

## Supplementary Information

### **Untapping the coordinative potential of a C-functional 1,4-diphosphabarrelene using two sets of complimentary ligand centres**

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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).

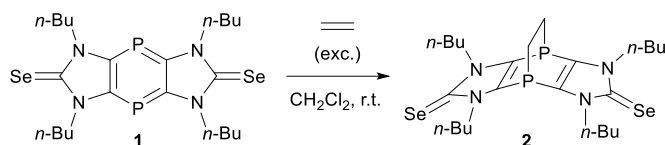
Elemental analyses were performed on a Elementar Vario Micro analysis device in quadruplicate or triplicate for each sample. All samples were prepared and weighed up in tin or silver sample containers using a micro-analytical balance in a glovebox. The mean C, H and N values are given for each compound.

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. 2363298 (4) and 2363297 (5), 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).

## 2. Experimental procedures and characterisation

### 2.1. Synthesis of 2



In a 20 mL Schlenk tube equipped with a stir bar 0.066 g (0.11 mmol, 1.0 eq.) of **1** were dissolved in 6 mL dichloromethane and the Argon atmosphere was exchanged for 1 atm ethene. After stirring for 1 h at ambient temperature the solution had turned orange and the solvent was removed *in vacuo* ( $\leq 0.05$  mbar). The resulting yellow to orange solid was washed four times with 2–4 mL *n*-pentane each and dried for 2 h ( $\leq 0.02$  mbar) yielding a yellow solid.

**Molecular formula:** C<sub>24</sub>H<sub>40</sub>N<sub>4</sub>P<sub>2</sub>Se<sub>2</sub>

**Molecular weight:** 604.48 g mol<sup>-1</sup>

**Yield:** 0.049 g (0.08 mmol, 71 %)

**Melting point:** 120 °C (dec.)

**EA:** calculated (%) C 47.69 H 6.67 N 9.27

found (%) C 46.85 H 6.66 N 9.20

**MS (pos. ESI):**  $m/z$  (%) = 604.107 (4) [M]<sup>+</sup>, 527.197 (100) [M–Se+H]<sup>+</sup>, 499.165 (25) [M–C<sub>2</sub>H<sub>4</sub>–Se+H]<sup>+</sup>.

**HRMS (pos. ESI):**  $m/z$  calculated for [C<sub>24</sub>H<sub>40</sub>N<sub>4</sub>P<sub>2</sub>Se<sub>2</sub>]<sup>+</sup>: 604.107; found: 604.107.

$m/z$  calculated for [C<sub>24</sub>H<sub>40</sub>N<sub>4</sub>P<sub>2</sub>Se<sub>2</sub>H]<sup>+</sup>: 605.1146; found: 605.1145.

**IR (ATR):**  $\tilde{\nu}$  / cm<sup>-1</sup> = 2959 (m,  $\nu_{as}(\text{CH}_3)$ ,  $\nu_s(\text{CH}_2)$ ), 2933 (m,  $\nu_{as}(\text{CH}_3)$ ,  $\nu_s(\text{CH}_2)$ ), 2871 (m,  $\nu_s(\text{CH}_3)$ ,  $\nu_{as}(\text{CH}_2)$ ).

**<sup>1</sup>H NMR** (500.04 MHz, 298.0 K, CDCl<sub>3</sub>):  $\delta$  / ppm = 0.96 (t,  $^3J_{\text{H,H}} = 7.4$  Hz, 12H, CH<sub>3</sub>), 1.38 (qm,  $^3J_{\text{H,H}} = 7.4$  Hz, 8H, CH<sub>2</sub>CH<sub>3</sub>), 1.67–1.82 (m, 12H, PCH<sub>2</sub>, NCH<sub>2</sub>CH<sub>2</sub>), 4.20–4.37 (m, 8H, NCH<sub>2</sub>).

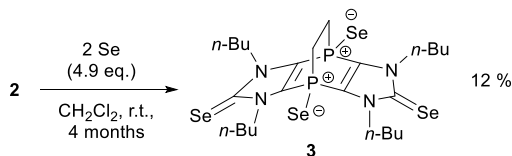
**<sup>13</sup>C{<sup>1</sup>H} NMR** (125.75 MHz, 298.0 K, CDCl<sub>3</sub>):  $\delta$  / ppm = 13.9 (s, CH<sub>3</sub>), 19.8 (dd,  $J_{\text{P,C}} = 4.6$  Hz, PCH<sub>2</sub>), 20.1 (m, CH<sub>2</sub>CH<sub>3</sub>), 32.0 (m, NCH<sub>2</sub>CH<sub>2</sub>), 48.9 (m, NCH<sub>2</sub>), 137.3 (dd,  $J_{\text{P,C}} = 4.6$  Hz, PC), 159.1 ( $s_{\text{sat}}$ ,  $^1J_{\text{Se,C}} = 233.4$  Hz, CSe).

**<sup>31</sup>P NMR** (202.44 MHz, 298.0 K, CDCl<sub>3</sub>):  $\delta$  / ppm = –94.7 (tm,  $^2J_{\text{P,H}} = 5.3$  Hz).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (202.44 MHz, 298.0 K, CDCl<sub>3</sub>):  $\delta$  / ppm = –94.7 (s).

**<sup>77</sup>Se NMR** (57.24 MHz, 298.0 K, CDCl<sub>3</sub>):  $\delta$  / ppm = 26.4 (s).

### 2.2. Generation of 3



In a 20 mL Schlenk tube 0.139 g (0.21 mmol, 1.0 eq.) of **2** and 0.081 g (1.03 mmol, 4.9 eq.) grey selenium were suspended in 4 mL dichloromethane and stirred at ambient temperature while the reaction course was monitored via  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. After 4 months no change in the composition of the reaction mixture was observed anymore and the contents were extracted with additional dichloromethane (twice 4 mL). The solvent was removed *in vacuo* ( $\leq 0.05$  mbar) yielding a yellow solid which was washed with twice 3 mL diethyl ether and three times 3 mL *n*-pentane. After drying for 2 h ( $\leq 0.02$  mbar) the product mixture was obtained as yellow solid and analysed by NMR spectroscopy.

**Molecular formula:**  $\text{C}_{24}\text{H}_{40}\text{N}_4\text{P}_2\text{Se}_2$

**Molecular weight:**  $762.44 \text{ g mol}^{-1}$

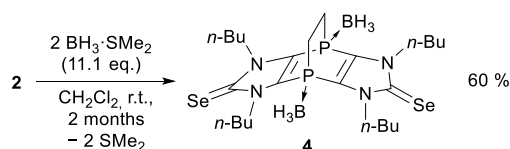
**Content in mixture:** 12 % ( $^{31}\text{P}$  NMR integration of isolated reaction mixture)

$^{31}\text{P}$  NMR (202.44 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta / \text{ppm} = -22.1$  (br  $s_{\text{sat}}$ ,  $^1J_{\text{Se,P}} = 856 \text{ Hz}$ ,  $^3J_{\text{P,P}} = 49 \text{ Hz}$ ).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202.44 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta / \text{ppm} = -21.8$  (d,  $^1J_{\text{Se,P}} = 856 \text{ Hz}$ ).

$^{77}\text{Se}$  NMR (57.24 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta / \text{ppm} = -438.2$  (d,  $^1J_{\text{Se,P}} = 856 \text{ Hz}$ , PSe), 43.6 (s, CSe).

### 2.3. Generation of **4**



To a solution of 0.112 g (0.19 mmol, 1.0 eq.) of **2** in 3 mL dichloromethane in a 15 mL Schlenk tube 0.20 mL (2.11 mmol, 11.1 eq.)  $\text{BH}_3\cdot\text{SMe}_2$  were added and the reaction solution was stirred at ambient temperature while the reaction course was monitored via  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. After 2 months no change in the composition of the reaction mixture was observed anymore and the solvent was removed *in vacuo* ( $\leq 0.05$  mbar). The resulting yellow residue was washed with three times 3 mL *n*-pentane and after drying for 2 h ( $\leq 0.02$  mbar) the product mixture was obtained as light yellow solid and analysed by NMR spectroscopy and SCXRD.

**Molecular formula:**  $\text{C}_{24}\text{H}_{46}\text{B}_2\text{N}_4\text{P}_2\text{Se}_2$

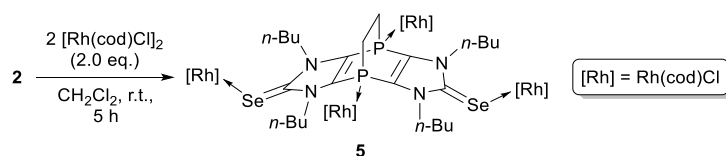
**Molecular weight:**  $632.17 \text{ g mol}^{-1}$

**Content in mixture:** 60 % ( $^{31}\text{P}$  NMR integration of isolated reaction mixture)

$^{31}\text{P}$  NMR (202.44 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta / \text{ppm} = -17.8$  (br s).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202.44 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta / \text{ppm} = -17.8$  (s).

### 2.4. Synthesis of **5**



In a 20 mL Schlenk tube 0.120 g (0.20 mmol, 1.0 eq.) of **2** and 0.195 g (0.40 mmol, 2.0 eq.)  $[\text{Rh}(\text{cod})\text{Cl}]_2$  were dissolved in 6 mL dichloromethane and stirred for 5 h at ambient temperature. The solvent was

removed *in vacuo* ( $\leq 0.05$  mbar) and the resulting yellow solid was extracted with three times 2–5 mL toluene. After evaporation of the solvent the oily residue was washed with six times 4–5 mL diethyl ether, three times with 5 mL *n*-pentane, and then dried for 3 h ( $\leq 0.02$  mbar) yielding a yellow solid.

**Molecular formula:** C<sub>56</sub>H<sub>88</sub>Cl<sub>4</sub>N<sub>4</sub>P<sub>2</sub>Rh<sub>4</sub>Se<sub>2</sub>

**Molecular weight:** 1590.66 g mol<sup>-1</sup>

**Yield:** 0.229 g (0.14 mmol, 73 %)

**Melting point:** 231 °C (dec.)

<b>EA:</b> calculated (%)	C 42.29	H 5.58	N 3.52
found (%)	C 42.13	H 5.77	N 3.56

**MS (pos. ESI):**  $m/z$  (%) = 1555.009 (25) [M-Cl]<sup>+</sup>, 1309.041 (86) [M-[Rh(cod)Cl]-Cl]<sup>+</sup>, 1063.073 (66), [M-2[Rh(cod)Cl]-Cl]<sup>+</sup>.

**HRMS (pos. ESI):**  $m/z$  calculated for [C<sub>56</sub>H<sub>88</sub>Cl<sub>3</sub>N<sub>4</sub>P<sub>2</sub>Rh<sub>4</sub>Se<sub>2</sub>]<sup>+</sup>: 1555.0088; found: 1555.0093.

**IR (ATR):**  $\tilde{\nu}$  / cm<sup>-1</sup> = 2997 (m,  $\nu_{as}(\text{CH}_3)$ ,  $\nu_s(\text{CH}_2)$ ), 2956 (m,  $\nu_{as}(\text{CH}_3)$ ,  $\nu_s(\text{CH}_2)$ ), 2872 (m,  $\nu_s(\text{CH}_3)$ ,  $\nu_{as}(\text{CH}_2)$ ), 2830 (w,  $\nu_s(\text{CH}_3)$ ,  $\nu_{as}(\text{CH}_2)$ ).

**<sup>1</sup>H NMR** (500.04 MHz, 298.0 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  / ppm = 1.17 (t, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, 12H, CH<sub>3</sub>), 1.45–1.57 (m, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, 8H, CH<sub>2</sub>CH<sub>3</sub>), 1.58–1.62 (m, 4H, PCH<sub>2</sub>), 1.64–1.79 (m, 16H, CH<sub>2</sub>CH<sub>3</sub>, CH<sub>2</sub>CH), 2.05–2.15 (m, 4H, CH<sub>2</sub>CH), 2.15–2.35 (m, 16H, NCH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH), 2.46–2.59 (m, 4H, CH<sub>2</sub>CH), 3.94 (m, 4H, CH), 4.20 (m, 4H, CH), 4.82 (m, 4H, CH), 5.50 (td, <sup>3</sup>J<sub>H,H</sub> = 12.5 Hz, <sup>4</sup>J<sub>P,H</sub> = 5.1 Hz, 4H, NCH<sub>2</sub>), 5.83 (m, 4H, CH), 5.98–6.09 (m, 4H, NCH<sub>2</sub>).

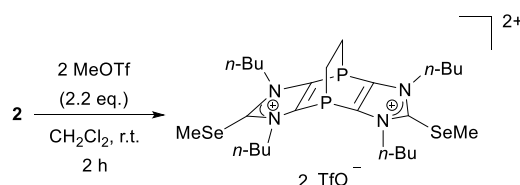
**<sup>13</sup>C{<sup>1</sup>H} NMR** (125.75 MHz, 298.0 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  / ppm = 14.3 (s, CH<sub>3</sub>), 17.8 (dd, <sup>1</sup>J<sub>Rh,C</sub> = 19.3 Hz, <sup>2</sup>J<sub>P,C</sub> = 9.7 Hz, PCH<sub>2</sub>), 20.9 (br s, CH<sub>2</sub>CH<sub>3</sub>), 28.8 (s, CH<sub>2</sub>CH), 30.8 (s, CH<sub>2</sub>CH), 31.4 (m, NCH<sub>2</sub>CH<sub>2</sub>), 32.3 (s, CH<sub>2</sub>CH), 33.3 (m, CH<sub>2</sub>CH), 51.6 (br s, NCH<sub>2</sub>), 72.7–73.0 (m, CH), 83.1–83.3 (m, CH), 109.7–110.0 (m, CH), 132.3 (d, <sup>2</sup>J<sub>Rh,C</sub> = 58.2 Hz, PC), 158.6 (s<sub>sat</sub>, <sup>1</sup>J<sub>Se,C</sub> = 209 Hz, CSe).

**<sup>31</sup>P NMR** (202.44 MHz, 298.0 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  / ppm = -21.8 (dm, <sup>1</sup>J<sub>Rh,P</sub> = 166.7 Hz).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (202.44 MHz, 298.0 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  / ppm = -21.8 (d, <sup>1</sup>J<sub>Rh,P</sub> = 166.7 Hz).

**<sup>77</sup>Se NMR** (57.24 MHz, 298.0 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$  / ppm = 167.8 (d, <sup>1</sup>J<sub>Rh,Se</sub> = 21.4 Hz).

## 2.5. Methylation of 2



In a 20 mL Schlenk tube 0.11 mL (1.02 mmol, 2.2 eq.) MeOTf were added dropwise to a solution of 0.281 g (0.47 mmol, 1.0 eq.) of **2** in 5 mL dichloromethane. After stirring for 2 h at ambient temperature the former orange solution had turned light yellow and the solvent was removed *in vacuo* ( $\leq 0.05$  mbar). The resulting light yellow, oily residue was washed with twice 5 mL *n*-pentane and dried for 2 h ( $\leq 0.02$  mbar) yielding a colourless solid.

**Molecular formula:** C<sub>28</sub>H<sub>46</sub>F<sub>6</sub>N<sub>4</sub>O<sub>6</sub>P<sub>2</sub>S<sub>2</sub>Se<sub>2</sub>



**Molecular weight:** 932.70 g mol<sup>-1</sup>

**Yield:** 0.401 g (0.44 mmol, 95 %)

**Melting point:** 102 °C

**EA:** calculated (%) C 36.06 H 4.97 N 6.01 S 6.87

found (%) C 35.61 H 5.01 N 5.88 S 7.56

**MS (pos. ESI):**  $m/z$  (%) = 785.106 (100) [M-OTf]<sup>+</sup>, 318.077 (68) [M-2OTf]<sup>2+</sup>.

**HRMS (pos. ESI):**  $m/z$  calculated for [C<sub>27</sub>H<sub>46</sub>F<sub>3</sub>N<sub>4</sub>O<sub>3</sub>P<sub>2</sub>SSe<sub>2</sub>]<sup>+</sup>: 785.1045; found: 785.1041.

**IR (ATR):**  $\tilde{\nu}$  / cm<sup>-1</sup> = 2963 (m,  $\nu_{as}(\text{CH}_3)$ ,  $\nu_s(\text{CH}_2)$ ), 2938 (m,  $\nu_{as}(\text{CH}_3)$ ,  $\nu_s(\text{CH}_2)$ ), 2878 (m,  $\nu_s(\text{CH}_3)$ ,  $\nu_{as}(\text{CH}_2)$ ).

**<sup>1</sup>H NMR** (500.04 MHz, 298.0 K, CDCl<sub>3</sub>):  $\delta$  / ppm = 0.93–1.06 (m, 12H, CH<sub>3</sub>(*n*-Bu)), 1.40–1.52 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 1.77–1.88 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 2.13–2.18 (m, 4H, PCH<sub>2</sub>), 2.45–2.49 (m, 6H, SeCH<sub>3</sub>), 4.40–4.54 (m, 8H, NCH<sub>2</sub>).

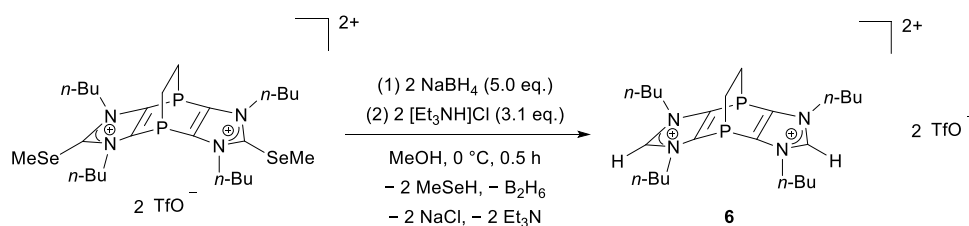
**<sup>13</sup>C{<sup>1</sup>H} NMR** (125.75 MHz, 298.0 K, CDCl<sub>3</sub>):  $\delta$  / ppm = 11.2 ( $s_{\text{sat}}$ ,  $^1J_{\text{Se,C}} = 56.9$  Hz, SeCH<sub>3</sub>), 13.7 (s, CH<sub>3</sub>(*n*-Bu)), 18.8 (dd,  $J_{\text{P,C}} = 5.6$  Hz, PCH<sub>2</sub>), 20.3 (m, CH<sub>2</sub>CH<sub>3</sub>), 33.7 (m, NCH<sub>2</sub>CH<sub>2</sub>), 51.0 (m, NCH<sub>2</sub>), 120.9 (q,  $^1J_{\text{F,C}} = 322$  Hz, CF<sub>3</sub>), 138.2 ( $s_{\text{sat}}$ ,  $^1J_{\text{Se,C}} = 181$  Hz, CSeCH<sub>3</sub>), 143.2 (dd,  $J_{\text{P,C}} = 9.8$  Hz,  $J_{\text{P,C}} = 7.0$  Hz, PC).

