

## Supporting Information

Nucleophilic Substitution Reactions in the  $[B_3H_8]^-$  Anion in the Presence of Lewis Acids

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## 1. Experimental

**Initial reagents and solvents.** NaBH<sub>4</sub>, PhCH<sub>2</sub>Cl, TiCl<sub>4</sub>, ZrCl<sub>4</sub>, AlCl<sub>3</sub>, I<sub>2</sub>, Et<sub>3</sub>N, Ph<sub>3</sub>P, Ph<sub>2</sub>P-(CH<sub>2</sub>)<sub>2</sub>-PPh<sub>2</sub> (dppe), and Ph<sub>3</sub>As (Aldrich) with a purity of at least 97% were used without additional purification. Triethylamine, pyridine, and aniline (Aldrich) were dried over KOH, distilled over CaH<sub>2</sub> (reduced pressure was used for aniline), and stored over 4 Å MS. Diglyme and tetrahydrofuran (Aldrich) were passed through neutral alumina (MN aluminum oxide 90 neutral). Dichloromethane, 1,2-dichloroethane, and acetonitrile were successively washed with acid, alkali, and water, dried over calcium chloride and distilled over calcium hydride. Hexane was washed with concentrated sulfuric acid and water, dried over calcium chloride, and distilled over calcium hydride [1]. After purification, all solvents were stored over activated molecular sieves (Fluka 3 Å).

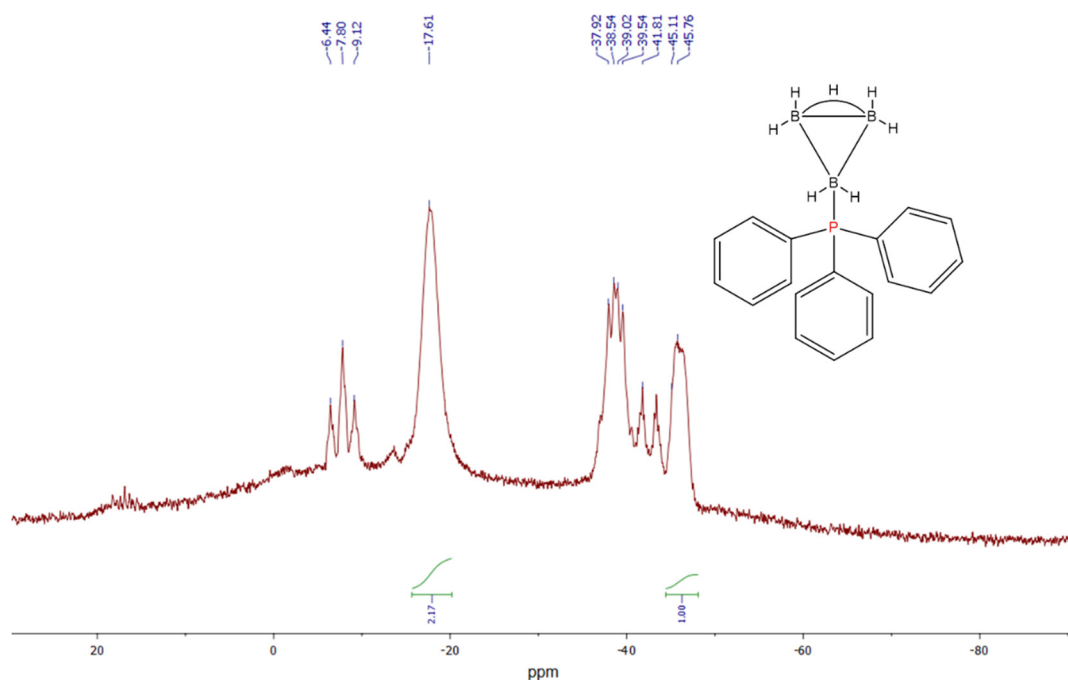
[Bu<sub>4</sub>NB<sub>3</sub>H<sub>8</sub>] was synthesized according to the method described [2] by the reaction between sodium tetrahydroborate and benzyl chloride in diglyme followed by the metathesis reaction with tetrabutylammonium bromide.

**Methods.** NMR spectra (<sup>1</sup>B, <sup>1</sup>H, <sup>13</sup>C) of solutions of the studied substances were recorded on a Bruker Avance II-300 spectrometer at frequencies of 96.32 MHz, 300.21 MHz, and 75.48 MHz, respectively, with internal deuterium stabilization. Boron trifluoride etherate (<sup>11</sup>B) and tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C) were used as external standards. IR spectra of the synthesized compounds were recorded on an INFRALUM FT-02 IR Fourier spectrometer (NPF AP Lumex, Russia) in the range 4000–400 cm<sup>−1</sup> with a resolution of 1 cm<sup>−1</sup>. Samples were prepared as KBr tablets or thin films.

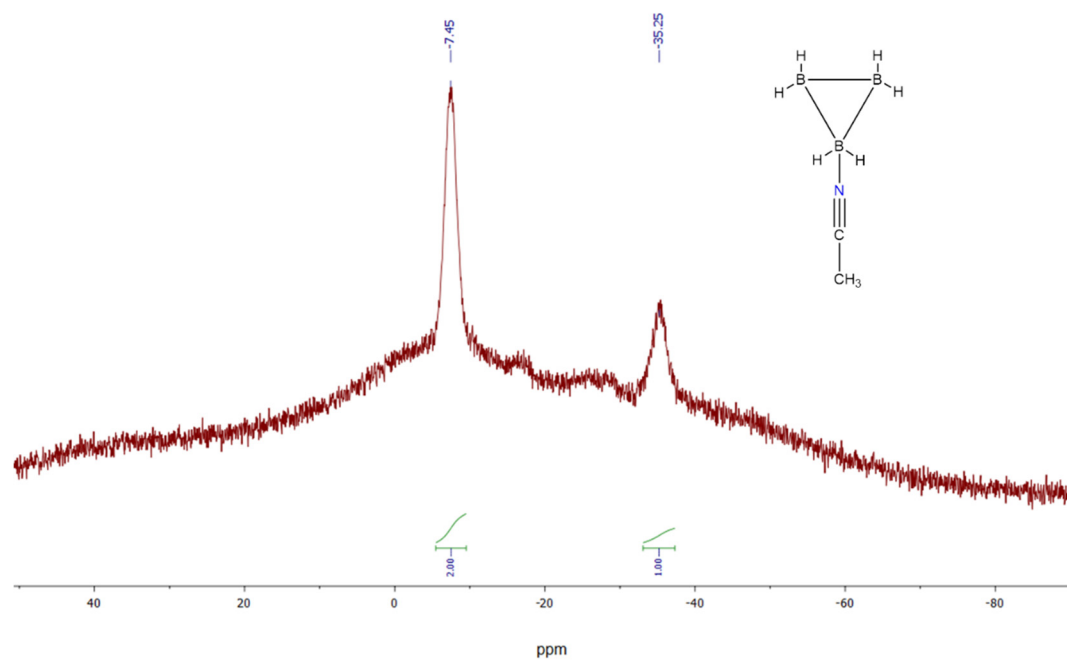
**X-ray single crystal diffraction** was carried out at the Shared Facility Center of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences by Grigoriev M.S. on an automatic four-circle Bruker KAPPA APEX II diffractometer with a two-dimensional detector [3] (MoK<sub>α</sub> radiation) at a temperature of 100 K. The unit cell parameters were refined over the entire data set. The structure was solved and refined using SHELX software [4] on F<sup>2</sup> using all data in the anisotropic approximation for all non-hydrogen atoms. All H atoms were localized from the difference Fourier synthesis of the electron density and were refined isotropically without any restrictions. Data processing was carried out by using OLEX program [5].

