Isolation of a Bis(imino)pyridine Molybdenum(I) Iodide Complex through Controlled Reduction and Interconversion of its Reaction Products

Electronic Supplementary Information

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Table S1. Crystallographic Data for (κ^6-*P*,*N*,*N*,*N*,*C*,*P*-^{Ph2PPr}PDI)MoI (**5**), (^{Ph2PPr}PDI)MoI (**6**), and (^{Ph2PPr}PDI)MoH_2 (**7**).

	5	**6**	**7**
chemical formula	$C_{39}H_{40}IMoN_3P_2$, $C_{3.995}H_{9.990}O$	$C_{39}H_{41}IMoN_3P_2$	$C_{39}H_{41}MoN_3P_2$
formula weight	909.64	836.53	709.63
crystal dimensions	0.34 x 0.30 x 0.25	0.305 x 0.203 x 0.048	0.200 x 0.170 x 0.130
crystal system	orthorhombic	tetragonal	triclinic
space group	P 21 21 21	P 43 21 2	P -1
a (Å)	10.9610(4)	10.343(3)	8.0248(3)
b (Å)	11.7192(3)	10.343(3)	10.4080(5)
c (Å)	32.6884(10)	33.282(10)	19.9821(9)
α (deg)	90	90	88.4317(7)
β (deg)	90	90	89.3949(7)
γ (deg)	90	90	89.6286(7)
V ($Å^3$)	4199.0(2)	3560.(2)	1668.20(13)
Z	4	4	2
T (°C)	100.(2)	123.(2)	123.(2)
ρcalcd (g cm^{-3})	1.439	1.561	1.413
μ (mm^{-1})	1.159	1.357	0.522
reflections collected	38146	28748	15238
data/restraints/parameters	7978/1/446	3312/0/211	6781/0/408
R_1 [I > 2σ(I)]	0.0401	0.0579	0.0332
wR_2 (all data)	0.1118	0.1572	0.0829
Goodness-of-fit	1.047	1.134	1.066
Largest peak, hole (e$Å^{-3}$)	1.295, -1.023	1.943, -1.622	0.882, -0.465

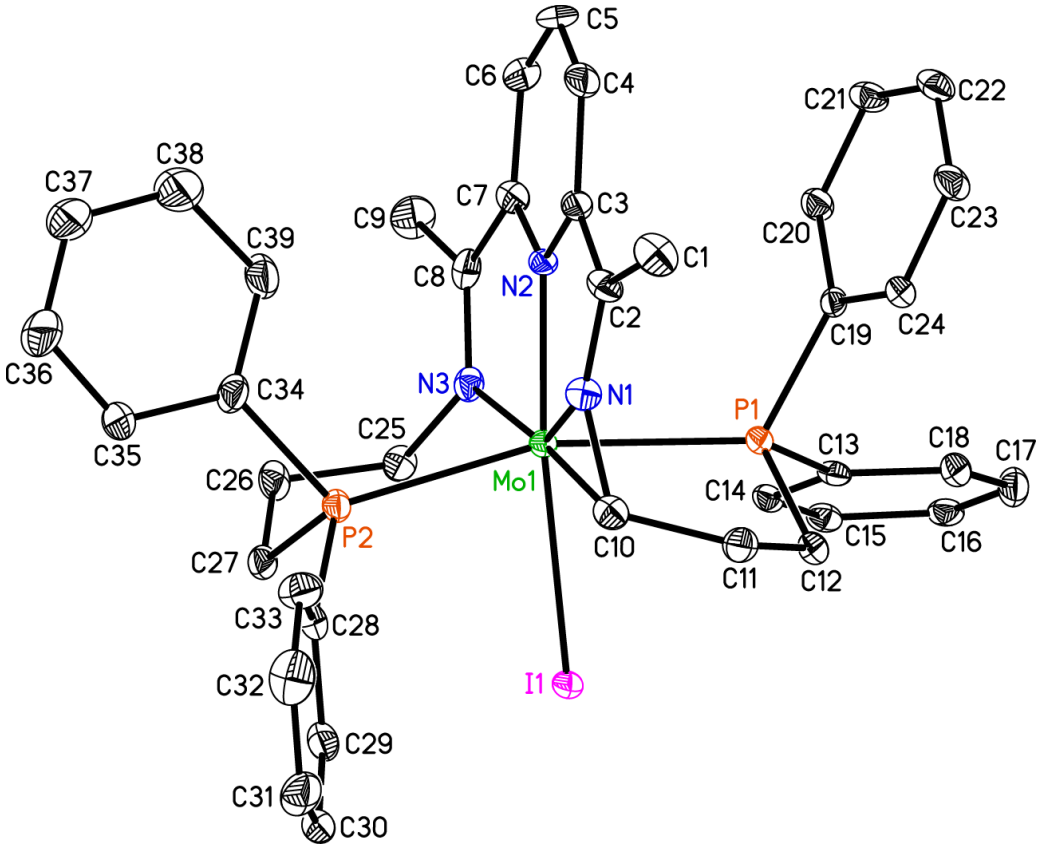

Figure S1. The molecular structure of **5** shown at 30% probability ellipsoids. Hydrogen atoms and co-crystallized ether are omitted for clarity.

Table S2. Metrical parameters for **5**.

I1-Mo1	2.8954(8)	C1-C2	1.491(12)	C21-C22	1.387(13)
Mo1-N1	1.952(7)	C2-C3	1.412(13)	C22-C23	1.387(12)
Mo1-N2	2.055(6)	C3-C4	1.418(12)	C23-C24	1.404(12)
Mo1-N3	2.141(7)	C4-C5	1.398(14)	C25-C26	1.527(11)
Mo1-C10	2.257(8)	C5-C6	1.380(14)	C26-C27	1.501(12)
Mo1-P1	2.471(2)	C6-C7	1.391(13)	C28-C33	1.380(12)
Mo1-P2	2.488(2)	C7-C8	1.408(13)	C28-C29	1.400(12)
P1-C13	1.822(8)	C8-C9	1.492(12)	C29-C30	1.387(12)
P1-C12	1.825(9)	C10-C11	1.523(11)	C30-C31	1.369(14)
P1-C19	1.834(8)	C11-C12	1.527(11)	C31-C32	1.362(16)
P2-C34	1.822(8)	C13-C18	1.381(11)	C32-C33	1.389(14)
P2-C28	1.835(9)	C13-C14	1.413(11)	C34-C39	1.367(14)
P2-C27	1.842(8)	C14-C15	1.381(11)	C34-C35	1.388(12)
N1-C2	1.322(11)	C15-C16	1.379(11)	C35-C36	1.388(13)
N1-C10	1.386(11)	C16-C17	1.396(12)	C36-C37	1.326(17)
N2-C7	1.386(11)	C17-C18	1.377(12)	C37-C38	1.364(16)
N2-C3	1.394(10)	C19-C24	1.387(11)	C38-C39	1.400(15)
N3-C8	1.328(12)	C19-C20	1.388(11)		
N3-C25	1.490(11)	C20-C21	1.384(11)		

