Pentacarbonylmethylmanganese(I) as a synthon for Mn(I) pincer catalysts

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General Methods. All reagents were procured from commercial sources and were used without further purification unless otherwise noted. Solvents were purified and collected from a PPT solvent system and stored over 3 Å molecular sieves. Molecular sieves were activated at 200 °C under vacuum (<100 mTorr) for 48 hours before use. Unless noted, all reactions were carried out under nitrogen in a VAC Genesis glove box or argon using standard Schlenk line techniques. Deuterated solvents were degassed by freeze-pump-thaw method and stored in the glove box in Strauss flasks. NMR experiments were performed on Varian Mercury-300 MHz, and Inova-400 MHz spectrometers. GCMS analysis of reaction mixtures was performed using an HP 5890 Series II GC coupled with a HP 5972 Series Mass Selective Detector. ATR-FTIR spectra were collected inside of a VAC Atmospheres Omni glovebox using a Bruker Alpha IR spectrometer with ALPHA-P Platinum ATR module (diamond crystal). Headspace analysis was obtained using a PerkinElmer Clarus 580 GC (thermal conductivity detector, Ar carrier gas). Hydrogenation reactions were carried out in a Parr instrument (4760 series, 100 mL) equipped with a heating mantle and temperature controller. Bis[(2-diisopropylphosphino]ethyl)amine (**H-PNP²**) was obtained from Sigma Aldrich. Ligands 4-methyl-2,6-bis(diphenylphosphinomethyl)phenol (**H-POP**), and 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine (**H-PNP¹**) were synthesized according to literature.[1,2]

Synthesis of MeMn(CO)$_5$. MeMn(CO)$_5$ was synthesized using modified literature procedure.[3] Inside a glovebox, sodium (147 mg, 6.4 mmol, 5 eq.) and potassium (25 mg, 0.64 mmol, 0.5 eq.) were added to 5 mL THF and allowed to stir vigorously for 10 mins. 500 mg $Mn_2(CO)_{10}$ (1.28 mmol, 1 eq.) was then added to the same THF solution. The reaction undergoes a series of color changes that end in a light grey-green color after overnight stirring. The reaction mixture was filtered using a glass-fritted funnel containing a plug of Celite (*Caution*: unreacted NaK should be handled with care*). The light green filtrate was collected and concentrated under vacuum to obtain a viscous green residue. 2 mL ether was added to the green residue and the resulting slurry of M[Mn(CO)$_5$] (M = Na, K) was transferred to a Schlenk flask and sealed with a gas-tight septum and brought out of the glovebox. The flask was cooled to 0 °C using an ice bath and an excess CH_3I (200 μL) was slowly added to the flask using a gas tight syringe (≈ 5 minutes). The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed under a flow of argon (the MeMn(CO)$_5$ product is sufficiently volatile that care should be taken not to use vacuum or warm bath). A cold finger (circulation was controlled to 0° C) was attached to the Schlenk flask and the flask evacuated and the product was allowed to sublime onto the cold finger under static vacuum at room temperature for 2 h. The flask was transferred to a glovebox and the vacuum released. The colorless crystals of MeMn(CO)$_5$ were transferred from the cold finger to a tared vial (TOC graphic) and stored at -35 °C (368 mg, 68 % yield). ^{1}H-NMR (d_6-benzene, 300 MHz, 298 K): δ -0.26 ppm (s, 3H, CH_3).

*When MeMn(CO)$_5$ is prepared as described, the celite pad containing the unreacted NaK is placed in a glass vial and covered in toluene. This vial is then cooled to 0 °C in a fume hood and treated dropwise with isopropanol.

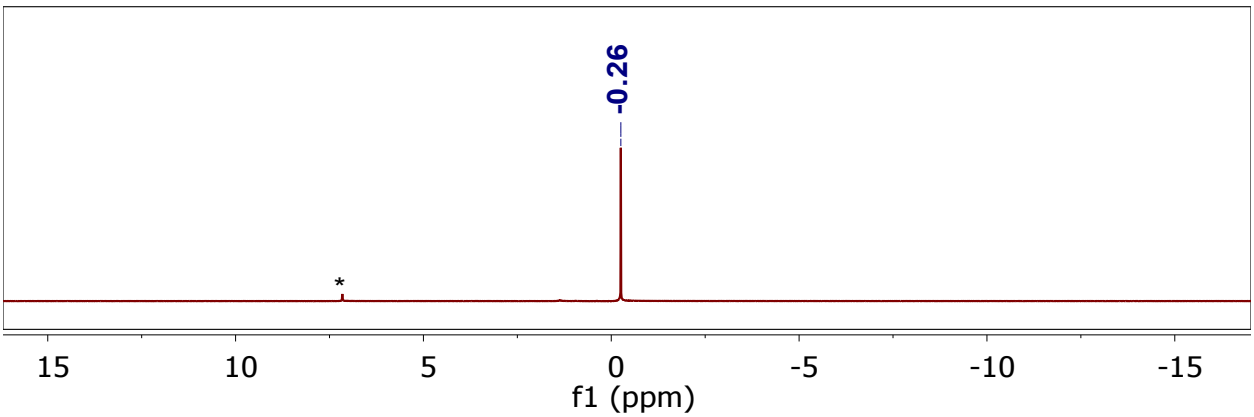

Figure S1. ^{1}H-NMR spectrum of MeMn(CO)$_5$ in d_6-benzene*.

