Supporting information

Reactions of (Mesityl)$_n$(Methyl)$_{2-n}$Silylene Complexes with Pyridine-*N*-oxide (*n* = 1 and 0): Formation of Silanone Complexes and a Disiloxanyloxy Complex

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3. NMR and IR spectra of **7a**, **7b**, **4a**, **8**, **9**, **11a** **11b** and **12** and ^{1}H NMR spectra of $HMe_2SiSiMesMe_2$, the resultant mixtures in the reaction of **7b** with 1 equivalent of pyridine-*N*-oxide (PNO) and in the reaction of **8** with 1 equivalent of PNO

4. References

1.1 General Procedure of X-ray crystal structure determination. The X-ray intensity data was collected on a RIGAKU XtaLAB P200 diffractometer using multi-layer mirror monochromated Mo-Kα radiation at 130 or 120 K. Empirical absorption corrections were applied. The structure was solved by direct and Fourier transform methods using the SHELX-97 systems.[1] All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters based on F^2 with all reflections. All hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters.

1.2 X-ray Crystal Structure Analysis of Cp*(OC)$_2$W{=SiMes(Me)}(SiMe$_3$) (7a) A single crystal suitable for X-ray crystal structure analysis was obtained by recrystallization from hexane solution of **7a**. The final residue *R*1 and the weighted *wR*2 were 0.0256 and 0.0646, respectively. Crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters are listed in Tables S1, S2, S3, and S4, respectively. ORTEP drawing of **7a** with atomic numbering schemes is shown in Figure S1.

1.3 X-ray Crystal Structure Analysis of Cp*(OC)$_2$Mo{=SiMes(Me)}(SiMe$_3$) (7b) A single crystal suitable for X-ray crystal structure analysis was obtained by recrystallization from toluene/hexane solution of **7b**. The final residue *R*1 and the weighted *wR*2 were 0.0269 and 0.0787, respectively. Crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters are listed in Tables S5, S6, S7, and S8, respectively. ORTEP drawing of **7b** with atomic numbering schemes is shown in Figure S2.

Table S1. Crystal data and structure refinement for complex **7a**.

Complex	Cp*(OC)$_2$W{=SiMes(Me)}(SiMe$_3$) (**7a**)
Empirical formula	$C_{25}H_{38}O_2Si_2W$
Formula weight	610.58
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*P*cab
Unit cell dimensions	a = 15.2435(14) Å
	b = 16.7605(14) Å
	c = 20.4763(16) Å
Volume (Å^3)	5231.5(8)
Z	8
D_{calc} (Mg / m^3)	1.550
Absorption coefficient (mm^{-1})	4.526
F(000)	2448
Crystal Size (mm^3)	0.20 × 0.09 × 0.04
Theta Range for data collection (°)	2.672 – 27.509
Index ranges	$-19 \le h \le 19$, $-21 \le k \le 21$, $-26 \le l \le 26$
Reflections collected	84216
Independent reflections [R(int)]	6014 [0.0610]
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	1.000 and 0.742
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6014 / 0 / 283
Goodness-of-fit on F^2	0.986
Final R indices[a] [$I > 2\sigma(I)$]	$R1$ = 0.0256, $wR2$ = 0.0646
R indices[a] (all data)	$R1$ = 0.0295, $wR2$ = 0.0661
Largest difference in peak and hole (eÅ^{-3})	1.500 and -1.686

[a] $R1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$.
$wR2 = [\Sigma[w\,(Fo^2 - Fc^2)^2] / \Sigma[w\,(Fo^2)^2]]^{0.5}$,
calc $w = 1 / [\sigma^2(Fo^2) + (0.0353P)^2]$ where $P = (Fo^2 + 2Fc^2) / 3$.

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **7a**. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	*x*	*y*	*z*	*U*(eq)[a)]
W	2335(1)	4086(1)	1716(1)	15(1)
Si(1)	3332(1)	3055(1)	1456(1)	21(1)
Si(2)	1785(1)	4183(1)	2925(1)	19(1)
O(1)	3906(1)	4212(1)	2687(1)	34(1)
O(2)	1334(1)	2522(1)	2085(1)	38(1)
C(1)	3317(2)	4146(1)	2333(1)	21(1)
C(2)	1728(2)	3101(1)	1963(1)	24(1)
C(3)	3763(2)	2294(2)	2045(1)	40(1)
C(4)	3937(1)	2817(1)	680(1)	19(1)
C(5)	4749(1)	3186(1)	547(1)	21(1)
C(6)	5189(1)	3006(1)	-28(1)	24(1)
C(7)	4866(1)	2446(1)	-467(1)	23(1)
C(8)	4076(2)	2068(1)	-323(1)	23(1)
C(9)	3609(2)	2248(1)	239(1)	21(1)
C(10)	5158(2)	3759(2)	1027(1)	28(1)
C(11)	5363(2)	2254(2)	-1090(1)	35(1)
C(12)	2757(2)	1810(2)	380(1)	32(1)
C(13)	2212(2)	5091(2)	3382(1)	33(1)
C(14)	2144(2)	3314(2)	3451(1)	30(1)
C(15)	550(2)	4196(2)	3009(1)	31(1)
C(16)	1819(2)	4422(1)	665(1)	24(1)
C(17)	2600(1)	4870(2)	780(1)	21(1)
C(18)	2440(2)	5402(1)	1304(1)	20(1)
C(19)	1554(2)	5296(1)	1511(1)	23(1)
C(20)	1174(2)	4683(2)	1120(1)	27(1)
C(21)	1670(2)	3859(2)	107(1)	45(1)
C(22)	3401(2)	4875(2)	346(1)	34(1)
C(23)	3046(2)	6036(2)	1552(2)	36(1)
C(24)	1083(2)	5851(2)	1974(2)	39(1)
C(25)	222(2)	4432(2)	1129(2)	47(1)

Table S3. Bond lengths [Å] and angles [deg] for **7a**.

W(1)-C(2)	1.959(2)	C(5)-C(6)	1.387(3)
W(1)-C(1)	1.961(2)	C(5)-C(10)	1.509(3)
W(1)-C(17)	2.359(2)	C(6)-C(7)	1.390(3)
W(1)-C(16)	2.360(2)	C(7)-C(8)	1.394(3)
W(1)-Si(1)	2.3628(6)	C(7)-C(11)	1.516(4)
W(1)-C(18)	2.367(2)	C(8)-C(9)	1.387(3)
W(1)-C(20)	2.372(2)	C(9)-C(12)	1.519(3)
W(1)-C(19)	2.389(2)	C(16)-C(20)	1.422(4)
W(1)-Si(2)	2.6178(7)	C(16)-C(17)	1.427(3)
Si(1)-C(3)	1.873(3)	C(16)-C(21)	1.499(3)
Si(1)-C(4)	1.881(2)	C(17)-C(18)	1.417(3)
Si(2)-C(15)	1.891(3)	C(17)-C(22)	1.511(3)
Si(2)-C(14)	1.892(3)	C(18)-C(19)	1.427(3)
Si(2)-C(13)	1.902(3)	C(18)-C(23)	1.497(4)
O(1)-C(1)	1.160(3)	C(19)-C(20)	1.426(3)
O(2)-C(2)	1.169(3)	C(19)-C(24)	1.508(3)
C(4)-C(9)	1.404(3)	C(20)-C(25)	1.511(4)
C(4)-C(5)	1.411(3)		
C(2)-W(1)-C(1)	103.71(10)	C(16)-W(1)-C(18)	58.34(8)
C(2)-W(1)-C(17)	139.43(9)	Si(1)-W(1)-C(18)	123.88(6)
C(1)-W(1)-C(17)	111.41(9)	C(2)-W(1)-C(20)	97.82(9)
C(2)-W(1)-C(16)	106.17(9)	C(1)-W(1)-C(20)	151.63(9)
C(1)-W(1)-C(16)	146.10(9)	C(17)-W(1)-C(20)	58.25(7)
C(17)-W(1)-C(16)	35.20(8)	C(16)-W(1)-C(20)	34.99(9)
C(2)-W(1)-Si(1)	75.28(7)	Si(1)-W(1)-C(20)	132.25(7)
C(1)-W(1)-Si(1)	72.01(7)	C(18)-W(1)-C(20)	58.23(8)
C(17)-W(1)-Si(1)	96.53(6)	C(2)-W(1)-C(19)	121.68(9)
C(16)-W(1)-Si(1)	100.55(6)	C(1)-W(1)-C(19)	116.79(9)
C(2)-W(1)-C(18)	155.39(9)	C(17)-W(1)-C(19)	57.99(8)
C(1)-W(1)-C(18)	97.53(8)	C(16)-W(1)-C(19)	58.08(8)
C(17)-W(1)-C(18)	34.89(9)	Si(1)-W(1)-C(19)	154.44(6)
C(18)-W(1)-C(19)	34.93(8)	C(8)-C(9)-C(12)	119.4(2)

C(20)-W(1)-C(19)	34.86(8)	C(4)-C(9)-C(12)	120.7(2)
C(2)-W(1)-Si(2)	69.91(7)	C(20)-C(16)-C(17)	107.8(2)
C(1)-W(1)-Si(2)	68.45(7)	C(20)-C(16)-C(21)	126.0(2)
C(17)-W(1)-Si(2)	142.09(7)	C(17)-C(16)-C(21)	125.7(2)
C(16)-W(1)-Si(2)	137.79(6)	C(20)-C(16)-W(1)	72.96(13)
Si(1)-W(1)-Si(2)	117.68(2)	C(17)-C(16)-W(1)	72.36(12)
C(18)-W(1)-Si(2)	107.56(6)	C(21)-C(16)-W(1)	126.55(18)
C(20)-W(1)-Si(2)	102.83(6)	C(18)-C(17)-C(16)	108.23(19)
C(19)-W(1)-Si(2)	87.36(6)	C(18)-C(17)-C(22)	125.5(2)
C(3)-Si(1)-C(4)	103.14(11)	C(16)-C(17)-C(22)	125.5(2)
C(3)-Si(1)-W(1)	125.34(9)	C(18)-C(17)-W(1)	72.87(13)
C(4)-Si(1)-W(1)	131.41(7)	C(16)-C(17)-W(1)	72.44(13)
C(15)-Si(2)-C(14)	104.23(13)	C(22)-C(17)-W(1)	128.29(16)
C(15)-Si(2)-C(13)	106.64(13)	C(17)-C(18)-C(19)	108.1(2)
C(14)-Si(2)-C(13)	103.69(14)	C(17)-C(18)-C(23)	126.7(2)
C(15)-Si(2)-W(1)	113.93(9)	C(19)-C(18)-C(23)	124.8(2)
C(14)-Si(2)-W(1)	113.44(9)	C(17)-C(18)-W(1)	72.25(13)
C(13)-Si(2)-W(1)	113.90(10)	C(19)-C(18)-W(1)	73.37(13)
O(1)-C(1)-W(1)	177.2(2)	C(23)-C(18)-W(1)	125.54(17)
O(2)-C(2)-W(1)	176.4(2)	C(20)-C(19)-C(18)	107.8(2)
C(9)-C(4)-C(5)	119.1(2)	C(20)-C(19)-C(24)	127.2(2)
C(9)-C(4)-Si(1)	120.86(16)	C(18)-C(19)-C(24)	124.1(2)
C(5)-C(4)-Si(1)	119.98(16)	C(20)-C(19)-W(1)	71.92(13)
C(6)-C(5)-C(4)	119.5(2)	C(18)-C(19)-W(1)	71.70(13)
C(6)-C(5)-C(10)	119.5(2)	C(24)-C(19)-W(1)	130.52(17)
C(4)-C(5)-C(10)	121.1(2)	C(16)-C(20)-C(19)	108.1(2)
C(5)-C(6)-C(7)	121.7(2)	C(16)-C(20)-C(25)	125.8(2)
C(6)-C(7)-C(8)	118.4(2)	C(19)-C(20)-C(25)	125.7(3)
C(6)-C(7)-C(11)	120.7(2)	C(16)-C(20)-W(1)	72.06(13)
C(8)-C(7)-C(11)	120.9(2)	C(19)-C(20)-W(1)	73.22(13)
C(9)-C(8)-C(7)	121.4(2)	C(25)-C(20)-W(1)	126.30(17)
C(8)-C(9)-C(4)	119.9(2)		

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (Å^2 × 10^3) for **7a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W(1)	15(1)	16(1)	15(1)	0(1)	1(1)	-1(1)
Si(1)	25(1)	18(1)	20(1)	1(1)	4(1)	3(1)
Si(2)	18(1)	23(1)	17(1)	-1(1)	2(1)	1(1)
O(1)	21(1)	48(1)	32(1)	1(1)	-7(1)	-2(1)
O(2)	45(1)	30(1)	38(1)	2(1)	1(1)	-19(1)
C(1)	19(1)	25(1)	20(1)	0(1)	-1(1)	-2(1)
C(2)	27(1)	25(1)	21(1)	-2(1)	-1(1)	-2(1)
C(3)	58(2)	34(2)	29(1)	8(1)	10(1)	21(1)
C(4)	19(1)	18(1)	19(1)	-1(1)	2(1)	2(1)
C(5)	16(1)	20(1)	25(1)	0(1)	-3(1)	3(1)
C(6)	15(1)	24(1)	32(1)	1(1)	4(1)	-1(1)
C(7)	20(1)	25(1)	23(1)	2(1)	5(1)	4(1)
C(8)	22(1)	22(1)	24(1)	-4(1)	-1(1)	-2(1)
C(9)	19(1)	19(1)	24(1)	2(1)	2(1)	-2(1)
C(10)	23(1)	28(1)	33(1)	-6(1)	-3(1)	-3(1)
C(11)	32(1)	39(2)	33(1)	-5(1)	11(1)	-2(1)
C(12)	28(1)	30(2)	37(1)	-9(1)	10(1)	-11(1)
C(13)	37(2)	36(2)	27(1)	-9(1)	-1(1)	0(1)
C(14)	32(1)	36(2)	21(1)	7(1)	-1(1)	2(1)
C(15)	23(1)	39(2)	31(1)	4(1)	8(1)	1(1)
C(16)	32(1)	21(1)	20(1)	3(1)	-7(1)	-2(1)
C(17)	23(1)	21(1)	20(1)	7(1)	1(1)	3(1)
C(18)	20(1)	16(1)	24(1)	4(1)	-4(1)	0(1)
C(19)	22(1)	24(1)	24(1)	7(1)	2(1)	6(1)
C(20)	18(1)	34(1)	29(1)	12(1)	-6(1)	-2(1)
C(21)	72(2)	39(2)	24(1)	-5(1)	-15(2)	-6(2)
C(22)	36(1)	35(2)	31(1)	16(1)	14(1)	13(1)
C(23)	35(2)	25(1)	47(2)	2(1)	-11(1)	-6(1)
C(24)	46(2)	38(2)	33(2)	7(1)	13(2)	23(1)
C(25)	25(1)	66(2)	49(2)	20(2)	-13(1)	-12(2)

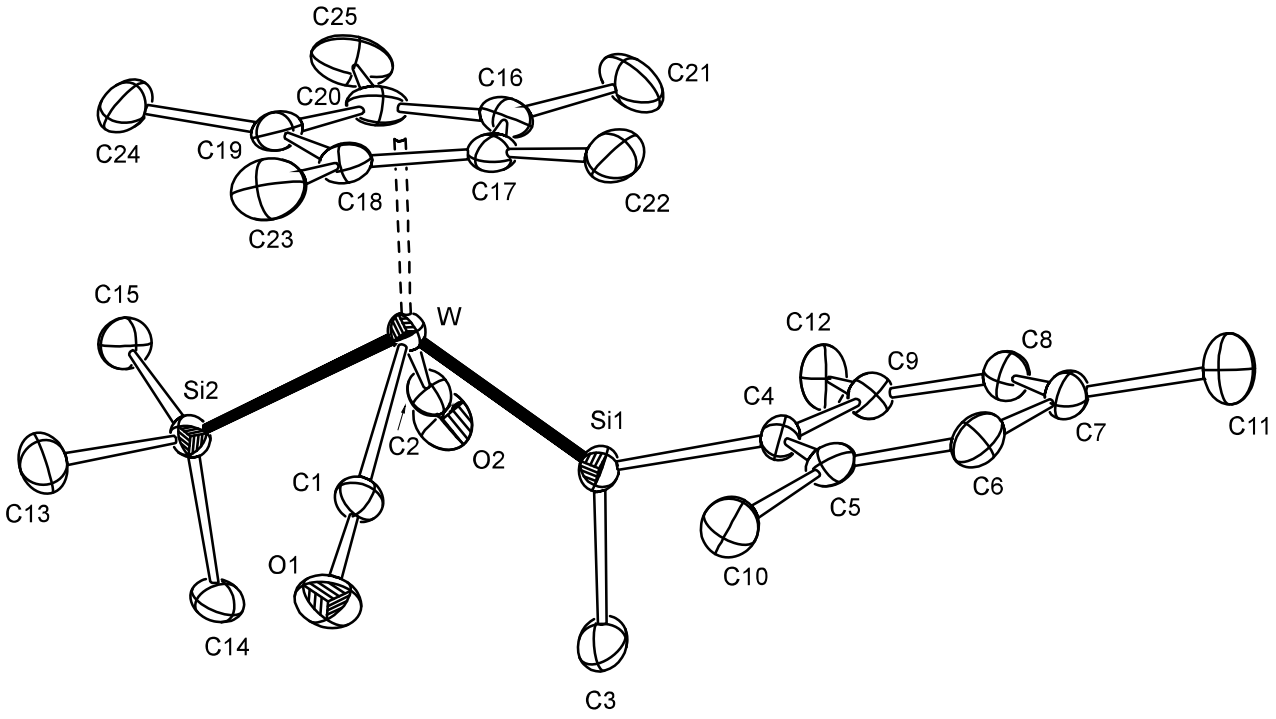

Figure S1. ORTEP drawing of **7a**. (thermal ellipsoids at the 50% probability level).

Table S5. Crystal data and structure refinement for complex **7b**.

