Supporting Information

Dehydrogenative Cross-Coupling of Primary Alcohols To Form Cross-Esters Catalyzed by a Manganese Pincer Complex

Uttam Kumar Das,[†] Yehoshoa Ben-David,[†] Gregory Leitus,[‡] Yael Diskin-Posner,[‡] and David Milstein[†*]

[†]Department of Organic Chemistry and [‡]Department of Chemical Research Support, Weizmann Institute of Science, Rehovot, 76100, Israel

E-mail: david.milstein@weizmann.ac.il

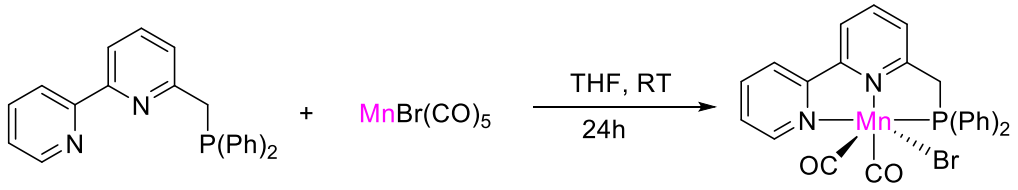
CONTENTS:

1. General Information:

All experiments were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glove box equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All non-deuterated solvents were refluxed over sodium/benzophenoneketyl and distilled under argon atmosphere. Deuterated solvents were used as received. All solvents were degassed with argon and kept in the glove box over 4Å molecular sieves. Most of the chemicals used in the experiments were purified according to standard procedures (vacuum distillation). ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded using Bruker Avance III 7T, Avance III 9.4T and Avance III 11.7T NMR spectrometers. All spectra were recorded at 298 K, unless otherwise noted. ^{1}H NMR and $^{13}C\{1H\}$ NMR chemical shifts are reported in ppm downfield from tetramethylsilane and referenced to the residual signals of an appropriate deuterated solvent. $^{31}P\{1H\}$ NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. NMR for C_6D_6 (7.16 ppm is solvent peak), toluene-d8 (7.00 and 2.1 ppm is solvent peak), and $CDCl_3$ (7.26 ppm is solvent peak) solution and reported in ppm (δ). NMR spectroscopy abbreviations: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet. GC–MS was carried out on HP 6890 (flame ionization detector and thermal conductivity detector) and HP 5973 (MS detector) instruments equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas. IR spectra were recorded on Thermo Nicolet 6700 FT-IR. The HRMS/ESI-MS was carried out on Micromass ZQ Mass Spectrometer.

2. Experimental procedures:

(a) Preparation and characterization of Mn(^{ph}PNN)(CO)$_2$Br (6)



6

To a solution of the ^{ph}PNN ligand (360 mg, 1.01 mmol) in 5 mL THF was added under argon atmosphere an orange solution of $Mn(CO)_5Br$ (275 mg, 1 mmol) in 10 mL THF and the reaction mixture was kept stirring at room temperature for 24 h (Note: The CO gas liberated needs to be removed occasionally in *vacuo*). The solution was evaporated in *vacuo*. The solid residue was washed with pentane (10 mL), which on evaporation gave a brown solid product in 88% (480 mg) yield. The brown crude product was dissolved in dichloromethane (15 mL), the solution was filtered and concentrated, layered with pentane and kept in the refrigerator (-30 °C) to obtain dark red crystals. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.48 (d, J_{PH} =11 Hz, 2H, PCH_2), 7.32 (m, 5H, $P(Ph)_2$), 7.41 (br, 1H), 7.45 (m, 3H), 7.73 (br, 1H), 7.82 (br, 1H), 7.95-8.02 (m, 5H), 9.46 (s, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 44.30 (d, J_{PC} = 20.1 Hz, PCH_2), 119.52, 121.69, 122.57 (d, J_{PC} = 8.8 Hz), 125.91 (d, J_{PC} = 9.8 Hz), 128.26 (d, J_{PC} = 9.8 Hz), 128.37 (d, J_{PC} = 9.3 Hz), 129.20 (d, J_{PC} = 2.0 Hz), 130.28 (d, J_{PC} = 9.8 Hz), 130.39 (d, J_{PC} = 2.1 Hz), 133.28 (d, J_{PC} = 38.5 Hz), 134.13 (d, J_{PC} = 10.3 Hz), 136.20, 137.08, 139.33 (d, J_{PC} = 43.9 Hz), 154.67, 156.00, 156.58 (d, J_{PC} = 4.2 Hz), 161.94 (d, J_{PC} = 8.4 Hz), 239.71(Mn-CO). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ = 87.37 ppm. IR (thin film, NaCl) = 1838 cm^{-1}(νCO) and 1917 cm^{-1}(νCO). Anal. Calcd. for $C_{25}H_{19}BrMnN_2O_2P$: C, 55.07; H, 3.51; N, 5.14 Found: C, 55.50; H, 3.53; N, 4.86. MS (ESI, DCM): 544 (100%, $[M-Br]^+$).

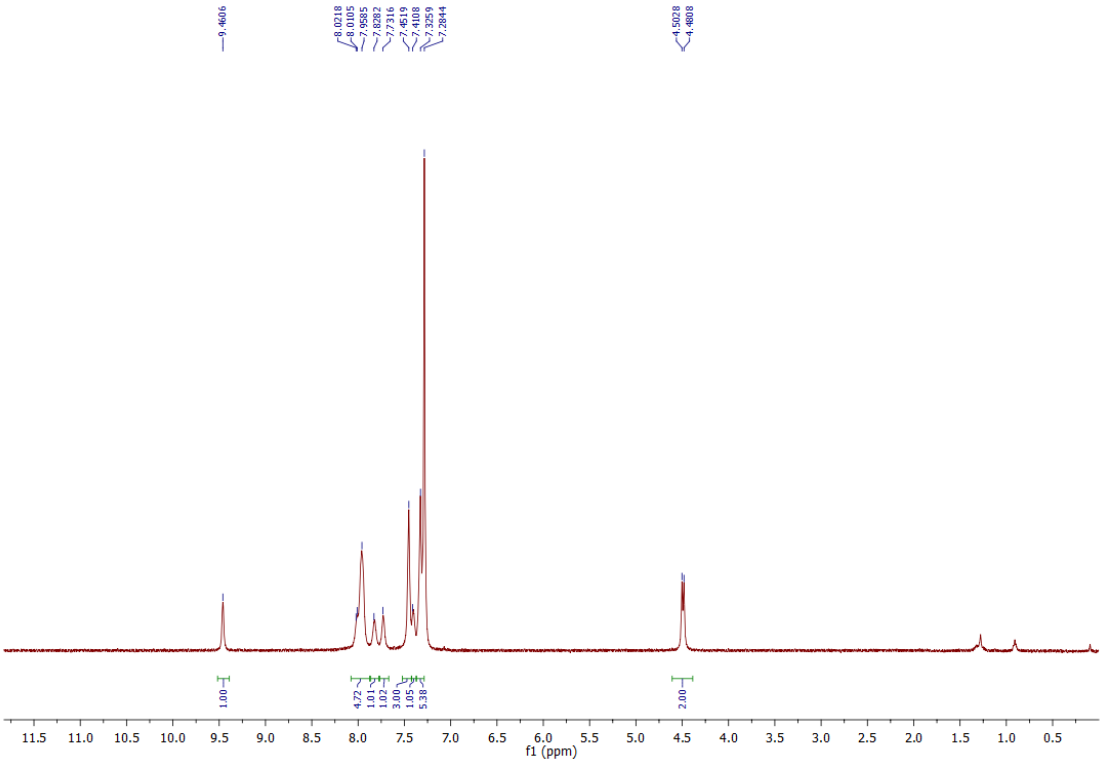


Figure S1. ^{1}H NMR spectrum of complex **6** at RT in $CDCl_3$ (500 MHz).