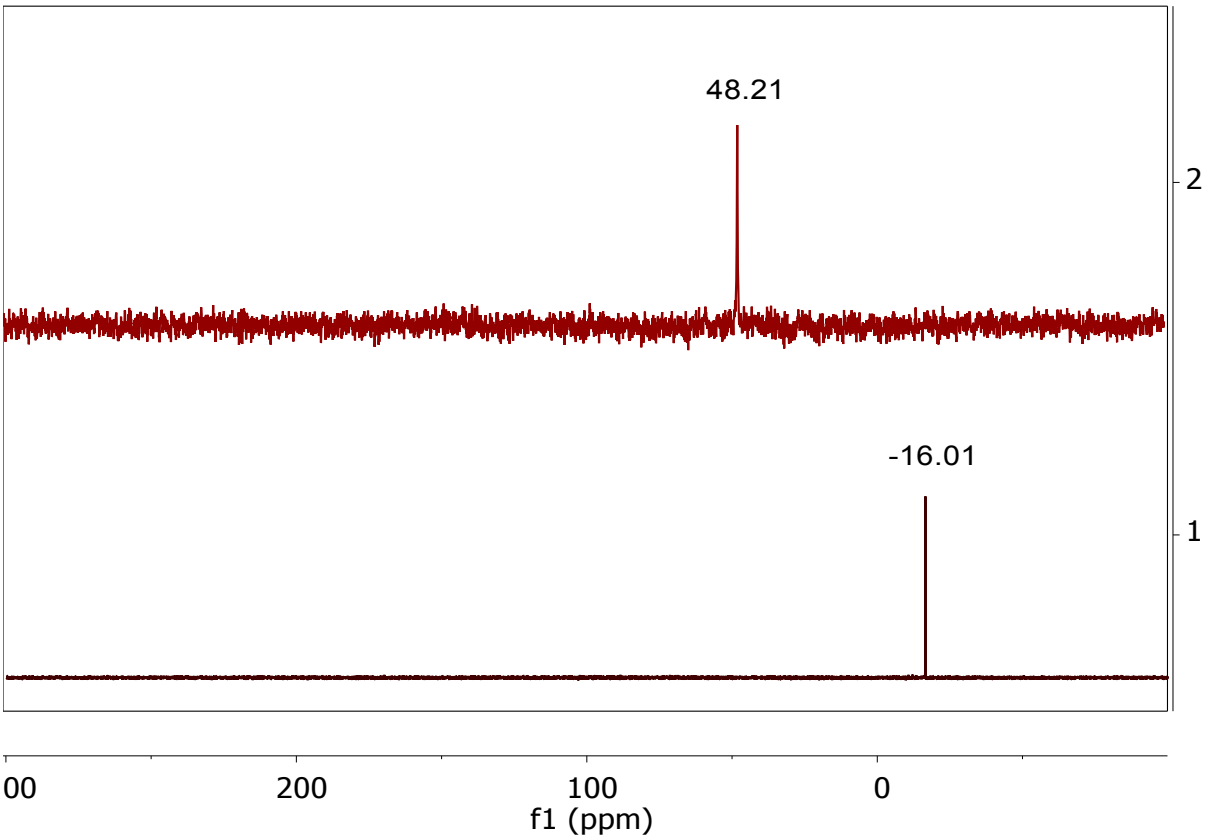

Figure S2. ^{31}P-NMR spectra showing reaction of **H-POP** with $MeMn(CO)_5$; (1) before addition of $MeMn(CO)_5$, and (2) after 2 h of addition of $MeMn(CO)_5$. The new peak at δ 48.21 ppm is assigned to **H-POP**$\{Mn(CO)_4(OCMe)\}_2$.