Complex	Cp*(OC)$_2$Mo{=Si(Me)Mes}(SiMe$_3$) (**7b**)
Empirical formula	$C_{25}H_{38}MoO_2Si_2$
Formula weight	522.67
Temperature (K)	130(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*P*cab
Unit cell dimensions	a = 15.221(2) Å
	b = 16.815(2) Å
	c = 20.546(3) Å
Volume (Å^3)	5258.6(12)
Z	8
D_{calc} (Mg / m^3)	1.320
Absorption coefficient (mm^{-1})	0.608
F(000)	2192
Crystal Size (mm^3)	0.10 × 0.10 × 0.05
Theta Range for data collection (°)	3.101 – 27.496
Index ranges	$-19 \le h \le 19$, $-21 \le k \le 21$, $-26 \le l \le 26$
Reflections collected	86685
Independent reflections [R(int)]	6023 [0.1247]
Absorption correction	Multi-scan
Maximum and minimum transmission	1.000 and 0.881
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6023 / 0 / 283
Goodness-of-fit on F^2	1.081
Final R indices[a] [$I > 2\sigma(I)$]	$R1$ = 0.0297, $wR2$ = 0.0732
R indices[a] (all data)	$R1$ = 0.0356, $wR2$ = 0.0774
Largest difference in peak and hole (eÅ^{-3})	0.972 and -0.719

[a] $R1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$.
$wR2 = [\Sigma[w\,(Fo^2 - Fc^2)^2] / \Sigma[w\,(Fo^2)^2]]^{0.5}$,
calc $w = 1 / [\sigma^2(Fo^2) + (0.0255P)^2 + 3.5191P]$ where $P = (Fo^2 + 2Fc^2) / 3$.

Table S6. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **7b**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	*x*	*y*	*z*	*U*(eq)[a)]
Mo	2334(1)	915(1)	1709(1)	14(1)
Si(1)	3322(1)	1945(1)	1456(1)	20(1)
Si(2)	1796(1)	824(1)	2919(1)	19(1)
O(1)	1329(1)	2471(1)	2081(1)	38(1)
O(2)	3912(1)	802(1)	2674(1)	33(1)
C(1)	1723(1)	1897(1)	1958(1)	23(1)
C(2)	3315(1)	862(1)	2322(1)	21(1)
C(3)	3739(2)	2708(1)	2043(1)	40(1)
C(4)	3933(1)	2181(1)	683(1)	19(1)
C(5)	3603(1)	2749(1)	243(1)	20(1)
C(6)	4072(1)	2926(1)	-322(1)	22(1)
C(7)	4859(1)	2546(1)	-467(1)	22(1)
C(8)	5183(1)	1990(1)	-28(1)	22(1)
C(9)	4742(1)	1811(1)	549(1)	20(1)
C(10)	2755(1)	3187(1)	383(1)	32(1)
C(11)	5357(2)	2737(1)	-1087(1)	33(1)
C(12)	5153(1)	1237(1)	1028(1)	28(1)
C(13)	558(2)	804(1)	3004(1)	30(1)
C(14)	2147(2)	1689(1)	3448(1)	29(1)
C(15)	2228(2)	-81(1)	3370(1)	32(1)
C(16)	2595(1)	140(1)	765(1)	21(1)
C(17)	1807(1)	580(1)	663(1)	24(1)
C(18)	1168(1)	311(1)	1120(1)	25(1)
C(19)	1563(1)	-301(1)	1507(1)	22(1)
C(20)	2443(1)	-395(1)	1293(1)	20(1)
C(21)	3386(2)	137(1)	328(1)	33(1)
C(22)	1643(2)	1140(2)	105(1)	47(1)
C(23)	214(2)	549(2)	1133(1)	47(1)
C(24)	1101(2)	-859(1)	1970(1)	38(1)
C(25)	3062(2)	-1023(1)	1535(1)	35(1)

Table S7. Bond lengths [Å] and angles [deg] for **7b**.

Mo-C(2)	1.956(2)	C(5)-C(6)	1.396(2)
Mo-C(1)	1.9617(19)	C(5)-C(10)	1.513(3)
Mo-Si(1)	2.3522(6)	C(6)-C(7)	1.390(3)
Mo-C(17)	2.3628(17)	C(7)-C(8)	1.390(3)
Mo-C(20)	2.3689(18)	C(7)-C(11)	1.516(3)
Mo-C(16)	2.3704(17)	C(8)-C(9)	1.394(3)
Mo-C(18)	2.3772(19)	C(9)-C(12)	1.515(3)
Mo-C(19)	2.3937(19)	C(16)-C(17)	1.424(3)
Mo-Si(2)	2.6217(6)	C(16)-C(20)	1.426(2)
Si(1)-C(3)	1.871(2)	C(16)-C(21)	1.503(3)
Si(1)-C(4)	1.8838(18)	C(17)-C(18)	1.427(3)
Si(2)-C(13)	1.892(2)	C(17)-C(22)	1.504(3)
Si(2)-C(14)	1.892(2)	C(18)-C(19)	1.432(3)
Si(2)-C(15)	1.899(2)	C(18)-C(23)	1.506(3)
O(1)-C(1)	1.164(2)	C(19)-C(20)	1.419(3)
O(2)-C(2)	1.166(2)	C(19)-C(24)	1.509(3)
C(4)-C(9)	1.406(3)	C(20)-C(25)	1.501(3)
C(4)-C(5)	1.408(2)		
C(2)-Mo-C(1)	103.46(8)	C(20)-Mo-C(16)	35.03(6)
C(2)-Mo-Si(1)	71.81(6)	C(2)-Mo-C(18)	151.48(7)
C(1)-Mo-Si(1)	74.98(6)	C(1)-Mo-C(18)	97.98(8)
C(2)-Mo-C(17)	146.49(7)	Si(1)-Mo-C(18)	132.83(5)
C(1)-Mo-C(17)	106.10(7)	C(17)-Mo-C(18)	35.03(7)
Si(1)-Mo-C(17)	101.04(5)	C(20)-Mo-C(18)	58.05(7)
C(2)-Mo-C(20)	97.82(7)	C(16)-Mo-C(18)	58.20(6)
C(1)-Mo-C(20)	155.46(8)	C(2)-Mo-C(19)	116.54(7)
Si(1)-Mo-C(20)	124.05(5)	C(1)-Mo-C(19)	122.12(8)
C(17)-Mo-C(20)	58.20(6)	Si(1)-Mo-C(19)	154.70(4)
C(2)-Mo-C(16)	111.93(7)	C(17)-Mo-C(19)	58.12(6)
C(1)-Mo-C(16)	139.04(7)	C(20)-Mo-C(19)	34.68(7)
Si(1)-Mo-C(16)	96.73(5)	C(16)-Mo-C(19)	58.01(6)
C(17)-Mo-C(16)	35.01(7)	C(18)-Mo-C(19)	34.94(7)

C(2)-Mo-Si(2)	67.99(6)	C(17)-C(16)-C(20)	107.68(16)
C(1)-Mo-Si(2)	69.81(5)	C(17)-C(16)-C(21)	125.96(18)
Si(1)-Mo-Si(2)	116.918(17)	C(20)-C(16)-C(21)	125.61(19)
C(17)-Mo-Si(2)	137.97(5)	C(17)-C(16)-Mo	72.20(10)
C(20)-Mo-Si(2)	108.03(4)	C(20)-C(16)-Mo	72.43(10)
C(16)-Mo-Si(2)	142.71(5)	C(21)-C(16)-Mo	128.68(13)
C(18)-Mo-Si(2)	102.98(5)	C(16)-C(17)-C(18)	108.21(16)
C(19)-Mo-Si(2)	87.77(4)	C(16)-C(17)-C(22)	125.3(2)
C(3)-Si(1)-C(4)	103.41(9)	C(18)-C(17)-C(22)	125.9(2)
C(3)-Si(1)-Mo	125.40(7)	C(16)-C(17)-Mo	72.78(10)
C(4)-Si(1)-Mo	131.08(6)	C(18)-C(17)-Mo	73.04(10)
C(13)-Si(2)-C(14)	103.95(10)	C(22)-C(17)-Mo	126.86(14)
C(13)-Si(2)-C(15)	106.63(10)	C(17)-C(18)-C(19)	107.84(17)
C(14)-Si(2)-C(15)	103.77(10)	C(17)-C(18)-C(23)	125.8(2)
C(13)-Si(2)-Mo	113.54(7)	C(19)-C(18)-C(23)	125.9(2)
C(14)-Si(2)-Mo	114.24(7)	C(17)-C(18)-Mo	71.93(11)
C(15)-Si(2)-Mo	113.70(7)	C(19)-C(18)-Mo	73.16(10)
O(1)-C(1)-Mo	176.54(18)	C(23)-C(18)-Mo	126.64(14)
O(2)-C(2)-Mo	177.21(17)	C(20)-C(19)-C(18)	107.71(16)
C(9)-C(4)-C(5)	119.19(16)	C(20)-C(19)-C(24)	124.43(19)
C(9)-C(4)-Si(1)	120.31(13)	C(18)-C(19)-C(24)	126.9(2)
C(5)-C(4)-Si(1)	120.46(14)	C(20)-C(19)-Mo	71.71(11)
C(6)-C(5)-C(4)	119.69(17)	C(18)-C(19)-Mo	71.90(11)
C(6)-C(5)-C(10)	119.43(17)	C(24)-C(19)-Mo	130.55(13)
C(4)-C(5)-C(10)	120.87(16)	C(19)-C(20)-C(16)	108.54(17)
C(7)-C(6)-C(5)	121.45(17)	C(19)-C(20)-C(25)	124.63(18)
C(6)-C(7)-C(8)	118.39(16)	C(16)-C(20)-C(25)	126.46(19)
C(6)-C(7)-C(11)	120.93(17)	C(19)-C(20)-Mo	73.62(11)
C(8)-C(7)-C(11)	120.67(18)	C(16)-C(20)-Mo	72.54(10)
C(7)-C(8)-C(9)	121.73(17)	C(25)-C(20)-Mo	125.40(13)
C(8)-C(9)-C(4)	119.50(17)	C(17)-C(18)-Mo	71.93(11)
C(8)-C(9)-C(12)	119.43(17)	C(19)-C(18)-Mo	73.16(10)
C(4)-C(9)-C(12)	121.05(16)		

Symmetry transformations used to generate equivalent atoms:

Table S8. Anisotropic displacement parameters (Å^2 × 10^3) for **7b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	18(1)	13(1)	11(1)	0(1)	0(1)	1(1)
Si(1)	28(1)	16(1)	16(1)	-1(1)	5(1)	-3(1)
Si(2)	22(1)	21(1)	14(1)	0(1)	2(1)	-1(1)
O(1)	50(1)	27(1)	38(1)	-2(1)	2(1)	19(1)
O(2)	24(1)	46(1)	30(1)	1(1)	-8(1)	2(1)
C(1)	29(1)	21(1)	18(1)	2(1)	0(1)	4(1)
C(2)	23(1)	22(1)	20(1)	-2(1)	3(1)	1(1)
C(3)	61(2)	34(1)	26(1)	-10(1)	11(1)	-22(1)
C(4)	21(1)	17(1)	17(1)	0(1)	2(1)	-2(1)
C(5)	22(1)	17(1)	20(1)	0(1)	2(1)	2(1)
C(6)	26(1)	21(1)	18(1)	4(1)	0(1)	2(1)
C(7)	24(1)	23(1)	19(1)	-1(1)	4(1)	-3(1)
C(8)	18(1)	21(1)	27(1)	-2(1)	3(1)	1(1)
C(9)	21(1)	16(1)	22(1)	0(1)	-3(1)	-2(1)
C(10)	31(1)	30(1)	34(1)	8(1)	10(1)	11(1)
C(11)	34(1)	38(1)	27(1)	7(1)	13(1)	4(1)
C(12)	26(1)	28(1)	29(1)	7(1)	-3(1)	3(1)
C(13)	26(1)	36(1)	29(1)	-3(1)	8(1)	-1(1)
C(14)	36(1)	34(1)	17(1)	-7(1)	2(1)	-3(1)
C(15)	41(1)	32(1)	23(1)	12(1)	1(1)	0(1)
C(16)	27(1)	19(1)	15(1)	-6(1)	1(1)	-4(1)
C(17)	36(1)	23(1)	13(1)	-4(1)	-7(1)	1(1)
C(18)	21(1)	31(1)	24(1)	-11(1)	-6(1)	2(1)
C(19)	26(1)	21(1)	19(1)	-6(1)	1(1)	-5(1)
C(20)	24(1)	16(1)	19(1)	-3(1)	-3(1)	-1(1)
C(21)	39(1)	33(1)	28(1)	-15(1)	15(1)	-12(1)
C(22)	81(2)	37(1)	22(1)	4(1)	-19(1)	7(1)
C(23)	27(1)	64(2)	51(1)	-22(1)	-14(1)	11(1)
C(24)	51(2)	33(1)	30(1)	-9(1)	13(1)	-22(1)
C(25)	40(1)	20(1)	43(1)	-2(1)	-9(1)	7(1)

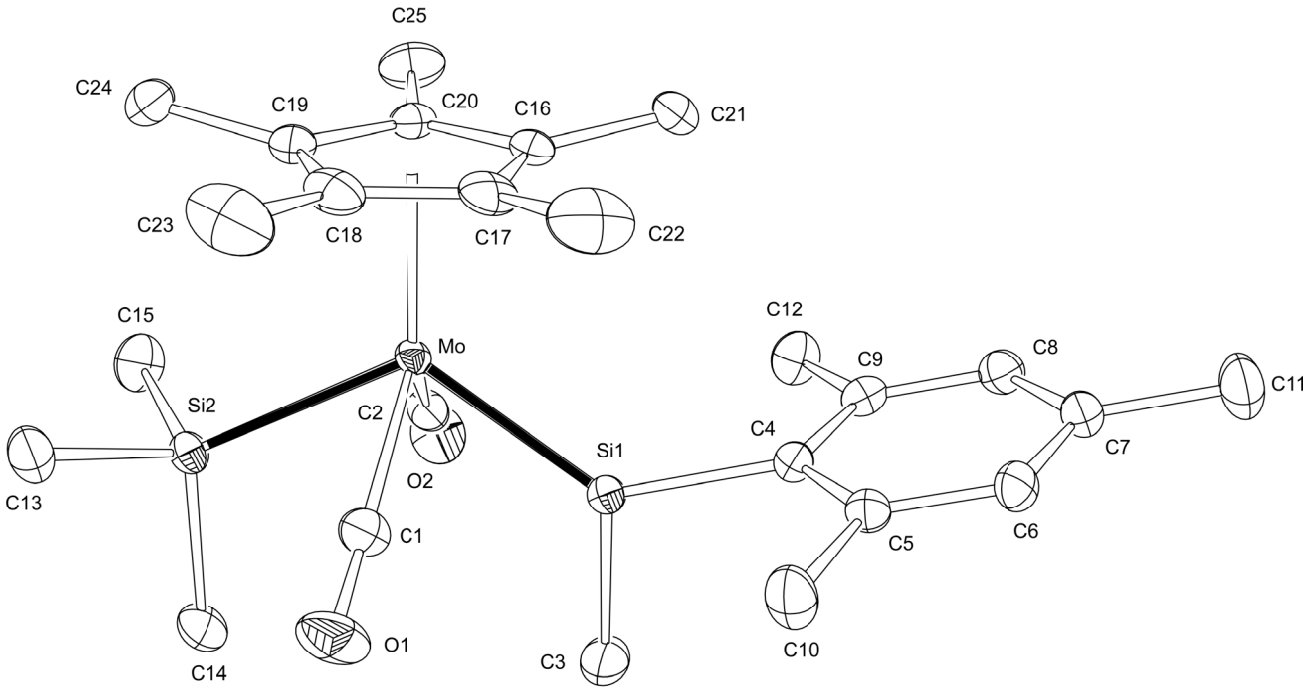

Figure S2. ORTEP drawing of **7b**. (thermal ellipsoids at the 50% probability level).

1.4 X-ray Crystal Structure Analysis of $Cp^*(OC)_2Mo(PMe_3)\{SiMes(Me)(OSiMe_3)\}$ (11b) A single crystal suitable for X-ray crystal structure analysis was obtained by recrystallization from toluene/hexane solution of **11b**. The final residue *R*1 and the weighted *wR*2 were 0.0483 and 0.1256, respectively. The unit cell contains one toluene molecule per two molecules of **11b**. Crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters are listed in Tables S9, S10, S11, and S12, respectively. ORTEP drawing of **11b** with atomic numbering schemes is shown in Figure S3.

Table S9. Crystal data and structure refinement for complex **11b**.

Complex	$Cp^*(OC)_2Mo(PMe_3)\{SiMe(Mes)(OSiMe_3)\}$ (**11b**)
Empirical formula	$C_{63}H_{94}Mo_2O_6Si_4$
Formula weight	1313.56
Temperature (K)	130(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	a = 36.982(7) Å
	b = 11.547(2) Å $\quad \beta$ = 100.183(4)°
	c = 16.211(3) Å
Volume (Å^3)	6814(2)
Z	4
D_{calc} (Mg / m^3)	1.281
Absorption coefficient (mm^{-1})	0.531
F(000)	2760
Crystal Size (mm^3)	0.17 × 0.17 × 0.10
Theta Range for data collection (°)	2.884 – 27.489
Index ranges	$-48 \le h \le 48$, $-14 \le k \le 14$, $-21 \le l \le 19$
Reflections collected	53779
Independent reflections [R(int)]	7781 [0.1276]
Absorption correction	Multi-scan
Maximum and minimum transmission	1.000 and 0.658
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7781 / 0 / 394
Goodness-of-fit on F^2	1.058
Final R indices[a] [$I > 2\sigma(I)$]	$R1$ = 0.0483, $wR2$ = 0.1256
R indices[a] (all data)	$R1$ = 0.0744, $wR2$ = 0.1328
Largest difference in peak and hole (eÅ^{-3})	0.711 and -1.199

[a] $R1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$.
$wR2 = [\Sigma[w\,(Fo^2 - Fc^2)^2] / \Sigma[w\,(Fo^2)^2]]^{0.5}$,
calc $w = 1 / [\sigma^2(Fo^2) + (0.0657P)^2]$ where $P = (Fo^2 + 2Fc^2) / 3$.

