

## **Supporting Information**

### **Facile Insertion of a Cyclic Alkyl(Amino) Carbene Carbon into the B-B Bond of Diboron(4) Reagents**

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# 1. Experimental Section and NMR Spectra

## 1.1 General Considerations

All reactions and subsequent manipulations were performed under an argon atmosphere using standard Schlenk techniques as reported previously.<sup>[S1]</sup> NMR spectra were recorded on a Bruker Avance 500 (<sup>1</sup>H, 500.1 MHz; <sup>13</sup>C, 125.8 MHz; <sup>11</sup>B, 160.4 MHz), Avance 400 (<sup>1</sup>H, 400.4 MHz; <sup>13</sup>C, 100.7 MHz; <sup>11</sup>B, 128.5 MHz) and Avance 200 (<sup>1</sup>H, 199.9 MHz; <sup>11</sup>B, 64.1 MHz), using C<sub>6</sub>D<sub>6</sub>. <sup>13</sup>C NMR spectra are broad-band proton-decoupled (<sup>13</sup>C{<sup>1</sup>H}). Assignment of the <sup>13</sup>C NMR data was supported by <sup>13</sup>C,<sup>1</sup>H correlation experiments. Chemical shifts are listed in parts per million (ppm) and were determined relative to internal C<sub>6</sub>D<sub>5</sub>H (<sup>1</sup>H,  $\delta$  = 7.16; C<sub>6</sub>D<sub>6</sub> natural-abundance carbon resonances C<sub>6</sub>D<sub>6</sub> (<sup>13</sup>C,  $\delta$  = 128.06; C<sub>6</sub>D<sub>6</sub>). Coupling constants are quoted in hertz. High resolution mass spectroscopy was measured on a Thermo Scientific Exactive Plus mass spectrometer, equipped with an Orbitrap Mass Analyzer. Measurements were accomplished using an ASAP/APCI source with a corona needle, and a carrier-gas (N<sub>2</sub>) temperature of 250 °C. The starting compounds cAAC<sup>Me</sup>, B<sub>2</sub>cat<sub>2</sub> and B<sub>2</sub>eg<sub>2</sub> were prepared according to published procedures.<sup>[S2-S5]</sup> The diboron reagents B<sub>2</sub>pin<sub>2</sub>, and B<sub>2</sub>neop<sub>2</sub> were a generous gift from AllyChem Co. Ltd.

## 1.2 Synthesis of the Compounds

### Synthesis of cAAC<sup>Me</sup>(Bpin)<sub>2</sub> **1**

In a Schlenk-tube B<sub>2</sub>pin<sub>2</sub> (178 mg, 700  $\mu$ mol) and cAAC<sup>Me</sup> (200 mg, 700  $\mu$ mol) were dissolved in 12 mL of toluene. After stirring the reaction mixture for 15 h at room temperature, the solvent was removed under reduced pressure. The residue was washed with 8 mL of *n*-hexane and dried *in vacuo*. Yield: 170 mg (315  $\mu$ mol, 45%) of a white solid.

**For X-Ray diffraction:** Single-crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent of a saturated solution of cAAC<sup>Me</sup>(Bpin)<sub>2</sub> in C<sub>6</sub>D<sub>6</sub>.

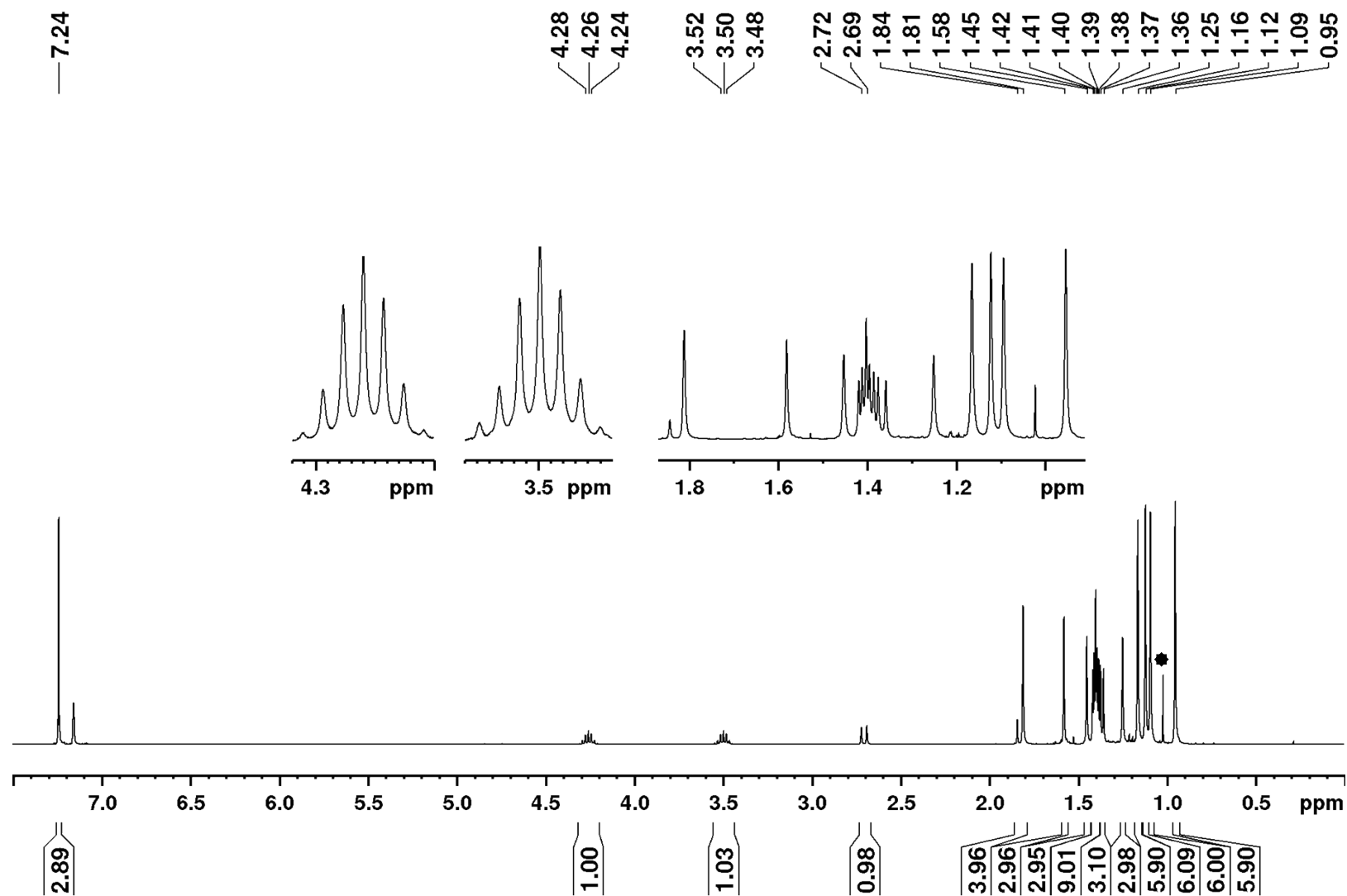
**Elemental analysis** for [C<sub>32</sub>H<sub>55</sub>B<sub>2</sub>NO<sub>4</sub>] [539.41 g/mol] Calc. (obs.): C 71.25 (71.25), H 10.28 (10.32), N 2.60 (2.67).

**<sup>1</sup>H-NMR** (400 MHz, 23 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) = 0.95 (s, 6 H, OC<sub>q</sub>CH<sub>3</sub>), 1.09 (s, 6 H, OC<sub>q</sub>CH<sub>3</sub>), 1.12 (s, 6 H, OC<sub>q</sub>CH<sub>3</sub>), 1.16 (s, 6 H, OC<sub>q</sub>CH<sub>3</sub>), 1.25 (s, 3 H, NC<sub>q</sub>CH<sub>3</sub>), 1.37 (d, 3 H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CHCH<sub>3</sub>), 1.39 (d, 3 H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CHCH<sub>3</sub>), 1.41 (d, 3 H, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, CHCH<sub>3</sub>), 1.42 (d, 3 H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CHCH<sub>3</sub>), 1.45 (s, 3 H, NC<sub>q</sub>CH<sub>3</sub>), 1.58 (s, 3 H, C<sub>q</sub>C<sub>q</sub>CH<sub>3</sub>), 1.81 (s, 3 H, C<sub>q</sub>C<sub>q</sub>CH<sub>3</sub>), 1.84 (d, 1 H, <sup>2</sup>J<sub>HH</sub> = 12 Hz, C<sub>q</sub>CH<sub>2</sub>), 2.71 (d, 1 H, <sup>2</sup>J<sub>HH</sub> = 12 Hz, C<sub>q</sub>CH<sub>2</sub>), 3.50 (qq, 1 H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CHCH<sub>3</sub>), 4.26 (qq, 1 H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CHCH<sub>3</sub>), 7.24 (overlapping m, 3H, <sub>aryl</sub>CH).

