

# SUPPORTING INFORMATION

## Synthesis, Crystal Structure, and Some Transformations of 9,12-Dichloro-*ortho*-carborane

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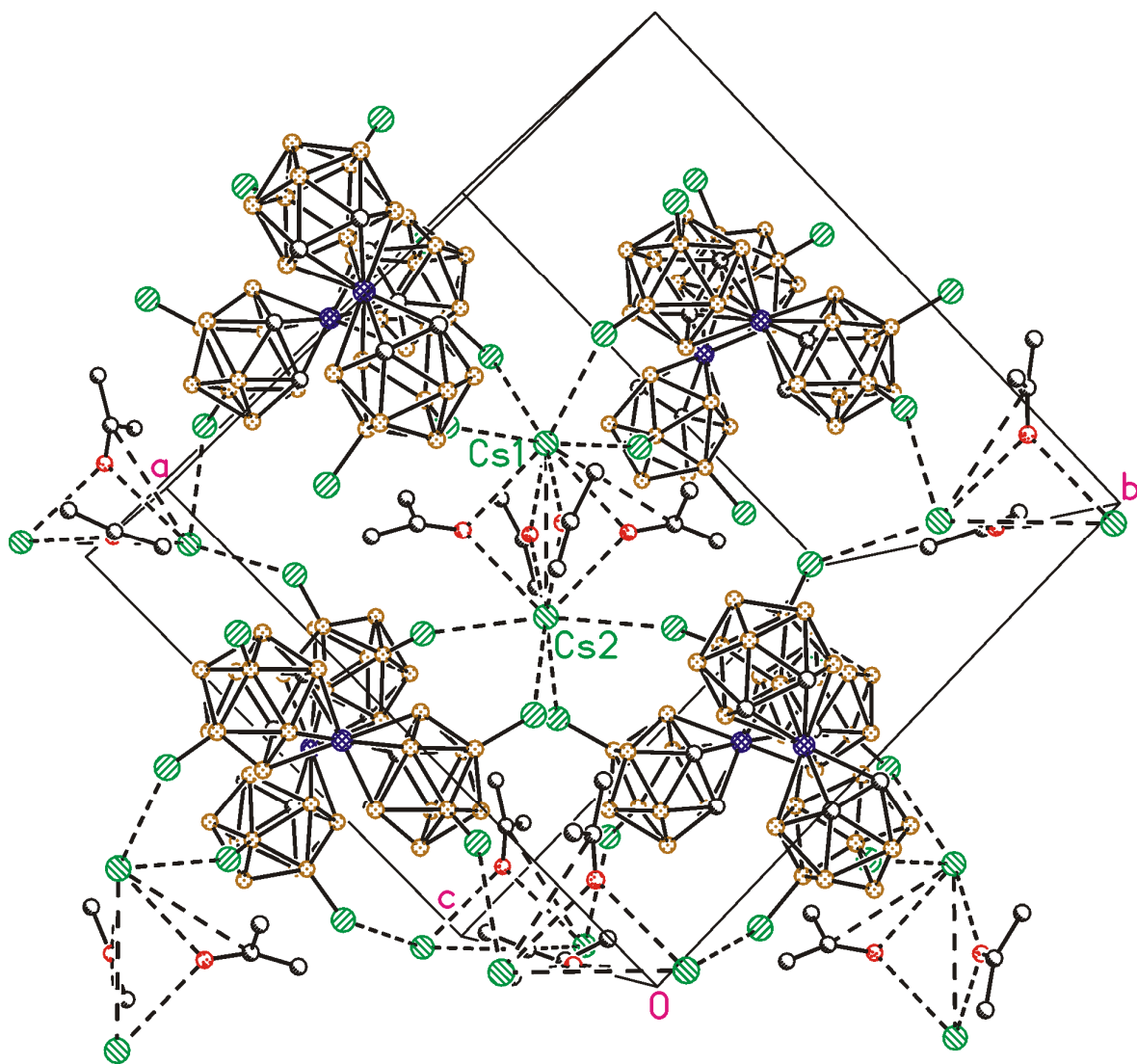
\* Correspondence: sivaev@ineos.ac.ru

Crystallographic data for compounds <b>2</b> , <b>3</b> , and <b>5'</b>	<b>2</b>
Crystal packing of compound <b>5'</b>	<b>3</b>
NMR spectra of compound <b>1</b>	<b>4</b>
Mass spectrum of compound <b>1</b>	<b>10</b>
NMR spectra of compound <b>2</b>	<b>11</b>
Mass spectrum of compound <b>2</b>	<b>17</b>
NMR spectra of compound <b>3</b>	<b>18</b>
Mass spectrum of compound <b>3</b>	<b>24</b>
NMR spectra of compound <b>4</b>	<b>25</b>
Mass spectrum of compound <b>4</b>	<b>31</b>
NMR spectra of compound <b>5</b>	<b>32</b>
Mass spectrum of compound <b>5</b>	<b>38</b>
NMR spectra of compound <b>6</b>	<b>39</b>
Mass spectrum of compound <b>6</b>	<b>45</b>

Table S1. Crystallographic data for compounds **2**, **3**, and **5'**.

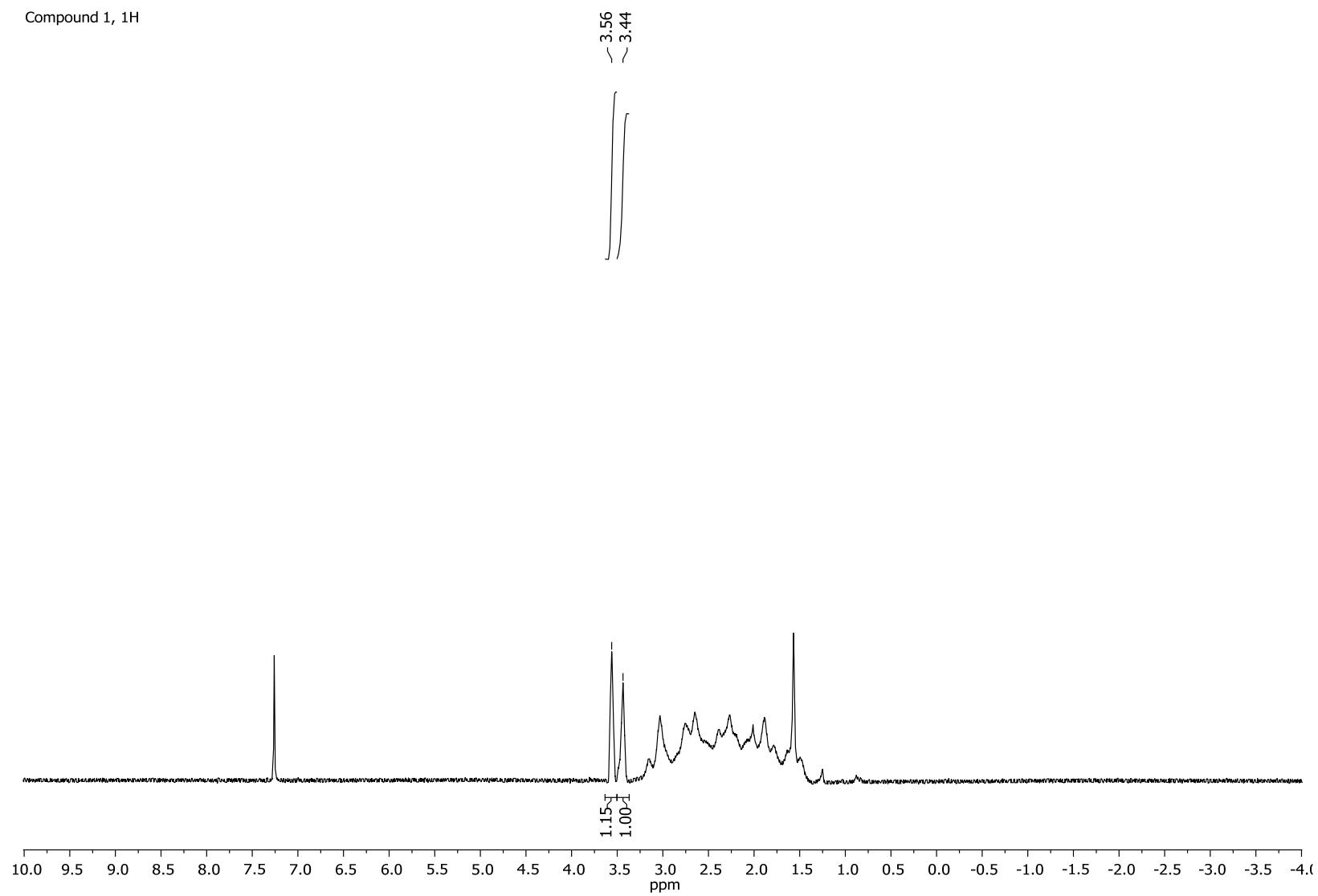
	<b>Compound 2</b>	<b>Compound 3</b>	<b>Compound 5'</b>
formula	C <sub>2</sub> H <sub>10</sub> B <sub>10</sub> Cl <sub>2</sub>	C <sub>2</sub> H <sub>9</sub> B <sub>10</sub> Cl <sub>3</sub>	C <sub>4</sub> H <sub>18</sub> B <sub>18</sub> Cl <sub>4</sub> Co <sup>-</sup> Cs <sup>+</sup> 2(C <sub>3</sub> H <sub>6</sub> O)
fw	213.10	247.54	710.56
crystal system	Orthorhombic	Monoclinic	Tetragonal
space group	<i>Pna</i> 2 <sub>1</sub>	<i>Cc</i>	<i>P4</i> <sub>1</sub> 2 <sub>1</sub> 2
<i>a</i> , Å	12.6461(7)	12.5845(9)	15.1995(3)
<i>b</i> , Å	7.1946(4)	7.0519(5)	15.1995(3)
<i>c</i> , Å	11.4596(7)	13.8263(10)	24.6019(7)
$\beta$ , deg.	90	113.098(3)	90
<i>V</i> , Å <sup>3</sup>	1042.64(10)	1128.65(14)	5683.6(3)
<i>Z</i>	4	4	8
$\rho_{\text{calc}}$ , g·cm <sup>-3</sup>	1.358	1.457	1.661
<i>F</i> (000)	424	488	2768
$\mu$ , mm <sup>-1</sup>	0.557	0.754	2.255
$\theta$ range, deg.	3.22 – 28.84	3.20 – 26.03	1.90 – 26.78
reflections collected	11782	5298	74784
independent reflections / <i>R</i> <sub>int</sub>	2715/0.0282	2197/0.0246	6074/0.0376
Completeness to theta $\theta$ , %	100	100	99.7
refined parameters	167	178	330
<i>GOF</i> ( <i>F</i> <sup>2</sup> )	1.103	1.124	1.051
reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	2548	2116	5678
<i>R</i> <sub>1</sub> ( <i>F</i> ) ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>a</sup>	0.0220	0.0296	0.0311
<i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ) (all data) <sup>b</sup>	0.0562	0.0700	0.0772
Largest diff. peak/hole, e·Å <sup>-3</sup>	0.145/-0.256	0.266/-0.269	1.290/-0.847

<sup>a</sup>  $R_1 = \sum |F_o - |F_c|| / \sum (F_o)$ ; <sup>b</sup>  $wR_2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2])^{1/2}$



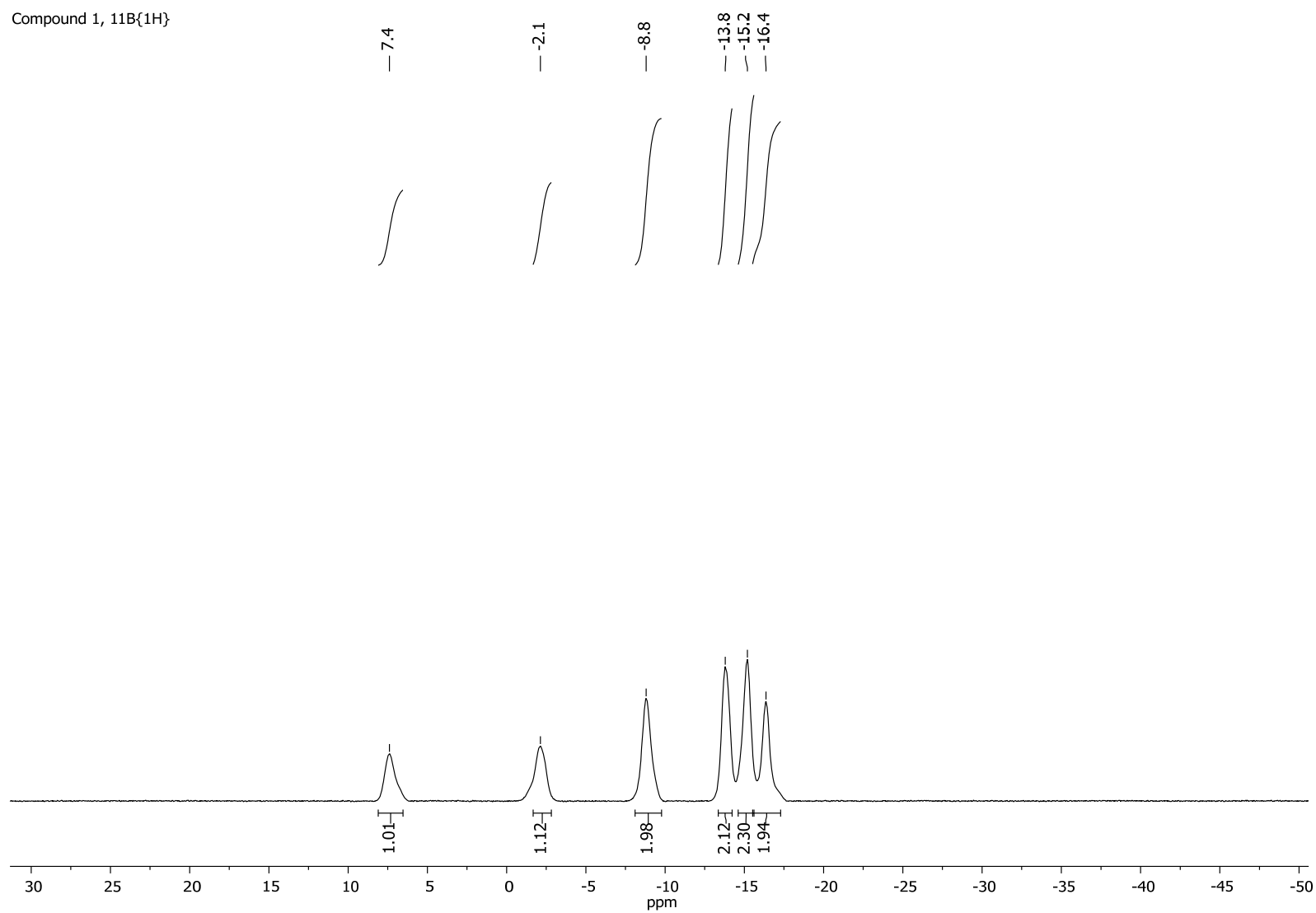
**Figure S1.** Crystal packing of  $\text{Cs}[9,9',12,12'\text{-Cl}_4\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]\cdot 2\text{Me}_2\text{CO}$  (5').

Compound 1, 1H



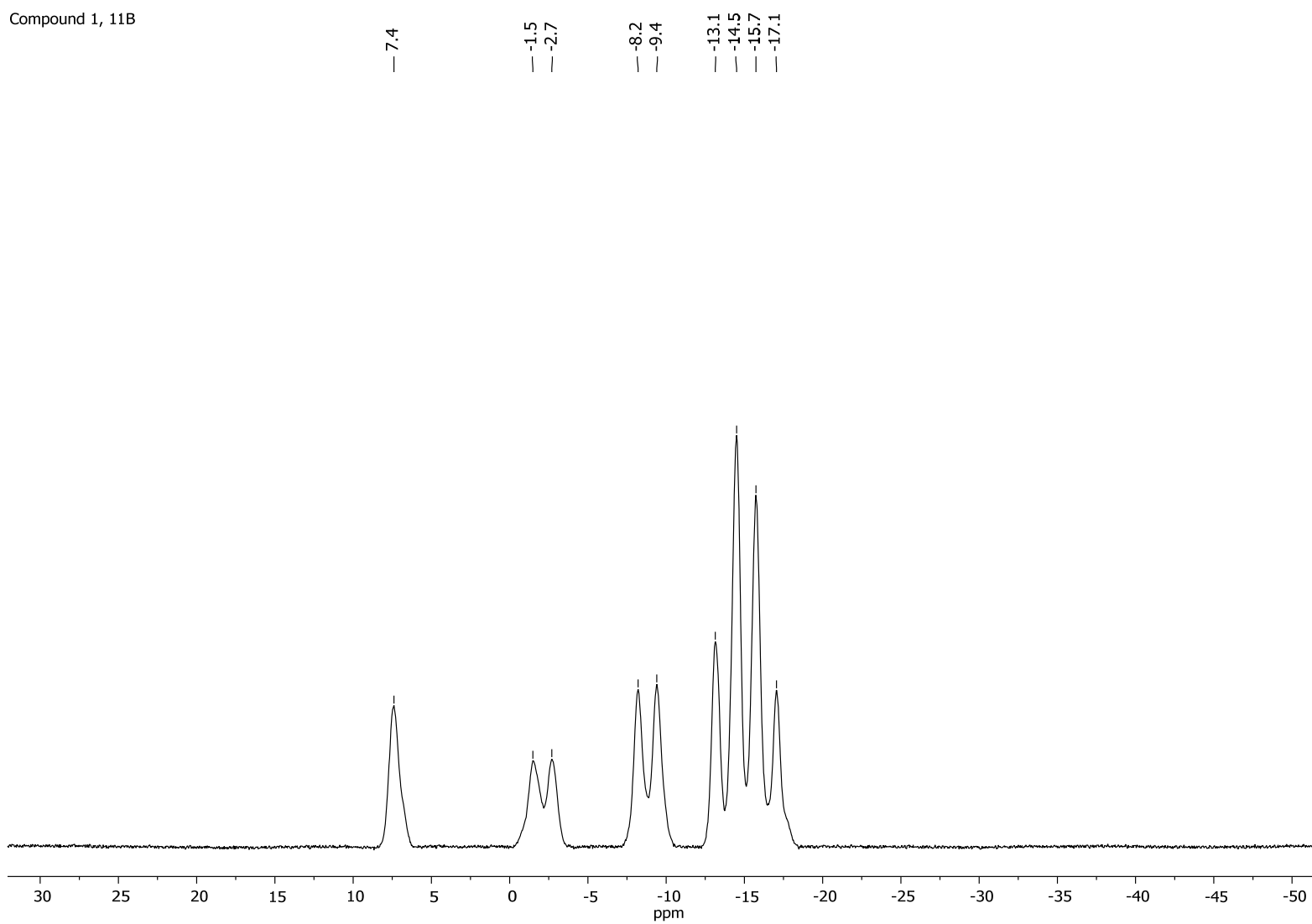
**Figure S1.**  $^1\text{H}$  NMR spectrum of 9-Cl-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  in  $\text{CDCl}_3$ .

Compound 1,  $^{11}\text{B}\{^1\text{H}\}$



**Figure S2.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of 9-Cl-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  in  $\text{CDCl}_3$ .

