Electronic Supporting Information

for

A synthon for unknown 1,3-zwitterions? – A K/OR phosphinidenoid complex with an additional Si-Cl function

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Abstract: Although the chemistry of frustrated Lewis pairs (FLPs) has seen tremendous developments, investigations on anionic, monomolecular FLPs are still scarce, and 1,3-zwitterions unknown. Herein, synthesis and reactions of a K/OR phosphinidenoid complex containing a Si-Cl function is reported, and this anionic "crypto-FLP" allow access to novel P-heterocyclic ligands via stepwise reactions.

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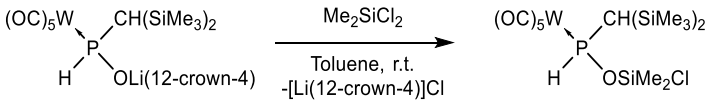
1. Experimental Procedures

General information.

All operations were performed under an argon atmosphere, using Schlenk techniques or a glove box. Before use, the argon is dried by phosphorus pentoxide and traces of oxygen are removed by a copper catalyst. The values of water and oxygen in the glovebox are kept under 0.1 ppm, each. All used solvents are purified before use, by fresh distillation from sodium wire. Additionally diethyl ether and toluene for glove box use were taken from a MBRAUN SPS800 solvent purification system. All NMR spectra were recorded at room temperature on a Bruker Avance I 300 MHz (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C, 59.9 for ^{29} Si and 121.5 MHz for ^{31}P) or a Bruker Avance III HD 500 MHz Prodigy (500.1 MHz for ^{1}H, 125.7 MHz for ^{13}C, 99.3 for ^{29} Si and 202.4 MHz for ^{31}P) spectrometer, respectively. Benzene-d_6 and THF-d_8 were used as solvents for NMR spectroscopy. ^{1}H and ^{13}C spectra were references to the residual proton resonances of these solvents. For ^{29}Si and ^{31}P NMR measurements a solution of Tetramethylsilane in $CDCl_3$ or 85% H_3PO_4, respectively, were used as external standards. All melting points were measured on a Büchi Type S device, in sealed capillaries, the values are not corrected. Elemental analyses were carried out on a Elementa Vario EL gas chromatograph. Mass spectra were recorded on a Thermo Finnigan MAT 95 XL in the case of EI spectra, and on a Thermo Fischer Scientific Orbitrap XL in the case of ESI spectra. All IR spectra were measured from solids on a Bruker Alpha Diamond ATR FTIR device. The UV/vis spectra were recorded on a Shimadzu UV-1650PC. Single crystal x-ray analyses were performed on a Bruker X8-KappaApexII diffractometer at 100 K. SHELXT-2014 and SHELXL-2014[1] program packages were used for solving the structures involving intrinsic phasing methods refined by full-matrix least-squares technique in anisotropic approximation for non-hydrogen atoms. P-bounded Hydrogen atoms were located by Fourier synthesis and refined isotropically, all other H atoms where included using a riding model on the bound carbon atom.



1 **2**

Preparation of complex **2**:

To a suspension of **1** (2,29 g, 3.2 mmol) in 30 mL toluene, 3.9 ml of dimethyldichlorosilane (4,13 g, 32.0 mmol, 10 eq.) were added at room temperature. After 4 days stirring all volatiles were removed in *vacuo* (10^{-2} mbar). The residue was extracted four times with 10 mL *n*-pentane and filtered to separate from [Li(12-crown-4)]Cl. After removal of the solvent in *vacuo* (10^{-2} mbar) a white solid was obtained. Traces of a rose-colored impurity were removed by washing with 0.5 mL acetonitrile at -40 °C. The white powder was then dried in *vacuo* (10^{-2} mbar).

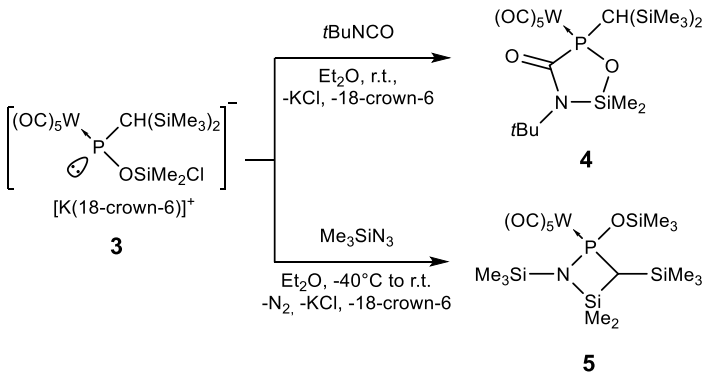
Yield: 1.542 g (2.467 mmol, 77 %). ^{1}H NMR (300,1 MHz, C_6D_6): δ [ppm] = 0.02 (s, 9H, Si-C*H*$_3$), 0.22 (s, 9H, Si-C*H*$_3$), 0.26 (s, 3H, O-Si-C*H*$_3$), 0.37 (s, 3H, O-Si-C*H*$_3$), 0.87 (d, 1H, P-C*H*, $^{2}J_{P,H}$ = 2.9 Hz), 8.33 (dd, 1H, $^{1}J_{P,H}$ = 334.2 Hz, $^{3}J_{H,H}$ = 1.2 Hz, $^{1}J_{C,H}$ = 7.6 Hz, P*H*). ^{13}C{^{1}H} NMR 125,5 MHz, C_6D_6): δ [ppm] = 0.2 (d_{sat}, $^{3}J_{P,C}$ = 2.1 Hz, $^{1}J_{Si,C}$ = 51.7 Hz, Si-*C*H$_3$), 2.0 (d_{sat}, $^{3}J_{P,C}$ = 3.6 Hz, $^{1}J_{Si,C}$ = 53.0 Hz, Si-*C*H$_3$), 3.2 (d_{sat}, $^{3}J_{P,C}$ = 6.2 Hz, $^{1}J_{Si,C}$ = 72.5 Hz, O-Si-*C*H$_3$), 26.5 (d_{sat}, $^{1}J_{P,C}$ = 10.0 Hz, $^{1}J_{Si,C}$ = 34.7 Hz, P-*C*), 197.3 (d_{sat}, $^{2}J_{P,C}$ = 7.5 Hz, $^{1}J_{W,C}$ = 125.7 Hz, *cis*-*C*O), 199.3 (d_{sat}, $^{2}J_{P,C}$ = 26.1 Hz, $^{1}J_{W,C}$ = 139.3 Hz, *trans*-*C*O). ^{29}Si{^{1}H} NMR (59,6 MHz, C_6D_6): δ [ppm] = 0.3 (d_{sat}, $^{2}J_{P,Si}$ = 5.6 Hz, *Si*Me$_3$), 2.2 (d, $^{2}J_{P,Si}$ = 9.5 Hz, *Si*Me$_3$), 13.1 (d, $^{2}J_{P,Si}$ = 14.8 Hz, *Si*Me$_2$Cl). ^{31}P NMR (121,4 MHz, C_6D_6): δ [ppm] = 82.3 (d_{sat}, $^{1}J_{W,P}$ = 278.5 Hz, $^{1}J_{P,H}$ = 334.2 Hz). IR (ATR Diamond, $\tilde{\nu}$ [cm^{-1}], selected peaks): 2364 (w, ν(PH)), 2070 (s, ν(CO)), 1979 (w, ν(CO)), 1896 (vs, ν(CO)), 1250 (s, ν(P-O-Si). MS (EI, 70 eV, ^{184}W, selected peaks): m/z (%) = 624.0 (20) [M]$^{\bullet+}$, 596.0 (8) [M-1 CO]$^{\bullet+}$, 568.0 (48) [M-2 CO]$^{\bullet+}$, 540.0 (10) [M-3 CO]$^{\bullet+}$, 512.0 (34) [M-4 CO]$^{\bullet+}$, 484.0 (30) [M-5 CO]$^{\bullet+}$, 146.9 (48) [$C_3H_8OPSi_2$]$^{\bullet+}$, 73.0 (100) [$SiMe_3$]$^{\bullet+}$. M.p. 76 °C. EA [%]: theor./exp. C 26.91/27.44, H 4.19/4.30.

2 **3**

Preparation of complex **3**:

To a solution of complex **2** (1.272 g, 2.04 mmol) in 10 mL diethyl ether a solution of KHMDS (405.9 mg, 2.04 mmol, 1.0 eq.) and 18-crown-6 (537.6 mg, 2.04 mmol, 1.0 eq.) in 18 mL diethyl ether was added slowly at room temperature. After 20 minutes of stirring, all volatiles were removed in *vacuo* (10^{-2} mbar). The orange residue was washed five times with 4 mL *n*-pentane and then dried in *vacuo* (10^{-2} mbar) to yield an orange solid.

Yield: 1.651 g (1.78 mmol, 88 %). ^{1}H NMR (300,1 MHz, THF-d_8): δ [ppm] = 0.07 (d, 9 H, $^{4}J_{P,H}$ = 1.2 Hz, Si(C*H*$_3$)$_3$), 0.19 (s, 9 H, Si(C*H*$_3$)$_3$), 0.36 (s, 3H, O-SiC*H*$_3$), 0.42 (s, 3H, O-SiC*H*$_3$), 1.68 (s, 1 H, P-C*H*), 3.62 (s, 24 H, C*H*$_2$). ^{13}C{^{1}H} NMR 75,5 MHz, THF-d_8): δ [ppm] = 1.6 (d_{sat}, $^{3}J_{P,H}$ = 12.6 Hz, $^{1}J_{Si,C}$ = 51.5 Hz, Si(*C*H$_3$)$_3$), 3.7 (d, $^{3}J_{P,C}$ = 5.2 Hz, O-Si-*C*H$_3$), 3.8 (s_{sat}, $^{1}J_{Si,C}$ = 50.8 Hz, Si(*C*H$_3$)$_3$), 4.0 (d, $^{3}J_{P,C}$ = 0.9 Hz, O-Si-*C*H$_3$), 26.9 (d, $^{1}J_{P,C}$ = 70.8 Hz, P-*C*H), 71.1 (s, CH$_2$), 206.8 (d_{sat}, $^{1}J_{W,C}$ = 127.6 Hz, $^{2}J_{P,C}$ = 6.7 Hz, *cis*-*C*O), 210.6 (d, $^{1}J_{W,P}$ = 127.6 Hz, $^{2}J_{P,C}$ = 15.4 Hz, *trans*-*C*O). ^{29}Si{^{1}H} NMR (59,6 MHz, THF-d_8): δ [ppm] = -5.7 (d, $^{2}J_{P,Si}$ = 27.5 Hz, *Si*Me$_3$), -1.1 (d, $^{2}J_{P,Si}$ = 3.2 Hz, *Si*Me$_3$), 6.0 (d, $^{2}J_{P,Si}$ = 11.9 Hz, O-*Si*(CH$_3$)$_2$). ^{31}P NMR (121,4 MHz, THF-d_8): δ [ppm] = 214.5 (s_{sat}, $^{1}J_{W,P}$ = 72.1 Hz). IR (ATR Diamond, $\tilde{\nu}$ [cm^{-1}], selected peaks): 2071 (w, ν(CO)), 2029 (m, ν(CO)), 1983 (w, ν(CO)), 1933 (w, ν(CO)), 1856 (vs, ν(CO)), 1250 (s, ν(P-O-Si). UV/vis 432 (0.582). ε_{432} = 2.5606·10^3 L·mol^{-1}·cm^{-1}.MS (ESI, positive, ^{184}W, selected peaks): m/z (%) = 303.1 (100) [M]$^{\bullet+}$. MS (ESI, negative, ^{184}W, selected peaks): m/z (%) = 531.0 (40) [M-SiMe$_2$Cl+H]$^{\bullet-}$. M.p. 89 °C. EA [%]: theor./exp. C 33.68/33.39, H 5.33/5.37.



3 **4** **5**

Preparation of complexes **4** and **5**:

Complex **4**: To a solution of complex **3** (503.4 mg, 0.54 mmol) in 6 mL diethyl ether 200 µL (173.6 mg, 1.75 mmol, 3.2 eq.) of *tert*-butyl isocyanate were added. After 90 minutes of stirring, all volatiles were removed in *vacuo* (10^{-2} mbar). The crude product was then purified by low-temperature chromatography under an argon atmosphere (-20 °C, h = 4 cm, ø = 3,5 cm, undried Al_2O_3. The used eluent was a mixture a *n*-pentane and diethyl ether (97:3). The product is contained in the first fraction. After removal of all volatiles in *vacuo* (10^{-2} mbar), a white solid was obtained which was further dried in *vacuo* (10^{-2} mbar).

Complex **4**: Yield: 85.2 mg (0.12 mmol, 23 %). ^{1}H NMR (300,1 MHz, C_6D_6): δ [ppm] = 0.11 (s, 3H, O-Si-*C*H_3), 0.24 (s, 9H, Si-*C*H_3), 0.29 (s, 3H, O-Si-*C*H_3), 0.34 (s, 9H, Si-*C*H_3), 1.25 (s, 9 H, *t*Bu), 1.43 (d, 1H, $^{2}J_{P,H}$ = 2.3 Hz, P-C*H*). ^{13}C{^{1}H} NMR 125,5 MHz, C_6D_6): δ [ppm] = 2.7 (d_{sat}, $^{3}J_{P,C}$ = 1.8 Hz, $^{1}J_{Si,C}$ = 52.3 Hz, Si-CH_3), 2.9 (s_{sat}, $^{1}J_{Si,C}$ = 69.2 Hz, O-Si-CH_3), 2.9 (d_{sat}, $^{3}J_{P,C}$ = 3.1 Hz, $^{1}J_{Si,C}$ = 53.1 Hz, Si-CH_3), 3.9 (s_{sat}, $^{1}J_{Si,C}$ = 69.1 Hz, O-Si-CH_3), 28.8 (s, N-C(*C*H_3)$_3$), 32.0 (d_{sat}, $^{1}J_{P,C}$ = 6.6 Hz, $^{1}J_{Si,C}$ = 31.2 Hz, P-*C*H), 55.8 (d, $^{1}J_{P,C}$ = 3.7 Hz, N-*C*(CH_3)$_3$), 183.6 (d, $^{1}J_{P,C}$ = 45.5 Hz, P-*C*-N), 197.6 (d_{sat}, $^{2}J_{P,C}$ = 3.7 Hz, $^{1}J_{W,C}$ = 129.9 Hz, *cis*-*C*O), 199.6 (d_{sat}, 1C, $^{2}J_{P,C}$ = 26.8 Hz, $^{1}J_{W,C}$ = 139.1 Hz, *trans*-*C*O). ^{15}N{^{1}H} NMR 50.7 MHz, C_6D_6): δ [ppm] = -232.5 (s). ^{29}Si{^{1}H} NMR (59,6 MHz, C_6D_6): δ [ppm] = 0.5 (d, $^{2}J_{P,Si}$ = 4.5 Hz, *Si*Me_3), 0.9 (d, $^{2}J_{P,Si}$ = 10.4 Hz, *Si*Me_3), 16.2 (d, $^{2}J_{P,Si}$ = 9.4 Hz, O-*Si*(CH_3)$_2$). ^{31}P NMR (202,4 MHz, C_6D_6): δ [ppm] = 116.5 ppm (s_{sat}, $^{1}J_{W,P}$ = 283.5 Hz). IR (ATR Diamond, $\tilde{\nu}$ [cm^{-1}], selected peaks): 2366 (w, ν(CO)), 2070 (m, ν(CO)), 1986 (m, ν(CO)), 1950 (sh, ν(CO)), 1940 (sh, ν(CO)), 1905 (vs, ν(CO)), 1641 (s, ν(C=O)),. MS (EI, 70 eV, ^{184}W, selected peaks): m/z (%) = 687.1 (38) $[M]^{\bullet+}$, 631.1 (30) [M-2 CO]$^{\bullet+}$, 603.1 (86) [M-3 CO]$^{\bullet+}$, 575.1 (100) [M-4 CO]$^{\bullet+}$, 474.0 (15) [M-3 CO-(^{t}BuN=$SiMe_2$)]$^{\bullet+}$, 73.1 (58) $[SiMe_3]^{\bullet+}$. M.p. 94 °C.

Complex **5**: To a solution of complex **3** (412.3 mg, 0.45 mmol) in 6 mL diethyl ether a solution of 80 µL (69.4 mg, 0.60 mmol, 1.3 eq.) trimethylsilyl azide in 2 mL diethyl ether. After 130 minutes of stirring, all volatiles were removed in *vacuo* (10^{-2} mbar). The residue was extracted four times with 2 mL *n*-pentane and filtered to separate from KCl. The crude product was washed eight times with 0.2 mL of acetonitrile at -40°C. Afterwards the crude product was dissolved in 1 mL of *n*-pentane, and cooled down to -40 °C. After 12 hours, 18-crown-6 crystallized from this solution. After separation from 18-crown-6, the solvent was removed in *vacuo* (10^{-2} mbar). A white solid was obtained, which was dried in *vacuo* (10^{-2} mbar).

Complex **5**: Yield: 52.4 mg (0.078 mmol, 17 %). ^{1}H NMR (500,1 MHz, C_6D_6): δ [ppm] = 0.19 (s, 9H, O-Si-(CH_3)$_3$), 0.19 (s, 3H, Si(CH_3)$_2$), 0.21 (s, 9H, P-CH-Si-CH_3), 0.22 (s, 9H, N-Si(CH_3)$_3$), 0.32 (s, 3H, Si(CH_3)$_2$), 1.45 (d, 1H, $^{2}J_{P,H}$ = 13.8 Hz, P-C*H*). ^{13}C{^{1}H} NMR 125,8 MHz, C_6D_6): δ [ppm] = 1.4 (d_{sat}, $^{3}J_{P,C}$ = 3.6 Hz, $^{1}J_{Si,C}$ = 52.7 Hz, O-Si(*C*H_3)$_3$), 2.1 (d, $^{3}J_{P,C}$ = 0.6 Hz, N-Si-*C*H_3), 2.2 (d_{sat}, $^{3}J_{P,C}$ = 2.2 Hz, $^{1}J_{Si,C}$ = 56.7 Hz, P-CH-Si(*C*H_3)$_3$), 3.4 (s_{sat}, $^{1}J_{Si,C}$ = 56.9 Hz, Si(*C*H_3)$_2$), 7.2 (d_{sat}, $^{3}J_{P,C}$ = 2.3 Hz, $^{1}J_{Si,C}$ = 53.4 Hz, Si(*C*H_3)$_2$), 38.2 (d_{sat},, $^{3}J_{P,C}$ = 9.7 Hz, $^{1}J_{Si,C}$ = 46.3 Hz, P-*C*H), 199.5 (d_{sat}, $^{1}J_{W,C}$ = 126.1 Hz, $^{2}J_{P,C}$ = 9.1 Hz, *cis*-*C*O), 200.0 (d_{sat}, $^{1}J_{W,C}$ = 135.7 Hz, $^{2}J_{P,C}$ = 28.3 Hz, *trans*-*C*O). ^{29}Si{^{1}H} NMR (59,6 MHz, C_6D_6): δ [ppm] = -4.3 (d_{sat}, $^{2}J_{P,Si}$ = 5.6 Hz, $^{1}J_{Si,C}$ = 52.8 Hz, CH-*Si*Me_3), 2.5 (s_{sat}, $^{1}J_{Si,C}$ = 56.9 Hz, N-*Si*Me_3), 12.5 (d, $^{2}J_{P,Si}$ = 25.3 Hz, O-*Si*Me_3), 14.1 (d, $^{2}J_{P,Si}$ = 15.3 Hz, CH-*Si*Me_2-N). ^{31}P NMR (121,4 MHz, C_6D_6): δ [ppm] = isomer 1 (95 %): 118.4 ppm (d_{sat}, $^{1}J_{W,P}$ = 318.3 Hz, $^{2}J_{P,H}$ = 13.8 Hz); isomer 2 (5 %): 117.1 ppm (d_{sat}, $^{1}J_{W,P}$ = 310.7 Hz, $^{2}J_{P,H}$ = 2.0 Hz). IR (ATR Diamond, $\tilde{\nu}$ [cm^{-1}], selected peaks): 2066 (s, ν(CO)), 1973 (w, ν(CO)), 1907 (vs, ν(CO)). MS (EI, 70 eV, ^{184}W, selected peaks): m/z (%) = 675.1 (19) $[M]^{\bullet+}$, 591.1 (100) [M-3 CO]$^{\bullet+}$, 535.1 (64) [M-5 CO]$^{\bullet+}$, 351.1 (39) [M-5 CO - W]$^{\bullet+}$, 73.0 (32) $[SiMe_3]^{\bullet+}$. M.p. 141 °C.

2. **Crystallographic data**

Complex **2** ($C_{14}H_{26}O_6Si_3PClW$): M = 624.89 g·mol^{-1}, monoclinic, $P2_1/c$, a = 9.3757(10) Å, b = 10.4164(9) Å, c = 25.134(3) Å, α = 90°, β = 93.912(4)°, γ = 90°, V = 2448.9(4) Å^3, Z = 4, $d_{calcd.}$ = 1.695 g·cm^{-3}, μ = 5.062 mm^{-1}, T = 100 K. A sum of 28078 reflections (5331 unique; R_{int} = 0.0773) were measured by a Bruker X8-KappaApexII diffractometer (monochromated Mo-$K\alpha$ radiation; λ = 0.71073 Å; empirical absorption correction with T_{min} = 0.5641 and T_{max} = 0.7460). Patterson methods were applied for the solution of the structure, refinement was performed by full-matrix-least squares fitting against F^2 for all reflections. Hydrogens were refined as rigid groups while other atoms were refined anisotropically. R values [$I>2\sigma(I)$]: R_1 = 0.0569, wR_2 = 0.0871. R values (all data): R_1 = 0.0800, wR_2 = 0.0962, min./max. electron difference 1.33/-1.87 e·Å^{-3}.

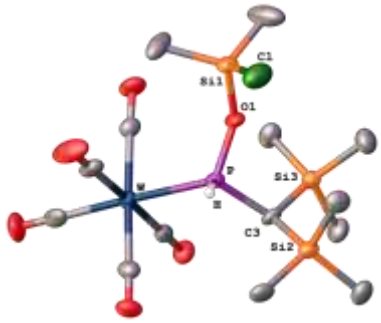


Figure S1. ORTEP drawing of the molecular structure of complex **2** in the solid state (ellipsoids are set at 50% probability level and hydrogen atoms except P-H are omitted for clarity). Selected bond lengths (Å) and angles (deg): P-W 2.476(2); P-C3 1.821(7); P-O1 1.623(5); Si1-O1 1.645(5); W-P-O 118.3(2); W-P-C3 117.4(3); O1-P-C3 103.7(3); P-O1-Si1 141.3(3).

Complex **4** ($C_{19}H_{34}NO_7Si_3PW$): M = 687.56 g·mol^{-1}, orthorombic, $P2_12_12_1$, a = 9.9978(4) Å, b = 13.3597(5) Å, c = 21.3413(9) Å, α = 90°, β = 90°, γ = 90°, V = 2850.5(2) Å^3, Z = 4, $d_{calcd.}$ = 1.602 g·cm^{-3}, μ = 4.270 mm^{-1}, T = 100 K. A sum of 25714 reflections (6863 unique; R_{int} = 0.0325) were measured by a Bruker X8-KappaApexII diffractometer (monochromated Mo-$K\alpha$ radiation; λ = 0.71073 Å; empirical absorption correction with T_{min} = 0.4896 and T_{max} = 0.7462). Patterson methods were applied for the solution of the structure, refinement was performed by full-matrix-least squares fitting against F^2 for all reflections. Hydrogens were refined as rigid groups while other atoms were refined anisotropically. R values [$I>2\sigma(I)$]: R_1 = 0.0175, wR_2 = 0.0363. R values (all data): R_1 = 0.0196, wR_2 = 0.0371, min./max. electron difference 0.68/-0.26 e·Å^{-3}.

Complex **5** ($C_{17}H_{34}NO_6Si_4PW$): M = 675.63 g·mol^{-1}, monoclinic, $P2_1/c$, a = 15.8672(11) Å, b = 16.5104(11) Å, c = 22.0806(15) Å, α = 90°, β = 91.193(3)°, γ = 90°, V = 5783.3(7) Å^3, Z = 8, $d_{calcd.}$ = 1.552 g·cm^{-3}, μ = 4.244 mm^{-1}, T = 100 K. A sum of 80534 reflections (13954 unique; R_{int} = 0.0474) were measured by a Bruker X8-KappaApexII diffractometer (monochromated Mo-$K\alpha$ radiation; λ = 0.71073 Å; empirical absorption correction with T_{min} = 0.4169 and T_{max} = 0.7461). Patterson methods were applied for the solution of the structure, refinement was performed by full-matrix-least squares fitting against F^2 for all reflections. Hydrogens were refined as rigid groups while other atoms were refined anisotropically. R values [$I>2\sigma(I)$]: R_1 = 0.0237, wR_2 = 0.0513. R values (all data): R_1 = 0.0316, wR_2 = 0.0542, min./max. electron difference 1.09/-0.76 e·Å^{-3}.

The primitive cell contains two independent molecules, having split layers (Figure S1).

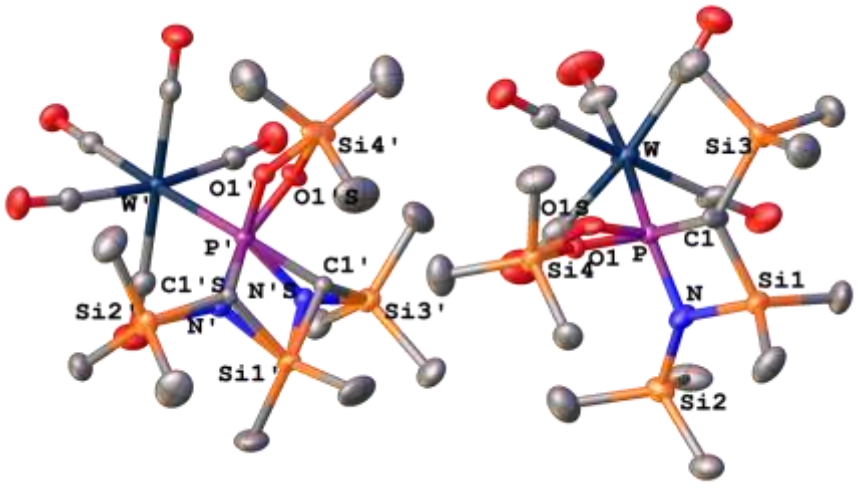


Figure S2: ORTEP drawing of the molecular structure of both independent molecules of complex **5** (cis) in the solid state (ellipsoids are set at 50% probability level and hydrogen atoms are omitted for clarity). Split layers: O1/O1S (0.76:0.24); O1´/O1´S (0.43:0.57); C1´/N´S and N´/C1´S (0.51:0.49).

ShelxT-2014 and ShelxL-2014-program-package was used for the solution and refinement.

The crystallographic data of complexes **2**, **4** and **5** were deposited at the Cambridge Crystallographic Data Centre and can be obtained free of charge via www.cam.ac.uk/data_request/cif. The CCDC numbers are **2**: 1963999, **4**: 1964000 and **5**: 1964001.

This material is available free of charge via the internet at http://pubs.acs.org.

2. NMR spectra of all new complexes

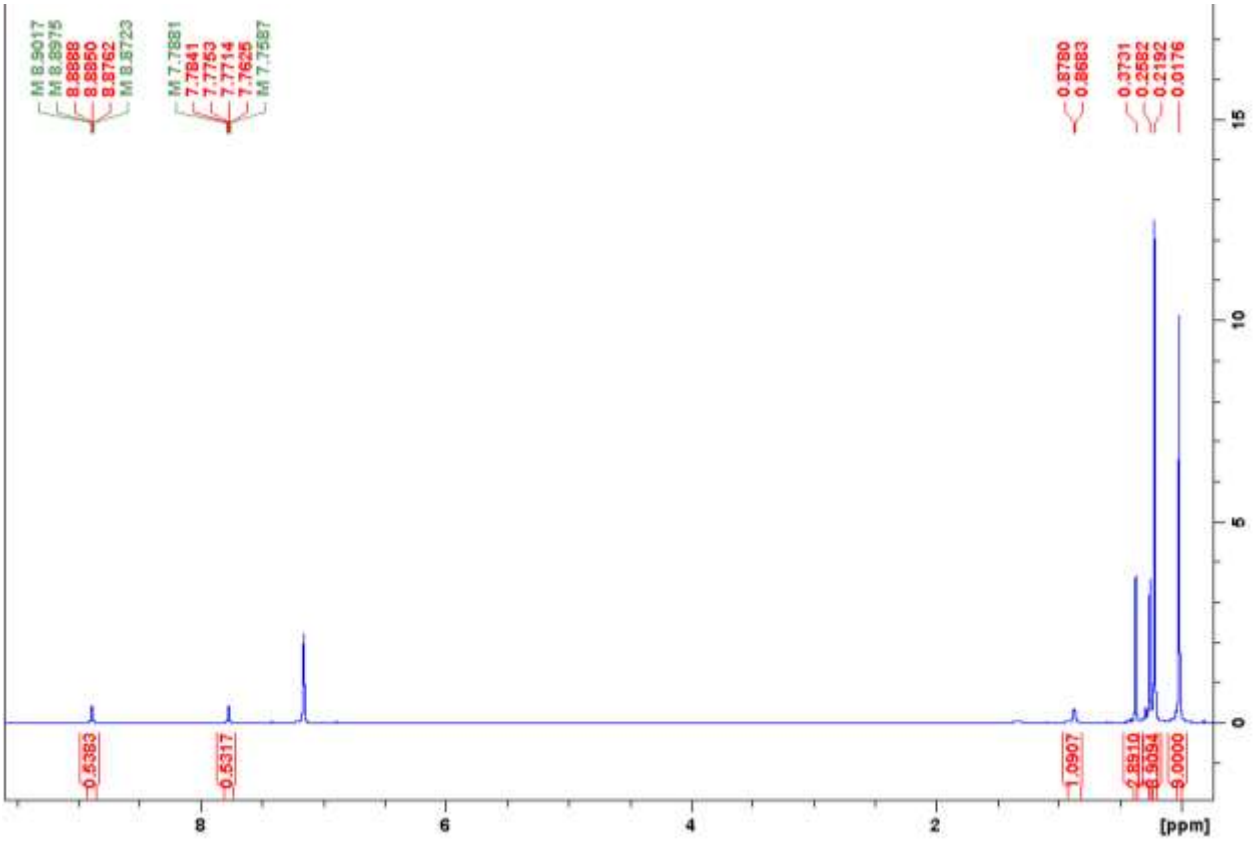


Figure S3: ^{1}H NMR spectrum of complex **2**.

