

SUPPORTING INFORMATION

Synthesis of 3-Aryl-*ortho*-carboranes with Sensitive Functional Groups

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Materials and Methods

3-Iodo-*ortho*-carborane (**1**) [54] and bis(triphenylphosphine)palladium dichloride [81] were prepared according to the literature procedure. Anhydrous cobalt dibromide was prepared by heating cobalt bromide hexahydrate at 160 °C under vacuum for 3 h and stored under argon atmosphere. Acetonitrile was dried using standard procedures [82]. All other chemical reagents were purchased from Sigma Aldrich, Acros Organics and ABCR and used as received. All reactions were carried out under argon atmosphere. The reaction progress was monitored by thin layer chromatography (Merck F254 silica gel on aluminum plates) and visualized using 0.5% PdCl₂ in 1% HCl in aq. MeOH (1:10). Acros Organics silica gel (0.060–0.200 mm) was used for column chromatography. The NMR spectra at 400 MHz (¹H), 128 MHz (¹¹B) and 100 MHz (¹³C) were recorded with Varian Inova 400 spectrometer. The residual signal of the NMR solvent relative to Me₄Si was taken as the internal reference for ¹H and ¹³C NMR spectra. ¹¹B NMR spectra were referenced using BF₃·Et₂O as external standard. Mass spectra (MS) were measured using Shimadzu LCMS-2020 instrument with DUIS ionization (ESI—Electrospray ionization and APCI—Atmospheric pressure chemical ionization). The measurements were done in a positive and negative ion modes with mass range from *m/z* 50 to *m/z* 2000. Isotope distribution were calculated using Isotope Distribution Calculator and Mass Spec Plotter [83].

Single crystal X-ray diffraction experiments for compounds **5–7** were carried out using SMART APEX2 CCD diffractometer ($\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$, graphite monochromator, ω -scans) at 120 K. Collected data were processed by the SAINT and SADABS programs incorporated into the APEX2 program package [84]. The structures were solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. The refinement was carried out with the SHELXTL program [85]. The CCDC numbers (2118711, 2118710, and 2118709 for **5**, **6**, and **7**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

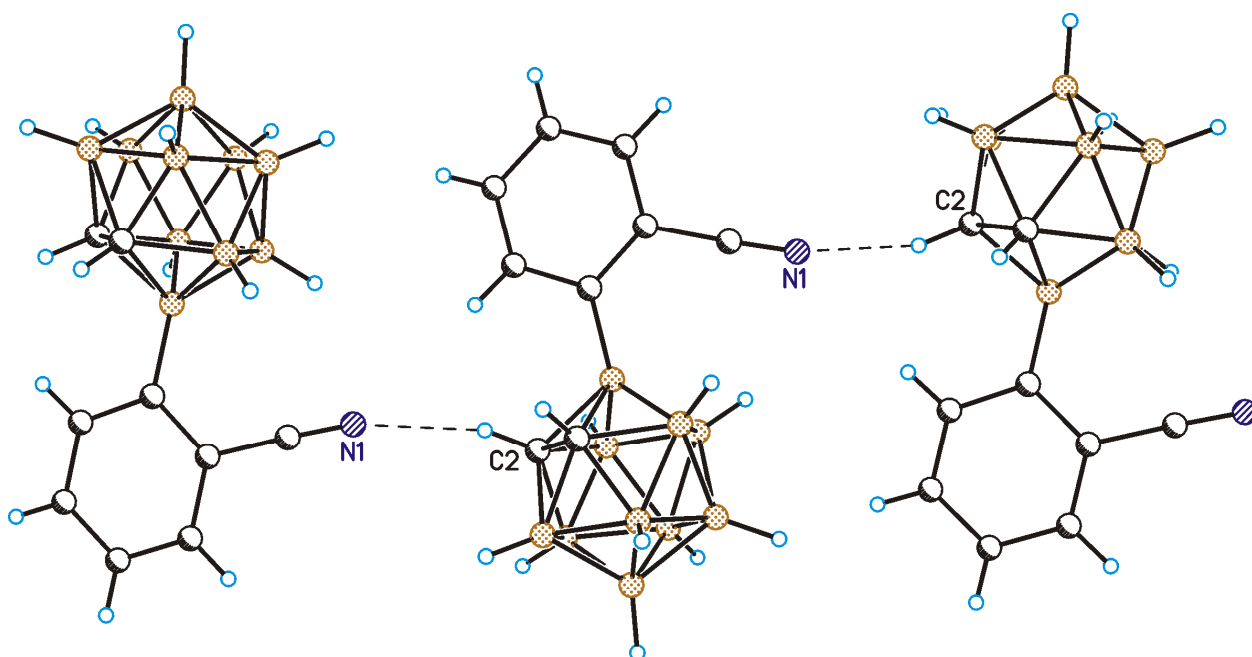


Figure S1. H-bonded chain in the crystal structure of compound **6**.

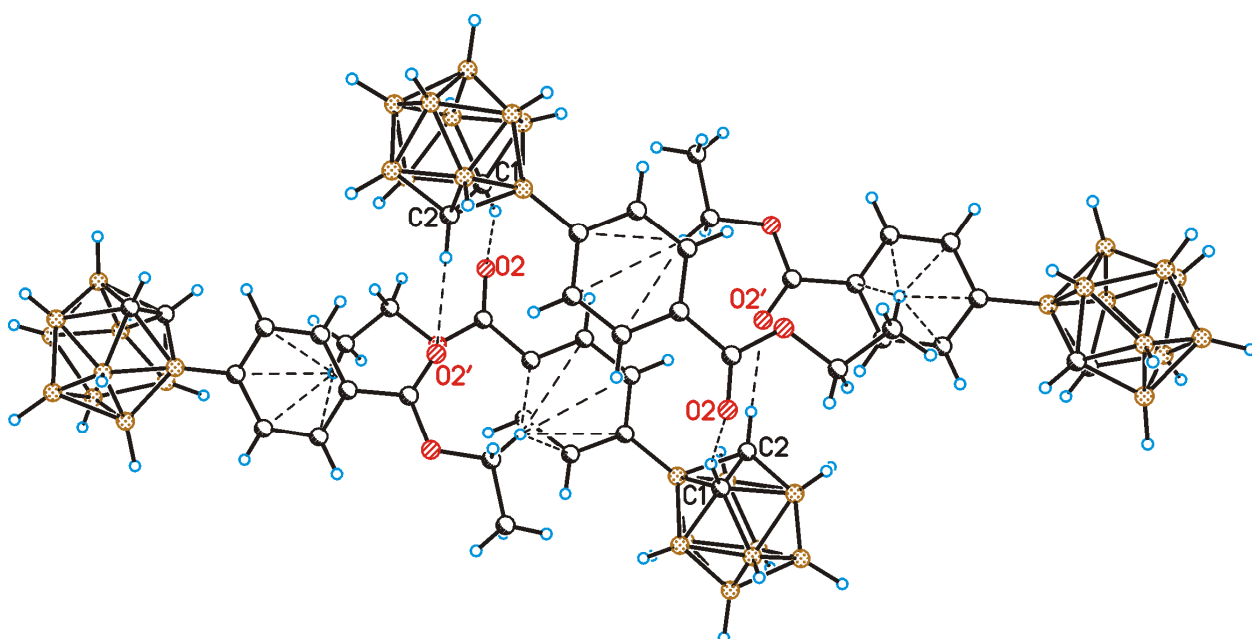
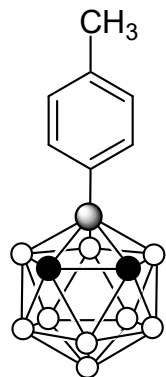


Figure S2. Fragment of the crystal packing of compound **10**. Tetramer formed by two molecules A and two molecules A' by means of H... π and C_{carb}-H...O intermolecular hydrogen bonds.

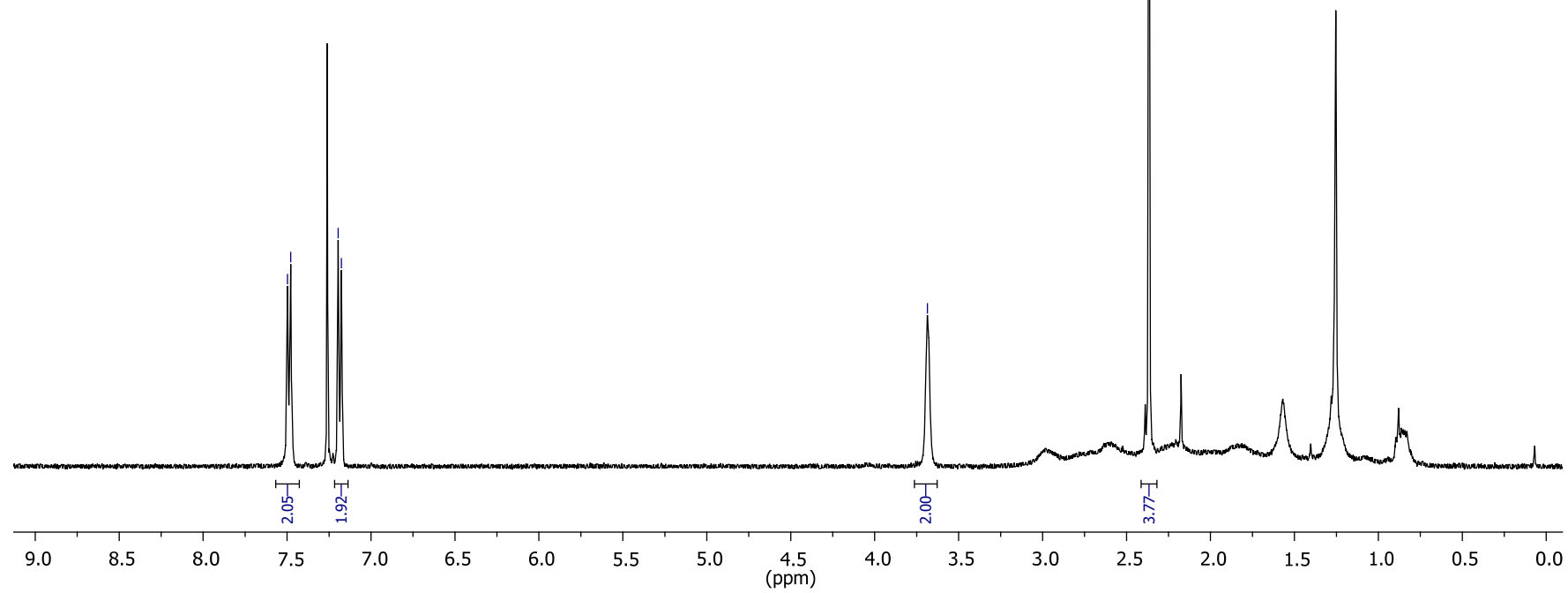
¹H, compound 2



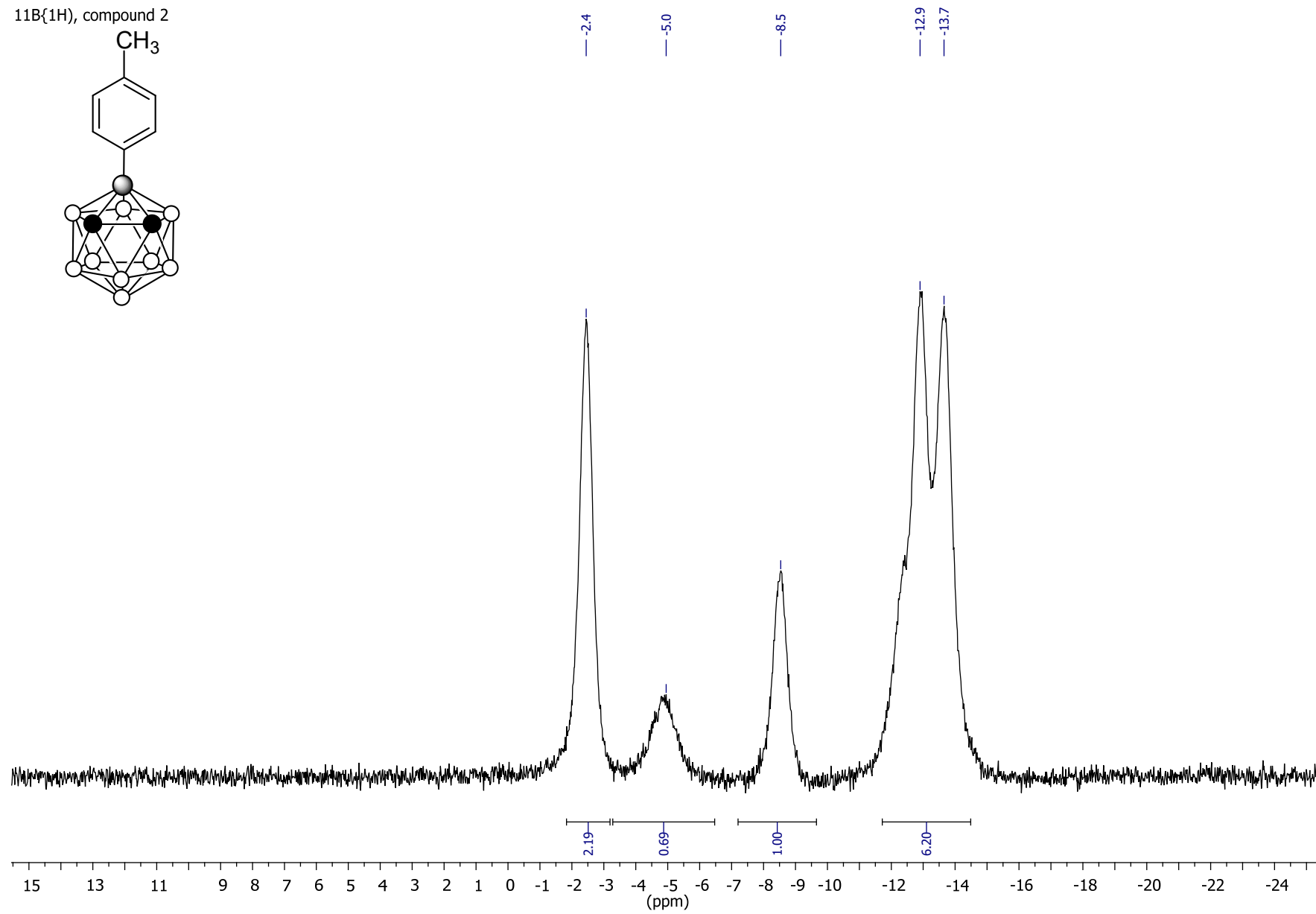
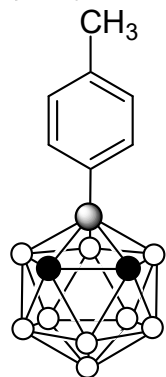
7.50
7.48
7.20
7.18