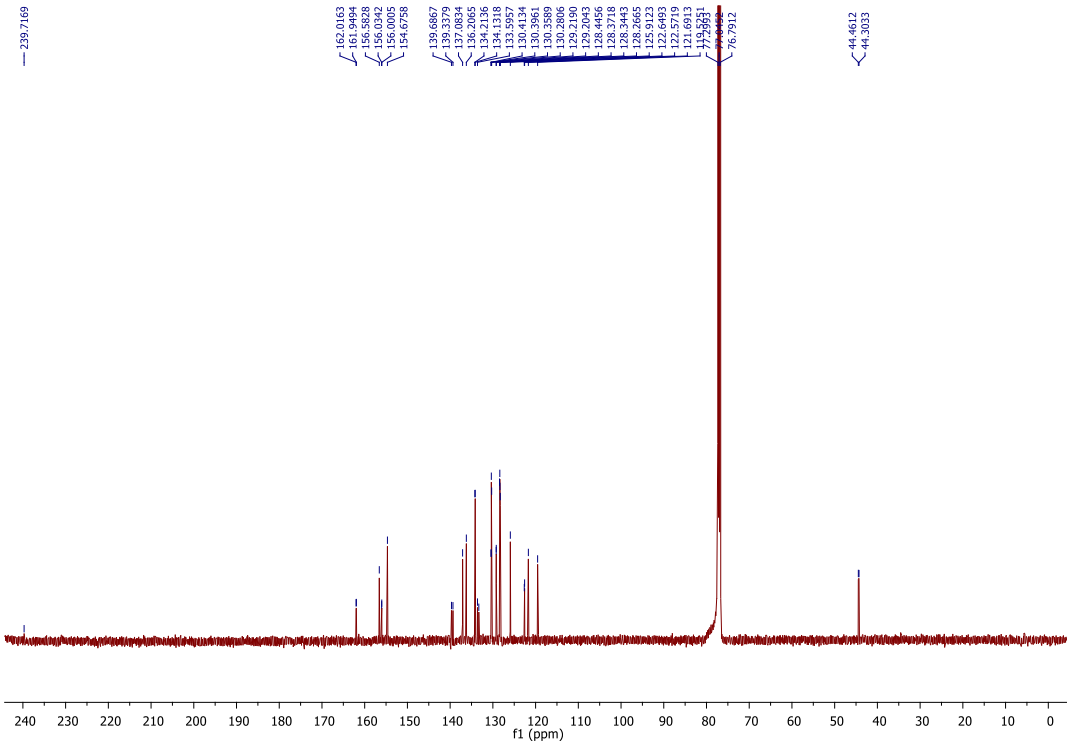


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of complex **6** at RT in $CDCl_3$ (126 MHz).

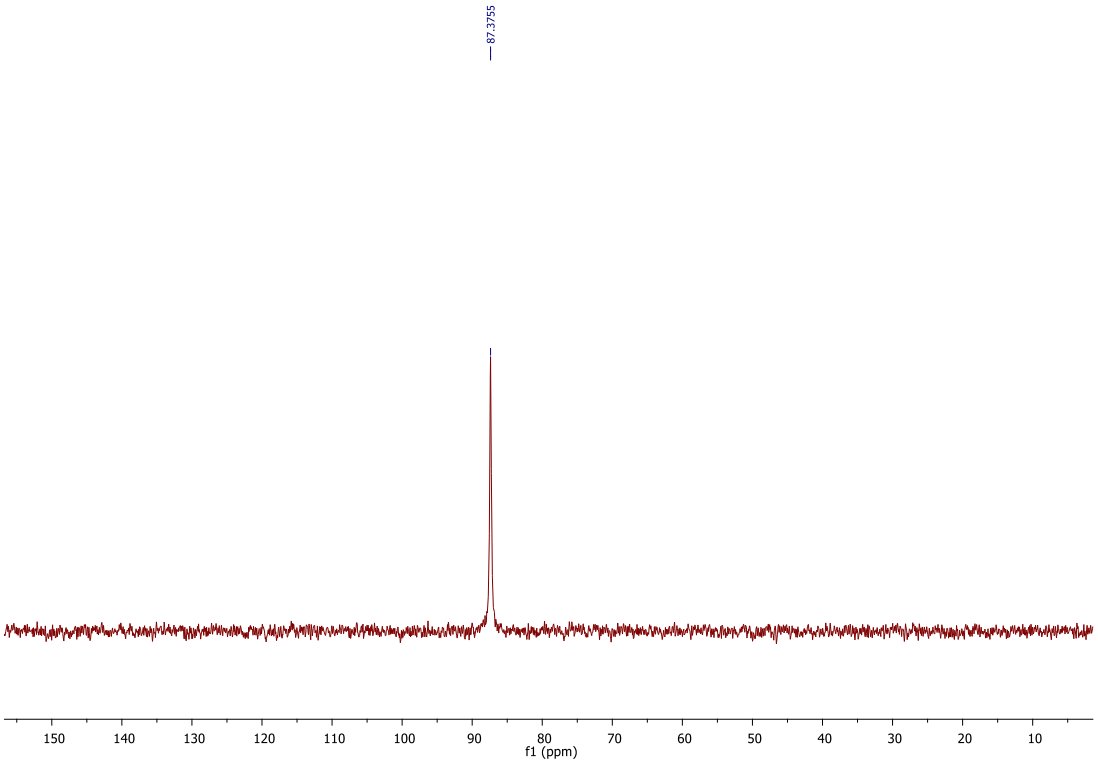


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of complex **6** at RT in $CDCl_3$ (202 MHz).

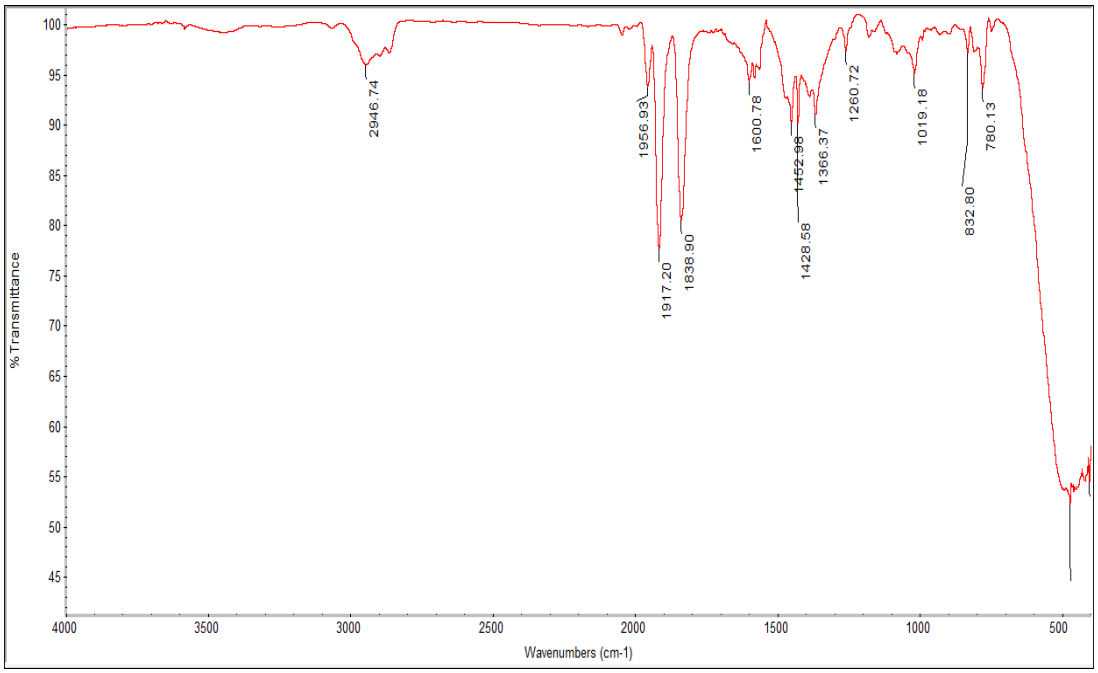
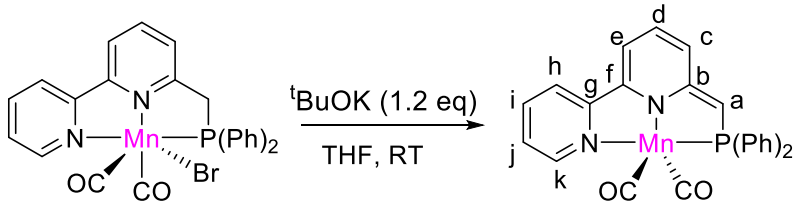


Figure S4. IR spectrum of complex **6** on NaCl plate**.**

(b) Procedure for the synthesis and characterization of Mn(^{Ph}PNN*)(CO)$_2$ (7)



