

Supporting Information

**Derivatization of sodium phosphide into silyl- and cyanophosphides and structure of a terminal silver phosphide**

Grégoire Le Corre,<sup>a</sup> and Hansjörg Grützmacher\*<sup>a</sup>

---

<sup>a</sup> *Department of Chemistry and Applied Biosciences, ETH Zürich, Switzerland*

E-mail:

\* [hgruetzmacher@ethz.ch](mailto:hgruetzmacher@ethz.ch)

## Table of Contents

1. GENERAL REMARKS.....	3
2. SYNTHESIS AND CHARACTERIZATION .....	4
3. SPECTRA.....	16
4. CRYSTALLOGRAPHIC DETAILS .....	41
5. THERMOGRAVIMETRIC DATA .....	48
REFERENCES .....	49

## 1. General Remarks

All experiments were performed under Ar atmosphere using standard Schlenk and vacuum-line techniques or in an MBraun glove box. Glassware was flame dried on a Schlenk line prior to use. Solvents were dried and stored over 4 Å molecular sieves under Ar with the exception of 1,2-difluorobenzene (DFB, 99 %, Fluorochem) and 1,2-diethoxyethane (DEE, 99 %, Acros) which were distilled over calcium hydride and stored under molecular sieves. Deuterated solvents were purchased from Eurisotop, degassed and distilled from the proper drying agent, and stored over 4 Å molecular sieves under Ar. The argon was provided by PANGAS and further purified with an MBraun >99 HP gas purification system. Air sensitive compounds were handled in a glovebox (MBraun lab master 130 or 150B-G). Small scale reactions were performed inside a glovebox.

Chlorotrimethylsilane (95 %, Acros Organics) and trimethylsilyl isocyanate (Tokyo Chemical Industry, 95 %) were re-condensed prior to use. Sodium in paraffin oil (99.8 %), dichlorodiphenylsilane (97 %), tetrachlorosilane (99.8 %) and cesium fluoride (99.9 %) were purchased from Acros Organics. Red phosphorus (> 97 %), chlorotriphenylsilane (95 %) and trimethylacetyl chloride (99 %) were purchased from Sigma Aldrich. 2,4,6-trimethylbenzoyl chloride (> 98 %) was purchased from Tokyo Chemical Industry. Phenyltrichlorosilane (97 %) was purchased from Alfa Aesar. Tetra n-butylphosphonium bromide (99 %) and tetraphenylphosphonium chloride (95 %) were both purchased from Acros Organics and dried in the presence of P<sub>2</sub>O<sub>5</sub> under vacuum at 75°C. BrCN (97 %) was purchased from Sigma-Aldrich and sublimed *in vacuo* before preparing a 1.0 M solution in DME. Na[2]<sup>[1]</sup>, phenyl cyanate,<sup>[2]</sup> triphenylsilyl isocyanate<sup>[3]</sup> and IPrMCl (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, M = Au, Ag, Cl)<sup>[4-6]</sup> were prepared according to literature procedures.

NMR measurements were carried out on Bruker Avance 200, 250, 300, 400, 500 MHz and 500 MHz Cryoprobe spectrometers at 298 K (unless indicated otherwise). Chemical shifts  $\delta$  are given as dimensionless numbers and the absolute values of the coupling constants are given in Hertz (Hz), the first atom mentioned in the subscript always refers to the atom that was used to observe the coupling. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), virtual triplet (vt), virtual doublet of doublets (vdd) and broad (br). NMR spectra were referenced to TMS (<sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si), H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) and Ag(NO<sub>3</sub>) (<sup>109</sup>Ag). <sup>31</sup>P-<sup>109</sup>Ag HMBC correlation was measured using a triple resonance broadband probehead (<sup>1</sup>H, <sup>31</sup>P, X).

X-ray single crystals suitable for X-ray diffraction were coated with perfluoroalkylether oil in a glovebox, transferred to a nylon loop and then transferred to the goniometer of an Oxford XCalibur diffractometer or D8-Venture diffractometer equipped with a copper X-ray tube ( $\lambda = 1.5406$  Å) or a molybdenum tube ( $\lambda = 0.7107$  Å). Preliminary data was collected to determine the crystal system. The space group was identified, and the data was processed using the Bruker SAINT+ or CrysAlis program and corrected for absorption using SADABS or the SCALE3 ABSPACK on CrysAlis absorption correction. The structures were solved using direct methods (XT) on OLEX2 completed by Fourier transformation and refined by full-matrix least-squares procedures (XL).

TGA/DSC measurements were performed on NETZSCH STA449F5 instrument connected to a EI-MS (AEOLOS III). About 5 mg of the samples was heated from 40 °C to 600 °C at a rate of 10 K min<sup>-1</sup> under argon flow. The line that transfers evolved gases from TGA to MS was maintained at 230 °C. The TGA data obtained during the measurement was analyzed using Netzsch Proteus – Thermal Analysis Software. Other melting points were determined using a Büchi apparatus and are not corrected.

Elemental analysis was performed by the ETH Zurich Microelemental Analysis service on a LECO TruSpec Micro apparatus.

## 2. Synthesis and Characterization

### Preparation of sodium phosphide (Na<sub>3</sub>P):

A dry and argon-flushed Schlenk flask equipped with a magnetic stirrer was charged with sodium pieces (24 g, 1.044 mol, 3 equivalents), DME (400 mL) and naphthalene (4.46 g, 34.8 mmol, 0.1 equivalent). The suspension was stirred at room temperature until a deep green color appeared and red phosphorus (10.8 g, 348 mmol, 1 equivalent) was added. The mixture was stirred at 75 °C for 14 h and cooled down to room temperature. The resulting black solid was collected by filtration, washed with diethyl ether (3x20 mL) and dried in vacuo to afford sodium phosphide (34.5 g, 345 mmol, 99 % yield) as a black powder. These materials can be used without further purification.

### Generation of tris(trimethylsilyl)phosphine **1** and bis(trimethylsilyl)phosphide **[2]**

A dry and argon-flushed Schlenk tube was charged with DME (0.5 mL), sodium phosphide (5 mg, 0.05 mmol), tetrabutylphosphonium bromide (16.9 mg, 0.05 mmol, 1 equivalent) and trimethylsilyl chloride (10.8 mg, 0.1 mmol, 2 equivalents). The tube was sealed and the suspension was sonicated for 3 days at 50 °C before analyzing the sample by <sup>31</sup>P{<sup>1</sup>H}-NMR, which indicated the presence of phosphine **1** (-251 ppm) and phosphide **[2]** (-290 ppm) as products of the reaction.

<sup>31</sup>P{<sup>1</sup>H}-NMR (121.5 MHz, DME, ppm): -252 (s, **1**), -290 (s, <sup>1</sup>J<sub>P,Si</sub> = 55 Hz, **[2]**)

### Preparation of tris(trimethylsilyl)phosphine **1**:

A dry and argon-flushed Schlenk flask equipped with a magnetic stirrer was charged with sodium phosphide (5.0 g, 50 mmol, 1 equivalent) and DME (150 mL). Trimethylsilyl chloride (21 mL, 165 mmol, 3.3 equivalents) was added and the resulting black suspension was stirred at 50 °C for 5 days before removing the solvent in vacuo. **1** was purified by distillation at 50°C under vacuum (0.02 mbar) and afforded as a colorless liquid (6.52 g, 52% yield).

<sup>31</sup>P-NMR (121.5 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): -252 (multiplet)

<sup>13</sup>C{<sup>1</sup>H}-NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): 4.2 (d, <sup>2</sup>J<sub>P,C</sub> = 11.3 Hz)

<sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): 0.31 (d, <sup>3</sup>J<sub>P,H</sub> = 4.4 Hz)

### Preparation of bis(triphenylsilyl)phosphide salt Na(18-c-6)(DME)<sub>0.5</sub>**[4]**:

A dry and argon-flushed Schlenk flask equipped with a magnetic stirrer was charged with sodium pieces (3.52 g, 153 mmol, 3 equivalents), DME (80 mL) and naphthalene (4.46 g, 34.8 mmol, 0.1 equivalent). The suspension was stirred at room temperature until a deep green color appeared and red phosphorus (1.58 g, 51 mmol, 1 equivalent) was added. The mixture was stirred overnight at 75 °C, after which chlorotriphenylsilane (30.1 g, 102 mmol, 2 equivalents) dissolved in 20 mL DME was added. The suspension was sonicated for 16 h at 75°C before filtering over celite and washing the solid with DME (3x100 mL). The filtrate was reduced to about 150 mL and 18-crown-6 (13.5 g, 51 mmol, 1 equivalent) dissolved in 20 mL DME was added. The resulting suspension was stirred for 20 minutes and the supernatant was removed by decantation. The solid was washed with toluene (2x300 mL) and diethyl ether (200 mL) and dried in vacuum to afford Na(18-c-6)(DME)<sub>0.5</sub>**[4]** as a yellow powder (25.5 g, 29.7 mmol, 60 % yield).

Crystals suitable for X-ray diffraction were grown from a concentrated solution generated from sonication of Na<sub>3</sub>P (50 mg, 0.5 mmol, 1 equivalent) and chlorotriphenylsilane (294.85 mg, 1 mmol, 2 equivalents) in DME (4 mL) and filtration with a syringe filter. The solution was layered

with 18-crown-6 (132 mg, 0.5 mmol, 1 equivalent) dissolved in DME (1 mL) to afford crystals of  $\text{Na}(18\text{-c-}6)(\text{DME})_{0.5}[\mathbf{4}]$ .

**Melting point:** 307 °C (DSC, decomp.)

**$^{31}\text{P}\{^1\text{H}\}$ -NMR** (121.5 MHz, THF- $d_8$ , ppm): -316 (s, Si satellites,  $^1J_{\text{P,Si}} = 86$  Hz)

**$^{13}\text{C}\{^1\text{H}\}$ -NMR** (125.8 MHz, THF- $d_8$ , ppm): 146.4 (d,  $^3J_{\text{P,C}} = 9.6$  Hz, Ph ipso), 137.1 (d,  $^3J_{\text{P,C}} = 3.4$  Hz, Ph ortho) 126.3 (two overlapping s, Ph para and meta) 72.6 (s, DME  $\text{CH}_3$ ), 70.5 (s, 18-c-6), 58.7 (s, DME  $\text{CH}_2$ )

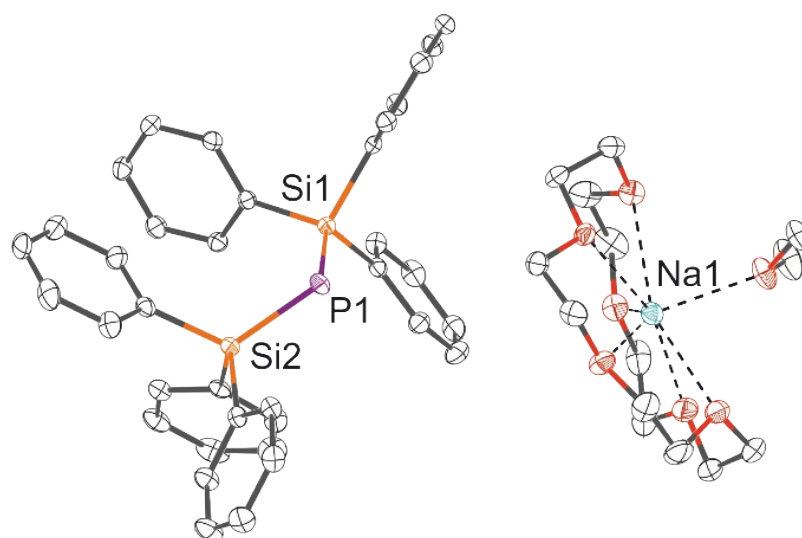
**$^{29}\text{Si}$ -NMR** (99.4 MHz, THF- $d_8$ , ppm): 0 (d,  $^1J_{\text{P,Si}} = 86$  Hz)

**$^1\text{H}$ -NMR** (500 MHz, THF- $d_8$ , ppm): 7.50-7.43 (m, 12H, Ph ortho), 7.27-7.14 (m, 18H, Ph para and meta), 3.55 (s, 24H, 18-c-6), 3.42 (s, 2H, DME  $\text{CH}_2$ ), 3.26 (s, 3H, DME  $\text{CH}_3$ )

**Elemental analysis for  $\text{C}_{50}\text{H}_{59}\text{O}_7\text{NaSi}_2\text{P}$  (%):**

Calc: C 68.08 H 6.74 N 0.00

Found: C 68.01 H 6.31 N 0.01



**Figure S1:** Plot of the structure of  $\text{Na}(18\text{-crown-}6)(\text{DME})_{0.5}[\mathbf{4}]$  (hydrogens omitted for clarity). Selected bond distances [Å] and angles [°]:  $[\mathbf{4}]$  P1-Si1 2.1878(5); P1-Si2 2.1939(5); Si1-P1-Si2 105.060(18)

#### Generation of bis(triphenylsilyl)phosphide salt $\text{Bu}_4\text{P}[\mathbf{4}]$ in diethoxyethane:

A dry and argon-flushed Schlenk flask equipped with a magnetic stirrer was charged with sodium phosphide (100 mg, 1 mmol), tetrabutylphosphonium bromide (339 mg, 1 mmol 1 equivalent) and DEE (3 mL). The suspension was heated at 120°C and chlorotriphenylsilane (590 mg, 2 mmol, 2 equivalents) dissolved in DEE (3 mL) was injected. The suspension was stirred for one hour at 120°C, after which  $^{31}\text{P}$ -NMR indicated the presence of phosphide  $[\mathbf{4}]$  and the absence of tris(triphenylsilyl)phosphine  $\mathbf{3}$  (see Figure S15 below). Signals in the -70 to 50 ppm region were identified as decomposition products of tetrabutylphosphonium bromide.

A similar reaction with three equivalents of chlorotriphenylsilane leads to the same outcome.

**$^{31}\text{P}\{^1\text{H}\}$ -NMR** (121.5 MHz, DME, ppm): -309 (s, Si satellites,  $^1J_{\text{P,Si}} = 86$  Hz)

### Tetraphenylphosphonium bis(trichlorosilyl)phosphide $\text{PPh}_4[5]$ :

Warning: The reaction of  $\text{Na}_3\text{P}$  with neat  $\text{SiCl}_4$  is highly exothermic and may generate a flame even under inert atmosphere. We highly recommend suspending  $\text{Na}_3\text{P}$  in DME before adding  $\text{SiCl}_4$  so as to avoid any violent reaction.

A dry and argon-flushed thin Schlenk flask was charged with sodium phosphide (1.4 g, 13.3 mmol, 1.4 equivalent), tetraphenylphosphonium chloride (3.3 g, 10 mmol, 1 equivalent). DME (40 mL) and tetrachlorosilane (2.29 mL, 20 mmol, 2 equivalents). The resulting suspension was sonicated at 50 °C for 4 days. The brown suspension was filtered and the solid was washed with DME (2x10 mL). The filtrate was reduced in vacuum and the resulting solid was redissolved in DCM (10 mL), the solution was reduced *in vacuo* until some precipitate appeared and diethyl ether (20 mL) was added. The resulting white solid was collected by filtration, washed with diethyl ether (3x20 mL), dried in high vacuum to yield as a white powder (2.14 g, 48 % yield). Crystals suitable for X-Ray diffraction were obtained from cooling down of a concentrated DCM solution.

**Melting point:** 140 °C (DSC)

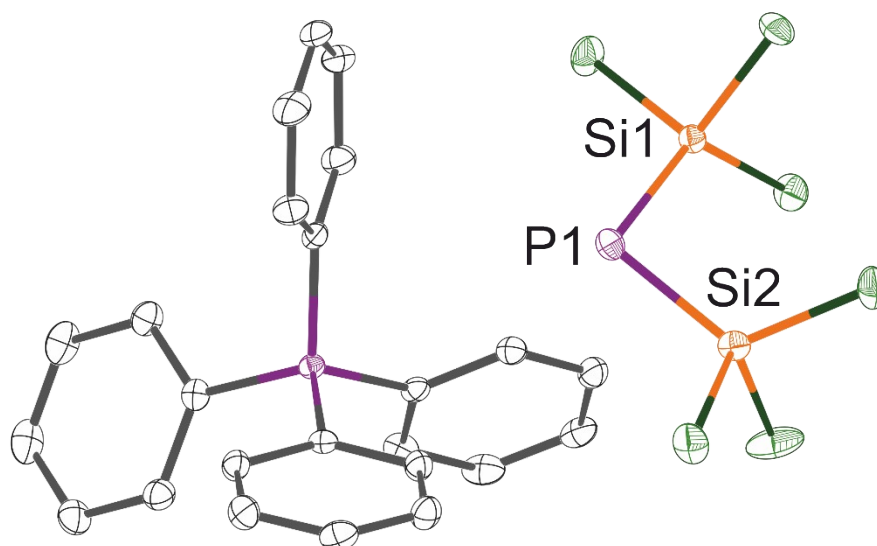
$^{31}\text{P}\{^1\text{H}\}$ -NMR (121.5 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm): 23 (s,  $\text{PPh}_4$ ), -173 (s, Si satellites,  $^1J_{\text{P,Si}} = 160$  Hz,  $\text{P-Si}$ )

$^{29}\text{Si}$ -NMR (99.4 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm): 11 (d,  $^1J_{\text{P,Si}} = 160$  Hz)

$^{13}\text{C}\{^1\text{H}\}$ -NMR (125.8 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm): 136.2 (d,  $^4J_{\text{P,C}} = 3.2$  Hz, para), 134.9 (d,  $^3J_{\text{P,C}} = 10.3$  Hz, meta), 131.1 (d,  $^2J_{\text{P,C}} = 12.9$  Hz, ortho), 117.9 (d,  $^3J_{\text{P,C}} = 89.6$  Hz, ipso)

$^1\text{H}$ -NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm): 7.90-8.00 (m, 4H, para), 7.27-7.86 (m, 8H, meta), 7.56-7.14 (m, 8H, ortho).

No elemental analysis is provided for this compound due to presence of large amounts of chloride impurity.



**Figure S2:** Structure of  $\text{PPh}_4[5]$  in the crystal (hydrogens omitted for clarity).

Selected bond distances [Å] and angles [°]: P1-Si1 2.1524(7); P1-Si2 2.1473(7); Si-Cl (average): 2.0658(7); Si1-P1-Si2 96.76(3)

## Reactivity study of PPh<sub>4</sub>[5] with electrophiles

A dry and argon-flushed NMR tube was charged with PPh<sub>4</sub>[5] (0.05 mmol) and DFB (0.5 mL). Benzoyl chloride or tetrachlorosilane was added in excess (5 equivalents) and the tube was heated at 50 °C. <sup>31</sup>P NMR showed no reaction after four hours of heating.

## Generation of bis(silyl)phosphides [8] and [9]:

Na<sub>3</sub>P (10 mg, 0.1 mmol, 1 equivalent) and tetra n-butylphosphonium bromide (33 mg, 0.1 mmol, 1 equivalent) and DME (0.5 mL) were added into a dry and argon-flushed NMR tube inside a glovebox. Two equivalents of either trichloro(phenyl)silane or diphenyldichlorosilane was added under argon and the suspension was sonicated at 75 °C overnight. The products were characterized by <sup>31</sup>P NMR which indicated presence of [8] (resp. [9]) among a complex mixture of products (Figures S28 and S29).

### [8]

<sup>31</sup>P{<sup>1</sup>H}-NMR (121.5 MHz, DME, ppm): -228 (s, Si satellites, <sup>1</sup>J<sub>P,Si</sub> = 131 Hz, *P*-Si)

### [9]

<sup>31</sup>P{<sup>1</sup>H}-NMR (121.5 MHz, DME, ppm): -270 (s, Si satellites, <sup>1</sup>J<sub>P,Si</sub> = 108 Hz, *P*-Si)

## (E/Z)-2,2-dimethyl-1-((triphenylsilyl)oxy)propylidene(triphenylsilyl)phosphane 10:

A dry and argon-flushed Schlenk flask was charged with sodium phosphide (1.0 g, 10 mmol, 1 equivalent), chlorotriphenylsilane (5.897 g, 20 mmol, 2 equivalents) and DME (40 mL). The mixture was sonicated at 75 °C for 18 hours, a magnetic stirrer was added and the suspension was subsequently cooled to -30 °C. Pivaloyl chloride (1.82 g, 10 mmol, 1 equivalent) was added dropwise while stirring and the suspension was warmed up overnight to room temperature. The solvent was removed *in vacuo*, toluene (100 mL) was added and the resulting suspension was filtered. The solid was extracted again with toluene (2x50 mL). The solvent was removed *in vacuo* from the combined filtrate and washings and the resulting solid was washed in hexane (2x20 mL). Drying *in vacuo* afforded 3.2 g (5.0 mmol, 50 % yield) of **10** as a sticky pale yellow solid.

Several impurities including hexaphenyldisiloxane are present in the product and could not be separated from it. Therefore, no elemental analysis is provided for this compound.

Due to the presence of two isomers and significant amounts of impurities and due to overlapping signals in the aromatic region, we only report <sup>1</sup>H-NMR signals in the aliphatic region.

Crystals suitable for X-Ray diffraction were obtained by slow evaporation of a concentrated solution of **10** in hexane.

<sup>31</sup>P{<sup>1</sup>H}-NMR (121.5 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): 109 (s), 98 (s)

<sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): 1.26 (s, isomer A), 1.15 (s, isomer B)

### **(E/Z)-(mesityl((triphenylsilyl)oxy)methylene)(triphenylsilyl)phosphane 11:**

A dry and argon-flushed Schlenk flask was charged with sodium phosphide (1.0 g, 10 mmol, 1 equivalent), chlorotriphenylsilane (5.897 g, 20 mmol, 2 equivalents) and DME (40 mL). The mixture was sonicated at 75 °C for 18 hours, a magnetic stirrer was added and the suspension was subsequently cooled to -30 °C. Mesityl chloride (1.82 g, 10 mmol, 1 equivalent) was added dropwise while stirring and the suspension was warmed up overnight to room temperature. The solvent was removed *in vacuo*, toluene (100 mL) was added and the resulting suspension was filtered. The solid was extracted again with toluene (2x50 mL). The solvent was removed *in vacuo* from the combined filtrate and washings and the resulting solid was washed in hexane (2x20 mL). Drying *in vacuo* afforded 4.5 g (6.4 mmol, 64 % yield) of **11** as a sticky pale yellow solid.

Several impurities including hexaphenyldisiloxane are present in the product and could not be separated from it. Therefore, no elemental analysis is provided for this compound. This material was pure enough for generation of **11**.

Due to the presence of two isomers and significant amounts of impurities and due to overlapping signals in the aromatic region, we only report <sup>1</sup>H-NMR signals in the aliphatic region.

Crystals suitable for X-Ray diffraction were obtained by slow evaporation of a concentrated solution of **11** in hexane.

<sup>31</sup>P{<sup>1</sup>H}-NMR (121.5 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): 131 (s), 105 (s)

<sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): isomer A 2.18 (s, 3H) and 1.82 (6H); isomer B 2.00 (s, 3H) and 1.84 (s, 6H)

### **Thermal decomposition of 10 and 11, attempt at generating the corresponding phosphalkynes by thermal elimination of hexaphenyldisiloxane.**

2-5 mg of **10** or **11** were charged into an aluminum crucible which was heated in a NETZSCH STA449F5 apparatus at a rate of 10 K/min (thermogravimetric curves on Figures S57 and S58). No traces of the corresponding phosphalkynes were detected in the QMS signal of the volatiles despite substantial loss of mass.

### **Generation of Mesitylphospacetylene 12**

A dry and argon-flushed 5mm NMR tube was charged with **11** (35 mg, 0.05 mmol), cesium fluoride (15 mg, 0.05 mmol, 1 equivalent) and THF (0.5 mL). The suspension was stirred at room temperature on a moving plate for five minutes and the sample was subsequently measured on a 300 MHz NMR, allowing for identification of **12** with a singlet at 1 ppm in <sup>31</sup>P{<sup>1</sup>H}-NMR and a doublet at 163.5 ppm (<sup>1</sup>J<sub>CP</sub> = 45 Hz) in <sup>13</sup>C{<sup>1</sup>H}-NMR. Attempts at isolating **12** from such a reaction mixture by distillation were unsuccessful, potentially due to the presence of cesium triphenylsilylanolate which can react with **12** under heating.

<sup>31</sup>P{<sup>1</sup>H}-NMR (121.5 MHz, THF, ppm): 1 (s)

<sup>13</sup>C{<sup>1</sup>H}-NMR (75.5 MHz, THF, ppm): 163.5 (d, <sup>1</sup>J<sub>C,P</sub> = 45 Hz)



### Preparation of sodium(18-crown-6) bis(cyano)phosphide Na(18-c-6)[6]

Warning: The reaction of Na<sub>3</sub>P with neat BrCN is highly exothermic and may generate a flame even under inert atmosphere. We highly recommend suspending BrCN in solution in DME before adding it to Na<sub>3</sub>P or suspending Na<sub>3</sub>P in DME before adding BrCN so as to avoid any violent reaction. Solid and liquid waste from the reactions was systematically quenched in diluted hydrogen peroxide to prevent formation of HCN from the waste.