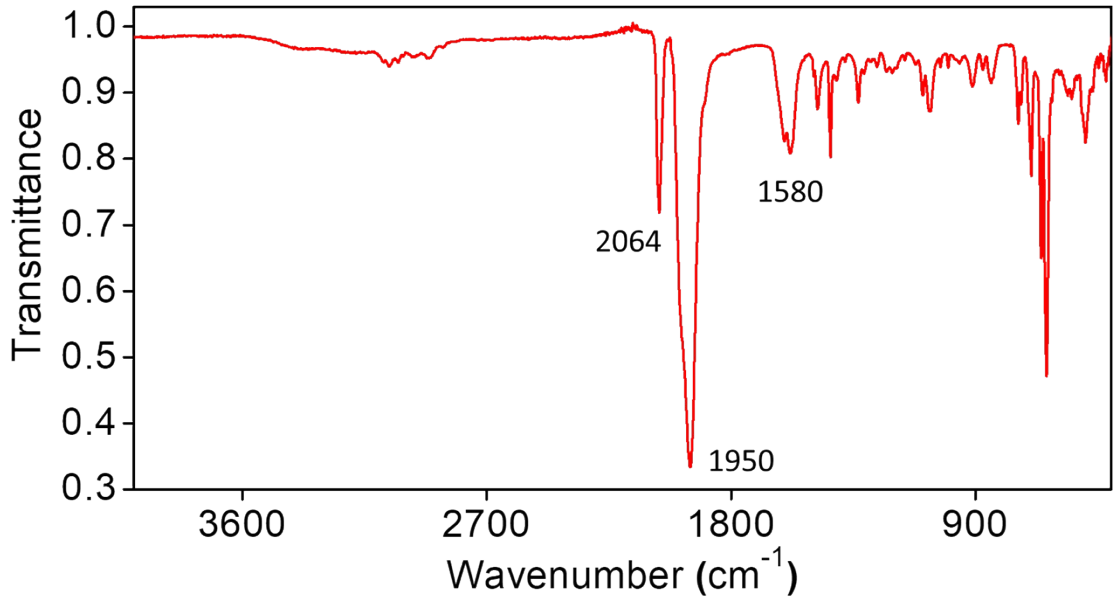

Figure S3. ATR-FTIR spectrum of **H-POP**$\{Mn(CO)_4(OCMe)\}_2$.

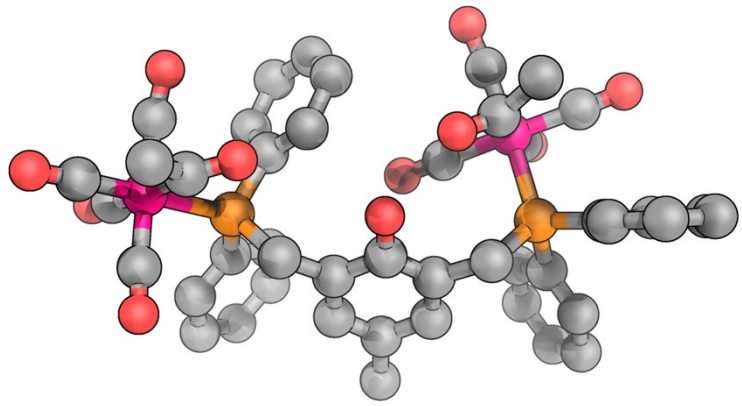

Figure S4. Connectivity structure of **H-POP**{$Mn(CO)_4(OCMe)$}$_2$ determined with XRD.

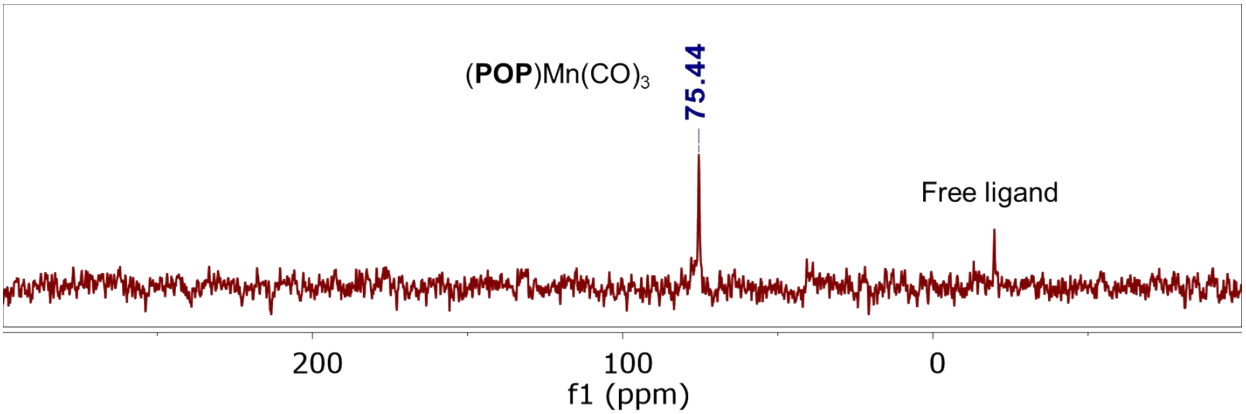

Figure S5. ^{31}P-NMR spectrum of the reaction mixture of 1:1 **H-POP** and $MeMn(CO)_5$ in toluene after heating at 120 °C for 12 h (matches literature).[1]