3.69

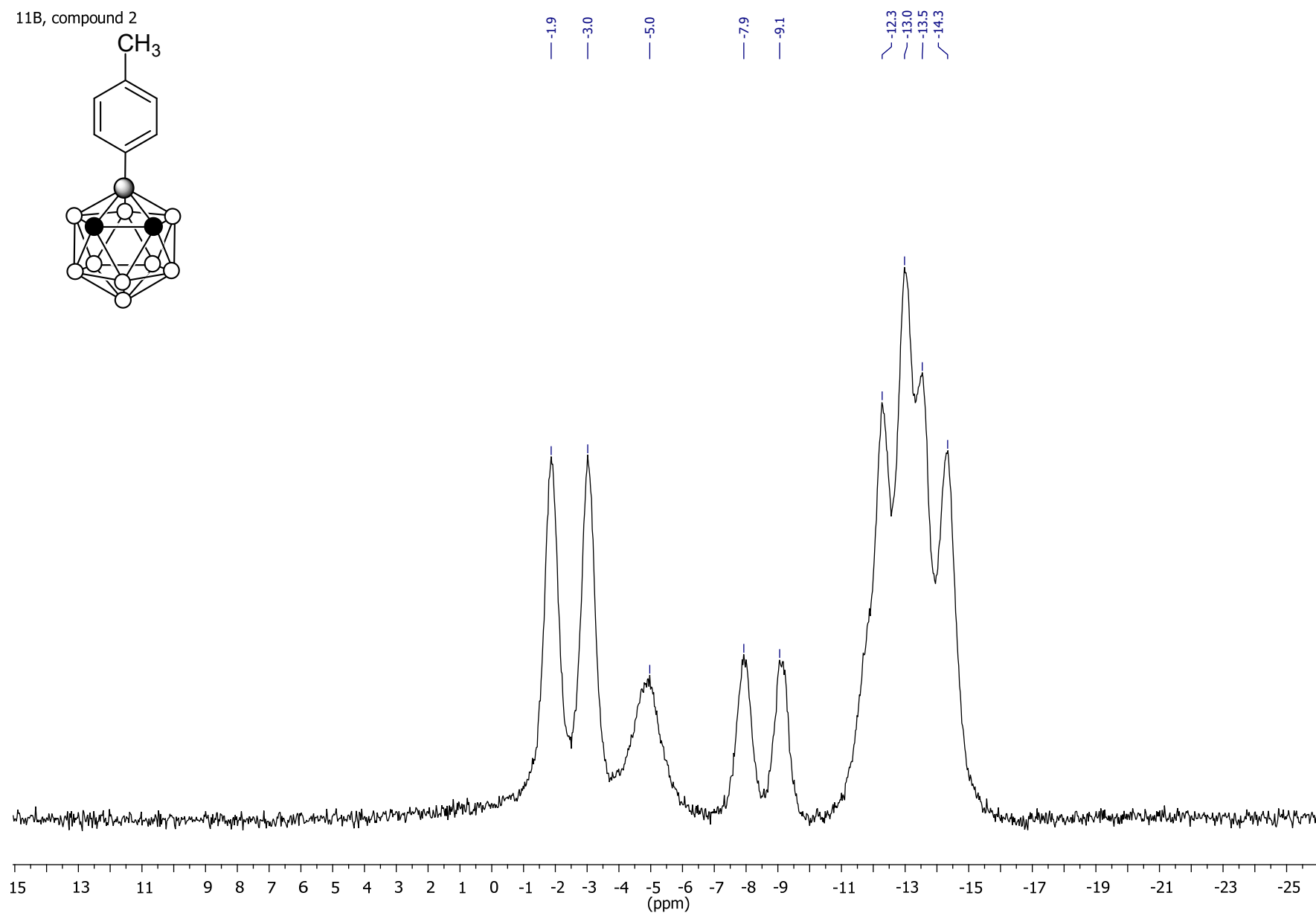
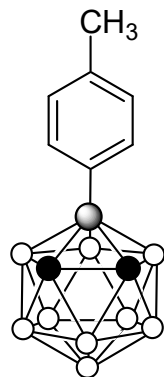
2.37



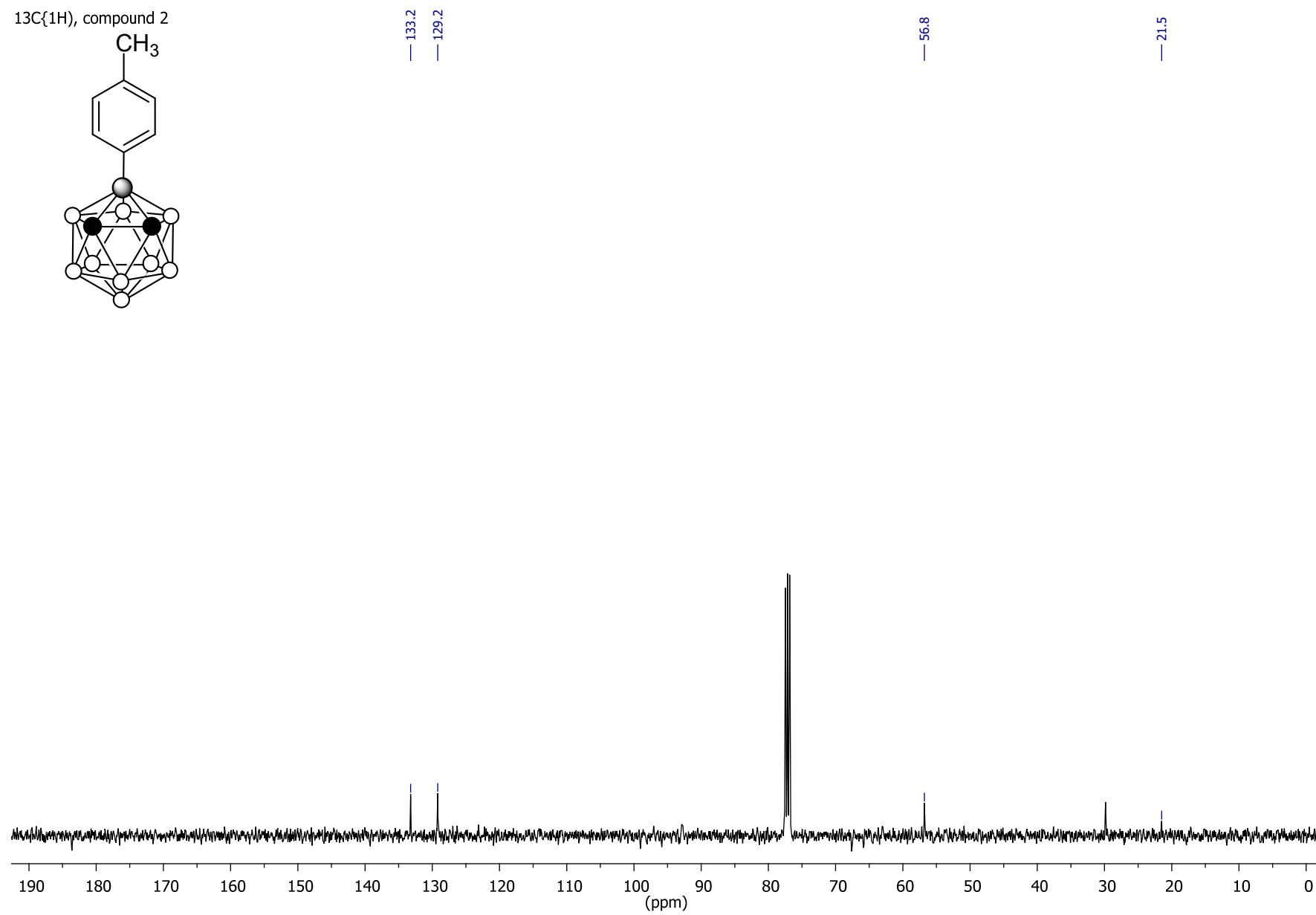
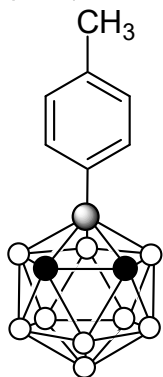
$^{11}\text{B}\{^1\text{H}\}$, compound 2

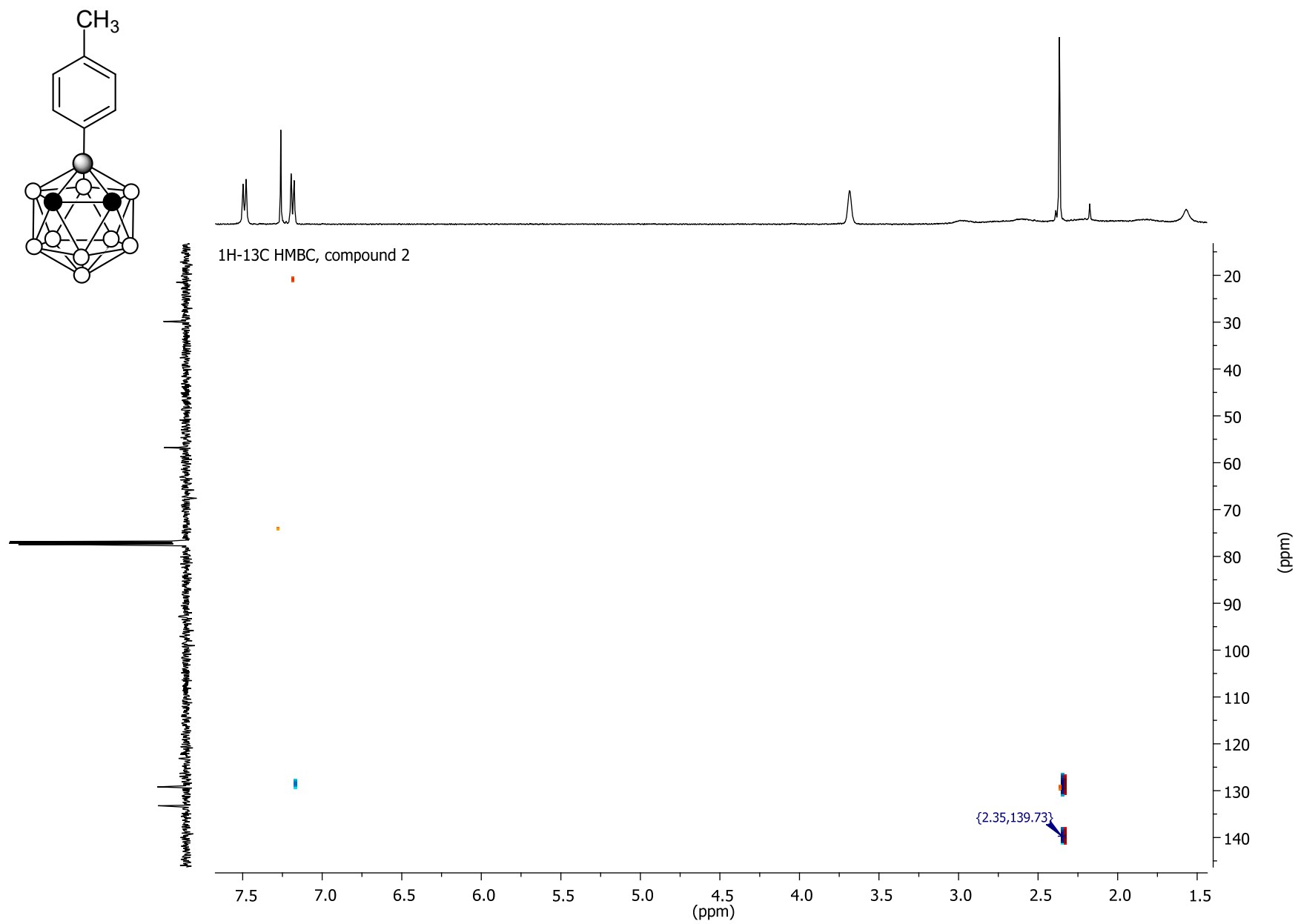


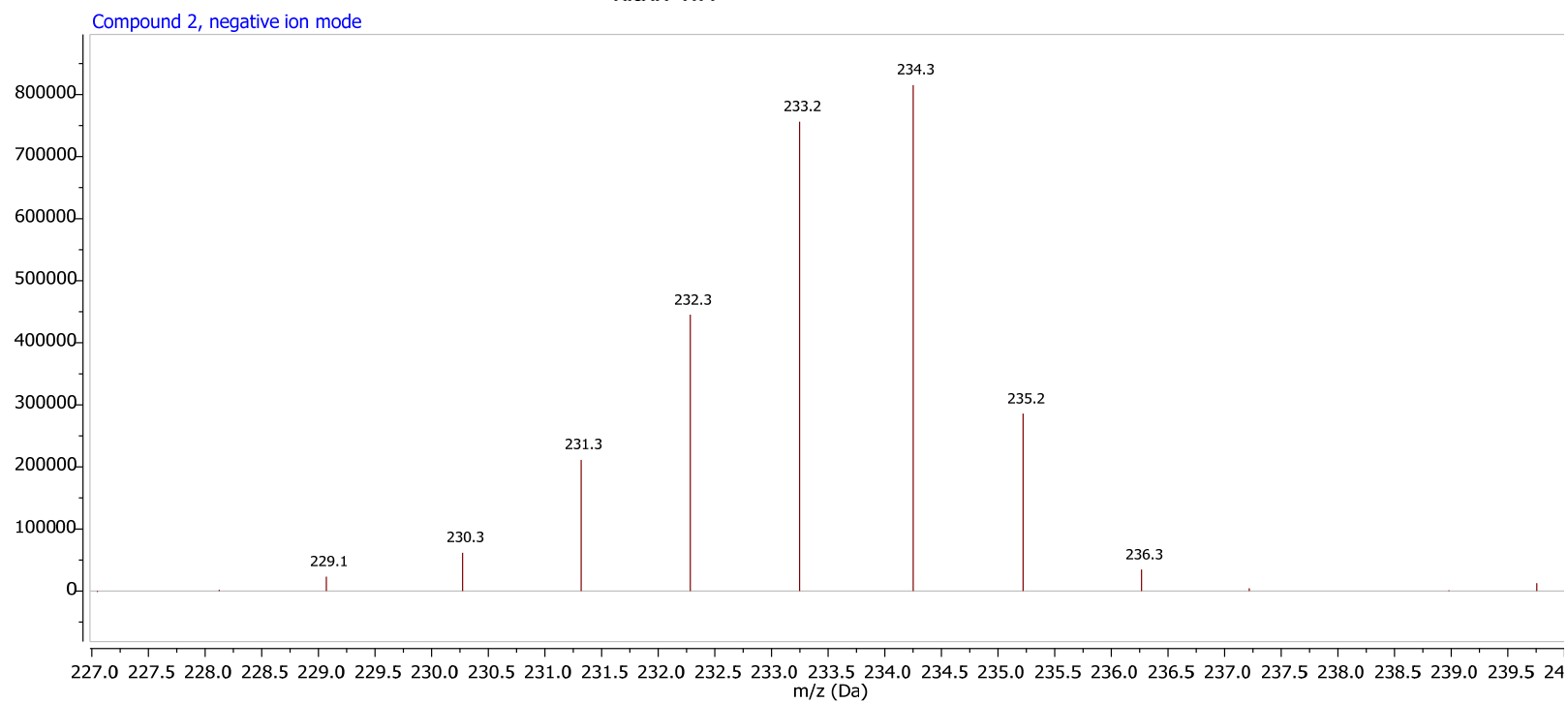
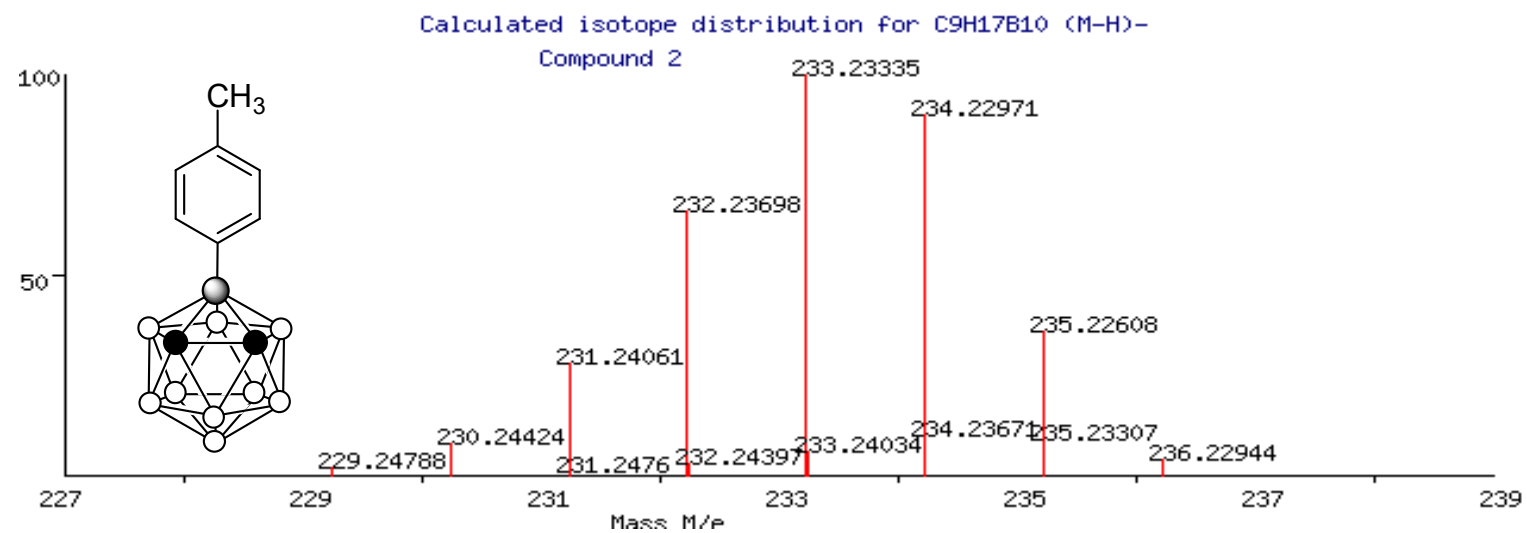
11B, compound 2