A dry and argon-flushed Schlenk tube was charged with sodium phosphide (300 mg, 3.0 mmol, 1 equivalent) and chlorotriphenylsilane (177 mg, 0.6 mmol, 0.20 equivalent) dissolved in DME (6 mL). 1.0 M Cyanogen bromide solution in DME (6 mL, 6 mmol, 2 equivalents) was added. The resulting suspension was sonicated for 16h at 50 °C, after which it was filtered. The solid was washed with THF (6 mL). The combined filtrate and washings were concentrated *in vacuo* to about 4-5 mL. 18-crown-6 (793 mg, 3 mmol, 1 equivalent) dissolved in hexane (15 mL) was added, the resulting suspension was stirred for 1h and the supernatant was removed by filtration. The solid was washed with toluene (15 mL) and diethylether (20 mL) before drying in vacuo which afforded Na(18-crown-6)[6] as a beige powder (475 mg, 43% yield).

<sup>31</sup>P{<sup>1</sup>H}-NMR (121.5 MHz, THF-d<sub>8</sub>, ppm): -193 (s)

<sup>13</sup>C{<sup>1</sup>H}-NMR (125.8 MHz, THF-d<sub>8</sub>, ppm): 132.0 (d, <sup>1</sup>J<sub>P,C</sub> = 105 Hz), 70.6 (s, 18-c-6)

<sup>1</sup>H-NMR (300 MHz, THF-d<sub>8</sub>, ppm): 3.64 (s)

### Reaction of Na(18-c-6)(DME)<sub>0.5</sub>[4] with phenyl cyanate

A dry and argon-flushed Schlenk flask equipped with a magnetic stirrer was charged with Na(18-c-6)(DME)<sub>0.5</sub>[4] (441 mg, 0.5 mmol) and DME (3 mL). The suspension was cooled at 0 °C and phenyl cyanate (59.5 mg, 0.5 mmol, 1 equivalent) dissolved in DME (2 mL) was added dropwise over one minute. After warming up to room temperature over 30 minutes, <sup>31</sup>P{<sup>1</sup>H}-NMR of a 0.5 mL aliquot showed the formation of [6] (-193 ppm), alongside [7] (-280 ppm).

<sup>31</sup>P{<sup>1</sup>H}-NMR (121.5 MHz, DME, ppm): -193 (s) ([6]), -280 ([7])

### Preparation of cyano(triphenylsilyl)phosphanide sodium salt Na(18-c-6)[7]

A dry and argon-flushed Schlenk flask equipped with a magnetic stirrer was charged Na(18-c-6)(DME)<sub>0.5</sub>[4] (8.82 g, 10 mmol, 1 equivalent) and DFB (30 mL). The suspension was cooled down to 0 °C and trimethylsilyl isocyanate (1.21 g, 10.5 mmol, 1.05 equivalent) dissolved in DFB (10 mL) was added dropwise over 5 minutes. The resulting clear suspension was filtered via cannula. The filtrate was layered with n-hexane (100 mL) and stirred gently until then-hexane and the DFB had mixed (the mixing process took about two minutes), causing the precipitation of Na(18-crown-6)[7]. The supernatant was removed by decantation and the solid was washed with toluene (2 x 40 mL) and diethyl ether (40 mL). The solid was dried in vacuo affording Na(18-crown-6)[7] as an off-white powder (4.77 g, 79 % yield). The analytical properties were found to be identical to the material obtained in the previously published procedure<sup>[7]</sup>.

**Melting point:** 171 °C (DSC, decomp.)

<sup>31</sup>P{<sup>1</sup>H}-NMR (121.5 MHz, THF-d<sub>8</sub>, ppm): -283 (s, <sup>1</sup>J<sub>P,Si</sub> = 67.6 Hz)

<sup>29</sup>Si{<sup>1</sup>H}-NMR (99.4 MHz, THF-d<sub>8</sub>, ppm): 0 (d, <sup>1</sup>J<sub>P,Si</sub> = 67.6 Hz)

<sup>13</sup>C{<sup>1</sup>H}-NMR (125.8 MHz, THF-d<sub>8</sub>, ppm): 143.0 (d, <sup>2</sup>J<sub>P,C</sub> = 10.1 Hz, Ph ipso), 139.5 (d, <sup>1</sup>J<sub>P,C</sub> = 111.3 Hz, CN), 136.7 (d, <sup>3</sup>J<sub>P,C</sub> = 2.3 Hz, Ph ortho), 127.8 (s, Ph para), 127.2 (s, Ph meta), 70.4 (s, 18-c-6)

<sup>1</sup>H-NMR (300 MHz, THF-d<sub>8</sub>, ppm): 7.72-7.65 (m, 6H, Ph ortho), 7.17-7.12 (m, 9H, Ph para and meta), 3.48 (s, 24H, 18-c-6)

**IR** (ATR, 298 K,  $\text{cm}^{-1}$ ): 3058 (w br), 2870 (w br), 2061 (m, CN), 1563 (w), 1479 (w), 1459 (w), 1424 (w), 1369 (w), 1351 (w), 1297 (w), 1241 (w), 1184 (w), 1090 (s br), 1064 (w), 996 (m), 945 (m), 834 (w), 808 (w), 747 (m), 704 (s), 696 (s), 678 (s), 620 (m), 582 (w), 551 (s), 501 (s), 488 (s), 475 (s), 440 (w), 422 (m)

### Reaction of Na[4] with trimethylsilyl isocyanate and generation of 13 and [7]

A dry and argon-flushed Schlenk flask was charged with sodium phosphide (500 mg, 5 mmol, 1 equivalent), chlorotriphenylsilane (2.948 g, 10 mmol, 2 equivalents) and DME (20 mL). The mixture was sonicated at 75 °C for 18 hours, a magnetic stirrer and DFB (40 mL) were added and the suspension was brought back to room temperature. Under vigorous stirring, trimethylsilyl isocyanate (576 mg, 5 mmol, 1 equivalent) dissolved in DFB (5 mL) was added over 5 minutes. An aliquot from the reaction mixture was analyzed via  $^{31}\text{P}$ -NMR.

$^{31}\text{P}\{^1\text{H}\}$ -NMR (121.5 MHz, DME/DFB, ppm): -244 (s, unidentified hydrolysis product), -255 (s,  $\text{P}(\text{SiMe}_3)(\text{SiPh}_3)_2$  **13**), -264 (s, unidentified), -281 (s, **[7]**)

### Reaction of Na[2] and trimethylsilyl isocyanate and generation of 1

A dry and argon-flushed 5mm NMR tube was charged with Na[2] (10 mg, 0.05 mmol), trimethylsilyl isocyanate (5.5 mg, 0.05 mmol, 1 equivalent) and THF- $d_8$  (0.5 mL) and the tube was shaken vigorously. **1** was identified as the major product of the reaction via multinuclear NMR.

$^{31}\text{P}\{^1\text{H}\}$ -NMR (121.5 MHz, THF- $d_8$ , ppm): -252 (s)

$^{13}\text{C}\{^1\text{H}\}$ -NMR (125.8 MHz, THF- $d_8$ , ppm): 4.2 (d,  $^2J_{\text{P,C}} = 11.3$  Hz)

$^1\text{H}$ -NMR (500 MHz, THF- $d_8$ , ppm): 0.29 (d,  $^3J_{\text{P,H}} = 4.4$  Hz)

### Preparation of copper complex 14 (IPrCu[7])

A dry and argon-flushed Schlenk tube equipped with a magnetic stirrer was charged with IPrCuCl (488 mg, 1 mmol, 1 equivalent) and THF (5 mL). The resulting solution was stirred at 0 °C (ice bath) and Na(18-crown-6)[7] (604 mg, 1 mmol, 1 equivalent) dissolved in THF (10 mL) was added dropwise over 5 minutes. After 15 minutes, the solvent was removed *in vacuo* and toluene (15 mL) was added. The resulting suspension was filtered via cannula, the solid was washed with toluene (2 x 3 mL) and the combined filtrate and washings were reduced to 15 mL. *n*-hexane (45 mL) was added slowly while stirring gently causing the precipitation of complex **11** as a colorless microcrystalline powder. The supernatant was removed by decantation and the solid was washed with *n*-hexane (2 x 15 mL) before drying the solid *in vacuo* to afford **11** as a yellowish powder (584 mg, 0.76 mmol, 76 % yield). Crystals suitable for X-ray diffraction were obtained by layering of a concentrated toluene solution of **14** with *n*-hexane.

**Melting point** (DSC): 157 °C (decomp.)

$^{31}\text{P}\{^1\text{H}\}$ -NMR (202.5 MHz,  $\text{C}_6\text{D}_6$ , ppm): -242 (s)

$^{29}\text{Si}\{^1\text{H}\}$ -NMR (99.4 MHz,  $\text{C}_6\text{D}_6$ , ppm): -4 (d,  $^1J_{\text{P,Si}} = 31.4$  Hz)

$^{13}\text{C}\{^1\text{H}\}$ -NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ , ppm): 181.4 (dm,  $^2J_{\text{P,C}} = 34.2$  Hz, NCN), 145.7 (s, Dipp ortho) 137.9 (d,  $^2J_{\text{P,C}} = 10.8$  Hz,  $\text{SiPh}_3$  ipso), 136.2 (d,  $^3J_{\text{P,C}} = 1.8$  Hz,  $\text{SiPh}_3$  ortho), 134.5 (s, Dipp ipso), 131.0 (s, Dipp para), 129.0 (s,  $\text{SiPh}_3$  meta), 128.3 (s,  $\text{SiPh}_3$  para), 124.5 (s, Dipp meta), 123.7 (d,  $^1J_{\text{P,C}} = 86.5$  Hz, PCN), 122.8 (s, NCH), 29.0 (s,  $\text{C}(\text{H})(\text{CH}_3)_2$ ), 25.2 (s,  $\text{CH}_3$ ), 23.8 (s,  $\text{CH}_3$ )

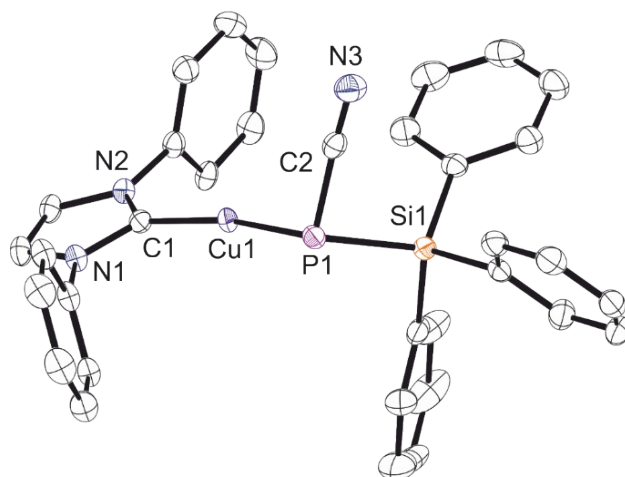
$^1\text{H}$ -NMR (500.1 MHz,  $\text{C}_6\text{D}_6$ , ppm): 7.74-7.68 (m, 6H,  $\text{SiPh}_3$  ortho), 7.29-7.25 (m, 2H, Dipp para), 7.17-7.13 (m, 3H,  $\text{SiPh}_3$  para), 7.09-7.04 (m, 10H,  $\text{SiPh}_3$  meta and Dipp meta), 6.21 (s, 2H, NCH), 2.46 (septet, 4H,  $^3J_{\text{H,H}} = 6.9$  Hz,  $\text{HC}(\text{CH}_3)_2$ ), 1.21 (d, 12H,  $^3J_{\text{H,H}} = 6.9$  Hz,  $\text{CH}_3$ ), 1.03 21 (d, 12H,  $^3J_{\text{H,H}} = 6.9$  Hz,  $\text{CH}_3$ )

IR (ATR, 298 K,  $\text{cm}^{-1}$ ): 3121 (w), 3069 (w), 2958 (m), 2921 (w), 2865 (w), 2116 (m, CN), 1592 (w), 1551 (w), 1465 (m br), 1408 (m), 1384 (m), 1362 (w), 1328 (w), 1286 (w), 1255 (w), 1216 (w), 1183 (w), 1157 (w), 1104 (m), 1059 (w), 1028 (w), 998 (w), 976 (w), 946 (w), 934 (w), 848 (w), 801 (m), 757 (m), 746 (m), 738 (m), 697 (s), 681 (m), 638 (w), 539 (w), 502 (m), 487 (s), 459 (m), 436 (m), 404 (m)

#### Elemental analysis for $\text{C}_{46}\text{H}_{51}\text{CuN}_3\text{PSi}$ (%):

Calc. C 71.89 H 6.69 N 5.47

Found C 71.78 H 6.29 N 5.65



**Figure S3:** Structure of **14** in the crystal (hydrogen atoms and  $i\text{Pr}$  groups mo omitted for clarity). Selected bond distances [Å] and angles [°]: Cu1-C1 1.910(2) Cu1-P1 2.1969(7) P1-C2 1.787(3) C2-N3 1.150(4) P1-Si1 2.2387(9) C1-Cu1-P1 167.07(7) Cu1-P1-C2 105.40(8) Cu1-P1-Si1 106.97(3) Si1-P1-C2 93.97(9)

## Preparation of silver complex **15** (IPrAg[7])

A dry and argon-flushed Schlenk tube equipped with a magnetic stirrer was charged with IPrAgCl (532 mg, 1 mmol, 1 equivalent) and THF (5 mL). The resulting solution was stirred at 0°C (ice bath) and Na(18-crown-6)[**7**] (604 mg, 1 mmol, 1 equivalent) dissolved in THF (10 mL) was added dropwise over 5 minutes. After 15 minutes, toluene (15 mL) was added and the solution was reduced to 10 mL under vacuum while the temperature was kept at 0°C. The resulting suspension was filtered via cannula, the solid was washed with toluene (2 x 3 mL) and the filtrate was kept at 0°C as well. The cooling was removed and *n*-hexane (45 mL) was added slowly while stirring gently causing the precipitation of complex **15** as a colorless microcrystalline powder. The supernatant was removed by decantation and the solid was washed with *n*-hexane (2 x 15 mL) before drying the solid *in vacuo* to afford **15** as a yellowish powder (597 mg, 0.73 mmol, 73 % yield). Crystals suitable for X-ray diffraction were obtained by layering of a concentrated toluene solution of **15** with *n*-hexane.

Note: due to the unstable character of complex **15**, no sample with satisfactory elemental analysis could be obtained by successive recrystallizations.

**Melting point** (DSC): 160°C (decomp.)

**<sup>109</sup>Ag-NMR** (23.3 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): 704 (d, <sup>1</sup>J<sub>P, <sup>109</sup>Ag</sub> = 219.2 Hz)

**<sup>31</sup>P{<sup>1</sup>H}-NMR** (202.5 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): -252 (d, <sup>1</sup>J<sub>P, <sup>109</sup>Ag</sub> = 219.2 Hz; <sup>1</sup>J<sub>P, <sup>107</sup>Ag</sub> = 197.2 Hz)

**<sup>29</sup>Si{<sup>1</sup>H}-NMR** (99.4 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): -3 (d, <sup>1</sup>J<sub>P, Si</sub> = 37.2 Hz)

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): 188.3 (m, NCN), 145.7 (s, Dipp ortho), 138.2 (d, <sup>2</sup>J<sub>P, C</sub> = 10.6 Hz, SiPh<sub>3</sub> ipso), 136.2 (d, <sup>3</sup>J<sub>P, C</sub> = 2.0 Hz, SiPh<sub>3</sub> ortho), 134.5 (s, Dipp ipso), 131.0 (s, Dipp para), 129.0 (s, SiPh<sub>3</sub> meta), 128.3 (s, SiPh<sub>3</sub> para), 125.1 (d, <sup>1</sup>J<sub>P, C</sub> = 93.8 Hz, PCN), 124.5 (s, Dipp meta), 123.1 (d, <sup>3</sup>J<sub>Ag, C</sub> = 5 Hz, NCH), 28.9 (s, C(H)(CH<sub>3</sub>)<sub>2</sub>), 25.0 (s, CH<sub>3</sub>), 23.8 (s, CH<sub>3</sub>)

**<sup>1</sup>H-NMR** (500.1 MHz, C<sub>6</sub>D<sub>6</sub>): 7.79-7.74 (m, 6H, SiPh<sub>3</sub> ortho), 7.26-7.22 (m, 2H, Dipp para), 7.17-7.13 (m, 3H, SiPh<sub>3</sub> para), 7.09-7.03 (m, 10H, SiPh<sub>3</sub> meta and Dipp meta), 6.26 (d, <sup>4</sup>J<sub>Ag, H</sub> = 1 Hz, 2H, NCH), 2.41 (septet, 4H, <sup>3</sup>J<sub>H, H</sub> = 6.8 Hz, HC(CH<sub>3</sub>)<sub>2</sub>), 1.16 (d, 12H, <sup>3</sup>J<sub>H, H</sub> = 6.8 Hz, CH<sub>3</sub>), 1.02 21 (d, 12H, <sup>3</sup>J<sub>H, H</sub> = 6.8 Hz, CH<sub>3</sub>)

**IR** (ATR, 298 K, cm<sup>-1</sup>): 3120 (w), 3068 (w), 2958 (m), 2922 (w), 2866 (w), 2164 (w), 2113 (m, CN), 1591 (w), 1552 (w), 1466 (w), 1427 (m br), 1410 (m), 1384 (m), 1362 (w), 1328 (w), 1289 (w), 1255 (w), 1216 (w), 1183 (w), 1157 (w), 1104 (m), 1059 (w), 1028 (w), 998 (w), 977 (w), 947 (w), 935 (w), 850 (w), 802 (m), 757 (m), 738 (m), 697 (m), 680 (s), 638 (m), 538 (w), 502 (s), 489 (s), 459 (s), 439 (m), 422 (m), 406 (m)

## Elemental analysis for C<sub>46</sub>H<sub>51</sub>AgN<sub>3</sub>PSi (%):

Calc. C 67.97 H 6.32 N 5.17

Found C 68.11 H 6.14 N 6.08

### Preparation of gold complex **16** (IPrAu[7])

In a glovebox, a vial equipped with a magnetic stirrer was charged with IPrAuCl (62.1 mg, 0.1 mmol, 1 equivalent) and THF (1 mL). The resulting solution was stirred vigorously and Na(18-crown-6)[7] (60.4 mg, 0.1 mmol, 1 equivalent) dissolved in THF (1 mL) was added dropwise over 1 minute. After 5 minutes, the solvent was removed *in vacuo* and toluene (2 mL) was added. The resulting suspension was filtered over celite and the solid was washed with toluene (2 x 0.2 mL). The combined filtrate and washings were layered with n-hexane (7 mL), which caused the formation of crystals of **16** suitable for X-Ray diffraction overnight. The supernatant was removed by decantation and the solid was washed with n-hexane (2 x 2 mL) before drying the solid *in vacuo* to afford **16** as a white powder (54 mg, 0.06 mmol, 60 % yield).

**Melting point** (DSC): 171°C (decomp.)

<sup>31</sup>P{<sup>1</sup>H}-NMR (202.5 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): -207 (s)

<sup>29</sup>Si{<sup>1</sup>H}-NMR (99.4 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): -2 (d, <sup>1</sup>J<sub>P,Si</sub> = 30.3 Hz)

<sup>13</sup>C{<sup>1</sup>H}-NMR (125.8 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): 195.8 (d, <sup>2</sup>J<sub>P,C</sub> = 58.6 Hz, NCN), 145.7 (s, Dipp ortho) 137.3 (d, <sup>2</sup>J<sub>P,C</sub> = 10.8 Hz, SiPh<sub>3</sub> ipso), 136.4 (d, <sup>3</sup>J<sub>P,C</sub> = 2.7 Hz, SiPh<sub>3</sub> ortho), 134.2 (s, Dipp ipso), 131.1 (s, Dipp para), 129.1 (s, SiPh<sub>3</sub> meta), 128.3 (s, SiPh<sub>3</sub> para), 124.4 (d, <sup>1</sup>J<sub>P,C</sub> = 85.6 Hz, PCN), 124.4 (s, Dipp meta), 123.1 (s, NCH), 29.0 (s, C(H)(CH<sub>3</sub>)<sub>2</sub>), 24.8 (s, CH<sub>3</sub>), 23.9 (s, CH<sub>3</sub>)

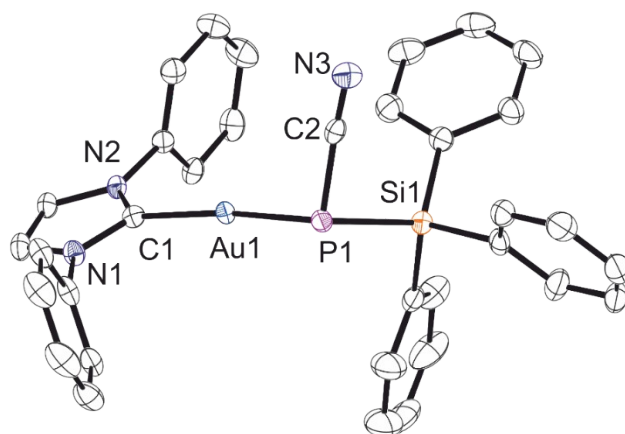
<sup>1</sup>H-NMR (500.1 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): 7.77-7.73 (m, 6H, SiPh<sub>3</sub> ortho), 7.27-7.23 (m, 2H, Dipp para), 7.19-7.14 (m, 3H, SiPh<sub>3</sub> para), 7.10-7.04 (m, 10H, SiPh<sub>3</sub> meta and Dipp meta), 6.21 (s, 2H, NCH), 2.46 (septet, 4H, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz, HC(CH<sub>3</sub>)<sub>2</sub>), 1.16 (d, 12H, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz, CH<sub>3</sub>), 1.02 21 (d, 12H, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz, CH<sub>3</sub>)

**IR** (ATR, 298 K, cm<sup>-1</sup>): 3069 (w), 3050 (w), 3022 (m), 2959 (w), 2868 (w), 2120 (m, CN), 1589 (w), 1559 (w), 1459 (m br), 1428 (m), 1409 (m), 1383 (w), 1364 (w), 1327 (w), 1302 (w), 1258 (w), 1208 (w), 1186 (w), 1109 (m br), 1061 (w), 1029 (w), 997 (w), 972 (w), 936 (w), 851 (w), 806 (m), 761 (m), 761 (s), 737 (s), 696 (s), 678 (m), 640 (m), 621 (w), 536 (s), 493 (s), 447 (m), 425 (m)

### Elemental analysis for C<sub>46</sub>H<sub>51</sub>AuN<sub>3</sub>PSi (%):

Calc. C 61.26 H 5.70 N 4.66

Found C 61.26 H 5.57 N 4.82



**Figure S4:** Structure of **16** in the crystal (hydrogen atoms and *iPr* groups omitted for clarity). Selected bond distances [Å] and angles [°]: Au1-C1 2.040(4) P1-Au1 2.3063(11) P1-C2 1.783(4) C2-N3 1.153(5) P1-Si1 2.2505(15) P1-Au1-C1 171.62(12) Au1-P1-C2 104.52(14) Au1-P1-Si1: 106.84(5) Si1-P1-C2 94.39(14)

**Table S1:** Comparison of structural and spectroscopic features in complexes **14-16**

Compound	<b>14</b>	<b>16</b>	<b>15</b>	Na(18-c-6)[ <b>3</b> ]
<b>C≡N distance (Å)</b>	1.150(4)	1.150(4)	1.153(5)	1.1607(15)
<b>P-C distance (Å)</b>	1.787(3)	1.778(3)	1.783(4)	1.7619(12)
<b>P-Si distance (Å)</b>	2.238(1)	2.239(1)	2.250(2)	2.2059(4)
<b>C≡N IR frequency (cm<sup>-1</sup>)</b>	2116(4)	2113(4)	2120(4)	2061(4)
<b><sup>1</sup>J<sub>P,Si</sub></b>	30	37	31	67