Synthesis of ***H-POP^{OMe}***. The synthesis route was adapted from literature.[1] In a 50 mL round bottom flask maintained at 0 °C and opened to air, dimethylamine (40% aq, 8.2 mL, 64.8 mmol) and *p*-methoxyphenol (2.5 g, 20 mmol) were mixed and formaldehyde (37% aq, 4.2 mL, 56 mmol) was added dropwise. The mixture was allowed to come to room temperature and then refluxed at 95 °C for 3h. After cooling to rt, solid NaCl was added to the reaction mixture and stirred for 10 mins to separate out the orange-brown organic layer. The top layer was collected and dried over anhydrous Na_2SO_4 to yield 2,6-bis[(dimethylamino)methyl]-4-methoxyphenol, **H-NON^{OMe}**. The crude oil product thus obtained was used for phosphination without further purification. Inside a glovebox, 100 mg of **H-NON^{OMe}** (0.42 mmol, 1 eq.) was mixed with Ph_2PH (235 mg, 1.26 mmol, 3 eq.) and transferred to a Strauss tube. The solution was subjected to one freeze-pump-thaw cycle and heated at 150 °C for 12 h. The solution was allowed to cool to room temperature and the reaction mixture was transferred to a tared vial using diethyl ether. Diethyl ether was removed under vacuum and petroleum ether (10 mL) was added to the mixture and vigorously stirred for 30 mins to extract out the unreacted Ph_2PH. The mixture was cooled to -35 °C and decanted, while cold, to remove the pet ether wash. This wash procedure was repeated 5 times and the viscous oil left behind was dried under vacuum during which it formed a white thick foam which eventually turned into a sticky transparent gel of **H-POP^{OMe}** (101 mg, 46% yield). ^{1}H-NMR (d_2-DCM, 300 MHz, 298 K, ppm): δ 3.36 (s, 3H, OCH_3), 3.41 (s, 4H, CH_2), 5.28 (s, 1H, O*H*), 6.14 (s, 2H, phenol ring C*H*), 7.3-7.4 (20H, (C_6H_5)$_2$P). ^{31}P-

NMR (d_2-DCM, 121 MHz, 298 K, ppm): δ -16.95 ppm. Note: The pet ether washes collected was pumped down under vacuum to recover the unreacted diphenylphosphine.

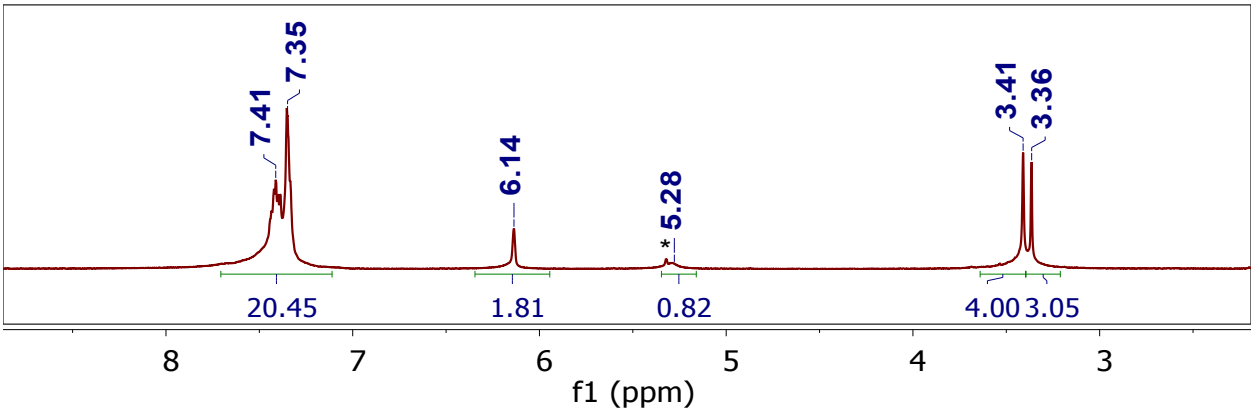

Figure S6. ^{1}H-NMR spectrum of **H-POP^{OMe}** in d_2-DCM*.