N1-Mo1-N2	72.3(3)	C34-P2-C27	101.8(4)	C7-C8-C9	121.5(9)
N1-Mo1-N3	143.5(3)	C28-P2-C27	104.5(4)	N1-C10-C11	117.6(7)
N2-Mo1-N3	72.6(3)	C34-P2-Mo1	117.8(3)	N1-C10-Mo1	59.2(4)
N1-Mo1-C10	37.6(3)	C28-P2-Mo1	117.6(3)	C11-C10-Mo1	121.5(5)
N2-Mo1-C10	109.2(3)	C27-P2-Mo1	111.8(3)	C10-C11-C12	114.7(7)
N3-Mo1-C10	176.4(3)	C2-N1-C10	144.8(8)	C11-C12-P1	111.3(6)
N1-Mo1-P1	83.5(2)	C2-N1-Mo1	127.9(6)	C18-C13-C14	118.0(7)
N2-Mo1-P1	89.26(18)	C10-N1-Mo1	83.3(5)	C18-C13-P1	121.6(6)
N3-Mo1-P1	105.66(18)	C7-N2-C3	120.6(7)	C14-C13-P1	120.3(6)
C10-Mo1-P1	77.6(2)	C7-N2-Mo1	121.0(5)	C15-C14-C13	120.5(7)
N1-Mo1-P2	97.4(2)	C3-N2-Mo1	118.4(5)	C16-C15-C14	119.7(8)
N2-Mo1-P2	106.22(18)	C8-N3-C25	117.4(7)	C15-C16-C17	120.9(7)
N3-Mo1-P2	83.12(18)	C8-N3-Mo1	119.0(6)	C18-C17-C16	118.5(8)
C10-Mo1-P2	93.4(2)	C25-N3-Mo1	122.6(5)	C17-C18-C13	122.3(8)
P1-Mo1-P2	164.06(7)	N1-C2-C3	108.4(7)	C24-C19-C20	119.9(7)
N1-Mo1-I1	123.3(2)	N1-C2-C1	125.5(8)	C24-C19-P1	122.1(6)
N2-Mo1-I1	161.34(18)	C3-C2-C1	126.0(8)	C20-C19-P1	117.9(6)
N3-Mo1-I1	93.15(18)	N2-C3-C2	112.5(7)	C21-C20-C19	120.9(8)
C10-Mo1-I1	85.7(2)	N2-C3-C4	119.5(8)	C20-C21-C22	119.9(8)
P1-Mo1-I1	82.96(5)	C2-C3-C4	128.0(8)	C21-C22-C23	119.5(7)
P2-Mo1-I1	83.29(5)	C5-C4-C3	118.8(9)	C22-C23-C24	120.8(7)
C13-P1-C12	106.3(4)	C6-C5-C4	120.9(8)	C19-C24-C23	119.0(7)
C13-P1-C19	100.4(3)	C5-C6-C7	120.2(9)	N3-C25-C26	111.0(6)
C12-P1-C19	104.4(4)	N2-C7-C6	119.9(8)	C27-C26-C25	115.5(7)
C13-P1-Mo1	124.9(3)	N2-C7-C8	112.0(8)	C26-C27-P2	112.9(6)
C12-P1-Mo1	103.4(3)	C6-C7-C8	127.9(8)	C33-C28-C29	118.6(8)
C19-P1-Mo1	115.7(2)	N3-C8-C7	114.7(7)	C33-C28-P2	119.6(7)
C34-P2-C28	101.2(4)	N3-C8-C9	123.7(9)	C29-C28-P2	121.4(7)

C30-C29-C28	119.8(8)	C39-C34-C35	116.7(8)	C36-C37-C38	118.0(10)
C31-C30-C29	120.5(9)	C39-C34-P2	121.0(7)	C37-C38-C39	121.3(11)
C32-C31-C30	120.1(9)	C35-C34-P2	122.2(7)	C34-C39-C38	120.8(10)
C31-C32-C33	120.3(10)	C36-C35-C34	120.7(10)		
C28-C33-C32	120.6(9)	C37-C36-C35	122.3(10)		

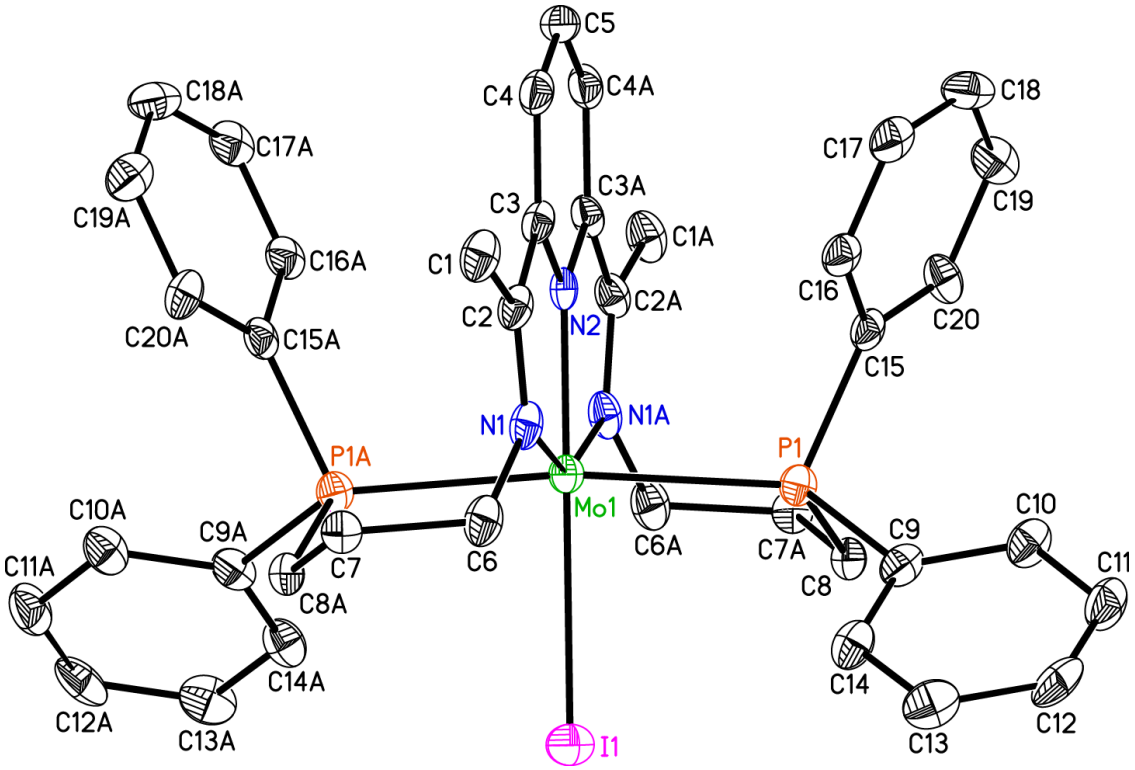

Figure S2. The molecular structure of **6** displayed at 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

Table S3. Metrical parameters for **6**.

