

Article

# How to Protect *ortho*-Carborane from Decapitation. Practical Synthesis of 3,6-Dihalogen Derivatives 3,6-X<sub>2</sub>- 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (X = Cl, Br, I)

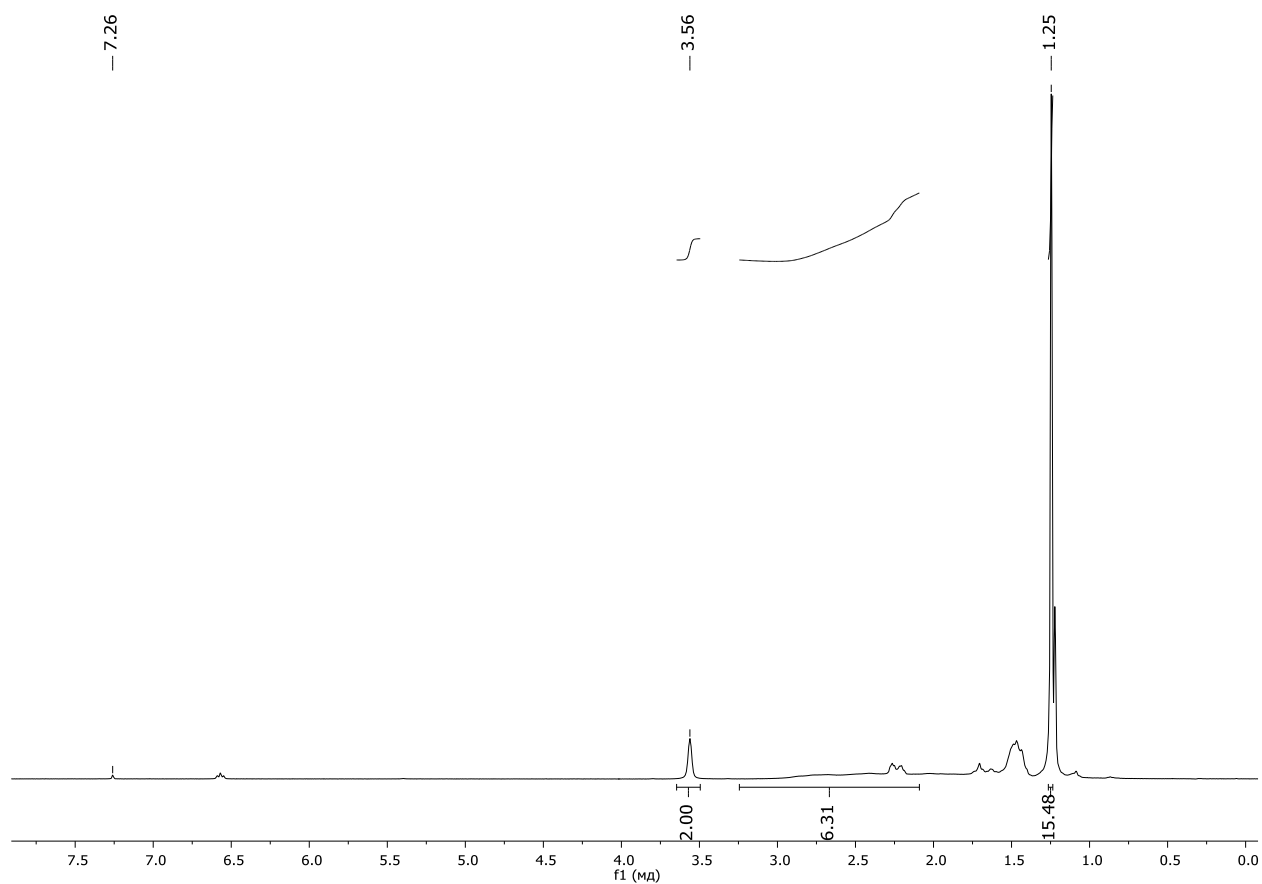
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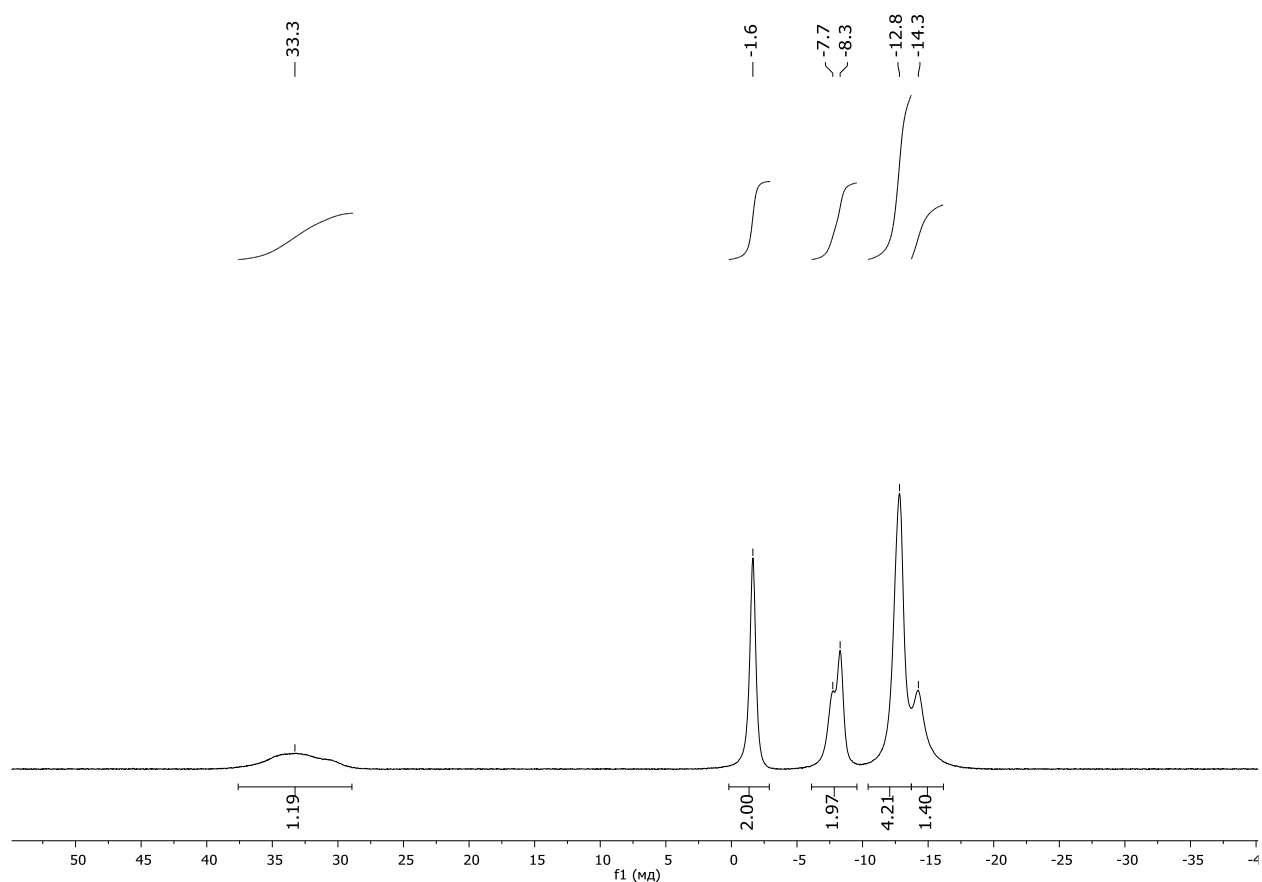
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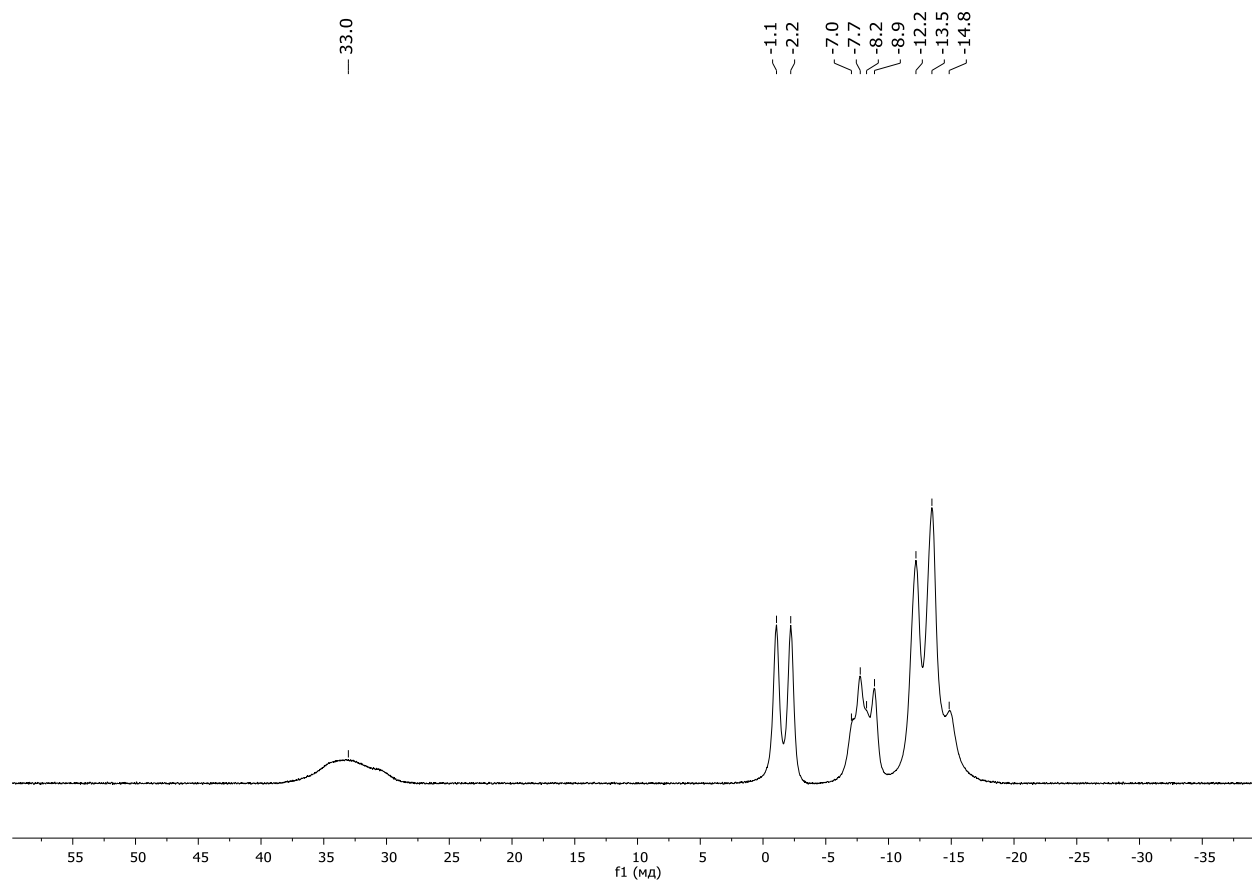
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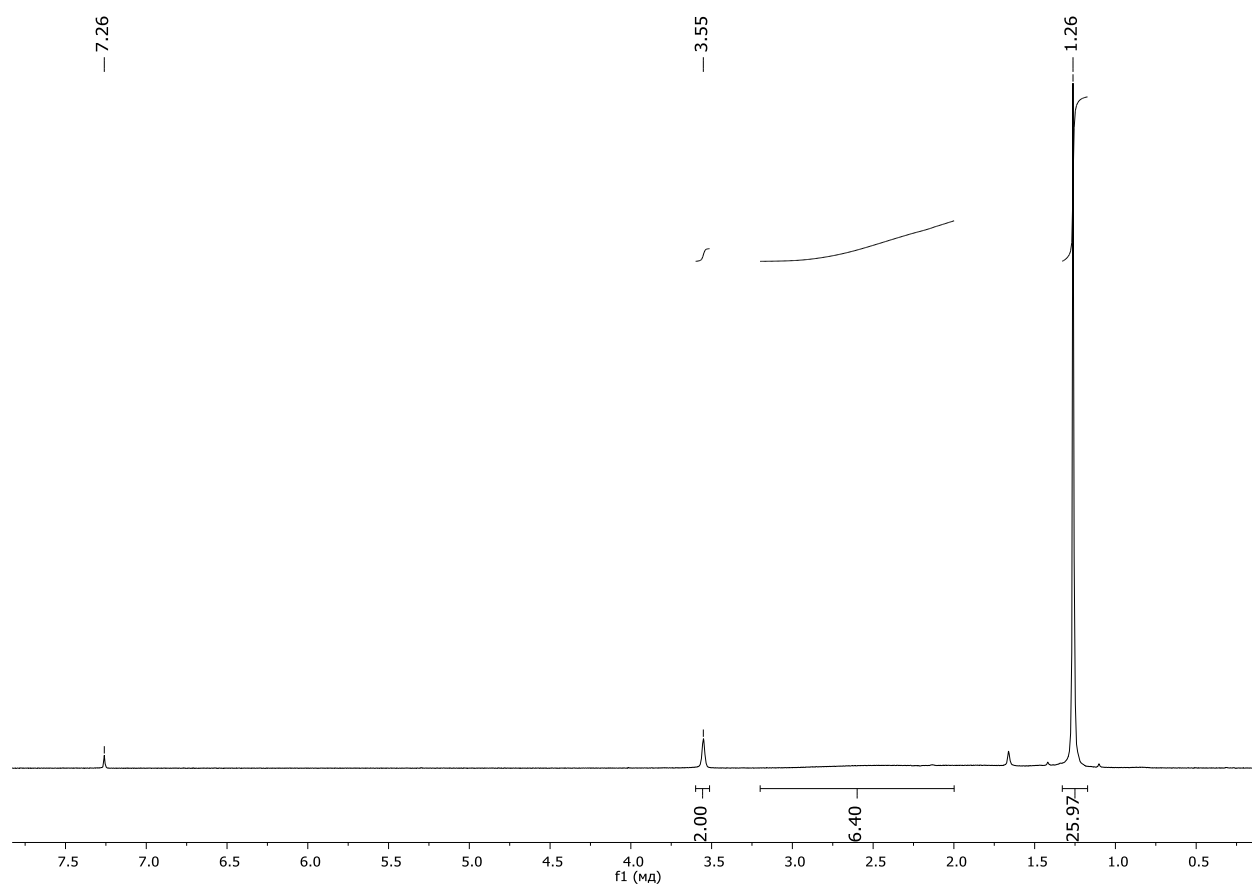
**Figure S1.** <sup>1</sup>H NMR spectrum of 3-Bpin-*ortho*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (**1**) in CDCl<sub>3</sub>.



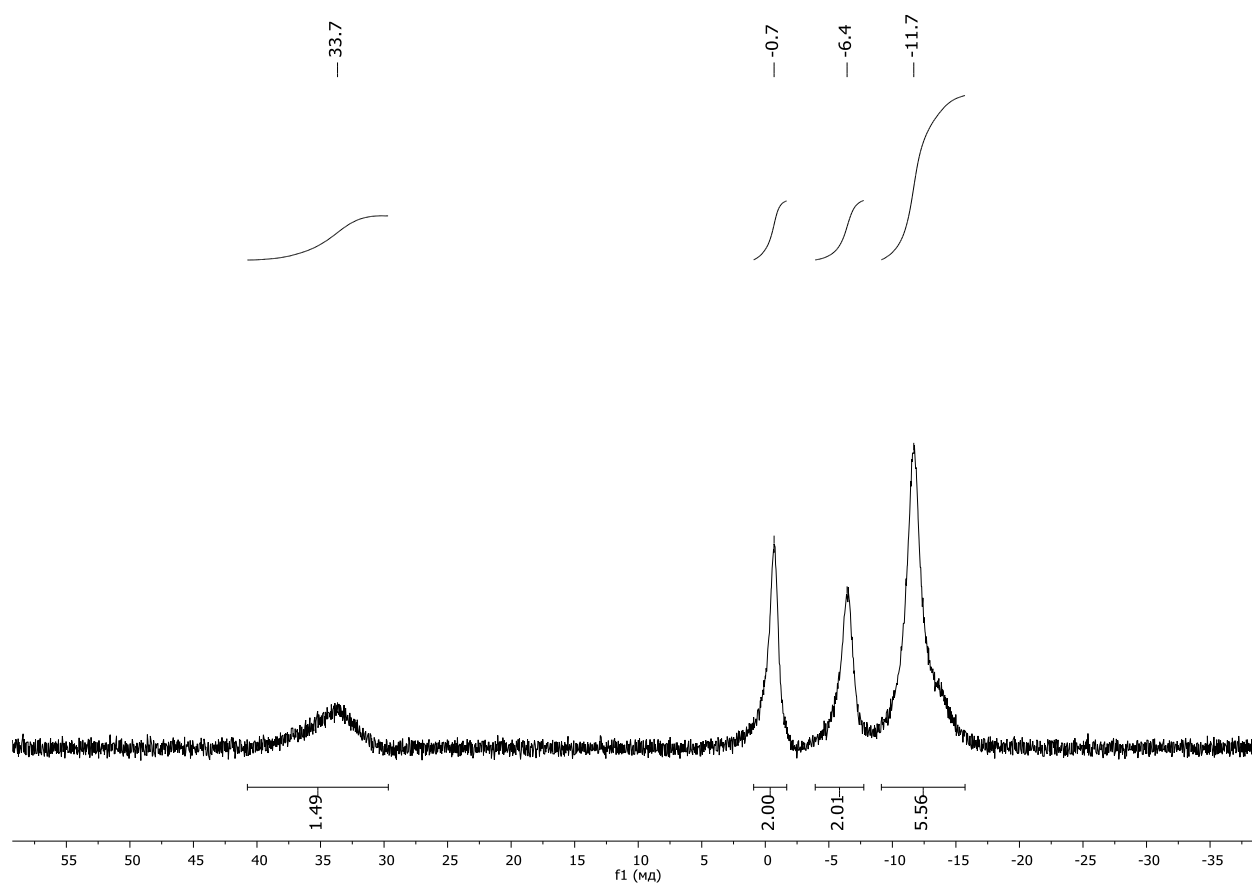
**Figure S2.** <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of 3-Bpin-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (**1**) in CDCl<sub>3</sub>.



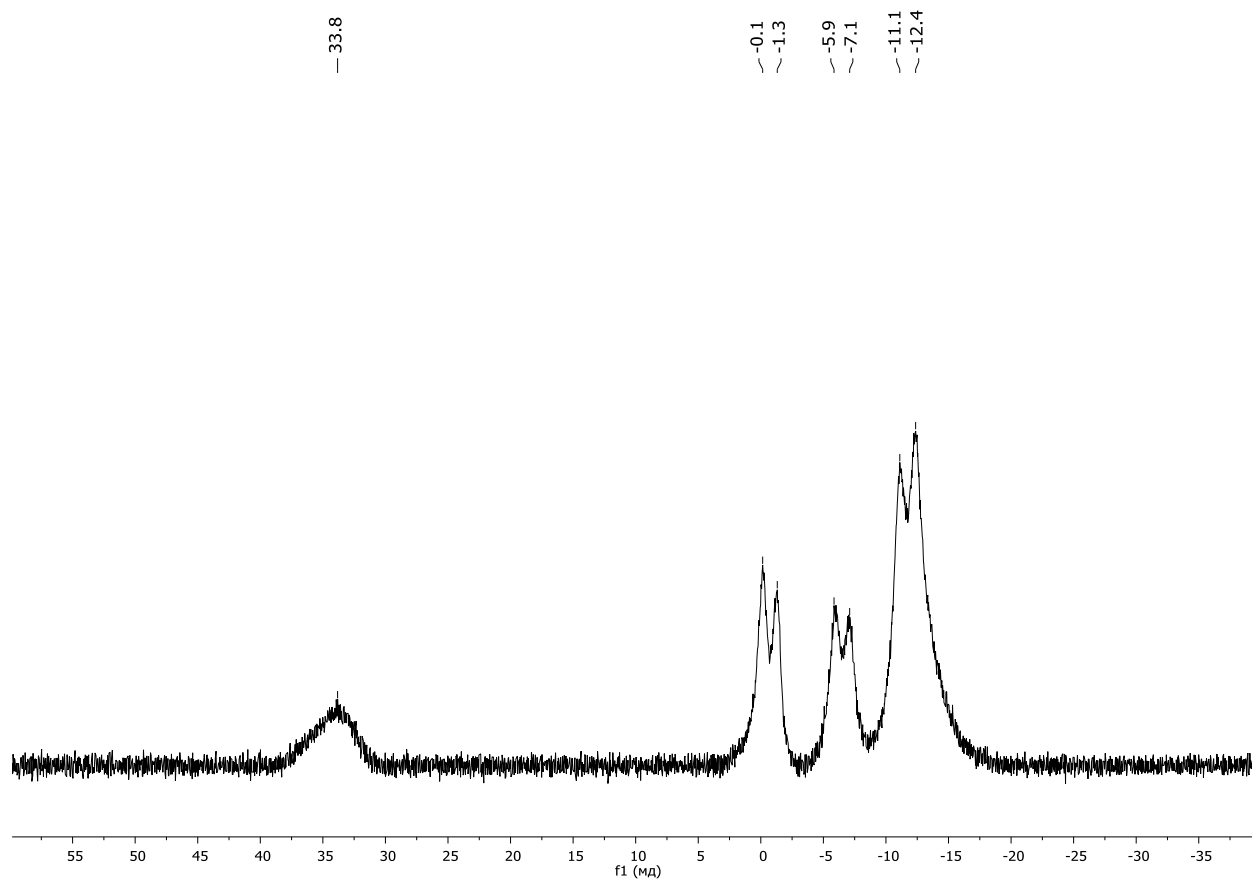
**Figure S3.**  $^{11}\text{B}$  NMR spectrum of 3-Bpin-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  (**1**) in  $\text{CDCl}_3$ .



