Supporting Information

Mono-, Di- and Tri-borylphosphine Analogues of Triarylphosphines

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Table S1. Crystal data

Compound	**I**	**L_1**	**L_2**
Empirical formula	$C_{10}H_8BClN_2$	$C_{22}H_{18}BN_2P$	$C_{26}H_{21}B_2N_4P$
Formula weight	202.44	352.16	442.06
Temperature/K	100(2)	100(2)	100(2)
Crystal system	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$	P-1	$Pca2_1$
a/Å	8.1003(2)	9.1263(8)	13.6850(7)
b/Å	3.79990(10)	10.6800(10)	19.4779(11)
c/Å	29.2151(7)	11.0452(10)	8.0751(5)
α/°	90	113.860(5)	90
β/°	96.5300(10)	102.299(6)	90
γ/°	90	105.052(6)	90
Volume/$Å^3$	893.42(4)	886.98(15)	2152.5(2)
Z	4	2	4
$\rho_{calc}mg/mm^3$	1.505	1.319	1.364
m/mm^{-1}	0.378	0.162	0.151
F(000)	416	368	920
Crystal size/mm^3	0.6 × 0.22 × 0.2	0.35 × 0.26 × 0.13	0.4 × 0.25 × 0.13
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection	2.806 to 55.252°	4.322 to 55.284°	2.09 to 55.062°
Index ranges	$-10 \le h \le 10$, $-4 \le k \le 4$, $-38 \le l \le 38$	$-11 \le h \le 11$, $-13 \le k \le 13$, $-14 \le l \le 14$	$-17 \le h \le 17$, $-25 \le k \le 24$, $-10 \le l \le 10$
Reflections collected	26625	30860	35926
Independent reflections	2069 [R_{int} = 0.0251, R_{sigma} = 0.0101]	4118 [R_{int} = 0.0600, R_{sigma} = 0.0350]	4951 [R_{int} = 0.0849, R_{sigma} = 0.0526]
Data/restraints/parameters	2069/0/135	4118/0/241	4951/5/310
Goodness-of-fit on F^2	1.124	1.014	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0279, wR_2 = 0.0820	R_1 = 0.0371, wR_2 = 0.0850	R_1 = 0.0433, wR_2 = 0.0907
Final R indexes [all data]	R_1 = 0.0296, wR_2 = 0.0834	R_1 = 0.0534, wR_2 = 0.0933	R_1 = 0.0625, wR_2 = 0.0992
Largest diff. peak/hole / e $Å^{-3}$	0.40/-0.20	0.36/-0.27	0.20/-0.30
Flack Parameter	n/a	n/a	-0.01(7)

Compound	**L_3**	**1**
Empirical formula	C30H24B3N6P	$C_{48}H_{36}B_2MoN_4O_4P_2$
Formula weight	531.95	912.31
Temperature/K	100(2)	100(2)
Crystal system	hexagonal	monoclinic
Space group	$P6_3$	$P2_1/n$
a/Å	14.3773(3)	9.87300(10)
b/Å	14.3773(3)	13.0201(2)
c/Å	7.2074(2)	33.2549(5)
α/°	90	90
β/°	90	90.6290(10)
γ/°	120	90
Volume/$Å^3$	1290.22(6)	4274.58(10)
Z	2	4
$\rho_{calc}mg/mm^3$	1.369	1.418
m/mm^{-1}	0.141	0.432
F(000)	552	1864
Crystal size/mm^3	0.49 × 0.27 × 0.25	0.42 × 0.36 × 0.28
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection	3.27 to 55.114°	3.36 to 55.254°
Index ranges	$-18 \le h \le 18$, $-18 \le k \le 18$, $-9 \le l \le 9$	$-12 \le h \le 12$, $-16 \le k \le 16$, $-43 \le l \le 43$
Reflections collected	45115	74957
Independent reflections	1987 [Rint = 0.0255, Rsigma = 0.0077]	9933 [R_{int} = 0.0365, R_{sigma} = 0.0206]
Data/restraints/parameters	1987/3/128	9933/4/562
Goodness-of-fit on F^2	1.058	1.025
Final R indexes [I>=2σ (I)]	R1 = 0.0270, wR2 = 0.0782	R_1 = 0.0243, wR_2 = 0.0583
Final R indexes [all data]	R1 = 0.0276, wR2 = 0.0792	R_1 = 0.0288, wR_2 = 0.0605
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.17	0.39/-0.39
Flack Parameter	-0.03(13)	n/a

