

Supporting Information

Synthesis of a 1-aza-2-phospha-acenaphthene complex profiting from coordination enabled chloromethane elimination

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1 General methods

All reactions were performed under dried and deoxygenated argon atmosphere using Schlenk or glovebox techniques. The used argon (>99.998%) was purified by a system of three columns (deoxygenation by a BTS copper catalyst (BASF PuriStar® R3-15S) at ca. 100 °C, removing moisture with silica gel, phosphorus pentoxide desiccant with indicator (Sicapent®) and calcium chloride). Glassware, spatulae, cannulae as well as filter papers were dried in a compartment dryer at 110 °C for at least one hour. Additionally, the glassware was heated with a heat gun (up to 550 °C) under active vacuum (<0.02 mbar) and filled with argon three times. Sterile syringes were purged with argon three times before use. The solvents were dried by standard procedures¹ by refluxing over proper desiccants under an argon atmosphere (*n*-pentane, petroleum ether 40/65 and toluene over sodium wire ($\varnothing = 2$ mm); diethyl ether stabilized with 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) and tetrahydrofuran over benzophenone and sodium wire) for several days and distilled before use. Alternatively, diethyl ether and toluene were dried using a MBraun SPS-800 solvent purification system. For filtration Schlenk frits or stainless steel cannulae ($\varnothing = 1$ mm and 2 mm) with Whatman® glass microfiber filters (grade GF/B) were used. After use, devices made of stainless steel were cleaned with acetone, water and diluted hydrochloric acid and glassware by storage in a concentrated solution of potassium hydroxide in isopropanol for at least two days and in diluted hydrochloric acid for one day. Afterwards, the glassware was washed with water and soap, acetone and petroleum ether 40/65. All joints were greased with OKS 1112 grease or with PTFE paste (Carl Roth). Vacuum was applied by a rotary vane pump (vacuubrand RZ6) enabling pressures 10^{-2} mbar.

NMR spectra were recorded on a Bruker Avance I 300 MHz, Bruker Avance I 400 MHz, Bruker Avance I 500 MHz or Bruker Avance III HD Ascend 500 MHz spectrometer at the NMR department of the University of Bonn and subsequently analyzed by the program *Mestrenova 14.2*. The calibration of the ¹H and ¹³C NMR spectra was done via the solvent residual signals relative to tetramethylsilane (<1% in CDCl₃) (C₆D₆: $\delta(^1\text{H}) = 7.16$ ppm and $\delta(^{13}\text{C}) = 128.06$ ppm).² All lock frequencies were calibrated internally against the ¹H signals of solutions of tetramethylsilane with a volume fraction of $\Phi \leq 1\%$ in the corresponding deuterated solvent. The used deuterated solvent C₆D₆ was dried over a potassium mirror, trap-to-trap recondensed and degassed by three freeze-pump-thaw cycles. The purified solvent was stored over 3 Å or 4 Å molecular sieves. The chemical shift (δ) is given in parts per million (ppm) and the coupling constant ($^nJ_{X,Y}$) in Hertz (Hz) as absolute values neglecting the sign where *n* is the number of bonds between the coupling nuclei X and Y. For assigning the multiplicity following abbreviations were used: s = singlet, d = doublet, dd = doublet of doublets, m = multiplet, sat = satellites and br = broad. For ¹H NMR spectra additionally the number of nuclei is given accordingly which is determined via integration. The ¹H and ¹³C NMR signals of compounds were assigned by a combination of COSY, NOESY, HMQC and HMBC experiments to unequivocally assign protons and carbon

resonances if necessary. All measurements were performed at ambient temperature (298 K) if not stated otherwise.

Mass spectra using electron impact ionization (EI) were performed on a Thermo Finnigan MAT 95 XL sector field instrument using an ionization energy of 70 eV. The calibration and referencing were done using perfluorokerosene (PFK). Only selected data are given for detected ions. The peaks are given in mass-to-charge ratio (m/z) while only the isotopomer with the highest relative abundance is represented. Additionally, the relative intensities of the peaks are given in parentheses and the proposed molecule fragments in square brackets if not stated otherwise.

ATR-IR spectra of solids were recorded in the spectral range of 4000–400 cm^{-1} on a Bruker Alpha FTIR spectrometer with a single-reflection ATR measurement attachment (Platinum-ATR Diamond) in a glovebox at ambient temperature. All analyses were performed using the programs *EZ OMNIC 7.3* of Fisher Scientific and *OPUS* of Bruker. Only selected wavenumbers of the absorption bands are given using reciprocal centimeters (cm^{-1}). The intensities of the bands are marked as very strong (vs), strong (s), medium (m), weak (w) or very weak (vw).

Elemental analyses were performed on a Elementar Vario Micro analysis device in quadruplicate or triplicate for each sample. All samples were prepared and weighed up in tin or silver sample containers using a micro-analytical balance in a glovebox. The mean C, H, N and S values are given for each compound.

Melting points were measured using an SRS DigiMelt device or a Büchi melting point determination device according to Dr. Tottoli. The samples were flame-sealed in a glass capillary ($\varnothing = 0.1$ mm) *in vacuo* (<0.02 mbar) and heated quickly (ca. 5 K/min) for a rough determination of the melting point or decomposition temperature. Afterwards, a heating rate of approximately 2 K/min was used until the sample melted or decomposed. The thermally treated samples were cooled to ambient temperature and studied by ^1H and/or ^{31}P NMR spectroscopy to confirm whether decomposition had occurred. No internal or external temperature corrections were performed.

Single crystal X-ray diffraction analyses were performed on a STOE IPDS-2T diffractometer, equipped with a low-temperature device (Oxford Cryostream 700 series) at 123(2) K or 180(2) K by using graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å). Intensities were measured by fine-slicing Φ and ω scans and corrected background, polarization and Lorentz effects. A semi-empirical absorption correction was applied for the data sets following Blessing's method.³ The structure was solved by direct methods and refined anisotropically by the least-squares procedure implemented in ShelX program system.⁴ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included isotropically refined using a riding model at the bound carbon atoms. The program *Olex2 1.5*⁵

of *OlexSys* was used for analyses and the ellipsoid representations of the molecular structures with the probability level set to 50%. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2250016 (**1**), CCDC-2250017 (**5**) and CCDC-2250018 (**6**) which can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

2 Experimental procedures and characterisation

Compound 1

A solution of 4.209 g (16.75 mmol, 1.0 eq.) of 8-dimethylamino-1-naphthyllithium etherate⁶ in 80 mL of diethyl ether was added to a solution of 6.6 mL (75.45 mmol, 4.5 eq.) of trichlorophosphane in 80 mL of diethyl ether while stirring at $-80\text{ }^{\circ}\text{C}$. The reaction mixture was slowly warmed up to ambient temperature and stirred for two days. The formed yellow suspension was filtered using a filter cannula, and the solid on the sinter was washed with diethyl ether ($3 \times 20\text{ mL}$). The filtrate and washings were combined and the solvent was removed *in vacuo* at ambient temperature to obtain a pale-yellow solid. The solid was further dried *in vacuo* at ambient temperature for 1 hour. The obtained analytical data were in accordance with literature.⁶ Yield: 4.37 g (16.1 mmol, 96%) (Lit.:⁶ 62%). ^1H NMR (400.13 MHz, 298 K, C_6D_6): δ / ppm = 9.12–6.76 (m, 6H; Ar-H), 2.15 (s, 6H; N(CH₃)₂). $^{31}\text{P}\{^1\text{H}\}$ NMR (162.00 MHz, 298 K, C_6D_6): δ / ppm = 130.6 (s).

Compound 5

Via $[\text{W}(\text{CO})_5(\text{CH}_2\text{Cl}_2)]$ (**2b**): A solution of 1.426 g (4.05 mmol, 1.1 eq.) of $[\text{W}(\text{CO})_6]$ in 240 mL of dichloromethane was photolyzed using a Hg vapor lamp at $-65\text{ }^{\circ}\text{C}$ for 1.5 hours. The generated $[\text{W}(\text{CO})_5(\text{CH}_2\text{Cl}_2)]$ (**2b**)⁷ solution was added *in situ* to 1.002 g (3.68 mmol, 1.0 eq.) of compound **1** and stirred for 4 hours at $-65\text{ }^{\circ}\text{C}$. The reaction mixture was warmed up to ambient temperature and stirred for another 15 hours. The solvent was removed *in vacuo* at ambient temperature obtaining a black solid. The product was extracted with three times 15 mL of diethyl ether via a filter cannula. Subsequently, the solvents were removed *in vacuo* at ambient temperature. Diethyl ether (20 mL) was added and the resulting solution was filtered through silica gel ($h = 1.5\text{ cm}$, $d = 2\text{ cm}$) at $-20\text{ }^{\circ}\text{C}$ using diethyl ether. The volatiles were removed *in vacuo* at ambient temperature, the product was obtained as yellow solid with minor impurities of $[\text{W}(\text{CO})_6]$. Yield: 0.12 g (0.22 mmol, 6%). Via $[\text{W}(\text{CO})_5(\text{CH}_3\text{CN})]$ (**2c**): A solution of 0.938 g (2.57 mmol, 1.2 eq.) $[\text{W}(\text{CO})_5(\text{CH}_3\text{CN})]$ (**2c**)⁸ in 6 mL of toluene was added via transfer cannula to a suspension of 0.600 g (2.20 mmol, 1.0 eq.) of compound **1** in 14 mL of toluene at ambient temperature. The reaction mixture was stirred for 25 hours at $50\text{ }^{\circ}\text{C}$ and another 114 hours at $70\text{ }^{\circ}\text{C}$. The obtained yellow supernatant and black solid were separated via filtration using a filter cannula at ambient temperature and extraction with three times 10 mL of toluene. All volatiles were

removed *in vacuo* at 40 °C. Afterwards, side products were removed via sublimation *in vacuo* at 45 °C. The raw product was further purified by filtration through dried silica gel (h = 1.5 cm, d = 2 cm) using diethyl ether at –20 °C. After removal of solvents *in vacuo* at ambient temperature, a yellow solid was obtained. Yield: 0.25 g (0.45 mmol, 20%). Mp 110–111 °C (dec.). Elemental analysis calcd (%) for C₁₆H₉NO₅PCIW: C 35.25, H 1.66, N 2.57; found: C 35.33, H 3.20, N 2.07. IR (ATR Diamond): ν_{\max} / cm⁻¹ = 1910 (s) (CO), 1993 (s) (CO), 2078 (m) (CO). ¹H NMR (500.04 MHz, 298 K, C₆D₆): δ / ppm = 7.70 (dd, ³J_{P,H} = 7.02 Hz, ³J_{H,H} = 6.99 Hz, 1H; C²-H), 7.44 (d, ³J_{H,H} = 8.21 Hz, 1H; C³-H), 7.17–7.03 (m, 3H; Ar-H), 6.16 (d, ³J_{H,H} = 7.13 Hz, 1H; C⁷-H), 2.91 (d, ³J_{P,H} = 14.04 Hz, 3H; N-CH₃). ¹³C{¹H} NMR (125.74 MHz, 298 K, C₆D₆): δ / ppm = 198.0 (d_{sat}, ²J_{P,C} = 38.0 Hz, ¹J_{W,C} = 174.5 Hz; *trans*-CO), 194.8 (d_{sat}, ²J_{P,C} = 8.4 Hz, ¹J_{W,C} = 125.9 Hz; *cis*-CO), 145.4 (d, ³J_{P,C} = 4.1 Hz; Ar-C⁸), 136.9 (d, ¹J_{P,C} = 46.5 Hz; Ar-C¹), 131.8 (d, ³J_{P,C} = 3.2 Hz; Ar-C^{4a}), 131.0 (s; Ar-C³H), 128.9 (d, ⁴J_{P,C} = 3.0 Hz; Ar-C⁴H), 128.3 (s; Ar-C⁵H), 127.1 (d, ²J_{P,C} = 6.8 Hz; Ar-C^{8a}), 126.5 (d, ²J_{P,C} = 21.8 Hz; Ar-C²H), 119.1 (s; Ar-C⁶H), 105.9 (d, ³J_{P,C} = 7.7 Hz; Ar-C⁷H), 28.8 (d, ²J_{P,C} = 8.8 Hz; N-CH₃). ³¹P{¹H} NMR (202.44 MHz, 298 K, C₆D₆): δ / ppm = 111.6 (s_{sat}, ¹J_{W,P} = 332.4 Hz). ³¹P NMR (202.44 MHz, 298 K, C₆D₆): δ / ppm = 111.6 (m_{sat}, ¹J_{W,P} = 332.4 Hz). MS (EI, 70 eV): *m/z* (%) = 544.9 (4) [M]⁺, 527.0 (2) [M-Cl+OH]⁺, 510.0 (1) [M-Cl]⁺, 454.0 (3) [M-Cl-2CO]⁺, 405.0 (15) [M-5CO]⁺, 186.1 (100) [M-W(CO)₅-Cl]⁺, 171.1 (5) [M-W(CO)₅-Cl-CH₃]⁺. HRMS (EI, 70 eV): *m/z* calcd for [C₁₆H₉NO₅PCIW]⁺: 544.9416; found: 544.9386.