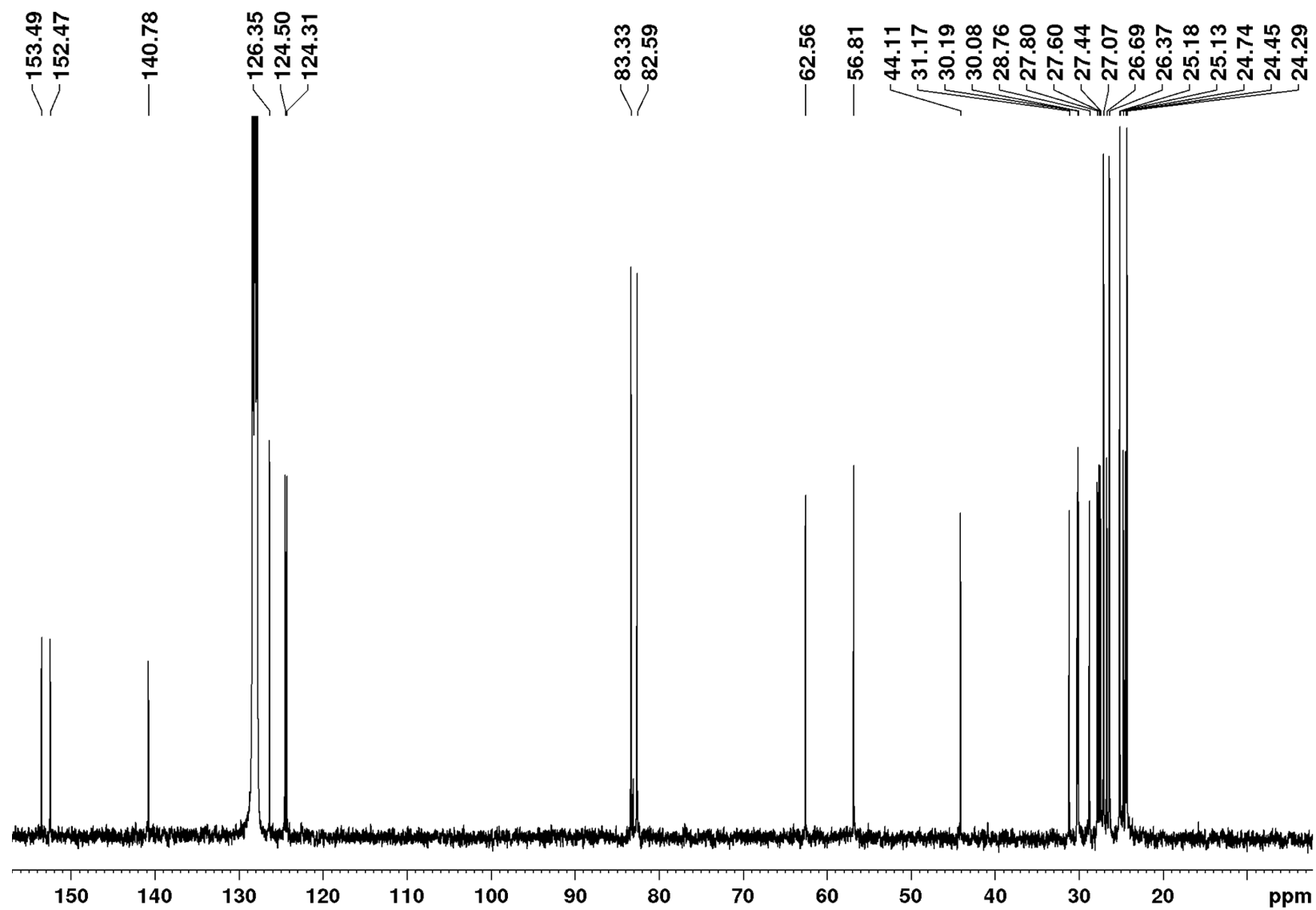
**$^{11}\text{B}$ -NMR** (128 MHz, 23 °C,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 32.0 (s).  **$^{13}\text{C}\{^1\text{H}\}$ -NMR** (100 MHz, 23 °C,  $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) = 24.3 ( $\text{OC}_q\text{CH}_3$ ), 24.5 ( $\text{CHCH}_3$ ), 24.7 ( $\text{CHCH}_3$ ), 25.2 ( $\text{OC}_q\text{CH}_3$ ), 26.4 ( $\text{OC}_q\text{CH}_3$ ), 26.7 ( $\text{CHCH}_3$ ), 27.1 ( $\text{OC}_q\text{CH}_3$ ), 27.4 ( $\text{NC}_q\text{CH}_3$ ), 27.6 ( $\text{CHCH}_3$ ), 27.8 ( $\text{CHCH}_3$ ), 28.8 ( $\text{CHCH}_3$ ), 30.1 ( $\text{NC}_q\text{CH}_3$ ), 30.2 ( $\text{C}_q\text{C}_q\text{CH}_3$ ), 31.2 ( $\text{C}_q\text{C}_q\text{CH}_3$ ), 44.1 ( $\text{BC}_q\text{C}_q$ ), 56.8 ( $\text{NC}_q\text{CH}_2$ ), 62.6 ( $\text{NC}_q\text{CH}_2$ ), 82.6 ( $\text{OC}_q$ ), 83.3 ( $\text{OC}_q$ ), 124.3 ( $m^{\text{dipp-CH}}$ ), 124.5 ( $m^{\text{dipp-CH}}$ ), 126.4 ( $p^{\text{dipp-CH}}$ ), 140.8 ( $i^{\text{dipp-CH}}$ ), 152.5 ( $o^{\text{dipp-CH}}$ ), 153.5 ( $o^{\text{dipp-CH}}$ ).

**HRMS-ASAP** (m/z):  $[\text{M} + \text{H}]^+$  calc. for  $\text{C}_{32}\text{H}_{55}\text{B}_2\text{NO}_4$ , 540.4390 found 540.4388.

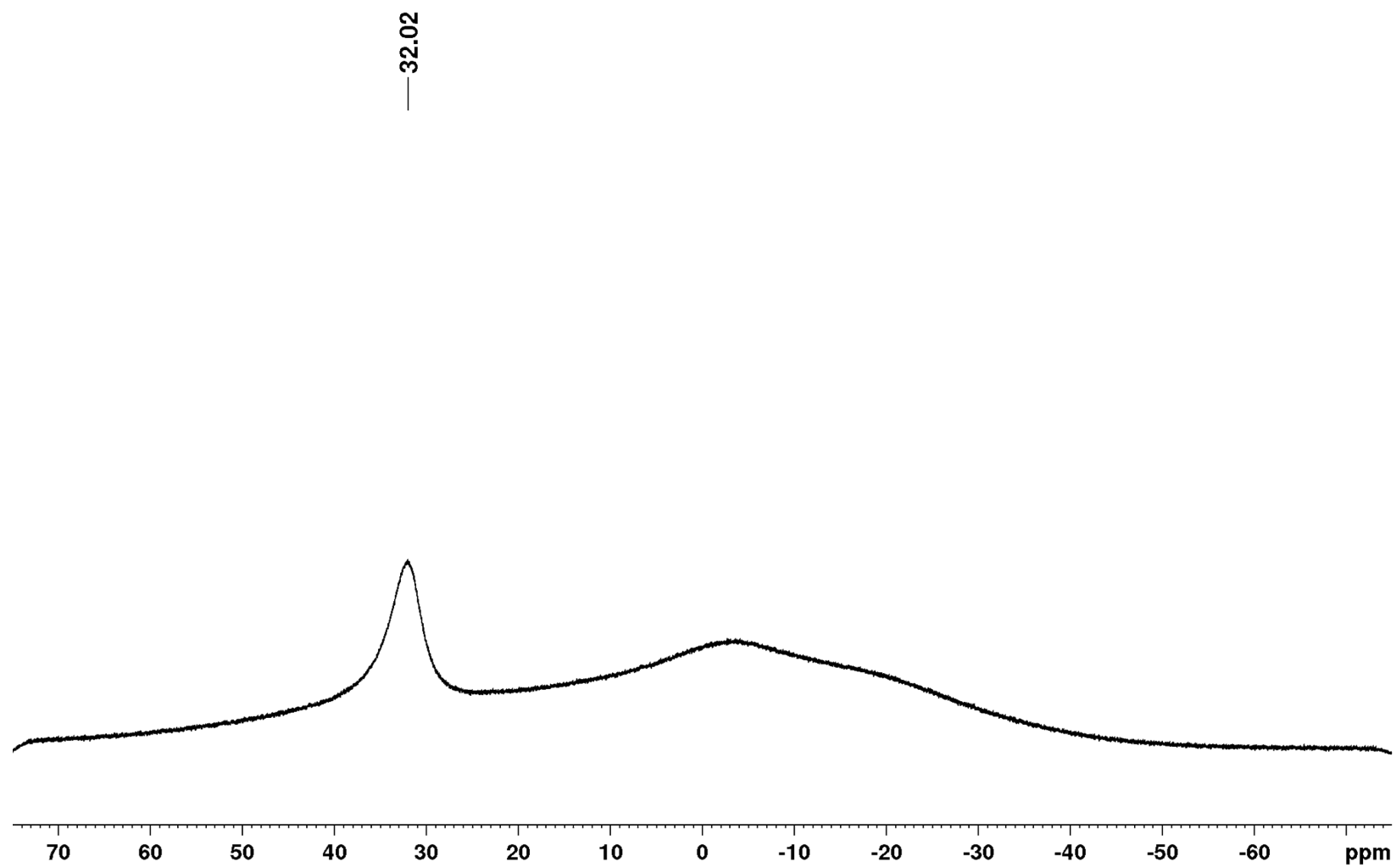
NMR spectra of cAAC<sup>Me</sup>(Bpin)<sub>2</sub> **1**



**Figure 1.** <sup>1</sup>H NMR spectrum of compound **1** in C<sub>6</sub>D<sub>6</sub> (400 MHz, 23 °C). Asterisk = residual starting material.



