

## SUPPORTING INFORMATION

### Synthesis of Bis(Carboranyl)amides 1,1'- $\mu$ -(CH<sub>2</sub>NH(O)C(CH<sub>2</sub>)<sub>n</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)<sub>2</sub> (n = 0, 1) and Attempt of Synthesis of Gadolinium Bis(Dicarbollide)

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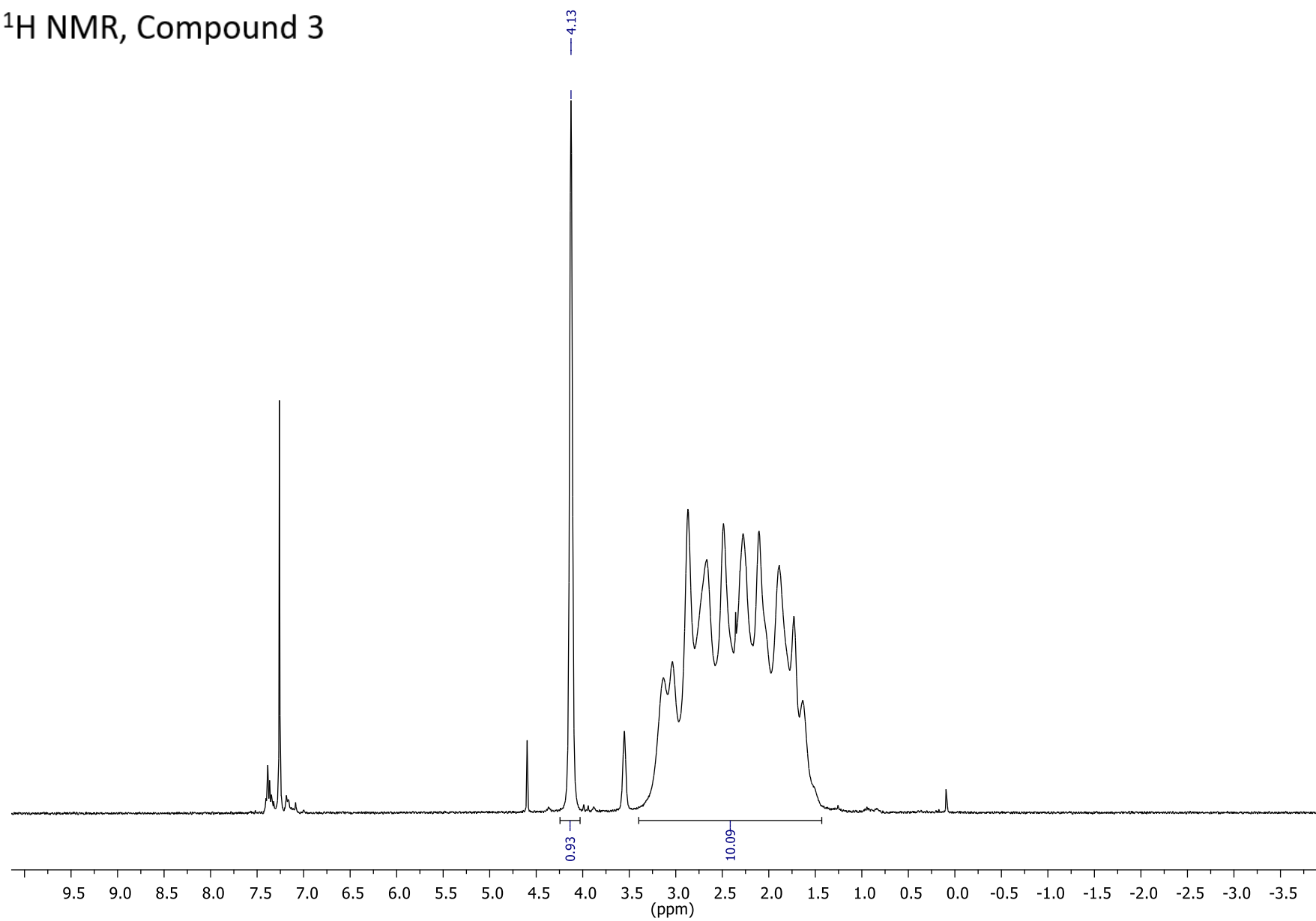
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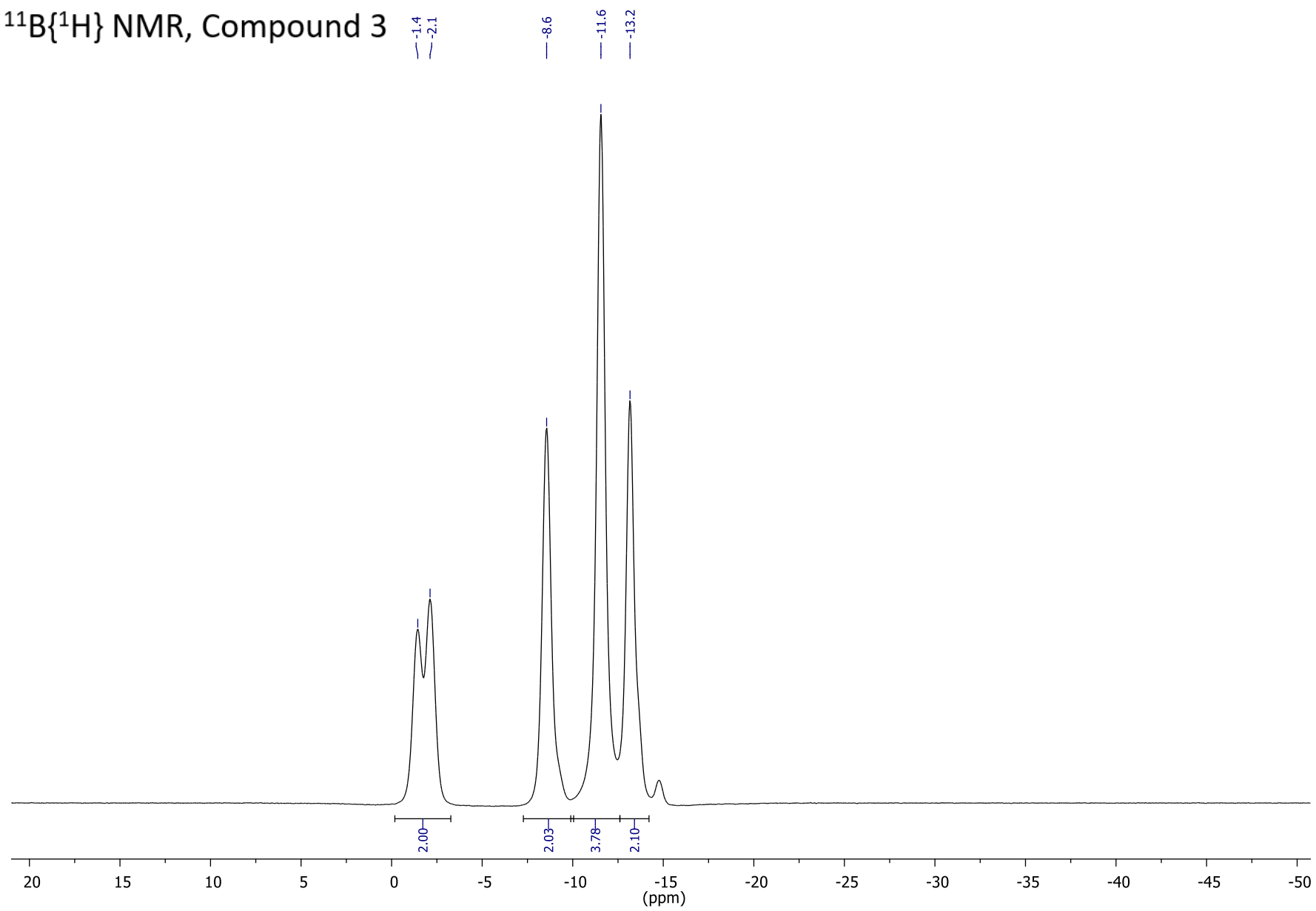
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NMR spectra of compound <b>3</b>	2
NMR spectra of compound <b>4</b>	5
NMR spectra of compound <b>6</b>	10
NMR spectra of compound <b>7</b>	13
NMR spectra of compound (Me <sub>3</sub> NH) <sub>2</sub> [ <b>8</b> ]	18
NMR spectra of compound (Me <sub>3</sub> NH) <sub>2</sub> [ <b>9</b> ]	23
NMR spectra of compound Cs <sub>2</sub> [ <b>9</b> ]	26
Geometry characteristics of compound <b>4</b>	29
Geometry and energies of [Gd(C <sub>2</sub> B <sub>9</sub> H <sub>11</sub> ) <sub>2</sub> (DME)] <sup>-</sup> rotamers	30