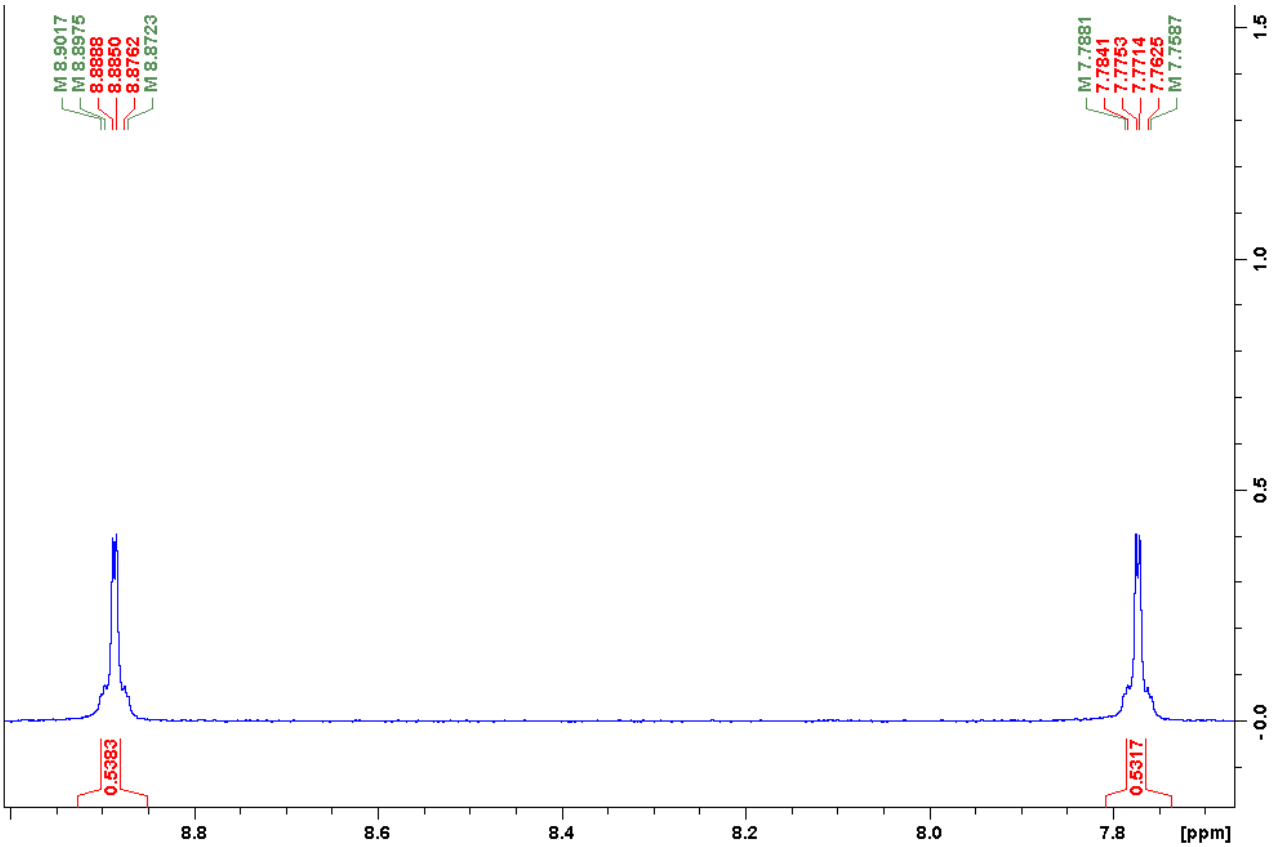


Figure S4: ^{1}H NMR spectrum of complex **2** (expansion).

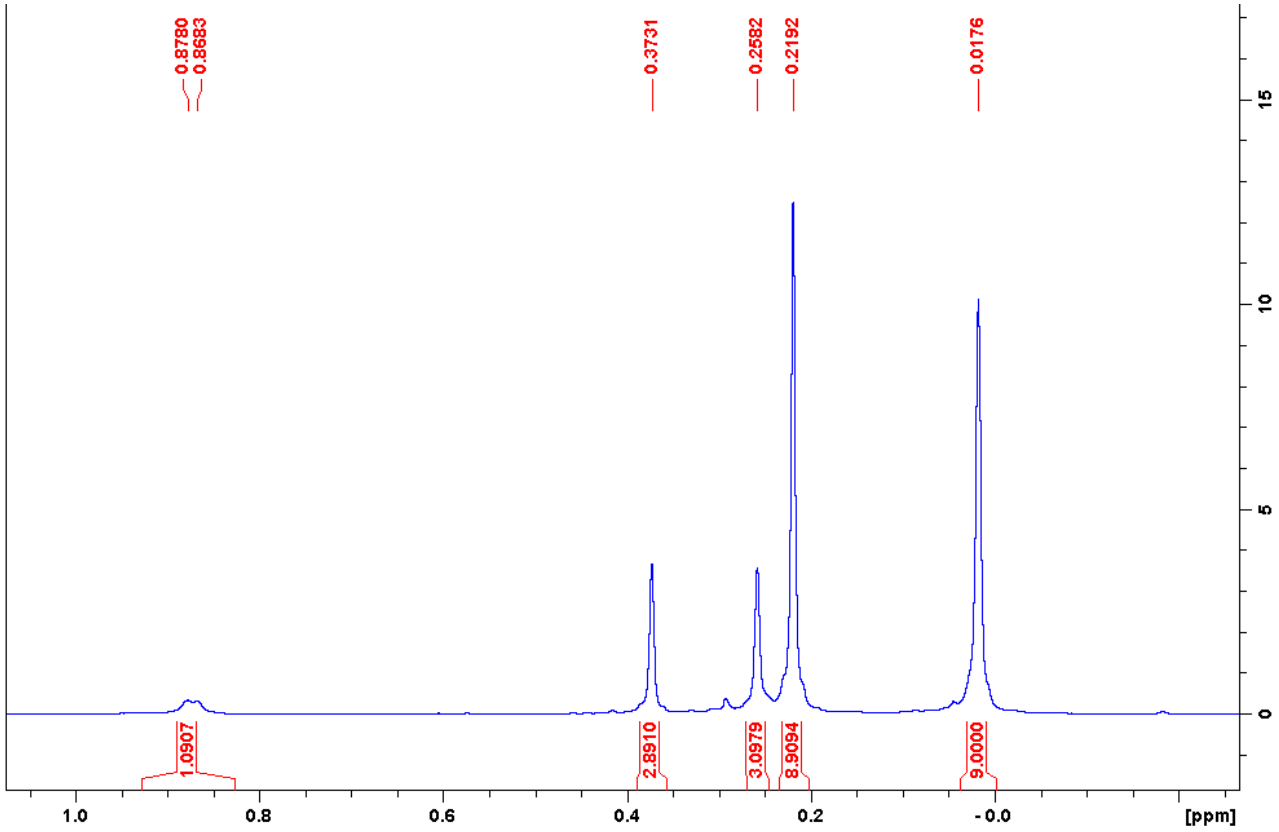


Figure S5: ^{1}H NMR spectrum of complex **2** (expansion).

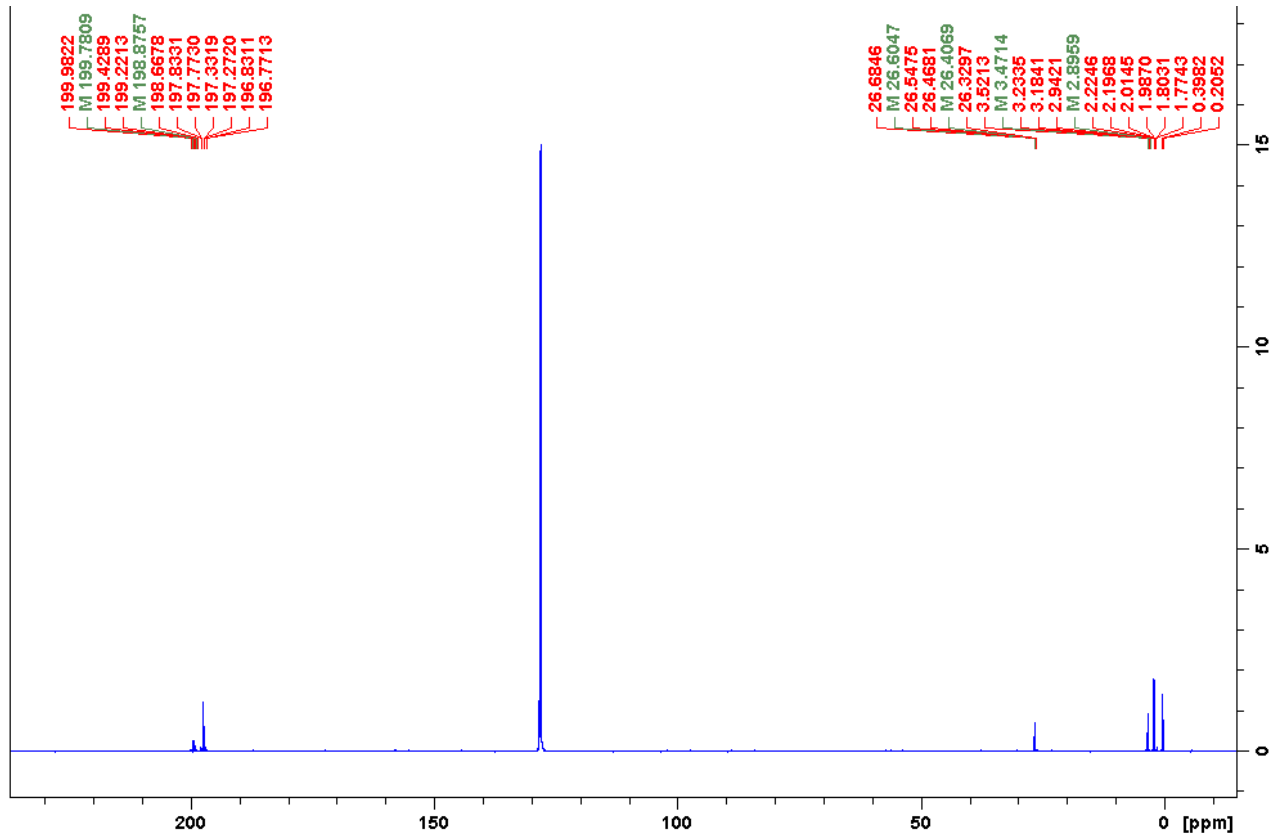


Figure S6: ^{13}C NMR spectrum of complex **2**.

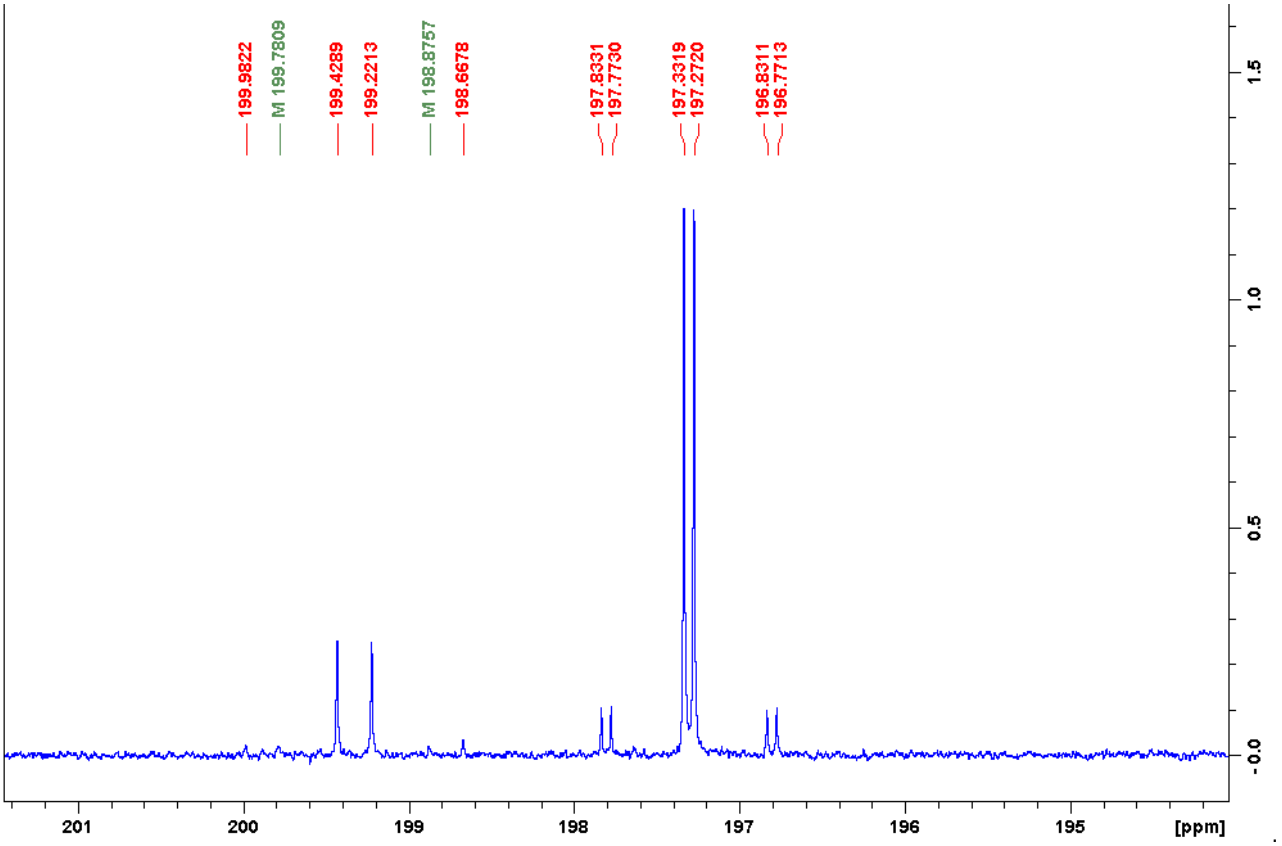


Figure S7: ^{13}C NMR spectrum of complex **2** (expansion).

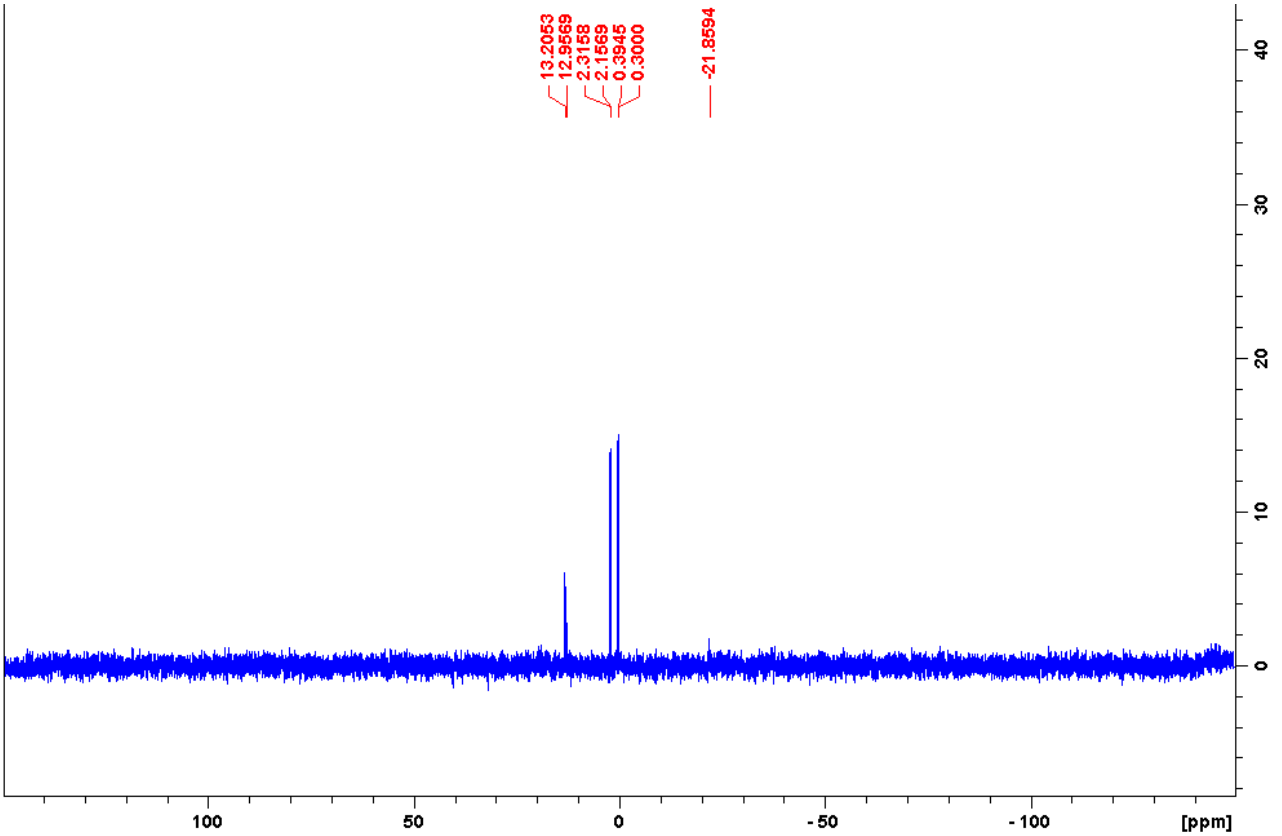


Figure S7: ^{29}Si NMR spectrum of complex **2**.

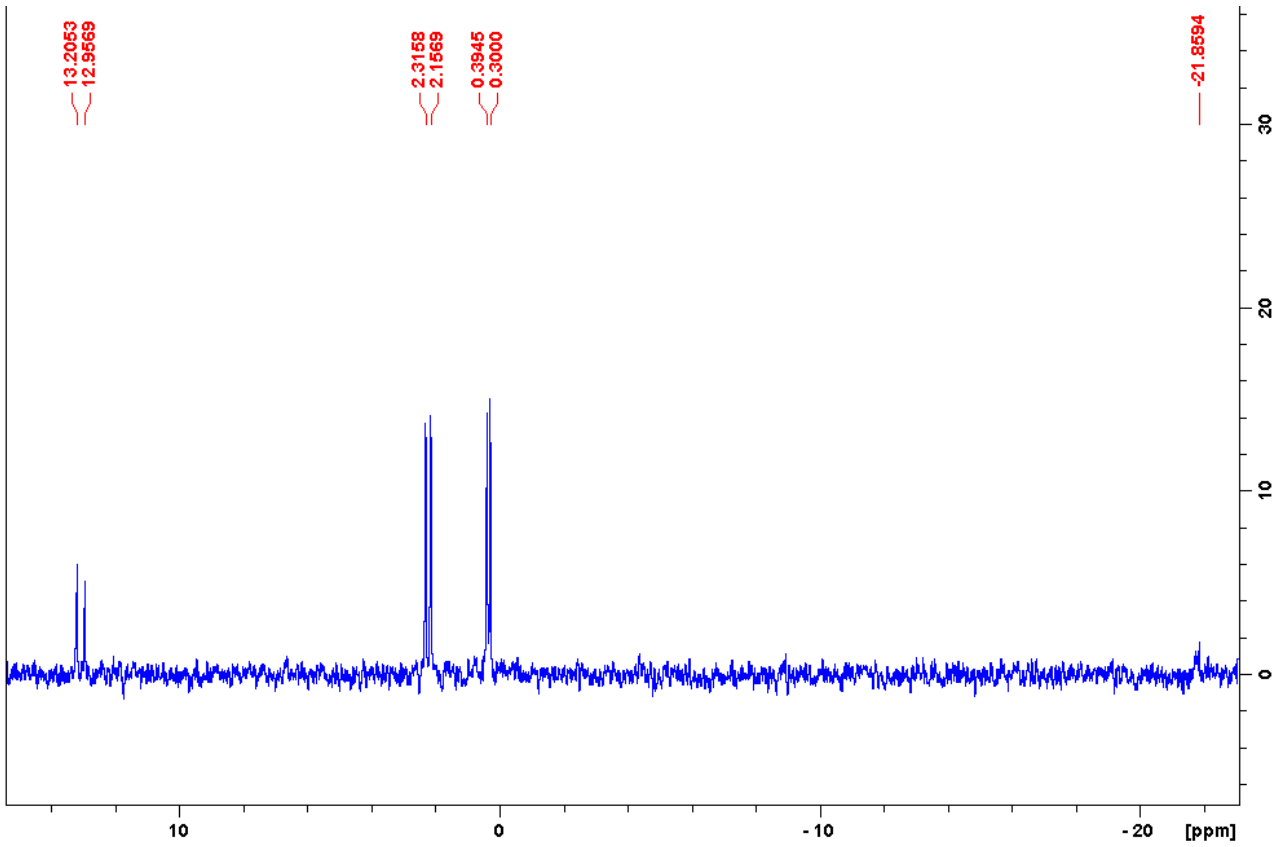


Figure S9: ^{29}Si NMR spectrum of complex **2** (expansion).

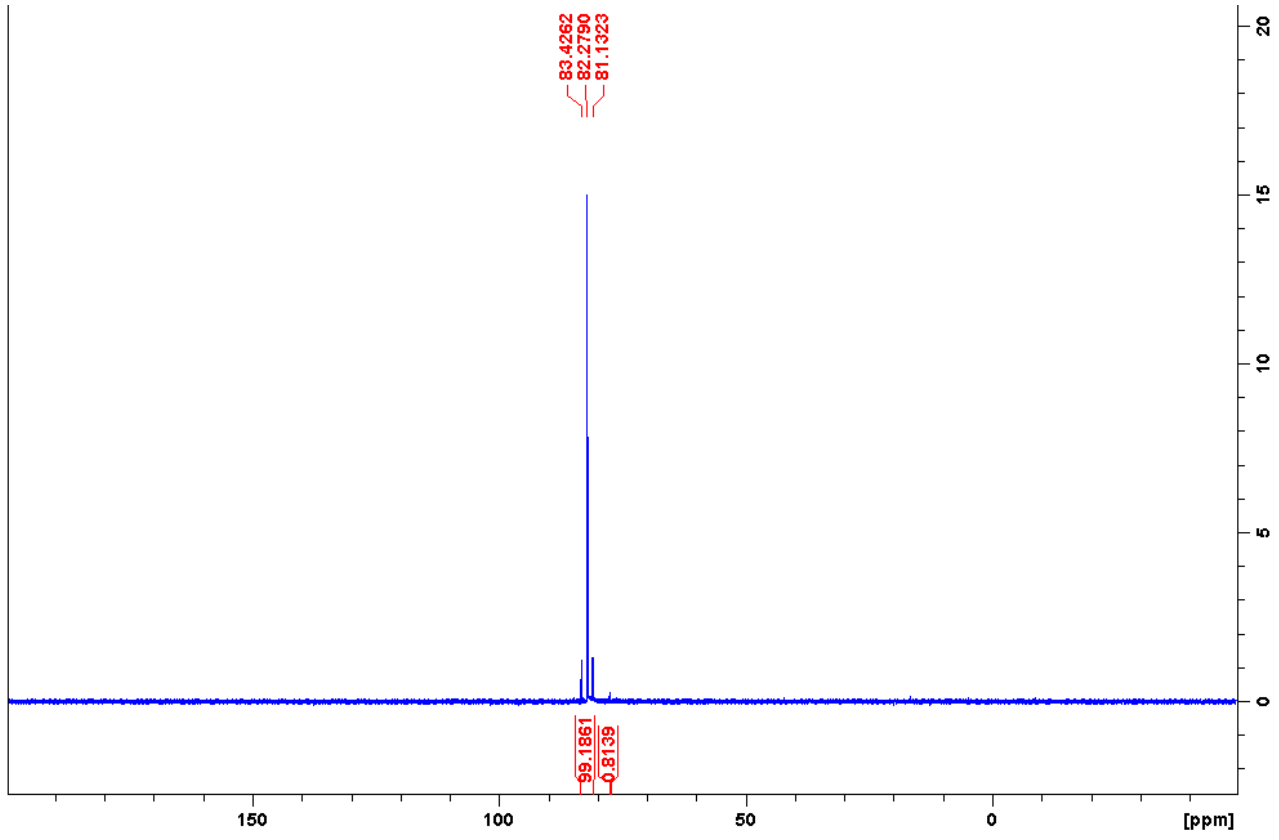


Figure S10: ^{31}P{^{1}H} NMR spectrum of complex **2**.

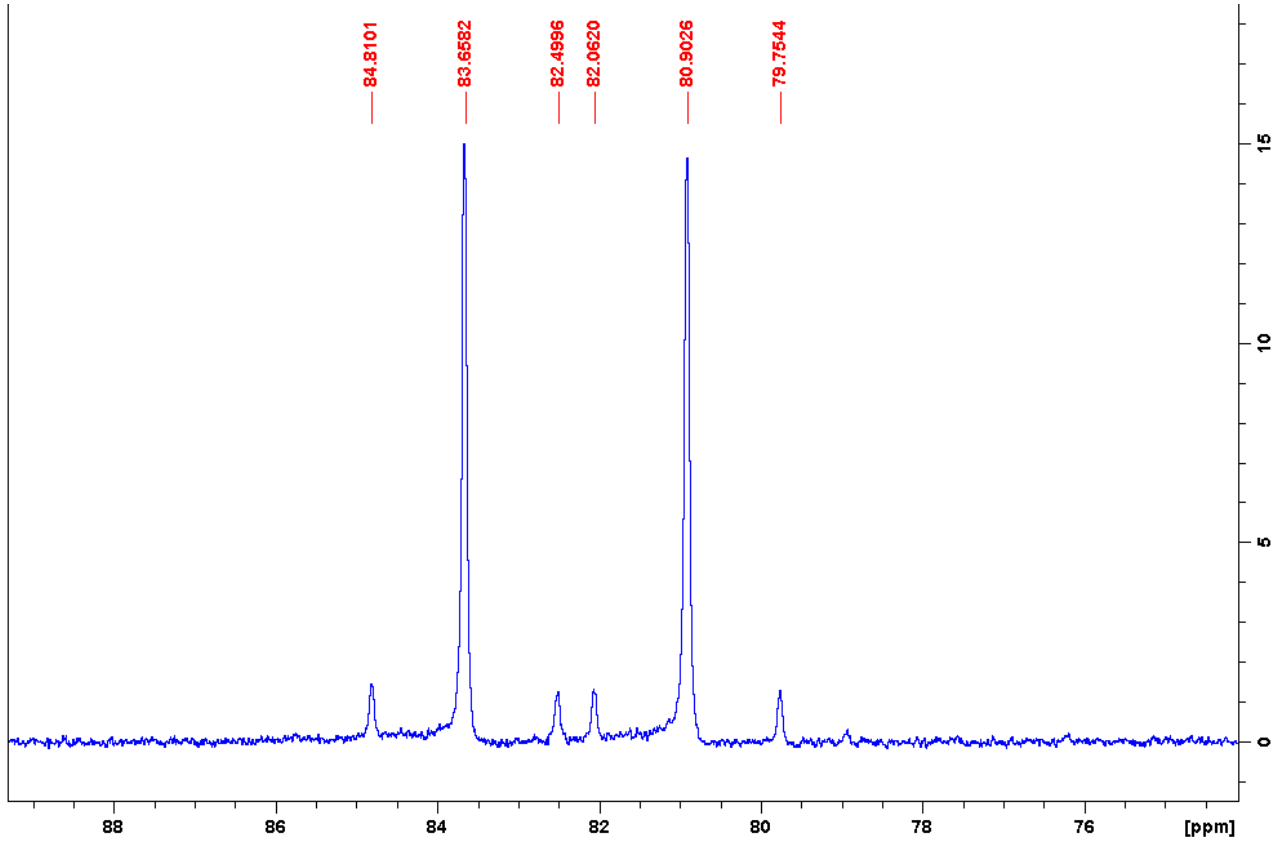


Figure S11: $^{31}P\{^{1}H\}$ NMR spectrum of complex **2** (expansion).