**Figure 2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **1** in  $\text{C}_6\text{D}_6$  (100 MHz, 23 °C).



**Figure 3.**  $^{11}\text{B}$  NMR spectrum of compound **1** in  $\text{C}_6\text{D}_6$  (128 MHz, 23 °C).

### Synthesis of cAAC<sup>Me</sup>(Bcat)<sub>2</sub> **2**

In a Schlenk-tube B<sub>2</sub>cat<sub>2</sub> (166 mg, 700 μmol) and cAAC<sup>Me</sup> (200 mg, 700 μmol) were dissolved in 12 mL of toluene. After stirring the reaction mixture for 15 h at room temperature, the solvent was removed under reduced pressure. The residue was washed with 8 mL of *n*-hexane and dried *in vacuo*. Yield: 266 mg (508 μmol, 73%) of a white solid.

**For X-Ray diffraction:** A saturated solution of cAAC<sup>Me</sup>(Bcat)<sub>2</sub> in *n*-hexane was cooled to -30 °C to obtain single-crystals suitable for X-ray diffraction.

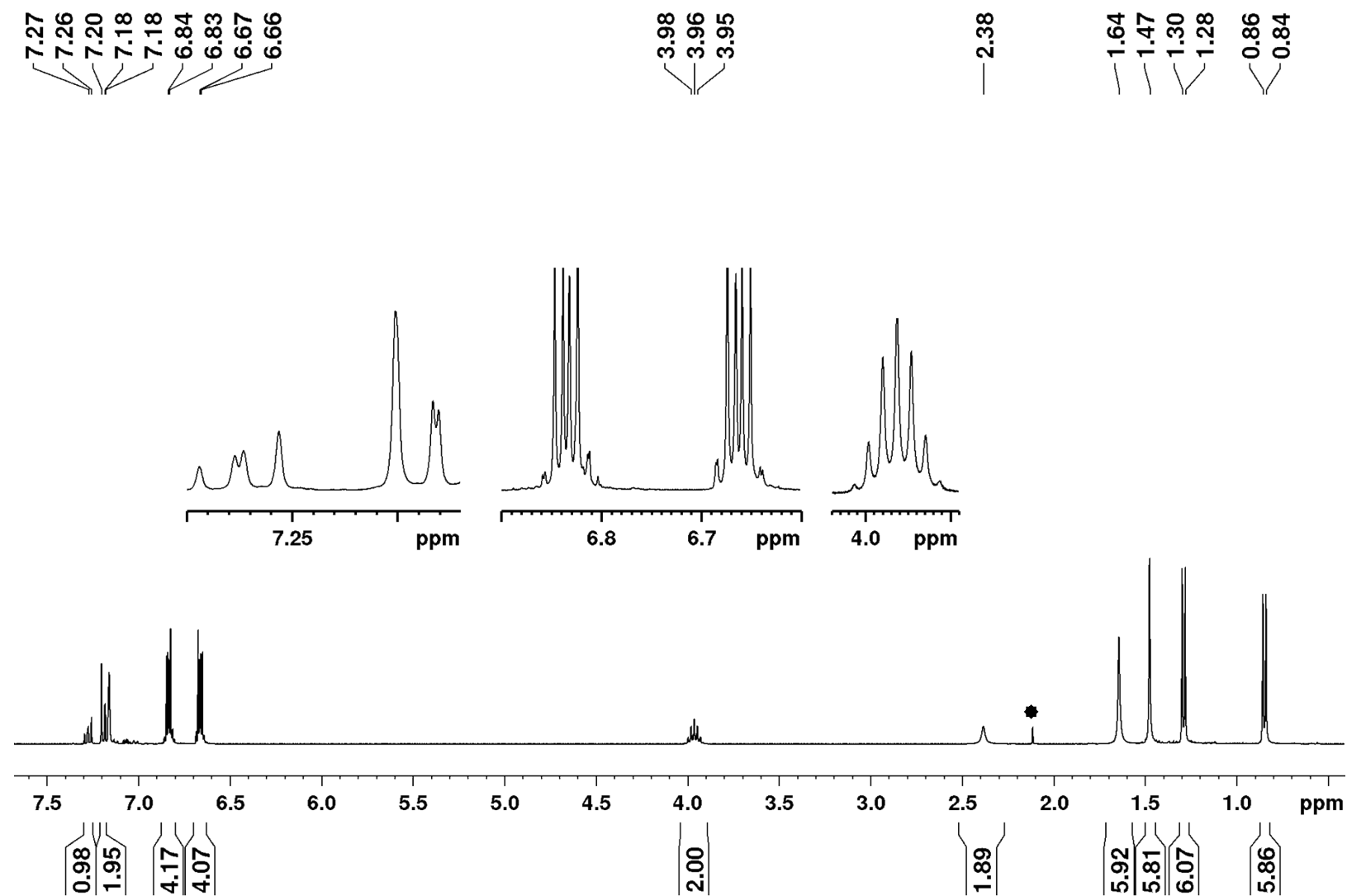
**Elemental analysis** for [C<sub>32</sub>H<sub>39</sub>B<sub>2</sub>NO<sub>4</sub>] [523.28 g/mol] Calc. (obs.): C 73.45 (74.02), H 7.51 (7.50), N 2.68 (2.78).

**<sup>1</sup>H-NMR** (400 MHz, 23 °C, C<sub>6</sub>D<sub>6</sub>): δ (ppm) = 0.85 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CHCH<sub>3</sub>), 1.29 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CHCH<sub>3</sub>), 1.47 (s, 6 H, NC<sub>q</sub>CH<sub>3</sub>), 1.64 (s, 6 H, C<sub>q</sub>C<sub>q</sub>CH<sub>3</sub>), 2.38 (s, 2 H, NC<sub>q</sub>CH<sub>2</sub>), 3.96 (qq, 2 H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CHCH<sub>3</sub>), 6.64 – 6.69 (m, 4 H, <sub>aryl</sub><sup>cat</sup>-CH), 6.81 – 6.86 (m, 4 H, <sub>aryl</sub><sup>cat</sup>-CH), 7.18 – 7.20 (m, 2 H, *m*<sup>dipp</sup>-CH), 7.26 – 7.30 (m, 1 H, *p*<sup>dipp</sup>-CH). **<sup>11</sup>B-NMR** (128 MHz, 23 °C, C<sub>6</sub>D<sub>6</sub>): δ (ppm) = 34.2 (s). **<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, 23 °C, C<sub>6</sub>D<sub>6</sub>): δ (ppm) = 24.5 (CHCH<sub>3</sub>), 25.3 (CHCH<sub>3</sub>), 28.0 (C<sub>q</sub>C<sub>q</sub>CH<sub>3</sub>), 28.4 (CHCH<sub>3</sub>), 30.7 (NC<sub>q</sub>CH<sub>3</sub>), 43.6 (C<sub>q</sub>C<sub>q</sub>CH<sub>3</sub>), 56.5 (NC<sub>q</sub>CH<sub>2</sub>), 63.6 (NC<sub>q</sub>CH<sub>2</sub>), 112.8 (<sub>aryl</sub><sup>cat</sup>-CH), 123.0 (<sub>aryl</sub><sup>cat</sup>-CH), 124.7 (*m*<sup>dipp</sup>-CH), 127.5 (*p*<sup>dipp</sup>-CH), 139.4 (*i*<sup>dipp</sup>-C<sub>q</sub>), 148.1 (<sub>aryl</sub><sup>cat</sup>-C<sub>q</sub>), 153.4 (*o*<sup>dipp</sup>-C<sub>q</sub>).