6 **7**

Under a nitrogen atmosphere, complex **6** (110 mg, 0.2 mmol), KO^{t}Bu (26 mg, 0.24 mmol) and 5 mL of THF were charged in a vial equipped with a stirring bar. The reaction mixture was allowed to stir for 1h at room temperature. Afterwards the solution was filtered through a Teflon syringe filter (0.2 µm). The solvent was evaporate in vacuum, washed with pentane and dried in vacuum. The pure compound Mn(^{Ph}PNN*)(CO)$_2$ was isolated in 83% yield. ^{1}H NMR (400 MHz, C_6D_6, RT): δ = 4.40 (s, 1H, H_a), 5.97 (d, J_{HH} = 6.0 Hz, 1H, H_c), 6.10 (t, J_{HH} = 6.0 Hz, 1H, H_d), 6.63-6.72 (m, 3H, H_e, H_i, H_j), 6.85 (d, J_{HH} = 8.0 Hz, 1H, H_h), 6.97 (t, J_{HH} = 7.0 Hz, 2H, Ph), 7.01 (t, J_{HH} = 7.0 Hz, 4H, Ph), 8.10 (t, J_{HH} = 8.8 Hz, 4H), 8.94 (d, J_{HH} = 4.8 Hz, 1H, H_k). ^{13}C{^{1}H} NMR (100 MHz, THF-d8, 25 °C): δ = 63.10 (d, J_{PC} = 67.3 Hz, C_a), 101.25 (C_e), 116.69 (d, J = 17.4 Hz, C_c), 120.10 (C_d), 123.86 (Ph), 127.22 (d, J = 9.1Hz, Ph), 127.7 (C_i), 131.36 (d, J = 9.9 Hz, Ph), 131.96 (C_j), 136.56 (C_h), 140.35 (d, J = 32.8 Hz, Ph), 153.41 (C_g), 154.41 (d J = 5.0 Hz, C_k), 160.89 (C_f), 170.93 (d, J = 24.8 Hz, C_b), 228.23 (d, J = 20.4 Hz, Mn-CO). ^{31}P{^{1}H} NMR (162 MHz, THF-d8, RT): δ 69.98. IR (NaCl, pellet, cm^{-1}): 1840, 1917 (1:1 ratio).

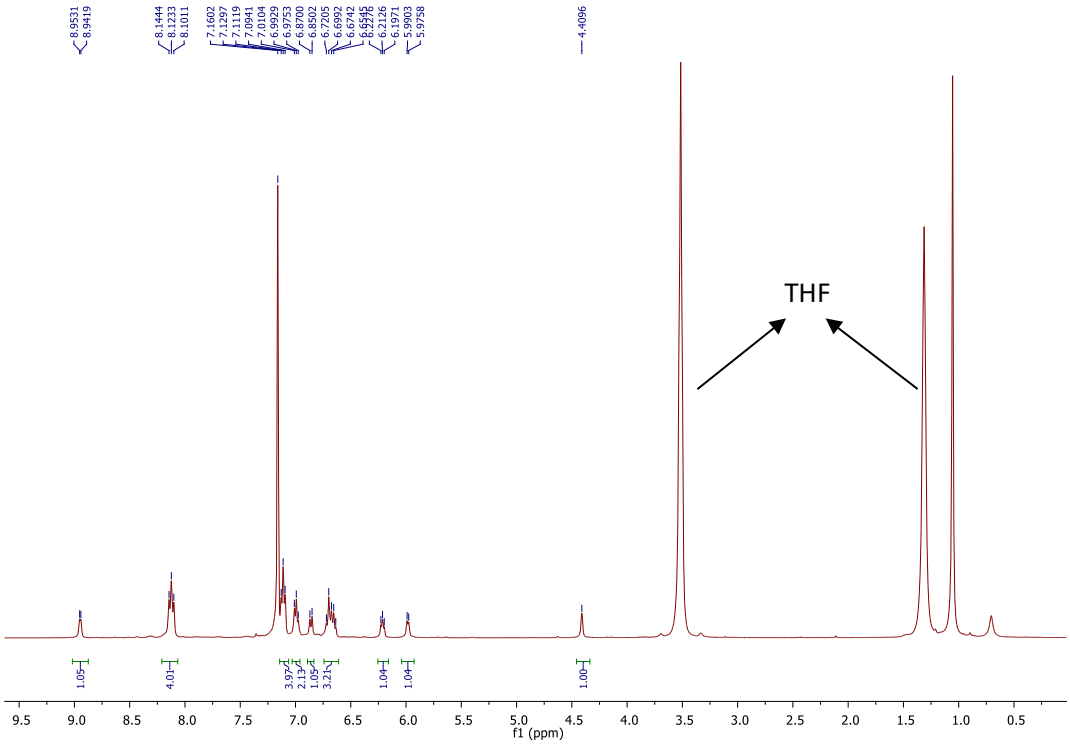


Figure S5. ^{1}H NMR spectrum of complex **7** at RT in C_6D_6 (400 MHz)

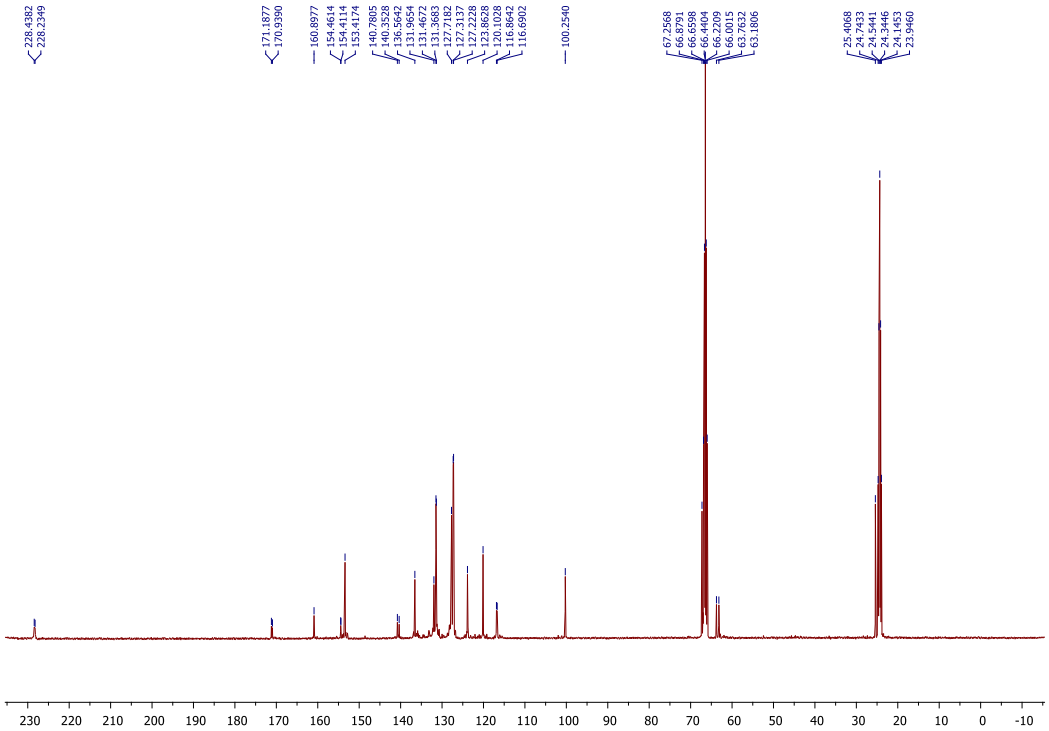


Figure S6. ^{13}C{^{1}H} NMR spectrum of complex **7** at RT in THF-d8 (100 MHz)

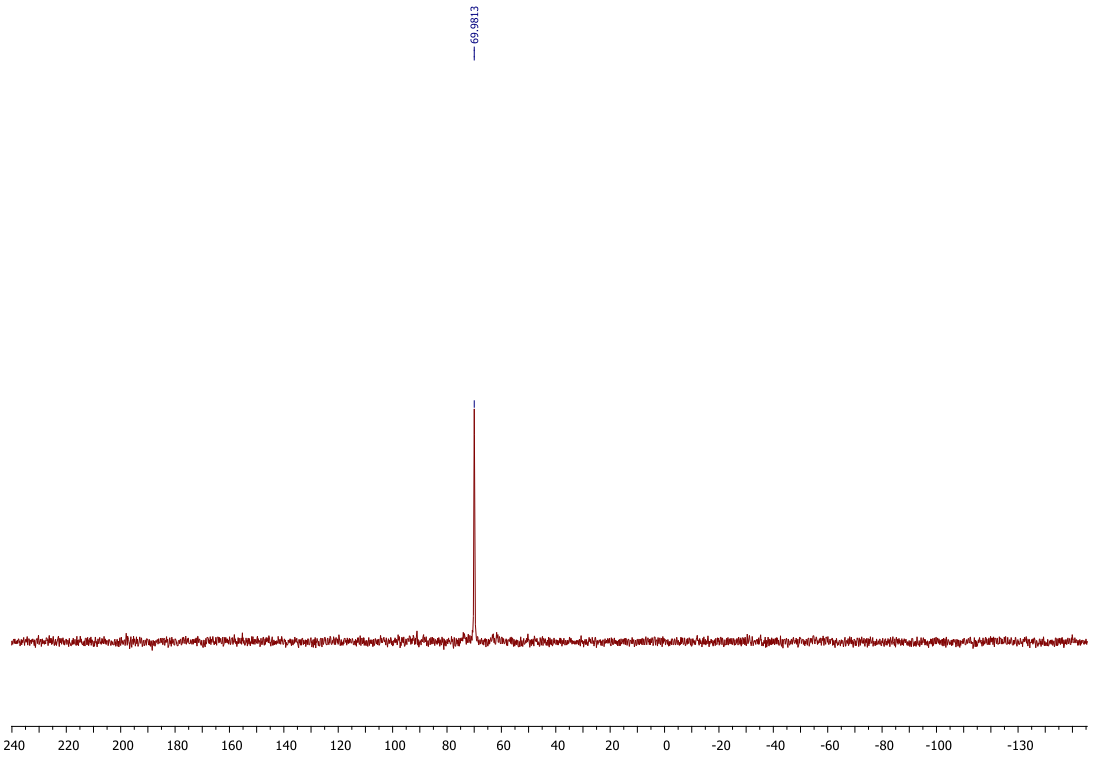


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of complex **7** at RT in THF-d8 (162 MHz)