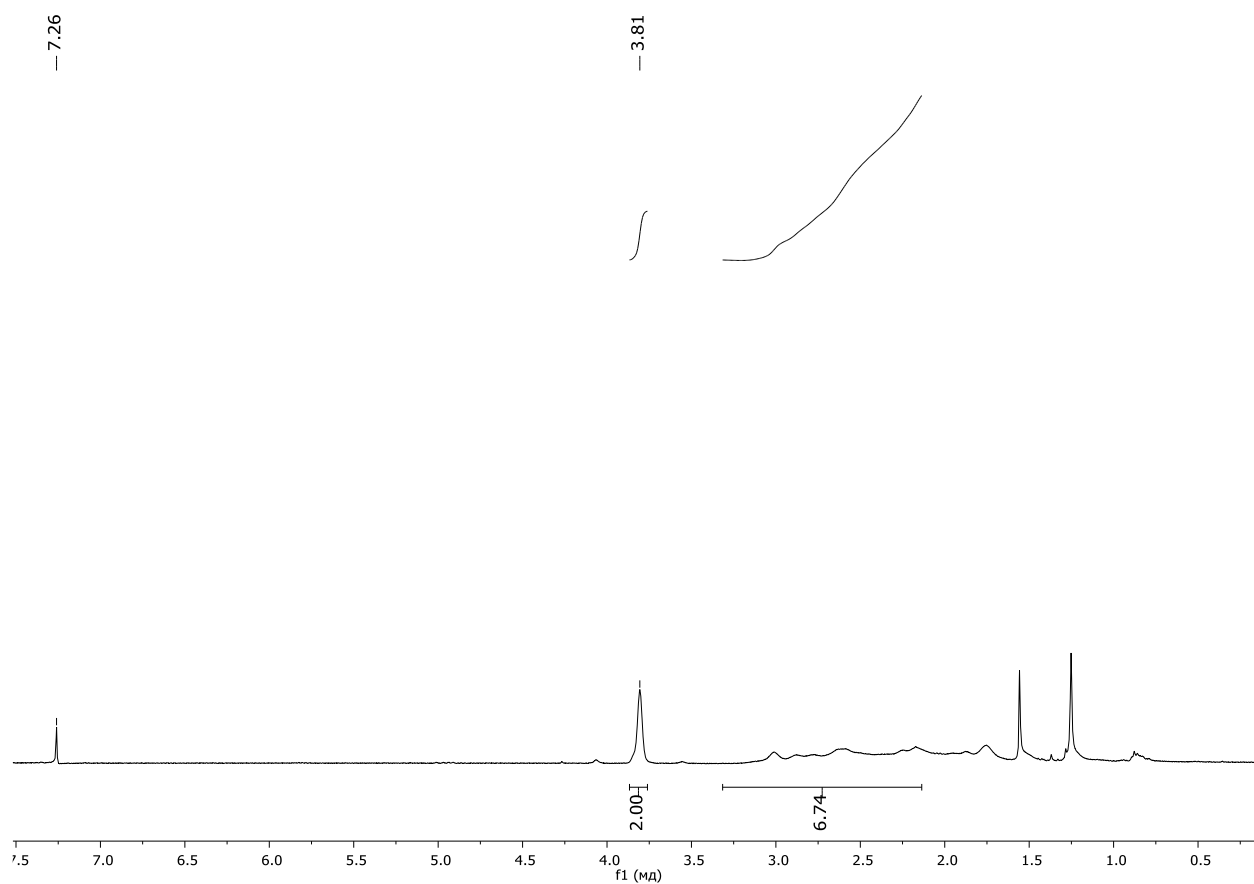
**Figure S4.**  $^1\text{H}$  NMR spectrum of 3,6-(Bpin) $_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**2**) in  $\text{CDCl}_3$ .



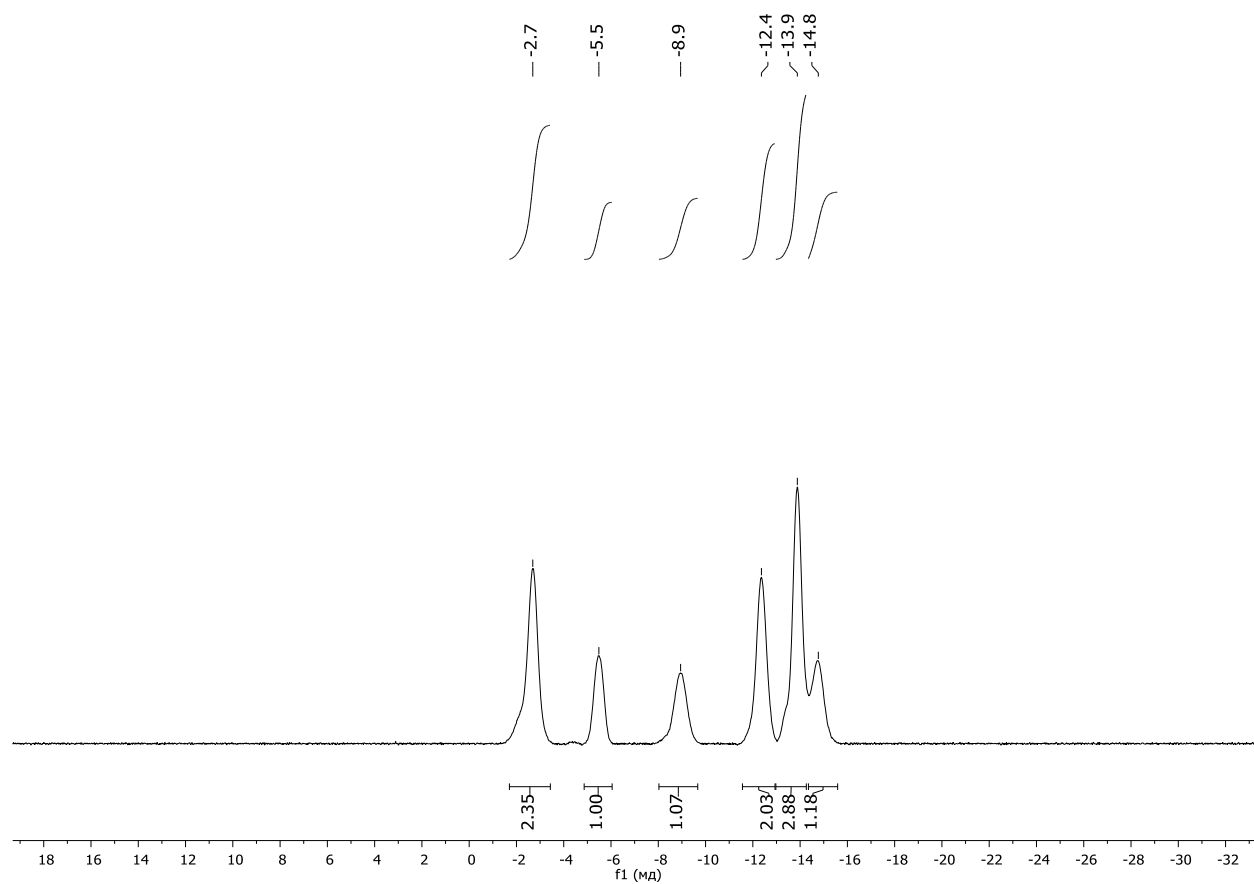
**Figure S5.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of 3,6-(Bpin) $_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**2**) in  $\text{CDCl}_3$ .



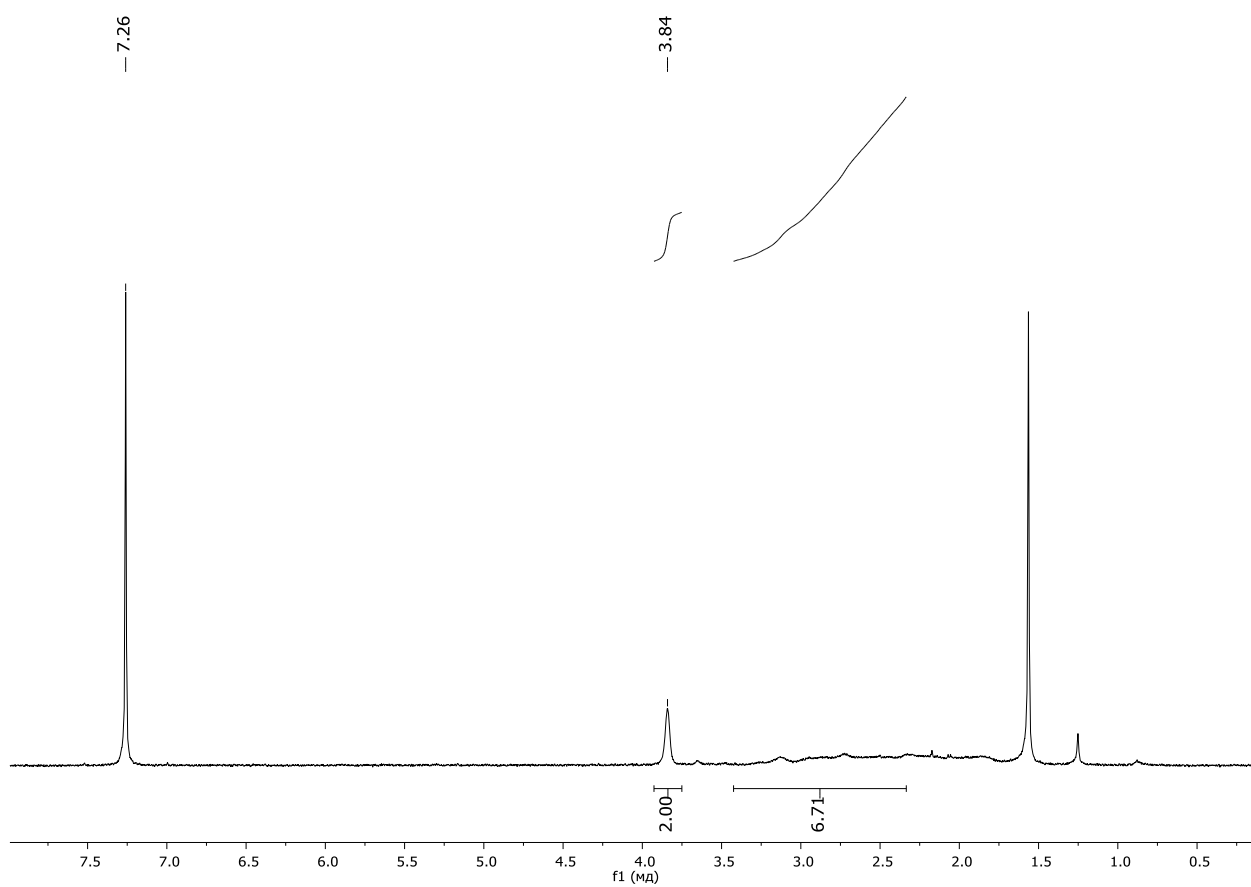
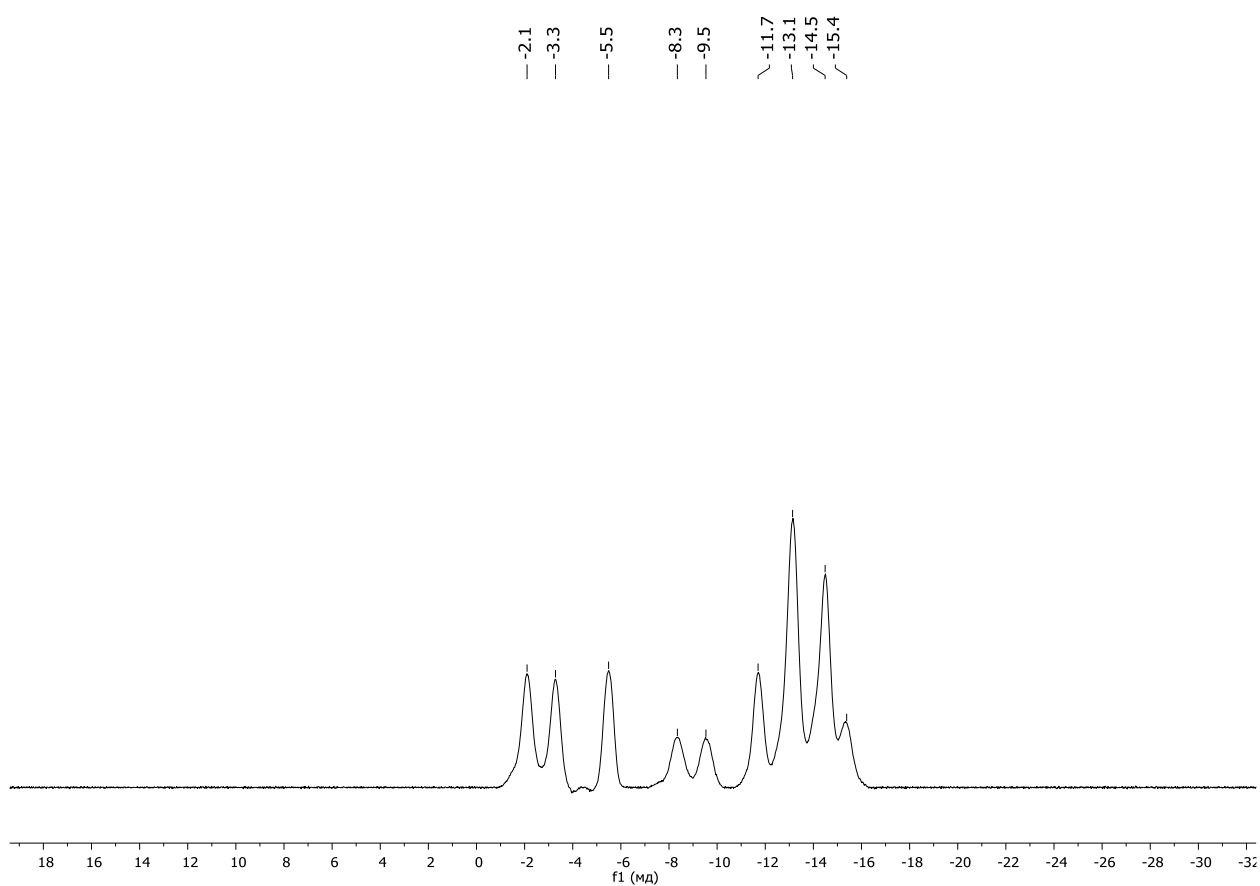
**Figure S6.**  $^{11}\text{B}$  NMR spectrum of 3,6-(Bpin) $_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**2**) in  $\text{CDCl}_3$ .

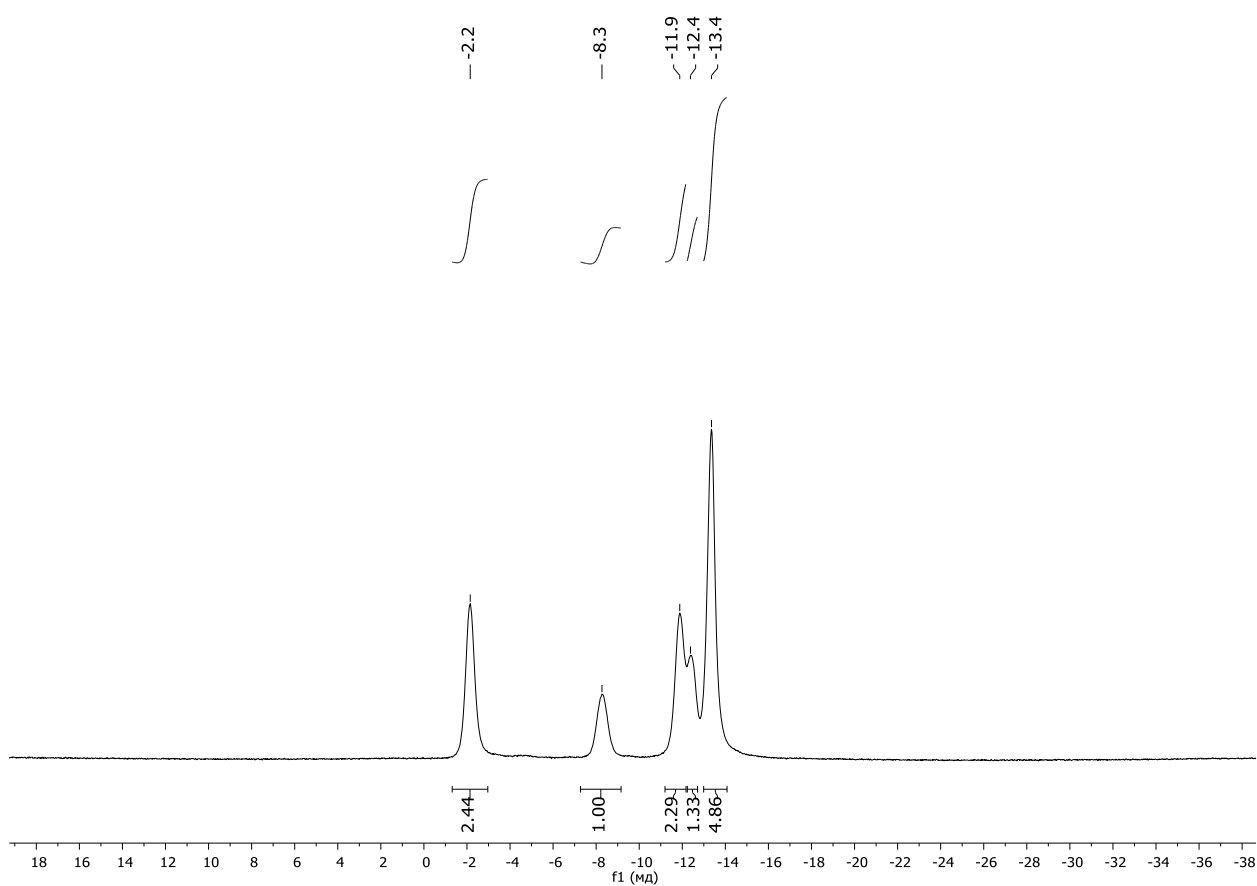


**Figure S7.**  $^1\text{H}$  NMR spectrum of 3-Cl-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  (**3**) in  $\text{CDCl}_3$ .

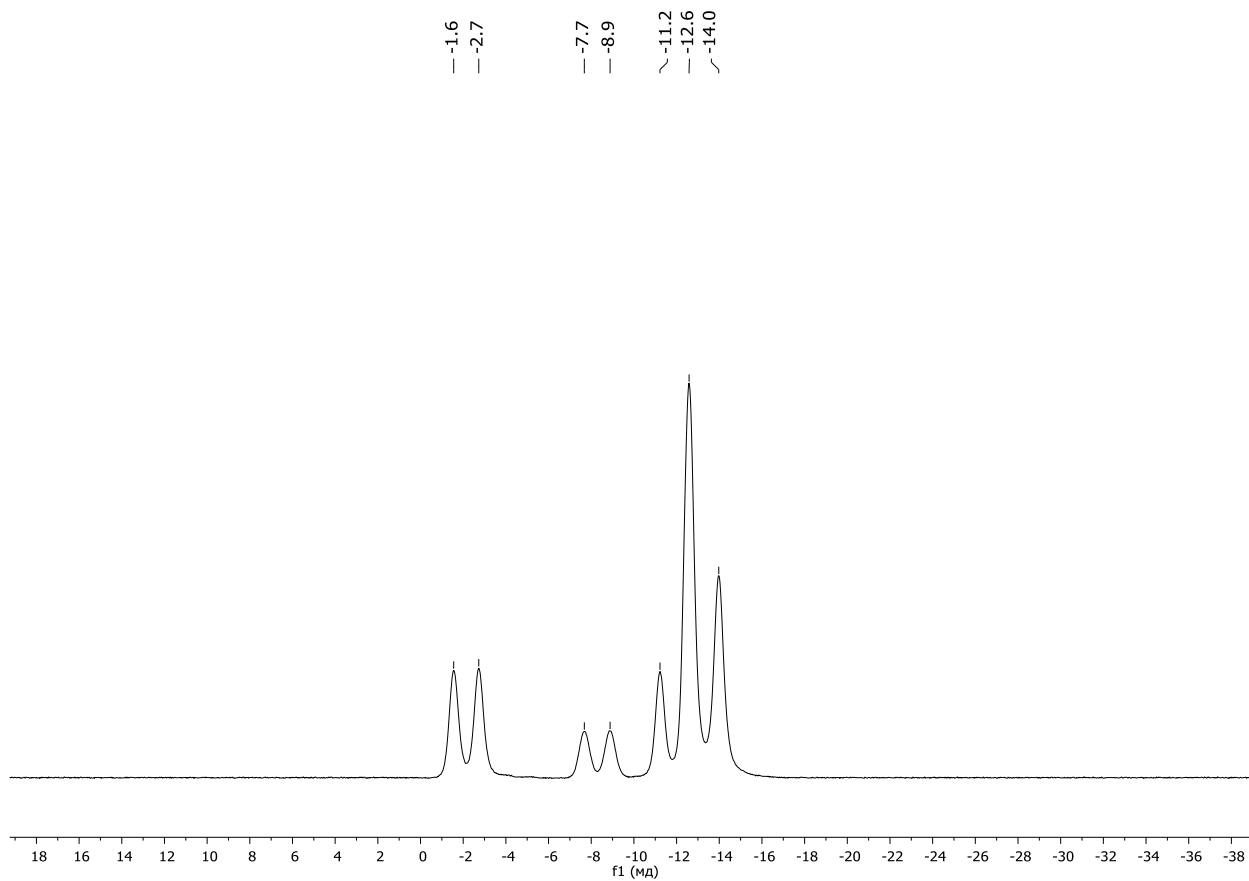


**Figure S8.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of 3-Cl-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  (**3**) in  $\text{CDCl}_3$ .