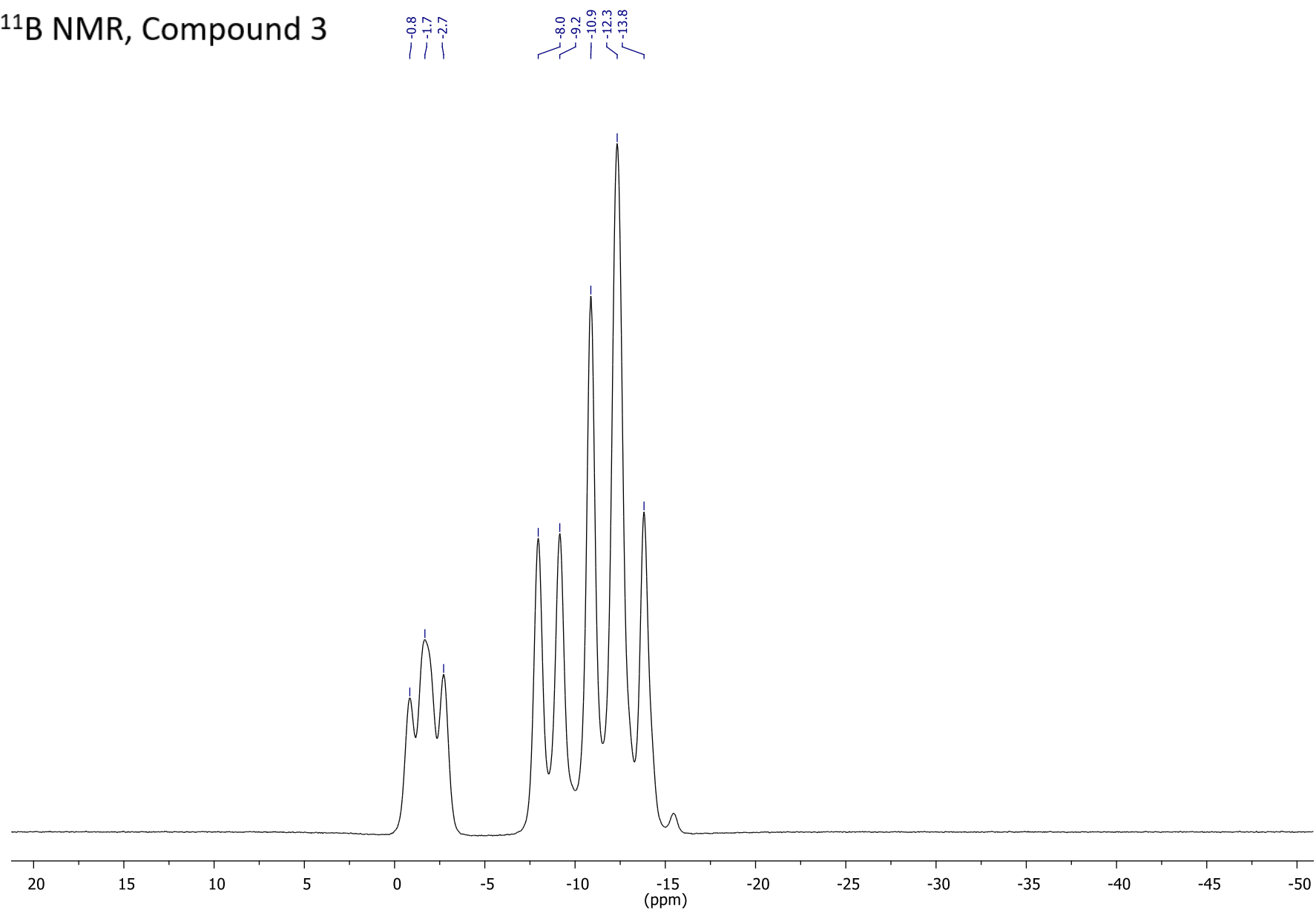
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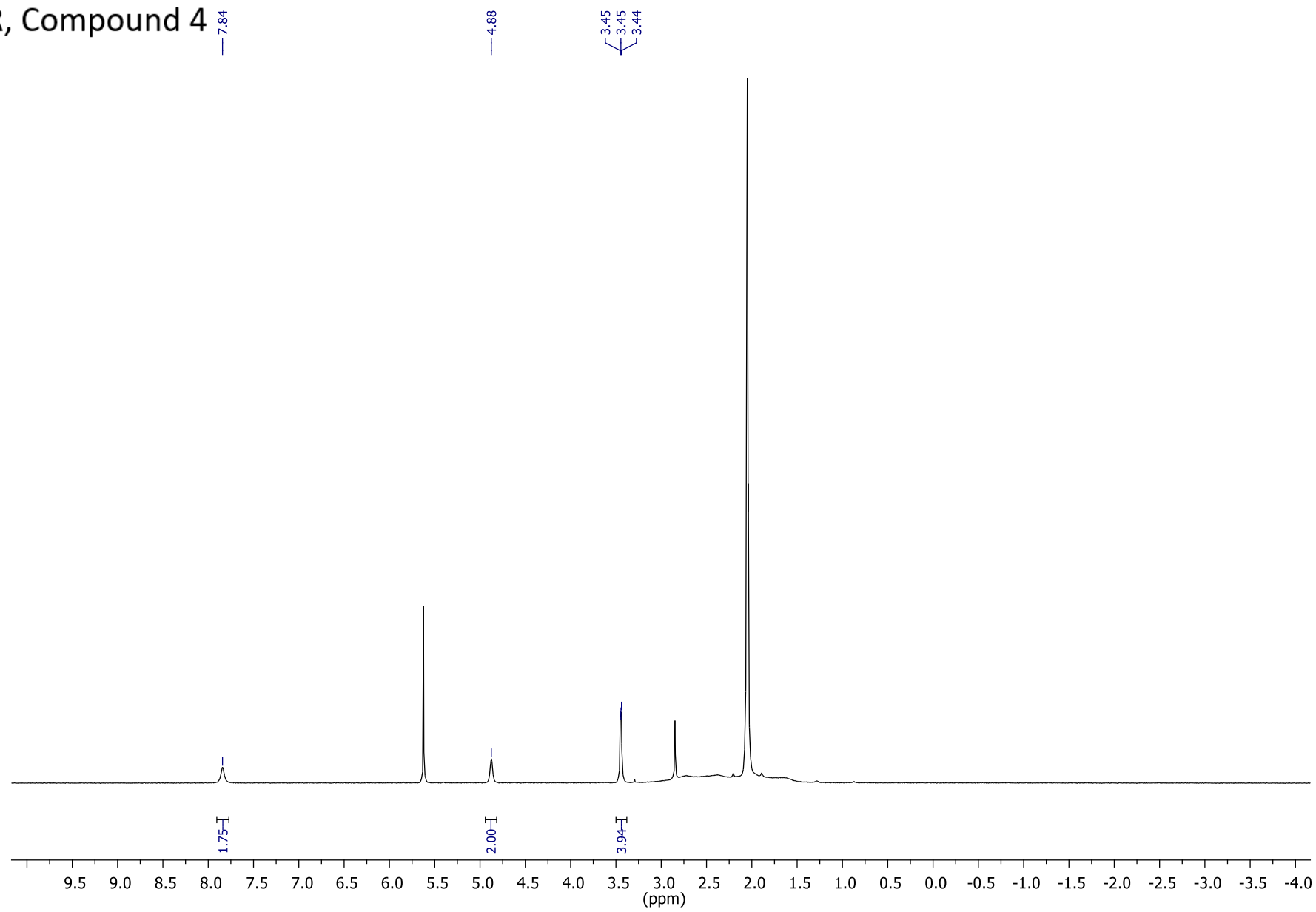
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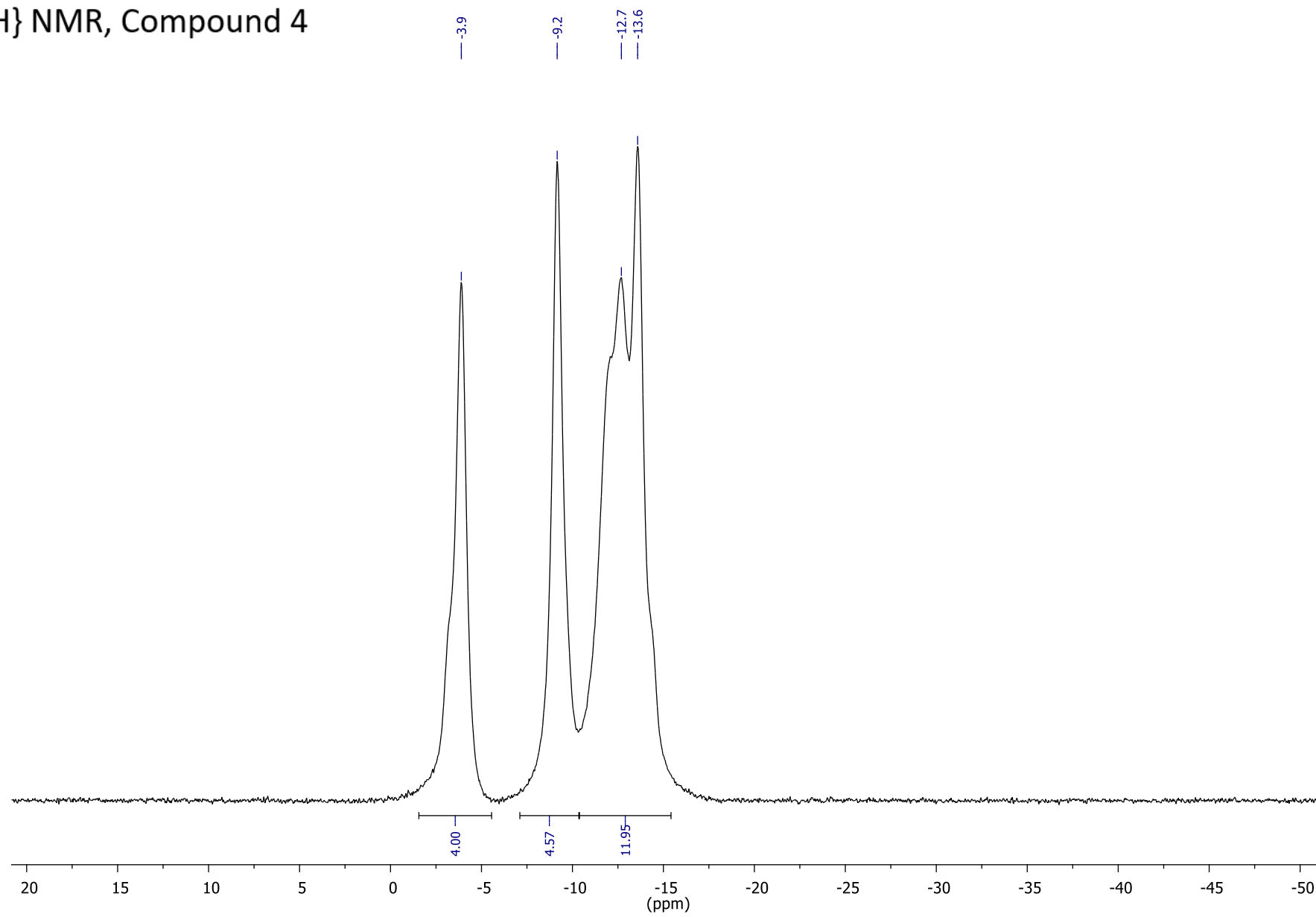
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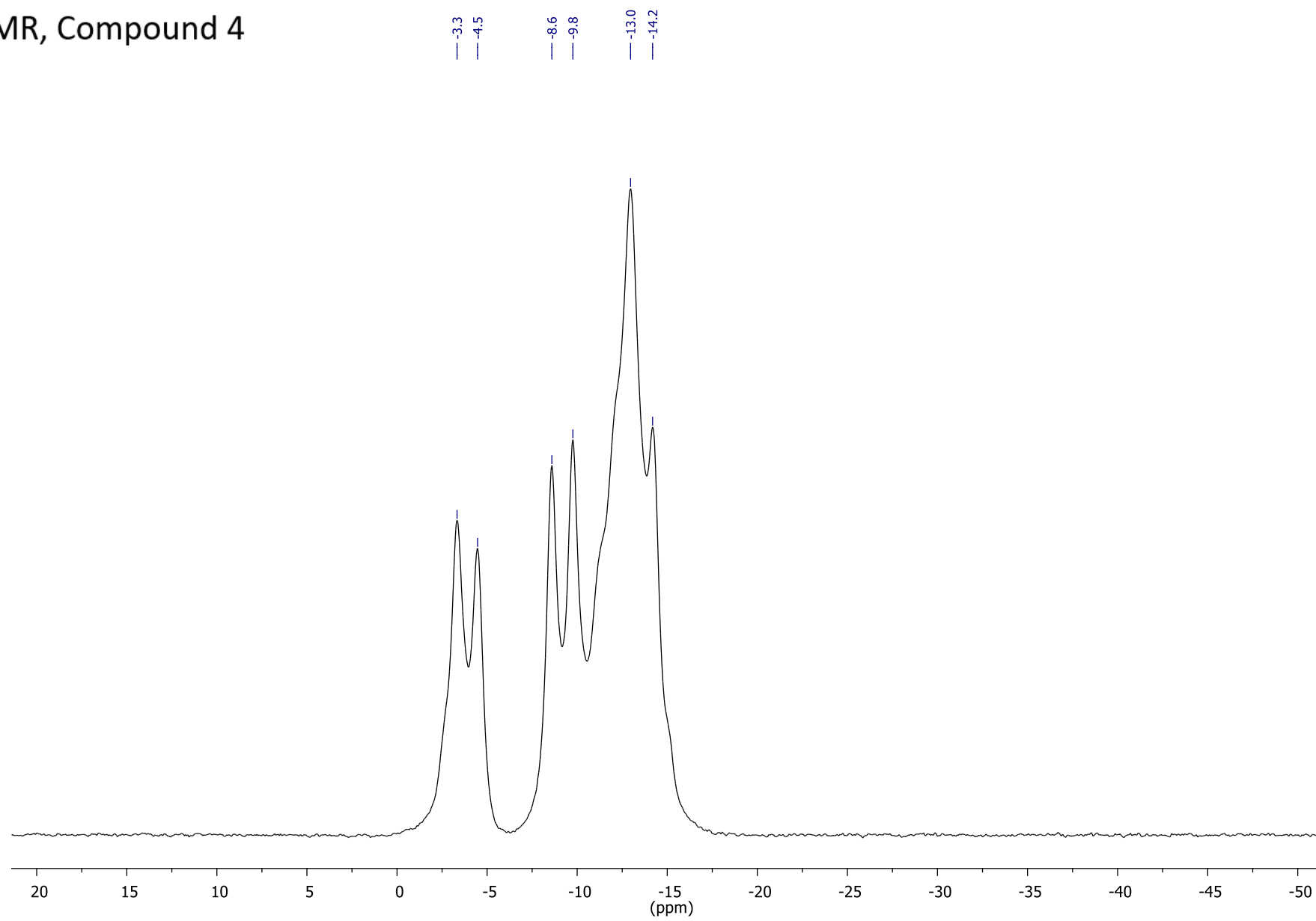
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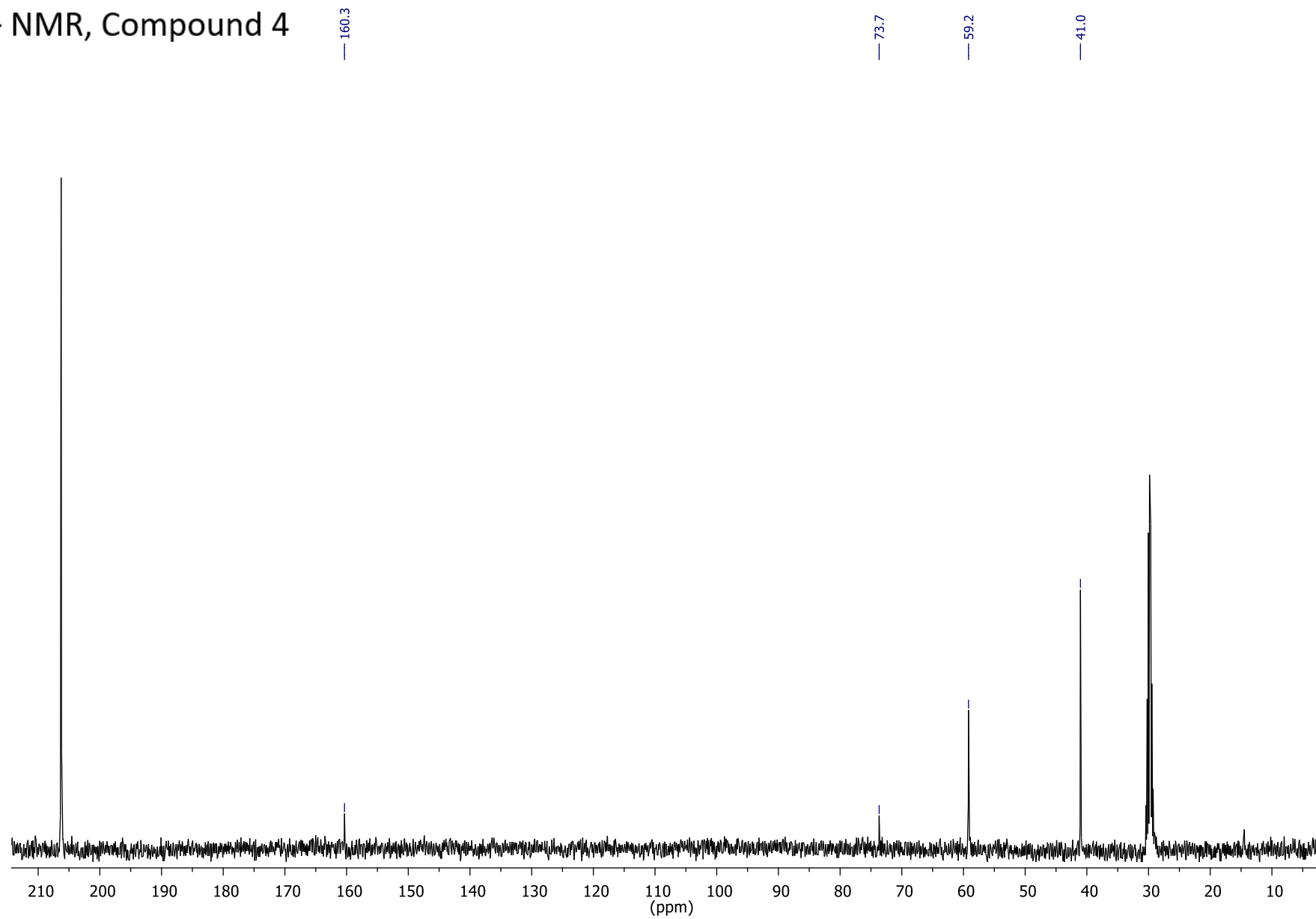
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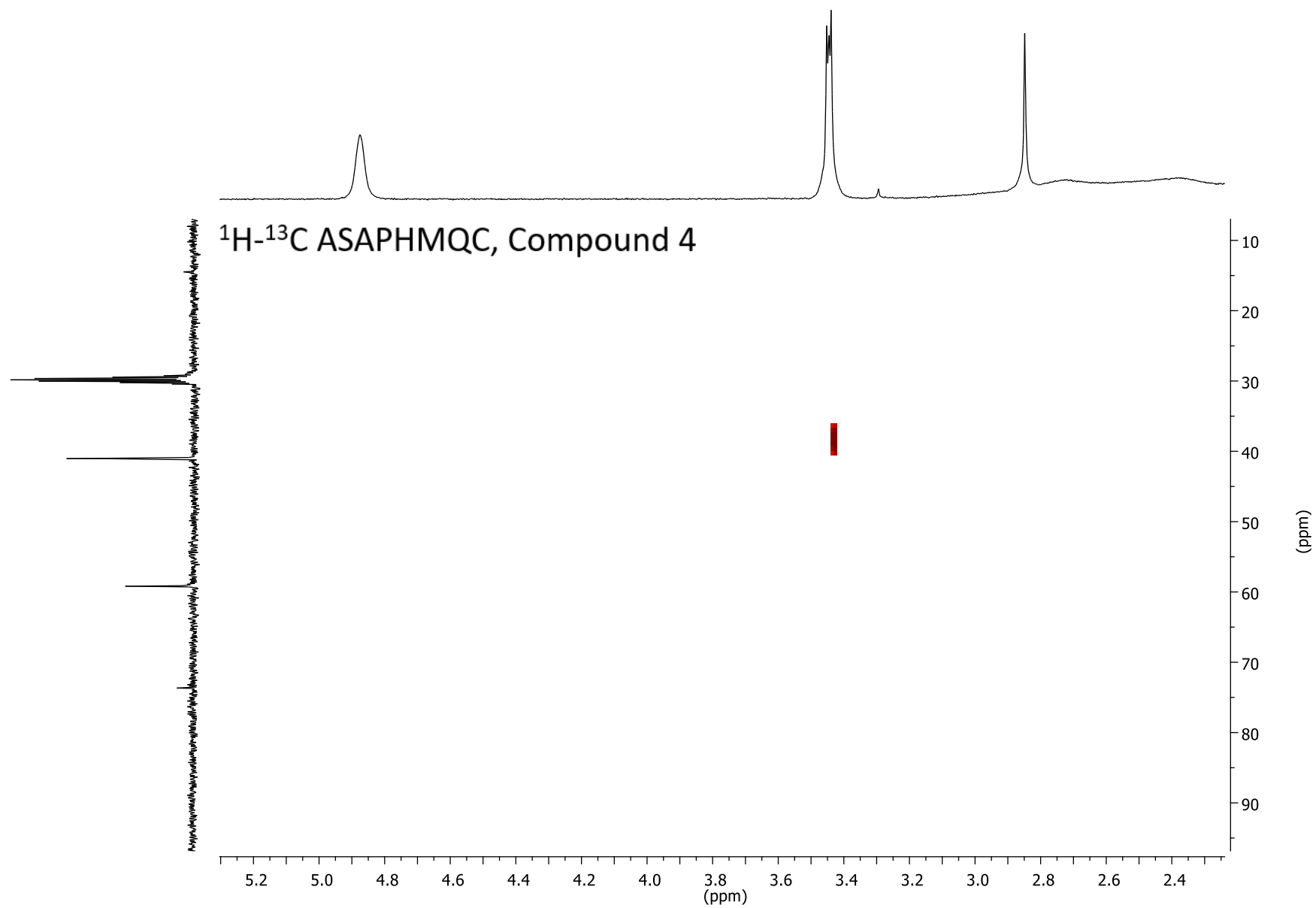
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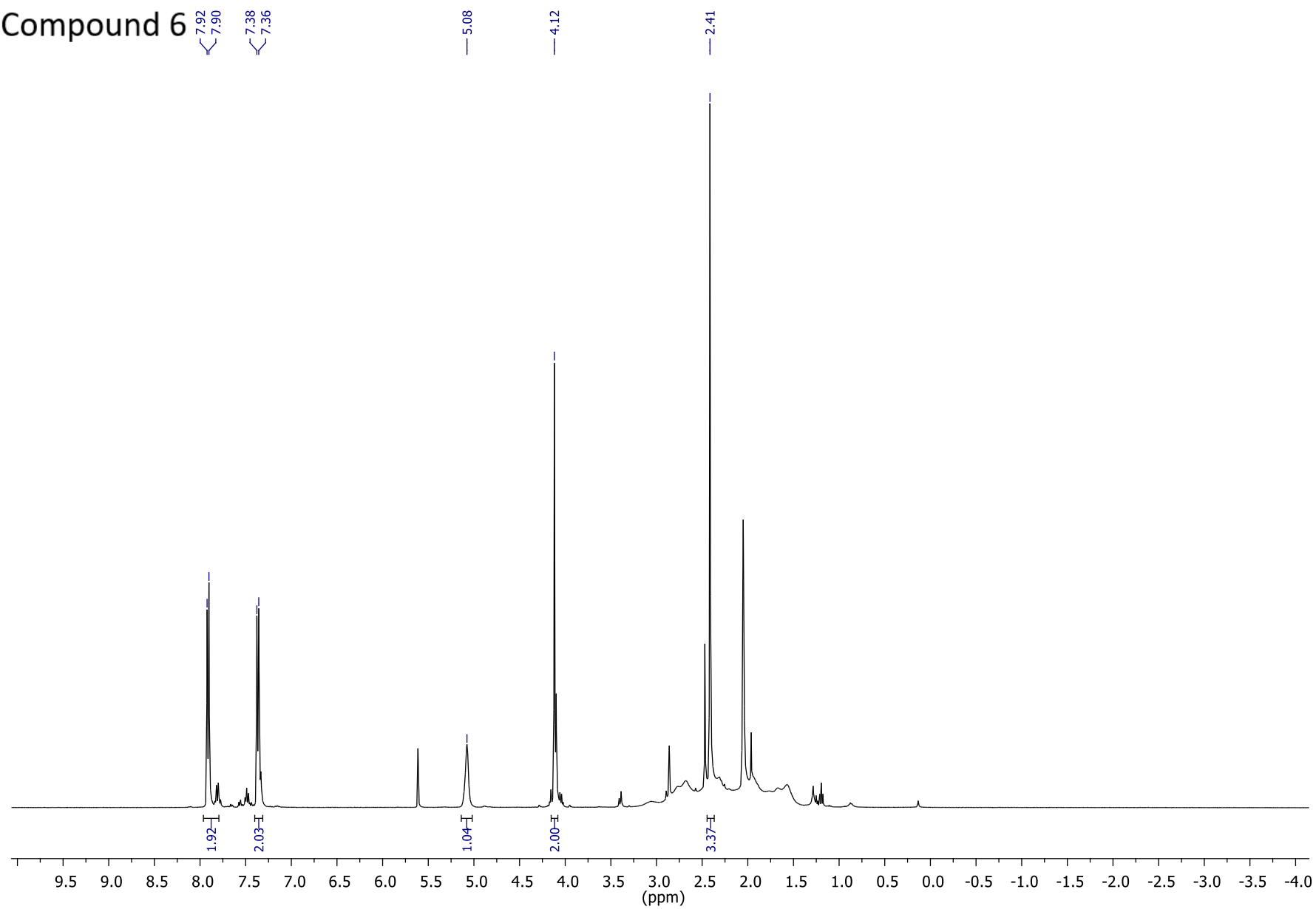
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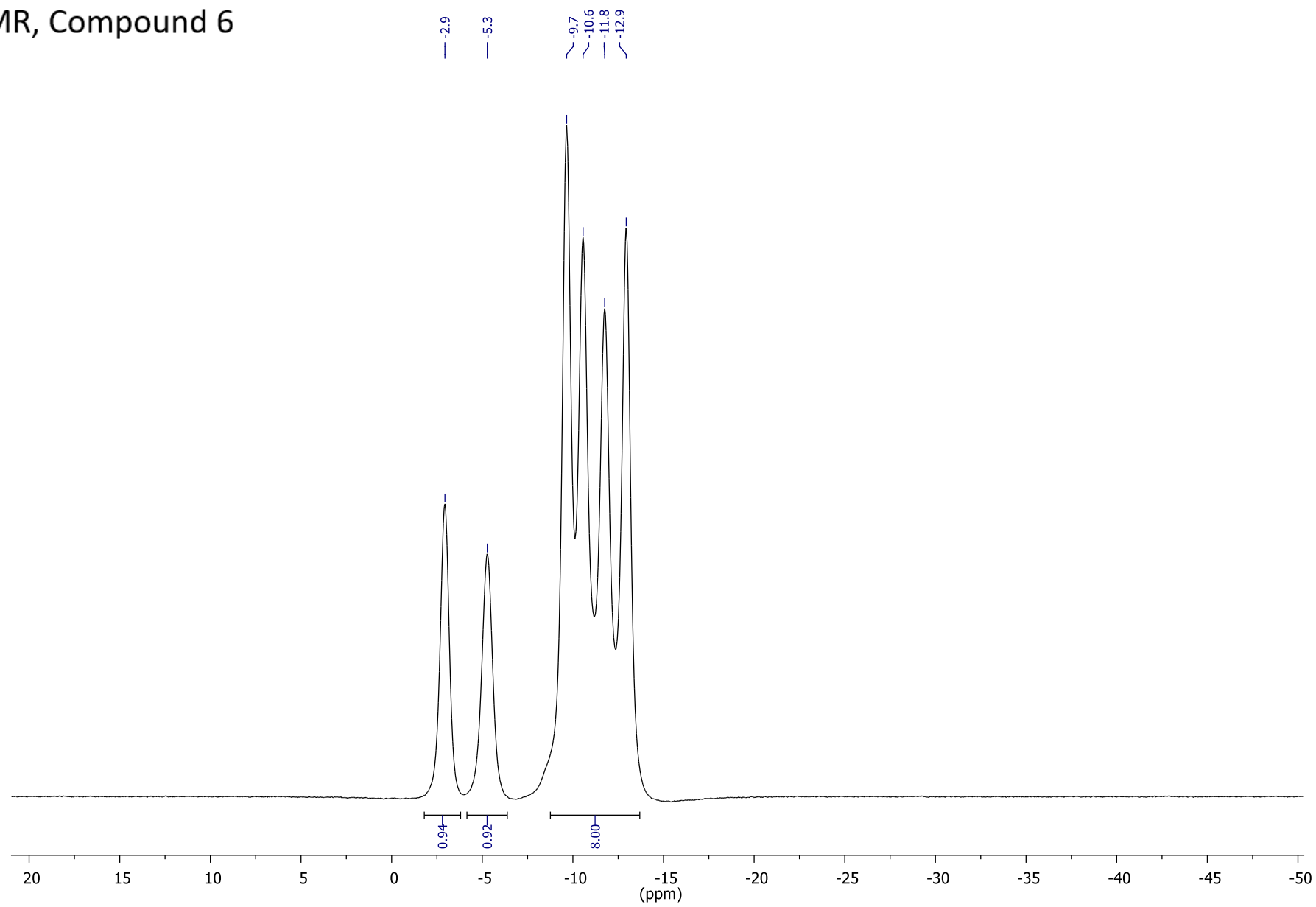




