

“Chemistry of thermally generated transient phosphanoxyl complexes”

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1) Crystallographic data:

Crystal structure data for complex **2** ($C_{34}H_{20}O_{11}P_2W_2$): $M = 1034.14$ g/mol, triclinic, $P\bar{1}$, $a = 10.2599(2)$ Å, $b = 11.1737(5)$ Å, $c = 16.8611(7)$ Å, $\alpha = 87.0036(15)^\circ$, $\beta = 83.4521(15)^\circ$, $\gamma = 62.6796(14)^\circ$, $V = 1706.16(13)$ Å³, $Z = 2$, $\rho_{\text{calcd.}} = 2.013$ g/cm³, $\mu = 6.890$ mm⁻¹, $T = 100$ K. A total of 32716 reflections were measured with a Bruker X8-KappaApexII diffractometer by using monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å), 10323 of which were unique ($R_{\text{int}} = 0.0420$, $R_{\text{sigma}} = 0.0470$). An empirical absorption correction was applied (min./max. transmission 0.3176/0.6478). The structure was solved by Patterson methods and refined by full-matrix least-squares fitting against F^2 for all reflections. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined as rigid groups. R values [$I > 2\sigma(I)$]: $R_1 = 0.0256$, $wR_2 = 0.0471$. R values (all data): $R_1 = 0.0283$, $wR_2 = 0.0484$, min./max. electron difference $-1.15/1.23$ e/Å³.

Crystal structure data for complex **3** ($C_{29}H_{20}O_7P_2W_2$): $M = 726.24$ g/mol, monoclinic, $P2_1/c$, $a = 12.7231(2)$ Å, $b = 12.8886(3)$ Å, $c = 19.6359(3)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 119.9890(10)^\circ$, $V = 2788.87(9)$ Å³, $Z = 4$, $\rho_{\text{calcd.}} = 1.730$ Mg/m³, $\mu = 4.302$ mm⁻¹, $T = 123(2)$ K. A total of 82246 reflections were measured with a STOE IPDS2T diffractometer by using monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å), 6705 of which were unique ($R_{\text{int}} = 0.0395$). An absorption correction by integration was applied (min./max. transmission 0.6263/0.7824). The structure was solved by Patterson methods and refined by full-matrix least-squares fitting against F^2 for all reflections. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined as rigid groups. R values [$I > 2\sigma(I)$]: $R_1 = 0.0297$, $wR_2 = 0.0555$. R values (all data): $R_1 = 0.0317$, $wR_2 = 0.0560$, min./max. electron difference $-1.019/1.266$ e/Å³.

Crystal structure data for complex **6b** ($C_{35}H_{25}O_6PSnW$): $M = 875.06$ g/mol, monoclinic, $P2_1/n$, $a = 12.7649(9)$ Å, $b = 16.8829(13)$ Å, $c = 15.0318(11)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 91.612(2)^\circ$, $V = 3228.6(4)$ Å³, $Z = 4$, $\rho_{\text{calcd.}} = 1.800$ g/cm³, $\mu = 4.427$ mm⁻¹, $T = 100$ K. A total of 38720 reflections were measured with a Bruker X8-KappaApexII diffractometer by using monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å), 7779 of which were unique ($R_{\text{int}} = 0.0306$). An empirical absorption correction was applied (min./max. transmission 0.5534/0.7459). The structure was solved by Patterson methods and refined by full-matrix least-squares fitting against F^2 for all reflections. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined as rigid groups. R values [$I > 2\sigma(I)$]: $R_1 = 0.0164$, $wR_2 = 0.0360$. R values (all data): $R_1 = 0.0199$, $wR_2 = 0.0374$, min./max. electron difference $-0.72/0.79$ e/Å³.

Crystal structure data for complex **6c** ($C_{35}H_{25}O_6PGeW$): $M = 828.96$ g/mol, monoclinic, $P2_1/n$, $a = 9.6516(2)$ Å, $b = 20.8528(6)$ Å, $c = 15.5258(3)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 90.4370(10)^\circ$, $V = 3124.68(13)$ Å³, $Z = 4$, $\rho_{\text{calcd.}} = 1.762$ g/cm³, $\mu = 4.737$ mm⁻¹, $T = 100(2)$ K. A total of 19231 reflections were measured with a Bruker X8-KappaApexII diffractometer by using monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å), 7437 of which were unique ($R_{\text{int}} = 0.0419$). A numerical absorption correction was applied (min./max. transmission 0.5050/0.7461). The structure was solved by Patterson methods and refined by full-matrix least-squares fitting against F^2 for all reflections. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined as rigid groups. R values [$I > 2\sigma(I)$]: $R_1 = 0.0341$, $wR_2 = 0.0576$. R values (all data): $R_1 = 0.0439$, $wR_2 = 0.0641$, min./max. electron difference $-0.87/1.35$ e/Å³.

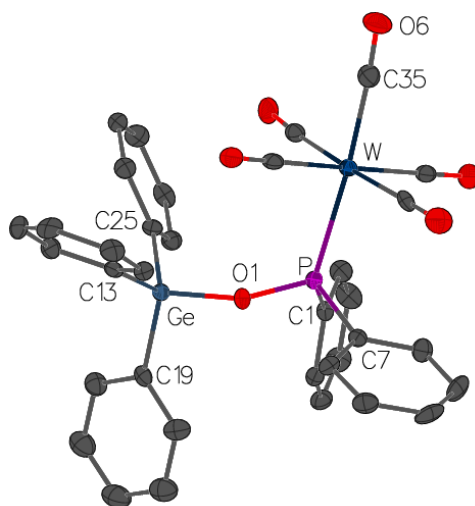


Figure S1. Molecular structure of complex **6c** (50 % probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (in Å) and angles (in °): W–P 2.4945(11), C1–P 1.830(4), C7–P 1.827(4), O1–P 1.600(3), O1–Ge 1.809(3), P–O1–Ge 140.67(17), W–P–C1 118.46(14), W–P–C7 111.85(14), W–P–O1 116.61(11), O1–P–C1 105.43(18), O1–P–C7 99.54(17), C1–P–C7 102.45(18).

Crystal structure data for complex **6d** ($C_{35}H_{25}O_6PSiW$): $M = 784.46$ g/mol, monoclinic, $P2_1/n$, $a = 9.6677(4)$ Å, $b = 21.2689(8)$ Å, $c = 15.2926(6)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 90.136(2)^\circ$, $V = 3144.5(2)$ Å³, $Z = 4$, $\rho_{\text{calcd.}} = 1.657$ g/cm³, $\mu = 3.808$ mm⁻¹, $T = 123(2)$ K. A total of 34914 reflections were measured with a Nonius KappaCCD diffractometer by using monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å), 7486 of which were unique ($R_{\text{int}} = 0.0659$). An empirical absorption correction was applied (min./max. transmission 0.5709/0.7461). The structure was solved by Patterson methods and refined by full-matrix least-squares fitting against F^2 for all reflections. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined as rigid groups. R values [$I > 2\sigma(I)$]: $R_1 = 0.0324$, $wR_2 = 0.0589$. R values (all data): $R_1 = 0.0561$, $wR_2 = 0.0650$, min./max. electron difference $-1.35/0.92$ e/Å³.

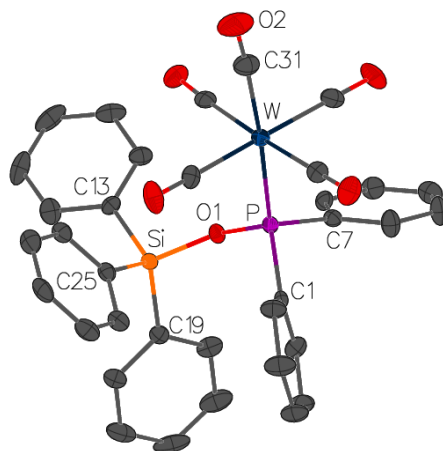


Figure S2. Molecular structure of complex **6d** (50 % probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (in Å) and angles (in °): W–P 2.4866(9), C1–P 1.835(4), C7–P 1.822(4), O1–P 1.609(2), O1–Si 1.662(2), P–O1–Si 146.27(17), W–P–C1 119.39(12), W–P–C7 113.02(12), W–P–O1 115.66(10), O1–P–C1 104.08(15), O1–P–C7 99.62(15), C1–P–C7 102.49(16).

X-Ray crystal structure solution and refinement has been done using ShelxS-97 and ShelxL-97,^{S1} respectively. The ORTEP drawings of the crystal structures were done with the OLEX² program.^{S2}

Crystallographic data of **2**, **3**, **6b**, **6c** and **6d** have been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC 1545939, 974093, 1545942, 1545941 and 1545940. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Reference:

(S1) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.

(S2) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339–341.

2) NMR spectra and simulation of complex 2:

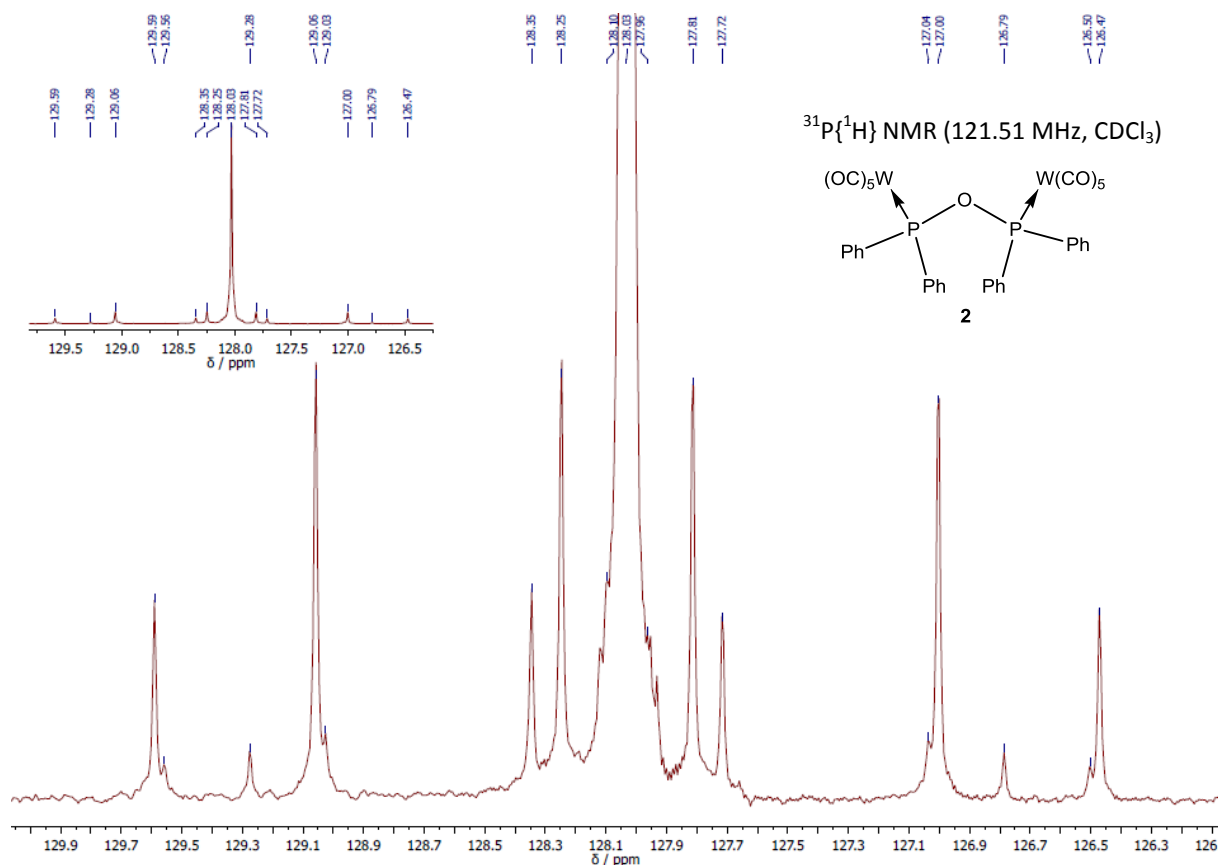


Figure S3: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **2**.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **2** displayed a complicated higher order spectrum. It consists of three overlapped spin systems; one A_2 system, one ABX system and one $AA'XX'$ system. This composition is due to the natural abundance of 14.31 % of the only NMR active tungsten nucleus ^{183}W . Thus there are three different configurations of the molecule that are represented by the three spin systems. But as the coupling constants are not just available from the spectrum itself, simulation is needed. Therefore the program gNMR^{S3a} was used. For the determination and assignment of the single spin systems the program WinDNMR^{S3b} was used.

The main signal belongs to the A_2 spin system and shows no coupling to other nuclei.

The ABX spin system has a phosphorus-phosphorus coupling constant of 64.64 Hz. The phosphorus-tungsten coupling constant is 300.98 Hz for the direct coupling and 1.43 Hz for the long range coupling constant.

For the $AA'XX'$ spin system the same coupling constants are valid, here additionally the tungsten-tungsten coupling is set to zero or very close to it.

The simulation of the whole spin system (see Figure S2) fits very well to the experimental NMR spectrum (see also Figure S1).

The different spin systems are asterisked with different colors to assign them to the A_2 (red), ABX (green) and $AA'XX'$ (blue) spin systems.

In the ^{13}C NMR spectrum of complex **2** all signals have a pseudo triplet (see Figure S3). In a similar case, a phosphorus decoupled carbon spectrum showed only singlets or doublets, respectively. This phenomenon is due to the very similar nuclei in the molecule representing a A_2X_2 spin system as a special case of a $AA'XX'$ spin system.

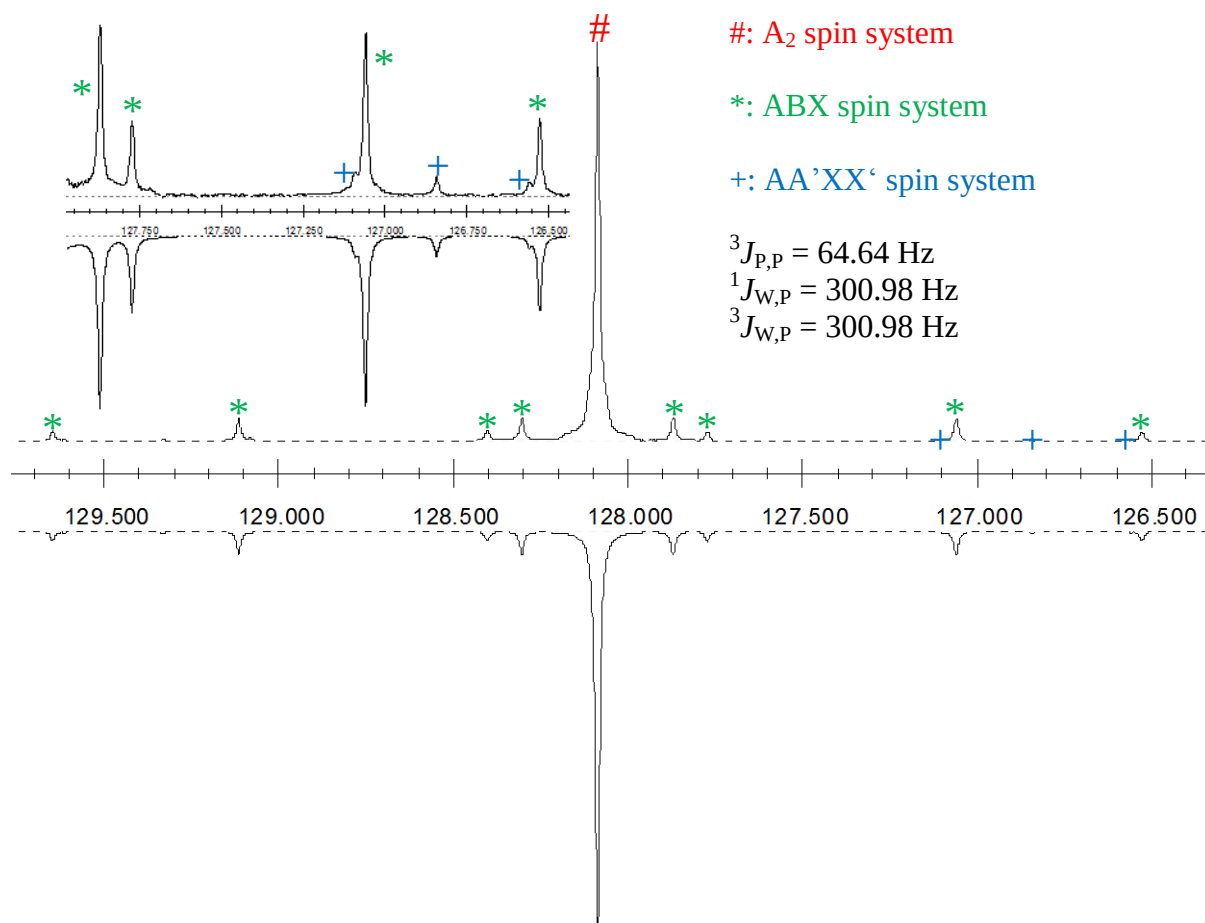


Figure S4: Simulated (bottom) and experimental (top) $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complex **2** and expansion of one region.

