Supporting Information for

Deoxydehydration of Polyols Catalyzed by a Molybdenum Dioxo-Complex Supported by a Dianionic ONO Pincer Ligand.

Randy Tran and Stefan M. Kilyanek.

Department of Chemistry and Biochemistry, University of Arkansas, 119 Chemistry Building 1 University of Arkansas Fayetteville, AR 72701

Email: kilyanek@uark.edu

Table of Contents

I. EXPERIMENTAL PROCEDURE.

General comments: Reagents were obtained from common commercial sources and used without further purification. Solvents were obtained anhydrous from Aldrich and placed over 3Å molecular sieves. All reactions were performed under inert atmosphere using standard Schlenk or glovebox techniques unless otherwise noted. The preparation of the ligand is a modified version of literature.[1] ^{1}H NMR was referenced to solvent residual signals (chloroform-*d* δ = 7.26 methylenechloride-d_2, δ = 5.32). DODH reaction yields were determined by use of an internal standard : (1,3,5-trimethoxybenzene, δ = 3.32 (s, 9H, OCH_3) δ = 6.13 (s, 3H, aryl H)) or (hexamethylcyclotrisiloxane, δ = 0.17 (s, 18H, CH_3)). Elemental analysis was performed by either the CENTC Elemental Analysis Facility at the University of Rochester or Midwest Microlabs (Indianpolis, IN).

Preliminary Kinetics Study. Reactions were carried out in J. Young high-pressure NMR tubes. The reactions were performed with 1:10:10 measured molar concentrations of catalyst:reductant:substrate. The tubes were charged with the starting materials (10 mmol of catalyst) and 0.7 mL of toluene-d8. The tube was placed in an oil bath preheated to 150 ℃. The tube was cooled and degreased to be monitored every hour by NMR. 1,3,5-trimethoxybenzene was used as an internal standard and triphenylphosphine was used as an external reference for ^{31}P NMR measurements.

X-Ray Crystallography for 1. (L = $OPPh_3$) A yellow, rod-shaped crystal of dimensions 0.078 x 0.078 x 0.270 mm was selected for structural analysis. Intensity data for this compound were collected using a D8 Quest diffractometer with a Bruker Photon II ccd area detector[4] and an Incoatec Iμs microfocus Mo Kα source (λ = 0.71073 Å). The sample was cooled to 100(2) K. Cell parameters were determined from a least-squares fit of 9717 peaks in the range 2.64 < θ <

30.02°. A total of 77479 data were measured in the range 2.290 < θ < 30.061° using ϕ and ω oscillation frames. The data were corrected for absorption by the empirical method[5] giving minimum and maximum transmission factors of 0.5191 and 0.6042. The data were merged to form a set of 13083 independent data with R(int) = 0.0482 and a coverage of 99.9 %.

The triclinic space group $P\ \bar{1}$ was determined by statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 [6]. The positions of hydrogens bonded to carbons were initially determined by geometry and were refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 (1.5 for methyl) times the isotropic equivalent displacement parameters of the bonded atoms. A total of 544 parameters were refined against 13083 data to give wR(F2) = 0.0744 and S = 1.007 for weights of $w = 1/[\sigma^2 (F^2) + (0.0320 P)^2 + 1.5000 P]$, where $P = [F_o^2 + 2F_c^2] / 3$. The final R(F) was 0.0288 for the 11584 observed, [F > 4 σ(F)], data. The largest shift/s.u. was 0.003 in the final refinement cycle. The final difference map had maxima and minima of 0.743 and -0.590 e/Å3, respectively.

X-Ray Crystallography for 2. (L = 5-coordinate) A yellow, needle-shaped crystal of dimensions 0.031 x 0.034 x 0.252 mm was selected for structural analysis. Intensity data for this compound were collected using a D8 Quest diffractometer with a Bruker Photon II cpad area detector[4] and an Incoatec Iμs microfocus Mo Kα source (λ = 0.71073 Å). The sample was cooled to 100(2) K. Cell parameters were determined from a least-squares fit of 9975 peaks in the range 2.21 < θ < 27.07°. A total of 52,537 data were measured in the range 2.208 < θ < 27.135° using ϕ and ω oscillation frames. The data were corrected for absorption by the empirical method[3] giving minimum and maximum transmission factors of 0.6042 and 0.6941. The data were merged to form a set of 6820 independent data with R(int) = 0.0742 and a coverage of 99.9 %.

The monoclinic space group $P2_1/c$ was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2.[6] The positions of hydrogens bonded to carbons were initially determined by geometry and were refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 (1.5 for methyl) times the isotropic equivalent displacement parameters of the bonded atoms. A total of 364 parameters were refined against 6820 data to give wR(F^2) = 0.1013 and S = 1.003 for weights of w = 1/[σ^2 (F2) + (0.0500 P)2 + 2.9200 P], where P = [F_o^2 + 2F_c^2] / 3. The final R(F) was 0.0342 for the 5132 observed, [$F > 4\sigma$ (F)], data. The largest shift/s.u. was 0.001 in the final refinement cycle. The final difference map had maxima and minima of 0.446 and -0.686 e/Å^3, respectively.

II. NMR characterizations

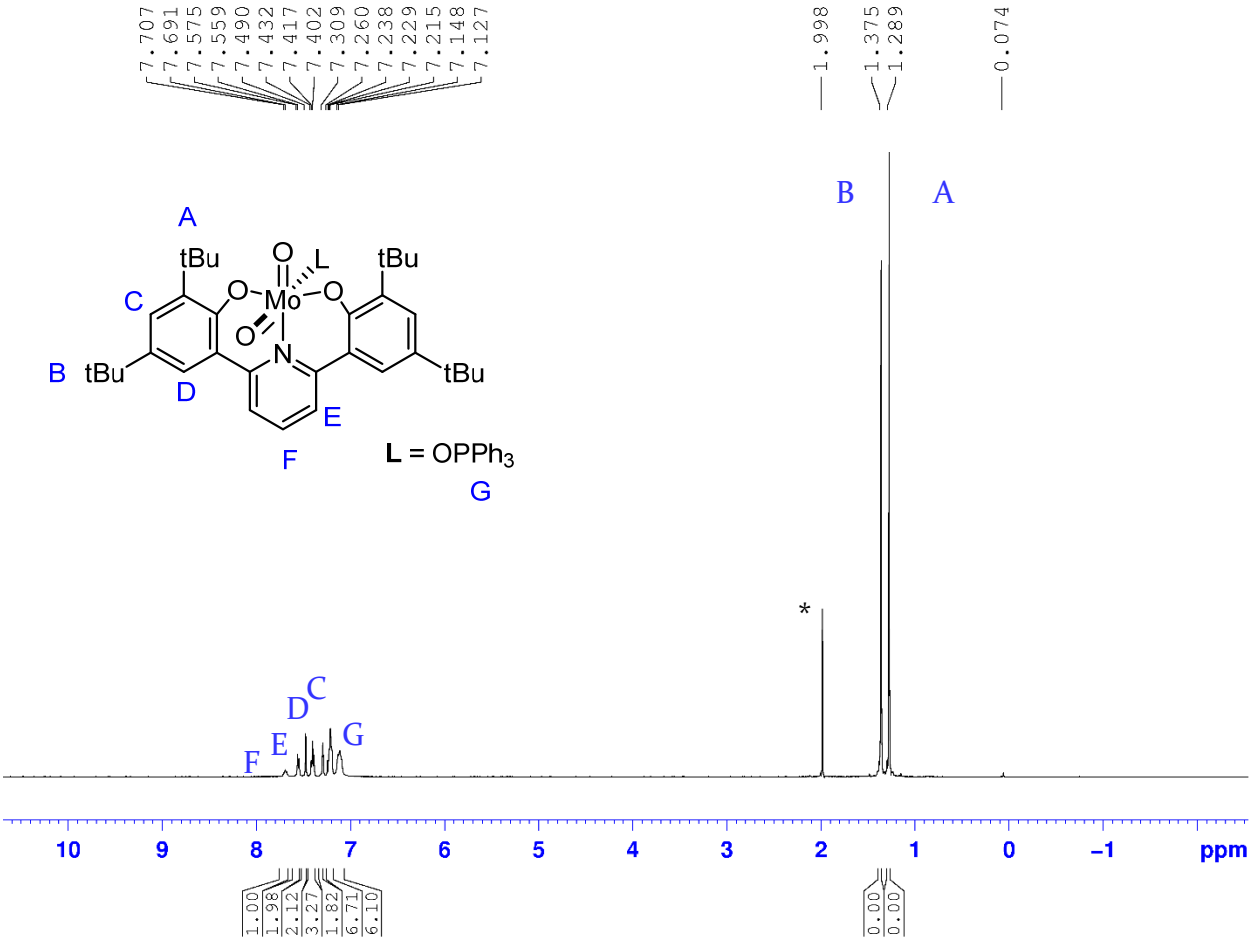


Figure S2 Catalyst **1** (^{1}H, 500 MHz, $CDCl_3$) The $OPPh_3$ is weakly bound in solution and the rate of dissociation/association is approximately that of the NMR timescale. "*" = acetonitrile

