Supporting Information for:

CO_2 Activation by Manganese Pincer Complexes Through Different Modes of Metal-Ligand Cooperation

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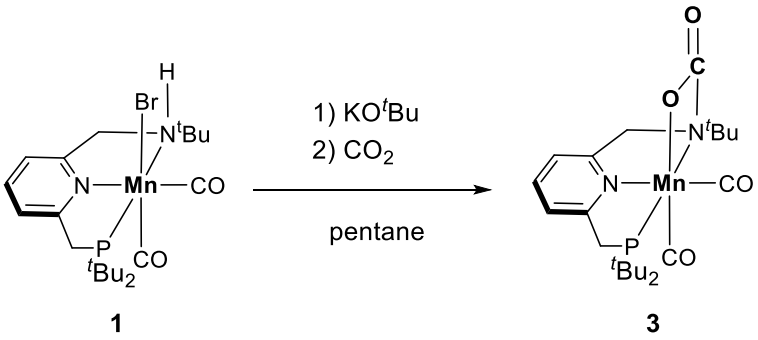
1. General information

All experiments were carried out in M-BRAUN Unilab 1200/780 glovebox under inert atmosphere of purified nitrogen or using standard Schlenk techniques. DCM, Et_2O and *n*-pentane were refluxed over sodium/benzophenone, distilled under argon atmosphere, and stored over 4 Å molecular sieves (MS).[1] Deuterated solvents were degassed with argon and kept in the glovebox over 4 Å MS. The [Mn(PNNH)$(CO)_2$(Br)] (**1**) and [Mn(PNN)$(CO)_2$(Br)] (**4**) were prepared according to the literature procedures described earlier.[2] ^{1}H NMR, $^{13}C\{^1H\}$ NMR, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AMX-500 NMR and AMX-400 NMR spectrometers and reported in ppm (δ). ^{1}H NMR, $^{13}C\{^1H\}$ NMR, and $^{13}C\{^1H\}$-DEPTQ NMR chemical shifts are referenced with respect to tetramethylsilane, while $^{31}P\{^1H\}$ NMR chemical shifts are reported referenced to an external 85% solution of phosphoric acid in D_2O. NMR spectroscopy abbreviations: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

2. Synthesis and characterization of new complexes

(i)**[Mn(PNN-COO)$(CO)_2$] (3)**



1 **3**

[Mn(PNNH)$(CO)_2$(Br)] (**1**) (200 mg, 0.39 mmol) and KO^{t}Bu (52 mg, 0.47 mmol) were suspended in 20 mL of pentane. The mixture was stirred at room temperature for 1 h. During the reaction time the original colorless suspension becomes a dark-blue solution. After filtration through a Teflon syringe filter (0.2 μm), the pentane solution was transferred into and Schlenk tube fitted with Young's cap. The Schlenk tube was evacuated twice by freeze-pump-thaw cycles and then filled with CO_2 (1 bar). This resulted in an immediate color change from dark blue to yellow which was followed by precipitation of a yellow powder. The reaction was kept under strong stirring for

an hour at room temperature. The yellow precipitate was decanted, washed with diethyl ether (10 mL) and dried *in vacuo* (152 mg, 82% yield). Clear Pale yellow crystals suitable for X-ray analysis were obtained from a CH_2Cl_2 concentrated solution of compound **3** layered with pentane and kept under nitrogen at room temperature for 24 hours.

$^{31}P\{^{1}H\}$ NMR (202.44 MHz, CD_2Cl_2, 25 °C): δ 117.6 (s).

$^{1}H\{^{31}P\}$ NMR (500.08 MHz, CD_2Cl_2, 25 °C): δ 1.30 (s, 9H, $(CH_3)_3CP$), 1.34 (s, 9H, $(CH_3)_3CP$), 1.55 (s, 9H, $(CH_3)_3CN$), 3.32 (d, $^{2}J_{HH}$ = 17.1 Hz, 1H, PCH*H*), 3.55 (d, $^{2}J_{HH}$ = 17.1 Hz, 1H, PC*H*H), 4.21 (d, $^{2}J_{HH}$ = 14.7 Hz, 1H, NCH*H*), 4.54 (d, $^{2}J_{HH}$ = 15.2 Hz, 1H, NCH*H*), 7.35 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H, $CH_{pyri(3)}$), 7.45 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H, $CH_{pyri(5)}$), 7.73 (t, $^{3}J_{HH}$ = 7.9 Hz, 1H, $CH_{pyri(4)}$).

^{1}H NMR (500.08 MHz, CD_2Cl_2, 25 °C): δ 1.30 (d, $^{3}J_{PH}$ = 12.8 Hz, 9H, $(CH_3)_3CP$), 1.34 (d, $^{3}J_{PH}$ = 13.2 Hz, 9H, $(CH_3)_3CP$), 1.55 (s, 9H, $(CH_3)_3CN$), 3.32 (dd, $^{2}J_{HH}$ = 17.1 Hz, $^{2}J_{PH}$ = 9.7 Hz, 1H, PCH*H*), 3.54 (dd, $^{2}J_{HH}$ = 17.1 Hz, $^{2}J_{PH}$ = 9.7 Hz, 1H, PC*H*H), 4.21 (d, $^{2}J_{HH}$ = 15.1 Hz, 1H, NCH*H*), 4.54 (d, $^{2}J_{HH}$ = 15.1 Hz, 1H, NCH*H*), 7.35 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H, $CH_{pyri(3)}$), 7.45 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H, $CH_{pyri(5)}$), 7.73 (t, $^{3}J_{HH}$ = 7.9 Hz, 1H, $CH_{pyri(4)}$).

$^{13}C\{^{1}H\}$ QDEPT NMR (125.75 MHz, CD_2Cl_2, 25 °C): δ 27.0 (s, $(CH_3)_3CN$), 28.9 (d,$^{2}J_{PC}$ = 3.7 Hz, $(CH_3)_3CP$), 29.3 (d,$^{2}J_{PC}$ = 3.7 Hz, $(CH_3)_3CP$), 35.5 (d, $^{1}J_{PC}$ = 12.0 Hz, CH_2P), 36.6 (d, $^{1}J_{PC}$ = 9.6 Hz, $(CH_3)_3CP$), 36.9 (d, $^{1}J_{PC}$ = 19.8 Hz, $(CH_3)_3CP$), 57.7 (s, CH_2N), 59.4 (s, $(CH_3)_3CN$), 119.6 (s, $CH_{pyri(5)}$), 121.1 (d, $^{3}J_{PC}$ = 8.2 Hz, $CH_{pyri(3)}$), 137.5 (s, $CH_{pyri(4)}$), 160.7 (d, $^{3}J_{PC}$ = 3.0 Hz, $CH_{pyri(6)}$), 161.2 (s, Mn–O–*C*=O), 162.7 (d, $^{2}J_{PC}$ = 7.0 Hz, $CH_{pyri(2)}$), 231.5 (bs, Mn-*C*O), 234.5 (bs, Mn-*C*O).

IR (NaCl thin film, cm^{-1}): 1917.7 (ν_{asym}, C≡O), 1824.0 (ν_{sym}, C≡O), 1716.3 (COO).

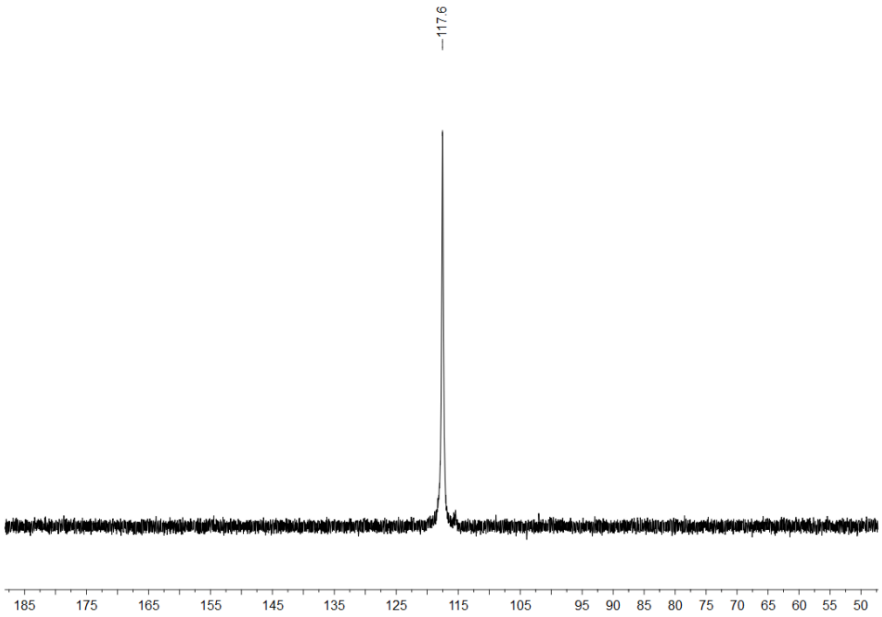


Figure S1. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 298 K) spectrum of [Mn(PNN-COO)$(CO)_2$] (**3**).

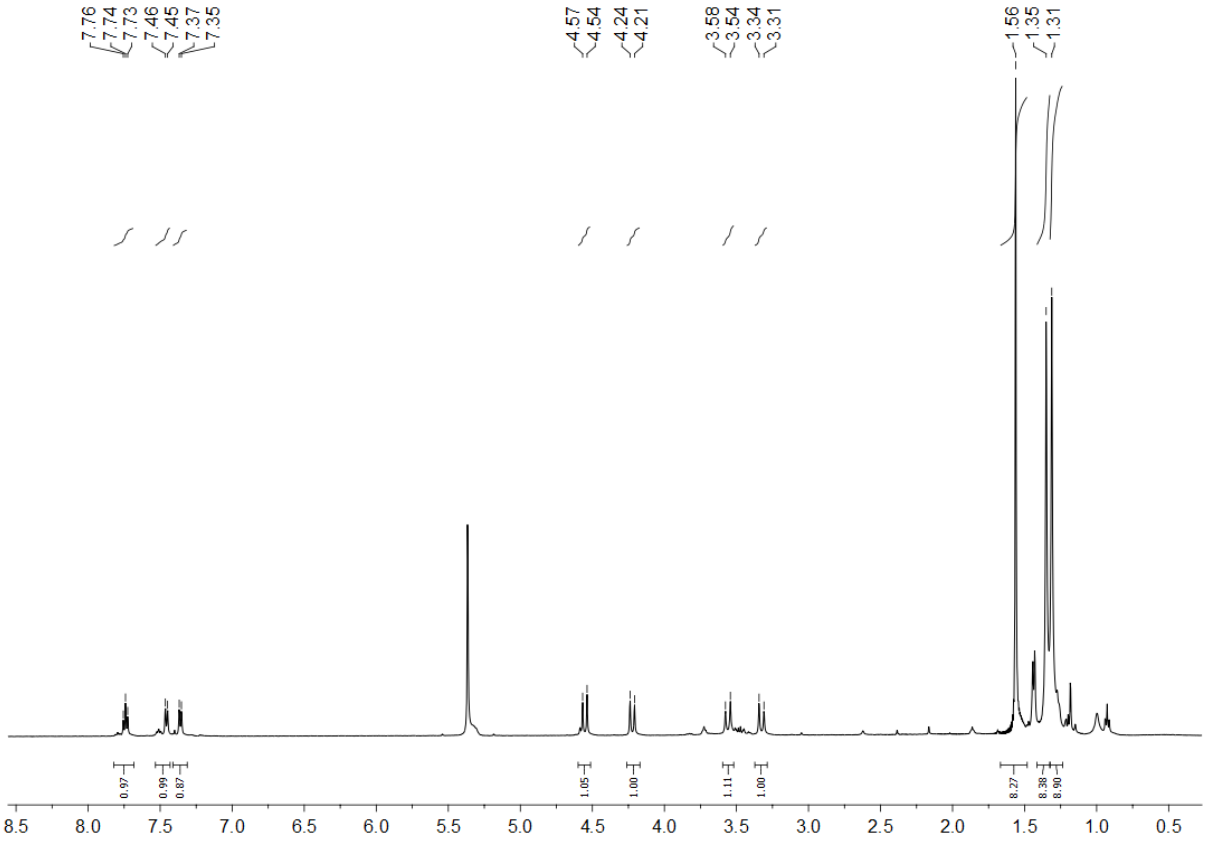


Figure S2. $^{1}H\{^{31}P\}$ NMR (CD_2Cl_2, 298 K) spectrum of [Mn(PNN-COO)$(CO)_2$] (**3**).

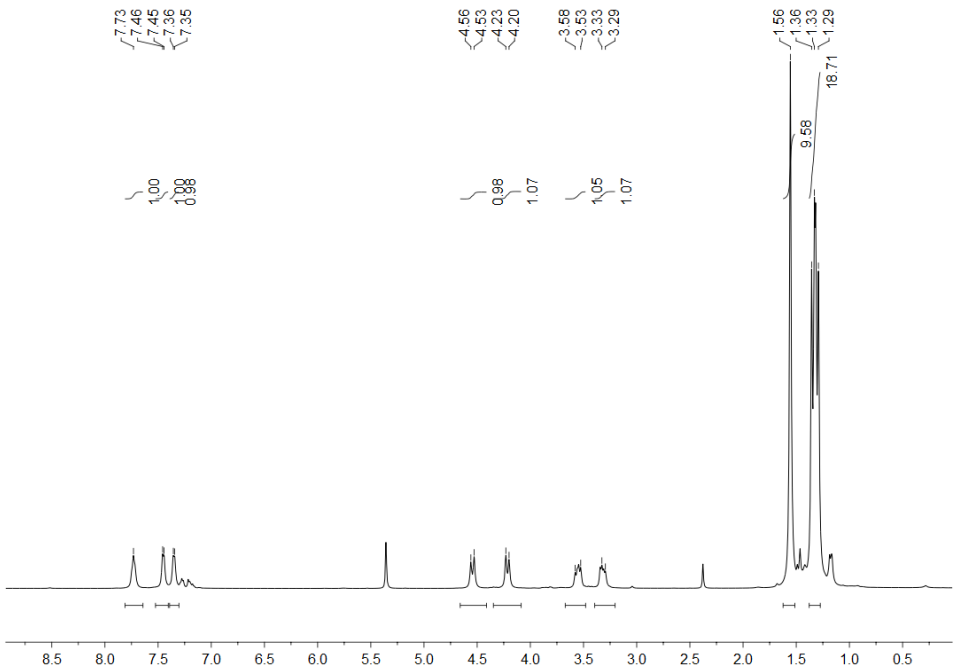


Figure S3. ^{1}H NMR (CD_2Cl_2, 298 K) spectrum of [Mn(PNN-COO)$(CO)_2$] (**3**).