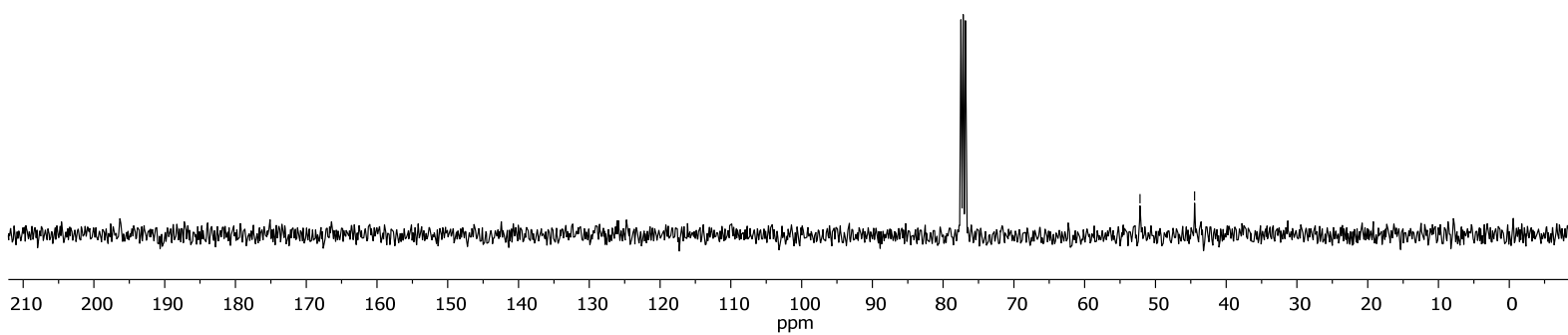
Compound 1, 11B



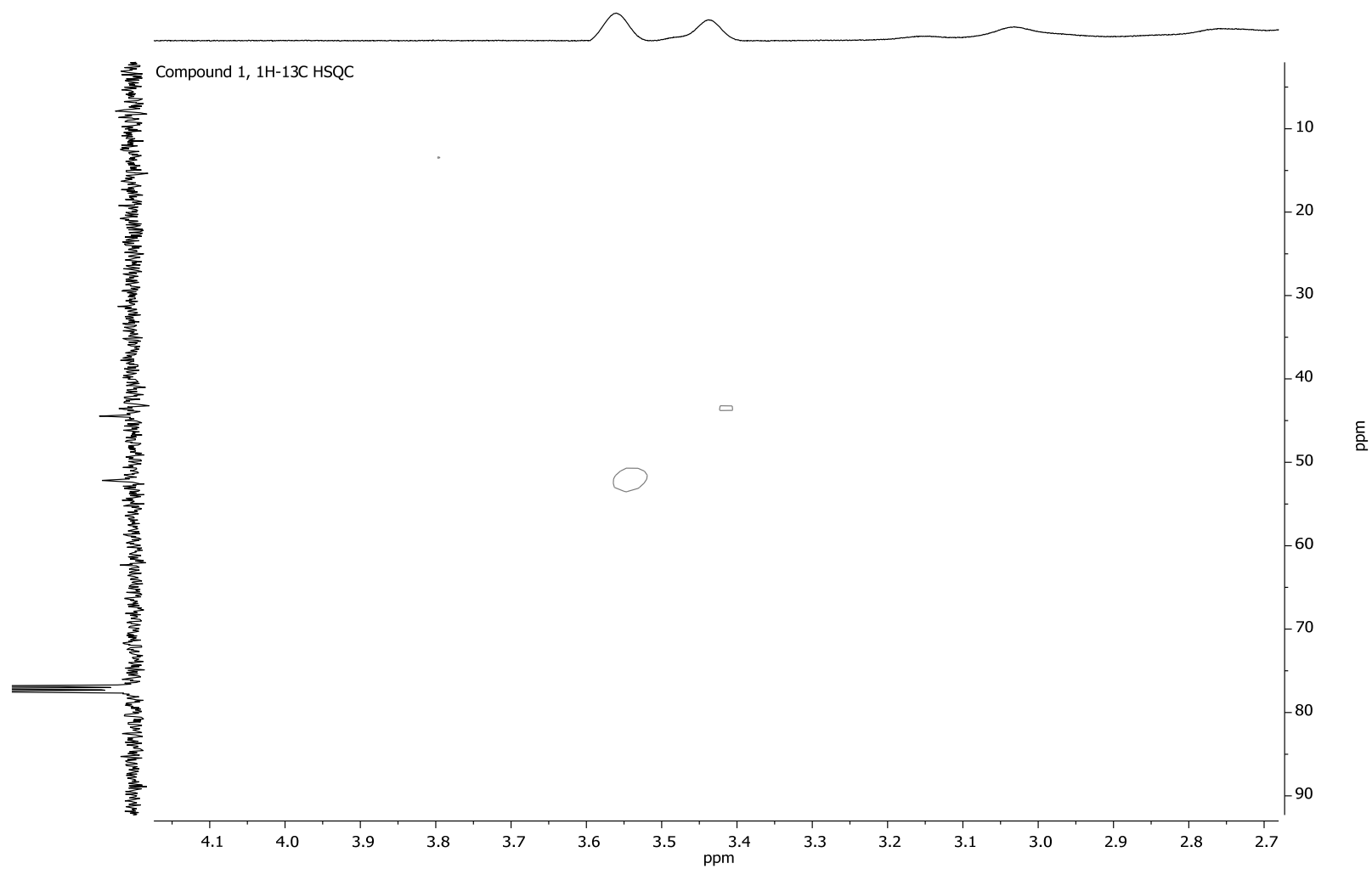
**Figure S3.**  $^{11}\text{B}$  NMR spectrum of 9-Cl-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  in  $\text{CDCl}_3$ .

Compound 1,  $^{13}\text{C}\{^1\text{H}\}$

— 52.2  
— 44.5

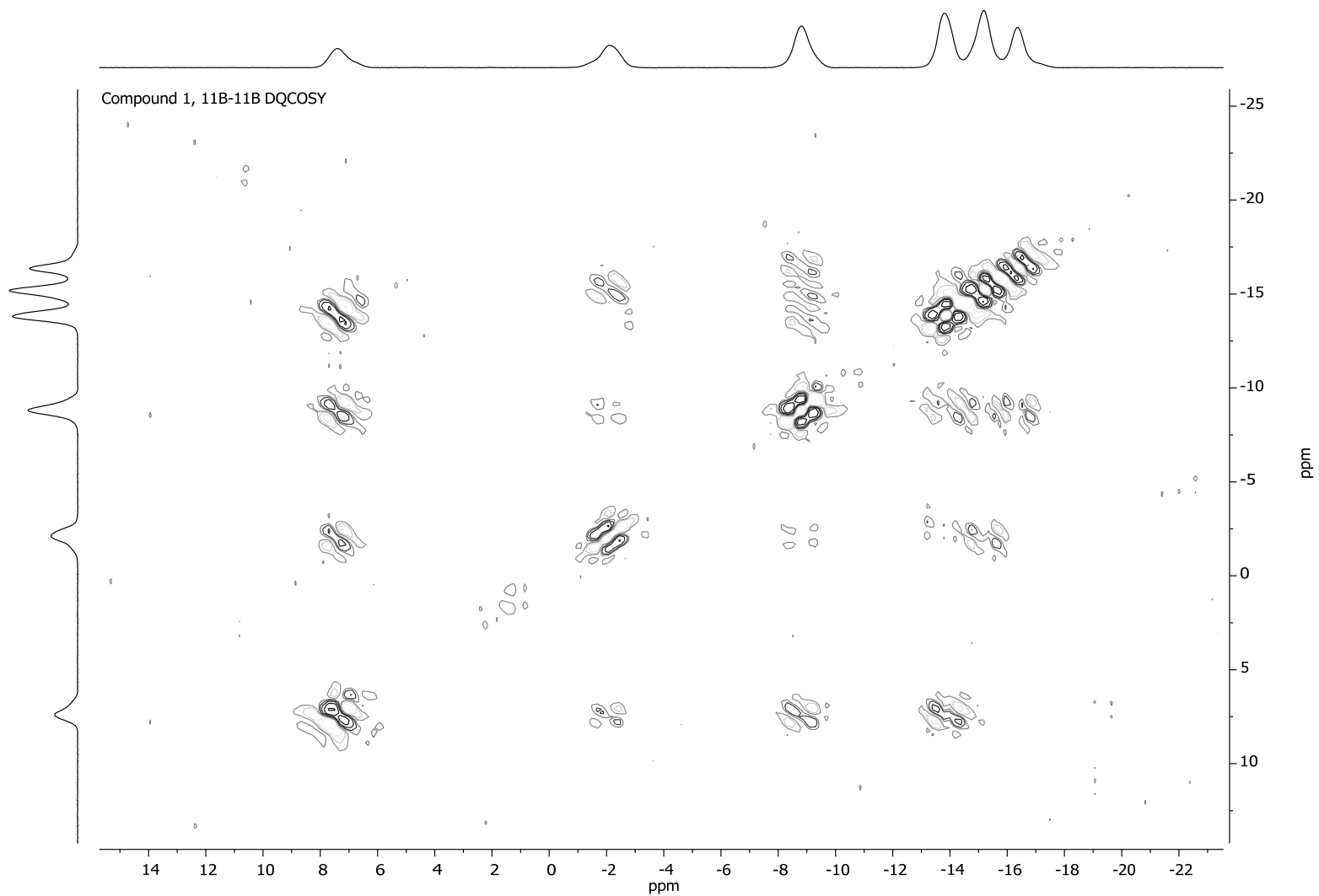


**Figure S4.**  $^{13}\text{C}$  NMR spectrum of 9-Cl-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  in  $\text{CDCl}_3$ .



**Figure S5.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of 9-Cl-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  in  $\text{CDCl}_3$ .





**Figure S6.**  $^{11}\text{B}$ - $^{11}\text{B}$  DQCOSY NMR spectrum of 9-Cl-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$  in  $\text{CDCl}_3$ .

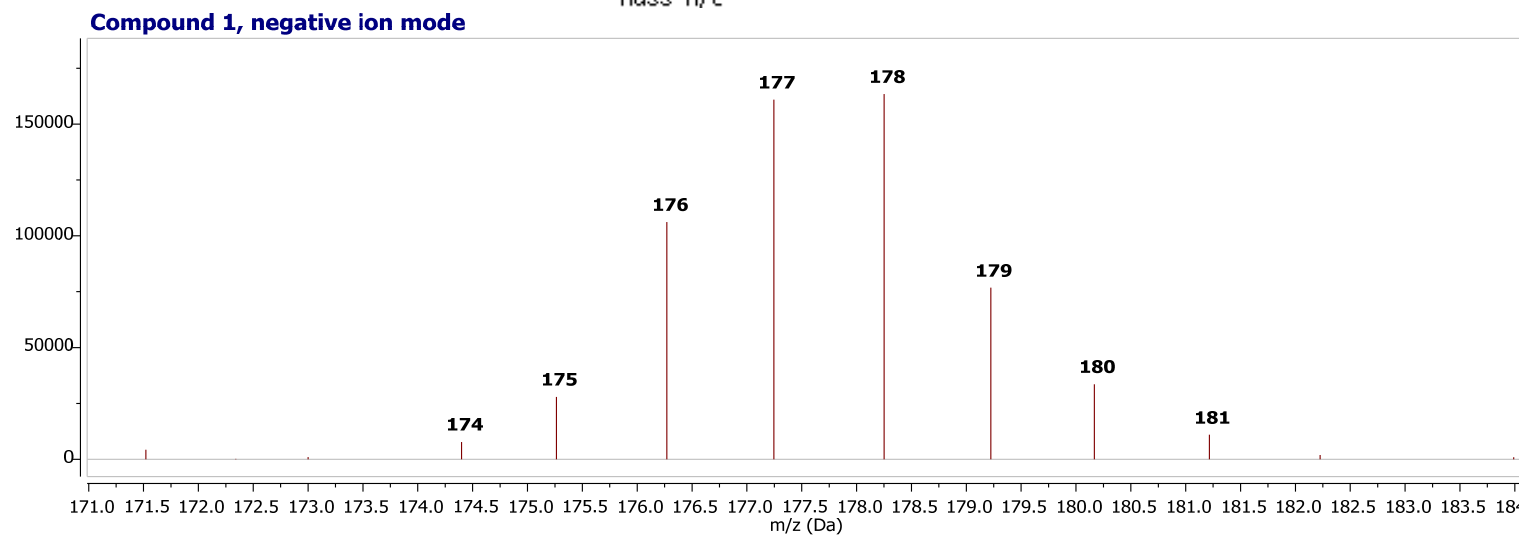
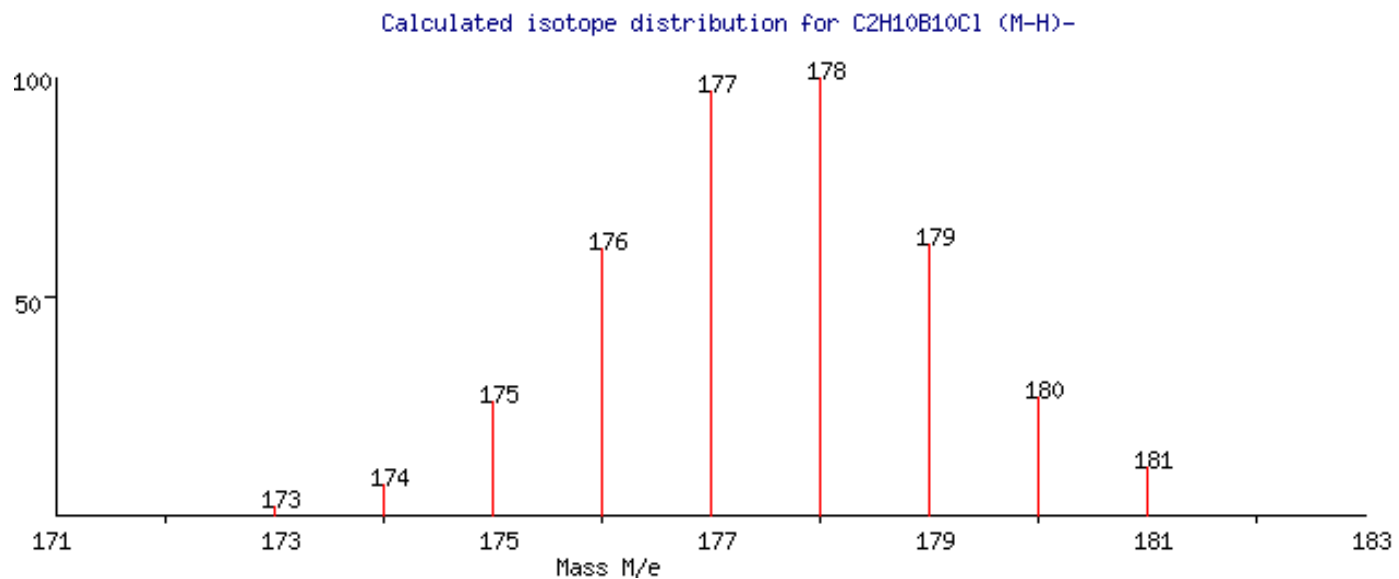
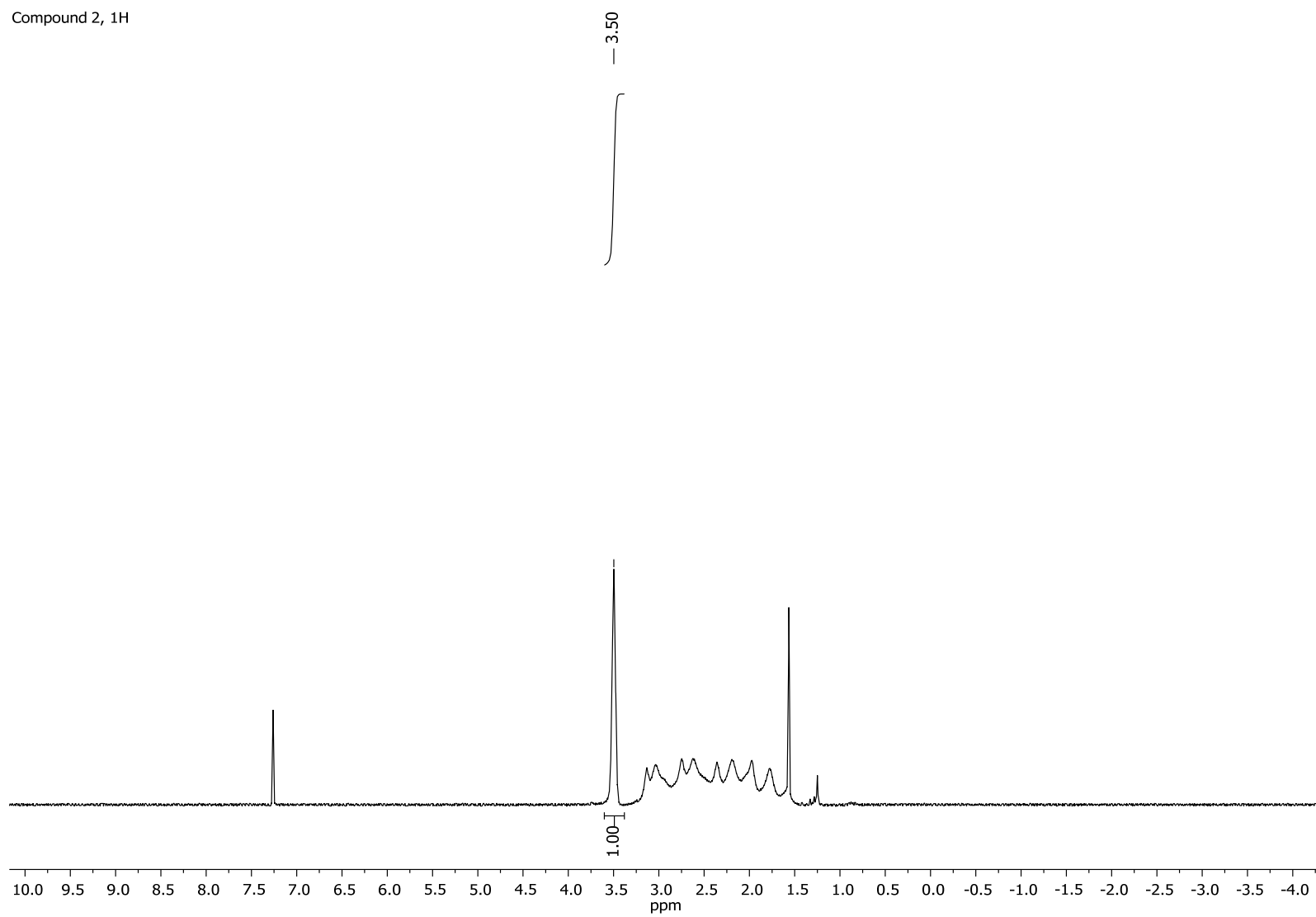


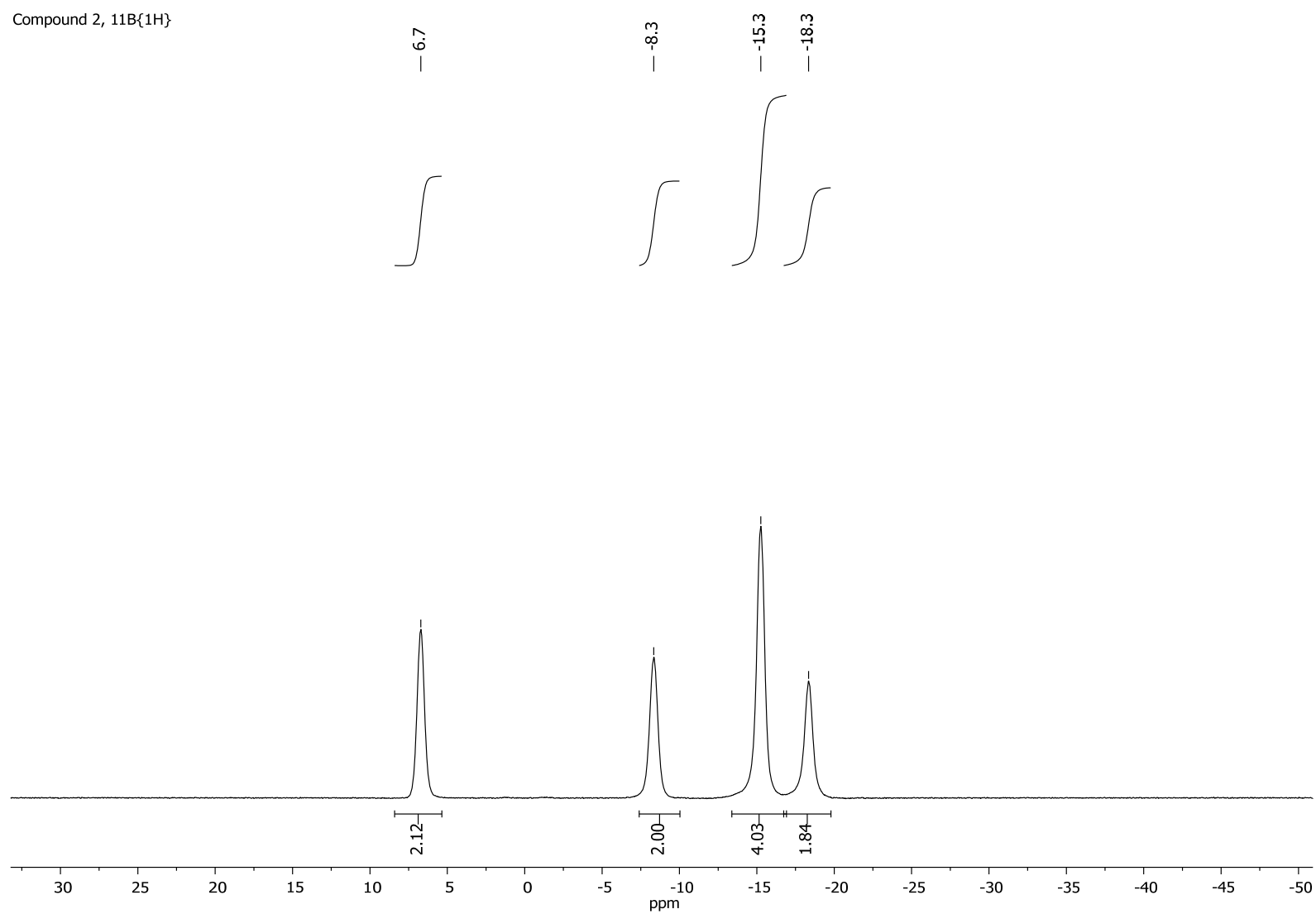
Figure S7. Mass-spectrum of 9-Cl-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>.