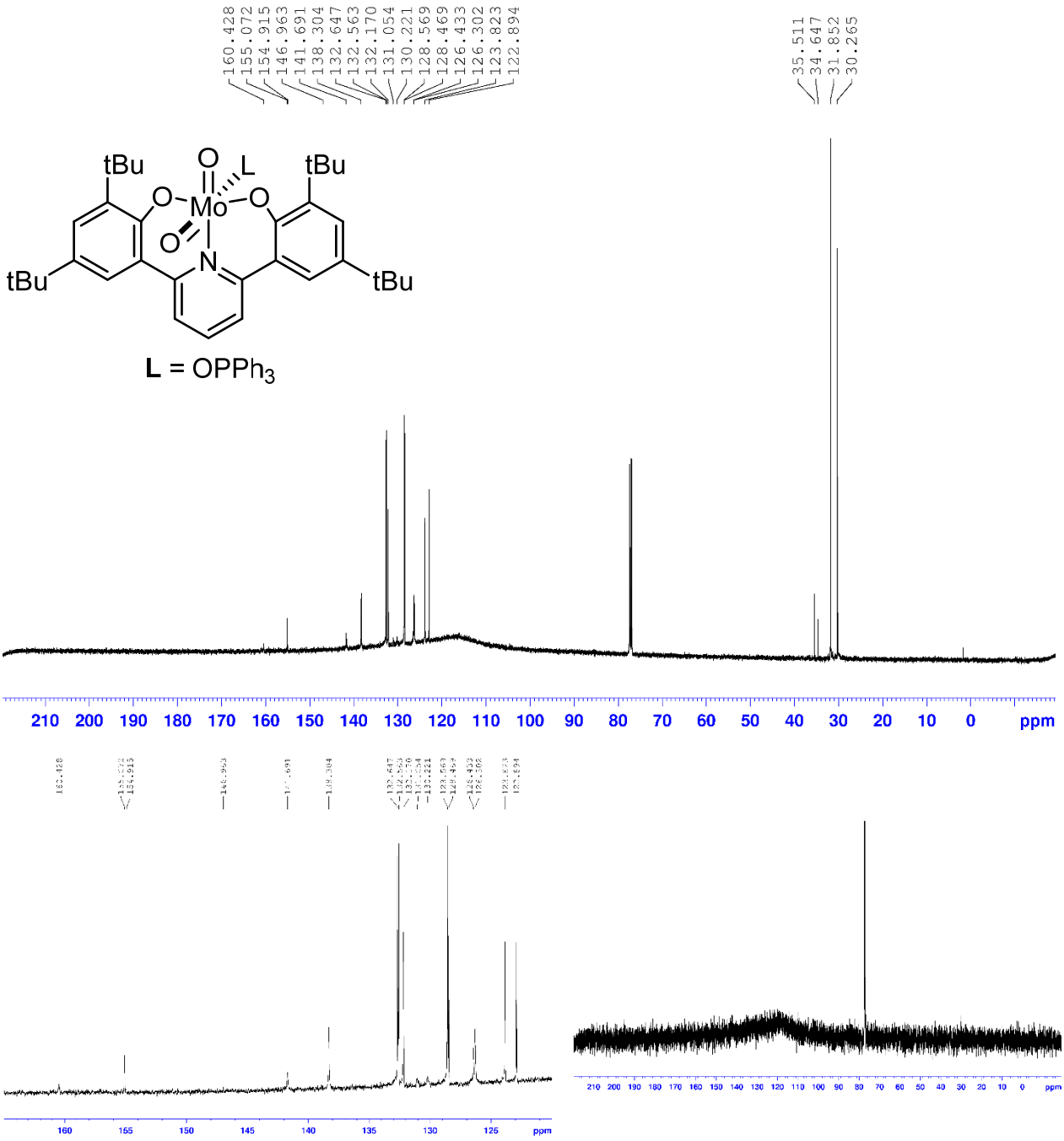


Figure S3 Catalyst **1** ($^{13}C\{^{1}H\}$, 500 MHz, $CDCl_3$) Bottom: aryl region

The broad baseline is a result of probe contamination the figure in the bottom right shows a chloroform blank of the NMR probe in question.

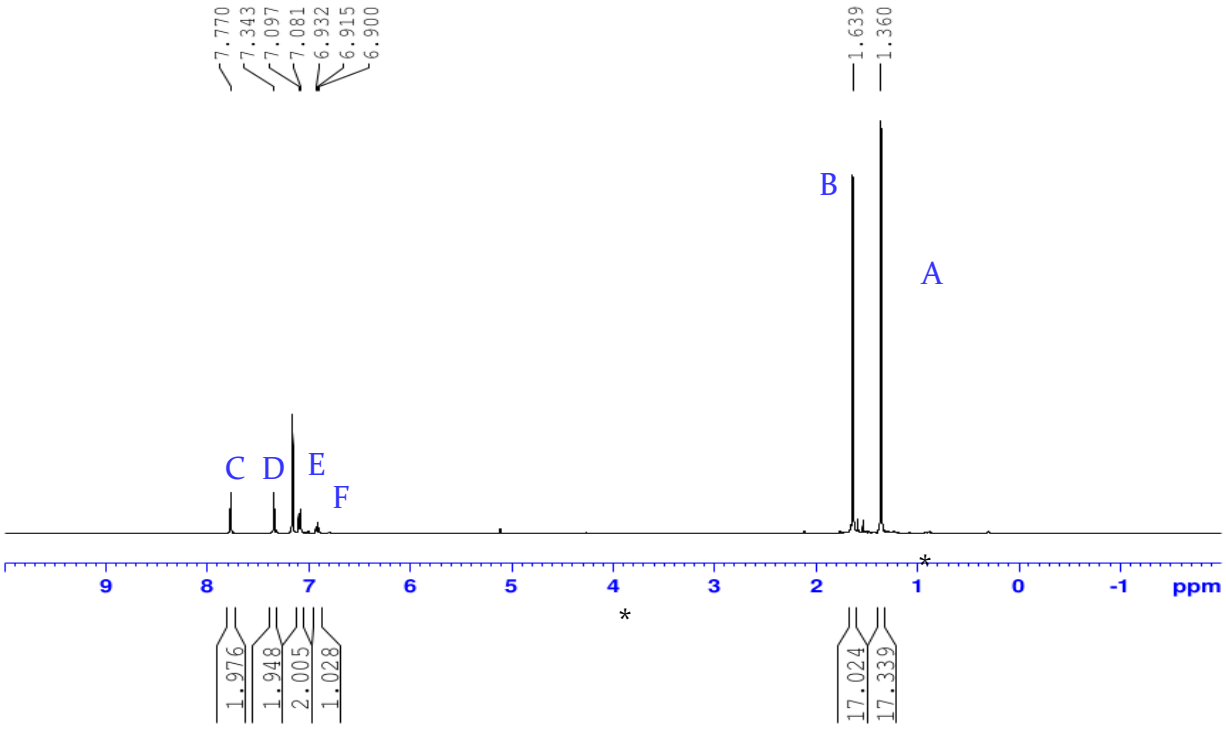
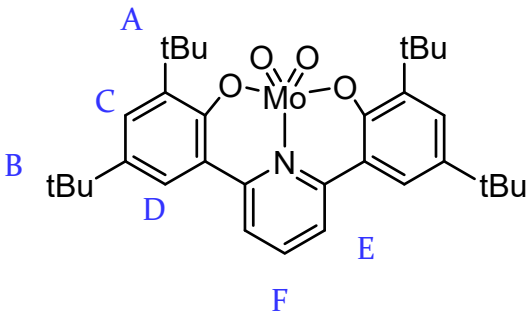


Figure S4 Catalyst **2** (^{1}H, 500 MHz, C_6D_6)



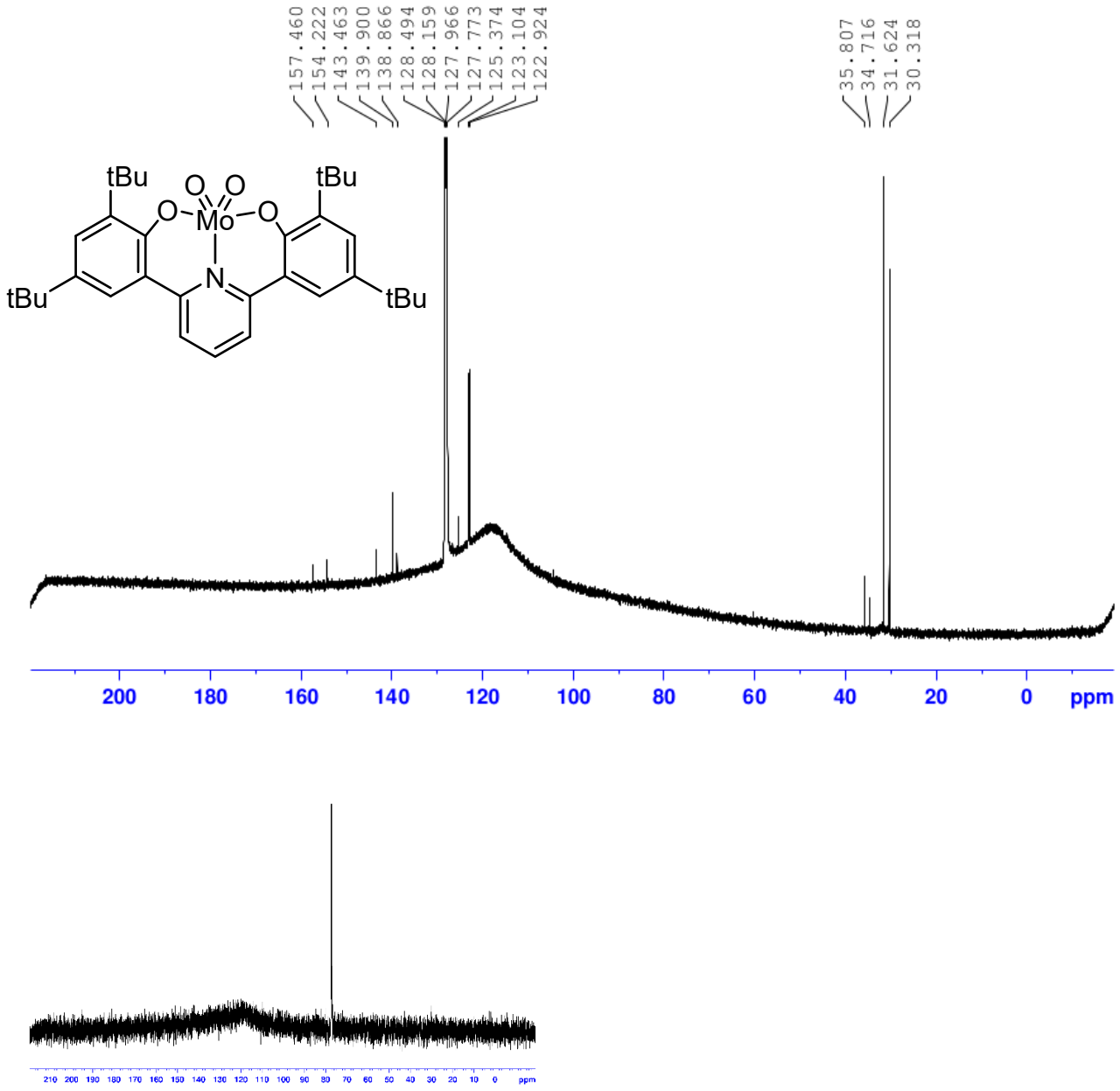


Figure S5 Catalyst **2** L = 5-coordinate ($^{13}C\{^{1}H\}$, 500 MHz, C_6D_6)

The broad baseline is a result of probe contamination the figure in the bottom right shows a chloroform blank of the NMR probe in question.

