Bisphosphine Phenol and Phenolate Complexes of Mn(I): Manganese(I) Catalyzed Tishchenko Reaction

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Crystallographic methods

Low-temperature X-ray diffraction data for **1** (Rlacy7), **1$_2$** (Rlacy8), **2** (Rlacy13), and **1$_2$H·OTf** (Rlacy18) were collected on a Rigaku XtaLAB Synergy diffractometer coupled to a Rigaku Hypix detector with either Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.54184 Å), from a PhotonJet micro-focus X-ray source at 100 K. The diffraction images were processed and scaled using the CrysAlisPro software.[1] The structures were solved through intrinsic phasing using SHELXT[2] and refined against F^2 on all data by full-matrix least squares with SHELXL[3] following established refinement strategies.[4] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bound to carbon were included in the model at geometrically calculated positions and refined using a riding model. Hydrogen atoms bound to oxygen were located in the difference Fourier synthesis and subsequently refined semi-freely with the help of distance restraints. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the Ueq value of the atoms they are linked to (1.5 times for methyl groups).

General Methods. All manipulations were performed under a dry, anaerobic argon atmosphere using Schlenk line techniques or in a nitrogen-filled VAC Atmosphere Genesis Glovebox unless otherwise stated. Reagents were purchased from commercial vendors and used without further purification unless specified. 3 Å molecular sieves were activated by heating ≥ 200 °C under vacuum (≈100 mTorr) for 48 h. Anhydrous solvents were purified using a Pure Process Technology solvent purification system and stored in a glovebox over 3 Å molecular sieves for at least 24 h before use. ^{1}H NMR spectra were recorded on a Varian Mercury-300 or Varian Inova-400 MHz spectrometer. Values of chemical shifts (ppm) are referenced to the residual solvent proton resonances. ^{31}P NMR spectra were recorded on a Varian Mercury-300 or Varian Inova-400 MHz spectrometer and referenced to an internal standard (capillary insert) of H_3PO_4 in D_2O. GCMS analysis of reaction mixtures was performed using an HP 5890 Series II GC coupled with a HP 5972 Series Mass Selective Detector. Transmission and 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). CHN combustion analyses were performed by Robertson Microlit Laboratories, NJ USA. *2,6-bis[(dimethylamino)methyl]-4-methylphenol (**H-NON**)* was synthesized open to air, following a reported procedure.[5]

*Synthesis of 4-methyl-2,6-bis[(diphenylphosphanyl)methyl]phenol (**H-POP**).* The ligand was synthesized using modified literature procedure.[6] Diphenylphosphine (3.352 g, 18 mmol, 4 eq.) and **H-NON** (1 g, 4.5 mmol, 1 eq.) were mixed together in a Schlenk flask (50 mL) and stirred overnight at 150 °C under argon. The flask was allowed to cool to room temperature and the reaction mixture was transferred to a 250 mL round bottom flask inside a glovebox. Pet ether (50 mL) was added to the mixture and vigorously stirred for 30 mins to extract out the unreacted $HPPh_2$ into the pet ether layer. 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 (solid at -35 °C) thus obtained was dried under vacuum during which it formed a white thick foam which eventually turned into a sticky transparent gel. The sticky material thus obtained showed single peak corresponding to the **H-POP** ligand in ^{31}P-NMR and was hence used without further purification (1.92 g, 85% yield). ^{1}H-NMR (d_3-MeCN, 300 MHz, 298 K, ppm): δ 1.84 (s, 3H, CH_3), 3.41 (s, 4H, CH_2), 6.19 (s, 1H, OH), 6.38 (s, 2H, *p*-cresol ring CH), 7.3-7.4 (20H, (C_6H_5)$_2$P). ^{31}P-NMR (d_3-MeCN, 121 MHz, 298 K, ppm): δ -15.9 ppm. ^{13}C-NMR (d_3-MeCN, 101 MHz, 298 K, ppm): δ 20.26 (s), 30.09 (d, J = 14.1 Hz), 101.06 (s), 124.69 (dd, J = 1 Hz, 6.1 Hz), 129.31 (d, J = 7.1 Hz), 129.74 (s), 130.23 (dd, J = 2 Hz, 8.1 Hz), 133.67 (d, J = 19.2 Hz), 139. 39 (d, 15.1 Hz), 159.47 (s). Note: The **H-POP** ligand is air sensitive and converts to the corresponding phosphine oxide when exposed to air. The pet ether washes collected was pumped down under vacuum to recover the unreacted diphenylphosphine (contains trace **H-POP** ligand).

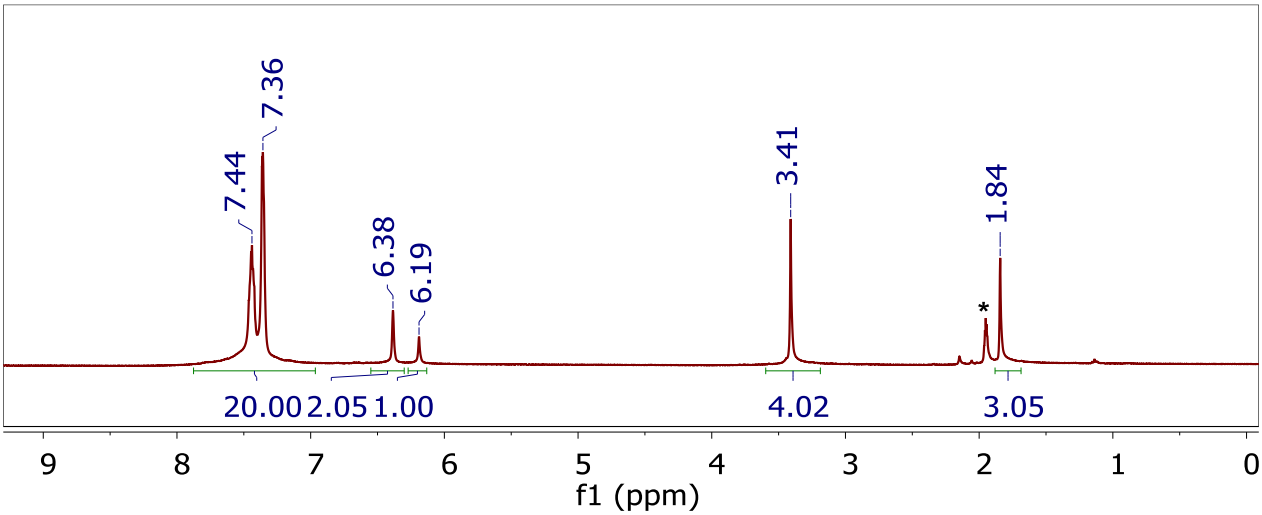

Figure S1. Room temperature ^{1}H-NMR spectrum of **H-POP** in d_3-MeCN*.

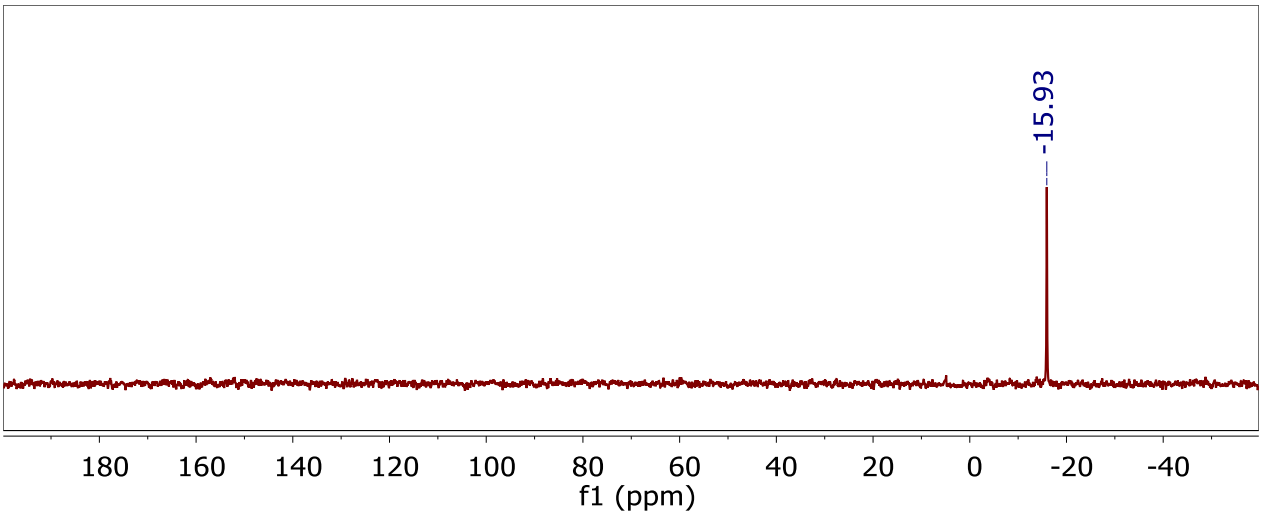

Figure S2. Room temperature ^{31}P-NMR spectrum of **H-POP** in d_3-MeCN.