Compound 6

Compound 5 (prepared *in situ* using 1.033 g (3.80 mmol, 1.0 eq.) of compound 1 and 1.373 g (3.76 mmol, 1.0 eq.) of [W(CO)₅(CH₃CN)]⁸) was passed as crude material through a column with moist silica gel (h = 8 cm, d = 1 cm) using 180 mL of a 1:1 diethyl ether/petrol ether (40/65) mixture at ambient temperature to obtain a yellow solution. All volatiles were removed *in vacuo* at 40 °C to obtain a yellow powder. Yield: 0.25 g (0.47 mmol, 12%). Mp 120–121 °C (dec.). Elemental analysis calcd (%) for C₁₆H₉NO₅PCIW: C 36.46, H 1.91, N 2.66; found: C 37.43, H 2.38, N 2.63. IR (ATR Diamond): ν_{\max} / cm⁻¹ = 1900 (s) (CO), 1982 (s) (CO), 2073 (s) (CO), 3473 (s) (OH). ¹H NMR (500.04 MHz, 298 K, C₆D₆): δ / ppm = 7.60 (dd, ³J_{P,H} = 7.18 Hz, ³J_{H,H} = 7.14 Hz, 1H; C²-H), 7.51 (d, ³J_{H,H} = 8.68 Hz, 1H; C³-H), 7.25–7.18 (m, 2H; Ar-H), 7.07 (d, ³J_{H,H} = 8.31 Hz, 1H; Ar-H), 6.11 (d, ³J_{H,H} = 7.27 Hz, 1H; C⁷-H), 2.90 (d, ³J_{P,H} = 9.44 Hz, 3H; N-CH₃), 2.85 (br s, 1H; P-OH). ¹³C{¹H} NMR (125.74 MHz, 298 K, C₆D₆): δ / ppm = 199.1 (d_{sat}, ²J_{P,C} = 29.4 Hz, ¹J_{W,C} = 140.3 Hz; *trans*-CO), 195.9 (d_{sat}, ²J_{P,C} = 9.0 Hz, ¹J_{W,C} = 125.0 Hz; *cis*-CO), 145.8 (d, ³J_{P,C} = 2.1 Hz, Ar-C⁸), 136.2 (d, ¹J_{P,C} = 51.1 Hz; Ar-C¹), 131.7 (d, ³J_{P,C} = 4.4 Hz; Ar-C^{4a}), 130.1 (s; Ar-C³H), 129.2 (s; Ar-C⁴H), 128.4 (s; Ar-C⁵H), 127.0 (d, ²J_{P,C} = 7.2 Hz; Ar-C^{8a}), 126.4 (d, ²J_{P,C} = 18.7 Hz; Ar-C²H), 117.2 (s; Ar-C⁶H), 102.8 (s; Ar-C⁷H), 29.0 (d, ²J_{P,C} = 11.8 Hz; N-CH₃). ³¹P{¹H} NMR (202.44 MHz, 298 K, C₆D₆): δ / ppm = 118.0 (s_{sat}, ¹J_{W,P} = 320.9 Hz). ³¹P NMR (202.44 MHz, 298 K, C₆D₆): δ / ppm = 118.0 (br s_{sat}, ¹J_{W,P} = 320.9 Hz). MS (EI, 70 eV): *m/z* (%) = 527.0 (18) [M]⁺, 471.0 (8) [M-2CO]⁺, 443.0 (12) [M-3CO]⁺, 415.0

(6) $[M-4CO]^+$, 387.0 (28) $[M-5CO]^+$, 203.1 (8) $[M-W(CO)_5]^+$, 186.1 (100) $[M-W(CO)_5-OH]^+$. HRMS (EI, 70 eV): m/z calcd for $[C_{16}H_{10}NO_6P^{182}W]^+$: 524.9728; found: 524.9745.

3 NMR spectra

Compound 1

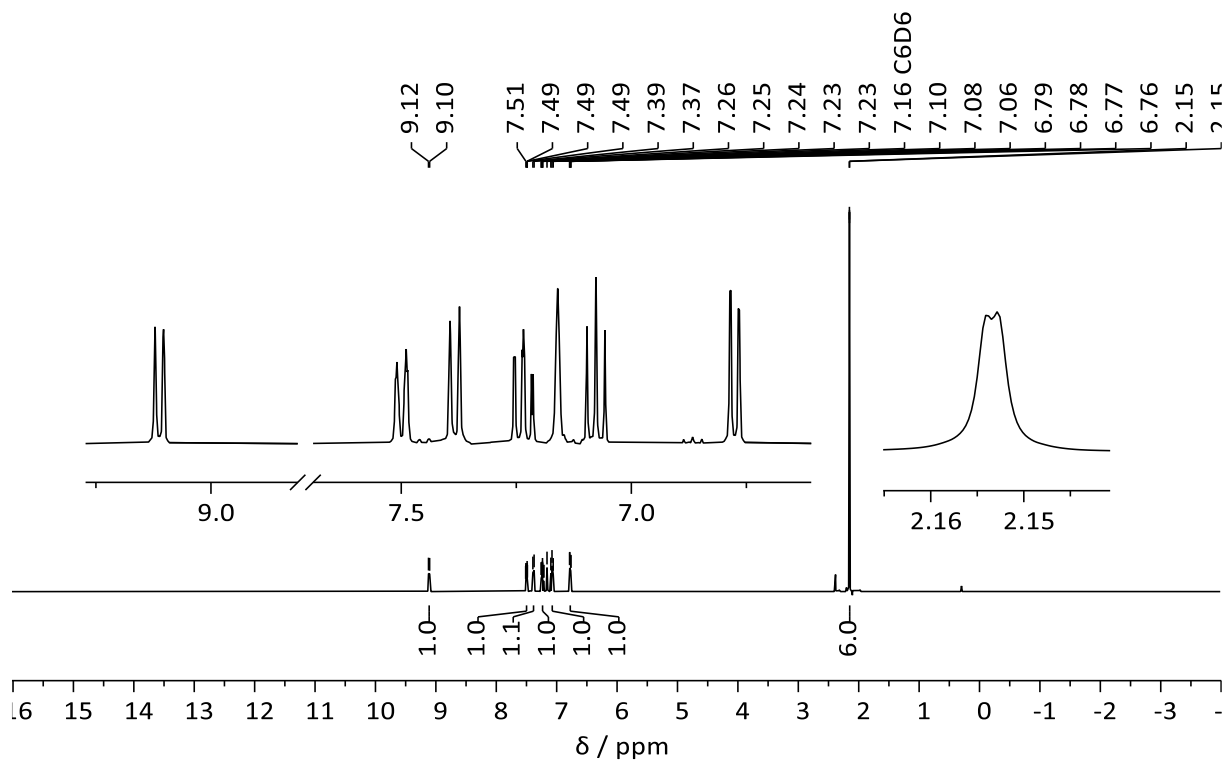


Figure S1 1H NMR spectrum (400.13 MHz, C_6D_6 , 298 K) of compound 1.

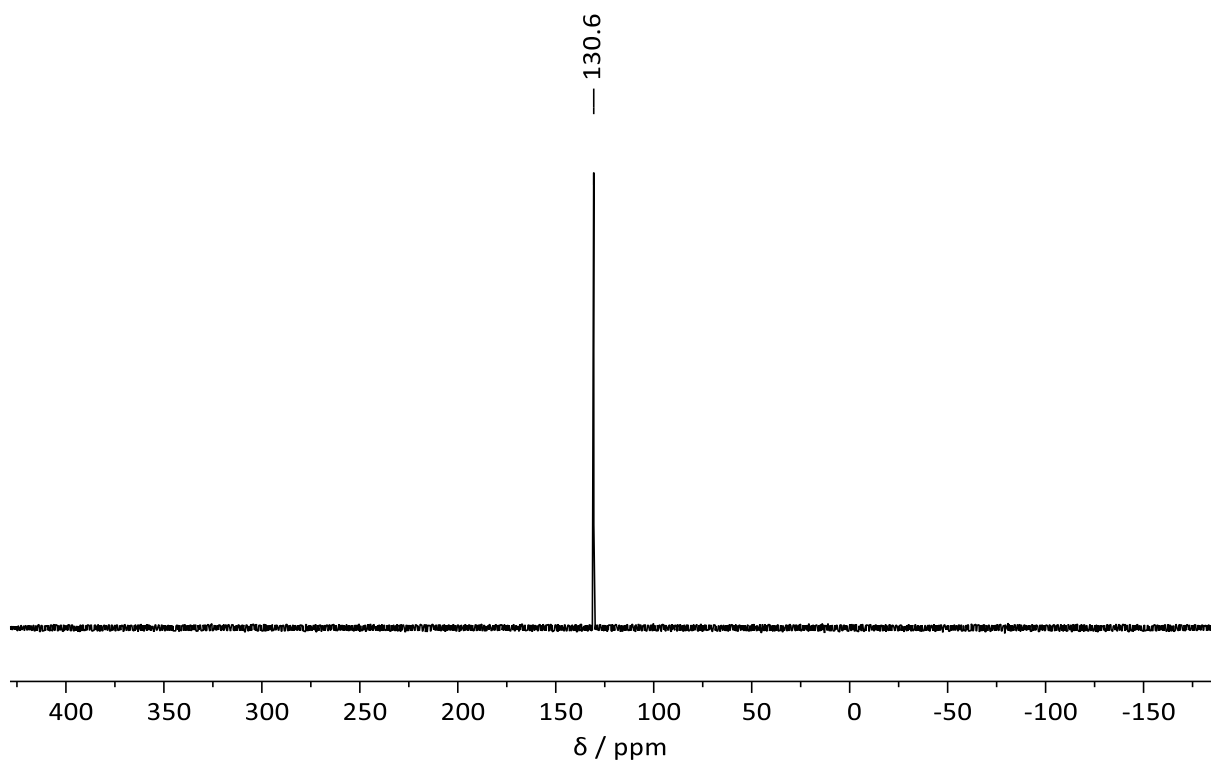


Figure S2 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162.00 MHz, C_6D_6 , 298 K) of compound **1**.

Reaction of **1** with **2a**

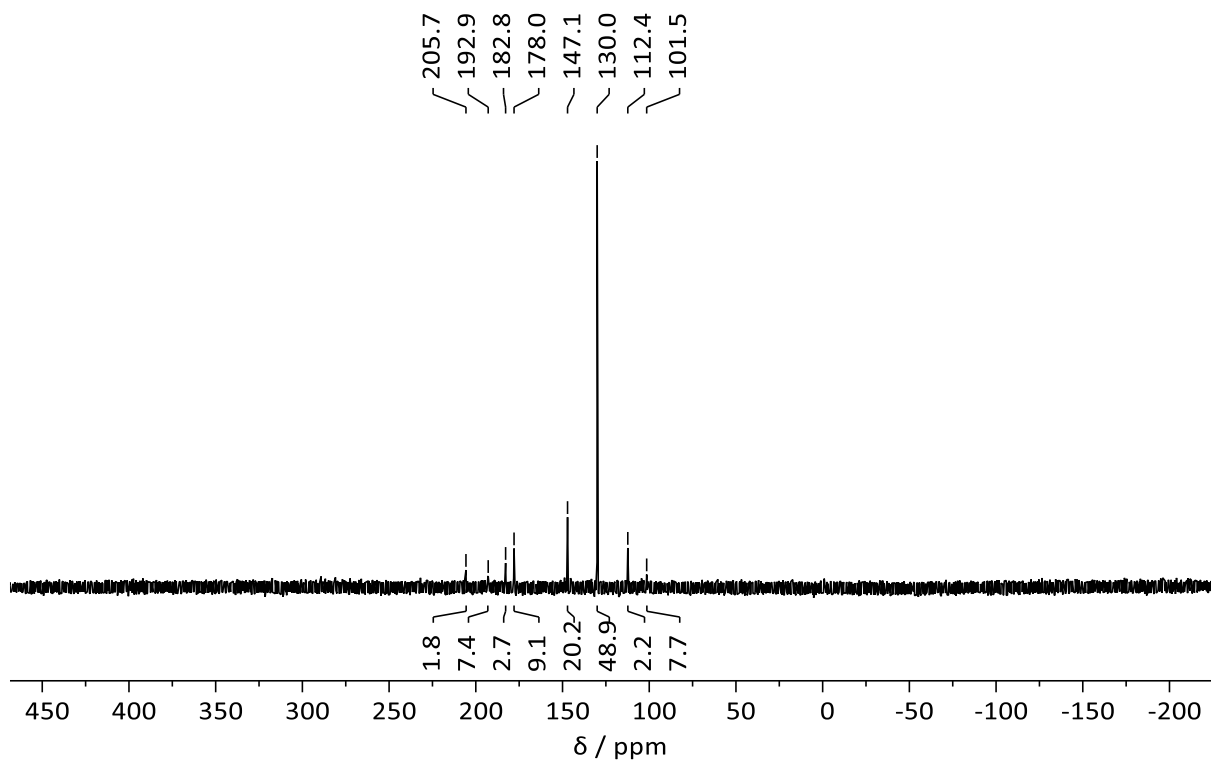


Figure S3 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121.51 MHz, THF, 298 K) of the reaction mixture of **1** with **2a**.

