Asymmetric Transfer Hydrogenation of Ketones With Well-Defined Manganese(I) PNN and PNNP Complexes

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Supporting Information

Table of Contents

Experimental Protocols for the Hydride Studies 2

Summary of $^{31}P\{^{1}H\}$ NMR Spectrum Chemical Shifts and IR CO Stretch Wavenumbers 3

NMR Spectra of Newly Synthesized Chemicals 4

NMR Spectra of Base Activation Studies 18

NMR Spectra of Hydride, Borohydride, and Ethoxide Species 23

Gas Chromatograph Readouts for the ATH of Ketones 37

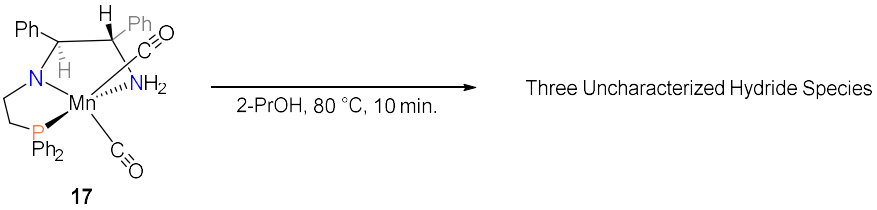
Characterization of Ethyl *p*-(1-hydroxyethyl)benzoate Alcohol Product 43

DFT Calculations for the Manganese Bromide, Manganese Borohydride, and Manganese Ethoxide Isomers 44

References 46

Experimental Protocols for the Hydride Studies

Attempted Synthesis of Mn(P–NH–NH_2)$(CO)_2$(H) mimicking catalytic conditions, (**20** and **20'**):

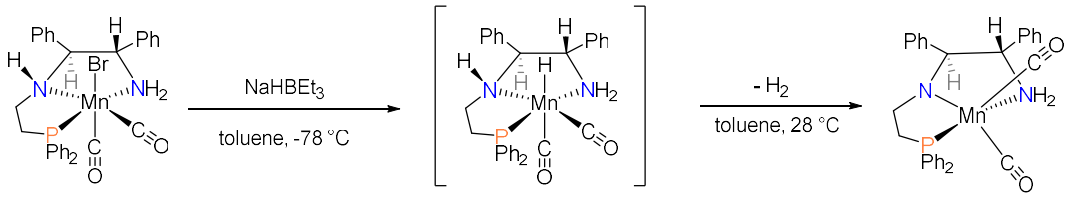


17

Mn(P–N–NH_2)$(CO)_2$ **17** (30 mg, 0.056 mmol, 1 equivalent) was weighed out in a 20 mL vial and then 2-PrOH (2 mL) was added. The solution immediately turned yellow presumably due to the formation of an alkoxide complex. The solution was stirred for 10 minutes, then the solvent was removed *in vacuo* to yield a yellow residue. The residue was redissolved in benzene, filtered through celite, and then the filtrate was removed *in vacuo* to yield a mixture of products including a three hydride species.

^{1}H NMR spectrum (600 MHz, C_6D_6) δ –4.12 (d, $^2J_{HP}$ = 71.6 Hz), –4.63 (d, $^2J_{HP}$ = 36 Hz), –4.73 (d, $^2J_{HP}$ = 38 Hz).

Attempted independent synthesis of Mn(P–NH–NH_2)$(CO)_2$(H) via sodium triethylborohydride, (**20** and **20'**):



16 20 17

Mn(P-NH-NH_2)$(CO)_2$(Br) **16** (50 mg, 0.081 mmol, 1 equivalent) was weighed out in a vial, dissolved in toluene (2 mL), and transferred to a 10 mL Schlenk flask. This was brought out of the glovebox, placed on the Schlenk line, and cooled to –78 °C. In the glovebox, $NaHBEt_3$ (0.08 mL of 1.0 M in toluene, 0.081 mmol, 1 equivalent) was diluted to 2 mL with toluene, then placed in a syringe. The needle of the syringe was stabbed into a rubber stopper and the syringe was brought out of the glovebox. The solution of $NaHBEt_3$ was added dropwise to the manganese precatalyst solution. The solution quickly became a lighter yellow colour. This reaction was allowed to warm to 28 °C, upon which the solution turned red indicating the presence of the five-coordinate Mn(P–N–NH_2)$(CO)_2$ compound **17**. This was confirmed to be the only product via the $^{31}P\{^1H\}$ and ^{1}H NMR spectra.

Summary of $^{31}P\{^{1}H\}$ NMR Spectrum Chemical Shifts and IR CO Stretch Wavenumbers

Table S1: Summary of $^{31}P\{^{1}H\}$ NMR Spectral Information and IR CO Stretch Wavenumbers

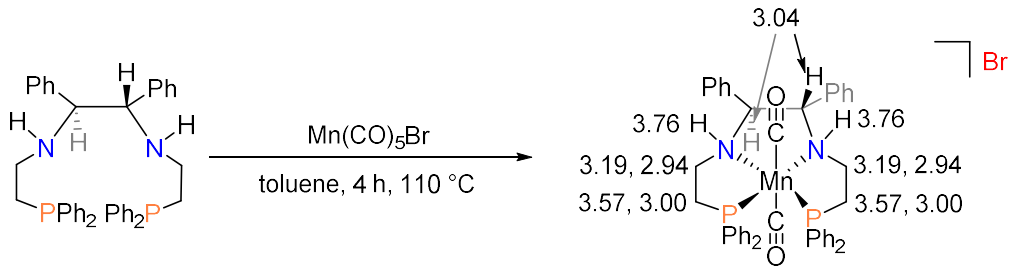
Complex	**$^{31}P\{^{1}H\}$ Spectrum Chemical Shift (ppm)**	**IR Spectrum (CO Stretch, cm^{-1})**
trans-[Mn(P–NH–NH–P)$(CO)_2$][Br], **14**	77.9	1930, 1854
fac-[Mn(P'–NH–NH_2)$(CO)_3$][Br], **15**	63.9	2032, 1955, 1914
syn mer-Mn(P–NH–NH_2)$(CO)_2$Br, **16**	83.1	1915, 1828
Mn(P–N–NH_2)$(CO)_2$, **17**	102.8	1890, 1808
syn mer-Mn(P–NH–NH_2)$(CO)_2(BH_4)$, **18**	89.2	1920, 1836
anti mer-Mn(P–NH–NH_2)$(CO)_2$(OEt), **19'**	84.1	1916, 1830

NMR Spectra of Newly Synthesized Chemicals

A Note on Solving NMR in the Following Studies:

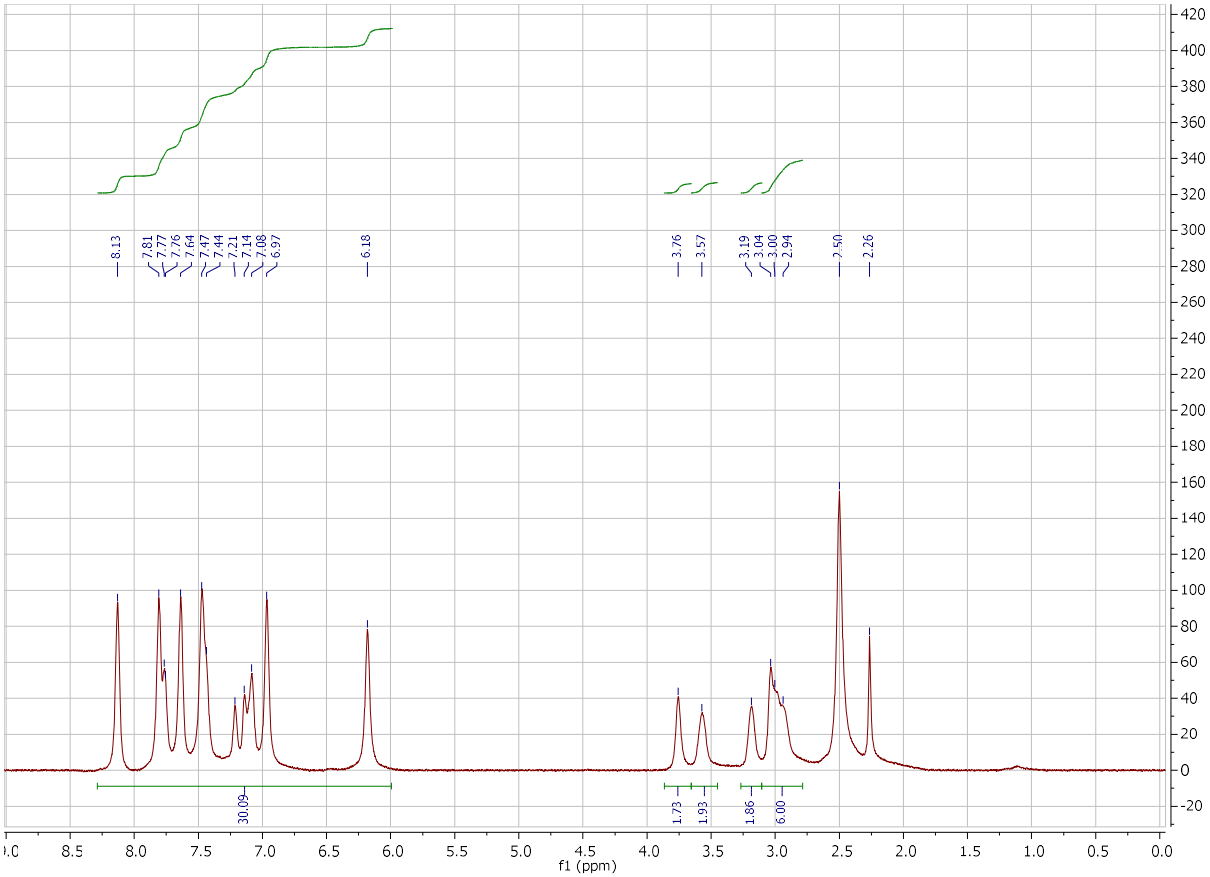
2D ^{1}H–^{13}C HSQC spectrum was used to locate the two C**H**Ph o the DPEN backbone in the ^{13}C range of 70–90 ppm, using the intensity in the ^{1}H to discern the major species, medium species, and minor species (when applicable). The 2D ^{1}H–^{1}H COSY spectrum was used to discern the connectivity of the DPEN backbone to the side arm, verifying how many protons were attached to each carbon through the HSQC. The 2D ^{1}H–^{1}H NOESY spectrum was used to place the protons on either the top or bottom of the plane formed by the PNN ligand, using the DPEN C**H**Ph as an anchor.

Figure S1 NMR and IR Spectroscopy for *trans*-[Mn(P–NH–NH–P)(CO)$_2$][Br] (**14**):

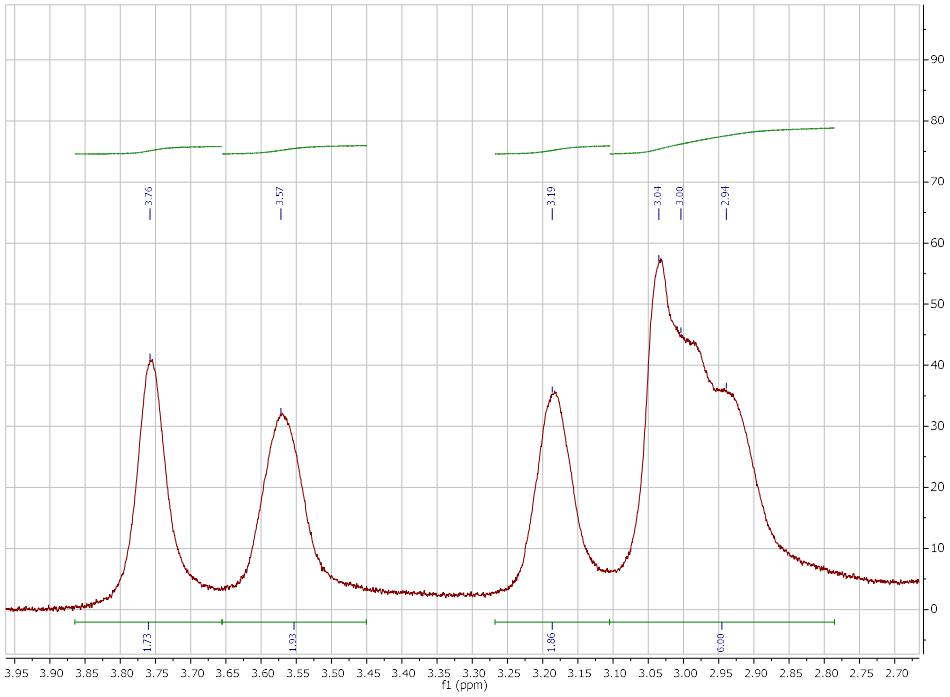


8 **14**

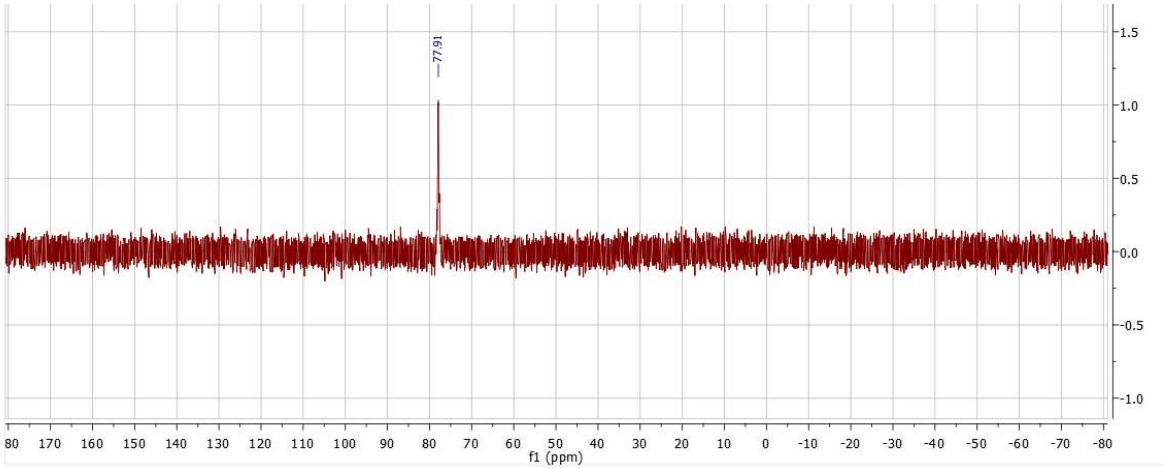
(a) ^{1}H NMR spectrum (600 MHz, DMSO-d_6):



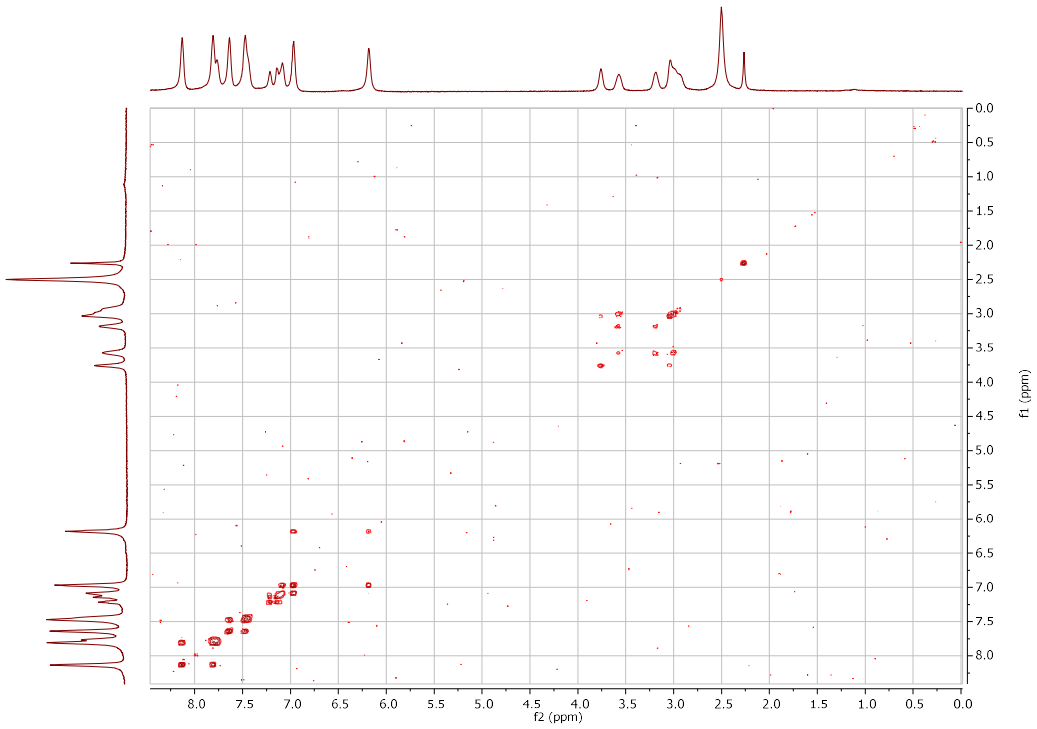
(b) ^{1}H NMR spectrum, zoom on CH_2, NH, CHPh region:



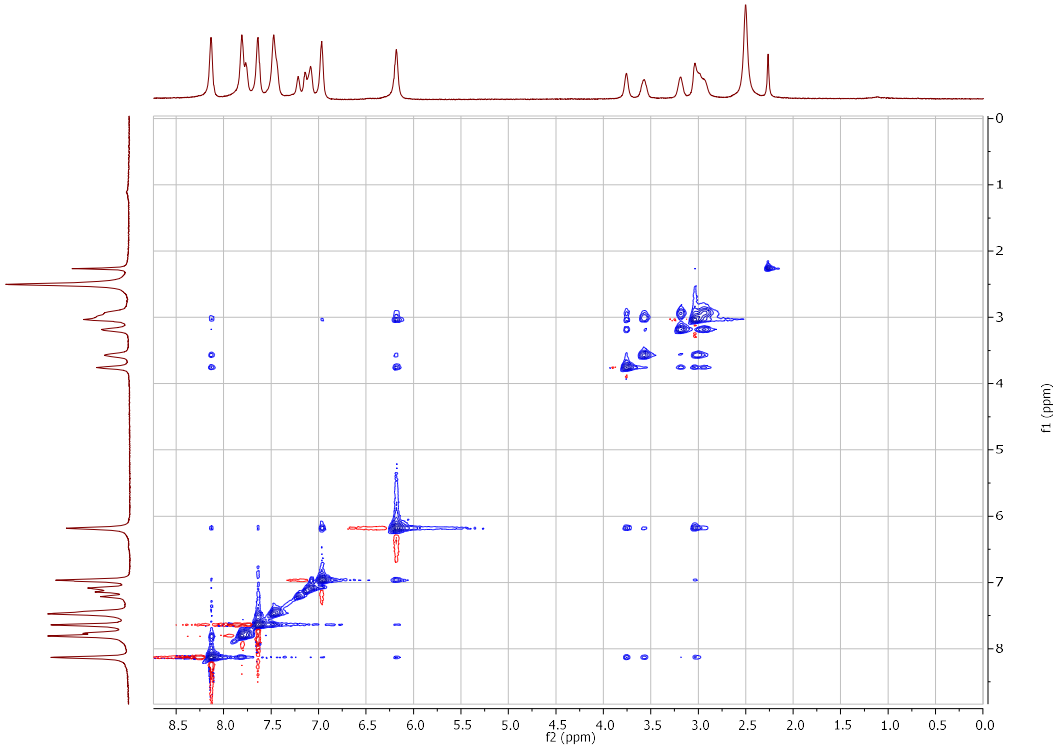
(c) $^{31}P\{^{1}H\}$ NMR spectrum (243 MHz, DMSO-d_6):



(d) 2D ^{1}H–^{1}H COSY spectrum (600 MHz, DMSO-d_6):

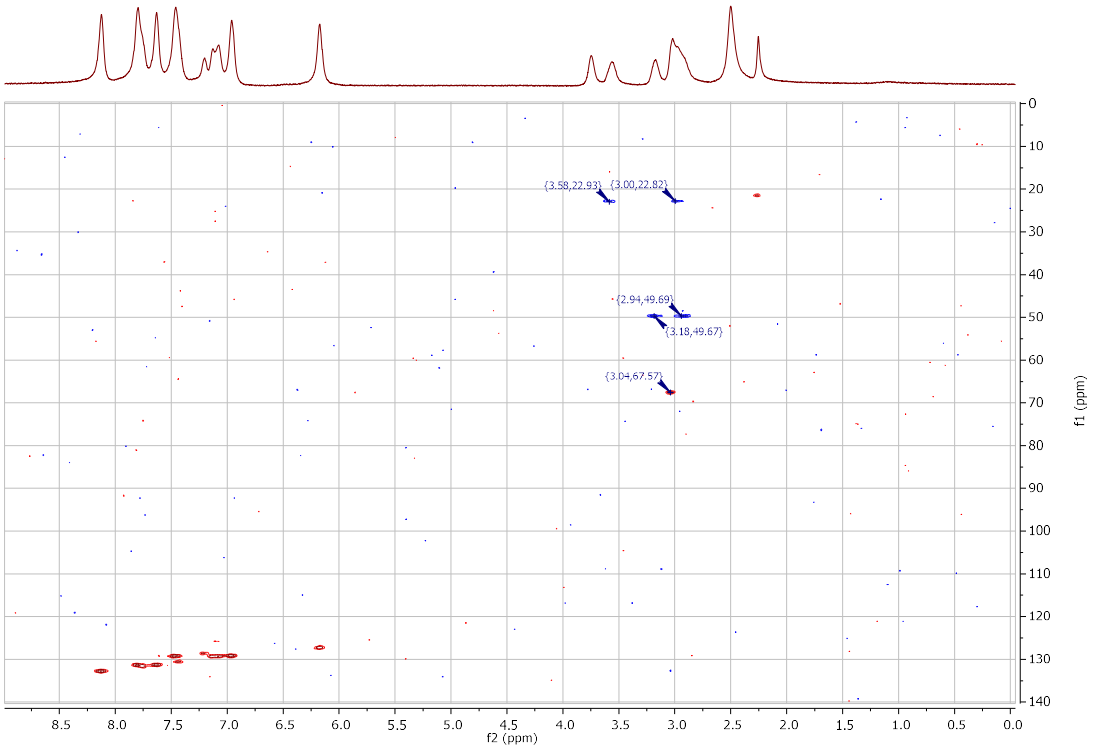


(e) 2D ^{1}H–^{1}H NOESY spectrum (600 MHz, DMSO-d_6):

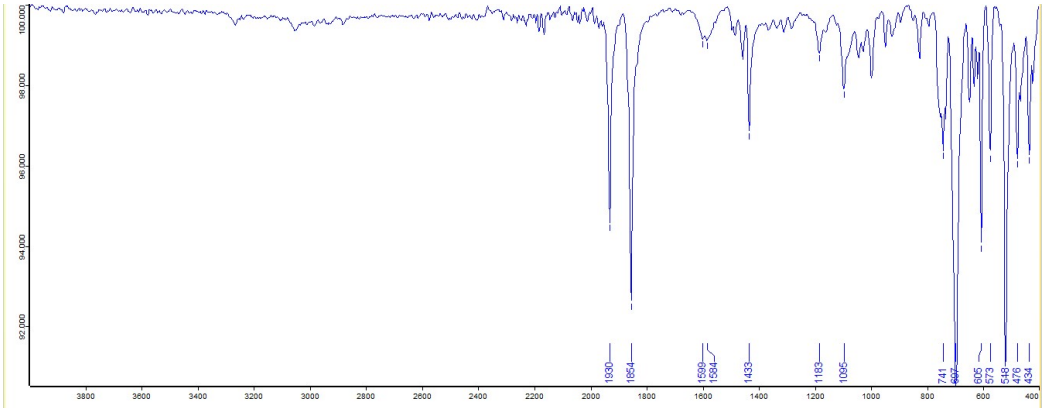


(f) 2D ^{1}H–^{13}C HSQC spectrum (500 MHz, DMSO-d_6):

2D ^{1}H–^{13}C HSQC spectrum displays the two C**H**Ph at (3.04, 67.57), the four protons of the two CH_2 adjacent to the amino donor at (3.19, 49.67) and (2.94, 49.69), the four protons of the two CH_2 adjacent to the diphenylphosphino donor at (3.57, 22.93) and (3.00, 22.82). There is no cross peak for the two amino protons at 3.75 ppm in the HSQC.