### 3. Spectra

#### NMR

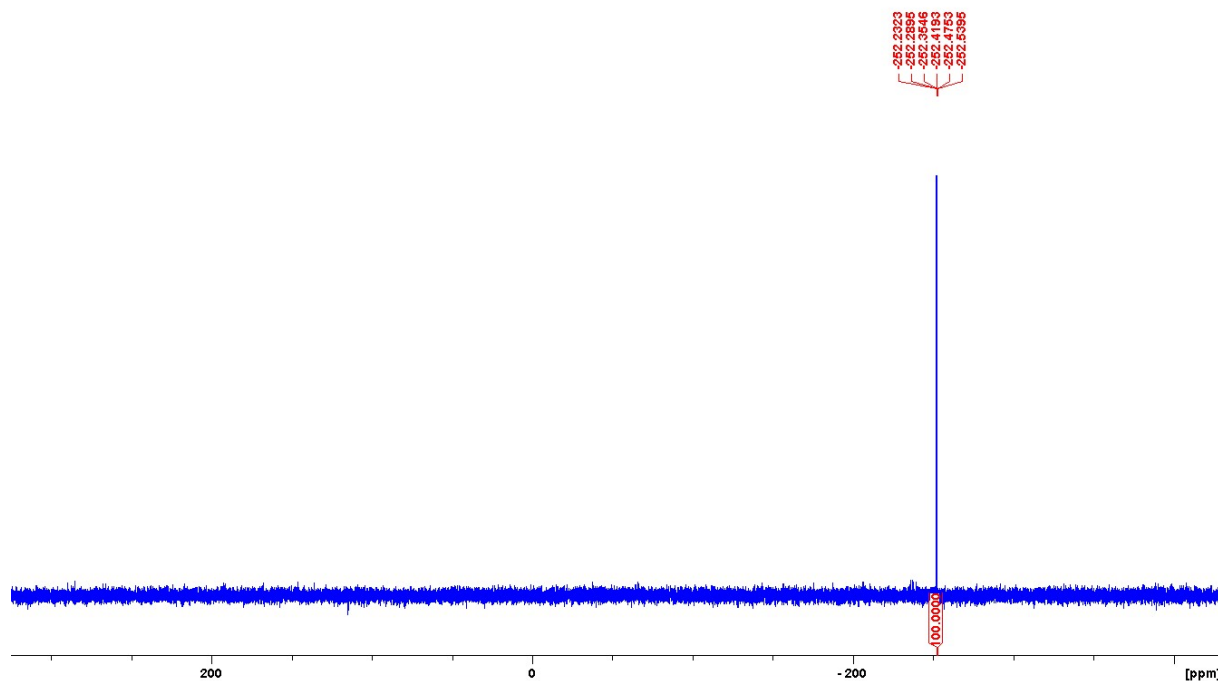


Figure S5:  $^{31}\text{P}$ -NMR Spectrum of **1**

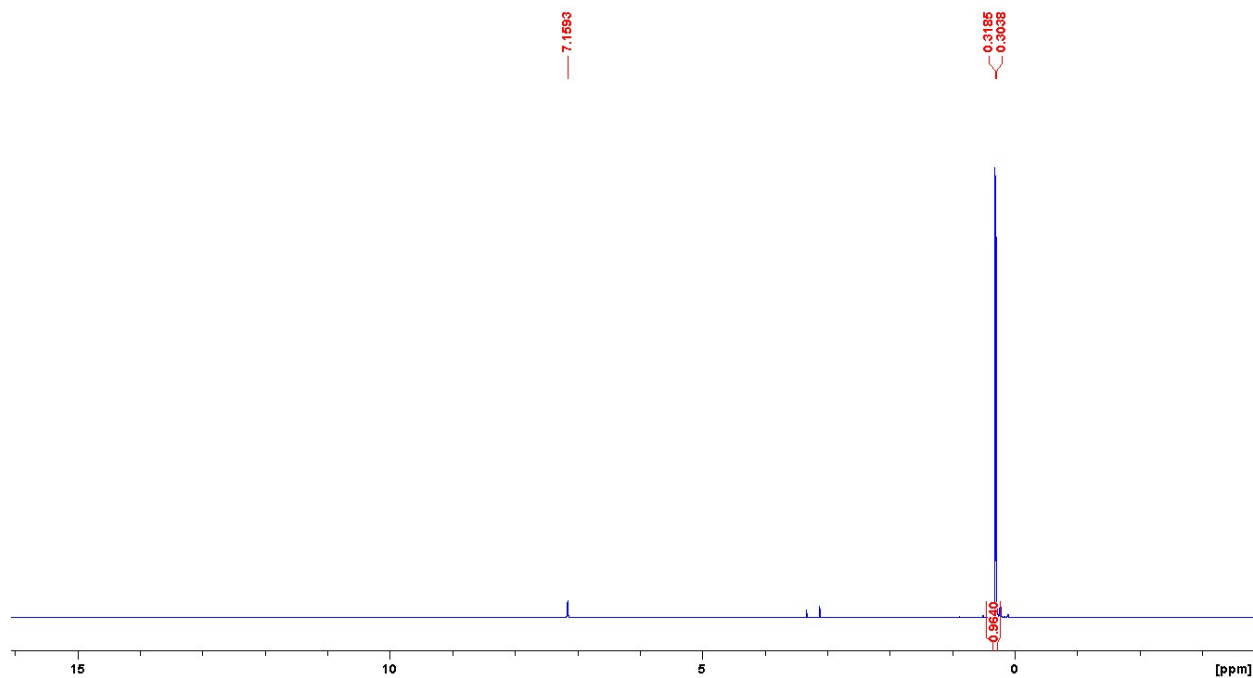
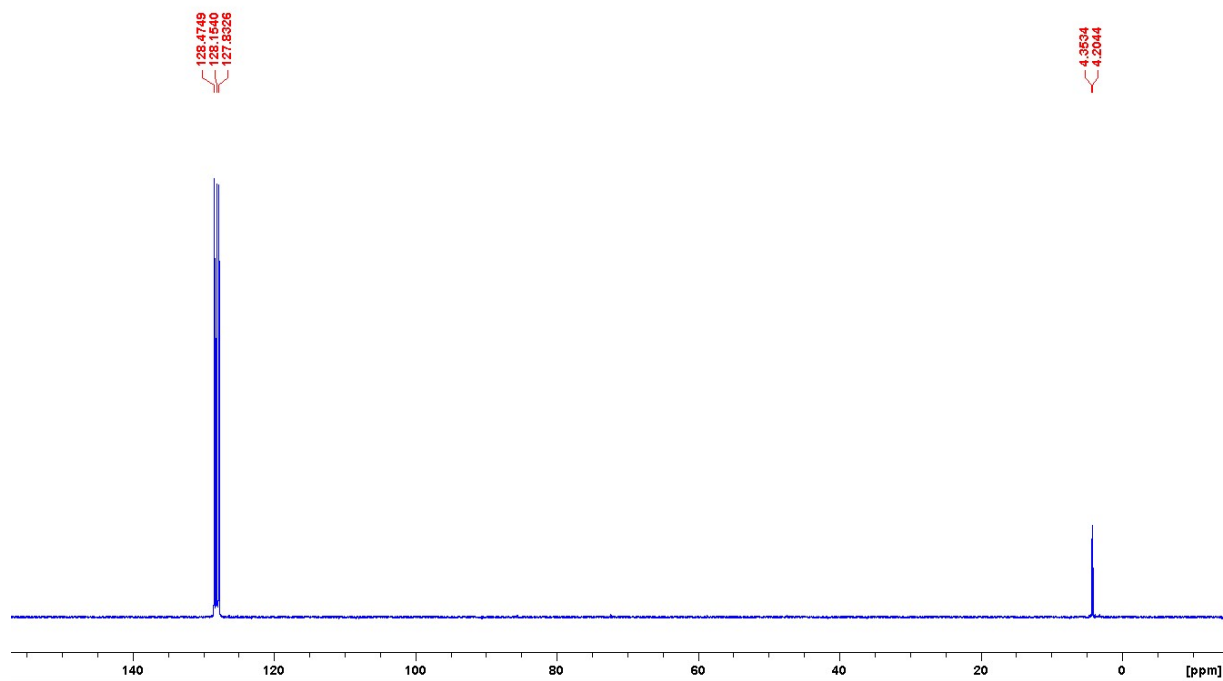
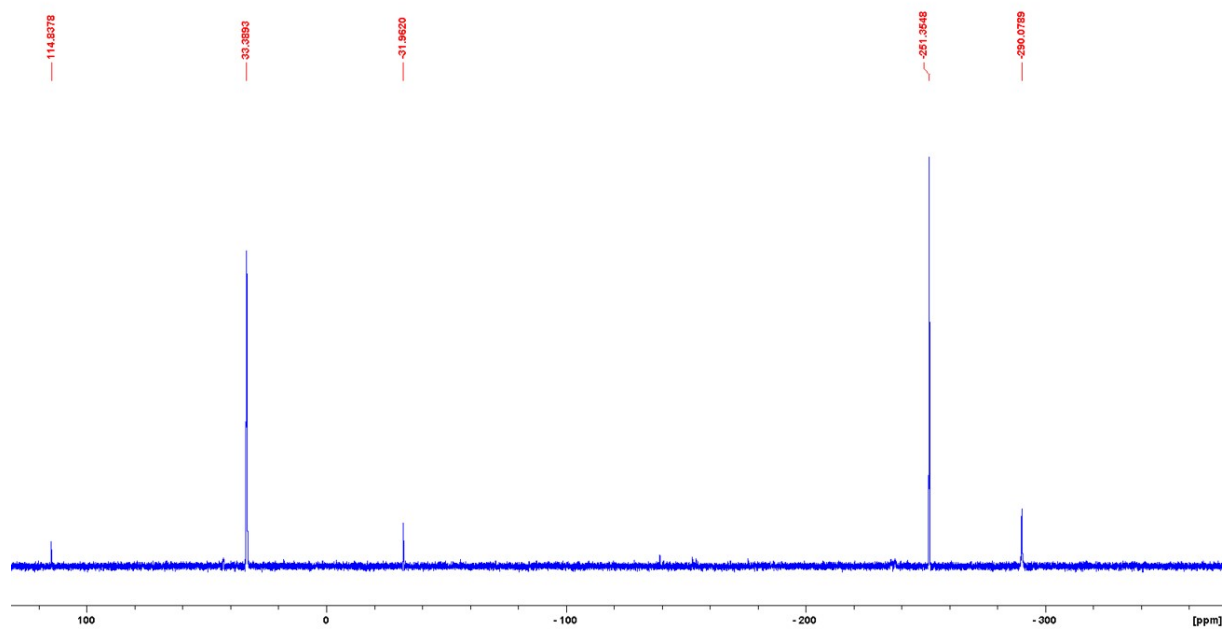


Figure S6:  $^1\text{H}$ -NMR spectrum of **1**



**Figure S7:**  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **1**



**Figure S8:**  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **1** and **2** generated by sonication of sodium phosphide in DME in presence of trimethylsilyl chloride and tetrabutylphosphonium bromide.



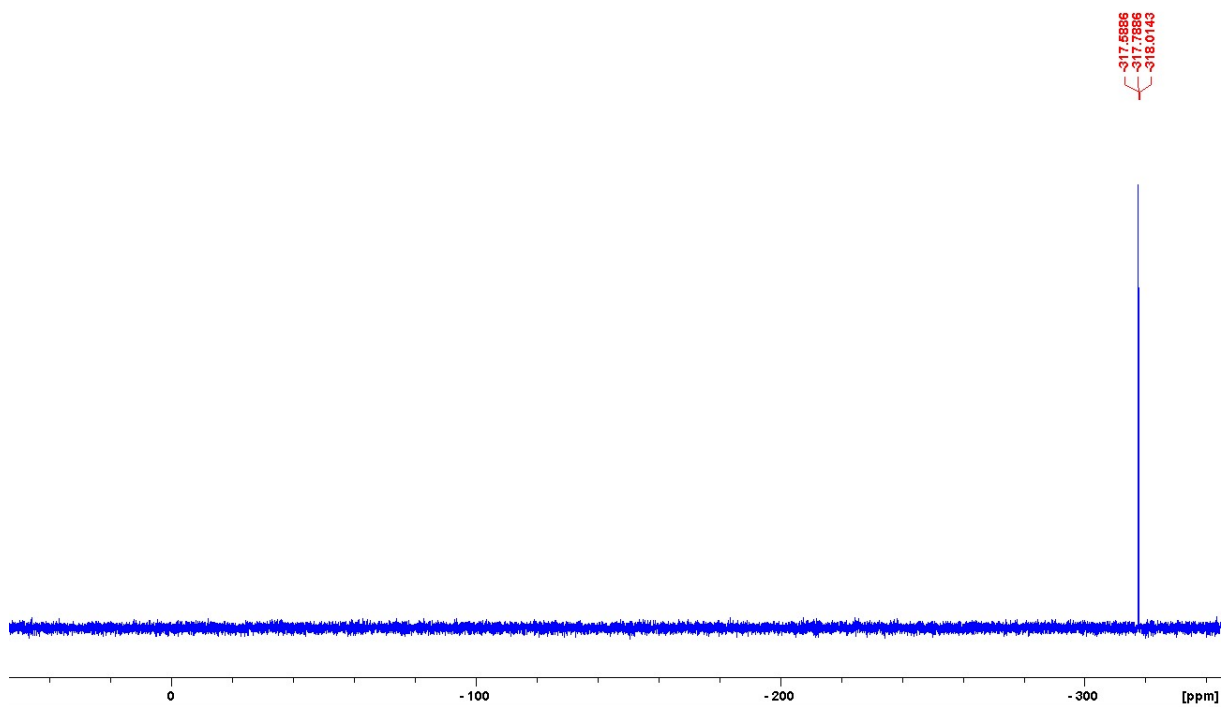


Figure S9:  $^{31}\text{P}$ -NMR Spectrum of  $\text{Na}(18\text{-c-}6)(\text{DME})_{0.5}[\mathbf{4}]$

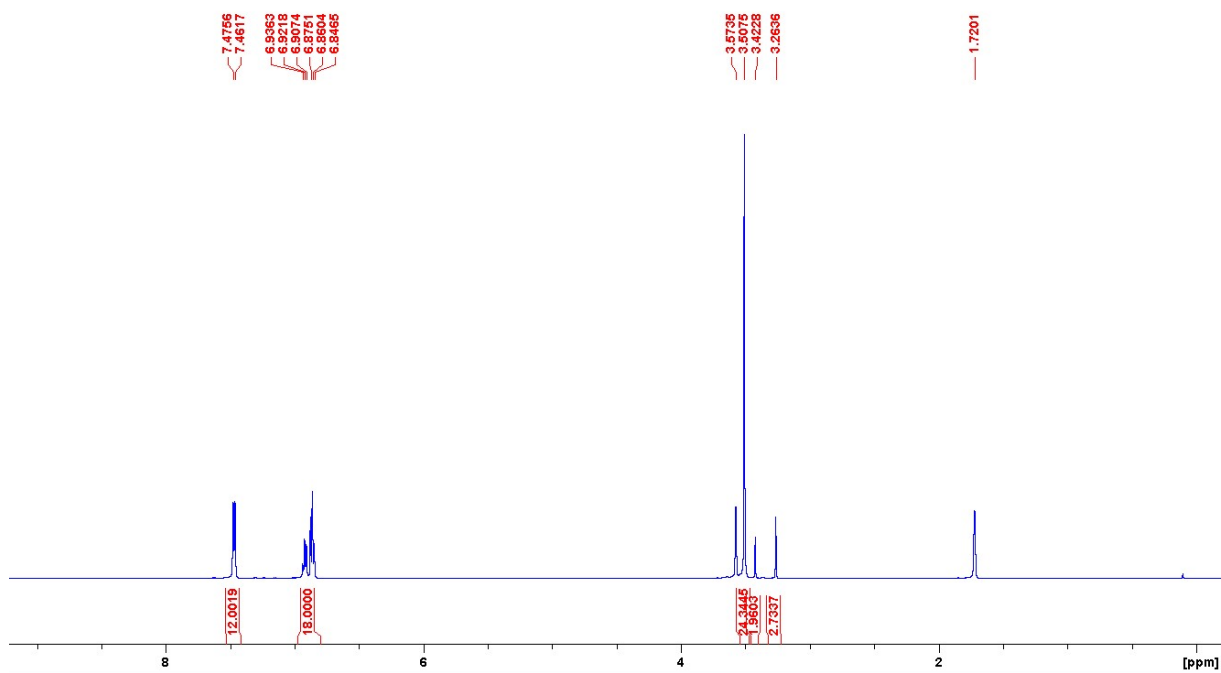
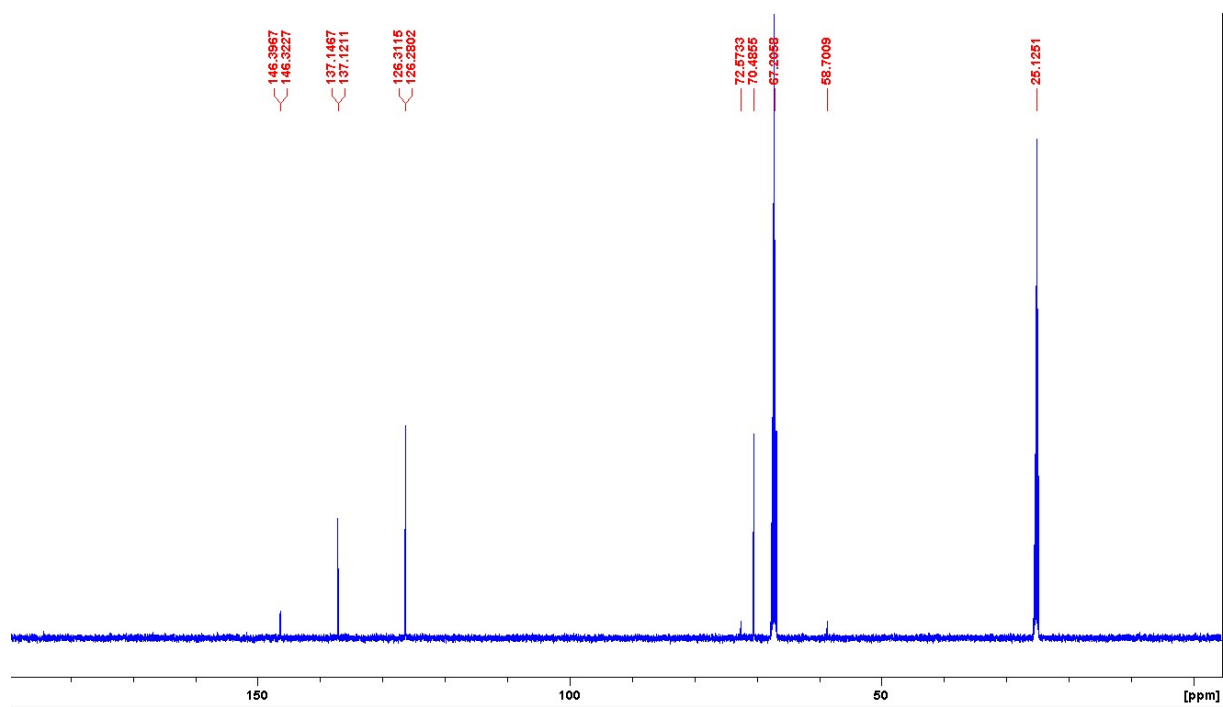
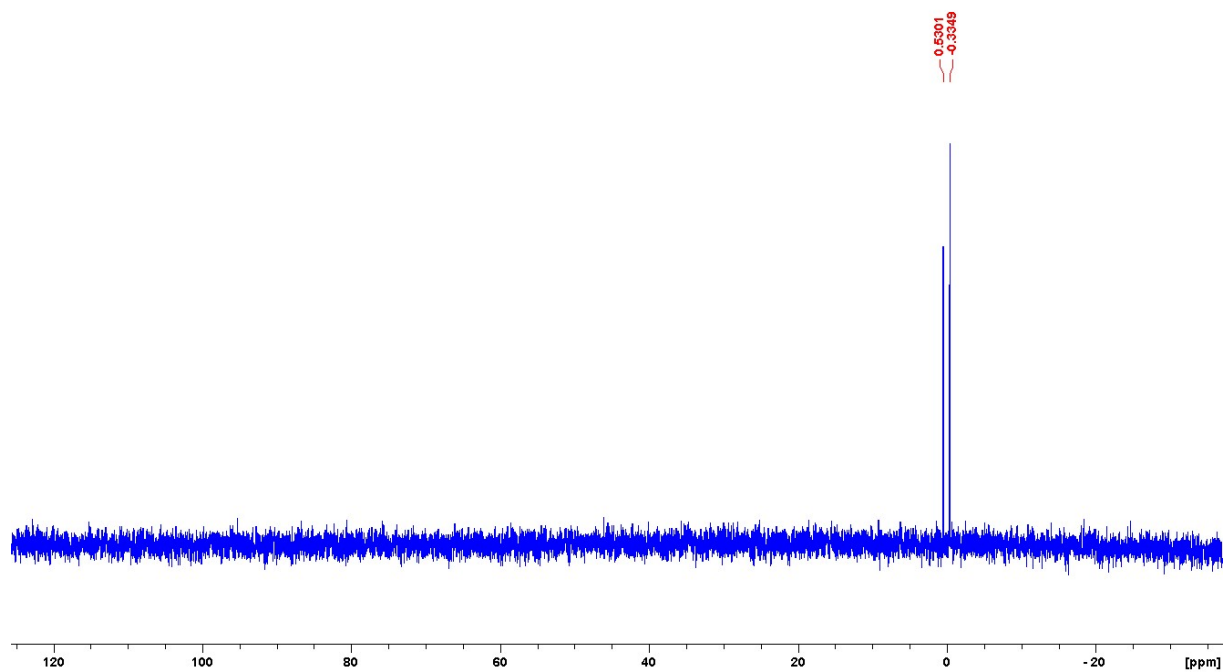


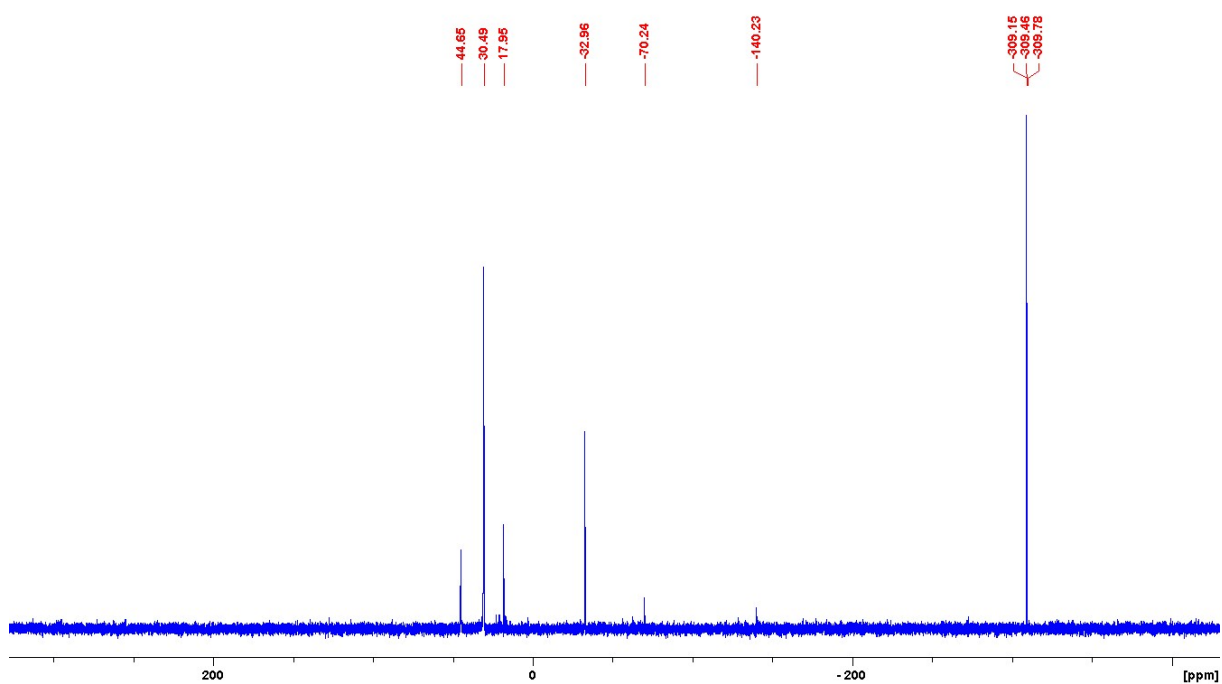
Figure S10:  $^1\text{H}$ -NMR spectrum of  $\text{Na}(18\text{-c-}6)(\text{DME})_{0.5}[\mathbf{4}]$



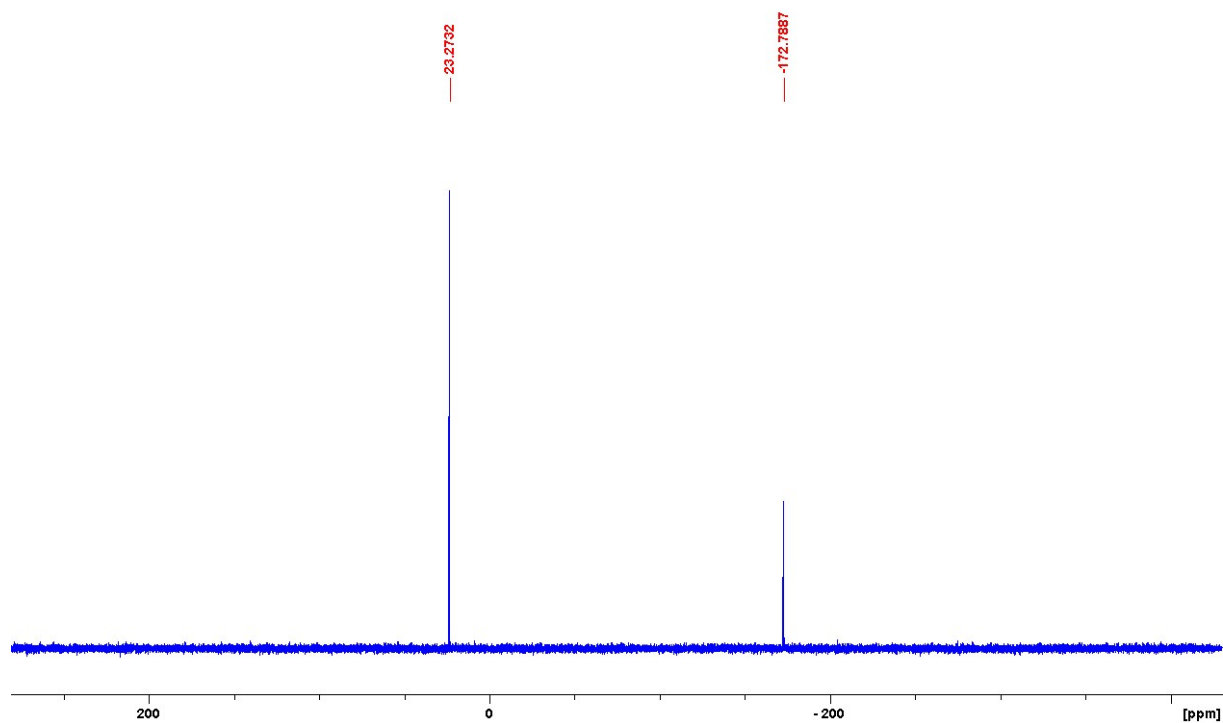
**Figure S11:**  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of  $\text{Na}(18\text{-c-}6)(\text{DME})_{0.5}$  [4]