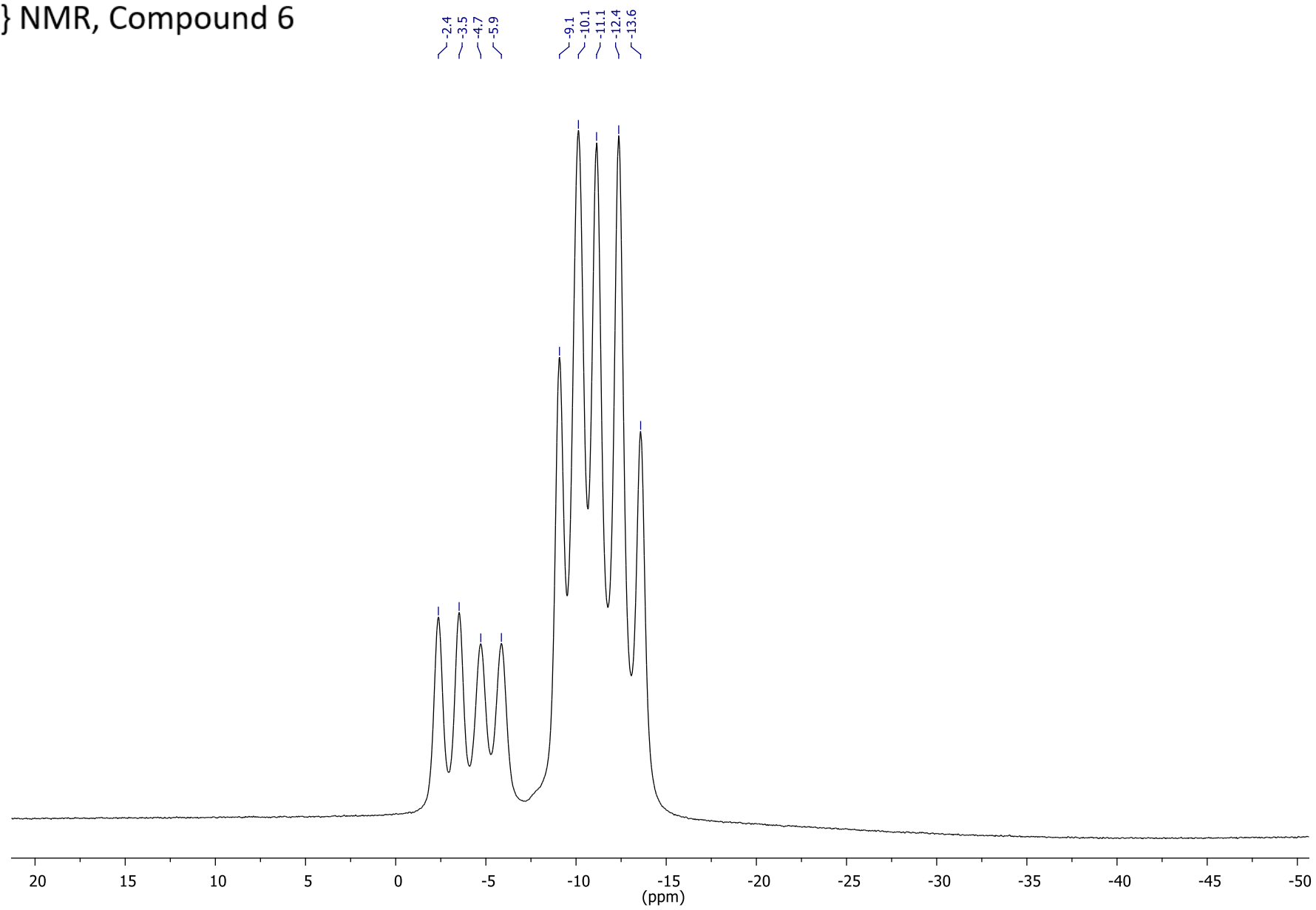
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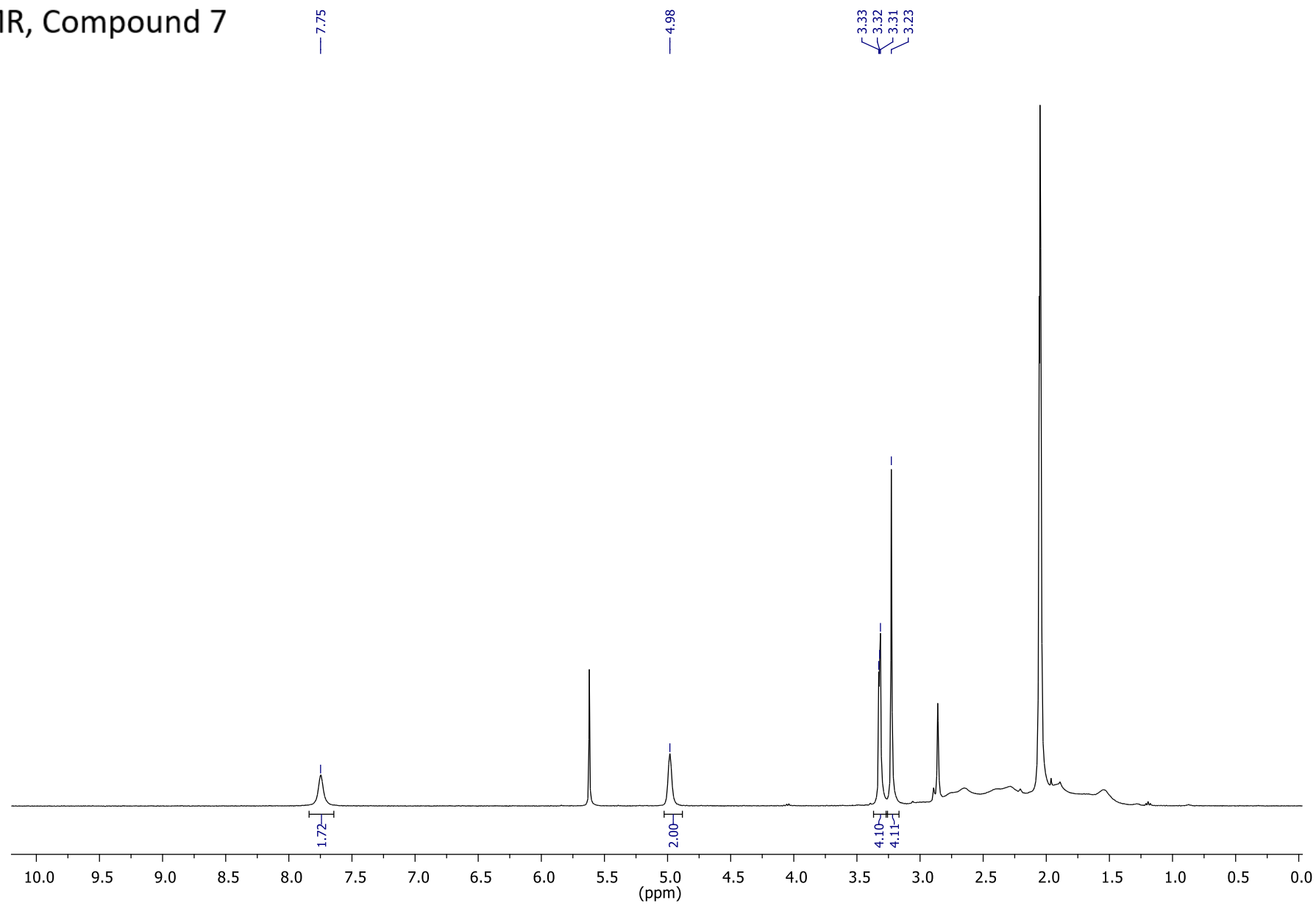
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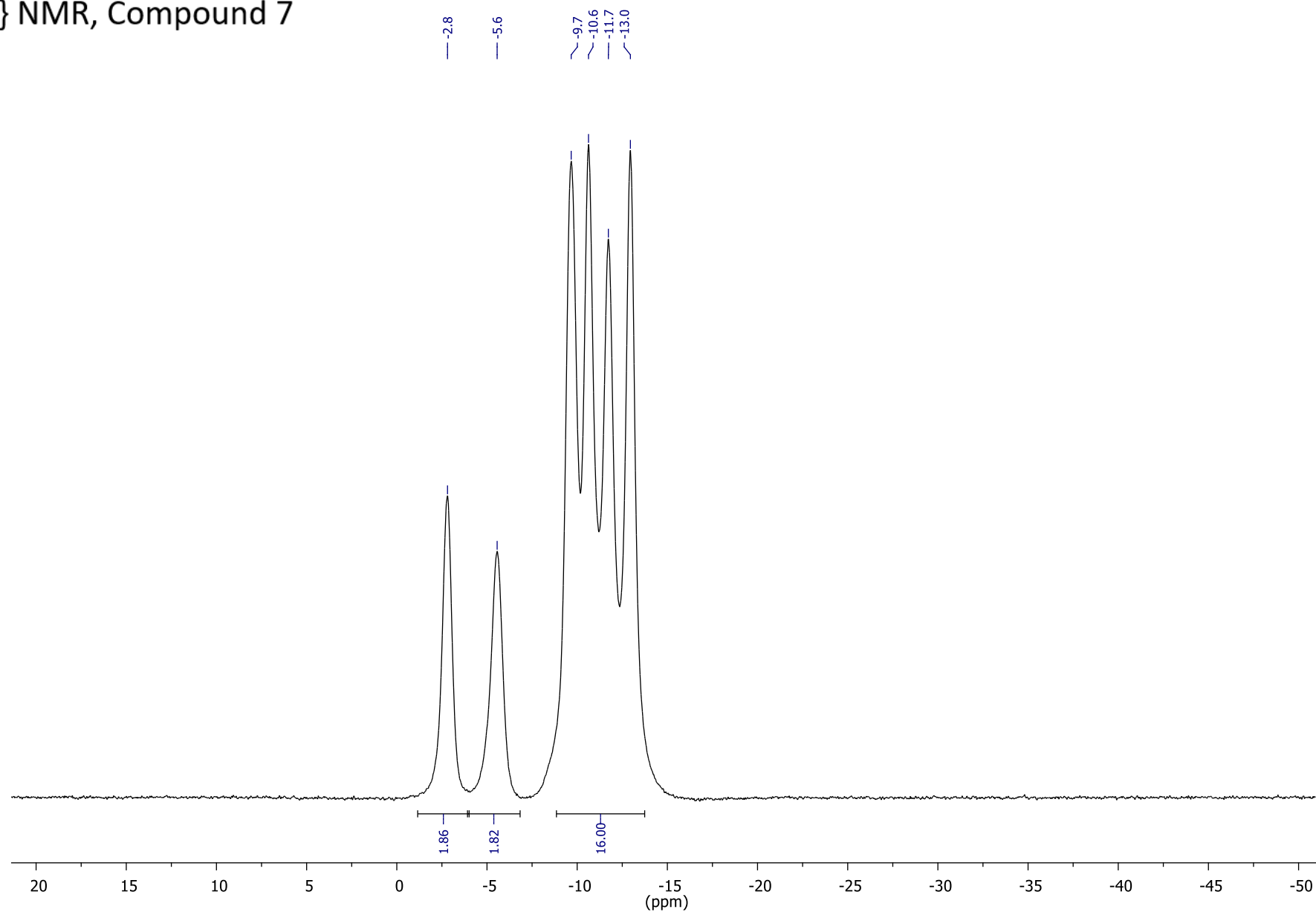
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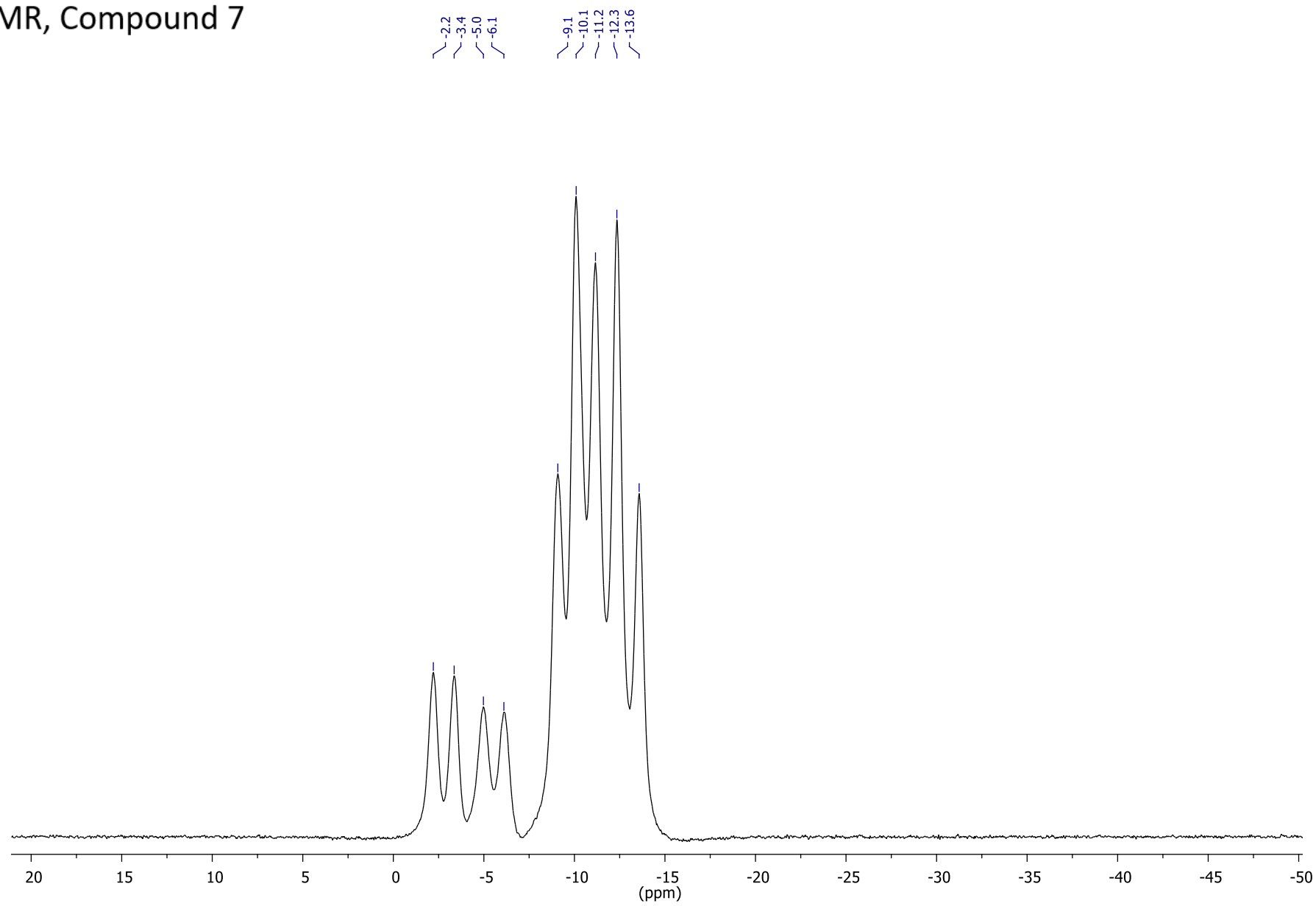
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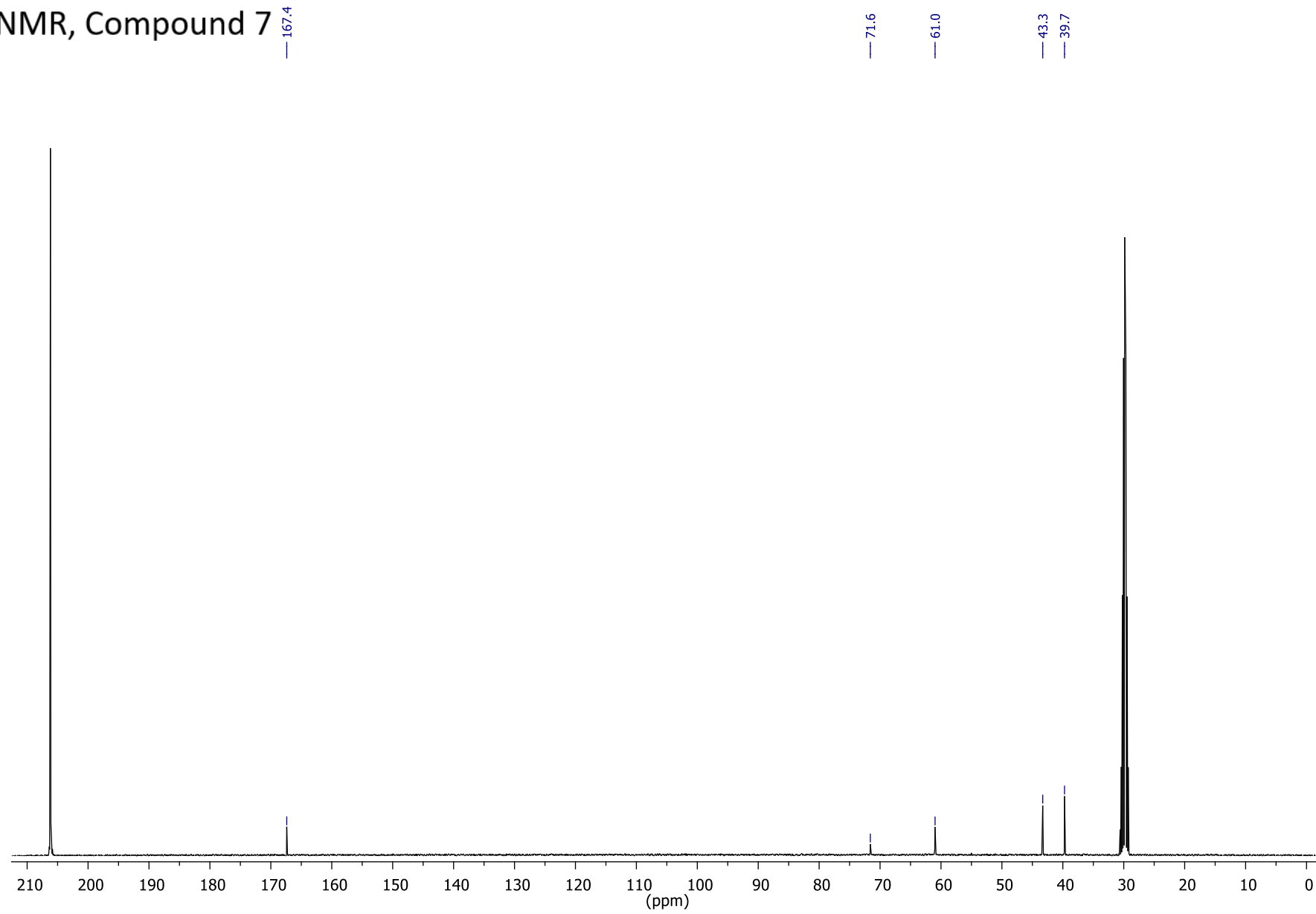
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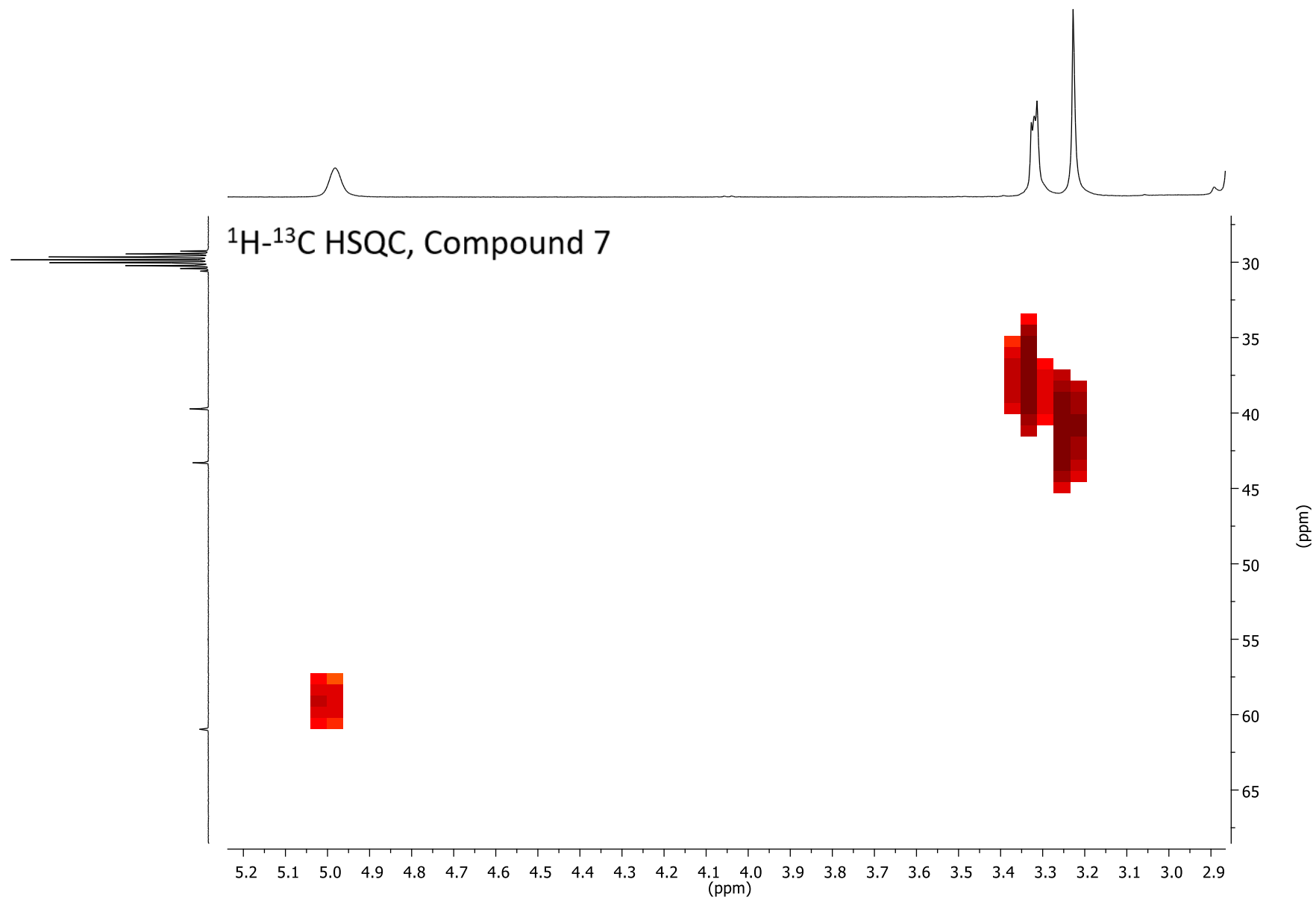
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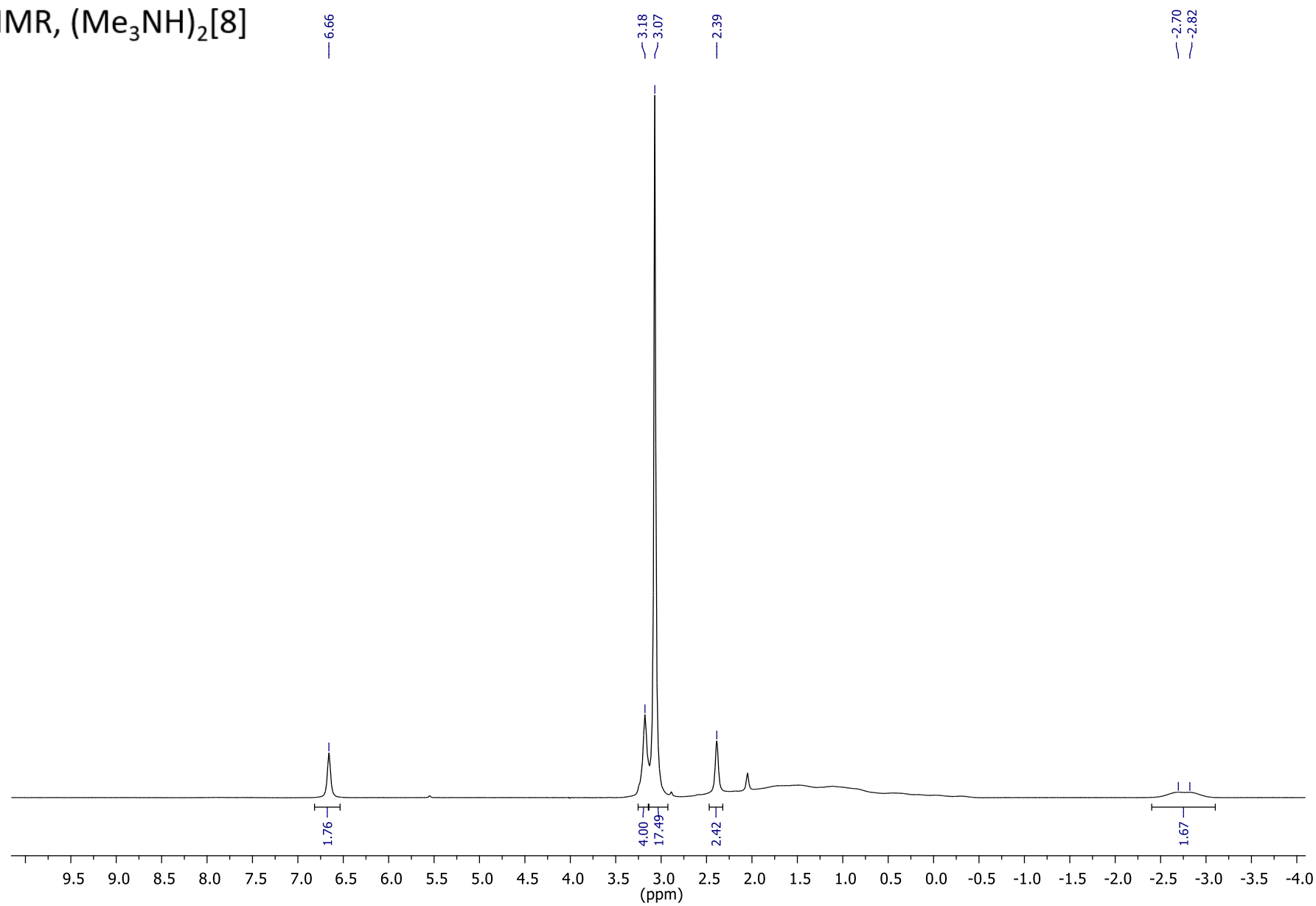
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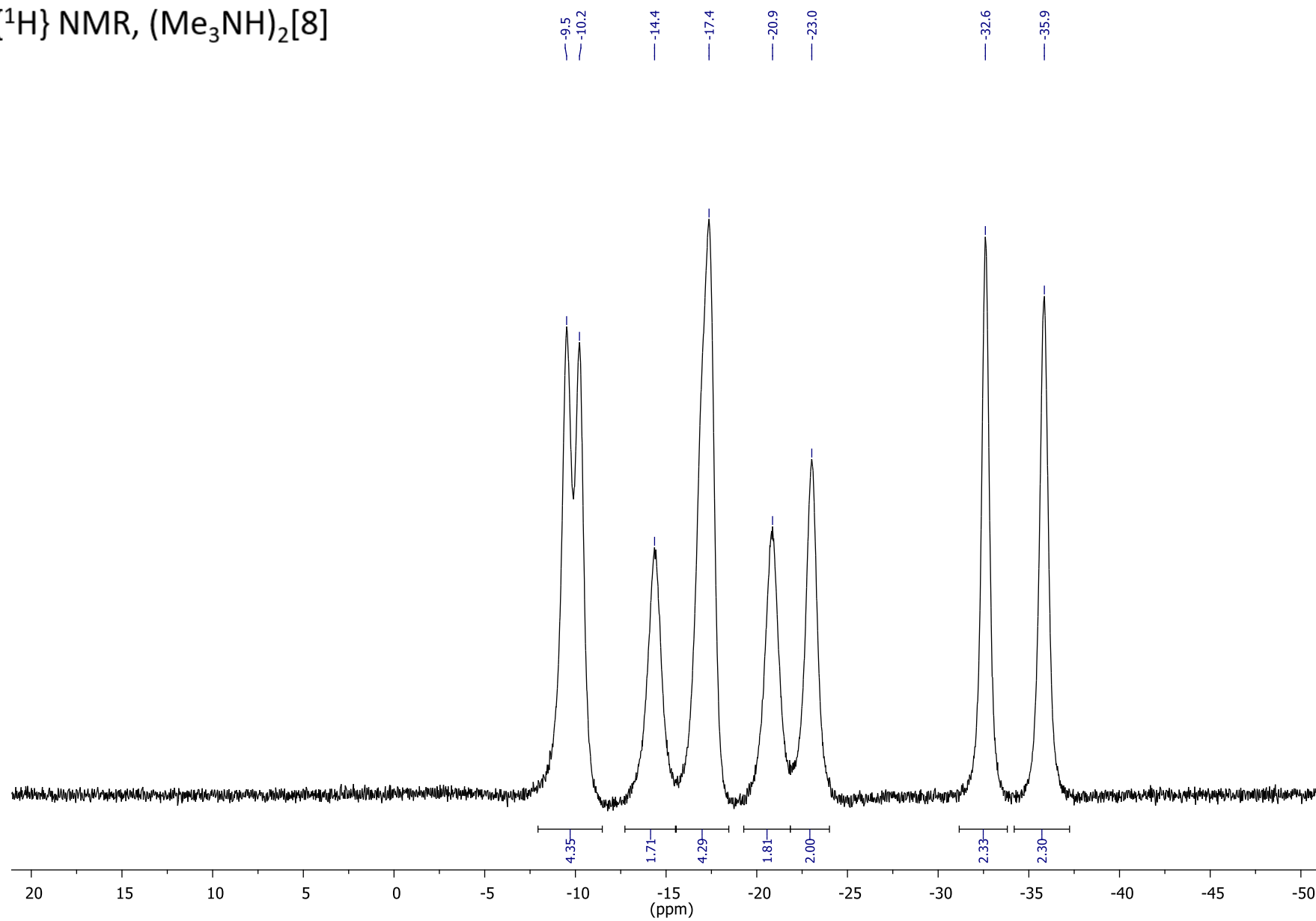