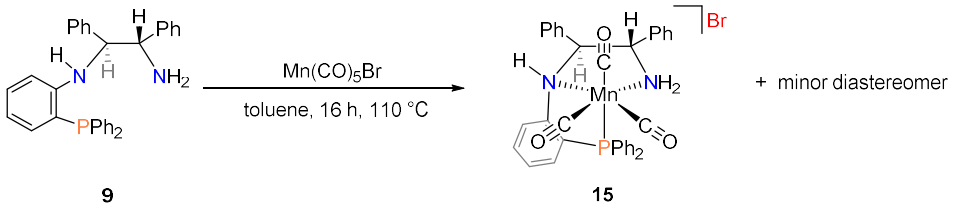


(g) IR Spectrum:



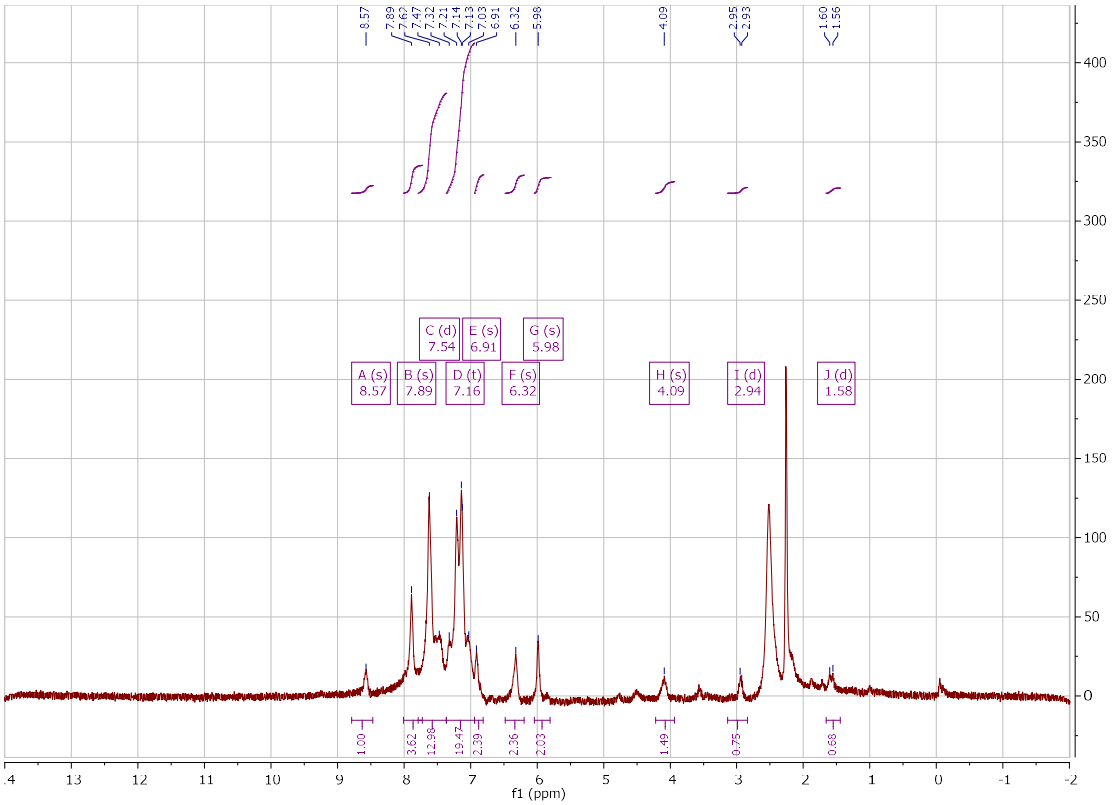
The CO stretches of manganese complex **14** are at 1930 cm^{-1} and 1854 cm^{-1}.

Figure S2 NMR and IR Spectroscopy for *fac*-[Mn(P–NH–NH_2)$(CO)_3$][Br] (**15**):

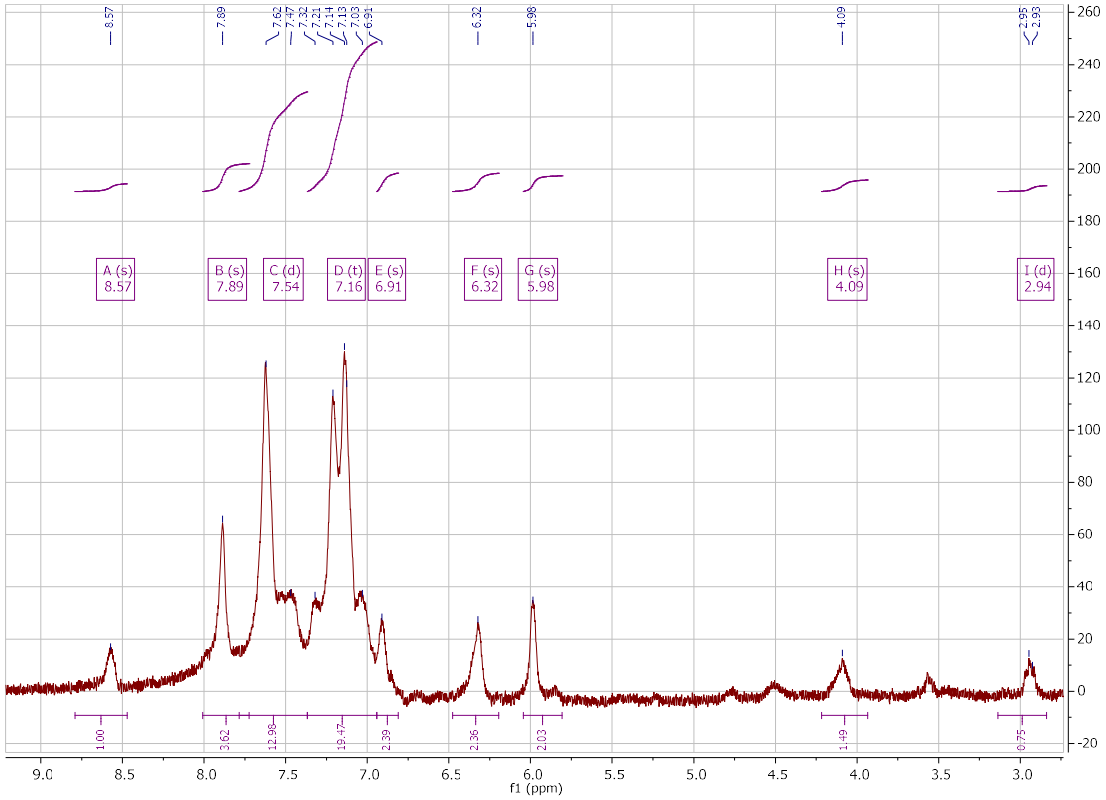


9 **15**

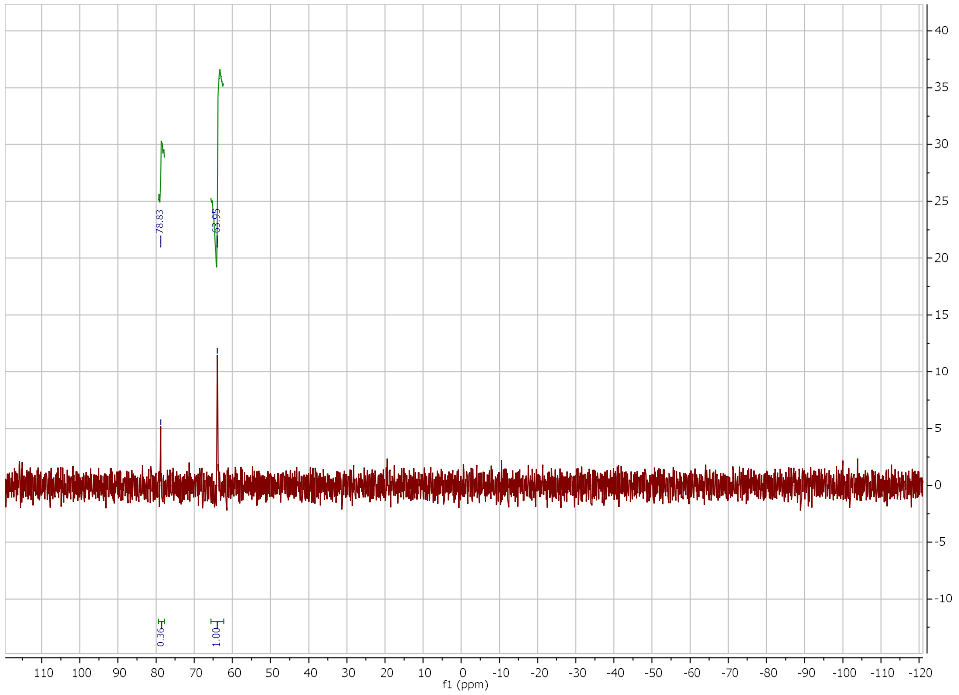
(a) ^{1}H NMR spectrum (600 MHz, DMSO-d_6):



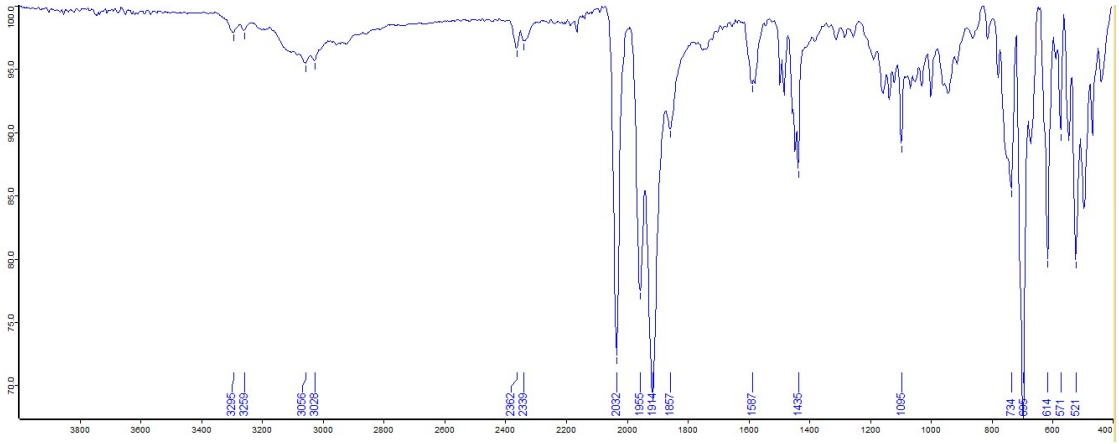
(b) Zoom in on ^{1}H NMR spectrum (600 MHz, d_6-DMSO) between δ 3.8 ppm – 8.0 ppm:



(c) ^{31}P{^{1}H} spectrum (243 MHz, DMSO-d_6):

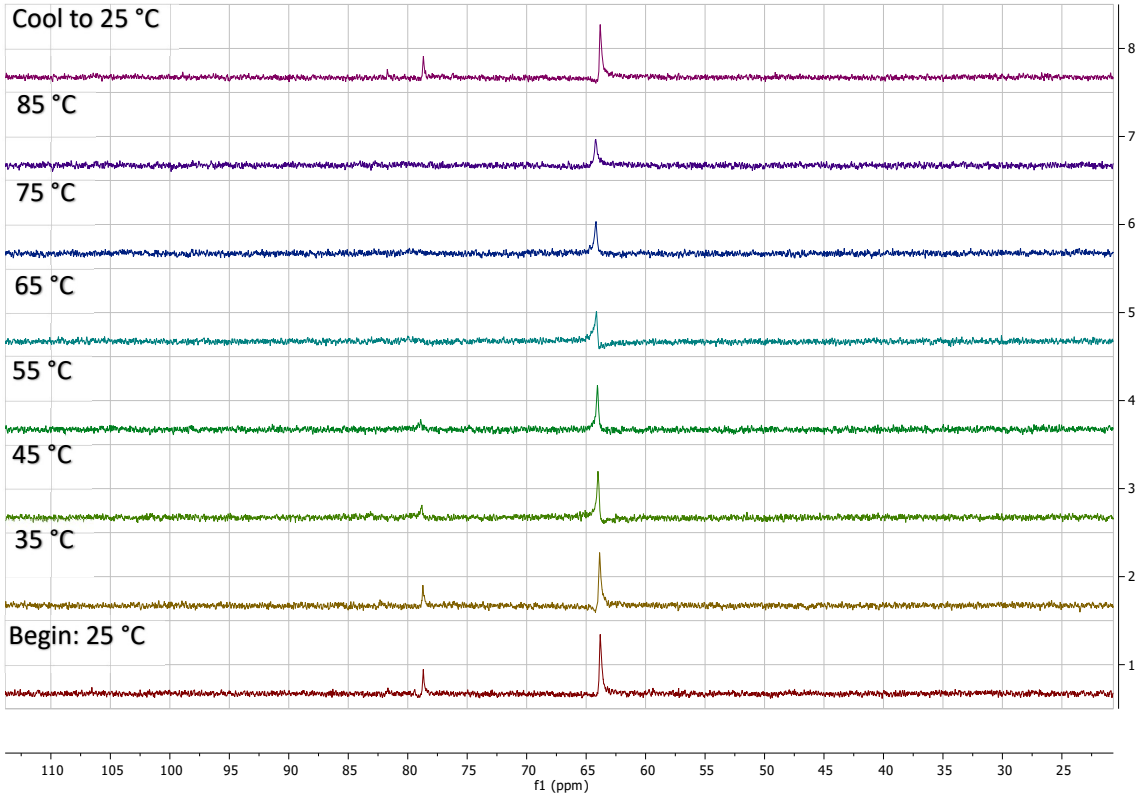


(d) IR Spectrum:



The CO stretches of manganese complex **15** are at 2032 cm^{-1}, 1955 cm^{-1}, and 1914 cm^{-1}.

(e) $^{31}P\{^{1}H\}$ Variable temperature NMR spectra heating from 25 °C to 85 °C, then back down to 25 °C.



(f) ^{1}H Variable temperature NMR spectra heating from 25 °C to 85 °C, then back down to 25 °C. Asterisks denote areas of change.

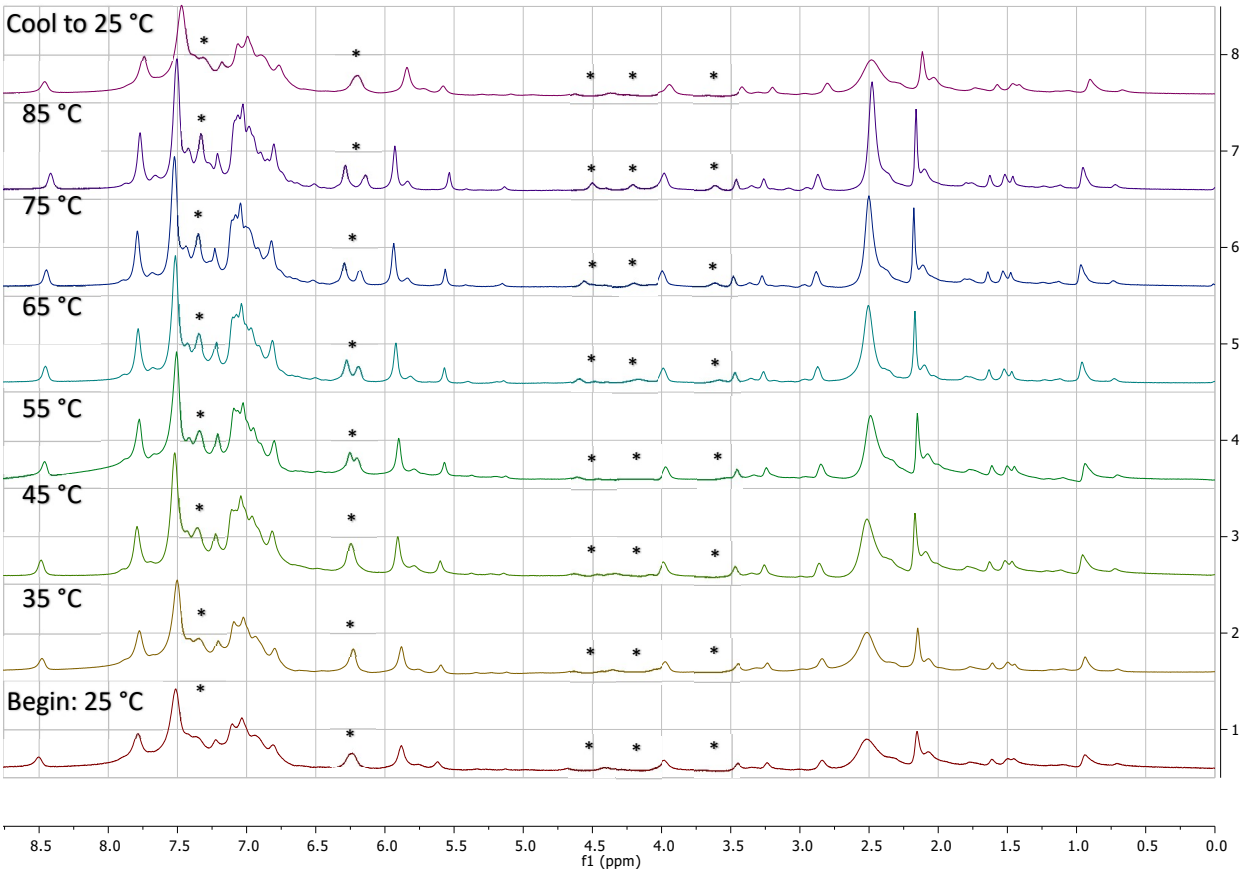
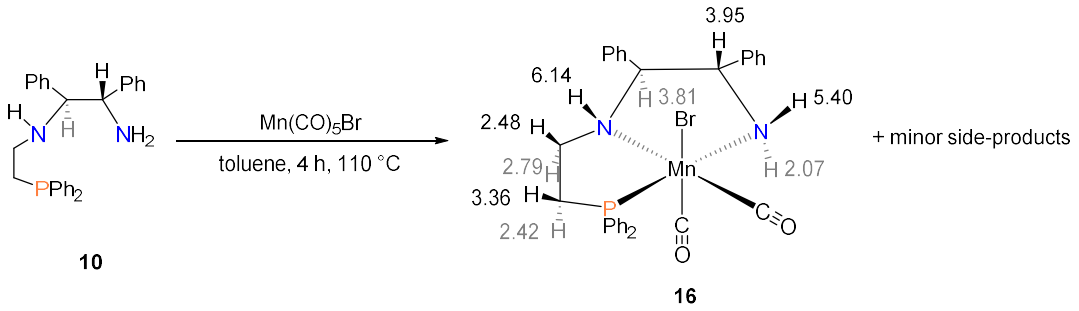
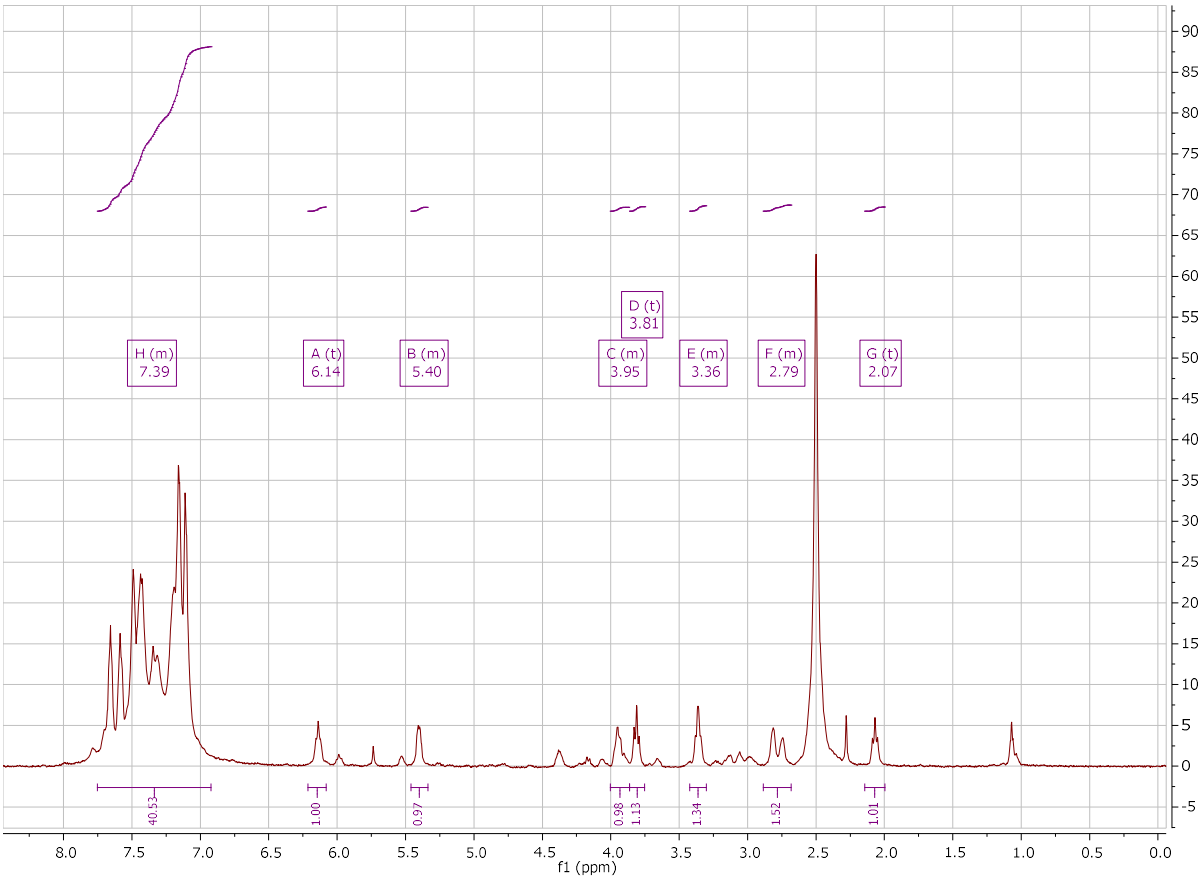