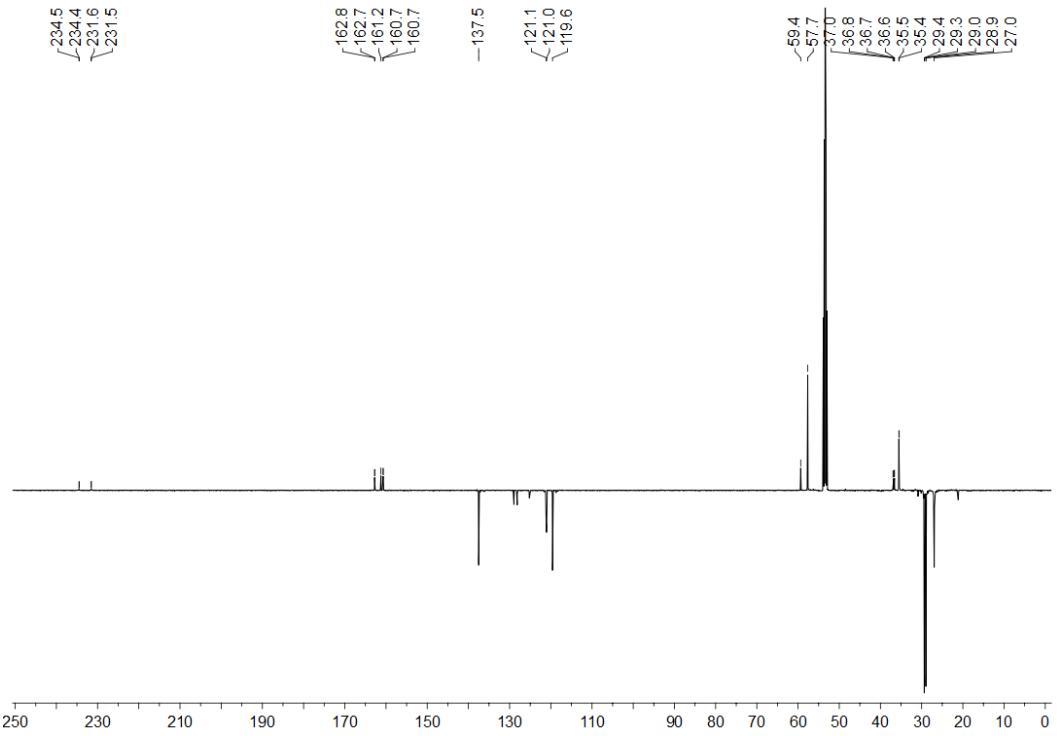


Figure S4. $^{13}C\{^{1}H\}$ QDEPT NMR (CD_2Cl_2, 298 K) spectrum of [Mn(PNN-COO)$(CO)_2$] (**3**).

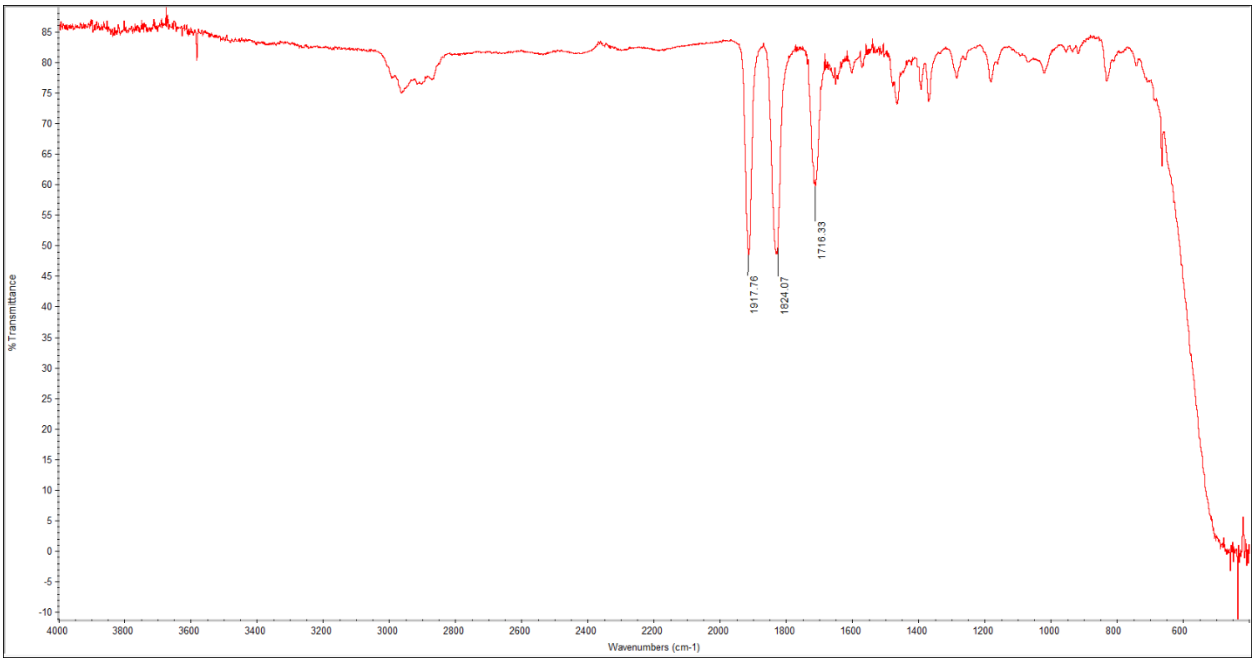
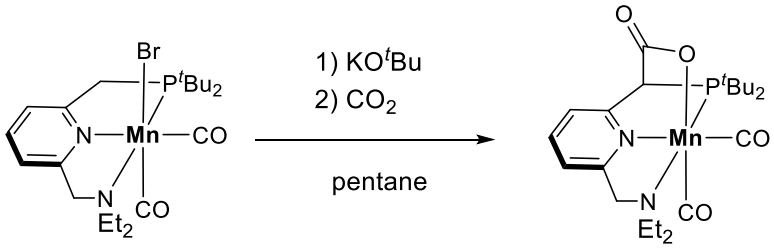


Figure S5. IR (NaCl thin film) spectrum of [Mn(PNN-COO)(CO)$_2$] (**3**).

(ii) [Mn(PNN-COO)(CO)$_2$] (3')



1' **3'**

[Mn(PNN)(CO)$_2$(Br)] (**1'**) (200 mg, 0.39 mmol) and KO^{t}Bu (52 mg, 0.47 mmol) were suspended in 20 mL of pentane. The mixture was stirred at room temperature for 1 h. During the reaction time the original colorless suspension becomes a dark-green solution. After filtration through a Teflon syringe filter (0.2 μm) the pentane solution was transferred into a Schlenk tube fitted with the Young's cap. The Schlenk tube was evacuated twice by freeze-pump-thaw cycles and then filled with CO_2 (1 bar). This resulted in an immediate color change from dark-green to orange which was followed by precipitation of an orange powder. The reaction was kept under strong stirring for an hour at room

temperature. The orange precipitate was decanted, washed with diethyl ether (10 mL) and dried *in vacuo* (132 mg, 78 % yield). Crystals suitable for X-ray analysis were obtained from a CH_2Cl_2 concentrated solution of compound **3'** layered with pentane and kept under nitrogen at -30ºC for 24 hours.

$^{31}P\{^{1}H\}$ NMR (162.08 MHz, $CDCl_3$, 25 °C): δ 143.2 (s).

$^{1}H\{^{31}P\}$ NMR (500.08 MHz, $CDCl_3$, 25 °C): δ 1.13 (m, 15H, apparent overlapped $N(CH_2C\mathit{H}_3)_2$ and $(C\mathit{H}_3)_3CP$), 1.53 (s, 9H, $(C\mathit{H}_3)_3CP$), 1.78 (m, 1H, $NC\mathit{H}HCH_3$), 1.88 (m, 1H, $NCH\mathit{H}CH_3$), 3.50 (m, 1H, $NC\mathit{H}HCH_3$), 3.69 (m, 1H, $NCH\mathit{H}CH_3$), 3.85 (d, $^{2}J_{HH}$ = 14.6 Hz, 1H, $NC\mathit{H}H$), 4.42 (d, $^{2}J_{HH}$ = 14.6 Hz, 1H, $NCH\mathit{H}$), 4.53 (s, 1H, $PC\mathit{H}$), 7.22 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, $C\mathit{H}_{pyri(3)}$), 7.54 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, $C\mathit{H}_{pyri(5)}$), 7.74 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, $C\mathit{H}_{pyri(4)}$).

^{1}H NMR (400.36 MHz, $CDCl_3$, 25 °C): δ 1.15 (m, 15H, overlapped $N(CH_2C\mathit{H}_3)_2$ and $(C\mathit{H}_3)_3CP$), 1.57 (d, $^{3}J_{PH}$ = 13.0 Hz, 9H, $(C\mathit{H}_3)_3CP$), 1.78 (m, 1H, $NC\mathit{H}HCH_3$), 1.88 (m, 1H, $NC\mathit{H}HCH_3$), 3.50 (m, 1H, $NC\mathit{H}HCH_3$), 3.69 (m, 1H, $NC\mathit{H}HCH_3$), 3.84 (d, $^{2}J_{HH}$ = 14.6 Hz, 1H, $NC\mathit{H}H$), 4.41 (d, $^{2}J_{HH}$ = 14.6 Hz, 1H, $NCH\mathit{H}$), 4.58 (d, $^{2}J_{HP}$ = 8.6 Hz, 1H, $PC\mathit{H}$), 7.20 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, $C\mathit{H}_{pyri(3)}$), 7.54 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, $C\mathit{H}_{pyri(5)}$), 7.73 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, $C\mathit{H}_{pyri(4)}$).

$^{13}C\{^{1}H\}$ QDEPT NMR (100.67 MHz, $CDCl_3$, 25 °C): δ 8.1 (s, $N(CH_2\mathit{C}H_3)_2$), 11.0 (s, $N(CH_2\mathit{C}H_3)_2$), 28.9 (d, $^{2}J_{PC}$ = 4.8 Hz, $(\mathit{C}H_3)_3CP$), 30.5 (m, $(\mathit{C}H_3)_3CP$), 37.3 (d, $^{1}J_{PC}$ = 6.0 Hz, $(CH_3)_3\mathit{C}P$), 37.5 (d, $^{1}J_{PC}$ = 10.5 Hz, $(CH_3)_3\mathit{C}P$), 46.4 (s, $N(\mathit{C}H_2CH_3)_2$), 53.8 (s, $N(\mathit{C}H_2CH_3)_2$), 60.7 (d, $^{1}J_{PC}$ = 3.8 Hz, $P\mathit{C}H$), 66.4 (s, $N\mathit{C}H_2$), 118.6 (s, $\mathit{C}H_{pyri(5)}$), 120.3 (d, $^{3}J_{PC}$ = 5.5 Hz, $\mathit{C}H_{pyri(3)}$), 138.2 (s, $\mathit{C}H_{pyri(4)}$), 159.6 (d, $^{3}J_{PC}$ = 2.0 Hz, $\mathit{C}H_{pyri(6)}$), 162.1 (d, $^{2}J_{PC}$ = 3.9 Hz, $\mathit{C}H_{pyri(2)}$), 174.1(d, $^{2}J_{PC}$ = 8.7 Hz, Mn–O–*C*=O), 232.7 (d, $^{2}J_{PC}$ = 11.5 Hz, Mn-*C*O), 233.9 (d, $^{2}J_{PC}$ = 21.6 Hz, Mn-*C*O).

IR (NaCl thin film, cm^{-1}): 1908.4 (ν_{asym}, C≡O), 1824.1 (ν_{sym}, C≡O), 1641.4 (COO).

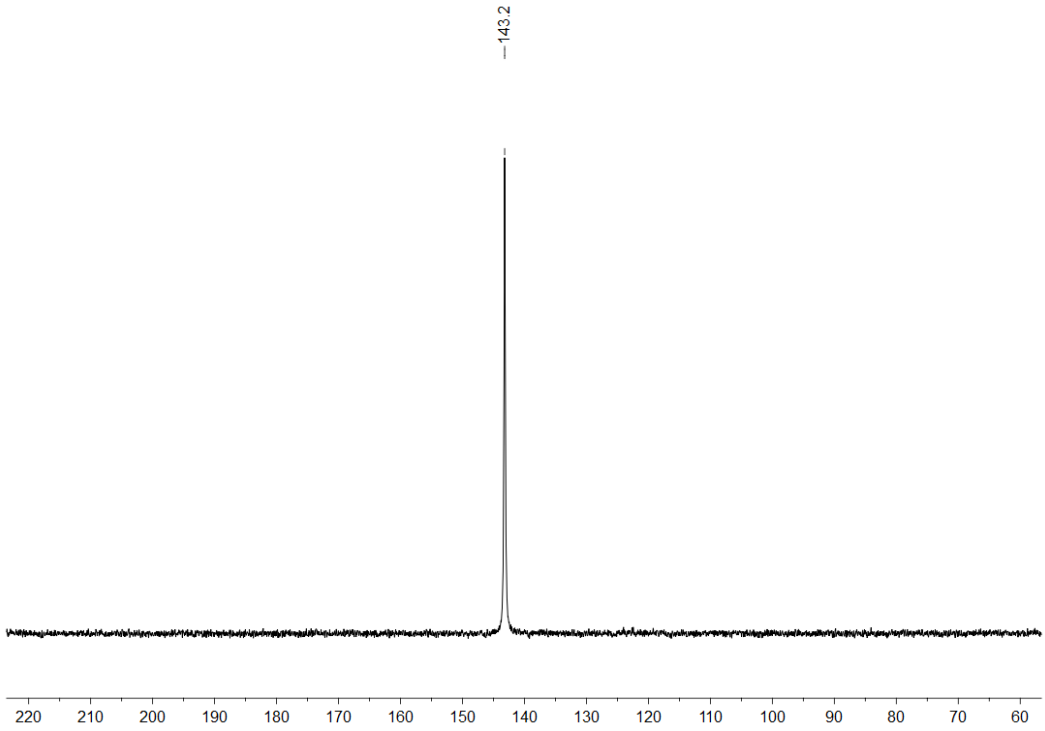


Figure S6. $^{31}P\{^{1}H\}$ NMR (298 K, $CDCl_3$) spectrum of [Mn(PNN-COO)$(CO)_2$] (**3'**).

