

## Supplementary Information

### Synthesis of P-bridged, planar bis(NHC) BCl<sub>3</sub> adducts

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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 80 °C for at least one hour. Additionally, the glassware was heated with a heat gun (up to 550 °C) under active vacuum ( $< 5 \cdot 10^{-2}$  mbar) and filled with argon. Sterile syringes were purged with argon three times before use. The solvents were dried by standard procedures by refluxing over proper desiccants under an argon atmosphere (*n*-pentane and toluene over sodium wire ( $\varnothing = 2$  mm); diethyl ether stabilised with 3,5-di-*t*-butyl-4-hydroxytoluene (BHT) and tetrahydrofuran over benzophenone and sodium wire; dichloromethane over calcium hydride) 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/A) were used. After use, devices made of stainless steel were cleaned with deionised water and acetone and glassware by storage in a concentrated solution of potassium hydroxide in isopropanol for at least two days and in diluted hydrochloric acid for at least four hours. Afterwards, the glassware was washed with water and soap, deionised water and acetone. 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 analysed by the program *MestReNova 14.2*. The calibration of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra was done via the solvent residual signals relative to tetramethylsilane (<1% in  $\text{CDCl}_3$ ) ( $\text{C}_6\text{D}_6$ :  $\delta(^1\text{H}) = 7.16$  ppm and  $\delta(^{13}\text{C}) = 128.06$  ppm,  $\text{CD}_2\text{Cl}_2$ :  $\delta(^1\text{H}) = 5.32$  ppm and  $\delta(^{13}\text{C}) = 53.84$  ppm).<sup>1</sup> All lock frequencies were calibrated internally against the  $^1\text{H}$  signals of solutions of tetramethylsilane with a volume fraction of  $\phi \leq 1\%$  in the corresponding deuterated solvent. The deuterated solvents were used without further purification and dried by storing over 3 Å ( $\text{CD}_2\text{Cl}_2$ ) or 4 Å ( $\text{C}_6\text{D}_6$ ) molecular sieves. The chemical shift ( $\delta$ ) 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  $^1\text{H}$  NMR spectra additionally the number of nuclei is given accordingly which is determined via integration. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals of compounds were assigned by a combination of COSY, HSQC 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 spectrometry using electrospray ionisation (ESI) or atmospheric-pressure chemical ionization (APCI) was performed on a Thermo Fisher Scientific Orbitrap XL mass spectrometer. 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.

UV/vis spectra were recorded in the spectral range of 200–700 nm on a *Shimadzu UV-1650PC* spectrometer with a double-beam optic photometric system with a maximum wavelength range of 190.0 to 1100 nm, a spectra band width of 2 nm and a wavelength accuracy of  $\pm 0.5$  nm with an automatic wavelength correction. An automatic baseline correction with the pure solvent was performed before the analyte solution was measured. The detector is a silicon photodiode with a photometric range of  $-0.5$  to 3.999 absorbance. Quartz glass cuvettes (*Hellma* precision cells *110-QC*) with dimensions of 46 mm  $\times$  12.5 mm  $\times$  12.5 mm, a light path length of 10 mm and a chamber volume of 350  $\mu$ L were used and closed with PTFE caps before measurement. Measurements were started with a circa  $10^{-5}$  molar solution of the respective compound and diluted until a sufficient spectrum was recorded. All spectra are normed to an absorbance of 1 a.u.; no extinction coefficient were determined. Absorbance wavelengths are given in nanometers (nm) with the relative absorbance (max. 1) and assignment to the associated transition in parentheses.

IR spectra of solids were recorded in the spectral range of 4000-400  $\text{cm}^{-1}$  on a Bruker Alpha FTIR spectrometer with a single-reflection diamond ATR measurement or a Shimadzu IRSpirit FTIR spectrometer with a single-reflection germanium ATR measurement attachment 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 centimetres ( $\text{cm}^{-1}$ ). The intensities of the bands are marked as very strong (vs), strong(s), medium (m), weak (w).

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 and N values are given for each compound.

Melting points were measured using a MPM-H2 device or a Büchi melting point determination device according to Dr. Tottoli. The samples were grease-sealed in a glass capillary ( $\varnothing = 0.1$  mm) in a glovebox and heated quickly (ca. 10 K/min) for a rough determination of the melting point or decomposition temperature. Afterwards, a heating rate of approximately 1 K/min was used until the sample melted or decomposed. No internal or external temperature corrections were performed.

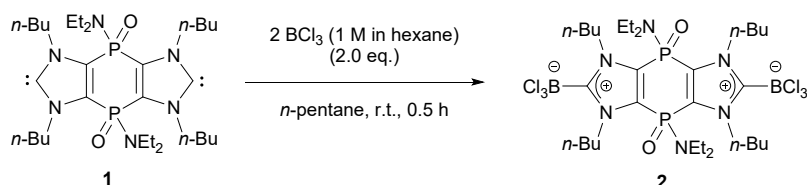
Single crystal X-ray diffraction analyses were performed on a Bruker D8-Venture diffractometer at 100 K by using monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.54178$  Å), a STOE IPDS-2T diffractometer at 123 K by using monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) or a STOE STADIVARI diffractometer at 100 K by using monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.54178$  Å). Intensities were measured by fine-slicing  $\phi$  and  $\omega$  scans and corrected background, polarisation and Lorentz effects. A semi-empirical absorption correction was applied for the data sets following Blessing's method.<sup>2</sup> The structure was solved by direct methods and refined anisotropically by the least-squares procedure implemented in SHELX program system.<sup>3</sup> 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* of *OlexSys*<sup>4</sup> 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. 2375703 (2), which can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Cyclovoltammetric measurements were performed in the glovebox with the potentiostat/galvanostat system *WaveNow<sup>XV</sup>*® of *Pine Research* over scan rates of 50–1600 mV s<sup>-1</sup>. For all measurements *Pine Research* ceramic screen-printed platinum electrodes containing an

Ag/AgCl reference electrode which combine working, counter and reference electrode on one ceramic plate were used. The measurements were carried out in a glass cell with a special PTFE insert at the bottom with a slit to fit the ceramic screen-printed electrode and a slit-volume of circa 1 mL. When using acetonitrile as solvent a 0.1 M solution of the electrolyte  $n\text{-Bu}_4\text{PF}_6$  was prepared. The electrolyte was dried thoroughly *in vacuo* ( $\leq 0.02$  mbar) at 80 °C for at least 24 hours before use. Acetonitrile was purified by drying over  $\text{CaH}_2$  and  $\text{P}_2\text{O}_5$ , trap-to-trap recondensation and degassing by three freeze-pump-thaw cycles. The analyte solutions were prepared with concentrations of 1–3 mmol L<sup>-1</sup>. For each measurements a background scan to determine the anodic and cathodic limits of the electrolyte solution was performed first, followed by analyte addition and the measurement of the open circuit potential and thus, the starting point of the experiments. The oxidation and reduction processes in both anodic and cathodic direction were determined carefully and investigated in isolated form if possible. In the end, cobaltocenium hexafluorophosphate (–1.35 V vs.  $\text{Fc}^{+/0}$ ) or ferrocene were added as internal reference to achieve the IUPAC recommended<sup>5</sup> referencing to the ferrocene/ferrocenium redox couple ( $\text{Fc}^{+/0}$ ). For the measurement and analysis of the experimental data the software *Aftermath* of *Pine Research* was used.

## 2. Experimental procedures and characterisation

### 2.1. Synthesis of 2



In a 50 mL Schlenk tube 0.44 mL (0.44 mmol, 2.0 eq.)  $\text{BCl}_3$  (1 M in hexane) were added dropwise to a solution of 0.131 g (0.22 mmol, 1.0 eq.) of **1** in 10 mL *n*-pentane. After stirring for 0.5 h the solvent was removed *in vacuo* ( $\leq 0.05$  mbar) yielding a beige solid which was purified via column chromatography at  $-20^\circ\text{C}$  ( $\text{Al}_2\text{O}_3$ ,  $h = 7$  cm,  $d = 1$  cm, eluent diethyl ether/dichloromethane) collecting the second fraction in dichloromethane. After solvent removal *in vacuo* ( $\leq 0.05$  mbar) the residue was washed with three times 1–1.5 mL *n*-pentane and dried for 3 h ( $\leq 0.02$  mbar) yielding a colourless solid.

**Reaction code:** TT-274 (35p5a032.20)

**Molecular formula:**  $\text{C}_{30}\text{H}_{56}\text{B}_2\text{Cl}_2\text{N}_6\text{O}_2\text{P}_2$

**Molecular weight:**  $829.09\text{ g mol}^{-1}$

**Yield:** 0.004 g (0.005 mmol, 2 %)

**Melting point:**  $> 220^\circ\text{C}$

**MS (EI, 70 eV):**  $m/z$  (%) = 675.3 (100)  $[\text{M}-\text{BCl}_4]^+$ , 594.3 (54)  $[\text{M}-2\text{BCl}_3]^+$ , 522.2 (35)  $[\text{M}-2\text{BCl}_3-\text{NEt}_2]^+$ , 466.1 (41)  $[\text{M}-2\text{BCl}_3-\text{NEt}_2-\text{C}_4\text{H}_8]^+$ , 72.0 (35)  $[\text{NET}_2]^+$ .

**IR (ATR):**  $\tilde{\nu} / \text{cm}^{-1} = 2962$  (w,  $\nu_{\text{as}}(\text{CH}_3)$ ,  $\nu_{\text{s}}(\text{CH}_2)$ ,  $\nu(\text{CH})$ ), 2873 (w,  $\nu_{\text{s}}(\text{CH}_3)$ ,  $\nu_{\text{as}}(\text{CH}_2)$ ).

**$^1\text{H}$  NMR** (500.14 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta / \text{ppm} = 1.00$  (m,  $^3J_{\text{H,H}} = 8.7$  Hz,  $^3J_{\text{H,H}} = 7.2$  Hz, 24H,  $\text{CH}_3$ ), 1.39–1.52 (m, 8,  $\text{NCH}_2\text{CH}_2\text{CH}_2$ ), 1.94–2.06 (m, 4H,  $\text{NCH}_2\text{CH}_2$ ), 2.13–2.25 (m, 4H,  $\text{NCH}_2\text{CH}_2$ ), 3.13–3.21 (m, 8H,  $\text{PNCH}_2$ ), 4.12–4.43 (br m, 4H,  $\text{NCH}_2$ ), 5.18–5.30 (br m, 4H,  $\text{NCH}_2$ ).

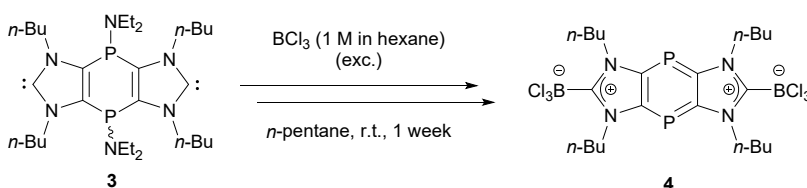
**$^{13}\text{C}\{^1\text{H}\}$  NMR** (125.78 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta / \text{ppm} = 13.7$  (s,  $\text{CH}_3$ ), 20.1 (s,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 34.2 (s,  $\text{NCH}_2\text{CH}_2$ ), 38.2 (d,  $J_{\text{P,C}} = 5.0$  Hz,  $\text{NCH}_2\text{CH}_3$ ), 51.7 (s,  $\text{NCH}_2$ ), 131.1 (d,  $J_{\text{P,C}} = 20.1$  Hz, PC), 132.3 (d,  $J_{\text{P,C}} = 20.2$  Hz, PC).

**$^{31}\text{P}$  NMR** (202.48 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta / \text{ppm} = -4.7$  (m).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (202.48 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta / \text{ppm} = -4.7$  (s).

**$^{11}\text{B}\{^1\text{H}\}$  NMR** (160.46 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta / \text{ppm} = 1.8$  (s).