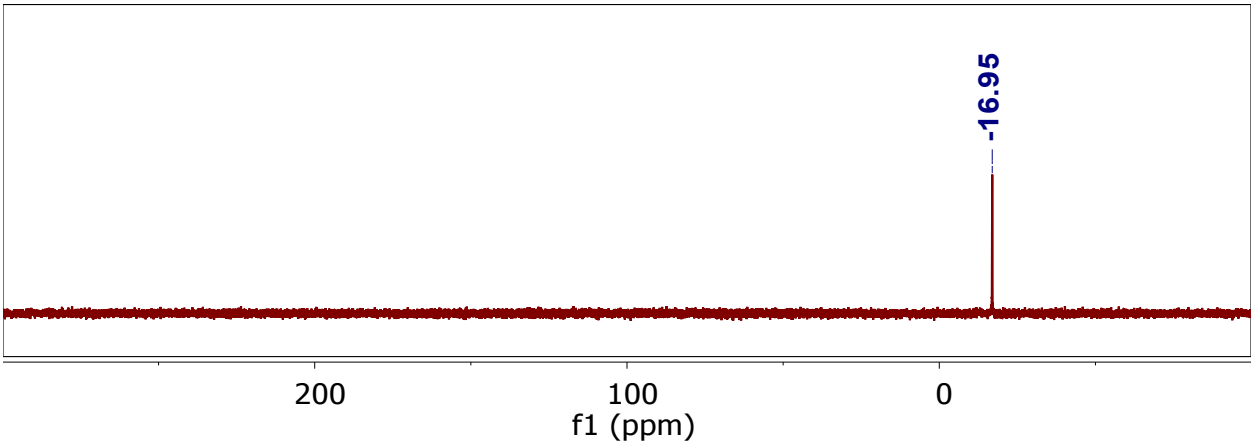

Figure S7. ^{31}P-NMR spectrum of **H-POP^{OMe}** in d_2-DCM.

Synthesis of ***H-POP$^{iPr,p\text{-}Me}$***. The synthesis route was adapted from literature.[1] 2,6-bis[(dimethylamino)methyl]-4-methylphenol, **H-NON**, (100 mg, 0.45 mmol, 1 eq.) was mixed with ^{i}Pr$_2$PH (160 mg, 1.35 mmol, 3 eq.) in a Straus tube. The solution was subjected to one cycle of freeze-pump-thaw and heated at 150 °C for 12 h. The excess ^{i}Pr$_2$PH was distilled out to yield pure **H-POP$^{iPr,p\text{-}Me}$** as a light-yellow oil (130 mg, 78% yield). ^{1}H-NMR (d_1-CHCl$_3$, 300 MHz, 298 K, ppm): δ 1.02-1.11 {24H, [(C*H*$_3$)$_2$CH]$_2$P}, 1.78 {4H, [(CH$_3$)$_2$C*H*]$_2$P}, 2.20 (s, 3H, *p*-cresol C*H*$_3$), 2.81 (s, 4H, C*H*$_2$), 6.71 (s, 2H, *p*-cresol C*H*). ^{31}P-NMR (d_1-CHCl$_3$, 121 MHz, 298 K, ppm): δ 2.27 ppm.

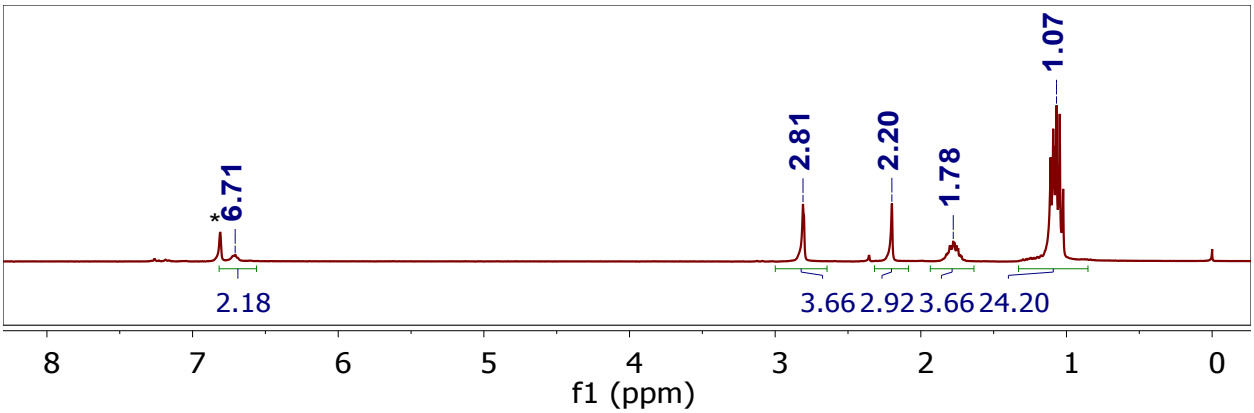

Figure S8. ^{1}H-NMR spectrum of **H-POP$^{iPr,p\text{-}Me}$** in d_1-$CHCl_3$*.