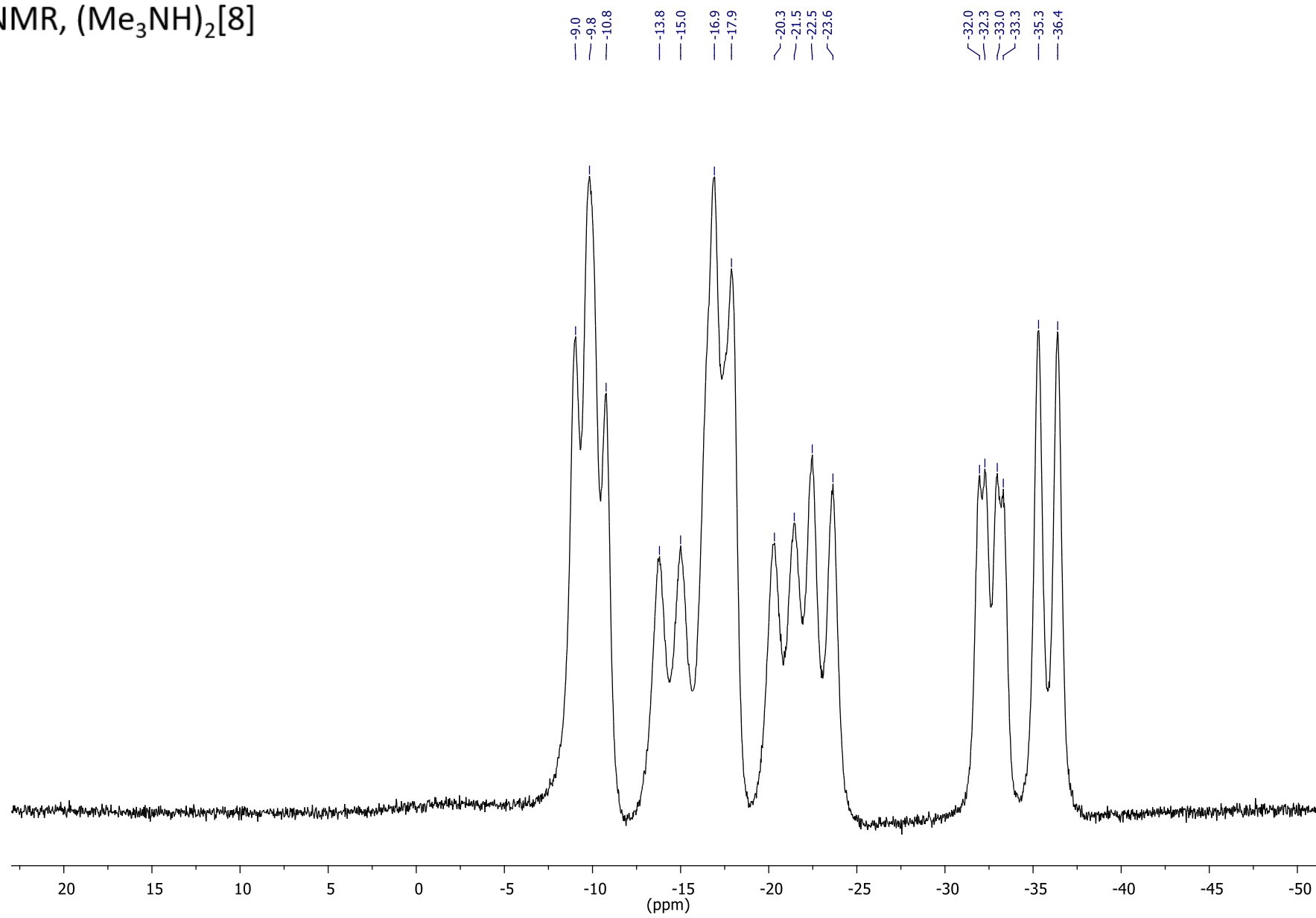
$^1\text{H}$  NMR,  $(\text{Me}_3\text{NH})_2[8]$