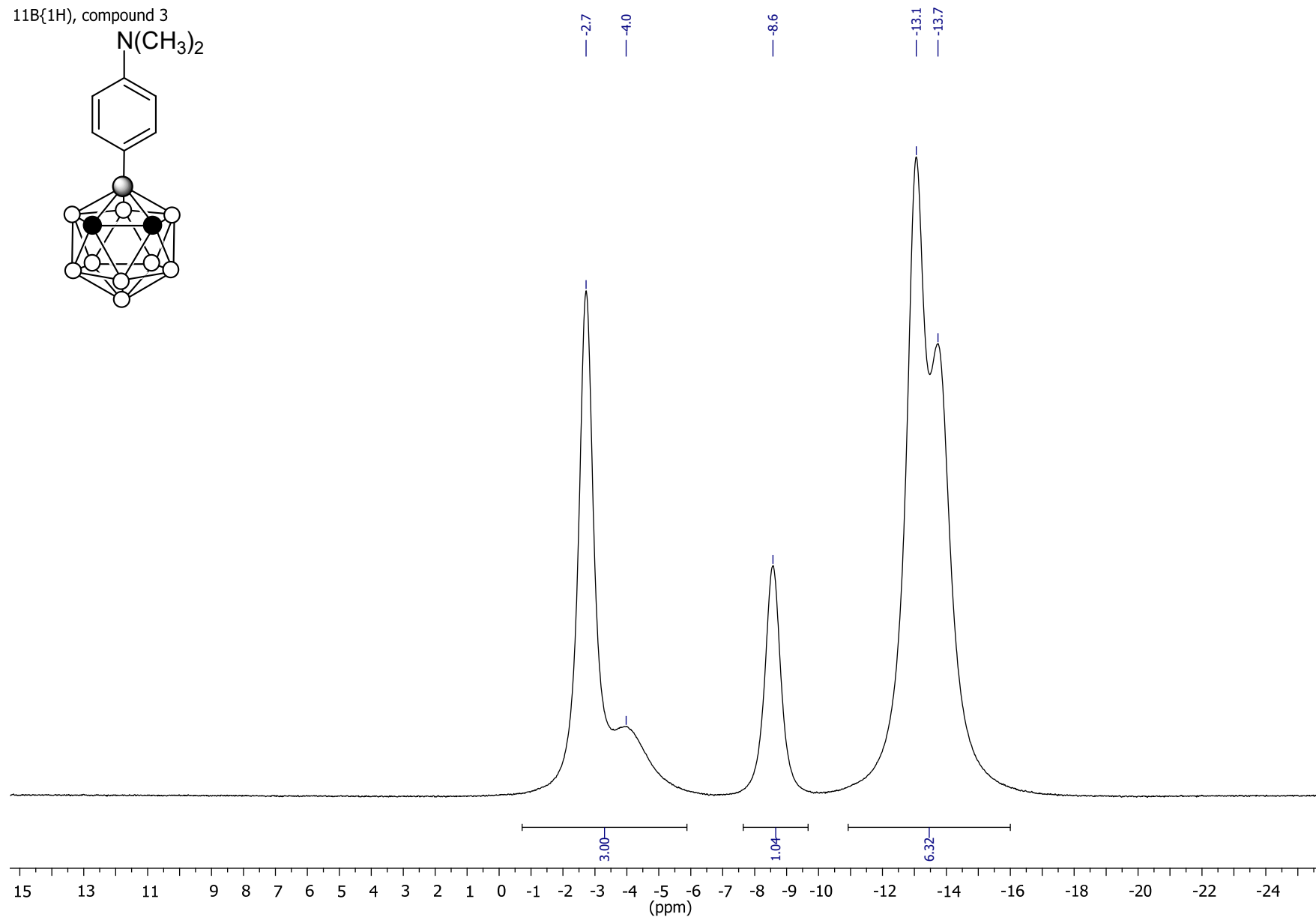
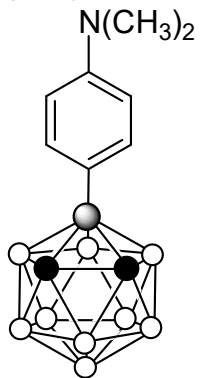
$^{13}\text{C}\{^1\text{H}\}$, compound 2



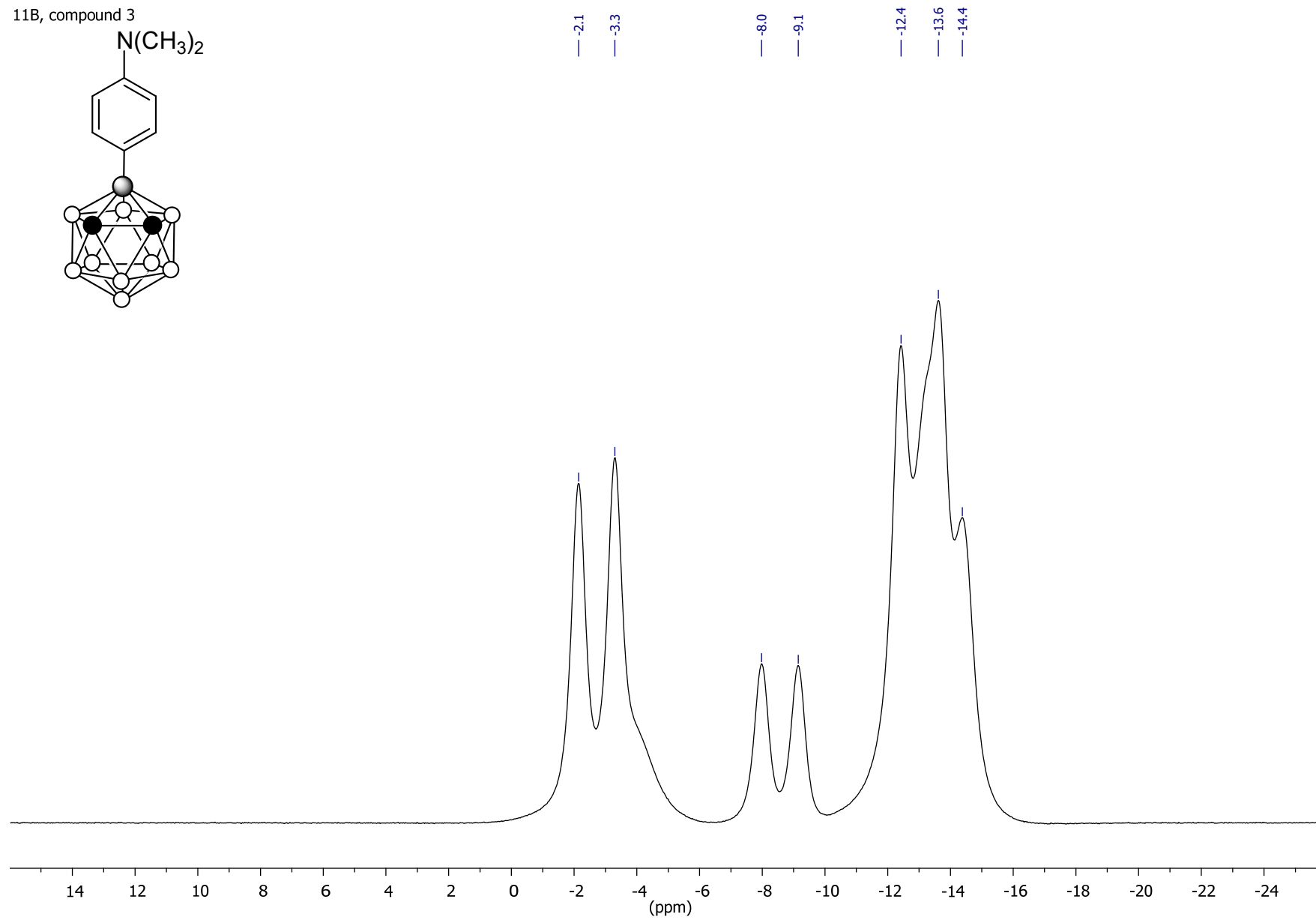
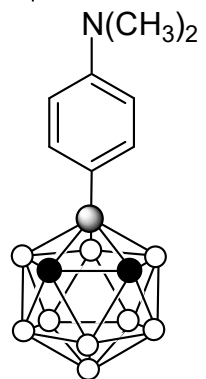




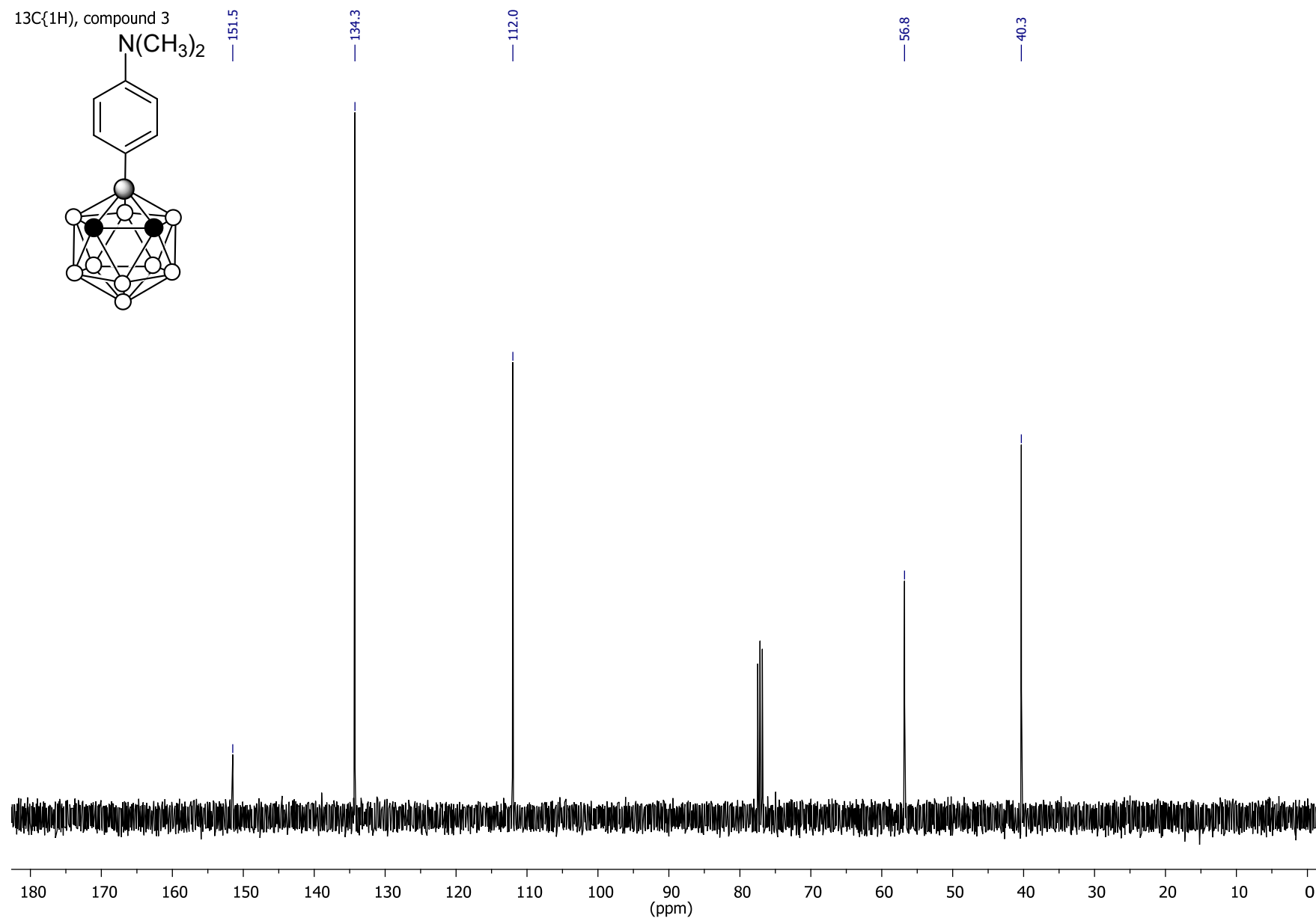
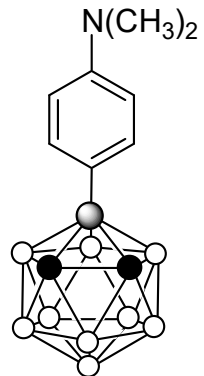
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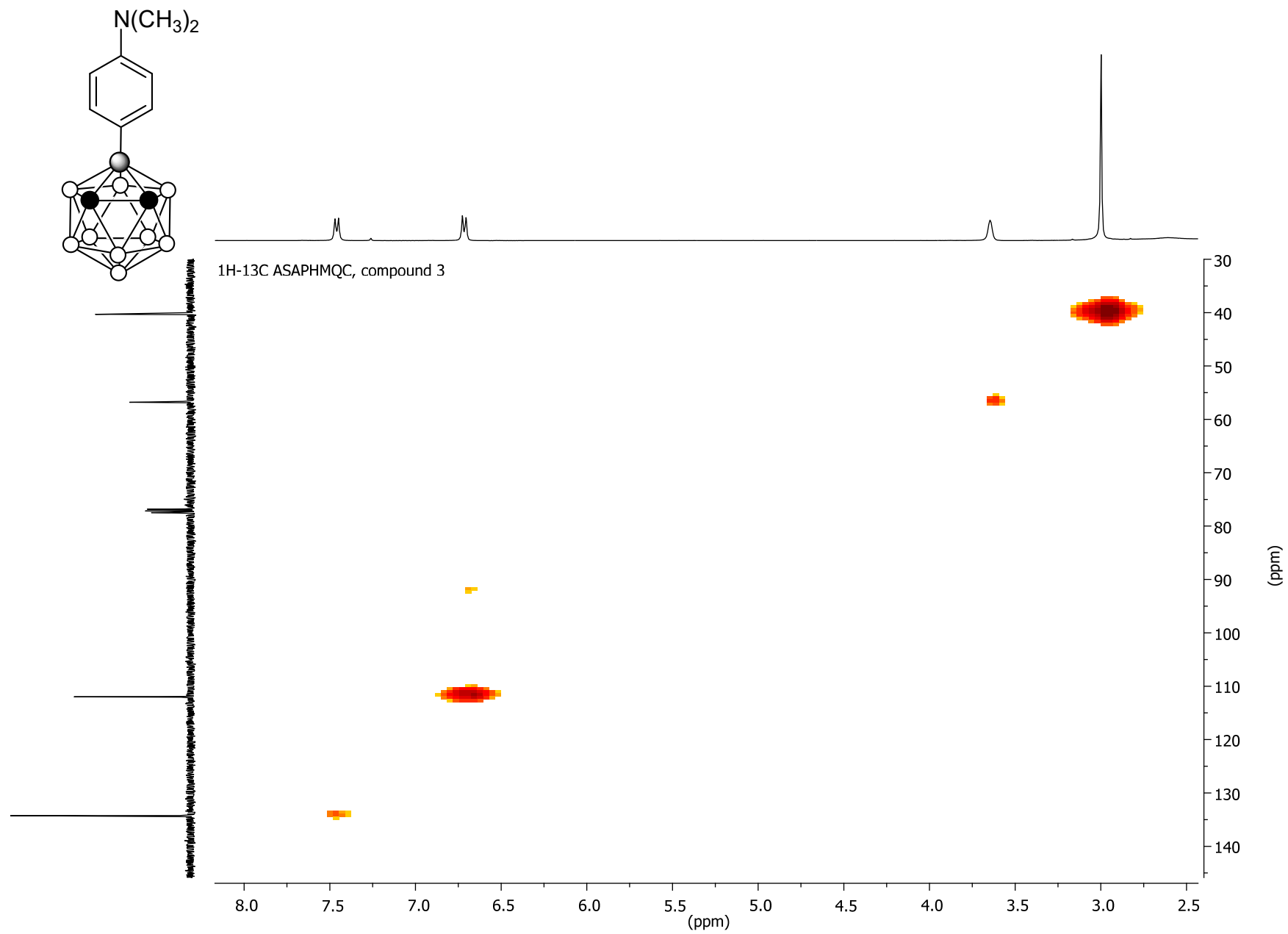