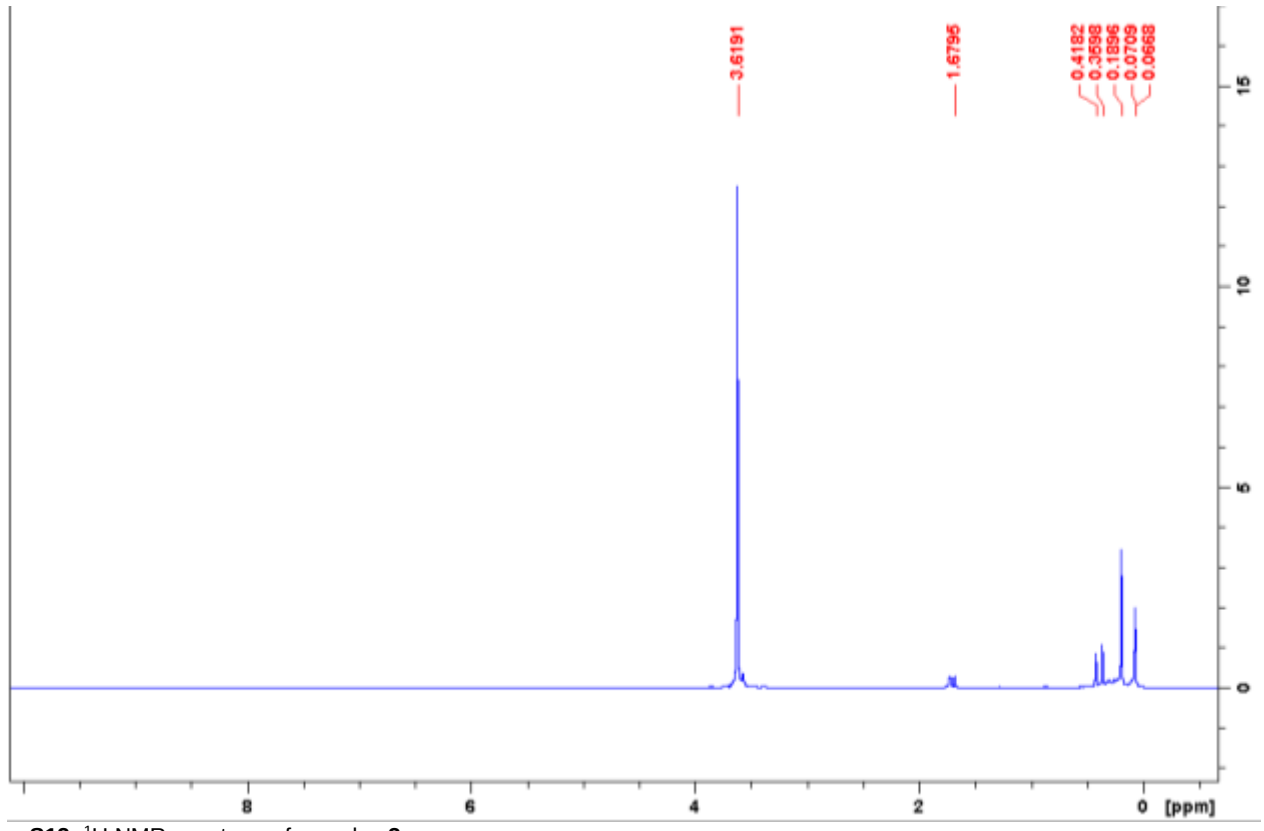


Figure S12: ^{1}H NMR spectrum of complex **3**.

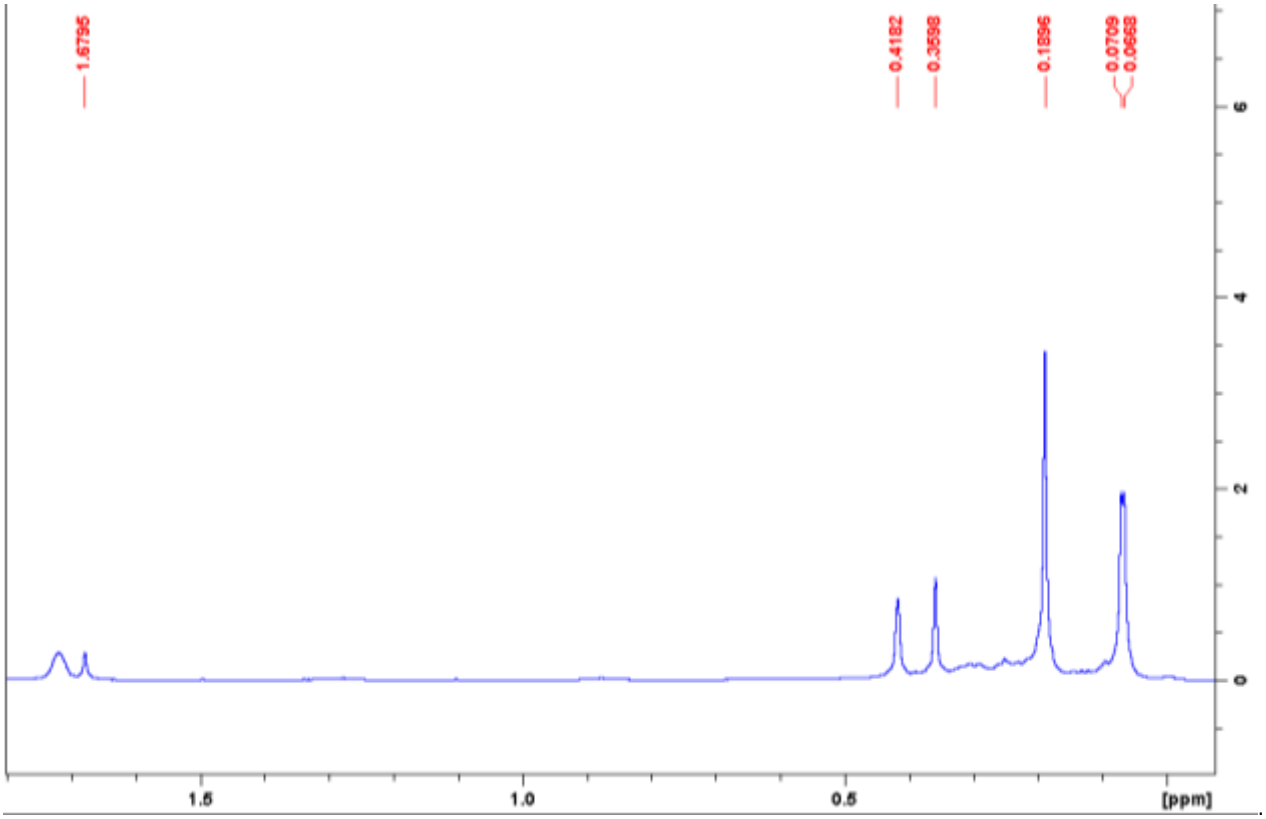


Figure S13: ^{1}H NMR spectrum of complex **3** (expansion).

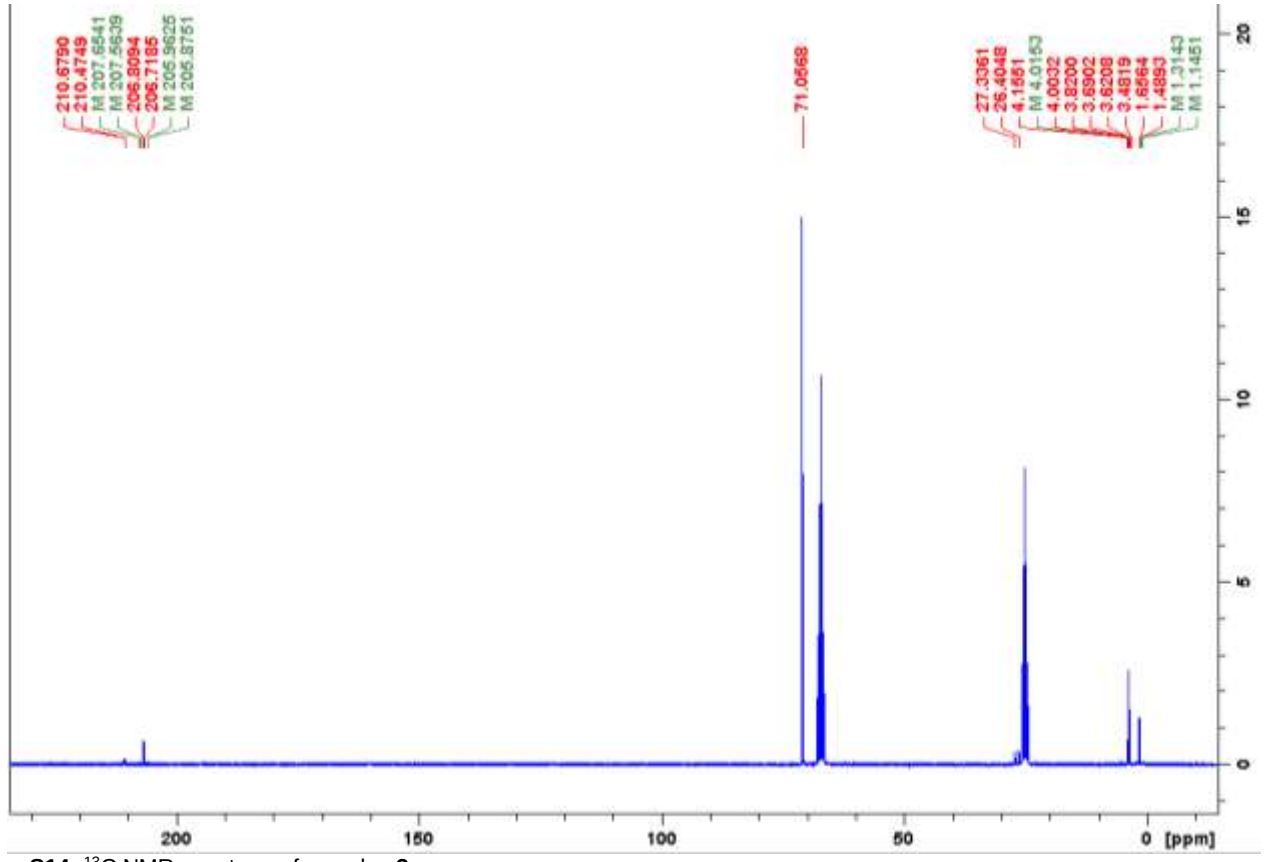


Figure S14: ^{13}C NMR spectrum of complex **3**.

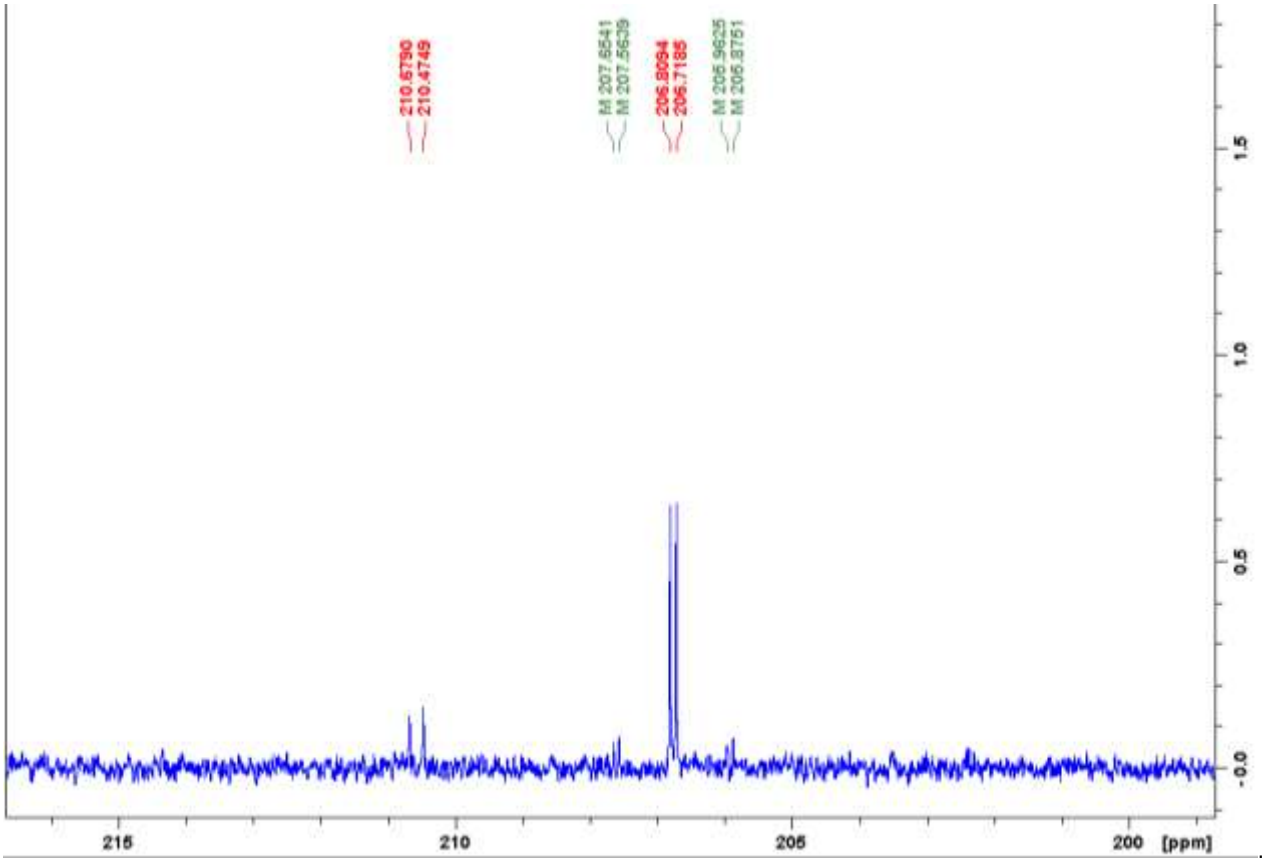


Figure S15: ^{13}C NMR spectrum of complex **3** (expansion).

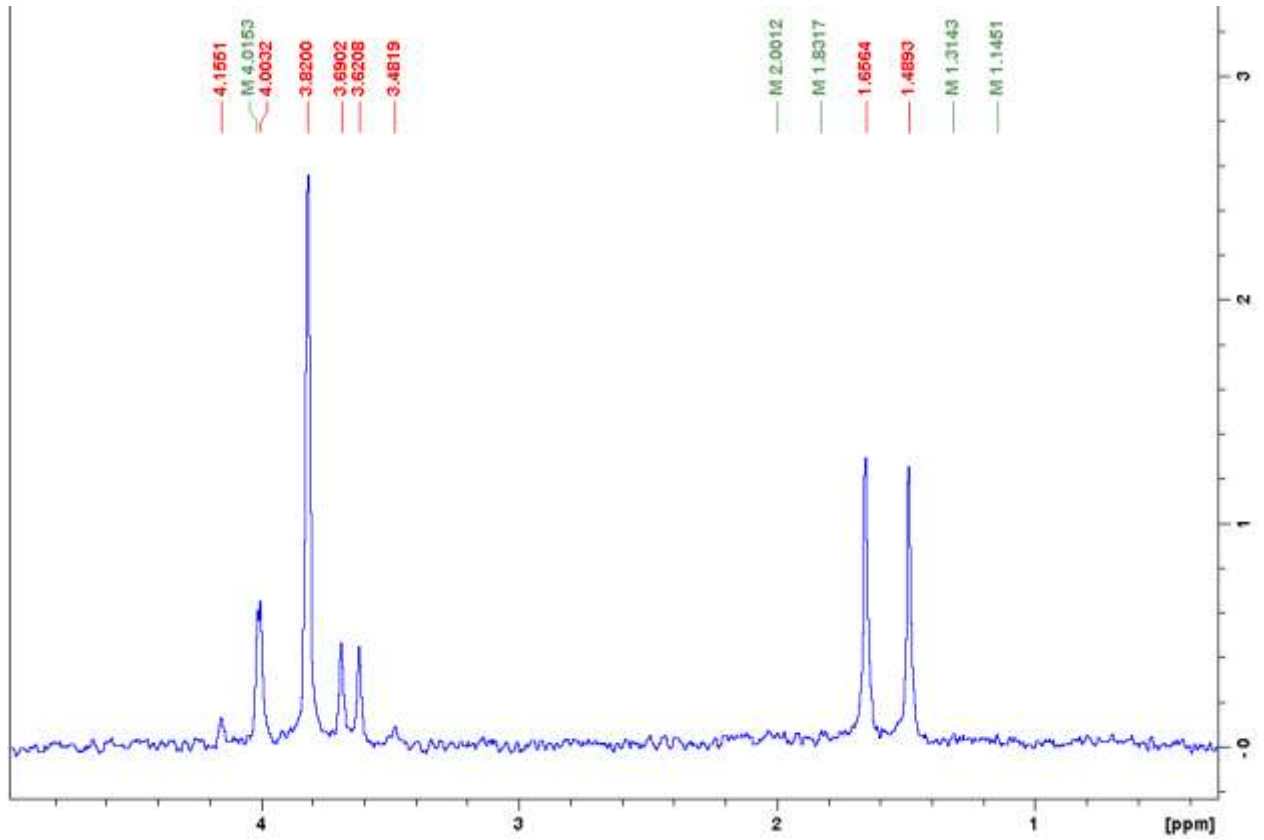


Figure S16: ^{13}C NMR spectrum of complex **3** (expansion).

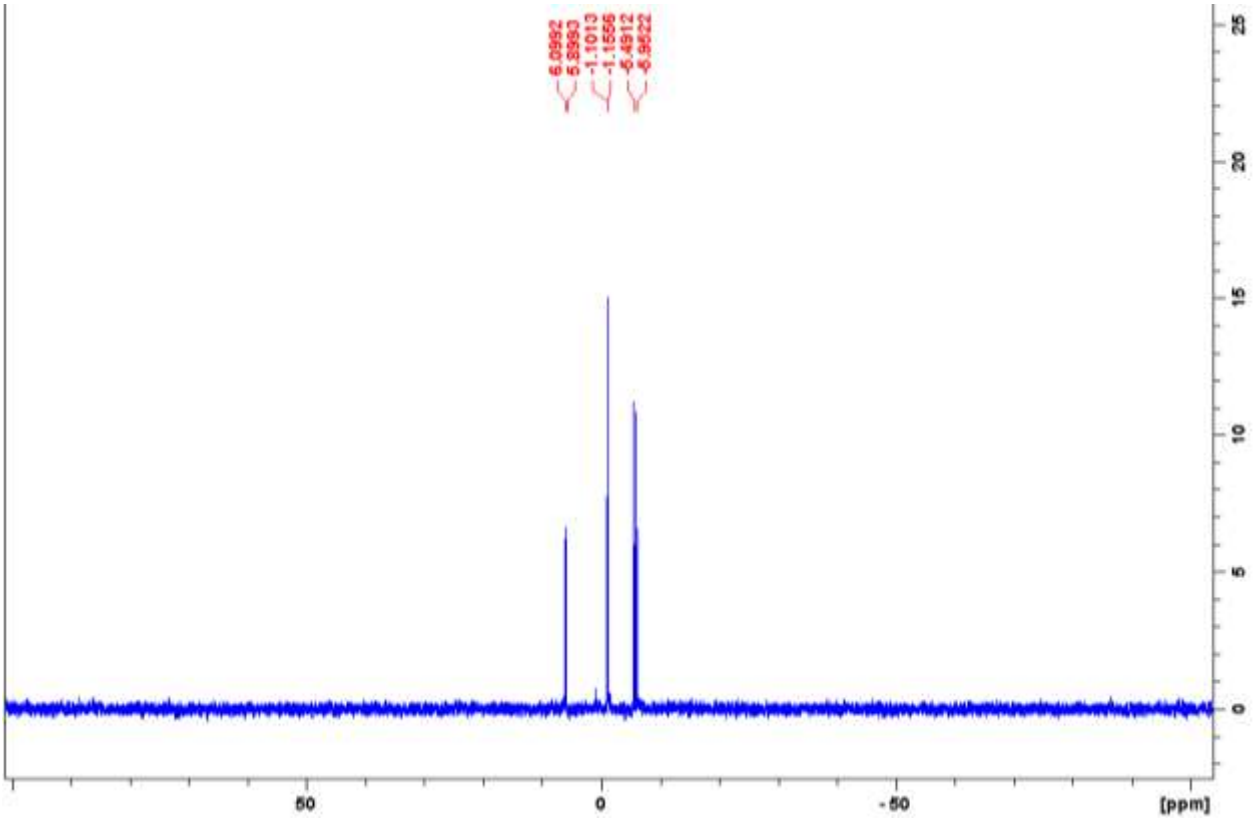


Figure S17: ^{29}Si NMR spectrum of complex **3**.

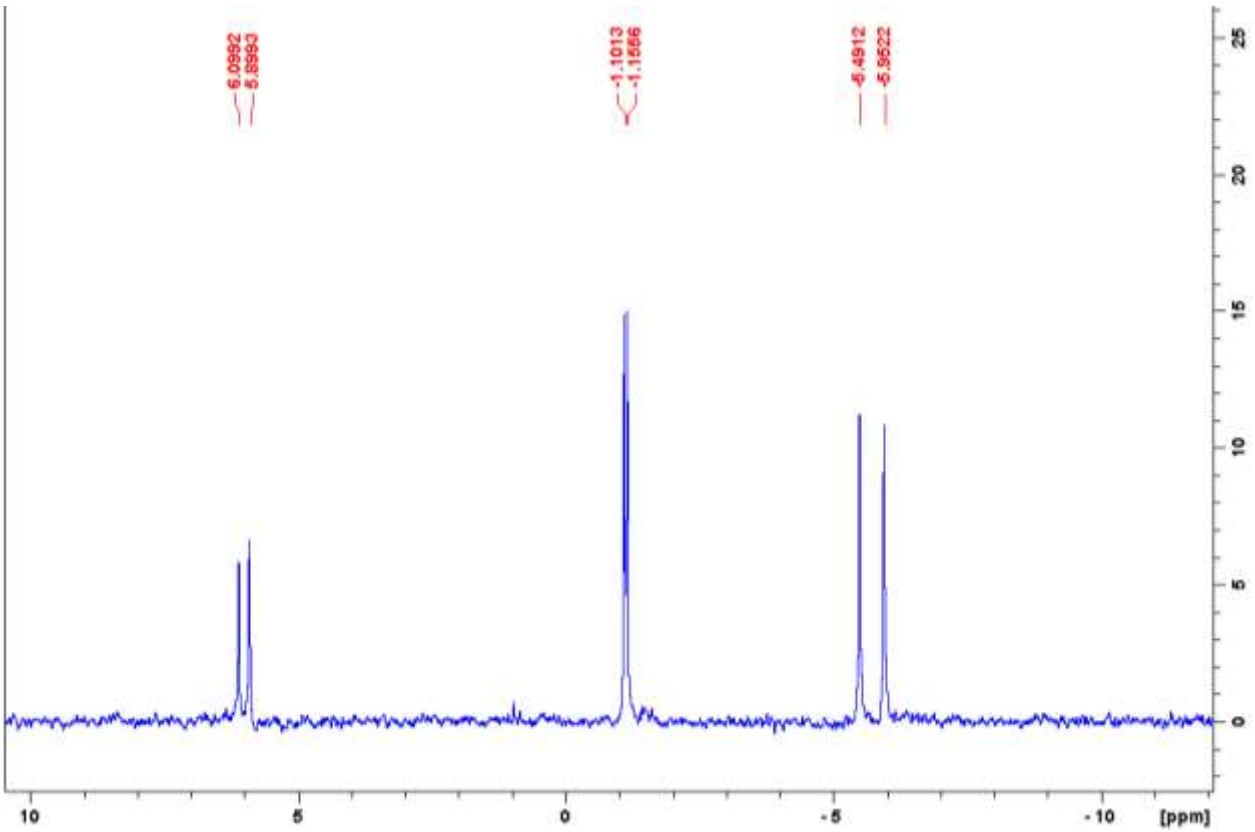


Figure S18: ^{29}Si NMR spectrum of complex **3** (expansion).

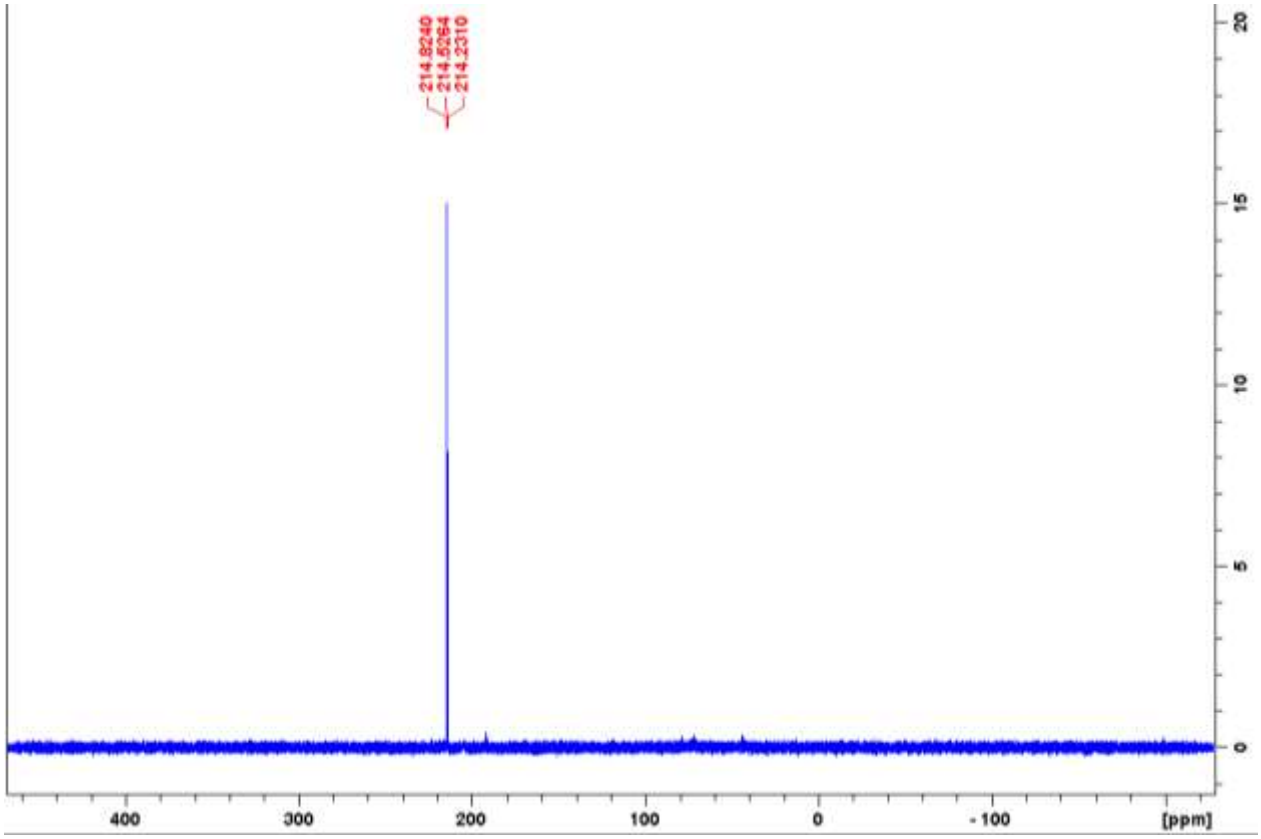


Figure S19: ^{31}P NMR spectrum of complex **3**.