**<sup>31</sup>P NMR** (202.44 MHz, 298.0 K, CDCl<sub>3</sub>):  $\delta$  / ppm = -94.5 (m).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (202.44 MHz, 298.0 K, CDCl<sub>3</sub>):  $\delta$  / ppm = -94.5 (s).

**<sup>77</sup>Se NMR** (57.24 MHz, 298.0 K, CDCl<sub>3</sub>):  $\delta$  / ppm = 115.8 (s).

## 2.6. Synthesis of 6



In a 50 mL Schlenk tube 0.315 g (8.10 mmol, 5.0 eq.) NaBH<sub>4</sub> were added to a solution of 1.511 g (1.62 mmol, 1.0 eq.) of the methylation product of **2** in 16 mL methanol at -20 °C which resulted in a darkening of the yellow solution and gas formation (MeSeH). After stirring for 20 min the gas evolution had stopped and 0.691 g (5.02 mmol, 3.1 eq.) [Et<sub>3</sub>NH]Cl were added. The suspension was let warm up to ambient temperature and the solvent was removed *in vacuo* ( $\leq 0.05$  mbar). The resulting yellow, oily residue was filtered over a bed of celite® and silica (d = 2 cm, h = 1 cm each) with 120 mL tetrahydrofuran. After solvent removal *in vacuo* ( $\leq 0.05$  mbar), extraction with three times 5–10 mL dichloromethane, followed by solvent evaporation, the light-yellow residue was washed with three times 10 mL *n*-pentane at -40 °C and dried for 3 h ( $\leq 0.02$  mbar) yielding a sticky, beige solid.

**Molecular formula:** C<sub>26</sub>H<sub>42</sub>F<sub>6</sub>N<sub>4</sub>O<sub>6</sub>P<sub>2</sub>S<sub>2</sub>

**Molecular weight:** 746.70 g mol<sup>-1</sup>

**Yield:** 0.805 g (1.08 mmol, 67 %)

**Melting point:** 121 °C

**MS (pos. ESI):**  $m/z$  (%) = 597.239 (100) [M-OTf]<sup>+</sup>, 210.128 (17) [M-2OTf-C<sub>2</sub>H<sub>4</sub>]<sup>2+</sup>,

**HRMS (pos. ESI):**  $m/z$  calculated for [C<sub>27</sub>H<sub>46</sub>F<sub>3</sub>N<sub>4</sub>O<sub>3</sub>P<sub>2</sub>S]<sup>+</sup>: 597.2399; found: 597.2396.

**IR (ATR):**  $\tilde{\nu}$  / cm<sup>-1</sup> = 3110 (w,  $\nu$ (CH)), 3040 (w,  $\nu$ (CH)), 2966 (w,  $\nu_{as}$ (CH<sub>3</sub>),  $\nu_s$ (CH<sub>2</sub>)), 2936 (w,  $\nu_{as}$ (CH<sub>3</sub>),  $\nu_s$ (CH<sub>2</sub>)).

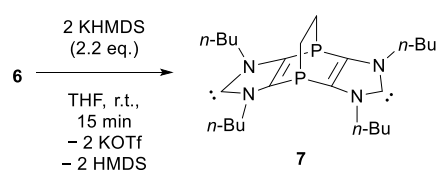
**<sup>1</sup>H NMR** (500.04 MHz, 298.0 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  / ppm = 0.97 (t, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, 12H, CH<sub>3</sub>), 1.35–1.44 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 1.87 (tt, <sup>3</sup>J<sub>H,H</sub> = 8.8 Hz, <sup>3</sup>J<sub>H,H</sub> = 6.8 Hz, 8H, CH<sub>2</sub>CH<sub>3</sub>), 2.10 (t, J<sub>P,H</sub> = 5.4 Hz, 4H, PCH<sub>2</sub>), 4.33 (t, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 8H, NCH<sub>2</sub>), 8.93 (t, <sup>4</sup>J<sub>P,H</sub> = 3.0 Hz, CH).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (125.75 MHz, 298.0 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  / ppm = 13.4 (s, CH<sub>3</sub>), 18.8 (dd, J<sub>P,C</sub> = 5.6 Hz, PCH<sub>2</sub>), 20.0 (m, CH<sub>2</sub>CH<sub>3</sub>), 33.0 (m, NCH<sub>2</sub>CH<sub>2</sub>), 49.9 (m, NCH<sub>2</sub>), 121.0 (q, <sup>1</sup>J<sub>F,C</sub> = 320.5 Hz, CF<sub>3</sub>), 138.8 (s, CH), 141.9 (dd, J<sub>P,C</sub> = 9.5 Hz, J<sub>P,C</sub> = 7.0 Hz, PC).

**<sup>31</sup>P NMR** (202.44 MHz, 298.0 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  / ppm = -97.4 (m).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (202.44 MHz, 298.0 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  / ppm = -97.4 (s).

## 2.7. Synthesis of 7



In a 50 mL Schlenk tube 0.397 g (1.99 mmol, 2.2 eq.) KHMDS in 5 mL THF were added to a suspension of 0.675 g (0.90 mmol, 1.0 eq.) of **6** in 15 mL THF via a transfer canula, resulting in an orange, slightly turbid solution. After stirring for 15 min at ambient temperature the solvent was removed *in vacuo* ( $\leq 0.05$  mbar) at the same temperature. The resulting yellow solid mixed with an orange, oily residue was extracted with three times 5–7 mL toluene. After removal of the solvent *in vacuo* ( $\leq 0.05$  mbar) at ambient temperature, washing with twice 10 mL *n*-pentane and drying for 4 h ( $\leq 0.02$  mbar) a beige solid was obtained.

**Molecular formula:** C<sub>24</sub>H<sub>40</sub>N<sub>4</sub>P<sub>2</sub>

**Molecular weight:** 446.56 g mol<sup>-1</sup>

**Yield:** 0.141 g (0.32 mmol, 36 %)

**Melting point:** 104 °C (dec.)

<b>EA:</b> calculated (%)	C 64.55	H 9.03	N 12.55
found (%)	C 63.44	H 8.96	N 12.37

**MS (pos. APCI):**  $m/z$  (%) = 483.300 (100) [M+2H<sub>2</sub>O+H]<sup>+</sup>, 465.289 (31) [M+H<sub>2</sub>O+H]<sup>+</sup>.

**HRMS (pos. APCI):**  $m/z$  calculated for [C<sub>24</sub>H<sub>43</sub>N<sub>4</sub>P<sub>2</sub>O]<sup>+</sup>: 465.2907; found: 465.2897.

**IR (ATR):**  $\tilde{\nu}$  / cm<sup>-1</sup> = 2957 (w,  $\nu_{as}$ (CH<sub>3</sub>),  $\nu_s$ (CH<sub>2</sub>)), 2931 (w,  $\nu_{as}$ (CH<sub>3</sub>),  $\nu_s$ (CH<sub>2</sub>)), 2871 (m,  $\nu_s$ (CH<sub>3</sub>),  $\nu_{as}$ (CH<sub>2</sub>)).

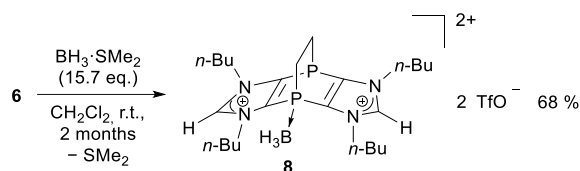
**<sup>1</sup>H NMR** (500.04 MHz, 298.0 K, THF-d<sub>8</sub>):  $\delta$  / ppm = 0.93 (t, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, 12H, CH<sub>3</sub>), 1.27–1.38 (m, 8H, CH<sub>2</sub>CH<sub>3</sub>), 1.60 (t, J<sub>P,H</sub> = 5.3 Hz, 4H, PCH<sub>2</sub>), 1.70–1.82 (m, 8H, NCH<sub>2</sub>CH<sub>2</sub>), 4.03–4.15 (m, 8H, NCH<sub>2</sub>).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.75 MHz, 298.0 K, THF- $d_8$ ):  $\delta$  / ppm = 14.3 (s,  $\text{CH}_3$ ), 19.8 (dd,  $J_{\text{P,C}} = 6.4$  Hz,  $\text{PCH}_2$ ), 20.8 (m,  $\text{CH}_2\text{CH}_3$ ), 35.7 (m,  $\text{NCH}_2\text{CH}_2$ ), 50.1 (m,  $\text{NCH}_2$ ), 140.4 (dd,  $J_{\text{P,C}} = 6.1$  Hz,  $J_{\text{P,C}} = 4.1$  Hz,  $\text{PC}$ ), 220.0 (br s,  $\text{C}^2$ ).

$^{31}\text{P}$  NMR (202.44 MHz, 298.0 K, THF- $d_8$ ):  $\delta$  / ppm = -94.8 (m).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202.44 MHz, 298.0 K, THF- $d_8$ ):  $\delta$  / ppm = -94.8 (s).

## 2.8. Generation of 8



In a 20 mL Schlenk tube 0.20 mL (2.11 mmol, 15.7 eq.)  $\text{BH}_3\cdot\text{SMe}_2$  were added to a solution of 0.100 g (0.13 mmol, 1.0 eq.) of **6** in 2.5 mL dichloromethane and the reaction solution was stirred at ambient temperature while the reaction course was monitored via  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. After 2 months no change in the composition of the reaction mixture was observed anymore and the solvent was removed *in vacuo* ( $\leq 0.05$  mbar). The resulting colourless residue was washed with three times 3 mL *n*-pentane and after drying for 2 h ( $\leq 0.02$  mbar) the product mixture was obtained as slightly sticky, colourless solid and analysed by NMR spectroscopy and SCXRD.

**Molecular formula:**  $\text{C}_{26}\text{H}_{45}\text{BF}_6\text{N}_4\text{O}_6\text{P}_2\text{S}_2$

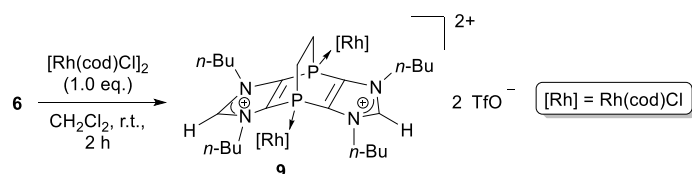
**Molecular weight:**  $760.54 \text{ g mol}^{-1}$

**Content in mixture:** 68 % ( $^{31}\text{P}$  NMR integration of isolated reaction mixture)

$^{31}\text{P}$  NMR (202.50 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  / ppm = -98.1 (br s), -13.3 (br s).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202.50 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  / ppm = -98.1 (d,  $^3J_{\text{P,P}} = 5.8$  Hz), -13.3 (br s).

## 2.9. Synthesis of 9



In a 20 mL Schlenk tube 0.079 g (0.11 mmol, 1.0 eq.) of **6** and 0.052 g (0.11 mmol, 1.0 eq.)  $[\text{Rh}(\text{cod})\text{Cl}]_2$  were dissolved in 4 mL dichloromethane and stirred for 2 h at ambient temperature yielding a yellow suspension. The solvent was removed *in vacuo* ( $\leq 0.05$  mbar) and the resulting yellow solid was washed with three times a mixture of 2 mL toluene / and 2 mL *n*-pentane each, twice 2 mL diethyl ether and three times 3–4 mL *n*-pentane and dried for 2 h ( $\leq 0.02$  mbar) yielding a yellow solid.

**Molecular formula:**  $\text{C}_{42}\text{H}_{66}\text{Cl}_2\text{F}_6\text{N}_4\text{O}_6\text{P}_2\text{Rh}_2\text{S}_2$

**Molecular weight:**  $1239.78 \text{ g mol}^{-1}$

**Yield:** 0.092 g (0.07 mmol, 67 %)

**Melting point:**  $> 250$  °C

<b>EA:</b> calculated (%)	C 40.69	H 5.37	N 4.52	S 5.17
found (%)	C 40.76	H 5.37	N 4.37	S 5.32

**MS (pos. ESI):**  $m/z$  (%) = 1089.1775 (4)  $[M-OTf]^+$ , 843.2086 (21)  $[M-[Rh(cod)Cl]-OTf]^+$ , 597.2401 (100)  $[M-2[Rh(cod)Cl]-OTf]^+$ .

**MS (neg. ESI):**  $m/z$  (%) = 149.1 (100)  $[OTf]^-$ .

**HRMS (pos. ESI):**  $m/z$  calculated for  $[C_{41}H_{66}Cl_2F_3N_4O_3P_2Rh_2S]^+$ : 1089.1765; found: 1089.1775.

**IR (ATR):**  $\tilde{\nu}$  /  $cm^{-1}$  = 3112 (w,  $\nu(CH)$ ), 3042 (w,  $\nu(CH)$ ), 2964 (m,  $\nu_{as}(CH_3)$ ,  $\nu_s(CH_2)$ ), 2878 (m,  $\nu_s(CH_3)$ ).

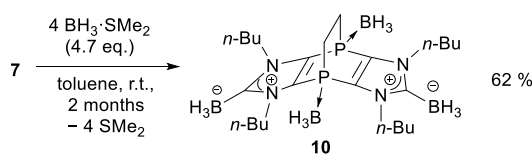
**$^1H$  NMR** (499.96 MHz, 298.0 K,  $CD_2Cl_2$ ):  $\delta$  / ppm = 1.09 (t,  $^3J_{H,H} = 7.4$  Hz, 12H,  $CH_3$ ), 1.57–1.67 (m, 8H,  $CH_2CH_3$ ), 2.05–2.16 (m, 12H,  $NCH_2CH_2$ ,  $PCH_2$ ), 2.30–2.39 (m, 8H,  $CH_2CH$ ), 2.42–2.52 (m, 4H,  $CH_2CH$ ), 2.53–2.63 (m, 4H,  $CH_2CH$ ), 4.30–4.36 (m, 4H,  $CH_2CH$ ), 4.93–5.01 (m, 4H,  $NCH_2$ ), 5.61–5.69 (m, 4H,  $NCH_2$ ), 5.84–5.89 (m, 4H,  $CH_2CH$ ), 8.55 (t,  $^4J_{P,H} = 3.3$  Hz, 2H,  $CH$ ).

**$^{13}C\{^1H\}$  NMR** (125.73 MHz, 298.0 K,  $CD_2Cl_2$ ):  $\delta$  / ppm = 13.9 (s,  $CH_3$ ), 17.8 (dd,  $^1J_{Rh,C} = 20.3$  Hz,  $^2J_{P,C} = 9.9$  Hz,  $PCH_2$ ), 20.5 (s,  $CH_2CH_3$ ), 29.2 (s,  $CH_2CH$ ), 32.1 (m,  $NCH_2CH_2$ ), 33.3 (m,  $CH_2CH$ ), 51.6 (d,  $^3J_{P,C} = 2.8$  Hz,  $NCH_2$ ), 74.5–74.7 (m,  $CH_2CH$ ), 112.6–112.8 (m,  $CH_2CH$ ), 121.0 (q,  $^1J_{F,C} = 320.8$  Hz,  $CF_3$ ), 134.8 (d,  $^2J_{Rh,C} = 55.0$  Hz,  $PC$ ), 140.1 (t,  $^3J_{P,C} = 3.5$  Hz,  $CH$ ).

**$^{31}P$  NMR** (202.41 MHz, 298.0 K,  $CD_2Cl_2$ ):  $\delta$  / ppm = -24.7 (br d,  $^1J_{Rh,P} = 167.8$  Hz).

**$^{31}P\{^1H\}$  NMR** (202.41 MHz, 298.0 K,  $CD_2Cl_2$ ):  $\delta$  / ppm = -24.7 (dd,  $^1J_{Rh,P} = 172$  Hz,  $^4J_{Rh,P} = 3$  Hz), -24.7 (dd,  $^1J_{Rh,P} = 163$  Hz,  $^4J_{Rh,P} = 4$  Hz).

## 2.10. Generation of 10



In a 15 mL Schlenk tube 0.05 mL (0.53 mmol, 4.7 eq.)  $BH_3 \cdot SMe_2$  were added to a solution of 0.050 g (0.11 mmol, 1.0 eq.) of **7** in 1.5 mL toluene and the reaction solution was stirred at ambient temperature while the reaction course was monitored via  $^{31}P\{^1H\}$  NMR spectroscopy. After 2 months no change in the composition of the reaction mixture was observed anymore and the solvent was removed *in vacuo* ( $\leq 0.05$  mbar). The resulting colourless residue was washed with three times 3 mL *n*-pentane and after drying for 4 h ( $\leq 0.02$  mbar) the product mixture was obtained as colourless solid and analysed by NMR spectroscopy and SCXRD.

**Molecular formula:**  $C_{24}H_{52}B_4N_4P_2$

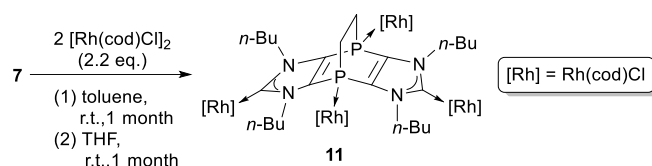
**Molecular weight:** 501.90  $g\ mol^{-1}$

**Content in mixture:** 62 % ( $^{31}P$  NMR integration of isolated reaction mixture)

**$^{31}P$  NMR** (202.50 MHz, 298.0 K,  $CD_2Cl_2$ ):  $\delta$  / ppm = -17.7 (br s).

**$^{31}P\{^1H\}$  NMR** (202.50 MHz, 298.0 K,  $CD_2Cl_2$ ):  $\delta$  / ppm = -17.7 (s).

## 2.11. Synthesis of 11



In a 20 mL Schlenk tube 0.050 g (0.11 mmol, 1.0 eq.) of **7** and 0.121 g (0.25 mmol, 2.2 eq.)  $[\text{Rh}(\text{cod})\text{Cl}]_2$  were dissolved in 3 mL toluene and stirred for 1 month at ambient temperature yielding an orange suspension. The solvent was evaporated *in vacuo* ( $\leq 0.05$  mbar) and the solids were redissolved in 5 mL THF and stirred for 1 month. After removal of the solvent *in vacuo* ( $\leq 0.05$  mbar) the yellow-brown residue was washed with eight times 5 mL *n*-pentane. After drying for 3 h ( $\leq 0.02$  mbar) a yellow-brown solid was obtained.