III. Quantitation of Yields by NMR Experiments

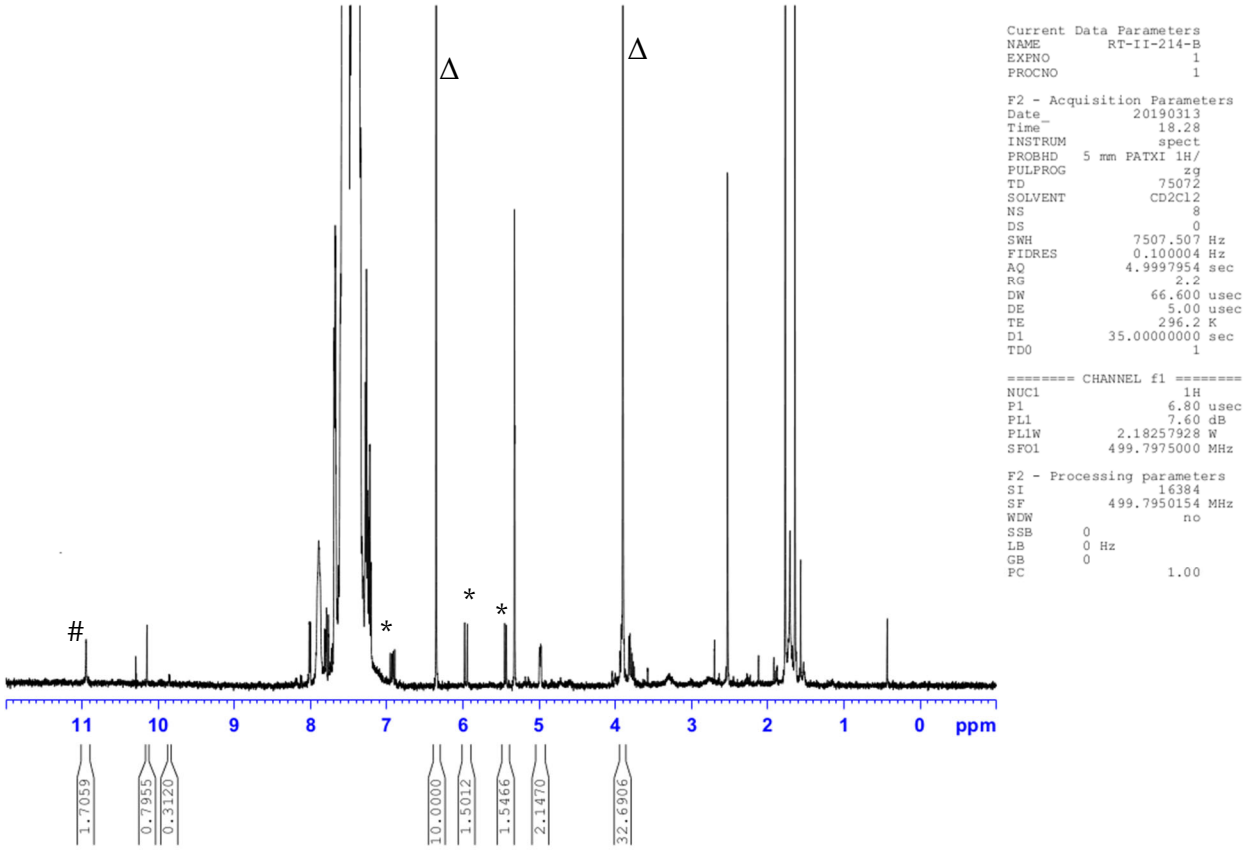


Figure S6 Catalyst **1**, PPh_3, 1-phenyl-1,2-ethanediol, 1,3,5-trimethoxybenzene 48h 150°C in chlorobenzene. ^1H NMR (^1H, 500 MHz, dcm-d2). A 0.35mL aliquot was taken from the reaction mixture and added to 0.35mL of dcm-d2.

"*" denotes styrene resonances tracked

"#" denotes free ligand (P3)

"Δ" denotes internal standard

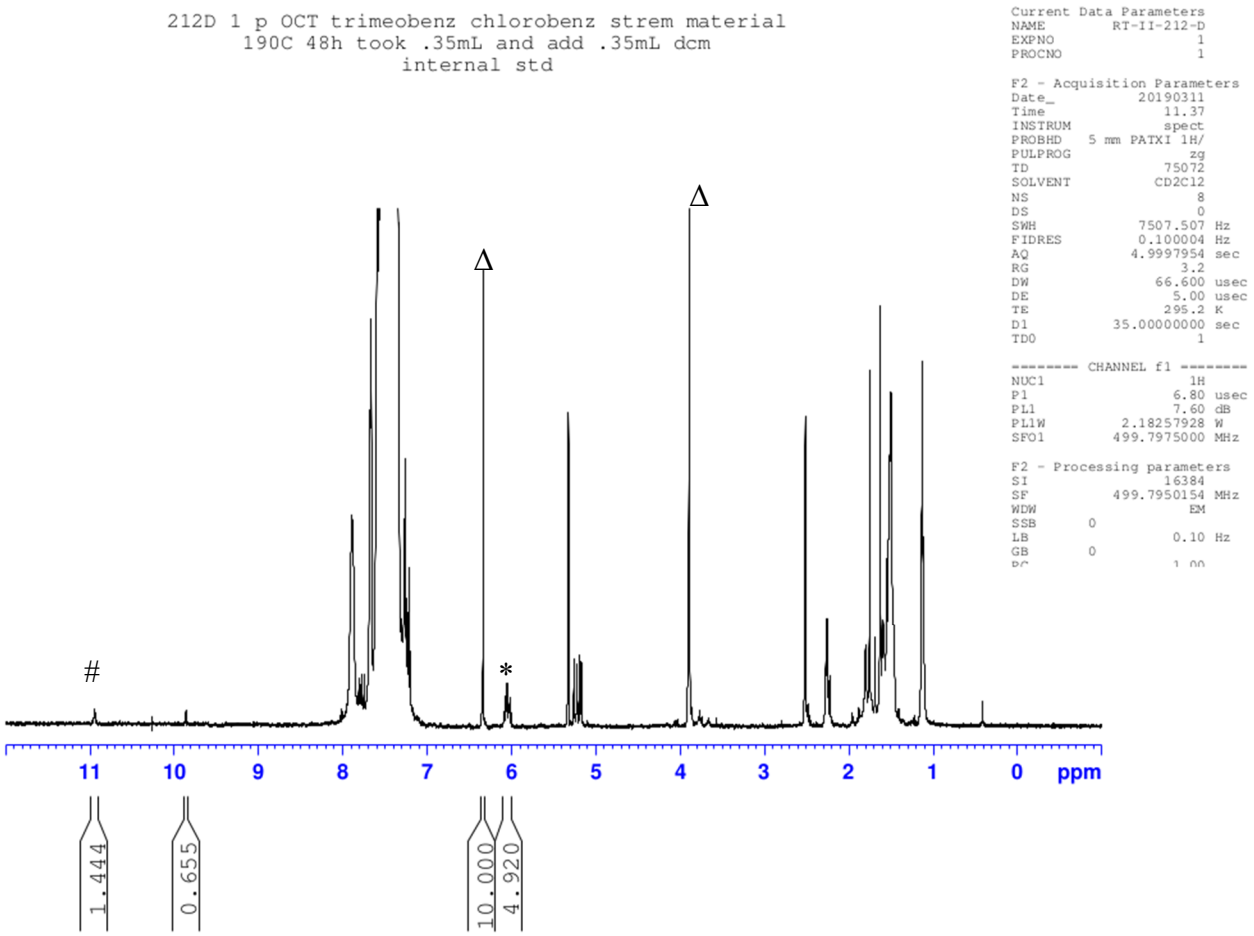


Figure S7 Catalyst **1**, PPh_3, 1,2-octanediol, 1,3,5-trimethoxybenzene 48h 190℃ in chlorobenzene. ^1H NMR (^1H, 500 MHz, dcm-d2) A 0.35mL aliquot was taken from the reaction mixture and added to 0.35mL of dcm-d2.

"*" denotes octene resonance tracked

"#" denotes free ligand (P3)