Table S10. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **11b**. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	*x*	*y*	*z*	*U*(eq)[a)]
Mo	8677(1)	7953(1)	5167(1)	37(1)
P	8146(1)	9120(1)	5320(1)	49(1)
Si(1)	8835(1)	6052(1)	6044(1)	40(1)
Si(2)	9328(1)	3968(1)	5703(1)	45(1)
O(1)	7996(1)	6377(3)	4628(2)	56(1)
O(2)	8838(1)	8789(3)	7018(2)	63(1)
O(3)	9073(1)	5129(2)	5547(1)	42(1)
C(1)	8251(1)	6918(4)	4880(2)	44(1)
C(2)	8769(1)	8400(4)	6355(2)	49(1)
C(3)	9174(1)	6224(4)	7058(2)	48(1)
C(4)	8422(1)	5166(4)	6279(2)	43(1)
C(5)	8258(1)	4293(4)	5729(2)	43(1)
C(6)	7973(1)	3610(4)	5938(2)	48(1)
C(7)	7844(1)	3749(4)	6684(2)	54(1)
C(8)	7994(1)	4627(5)	7203(2)	56(1)
C(9)	8273(1)	5349(4)	7019(2)	49(1)
C(10)	8354(1)	4037(4)	4874(2)	47(1)
C(11)	7540(1)	2982(5)	6896(3)	70(2)
C(12)	8399(1)	6305(4)	7630(2)	58(1)
C(13)	9137(1)	2906(4)	6371(2)	58(1)
C(14)	9807(1)	4330(5)	6228(3)	63(1)
C(15)	9351(1)	3322(4)	4656(2)	50(1)
C(16)	7896(1)	8566(5)	6114(3)	65(1)
C(17)	7783(1)	9258(5)	4404(3)	67(1)
C(18)	8217(1)	10623(5)	5663(3)	69(1)
C(19)	8754(1)	8355(4)	3787(2)	42(1)
C(20)	8999(1)	7440(4)	4105(2)	41(1)
C(21)	9257(1)	7902(4)	4783(2)	41(1)
C(22)	9171(1)	9091(4)	4879(2)	41(1)
C(23)	8860(1)	9371(4)	4256(2)	40(1)
C(24)	8468(1)	8302(5)	2996(2)	57(1)

C(25)	9022(1)	6276(4)	3708(2)	50(1)
C(26)	9606(1)	7332(4)	5195(3)	50(1)
C(27)	9397(1)	9930(4)	5464(2)	54(1)
C(28)	8721(1)	10569(4)	4042(2)	49(1)
C(31)	160(3)	10273(10)	7281(6)	40(3)
C(32)	151(4)	8988(14)	7343(8)	46(3)
C(33)	101(5)	8485(19)	7237(11)	78(6)
C(34)	350(2)	9091(11)	6904(5)	61(3)
C(35)	356(2)	10407(13)	6922(6)	54(4)
C(36)	87(2)	10880(10)	7342(5)	41(2)
C(37)	447(3)	10855(14)	6822(9)	70(4)

Table S11. Bond lengths [Å] and angles [deg] for **11b**.

Mo-C(2)	1.964(3)	C(19)-C(23)	1.415(6)
Mo-C(1)	1.968(4)	C(19)-C(20)	1.428(6)
Mo-C(20)	2.336(3)	C(19)-C(24)	1.511(5)
Mo-C(21)	2.338(3)	C(20)-C(21)	1.426(5)
Mo-C(19)	2.351(3)	C(20)-C(25)	1.500(6)
Mo-C(22)	2.363(4)	C(21)-C(22)	1.424(5)
Mo-C(23)	2.383(4)	C(21)-C(26)	1.495(5)
Mo-P	2.4313(10)	C(22)-C(23)	1.427(5)
Mo-Si(1)	2.6241(12)	C(22)-C(27)	1.502(5)
P-C(17)	1.823(4)	C(23)-C(28)	1.496(6)
P-C(16)	1.828(4)	C(31)-C(36)	0.764(10)
P-C(18)	1.828(6)	C(31)-C(35)	1.018(13)
Si(1)-O(3)	1.676(2)	C(31)-C(36)#1	1.377(11)
Si(1)-C(3)	1.893(3)	C(31)-C(31)#1	1.48(2)
Si(1)-C(4)	1.932(4)	C(31)-C(32)	1.49(2)
Si(2)-O(3)	1.633(3)	C(31)-C(37)	1.554(14)
Si(2)-C(13)	1.857(5)	C(31)-C(34)	1.698(14)
Si(2)-C(15)	1.870(4)	C(31)-C(32)#1	2.03(2)
Si(2)-C(14)	1.872(4)	C(32)-C(33)	0.62(2)
O(1)-C(1)	1.145(5)	C(32)-C(34)	1.118(19)
O(2)-C(2)	1.152(4)	C(32)-C(32)#1	1.31(3)
C(4)-C(5)	1.410(6)	C(32)-C(33)#1	1.377(16)
C(4)-C(9)	1.422(4)	C(32)-C(35)	1.98(2)
C(5)-C(6)	1.403(5)	C(33)-C(33)#1	1.23(4)
C(5)-C(10)	1.521(4)	C(33)-C(34)	1.34(2)
C(6)-C(7)	1.386(5)	C(34)-C(35)	1.520(19)
C(7)-C(8)	1.372(7)	C(35)-C(37)	0.654(15)
C(7)-C(11)	1.517(6)	C(35)-C(36)	1.409(13)
C(8)-C(9)	1.398(6)	C(36)-C(36)#1	0.891(18)
C(9)-C(12)	1.502(6)	C(36)-C(37)	1.697(14)
C(2)-Mo-C(1)	112.63(16)	C(2)-Mo-C(20)	140.05(13)
C(1)-Mo-C(20)	99.38(14)	C(17)-P-C(16)	102.4(2)

C(2)-Mo-C(21)	105.05(13)	C(17)-P-C(18)	102.2(2)
C(1)-Mo-C(21)	131.02(14)	C(16)-P-C(18)	100.5(2)
C(20)-Mo-C(21)	35.52(11)	C(17)-P-Mo	117.22(16)
C(2)-Mo-C(19)	148.43(18)	C(16)-P-Mo	113.34(15)
C(1)-Mo-C(19)	96.93(13)	C(18)-P-Mo	118.74(15)
C(20)-Mo-C(19)	35.47(14)	O(3)-Si(1)-C(3)	99.32(14)
C(21)-Mo-C(19)	58.71(12)	O(3)-Si(1)-C(4)	104.99(16)
C(2)-Mo-C(22)	92.38(15)	C(3)-Si(1)-C(4)	108.01(16)
C(1)-Mo-C(22)	154.95(12)	O(3)-Si(1)-Mo	110.91(10)
C(20)-Mo-C(22)	58.85(13)	C(3)-Si(1)-Mo	115.63(15)
C(21)-Mo-C(22)	35.26(13)	C(4)-Si(1)-Mo	116.19(11)
C(19)-Mo-C(22)	58.30(11)	O(3)-Si(2)-C(13)	111.31(15)
C(2)-Mo-C(23)	114.10(17)	O(3)-Si(2)-C(15)	107.65(16)
C(1)-Mo-C(23)	125.02(13)	C(13)-Si(2)-C(15)	110.4(2)
C(20)-Mo-C(23)	58.61(14)	O(3)-Si(2)-C(14)	111.20(19)
C(21)-Mo-C(23)	58.48(13)	C(13)-Si(2)-C(14)	108.1(2)
C(19)-Mo-C(23)	34.79(13)	C(15)-Si(2)-C(14)	108.14(18)
C(22)-Mo-C(23)	34.99(11)	Si(2)-O(3)-Si(1)	141.70(15)
C(2)-Mo-P	75.99(10)	O(1)-C(1)-Mo	172.4(3)
C(1)-Mo-P	74.46(12)	O(2)-C(2)-Mo	171.6(4)
C(20)-Mo-P	137.87(10)	C(5)-C(4)-C(9)	116.8(3)
C(21)-Mo-P	146.84(11)	C(5)-C(4)-Si(1)	121.5(2)
C(19)-Mo-P	102.87(10)	C(9)-C(4)-Si(1)	121.7(3)
C(22)-Mo-P	112.26(10)	C(6)-C(5)-C(4)	120.6(3)
C(23)-Mo-P	90.31(9)	C(6)-C(5)-C(10)	114.7(4)
C(2)-Mo-Si(1)	72.88(14)	C(4)-C(5)-C(10)	124.7(3)
C(1)-Mo-Si(1)	73.32(11)	C(7)-C(6)-C(5)	122.3(4)
C(20)-Mo-Si(1)	95.37(11)	C(8)-C(7)-C(6)	117.1(4)
C(21)-Mo-Si(1)	89.80(10)	C(8)-C(7)-C(11)	122.0(4)
C(19)-Mo-Si(1)	128.89(11)	C(6)-C(7)-C(11)	120.9(5)
C(22)-Mo-Si(1)	117.80(10)	C(7)-C(8)-C(9)	123.0(3)
C(23)-Mo-Si(1)	148.24(8)	C(8)-C(9)-C(4)	120.2(4)
P-Mo-Si(1)	121.02(3)	C(8)-C(9)-C(12)	116.8(3)
C(4)-C(9)-C(12)	123.0(4)	C(36)-C(31)-C(31)#1	67.0(14)
C(23)-C(19)-C(20)	108.7(3)	C(35)-C(31)-C(31)#1	169.0(11)

C(23)-C(19)-C(24)	125.1(4)	C(36)#1-C(31)-C(31)#1	30.7(5)
C(20)-C(19)-C(24)	125.5(4)	C(36)-C(31)-C(32)	153.4(18)
C(23)-C(19)-Mo	73.82(18)	C(35)-C(31)-C(32)	102.6(14)
C(20)-C(19)-Mo	71.70(18)	C(36)#1-C(31)-C(32)	117.0(10)
C(24)-C(19)-Mo	128.0(2)	C(31)#1-C(31)-C(32)	86.5(7)
C(21)-C(20)-C(19)	107.3(4)	C(36)-C(31)-C(37)	87.2(16)
C(21)-C(20)-C(25)	125.8(4)	C(35)-C(31)-C(37)	17.1(13)
C(19)-C(20)-C(25)	126.1(3)	C(36)#1-C(31)-C(37)	123.7(10)
C(21)-C(20)-Mo	72.31(17)	C(31)#1-C(31)-C(37)	154.1(7)
C(19)-C(20)-Mo	72.83(17)	C(32)-C(31)-C(37)	119.3(11)
C(25)-C(20)-Mo	128.2(3)	C(36)-C(31)-C(34)	164.3(16)
C(22)-C(21)-C(20)	108.2(3)	C(35)-C(31)-C(34)	62.3(11)
C(22)-C(21)-C(26)	124.5(3)	C(36)#1-C(31)-C(34)	156.7(9)
C(20)-C(21)-C(26)	125.9(4)	C(31)#1-C(31)-C(34)	126.1(6)
C(22)-C(21)-Mo	73.33(18)	C(32)-C(31)-C(34)	40.4(8)
C(20)-C(21)-Mo	72.17(17)	C(37)-C(31)-C(34)	79.3(8)
C(26)-C(21)-Mo	130.6(3)	C(36)-C(31)-C(32)#1	113.6(15)
C(21)-C(22)-C(23)	108.0(3)	C(35)-C(31)-C(32)#1	141.2(14)
C(21)-C(22)-C(27)	125.5(3)	C(36)#1-C(31)-C(32)#1	77.6(8)
C(23)-C(22)-C(27)	126.2(4)	C(31)#1-C(31)-C(32)#1	46.9(5)
C(21)-C(22)-Mo	71.4(2)	C(32)-C(31)-C(32)#1	39.8(10)
C(23)-C(22)-Mo	73.2(2)	C(37)-C(31)-C(32)#1	158.3(10)
C(27)-C(22)-Mo	126.6(2)	C(34)-C(31)-C(32)#1	79.3(7)
C(19)-C(23)-C(22)	107.8(3)	C(33)-C(32)-C(34)	97(3)
C(19)-C(23)-C(28)	126.2(3)	C(33)-C(32)-C(32)#1	83(3)
C(22)-C(23)-C(28)	125.1(4)	C(34)-C(32)-C(32)#1	162.4(18)
C(19)-C(23)-Mo	71.4(2)	C(33)-C(32)-C(33)#1	63(4)
C(22)-C(23)-Mo	71.8(2)	C(34)-C(32)-C(33)#1	160.1(19)
C(28)-C(23)-Mo	131.0(2)	C(32)#1-C(32)-C(33)#1	26.7(9)
C(36)-C(31)-C(35)	103.7(18)	C(33)-C(32)-C(31)	157(4)
C(36)-C(31)-C(36)#1	36.7(11)	C(34)-C(32)-C(31)	80.0(12)
C(35)-C(31)-C(36)#1	140.4(12)	C(32)#1-C(32)-C(31)	93.3(7)
C(33)#1-C(32)-C(31)	118.6(14)	C(37)-C(35)-C(31)	136(3)
C(33)-C(32)-C(35)	142(3)	C(37)-C(35)-C(36)	105(3)
C(34)-C(32)-C(35)	49.9(10)	C(31)-C(35)-C(36)	31.8(7)

C(32)#1-C(32)-C(35)	122.7(7)	C(37)-C(35)-C(34)	142(2)
C(33)#1-C(32)-C(35)	148.7(15)	C(31)-C(35)-C(34)	81.4(12)
C(31)-C(32)-C(35)	30.2(6)	C(36)-C(35)-C(34)	112.9(10)
C(33)-C(32)-C(31)#1	127(4)	C(37)-C(35)-C(32)	171(2)
C(34)-C(32)-C(31)#1	125.7(14)	C(31)-C(35)-C(32)	47.3(10)
C(32)#1-C(32)-C(31)#1	46.9(5)	C(36)-C(35)-C(32)	79.0(9)
C(33)#1-C(32)-C(31)#1	72.0(10)	C(34)-C(35)-C(32)	34.2(7)
C(31)-C(32)-C(31)#1	46.7(8)	C(31)-C(36)-C(36)#1	112.4(13)
C(35)-C(32)-C(31)#1	76.7(7)	C(31)-C(36)-C(31)#1	82.3(18)
C(32)-C(33)-C(33)#1	90(3)	C(36)#1-C(36)-C(31)#1	30.8(5)
C(32)-C(33)-C(34)	56(3)	C(31)-C(36)-C(35)	44.6(12)
C(33)#1-C(33)-C(34)	145.4(9)	C(36)#1-C(36)-C(35)	157.0(8)
C(32)-C(33)-C(32)#1	70(4)	C(31)#1-C(36)-C(35)	126.6(12)
C(33)#1-C(33)-C(32)#1	26.9(9)	C(31)-C(36)-C(37)	66.1(14)
C(34)-C(33)-C(32)#1	123.5(19)	C(36)#1-C(36)-C(37)	174.8(15)
C(32)-C(34)-C(33)	27.5(10)	C(31)#1-C(36)-C(37)	148.4(10)
C(32)-C(34)-C(35)	95.8(11)	C(35)-C(36)-C(37)	21.9(9)
C(33)-C(34)-C(35)	121.4(11)	C(35)-C(37)-C(31)	27.3(17)
C(32)-C(34)-C(31)	59.6(10)	C(35)-C(37)-C(36)	53.4(18)
C(33)-C(34)-C(31)	85.2(10)	C(31)-C(37)-C(36)	26.7(4)
C(35)-C(34)-C(31)	36.3(5)		

Symmetry transformations used to generate equivalent atoms:

#1 −x, y, −z+3/2

Table S12. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **11b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	24(1)	73(1)	15(1)	1(1)	5(1)	12(1)
P	33(1)	84(1)	34(1)	16(1)	15(1)	23(1)
Si(1)	29(1)	74(1)	17(1)	1(1)	7(1)	15(1)
Si(2)	33(1)	77(1)	26(1)	-7(1)	6(1)	18(1)
O(1)	33(1)	86(2)	46(2)	17(2)	-4(1)	-1(2)
O(2)	68(2)	96(3)	22(1)	-5(1)	6(1)	31(2)
O(3)	27(1)	75(2)	25(1)	-3(1)	7(1)	11(1)
C(1)	34(2)	74(3)	26(2)	15(2)	8(1)	13(2)
C(2)	46(2)	80(3)	21(2)	-4(2)	7(1)	30(2)
C(3)	43(2)	80(3)	21(2)	-2(2)	2(1)	18(2)
C(4)	32(2)	76(3)	23(2)	10(2)	8(1)	19(2)
C(5)	30(2)	75(3)	26(2)	8(2)	10(1)	17(2)
C(6)	30(2)	72(3)	43(2)	14(2)	10(2)	18(2)
C(7)	32(2)	95(4)	40(2)	26(2)	15(2)	19(2)
C(8)	44(2)	100(4)	29(2)	24(2)	20(2)	33(2)
C(9)	36(2)	88(3)	25(2)	14(2)	12(1)	26(2)
C(10)	37(2)	75(3)	30(2)	-1(2)	10(1)	7(2)
C(11)	43(2)	111(5)	63(3)	28(3)	25(2)	13(2)
C(12)	53(2)	100(4)	26(2)	5(2)	18(2)	27(2)
C(13)	62(2)	87(4)	27(2)	0(2)	14(2)	31(2)
C(14)	41(2)	93(4)	49(2)	-18(2)	-7(2)	26(2)
C(15)	39(2)	78(3)	34(2)	-9(2)	12(2)	9(2)
C(16)	42(2)	108(4)	53(2)	24(3)	28(2)	34(2)
C(17)	36(2)	106(4)	58(3)	37(3)	9(2)	27(2)
C(18)	74(3)	83(4)	59(3)	13(3)	37(2)	33(3)
C(19)	30(2)	80(3)	16(1)	-6(2)	9(1)	-11(2)
C(20)	32(2)	72(3)	21(2)	-13(2)	12(1)	-6(2)
C(21)	24(2)	74(3)	25(2)	-15(2)	9(1)	1(2)

C(22)	29(2)	67(3)	26(2)	-16(2)	5(1)	2(2)
C(23)	28(2)	74(3)	20(1)	-3(2)	9(1)	1(2)
C(24)	53(2)	94(4)	20(2)	5(2)	-2(2)	-16(2)
C(25)	53(2)	74(3)	27(2)	-16(2)	17(2)	-17(2)
C(26)	27(2)	72(3)	52(2)	-20(2)	8(2)	7(2)
C(27)	43(2)	72(3)	41(2)	-21(2)	-4(2)	12(2)
C(28)	40(2)	79(3)	29(2)	7(2)	10(1)	10(2)
C(31)	31(5)	57(8)	27(4)	5(5)	-4(3)	10(5)
C(32)	29(5)	79(12)	21(5)	-4(6)	-14(4)	0(6)
C(33)	51(9)	129(18)	40(6)	-34(9)	-28(5)	19(10)
C(34)	29(4)	112(9)	39(4)	-36(5)	-3(3)	19(5)
C(35)	18(4)	125(14)	23(4)	-2(6)	12(3)	-5(5)
C(36)	31(5)	70(8)	20(4)	-1(5)	3(3)	-7(5)
C(37)	48(7)	104(11)	66(7)	32(6)	27(5)	-19(6)