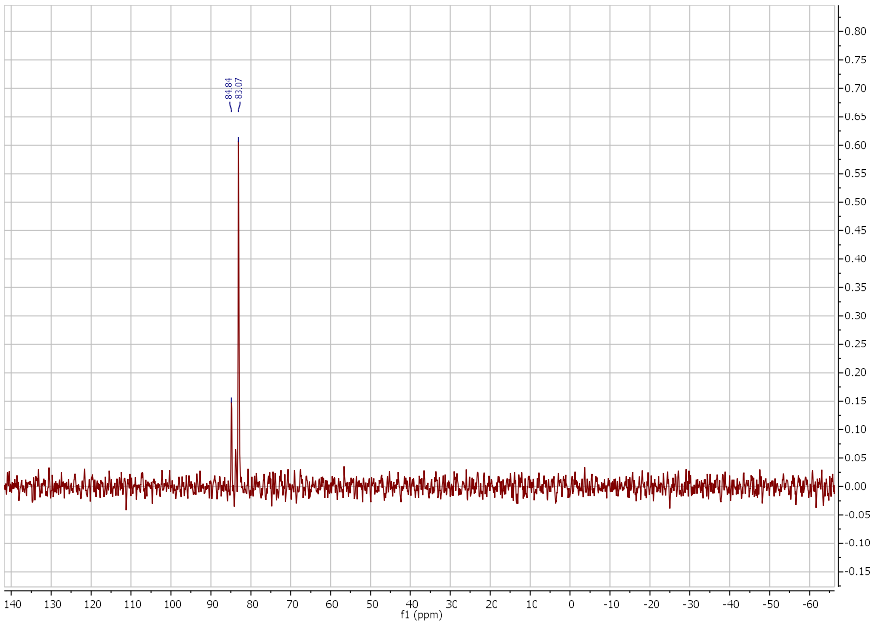
Figure S3 NMR and IR Spectroscopy for *syn mer*-Mn(P–NH–NH_2)$(CO)_2$Br (**16**):



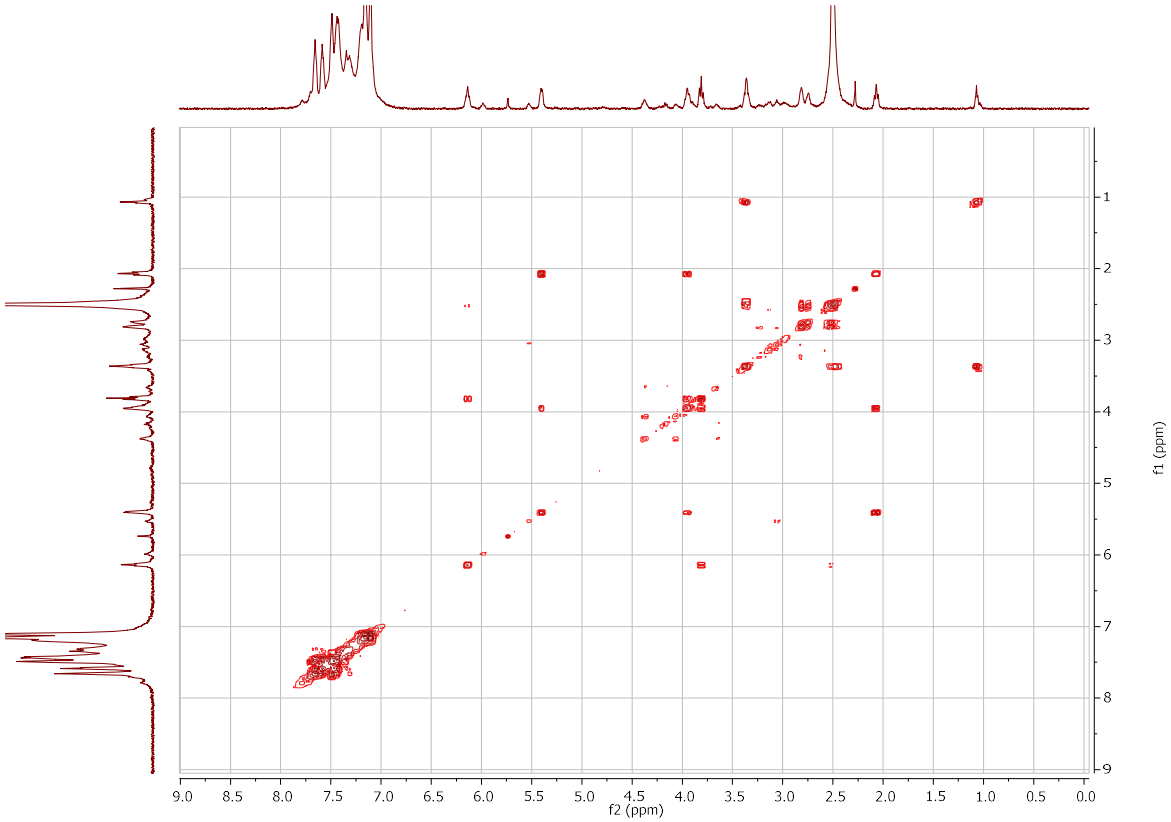
(a) ^{1}H NMR spectrum (600 MHz, DMSO-d_6):



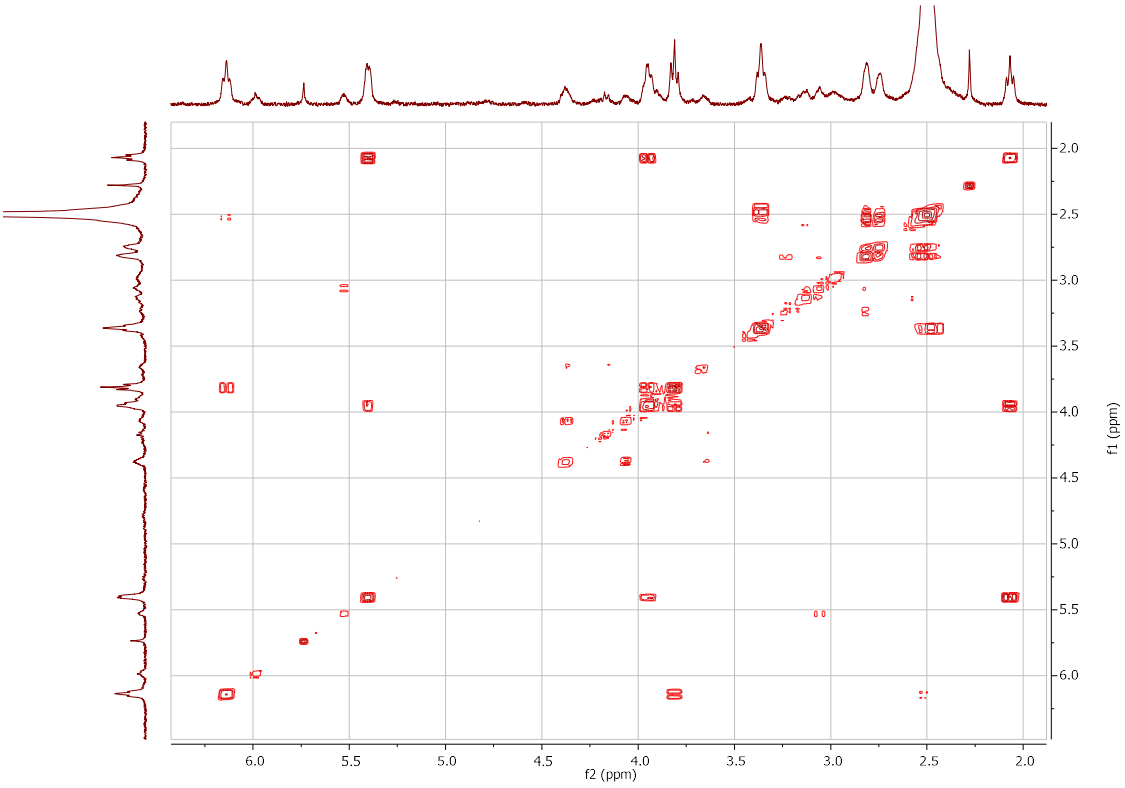
(b) $^{31}P\{^{1}H\}$ NMR spectrum (243 MHz, DMSO-d_6):



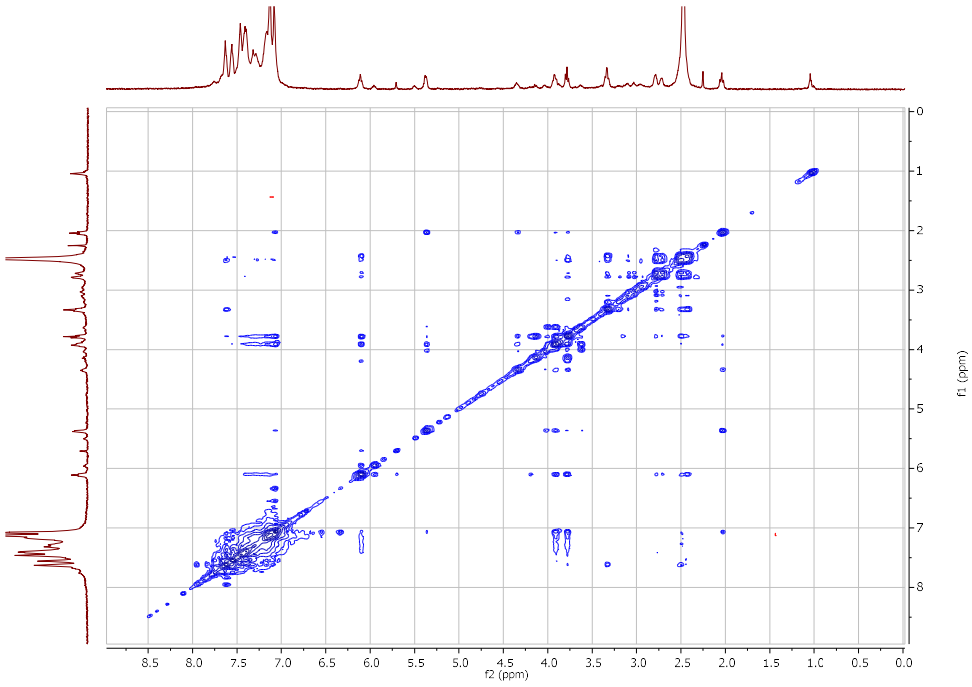
(c) 2D ^{1}H–^{1}H COSY spectrum (600 MHz, DMSO-d_6):



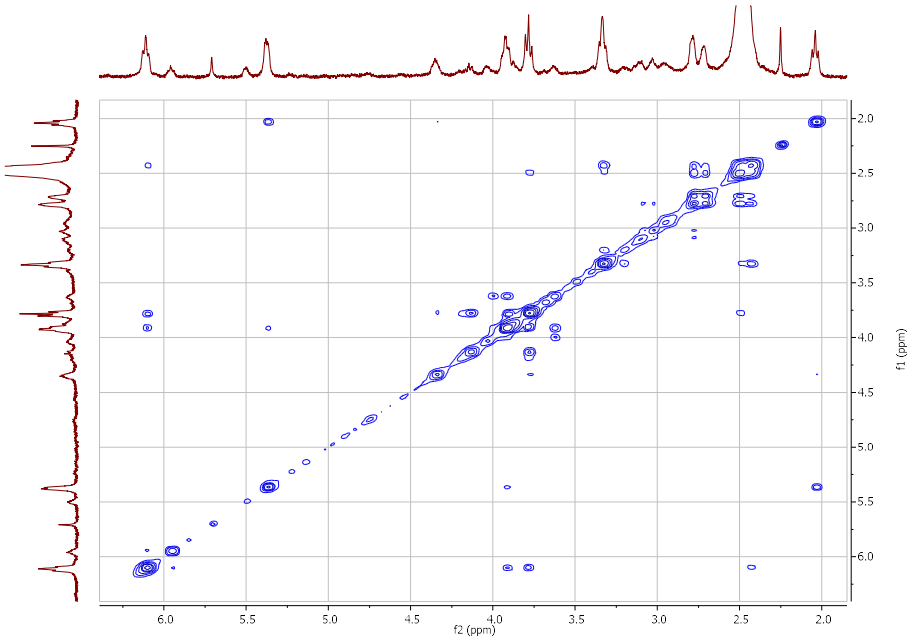
(d) Zoom in on 2D ^{1}H–^{1}H COSY spectrum (600 MHz, DMSO-d_6) between δ 2.0 ppm – 6.5 ppm:



(e) 2D ^{1}H–^{1}H NOESY spectrum (600 MHz, DMSO-d_6):

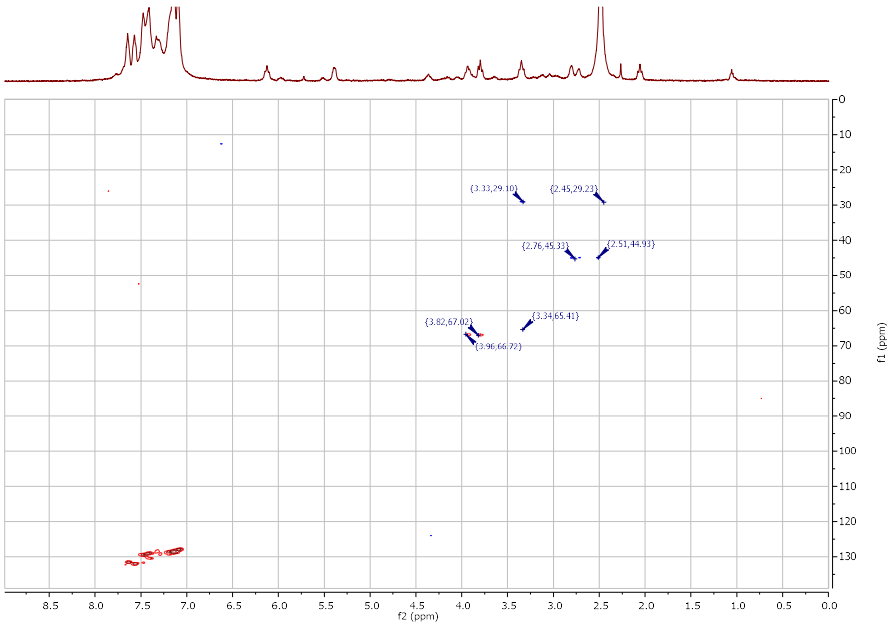


(f) Zoom in on 2D ^{1}H–^{1}H NOESY spectrum (600 MHz, DMSO-d_6) between δ 0.6 ppm – 4.1 ppm:

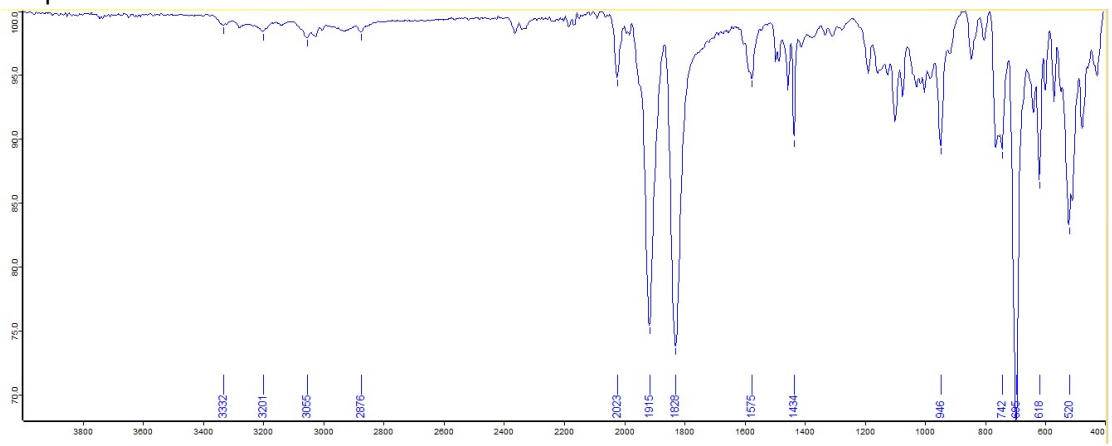


(g) 2D ^{1}H–^{13}C HSQC spectrum (500 MHz, DMSO-d_6):

2D ^{1}H–^{13}C HSQC spectrum displays the two C**H**Ph at (3.95, 66.88) and (3.81, 66.97), the two protons of the CH_2 adjacent to the amino donor at (2.79, 45.28) and (2.48, 44.99), the two protons of the CH_2 adjacent to the diphenylphosphino donor at (3.36, 29.10) and (2.42, 29.23). There is no cross peak for the three amino protons at 6.14, 5.40, and 2.07 ppm in the HSQC. The cross peak at (3.33, 65.41) and the proton with the most upfield shift (1.09 ppm) is from diethyl ether.



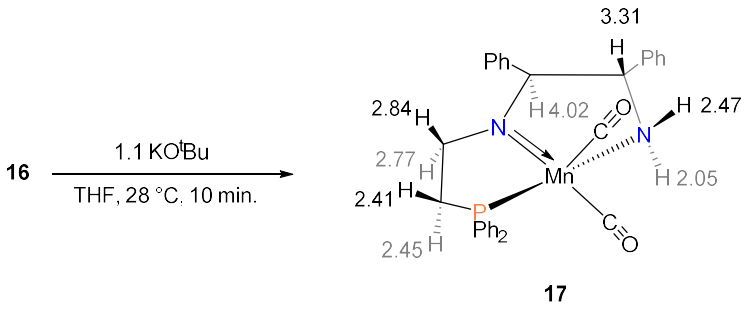
(h) IR Spectrum:



The CO stretches of precatalyst **16** are at 1915 cm^{-1} and 1828 cm^{-1}. The slight impurity at 2023 cm^{-1} suggests a side-product in the form $[Mn(P–NH–NH_2)(CO)_3][Br]$ was present in small quantities.