I1-Mo1	2.8993(18)	C1-C2	1.526(15)	C12-C13	1.37(2)
Mo1-N2	1.984(11)	C2-C3	1.436(16)	C13-C14	1.405(16)
Mo1-N1	2.122(9)	C3-C4	1.390(15)	C15-C20	1.387(16)
Mo1-P1	2.488(3)	C4-C5	1.379(14)	C15-C16	1.406(16)
P1-C15	1.828(12)	C6-C7	1.523(15)	C16-C17	1.354(17)
P1-C8	1.830(11)	C7A-C8	1.539(14)	C17-C18	1.372(19)
P1-C9	1.837(11)	C9-C14	1.373(17)	C18-C19	1.380(19)
N1-C2	1.305(15)	C9-C10	1.383(16)	C19-C20	1.392(17)
N1-C6	1.466(16)	C10-C11	1.389(16)		
N2-C3	1.407(12)	C11-C12	1.361(19)		

N2-Mo1-N1	74.2(3)	C2-N1-Mo1	118.4(8)	C14-C9-P1	120.2(9)
N1-Mo1-N1A	148.4(6)	C6-N1-Mo1	120.2(8)	C10-C9-P1	121.1(9)
N1-Mo1-P1A	77.2(2)	C3-N2-C3A	115.9(12)	C9-C10-C11	120.5(12)
N2-Mo1-P1	93.62(7)	C3-N2-Mo1	122.0(6)	C12-C11-C10	120.8(12)
N1-Mo1-P1	104.9(2)	N1-C2-C3	115.2(10)	C11-C12-C13	119.6(11)
P1-Mo1-P1A	172.76(15)	N1-C2-C1	125.4(11)	C12-C13-C14	120.0(13)
N2-Mo1-I1	180.00(6)	C3-C2-C1	119.4(10)	C9-C14-C13	120.5(11)
N1-Mo1-I1	105.8(3)	C4-C3-N2	121.8(10)	C20-C15-C16	117.5(11)
P1-Mo1-I1	86.38(7)	C4-C3-C2	128.1(10)	C20 -C15-P1	125.9(9)
C15-P1-C8	106.3(5)	N2-C3-C2	110.1(9)	C16-C15-P1	116.5(9)
C15-P1-C9	99.9(5)	C5-C4-C3	120.8(11)	C17-C16-C15	120.8(12)
C8-P1-C9	100.0(5)	C4-C5-C4A	118.9(14)	C16-C17-C18	121.5(12)
C15-P1-Mo1	111.3(3)	N1-C6-C7	111.9(9)	C17-C18-C19	119.5(12)
C8-P1-Mo1	110.7(3)	C6-C7-C8A	113.3(9)	C18-C19-C20	119.5(12)
C9-P1-Mo1	126.6(4)	C7A-C8-P1	118.6(8)	C15-C20-C19	121.2(12)
C2-N1-C6	119.9(10)	C14-C9-C10	118.6(10)		

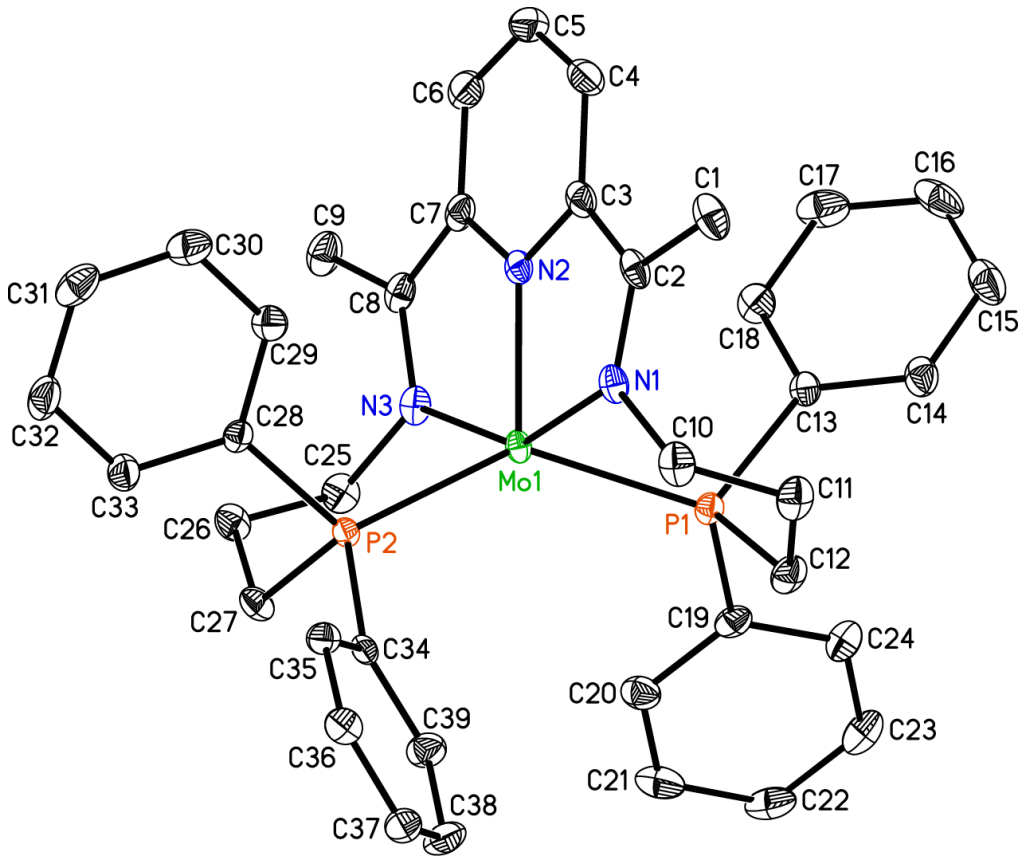

Figure S3. The molecular structure of **7** displayed at 30% probability ellipsoids. Hydrogen atoms omitted for clarity (Note: the dihydrogen ligand of **7** was not located in the difference map).

Table S4. Metrical parameters for **7**.