Compound 2, 1H



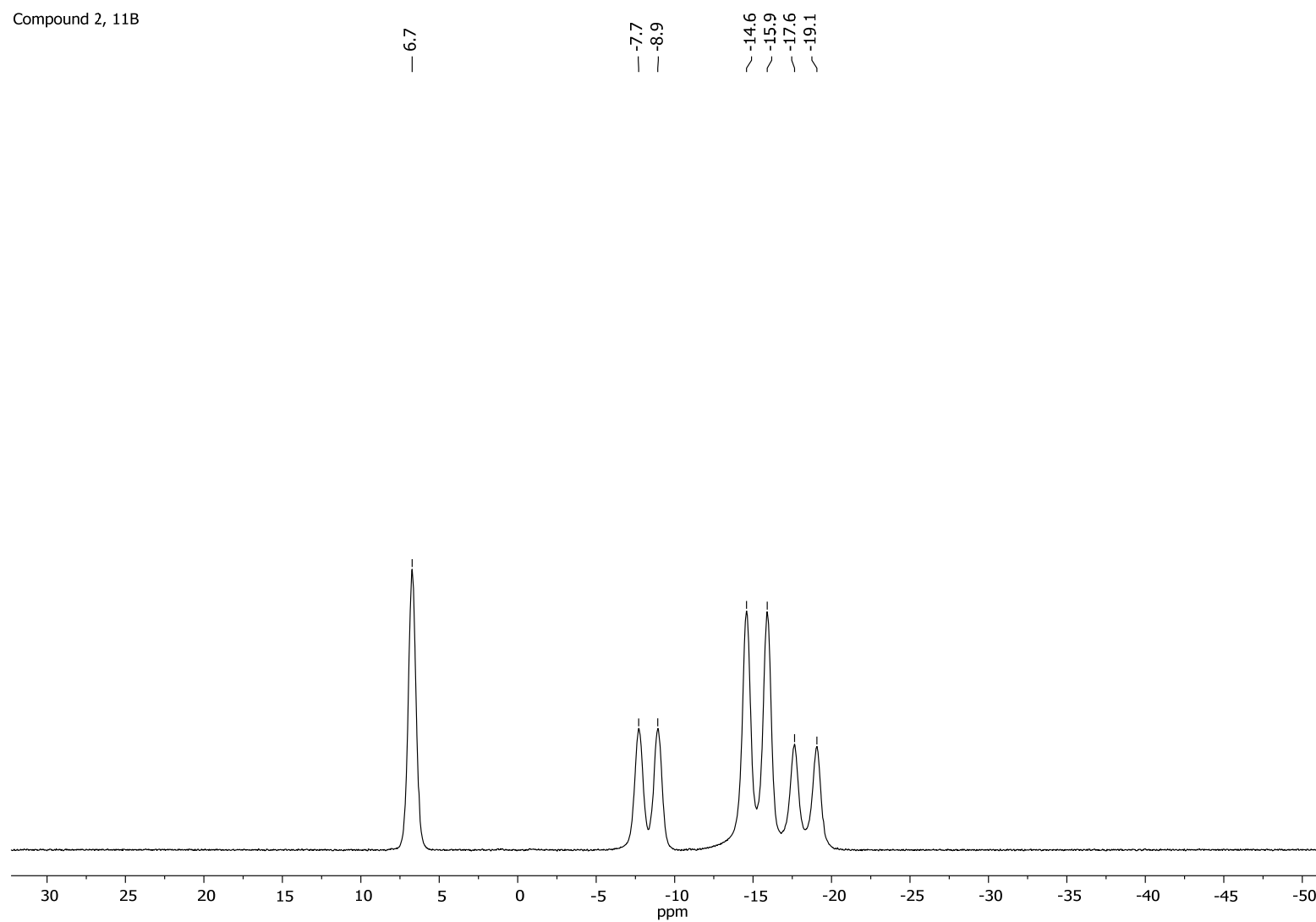
**Figure S8.**  $^1\text{H}$  NMR spectrum of 9,12- $\text{Cl}_2$ -1,2- $\text{C}_{20}\text{H}_{38}$  in  $\text{CDCl}_3$ .

Compound 2,  $11B\{^1H\}$



**Figure S9.**  $^{11}B\{^1H\}$  NMR spectrum of 9,12-Cl<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> in CDCl<sub>3</sub>.

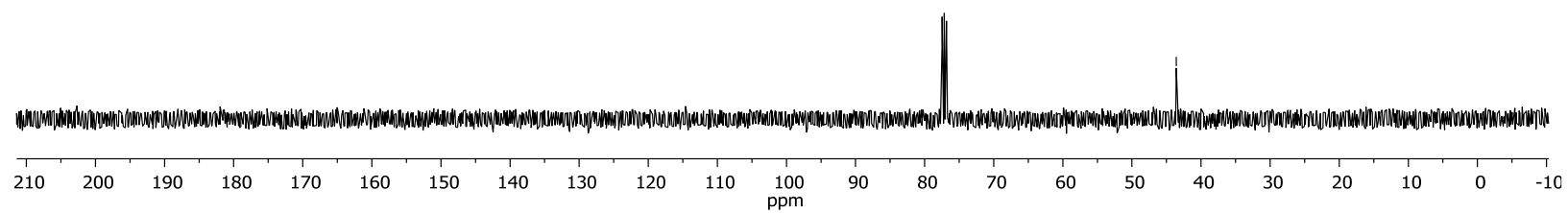
Compound 2, 11B



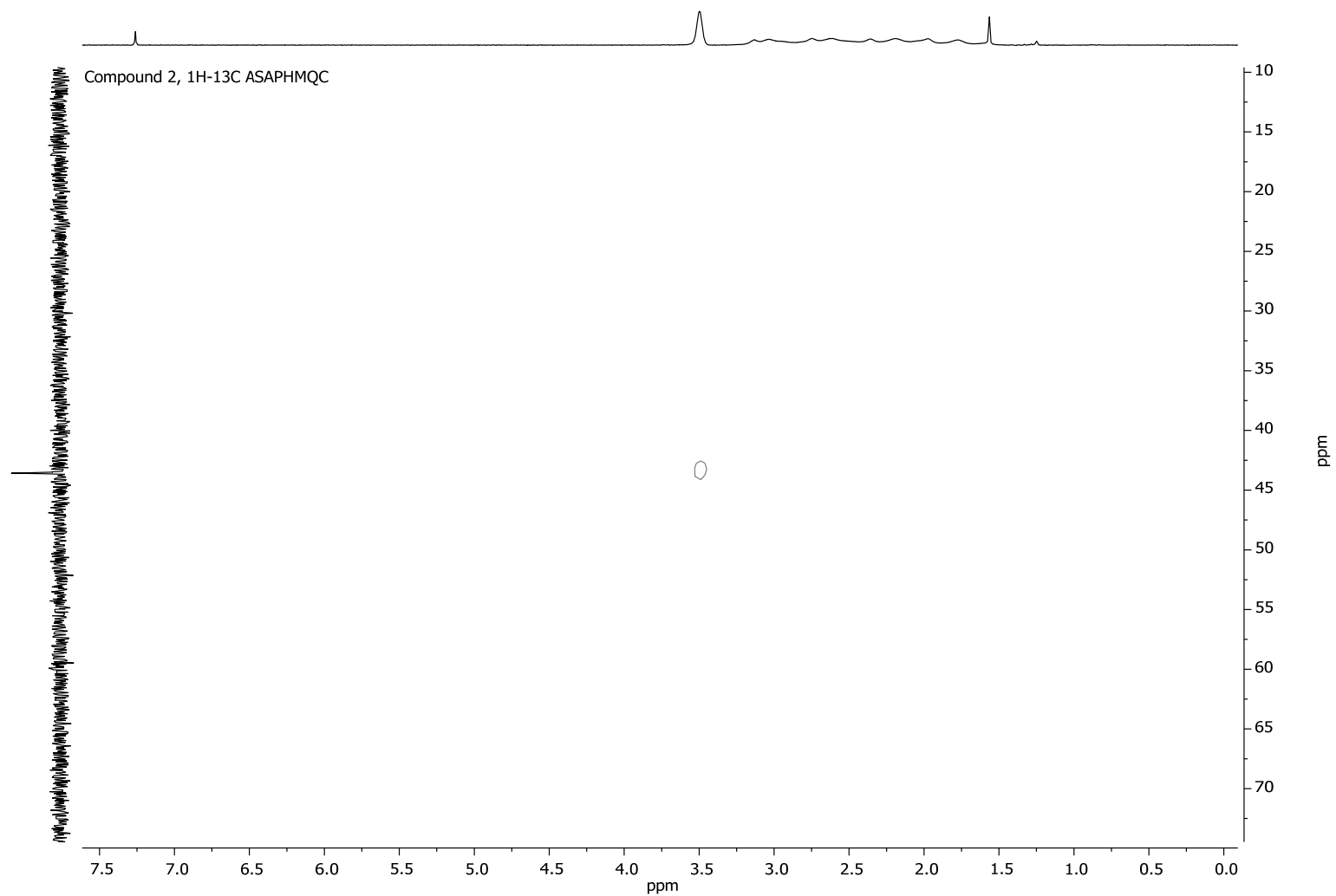
**Figure S10.**  $^{11}\text{B}$  NMR spectrum of 9,12- $\text{Cl}_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  in  $\text{CDCl}_3$ .

Compound 2,  $^{13}\text{C}\{^1\text{H}\}$

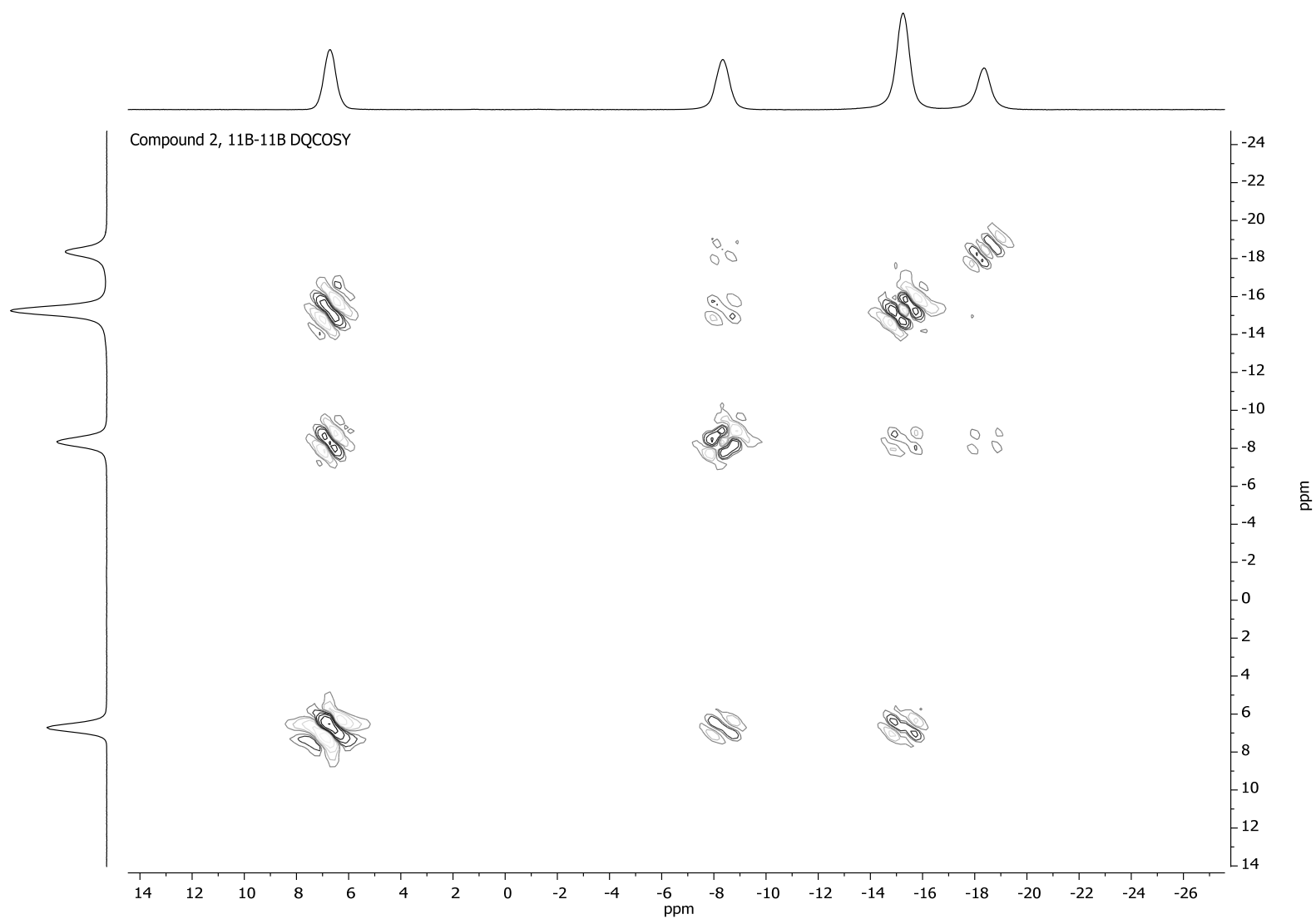
— 43.6



**Figure S11.**  $^{13}\text{C}$  NMR spectrum of 9,12- $\text{Cl}_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  in  $\text{CDCl}_3$ .



**Figure S12.**  $^1\text{H}$ - $^{13}\text{C}$  ASAPHMQC NMR spectrum of 9,12- $\text{Cl}_2$ -1,2- $\text{C}_{20}\text{H}_{10}$  in  $\text{CDCl}_3$ .



**Figure S13.**  $^{11}\text{B}$ - $^{11}\text{B}$  DQCOSY NMR spectrum of 9,12- $\text{Cl}_2$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  in  $\text{CDCl}_3$ .



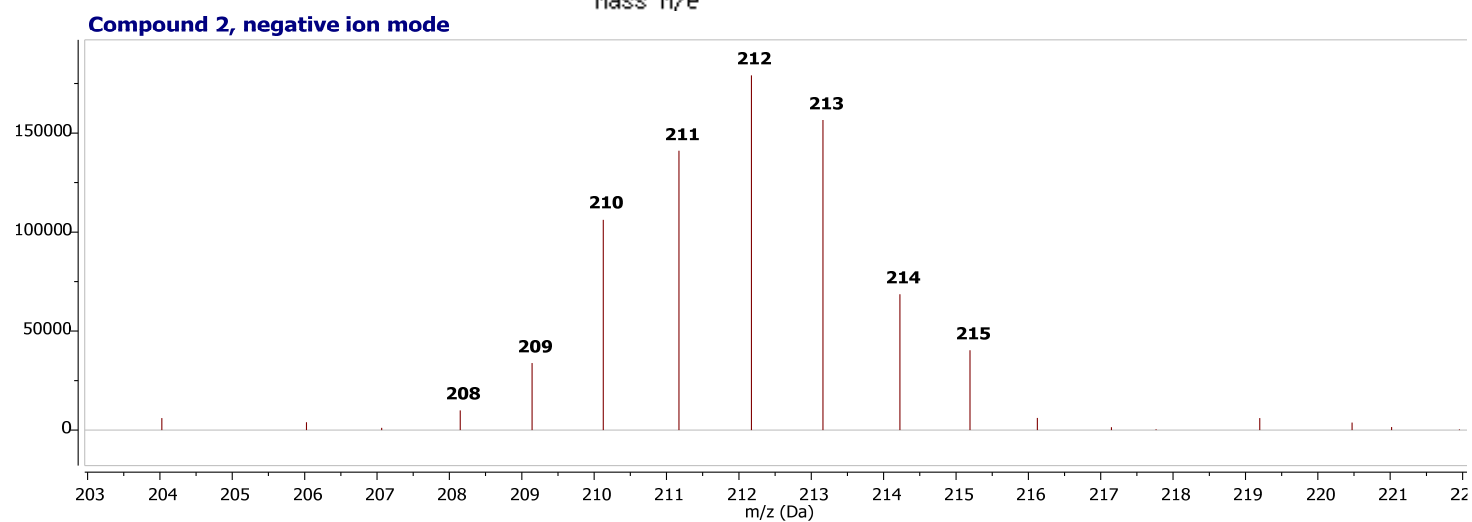
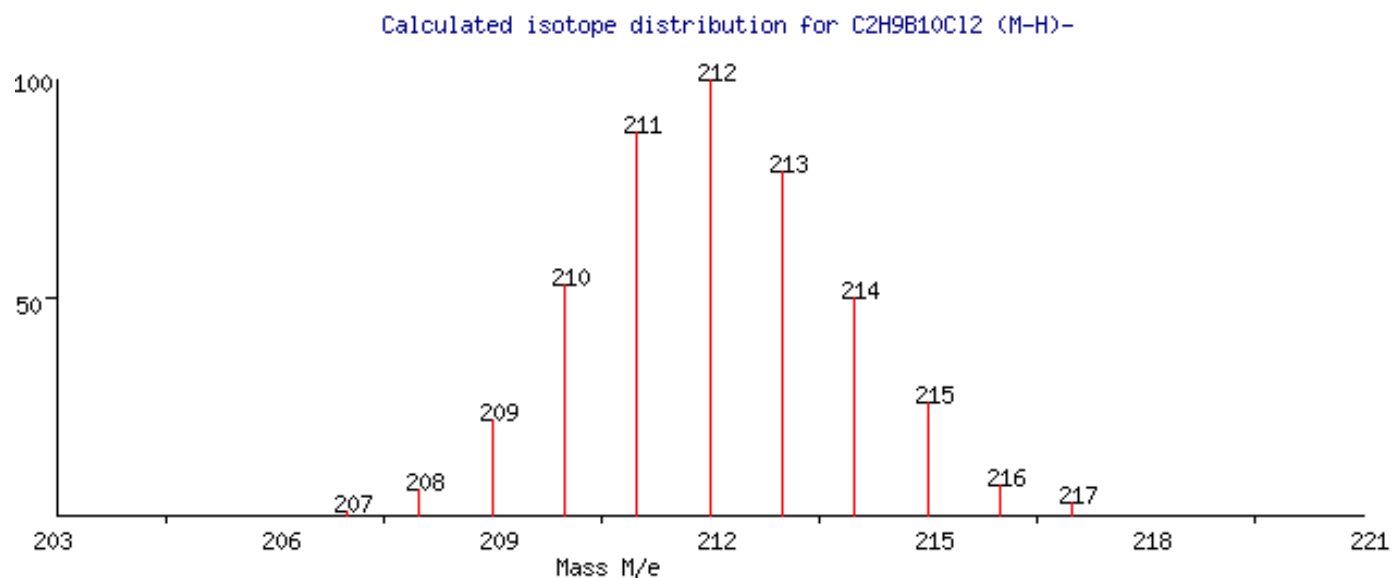
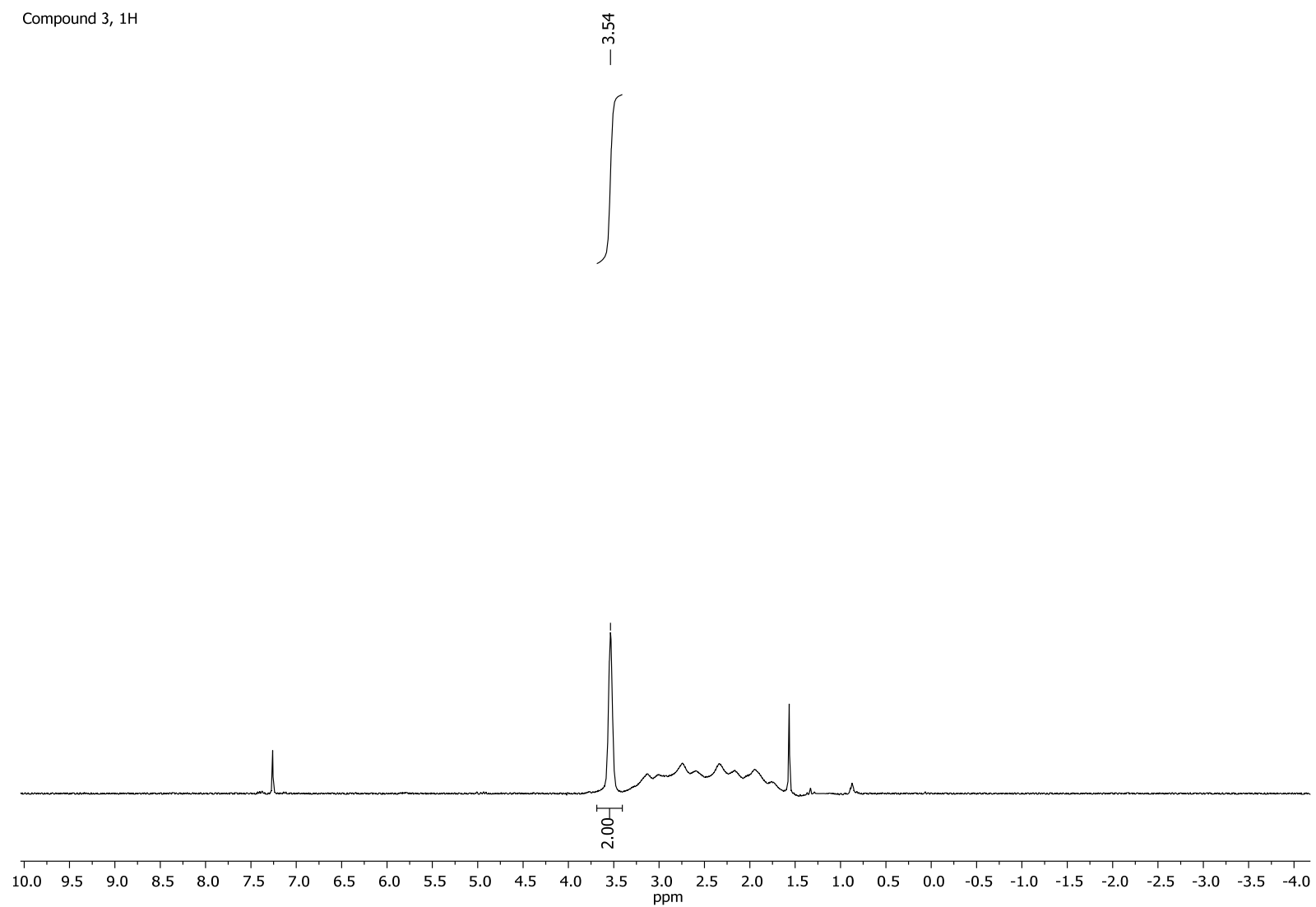