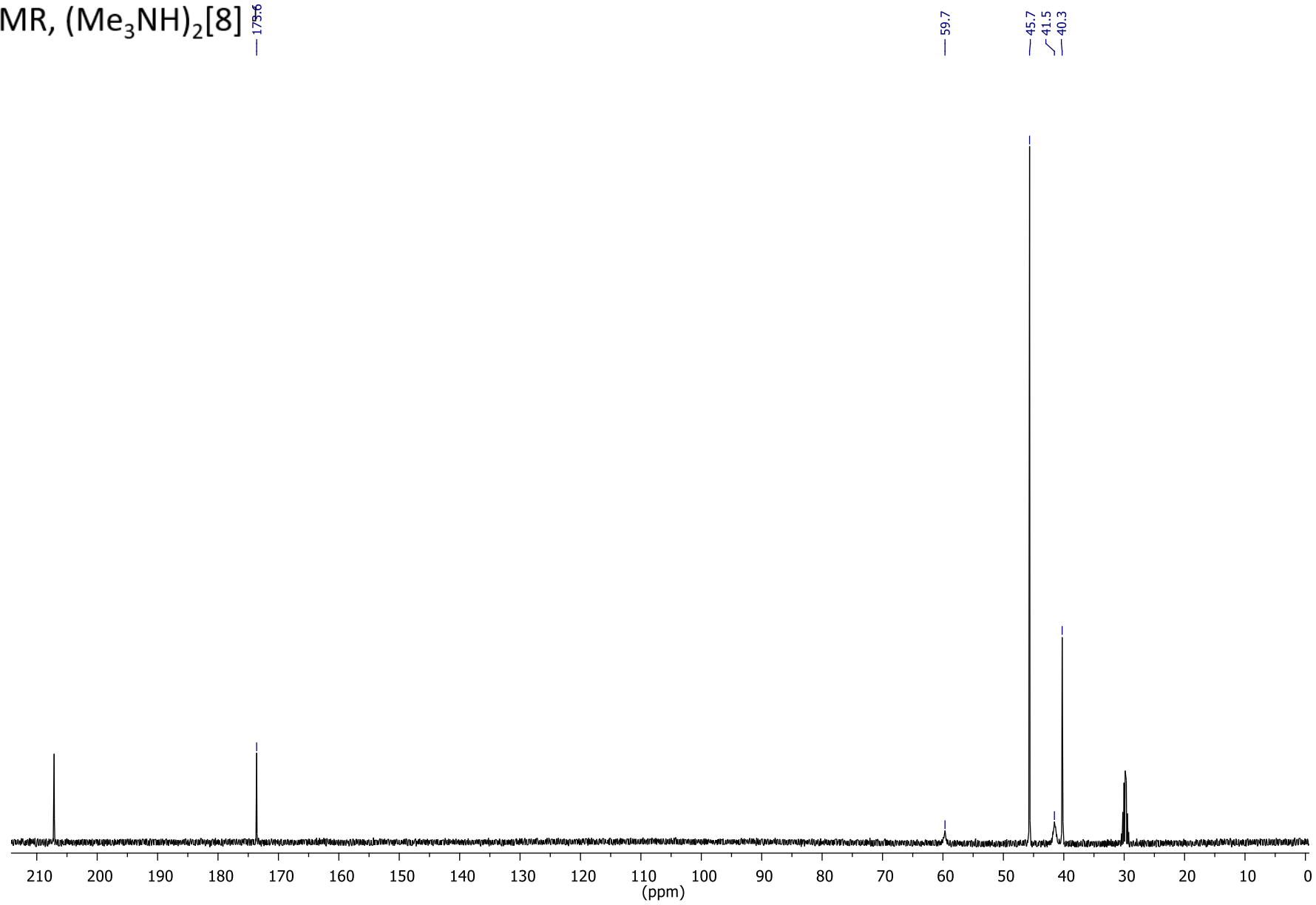
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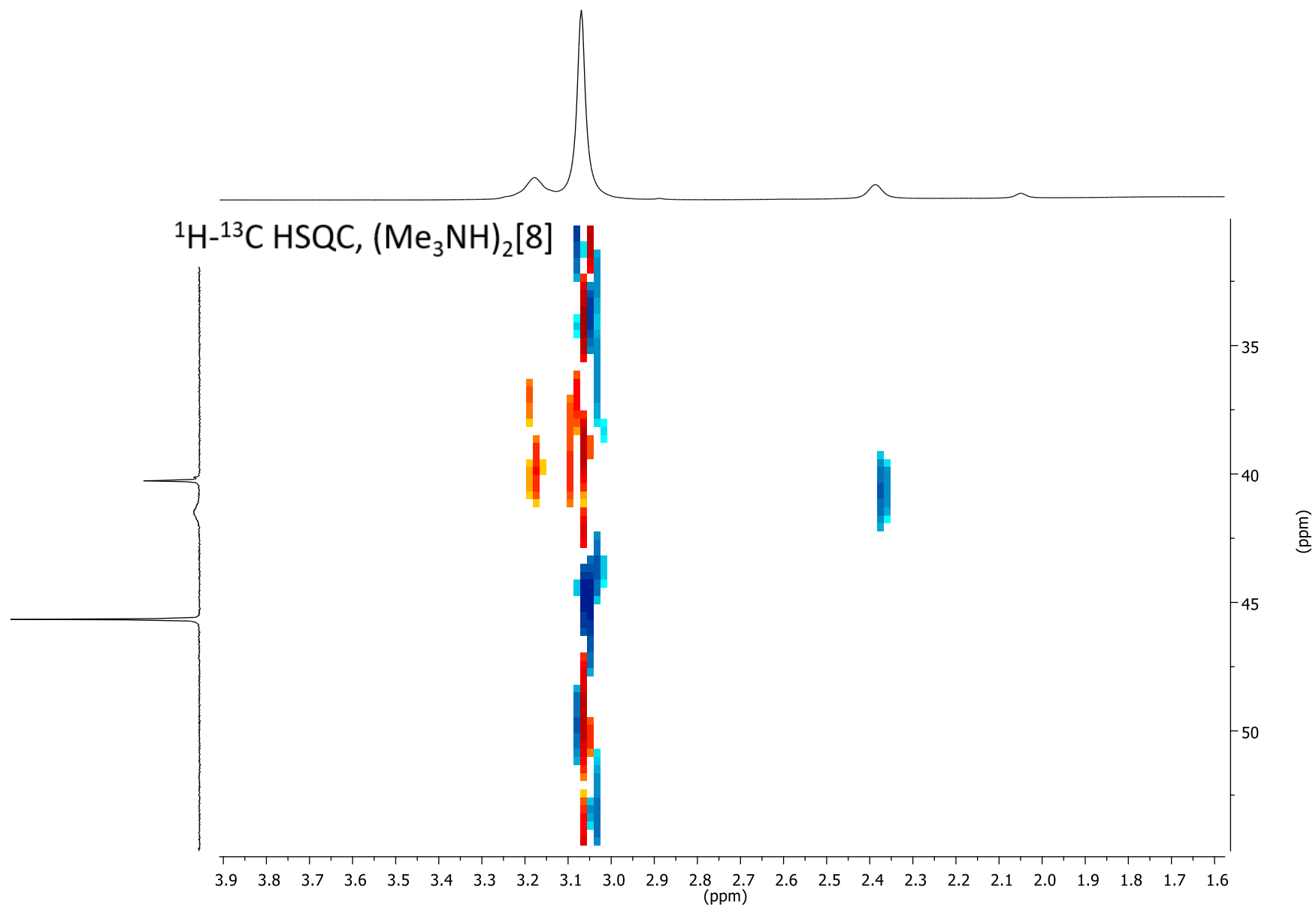