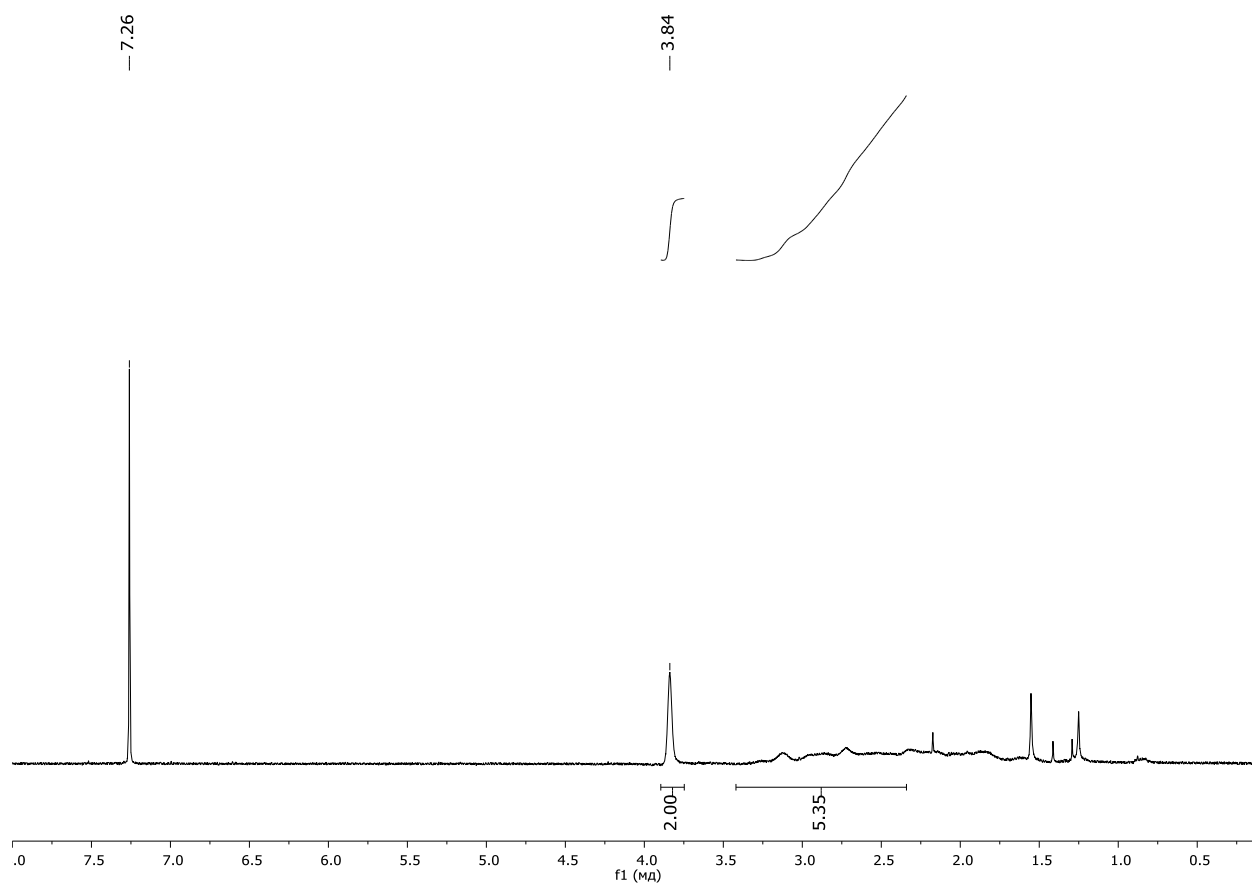




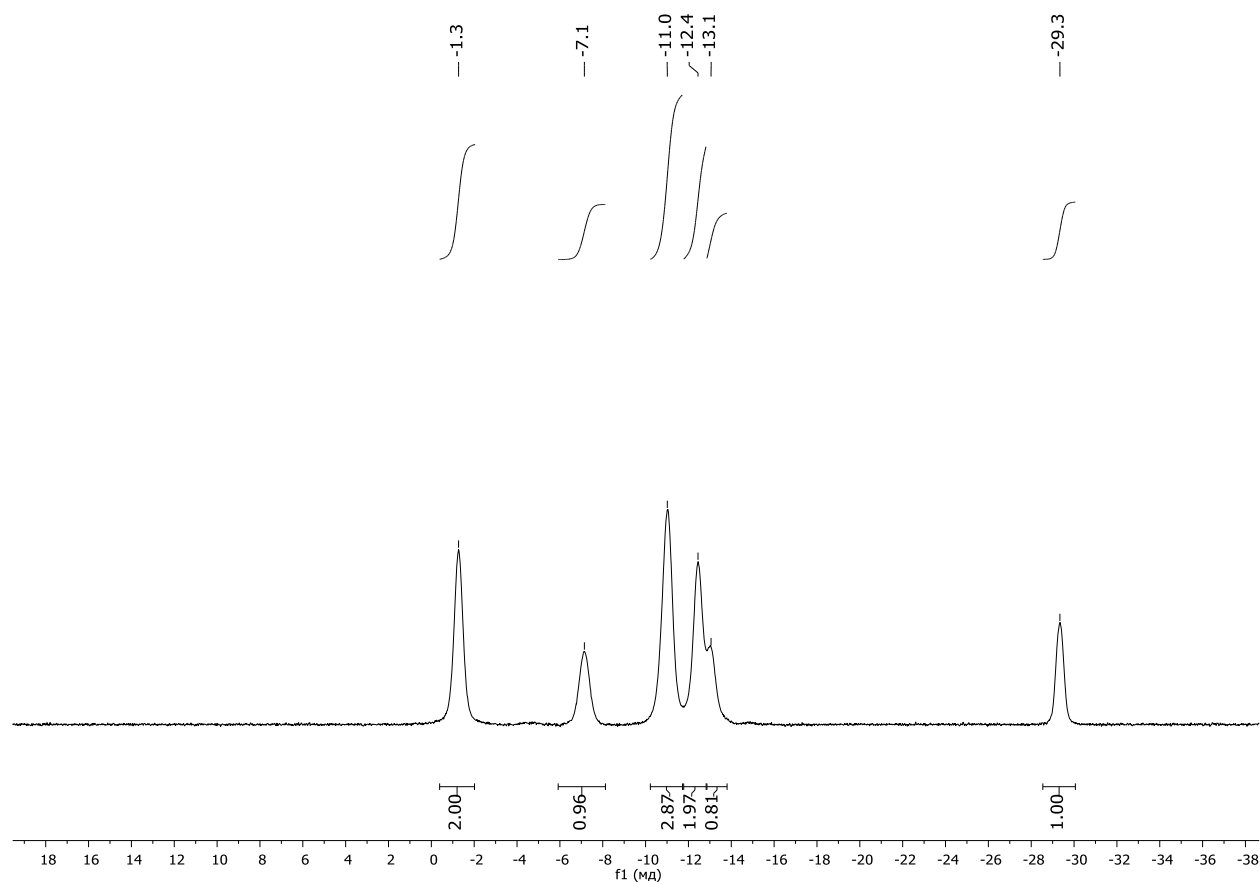
**Figure S11.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of 3-Br-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  (**4**) in  $\text{CDCl}_3$ .



**Figure S12.**  $^{11}\text{B}$  NMR spectrum of 3-Br-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  (**4**) in  $\text{CDCl}_3$ .

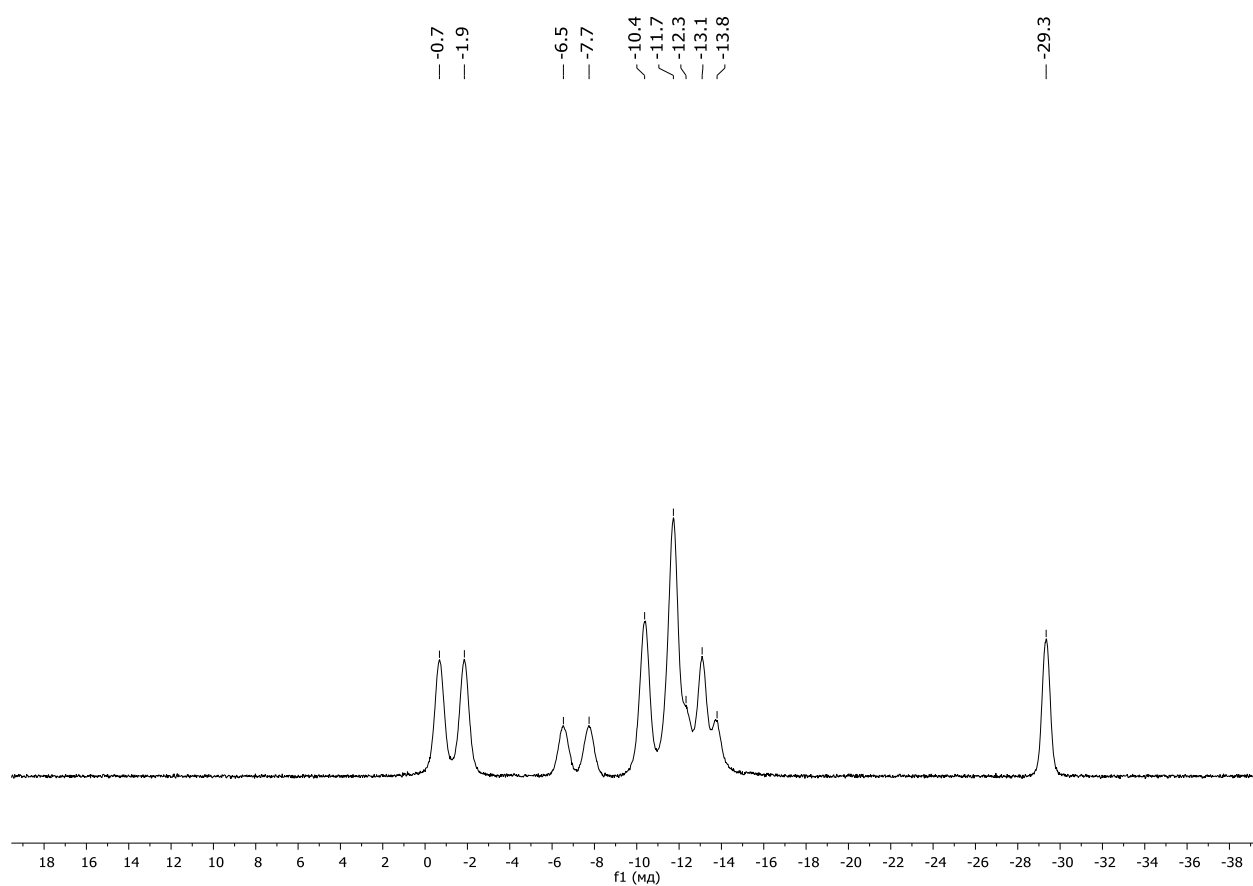


**Figure S13.**  $^1\text{H}$  NMR spectrum of 3-I-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  (**5**) in  $\text{CDCl}_3$ .

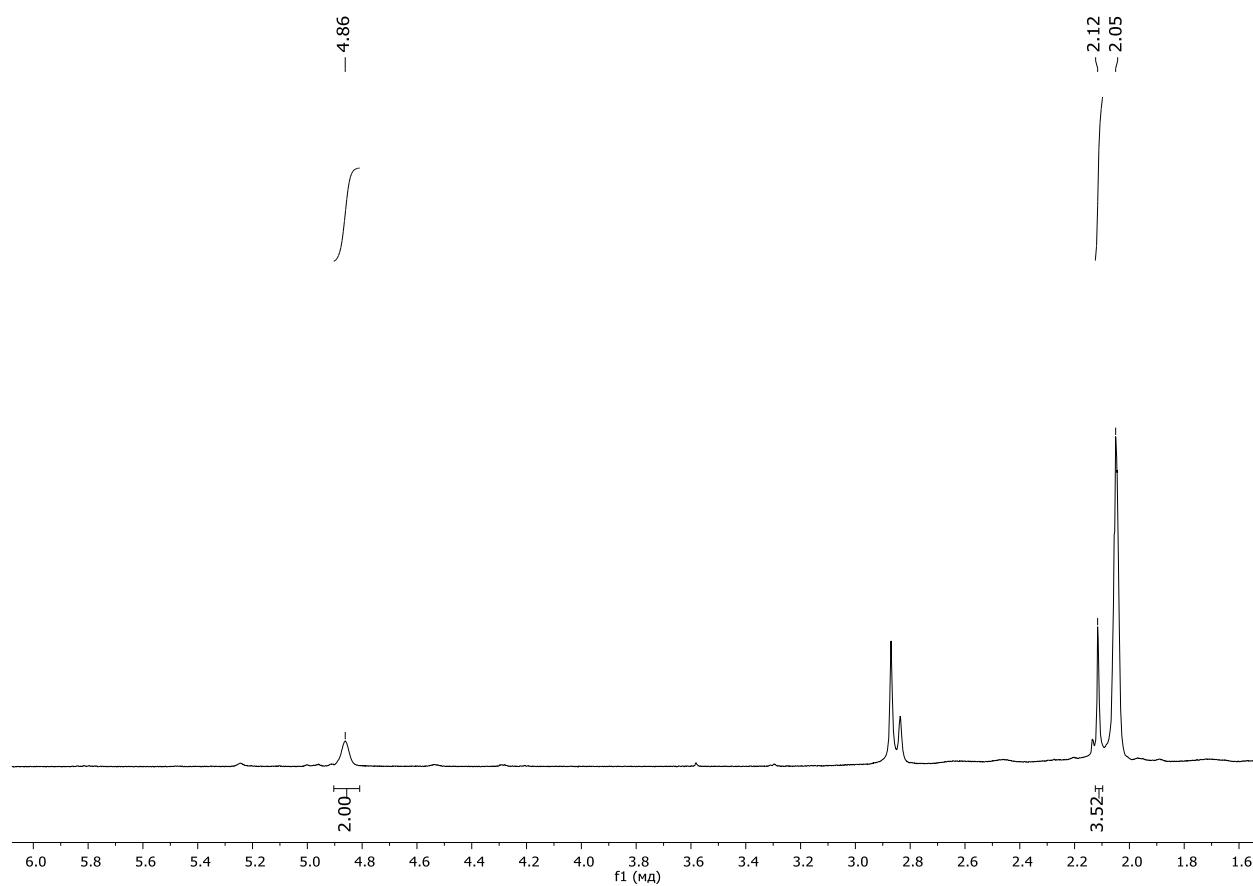


**Figure S14.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of 3-I-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  (**5**) in  $\text{CDCl}_3$ .

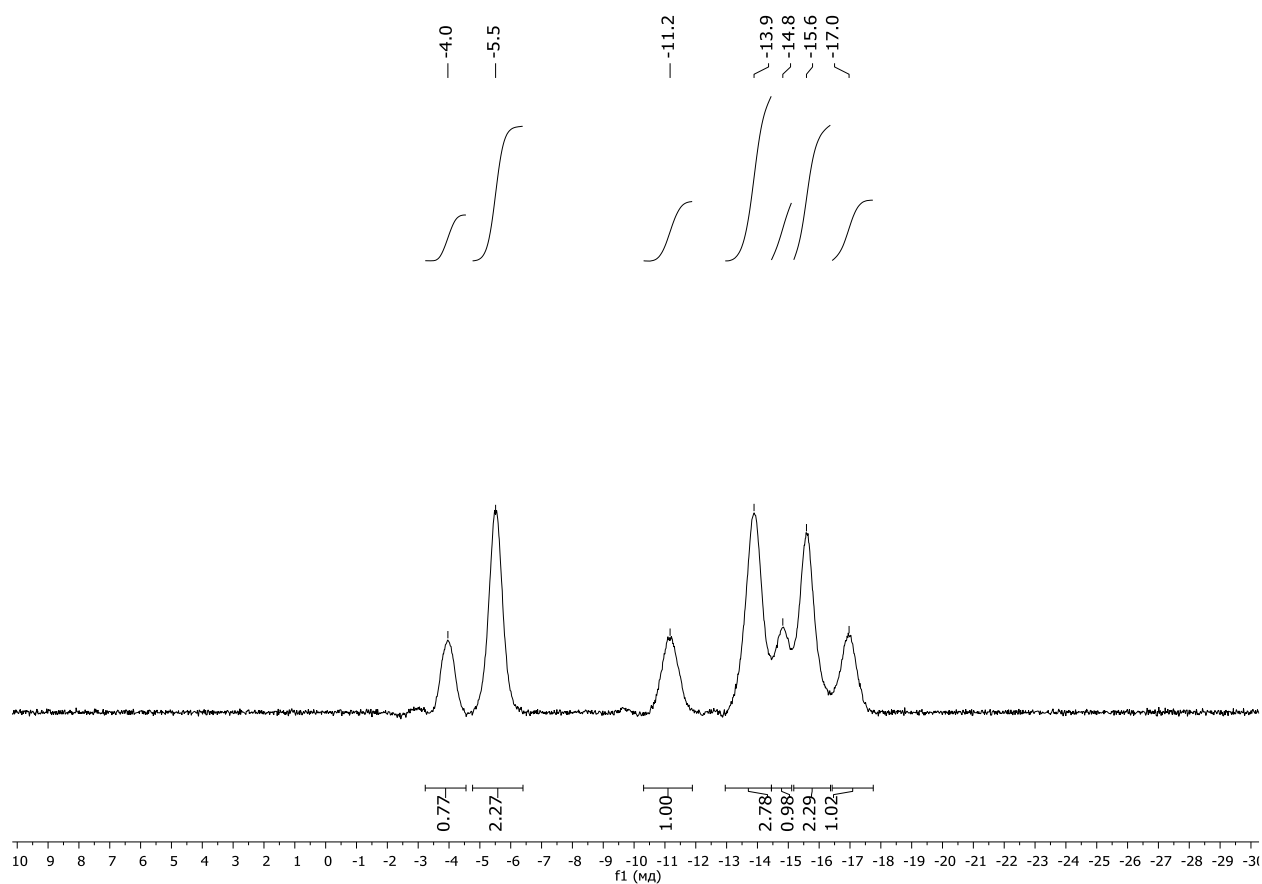




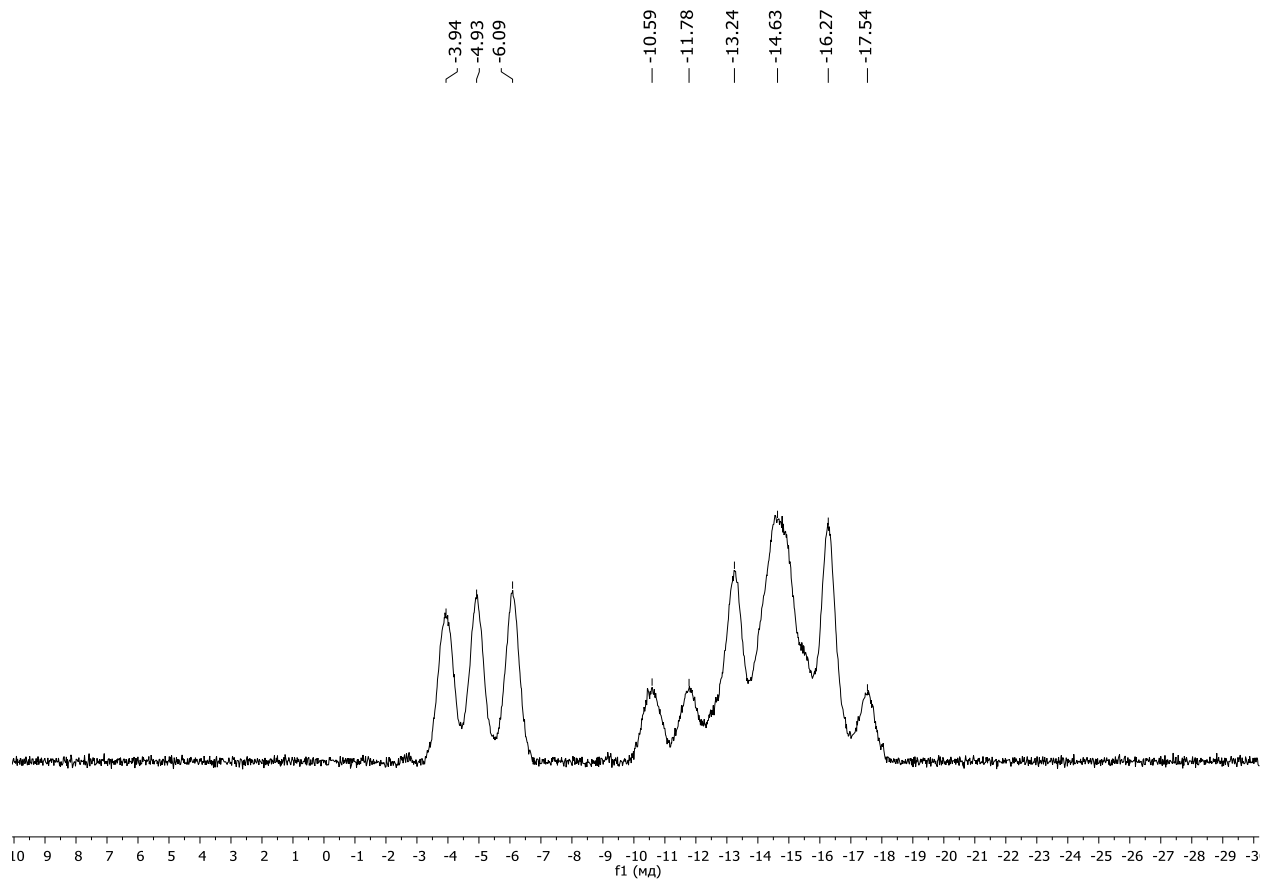
**Figure S15.**  $^{11}\text{B}$  NMR spectrum of 3-I-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  (**5**) in  $\text{CDCl}_3$ .