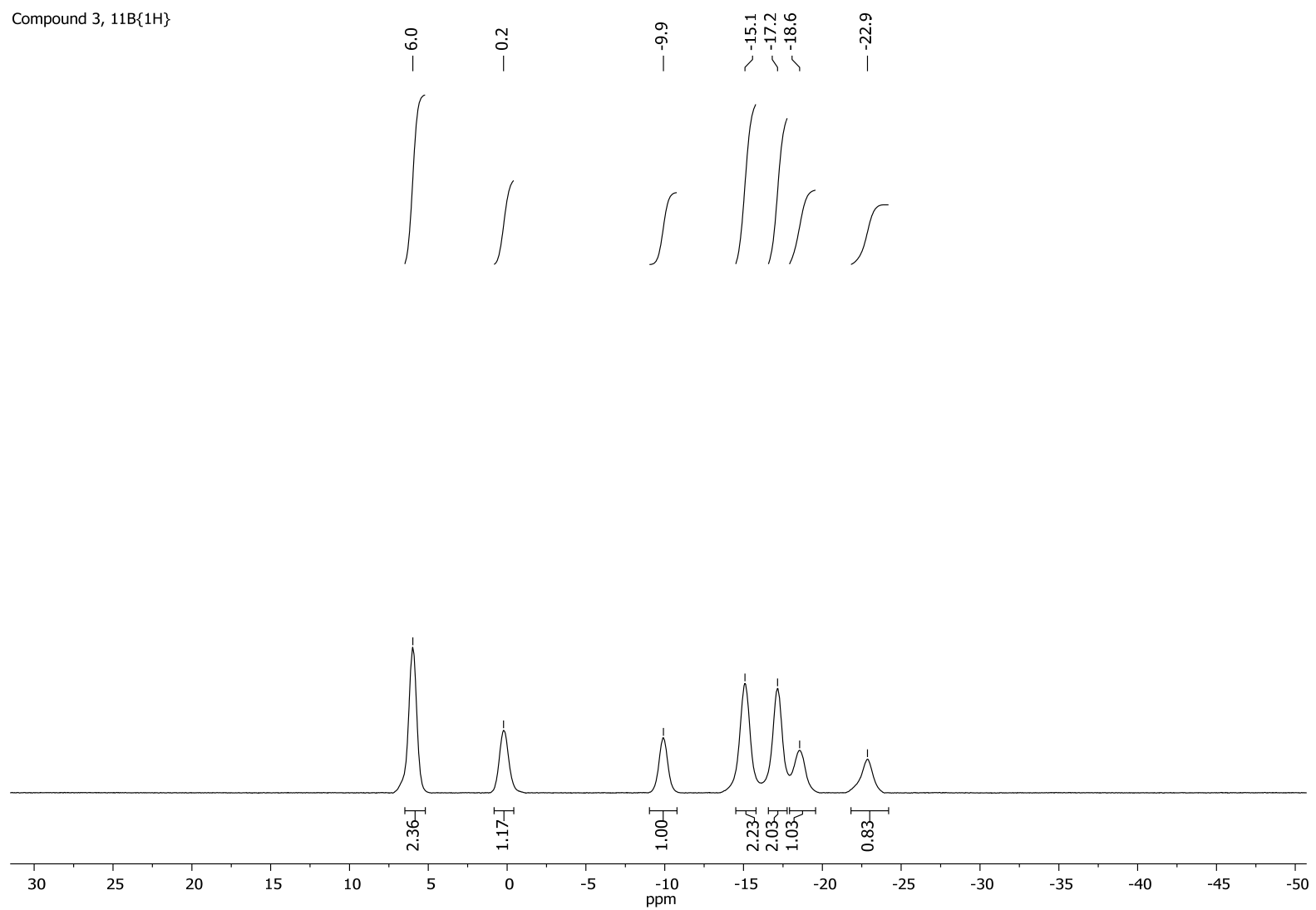
Figure S14. Mass-spectrum of 9,12-Cl<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>.

Compound 3, 1H



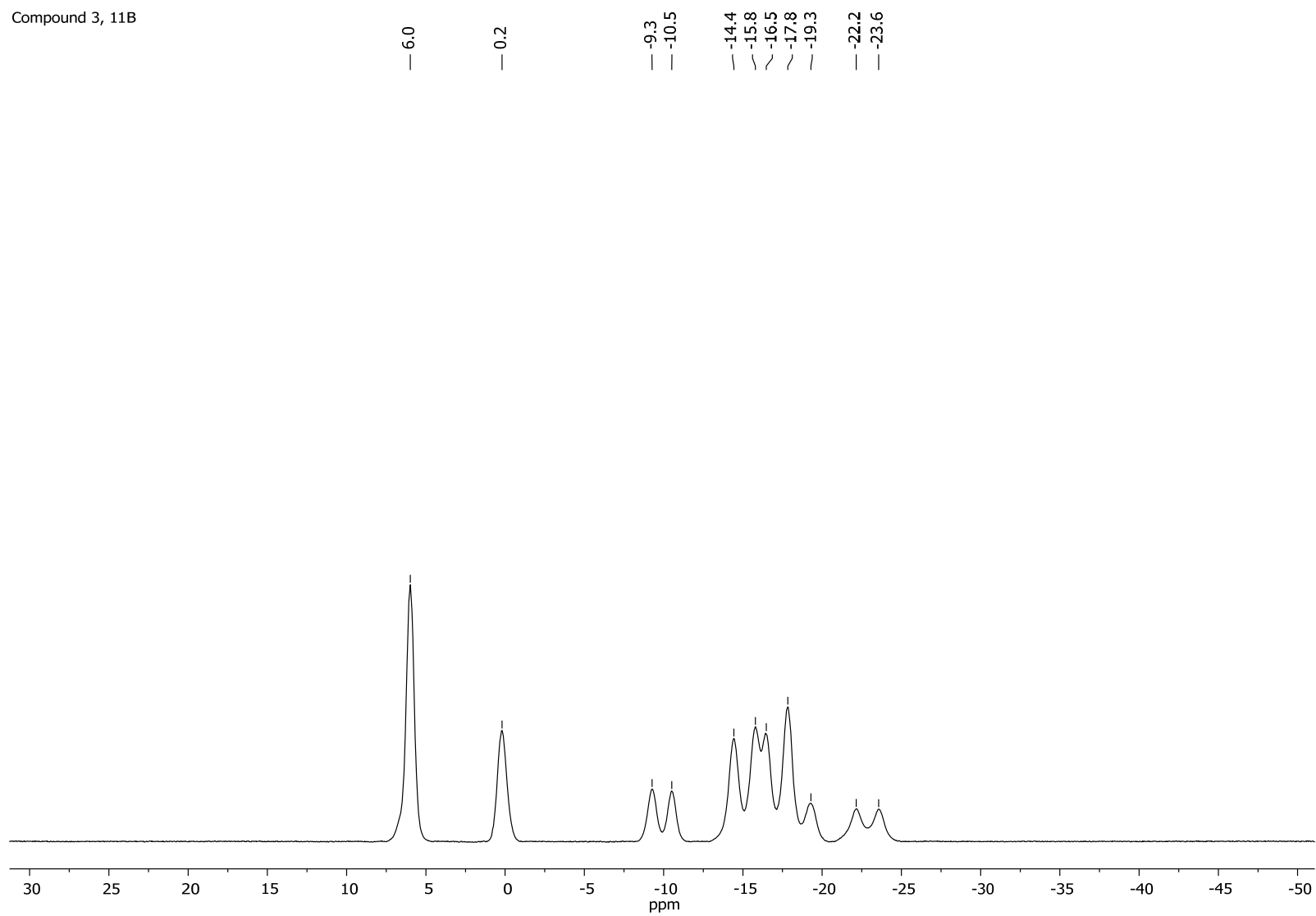
**Figure S15.**  $^1\text{H}$  NMR spectrum of 8,9,12- $\text{Cl}_3$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_9$  in  $\text{CDCl}_3$ .

Compound 3,  $^{11}\text{B}\{^1\text{H}\}$



**Figure S16.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of 8,9,12- $\text{Cl}_3$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_9$  in  $\text{CDCl}_3$ .

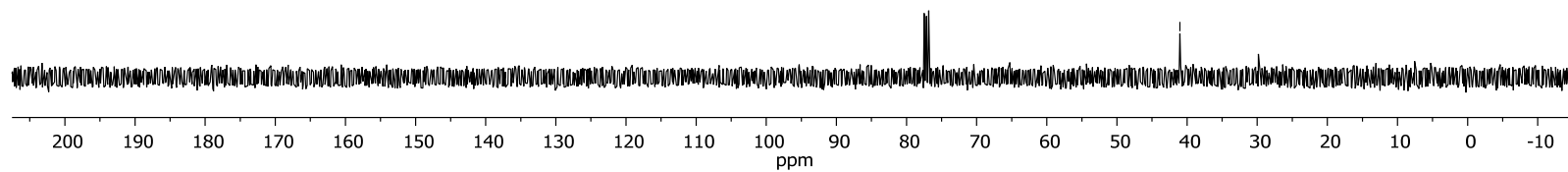
Compound 3, 11B



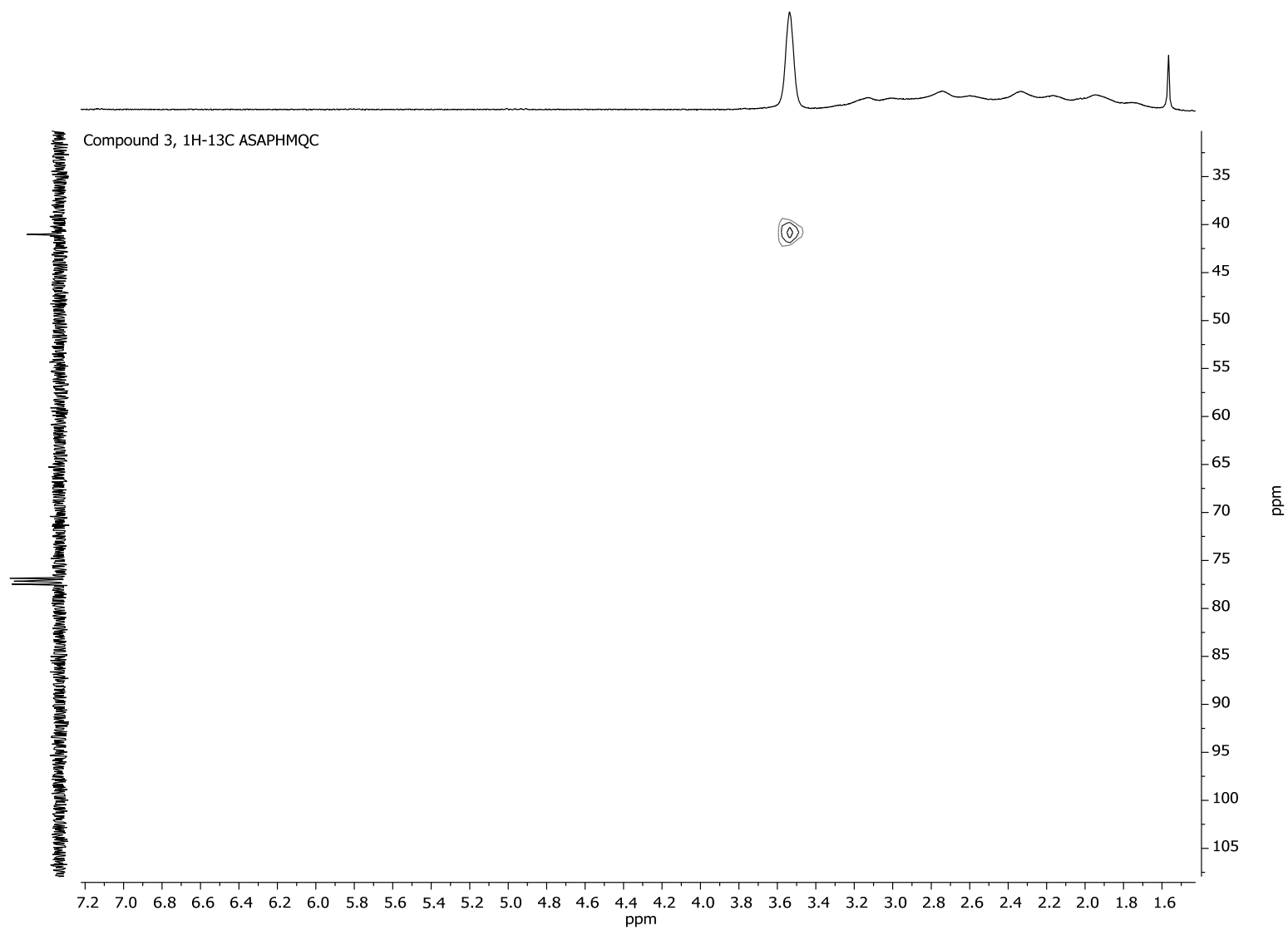
**Figure S17.**  $^{11}\text{B}$  NMR spectrum of 8,9,12- $\text{Cl}_3$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_9$  in  $\text{CDCl}_3$ .

Compound 3,  $^{13}\text{C}\{^1\text{H}\}$

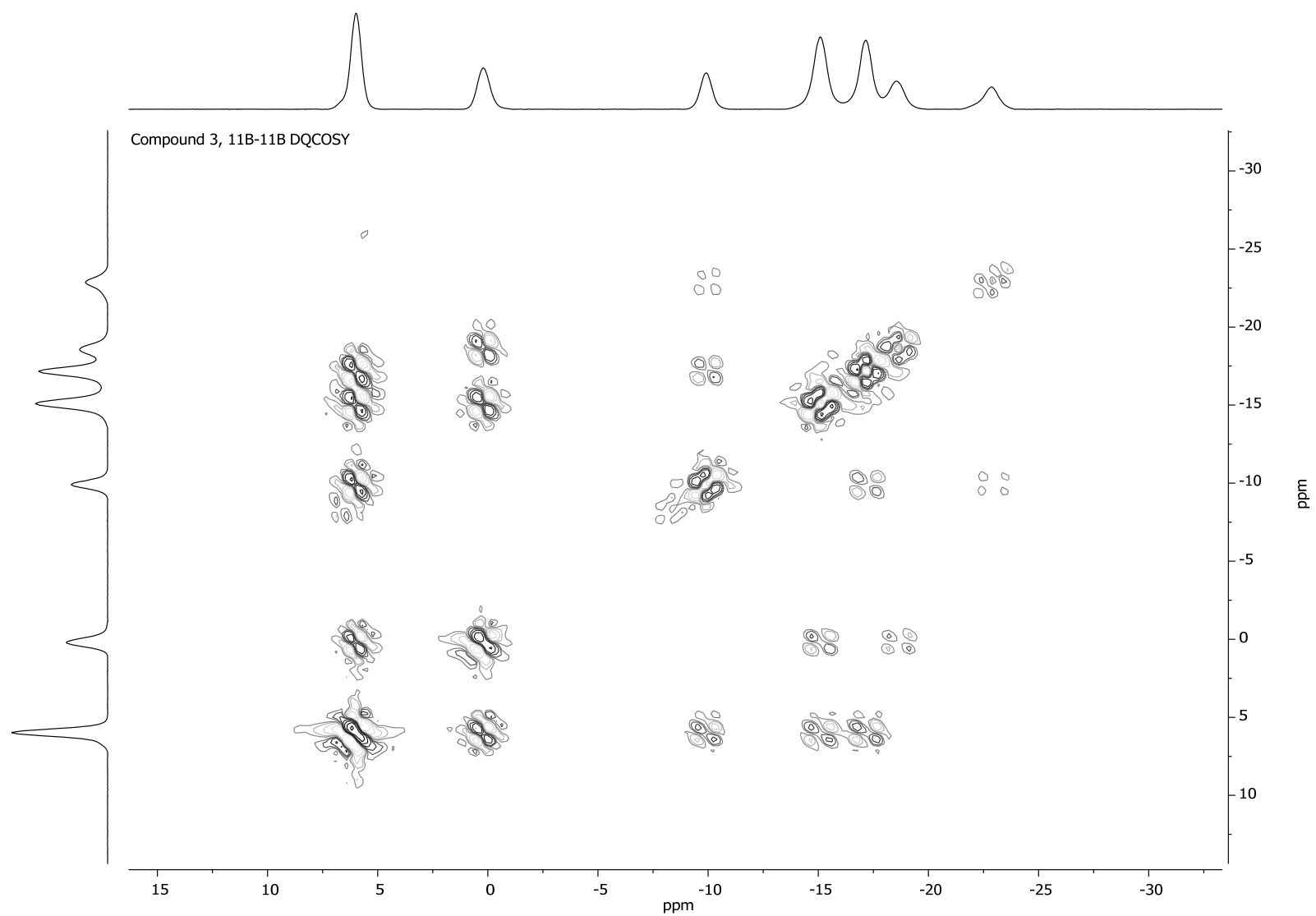
— 41.0



**Figure S18.**  $^{13}\text{C}$  NMR spectrum of 8,9,12- $\text{Cl}_3$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_9$  in  $\text{CDCl}_3$ .



**Figure S19.**  $^1\text{H}$ - $^{13}\text{C}$  ASAPHMQC NMR spectrum of 8,9,12- $\text{Cl}_3$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_9$  in  $\text{CDCl}_3$ .



**Figure S20.**  $^{11}\text{B}$ - $^{11}\text{B}$  DQCOSY NMR spectrum of 8,9,12- $\text{Cl}_3$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_9$  in  $\text{CDCl}_3$ .