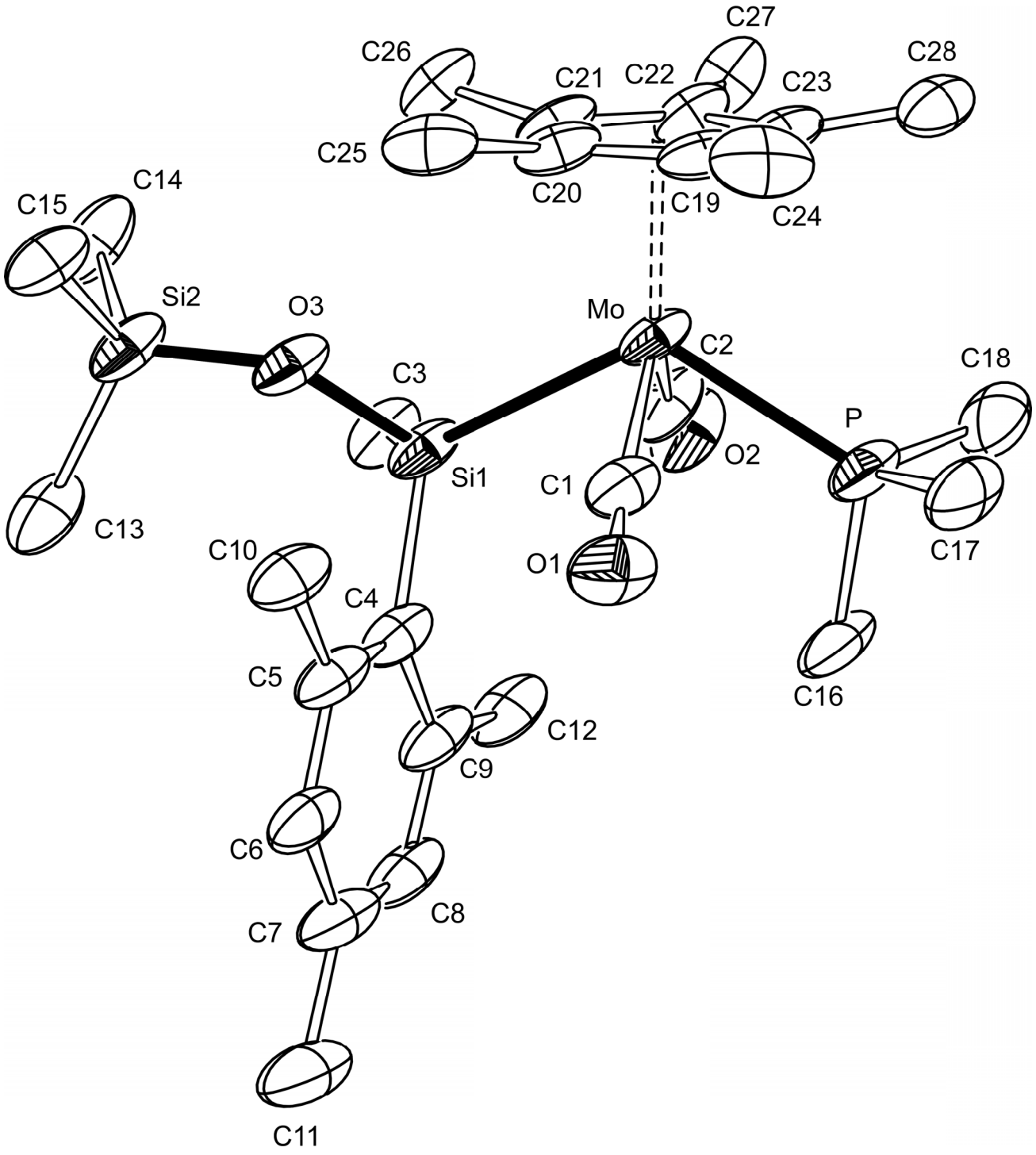

Figure S3. ORTEP drawing of **11b**. (thermal ellipsoids at the 50% probability level).

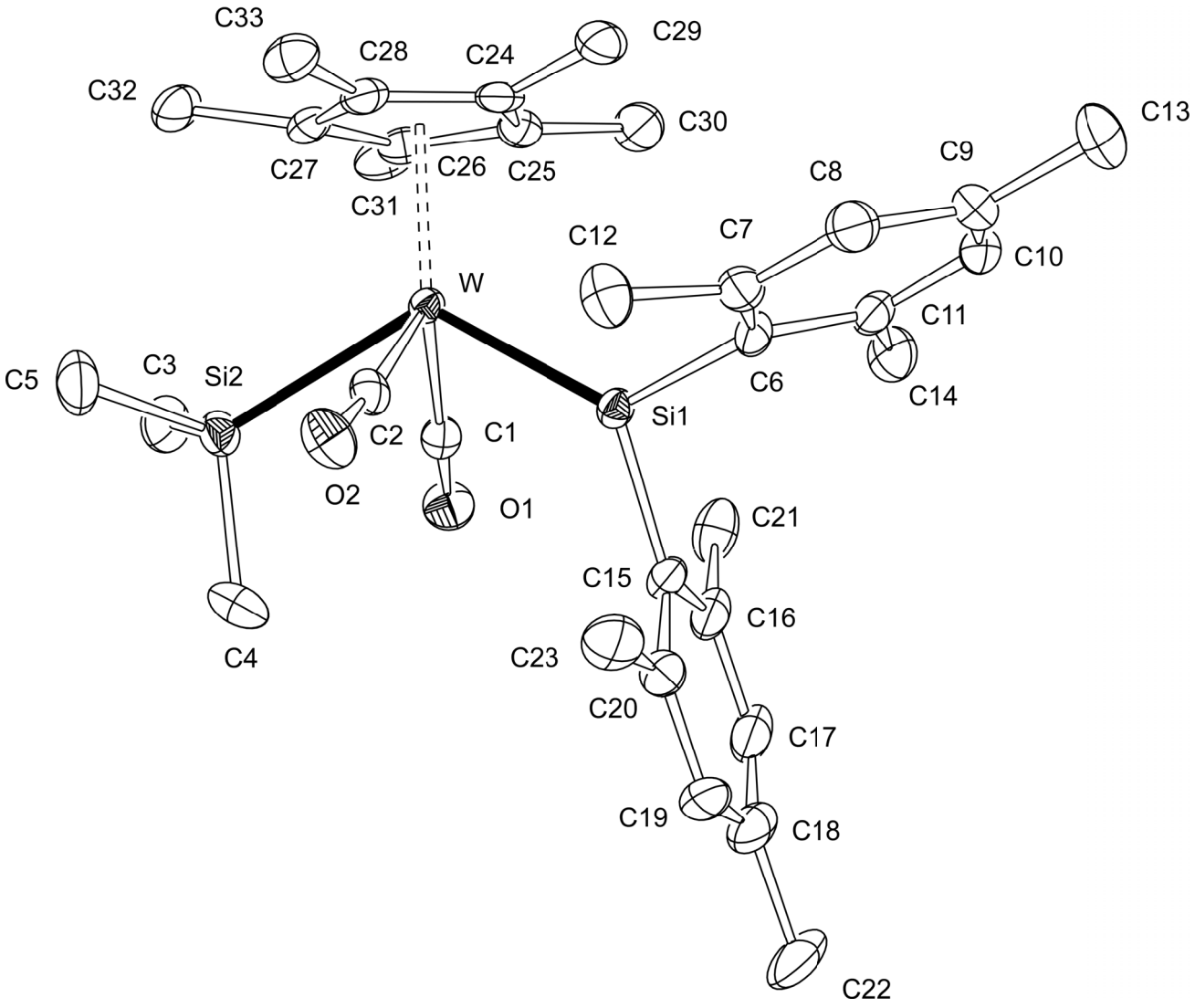

Figure S4. ORTEP drawing of **6a**. (thermal ellipsoids at the 50% probability level).

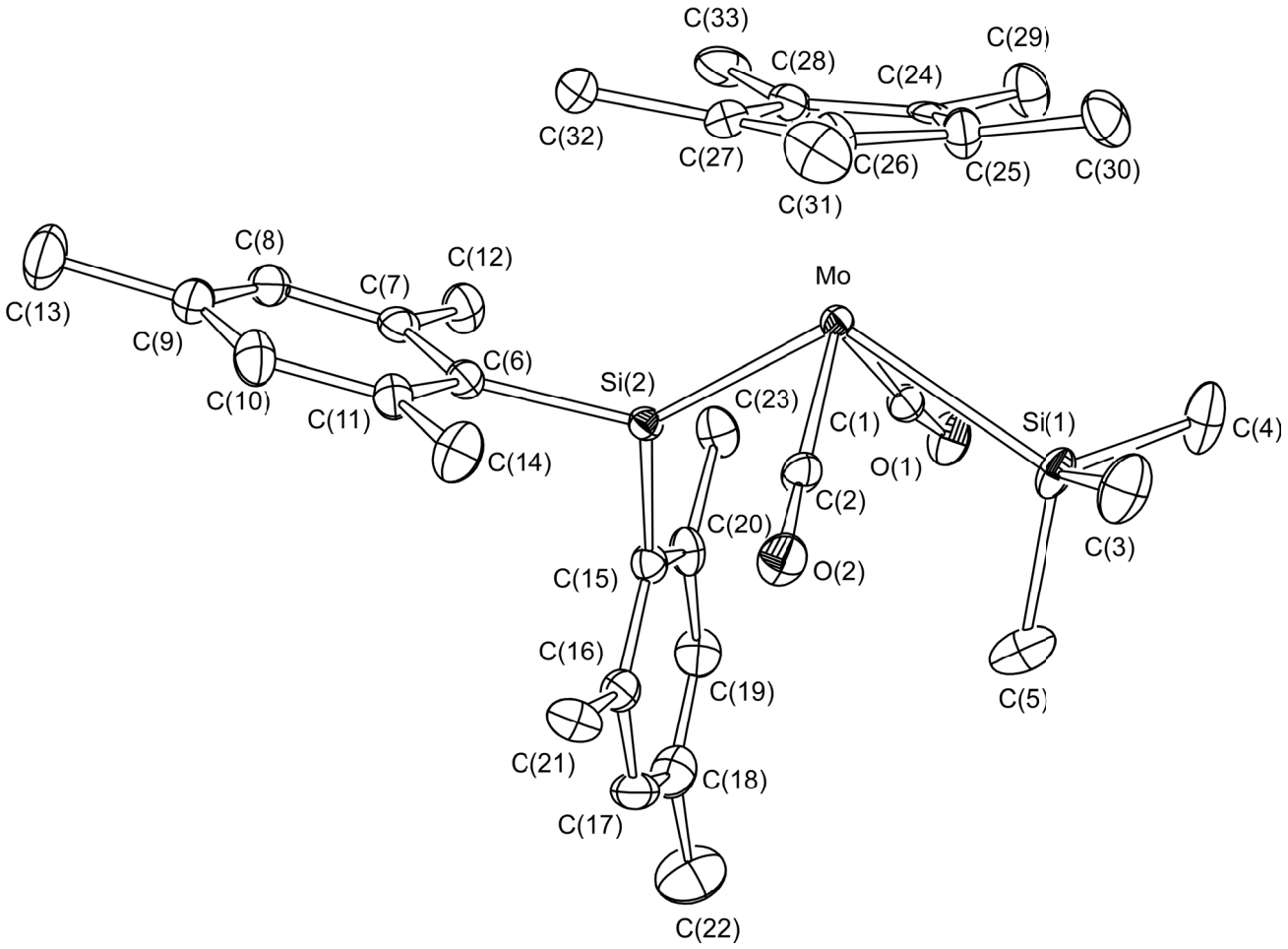

Figure S5. ORTEP drawing of **6b**. (thermal ellipsoids at the 50% probability level).

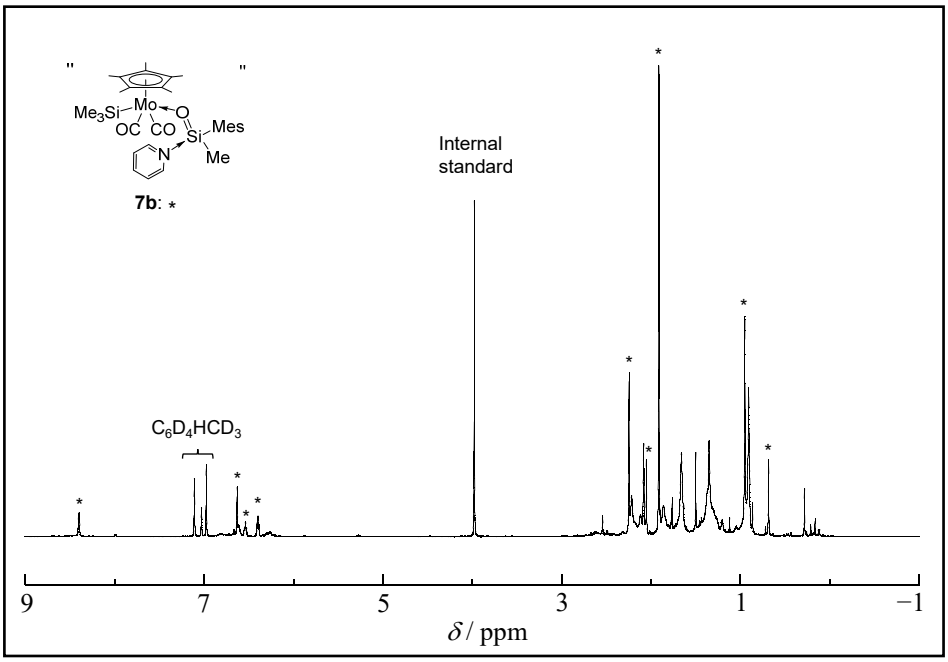

Figure S6. ^{1}H NMR spectrum of the reaction of **7b** with 1 equiv. of PNO (-15 °C, 600 MHz, C_7D_8).

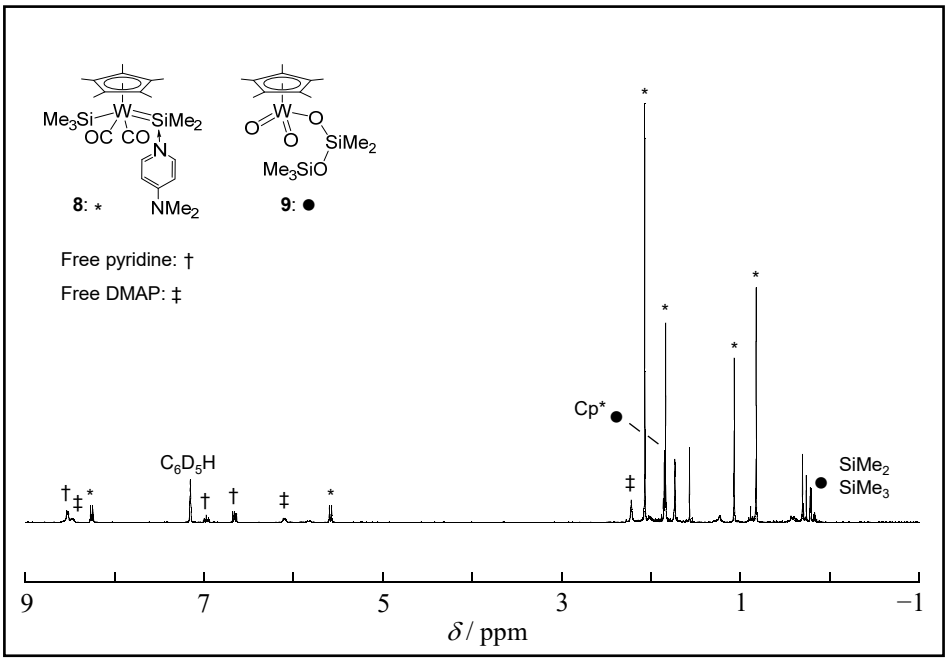

Figure S7. ^{1}H NMR spectrum of the reaction of **8** with 1 equiv. of PNO in C_6D_6 at 40 °C for 1 h (300 MHz, C_6D_6).

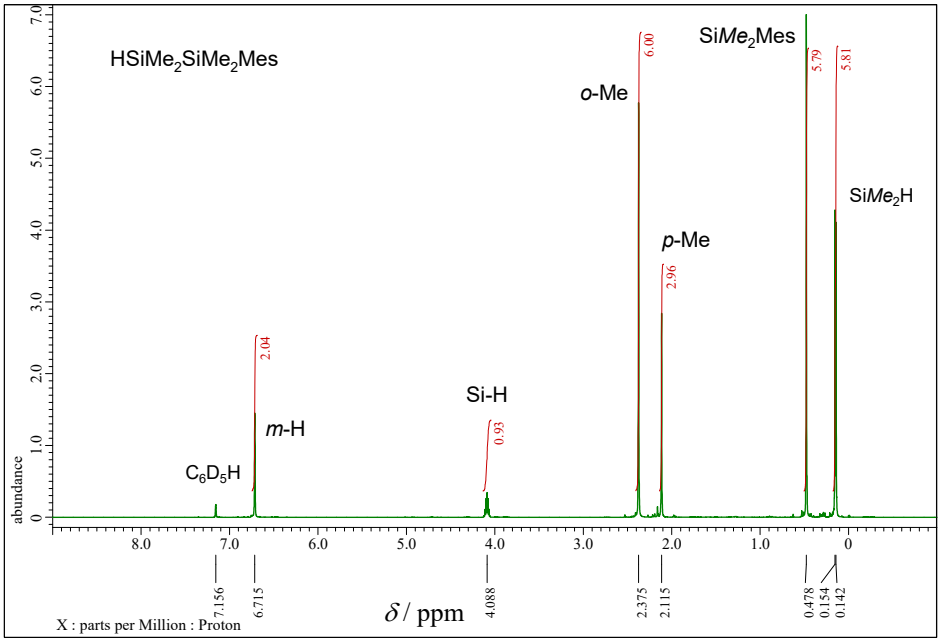

Figure S8. ^{1}H NMR spectrum of HMe2SiSiMe2Mes[2] (400 MHz, C_6D_6).

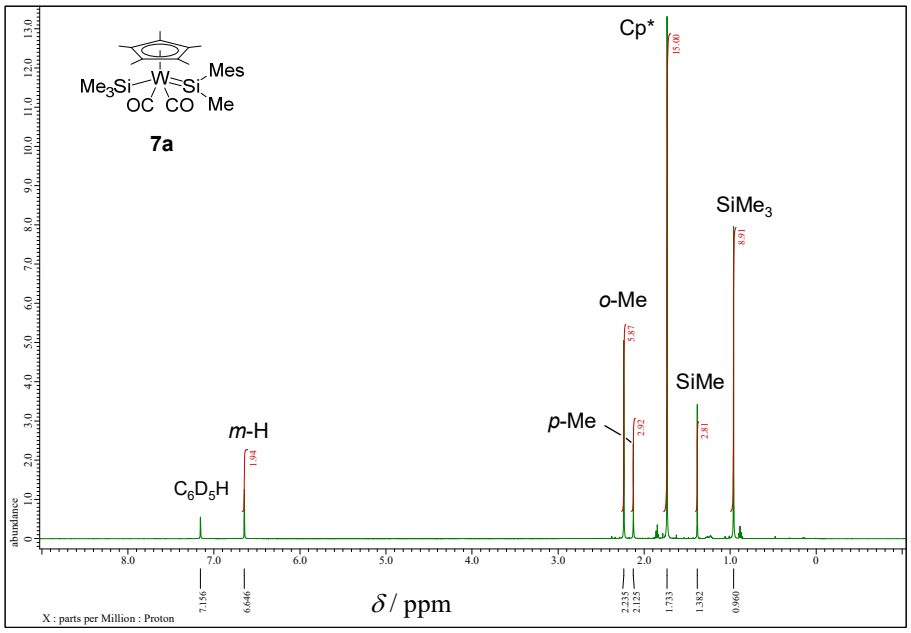

Figure S9. ^{1}H NMR spectrum of **7a** (600 MHz, C_6D_6).