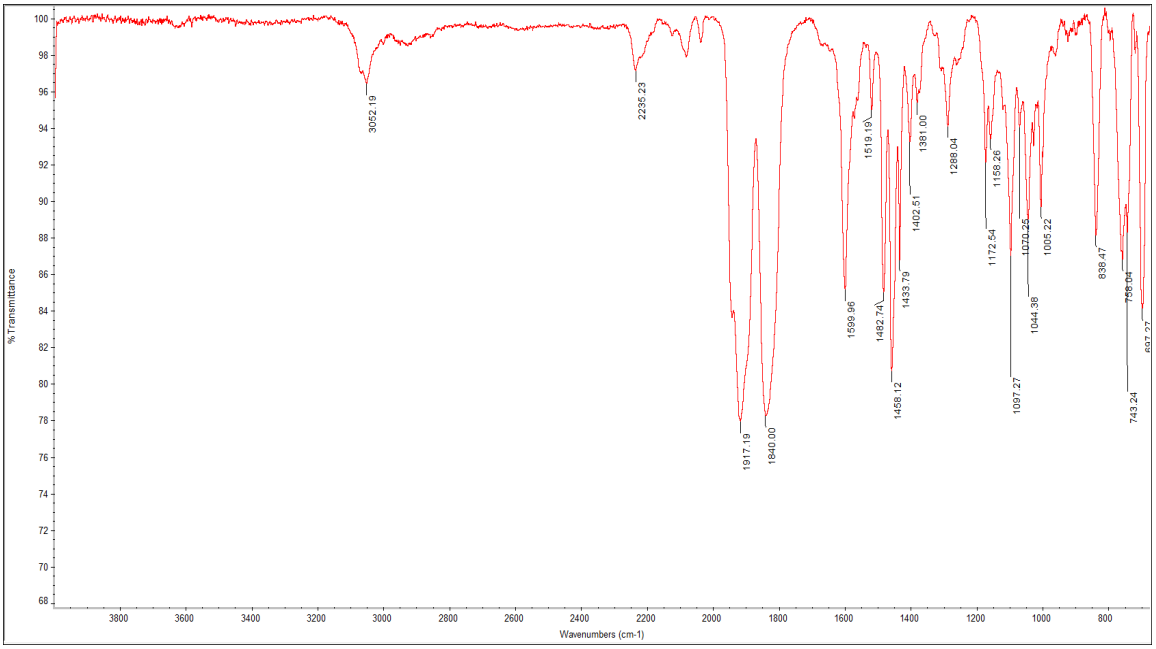
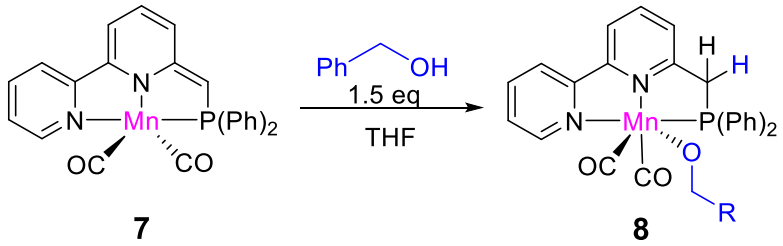


Figure S8. IR spectrum of complex **7** on NaCl plate

(c) Synthesis and characterization of Mn(^{Ph}PNN)(OCH$_2$Ph)(CO)$_2$ (8)



In a vial, complex **7** (232 mg, 0.5 mmol) and Benzyl alcohol (81 mg, 0.75 mmol) were mixed in 5 ml THF and stirred for 15 min at RT. The brown solution was evacuated and the solid was extracted with toluene. The toluene solution was filtered through a 0.2 µm Teflon filter. The solvent was evaporated in *vacuo*. The solid residue was washed with pentane (2 mL), and dried to give a dark brown solid product (79% yield). The crude product was dissolved in toluene (5 mL) and the solution was filtered and concentrated and kept in the refrigerator (-30 °C) to obtain dark brown crystals. ^{1}H NMR (Toluene-d8, 300 MHz): δ = 3.77 (d, *J* = 9.1 Hz, 2H, P(CH$_2$), 4.47 (dd, *J* = 13.2, 16.2 Hz, 2H, OCH$_2$Ph), 6.39 (t, *J* = 6.3 Hz, 1H), 7.02-7.31 (m, 15H), 7.76 (br, 2H), 8.01 (t, *J* = 8.4 Hz, 2H), 8.88 (d, *J* = 4.8 Hz, 1H). ^{13}C{^{1}H} NMR (Toluene-d8, 100 MHz): δ = 44.6 (d, J_{PC} = 19.6 Hz, P(C*H$_2$), 74.5 (OC*H$_2$Ph), 119.0, 121.1, 122.0 (d, *J* = 9.8 Hz), 123.7, 126.0, 126.4, 127.1, 127.4, 126.6, 126.7, 128.3, 129.9, 132.5 (d, *J* = 9.8 Hz), 133.1 (d, *J* = 10.6 Hz), 134.8, 135.9, 149.0, 153.2, 156.3 (d, *J* = 4.0 Hz), 157.1, 161.3 (d, *J* = 9.3 Hz), 220.9 (d, *J* = 11.3 Hz, Mn-CO), 230.1, ((d, *J* = 23.6 Hz, Mn-CO). ^{31}P{^{1}H} NMR (toluene-d8, 162 MHz): δ = 91.43 ppm. IR (thin film, NaCl) = 1840 cm^{-1}(*v*CO) and 1916 cm^{-1}(*v*CO).

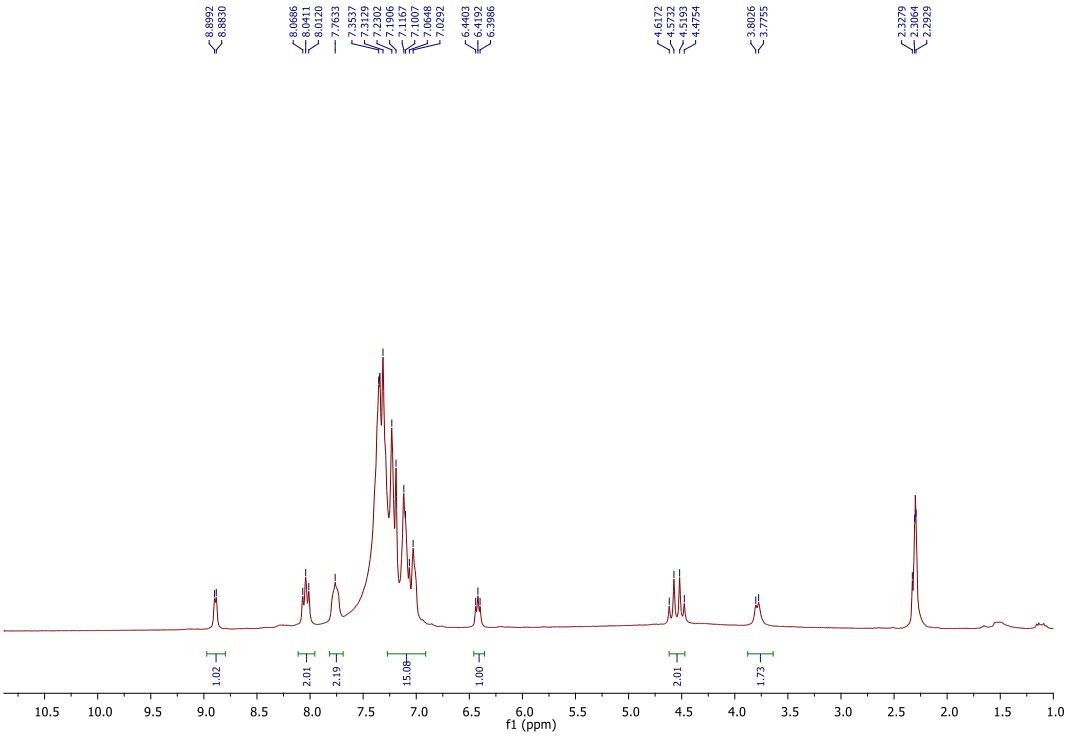


Figure S9. ^{1}H NMR spectrum of complex **8** at RT in Tol-d8 (300 MHz)