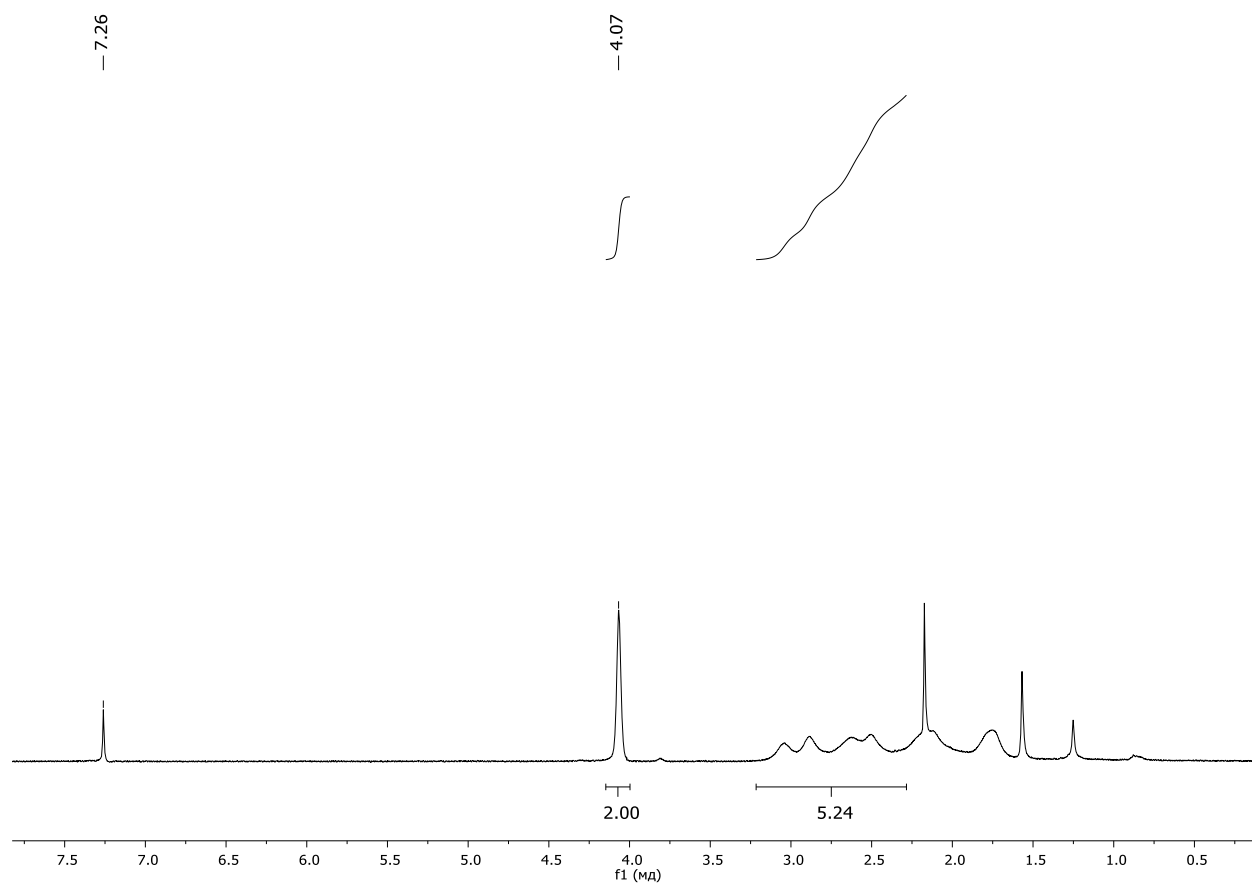
**Figure S16.**  $^1\text{H}$  NMR spectrum of 3-AcO-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  (**6**) in acetone- $d_6$ .



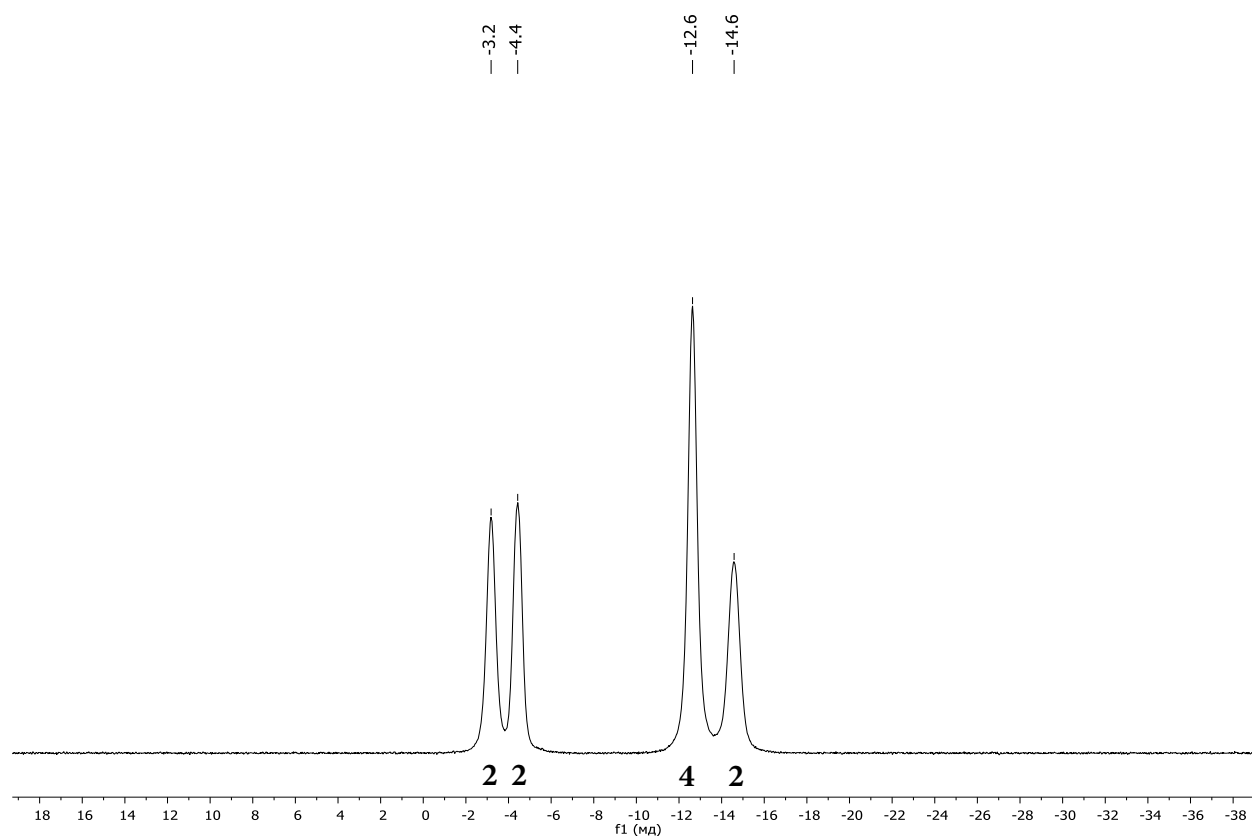
**Figure S17.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of 3-AcO-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  (**6**) in acetone- $d_6$ .



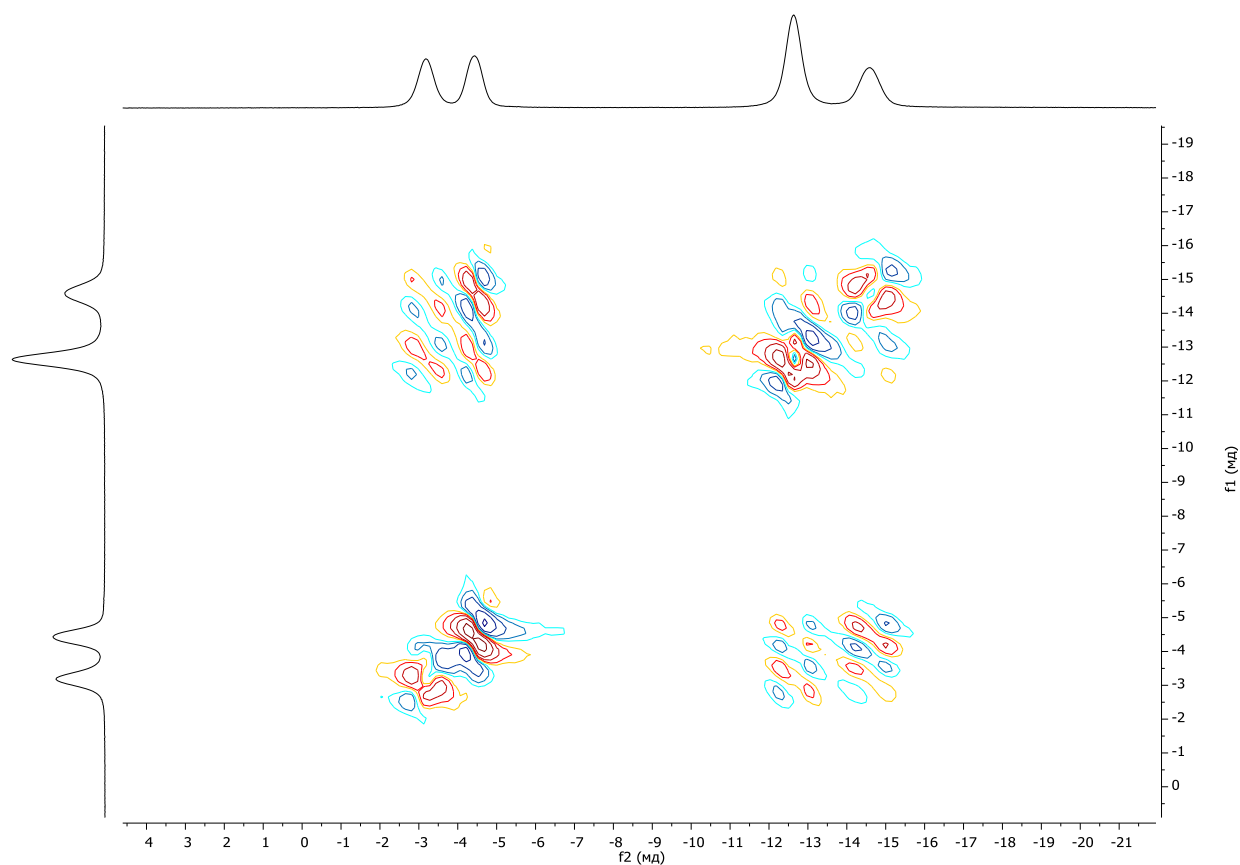
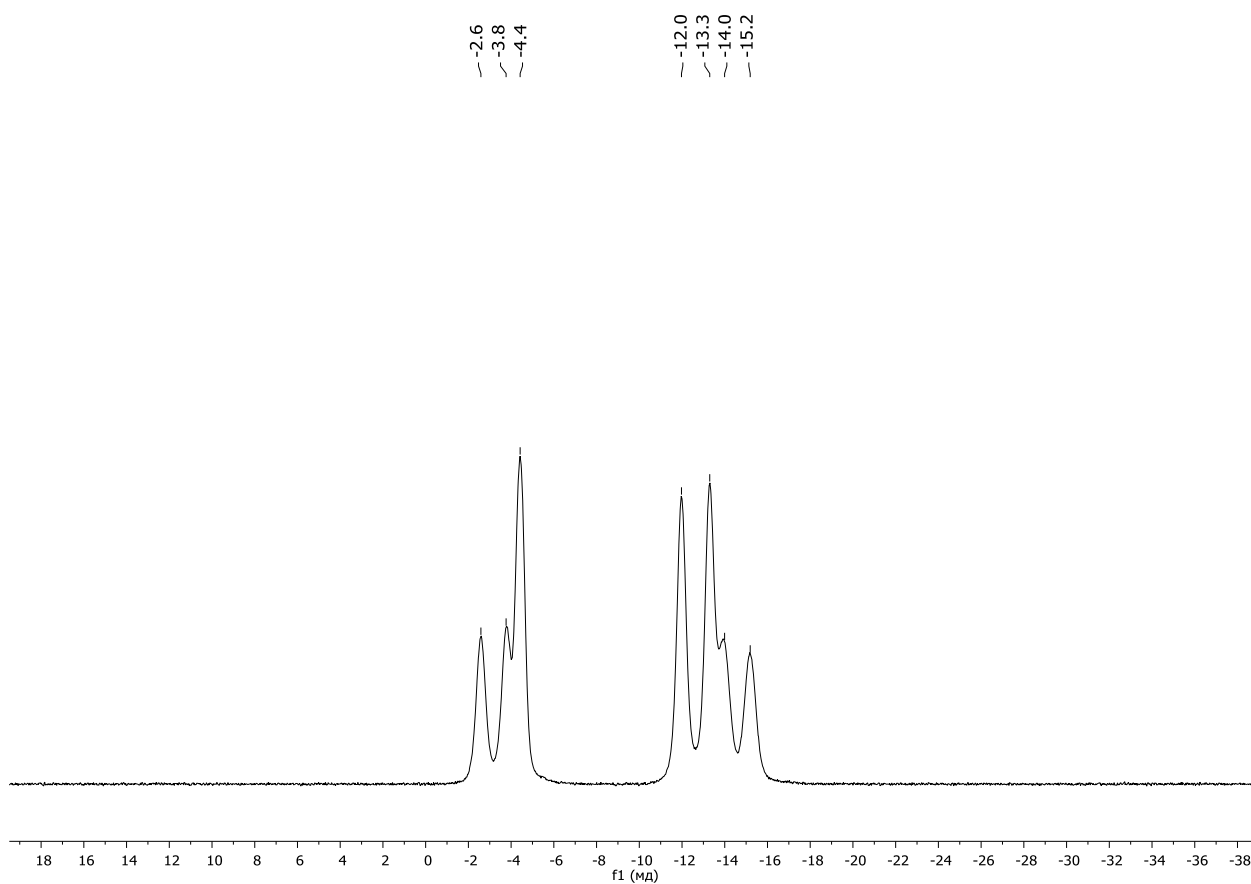
**Figure S18.**  $^{11}\text{B}$  NMR spectrum of 3-AcO-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  (**6**) in acetone- $d_6$ .

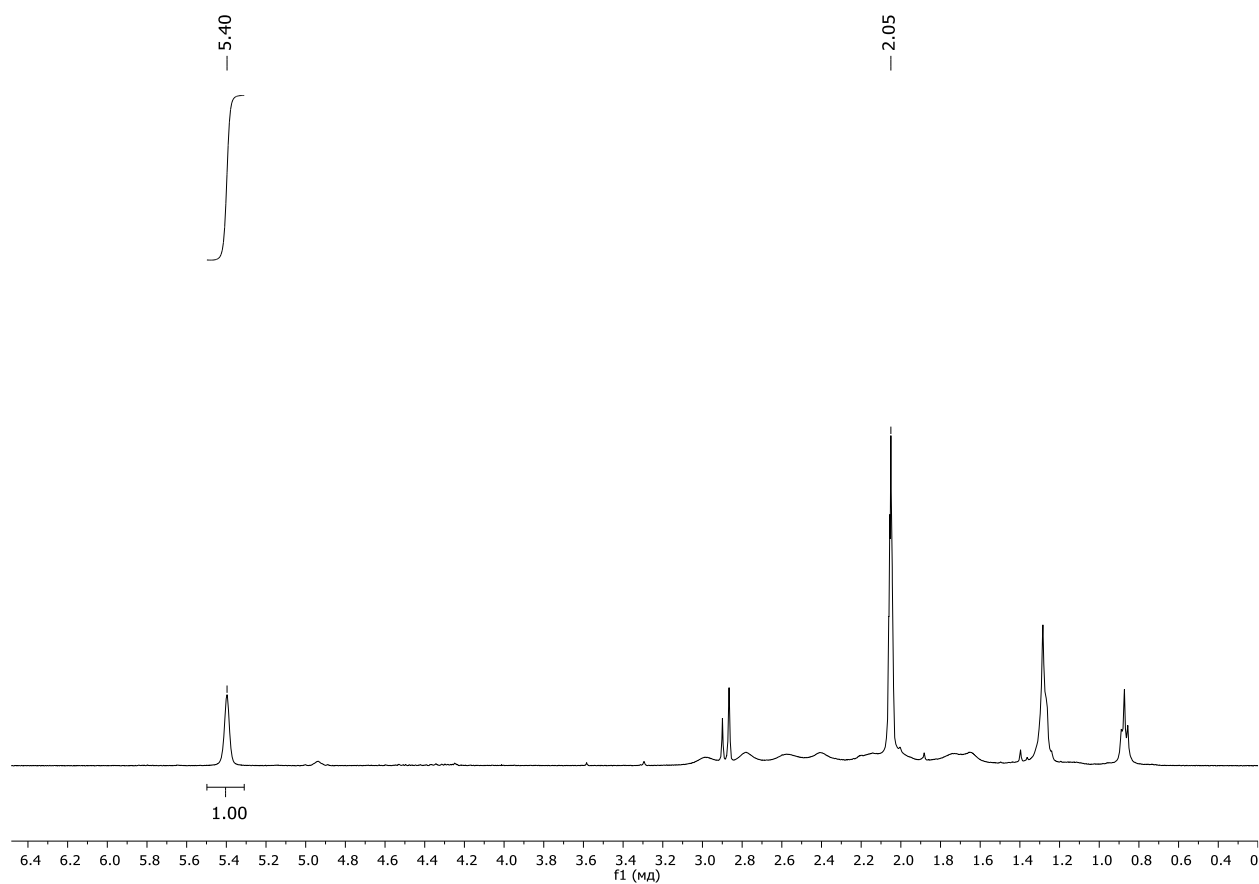


**Figure S19.** <sup>1</sup>H NMR spectrum of 3,6-Cl<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**7**) in CDCl<sub>3</sub>.

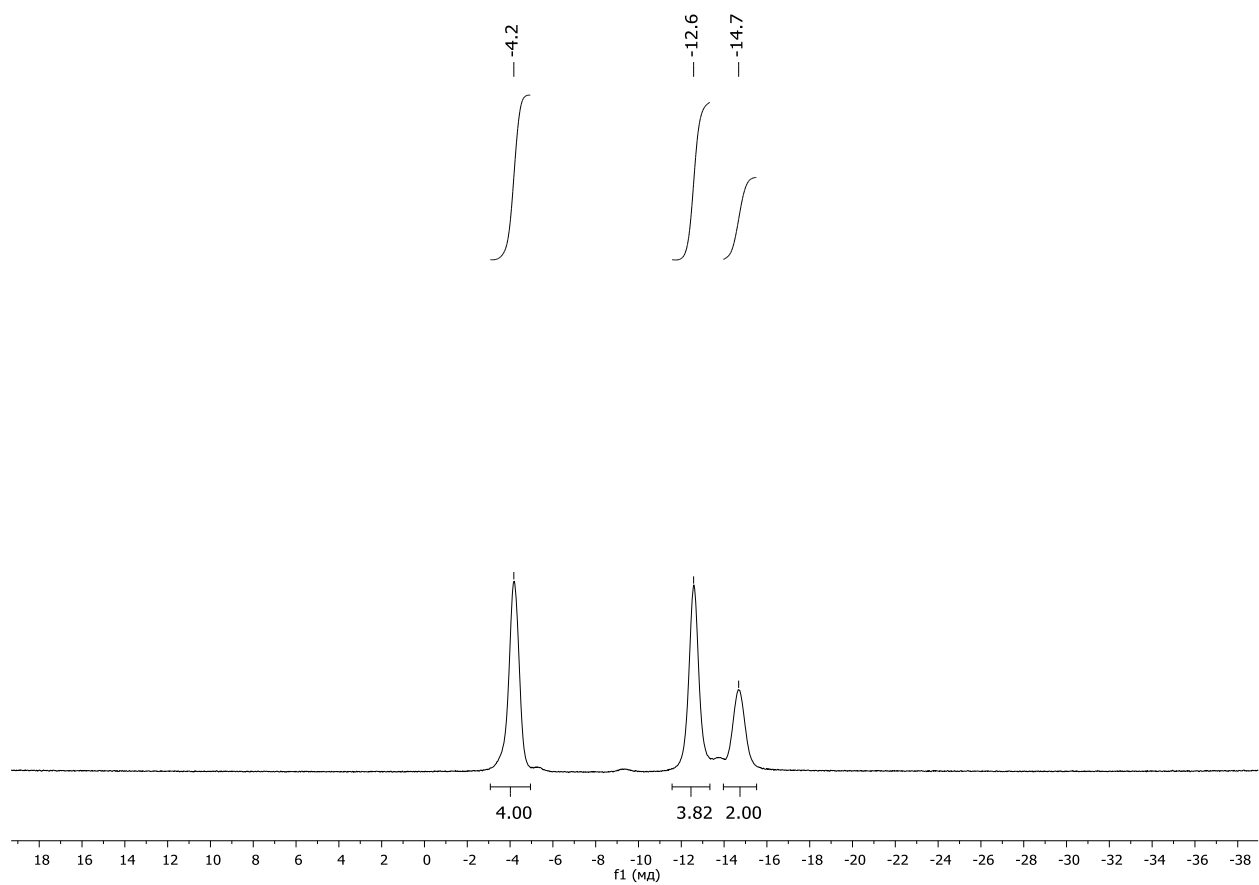


**Figure S20.** <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of 3,6-Cl<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**7**) in CDCl<sub>3</sub>.