Mo1-N2	2.056(2)	C2-C3	1.416(4)	C21-C22	1.376(4)
Mo1-N3	2.098(2)	C3-C4	1.405(4)	C22-C23	1.387(4)
Mo1-N1	2.098(2)	C4-C5	1.387(4)	C23-C24	1.394(4)
Mo1-P2	2.4103(6)	C5-C6	1.368(4)	C25-C26	1.529(4)
Mo1-P1	2.4123(6)	C6-C7	1.408(4)	C26-C27	1.530(3)
P1-C13	1.837(2)	C7-C8	1.407(4)	C28-C29	1.379(3)
P1-C19	1.844(3)	C8-C9	1.507(3)	C28-C33	1.400(3)
P1-C12	1.848(2)	C10-C11	1.526(4)	C29-C30	1.400(4)
P2-C28	1.835(2)	C11-C12	1.531(4)	C30-C31	1.378(4)
P2-C34	1.841(2)	C13-C18	1.386(4)	C31-C32	1.382(4)
P2-C27	1.842(2)	C13-C14	1.394(4)	C32-C33	1.379(4)
N1-C2	1.345(3)	C14-C15	1.380(4)	C34-C35	1.383(3)
N1-C10	1.470(3)	C15-C16	1.365(5)	C34-C39	1.392(3)
N2-C3	1.394(3)	C16-C17	1.390(5)	C35-C36	1.398(3)
N2-C7	1.400(3)	C17-C18	1.397(4)	C36-C37	1.373(4)
N3-C8	1.349(3)	C19-C24	1.397(4)	C37-C38	1.380(4)
N3-C25	1.481(3)	C19-C20	1.404(4)	C38-C39	1.396(4)
C1-C2	1.505(3)	C20-C21	1.392(4)		

N2-Mo1-N3	73.86(8)	C8-N3-C25	117.2(2)	C13-C18-C17	120.5(3)
N2-Mo1-N1	73.41(8)	C8-N3-Mo1	119.47(17)	C24-C19-C20	118.2(2)
N3-Mo1-N1	147.13(8)	C25-N3-Mo1	122.38(16)	C24-C19-P1	121.4(2)
N2-Mo1-P2	115.81(5)	N1-C2-C3	114.2(2)	C20-C19-P1	120.43(19)
N3-Mo1-P2	87.19(6)	N1-C2-C1	123.7(2)	C21-C20-C19	120.5(3)
N1-Mo1-P2	104.39(5)	C3-C2-C1	122.1(2)	C22-C21-C20	120.6(3)
N2-Mo1-P1	105.77(5)	N2-C3-C4	120.2(2)	C21-C22-C23	119.8(3)
N3-Mo1-P1	109.54(6)	N2-C3-C2	111.7(2)	C22-C23-C24	120.1(3)
N1-Mo1-P1	82.36(6)	C4-C3-C2	128.2(2)	C23-C24-C19	120.8(3)
P2-Mo1-P1	138.15(2)	C5-C4-C3	119.7(3)	N3-C25-C26	111.3(2)
C13-P1-C19	103.16(11)	C6-C5-C4	120.7(3)	C25-C26-C27	114.1(2)
C13-P1-C12	103.70(12)	C5-C6-C7	120.2(3)	C26-C27-P2	112.04(17)
C19-P1-C12	100.32(12)	N2-C7-C8	112.3(2)	C29-C28-C33	118.6(2)
C13-P1-Mo1	114.25(8)	N2-C7-C6	119.9(2)	C29-C28-P2	118.89(18)
C19-P1-Mo1	123.61(9)	C8-C7-C6	127.8(2)	C33-C28-P2	122.51(19)
C12-P1-Mo1	109.36(9)	N3-C8-C7	114.3(2)	C28-C29-C30	120.4(2)
C28-P2-C34	102.94(11)	N3-C8-C9	123.7(2)	C31-C30-C29	119.9(3)
C28-P2-C27	101.34(12)	C7-C8-C9	122.0(2)	C30-C31-C32	120.3(3)
C34-P2-C27	102.47(11)	N1-C10-C11	111.0(2)	C33-C32-C31	119.6(3)
C28-P2-Mo1	118.86(8)	C10-C11-C12	115.0(2)	C32-C33-C28	121.2(3)
C34-P2-Mo1	118.33(7)	C11-C12-P1	115.07(18)	C35-C34-C39	118.7(2)
C27-P2-Mo1	110.46(8)	C18-C13-C14	118.6(2)	C35-C34-P2	121.60(18)
C2-N1-C10	117.9(2)	C18-C13-P1	117.21(19)	C39-C34-P2	119.67(19)
C2-N1-Mo1	119.77(16)	C14-C13-P1	124.2(2)	C34-C35-C36	120.7(2)
C10-N1-Mo1	121.37(17)	C15-C14-C13	120.9(3)	C37-C36-C35	120.1(2)
C3-N2-C7	119.2(2)	C16-C15-C14	120.4(3)	C36-C37-C38	120.0(2)
C3-N2-Mo1	120.72(16)	C15-C16-C17	120.2(3)	C37-C38-C39	120.0(3)
C7-N2-Mo1	119.96(16)	C16-C17-C18	119.5(3)	C34-C39-C38	120.5(3)