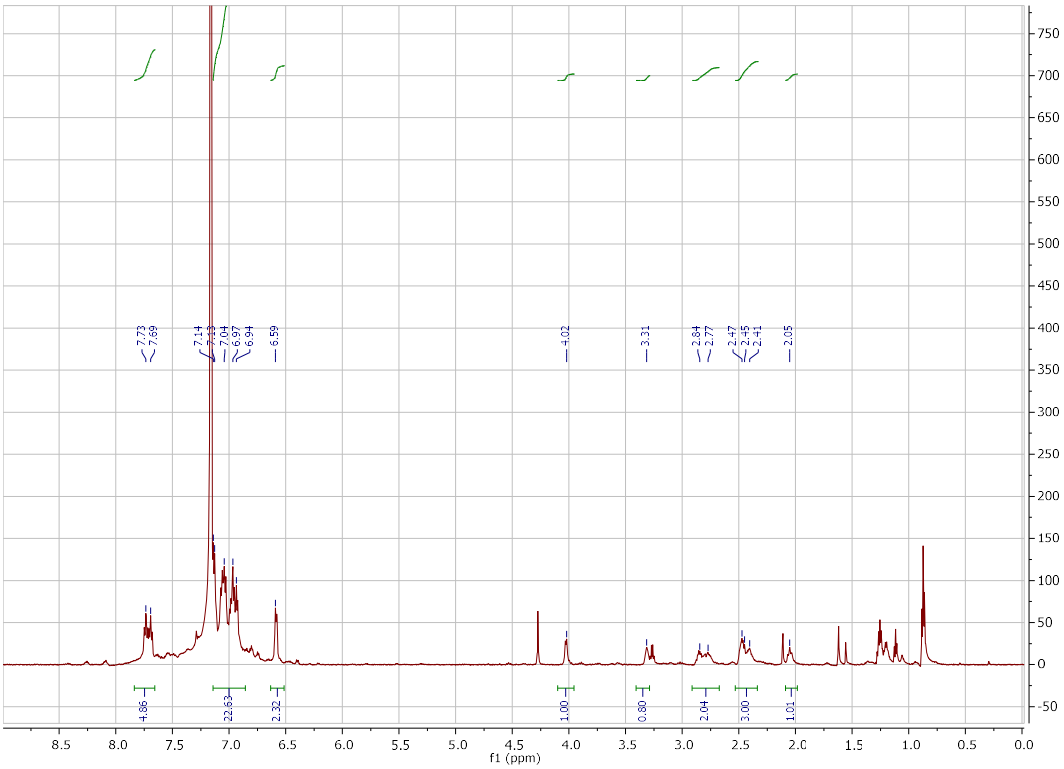
NMR Spectra of Base Activation Studies

Figure S4 NMR and IR Spectroscopy for $Mn(P–N–NH_2)(CO)_2$ (**17**):

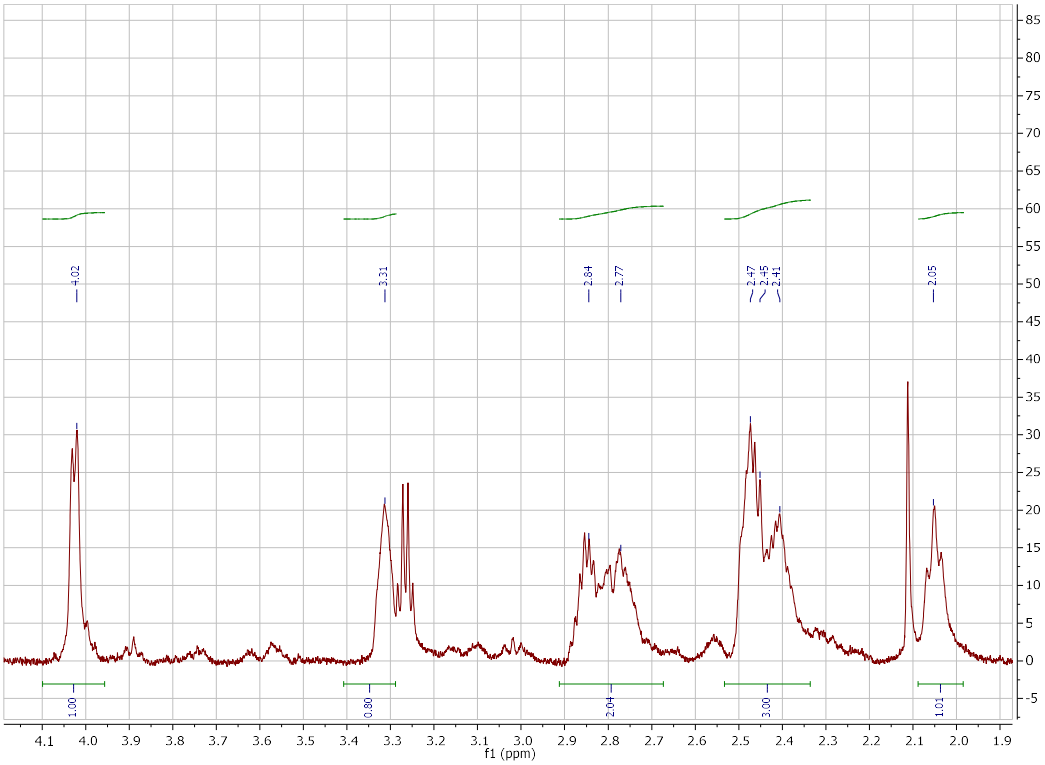


17

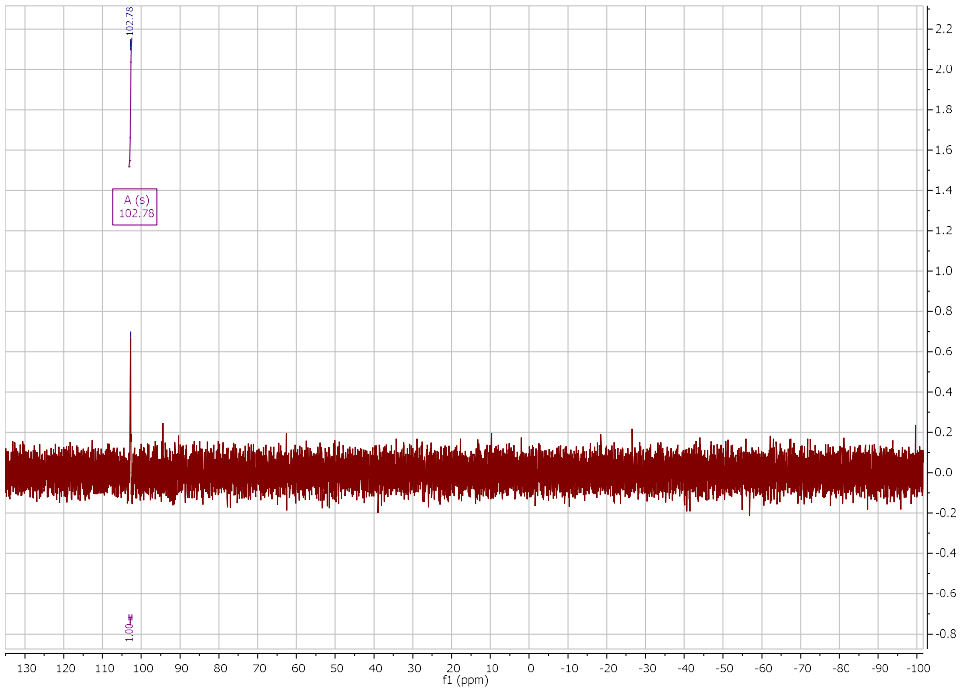
(a) ^{1}H NMR spectrum (600 MHz, C_6D_6):



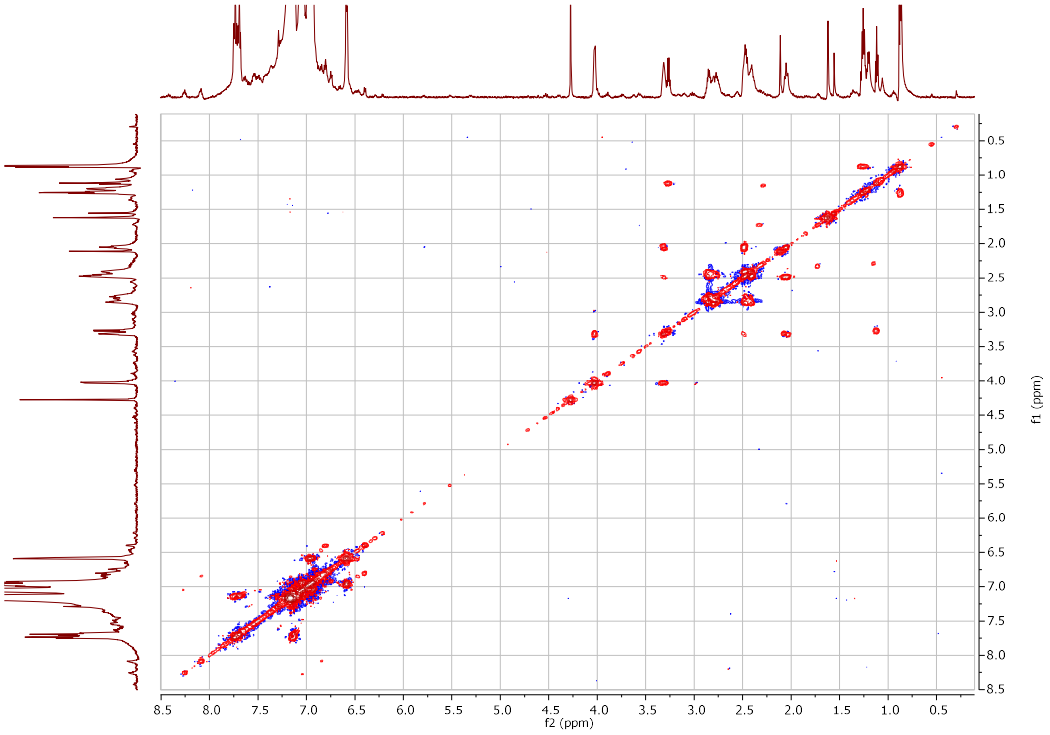
(b) Zoom in on ^{1}H NMR spectrum (600 MHz, C_6D_6) between δ 1.9 ppm – 4.2 ppm:



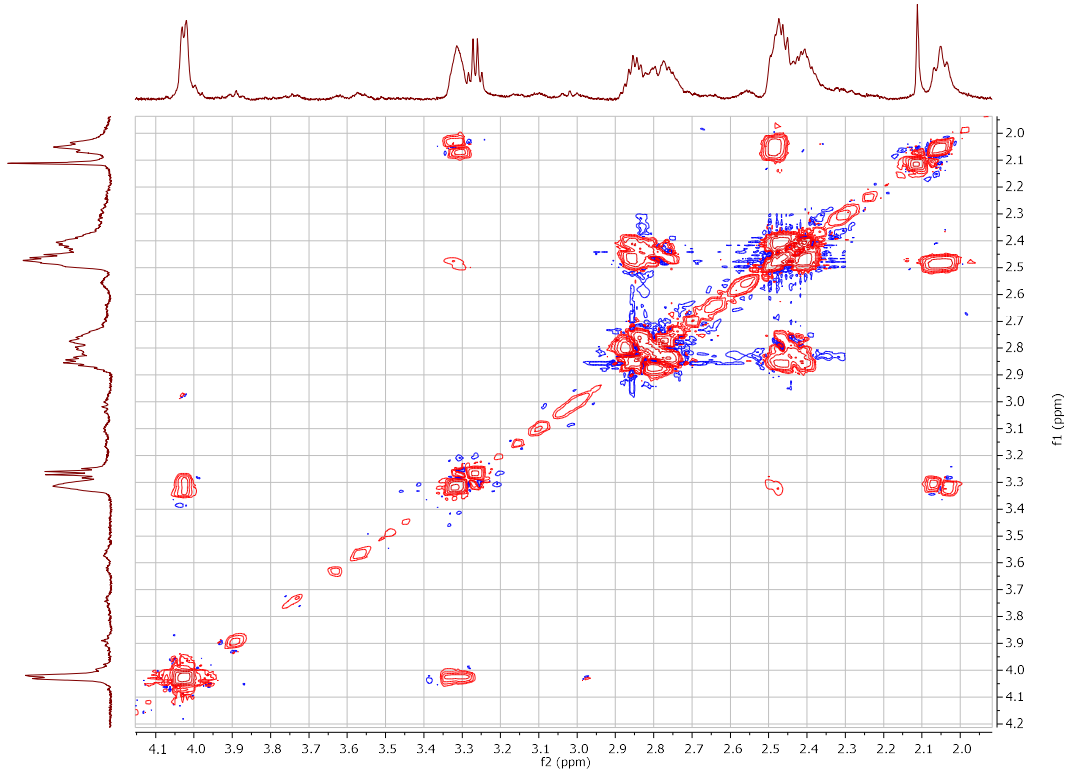
(c) $^{31}P\{^{1}H\}$ NMR spectrum (253 MHz, C_6D_6):



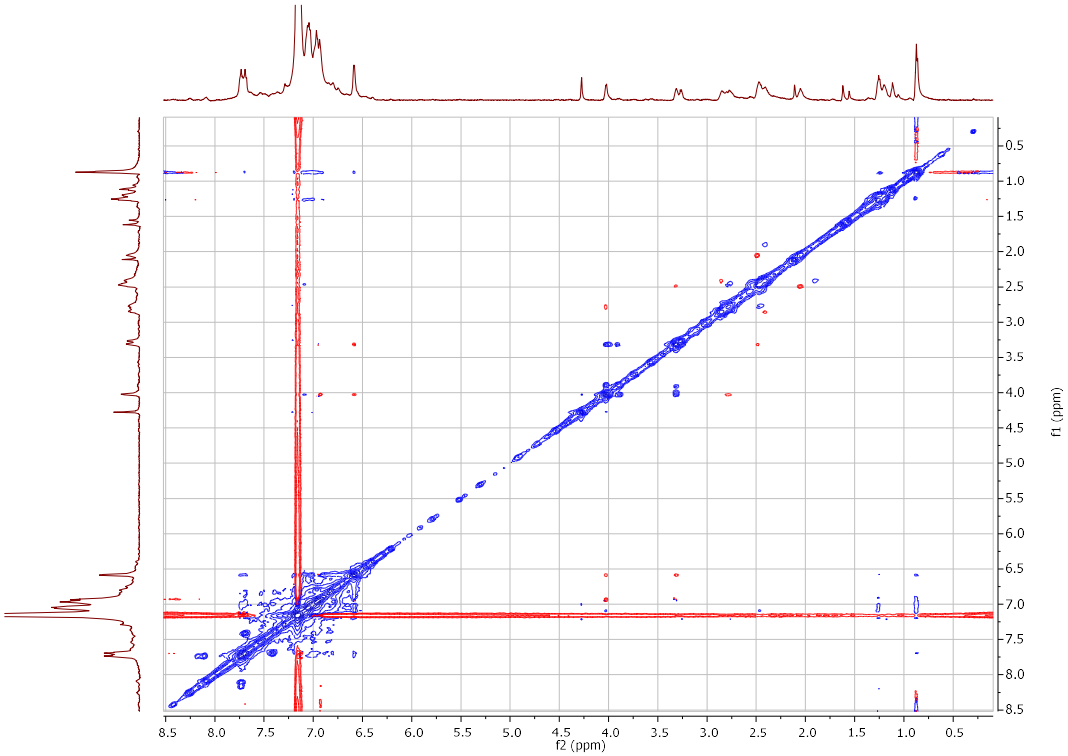
(d) 2D ^{1}H–^{1}H COSY spectrum (600 MHz, C_6D_6):



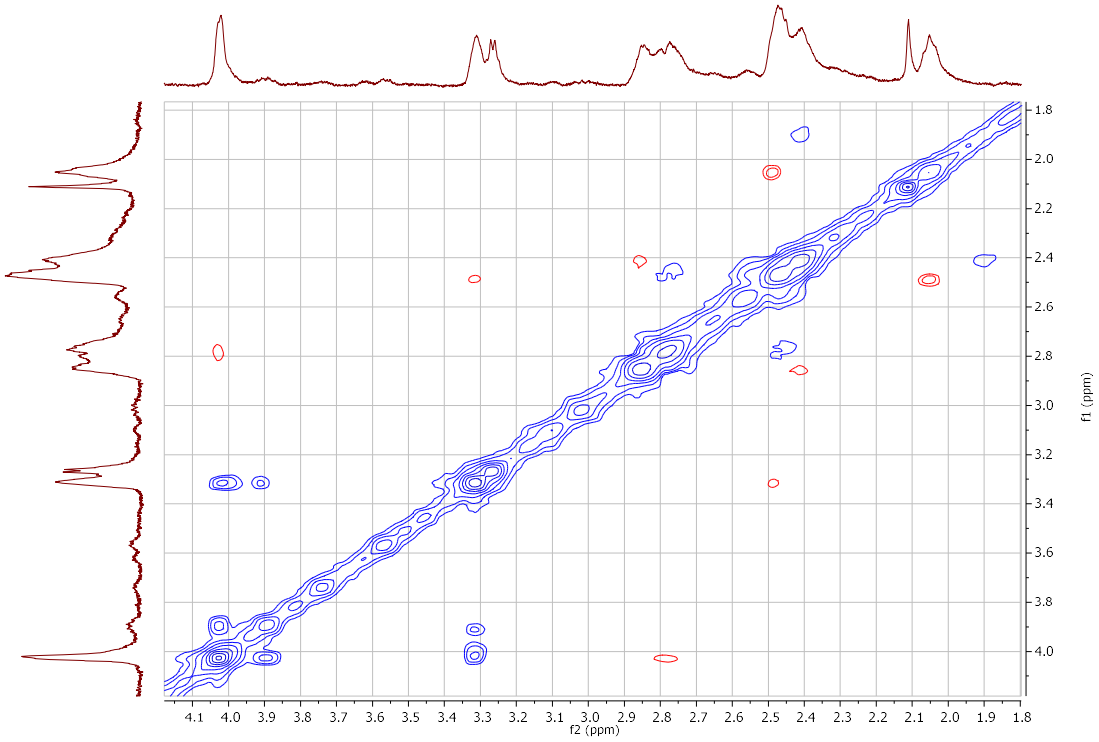
(e) Zoom in on 2D ^{1}H–^{1}H COSY spectrum (600 MHz, C_6D_6) between δ 1.9 ppm – 4.2 ppm:



(f) 2D ^{1}H–^{1}H NOESY spectrum (600 MHz, C_6D_6):

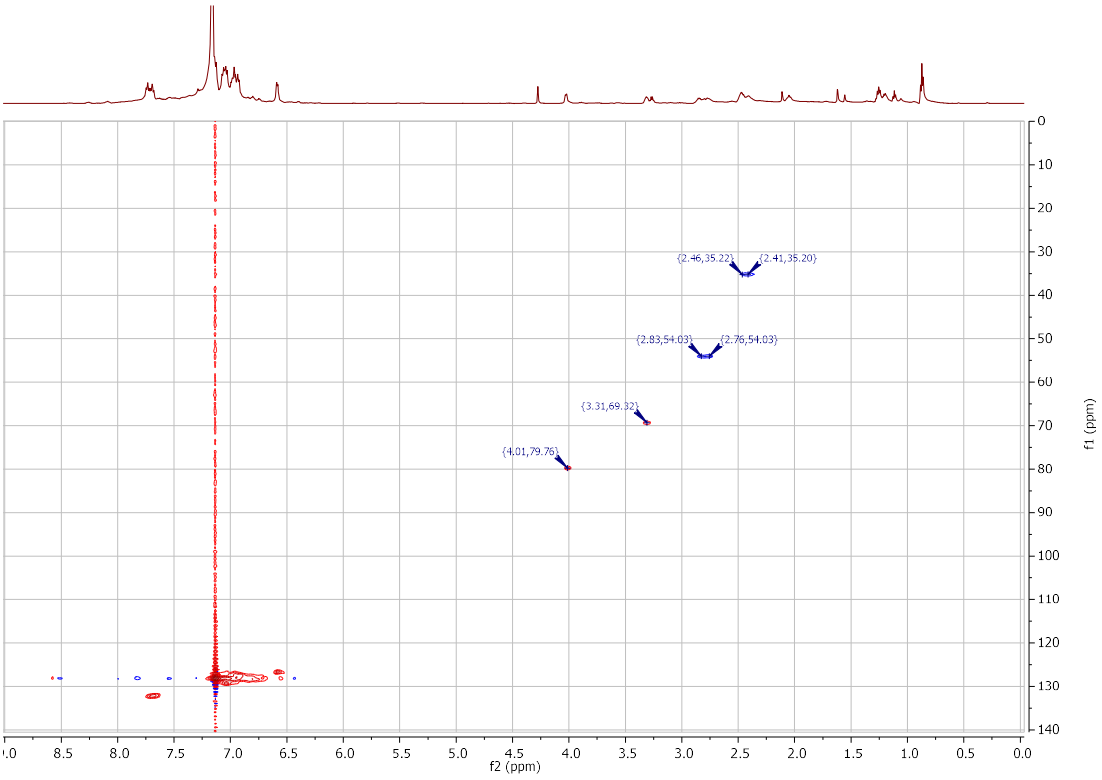


(g) Zoom in on 2D ^{1}H–^{1}H NOESY spectrum (600 MHz, C_6D_6) between δ 1.8 ppm – 4.2 ppm:

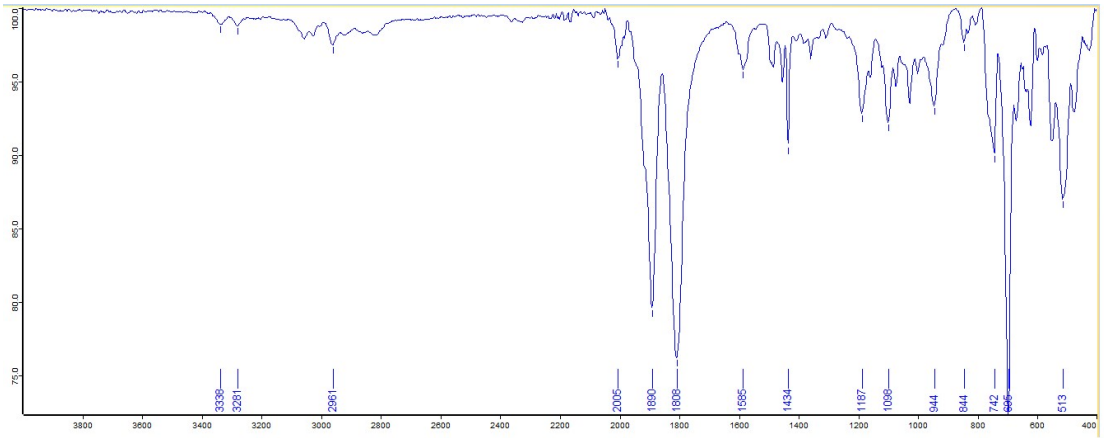


(h) 2D $^{1}H–^{13}C$ HSQC spectrum (500 MHz, C_6D_6):

2D $^{1}H–^{13}C$ HSQC spectrum displays the two C**H**Ph protons at (4.02, 79.76) and (3.31, 69.32), the two protons of the CH_2 adjacent to the amino donor are found at (2.84, 54.03) and (2.77, 54.03), and the two protons of the CH_2 adjacent to the diphenylphosphine at (2.45, 35.22) and (2.41, 35.20). There is no cross peak for the amino group proton at 2.05 ppm, while no conclusion can be drawn for the amino proton at 2.47 ppm since it is shrouded by the CH_2 proton at 2.45 ppm.



