR of **5a**



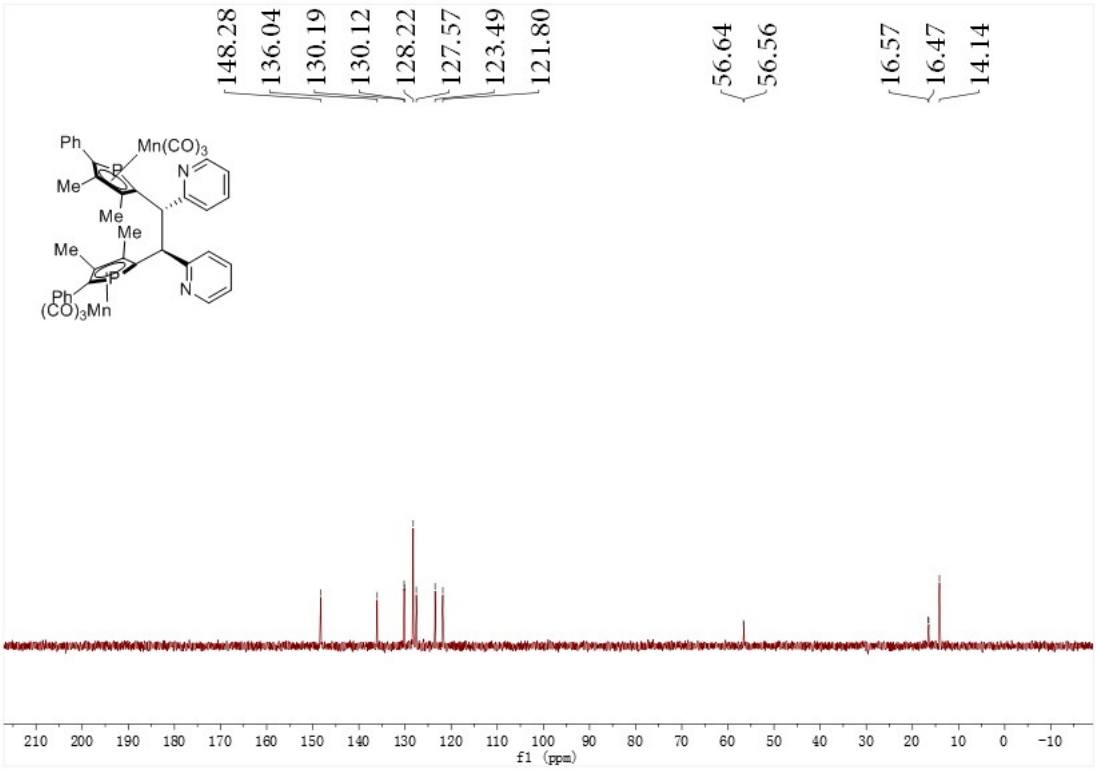
$^{31}P\{^{1}H\}$ ($CDCl_3$, 121 MHz) NMR of **5b**



