

*Electronic Supplementary Information for*

**Borane-Catalysed Dinitrogen Borylation by 1,3-B–H Bond Addition**

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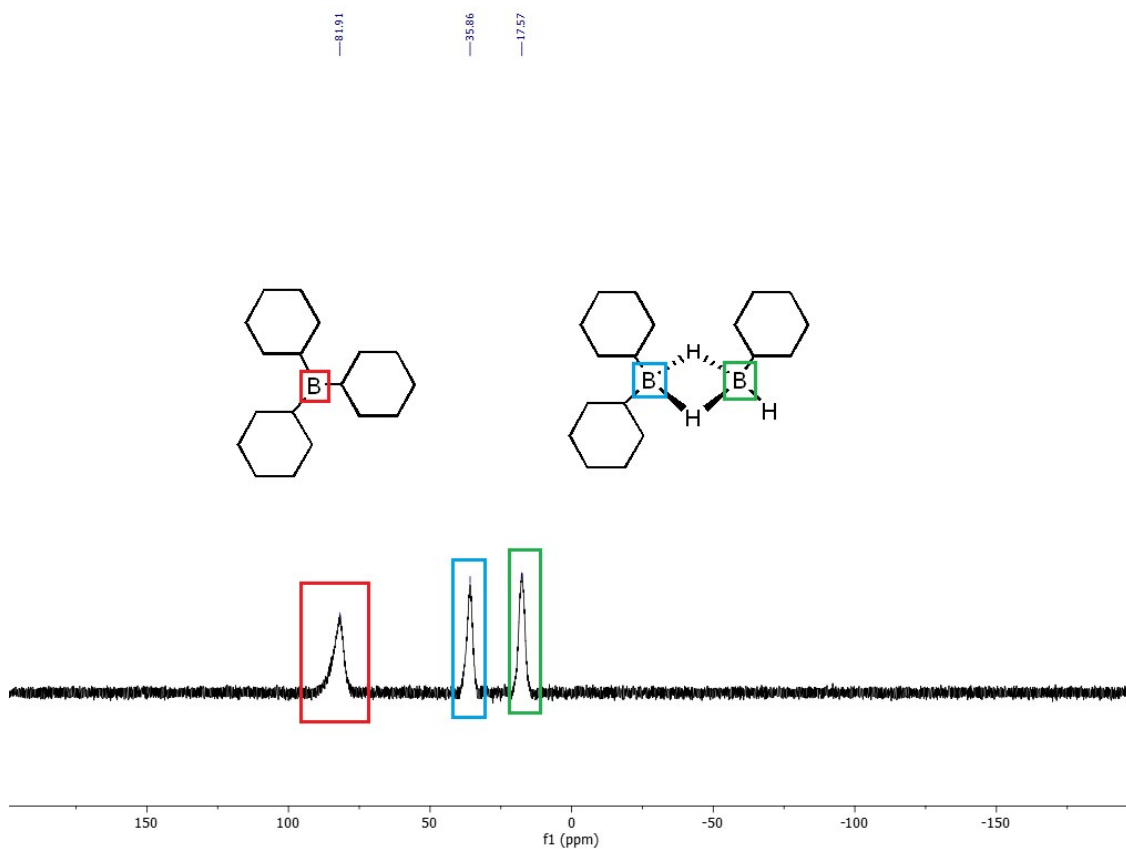
# 1. Characterization Data of New Compounds

## 1.1. Generation of tricyclohexyldiborane

HBCy<sub>2</sub> (13.8 mg, 77 μmol) was introduced in a flask in a glovebox and was partially dissolved in 0.5 mL of C<sub>6</sub>D<sub>6</sub>. The solution was then heated at 60 °C for 1 h to give a homogeneous solution that was subsequently analyzed by NMR.

<sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>6</sub>) δ 81.9 (BCy<sub>3</sub>), 35.9 (Cy<sub>2</sub>BH<sub>2</sub>BHCy), 17.6 (Cy<sub>2</sub>BH<sub>2</sub>BHCy).

**Figure S1.** <sup>11</sup>B NMR spectrum (128.4 MHz, C<sub>6</sub>D<sub>6</sub>).



## 1.2. Compound 7

Figure S2.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_6\text{D}_6$ )

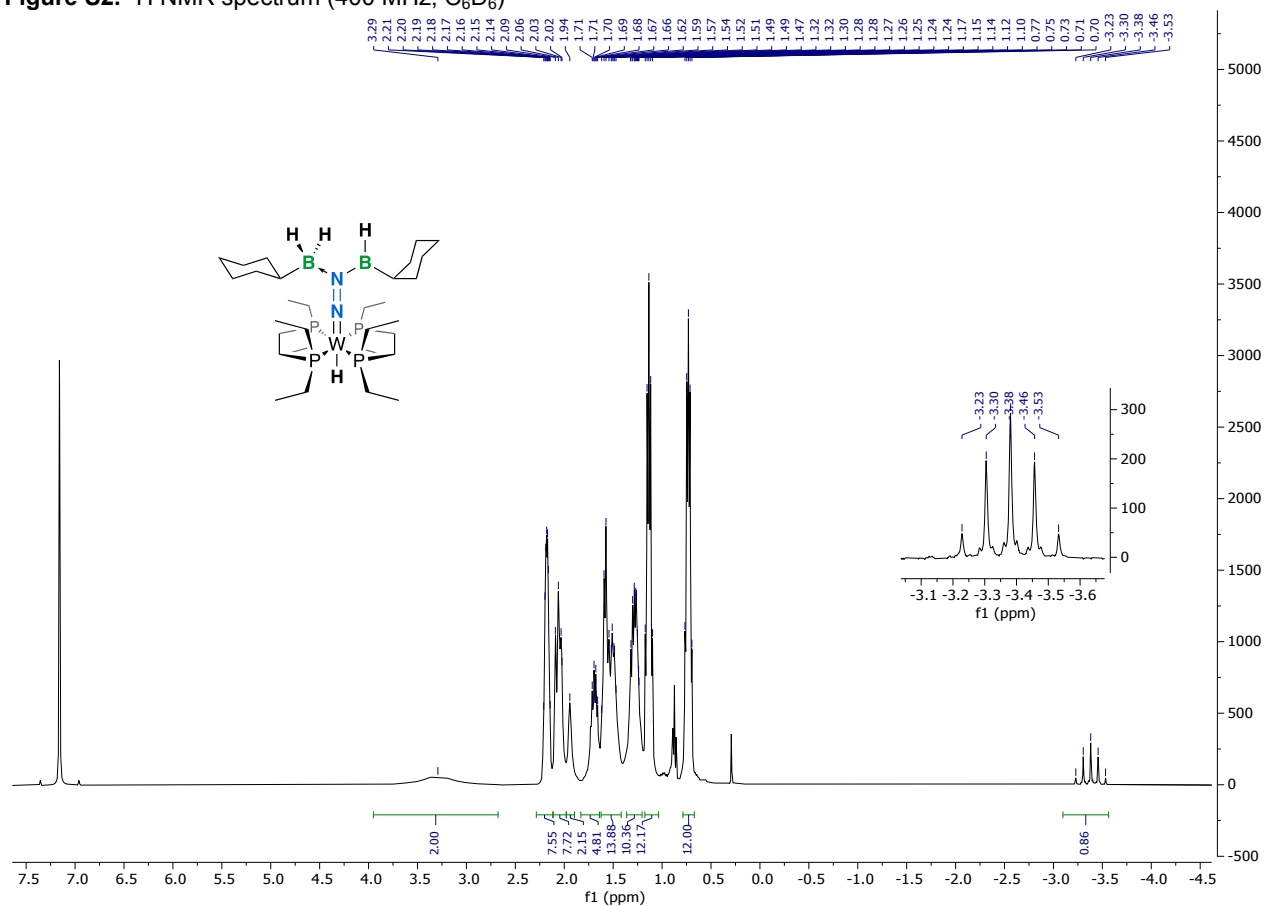


Figure S3.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $\text{C}_6\text{D}_6$ )

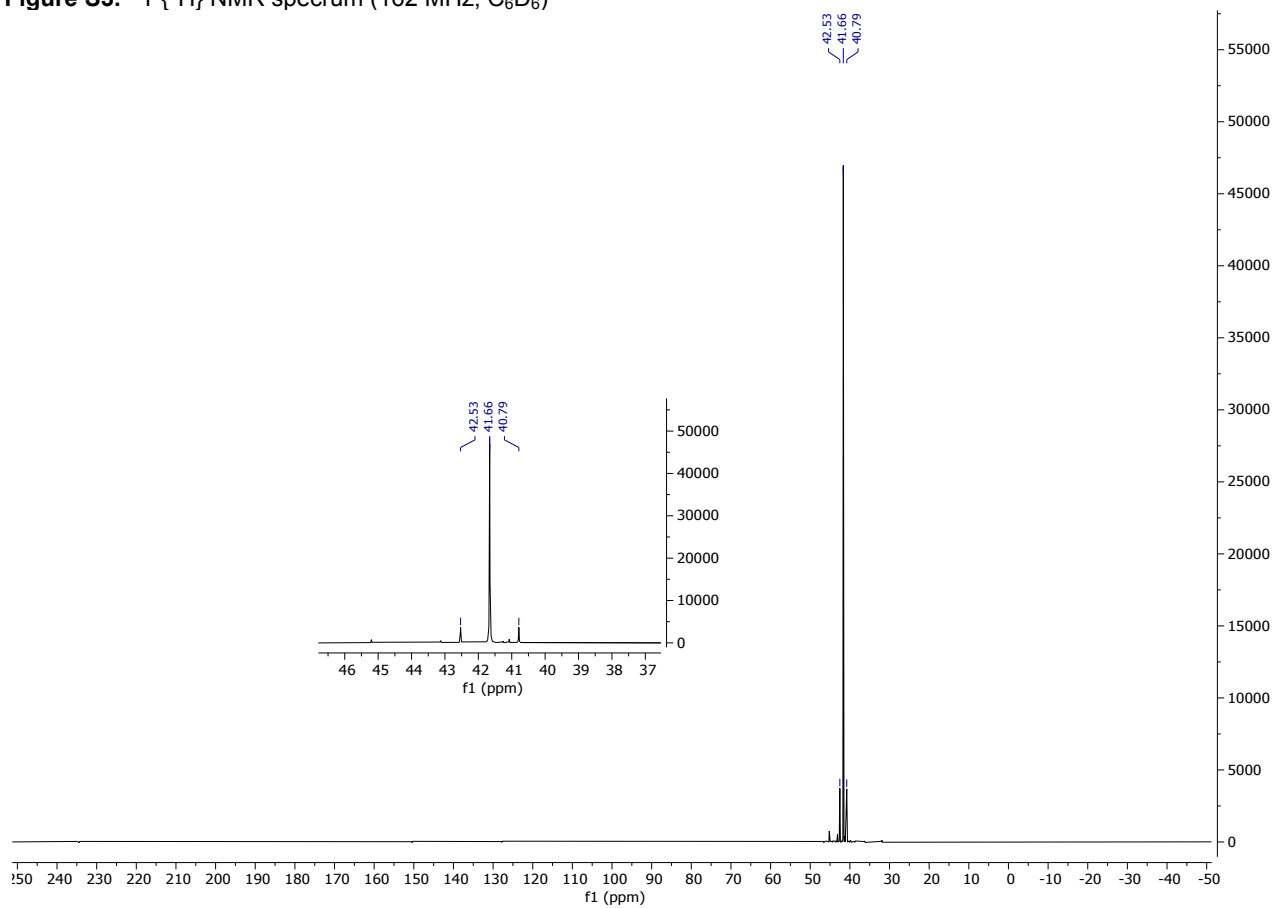


Figure S4.  $^{11}\text{B}$  NMR spectrum (128.4 MHz,  $\text{C}_6\text{D}_6$ )

