SUPPORTING INFORMATION

1,1'-BIFUNCTIONAL AMINOPHOSPHANE COMPLEXES VIA N-H BOND INSERTIONS OF A LI/CL PHOSPHINIDENOID COMPLEX AND FIRST STUDIES ON N/P MONO FUNCTIONALIZATIONS

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Content

1. NMR spectra and crystal structure data for **3** S2-S3
2. NMR spectra and crystal structure data for **4** S4-S5
3. NMR spectra and crystal structure data for **5** S6-S7
4. NMR spectra and crystal structure data for **6** S8-S9
5. NMR spectra and crystal structure data for **7** S10-S11
6. NMR spectra and crystal structure data for **8** S12-S13
7. NMR spectra and crystal structure data for **9** S14-S15
8. NMR spectra and crystal structure data for **10** S16-S17
9. NMR spectra for **12** S18-S19
10. NMR spectra for **13** S20-S21
11. NMR spectra and crystal structure data for **14** S22-S23
12. NMR spectra and crystal structure data for **17** S24-S25
13. NMR spectra and crystal structure data for **19** S26-S27

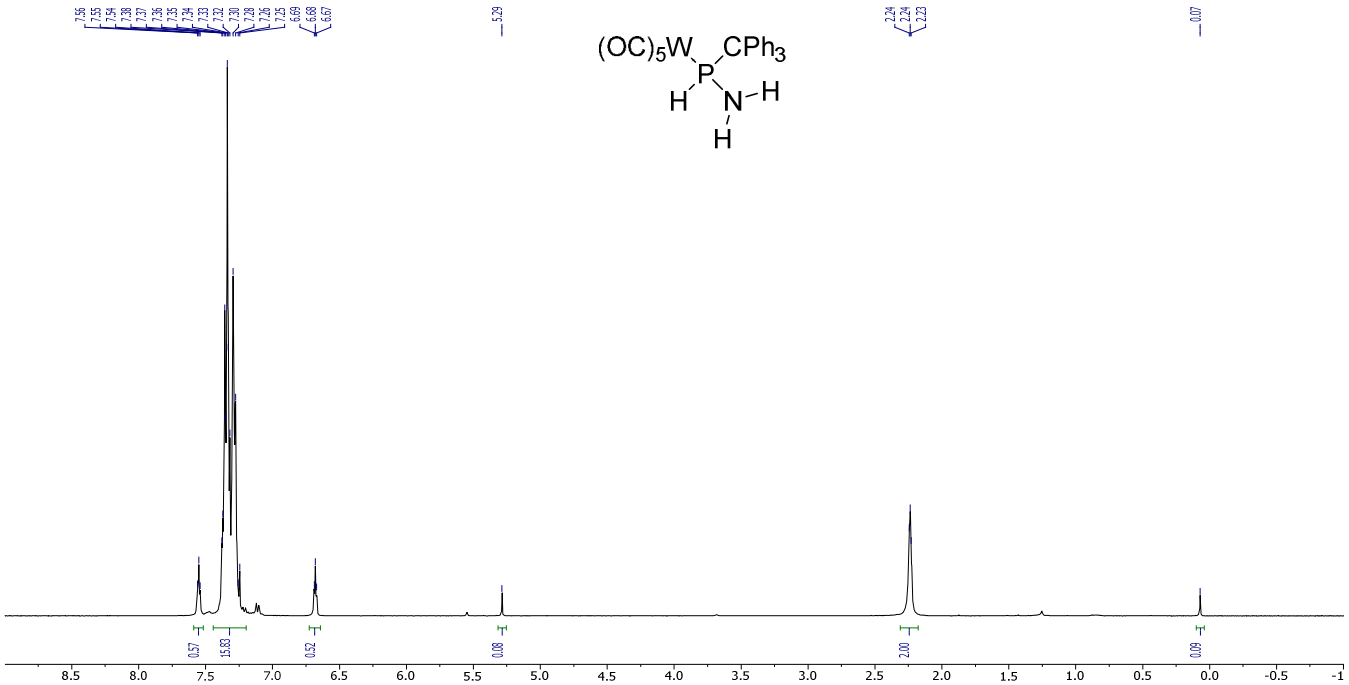

Figure S1: ^{1}H NMR spectrum of **3** in $CDCl_3$ at 400.1 MHz.

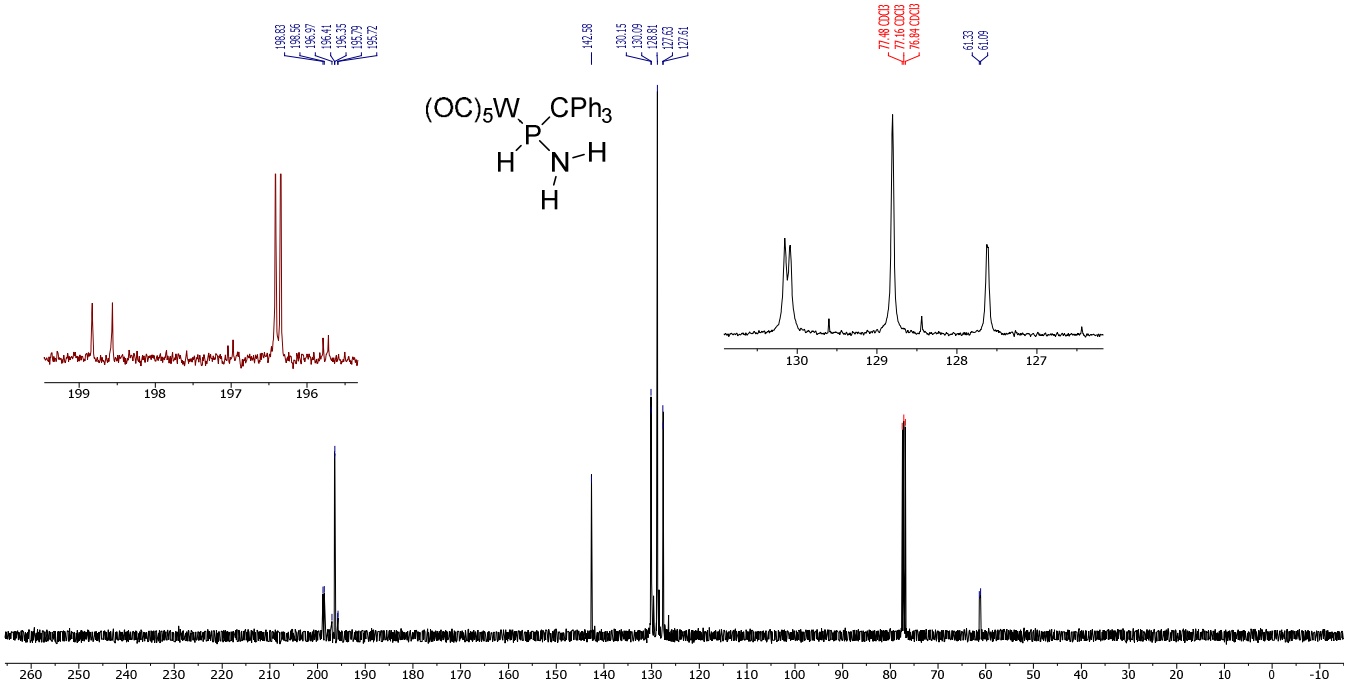

Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$ at 100.6 MHz.

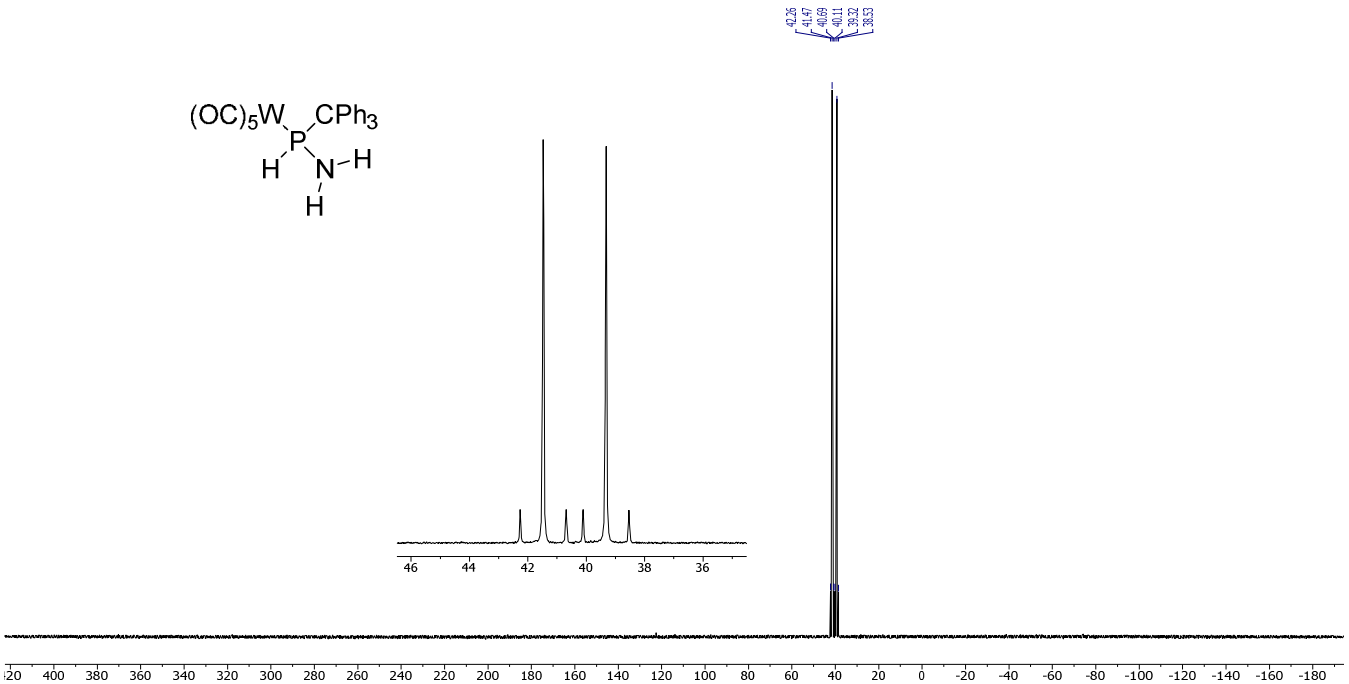

Figure S3: ^{31}P NMR spectrum of **3** in $CDCl_3$ at 162.0 MHz.

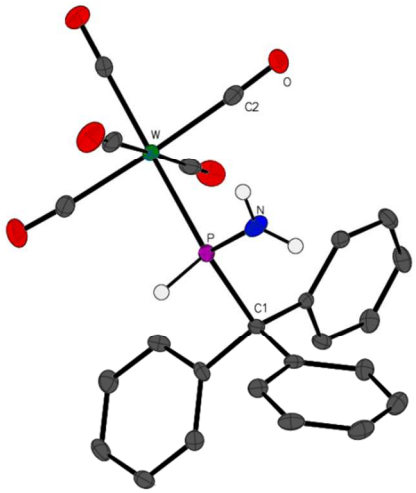

Figure S4: Crystal structure of **3**. Suitable single-crystals of **3** were obtained from a concentrated diethyl ether solution at 4 °C. Data were collected with a Bruker X8-KappaApexII diffractometer equipped with a low-temperature device at 100 K by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by intrinsic phasing methods (SHELXT 2015) and refined by full-matrix least squares on F^2 (SHELXL 2015)[1]: $C_{24}H_{18}NO_5PW$, Mr = 615.21, crystal dimensions 0.22 × 0.08 × 0.04 mm^3, monoclinic, space group $P2_1/c$, Z =4, a = 7.2639(9) Å, b = 16.750(2) Å, c = 18.608(2) Å, α =90°, β =98.941(4)°, γ =90°, V = 2236.6(5) $Å^3$, d_{calcd} = 1.827 g cm^{-3}, μ = 5.272 mm^{-1}, transmission factors (min/max) 0.3194/0.7459, empirical absorption correction, $2\theta_{max}$ = 55.996°, no. of unique data 5339, R_{int} = 0.06, R_1 (for I >2σ(I)) = 0.0250, wR_2 (for all data) = 0.0637, final R_1 = 0.0306, goodness of fit 1.029, ΔF (max/min) = 2.21 /−1.34 e $Å^{-3}$. CCDC 1529744 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

[1] Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

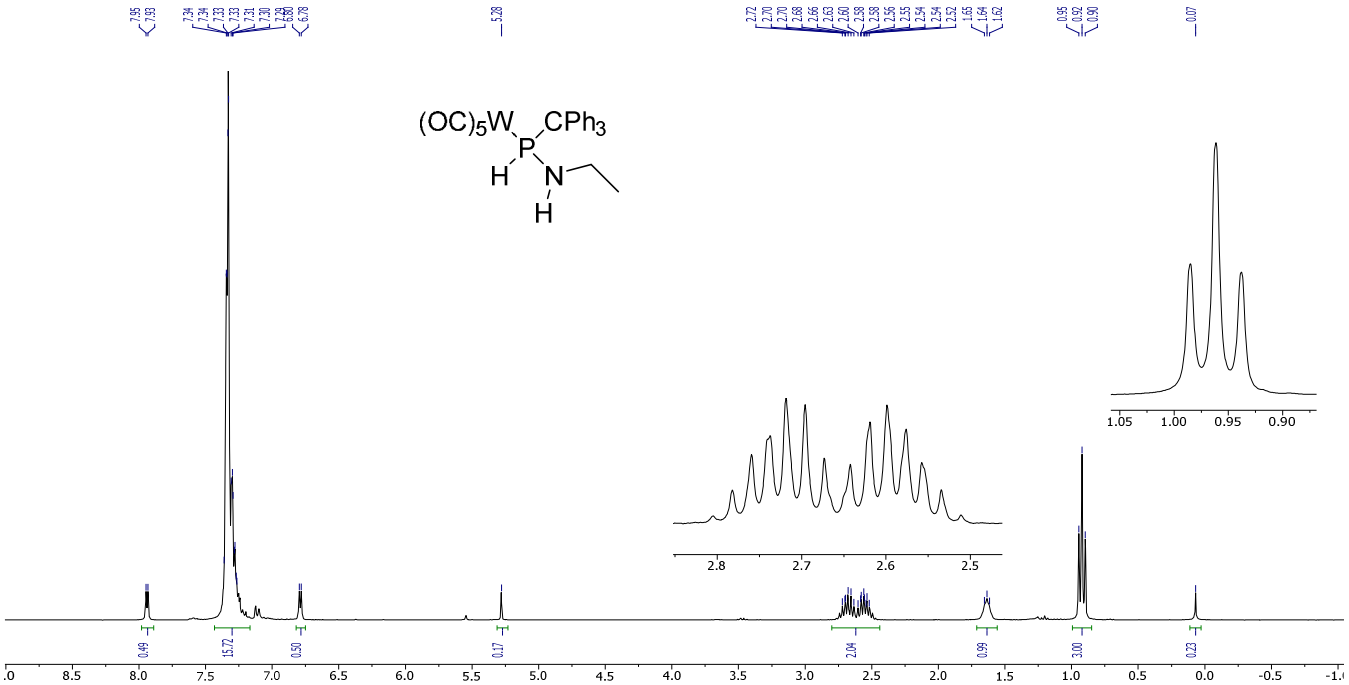

Figure S5: ^{1}H NMR spectrum of **4** in $CDCl_3$ at 300.1 MHz.

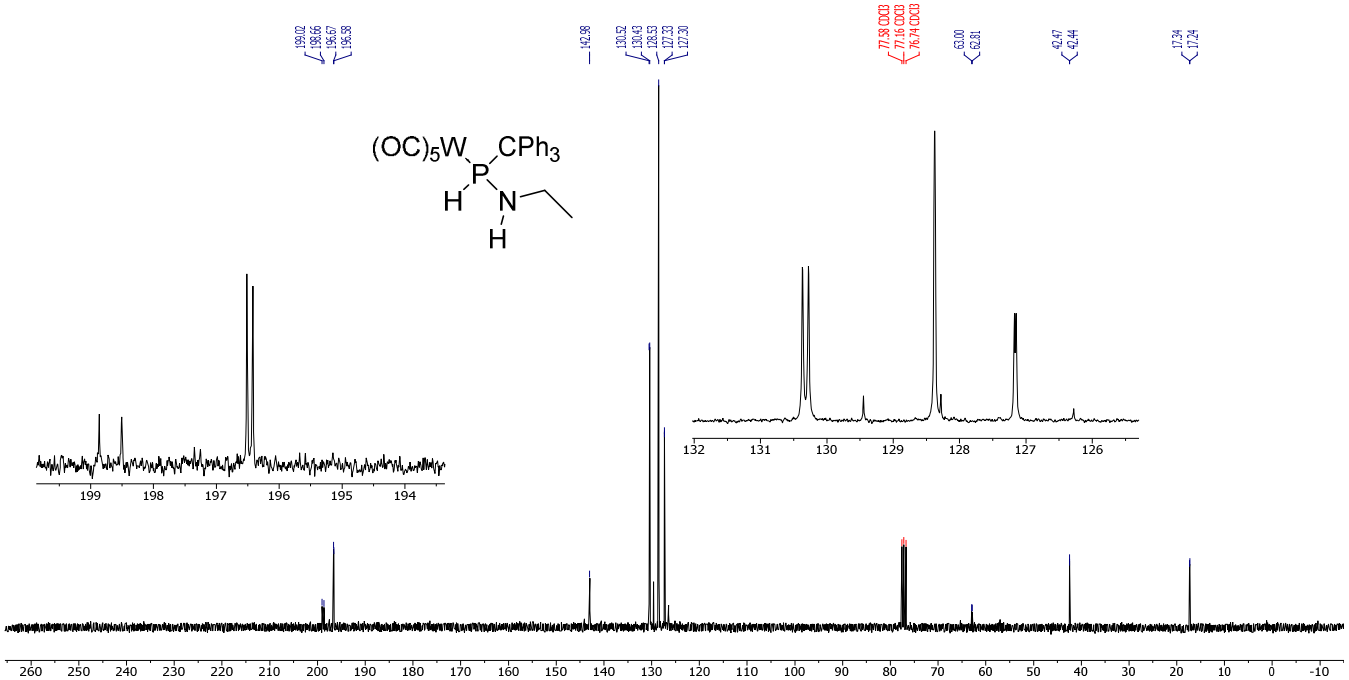

Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$ at 75.5 MHz.