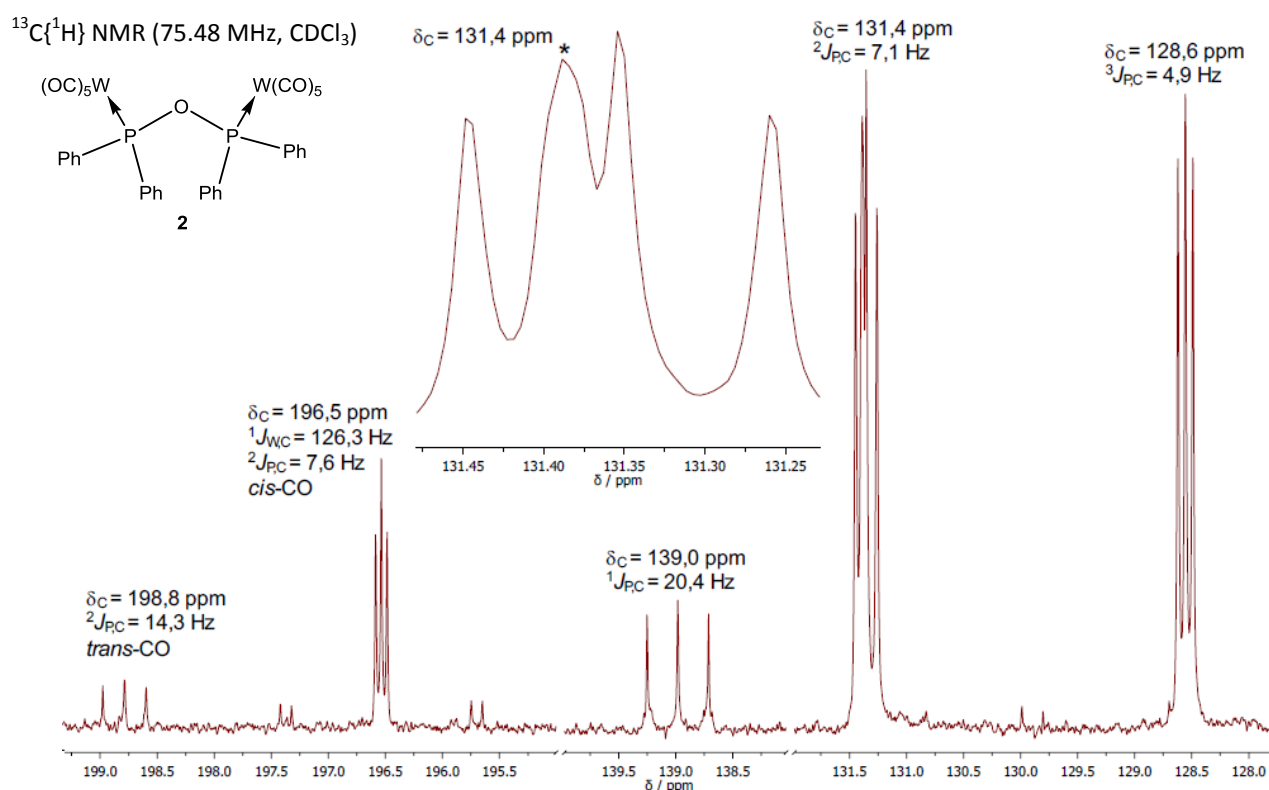


Figure S5: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **2**.

Reference:

(S3) (a) gNMR, Budzeelar, P. H., *IvorySoft* **2006**, Version 5.0.6.0; (b) Reich, H. J. *J. Chem. Educ.* **1995**, 72, 1086.

3) NMR spectra of the isolated compounds:

a) NMR spectra of complex 2:

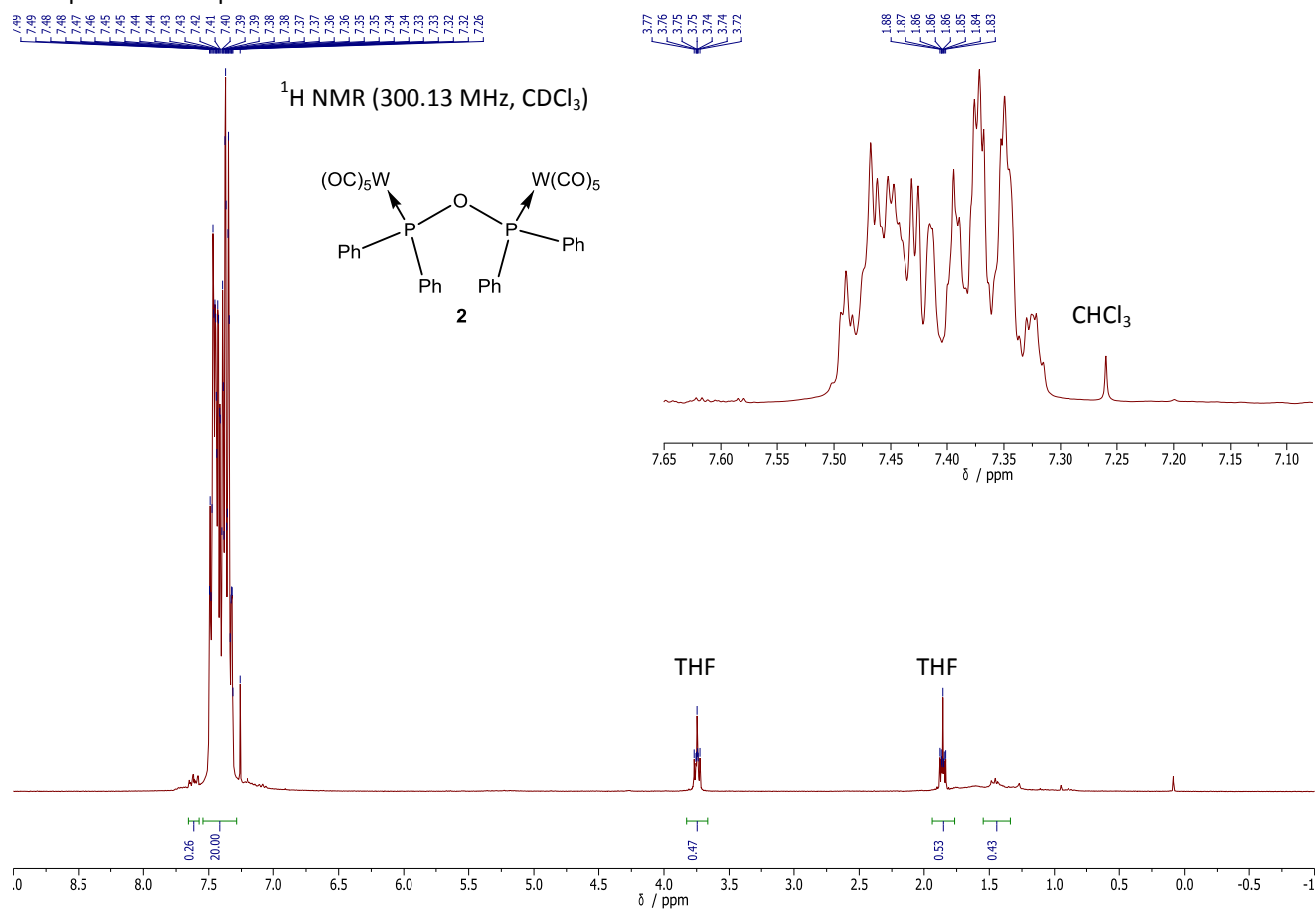


Figure S6: ¹H NMR spectrum of complex 2.

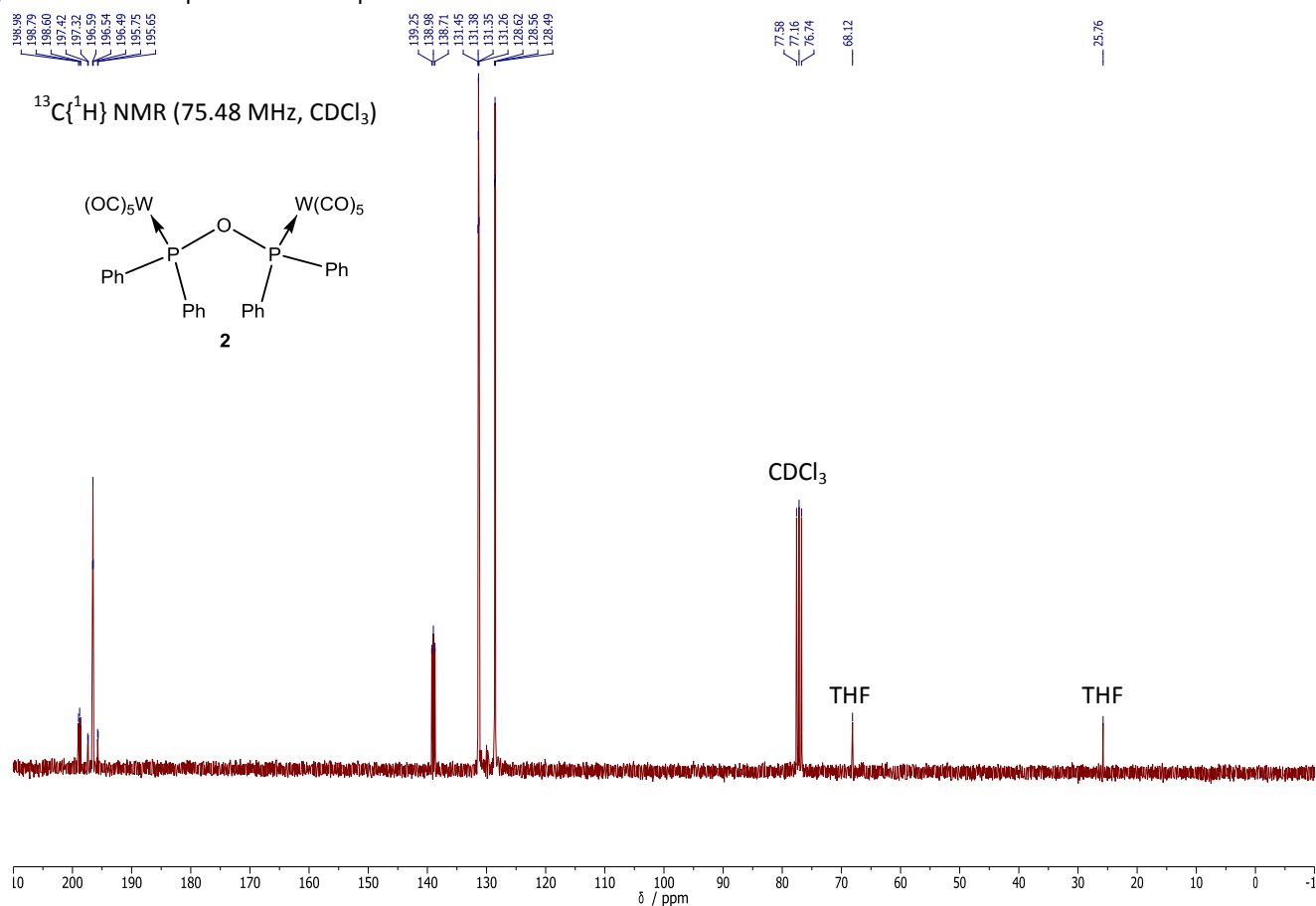


Figure S7: ¹³C{¹H} NMR spectrum of complex 2.

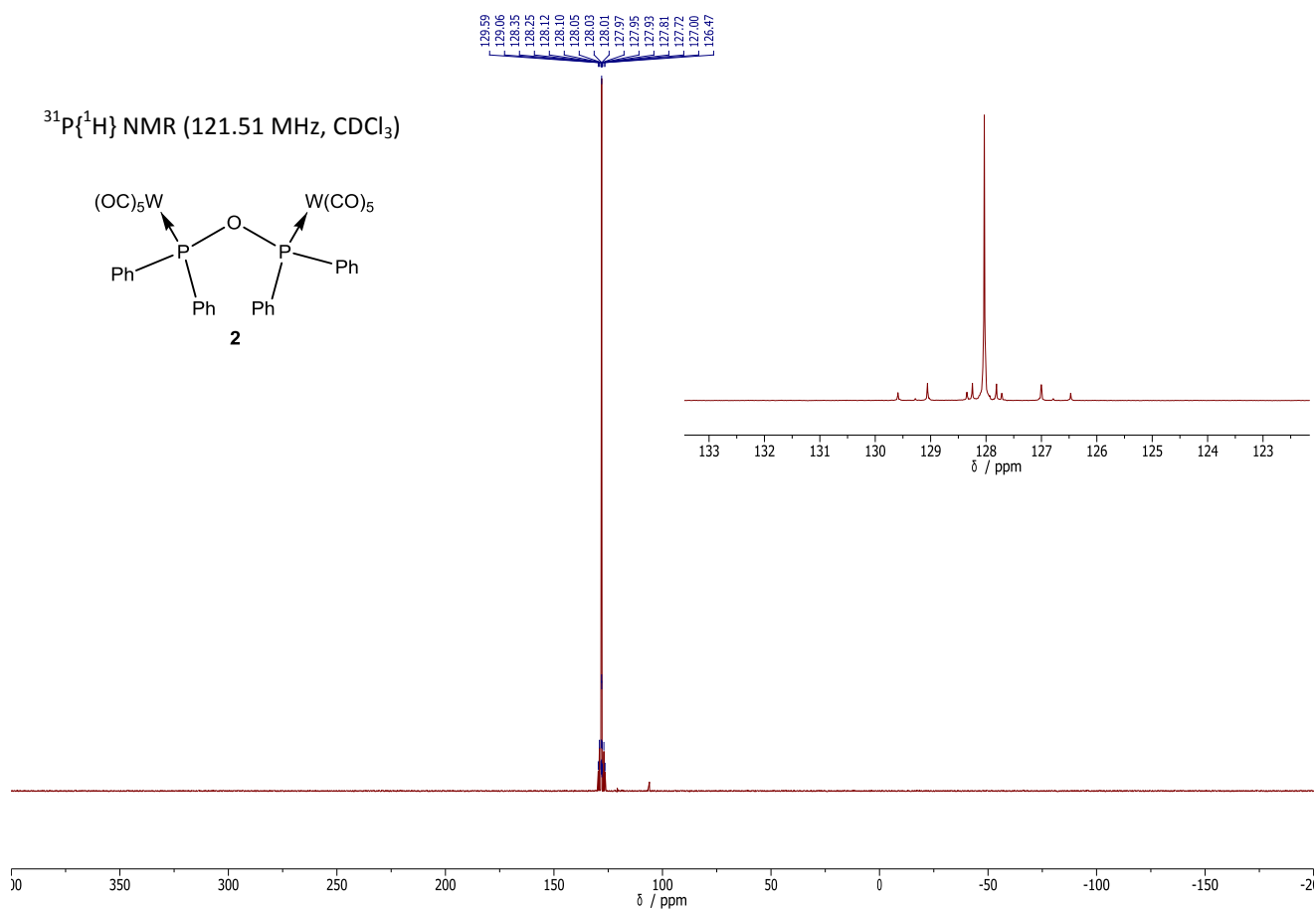


Figure S8: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **2**.

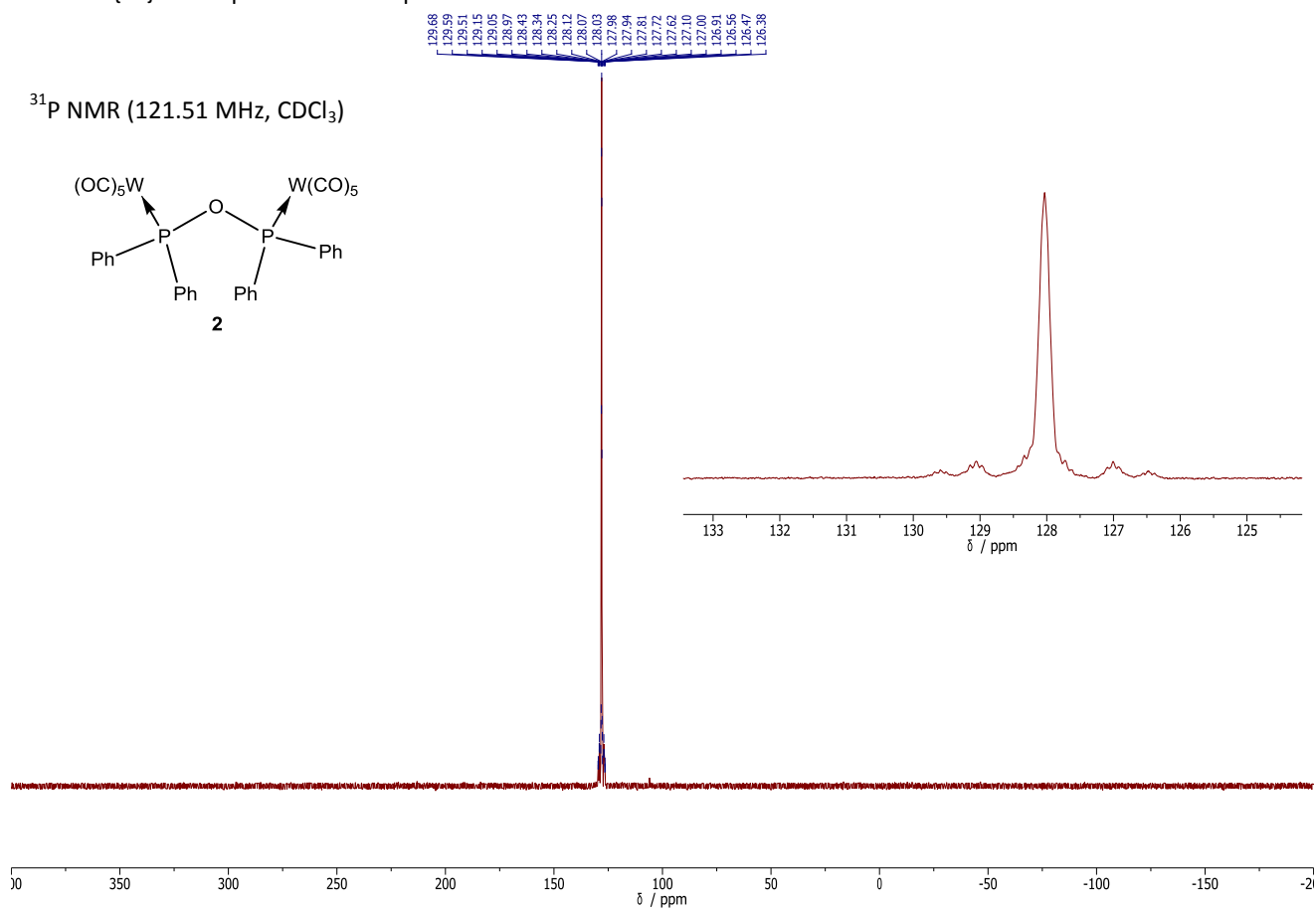


Figure S9: ^{31}P NMR spectrum of complex **2**.

b) NMR spectra of complex 3:

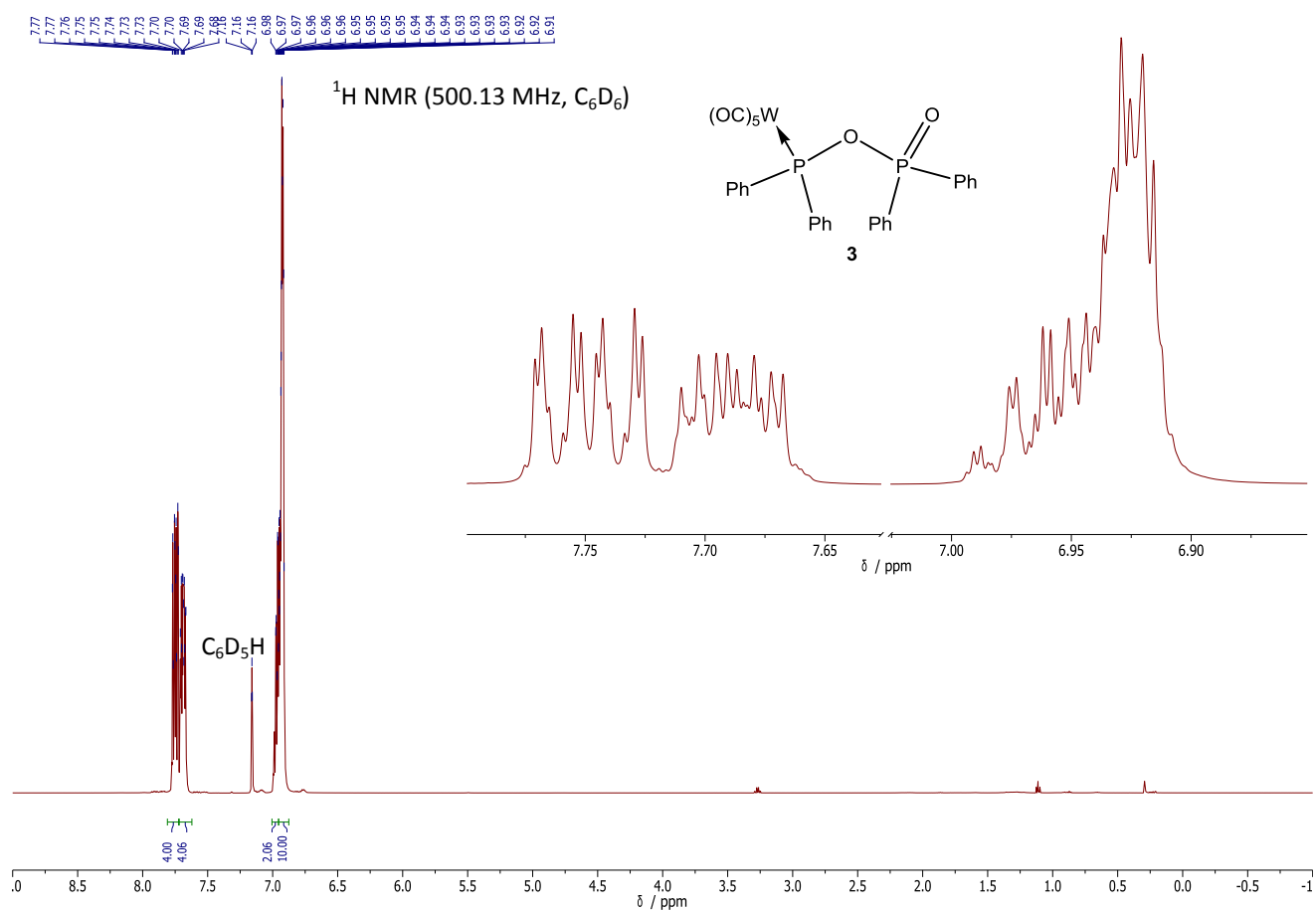


Figure S10: ¹H NMR spectrum of complex 3.

