

Electronic Supporting Information

**Zinc hydridotriphenylborates supported by a neutral macrocyclic  
polyamine**

Debabrata Mukherjee, Ann-Kristin Wiegand, Thomas P. Spaniol, and Jun Okuda\*

Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52056 Aachen, Germany.

**Table of Contents**

<b>General remarks.....</b>	<b>S1</b>
<b>Synthetic procedures and spectroscopic data for 1-11.....</b>	<b>S2</b>
<b>Hydroboration catalysis using 1.....</b>	<b>S21</b>
<b>Crystal structure analysis.....</b>	<b>S25</b>
<b>References.....</b>	<b>S27</b>

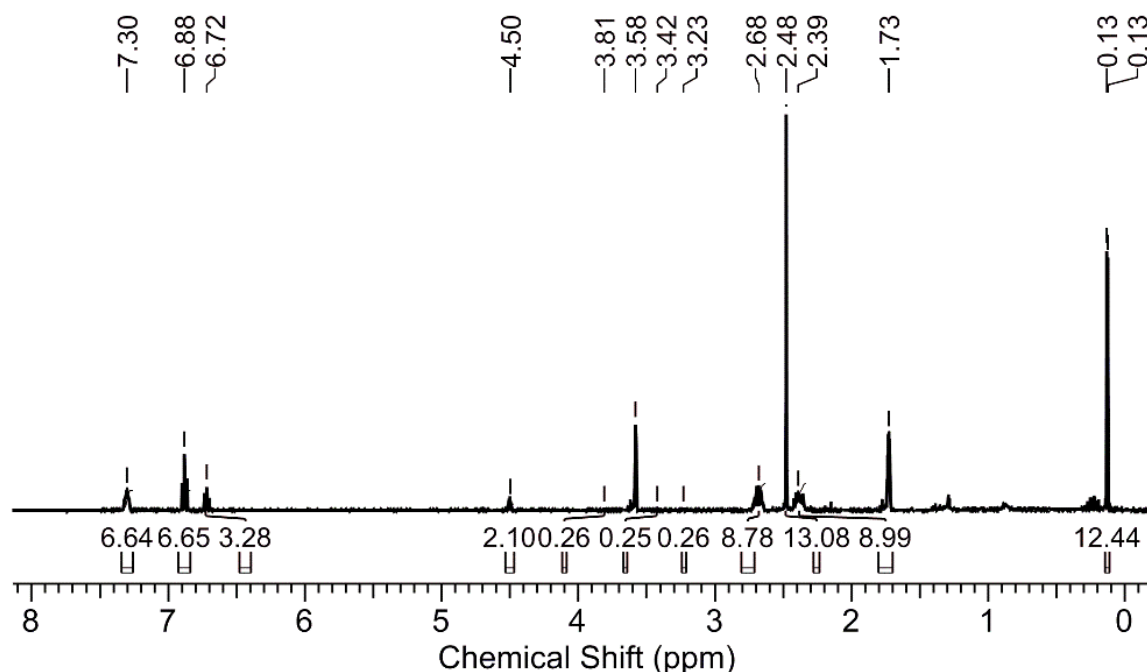
**General remarks.**

All reactions were performed under a dry argon atmosphere using standard Schlenk techniques or under argon atmosphere in a glovebox, unless otherwise indicated. Prior to use, glassware were dried overnight at 130 °C and solvents were dried, distilled, and degassed using standard methods.  $[\text{Zn}\{\text{N}(\text{SiHMe}_2)_2\}_2]$ ,<sup>S1</sup>  $\text{Me}_4\text{TACD}$ ,<sup>S2</sup>  $\text{KHBPh}_3$ <sup>S3</sup> were synthesized following literature procedures.  $^1\text{H}$  NMR spectrum of isolated  $\text{KHBPh}_3$  in  $\text{THF-}d_8$  suggests the composition as  $[\text{KHBPh}_3(\text{thf})_{0.625}]$ .  $\text{HN}(\text{SiHMe}_2)_2$  was purchased from Alfa Aesar and dried and degassed prior storing over molecular sieves inside the glovebox.  $\text{BPh}_3$  (95%) was purchased from abcr and purified by sublimation before use.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{11}\text{B}$ , and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker Avance-III spectrometer at ambient temperature unless otherwise mentioned. Chemical shifts ( $\delta$  in ppm) in the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were referenced to the residual signals of the deuterated solvents. Abbreviations for NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), sep (septet), br (broad). FT-IR spectra were recorded on KBr pellets using an AVATAR 360 FT-IR spectrometer. Elemental analyses were performed on an *elementar vario EL* machine. X-ray diffraction data were collected on a Bruker APEX II diffractometer. Single crystal diffraction data were reported in crystallographic information files (cif) accompanying this document.

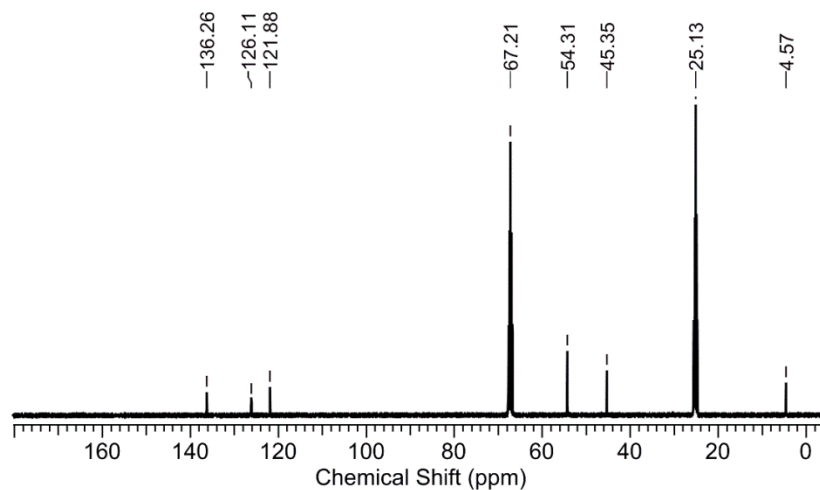
## Synthetic procedures and spectroscopic data for 1-11.

### [(L)Zn{N(SiHMe<sub>2</sub>)<sub>2</sub>}][HBPh<sub>3</sub>] (1).

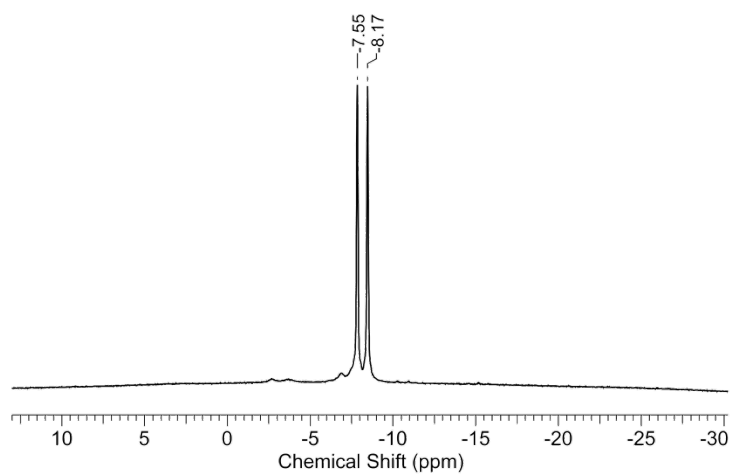
A solution of [Zn{N(SiHMe<sub>2</sub>)<sub>2</sub>}<sub>2</sub>] (0.289 g, 0.876 mmol) and L (0.200 g, 0.876 mmol) in 5 mL of THF was stirred for 10 min. BPh<sub>3</sub> (0.212 g, 0.876 mmol) in 2 mL of THF was added to this mixture and stirred for additional 24 h. A small amount of white solid precipitated during this time which was removed by filtration. The filtrate was evaporated under reduced pressure to give a colorless solid. The solid was washed with *n*-pentane (3×5 mL) and dried under vacuum to afford analytically pure **1** (0.387 g, 0.578 mmol, 66%) as a colorless powder. <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>): δ 7.30 (m, 6 H, *o*-Ph), 6.88 (m, 6 H, *m*-Ph), 6.72 (m, 3 H, *p*-Ph), 4.50 (m, 2 H, SiHMe<sub>2</sub>), 3.81-3.23 (q, <sup>1</sup>J<sub>BH</sub> = 76 Hz, 1 H, BH), 2.68 (m, 8 H, NCH<sub>2</sub>), 2.48 (s, 12 H, NMe), 2.39 (m, 8 H, NCH<sub>2</sub>), 0.13 (d, <sup>3</sup>J<sub>HH</sub> = 3.01 Hz, 12 H, SiHMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, THF-*d*<sub>8</sub>): δ 136.3 (*o*-Ph), 126.1 (*m*-Ph), 121.9 (*p*-Ph), 54.3 (CH<sub>2</sub>), 45.4 (NMe), 4.6 (SiHMe<sub>2</sub>). <sup>11</sup>B NMR (128 MHz, THF-*d*<sub>8</sub>): δ -7.9 (d, <sup>1</sup>J<sub>BH</sub> = 79 Hz). <sup>29</sup>Si NMR (79.5 MHz, THF-*d*<sub>8</sub>): δ -15.1. IR (KBr, cm<sup>-1</sup>): 2221-2083 (ν<sub>SiH</sub> and ν<sub>BH</sub>). Anal. Calc. for C<sub>35</sub>H<sub>58</sub>BN<sub>5</sub>Si<sub>2</sub>Zn: C, 61.02; H, 8.74; N, 10.46. Found: C, 61.71; H, 8.01; N, 10.10.



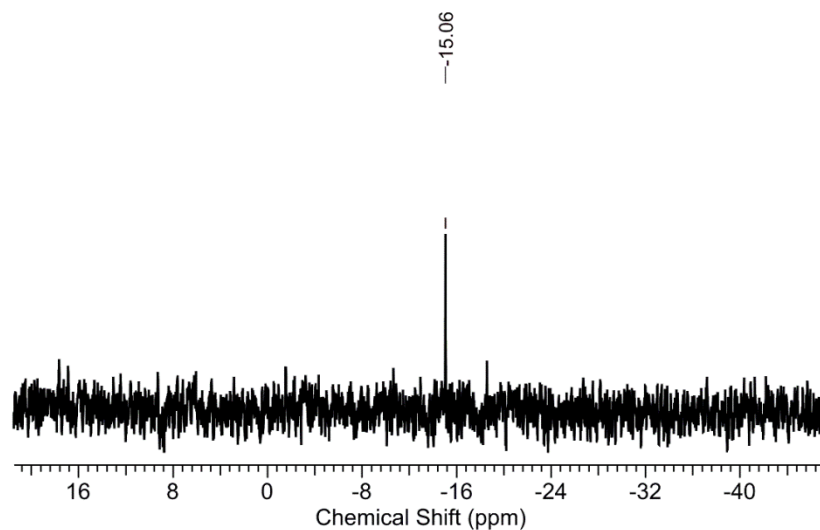
**Figure 1.** <sup>1</sup>H NMR spectrum of [(L)Zn{N(SiHMe<sub>2</sub>)<sub>2</sub>}][HBPh<sub>3</sub>] (**1**) in THF-*d*<sub>8</sub>.



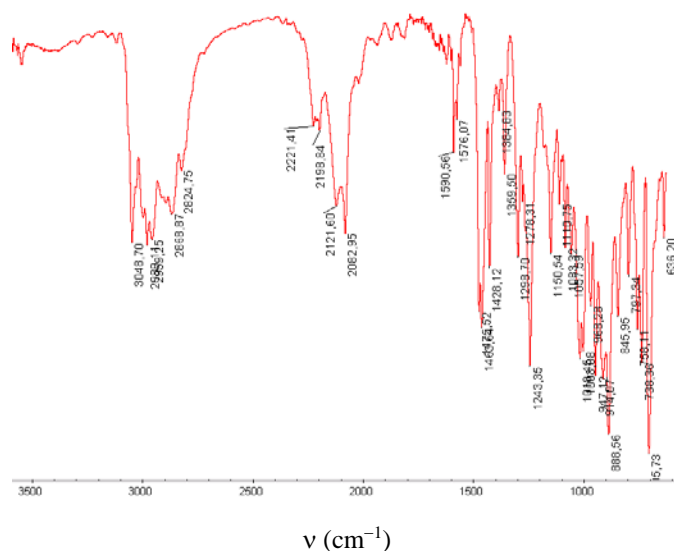
**Figure 2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L})\text{Zn}\{\text{N}(\text{SiHMe}_2)_2\}][\text{HBPh}_3]$  (**1**) in  $\text{THF-}d_8$ .



**Figure 3.**  $^{11}\text{B}$  NMR spectrum of  $[(\text{L})\text{Zn}\{\text{N}(\text{SiHMe}_2)_2\}][\text{HBPh}_3]$  (**1**) in  $\text{THF-}d_8$ .



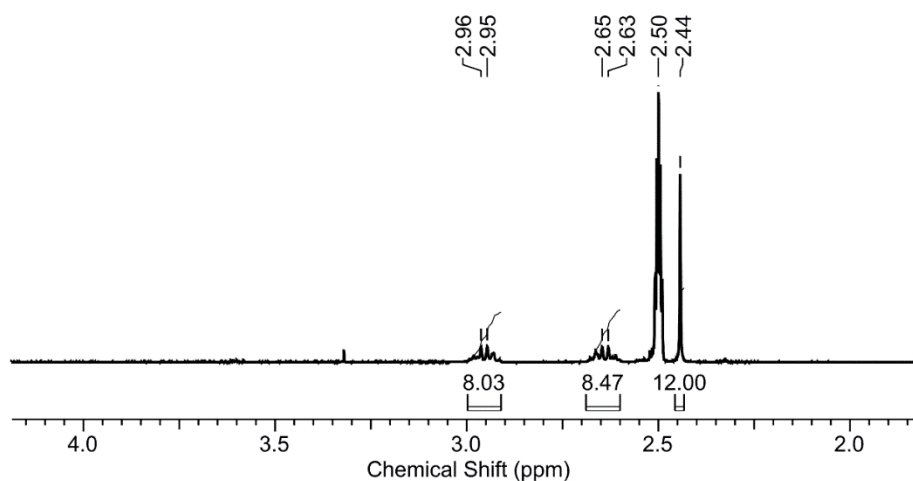
**Figure 4.**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L})\text{Zn}\{\text{N}(\text{SiHMe}_2)_2\}][\text{HBPh}_3]$  (**1**) in  $\text{THF-}d_8$ .