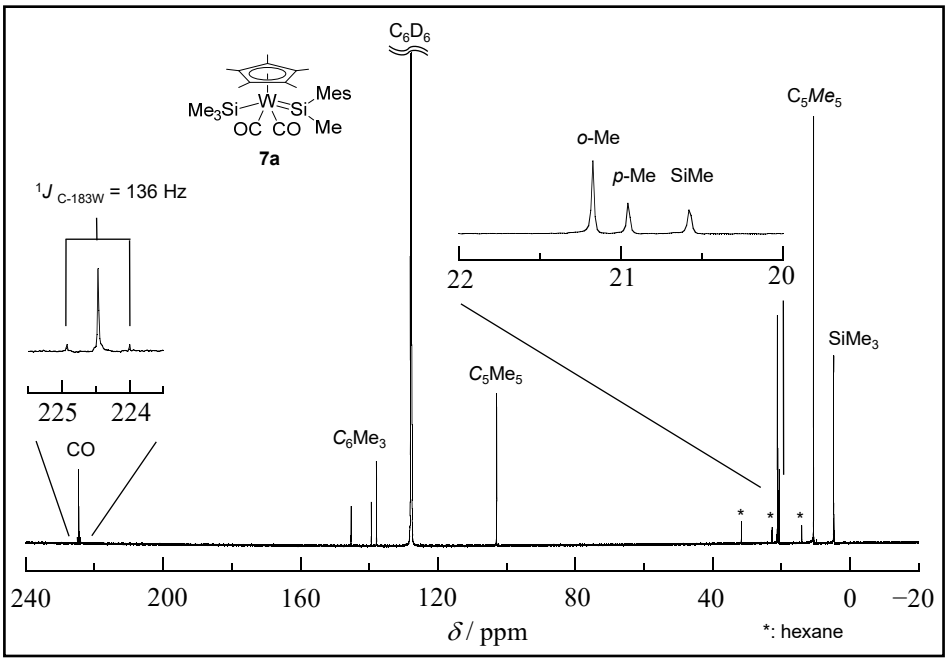

Figure S10. ^{13}C NMR spectrum of **7a** (150.9 MHz, C_6D_6).

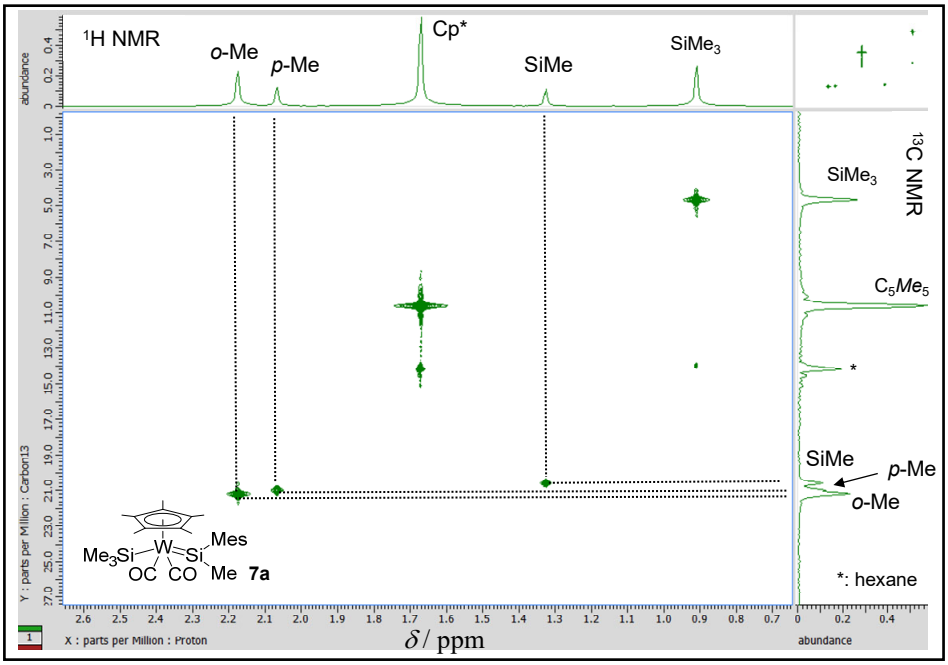

Figure S11. HMQC (^1H, ^{13}C) spectrum of **7a** (C_6D_6).

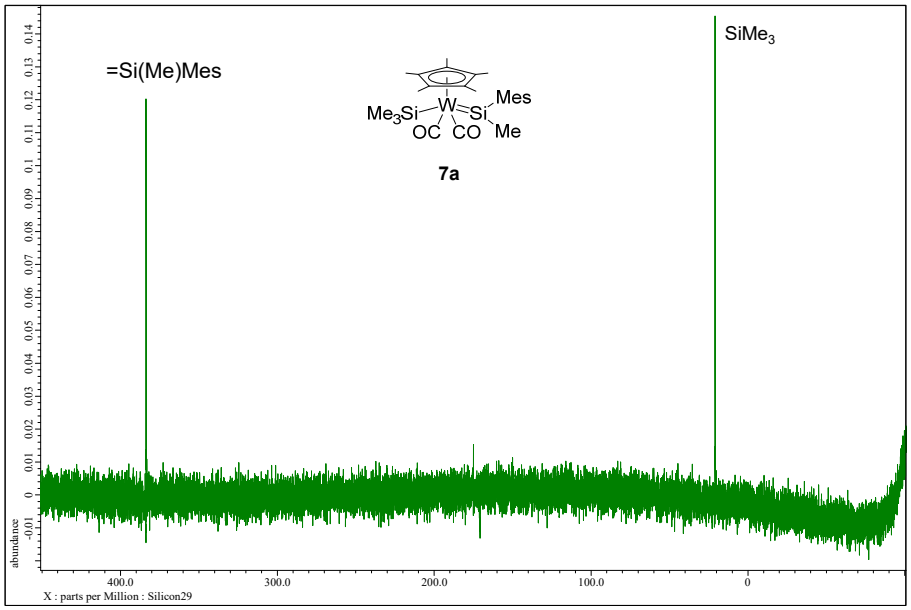

Figure S12. ^{29}Si NMR spectrum of **7a** (119.2 MHz, C_6D_6).

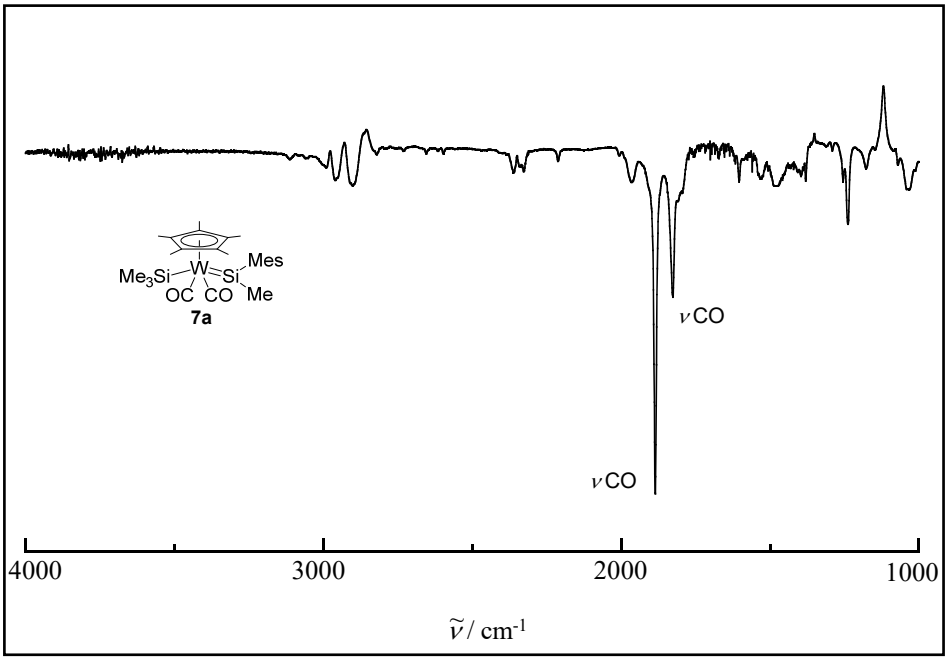

Figure S13. IR spectrum of **7a** (C_6H_6).

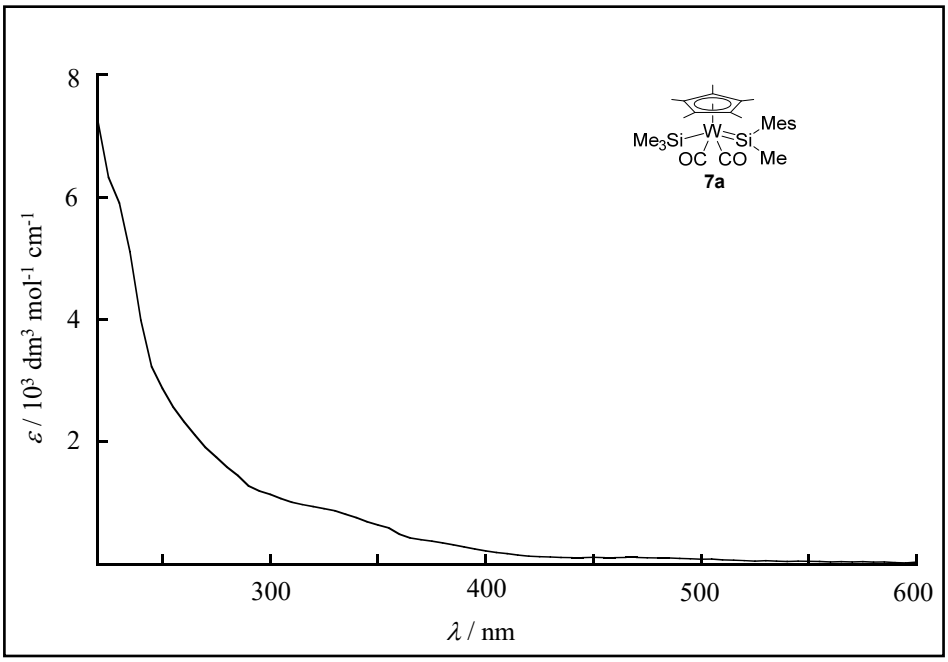

Figure S14. UV-vis spectrum of **7a** (hexane).

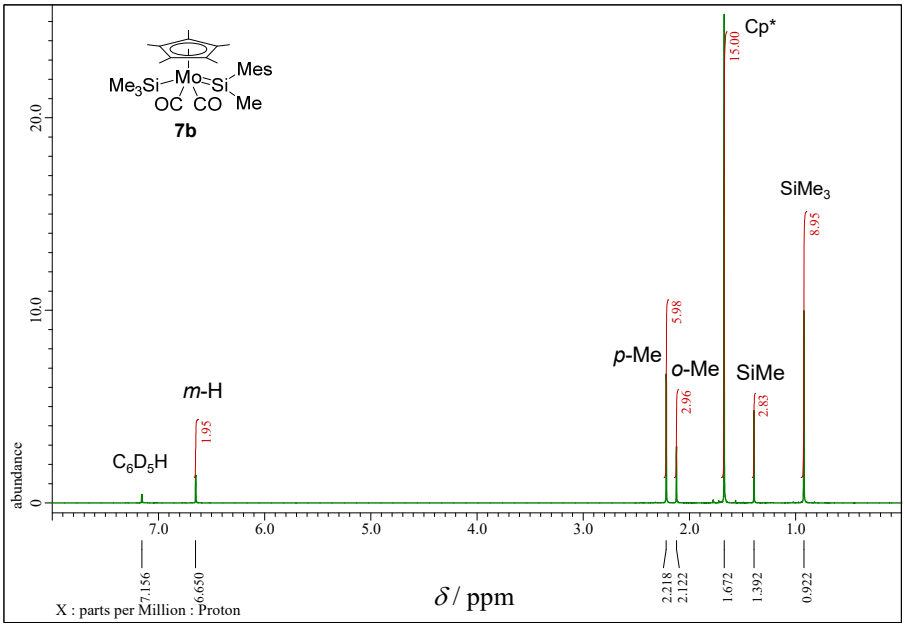

Figure S15. ^{1}H NMR spectrum of **7b** (400 MHz, C_6D_6).

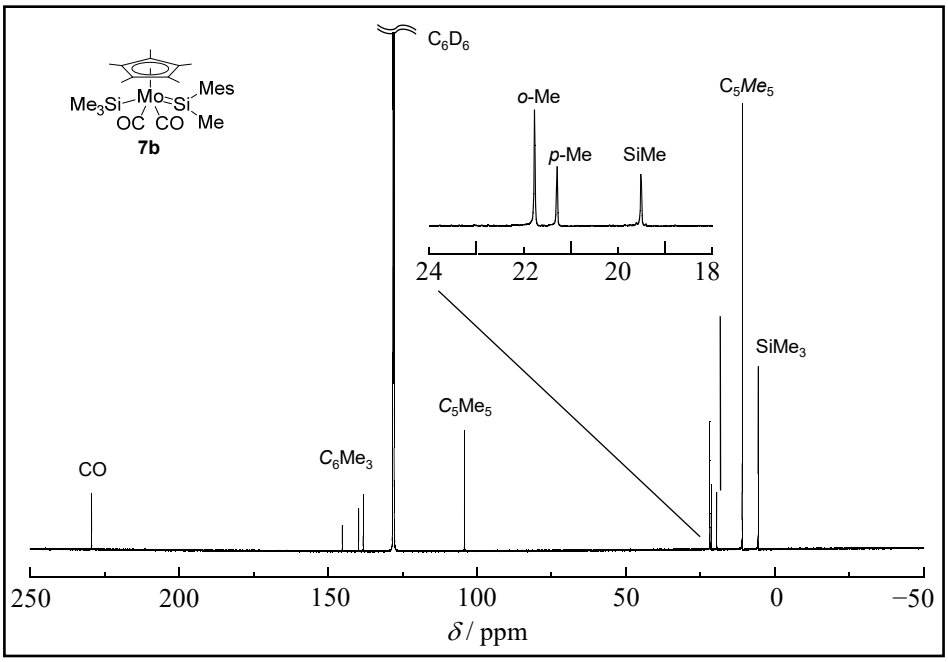

Figure S16. ^{13}C NMR spectrum of **7b** (150.6 MHz, C_6D_6).

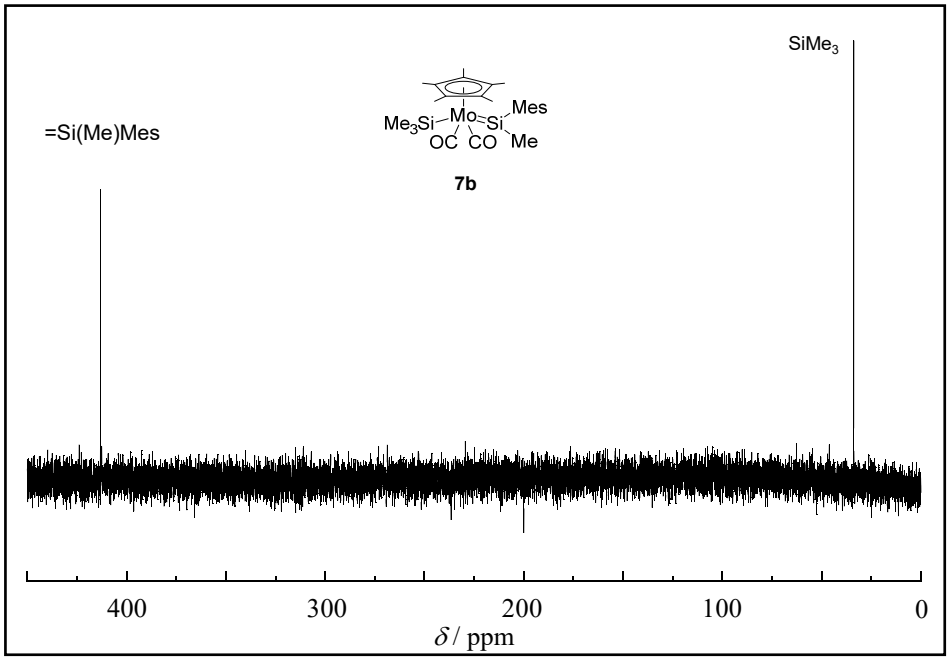

Figure S17. ^{29}Si NMR spectrum of **7b** (119.2 MHz, C_6D_6).

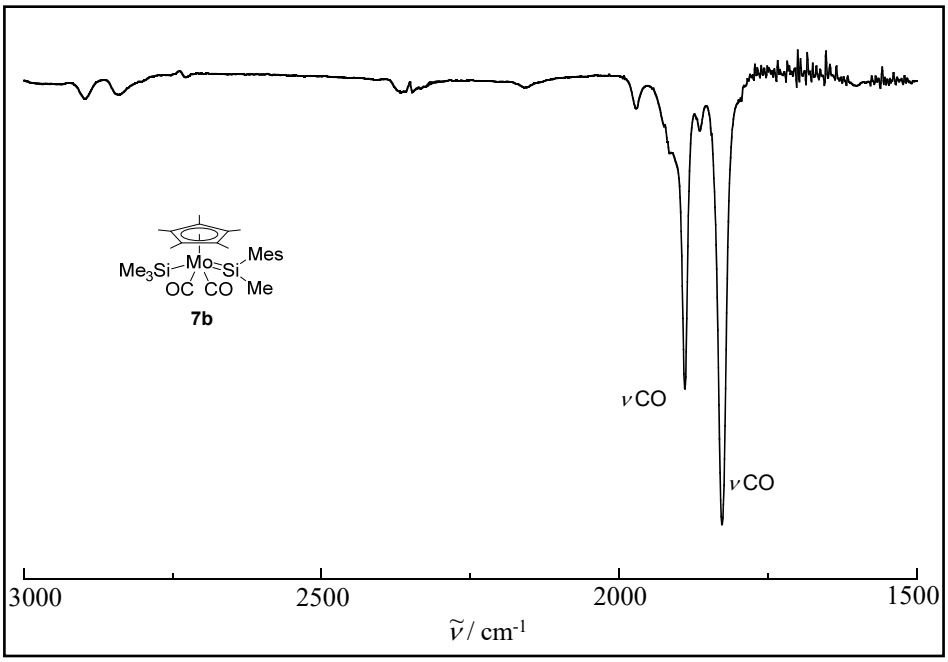

Figure S18. IR spectrum of **7b** (C_7H_8).