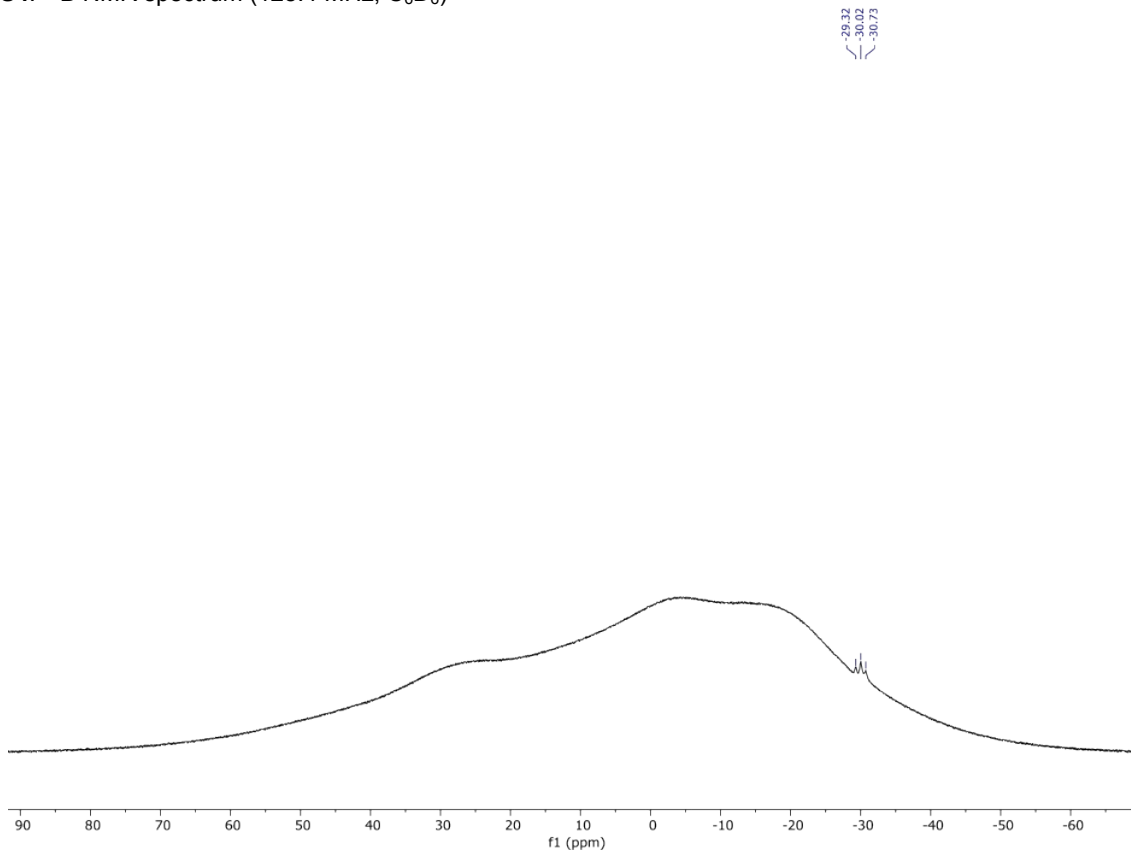
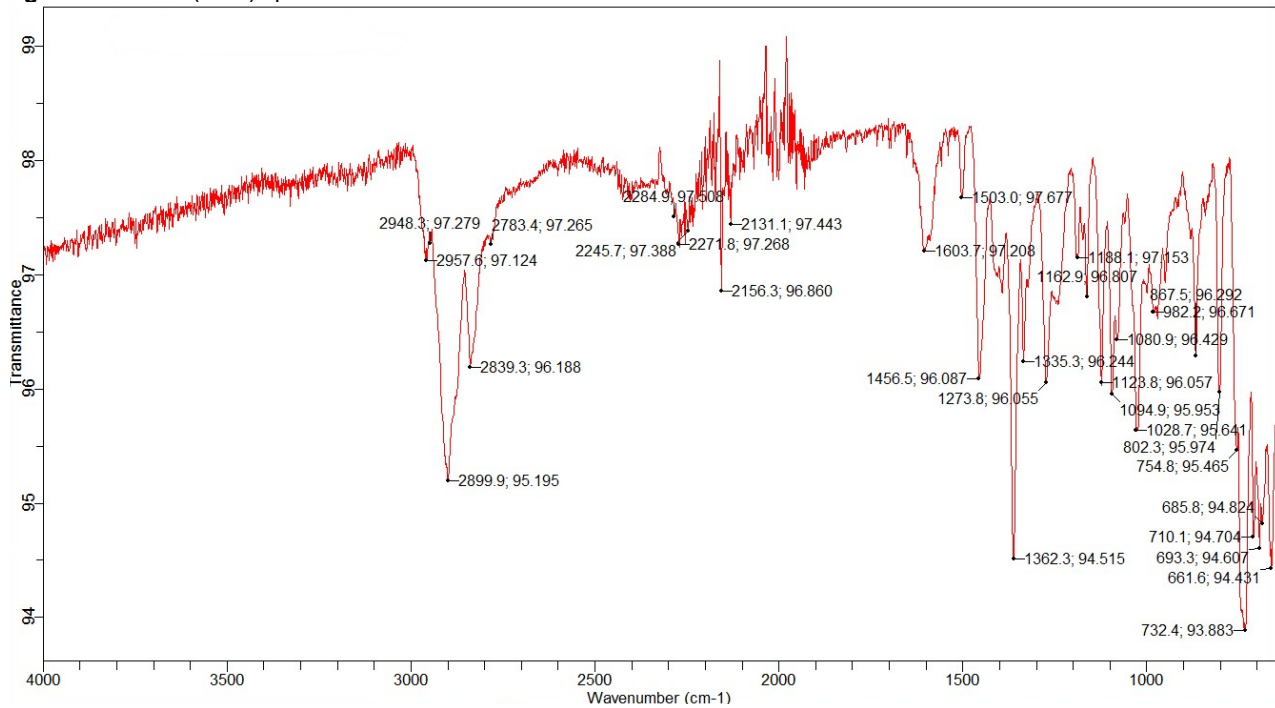


Figure S5. FT IR (ATR) spectrum.

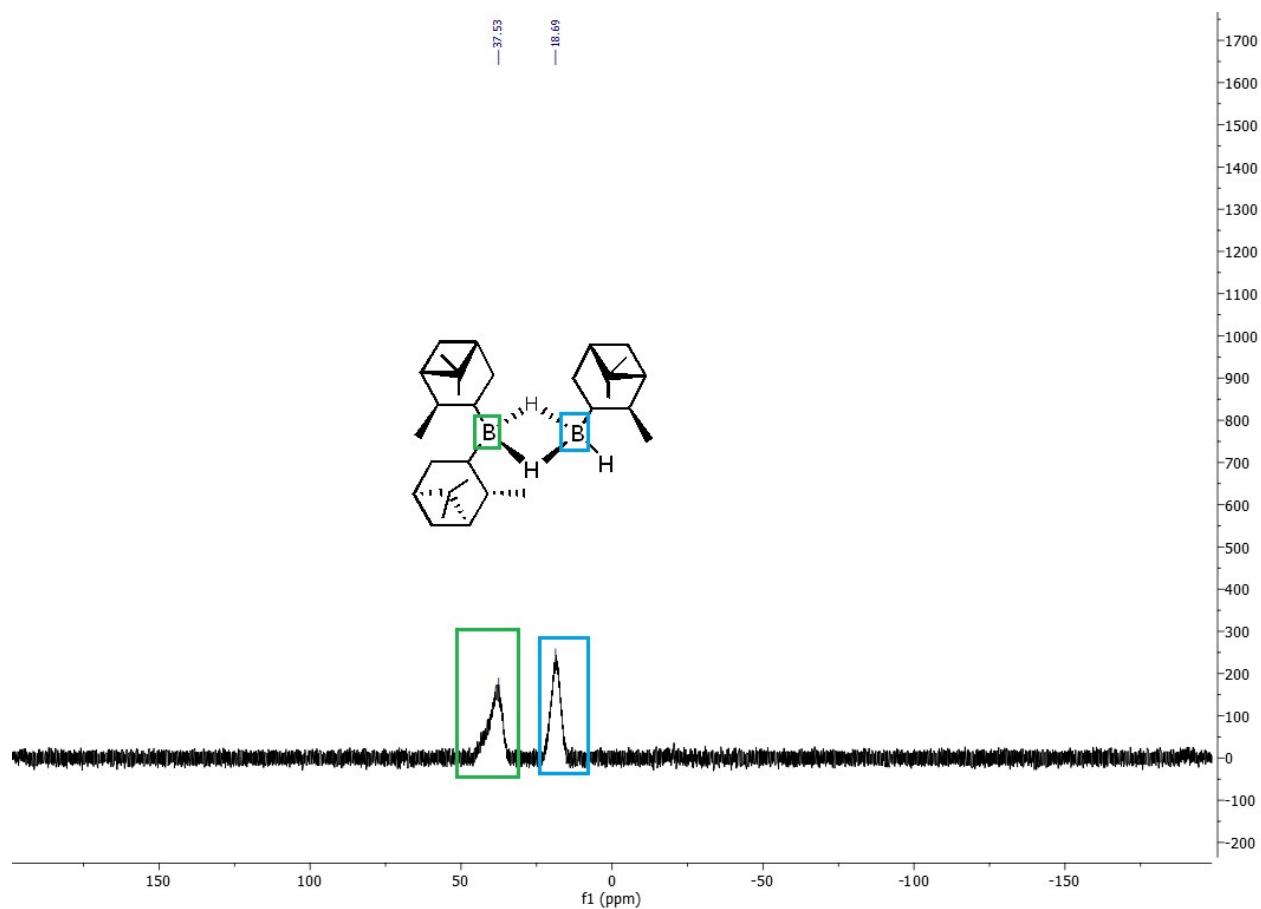


### 1.3. Generation of triisopinocampheylborane

HBIPC<sub>2</sub> (17.2 mg, 60 μmol) is introduced in a flask in a glovebox and is dissolved in 0.5 mL of C<sub>6</sub>D<sub>6</sub> giving a homogeneous solution that was subsequently analyzed by NMR.

**RMN <sup>11</sup>B** (128 MHz, C<sub>6</sub>D<sub>6</sub>) δ 37.5 (IPC<sub>2</sub>BH<sub>2</sub>BHIPC), 18.7 (IPC<sub>2</sub>BH<sub>2</sub>BHIPC).

**Figure S6.** <sup>11</sup>B NMR spectrum (128.4 MHz, C<sub>6</sub>D<sub>6</sub>) with exponential apodization and multiple point baseline correction.



## 1.4. Compound 8

Figure S7.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_6\text{D}_6$ )

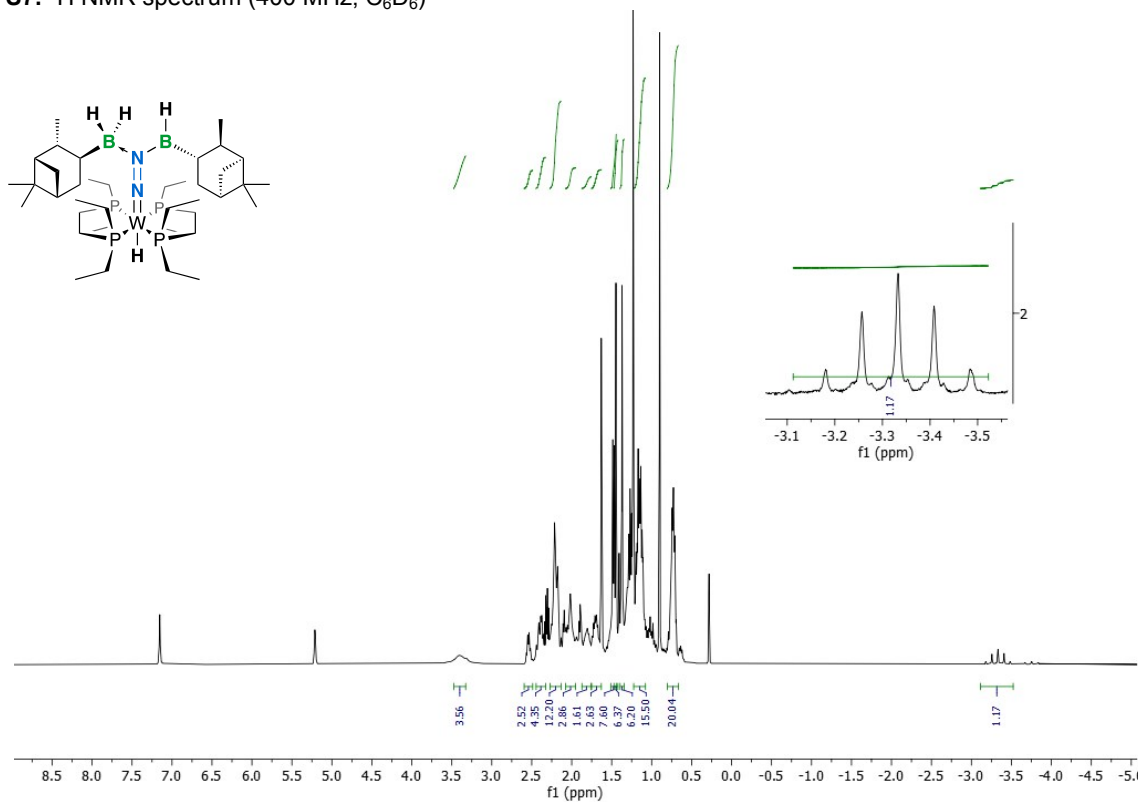


Figure S8.  $^{31}\text{P}$  NMR spectrum (162 MHz,  $\text{C}_6\text{D}_6$ )