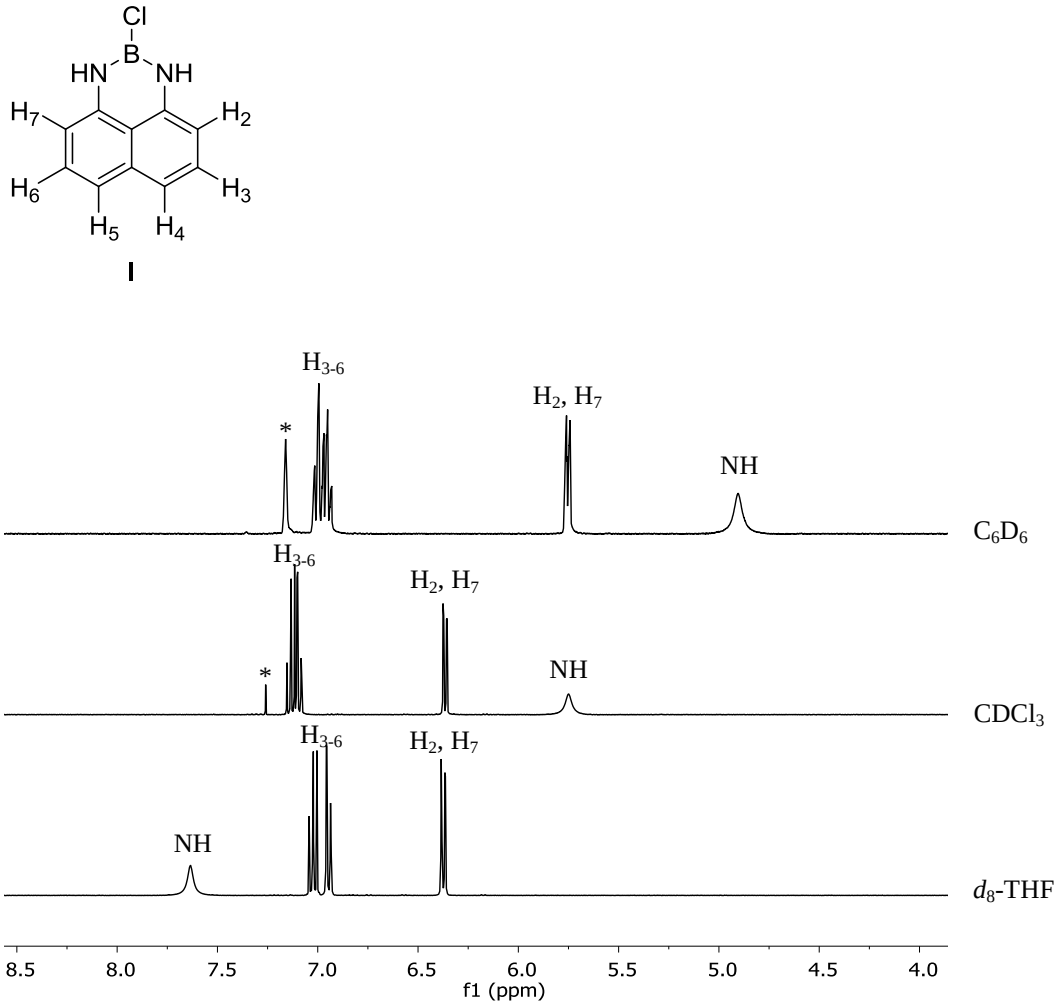

Figure S1. ^{1}H NMR spectra of **I** in different solvents. Top: C_6D_6, Middle: $CDCl_3$, bottom: d_8-THF. *: residual solvent peak.