**Elemental analysis** (C,H,N) was carried out at automatic gas analyzer CHNS-3 FA 1108 Elemental Analyser (Carlo Erba). The B determination using the ICP MS method was carried out at inductively coupled plasma atomic emission spectrometer iCAP 6300 Duo in shared experimental facilities supported by IGIC RAS state assignment FCUE “IREA” NRC “Kurchatov institute”.

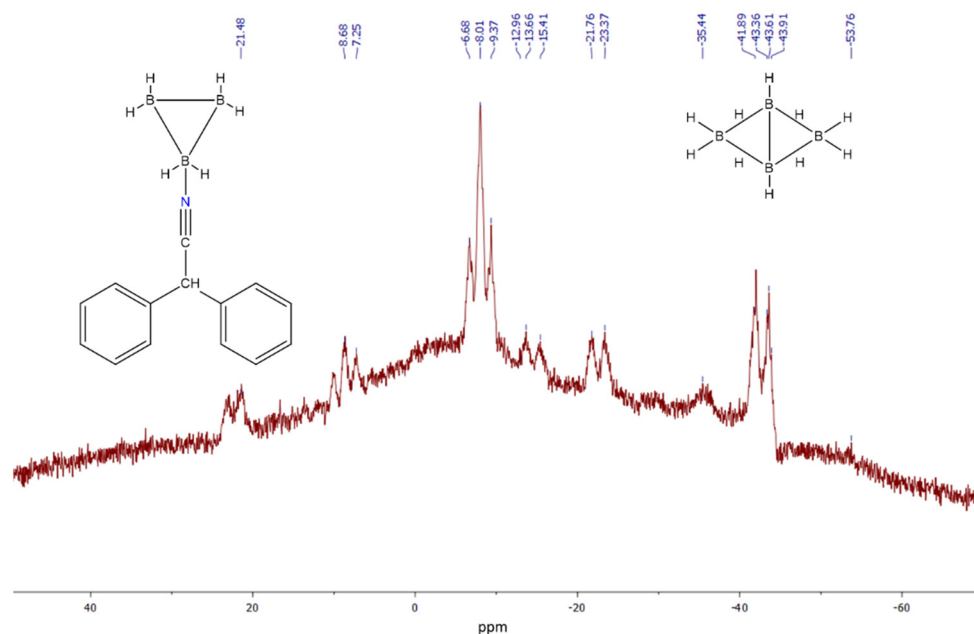
## 2. NMR spectra



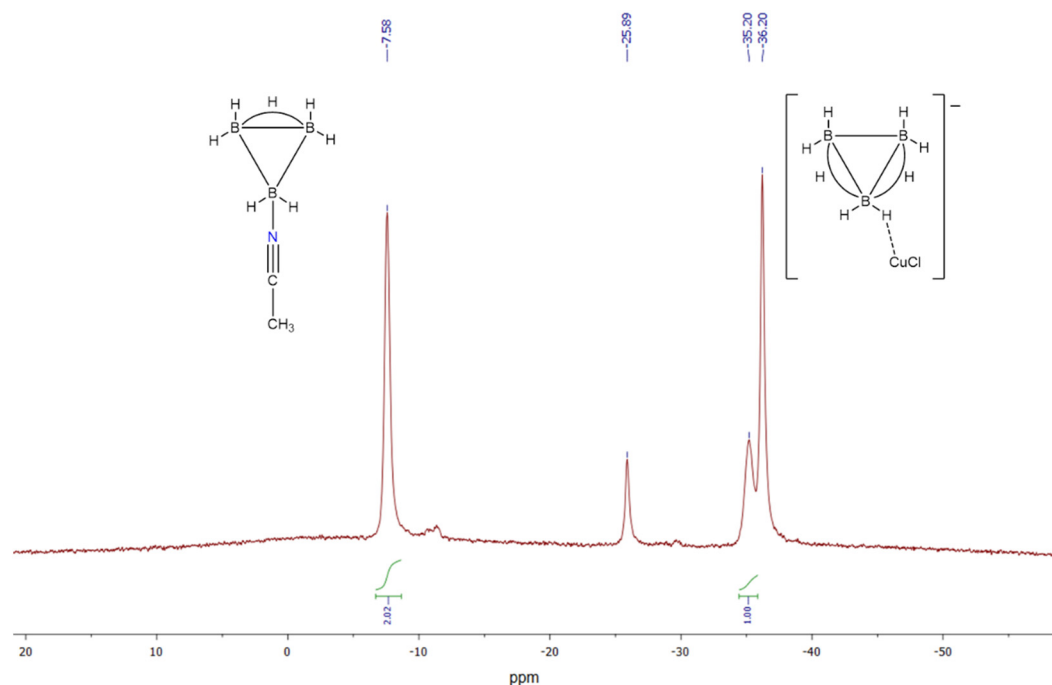
**Figure S1.**  $^{11}\text{B}$  NMR spectrum of a mixture of TBA[B<sub>3</sub>H<sub>8</sub>], PPh<sub>3</sub> and TiCl<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> 30 min after the beginning of the reaction. [B<sub>3</sub>H<sub>7</sub>PPh<sub>3</sub>] ( $\delta$  -17.61 ppm, -45.76 ppm) at 298 K.



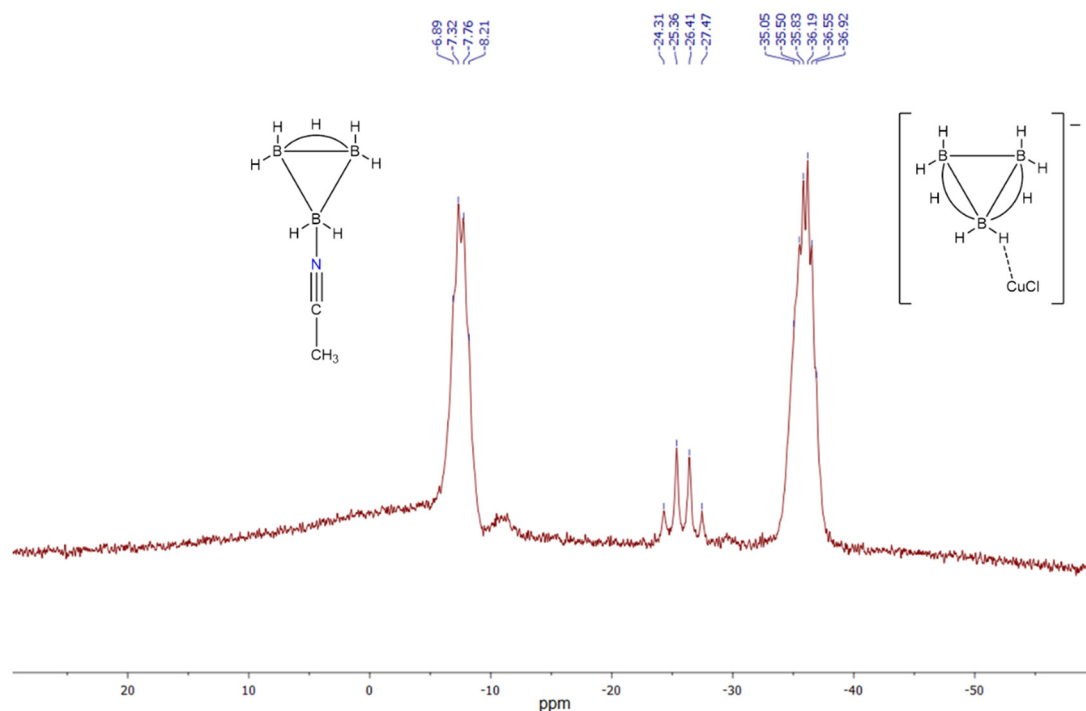
**Figure S2.**  $^{11}\text{B}$  NMR spectrum of a mixture of TBA[B<sub>3</sub>H<sub>8</sub>], CH<sub>3</sub>CN and AlCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> 2h after the beginning of the reaction. [B<sub>3</sub>H<sub>7</sub>NCCH<sub>3</sub>] ( $\delta$  -7.45 ppm, -35.25 ppm) at 298 K.