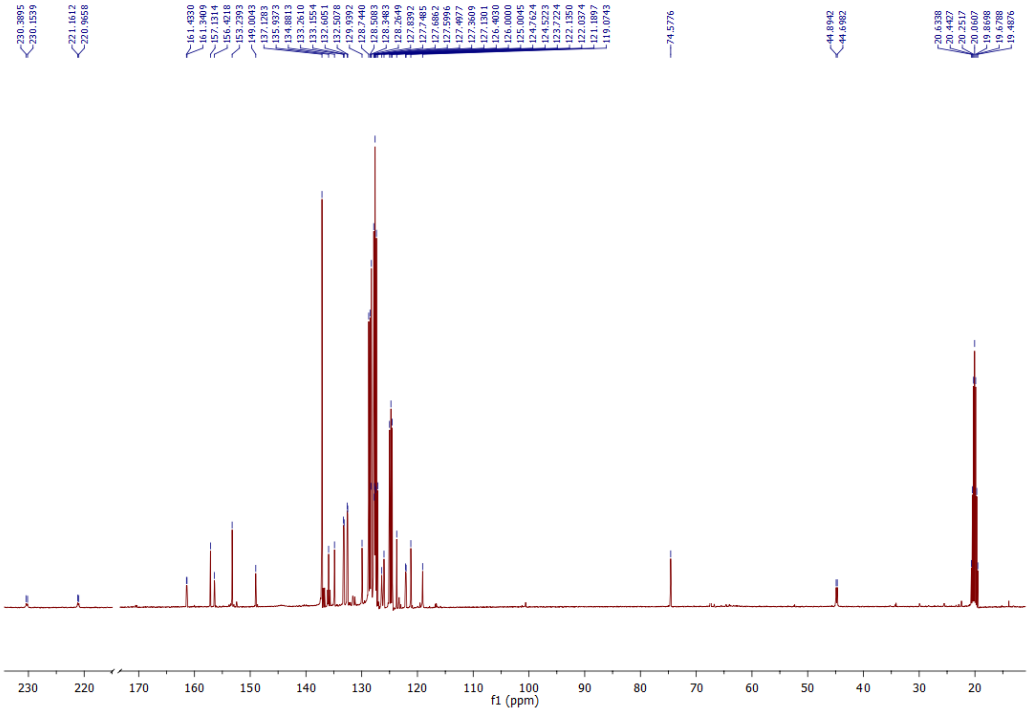
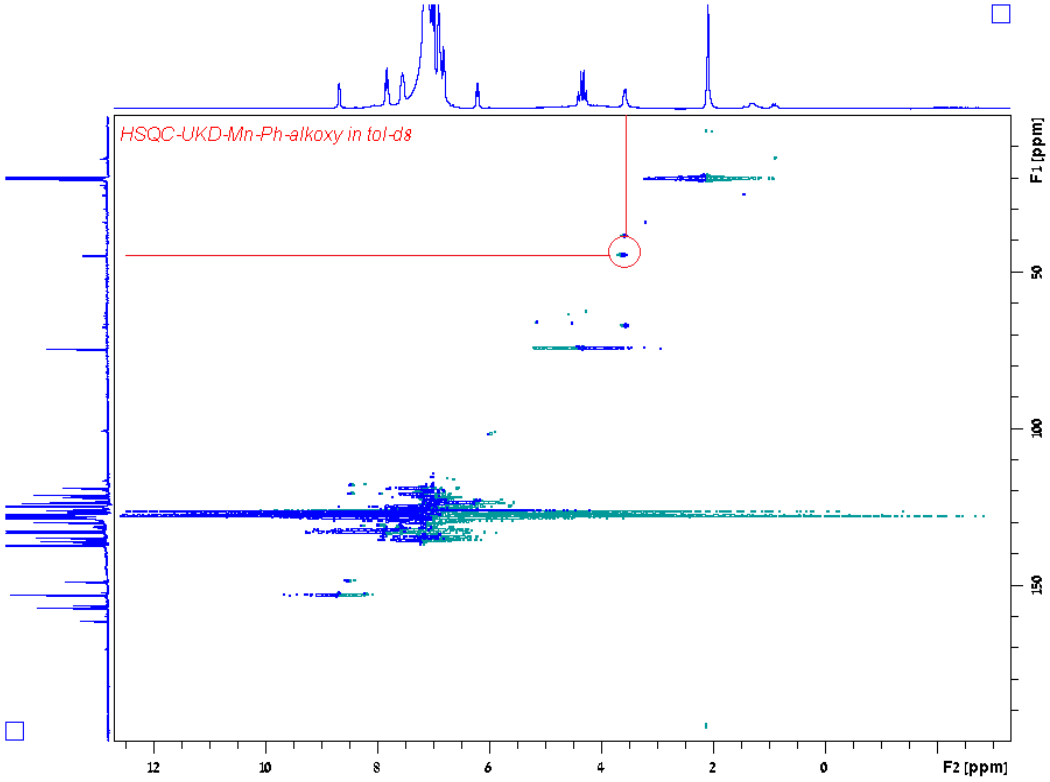
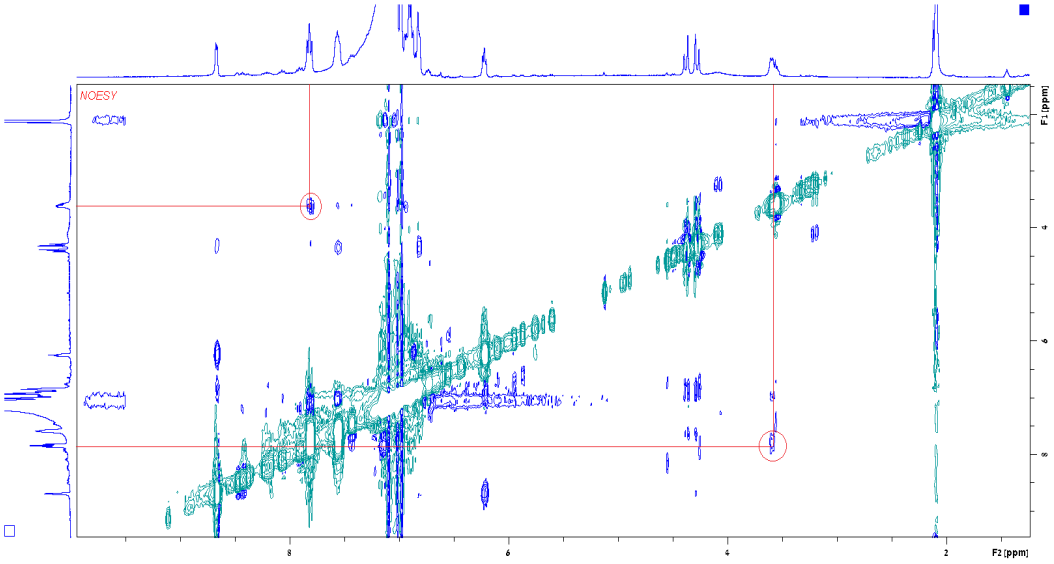


Figure S10. ^{13}C{^{1}H} NMR spectrum of complex **8** at RT in tol-d8 (100 MHz)



Figures S11. Phase sensitive HSQC NMR spectrum (500.08 MHz , 125.76 MHz, toluene-d8 , 298 K) of complex **8**.



Figures S12. NOESY NMR spectrum (400 MHz, toluene-d8, 298 K) of complex **8**.