**Molecular formula:**  $\text{C}_{56}\text{H}_{88}\text{Cl}_4\text{N}_4\text{P}_2\text{Rh}_4$

**Molecular weight:**  $1432.72 \text{ g mol}^{-1}$

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

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

**MS (pos. ESI):**  $m/z$  (%) = 693.2484 (100)  $[\text{M}-3(\text{Rh}(\text{cod})\text{Cl})+\text{H}]^+$ , 939.2165 (72)  $[\text{M}-2(\text{Rh}(\text{cod})\text{Cl})+\text{H}]^+$ :

**HRMS (pos. ESI):**  $m/z$  calculated  $[\text{C}_{56}\text{H}_{88}\text{Cl}_4\text{N}_4\text{P}_2\text{Rh}_4\text{H}]^+$ : 1433.1510; found: 1433.1508.

**IR (ATR):**  $\tilde{\nu} / \text{cm}^{-1}$  = 2982 (w,  $\nu_{\text{as}}(\text{CH}_3)$ ,  $\nu_s(\text{CH}_2)$ ,  $\nu(\text{CH})$ ), 2964 (w,  $\nu_{\text{as}}(\text{CH}_3)$ ,  $\nu_s(\text{CH}_2)$ ), 2871 (w,  $\nu_s(\text{CH}_3)$ ).

**$^1\text{H}$  NMR** (500.18 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta / \text{ppm}$  = 1.19 (t,  $^3J_{\text{H,H}} = 7.2$  Hz, 12H,  $\text{CH}_3$ ), 1.62–1.74 (m, 8H,  $\text{CH}_2\text{CH}_3$ ), 1.49–1.58 (m, 4H,  $\text{PCH}_2$ ), 1.85–1.99 (m, 16H,  $\text{CH}_2\text{CH}$ ), 2.19–3.30 (m, 8H,  $\text{CH}_2\text{CH}$ ), 2.39 (m, 12H,  $\text{NCH}_2\text{CH}_2$ ), 2.49 (m, 4H,  $\text{CH}_2\text{CH}$ ), 2.62 (m, 4H,  $\text{CH}_2\text{CH}$ ), 3.11–3.20 (m, 4H,  $\text{CH}_2\text{CH}$ ), 3.92–4.02 (m, 4H,  $\text{CH}_2\text{CH}$ ), 4.87–5.05 (m, 4H,  $\text{CH}_2\text{CH}$ ), 5.33–5.43 (m, 4H,  $\text{NCH}_2$ ), 5.68–5.79 (m, 4H,  $\text{NCH}_2$ ), 5.80–5.91 (m, 4H,  $\text{CH}_2\text{CH}$ ).

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (125.78 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta / \text{ppm}$  = 14.2 (s,  $\text{CH}_3$ ), 18.0 (dd,  $^1J_{\text{Rh,C}} = 23.1$  Hz,  $^2J_{\text{P,C}} = 8.8$  Hz,  $\text{PCH}_2$ ), 21.2 (s,  $\text{CH}_2\text{CH}_3$ ), 28.9 (s,  $\text{CH}_2\text{CH}$ ), 29.2 (s,  $\text{CH}_2\text{CH}$ ), 33.5 (m,  $\text{NCH}_2\text{CH}_2$ ), 33.1 (m,  $\text{CH}_2\text{CH}$ ), 34.0 (m,  $\text{CH}_2\text{CH}$ ), 52.1 (m,  $\text{NCH}_2$ ), 70.2 (m,  $\text{CH}_2\text{CH}$ ), 72.7 (m,  $\text{CH}_2\text{CH}$ ), 98.3 (m,  $\text{CH}_2\text{CH}$ ), 111.0 (m,  $\text{CH}_2\text{CH}$ , 2<sup>nd</sup> isomer), 110.2 (m,  $\text{CH}_2\text{CH}$ , 1<sup>st</sup> isomer), 134.2 (dd,  $J_{\text{Rh,C}} = 53.0$  Hz,  $J_{\text{P,C}} = 3.2$  Hz,  $\text{PC}$ ), 191.7 (t,  $^1J_{\text{Rh,P}} = 52.4$  Hz,  $\text{CRh}$ ).

**$^{31}\text{P}$  NMR** (202.50 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta / \text{ppm}$  = -33.8 (d,  $^1J_{\text{Rh,P}} = 160.8$  Hz, 1<sup>st</sup> isomer), -29.5 (d,  $^1J_{\text{Rh,P}} = 163.5$  Hz, 2<sup>nd</sup> isomer)(ratio 2.8:1).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (202.50 MHz, 298.0 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta / \text{ppm}$  = -33.8 (d,  $^1J_{\text{Rh,P}} = 160.8$  Hz, 1<sup>st</sup> isomer), -29.5 (d,  $^1J_{\text{Rh,P}} = 163.7$  Hz, 2<sup>nd</sup> isomer)(ratio 2.9:1).

### 3. NMR spectra

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

#### 3.1. 2

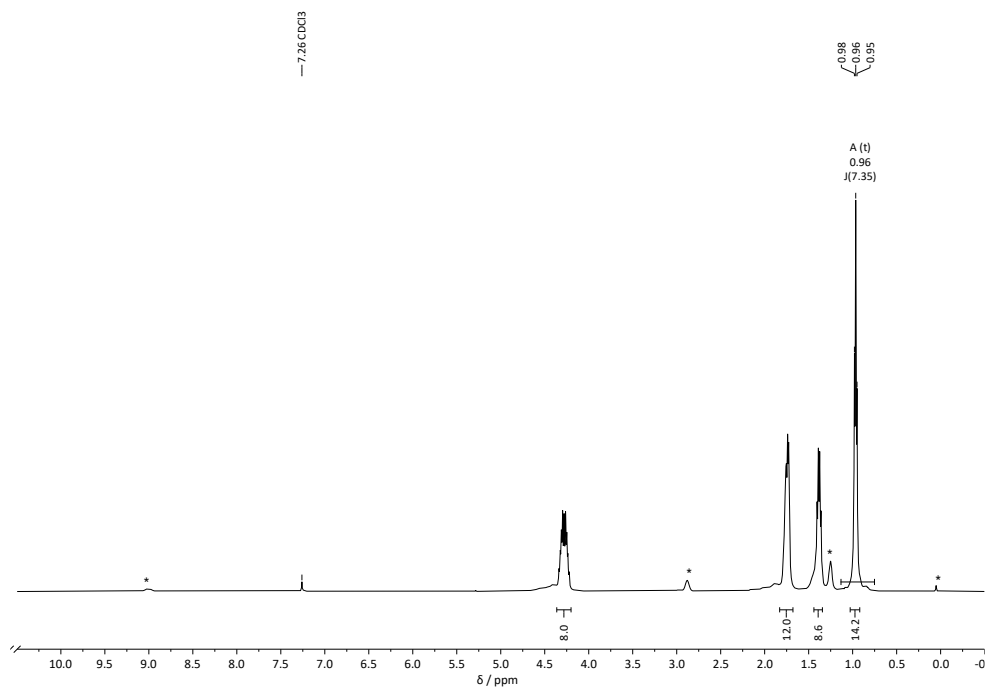


Figure S1 <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 499.96 Hz, 298.0 K) of **2**.

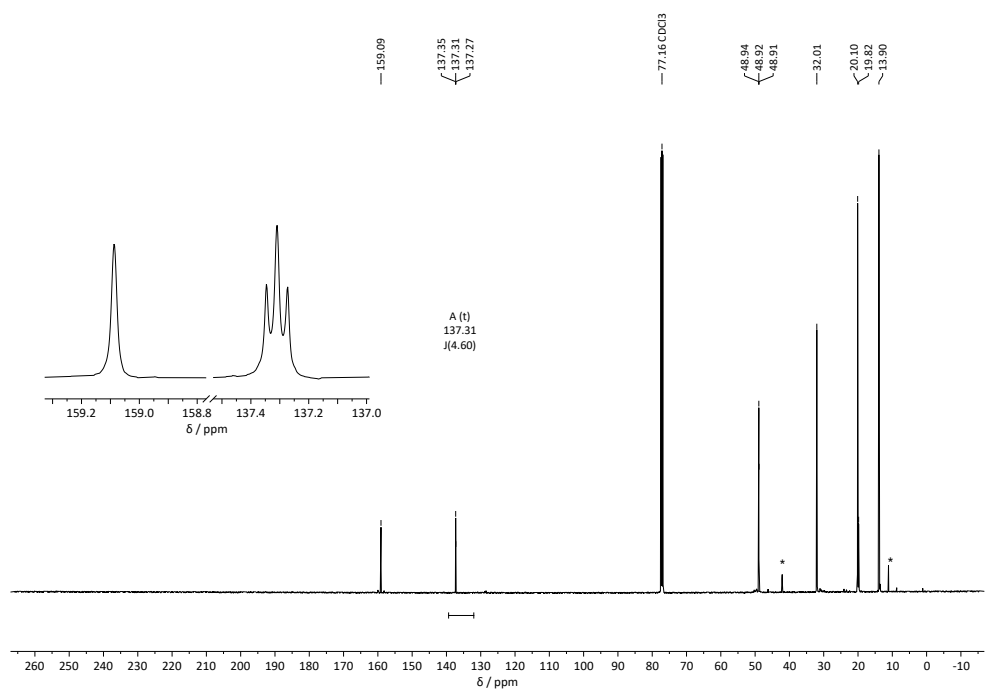
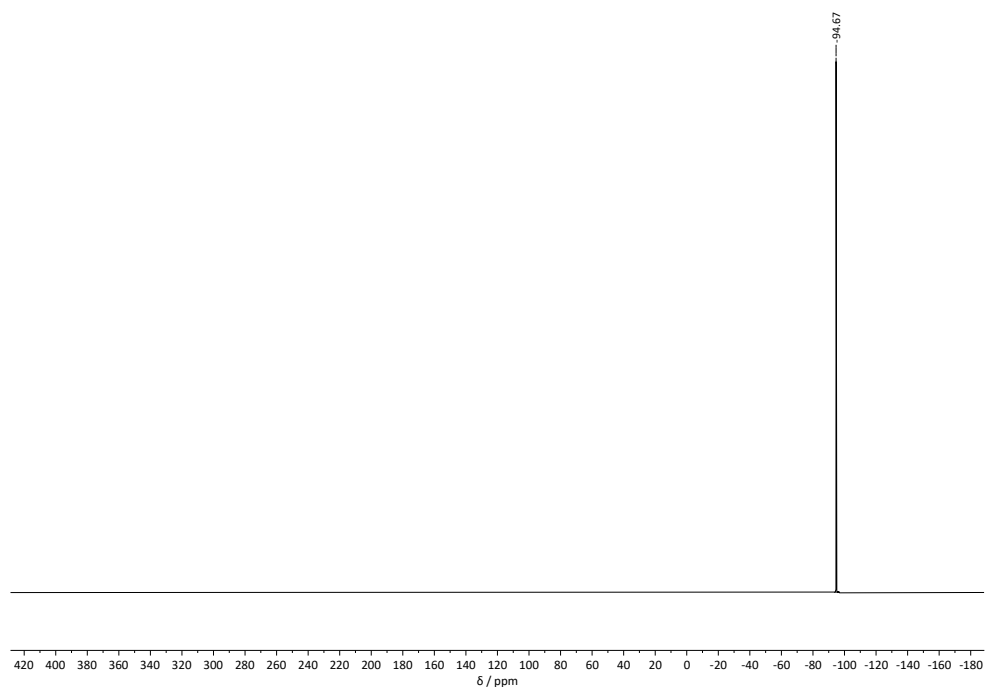
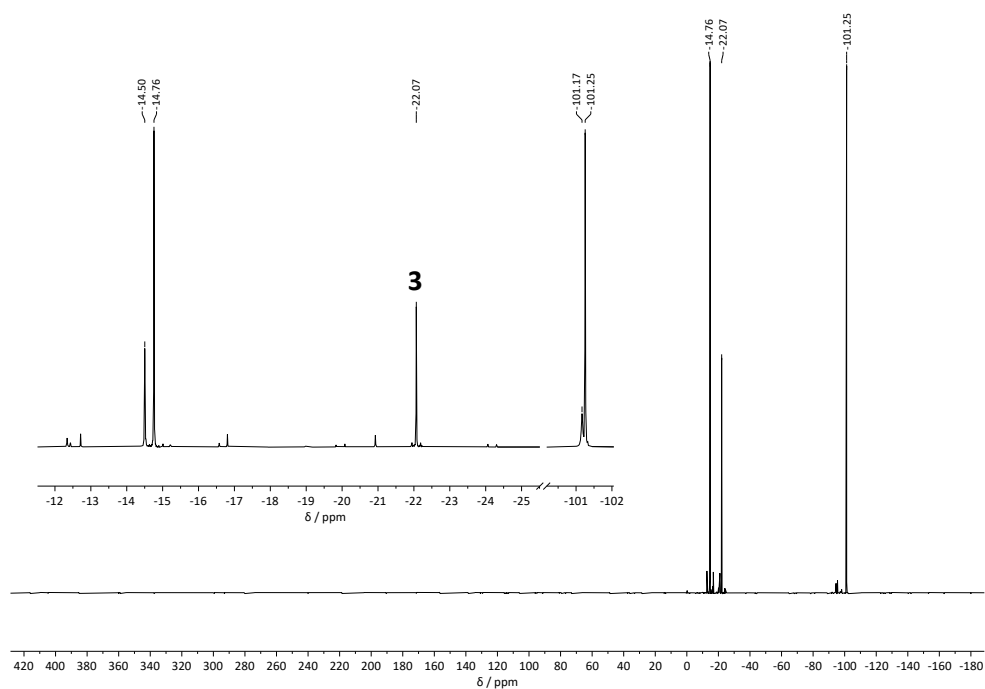


Figure S2 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CDCl<sub>3</sub>, 125.73 Hz, 298.0 K) of **2**.



**Figure S3**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ , 202.41 Hz, 298.0 K) of **2**.

### 3.2. **3** in reaction mixture



**Figure S4**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 202.50 Hz, 298.0 K) of **3** in reaction mixture.

### 3.3. 4 in reaction mixture

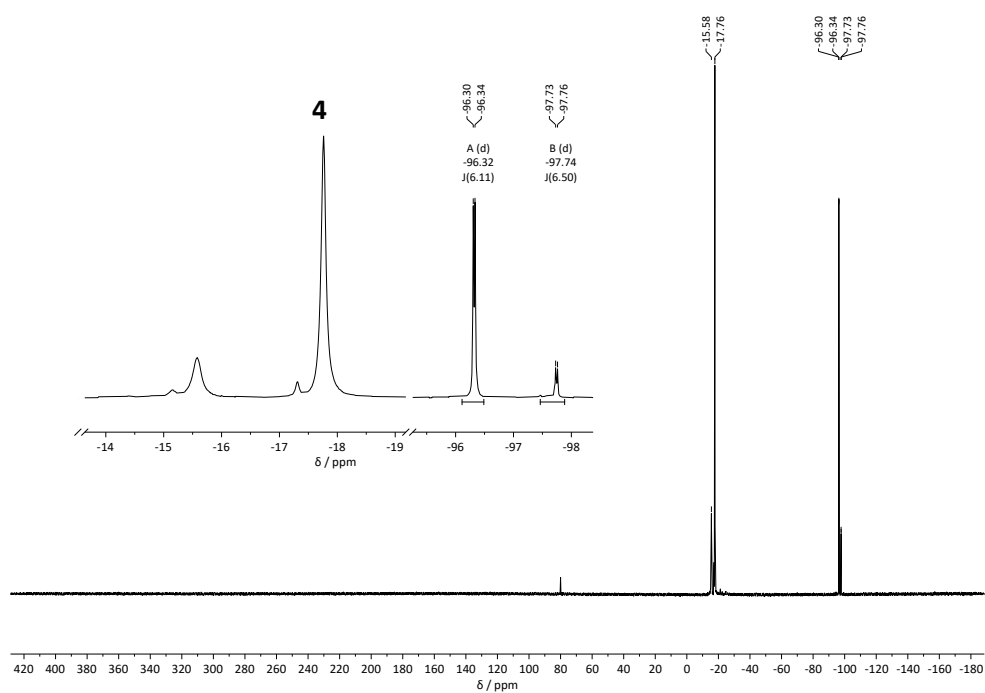


Figure S5  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 202.50 Hz, 298.0 K) of **4** in reaction mixture.