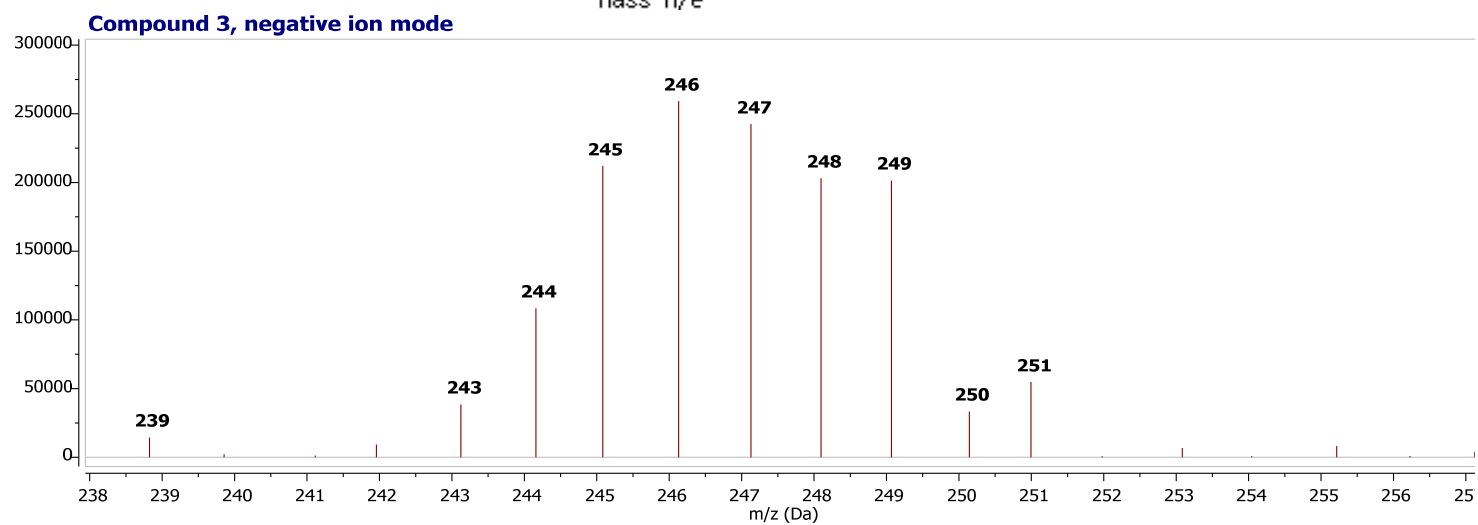
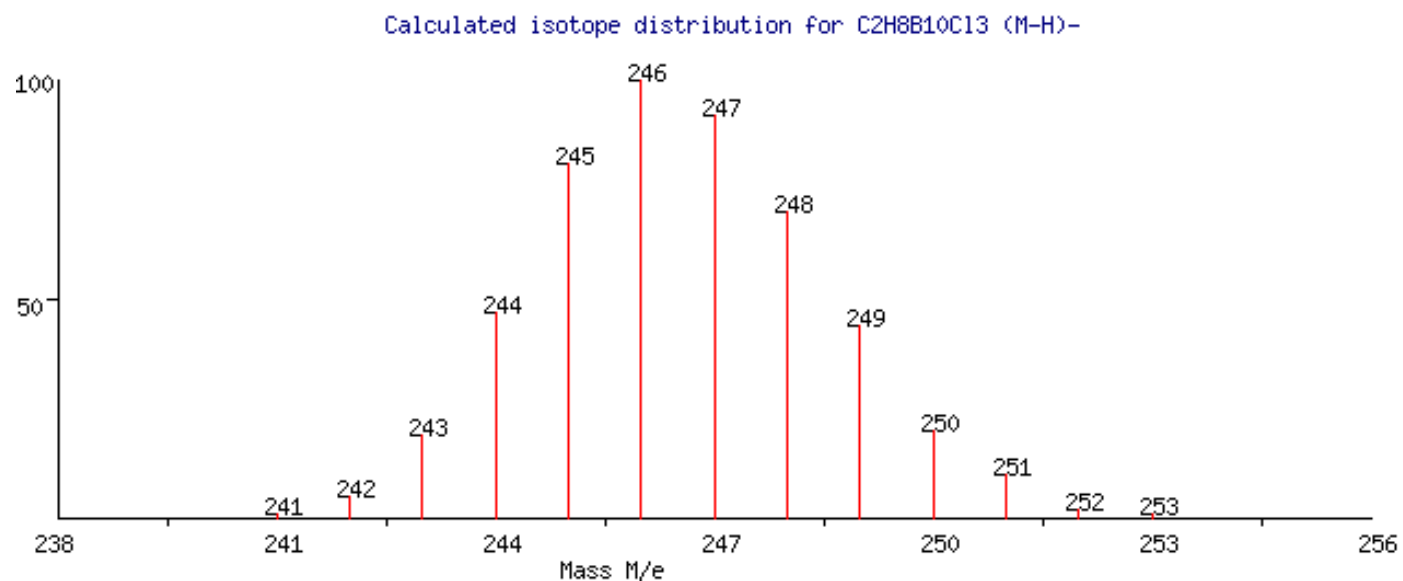
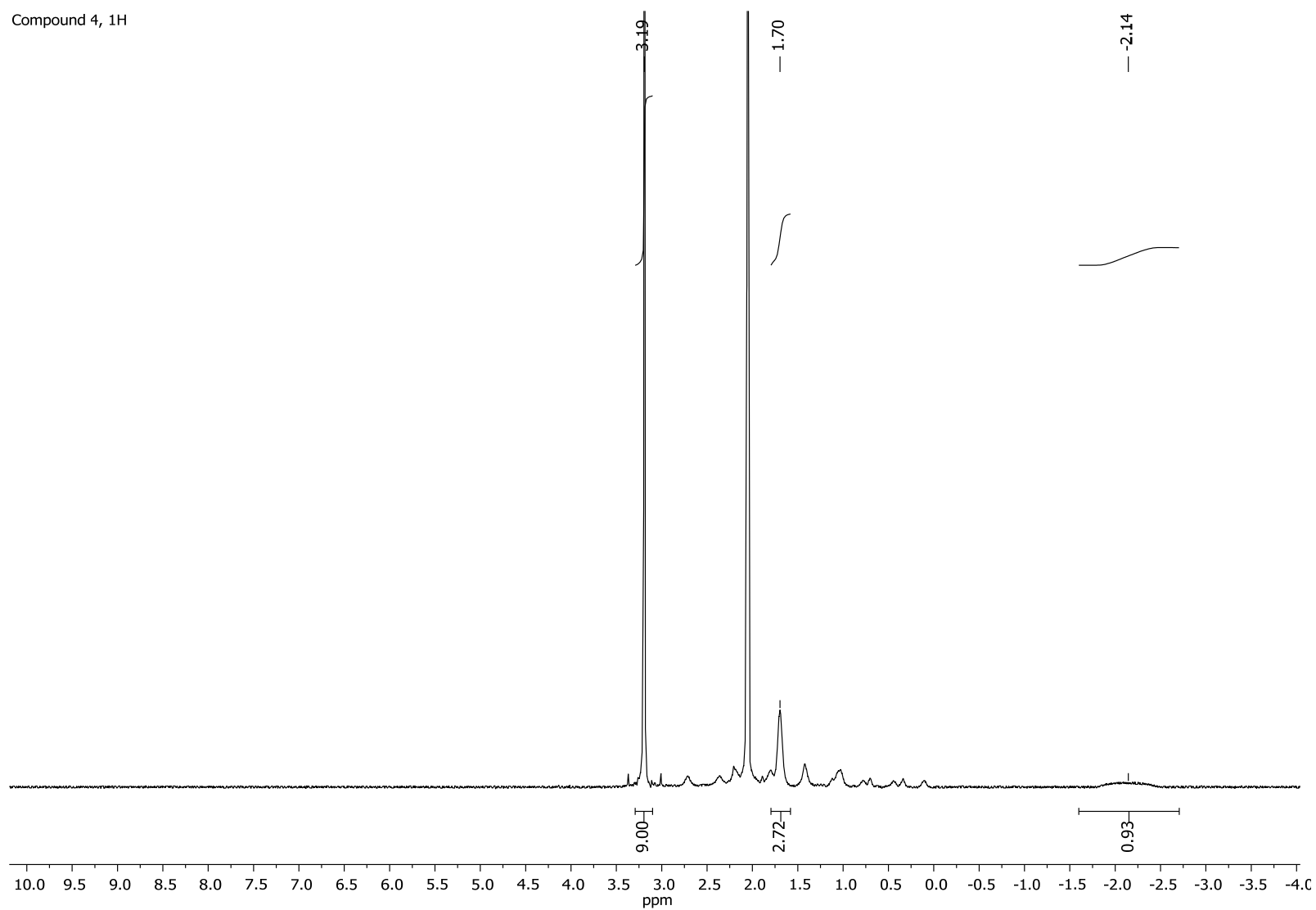


Figure S21. Mass-spectrum of 8,9,12-Cl<sub>3</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>9</sub>.

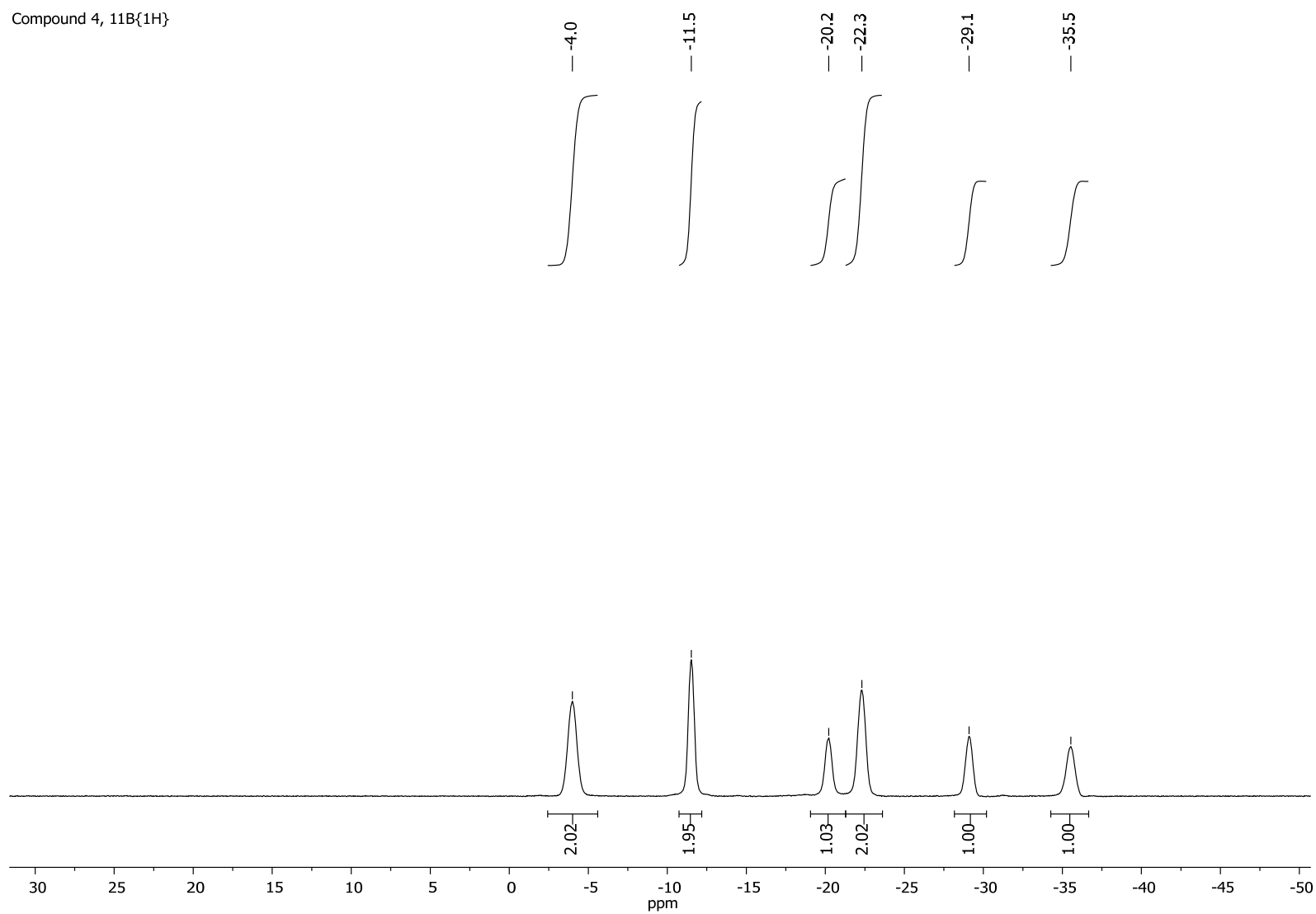


Compound 4, 1H



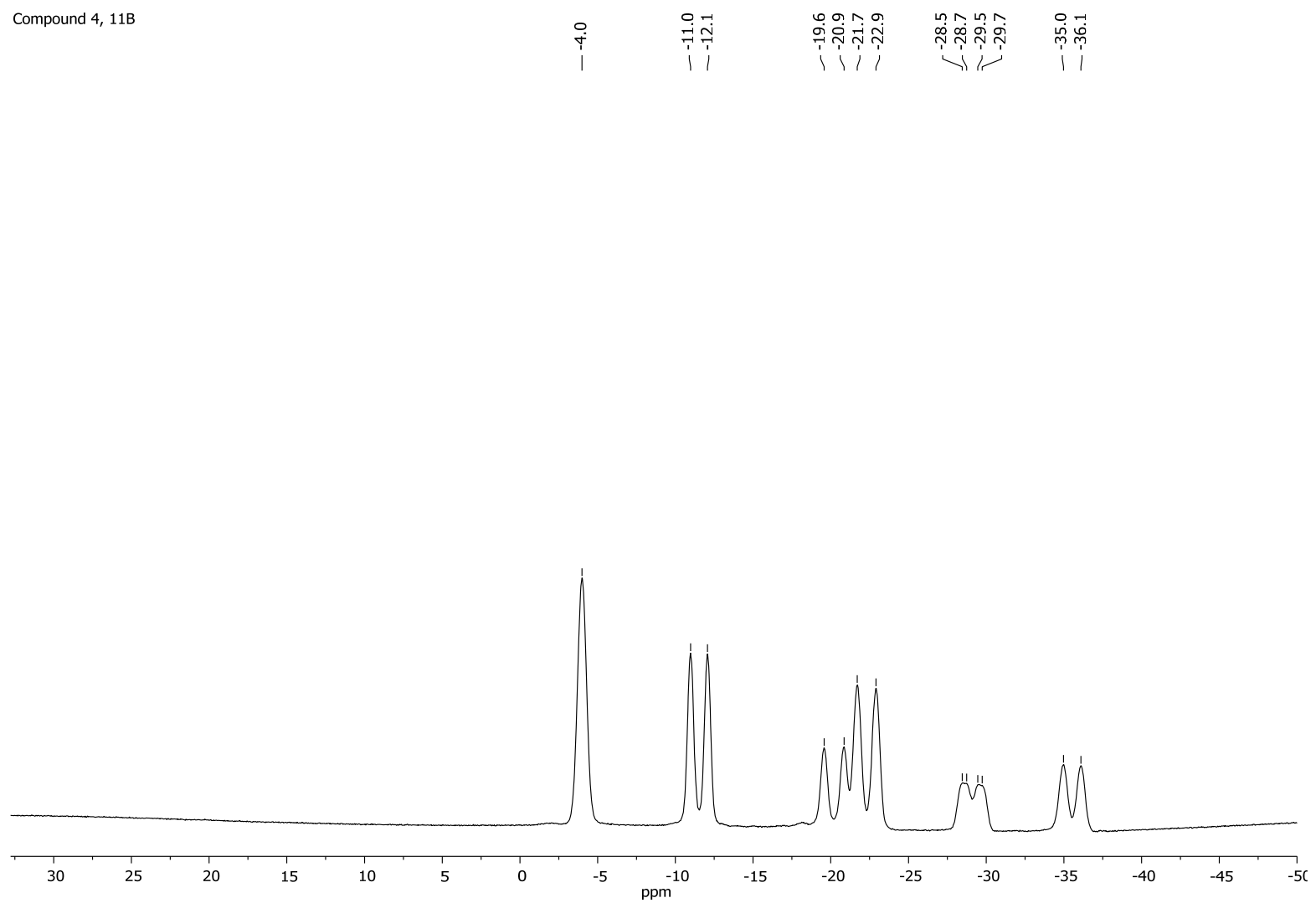
**Figure S22.**  $^1\text{H}$  NMR spectrum of  $(\text{Me}_3\text{NH})[5,6\text{-Cl}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]$  in  $\text{acetone-}d_6$ .

Compound 4,  $^{11}\text{B}\{^1\text{H}\}$



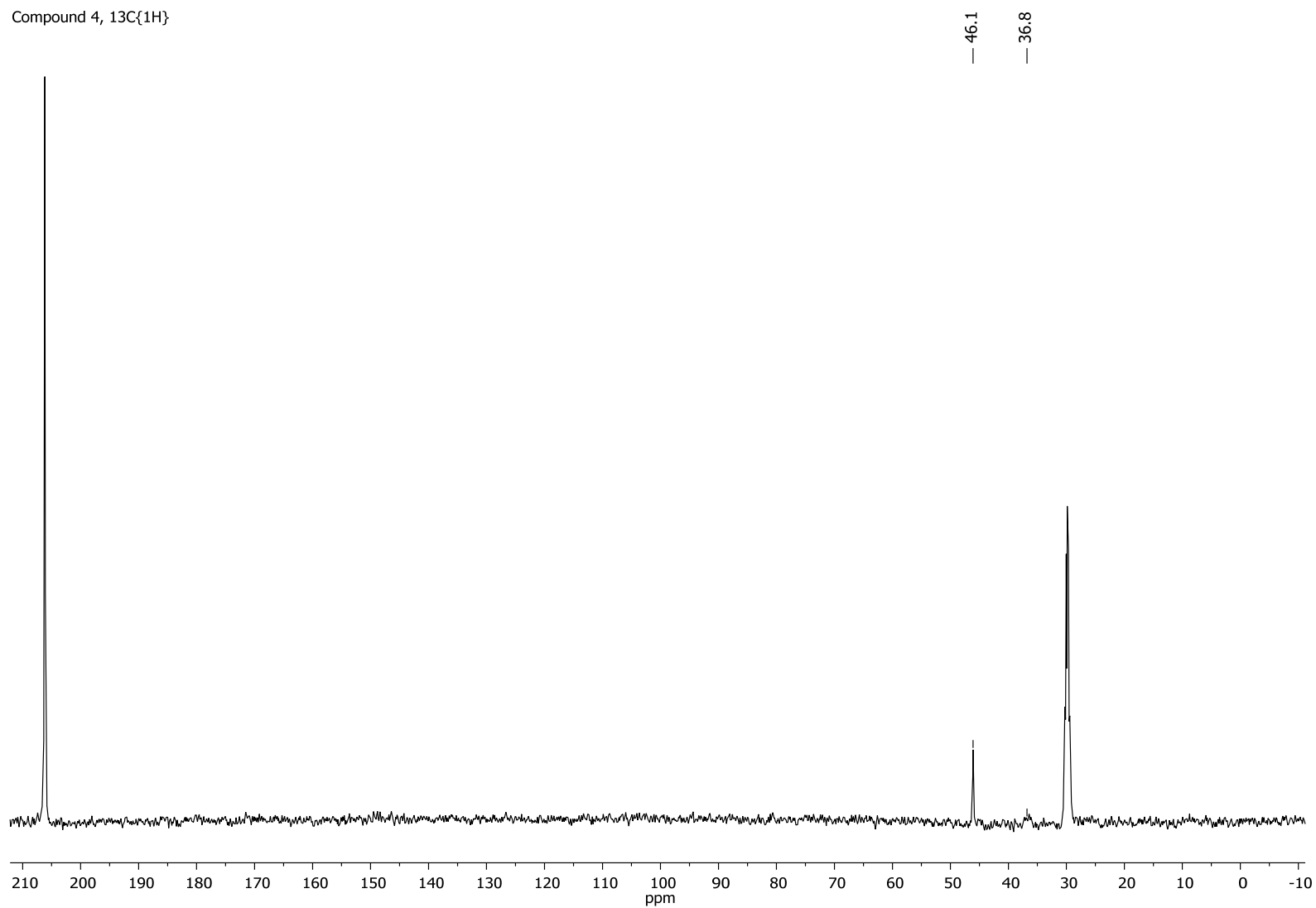
**Figure S23.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $(\text{Me}_3\text{NH})[5,6\text{-Cl}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]$  in  $\text{acetone-}d_6$ .

Compound 4, 11B

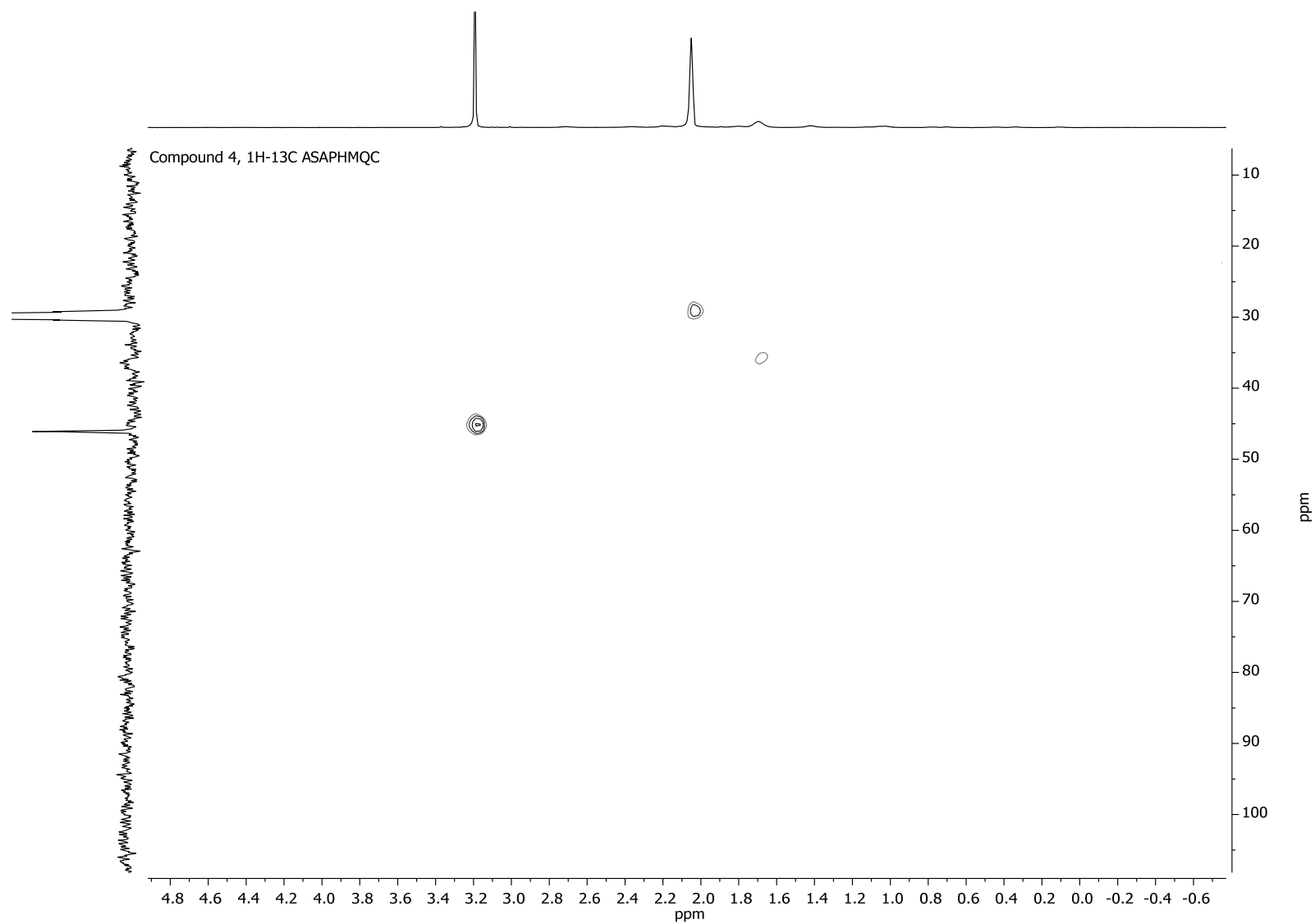


**Figure S24.**  $^{11}\text{B}$  NMR spectrum of  $(\text{Me}_3\text{NH})[5,6\text{-Cl}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]$  in acetone- $d_6$ .