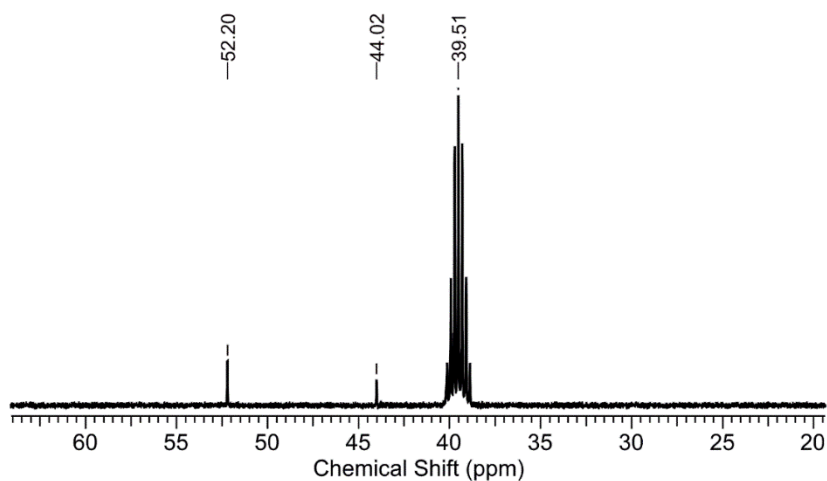
**Figure 5.** Solid-state IR (KBr) spectrum of  $[(L)Zn\{N(SiHMe_2)_2\}][HBPh_3]$  (**1**).

### $[(L)ZnCl]Cl$ (**2**).

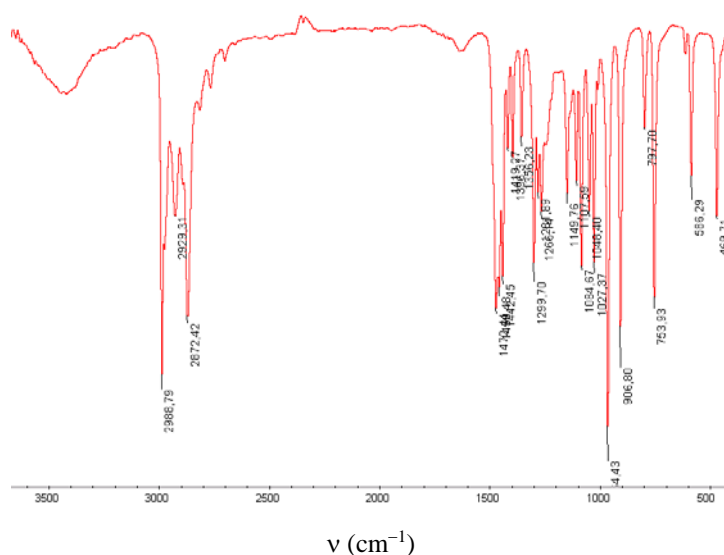
A solution of  $ZnCl_2$  (0.015 g, 0.109 mmol) in 2 mL of THF was layered on top of solution of **L** (0.025 g, 0.109 mmol) in 2 mL of THF. A colorless solid precipitated within 30 min. The solid was washed with *n*-pentane (3×5 mL) and dried under vacuum to give analytically pure **2** (0.035 g, 0.097 mmol, 89%) as a colorless powder.  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ):  $\delta$  2.95 (m, 8 H,  $NCH_2$ ), 2.64 (m, 8 H,  $NCH_2$ ), 2.44 (s, 12 H,  $NMe$ ).  $^{13}C\{^1H\}$  NMR (100 MHz,  $DMSO-d_6$ ):  $\delta$  52.2 ( $CH_2$ ), 44.0 ( $NMe$ ). Anal. Calc. for  $C_{12}H_{28}Cl_2N_4Zn$ : C, 39.52; H, 7.74, N, 15.36. Found: C, 39.96; H, 7.48; N, 15.17.



**Figure 6.**  $^1H$  NMR spectrum of  $[(L)ZnCl][Cl]$  (**2**) in  $DMSO-d_6$ .



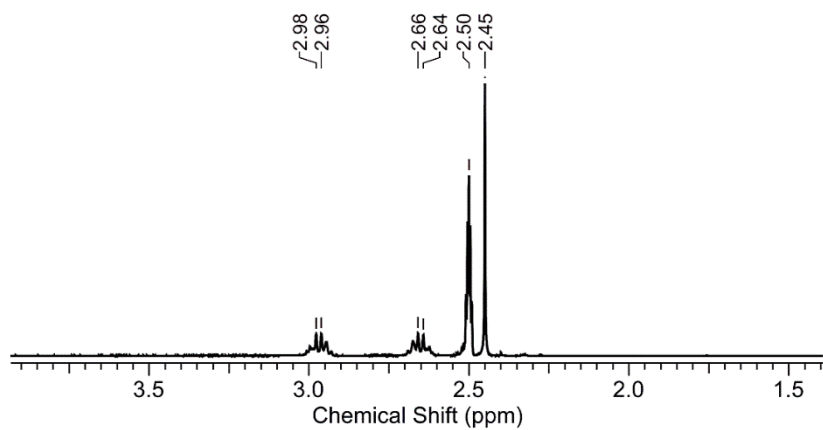
**Figure 7.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L})\text{ZnCl}][\text{Cl}]$  (**2**) in  $\text{DMSO-}d_6$ .



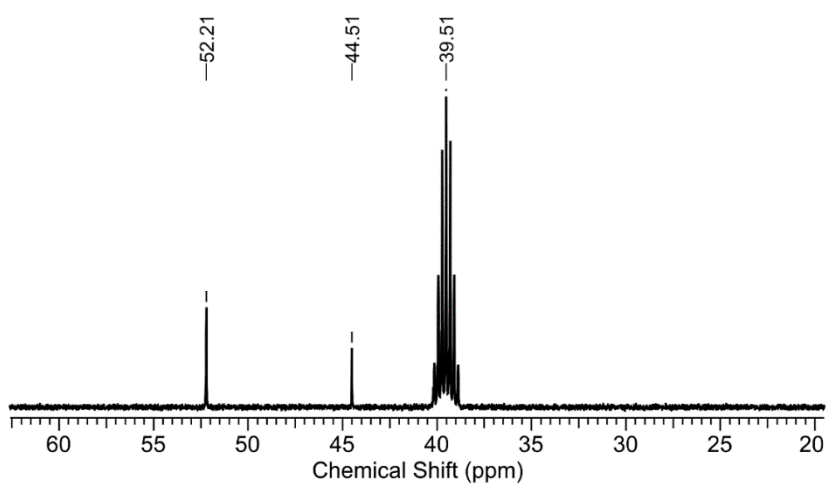
**Figure 8.** Solid-state IR (KBr) spectrum of  $[(\text{L})\text{ZnCl}][\text{Cl}]$  (**2**).

### **$[(\text{L})\text{ZnBr}]\text{Br}$ (**3**).**

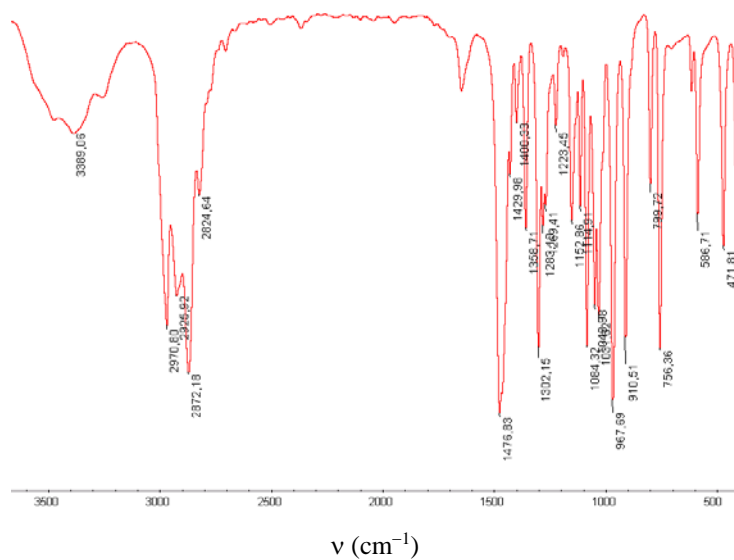
Starting from  $\text{ZnBr}_2$  (0.025 g, 0.109 mmol) and **L** (0.025 g, 0.109 mmol) **3** (0.043 g, 0.096 mmol, 87%) was prepared in a similar fashion as **2** and isolated as a colorless powder.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  2.97 (m, 8 H,  $\text{NCH}_2$ ), 2.65 (m, 8 H,  $\text{NCH}_2$ ), 2.45 (s, 12 H,  $\text{NMe}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  52.2 ( $\text{CH}_2$ ), 44.5 ( $\text{NMe}$ ). Anal. Calc. for  $\text{C}_{12}\text{H}_{28}\text{Br}_2\text{N}_4\text{Zn}$ : C, 31.78; H, 6.22, N, 12.35. Found: C, 31.97; H, 6.10; N, 12.33.



**Figure 9.**  $^1\text{H}$  NMR spectrum of  $[(\text{L})\text{ZnBr}][\text{Br}]$  (**3**) in  $\text{DMSO-}d_6$ .



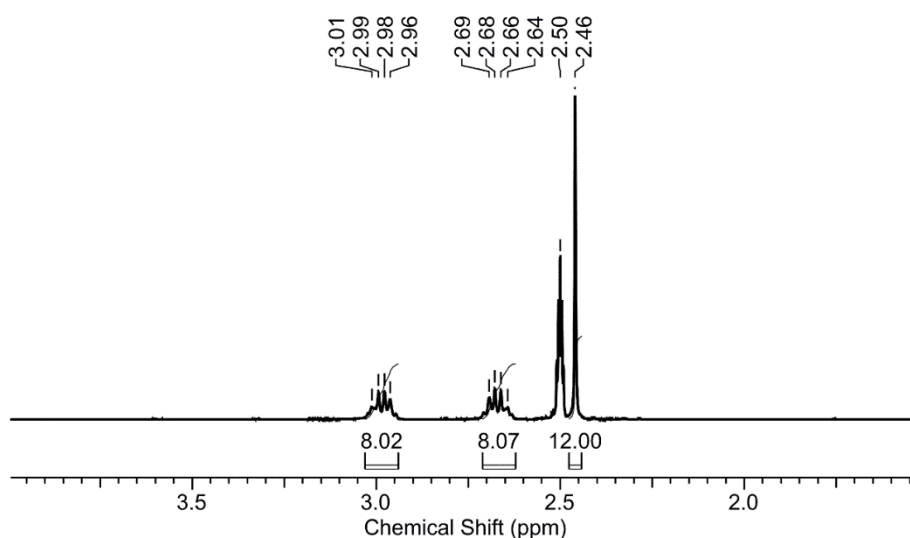
**Figure 10.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L})\text{ZnBr}][\text{Br}]$  (**3**) in  $\text{DMSO-}d_6$ .



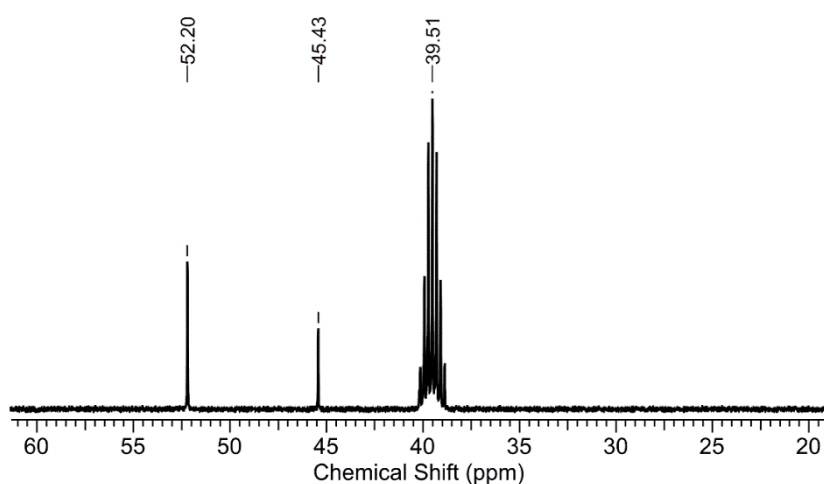
**Figure 11.** Solid-state IR (KBr) spectrum of  $[(\text{L})\text{ZnBr}][\text{Br}]$  (**3**).

**[(L)ZnI][I] (4).**

Starting from  $\text{ZnI}_2$  (0.035 g, 0.109 mmol) and L (0.025 g, 0.109 mmol) **4** (0.050 g, 0.091 mmol, 84%) was prepared in a similar fashion as **2** and isolated as a colorless powder.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  2.98 (m, 8 H,  $\text{NCH}_2$ ), 2.75 (m, 8 H,  $\text{NCH}_2$ ), 2.46 (s, 12 H,  $\text{NMe}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  52.2 ( $\text{CH}_2$ ), 45.4 ( $\text{NMe}$ ). **4** is sparingly soluble in THF, but NMR spectroscopic characterization was possible in  $\text{THF-}d_8$  and in  $\text{DMSO-}d_6$ .  $^1\text{H}$  NMR (400 MHz,  $\text{THF-}d_8$ ):  $\delta$  3.72 (m, 8 H,  $\text{NCH}_2$ ), 2.56 (m, 8 H,  $\text{NCH}_2$ ), 2.51 (s, 12 H,  $\text{NMe}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{THF-}d_8$ ):  $\delta$  54.5 ( $\text{CH}_2$ ), 46.3 ( $\text{NMe}$ ). Anal. Calc. for  $\text{C}_{12}\text{H}_{28}\text{I}_2\text{N}_4\text{Zn}$ : C, 26.32; H, 5.15, N, 10.23. Found: C, 26.28; H, 5.15; N, 10.24.