### 2.2. Generation of 4



In a 15 mL Schlenk tube 0.46 mL (0.46 mmol, 6.0 eq.) BCl<sub>3</sub> (1 M in hexane) were added dropwise to a solution of 0.043 g (0.08 mmol, 1.0 eq.) of **3** in 3 mL *n*-pentane. After stirring for 4 h at ambient temperature the solvent was removed *in vacuo* ( $\leq 0.05$  mbar) yielding a light-yellow solid. After washing with three times 3–6 mL *n*-pentane and drying for 1 h ( $\leq 0.02$  mbar) a light-yellow solid was obtained.

**Reaction code:** TT-369 (09t4a101.21), TT-933 (TAT231020p5a054)

**Molecular formula:** C<sub>22</sub>H<sub>36</sub>B<sub>2</sub>Cl<sub>6</sub>N<sub>4</sub>P<sub>2</sub>

**Molecular weight:** 652.83 g mol<sup>-1</sup>

**Yield:** not determined due to remaining impurities

**Melting point** not determined due to remaining impurities

**Content in mixture:** up to 94 % (<sup>31</sup>P{<sup>1</sup>H} NMR integration of isolated reaction mixture)

**MS (pos. ESI):** *m/z* (%) = 569.170 (10) [M–BCl<sub>3</sub>+O<sub>2</sub>+3H]<sup>+</sup>, 533.193 (27) [M–BCl<sub>4</sub>+O<sub>2</sub>+2H]<sup>+</sup>, 453.254 (100) [M–2BCl<sub>3</sub>+O<sub>2</sub>+3H]<sup>+</sup>, 437.259 (80) [M–2BCl<sub>3</sub>+OH+2H]<sup>+</sup>, 227.131 (80) [M–2BCl<sub>3</sub>+O<sub>2</sub>+4H]<sup>2+</sup>.

**MS (neg. ESI):** *m/z* (%) = 669.074 (41) [M+OH]<sup>-</sup>, 685.0685 (14) [M+O<sub>2</sub>+H]<sup>-</sup>.

**HRMS (neg. ESI):** *m/z* calculated [C<sub>22</sub>H<sub>36</sub>B<sub>2</sub>Cl<sub>6</sub>N<sub>4</sub>P<sub>2</sub>OH]<sup>-</sup>: 669.0746; found: 669.0743.

**IR (ATR):**  $\tilde{\nu}$  / cm<sup>-1</sup> = 2963 (w,  $\nu_{as}$ (CH<sub>3</sub>),  $\nu_s$ (CH<sub>2</sub>),  $\nu$ (CH)), 2934 (w,  $\nu_{as}$ (CH<sub>3</sub>),  $\nu_s$ (CH<sub>2</sub>),  $\nu$ (CH)), 2876 (w,  $\nu_s$ (CH<sub>3</sub>),  $\nu_{as}$ (CH<sub>2</sub>)).

**<sup>1</sup>H NMR** (500.14 MHz, 298.0 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  / ppm = 1.07 (t, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, 12H, CH<sub>3</sub>), 1.52–1.65 (m, 8H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.16–2.27 (m, 8H, NCH<sub>2</sub>CH<sub>2</sub>), 4.83–4.90 (m, 4H, NCH<sub>2</sub>), 5.19–5.26 (m, 4H, NCH<sub>2</sub>).

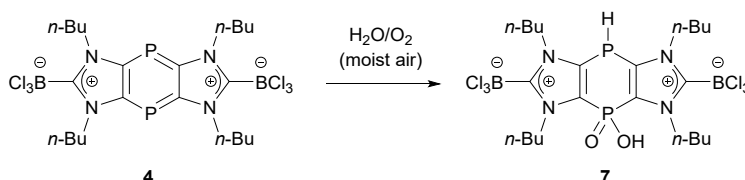
**<sup>13</sup>C{<sup>1</sup>H} NMR** (125.78 MHz, 298.0 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  / ppm = 13.7 (m, CH<sub>3</sub>), 20.4 (m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 31.2 (m, NCH<sub>2</sub>CH<sub>2</sub>), 50.5–50.9 (m, NCH<sub>2</sub>), 155.7 (d, J<sub>P,C</sub> = 24.7 Hz, PC), 162.7 (br m, CBCl<sub>3</sub>).

**<sup>31</sup>P NMR** (162.00 MHz, 298.0 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  / ppm = 118.6 (s).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (162.00 MHz, 298.0 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  / ppm = 118.6 (s).

**<sup>11</sup>B{<sup>1</sup>H} NMR** (128.38 MHz, 298.0 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  / ppm = 2.1 (br s).

### 2.3. Generation of **7**



In a 10 mL vial 0.005 g (<0.01 mmol, 1.0 eq.) of **4** in 94 % purity were exposed to moist air for 1.5 h leading to fading of the yellow colour. The beige solid was analysed via NMR spectroscopy.

**Reaction code:** TT-369-4 (10m3a041.21)

**Molecular formula:** C<sub>22</sub>H<sub>38</sub>B<sub>2</sub>Cl<sub>6</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>

**Molecular weight:** 686.84 g mol<sup>-1</sup>

**Content in mixture:** 91 % (<sup>31</sup>P{<sup>1</sup>H} NMR integration of reaction mixture)

**MS (neg. ESI):**  $m/z$  (%) = 685.0685 (16)  $[M-H]^-$ .

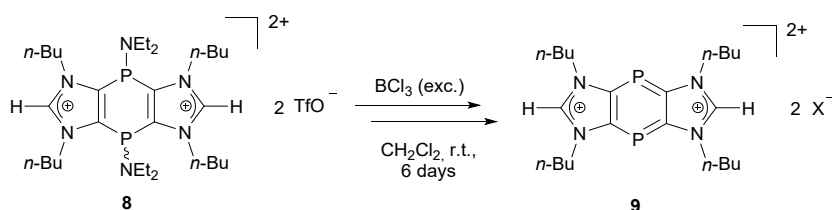
**HRMS (neg. ESI):**  $m/z$  calculated  $[C_{22}H_{36}B_2Cl_6N_4P_2OH]^-$ : 669.0746; found: 669.0743.

**$^{31}P$  NMR** (121.51 MHz, 298.0 K,  $CH_2Cl_2$ ):  $\delta$  / ppm = -127.5 (d,  $^1J_{P,H}$  = 234.4 Hz, PH), 14.2 (s,  $P(O)OH$ ).

**$^{31}P\{^1H\}$  NMR** (121.51 MHz, 298.0 K,  $CH_2Cl_2$ ):  $\delta$  / ppm = -127.5 (s, PH), 14.2 (s,  $P(O)OH$ ).

**$^{11}B\{^1H\}$  NMR** (96.29 MHz, 298.0 K,  $CH_2Cl_2$ ):  $\delta$  / ppm = 2.1 (br s).

## 2.4. Generation of 9



In a 50 mL *Young*® flask in the glovebox 1.15 mL (1.15 mmol, 6.0 eq.)  $BCl_3$  (1 M in hexane) were added dropwise to a solution of 0.165 g (0.19 mmol, 1.0 eq.) of **8** in 4 mL dichloromethane leading to a colour change from orange over brown and green to yellow. After stirring for 6 h at ambient temperature the solvent was removed *in vacuo* ( $\leq 0.05$  mbar) yielding a yellow to orange, oily solid which was redissolved in 3 mL dichloromethane and another 1.15 mL (1.15 mmol, 6.0 eq.)  $BCl_3$  (1 M in hexane) were added yielding a colour change from red to yellow. After stirring overnight another 1.15 mL (1.15 mmol, 6.0 eq.)  $BCl_3$  (1 M in hexane) were added. After stirring for 19 h the solvent was removed *in vacuo* ( $\leq 0.05$  mbar) yielding a yellow, slightly sticky solid which was washed with five times 2 mL *n*-pentane. After drying for 4 h ( $\leq 0.02$  mbar) a yellow solid was obtained.

**Reaction code:** TT-888 (TAT230821p5a014)

**Molecular formula:**  $C_{22}H_{38}B_2Cl_6N_4P_2$  ( $X = BCl_4$ ),  $C_{22}H_{38}N_4P_2$  (only cation)

**Molecular weight:** 725.74 g  $mol^{-1}$  ( $X = BCl_4$ ), 420.52 g  $mol^{-1}$  (only cation)

**Yield:** not determined due to remaining impurities

**Melting point:** not determined due to remaining impurities

**Content in mixture:** 100 % ( $^{31}P$  NMR integration of isolated reaction mixture; impurities in  $^{11}B\{^1H\}$  and  $^1H$  NMR spectra)

**MS (pos. ESI):**  $m/z$  (%) = 603.214 (55)  $[M+OTf+O_2+H]^+$ , 569.208 (7)  $[M+OTf]^+$ , 219.133 (27)  $[M+2H_2O]^+$ , 453.254 (100)  $[M+O_2+H]^+$ , 437.259 (80)  $[M+OH]^+$ , 210.128 (4)  $[M]^{2+}$ .  
(M = cation)

**MS (neg. ESI):**  $m/z$  (%) = 148.949 (100)  $[OTf]^-$ .

**HRMS (pos. ESI):**  $m/z$  calculated  $[C_{22}H_{38}N_4P_2OH]^+$ : 437.2594; found: 437.2591.

$m/z$  calculated  $[C_{22}H_{38}N_4P_2F_3S_1O_3]^+$ : 569.2086; found: 569.2083.

**IR (ATR):**  $\tilde{\nu}$  /  $cm^{-1}$  = 3140 (w,  $\nu(CH)$ ), 3069 (w,  $\nu(CH)$ ), 2963 (w,  $\nu_{as}(CH_3)$ ,  $\nu_s(CH_2)$ ), 2936 (w,  $\nu_{as}(CH_3)$ ,  $\nu_s(CH_2)$ ), 2875 (w,  $\nu_s(CH_3)$ ,  $\nu_{as}(CH_2)$ ).

**$^1H$  NMR** (499.96 MHz, 298.0 K,  $CD_2Cl_2$ ):  $\delta$  / ppm = 1.06 (t,  $^3J_{H,H}$  = 7.5 Hz, 12H,  $CH_3$ ), 1.48–1.60 (m, 8H,  $NCH_2CH_2CH_2$ ), 2.17–2.26 (m, 8H,  $NCH_2CH_2$ ), 4.81 (t,  $^3J_{H,H}$  = 7.8 Hz, 8H,  $NCH_2$ ), 9.58 (s, 2H,  $CH$ ).



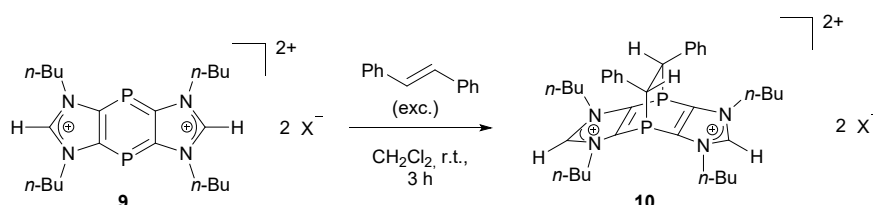
$^{13}\text{C}\{^1\text{H}\}$  NMR (125.73 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  / ppm = 13.6 (s,  $\text{CH}_3$ ), 20.4 (s,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 30.9 (m,  $\text{NCH}_2\text{CH}_2$ ), 50.8 (dd,  $J_{\text{P,C}} = 4.3$  Hz,  $\text{NCH}_2$ ), 144.4 (t,  $^3J_{\text{P,C}} = 3.0$  Hz, CH), 154.5 (t,  $J_{\text{P,C}} = 26.7$  Hz, PC).

$^{31}\text{P}$  NMR (202.41 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  / ppm = 121.3 (s).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202.41 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  / ppm = 121.3 (s).

$^{11}\text{B}\{^1\text{H}\}$  NMR (160.41 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  / ppm = 6.5 (s,  $\text{BCl}_4$ ).

## 2.5. Generation of 10



A solution of circa 0.050 g of a mixture containing approximately 50 % of **9** (according to  $^{31}\text{P}$  NMR spectroscopy) in 3 mL dichloromethane were added to an excess (0.080 g (0.44 mmol)) of *trans*-diphenylethene in a 15 mL Schlenk tube. After stirring for 3 h the solvent was removed *in vacuo* ( $\leq 0.05$  mbar) and the yellow residue was extracted with three times 2–4 mL THF. After solvent removal *in vacuo* ( $\leq 0.05$  mbar) the yellow solid was washed with 5 mL diethyl ether, 5 mL toluene and three times 5 mL *n*-pentane at  $-40$  °C. After drying for 2 h the light-yellow solid was analysed via  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy.