**Figure S12:**  $^{29}\text{Si}\{^1\text{H}\}$ -NMR spectrum of  $\text{Na}(18\text{-c-}6)(\text{DME})_{0.5}$  [4]



**Figure S13:**  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of  $\text{Bu}_4\text{P}[\mathbf{4}]$  generated in DEE



**Figure S14:**  $^{31}\text{P}\{^1\text{H}\}$ -NMR Spectrum of  $\text{Ph}_4\text{P}[\mathbf{5}]$

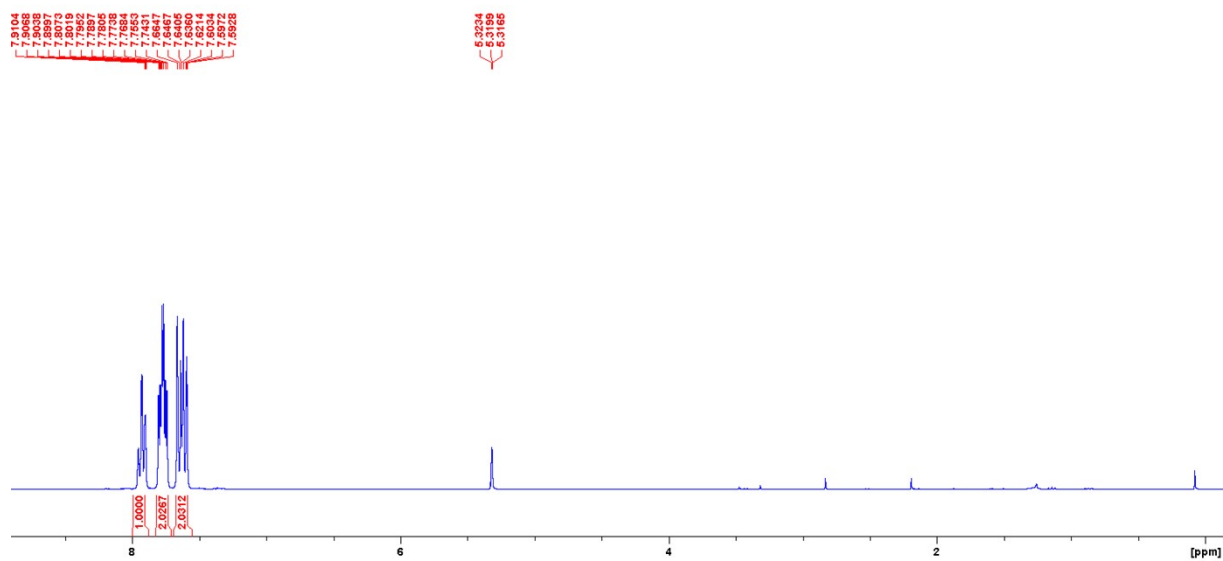


Figure S15:  $^1\text{H}$ -NMR spectrum of  $\text{Ph}_4\text{P}[5]$

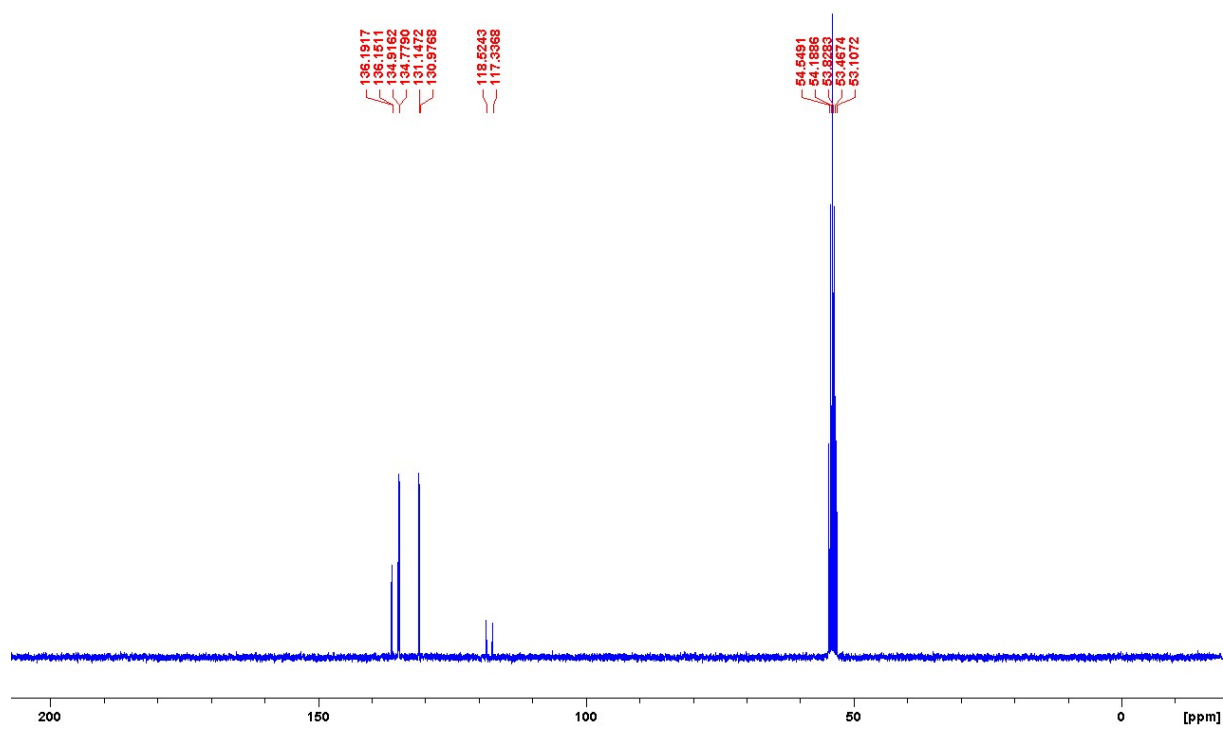


Figure S16:  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of  $\text{Ph}_4\text{P}[5]$

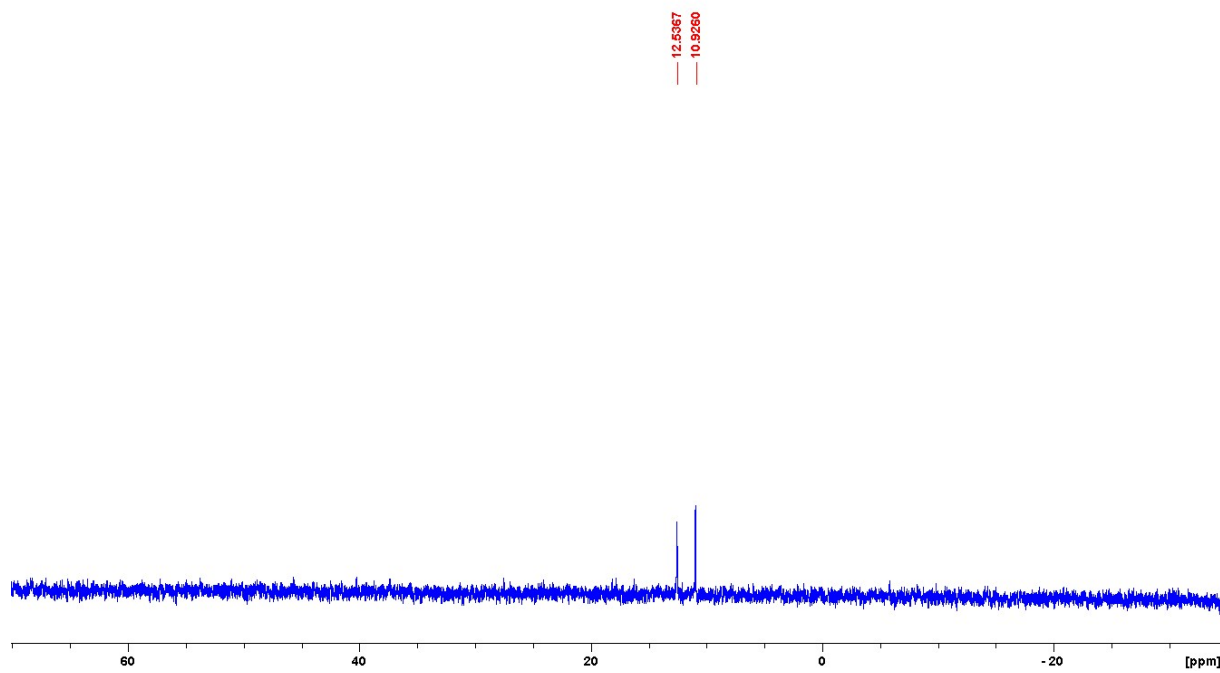


Figure S17:  $^{29}\text{Si}\{^1\text{H}\}$ -NMR spectrum of  $\text{Ph}_4\text{P}[5]$

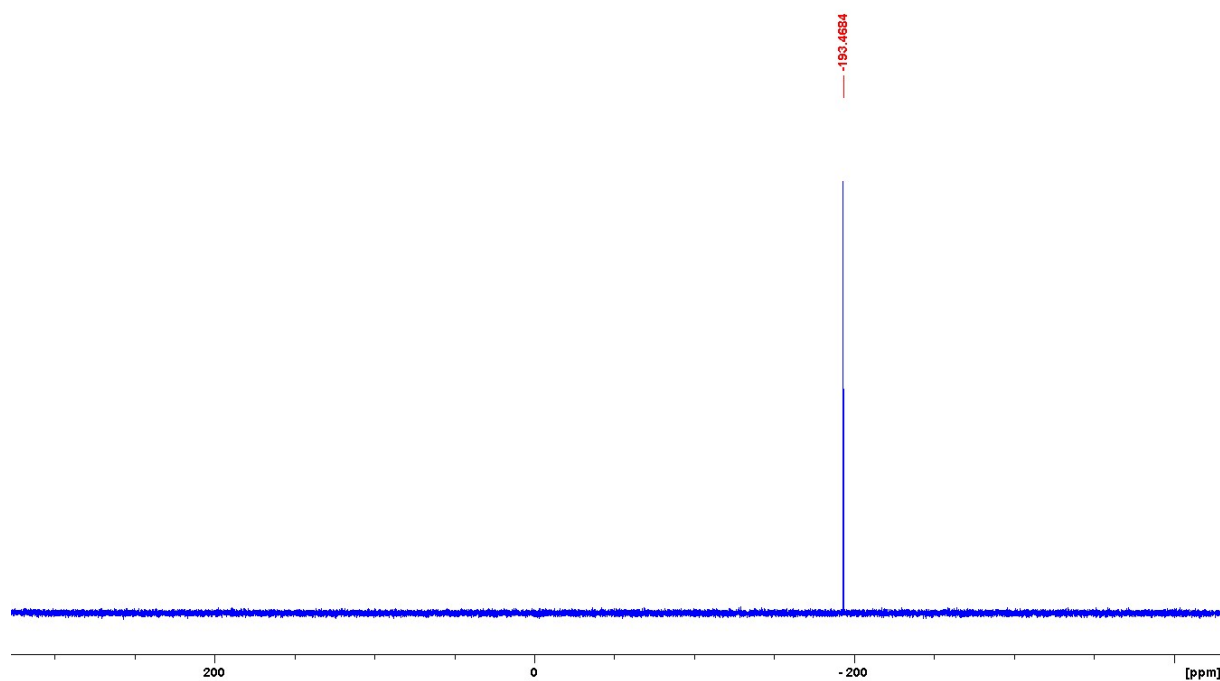


Figure S18:  $^{31}\text{P}\{^1\text{H}\}$ -NMR Spectrum of  $\text{Na}(18\text{-crown-6})[6]$

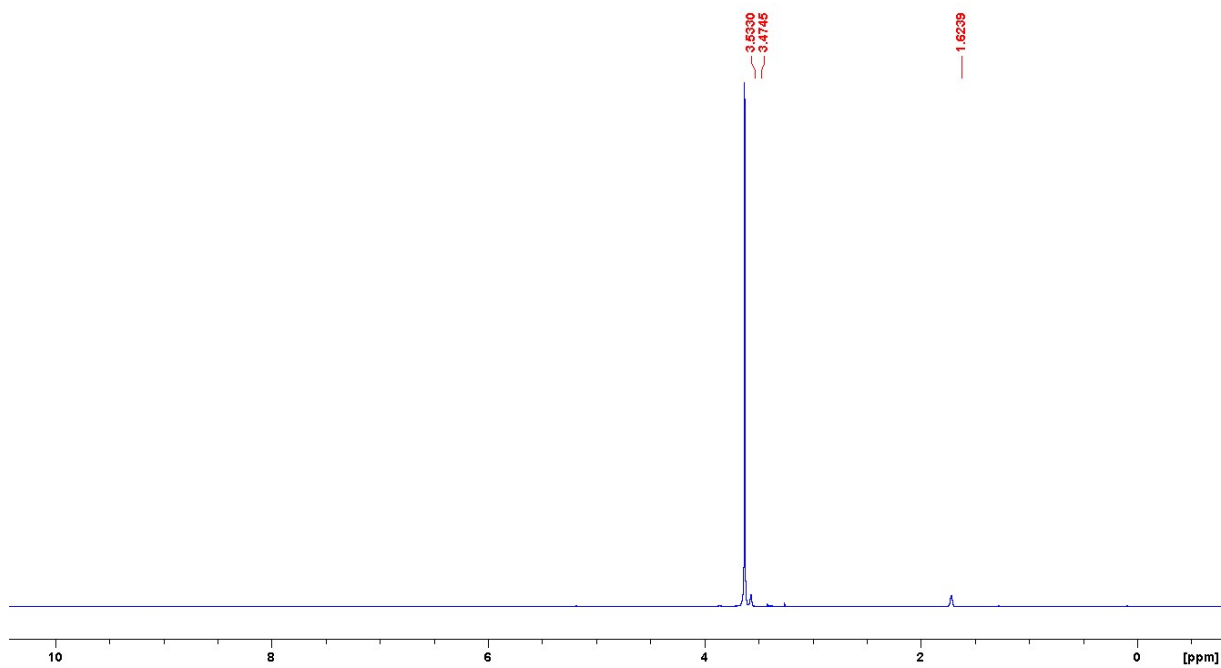


Figure S19:  $^1\text{H}$ -NMR Spectrum of  $\text{Na}(18\text{-crown-6})[\text{6}]$

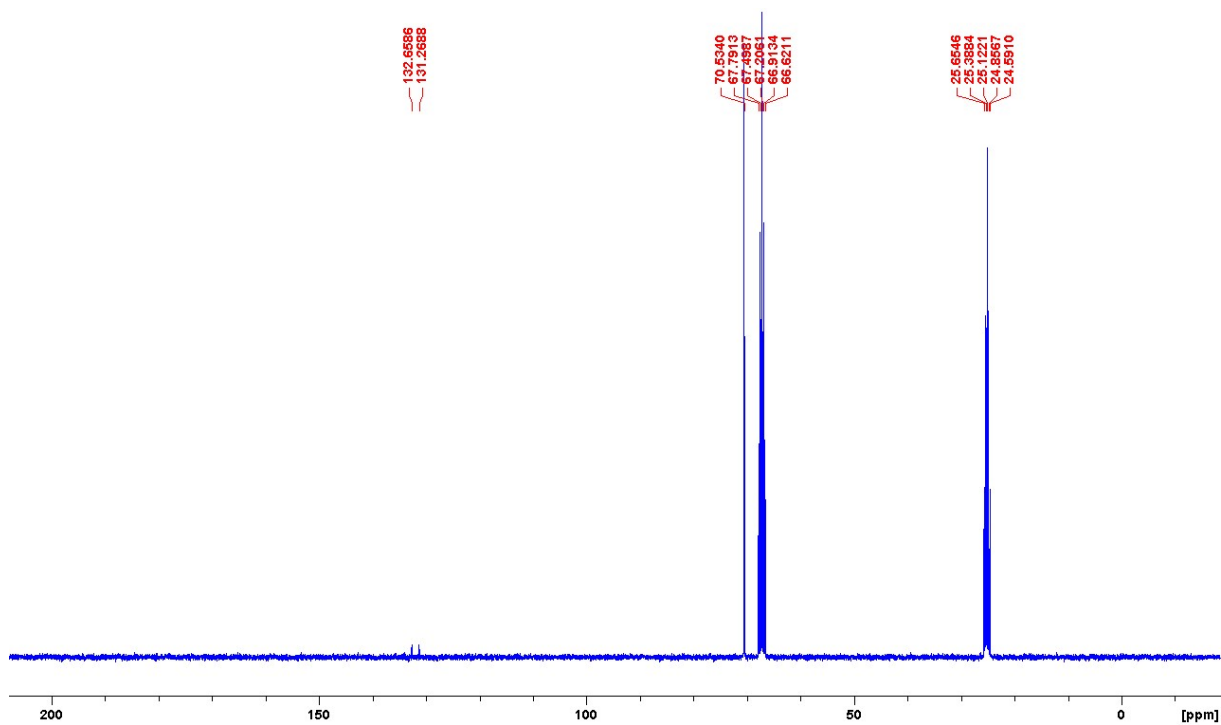
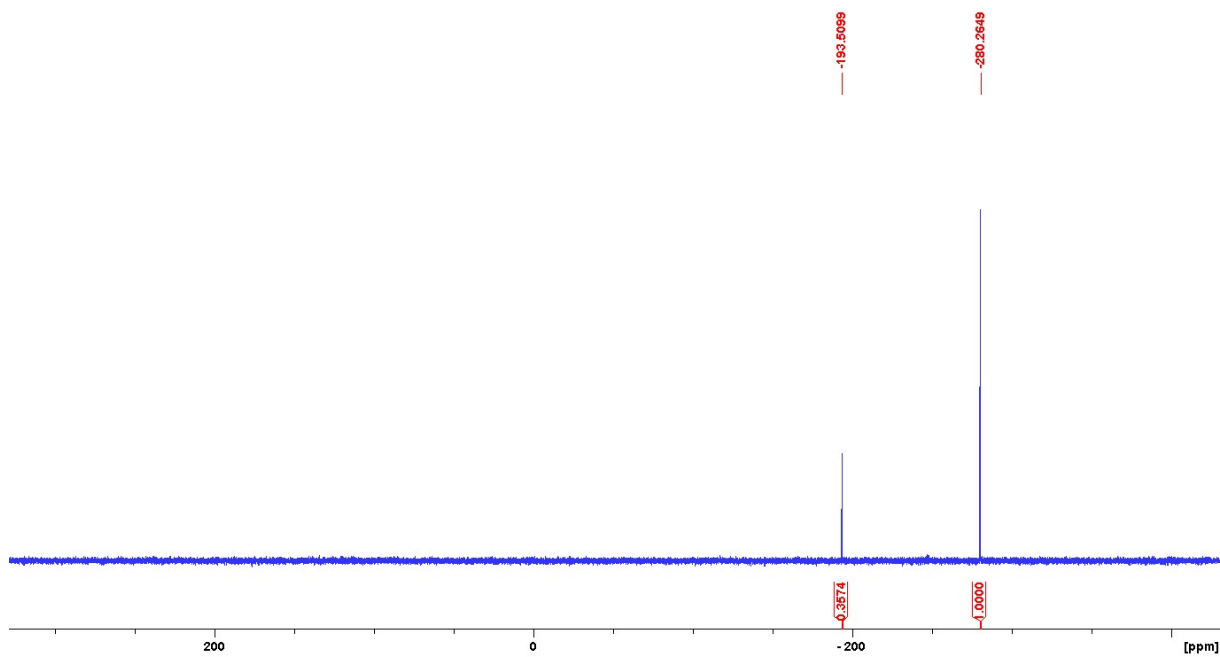
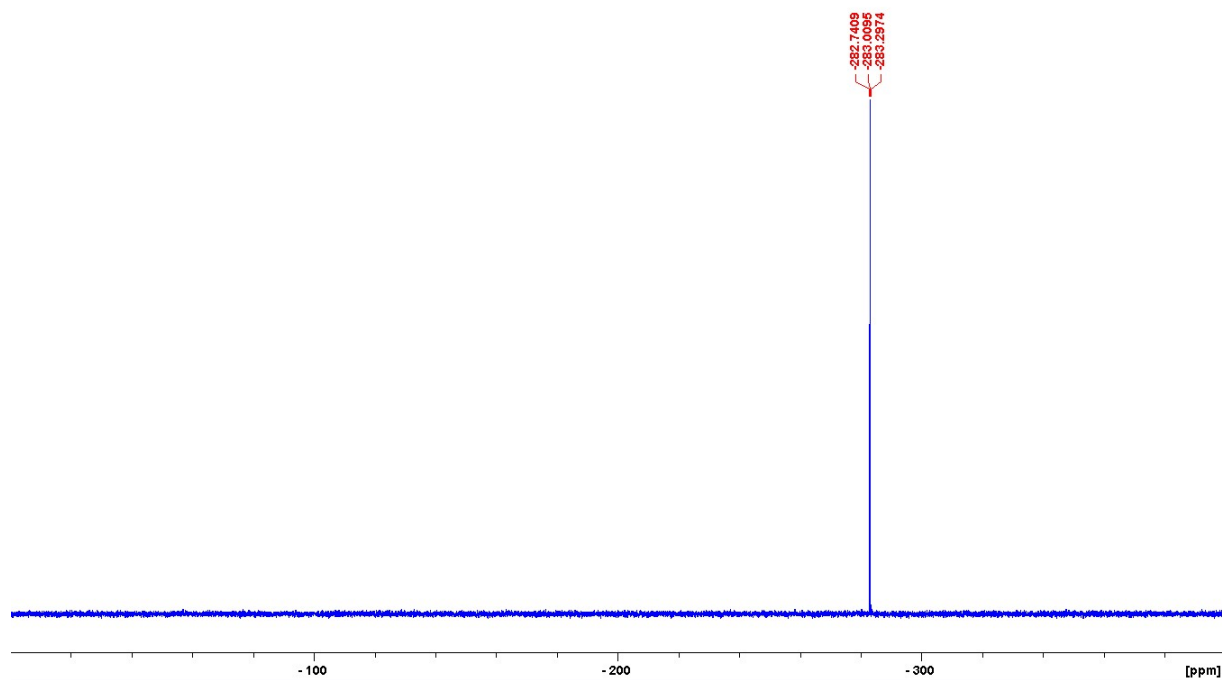


Figure S20:  $^{13}\text{C}\{^1\text{H}\}$ -NMR Spectrum of  $\text{Na}(18\text{-crown-6})[\text{6}]$



**Figure S21:**  $^{31}\text{P}\{^1\text{H}\}$ -NMR Signal of [6] and [7] in the reaction mixture of Na(18-crown-6)[4] with phenyl cyanate