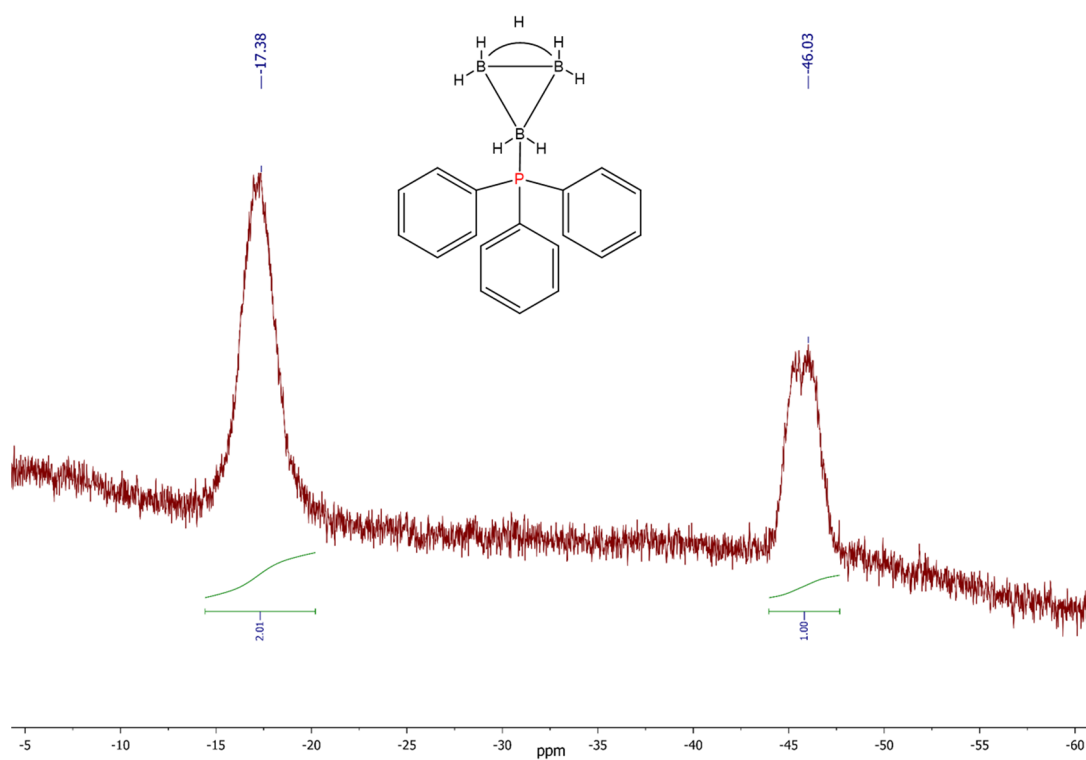
**Figure S3.**  $^{11}\text{B}$  NMR spectrum of a mixture of TBA[B<sub>3</sub>H<sub>8</sub>], Ph<sub>2</sub>CHCN and AlCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> 2h after the beginning of the reaction. [B<sub>3</sub>H<sub>7</sub>NCCH<sub>2</sub>Ph] ( $\delta$  -7.65 ppm, -35.44 ppm), [B<sub>4</sub>H<sub>10</sub>] ( $\delta$  -8.01 ppm, -43.46 ppm) at 298 K.



**Figure S4.**  $^{11}\text{B}$ - $^1\text{H}$  NMR spectrum of a mixture of TBA[B<sub>3</sub>H<sub>8</sub>] and CuCl in CD<sub>3</sub>CN 30 min after the beginning of the reaction. [B<sub>3</sub>H<sub>7</sub>NCCH<sub>3</sub>] ( $\delta$  -7.58 ppm, -35.20 ppm), [B<sub>3</sub>H<sub>7</sub>HCuCl]<sup>-</sup> ( $\delta$  -36.20 ppm) at 298 K.



**Figure S5.**  $^{11}\text{B}$  NMR spectrum of a mixture of  $\text{TBA}[\text{B}_3\text{H}_8]$  and  $\text{CuCl}$  in  $\text{CD}_3\text{CN}$  30 min after the beginning of the reaction.  $[\text{B}_3\text{H}_7\text{NCCH}_3]$  ( $\delta$  -7.58 ppm, -35.20 ppm),  $[\text{BH}_3\text{NCCH}_3]$  ( $\delta$  -25.8 ppm),  $[\text{B}_3\text{H}_7\text{HCuCl}]$  ( $\delta$  -36.20 ppm) at 298 K.



**Figure S6.**  $^{11}\text{B}$ - $^1\text{H}$  NMR spectrum of crystal solution  $[\text{B}_3\text{H}_7\text{PPh}_3]$  in  $\text{CD}_2\text{Cl}_2$  at 298 K.

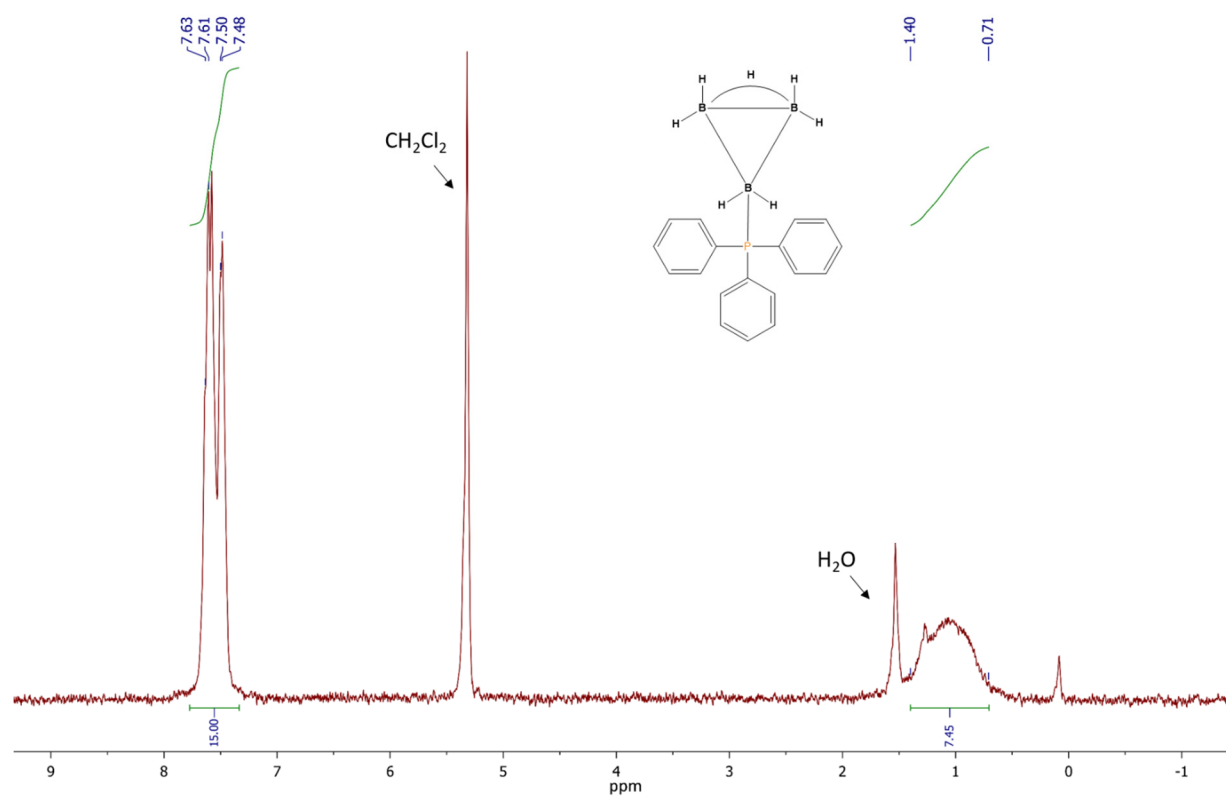


Figure S7.  $^1\text{H}$  NMR spectrum of crystal solution  $[\text{B}_3\text{H}_7\text{PPh}_3]$  in  $\text{CD}_2\text{Cl}_2$  at 298 K.