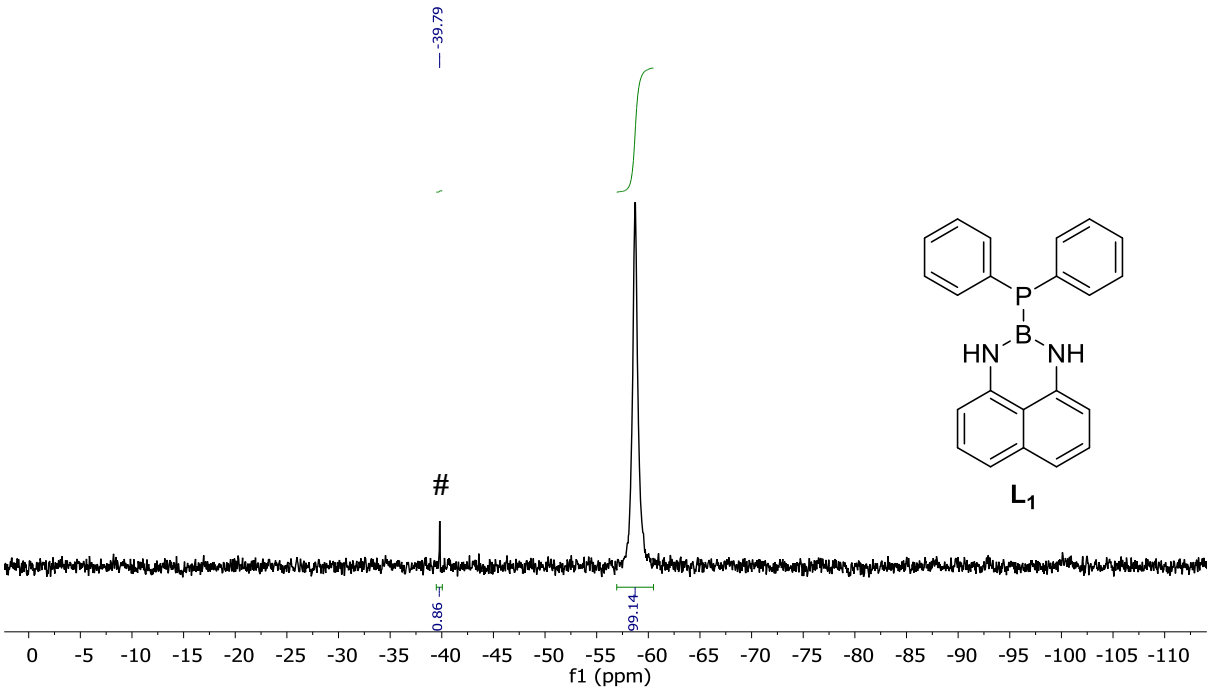

Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum of $\mathbf{L_1}$ in $CDCl_3$. Impurity #: Ph_2PH.