**Figure S22:**  $^{31}\text{P}\{^1\text{H}\}$ -NMR Spectrum of Na(18-c-6)[7] in  $\text{THF-d}_8$

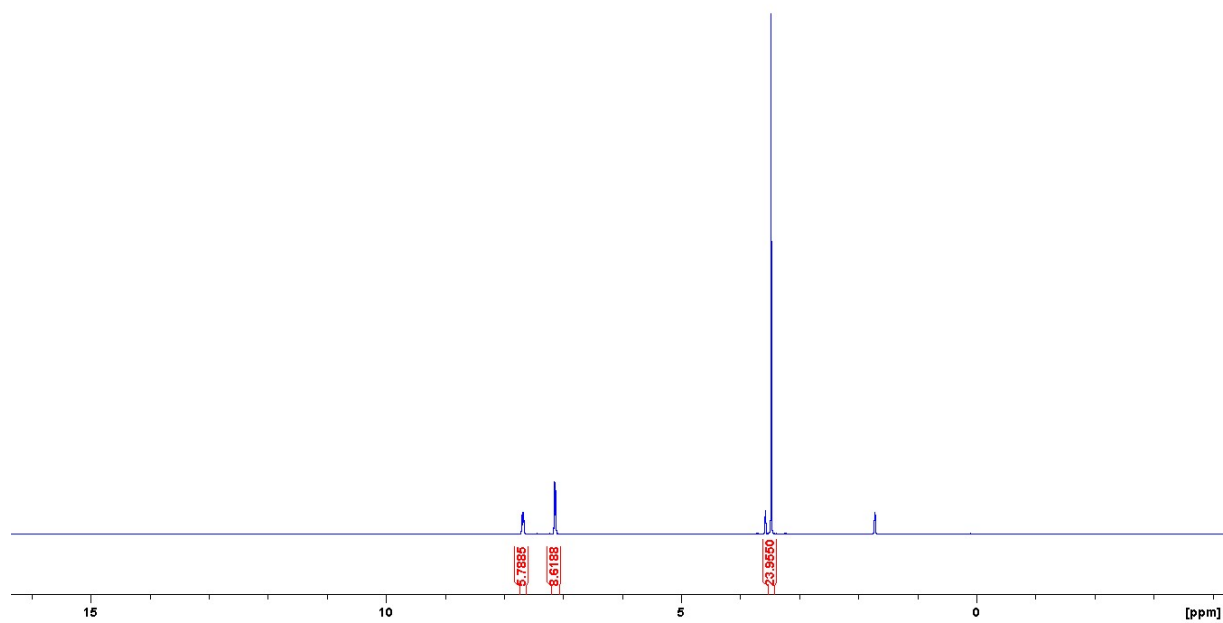


Figure S23:  $^1\text{H}$ -NMR Spectrum of Na(18-c-6)[7] in THF- $\text{d}_8$

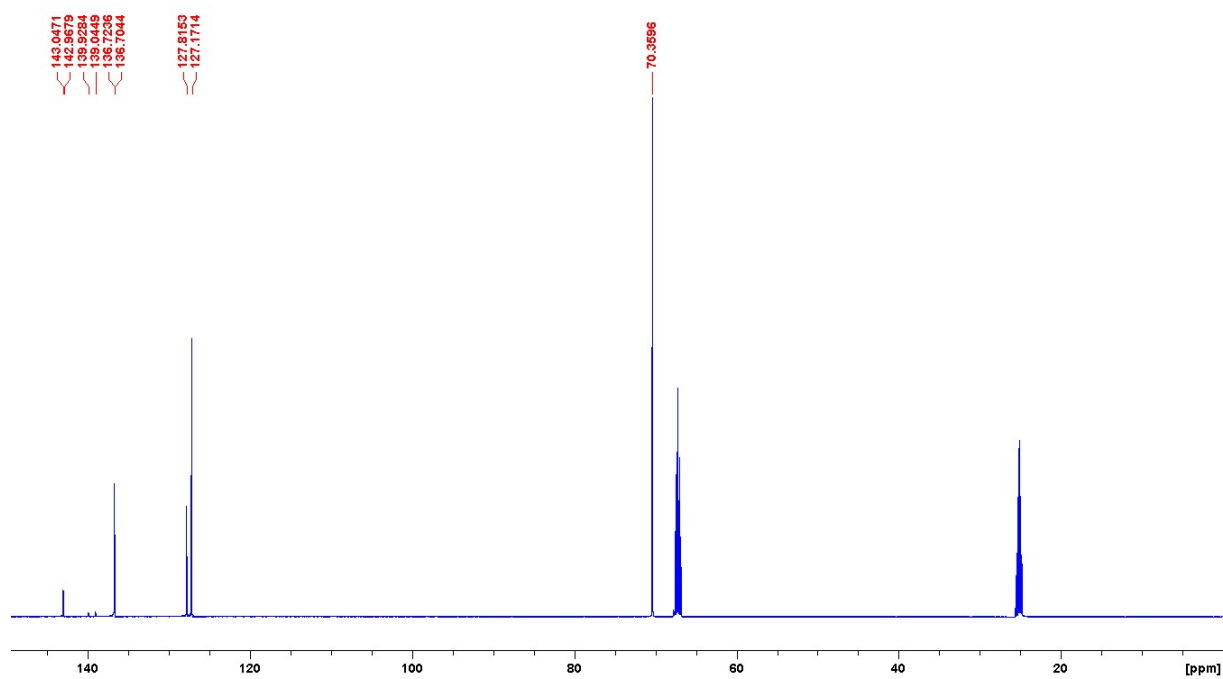


Figure S24:  $^{13}\text{C}\{^1\text{H}\}$ -NMR Spectrum of Na(18-c-6)[7] in THF- $\text{d}_8$



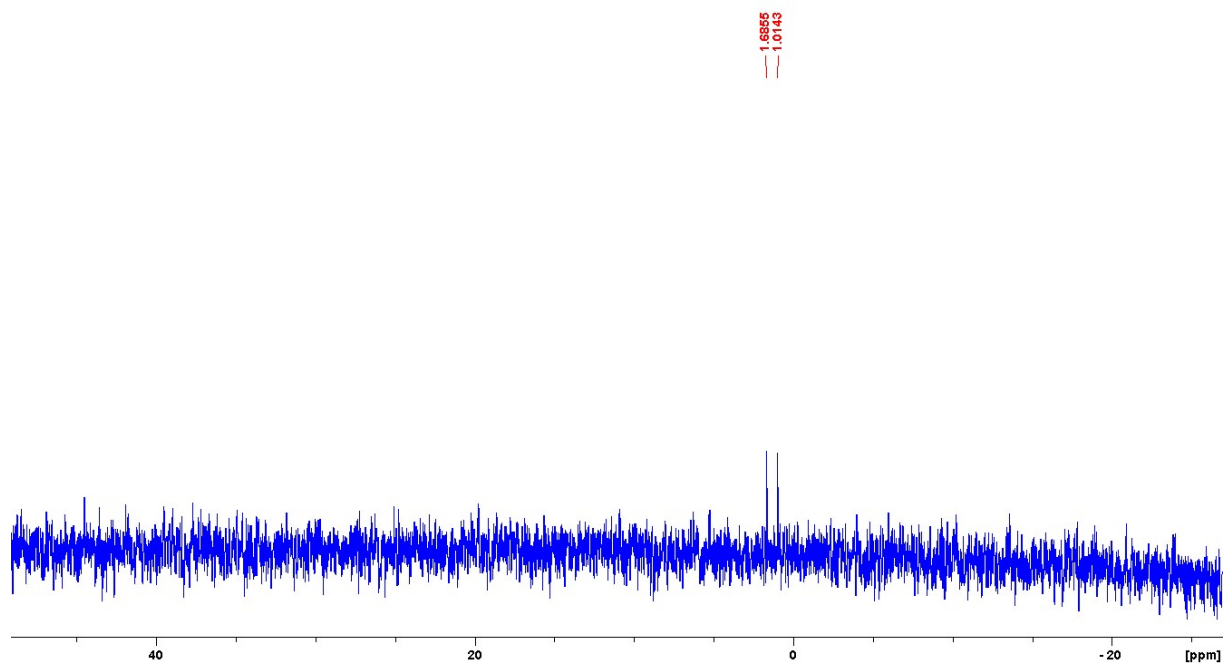


Figure S25:  $^{29}\text{Si}\{^1\text{H}\}$ -NMR Spectrum of  $\text{Na}(18\text{-c-}6)[7]$  in  $\text{THF-d}_8$

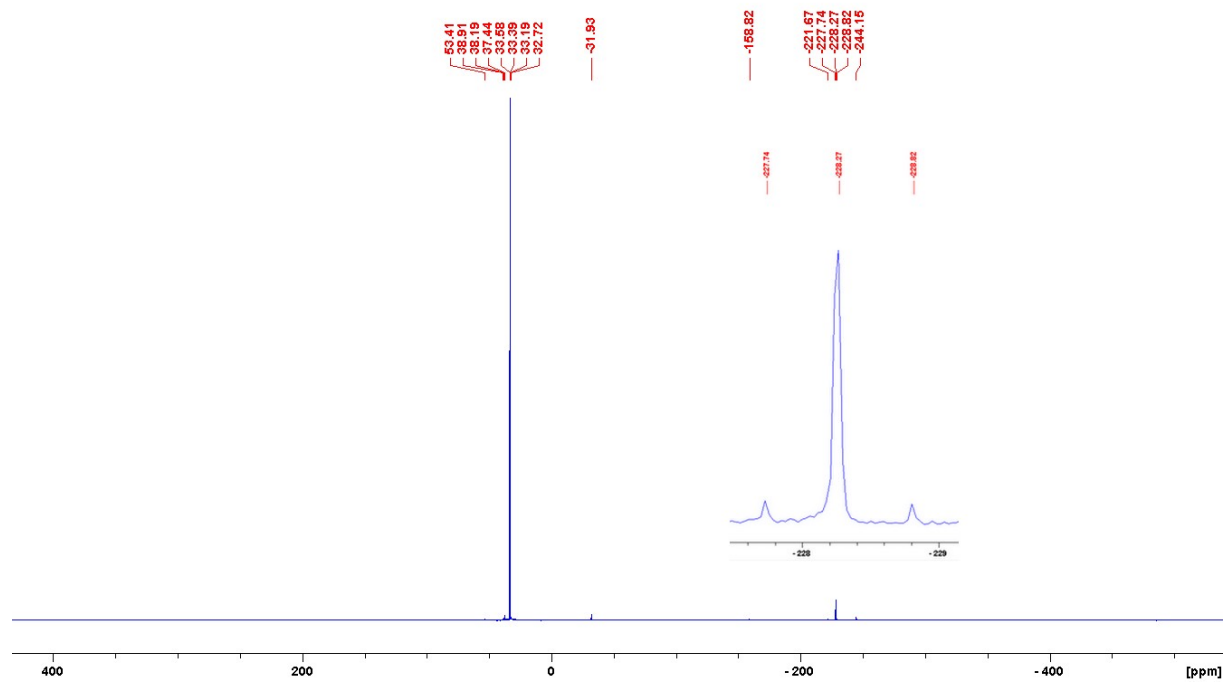


Figure S26:  $^{31}\text{P}\{^1\text{H}\}$ -NMR signal of **[8]** in the reaction mixture

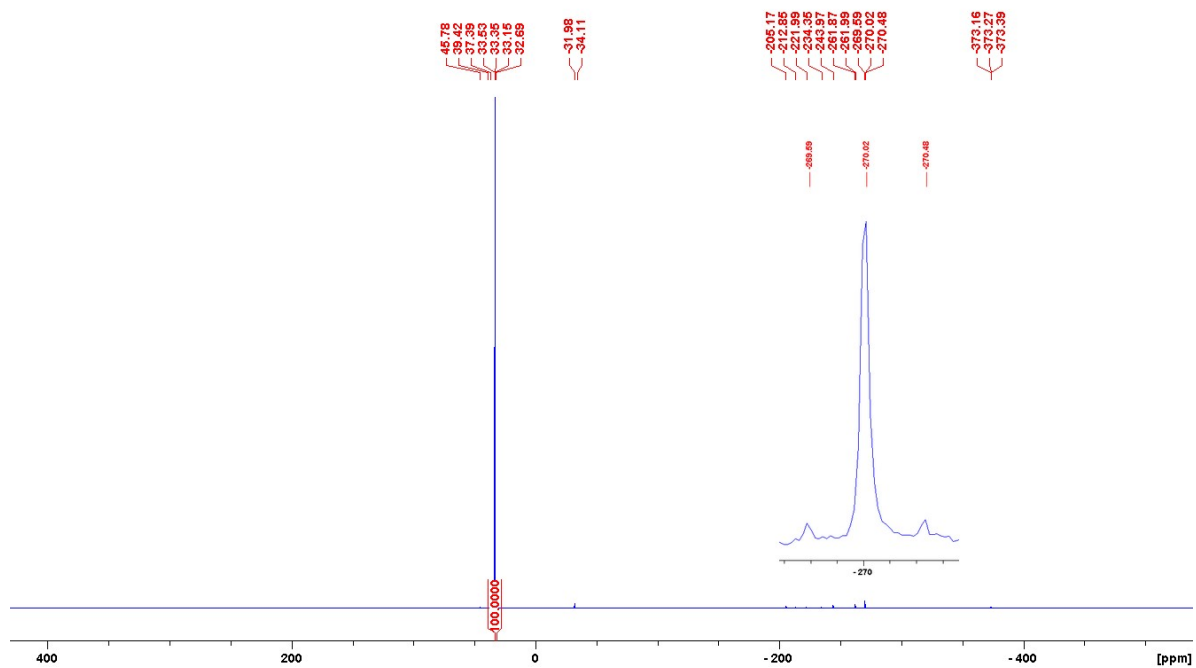


Figure S27:  $^{31}\text{P}\{^1\text{H}\}$ -NMR signal of **[9]** in the reaction mixture

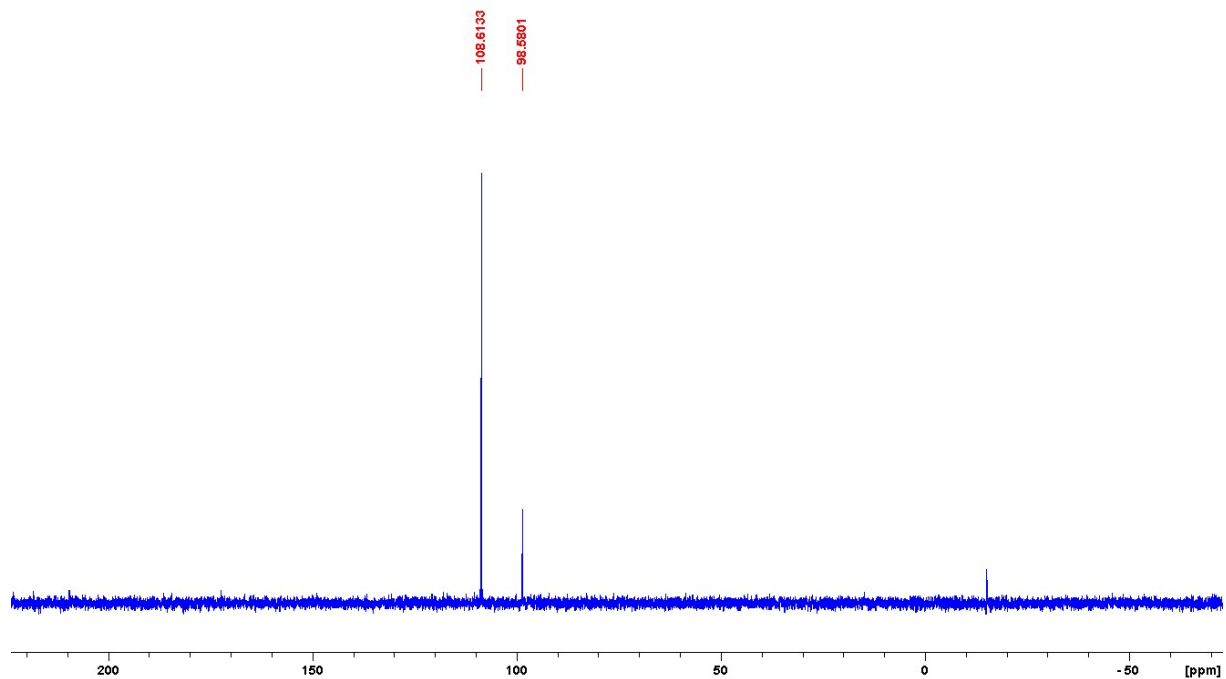


Figure S28:  $^{31}\text{P}\{^1\text{H}\}$ -NMR Spectrum of **10** E-Z mixture

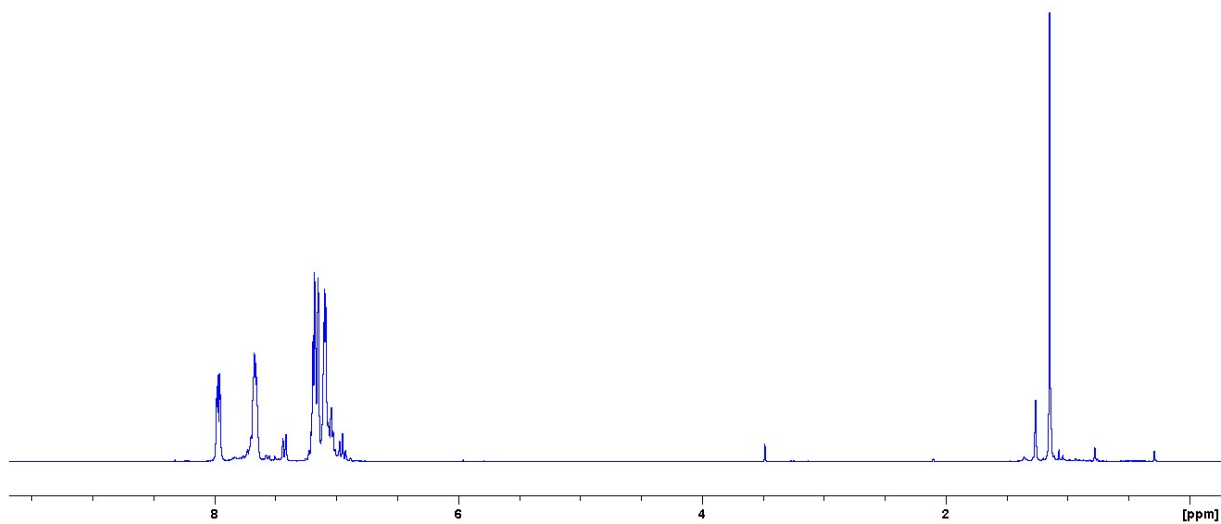


Figure S29:  $^1\text{H}$ -NMR Spectrum of **10** E-Z mixture

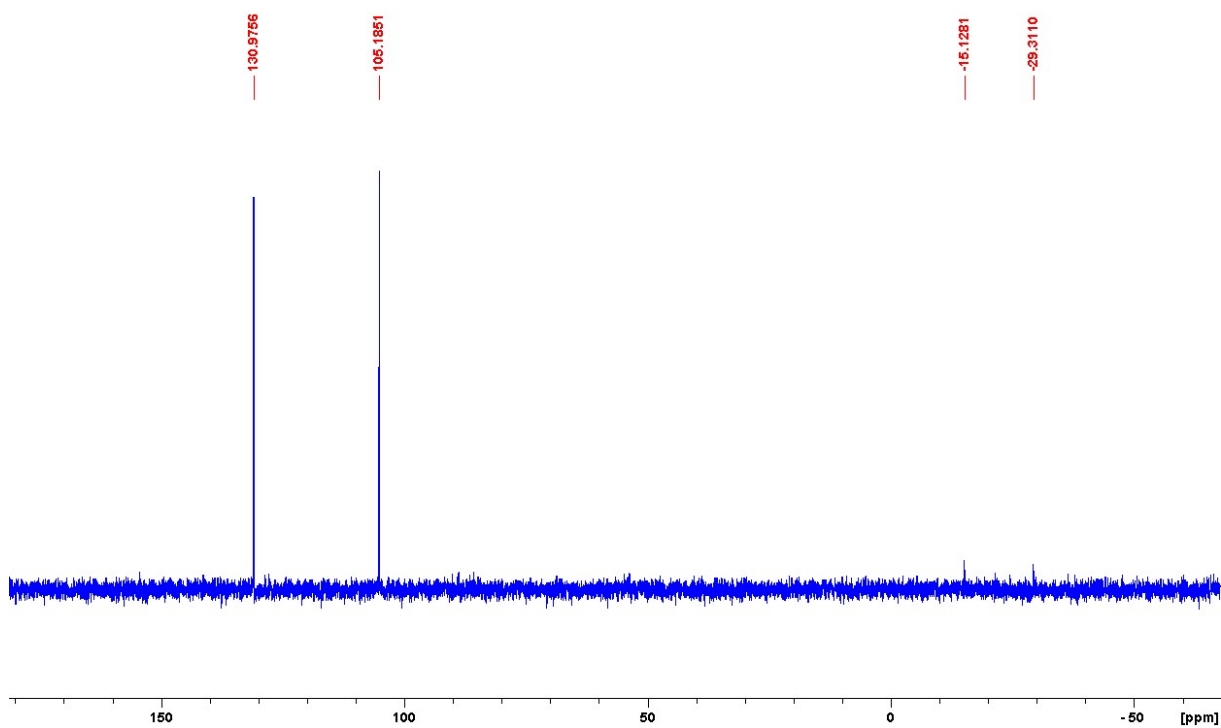
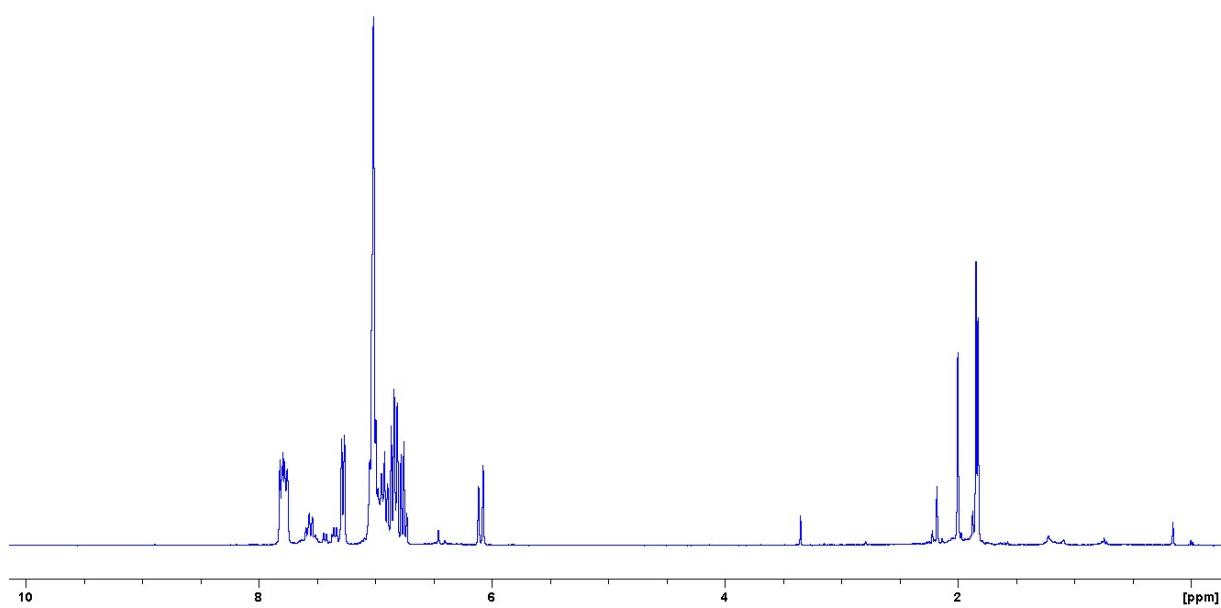
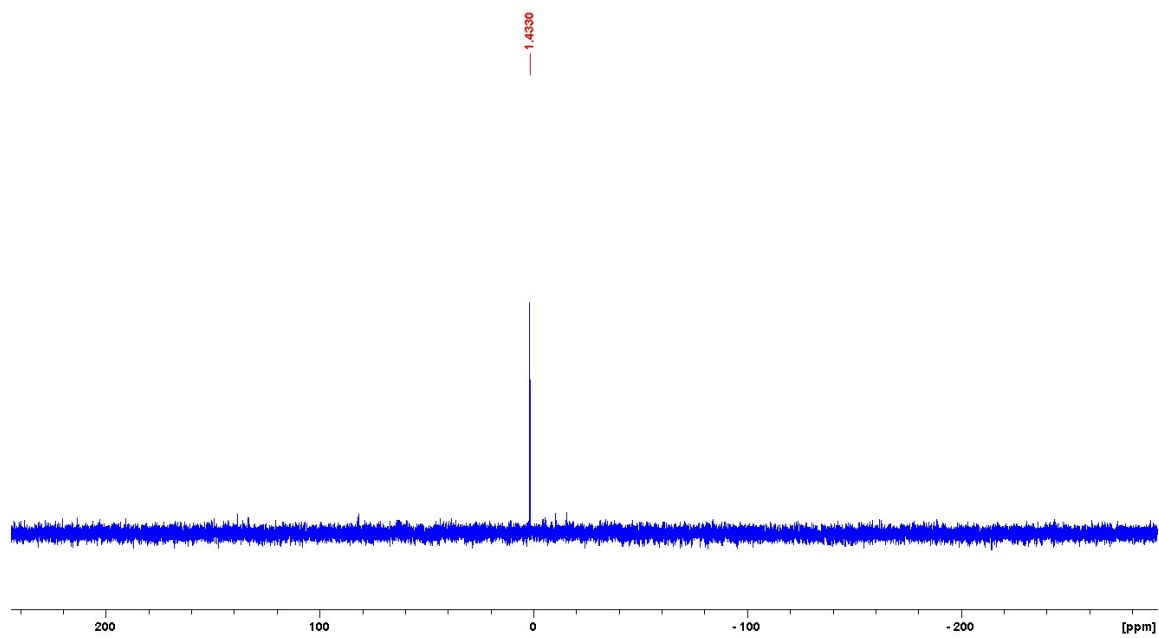