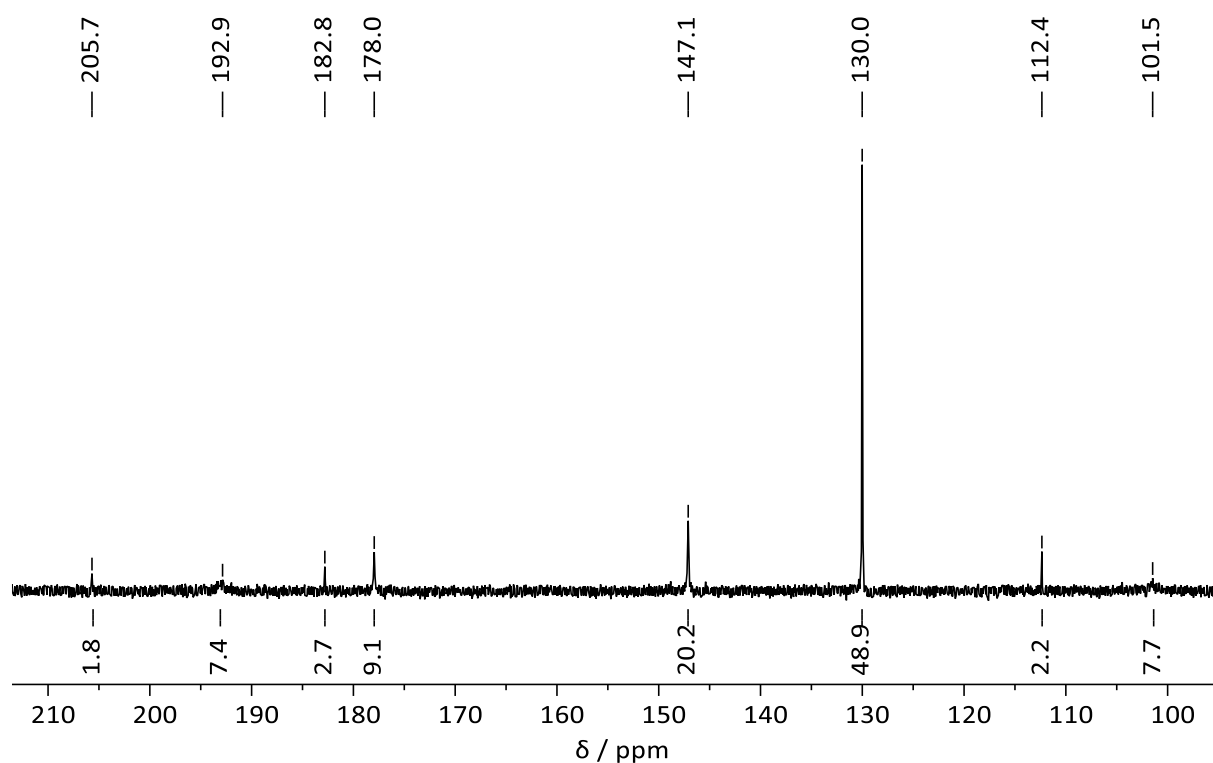


Figure S4 Zoom into the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121.51 MHz, THF, 298 K) of the reaction mixture of **1** with **2a** (Figure S3).

Reaction of **1** with **2b**

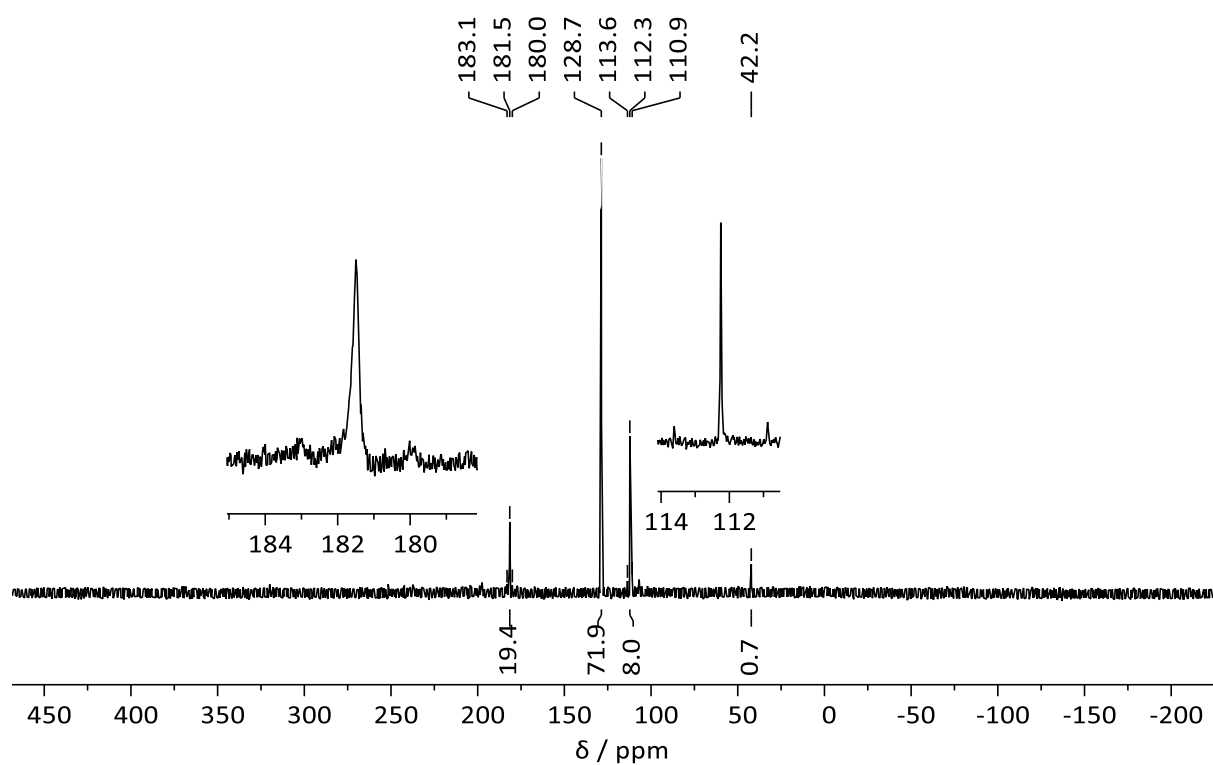


Figure S5 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121.51 MHz, CH_2Cl_2 , 298 K) of the reaction mixture of **1** with **2b**.

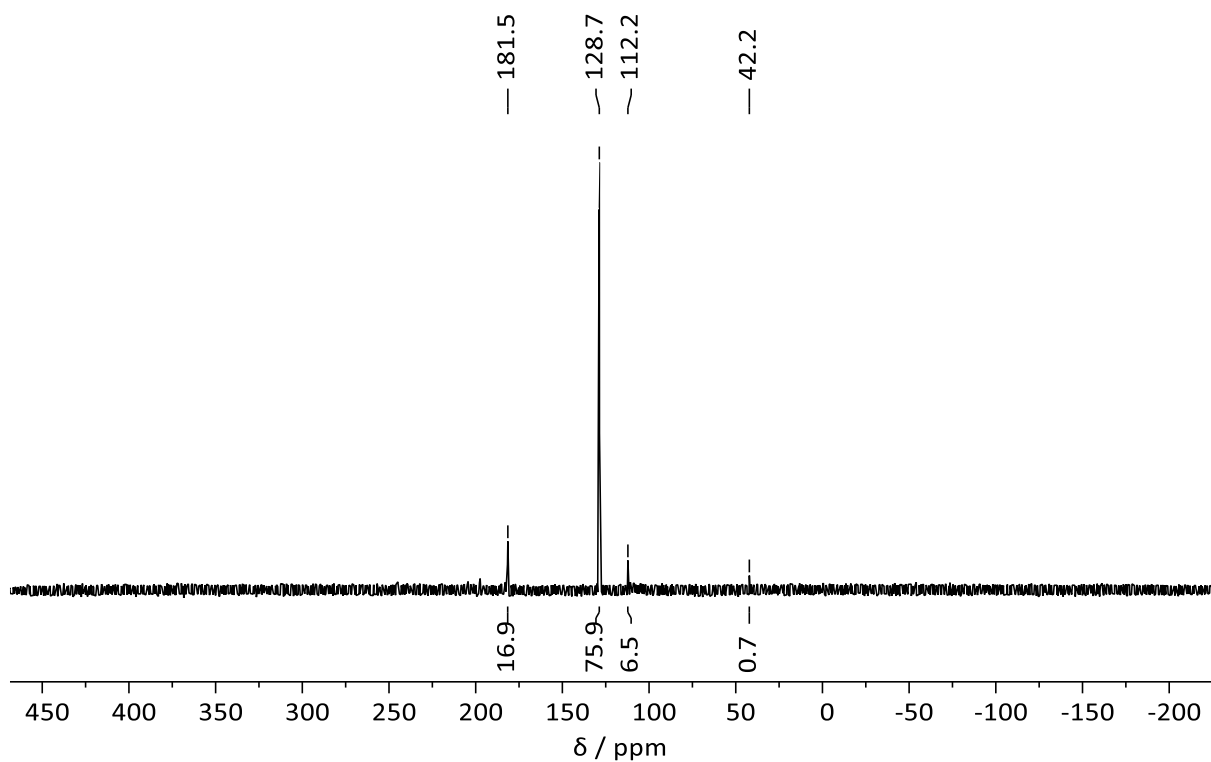


Figure S6 ^{31}P NMR spectrum (121.51 MHz, CH_2Cl_2 , 298 K) of the reaction mixture of **1** with **2b**.

Compound 5

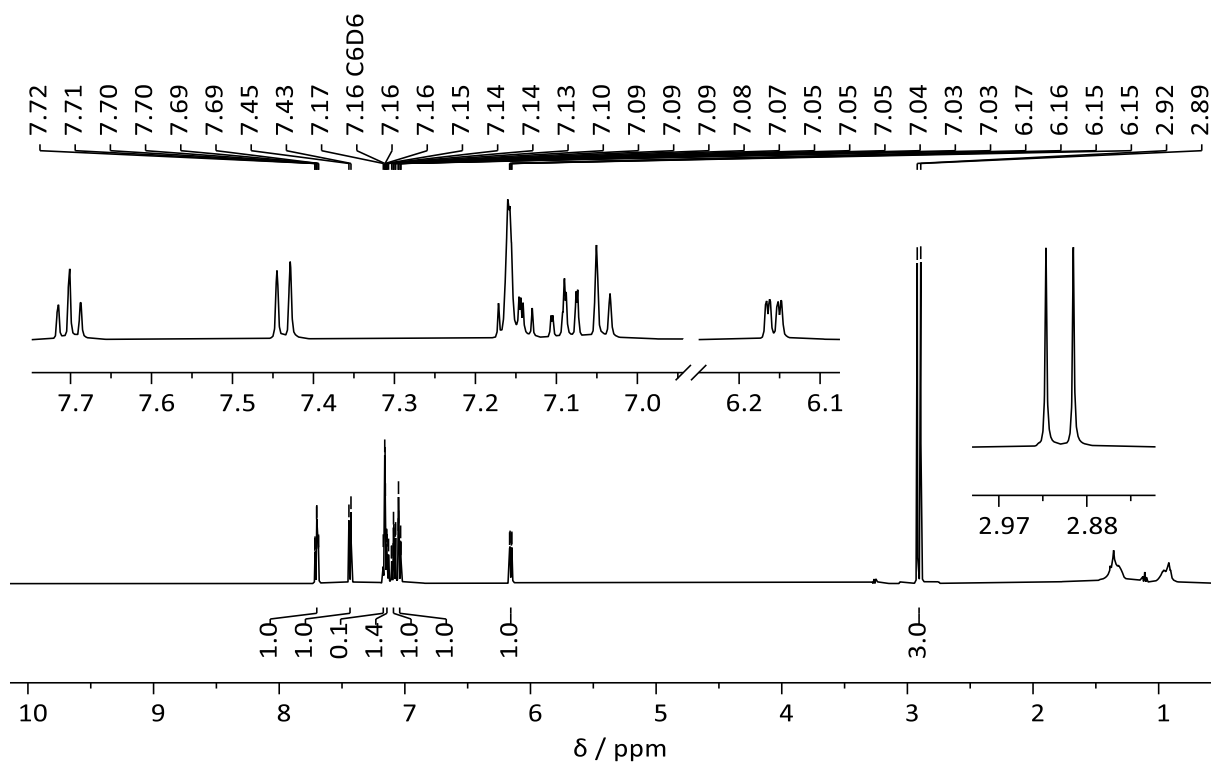


Figure S7 ^1H NMR spectrum (500.04 MHz, C_6D_6 , 298 K) of complex **5**.

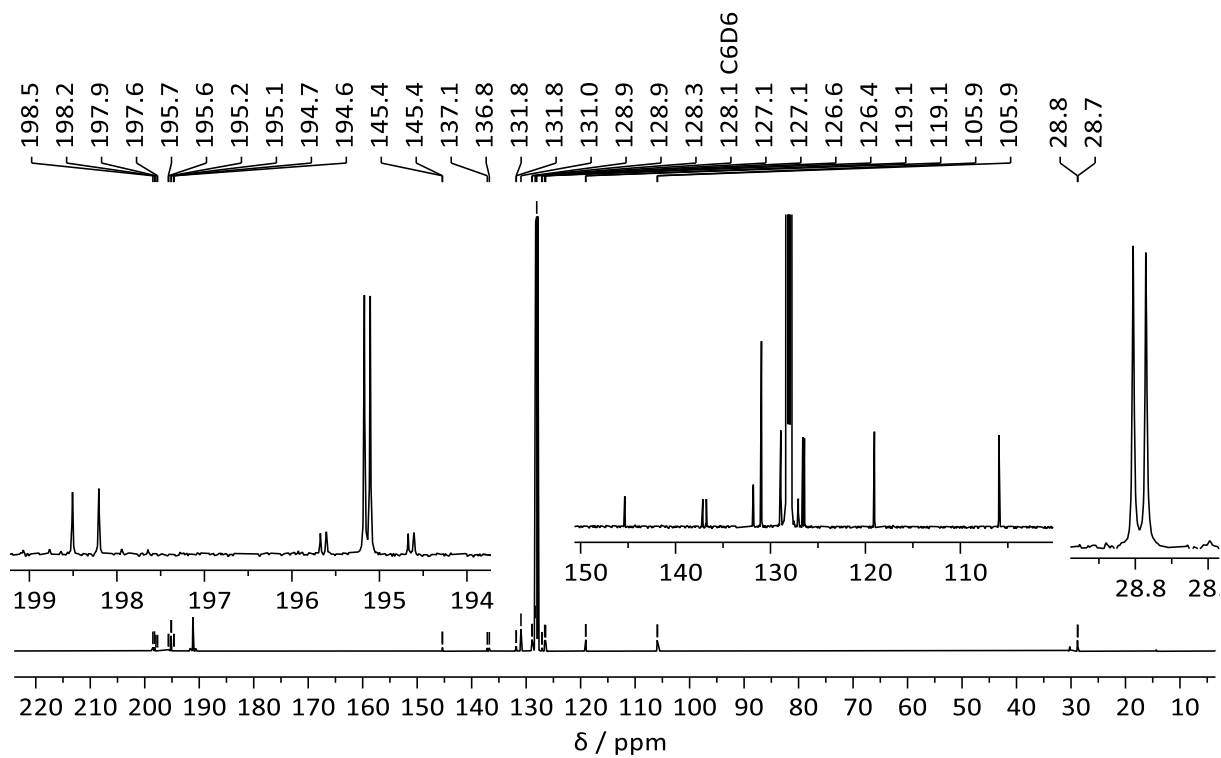


Figure S8 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125.75 MHz, C₆D₆, 298 K) of complex 5.