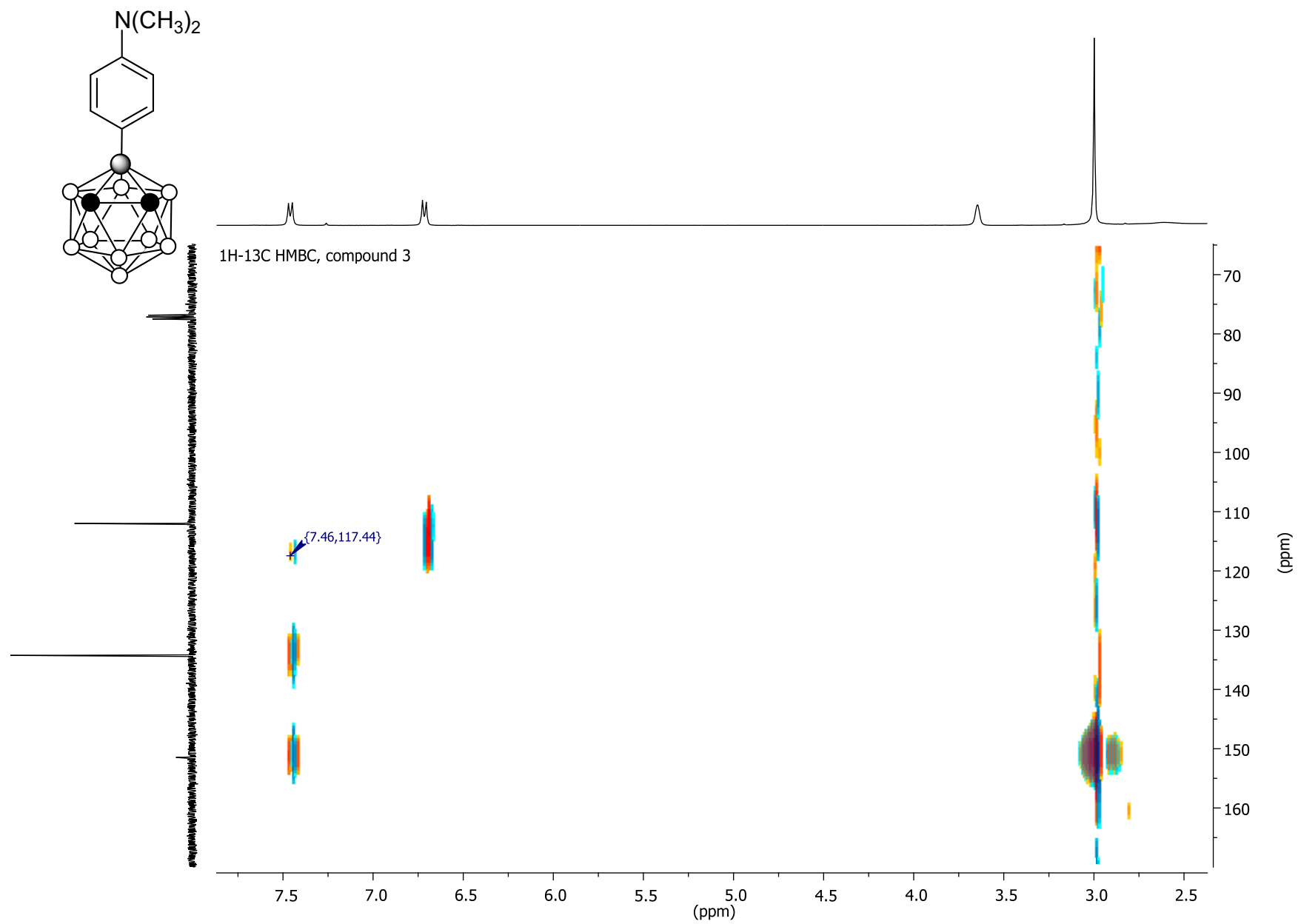
11B, compound 3

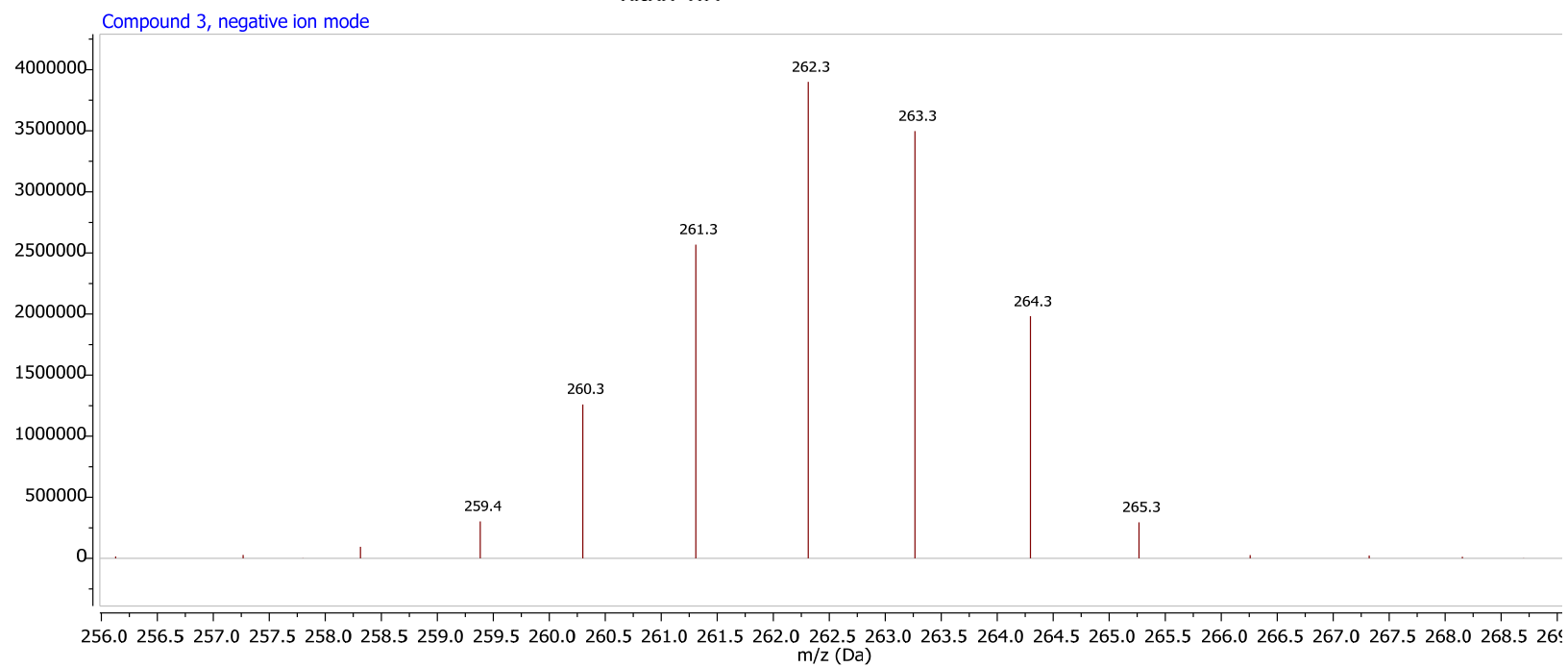
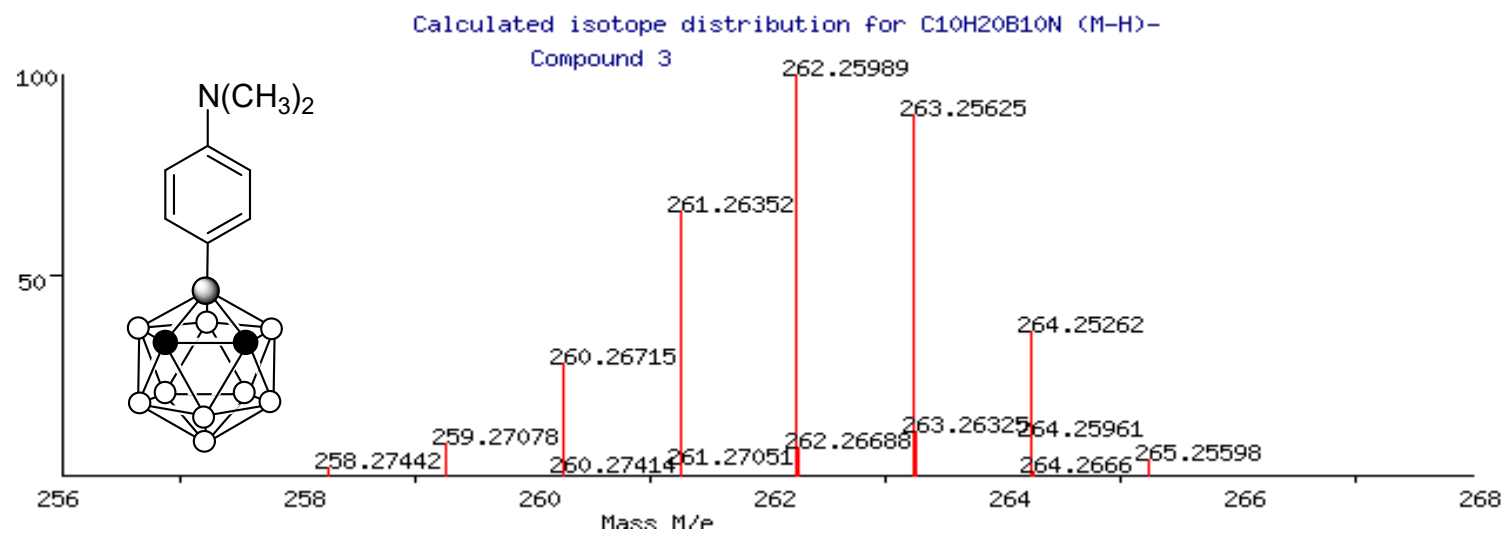


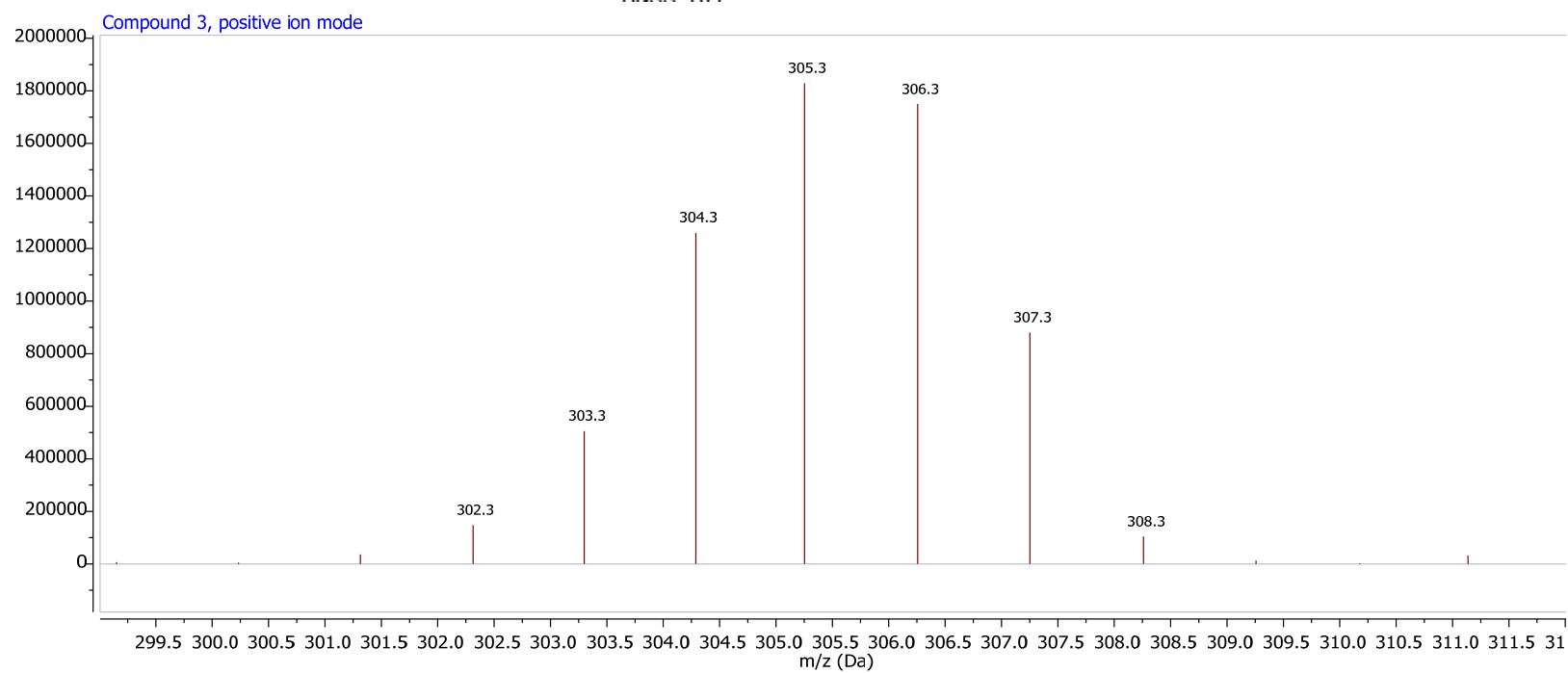
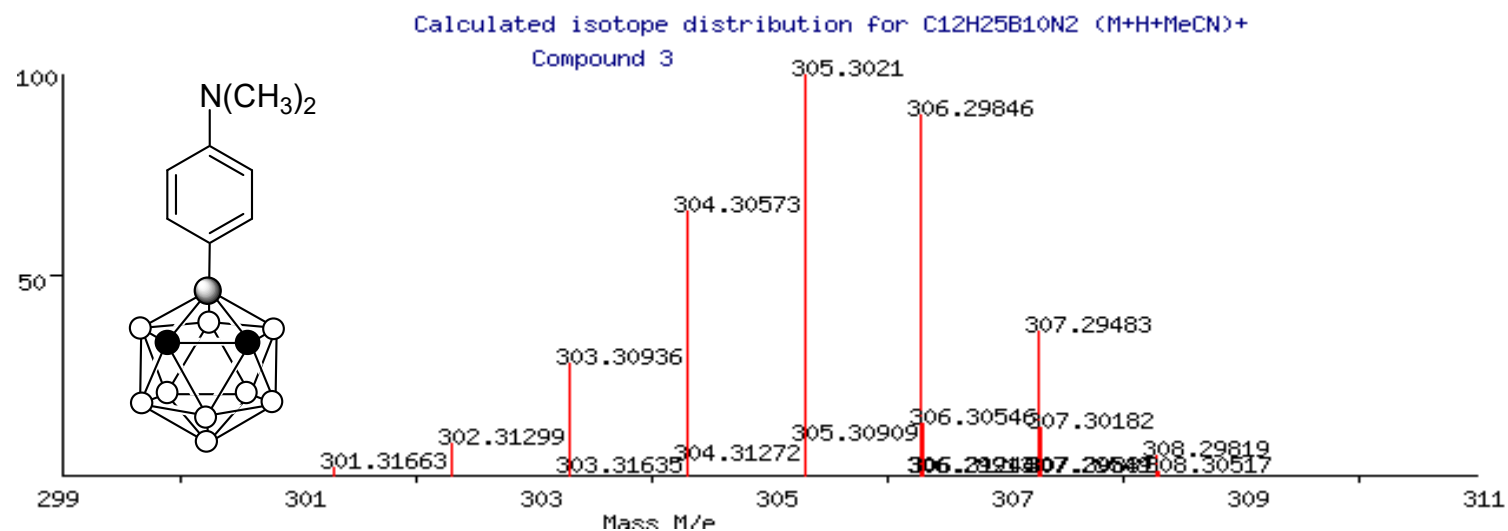
$^{13}\text{C}\{^1\text{H}\}$, compound 3