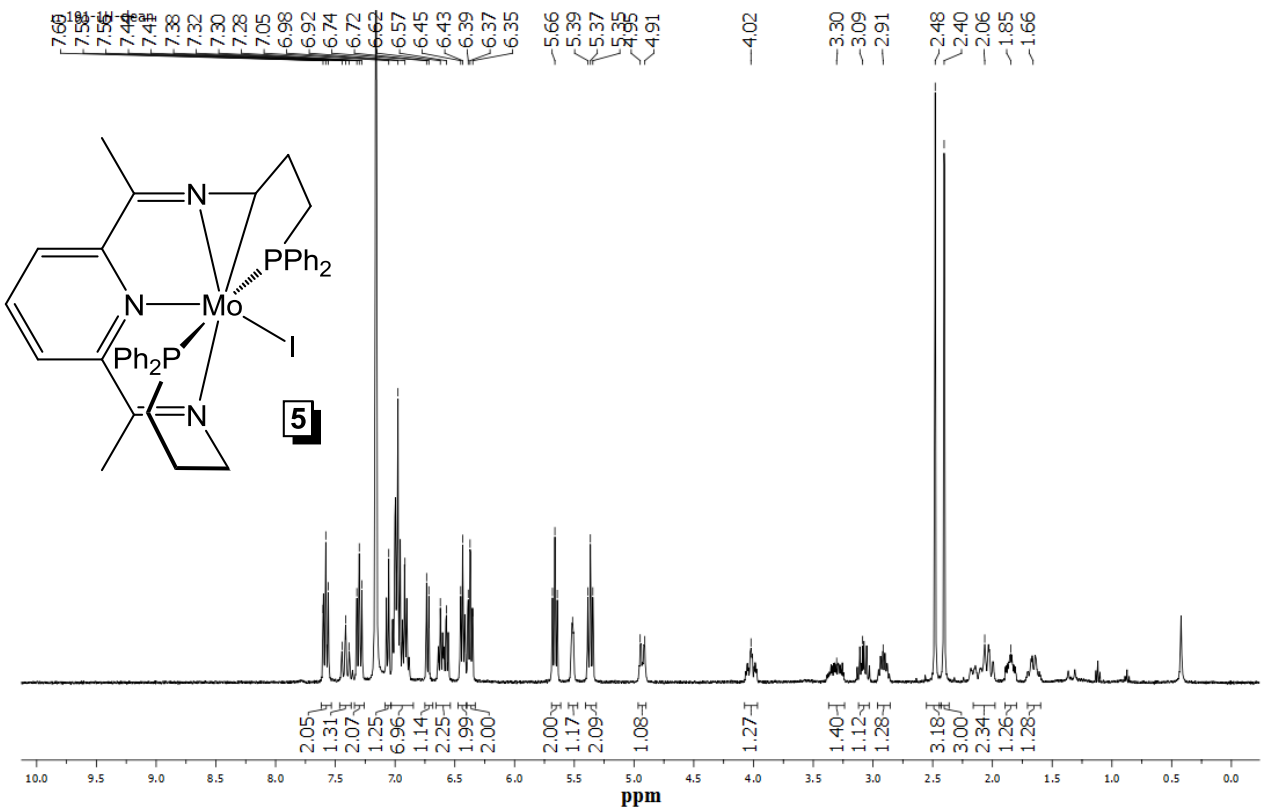

Figure S4. ^{1}H NMR spectrum of (κ^{6}-*P*,*N*,*N*,*N*,*C*,*P*-^{Ph2PPr}PDI)MoI **(5)** in benzene-d_6.

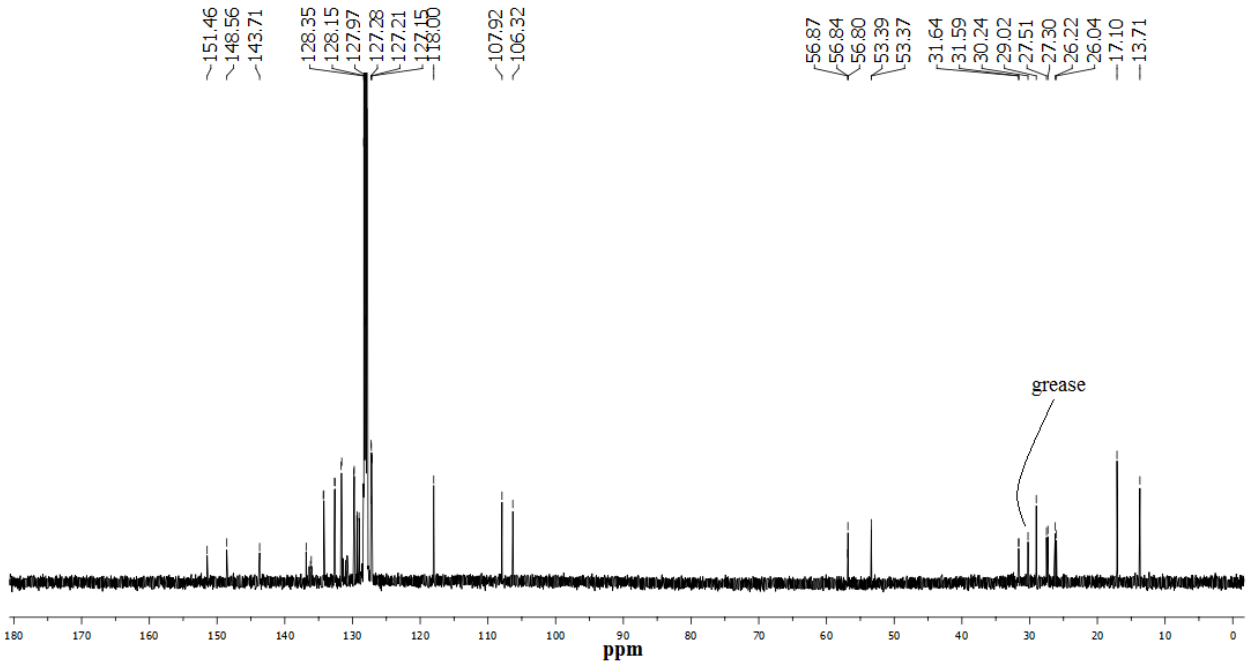

Figure S5. ^{13}C NMR spectrum of (κ^{6}-*P*,*N*,*N*,*N*,*C*,*P*-^{Ph2PPr}PDI)MoI **(5)** in benzene-d_6.

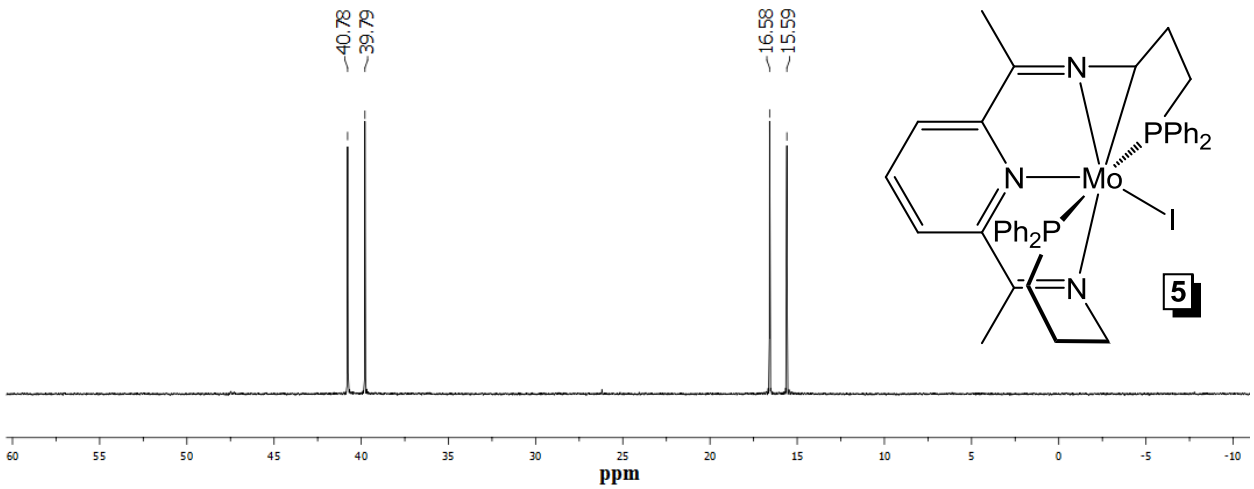

Figure S6. ^{31}P NMR spectrum of (κ^6-*P*,*N*,*N*,*N*,*C*,*P*-^{Ph2PPr}PDI)MoI **(5)** in benzene-d_6.