**Figure 12.**  $^1\text{H}$  NMR spectrum of  $[(\text{L})\text{ZnI}][\text{I}]$  (**4**) in  $\text{DMSO-}d_6$ .



**Figure 13.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L})\text{ZnI}][\text{I}]$  (**4**) in  $\text{DMSO-}d_6$ .

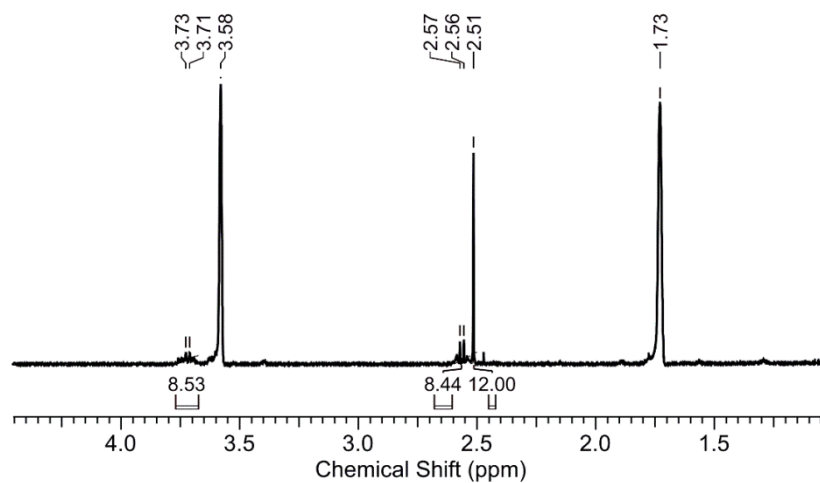


Figure 14.  $^1\text{H}$  NMR spectrum of  $[(\text{L})\text{ZnI}][\text{I}]$  (**4**) in  $\text{THF-}d_8$ .

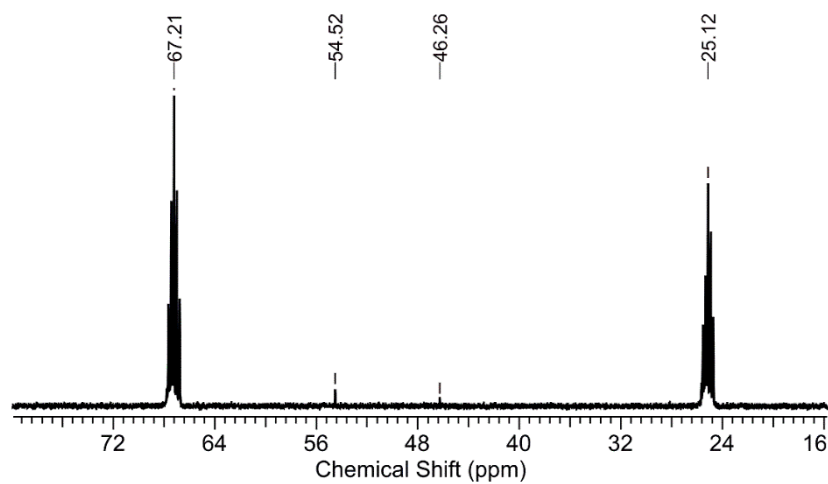


Figure 15.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L})\text{ZnI}][\text{I}]$  (**4**) in  $\text{THF-}d_8$ .

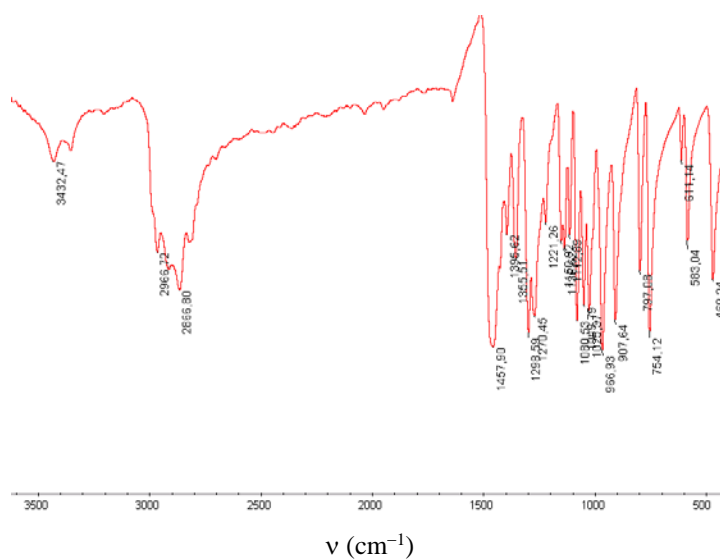
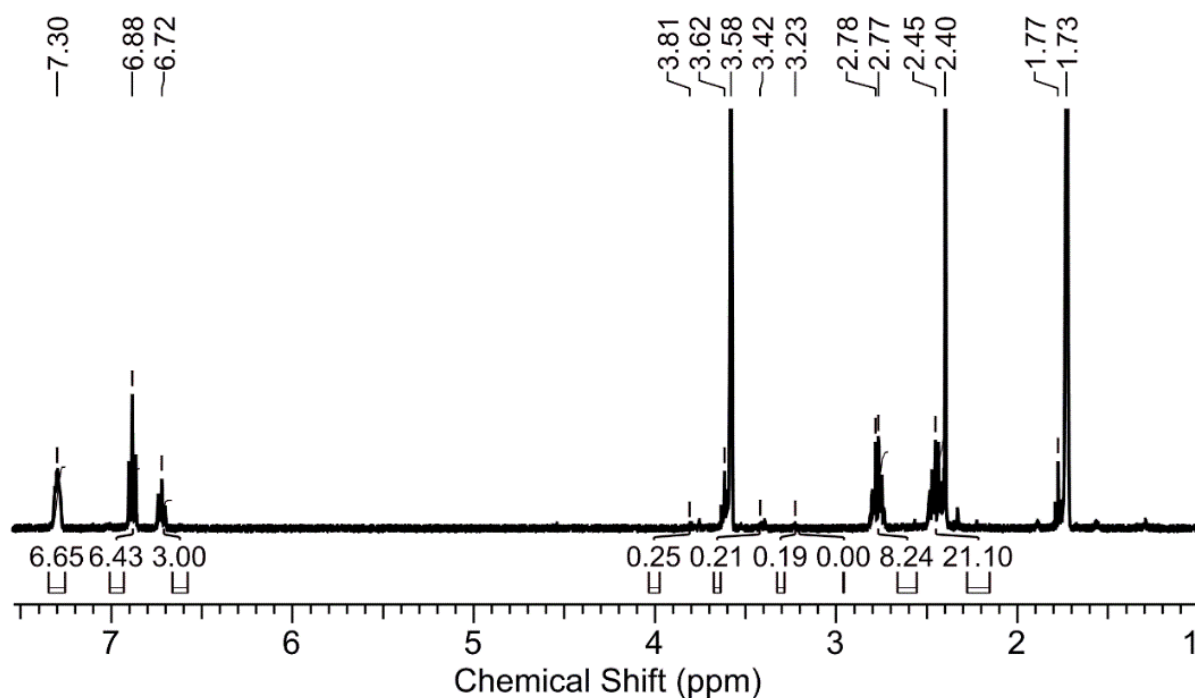


Figure 16. Solid-state IR (KBr) spectrum of  $[(\text{L})\text{ZnI}][\text{I}]$  (**4**).

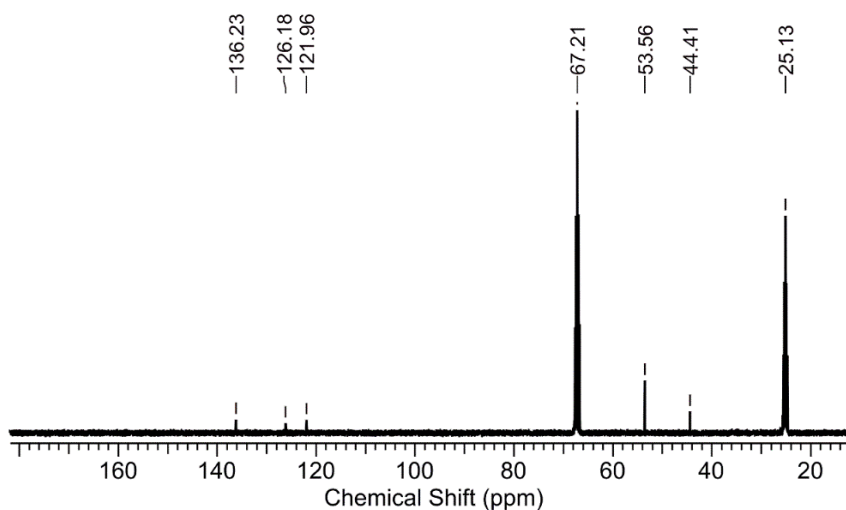


**[(L)ZnCl][HBPh<sub>3</sub>] (5).**

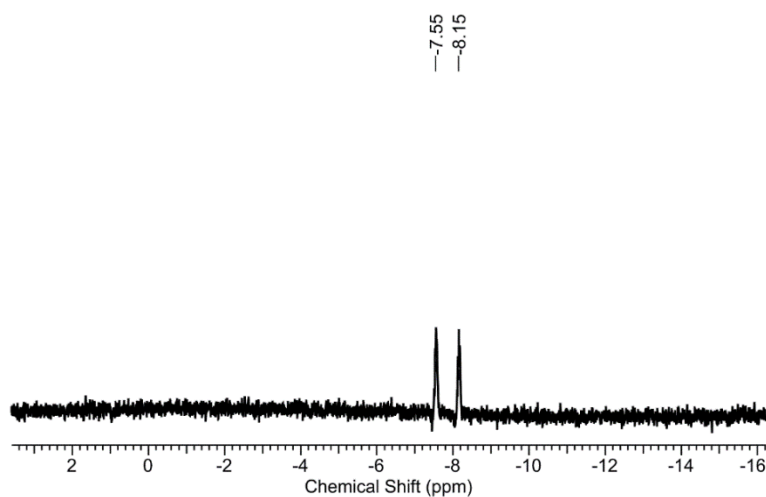
ZnCl<sub>2</sub> (0.015 g, 0.109 mmol) and L (0.025 g, 0.109 mmol) was stirred in 2 mL of THF for 30 min to give a colorless suspension. To this mixture, solid [KHBPh<sub>3</sub>(thf)<sub>0.625</sub>] (0.036 g, 0.109 mmol) was added and stirred for additional 18 h. The suspension was filtered and the filtrate was evaporated under reduced pressure to give a colorless solid. The solid was washed with *n*-pentane (3×5 mL) and dried under vacuum to afford analytically pure **5** (0.052 g, 0.091 mmol, 83%) as a white powder. <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>): δ 7.30 (m, 6 H, *o*-Ph), 6.88 (m, 6 H, *m*-Ph), 6.72 (m, 3 H, *p*-Ph), 3.81-3.23 (q, <sup>1</sup>J<sub>BH</sub> = 76 Hz, 1 H, BH), 2.76 (m, 8 H, NCH<sub>2</sub>), 2.45 (s, 12 H, NMe), 2.40 (m, 8 H, NCH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, THF-*d*<sub>8</sub>): δ 136.2 (*o*-Ph), 126.2 (*m*-Ph), 122.0 (*p*-Ph), 53.6 (CH<sub>2</sub>), 44.4 (NMe). <sup>11</sup>B NMR (128 MHz, THF-*d*<sub>8</sub>): δ -7.9 (d, <sup>1</sup>J<sub>BH</sub> = 77 Hz). IR (KBr, cm<sup>-1</sup>): 2184-2000 (ν<sub>BH</sub>). Anal. Calc. for C<sub>30</sub>H<sub>44</sub>BClN<sub>4</sub>Zn: C, 62.96; H, 7.75, N, 9.79. Found: C, 62.76; H, 8.03; N, 9.23.



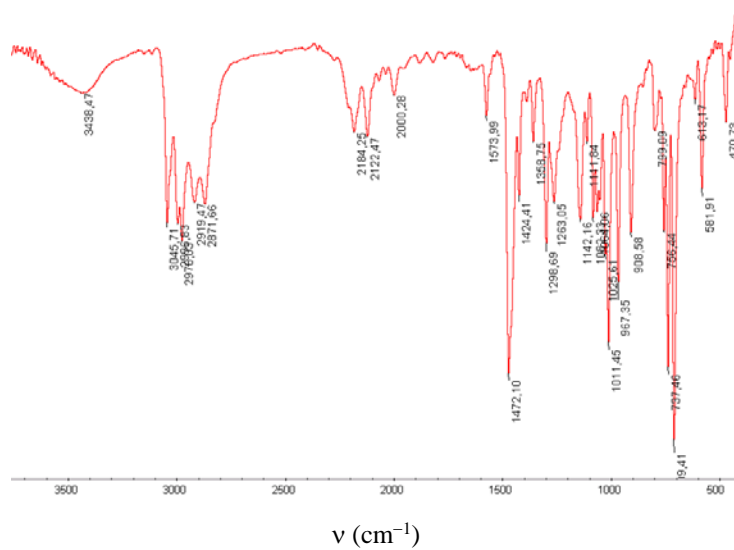
**Figure 17.** <sup>1</sup>H NMR spectrum of [(L)ZnCl][HBPh<sub>3</sub>] (**5**) in THF-*d*<sub>8</sub>.



**Figure 18.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L})\text{ZnCl}][\text{HBPh}_3]$  (**5**) in  $\text{THF-}d_8$ .