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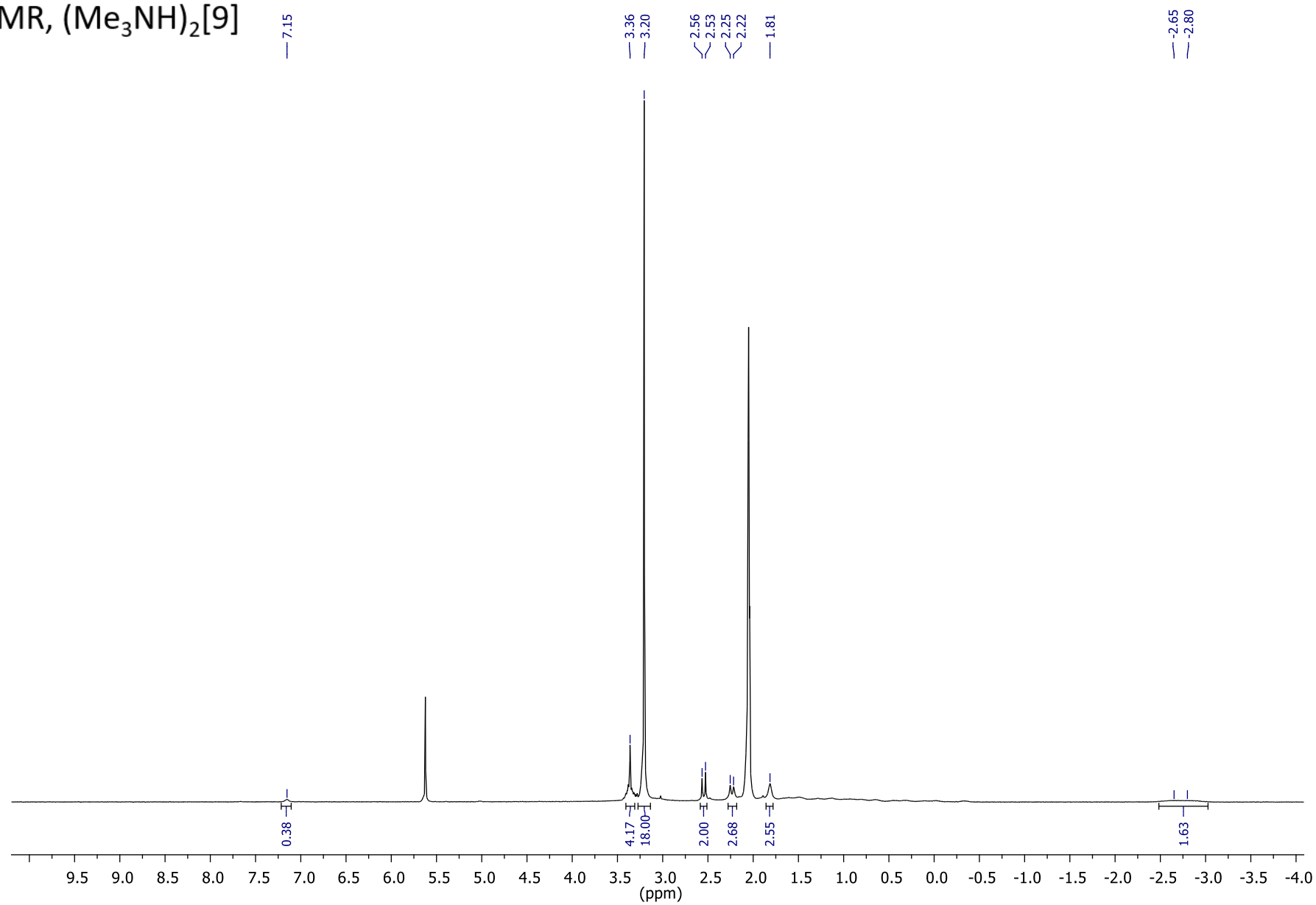