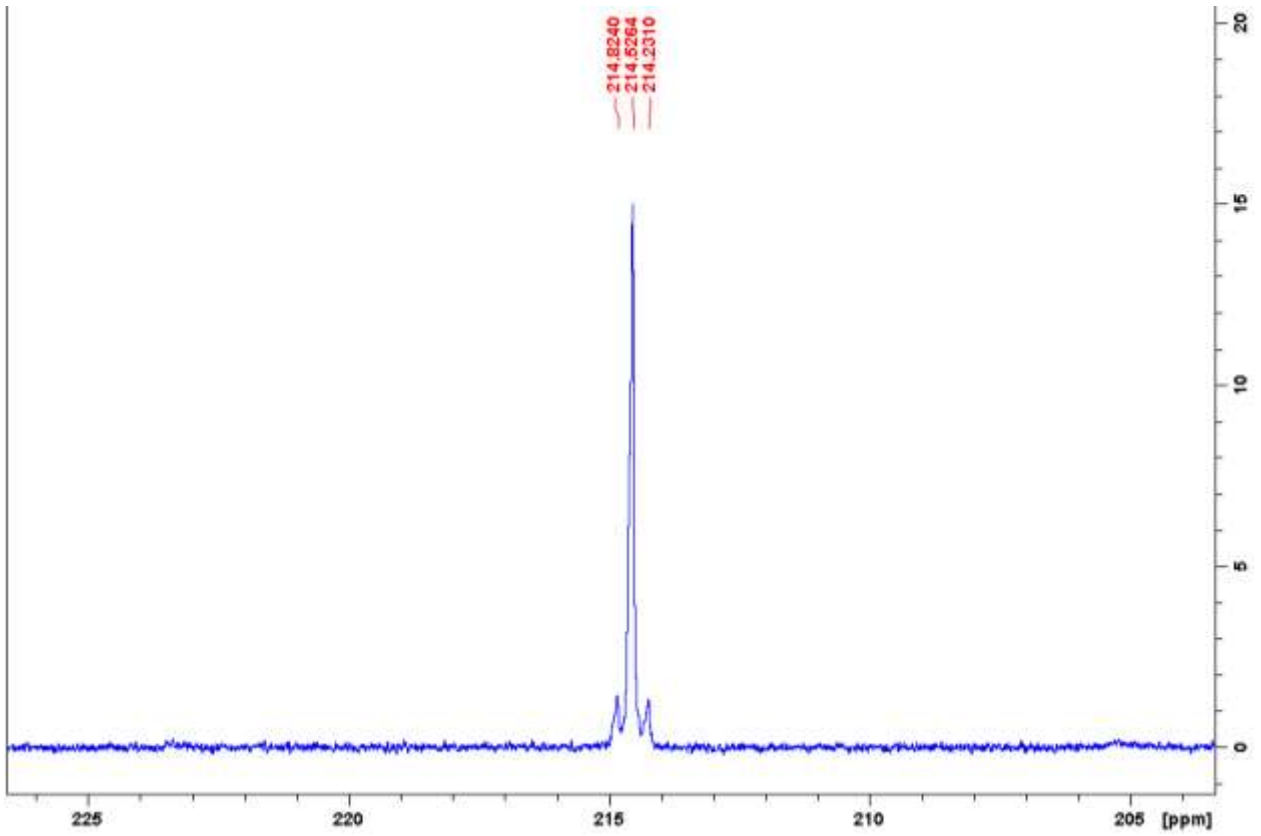


Figure S20: ^{31}P NMR spectrum of complex **3** (expansion).

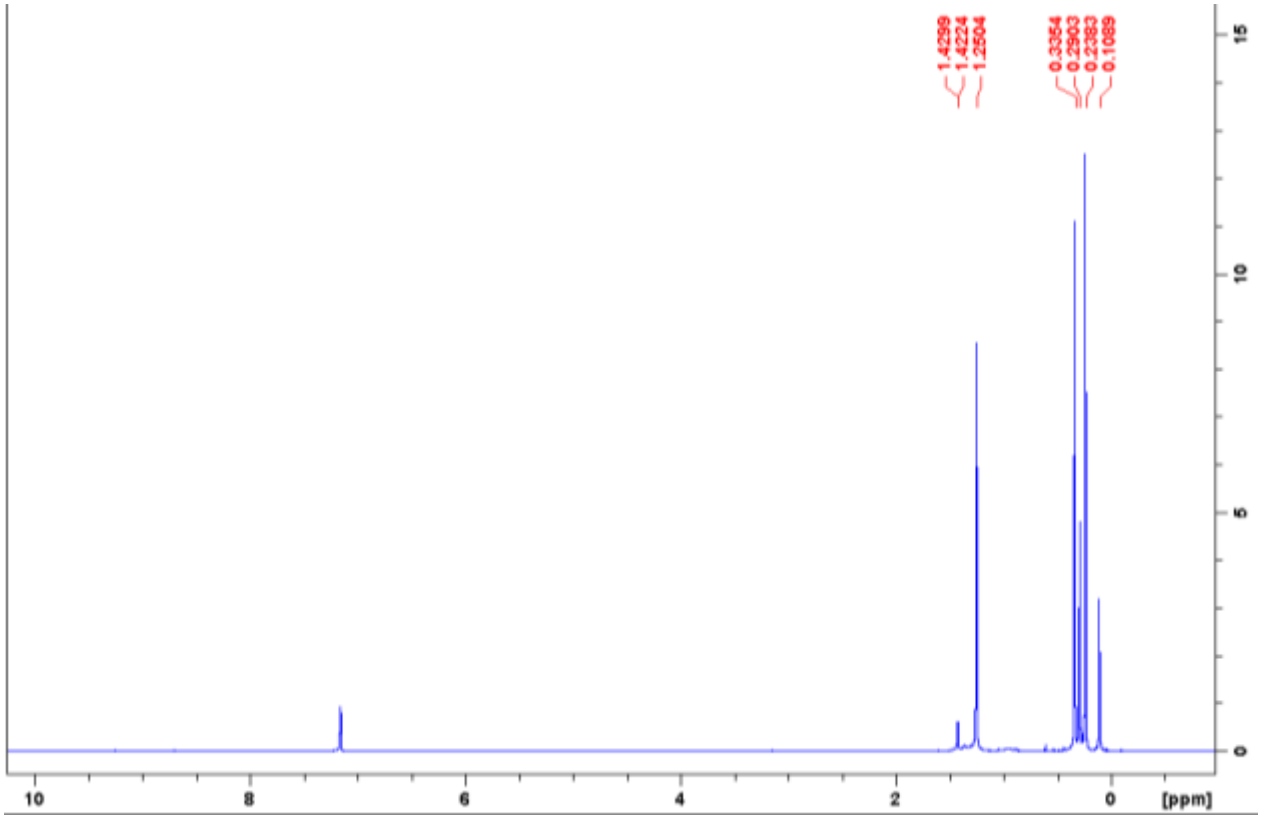


Figure S21: ^{1}H NMR spectrum of complex **4**.

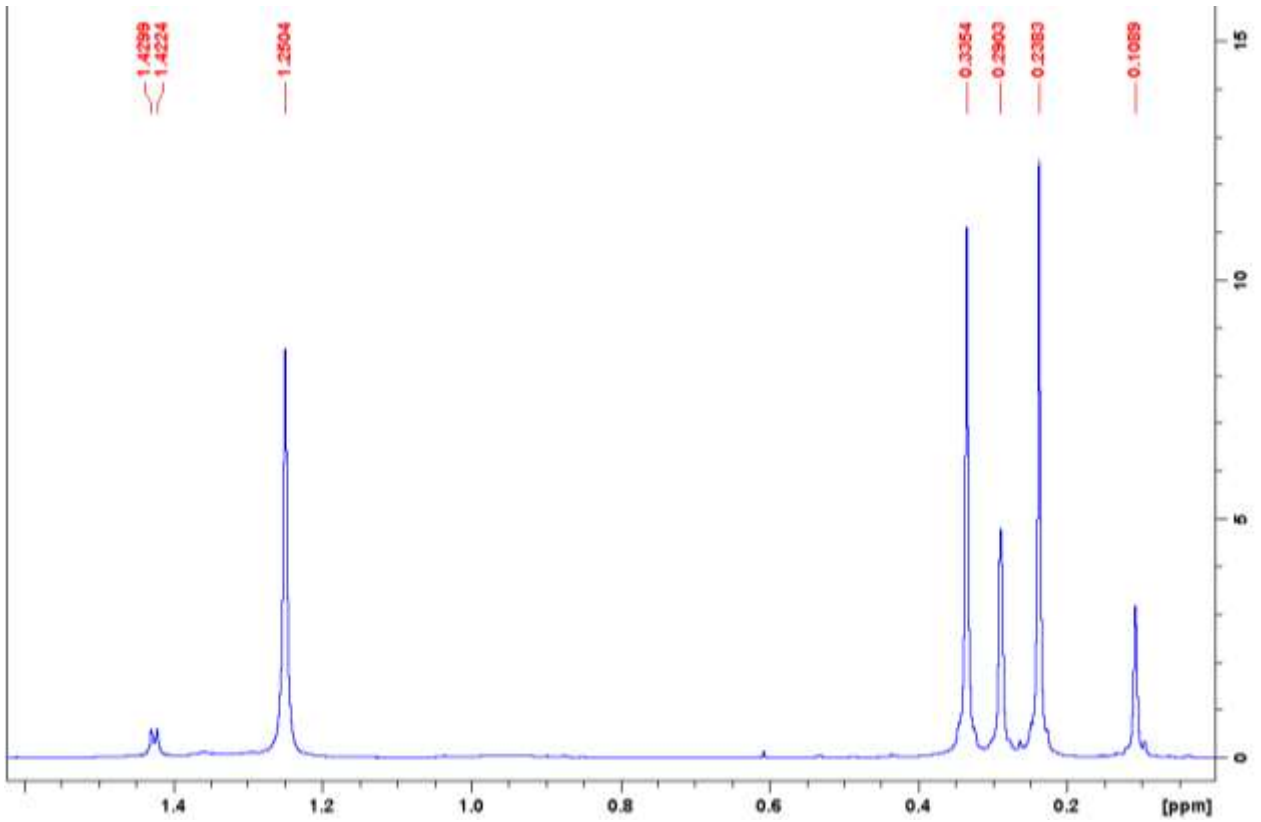


Figure S22: ^{1}H NMR spectrum of complex **4** (expansion).

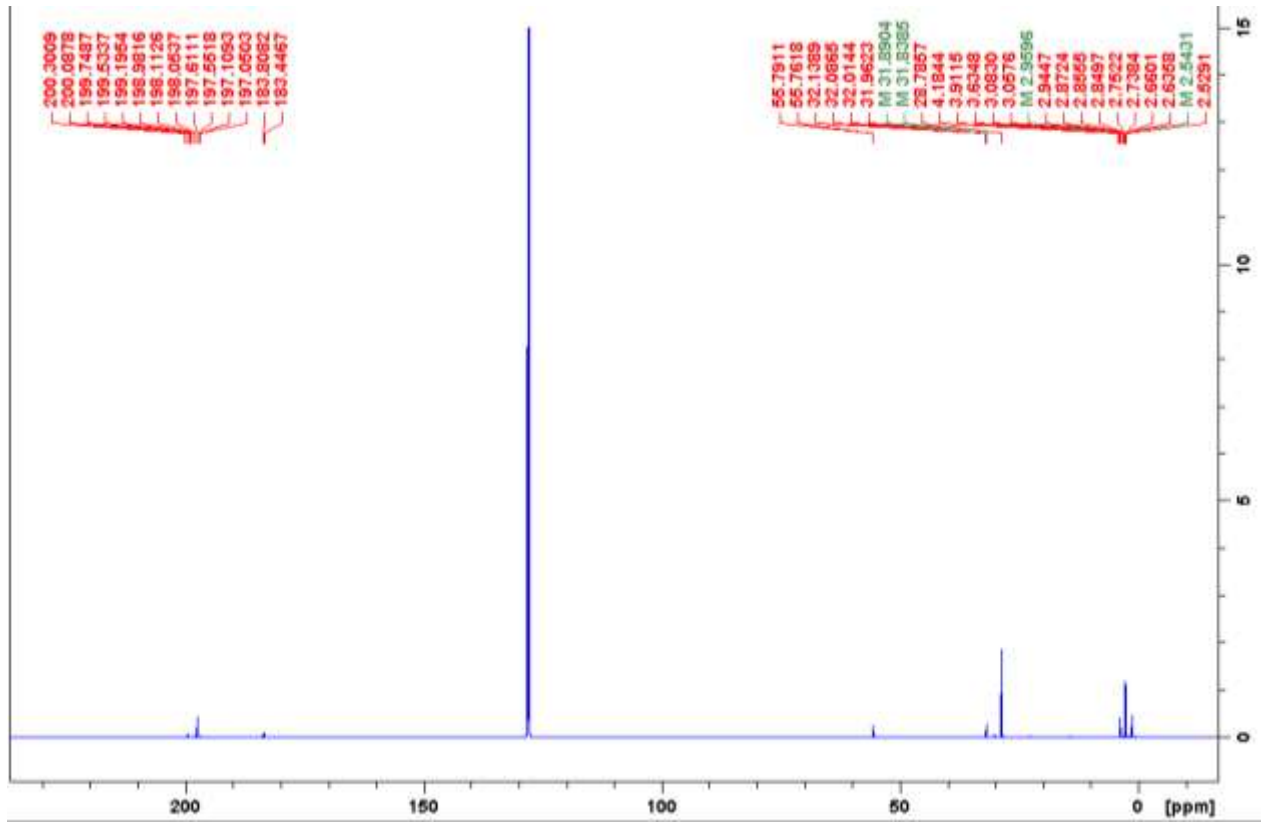


Figure S23: ^{13}C NMR spectrum of complex **4**.

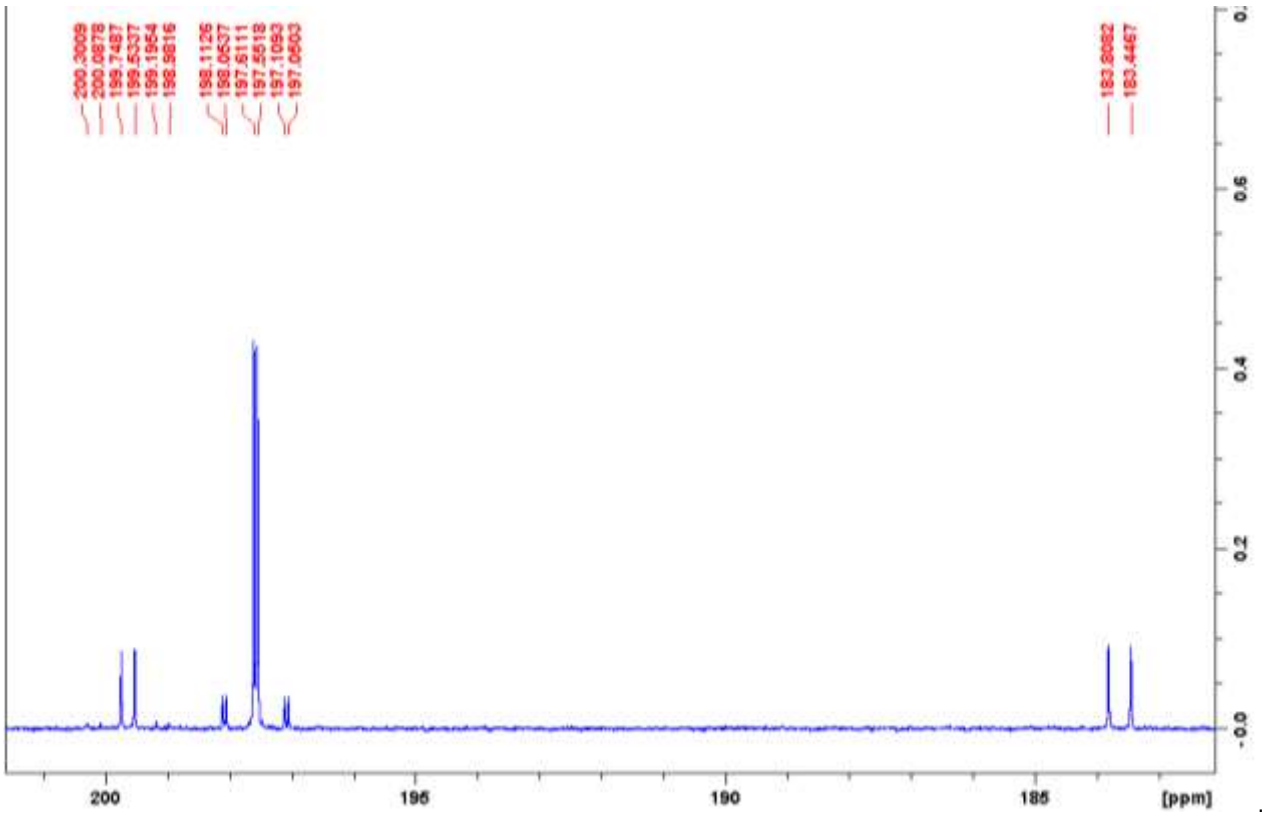


Figure S24: ^{13}C NMR spectrum of complex **4** (expansion).

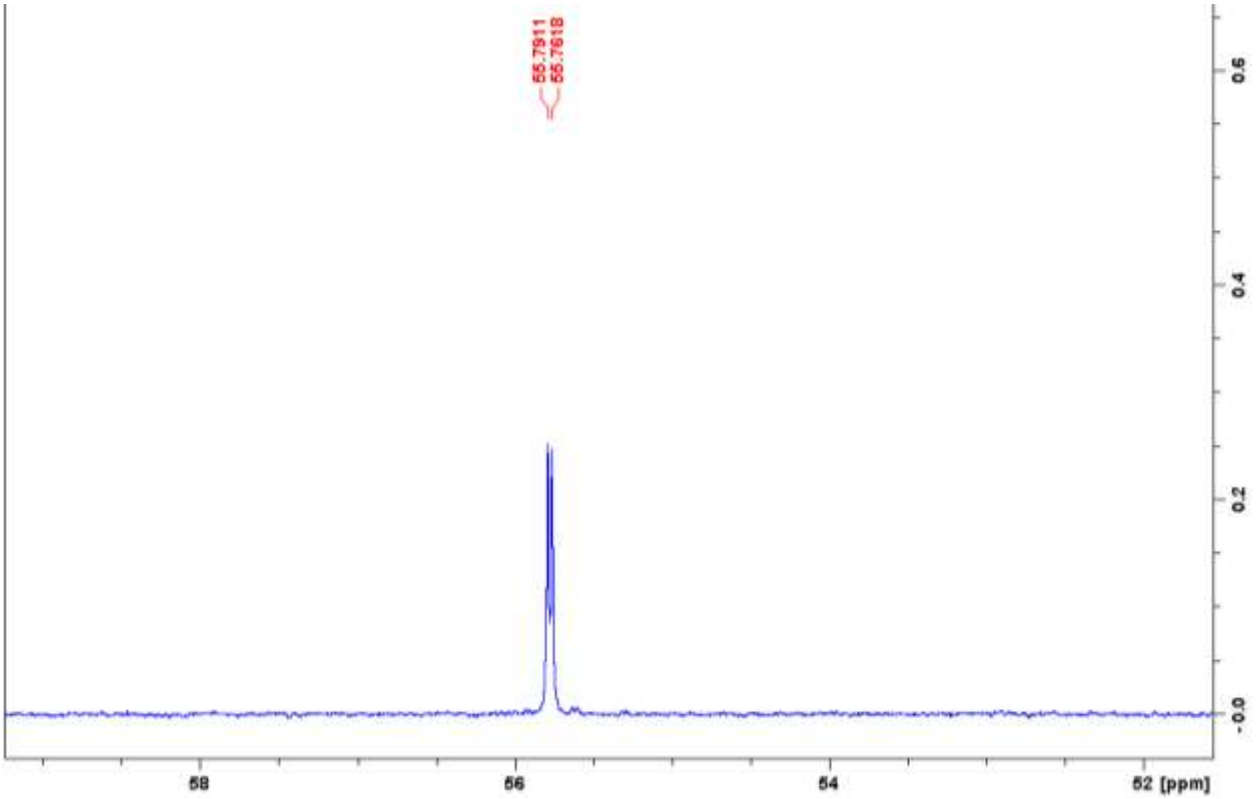


Figure S25: ^{13}C NMR spectrum of complex **4** (expansion).

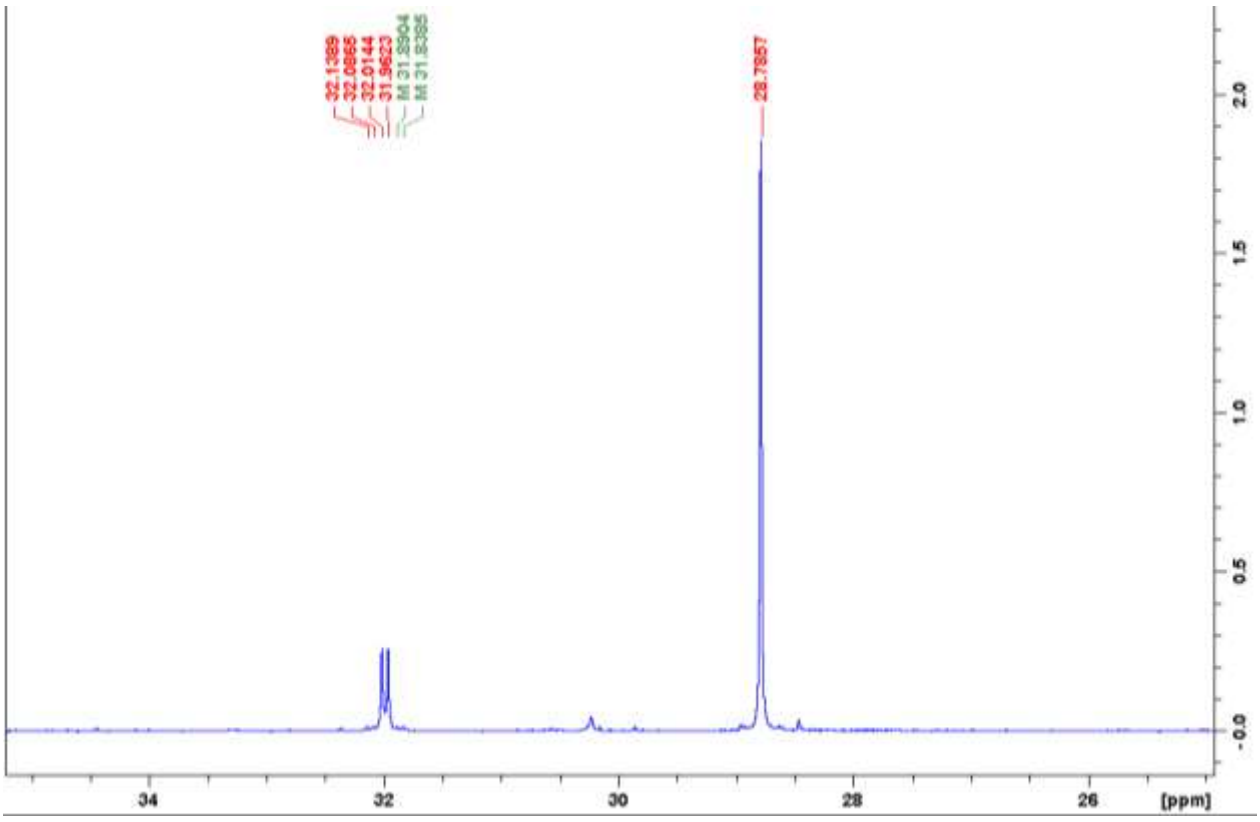


Figure S26: ^{13}C NMR spectrum of complex **4** (expansion).

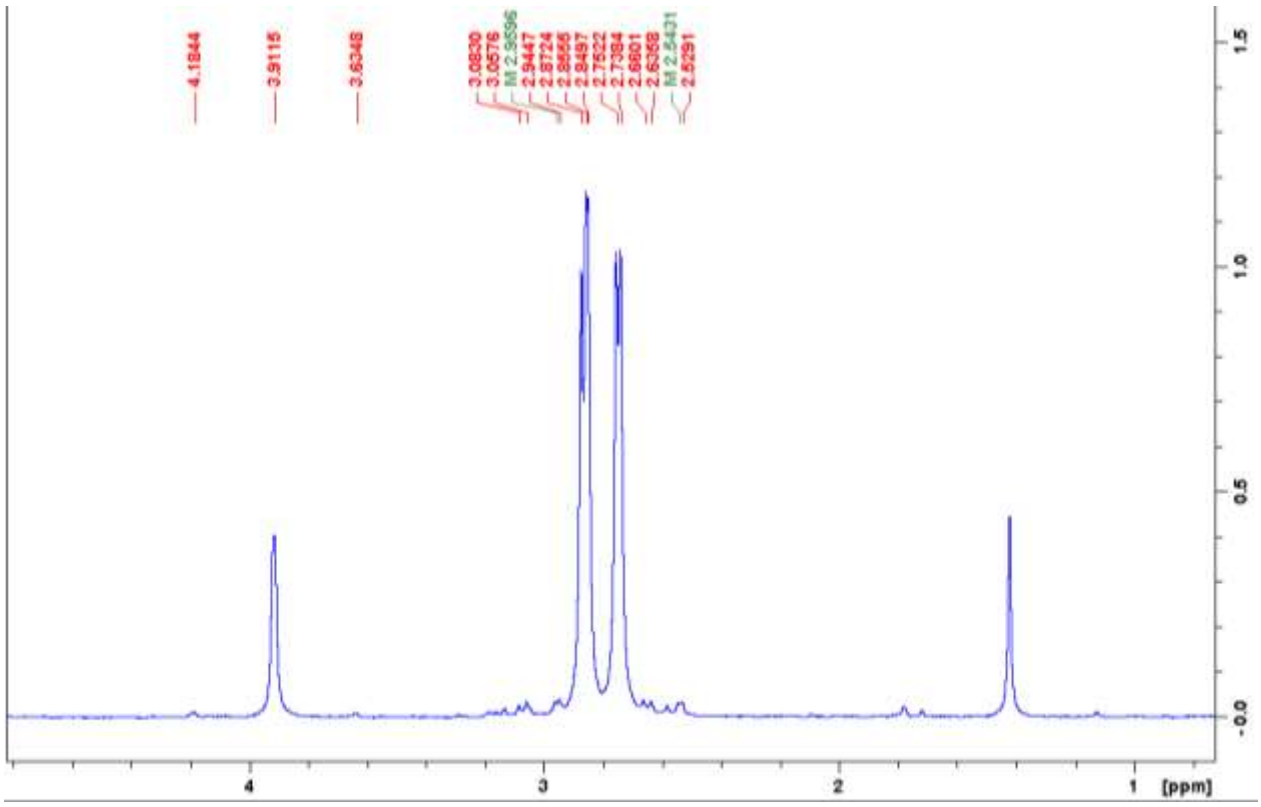


Figure S27: ^{13}C NMR spectrum of complex **4** (expansion).

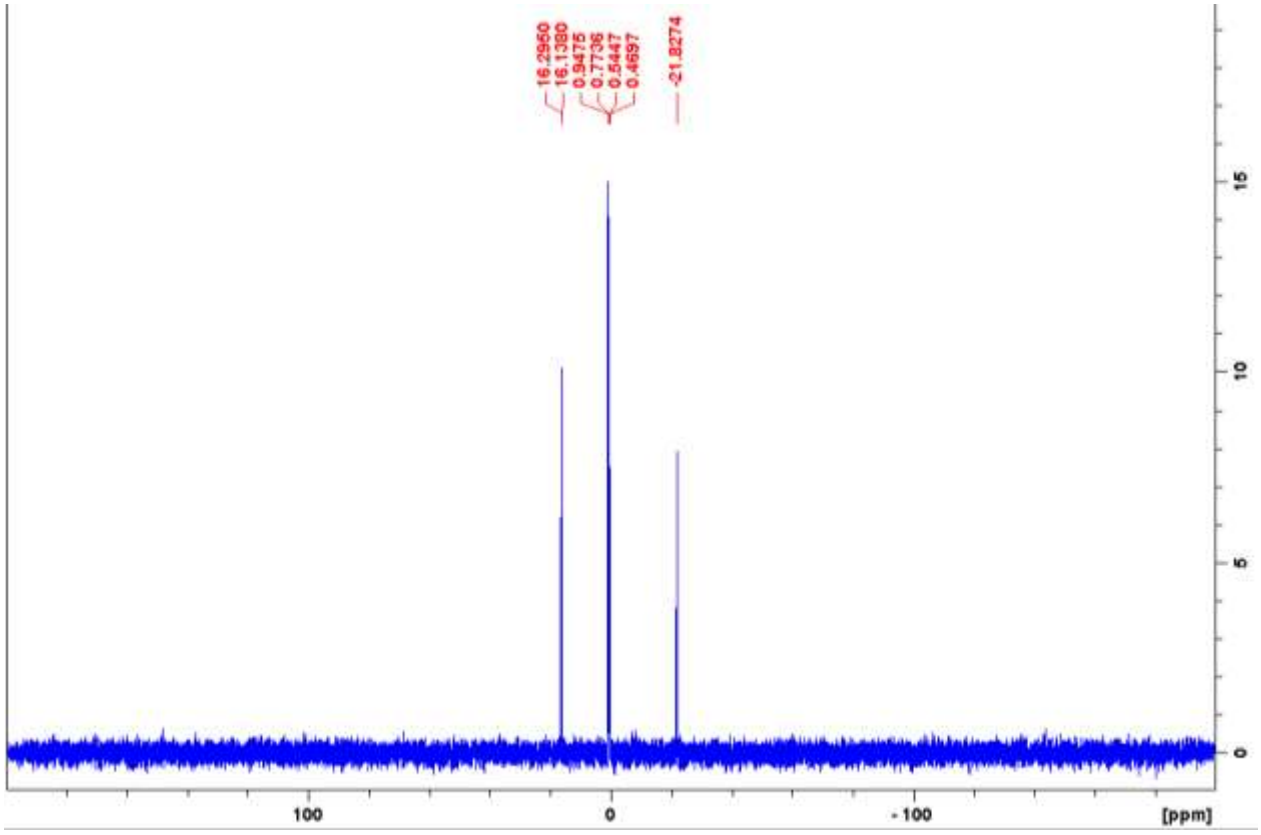


Figure S28: ^{29}Si NMR spectrum of complex **4**.