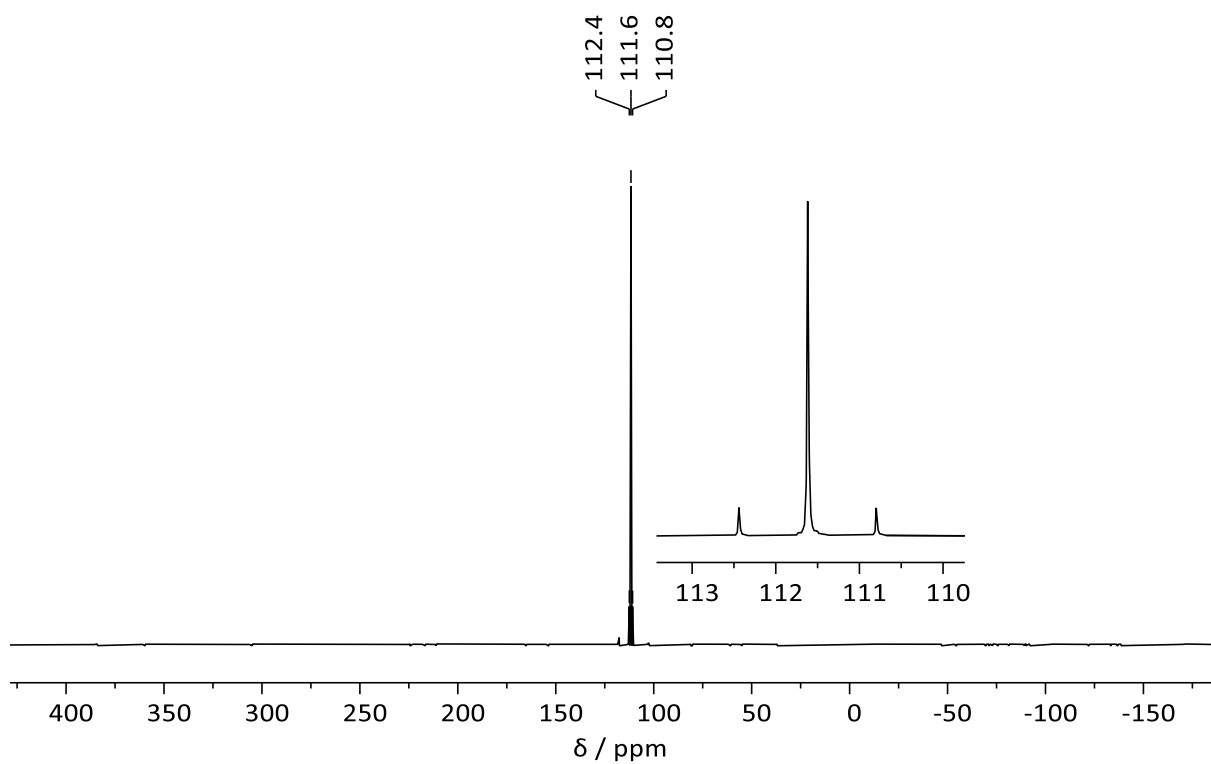


Figure S9 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202.44 MHz, C₆D₆, 298 K) of complex 5.

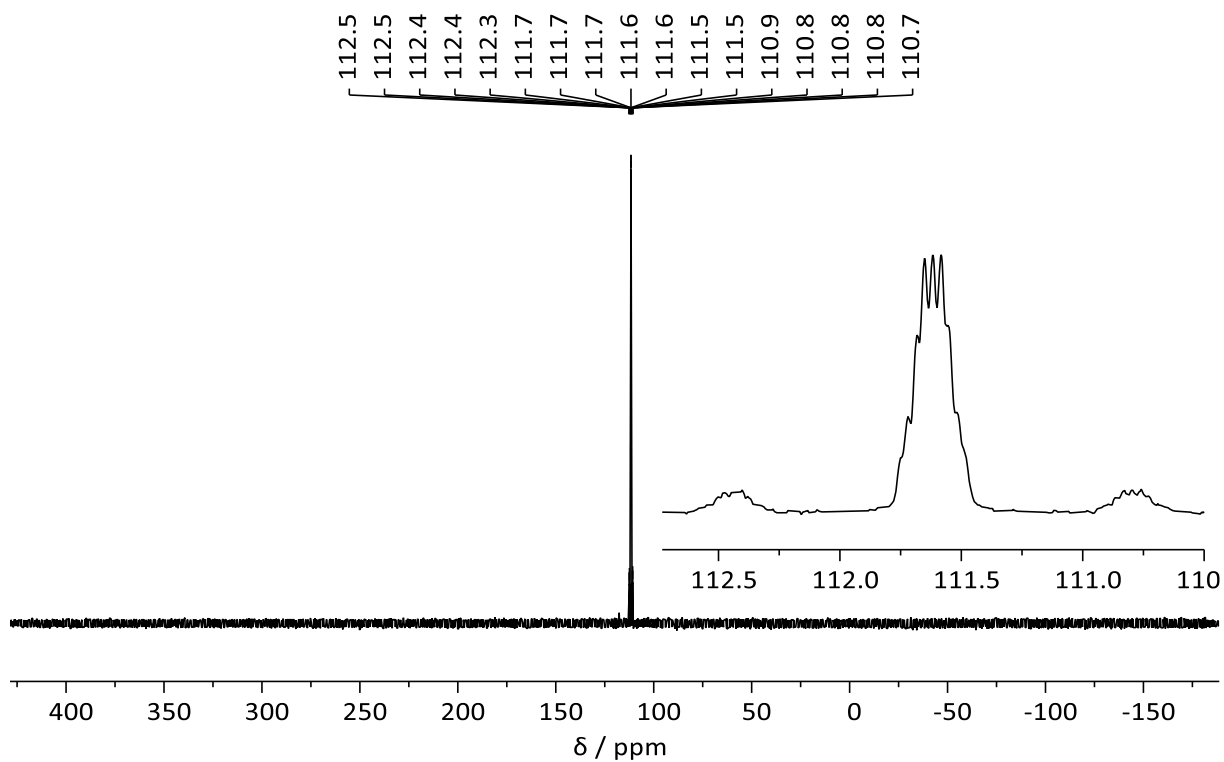


Figure S10 ^{31}P NMR spectrum (202.44 MHz, C_6D_6 , 298 K) of complex 5.

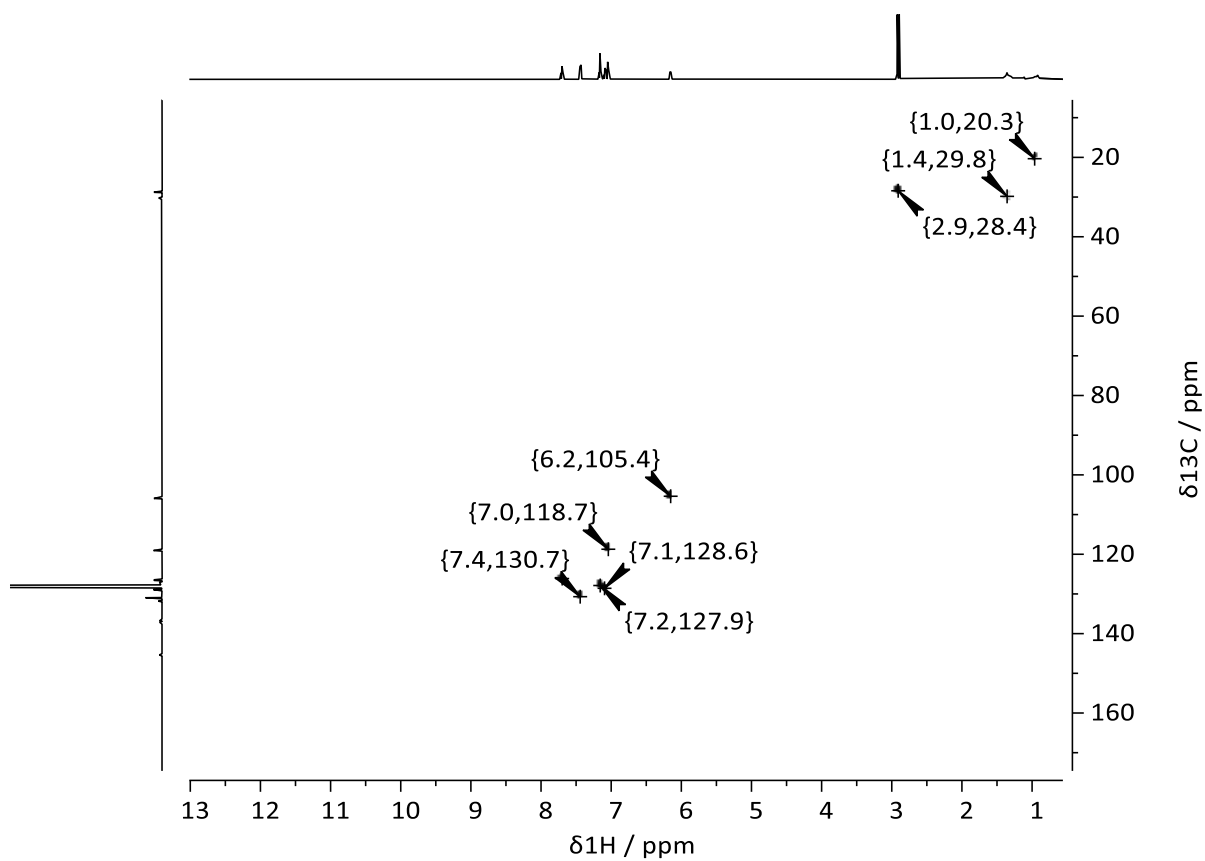


Figure S11 ^1H , ^{13}C HSQC NMR spectrum (500.04 MHz, 125.75 MHz, C_6D_6 , 298 K) of complex 5.

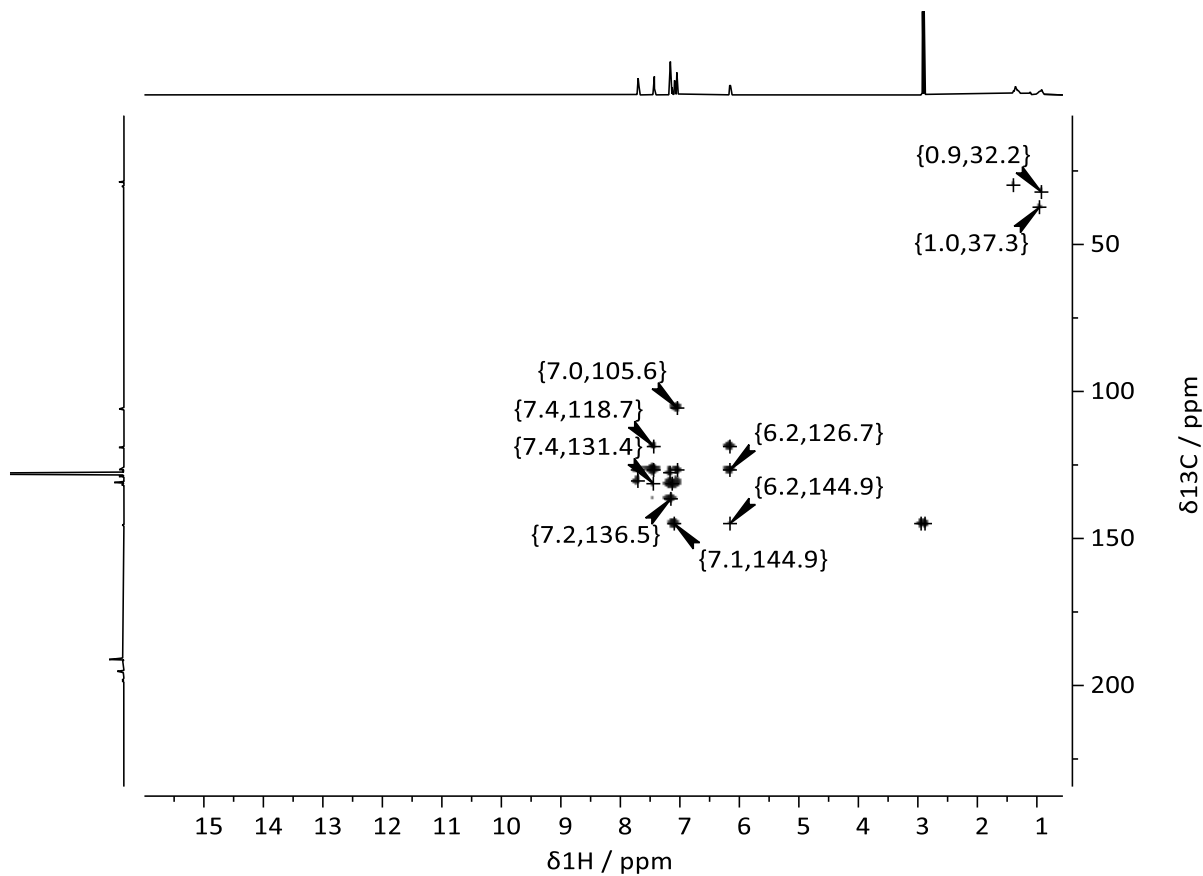


Figure S12 ^1H , ^{13}C HMBC NMR spectrum (500.04 MHz, 125.75 MHz, C_6D_6 , 298 K) of complex 5.