**Reaction code:** TT-906 (TAT230828m3a004)

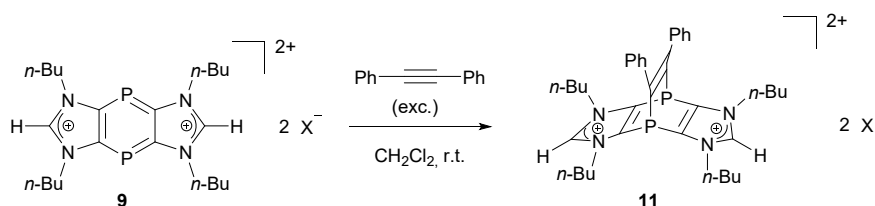
**Molecular formula:**  $\text{C}_{36}\text{H}_{50}\text{N}_4\text{P}_2\text{X}_2$  (**10** with unknown counter ions X)

**Molecular weight:** 600.77 g  $\text{mol}^{-1}$  (only **10**)

**Content in mixture:** 100 % ( $^{31}\text{P}\{^1\text{H}\}$  NMR integration of isolated reaction mixture)

$^{31}\text{P}\{^1\text{H}\}$  NMR (121.51 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  / ppm =  $-80.6$  (s).

## 2.6. Generation of 11



0.010 g of a mixture containing 100 % of **9** (according to  $^{31}\text{P}$  NMR spectroscopy) ( $\approx 0.01$  mmol, 1.0 eq.) and 0.046 g (0.26 mmol,  $\approx 26$  eq.) diphenylethyne were dissolved in 0.5 mL dichloromethane in a *J Young*<sup>®</sup> NMR tube yielding a clear, yellow solution that was analysed via  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy.

**Reaction code:** TT-900 (TAT230823m3a042)

**Molecular formula:**  $\text{C}_{36}\text{H}_{48}\text{N}_4\text{P}_2\text{X}_2$  (**11** with unknown counter ions X)

**Molecular weight:** 598.33 g  $\text{mol}^{-1}$  (only **11**)

**Content in mixture:** 43 % ( $^{31}\text{P}\{^1\text{H}\}$  NMR integration of reaction mixture)

$^{31}\text{P}\{^1\text{H}\}$  NMR (121.51 MHz, 298.0 K,  $\text{CH}_2\text{Cl}_2$ ):  $\delta$  / ppm = -81.2 (s).

### 3. NMR spectra

Impurities (solvent peaks, grease peaks) are marked with \* in the spectra.

#### 3.1. 2

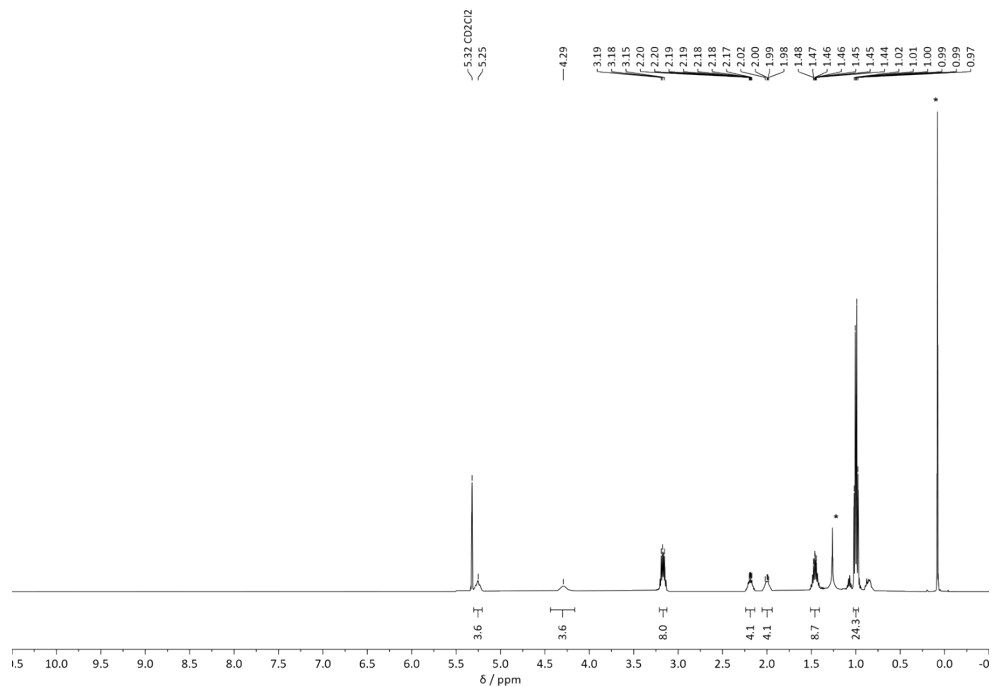


Figure S1  $^1\text{H}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 500.14 Hz, 298.0 K) of **2**.

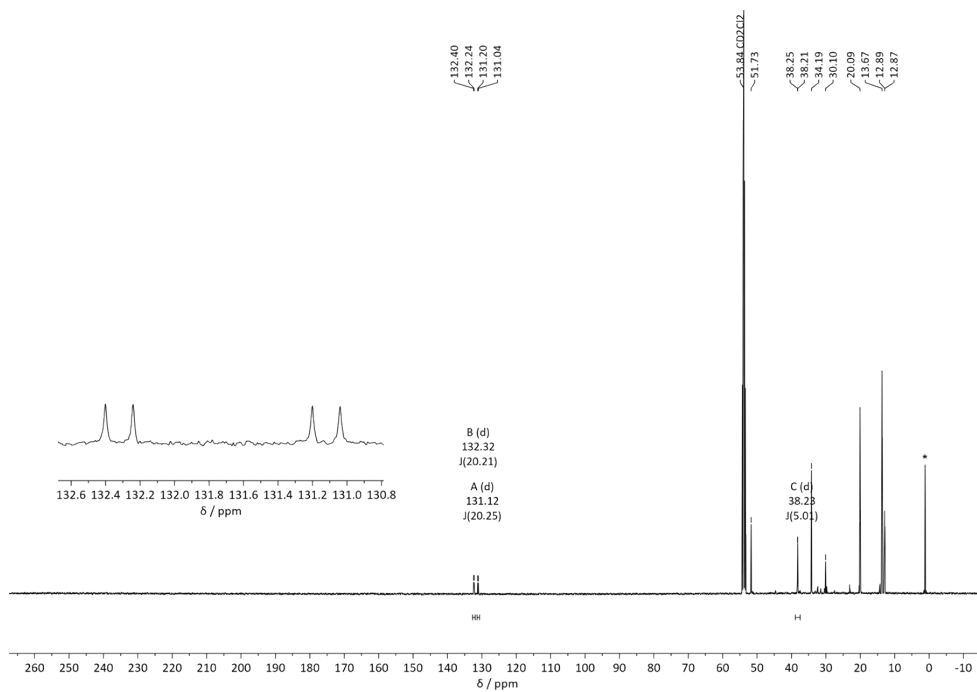
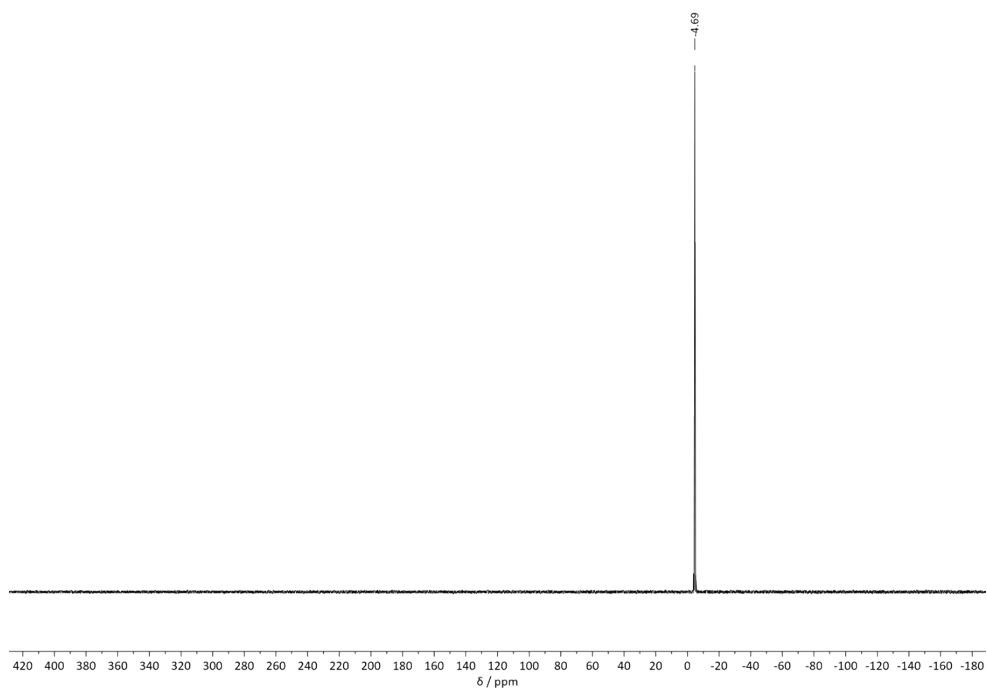
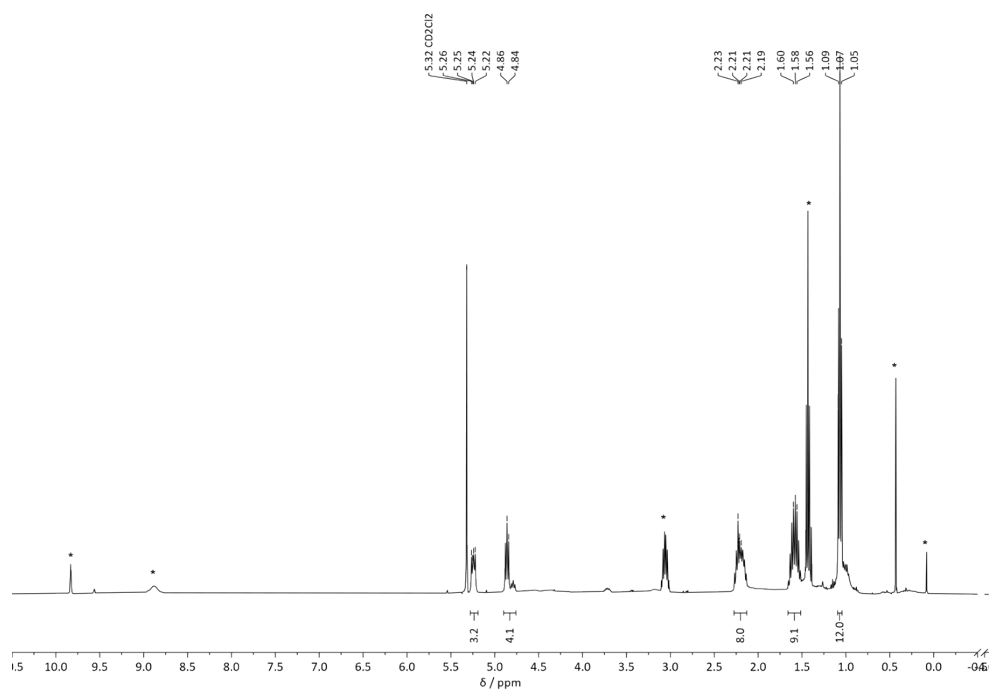


Figure S2  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 125.78 Hz, 298.0 K) of **2**.