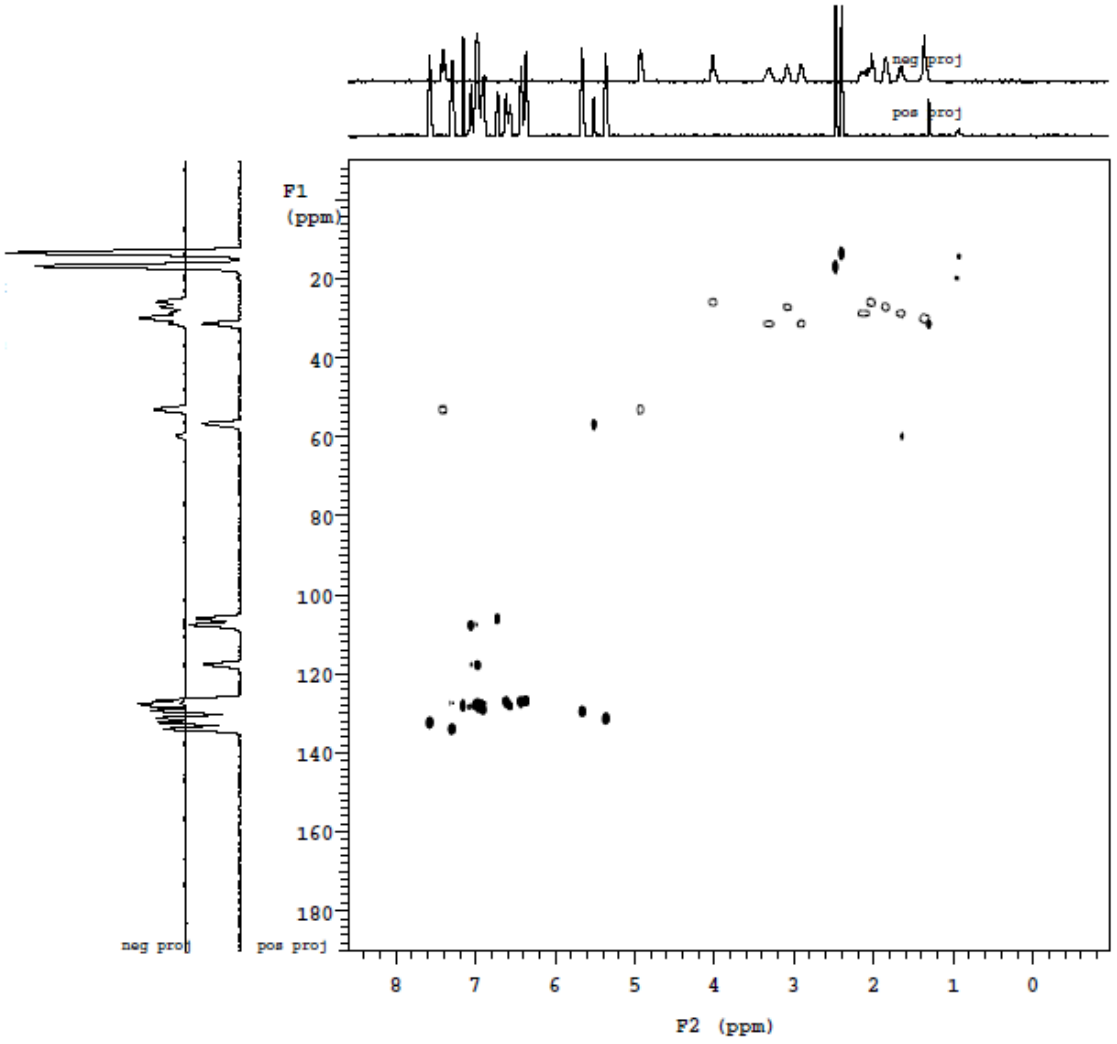

Figure S7. gHSQCAD NMR spectrum of **5** in benzene-d_6.

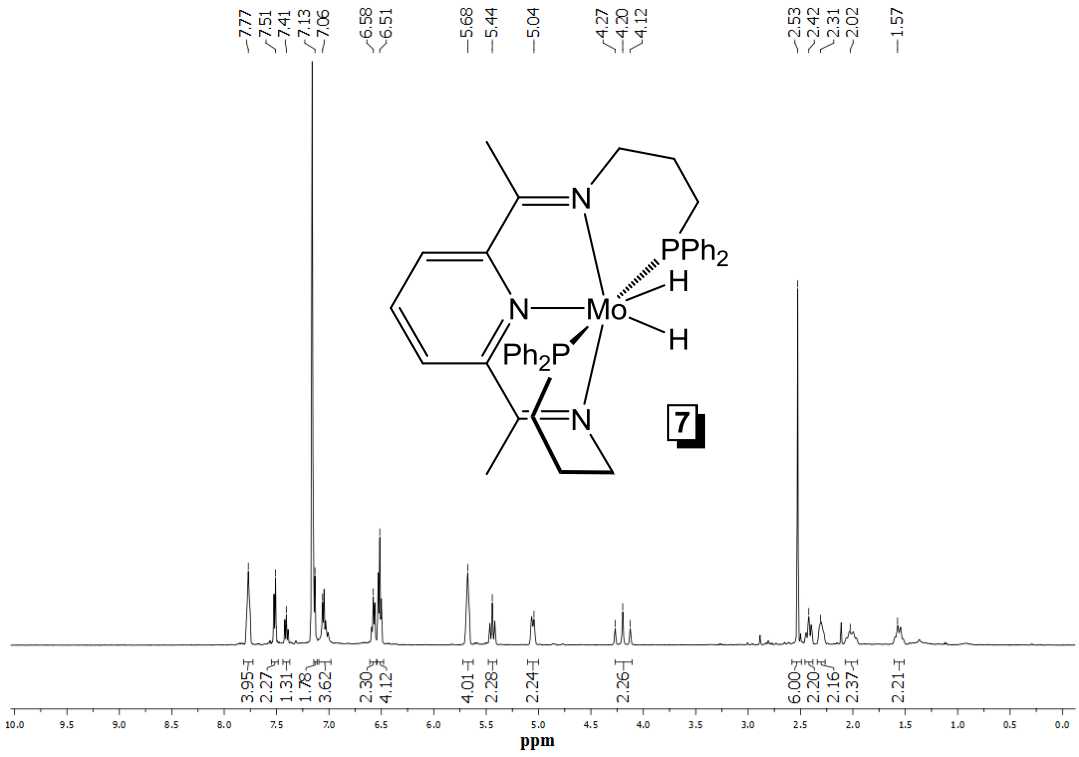

Figure S8. ^{1}H NMR spectrum of (^{Ph2PPr}PDI)MoH$_2$ (**7**) in benzene-d_6.