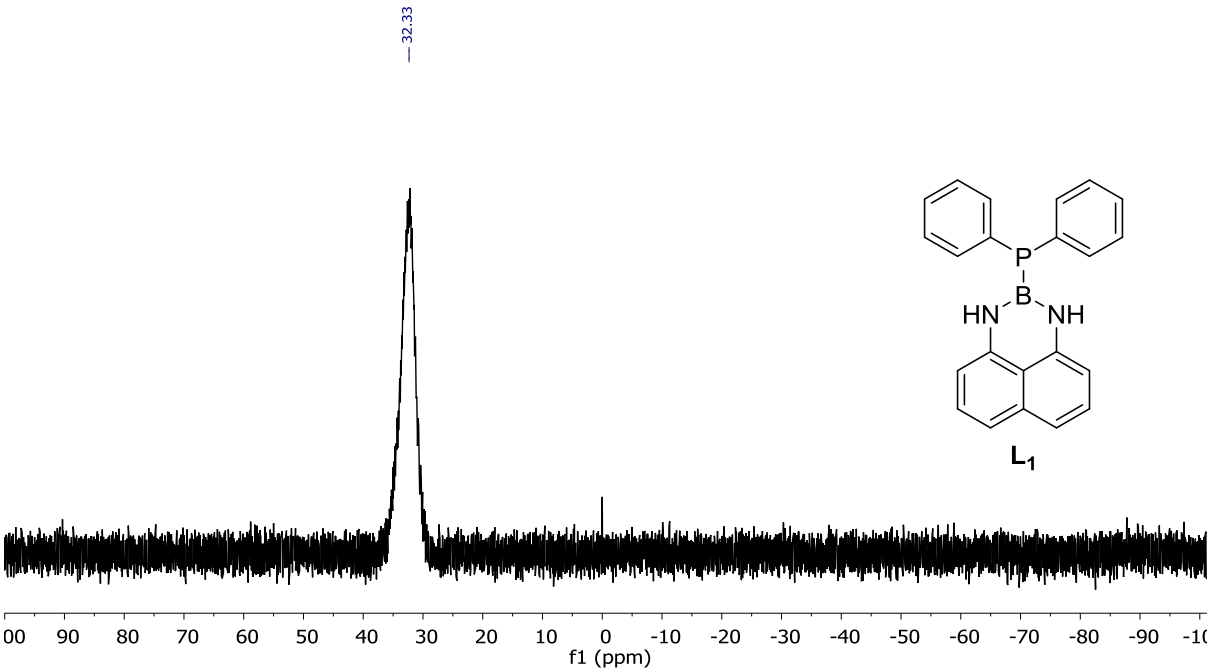

Figure S3. $^{11}B\{^{1}H\}$ NMR spectrum of $\mathbf{L_1}$ in $CDCl_3$.

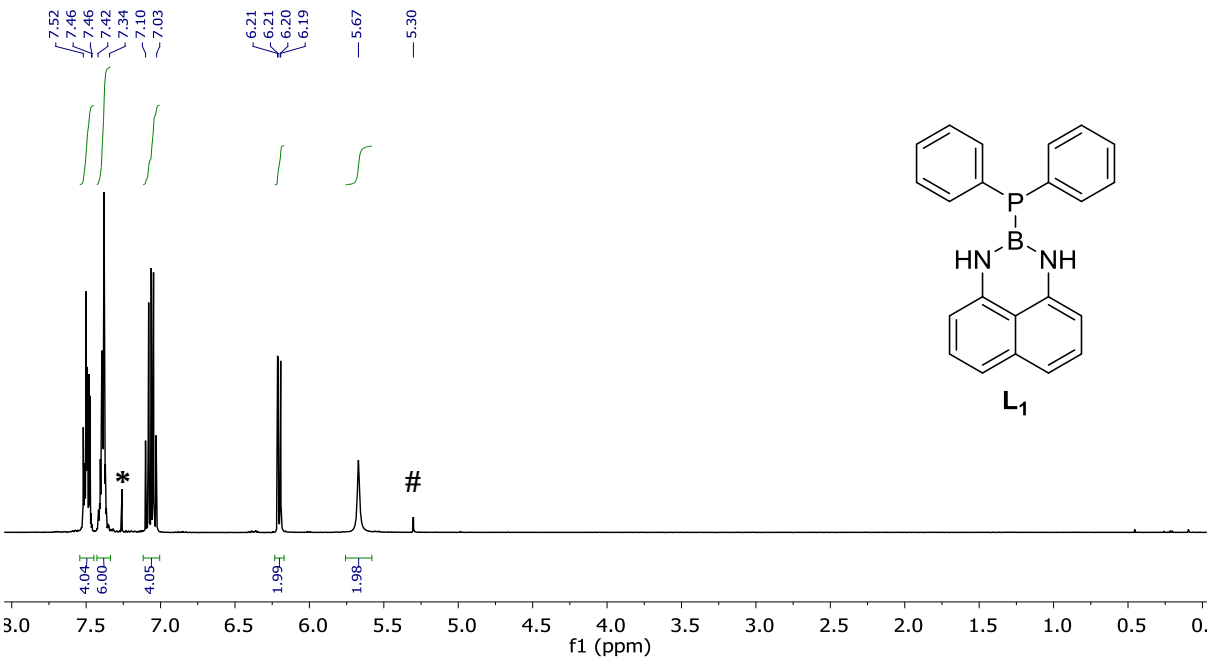

Figure S4. ^{1}H NMR spectrum of $\mathbf{L_1}$ in $CDCl_3$ (*: $CHCl_3$; impurity #: CH_2Cl_2).