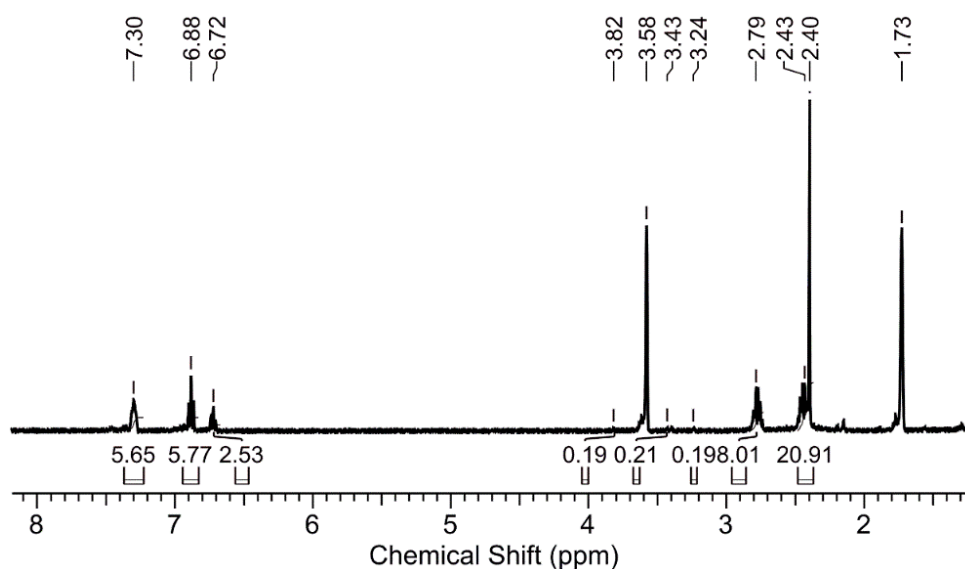
**Figure 19.**  $^{11}\text{B}$  NMR spectrum of  $[(\text{L})\text{ZnCl}][\text{HBPh}_3]$  (**5**) in  $\text{THF-}d_8$ .



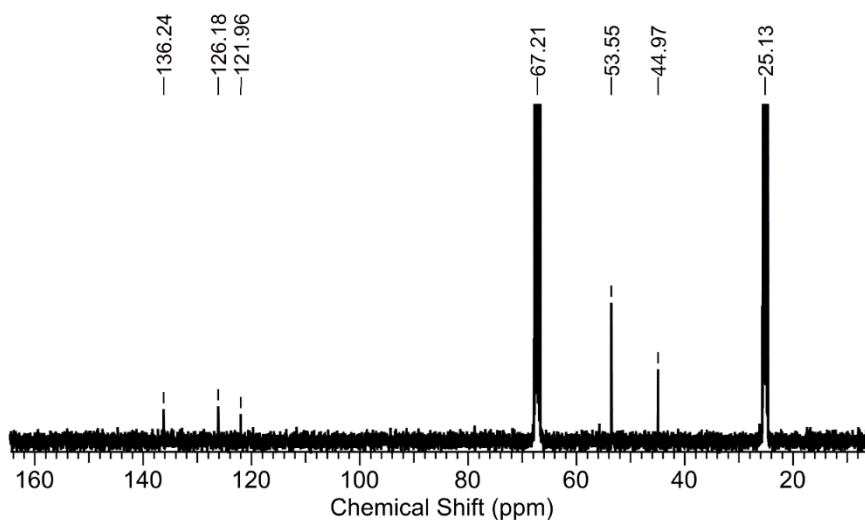
**Figure 20.** Solid-state IR (KBr) spectrum of  $[(\text{L})\text{ZnCl}][\text{HBPh}_3]$  (**5**).

**[(L)ZnBr][HBPh<sub>3</sub>] (6).**

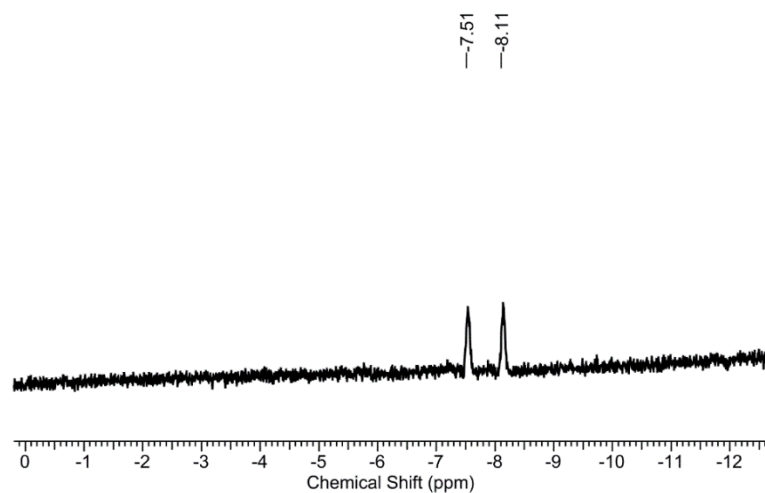
Starting from ZnBr<sub>2</sub> (0.025 g, 0.109 mmol), L (0.025 g, 0.109 mmol), and [KHBPh<sub>3</sub>(thf)<sub>0.625</sub>] (0.036 g, 0.109 mmol) **6** (0.055 g, 0.089 mmol, 82%) was prepared in a similar fashion as **5** and isolated as a colorless powder. <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>): δ 7.30 (m, 6 H, *o*-Ph), 6.88 (m, 6 H, *m*-Ph), 6.72 (m, 3 H, *p*-Ph), 3.82-3.24 (q, <sup>1</sup>J<sub>BH</sub> = 76 Hz, 1 H, BH), 2.79 (m, 8 H, NCH<sub>2</sub>), 2.43 (m, 8 H, NCH<sub>2</sub>), 2.40 (s, 12 H, NMe). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, THF-*d*<sub>8</sub>): δ 136.2 (*o*-Ph), 126.2 (*m*-Ph), 122.0 (*p*-Ph), 53.6 (CH<sub>2</sub>), 45.0 (NMe). <sup>11</sup>B NMR (128 MHz, THF-*d*<sub>8</sub>): δ -7.8 (d, <sup>1</sup>J<sub>BH</sub> = 77 Hz). IR (KBr, cm<sup>-1</sup>): 2188-1999 (ν<sub>BH</sub>). Anal. Calc. for C<sub>30</sub>H<sub>44</sub>BBrN<sub>4</sub>Zn: C, 58.42; H, 7.19, N, 9.08. Found: C 58.88; H, 7.42; N, 8.51.



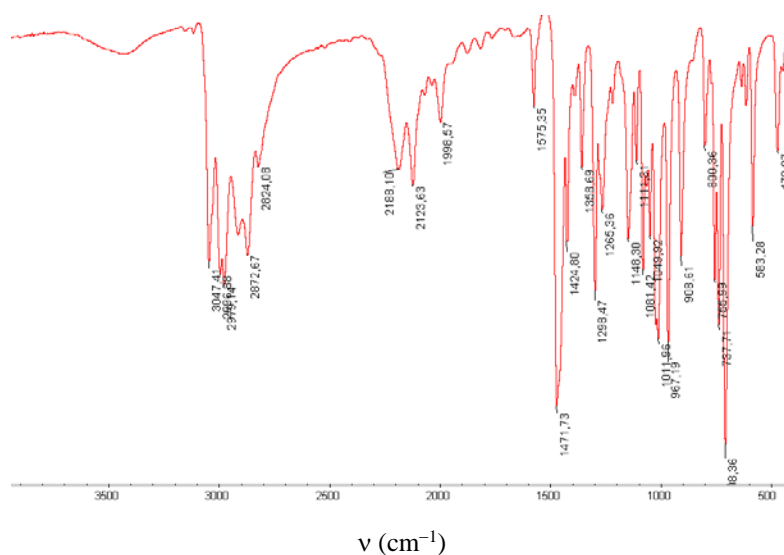
**Figure 21.** <sup>1</sup>H NMR spectrum of [(L)ZnBr][HBPh<sub>3</sub>] (6) in THF-*d*<sub>8</sub>.



**Figure 22.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [(L)ZnBr][HBPh<sub>3</sub>] (6) in THF-*d*<sub>8</sub>.



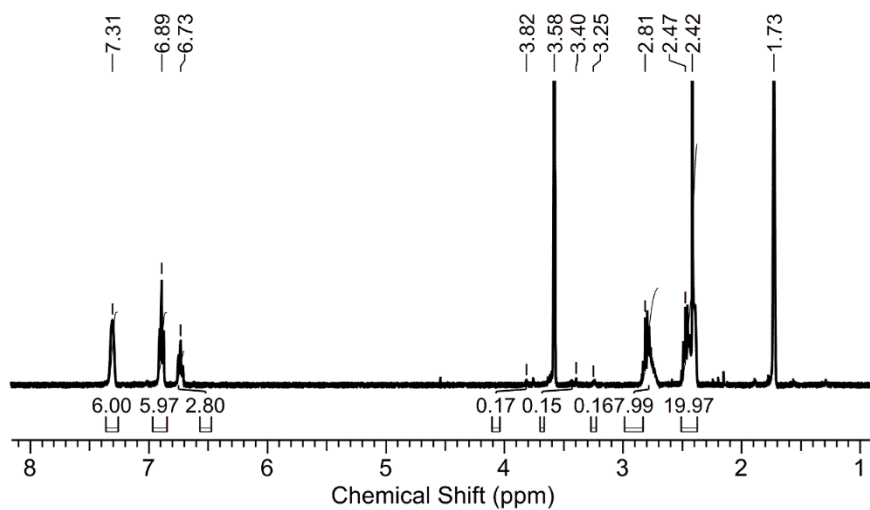
**Figure 23.**  $^{11}\text{B}$  NMR spectrum of  $[(\text{L})\text{ZnBr}][\text{HBPh}_3]$  (**6**) in  $\text{THF-}d_8$ .



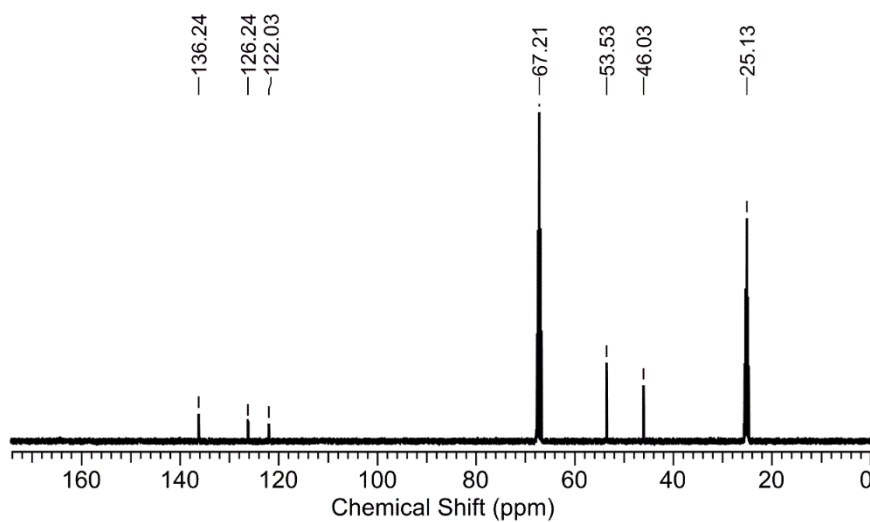
**Figure 24.** Solid-state IR (KBr) spectrum of  $[(\text{L})\text{ZnBr}][\text{HBPh}_3]$  (**6**).

### $[(\text{L})\text{ZnI}][\text{HBPh}_3]$ (**7**).

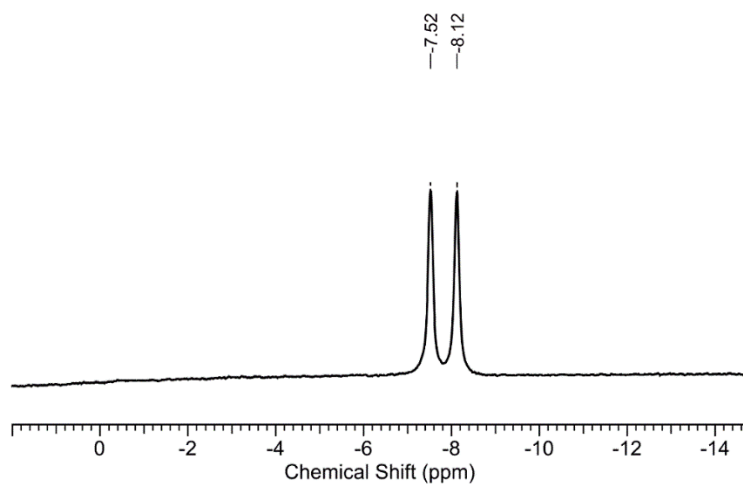
Starting from  $\text{ZnI}_2$  (0.035 g, 0.109 mmol), **L** (0.025 g, 0.109 mmol), and  $[\text{KHBPh}_3(\text{thf})_{0.625}]$  (0.036 g, 0.109 mmol) **7** was prepared in a similar fashion as **5** and isolated as a colorless powder in a similar fashion (0.053 g, 0.080 mmol, 73%).  $^1\text{H}$  NMR (400 MHz,  $\text{THF-}d_8$ ):  $\delta$  7.31 (m, 6 H, *o*-Ph), 6.89 (m, 6 H, *m*-Ph), 6.73 (m, 3 H, *p*-Ph), 3.82–3.25 (q,  $^1J_{\text{BH}} = 76$  Hz, 1 H, BH), 2.81 (m, 8 H,  $\text{NCH}_2$ ), 2.47 (m, 8 H,  $\text{NCH}_2$ ), 2.42 (s, 12 H, NMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{THF-}d_8$ ):  $\delta$  136.2 (*o*-Ph), 126.2 (*m*-Ph), 122.0 (*p*-Ph), 53.5 ( $\text{CH}_2$ ), 46.0 (NMe).  $^{11}\text{B}$  NMR (128 MHz,  $\text{THF-}d_8$ ):  $\delta$  -7.8 (d,  $^1J_{\text{BH}} = 77$  Hz). IR (KBr,  $\text{cm}^{-1}$ ): 2205–2018 ( $\nu_{\text{BH}}$ ). Anal. Calc. for  $\text{C}_{30}\text{H}_{44}\text{BIN}_4\text{Zn}$ : C, 54.28; H, 6.68; N, 8.55. Found: C, 54.48; H, 7.01; N, 8.97.