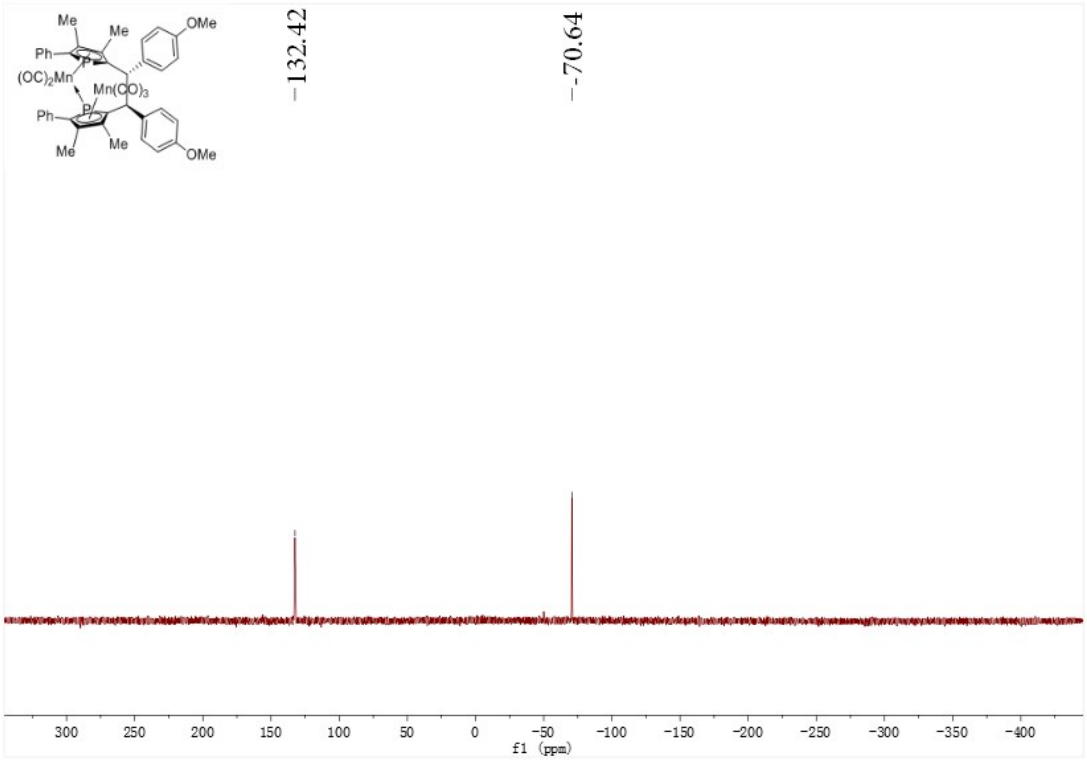
^{1}H ($CDCl_3$, 300 MHz) NMR of **5b**



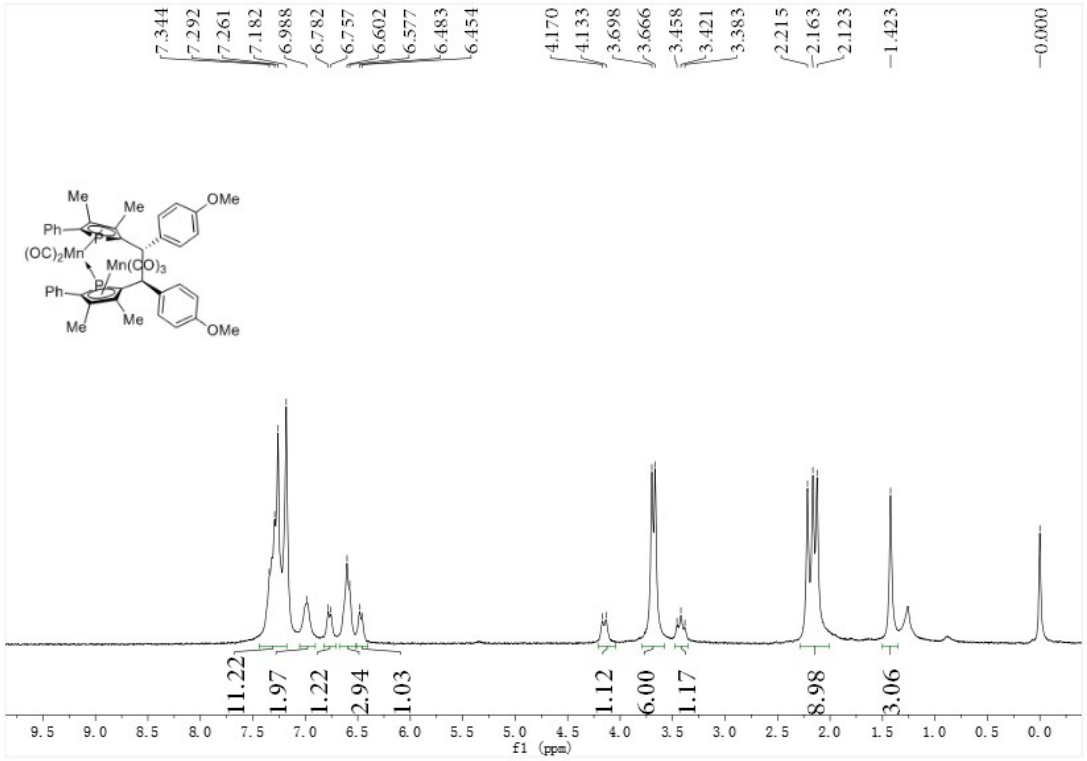
$^{13}C\{^{1}H\}$ ($CDCl_3$, 75 MHz) NMR of **5b**



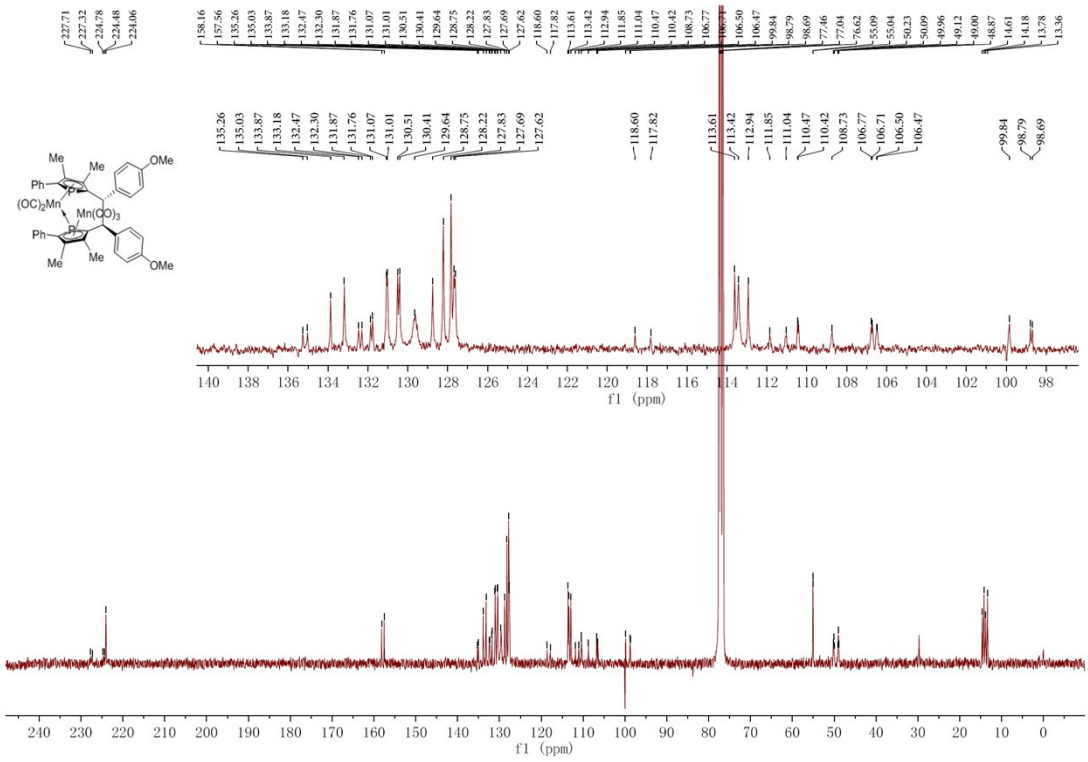
Dept135 ($CDCl_3$, 75 MHz) NMR of **5b**