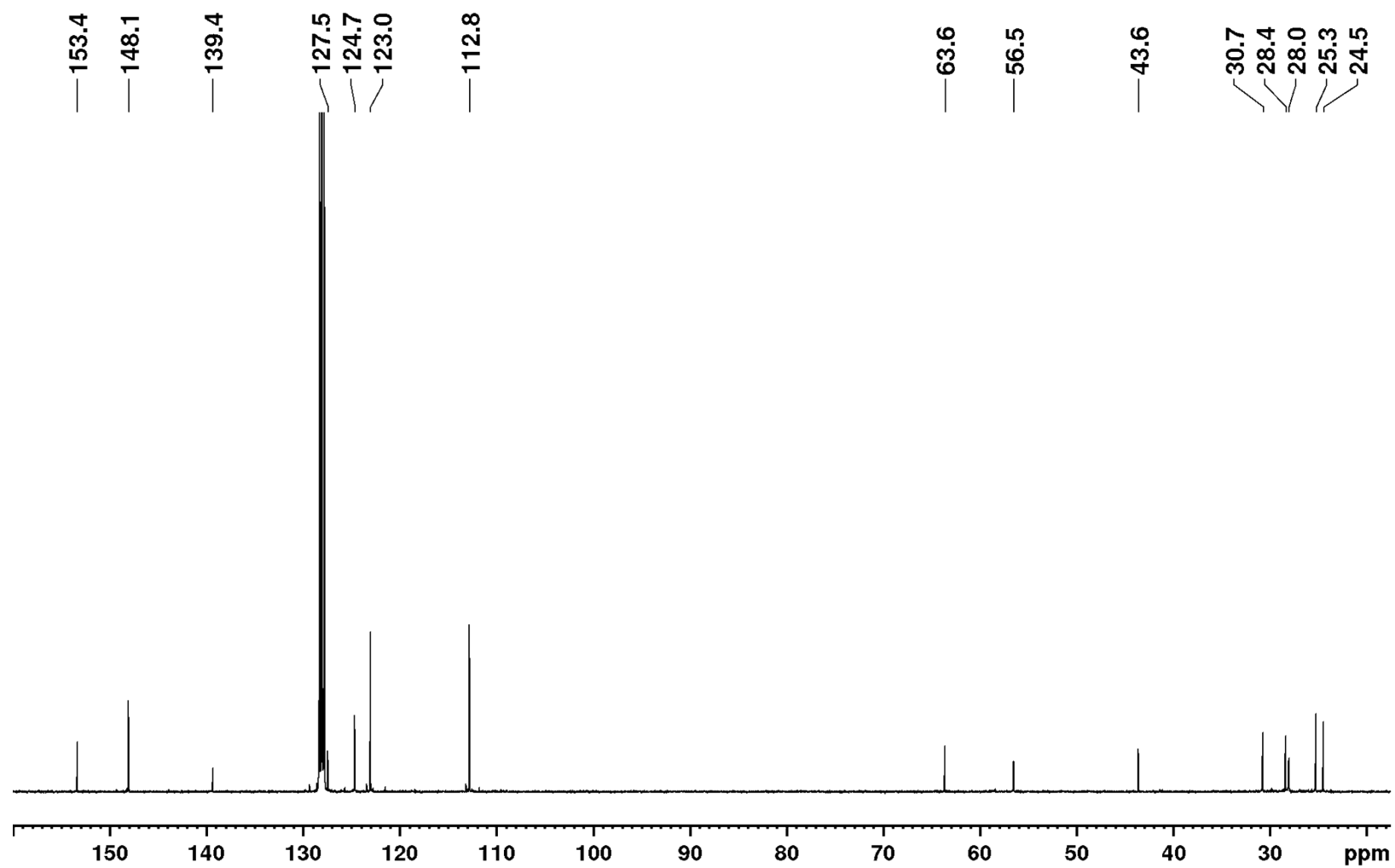
**HRMS-ASAP** (m/z): [M + H]<sup>+</sup> calc. for C<sub>32</sub>H<sub>39</sub>B<sub>2</sub>NO<sub>4</sub>, 524.3138 found 524.3132.



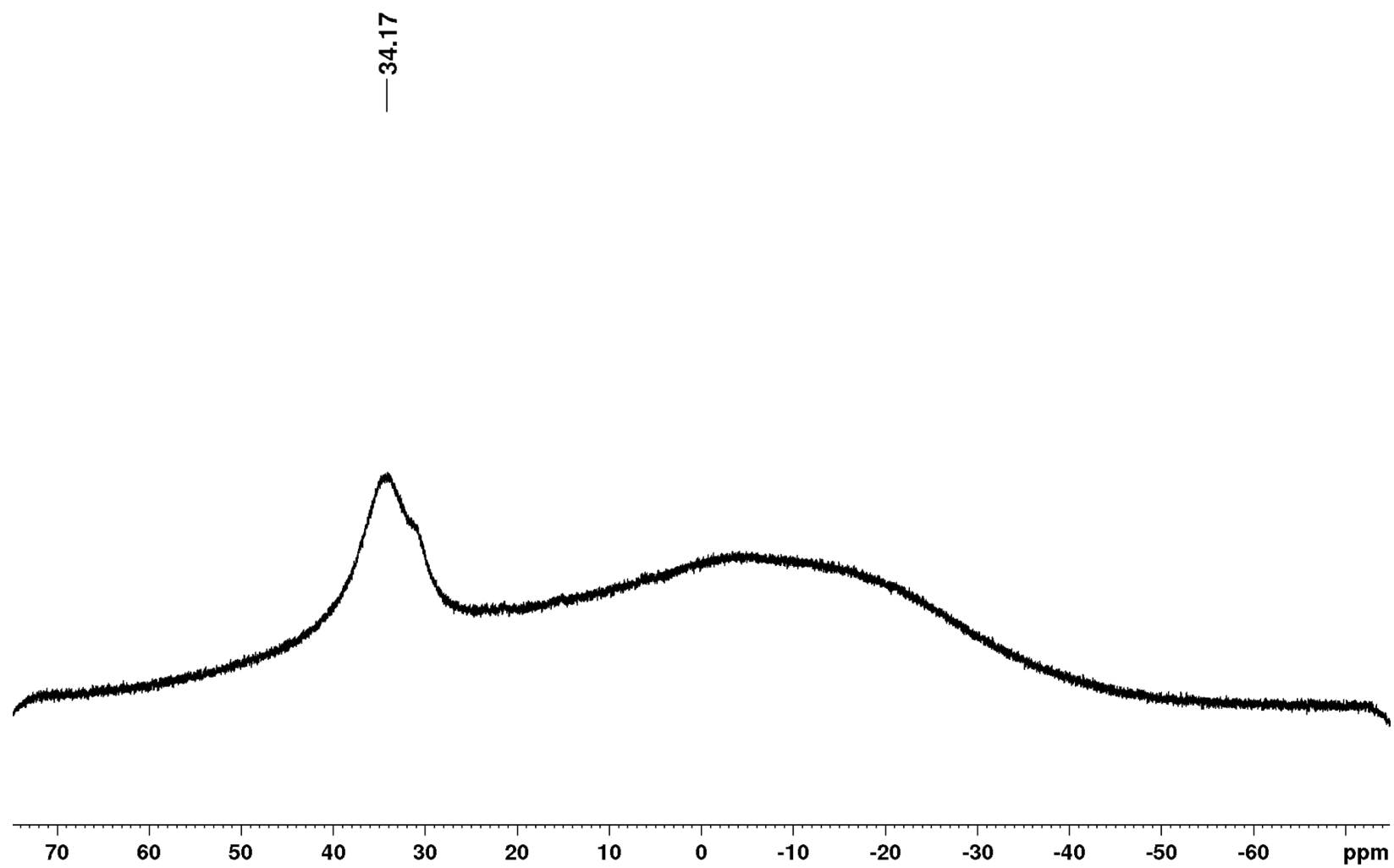
NMR spectra of  $B_2cat_2 \cdot cAAC^{Me}$  **BBA 2**



**Figure 4.**  $^1H$  NMR spectrum of compound **2** in  $C_6D_6$  (400 MHz, 23 °C). Asterisk = residual toluene.



**Figure 5.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **2** in  $\text{C}_6\text{D}_6$  (100 MHz, 23 °C).



**Figure 6.**  $^{11}\text{B}$  NMR spectrum of compound **2** in  $\text{C}_6\text{D}_6$  (128 MHz, 23 °C).

### Synthesis of cAAC<sup>Me</sup>(Bneop)<sub>2</sub> **3**

In a Schlenk-tube B<sub>2</sub>neop<sub>2</sub> (158 mg, 700 μmol) and cAAC<sup>Me</sup> (200 mg, 700 μmol) were dissolved in 12 mL of toluene. After stirring the reaction mixture for 15 h at room temperature, the solvent was removed under reduced pressure. The residue was washed with 5 mL of *n*-hexane and dried *in vacuo*. Yield: 183 mg (357 μmol, 51%) of an off white solid.