### 3.4. 5

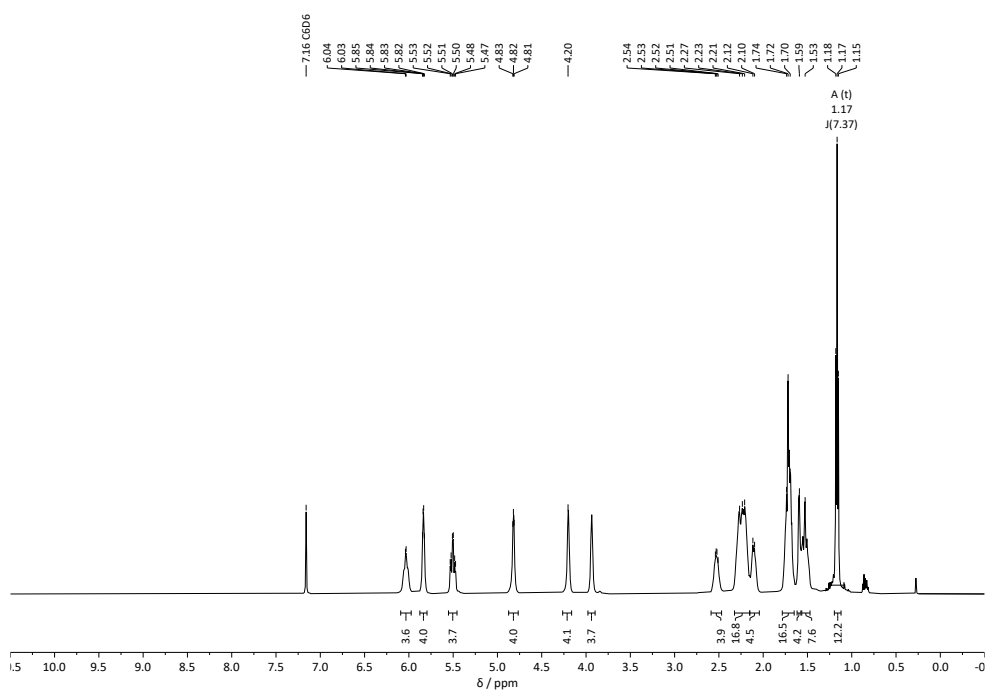
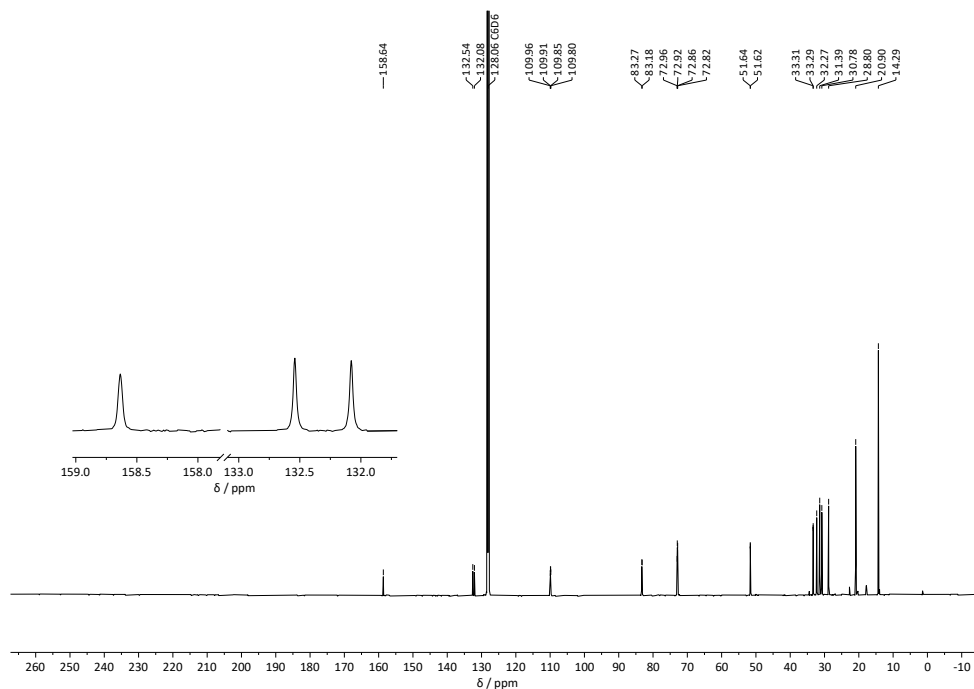
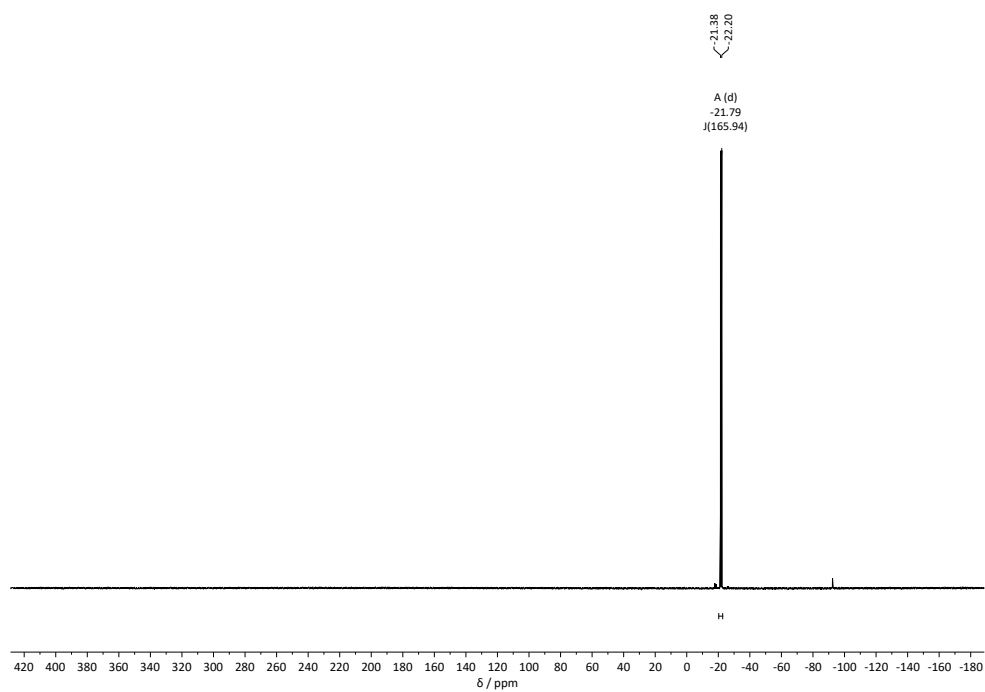


Figure S6  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , 499.96 Hz, 298.0 K) of **5**.





**Figure S7**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , 125.73 Hz, 298.0 K) of **5**.



**Figure S8**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , 202.41 Hz, 298.0 K) of **5**.

### 3.5. Methylation product of 2

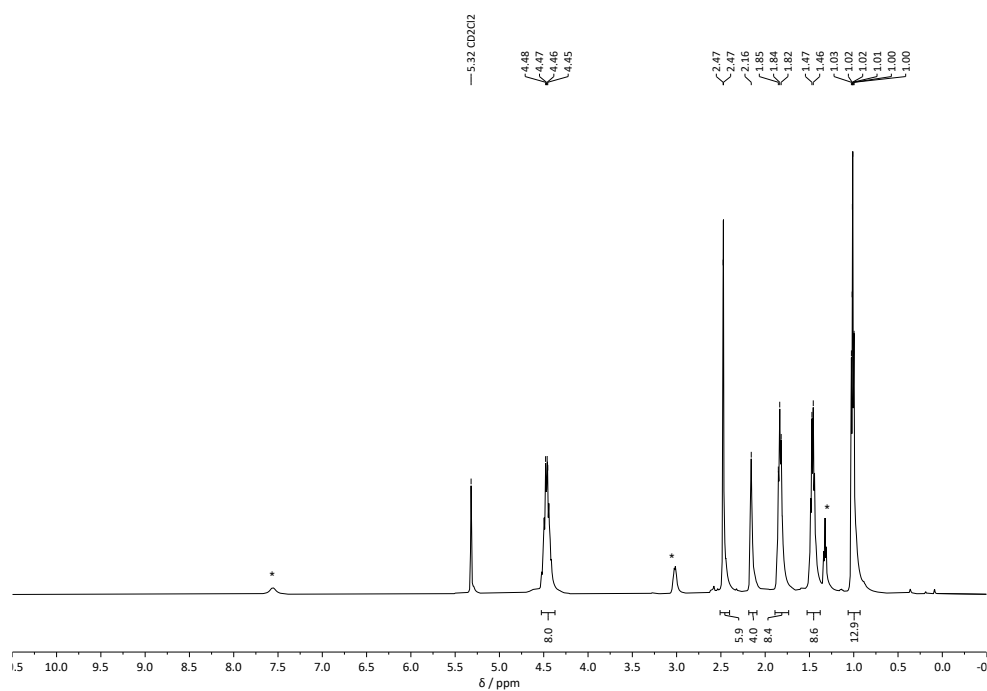


Figure 9  $^1\text{H}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 499.96 Hz, 298.0 K) of the methylation product of 2.

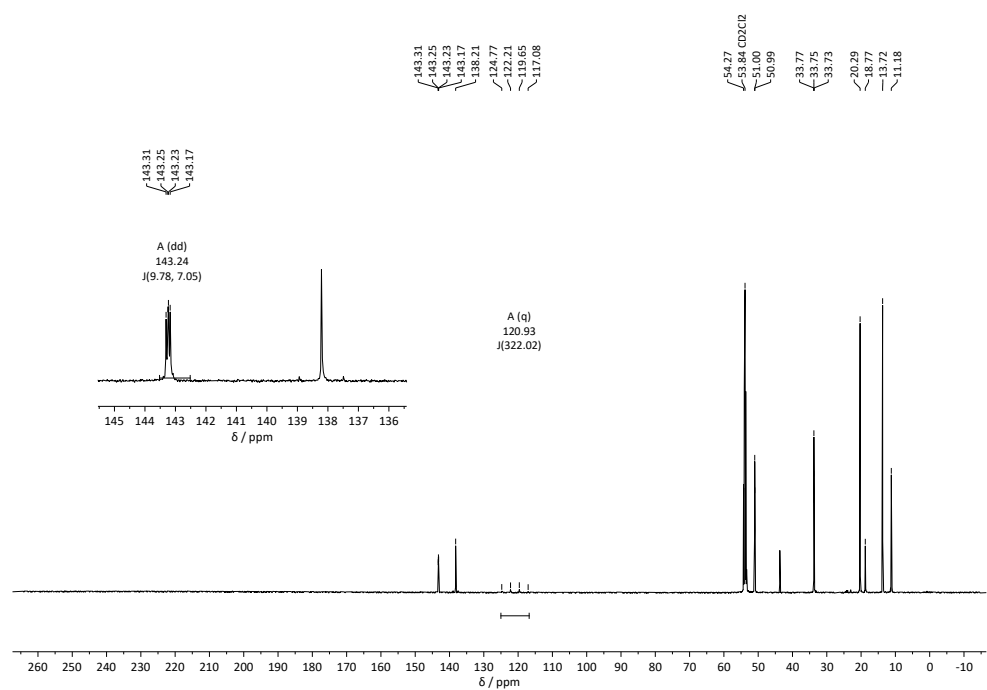
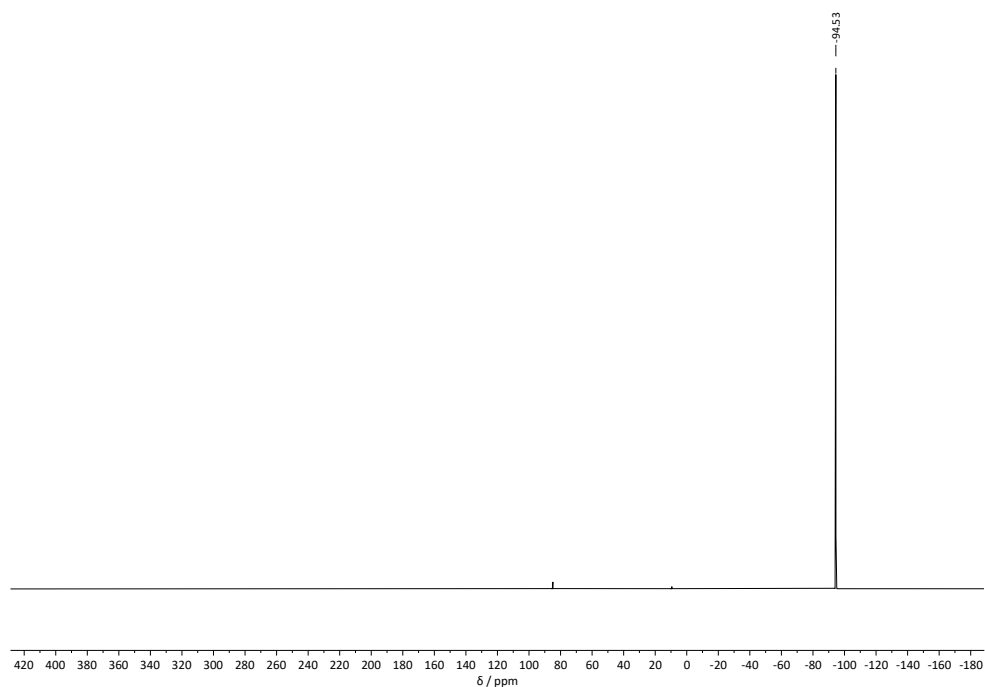
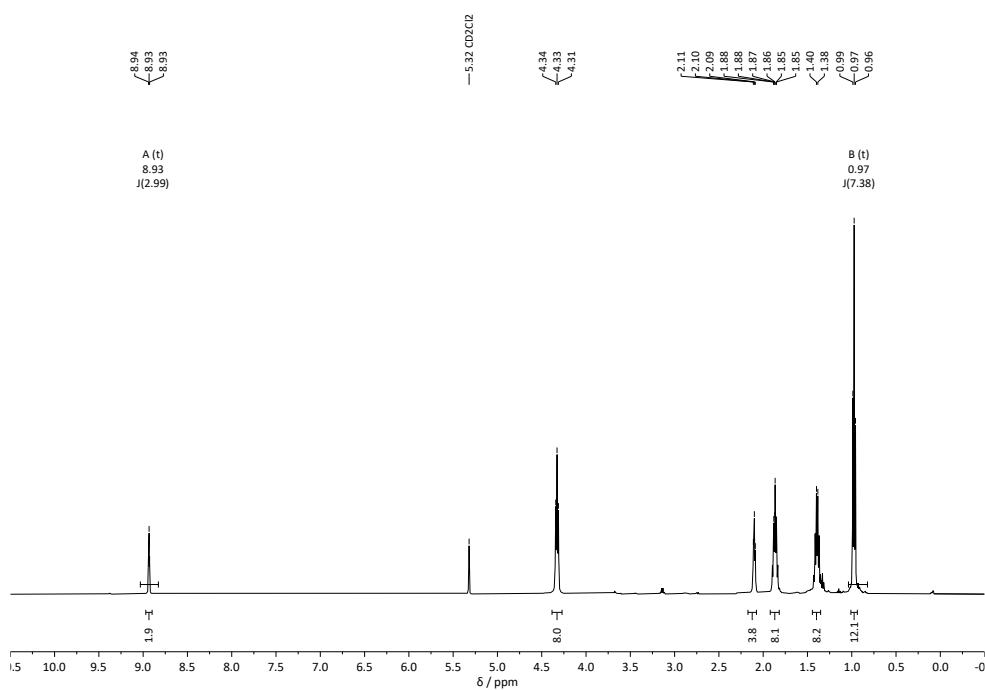


Figure S10  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 125.75 Hz, 298.0 K) of 4a.

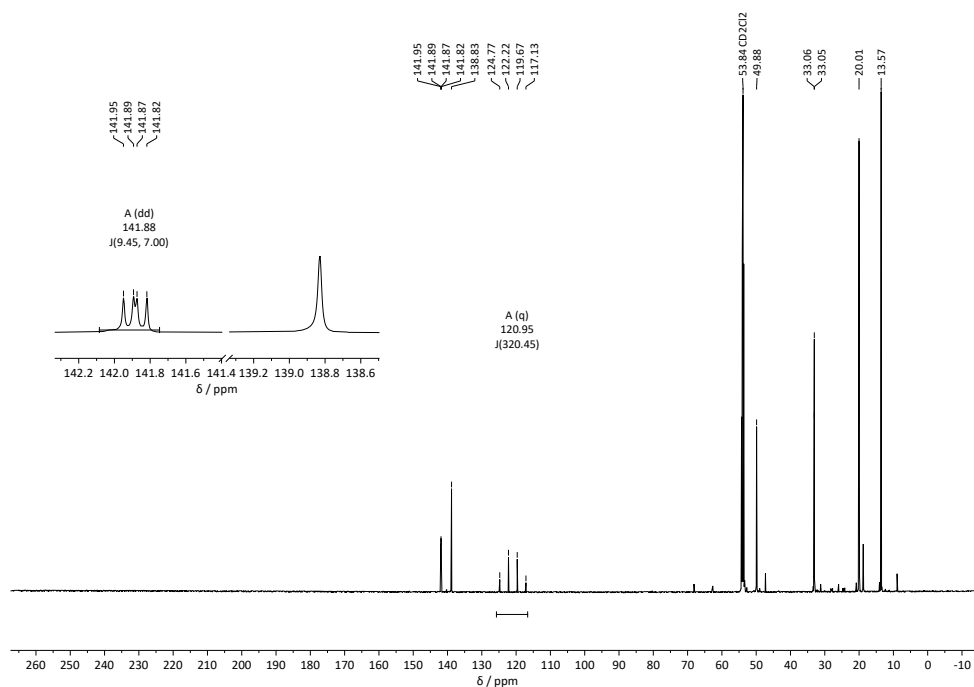


**Figure S11**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 202.41 Hz, 298.0 K) of the methylation product of **2**.