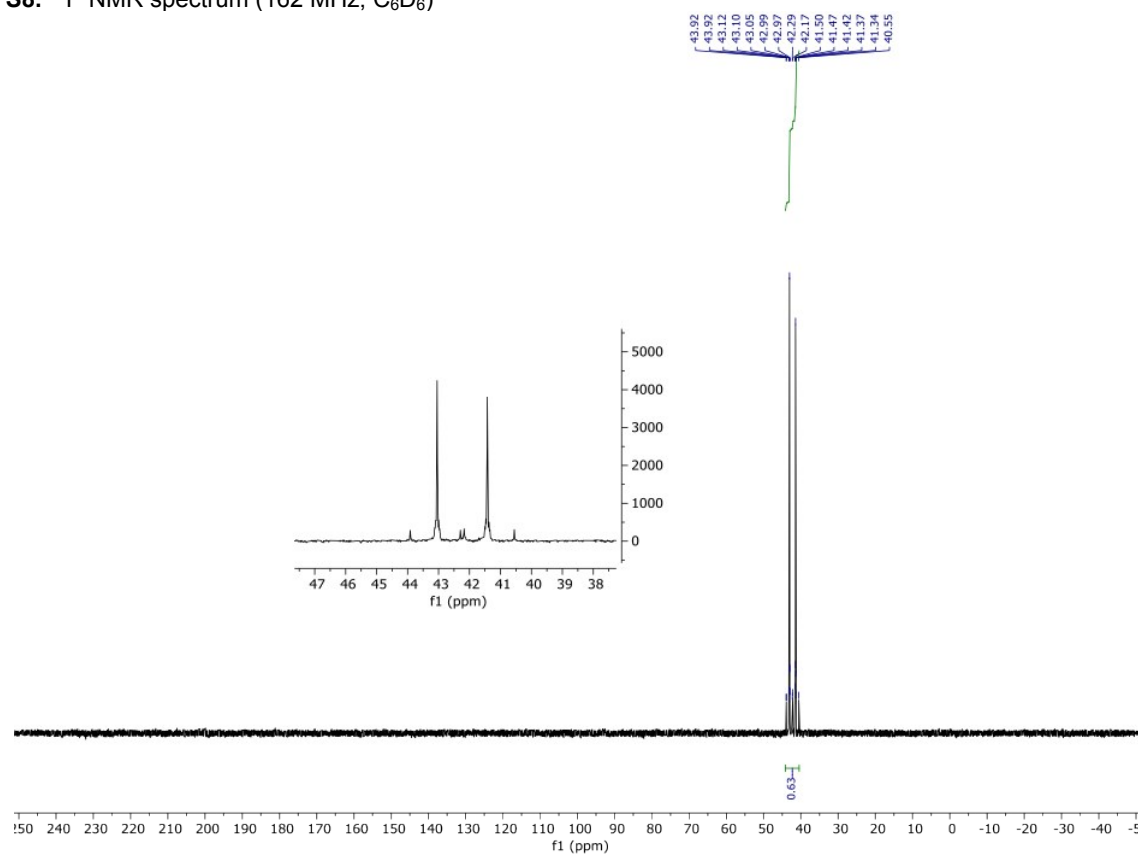


Figure S9.  $^{11}\text{B}$  NMR spectrum (128.4 MHz,  $\text{C}_6\text{D}_6$ )

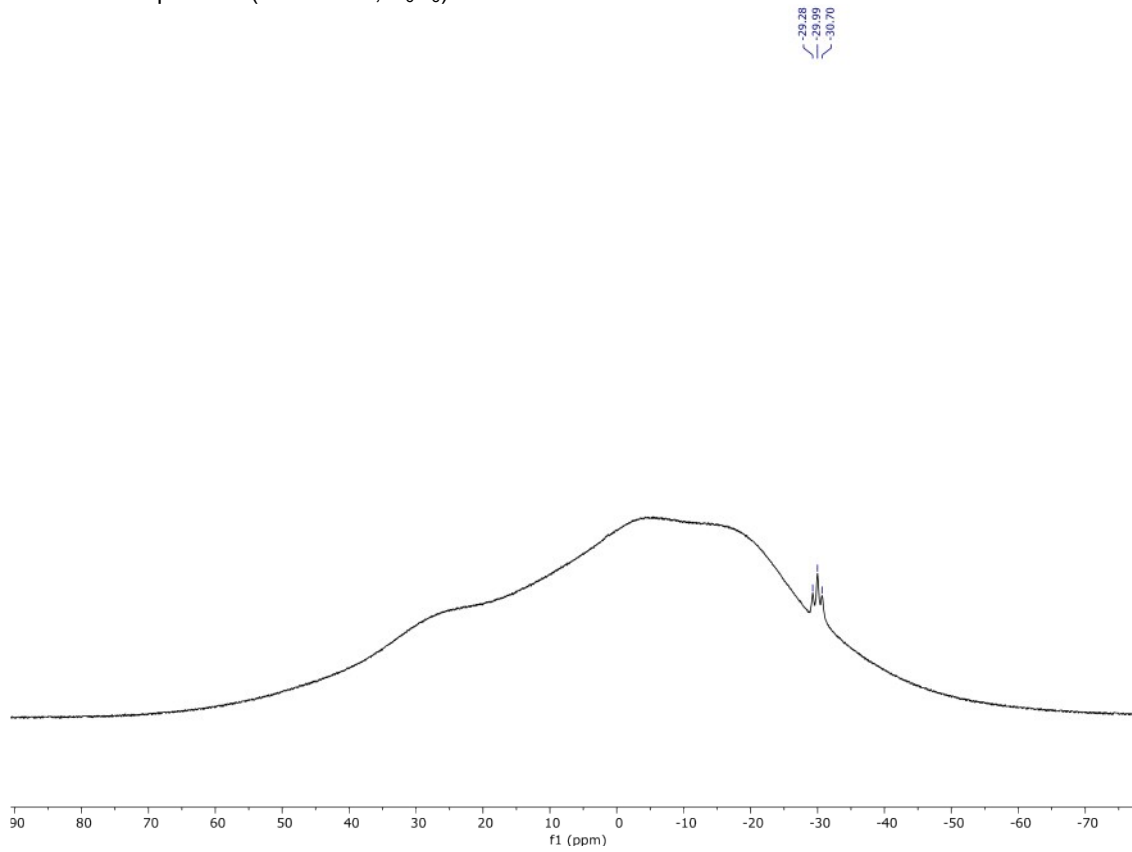
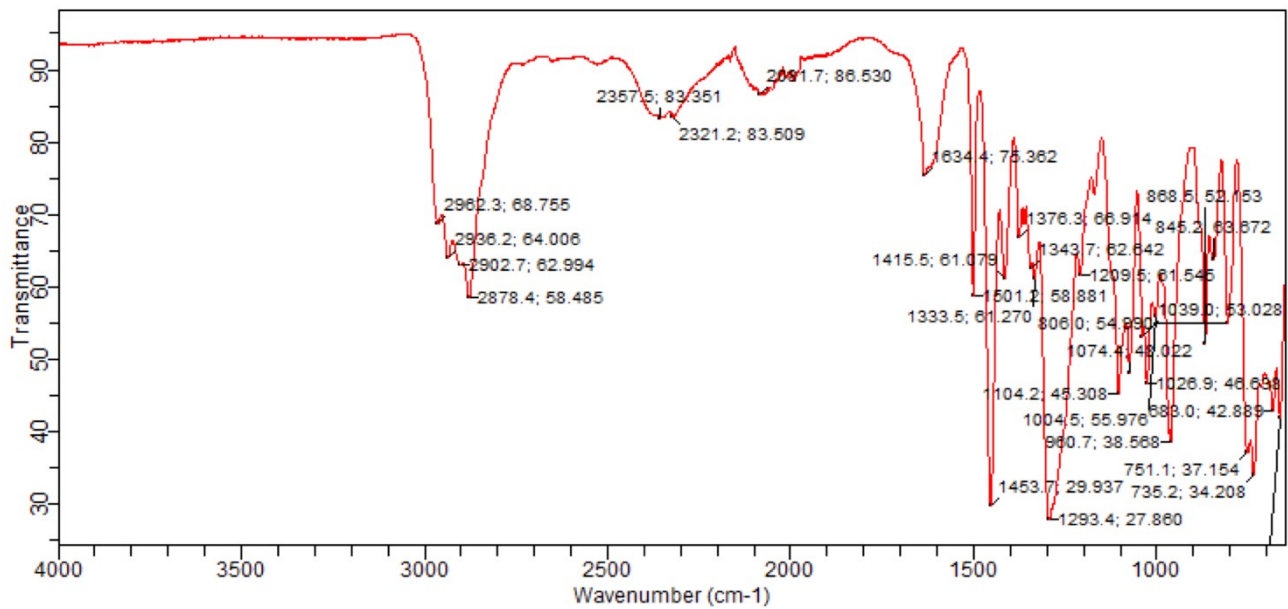