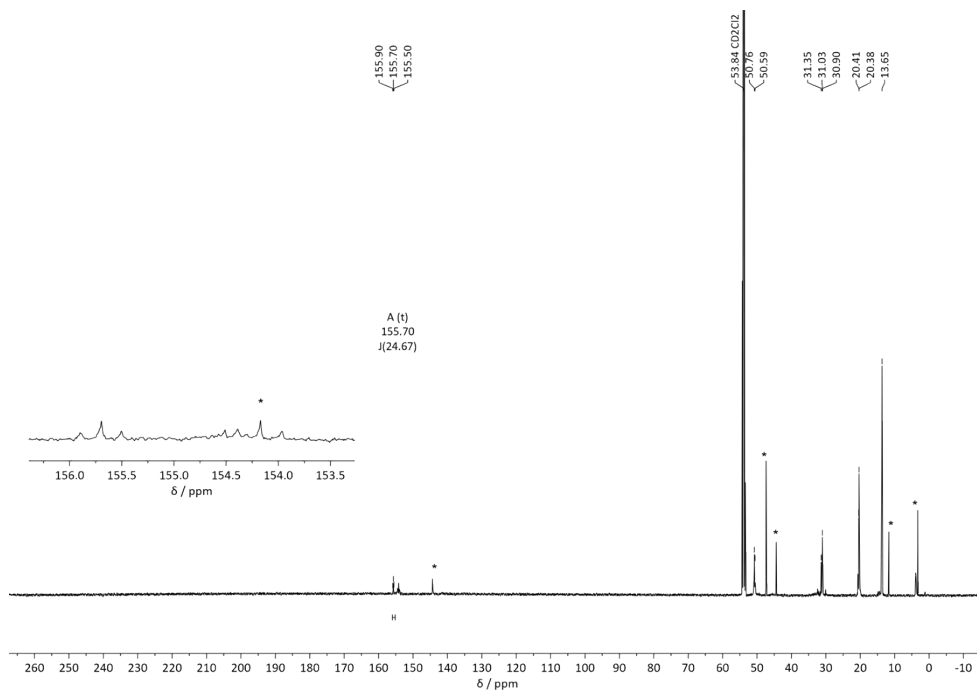


**Figure S3**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 202.48 Hz, 298.0 K) of **2**.

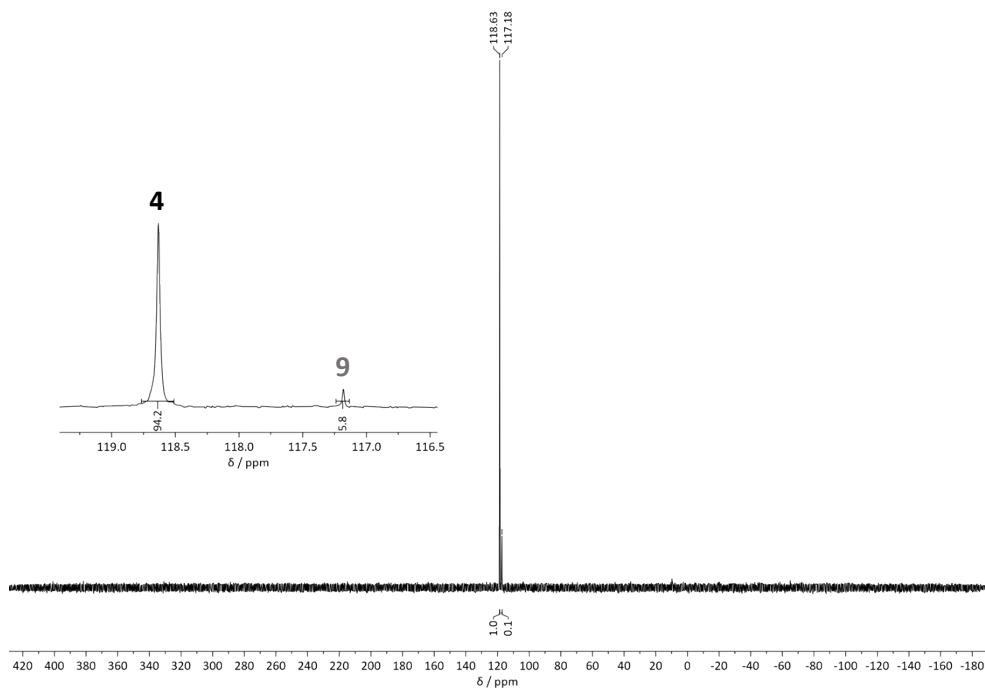
### 3.2. **4** (containing impurities)



**Figure S4**  $^1\text{H}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 400.13 Hz, 298.0 K) of **4**.



**Figure S5**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 125.78 Hz, 298.0 K) of **4**.



**Figure S6**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 162.00 Hz, 298.0 K) of **4** (94 % purity).

### 3.3. 7 in reaction mixture

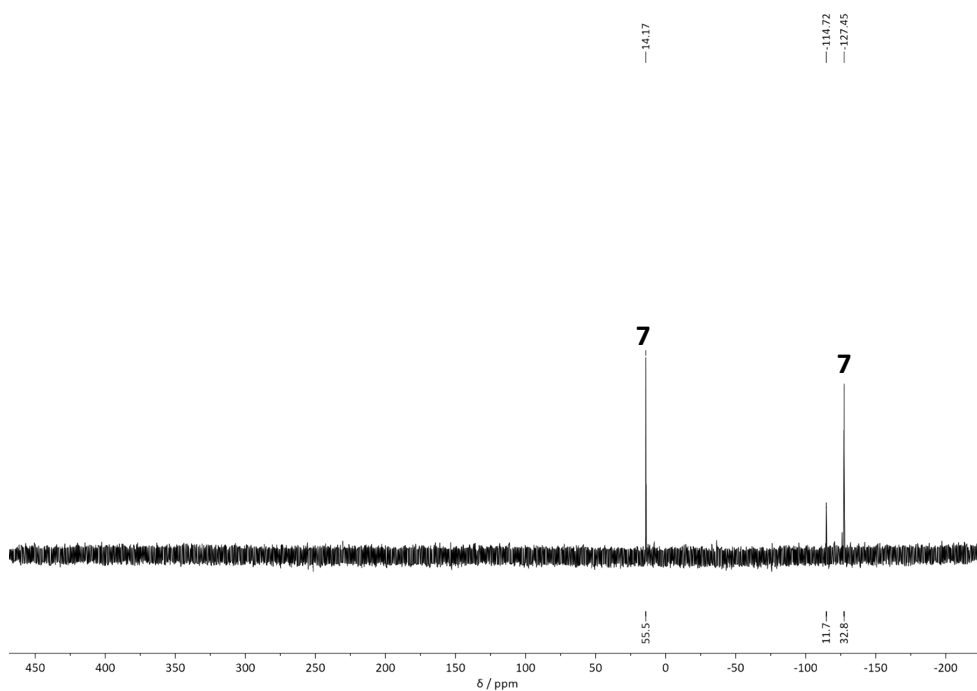


Figure S7  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CH}_2\text{Cl}_2$ , 121.51 Hz, 298.0 K) of 7 in reaction mixture.

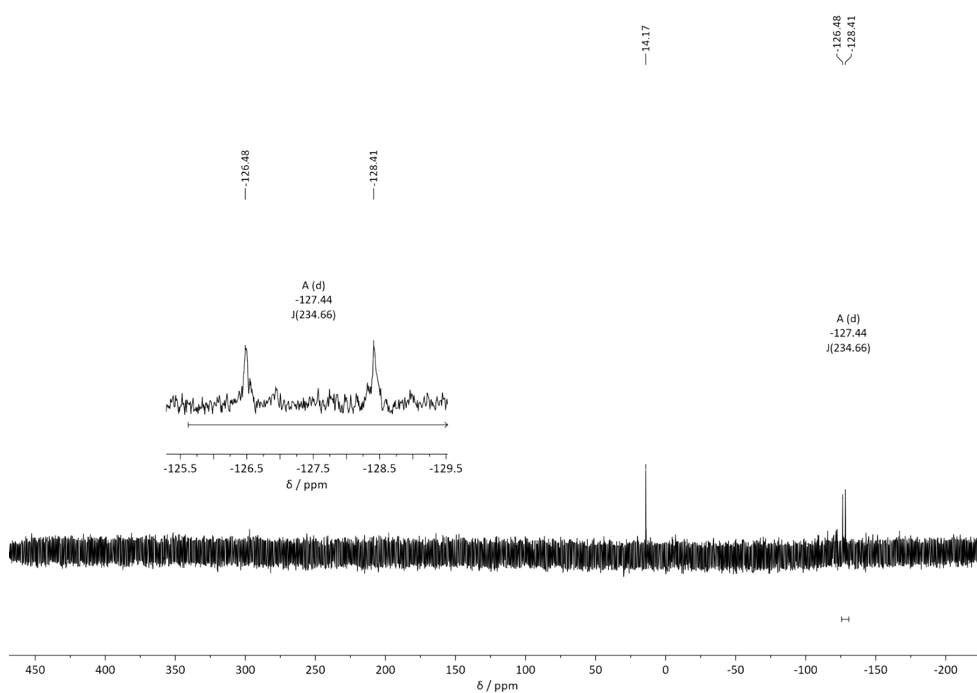


Figure S8  $^{31}\text{P}$  NMR spectrum ( $\text{CH}_2\text{Cl}_2$ , 121.51 Hz, 298.0 K) of 7 in reaction mixture.

### 3.4. 9 (containing impurities)

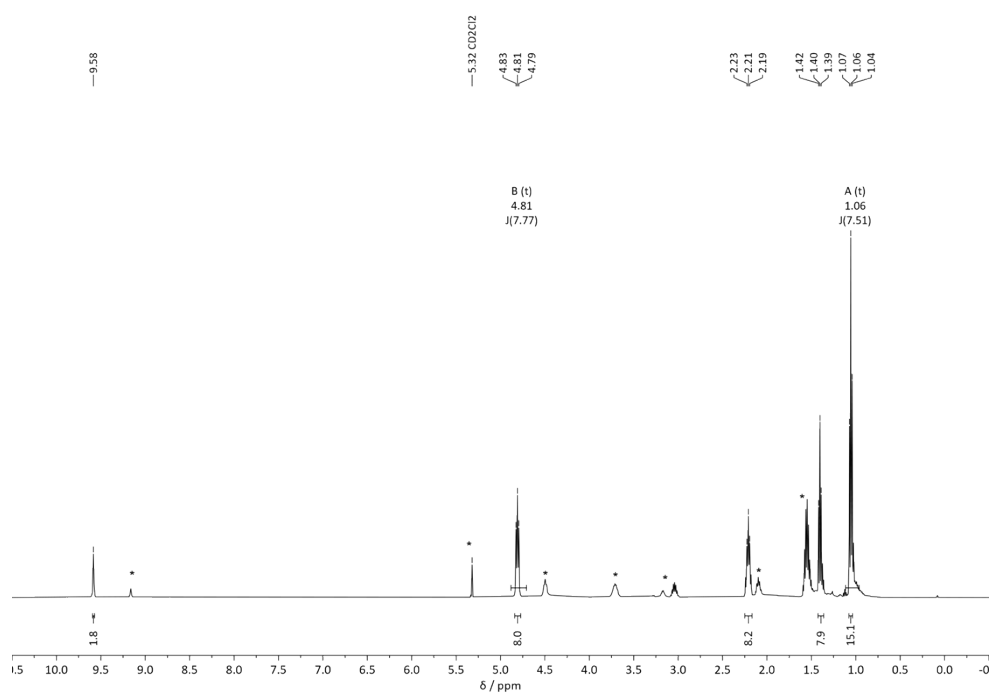


Figure S9 <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 499.96 Hz, 298.0 K) of **9**.