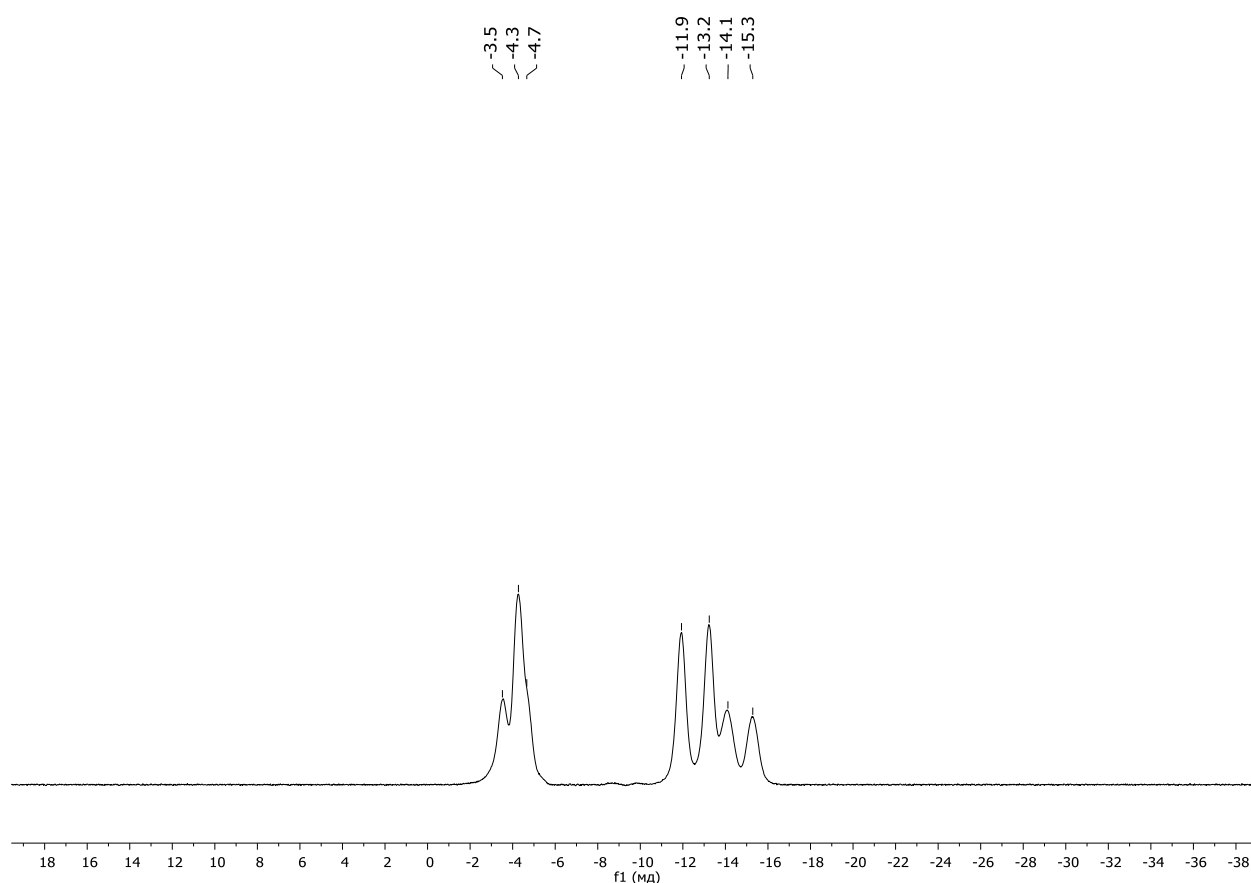




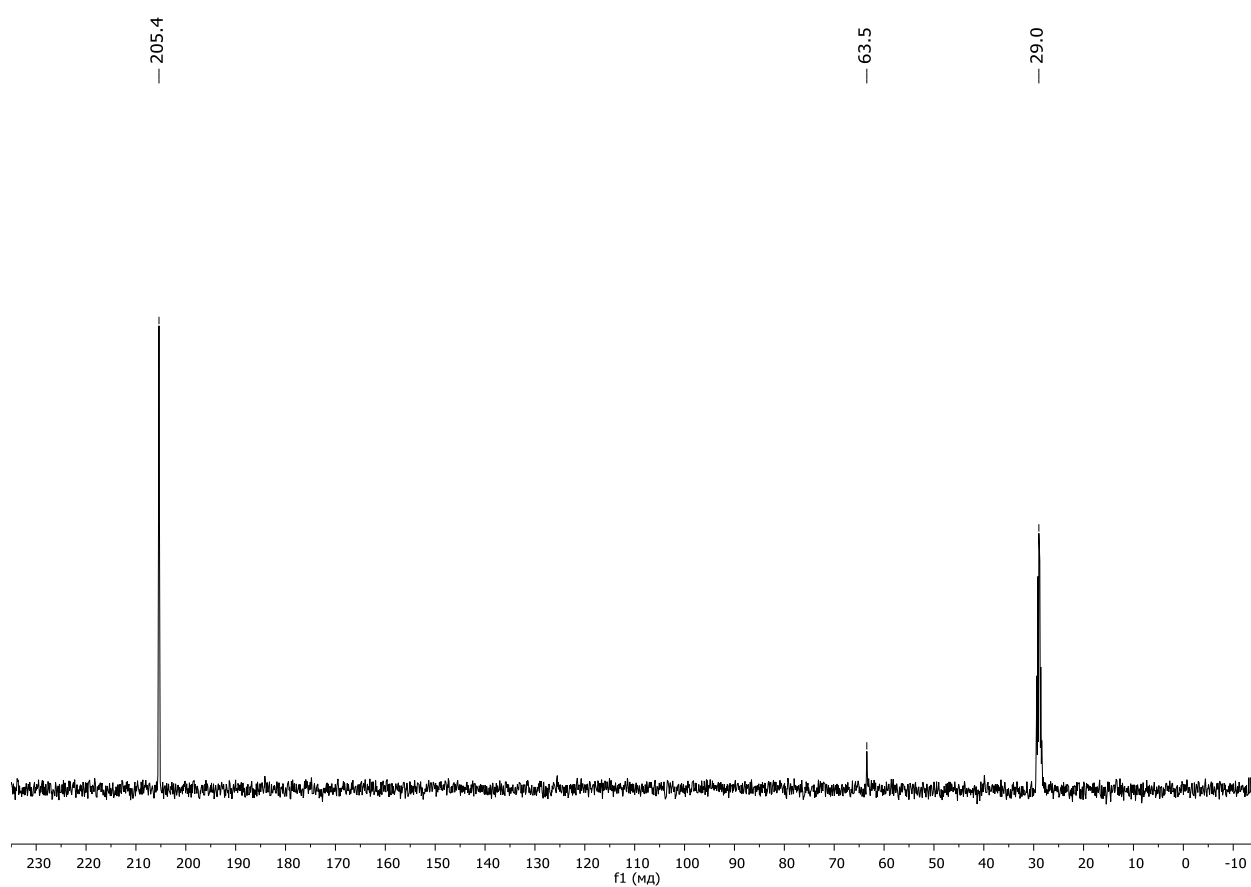
**Figure S23.** <sup>1</sup>H NMR spectrum of 3,6-Cl<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**7**) in acetone-*d*<sub>6</sub>.



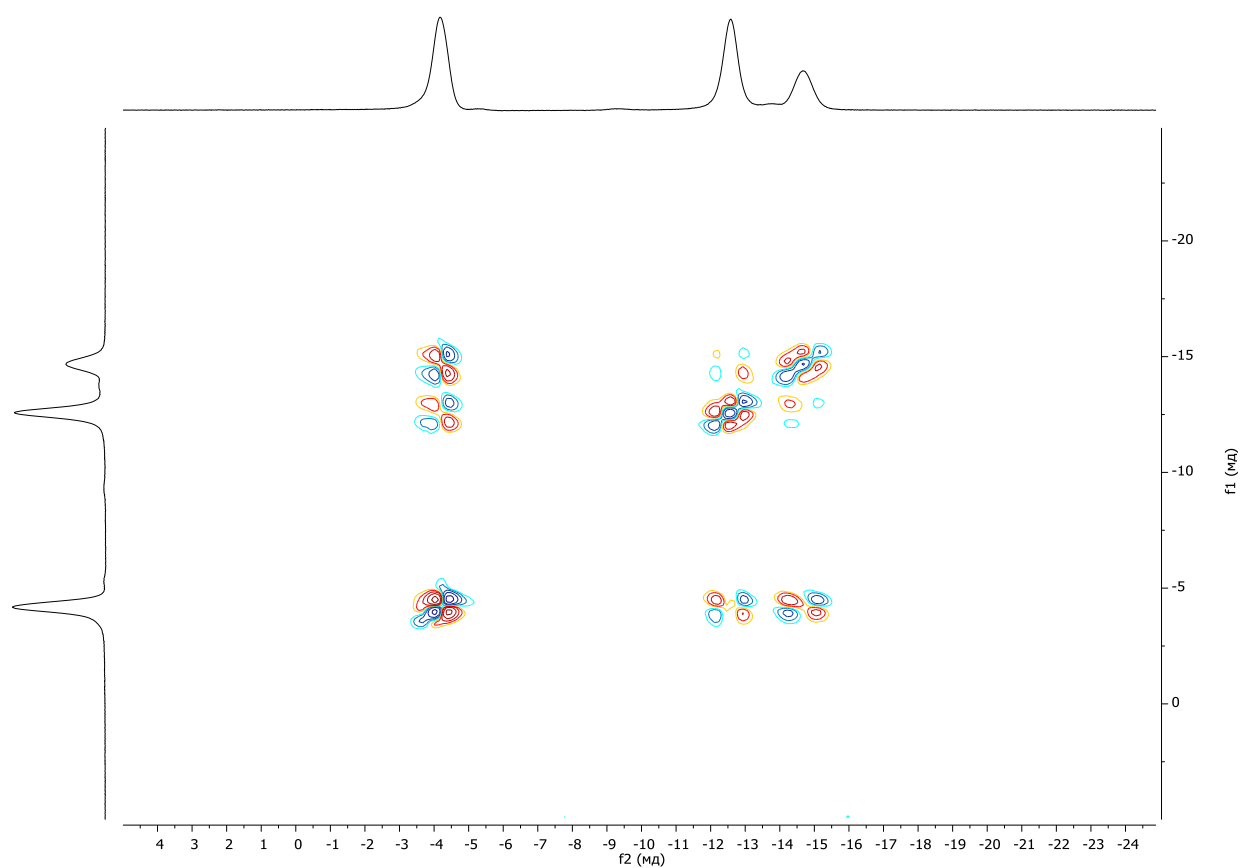
**Figure S24.** <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of 3,6-Cl<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**7**) in acetone-*d*<sub>6</sub>.



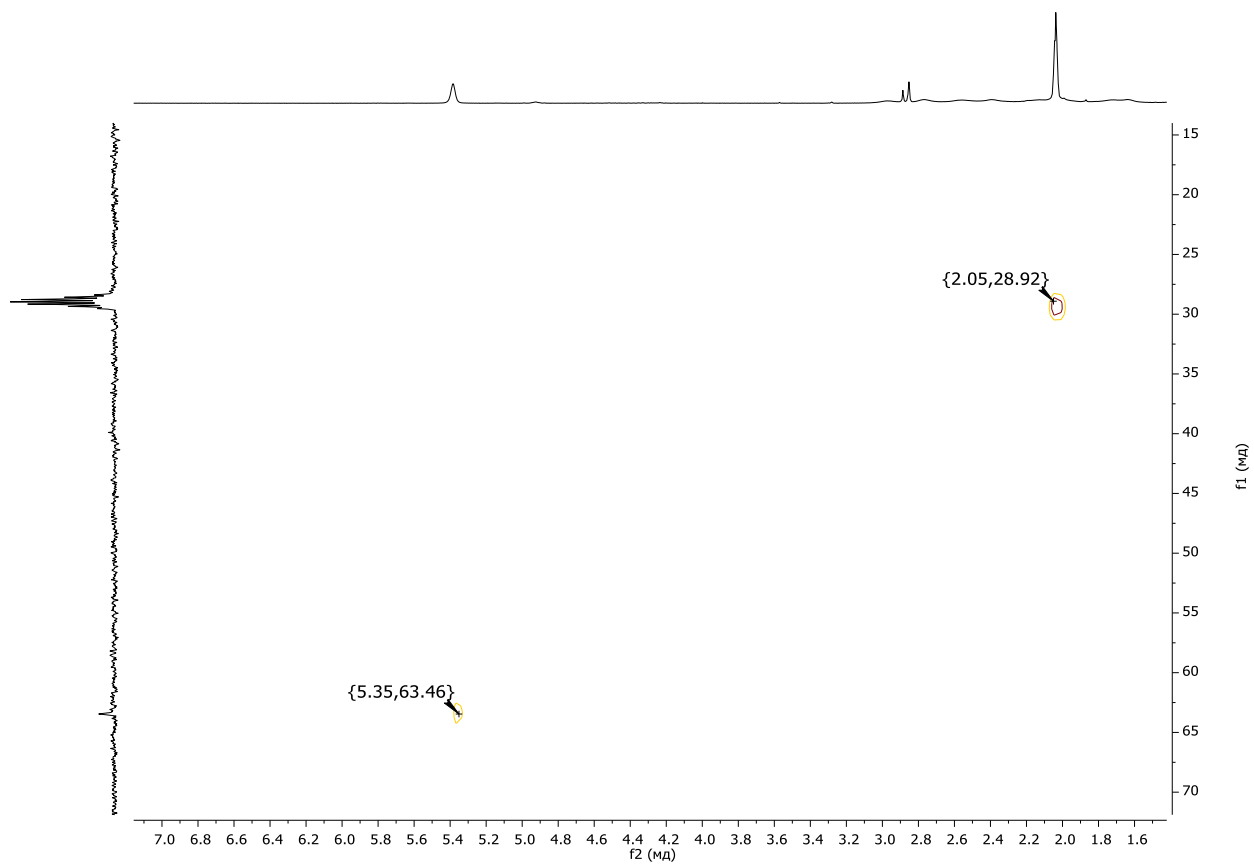
**Figure S25.**  $^{11}\text{B}$  NMR spectrum of 3,6- $\text{Cl}_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**7**) in acetone- $d_6$ .



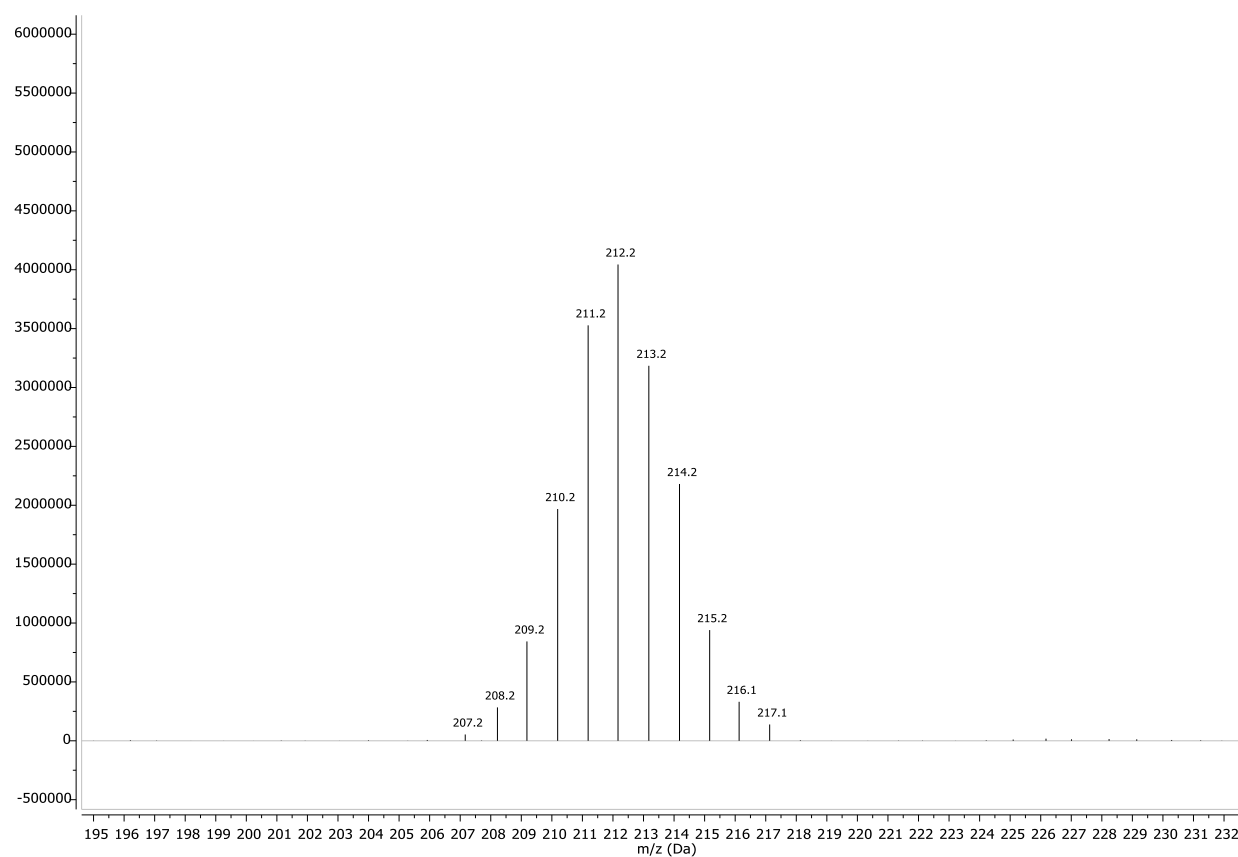
**Figure S26.**  $^{13}\text{C}$  NMR spectrum of 3,6- $\text{Cl}_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**7**) in acetone- $d_6$ .



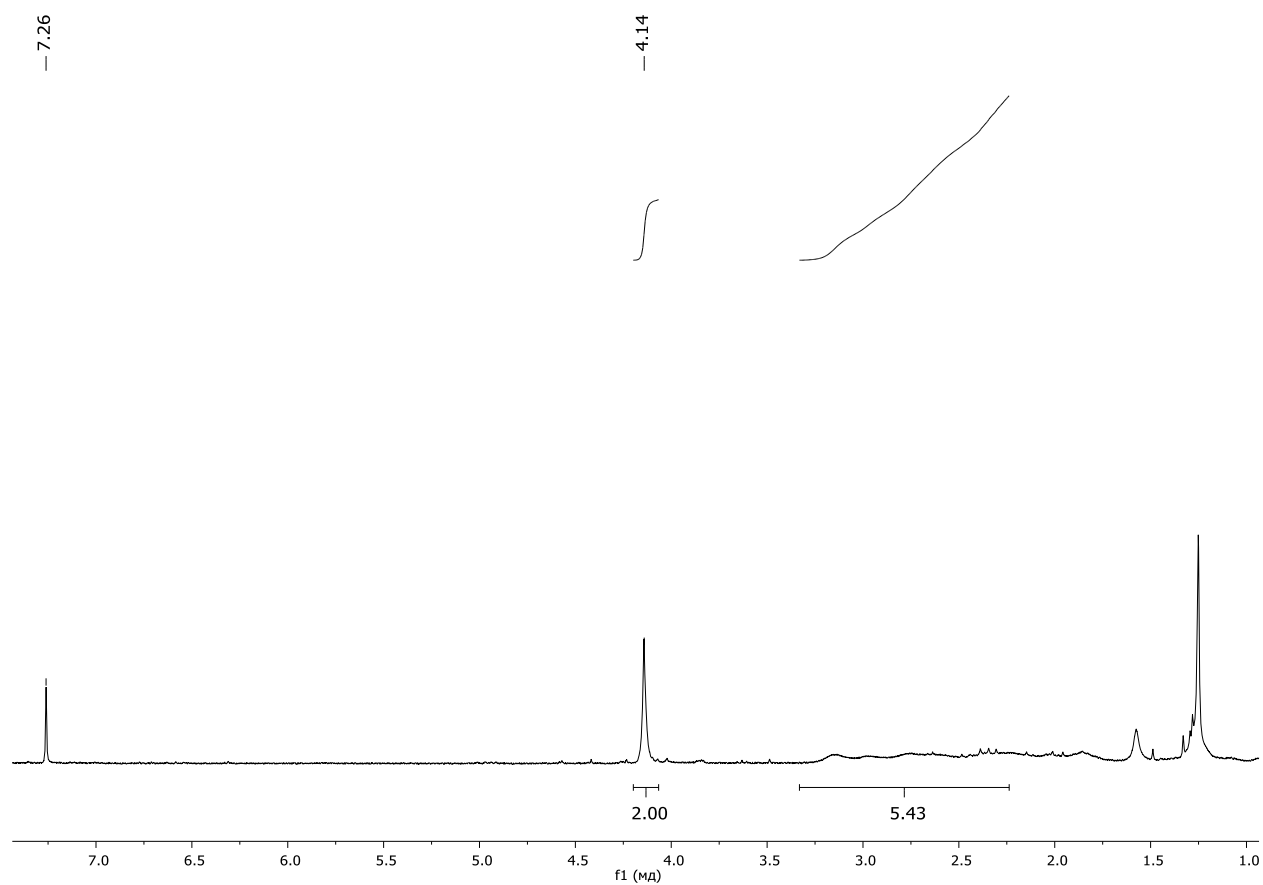
**Figure S27.**  $^{11}\text{B}$ - $^{11}\text{B}$  gDQCOSY NMR spectrum of 3,6- $\text{Cl}_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**7**) in acetone- $d_6$ .



**Figure S28.**  $^1\text{H}$ - $^{13}\text{C}$  HMQC NMR spectrum of 3,6- $\text{Cl}_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**7**) in acetone- $d_6$ .