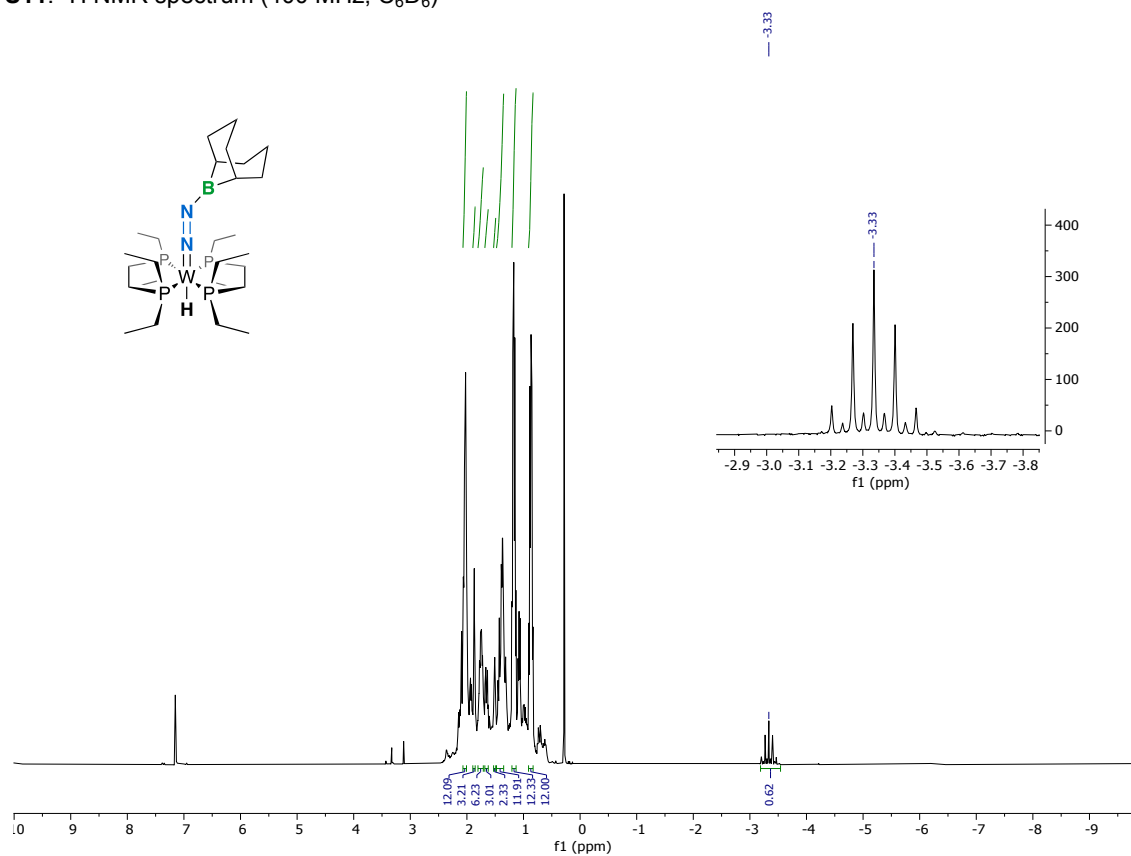
Fig. S10. FT IR (ATR) spectrum





## 1.5. Compound **9** in the reaction mixture

**Figure S11.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_6\text{D}_6$ )



**Figure S12.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $\text{C}_6\text{D}_6$ )

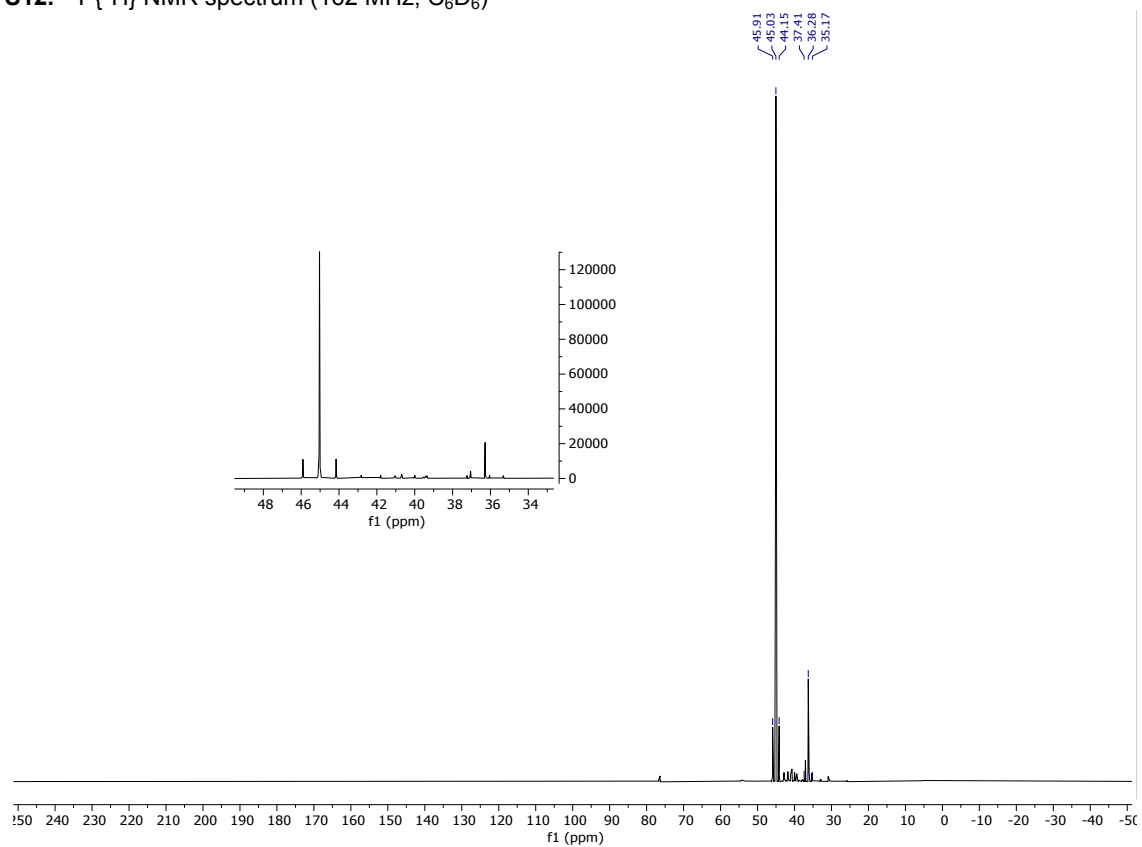


Figure S13.  $^{11}\text{B}$  NMR spectrum (128.4 MHz,  $\text{C}_6\text{D}_6$ )

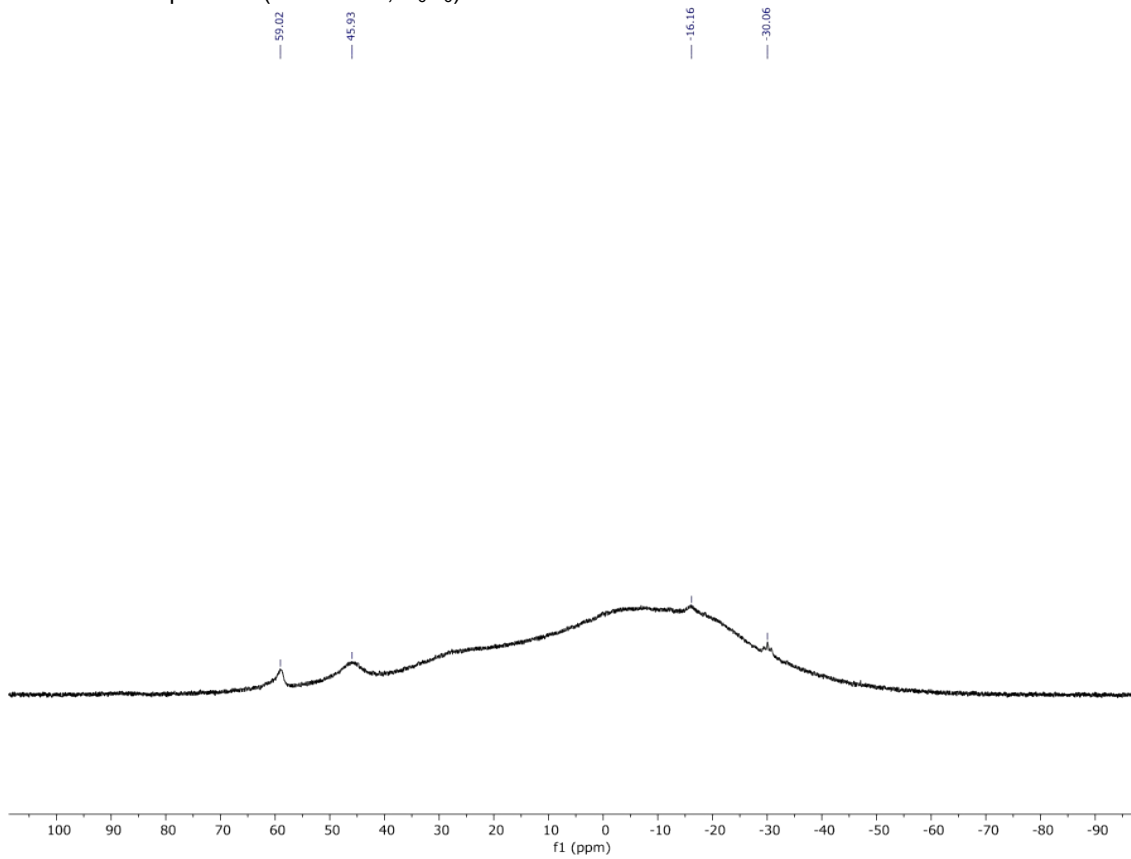
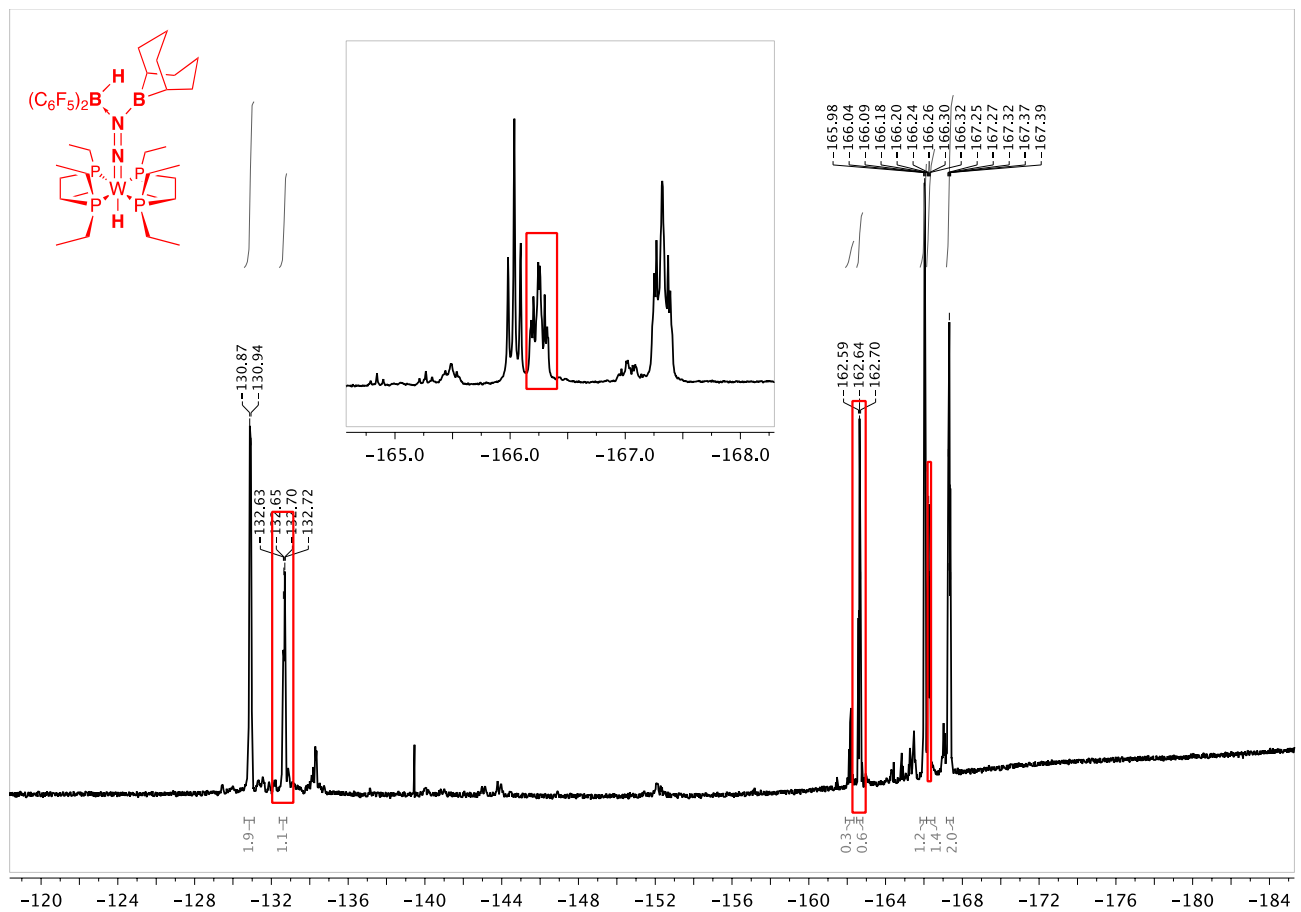


Figure S14.  $^{19}\text{F}$  NMR spectrum (377 MHz,  $\text{C}_6\text{D}_6$ )



### Diffusion-ordered spectroscopy (DOSY)

This experiment was run on a Bruker Avance NEO 600, directly on the reaction mixture of **2**, 9-BBN and catalytic amounts of **1**. After 14 d of heating the C<sub>6</sub>D<sub>6</sub> solution, **2** and **9** are present in a ca. 25:75 mixture according to <sup>31</sup>P NMR integration. Diffusion coefficients are expressed in cm<sup>2</sup>·s<sup>-1</sup>. Gaussian fit to diffusion peak intensities gives a diffusion coefficient D of 5.07·10<sup>-6</sup> cm<sup>2</sup>·s<sup>-1</sup> for [W(depe)<sub>2</sub>(N<sub>2</sub>)<sub>2</sub>] (**2**) and 4.64·10<sup>-6</sup> cm<sup>2</sup>·s<sup>-1</sup> for **9**. Using the Stokes-Einstein equation, the Stokes radius of **2** and **9** were estimated to 6.1 and 6.7 Å, respectively. The closeness of these radii indeed suggests that **9** is monomeric in solution.