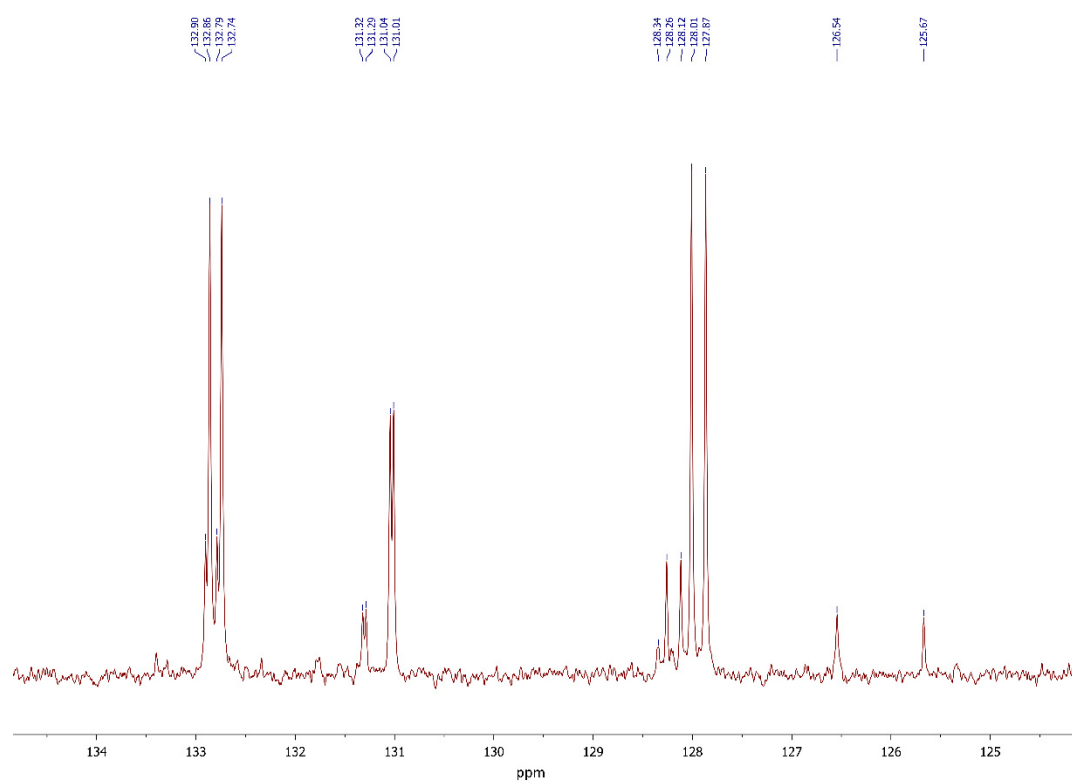


Figure S8.  $^{13}\text{C}$  NMR spectrum of crystal solution  $[\text{B}_3\text{H}_7\text{PPh}_3]$  in  $\text{CD}_2\text{Cl}_2$  at 298 K.

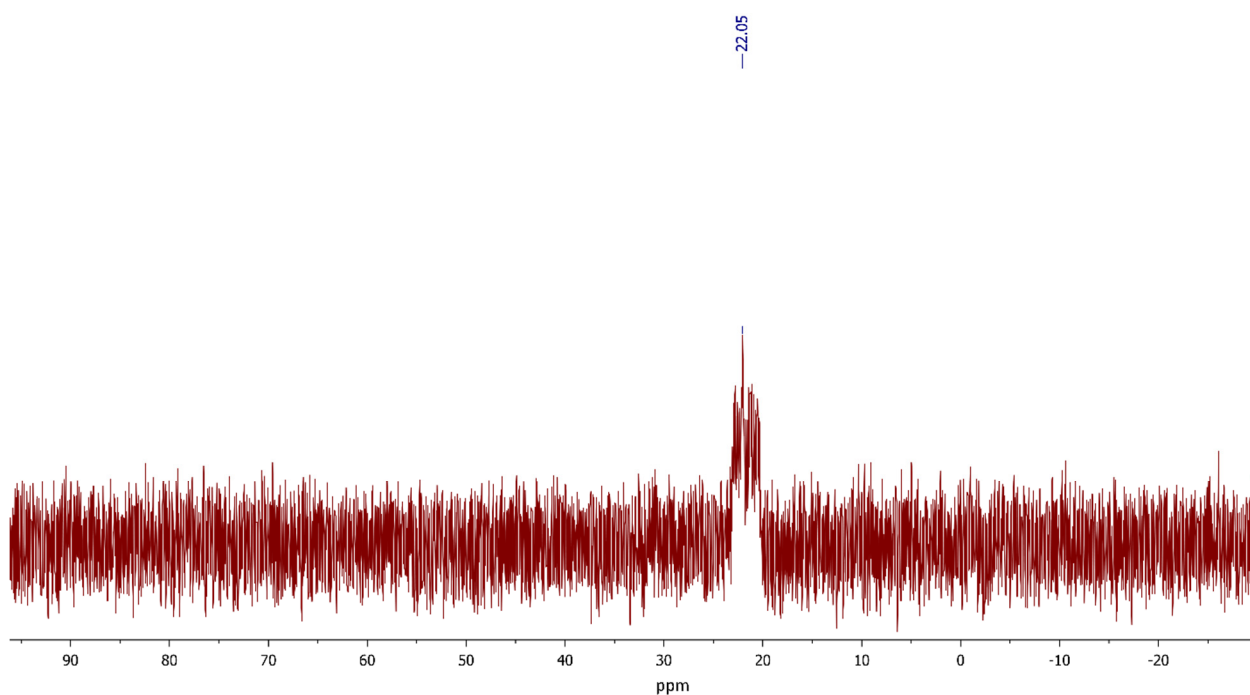


Figure S9.  $^{31}\text{P}$  NMR spectrum of crystal solution  $[\text{B}_3\text{H}_7\text{PPh}_3]$  in  $\text{CD}_2\text{Cl}_2$  at 298 K.