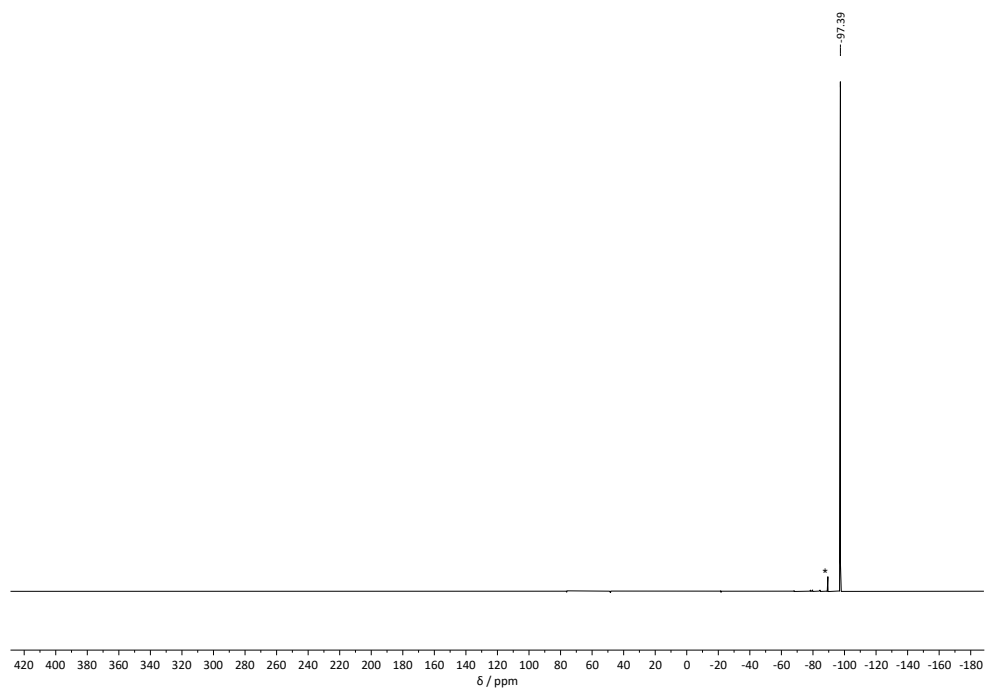
### 3.6. 6



**Figure S12**  $^1\text{H}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 500.04 Hz, 298.0 K) of **6**.



**Figure S13**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 125.75 Hz, 298.0 K) of **6**.



**Figure S14**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 202.41 Hz, 298.0 K) of **6**.

3.7. 7

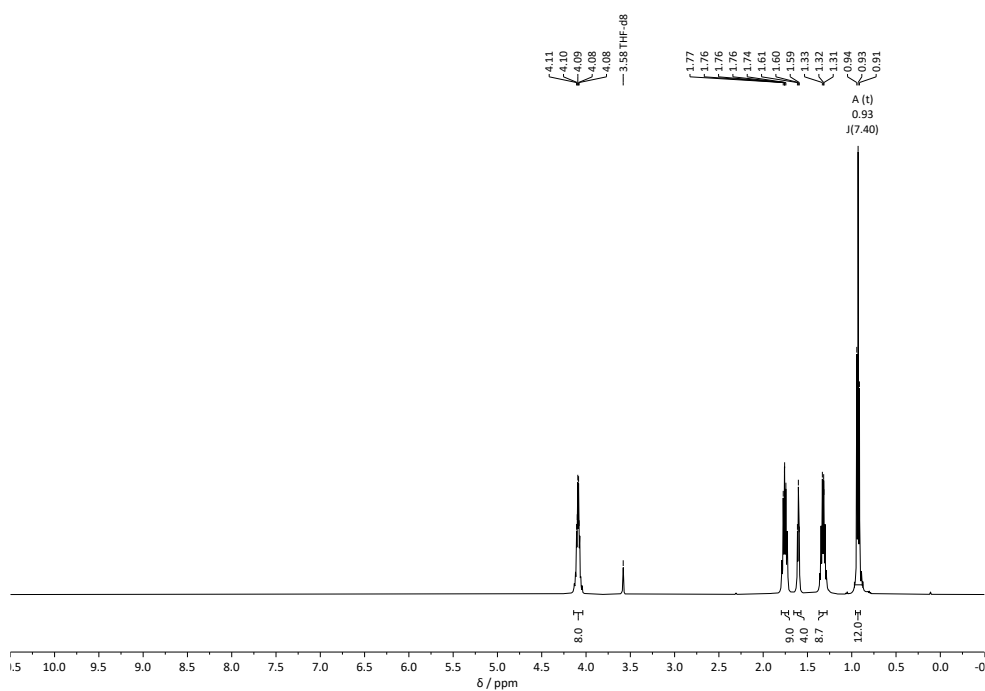


Figure S15  $^1\text{H}$  NMR spectrum (THF- $d_8$ , 499.96 Hz, 298.0 K) of **7**.

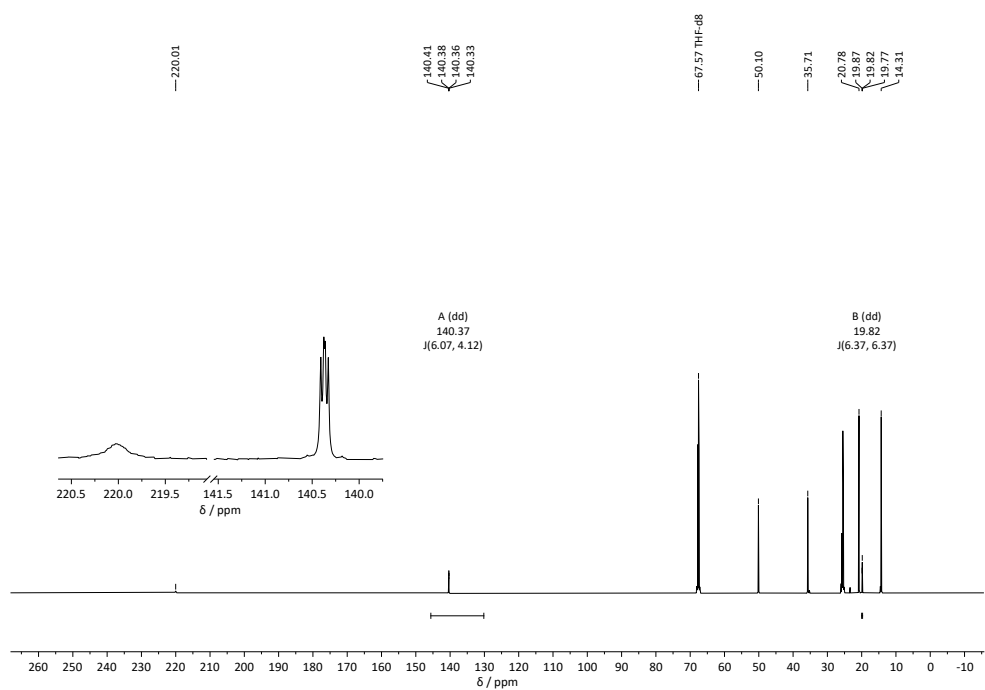


Figure S16  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (THF- $d_8$ , 125.73 Hz, 298.0 K) of **7**.

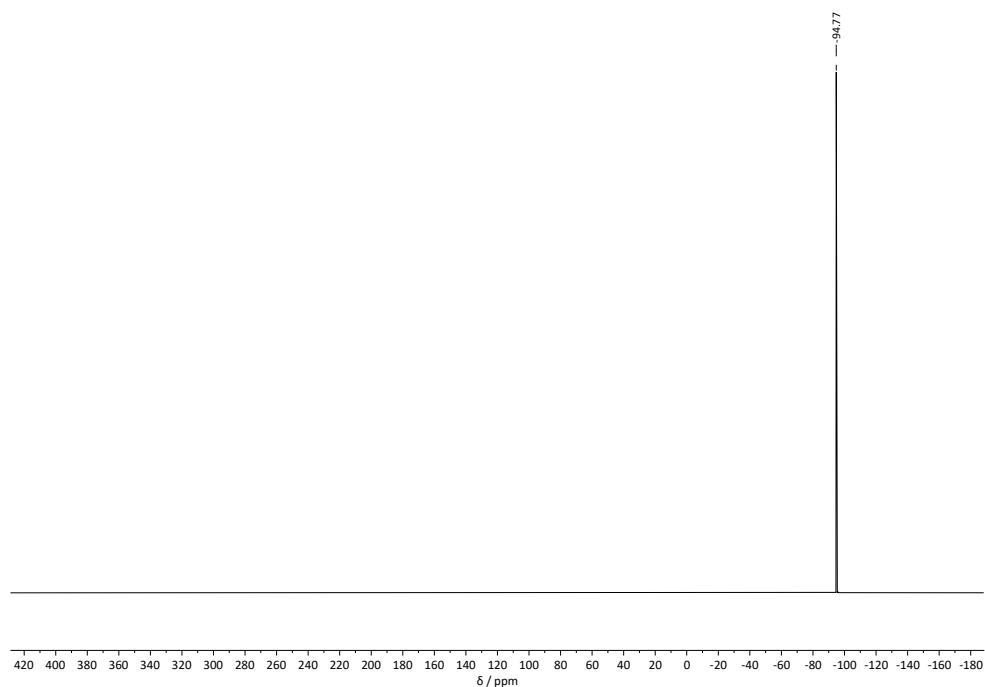


Figure S17  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{THF-d}_8$ , 202.41 Hz, 298.0 K) of **7**.

### 3.8. **8** in reaction mixture

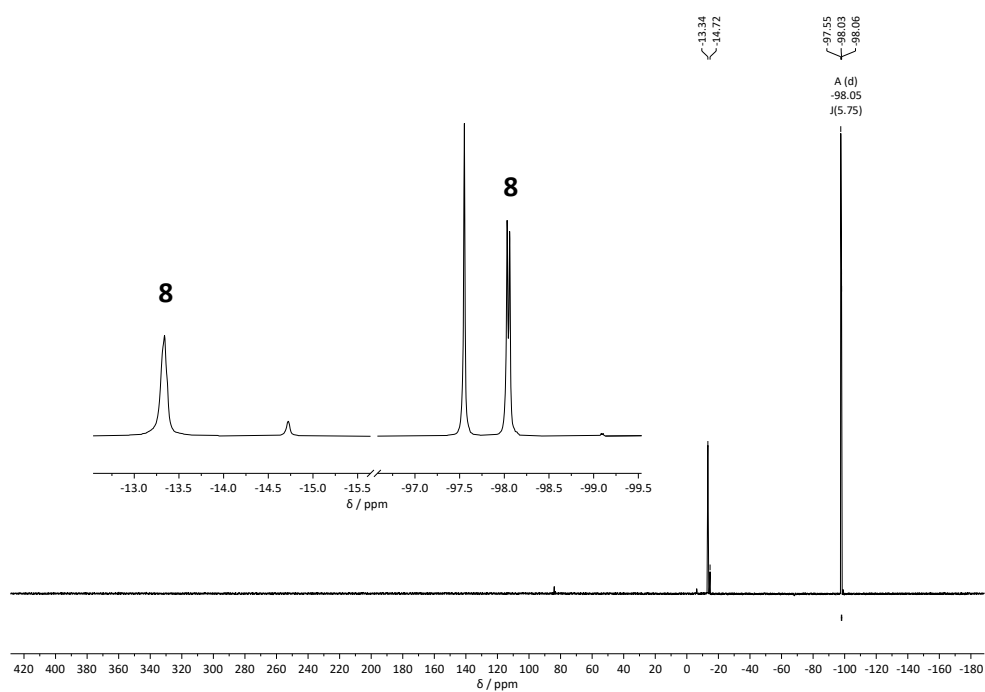


Figure S18  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 202.50 Hz, 298.0 K) of **8**.

3.9. 9

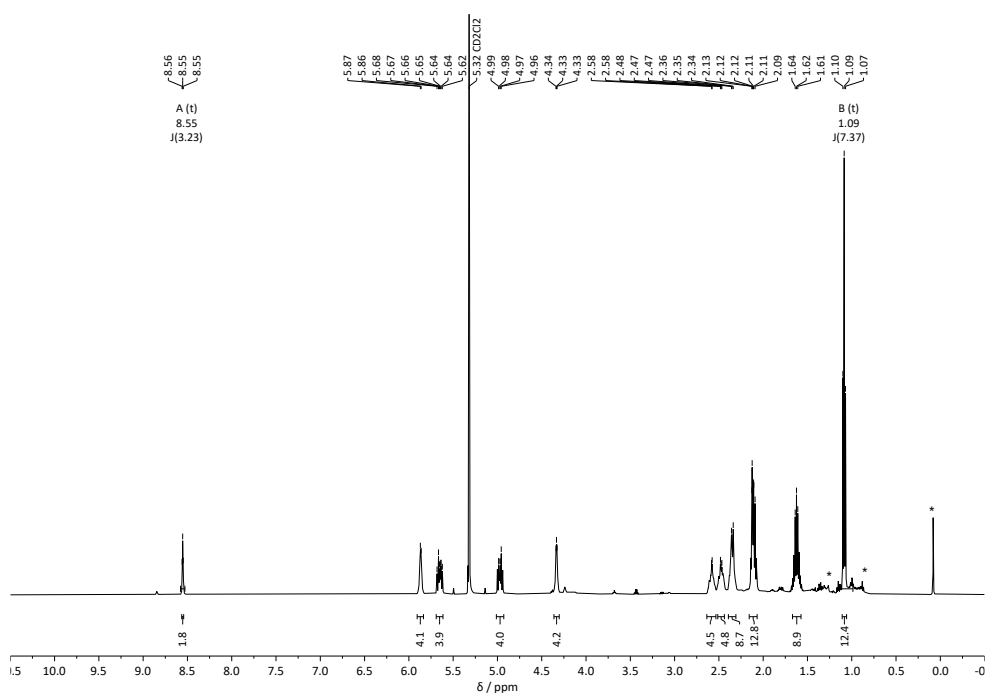


Figure S19 <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 499.96 Hz, 298.0 K) of 9.

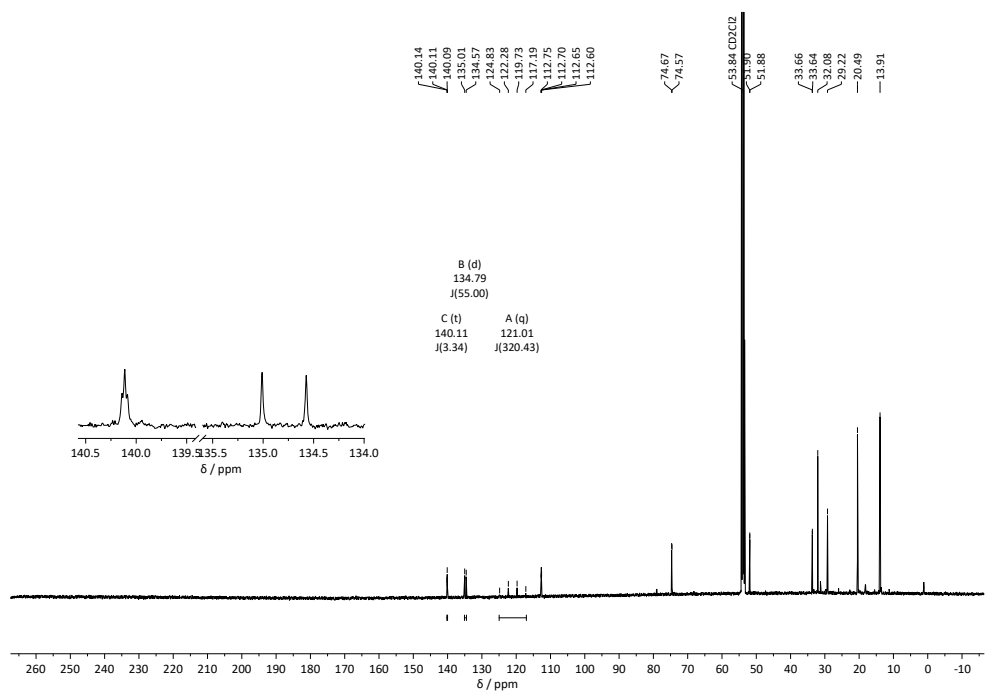
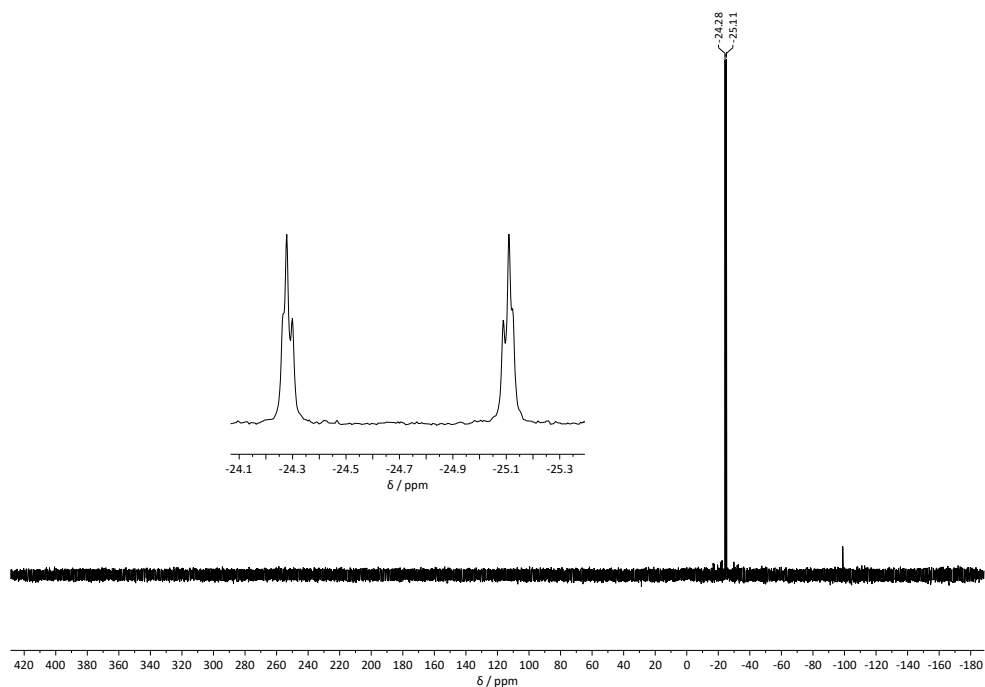
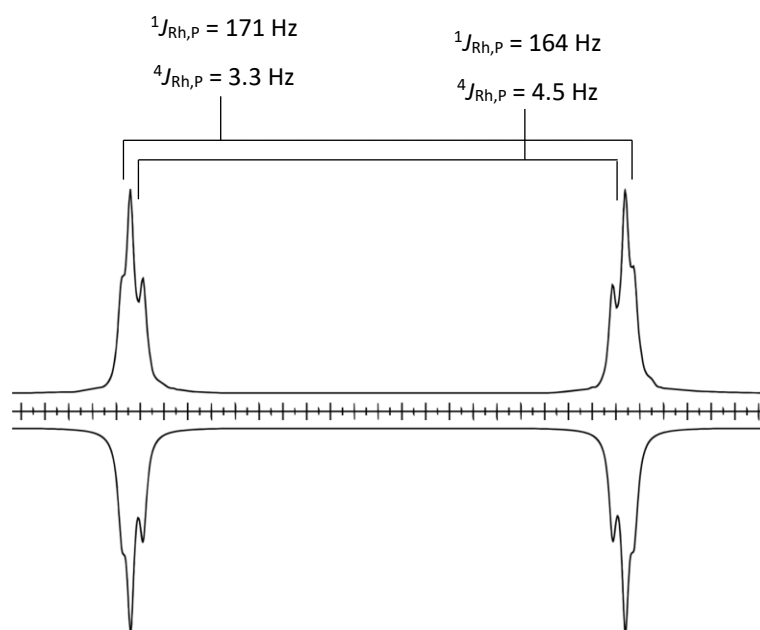


Figure S20 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 125.73 Hz, 298.0 K) of 9.