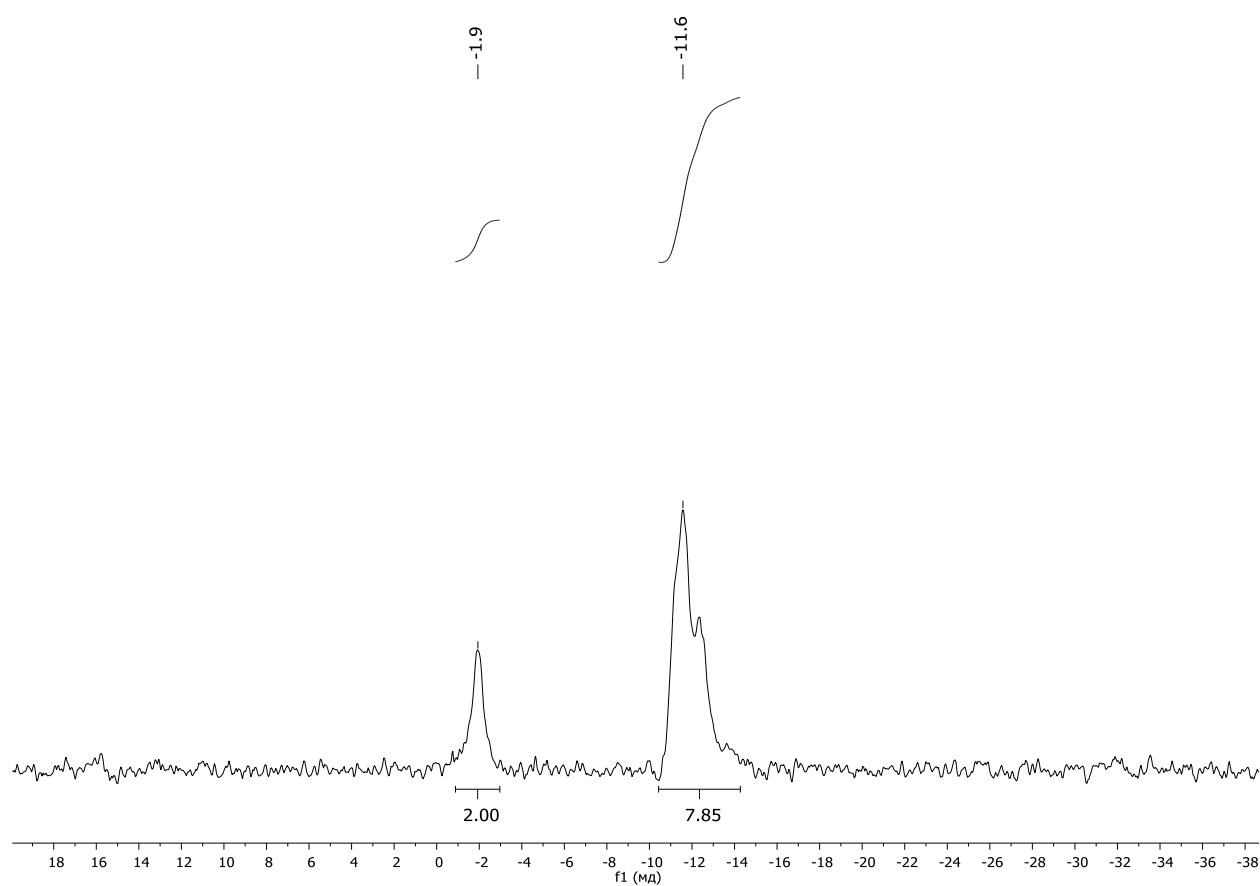


**Figure S29.** Mass-spectrum (DUIS) of 3,6-Cl<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**7**).

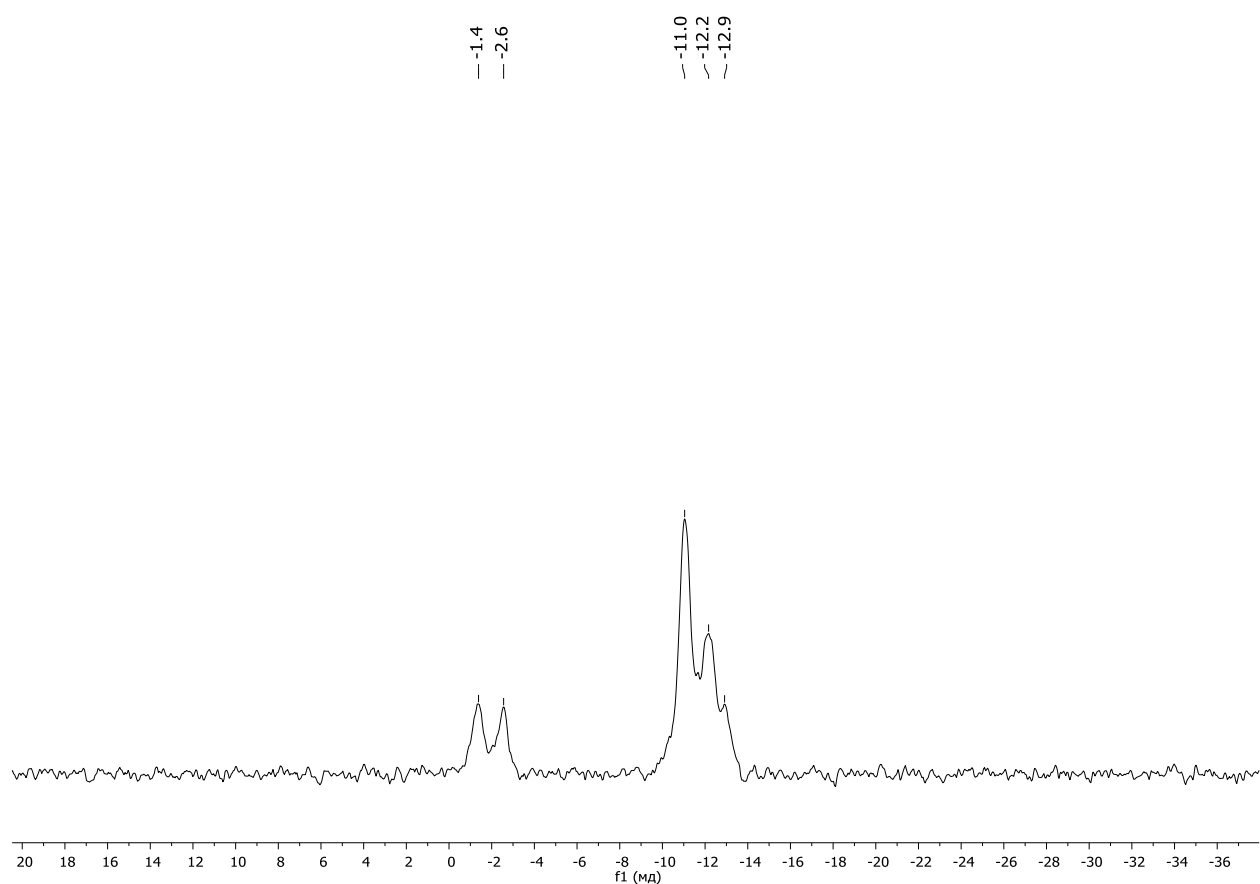


**Figure S30.** <sup>1</sup>H NMR spectrum of 3,6-Br<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**8**) in CDCl<sub>3</sub>.

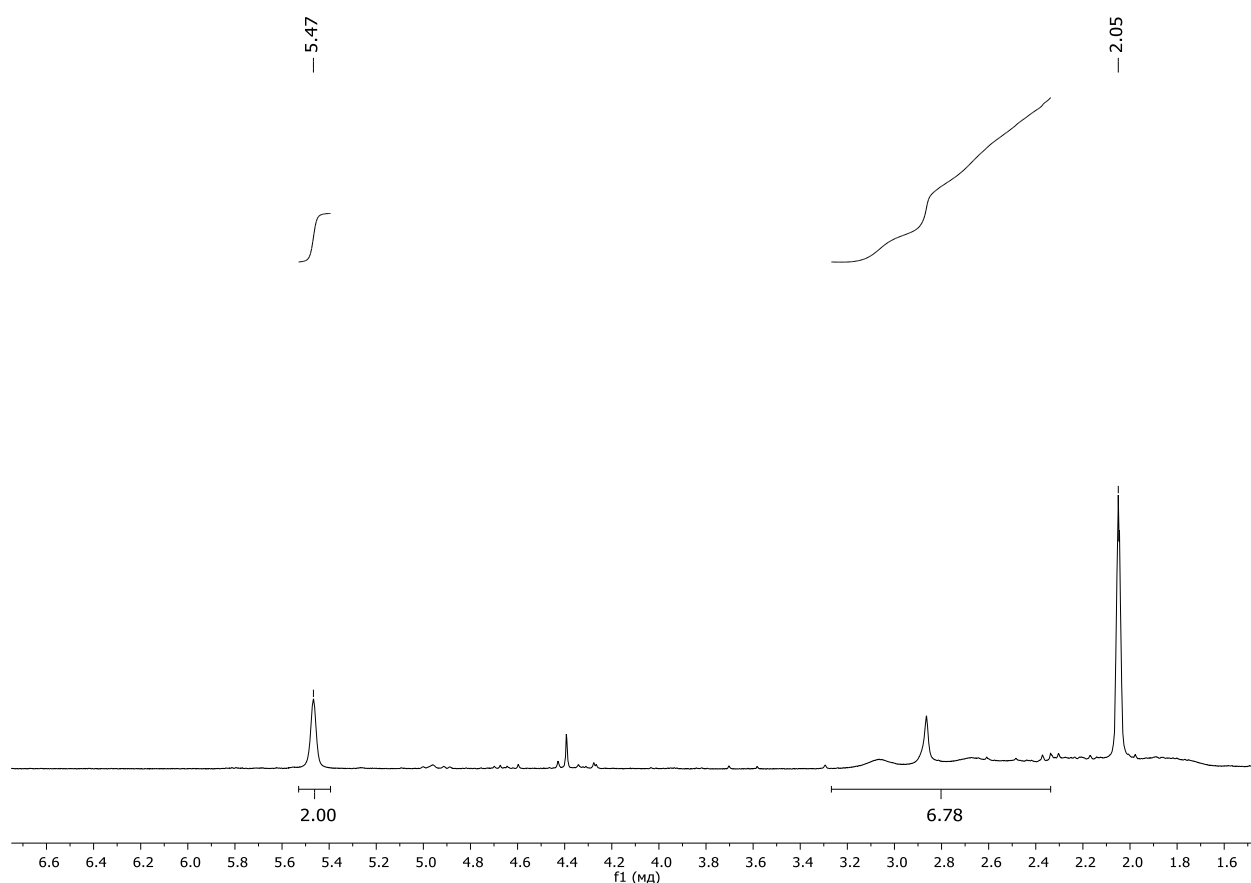




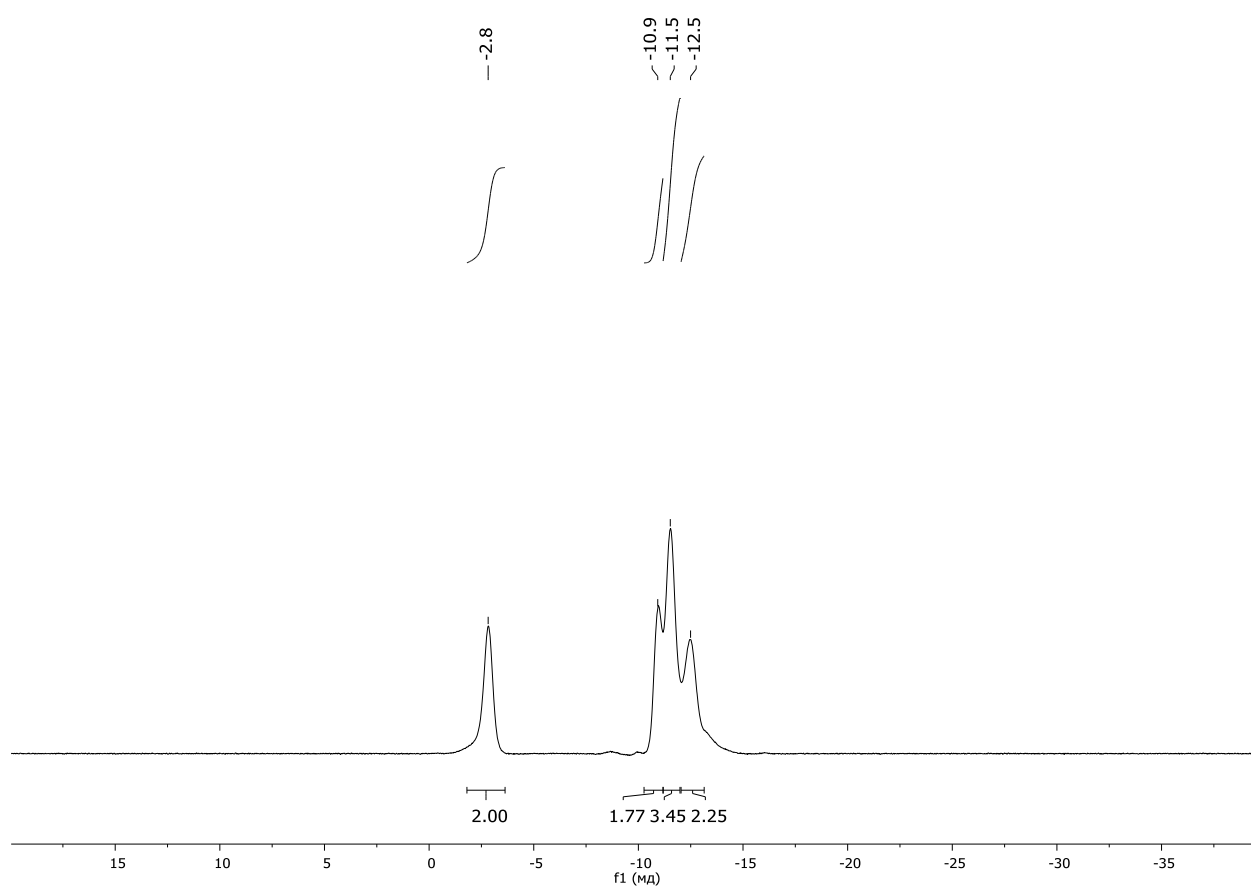
**Figure S31.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of 3,6- $\text{Br}_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**8**) in  $\text{CDCl}_3$ .



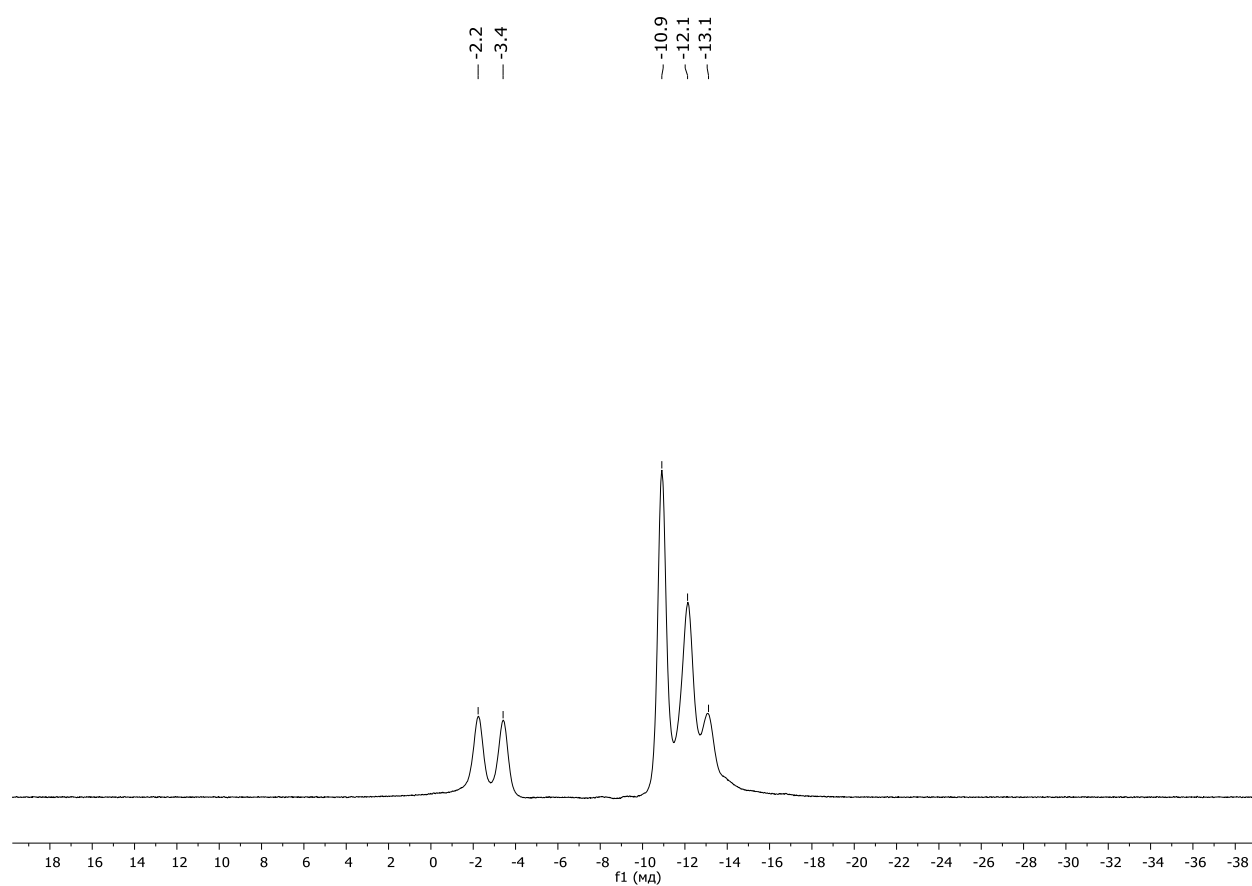
**Figure S32.**  $^{11}\text{B}$  NMR spectrum of 3,6- $\text{Br}_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**8**) in  $\text{CDCl}_3$ .



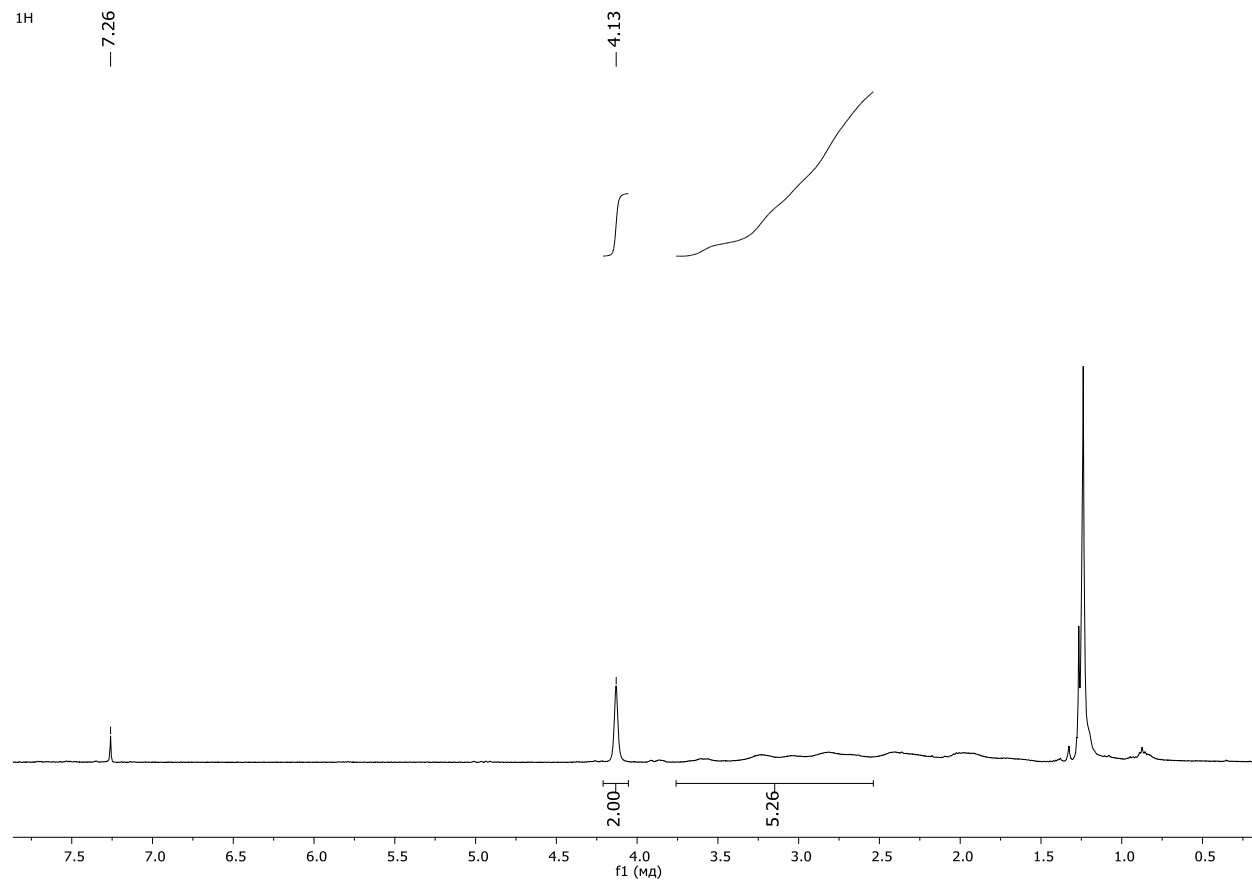
**Figure S33.** <sup>1</sup>H NMR spectrum of 3,6-Br<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**8**) in acetone-*d*<sub>6</sub>.