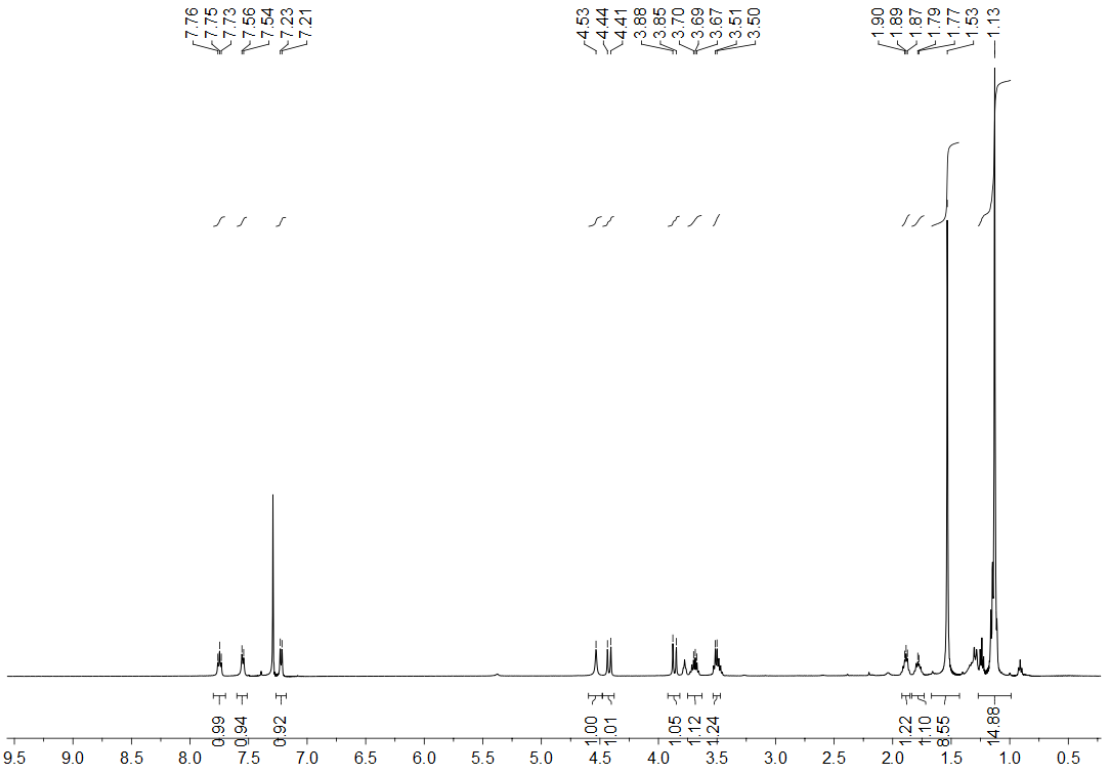


Figure S7. $^{1}H\{^{31}P\}$ NMR (298 K, $CDCl_3$) spectrum [Mn(PNN-COO)$(CO)_2$] (**3'**).

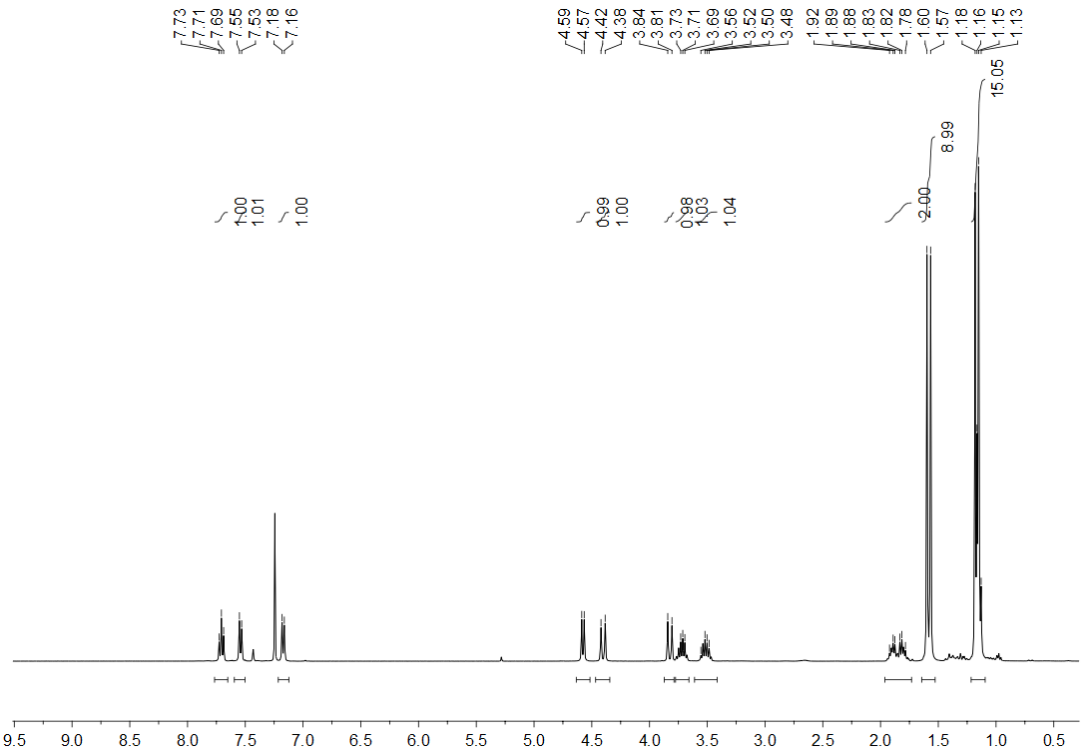


Figure S8. ^{1}H NMR (298 K, $CDCl_3$) spectrum [Mn(PNN-COO)$(CO)_2$] (**3'**).

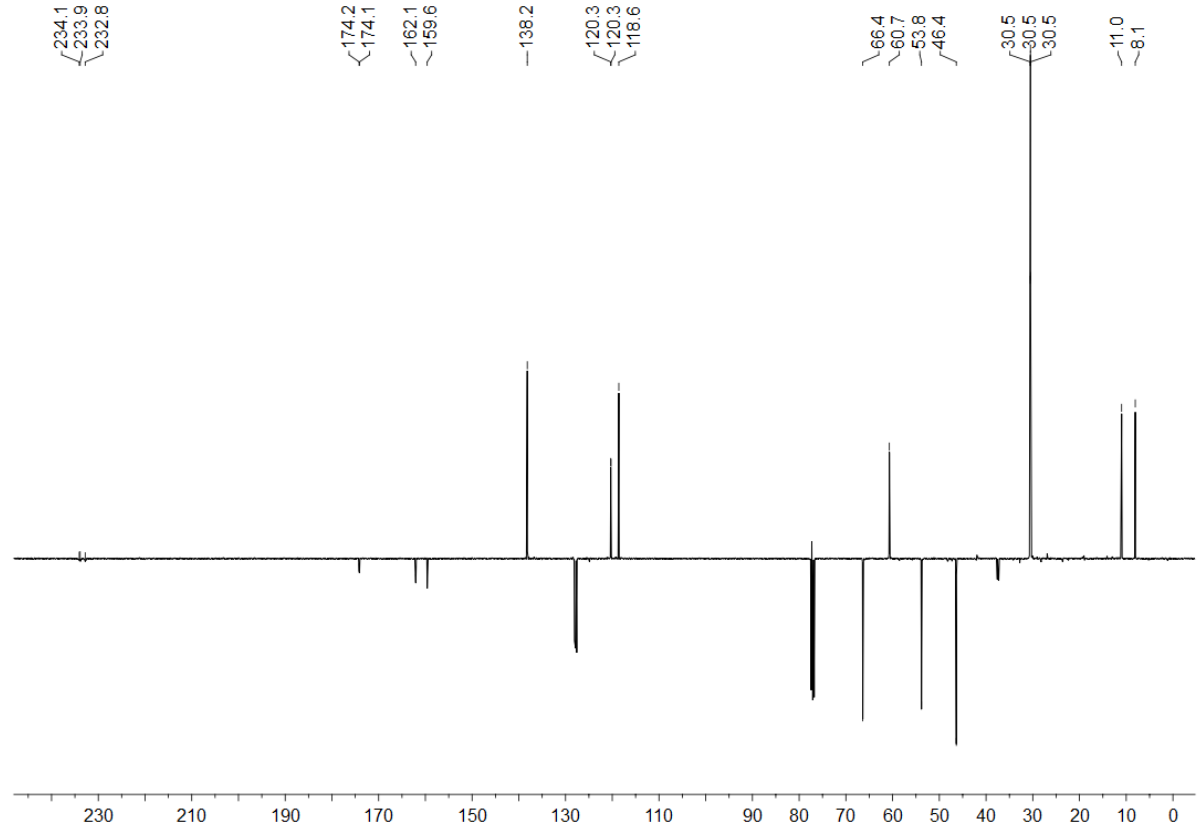


Figure S9. $^{13}C\{^{1}H\}$ NMR (298 K, $CDCl_3$) spectrum of [Mn(PNN-COO)$(CO)_2$] (**3'**).

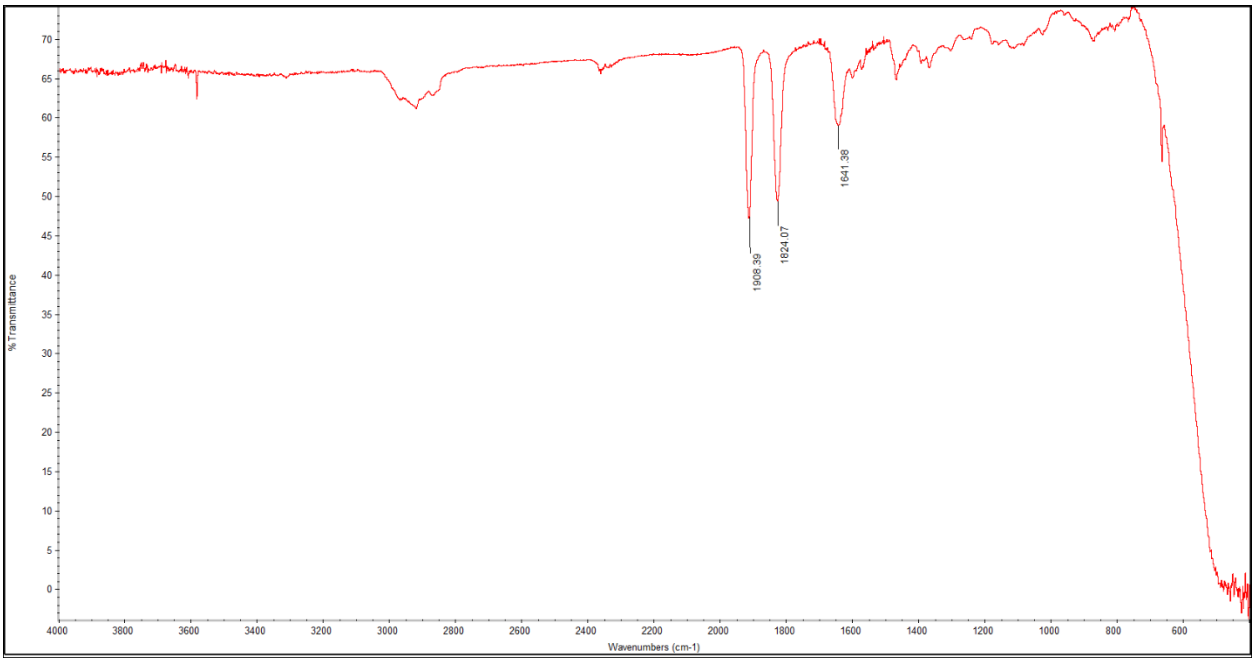
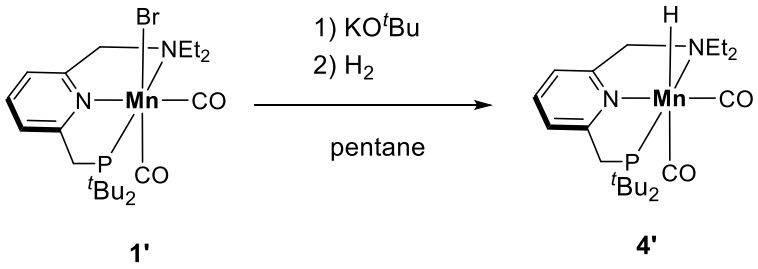


Figure S10. IR (NaCl thin film) spectrum of [Mn(PNN-COO)(CO)$_2$] (**3'**).

(iii) [Mn(PNN)(H)(CO)$_2$] (4')



1' **4'**

[Mn(PNN)(CO)$_2$(Br)] (**1'**) (200 mg, 0.39 mmol) and KO^{t}Bu (52 mg, 0.47 mmol) were suspended in 20 mL of pentane. The mixture was stirred at room temperature for 1 h. During the reaction time the original colorless suspension becomes a dark-green solution. After filtration through a Teflon syringe filter (0.2 µm) the pentane solution was transferred into a Schlenk tube fitted with a Young's cap. The Schlenk tube was evacuated twice by freeze-pump-thaw cycles and then filled with H_2 (1 bar). This resulted in an immediate color change from dark-green to yellow which was followed by precipitation of a red powder. The reaction was kept under strong stirring for an hour at room temperature. The

red precipitate was decanted, washed with diethyl ether (10 mL) and dried *in vacuo* (151 mg, 89 % yield). Clear pale yellow crystals suitable for X-ray analysis were obtained from a CH_2Cl_2 concentrated solution of **4'** layered with pentane and kept under nitrogen at ambient temperature.

$^{31}P\{^{1}H\}$ NMR (162.08 MHz, C_6D_6, 25 °C): δ 143.1 (s).

$^{1}H\{^{31}P\}$ NMR (500.08 MHz, C_6D_6, 25 °C): δ – 1.51 (s, 1H, Mn-*H*), 0.59 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, $N(CH_2CH_3)$), 1.20 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, 3H, $N(CH_2CH_3)$), 1.22 (s, 9H, $(CH_3)_3CP$), 1.40 (s, 9H, $(CH_3)_3CP$), 2.03 (m, 1H, $NCHHCH_3$), 2.12 (m, 1H, $NCHHCH_3$), 2.88 (d, $^{2}J_{HH}$ = 16.5 Hz, 1H, PC*H*H), 2.94 (d, $^{2}J_{HH}$ = 16.5 Hz, 1H, PCH*H*), 3.20 (d, $^{2}J_{HH}$ = 13.8 Hz, 1H, NCH*H*), 3.29 (m, 2H, NCH_2CH_3), 3.69 (d, $^{2}J_{HH}$ = 13.8 Hz, 1H, NC*H*H), 6.27 (d, $^{3}J_{HH}$ = 7.7 Hz, 1H, $CH_{pyri(3)}$), 6.51 (d, $^{3}J_{HH}$ = 7.7 Hz, 1H, $CH_{pyri(5)}$), 6.74 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, $CH_{pyri(4)}$).

^{1}H NMR (400.36 MHz, C_6D_6, 25 °C): δ – 1.52 (d, $^{2}J_{HP}$ = 55.5 Hz, 1H, Mn-*H*), 0.58 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, $N(CH_2CH_3)$), 1.19 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, 3H, $N(CH_2CH_3)$), 1.21 (d, $^{3}J_{PH}$ = 11.8 Hz, 9H, $(CH_3)_3CP$), 1.39 (d, $^{3}J_{PH}$ = 11.8 Hz, 9H, $(CH_3)_3CP$), 2.02 (m, 1H, $NCHHCH_3$), 2.12 (m, 1H, $NCHHCH_3$), 2.87 (dd, $^{2}J_{HH}$ = 16.5 Hz, $^{2}J_{HP}$ = 9.2 Hz, 1H, PC*H*H), 2.93 (dd, $^{2}J_{HH}$ = 16.5 Hz, $^{2}J_{HP}$ = 9.2 Hz, 1H, PCH*H*), 3.20 (d, $^{1}J_{HH}$ = 13.8 Hz, 1H, NCH*H*), 3.28 (m, 2H, NCH_2CH_3), 3.68 (d, $^{1}J_{HH}$ = 13.8 Hz, 1H, NC*H*H), 6.27 (d, $^{3}J_{HH}$ = 7.7 Hz, 1H, $CH_{pyri(3)}$), 6.52 (d, $^{3}J_{HH}$ = 7.7 Hz, 1H, $CH_{pyri(5)}$), 6.75 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, $CH_{pyri(4)}$).