**Figure S21**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 202.41 Hz, 298.0 K) of **9**.

### 3.10. Simulated $^{31}\text{P}\{^1\text{H}\}$ NMR signal of **9**



**Figure S22.** Experimental  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **9** (top) and simulated spectrum (bottom).



### 3.11. 10 in reaction mixture

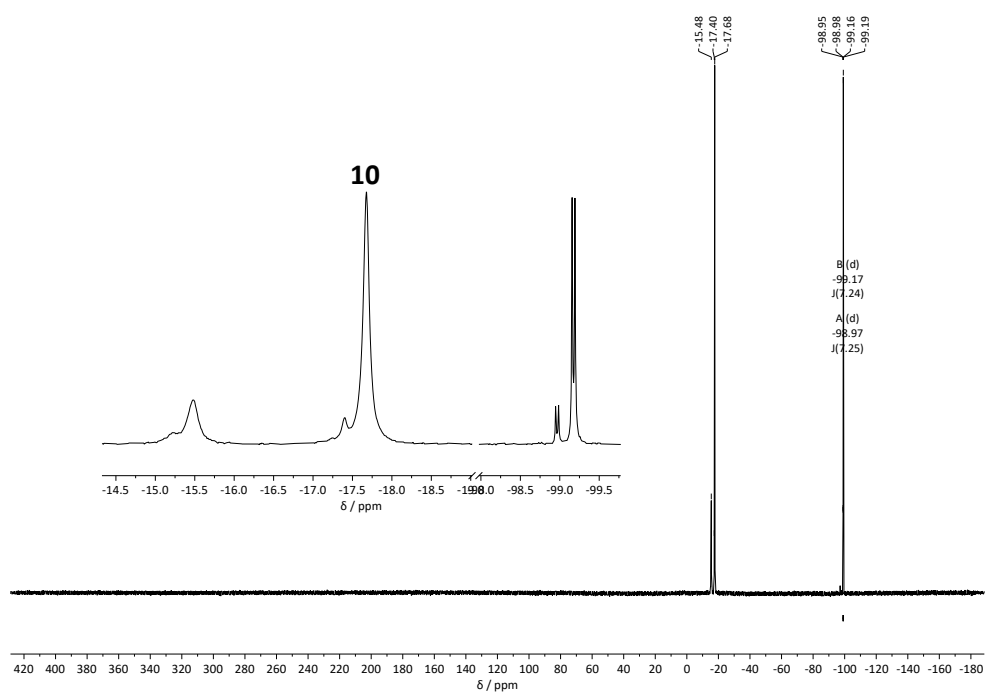


Figure S23  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 202.50 Hz, 298.0 K) of **10**.

### 3.12. 11

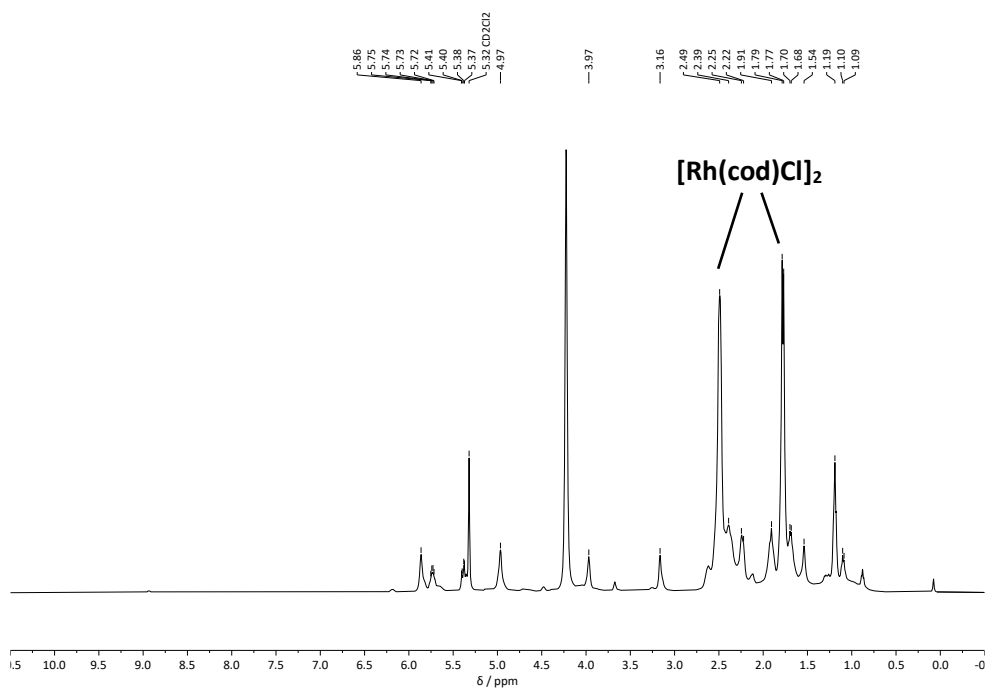


Figure S24  $^1\text{H}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 500.18 Hz, 298.0 K) of **11**.

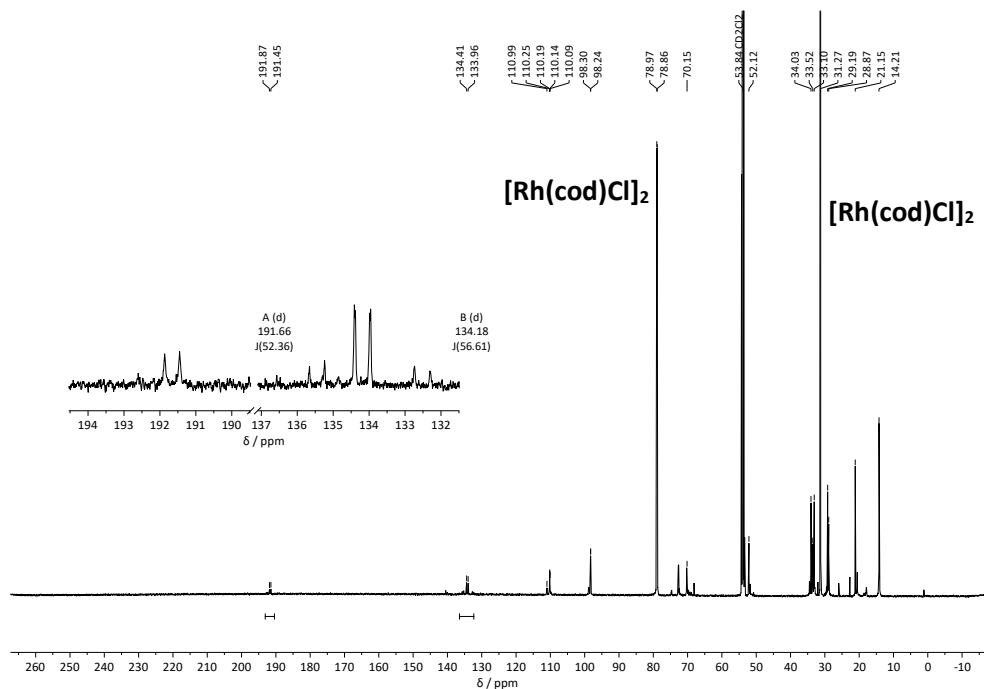


Figure S25 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 125.73 Hz, 298.0 K) of **7a**.

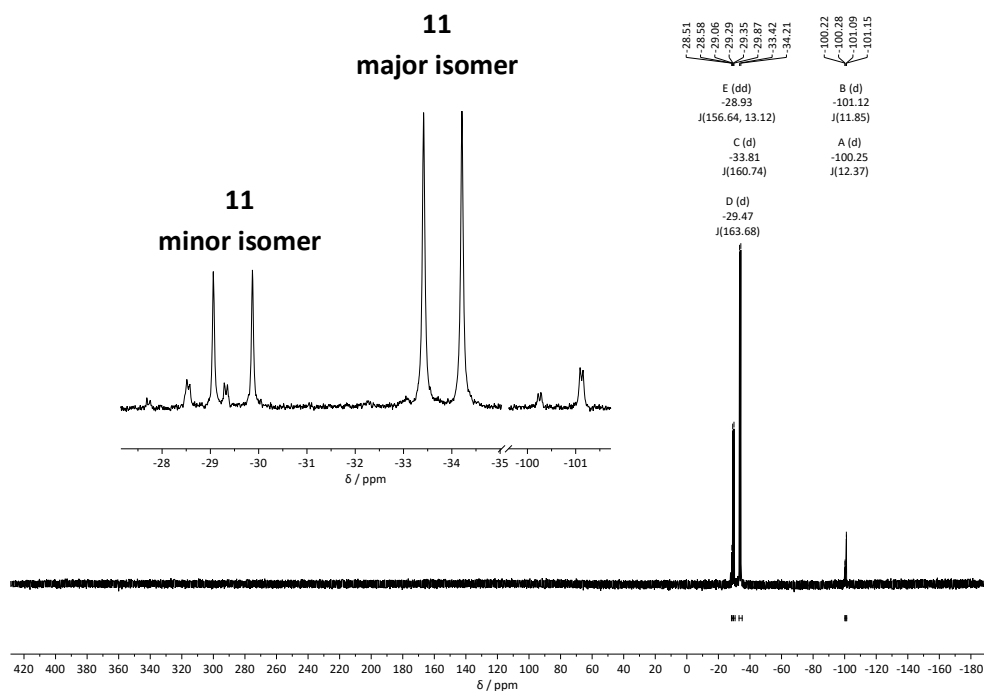
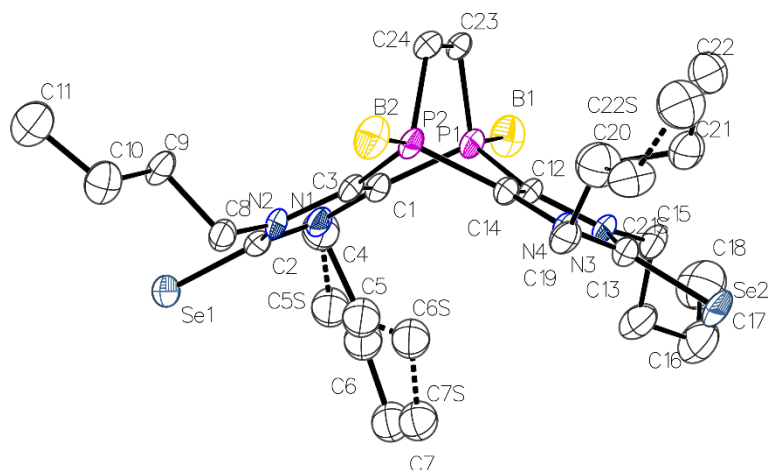


Figure S26 <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, 202.50 Hz, 298.0 K) of **11**.

## 4. Single crystal X-ray diffraction studies

### 4.1. 4



**Figure S27** Molecular structure of **4** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms and solvent molecules were omitted for clarity.

**Table S1.** Crystal data and structure refinements for **4**.

Identification code	GSTR830, TT-893 // GXraycu_7878f
Crystal habitus	clear colourless plate
Device type	Bruker D8 Venture
Empirical formula	C <sub>25</sub> H <sub>48</sub> B <sub>2</sub> Cl <sub>2</sub> N <sub>4</sub> P <sub>2</sub> Se <sub>2</sub>
Moiety formula	C <sub>25</sub> H <sub>48</sub> B <sub>2</sub> Cl <sub>2</sub> N <sub>4</sub> P <sub>2</sub> Se <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub>
Formula weight / g mol <sup>-1</sup>	717.05
T / K	100.0
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> / Å	9.5526(7)
<i>b</i> / Å	15.9233(12)
<i>c</i> / Å	23.092(2)
$\alpha$ / °	90
$\beta$ / °	101.475(6)
$\gamma$ / °	90
<i>V</i> / Å <sup>3</sup>	3442.3(5)
<i>Z</i>	4
$\rho_{calc}$ / g cm <sup>-3</sup>	1.384
$\mu$ / mm <sup>-1</sup>	5.147
<i>F</i> (000)	1472.0
Crystal size / mm <sup>3</sup>	0.12 × 0.08 × 0.01
Absorption correction	multi-scan
<i>T</i> <sub>min</sub> ; <i>T</i> <sub>max</sub>	0.4963; 0.7538
Radiation	Cu-K $\alpha$ ( $\lambda$ = 1.54178 Å)
2 $\theta$ range for data collection / °	6.788 to 135.488
Completeness to $\theta$	0.999
Index ranges	-11 ≤ <i>h</i> ≤ 11, -19 ≤ <i>k</i> ≤ 19, -27 ≤ <i>l</i> ≤ 27
Reflections collected	51353
Independent reflections	6234 ( <i>R</i> <sub>int</sub> = 0.1538, <i>R</i> <sub><math>\sigma</math></sub> = 0.0841)
Data / restraints / parameters	6234 / 121 / 405
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.021
Final <i>R</i> indexes ( <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> ))	<i>R</i> <sub>1</sub> = 0.0527, $\omega$ <i>R</i> <sub>2</sub> = 0.1219
Final <i>R</i> indexes (all data)	<i>R</i> <sub>1</sub> = 0.0856, $\omega$ <i>R</i> <sub>2</sub> = 0.1382
Largest diff. peak / hole / e Å <sup>-3</sup>	1.10 / -0.86

**Table S2.** Bond lengths for **4**.

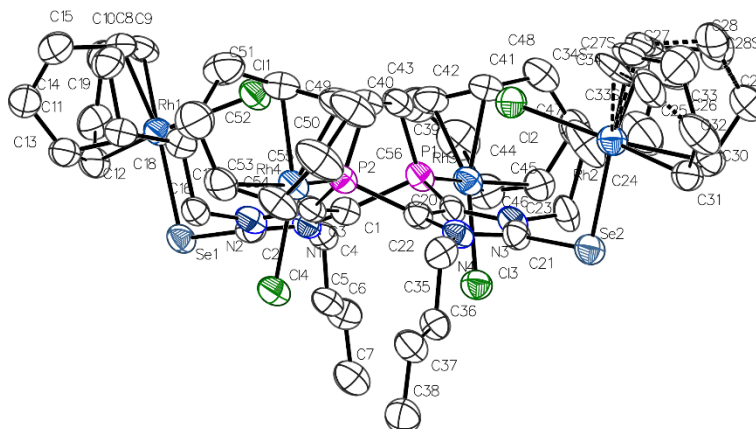
Atom	Atom	Length / Å	Atom	Atom	Length / Å
Se1	C2	1.837(4)	C1	C3	1.361(7)
Se2	C13	1.847(4)	C4	C5	1.662(13)
P1	C1	1.806(5)	C4	C5S	1.484(8)
P1	C12	1.802(4)	C5	C6	1.503(9)
P1	C23	1.835(5)	C5S	C6S	1.505(9)
P1	B1	1.906(7)	C6	C7	1.508(9)
P2	C3	1.801(5)	C6S	C7S	1.504(9)
P2	C14	1.814(5)	C8	C9	1.517(6)
P2	C24	1.827(5)	C9	C10	1.512(8)
P2	B2	1.909(7)	C10	C11	1.509(8)
N1	C1	1.394(6)	C12	C14	1.357(7)
N1	C2	1.358(6)	C15	C16	1.512(8)
N1	C4	1.463(7)	C16	C17	1.528(8)
N2	C2	1.359(6)	C17	C18	1.503(11)
N2	C3	1.381(6)	C19	C20	1.487(8)
N2	C8	1.474(6)	C20	C21	1.455(7)
N3	C12	1.387(5)	C20	C21S	1.448(8)
N3	C13	1.354(6)	C21	C22	1.513(12)
N3	C15	1.467(7)	C21S	C22S	1.502(17)
N4	C13	1.371(6)	C23	C24	1.538(7)
N4	C14	1.371(6)	Cl1	C27	1.759(6)
N4	C19	1.460(7)	Cl2	C27	1.764(6)

**Table S3.** Bond angles for **4**.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C1	P1	C23	99.3(2)	C1	C3	P2	120.1(3)
C1	P1	B1	122.2(3)	C1	C3	N2	107.5(4)
C12	P1	C1	97.3(2)	N1	C4	C5	101.6(5)
C12	P1	C23	99.0(2)	N1	C4	C5S	121.5(7)
C12	P1	B1	121.6(2)	C6	C5	C4	111.1(8)
C23	P1	B1	112.8(3)	C4	C5S	C6S	111.0(8)
C3	P2	C14	97.8(2)	C5	C6	C7	110.2(9)
C3	P2	C24	99.0(2)	C5S	C6S	C7S	112.1(8)
C3	P2	B2	120.8(3)	N2	C8	C9	112.4(4)
C14	P2	C24	99.2(2)	C10	C9	C8	111.2(4)
C14	P2	B2	122.3(2)	C11	C10	C9	114.1(5)
C24	P2	B2	113.4(3)	N3	C12	P1	132.6(4)
C1	N1	C4	126.5(4)	C14	C12	P1	120.3(3)
C2	N1	C1	109.0(4)	C14	C12	N3	106.9(4)
C2	N1	C4	124.5(4)	N3	C13	Se2	126.5(3)
C2	N2	C3	109.3(4)	N3	C13	N4	107.2(3)
C2	N2	C8	124.1(4)	N4	C13	Se2	126.3(3)
C3	N2	C8	126.6(4)	N4	C14	P2	131.7(4)
C12	N3	C15	127.1(4)	C12	C14	P2	119.9(3)
C13	N3	C12	109.0(4)	C12	C14	N4	108.3(4)
C13	N3	C15	123.9(4)	N3	C15	C16	112.6(4)
C13	N4	C14	108.4(4)	C15	C16	C17	112.7(5)
C13	N4	C19	125.0(4)	C18	C17	C16	114.2(5)
C14	N4	C19	126.6(4)	N4	C19	C20	113.6(5)
N1	C1	P1	132.7(4)	C21	C20	C19	123.3(6)
C3	C1	P1	120.1(3)	C21S	C20	C19	117.4(7)
C3	C1	N1	107.1(4)	C20	C21	C22	114.6(7)

N1	C2	Se1	126.4(4)	C20	C21S	C22S	112.7(12)
N1	C2	N2	107.1(4)	C24	C23	P1	116.5(3)
N2	C2	Se1	126.5(4)	C23	C24	P2	116.5(3)
N2	C3	P2	132.3(4)	Cl1	C27	Cl2	110.3(3)

#### 4.2. 5



**Figure S28** Molecular structure of **5** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms and solvent molecules were omitted for clarity.