Compound 6

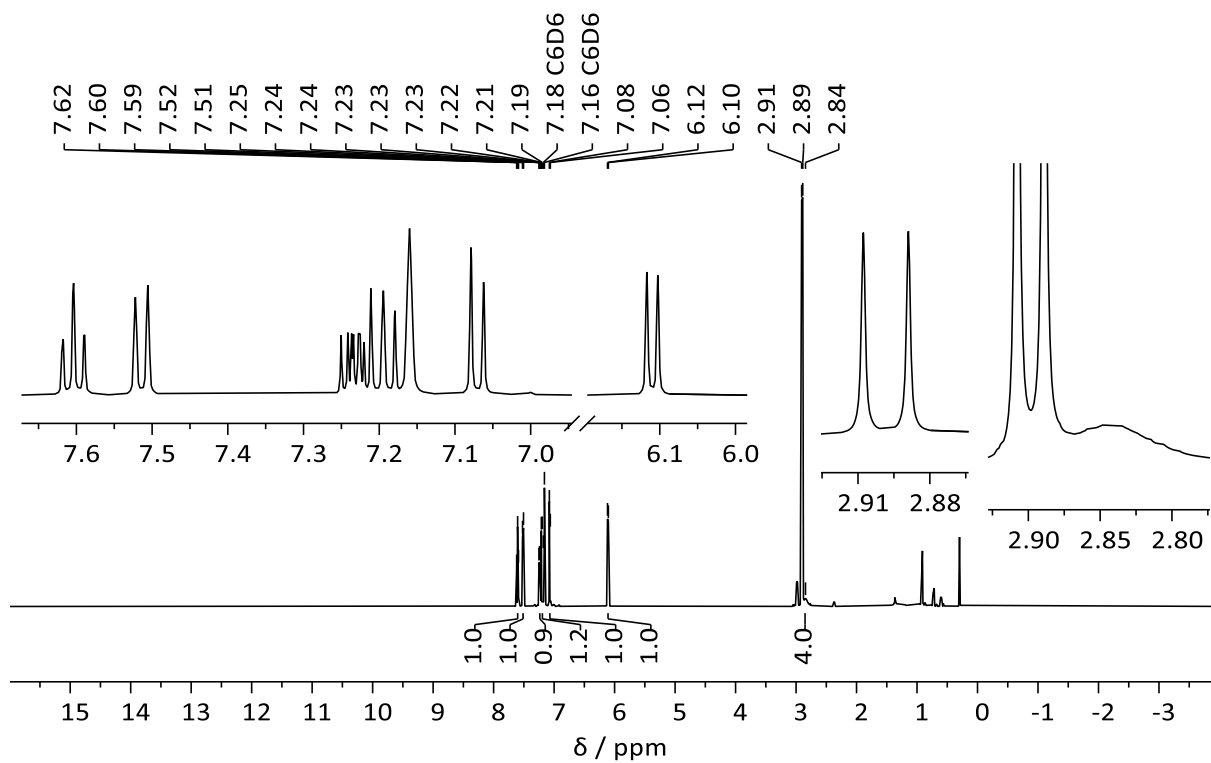


Figure S13 ^1H NMR spectrum (500.04 MHz, C_6D_6 , 298 K) of complex 6.

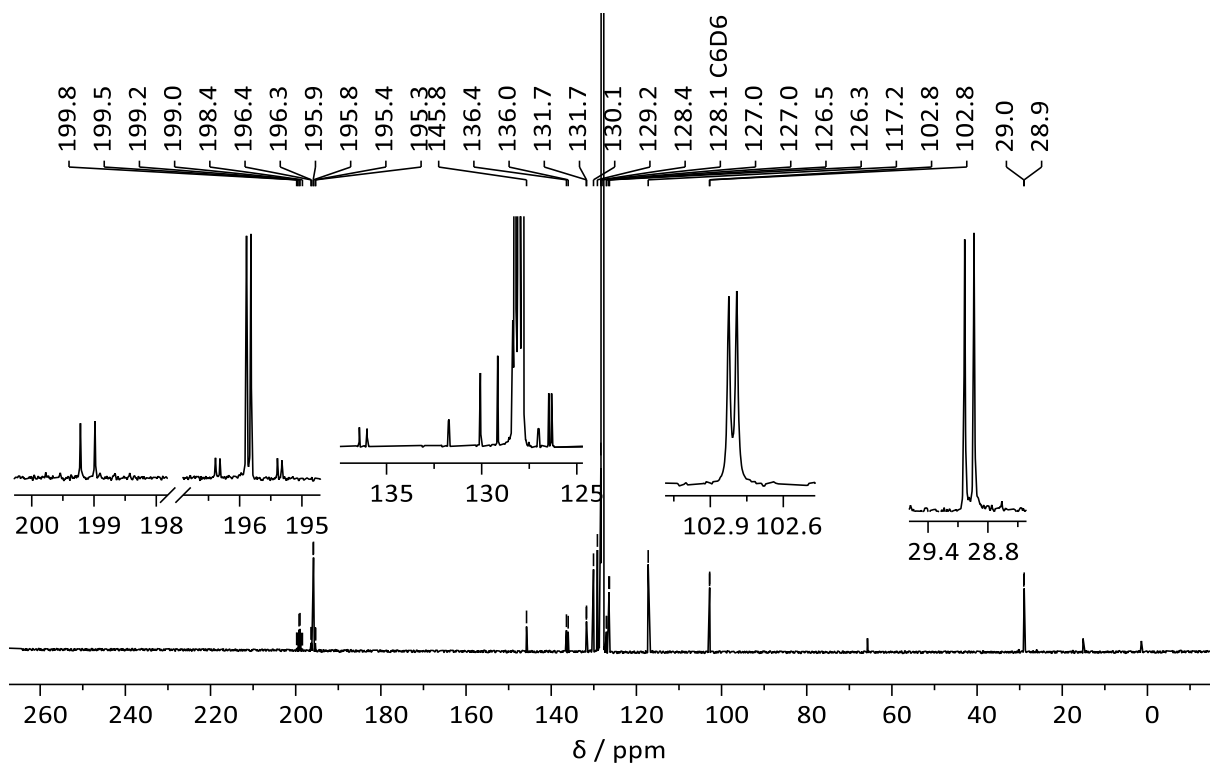


Figure S14 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125.75 MHz, C_6D_6 , 298 K) of complex **6**.

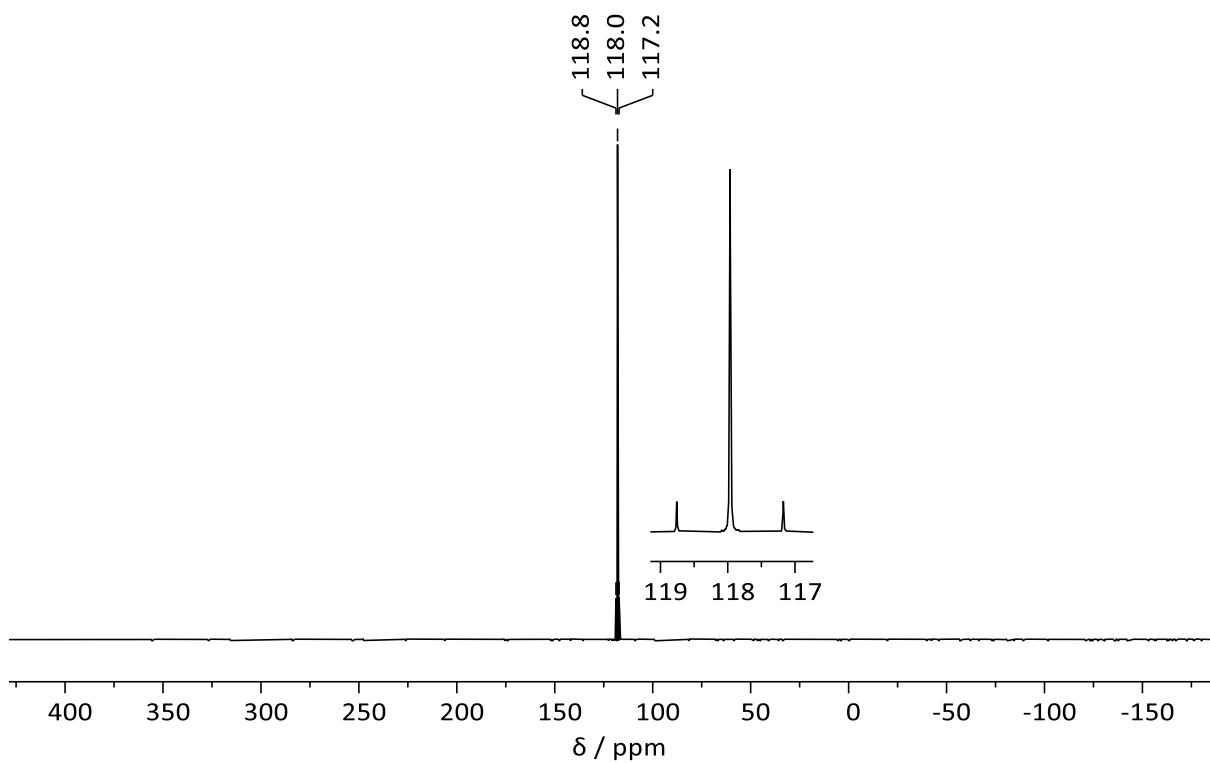


Figure S15 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202.44 MHz, C_6D_6 , 298 K) of complex **6**.

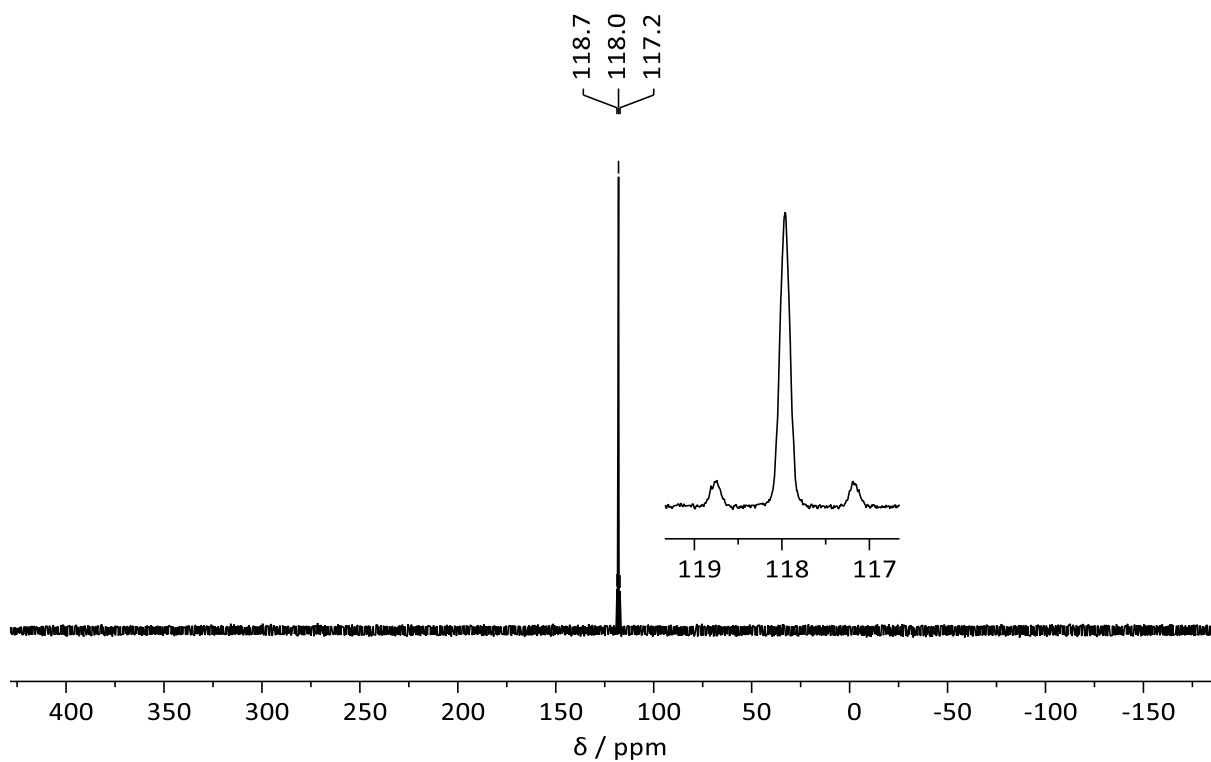


Figure S16 ³¹P NMR spectrum (202.44 MHz, C₆D₆, 298 K) of complex 6.