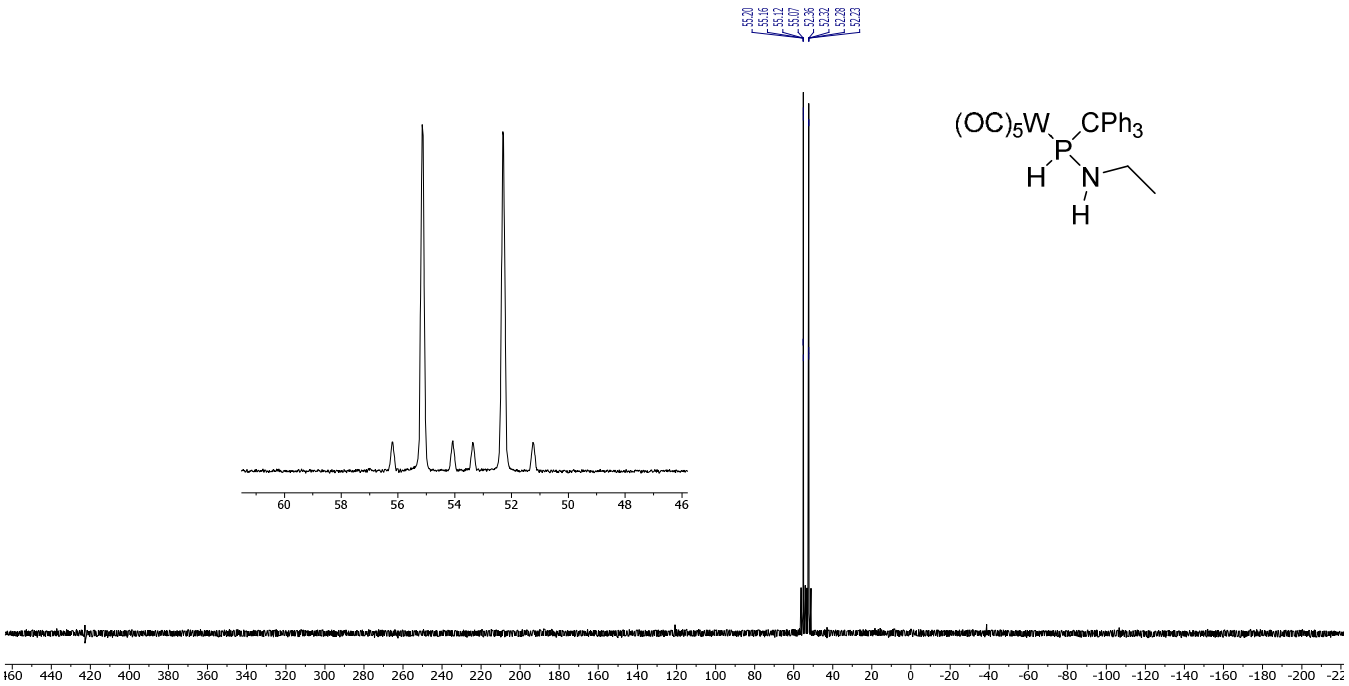

Figure S7: ^{31}P NMR spectrum of **4** in $CDCl_3$ at 121.5 MHz.

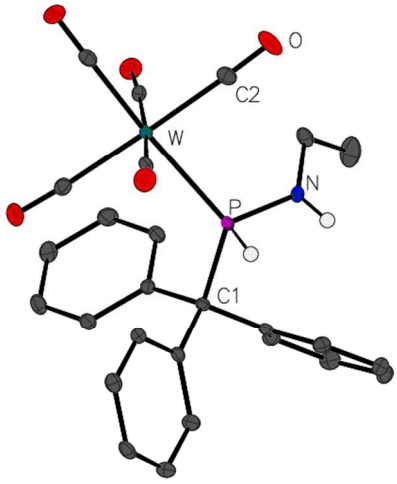

Figure S8: Crystal structure of **4**. Suitable single-crystals of **4** were obtained from a concentrated diethyl ether solution at 4 °C. Data were collected with a Bruker D8-Venture diffractometer equipped with a low-temperature device at 100 K by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by intrinsic phasing methods (SHELXT 2015) and refined by full-matrix least squares on F^2 (SHELXL 2015)[1]: $C_{26}H_{22}NO_5PW$, Mr = 643.26, crystal dimensions 0.24 × 0.18 × 0.16 mm^3, monoclinic, space group C2/c, Z =8, a = 11.1776(4) Å, b = 11.1777(4) Å, c = 19.2814(7) Å, α =90°, β =95.4332(13)°, γ =90°, V = 2398.19(15) $Å^3$, d_{calcd} = 1.782 g cm^{-3}, μ = 4.921 mm^{-1}, transmission factors (min/max) 0.3579/0.7459, empirical absorption correction, $2\theta_{max}$ = 55.998°, no. of unique data 5774, R_{int} = 0.0421, R_1 (for I >2σ(I)) = 0.0180, wR_2 (for all data) = 0.0460, final R_1 = 0.0203, goodness of fit 1.078, ΔF (max/min) = 0.53 /−2.49 e $Å^{-3}$. CCDC 1529740 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

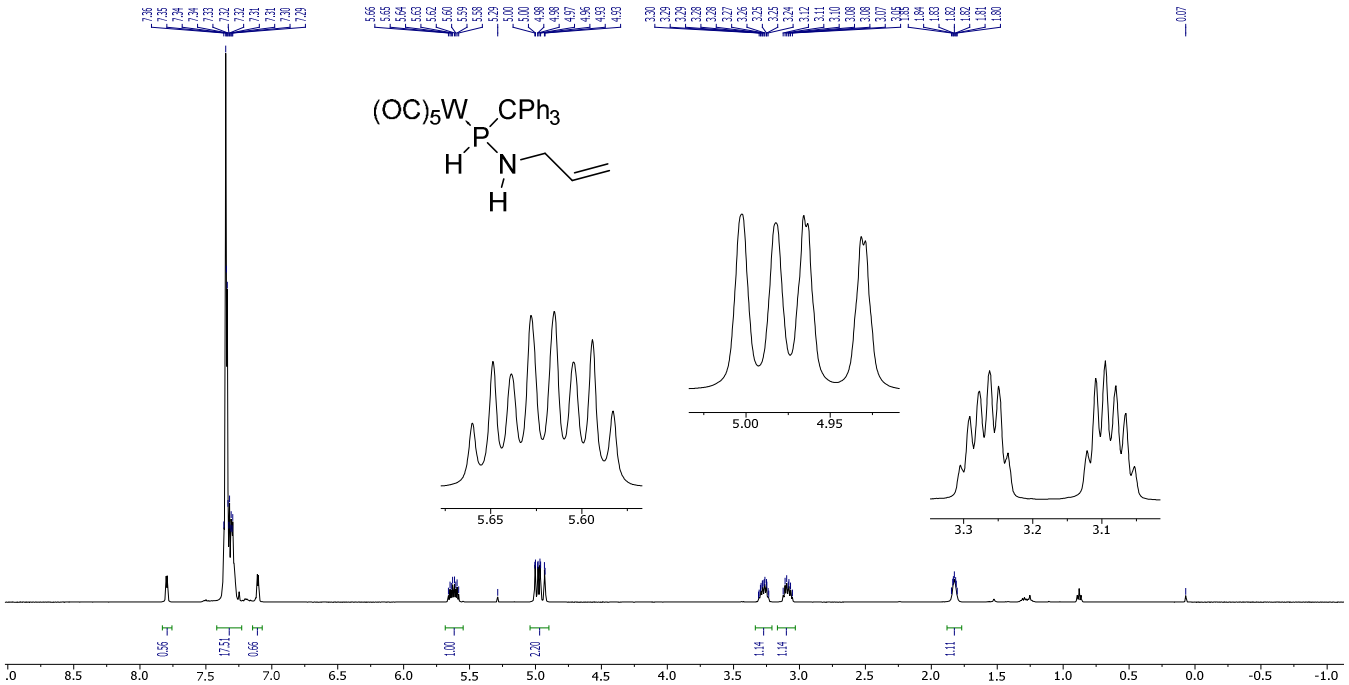

Figure S9: ^{1}H NMR spectrum of **5** in $CDCl_3$ at 500.2 MHz.

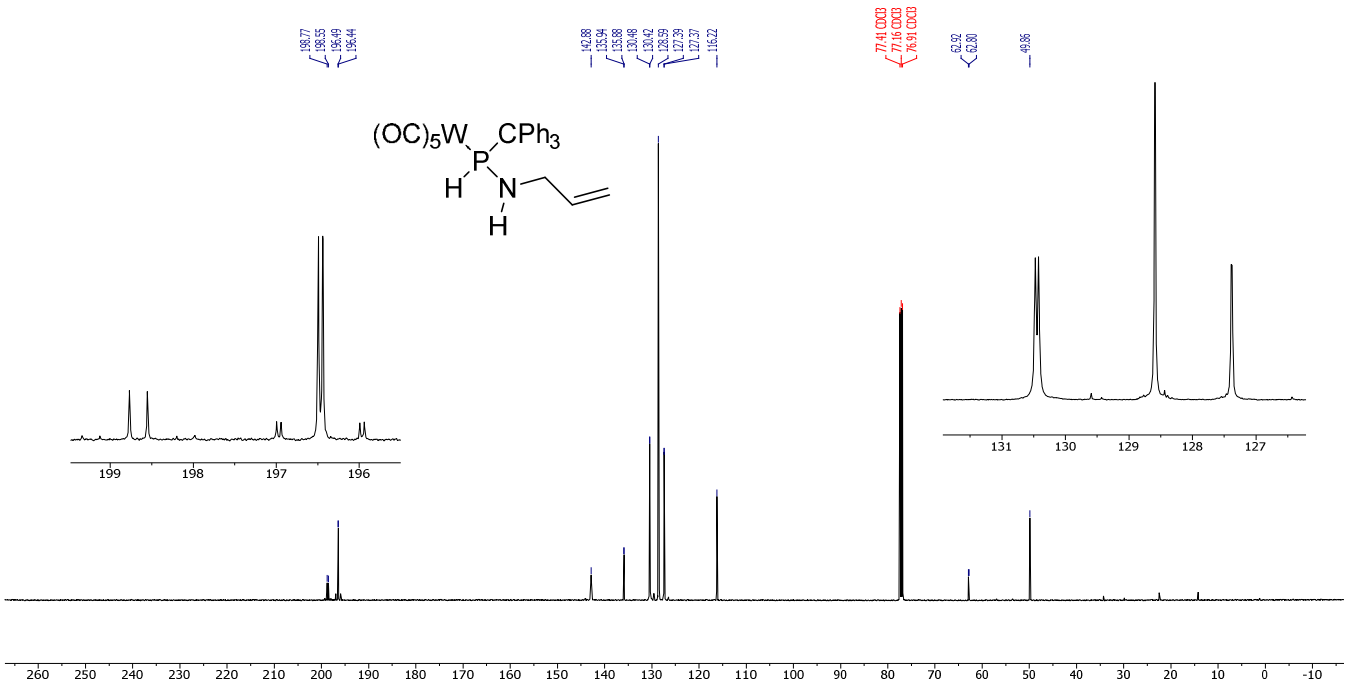

Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$ at 125.8 MHz.

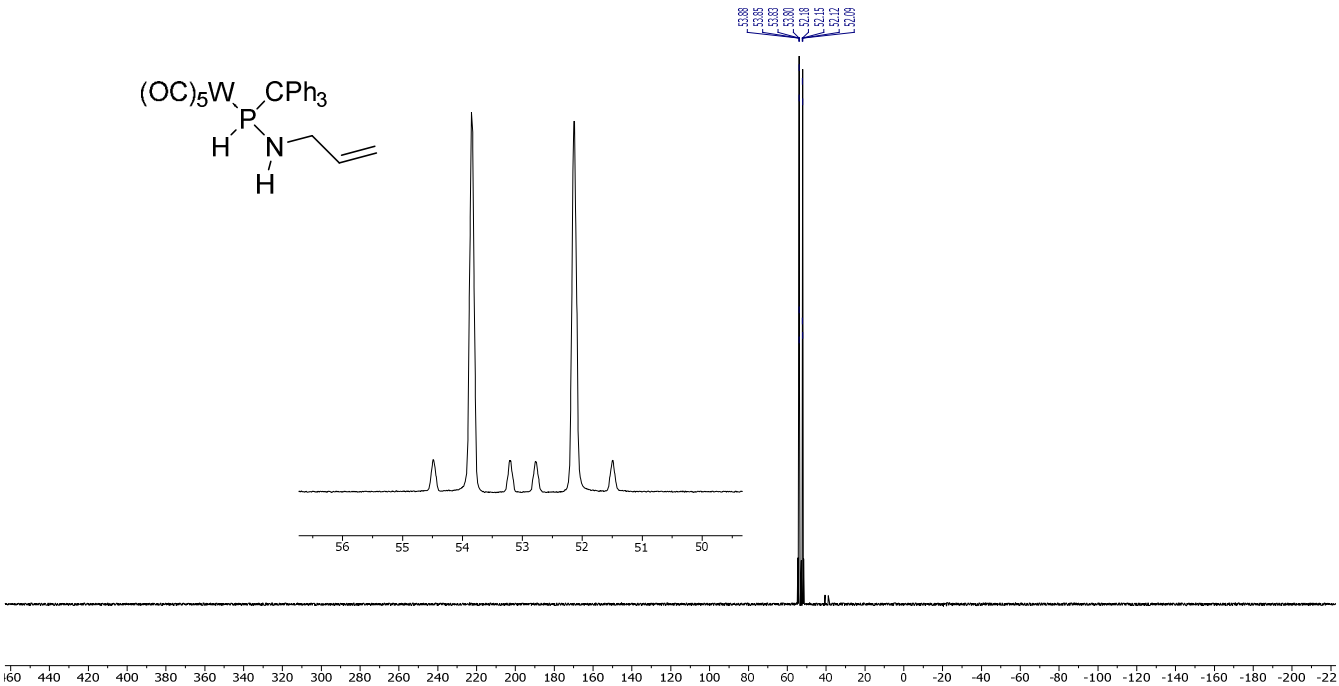

Figure S11: ^{31}P NMR spectrum of **5** in $CDCl_3$ at 202.5 MHz.

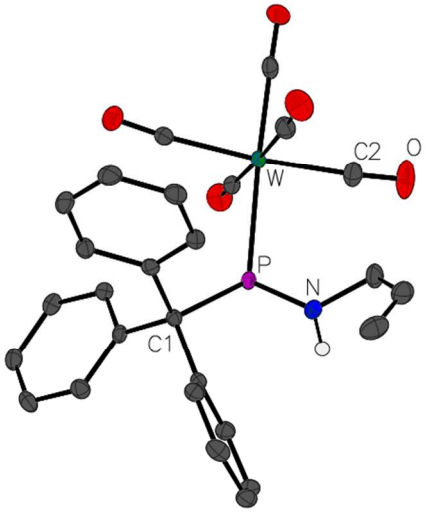

Figure S12: Crystal structure of **5**. Suitable single-crystals of **5** were obtained from a concentrated diethyl ether solution at 4 °C. Data were collected with a Bruker D8-Venture diffractometer equipped with a low-temperature device at 123 K by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by intrinsic phasing methods (SHELXT 2015) and refined by full-matrix least squares on F^2 (SHELXL 2015)[1]: $C_{27}H_{22}NO_5PW$, Mr = 655.27, crystal dimensions 0.11 × 0.05 × 0.04 mm^3, monoclinic, space group $P2_1/c$, Z =4, a = 10.9081(7) Å, b = 11.6721(7) Å, c = 19.6053(13) Å, α =90°, β =96.509(2)°, γ =90°, V = 2480.1(3) $Å^3$, d_{calcd} = 1.755 g cm^{-3}, μ = 4.761 mm^{-1}, transmission factors (min/max) 0.5177/0.7459, empirical absorption correction, $2\theta_{max}$ = 55.998°, no. of unique data 5983, R_{int} = 0.0600, R_1 (for I >2σ(I)) = 0.0188, wR_2 (for all data) = 0.0408, final R_1 = 0.0257, goodness of fit 1.053, ΔF (max/min) = 0.55 /−0.84 e $Å^{-3}$. CCDC 1529742 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

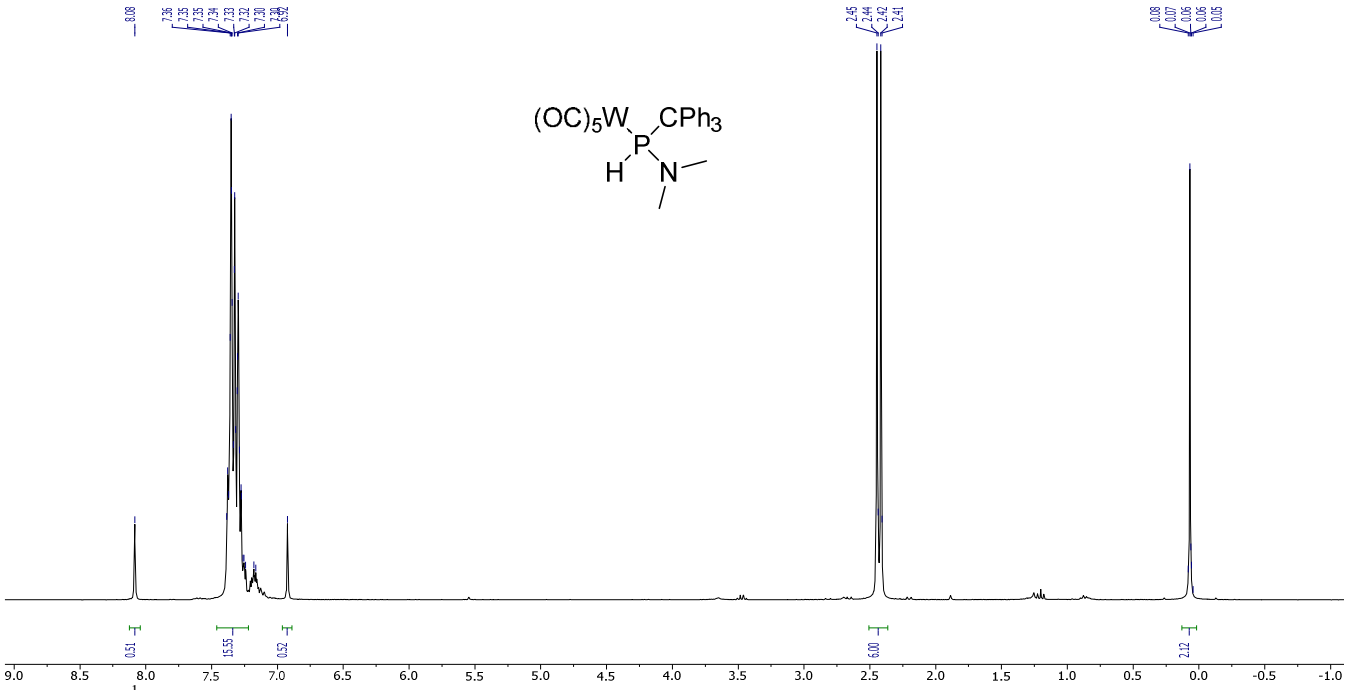

Figure S13: ^{1}H NMR spectrum of **6** in $CDCl_3$ at 300.1 MHz.