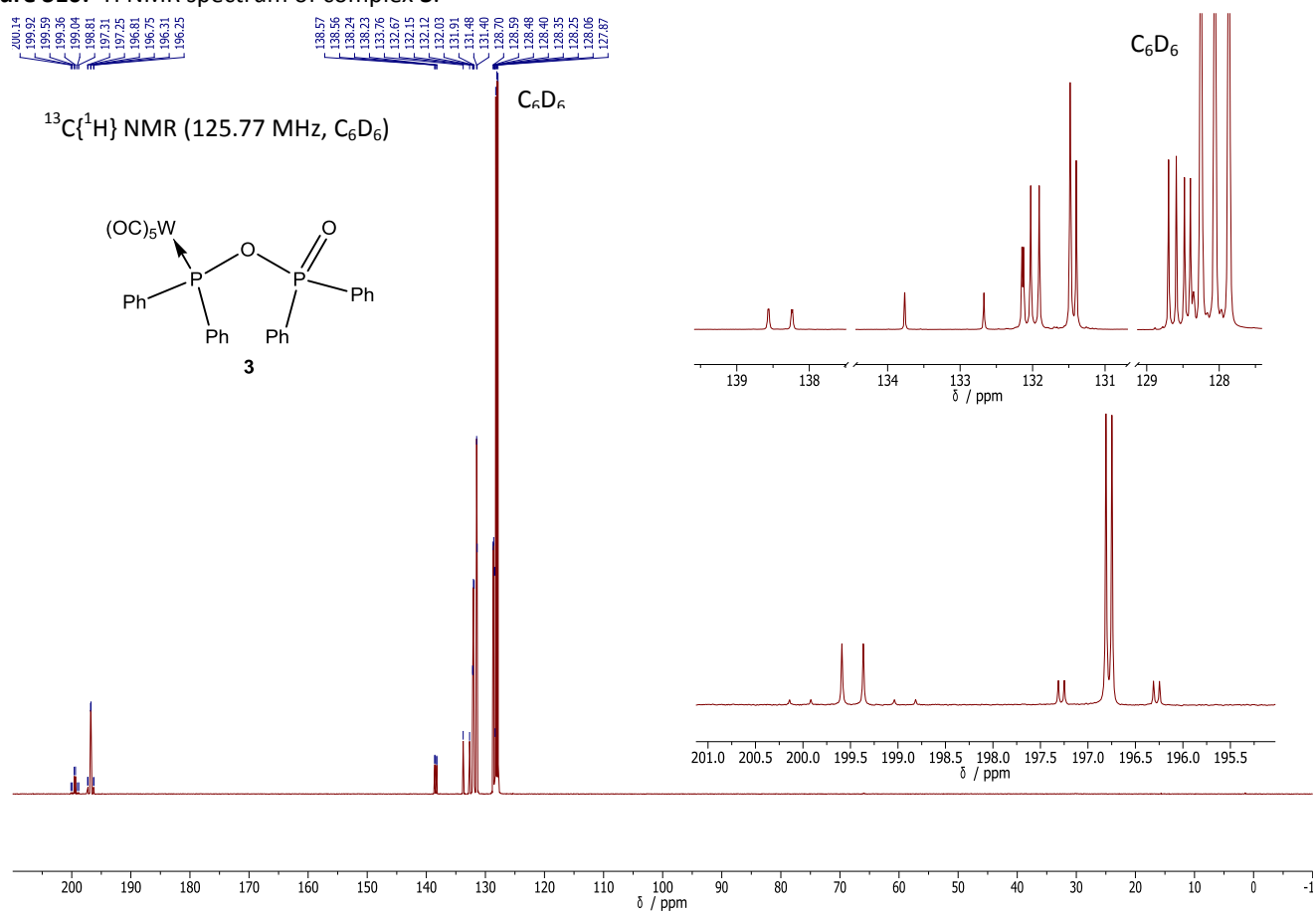


Figure S11: ¹³C{¹H} NMR spectrum of complex 3.

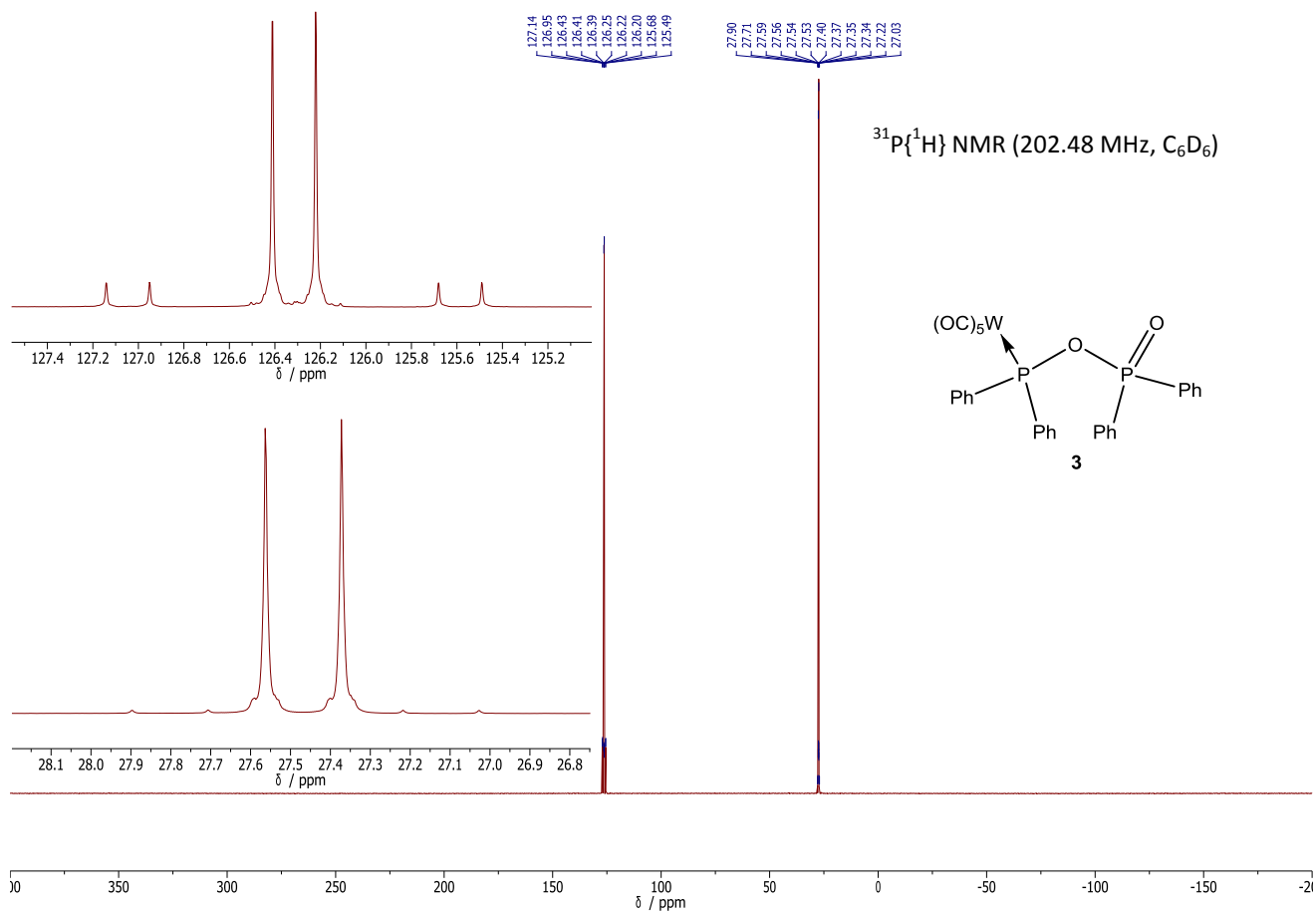


Figure S12: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **3**.

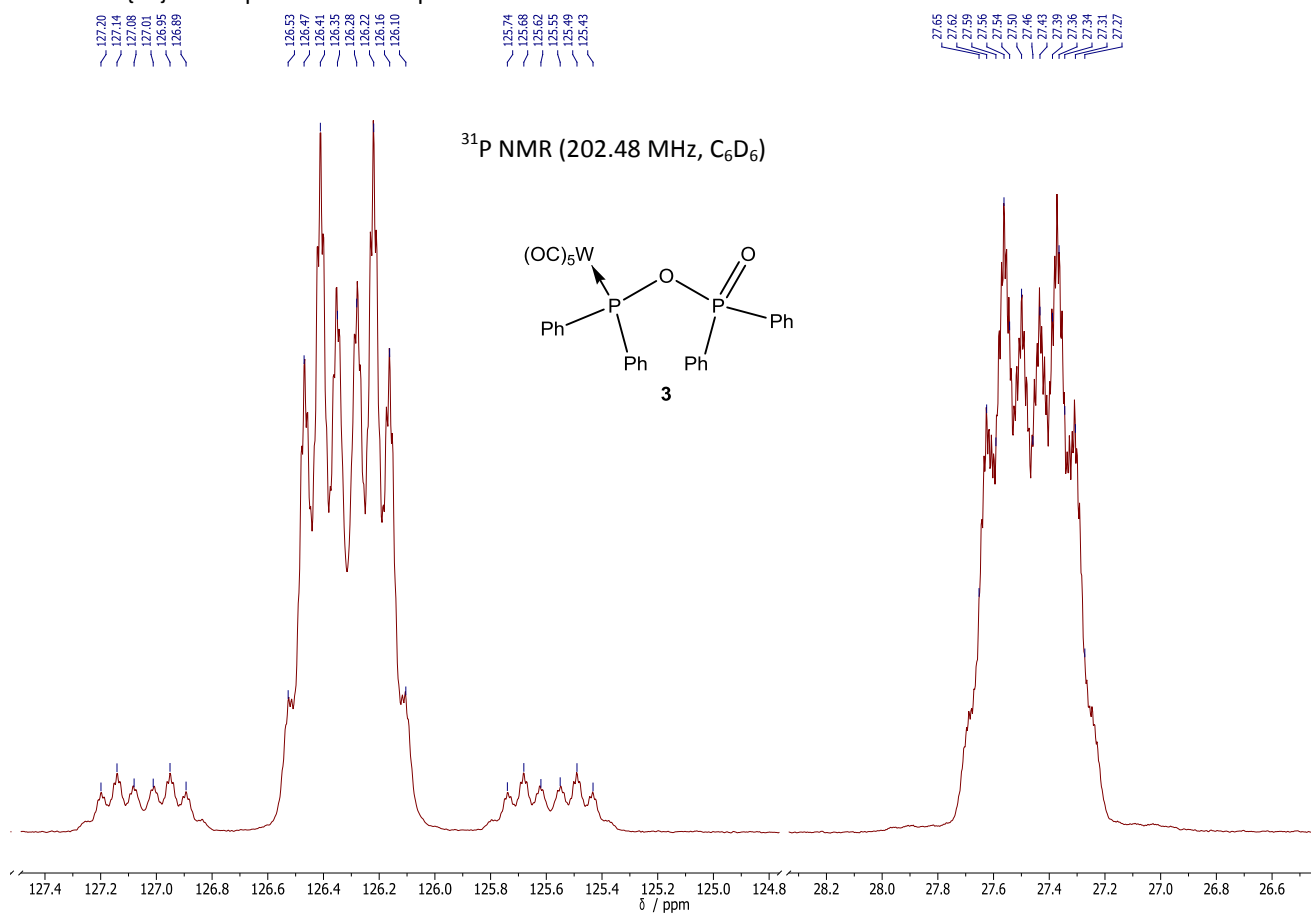


Figure S13: ^{31}P NMR spectrum of complex **3**.

c) NMR spectra of complex **6a**:

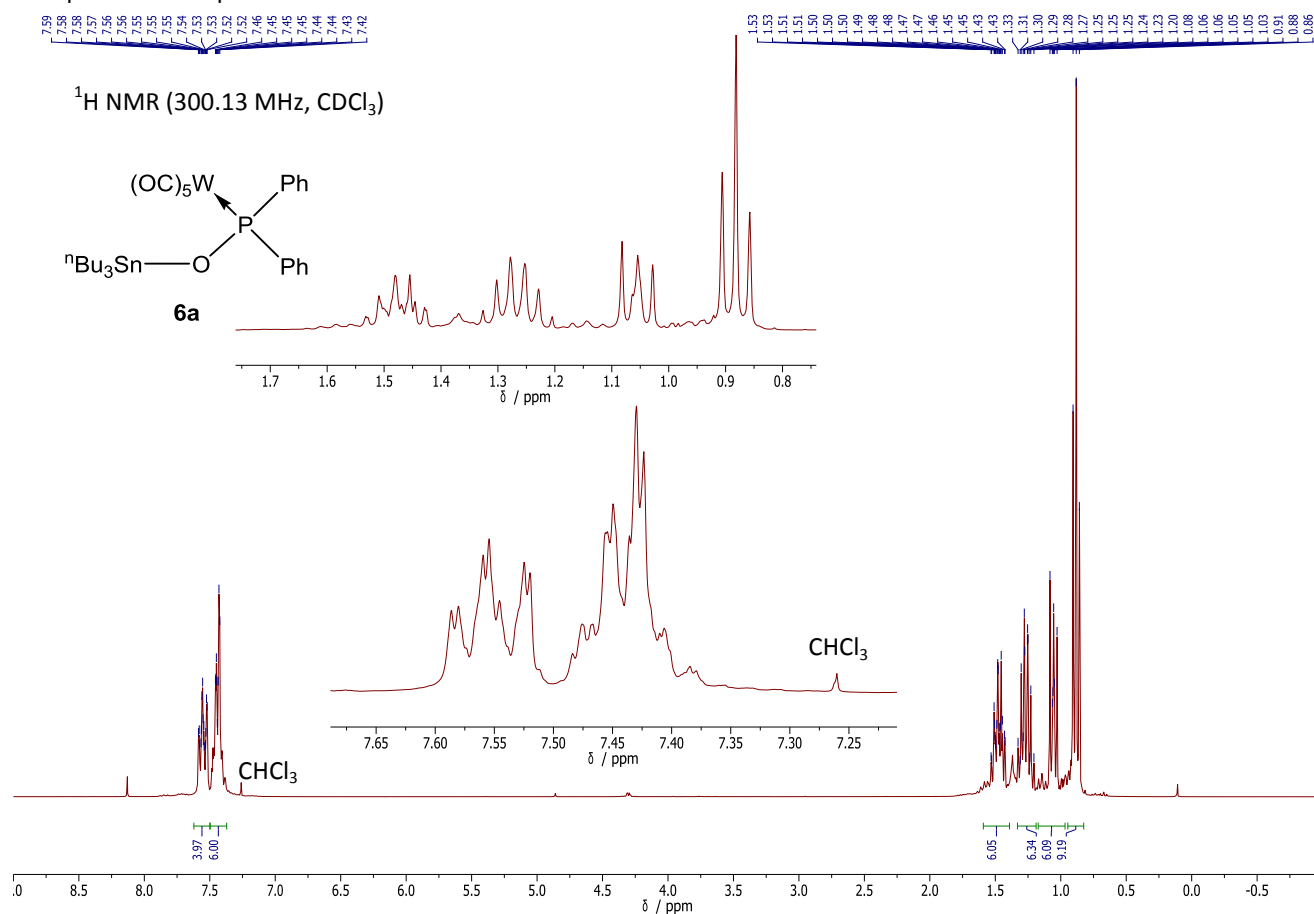


Figure S14: ¹H NMR spectrum of complex **6a**.