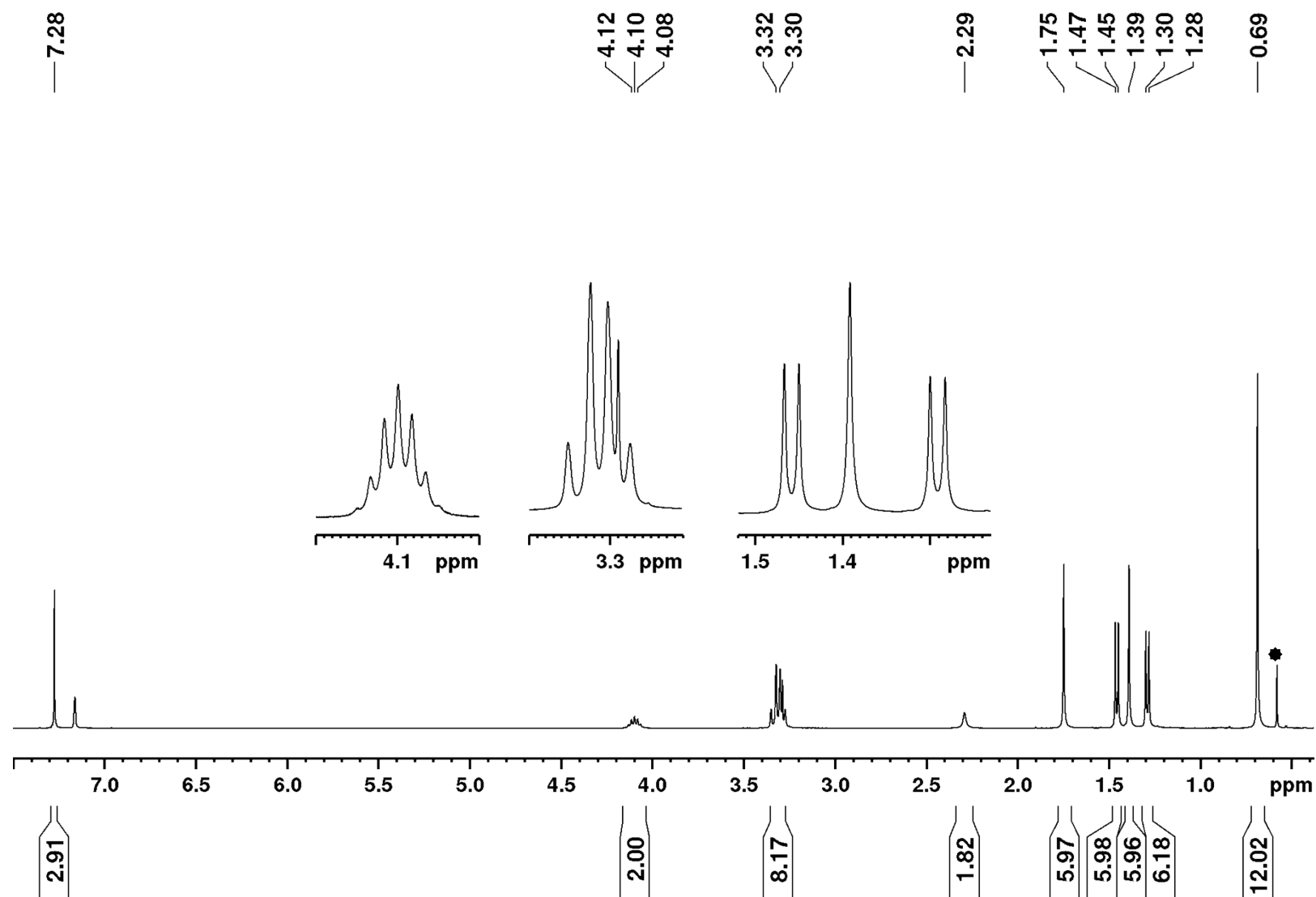
**For X-Ray diffraction:** Single-crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent of a saturated solution of cAAC<sup>Me</sup>(Bneop)<sub>2</sub> in C<sub>6</sub>D<sub>6</sub>.

**Elemental analysis** for [C<sub>30</sub>H<sub>51</sub>B<sub>2</sub>NO<sub>4</sub>] [511.35 g/mol] Calc. (obs.): C 70.46 (70.38), H 10.05 (10.04), N 2.74 (2.82).

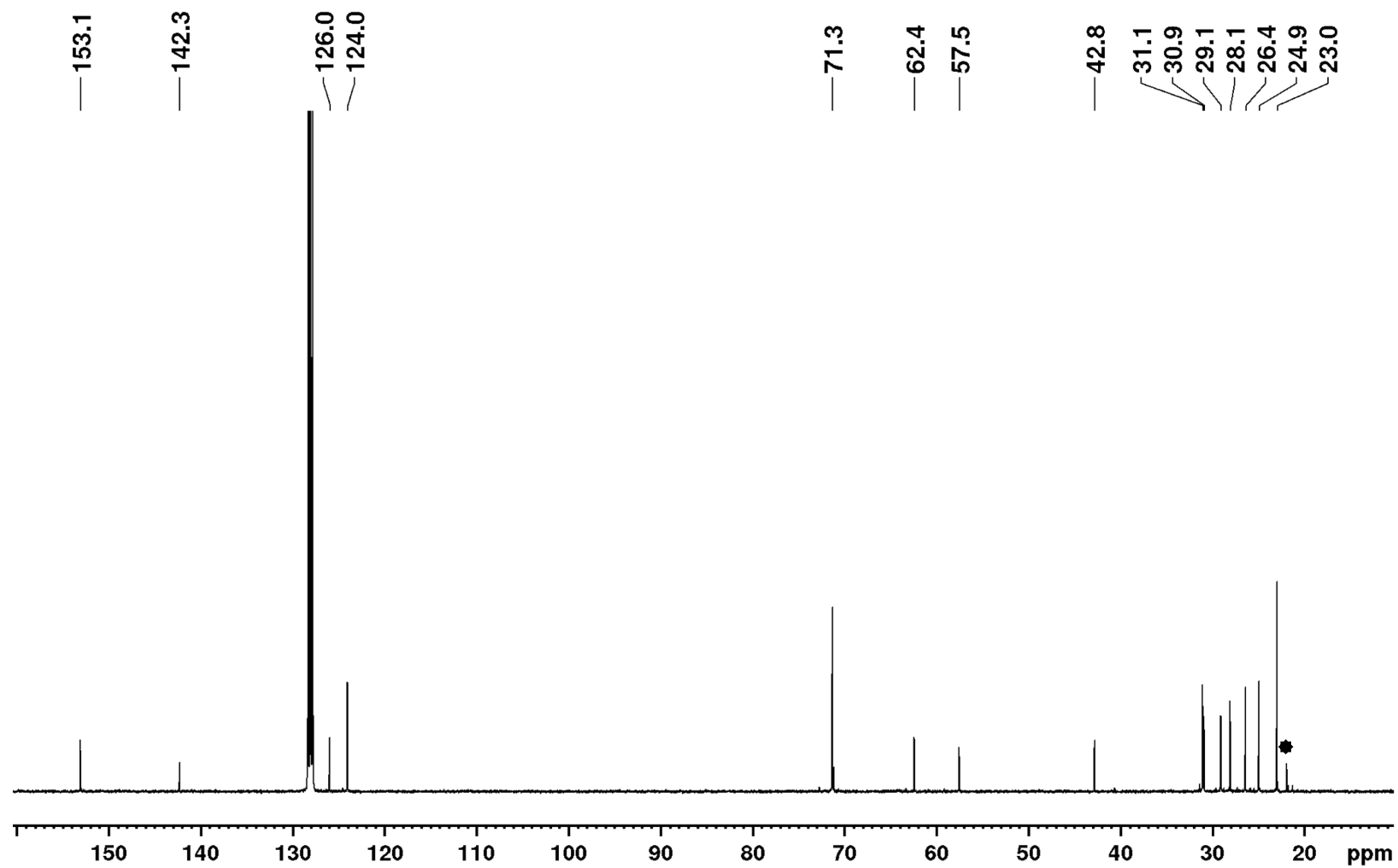
**<sup>1</sup>H-NMR** (400 MHz, 23 °C, C<sub>6</sub>D<sub>6</sub>): δ (ppm) = 0.69 (s, 12 H, OCH<sub>2</sub>C<sub>q</sub>CH<sub>3</sub>), 1.29 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CHCH<sub>3</sub>), 1.39 (s, 6 H, NC<sub>q</sub>CH<sub>3</sub>), 1.46 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CHCH<sub>3</sub>), 1.75 (s, 6 H, C<sub>q</sub>C<sub>q</sub>CH<sub>3</sub>), 2.29 (s, 2 H, NC<sub>q</sub>CH<sub>2</sub>), 3.31 (m, 8 H, OCH<sub>2</sub>), 4.10 (qq, 2 H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CHCH<sub>3</sub>), 7.28 (s, 3 H, <sub>aryl</sub>CH). **<sup>11</sup>B-NMR** (128 MHz, 23 °C, C<sub>6</sub>D<sub>6</sub>): δ (ppm) = 29.2 (s). **<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, 23 °C, C<sub>6</sub>D<sub>6</sub>): δ (ppm) = 23.0 (OCH<sub>2</sub>C<sub>q</sub>CH<sub>3</sub>), 24.9 (CHCH<sub>3</sub>), 26.4 (CHCH<sub>3</sub>), 28.1 (CHCH<sub>3</sub>), 29.1 (C<sub>q</sub>C<sub>q</sub>CH<sub>3</sub>), 30.9 (NC<sub>q</sub>CH<sub>3</sub>), 31.1 (OCH<sub>2</sub>C<sub>q</sub>CH<sub>3</sub>), 42.8 (C<sub>q</sub>C<sub>q</sub>CH<sub>3</sub>), 57.5 (NC<sub>q</sub>CH<sub>2</sub>), 62.4 (NC<sub>q</sub>CH<sub>3</sub>), 71.3 (OCH<sub>2</sub>), 124.0 (*m*<sup>dipp</sup>-CH), 126.0 (*p*<sup>dipp</sup>-CH), 142.3 (*i*<sup>dipp</sup>-C<sub>q</sub>), 153.1 (*o*<sup>dipp</sup>-C<sub>q</sub>). **<sup>13</sup>C{<sup>1</sup>H}[<sup>11</sup>B]-NMR** (75 MHz, 23 °C, C<sub>6</sub>D<sub>6</sub>): δ (ppm) = 64.1 (BC<sub>q</sub>).