$^{13}C\{^{1}H\}$ NMR (100.67 MHz, C_6D_6, 25 °C): δ 7.7 (s, $N(CH_2CH_3)_2$), 11.3 (s, $N(CH_2CH_3)_2$), 28.9 (d,$^{2}J_{PC}$ = 4.8 Hz, $(CH_3)_3CP$), 30.6 (d,$^{2}J_{PC}$ = 2.8 Hz, $(CH_3)_3CP$), 35.0 (d,$^{1}J_{PC}$ = 16.1 Hz, $(CH_3)_3CP$), 36.8 (d, $^{1}J_{PC}$ = 10.7 Hz, PCH_2), 37.3 (d,$^{1}J_{PC}$ = 7.4 Hz, $(CH_3)_3CP$), 52.8 (s, $N(CH_2CH_3)_2$), 53.4 (s, $N(CH_2CH_3)_2$), 66.4 (s, NCH_2), 117.2 (s,$CH_{pyri(5)}$), 118.8 (d, $^{3}J_{PC}$ = 7.7 Hz, $CH_{pyri(3)}$), 132.3 (s, $CH_{pyri(4)}$), 158.2 (d, $^{3}J_{PC}$ = 3.3 Hz, $CH_{pyri(6)}$), 161.7 (d, $^{2}J_{PC}$ = 7.0 Hz, $CH_{pyri(2)}$), 227.3 (d, $^{2}J_{PC}$ = 13.2 Hz, Mn-*C*O), 238.5 (d, $^{2}J_{PC}$ = 17.6 Hz, Mn-*C*O).

IR (NaCl thin film, cm^{-1}): 1886.2 (ν_{asym}, C≡O), 1798.3 (ν_{sym}, C≡O).

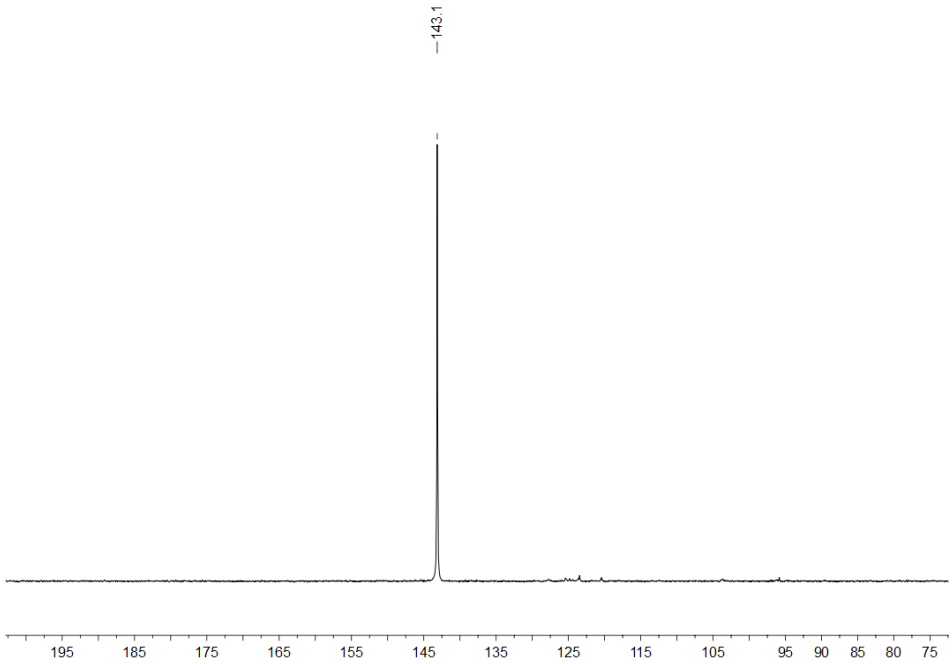


Figure S11. $^{31}P\{^{1}H\}$ NMR (298 K, C_6D_6) spectrum of [Mn(PNN)(H)$(CO)_2$] (**4'**).

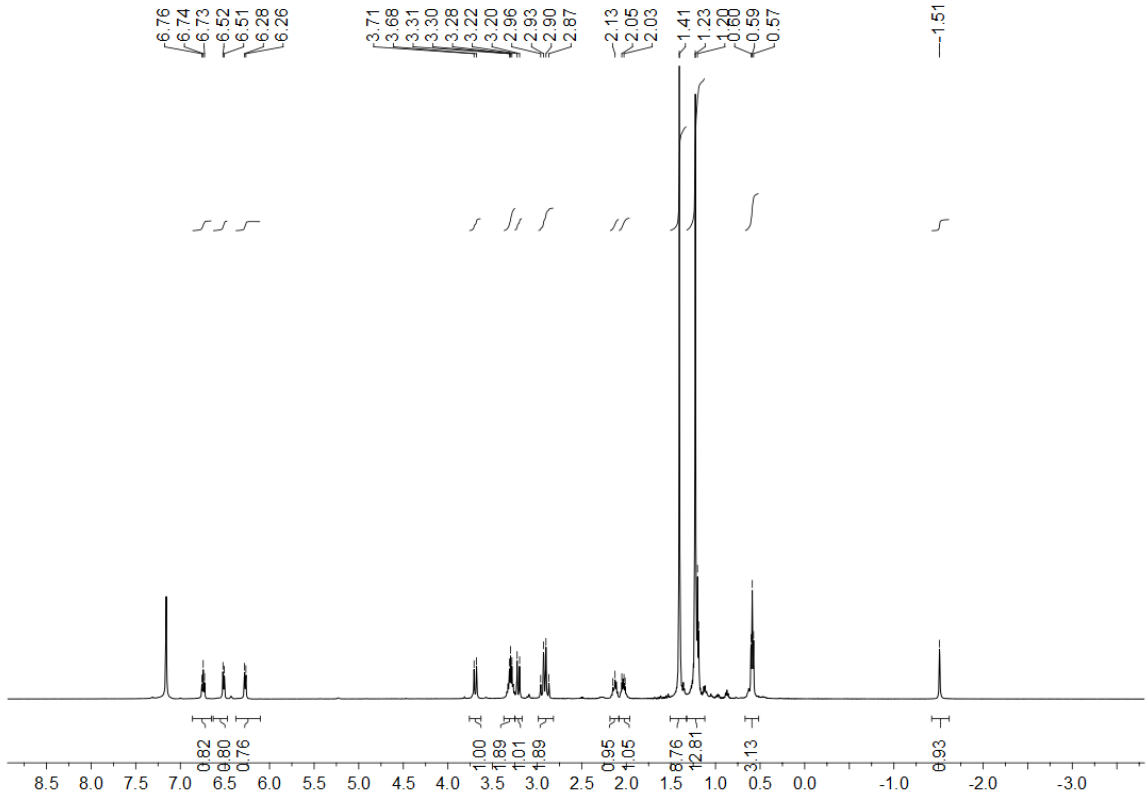


Figure S12. $^{1}H\{^{31}P\}$ NMR (298 K, $CDCl_3$) spectrum [Mn(PNN)(H)$(CO)_2$] (**4'**).

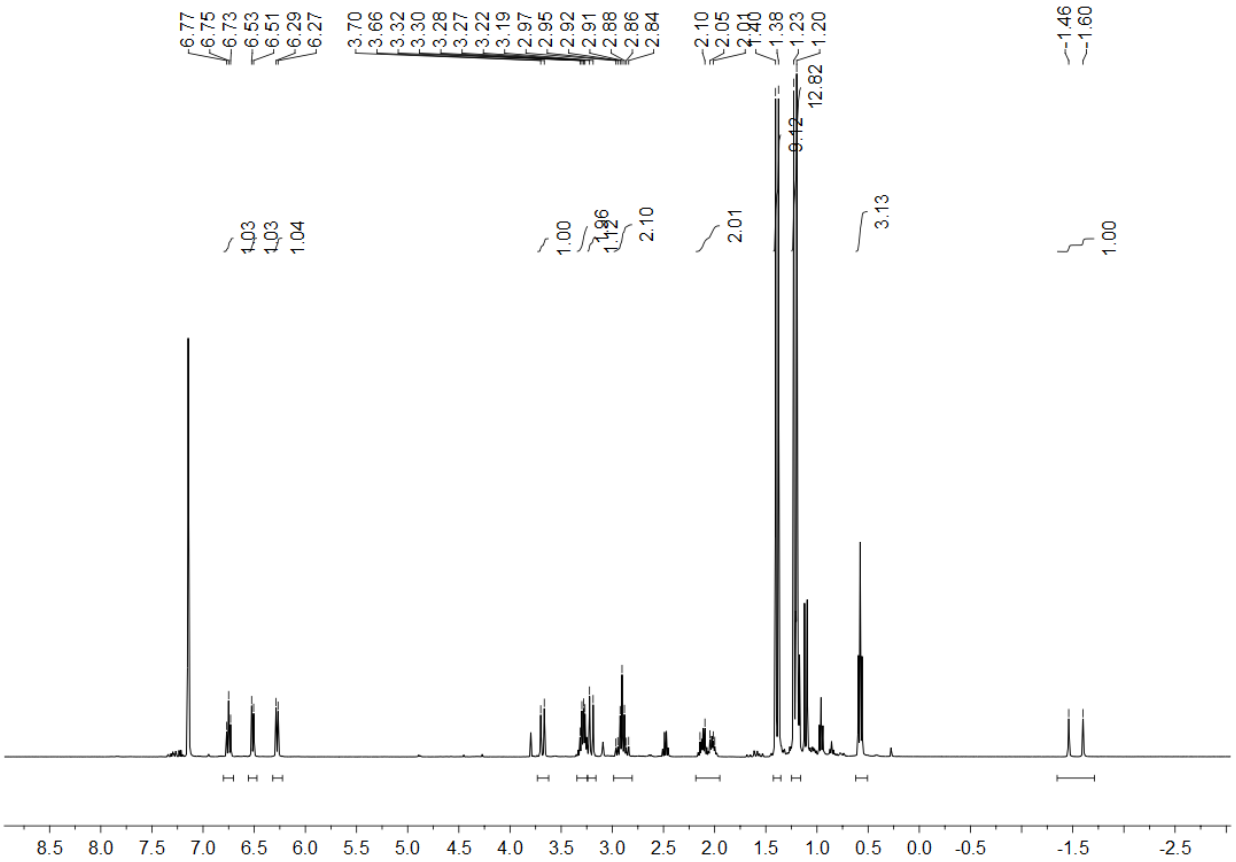


Figure S13. ^{1}H NMR (298 K, $CDCl_3$) spectrum of [Mn(PNN)(H)$(CO)_2$] (**4'**).

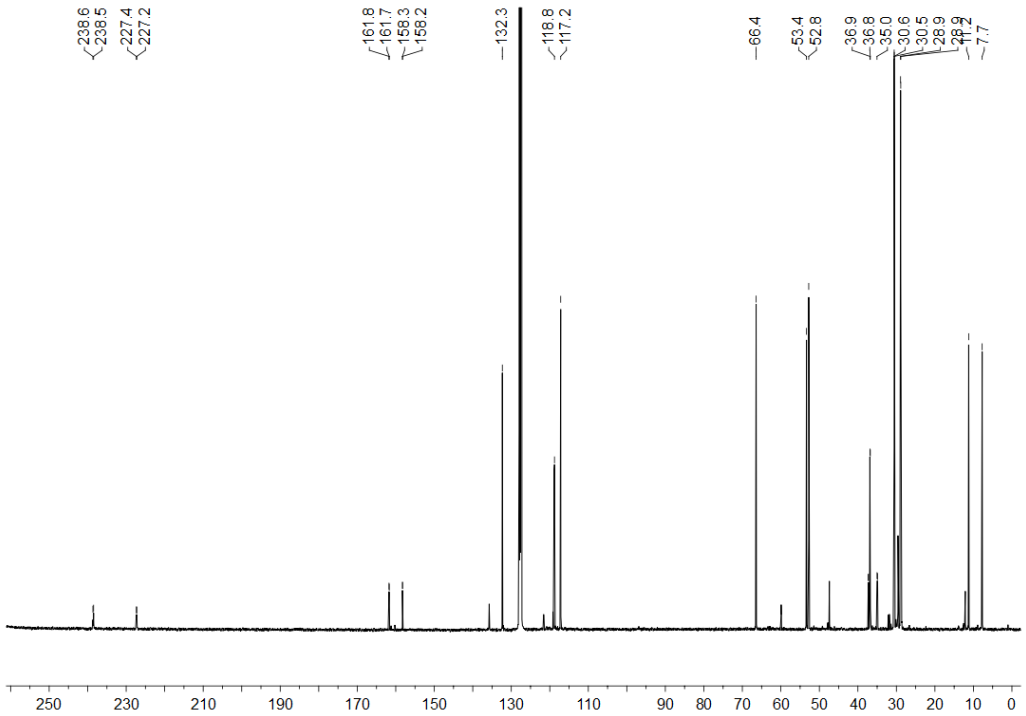


Figure S14. $^{13}C\{^{1}H\}$ NMR (298 K, $CDCl_3$) spectrum of [Mn(PNN)(H)$(CO)_2$] (**4'**).

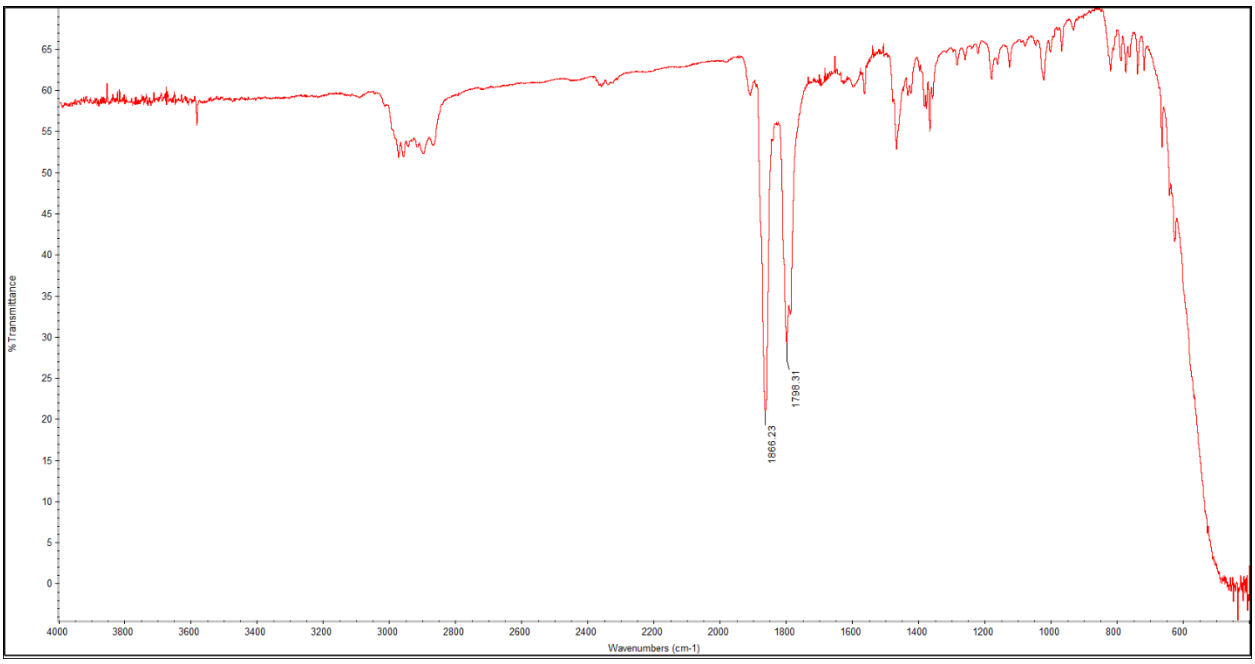
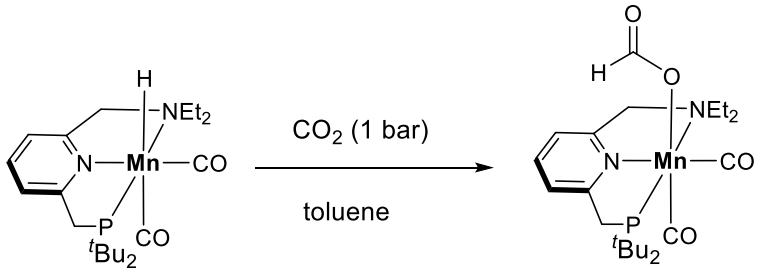


Figure S15. IR (NaCl thin film) spectrum of [Mn(PNN)(H)(CO)$_2$] (**4'**).