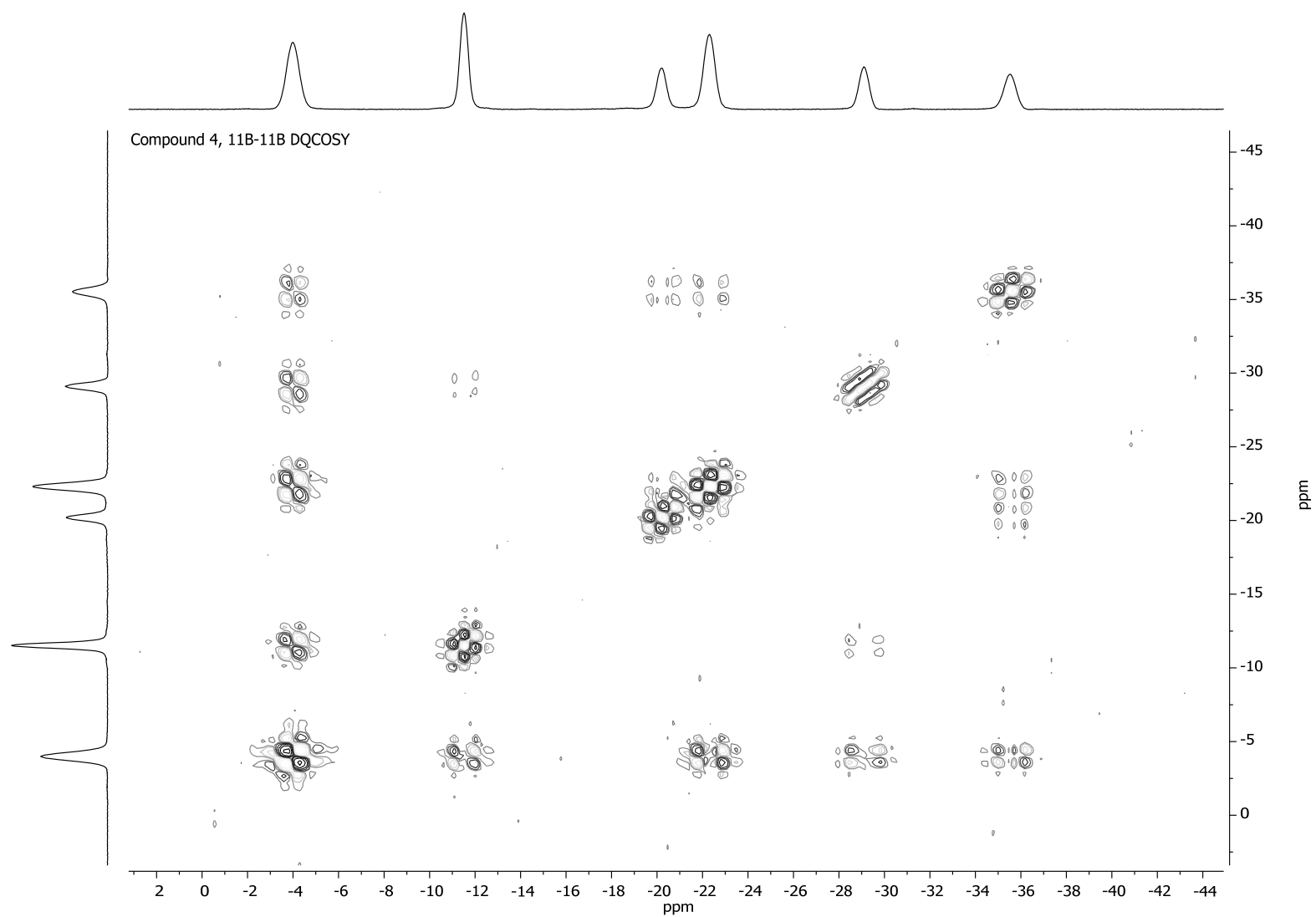
Compound 4,  $^{13}\text{C}\{^1\text{H}\}$



**Figure S25.**  $^{13}\text{C}$  NMR spectrum of  $(\text{Me}_3\text{NH})[5,6\text{-Cl}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]$  in acetone- $d_6$ .



**Figure S26.**  $^1\text{H}$ - $^{13}\text{C}$  ASAPHMQC NMR spectrum of  $(\text{Me}_3\text{NH})[5,6\text{-Cl}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]$  in acetone- $d_6$ .



**Figure S27.**  $^{11}\text{B}$ - $^{11}\text{B}$  DQCOSY NMR spectrum of  $(\text{Me}_3\text{NH})[5,6\text{-Cl}_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]$  in acetone- $d_6$ .

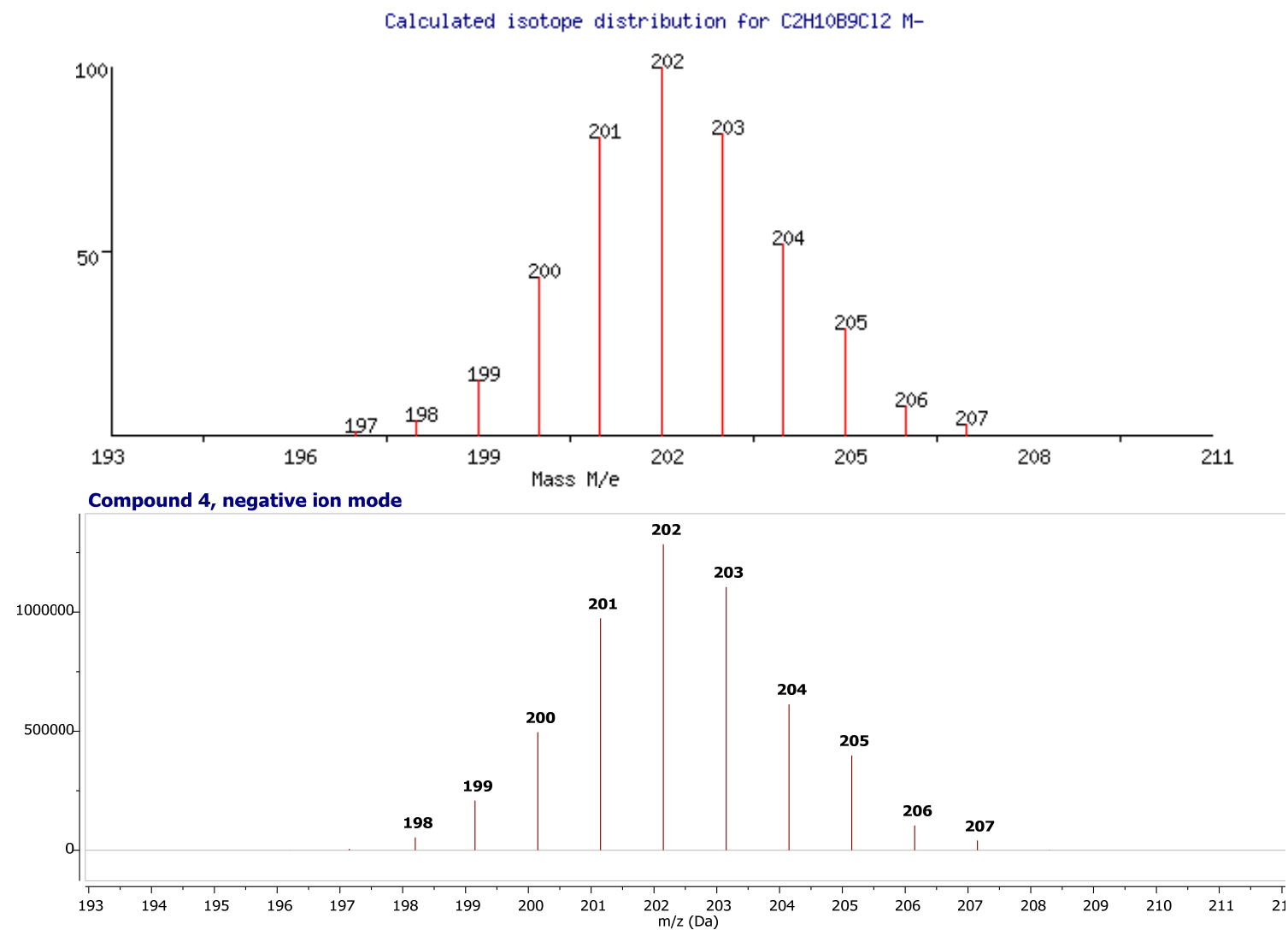
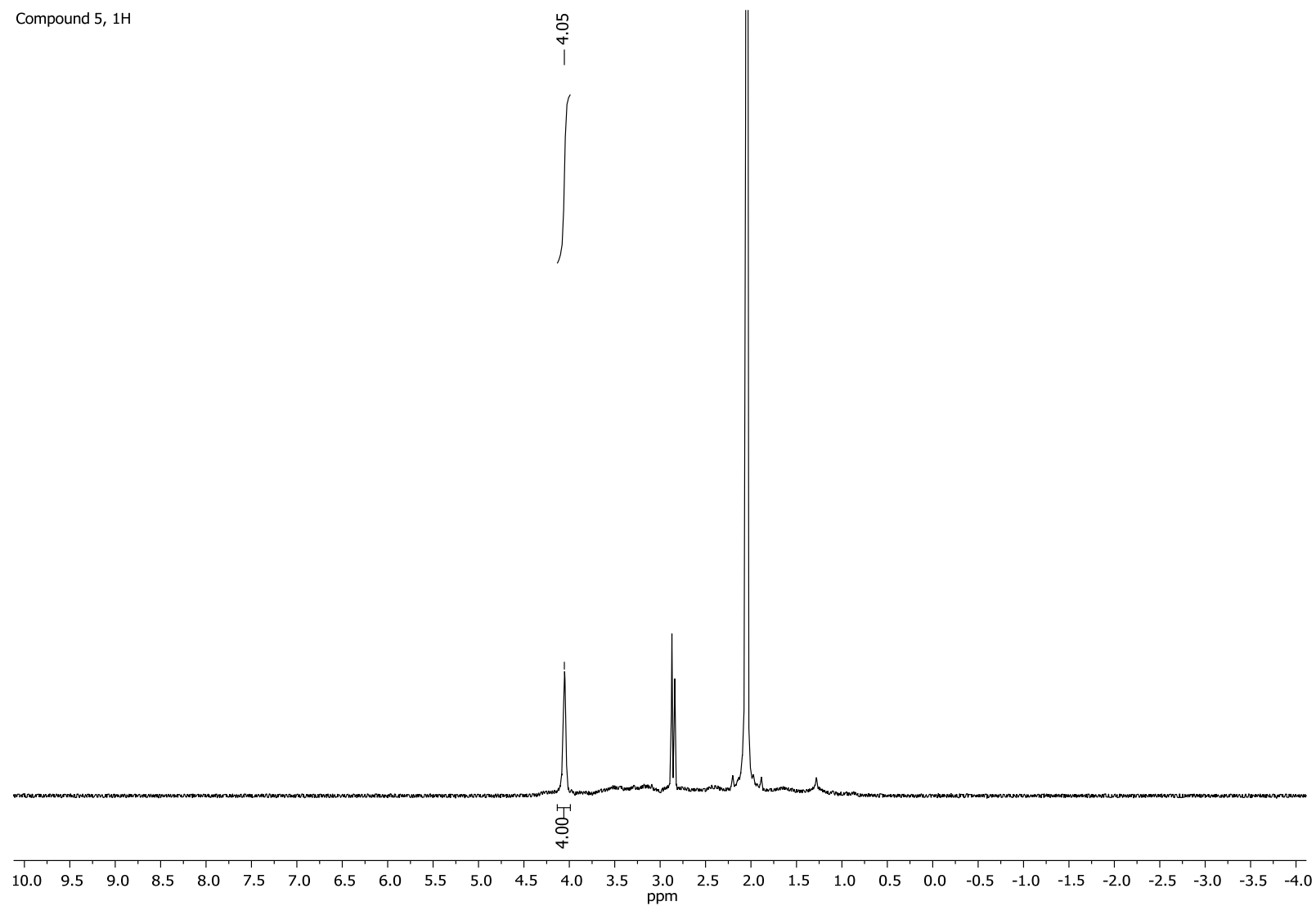


Figure S28. Mass-spectrum of the [5,6-Cl<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>-</sup> anion.

Compound 5, 1H



**Figure S29.**  $^1\text{H}$  NMR spectrum of  $\text{K}[9,9',12,12'\text{-Cl}_4\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]$  in acetone- $d_6$ .



Compound 5,  $^{11}\text{B}\{^1\text{H}\}$

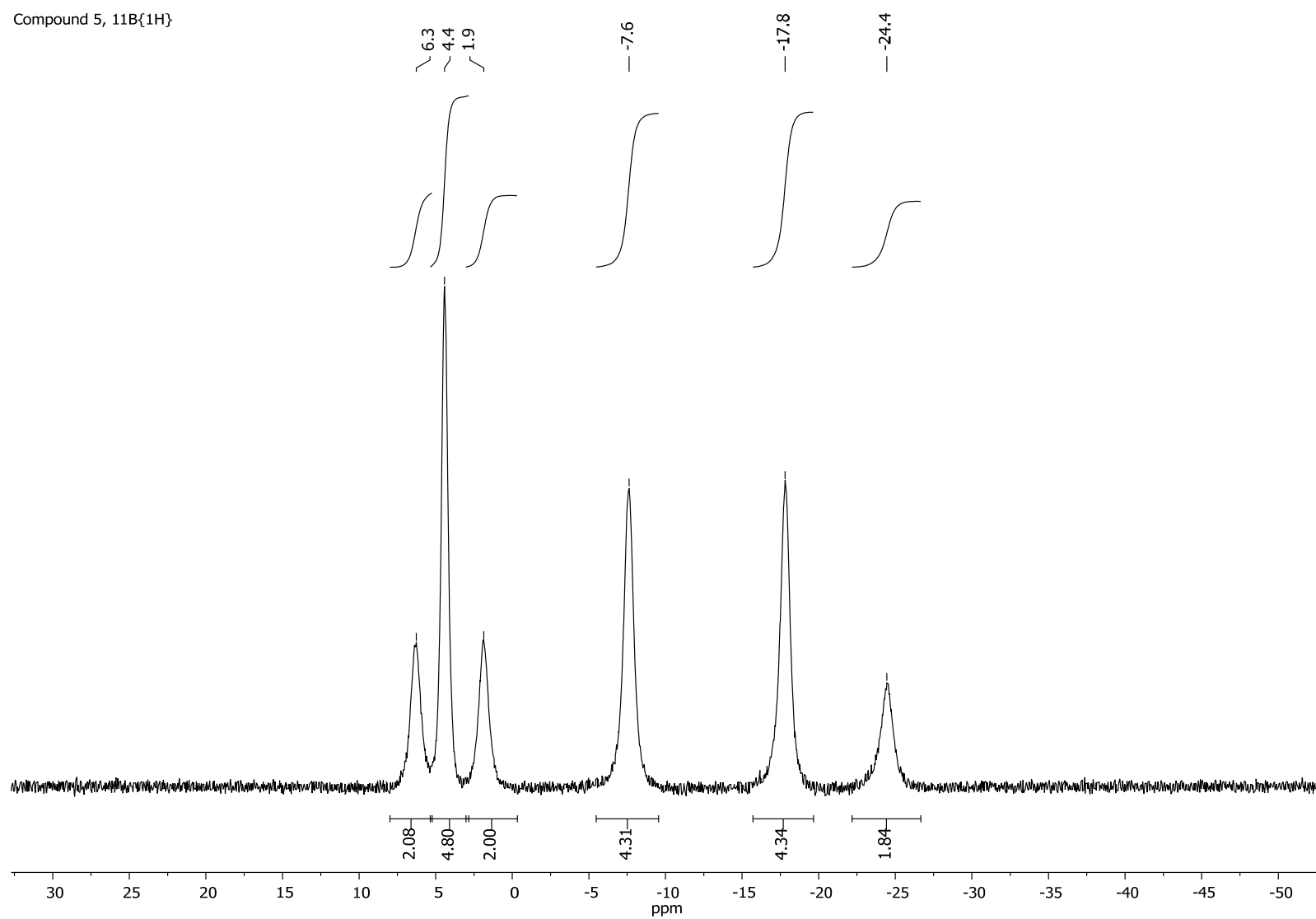
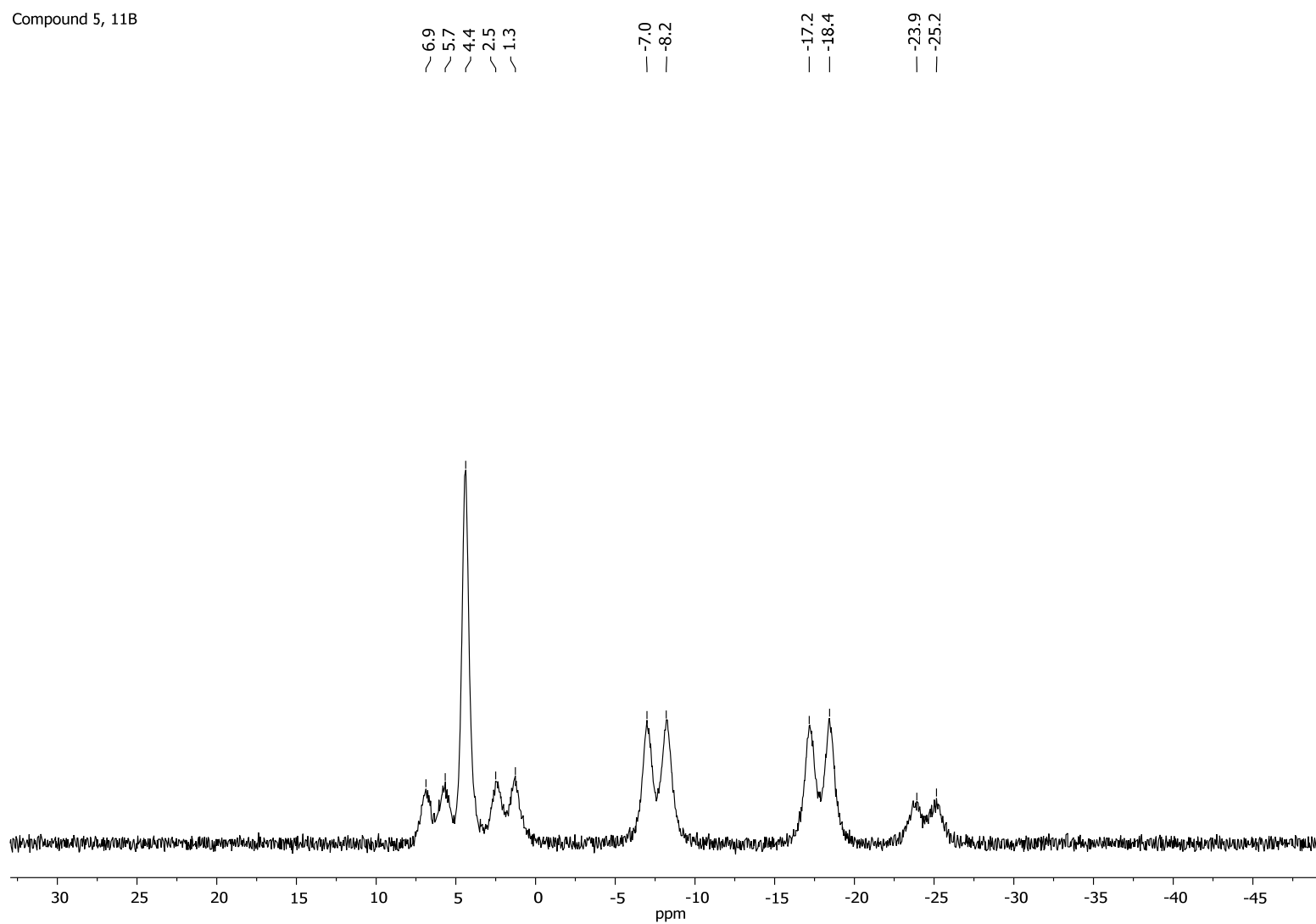
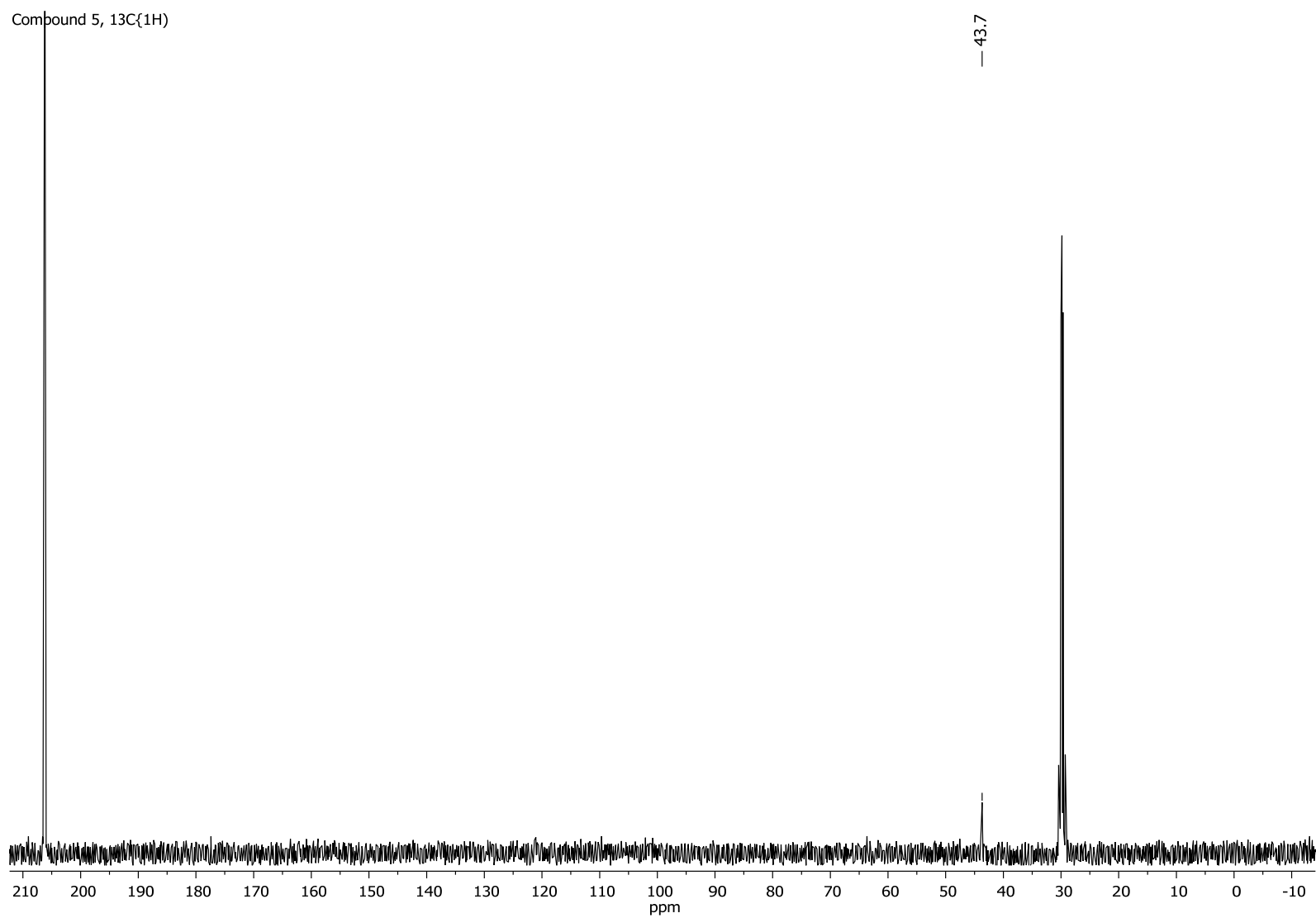


Figure S30.  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum of  $\text{K}[9,9',12,12'\text{-Cl}_4\text{-3,3'-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]$  in acetone- $d_6$ .