**HRMS-ASAP** (m/z): [M + H]<sup>+</sup> calc. for C<sub>30</sub>H<sub>51</sub>B<sub>2</sub>NO<sub>4</sub>, 512.4077 found 512.4074.

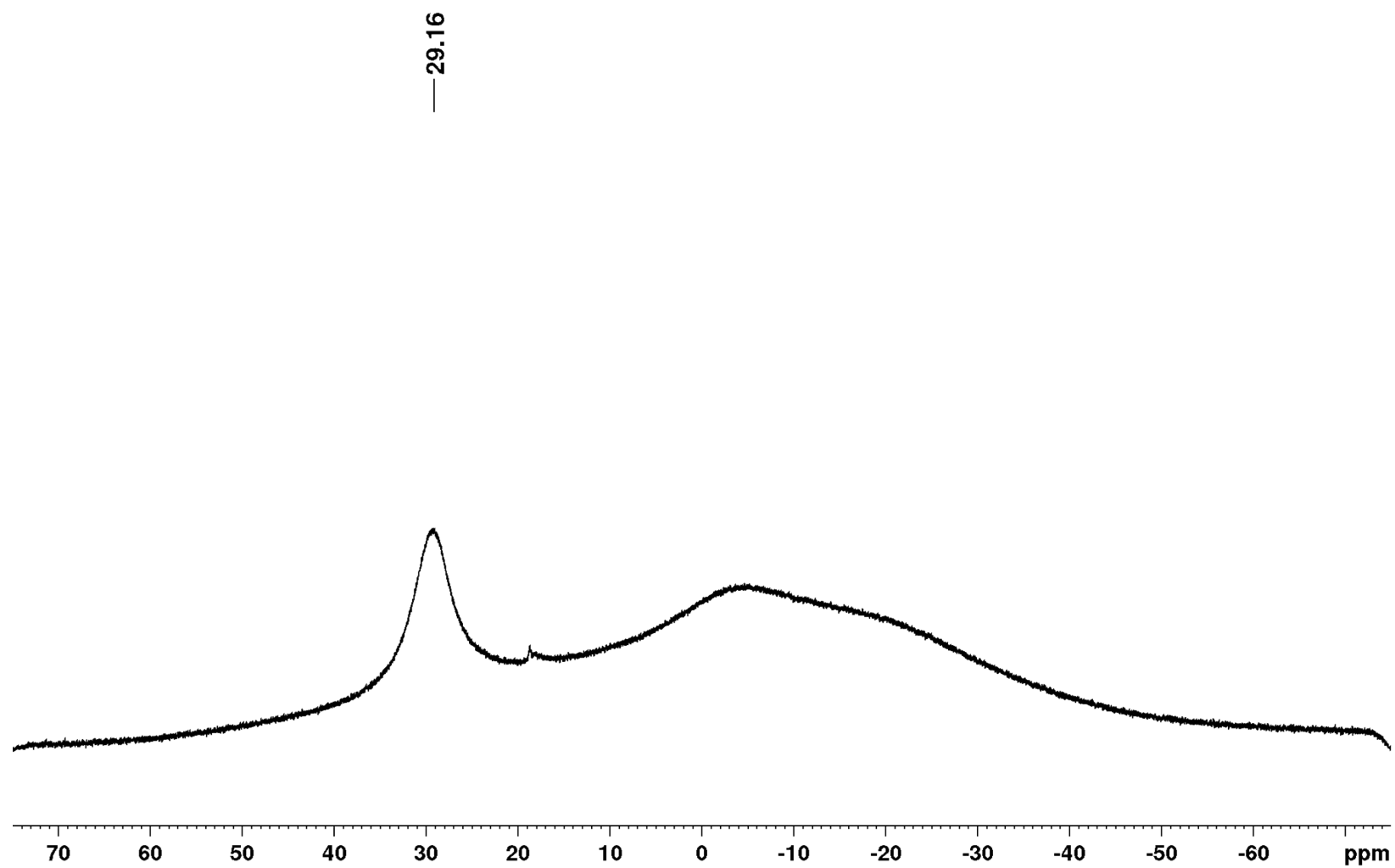
NMR spectra of cAAC<sup>Me</sup>(Bneop)<sub>2</sub> **3**



**Figure 7.** <sup>1</sup>H NMR spectrum of compound **3** in C<sub>6</sub>D<sub>6</sub> (400 MHz, 23 °C). Asterisk = unknown impurity.



**Figure 8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **3** in  $\text{C}_6\text{D}_6$  (125 MHz, 23 °C). Asterisk =unknown impurity.



**Figure9.**  $^{11}\text{B}$  NMR spectrum of compound **3** in  $\text{C}_6\text{D}_6$  (128 MHz, 23 °C).

#### Synthesis of cAAC<sup>Me</sup>(Beg)<sub>2</sub> **4**

In a Schlenk-tube B<sub>2</sub>eg<sub>2</sub> (99 mg, 700 μmol) and cAAC<sup>Me</sup> (200 mg, 700 μmol) were dissolved in 12 mL of toluene. After stirring the reaction mixture for 15 h at room temperature, the solvent was removed under reduced pressure. The residue was washed with 5 mL of *n*-hexane and dried *in vacuo*. Yield: 188 mg (441 μmol, 63%) of a white solid.

**For X-Ray diffraction:** Single-crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent of a saturated solution of cAAC<sup>Me</sup>(Beg)<sub>2</sub> in C<sub>6</sub>D<sub>6</sub>.

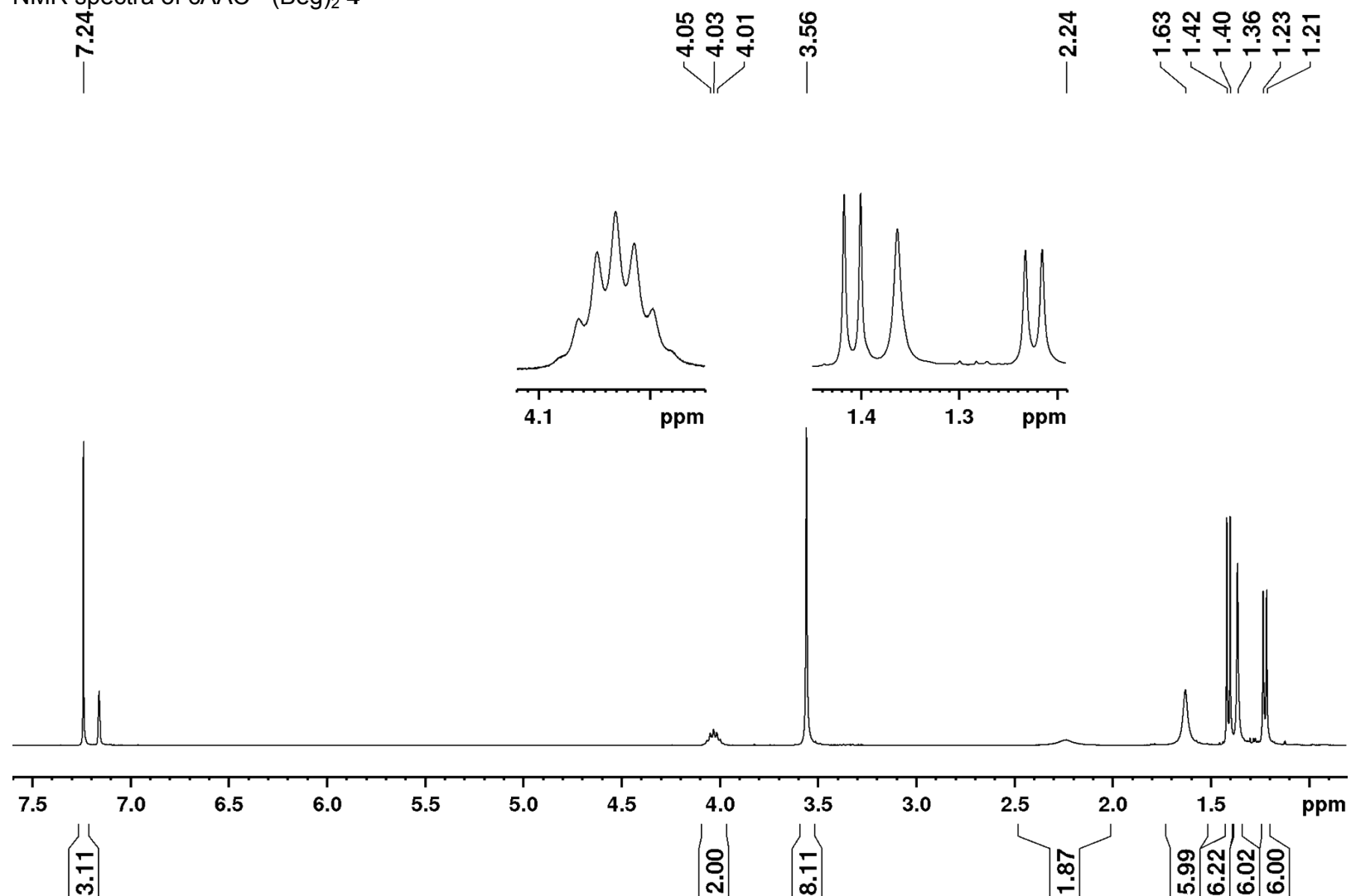
**Elemental analysis** for [C<sub>24</sub>H<sub>39</sub>B<sub>2</sub>NO<sub>4</sub>] [427.19 g/mol] Calc. (obs.): C 67.48 (67.00), H 9.20 (9.30), N 3.28 (3.00).