(iv) [Mn(PNN)(OCOH)(CO)$_2$] (10)



4' **5'**

[Mn(PNN)(CO)$_2$(H)] (**4'**) (40 mg) was dissolved in toluene in an NMR tube fitted with Young's valve. NMR tube was degassed using freeze-pump-thaw cycle and refilled with 1 bar of CO_2 at room temperature. The color of the reaction mixture turned to yellow from orange in 15 minutes. NMR spectroscopy showed clean formation of a new complex characterized as [Mn(PNN)(CO)$_2$(OCOH)] (**5'**). Leaving the sample overnight at room temperature under CO_2 atmosphere resulted in the

formation of yellow crystals. The mother liquor was decanted and crystals were dried to obtain yellow crystalline solid (42 mg) in 95% yield.

$^{31}P\{^{1}H\}$ NMR (162.08 MHz, CD_2Cl_2, 25 °C): δ 120.6 (s).

$^{1}H\{^{31}P\}$ NMR (500.08 MHz, CD_2Cl_2, 25 °C): δ 0.54 (t, $^{3}J_{HH}$ = 6.6 Hz, 3H, NCH_2CH_3), 0.61 (t, $^{3}J_{HH}$ = 6.6 Hz, 3H, NCH_2CH_3), 0.75 (s, 3H, $(CH_3)_3CP$), 0.77 (s, 6H, $(CH_3)_3CP$), 0.84 (s, 9H, $(CH_3)_3CP$), 1.77 (m, 1H, $NCHHCH_3$), 2.06 (m, 1H, $NCHHCH_3$), 2.23 (m, 1H, $NCHHCH_3$), 2.70 (m, 1H, $NCHHCH_3$), 2.93 (d, $^{2}J_{HH}$ = 16.5 Hz, 1H, PCH*H*), 3.23 (d, $^{2}J_{HH}$ = 16.5 Hz, 1H, PCH*H*), 3.36 (d, $^{2}J_{HH}$ = 15.0 Hz, 1H, NC*H*H), 3.70 (d, $^{2}J_{HH}$ = 15.0 Hz, 1H, NC*H*H), 6.82 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H, $CH_{pyri(3)}$), 7.07 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H, $CH_{pyri(5)}$), 7.31 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H, $CH_{pyri(4)}$), 8.40 (s, 1H, OCO*H*).

^{1}H NMR (500.08 MHz, CD_2Cl_2, 25 °C): δ 0.54 (t, $^{3}J_{HH}$ = 6.6 Hz, 3H, NCH_2CH_3), 0.61 (t, $^{3}J_{HH}$ = 6.6 Hz, 3H, NCH_2CH_3), 0.75 (d, $^{2}J_{HP}$ = 12.2 Hz, 3H, $(CH_3)_3CP$), 0.77 (d, $^{2}J_{HP}$ = 12.2 Hz, 6H, $(CH_3)_3CP$), 0.84 (d, $^{2}J_{HP}$ = 12.2 Hz, 9H, $(CH_3)_3CP$), 1.77 (m, 1H, $NCHHCH_3$), 2.06 (m, 1H, $NCHHCH_3$), 2.23 (m, 1H, $NCHHCH_3$), 2.70 (m, 1H, $NCHHCH_3$), 2.93 (dd, $^{2}J_{HH}$ = 16.5 Hz, $^{2}J_{HP}$ = 8.8 Hz, 1H, PCH*H*), 3.23 (dd, $^{2}J_{HH}$ = 16.5 Hz, $^{2}J_{HP}$ = 8.8 Hz, 1H, PCH*H*), 3.36 (d, $^{2}J_{HH}$ = 15.0 Hz, 1H, NC*H*H), 3.70 (d, $^{2}J_{HH}$ = 15.0 Hz, 1H, NC*H*H), 6.82 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H, $CH_{pyri(3)}$), 7.07 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H, $CH_{pyri(5)}$), 7.31 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H, $CH_{pyri(4)}$), 8.40 (s, 1H, OCO*H*).

$^{13}C\{^{1}H\}$ NMR (100.67 MHz, CD_2Cl_2, 25 °C): δ 7.4 (s, $N(CH_2CH_3)_2$), 10.4 (s, $N(CH_2CH_3)_2$), 29.8 (d, $^{2}J_{PC}$ = 4.2 Hz, $(CH_3)_3CP$), 30.1 (d, $^{2}J_{PC}$ = 3.2 Hz, $(CH_3)_3CP$), 31.6 (d, $^{1}J_{PC}$ = 24.4 Hz, $(CH_3)_3CP$), 35.6 (d, $^{1}J_{PC}$ = 12.5 Hz, PCH_2), 37.0 (d, $^{1}J_{PC}$ = 18.4 Hz, $(CH_3)_3CP$), 46.5 (s, $N(CH_2CH_3)_2$), 51.6 (s, $N(CH_2CH_3)_2$), 62.6 (s, NCH_2), 119.5 (s, $CH_{pyri(5)}$), 121.5 (d, $^{3}J_{PC}$ = 7.7 Hz, $CH_{pyri(3)}$), 137.4 (s, $CH_{pyri(4)}$), 161.0 (d, $^{3}J_{PC}$ = 3.3 Hz, $CH_{pyri(6)}$), 163.1 (d, $^{2}J_{PC}$ = 7.0 Hz, $CH_{pyri(2)}$), 171.8 (s, OCOH), 231.9 (d, $^{2}J_{PC}$ = 18.2 Hz, Mn-CO), 232.0 (d, $^{2}J_{PC}$ = 17.6 Hz, Mn-CO).

IR (NaCl thin film, cm^{-1}): 1912.3 (ν_{asym}, C≡O), 1823.1 (ν_{sym}, C≡O), 1588.2 (OCOH).

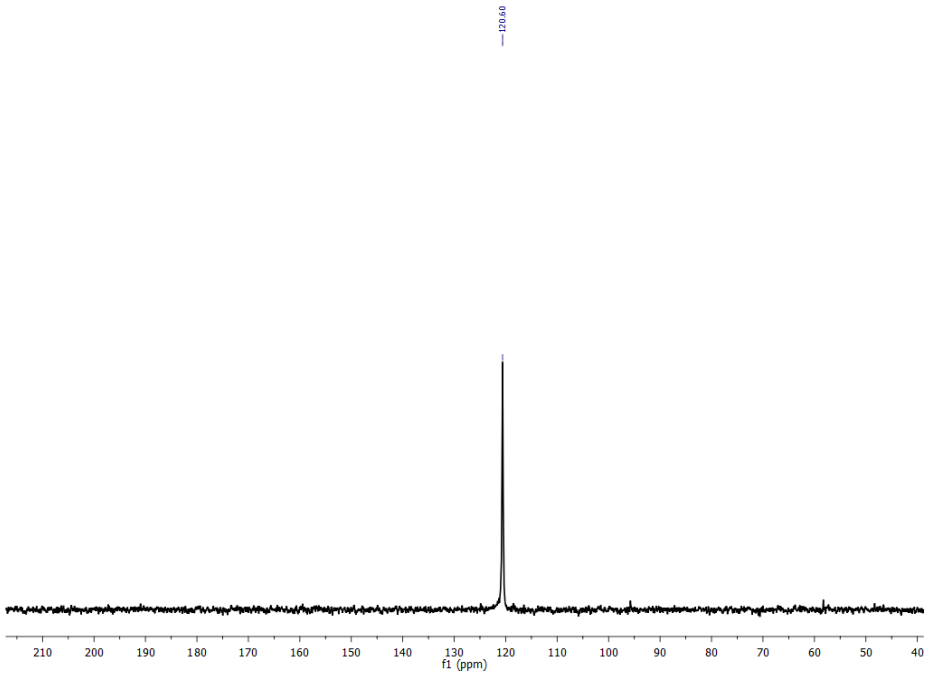


Figure S16. $^{31}P\{^{1}H\}$ NMR (298 K, CD_2Cl_2) spectrum of [Mn(PNN)(OCOH)$(CO)_2$] (**5'**).

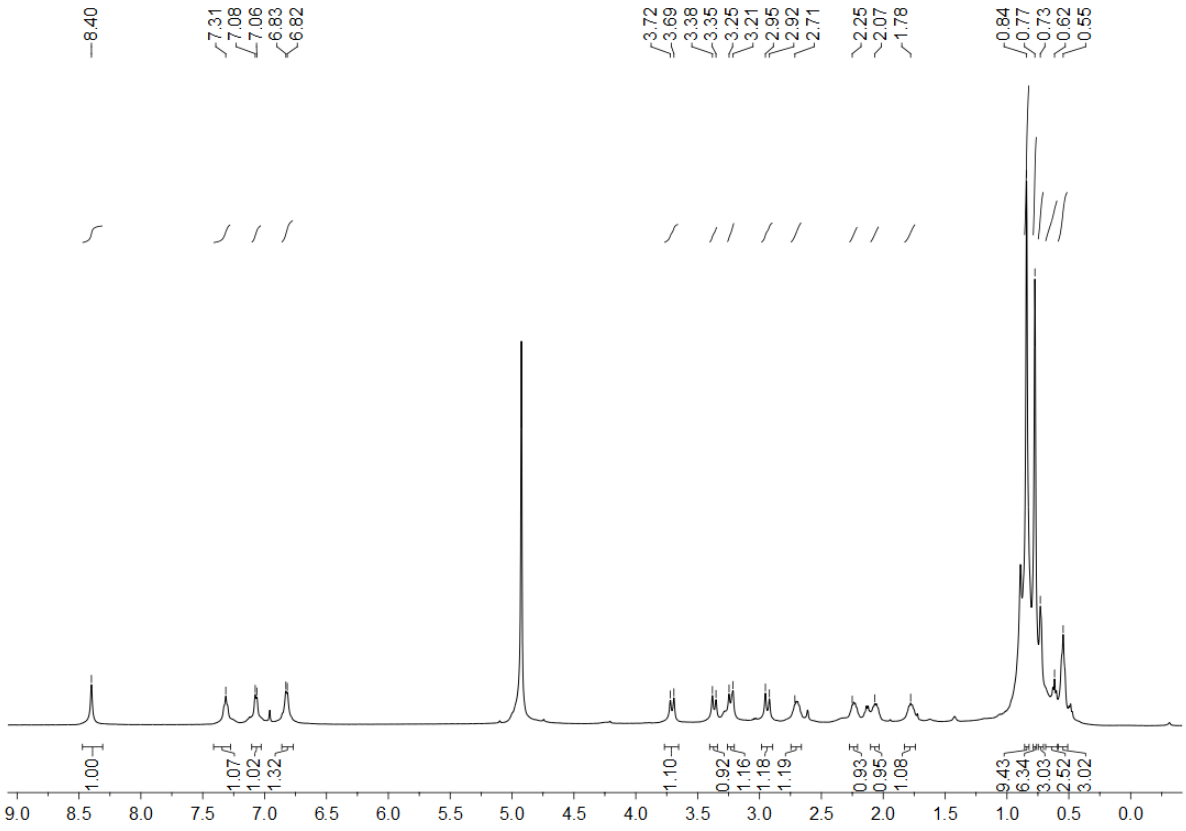


Figure S17. $^{1}H\{^{31}P\}$ NMR (298 K, CD_2Cl_2) spectrum of [Mn(PNN)(OCOH)$(CO)_2$] (**5'**).

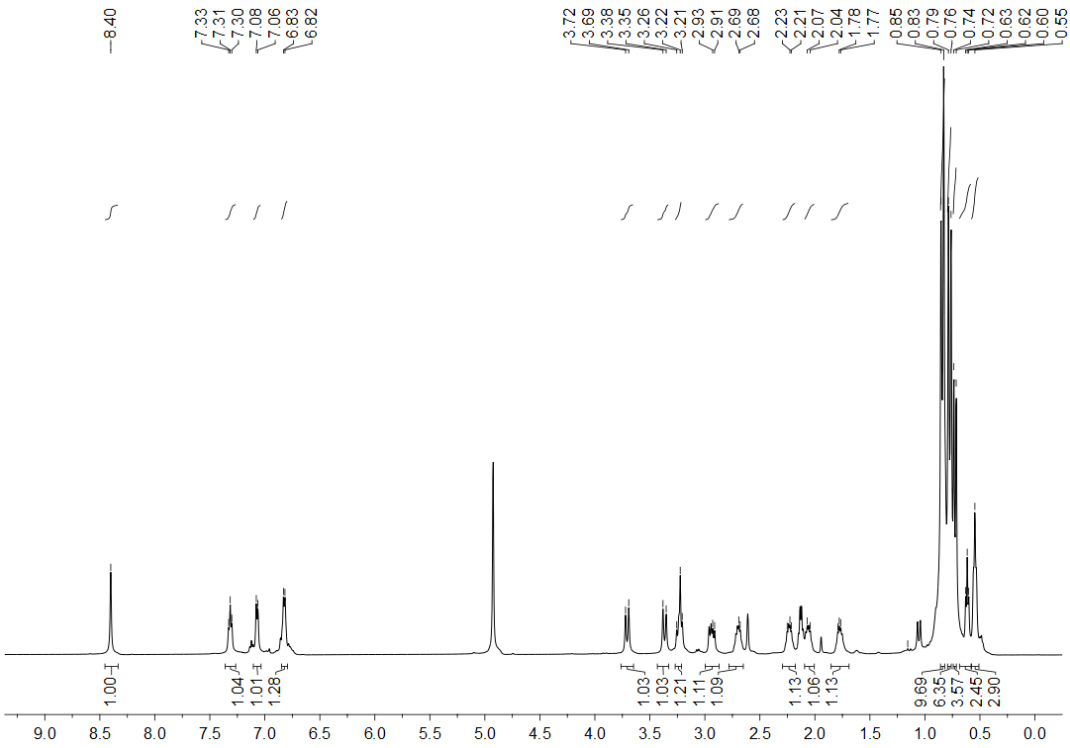


Figure S18. ^{1}H NMR (298 K, CD_2Cl_2) spectrum of [Mn(PNN)(OCOH)$(CO)_2$] (**5'**).