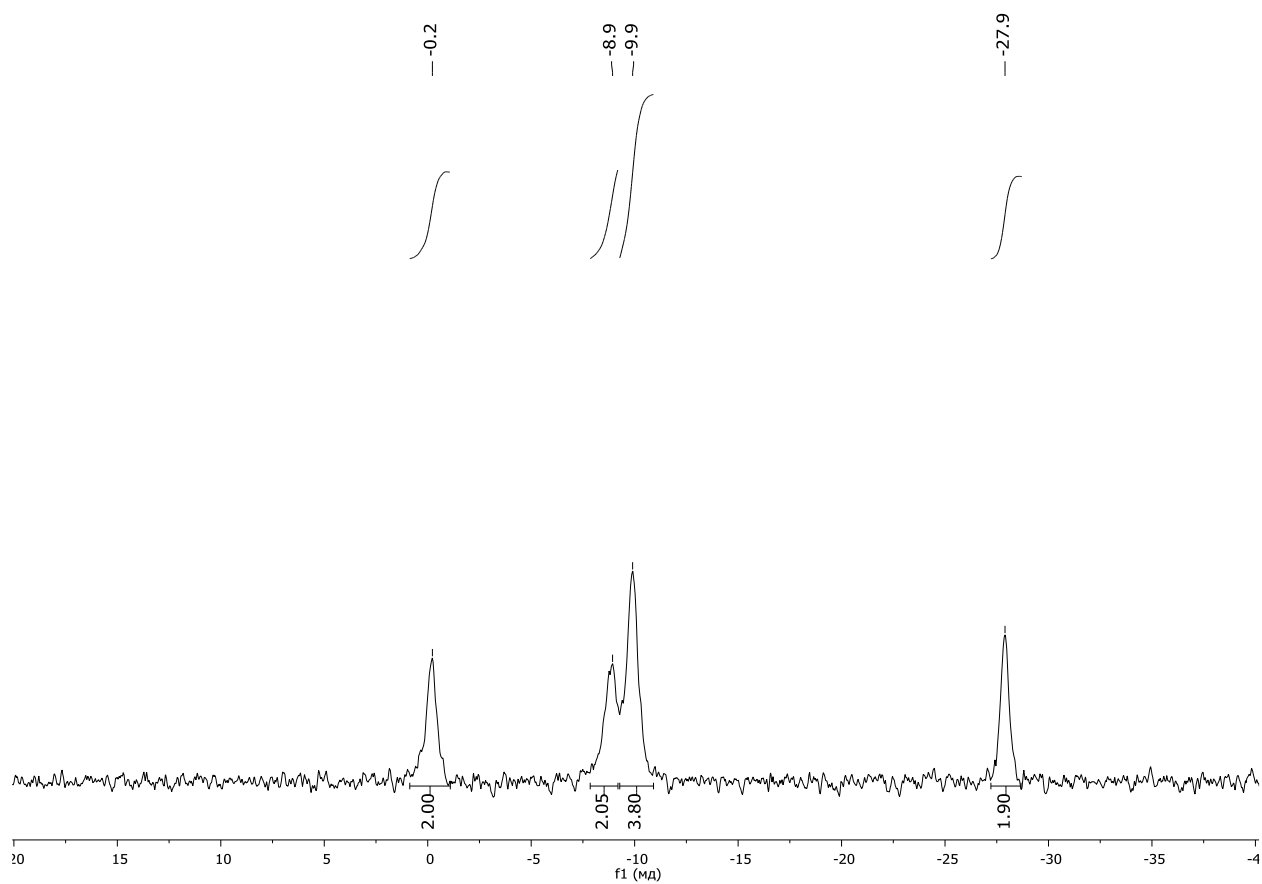
**Figure S34.** <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of 3,6-Br<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**8**) in acetone-*d*<sub>6</sub>.



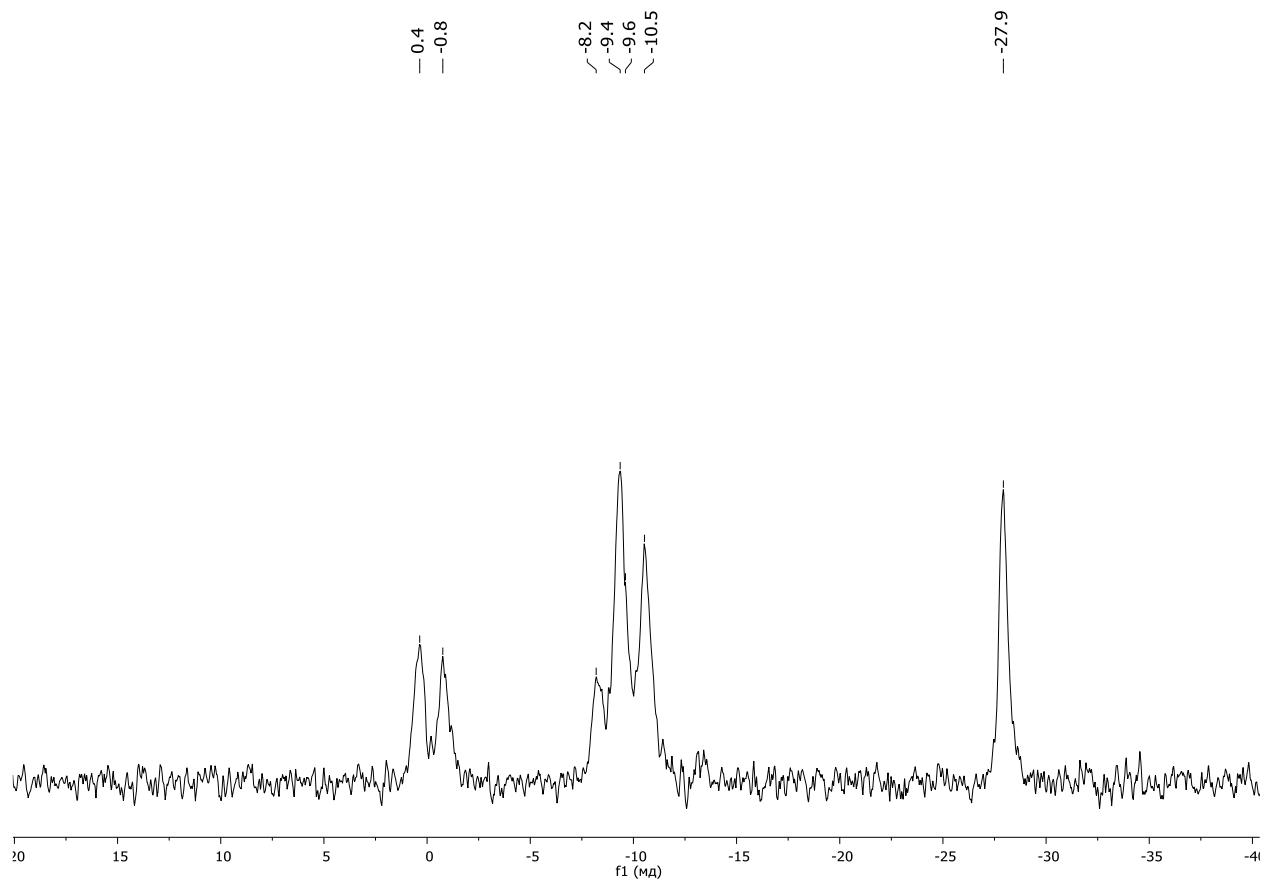
**Figure S35.**  $^{11}\text{B}$  NMR spectrum of 3,6-Br<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**8**) in acetone-*d*<sub>6</sub>.



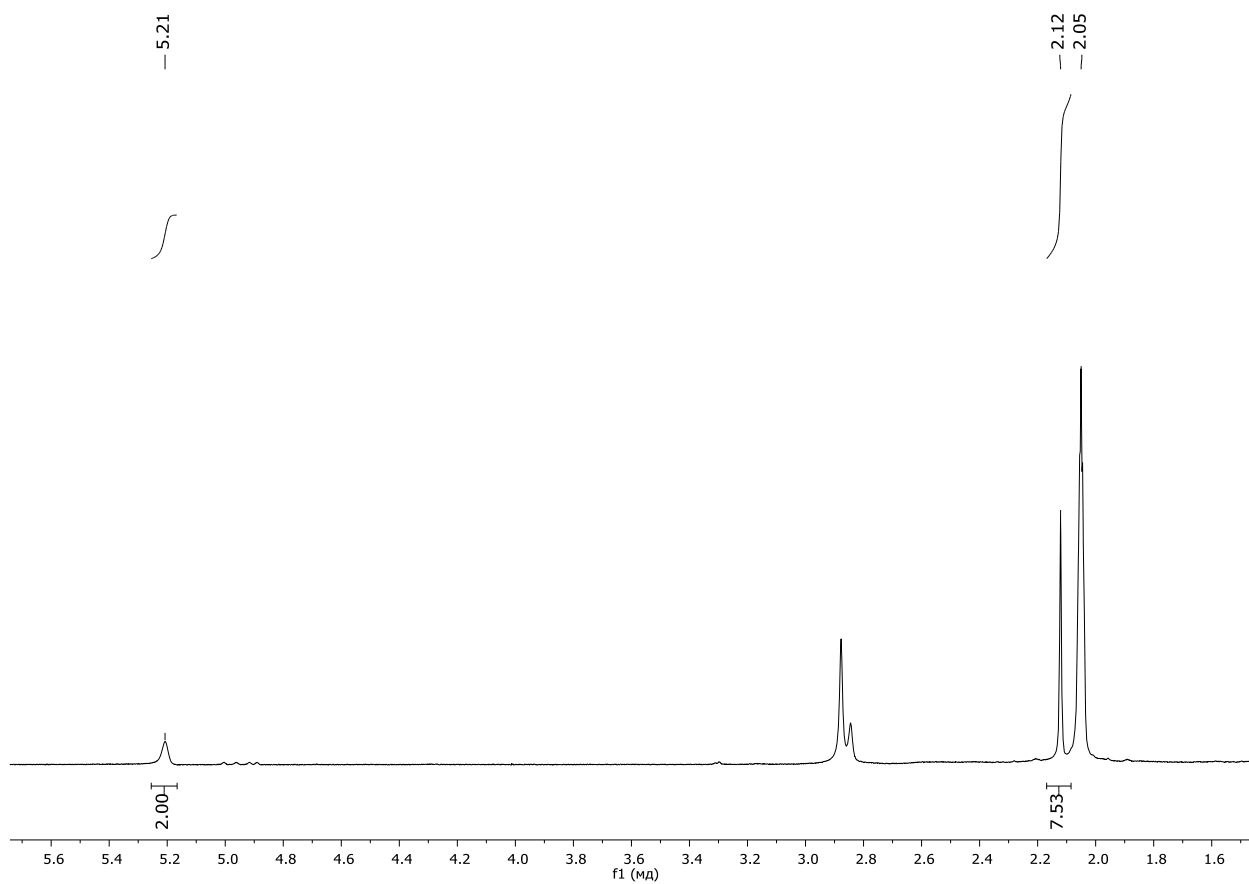
**Figure S36.**  $^1\text{H}$  NMR spectrum of 3,6-I<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**9**) in CDCl<sub>3</sub>.



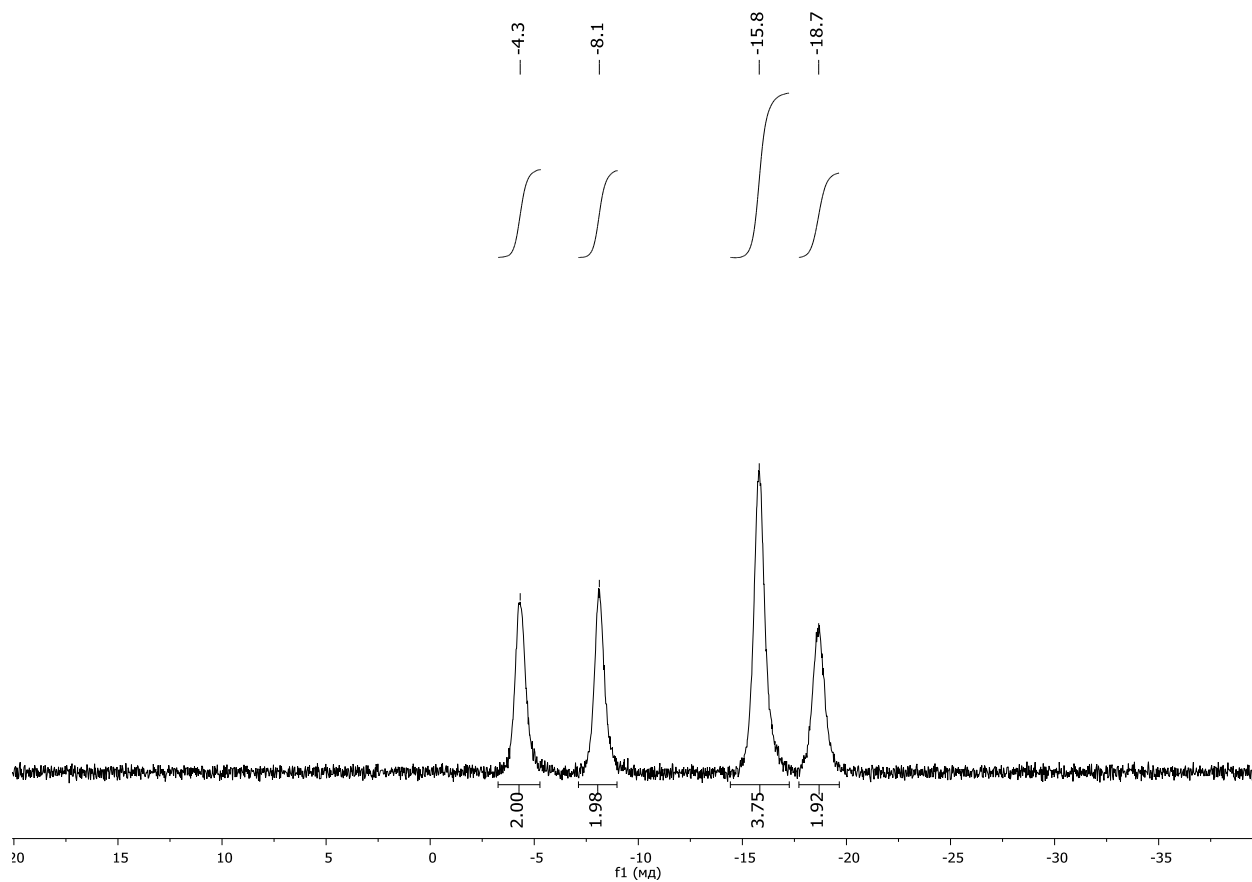
**Figure S37.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of 3,6- $\text{I}_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**9**) in  $\text{CDCl}_3$ .



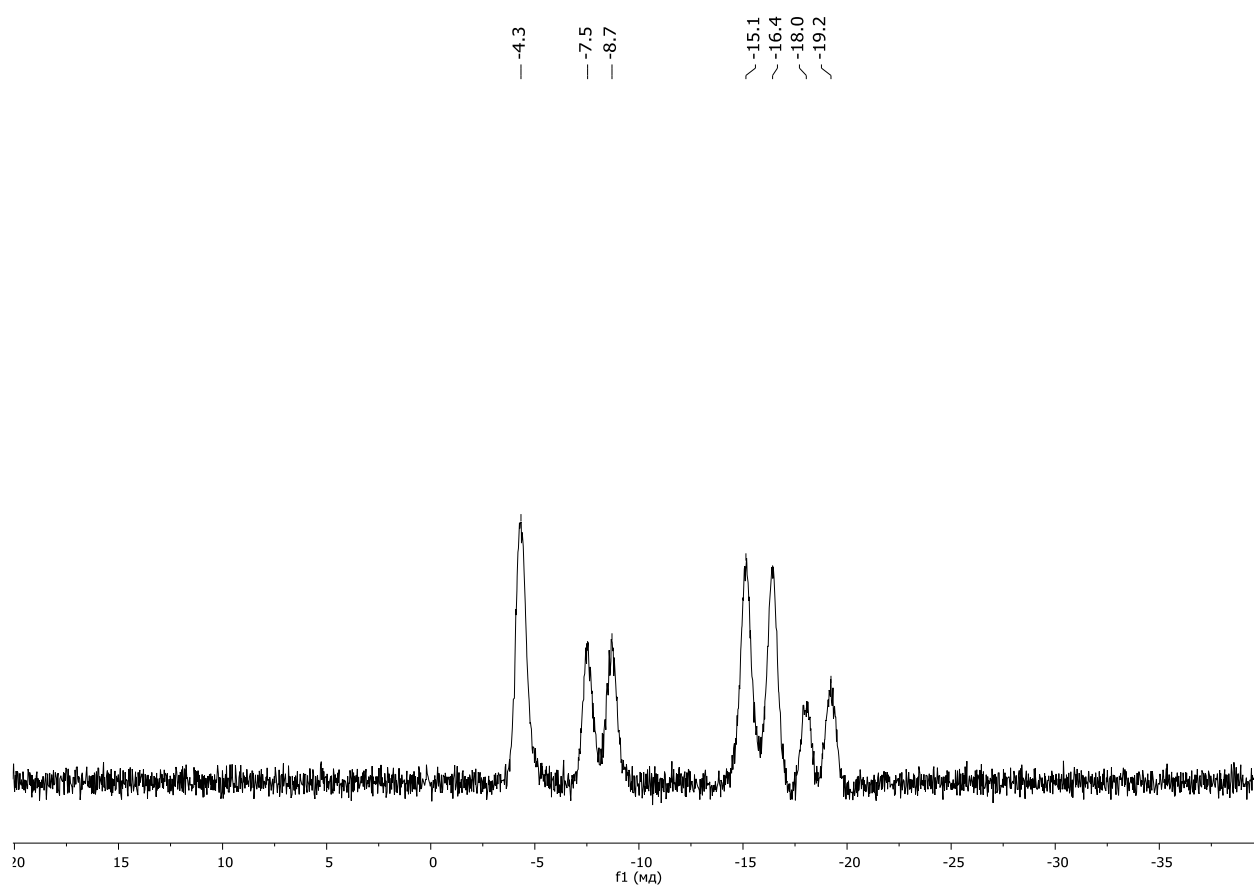
**Figure S38.**  $^{11}\text{B}$  NMR spectrum of 3,6- $\text{I}_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  (**9**) in  $\text{CDCl}_3$ .



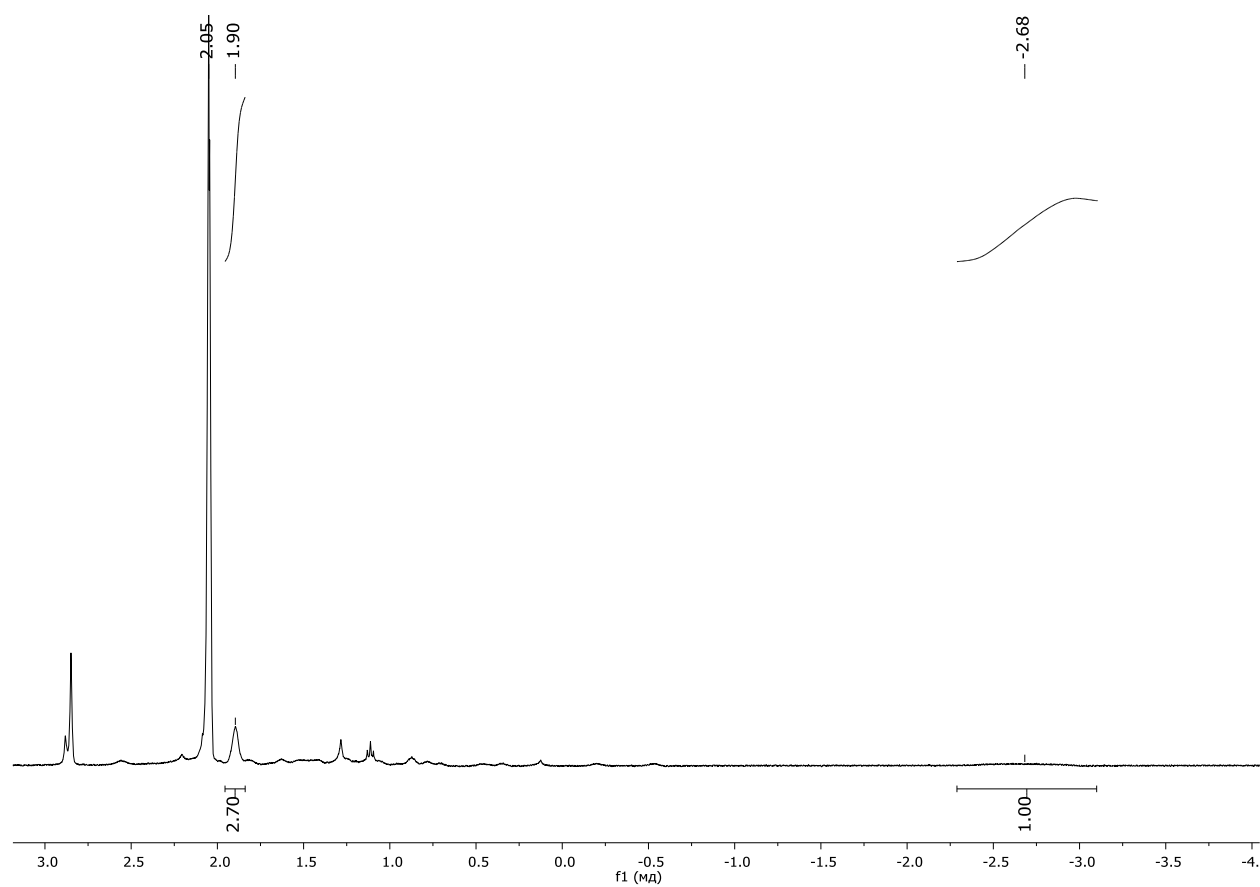
**Figure S39.**  $^1\text{H}$  NMR spectrum of 3,6-(AcO)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**10**) in acetone-*d*<sub>6</sub>.