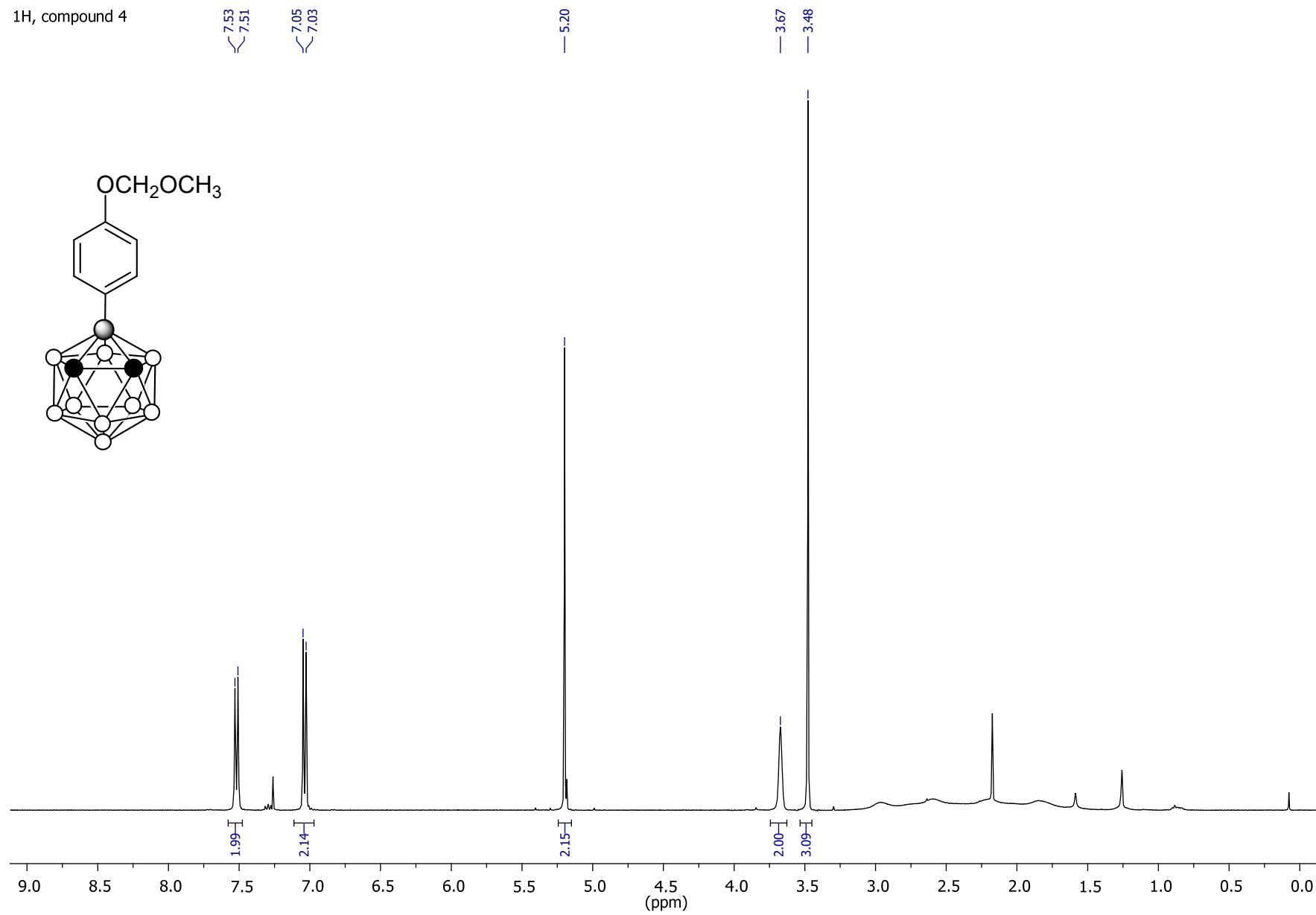




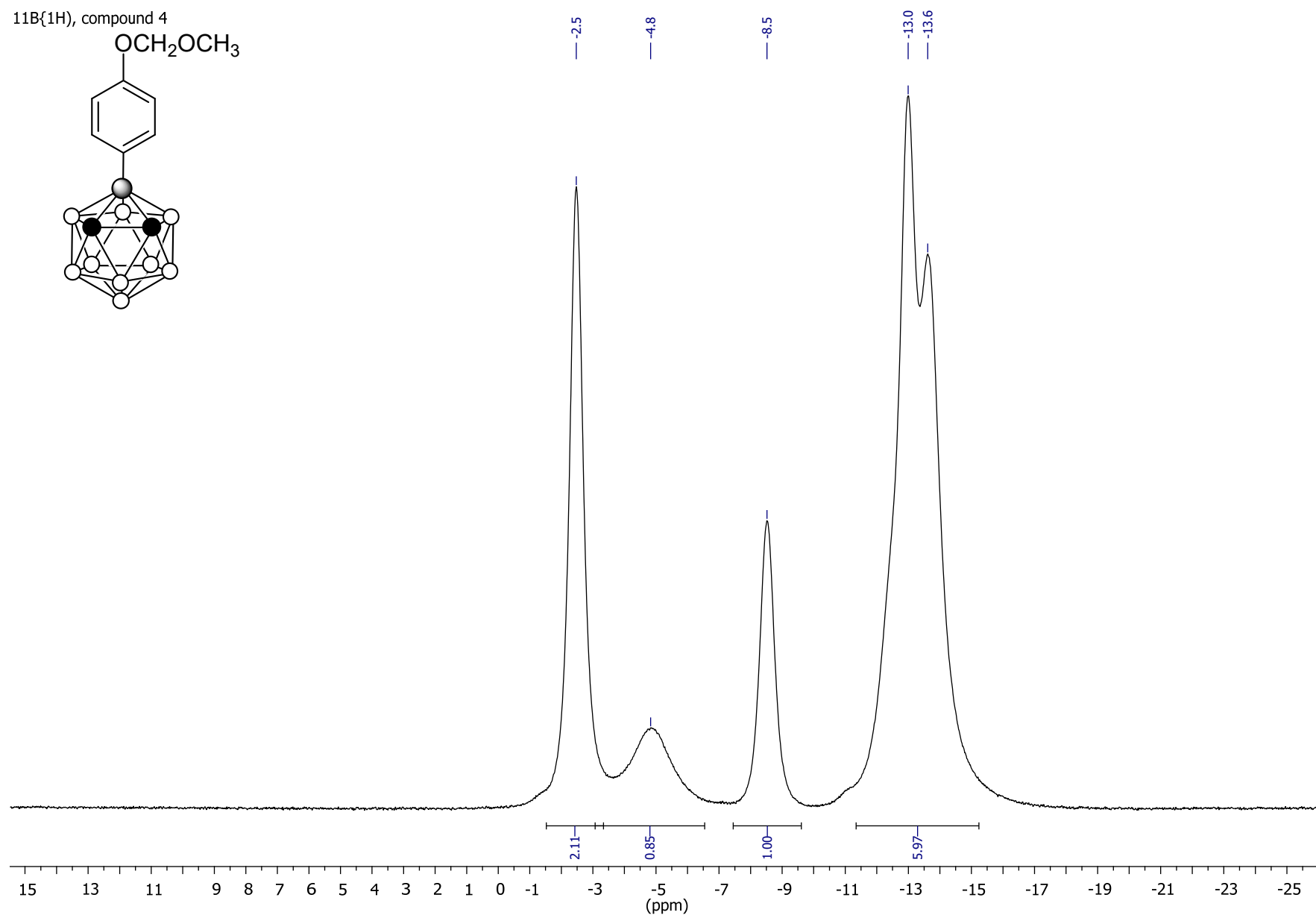
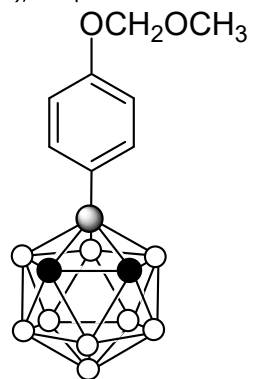




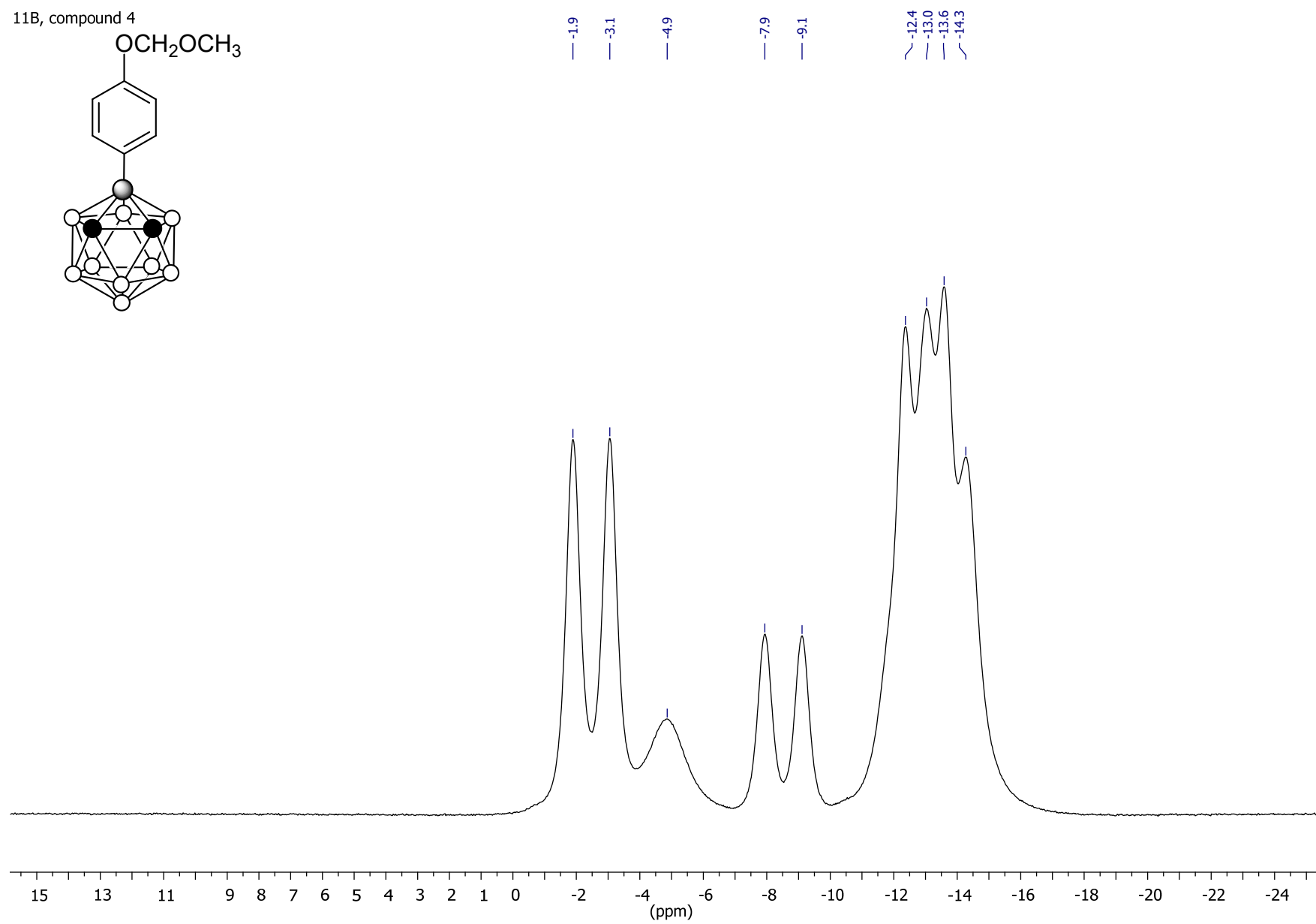
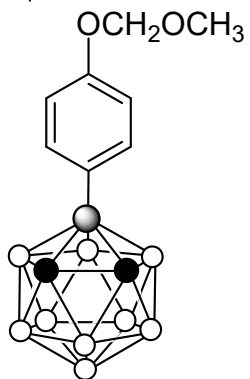
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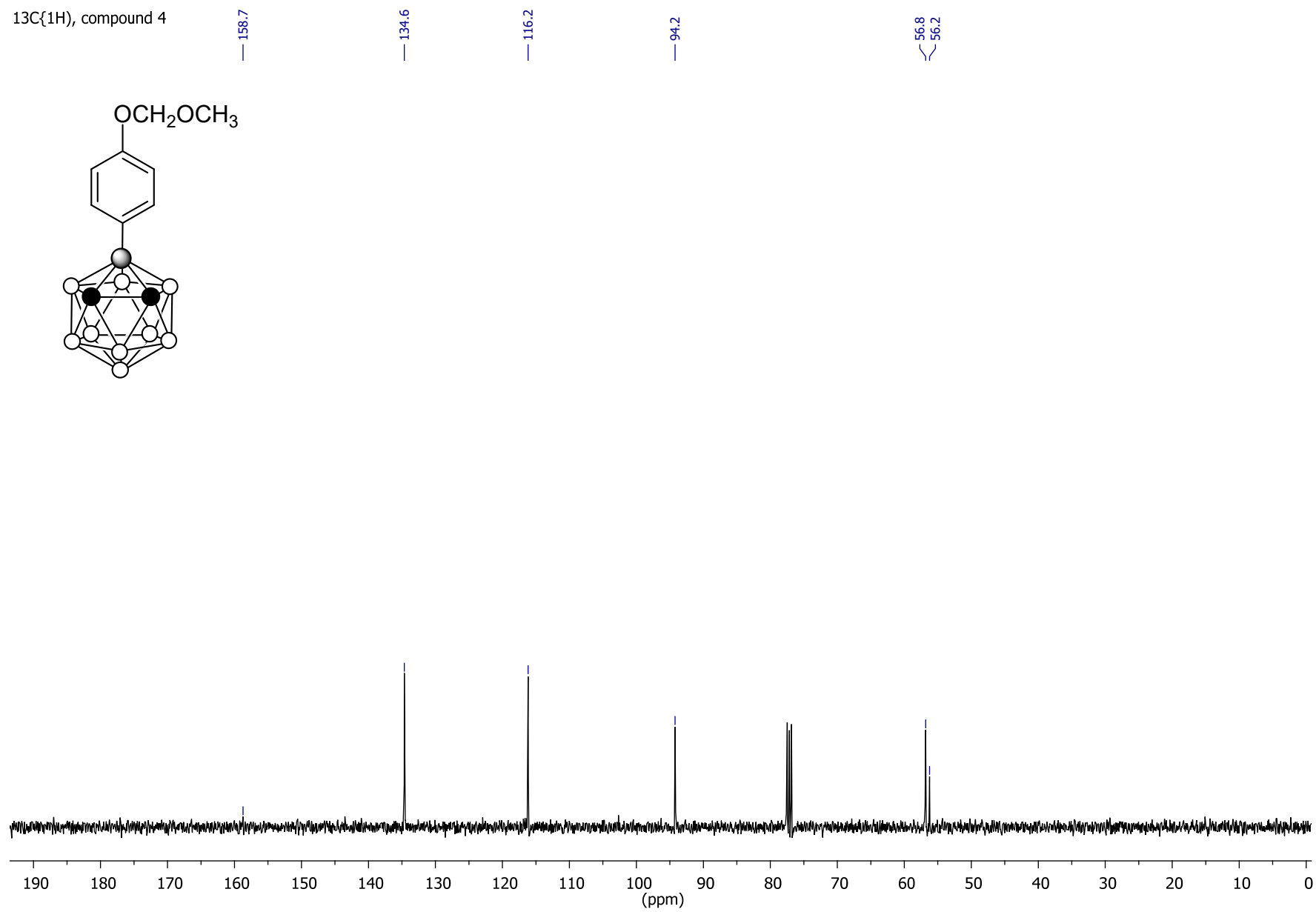
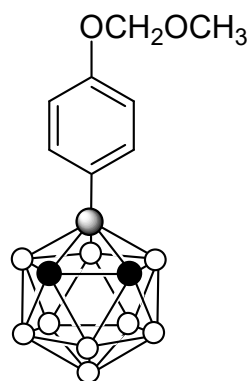
$^{11}\text{B}\{^1\text{H}\}$, compound 4