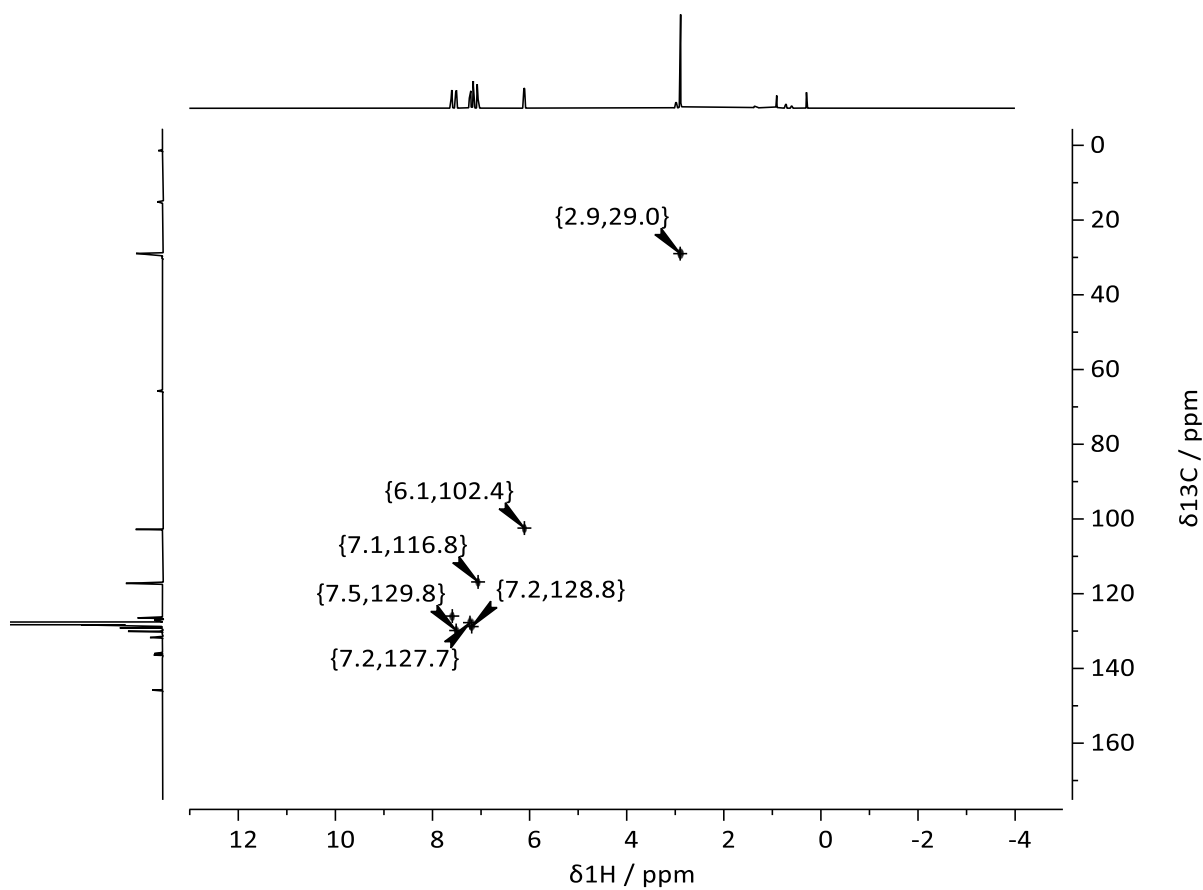


Figure S17 ¹H, ¹³C HSQC NMR spectrum (500.04 MHz, ¹³C, 125.75 MHz, C₆D₆, 298 K) of complex 6.

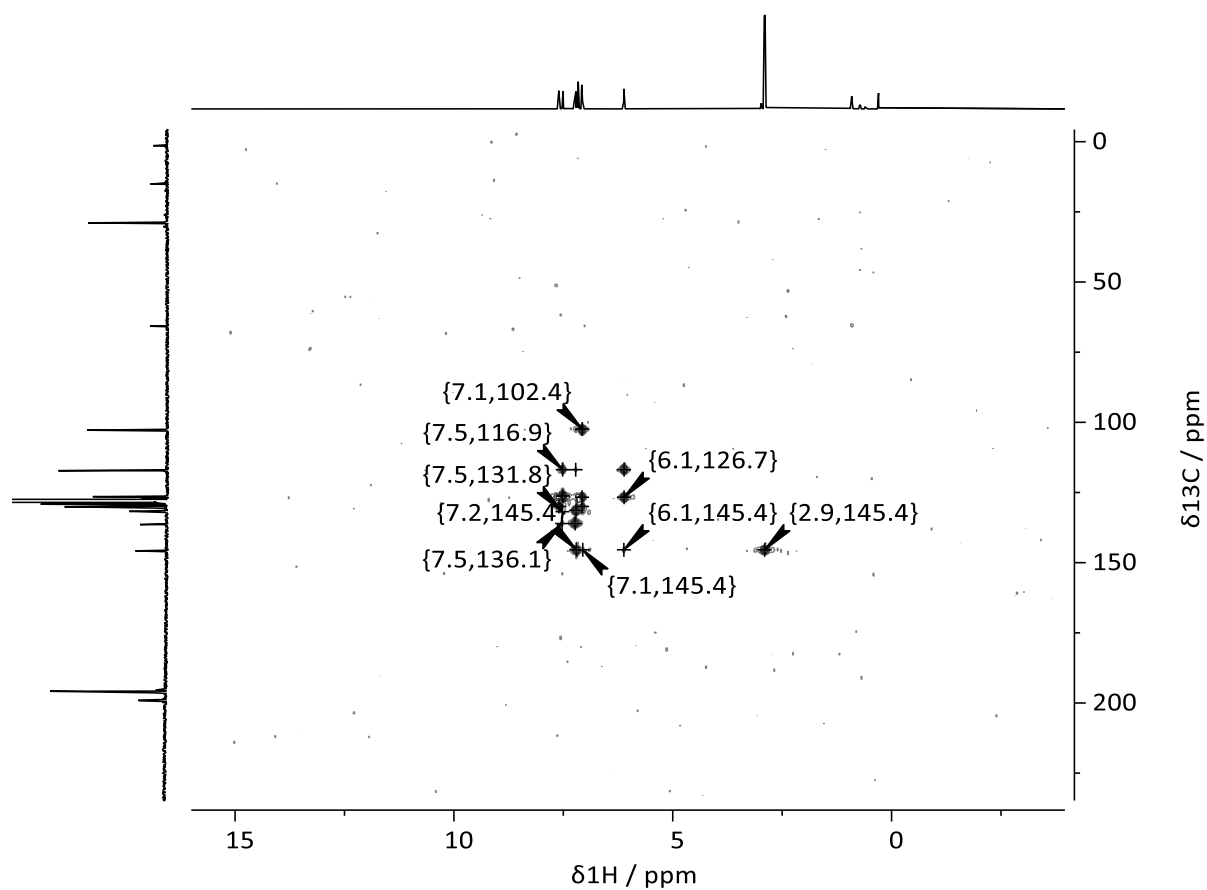


Figure S18 ^1H , ^{13}C HMBC NMR spectrum (500.04 MHz, 125.75 MHz, C_6D_6 , 298 K) of complex 6.

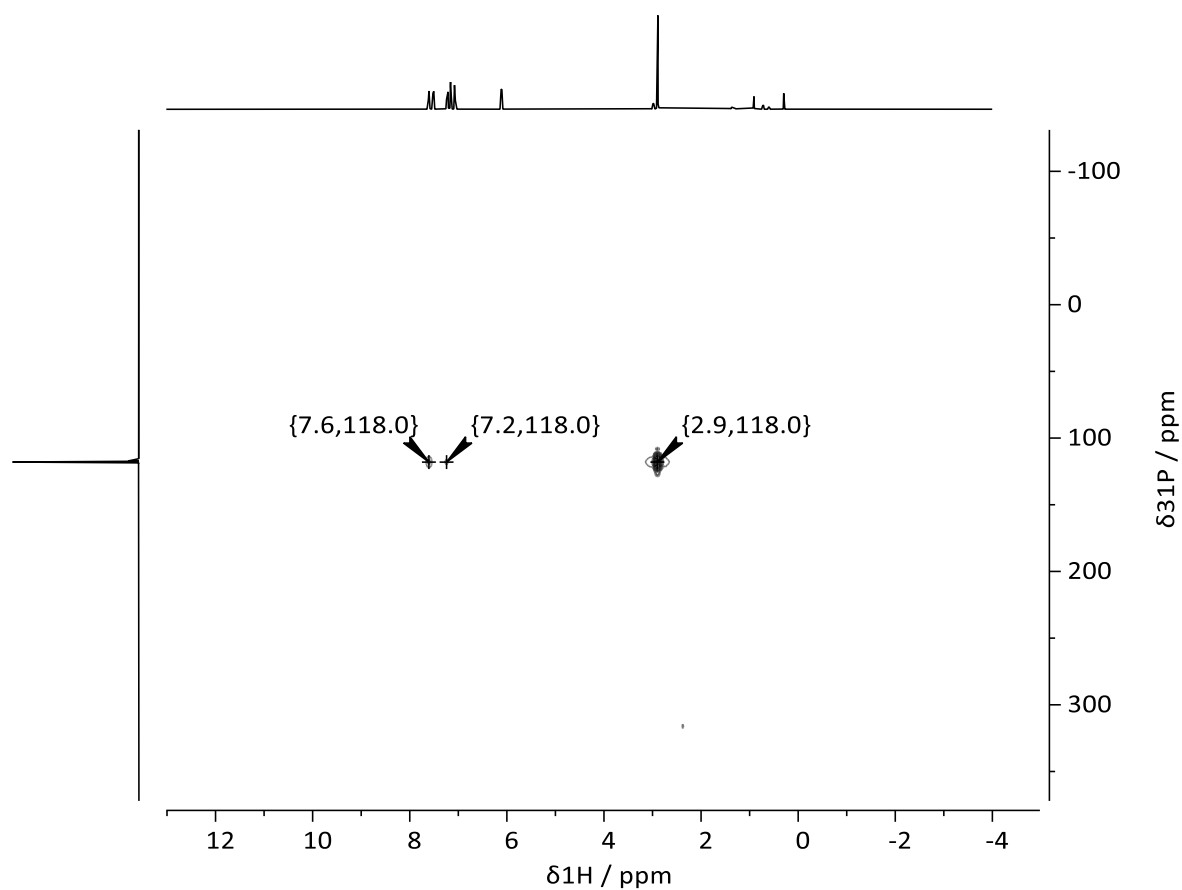


Figure S19 ^1H , ^{31}P HMBC NMR spectrum (500.04 MHz, 202.44 MHz, C_6D_6 , 298 K) of complex 6.

4 X-ray diffraction studies

Compound 1

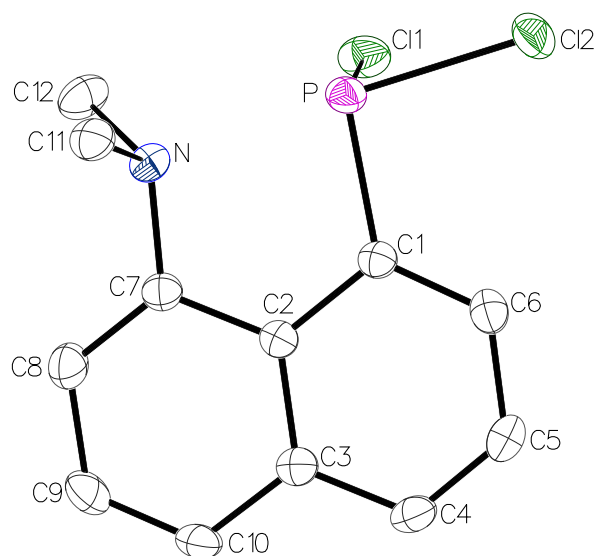


Figure S20 Molecular structure of **1** in the single crystal lattice at 123(2) K. Thermal ellipsoids are set at 50% probability. Hydrogen atoms were omitted for clarity. Suitable single crystals were obtained as clear colorless blocks by vapor diffusion of *n*-pentane into a concentrated solution of 19 mg of **1** in 0.8 mL of diethyl ether at ambient temperature in a glovebox. CCDC 2250016.

Table S1 Crystal data and structure refinements for **1**.

| | |
|--|---|
| Identification code | GSTR720, TB-017 // GXray6598 |
| Crystal habitus | clear colorless block |
| Device type | STOE IPDS-2T |
| Empirical formula | C ₁₂ H ₁₂ Cl ₂ NP |
| Moiety formula | C ₁₂ H ₁₂ Cl ₂ NP |
| Formula weight / g/mol | 272.10 |
| <i>T</i> / K | 123(2) |
| Crystal system | orthorhombic |
| Space group | <i>P</i> 2 ₁ 2 ₁ 2 ₁ |
| <i>a</i> / Å | 9.5389(6) |
| <i>b</i> / Å | 9.7198(5) |
| <i>c</i> / Å | 13.2575(6) |
| α / ° | 90 |
| β / ° | 90 |
| γ / ° | 90 |
| <i>V</i> / Å ³ | 1229.19(11) |
| <i>Z</i> | 4 |
| ρ_{calc} / g/cm ³ | 1.470 |
| μ / mm ⁻¹ | 0.628 |
| <i>F</i> (000) | 560.0 |
| Crystal size / mm ³ | 0.31 × 0.29 × 0.25 |

| | |
|--|---|
| Absorption correction | Integration |
| Min. and max. transmission | 0.9052 and 0.9803 |
| Radiation | Mo-K α ($\lambda = 0.71073$ Å) |
| 2 θ range for data collection / ° | 5.984 to 55.994 |
| Completeness to θ | 0.986 |
| Index ranges | $-8 \leq h \leq 12$, $-11 \leq k \leq 12$, $-15 \leq l \leq 17$ |
| Reflections collected | 4445 |
| Independent reflections | 2932 ($R_{int} = 0.0141$, $R_{\sigma} = 0.0252$) |
| Data / restraints / parameters | 2932 / 0 / 147 |
| Goodness-of-fit on F^2 | 0.958 |
| Final R indexes ($I \geq 2\sigma(I)$) | $R_1 = 0.0209$, $\omega R_2 = 0.0463$ |
| Final R indexes (all data) | $R_1 = 0.0255$, $\omega R_2 = 0.0470$ |
| Largest diff. peak and hole / e/Å ³ | 0.22 and -0.18 |
| Flack parameter | -0.04(2) |

Compound 5

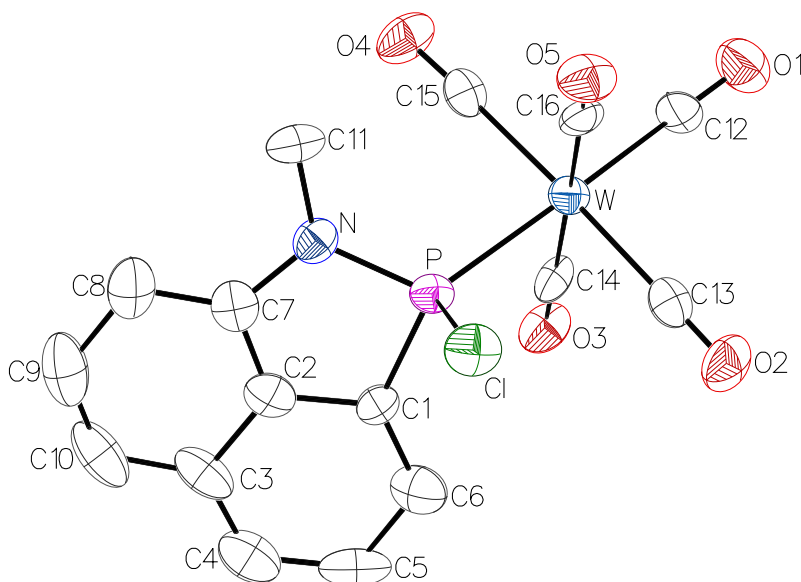


Figure S21 Molecular structure of **5** in the single crystal lattice at 180(2) K. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity. Suitable single crystals were obtained as clear light yellow blocks by slow evaporation of solvent from 2.5 mL of a saturated solution of **5** in *n*-pentane at ambient temperature in a glovebox. CCDC 2250017.