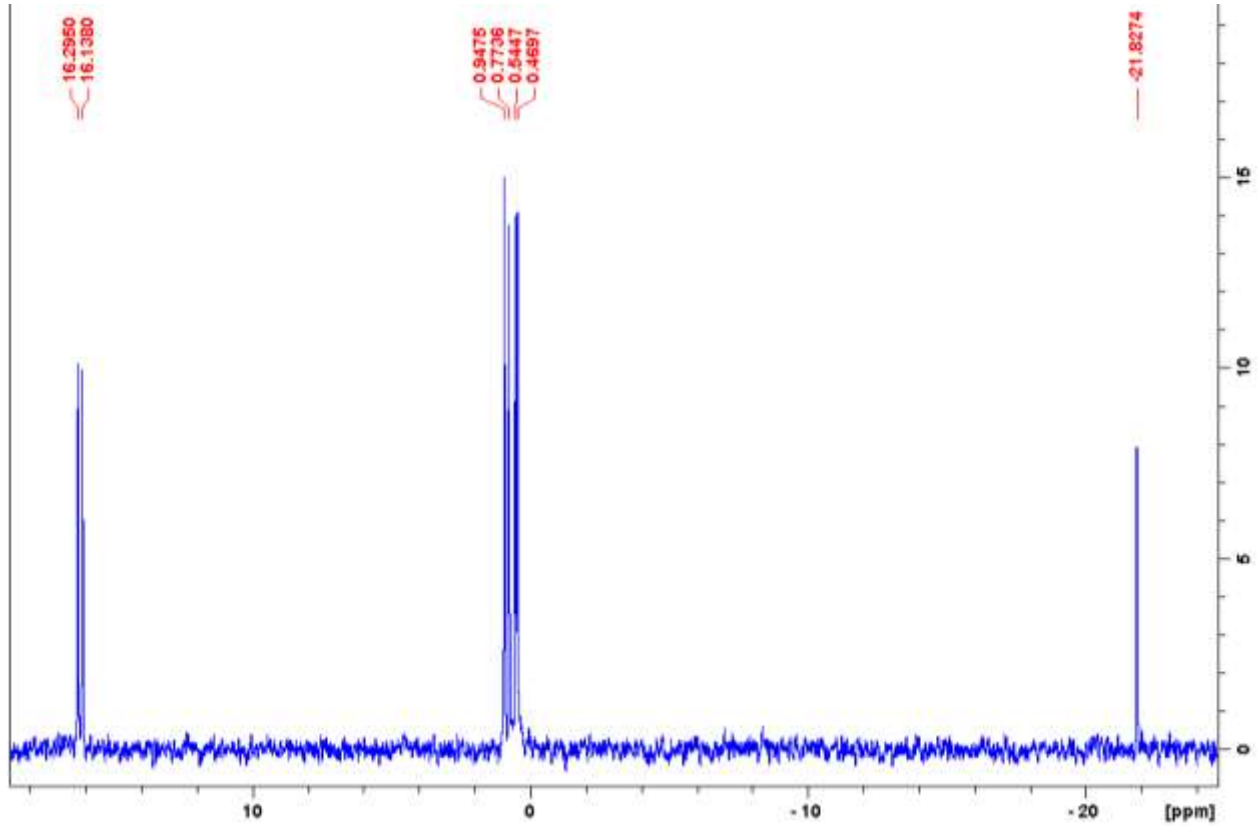


Figure S29: ^{29}Si NMR spectrum of complex **4** (expansion).

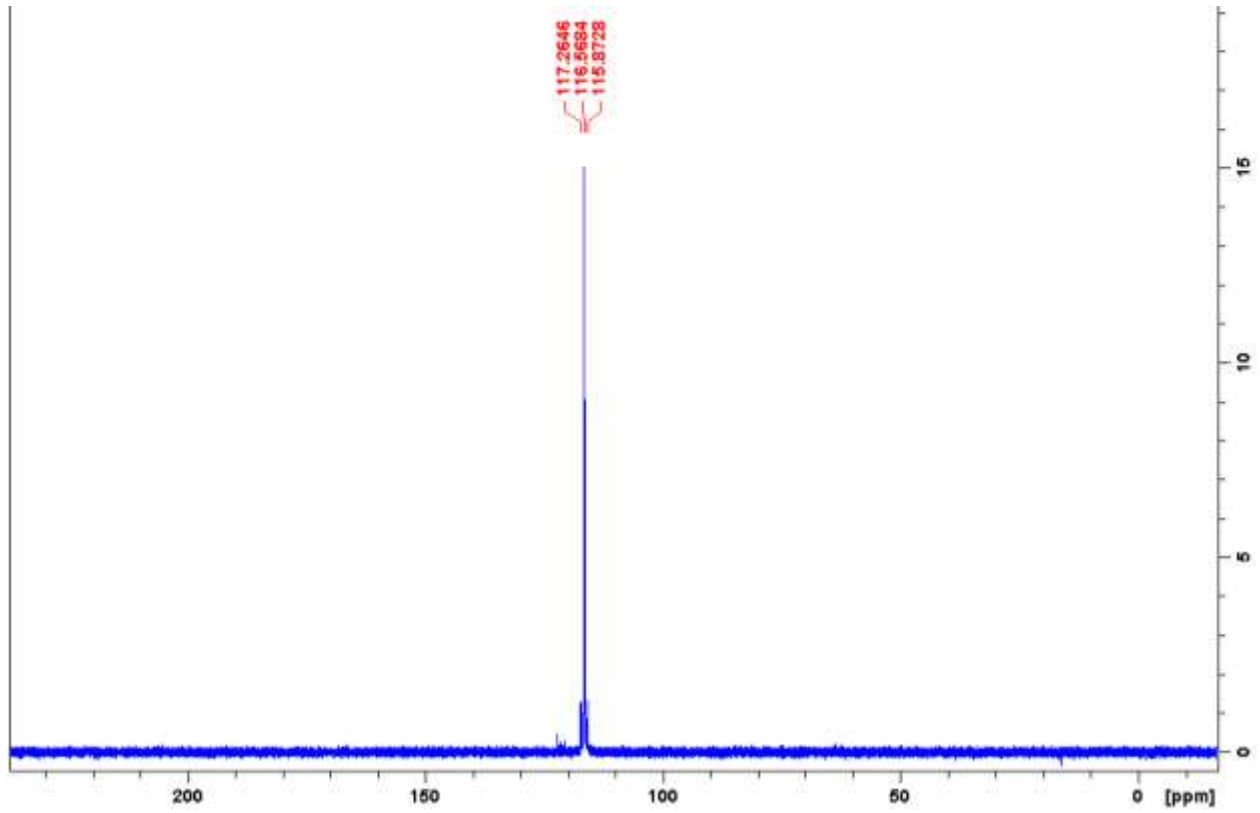


Figure S30: ^{31}P NMR spectrum of complex **4**.

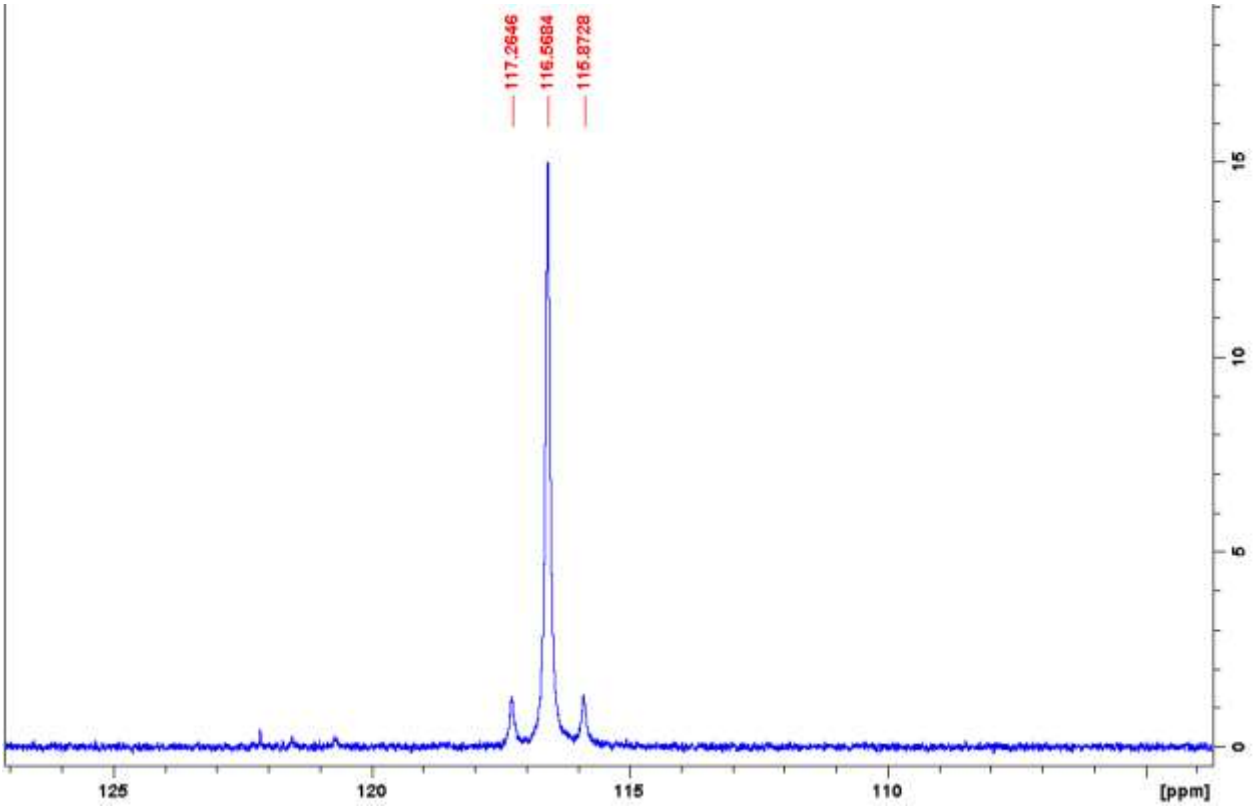


Figure S31: ^{31}P NMR spectrum of complex **4** (expansion).

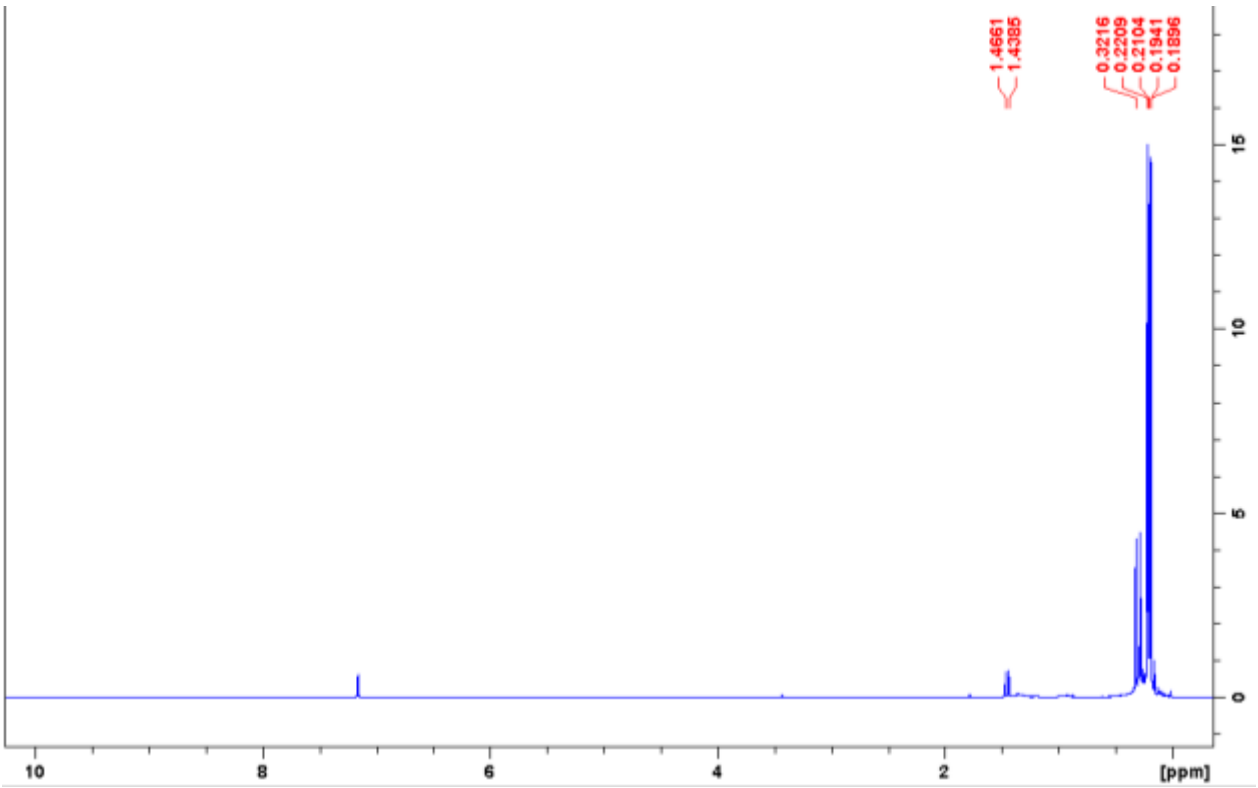


Figure S32: ^{1}H NMR spectrum of complex **5**.

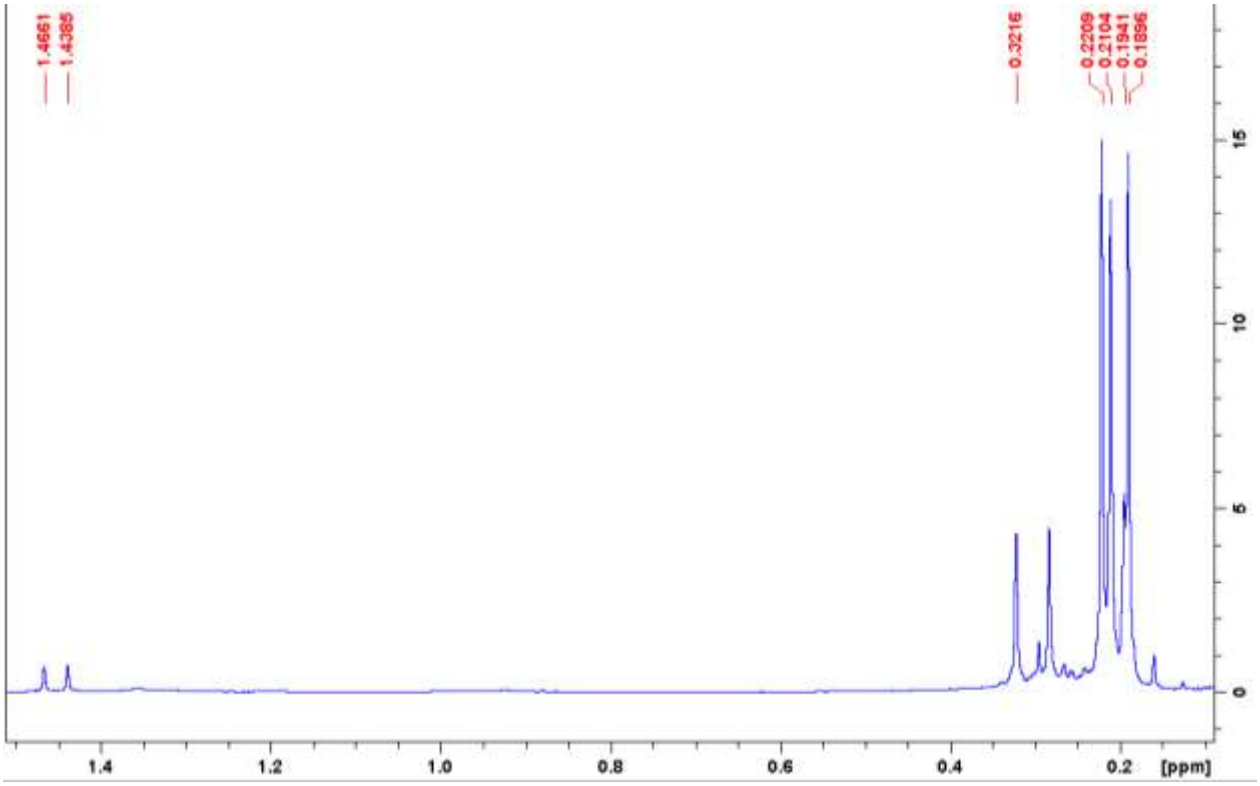


Figure S33: ^{1}H NMR spectrum of complex **5** (expansion).

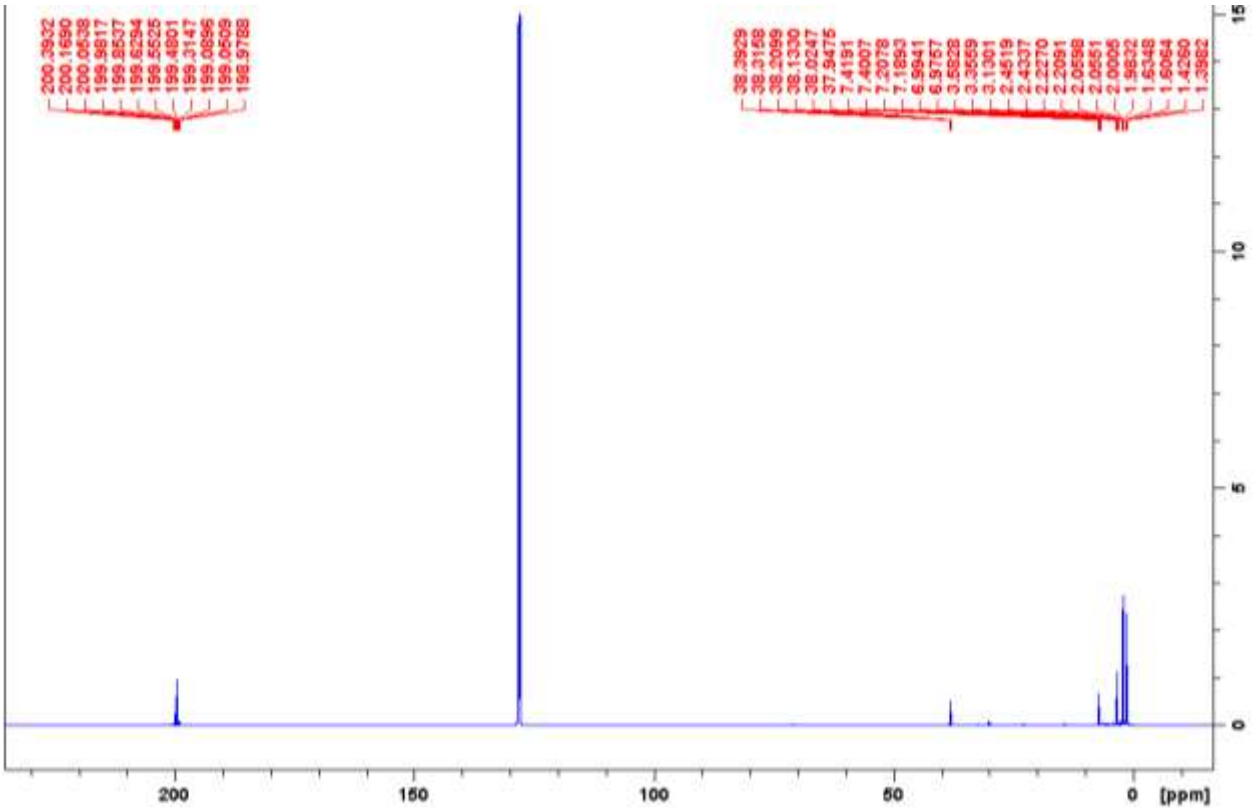


Figure S34: ^{13}C NMR spectrum of complex **5**.

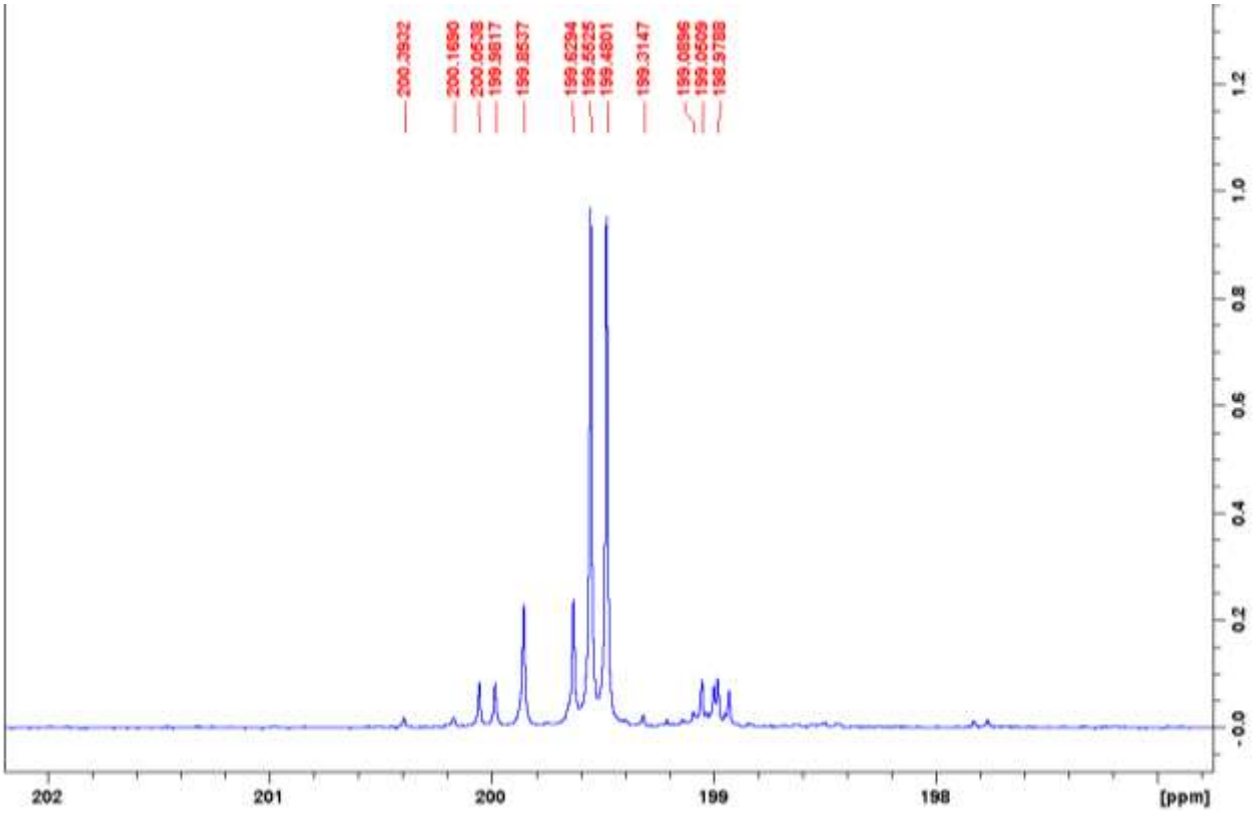


Figure S35: ^{13}C NMR spectrum of complex **5** (expansion).

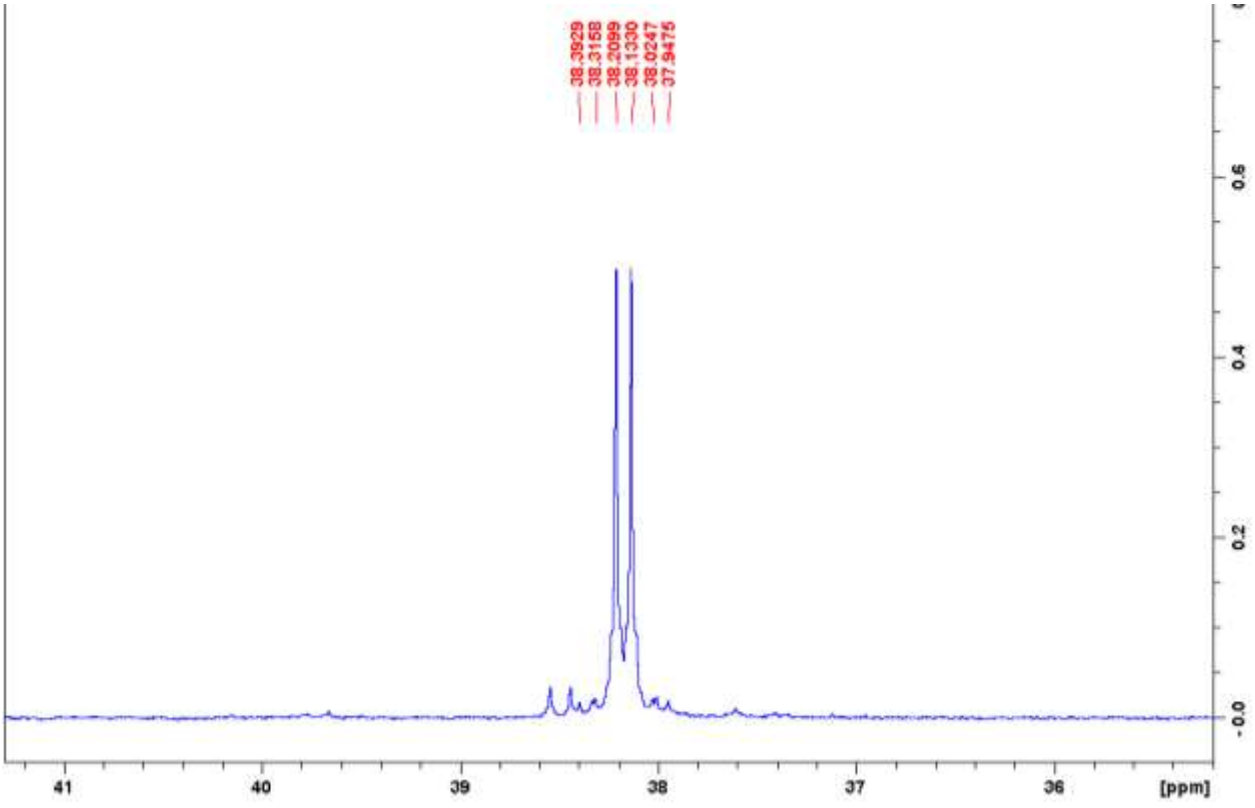


Figure S36: ^{13}C NMR spectrum of complex **5** (expansion).

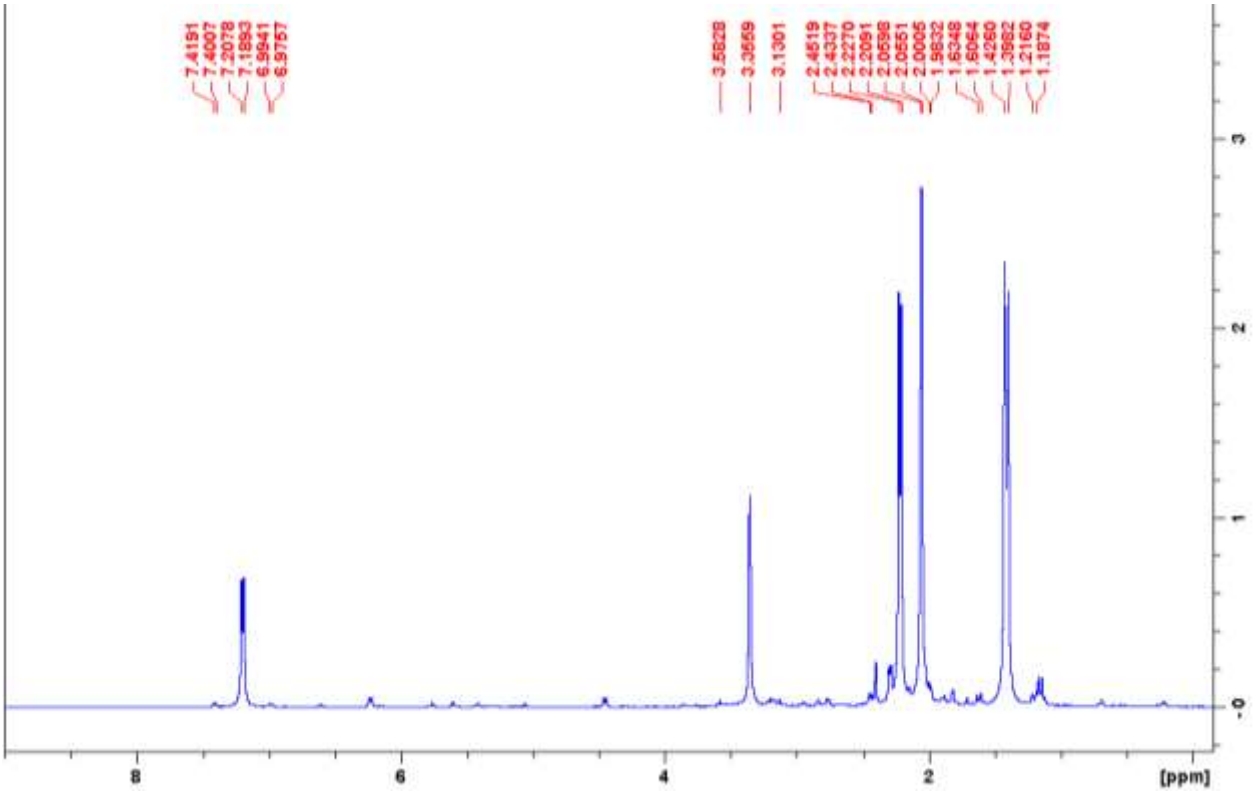


Figure S37: ^{13}C NMR spectrum of complex **5** (expansion).