**Figure S15.** <sup>1</sup>H-DOSY NMR experiment (600 MHz, C<sub>6</sub>D<sub>6</sub>). On the vertical axis one read the diffusion units (cm<sup>2</sup>·s<sup>-1</sup>)

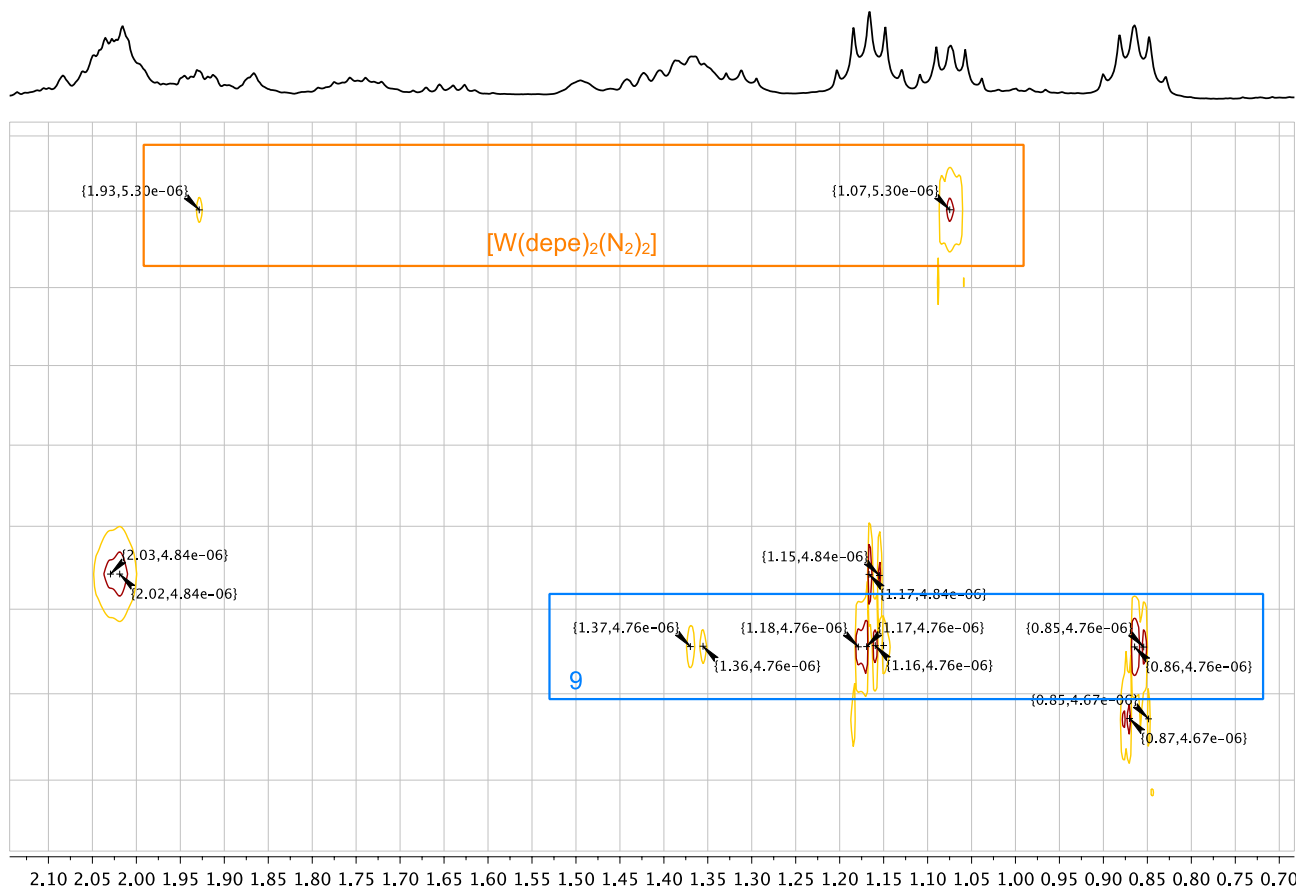




Figure S18.  $^{11}\text{B}$  NMR spectrum (128.4 MHz,  $\text{C}_6\text{D}_6$ )

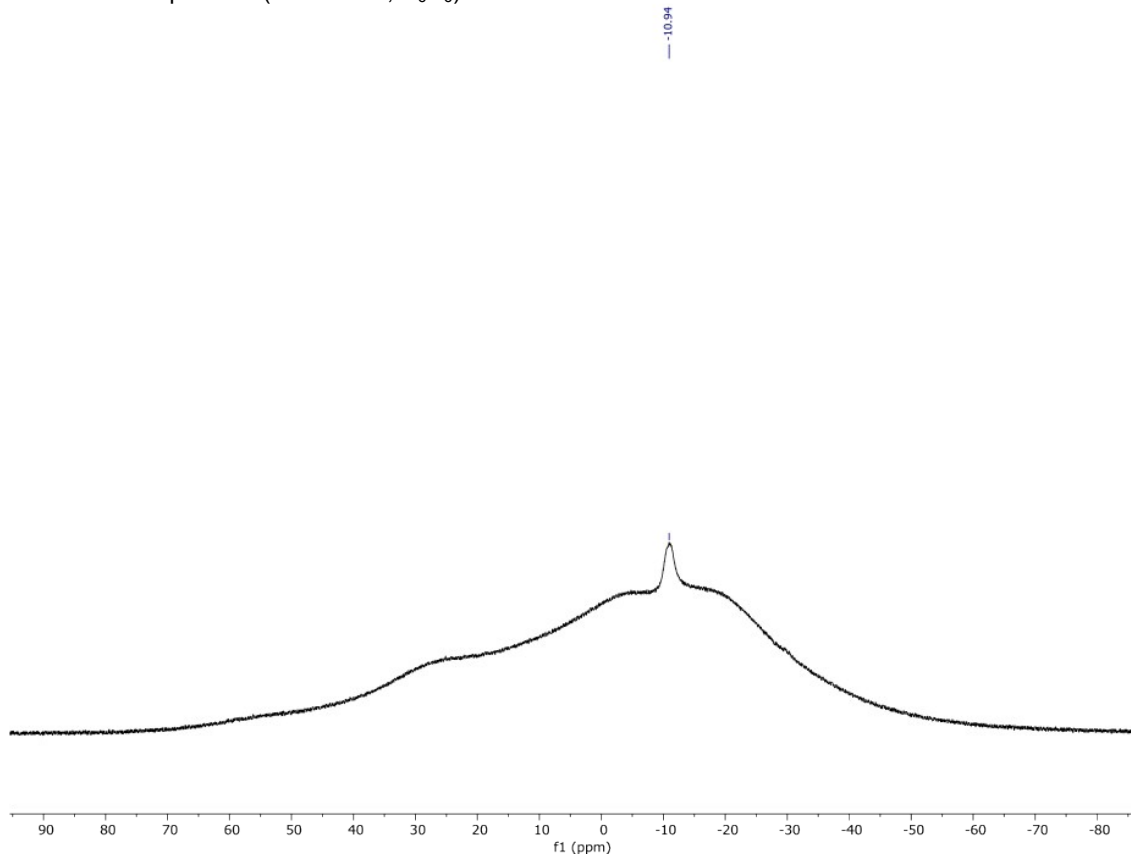


Figure S19.  $^{19}\text{F}$  NMR spectrum (377 MHz,  $\text{C}_6\text{D}_6$ )

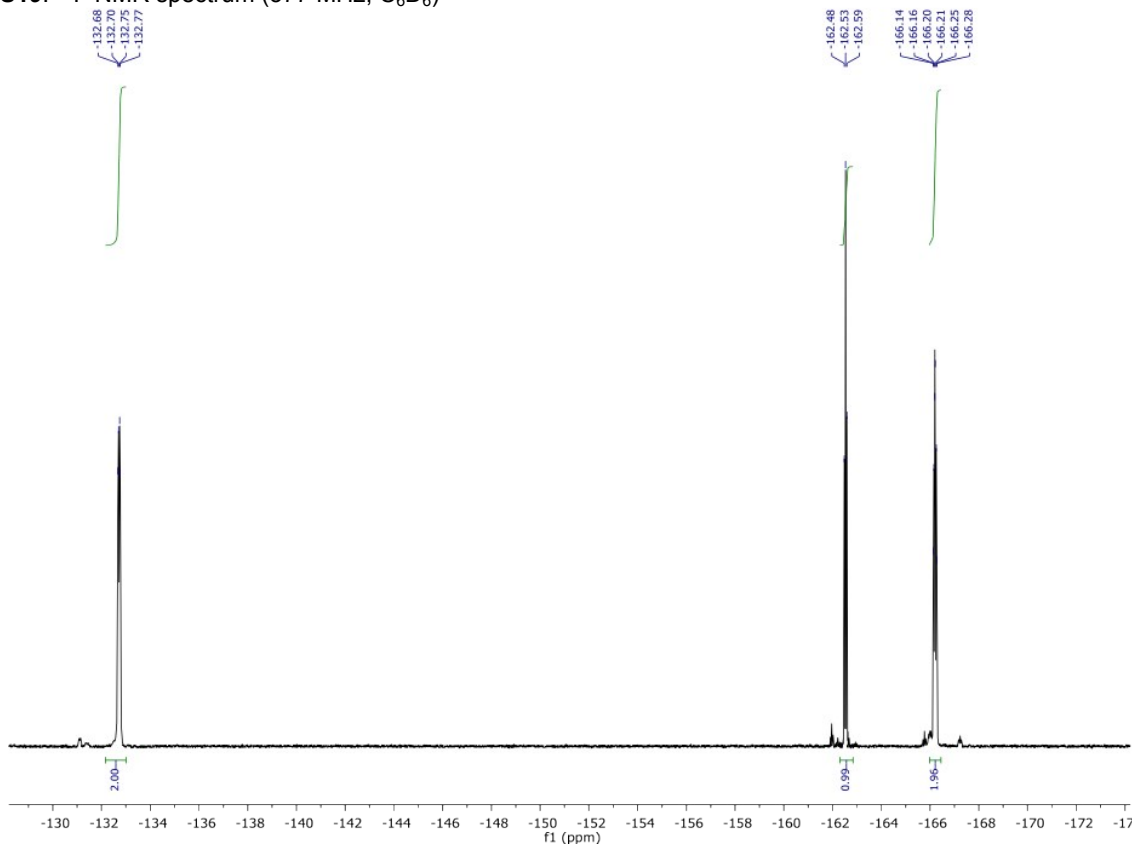
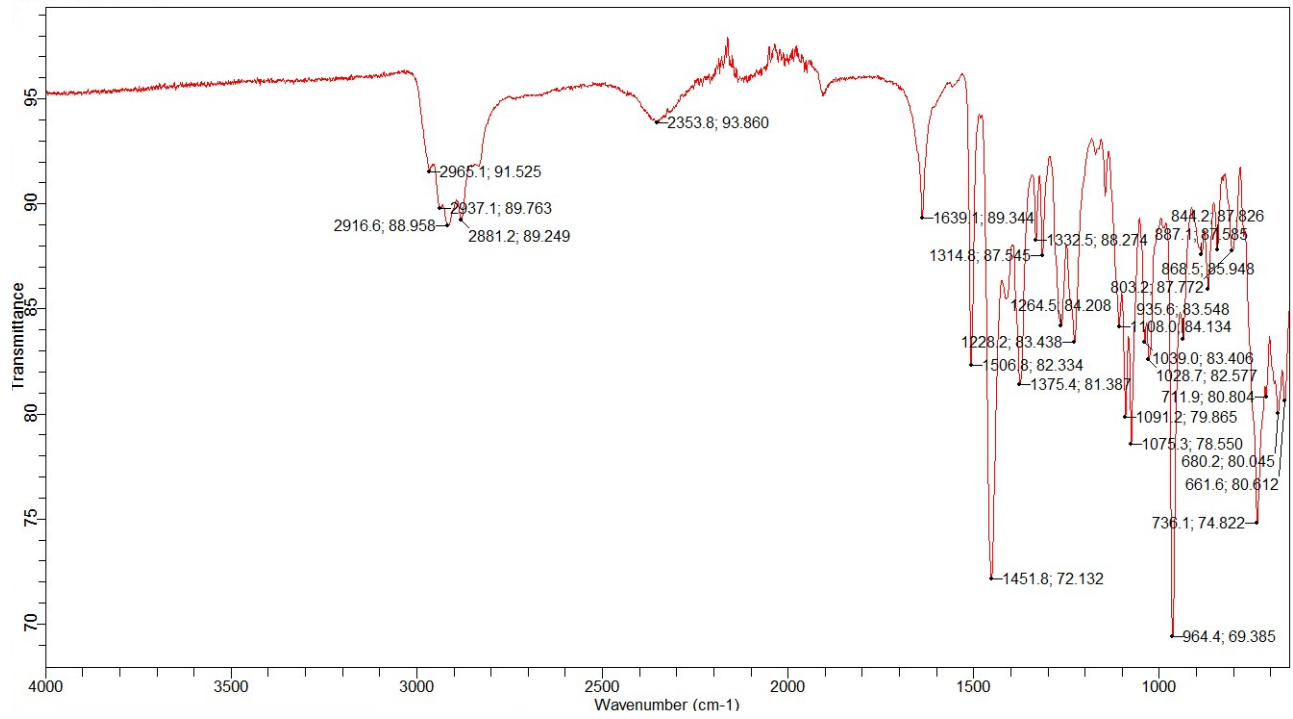