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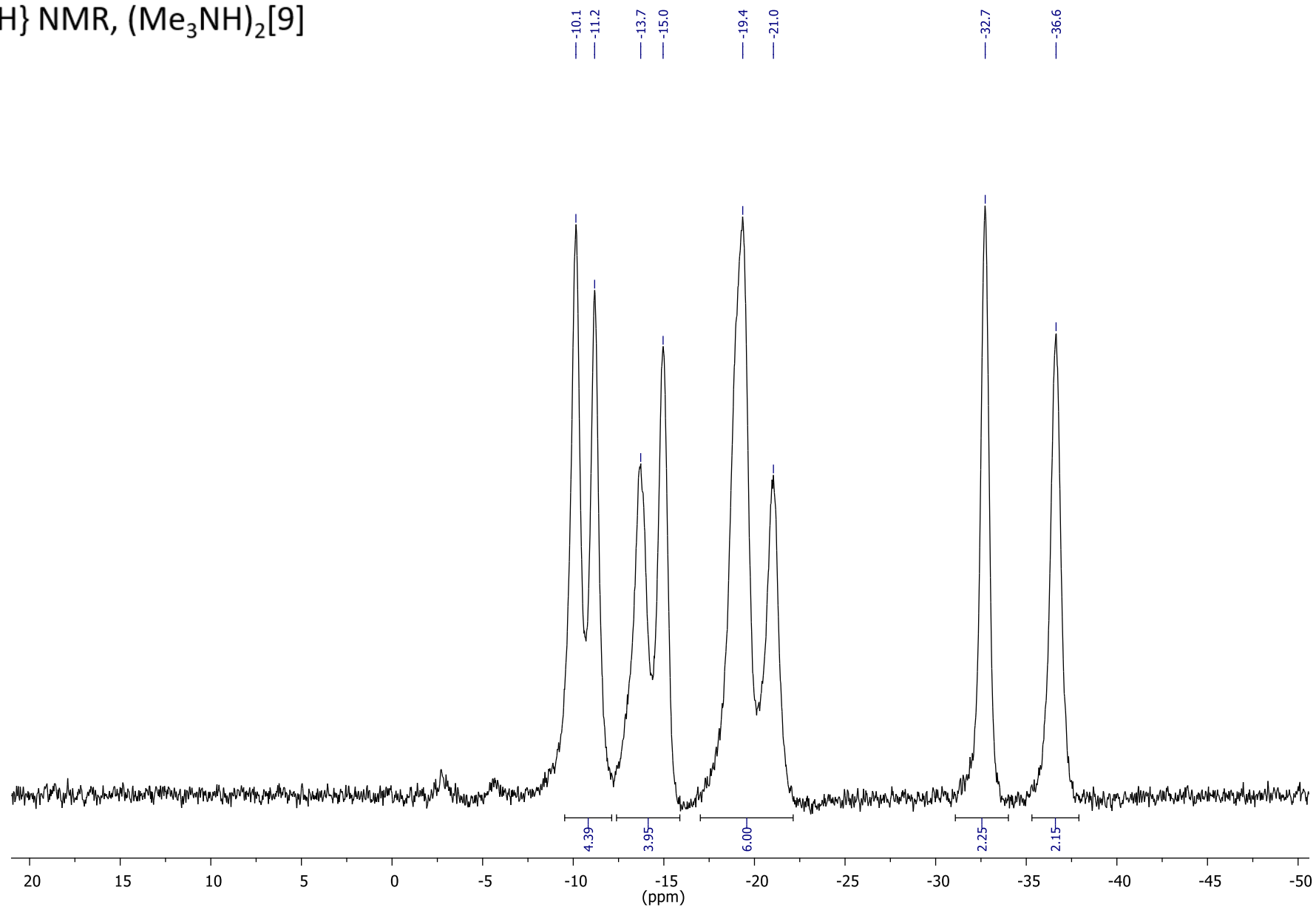




$^1\text{H}$  NMR,  $(\text{Me}_3\text{NH})_2[9]$

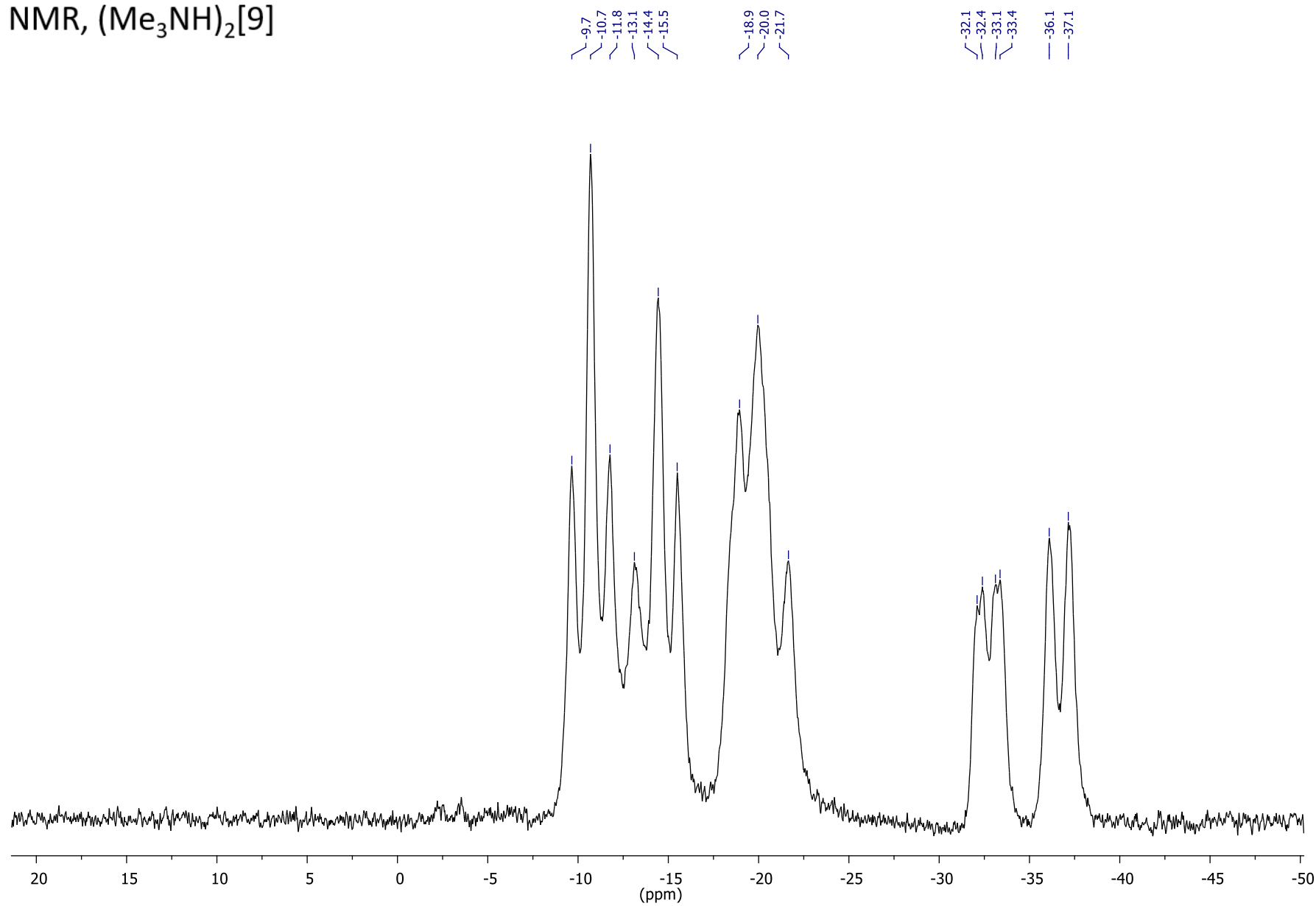


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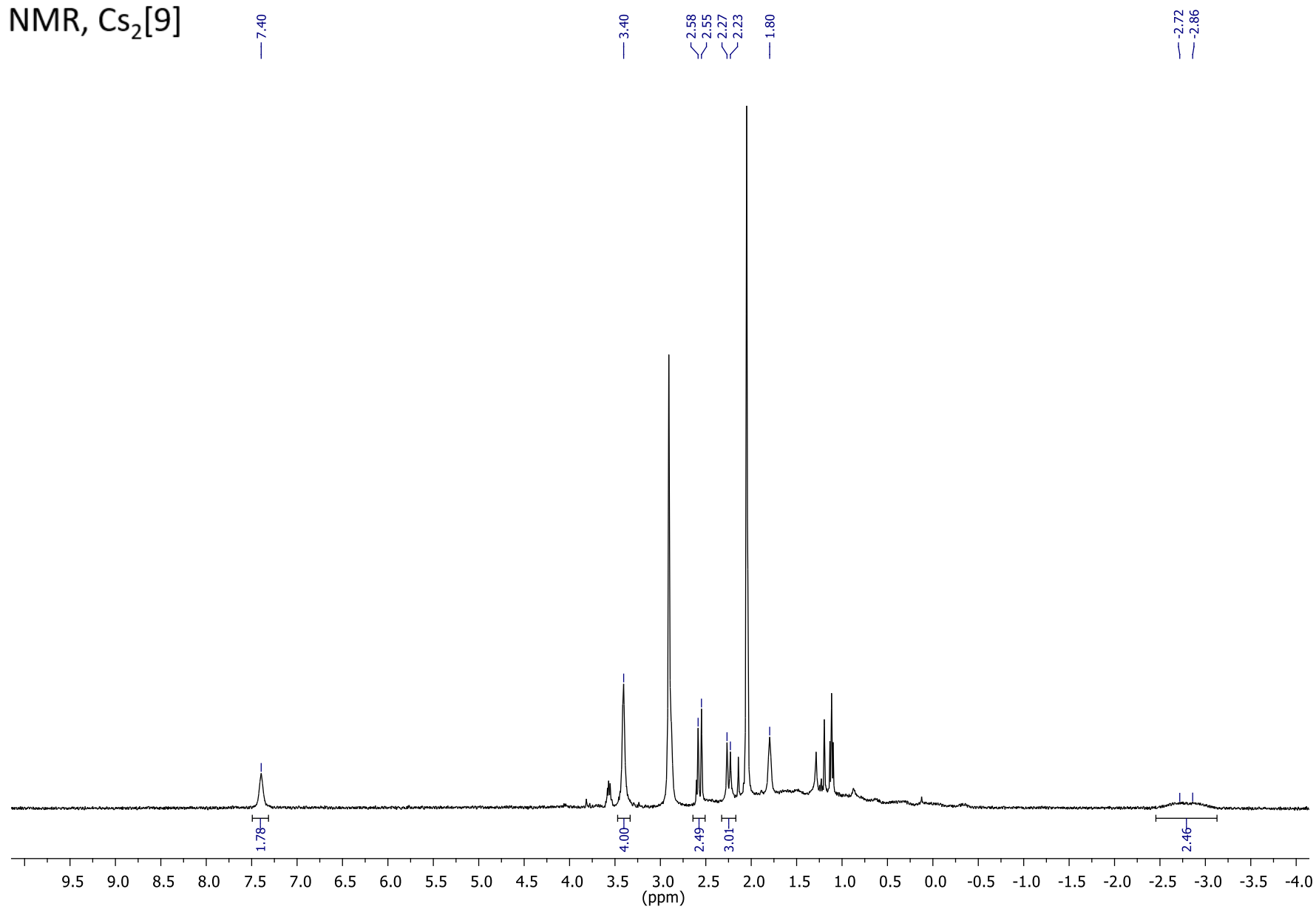