Table S2 Crystal data and structure refinements for 5.

| | |
|--|--|
| Identification code | GSTR729, TB053P.K // GXray6649 |
| Crystal habitus | clear light yellow block |
| Device type | STOE IPDS-2T |
| Empirical formula | C ₁₆ H ₉ CINO ₅ PW |
| Moiety formula | C ₁₆ H ₉ CINO ₅ PW |
| Formula weight / g/mol | 545.51 |
| <i>T</i> / K | 180 |
| Crystal system | monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>n</i> |
| <i>a</i> / Å | 11.8259(10) |
| <i>b</i> / Å | 12.6614(8) |
| <i>c</i> / Å | 12.5663(10) |
| α / ° | 90 |
| β / ° | 110.673(6) |
| γ / ° | 90 |
| <i>V</i> / Å ³ | 1760.4(2) |
| <i>Z</i> | 4 |
| ρ_{calc} / g/cm ³ | 2.058 |
| μ / mm ⁻¹ | 6.830 |
| <i>F</i> (000) | 1032.0 |
| Crystal size / mm ³ | 0.15 × 0.08 × 0.06 |
| Absorption correction | integration |
| Min. and max. transmission | 0.1867 and 0.4901 |
| Radiation | Mo-K α (λ = 0.71073 Å) |
| 2 θ range for data collection / ° | 5.88 to 55.984 |
| Completeness to θ | 0.982 |
| Index ranges | -15 ≤ <i>h</i> ≤ 14, -14 ≤ <i>k</i> ≤ 16, -12 ≤ <i>l</i> ≤ 16 |
| Reflections collected | 8798 |
| Independent reflections | 4202 (<i>R</i> _{int} = 0.0783, <i>R</i> _σ = 0.2145) |
| Data / restraints / parameters | 4902 / 0 / 227 |
| Goodness-of-fit on <i>F</i> ² | 0.530 |
| Final <i>R</i> indexes (<i>I</i> ≥ 2 σ (<i>I</i>)) | <i>R</i> ₁ = 0.0315, ωR ₂ = 0.0433 |
| Final <i>R</i> indexes (all data) | <i>R</i> ₁ = 0.0994, ωR ₂ = 0.0517 |
| Largest diff. peak and hole / e/Å ³ | 0.80 and -1.10 |

Compound 6

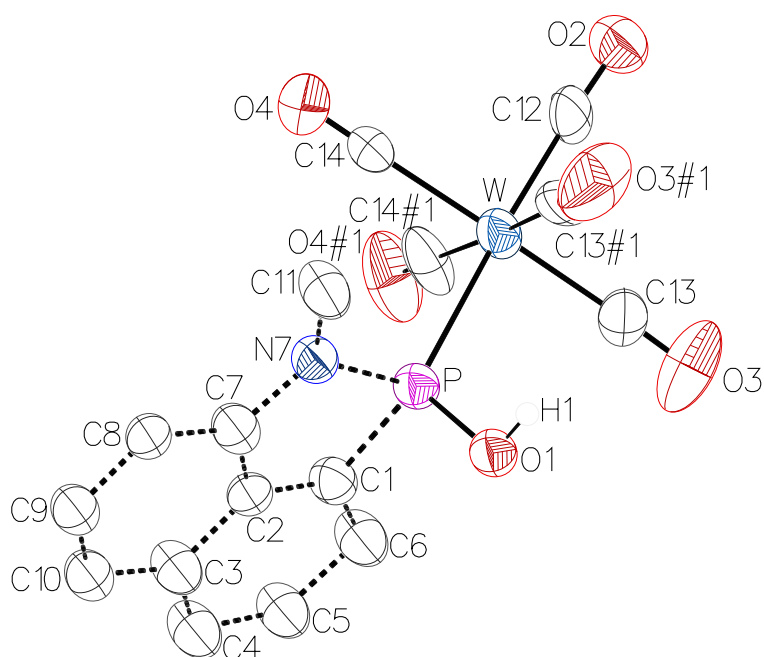


Figure S22 Molecular structure of **6** in the single crystal lattice at 180(2) K. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity. Suitable single crystals were obtained as clear light yellow plates by vapor diffusion of *n*-pentane into a concentrated solution of 9 mg of **6** in 0.25 mL of diethyl ether at ambient temperature in a glovebox. Due to the rather low quality data set, the structure of **6** was added to the ESI but not discussed in the main body of the manuscript. CCDC 2250018.

Table S3 Crystal data and structure refinements for **6**.

| | |
|--|--|
| Identification code | GSTR743, TB037P.K // GXray6650 |
| Crystal habitus | clear light yellow plate |
| Device type | STOE IPDS-2T |
| Empirical formula | C ₁₆ H ₁₀ NO ₆ PW |
| Moiety formula | C ₁₆ H ₁₀ NO ₆ PW |
| Formula weight / g/mol | 527.07 |
| <i>T</i> / K | 123 |
| Crystal system | monoclinic |
| Space group | <i>I</i> 2/ <i>m</i> |
| <i>a</i> / Å | 9.1981(5) |
| <i>b</i> / Å | 14.8394(12) |
| <i>c</i> / Å | 13.0755(8) |
| α / ° | 90 |
| β / ° | 102.642(6) |
| γ / ° | 90 |
| <i>V</i> / Å ³ | 1741.5(2) |
| <i>Z</i> | 4 |
| ρ_{calc} / g/cm ³ | 2.010 |
| μ / mm ⁻¹ | 6.756 |
| <i>F</i> (000) | 1000.0 |

| | |
|--|--|
| Crystal size / mm ³ | 0.18 × 0.15 × 0.05 |
| Absorption correction | integration |
| Min. and max. transmission | 0.1279 and 0.3453 |
| Radiation | Mo-K α (λ = 0.71073 Å) |
| 2 θ range for data collection / ° | 4.21 to 50.488 |
| Completeness to θ | 0.962 |
| Index ranges | -10 ≤ <i>h</i> ≤ 10, -17 ≤ <i>k</i> ≤ 17, -15 ≤ <i>l</i> ≤ 15 |
| Reflections collected | 4632 |
| Independent reflections | 1587 (<i>R</i> _{int} = 0.1460, <i>R</i> _{σ} = 0.1049) |
| Data / restraints / parameters | 1587 / 183 / 165 |
| Goodness-of-fit on <i>F</i> ² | 1.135 |
| Final <i>R</i> indexes (<i>I</i> ≥ 2 σ (<i>I</i>)) | <i>R</i> ₁ = 0.0768, ωR ₂ = 0.2047 |
| Final <i>R</i> indexes (all data) | <i>R</i> ₁ = 0.0915, ωR ₂ = 0.2164 |
| Largest diff. peak and hole / e/Å ³ | 2.27 and -3.49 |

Table S4 Bond lengths for 6.

| Atom | Atom | Bond length / Å | Atom | Atom | Bond length / Å |
|------|------------------|-----------------|------|------|-----------------|
| W | P | 2.458(5) | N7 | C11 | 1.48(4) |
| W | C12 | 1.95(2) | C1 | C6 | 1.37(4) |
| W | C13 | 2.028(17) | C1 | C2 | 1.34(3) |
| W | C13 ¹ | 2.028(17) | C4 | C5 | 1.43(5) |
| W | C14 ¹ | 2.062(18) | C4 | C3 | 1.37(3) |
| W | C14 | 2.062(18) | C5 | C6 | 1.44(4) |
| P | O1 | 1.609(14) | C7 | C2 | 1.3900 |
| P | N7 | 1.78(2) | C7 | C8 | 1.3900 |
| P | C1 | 1.84(3) | C2 | C3 | 1.3900 |
| O2 | C12 | 1.18(3) | C3 | C10 | 1.3900 |
| O3 | C13 | 1.14(2) | C10 | C9 | 1.3900 |
| O4 | C14 | 1.09(2) | C9 | C8 | 1.3900 |
| N7 | C7 | 1.38(2) | | | |

¹+X,1-Y,+Z

Table S5 Bond angles for **6**.

| Atom | Atom | Atom | Angle / ° | Atom | Atom | Atom | Angle / ° |
|------------------|------|------------------|-----------|------|------|------|-----------|
| C12 | W | P | 177.1(6) | C11 | N7 | P | 123.7(18) |
| C12 | W | C13 | 87.4(6) | C6 | C1 | P | 124(3) |
| C12 | W | C13 ¹ | 87.4(6) | C2 | C1 | P | 108.8(18) |
| C12 | W | C14 ¹ | 92.6(6) | C2 | C1 | C6 | 127(3) |
| C12 | W | C14 | 92.6(6) | C3 | C4 | C5 | 119(3) |
| C13 ¹ | W | P | 90.6(5) | C4 | C5 | C6 | 124(3) |
| C13 | W | P | 90.6(5) | C1 | C6 | C5 | 111(3) |
| C13 | W | C13 ¹ | 90.3(10) | N7 | C7 | C2 | 111.6(15) |
| C13 | W | C14 ¹ | 92.3(9) | N7 | C7 | C8 | 128.4(15) |
| C13 ¹ | W | C14 | 92.3(9) | C2 | C7 | C8 | 120.0 |
| C13 ¹ | W | C14 ¹ | 177.5(7) | C1 | C2 | C7 | 117.7(16) |
| C13 | W | C14 | 177.5(7) | C1 | C2 | C3 | 122.3(16) |
| C14 | W | P | 89.5(4) | C3 | C2 | C7 | 120.0 |
| C14 ¹ | W | P | 89.5(4) | C4 | C3 | C2 | 117(2) |
| C14 ¹ | W | C14 | 85.2(12) | C4 | C3 | C10 | 123(2) |
| O1 | P | W | 112.2(5) | C2 | C3 | C10 | 120.0 |
| O1 | P | N7 | 102.6(8) | C3 | C10 | C9 | 120.0 |
| O1 | P | C1 | 104.5(10) | C8 | C9 | C10 | 120.0 |
| N7 | P | W | 114.2(8) | C9 | C8 | C7 | 120.0 |
| N7 | P | C1 | 88.3(15) | O2 | C12 | W | 176.9(19) |
| C1 | P | W | 130.0(9) | O3 | C13 | W | 175.4(16) |
| C7 | N7 | P | 112.4(17) | O4 | C14 | W | 178(2) |
| C7 | N7 | C11 | 122(2) | | | | |

¹+X,1-Y,+Z

5 Theoretical investigations

Computational details

All the geometric and energy calculations have been performed using ORCA 5.0 program⁹ by means of the PBE0¹⁰-D4¹¹ method in combination with the def2-TZVP¹² basis set. The solvent effects have been modeled using the CPCM continuum model¹³ and taken into consideration for both optimization and energy calculations. The minimum or transition state nature of the compounds have been determined by frequency calculations. All minima have zero imaginary frequencies and the transition state have only one imaginary frequency that connects the starting and final products. The transition states have been computed using the NEB-TS (Nudged Elastic Band with TS optimization)¹⁴ methodology as implemented in ORCA 5.0 program. The NBO analysis¹⁵ was performed using the NBO7.0 program¹⁶ at the same level of theory.

Computed structures

Cartesian coordinates (in Å) for all computed species. Geometries are computed at the CPCM(CH₂Cl₂)/PBE0-D4/def2-TZVP level of theory.