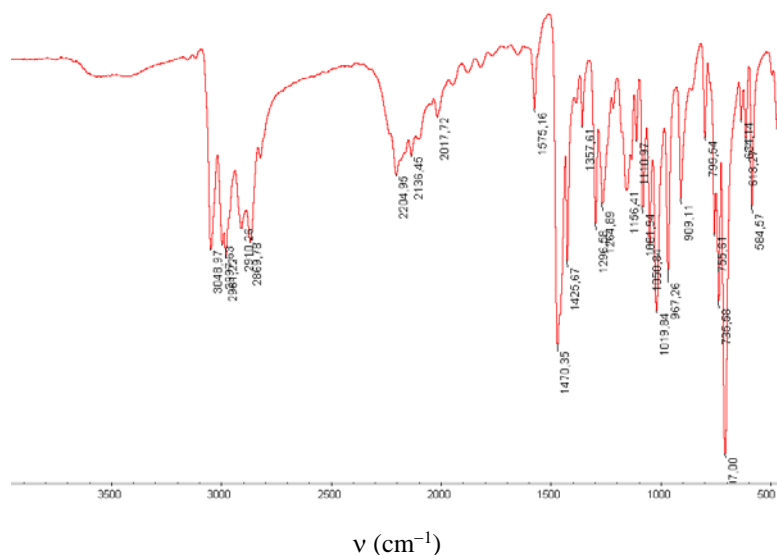
**Figure 25.**  $^1\text{H}$  NMR spectrum of  $[(\text{L})\text{ZnI}][\text{HBPh}_3]$  (**7**) in  $\text{THF-}d_8$ .



**Figure 26.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L})\text{ZnI}][\text{HBPh}_3]$  (**7**) in  $\text{THF-}d_8$ .



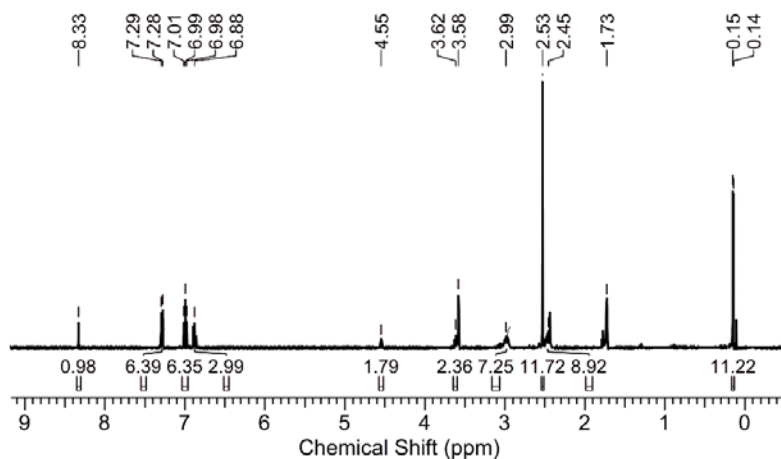
**Figure 27.**  $^{11}\text{B}$  NMR spectrum of  $[(\text{L})\text{ZnI}][\text{HBPh}_3]$  (**7**) in  $\text{THF-}d_8$ .



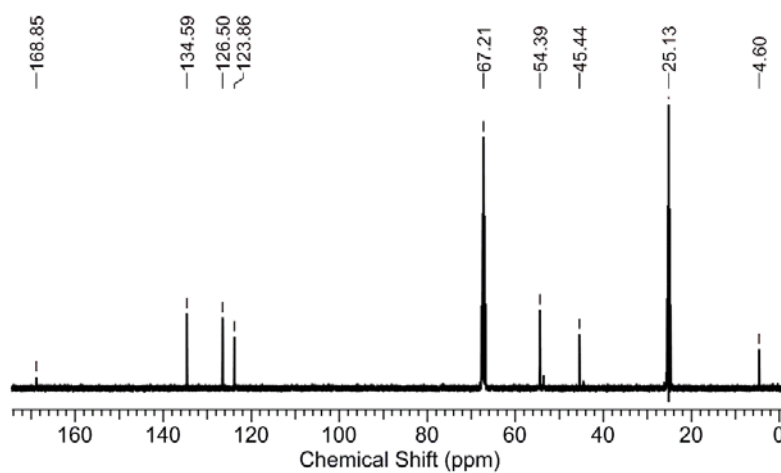
**Figure 28.** Solid-state IR (KBr) spectrum of [(L)ZnI][HBPh<sub>3</sub>] (**7**).

**[(L)Zn{N(SiHMe<sub>2</sub>)<sub>2</sub>}[HCO<sub>2</sub>BPh<sub>3</sub>]] (**8**).**

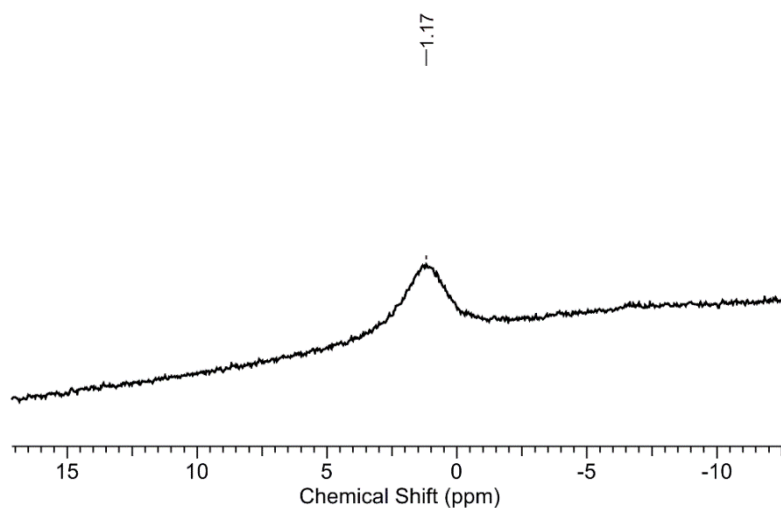
In a 25 mL Schlenk tube a solution of **1** (0.045 g, 0.067 mmol) 1 mL of THF was degassed following three freeze-pump-thaw cycles. The head space was then filled with CO<sub>2</sub> (1 atm). After 10 min, all the volatiles were removed under reduced pressure to give a colorless solid. The solid was washed with *n*-pentane (3×5 mL) and dried under vacuum to afford analytically pure **8** (0.039 g, 0.055 mmol, 81%) as a colorless powder. <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>): δ 8.33 (s, 1 H, HCO<sub>2</sub>), 7.28 (m, 6 H, *o*-Ph), 6.99 (m, 6 H, *m*-Ph), 6.88 (m, 3 H, *p*-Ph), 4.55 (m, 2 H, SiHMe<sub>2</sub>), 2.99 (m, 8 H, NCH<sub>2</sub>), 2.53 (s, 12 H, NMe), 2.45 (m, 8 H, NCH<sub>2</sub>), 0.15 (d, <sup>3</sup>J<sub>HH</sub> = 3.08 Hz, 12H, SiHMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, THF-*d*<sub>8</sub>): δ 168.9 (HCO<sub>2</sub>), 134.6 (*o*-Ph), 126.5 (*m*-Ph), 123.9 (*p*-Ph), 54.4 (CH<sub>2</sub>), 45.5 (NMe), 4.6 (SiHMe<sub>2</sub>). <sup>11</sup>B NMR (128 MHz, THF-*d*<sub>8</sub>): δ 1.2 (br, s). <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, THF-*d*<sub>8</sub>): δ -13.3. IR (KBr, cm<sup>-1</sup>): 2227 (ν<sub>SiH</sub>), 2116 (ν<sub>SiH</sub>), 1677 (ν<sub>CO</sub>), 1634 (ν<sub>CO</sub>). Anal. Calc. for C<sub>35</sub>H<sub>58</sub>BN<sub>5</sub>O<sub>2</sub>Si<sub>2</sub>Zn: C, 58.94; H, 8.20; N, 9.82. Found: C, 59.17; H, 8.09; N, 10.05.



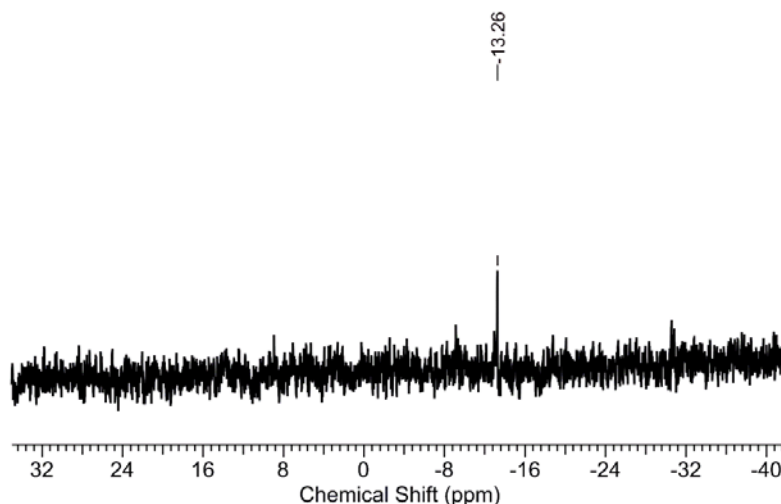
**Figure 29.**  $^1\text{H}$  NMR spectrum of  $[(\text{L})\text{Zn}\{\text{N}(\text{SiHMe}_2)_2\}][\text{HCO}_2\text{BPh}_3]$  (**8**) in  $\text{THF-}d_8$ .



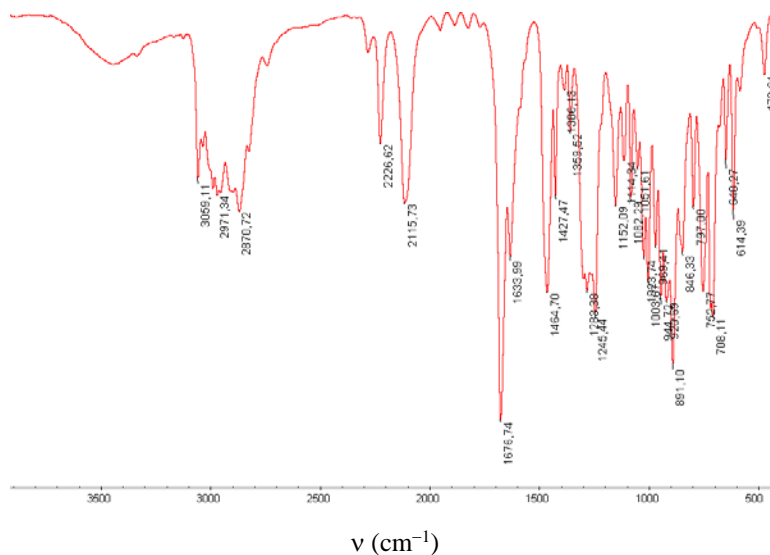
**Figure 30.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L})\text{Zn}\{\text{N}(\text{SiHMe}_2)_2\}][\text{HCO}_2\text{BPh}_3]$  (**8**) in  $\text{THF-}d_8$ .



**Figure 31.**  $^{11}\text{B}$  NMR spectrum of  $[(\text{L})\text{Zn}\{\text{N}(\text{SiHMe}_2)_2\}][\text{HCO}_2\text{BPh}_3]$  (**8**) in  $\text{THF-}d_8$ .



**Figure 32.**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L})\text{Zn}\{\text{N}(\text{SiHMe}_2)_2\}][\text{HCO}_2\text{BPh}_3]$  (**8**) in  $\text{THF-}d_8$ .

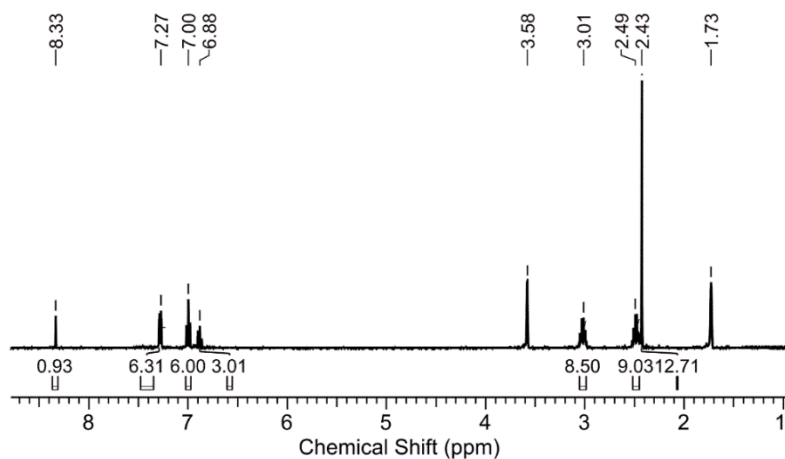


**Figure 33.** Solid-state IR (KBr) spectrum of  $[(\text{L})\text{Zn}\{\text{N}(\text{SiHMe}_2)_2\}][\text{HCO}_2\text{BPh}_3]$  (**8**).

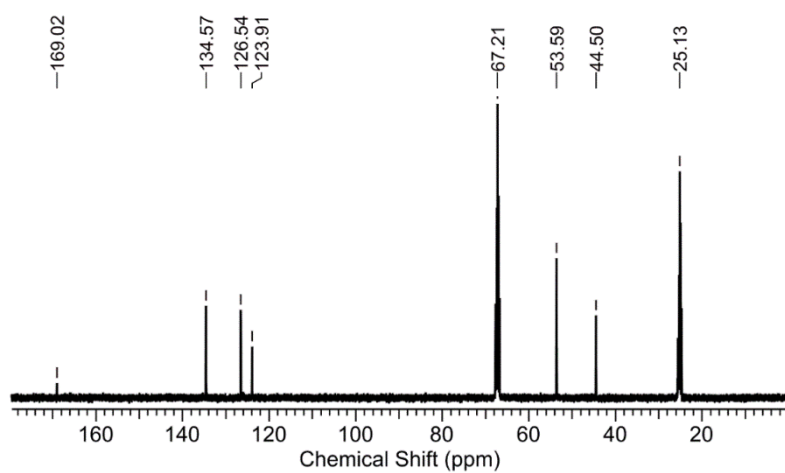
### $[(\text{L})\text{ZnCl}][\text{HCO}_2\text{BPh}_3]$ (**9**).