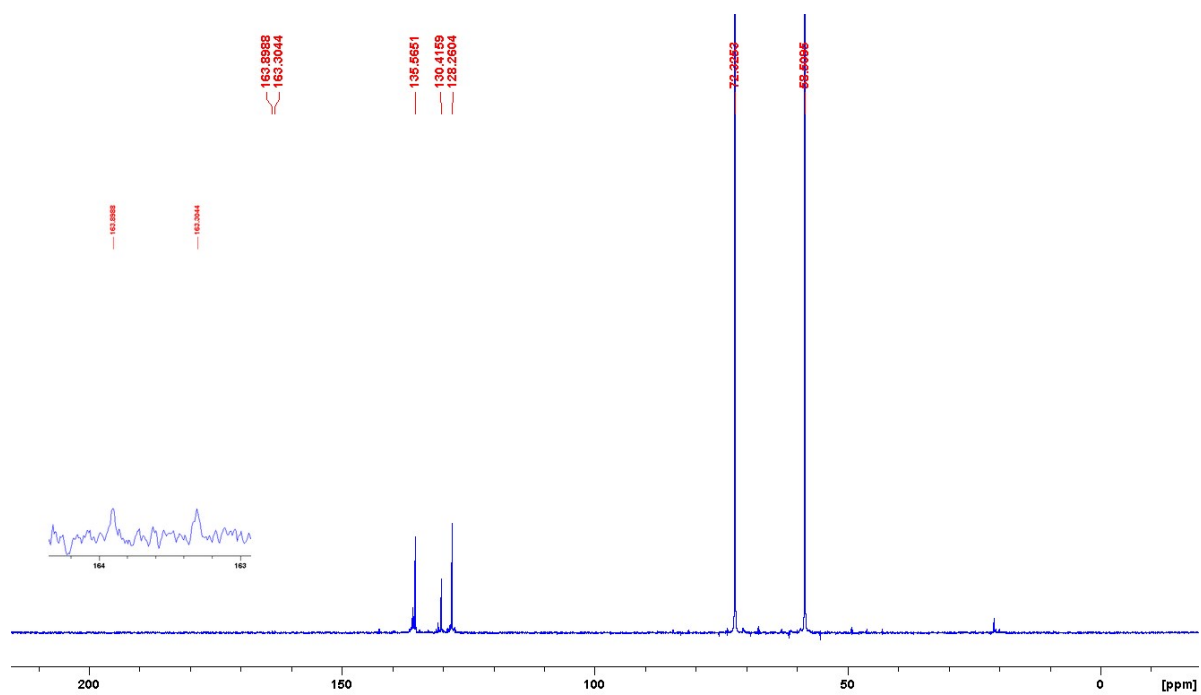
Figure S30:  $^{31}\text{P}\{^1\text{H}\}$ -NMR Spectrum of **11** E-Z mixture



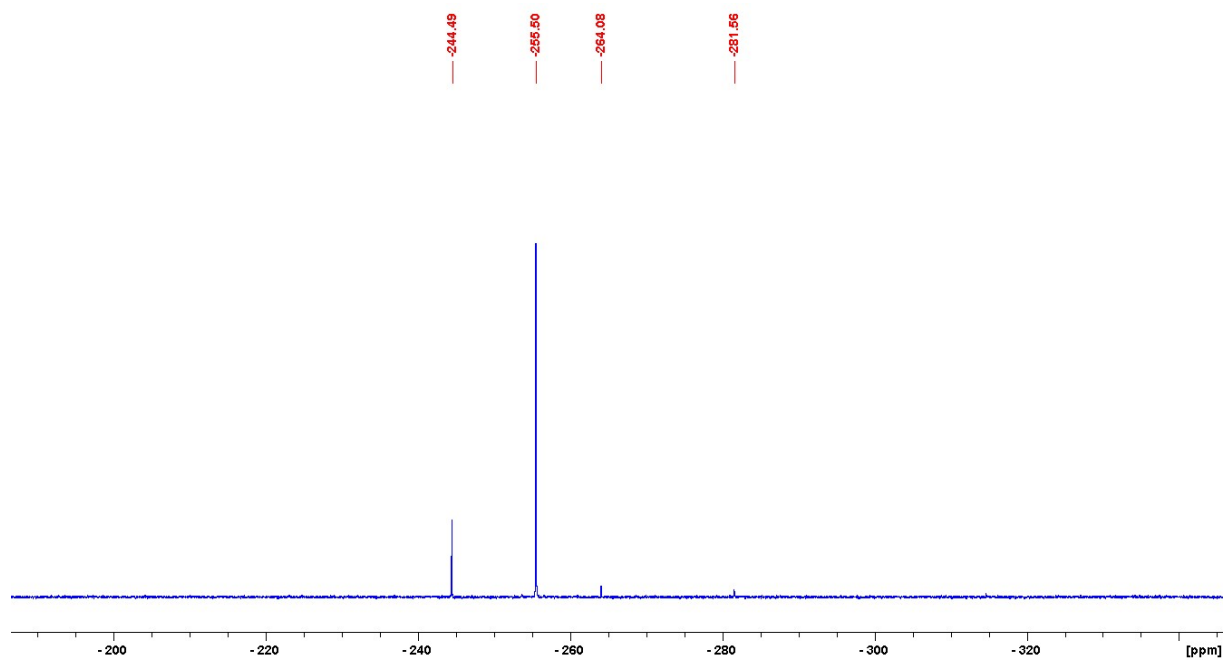
**Figure S31:**  $^1\text{H}$ -NMR Spectrum of **11** E-Z mixture



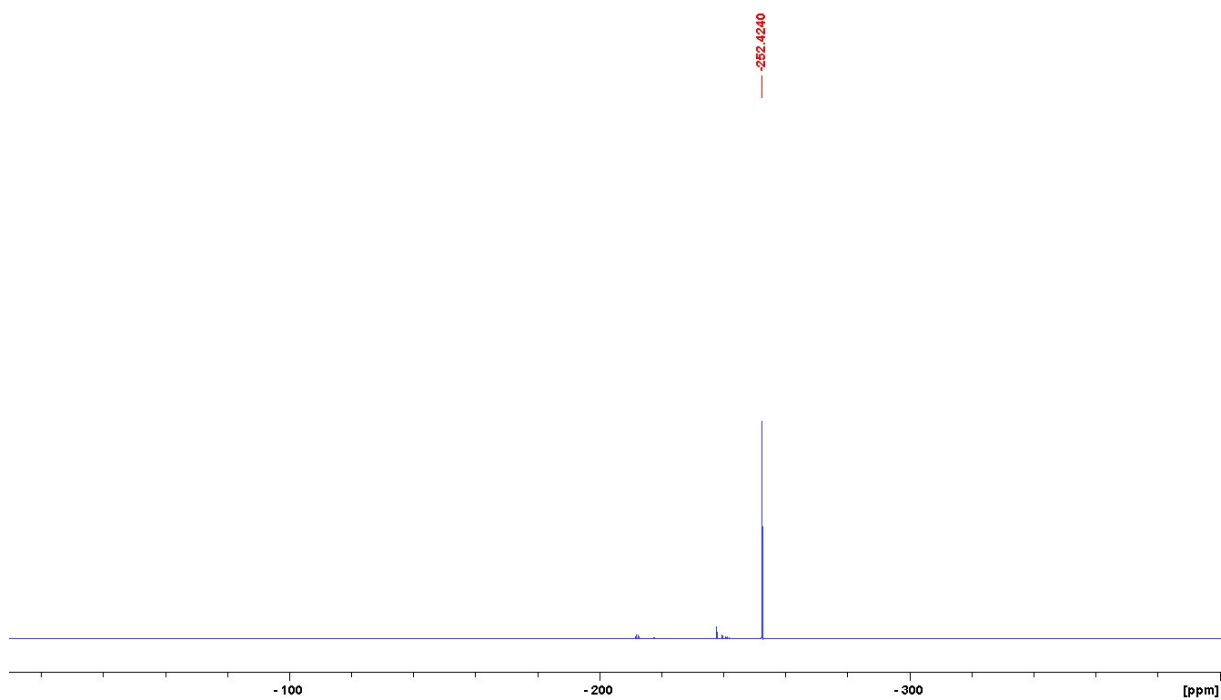
**Figure S32:**  $^{31}\text{P}\{^1\text{H}\}$ -NMR Signal of **12** in the reaction mixture



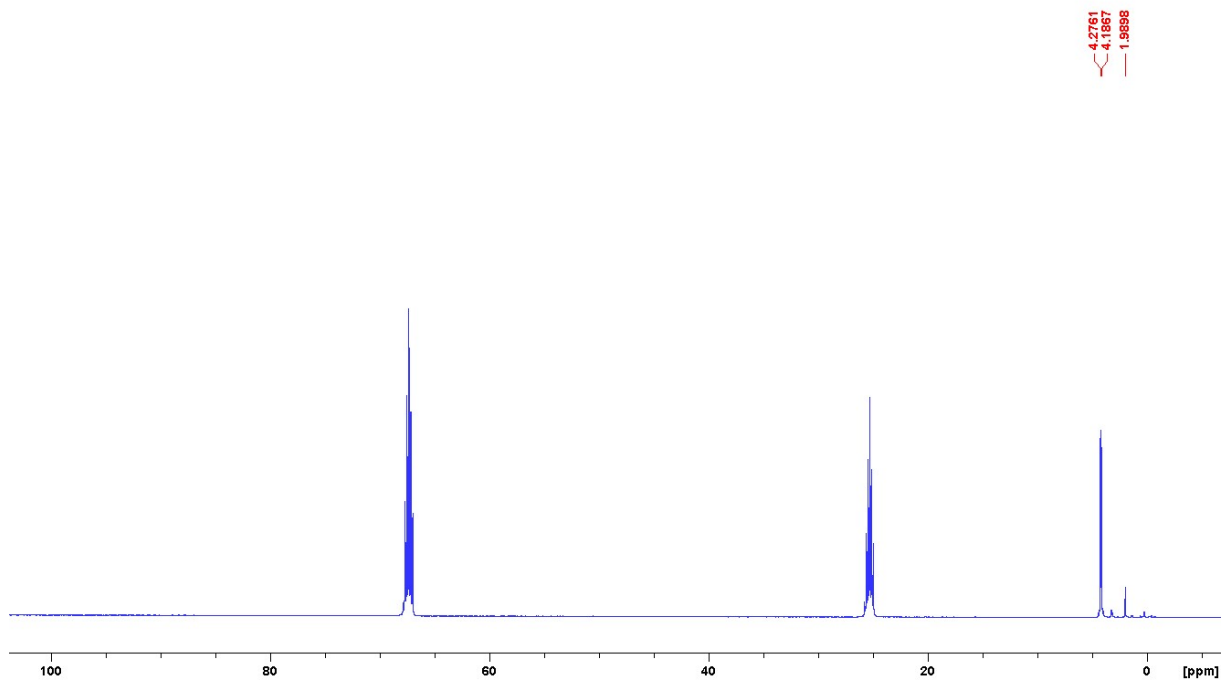
**Figure S33:**  $^{13}\text{C}\{^1\text{H}\}$ -NMR Signal of the sp carbon of **12** in the reaction mixture



**Figure S34:**  $^{31}\text{P}\{^1\text{H}\}$ -NMR Spectrum of the reaction mixture of **[4]** with trimethylsilyl isocyanate in absence of 18-crown-6, signal of **13**



**Figure S35:**  $^{31}\text{P}\{^1\text{H}\}$ -NMR Spectrum of the reaction mixture of **[2]** with trimethylsilyl isocyanate, signal of **1**



**Figure S36:**  $^{13}\text{C}\{^1\text{H}\}$ -NMR Spectrum of the reaction mixture of **[2]** with trimethylsilyl isocyanate, signal of **1**

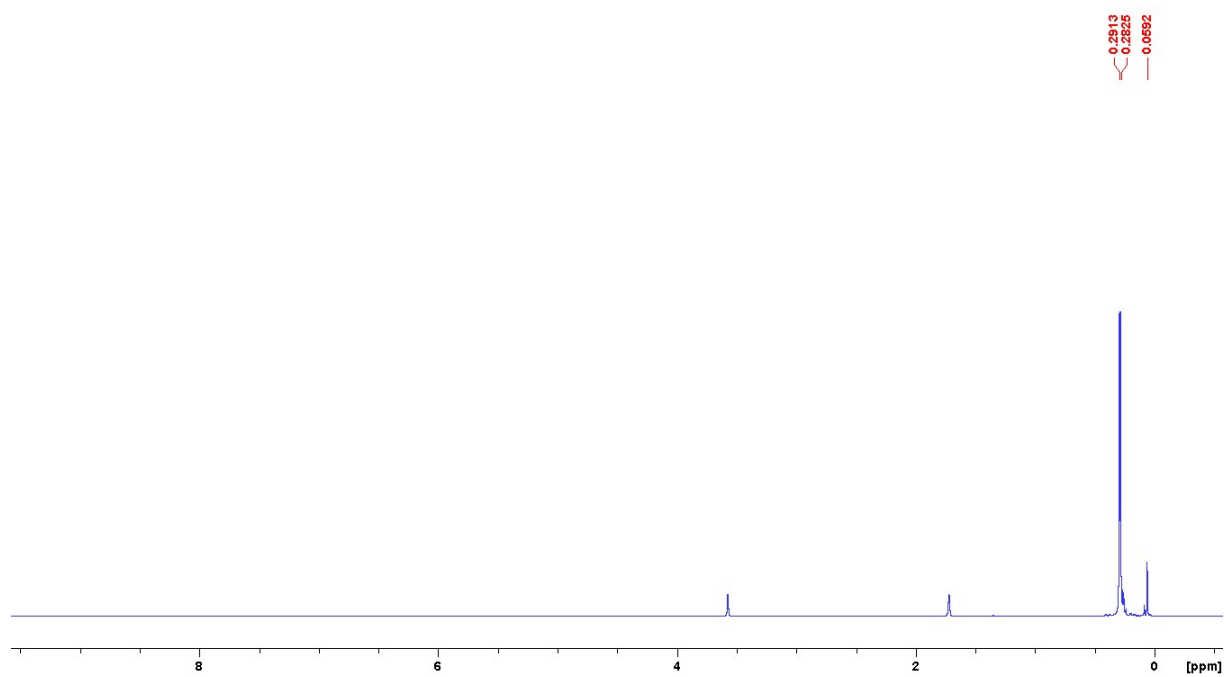


Figure S37:  $^1\text{H}$ -NMR Spectrum of the reaction mixture of **[2]** with trimethylsilyl isocyanate, signal of **1**

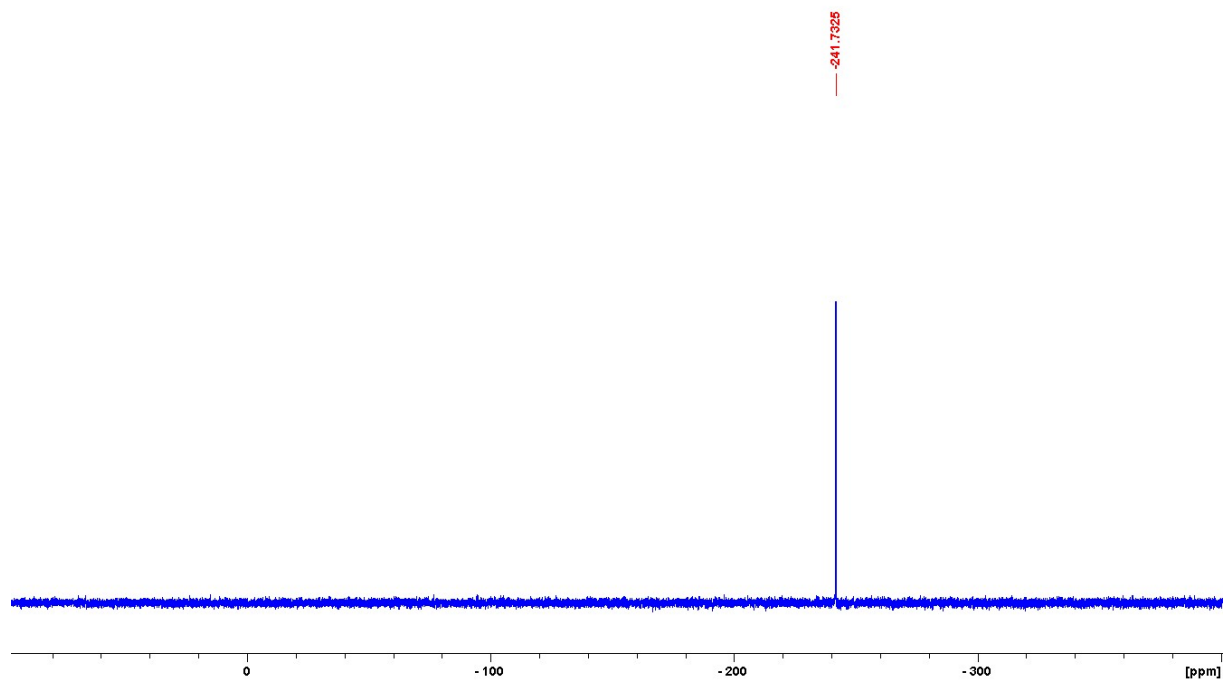


Figure S38:  $^{31}\text{P}\{^1\text{H}\}$ -NMR Spectrum of **14** in  $\text{C}_6\text{D}_6$

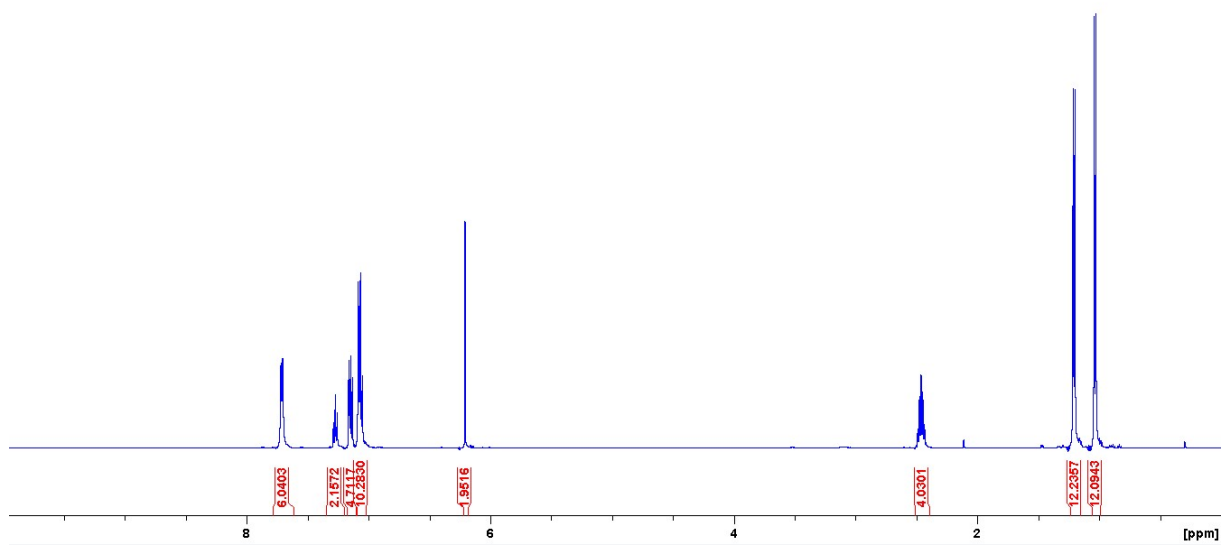


Figure S39:  $^1\text{H}$ -NMR Spectrum of **14** in  $\text{C}_6\text{D}_6$

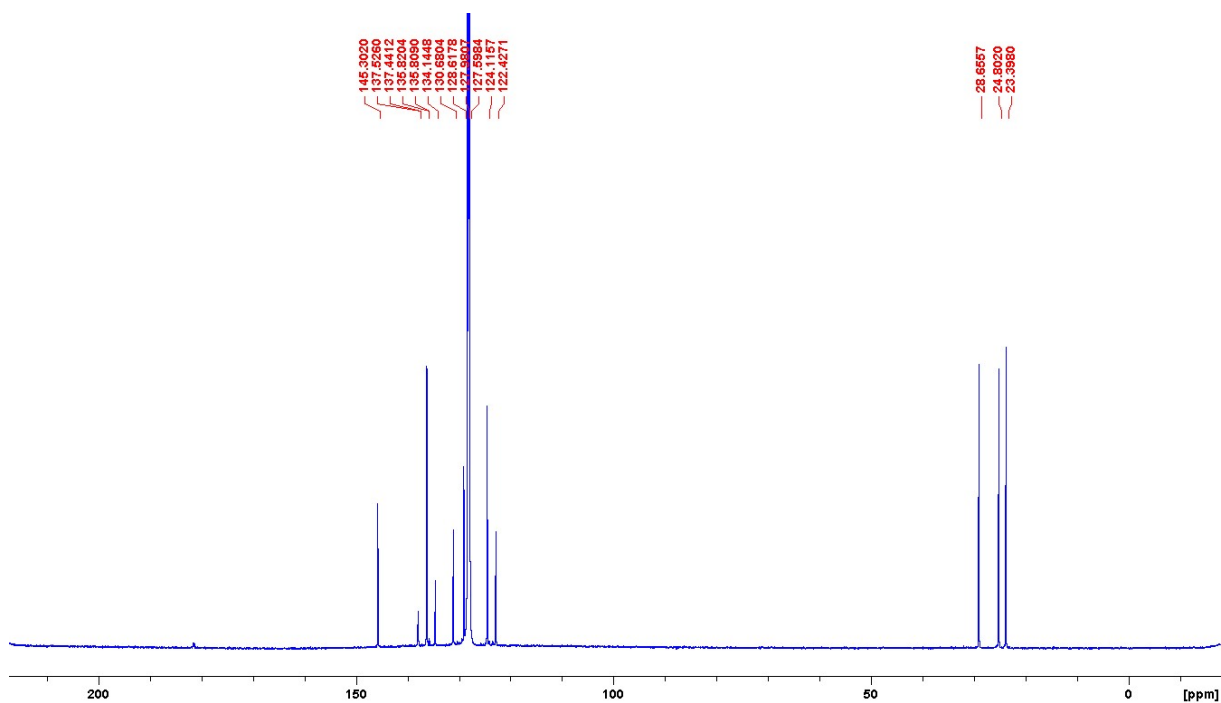
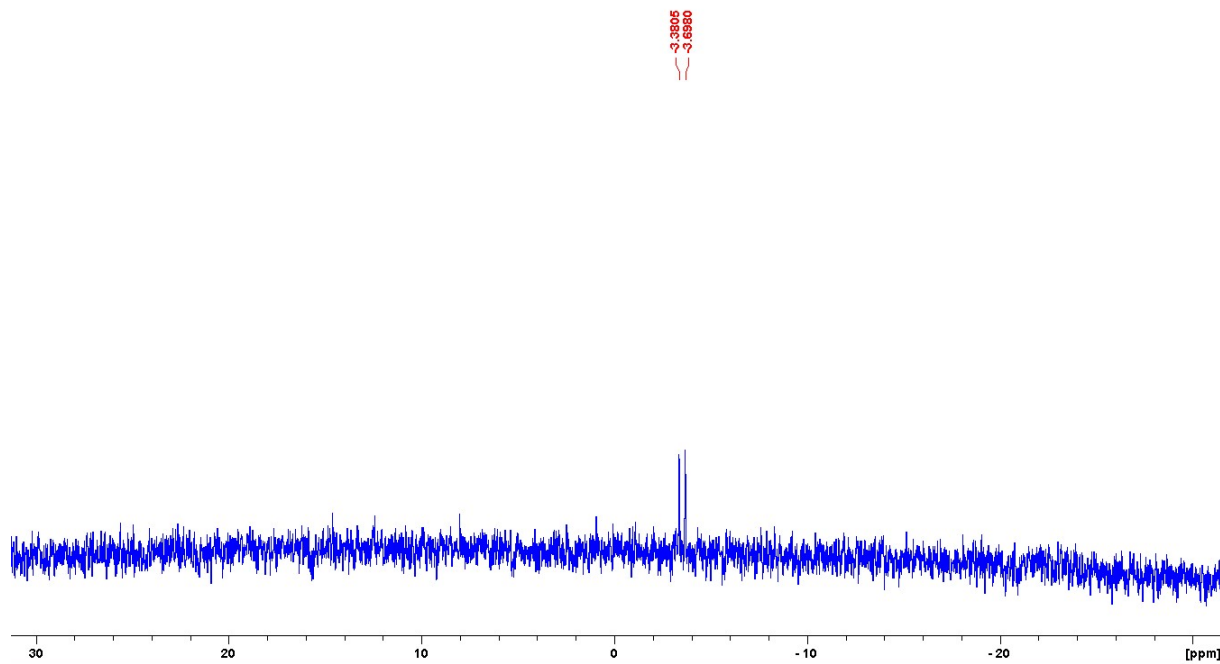
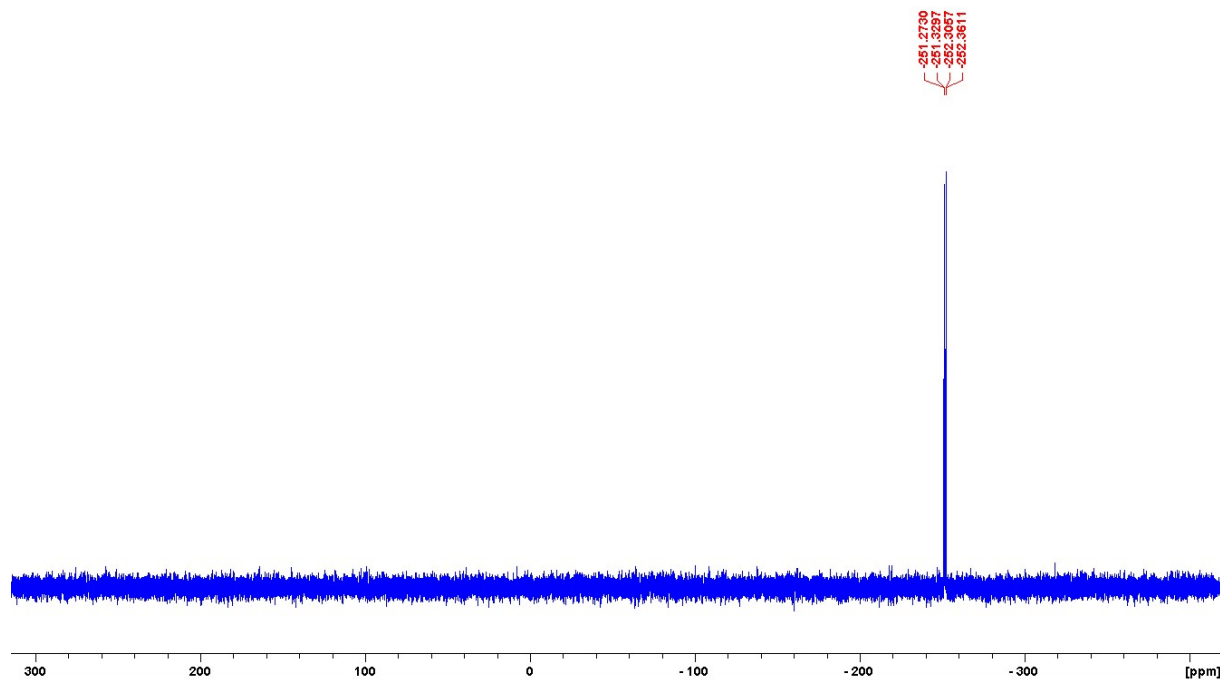