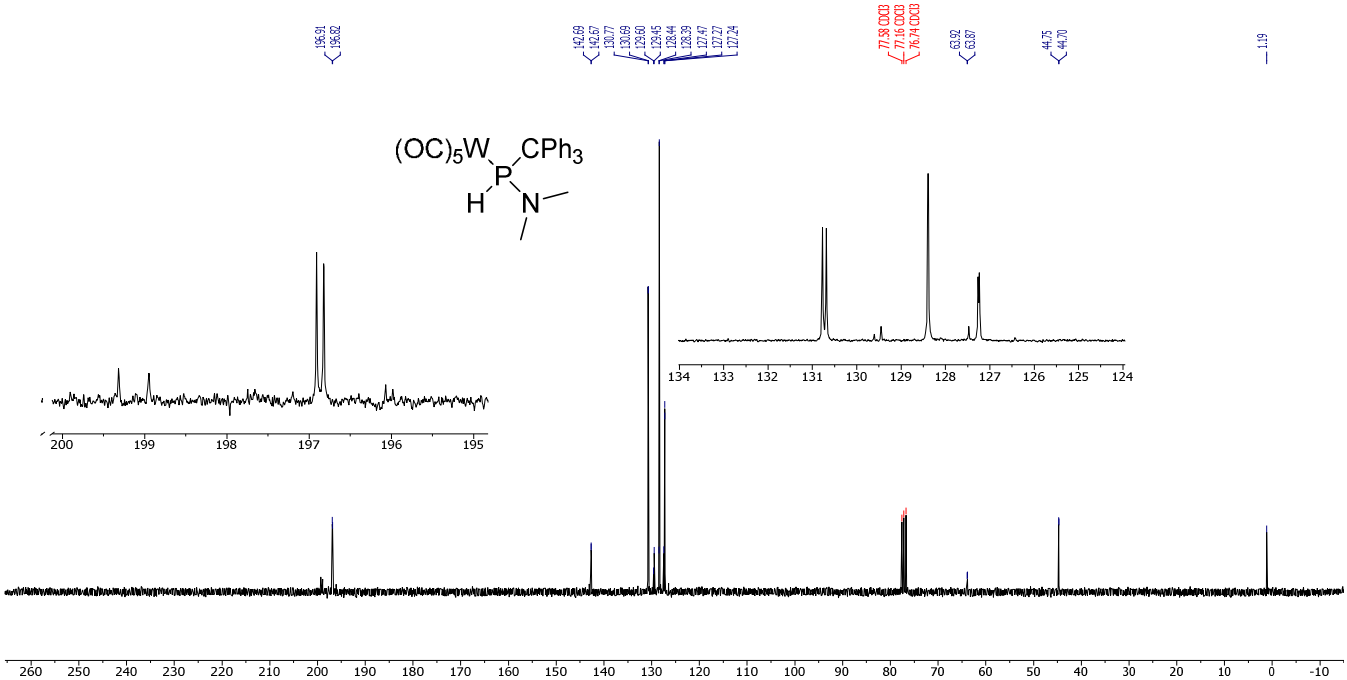

Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$ at 75.5 MHz.

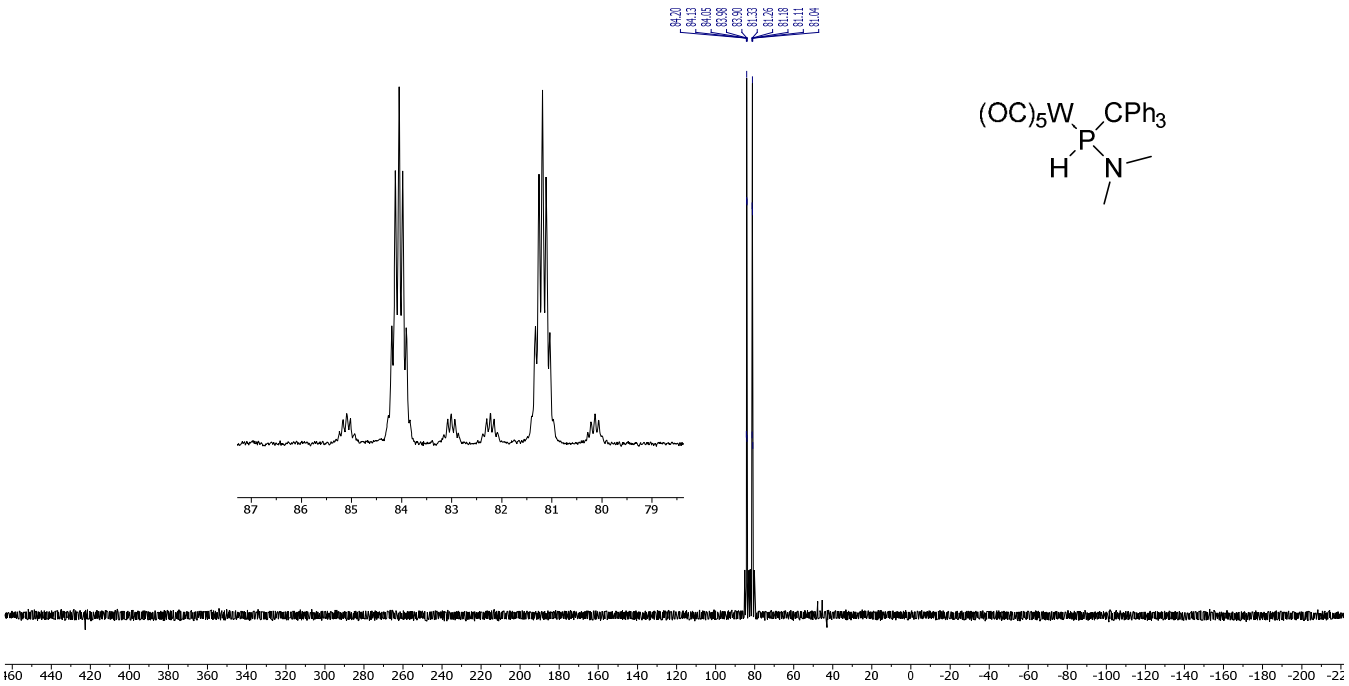

Figure S15: ^{31}P NMR spectrum of **6** in $CDCl_3$ at 121.5 MHz.

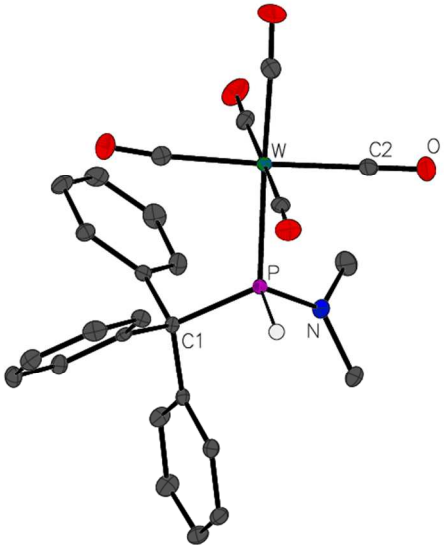

Figure S16: Crystal structure of **6**. Suitable single-crystals of **6** were obtained from a concentrated diethyl ether solution at 4 °C. Data were collected with a Bruker D8-Venture diffractometer equipped with a low-temperature device at 100 K by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by intrinsic phasing methods (SHELXT 2015) and refined by full-matrix least squares on F^2 (SHELXL 2015)[1]: $C_{26}H_{22}NO_5PW$, Mr = 643.26, crystal dimensions 0.24 × 0.18 × 0.16 mm^3, monoclinic, space group C2/c, Z =8, a = 31.6772(9) Å, b = 11.5478(3) Å, c = 13.5495(4) Å, α =90°, β =99.2472(9)°, γ =90°, V = 4892.0(2) $Å^3$, d_{calcd} = 1.747 g cm^{-3}, μ = 4.825 mm^{-1}, transmission factors (min/max) 0.4351/0.7459, empirical absorption correction from equivalents, $2\theta_{max}$ = 55.996°, no. of unique data 5896, R_{int} = 0.0351, R_1 (for I >2σ(I)) = 0.01498, wR_2 (for all data) = 0.0370, final R_1 = 0.0157, goodness of fit 1.141, ΔF (max/min) = 0.45 /−1.01 e $Å^{-3}$. CCDC 1529738 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

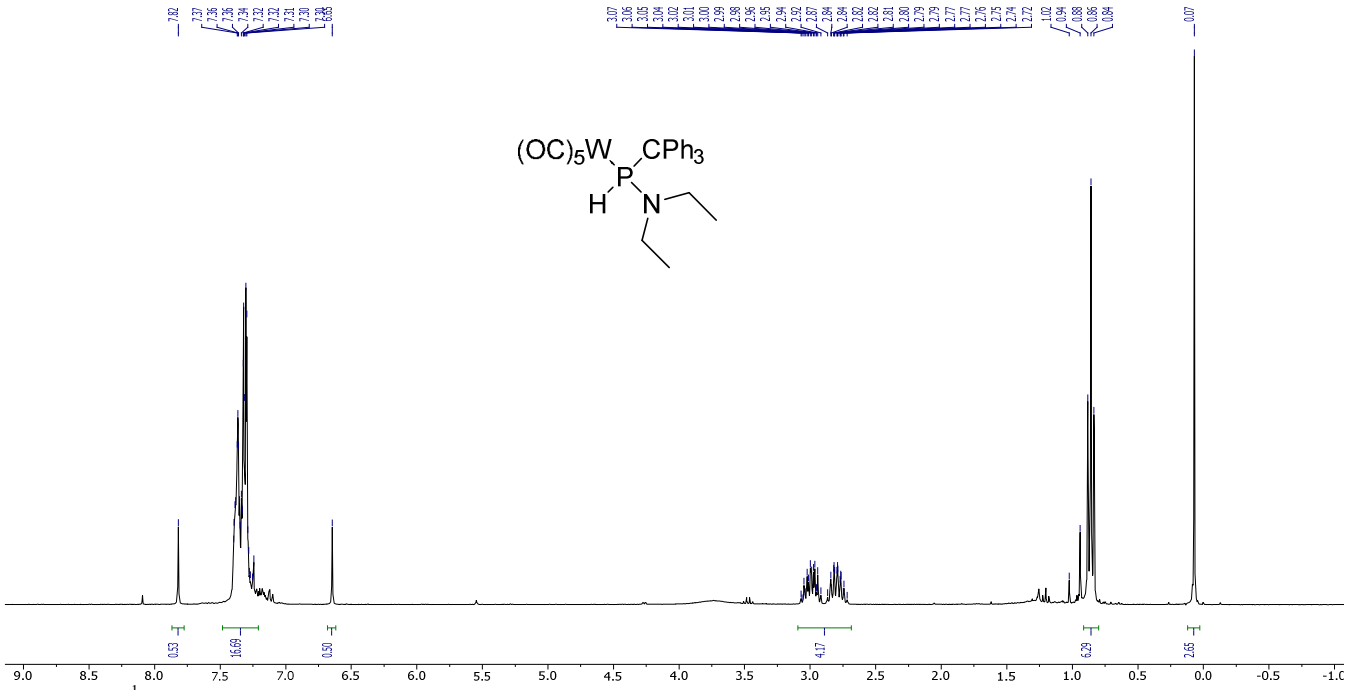

Figure S17: ^{1}H NMR spectrum of **7** in $CDCl_3$ at 300.1 MHz.

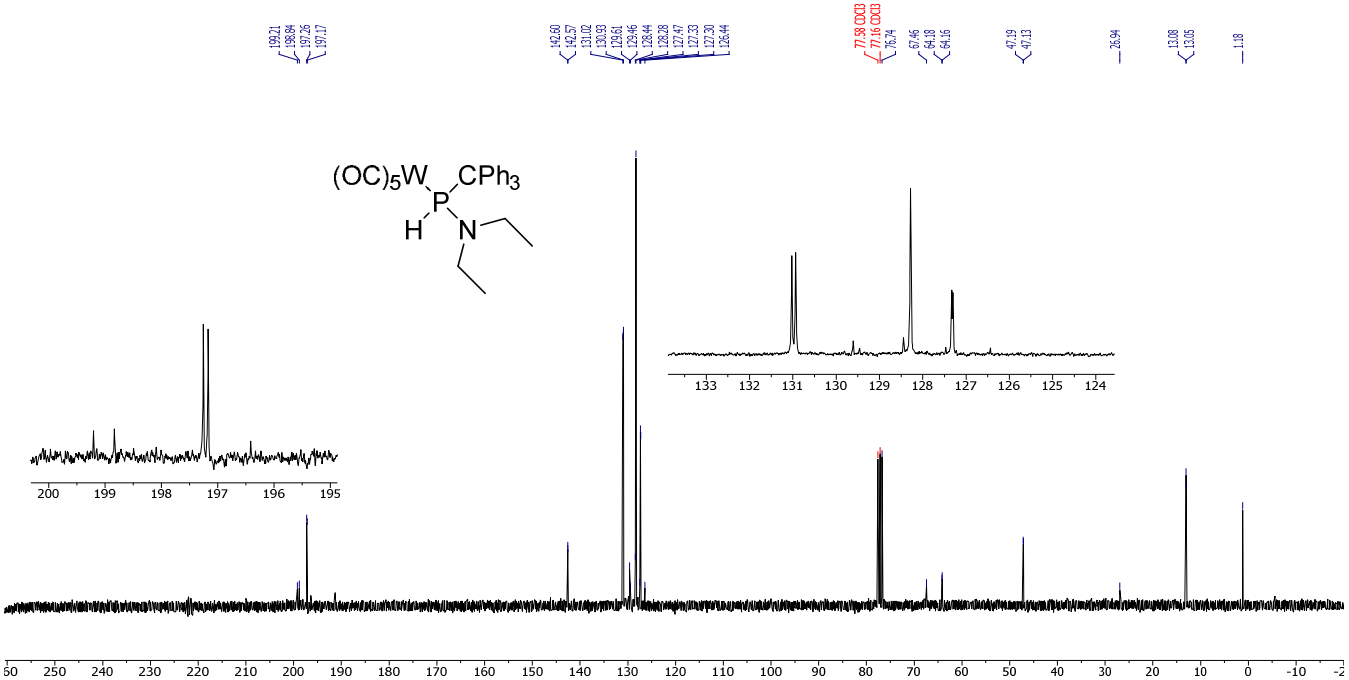

Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum of **7** in $CDCl_3$ at 75.5 MHz.