Complex **9** was prepared from **5** (0.027 g, 0.047 mmol) and  $\text{CO}_2$  (1 atm) in a similar fashion as **8** and isolated as a colorless solid (0.019 g, 0.031 mmol, 66%).  $^1\text{H}$  NMR (400 MHz,  $\text{THF-}d_8$ ):  $\delta$  8.34 (s, 1 H,  $\text{HCO}_2$ ), 7.27 (m, 6 H, *o*-Ph), 7.00 (m, 6 H, *m*-Ph), 6.88 (m, 3 H, *p*-Ph), 3.01 (m, 8 H,  $\text{NCH}_2$ ), 2.49 (m, 8 H,  $\text{NCH}_2$ ), 2.43 (s, 12 H, NMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{THF-}d_8$ ):  $\delta$  169.0 ( $\text{HCO}_2$ ), 134.6 (*o*-Ph), 126.5 (*m*-Ph), 123.9 (*p*-Ph), 53.6 ( $\text{CH}_2$ ), 44.5 (NMe).  $^{11}\text{B}$  NMR (128 MHz,  $\text{THF-}d_8$ ):  $\delta$  3.3 (br, s). IR (KBr,  $\text{cm}^{-1}$ ): 1672 ( $\nu_{\text{CO}}$ ). Anal. Calc. for  $\text{C}_{31}\text{H}_{44}\text{BClN}_4\text{O}_2\text{Zn}$ : C, 60.41; H, 7.20; N, 9.09. Found: C, 60.24; H, 7.07; N, 9.52.

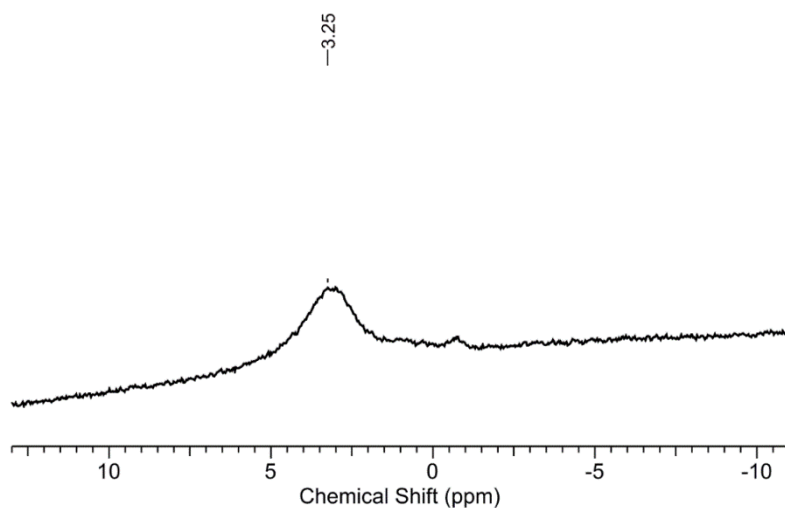




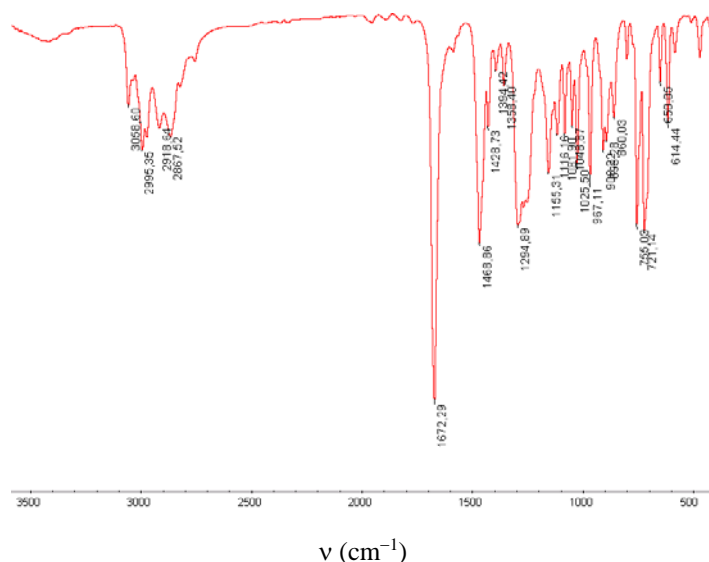
**Figure 34.**  $^1\text{H}$  NMR spectrum of  $[(\text{L})\text{ZnCl}][\text{HCO}_2\text{BPh}_3]$  (**9**) in  $\text{THF-}d_8$ .



**Figure 35.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L})\text{ZnCl}][\text{HCO}_2\text{BPh}_3]$  (**9**) in  $\text{THF-}d_8$ .



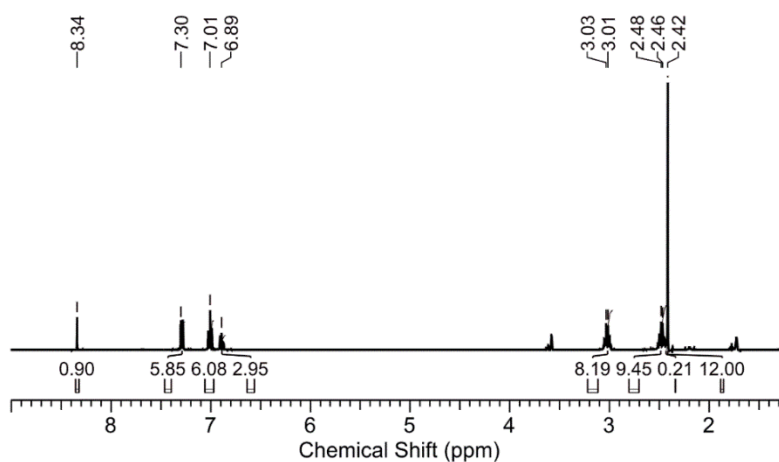
**Figure 36.**  $^{11}\text{B}$  NMR spectrum of  $[(\text{L})\text{ZnCl}][\text{HCO}_2\text{BPh}_3]$  (**9**) in  $\text{THF-}d_8$ .



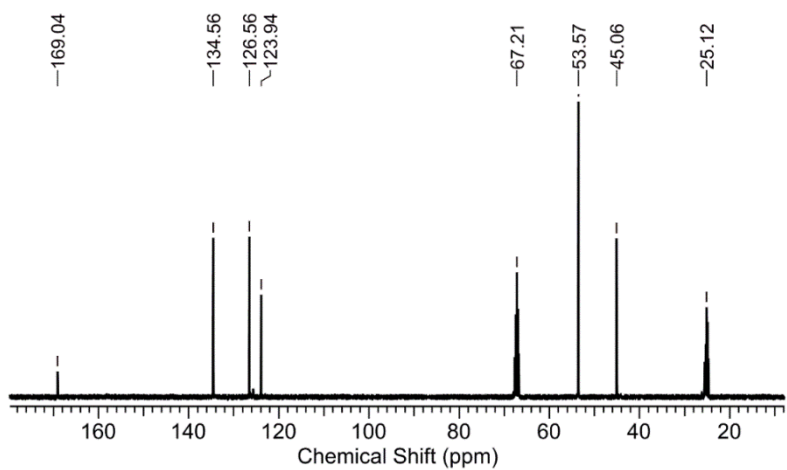
**Figure 37.** Solid-state IR (KBr) spectrum of  $[(L)ZnCl][HCO_2BPh_3]$  (**9**).

### $[(L)ZnBr][HCO_2BPh_3]$ (**10**)

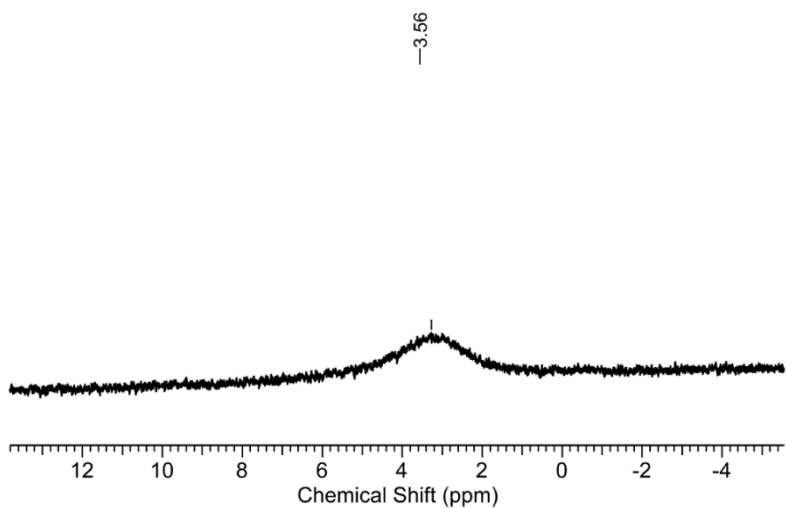
Complex **10** was prepared from **6** (0.016 g, 0.026 mmol) and  $CO_2$  (1 atm) as **8** and isolated as a colorless solid (0.019 g, 0.031 mmol, 66%).  $^1H$  NMR (400 MHz,  $THF-d_8$ ):  $\delta$  8.34 (s, 1 H,  $HCO_2$ ), 7.30 (m, 6 H, *o*-Ph), 7.01 (m, 6 H, *m*-Ph), 6.89 (m, 3 H, *p*-Ph), 3.02 (m, 8 H,  $NCH_2$ ), 2.47 (m, 8 H,  $NCH_2$ ), 2.42 (s, 12 H,  $NMe$ ).  $^{13}C\{^1H\}$  NMR (100 MHz,  $THF-d_8$ ):  $\delta$  169.0 ( $HCO_2$ ), 134.6 (*o*-Ph), 126.6 (*m*-Ph), 123.9 (*p*-Ph), 53.6 ( $CH_2$ ), 45.1 ( $NMe$ ).  $^{11}B$  NMR (128 MHz,  $THF-d_8$ ):  $\delta$  3.6 (br, s). IR (KBr,  $cm^{-1}$ ): 1675 ( $\nu_{CO}$ ). Anal. Calc. for  $C_{31}H_{44}BBrN_4O_2Zn$ : C, 56.35; H, 6.71, N, 8.48. Found: C, 56.33; H, 6.60; N, 8.61.



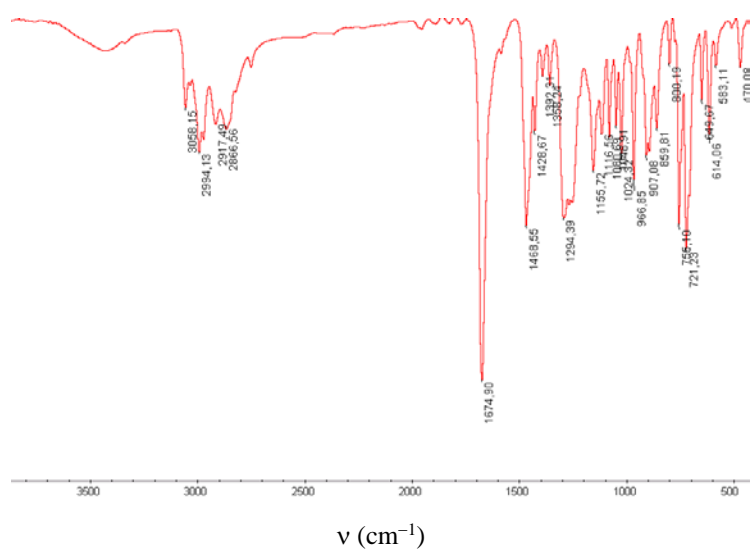
**Figure 38.**  $^1H$  NMR spectrum of  $[(L)ZnBr][HCO_2BPh_3]$  (**10**) in  $THF-d_8$ .



**Figure 39.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L})\text{ZnBr}][\text{HCO}_2\text{BPh}_3]$  (**10**) in  $\text{THF-}d_8$ .



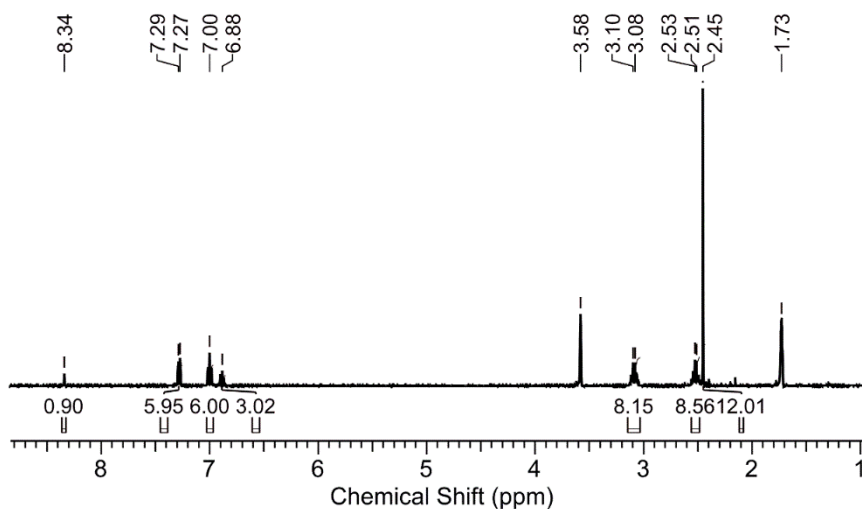
**Figure 40.**  $^{11}\text{B}$  NMR spectrum of  $[(\text{L})\text{ZBr}][\text{HCO}_2\text{BPh}_3]$  (**10**) in  $\text{THF-}d_8$ .