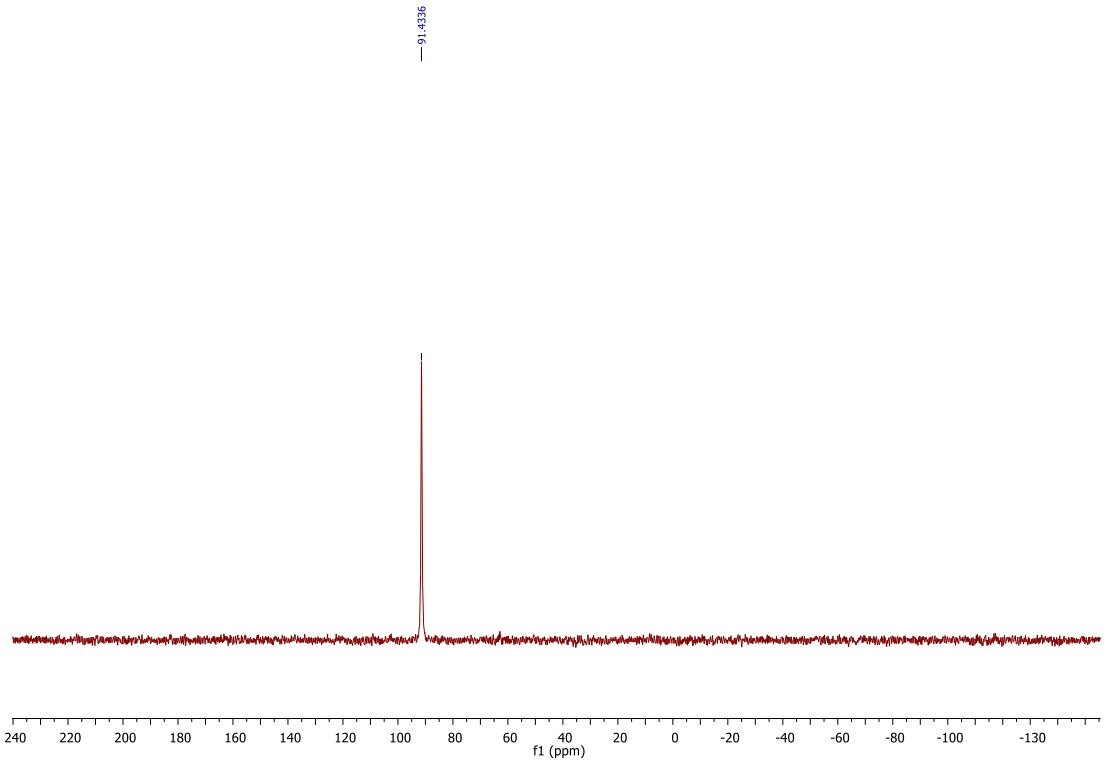


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of complex **8** at RT in tol-d8 (162 MHz)

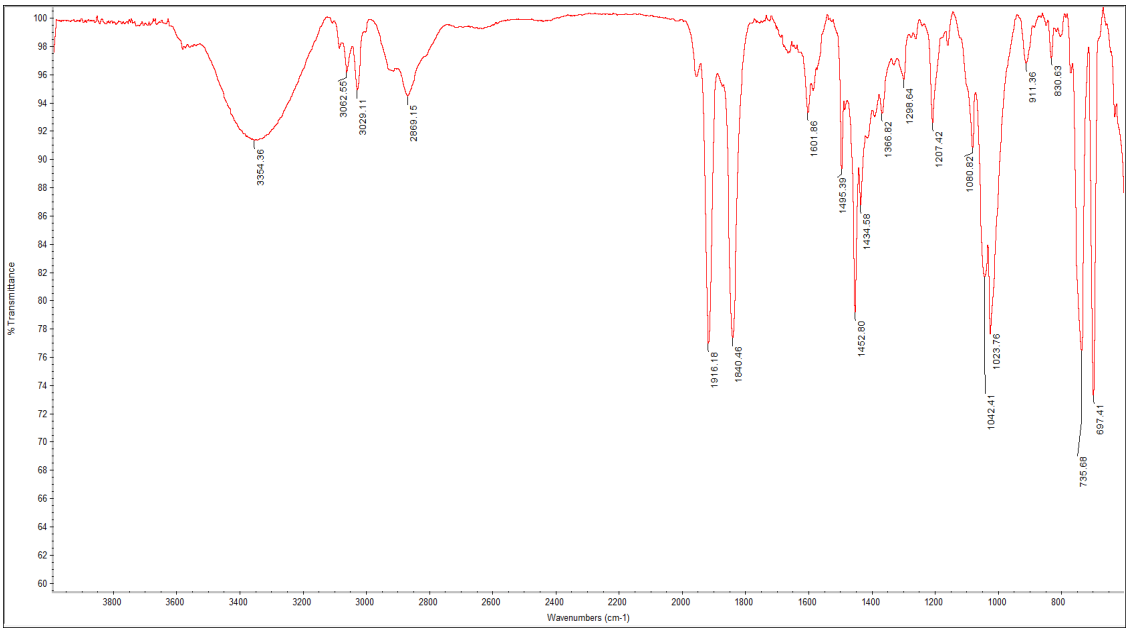


Figure S14. IR spectrum of complex **8** on NaCl plate

(d) Mechanistic study.

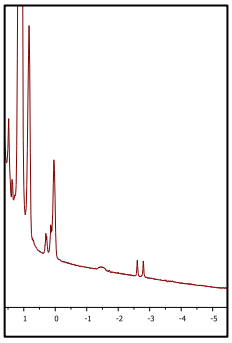


Figure S15. ^{1}H NMR (300 MHz) of the hydrido complex **11** upon heating of complex **8** in toluene at 120 °C**.**

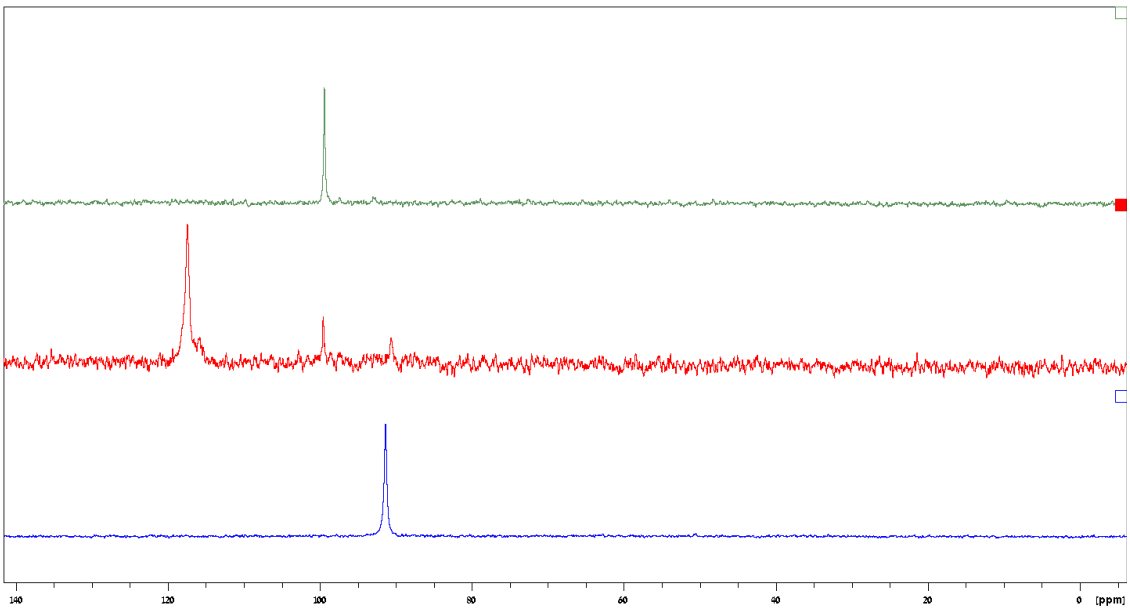


Figure S16. ^{31}P{^{1}H} NMR (121 MHz) of (below) complex **8** in toluene, (middle) heating of complex **8** + 1.5 equivalent of benzyl alcohol in toluene at 120 °C for 12h and (above) hydrido complex **11** (prepared from 1:1 complex **6** + $NaHBEt_3$) in toluene.

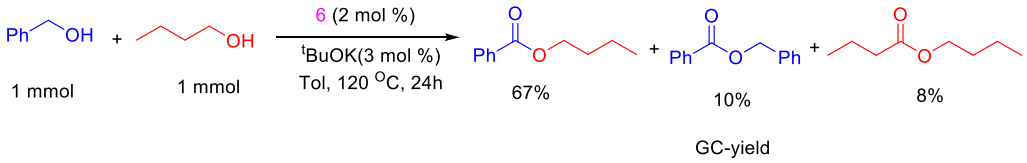
(e) General procedure for the catalytic reactions:

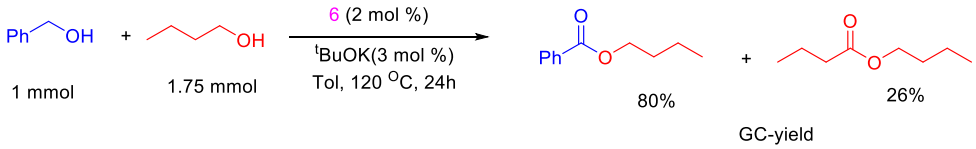
Table 1: In a glove box, 0.02 mmol of complex (**1-6** as mentioned in Table 1) and 0.03 mmol of ^{t}BuOK were charged in a 20 mL vial in 2 mL of the respective solvent. This mixture was stirred for 3 min and 1 mmol of benzyl alcohol was added and stirred for another 1 min. Finally methanol (according to Table 1) was added to this mixture. The reaction mixture was transferred to a 50 mL Schlenk tube and taken out of the glove box. The tube was kept in an oil bath pre-heated (as mentioned in Table 1) and stirred for the specified time (Table 1). The reaction mixture was then cooled to room temperature and the generated H_2 was vented off after which mesitylene (1 mmol) was added as an internal standard. Conversion and yield of the product was determined by GC-MS or ^{1}H NMR spectroscopy.