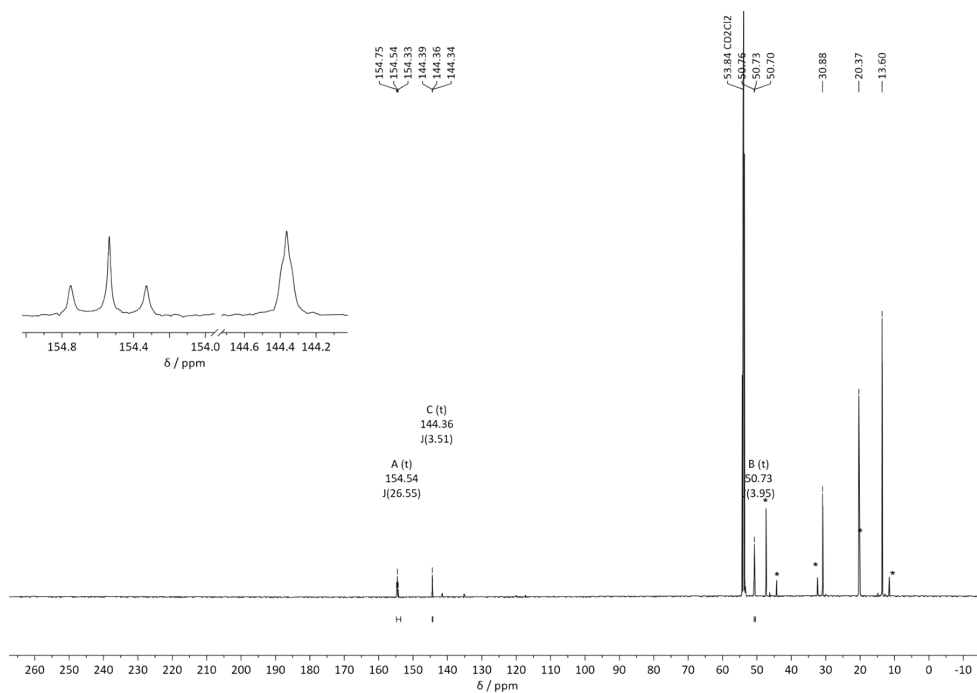
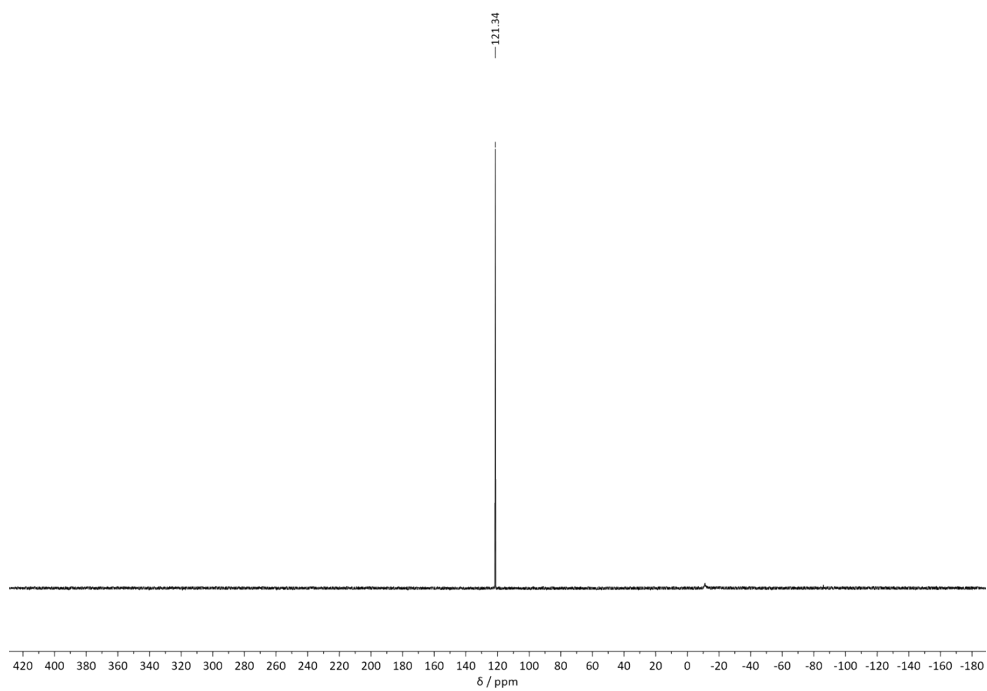
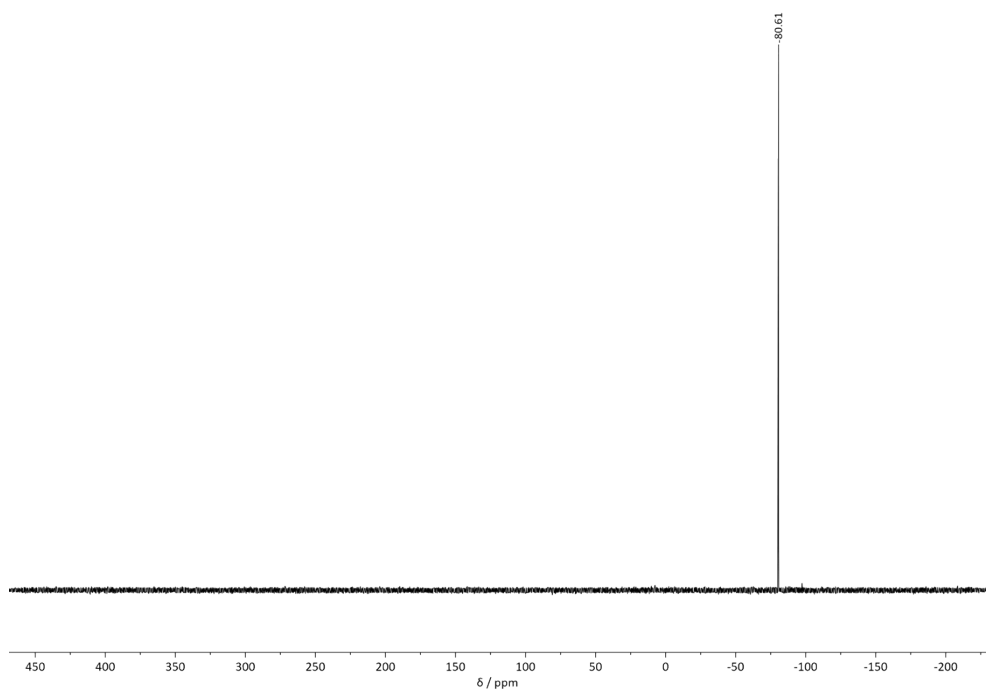


Figure S10 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 125.73 Hz, 298.0 K) of **9**.



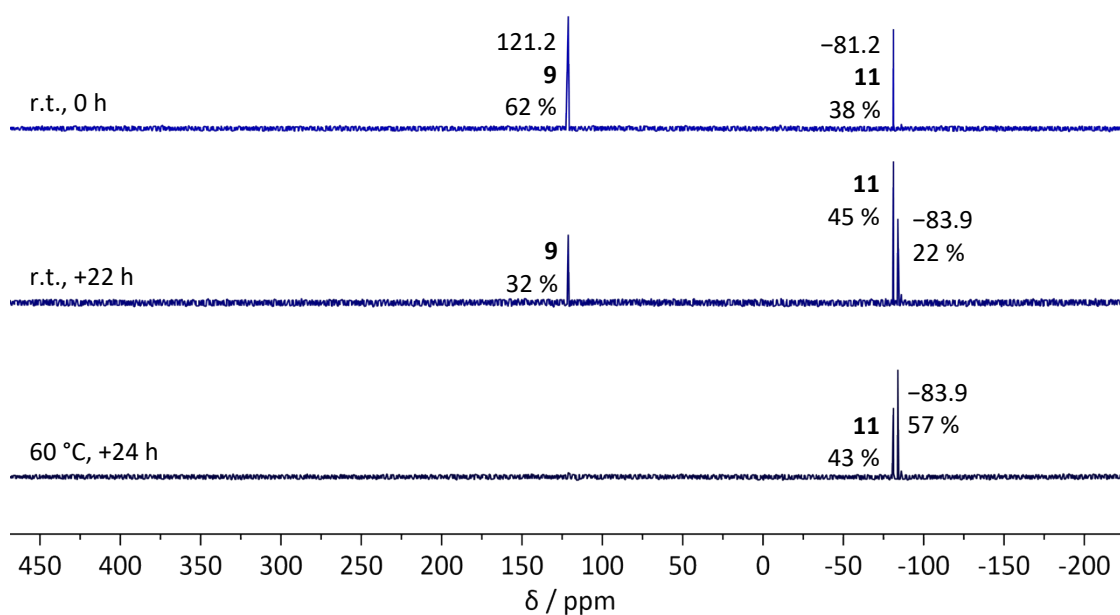
**Figure S11**  $^{31}\text{P}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 202.41 Hz, 298.0 K) of **9**.

### 3.5. **10** in reaction mixture



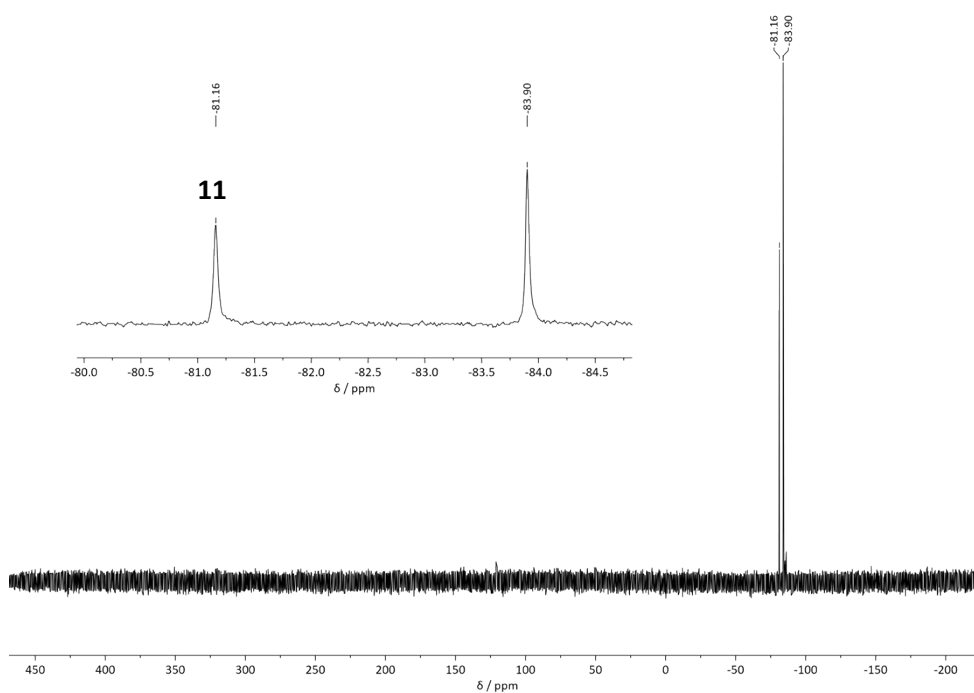
**Figure S12**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 121.51 Hz, 298.0 K) of **10** in reaction mixture.





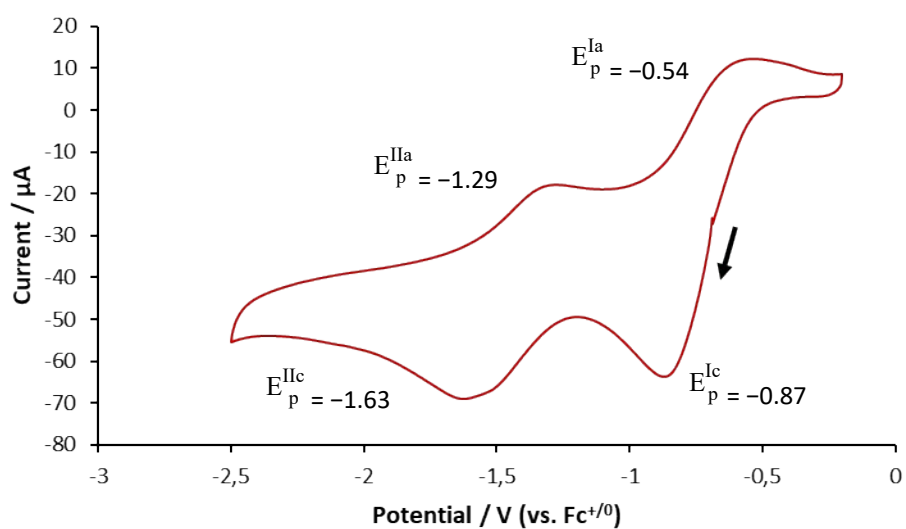
**Figure S13**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the reaction of **9** with an excess of diphenylethyne in  $\text{CH}_2\text{Cl}_2$ .