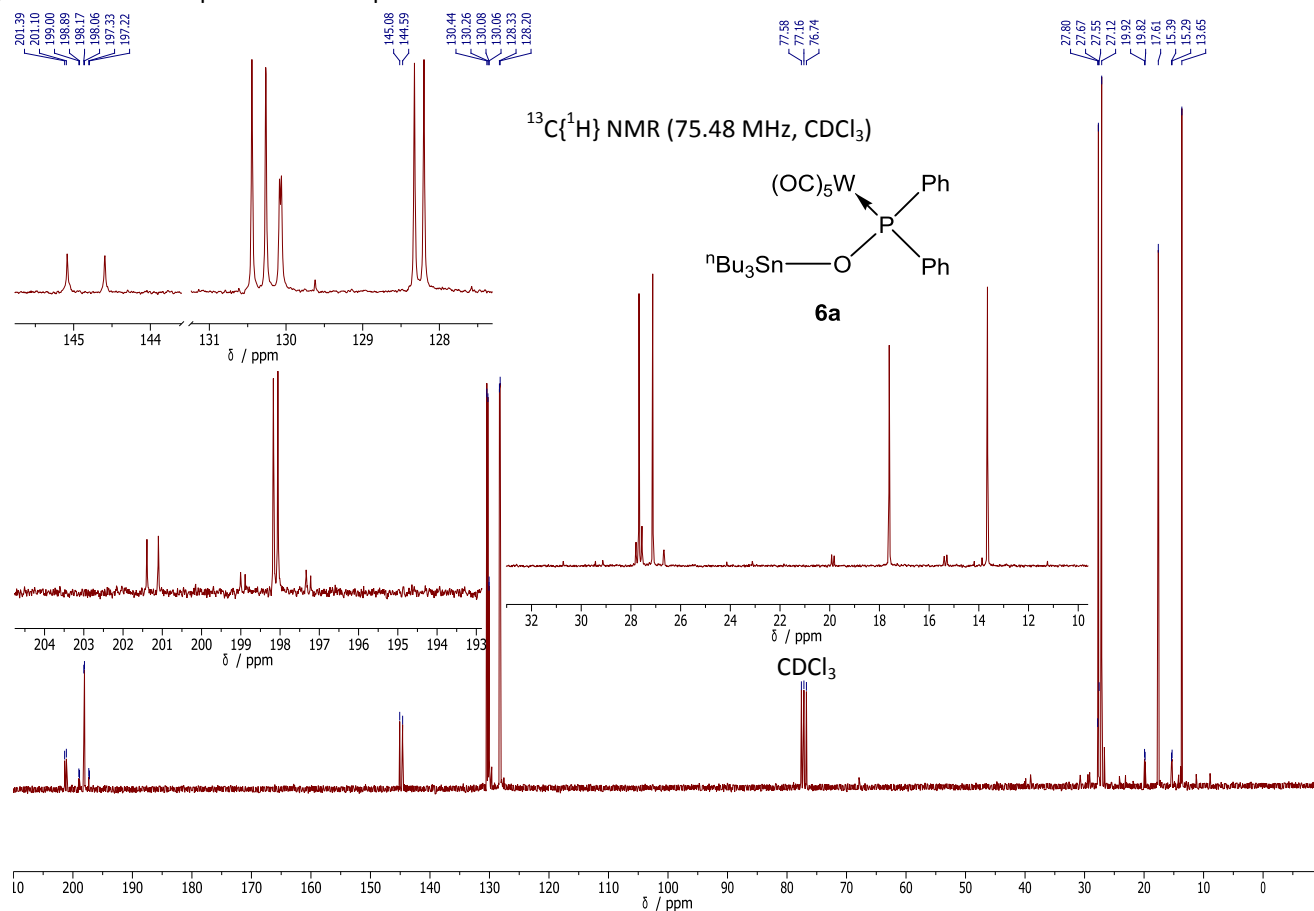


Figure S15: ¹³C{¹H} NMR spectrum of complex **6a**.

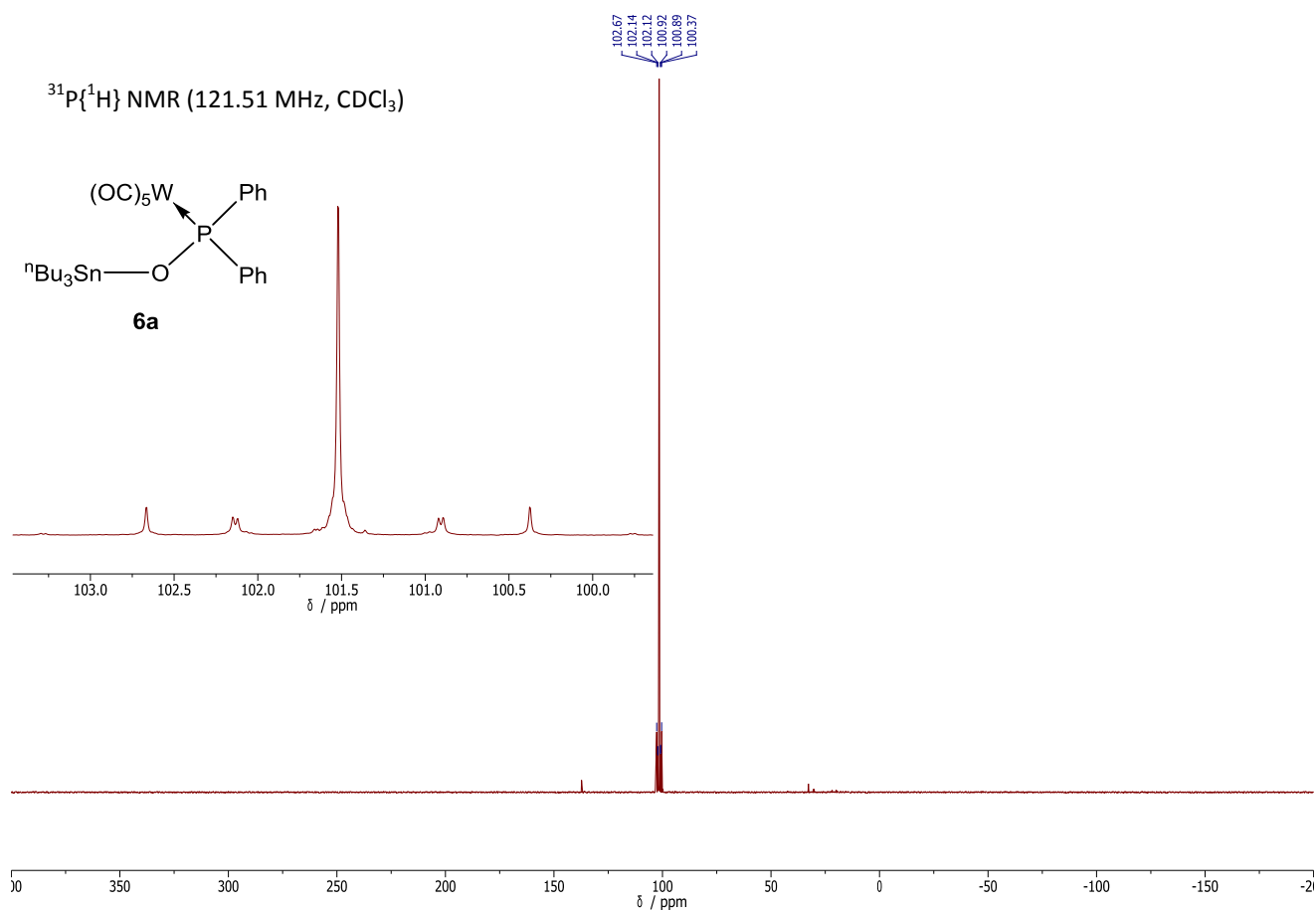


Figure S16: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **6a**.

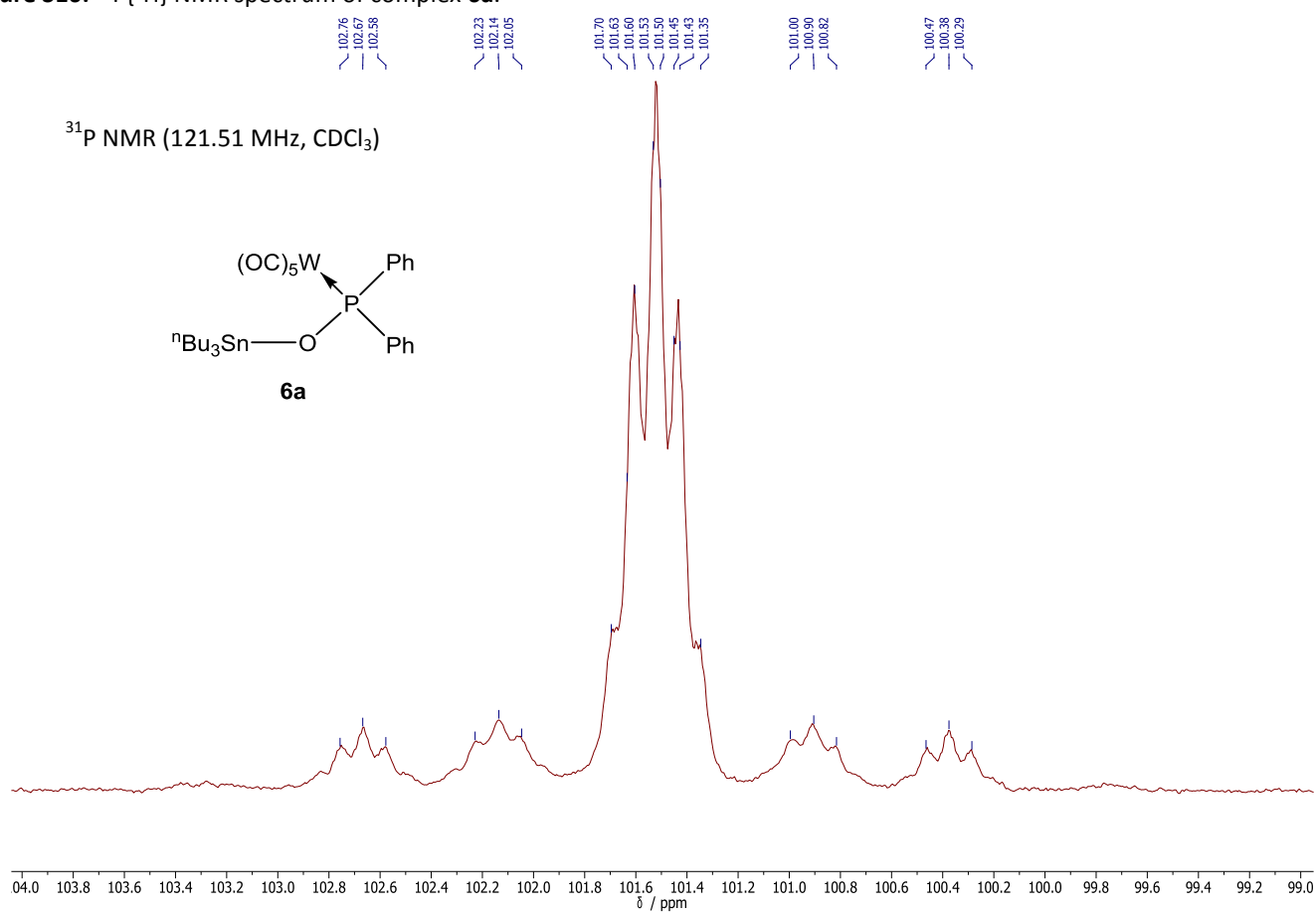


Figure S17: ^{31}P NMR spectrum of complex **6a**.

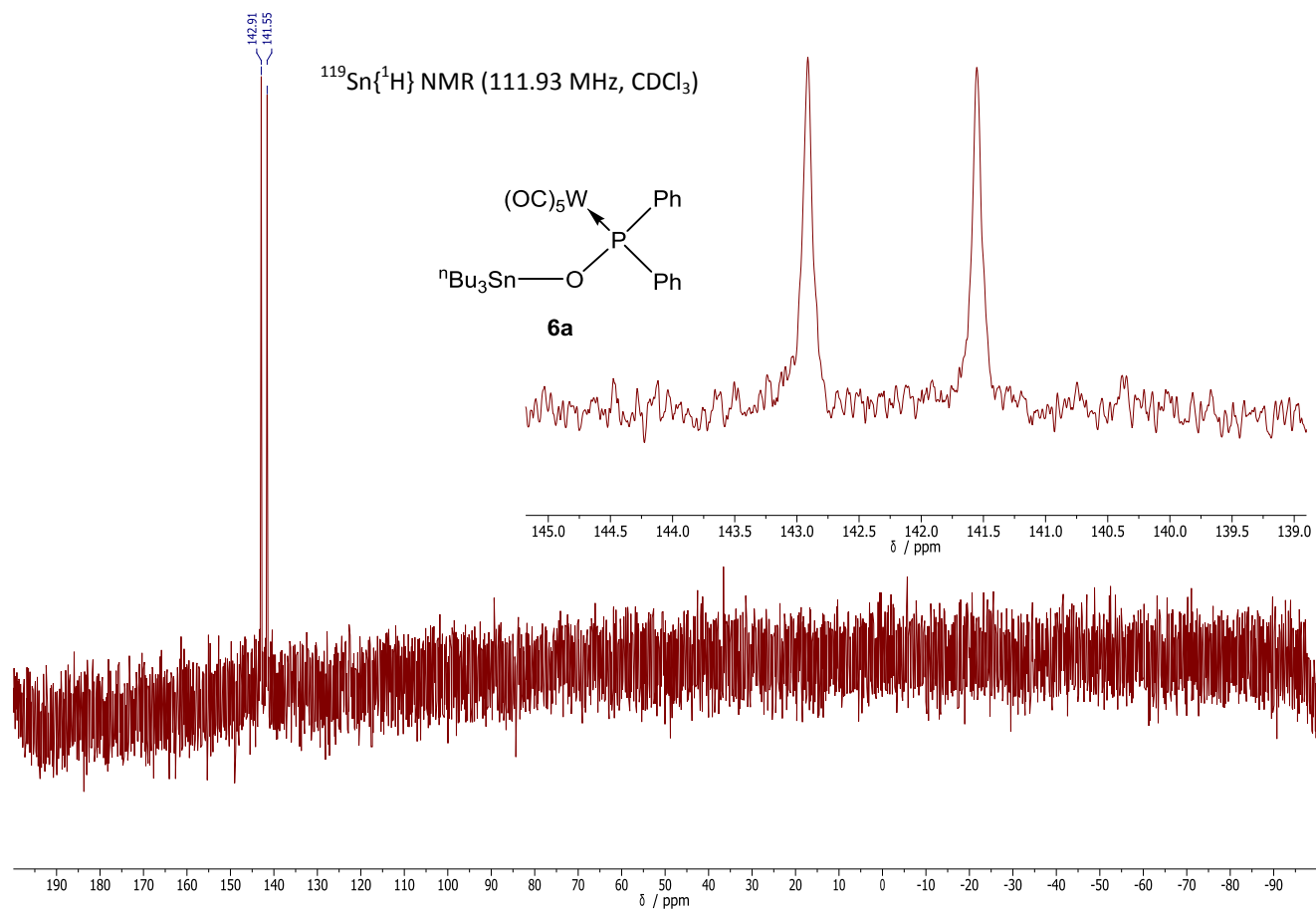


Figure S18: $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of complex **6a**.

d) NMR spectra of complex **6b:**

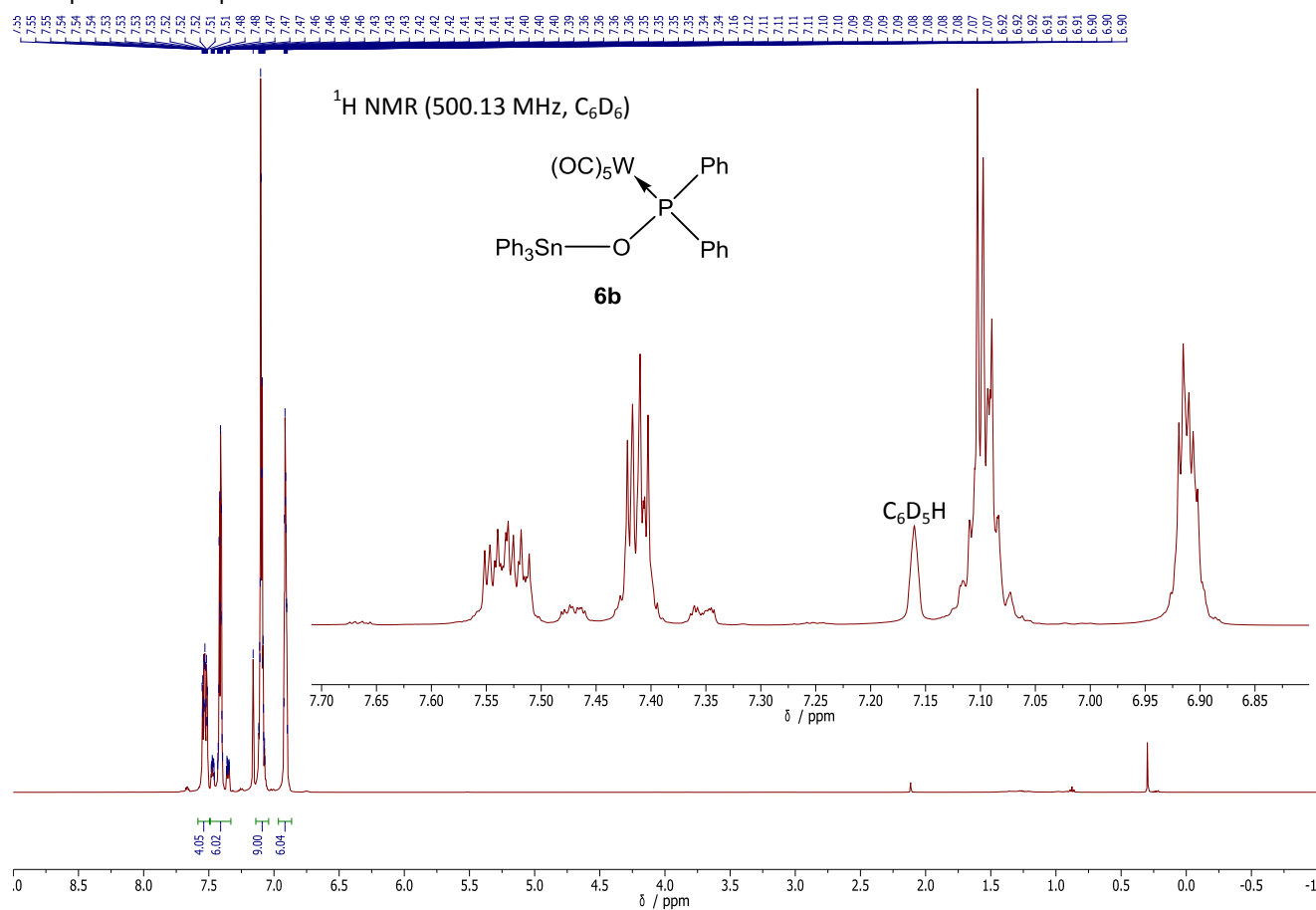


Figure S19: ^1H NMR spectrum of complex **6b**.