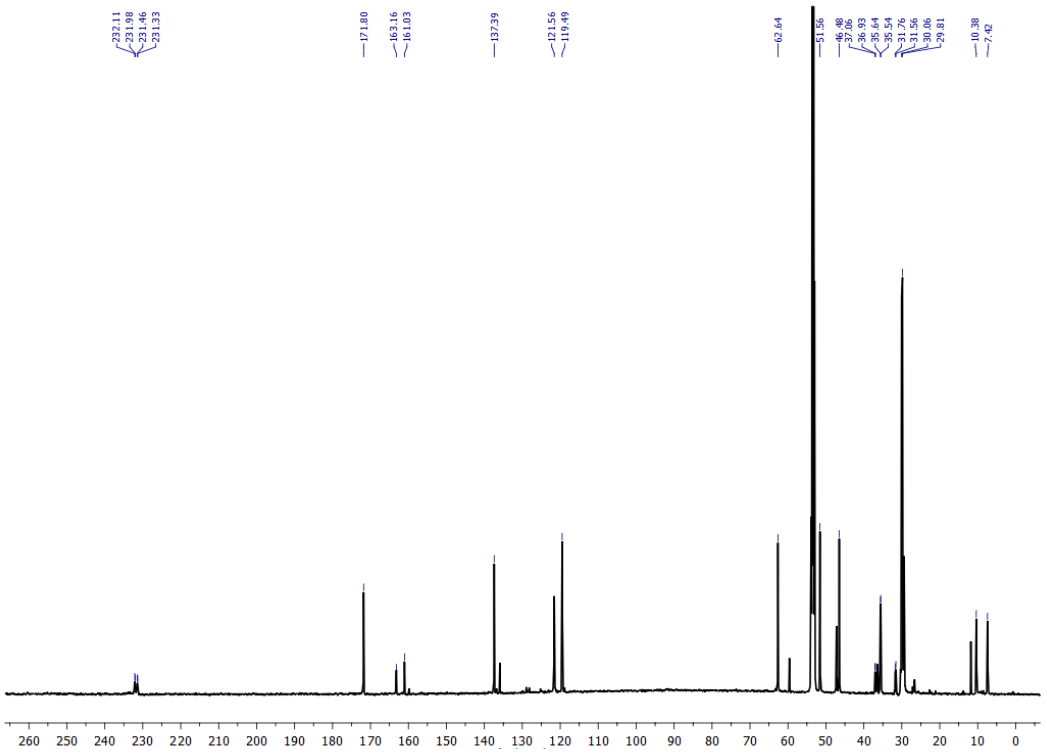


Figure S19. $^{13}C\{^{1}H\}$ NMR (298 K, CD_2Cl_2) spectrum of [Mn(PNN)(OCOH)$(CO)_2$] (**5'**).

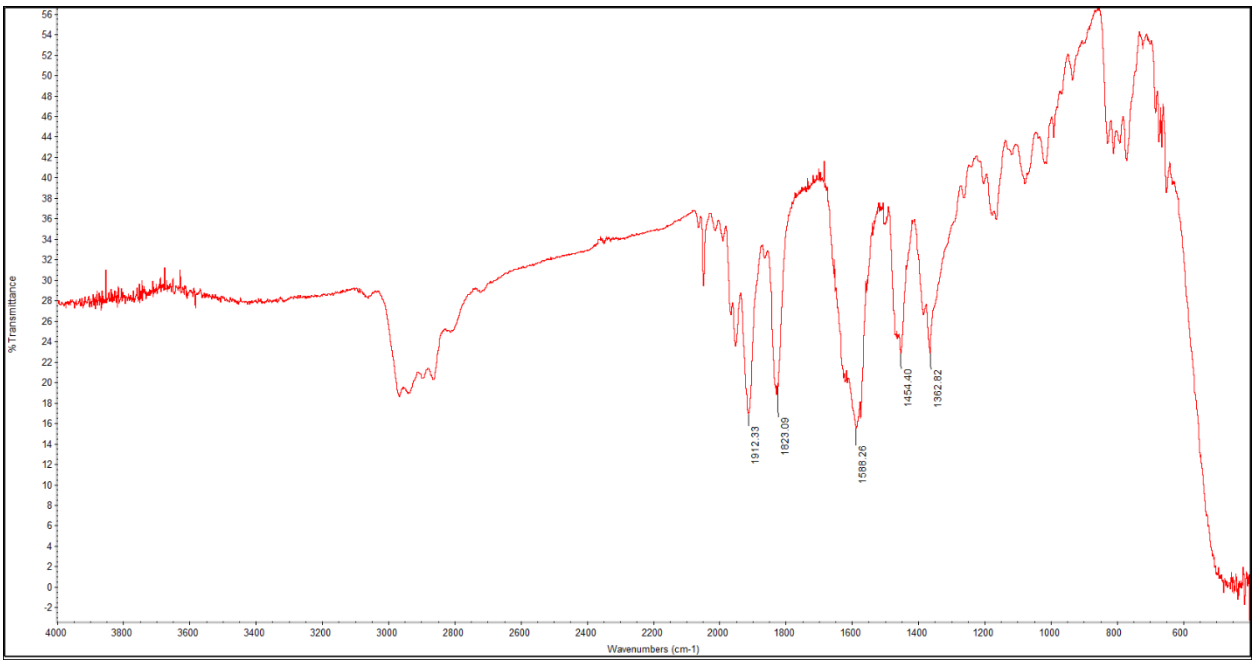
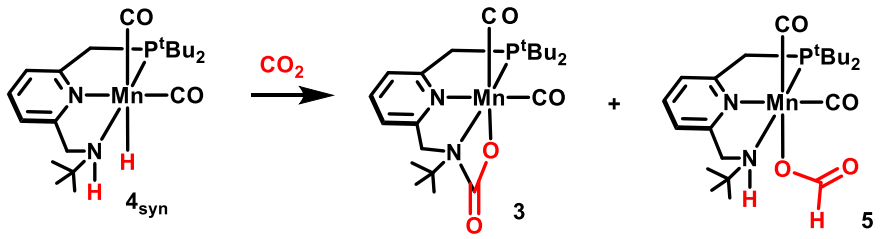


Figure S20. IR (NaCl thin film) spectrum of [Mn(PNN)(OCOH)(CO)$_2$] (**5'**).

3. Reaction of Complex 7 with CO_2



Complex **4$_{syn}$** was *in-situ* prepared by the reaction of complex **2** (20 mg, 0.04 mmol, toluene-d8) with H_2 gas (2 bar) in a Young's NMR tube as per the earlier reported procedure.[2a] The formation of complex **4$_{syn}$** was confirmed by the NMR spectroscopy. 4 bar of CO_2 was then added to the same NMR tube and the reaction was monitored by the NMR spectroscopy. The NMR and IR spectroscopy showed the formation of mixture of two complexes that stayed same at room temperature till 24 h. We were unable to separate/isolate the complexes by crystallization. We present here the NMR spectra of the resulting reaction mixture where we can observe the signals

corresponding to the CO_2 bound complex **3** based on the characterization details described above as well as for the complex **5** whose characteristic signals match with the similar manganese formate complexes reported earlier in literature.[3]

Characteristic spectral signals for complex 5 elucidated from the reaction mixture (Figures S21-24):

$^{31}P\{^1H\}$ NMR (162.08 MHz, Tol-d_8, 25 °C): δ 116.0 (s).

^1H NMR (500.08 MHz, Tol-d_8, 25 °C): δ 8.34 (*H*COOMn).

$^{13}C\{^1H\}$ NMR (125.74 MHz, Tol-d_8, 25 °C): δ 173.9 (H*C*OOMn).

IR (NaCl thin film, cm^{-1}): 1599.2 (COO).

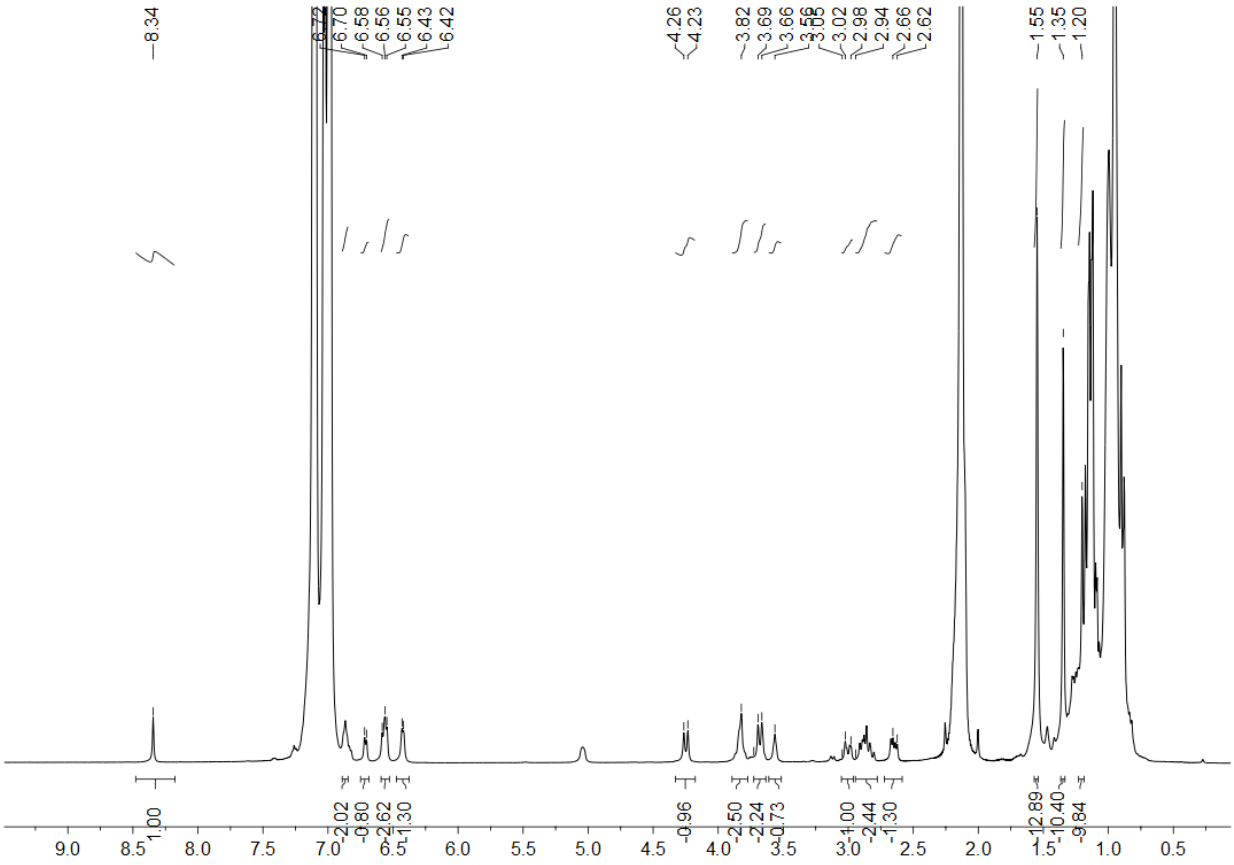


Figure S21. ^1H NMR (298 K, Tol-d_8) spectrum of the reaction of complex $\mathbf{4_{syn}}$ with CO_2.

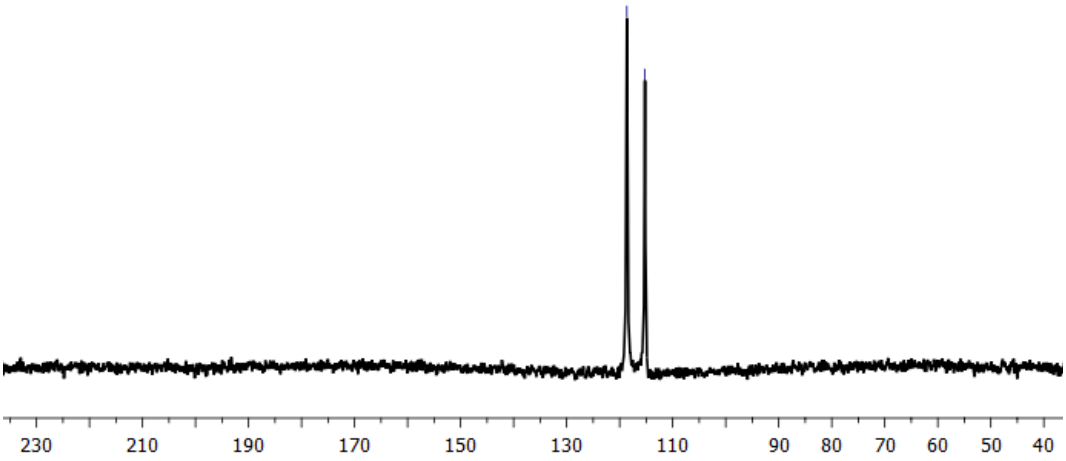


Figure S22. $^{31}P\{^{1}H\}$ NMR (298 K, Tol-d_8) spectrum of the reaction of complex $\mathbf{4_{syn}}$ with CO_2.

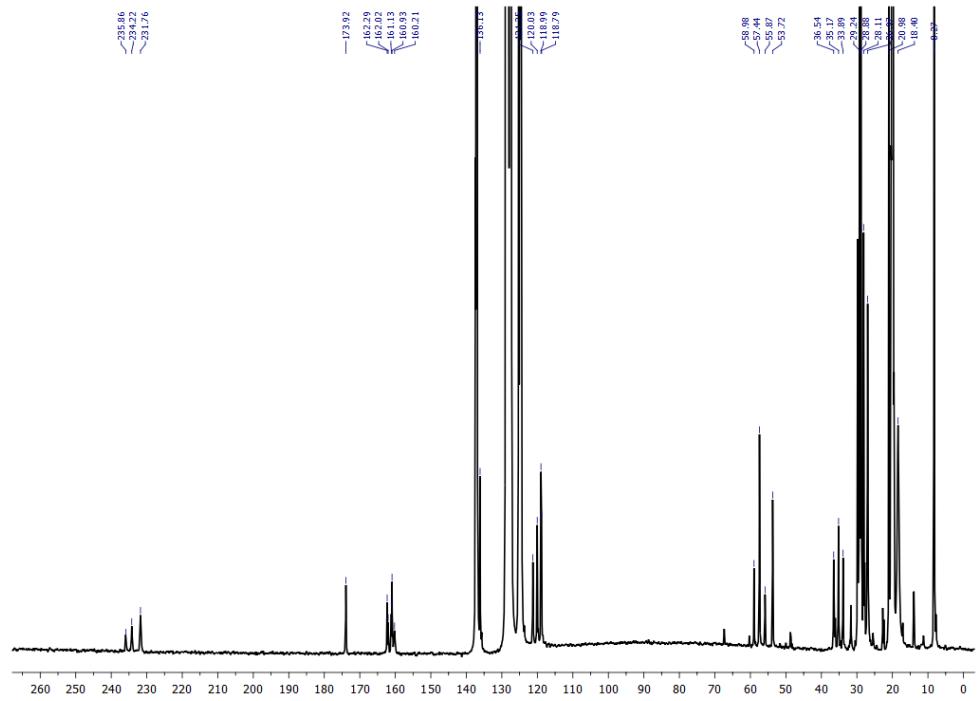


Figure S23. $^{13}C\{^{1}H\}$ NMR (298 K, Tol-d_8) spectrum of the reaction of complex $\mathbf{4_{syn}}$ with CO_2.