*Synthesis of **POP**Mn(CO)$_3$ (**1**) and {**POP**Mn(CO)$_3$}$_2$ (**1$_2$**).* Anhydrous Me_3NO (45 mg, 0.6 mmol, 6 eq.) was added to a solution of $Mn_2(CO)_{10}$ (39 mg, 0.1 mmol, 1 eq.) in DCM (2 mL) and allowed to stir for 2 h. The reaction mixture was cooled to -35 °C and a cold solution of **H-POP** ligand (97 mg, 0.19 mmol) in DCM (1 mL) was added to the reaction. After stirring the mixture for another 16 h, the solution was filtered. The filtrate was concentrated to 1 mL, layered under ether and stored at -35 °C to yield orange crystals of **1** suitable for xray diffraction (50 mg, 39% crystalline yield). ^{1}H-NMR (d_2-DCM, 300 MHz, 298 K, ppm): δ 2.23 (s, 3H, CH_3), 3.82 (m, 4H, CH_2), 6.98 (s, 2H, *p*-cresol ring C*H*), 7.4-7.7 (20H, (C$_6H_5$)$_2$P). ^{31}P-NMR (d_2-DCM, 121 MHz, 298 K, ppm): δ 75.69 ppm. FTIR-ATR (cm^{-1}): 2027, 1937, 1886. Anal Calcd. (found) for **1**·(CH$_2$Cl$_2$)$_{1/6}$*, $C_{36}H_{29}MnO_4P_2$·(CH$_2$Cl$_2$)$_{0.17}$: %C 66.15 (66.01); %H 4.50 (4.84); %N 0.00 (none found). *Compound **1** was isolated as a crystalline material containing 1/6th DCM for every molecule of **1** (figure S4).

Layering the filtrate under ether and storing at room temperature instead of -35 °C yielded yellow crystals of ***1$_2$*** (40 mg, 31% crystalline yield). Crystals suitable for xray diffraction were obtained from repeating the synthesis in THF, layering the filtrate under hexane and storing at -35 °C. ^{1}H-NMR (d_2-DCM, 300 MHz, 298 K, ppm): δ 1.87 (s, 3H, CH_3), 3.54 (d, 2H, CH_2), 4.19 (d, 2H, CH_2), 5.50 (s, 1H, *p*-cresol ring C*H*), 6.76 (s, 1H, *p*-cresol ring C*H*), 7.4-7.9 (20H, (C$_6H_5$)$_2$P). ^{31}P-NMR (d_2-DCM, 121 MHz, 298 K, ppm): δ 64.41, 77.61 ppm. FTIR-ATR (cm^{-1}) 2035, 1946, 1886, 1845. Anal Calcd. (found) for **1$_2$**, $C_{72}H_{58}Mn_2O_8P_4$: %C 67.30 (67.08); %H 4.55 (4.90); %N 0.00 (none found).

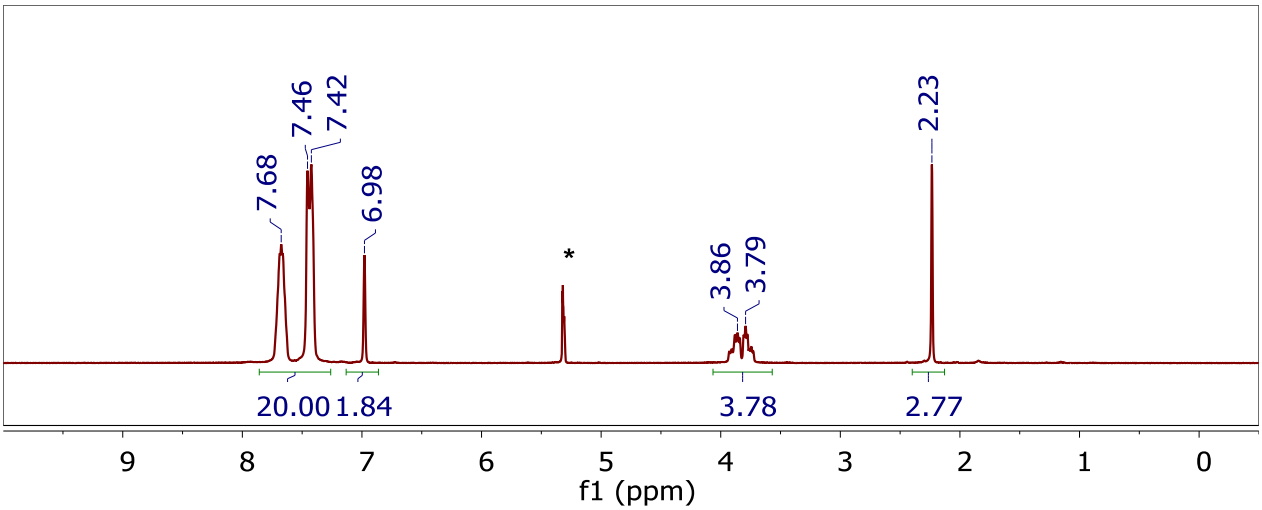

Figure S3. Room temperature ^{1}H-NMR spectrum of **POP**Mn(CO)$_3$ (**1**) in d_2-DCM*.

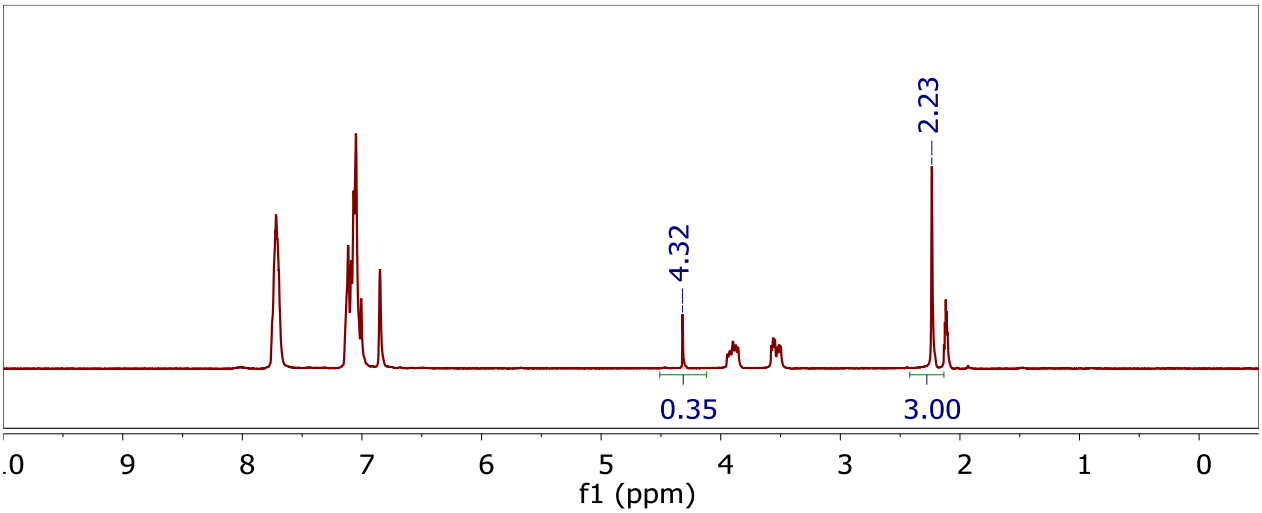

Figure S4. *Room temperature ^{1}H-NMR spectrum of **POP**Mn(CO)$_3$ (**1**) in d_8-toluene. Note the presence of DCM, which corresponds to 1 DCM to every 6 molecules of **1** consistent with our CHN analysis.