**Table S4.** Crystal data and structure refinements for **5**.

Identification code	GSTR816, TT-808 // GXray7481_3d
Crystal habitus	clear yellow plate
Device type	STOE STADIVARI
Empirical formula	C <sub>70</sub> H <sub>104</sub> Cl <sub>4</sub> N <sub>4</sub> P <sub>2</sub> Rh <sub>4</sub> Se <sub>2</sub>
Moiety formula	C <sub>56</sub> H <sub>88</sub> Cl <sub>4</sub> N <sub>4</sub> P <sub>2</sub> Rh <sub>4</sub> Se <sub>2</sub> , 2 C <sub>7</sub> H <sub>8</sub>
Formula weight / g mol <sup>-1</sup>	1774.87
T / K	100
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> / Å	13.2812(4)
<i>b</i> / Å	15.1399(5)
<i>c</i> / Å	20.6038(7)
$\alpha$ / °	109.729(2)
$\beta$ / °	92.124(3)
$\gamma$ / °	106.197(2)
<i>V</i> / Å <sup>3</sup>	3705.3(2)
<i>Z</i>	2
$\rho_{calc}$ / g cm <sup>-3</sup>	1.591
$\mu$ / mm <sup>-1</sup>	10.254
<i>F</i> (000)	1796.0
Crystal size / mm <sup>3</sup>	0.12 × 0.1 × 0.05
Absorption correction	multi-scan
<i>T</i> <sub>min</sub> ; <i>T</i> <sub>max</sub>	0.0800; 0.2369
Radiation	Cu-K $\alpha$ ( $\lambda$ = 1.54178 Å)
2 $\theta$ range for data collection / °	9.218 to 141.094
Completeness to $\theta$	0.987
Index ranges	-16 ≤ <i>h</i> ≤ 15, -15 ≤ <i>k</i> ≤ 18, -24 ≤ <i>l</i> ≤ 11
Reflections collected	54383
Independent reflections	13818 ( <i>R</i> <sub>int</sub> = 0.0458, <i>R</i> <sub><math>\sigma</math></sub> = 0.0426)
Data / restraints / parameters	13851 / 1132 / 896
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.107
Final <i>R</i> indexes ( <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> ))	<i>R</i> <sub>1</sub> = 0.0697, $\omega R$ <sub>2</sub> = 0.1723

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

$R_1 = 0.0951$ ,  $\omega R_2 = 0.1874$   
1.50 / -1.35

**Table S5.** Bond lengths for 5.

Atom	Atom	Length / $\text{\AA}$	Atom	Atom	Length / $\text{\AA}$
Rh1	Se1	2.5039(12)	C24	C25	1.459(18)
Rh1	Cl1	2.401(2)	C25	C26	1.52(2)
Rh1	C8	2.108(10)	C27	C28	1.51(3)
Rh1	C9	2.124(10)	C27	C34	1.36(3)
Rh1	C12	2.111(9)	C28	C29	1.38(2)
Rh1	C13	2.140(10)	C27S	C28S	1.51(3)
Rh2	Se2	2.4996(12)	C27S	C34S	1.35(4)
Rh2	Cl2	2.378(2)	C28S	C29	1.62(3)
Rh2	C27	2.16(2)	C29	C30	1.520(15)
Rh2	C27S	2.15(3)	C30	C31	1.386(16)
Rh2	C30	2.106(11)	C31	C32	1.521(15)
Rh2	C31	2.122(11)	C32	C33	1.61(3)
Rh2	C34	2.10(2)	C32	C33S	1.41(3)
Rh2	C34S	2.16(2)	C33	C34	1.53(3)
Rh3	Cl3	2.358(2)	C33S	C34S	1.47(3)
Rh3	P1	2.256(2)	C35	C36	1.539(13)
Rh3	C41	2.121(10)	C36	C37	1.525(14)
Rh3	C42	2.122(11)	C37	C38	1.522(16)
Rh3	C45	2.224(11)	C39	C40	1.546(12)
Rh3	C46	2.228(11)	C41	C42	1.366(15)
Rh4	Cl4	2.361(2)	C41	C48	1.535(15)
Rh4	P2	2.261(2)	C42	C43	1.525(15)
Rh4	C49	2.143(10)	C43	C44	1.505(17)
Rh4	C50	2.133(11)	C44	C45	1.527(16)
Rh4	C53	2.223(12)	C45	C46	1.379(16)
Rh4	C54	2.231(11)	C46	C47	1.504(16)
Se1	C2	1.870(9)	C47	C48	1.516(16)
Se2	C21	1.869(9)	C49	C50	1.417(16)
P1	C1	1.828(9)	C49	C56	1.502(11)
P1	C20	1.823(9)	C50	C51	1.494(12)
P1	C39	1.851(9)	C51	C52	1.472(12)
P2	C3	1.820(9)	C52	C53	1.465(12)
P2	C22	1.834(10)	C53	C54	1.371(17)
P2	C40	1.864(9)	C54	C55	1.470(12)
N1	C1	1.387(11)	C55	C56	1.460(11)
N1	C2	1.349(12)	C57	C58	1.3900
N1	C4	1.472(11)	C57	C62	1.3900
N2	C2	1.354(11)	C57	C63	1.5399(10)
N2	C3	1.385(11)	C58	C59	1.3900
N2	C16	1.477(12)	C59	C60	1.3900
N3	C20	1.375(12)	C60	C61	1.3900
N3	C21	1.363(12)	C61	C62	1.3900
N3	C23	1.470(13)	C64	C65	1.3900
N4	C21	1.339(12)	C64	C69	1.3900
N4	C22	1.383(11)	C64	C70	1.44(4)
N4	C35	1.473(12)	C65	C66	1.3900
C1	C3	1.342(13)	C66	C67	1.3900
C4	C5	1.490(13)	C67	C68	1.3900
C5	C6	1.529(13)	C68	C69	1.3900
C6	C7	1.523(14)	C64S	C65S	1.3900
C8	C9	1.390(14)	C64S	C69S	1.3900

C8	C15	1.520(14)	C64S	C70S	1.44(3)
C9	C10	1.523(13)	C65S	C66S	1.3900
C10	C11	1.534(14)	C66S	C67S	1.3900
C11	C12	1.496(15)	C67S	C68S	1.3900
C12	C13	1.407(15)	C68S	C69S	1.3900
C13	C14	1.497(15)	C57A	C58A	1.3900
C14	C15	1.544(14)	C57A	C62A	1.3900
C16	C17	1.531(13)	C57A	C63A	1.530(16)
C17	C18	1.511(14)	C58A	C59A	1.3900
C18	C19	1.538(15)	C59A	C60A	1.3900
C20	C22	1.333(13)	C60A	C61A	1.3900
C23	C24	1.565(15)	C61A	C62A	1.3900

**Table S6.** Bond angles for **5**.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
Cl1	Rh1	Se1	95.02(6)	C13	C12	C11	125.3(10)
C8	Rh1	Se1	156.4(3)	C12	C13	Rh1	69.6(6)
C8	Rh1	Cl1	89.6(3)	C12	C13	C14	123.4(10)
C8	Rh1	C9	38.4(4)	C14	C13	Rh1	114.8(7)
C8	Rh1	C12	97.8(4)	C13	C14	C15	111.5(9)
C8	Rh1	C13	80.3(4)	C8	C15	C14	110.6(9)
C9	Rh1	Se1	164.3(3)	N2	C16	C17	110.0(7)
C9	Rh1	Cl1	88.8(3)	C18	C17	C16	111.3(8)
C9	Rh1	C13	89.4(4)	C17	C18	C19	109.7(8)
C12	Rh1	Se1	87.9(3)	N3	C20	P1	130.0(7)
C12	Rh1	Cl1	154.4(3)	C22	C20	P1	120.7(7)
C12	Rh1	C9	82.3(4)	C22	C20	N3	108.5(8)
C12	Rh1	C13	38.7(4)	N3	C21	Se2	125.3(7)
C13	Rh1	Se1	90.5(3)	N4	C21	Se2	127.1(7)
C13	Rh1	Cl1	165.8(3)	N4	C21	N3	107.5(8)
Cl2	Rh2	Se2	94.36(6)	N4	C22	P2	127.2(7)
C27	Rh2	Se2	149.8(7)	C20	C22	P2	121.9(7)
C27	Rh2	Cl2	89.0(6)	C20	C22	N4	107.3(8)
C27S	Rh2	Se2	170.5(8)	N3	C23	C24	109.8(9)
C27S	Rh2	Cl2	89.6(7)	C25	C24	C23	112.8(11)
C27S	Rh2	C34S	36.5(10)	C24	C25	C26	111.7(14)
C30	Rh2	Se2	89.2(3)	C28	C27	Rh2	112.4(15)
C30	Rh2	Cl2	161.8(3)	C34	C27	Rh2	69.1(13)
C30	Rh2	C27	79.1(7)	C34	C27	C28	123(2)
C30	Rh2	C27S	84.4(8)	C29	C28	C27	110.5(18)
C30	Rh2	C31	38.3(4)	C28S	C27S	Rh2	109.7(17)
C30	Rh2	C34S	98.0(7)	C34S	C27S	Rh2	72.2(14)
C31	Rh2	Se2	88.8(3)	C34S	C27S	C28S	123(2)
C31	Rh2	Cl2	159.4(3)	C27S	C28S	C29	116.6(17)
C31	Rh2	C27	98.4(7)	C28	C29	C30	117.6(12)
C31	Rh2	C27S	90.5(8)	C30	C29	C28S	108.8(12)
C31	Rh2	C34S	80.8(7)	C29	C30	Rh2	112.1(8)
C34	Rh2	Se2	171.3(7)	C31	C30	Rh2	71.5(7)
C34	Rh2	Cl2	90.8(7)	C31	C30	C29	124.6(10)
C34	Rh2	C27	37.1(9)	C30	C31	Rh2	70.2(6)
C34	Rh2	C30	88.0(8)	C30	C31	C32	123.2(10)
C34	Rh2	C31	83.9(7)	C32	C31	Rh2	111.0(8)
C34S	Rh2	Se2	152.2(8)	C31	C32	C33	110.2(12)
C34S	Rh2	Cl2	87.1(7)	C33S	C32	C31	116.8(13)
P1	Rh3	Cl3	86.29(9)	C34	C33	C32	114.1(16)
C41	Rh3	Cl3	163.5(3)	C27	C34	Rh2	73.8(13)

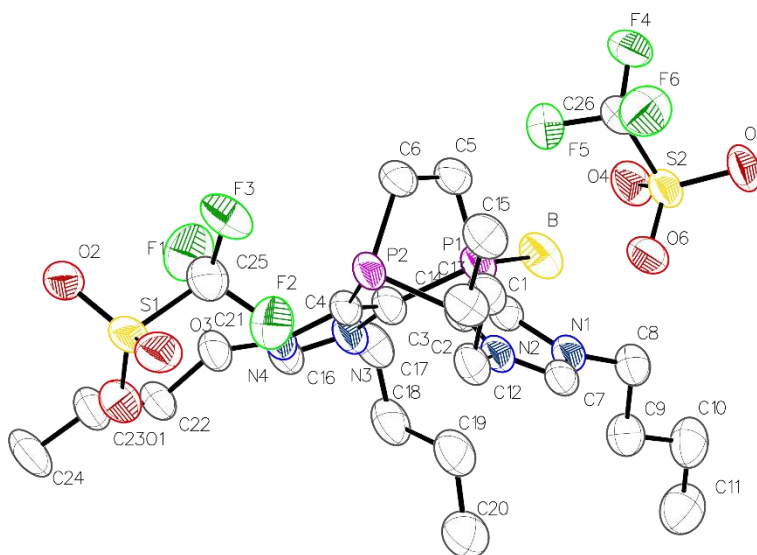
C41	Rh3	P1	96.2(3)	C27	C34	C33	126(2)
C41	Rh3	C42	37.6(4)	C33	C34	Rh2	112.1(16)
C41	Rh3	C45	89.4(4)	C32	C33S	C34S	115(2)
C41	Rh3	C46	81.4(4)	C27S	C34S	Rh2	71.3(15)
C42	Rh3	Cl3	158.9(3)	C27S	C34S	C33S	122(2)
C42	Rh3	P1	93.0(3)	C33S	C34S	Rh2	110.8(17)
C42	Rh3	C45	81.3(4)	N4	C35	C36	110.0(8)
C42	Rh3	C46	96.0(4)	C37	C36	C35	111.1(9)
C45	Rh3	Cl3	93.1(3)	C38	C37	C36	109.0(10)
C45	Rh3	P1	162.3(3)	C40	C39	P1	117.5(6)
C45	Rh3	C46	36.1(4)	C39	C40	P2	116.7(6)
C46	Rh3	Cl3	91.0(3)	C42	C41	Rh3	71.2(6)
C46	Rh3	P1	161.5(3)	C42	C41	C48	125.1(10)
P2	Rh4	Cl4	87.76(8)	C48	C41	Rh3	113.6(7)
C49	Rh4	Cl4	158.8(3)	C41	C42	Rh3	71.2(6)
C49	Rh4	P2	93.8(3)	C41	C42	C43	126.1(10)
C49	Rh4	C53	92.2(4)	C43	C42	Rh3	109.8(7)
C49	Rh4	C54	80.8(4)	C44	C43	C42	114.7(10)
C50	Rh4	Cl4	162.1(3)	C43	C44	C45	112.3(10)
C50	Rh4	P2	95.6(3)	C44	C45	Rh3	111.2(8)
C50	Rh4	C49	38.7(4)	C46	C45	Rh3	72.1(7)
C50	Rh4	C53	80.2(4)	C46	C45	C44	122.4(11)
C50	Rh4	C54	92.4(4)	C45	C46	Rh3	71.8(7)
C53	Rh4	Cl4	91.8(3)	C45	C46	C47	124.7(11)
C53	Rh4	P2	164.3(3)	C47	C46	Rh3	108.9(8)
C53	Rh4	C54	35.9(4)	C46	C47	C48	114.9(10)
C54	Rh4	Cl4	90.4(3)	C47	C48	C41	114.5(9)
C54	Rh4	P2	159.8(3)	C50	C49	Rh4	70.3(6)
C2	Se1	Rh1	100.1(3)	C50	C49	C56	124.1(11)
C21	Se2	Rh2	99.8(3)	C56	C49	Rh4	111.9(7)
C1	P1	Rh3	118.1(3)	C49	C50	Rh4	71.0(6)
C1	P1	C39	96.3(4)	C49	C50	C51	125.4(10)
C20	P1	Rh3	121.9(3)	C51	C50	Rh4	112.2(7)
C20	P1	C1	97.7(4)	C52	C51	C50	116.3(10)
C20	P1	C39	96.6(4)	C53	C52	C51	116.9(10)
C39	P1	Rh3	120.7(3)	C52	C53	Rh4	111.2(8)
C3	P2	Rh4	124.1(3)	C54	C53	Rh4	72.4(7)
C3	P2	C22	97.4(4)	C54	C53	C52	121.9(12)
C3	P2	C40	96.5(4)	C53	C54	Rh4	71.7(7)
C22	P2	Rh4	117.4(3)	C53	C54	C55	125.9(12)
C22	P2	C40	96.6(4)	C55	C54	Rh4	108.8(8)
C40	P2	Rh4	119.2(3)	C56	C55	C54	118.7(10)
C1	N1	C4	128.7(8)	C55	C56	C49	116.4(9)
C2	N1	C1	108.1(7)	C58	C57	C62	120.0
C2	N1	C4	123.1(7)	C58	C57	C63	123.8(15)
C2	N2	C3	108.2(7)	C62	C57	C63	116.2(15)
C2	N2	C16	124.7(7)	C57	C58	C59	120.0
C3	N2	C16	126.0(7)	C58	C59	C60	120.0
C20	N3	C23	127.5(8)	C61	C60	C59	120.0
C21	N3	C20	107.8(8)	C62	C61	C60	120.0
C21	N3	C23	124.0(8)	C61	C62	C57	120.0
C21	N4	C22	108.9(8)	C65	C64	C69	120.0
C21	N4	C35	123.0(8)	C65	C64	C70	122(2)
C22	N4	C35	128.0(8)	C69	C64	C70	118(3)
N1	C1	P1	126.8(7)	C64	C65	C66	120.0
C3	C1	P1	121.9(7)	C67	C66	C65	120.0
C3	C1	N1	107.9(8)	C68	C67	C66	120.0
N1	C2	Se1	126.0(7)	C67	C68	C69	120.0



N1	C2	N2	108.1(7)	C68	C69	C64	120.0
N2	C2	Se1	125.6(7)	C65S	C64S	C69S	120.0
N2	C3	P2	131.0(7)	C65S	C64S	C70S	115(2)
C1	C3	P2	120.6(7)	C69S	C64S	C70S	124(2)
C1	C3	N2	107.6(8)	C64S	C65S	C66S	120.0
N1	C4	C5	111.3(7)	C67S	C66S	C65S	120.0
C4	C5	C6	111.8(8)	C68S	C67S	C66S	120.0
C7	C6	C5	112.6(8)	C69S	C68S	C67S	120.0
C9	C8	Rh1	71.4(6)	C68S	C69S	C64S	120.0
C9	C8	C15	125.8(9)	C58A	C57A	C62A	120.0
C15	C8	Rh1	112.7(7)	C58A	C57A	C63A	127.5(18)
C8	C9	Rh1	70.2(6)	C62A	C57A	C63A	112.5(18)
C8	C9	C10	124.7(9)	C57A	C58A	C59A	120.0
C10	C9	Rh1	112.8(7)	C58A	C59A	C60A	120.0
C9	C10	C11	111.4(9)	C61A	C60A	C59A	120.0
C12	C11	C10	113.6(9)	C62A	C61A	C60A	120.0
C11	C12	Rh1	109.6(7)	C61A	C62A	C57A	120.0
C13	C12	Rh1	71.8(6)				

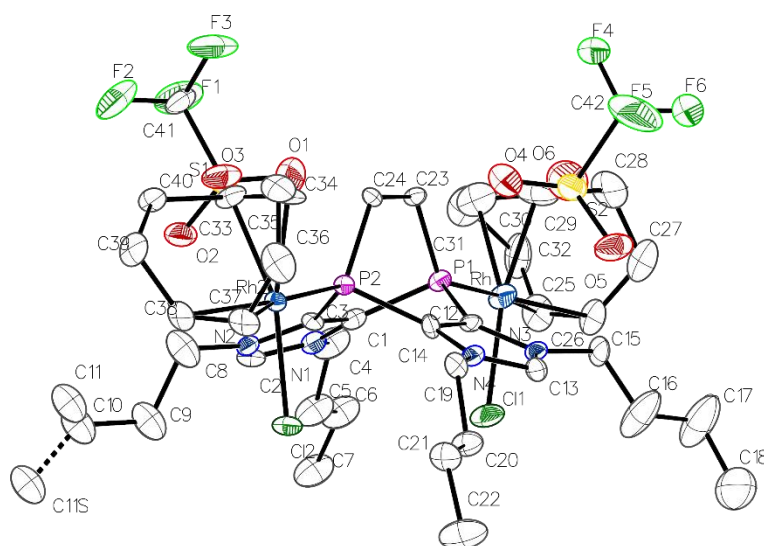
Due to the lower quality of the structures determined from single crystals of 8–11 no discussion of any structural parameters was performed. However, the composition of the (main) product could be confirmed as evidenced by the figures below.