"Δ" denotes internal standard

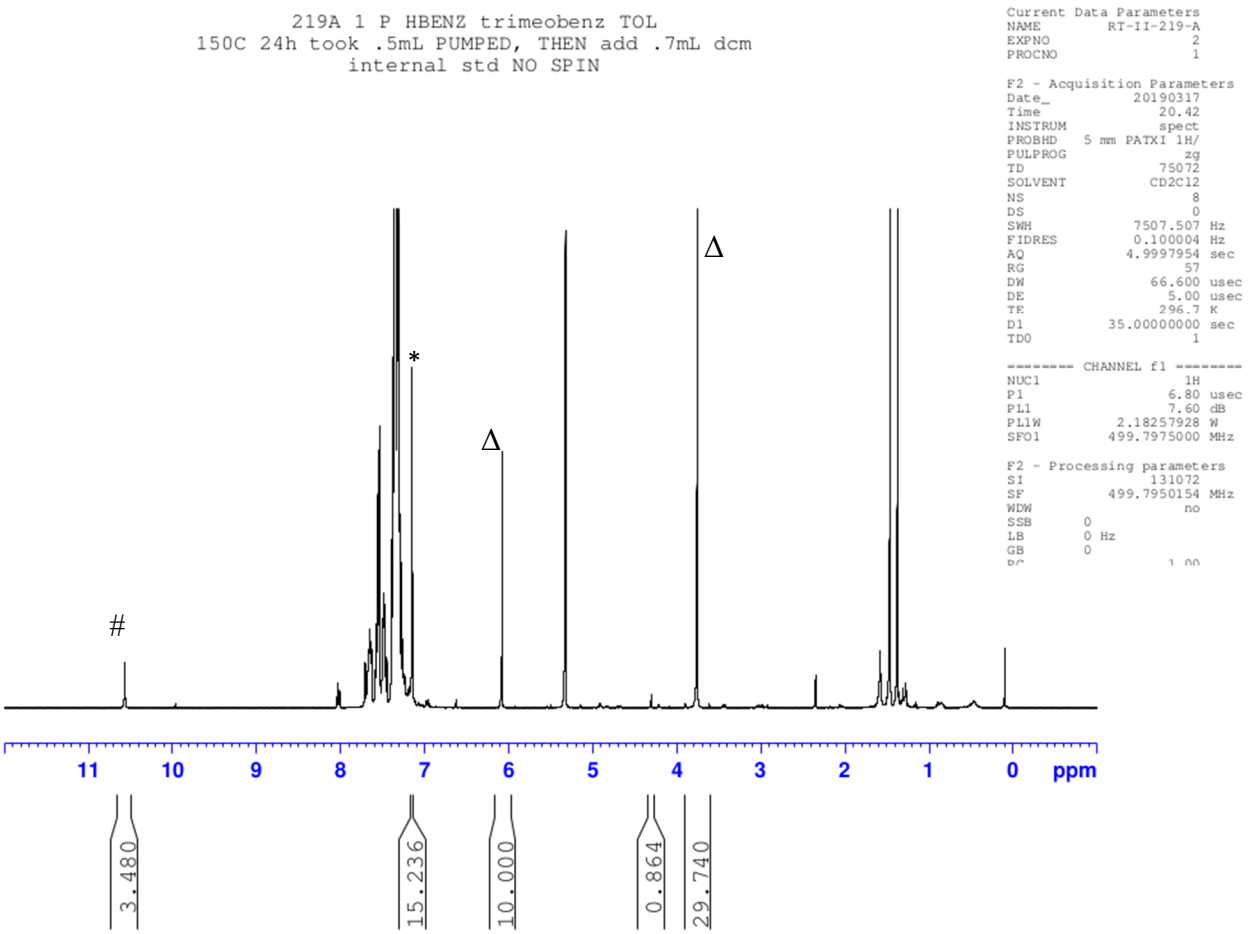


Figure S8 Catalyst **1**, PPh_3, (R,R)-(+)-hydrobenzoin, 1,3,5-trimethoxybenzene 48h 190°C in chlorobenzene. ^1H NMR (^1H, 500 MHz, dcm-d2). A 0.5mL aliquot was taken and volatiles removed then it was dissolved in 0.7mL of dcm-d2

"*" denotes stilbene resonance tracked

"#" denotes free ligand (P3)

"Δ" denotes internal standard

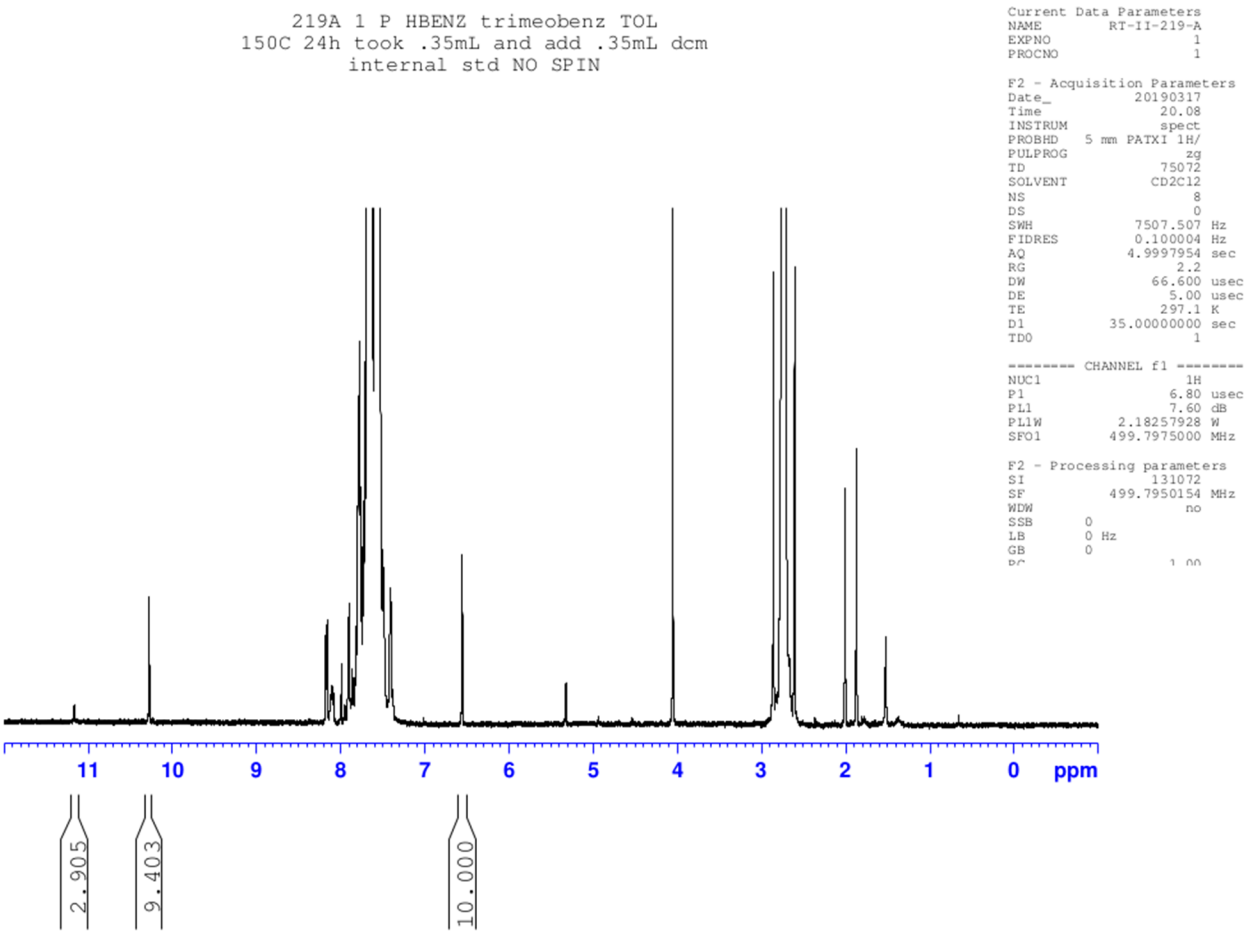


Figure S9 Catalyst **1**, PPh_3, (R,R)-(+)-hydrobenzoin, 1,3,5-trimethoxybenzene 48h 190°C in chlorobenzene. ^1H NMR (^1H, 500 MHz, dcm-d2) A 0.35mL aliquot was taken from the reaction mixture and added to 0.35mL of dcm-d2.

"*" denotes benzaldehyde resonance tracked

"#" denotes free ligand (P3)

"Δ" denotes internal standard

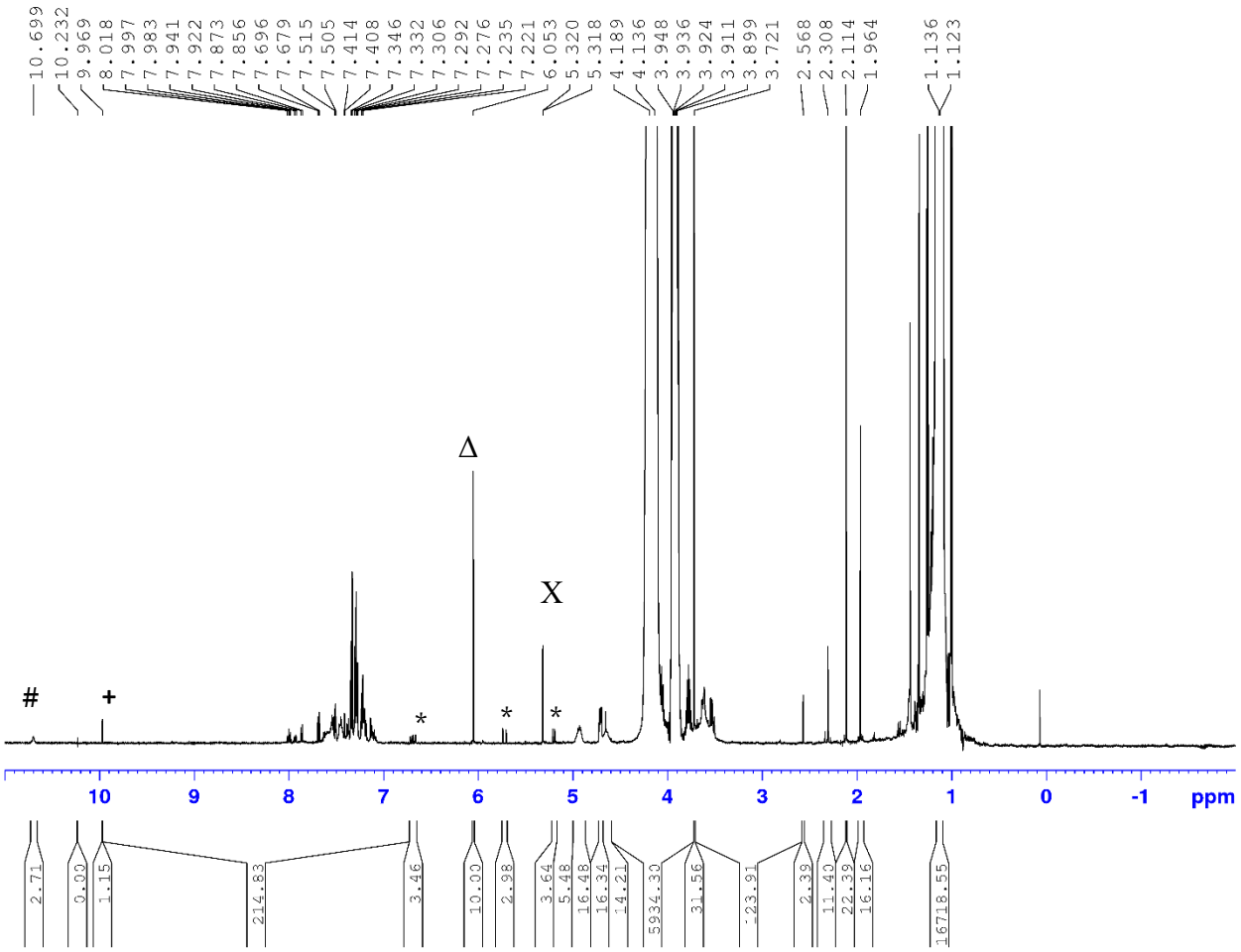


Figure S10 Catalyst **1** L = $OPPh_3$, PPh_3, 1-phenyl-1,2-ethanediol, 1,3,5-trimethoxybenzene in 2-propanol 48h 150°C (^1H, 500 MHz, dcm-d2)