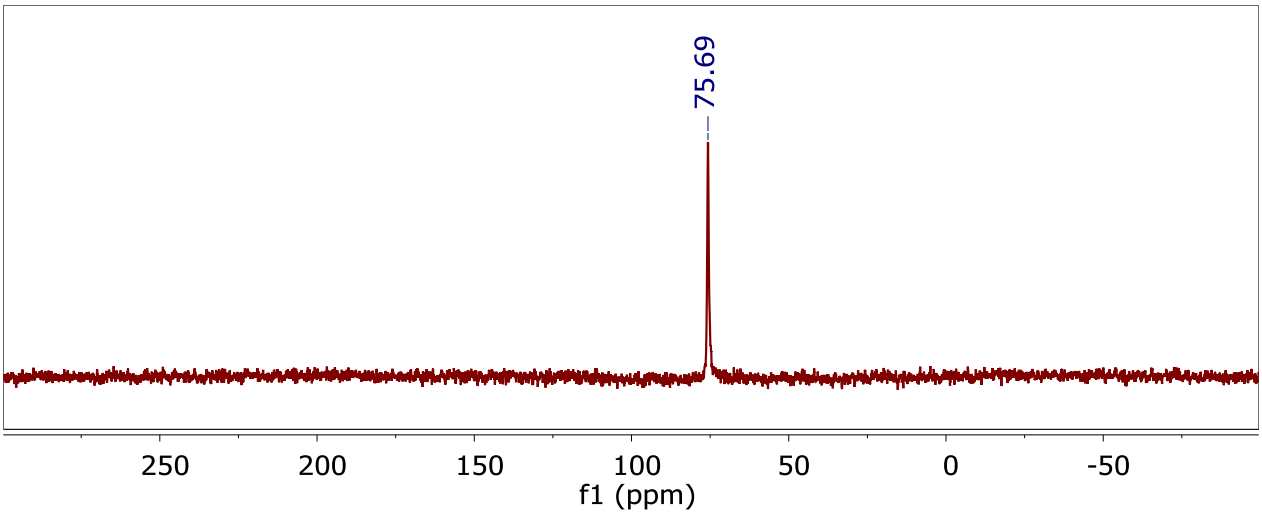

Figure S5. Room temperature ^{31}P-NMR spectrum of **POP**Mn(CO)$_3$ (**1**) in d_2-DCM.

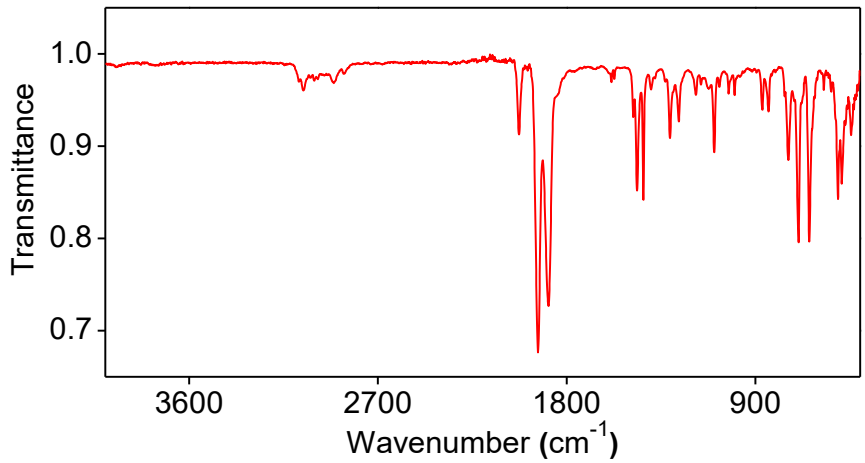

Figure S6. ATR-FTIR spectrum of **POP**Mn(CO)$_3$ (**1**).

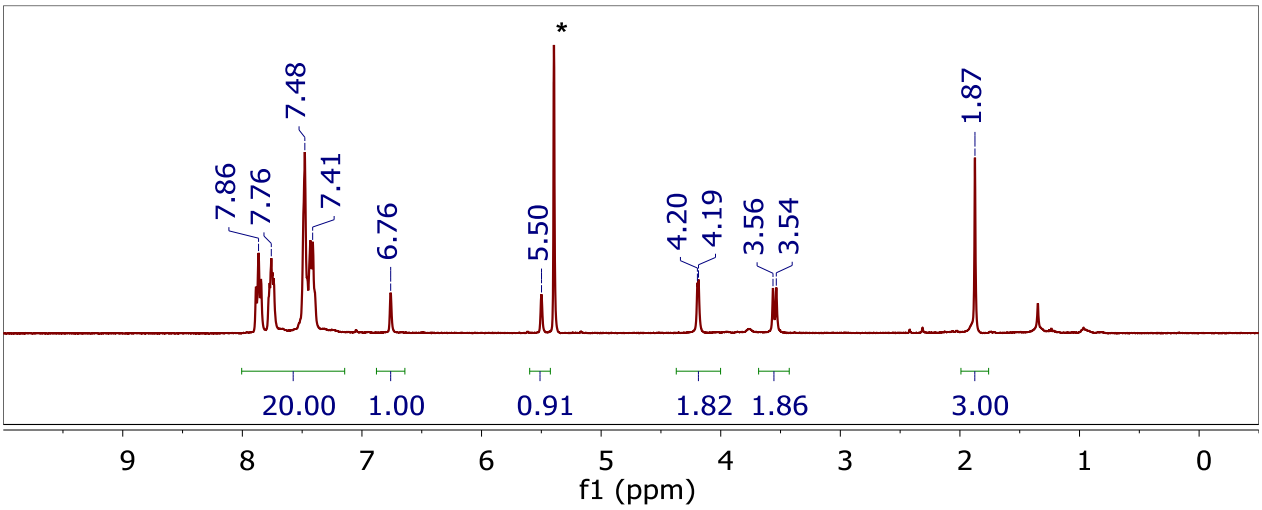

Figure S7. Room temperature ^{1}H-NMR spectrum of {**POP**Mn(CO)$_3$}$_2$ (**1$_2$**) in d_2-DCM*.

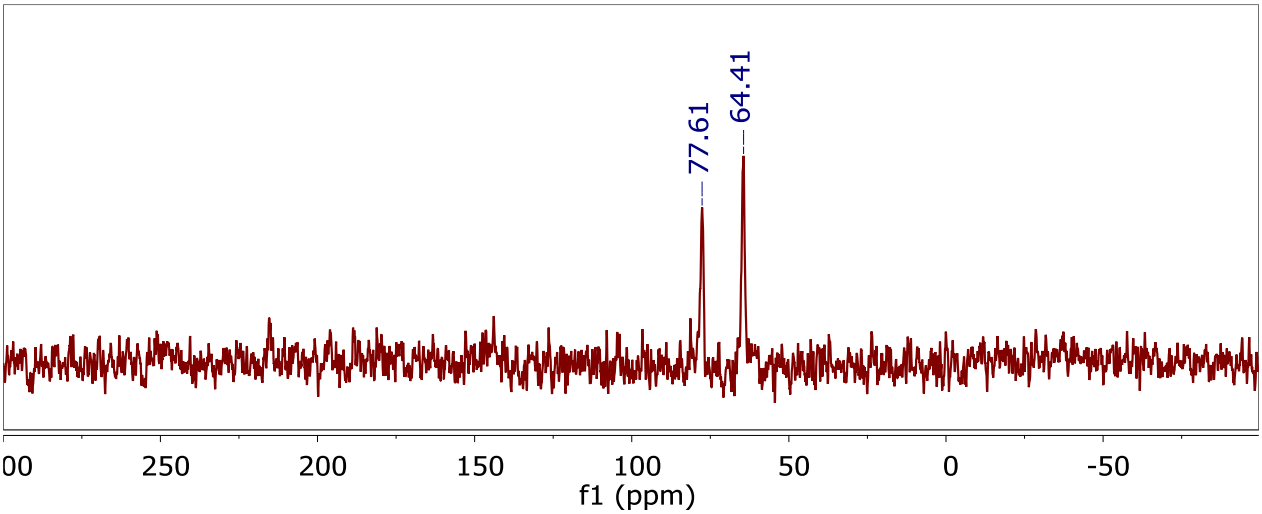

Figure S8. Room temperature ^{31}P-NMR spectrum of {**POP**Mn(CO)$_3$}$_2$ (**1$_2$**) in d_2-DCM.

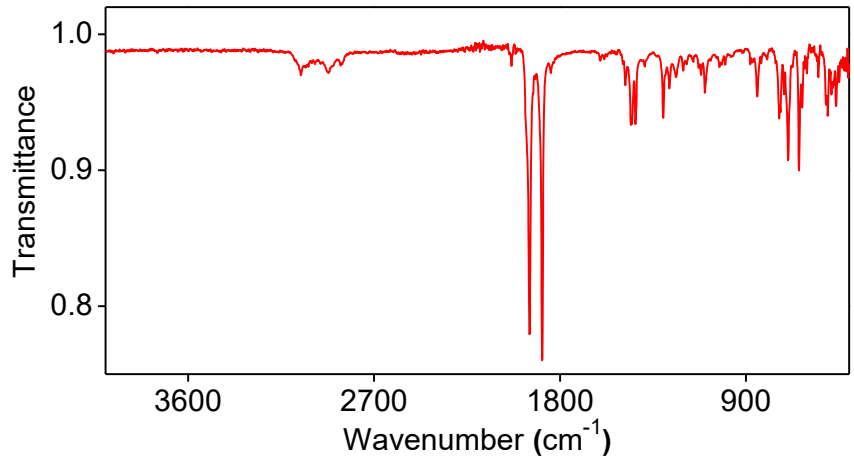

Figure S9. ATR-FTIR spectrum of {**POP**Mn(CO)$_3$}$_2$ (**1$_2$**).