(i) IR Spectrum:

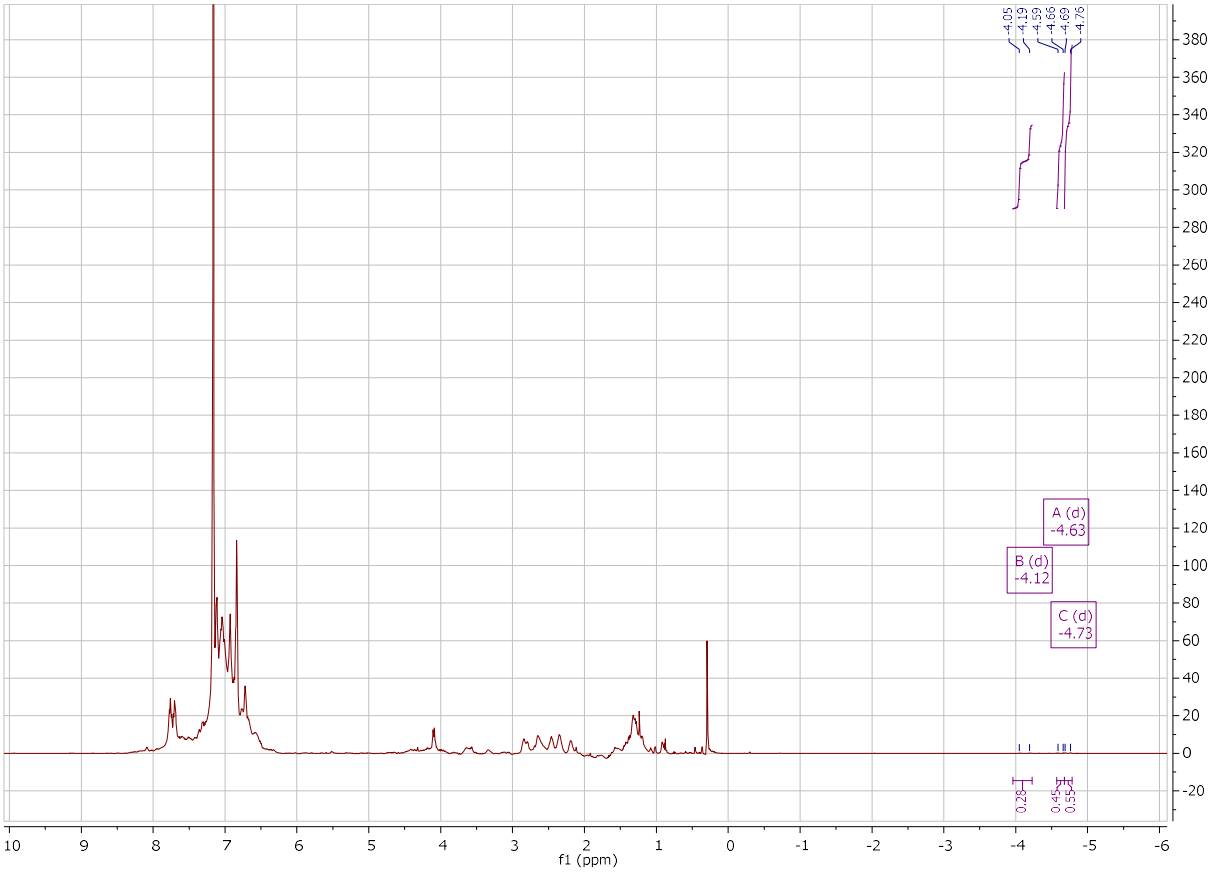


The CO stretches of deprotonated complex **17** are at 1890 cm^{-1} and 1808 cm^{-1}.

NMR Spectra of Hydride, Borohydride, and Ethoxide Species

Figure S5 NMR and IR Spectroscopy for the attempted synthesis of $Mn(P–NH–NH_2)(CO)_2H$ (**20**):

(a) ^1H NMR spectrum (600 MHz, C_6D_6):



(b) Zoom in on ^{1}H NMR spectrum (600 MHz, C_6D_6) in the hydride region

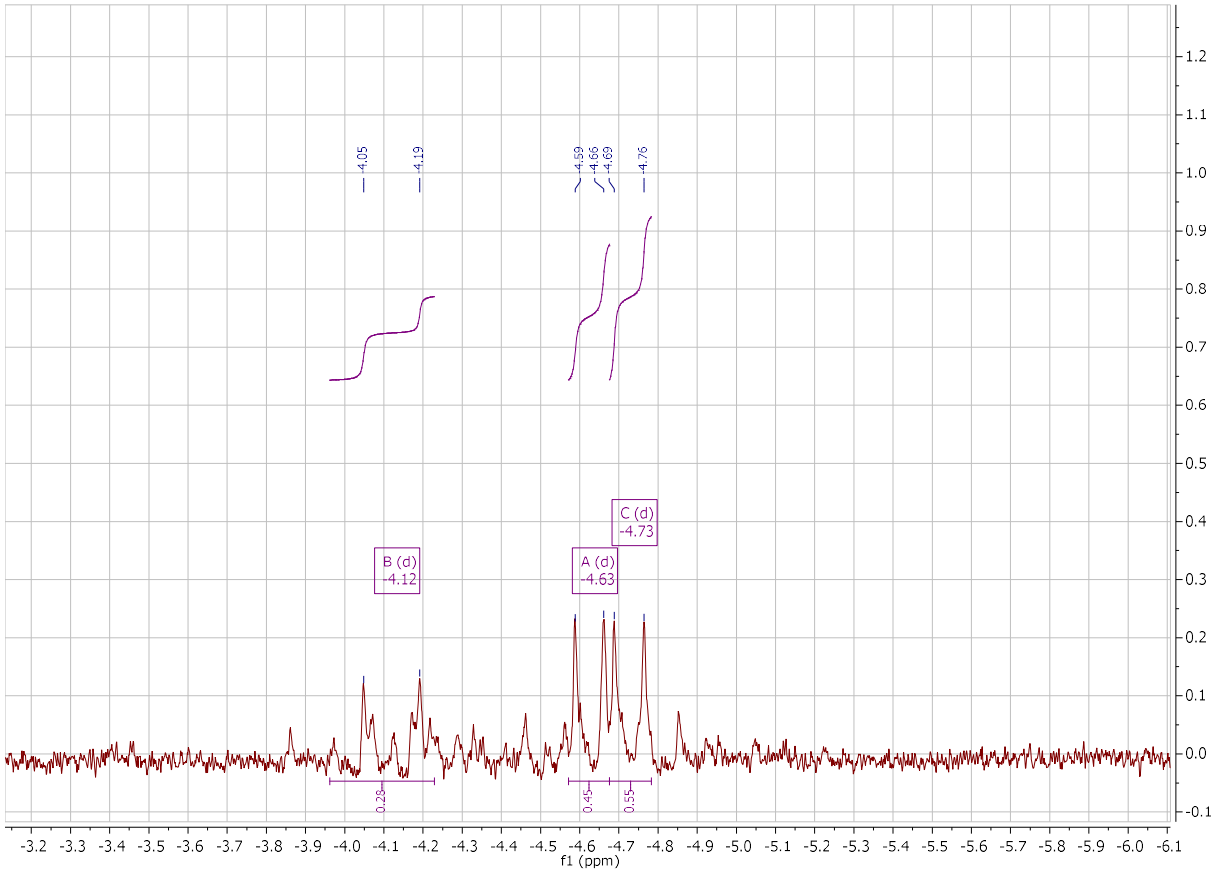
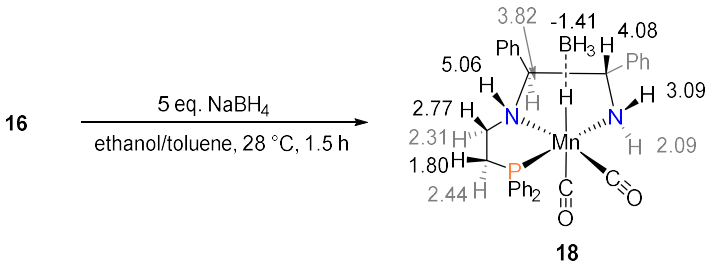
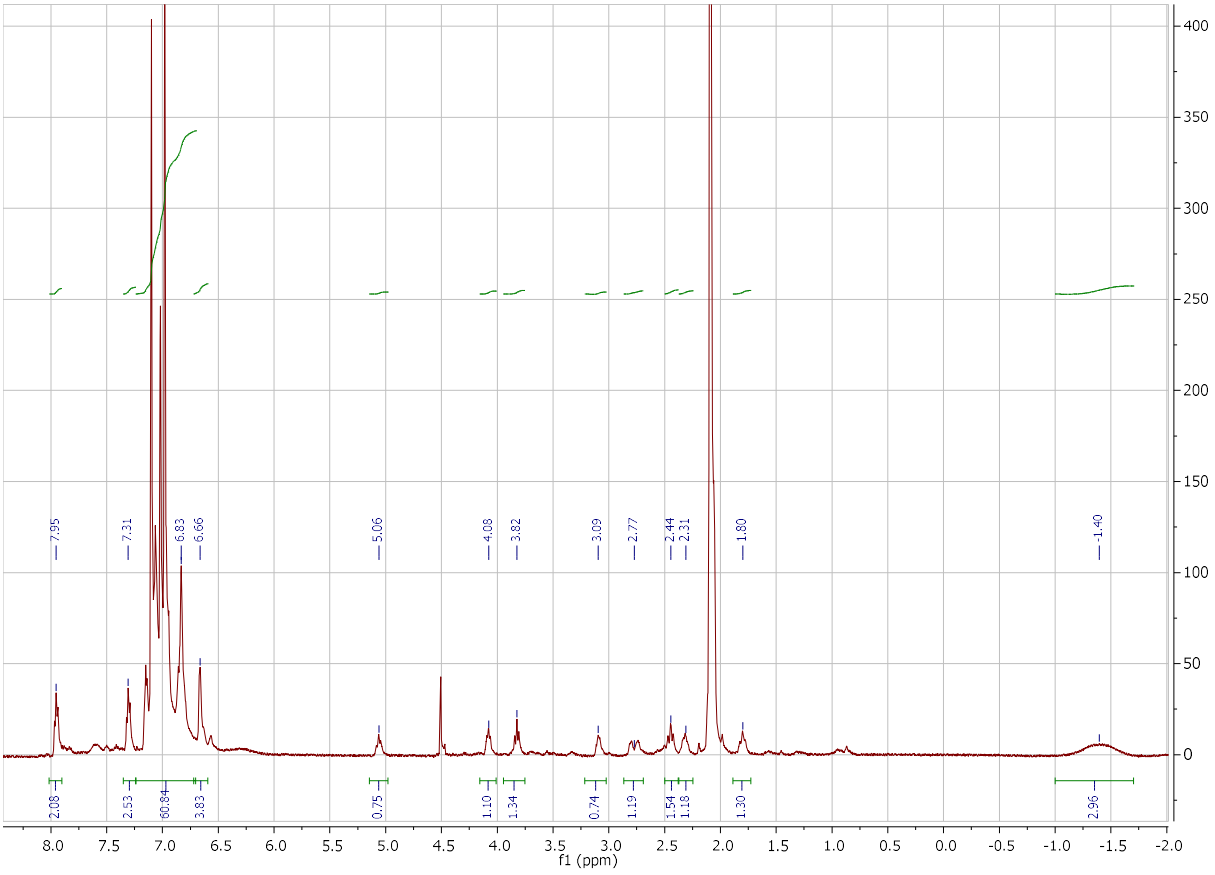


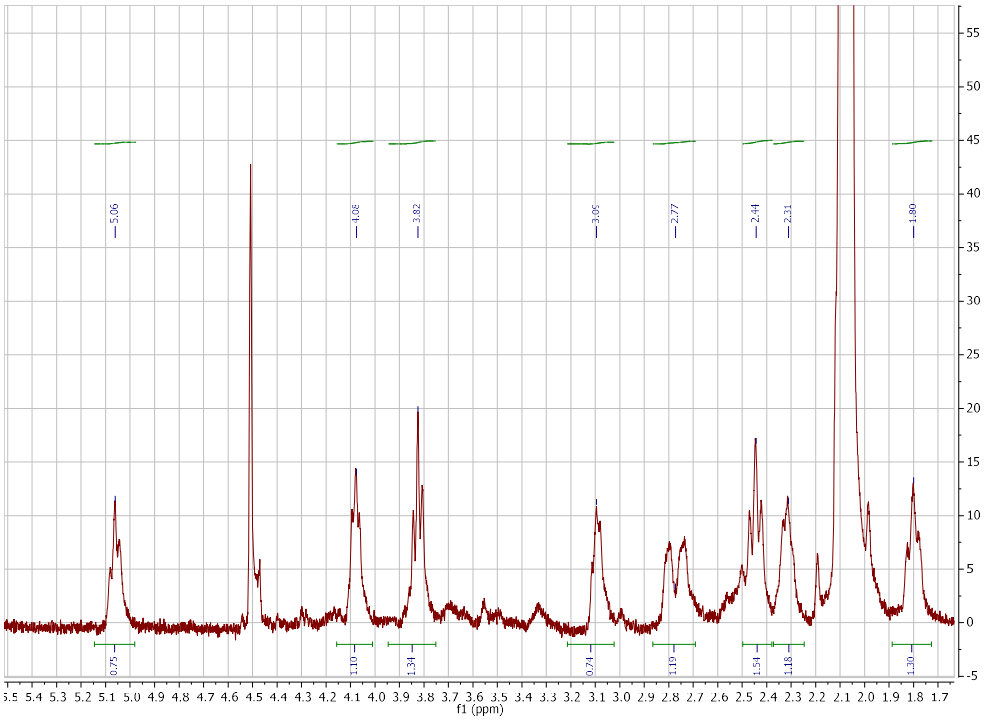
Figure S6 NMR and IR Spectroscopy for *syn mer*-Mn(P–NH–NH_2)$(CO)_2(BH_4)$ (**18**):



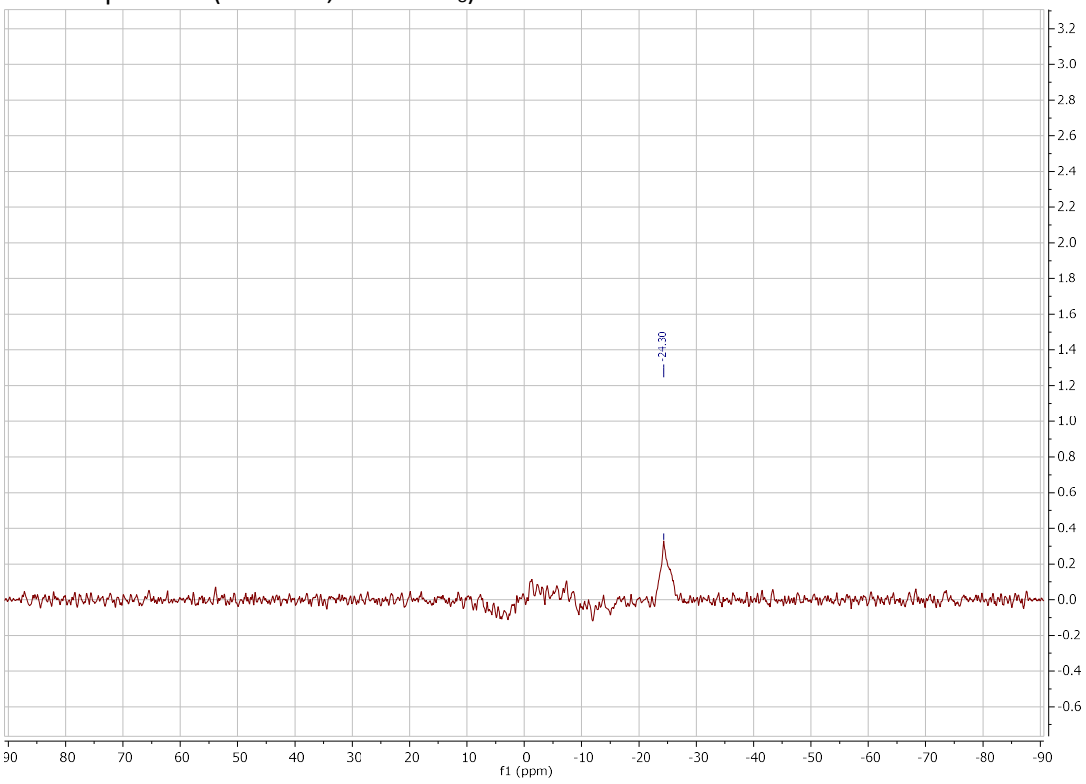
(a) ^{1}H NMR spectrum (600 MHz, toluene-d_8):



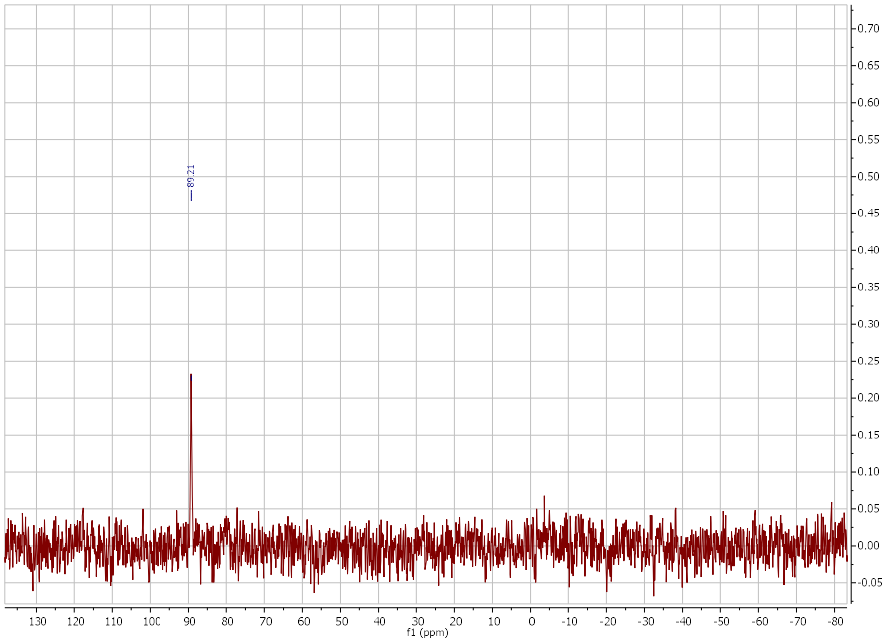
(b) Zoom in on ^{1}H NMR spectrum (600 MHz, toluene-d_8) between δ 1.7 ppm – 5.5 ppm:



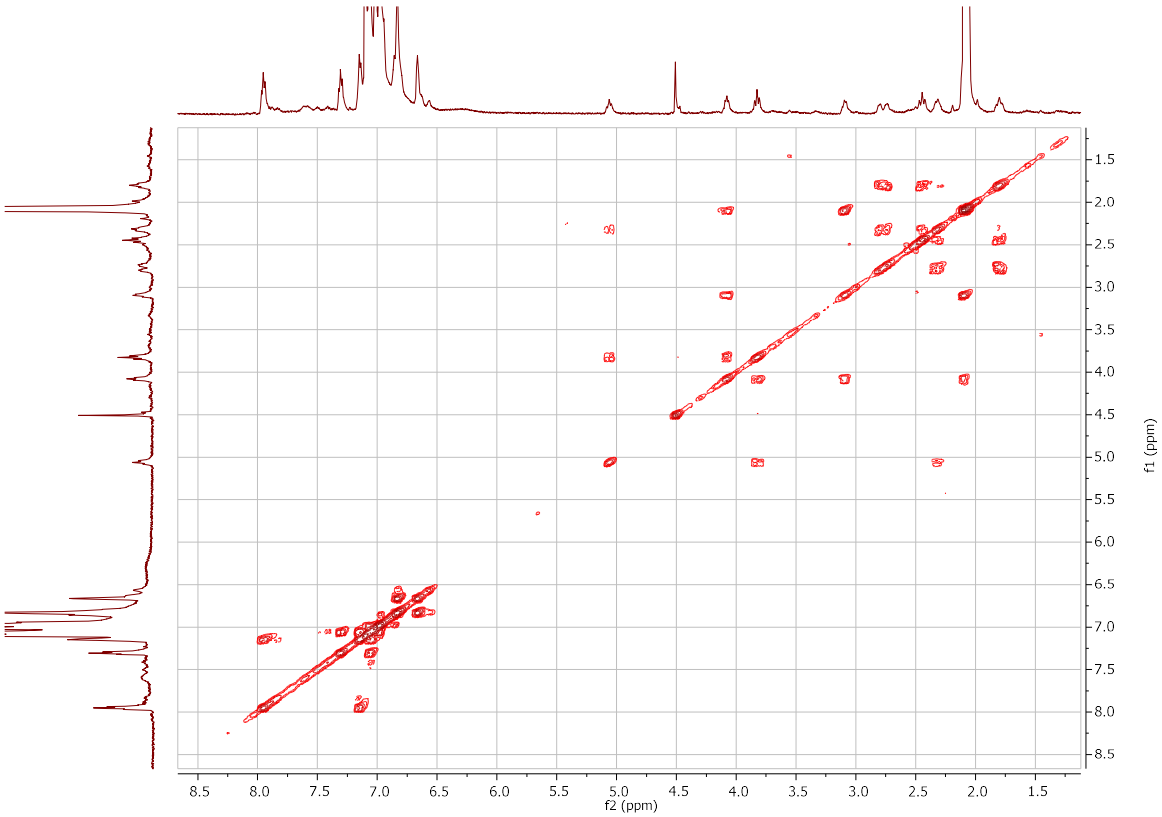
(c) ^{11}B NMR spectrum (192 MHz, toluene-d_8):