3

| | | | |
|----|------------------|-------------------|------------------|
| W | 7.07991466235873 | 5.84702326169664 | 5.26540807331311 |
| Cl | 6.96942711385361 | 8.13064581012577 | 1.95435271660310 |
| P | 6.02131542772173 | 7.56591274645321 | 3.69300420971700 |
| O | 8.58348848913192 | 4.07696150680148 | 7.38107477315744 |
| O | 9.78471125735484 | 7.50153927477836 | 4.89650734457027 |
| O | 6.24165023665105 | 7.67382021134318 | 7.74203077270962 |
| O | 4.49466922592716 | 4.11984269628327 | 5.96936696189867 |
| O | 8.16613842153481 | 3.68491452842373 | 3.19098663271277 |
| N | 5.02739970460208 | 5.89647029057217 | 1.93957925444343 |
| C | 4.28215693387434 | 8.08138012146799 | 3.48404240077275 |
| C | 3.56175086708208 | 7.75091185787813 | 2.30930206380989 |
| C | 2.35205999353413 | 8.43171343826226 | 2.01828012329339 |
| C | 1.79645572342308 | 9.28098376603509 | 2.99788544411540 |
| H | 0.85855390731282 | 9.78230926517846 | 2.78456415191592 |
| C | 2.42589010382362 | 9.45750151432881 | 4.19889609622386 |
| H | 1.98569129911275 | 10.08520330191173 | 4.96441192765677 |
| C | 3.69285482289299 | 8.89458403977429 | 4.42464631367463 |

| | | | |
|----|------------------|------------------|-------------------|
| H | 4.21595226763836 | 9.15168374934172 | 5.33521534846404 |
| C | 4.01688672742581 | 6.75530518640574 | 1.42050150908675 |
| C | 3.41102745466508 | 6.58543357021574 | 0.20301460369065 |
| H | 3.76613194011097 | 5.82950978235823 | -0.48622986836907 |
| C | 2.28241289707212 | 7.35400424013099 | -0.13754593697830 |
| H | 1.81650991951754 | 7.20837204469346 | -1.10515090779939 |
| C | 1.73660796451049 | 8.22472650487414 | 0.76477379938035 |
| H | 0.82632712323602 | 8.76687303263954 | 0.53373775238166 |
| C | 5.91287485291334 | 5.33480640563941 | 0.92603589806027 |
| H | 6.26636171510558 | 6.11887483768336 | 0.26103304700855 |
| H | 5.40324650186917 | 4.56576763027299 | 0.33371910850102 |
| H | 6.76882944147048 | 4.87279070805026 | 1.41356397840182 |
| C | 8.02693729110703 | 4.71781527881409 | 6.60864211643501 |
| C | 8.80912797732245 | 6.92200251441040 | 5.00535186772634 |
| C | 6.52467491383600 | 7.05642325823077 | 6.82569187999411 |
| C | 5.39482867947078 | 4.75295384021900 | 5.66316132881528 |
| C | 7.73986484347699 | 4.49395159529111 | 3.87661335402915 |
| C | 4.38376363949131 | 4.81473404424542 | 2.68953379744952 |
| H | 5.14842744968074 | 4.17124878226622 | 3.12052415568302 |
| H | 3.76793373370817 | 5.22919857811736 | 3.48649530396254 |
| H | 3.74997532880539 | 4.21211300474226 | 2.02790788522483 |
| Cl | 6.65082500737399 | 9.35233452004272 | 4.68384941826350 |

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| | | | |
|----|------------------|------------------|------------------|
| W | 7.22970915112822 | 6.34923342952890 | 5.04776930763001 |
| Cl | 6.92238773746470 | 8.60885713102440 | 2.07766272952613 |
| P | 5.91499375941899 | 7.25764158450270 | 3.24517534652937 |
| O | 8.92913961273610 | 5.62978661671349 | 7.63387603645660 |
| O | 7.93178762089463 | 9.37899235161953 | 5.76934052181307 |
| O | 4.54911090923359 | 6.19904839696365 | 6.78291734547722 |
| O | 7.03652594432847 | 3.20168676000497 | 4.54897968726269 |
| O | 9.80473948965542 | 6.33579572361170 | 3.16505487161738 |
| N | 5.18983965875629 | 6.21562532336484 | 1.81461370662098 |
| C | 4.34701253193105 | 8.09117061482202 | 3.40837113659084 |
| C | 3.58058361064472 | 7.91030598559198 | 2.24385285651509 |

| | | | |
|----|------------------|-------------------|-------------------|
| C | 2.39221010578073 | 8.62485424432739 | 2.02064943786325 |
| C | 1.97020490803874 | 9.49623310809835 | 3.05030472452278 |
| H | 1.05477039807153 | 10.06264467598312 | 2.91910571082493 |
| C | 2.70215311140404 | 9.62565851986291 | 4.20505508415815 |
| H | 2.35915076199578 | 10.28881828010306 | 4.99042795218730 |
| C | 3.91672255030638 | 8.93603600915103 | 4.39816755114003 |
| H | 4.47366720500463 | 9.10600624767089 | 5.31811377742675 |
| C | 4.04993144481200 | 6.98878687029927 | 1.30760260813645 |
| C | 3.41123085740973 | 6.78539442751603 | 0.12194830497234 |
| H | 3.76328282985742 | 6.06772346877981 | -0.60826586351052 |
| C | 2.23941347988725 | 7.53198592446783 | -0.12904396768782 |
| H | 1.72631134358715 | 7.38395829550544 | -1.07136997701179 |
| C | 1.72927918425245 | 8.41076497845713 | 0.79294681208021 |
| H | 0.81291400007692 | 8.95101263193435 | 0.58355272995419 |
| C | 4.66083457933993 | 4.95687165988275 | 2.42848496245985 |
| H | 4.08217058950707 | 4.43834040851932 | 1.66647413046519 |
| H | 4.02496905767297 | 5.20312526227603 | 3.27781752048535 |
| H | 5.50089485105818 | 4.34409718766605 | 2.73997306822752 |
| C | 8.32094491447399 | 5.87549026621581 | 6.70339596256106 |
| C | 7.63343230689455 | 8.31191272642029 | 5.51656195130974 |
| C | 5.50808151812397 | 6.27976455046250 | 6.17707685808791 |
| C | 7.06870464465137 | 4.33052286383411 | 4.70022304473990 |
| C | 8.89302281986841 | 6.34471234108934 | 3.84795896862468 |
| C | 6.19455007217639 | 5.85931163418368 | 0.78188401584775 |
| H | 6.47024603050140 | 6.74474702086663 | 0.21829708294500 |
| H | 7.06311005667989 | 5.43276294651918 | 1.28273439352347 |
| H | 5.75518765646984 | 5.11219183675718 | 0.12280268325885 |
| Cl | 4.70102502590430 | 9.92401661540130 | 7.68179534636763 |

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| | | | |
|----|------------------|------------------|------------------|
| W | 7.39343842922752 | 6.30972876517602 | 5.13962849461994 |
| Cl | 7.67066825039689 | 7.74290928279886 | 1.62024513714045 |
| P | 6.31555463963075 | 6.89421050294652 | 3.00181289099585 |
| O | 8.65390224088256 | 5.67157545563770 | 7.97175207146237 |
| O | 8.56245795775288 | 9.27381221605304 | 5.32544980249949 |

| | | | |
|----|-------------------|-------------------|-------------------|
| O | 4.69033549448592 | 7.23658878244831 | 6.55523851856352 |
| O | 6.23929093296675 | 3.33819714983158 | 5.01479085693439 |
| O | 10.08220575625193 | 5.40235766270072 | 3.67021889319377 |
| N | 5.47832514776595 | 5.75424596812059 | 2.09056238117059 |
| C | 4.95735969666654 | 8.06165417372944 | 2.90471079624949 |
| C | 3.98590559393018 | 7.52224142400358 | 2.05333708457757 |
| C | 2.81505094562041 | 8.20965926513104 | 1.71287412026994 |
| C | 2.64909148432730 | 9.48554135152488 | 2.29215318130810 |
| H | 1.76005462129602 | 10.06189233906008 | 2.06037738744571 |
| C | 3.59893374439454 | 10.00573756884647 | 3.14397793326252 |
| H | 3.44426130998714 | 10.98682399561413 | 3.57773769729187 |
| C | 4.77488184016299 | 9.30111564996997 | 3.46324311966301 |
| H | 5.51219283091870 | 9.74295500118437 | 4.12369565082939 |
| C | 4.28791553219846 | 6.23770898261112 | 1.55884833497767 |
| C | 3.42331774622918 | 5.63066154499832 | 0.68785100726811 |
| H | 3.62196133946423 | 4.64828853455729 | 0.27801357332418 |
| C | 2.23775148939919 | 6.32095005086953 | 0.33363794690789 |
| H | 1.55390361183023 | 5.83427923176710 | -0.35256881565835 |
| C | 1.92456222587637 | 7.56382829691573 | 0.82042947124367 |
| H | 1.00544014243251 | 8.05690435385920 | 0.52622646671565 |
| C | 6.03956103088405 | 4.49244551357872 | 1.66559319243145 |
| H | 6.26445487499169 | 4.50619454752005 | 0.59551240239977 |
| H | 5.34216830221334 | 3.67841536243025 | 1.87468787921906 |
| H | 6.96485797602980 | 4.30405036038425 | 2.20865235344697 |
| C | 8.20122623367820 | 5.89905157829233 | 6.94533390094204 |
| C | 8.13655255513632 | 8.21766818677602 | 5.25294501496327 |
| C | 5.66050867536725 | 6.90819461856524 | 6.05186328623193 |
| C | 6.65665278599397 | 4.39969833280643 | 5.04731903947984 |
| C | 9.11870561727105 | 5.71928829217352 | 4.19130807792789 |
| C | 5.33491189601648 | 9.50873301454719 | -0.49787932855605 |
| H | 5.34226798995414 | 9.84484594681702 | 0.53494334704494 |
| H | 6.26487469460233 | 9.77330011209382 | -0.99401796499341 |
| H | 5.16090565977680 | 8.43793921637285 | -0.55145850657499 |
| Cl | 3.99716750398829 | 10.33351592728505 | -1.33976805622012 |

TS1Imaginary frequency: -88.10 cm⁻¹

| | | | |
|----|-------------------|-------------------|-------------------|
| W | 2.17031514864269 | -0.94857333254768 | 2.03066789415001 |
| Cl | 2.00384938495852 | 1.42736503349493 | -1.13702403766733 |
| P | 0.95990842996180 | 0.39400575034640 | 0.28700231114509 |
| O | 3.76899231464546 | -2.42227757878625 | 4.31027567535195 |
| O | 4.78651387715441 | 0.82141262824927 | 1.46986717623332 |
| O | 0.97829584925853 | 0.82446867501747 | 4.41784502132708 |
| O | -0.18321330957442 | -2.94539412439683 | 2.78048267723542 |
| O | 3.41216602576378 | -3.18641943691954 | 0.14903420143708 |
| N | 0.15119104685186 | -0.76847603778958 | -1.11340809112413 |
| C | -0.63046778510778 | 1.24437627574150 | 0.34177740568191 |
| C | -1.36684495098551 | 1.02381810122156 | -0.83628438821727 |
| C | -2.53425827318191 | 1.75129233569782 | -1.13284932814370 |
| C | -3.00476071698664 | 2.64237924586064 | -0.14513495157284 |
| H | -3.90499033725514 | 3.21640313465363 | -0.33536789615747 |
| C | -2.33508620302973 | 2.77642280384184 | 1.04548547257558 |
| H | -2.71610479109014 | 3.45051339806468 | 1.80339643401515 |
| C | -1.12515391079171 | 2.09959645073141 | 1.29271492722939 |
| H | -0.56562252150127 | 2.29970109098402 | 2.19507533195600 |
| C | -0.90053843590858 | 0.04459601000924 | -1.71383347697129 |
| C | -1.49139280235420 | -0.17301827691717 | -2.92226362773534 |
| H | -1.13799923792380 | -0.93509190535079 | -3.60526705614910 |
| C | -2.61758358675411 | 0.60878247565556 | -3.26003087264195 |
| H | -3.08754286139551 | 0.45078161632290 | -4.22310031133807 |
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| H | -4.03423059044556 | 2.08442709892729 | -2.65004765059525 |
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| H | 0.25439495333331 | -2.57416707880986 | -0.02917335949578 |
| C | 3.18995777331032 | -1.88442440813333 | 3.48152231344779 |
| C | 3.83048666751955 | 0.24030215166561 | 1.66924874554546 |
| C | 1.40897443622691 | 0.27492455823396 | 3.52006523913811 |

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| C | 0.63150970780723 | -2.20279753497999 | 2.47394514785087 |
| C | 2.94775627975778 | -2.34330224172846 | 0.76999010194964 |
| C | 1.11653715896835 | -1.30785433699890 | -2.09805511079766 |
| H | 1.42800603980479 | -0.52406048644031 | -2.77944225594194 |
| H | 1.97620242207929 | -1.70675463805559 | -1.56588092798266 |
| H | 0.63181226749365 | -2.11338215783126 | -2.64895738842919 |
| Cl | 1.90613740204441 | 2.74200358279289 | 1.77749711576015 |

TS2

Imaginary frequency: -579.50 cm⁻¹

| | | | |
|----|-------------------|-------------------|-------------------|
| W | 1.71117964114216 | -0.99118380983155 | 2.28761287285577 |
| Cl | 2.73203825174236 | 1.29595570462789 | -0.52842694505741 |
| P | 1.16255270869358 | 0.22586784556310 | 0.22270539041593 |
| O | 2.31335166408186 | -2.15061871218780 | 5.17097228931578 |
| O | 2.42760088287007 | 1.85976309381259 | 3.52290725131889 |
| O | -1.37363949598353 | -0.66795453285568 | 3.03735905413373 |
| O | 1.23053235841087 | -4.02864476383343 | 1.42281918922950 |
| O | 4.75333100928350 | -1.34410473313729 | 1.37518031659408 |
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| C | -2.55743811947402 | 1.36913026006210 | -0.38266395305955 |
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| H | -1.85810198079438 | 3.93079913441659 | 1.74382287816606 |
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| H | -1.70590066906084 | -1.79812430908462 | -2.52808119153911 |
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| H | 0.28755300118132 | -2.59781646718264 | -0.69211171216330 |
| H | 1.90274895488446 | -2.08201264679533 | -1.25475377668287 |
| C | 2.10060995363267 | -1.74481038164321 | 4.12433977377766 |
| C | 2.15438177765736 | 0.85310978396349 | 3.06092779093136 |
| C | -0.26929856090165 | -0.78503504194283 | 2.77829913810763 |
| C | 1.37943745187229 | -2.92908730424967 | 1.68496593041712 |
| C | 3.67043695227928 | -1.21414236947306 | 1.70413576213799 |
| C | 1.04375127424536 | 0.25472738342449 | -2.89724501411777 |
| H | 0.81946282483879 | 1.26773451911042 | -2.61248559515912 |
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| Cl | 1.71077968907833 | 1.16933921143622 | -4.98956181371319 |

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