*Synthesis of {**H-POP**}{Mn(CO)$_4$Br}$_2$ (**2**).* A solution of **H-POP** (100 mg, 0.2 mmol, 1 eq.) and MnBr(CO)$_5$ (100 mg, 0.4 mmol, 2 eq.) in THF (5 mL) was stirred for 12 h at room temperature. The solution was layered under hexane to yield light orange crystals of **2**•THF (172 mg, 80% crystalline yield). ^{1}H-NMR (d_2-DCM, 300 MHz, 298 K, ppm): δ 1.48 (s, 3H, C*H*$_3$), 3.94 (d, 4H, C*H*$_2$), 5.47 (s, 2H, *p*-cresol ring C*H*), 6.52 (s, 1H, O*H*), 7.4-7.7 (20H, (C$_6$*H*$_5$)$_2$P). ^{31}P-NMR (d_2-DCM, 121 MHz, 298 K, ppm): δ 40.4 ppm. FTIR-ATR (cm^{-1}): 3310, 2086, 1996, 1951, 1911. Anal Calcd. (found) for **2**•THF, $C_{45}H_{38}Br_2Mn_2O_{10}P_2$: %C 50.49 (50.91); %H 3.58 (3.63); %N 0.00 (none found).

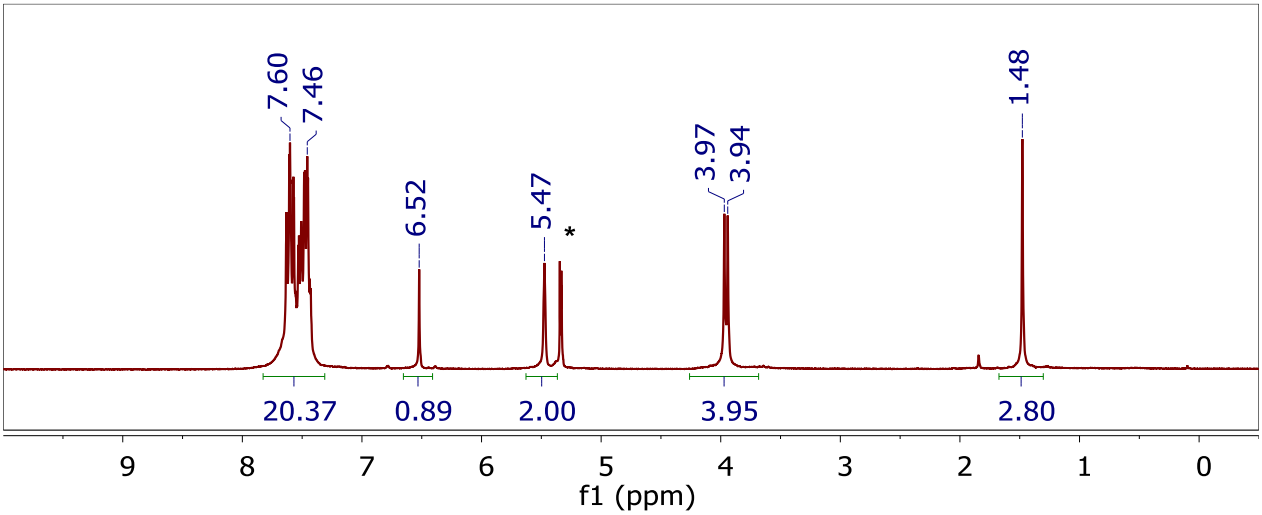

Figure S10. Room temperature ^{1}H-NMR spectrum of {**H-POP**}{Mn(CO)$_4$Br}$_2$ (**2**) in d_2-DCM*.

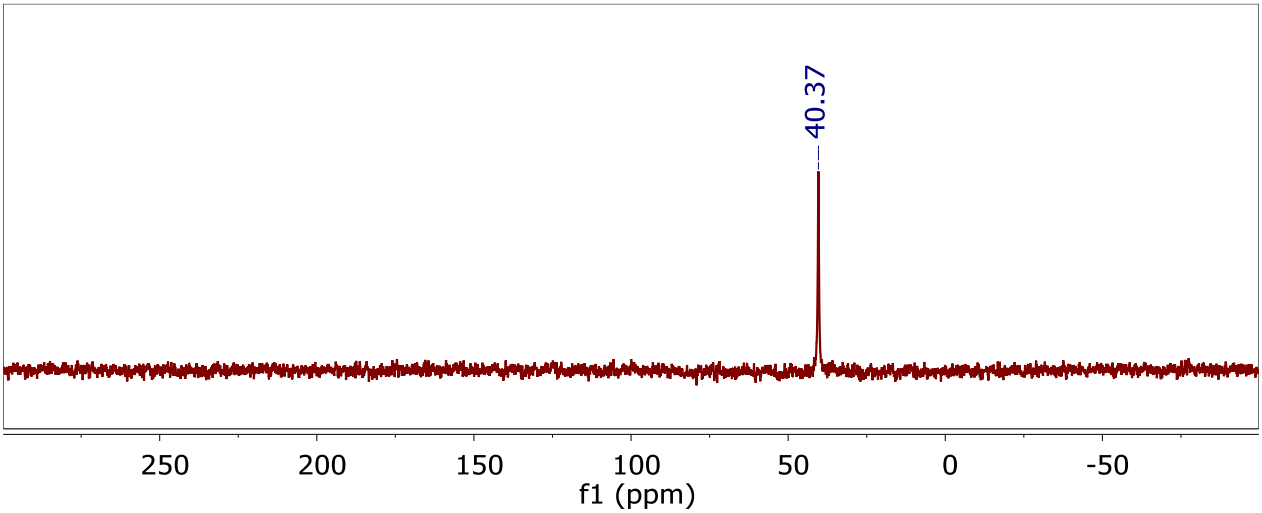

Figure S11. Room temperature ^{31}P-NMR spectrum of {**H-POP**}{Mn(CO)$_4$Br}$_2$ (**2**) in d_2-DCM.

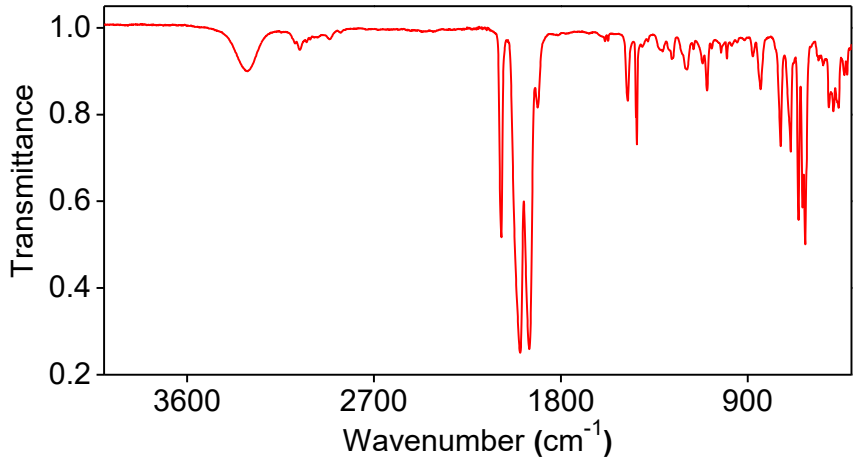

Figure S12. ATR-FTIR spectrum of {**H-POP**}{$Mn(CO)_4Br$}$_2$ (**2**).

Synthesis of ***1****·HBr*. A THF solution of **H-POP** (100 mg, 0.2 mmol, 1.05 eq.) and $MnBr(CO)_5$ (52 mg, 0.19 mmol, 1 eq.) in a 25 mL Straus tube (without a stir bar) was subjected to 3 cycles of freeze-pump-thaw and heated at 50 °C for 24 h. After allowing the solution to cool to room temperature, the solution was subjected to a second set of freeze-pump-thaw (3 cycles) and heated at 50 °C for another 24 h. ^{31}P-NMR of an aliquot of the reaction mixture at this point showed peak(s) only at 55 ppm. The solvent was removed under vacuum and the residue was washed with hexane. The yellow solid thus obtained was dried under vacuum to obtain the compound as a THF adduct, **1**·HBr·THF (144 mg, 100% yield). Anal Calcd. (found) for **1**·HBr·THF, $C_{40}H_{38}BrMnO_5P_2$: %C 60.39 (60.03); %H 4.47 (4.81); %N 0.00 (none found). FTIR-ATR (cm^{-1}): 3300, 2030, 1947, 1907, 1845.

The above residue was washed with toluene:Et_2O (50:50) mixture and the insoluble yellow solid was collected on a frit and dried under vacuum to give [**1H**]Br. ^{1}H-NMR (d_2-DCM, 300 MHz, 298 K, ppm): δ 1.52 (s, 3H, C*H*$_3$), 3.98 (s, 4H, C*H*$_2$), 5.59 (s, 2H, *p*-cresol ring C*H*), 6.45 (s, 1H, O*H*), 7.3-7.6 (20H, (C$_6$*H*$_5$)$_2$P). ^{31}P-NMR (THF, 121 MHz, 298 K, ppm): δ 50.35 ppm. FTIR-ATR (cm^{-1}): 3300, 2034, 1947, 1907.