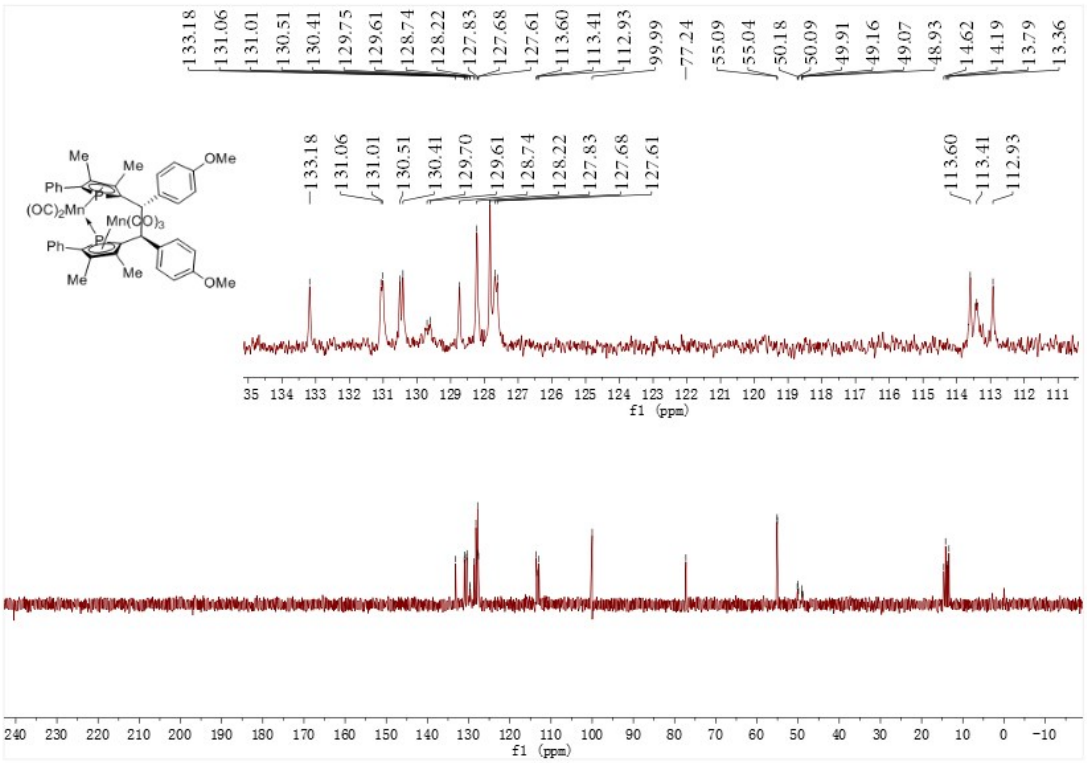
^{31}P {^{1}H} ($CDCl_3$, 121 MHz) NMR of **7a**