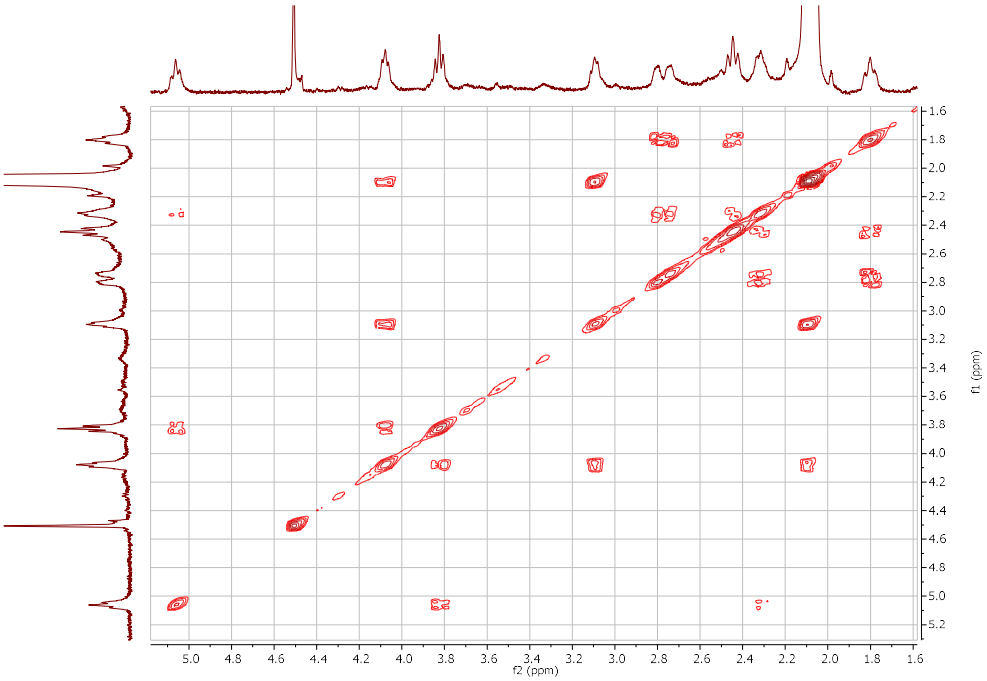
(d) $^{31}P\{^{1}H\}$ NMR spectrum (243 MHz, toluene-d_8):



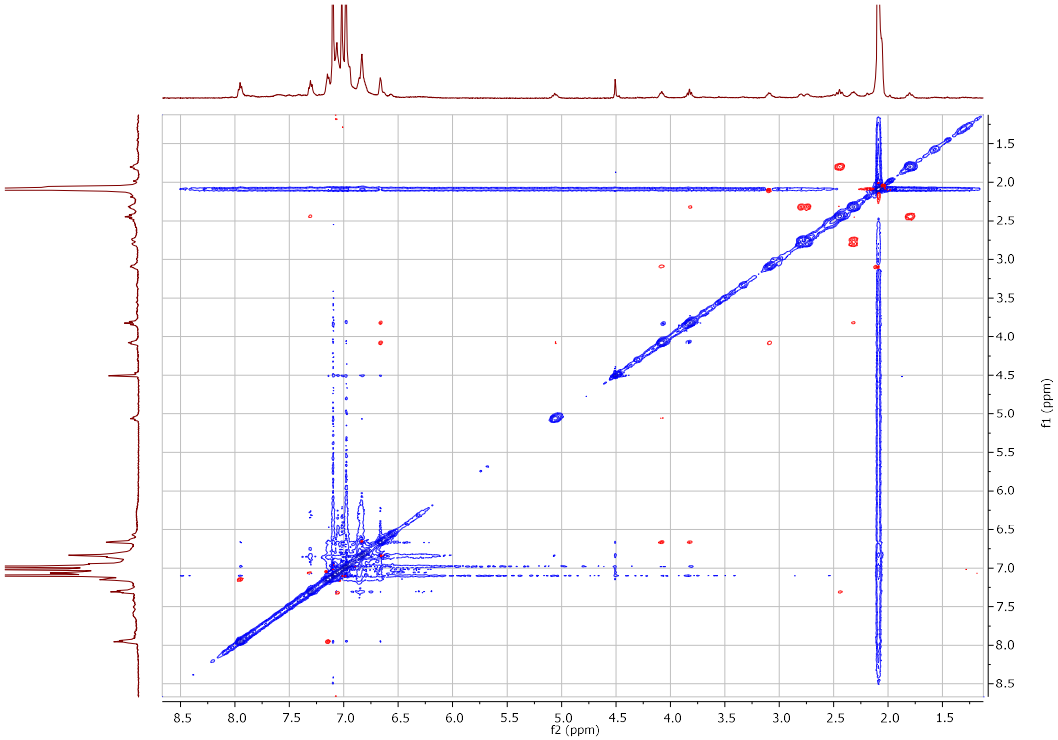
(e) 2D ^{1}H–^{1}H COSY spectrum (600 MHz, toluene-d_8):



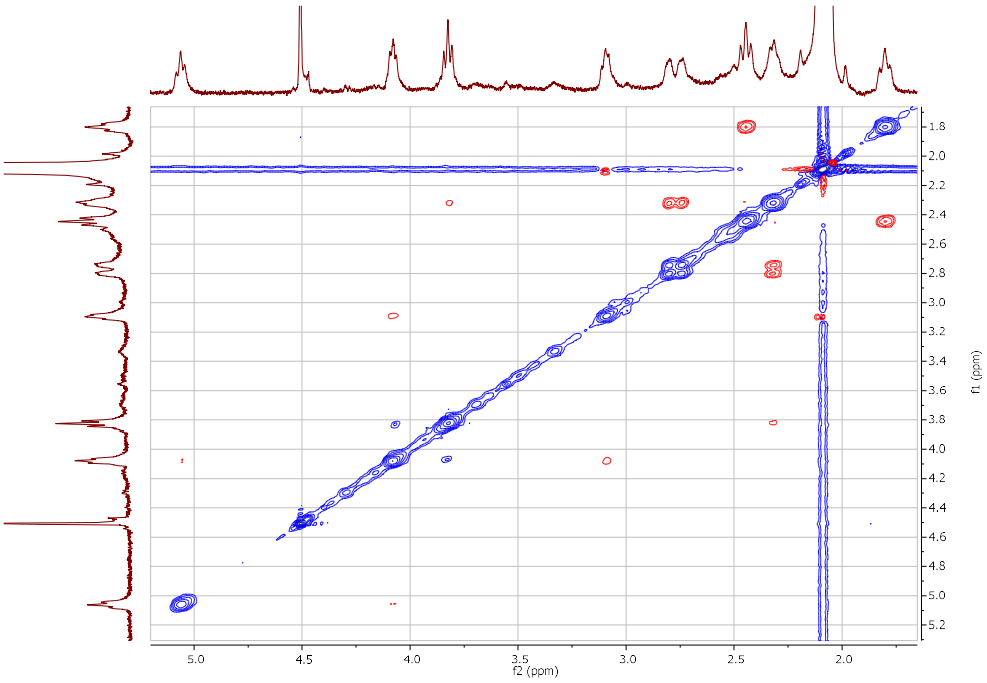
(f) Zoom in on 2D ^{1}H–^{1}H COSY spectrum (600 MHz, toluene-d_8) between δ 1.6 ppm – 5.3 ppm:



(g) 2D ^{1}H–^{1}H NOESY spectrum (600 MHz, toluene-d_8):

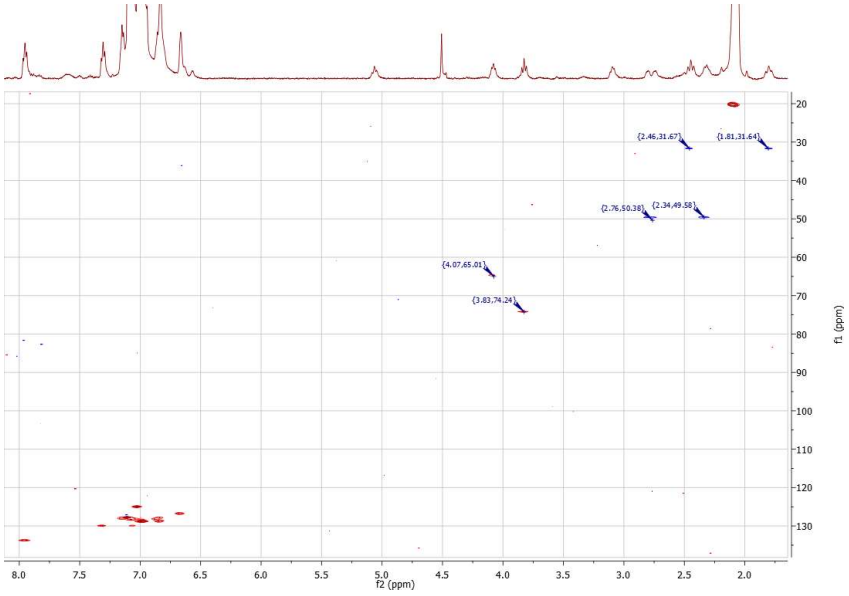


(h) Zoom in on 2D ^{1}H–^{1}H NOESY spectrum (600 MHz, toluene-d_8) between δ 1.7 ppm – 5.1 ppm:

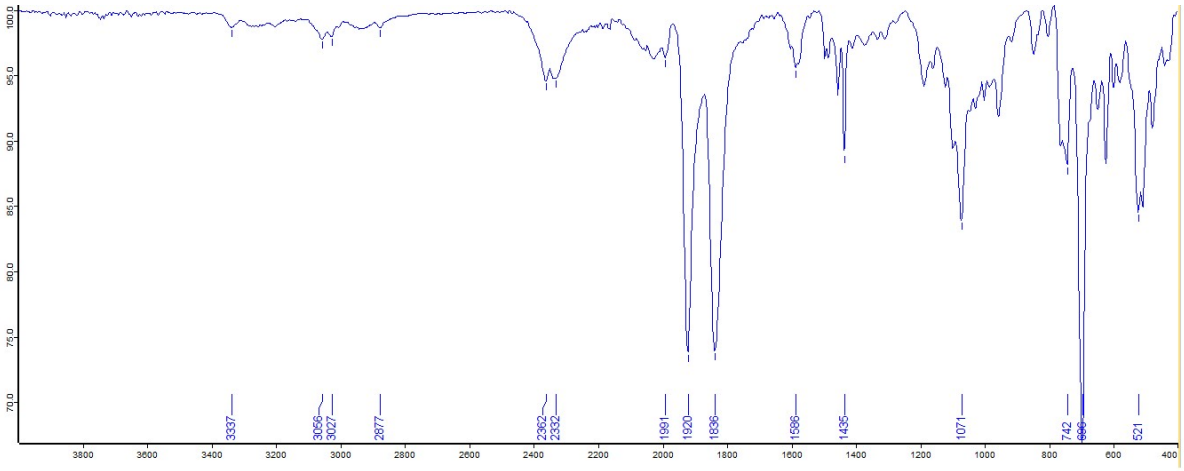


(i) 2D ^{1}H–^{13}C HSQC spectrum (600 MHz, toluene-d_8):

Explanation: 2D ^{1}H–^{13}C HSQC spectrum displays the two C**H**Ph at (4.08, 65.01) and (3.82, 74.24), the two protons of the CH_2 adjacent to the secondary amino donor at (2.77, 50.39) and (2.31, 49.58), the two protons of the CH_2 adjacent to the diphenylphosphino donor at (2.44, 31.67) and (1.80, 31.64). There is no cross peak for the three amino protons at 5.06, 3.09, and 2.09 ppm in the HSQC.

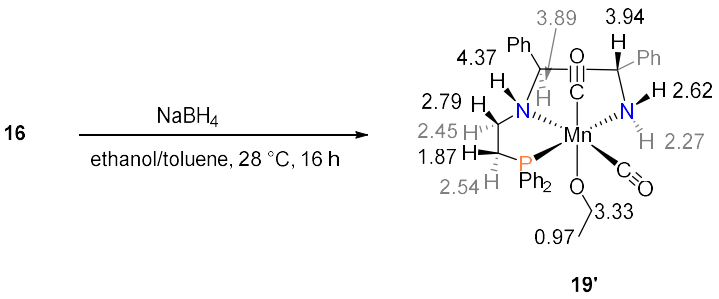


(j) IR Spectrum:



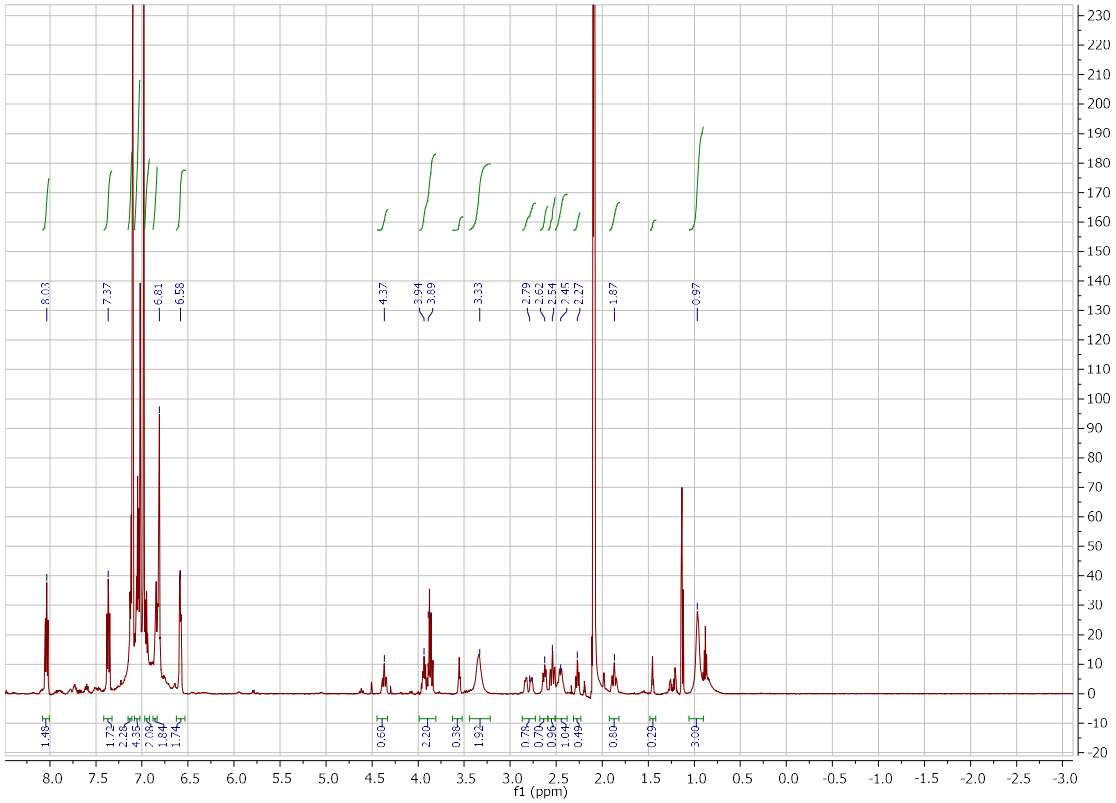
The CO stretches of the borohydride complex **18** are at 1920 cm^{-1} and 1836 cm^{-1}.

Figure S7 NMR and IR Spectroscopy for *anti mer*-Mn(P–NH–NH_2)$(CO)_2$(OEt) (**19'**):

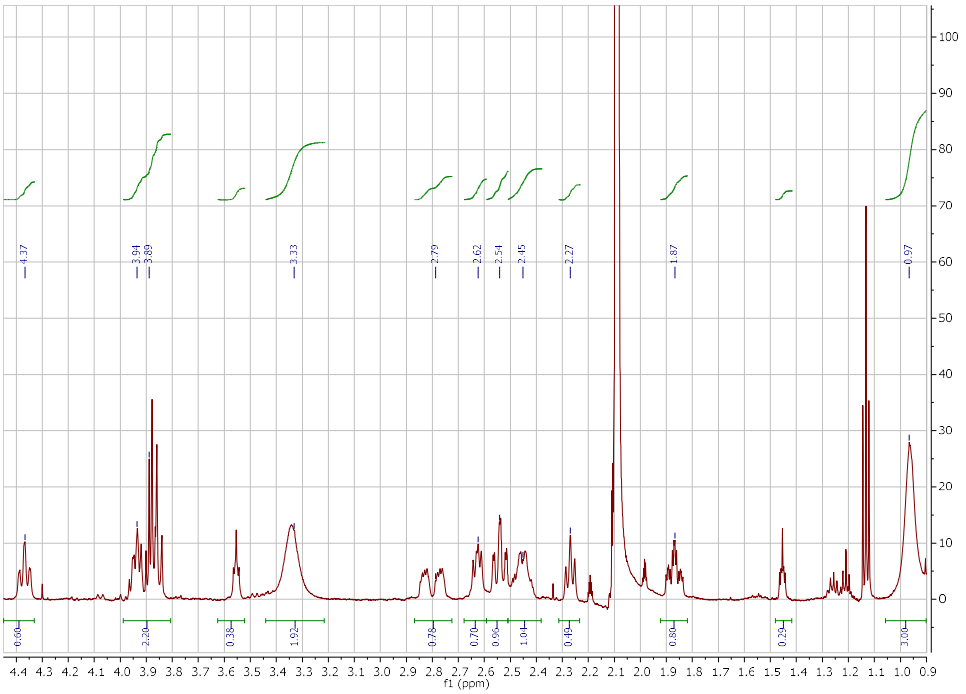


19'

(a) ^{1}H NMR spectrum (600 MHz, toluene-d_8):

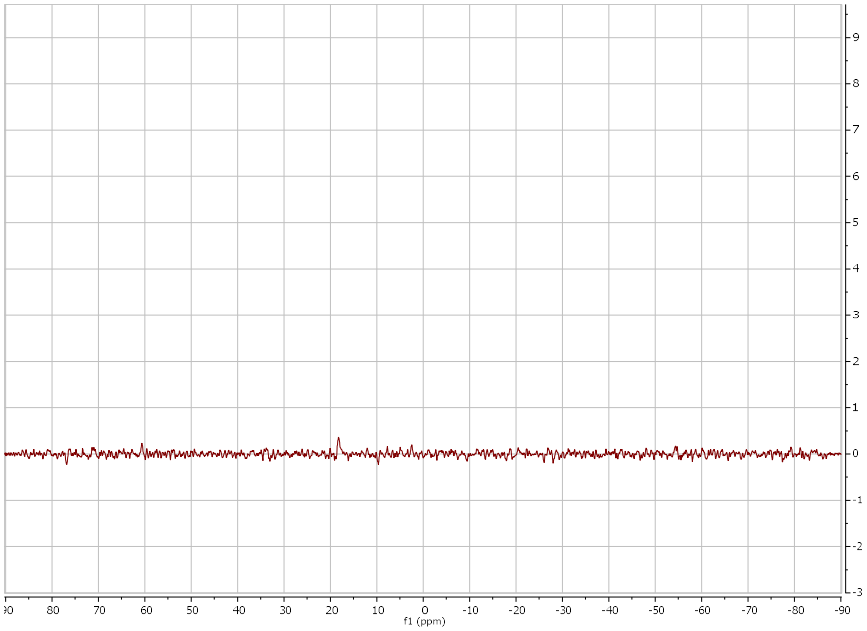


(b) Zoom in on ^{1}H NMR spectrum (600 MHz, toluene-d_8) between δ 0.9 ppm – 4.8 ppm:

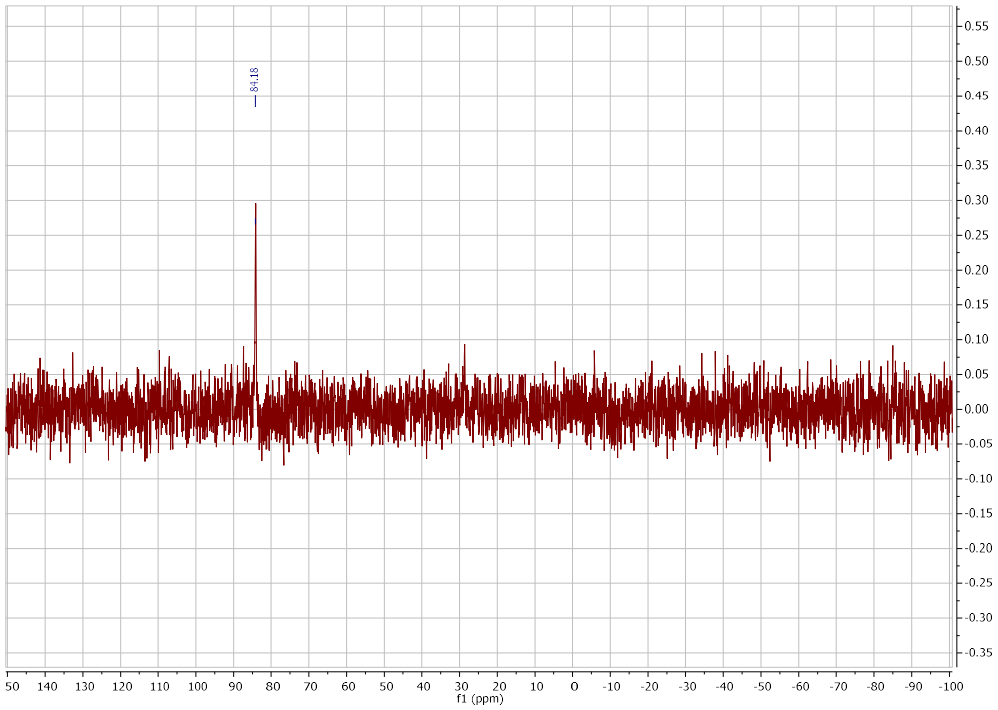


(c) ^{11}B NMR spectrum (192 MHz, toluene-d_8):