### 3.6. **11** in reaction mixture

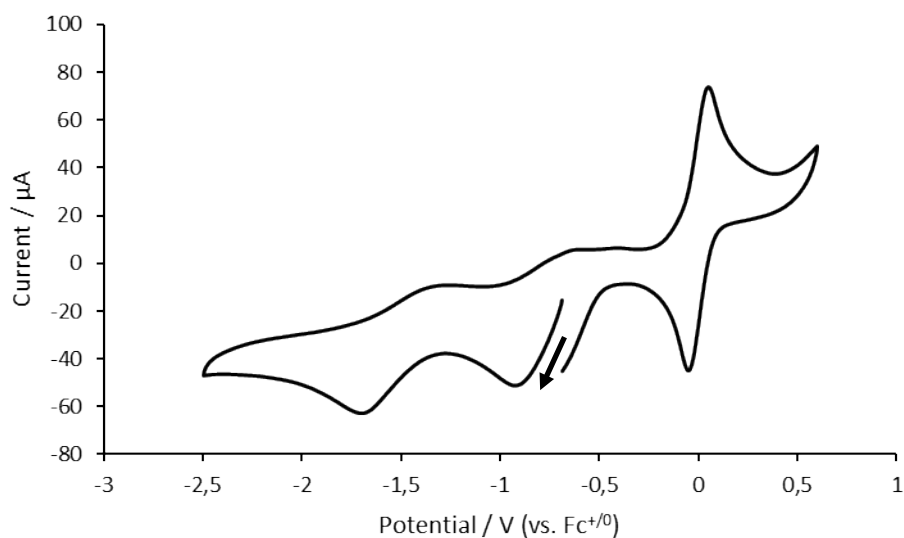


**Figure S14**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 202.41 Hz, 298.0 K) of **11** in reaction mixture (bottom spectrum of figure above).

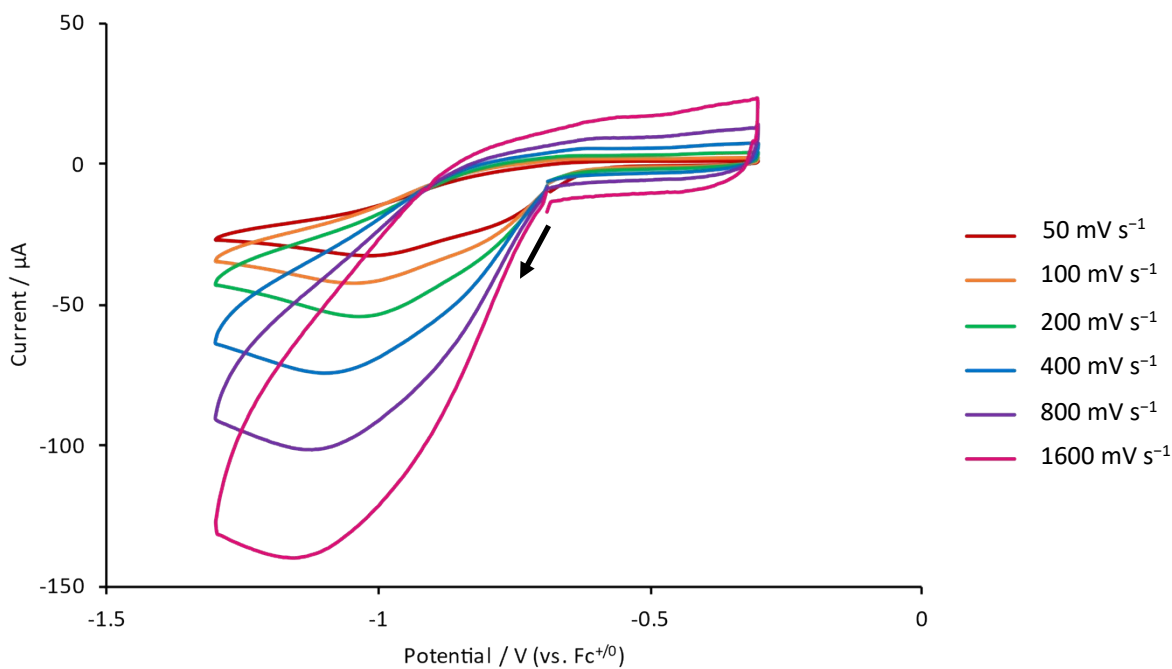
#### 4. Cyclic voltammetric studies



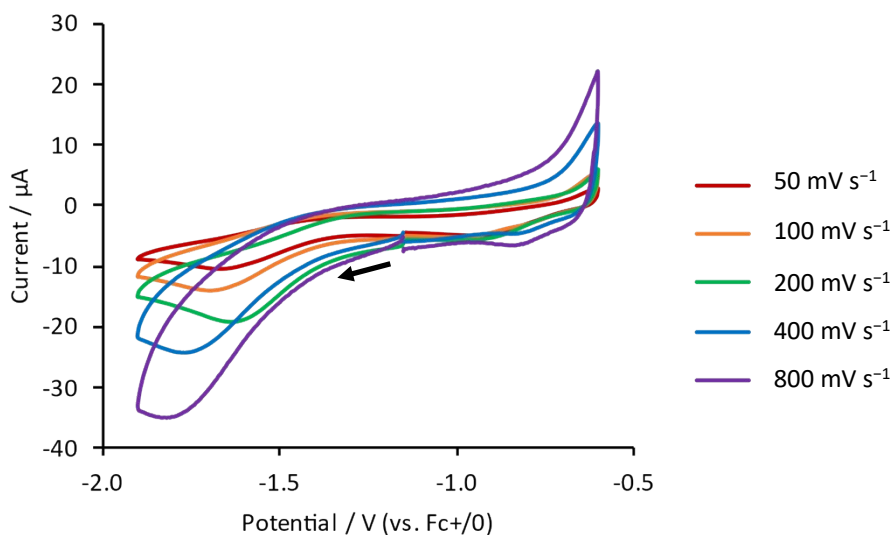
**Figure S15** Cyclic voltammogram of **9** (circa 1 mM) at a Pt electrode in a 0.1 M  $n\text{-Bu}_4\text{PF}_6/\text{MeCN}$  solution at a scan rate of  $200 \text{ mV s}^{-1}$ ; measurement with cathodic initial scan direction (indicated by an arrow) of the two reduction processes; potentials are referenced against  $\text{Fc}^{+/0}$ .



**Figure S16** Cyclic voltammogram of **9** (circa 1 mM) with ferrocene as internal reference at a Pt electrode in a 0.1 M  $n\text{-Bu}_4\text{PF}_6/\text{MeCN}$  solution at a scan rate of  $200 \text{ mV s}^{-1}$ ; measurement with cathodic initial scan direction (indicated by an arrow); potentials are referenced against  $\text{Fc}^{+/0}$ .



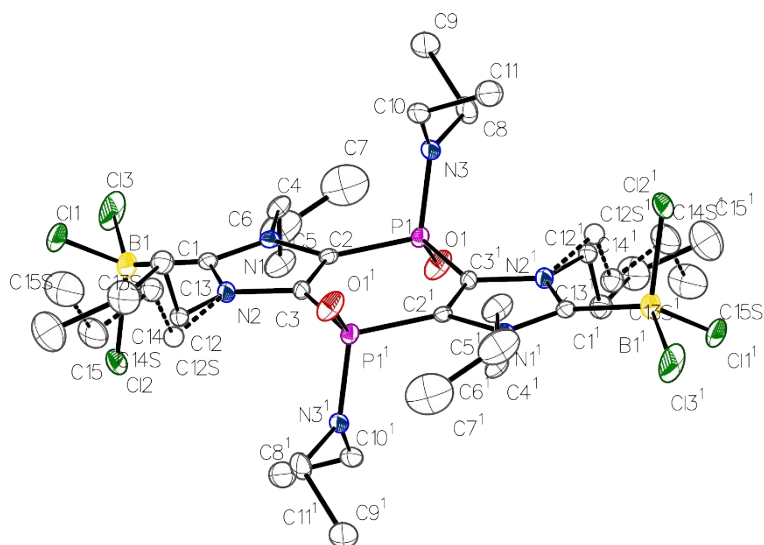
**Figure S17.** Cyclic voltammogram of the first reduction process of **9** (circa 1 mM) with ferrocene as internal reference at a Pt electrode in a 0.1 M  $n\text{-Bu}_4\text{PF}_6/\text{MeCN}$  solution at various scan rates; measurement with cathodic initial scan direction (indicated by an arrow); potentials are referenced against  $\text{Fc}^{+/0}$ .



**Figure S18.** Cyclic voltammogram of the second reduction process of **9** (circa 1 mM) with ferrocene as internal reference at a Pt electrode in a 0.1 M  $n\text{-Bu}_4\text{PF}_6/\text{MeCN}$  solution at various scan rates; measurement with cathodic initial scan direction (indicated by an arrow); potentials are referenced against  $\text{Fc}^{+/0}$ .

## 5. Single crystal X-ray diffraction studies

### 5.1. 2



**Figure S19** Molecular structure of **2** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms were omitted for clarity.

**Table S1.** Crystal data and structure refinements for **2**.

Identification code	TT-274 // GXraycu_6489f
Crystal habitus	clear colourless prism
Device type	Bruker D8 Venture
Empirical formula	C <sub>30</sub> H <sub>56</sub> B <sub>2</sub> Cl <sub>6</sub> N <sub>6</sub> O <sub>2</sub> P <sub>2</sub>
Moiety formula	C <sub>30</sub> H <sub>56</sub> B <sub>2</sub> Cl <sub>6</sub> N <sub>6</sub> O <sub>2</sub> P <sub>2</sub>
Formula weight / g mol <sup>-1</sup>	829.06
T / K	123
Crystal system	triclinic
Space group	P-1
<i>a</i> / Å	9.9165(4)
<i>b</i> / Å	10.3070(4)
<i>c</i> / Å	11.5166(5)
$\alpha$ / °	115.6440(10)
$\beta$ / °	92.465(2)
$\gamma$ / °	97.618(2)
<i>V</i> / Å <sup>3</sup>	1045.14(7)
<i>Z</i>	1
$\rho_{calc}$ / g cm <sup>-3</sup>	1.317
$\mu$ / mm <sup>-1</sup>	4.752
<i>F</i> (000)	436.0
Crystal size / mm <sup>3</sup>	0.32 × 0.16 × 0.12
Absorption correction	multi-scan
<i>T</i> <sub>min</sub> ; <i>T</i> <sub>max</sub>	0.4836; 0.7535
Radiation	Cu-K $\alpha$ ( $\lambda$ = 1.54178 Å)
2 $\theta$ range for data collection / °	9.054 to 145.154
Completeness to $\theta$	0.983
Index ranges	-12 ≤ <i>h</i> ≤ 12, -12 ≤ <i>k</i> ≤ 12, -14 ≤ <i>l</i> ≤ 14
Reflections collected	12580
Independent reflections	4054 ( <i>R</i> <sub>int</sub> = 0.0475, <i>R</i> <sub><math>\sigma</math></sub> = 0.0469)
Data / restraints / parameters	4054 / 226 / 254
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.071

Final  $R$  indexes ( $I \geq 2\sigma(I)$ )  
 Final  $R$  indexes (all data)  
 Largest diff. peak / hole /  $e \text{ \AA}^{-3}$

$R_1 = 0.0598$ ,  $\omega R_2 = 0.1500$   
 $R_1 = 0.0681$ ,  $\omega R_2 = 0.1584$   
 1.39 / -1.03

**Table S2.** Bond lengths for 2.

Atom	Atom	Length / $\text{\AA}$	Atom	Atom	Length / $\text{\AA}$
Cl1	B1	1.854(4)	N3	C10	1.469(4)
Cl2	B1	1.874(4)	C1	B1	1.641(5)
Cl3	B1	1.834(4)	C2	C3	1.368(4)
P1	O1	1.466(2)	C3	P1 <sup>1</sup>	1.808(3)
P1	N3	1.638(3)	C4	C5	1.528(4)
P1	C2	1.800(3)	C5	C6	1.526(5)
P1	C3 <sup>1</sup>	1.808(3)	C6	C7	1.502(8)
N1	C1	1.347(4)	C8	C9	1.521(5)
N1	C2	1.390(4)	C10	C11	1.525(5)
N1	C4	1.483(4)	C13	C14	1.528(3)
N2	C1	1.356(4)	C13	C12	1.517(4)
N2	C3	1.390(4)	C14	C15	1.517(4)
N2	C12	1.503(3)	C13S	C14S	1.528(3)
N2	C12S	1.503(3)	C13S	C12S	1.517(4)
N3	C8	1.478(4)	C14S	C15S	1.517(4)