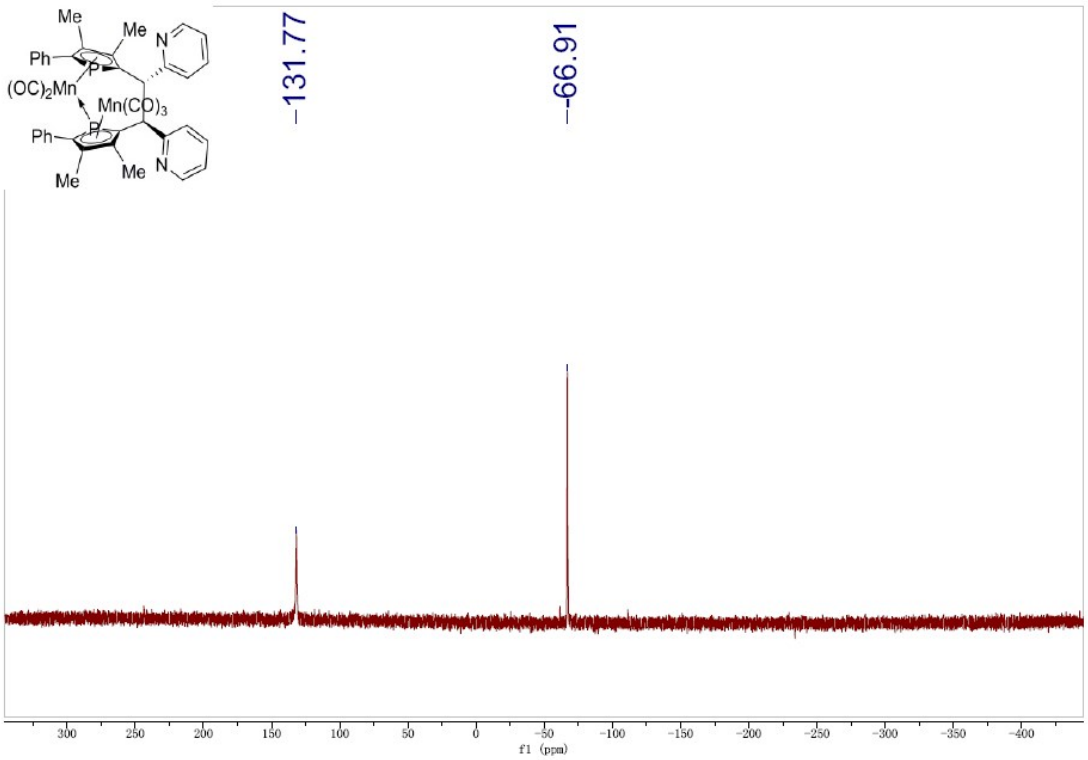
^{1}H ($CDCl_3$, 300 MHz) NMR of **7a**



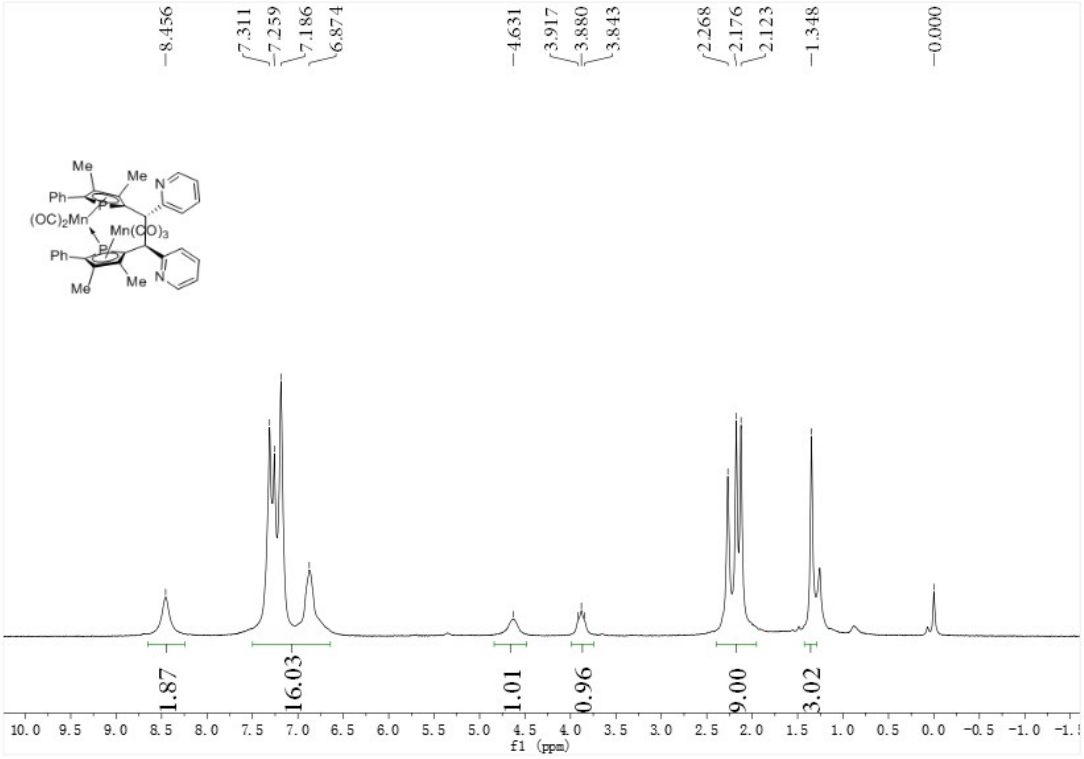
$^{13}C\{^{1}H\}$ ($CDCl_3$, 75 MHz) NMR of Complex **7a**



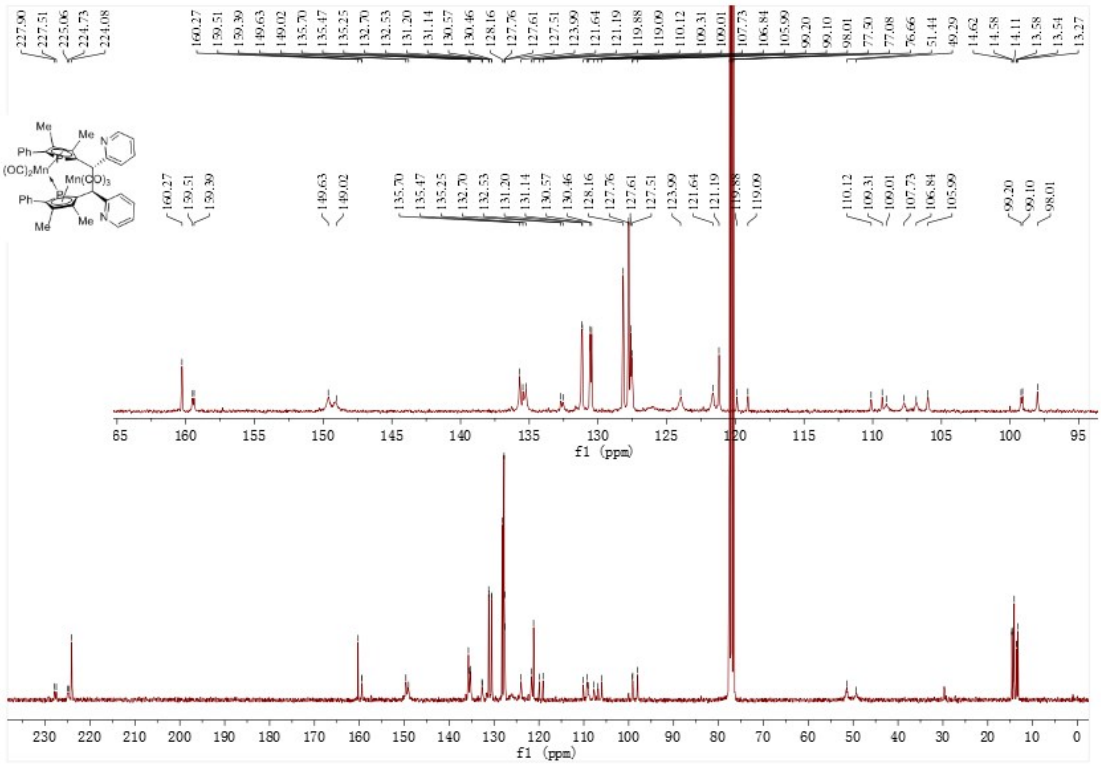
Dept135 ($CDCl_3$, 75 MHz) NMR of **7a**