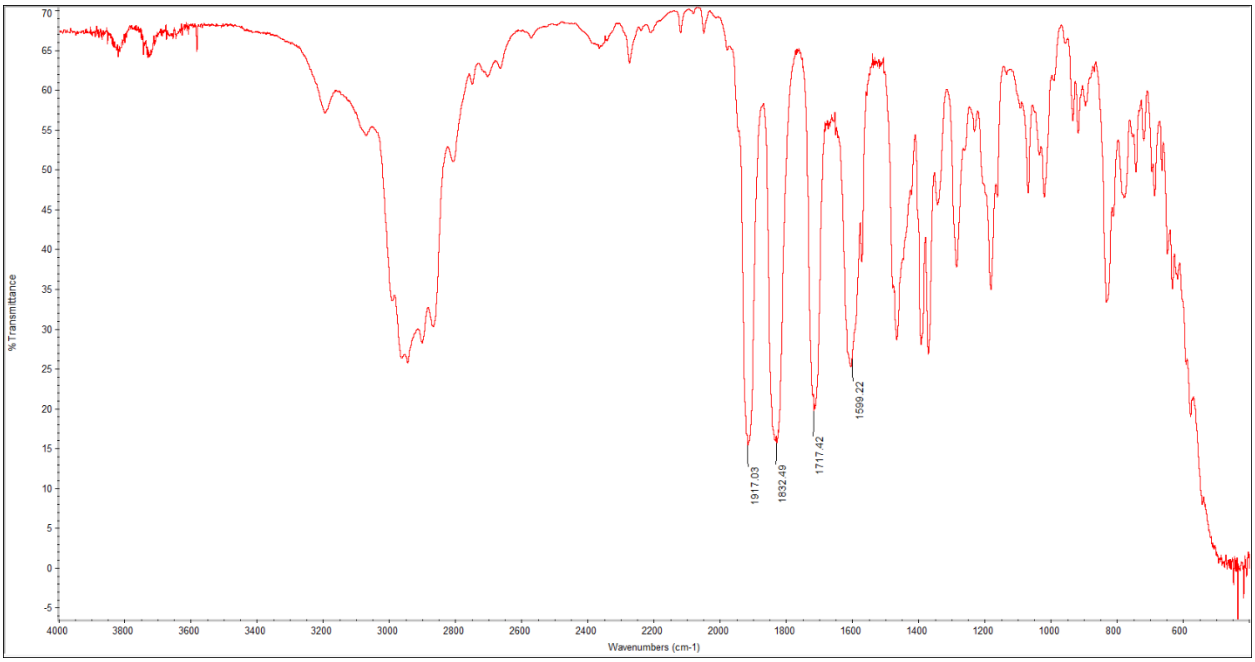
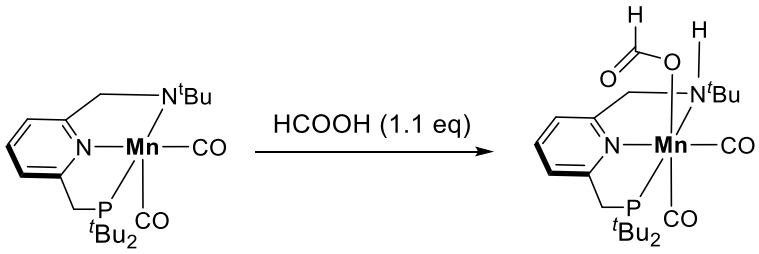


Figure S24. IR (NaCl thin film) spectrum of the reaction of complex $\mathbf{4_{syn}}$ with CO_2.

Independent synthesis of [Mn(PNNH)(OCOH)(CO)$_2$] (5)



2 **5**

Complex **2** (20 mg, 0.046 mmol) was dissolved in 1 mL of pentane and the dark blue solution of **2** was added to HCOOH (2.4 mg, 0.05 mmol) which resulted in an immediate color change to yellow. The resulting solution was kept in freezer at -30ºC for 15 minutes to obtain a crystalline yellow solid. The pentane was decanted and the resulting solid was dried in vacuum to remove the pentane and traces of formic acid. Isolated yield: 17 mg, 77%.

$^{31}P\{^1H\}$ NMR (202.44 MHz, CD_2Cl_2, 25 °C): δ 116.0 (s).

$^1H\{^{31}P\}$ NMR (500.08 MHz, Tol-d_8, 25 °C): δ 0.98 (s, 9H, $(CH_3)_3CP$), 1.26 (s, 9H, $(CH_3)_3CP$), 1.40 (s, 9H, $(CH_3)_3CN$), 2.83 (d, $^2J_{HH}$ = 16.7 Hz, 1H, PCH*H*), 3.17 (d, $^2J_{HH}$ = 16.7 Hz, 1H, PC*H*H),

3.84 (m, 3H, NCH_2, NH), 6.48 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C$H_{pyri(3)}$), 6.65 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C$H_{pyri(5)}$), 6.95 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C$H_{pyri(4)}$), 8.16 (s, OCO*H*).

^{1}H NMR (500.08 MHz, Tol-d_8, 25 °C): δ 0.98 (d, $^3J_{PH}$ = 11.2 Hz, 9H, (CH_3)$_3$CP), 1.26 (d, $^3J_{PH}$ = 11.2 Hz, 9H, (CH_3)$_3$CP), 1.40 (s, 9H, (CH_3)$_3$CN), 2.83 (dd, $^2J_{HH}$ = 16.7 Hz, $^2J_{PH}$ = 12.8 Hz, 1H, PCH*H*), 3.17 (dd, $^2J_{HH}$ = 16.7 Hz, $^2J_{PH}$ = 12.8 Hz, 1H, PC*H*H), 3.84 (m, 3H, NCH_2, NH), 6.48 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C$H_{pyri(3)}$), 6.65 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C$H_{pyri(5)}$), 6.95 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C$H_{pyri(4)}$), 8.16 (s, OCO*H*).

^{13}C{^{1}H} NMR (125.75 MHz, Tol-d_8, 25 °C): δ 28.2 (s, (*C*H$_3$)$_3$CN), 29.0 (d,$^2J_{PC}$ = 5.7 Hz, (*C*H$_3$)$_3$CP), 30.0 (d,$^2J_{PC}$ = 5.7 Hz, (*C*H$_3$)$_3$CP), 34.3 (d, $^1J_{PC}$ = 12.8 Hz, *C*H$_2$P), 36.2 (d, $^1J_{PC}$ = 5.8 Hz, (CH$_3$)$_3$*C*P), 36.5 (d, $^1J_{PC}$ = 15.3 Hz, (CH$_3$)$_3$*C*P), 53.6 (s, *C*H$_2$N), 55.3 (s, (CH$_3$)$_3$*C*N), 117.5 (s, *C*H$_{pyri(5)}$), 120.4 (d, $^3J_{PC}$ = 12.8 Hz, *C*H$_{pyri(3)}$), 136.1 (s, *C*H$_{pyri(4)}$), 162.1 (d, $^3J_{PC}$ = 3.0 Hz, *C*H$_{pyri(6)}$), 162.4 (d, $^2J_{PC}$ = 5.0 Hz, *C*H$_{pyri(2)}$), 171.2 (s, Mn–O–*C*=O), 232.9 (bs, Mn-*C*O), 235.1 (bs, Mn-*C*O).

IR (NaCl thin film, cm^{-1}): 1917.0 (ν_{asym}, C≡O), 1828.8 (ν_{sym}, C≡O), 1713.9 (COO).

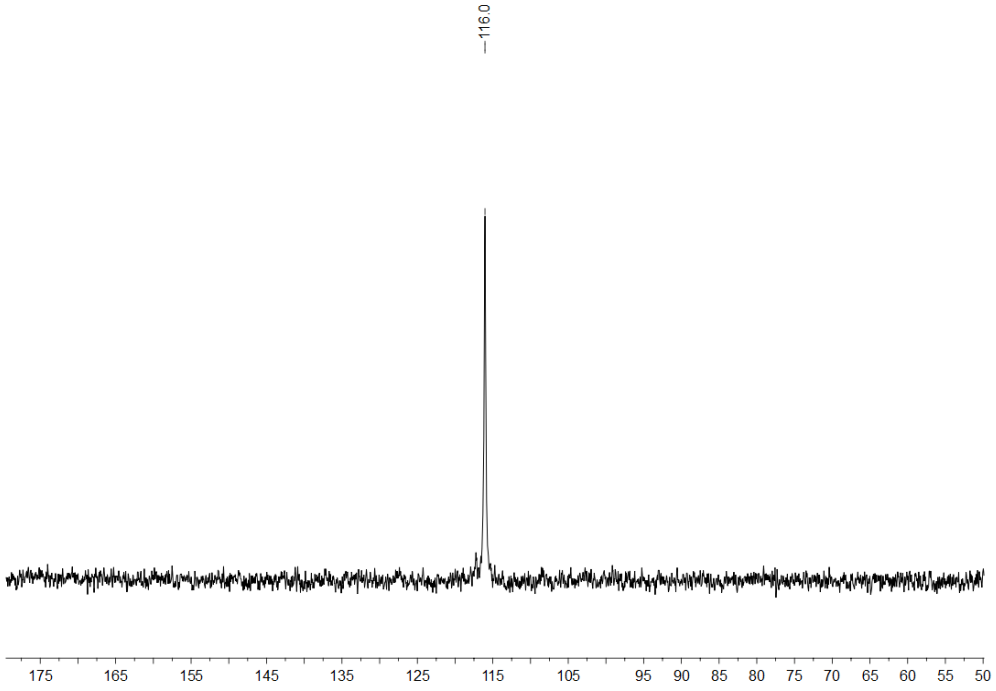


Figure S25. ^{31}P {^{1}H} NMR (298 K, Tol-d_8) spectrum of [Mn(PNNH)(OCOH)(CO)$_2$] (**5**).

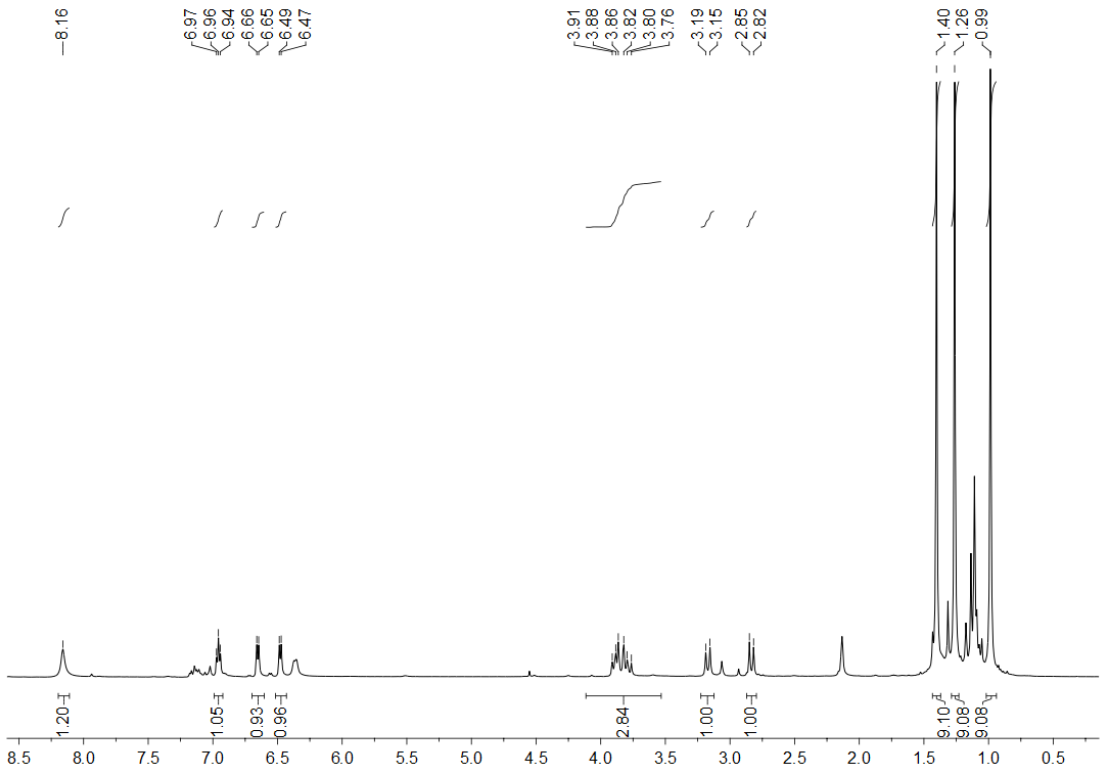


Figure S26. $^{1}H\{^{31}P\}$ NMR (298 K, Tol-d_8) spectrum of [Mn(PNNH)(OCOH)$(CO)_2$] (**5**).

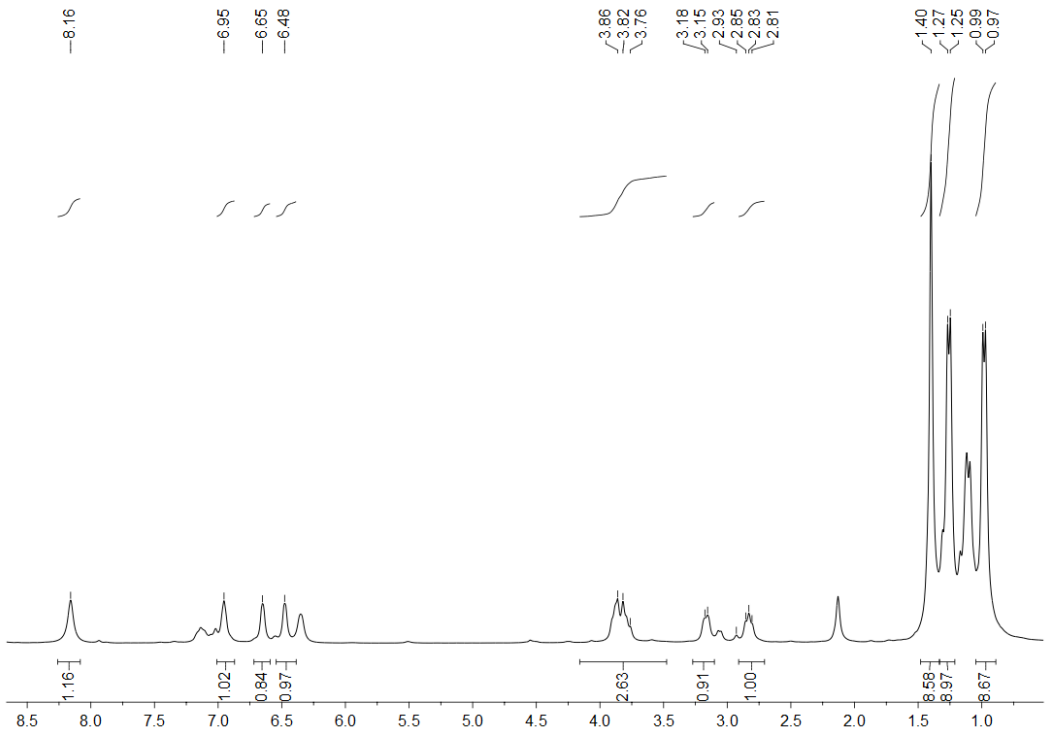


Figure S27. ^{1}H NMR (298 K, Tol-d_8) spectrum of [Mn(PNNH)(OCOH)$(CO)_2$] (**5**).