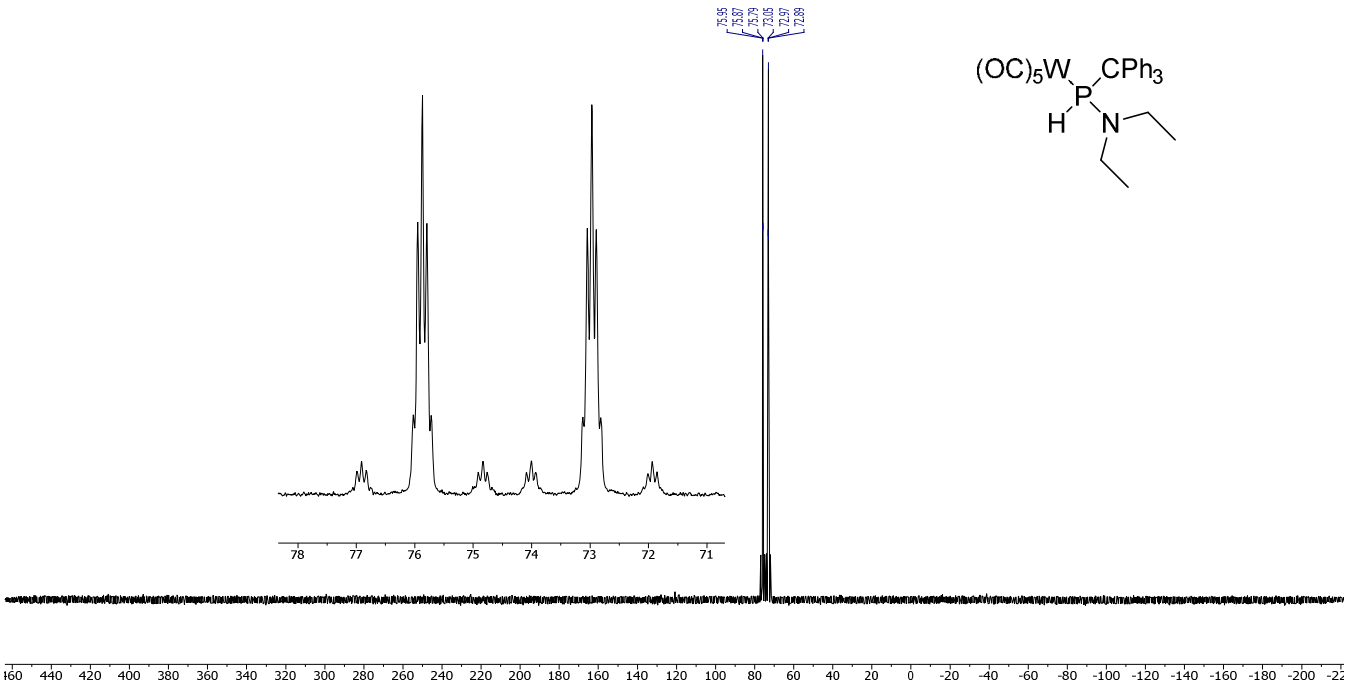

Figure S19: ^{31}P NMR spectrum of **7** in $CDCl_3$ at 121.5 MHz.

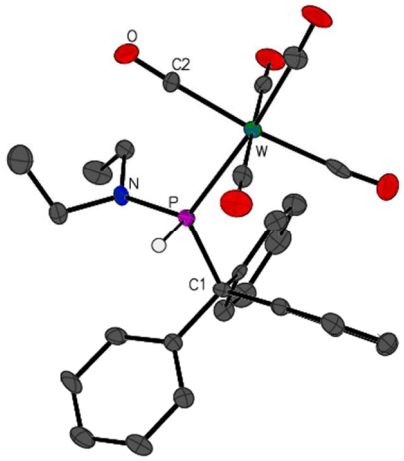

Figure S20: Crystal structure of **7**. Suitable single-crystals of **7** were obtained from a concentrated diethyl ether solution at 4 °C. Data were collected with a Bruker X8-KappaApexII diffractometer equipped with a low-temperature device at 100(2) K by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by intrinsic phasing methods (SHELXT 2015) and refined by full-matrix least squares on F^2 (SHELXL 2015)[1]: $C_{28}H_{26}NO_5PW$, Mr = 671.32, crystal dimensions 0.35 × 0.20 × 0.10 mm^3, triclinic, space group P-1, Z =4, a = 10.7367(7) Å, b = 15.6770(10) Å, c = 17.4538(10) Å, α = 104.204(3)°, β = 98.484(3)°, γ =104.184(3)°, V = 2692.9(3) $Å^3$, d_{calcd} = 1.656 g cm^{-3}, μ = 4.386 mm^{-1}, transmission factors (min/max) 0.0734/0.2638, empirical absorption correction, $2\theta_{max}$ = 53.998°, no. of unique data 13114, R_{int} = 0.0700, R_1 (for I >2σ(I)) = 0.0461, wR_2 (for all data) = 0.1134, final R_1 = 0.0605, goodness of fit 1.052, ΔF (max/min) = 2.50 /−2.35 e $Å^{-3}$. CCDC 1529747 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

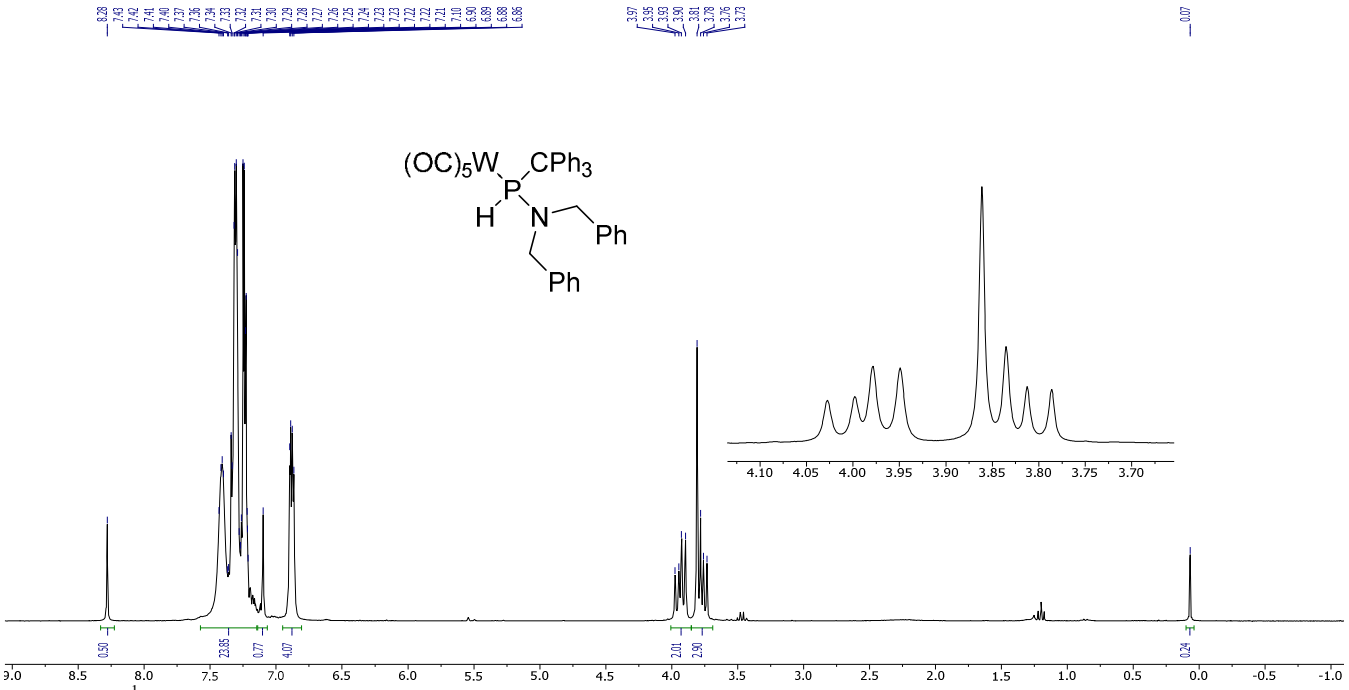

Figure S21: ^{1}H NMR spectrum of **8** in $CDCl_3$ at 300.1 MHz.

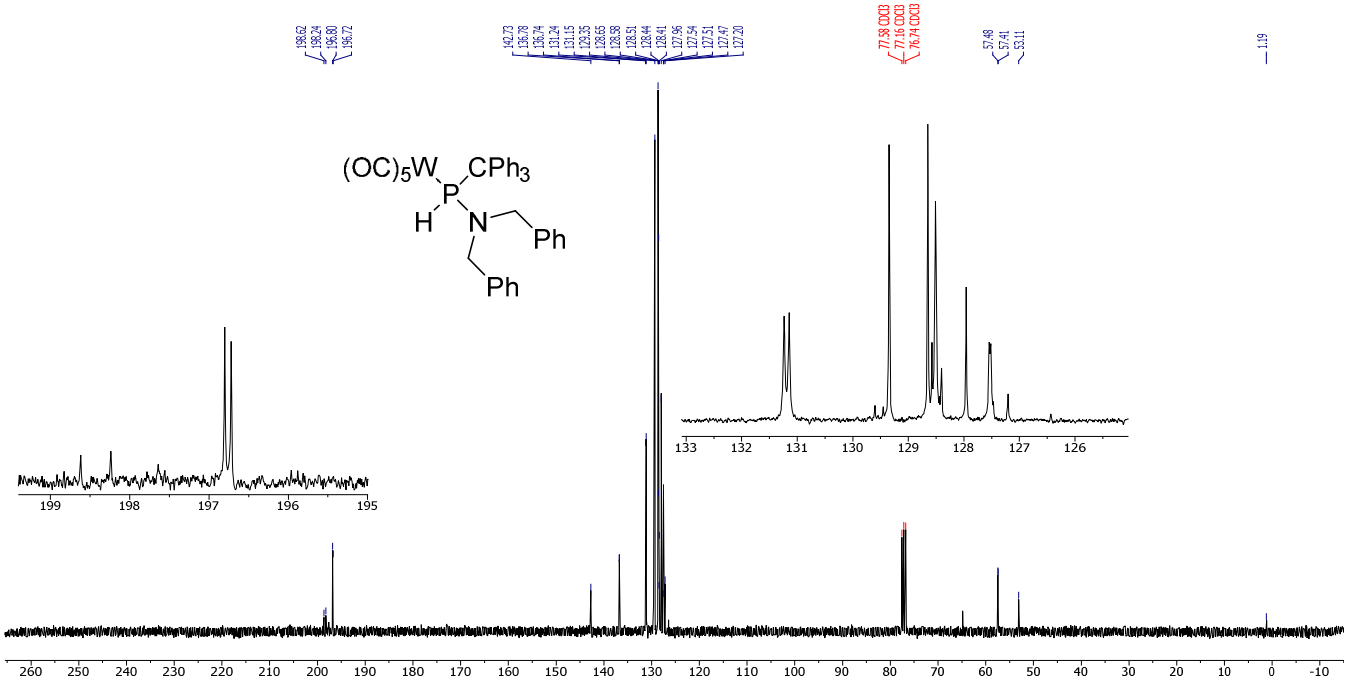

Figure S22: $^{13}C\{^{1}H\}$ NMR spectrum of **8** in $CDCl_3$ at 75.5 MHz.

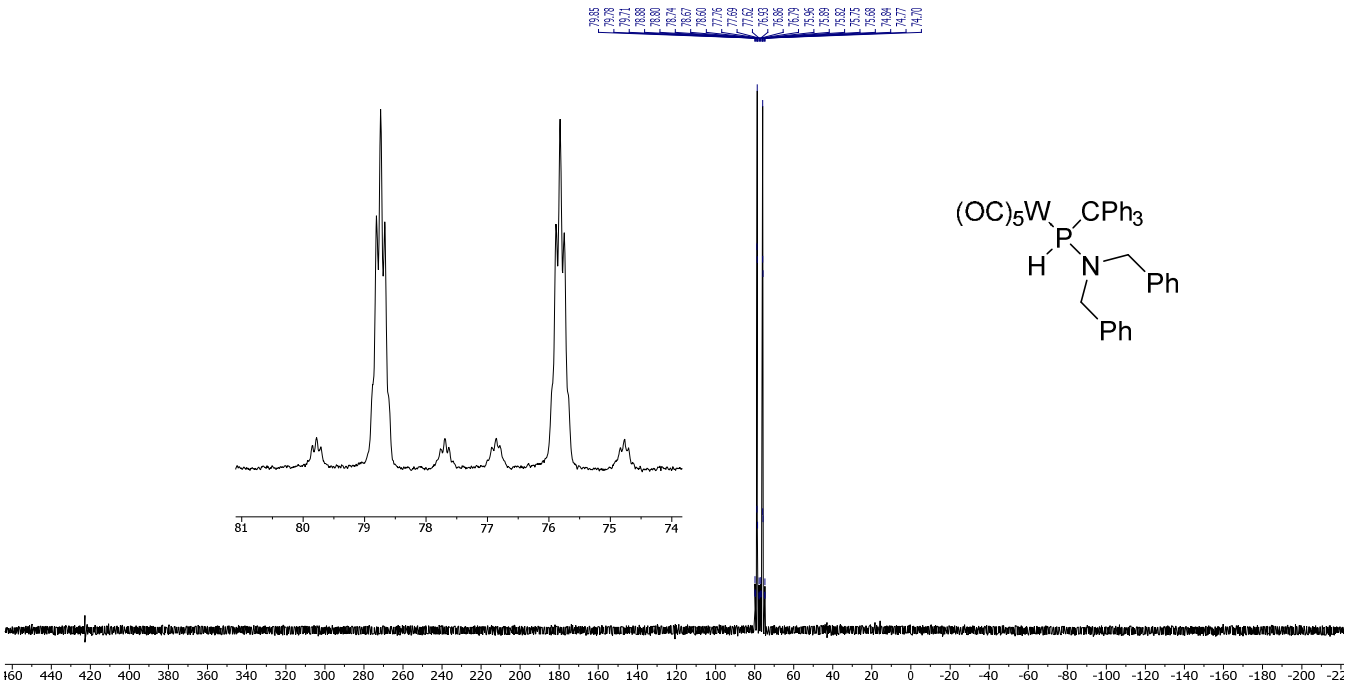

Figure S23: ^{31}P NMR spectrum of **8** in $CDCl_3$ at 121.5 MHz.

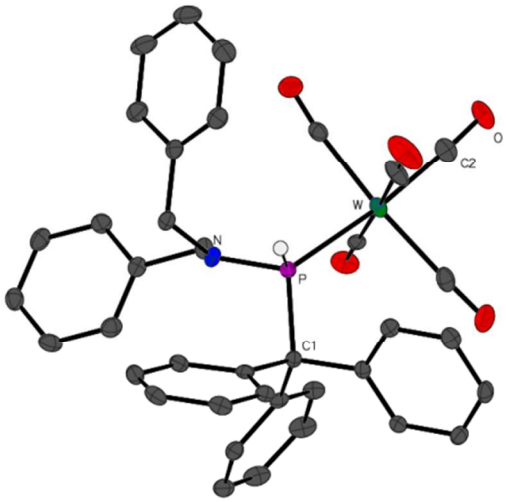

Figure S24: Crystal structure of **8**. Suitable single-crystals of **8** were obtained from a concentrated diethyl ether solution at 4 °C. Data were collected with a Bruker D8-Venture diffractometer equipped with a low-temperature device at 99.99 K by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by intrinsic phasing methods (SHELXT 2015) and refined by full-matrix least squares on F^2 (SHELXL 2015)[1]: $C_{38}H_{30}NO_5PW$, Mr = 795.45, crystal dimensions 0.27 × 0.22 × 0.16 mm^3, triclinic, space group $P\bar{1}$, Z =2, a = 10.419(4) Å, b = 10.508(5) Å, c = 16.971(8) Å, α =84.29(2)°, β =78.87(2)°, γ =64.441(19)°, V = 1644.5(12) $Å^3$, d_{calcd} = 1.606 g cm^{-3}, μ = 3.606 mm^{-1}, transmission factors (min/max) 0.4719/0.7459, empirical absorption correction, $2\theta_{max}$ = 55.998°, no. of unique data 7851, R_{int} = 0.0550, R_1 (for I >2σ(I)) = 0.0214, wR_2 (for all data) = 0.0455, final R_1 = 0.0264, goodness of fit 1.048, ΔF (max/min) = 0.83 /−1.17 e $Å^{-3}$. CCDC 1529739 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

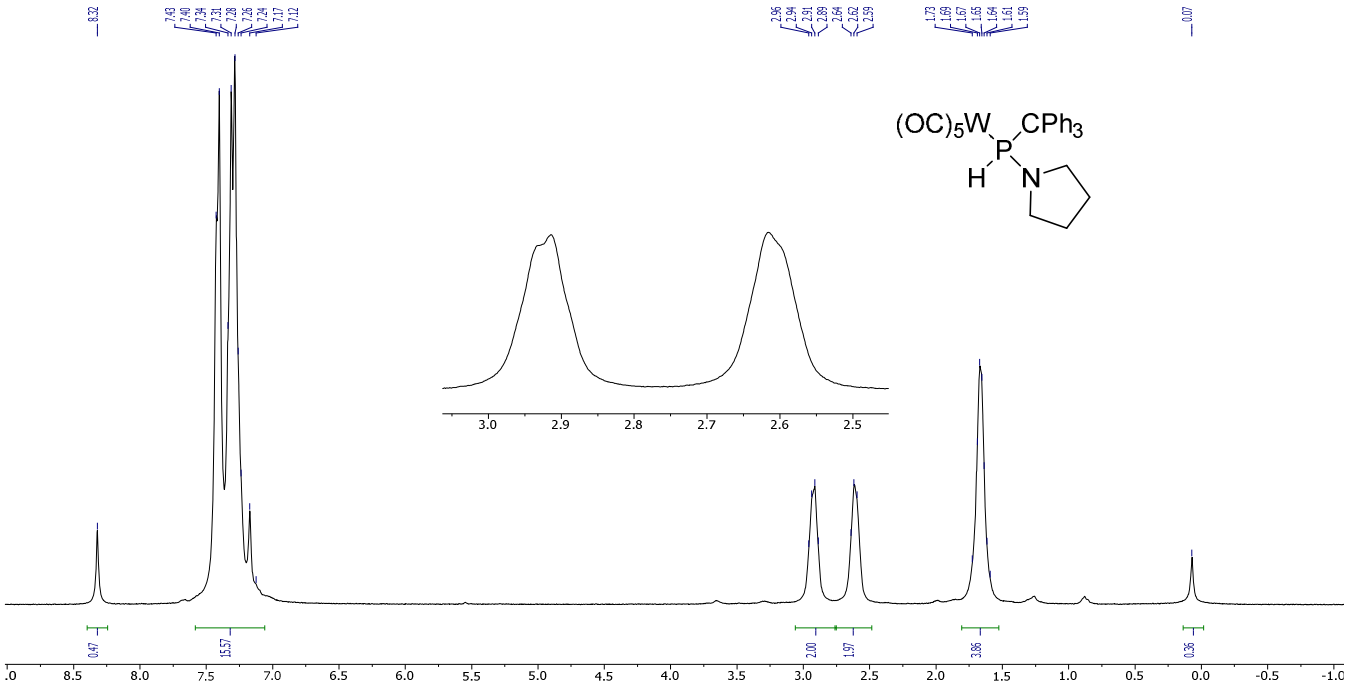

Figure S25: ^{1}H NMR spectrum of **9** in $CDCl_3$ at 300.1 MHz.