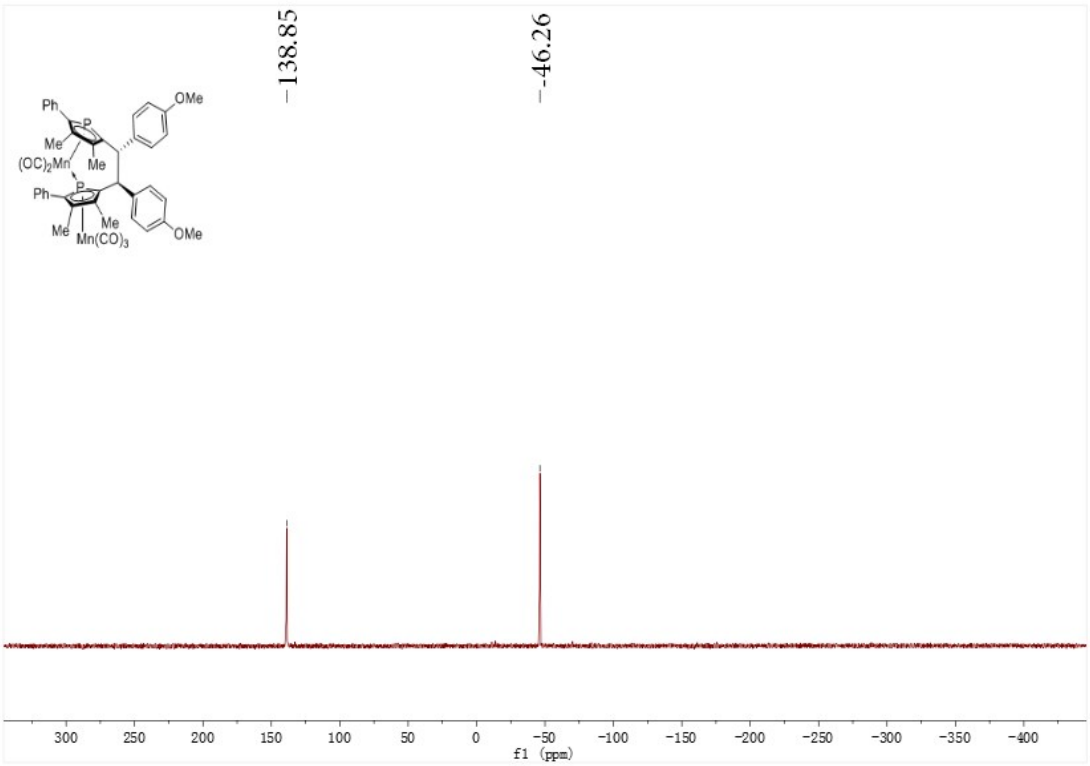
^{31}P {^{1}H} ($CDCl_3$, 121 MHz) NMR of **7b**