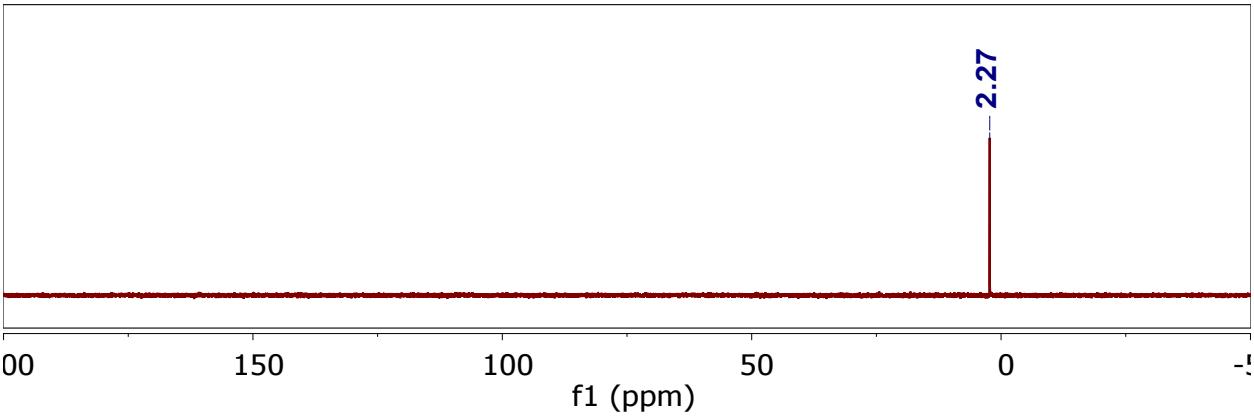

Figure S9. ^{1}H-NMR spectrum of **H-POP$^{iPr,p\text{-}Me}$** in d_1-$CHCl_3$.

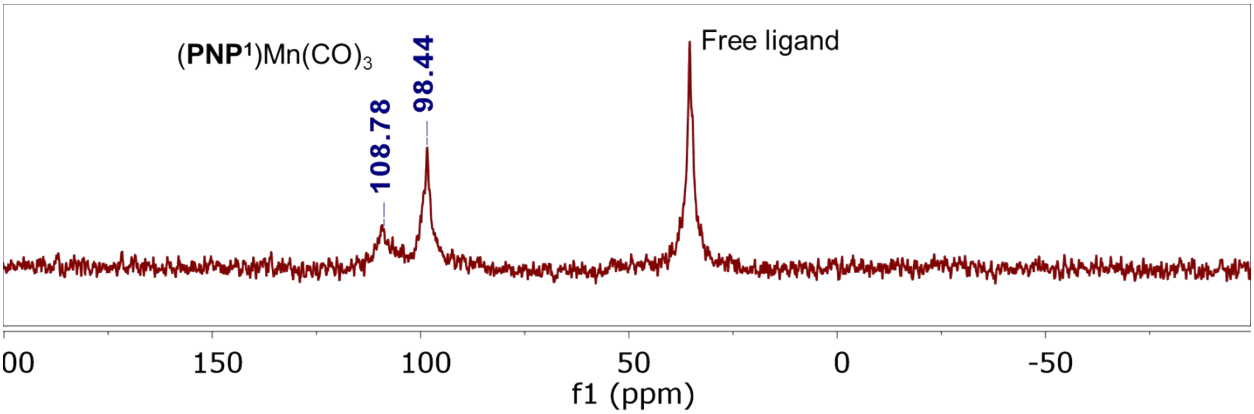

Figure S10. ^{31}P-NMR spectrum of the reaction mixture of 1:1 **H-PNP^{1}** and $MeMn(CO)_5$ in toluene after heating at 120 °C for 12 h.

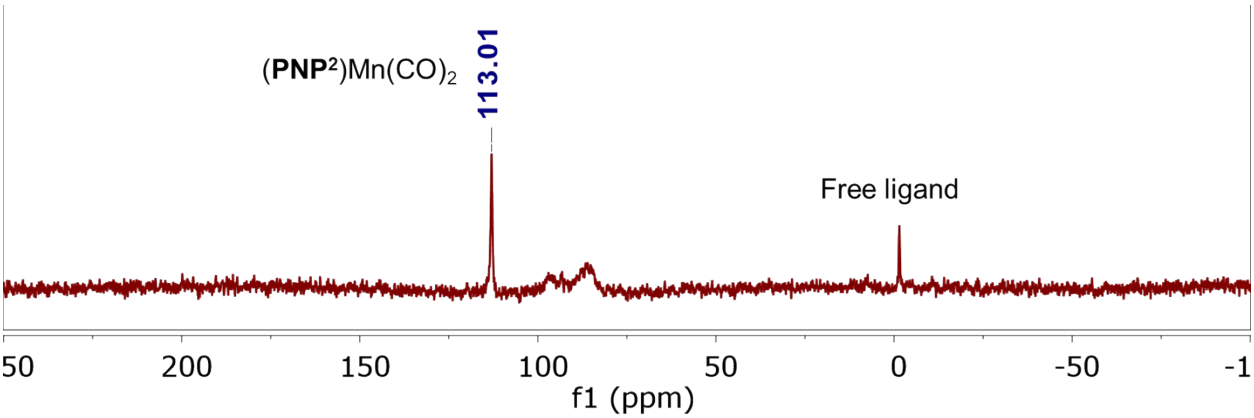

Figure S11. ^{31}P-NMR spectrum of the reaction mixture of 1:1 **H-PNP²** and $MeMn(CO)_5$ in toluene after heating at 120 °C for 12 h.