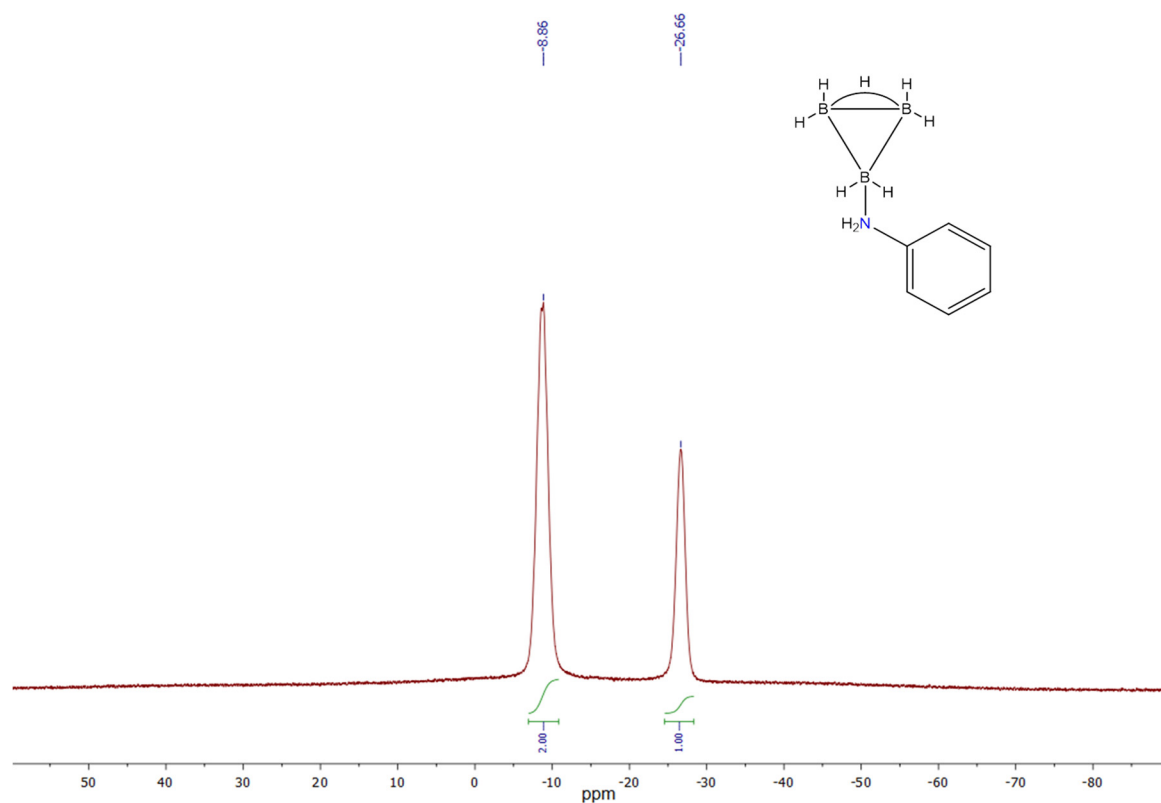
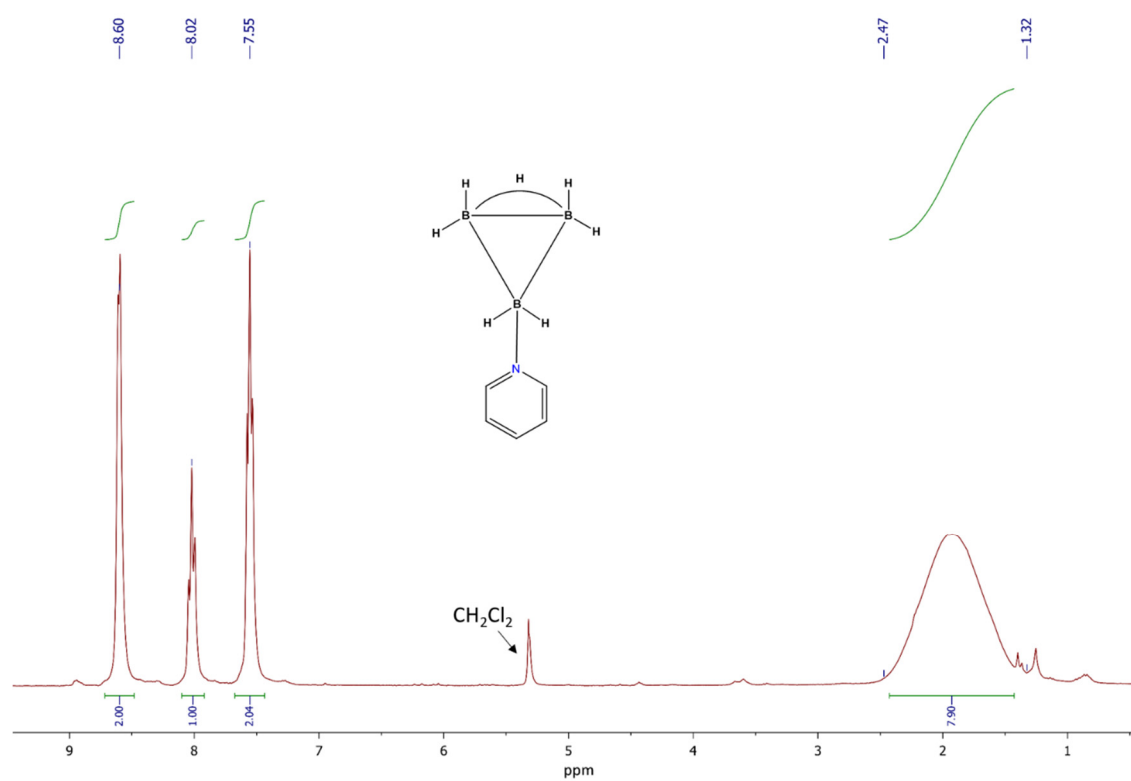
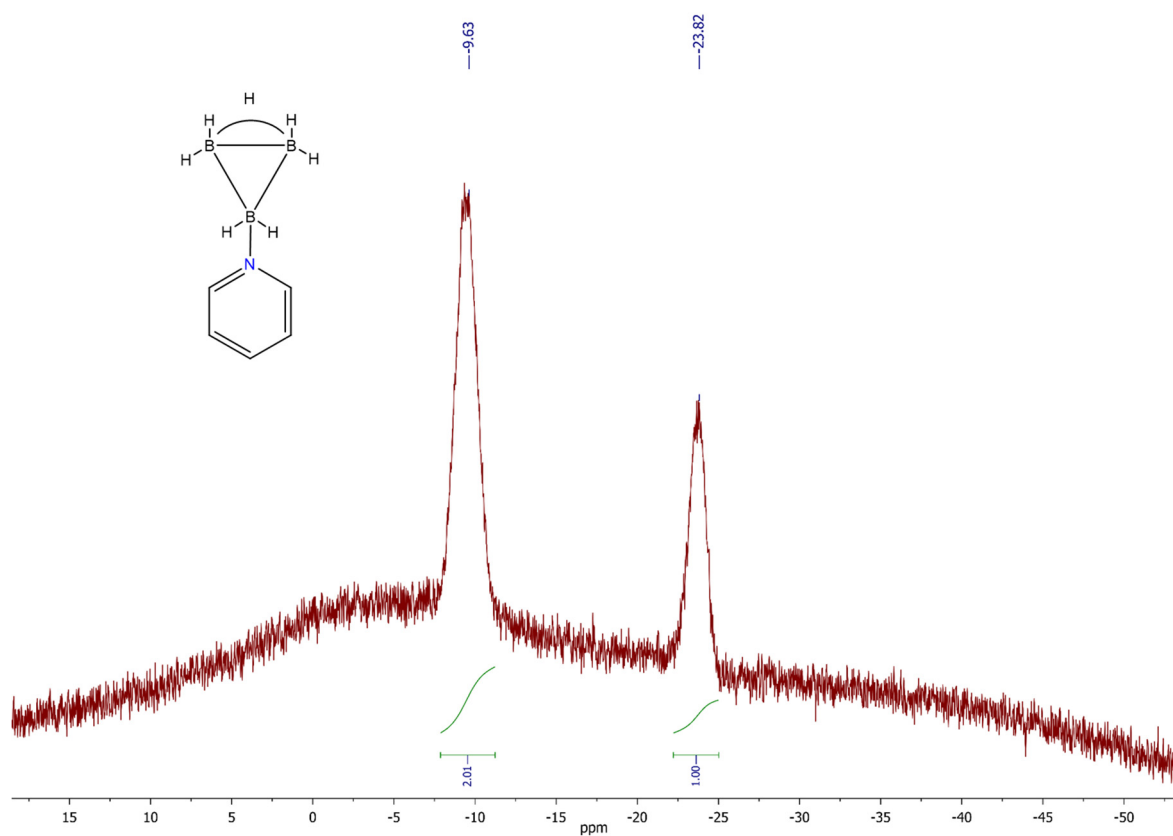


Figure S10.  $^{11}\text{B}$ - $^1\text{H}$  NMR spectrum of crystal solution  $[\text{B}_3\text{H}_7\text{NH}_2\text{Ph}]$  in  $\text{CD}_2\text{Cl}_2$  at 298 K.