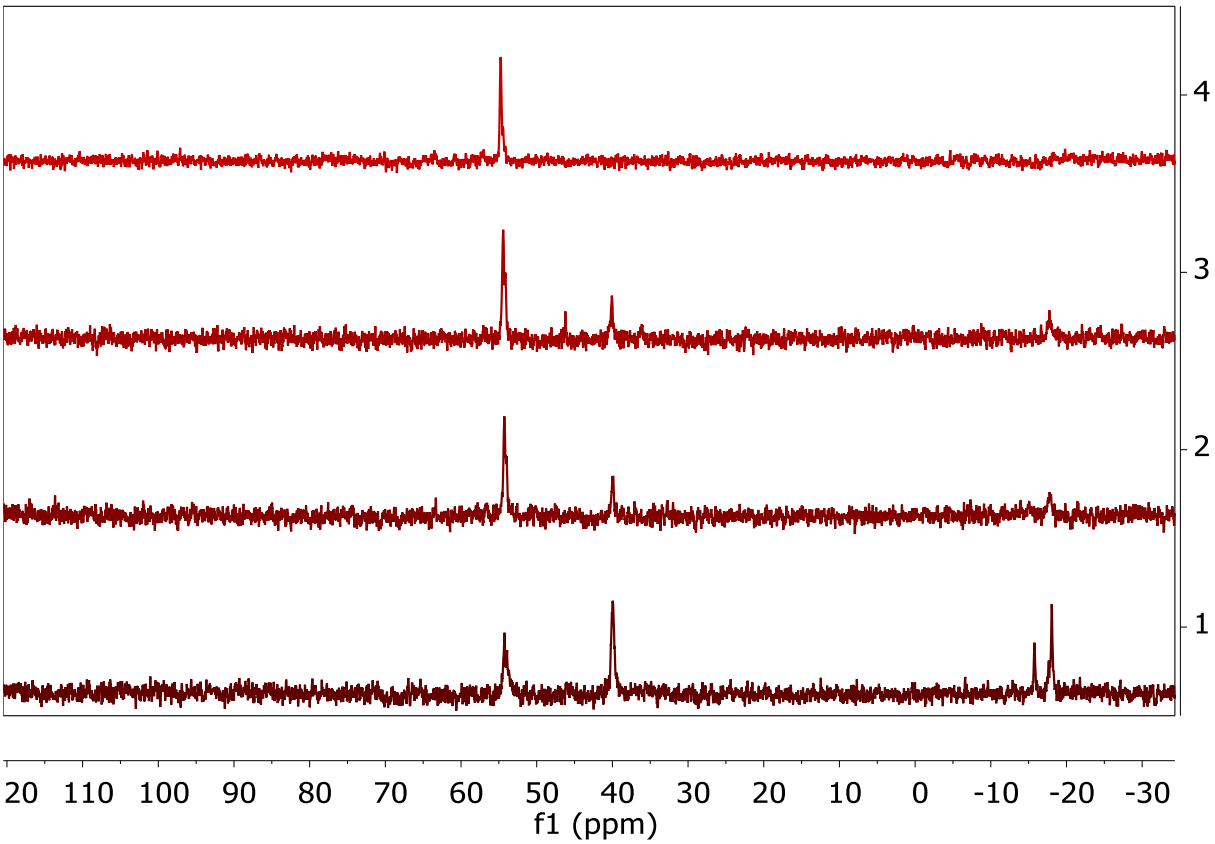

Figure S13. Reaction of **H-POP** with $MnBr(CO)_5$ monitored using ^{31}P-NMR. Spectra after 1) 12 h at room temperature, 2) additional 12 h at 50 °C, 3) one freeze-pump-thaw cycle, and 4) additional 12 h at 50 °C.

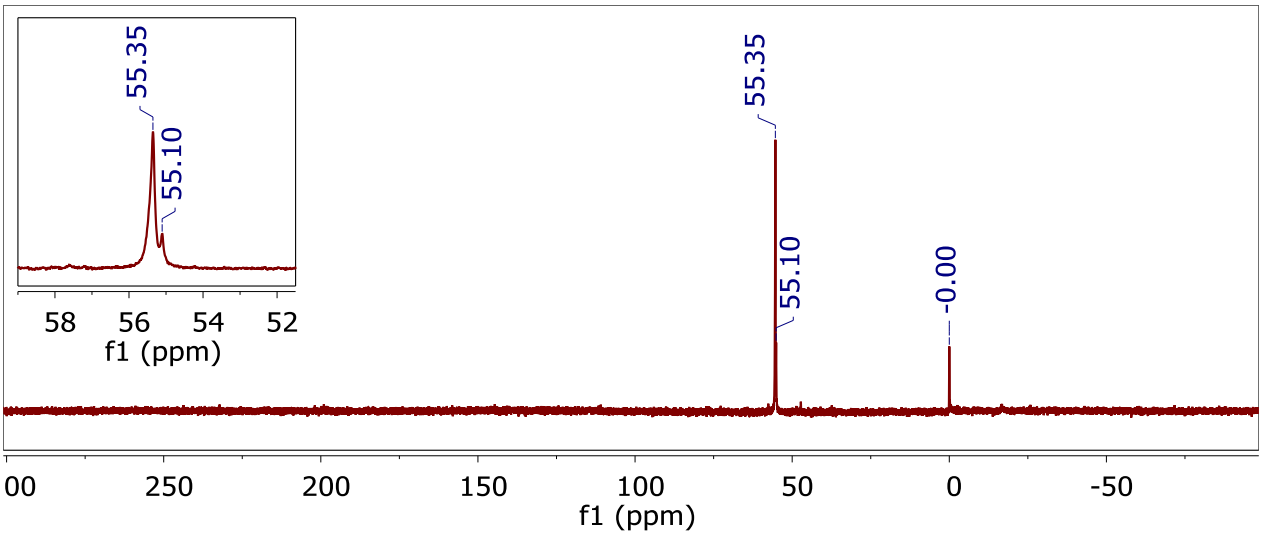

Figure S14. Room temperature ^{31}P-NMR spectrum of **1**·HBr in THF with an internal standard (capillary insert) of H_3PO_4 in D_2O.

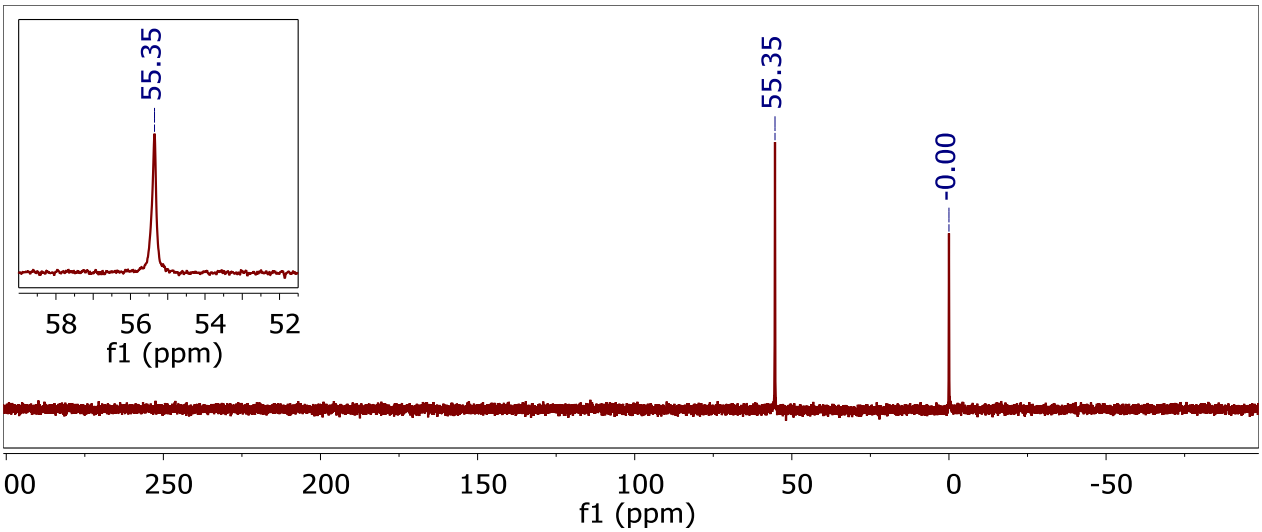

Figure S15. Room temperature ^{31}P-NMR spectrum of [**1H**]Br in THF with an internal standard (capillary insert) of H_3PO_4 in D_2O.