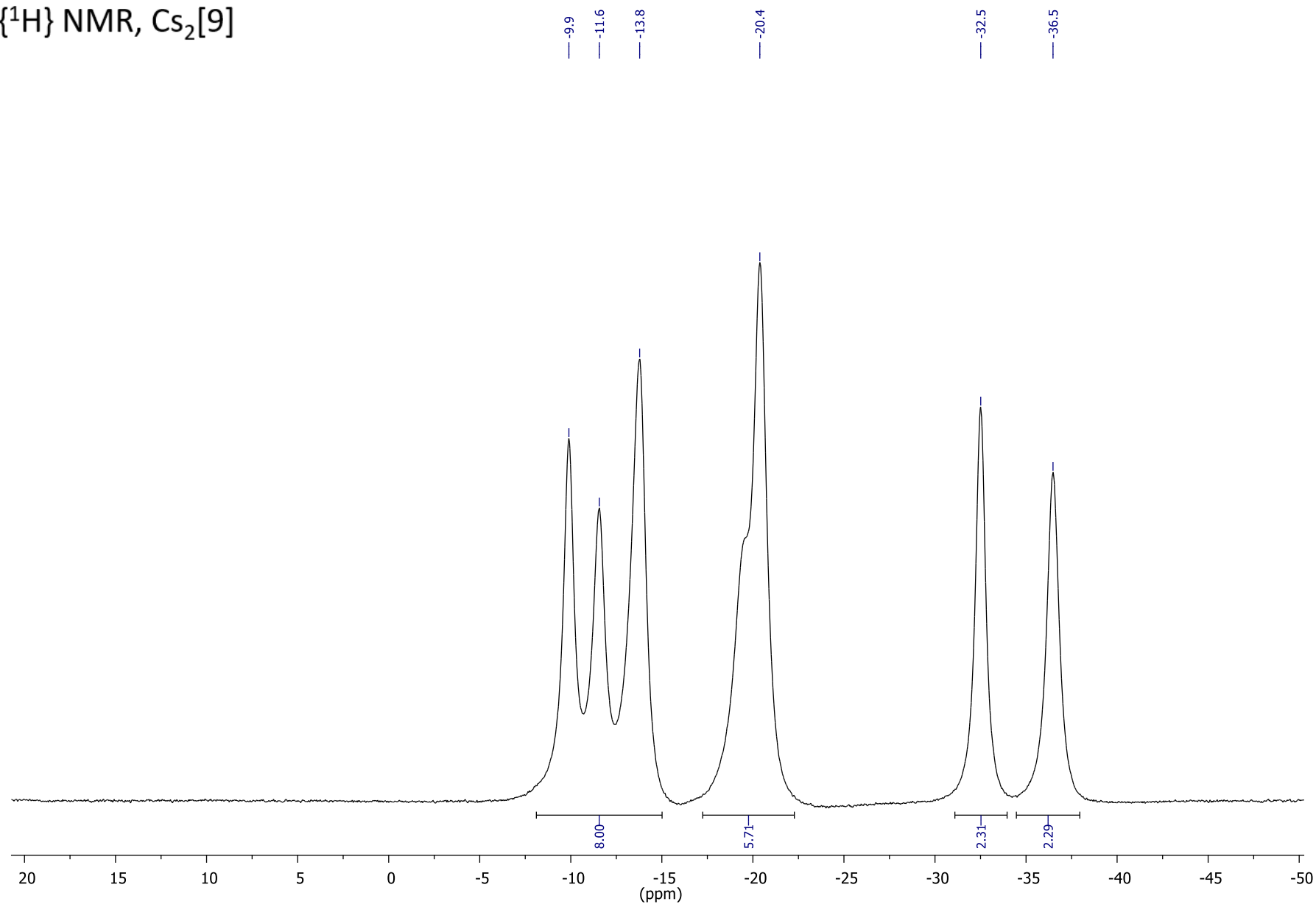
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$^1\text{H}$  NMR,  $\text{Cs}_2[9]$



$^{11}\text{B}\{^1\text{H}\}$  NMR,  $\text{Cs}_2[9]$



$^{11}\text{B}$  NMR,  $\text{Cs}_2[9]$

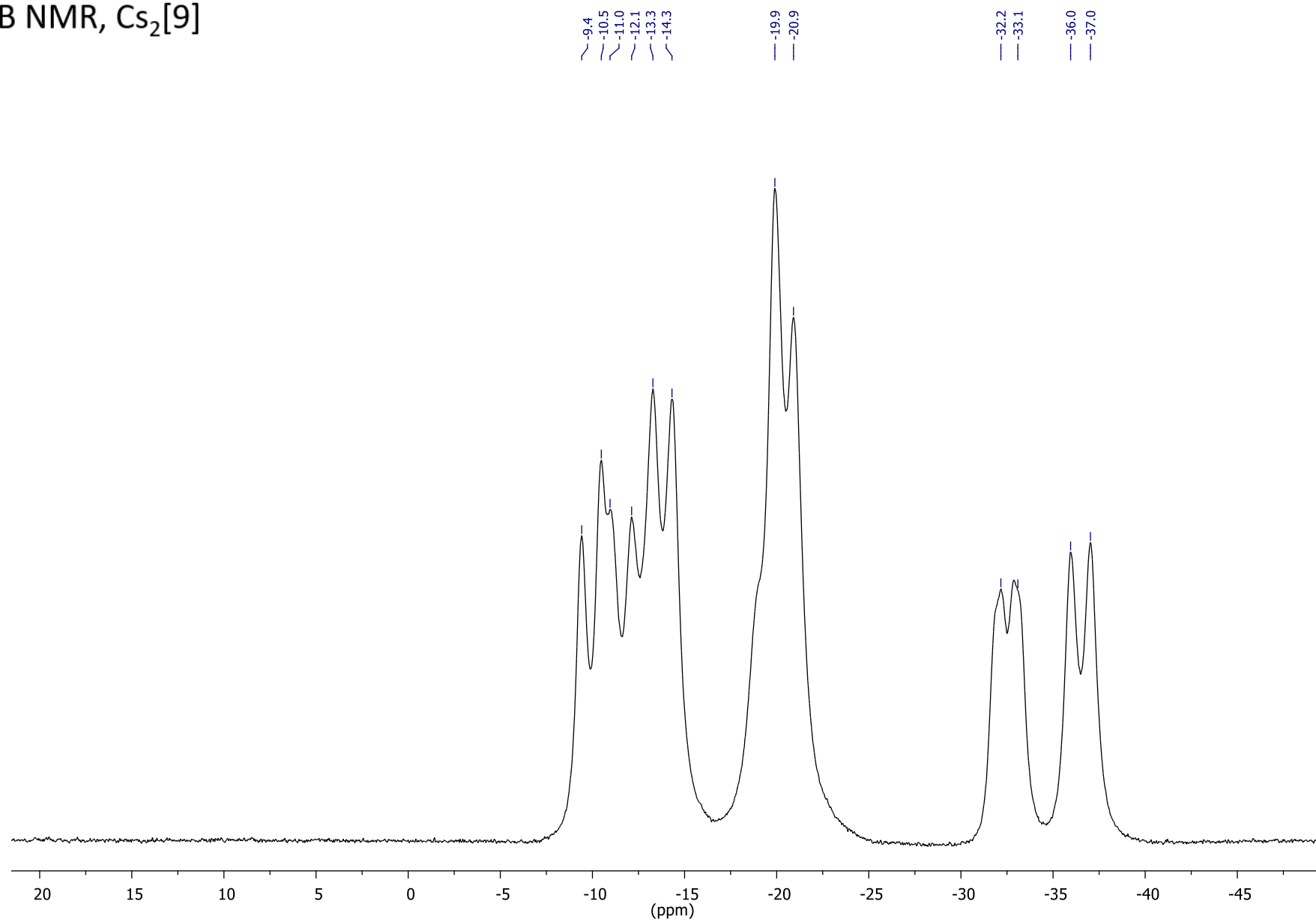


Table S1. Selected geometry characteristics (distance in Å, angles in deg.) of compound **5** as obtained from X-ray study and quantum chemical calculation.

Angle or contact	X-ray	Calculation
C2-C1-C3-N1	166.3(2)	-177.5
C1-C3-N1-C4	179.2(2)	-174.6
C3-N1-C4-C4'	-117.7(2)	-86.3
N1-C4-C4'-N1'	63.6(2)	68.6
C3'-N1'C4'-C4	-119.6(2)	176.3
C1'-C3'-N1'-C4'	176.4(2)	-179.9
C2'-C1'-C3'-N1'	170.4(2)	178.3
B3-H3...H4'-B4'	2.60	2.86
B4-H4...H3'-B3'	2.51	—
N1-H1...O1'	intermol.	—
H...O	2.09	—
N...O	2.860(2)	—
<NHO	146	—
N1'-H1'...O1	intermol.	intramol.
H...O	2.12	2.06
N...O	2.899(2)	2.937
<NHO	147	144

Table S2. Energies (relative to the most favored isomer in kcal/mol) and principal geometry of  $[\text{Gd}(\text{C}_2\text{B}_9\text{H}_{11})_2(\text{DME})]^-$  rotamers.

	1	2	3	4	5	6	7	8	9
$\Delta E$	13.4	5.8	3.0	6.4	5.3	0.0	3.1	7.4	3.1
D1	27.24	-14.25	-15.39	13.21	30.30	165.22	179.28	87.22	165.93
D2	8.69	125.28	-164.85	-127.32	-152.45	163.30	-145.98	125.03	-125.14
D3	35.93	111.03	-180.24	-114.11	-122.15	-31.48	33.30	-147.75	40.79

D1 = centroid O...O and centroid C-C of first cage:  $\text{cent}_{\text{OO}}\text{-Gd-B}_{\text{ax}}\text{-cent}_{\text{CC}}$  dihedral.

D2 = centroid O...O and centroid C'-C' of second cage:  $\text{cent}_{\text{OO}}\text{-Gd-B}'_{\text{ax}}\text{-cent}_{\text{C}'\text{C}'}$  dihedral.

D3 = sum of D1 and D2.

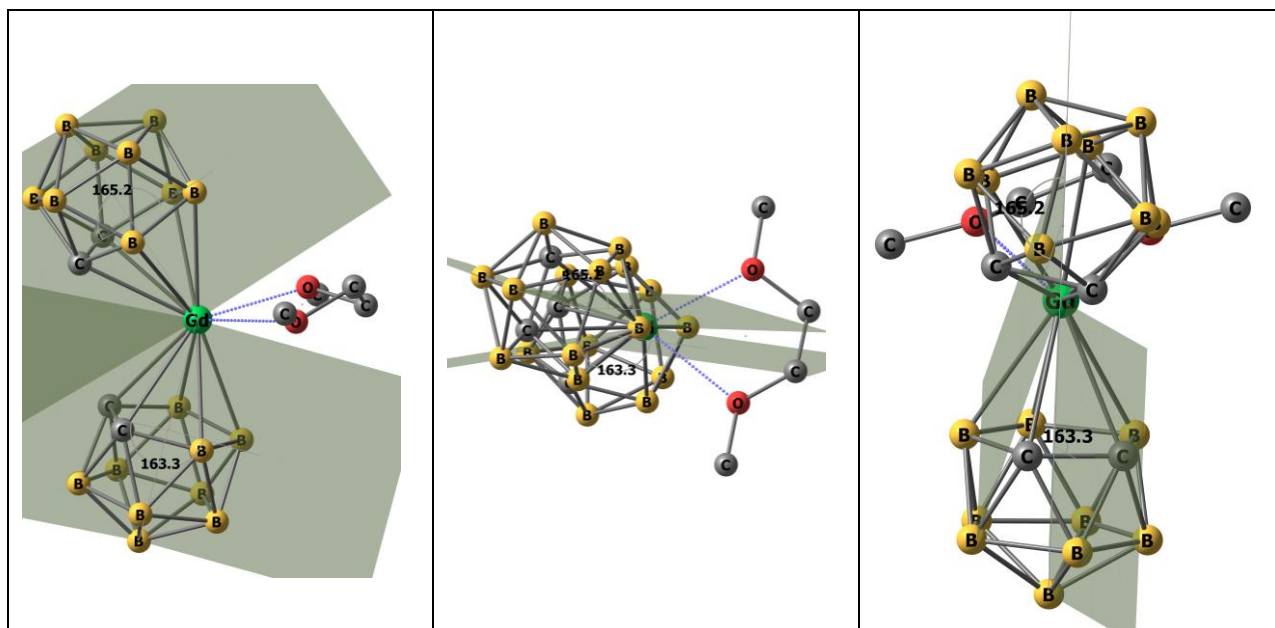


Figure S1. Optimized geometry of the most favored isomer of  $[\text{Gd}(\text{C}_2\text{B}_9\text{H}_{11})_2(\text{DME})]^-$  (three projections). Dihedrals D1 and D2 projected as olive planes, hydrogen atoms omitted for clarity.