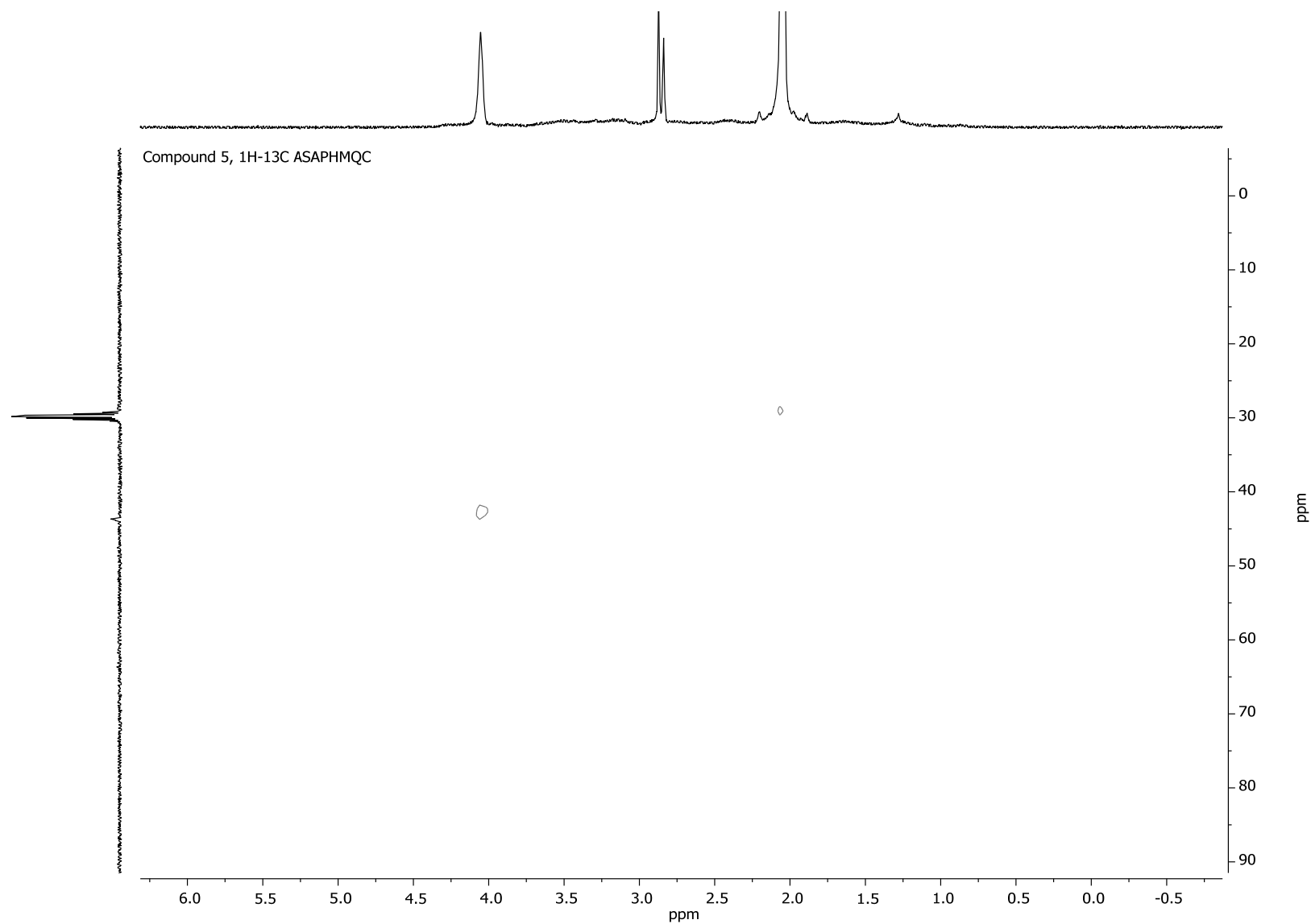
Compound 5, 11B



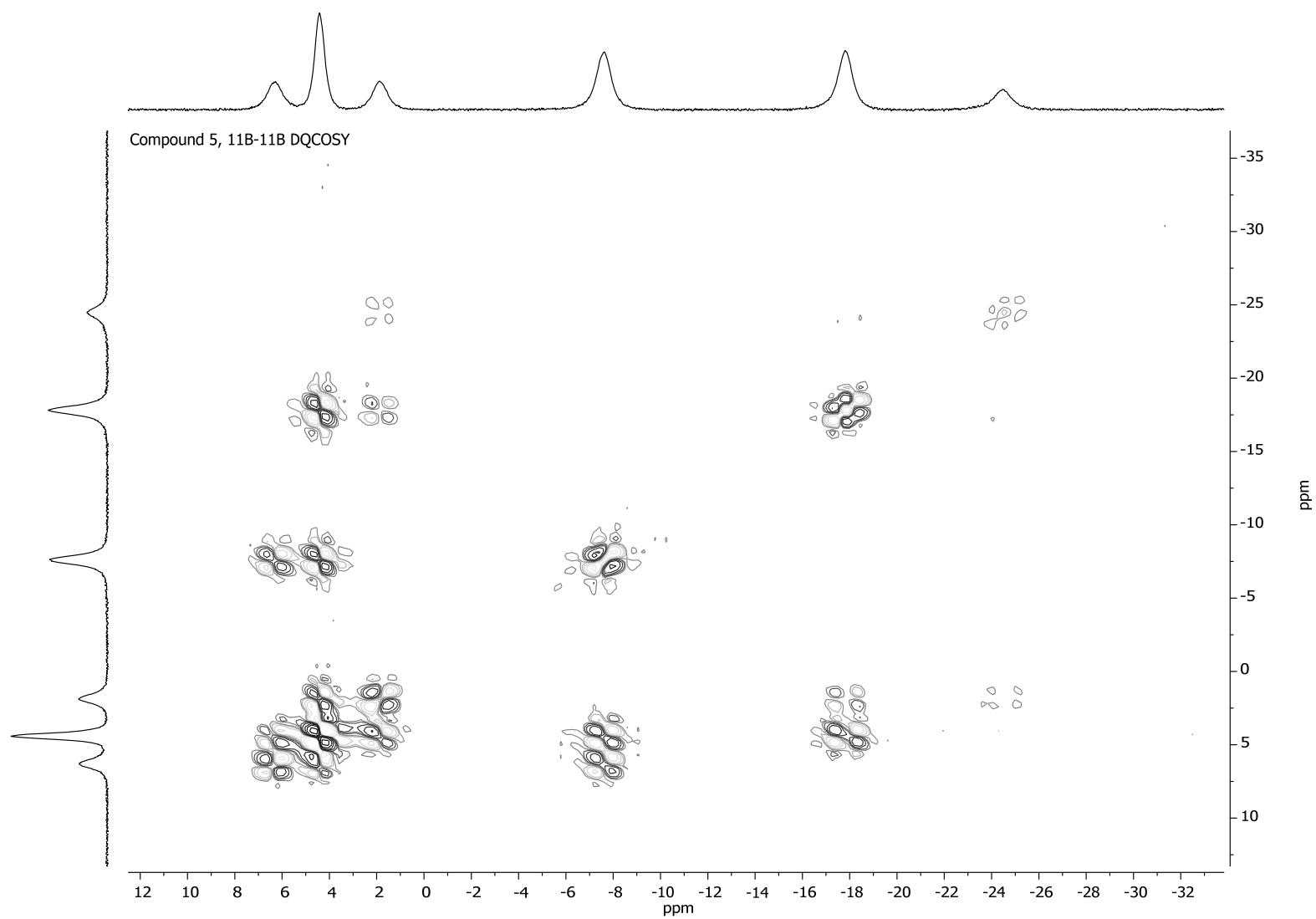
**Figure S31.**  $^{11}\text{B}$  NMR spectrum of  $\text{K}[9,9',12,12'\text{-Cl}_4\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]$  in acetone- $d_6$ .



**Figure S32.**  $^{13}\text{C}$  NMR spectrum of  $\text{K}[9,9',12,12'\text{-Cl}_4\text{-3,3'}\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]$  in acetone- $d_6$ .



**Figure S33.**  $^1\text{H}$ - $^{13}\text{C}$  ASAPHMQC NMR spectrum of  $\text{K}[9,9',12,12'\text{-Cl}_4\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]$  in acetone- $d_6$ .



**Figure S34.**  $^{11}\text{B}$ - $^{11}\text{B}$  DQCOSY NMR spectrum of  $\text{K}[9,9',12,12'\text{-Cl}_4\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_9)_2]$  in acetone- $d_6$ .

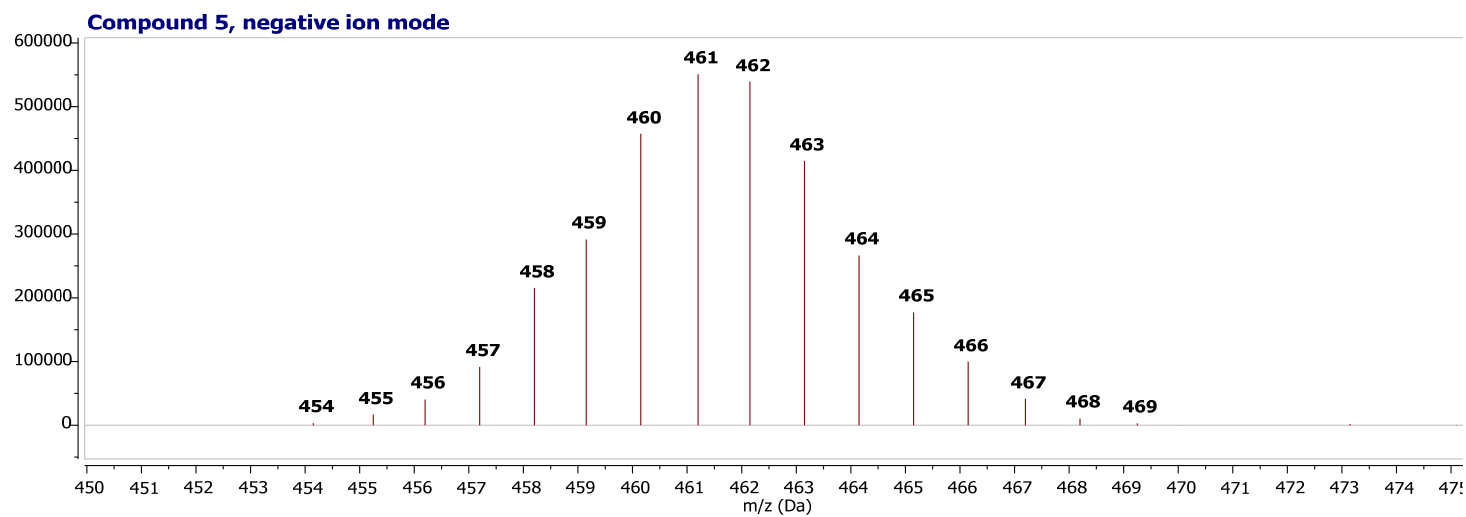
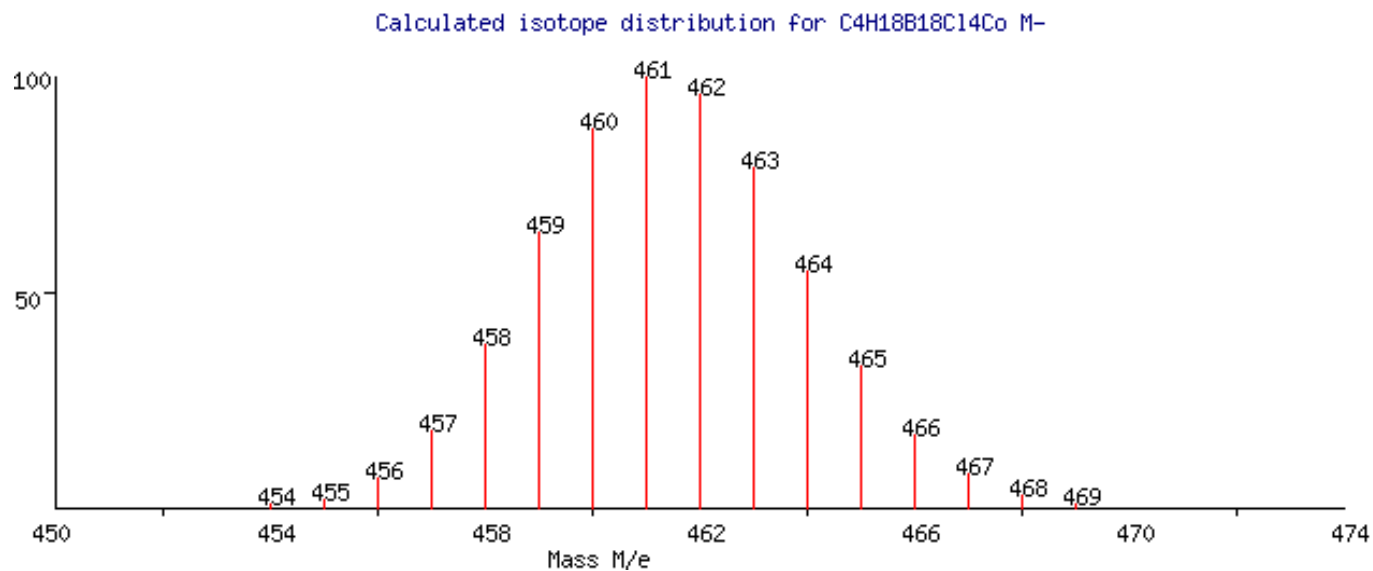
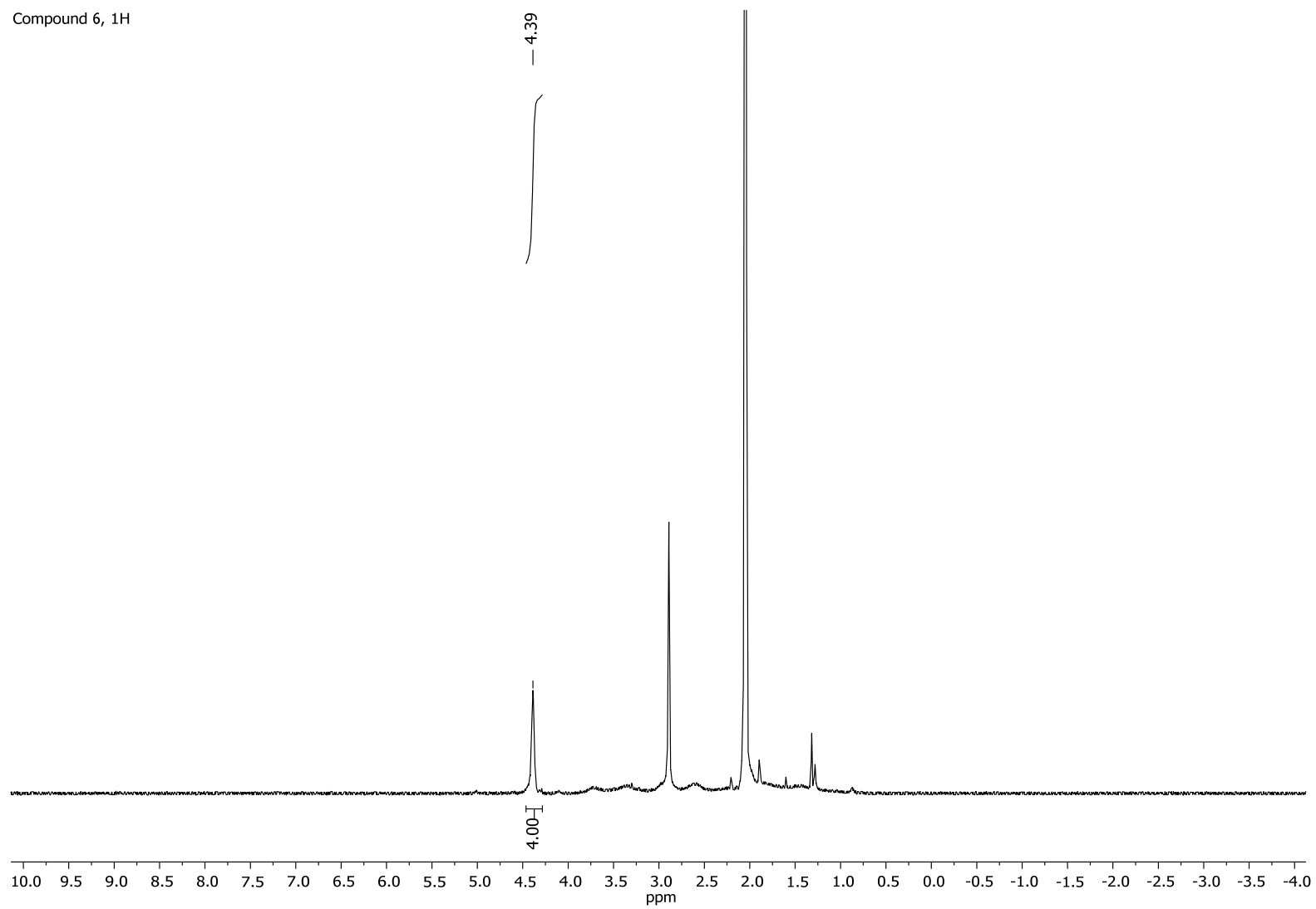


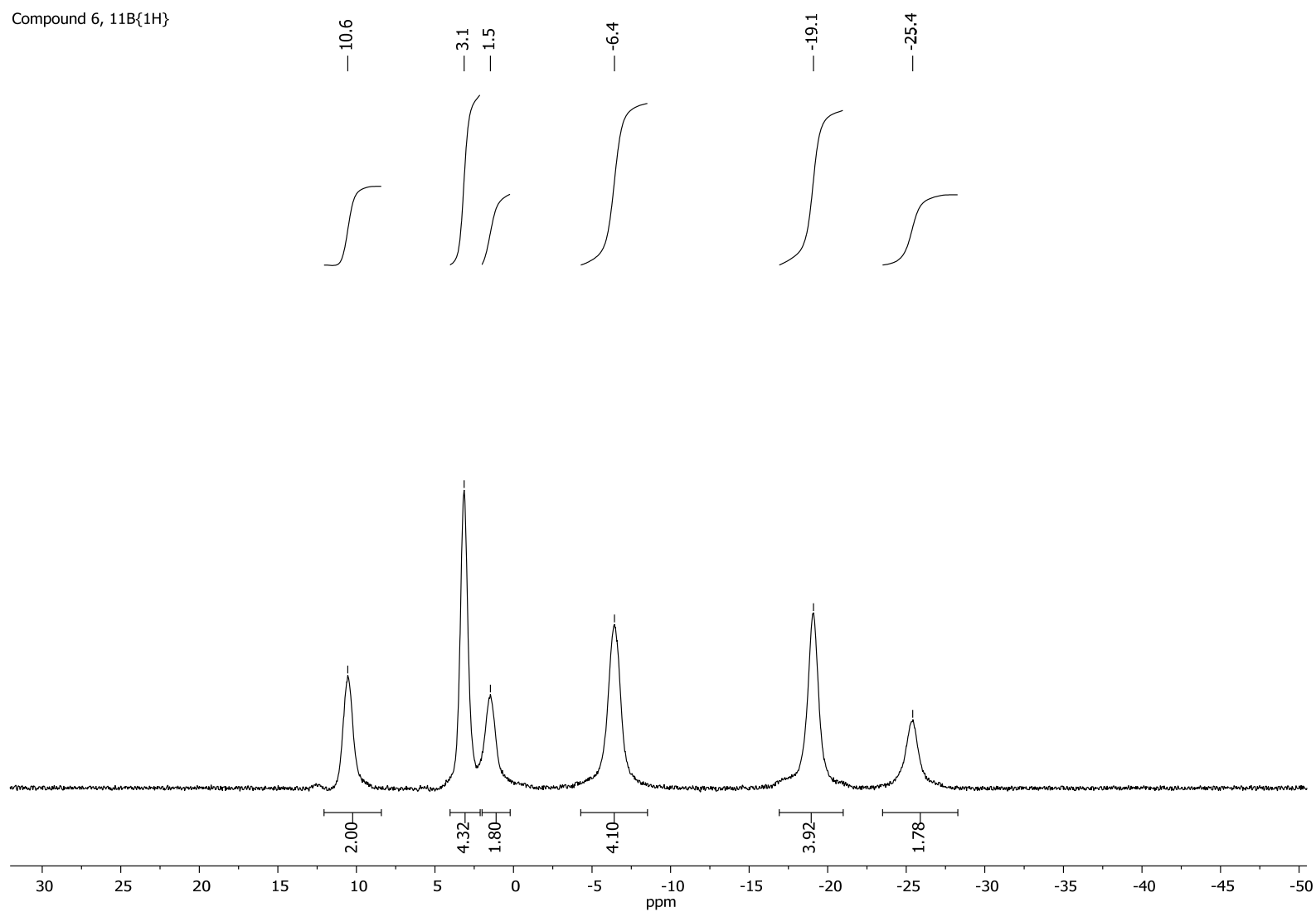
Figure S35. Mass-spectrum of the [9,9',12,12'-Cl<sub>4</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)<sub>2</sub>]<sup>-</sup> anion.