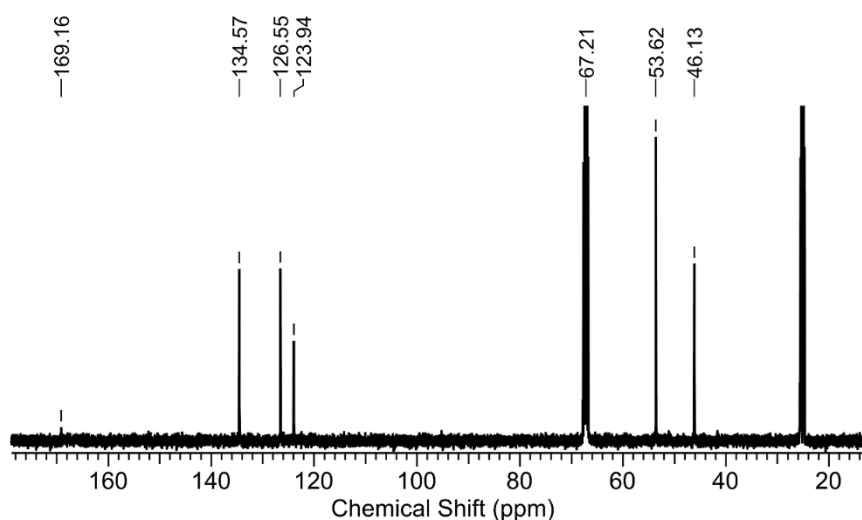
**Figure 41.** Solid-state IR (KBr) spectrum of  $[(\text{L})\text{ZnBr}][\text{HCO}_2\text{BPh}_3]$  (**8**).

### **[(L)ZnI][HCO<sub>2</sub>BPh<sub>3</sub>] (11)**

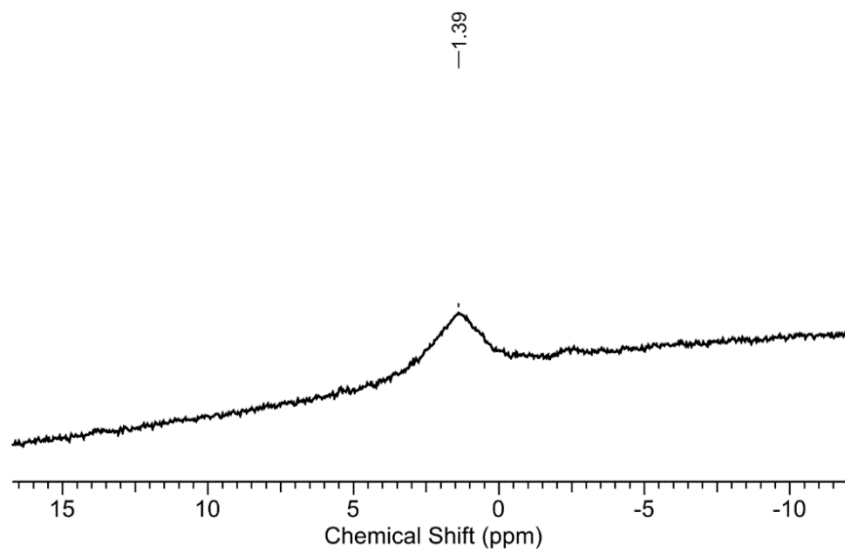
Complex **11** was prepared from **7** (0.030 g, 0.045 mmol) and CO<sub>2</sub> (1 atm) in a similar fashion as **8** and as a colorless solid (0.024 g, 0.034 mmol, 75%). <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>): δ 8.33 (s, 1 H, HCO<sub>2</sub>), 7.28 (m, 6 H, *o*-Ph), 7.00 (m, 6 H, *m*-Ph), 6.88 (m, 3 H, *p*-Ph), 3.09 (m, 8 H, NCH<sub>2</sub>), 2.53 (m, 8 H, NCH<sub>2</sub>), 2.45 (s, 12 H, NMe). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, THF-*d*<sub>8</sub>): δ 169.2 (HCO<sub>2</sub>), 134.6 (*o*-Ph), 126.6 (*m*-Ph), 123.9 (*p*-Ph), 53.6 (CH<sub>2</sub>), 46.1 (NMe). <sup>11</sup>B NMR (128 MHz, THF-*d*<sub>8</sub>): δ 1.4 (br, s). IR (KBr, cm<sup>-1</sup>): 1679 (ν<sub>CO</sub>). Anal. Calc. for C<sub>31</sub>H<sub>44</sub>BN<sub>4</sub>O<sub>2</sub>Zn: C, 52.60; H, 6.27, N, 7.92. Found: C, 52.86; H, 6.17; N, 8.26.



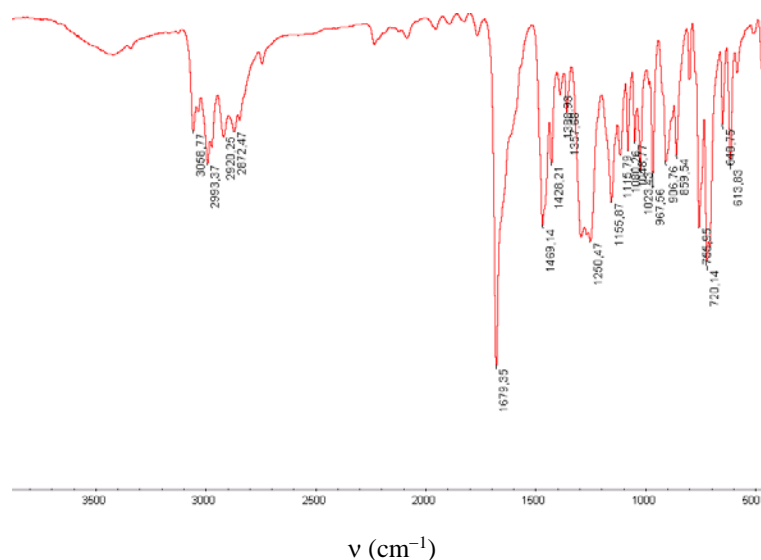
**Figure 42.** <sup>1</sup>H NMR spectrum of [(L)ZnI][HCO<sub>2</sub>BPh<sub>3</sub>] (**11**) in THF-*d*<sub>8</sub>.



**Figure 43.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [(L)ZnI][HCO<sub>2</sub>BPh<sub>3</sub>] (**11**) in THF-*d*<sub>8</sub>.



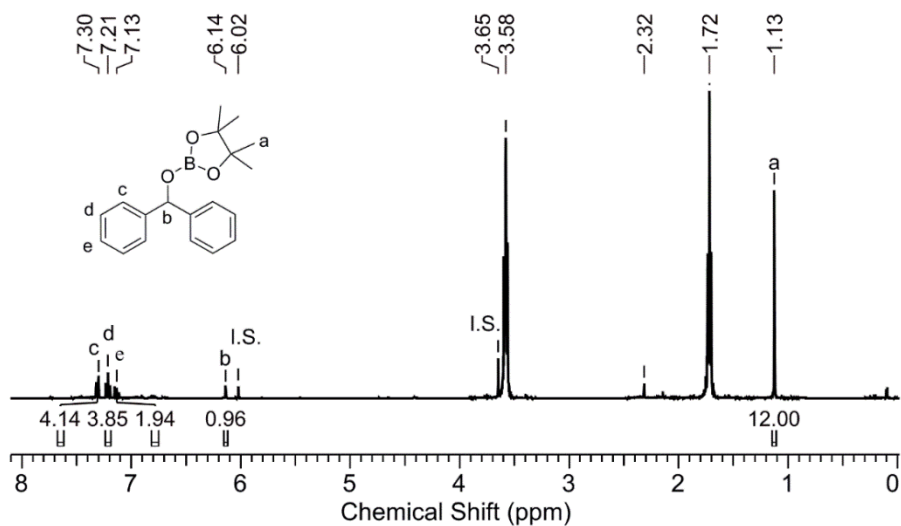
**Figure 44.**  $^{11}\text{B}$  NMR spectrum of  $[(\text{L})\text{ZnI}][\text{HCO}_2\text{BPh}_3]$  (**11**) in  $\text{THF-}d_8$ .



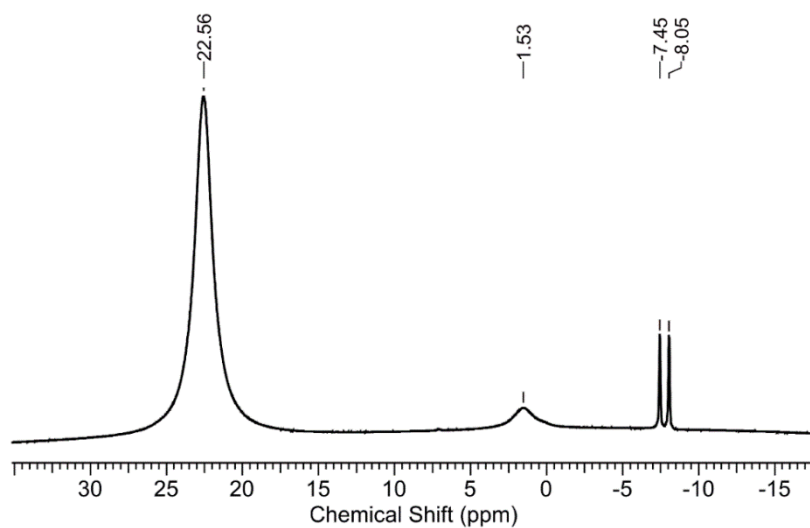
**Figure 45.** Solid-state IR (KBr) spectrum of  $[(\text{L})\text{ZnI}][\text{HCO}_2\text{BPh}_3]$  (**11**).

### Hydroboration catalysis using **1**.

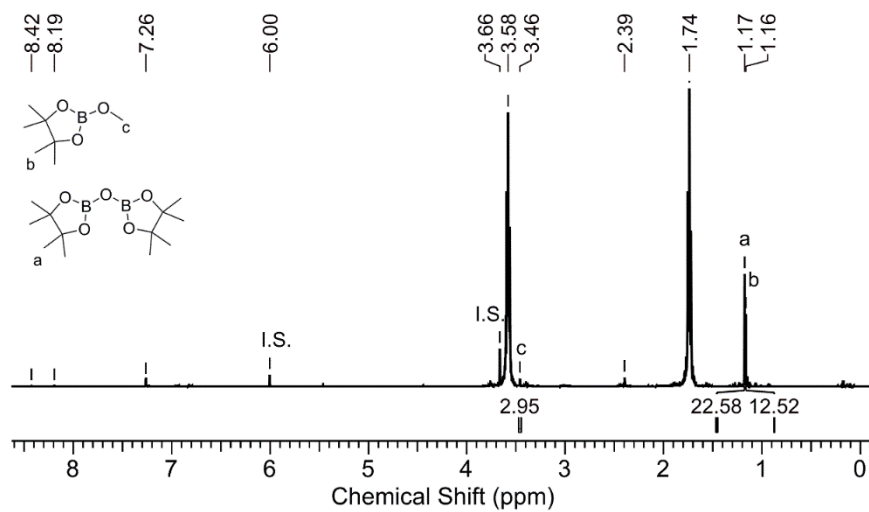
The hydroboration catalysis was performed on NMR-scale. A 5 mL aliquot of 0.06 M stock solution of 1,3,5-trimethoxybenzene (internal standard) in THF was prepared ( $\text{THF}:\text{THF-}d_8 = 2:1$ ). A Teflon-sealed NMR tube was charged with substrate (0.21 mmol), HBpin (0.21 mmol), **1** (0.021 mmol) and 0.45 mL of the stock solution. Preheated oil bath was used for the catalysis at  $60\text{ }^\circ\text{C}$ . For  $\text{CO}_2$  hydroboration, the reaction mixture in a Teflon-sealed NMR tube was degassed by three freeze-pump-thaw cycles, followed by filling the headspace with  $\text{CO}_2$  (1 atm). Reaction progress was monitored by  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectroscopy and compared with the literature.<sup>S4</sup>



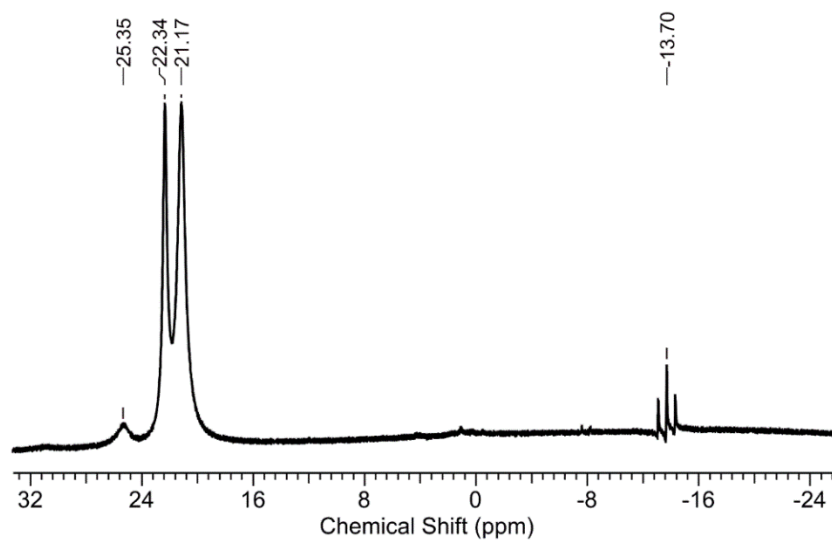
**Figure 46.**  $^1\text{H}$  NMR spectrum for the hydroboration of benzophenone in  $\text{THF-}d_8$ .



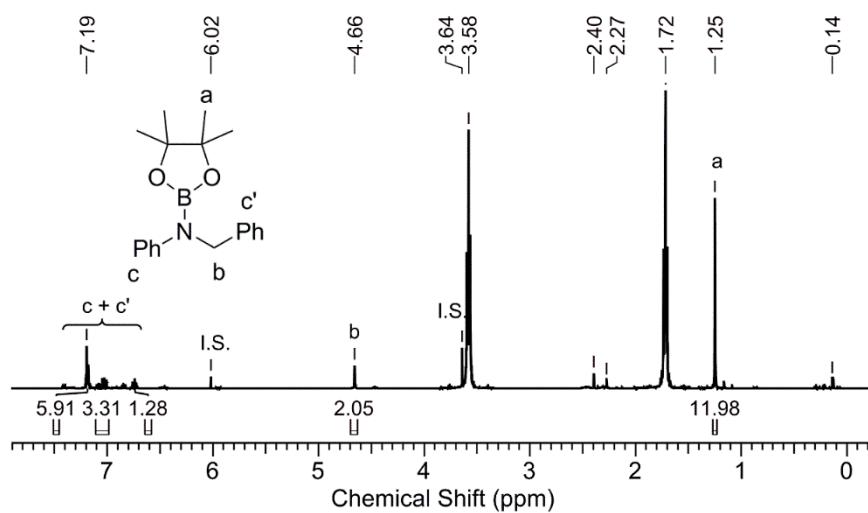
**Figure 47.**  $^{11}\text{B}$  NMR spectrum for the hydroboration of benzophenone in  $\text{THF-}d_8$ .