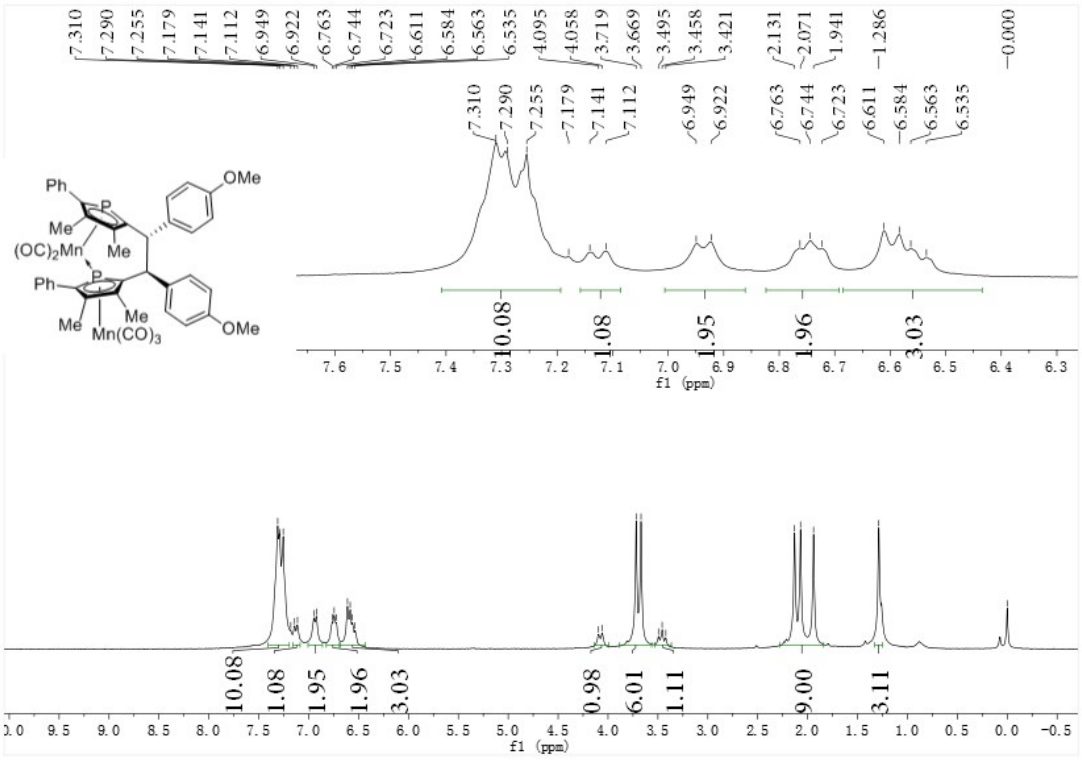
^{1}H ($CDCl_3$, 300 MHz) NMR of **7b**



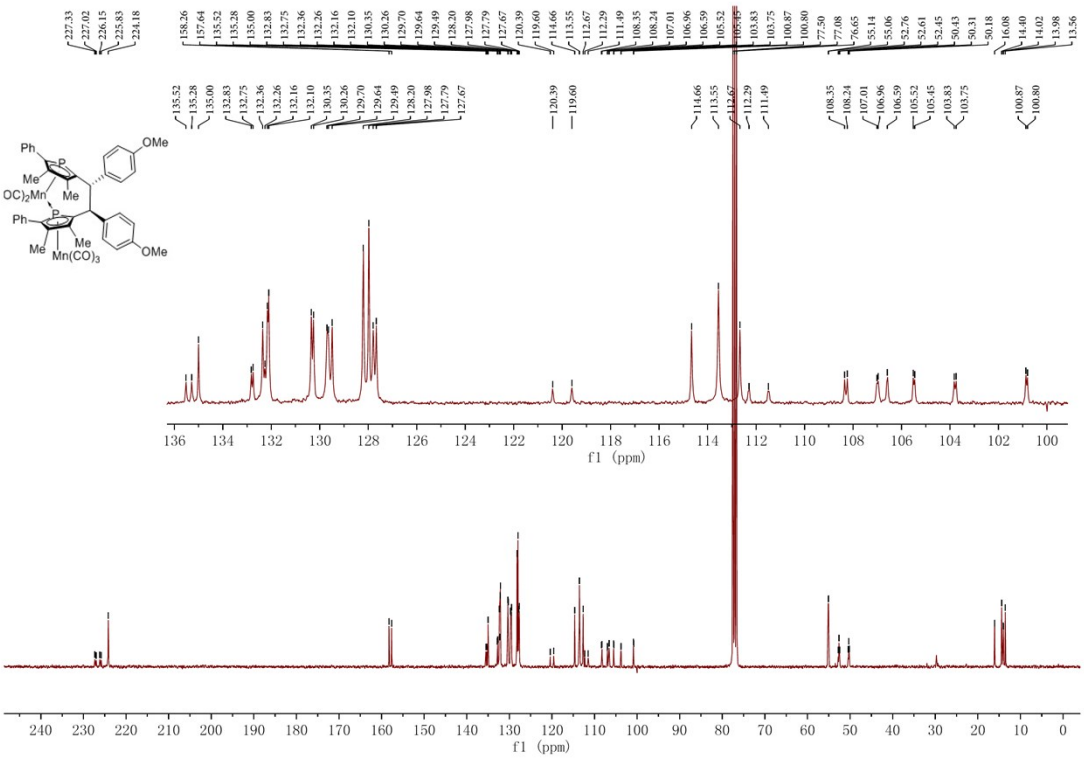
$^{13}C\{^{1}H\}$ ($CDCl_3$, 75 MHz) NMR of **7b**



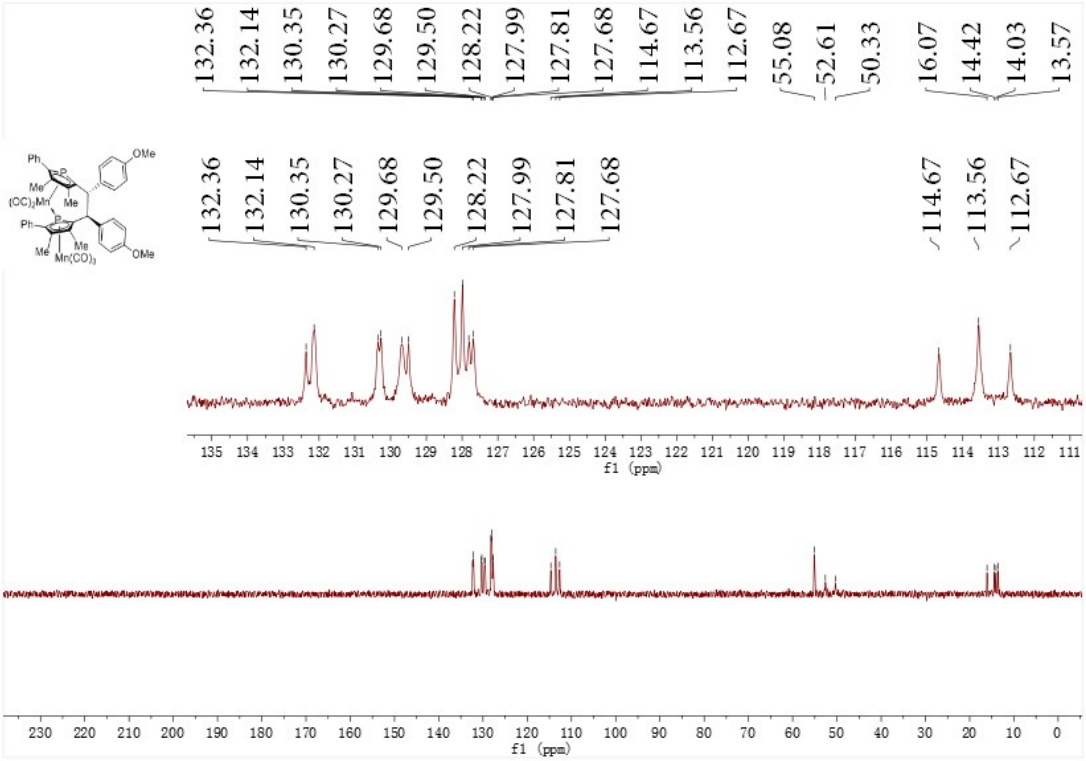
$^{31}P\ \{^{1}H\}$ ($CDCl_3$, 121 MHz) NMR of **8a**