Figure S40:  $^{13}\text{C}\{^1\text{H}\}$ -NMR Spectrum of **14** in  $\text{C}_6\text{D}_6$





**Figure S41:**  $^{29}\text{Si}\{^1\text{H}\}$ -NMR spectrum of **14** in  $\text{C}_6\text{D}_6$



**Figure S42:**  $^{31}\text{P}\{^1\text{H}\}$ -NMR Spectrum of **15** in  $\text{C}_6\text{D}_6$

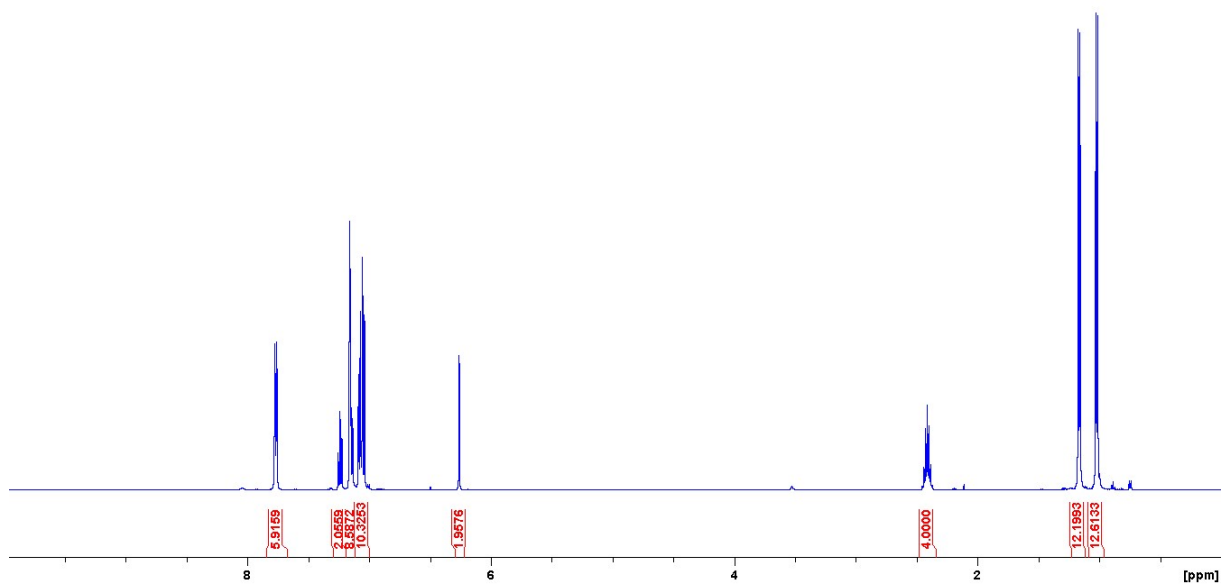


Figure S43:  $^1\text{H}$ -NMR spectrum of **15** in  $\text{C}_6\text{D}_6$

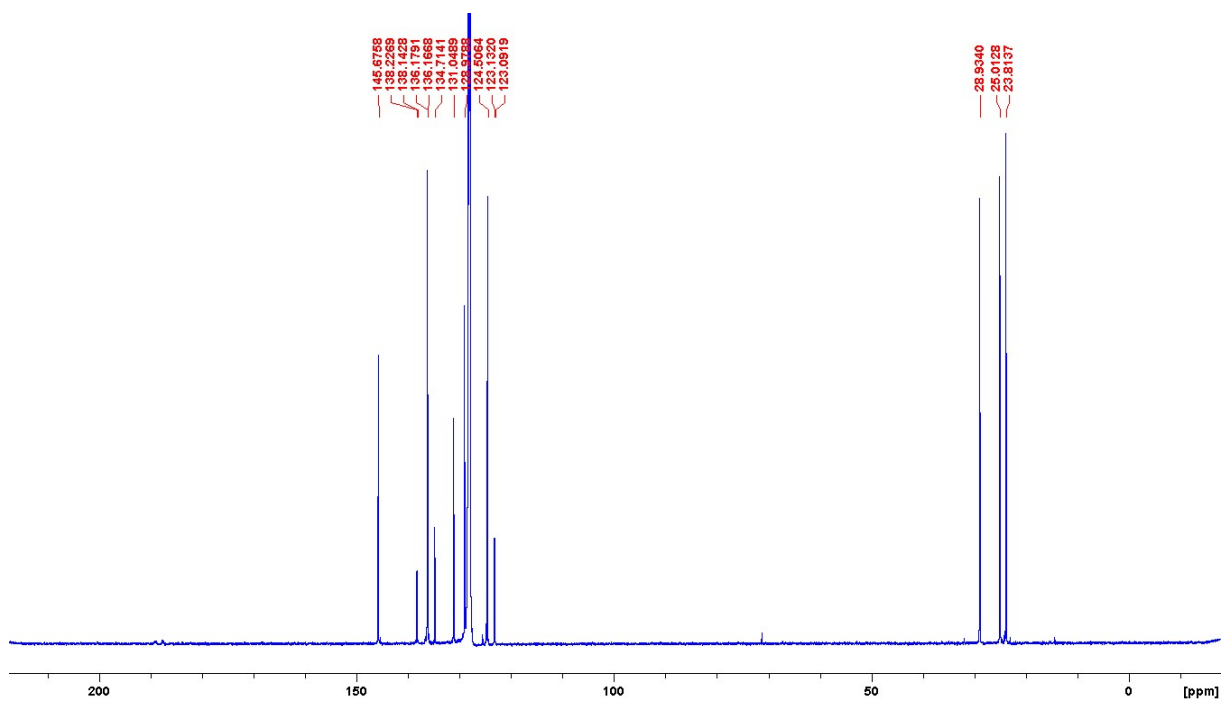
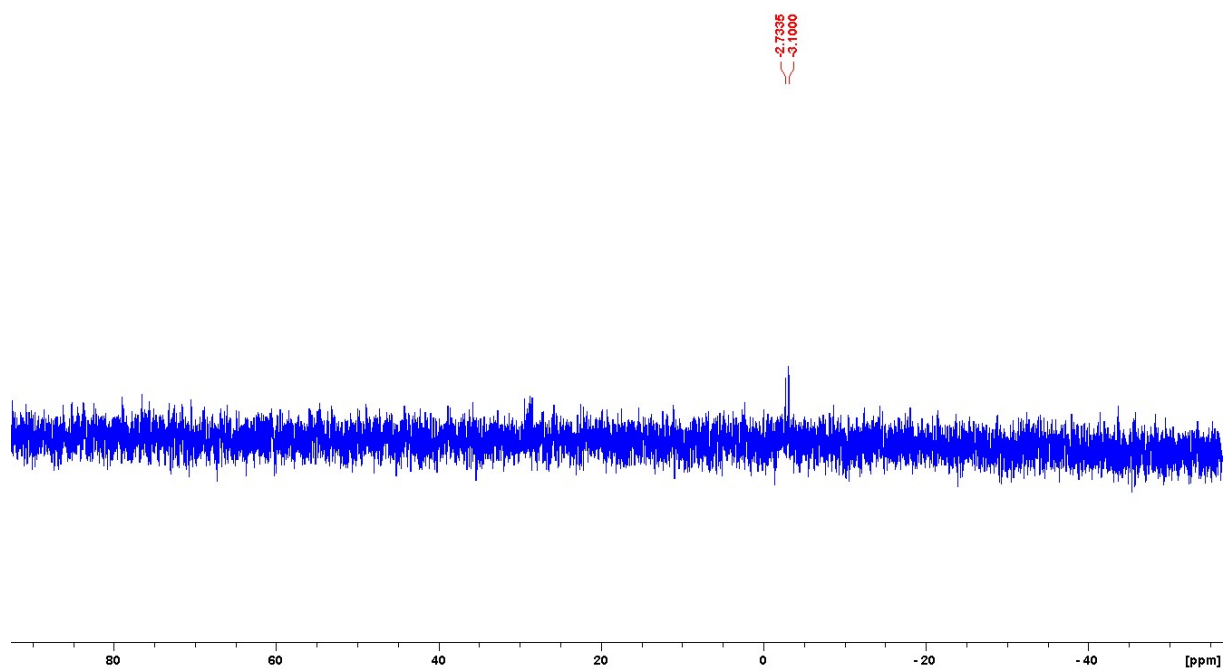
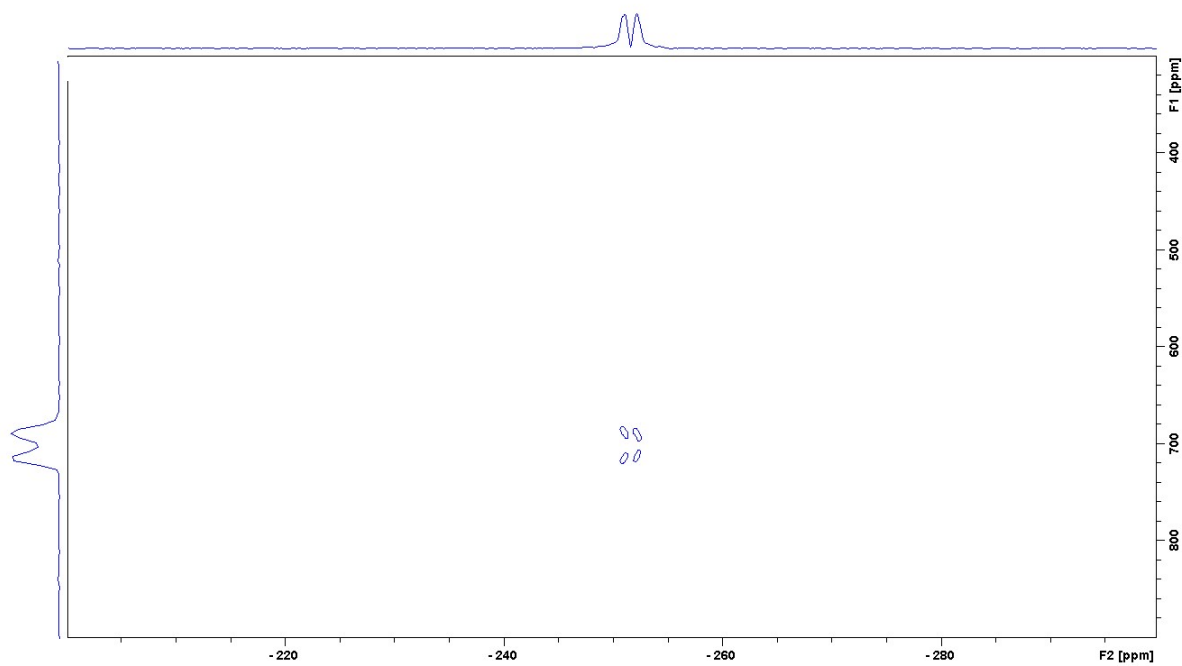


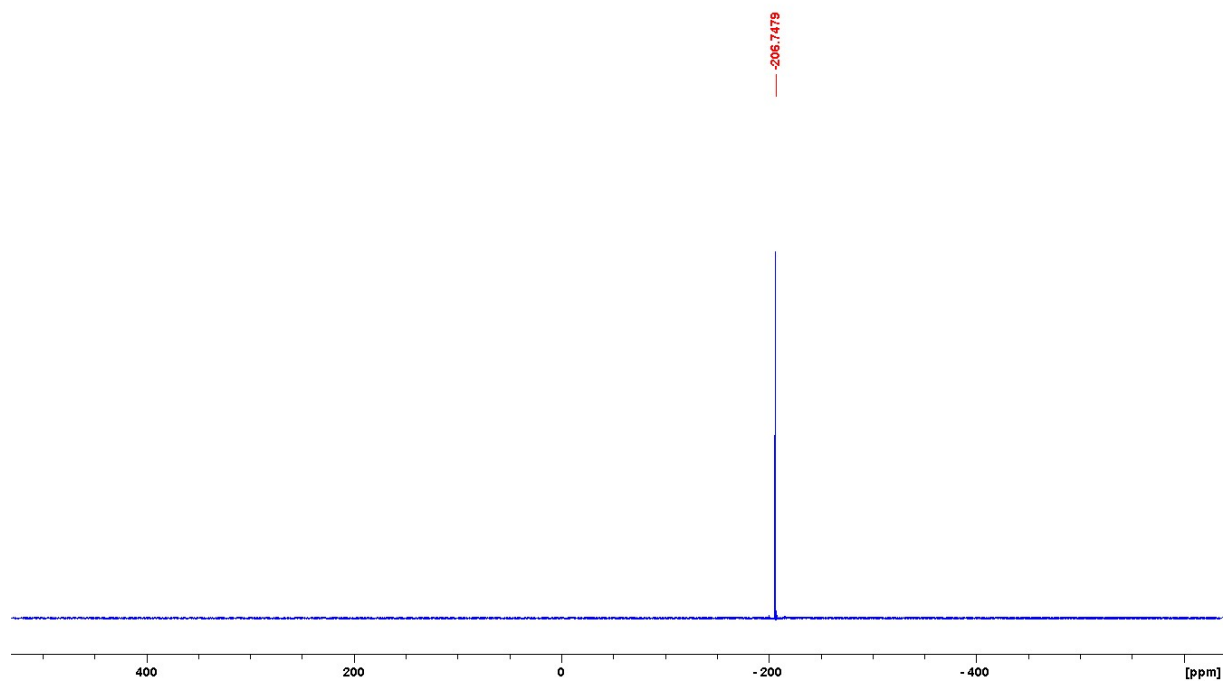
Figure S44:  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **15** in  $\text{C}_6\text{D}_6$



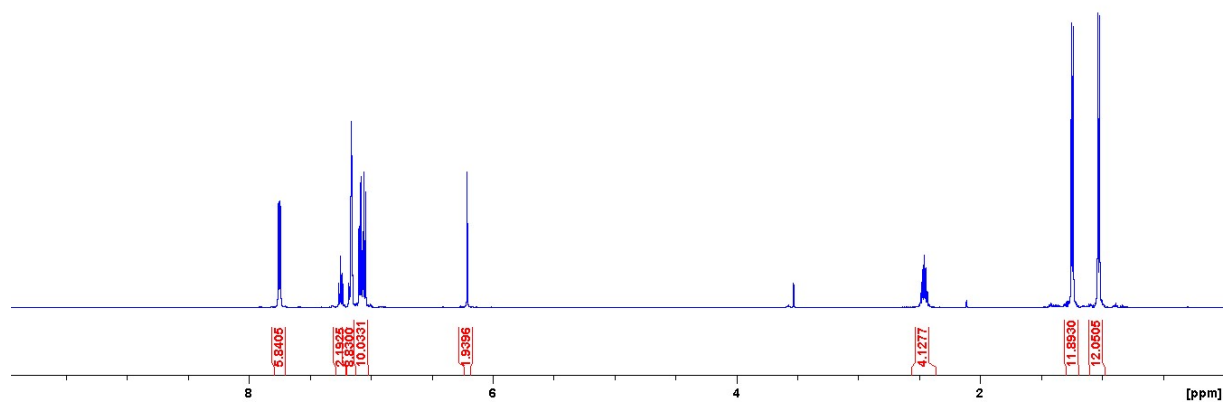
**Figure S45:**  $^{29}\text{Si}\{^1\text{H}\}$ -NMR spectrum of **15** in  $\text{C}_6\text{D}_6$



**Figure S46:**  $^{109}\text{Ag}$ - $^{31}\text{P}$  HMBC spectrum of **15** in  $\text{C}_6\text{D}_6$



**Figure S47:**  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **16** in  $\text{C}_6\text{D}_6$



**Figure S48:**  $^1\text{H}$ -NMR spectrum of **16** in  $\text{C}_6\text{D}_6$

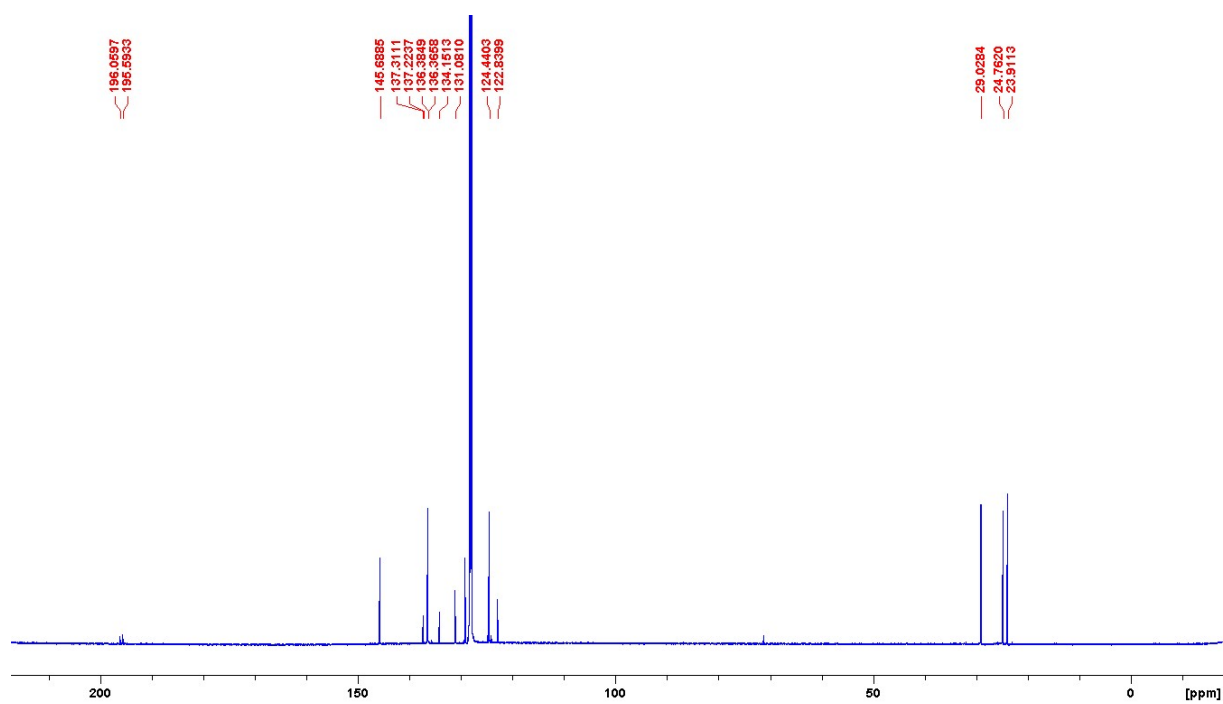


Figure S49:  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **16** in  $\text{C}_6\text{D}_6$

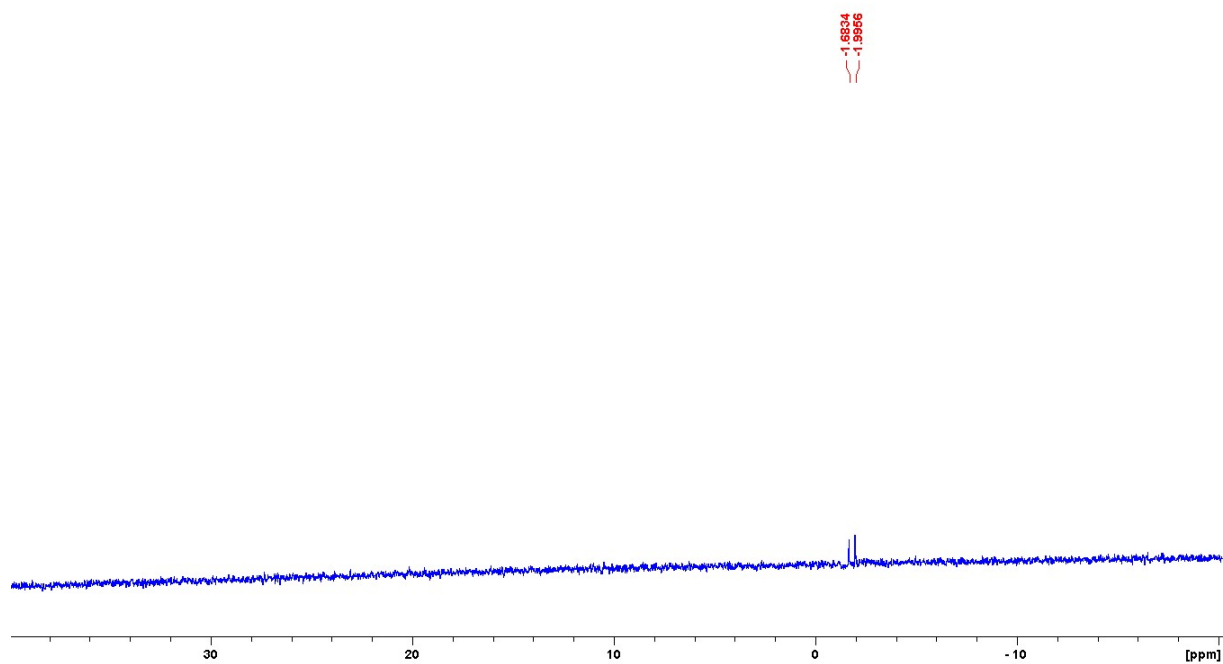


Figure S50:  $^{29}\text{Si}\{^1\text{H}\}$ -NMR spectrum of **16** in  $\text{C}_6\text{D}_6$

# IR

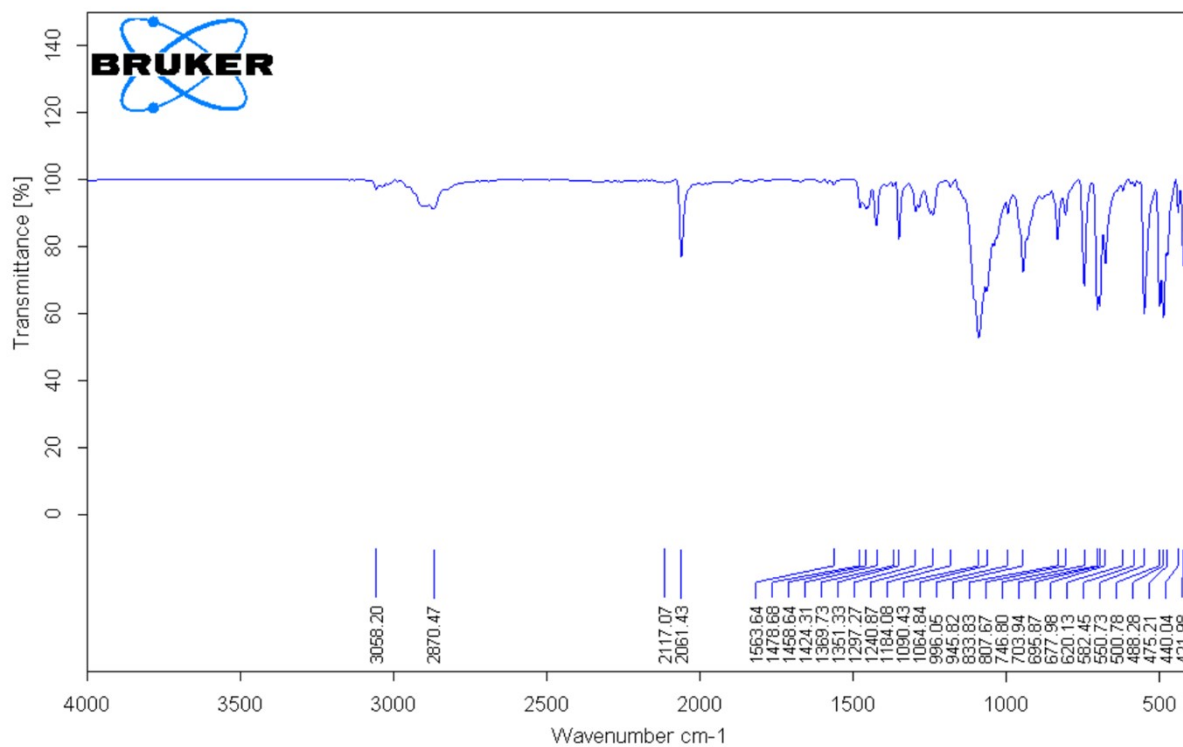


Figure S51: IR spectrum (ATR) of Na(18-crown-6)[7]