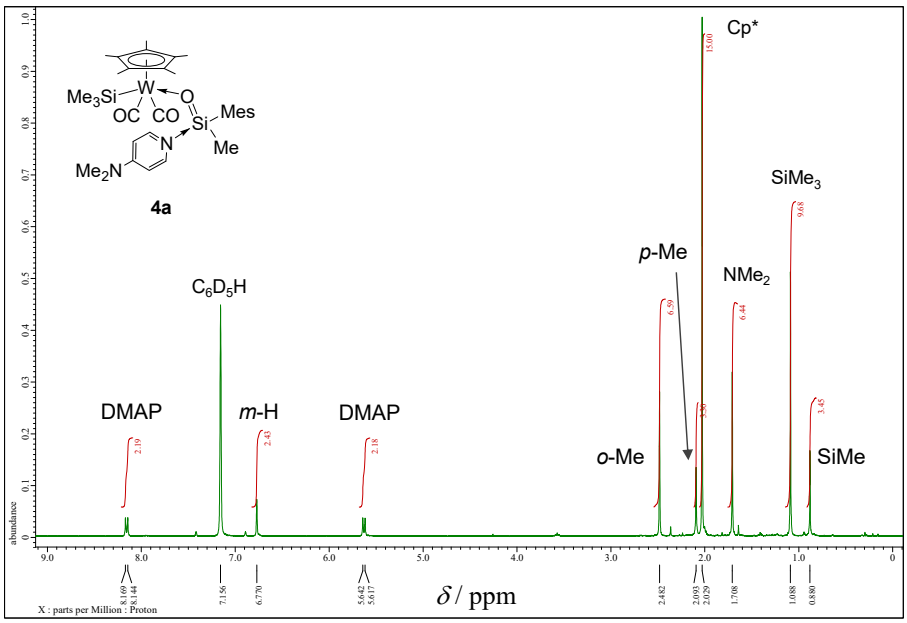

Figure S19. ^{1}H NMR spectrum of **4a** (300 MHz, C_6D_6).

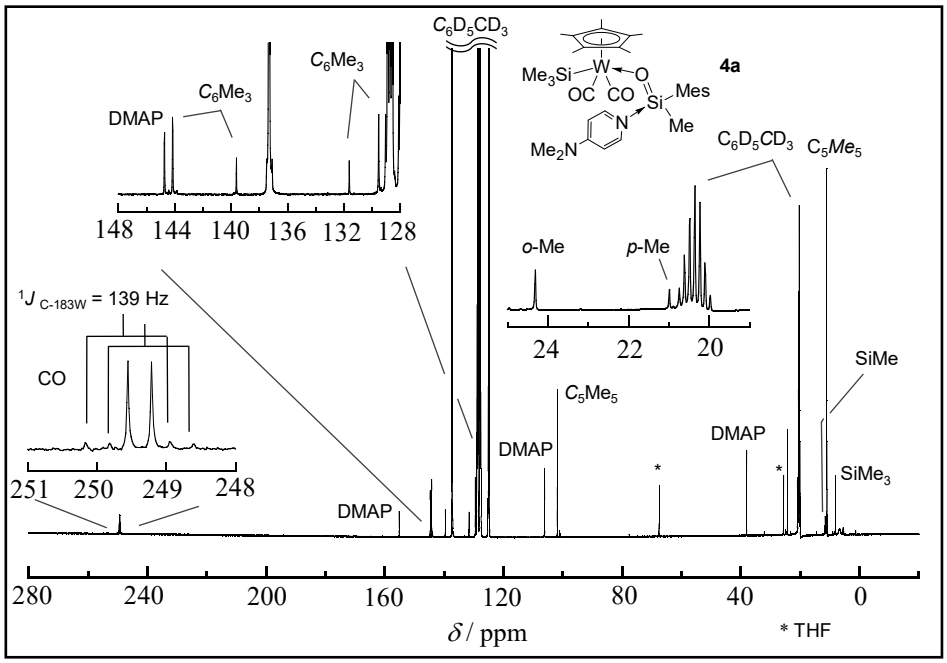

Figure S20. ^{13}C NMR spectrum of **4a** (150.6 MHz, 228 K, C_7D_8).

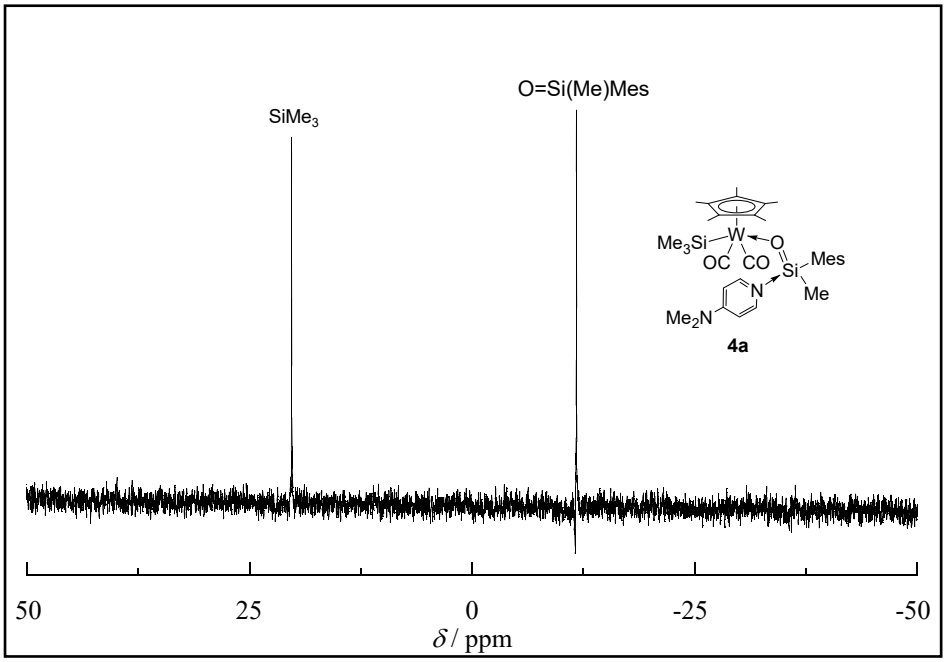

Figure S21. ^{29}Si NMR spectrum of **4a** (119.2 MHz, 228 K, C_7D_8).

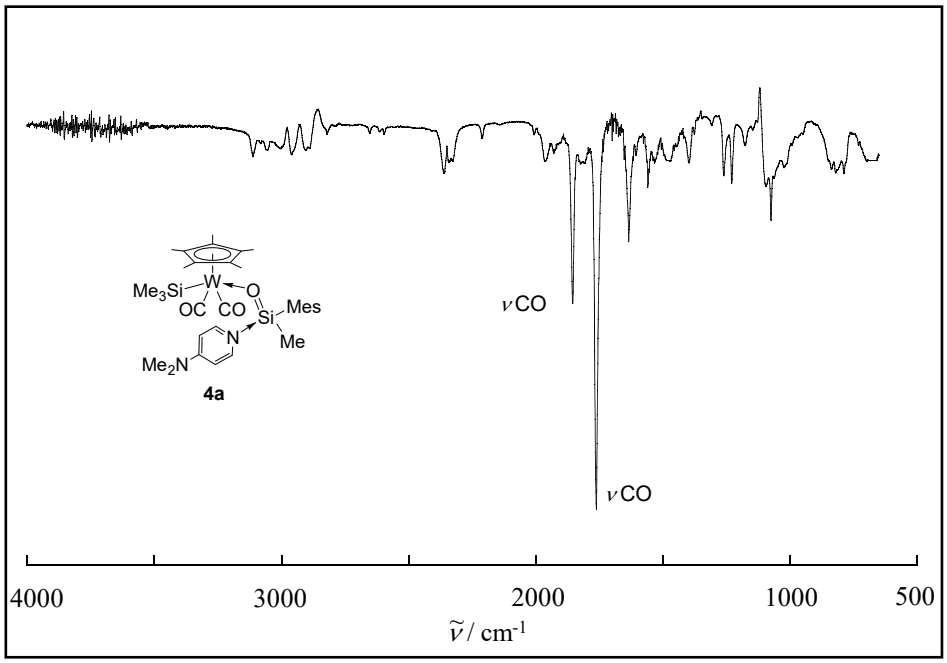

Figure S22. IR spectrum of **4a** (C_6H_6).

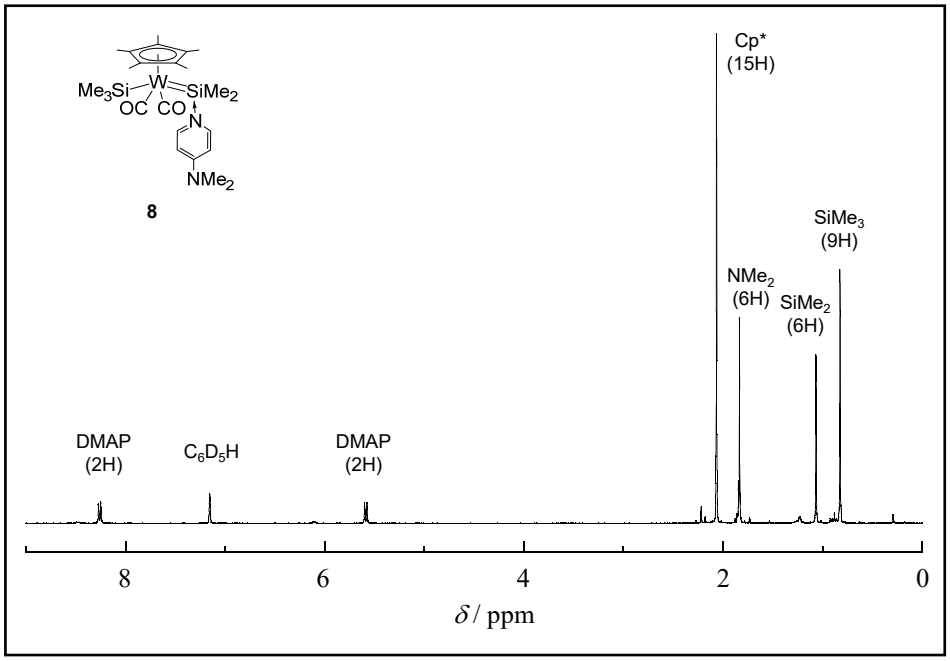

Figure S23. ^{1}H NMR spectrum of **8** (400 MHz, C_6D_6).

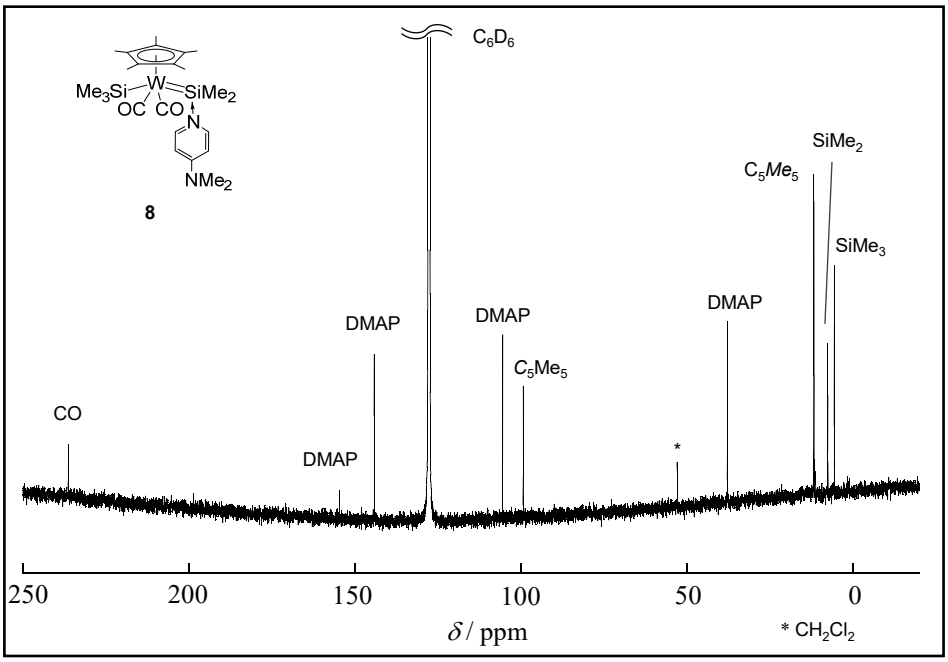

Figure S24. ^{13}C NMR spectrum of **8** (150.9 MHz, C_6D_6).

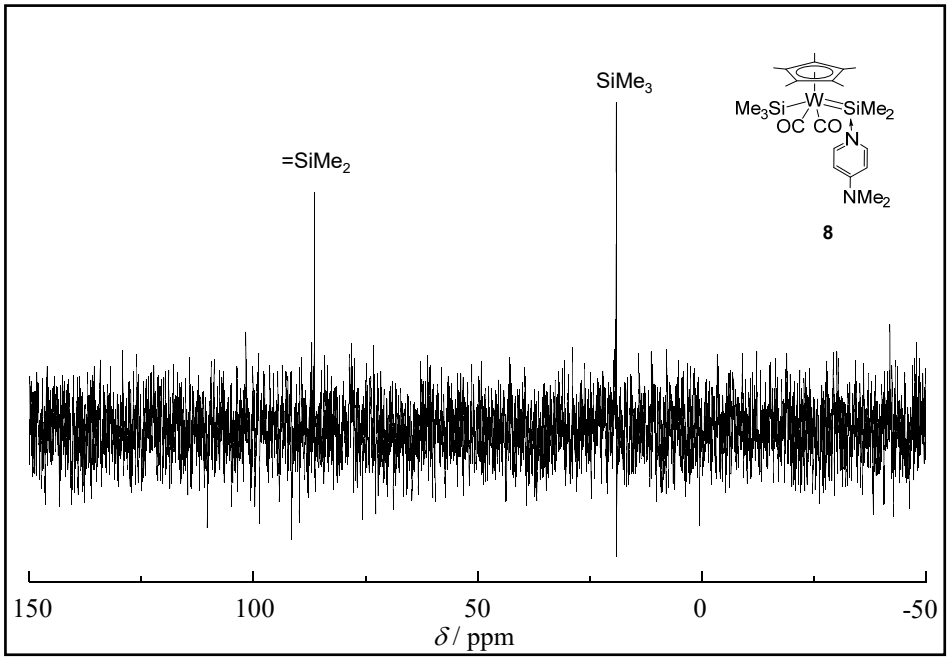

Figure S25. ^{29}Si NMR spectrum of **8** (119.2 MHz, C_6D_6).

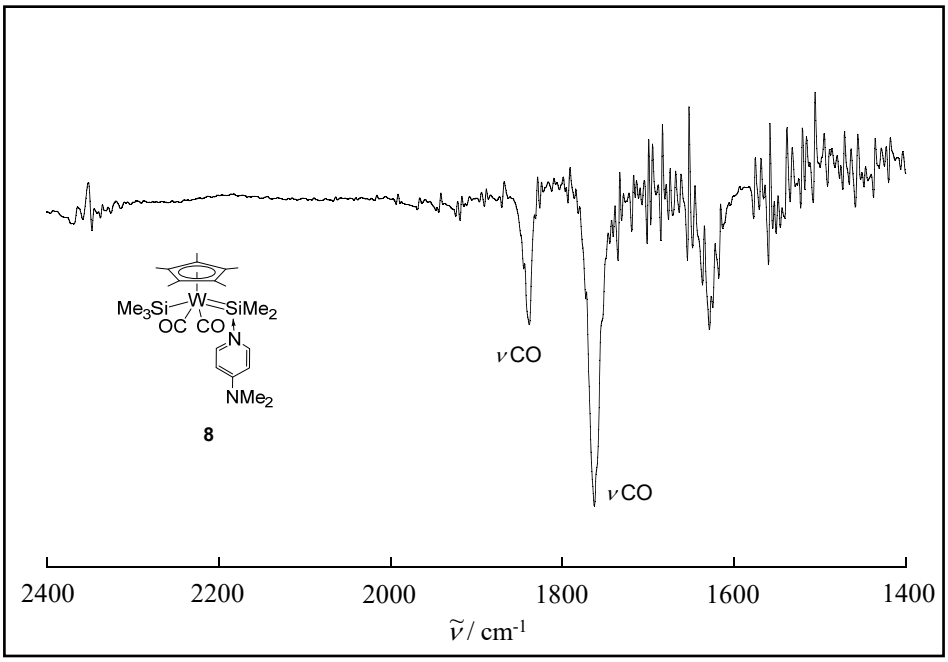

Figure S26. IR spectrum of **8** (KBr).

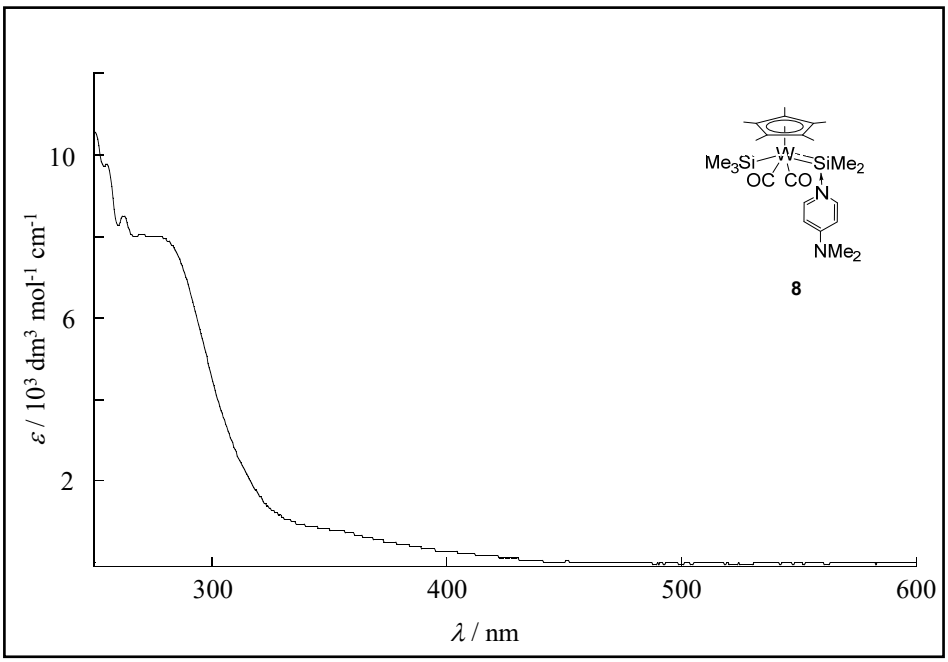

Figure S27. UV-vis spectrum of **8** (hexane).