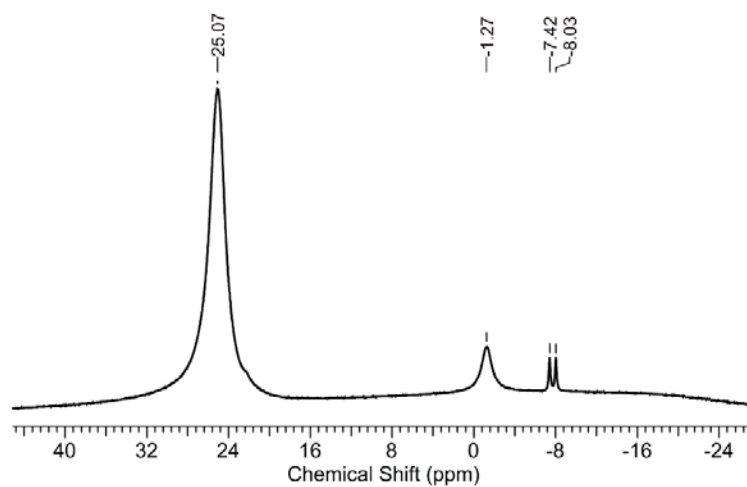
**Figure 48.**  $^1\text{H}$  NMR spectrum for the hydroboration of  $\text{CO}_2$  in  $\text{THF-}d_8$ .



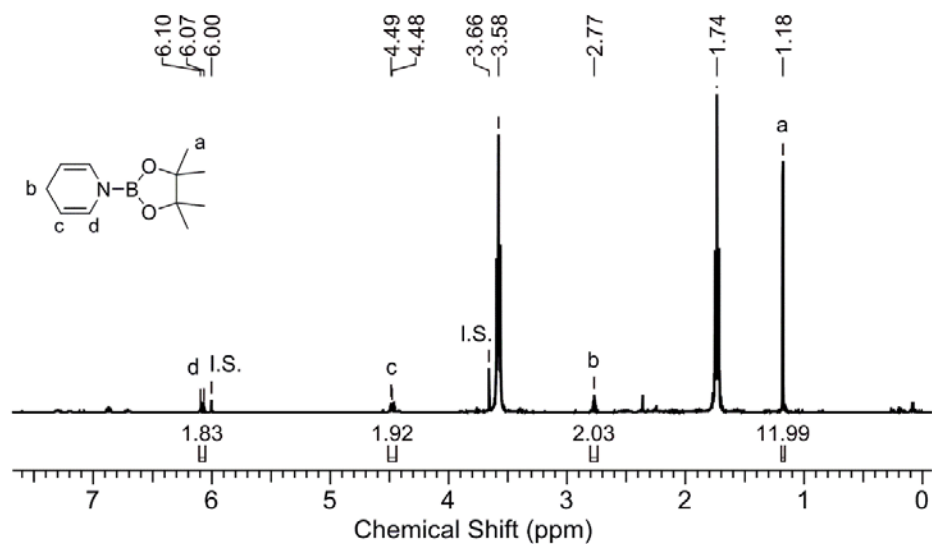
**Figure 49.**  $^{11}\text{B}$  NMR spectrum for the hydroboration of  $\text{CO}_2$  in  $\text{THF-}d_8$ .



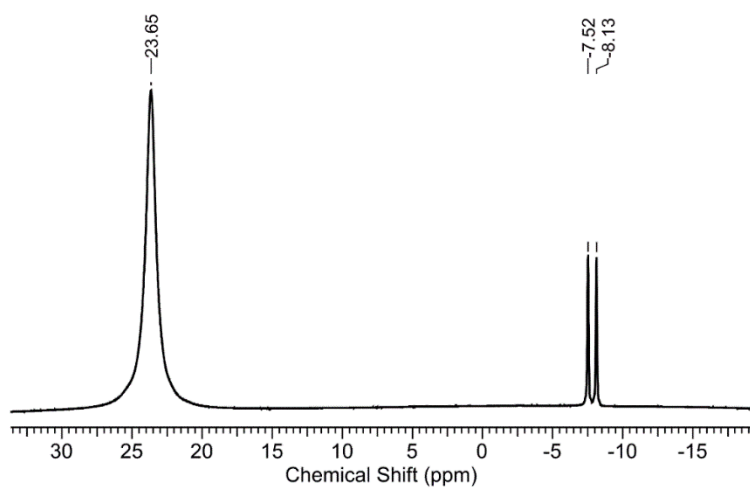
**Figure 50.**  $^1\text{H}$  NMR spectrum for the hydroboration of *N*-benzylideneaniline in  $\text{THF-}d_8$ .



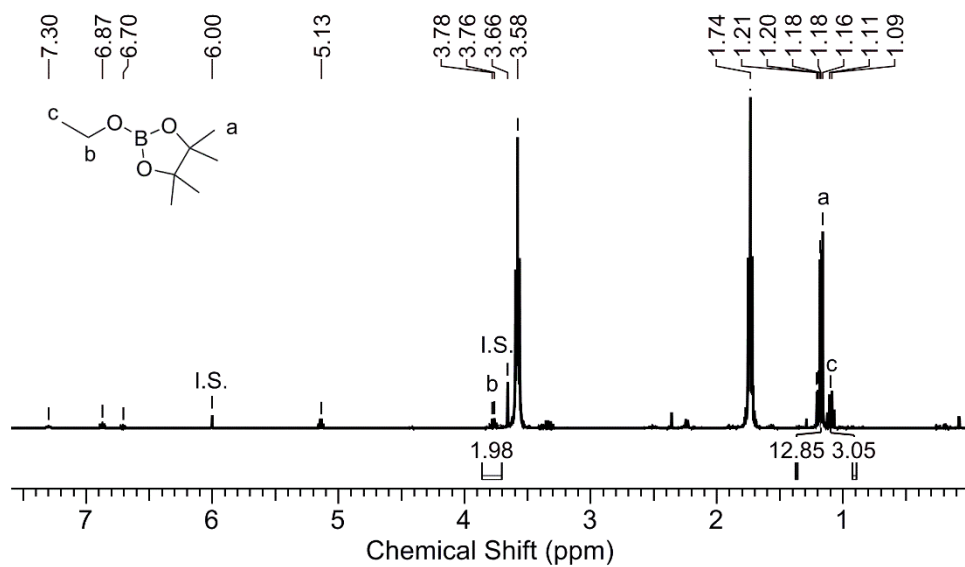
**Figure 51.**  $^{11}\text{B}$  NMR spectrum for the hydroboration of *N*-benzylideneaniline in  $\text{THF-}d_8$ .



**Figure 52.**  $^1\text{H}$  NMR spectrum for the hydroboration of pyridine in  $\text{THF-}d_8$ .

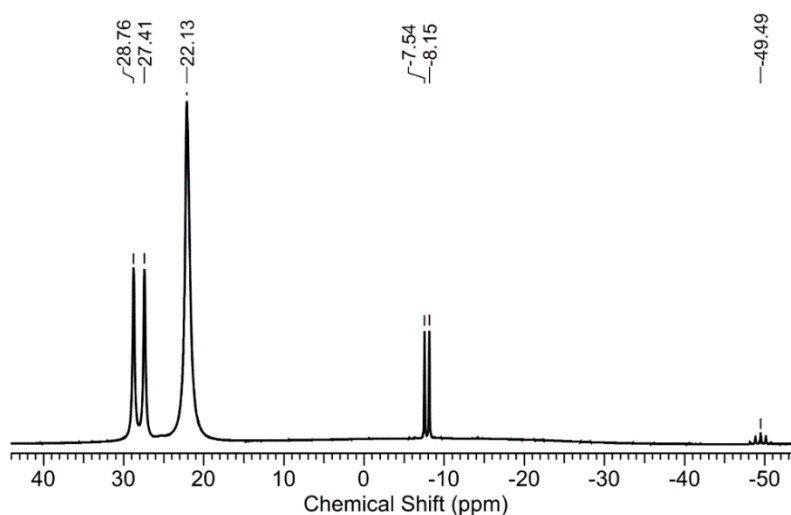


**Figure 53.**  $^{11}\text{B}$  NMR spectrum for the hydroboration of pyridine in  $\text{THF-}d_8$ .



**Figure 54.**  $^1\text{H}$  NMR spectrum for the hydroboration of ethylacetate in  $\text{THF-}d_8$ .





**Figure 55.**  $^1\text{H}$  NMR spectrum for the hydroboration of ethylacetate in  $\text{THF-}d_8$ .

### Crystal structure analysis.

Single-crystal X-ray diffraction measurements of **4**, **7** and **11** were performed on a Bruker AXS diffractometer equipped with an Incoatec microsource and an APEX area detector using  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), multilayer optics and  $\omega$ -scans. Temperature control was achieved with an Oxford cryostream 700. The SMART program was used for data collection and unit cell determination. Processing of the raw data frame was performed using SAINT+,<sup>S5</sup> multi scan absorption corrections were applied with SADABS.<sup>S6</sup> The structures were solved by direct methods (SIR-92).<sup>S7</sup> The crystal lattice of **4** contains two crystallographically independent molecules of THF that are disordered, one of them around a crystallographic inversion center. Disorder was also found in **7** for the carbon atoms C1–C8 of the ligand  $\text{Me}_4\text{TACD}$ , as well as in **11** for all carbon atoms C1–C12 and all nitrogen atoms N1–N4 of the ligand  $\text{Me}_4\text{TACD}$  and the iodine atom I1. In each case, the disorder could be modeled with split positions. The Refinements were performed against  $F^2$  with the program SHELXL-2013 using all reflections, as implemented in the program system WinGX.<sup>S8,9</sup> Hydrogen atoms were included as riding on calculated positions with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{non-H})$ , except for the atoms bound to boron (H1 in **7** that was localized in a difference Fourier map and refined in its position with isotropic displacement parameters  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{B})$ . All non-hydrogen atoms were refined anisotropically. Refinement results are given in Table S1. Graphical representations were performed with the program DIAMOND.<sup>S10</sup> CCDC-1539861 (**4**), -1539862 (**7**), -1539863 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S1.** Crystal data and structure refinement.

	<b>4</b>	<b>7</b>	<b>11</b>
chemical formula	2(C <sub>12</sub> H <sub>28</sub> IN <sub>4</sub> Zn), 2I, 3(C <sub>4</sub> H <sub>8</sub> O)	C <sub>12</sub> H <sub>28</sub> IN <sub>4</sub> Zn, C <sub>18</sub> H <sub>16</sub> B, C <sub>4</sub> H <sub>8</sub> O	C <sub>12</sub> H <sub>28</sub> IN <sub>4</sub> Zn, C <sub>19</sub> H <sub>16</sub> BO <sub>2</sub>
fw (g·mol <sup>-1</sup> )	1311.42	745.87	707.78
space group	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/c</i>	<i>Pbca</i>
crystal size (mm)	0.16×0.22×0.22	0.21×0.27×0.31	0.30×0.30×0.37
unit cell parameters			
<i>a</i> (Å)	7.936(2)	16.619(5)	17.691(2)
<i>b</i> (Å)	12.276(3)	9.831(3)	20.439(3)
<i>c</i> (Å)	25.751(7)	21.995(7)	17.778(2)
β (°)	94.987(6)	103.977(5)	
(Å <sup>3</sup> )	2499.2(11)	3847.2(19)	1552.4(4)
<i>Z</i>	2	4	8
<i>T</i> (K)	100(2)	100(2)	100(2)
μ(Mo K <sub>α</sub> ) (mm <sup>-1</sup> )	3.470	1.621	1.758
reflns	22658	31105	56175
independent reflns ( <i>R</i> <sub>int.</sub> )	5153 (0.0993)	7201 (0.1128)	6662 (0.1187)
observed reflns	3429	4782	4253
parameters	238	379	358
goodness of fit on <i>F</i> <sup>2</sup>	1.024	0.929	1.017
final R indices			
<i>R</i> 1, <i>wR</i> 2 [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.0590, 0.1357	0.0471, 0.0974	0.0590, 0.1458
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0949, 0.1489	0.0792, 0.1048	0.0983, 0.1685

## 5. References.

- S1 Y. Liang and R. Anwender, *Dalton Trans.*, 2006, 1909-1918.
- S2 J. Coates, D. Hadi and S. Lincoln, *Aus. J. Chem.*, 1982, **35**, 903-909.
- S3 N. M. Yoon, K. E. Kim and J. Kang, *J. Org. Chem.*, 1986, **51**, 226-229.
- S4 (a) D. Mukherjee, H. Osseili, T. P. Spaniol and J. Okuda, *J. Am. Chem. Soc.*, 2016, **138**, 10790-10793; (b) D. Mukherjee, S. Shirase, T. P. Spaniol, K. Mashima and J. Okuda, *Chem. Commun.*, 2016, **52**, 13155-13158.
- S5 Bruker, SAINT-Plus, Bruker AXS Inc., Madison, Wisconsin, USA, 1999.
- S6 Bruker, SADABS, Bruker AXS Inc. Madison, Wisconsin, USA, 2004.
- S7 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.* 1993, **26**, 343-350.
- S8 G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2008, **64**, 112–122.
- S9 L. J. Farrugia, *J. Appl. Crystallogr.* 2012, **45**, 849-854.
- S10 K. Brandenburg, DIAMOND, Crystal Impact GbR, Bonn, Germany, 2017.