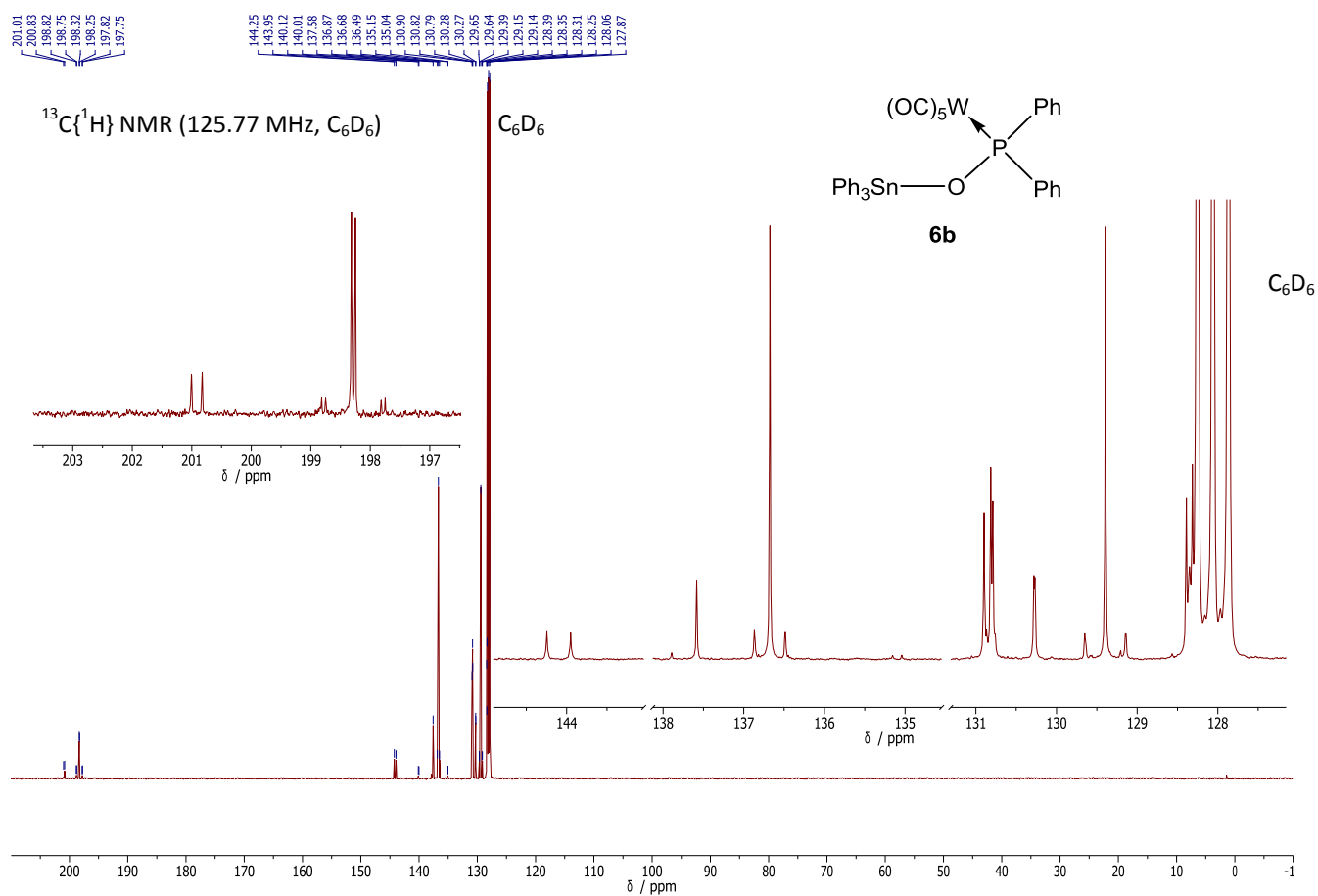


Figure S20: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **6b**.

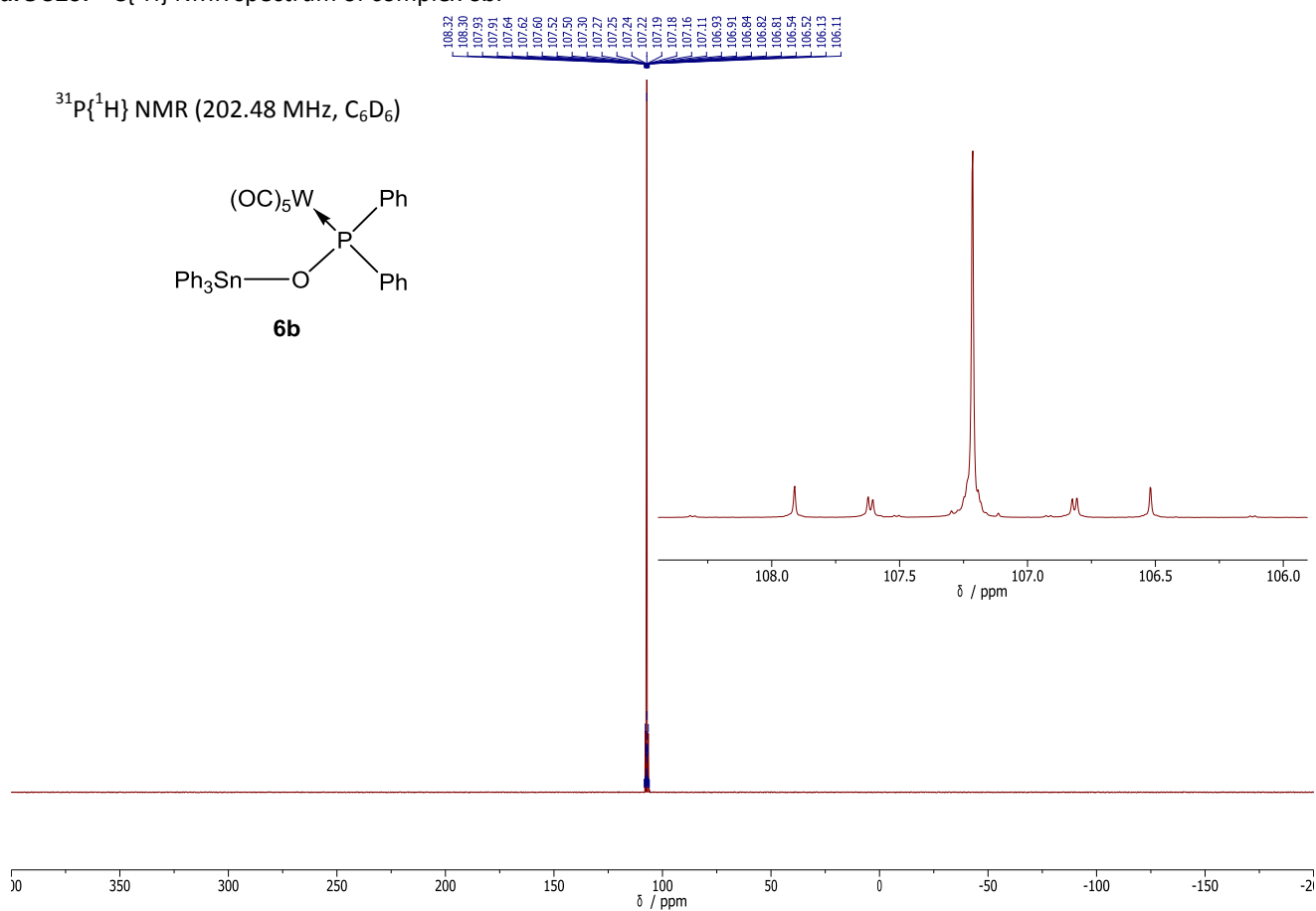


Figure S21: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **6b**.

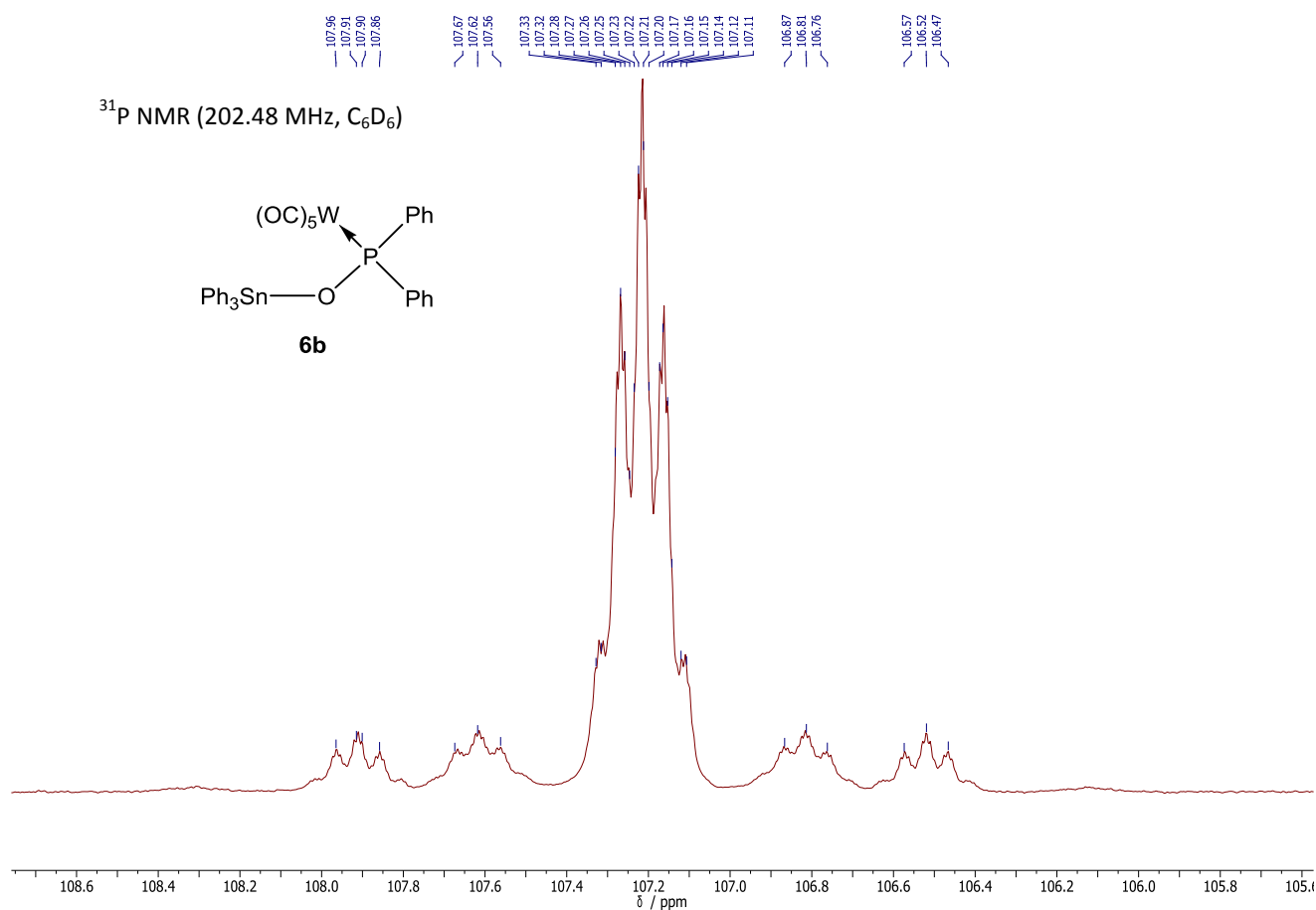


Figure S22: ³¹P NMR spectrum of complex **6b**.

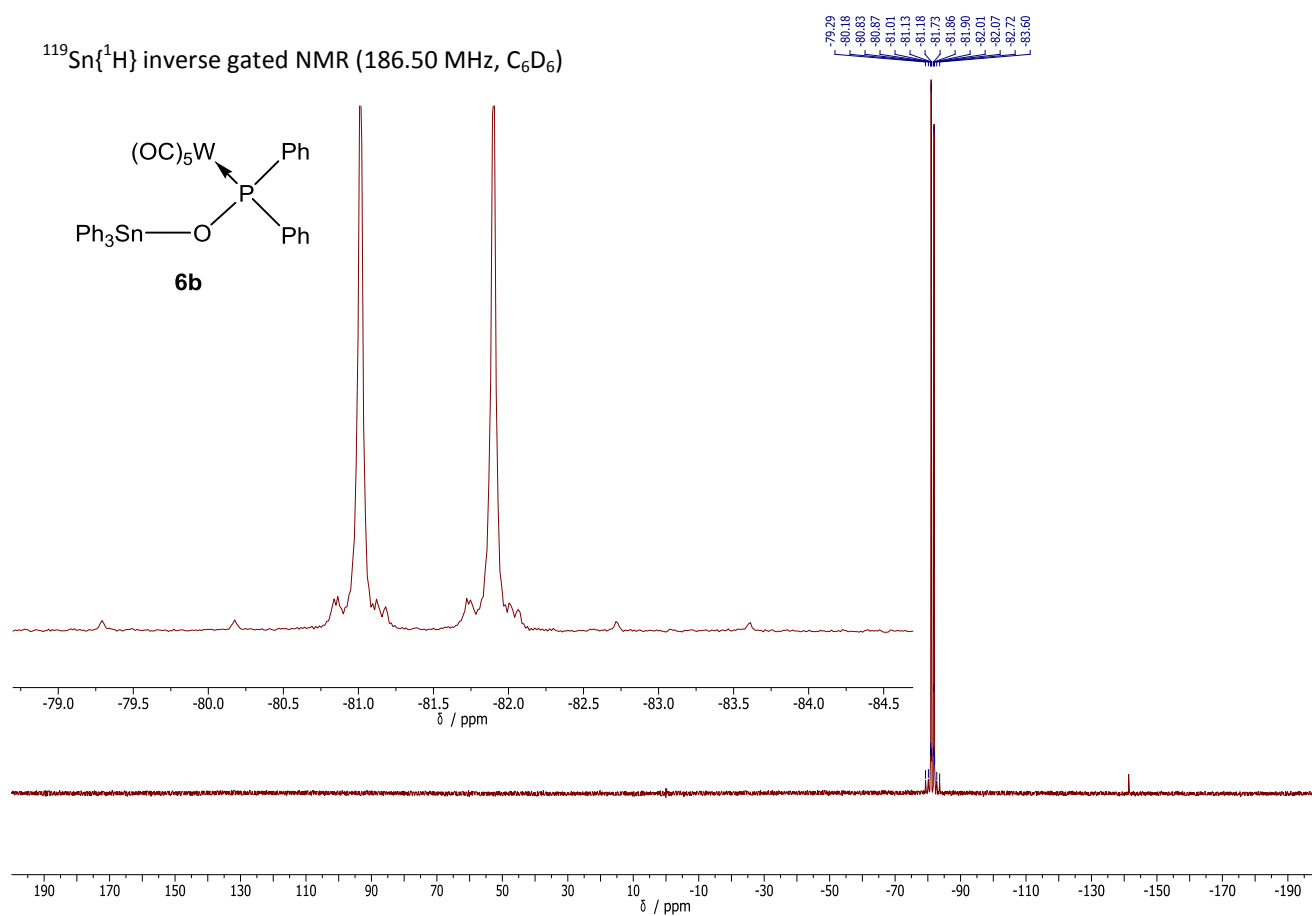


Figure S23: ¹¹⁹Sn{¹H} inverse gated NMR spectrum of complex **6b**.

e) NMR spectra of complex **6c**:

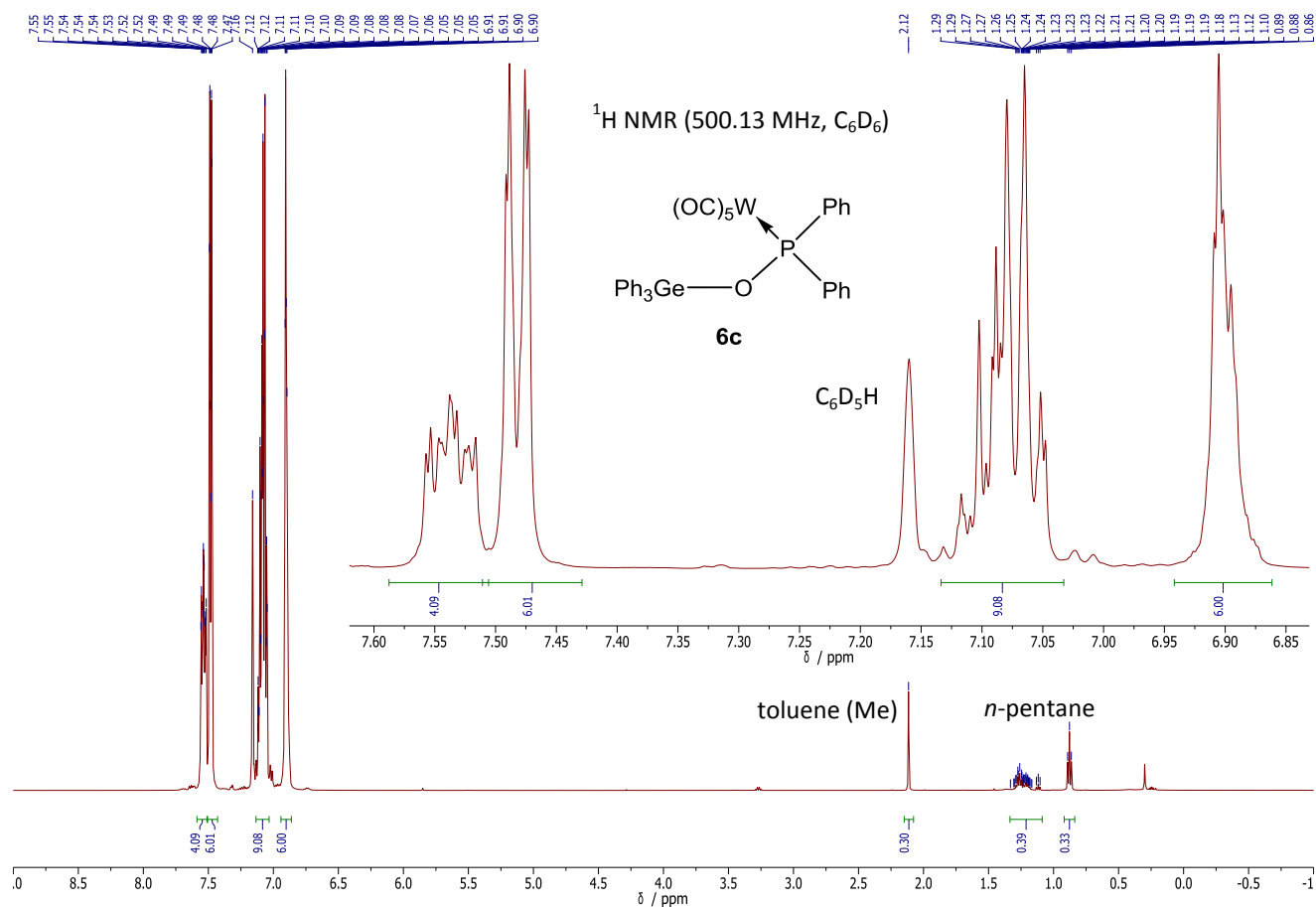


Figure S24: ^1H NMR spectrum of complex **6c**.