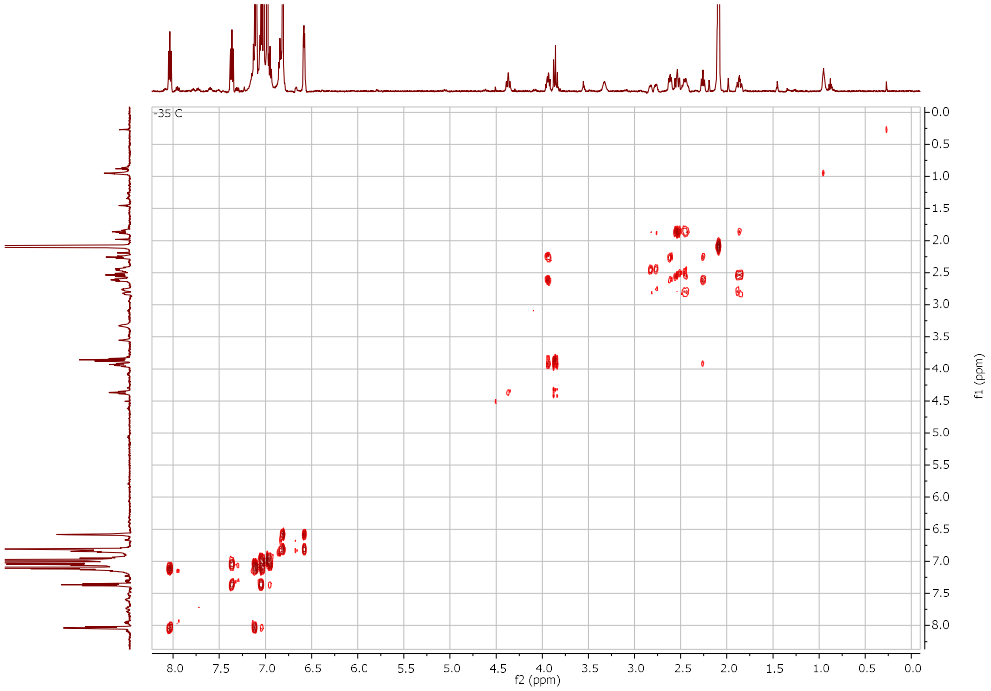
No peaks are present in the ^{11}B NMR spectrum.



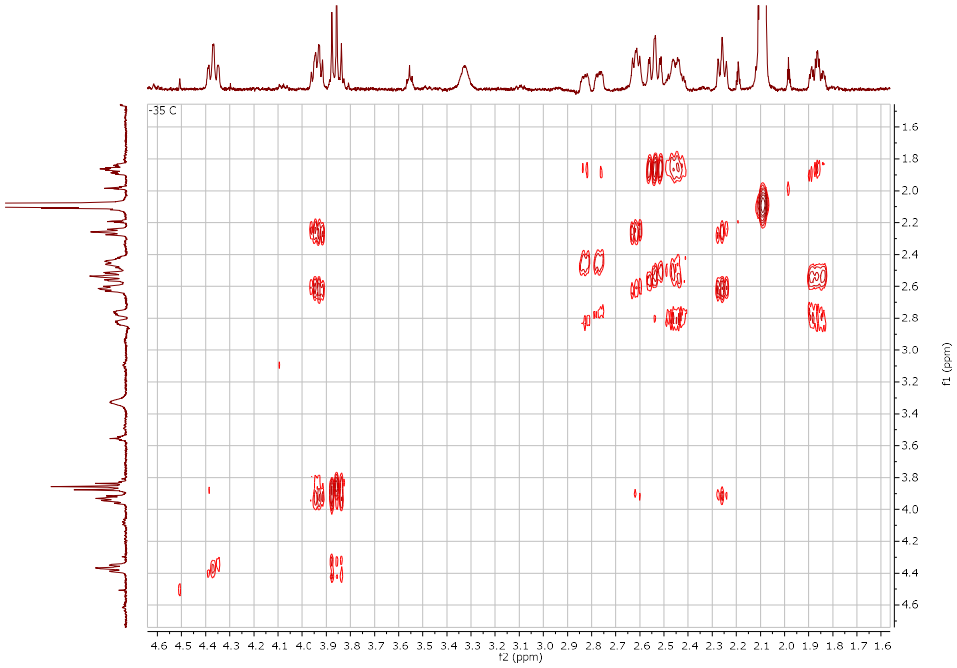
(d) $^{31}P\{^{1}H\}$ NMR spectrum (243 MHz, toluene-d_8):



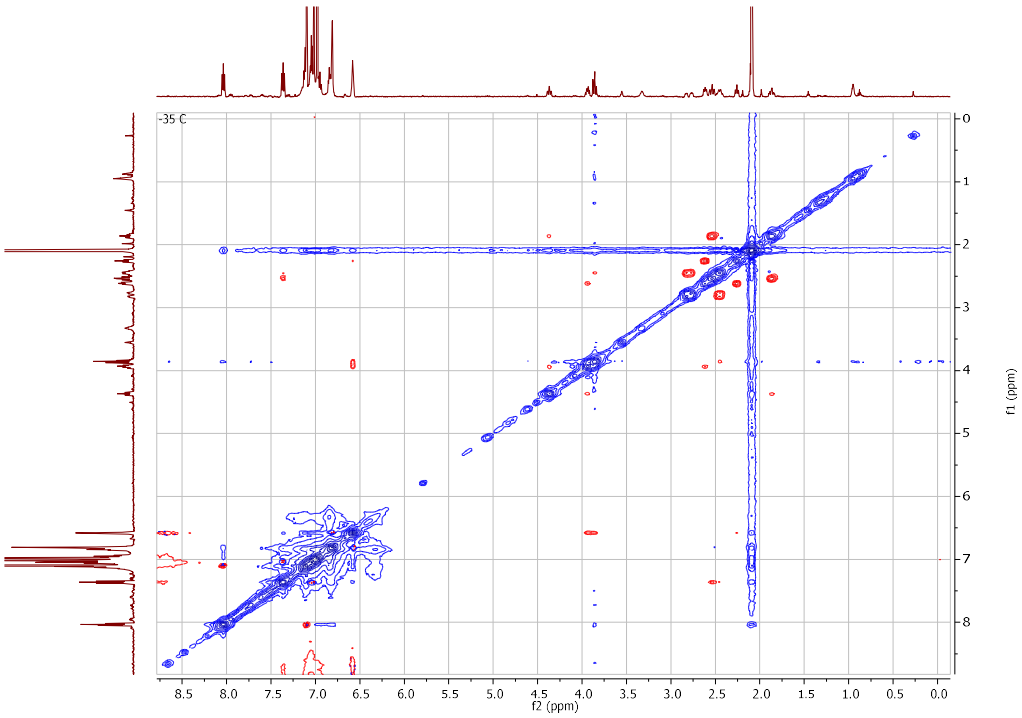
(e) 2D ^{1}H–^{1}H COSY spectrum (600 MHz, toluene-d_8):



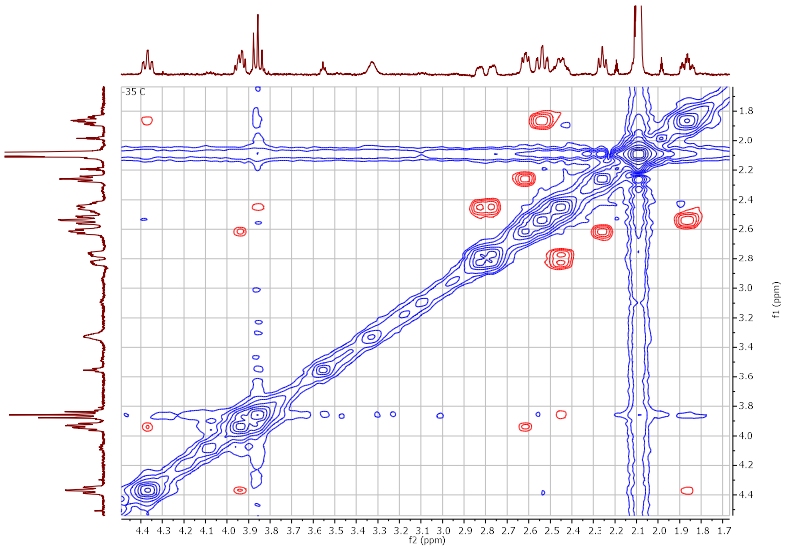
(f) Zoom in on 2D ^{1}H–^{1}H COSY spectrum (600 MHz, toluene-d_8) between δ 1.0 ppm – 4.5 ppm:



(g) 2D ^{1}H–^{1}H NOESY spectrum (600 MHz, toluene-d_8):

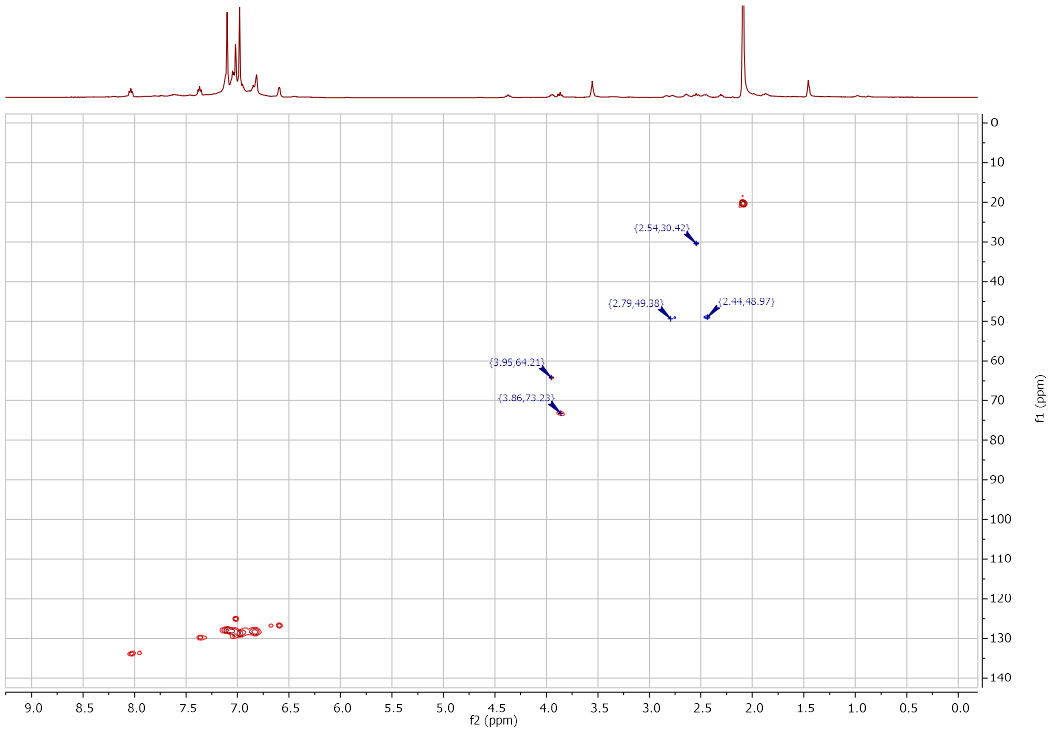


(h) Zoom in on 2D ^{1}H–^{1}H NOESY spectrum (600 MHz, toluene-d_8) between δ 1.7 ppm – 4.4 ppm:

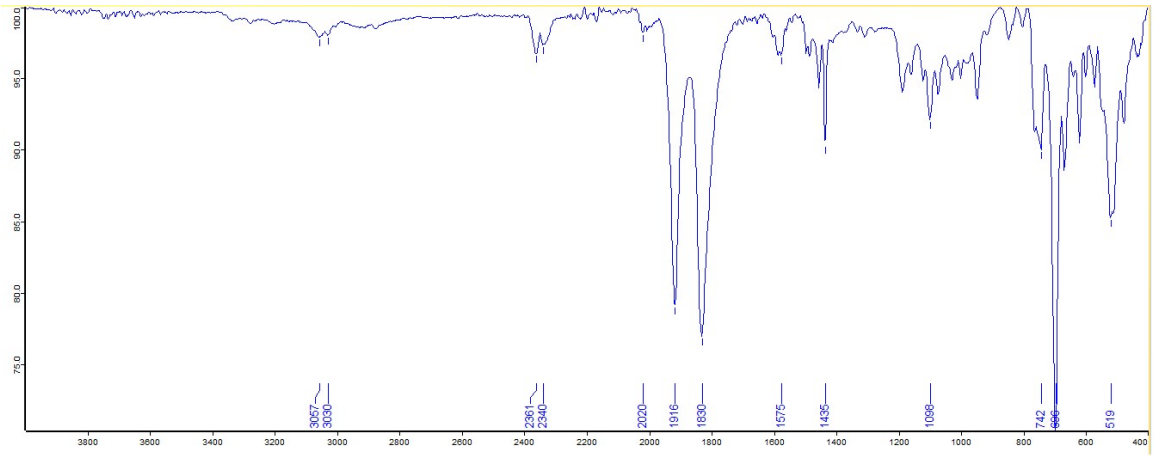


(i) 2D ^{1}H–^{13}C HSQC spectrum (600 MHz, toluene-d_8):

2D ^{1}H–^{13}C HSQC spectrum displays the two C**H**Ph at (3.94, 64.21) and (3.89, 73.23), the two protons of the CH_2 adjacent to the secondary amino donor at (2.79, 49.38) and (2.45, 48.97), the two protons of the CH_2 adjacent to the diphenylphosphino donor at (2.54, 30.42) and no cross peak was found for the proton at 1.87. There is no cross peak for the three amino protons at 4.37, 2.62, and 2.27 ppm in the HSQC spectrum.



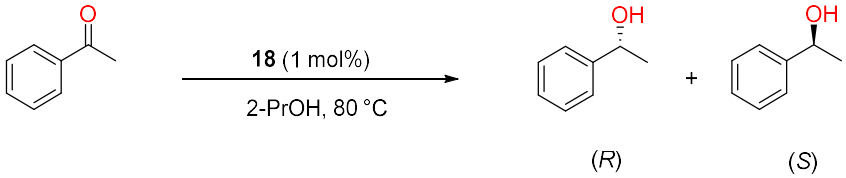
(j) IR spectrum:



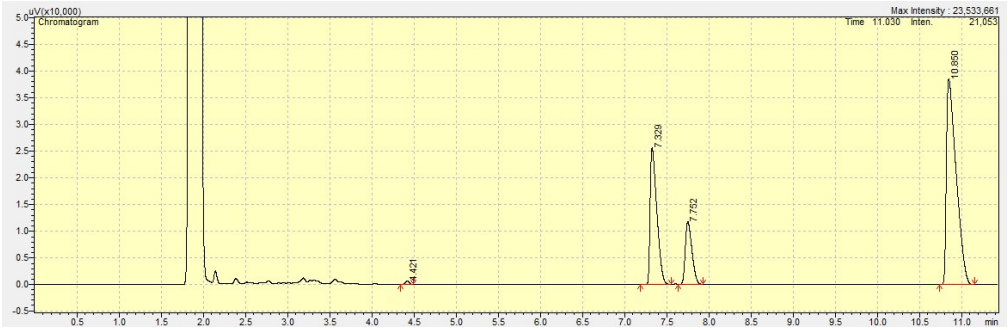
The CO stretches of the *anti* ethoxide complex **19'** are at 1916 cm^{-1} and 1830 cm^{-1}.

Gas Chromatograph Readouts for the ATH of Ketones

Figure S8 Gas chromatograph readout for the ATH of acetophenone.

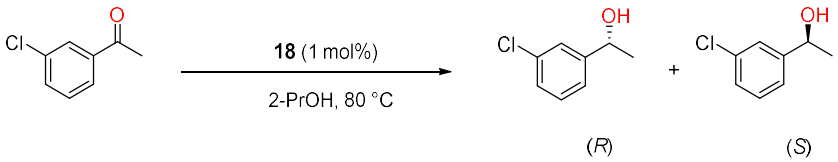


Oven Temperature: 130 °C

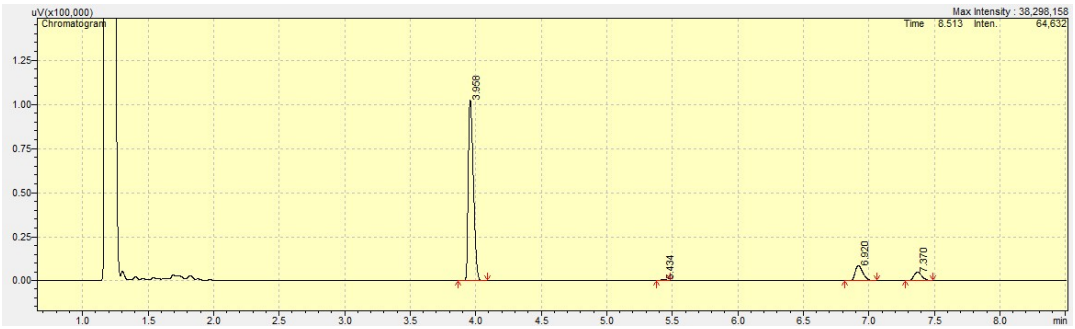


Retention time: acetophenone: 4.421 min.; (*R*)-1-phenylethanol: 7.329 min.; (*S*)-1-phenylethanol: 7.752 min.; di-*tert*-butylbenzene (standard): 10.850 min..

Figure S9 Gas chromatograph readout for the ATH of *m*-chloroacetophenone.

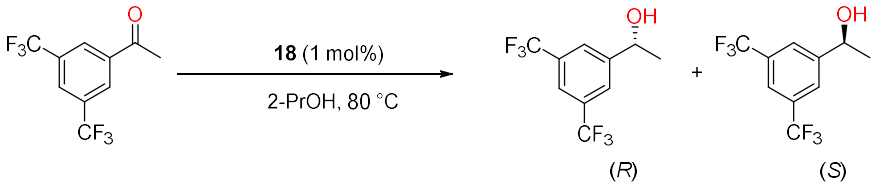


Oven Temperature: 145 °C

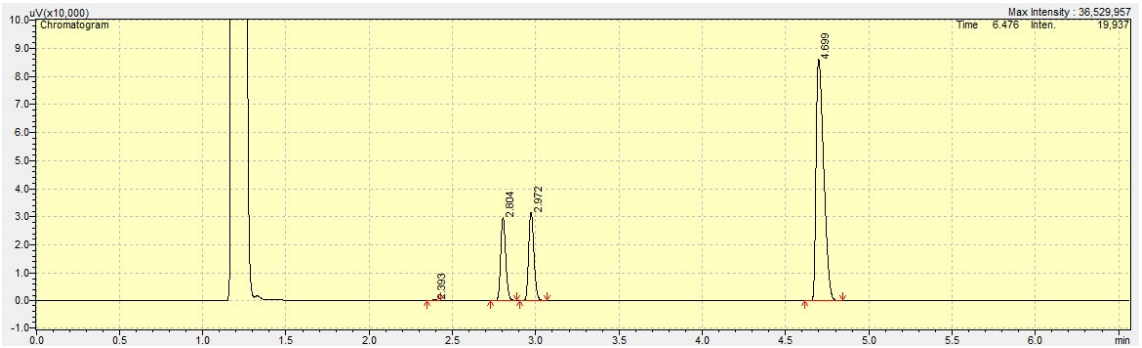


Retention time: *m*-chloroacetophenone: 5.434 min.; (*R*)-1-(*m*-chlorophenyl)ethan-1-ol: 6.920 min.; (*S*)-1-(*m*-chlorophenyl)ethan-1-ol: 7.370 min.; di-*tert*-butylbenzene (standard): 3.958 min..

Figure S10 Gas chromatograph readout for the ATH of 3',5'-bis(trifluoromethyl)acetophenone.