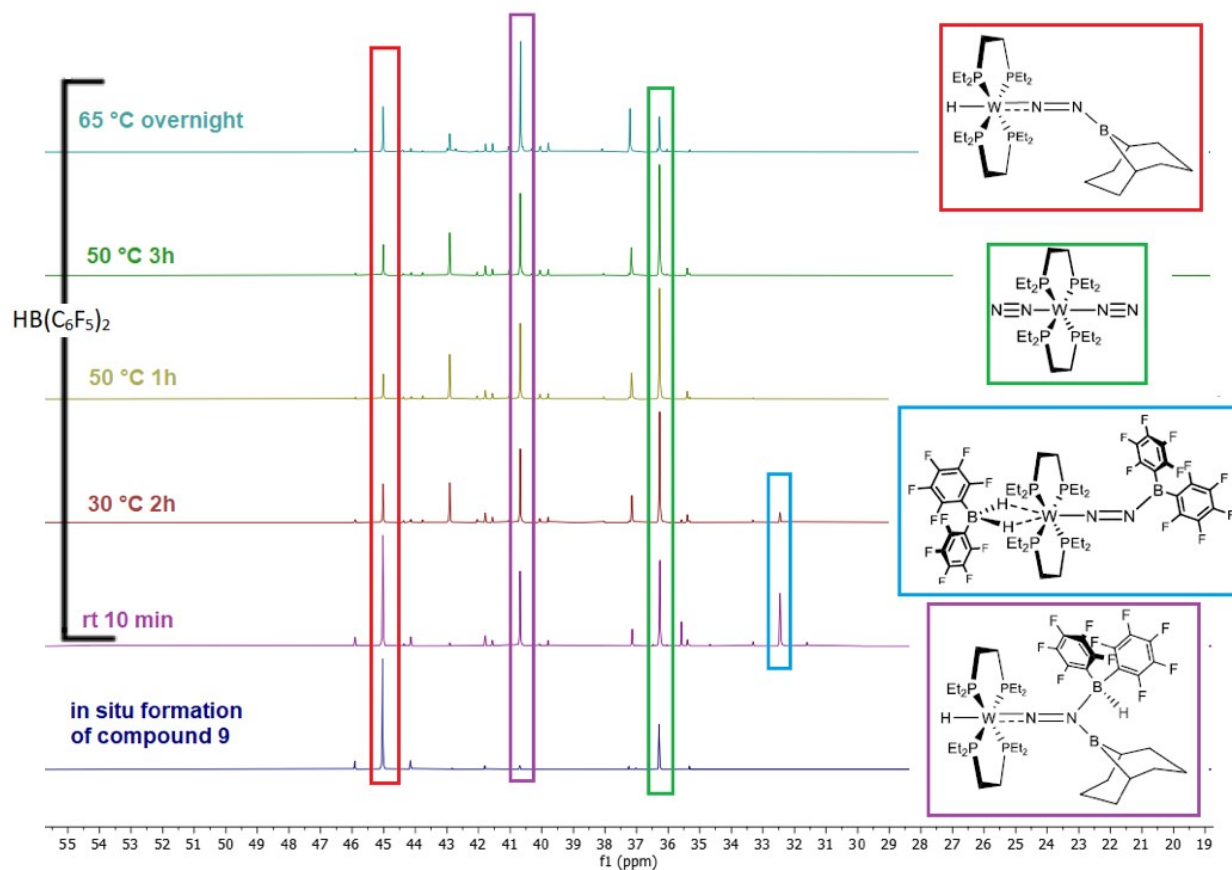
Figure S20. FT IR (ATR) spectrum



### 1.7. Reaction between compound **9** and $\text{HB}(\text{C}_6\text{F}_5)_2$ (**1**)

Compound **9** was formed *in-situ* and then  $\text{HB}(\text{C}_6\text{F}_5)_2$  (**1**) was added. We monitored the reaction by NMR spectroscopy. Four different products were observed during the reaction leading mainly to the formation of compound **10**.

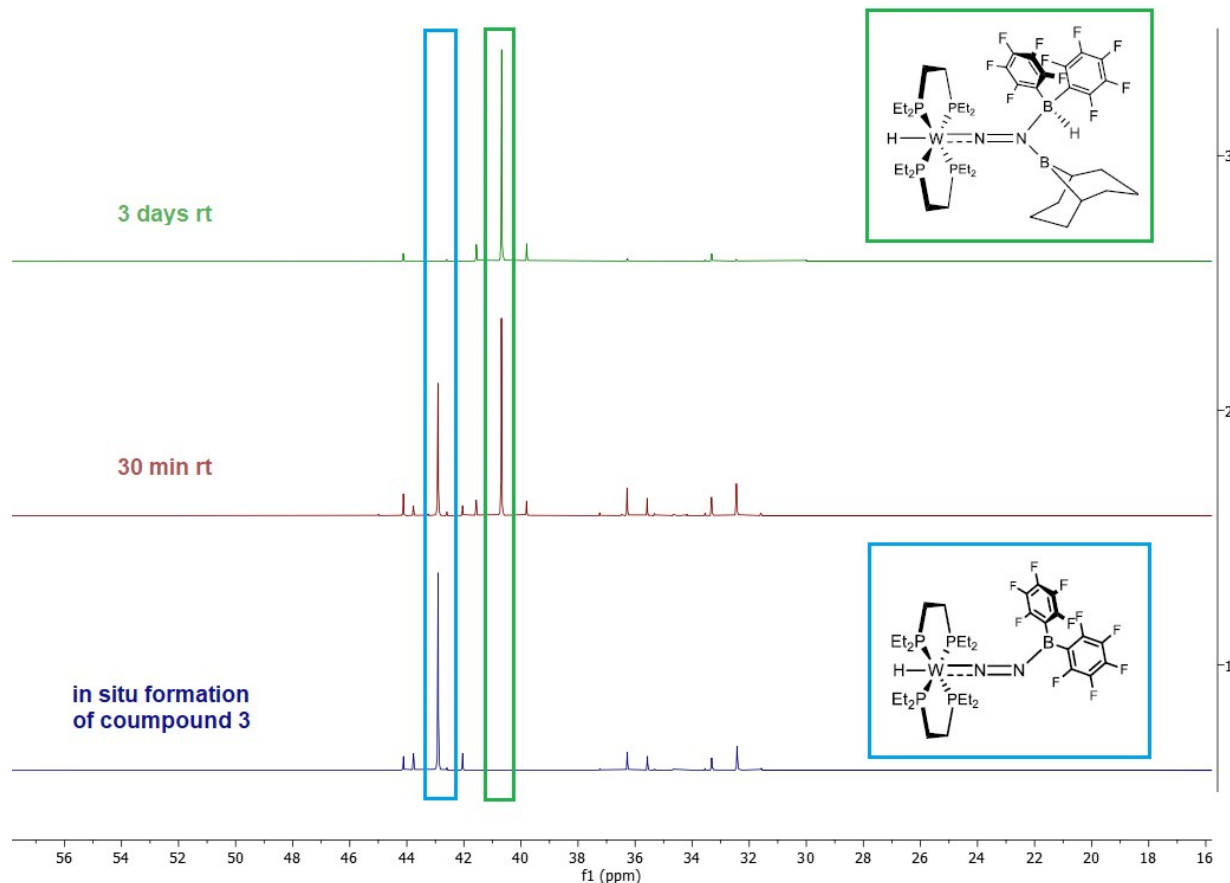
**Figure S21.** Stacked  $^{31}\text{P}$  NMR spectra (162 MHz,  $\text{C}_6\text{D}_6$ ) monitoring the reaction of **9** with  $\text{HB}(\text{C}_6\text{F}_5)_2$



### 1.8. Reaction between compound **3** and 9-BBN

Compound **3** was formed *in-situ* and then 9-BBN was added. We monitored the reaction by NMR spectroscopy leading mainly to the formation of compound **10**.

**Figure S22.** Stacked  $^{31}\text{P}$  NMR spectra (162 MHz,  $\text{C}_6\text{D}_6$ ) monitoring the reaction of **3** with 9-BBN



### 1.9. Reaction between compound **10** and Lewis bases

After formation of compound **10** *in-situ*, a drop (excess) of  $\text{PMe}_3$ ,  $\text{C}_5\text{H}_5\text{N}$  or TMEDA was added. After prolonged heating no reaction could be observed in any cases.

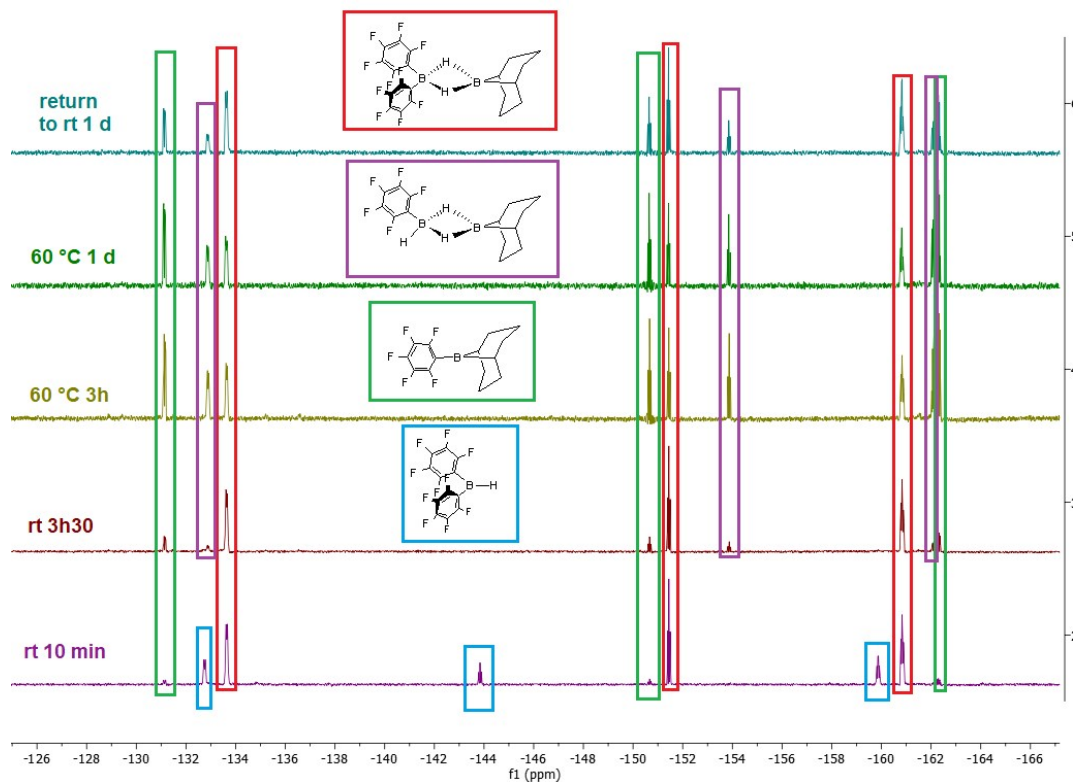
After formation of compound **10** *in-situ*, one equivalent of compound **2** was added and prolonged heating gave no reaction (only traces of compound **3** could be observed).