#### 4.3. 8



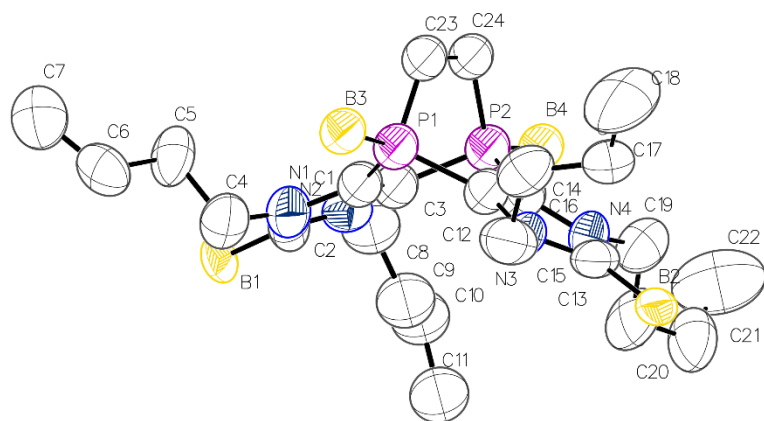
**Figure S29.** Molecular structure of **8** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms were omitted for clarity.

4.4. 9



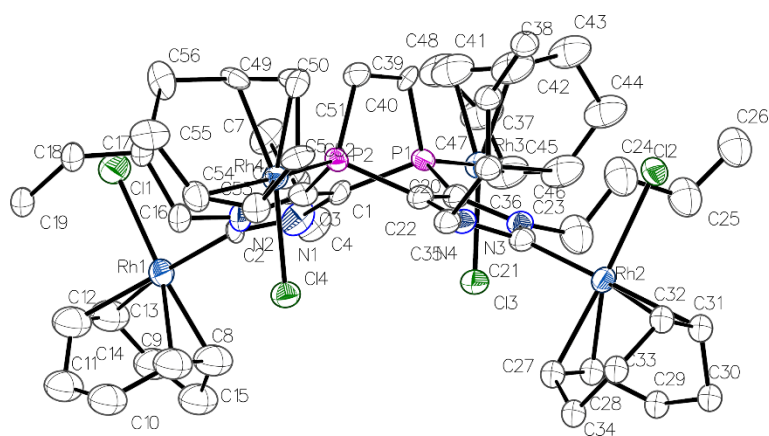
**Figure S30.** Molecular structure of **9** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms and solvent molecules were omitted for clarity.

4.5. 10



**Figure S31.** Molecular structure of **10** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms and solvent molecules were omitted for clarity.

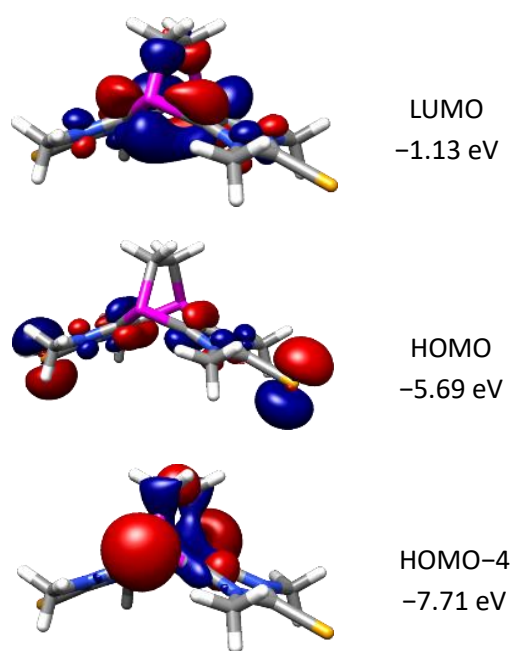
4.6. 11



**Figure S32.** Molecular structure of **11** in the single crystal. Thermal ellipsoids are set at 50 % probability level. Hydrogen atoms and solvent molecules were omitted for clarity.

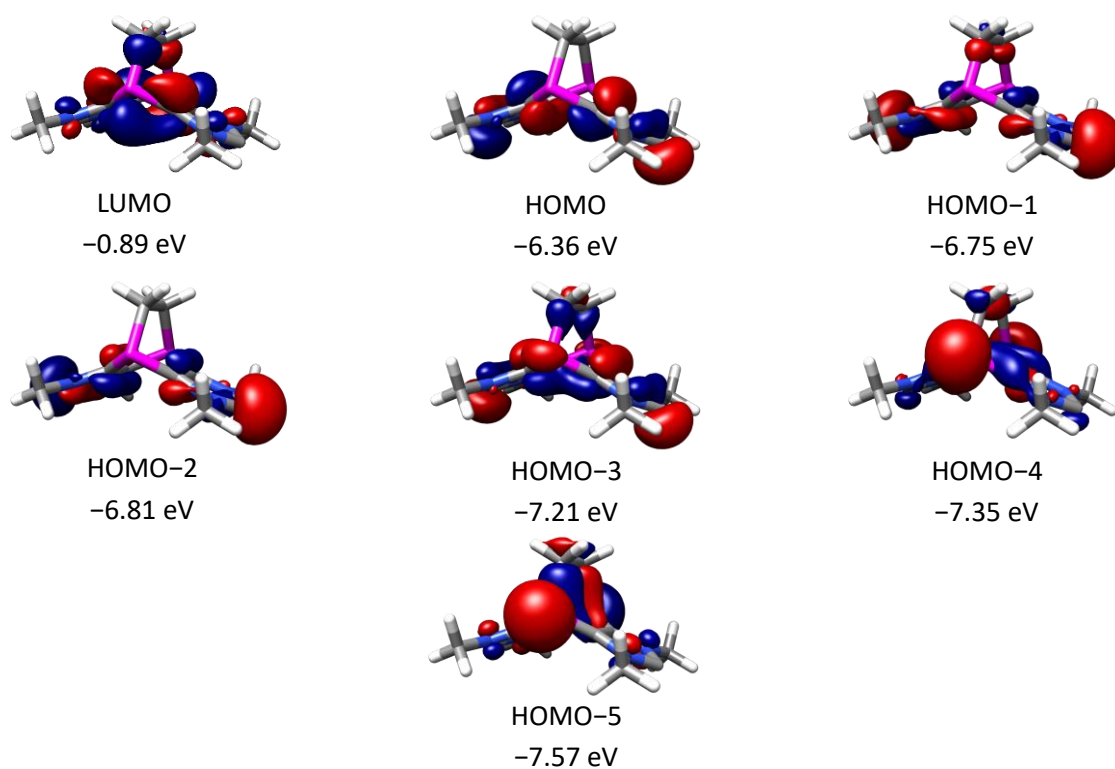
## 5. Additional figures

### 5.1. FMOs of 2



*Figure S33* Selected FMOs of compound **2<sup>Me</sup>**.

### 5.2. FMOs of 7



*Figure S34* Selected FMOs of compound **7<sup>Me</sup>**.

## 6. Computational details

All geometric optimisation and energy calculations were performed with *ORCA 5.0*.<sup>5,6</sup> Structures were optimised at the TPSS-D4/def2-TZVP/CPCM<sub>THF</sub> level of theory which combines the TPSS<sup>7</sup> meta-GGA density functional with the charge dependent atom-pairwise DFT-D4 dispersion correction which uses the D4(EEQ)-ATM dispersion model<sup>8</sup> and the def2-TZVP basis set<sup>9-12</sup> using the conductor-like polarisable continuum model (CPCM)<sup>13</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>14</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>6,15</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>16</sup> with the larger def2-QZVP basis set.<sup>9-12</sup> NICS(1) values were calculated at the B3LYP-D4/def2-TZVPPD level of theory combining the hybrid functional B3LYP<sup>17</sup> with the def2-TZVPPD basis set<sup>9-12</sup> and using the NMR module of *ORCA 5.0* utilising Gauge including atomic orbitals (GIAOs).<sup>18</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>9,19</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>20</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. **1**<sup>Me</sup>

**Table S7.** Computational data for **1**<sup>Me</sup>.

<b>1</b> <sup>Me</sup>			
$E = -6097.147735690066$			
$E_{ZPE} = 0.21546057$			
$E_T = 0.01970719$			
$E_S = -0.06819458$			
C	-6.63660	-6.76350	-0.57438
C	-7.01810	-5.46794	-0.98979
C	-4.58926	-4.59093	-0.48861
C	-4.20813	-5.88621	-0.07202
P	-6.11505	-3.97317	-1.07857
P	-5.11074	-7.38130	0.01539
N	-7.76343	-7.56272	-0.71510
N	-8.35413	-5.55730	-1.35753
N	-3.46237	-3.79177	-0.34810
N	-2.87256	-5.79650	0.29726

C	-9.13716	-4.42944	-1.84950
H	-9.15479	-3.64136	-1.09138
H	-8.68712	-4.04651	-2.76985
H	-10.14786	-4.78917	-2.04432
C	-7.79637	-8.98343	-0.38623
H	-7.06122	-9.51543	-0.99657
H	-7.56282	-9.11693	0.67388
H	-8.80108	-9.34835	-0.60113
C	-2.08982	-6.92415	0.79013
H	-2.05535	-7.70533	0.02542
H	-1.08449	-6.55997	1.00360
H	-2.55170	-7.31810	1.69986
C	-3.42922	-2.37115	-0.67734
H	-2.42210	-2.00828	-0.47040
H	-3.67088	-2.23765	-1.73562
H	-4.15839	-1.83731	-0.06143
Se	-0.70978	-3.90794	0.48230
C	-2.40381	-4.51871	0.13232
C	-8.82250	-6.83540	-1.19380
Se	-10.51670	-7.44603	-1.54318

## 6.2. 2<sup>Me</sup>

**Table S8.** Computational data for 2<sup>Me</sup>.

2<sup>Me</sup>

$E = -6175.906245036859$

$E_{ZPE} = 0.27120048$

$E_T = 0.02213321$

$E_S = -0.07289518$

---

C	-5.37582	-7.63244	0.34730
C	-6.00388	-6.84459	-0.57853
C	-3.86284	-5.22939	-0.65073
C	-3.23837	-6.01434	0.27960
P	-5.66913	-5.06727	-0.75398
P	-4.14421	-6.98707	1.51812
N	-5.94910	-8.89262	0.27088
N	-6.95474	-7.63168	-1.20980
N	-2.87343	-4.55403	-1.34895
N	-1.87401	-5.81072	0.13958
C	-7.85496	-7.21076	-2.27926
H	-8.89039	-7.35653	-1.96349
H	-7.66639	-6.15564	-2.48089
H	-7.66454	-7.80722	-3.17446
C	-5.57990	-10.06176	1.06346
H	-4.77313	-9.76973	1.73680
H	-6.44502	-10.40480	1.63533
H	-5.24747	-10.86285	0.39922
C	-0.81910	-6.46067	0.91186
H	-1.29441	-7.12108	1.63794
H	-0.17614	-7.03549	0.24133
H	-0.22038	-5.70390	1.42360
C	-3.07639	-3.61198	-2.44573
H	-2.55019	-3.96840	-3.33401
H	-4.14763	-3.54890	-2.64048
H	-2.68497	-2.63150	-2.16487
C	-1.64151	-4.91219	-0.86810

C	-6.92195	-8.90032	-0.69383
C	-5.21515	-5.55503	2.12302
C	-5.91185	-4.66151	1.07402
H	-5.95714	-6.02237	2.77811
H	-5.57834	-3.62400	1.17603
Se	-7.96161	-10.33376	-1.21020
Se	-0.00154	-4.31842	-1.46886
H	-6.99619	-4.67496	1.22198
H	-4.55069	-4.95579	2.75330

### 6.3. Ethene

**Table S9.** Computational data for ethene.

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**Ethene**  
 $E = -78.726416921569$   
 $E_{ZPE} = 0.050233$   
 $E_T = 0.00305219$   
 $E_S = -0.02487869$

---

C	-2.62830	0.55359	-0.00020
H	-3.71536	0.51851	0.00021
H	-2.11074	-0.40296	-0.00059
C	-1.96480	1.70925	-0.00023
H	-2.48236	2.66580	0.00016
H	-0.87774	1.74433	-0.00064

### 6.4. 2<sup>Me</sup>-TS

**Table S10.** Computational data for 2<sup>Me</sup>-TS.

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**2<sup>Me</sup>-TS**  
 $E = -6175.861062308280$   
 $E_{ZPE} = 0.26772679$   
 $E_T = 0.02197965$   
 $E_S = -0.07280527$   
 $imf = -283.83 \text{ cm}^{-1}$

---

C	-0.43619	-1.65116	-0.11573
C	-1.05269	-0.84065	-1.06094
C	1.08505	0.73447	-1.09954
C	1.70310	-0.07906	-0.15760
P	-0.64496	0.83599	-1.45275
P	0.91515	-1.21925	0.94158
N	-1.26326	-2.75388	0.06596
N	-2.23436	-1.47936	-1.42220
N	2.03002	1.67339	-1.49804
N	3.00392	0.39329	-0.01675
C	-3.19951	-0.98036	-2.39753
H	-4.00507	-0.44110	-1.89129
H	-2.67656	-0.30921	-3.08124
H	-3.61570	-1.83168	-2.93789
C	-0.99240	-3.85848	0.98106
H	0.07879	-4.07054	0.96266
H	-1.29991	-3.59185	1.99633
H	-1.56238	-4.72382	0.64058
C	4.01804	-0.17080	0.86937
H	3.72634	-1.19447	1.11070

H	4.97897	-0.15796	0.35262
H	4.09045	0.42143	1.78563
C	1.79646	2.73514	-2.47220
H	2.75981	3.02026	-2.89707
H	1.12989	2.35356	-3.24830
H	1.33989	3.60143	-1.98467
C	3.21280	1.46706	-0.83919
C	-2.36872	-2.65684	-0.73682
C	-0.43391	0.64055	1.86171
C	-1.05718	1.45518	0.91451
H	-1.02973	-0.08439	2.40830
H	-0.64516	2.43869	0.70937
H	0.45095	1.00736	2.37348
H	-2.12310	1.34273	0.74018
Se	-3.74677	-3.86910	-0.89253
Se	4.77933	2.41522	-1.03229

## 6.5. $7^{\text{Me}}$

**Table S11.** Computational data for  $7^{\text{Me}}$ .

$7^{\text{Me}}$			
$E = -1370.391081703325$			
$E_{\text{ZPE}} = 0.26654919$			
$E_{\text{T}} = 0.01877921$			
$E_{\text{S}} = -0.06430423$			
C	-5.39778	-7.62016	0.36742
C	-6.01740	-6.83777	-0.56914
C	-3.83819	-5.25330	-0.68087
C	-3.22100	-6.03346	0.25880
P	-5.64319	-5.07139	-0.77853
P	-4.14061	-6.97555	1.51144
N	-6.01100	-8.86487	0.29941
N	-6.98205	-7.63943	-1.16656
N	-2.82294	-4.61397	-1.38121
N	-1.85607	-5.83633	0.09010
C	-7.87637	-7.19721	-2.23412
H	-8.49409	-8.04871	-2.51849
H	-8.51183	-6.37988	-1.88148
H	-7.29479	-6.85478	-3.09446
C	-5.64667	-10.01145	1.12889
H	-4.59690	-10.27296	0.96947
H	-5.80272	-9.77810	2.18585
H	-6.28520	-10.84446	0.83594
C	-0.82241	-6.49241	0.88784
H	-0.89878	-7.57829	0.78354
H	0.14392	-6.15088	0.51768
H	-0.93160	-6.22376	1.94227
C	-3.04192	-3.68254	-2.48571
H	-2.06378	-3.35941	-2.84114
H	-3.58710	-4.17786	-3.29394
H	-3.61591	-2.81750	-2.14190
C	-1.57360	-4.96132	-0.92963
C	-6.99946	-8.91242	-0.65248
C	-5.18493	-5.51323	2.10658
C	-5.87026	-4.62462	1.04719
H	-5.93161	-5.95733	2.77250



H	-5.51579	-3.59219	1.12874
H	-6.95364	-4.61380	1.20310
H	-4.50764	-4.91524	2.72451

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