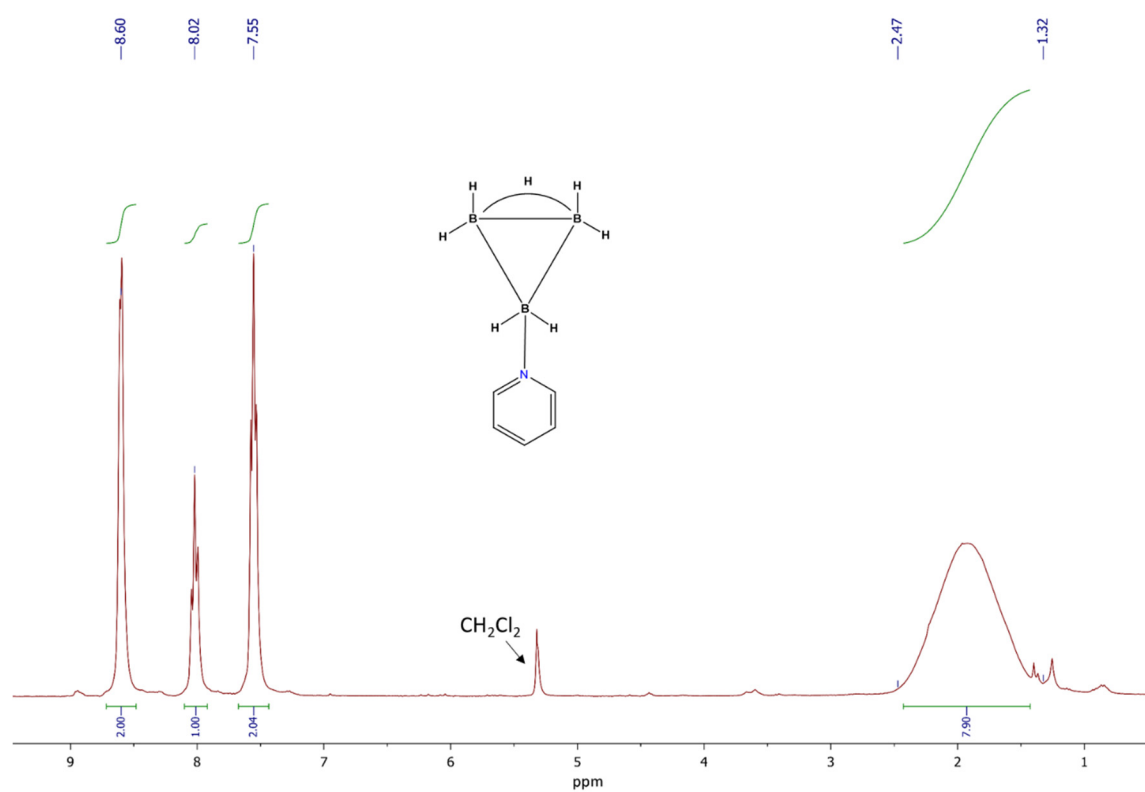


**Figure S11.**  $^1\text{H}$  NMR spectrum of crystal solution  $[\text{B}_3\text{H}_7\text{NH}_2\text{Ph}]$  in  $\text{CD}_2\text{Cl}_2$  at 298 K.



**Figure S12.**  $^{11}\text{B}$  NMR spectrum of solution  $[\text{B}_3\text{H}_7\text{Py}]$  in  $\text{CD}_2\text{Cl}_2$  at 298 K.





**Figure S13.**  $^1\text{H}$  NMR spectrum of crystal solution  $[\text{B}_3\text{H}_7\text{Py}]$  in  $\text{CD}_2\text{Cl}_2$  at 298 K.

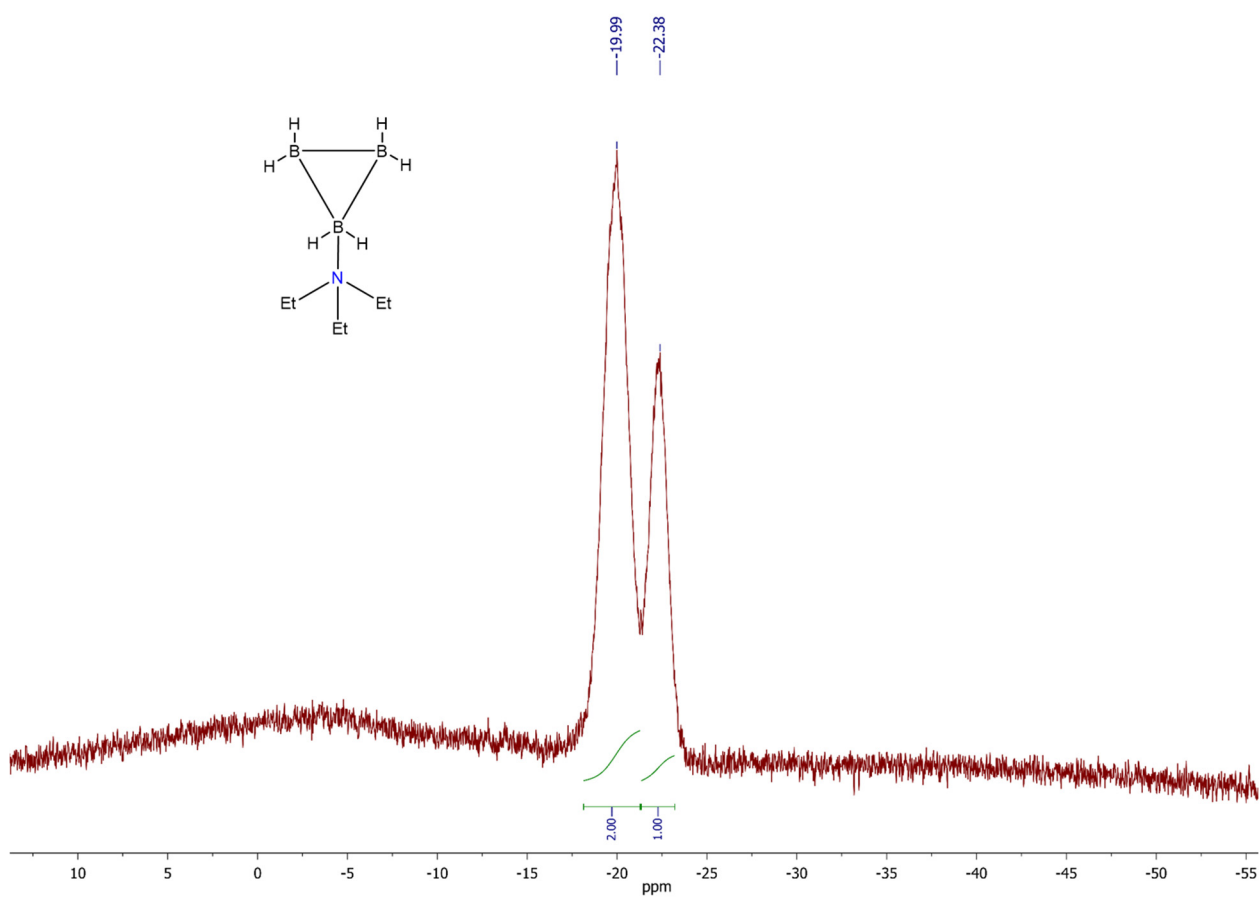


Figure S14.  $^{11}\text{B}$  NMR spectrum of solution  $[\text{B}_3\text{H}_7\text{Et}_3\text{N}]$  in  $\text{CD}_2\text{Cl}_2$  at 298 K.