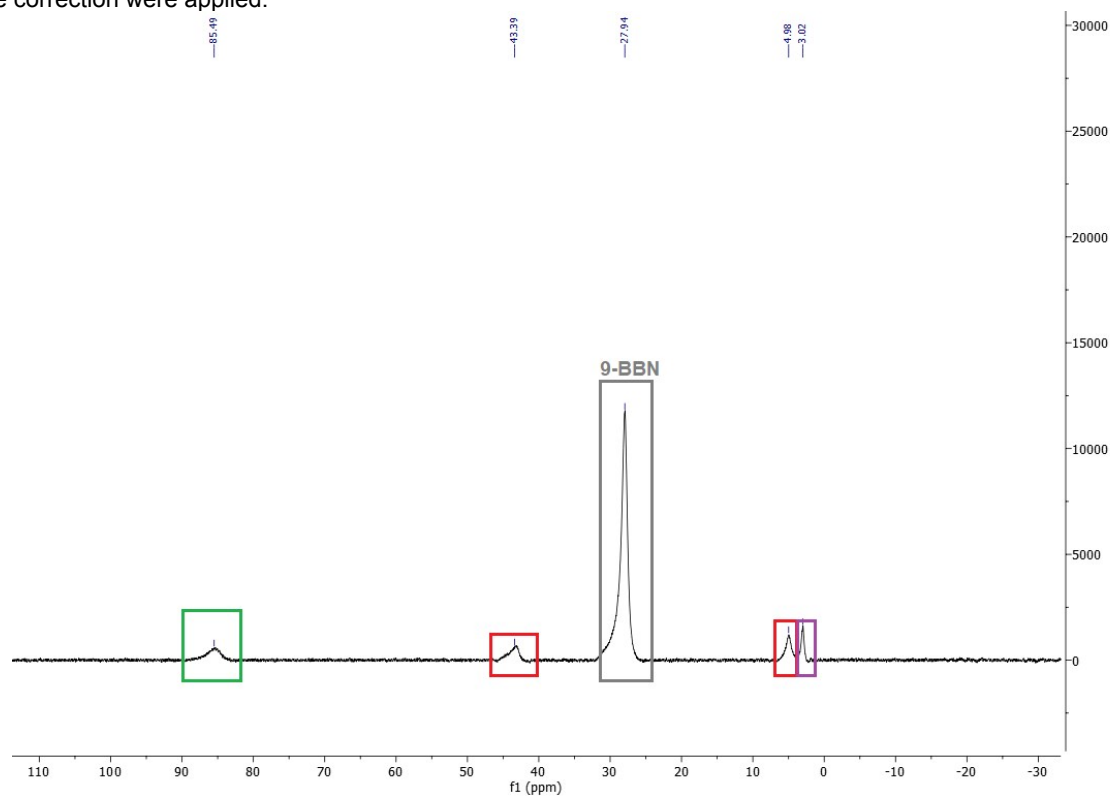
## 1.10. Reaction between 9-BBN and $\text{HB}(\text{C}_6\text{F}_5)_2$ (**1**)

In a glovebox, 9-BBN (2.6 mg, 21  $\mu\text{mol}$ , 1.0 equiv.) and  $\text{HB}(\text{C}_6\text{F}_5)_2$  (**1**, 0.8, 2.3  $\mu\text{mol}$ , 0.11 equiv.) were weighed in a 4-mL vial and solubilized in 0.5 mL of  $\text{C}_6\text{D}_6$ . The reaction was monitored by NMR spectroscopy and led to an equilibrated mixture between at least three compounds.

**Figure S23.** Stacked  $^{31}\text{P}$  NMR spectra (162 MHz,  $\text{C}_6\text{D}_6$ ) monitoring the reaction of  $\text{HB}(\text{C}_6\text{F}_5)_2$  with 9-BBN



**Figure S24.**  $^{11}\text{B}$  NMR spectrum after cooling to RT for 1 day (128.4 MHz,  $\text{C}_6\text{D}_6$ ). Exponential apodization and multiple point baseline correction were applied.



# 1.11. Compound 11

Figure S25.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{C}_6\text{D}_6$ )

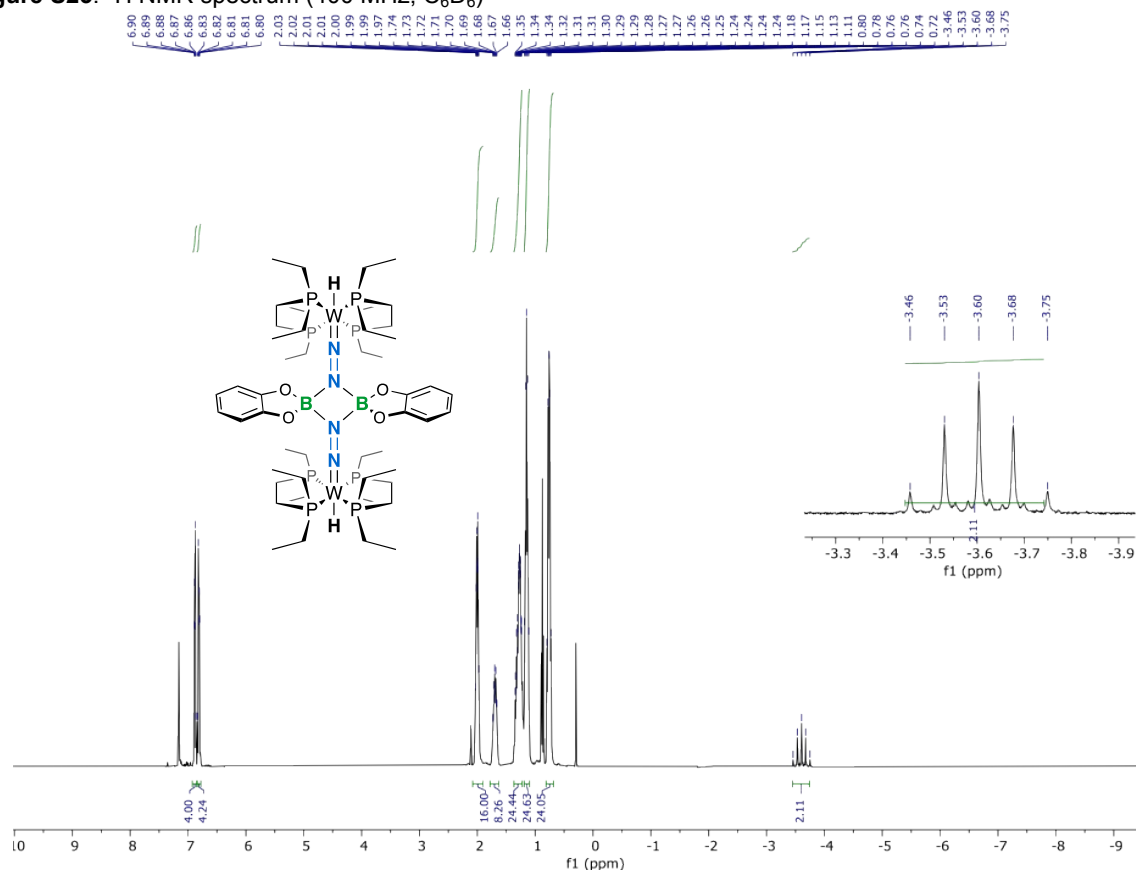


Figure S26.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz,  $\text{C}_6\text{D}_6$ )

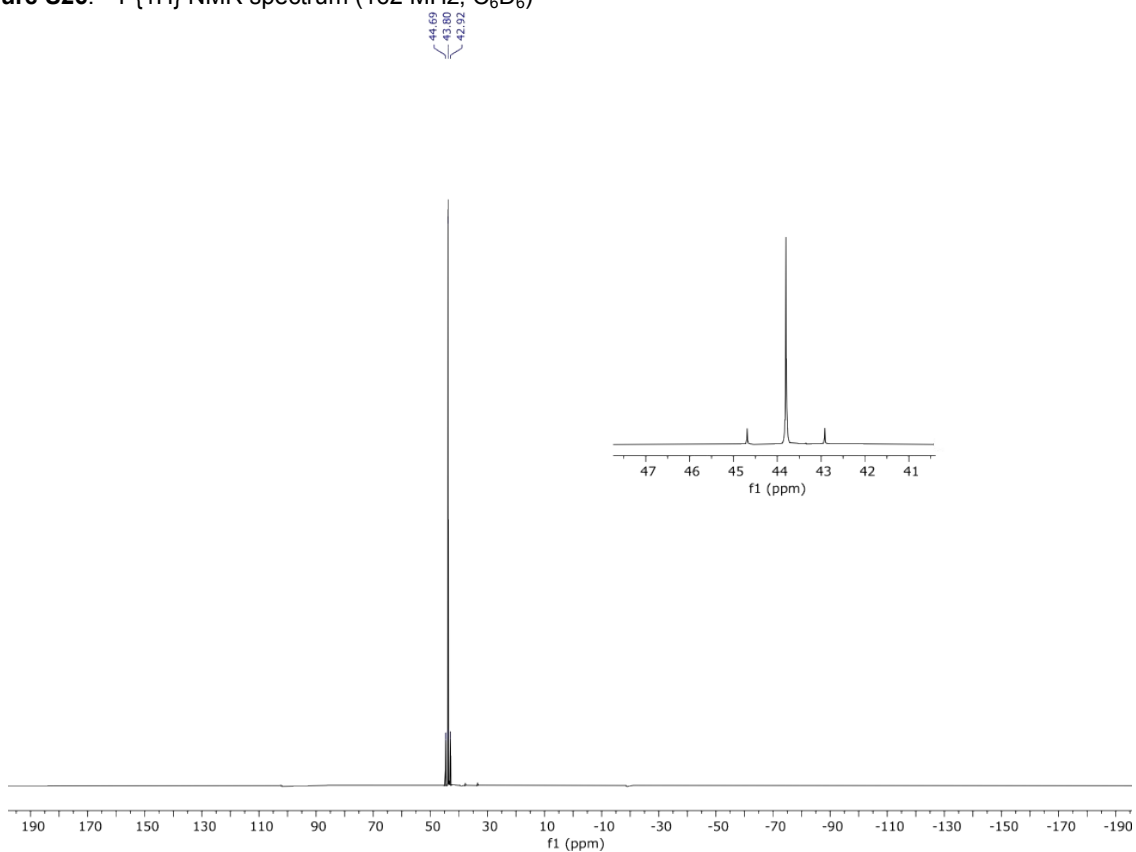
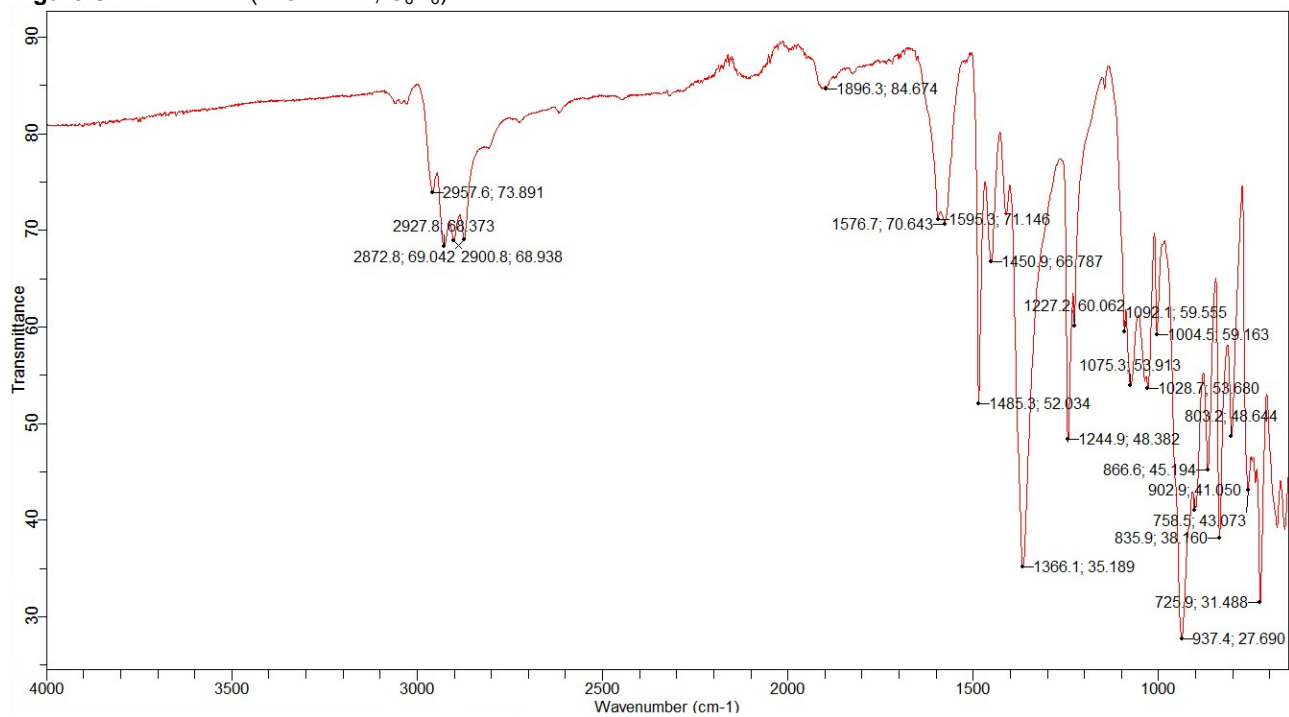