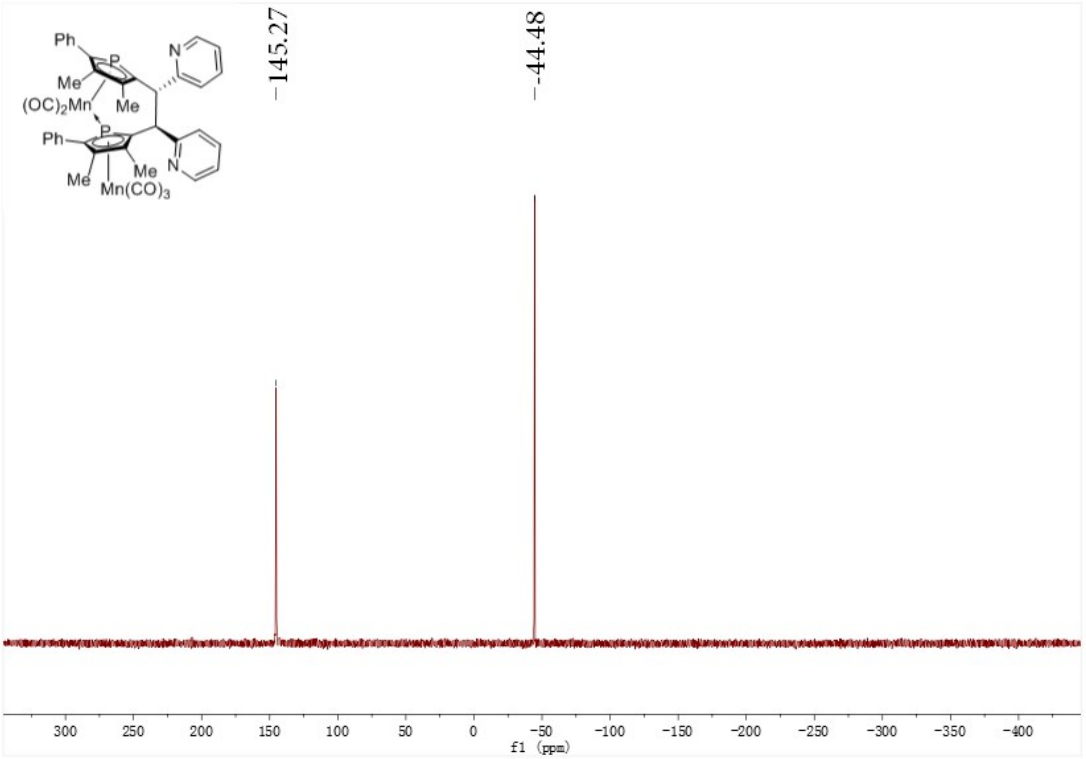
^{1}H ($CDCl_3$, 300 MHz) NMR of **8a**



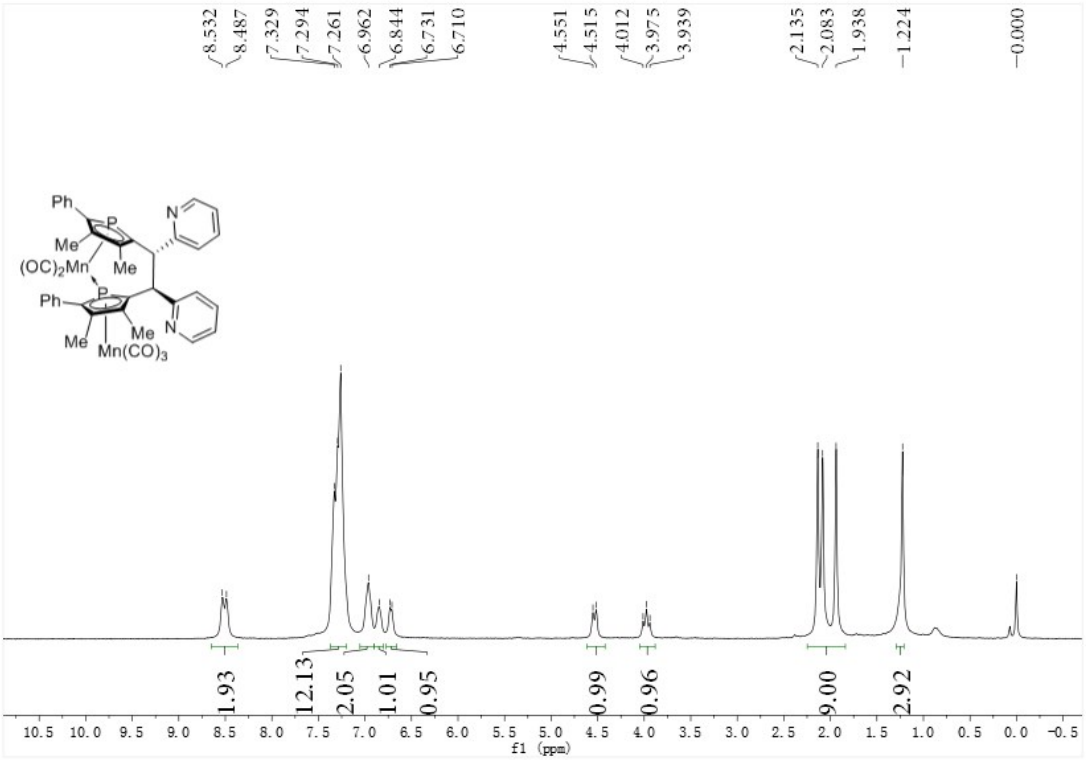
$^{13}C\{^{1}H\}$ ($CDCl_3$, 75 MHz) NMR of **8a**