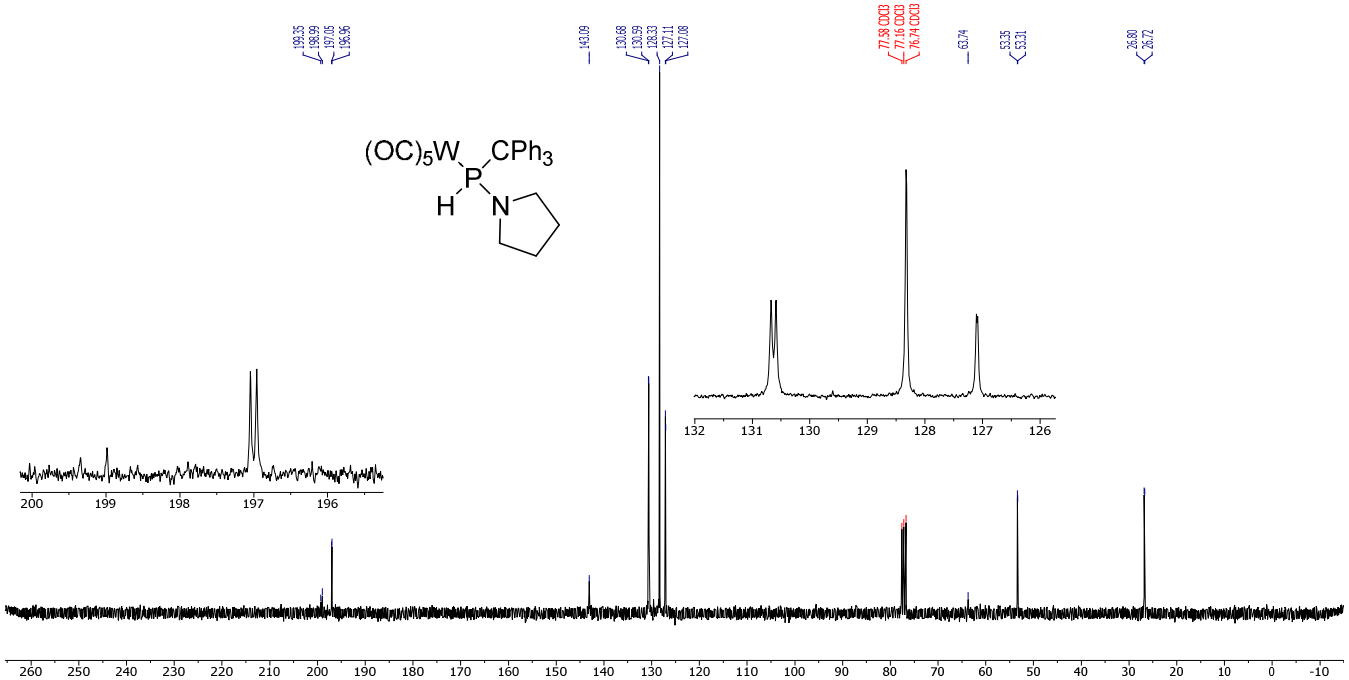

Figure S26: $^{13}C\{^{1}H\}$ NMR spectrum of **9** in $CDCl_3$ at 75.5 MHz.

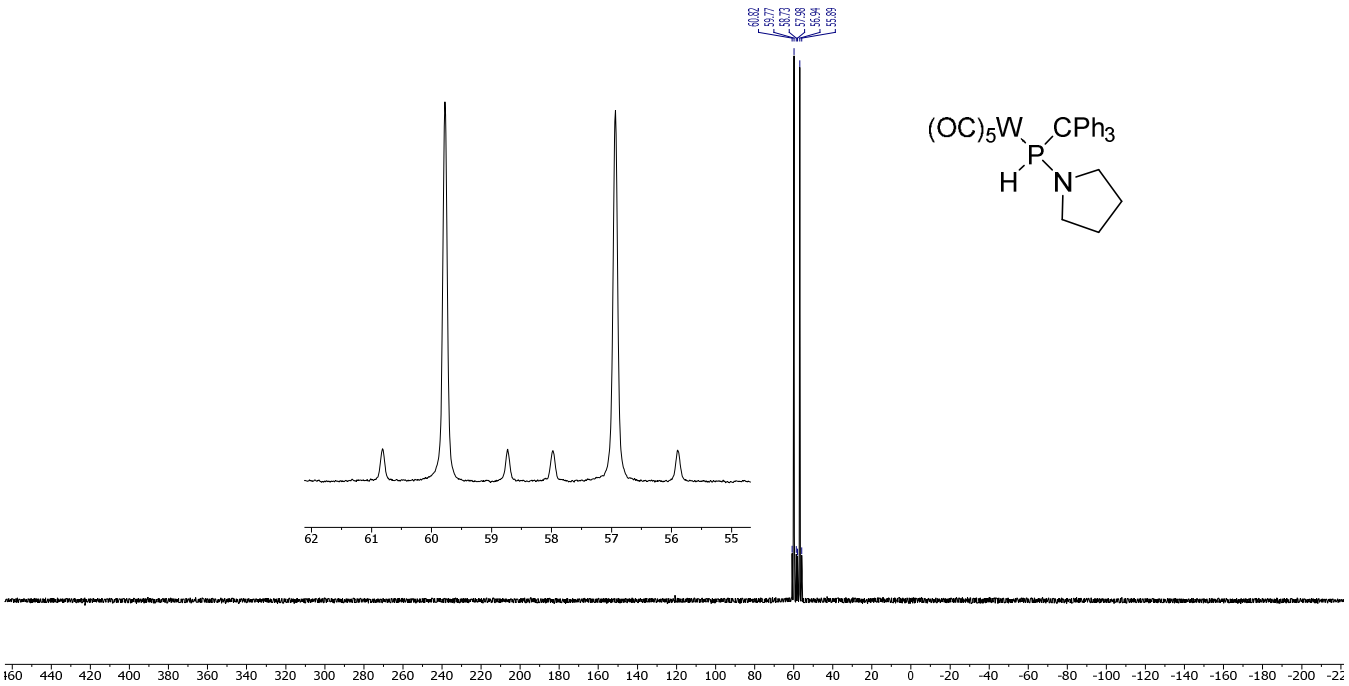

Figure S27: ^{31}P NMR spectrum of **9** in $CDCl_3$ at 121.5 MHz.

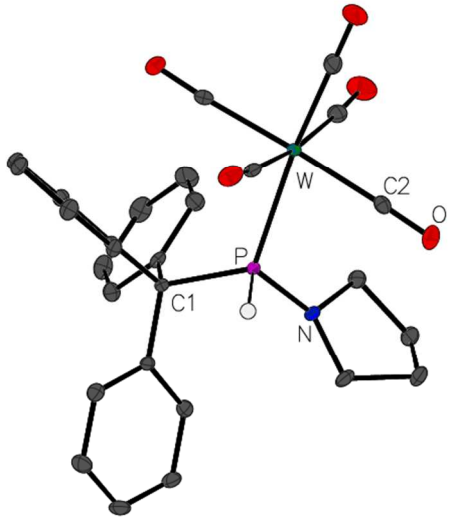

Figure S28: Crystal structure of **9**. Suitable single-crystals of **9** were obtained from a concentrated diethyl ether solution at 4 °C. Data were collected with a Bruker D8-Venture diffractometer equipped with a low-temperature device at 99.99 K by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by intrinsic phasing methods (SHELXT 2015) and refined by full-matrix least squares on F^2 (SHELXL 2015)[1]: $C_{28}H_{24}NO_5PW$, Mr = 669.30, crystal dimensions 0.26 × 0.24 × 0.2 mm^3, triclinic, space group $P\bar{1}$, Z =2, a = 10.0227(4) Å, b = 10.6252(4) Å, c = 13.1760(5) Å, α =76.5244(14)°, β =75.7674(14)°, γ =75.8317(13)°, V = 1296.22(9) $Å^3$, d_{calcd} = 1.715 g cm^{-3}, μ = 4.556 mm^{-1}, transmission factors (min/max) 0.4188/0.7459, empirical absorption correction, $2\theta_{max}$ = 55.99°, no. of unique data 6245, R_{int} = 0.0449, R_1 (for I >2σ(I)) = 0.0158, wR_2 (for all data) = 0.0385, final R_1 = 0.0175, goodness of fit 1.087, ΔF (max/min) = 0.49 /−1.39 e $Å^{-3}$. CCDC 1529741 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

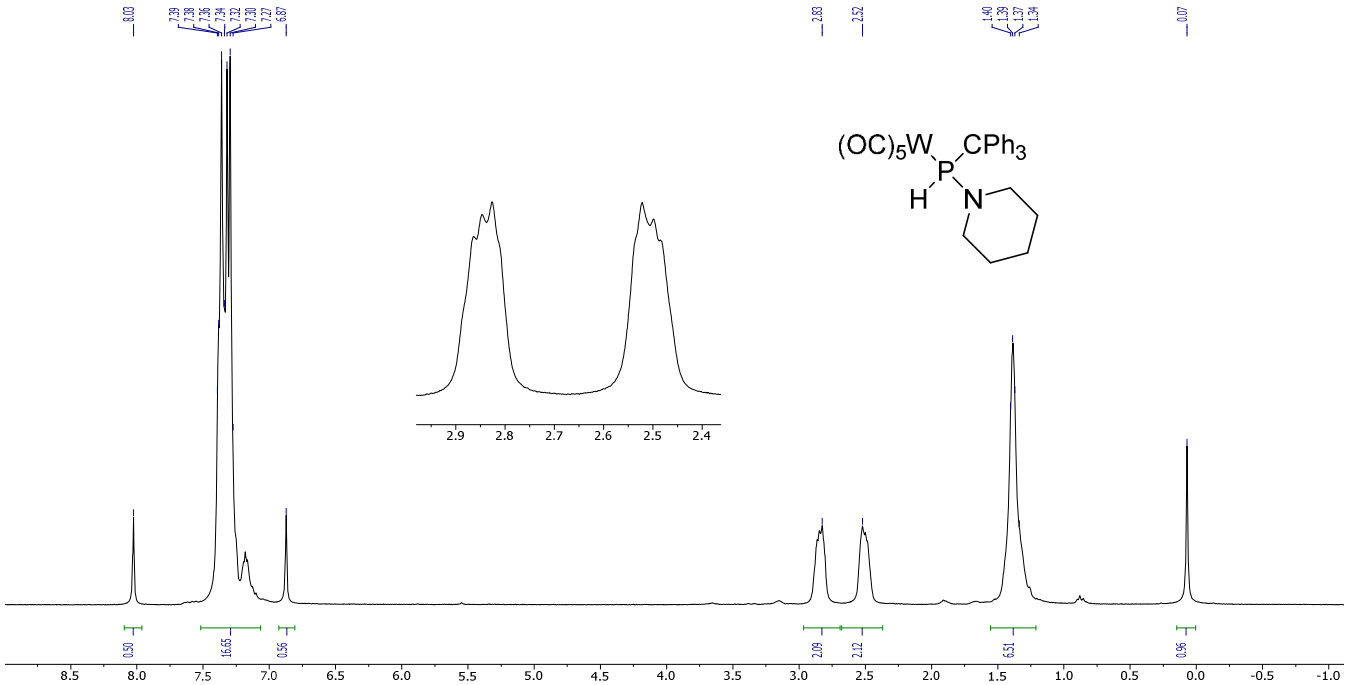

Figure S29: ^{1}H NMR spectrum of **10** in $CDCl_3$ at 300.1 MHz.

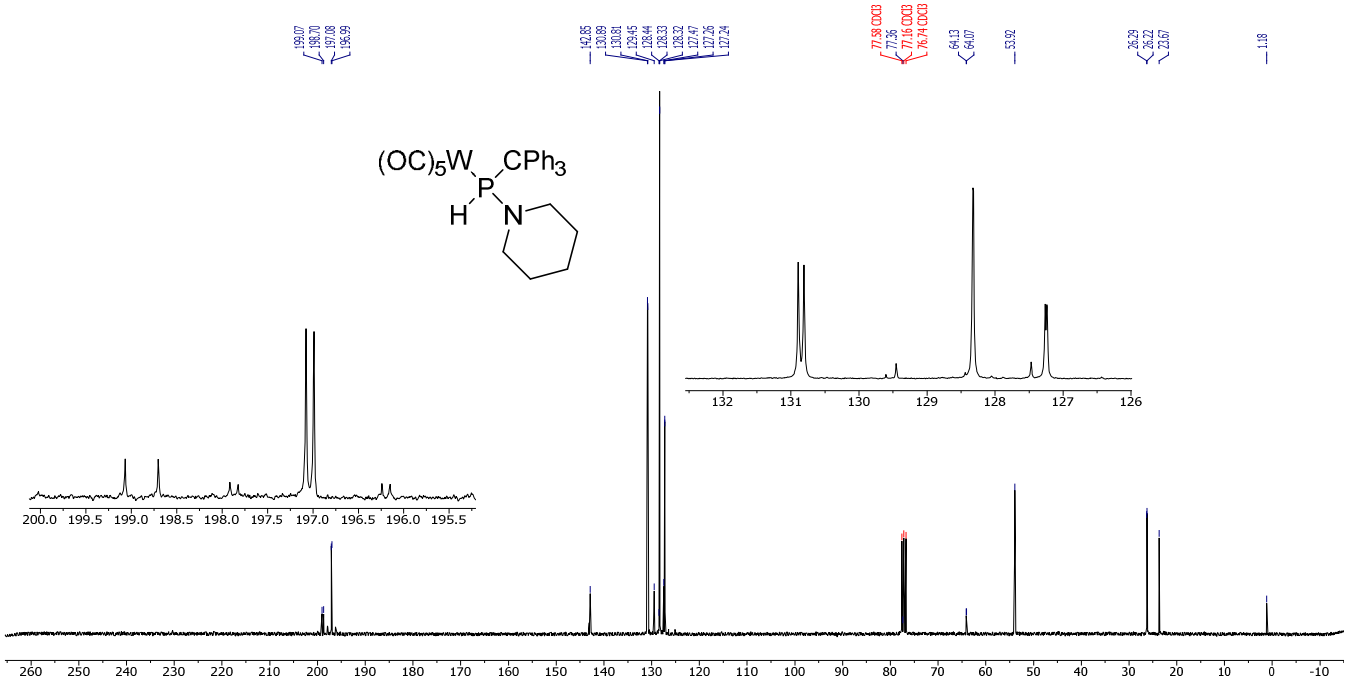

Figure S30: $^{13}C\{^{1}H\}$ NMR spectrum of **10** in $CDCl_3$ at 75.5 MHz.

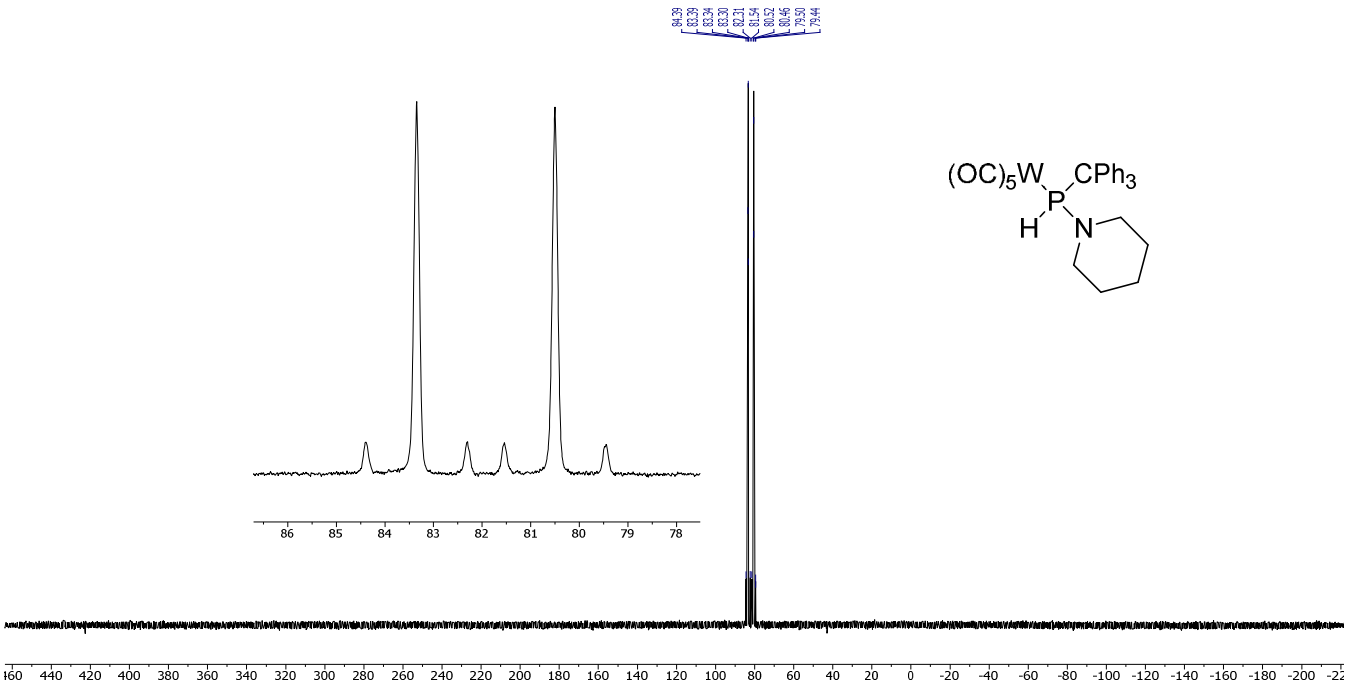

Figure S31: ^{31}P NMR spectrum of **10** in $CDCl_3$ at 121.5 MHz.