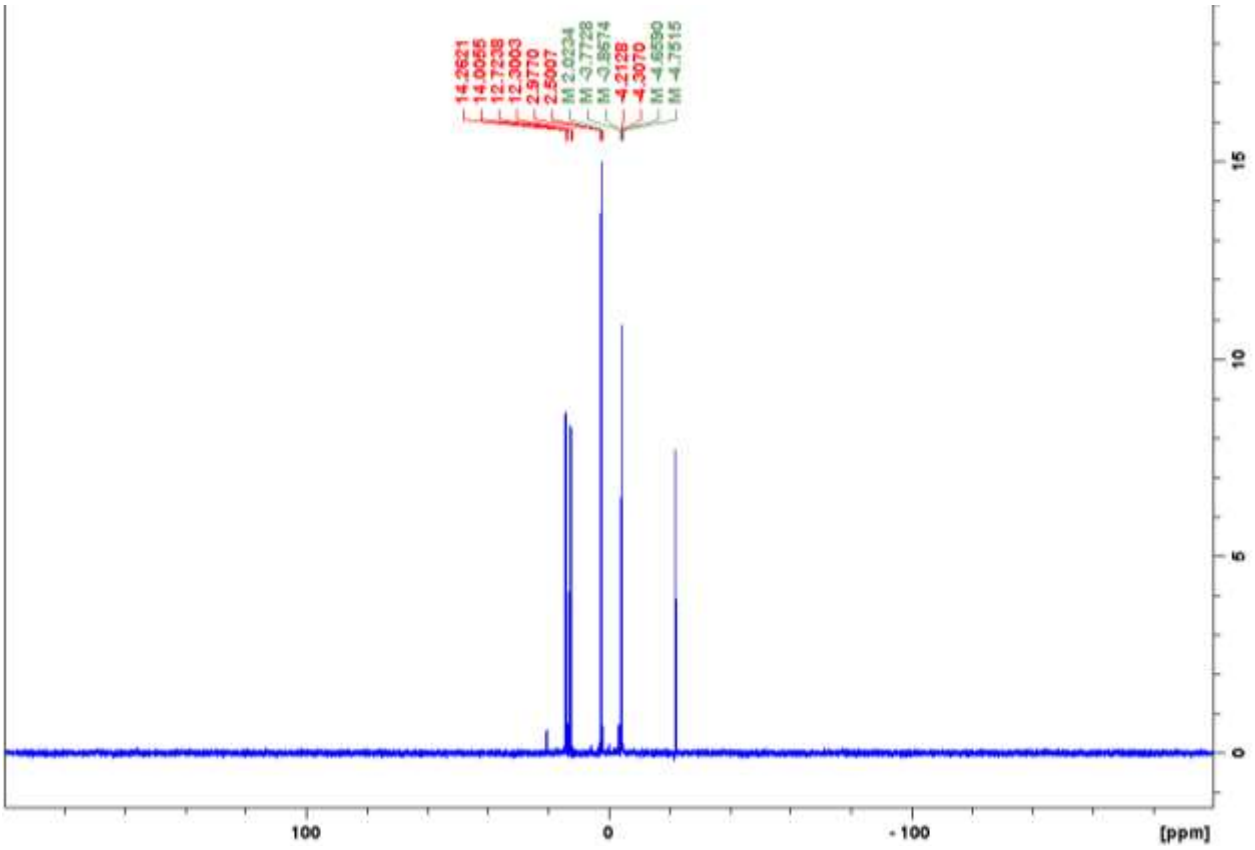


Figure S38: ^{29}Si NMR spectrum of complex **5**.

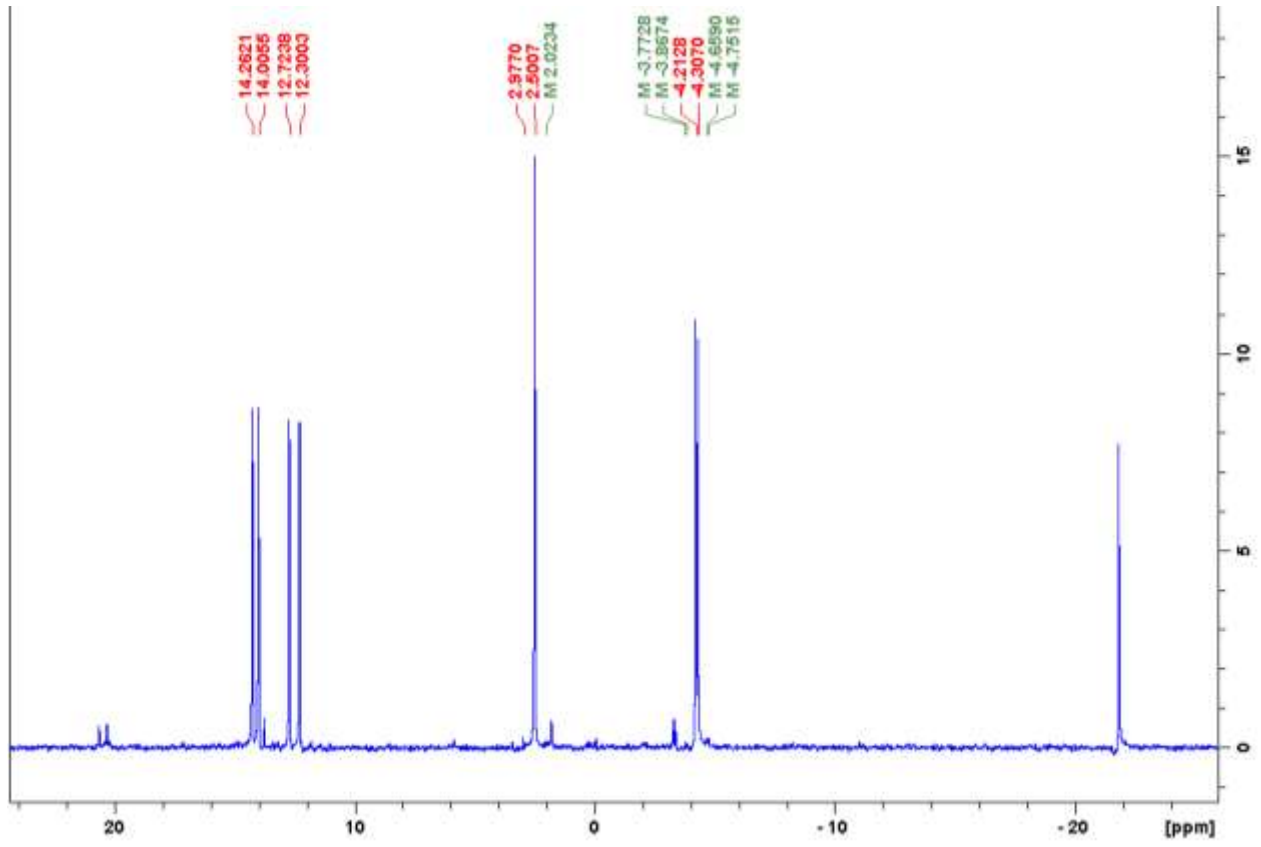


Figure S39: ^{29}Si NMR spectrum of complex **5** (expansion).

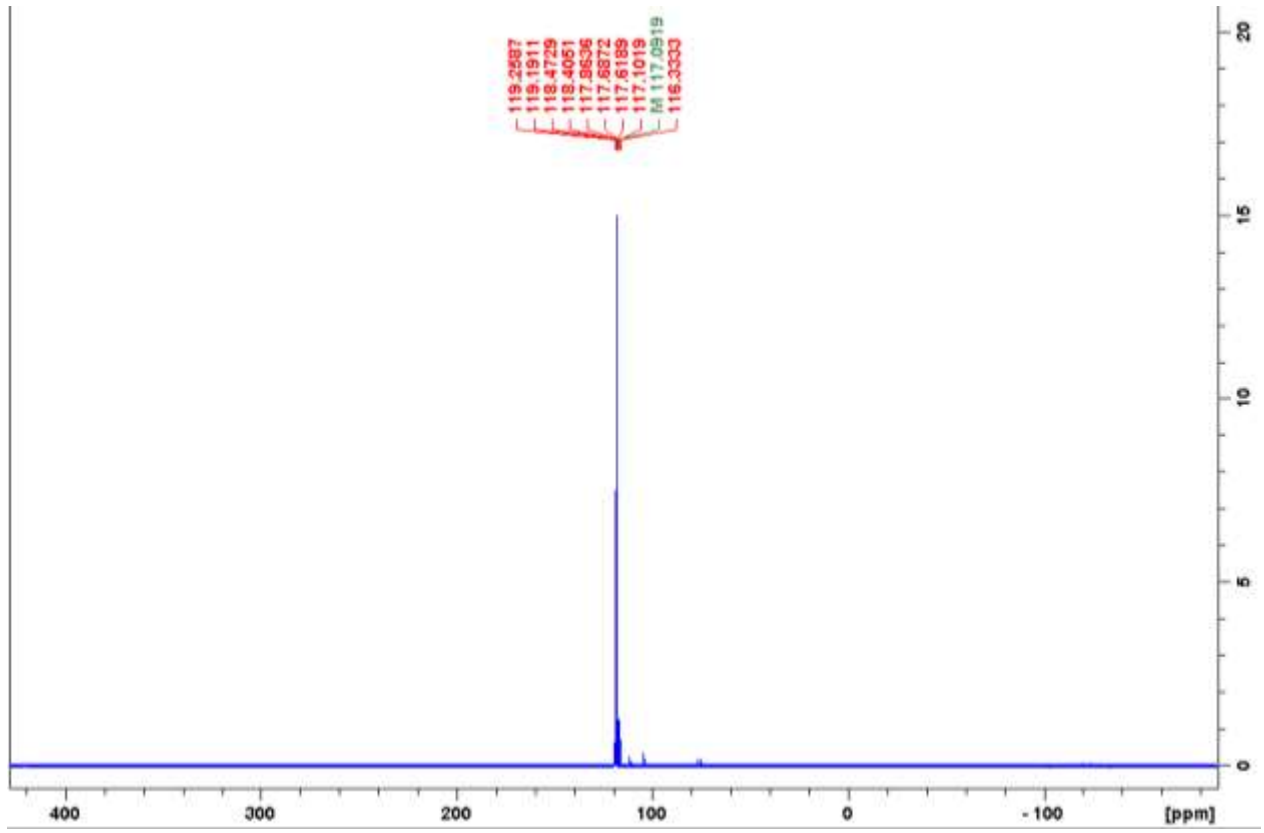


Figure S40: ^{31}P NMR spectrum of complex **5**.

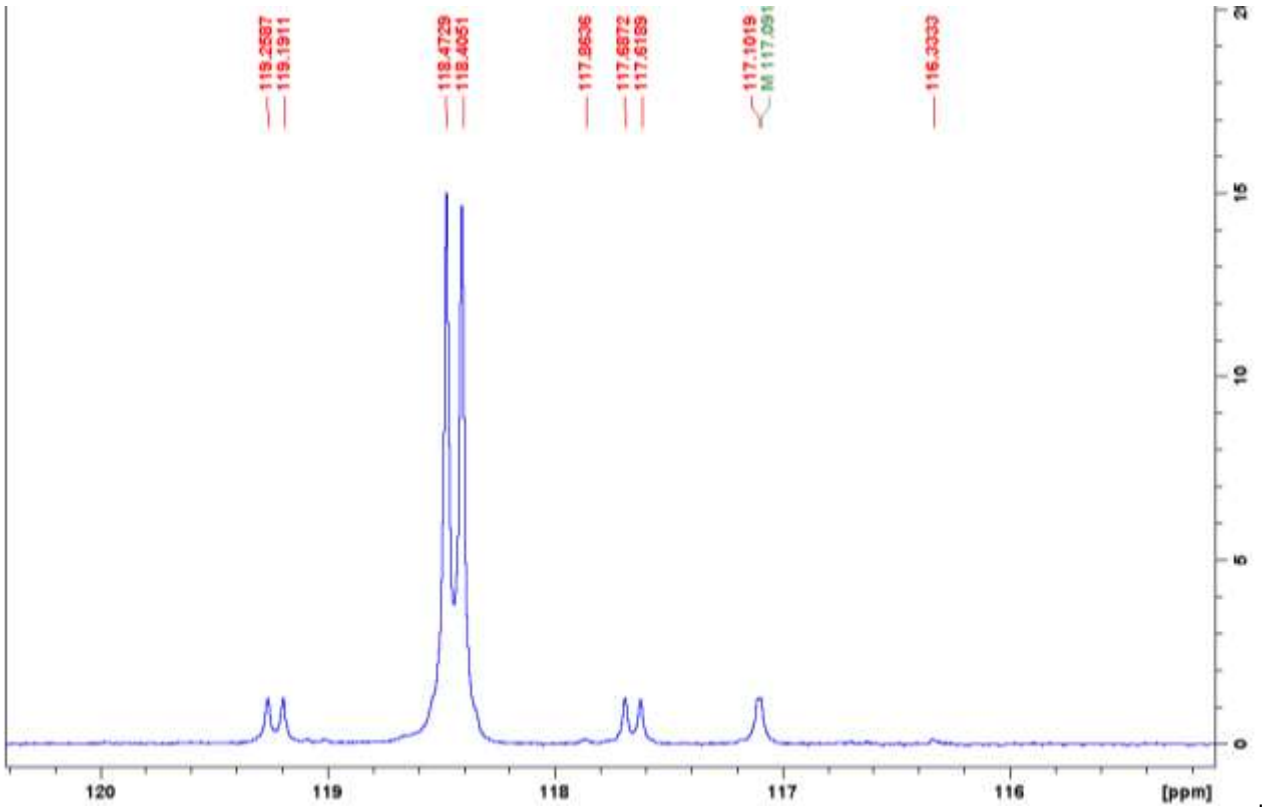


Figure S41: ^{31}P NMR spectrum of complex **5** (expansion).

4. Computational part

4.1 Computational details.

Quantum chemical calculations were performed with the ORCA electronic structure program package.[2] All geometry optimizations were run in redundant internal coordinates with tight convergence criteria, using the B3LYP[3] functional together with the powerful speeding up RIJCOSX algorithm[4] and the Ahlrichs' segmented def2-TZVP basis set.[5] For W atoms the [SD(60,MWB)][6] effective core potencial was used. In all optimizations and energy evaluations, the latest Grimme's semiempirical atom-pair-wise correction (DFT-D3 methods), taking into account the major part of the contribution of dispersion forces to the energy, was included.[7] Harmonic frequency calculations verified the nature of the computed species as minima or TS (transition state) structures, featuring none or only one negative eigenvalues, respectively. Moreover, all TS structures were confirmed by intrinsic reaction coordinate (IRC) calculations. From these geometries, all reported electronic data were obtained by means of single-point (SP) calculations using the same functional as well as the more polarized def2-TZVPP[5,8] basis set. Reported energies were corrected for the Gibbs energy term at the optimization level and obtained by means of the recently developed near linear scaling domain-based local pair natural orbital (DLPNO) method[9] to achieve coupled cluster theory with single-double and perturbative triple excitations (CCSD(T)).[10] Due to convergence problems at higher computational levels for **7a** and its formation and decomposition TSs, the conversion **3a**→**10a** was quoted using energies at the optimization level. Solvent effects (tetrahydrofurane) were taken into account via the COSMO solvation model[11] for both geometry optimizations and energy SP calculations.

4.2 Stability of oxaphosphasiliranes.

Theoretical investigations revealed that conversion of (model) complex **3'** into the hypothetical oxaphosphasilirane complex is significantly endergonic (ΔE_{ZPE} = 29.24 kcal/mol), in agreement with the experimental non observation of the cyclic species. Furthermore, the six-membered cyclic dimer turned out to be 32.72 kcal/mol more stable than oxaphosphasilirane (non ZPE-corrected at the B3LYP-D3/def2-TZVPecp level).

The ring strain energy (RSE) of phosphasilirane and its 2,3,3-trimethyl-derivative was computed by evaluating the energetics of appropriate homodesmotic reactions (Scheme 5), similar to those used for other three-[12] or four-membered[13] saturated phosphorus heterocycles. In such reactions, for the cleavage of every endocyclic X–Y (or X=Y) bond, a $H_nX–YH_m$ (or $H_nX=YH_m$) reagent is used, the valences of X and Y being completed with H atoms. In reactants and products, the number of every type of bonds (single/double) between X and Y, with the same hybridization states in X and Y, must be conserved, as well as the number of sp^3, sp^2, and sp-hybridized (and non-hybridized, in case) atoms of every element with 0, 1, 2, or 3 H atoms attached. By averaging the opposites of the zero point-corrected energies for the three homodesmotic endocyclic bond cleavage reactions RSE values of 34.22 (R = H) and 35.18 kcal/mol (R = Me) were obtained.

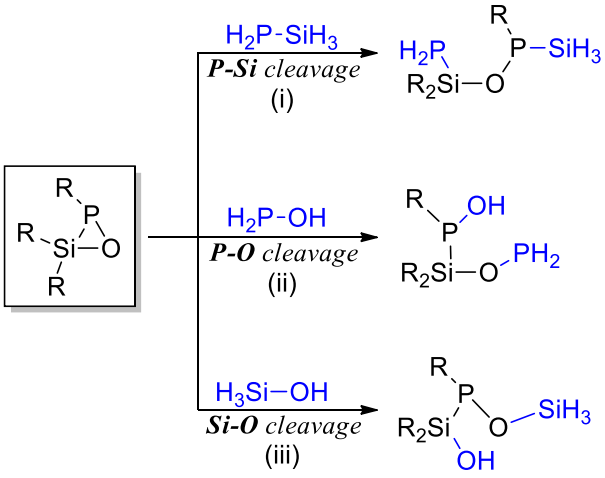


Figure S42: Homodesmotic reactions used for the estimation of RSE for oxaphosphasiliranes.

4.3 Computed optical transitions in 3a'.

TD-DFT studies ($COSMO_{THF}$/B3LYP-D3/def2-TZVPecp) on the model species **3'** predict a lowest-energy absorption at 450.1 nm (f = 0.0627) corresponding mainly to a HOMO→LUMO+2 transition from a phosphorus p-type orbital to a carbonyl ligand-based empty MO (Figure S42).

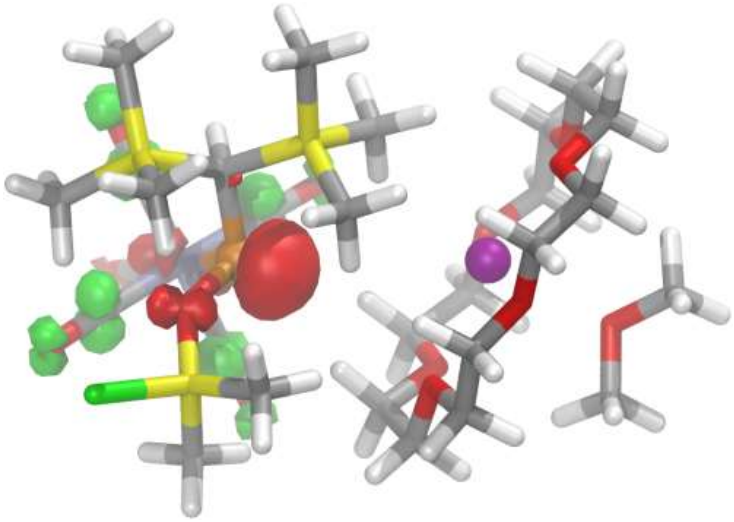
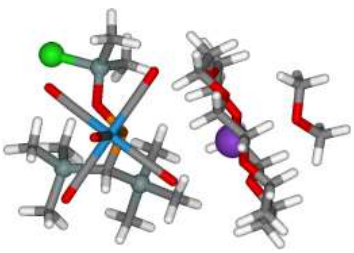


Figure S43: Calculated ($COSMO_{THF}$/B3LYP-D3/def2-TZVPecp) electron difference isosurfaces (isovalues, in au: +0.005 green and -0.005 red) for the predicted optical transition of **3'** at 450 nm.

According to these calculations two less intense bands are expected at 355.9 nm (f = 0.0353) and 326.5 nm (f = 0.0251), corresponding to HOMO-2→LUMO+1 and HOMO-1→LIMO+3 transitions, respectively.

4.4 Computed structures.

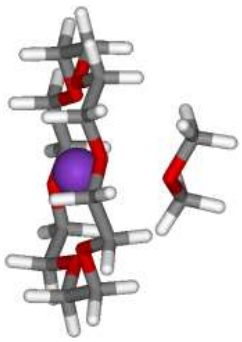
Cartesian coordinates (in Å) and energies (in hartrees) for all computed species. Geometries, zero-point energy correction (ZPE) and Gibbs energy correction (G_{corr}) at the COSMO(THF)/B3LYP-D3/def2-TZVP level, whereas electronic energies are computed at the COSMO(THF)/CCSD(T)/def2-TZVPP level unless otherwise stated.



3' E = -4415.16175925371 au ($COSMO_{THF}$/B3LYP-D3-def2-TZVPecp)
ZPE = 0.81443986
G_{corr} = 0.03393916 au

P	-0.010167	-0.025147	0.020268	O	2.252294	-2.399894	2.297169
W	0.052945	-0.101628	2.672300	C	1.497252	1.352633	2.618678
C	0.143776	-0.136892	4.676647	O	2.304790	2.175801	2.614643
O	0.177362	-0.155854	5.836231	O	-1.019770	1.271332	-0.437354
C	-1.371513	1.380538	2.619044	Si	-0.773119	2.773196	-0.990700
O	-2.143578	2.226932	2.542314	Cl	-2.698074	3.615073	-1.107800
C	-1.394213	-1.558153	2.666164	C	0.198944	3.834854	0.184279
O	-2.190593	-2.388205	2.648954	H	0.276780	4.854719	-0.197788
C	1.465042	-1.571947	2.450707	H	-0.283270	3.867458	1.161713

H	1.207247	3.440950	0.320155	H	3.144874	-0.234030	0.759604
C	-0.091885	2.792808	-2.719327	H	4.426018	0.786253	1.441529
H	0.057312	3.817659	-3.065479	C	5.122271	-1.059909	0.634466
H	0.863372	2.267627	-2.754108	H	5.157645	-1.479787	1.646672
H	-0.775562	2.291293	-3.405964	H	6.131126	-0.727456	0.360549
C	-1.093159	-1.421935	-0.613021	O	4.670676	-2.045028	-0.282389
H	-1.094800	-2.202188	0.154288	C	5.559587	-3.144473	-0.391435
Si	-2.926634	-1.056805	-0.891408	H	5.738758	-3.586852	0.596219
C	-3.746097	-0.029870	0.450186	H	6.520197	-2.807306	-0.799951
H	-3.636786	-0.482075	1.435936	C	4.953215	-4.192586	-1.287051
H	-3.344920	0.979642	0.485571	H	3.961653	-4.475834	-0.917248
H	-4.816568	0.029397	0.230274	H	5.593357	-5.082967	-1.280520
C	-3.847898	-2.705657	-0.903262	O	4.853402	-3.675481	-2.608585
H	-4.922516	-2.525409	-1.000613	C	4.294756	-4.594221	-3.534443
H	-3.542138	-3.360426	-1.718819	H	3.244165	-4.791327	-3.289536
H	-3.684417	-3.238718	0.037097	H	4.834201	-5.548371	-3.498755
C	-3.219020	-0.203520	-2.543641	C	4.416496	-4.025423	-4.923650
H	-2.713282	0.761297	-2.576397	H	4.037103	-4.758363	-5.646054
H	-2.866205	-0.805295	-3.383761	H	5.470327	-3.832954	-5.155847
H	-4.288651	-0.027611	-2.686696	O	3.675893	-2.815643	-5.017414
Si	-0.153831	-2.186258	-2.054280	C	3.843304	-2.181617	-6.278209
C	-1.103259	-3.535271	-2.968317	H	3.525997	-2.853960	-7.084628
H	-1.974094	-3.140945	-3.495045	H	4.901219	-1.936726	-6.433633
H	-0.447961	-4.000991	-3.710353	C	3.008543	-0.931300	-6.334094
H	-1.445765	-4.316579	-2.286519	H	1.956851	-1.169464	-6.137145
C	0.358856	-0.911208	-3.340835	H	3.076961	-0.505512	-7.342466
H	0.932525	-0.097294	-2.898359	O	3.486296	0.002898	-5.375544
H	0.966275	-1.393085	-4.111569	C	2.761443	1.226390	-5.403504
H	-0.508636	-0.470521	-3.834126	H	1.705424	1.039432	-5.179503
C	1.383787	-3.011634	-1.347240	H	2.827966	1.681051	-6.399209
H	1.991093	-2.336733	-0.742744	C	3.342705	2.179309	-4.393760
H	1.092874	-3.842612	-0.699359	H	4.408006	2.346783	-4.592791
H	2.008576	-3.425404	-2.141348	H	2.822975	3.140983	-4.479873
K	3.773108	-1.061187	-2.730321	O	6.491828	-0.645212	-2.955342
O	3.171716	1.643883	-3.089909	C	6.869780	0.720871	-2.982133
C	3.555410	2.546767	-2.060513	H	7.951921	0.829989	-2.849087
H	2.931899	3.447953	-2.099824	H	6.583896	1.189507	-3.931563
H	4.599223	2.850935	-2.197773	H	6.350124	1.209659	-2.161384
C	3.372020	1.873944	-0.728205	C	7.155396	-1.418737	-3.940109
H	2.347657	1.494444	-0.627375	H	6.829724	-2.447822	-3.807537
H	3.555974	2.601068	0.071073	H	6.896822	-1.077520	-4.949854
O	4.285109	0.788656	-0.626526	H	8.242836	-1.360272	-3.817839
C	4.174366	0.107189	0.619649				

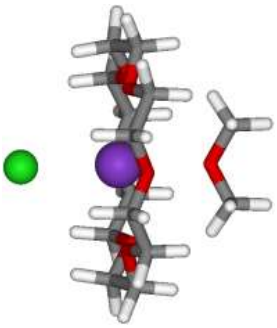


[K(18c6)(OMe$_2$)]$^+$

E = -1677.78215515772 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)
E = -1675.36410242961 au
G_{corr} = 0.39465928 au

K	0.112813	0.065833	-0.028964	C	2.291318	-0.936145	2.708058
O	0.099703	0.009660	2.795311	O	2.493082	-0.482644	1.376303
C	1.376364	0.023181	3.421322	C	3.421737	-1.279512	0.651210

C	3.551687	-0.740156	-0.748072	H	0.769958	-1.770557	-3.353730
O	2.330851	-0.946555	-1.448908	H	1.143868	-0.487165	-4.524778
C	2.383581	-0.473828	-2.789570	H	-1.571927	-1.079574	-3.242430
C	1.056588	-0.716802	-3.456330	H	-1.191866	0.117105	-4.499455
O	0.073993	0.117636	-2.856321	H	-3.143123	0.857832	-3.278815
C	-1.220565	-0.055173	-3.417126	H	-1.791614	1.955679	-2.930537
C	-2.165064	0.935057	-2.789576	H	-4.133260	1.572177	-1.204384
O	-2.287323	0.648883	-1.402099	H	-2.731558	2.566983	-0.757333
C	-3.148750	1.553506	-0.722568	H	-3.675081	0.068891	0.731805
C	-3.315864	1.104918	0.703973	H	-4.064653	1.739800	1.192231
O	-2.071296	1.203780	1.385789	H	-2.496113	-0.278717	2.767830
C	-2.164246	0.766298	2.736514	H	-2.896617	1.374375	3.280480
C	-0.824260	0.901132	3.406700	H	-0.459816	1.931978	3.326469
H	1.286275	-0.279815	4.471046	H	-0.935282	0.659065	4.470170
H	1.796440	1.035524	3.393140	O	1.131974	2.585385	-0.291462
H	1.856706	-1.943276	2.700857	C	1.282523	3.273087	0.940616
H	3.246964	-0.978850	3.243785	H	1.867754	4.189329	0.809927
H	3.082947	-2.322254	0.623066	H	0.306483	3.532253	1.366374
H	4.403184	-1.250620	1.139007	H	1.810543	2.605635	1.619339
H	4.370519	-1.261665	-1.257422	C	0.506493	3.378970	-1.288599
H	3.788772	0.330152	-0.719674	H	0.438376	2.768784	-2.187136
H	3.166671	-1.003333	-3.344814	H	-0.499213	3.682923	-0.975269
H	2.618493	0.597308	-2.799737	H	1.095334	4.278066	-1.498674

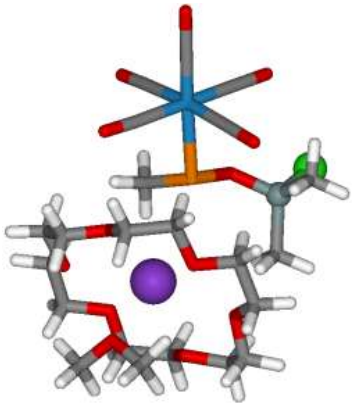


[K(18c6)(OMe_2)]Cl

E = -2138.13037282362 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)
E = -2135.2685990929 au
G_{corr} = 0.3923169 au