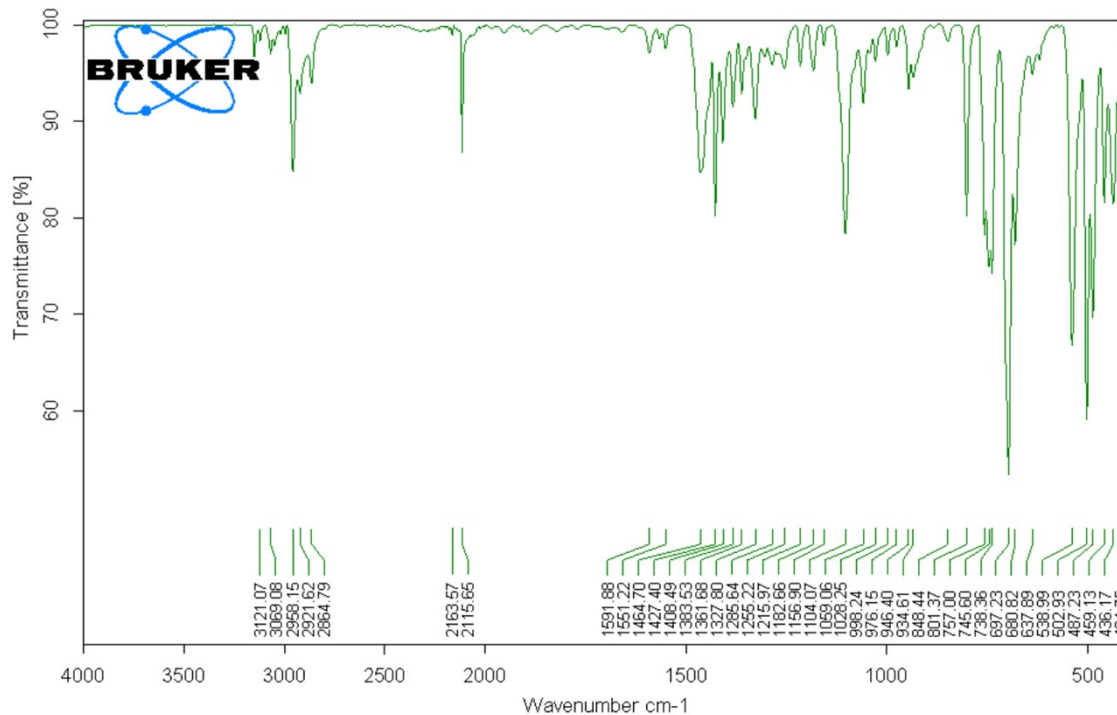


Figure S52: IR spectrum of 14

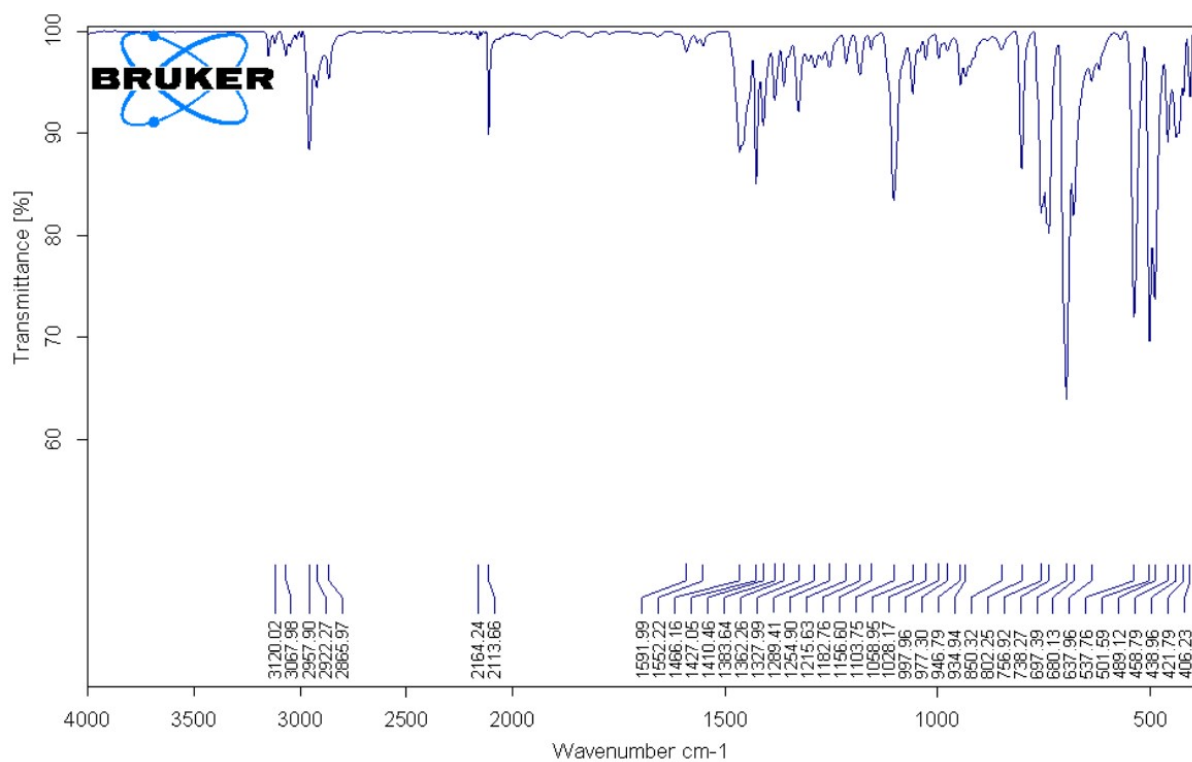


Figure S53: IR spectrum of 15

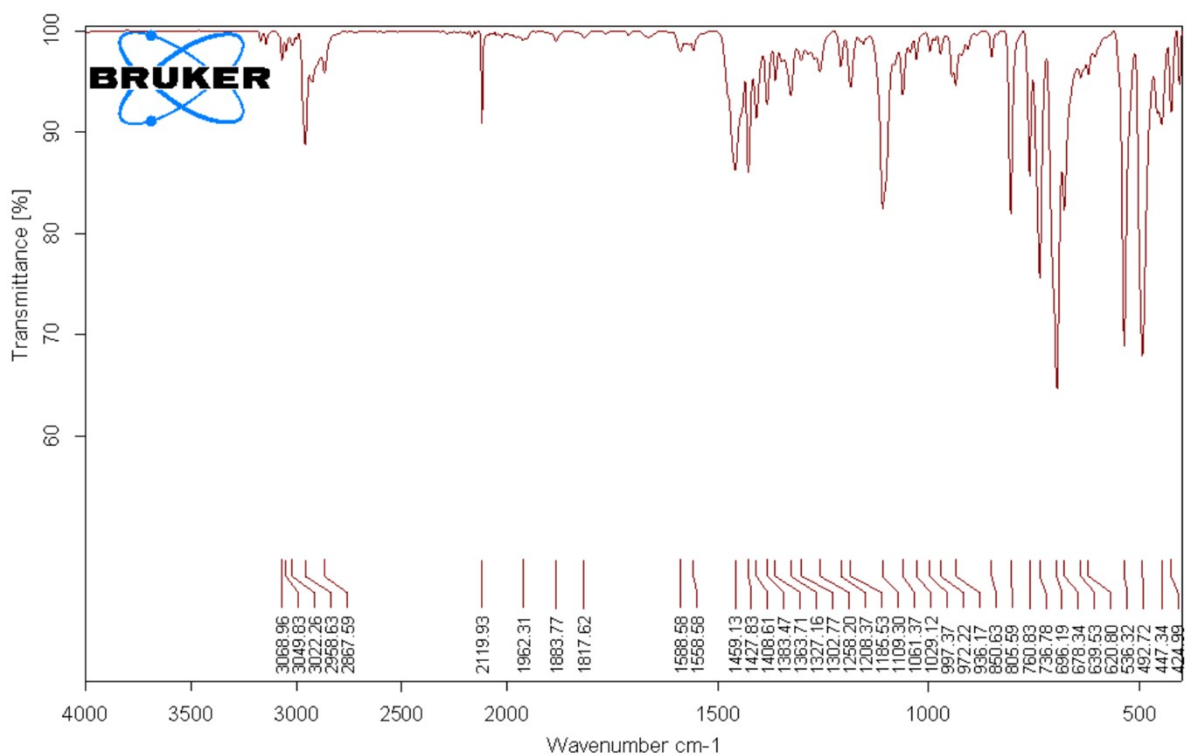


Figure S54: IR spectrum of 16

#### 4. Crystallographic details

**Table S2:** Crystal data and structure refinement for Ph4P[5]

Identification code	GLC20963_0m
Empirical formula	C <sub>1.81</sub> H <sub>1.51</sub> Cl <sub>0.45</sub> P <sub>0.15</sub> Si <sub>0.15</sub>
Formula weight	48.24
Temperature/K	100.02
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	13.2251(5)
b/Å	14.2041(5)
c/Å	15.3777(5)
α/°	90
β/°	100.5010(10)
γ/°	90
Volume/Å <sup>3</sup>	2840.33(17)
Z	53
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.495
μ/mm <sup>-1</sup>	0.816
F(000)	1296.0
Crystal size/mm <sup>3</sup>	0.22 × 0.16 × 0.14
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.714 to 60.148
Index ranges	-18 ≤ h ≤ 18, -20 ≤ k ≤ 19, -21 ≤ l ≤ 21
Reflections collected	68524
Independent reflections	8192 [R <sub>int</sub> = 0.0697, R <sub>sigma</sub> = 0.0408]
Data/restraints/parameters	8192/0/307
Goodness-of-fit on F <sup>2</sup>	1.076
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0366, wR <sub>2</sub> = 0.0700
Final R indexes [all data]	R <sub>1</sub> = 0.0631, wR <sub>2</sub> = 0.0811
Largest diff. peak/hole / e Å <sup>-3</sup>	0.56/-0.52



**Table S3:** Crystal data and structure refinement for Na(18-crown-6)(DME)<sub>0.5</sub>[4]

Identification code	GLC3010
Empirical formula	C <sub>50</sub> H <sub>59</sub> NaO <sub>7</sub> PSi <sub>2</sub>
Formula weight	882.11
Temperature/K	100.01(15)
Crystal system	triclinic
Space group	P-1
a/Å	12.2084(3)
b/Å	12.5732(4)
c/Å	16.8295(5)
α/°	98.695(2)
β/°	107.907(2)
γ/°	101.613(2)
Volume/Å <sup>3</sup>	2344.08(12)
Z	2
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.250
μ/mm <sup>-1</sup>	0.169
F(000)	938.0
Crystal size/mm <sup>3</sup>	0.45 × 0.25 × 0.15
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.396 to 61.754
Index ranges	-17 ≤ h ≤ 16, -17 ≤ k ≤ 18, -24 ≤ l ≤ 23
Reflections collected	73742
Independent reflections	13648 [R <sub>int</sub> = 0.0413, R <sub>sigma</sub> = 0.0358]
Data/restraints/parameters	13648/0/551
Goodness-of-fit on F <sup>2</sup>	1.017
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0393, wR <sub>2</sub> = 0.0861
Final R indexes [all data]	R <sub>1</sub> = 0.0564, wR <sub>2</sub> = 0.0938
Largest diff. peak/hole / e Å <sup>-3</sup>	0.39/-0.27

**Table S4:** Crystal data and structure refinement for **E-10**

Identification code	tBuCOPTPS
Empirical formula	$C_{10.25}H_{9.75}O_{0.25}P_{0.25}Si_{0.5}$
Formula weight	158.72
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	23.112(2)
b/Å	13.4449(12)
c/Å	11.1997(10)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å <sup>3</sup>	3480.1(5)
Z	16
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.212
$\mu/\text{mm}^{-1}$	0.179
F(000)	1344.0
Crystal size/mm <sup>3</sup>	0.6 × 0.3 × 0.15
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/ $^\circ$	4.648 to 53.052
Index ranges	-28 ≤ h ≤ 28, -16 ≤ k ≤ 16, -14 ≤ l ≤ 14
Reflections collected	88609
Independent reflections	7179 [ $R_{\text{int}} = 0.1415$ , $R_{\text{sigma}} = 0.0486$ ]
Data/restraints/parameters	7179/1/409
Goodness-of-fit on F <sup>2</sup>	1.064
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0328$ , $wR_2 = 0.0799$
Final R indexes [all data]	$R_1 = 0.0363$ , $wR_2 = 0.0852$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.33/-0.38
Flack parameter	0.03(3)

**Table S5:** Crystal data and structure refinement for **Z-11**

Identification code	GLC2117_0m
Empirical formula	$C_{9.68}H_{8.63}O_{0.21}P_{0.21}Si_{0.42}$
Formula weight	146.72
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.8439(2)
b/Å	17.8101(3)
c/Å	21.7832(4)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å <sup>3</sup>	3819.05(12)
Z	19
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.212
$\mu/\text{mm}^{-1}$	1.496
F(000)	1472.0
Crystal size/mm <sup>3</sup>	0.21 × 0.18 × 0.15
Radiation	CuK $\alpha$ ( $\lambda = 1.54178$ )
2 $\Theta$ range for data collection/ $^\circ$	6.41 to 145.176
Index ranges	-10 ≤ h ≤ 12, -22 ≤ k ≤ 22, -26 ≤ l ≤ 26
Reflections collected	62386
Independent reflections	7558 [ $R_{\text{int}} = 0.0632$ , $R_{\text{sigma}} = 0.0310$ ]
Data/restraints/parameters	7558/0/454
Goodness-of-fit on F <sup>2</sup>	1.041
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0312$ , $wR_2 = 0.0762$
Final R indexes [all data]	$R_1 = 0.0362$ , $wR_2 = 0.0806$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.30/-0.17
Flack parameter	-0.002(8)

**Table S6:** Crystal data and structure refinement for **14**

Identification code	CuCN
Empirical formula	$C_{9.68}H_{10.74}Cu_{0.21}N_{0.63}P_{0.21}Si_{0.21}$
Formula weight	161.79
Temperature/K	100.0
Crystal system	orthorhombic
Space group	Pca2 <sub>1</sub>
a/Å	21.5909(6)
b/Å	10.7125(3)
c/Å	18.4005(4)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å <sup>3</sup>	4255.90(19)
Z	19
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.199
$\mu/\text{mm}^{-1}$	0.613
F(000)	1624.0
Crystal size/mm <sup>3</sup>	0.33 × 0.15 × 0.07
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/ $^\circ$	4.374 to 53.47
Index ranges	-27 ≤ h ≤ 27, -13 ≤ k ≤ 13, -23 ≤ l ≤ 23
Reflections collected	74787
Independent reflections	9020 [ $R_{\text{int}} = 0.0462$ , $R_{\text{sigma}} = 0.0327$ ]
Data/restraints/parameters	9020/1/477
Goodness-of-fit on F <sup>2</sup>	1.049
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0242$ , $wR_2 = 0.0500$
Final R indexes [all data]	$R_1 = 0.0311$ , $wR_2 = 0.0547$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.20/-0.19
Flack parameter	-0.018(4)

**Table S7:** Crystal data and structure refinement for **15**

Identification code	exp_5191
Empirical formula	C <sub>10.22</sub> H <sub>11.33</sub> Ag <sub>0.22</sub> N <sub>0.67</sub> P <sub>0.22</sub> Si <sub>0.22</sub>
Formula weight	180.63
Temperature/K	100.01(10)
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	9.5649(2)
b/Å	20.0490(3)
c/Å	21.8272(3)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	4185.73(12)
Z	18
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.290
μ/mm <sup>-1</sup>	0.583
F(000)	1696.0
Crystal size/mm <sup>3</sup>	0.22 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.732 to 58.028
Index ranges	-12 ≤ h ≤ 12, -26 ≤ k ≤ 26, -29 ≤ l ≤ 23
Reflections collected	36466
Independent reflections	9768 [R <sub>int</sub> = 0.0321, R <sub>sigma</sub> = 0.0348]
Data/restraints/parameters	9768/0/477
Goodness-of-fit on F <sup>2</sup>	1.037
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0278, wR <sub>2</sub> = 0.0574
Final R indexes [all data]	R <sub>1</sub> = 0.0316, wR <sub>2</sub> = 0.0590
Largest diff. peak/hole / e Å <sup>-3</sup>	0.41/-0.26
Flack parameter	0.202(6)

**Table S8:** Crystal data and structure refinement for **16**

Identification code	AuCN
Empirical formula	$C_{9.68}H_{10.74}Au_{0.21}N_{0.63}P_{0.21}Si_{0.21}$
Formula weight	189.88
Temperature/K	100.0
Crystal system	orthorhombic
Space group	Pca2 <sub>1</sub>
a/Å	21.8306(7)
b/Å	10.5494(3)
c/Å	18.6773(6)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å <sup>3</sup>	4301.4(2)
Z	19
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.393
$\mu/\text{mm}^{-1}$	3.519
F(000)	1824.0
Crystal size/mm <sup>3</sup>	0.26 × 0.24 × 0.2
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/ $^\circ$	4.434 to 52.034
Index ranges	-26 ≤ h ≤ 26, -13 ≤ k ≤ 13, -23 ≤ l ≤ 23
Reflections collected	93534
Independent reflections	8447 [ $R_{\text{int}} = 0.0876$ , $R_{\text{sigma}} = 0.0311$ ]
Data/restraints/parameters	8447/1/478
Goodness-of-fit on F <sup>2</sup>	1.008
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0191$ , $wR_2 = 0.0373$
Final R indexes [all data]	$R_1 = 0.0238$ , $wR_2 = 0.0388$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.46/-1.08
Flack parameter	0.001(2)

## 5. Thermogravimetric data

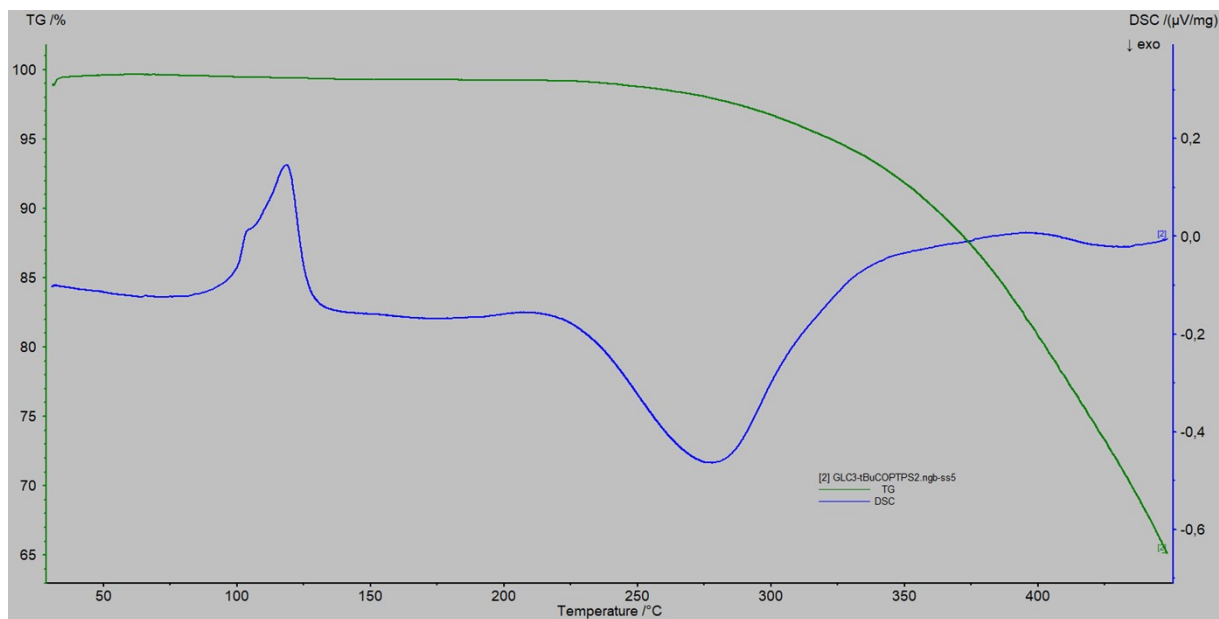


Figure S55:TGA/DSC signal of 10

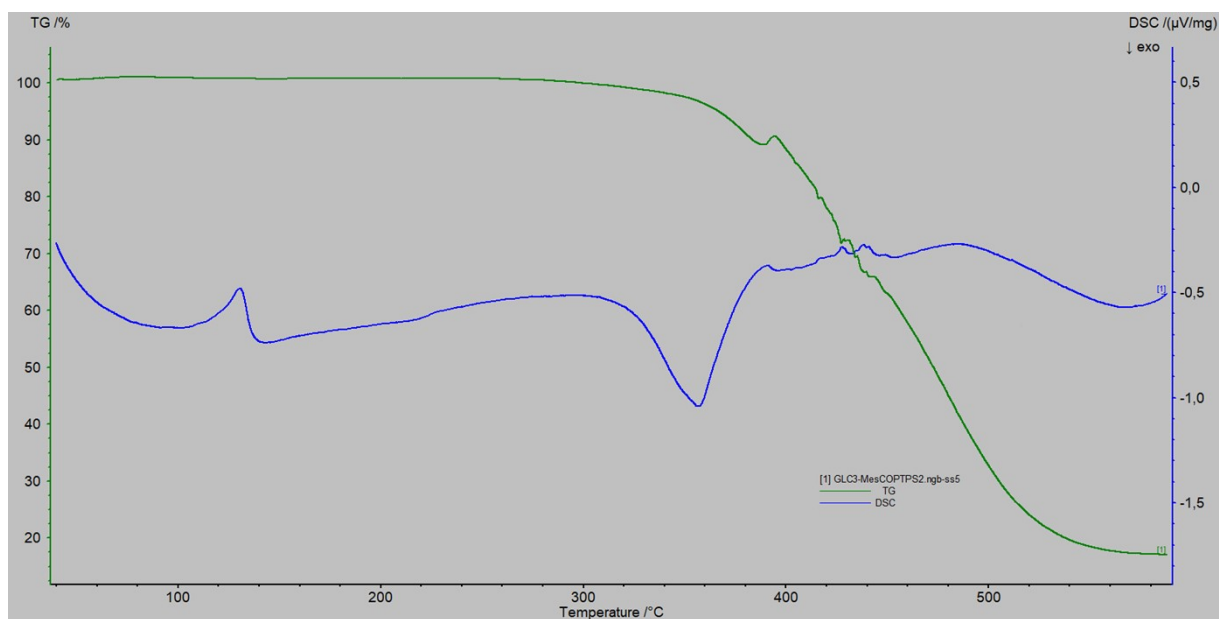


Figure S56: TGA/DSC signal of 11

## References

- [1] F. Uhlig, R. Hummeltenberg, *J. Organomet. Chem.* **1993**, *452*, C9-C10.
- [2] R. A. Moss, G. Chu, R. R. Sauers, *J. Am. Chem. Soc.* **2005**, *127*, 2408-2409.
- [3] G. S. Forbes, H. H. Anderson, *J. Am. Chem. Soc.* **1948**, *70*, 1043-1044.
- [4] H. Kaur, F. K. Zinn, E. D. Stevens, S. P. Nolan, *Organometallics* **2004**, *23*, 1157-1160.
- [5] P. de Frémont, N. M. Scott, E. D. Stevens, S. P. Nolan, *Organometallics* **2005**, *24*, 2411-2418.
- [6] P. de Frémont, N. M. Scott, E. D. Stevens, T. Ramnial, O. C. Lightbody, C. L. B. Macdonald, J. A. C. Clyburne, C. D. Abernethy, S. P. Nolan, *Organometallics* **2005**, *24*, 6301-6309.
- [7] G. Le Corre, J. J. Gamboa-Carballo, Z. Li, H. Grützmacher, *Angew. Chem. Int. Ed.* **2021**, *60*, 24817-24822.