<sup>1</sup>1-X,-Y,1-Z

**Table S3.** Bond angles for 2.

Atom	Atom	Atom	Angle / $^\circ$	Atom	Atom	Atom	Angle / $^\circ$
O1	P1	N3	113.94(14)	C3	C2	N1	106.7(2)
O1	P1	C2	113.53(14)	N2	C3	P1 <sup>1</sup>	123.6(2)
O1	P1	C3 <sup>1</sup>	114.16(13)	C2	C3	P1 <sup>1</sup>	129.5(2)
N3	P1	C2	106.53(13)	C2	C3	N2	106.6(2)
N3	P1	C3 <sup>1</sup>	107.52(13)	N1	C4	C5	112.2(3)
C2	P1	C3 <sup>1</sup>	99.99(13)	C6	C5	C4	110.4(3)
C1	N1	C2	110.3(2)	C7	C6	C5	114.0(4)
C1	N1	C4	127.7(2)	N3	C8	C9	112.9(3)
C2	N1	C4	121.9(2)	N3	C10	C11	113.8(3)
C1	N2	C3	110.0(2)	C12	C13	C14	113.9(3)
C1	N2	C12	130.4(3)	C15	C14	C13	114.3(4)
C1	N2	C12S	122.6(3)	Cl1	B1	Cl2	110.3(2)
C3	N2	C12	119.0(3)	Cl3	B1	Cl1	106.4(2)
C3	N2	C12S	126.0(3)	Cl3	B1	Cl2	109.3(2)
C8	N3	P1	119.5(2)	C1	B1	Cl1	111.3(2)
C10	N3	P1	120.4(2)	C1	B1	Cl2	103.4(2)
C10	N3	C8	118.8(3)	C1	B1	Cl3	116.2(3)
N1	C1	N2	106.4(2)	C12S	C13S	C14S	107.0(3)
N1	C1	B1	129.3(3)	C15S	C14S	C13S	111.3(3)
N2	C1	B1	123.6(3)	N2	C12	C13	118.4(3)
N1	C2	P1	123.0(2)	N2	C12S	C13S	106.2(2)
C3	C2	P1	130.4(2)				

<sup>1</sup>1-X,-Y,1-Z

## 6. Computational details

All geometric optimisation and energy calculations were performed with *ORCA 5.0*.<sup>6,7</sup> Structures were optimised at the TPSS-D4/def2-TZVP/CPCM<sub>THF</sub> level of theory which combines the TPSS<sup>8</sup> meta-GGA density functional with the charge dependent atom-pairwise DFT-D4 dispersion correction which uses the D4(EEQ)-ATM dispersion model<sup>9</sup> and the def2-TZVP basis set<sup>10–13</sup> using the conductor-like polarisable continuum model (CPCM)<sup>14</sup> for THF ( $\epsilon = 7.25$ ). The minimum or transition state nature of the compounds has been determined by numerical frequency calculations. All minima have zero imaginary frequencies below  $-50 \text{ cm}^{-1}$  which can be the numerical error according to the *ORCA 5.0.4* manual.<sup>15</sup> If single imaginary frequencies between 0 and  $-50 \text{ cm}^{-1}$  appeared they were checked carefully and in all cases only belonged to small rotations of *N*-Me substituent whose contributions in energy difference fall within the method's error margins. Transition states possess only one imaginary frequency that describes the transition from starting material to product. The transition state has been computed with the help of the nudge elastic band optimiser (NEB)<sup>7,16</sup> as implemented in *ORCA 5.0*. Single-point calculations were performed at the PW6B95-D4/def2-QZVP/CPCM<sub>THF</sub> level of theory which combines the PW6B95 hybrid-meta-GGA functional<sup>17</sup> with the larger def2-QZVP basis set.<sup>10–13</sup> NICS(1) values were calculated at the B3LYP-D4/def2-TZVPPD level of theory combining the hybrid functional B3LYP<sup>18</sup> with the def2-TZVPPD basis set<sup>10–13</sup> and using the NMR module of *ORCA 5.0* utilising Gauge including atomic orbitals (GIAOs).<sup>19</sup> Values were obtained by calculating the NICS(1) value of benzene at the same levels of theory. The B3LYP functional was chosen here for general comparability as it is often used, performed well for the synthesised systems in a self-conducted small study and gave reliable results with relatively low resource cost. The density-fitting RI-J (def2/J)<sup>10,20</sup> approach was used to accelerate geometry optimisations, numerical frequency and single point energy calculations.

The graphical representations of the calculated structures and their frontier molecular orbitals (FMOs) were generated with *UCSF Chimera 1.15*.<sup>21</sup>

Below are listed the optimised cartesian coordinates (in Å) with electronic energies (in Hartree) in THF solution. All structures of new compounds were computed as model compounds with *N*-methyl instead of *N*-*n*-butyl substitution to save computational costs. Zero point energies ( $E_{ZPE}$ ), thermal corrections ( $E_T$ ) at 298.15 K and entropy corrections ( $E_S$ ) were taken from the optimisation calculations.

### 6.1. **3<sup>Me</sup>**

**Table S4.** Computational data for **3<sup>Me</sup>**.

<b>3<sup>Me</sup></b>			
$E = -1561.223420154035$			
$E_{ZPE} = 0.37508751$			
$E_T = 0.02563652$			
$E_S = -0.07729428$			
C	-8.05401	-0.57169	-1.50079
C	-5.95317	0.23473	-0.99877
C	-6.64951	1.25414	-1.60327
C	-4.47329	2.88017	-1.35732
C	-3.77656	1.86052	-0.75373
C	-2.37251	3.68674	-0.85512
P	-6.04904	2.83793	-2.25441
N	-3.60553	3.97291	-1.37736
N	-2.50647	2.37383	-0.48826
N	-6.82113	-0.85784	-0.97822

N	-7.91983	0.74108	-1.86815
N	-5.39708	2.19589	-3.79148
N	-5.02718	0.91986	1.43490
P	-4.37716	0.27674	-0.10246
C	-3.97671	5.32187	-1.80788
H	-3.08214	5.93989	-1.73713
H	-4.34169	5.31664	-2.83676
H	-4.75703	5.71877	-1.15272
C	-1.38116	1.58928	0.02271
H	-0.54445	2.27484	0.15374
H	-1.62960	1.12422	0.97860
H	-1.11532	0.81060	-0.69736
C	-3.96995	1.38538	2.34956
H	-3.40822	2.20104	1.89007
H	-4.45736	1.77462	3.24963
H	-3.27154	0.58787	2.65645
C	-5.90138	-0.04009	2.13136
H	-6.76604	-0.28029	1.50973
H	-5.38795	-0.97322	2.42066
H	-6.26427	0.44405	3.04411
C	-4.52922	3.16054	-4.48954
H	-5.04894	4.08978	-4.78016
H	-3.66612	3.40758	-3.86844
H	-4.16314	2.67748	-5.40160
C	-6.45174	1.72322	-4.70539
H	-7.00939	0.90546	-4.24470
H	-7.15411	2.51665	-5.01385
H	-5.96209	1.33507	-5.60472
C	-9.04469	1.52530	-2.38059
H	-8.79866	1.98269	-3.34081
H	-9.88383	0.84119	-2.50349
H	-9.30545	2.30990	-1.66514
C	-6.45144	-2.20563	-0.54283
H	-6.11361	-2.20216	0.49536
H	-7.33965	-2.82936	-0.63914
H	-5.65163	-2.59431	-1.17900

## 6.2. $4^{\text{Me}}$

Table S5. Computational data for  $42^{\text{Me}}$ .

### $42^{\text{Me}}$

$$E = -4105.331649950909$$

$$E_{\text{ZPE}} = 0.23292046$$

$$E_{\text{T}} = 0.027143$$

$$E_{\text{S}} = -0.08314802$$

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C	-6.61914	-6.78161	-0.54561
C	-7.00565	-5.50266	-0.99622
C	-4.60714	-4.57362	-0.51250
C	-4.21815	-5.85425	-0.06901
P	-6.13858	-3.99262	-1.11646
P	-5.09047	-7.36020	0.06791
N	-7.74934	-7.59177	-0.67489
N	-8.33907	-5.61775	-1.37210
N	-3.47791	-3.76249	-0.38158
N	-2.88175	-5.74099	0.29734
C	-9.09164	-4.47355	-1.90145

H	-10.00167	-4.82718	-2.37484
H	-9.32850	-3.78905	-1.08383
H	-8.46288	-3.97211	-2.64144
C	-7.72869	-9.01980	-0.31650
H	-8.38084	-9.19701	0.53725
H	-6.70095	-9.27557	-0.05515
H	-8.04748	-9.61660	-1.16827
C	-2.12864	-6.88641	0.82334
H	-2.45201	-7.08853	1.84696
H	-1.06672	-6.66505	0.79832
H	-2.34000	-7.74815	0.18524
C	-3.49347	-2.34020	-0.76227
H	-2.73553	-2.15289	-1.52028
H	-3.31527	-1.72061	0.11478
H	-4.48116	-2.12303	-1.17121
C	-2.43723	-4.47360	0.11432
C	-8.79059	-6.87929	-1.16770
B	-0.91839	-4.00351	0.46068
B	-10.32076	-7.33795	-1.47837
Cl	-11.44517	-6.19047	-0.50368
Cl	-10.58547	-7.13813	-3.33024
Cl	-10.73066	-9.08346	-1.00769
Cl	-0.57514	-2.19964	0.20476
Cl	-0.61529	-4.40808	2.26977
Cl	0.22545	-4.99230	-0.65928

### 6.3. $\text{BCl}_3$

Table S6. Computational data for  $\text{BCl}_3$ .

#### $\text{BCl}_3$

$E = -1406.774558275043$

$E_{\text{ZPE}} = 0.007326$

$E_{\text{T}} = 0.00444425$

$E_{\text{S}} = -0.03404358$

B	0.84887	-0.06810	0.00071
Cl	-0.02568	1.44555	0.00076
Cl	2.59712	-0.06760	0.00106
Cl	-0.02481	-1.58225	0.00037

### 6.4. $(\text{Me}_2\text{N})\text{BCl}_2$

Table S7. Computational data for  $(\text{Me}_2\text{N})\text{BCl}_2$ .

#### $(\text{Me}_2\text{N})\text{BCl}_2$

$E = -1081.006494325866$

$E_{\text{ZPE}} = 0.08853845$

$E_{\text{T}} = 0.00773965$

$E_{\text{S}} = -0.04127873$

B	0.82133	-0.01391	0.08734
Cl	-0.13139	0.09847	1.59532
Cl	-0.01970	-0.73589	-1.31498
N	2.13358	0.43114	0.00932
C	2.86377	1.02963	1.13331
H	3.75447	0.42974	1.35372
H	3.18408	2.04278	0.86395



H	2.22946	1.07351	2.01712
C	2.95294	0.35718	-1.20642
H	3.84207	-0.25413	-1.01296
H	2.38168	-0.08299	-2.02208
H	3.27760	1.36467	-1.49114

## 6.5. 5<sup>Me</sup>

Table S8. Computational data for 41a<sup>Me</sup>.