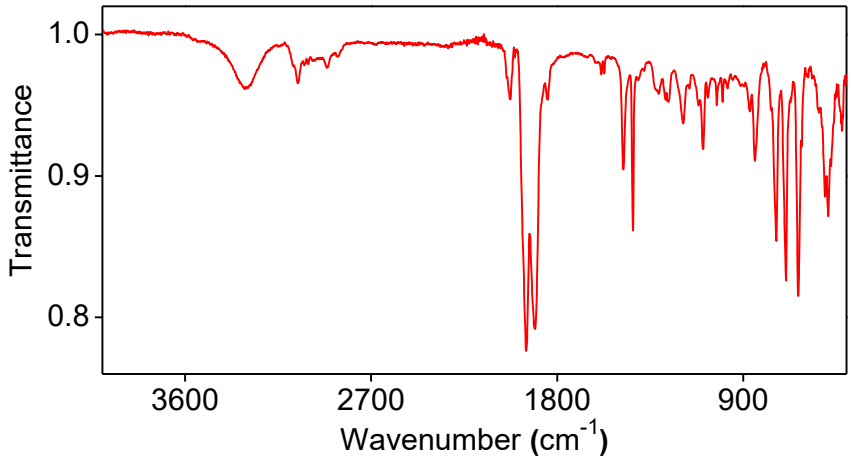

Figure S16. ATR-FTIR spectrum of **1**·HBr.

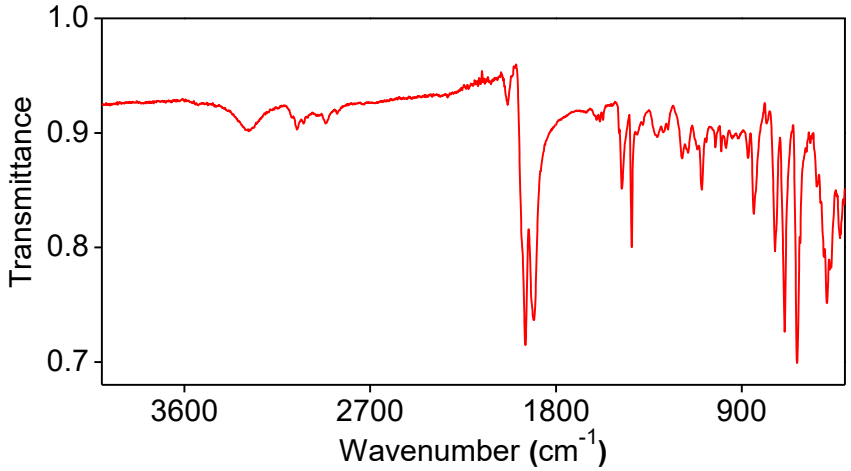

Figure S17. ATR-FTIR spectrum of [**1H**]Br.

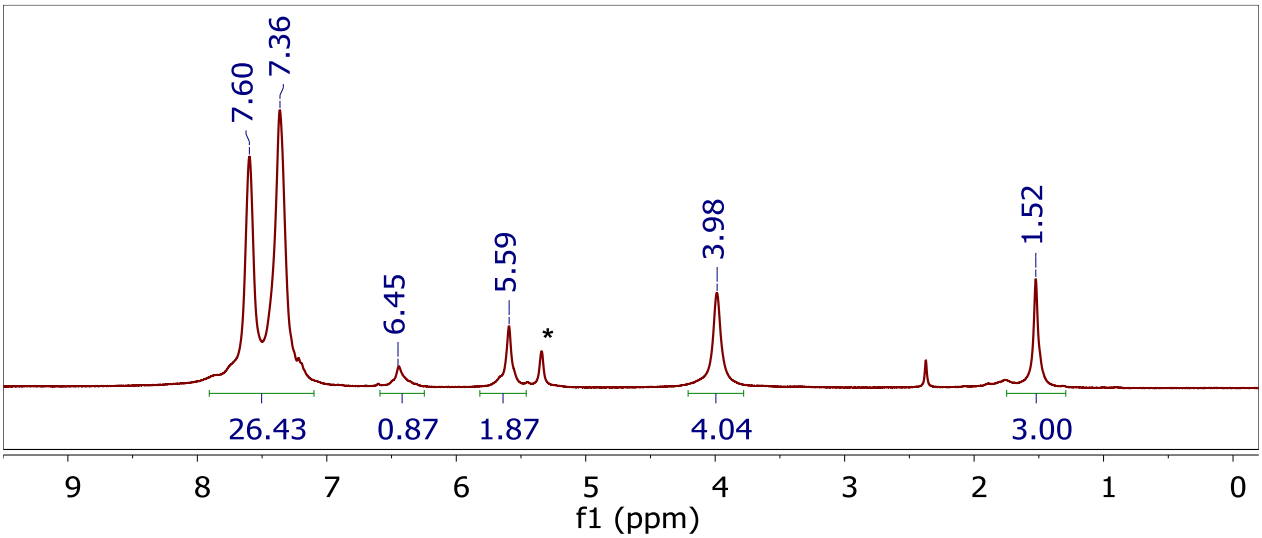

Figure S18. Room temperature ^{1}H-NMR spectrum of [**1H**]Br in d_2-DCM*.

*Synthesis of **1** from [**1H**]Br*. A solution of [**1H**]Br (30 mg, 0.041 mmol) in THF (500 μL) was cooled to -35 °C and Et_3N (20 μL, excess) was added. The reaction mixture was allowed to warm to room temperature and then stirred for 16 h. The white precipitate formed was filtered out using a frit and was characterized to be [Et_3NH]Br by ^{1}H-NMR. The yellow filtrate obtained was collected and solvent pumped off under vacuum to yield **1** as a yellow solid (25 mg, 96% yield). The same procedure when repeated for **1**·HBr (the mixture of two species) yielded mixture of **1** and $\mathbf{1}_2$ as evident from ^{31}P-NMR of reaction mixture.

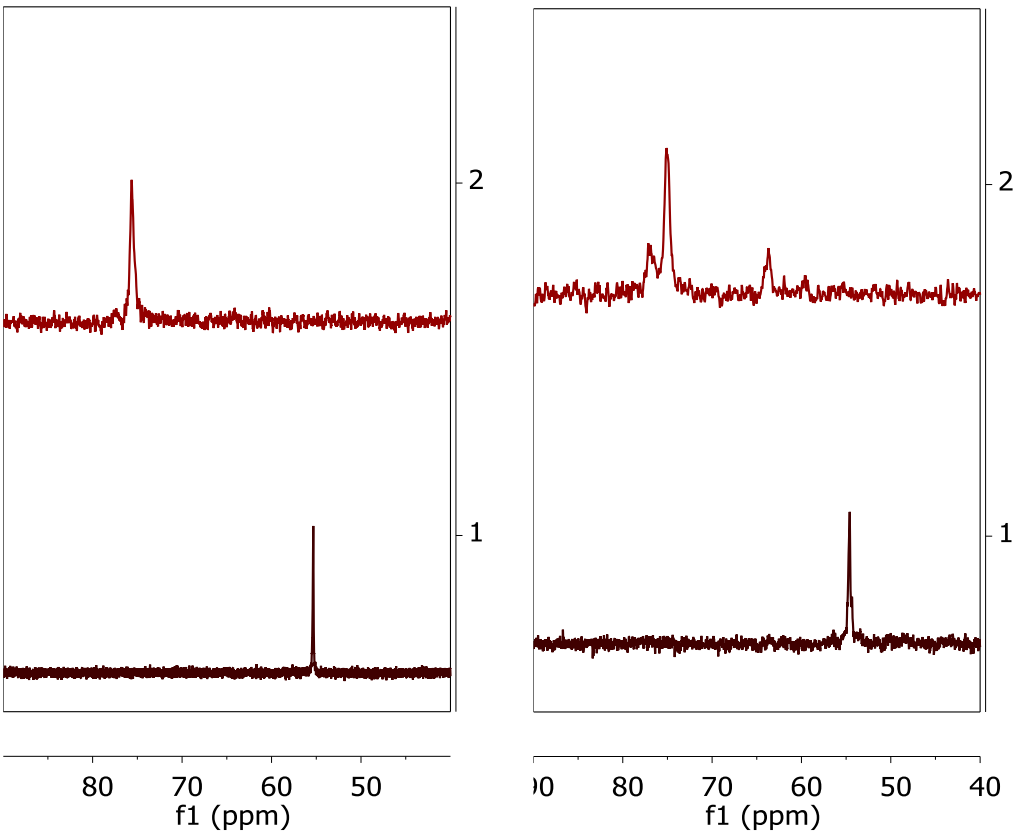

Figure S19. ^{31}P-NMR spectra showing reaction of **1**·HBr with Et_3N in THF; 1) before and 2) after. Note the conversion of [**1H**]Br to **1** (on left), and the conversion of **1**·HBr to a mixture of **1** and $\mathbf{1}_2$ (on right).