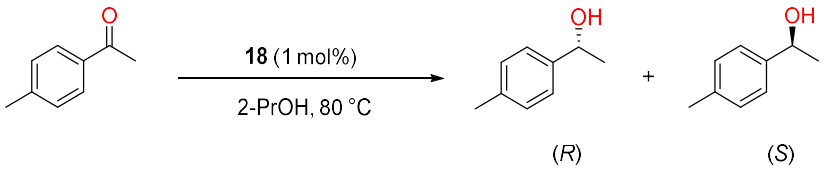


Oven Temperature: 140 °C

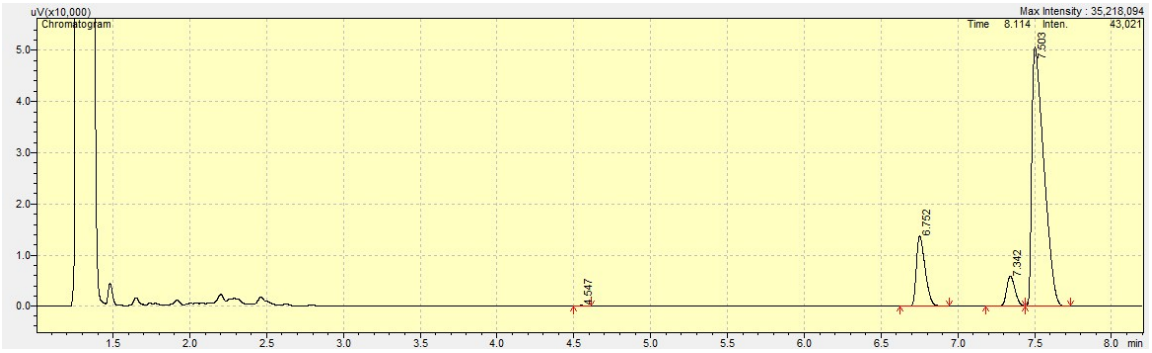


Retention time: 3',5'-bis(trifluoromethyl)acetophenone: 2.939 min.; (*S*)- 1-(3',5'-bis(trifluoromethyl)-phenyl)ethanol: 2.804 min.; (*R*)-1-(3',5'-bis(trifluoromethyl)phenyl)ethanol: 2.972 min.; di-*tert*-butylbenzene (standard): 4.699 min..

Figure S11 Gas chromatograph readout for the ATH of *p*-methylacetophenone.

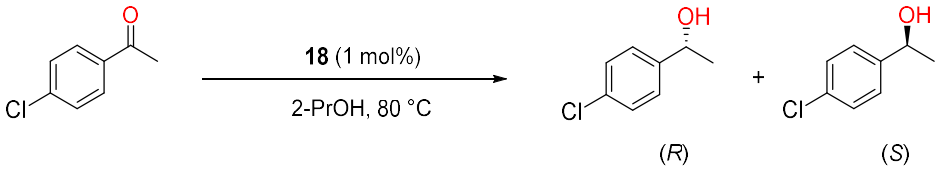


Oven Temperature: 130 °C

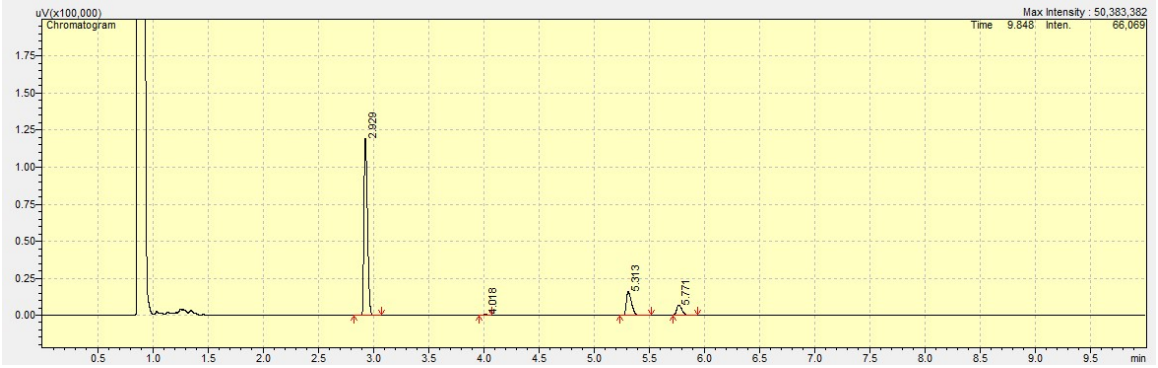


Retention time: *p*-methylacetophenone: 4.547 min.; (*R*)-1-(*p*-tolyl)ethan-1-ol: 6.752 min.; (*S*)-1-(*p*-tolyl)ethan-1-ol: 7.342 min.; di-*tert*-butylbenzene (standard): 7.503 min..

Figure S12 Gas chromatograph readout for the ATH of *p*-chloroacetophenone.

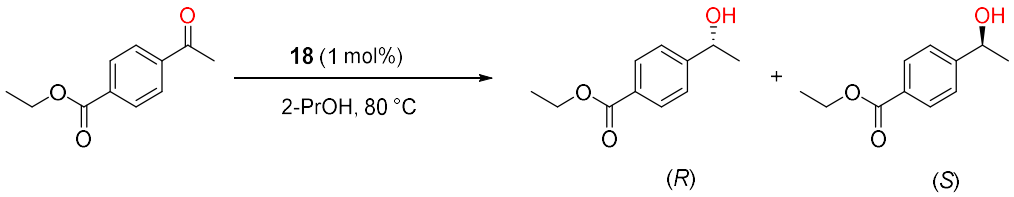


Oven Temperature: 145 °C



Retention time: *p*-chloroacetophenone: 4.018 min.; (*R*)-1-(*p*-chlorophenyl)ethan-1-ol: 5.313 min.; (*S*)-1-(*p*-chlorophenyl)ethan-1-ol: 5.771 min.; di-*tert*-butylbenzene (standard): 2.929 min..

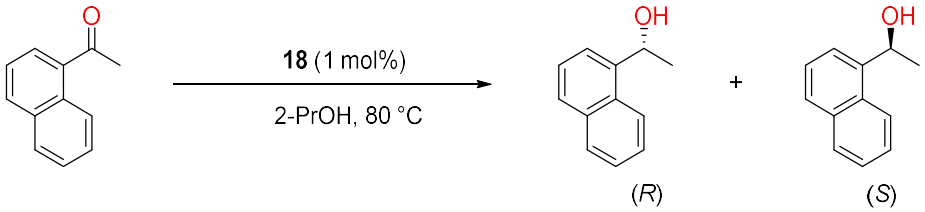
Figure S13 Gas chromatograph readout for the ATH of *p*-acetylbenzoate ethyl ester.



Oven Temperature: 180 °C

Retention time: *p*-acetylbenzoate ethyl ester: 2.686 min.; ethyl (*R*)-*p*-(1-hydroxyethyl)benzoate: 5.726 min.; ethyl (*S*)-*p*-(1-hydroxyethyl)benzoate: 5.885 min.; di-*tert*-butylbenzene (standard): 1.853 min..

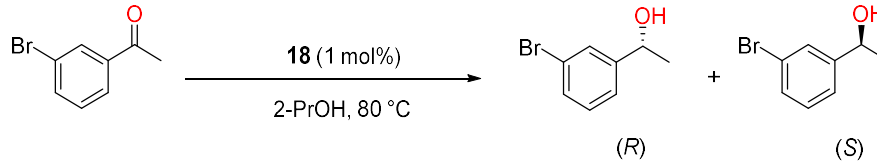
Figure S14 Gas chromatograph readout for the ATH of 1-acetonaphthone.



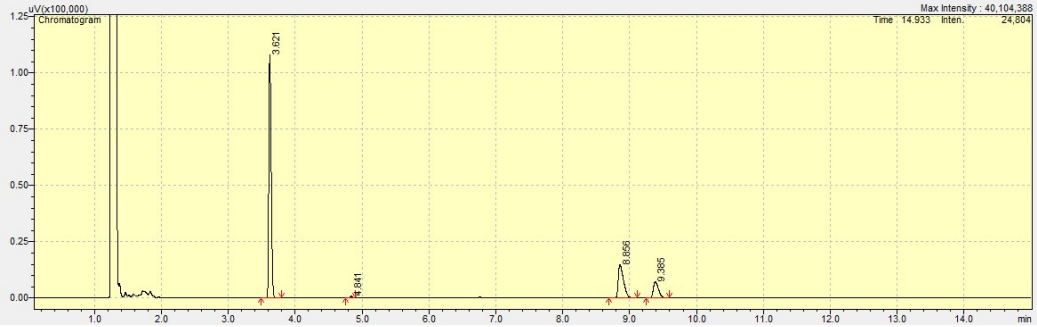
Oven Temperature: 150 °C

Retention time: 1-acetonaphthone: 8.298 min.; (*R*)-1-(naphthalen-1-yl)ethan-1-ol: 19.331 min.; (*R*)-1-(naphthalen-1-yl)ethan-1-ol: 21.275 min.; di-*tert*-butylbenzene (standard): 2.615 min..

Figure S15 Gas chromatograph readout for the ATH of *m*-bromoacetophenone.

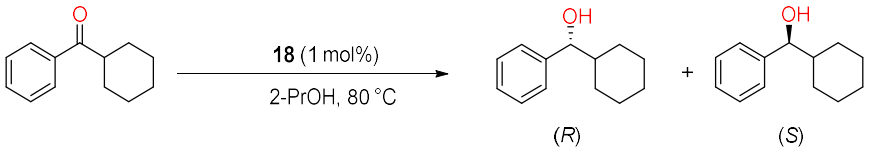


Oven Temperature: 145 °C

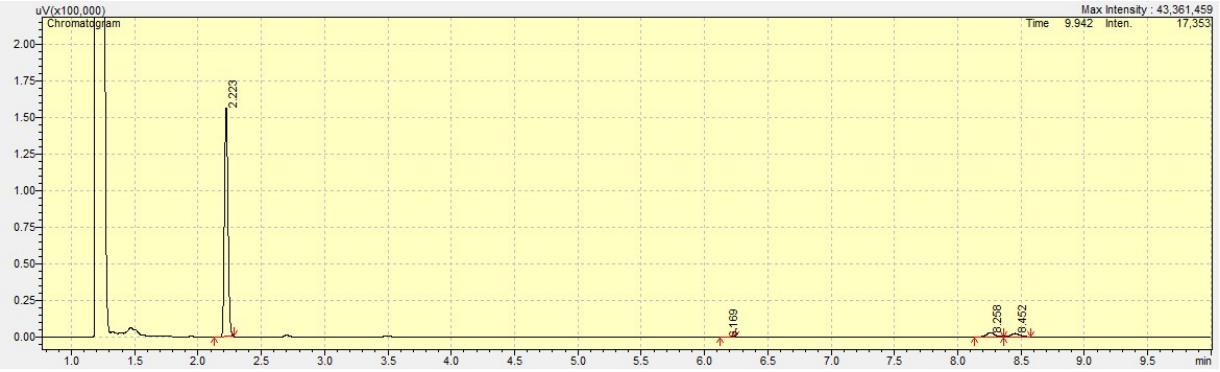


Retention time: *m*-bromoacetophenone: 4.841 min.; (*R*)-1-(*m*-bromophenyl)ethan-1-ol: 8.856 min.; (*S*)-1-(*m*-bromophenyl)ethan-1-ol: 9.385 min.; di-*tert*-butylbenzene (standard): 3.621 min..

Figure S16 Gas chromatograph readout for the ATH of cyclohexylphenylketone.

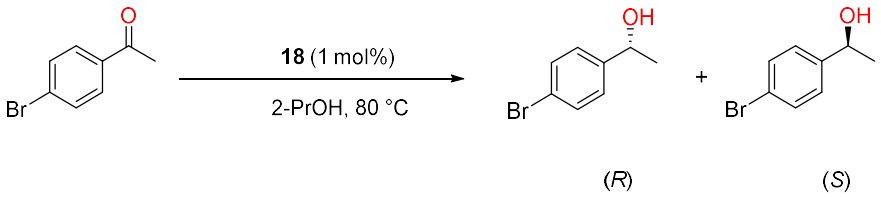


Oven Temperature: 170 °C

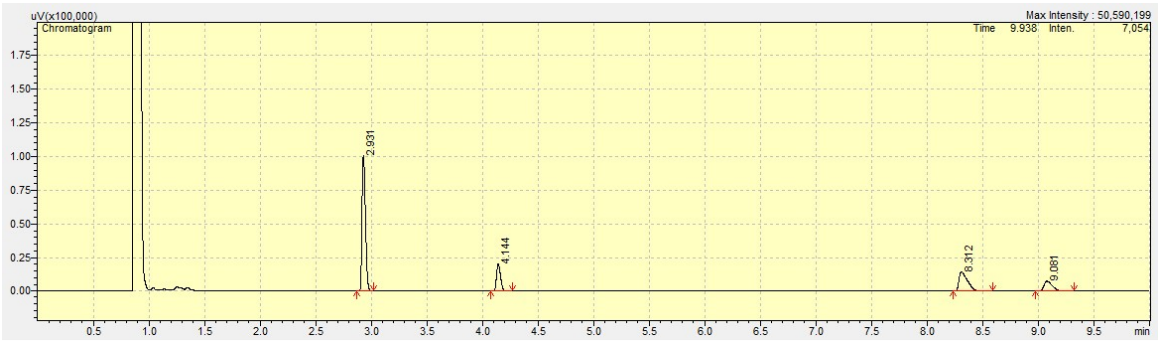


Retention time: cyclohexylphenylketone: 8.169 min.; (*R*)-cyclohexyl(phenyl)methanol: 8.258 min.; (*S*)-cyclohexyl(phenyl)methanol: 8.452 min.; di-*tert*-butylbenzene (standard): 2.223 min..

Figure S17 Gas chromatograph readout for the ATH of *p*-bromoacetophenone.



Oven Temperature: 145 °C

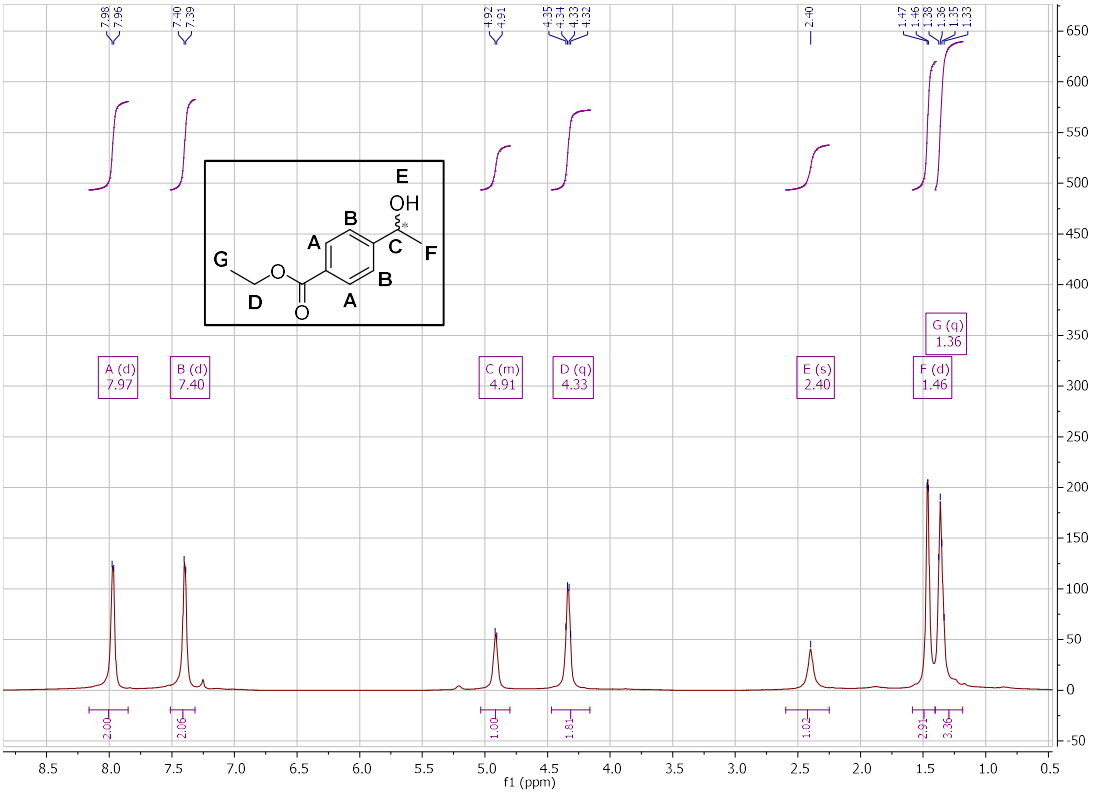


Retention time: *p*-bromoacetophenone: 4.144 min.; (*R*)-1-(*p*-bromophenyl)ethan-1-ol: 8.314 min.; (*S*)-1-(*p*-bromophenyl)ethan-1-ol: 9.081 min.; di-*tert*-butylbenzene (standard): 2.931 min..

Characterization of Ethyl *p*-(1-hydroxyethyl)benzoate Alcohol Product

After catalysis, the reaction solution was cooled to 28 °C. The solvent was removed *in vacuo* and an ^{1}H NMR spectrum was taken of the residue without any purification.

Figure S18 ^{1}H NMR of ethyl *p*-(1-hydroxyethyl)benzoate (600 MHz, $CDCl_3$)

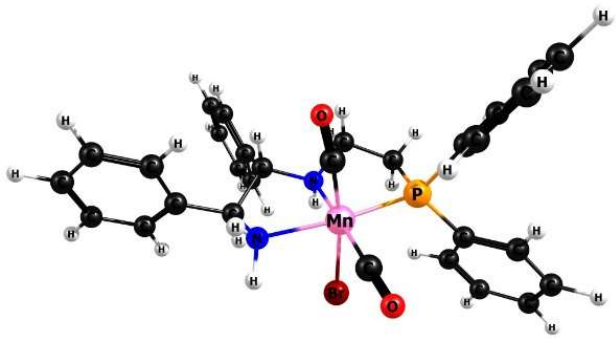


DFT Calculations for the Manganese Bromide, Manganese Borohydride, and Manganese Ethoxide Isomers

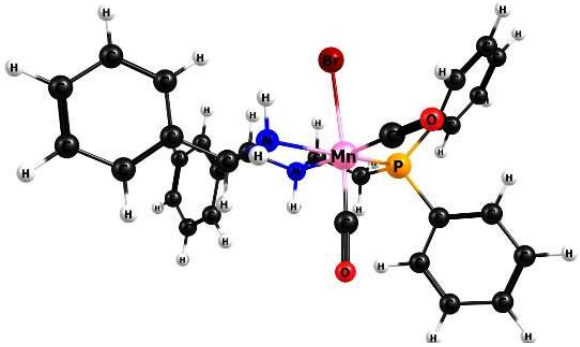
Structural Information

The DFT calculations were done with Gaussian09[1] using the functional PBEPBE and the basis set 6-31+G* for all atoms apart from the manganese which was treated with the SDD effective core potential. An ultrafine integration grid was employed, and the optimized structures had no imaginary modes. The GIAO method was used to calculate the ^{1}H NMR isotropic shielding constants. The calculated structures and relative energies of the diastereomers of **16** and **16'**, **18** and **18'**, as well as **19** and **19'** are shown in the Figure below.

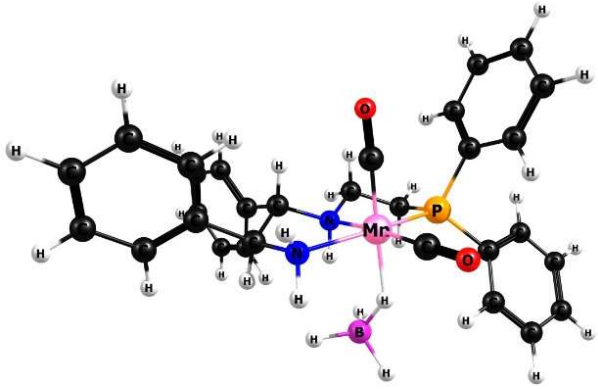
Figure S19 Structures of pairs of isomers calculated using DFT methods along with their relative energies (the lower of the two for each pair is set as zero energy).



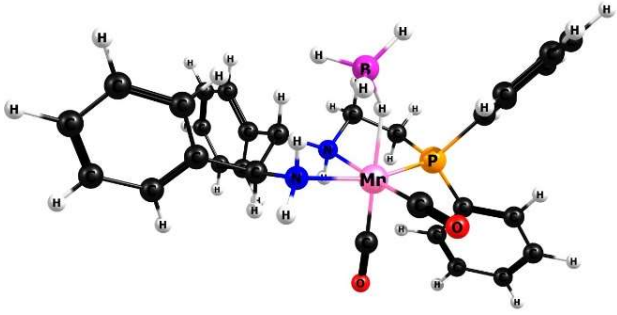
16 ΔG_{rel} = 0.0 Kcal/mol



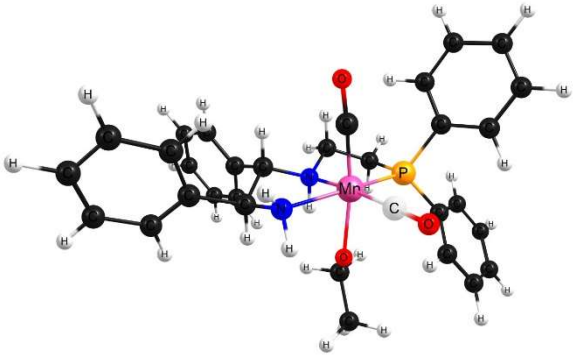
16' ΔG_{rel} = 1.4 Kcal/mol



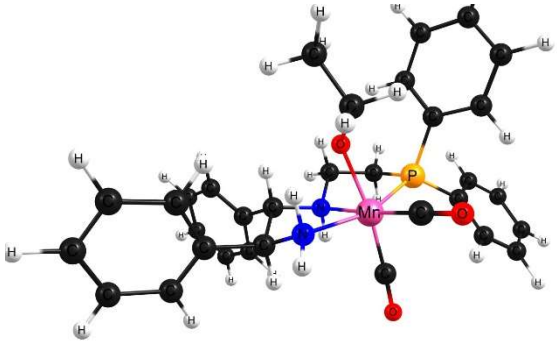
18 ΔG_{rel} = 0.0 Kcal/mol



18' ΔG_{rel} = 3.8 Kcal/mol



19 ΔG_{rel} = 4.0 Kcal/mol



19' ΔG_{rel} = 0.0 Kcal/mol

References

1. , Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.;Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J. and Fox, D. J. Gaussian 09, Revision or B.01 or D.01 Gaussian, Inc., Wallingford CT, 2009.