K	-0.008527	-0.140862	-0.011867	H	4.396580	-1.122623	1.140097
O	0.075553	0.106918	2.797586	H	4.375420	-1.056915	-1.236577
C	1.334512	0.095568	3.447484	H	3.712256	0.503842	-0.694305
C	2.252980	-0.846886	2.712836	H	3.165427	-0.870038	-3.339212
O	2.500912	-0.334450	1.411269	H	2.564371	0.714390	-2.795678
C	3.408514	-1.131013	0.663008	H	0.770075	-1.701477	-3.295705
C	3.527121	-0.576411	-0.732989	H	1.134646	-0.470768	-4.526341
O	2.327923	-0.836704	-1.446469	H	-1.559280	-1.069050	-3.165082
C	2.365711	-0.364202	-2.783505	H	-1.252548	0.068827	-4.498894
C	1.044661	-0.650525	-3.447710	H	-3.190417	0.827654	-3.278617
O	0.052714	0.200514	-2.892562	H	-1.861177	1.967885	-2.978933
C	-1.247142	-0.045982	-3.407758	H	-4.182195	1.547090	-1.220301
C	-2.208953	0.942683	-2.801887	H	-2.817926	2.587307	-0.755932
O	-2.306812	0.689237	-1.410808	H	-3.645911	0.029825	0.697534
C	-3.199011	1.558198	-0.733675	H	-4.152118	1.668779	1.172454
C	-3.357284	1.087546	0.688162	H	-2.473794	-0.286356	2.719025
O	-2.132303	1.259050	1.387593	H	-2.974749	1.327429	3.280072
C	-2.206253	0.776876	2.723025	H	-0.550725	2.007677	3.332729
C	-0.876705	0.962141	3.405659	H	-0.988285	0.712316	4.468187
H	1.224599	-0.247619	4.483887	O	1.317083	2.366653	-0.398566
H	1.762685	1.105336	3.467225	C	1.586392	2.955530	0.861590
H	1.792289	-1.839652	2.642866	H	2.136818	3.896816	0.746940
H	3.192938	-0.938692	3.271283	H	0.656717	3.155911	1.408102
H	3.055904	-2.168711	0.621773	H	2.189652	2.244080	1.420256

C	0.559231	3.210960	-1.247016	H	1.087990	4.151924	-1.439700
H	0.411650	2.672397	-2.180363	Cl	-1.153999	-2.897630	0.317493
H	-0.416706	3.442120	-0.802648				



3a

E = -3597.88687158147 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)
E = -3592.62284062254 au
G_{corr} = 0.52871640 au

P	0.583931	-0.596461	0.136337	H	4.186933	-3.198771	2.576574
W	-0.020584	-0.448218	2.712704	H	5.266772	-3.276923	1.164078
C	-0.475120	-0.265067	4.660335	O	3.242423	-3.397303	0.748592
O	-0.752228	-0.158064	5.781247	C	3.188600	-4.813002	0.743185
C	-1.139104	1.215413	2.242401	H	3.115308	-5.193285	1.769150
O	-1.769236	2.132623	1.961720	H	4.097912	-5.219372	0.283759
C	-1.656723	-1.618566	2.295793	C	1.972720	-5.258139	-0.025848
O	-2.560612	-2.275275	2.023168	H	1.071731	-4.806324	0.404354
C	1.045590	-2.157261	3.110601	H	1.877227	-6.348128	0.048681
O	1.608535	-3.127533	3.371413	O	2.116132	-4.872826	-1.386041
C	1.655516	0.716939	2.897865	C	0.998323	-5.206662	-2.193985
O	2.599683	1.373510	2.971926	H	0.128668	-4.606333	-1.904972
O	-0.334792	0.638420	-0.621679	H	0.739384	-6.265257	-2.071041
Si	0.268149	2.019996	-1.242099	C	1.355379	-4.966570	-3.636977
Cl	-1.429746	3.129133	-1.795345	H	0.516053	-5.274599	-4.272184
C	1.198273	3.033597	0.006407	H	2.228496	-5.571563	-3.908393
H	1.561780	3.959167	-0.444758	O	1.646103	-3.589372	-3.842638
H	0.563616	3.287875	0.855620	C	2.104743	-3.335231	-5.163058
H	2.058376	2.474809	0.380893	H	1.341913	-3.634349	-5.892173
C	1.256899	1.708763	-2.781402	H	3.012779	-3.918606	-5.358757
H	1.560261	2.644643	-3.254844	C	2.390183	-1.868592	-5.334689
H	2.156631	1.146243	-2.524436	H	1.503827	-1.275445	-5.077674
H	0.675744	1.127440	-3.500031	H	2.631195	-1.681237	-6.388050
C	-0.361819	-2.017587	-0.583709	O	3.482262	-1.492578	-4.505953
H	-0.018377	-2.931175	-0.095708	C	3.878286	-0.143584	-4.720808
H	-0.177008	-2.102973	-1.657925	H	3.009601	0.516402	-4.632594
H	-1.437498	-1.927691	-0.426379	H	4.294892	-0.028300	-5.728977
K	3.011201	-2.206694	-1.745879	C	4.923403	0.249104	-3.709216
O	4.374540	0.143025	-2.404538	H	5.807656	-0.393427	-3.795280
C	5.164869	0.763022	-1.399353	H	5.230452	1.281677	-3.913422
H	5.154297	1.851395	-1.533164	O	5.316196	-3.727431	-1.946188
H	6.202816	0.417312	-1.469482	C	6.505357	-2.966920	-2.069361
C	4.597445	0.420272	-0.047086	H	7.388590	-3.584711	-1.869992
H	3.535096	0.685929	-0.000401	H	6.596214	-2.539769	-3.075149
H	5.131482	0.990857	0.722108	H	6.447263	-2.165386	-1.336187
O	4.747418	-0.975161	0.172591	C	5.261039	-4.814685	-2.852442
C	4.295603	-1.384995	1.459645	H	4.333014	-5.345905	-2.653305
H	3.278461	-1.021798	1.627440	H	5.266784	-4.461409	-3.890778
H	4.949055	-0.969273	2.235690	H	6.110381	-5.491903	-2.705801
C	4.310037	-2.887830	1.533266				

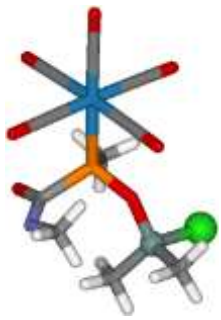
TS(**3a**+MeNCO→**6a**)

E = -2124.88054640556 au

G_{corr} = 0.15152822 au

v = -86.40 cm^{-1}

P	0.202961	0.140831	-0.258511	H	-1.951324	4.013372	-0.247750
W	0.700718	0.208948	2.308538	H	-0.408803	4.025178	-1.108007
C	0.990507	0.270172	4.298465	C	-0.940877	1.574789	-3.302267
O	1.125801	0.294381	5.450487	H	-1.319767	2.230144	-4.089109
C	-0.017503	2.132265	2.222521	H	0.144565	1.681283	-3.253004
O	-0.422031	3.204576	2.126762	H	-1.167950	0.541799	-3.571443
C	-1.223940	-0.500323	2.449774	C	-0.444851	-1.530081	-0.702388
O	-2.299995	-0.903401	2.462684	H	0.352018	-2.259881	-0.553652
C	1.401189	-1.714033	2.147053	H	-0.732879	-1.549005	-1.755786
O	1.791494	-2.789518	2.018999	H	-1.304894	-1.810527	-0.091805
C	2.587834	0.905864	1.902546	N	2.862533	1.295045	-1.950190
O	3.640833	1.295610	1.646494	C	2.486060	0.139253	-1.909542
O	-1.237149	1.022516	-0.461847	O	2.491453	-1.029858	-2.107108
Si	-1.703319	2.013761	-1.665413	C	2.370384	2.518617	-1.382197
Cl	-3.782700	1.714991	-1.861361	H	2.163285	3.239995	-2.174315
C	-1.473226	3.798257	-1.204415	H	1.457044	2.330304	-0.812125
H	-1.898119	4.454932	-1.966152	H	3.119818	2.946388	-0.715541

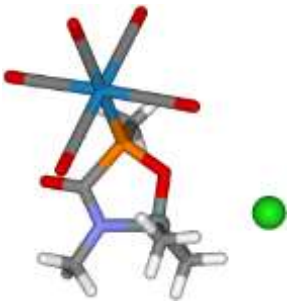


6a^{-}

E = -2124.90602346989 au

G_{corr} = 0.15283834 au

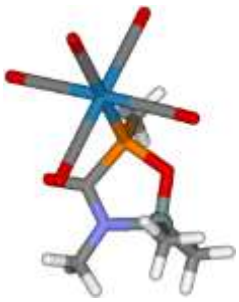
P	0.299588	0.162426	-0.186920	H	-2.105748	4.068509	-0.660269
W	0.861370	0.110592	2.294463	H	-0.649250	4.324327	-1.635555
C	1.275001	0.064448	4.274618	C	-0.677113	1.517080	-3.461260
O	1.501304	0.039569	5.406281	H	-1.210488	1.971080	-4.298856
C	0.177088	2.049987	2.407596	H	0.365791	1.838788	-3.486840
O	-0.217220	3.125886	2.441755	H	-0.697108	0.433981	-3.588283
C	-1.054527	-0.561282	2.622226	C	-0.681592	-1.262818	-0.754994
O	-2.128499	-0.930968	2.790233	H	-0.143883	-2.177874	-0.518623
C	1.511448	-1.828992	2.036173	H	-0.846523	-1.222585	-1.830680
O	1.863863	-2.909429	1.881829	H	-1.638846	-1.256163	-0.233260
C	2.766662	0.796728	1.882269	N	2.439859	1.228812	-1.700294
O	3.822614	1.180306	1.660109	C	1.774026	0.161179	-1.395965
O	-0.677880	1.425779	-0.550275	O	2.003323	-1.018364	-1.775076
Si	-1.461502	2.027564	-1.863381	C	2.137811	2.516895	-1.115885
Cl	-3.393048	1.199798	-1.822439	H	1.577134	3.156531	-1.810947
C	-1.634622	3.853399	-1.620781	H	1.569076	2.487254	-0.180495
H	-2.241958	4.292353	-2.414323	H	3.073018	3.041851	-0.901755



4a·Cl^- E = -2124.94128271413 au

G_{corr} = 0.15620252 au

P	-0.043618	0.396899	0.406709	H	-0.654234	-1.112905	-3.077613
W	2.369848	0.130263	-0.210268	H	-2.338059	-1.566740	-3.387783
C	4.318805	-0.109449	-0.733866	C	-3.900875	0.445573	-1.206799
O	5.423362	-0.247227	-1.025597	H	-4.071202	1.281412	-1.886473
C	1.990456	1.247871	-1.914939	H	-4.597209	-0.360853	-1.452727
O	1.766585	1.860263	-2.852591	H	-4.089560	0.763097	-0.179177
C	2.830793	1.849786	0.831694	C	-0.492795	1.379691	1.863478
O	3.080499	2.801007	1.420134	H	-0.009023	0.938644	2.736122
C	2.662018	-0.980501	1.500926	H	-1.573588	1.390211	2.004102
O	2.837865	-1.595956	2.451058	H	-0.127478	2.398121	1.732317
C	1.840390	-1.590770	-1.212912	N	-1.861455	-1.437533	-0.199435
O	1.530312	-2.549989	-1.758571	C	-0.914994	-1.225059	0.736396
O	-1.031622	0.931428	-0.762883	O	-0.606430	-1.974301	1.656304
Si	-2.158924	-0.136147	-1.399350	C	-2.615922	-2.688725	-0.154029
Cl	-2.490734	2.695018	-3.578017	H	-1.934701	-3.535868	-0.071441
C	-1.683284	-0.749085	-3.075370	H	-3.292380	-2.704302	0.702430
H	-1.780228	0.074387	-3.784160	H	-3.201341	-2.792038	-1.065893



4a E = -1665.05925861602 au

G_{corr} = 0.15659634 au

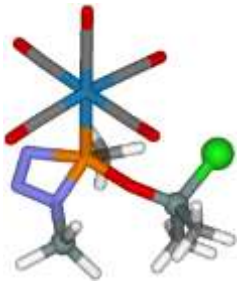
P	-0.050074	0.391514	0.451359	H	-2.248906	-1.495698	-3.423408
W	2.340677	0.121003	-0.220251	C	-3.879339	0.469945	-1.275666
C	4.280637	-0.113713	-0.796637	H	-4.006602	1.322136	-1.947094
O	5.374429	-0.244043	-1.121953	H	-4.584118	-0.306088	-1.584857
C	1.906401	1.186963	-1.934663	H	-4.132418	0.782244	-0.261090
O	1.636720	1.771995	-2.880711	C	-0.489527	1.358288	1.919339
C	2.813228	1.870980	0.769208	H	-0.001180	0.903804	2.782641
O	3.063976	2.838796	1.327352	H	-1.569017	1.370004	2.069018
C	2.691649	-0.954847	1.509300	H	-0.119677	2.376495	1.799744
O	2.893567	-1.553662	2.462782	N	-1.871501	-1.455282	-0.176342
C	1.796566	-1.632132	-1.155020	C	-0.924103	-1.235323	0.766999
O	1.468639	-2.607832	-1.659154	O	-0.616282	-1.989070	1.677995
O	-1.063193	0.937967	-0.707009	C	-2.607469	-2.720470	-0.142302
Si	-2.145685	-0.162125	-1.359077	H	-1.911357	-3.558813	-0.117621
C	-1.617115	-0.685144	-3.052162	H	-3.245206	-2.771848	0.740997
H	-1.699296	0.150091	-3.751270	H	-3.229399	-2.802127	-1.031974
H	-0.583017	-1.032800	-3.048680				

TS(**3a**+H_3SiN_3→**7a**) E = -2375.5397046262 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)

G_{corr} = 0.13513757 au

v = -233.44 cm^{-1}

P	0.380747	0.388138	-0.605810	H	-2.432961	3.946138	-0.317761
W	0.509109	0.390035	2.013637	H	-2.010012	4.227369	-2.016270
C	0.610078	0.357824	4.017367	C	-2.590806	1.195001	-3.266983
O	0.643761	0.331220	5.176930	H	-3.624240	1.405564	-3.550539
C	-0.914026	1.870627	2.032918	H	-1.927636	1.682537	-3.985970
O	-1.694699	2.713545	2.019910	H	-2.430263	0.117591	-3.324197
C	-0.961507	-1.045521	1.993265	C	-0.473824	-1.135987	-1.199053
O	-1.786025	-1.845905	1.961974	H	0.129042	-1.987123	-0.878965
C	1.963144	-1.053847	1.824475	H	-0.521508	-1.142583	-2.290288
O	2.785348	-1.850663	1.714435	H	-1.478597	-1.245823	-0.792565
C	1.953587	1.852504	1.901667	N	3.498996	1.526767	-1.050507
O	2.750088	2.679387	1.855460	N	3.301496	0.321046	-1.352666
O	-0.690534	1.579776	-1.124802	N	2.500821	-0.498940	-1.523871
Si	-2.238480	1.830185	-1.556522	Si	5.098799	2.107937	-0.687190
Cl	-3.500610	0.746253	-0.259327	H	5.649039	1.513830	0.558118
C	-2.630948	3.631072	-1.342937	H	6.067599	1.840595	-1.784038
H	-3.679747	3.828935	-1.572934	H	4.951118	3.566796	-0.508553



7a E = -2375.57521406692 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)

G_{corr} = 0.14030522 au

P	0.819457	0.042282	-0.354958	H	-1.480198	4.127336	-0.139141
W	0.761962	0.107328	2.233594	H	-0.732203	4.343537	-1.729128
C	0.712691	0.190216	4.241508	C	-1.703105	1.533804	-3.214789
O	0.680414	0.240231	5.398488	H	-2.608349	1.974816	-3.637543
C	-0.042029	1.999421	2.145653	H	-0.844991	1.884113	-3.794224
O	-0.494543	3.053898	2.129722	H	-1.767503	0.450251	-3.319068
C	-1.114797	-0.721938	2.101619	C	-0.221895	-1.157178	-1.264693
O	-2.150903	-1.205769	1.996673	H	0.000998	-2.157513	-0.897417
C	1.555734	-1.794192	2.346540	H	0.012467	-1.112132	-2.329782
O	1.981383	-2.853757	2.461445	H	-1.278341	-0.939212	-1.116826
C	2.652947	0.904640	2.089934	N	2.107726	0.798738	-1.272357
O	3.703043	1.346687	1.946614	N	3.032706	-0.251881	-1.088506
O	-0.161071	1.453830	-0.751305	N	2.382019	-1.133812	-0.508796
Si	-1.496543	2.033511	-1.432668	Si	2.442121	2.466595	-1.649500
Cl	-3.170470	1.229372	-0.412102	H	3.850171	2.515086	-2.107224
C	-1.563782	3.874913	-1.196788	H	1.562885	2.957468	-2.735441
H	-2.498029	4.286393	-1.583864	H	2.276376	3.357201	-0.477263

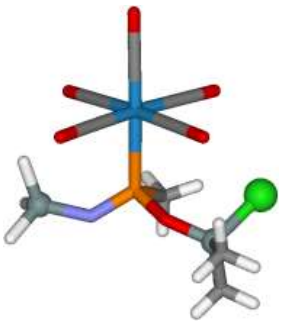
TS(**7a**→**8a^t**+N_2) E = -2375.57048032988 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)

G_{corr} = 0.13849365 au

v = -478.21 cm^{-1}

P	0.779246	0.122522	-0.368833	O	-2.161105	-1.139241	2.024059
W	0.774556	0.128655	2.218239	C	1.529712	-1.790051	2.316470
C	0.742247	0.206810	4.227549	O	1.930051	-2.859795	2.420538
O	0.717506	0.259441	5.384213	C	2.682608	0.893026	2.079134
C	-0.005300	2.030587	2.151347	O	3.741807	1.314807	1.949835
O	-0.449901	3.088709	2.144980	O	-0.204721	1.471536	-0.730173
C	-1.115570	-0.671941	2.109812	Si	-1.537537	2.036372	-1.446227

Cl	-3.206441	1.186419	-0.468681	H	0.043223	-2.126404	-0.866617
C	-1.623609	3.869697	-1.179519	H	0.052981	-1.115606	-2.326325
H	-2.553544	4.279503	-1.578184	H	-1.259744	-0.947444	-1.133914
H	-1.563703	4.103660	-0.115986	N	2.055576	0.780721	-1.312426
H	-0.785228	4.353556	-1.686532	N	3.102490	-0.414069	-1.057692
C	-1.673783	1.544167	-3.233584	N	2.465360	-1.240252	-0.481784
H	-2.570872	1.975188	-3.682995	Si	2.396862	2.442633	-1.633377
H	-0.801711	1.910364	-3.780910	H	3.802314	2.478994	-2.109267
H	-1.719568	0.460505	-3.345193	H	1.536889	3.023526	-2.698655
C	-0.195236	-1.142860	-1.264286	H	2.280496	3.330544	-0.446606



8a^{t} E = -2266.15736803255 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)

G_{corr} = 0.13285871 au

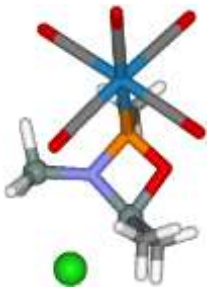
P	-0.016071	-0.007256	0.124995	H	-1.139949	4.784874	2.322280
W	2.570084	-0.040512	0.064559	H	0.222659	4.373601	1.264185
C	4.585141	-0.094369	-0.020072	H	-1.423786	4.426006	0.609286
O	5.741463	-0.124732	-0.064440	C	-2.789305	1.918567	2.359605
C	2.592613	1.880641	0.790558	H	-3.133387	2.550061	3.181440
O	2.595607	2.958048	1.187531	H	-3.456324	2.064194	1.506307
C	2.586152	-0.753918	1.988307	H	-2.855456	0.876312	2.674074
O	2.592754	-1.146924	3.068472	C	-0.689203	-1.047316	1.476985
C	2.408008	-1.968929	-0.638437	H	-0.378933	-2.076806	1.291120
O	2.306146	-3.052761	-1.005940	H	-1.779652	-0.999929	1.461407
C	2.446986	0.749912	-1.836607	H	-0.313940	-0.737004	2.452118
O	2.379630	1.227202	-2.877816	N	-0.855803	-0.322229	-1.176925
O	-0.531131	1.490233	0.608064	Si	-0.642958	-1.208172	-2.572995
Si	-1.052941	2.364131	1.876571	H	-1.454824	-0.643975	-3.693484
Cl	0.155591	1.928174	3.548210	H	0.756908	-1.293855	-3.091933
C	-0.824296	4.161012	1.483844	H	-1.086013	-2.636288	-2.460727

TS(**8a^{t}** →**9a^{o}**) E = -2266.14736241221 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)

G_{corr} = 0.13348181 au

v = -157.38 cm^{-1}

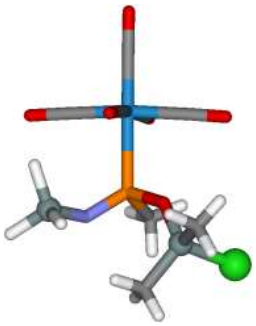
P	0.078614	0.380535	0.612222	H	-0.644907	4.350176	2.969776
W	2.577741	0.261965	0.084208	H	0.758184	3.530297	2.274673
C	4.557183	0.207017	-0.335714	H	-0.531007	4.101110	1.211052
O	5.687254	0.172426	-0.574772	C	-3.004079	1.924067	2.071783
C	2.531340	2.308769	-0.160501	H	-3.552734	2.439962	2.861408
O	2.505318	3.449836	-0.269785	H	-3.251761	2.361929	1.105698
C	2.913962	0.558356	2.096463	H	-3.323824	0.879324	2.062563
O	3.073222	0.732585	3.217942	C	-0.805929	-1.191765	0.324864
C	2.542601	-1.768324	0.400039	H	-0.721474	-1.456514	-0.730875
O	2.517305	-2.901500	0.589805	H	-1.858441	-1.067358	0.585057
C	2.056717	-0.023069	-1.884408	H	-0.367780	-1.991209	0.923991
O	1.742075	-0.192334	-2.976814	N	-0.815850	1.595983	0.059223
O	-0.226933	0.624035	2.207457	Si	-1.000512	2.413282	-1.394573
Si	-1.164996	2.012061	2.377150	H	-1.959507	1.764861	-2.342167
Cl	-1.181076	1.889998	4.576957	H	-1.546889	3.775026	-1.134250
C	-0.322254	3.663322	2.185799	H	0.257913	2.591994	-2.176713



9a^{O} E = -2266.16928483815 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)

G_{corr} = 0.13470769 au

P	0.584223	0.244643	1.118478	H	-2.923890	3.110344	2.485388
W	2.595410	-0.159184	-0.375095	H	-2.523706	1.484963	3.040186
C	4.221000	-0.404095	-1.563088	H	-1.381302	2.805893	3.328249
O	5.152035	-0.539752	-2.230922	C	-0.781876	3.443969	-0.115158
C	2.996579	1.853677	-0.147972	H	-1.601419	4.151016	-0.238832
O	3.202426	2.972358	-0.016297	H	0.091799	3.958985	0.289377
C	3.707263	-0.580118	1.301879	H	-0.521301	3.058734	-1.104166
O	4.319305	-0.815384	2.244908	C	0.439439	-0.892832	2.535205
C	2.105344	-2.150530	-0.539498	H	0.323096	-1.914446	2.168270
O	1.838967	-3.264235	-0.622927	H	-0.426115	-0.619460	3.140276
C	1.382780	0.296857	-1.980366	H	1.345642	-0.841883	3.140760
O	0.690132	0.565491	-2.852584	N	-0.962475	0.342222	0.441281
O	0.423860	1.714695	1.709203	Si	-1.834992	-0.820222	-0.487399
Si	-1.255470	2.013388	0.994879	H	-2.138330	-0.390253	-1.868196
Cl	-3.443362	1.856428	-0.101828	H	-0.928562	-1.998194	-0.584127
C	-2.106326	2.402670	2.617904	H	-3.074409	-1.287752	0.172756



8a^{g} E = -2266.1596493885 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)

G_{corr} = 0.13322733 au

P	0.050534	0.381813	0.360695	H	-1.279798	4.301989	3.733056
W	2.575391	0.208840	-0.146414	H	0.368624	3.653386	3.641148
C	4.558633	0.154952	-0.521005	H	-0.360839	4.418382	2.220444
O	5.697787	0.132447	-0.726296	C	-2.863295	2.268917	1.653007
C	2.501339	2.259189	-0.335707	H	-3.607994	2.715423	2.315846
O	2.438380	3.403122	-0.409311	H	-2.763112	2.889181	0.760810
C	2.866509	0.432076	1.876117	H	-3.210472	1.284760	1.339231
O	3.004023	0.549679	3.010001	C	-0.642963	-1.140026	1.095253
C	2.498259	-1.825809	0.110890	H	-0.592414	-1.942395	0.358540
O	2.442295	-2.964445	0.264371	H	-1.685862	-0.974547	1.372095
C	2.108695	-0.062629	-2.134092	H	-0.070572	-1.426568	1.978001
O	1.834679	-0.245186	-3.233911	N	-0.986173	0.838231	-0.747207
O	-0.057851	1.396658	1.674999	Si	-0.968213	2.103877	-1.842842
Si	-1.228779	2.152371	2.521305	H	-1.975699	1.874833	-2.919961
Cl	-1.570552	0.989911	4.252601	H	-1.327706	3.433338	-1.248608
C	-0.563536	3.787556	3.089745	H	0.330156	2.347520	-2.545242

TS(**8a^{g}**→**9a^{N}**) E = -2266.15771809032 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)

G_{corr} = 0.13321991 au

v = -109.92 cm^{-1}

P	0.078614	0.380535	0.612222	H	-0.644907	4.350176	2.969776
W	2.577741	0.261965	0.084208	H	0.758184	3.530297	2.274673
C	4.557183	0.207017	-0.335714	H	-0.531007	4.101110	1.211052
O	5.687254	0.172426	-0.574772	C	-3.004079	1.924067	2.071783
C	2.531340	2.308769	-0.160501	H	-3.552734	2.439962	2.861408
O	2.505318	3.449836	-0.269785	H	-3.251761	2.361929	1.105698
C	2.913962	0.558356	2.096463	H	-3.323824	0.879324	2.062563
O	3.073222	0.732585	3.217942	C	-0.805929	-1.191765	0.324864
C	2.542601	-1.768324	0.400039	H	-0.721474	-1.456514	-0.730875
O	2.517305	-2.901500	0.589805	H	-1.858441	-1.067358	0.585057
C	2.056717	-0.023069	-1.884408	H	-0.367780	-1.991209	0.923991
O	1.742075	-0.192334	-2.976814	N	-0.815850	1.595983	0.059223
O	-0.226933	0.624035	2.207457	Si	-1.000512	2.413282	-1.394573
Si	-1.164996	2.012061	2.377150	H	-1.959507	1.764861	-2.342167
Cl	-1.181076	1.889998	4.576957	H	-1.546889	3.775026	-1.134250
C	-0.322254	3.663322	2.185799	H	0.257913	2.591994	-2.176713

$9a^N$ E = -2266.16149333733 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)

G_{corr} = 0.13323559 au

P	0.155515	0.340769	0.687997	H	-0.774779	4.341133	2.975436
W	2.612961	0.231602	0.091021	H	0.728097	3.577868	2.453804
C	4.589101	0.185138	-0.368384	H	-0.375572	4.232518	1.241602
O	5.712309	0.157286	-0.629352	C	-3.017148	1.965851	1.947908
C	2.545877	2.277517	-0.164961	H	-3.518459	2.492949	2.758155
O	2.496655	3.415070	-0.291402	H	-3.332984	2.383267	0.988901
C	3.005304	0.530953	2.097993	H	-3.337426	0.920584	1.975069
O	3.199664	0.705524	3.212219	C	-0.800582	-1.154191	0.274453
C	2.586244	-1.801154	0.402818	H	-0.743809	-1.329570	-0.801765
O	2.560596	-2.934644	0.584538	H	-1.842266	-1.020798	0.569274
C	2.074887	-0.052929	-1.872447	H	-0.376878	-2.017591	0.789569
O	1.755252	-0.217824	-2.963679	N	-0.735300	1.659553	0.248965
O	-0.194541	0.605827	2.253615	Si	-1.080495	2.375037	-1.256016
Si	-1.149985	2.039961	2.102217	H	-2.071934	1.604062	-2.058797
Cl	-1.302265	1.929986	4.496110	H	-1.651419	3.723959	-1.021249
C	-0.326510	3.718005	2.202684	H	0.129368	2.511126	-2.108740

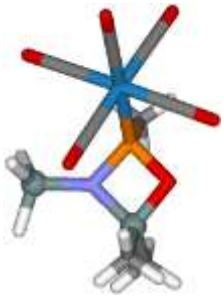
TS(**$9a^N$**→**$9a^O$**) E = -2266.15685584363 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)