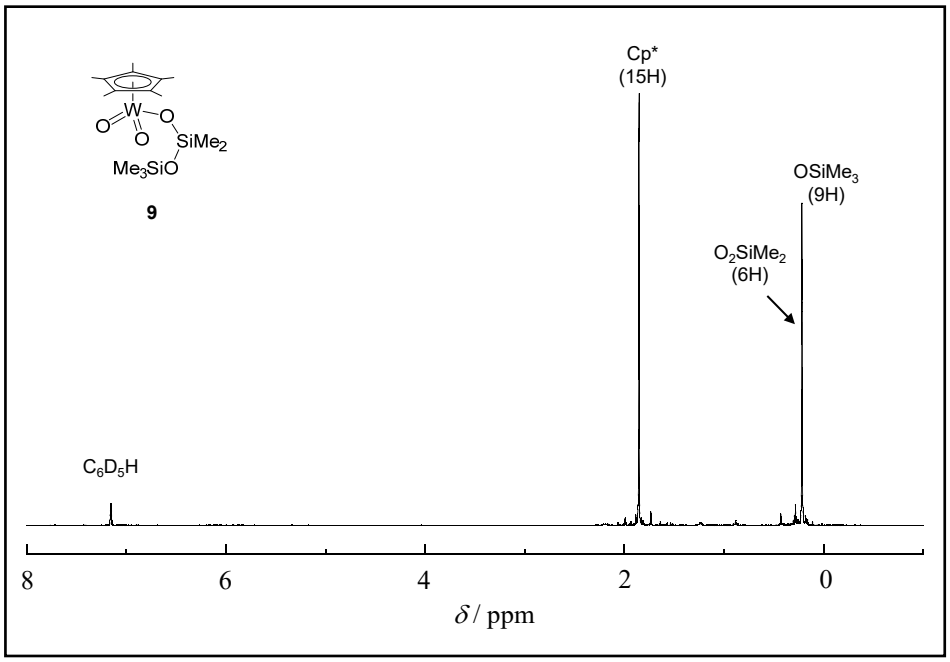

Figure S28. ^{1}H NMR spectrum of **9** (400 MHz, C_6D_6).

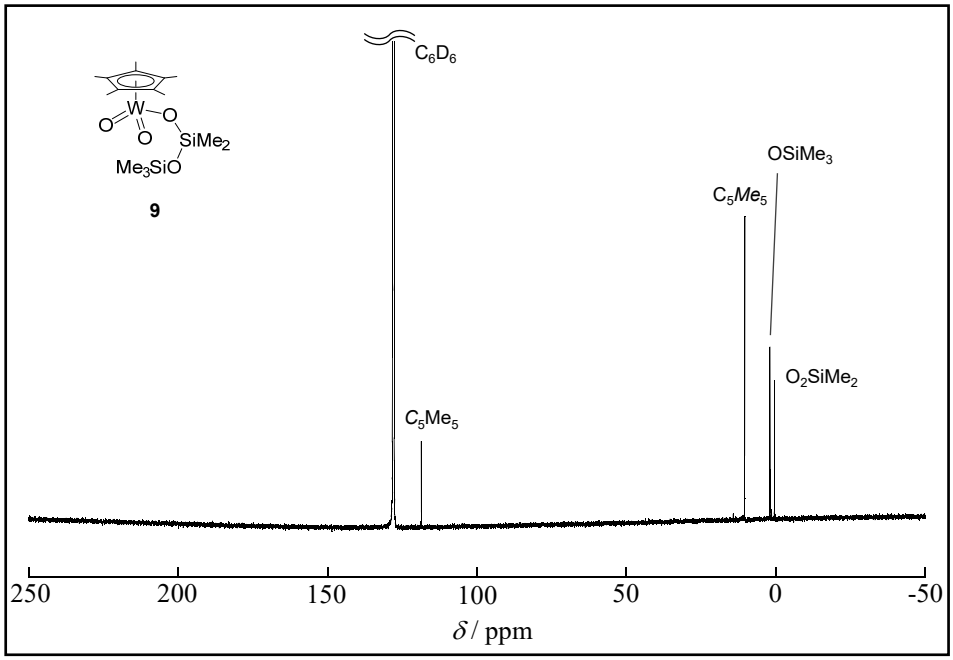

Figure S29. ^{13}C NMR spectrum of **9** (150.9 MHz, C_6D_6)

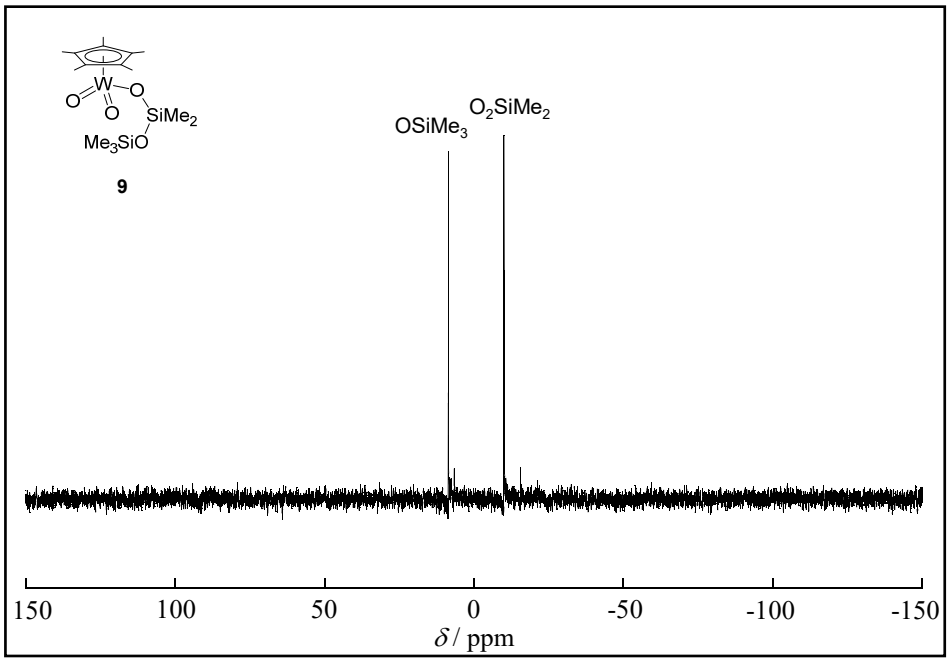

Figure S30. ^{29}Si NMR spectrum of **9** (79.4 MHz, C_6D_6).

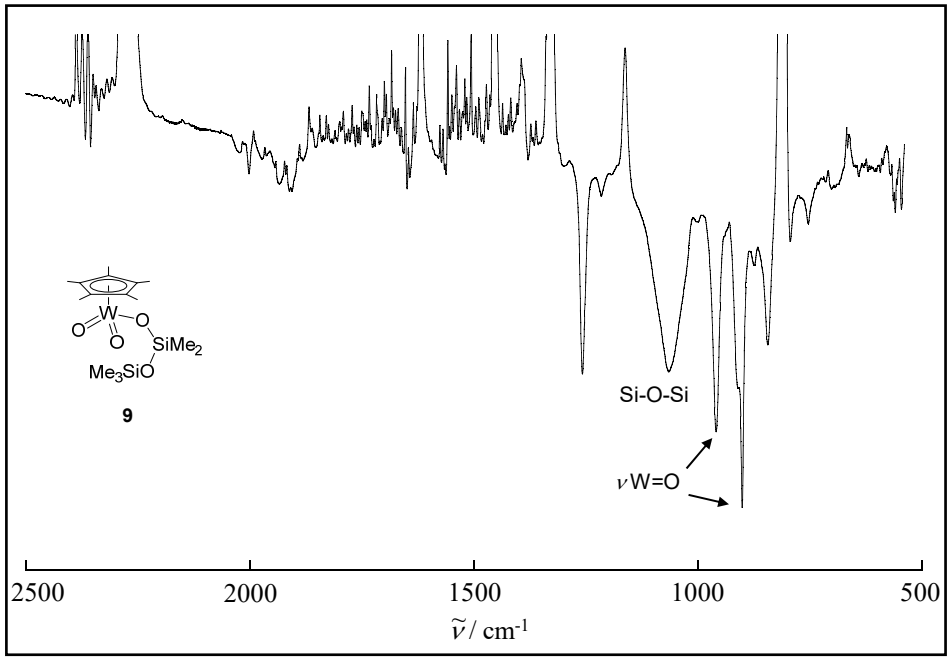

Figure S31. IR spectrum of **9** (C_6D_6).

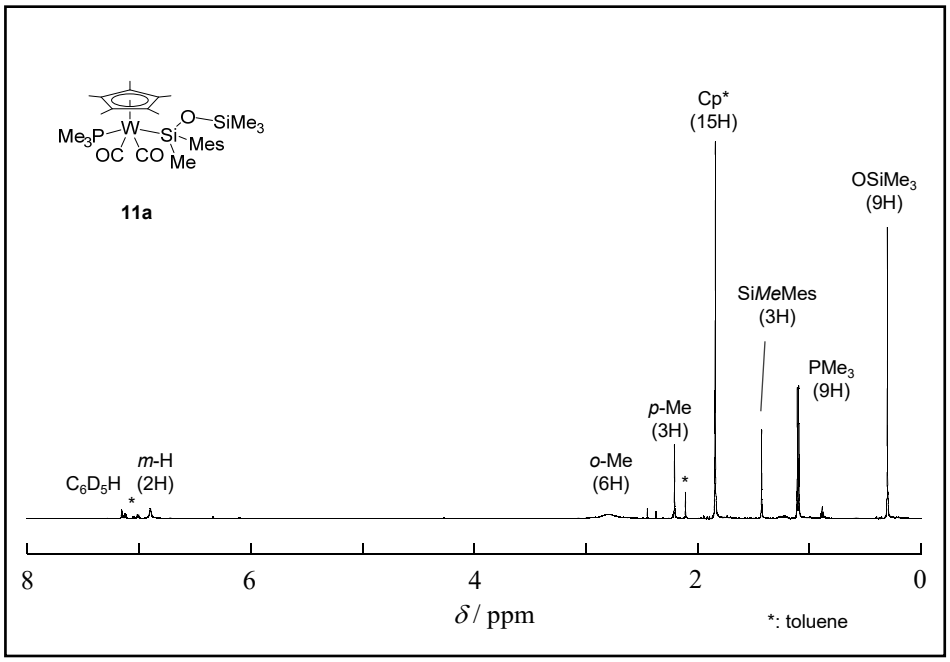

Figure S32. ^{1}H NMR spectrum of **11a** (600 MHz, C_6D_6).

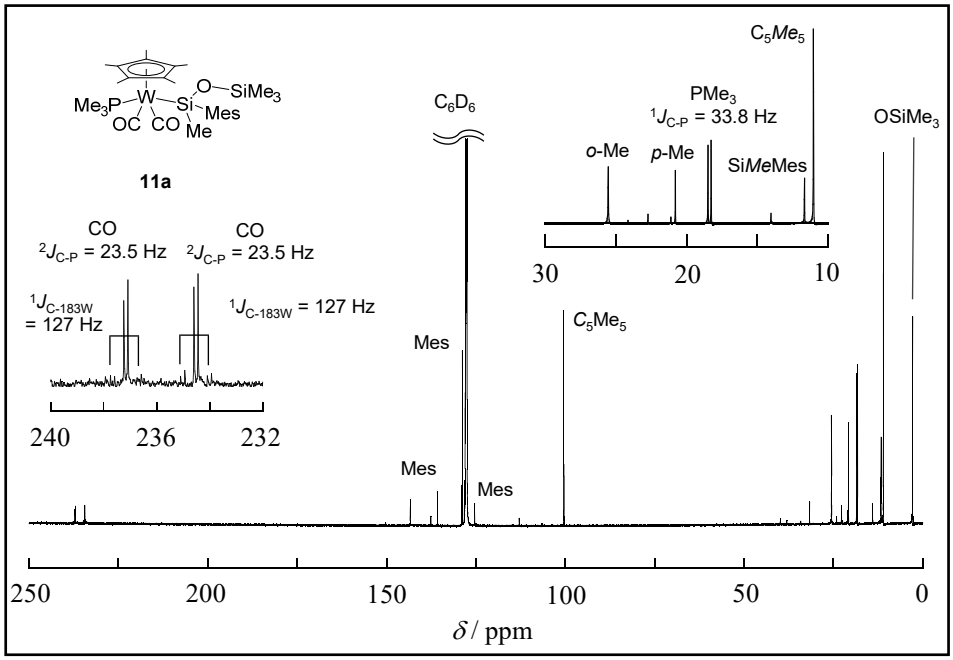

Figure S33. ^{13}C NMR spectrum of **11a** (150.9 MHz, C_6D_6).

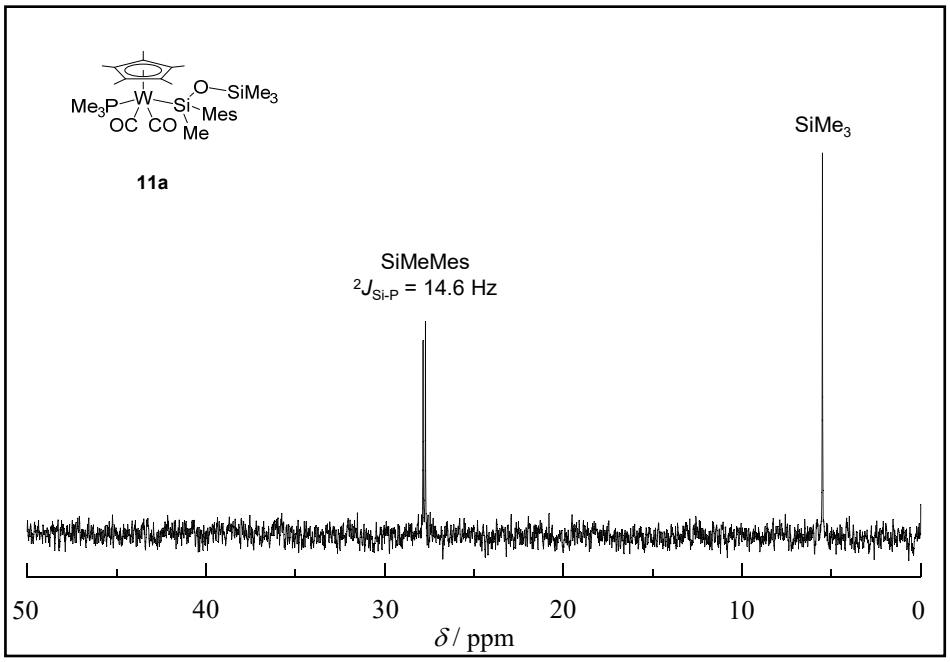

Figure S34. ^{29}Si NMR spectrum of **11a** (119.2 MHz, C_6D_6).

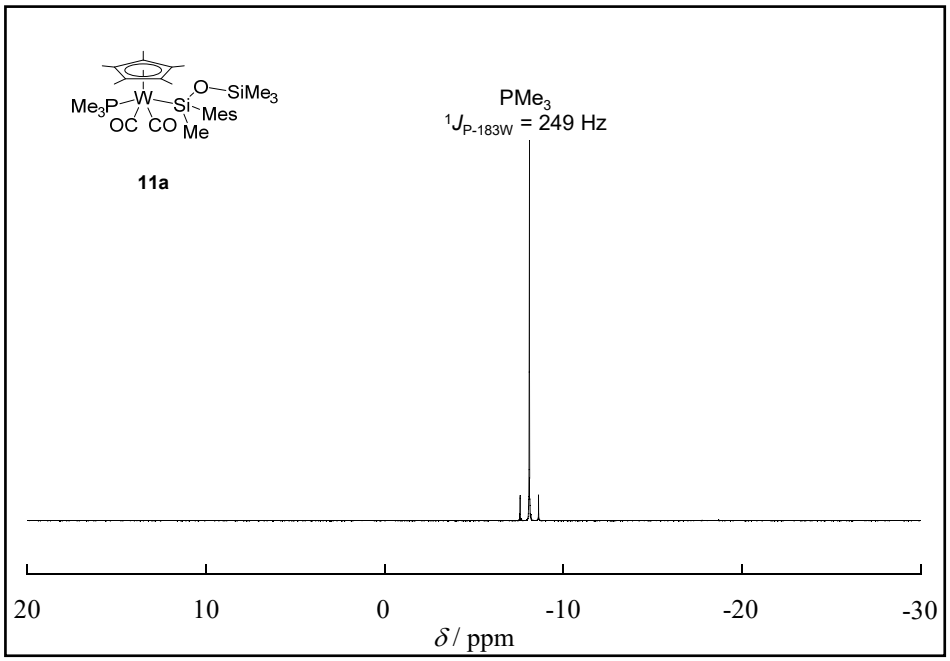

Figure S35. ^{31}P NMR spectrum of **11a** (242.9 MHz, C_6D_6).

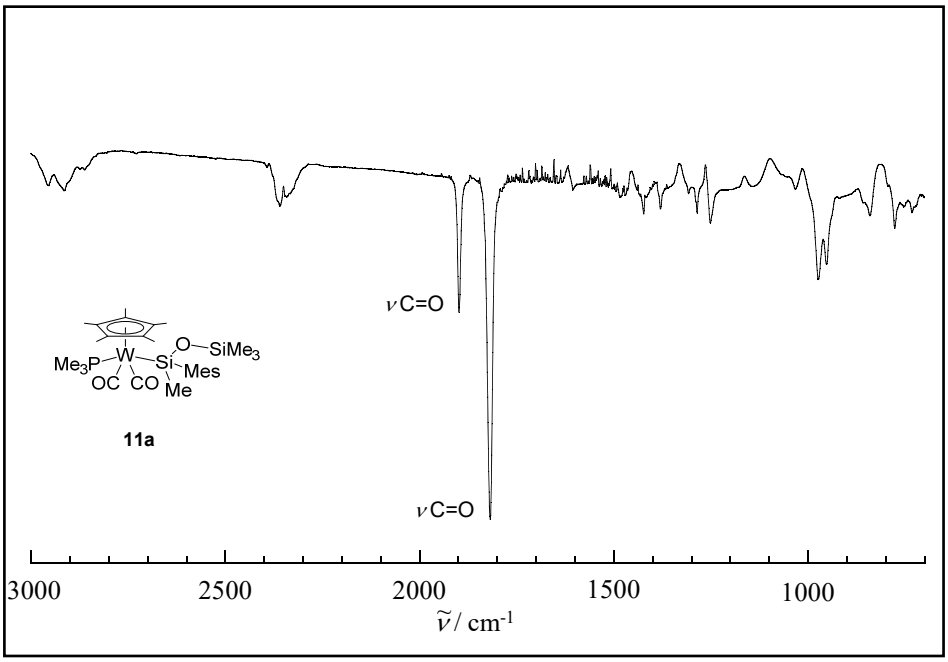

Figure S36. IR spectrum of **11a** (C_6D_6).