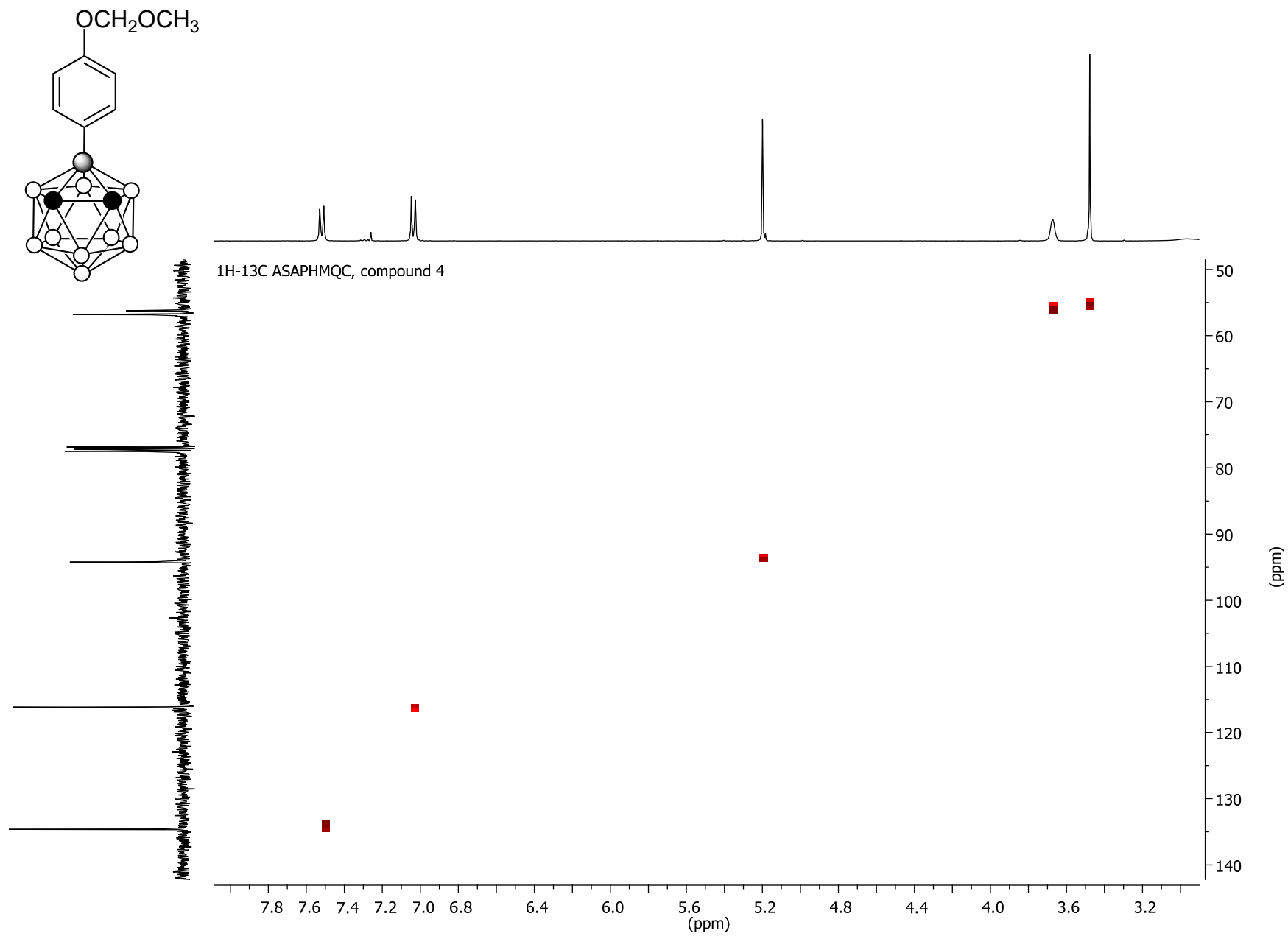


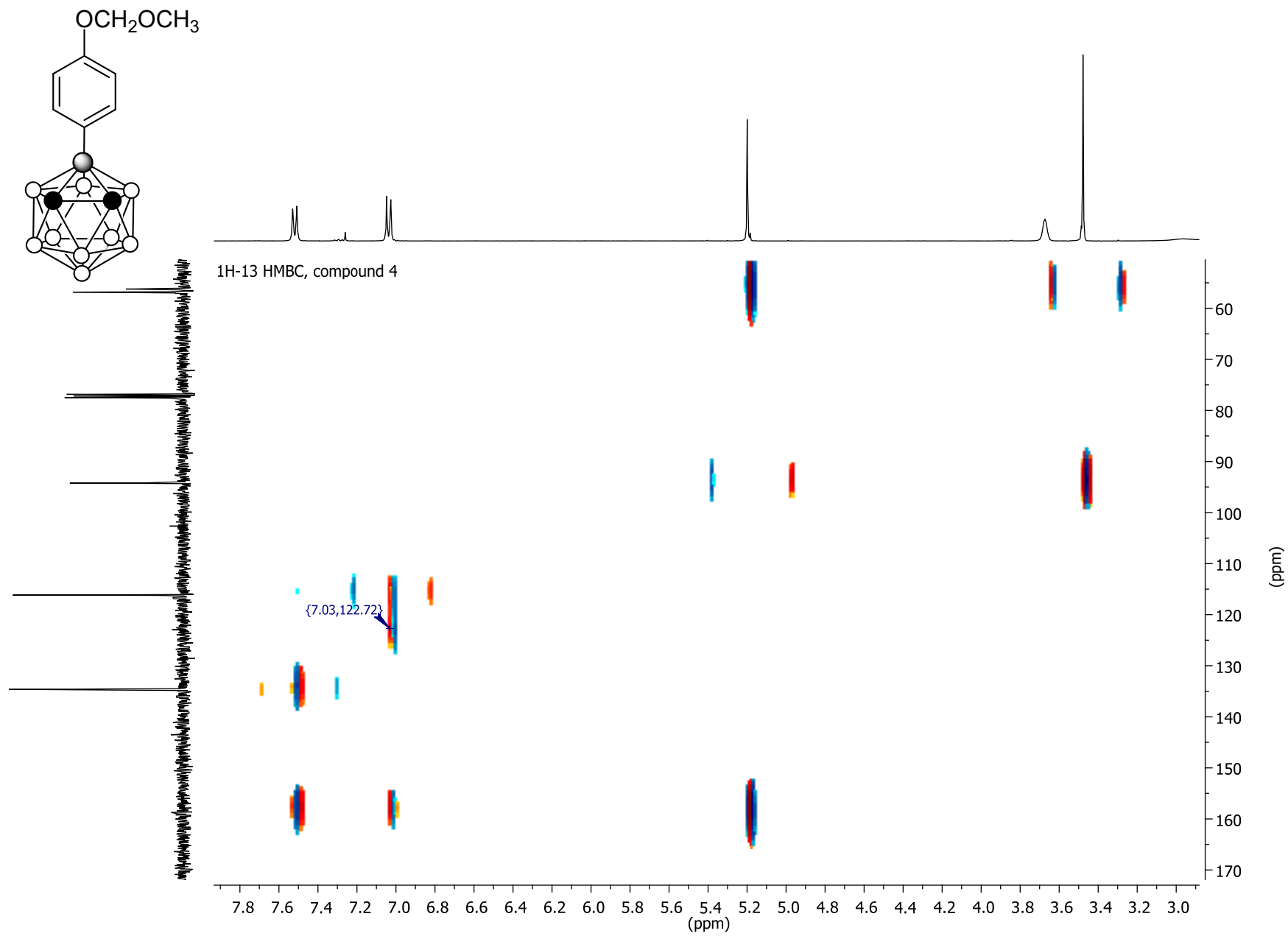
11B, compound 4

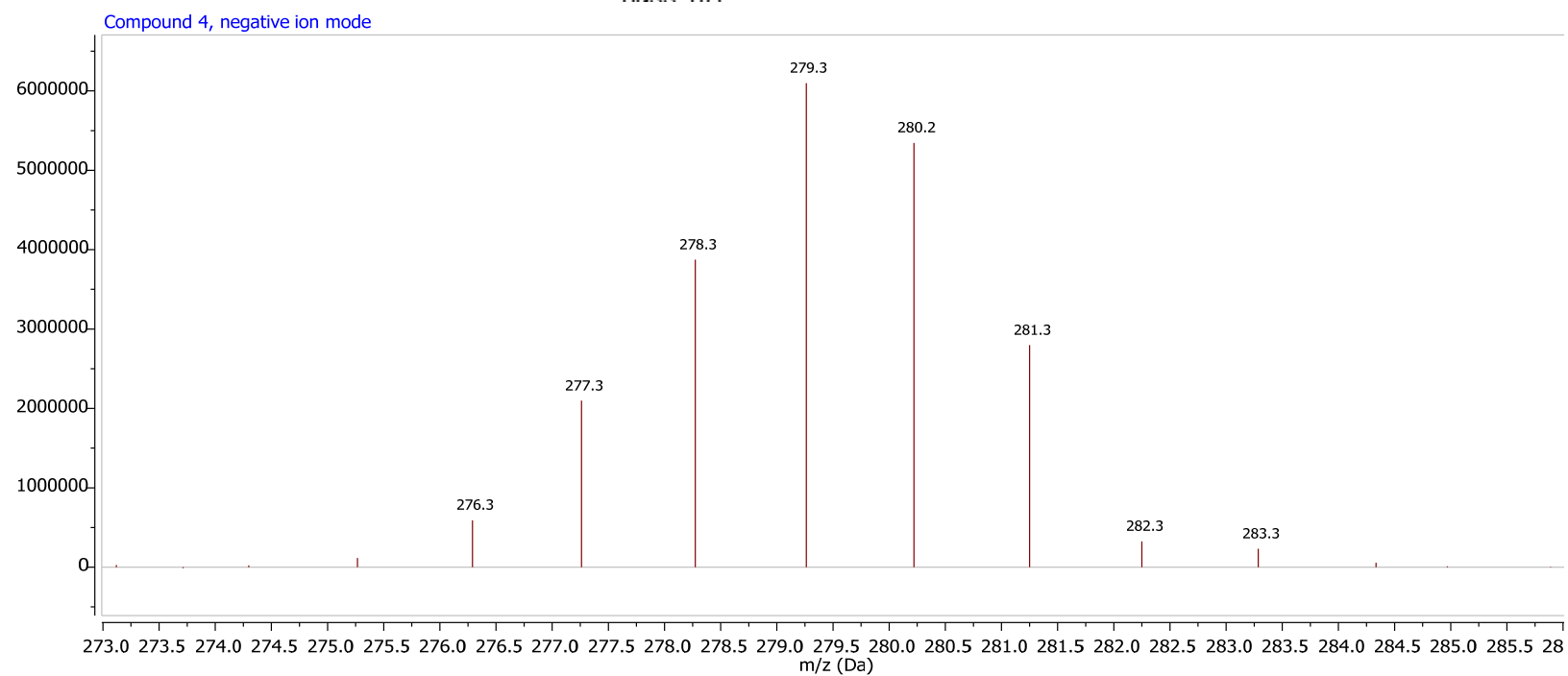
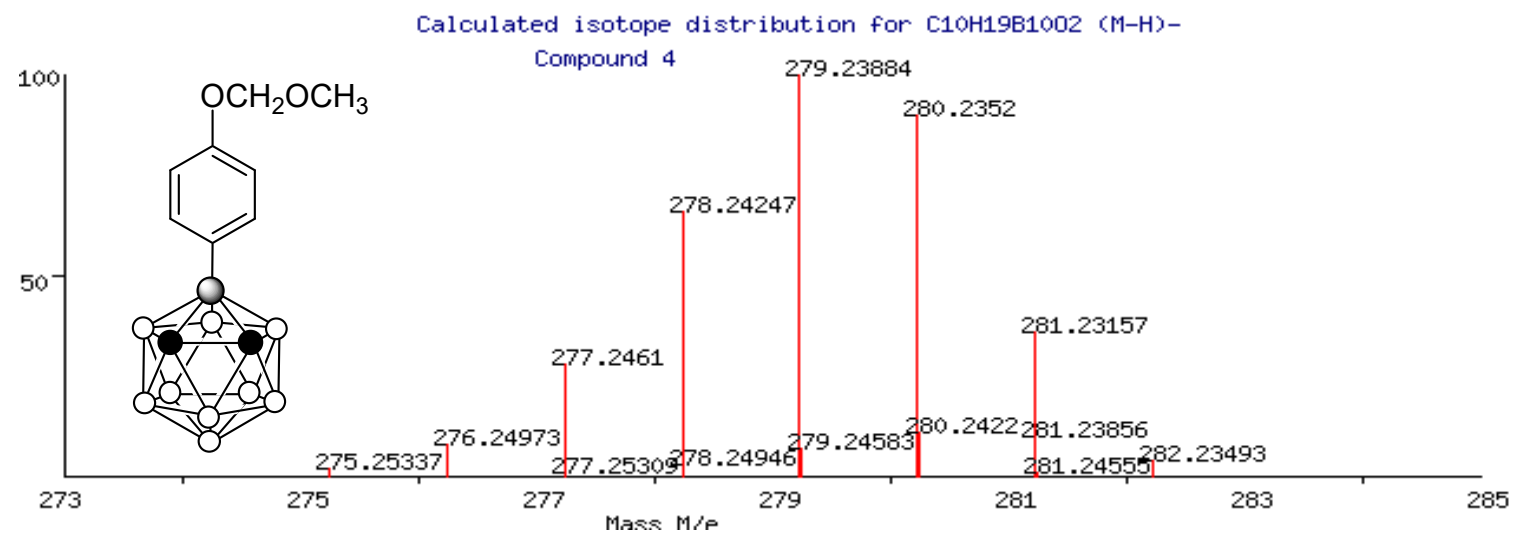