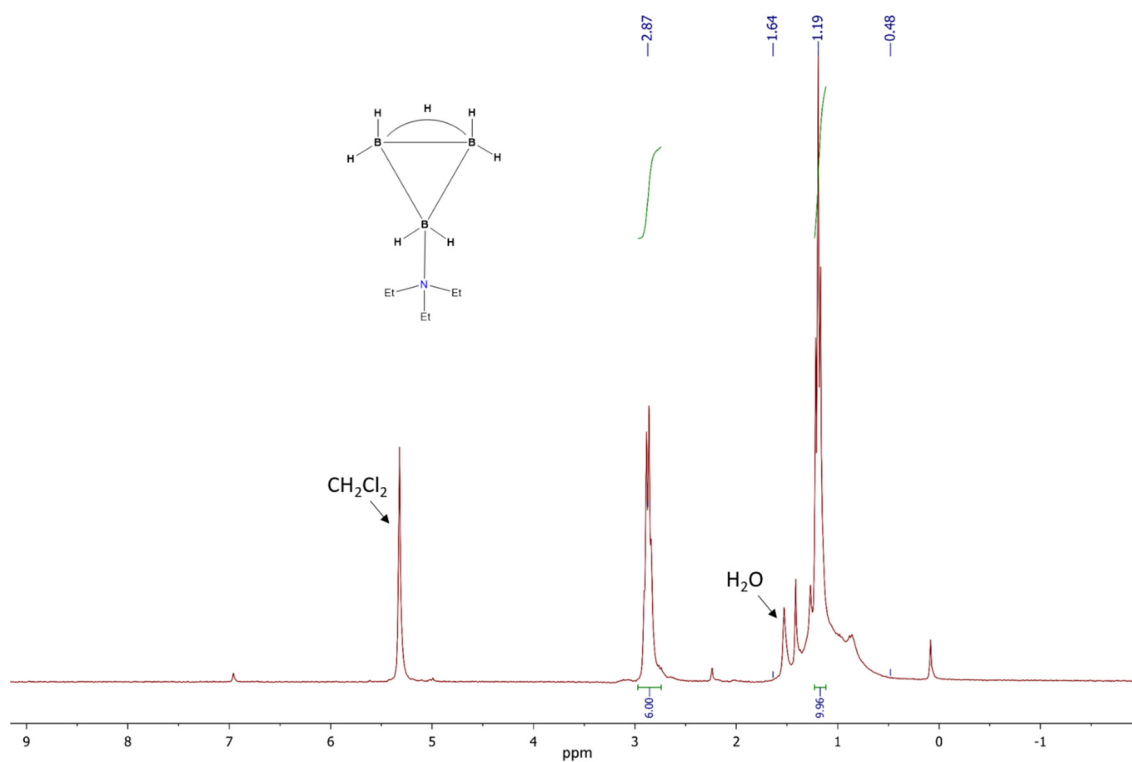
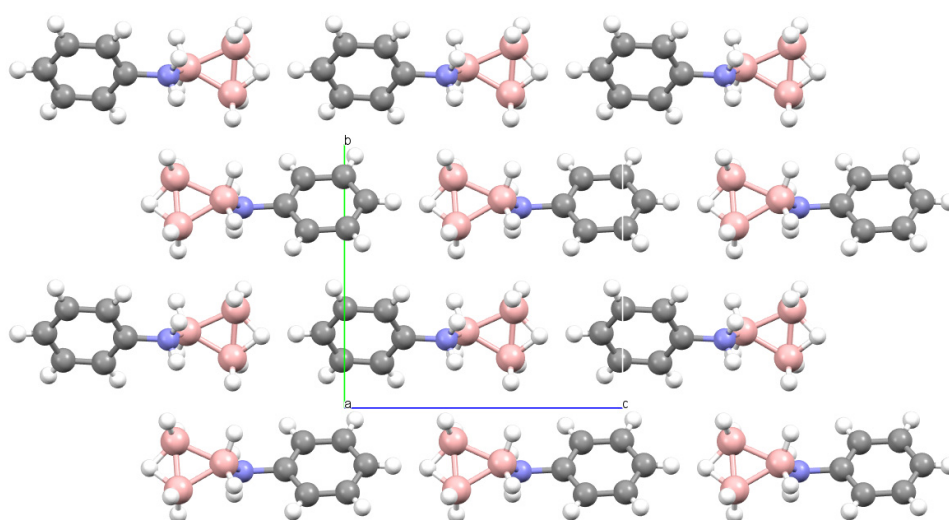


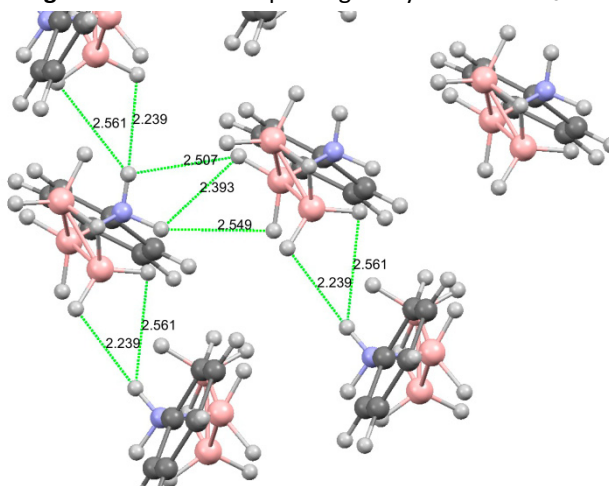
Figure S15.  $^1\text{H}$  NMR spectrum of solution  $[\text{B}_3\text{H}_7\text{Et}_3\text{N}]$  in  $\text{CD}_2\text{Cl}_2$  at 298 K.

### 3. X-ray diffraction

The packing in the crystal  $\text{PhNH}_2 \cdot \text{B}_3\text{H}_7$  (Figure 5, 6), apparently, occurs mainly due to the formation of dihydrogen bonds  $\text{N-H} \cdots \text{H-B}$ . Therefore, in stacks, binding is mainly carried out through the formation of the  $\text{N1-H1D} \cdots \text{H1A-B1}$  interaction ( $2.39(4) \text{ \AA}$ ), and between stacks located antiparallelly binding is realized due to the presence of a rather short contact  $\text{N1-H1C} \cdots \text{H2B-B2}$  ( $2.24(5) \text{ \AA}$ ) (Figures 5 and 6). The  $\text{C4-H4A} \cdots \text{H3B-B3}$  distance is  $2.35(4) \text{ \AA}$ ; this is the way of the interaction between the aryl and borohydride fragments.



**Figure S16.** Molecular packing in crystal  $\text{PhNH}_2 \cdot \text{B}_3\text{H}_7$



**Figure S17.** Possible intermolecular contacts in crystal  $\text{PhNH}_2 \cdot \text{B}_3\text{H}_7$ .

Table S1. Time of the substituted products formation in the reaction of  $[\text{B}_3\text{H}_8]^-$  with  $\text{CH}_3\text{CN}$  and THF

Lewis acid	Time/solvent		
	$\text{CH}_2\text{Cl}_2$	$\text{CH}_3\text{CN}$	THF
$\text{TiCl}_4$	30-40 min	30-40 min	1.5 h
$\text{ZrCl}_4$	30-40 min	30-40 min	1.5 h

<b>HfCl<sub>4</sub></b>	30-40 min	30-40 min	1.5 h
<b>AlCl<sub>3</sub></b>	30-40 min	30-40 min	1.5 h
<b>CuCl</b>	Has not observed (only the complex has been formed)	12 h	12 h
<b>CoCl<sub>2</sub></b>	Has not observed (only the complex has been formed)	Has not observed (only the complex has been formed)	Has not observed (only the complex has been formed)
<b>ZnCl<sub>2</sub></b>	Has not observed (only the complex has been formed)	Has not observed (only the complex has been formed)	Has not observed (only the complex has been formed)
<b>MnCl<sub>2</sub></b>	Has not observed (only the complex has been formed)	Has not observed (only the complex has been formed)	Has not observed (only the complex has been formed)

**Table S2.** Main crystallographic data, experimental parameters and characteristics of structure refinement for Ph<sub>3</sub>P·B<sub>3</sub>H<sub>7</sub>