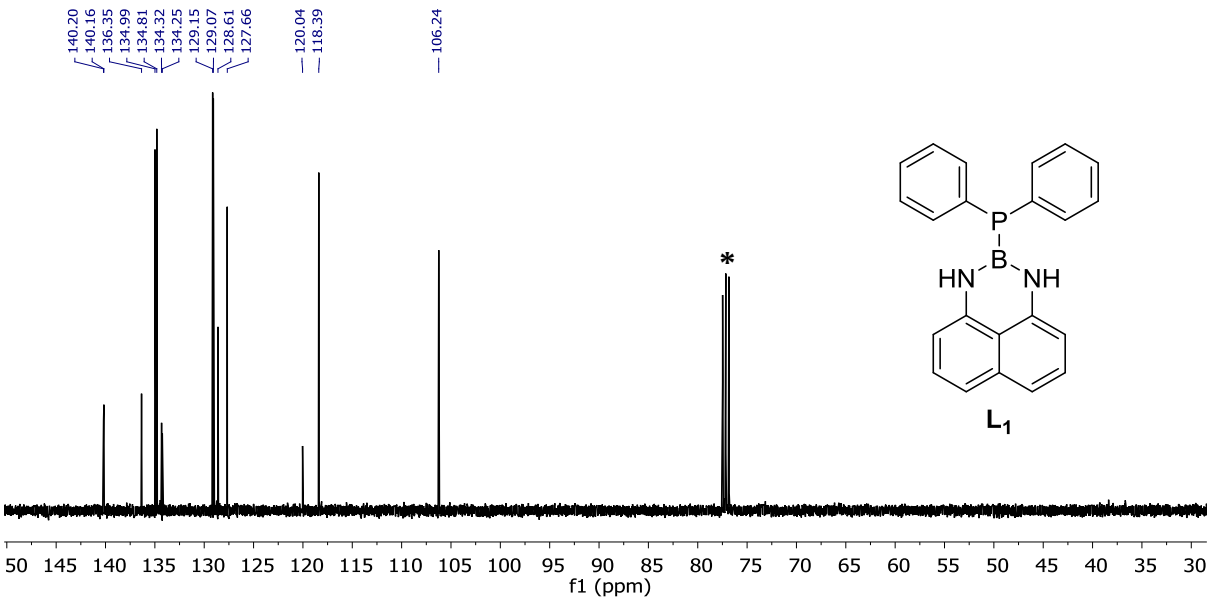

Figure S5. ^{13}C NMR spectrum of $\mathbf{L_1}$ in $CDCl_3$ (*: $CHCl_3$).

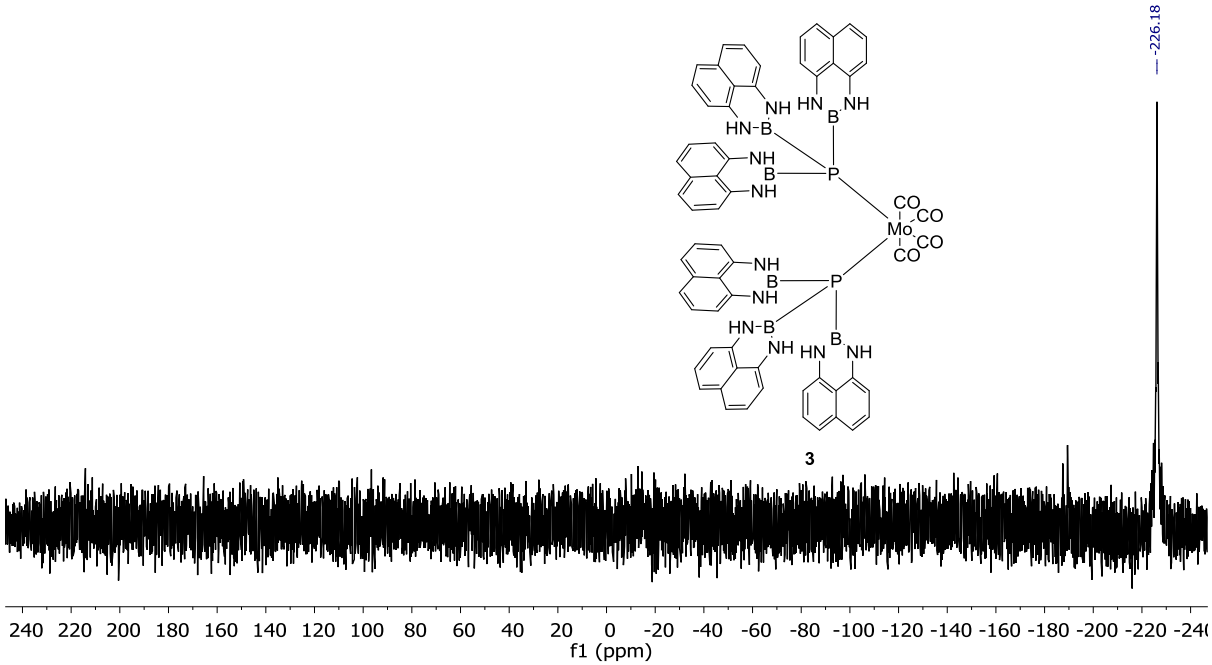

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in C_6D_6.