"*" denotes styrene resonances tracked

"#" denotes free ligand (P3)

"+" denotes aldehyde

"Δ" denotes internal standard

"X" denotes CD_2Cl_2

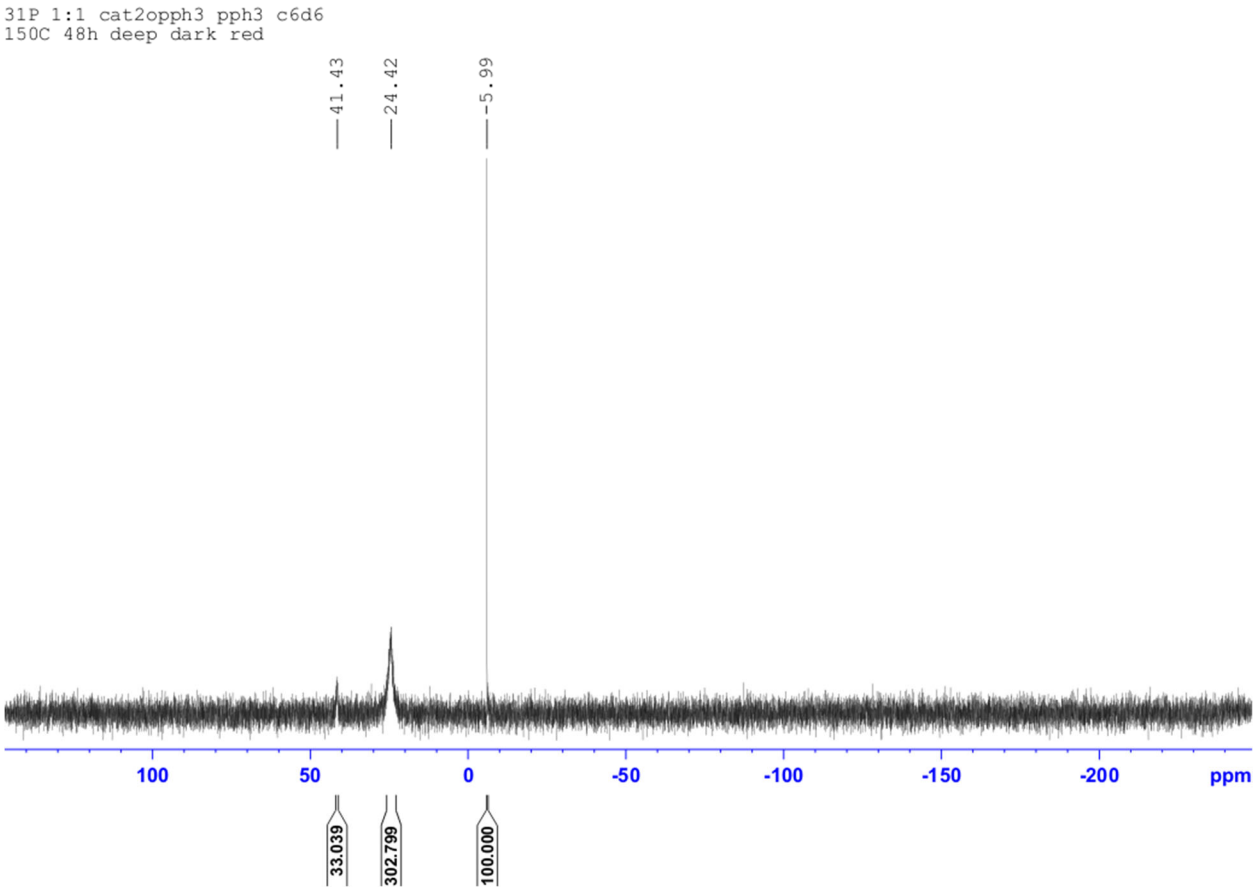


Figure S11 ^{31}P NMR of a 1:1 molar ratio of **1** and PPh_3 in C_6D_6 after heating for 48 hours at 150℃

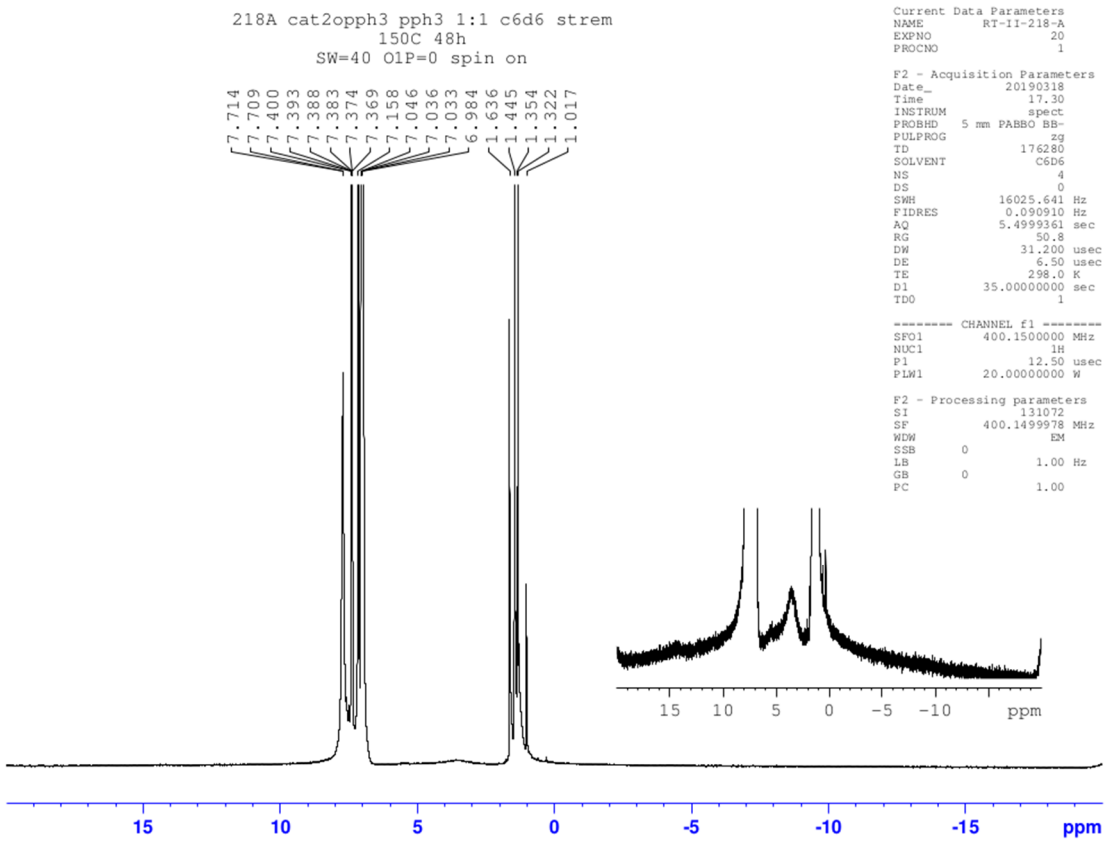


Figure S12 ^{31}P NMR of a 1:1 molar ratio of **1** and PPh_3 in C_6D_6 after heating for 48 hours at 150℃

IV. Kinetics Studies

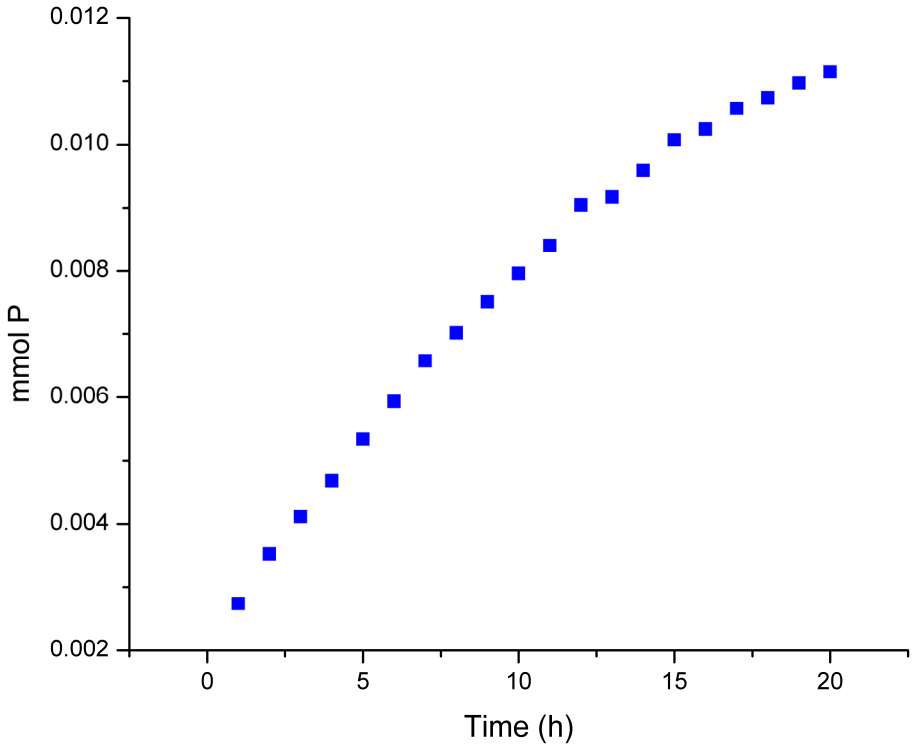


Figure S14. Monitored growth of styrene versus time.