Formula	C <sub>18</sub> H <sub>22</sub> B <sub>3</sub> P
FW	301.75
T, K	100(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	16.3802(4)
b/Å	11.5664(3)
c/Å	17.9927(4)
α/°	90
β/°	96.8160(10)
γ/°	90
V, Å <sup>3</sup>	3384.80(14)
Z	8
Q <sub>calc</sub> /g/cm <sup>3</sup>	1.184
μ/mm <sup>-1</sup>	0.154
F(000)	1280.0
Crystal size, mm	0.340 × 0.260 × 0.200

radiation, $\lambda$ , Å	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\theta$ range, °	8.302 to 59.992
Number of reflections: collected independent (N) [Rint]	18495 4898 [0.0264],
R1, wR2 for No	R <sub>1</sub> = 0.0352, wR <sub>2</sub> = 0.0863
R1, wR2 for N	R <sub>1</sub> = 0.0800, wR <sub>2</sub> = 0.1404
$\Delta\rho_{\max}/\Delta\rho_{\min}$ , e/Å <sup>3</sup>	0.38/-0.22

**Table S3.** Selected bond lengths and bond angles in the structure of Ph<sub>3</sub>P·B<sub>3</sub>H<sub>7</sub>

Bond	Length, Å	Bond angle	Angle, °	Bond angle	Angle, °
P1-C11	1.812(1)	C11-P1-C21	106.03(5)	B1-B2-H23	102.2(7)
P1-C21	1.816(1)	C11-P1-C31	106.58(5)	H2A-B2-H2B	118(1)
P1-C31	1.808(1)	C11-P1-B1	108.64(5)	H2A-B2-B3	119.4(9)
P1-B1	1.926(1)	C21-P1-C31	105.83(5)	H2A-B2-H23	103(1)
B1-H1A	1.10(2)	C21-P1-B1	117.51(5)	H2B-B2-B3	117.7(8)
B1-H1B	1.10(2)	C31-P1-B1	111.62(5)	H2B-B2-H23	104(1)
B1-B2	1.804(2)	P1-B1-H1A	102.0(9)	B3-B2-H23	41.1(7)
B1-B3	1.821(2)	P1-B1-H1B	107.4(9)	B1-B3-B2	60.10(8)
B2-H1A	1.65(2)	P1-B1-B2	125.02(9)	B1-B3-H3A	111.6(8)
B2-H2A	1.10(2)	P1-B1-B3	110.91(8)	B1-B3-H3B	109.5(8)
B2-H2B	1.11(2)	H1A-B1-H1B	104(1)	B1-B3-H23	108.3(8)
B2-B3	1.779(2)	H1A-B1-B2	63.8(9)	B2-B3-H3A	121.9(8)
B2-H23	1.33(2)	H1A-B1-B3	122.6(9)	B2-B3-H3B	120.8(8)
B3-H3A	1.12(2)	H1B-B1-B2	127.4(9)	B2-B3-H23	48.2(8)
B3-H3B	1.10(1)	H1B-B1-B3	108.8(9)	H3A-B3-H3B	116(1)
B3-H23	1.17(2)	B2-B1-B3	58.79(7)	H3A-B3-H23	105(1)
		B1-B2-H2A	115.1(9)	H3B-B3-H23	107(1)
		B1-B2-H2B	112.1(8)	B2-H23-B3	91(1)
		B1-B2-B3	61.11(8)		

**Table S4.** Main crystallographic data, experimental parameters and characteristics of structure refinement for PhNH<sub>2</sub>·B<sub>3</sub>H<sub>7</sub>.

Formula	C <sub>6</sub> H <sub>14</sub> B <sub>3</sub> N
FW	132.61
T, K	100(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub>
a/Å	4.9391(12)
b/Å	9.067(2)
c/Å	9.629(2)

$\alpha/^\circ$	90
$\beta/^\circ$	96.807(11)
$\gamma/^\circ$	90
$V, \text{\AA}^3$	428.17(17)
$Z$	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.029
$\mu/\text{mm}^{-1}$	0.055
$F(000)$	144
Crystal size, mm	0.400×0.200×0.120
radiation, $\lambda, \text{\AA}$	MoK $\alpha$ ( $\lambda = 0.71073$ )
$2\theta$ range, $^\circ$	8.310 to 59.938
Number of reflections: collected independent (N) [Rint]	5531 2415 [0.0407]
$R_1, wR_2$ for No	$R_1 = 0.0460, wR_2 = 0.1141$
$R_1, wR_2$ for $N$	$R_1 = 0.0590, wR_2 = 0.1224$
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}, \text{e/\AA}^3$	0.26/-0.16

**Table S5.** Selected bond lengths and bond angles in the structure of  $\text{PhNH}_2 \cdot \text{B}_3\text{H}_7$ 

Bond	Length, $\text{\AA}$	Bond angle	Angle, $^\circ$	Bond angle	Angle, $^\circ$
N1-H1C	0.88(4)	H1C-N1-H1D	100(3)	H1A-B1-H1B	108(2)
N1-H1D	0.95(3)	H1C-N1-C1	110(2)	H1A-B1-B2	129(2)
N1-C1	1.478(2)	H1C-N1-B1	110(2)	H1A-B1-B3	80(2)
N1-B1	1.608(3)	H1D-N1-C1	109(2)	H1B-B1-B2	87(1)
C1-C2	1.385(3)	H1D-N1-B1	111(2)	H1B-B1-B3	131(1)
C1-C6	1.385(3)	C1-N1-B1	115.0(2)	B2-B1-B3	55.7(1)
C2-H2C	0.93(3)	N1-C1-C2	119.2(2)	B1-B2-H2A	100(2)
C2-C3	1.392(3)	N1-C1-C6	119.6(2)	B1-B2-H2B	115(1)
C3-H3C	0.92(3)	C2-C1-C6	121.3(2)	B1-B2-H23	110(2)
C3-C4	1.387(3)	C1-C2-H2C	116(2)	B1-B2-B3	61.6(1)
C4-H4A	0.94(2)	C1-C2-C3	119.0(2)	H2A-B2-H2B	120(2)
C4-C5	1.383(3)	H2C-C2-C3	125(2)	H2A-B2-H23	105(2)
C5-H5A	1.00(3)	C2-C3-H3C	120(2)	H2A-B2-B3	123(2)
C5-C6	1.396(3)	C2-C3-C4	120.4(2)	H2B-B2-H23	107(2)
C6-H6A	0.95(3)	H3C-C3-C4	119(2)	H2B-B2-B3	116(1)
B1-H1A	1.08(3)	C3-C4-H4A	118(2)	H23-B2-B3	49(2)
B1-H1B	1.15(3)	C3-C4-C5	119.9(2)	B2-H23-B3	83(2)
B1-B2	1.847(3)	H4A-C4-C5	121(2)	B1-B3-B2	62.6(1)
B1-B3	1.830(3)	C4-C5-H5A	124(2)	B1-B3-H23	108(2)
B2-H2A	1.08(3)	C4-C5-C6	120.4(2)	B1-B3-H3A	106(2)

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B2-H2B	1.11(3)	H5A-C5-C6	116(2)	B1-B3-H3B	116(1)
B2-H23	1.27(4)	C1-C6-C5	119.0(2)	B2-B3-H23	47(2)
B2-B3	1.719(4)	C1-C6-H6A	119(2)	B2-B3-H3A	123(2)
H23-B3	1.32(4)	C5-C6-H6A	122(2)	B2-B3-H3B	114(1)
B3-H3A	1.16(4)	N1-B1-H1A	109(2)	H23-B3-H3A	101(2)
B3-H3B	1.11(3)	N1-B1-H1B	109(1)	H23-B3-H3B	104(2)
		N1-B1-B2	111.0(2)	H3A-B3-H3B	120(2)
		N1-B1-B3	112.5(2)		

## References

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