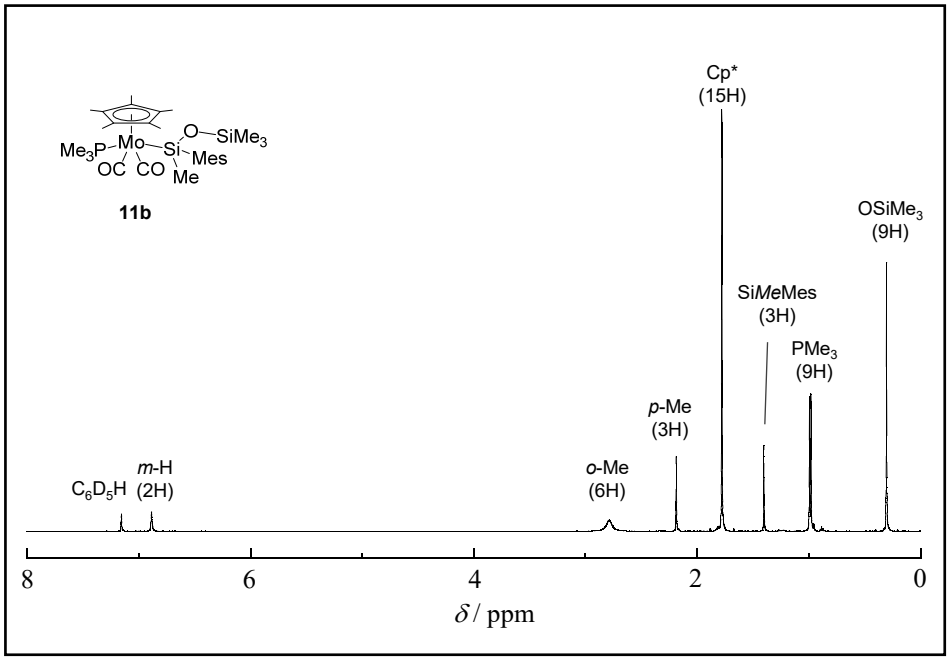

Figure S37. ^{1}H NMR spectrum of **11b** (600 MHz, C_6D_6).

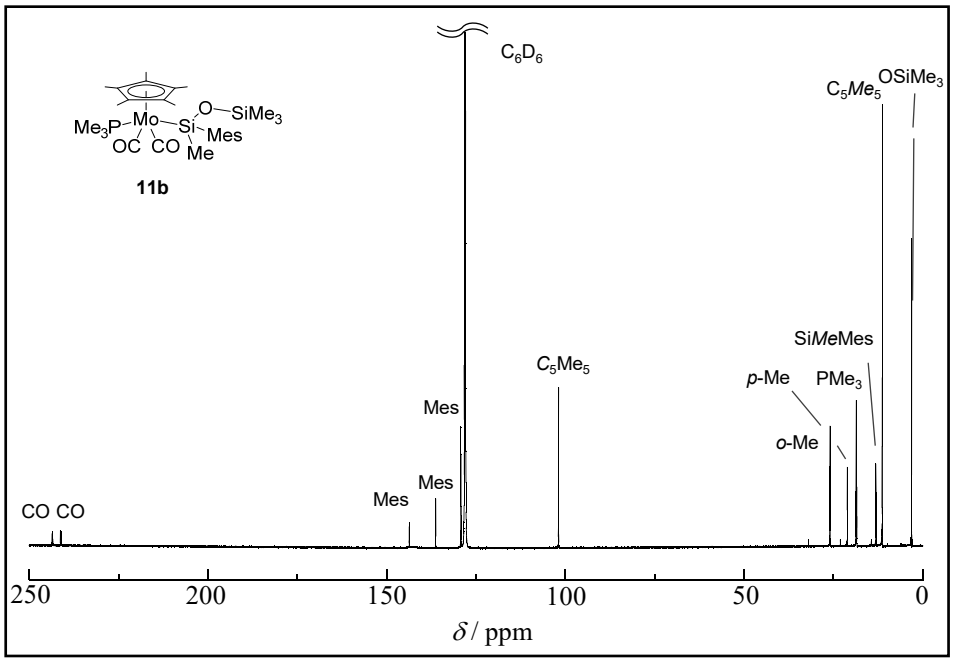

Figure S38. ^{13}C NMR spectrum of **11b** (150.9 MHz, C_6D_6).

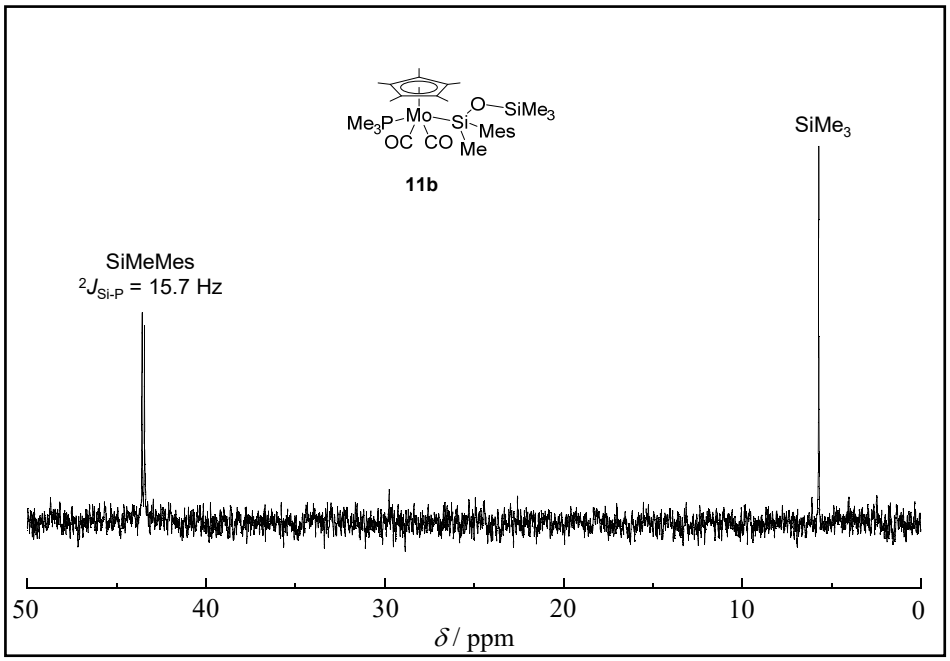

Figure S39. ^{29}Si NMR spectrum of **11b** (119.2 MHz, C_6D_6).

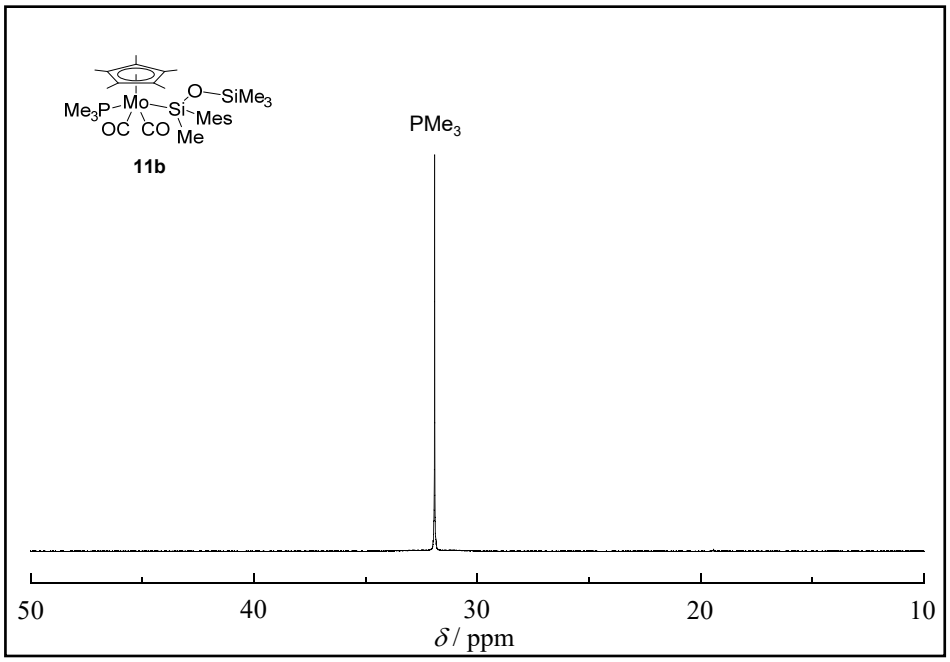

Figure S40. ^{31}P NMR spectrum of **11b** (242.9 MHz, C_6D_6).

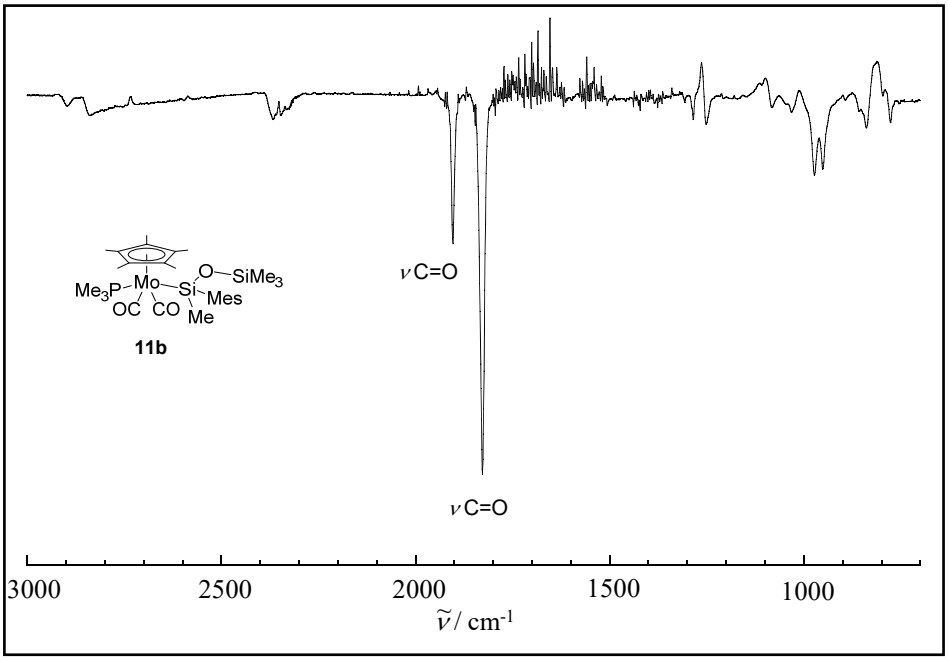

Figure S41. IR spectrum of **11b** (toluene).

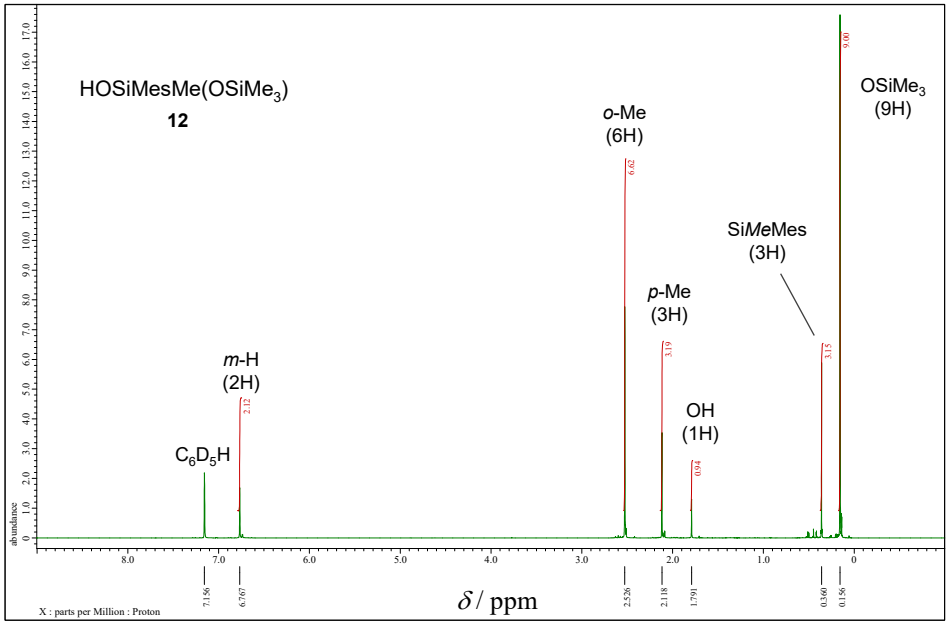

Figure S42. ^{1}H NMR spectrum of **12** (600 MHz, C_6D_6).

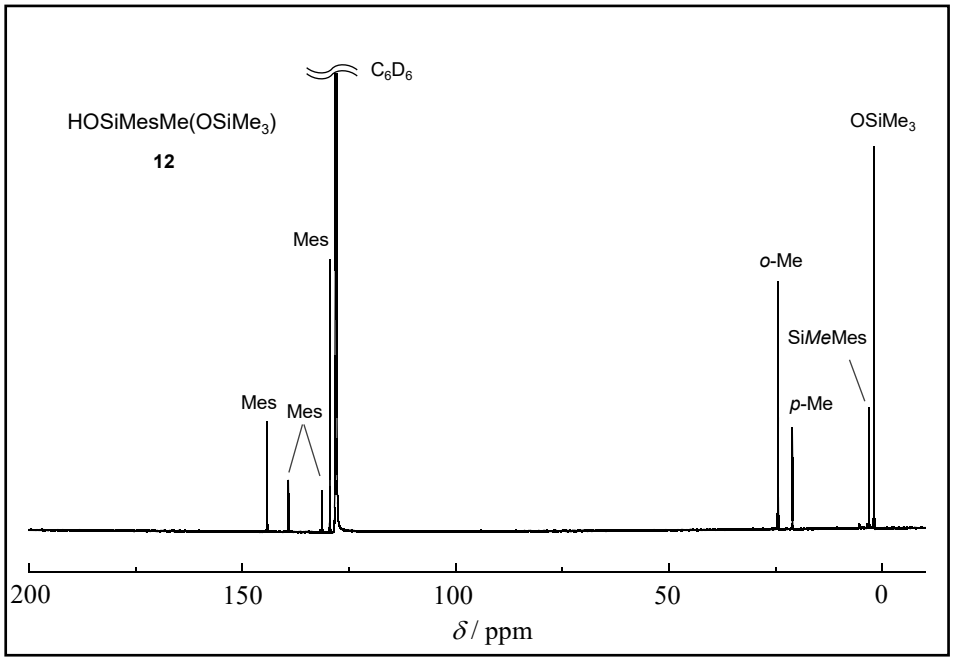

Figure S43. ^{13}C NMR spectrum of **12** (150.9 MHz, C_6D_6).

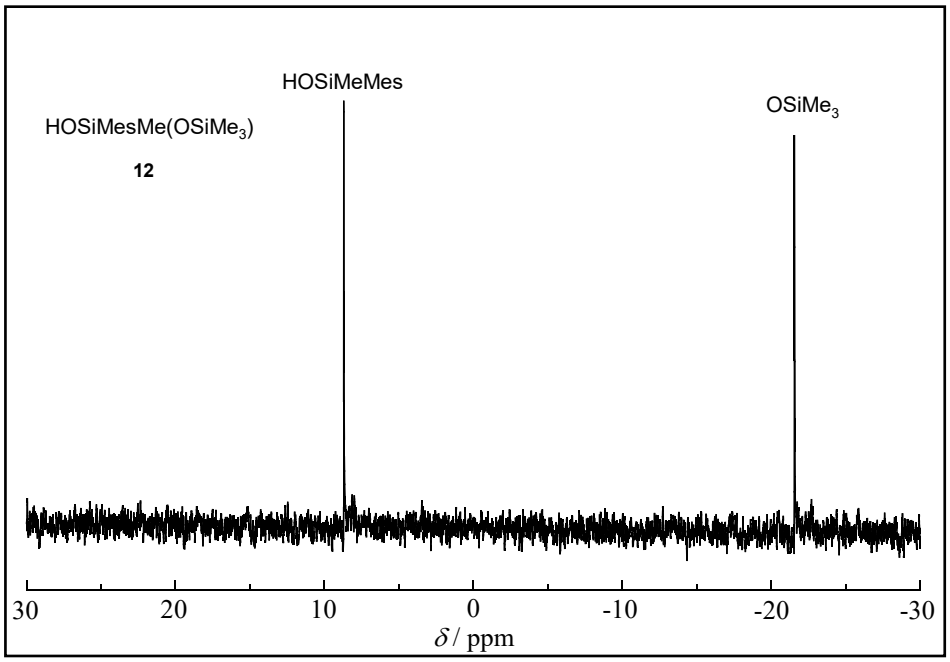

Figure S44. ^{29}Si NMR spectrum of **12** (119.2 MHz, C_6D_6).

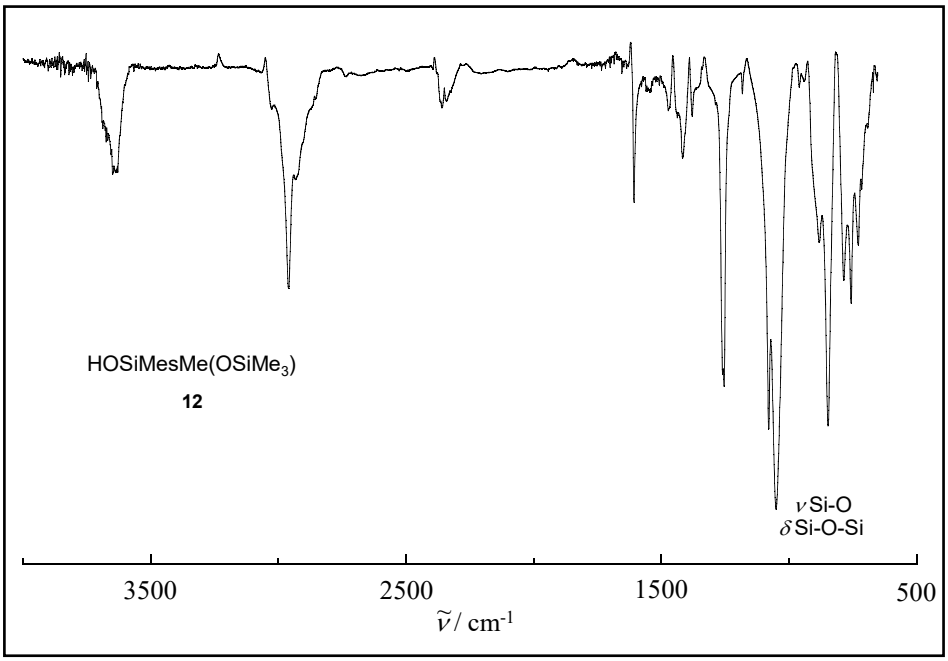

Figure S45. IR spectrum of **12** (C_6D_6).

References

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2. J. Braddock-Wilking, M. Y. Chiang, P. P. Gaspar, *Organometallics* 1993, **12**, 197.