$^{13}\text{C}\{^1\text{H}\}$, compound 4

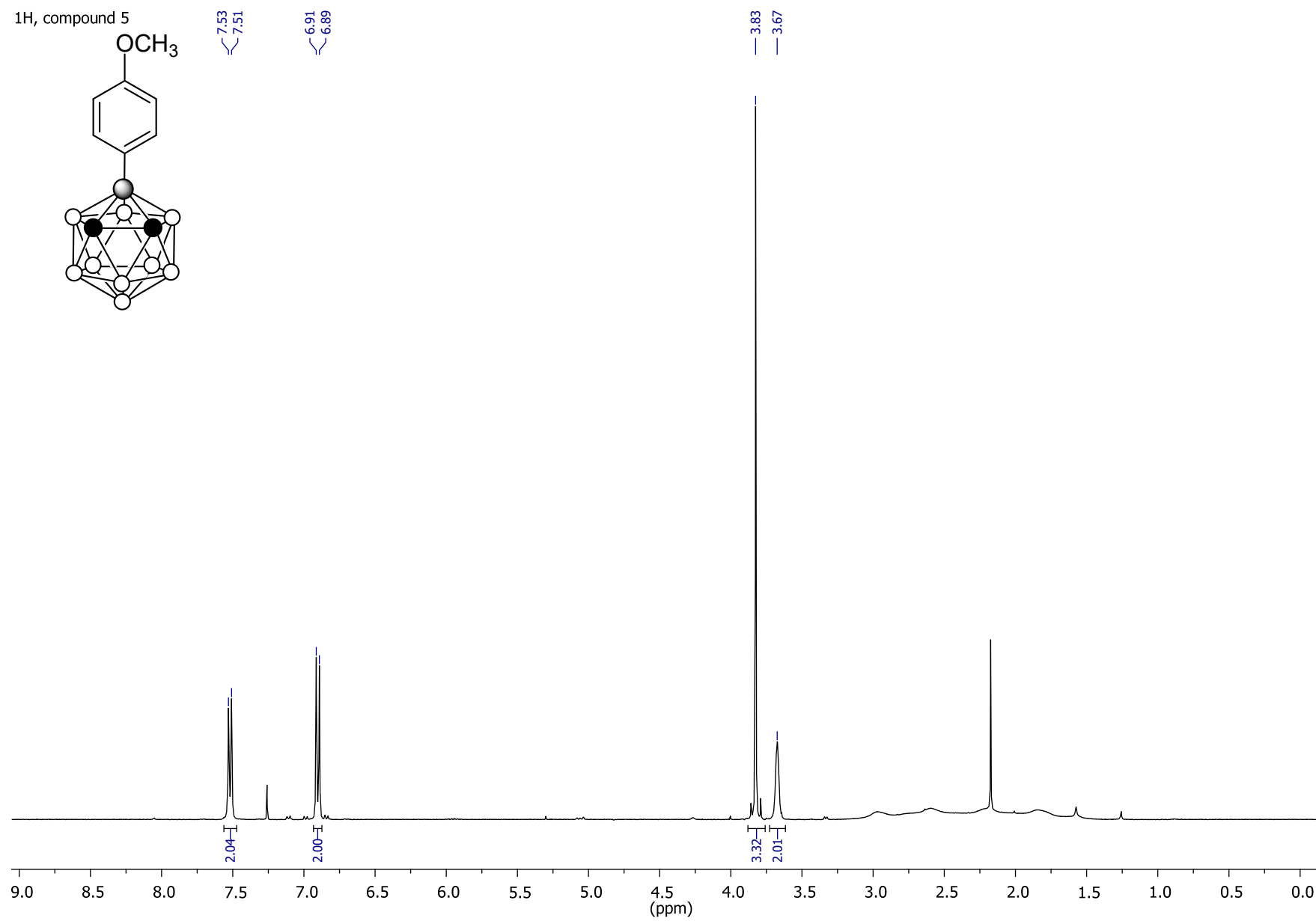
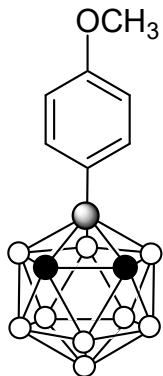




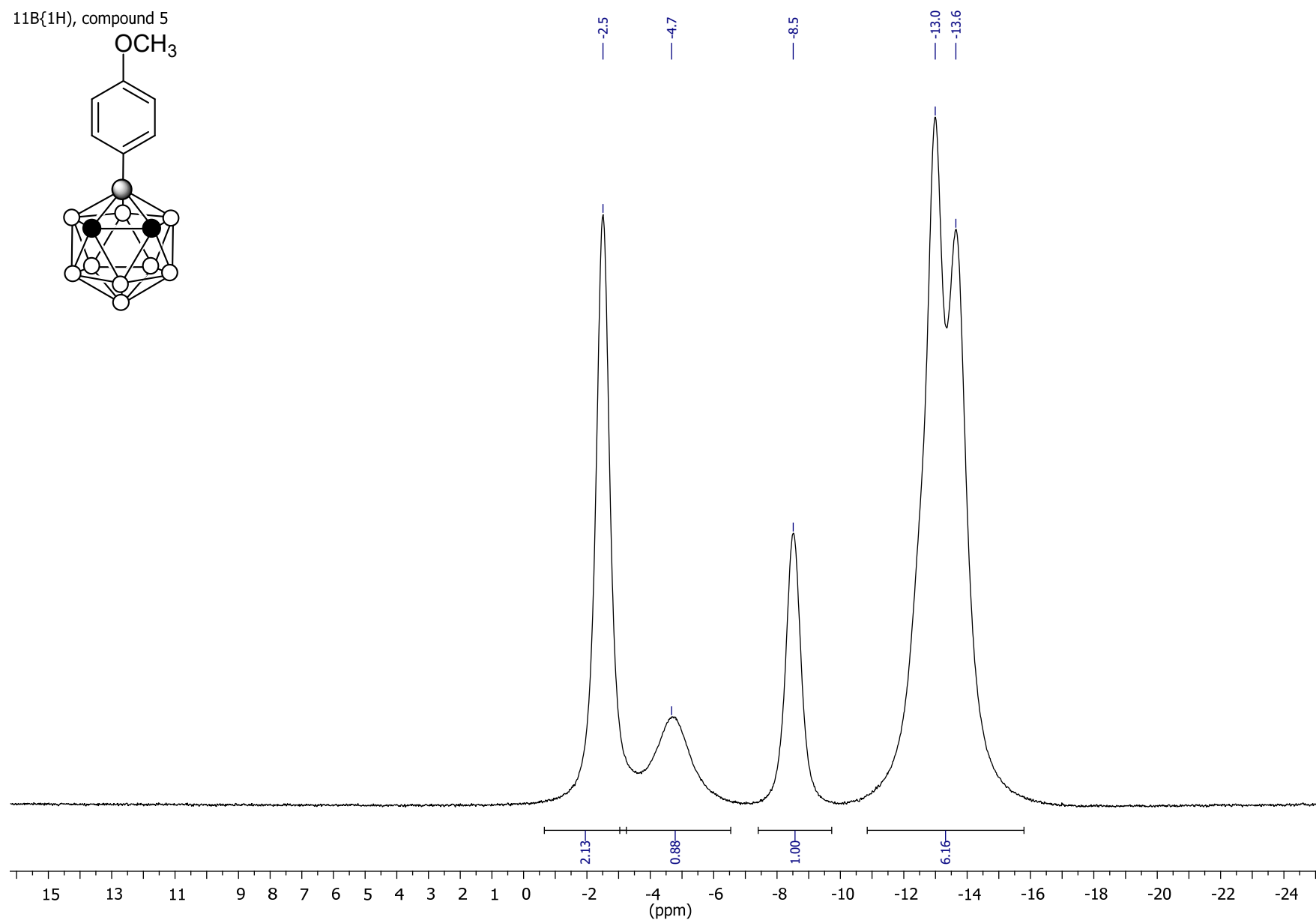
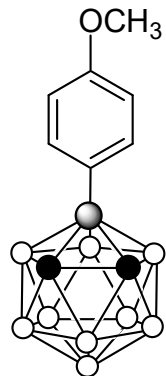




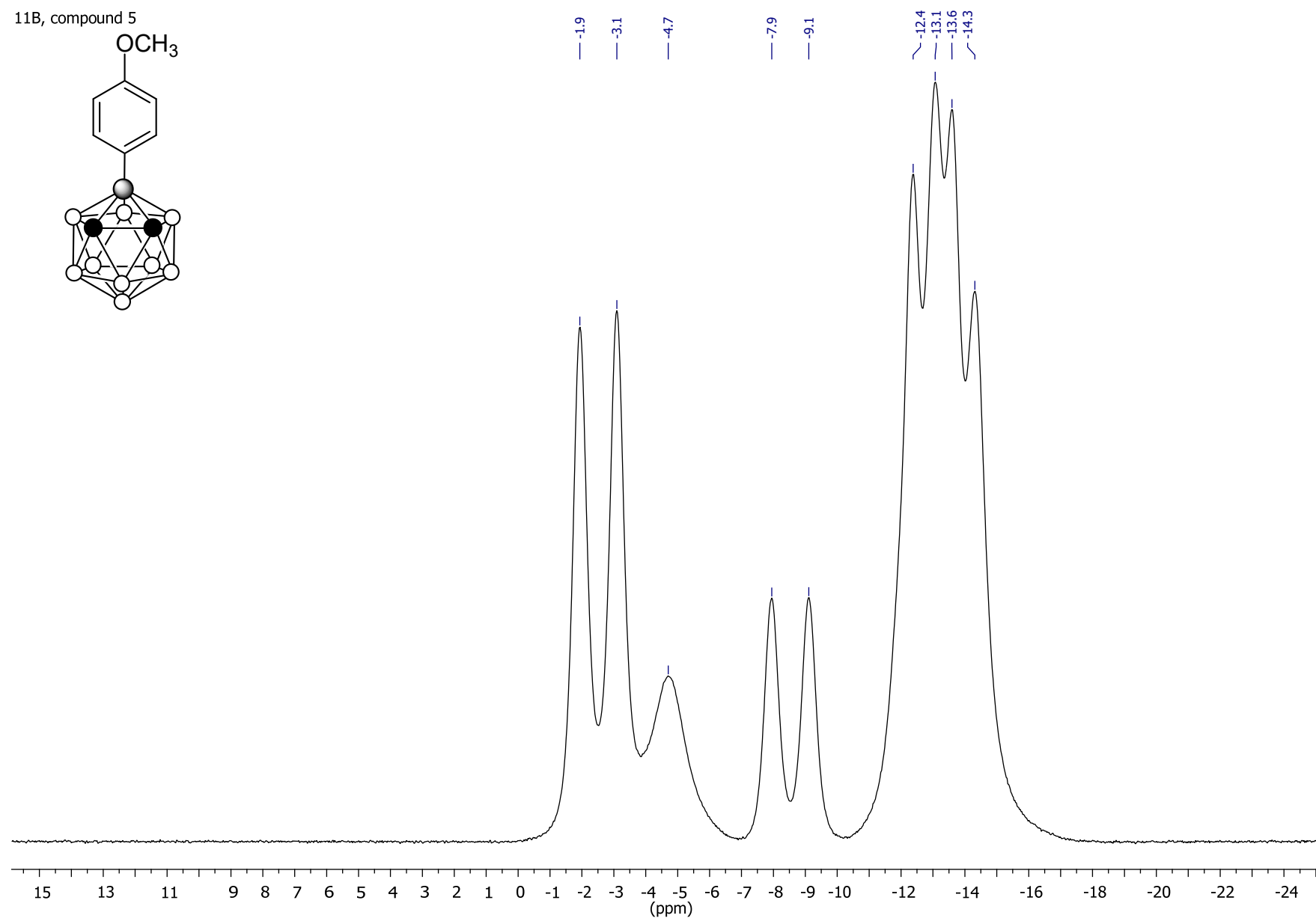
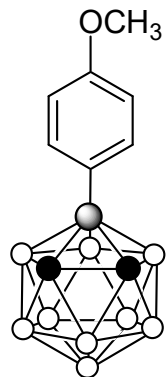
¹H, compound 5



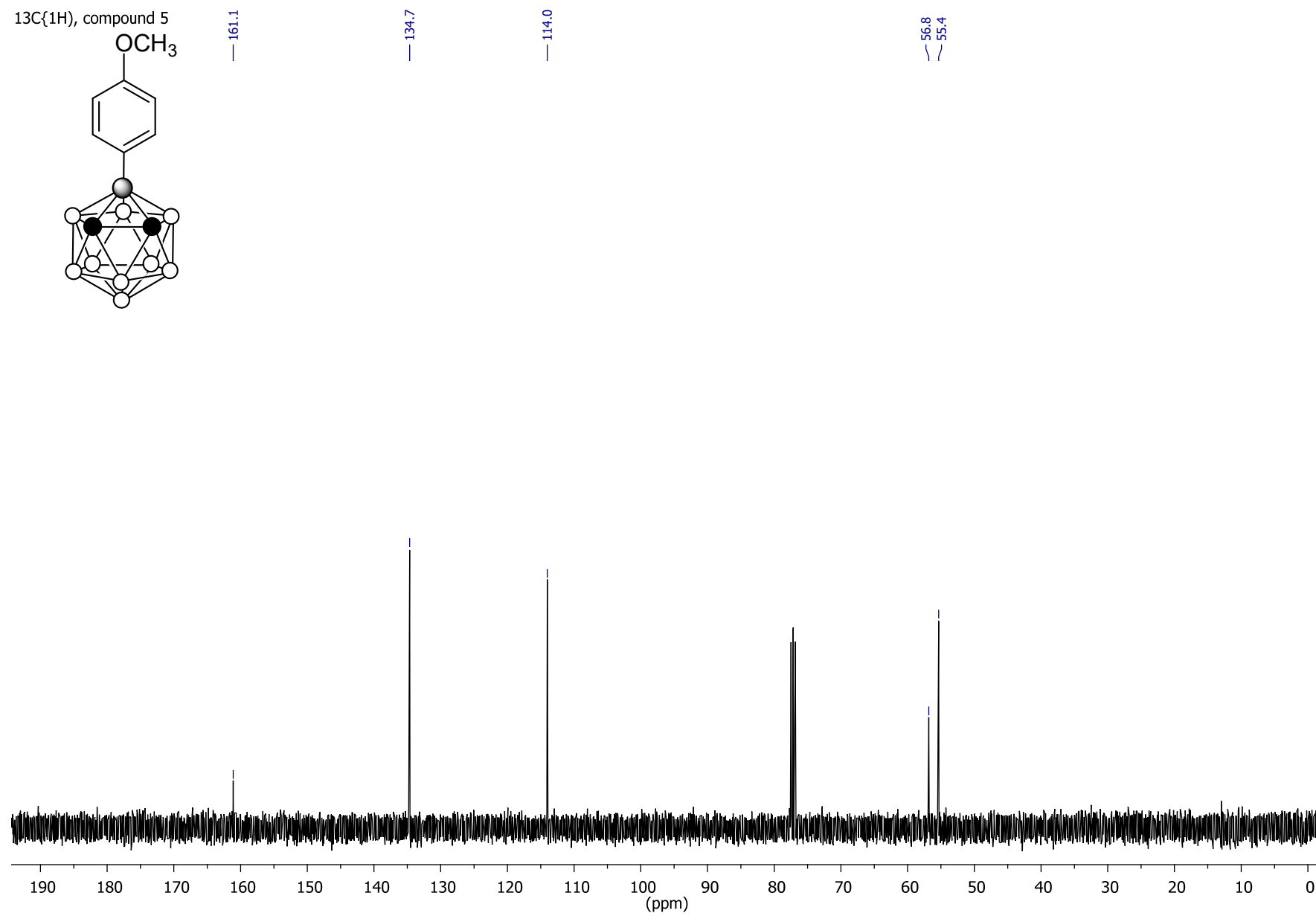
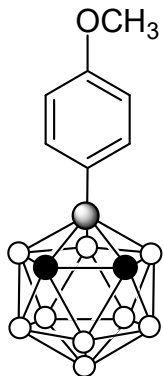
$^{11}\text{B}\{^1\text{H}\}$, compound 5