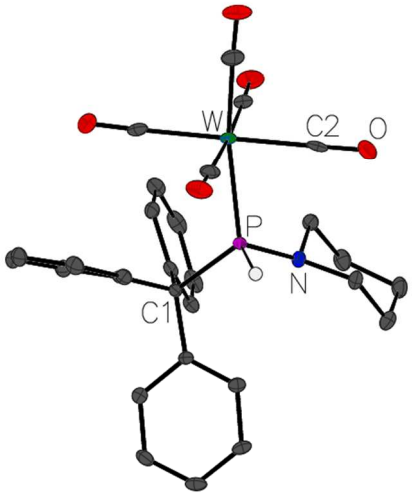

Figure S32: Crystal structure of **10**. Suitable single-crystals of **10** were obtained from a concentrated diethyl ether solution at 4 °C. Data were collected with a Bruker D8-Venture diffractometer equipped with a low-temperature device at 100 K by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by intrinsic phasing methods (SHELXT 2015) and refined by full-matrix least squares on F^2 (SHELXL 2015)[1]: $C_{29}H_{26}NO_5PW$, Mr = 683.33, crystal dimensions 0.15 × 0.08 × 0.06 mm^3, monoclinic, space group $P2_1/c$, Z =8, a = 14.7592(5) Å, b = 32.0367(10) Å, c = 11.2598(4) Å, α =90°, β =91.4175(12)°, γ =90°, V = 5322.4(3) $Å^3$, d_{calcd} = 1.706 g cm^{-3}, μ = 4.440 mm^{-1}, transmission factors (min/max) 0.5079/0.7459, empirical absorption correction, $2\theta_{max}$ = 56°, no. of unique data 12836, R_{int} = 0.0403, R_1 (for I >2σ(I)) = 0.0276, wR_2 (for all data) = 0.0559, final R_1 = 0.0333, goodness of fit 1.161, ΔF (max/min) = 1.30 /−2.30 e $Å^{-3}$. CCDC 1529737 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

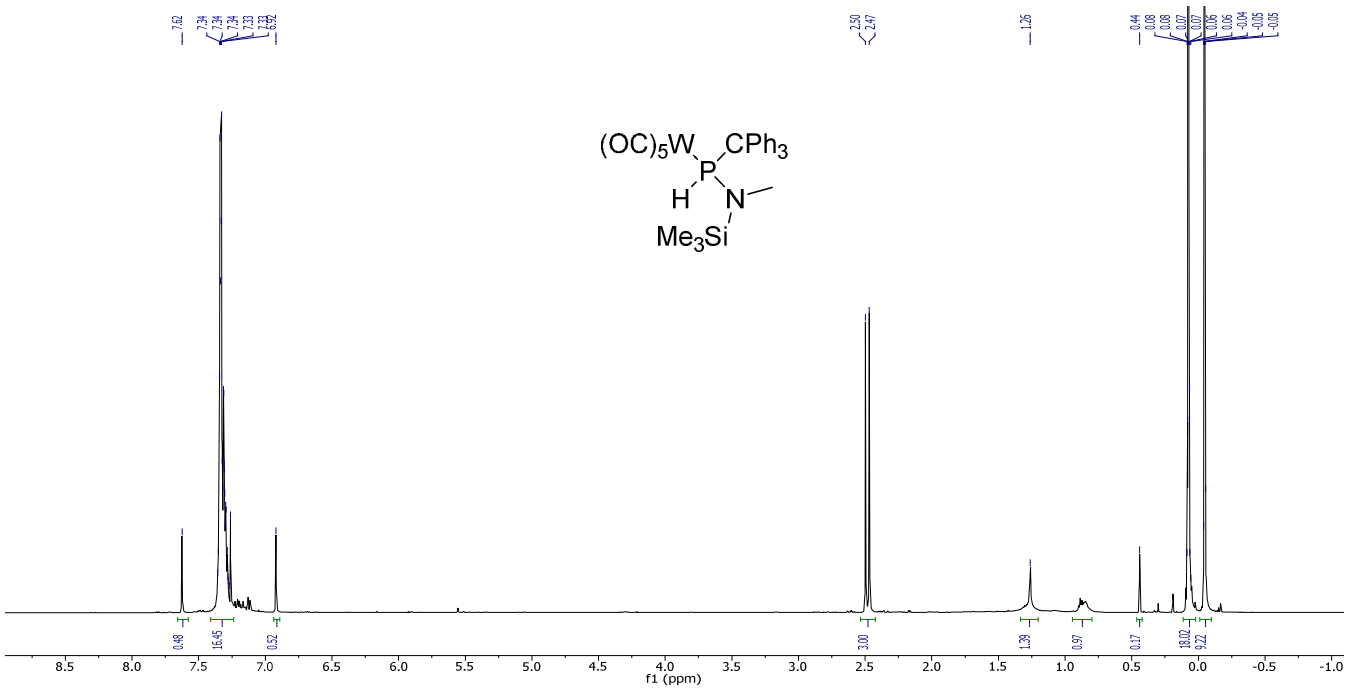

Figure S33: ^{1}H NMR spectrum of **12** in $CDCl_3$ at 500.2 MHz.

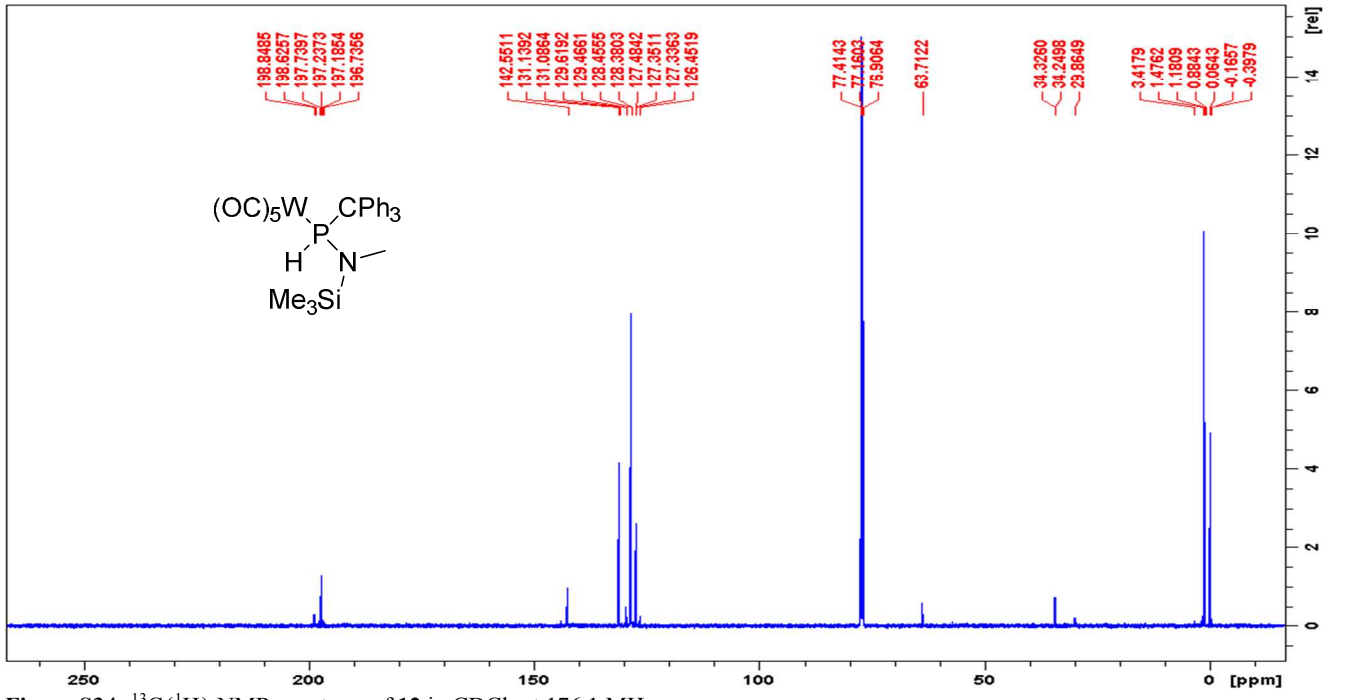

Figure S34: $^{13}C\{^{1}H\}$ NMR spectrum of **12** in $CDCl_3$ at 176.1 MHz.

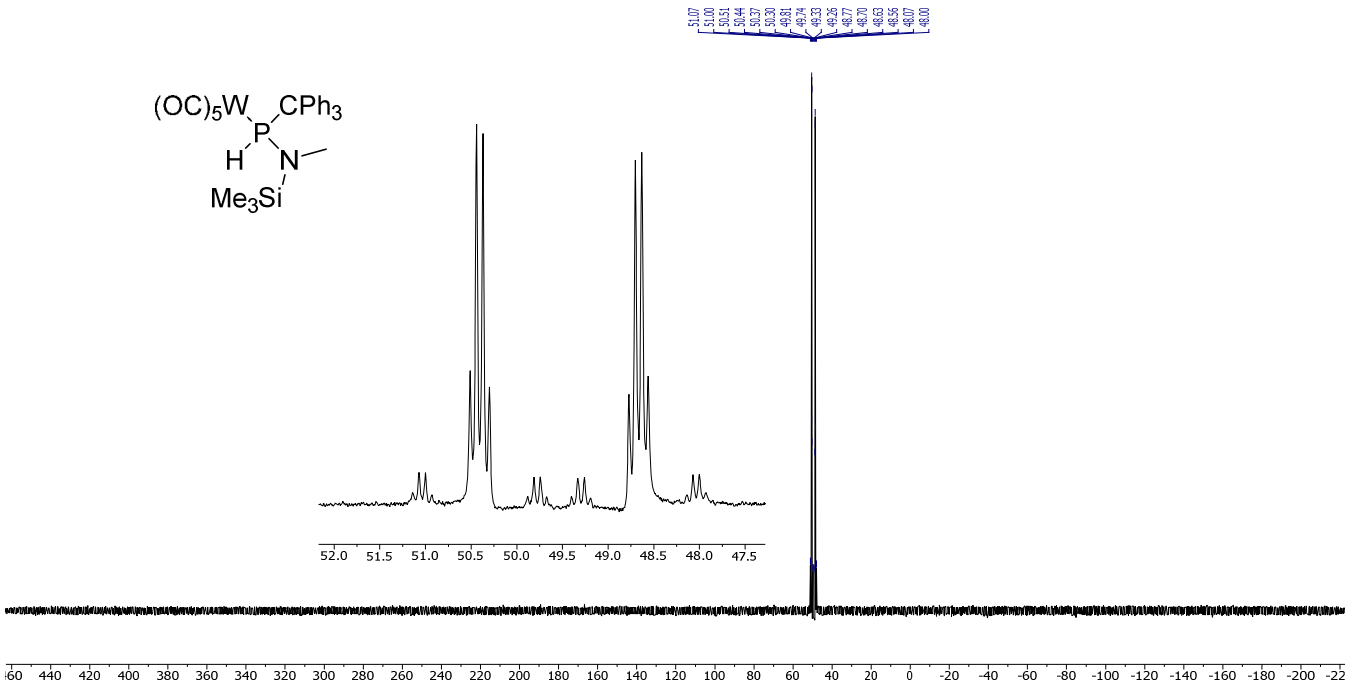

Figure S35: ^{31}P NMR spectrum of **12** in $CDCl_3$ at 202.5 MHz.

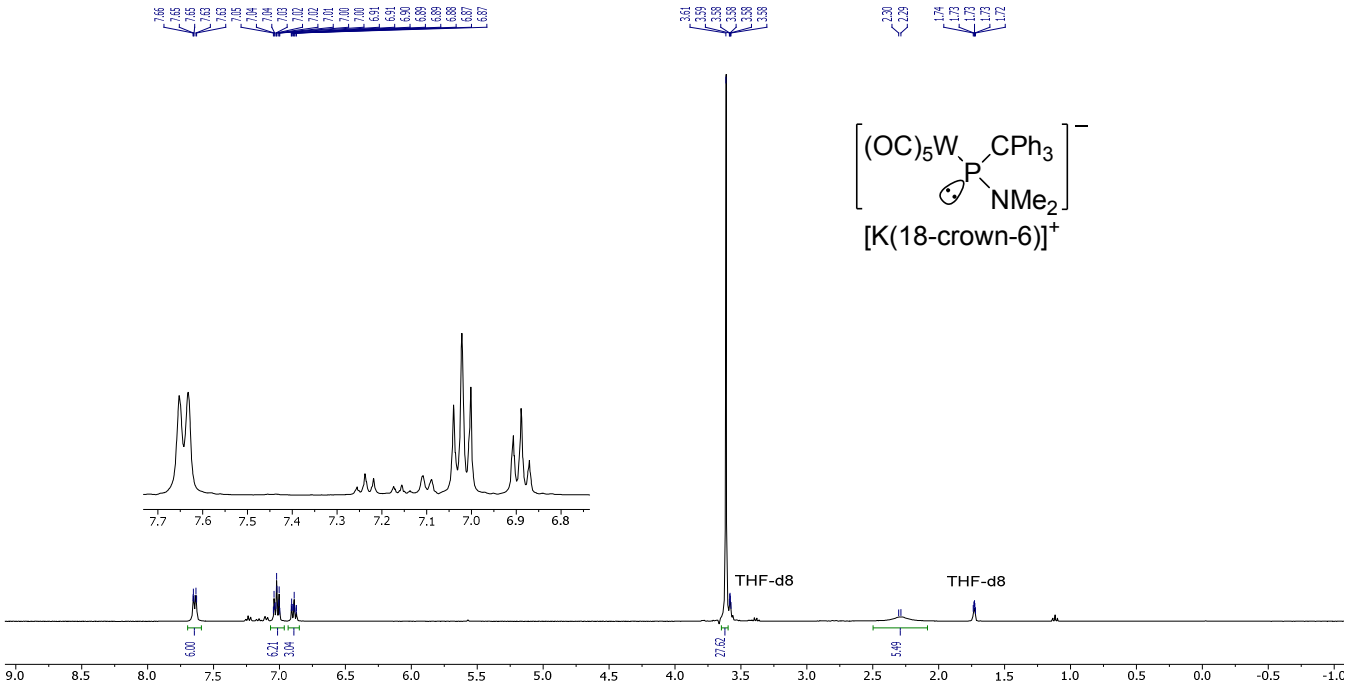

Figure S36: ^{1}H NMR spectrum of **13** in THF-d8 at 400.1 MHz.

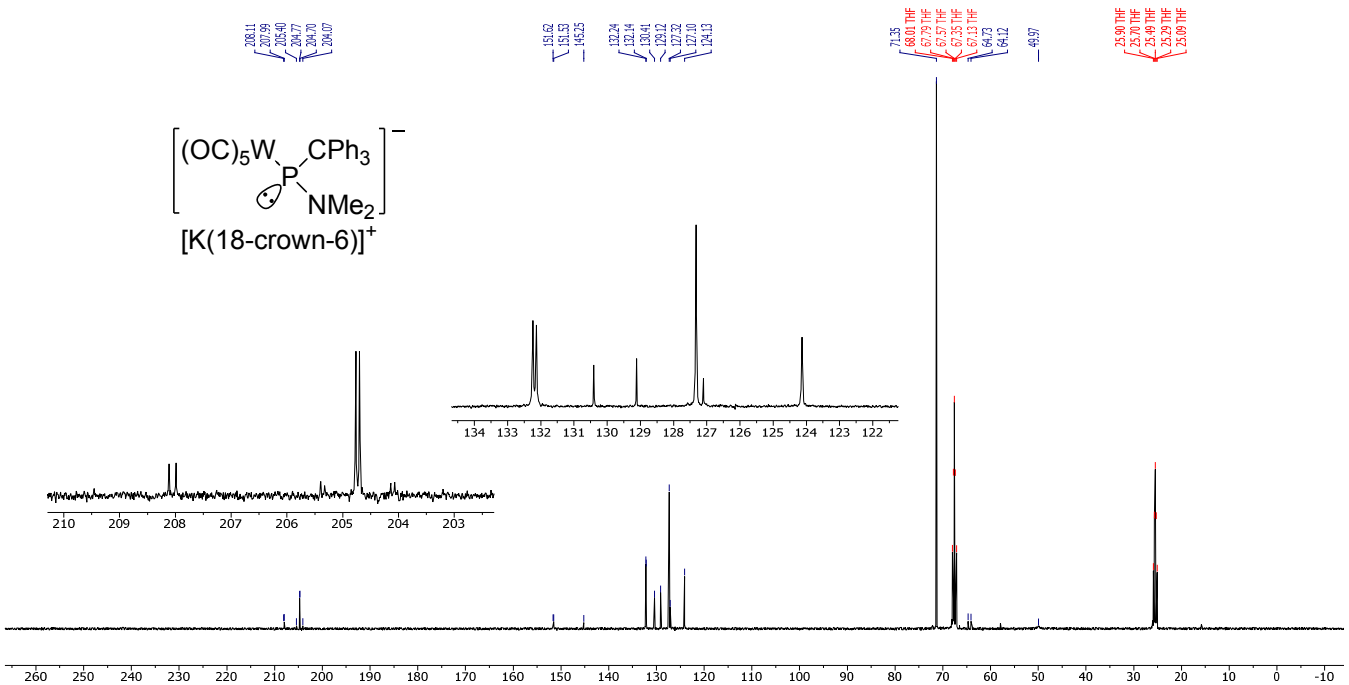

Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum of **13** in THF-d8 at 100.6 MHz.