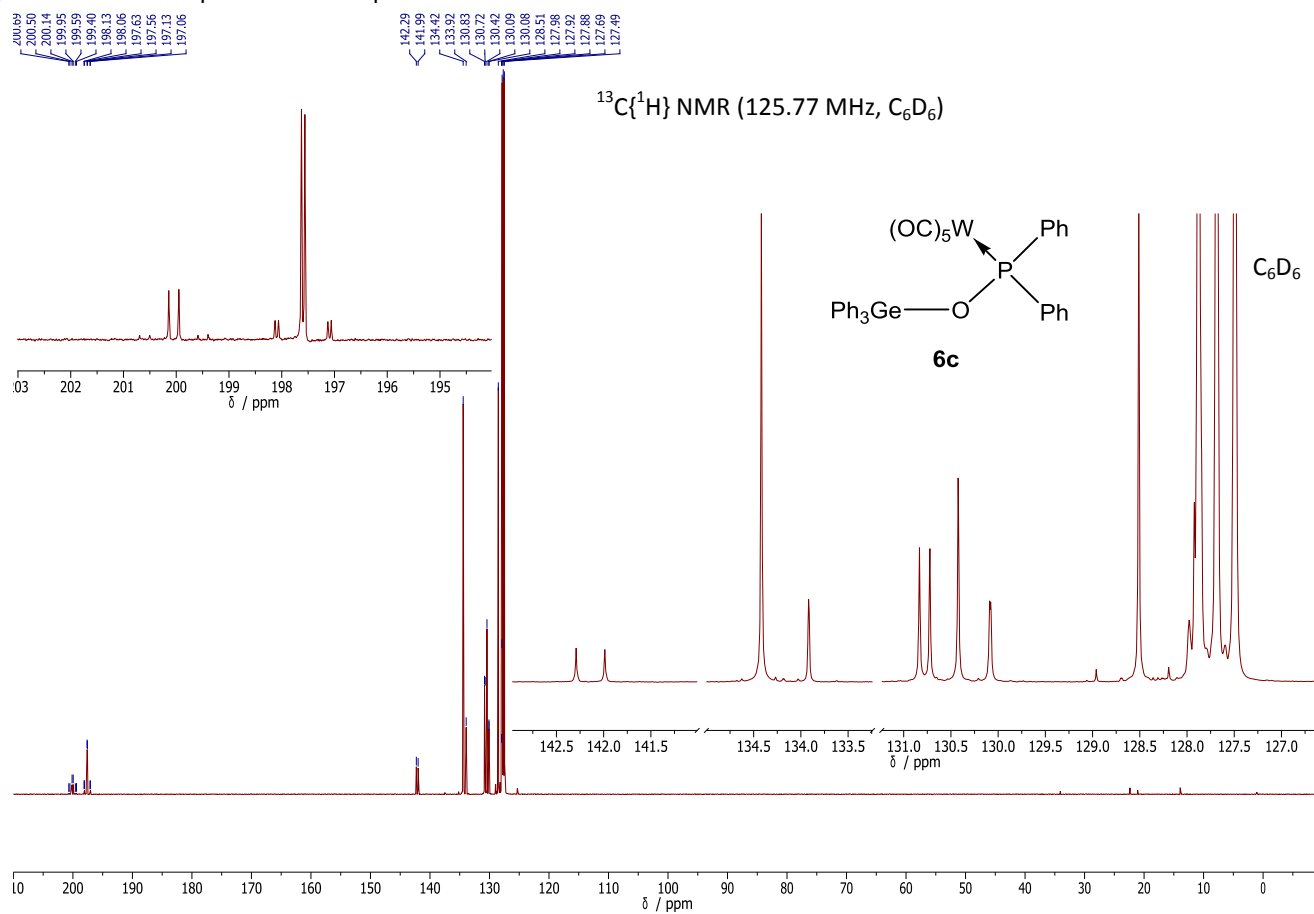


Figure S25: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **6c**.

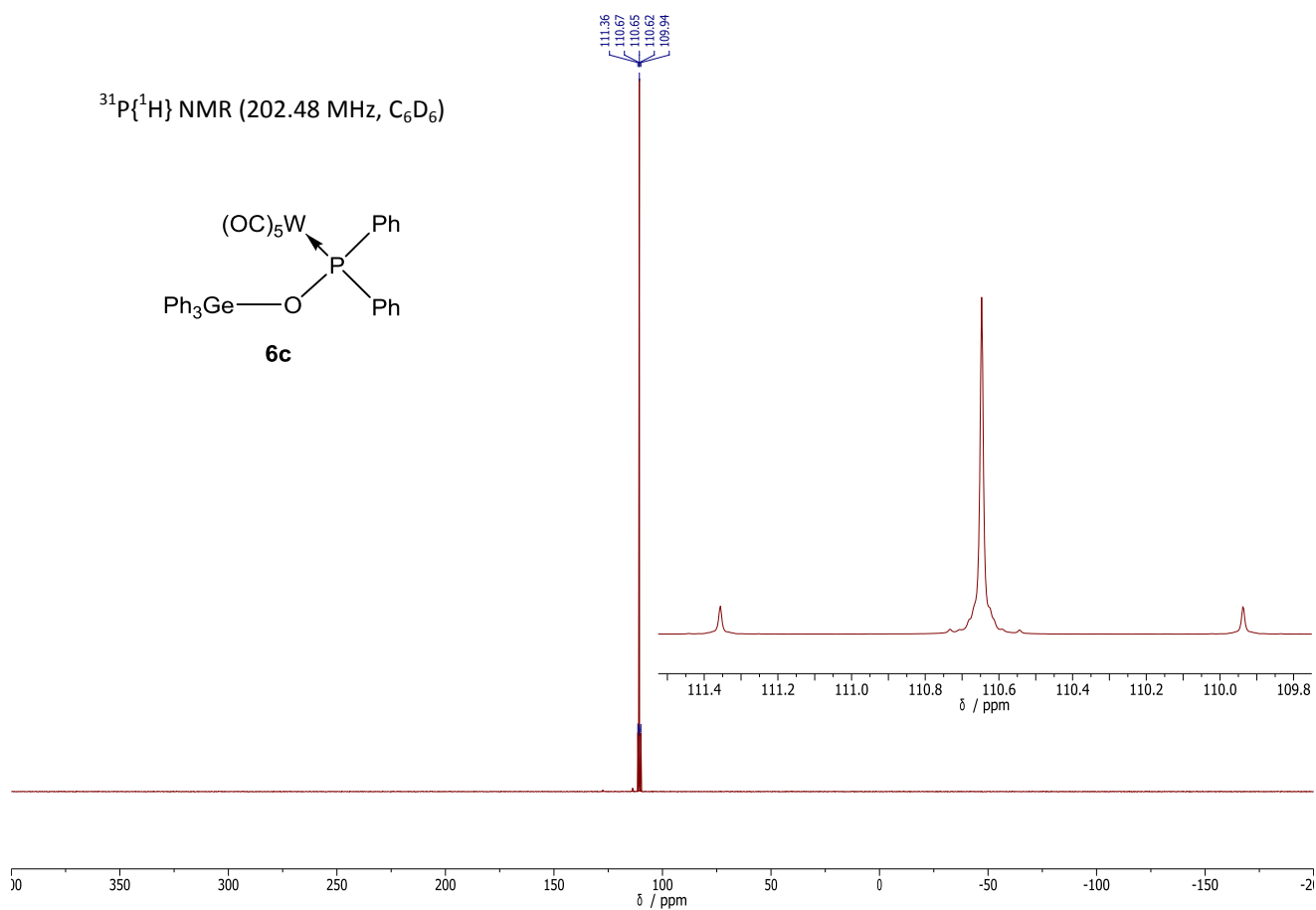


Figure S26: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **6c**.

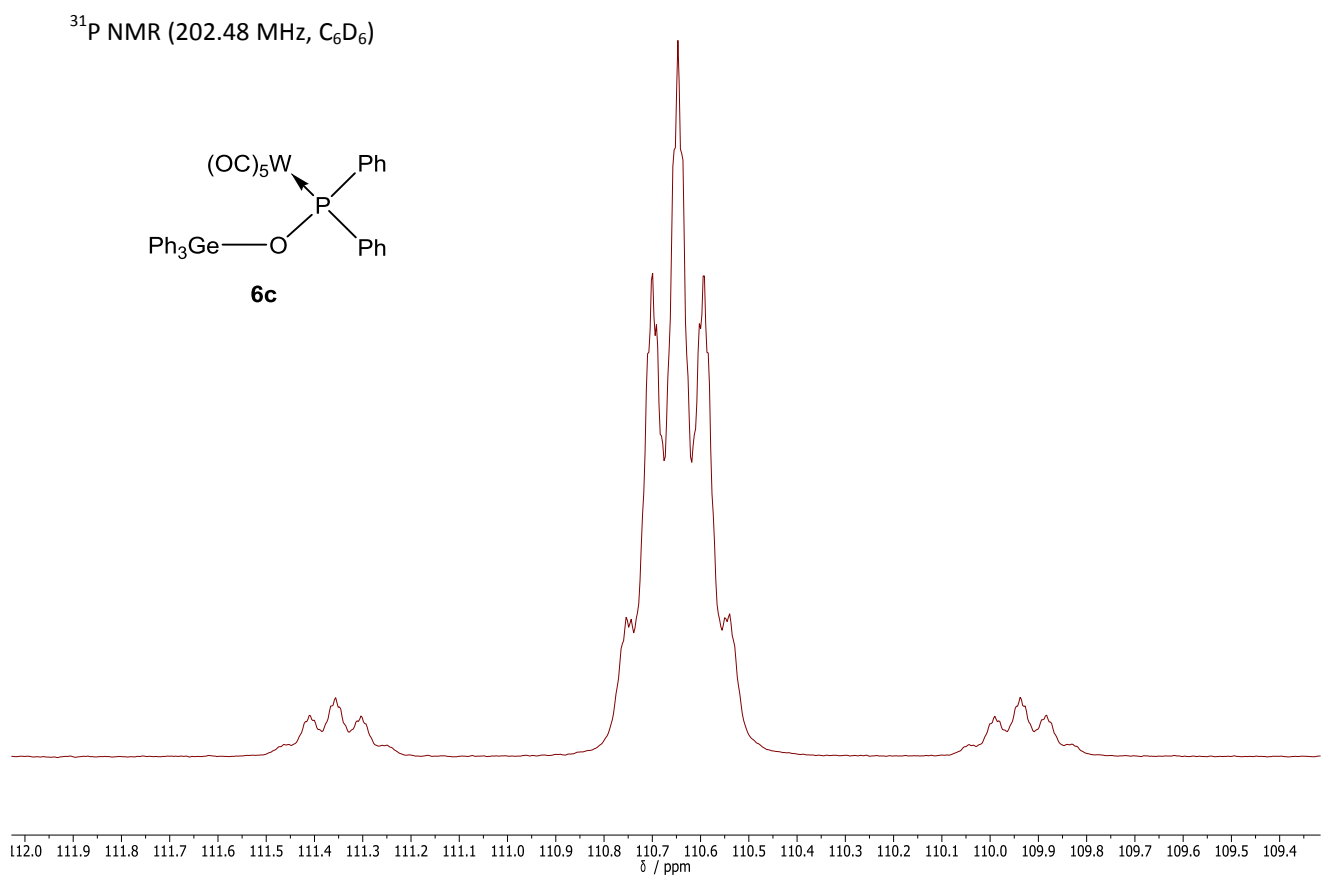


Figure S27: ^{31}P NMR spectrum of complex **6c**.

f) NMR spectra of complex **6d:**

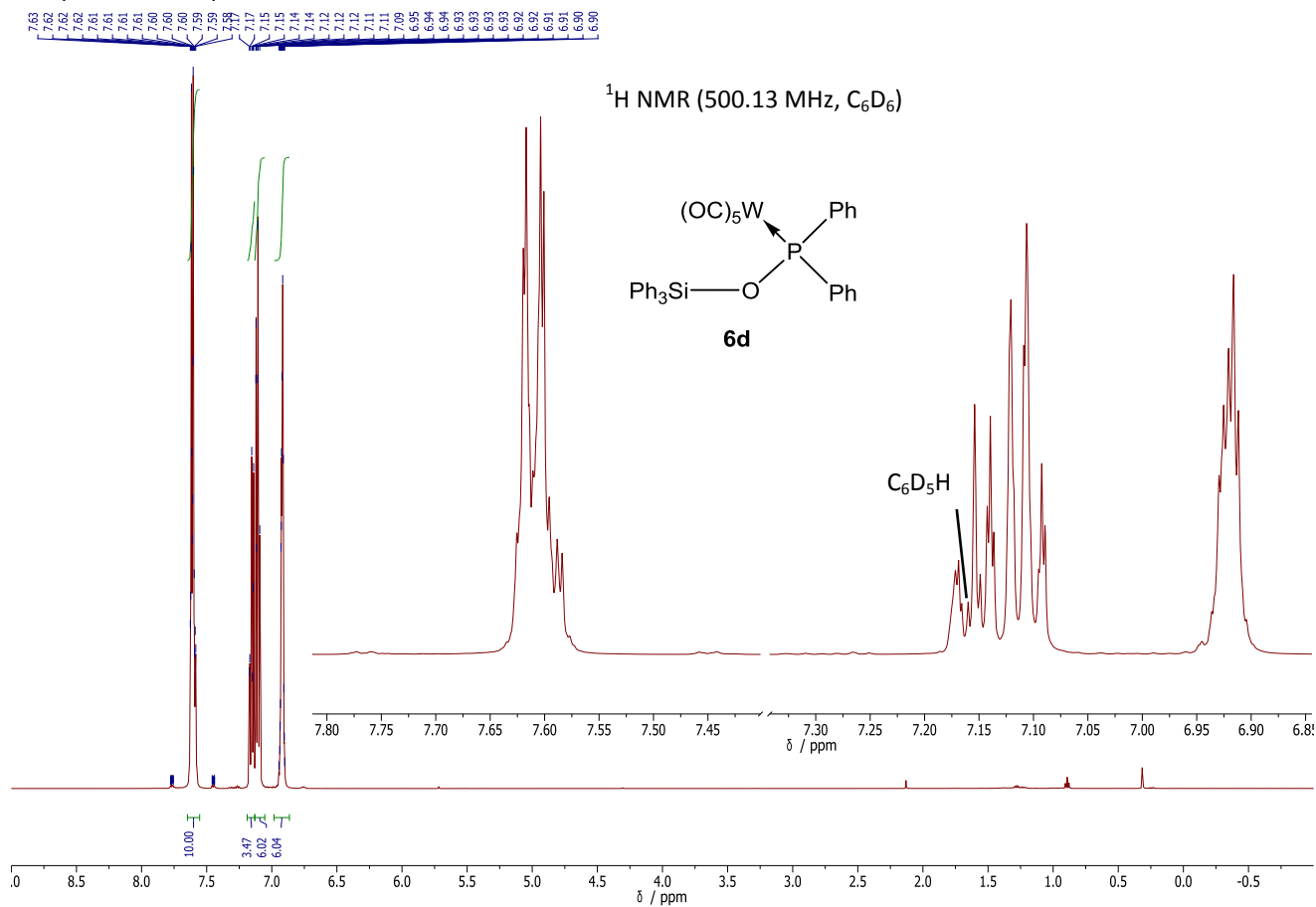


Figure S28: ^1H NMR spectrum of complex **6d**.

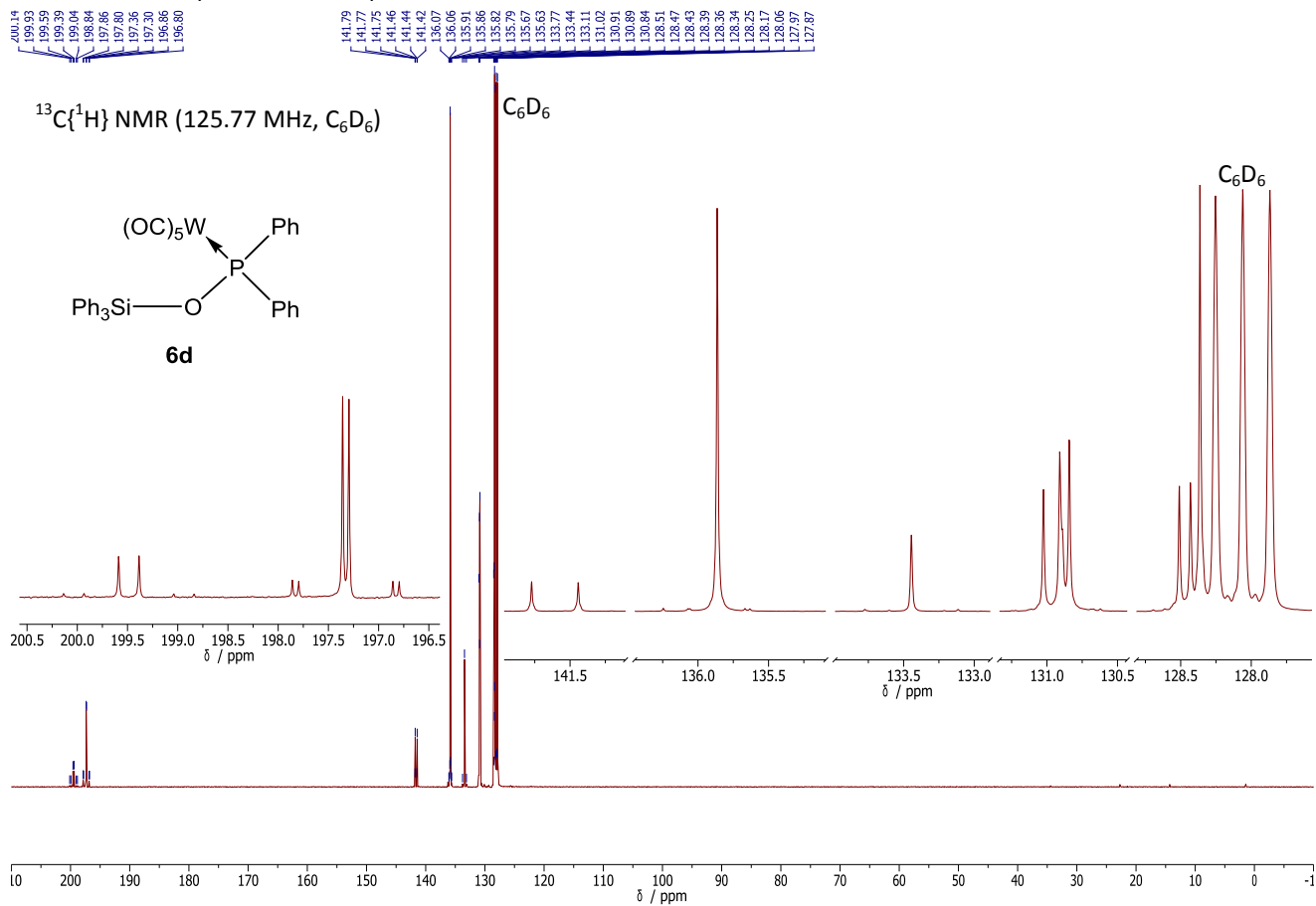


Figure S29: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **6d**.