*Mn(I) catalyzed Tishchenko reaction with $MeMn(CO)_5$ and **H-POP***. Similar catalysis conditions as in literature was employed.[1] To a solution containing 0.01 mmol of $MeMn(CO)_5$ and **H-POP** in d_8-toluene (500 μL) was added 26 μL (0.25 mmol) of benzaldehyde. The solution was transferred to a J-Young tube and the reaction mixture was heated at 120 °C for 24 h. The yield of benzyl benzoate was determined using ^{1}H-NMR from the integration (*I*) of the signals at 5.13 ppm (s, CH_2, benzyl benzoate) and 9.60 (s, C*H*O, benzaldehyde). Yield calculation was done as follows:

$$\%\ yield = \frac{I_{5.13\ ppm}}{I_{5.13\ ppm} + I_{9.60\ ppm}} \times 100$$

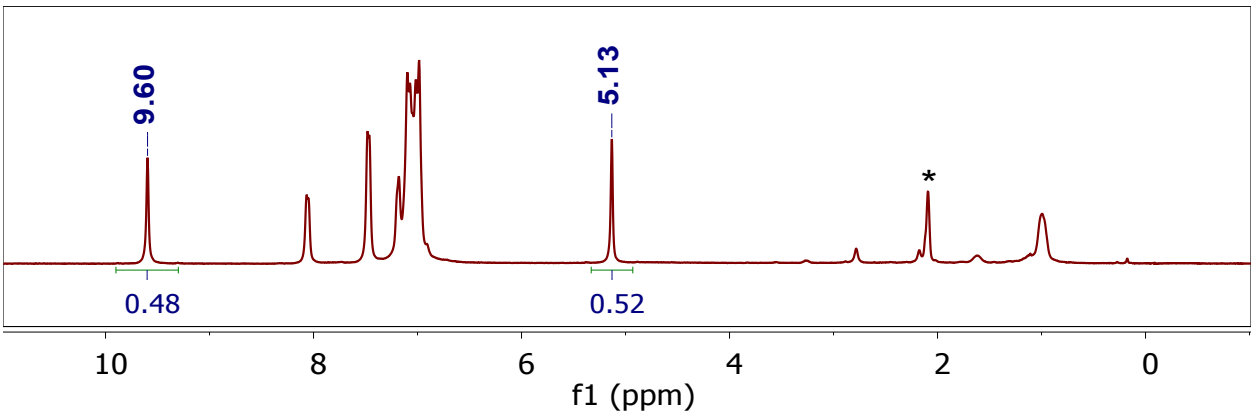

Figure S12: ^{1}H-NMR spectrum in d_8-toluene* obtained for the conversion of benzaldehyde to benzyl benzoate catalyzed by *in situ* generated (**POP$^{iPr,p\text{-}Me}$**)$Mn(CO)_3$ from $MeMn(CO)_5$ and **H-POP$^{iPr,p\text{-}Me}$**.

*Mn(I) catalyzed coupling of benzylamine and benzyl alcohol with $MeMn(CO)_5$ and **H-PNP¹***. Similar catalysis conditions as in literature was employed.[4] To a solution containing 0.015 mmol of $MeMn(CO)_5$, and **H-PNP¹** in benzene (2 mL) in a glass pressure tube (25 mL) was added 0.5 mmol of benzyl alcohol, and benzylamine. The mixture was heated at 135 °C for 60 h in a fume hood. The reaction mixture was then cooled in an ice bath and the pressure was slowly released. 0.5 mmol (53 μL) of toluene was added to the mixture. The solution was quickly filtered through a small celite plug. 100 μL of the reaction mixture was mixed with 400 μL $CDCl_3$ and analyzed by ^{1}H-NMR using the toluene as an internal standard.