Table 2: To a mixture of 0.02 mmol of complex **6** and 0.03 mmol KO^{t}Bu at room temperature (or 0.02 mmol of complex **7** in absence of any base) was added 1 mmol of alcohol in 2 mL toluene. This solution was stirred for 5 min and 10-20 mmol (as mentioned in Table 2) of methanol was added and placed in a Teflon Schlenk tube under N_2. The tube was heated at 120 ºC with stirring for 24h. The reaction mixture was then cooled in a water bath and the formed H_2 was vented off. The formation of methyl ester was determined by GC-MS and ^{1}H NMR spectroscopy. Isolated yield of the product was determined after column chromatography.

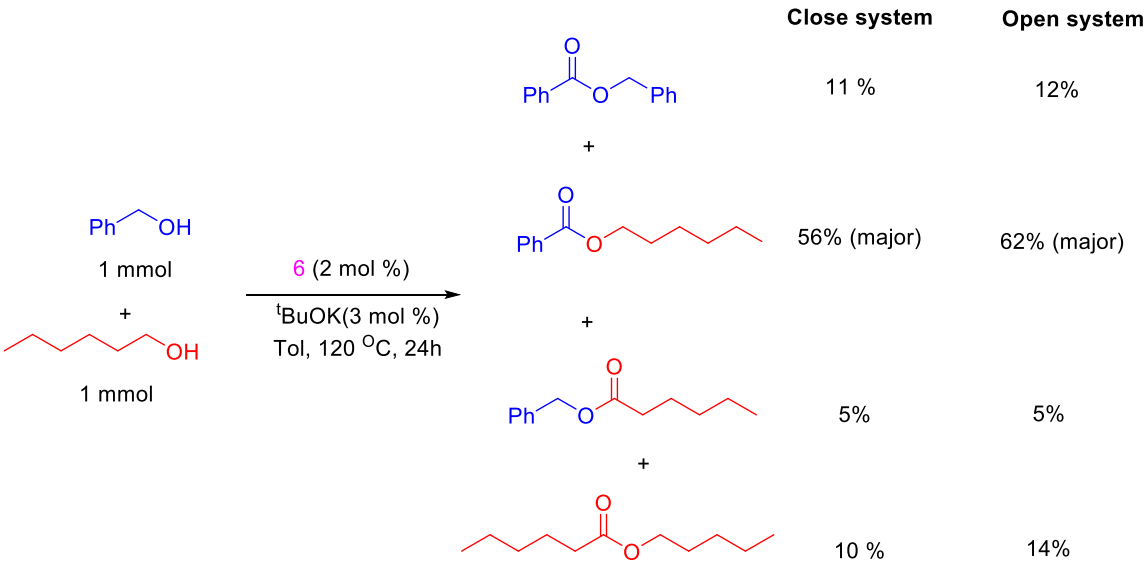
Table 3: To a mixture of 0.02 mmol of complex **6** and 0.03 mmol KO^{t}Bu at room temperature (or 0.02 mmol of complex **7** in absence of any base) was added 1 mmol of alcohol in 2 mL toluene. This solution was stirred for 5 min and y mmol (as mentioned in Table 3) of primary alcohol was added and placed in a Teflon Schlenk tube under N_2. The tube was heated at 120 ºC with stirring for 24h. The reaction mixture was then cooled in a water bath and the formed H_2 was vented off. The formation of methyl ester was analyzed by GC-MS and ^{1}H NMR. Isolated yield of the product was determined after column chromatography. The products are reported.[1-7]

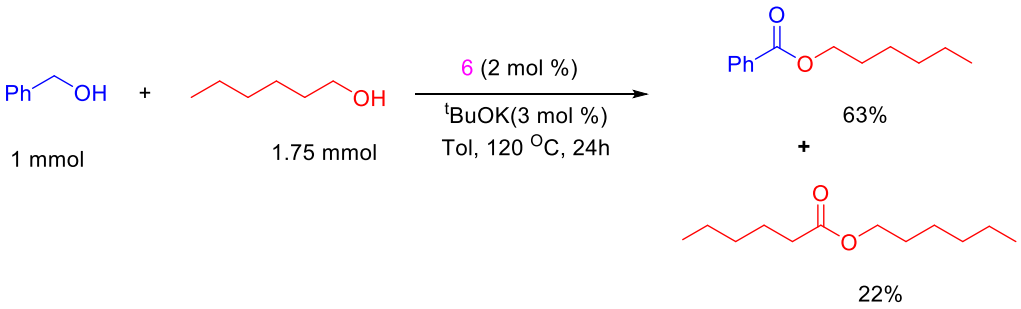
Reaction between benzyl alcohol and 1-butanol





Reaction between benzyl alcohol and 1-hexanol (in close system and open system)





(e) ^{1}H and ^{13}C NMR data of some isolated ester products.

Methyl benzoate:[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.91 (s, 3H), 7.41 (t, *J* = 7.5, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 52.1, 128.3, 129.5, 130.1, 132.9, 167.1.

Methyl 4-chloro benzoate:[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.85 (s, 3H), 7.33 (d, *J* = 7.8 Hz, 2H) 7.90 (d, *J* = 8.1 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ = 52.2, 128.5, 128.7, 131.1, 139.4, 166.3.

Methyl 4-methoxy benzoate:[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.79 (s, 3H), 3.82 (s, 3H), 7.84-7.86 (m, 2H) 7.92-7.94 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ = 51.9, 54.4, 113.6, 122.6, 131.5, 163.4, 166.9.

Methyl hexanoate:[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.83 (t, *J* = 6.9 Hz, 3H), 1.21-1.26 (m, 4H), 1.52-1.59 (m, 2H), 2.23 (t, *J* = 7.2 Hz, 2H), 3.61 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 14.0, 22.4. 26.6, 31.3, 34.1, 51.4, 174.3.

Methyl octanoate:[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.88 (t, *J* = 6.6 Hz, 3H), 1.25-1.32 (m, 8H), 1.59-1.65 (m, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 3.66 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 14.0, 22.6, 24.9, 28.9, 29.1, 31.6, 34.1, 51.4, 174.3.

Ethyl benzoate:[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.39 (t, *J* = 7.1 Hz, 3H), 4.38 (q, *J* = 7.1 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.81-7.54 (m, 1H), 7.98-8.09 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ = 14.45, 61.6, 128.4, 129.6, 130.6, 132.9, 166.7.

Propyl benzoate:[2]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 7.2 Hz, 3H), 1.55-1.70 (m, 2H), 4.12 (t, *J* = 6.6 Hz, 2H), 7.23-7.41 (m, 3H), 7.87-7.96 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ = 10.6, 22.2, 66.6, 128.3, 129.6, 130.54, 132.9, 166.6.

3. X-ray diffraction data of crystals and structure determination:

Crystal data of complexes **6** and **8** were measured at 100 K on a Rigaku XtaLab pro diffractometer equipped with PILATUS 200 detector with [λ(Mo-Kα) = 0.71073 Å] and [λ(Cu-Kα) = 1.54184 Å] radiation respectively. Crystal data of complexes **6** and **8** were processed with CrystalAlis^{pro} 1.171.38.41 (Rigaku OD, 2015). Structures were solved with SHELXT.[8] Structures were refined with full matrix least-squares refinement based on F^2 with SHELXL.[9] Full details can be found in the CIF files, Tables S3.