*Synthesis of **1**·HX from **1**.* A 1:1 solution of THF and aqueous HX w/w% (X=Cl 38%, Br 48%, and I 57%) in a Schlenk flask was subjected to 2 cycles of freeze-pump-thaw to get rid of O_2. Using a syringe, 100 μL of the above solution was transferred to a J-Young tube containing 500 μL solution of **1** (25 mg, 0.039 mmol) in THF, under a flow of argon. The tube was immediately sealed and subjected again to 2 cycles of freeze-pump-thaw. The reaction was allowed to stand at room temperature for 16 h. ^{31}P-NMR spectrum of the reaction mixture showed peaks at 57.85, 55.35, and 53.92 ppm corresponding to **1**·HCl, **1**·HBr and **1**·HI respectively. The reaction mixture was transferred to a Schlenk flask under a positive Argon flow and solvent pumped off under vacuum. FTIR-ATR spectra of the yellow solid residue left behind showed OH stretch at 3360, 3300, 3255 cm^{-1} for **1**·HCl, **1**·HBr and **1**·HI respectively.

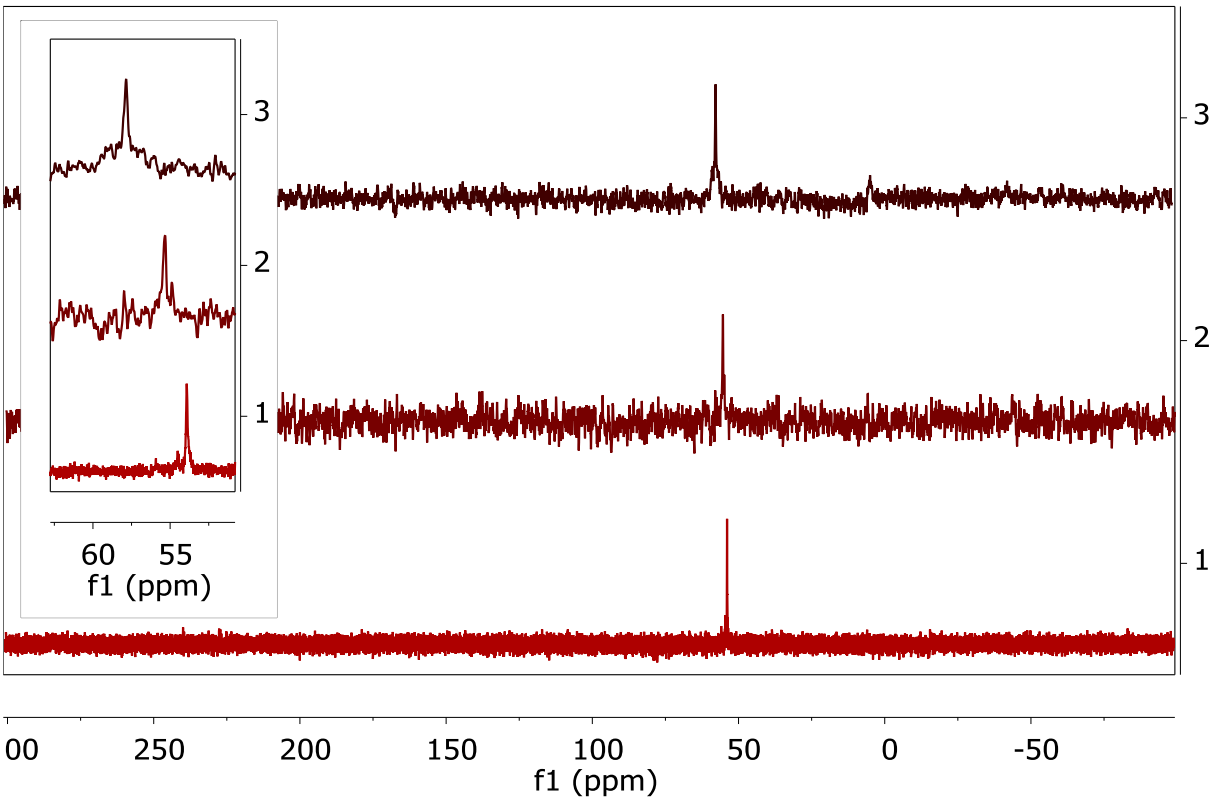

Figure S20. Synthesis of **1**·HX from **1**; ^{31}P-NMR spectra of reaction mixture in THF after 16 hours of addition of HX to **1** for X = 1) I, 2) Br, and 3) Cl.

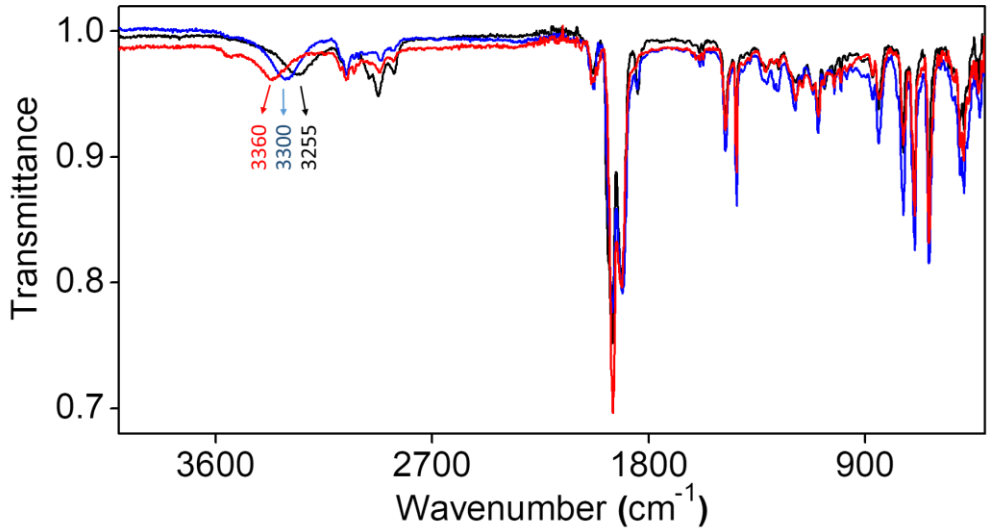

Figure S21. ATR-FTIR spectrum of **1**·HX; X= I (red), Br (blue), and Cl (black).

Synthesis of ***1₂H-OTf*** *from* ***1****·HBr*. To a solution of **1**·HBr (50 mg, 0.069 mmol) in DCM (2 mL) was added 18 mg of AgOTf (0.07 mmol, 1 eq.) and the solution was stirred for 16 h at room temperature. The reaction mixture was filtered and the orange filtrate was collected. The solvent was removed *in vacuo* and the residue was dissolved in minimal amount of THF (~ 1 mL) with a drop of DCM. Crystals suitable for XRD were obtained from this saturated solution and allowing it stand at room temperature for 24 h. ^{31}P-NMR (DCM, 121 MHz, 298 K, ppm): δ 63.52 (d, J = 43.56 Hz), 73.22 (d, J = 43.56 Hz) ppm. FTIR-ATR (cm^{-1}): 1963, 1900. The compound could not be obtained as an analytically pure material and was not further characterized.

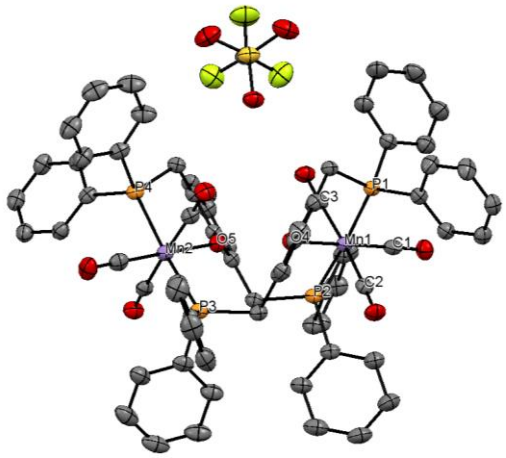

Figure S22. Molecular structure of **1₂H-OTf**; H-atoms and solvent molecules have been removed for clarity (ellipsoids at 50% probability). Color scheme: Mn = purple; O = red; P = orange; C = grey; S = yellow; F = green. Selected bond distances (Å) and angles (°): Mn1–O4 = 2.085(2); Mn1–P1 = 2.2963(8); Mn1–P2 = 2.3124(8); Mn1–C_{ave} = 1.84 (±0.05); O4-O5 = 2.388(3); C22–O4–Mn1 = 121.9(2); P1–Mn1–P2 = 174.58(4).