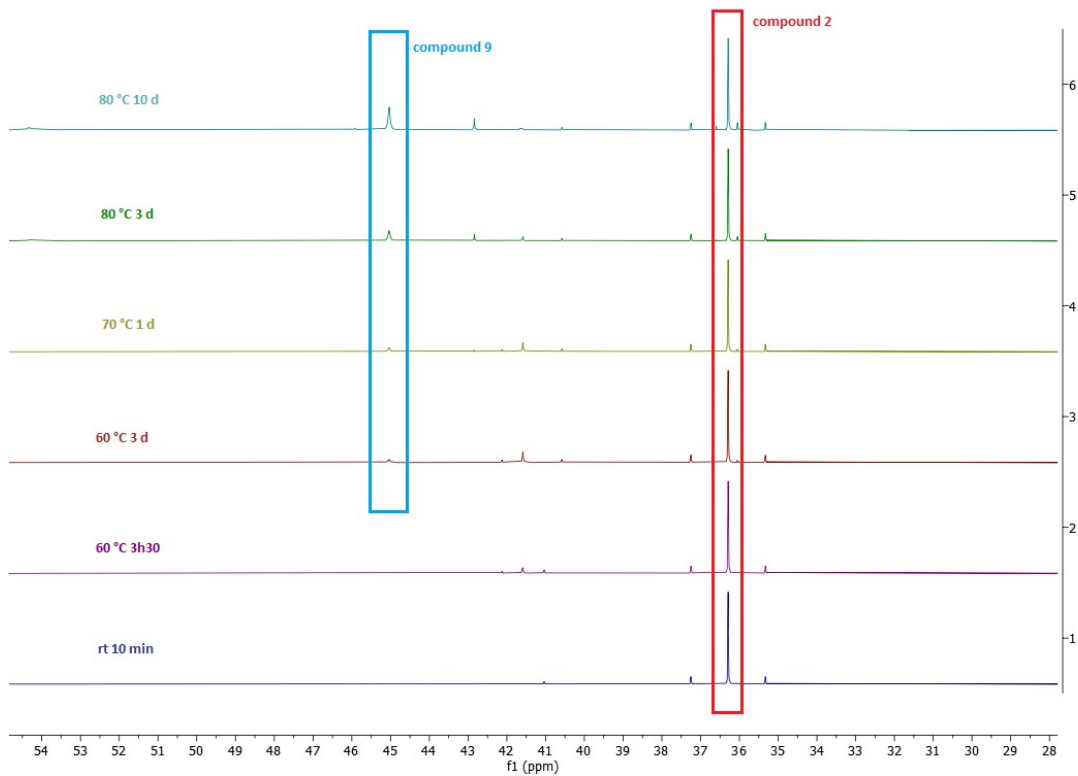
Figure S27.  $^{11}\text{B}$  NMR (128.4 MHz,  $\text{C}_6\text{D}_6$ )



### 1.12. Formation of complex **9** with HBcat as a catalyst

In a glovebox, *trans*-[W(N<sub>2</sub>)<sub>2</sub>(depe)<sub>2</sub>] (**2**, 19.7 mg, 30 μmol, 1.0 equiv.), 9-BBN (3.8 mg, 30 μmol, 1.0 equiv.) and HBcat (0.5 μL of a 10% solution in C<sub>6</sub>D<sub>6</sub>, 2.3 μmol, 0.11 equiv.) were weighted in a 4-mL vial and dissolved in 0.5 mL of C<sub>6</sub>D<sub>6</sub>. The resulting solution was transferred to an NMR tube equipped with a J. Young valve and the reaction was monitored by NMR spectroscopy.

**Figure S28.** Stacked <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>)

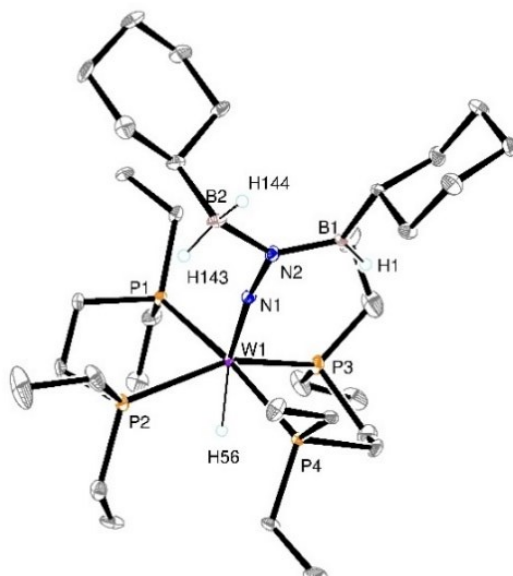


## 2. Crystallography

### 2.1. Data Collection and Refinement

Data for compounds **7**, **10** and **11** were collected at low temperature (100 K) on a Bruker Kappa Apex II diffractometer using a Mo-K $\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ) micro-source and equipped with an Oxford Cryosystems Cryostream Cooler Device. The structures have been solved by Direct Methods and refined by means of least-squares procedures using the SHELXS97<sup>[S1]</sup> program included in the softwares package WinGX version 1.63<sup>[S2]</sup> or with the aid of the software package Crystal<sup>[S3]</sup>. The Atomic Scattering Factors were taken from International tables for X-Ray Crystallography<sup>[S4]</sup>. Hydrogen atoms bonding with boron and tungsten were anisotropically refined; all other hydrogen atoms were placed geometrically and refined using a riding model. All non-hydrogens atoms were anisotropically refined. Drawing of molecules in the following figures were performed with the program ORTEP32<sup>[S5]</sup> with 30% probability displacement ellipsoids for non-hydrogen atoms. The crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers **CCDC 2058894-2058896**.

## 2.2. X-ray Analysis of Compound 7 (CCDC 2058894)

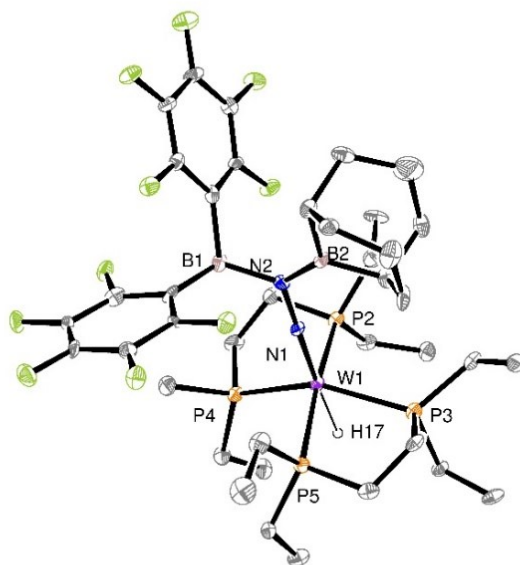


**Figure S29.** X-ray crystal structure of complex **7**, with ellipsoids set at the 30% probability level; hydrogen atoms omitted for clarity at the exception of those bound to heteroatoms.

**Table S1.** Crystallographic data for **7**.

Chemical formula	C <sub>32</sub> H <sub>74</sub> B <sub>2</sub> N <sub>2</sub> P <sub>4</sub> W
Mr	816.32
Crystal system, space group	Monoclinic, P2 <sub>1</sub> /n
Temperature (K)	100 K
a, b, c (Å)	12.04190 (2), 20.70460 (3), 15.84060 (3)
α, β, γ (°)	92.842 (3)
V (Å <sup>3</sup> )	3944.56 (2)
Z	4
Radiation type	Mo Kα radiation, λ = 0.71073 Å
μ (mm <sup>-1</sup> )	3.11
Crystal size (mm)	0.10 × 0.04 × 0.02
Data collection	
Diffractometer	Bruker Kappa APEX II diffractometer
Absorption correction	multi-scan SADABS (Siemens, 1996)
Tmin, Tmax	0.84, 0.94
No. of measured, independent and observed [ I  > 2σ(I)] reflections	113933, 9696, 6634
Rint	0.138
θmax (°)	28.3
Refinement	
R[F <sup>2</sup> > 2σ(F <sup>2</sup> )], wR(F <sup>2</sup> ), S	0.049, 0.024, 09.0
No. of reflections	6630
No. of parameters	382
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρmax, Δρmin (e Å <sup>-3</sup> )	4.80, -4.01

### 2.3. X-ray Analysis of Compound **10** (CCDC 2058896)

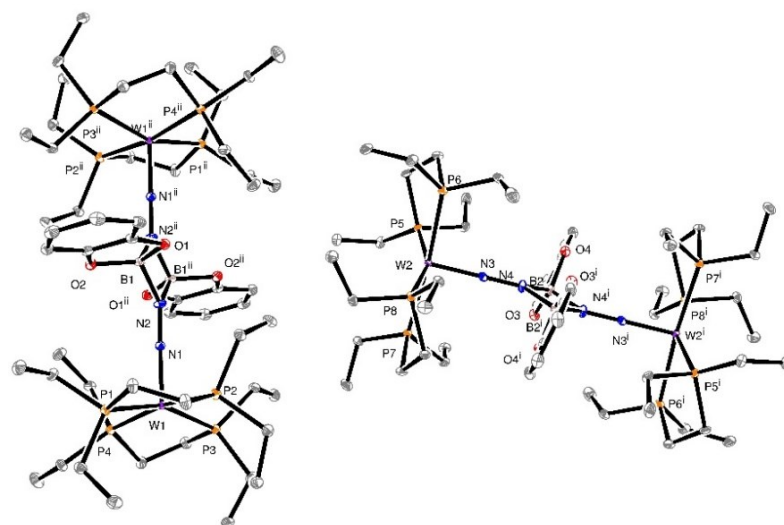


**Figure S30.** X-ray crystal structure of complex **10**, with ellipsoids set at the 30% probability level; hydrogen atoms omitted for clarity at the exception of those bound to heteroatoms.

**Table S2.** Crystallographic data for **10**.

Chemical formula	C <sub>87</sub> H <sub>136</sub> B <sub>4</sub> F <sub>20</sub> N <sub>4</sub> P <sub>8</sub> W <sub>2</sub>
Mr	2276.76
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	110 K
a, b, c (Å)	21.15760 (4), 19.95340 (4), 23.90660 (4)
α, β, γ (°)	106.795 (3)
V (Å <sup>3</sup> )	9662.06 (13)
Z	4
Radiation type	Mo Kα radiation, λ = 0.71073 Å
μ (mm <sup>-1</sup> )	2.60
Crystal size (mm)	0.12 × 0.07 × 0.02
Data collection	
Diffractometer	Bruker Kappa APEX II diffractometer
Absorption correction	multi-scan SADABS (Siemens, 1996)
Tmin, Tmax	0.71, 0.95
No. of measured, independent and observed [ I  > 2σ(I)] reflections	77544, 8550, 4245
Rint	0.166
θmax (°)	25.1
Refinement	
R[F <sup>2</sup> > 2σ(F <sup>2</sup> )], wR(F <sup>2</sup> ), S	0.041, 0.041, 0.92
No. of reflections	4240
No. of parameters	566
H-atom treatment	H atoms parameters constrained
Δpmax, Δpmin (e Å <sup>-3</sup> )	1.30 –1.88

## 2.4. X-ray Analysis of Compound **11** (CCDC 2058895)



**Figure S31.** X-ray crystal structure of complex **11**, with ellipsoids set at the 30% probability level; hydrogen atoms omitted for clarity at the exception of those bound to heteroatoms.

**Table S3.** Crystallographic data for **11**.

Chemical formula	C <sub>52</sub> H <sub>106</sub> B <sub>2</sub> N <sub>4</sub> O <sub>4</sub> P <sub>8</sub> W <sub>2</sub>
Mr	1488.55
Crystal system, space group	Triclinic, P-1
Temperature (K)	110 K
a, b, c (Å)	12.6243 (9), 15.7892 (11), 16.1110 (12)
α, β, γ (°)	91.132 (2), 91.227 (2), 92.249 (2)
V (Å <sup>3</sup> )	3207.5 (4)
Z	2
Radiation type	Mo Kα radiation, λ = 0.71073 Å
μ (mm <sup>-1</sup> )	3.83
Crystal size (mm)	0.12 × 0.08 × 0.02
Data collection	
Diffractometer	Bruker Kappa APEX II diffractometer
Absorption correction	multi-scan SADABS (Siemens, 1996)
Tmin, Tmax	0.77, 0.93
No. of measured, independent and observed [ I  > 2σ(I)] reflections	86276, 18961, 14292
Rint	0.061
θmax (°)	30.2
Refinement	
R[F <sup>2</sup> > 2σ(F <sup>2</sup> )], wR(F <sup>2</sup> ), S	0.033, 0.032, 1.07
No. of reflections	13329
No. of parameters	675
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρmax, Δρmin (e Å <sup>-3</sup> )	1.56, -1.09



### 3. References

- [S1] SHELX97 [Includes SHELXS97, SHELXL97, CIFTAB] - Programs for Crystal Structure Analysis (Release 97-2). G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
- [S2] L. J. Farrugia, *J. Appl. Crystallogr.* 1999, **32**, 837.
- [S3] CRYSTALS version 12: software for guided crystal structure analysis, P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Cryst.* 2003, **36**, 1487.
- [S4] International Tables for X-Ray Crystallography Vol. IV, Kynoch press, Birmingham, England, 1974.
- [S5] L. J. Farrugia, *J. Appl. Crystallogr.* 1997, **30**, 565.