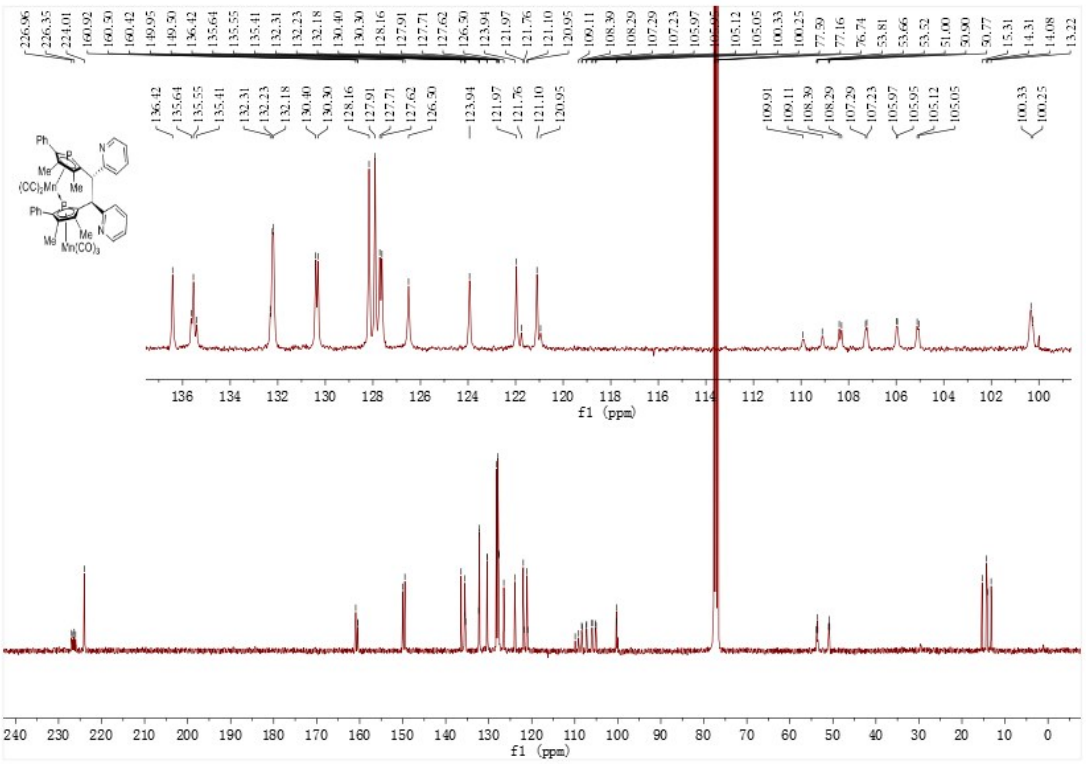
Dept135 ($CDCl_3$, 75 MHz) NMR of **8a**



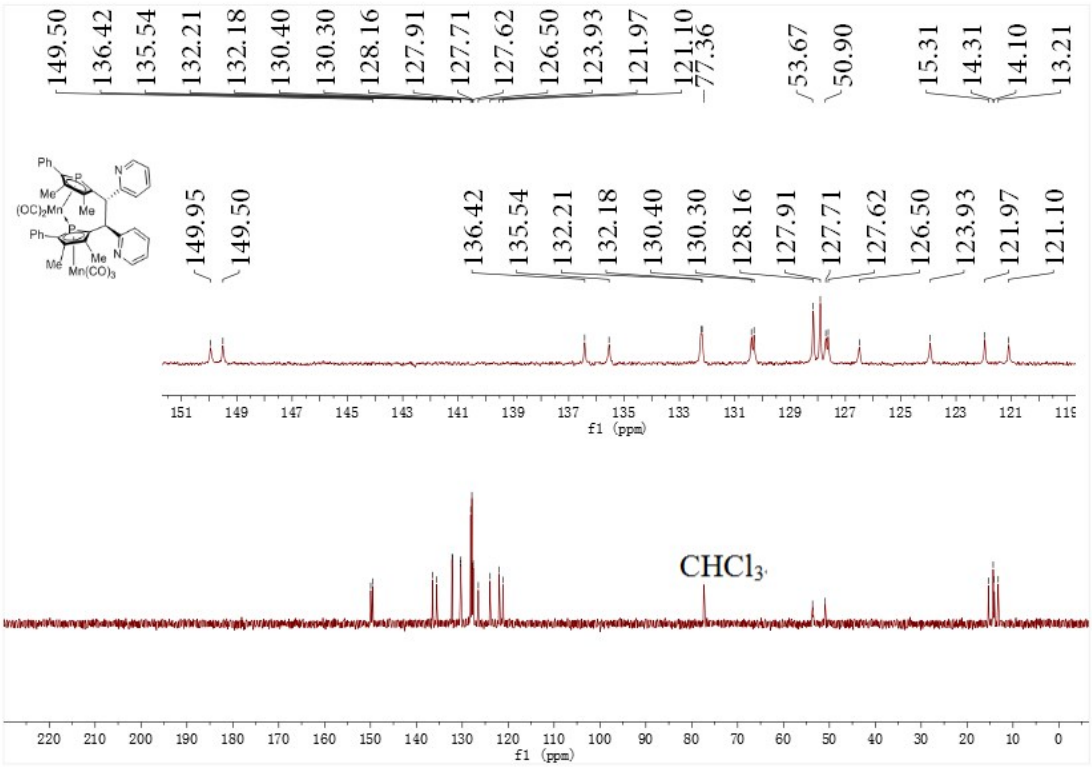
^{31}P ($CDCl_3$, 121 MHz) NMR of **8b**



^{1}H ($CDCl_3$, 300 MHz) NMR of **8b**



$^{13}C\{^{1}H\}$ ($CDCl_3$, 75 MHz) NMR of **8b**



Dept135 ($CDCl_3$, 75 MHz) NMR of **8b**