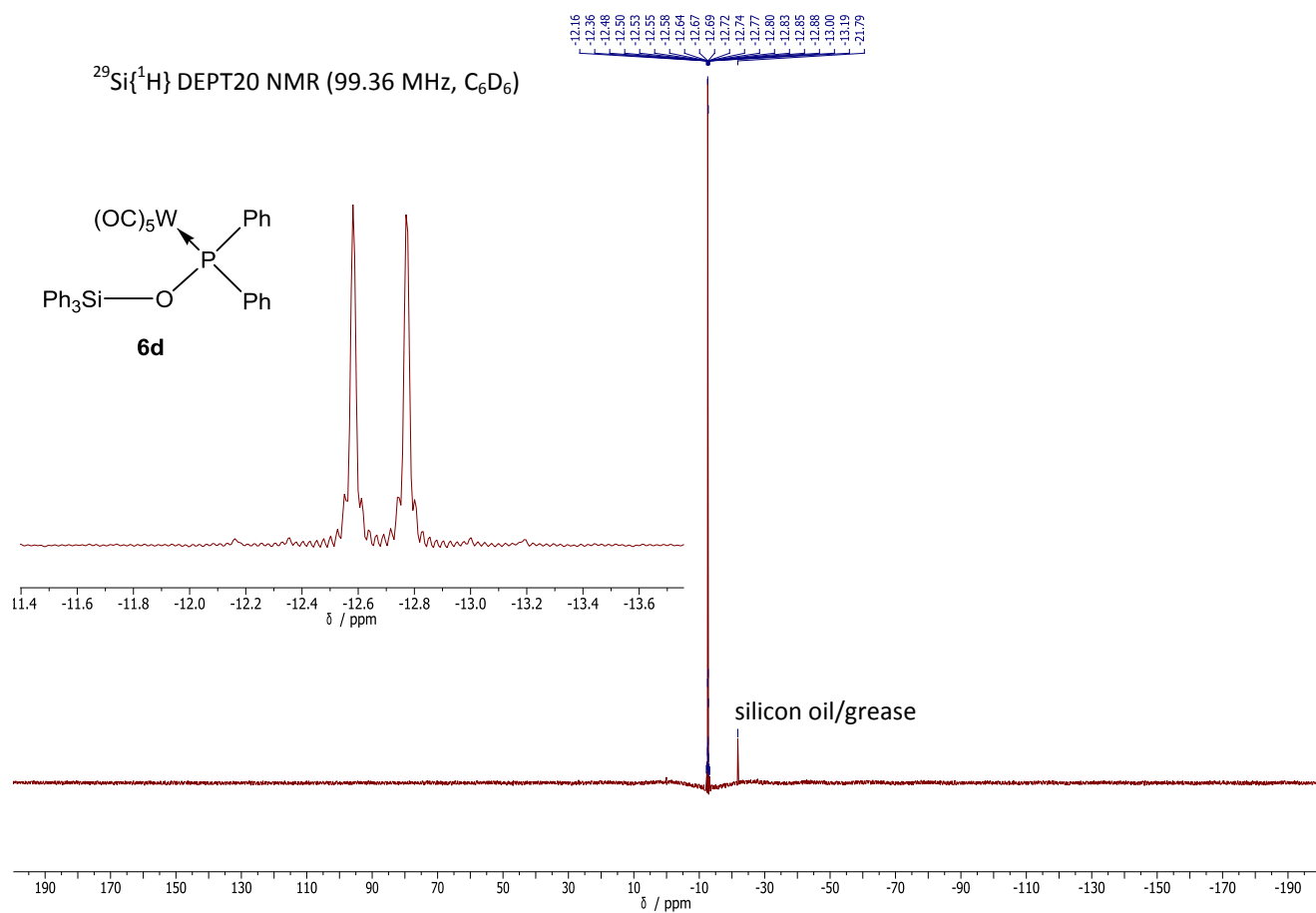


Figure S30: $^{29}\text{Si}\{^1\text{H}\}$ DEPT20 NMR spectrum of complex **6d**.

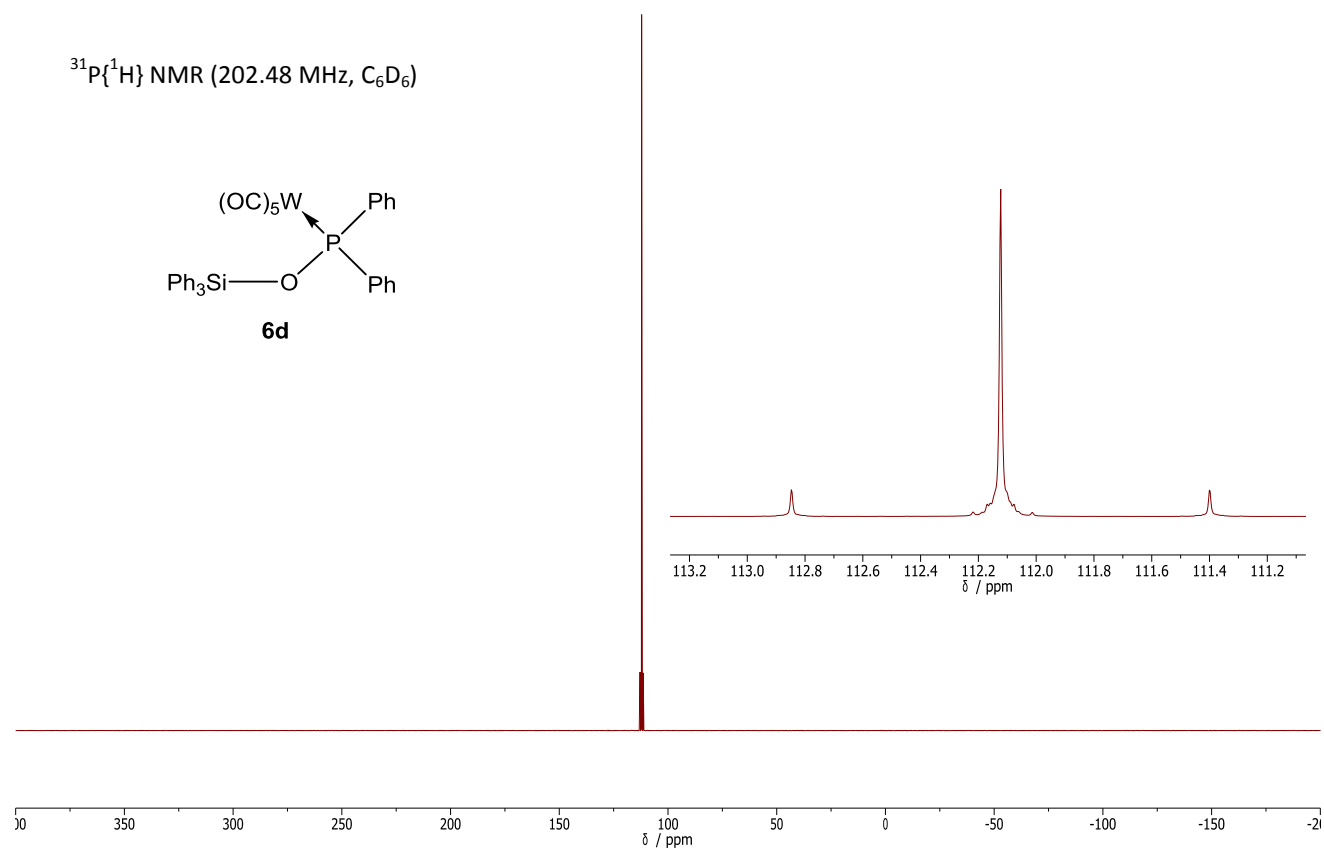


Figure S31: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **6d**.

^{31}P NMR (202.48 MHz, C_6D_6)

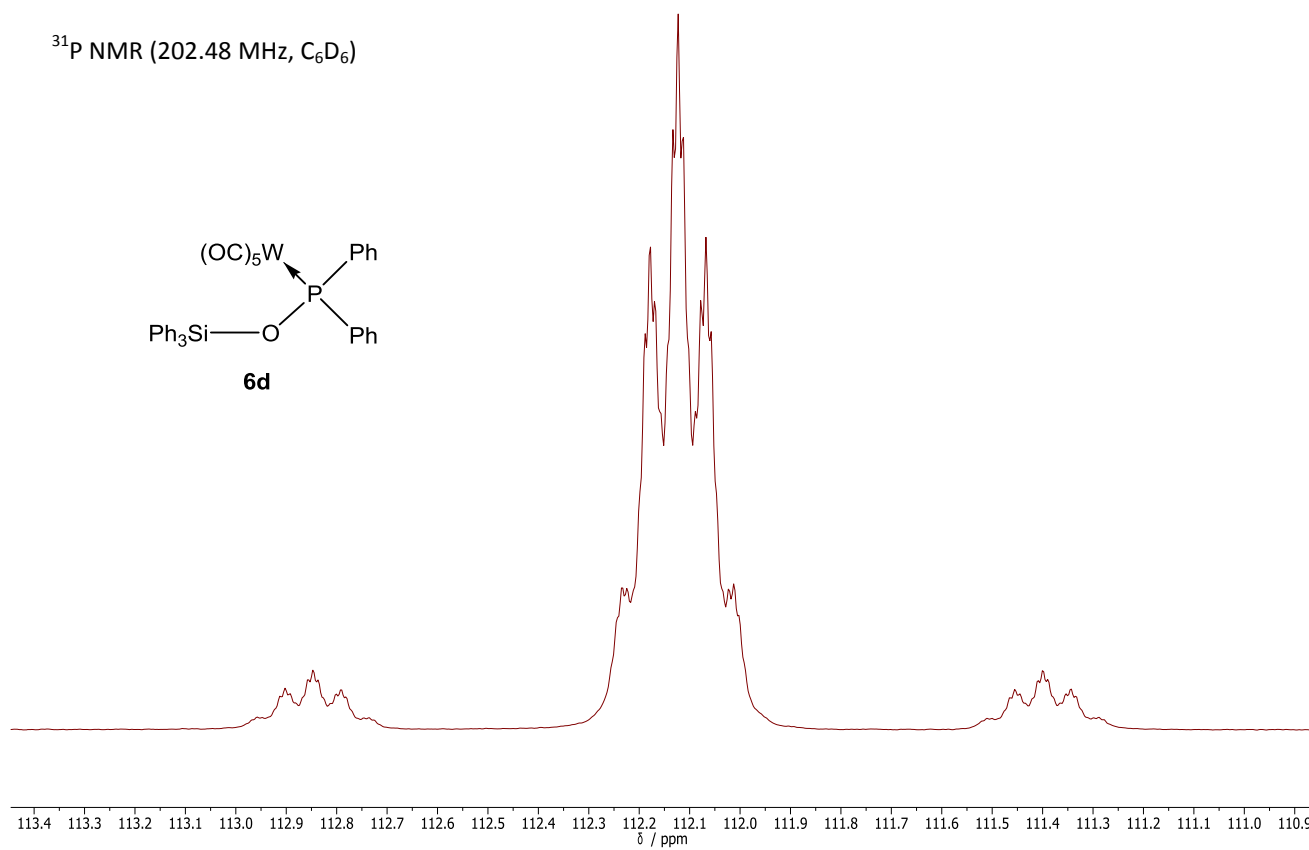
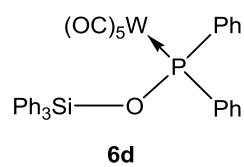


Figure S32: ^{31}P NMR spectrum of complex **6d**.

4) EPR spectra of complex 1 and measurement details:

Additionally, X-band continuous wave electron paramagnetic resonance spectroscopy (cw-EPR) was employed to detect the presence and development of any paramagnetic species during the course of the decomposition of complex **1**. At time zero the only paramagnetic species in the frozen sample was shown to be a weak nitroxide signal, attributed to a leftover from synthesis. Thawing the sample, heating it to 80 °C for 2 min, freezing it immediately in liquid nitrogen with subsequent measurement would let the decomposition proceed. Several such thaw/heat/freeze cycles were performed, each followed by EPR measurements (Figure S4). The result of multiple trials showed that the initial amount of remnant nitroxide signal varies and goes away very quickly. More interestingly, another signal appears slowly with the progress of the reaction. The intensity of this signal seems independent of the amount of the initial nitroxide, it grows with increasing reaction time and its large field spread suggests that it may stem from a metal-containing compound. Although it might not be possible to determine the identity of the contributing paramagnetic compound(s) at this point, its/their detection through the course of the reaction can serve as an evidence for a radical-mediated pathway for the reaction. Furthermore, the same anisotropic signal contributes to the spectrum of the liquid solution of the final product of the freeze/thaw cycles (t_{∞}) at room temperature (Figure S5), indicating that this compound is at least partially present in the final solution, although other species seem to be present in this final mixture.

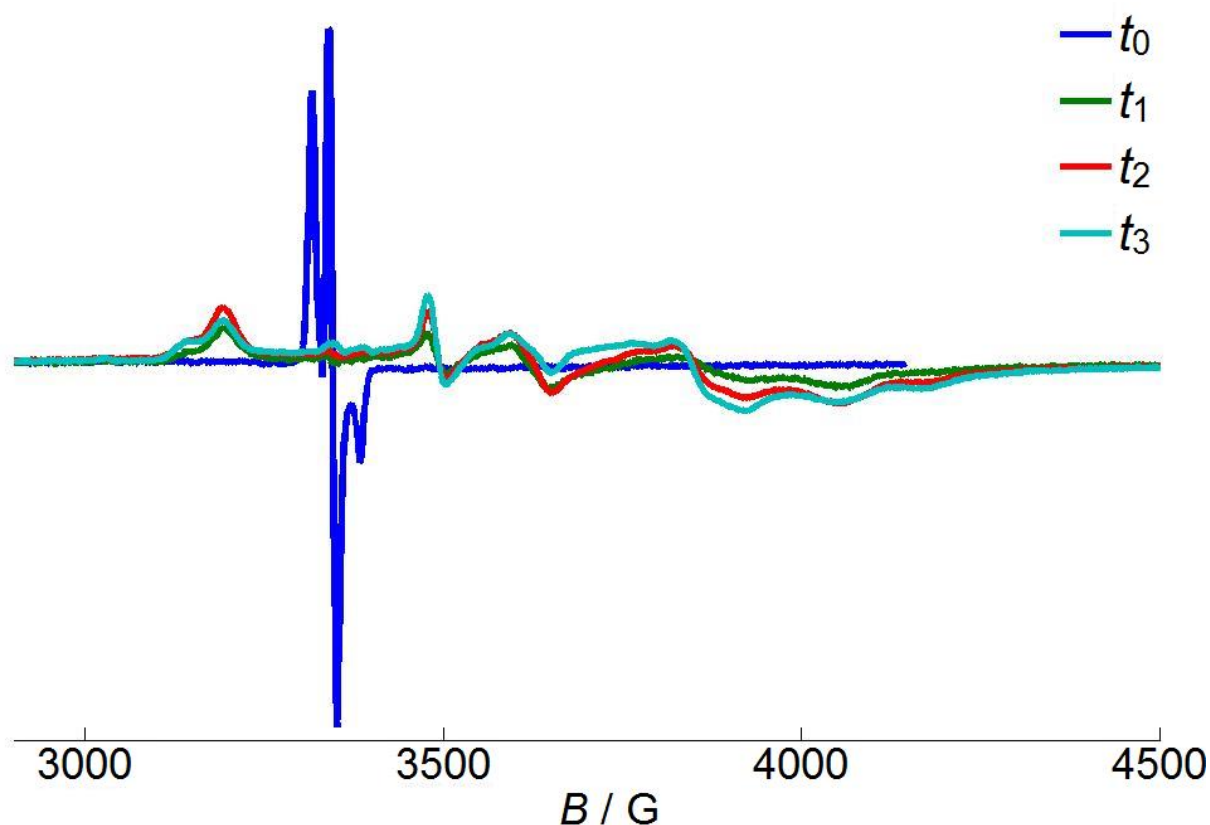


Figure S33: X-band cw-EPR spectra of a toluene- d_8 solution of complex **1** as a function of time at 100 K.

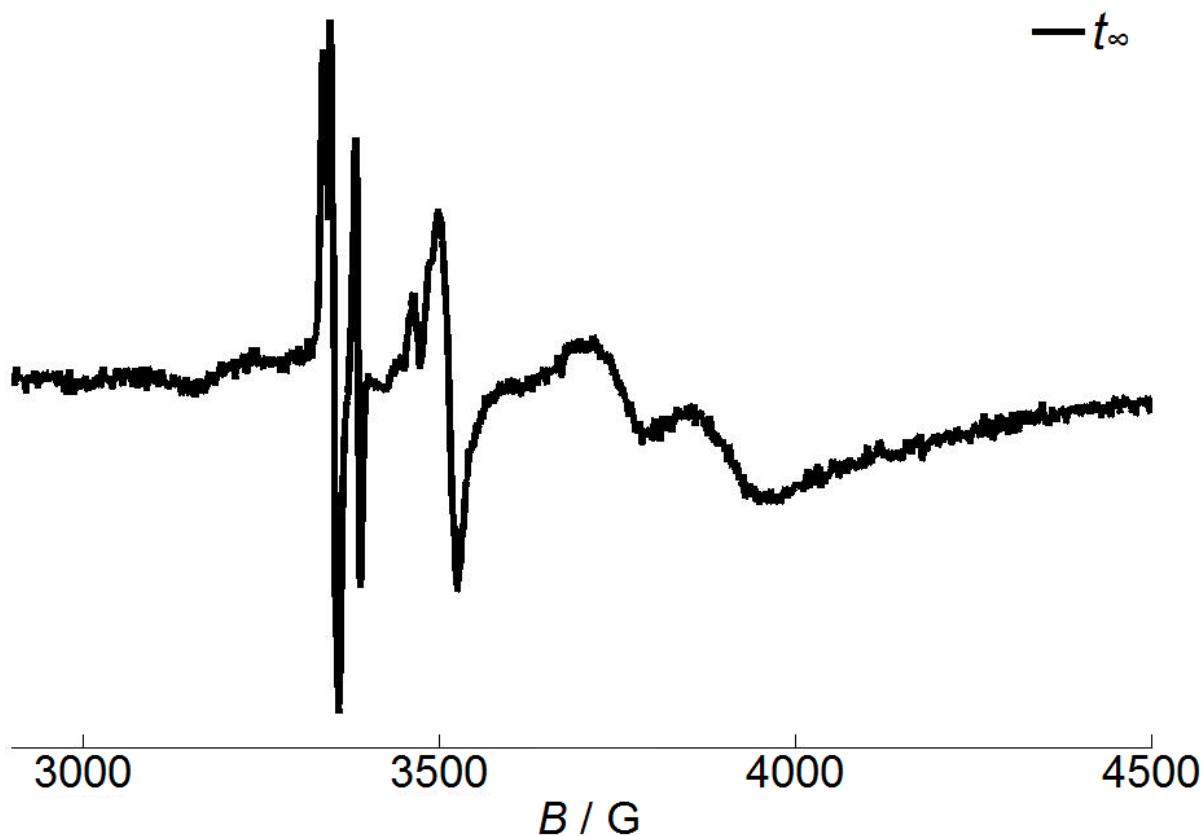


Figure S34: X-band cw-EPR spectra of the final solution of complex **1** at room temperature.