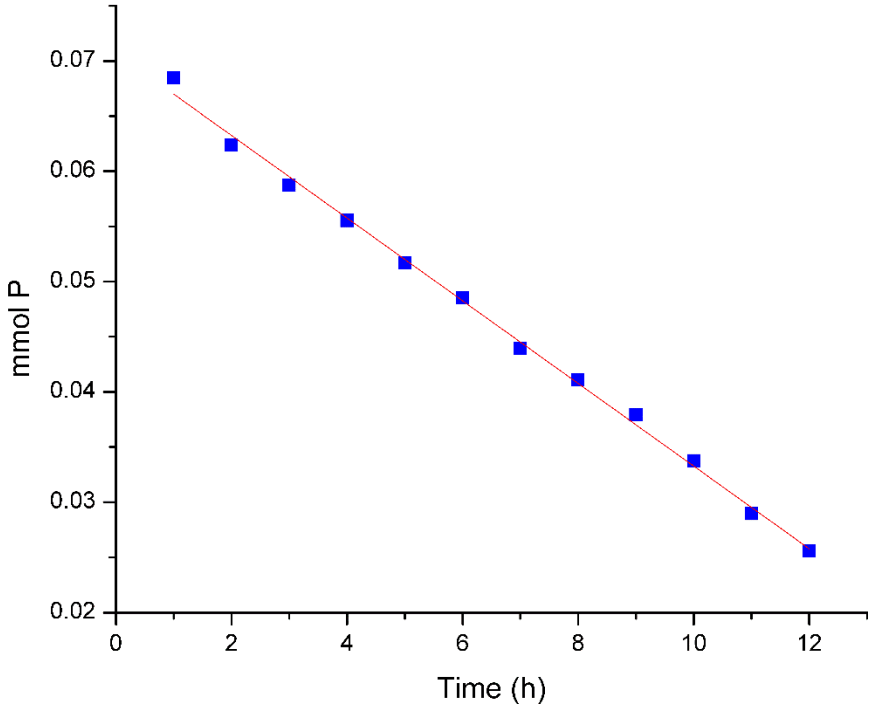


Figure S15. Monitored consumption of diol vs time.

V. Determination of Yields for Catalytic Reactions

NMR Method.

$$\frac{int\ P}{int\ std} * \frac{H\ std}{H\ P} * \frac{mmol\ std}{sample} * \frac{vol\ reaction}{vol\ aliquot} = mmol\ P$$

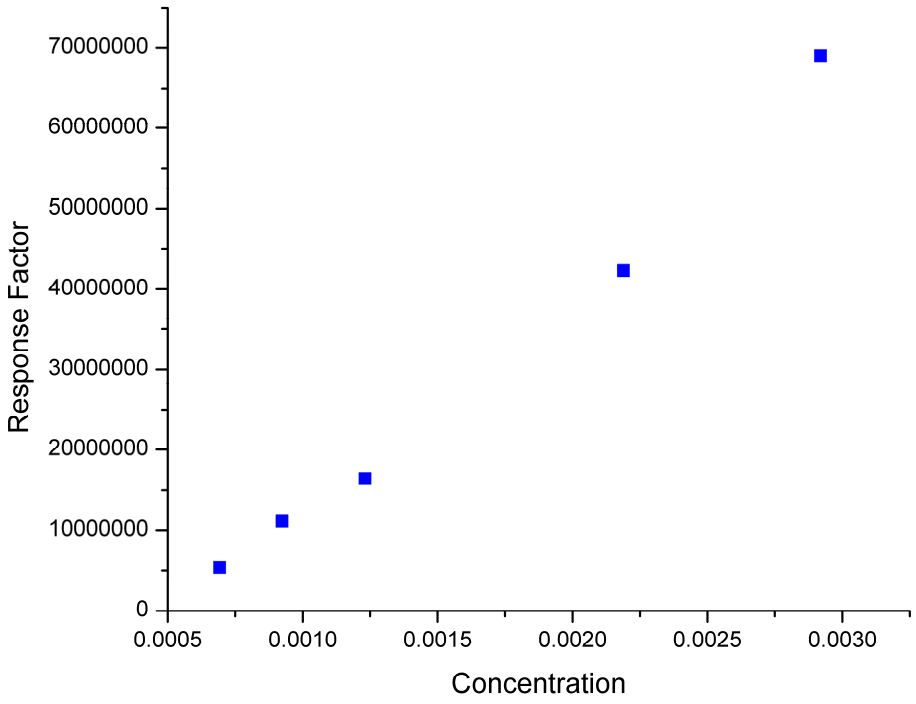
Int:	Analyte	H's	std int:	std H's	Std mmol in tube	mmol P	adjusted mmol
5.1172	Octene	1	10	3	0.008095	0.012427138	0.355061086
0.681	Heptaldehyde	6				0.001653811	0.047251739

Initial diol mmol	% Yield
0.558025029	63.63%
	8.47%

$$\frac{5.1172}{10} * \frac{3}{1} * 0.008095 * \frac{10}{0.35} = 0.355061086$$

$$\frac{0.355061086}{0.558025029} * 100 = 63.63\%$$

GC/MS



$R^2 = 0.98973$, y=2.819497E+10x – 1.602562E+07

Response Factor	Conc from curve	mmol in vial	Initial diol	conversion
1083033176	3.90E-02	0.042878736	0.087589117	51.05%

$$\frac{RF + 1.602562\text{E} + 07}{2.819497\text{E} + 10} = 0.034387192\ \text{M}$$

Took 1 mL (V_1) aliquot from reaction then column separation through a silica plug. Analytes of non interest were flushed off with toluene while the analyte of interest was flushed off with acetone and pumped it down and then added 0.4mL acetone and 0.8mL of pentane and naphthalene. The measured volume was 1.1mL (V_2).

$$C_{rxn}V_1 = C_{curve}V_2$$

$$C_{rxn}(1mL) = 0.0389807(1.1mL)$$

$$mmol_{rxn} = 0.042878736$$

$$\frac{0.042878736}{0.087589117} * 100 = 51.05\%$$

VI. Table of Catalytic Reactions

Table S1

Substrate	Reductant	Catalyst **1** %C=C(%C=O)	Conversion	Catalyst **2** %C=C(%C=O)	Conversion
1-phenyl-1,2-ethanediol	PPh_3	31(9)	57	31(5)	63
	PPh_3	21(5)[a,b]	71	-	-
	PPh_3	21(15)[a,b]	>99	-	-
	Zinc	36(9)	53	30(12)	68
	Carbon	37(11)	59	46(14)	86
	Na_2SO_3	29((9)	42	26.5(11)	55
	2-propanol	6(2), 1[c]	60.5	18(1)[b], 1.5[b,c]	21
	3-octanol	10(13)	64	18(16)	-
(R,R)-(+)-Hydrobenzoin	PPh_3	62(21)	98	46(41)	>99
	Zinc	48(44)	>99	38(38)	>99
	Na_2SO_3	48(46)	94	39(40)	>99
	Carbon	54(42)	96	40(40)	>99
	2-propanol	42(18), 6[c]	-	-	-
1,2-Octanediol	PPh_3	59(6)[a]	98	25(8)[b]	47[d]
	Carbon	18(18)[a,b]	>99	trace	>99[d]
	3-octanol	4(4)[a,b]	8	14(20)	>99[d]
	PPh_3	14(0)	-	-	-
	Zinc	0(0)	-	0(0)	-
	Carbon	0(0)	-	0(0)	-
	Na_2SO_3	0(0)	-	0(0)	-
(+)-Diethyl L-tartrate	PPh_3 10 pct	18(0)	70[d]	-	-
	PPh_3 1 pct	2(0)[e]	51	-	-
	Zinc	6(0)	37	-	-
	Carbon	9(0)	38	-	-
	Na_2SO_3	5(0)	51	-	-
	2-propanol	26(0) 3 equiv	-	-	-
trans-1,2-cyclohexanediol	PPh_3	1(0)	-	-	-
	Zinc	0(0)	-	-	-
	Carbon	0(0)	-	-	-
	Na_2SO_3	0(0)	-	-	-
	2-propanol	0(0)	-	-	-

[a]Reactions were at performed in chlorobenzene at 190°C. [b]Reaction data from single run. [c]Equivalents of acetone formed. [d]Conversion by GC/MS. [e]Reactions were run at 1% catalyst loading.

Table S2

Catalyst	Experiment Code	Substrate	Reductant	%C=C	%C=O	Total yield	NMR conversion	GC/MS conversion	Average %C=C	Average %C=O	Average conversion
1	44A-48-A	1-Phenyl-1,2-ethanediol	PPh_3	35	5	40	58	79	30.5	9	57
	212C	1-Phenyl-1,2-ethanediol	PPh_3	26	13	39	56	55			
190C ClBenz	215A	1-Phenyl-1,2-ethanediol	PPh_3	21	15		>99	>99			
	46B/56B	1-Phenyl-1,2-ethanediol	Zinc	34	10	44	56	NA	36	9	52.5
	51E/60H	1-Phenyl-1,2-ethanediol	Zinc	38	8	46	49	60			
	46E/56E	1-Phenyl-1,2-ethanediol	Carbon	45	11	56	58	57	37	10.5	59
	49E-60B	1-Phenyl-1,2-ethanediol	Carbon	29	10	39	60	59			
	49B-56H	1-Phenyl-1,2-ethanediol	Na_2SO_3	30	11	41	44	49	29		42.5
	53B-60K	1-Phenyl-1,2-ethanediol	Na_2SO_3	28	6	34	41	31			
	123A	1-Phenyl-1,2-ethanediol	2-propanol	7	2	9	61	NA	6		60.5, 1 eq of acetone formed
	126C	1-Phenyl-1,2-ethanediol	2-propanol	5	2	7	60	NA			1 eq of acetone formed
190C ClBenz	214A	1-Phenyl-1,2-ethanediol	3-octanol	8	33		>99	>99			
150C ClBenz	214B	1-Phenyl-1,2-ethanediol	PPh_3	21	5	26	71	75			
Neat 3-octanol	208A	1-Phenyl-1,2-ethanediol	3-octanol	12	3	15	38	41			
	208B	1-Phenyl-1,2-ethanediol	3-octanol	8	10		59	45	10	13.5	64.5
	212E	1-Phenyl-1,2-ethanediol	3-octanol	12	17		70	55			