Compound 6,  $^1\text{H}$



**Figure S36.**  $^1\text{H}$  NMR spectrum of  $\text{Cs}[8,8',9,9',12,12'\text{-Cl}_6\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_8)_2]$  in  $\text{acetone-}d_6$ .

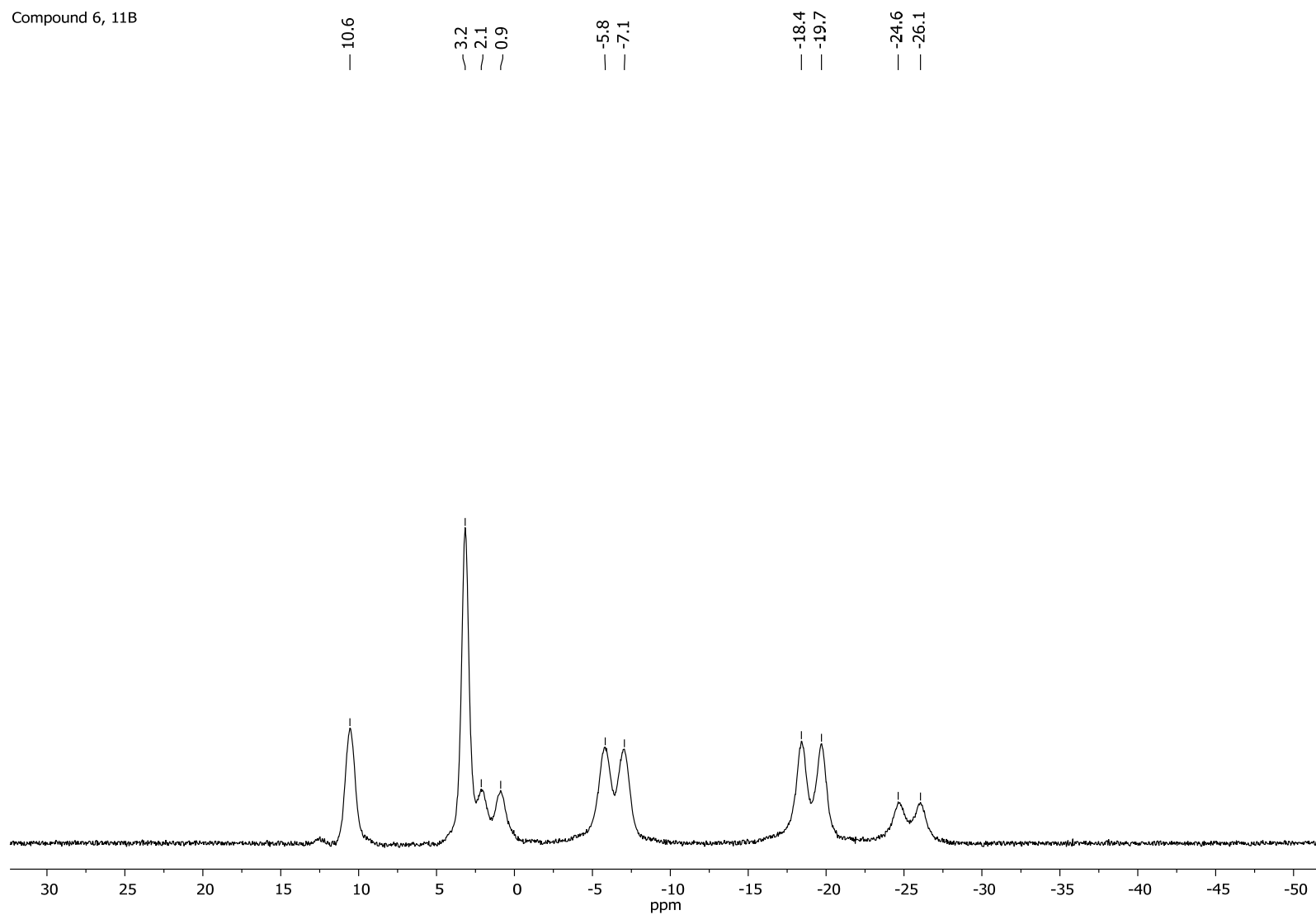
Compound 6,  $^{11}\text{B}\{^1\text{H}\}$



**Figure S36.**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $\text{Cs}[8,8',9,9',12,12'\text{-Cl}_6\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_8)_2]$  in  $\text{acetone-}d_6$ .



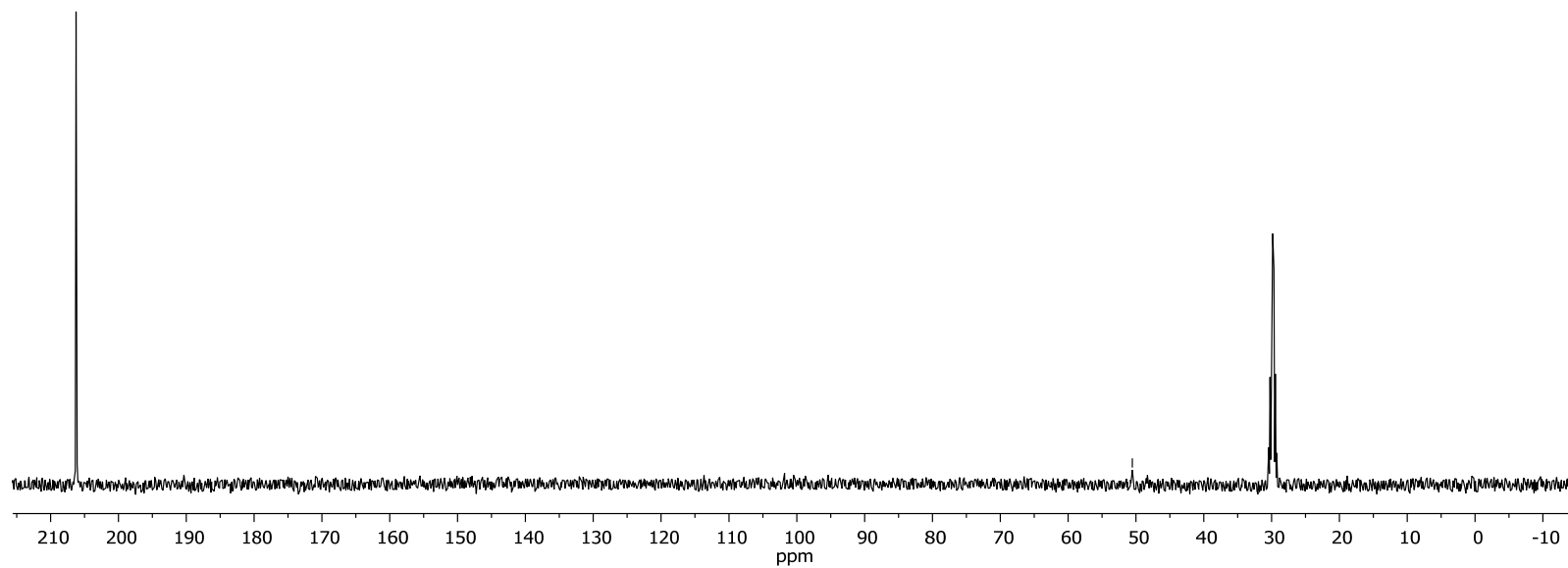
Compound 6, 11B



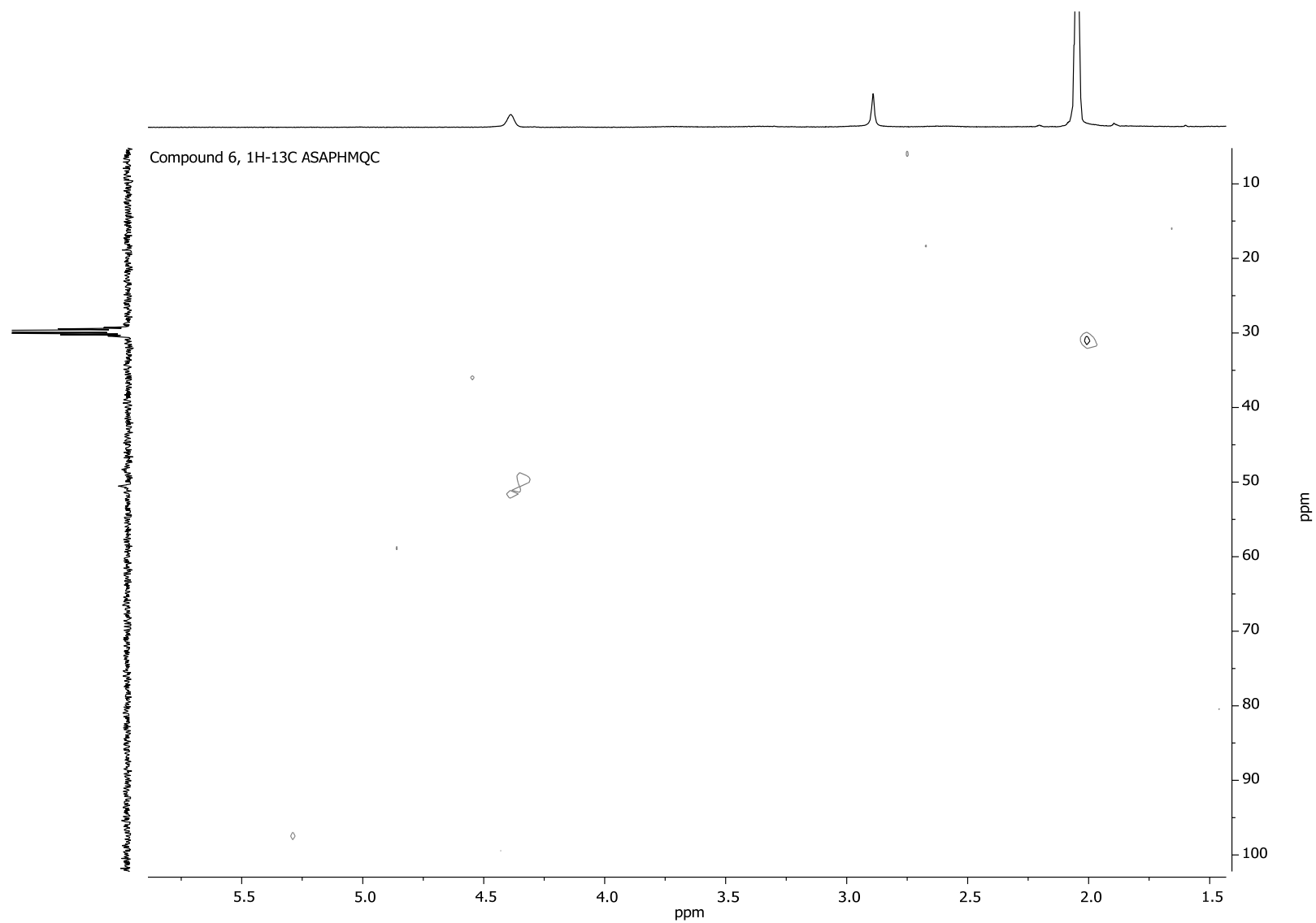
**Figure S38.**  $^{11}\text{B}$  NMR spectrum of  $\text{Cs}[8,8',9,9',12,12'\text{-Cl}_6\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_8)_2]$  in  $\text{acetone-}d_6$ .

Compound 6,  $^{13}\text{C}\{^1\text{H}\}$

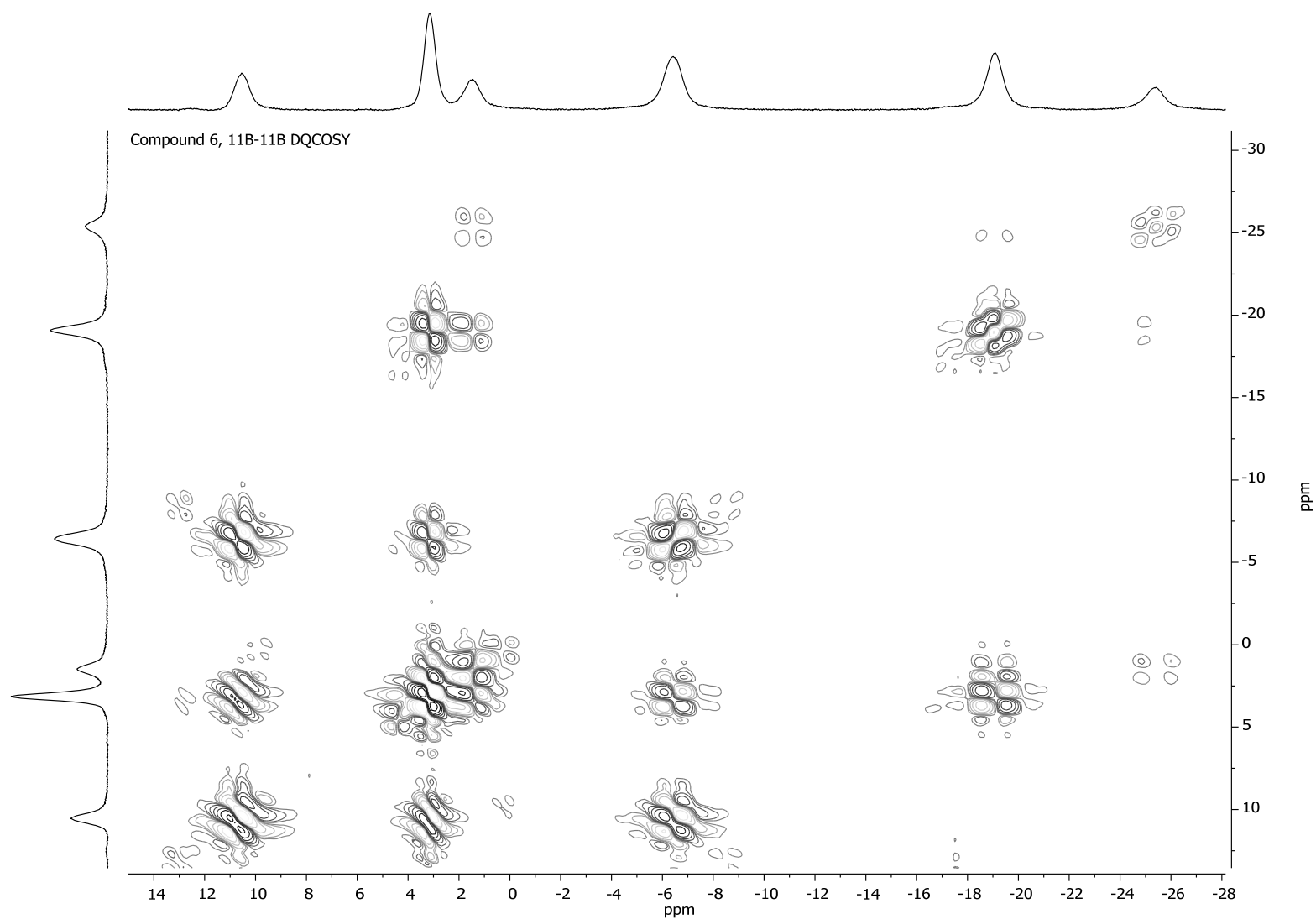
— 50.5



**Figure S39.**  $^{13}\text{C}$  NMR spectrum of  $\text{Cs}[8,8',9,9',12,12'\text{-Cl}_6\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_8)_2]$  in acetone- $d_6$ .



**Figure S40.**  $^1\text{H}$ - $^{13}\text{C}$  ASAPHMQC NMR spectrum of  $\text{Cs}[8,8',9,9',12,12'\text{-Cl}_6\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_8)_2]$  in acetone- $d_6$ .



**Figure S41.**  $^{11}\text{B}$ - $^{11}\text{B}$  DQCOSY NMR spectrum of  $\text{Cs}[8,8',9,9',12,12'\text{-Cl}_6\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_8)_2]$  in acetone- $d_6$ .

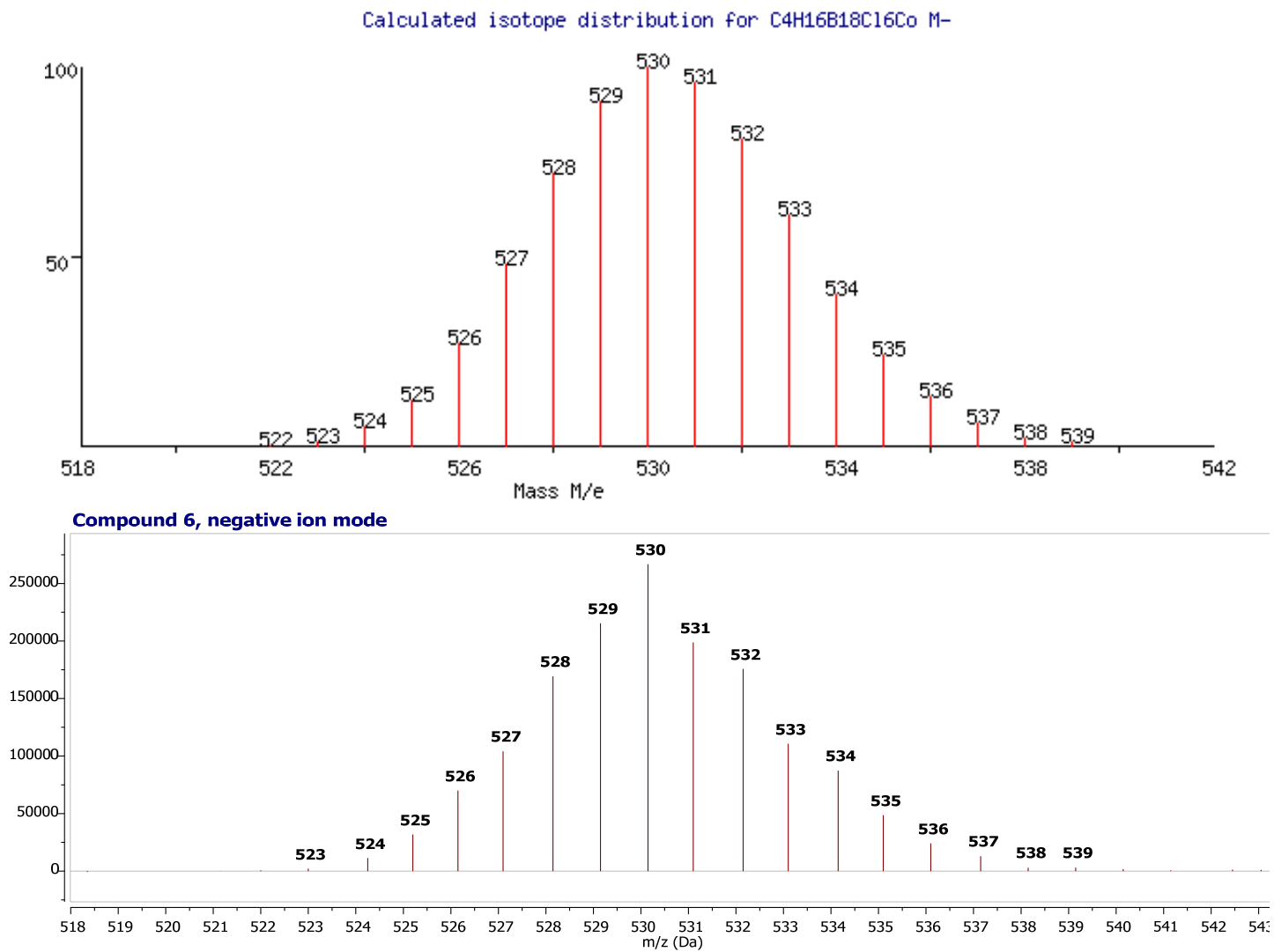


Figure S42. Mass-spectrum of the [8,8',9,9',12,12'-Cl<sub>6</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>)<sub>2</sub>]<sup>-</sup> anion.