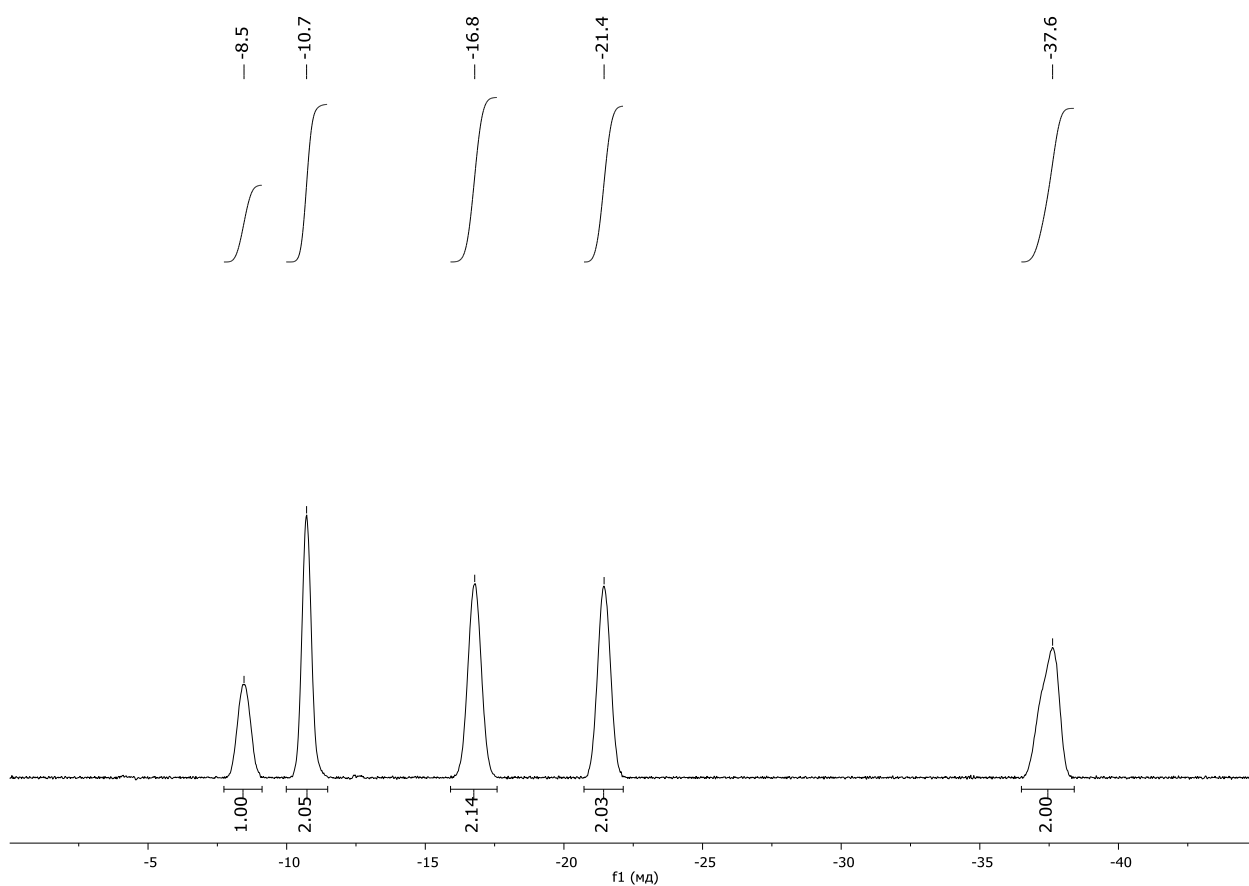
**Figure S40.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of 3,6-(AcO)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**10**) in acetone-*d*<sub>6</sub>.



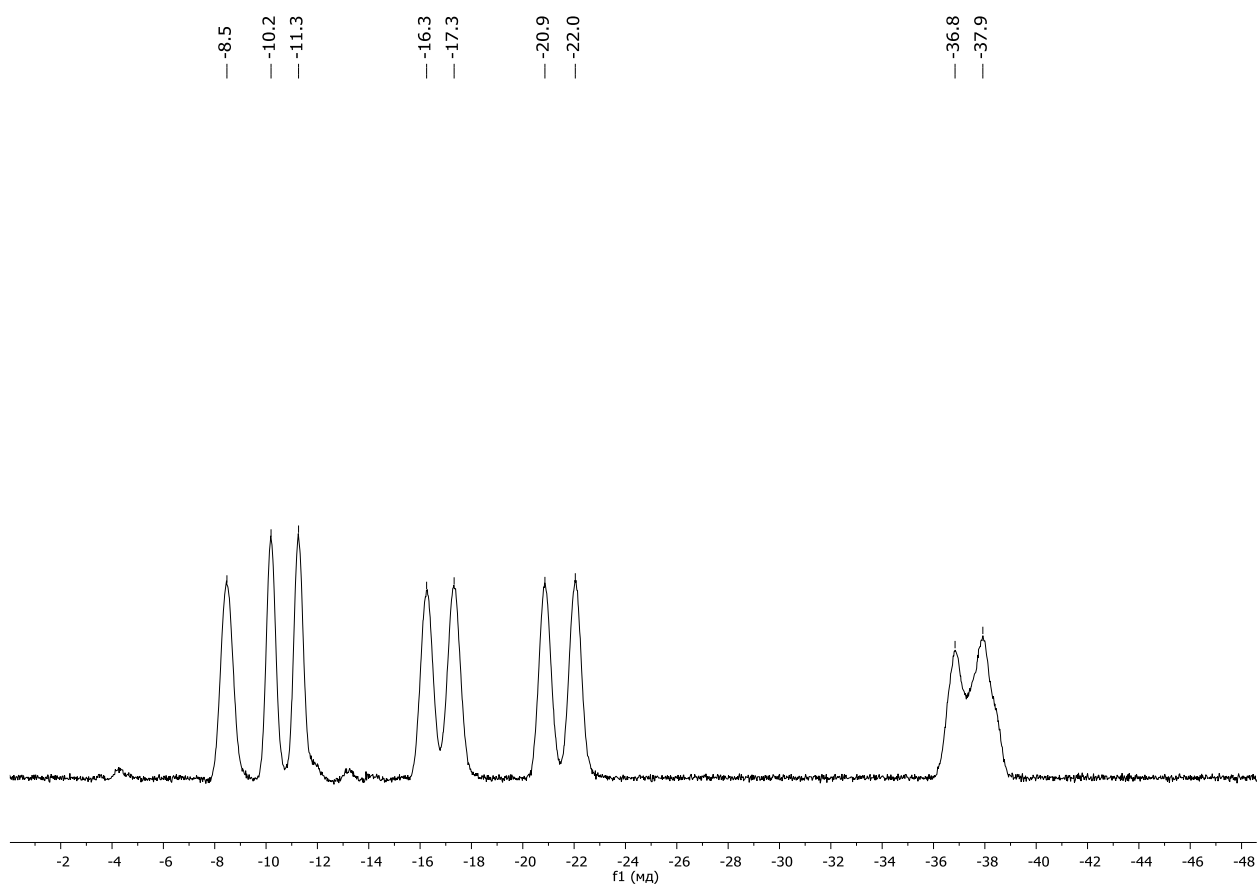
**Figure S41.**  $^{11}\text{B}$  NMR spectrum of 3,6-(AcO) $_2$ -1,2-C $_2\text{B}_{10}\text{H}_{10}$  (**10**) in acetone- $d_6$ .



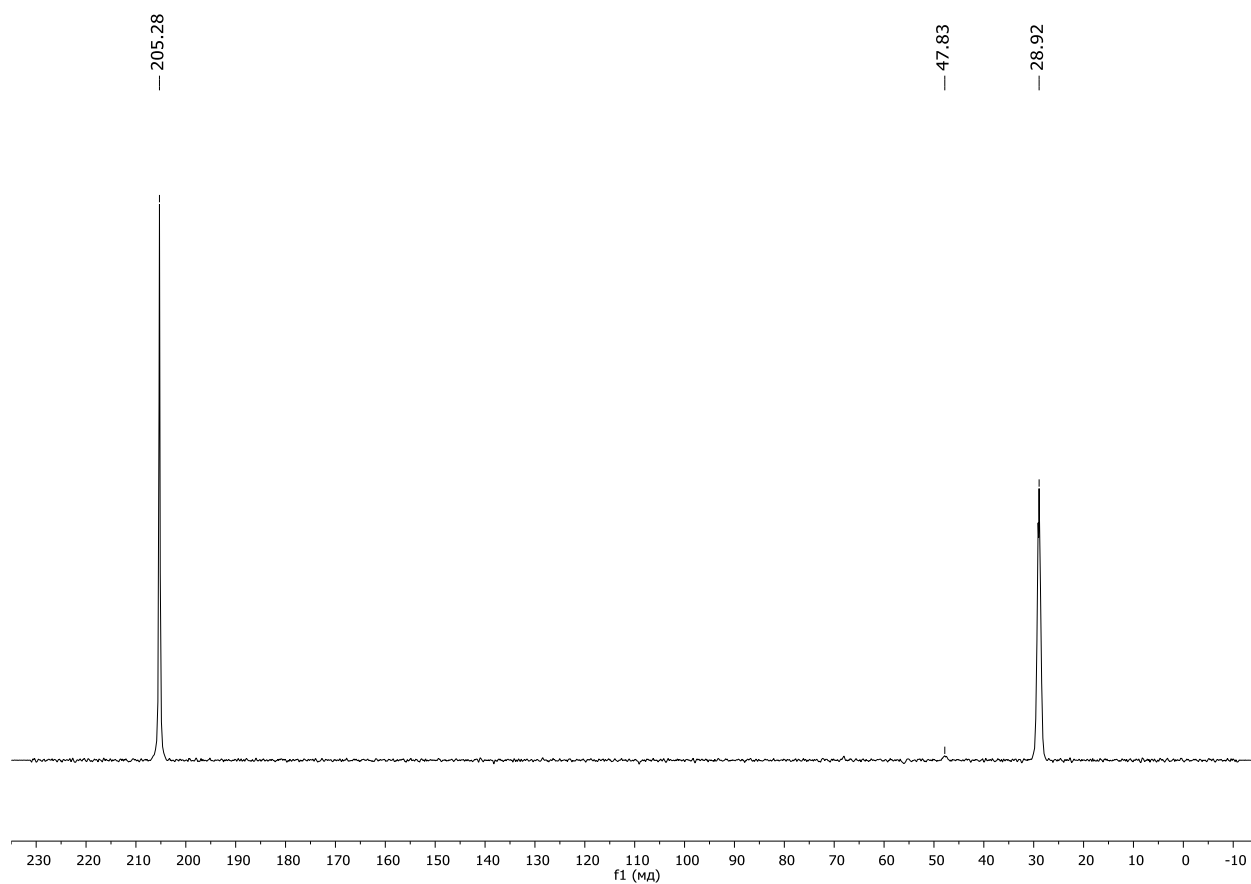
**Figure S42.**  $^1\text{H}$  NMR spectrum of Cs[3-Cl-7,8-C $_2\text{B}_9\text{H}_{11}$ ] (**11**) in acetone- $d_6$ .



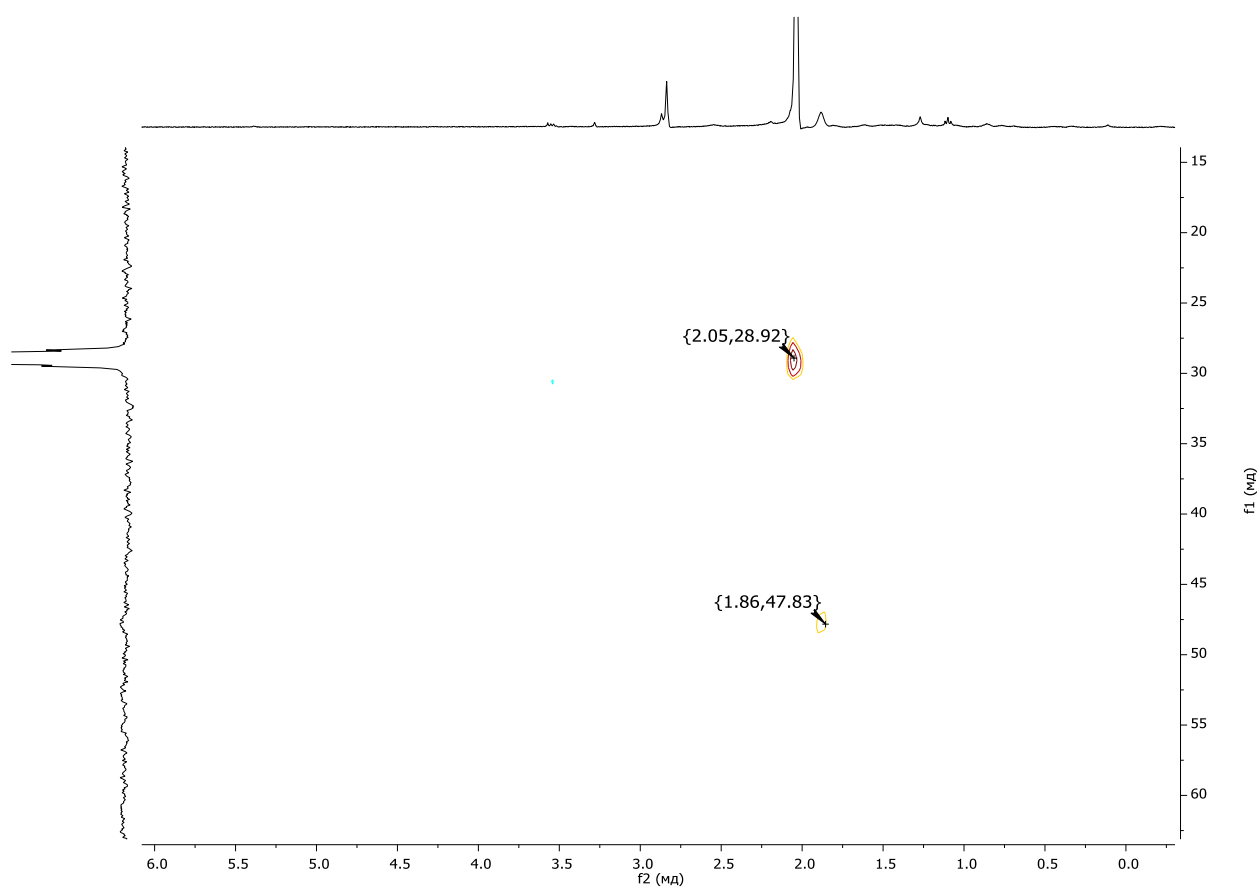
**Figure S43.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $\text{Cs}[3\text{-Cl-7,8-C}_2\text{B}_9\text{H}_{11}]$  (**11**) in acetone- $d_6$ .



**Figure S44.**  $^{11}\text{B}$  NMR spectrum of  $[3\text{-Cl-7,8-C}_2\text{B}_9\text{H}_{11}]$  (**11**) in acetone- $d_6$ .

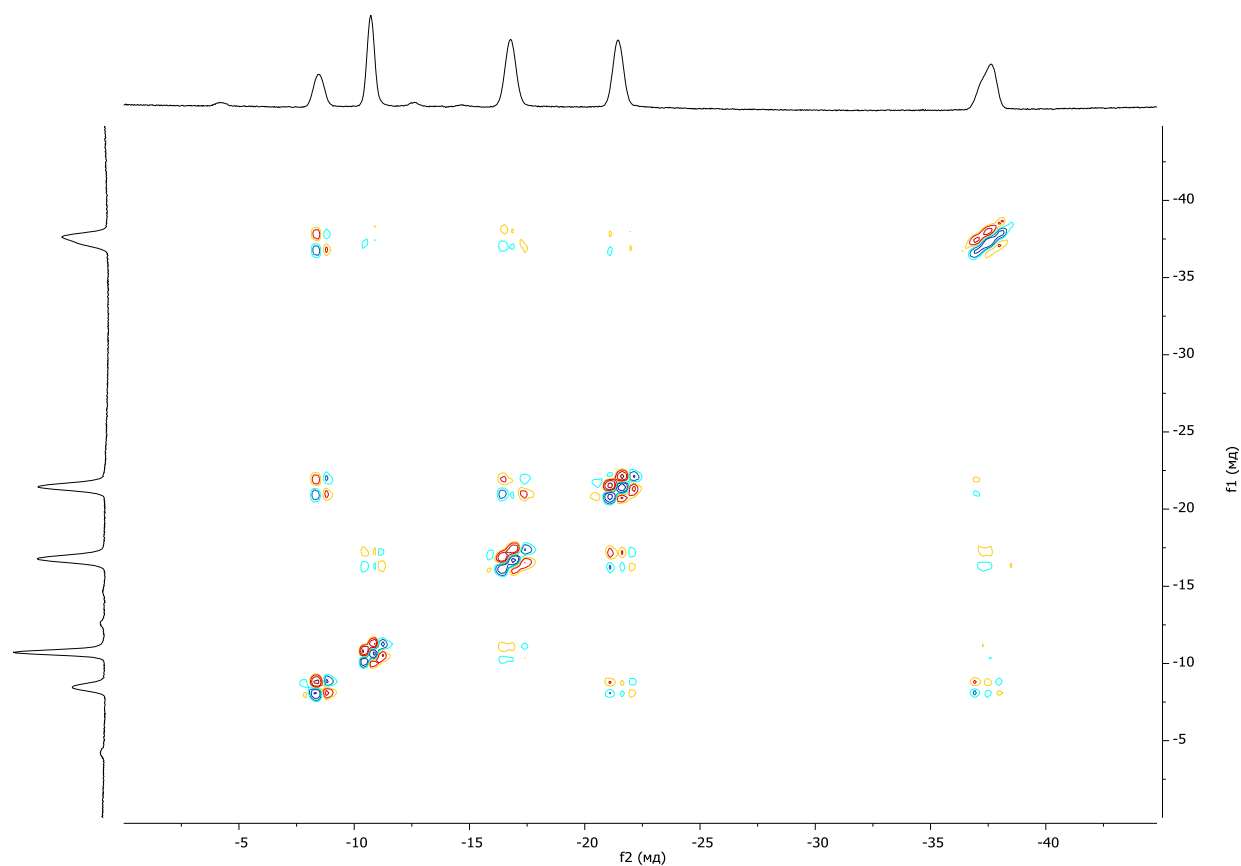


**Figure S45.**  $^{13}\text{C}$  NMR spectrum of  $\text{Cs}[3\text{-Cl-7,8-C}_2\text{B}_9\text{H}_{11}]$  (**11**) in  $\text{acetone-}d_6$ .

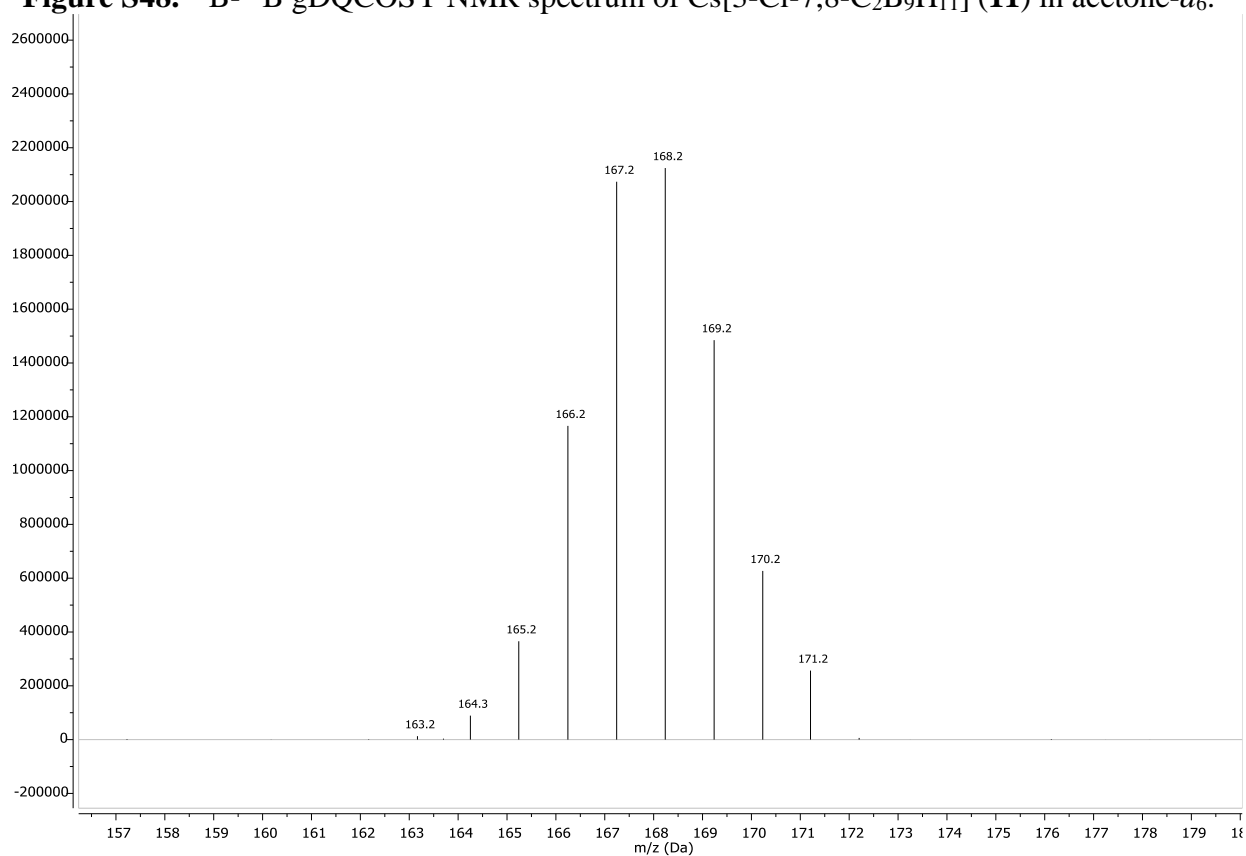


**Figure S46.**  $^1\text{H}$ - $^{13}\text{C}$  HMQC NMR spectrum of  $\text{Cs}[3\text{-Cl-7,8-C}_2\text{B}_9\text{H}_{11}]$  (**11**) in  $\text{acetone-}d_6$ .





**Figure S48.**  $^{11}\text{B}$ - $^{11}\text{B}$  gDQCOSY NMR spectrum of  $\text{Cs}[3\text{-Cl-7,8-C}_2\text{B}_9\text{H}_{11}]$  (**11**) in acetone- $d_6$ .



**Figure S48.** Mass-spectrum (DUIS) of  $\text{Cs}[3\text{-Cl-7,8-C}_2\text{B}_9\text{H}_{11}]$  (**11**).