**<sup>1</sup>H-NMR** (400 MHz, 23 °C, C<sub>6</sub>D<sub>6</sub>): δ (ppm) = 1.22 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CHCH<sub>3</sub>), 1.36 (s, 6 H, C<sub>q</sub>C<sub>q</sub>CH<sub>3</sub>), 1.41 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CHCH<sub>3</sub>), 1.63 (br, 6 H, NC<sub>q</sub>CH<sub>3</sub>), 2.24 (br, 2H, NC<sub>q</sub>CH<sub>2</sub>), 3.56 (s, 8 H, OCH<sub>2</sub>), 4.03 (qq, 2 H, <sup>3</sup>J<sub>HH</sub> = 7, CHCH<sub>3</sub>), 7.24 (s, 3H, <sub>aryl</sub>CH). **<sup>11</sup>B-NMR** (128 MHz, 23 °C, C<sub>6</sub>D<sub>6</sub>): δ (ppm) = 33.2 (s). **<sup>13</sup>C{<sup>1</sup>H}-NMR** (100 MHz, 23 °C, C<sub>6</sub>D<sub>6</sub>): δ (ppm) = 24.5 (CHCH<sub>3</sub>), 26.0 (CHCH<sub>3</sub>), 28.0 (CHCH<sub>3</sub>), 28.0 (NC<sub>q</sub>CH<sub>3</sub>), 30.6 (C<sub>q</sub>C<sub>q</sub>CH<sub>3</sub>), 42.6 (C<sub>q</sub>C<sub>q</sub>CH<sub>3</sub>), 56.6 (NC<sub>q</sub>CH<sub>2</sub>), 62.9 (NC<sub>q</sub>CH<sub>3</sub>), 65.0 (OCH<sub>2</sub>), 124.2 (*m*<sup>dipp</sup>-CH), 126.8 (*p*<sup>dipp</sup>-CH), 140.5 (*i*<sup>dipp</sup>-C<sub>q</sub>), 153.4 (*o*<sup>dipp</sup>-C<sub>q</sub>).

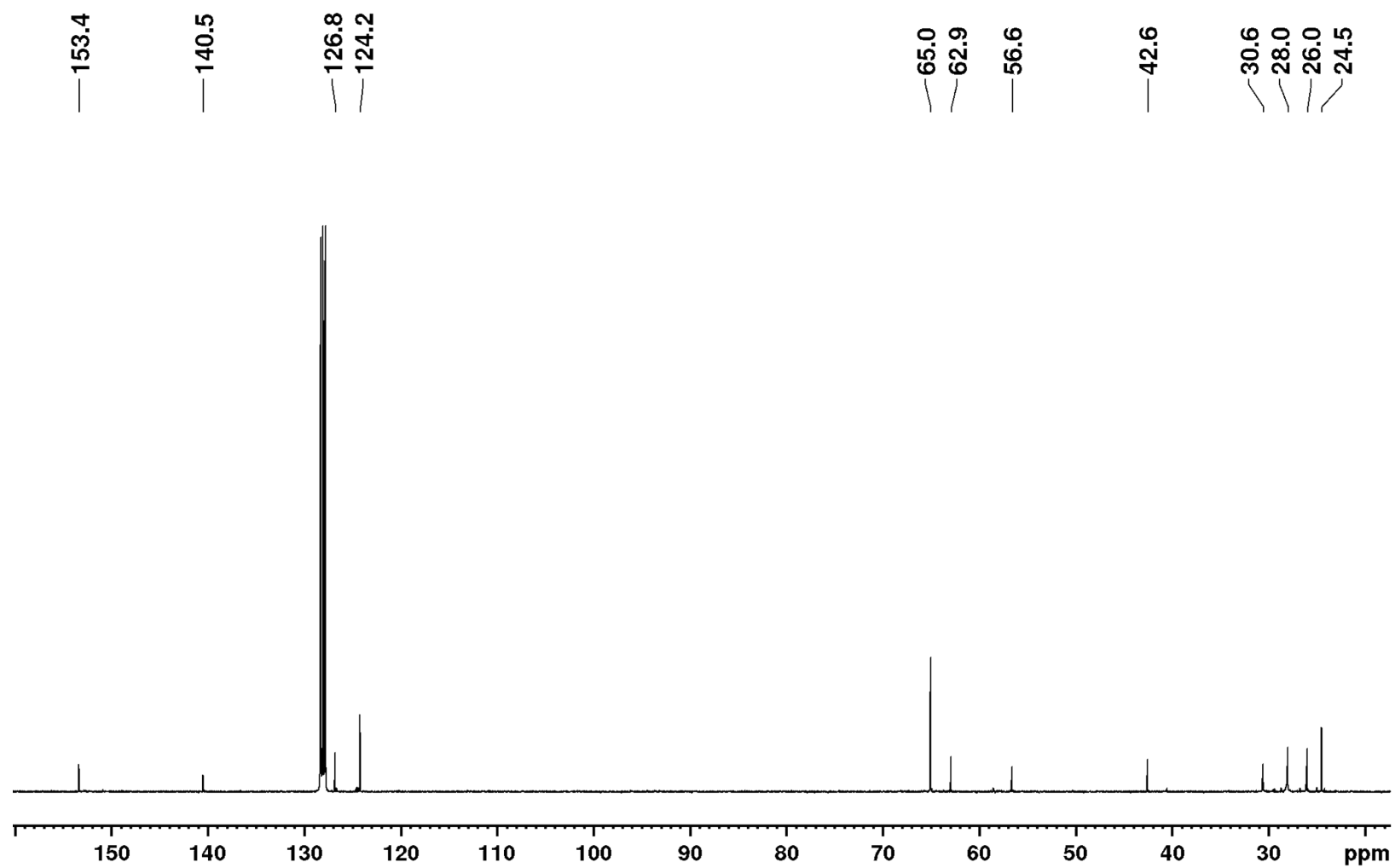
**HRMS-ASAP** (m/z): [M + H]<sup>+</sup> calc. for C<sub>24</sub>H<sub>39</sub>B<sub>2</sub>NO<sub>4</sub>, 428.3138 found 428.3135.



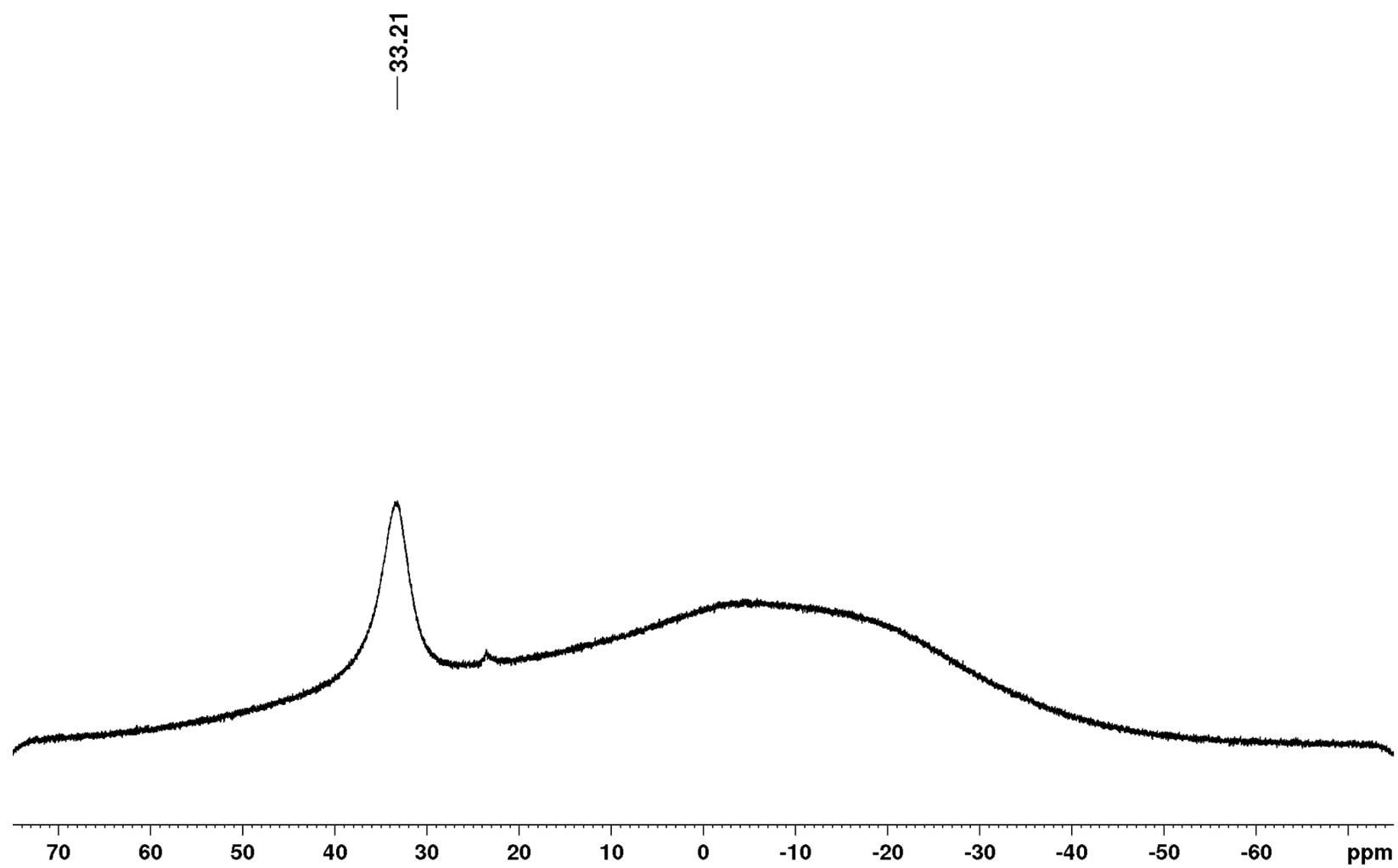
NMR spectra of cAAC<sup>Me</sup>(Beg)<sub>2</sub> **4**