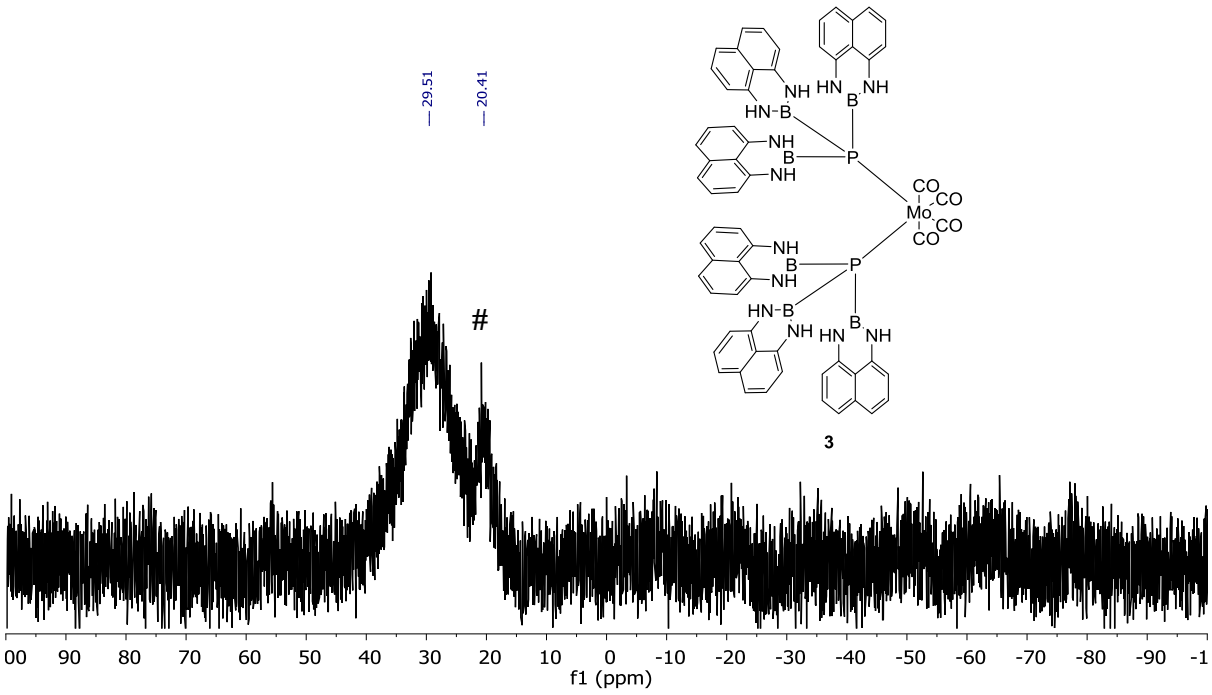

Figure S7. $^{11}B\{^{1}H\}$ NMR spectrum of **3** in C_6D_6. Impurity #: tentatively assigned as B-OH hydrolysis product. The undulations in the baseline are due to baseline correction of a weak sample run in a borosilicate tube.