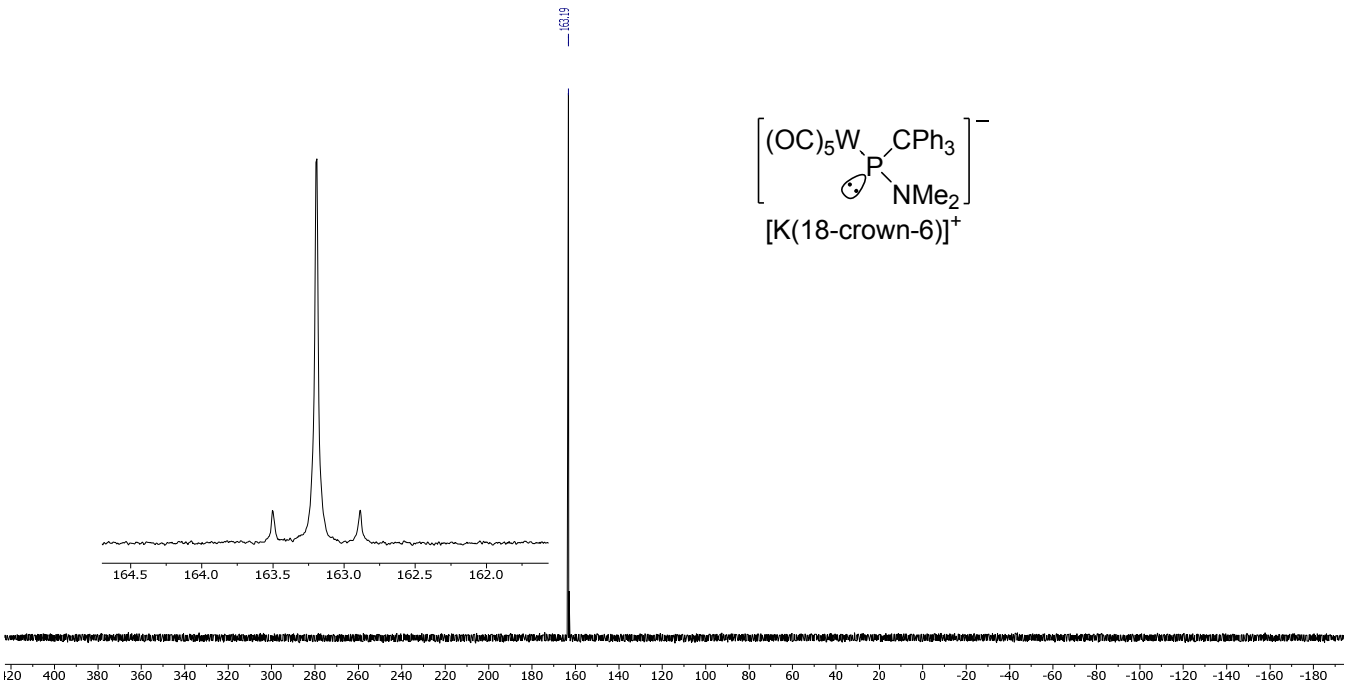

Figure S38: $^{31}P\{^{1}H\}$ NMR spectrum of **13** in THF-d8 at 162.0 MHz.

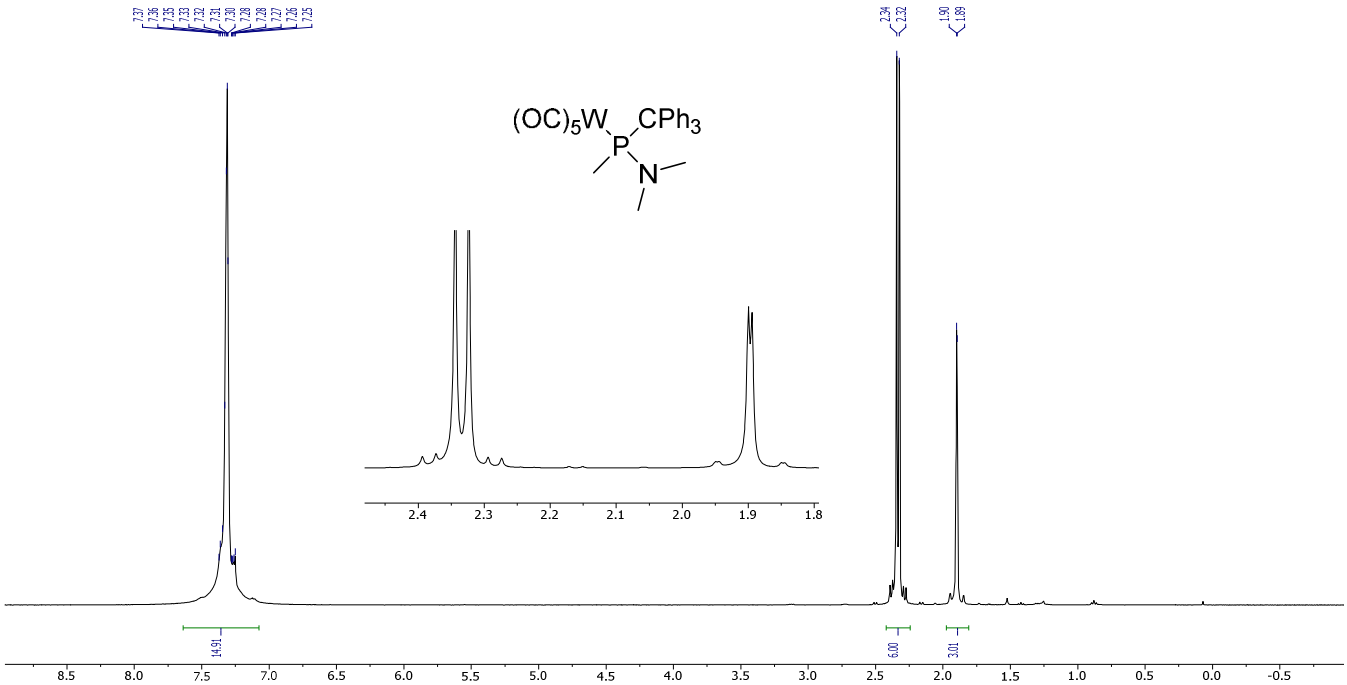

Figure S39: ^{1}H NMR spectrum of **14** in $CDCl_3$ at 400.1 MHz.

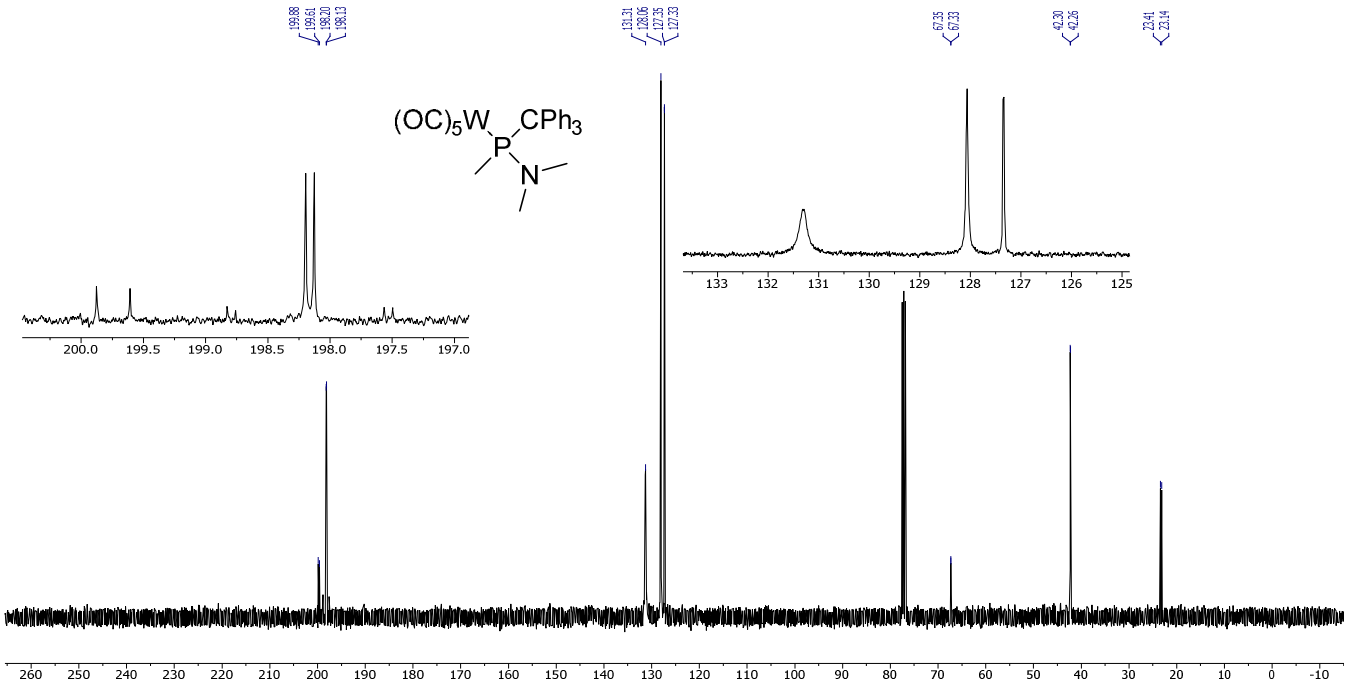

Figure S40: $^{13}C\{^{1}H\}$ NMR spectrum of **14** in $CDCl_3$ at 100.6 MHz.

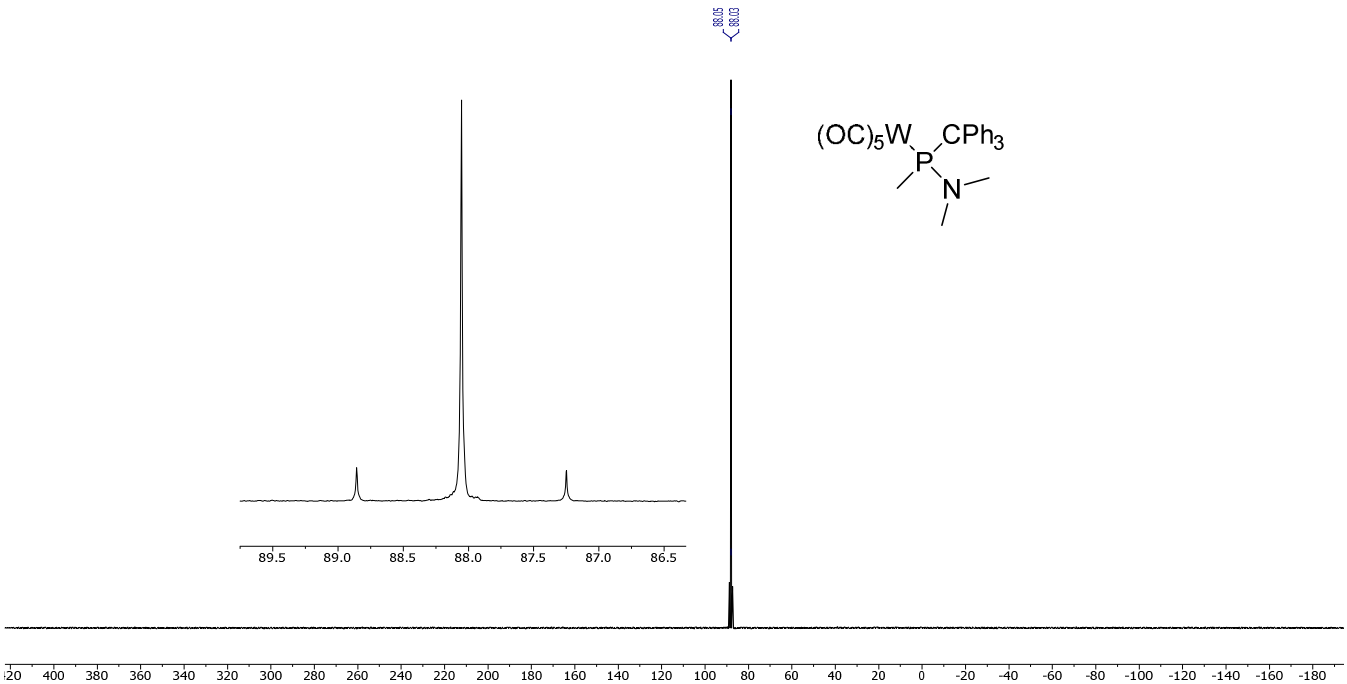

Figure S41: $^{31}P\{^{1}H\}$ NMR spectrum of **14** in $CDCl_3$ at 162.0 MHz.

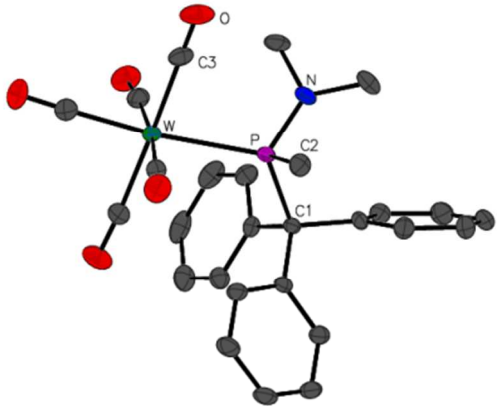

Figure S42: Crystal structure of **14**. Suitable single-crystals of **14** were obtained from a concentrated diethyl ether solution at 4 °C. Data were collected with a Bruker D8-Venture diffractometer equipped with a low-temperature device at 123 K by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by intrinsic phasing methods (SHELXT 2015) and refined by full-matrix least squares on F^2 (SHELXL 2015)[1]: $C_{27}H_{24}NO_5PW$, Mr = 657.29, crystal dimensions 0.22 × 0.21 × 0.17 mm^3, triclinic, space group P-1, Z =4, a = 10.5144(6) Å, b = 15.2601(10) Å, c = 16.9086(11) Å, α =105.035(2)°, β =102.792(2)°, γ =91.822(2)°, V = 2543.6(3) $Å^3$, d_{calcd} = 1.716 g cm^{-3}, μ = 4.642 mm^{-1}, transmission factors (min/max) 0.5165/0.7459, empirical absorption correction, $2\theta_{max}$ = 55.998°, no. of unique data 12269, R_{int} = 0.0521, R_1 (for I >2σ(I)) = 0.0182, wR_2 (for all data) = 0.0416, final R_1 = 0.0249, goodness of fit 1.099, ΔF (max/min) = 0.69 /−1.11 e $Å^{-3}$. CCDC 1529743 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

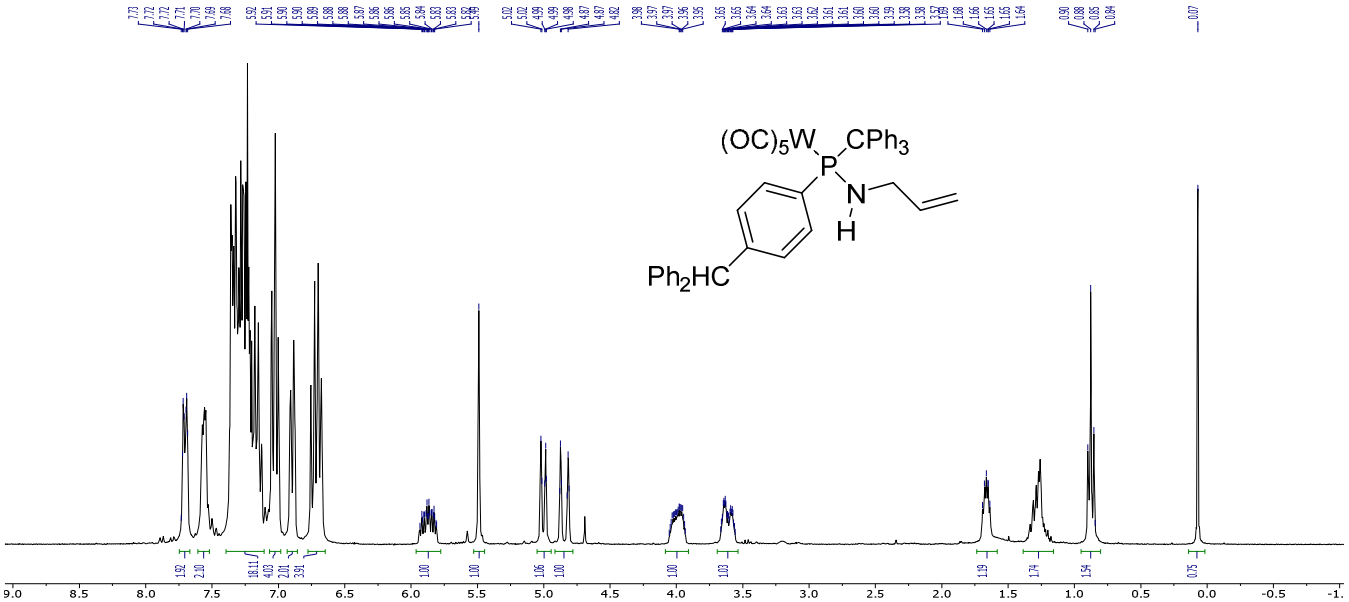

Figure S43: ^{1}H NMR spectrum of **17** in $CDCl_3$ at 300.1 MHz.