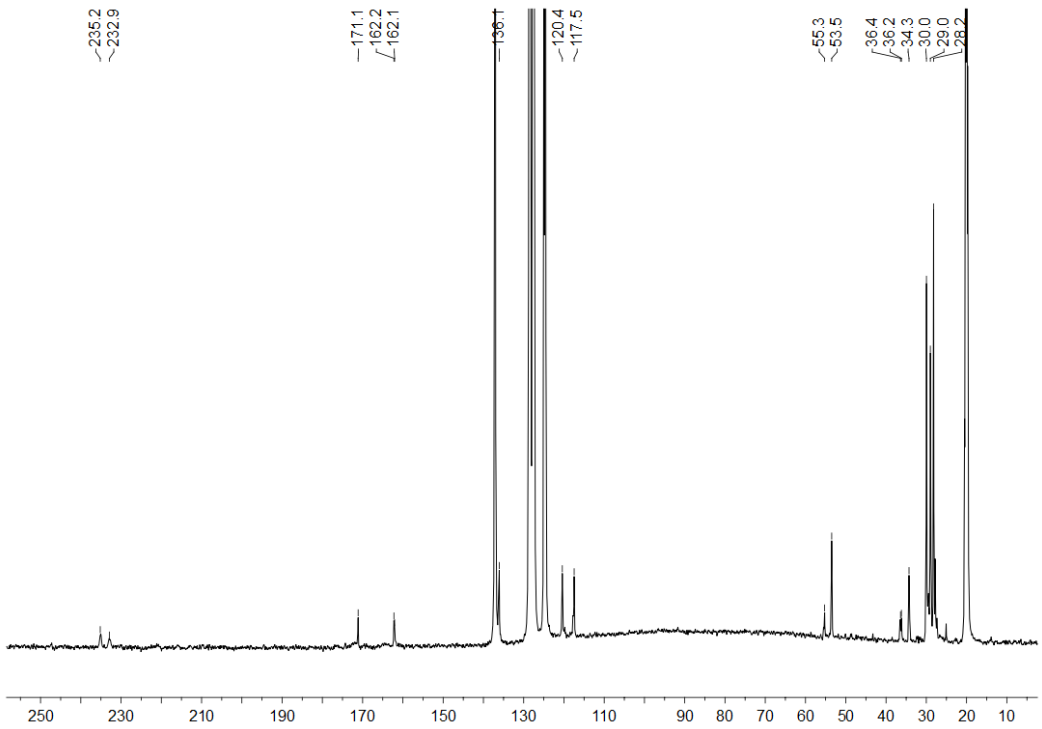


Figure S28. ^{13}C NMR (298 K, Tol-d_8) spectrum of [Mn(PNNH)(OCOH)(CO)$_2$] (**5**).

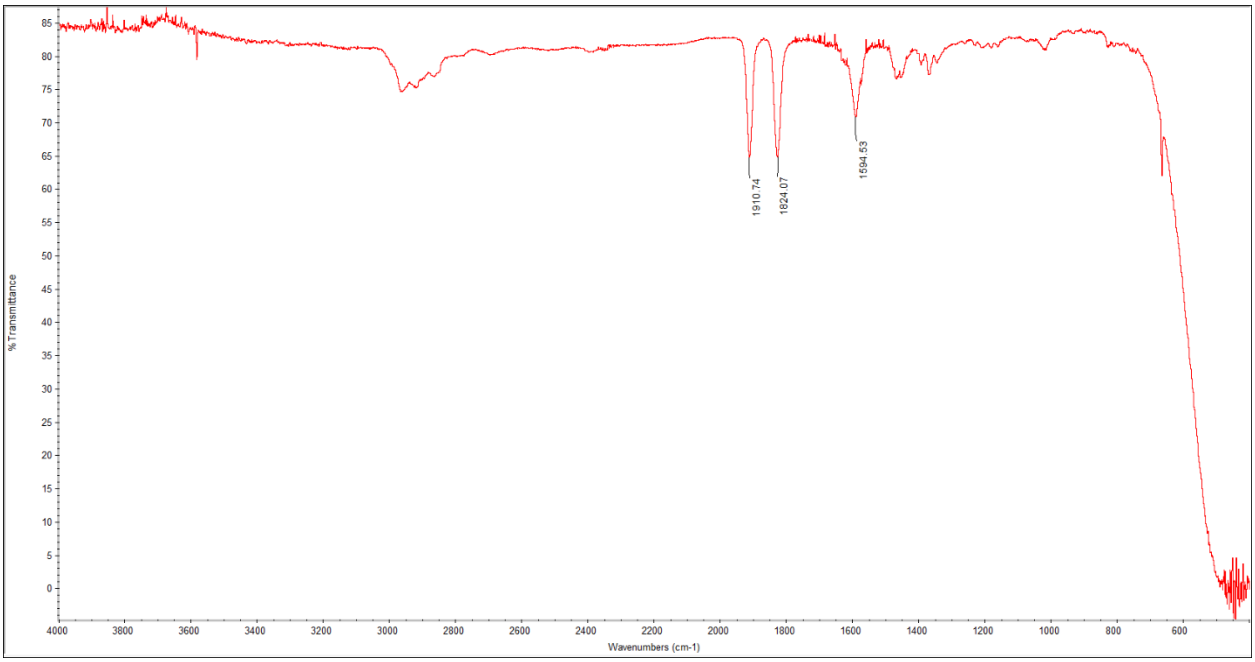


Figure S29. IR (NaCl thin film) spectrum of [Mn(PNNH)(OCOH)(CO)$_2$] (**5**).

4. Crystallographic Details

Table S1. Crystallographic data for complexes **3, 3'**, **4'** and **5'**.

Complex	**3**	**3'**	**4'**	**5'**
CCDC number	1938928	1938927	1938929	1938926
Formula	$2(C_{22}H_{34}MnN_2O_4P), C_7H_8$	$C_{22}H_{34}MnN_2O_4P$	$C_{21}H_{36}MnN_2O_2P$	$C_{22}H_{36}MnN_2O_4P$
Fw	1044.97	476.42	433.43	478.44
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a(Å)	18.0388(14)	11.0332(4)	12.5824(8)	12.713(3)
b(Å)	10.3918(9)	11.6911(4)	14.2411(7)	14.096(3)
c(Å)	14.3680(12)	17.3894(7)	13.1504(8)	13.603(3)
α (deg)	90(-)	90(-)	90(-)	90(-)
β (deg)	105.838(2)	96.460(4)	107.519(7)	102.34 (3)
γ (deg)	90(-)	90(-)	90(-)	90(-)
V(Å^3)	2591.1(4)	2228.82(14)	2247.1(2)	2381.3(8)
Z	2	4	4	4
D_{calc} (g/cm^3)	1.339	1.420	1.284	1.335
μ (mm^{-1})	0.605	5.750	0.676	0.651
λ(Å)	0.71073	1.54184	0.71073	0.71073
Data with $I>2\sigma(I)$, parameters	5243, 326	2073, 279	5272, 259	5257, 283
GOF on F^2	1.030	1.064	1.040	1.025
R1[a]	0.0355	0.0268	0.0439	0.0294
wR2 [b]	0.0718	0.0655	0.1103	0.0681

X-ray diffraction data were collected at 100 K. The diffraction data of **3** and **5'** were collected on a Bruker APEX-II Kappa CCD diffractometer with Mo radiation and processed with software Bruker KappaApex CCD. The diffraction data of **3'** and **4'** were collected using Cu- and Mo-

radiation accordingly on a Rigaku XtaLABPRO dual source diffractometer and processed with CrysAlisPRO.

The structures were solved by direct methods using SHELXT. All non-hydrogen atoms were further refined by SHELXL with anisotropic displacement parameters. Hydrogen atoms were assigned isotropic displacement parameters. Although the data for complex **3'** resolution is very low the refinement is stable and no restraints or constraints have been applied. In Complex **4'** one of the CO groups is disordered over two positions. The hydride was not seen and it was placed in calculated position and fixed during refinement. Crystallographic data and refinement parameters are summarized in Table S1.

5. Details of Catalytic experiments

In a steel autoclave, a manganese complex (**2** or **2'**, 0.05 mmol) and KOH (280 mg, 5 mmol) were dissolved in THF (2 mL). The autoclave was pressurized with CO_2 (30 bar) and H_2 (30 bar) and heated at 110 ^oC for 60 h. After 60 h, autoclave was cooled to room temperature and the gases were released slowly. The THF was removed in vacuum and the residue was dissolved in D_2O to which acetamide (30 mg, 0.5 mmol) was added as an internal standard. The yield of formate salt was calculated by the ^1H NMR spectroscopy using acetamide as an internal standard (Figures S30-S31).

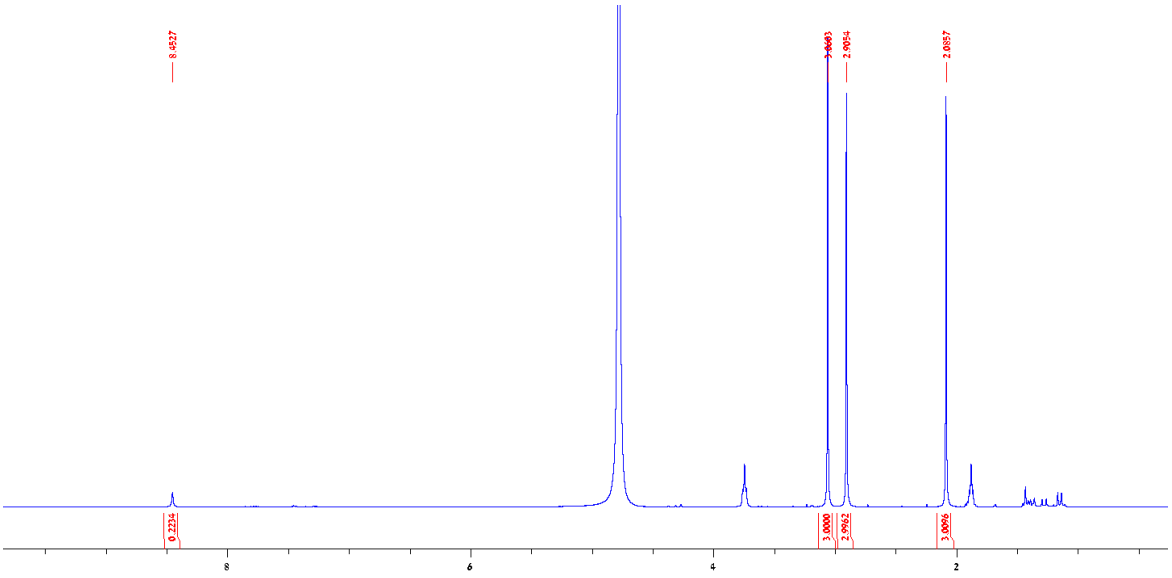


Figure S30. ^{1}H NMR spectrum of the crude reaction mixture for the formation of formate using complex **2** as a precatalyst. Signal at δ 8.452 is of formate and at δ 3.06, 2.90 and 2.08 are due to C*H*$_3$ protons of dimethyl acetamide.

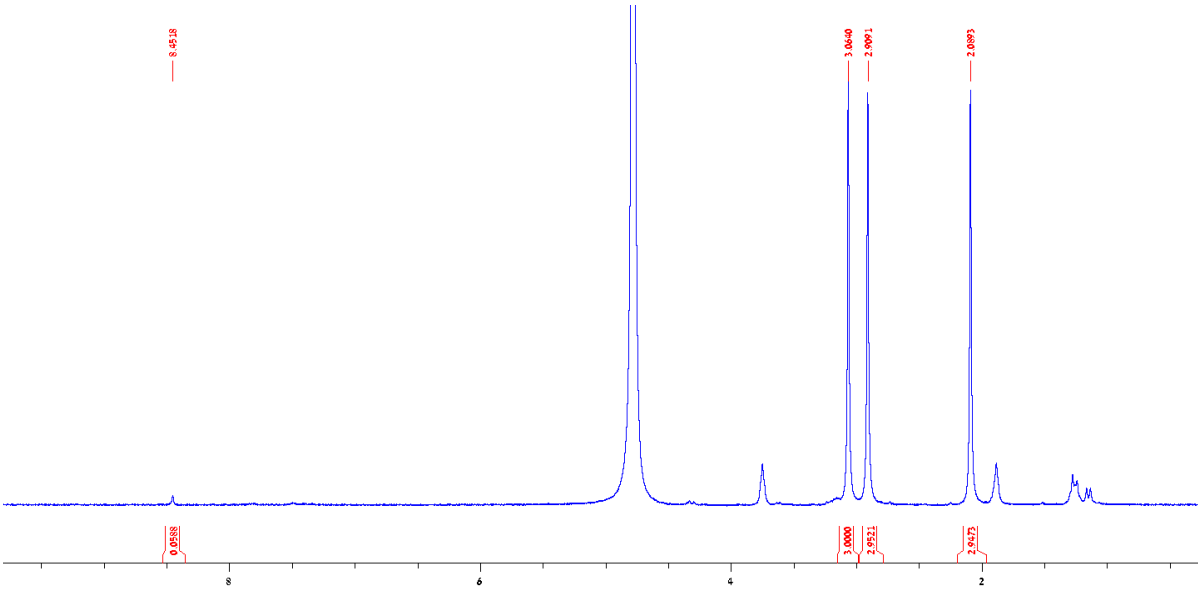


Figure S31. ^{1}H NMR spectrum of the crude reaction mixture for the formation of formate using complex **2'** as a precatalyst. Signal at δ 8.452 is of formate and at δ 3.06, 2.90 and 2.08 are due to C*H*$_3$ protons of dimethyl acetamide.

6. References

1. W. L. F. Armarego, D. D. Perrin, *Purification of Laboratory Chemicals*, 4th Edition, Butterworth-Heinemann: Oxford, *2000*.
2. (a) N. A. Espinosa-Jalapa, A. Nerush, L. J. W. Shimon, G. Leitus, L. Avram, Y. Ben-David, D. Milstein *Chem. Eur. J.* **2017**, *23*, 5934-5938; (b) N. A. Espinosa-Jalapa, A. Kumar, G. Leitus, Y. Diskin-Posner and D. Milstein, *J. Am. Chem. Soc.*, 2017, **139**, 11722–11725.
3. (a) F. Bertini, M. Glatz, N. Gorgas, B. Stoger, M. Peruzzini, L. F. Veiros, K. Kirchner and L. Gonsalvi, *Chem. Sci.*, 2017, **8**, 5024-5029; (b) F. Bertini, M. Glatz, N. Gorgas, B. Stoger, M. Peruzzini, L. F. Veiros, K. Kirchner and L. Gonsalvi, *ACS Catal.*, 2019, **9**, 632-639.