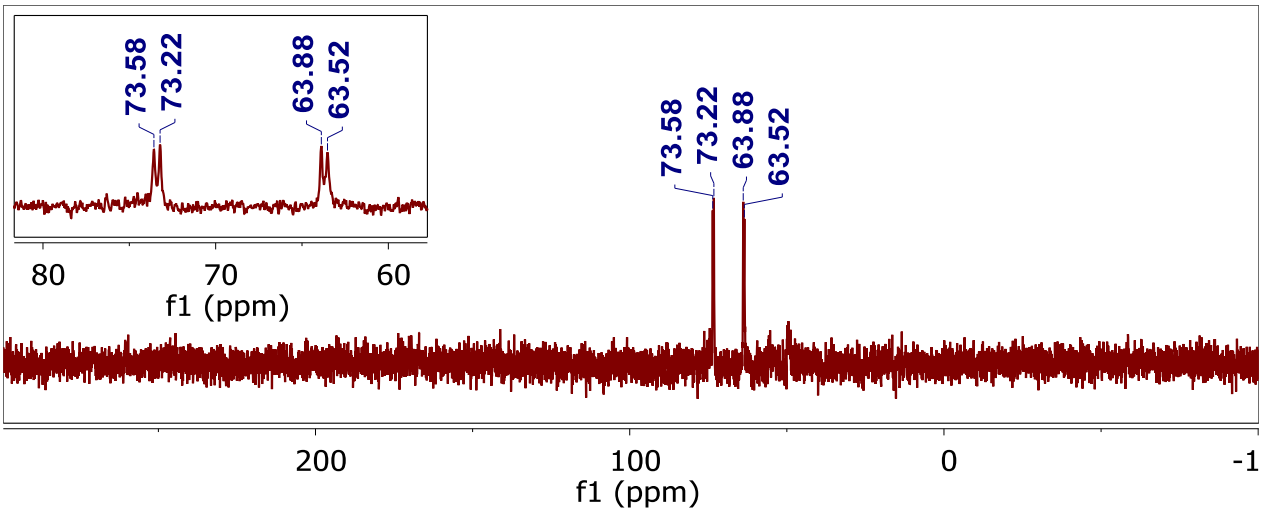

Figure S23. Room temperature ^{31}P-NMR spectrum of **1_2H-OTf** in DCM.

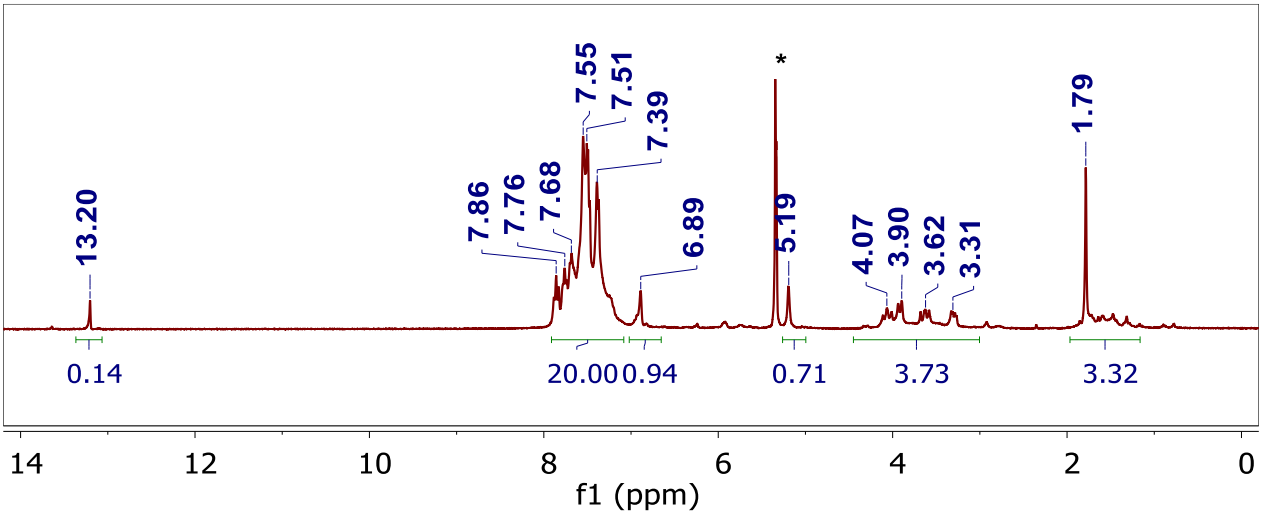

Figure S24. Room temperature ^{1}H-NMR spectrum of **1_2H-OTf** in DCM.

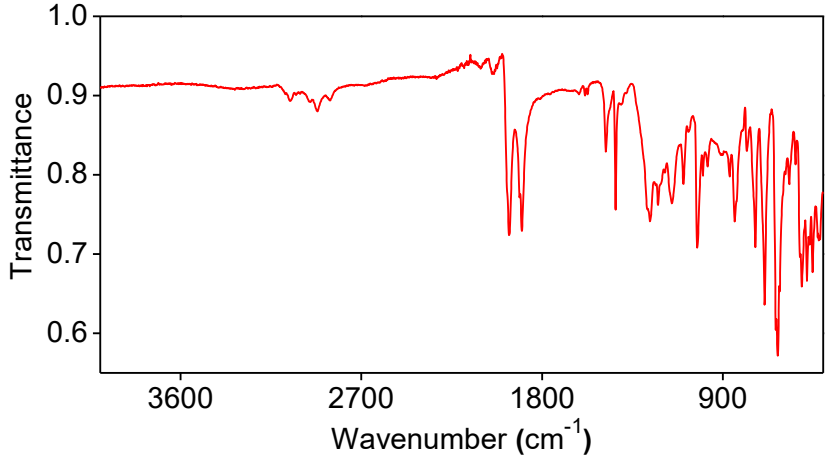

Figure S25. ATR-FTIR spectrum of **1_2H-OTf**.

General procedure for benzaldehyde to benzyl benzoate conversion. To a solution of 0.008 mmol of catalyst in d_8-toluene (500 μL) was added 20 μL (0.2 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 5.12 ppm (s, CH_2, benzyl benzoate) and 9.60 (s, C*H*O, benzaldehyde). Yield calculation was done as follows:

$$\%\ yield = \frac{I_{5.12\ ppm}}{I_{5.12\ ppm} + I_{9.60\ ppm}} \times 100$$

Table S1. Conversion of benzaldehyde to benzyl benzoate in presence of various catalysts

No.	Catalyst	Time	Yield (%)
1	**1**	24 h	26
2	**1**	40 h	31
3	**1**	60 h	40
4	**1**	4 days	50
5	**1**$_2$	24 h	52
6	-	24 h	0
7	**H-POP**	24 h	0
8	**H-POP** + $MnBr_2$	24 h	0
9	$MnBr(CO)_5$	24 h	0
10	**2**	24 h	0
11	**1**·HBr	24 h	0

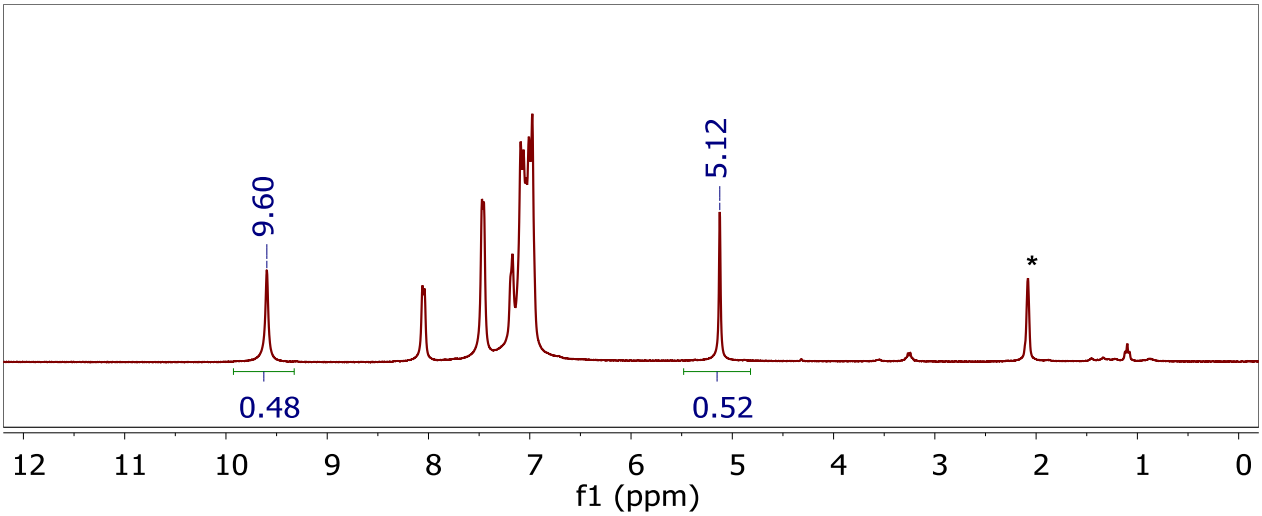

Figure S22: ^{1}H-NMR spectrum in d_8-toluene* obtained for the conversion of benzaldehyde to benzyl benzoate catalyzed by {**POP**Mn(CO)$_3$}$_2$.

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