1											
190C ClBenz	203A	1,2-octanediol	PPh_3	54	3	57	96	>99	59	5.5	97.5
190C ClBenz	212D	1,2-octanediol	PPh_3	64	8	72	99	>99			
190C ClBenz	216D	1,2-octanediol	Carbon	18	18						
190C ClBenz	218D	1,2-octanediol	3-octanol	4	4	8	-	41			
	52B/53H	1,2-octanediol	PPh_3	14	0	14	-	-			
	44C/48C	1,2-octanediol	PPh_3	0	0	0					
	56D/46D	1,2-octanediol	Zinc	0	0	0			0	0	
NMR rxn	52C/53I	1,2-octanediol	Zinc	0	0	0			0	0	
	51A/60D	1,2-octanediol	Carbon	0	0	0			0	0	
	53A/60J	1,2-octanediol	Carbon	0	0	0			0	0	
	51D/60G	1,2-octanediol	Na_2SO_3	0	0	0			0	0	
	53D/60M	1,2-octanediol	Na_2SO_3	0	0	0			0	0	
1	Experiment Code	Substrate	Reductant	%C=C	%C=O	Total yield	NMR conversion	GC/MS conversion	Average %C=C	Average%C=O	Average conversion
1% catalyst load	89C/93B	(+)-Diethyl L-tartrate	PPh_3	2	0	2	53	90	2	0	50.5
1% catalyst load	93G/95A	(+)-Diethyl L-tartrate	PPh_3	2	0	2	48	95			
	89D/93C	(+)-Diethyl L-tartrate	PPh_3	17	0	17		63	18	0	
	89E/93D	(+)-Diethyl L-tartrate	PPh_3	19	0	19		77			
	91A/93E	(+)-Diethyl L-tartrate	Zinc	5	0	5		58	5.5	0	37
	91B/93F	(+)-Diethyl L-tartrate	Zinc	6	0	6	37	48			

	92A/94A	(+)-Diethyl L-tartrate	Carbon	9	0	9	38	42	8.5	0	38
	92B/94B	(+)-Diethyl L-tartrate	Carbon	8	0	8	38	73			
	92C/94C	(+)-Diethyl L-tartrate	Na_2SO_3	4	0	4		48	5	0	
	93H/95B	(+)-Diethyl L-tartrate	Na_2SO_3	6	0	6		53			3.33 eq of acetone formed
	131B/133A	(+)-Diethyl L-tartrate	2-propanol	24	0	24	NA	NA	25.5	0	3 eq of acetone formed
1	212B	(R,R)-(+)-hydrobenzoin	PPh_3	57	24	81	>99	NA	62	21.5	98
	219A	(R,R)-(+)-hydrobenzoin	PPh_3	67	19	86	96				
	46C-66C	(R,R)-(+)-hydrobenzoin	Zinc	48	50	98	>99		48	44	>99
	51F-66H	(R,R)-(+)-hydrobenzoin	Zinc	48	38	87	>99				
	49C-66E	(R,R)-(+)-hydrobenzoin	Na_2SO_3	55	49	103			48	46	93.5
	53C2	(R,R)-(+)-hydrobenzoin	Na_2SO_3	41	43	84					
	49F2	(R,R)-(+)-hydrobenzoin	Carbon	66	39	105			54	41.5	95.5
	46F2	(R,R)-(+)-hydrobenzoin	Carbon	42	44	86					
	130A/131A	(R,R)-(+)-hydrobenzoin	2-propanol	42	19		NA	NA	42	18	4.8 eq of acetone formed
	132A/134C	(R,R)-(+)-hydrobenzoin	2-propanol	42	17		NA	NA			6.9 eq of acetone formed
1	102A/104B	Trans-cyclohexanediol	PPh_3	1	0	1	-	-	1	0	-
	102B/104C	Trans-cyclohexanediol	PPh_3	1	0	1	-	-			
	105A/107C	Trans-cyclohexanediol	Zinc	0	0	0	-	-	0	0	-
	105B/107C	Trans-cyclohexanediol	Zinc	0	0	0	-	-			
	107A/109C	Trans-cyclohexanediol	Na_2SO_3	0	0	0	-	-	0	0	-
	110C/111F	Trans-cyclohexanediol	Na_2SO_3	0	0	0	-	-			
	110A/111D	Trans-cyclohexanediol	Carbon	0	0	0	-	-	0	0	-
	110B/111E	Trans-cyclohexanediol	Carbon	0	0	0	-	-			
	132C/134E	Trans-cyclohexanediol	2-propanol	0	0	0	-	-	0	0	-
	134A/135A	Trans-cyclohexanediol	2-propanol	0	0	0	-	-			
2	36A-42A	1-Phenyl-1,2-ethanediol	PPh_3	35	6	41	63	81	31	5	63.5
	54A-61A	1-Phenyl-1,2-ethanediol	PPh_3	27	4	31	64	59			
	40D-42F	1-Phenyl-1,2-ethanediol	Zinc	29	10	39	63	73	30	12	68
	54D-61D	1-Phenyl-1,2-ethanediol	Zinc	31	14	45	73	70			
	55C-61I	1-Phenyl-1,2-ethanediol	Na_2SO_3	39	16	55	88	>99	46	14	85.5
	40E-42G	1-Phenyl-1,2-ethanediol	Na_2SO_3	53	12	65	83	98			
	57C-62-G	1-Phenyl-1,2-ethanediol	Carbon	22	12	34	40	33	26.5	11	54.5

	55F-62D	1-Phenyl-1,2-ethanediol	Carbon	31	10	41	69	56			
	57A-66N	1-Phenyl-1,2-ethanediol	2-propanol	18	1	19	21	NA		1.5 equiv	
2	61C-54C	1,2-octanediol	PPh_3	4	0	4	6		5.5	0.5	18
	42C-36C	1,2-octanediol	PPh_3	7	1		30				
	61F-54F	1,2-octanediol	Zinc	0	0	0	0	0	0	0	0
	61H-55B	1,2-octanediol	Zinc	0	0	0	0	0			
	62C-58A	1,2-octanediol	Carbon	10	0		30		5	0	15
	62K-58A	1,2-octanediol	Na_2SO_3	0	0	0	0	0	0	0	0
	62J-57F	1,2-octanediol	Na_2SO_3	0	0	0	0	0			
2	36B2-66A	(R,R)-(+)-hydrobenzoin	PPh_3	51	47	98			45.5	41	
	54B2-66I	(R,R)-(+)-hydrobenzoin	PPh_3	40	35	75					
	54E-66K	(R,R)-(+)-hydrobenzoin	Zinc	38	36	74			37.5	37.5	
	55A/66L	(R,R)-(+)-hydrobenzoin	Zinc	37	39	76					
	55D/66M	(R,R)-(+)-hydrobenzoin	Carbon	40	44	84			39	39.5	
	57A/66N	(R,R)-(+)-hydrobenzoin	Na_2SO_3	38	35	73					
	57D/660	(R,R)-(+)-hydrobenzoin	Na_2SO_3	39	46	85			39.5	39.5	
	57E/66P	(R,R)-(+)-hydrobenzoin	Na2SO3	40	33	73					

2	Experiment Code	Substrate	Reductant	%C=C	%C=O	Total yield	NMR conversion	GC/MS conversion	Average %C=C	Average%C=O	Average conversion
190C ClBenz	220A	sty-diol	3-octanol	18	16	34					
190C ClBenz	218C	1,2-octanediol	3-octanol	14	20	34					
190C ClBenz	216C	1,2-octanediol	PPh_3	25	8	33		47			
190C ClBenz	216E	1,2-octanediol	Carbon	trace	0						

Yields for alkene DODH product are similar or slightly higher than those reported using ammonium heptamolybdate as catalyst.[2] However, the bulk of our reactions are performed at a slightly lower temperature than the recent report. Additionally, here we provide conversion data showing 44% to >99% conversion. When our results are compared to those of Fristrup and coworkers[3] we see similar conversions. As is precedented in the literature, some reactions show >99% conversion and yields of 70% and below.

VII. X-ray crystallography

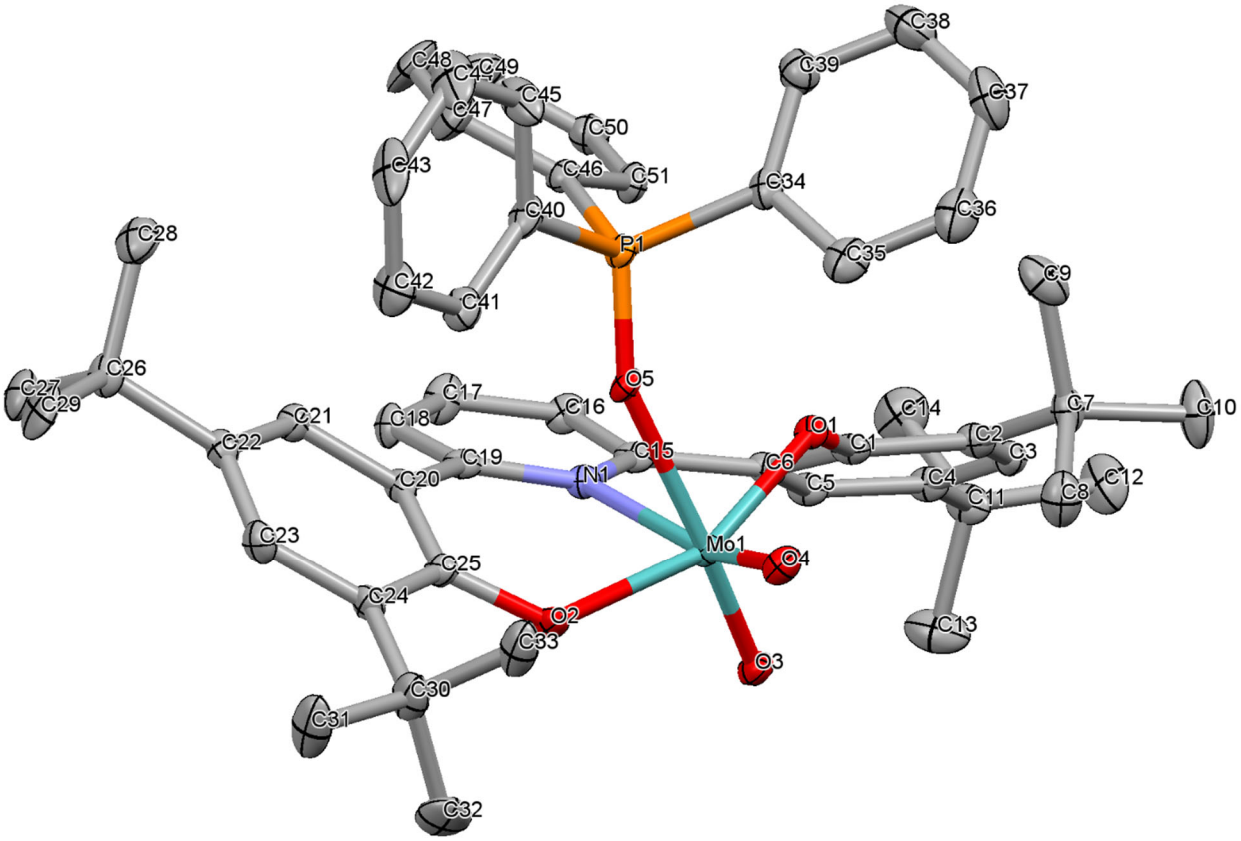


Figure S16 X-ray structure of **1** L=OPPh$_3$. The displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms were omitted for clarity.