G_{corr} = 0.13282652 au

v = -8.48 cm^{-1}

P	0.161080	0.373746	0.530095	O	1.936300	-0.870810	-2.862766
W	2.619191	0.249309	0.059634	O	-0.284823	0.628389	2.084256
C	4.621515	0.139855	-0.297252	Si	-1.175627	2.051596	1.770295
O	5.751975	0.073855	-0.500666	Cl	-1.655125	1.837372	5.335384
C	2.546378	2.178944	-0.654676	C	-0.375287	3.562697	2.463997
O	2.479552	3.256484	-1.038830	H	-0.411706	3.495508	3.551316
C	2.927355	1.006920	1.963261	H	0.661715	3.634857	2.131195
O	3.076018	1.433983	3.012785	H	-0.908029	4.463073	2.148201
C	2.595823	-1.666771	0.819201	C	-2.997985	1.906284	2.036192
O	2.567570	-2.728624	1.249631	H	-3.194812	1.813446	3.106768
C	2.194615	-0.469892	-1.818763	H	-3.495977	2.803529	1.657451

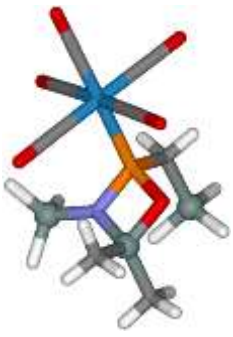
H	-3.403040	1.039554	1.510448	N	-0.714480	1.752738	0.072630
C	-0.821047	-1.062498	0.012262	Si	-0.981561	2.480614	-1.463696
H	-0.746524	-1.168994	-1.071903	H	-2.359102	2.231876	-1.957469
H	-1.865025	-0.932236	0.298013	H	-0.785549	3.945882	-1.372158
H	-0.418545	-1.963824	0.476919	H	-0.025365	1.899982	-2.434194



10a E = -1805.83281367963 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)

G_{corr} = 0.13431119 au

P	0.053435	0.067087	0.031985	H	-3.647316	0.874423	0.234575
W	2.545630	-0.041649	-0.010196	H	-3.660391	2.384064	1.168279
C	4.586162	-0.086450	-0.056121	C	-0.830106	3.748691	0.217648
O	5.733947	-0.106489	-0.083359	H	-1.194915	4.327833	-0.634896
C	2.558005	0.794696	1.882082	H	-1.176511	4.241823	1.128902
O	2.543876	1.261007	2.926143	H	0.260186	3.765565	0.202343
C	2.482512	-1.925988	0.825690	C	-0.847777	-1.504834	0.074201
O	2.437019	-2.972492	1.289314	H	-0.576651	-2.090367	-0.806318
C	2.448714	-0.886993	-1.886163	H	-0.553760	-2.062384	0.964447
O	2.383381	-1.367531	-2.925027	H	-1.923385	-1.328754	0.083142
C	2.537019	1.848897	-0.831814	N	-0.736867	1.031291	-1.135079
O	2.514627	2.902336	-1.280907	Si	-0.653622	1.042772	-2.861116
O	-0.665848	0.967224	1.208559	H	-1.628068	2.051791	-3.330490
Si	-1.466877	2.015786	0.127684	H	0.702489	1.395637	-3.338705
C	-3.308740	1.911363	0.247966	H	-0.999015	-0.292738	-3.401851
H	-3.767846	2.436292	-0.593889				



10b E = -2093.17149927917 au

G_{corr} = 0.1462388 au

P	0.856839	0.373031	1.285194	O	0.707103	1.935024	1.781197
W	2.637614	-0.135025	-0.395821	Si	-0.849091	2.156551	1.115132
C	4.073256	-0.518417	-1.794038	C	-2.146651	2.663654	2.328502
O	4.882497	-0.729421	-2.581278	H	-3.125672	2.633145	1.842285
C	3.336747	1.794221	-0.127904	H	-2.176914	2.018722	3.204932
O	3.698330	2.867027	0.033764	H	-1.969469	3.691738	2.654135
C	3.892471	-0.810110	1.095128	C	-0.807828	3.276601	-0.355774
O	4.588021	-1.193328	1.920762	H	-1.749414	3.210777	-0.907018
C	1.858332	-2.032661	-0.573923	H	-0.676367	4.314614	-0.041039
O	1.411103	-3.085886	-0.648851	H	0.003806	3.013327	-1.033554
C	1.358434	0.536084	-1.864930	C	0.878788	-0.627123	2.798593
O	0.640808	0.913298	-2.674074	H	0.846106	-1.671211	2.469454

H	1.865471	-0.484431	3.249911	H	-1.843989	-1.959342	0.843947
N	-0.759615	0.438209	0.738153	Si	-0.445269	-0.355827	4.112904
Si	-1.756822	-0.756343	-0.016105	H	-0.206300	-1.311183	5.218955
H	-3.094949	-0.152379	-0.191912	H	-0.373390	1.023847	4.640607
H	-1.211968	-1.168525	-1.329368	H	-1.794421	-0.591154	3.553785

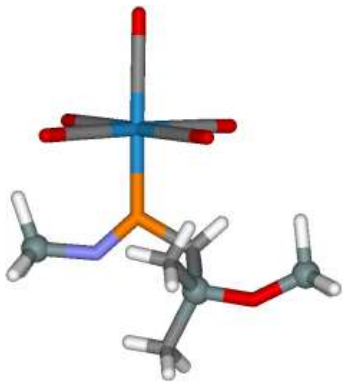
TS(**10b**→**11b**)

E = -2093.10878483968 au

G_{corr} = 0.14672107 au

v = -326.01 cm^{-1}

P	0.803136	-0.341662	0.869961	H	-3.038715	2.407957	2.515674
W	2.587421	-0.910825	-0.672003	C	-0.269088	2.884646	0.388313
C	4.186379	-1.271532	-1.913669	H	-0.783169	2.694944	-0.554505
O	5.085918	-1.465346	-2.591957	H	-0.473297	3.908141	0.706519
C	3.453255	0.885533	-0.119544	H	0.805485	2.803241	0.207318
O	3.909346	1.886149	0.189545	C	0.878418	0.208310	2.464931
C	3.550231	-1.871030	0.887513	H	0.113305	-0.175850	3.136217
O	4.071915	-2.395448	1.757929	H	1.820350	0.454803	2.938398
C	1.706037	-2.703112	-1.251575	N	-0.717100	0.105046	0.549146
O	1.221593	-3.684090	-1.574767	Si	-1.819759	-0.479909	-0.663473
C	1.553393	0.069816	-2.166942	H	-1.095387	-1.376804	-1.590528
O	0.960283	0.626932	-2.969391	H	-2.932554	-1.222459	-0.031694
O	-0.371547	2.575100	3.100299	H	-2.370552	0.676526	-1.403644
Si	-0.803093	1.686565	1.722901	Si	-0.240042	2.482029	4.721278
C	-2.638213	1.497884	2.065954	H	1.181184	2.336380	5.121982
H	-3.208630	1.274488	1.162088	H	-0.782708	3.719942	5.328237
H	-2.804462	0.675926	2.768144	H	-0.991737	1.315215	5.253100

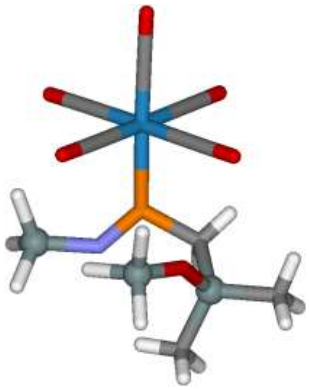


11b

E = -2093.15162908909 au

G_{corr} = 0.14784220 au

P	0.132314	-0.424288	0.442200	H	-3.185543	2.644724	2.324394
W	2.368880	-0.701190	-0.511845	C	-0.212050	2.996437	0.961037
C	4.258398	-0.950270	-1.278344	H	-0.439044	2.615445	-0.037684
O	5.311609	-1.086629	-1.703514	H	-0.689015	3.974630	1.058368
C	2.942790	1.116489	0.278333	H	0.866613	3.140724	1.037449
O	3.270092	2.116545	0.727242	C	-0.047013	0.129430	2.140046
C	2.942954	-1.598212	1.257892	H	-0.694429	-0.571239	2.674425
O	3.250512	-2.072904	2.251716	H	0.937558	0.129790	2.610042
C	1.786113	-2.533941	-1.293114	N	-1.280103	-0.594674	-0.165643
O	1.456077	-3.541816	-1.715206	Si	-1.863826	-1.048112	-1.717447
C	1.755789	0.233350	-2.256370	H	-2.626768	0.090235	-2.281958
O	1.414134	0.759147	-3.210888	H	-0.788401	-1.415270	-2.674303
O	-0.400883	2.445676	3.763710	H	-2.771694	-2.208578	-1.564088
Si	-0.848078	1.855477	2.289646	Si	0.829355	2.459941	4.848349
C	-2.694293	1.673278	2.234929	H	2.103333	2.100037	4.178086
H	-2.989294	1.218012	1.287230	H	0.937743	3.815850	5.427811
H	-3.045596	1.031330	3.045691	H	0.559366	1.478083	5.923562



11b^{conf} E = -2093.15372257683 au

G_{corr} = 0.14456259 au

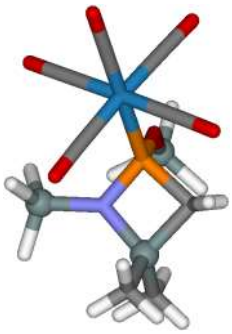
P	-0.033412	0.150381	0.034797	H	-1.715574	5.141340	1.115107
W	2.409073	0.046440	-0.114641	C	-3.196811	2.476464	-0.197593
C	4.459299	0.001970	-0.178567	H	-3.872341	2.300068	0.642799
O	5.603326	-0.017148	-0.206805	H	-3.573727	3.331659	-0.763730
C	2.465788	2.078494	0.259306	H	-3.216798	1.594458	-0.841381
O	2.497867	3.198334	0.485707	C	-0.794923	1.225232	1.254753
C	2.467432	-0.309616	1.920800	H	-1.632309	0.709206	1.729358
O	2.497582	-0.503781	3.047173	H	-0.054668	1.492458	2.009745
C	2.312510	-1.989850	-0.480165	N	-1.155750	-0.506650	-0.804413
O	2.250551	-3.112588	-0.681246	Si	-1.133394	-1.530855	-2.185120
C	2.353264	0.377753	-2.158392	H	-1.961542	-0.909653	-3.244804
O	2.333316	0.553483	-3.286814	H	0.228662	-1.762939	-2.730957
O	-0.471367	3.077647	-0.884561	H	-1.722384	-2.840967	-1.819952
Si	-1.465474	2.794875	0.402557	Si	-0.313385	3.109929	-2.514094
C	-1.336290	4.228045	1.579599	H	-1.274735	4.068837	-3.105980
H	-1.917890	4.038935	2.485059	H	1.070808	3.524676	-2.826135
H	-0.296667	4.396740	1.869035	H	-0.561055	1.762949	-3.076304

TS(**11b**^{conf}→**5b**) E = -2093.09613232758 au

G_{corr} = 0.14672819 au

v = -247.83cm^{-1}

P	-0.011646	-0.028196	-0.002136	H	-3.754488	-1.670585	-1.965280
W	2.477944	-0.000204	0.002768	C	-3.820533	0.154248	0.642387
C	4.513973	0.105986	0.032084	H	-4.737848	0.486009	0.148981
O	5.660267	0.166112	0.045827	H	-4.024710	-0.810112	1.114810
C	2.508327	-0.735336	-1.922224	H	-3.533556	0.858114	1.421380
O	2.515856	-1.130656	-2.996978	C	-1.070923	1.188538	-0.864561
C	2.365850	1.912907	-0.763426	H	-1.138465	2.115104	-0.299319
O	2.285645	2.969749	-1.195533	H	-0.803044	1.369515	-1.904491
C	2.360669	0.761077	1.920210	N	-0.996771	-0.262769	1.232550
O	2.273498	1.190539	2.976966	Si	-0.910942	-1.095128	2.714468
C	2.558988	-1.916822	0.765000	H	-1.773474	-2.306776	2.691294
O	2.617798	-2.980192	1.185393	H	0.472779	-1.528608	3.042655
O	-0.791249	-1.245892	-1.030633	H	-1.397119	-0.240018	3.827881
Si	-2.458221	-0.050751	-0.611569	Si	-0.507522	-2.905623	-1.060060
C	-3.285458	-0.701442	-2.152998	H	-1.662939	-3.493778	-1.759965
H	-4.083335	-0.004307	-2.426853	H	0.751307	-3.147300	-1.785002
H	-2.595996	-0.802189	-2.990057	H	-0.412554	-3.403330	0.326190



5b E = -2093.17465640066 au

G_{corr} = 0.14785031 au

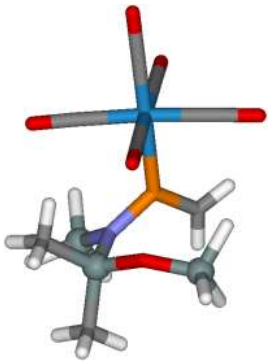
P	-0.002165	0.225258	-0.102278	H	-3.877559	1.292332	-2.617793
W	2.481069	-0.023168	0.143591	C	-0.925924	0.580385	-3.864286
C	4.491116	-0.240934	0.374687	H	-1.228014	-0.301014	-4.435739
O	5.624902	-0.370471	0.511526	H	-1.305445	1.463247	-4.384388
C	2.735294	1.882213	-0.598300	H	0.164821	0.624902	-3.857016
O	2.854586	2.940532	-1.021572	C	-0.775035	1.684747	-0.907930
C	2.283341	0.751811	2.049782	N	-0.832067	-0.790427	-1.180570
O	2.154945	1.190506	3.098769	Si	-0.777111	-2.518597	-1.338941
C	2.166080	-1.924711	0.883319	H	-1.784325	-2.879627	-2.360705
O	1.987556	-2.977356	1.298666	H	0.559442	-2.984979	-1.768084
C	2.578090	-0.744687	-1.781513	H	-1.104347	-3.164770	-0.048525
O	2.615372	-1.123329	-2.862511	Si	-2.301557	-0.170018	1.849317
O	-0.735778	0.060161	1.330020	H	-2.236191	-0.197942	3.321240
Si	-1.596655	0.499197	-2.132037	H	-3.148236	0.948875	1.380537
C	-3.454922	0.423107	-2.107637	H	-2.824600	-1.443515	1.315397
H	-3.806140	-0.473413	-2.624812	H	-1.440245	2.221133	-0.232495
H	-3.840459	0.402643	-1.087121	H	-0.044448	2.381051	-1.313506

TS(**10b**→**12b**) E = -2093.11407014306 au

G_{corr} = 0.14567283 au

v = -319.13 cm^{-1}

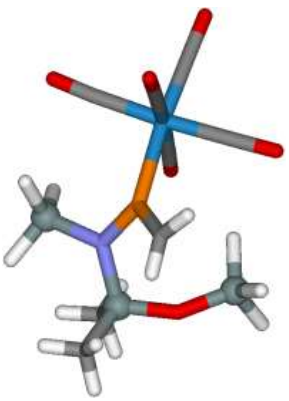
P	-0.012743	-0.019946	0.037362	H	-3.573932	-1.702215	-2.518035
W	2.464932	-0.035182	-0.003666	C	-0.604659	-3.119014	-2.152754
C	4.507169	-0.037646	-0.032910	H	-0.883054	-4.085362	-1.725933
O	5.654234	-0.039747	-0.051721	H	-0.881519	-3.122752	-3.209177
C	2.402140	-0.319798	-2.049049	H	0.477916	-3.010029	-2.076123
O	2.342233	-0.489284	-3.178317	C	-0.962568	1.379253	0.299188
C	2.419728	2.010619	-0.290894	H	-1.940724	1.228649	0.746368
O	2.382779	3.142250	-0.454325	H	-0.441835	2.260968	0.654849
C	2.466667	0.244452	2.044691	N	-0.874240	-1.462865	0.356912
O	2.462234	0.400700	3.178159	Si	-0.967730	-2.323292	1.862154
C	2.422527	-2.078084	0.253576	H	-1.301146	-3.726438	1.536361
O	2.366370	-3.214826	0.380719	H	0.336380	-2.235382	2.552933
O	-0.742197	-0.237359	-1.665946	H	-2.014073	-1.754782	2.741664
Si	-1.463513	-1.752992	-1.260125	Si	-1.419059	1.423556	-1.954484
C	-3.296700	-1.707498	-1.461767	H	-2.711298	2.029840	-1.541001
H	-3.739385	-2.595299	-1.003106	H	-0.327788	2.378210	-2.230013
H	-3.726120	-0.827258	-0.979875	H	-1.826422	0.952290	-3.327039



12b E = -2093.16537941816 au

G_{corr} = 0.14720991 au

P	0.459595	-0.697076	1.029834	H	-2.539162	3.335390	2.444086
W	2.584582	-0.402862	-0.215427	C	-0.515660	3.086831	-0.159741
C	4.294864	-0.256107	-1.308462	H	-1.254608	2.957635	-0.953838
O	5.255853	-0.185058	-1.931925	H	-0.540687	4.130255	0.162203
C	2.880580	1.527229	0.469020	H	0.469848	2.882761	-0.579344
O	3.091662	2.589468	0.835232	C	0.056765	-1.891096	2.086207
C	3.605535	-1.098573	1.440792	H	-0.915593	-1.959346	2.555554
O	4.147982	-1.480485	2.372286	H	0.792047	-2.646520	2.332369
C	2.358591	-2.343936	-0.893476	N	-0.886305	0.268361	0.734510
O	2.238124	-3.418748	-1.263888	Si	-2.259310	-0.470877	-0.064500
C	1.456199	0.305935	-1.790307	H	-3.021355	0.612380	-0.721957
O	0.803823	0.700897	-2.643338	H	-1.748497	-1.432760	-1.064432
O	0.322802	2.072078	2.359449	H	-3.140435	-1.179579	0.890860
Si	-0.889149	1.954920	1.260036	Si	0.880592	1.633386	3.840343
C	-2.529858	2.313977	2.055943	H	2.144370	0.884821	3.671346
H	-3.354915	2.219886	1.346637	H	1.125322	2.855922	4.636233
H	-2.714402	1.629741	2.887288	H	-0.111604	0.778655	4.532156



12b^{conf} E = -2093.1652141456 au

G_{corr} = 0.14747751 au

P	0.089420	0.181732	0.016405	C	-1.621440	1.066023	3.972423
W	2.556331	-0.190553	-0.024027	H	-1.931581	0.121737	4.423355
C	4.584599	-0.308092	-0.050529	H	-0.568289	1.230853	4.211561
O	5.731193	-0.359433	-0.062708	H	-2.204876	1.863665	4.438743
C	2.520092	-2.116231	0.720780	C	-3.654000	0.751015	1.652498
O	2.568606	-3.187088	1.121400	H	-3.952106	-0.248209	1.977852
C	2.390027	-0.959698	-1.937199	H	-4.329743	1.474749	2.114119
O	2.274210	-1.386821	-2.991295	H	-3.781030	0.806263	0.569396
C	2.711653	1.714535	-0.813018	C	-0.811286	0.924466	-1.140003
O	2.808948	2.761928	-1.260040	H	-1.864247	1.146272	-1.040636
C	2.579611	0.555845	1.898317	H	-0.316835	1.226240	-2.053802
O	2.557182	0.964288	2.966821	N	-0.806049	-0.097796	1.405260
O	-1.490240	2.574604	1.547830	Si	-0.608964	-1.657044	2.199872
Si	-1.897037	1.102721	2.132556	H	-1.861542	-1.923580	2.935847

H	-0.396611	-2.690735	1.168656	H	-0.515446	4.119854	-0.222573
H	0.528818	-1.647214	3.143734	H	-0.445037	4.818852	2.093485
Si	-0.327179	3.666924	1.171281	H	1.014385	3.061583	1.318755

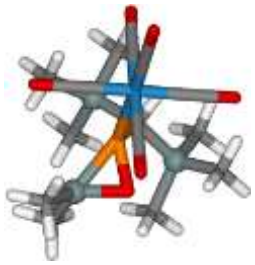
TS(**12b**^{conf}→**5b**)

E = -2093.08166957589 au

G_{corr} = 0.14757222 au

v = -232.35 cm^{-1}

P	-0.004925	0.002368	0.002535	H	-2.025582	2.205676	-3.534074
W	-0.000229	-0.009888	2.434157	C	0.257407	0.221025	-3.960350
C	0.120598	-0.062108	4.484383	H	-0.440423	0.235855	-4.799471
O	0.190467	-0.092668	5.625130	H	1.041527	0.962315	-4.148903
C	-0.781955	-1.926127	2.496825	H	0.751198	-0.751862	-3.911985
O	-1.190116	-2.989927	2.571772	C	1.210864	0.165112	-1.236904
C	1.901218	-0.810304	2.289271	H	1.608790	-0.800075	-1.547862
O	2.949244	-1.254306	2.193860	H	1.983340	0.907965	-1.060325
C	0.846541	1.881030	2.461995	N	-1.121648	-0.611427	-1.036772
O	1.343373	2.908097	2.499179	Si	-2.701246	-1.284816	-0.739040
C	-1.912436	0.776292	2.547995	H	-3.258327	-1.680488	-2.047795
O	-2.967570	1.206175	2.628695	H	-2.578634	-2.466308	0.138420
O	-0.473671	1.892914	-0.909951	H	-3.601899	-0.301768	-0.093349
Si	-0.539123	0.631970	-2.289716	Si	-1.415661	3.162589	-0.402185
C	-2.197182	1.296585	-2.948460	H	-2.759499	2.697230	0.006872
H	-2.629054	0.561213	-3.633012	H	-0.748532	3.784545	0.759626
H	-2.942158	1.524836	-2.183124	H	-1.540022	4.141408	-1.503205



Oxaphosphasilirane complex

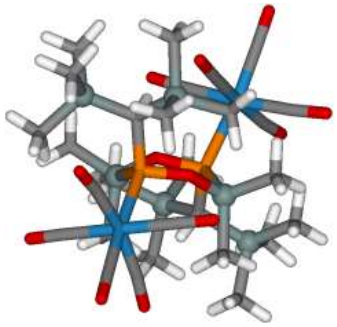
E = -2276.98214126538 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)

ZPE = 0.36147866

G_{corr} = 0.29386259 au

P	-0.307508	0.080004	0.216011	H	-2.018993	-1.477016	0.380888
W	-0.050348	0.074156	2.732042	Si	-2.952088	-0.301999	-1.452558
C	0.209012	0.075712	4.743556	C	-3.771789	0.958654	-0.333459
O	0.357479	0.078884	5.884623	H	-4.125586	0.498506	0.590973
C	0.309153	2.106457	2.633305	H	-3.081325	1.762604	-0.074532
O	0.500512	3.232520	2.561685	H	-4.634690	1.399684	-0.839672
C	-2.062617	0.460436	2.970371	C	-4.186406	-1.672092	-1.811830
O	-3.178938	0.664899	3.123807	H	-5.095812	-1.233883	-2.231963
C	-0.467474	-1.938848	2.757081	H	-3.805239	-2.398740	-2.531424
O	-0.717735	-3.058247	2.759921	H	-4.462782	-2.207651	-0.901079
C	1.950555	-0.328811	2.438079	C	-2.480794	0.528869	-3.065019
O	3.057345	-0.555073	2.247644	H	-1.860916	1.407784	-2.891158
O	-0.521161	1.619024	-0.524054	H	-1.960796	-0.139905	-3.751134
Si	0.988863	1.153131	-1.141375	H	-3.399579	0.858553	-3.558429
C	1.101906	0.908772	-2.972575	Si	-0.676028	-2.653014	-1.234099
H	2.010885	0.352721	-3.211863	C	-1.721776	-4.121059	-0.715291
H	0.244715	0.382434	-3.381110	H	-2.730100	-4.069244	-1.127729
H	1.169486	1.887972	-3.455443	H	-1.261268	-5.048469	-1.065526
C	2.433867	2.079896	-0.442398	H	-1.801980	-4.175672	0.372642
H	3.370068	1.605522	-0.743638	C	-0.555447	-2.602202	-3.105256
H	2.430475	3.101556	-0.833129	H	0.073954	-1.784569	-3.457166
H	2.399747	2.127316	0.644634	H	-0.104151	-3.535997	-3.451433
C	-1.496761	-1.089706	-0.502477	H	-1.533071	-2.509831	-3.580454

C	1.057748	-2.882585	-0.544981	H	1.062957	-2.937792	0.544568
H	1.731778	-2.078908	-0.844899	H	1.468158	-3.821547	-0.926135



Oxaphosphasilirane complex cyclic dimer E = -4554.06858009 au (COSMO$_{THF}$/B3LYP-D3-def2-TZVPecp)

P	5.162117	-4.219248	-0.470855	C	8.627610	-2.813358	-1.268714
C	6.278700	-4.619986	0.925394	H	9.452343	-2.382389	-1.837221
H	7.283123	-4.619437	0.484114	H	8.771109	-2.539850	-0.223220
Si	6.457155	-3.315580	2.328292	H	8.702969	-3.895395	-1.347478
C	6.717534	-1.560475	1.719822	P	6.706263	-3.022521	-4.014395
H	7.634140	-1.440752	1.144830	C	5.361945	-2.103743	-4.841663
H	5.882078	-1.195856	1.127623	H	4.617139	-1.955738	-4.050846
H	6.804343	-0.923165	2.604513	Si	5.744144	-0.288638	-5.374012
C	8.029194	-3.781511	3.250662	C	7.493213	0.281510	-4.987457
H	8.236249	-3.018680	4.005883	H	8.166487	0.014313	-5.801679
H	7.974214	-4.743696	3.758551	H	7.483585	1.372630	-4.916979
H	8.881086	-3.810835	2.566516	H	7.918547	-0.098588	-4.065766
C	5.009868	-3.204823	3.515064	C	4.468412	0.751841	-4.467430
H	4.130109	-2.773263	3.039949	H	4.654151	1.815295	-4.635814
H	4.722364	-4.147846	3.969815	H	3.468018	0.522314	-4.841445
H	5.309639	-2.522863	4.316306	H	4.459657	0.577351	-3.390816
Si	6.170970	-6.417294	1.627751	C	5.564056	0.104281	-7.203737
C	7.909867	-7.118185	1.541500	H	6.323008	-0.385413	-7.810701
H	8.594812	-6.540045	2.164917	H	4.586417	-0.115352	-7.626899
H	7.909284	-8.146743	1.911428	H	5.724256	1.183672	-7.291510
H	8.307543	-7.126927	0.526816	Si	4.314356	-3.033154	-6.158694
C	5.611351	-6.557665	3.414919	C	2.757469	-2.009556	-6.424958
H	4.560359	-6.307382	3.547132	H	2.932884	-1.023705	-6.851054
H	5.734906	-7.610050	3.687764	H	2.102217	-2.554251	-7.110438
H	6.199613	-5.967673	4.115481	H	2.219903	-1.881615	-5.484204
C	4.996436	-7.524986	0.668796	C	5.190797	-3.311926	-7.791907
H	3.995738	-7.101845	0.586163	H	6.038668	-3.988722	-7.689723
H	5.349045	-7.775824	-0.328652	H	4.474551	-3.788719	-8.467448
H	4.908760	-8.463513	1.222411	H	5.539196	-2.397952	-8.265978
W	2.642514	-3.899609	-0.086256	C	3.719952	-4.711474	-5.582563
C	0.685725	-3.442187	0.144092	H	4.530586	-5.429141	-5.482297
O	-0.422790	-3.163157	0.274349	H	3.195680	-4.645318	-4.631278
C	2.037711	-5.733489	-0.805399	H	3.016172	-5.092775	-6.327998
O	1.616844	-6.737709	-1.163084	W	8.821492	-3.652521	-5.341992
C	2.590664	-4.757727	1.785974	C	10.404622	-4.262409	-6.442885
O	2.468094	-5.266815	2.804781	O	11.293563	-4.617033	-7.081035
C	3.100749	-2.030492	0.655719	C	7.710381	-5.295303	-5.917442
O	3.304223	-0.974090	1.048123	O	7.089074	-6.219029	-6.185319
C	2.578077	-3.082544	-1.969465	C	9.679937	-4.741331	-3.827307
O	2.503299	-2.601366	-3.007364	O	10.283280	-5.339544	-3.056011
O	5.722172	-2.774297	-1.034152	C	9.867328	-2.044077	-4.604384
Si	7.001512	-2.146199	-1.892644	O	10.468817	-1.173905	-4.161833
C	6.922297	-0.301951	-1.682397	C	8.345763	-2.539532	-7.009170
H	7.848010	0.170364	-2.010150	O	8.229346	-1.929186	-7.971840
H	6.092732	0.155660	-2.215369	O	5.932199	-4.382768	-3.507170
H	6.800014	-0.090967	-0.619659	Si	5.766652	-5.513823	-2.307354

C	4.441450	-6.687773	-2.861199	C	7.354415	-6.458419	-2.065045
H	4.236486	-7.444371	-2.106245	H	7.166493	-7.363639	-1.488685
H	4.796125	-7.196199	-3.761027	H	7.723023	-6.767017	-3.045637
H	3.510948	-6.183276	-3.104677	H	8.144770	-5.901250	-1.568848

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