### 41a<sup>Me</sup>

$E = -4374.934386266487$

$E_{ZPE} = 0.39746753$

$E_T = 0.0360935$

$E_S = -0.09914472$

C	-8.01249	-0.52527	-1.52121
C	-5.96264	0.26159	-1.00230
C	-6.65024	1.26922	-1.63053
C	-4.48790	2.89130	-1.37944
C	-3.80106	1.87918	-0.75762
C	-2.42762	3.66510	-0.88475
P	-6.06822	2.86641	-2.28137
N	-3.63241	3.98749	-1.41863
N	-2.53085	2.36846	-0.49213
N	-6.80804	-0.83741	-0.97635
N	-7.91710	0.76971	-1.91422
N	-5.42096	2.24482	-3.81315
N	-5.01053	0.89725	1.42960
P	-4.37864	0.27893	-0.10942
C	-4.05054	5.30380	-1.93431
H	-3.98563	6.03923	-1.13452
H	-3.41885	5.59965	-2.76943
H	-5.08700	5.20910	-2.26173
C	-1.44274	1.54783	0.06623
H	-0.53181	1.75129	-0.49479
H	-1.29195	1.78484	1.11799
H	-1.72955	0.50187	-0.05064
C	-3.93562	1.34296	2.33991
H	-3.40569	2.19413	1.90859
H	-4.41172	1.68007	3.26537
H	-3.21390	0.54911	2.59022
C	-5.88661	-0.07454	2.11551
H	-6.77765	-0.26716	1.51546
H	-5.38731	-1.02822	2.35013
H	-6.20856	0.38497	3.05466
C	-4.57139	3.23431	-4.50741
H	-5.10268	4.16429	-4.76592
H	-3.69578	3.47222	-3.90123
H	-4.22061	2.76958	-5.43366
C	-6.47781	1.76277	-4.72592
H	-7.00170	0.91356	-4.28364
H	-7.20688	2.54090	-5.00276
H	-5.98491	1.41343	-5.63806
C	-8.97887	1.59332	-2.52000
H	-9.30819	1.15169	-3.45825
H	-9.81428	1.67019	-1.82657
H	-8.55732	2.58372	-2.69771

C	-6.39969	-2.16527	-0.48801
H	-6.78899	-2.33622	0.51431
H	-6.78613	-2.92007	-1.17097
H	-5.30892	-2.18945	-0.48135
B	-1.06726	4.53867	-0.75819
B	-9.23145	-1.58327	-1.67559
Cl	-0.43959	4.42378	1.00766
Cl	-1.25459	6.33798	-1.17927
Cl	0.17564	3.77427	-1.95604
Cl	-10.83682	-0.84517	-2.24866
Cl	-9.53557	-2.39409	-0.00887
Cl	-8.67591	-2.86408	-2.94561

## 6.6. 6<sup>Me</sup>

Table S9. Computational data for 6<sup>Me</sup>.

6<sup>Me</sup>

$E = -5026.55432574901$

$E_{ZPE} = 0.23633635$

$E_T = 0.03045269$

$E_S = -0.08982677$

---

C	-6.64300	-6.79678	-0.57229
C	-7.01954	-5.55602	-1.02938
C	-4.55755	-4.61026	-0.54463
C	-4.17643	-5.85342	-0.09824
P	-6.09423	-4.02979	-1.28666
P	-5.07393	-7.40947	0.07015
N	-7.76828	-7.60605	-0.64817
N	-8.35315	-5.65196	-1.37990
N	-3.45701	-3.77885	-0.39941
N	-2.86161	-5.73580	0.31561
C	-9.12482	-4.50977	-1.89413
H	-9.91788	-4.87843	-2.53937
H	-9.53984	-3.94595	-1.05827
H	-8.44254	-3.88286	-2.47381
C	-7.74860	-9.02698	-0.25553
H	-8.49383	-9.20086	0.51713
H	-6.75522	-9.24741	0.13887
H	-7.94639	-9.65096	-1.12549
C	-2.08662	-6.86942	0.84889
H	-2.29940	-6.98520	1.91238
H	-1.02834	-6.67977	0.69109
H	-2.37741	-7.76592	0.29892
C	-3.47771	-2.36671	-0.82150
H	-2.58194	-2.14919	-1.39698
H	-3.54046	-1.71800	0.05129
H	-4.35729	-2.22737	-1.45368
C	-2.42101	-4.46316	0.14828
C	-8.81912	-6.90556	-1.14295
B	-0.93339	-3.96062	0.56805
B	-10.34794	-7.36471	-1.44912
Cl	-11.48201	-6.19461	-0.51774
Cl	-10.60407	-7.21093	-3.30902
Cl	-10.75523	-9.10217	-0.94477
Cl	-0.68378	-2.12493	0.46431
Cl	-0.63434	-4.47649	2.34939

Cl	0.27496	-4.81658	-0.59102
Cl	-6.85162	-2.89091	0.31603
Cl	-4.36911	-8.41072	-1.65344

## 6.7. $9^{\text{Me}}$

**Table S10.** Computational data for  $9^{\text{Me}}$ .

$g^{\text{Me}}$

$E = -1292.581999195648$

$E_{\text{ZPE}} = 0.2383914$

$E_{\text{T}} = 0.01632579$

$E_{\text{S}} = -0.05945547$

---

C	C	C	C
C	C	C	C
C	C	C	C
C	C	C	C
P	P	P	P
P	P	P	P
N	N	N	N
N	N	N	N
N	N	N	N
N	N	N	N
C	C	C	C
H	H	H	H
H	H	H	H
H	H	H	H
C	C	C	C
H	H	H	H
H	H	H	H
H	H	H	H
C	C	C	C
H	H	H	H
H	H	H	H
H	H	H	H
C	C	C	C
H	H	H	H
H	H	H	H
H	H	H	H
C	C	C	C
C	C	C	C
H	H	H	H
H	H	H	H

## 6.8. Ghadwal's 1,4-diphosphinine<sup>22</sup>

**Table 11.** Computational data for Ghadwal's 1,4-diphosphinine.

$E = -3469.113732200630$

$E_{\text{ZPE}} = 1.26824462$

$E_{\text{T}} = 0.07373852$

$E_{\text{S}} = -0.16865406$

---

P	0.04937	-0.03435	0.02538
N	1.12552	-0.12197	2.55155
N	-0.55035	-0.20827	3.94604
C	0.80539	-0.20100	3.86677

C	-0.03232	-0.08297	1.77104
C	-1.11308	-0.11160	2.67134
C	2.42963	-0.15271	1.92185
C	2.98977	-1.40789	1.64605
C	4.21503	-1.41488	0.97132
H	4.69030	-2.36401	0.74216
C	4.82610	-0.22575	0.58492
H	5.77439	-0.25477	0.05595
C	4.23422	1.00204	0.87316
H	4.72670	1.92126	0.57074
C	3.01760	1.07125	1.55678
C	2.32581	-2.70802	2.05898
H	1.34118	-2.48025	2.47833
C	3.14668	-3.41275	3.15586
H	4.13960	-3.68470	2.78165
H	2.63621	-4.32835	3.47230
H	3.27402	-2.76659	4.03019
C	2.10244	-3.63046	0.84798
H	1.50425	-3.12956	0.07984
H	1.57370	-4.53587	1.16404
H	3.05483	-3.93294	0.40021
C	2.39606	2.41794	1.89190
H	1.53598	2.25119	2.54849
C	3.38189	3.33737	2.63608
H	2.87699	4.27121	2.90425
H	3.75705	2.87742	3.55481
H	4.23973	3.58685	2.00325
C	1.88539	3.11584	0.61996
H	1.39471	4.05977	0.87940
H	2.71450	3.33348	-0.06170
H	1.16494	2.48757	0.08803
C	-1.35178	-0.12649	5.14796
C	-2.04937	-1.27680	5.56304
C	-2.80249	-1.15513	6.73325
H	-3.35747	-2.00972	7.10331
C	-2.85504	0.04795	7.43605
H	-3.44649	0.11257	8.34488
C	-2.16875	1.16656	6.97827
H	-2.23428	2.10166	7.52636
C	-1.39498	1.10665	5.81440
C	-1.98254	-2.59176	4.79479
H	-1.99871	-2.35195	3.72407
C	-0.67590	-3.36565	5.06325
H	0.20902	-2.81541	4.73473
H	-0.56982	-3.58624	6.13092
H	-0.69748	-4.31407	4.51640
C	-3.18701	-3.49897	5.08003
H	-4.13377	-2.96726	4.94631
H	-3.16921	-4.35082	4.39382
H	-3.15362	-3.89478	6.10075
C	-0.67573	2.34372	5.30793
H	-0.03066	2.06182	4.47095
C	0.22568	2.96287	6.38963
H	-0.36633	3.32842	7.23517
H	0.77475	3.81204	5.96960
H	0.94972	2.23409	6.76677
C	-1.69385	3.36920	4.77207
H	-2.29836	2.93624	3.96859

H	-1.16880	4.24628	4.37885
H	-2.36681	3.69991	5.57040
C	1.73164	-0.23781	4.98735
C	1.35566	-0.80687	6.22036
H	0.37979	-1.24956	6.35189
C	2.24585	-0.82316	7.28602
H	1.94117	-1.27486	8.22473
C	3.51912	-0.26717	7.15218
H	4.20978	-0.27805	7.99002
C	3.89988	0.30283	5.93668
H	4.88465	0.74468	5.82211
C	3.02016	0.31468	4.86231
H	3.33587	0.76680	3.93448
P	-2.84299	-0.02512	2.43712
N	-3.91914	0.06276	-0.08904
N	-2.24326	0.14892	-1.48353
C	-3.59901	0.14180	-1.40426
C	-2.76131	0.02358	0.69146
C	-1.68054	0.05215	-0.20884
C	-5.22327	0.09380	0.54061
C	-5.78331	1.34910	0.81606
C	-7.00861	1.35635	1.49072
H	-7.48380	2.30558	1.71964
C	-7.61982	0.16737	1.87735
H	-8.56815	0.19662	2.40626
C	-7.02805	-1.06054	1.58943
H	-7.52064	-1.97965	1.89201
C	-5.81139	-1.13002	0.90591
C	-5.11920	2.64908	0.40290
H	-4.13467	2.42114	-0.01660
C	-5.94012	3.35383	-0.69395
H	-6.93295	3.62598	-0.31964
H	-5.42955	4.26932	-1.01053
H	-6.06767	2.70761	-1.56819
C	-4.89553	3.57160	1.61378
H	-4.29722	3.07071	2.38183
H	-4.36678	4.47695	1.29754
H	-5.84781	3.87417	2.06171
C	-5.19000	-2.47684	0.57106
H	-4.32969	-2.31027	-0.08528
C	-6.17577	-3.39611	-0.17340
H	-5.67102	-4.33014	-0.44122
H	-6.55040	-2.93620	-1.09236
H	-7.03395	-3.64525	0.45911
C	-4.67989	-3.17477	1.84319
H	-4.18916	-4.11874	1.58396
H	-5.50929	-3.39237	2.52452
H	-3.95962	-2.54655	2.37542
C	-1.44192	0.06704	-2.68550
C	-0.74429	1.21728	-3.10066
C	0.00864	1.09557	-4.27099
H	0.56362	1.95013	-4.64112
C	0.06099	-0.10751	-4.97380
H	0.65231	-0.17217	-5.88272
C	-0.62531	-1.22607	-4.51592
H	-0.55993	-2.16118	-5.06402
C	-1.39892	-1.16611	-3.35195
C	-0.81094	2.53226	-2.33243

H	-0.79519	2.29246	-1.26170
C	-2.11724	3.30656	-2.60130
H	-3.00242	2.75666	-2.27288
H	-2.22302	3.52702	-3.66903
H	-2.09545	4.25506	-2.05458
C	0.39396	3.43901	-2.61731
H	1.34046	2.90687	-2.48339
H	0.37637	4.29083	-1.93106
H	0.36101	3.83489	-3.63802
C	-2.11822	-2.40312	-2.84539
H	-2.76317	-2.12116	-2.00834
C	-3.01980	-3.02217	-3.92701
H	-2.42790	-3.38778	-4.77260
H	-3.56893	-3.87129	-3.50692
H	-3.74381	-2.29332	-4.30408
C	-1.10015	-3.42869	-2.30965
H	-0.49555	-2.99581	-1.50619
H	-1.62524	-4.30575	-1.91642
H	-0.42728	-3.75944	-3.10803
C	-4.52526	0.17877	-2.52482
C	-4.14924	0.74778	-3.75784
H	-3.17331	1.19031	-3.88940
C	-5.03946	0.76421	-4.82347
H	-4.73475	1.21588	-5.76218
C	-6.31280	0.20840	-4.68960
H	-7.00349	0.21940	-5.52742
C	-6.69361	-0.36157	-3.47410
H	-7.67843	-0.80329	-3.35950
C	-5.81385	-0.37356	-2.39976
H	-6.12959	-0.82565	-1.47192

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