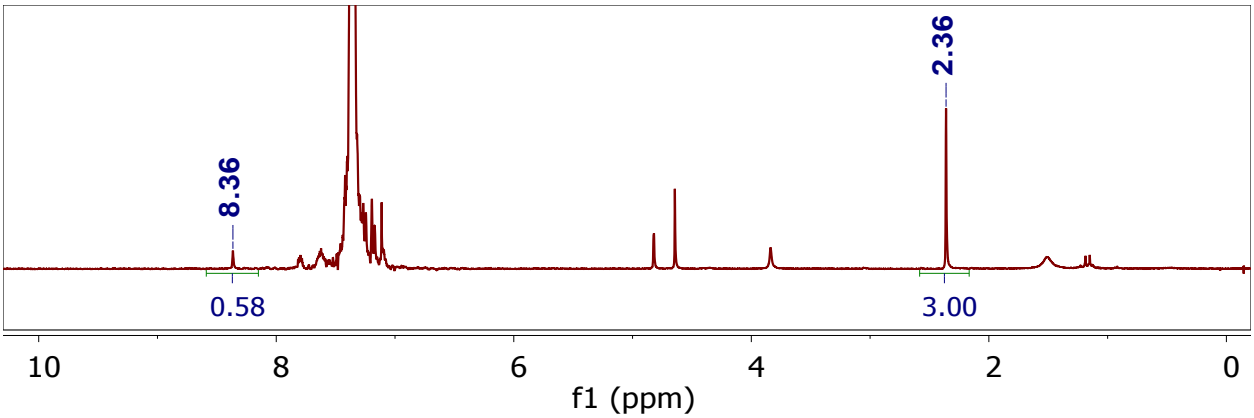

Figure S13: ^{1}H-NMR spectrum in d_1-$CHCl_3$ obtained for the coupling of benzylamine and benzyl alcohol catalyzed by *in situ* generated (**PNP^1**)$Mn(CO)_2$ from $MeMn(CO)_5$ and **H-PNP^1**.

*Mn(I) catalyzed hydrogenation of benzaldehyde with $MeMn(CO)_5$ and **H-PNP^2***. Similar catalysis conditions as in literature were employed.[5] To a solution containing 0.01 mmol of $MeMn(CO)_5$, and **H-PNP^2** in toluene (1 mL) was added 106 mg of benzaldehyde (1 mmol). The solution was transferred to the 100 mL Parr hydrogenator vessel under a flow of argon and quickly sealed. The hydrogenator was purged 3 times with hydrogen and then pressurized to 50 bar H_2. The mixture was heated at 100 °C for 24 h. After the reaction time the reactor was cooled to room temperature, slowly depressurized, and the solution was transferred to a vial open to air. 100 μL of the reaction mixture was mixed with 400 μL $CDCl_3$ and analyzed by ^{1}H-NMR, which showed complete conversion of benzaldehyde (δ 9.6 ppm, s, C*H*O) to benzyl alcohol (δ 4.6 ppm, s, CH_2).

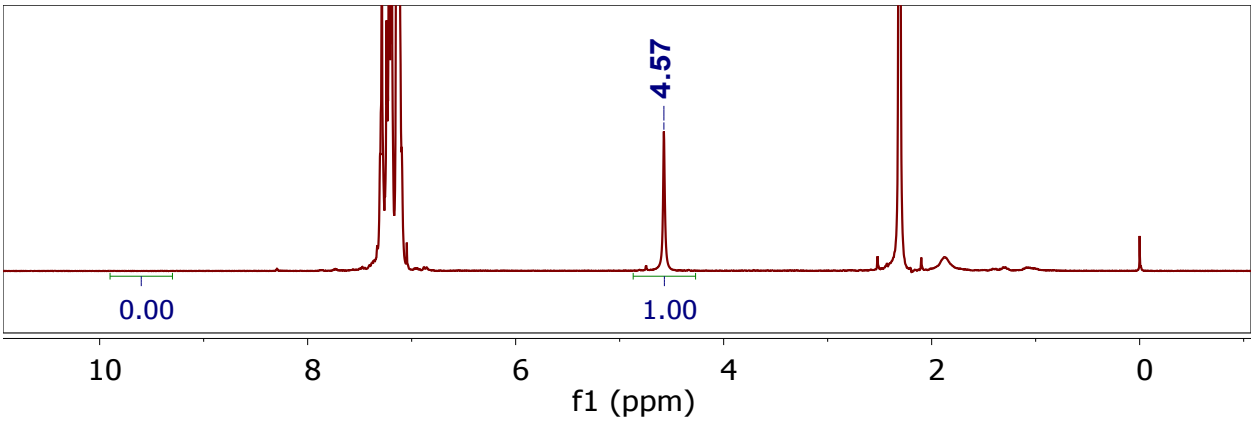

Figure S14: ^{1}H-NMR spectrum in d_1-$CHCl_3$ obtained for the hydrogenation of benzaldehyde to benzyl alcohol catalyzed by *in situ* generated (**PNP^2**)$Mn(CO)_2$ from $MeMn(CO)_5$ and **H-PNP^2**.

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