Table S3. Crystal data and structure refinement for **1** L = $OPPh_3$.

Empirical formula	C_{51} H_{58} Mo N O_5 P	
Formula weight	891.89	
Crystal system	triclinic	
Space group	$P\ \bar{1}$	
Unit cell dimensions	a = 9.9185(2) Å	□= 97.5508(10)°
	b = 14.9484(4) Å	□= 105.1882(8)°
	c = 16.3217(4) Å	□= 102.4915(8)°
Volume	2234.25(9) $Å^3$	
Z, Z'	2, 1	
Density (calculated)	1.326 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	936	
Absorption coefficient	0.377 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.6042 and 0.5191	
Theta range for data collection	2.290 to 30.061°	
Reflections collected	77479	
Independent reflections	13083 [R(int) = 0.0482]	
Data / restraints / parameters	13083 / 0 / 544	
$wR(F^2$ all data)	$wR2$ = 0.0744	
R(F obsd data)	$R1$ = 0.0288	
Goodness-of-fit on F^2	1.007	
Observed data [I > 2□(I)]	11584	
Largest and mean shift / s.u.	0.003 and 0.000	
Largest diff. peak and hole	0.743 and -0.590 e/$Å^3$	

$wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$

$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

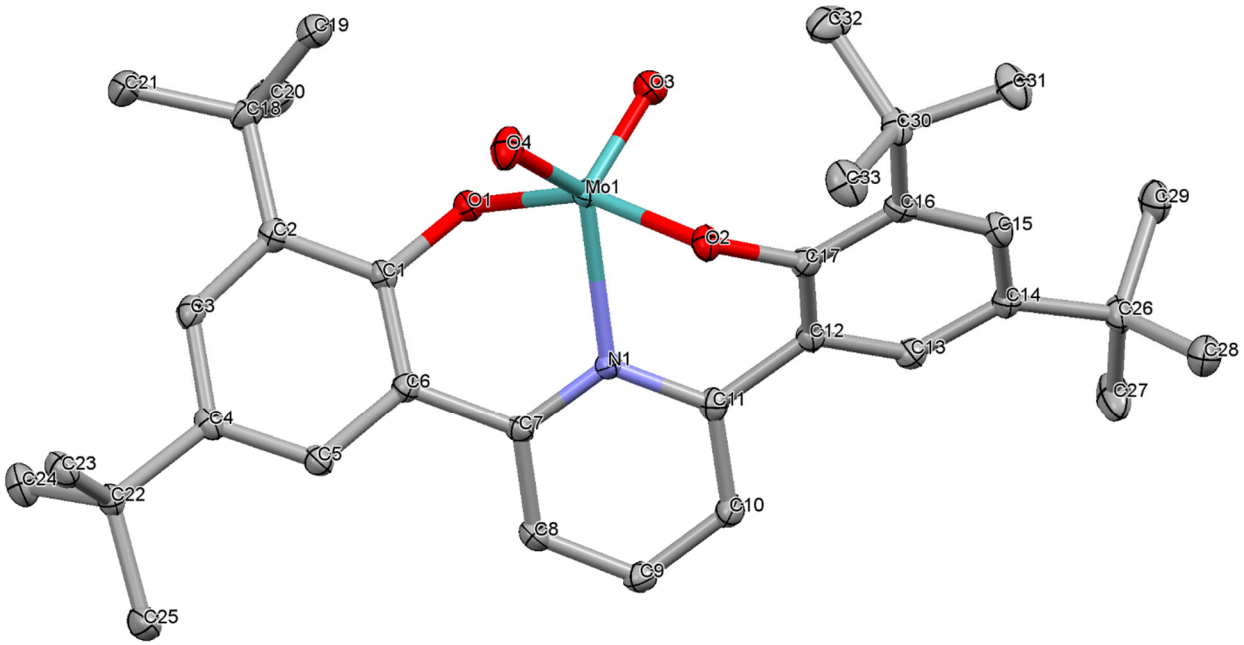


Figure S17. X-ray structure of **2** L=5-coordinate. The displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms were omitted for clarity.

Table S4. Crystal data and structure refinement for **2** L = 5-coordinate.

Empirical formula	C_{33} H_{43} Mo N O_4	
Formula weight	613.62	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.6718(6) Å	□= 90°
	b = 11.7729(4) Å	□= 118.4751(14)°
	c = 16.8857(6) Å	□= 90°
Volume	3088.05(19) $Å^3$	
Z, Z'	4, 1	
Density (calculated)	1.320 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	1288	
Absorption coefficient	0.461 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.6941 and 0.6042	
Theta range for data collection	2.208 to 27.135°	
Reflections collected	52537	
Independent reflections	6820 [R(int) = 0.0742]	
Data / restraints / parameters	6820 / 0 / 364	
$wR(F^2$ all data)	$wR2$ = 0.1013	
R(F obsd data)	$R1$ = 0.0342	
Goodness-of-fit on F^2	1.003	
Observed data [I > 2□(I)]	5132	
Largest and mean shift / s.u.	0.001 and 0.000	
Largest diff. peak and hole	0.446 and -0.686 e/$Å^3$	

$wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$

$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

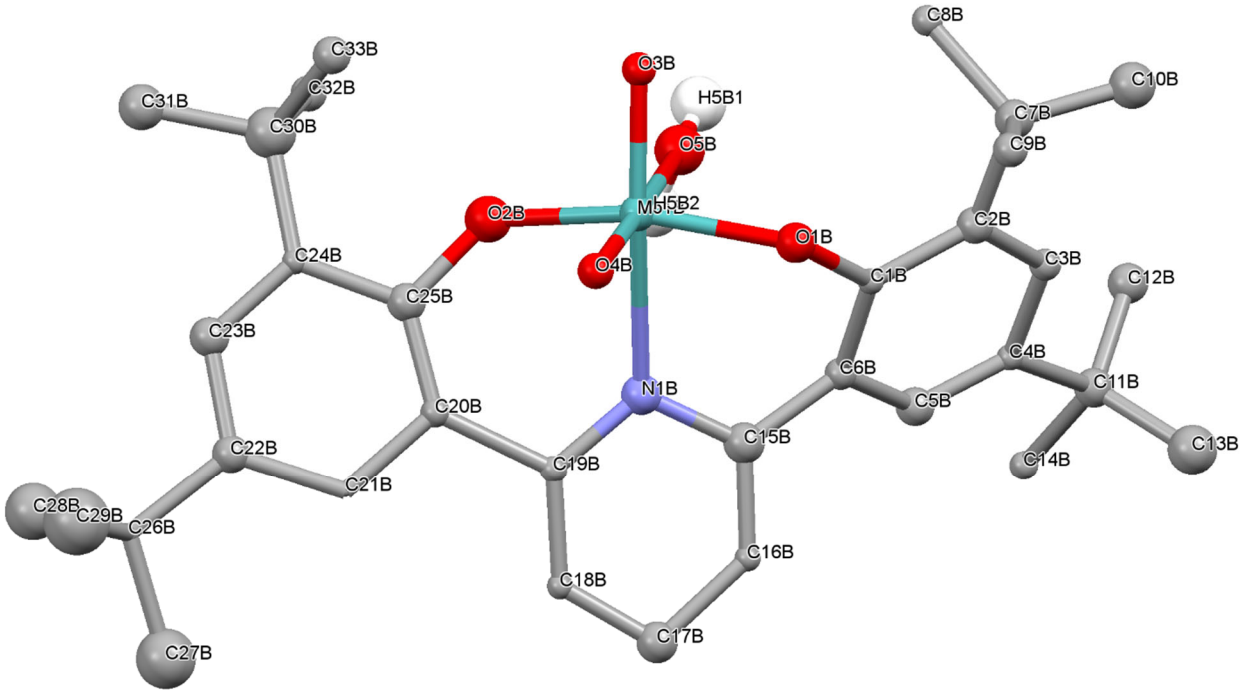


Figure S18. X-Ray structure of hydrated complex. Figure is provided to demonstrate atom connectivity.

Acknowledgements

The authors thank the National Science Foundation (grant CHE-0130835) and the University of Oklahoma for funds to purchase of the X-ray instrument and computers. This structure was determined by Douglas R. Powell.

VIII. References

(1) Fu, R.; Bercaw, J. E.; Labinger, J. A. Intra- and Intermolecular C–H Activation by Bis(Phenolate)Pyridineiridium(III) Complexes. *Organometallics* **2011**, *30* (24), 6751–6765. https://doi.org/10.1021/om201069k.

(2) Navarro, C. A.; John, A. Deoxydehydration Using a Commercial Catalyst and Readily Available Reductant. *Inorganic Chemistry Communications* **2019**, *99*, 145–148. https://doi.org/10.1016/j.inoche.2018.11.015.

(3) Dethlefsen, J. R.; Lupp, D.; Teshome, A.; Nielsen, L. B.; Fristrup, P. Molybdenum-Catalyzed Conversion of Diols and Biomass-Derived Polyols to Alkenes Using Isopropyl Alcohol as Reductant and Solvent. *ACS Catalysis* **2015**, 3638–3647. https://doi.org/10.1021/acscatal.5b00427.

(4) (a) Data Collection: APEX2 (2007) Bruker AXS Inc., Madison, Wisconsin, USA. (b) Data Reduction: SAINT (2007) Bruker AXS Inc., Madison, Wisconsin, USA.

(5) L. Krause, R. Herbst-Irmer, G. M. Sheldrick, and D. Stalke (2015). *J. Appl. Cryst., 48*, 3-10.

(6) (a) G. M. Sheldrick (2015). *Acta Cryst., A71*, 3-8. (b) G. M. Sheldrick (2015). *Acta Cryst., C71*, 3-8.

(7) S. Parsons, H. D. Flack, and T. Wagner (2013). *Acta Cryst., B69*, 249-259.