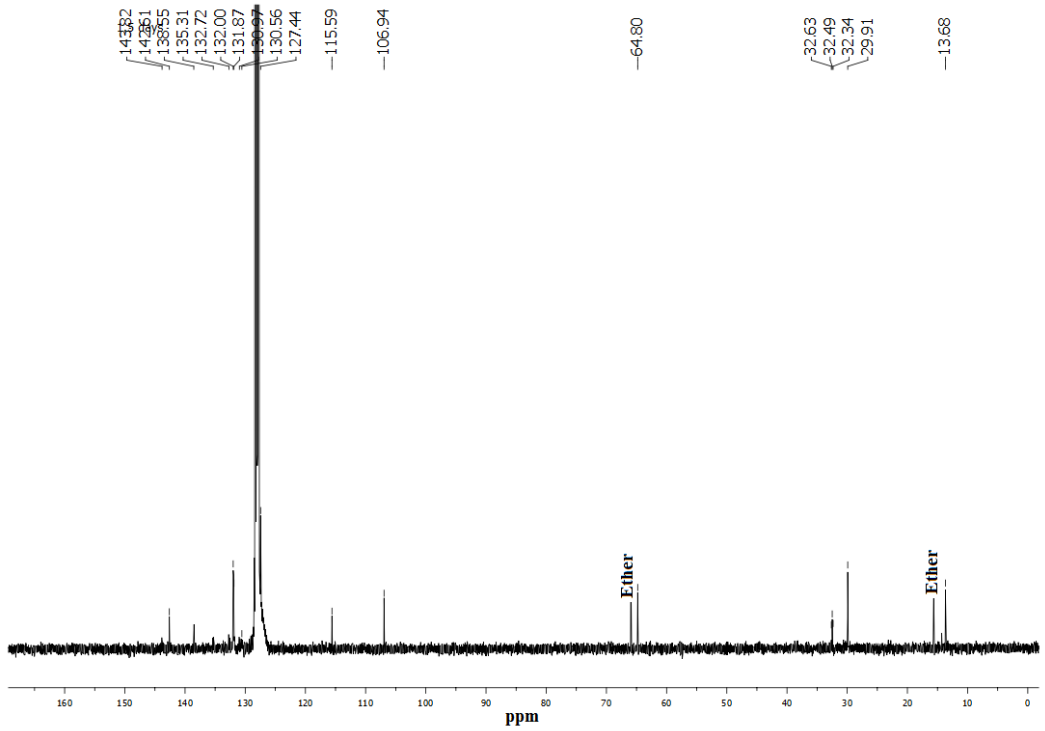

Figure S9. ^{13}C NMR spectrum of (^{Ph2PPr}PDI)MoH$_2$ (**7**) in benzene-d_6.

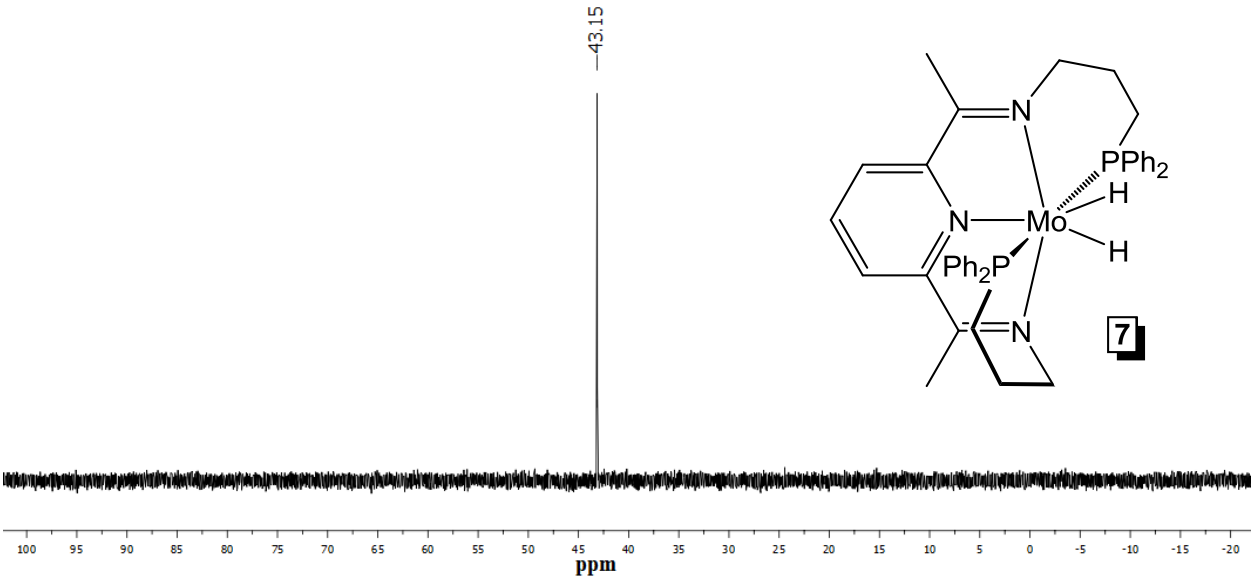

Figure S10. ^{31}P NMR spectrum of (^{Ph2PPr}PDI)MoH$_2$ (**7**) in benzene-d_6.