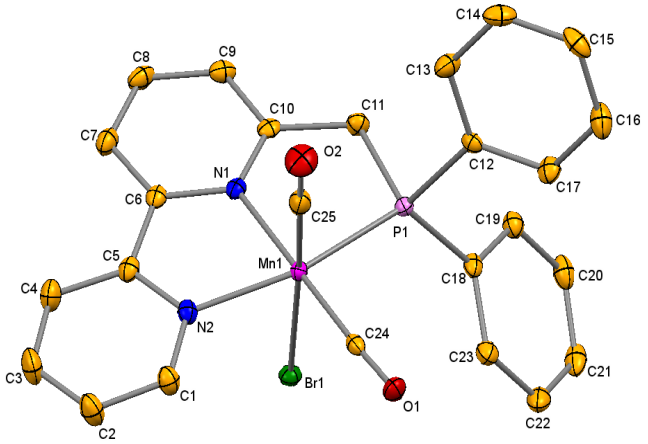


Figure S17. ORTEP presentation of complex **6**. The thermal ellipsoids are drawn at 50% probability. All hydrogen atoms are omitted for clarity.

Table S1: Selected bond lengths and bond angles of complex **6.**

Bond Angles in (°)		Bond lengths in Å	
P1-Mn1-N1	84.62(4)	Mn1-P1	2.2353(4)
P1-Mn1-N2	163.12(4)	Mn1-N1	2.0301(12)
P1-Mn1-C24	94.49(5)	Mn1-N2	2.0276(13)
P1-Mn1-Br1	91.018(13)	Mn1-Br1	2.5429(3)
N1-Mn1-N2	79.09(5)	Mn1-C24	1.7801(15)
N1-Mn1-C24	178.13(6)	Mn1-C25	1.770(3)
Mn1-C24-O1	176.51(13)	O1-C24	1.1611(18)
Mn1-C25-O2	175.9(3)	O2-C25	1.188(4)
Br1-Mn1-C25	176.22(11)	C10-C11	1.509(2)
C24-Mn1-C25	86.75(12)	P1-C11	1.8604(15)
C10-C11-P1	111.67(10)	N2-C1	1.340(2)

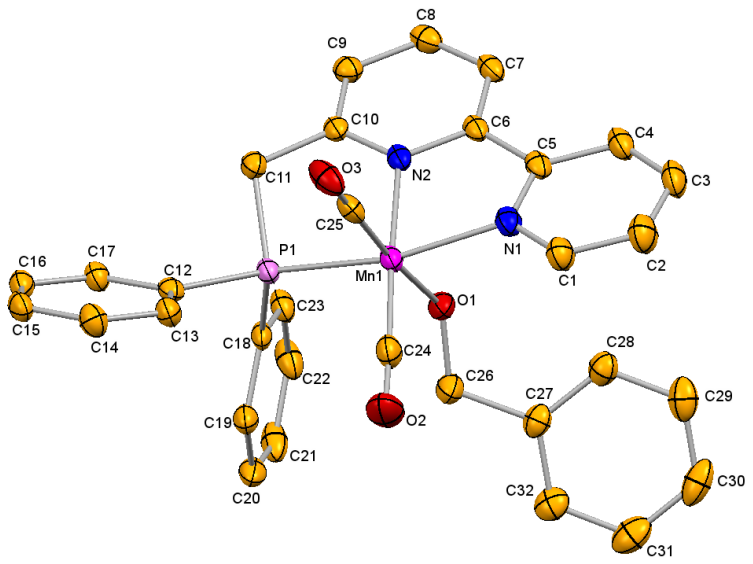


Figure S18. ORTEP presentation of complex **8**. The thermal ellipsoids are drawn at 50% probability. All hydrogen atoms are omitted for clarity.

Table S2: Selected bond lengths and bond angles of complex **8.**

Bond Angles in (°)		Bond lengths in Å	
P1-Mn1-O1	88.61(4)	Mn1-P1	2.2359(6)
P1-Mn1-N1	160.90(5)	Mn1-O1	2.002(1)
P1-Mn1-N2	82.86(5)	Mn1-N1	2.035(2)
P1-Mn1-C24	97.84(7)	Mn1-N2	2.035(2)
P1-Mn1-C25	93.10(7)	Mn1-C24	1.780(2)
O1-Mn1-N1	83.04(6)	Mn1-C25	1.769(2)
O1-Mn1-N2	78.49(6)	O1-C26	1.389(2)
O1-Mn1-C24	97.24(8)	O2-C24	1.168(3)
O1-Mn1-C25	174.82(8)	O3-C25	1.173(2)
N1-Mn1-N2	78.66(7)	C10-C11	1.499(3)
Mn1-C24-O2	176.7(2)	P1-C11	1.851(2)
Mn1-C25-O3	176.7(2)	P1-C12	1.818(2)
C24-Mn1-C25	87.37(9)	P1-C18	1.820(2)

Table S3: Crystal data summary of complex **6** and **8**.

	Complex **6**	Complex **8**
Identification code	CCDC 1878333	CCDC 1878332
Empirical formula	$C_{25}H_{19}BrMnN_2O_2P$	$C_{32}H_{26}MnN_2O_3P$
Formula weight	545.24	572.46
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	1.54184 Å
Crystal system, space group	Monoclinic, *P 2₁/c*	Monoclinic, *P 2₁/c*
Unit cell dimensions	a = 12.9669(4) Å,	a = 9.76630(10) Å,
	b = 13.8740(4) Å,	b = 16.9042(2) Å,
	c = 12.3572(4) Å	c = 16.0896(2) Å
	α = 90°,	α = 90°
	β = 93.057(3)°,	β = 97.9510(10)°
	γ = 90°	γ = 90°
Volume	2219.93(12)Å^3	2630.72(5)Å^3
Z, Calculated density	4, 1.631 Mgm^{-3}	4, 1.445 Mgm^{-3}
Absorption coefficient	2.493 mm^{-1}	4.962 mm^{-1}
F(000)	1096	1184
Crystal size	0.272 x 0.196 x 0.092 mm	0.048 x 0.031 x 0.025 mm
Theta range for data collection	3.473 to 26.020 deg.	4.571 to 68.239 deg.
Limiting indices	-16<=h<=16,	-11<=h<=11,
	-17<=k<=17,	-20<=k<=12,
	-15<=l<=15	-19<=l<=19
Reflections collected / unique	44170 / 4358	19848 / 4815
	[R(int) = 0.0334]	[R(int) = 0.0344]
Completeness to theta	99.7%	99.9%
Max. and min. transmission	1.000 and 0.212	1.000 and 0.921
Data / restraints / parameters	4358 / 6 / 317	4815 / 0 / 360
Goodness-of-fit on F^2	1.053	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0188, wR2 = 0.0445	R1 = 0.0328, wR2 = 0.0798
R indices (all data)	R1 = 0.0200, wR2 = 0.0449	R1 = 0.0372, wR2 = 0.0817
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	0.385 and -0.253 e.A^{-3}	0.392 and -0.371 e.A^{-3}

4. References:

1) Yamamoto, N.; Obora, Y.; Ishii, Y. Iridium-Catalyzed Oxidative Methyl Esterification of Primary Alcohols and Diols with Methanol. *J. Org. Chem*. **2011**, *76*, 2937–2941.
2) Wang, A.; Jiang, H. Palladium-Catalyzed Cleavage Reaction of Carbon−Carbon Triple Bond with Molecular Oxygen Promoted by Lewis Acid. *J. Am. Chem. Soc*. **2008**, *130*, 5030–5031
3) Cheng, J.; Zhu, M.; Wang, C.; Li, J.; Jiang, X.; Wei, Y.; Tang, W.; Xuea, D.; Xiao, J. Chemoselective Dehydrogenative Esterification of Aldehydes and Alcohols with a Dimeric Rhodium(II) Catalyst. *Chem. Sci*. **2016**, *7*, 4428–4434.
4) Liu, C.; Wang, J.; Meng, L.; Deng, Y.; Li, Y.; Lei, A. Palladium-Catalyzed Aerobic Oxidative Direct Esterification of Alcohols. *Angew. Chem. Int. Ed.* **2011**, *50*, 5144–5148.
5) Iwasaki, T.; Maegawa, Y.; Hayashi, Y.; Ohshima, T.; Mashima, K. Transesterification of Various Methyl Esters under Mild Conditions Catalyzed by Tetranuclear Zinc Cluster. *J. Org. Chem.* **2008**, *73*, 5147–5150.
6) Wang, Q.-Q.; Wang, Z.-X.; Xu, Y.-S.; Zhang, X.-Y.; Fan, X.-S. Bu4NI-Catalyzed and ^{t}BuOOH-Oxidized Esterification of Aldehydes with Alkyl Halides in Water. *Asian J. Org. Chem.* **2016**, *5*, 1304–1308.
7) Kong, W.; Li, B.; Xu, X.; Song, Q. Fe-Catalyzed Aerobic Oxidative C−CN Bond Cleavage of Arylacetonitriles Leading to Various Esters. *J. Org. Chem.* **2016**, **81**, 8436−8443.
8) Sheldrick, G. M. *SHELXT* -Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst.* **2015**, *A71*, 3–8.
9) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8.