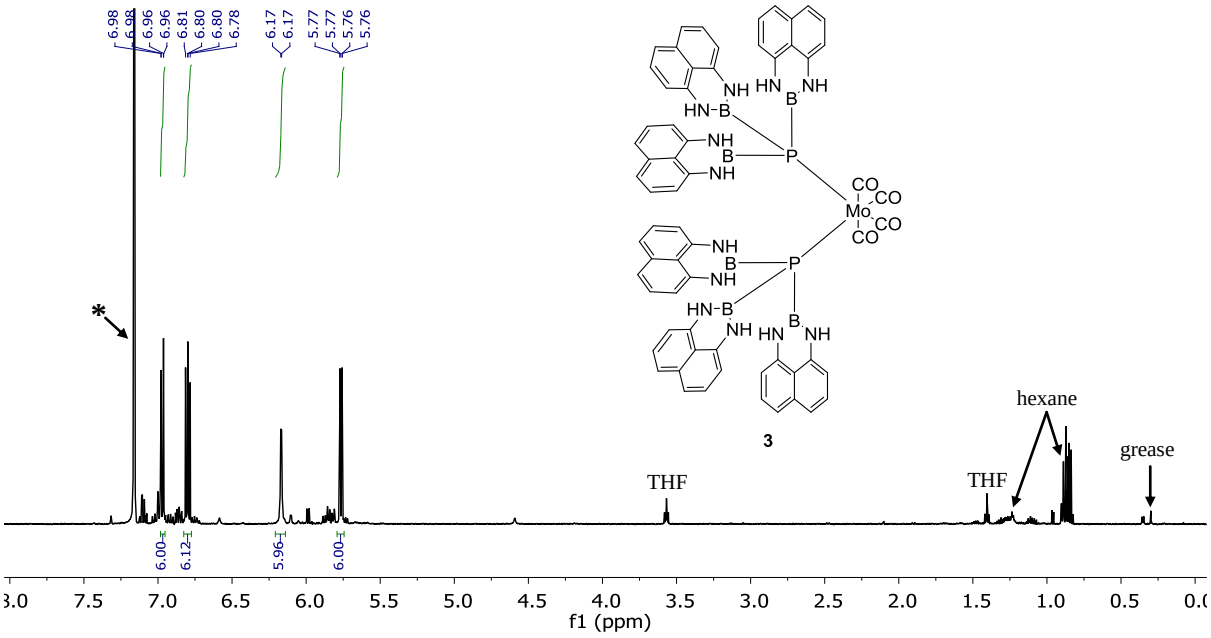

Figure S8. ^{1}H NMR spectrum of **3** in C_6D_6 (*: C_6D_5H).

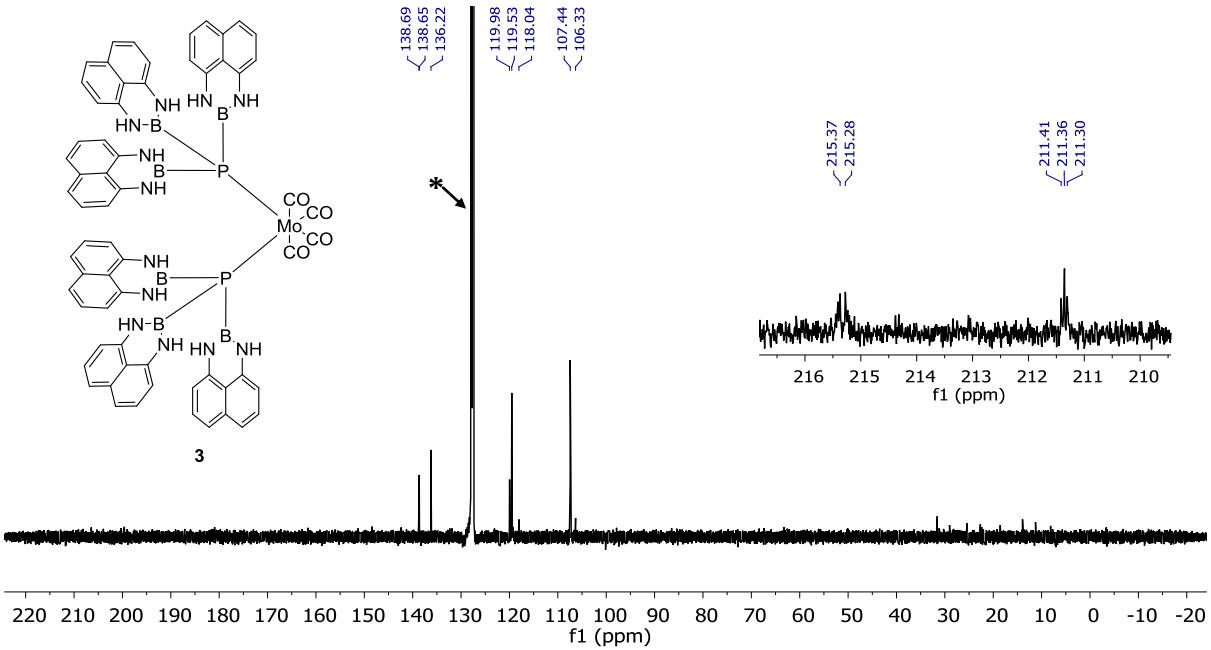

Figure S9. ^{13}C NMR spectrum of **3** in C_6D_6 (*: C_6D_5H).