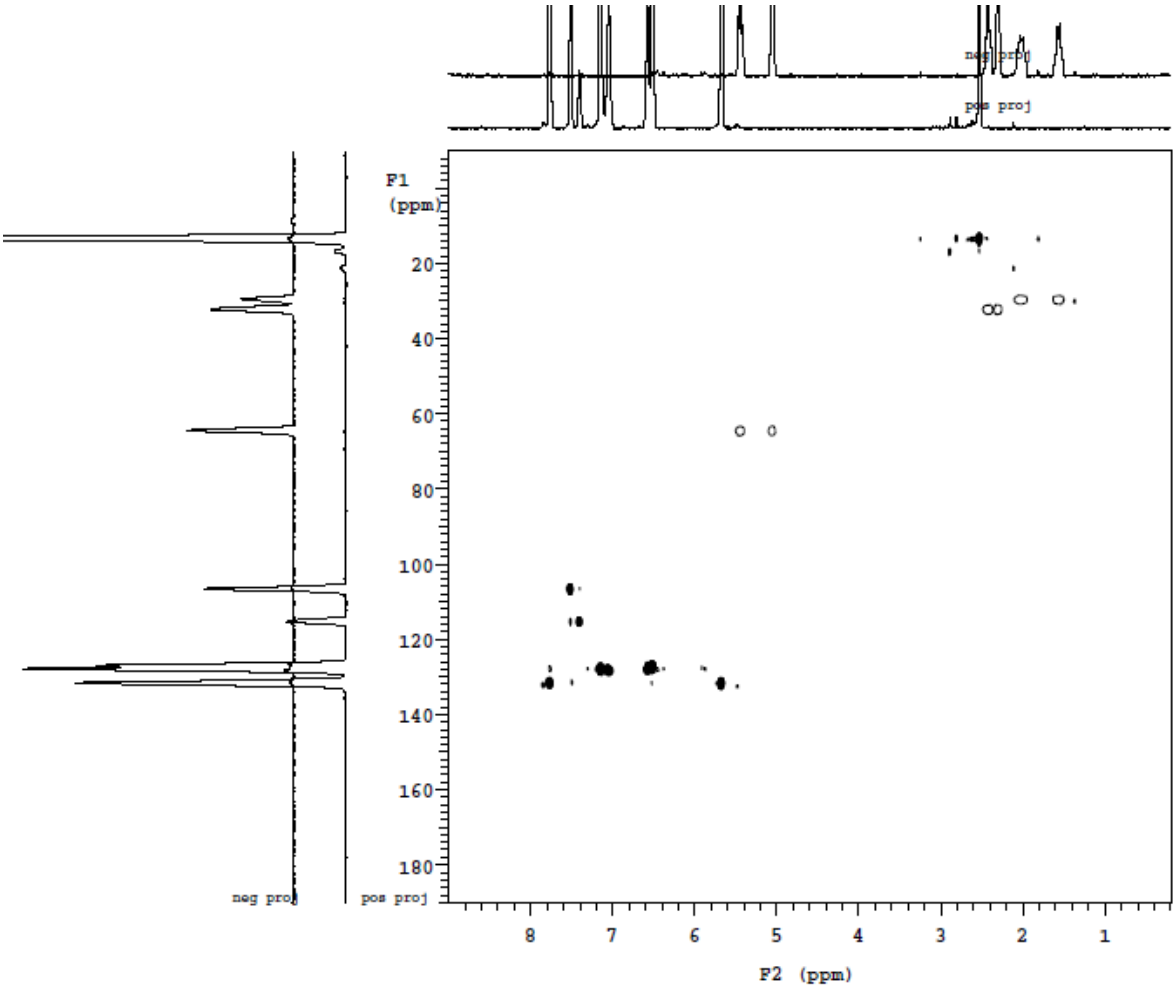

Figure S11. gHSQCAD NMR spectrum of (^{Ph2PPr}PDI)MoH$_2$ (**7**) in benzene-d_6.

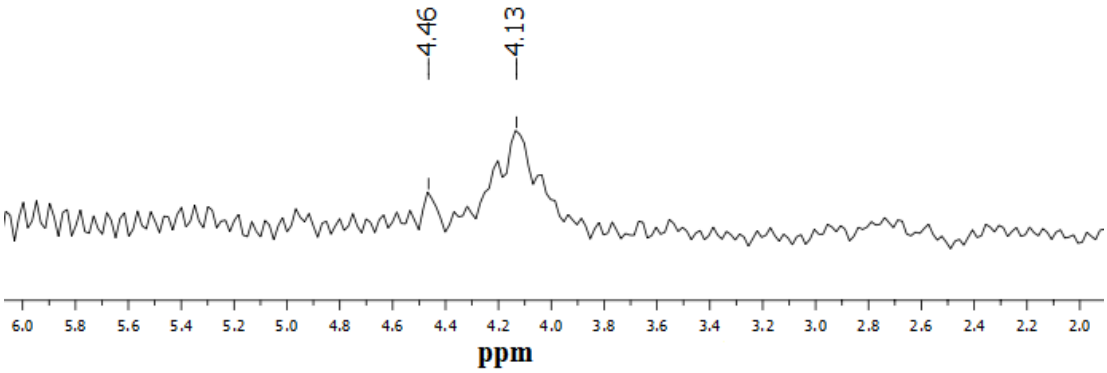

Figure S12. ^{2}H NMR spectrum of **7-*d*$_2$** in benzene-d_6.

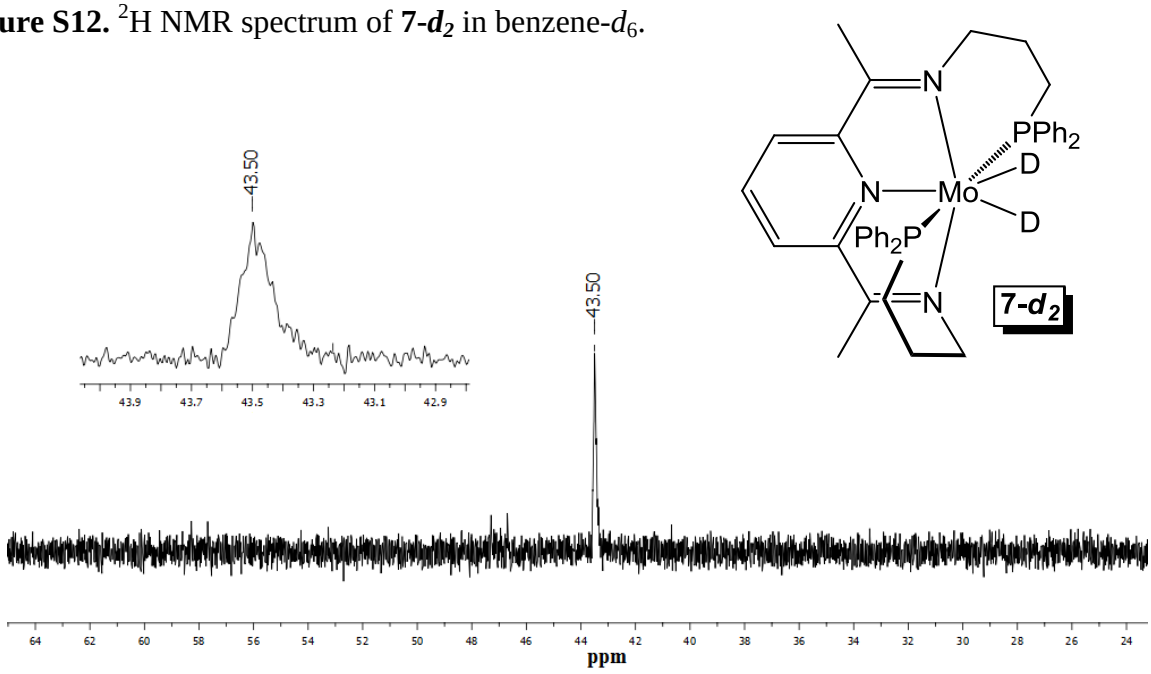

Figure S13. ^{31}P NMR spectrum of **7-*d*$_2$** in benzene-d_6.