**Figure 10.** <sup>1</sup>H NMR spectrum of compound **4** in C<sub>6</sub>D<sub>6</sub> (400 MHz, 23 °C).



**Figure 11.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4** in  $\text{C}_6\text{D}_6$  (100 MHz, 23 °C).



**Figure 12.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of compound **4** in  $\text{C}_6\text{D}_6$  (128 MHz, 23 °C).

## 2. Crystallographic Details

Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Bruker X8 Apex-2 diffractometer, with CCD area detector and mirror-monochromated Mo- $K_{\alpha}$  radiation, equipped with an Oxford Cryosystems low-temperature device. Data were collected at 100 K. The images were processed with the Bruker software packages and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were included in calculated positions and refined using a riding model. Extinction corrections were applied as required. Crystallographic calculations were performed using the SHELXTL software package.<sup>[S6]</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factors calculations. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.s CCDC 1567431- 1567434 (compounds **1** – **4**). Copies of the data can be obtained free of charge on application to the CSD.

**Table S1.** Crystal data and structure refinement for cAAC<sup>Me</sup>(Bpin)<sub>2</sub> **1**.

cAAC <sup>Me</sup> (Bpin) <sub>2</sub> <b>1</b>	
Identification code	CCDC 1567431
Empirical formula	C <sub>32</sub> H <sub>55</sub> B <sub>2</sub> NO <sub>4</sub>
Formula weight [g/mol]	539.39
Temperature [K]	100
Wavelength [Å]	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	<i>a</i> = 10.8403(14) Å <i>b</i> = 10.8459(14) Å <i>c</i> = 15.907(2) Å $\alpha$ = 91.467 ° $\beta$ = 103.418 ° $\gamma$ = 116.778 °
Volume [Å <sup>3</sup> ]	1605.7(4)
<i>Z</i>	2
Density (calculated) [g/cm <sup>3</sup> ]	1.259
Absorption coefficient [mm <sup>-1</sup> ]	0.070
<i>F</i> (000)	592
$\Theta$ range [°]	2.188 - 26.065
No. of reflections collected	20966
No. of unique reflections	6392 [ <i>R</i> <sub>int</sub> = 0.0568]
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	4836
Data / restraints / parameters	6392 / 0 / 368
GooF	1.028
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0563, <i>wR</i> <sub>2</sub> = 0.1469
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0763, <i>wR</i> <sub>2</sub> = 0.1630
Largest diff. peak and hole [e Å <sup>3</sup> ]	0.477 and -0.352
Diffractometer	Bruker Smart Apex 2

**Table S2.** Crystal data and structure refinement for cAAC<sup>Me</sup>(Bcat)<sub>2</sub> **2**.

cAAC <sup>Me</sup> (Bcat) <sub>2</sub> <b>2</b>	
Identification code	CCDC 1567432
Empirical formula	C <sub>32</sub> H <sub>39</sub> B <sub>2</sub> NO <sub>4</sub>
Formula weight [g/mol]	523.26
Temperature [K]	100
Wavelength [Å]	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> /n
Unit cell dimensions	<i>a</i> = 14.325(2) Å <i>b</i> = 12.0505(18) Å <i>c</i> = 17.419(3) Å $\alpha$ = 90 ° $\beta$ = 113.316(4)° $\gamma$ = 90 °
Volume [Å <sup>3</sup> ]	2761.4(7)
<i>Z</i>	4
Density (calculated) [g/cm <sup>3</sup> ]	1.259
Absorption coefficient [mm <sup>-1</sup> ]	0.080
<i>F</i> (000)	1120
$\Theta$ range [°]	1.567 - 26.116
No. of reflections collected	33371
No. of unique reflections	5462 [ <i>R</i> <sub>int</sub> = 0.0486]
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	4633
Data / restraints / parameters	5462 / 0 / 360
GooF	1.039
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0393, <i>wR</i> <sub>2</sub> = 0.0959
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0481, <i>wR</i> <sub>2</sub> = 0.1020
Largest diff. peak and hole [e Å <sup>3</sup> ]	0.340 and -0.254
Diffractometer	Bruker Smart Apex 2

**Table S3.** Crystal data and structure refinement for cAAC<sup>Me</sup>(Bneop)<sub>2</sub> **3**.

cAAC <sup>Me</sup> (Bneop) <sub>2</sub> <b>3</b>	
Identification code	CCDC 1567433
Empirical formula	C <sub>30</sub> H <sub>51</sub> B <sub>2</sub> NO <sub>4</sub>
Formula weight [g/mol]	511.34
Temperature [K]	100
Wavelength [Å]	0.71073
Crystal system	Orthorhombic
Space group	<i>P</i> na2 <sub>1</sub>
Unit cell dimensions	<i>a</i> = 19.384(2) Å <i>b</i> = 10.3921(13) Å <i>c</i> = 15.1929(19) Å $\alpha$ = 90 ° $\beta$ = 90 ° $\gamma$ = 90 °
Volume [Å <sup>3</sup> ]	3060.5(6)
<i>Z</i>	4
Density (calculated) [g/cm <sup>3</sup> ]	1.110
Absorption coefficient [mm <sup>-1</sup> ]	0.071
<i>F</i> (000)	1120
$\Theta$ range [°]	2.101 - 26.423
No. of reflections collected	39145
No. of unique reflections	6267 [ <i>R</i> <sub>int</sub> = 0.0407]
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	5907
Data / restraints / parameters	6267 / 1 / 346
GooF	1.022
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0345, <i>wR</i> <sub>2</sub> = 0.0877
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0377, <i>wR</i> <sub>2</sub> = 0.0902
Largest diff. peak and hole [e Å <sup>3</sup> ]	0.226 and -0.156
Diffractometer	Bruker Smart Apex 2

**Table S4.** Crystal data and structure refinement for cAAC<sup>Me</sup>(Beg)<sub>2</sub> **4**.

cAAC <sup>Me</sup> (Beg) <sub>2</sub> <b>4</b>	
Identification code	CCDC 1567434
Empirical formula	C <sub>24</sub> H <sub>39</sub> B <sub>2</sub> NO <sub>4</sub>
Formula weight [g/mol]	427.18
Temperature [K]	100
Wavelength [Å]	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	<i>a</i> = 9.5144(9) Å <i>b</i> = 15.1352(14) Å <i>c</i> = 18.5970(17) Å $\alpha$ = 113.046(2)° $\beta$ = 95.252(2)° $\gamma$ = 95.926(2)°
Volume [Å <sup>3</sup> ]	2425.5(4)
<i>Z</i>	4
Density (calculated) [g/cm <sup>3</sup> ]	1.170
Absorption coefficient [mm <sup>-1</sup> ]	0.076
<i>F</i> (000)	928
$\Theta$ range [°]	2.175 – 25.965
No. of reflections collected	21765
No. of unique reflections	9509 [ <i>R</i> <sub>int</sub> = 0.0253]
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	7022
Data / restraints / parameters	9509 / 0 / 575
GooF	1.011
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0428, <i>wR</i> <sub>2</sub> = 0.0945
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0685, <i>wR</i> <sub>2</sub> = 0.1066
Largest diff. peak and hole [e Å <sup>-3</sup> ]	0.291 and -0.265
Diffractometer	Bruker Smart Apex 2



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