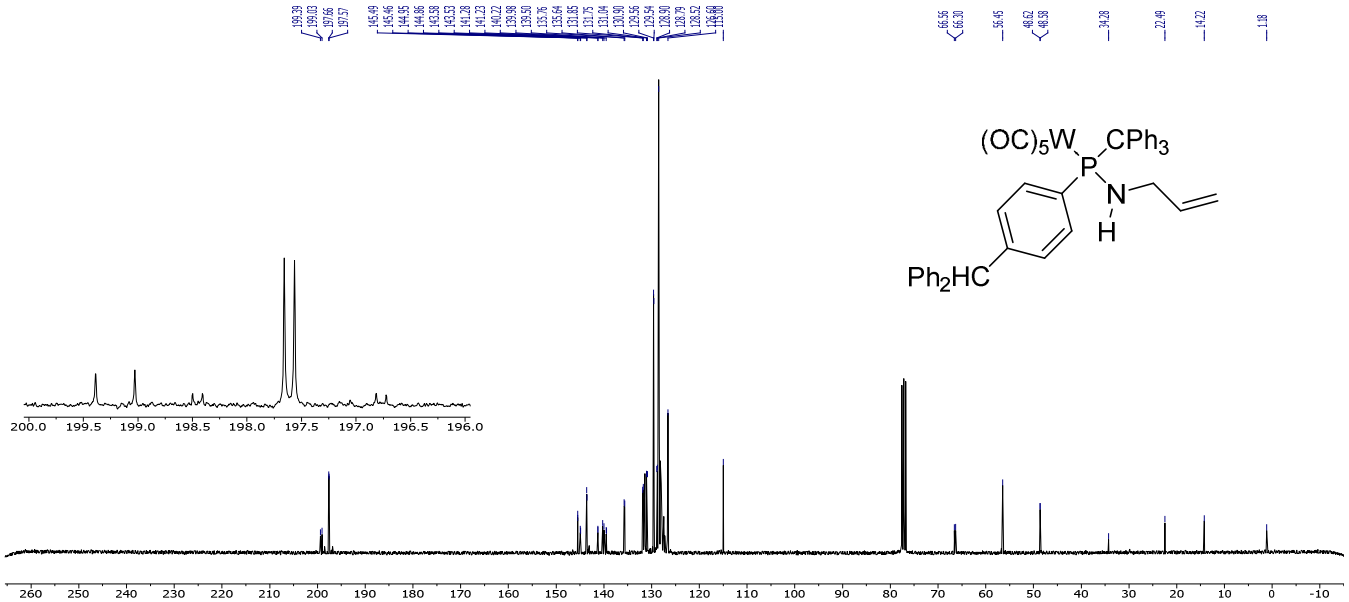

Figure S44: $^{13}C\{^{1}H\}$ NMR spectrum of **17** in $CDCl_3$ at 75.5 MHz.

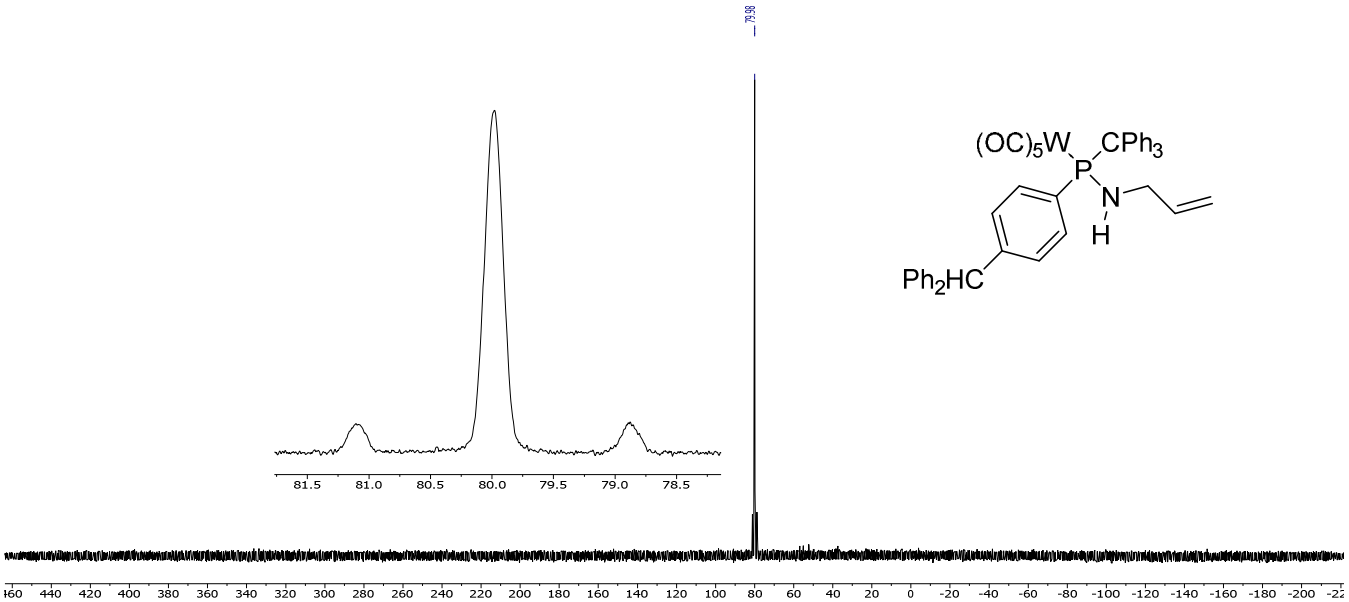

Figure S45: $^{31}P\{^{1}H\}$ NMR spectrum of **17** in $CDCl_3$ at 121.5 MHz.

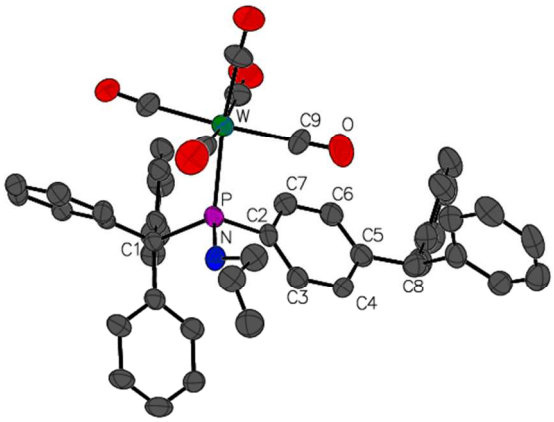

Figure S46: Crystal structure of **17**. Suitable single-crystals of **17** were obtained from a concentrated diethyl ether solution at 4 °C. Data were collected with a Bruker X8-KappaApexII diffractometer equipped with a low-temperature device at 100 K by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by intrinsic phasing methods (SHELXT 2015) and refined by full-matrix least squares on F^2 (SHELXL 2015)[1]: $C_{50}H_{46}NO_6PW$, Mr = 671.70, crystal dimensions 0.18 × 0.12 × 0.04 mm^3, monoclinic, space group $P2_1/n$, Z =4, a = 13.3276(15) Å, b = 19.649(2) Å, c = 18.692(2) Å, α =90°, β =107.734(4)°, γ =90°, V = 4662.3(9) $Å^3$, d_{calcd} = 1.384 g cm^{-3}, μ = 2.559 mm^{-1}, transmission factors (min/max) 0.4106/0.6478, empirical absorption correction, $2\theta_{max}$ = 51.996°, no. of unique data 8792, R_{int} = 0.0524, R_1 (for I >2σ(I)) = 0.0659, wR_2 (for all data) = 0.1631, final R_1 = 0.1077, goodness of fit 1.101, ΔF (max/min) = 4.33 /−2.54 e $Å^{-3}$. CCDC 1529745 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

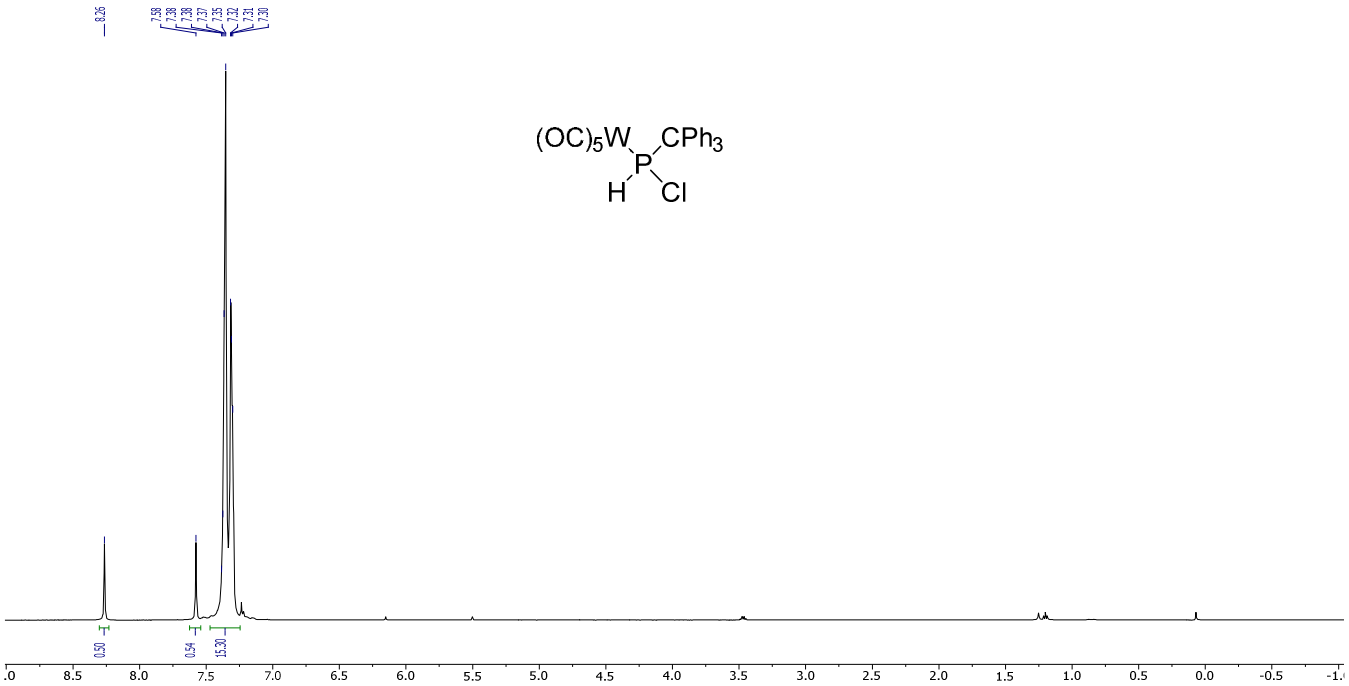

Figure S47: ^{1}H NMR spectrum of **19** in $CDCl_3$ at 500.2 MHz.

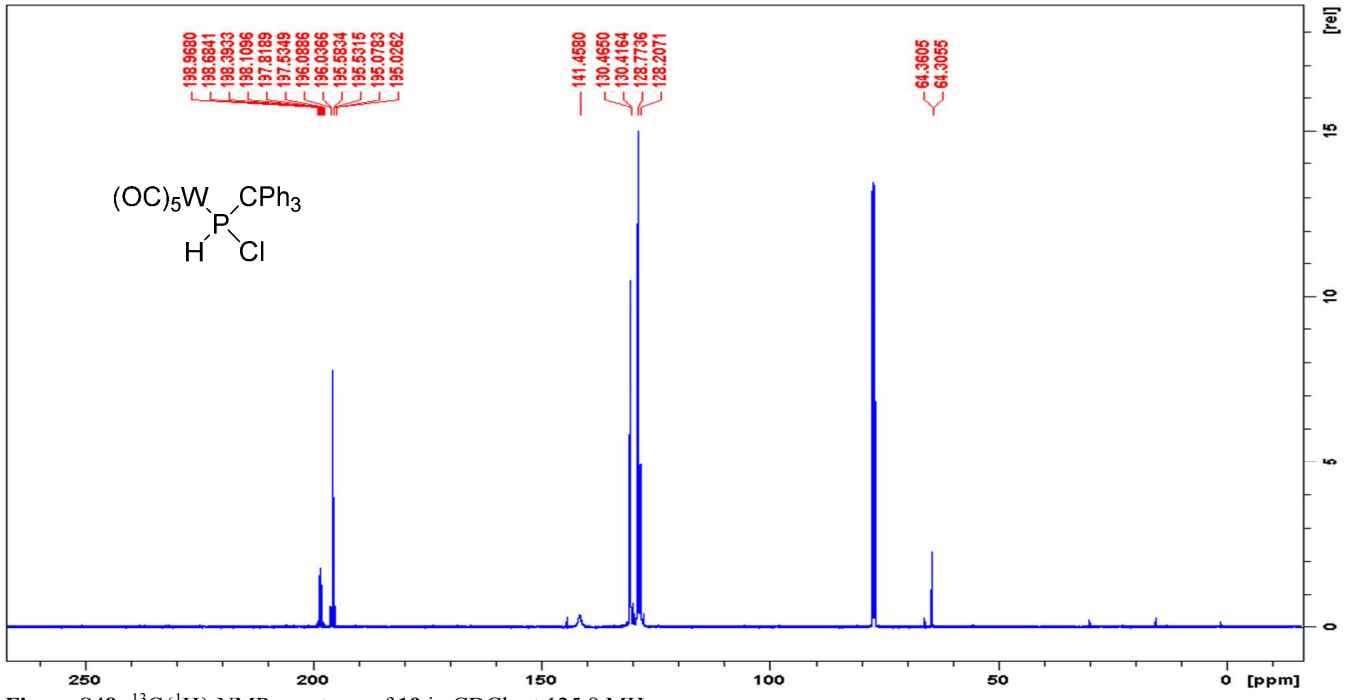

Figure S48: $^{13}C\{^{1}H\}$ NMR spectrum of **19** in $CDCl_3$ at 125.8 MHz.

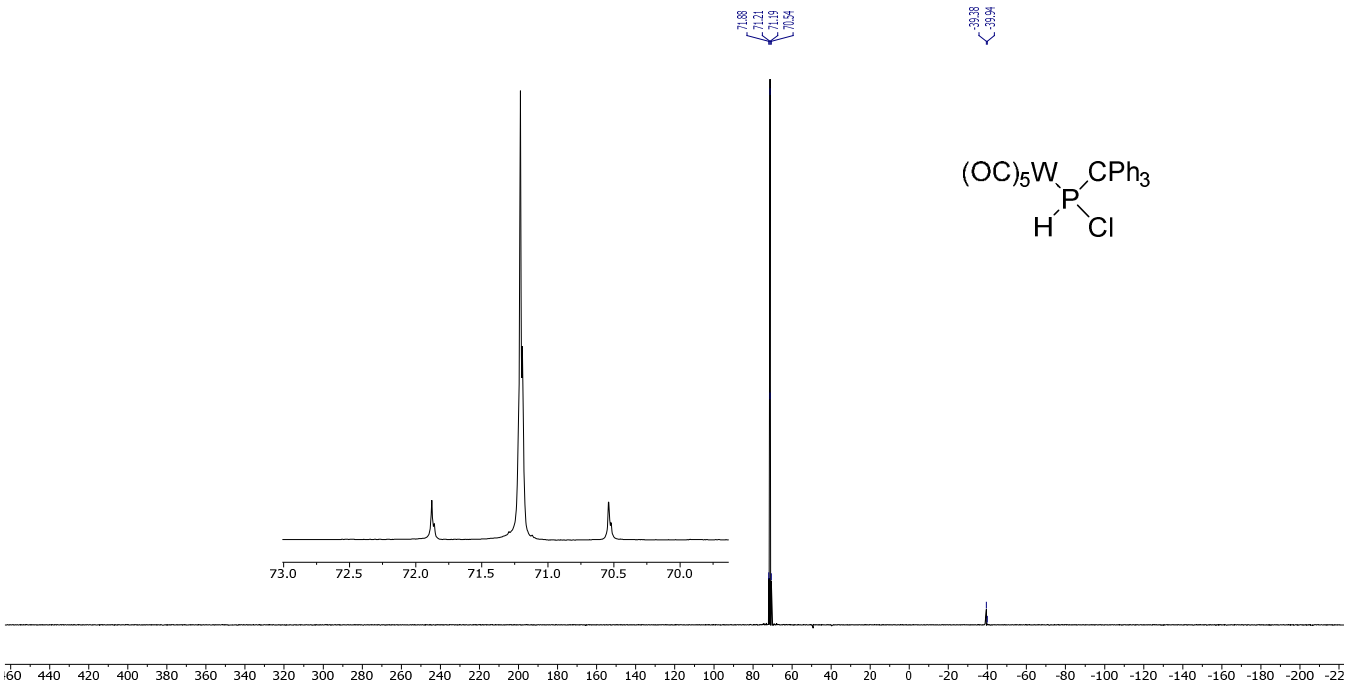

Figure S49: $^{31}P\{^{1}H\}$ NMR spectrum of **19** in $CDCl_3$ at 202.5 MHz.

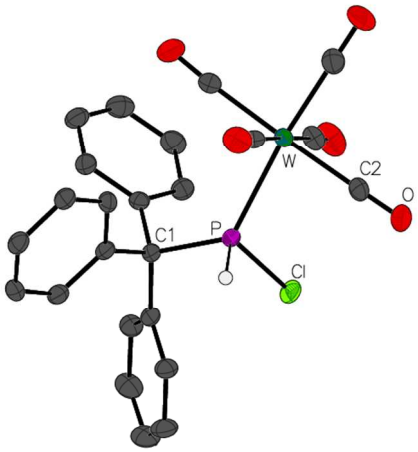

Figure S50: Crystal structure of **19**. Suitable single-crystals of **19** were obtained from a concentrated diethyl ether solution at 4 °C. Data were collected with a Nonius KappaCCD diffractometer equipped with a low-temperature device at 123 K by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by intrinsic phasing methods (SHELXT 2015) and refined by full-matrix least squares on F^2 (SHELXL 2015)[1]: $C_{24}H_{16}ClO_5PW$, Mr = 634.64, crystal dimensions 0.6 × 0.6 × 0.12 mm^3, triclinic, space group P-1, Z =2, a = 9.6127(4) Å, b = 10.5143(4) Å, c = 11.6185(5) Å, α =90.087(2)°, β =97.409(1)°, γ =94.466(1)°, V = 1160.87(8) $Å^3$, d_{calcd} = 1.816 g cm^{-3}, μ = 5.192 mm^{-1}, transmission factors (min/max) 0.3907/0.6478, multi-scan absorption correction, $2\theta_{max}$ = 55.992°, no. of unique data 5574, R_{int} = 0.0304, R_1 (for I >2σ(I)) = 0.0259, wR_2 (for all data) = 0.0714, final R_1 = 0.0294, goodness of fit 1.052, ΔF (max/min) = 1.97 /−1.65 e $Å^{-3}$. CCDC 1529746 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.