Experimental details:

The EPR spectra were recorded on an Bruker ELEXSYS E580 EPR spectrometer which was equipped with ER 4122 Super High Sensitivity (SHQ) resonator for measurements at X-band microwave frequency. The temperature was controlled with an Oxford ESR900 in combination with a temperature controlling unit ITC503S. The presented spectra are collected at 9.39 GHz frequency under 10 mW microwave power and 1 G modulation amplitude. The samples were prepared by filling a solution of complex **1** in dry and degassed toluene- d_8 ($c = 1$ mmol/L) in a glass EPR tube, that was sealed by melting under reduced pressure and freezing the solution in liquid nitrogen.

5) Computational details on the theoretical calculations:

The TURBOMOLE suite of programs^{S4} was used for all DFT calculations. All structures are fully optimized at the TPSS-D3/def2-TZVP + COSMO (toluene) level of theory, which combines the TPSS meta-GGA density functional^{S5} with the BJ-damped DFT-D3 dispersion correction^{S6,S7} and the large def2-TZVP AO basis set^{S8-S10}, together with the COSMO (for toluene solvent: dielectric constant $\epsilon_r = 2.38$, $R_{\text{sol}} = 3.48$ Å) solvation model^{S11}. The density-fitting RI-J approach^{S12,S13} is used to accelerate the geometry optimization and harmonic frequency calculations. Vibrational frequency analysis is used to identify the nature of located stationary points and to provide thermal and free-energy corrections according to the modified ideal gas–rigid rotor–harmonic oscillator model.^{S14} The structures are characterized as true minima (with no imaginary frequency) or transition states (with only one imaginary frequency). Better free energies in THF solution are obtained from the sum of TPSS-D3/def2-QZVP single-point energies,^{S9} COSMO-RS^{S15} solvation free energies (used the BP_TZVP_C30_1301.ctd parameter and $G_{\text{sol}} = \text{reference}$ option) and TPSS-D3/def2-TZVP thermal corrections at 298.15 K and 1 atm (*i.e.*, 0.04 mol/L gas). In our discussion, the final TPSS-D3/def2-QZVP + COSMO-RS(toluene) free energies (in kcal/mol) are used unless specified otherwise. For open-shell radical species, the spin densities are computed according to a Mulliken population analysis at the TPSS-D3/def2-TZVP + COSMO (toluene) level.

References:

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Table S1: The TPSS-D3/def2-TZVP + COSMO(toluene) computed lowest imaginary frequency (f_{im}), enthalpic (H_c) and Gibbs free-energy (G_c) corrections; the COSMO-RS(toluene) computed solvation enthalpic (H_{sol}) and Gibbs free-energy (G_{sol}) corrections; the TPSS-D3/def2-TZVP + COSMO(toluene) electronic energies (E_{cos}); the TPSS-D3/def2-QZVP single-point and relative electronic energies (E_{tot} and E_e); the final Gibbs free-energies (G) including relative electronic energy E_e , COSMO-RS(toluene) solvation free-energy G_{sol} and thermal correction G_c . Each structure is labeled either by its molecular formula or a specific name, such as **T** for TEMP and **W** for W(CO)₅. Loose complexes and high-lying isomers are further indicated by the sign of . and ', respectively. Transition structures (with only one imaginary frequency) are indicated by the "TS" prefix, followed by the labeling for two connected key intermediates.

Species	$f_{\text{im}} /$ cm^{-1}	$H_c /$ kcal/mol	$G_c /$ kcal/mol	$H_{\text{sol}} /$ kcal/mol	$G_{\text{sol}} /$ kcal/mol	$E_{\text{cos}} /$ E_h	$E_{\text{tot}} /$ E_h	$E_e /$ kcal/mol	$G /$ kcal/mol
1	0	326.04	262.69	-25.16	-14.97	-1923.34810	-1923.44404		
2	0	314.09	232.96	-31.21	-20.21	-2953.91357	-2954.04615		
2O	0	317.19	235.34	-32.48	-21.22	-3029.14674	-3029.28442		
3	0	282.77	216.79	-30.59	-19.38	-2394.92087	-2395.02914		
3W	0	317.49	234.01	-33.44	-21.87	-3029.21724	-3029.35632		
4	0	157.43	107.22	-20.07	-10.88	-1514.54213	-1514.60969		
4'	0	157.14	106.79	-20.51	-11.13	-1514.53763	-1514.60645		
4.1	0	485.02	389.60	-36.38	-24.32	-3437.89990	-3438.06527		
4.7b	0	341.84	266.24	-34.58	-22.52	-2424.74489	-2424.85321		
4.7d	0	344.03	271.06	-32.82	-20.95	-2500.09265	-2500.20775		
4H	0	164.62	114.11	-21.43	-12.05	-1515.18359	-1515.25077		
4W	0	191.74	123.68	-22.57	-12.87	-2148.85436	-2148.95307		
6b	0	337.44	263.38	-33.63	-22.03	-2424.22634	-2424.33344		
6b'	0	337.72	263.43	-35.77	-23.78	-2424.20082	-2424.30827		
6d	0	338.93	267.32	-31.08	-19.61	-2499.59025	-2499.70535		
6d'	0	339.15	267.31	-33.90	-22.05	-2499.54417	-2499.65991		
7b (HSnPh ₃)	0	182.91	143.55	-20.89	-11.36	-910.18385	-910.22206		
7d (HSiPh ₃)	0	184.90	147.41	-18.63	-9.36	-985.53393	-985.57992		
8b (SnPh ₃)	0	178.41	139.88	-21.10	-11.52	-909.56092	-909.59878		
8bT	0	346.05	291.59	-25.91	-15.48	-1318.40192	-1318.46868		
8d (SiPh ₃)	0	179.50	142.92	-18.95	-9.60	-984.88634	-984.93182		
8d.4H	0	345.15	271.82	-33.27	-21.45	-2500.09483	-2500.21010		
8dT	0	348.07	297.07	-23.77	-13.57	-1393.75857	-1393.83294		
9 (Ph ₂ PO)	0	123.20	91.69	-17.48	-8.89	-880.24480	-880.28145		
9T	0	290.97	244.63	-22.71	-12.89	-1289.02681	-1289.09287		
OT₂	0	338.32	294.22	-16.72	-8.27	-892.77387	-892.83338		
T (TEMP)	0	166.21	137.05	-10.97	-3.80	-408.75504	-408.78188		
T.6b	0	505.11	417.07	-40.33	-27.59	-2832.99817	-2833.13273		
T.6d	0	506.25	418.84	-37.42	-24.72	-2908.35765	-2908.50110		
TH (TEMP-H)	0	174.39	145.23	-10.94	-3.73	-409.40972	-409.43815		
TO (TEMPO)	0	170.15	139.86	-12.11	-4.69	-484.01700	-484.04622		
TOH	0	177.21	146.73	-11.78	-4.42	-484.62616	-484.65802		
TS4/4'	-44	156.72	107.04	-19.95	-10.80	-1514.53635	-1514.60502		
TS4/8b	-273	340.40	266.26	-34.89	-22.83	-2424.74030	-2424.84833		
TS4/8d	-688	341.28	268.98	-32.89	-21.09	-2500.08042	-2500.19534		
TS4H/4	-883	329.48	264.68	-27.61	-17.14	-1923.96804	-1924.06441		
TS7b/8b	-149	349.29	295.22	-27.45	-16.66	-1318.94404	-1319.01025		
TS7d/8d	-1476	350.45	298.05	-25.11	-14.55	-1394.28208	-1394.35657		
W (W(CO) ₅)	0	32.64	0.56	-7.49	-0.85	-634.19513	-634.19906		
W.OT	0	204.65	155.27	-17.86	-9.31	-1118.29021	-1118.35020		
W.T	0	201.34	154.64	-15.29	-7.18	-1043.05687	-1043.11329		

W.TH 0 209.82 162.62 -17.27 -8.86 -1043.69103 -1043.74769

Reactions	$f_{\text{im}} /$ cm^{-1}	$H_c /$ kcal/mol	$G_c /$ kcal/mol	$H_{\text{sol}} /$ kcal/mol	$G_{\text{sol}} /$ kcal/mol	$E_{\text{cos}} /$ E_h	$E_{\text{tot}} /$ E_h	$E_e /$ kcal/mol	$G /$ kcal/mol
1	0	326.04	262.69	-25.16	-14.97	-1923.34810	-1923.44404	0.0	0.0
4 + T (TEMP)	0	323.64	244.27	-31.03	-14.68	-1923.29717	-1923.39157	32.9	14.8
5 + TO	0	324.63	245.50	-31.53	-14.96	-1923.27530	-1923.36985	46.6	29.4
4'	0	157.14	106.79	-20.51	-11.13	-1514.53763	0.00000	0.0	0.0
9 + W	0	155.84	92.25	-24.96	-9.73	-1514.43993	-1514.48051	79.0	65.9
TS4/4'	-44	156.72	107.04	-19.95	-10.80	-1514.53635	-1514.60502	0.9	1.5
4	0	157.43	107.22	-20.07	-10.88	-1514.54213	-1514.60969	-2.0	-1.3
T + TO	0	336.36	276.91	-23.08	-8.49	-892.77203	-892.82810	0.0	0.0
OT ₂	0	338.32	294.22	-16.72	-8.27	-892.77387	-892.83338	-3.3	14.2
4 + 4	0	314.86	214.44	-40.13	-21.75	-3029.08426	-3029.21938	0.0	0.0
4 + 4'	0	314.57	214.01	-40.57	-22.01	-3029.07977	-3029.21614	2.0	1.3
2O	0	317.19	235.34	-32.48	-21.22	-3029.14674	-3029.28442	-40.8	-19.4
3W	0	317.49	234.01	-33.44	-21.87	-3029.21724	-3029.35632	-85.9	-66.5
3 + W	0	315.41	217.35	-38.07	-20.22	-3029.11601	-3029.22819	-5.5	-1.1
4W + 9	0	314.94	215.36	-40.05	-21.75	-3029.09916	-3029.23452	-9.5	-8.6
3W + T	0	483.70	371.06	-44.41	-25.68	-3437.97228	-3438.13821	0.0	0.0
3 + W.T	0	484.11	371.43	-45.88	-26.56	-3437.97774	-3438.14243	-2.7	-3.2
2O + T	0	483.39	372.39	-43.45	-25.03	-3437.90178	-3438.06630	0.0	0.0
2 + TO	0	484.24	372.82	-43.32	-24.90	-3437.93057	-3438.09237	-16.4	-15.8
3W + 4	0	474.92	341.23	-53.50	-32.75	-4543.75937	-4543.96601	0.0	0.0
3 + 4W	0	474.51	340.46	-53.16	-32.24	-4543.77524	-4543.98220	-10.2	-10.4
4H + T	0	330.83	251.16	-32.39	-15.85	-1923.93863	-1924.03265	0.0	0.0
TS4H/4	-883	329.48	264.68	-27.61	-17.14	-1923.96804	-1924.06441	-19.9	-7.7
4 + TH	0	331.82	252.45	-31.01	-14.61	-1923.95185	-1924.04784	-9.5	-7.0
1	0	326.04	262.69	-25.16	-14.97	-1923.34810	-1923.44404	0.0	0.0
9T + W	0	323.61	245.20	-30.20	-13.73	-1923.22194	-1923.29193	95.5	79.2
4 + 1	0	483.47	369.90	-45.23	-25.85	-3437.89023	-3438.05373	0.0	0.0
4W + 9T	0	482.71	368.31	-45.28	-25.75	-3437.88118	-3438.04594	4.9	3.4
2 + TO	0	484.24	372.82	-43.32	-24.90	-3437.93057	-3438.09237	-24.3	-20.4
4.1	0	485.02	389.60	-36.38	-24.32	-3437.89990	-3438.06527	-7.2	14.0
4 + 7b	0	340.35	250.77	-40.95	-22.23	-2424.72599	-2424.83175	0.0	0.0
4.7b	0	341.84	266.24	-34.58	-22.52	-2424.74489	-2424.85321	-13.5	1.7
4.7b'	0	341.86	266.76	-33.64	-21.91	-2424.74363	-2424.85147	-12.4	3.9
TS4/8b	-273	340.40	266.26	-34.89	-22.83	-2424.74030	-2424.84833	-10.4	4.5
4H + 8b	0	343.03	253.99	-42.53	-23.57	-2424.74451	-2424.84955	-11.2	-9.3
4 + 8b	0	335.85	247.10	-41.17	-22.40	-2424.10305	-2424.20847	0.0	0.0

6b	0	337.44	263.38	-33.63	-22.03	-2424.22634	-2424.33344	-78.4	-61.8
4' + 8b	0	335.55	246.67	-41.61	-22.66	-2424.09855	-2424.20523	2.0	1.3
6b'	0	337.72	263.43	-35.77	-23.78	-2424.20082	-2424.30827	-62.6	-47.7
8b + T	0	344.62	276.93	-32.07	-15.33	-1318.31595	-1318.38066	0.0	0.0
8bT	0	346.05	291.59	-25.91	-15.48	-1318.40192	-1318.46868	-55.2	-40.7
T + 7b	0	349.12	280.60	-31.86	-15.16	-1318.93889	-1319.00394	0.0	0.0
TS7b/8b	-149	349.29	295.22	-27.45	-16.66	-1318.94404	-1319.01025	-4.0	9.2
TH + 8b	0	352.80	285.11	-32.05	-15.26	-1318.97064	-1319.03693	-20.7	-16.3
TO + 7b	0	353.07	283.41	-33.00	-16.05	-1394.20085	-1394.26828	0.0	0.0
TOH + 8b	0	355.62	286.61	-32.88	-15.94	-1394.18708	-1394.25680	7.2	10.5
8bT + 4	0	503.48	398.81	-45.97	-26.36	-2832.94405	-2833.07837	0.0	0.0
T.6b	0	505.11	417.07	-40.33	-27.59	-2832.99817	-2833.13273	-34.1	-17.1
6b + T	0	503.65	400.43	-44.59	-25.83	-2832.98137	-2833.11532	-23.2	-21.0
T + 7d	0	351.11	284.46	-29.60	-13.17	-1394.28896	-1394.36180	0.0	0.0
TS7d/8d	-1476	350.45	298.05	-25.11	-14.55	-1394.28208	-1394.35657	3.3	15.5
TH + 8d	0	353.88	288.15	-29.89	-13.33	-1394.29606	-1394.36998	-5.1	-1.6
4 + 7d	0	342.33	254.63	-38.70	-20.24	-2500.07606	-2500.18961	0.0	0.0
4.7d	0	344.03	271.06	-32.82	-20.95	-2500.09265	-2500.20775	-11.4	4.3
TS4/8d	-688	341.28	268.98	-32.89	-21.09	-2500.08042	-2500.19534	-3.6	9.9
8d.4H	0	345.15	271.82	-33.27	-21.45	-2500.09483	-2500.21010	-12.9	3.1
4H + 8d	0	344.11	257.02	-40.38	-21.65	-2500.06994	-2500.18259	4.4	5.4
4 + 8d	0	336.93	250.14	-39.02	-20.48	-2499.42848	-2499.54151	0.0	0.0
6d	0	338.93	267.32	-31.08	-19.61	-2499.59025	-2499.70535	-102.8	-84.8
4' + 8d	0	336.63	249.71	-39.46	-20.73	-2499.42398	-2499.53827	2.0	1.3
6d'	0	339.15	267.31	-33.90	-22.05	-2499.54417	-2499.65991	-74.3	-58.7
T + 8d	0	345.70	279.97	-29.92	-13.40	-1393.64138	-1393.71371	0.0	0.0
8dT	0	348.07	297.07	-23.77	-13.57	-1393.75857	-1393.83294	-74.8	-57.9
8dT + 4	0	505.50	404.28	-43.83	-24.44	-2908.30071	-2908.44263	0.0	0.0
T.6d	0	506.25	418.84	-37.42	-24.72	-2908.35765	-2908.50110	-36.7	-22.4
6d + T	0	505.13	404.38	-42.05	-23.41	-2908.34529	-2908.48723	-28.0	-26.9
4 + W	0	190.07	107.78	-27.55	-11.72	-2148.73726	-2148.80875	0.0	0.0
4W	0	191.74	123.68	-22.57	-12.87	-2148.85436	-2148.95307	-90.6	-75.8
TO + W	0	202.79	140.43	-19.60	-5.54	-1118.21213	-1118.24528	0.0	0.0
W.OT	0	204.65	155.27	-17.86	-9.31	-1118.29021	-1118.35020	-65.8	-54.8
T + W	0	198.85	137.61	-18.45	-4.65	-1042.95017	-1042.98094	0.0	0.0
W.T	0	201.34	154.64	-15.29	-7.18	-1043.05687	-1043.11329	-83.1	-68.6
TH + W	0	207.03	145.80	-18.43	-4.58	-1043.60485	-1043.63721	0.0	0.0
W.TH	0	209.82	162.62	-17.27	-8.86	-1043.69103	-1043.74769	-69.3	-56.8

3W	0	317.49	234.01	-33.44	-21.87	-3029.21724	-3029.35632	0.0	0.0
3 + W	0	315.41	217.35	-38.07	-20.22	-3029.11601	-3029.22819	80.4	65.4