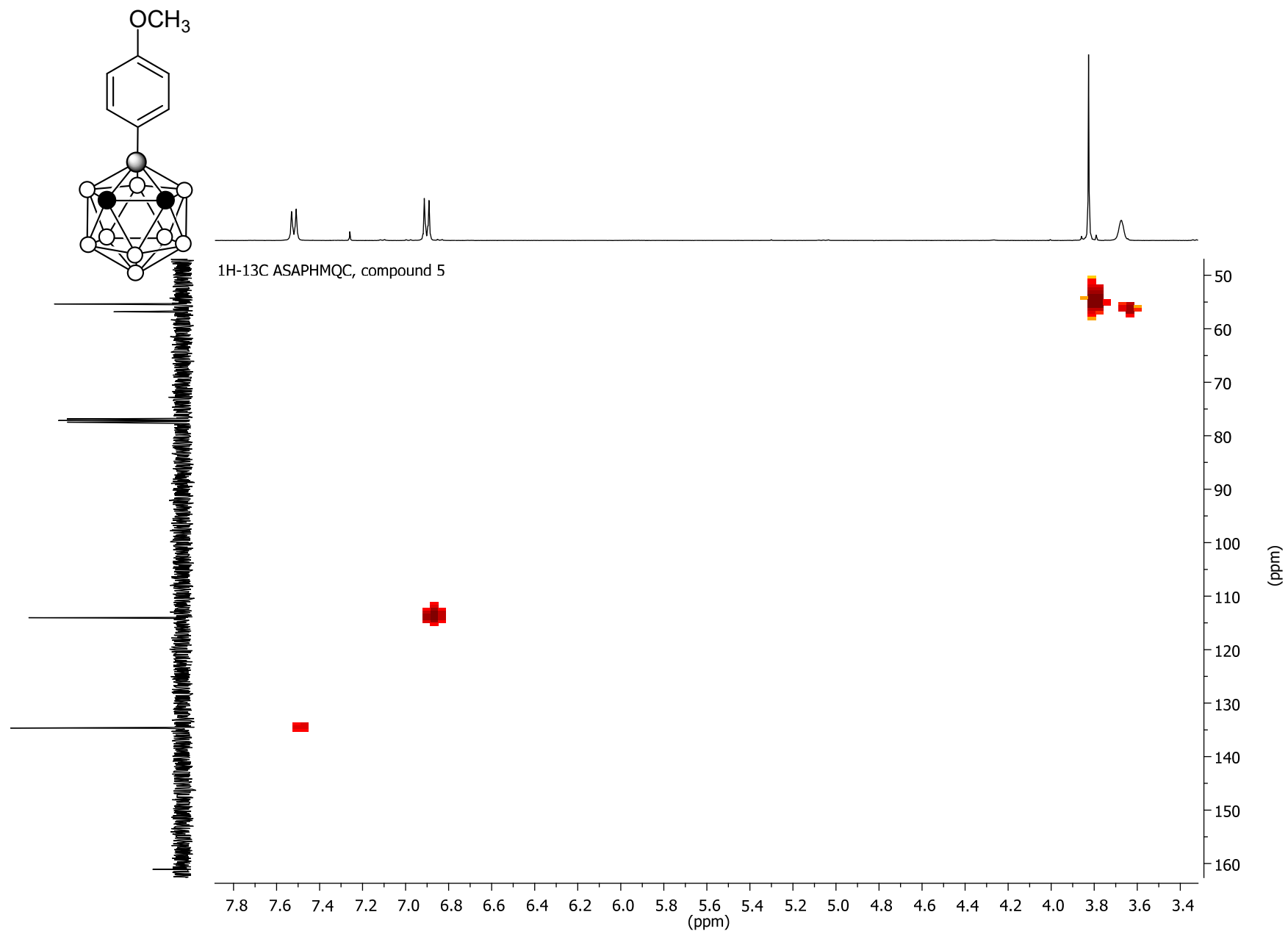


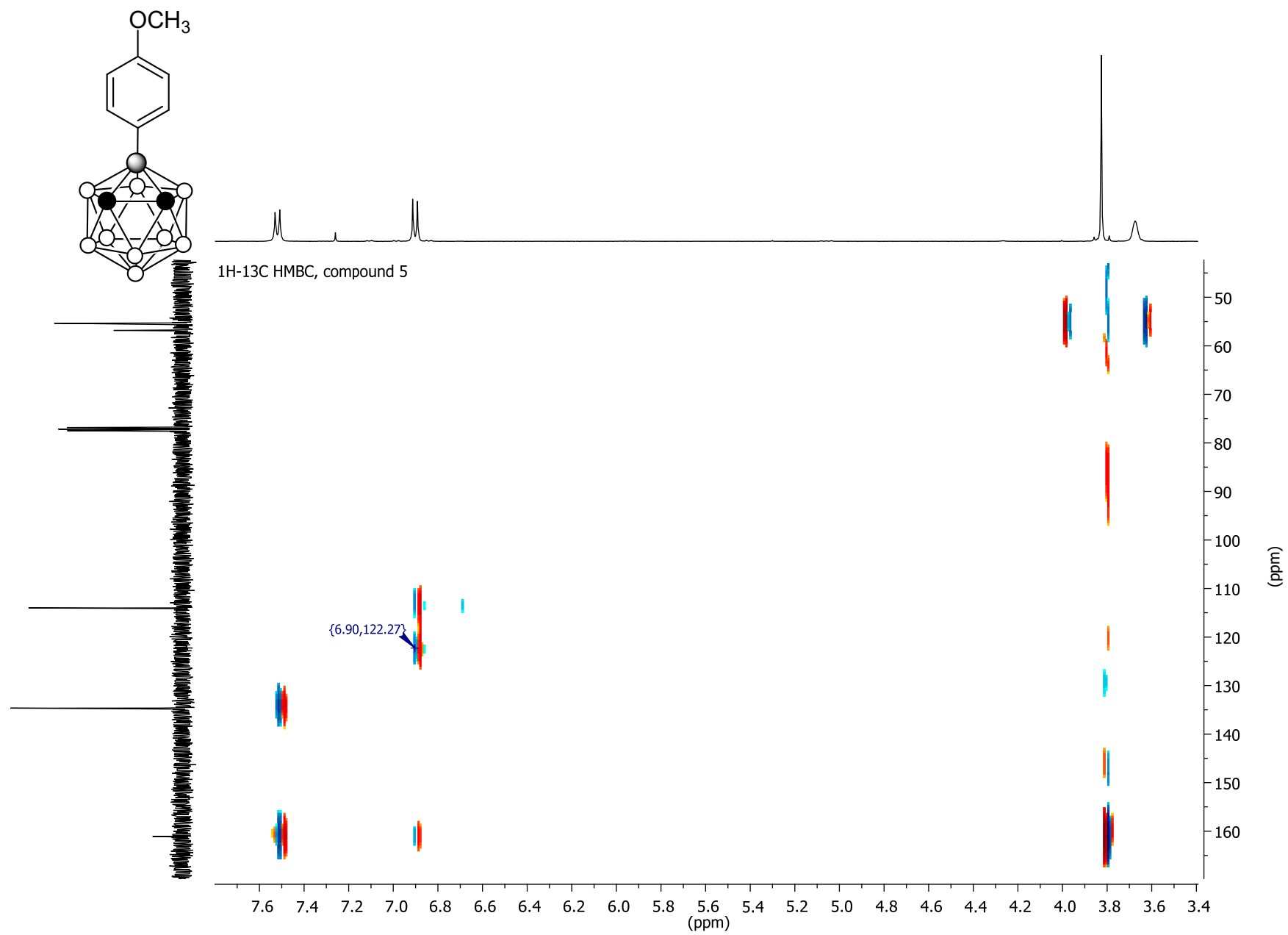
11B, compound 5

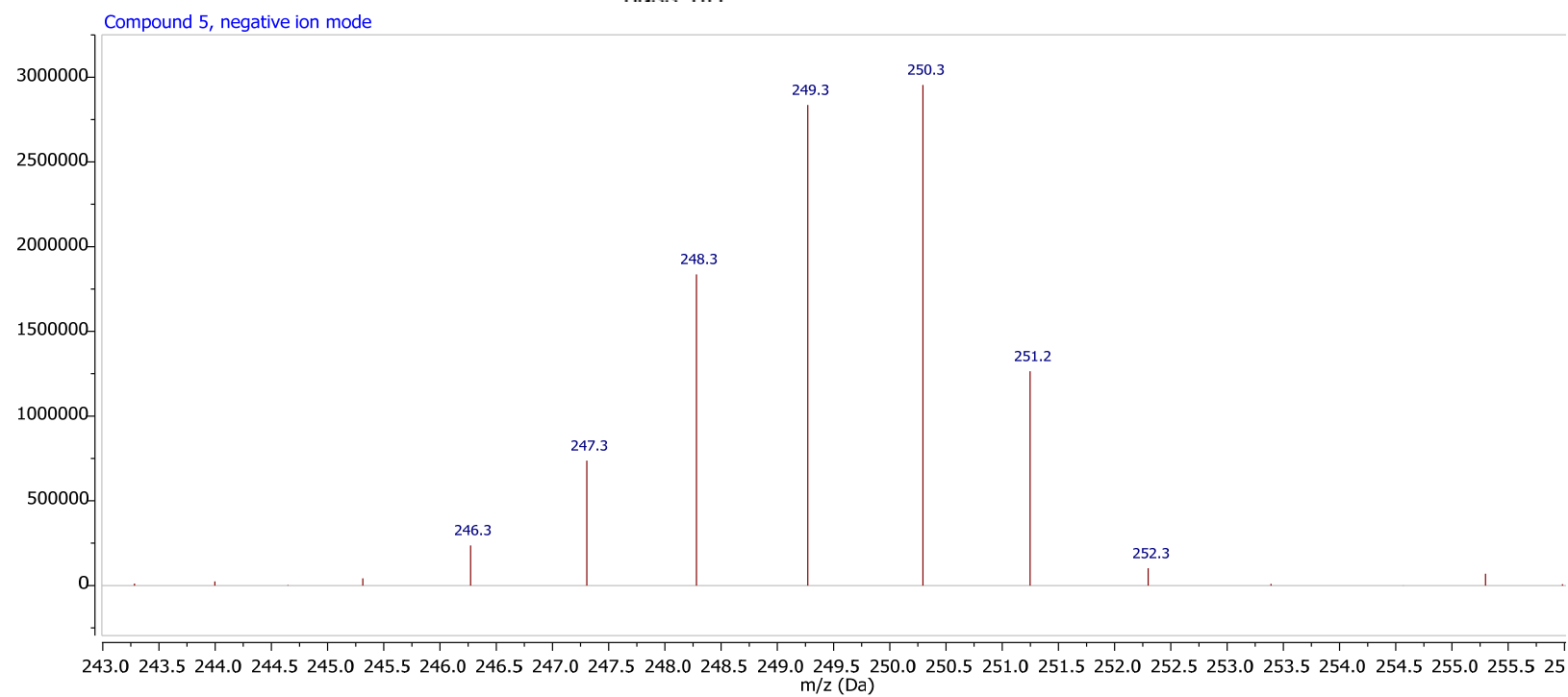
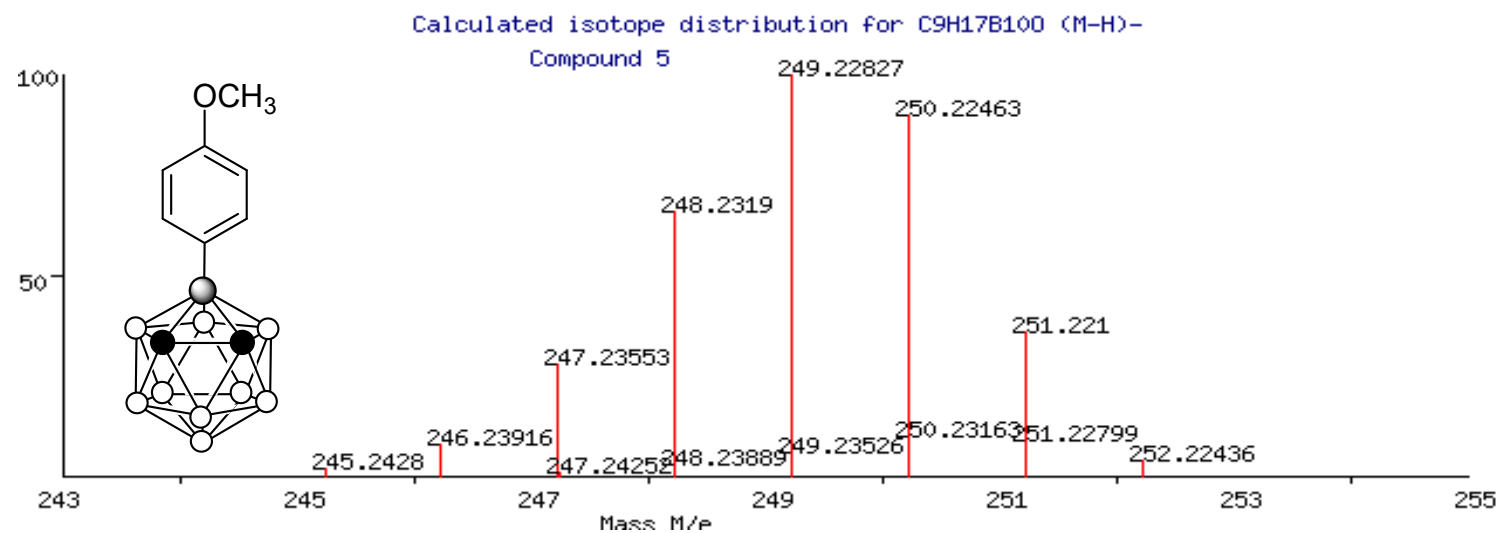


$^{13}\text{C}\{^1\text{H}\}$, compound 5

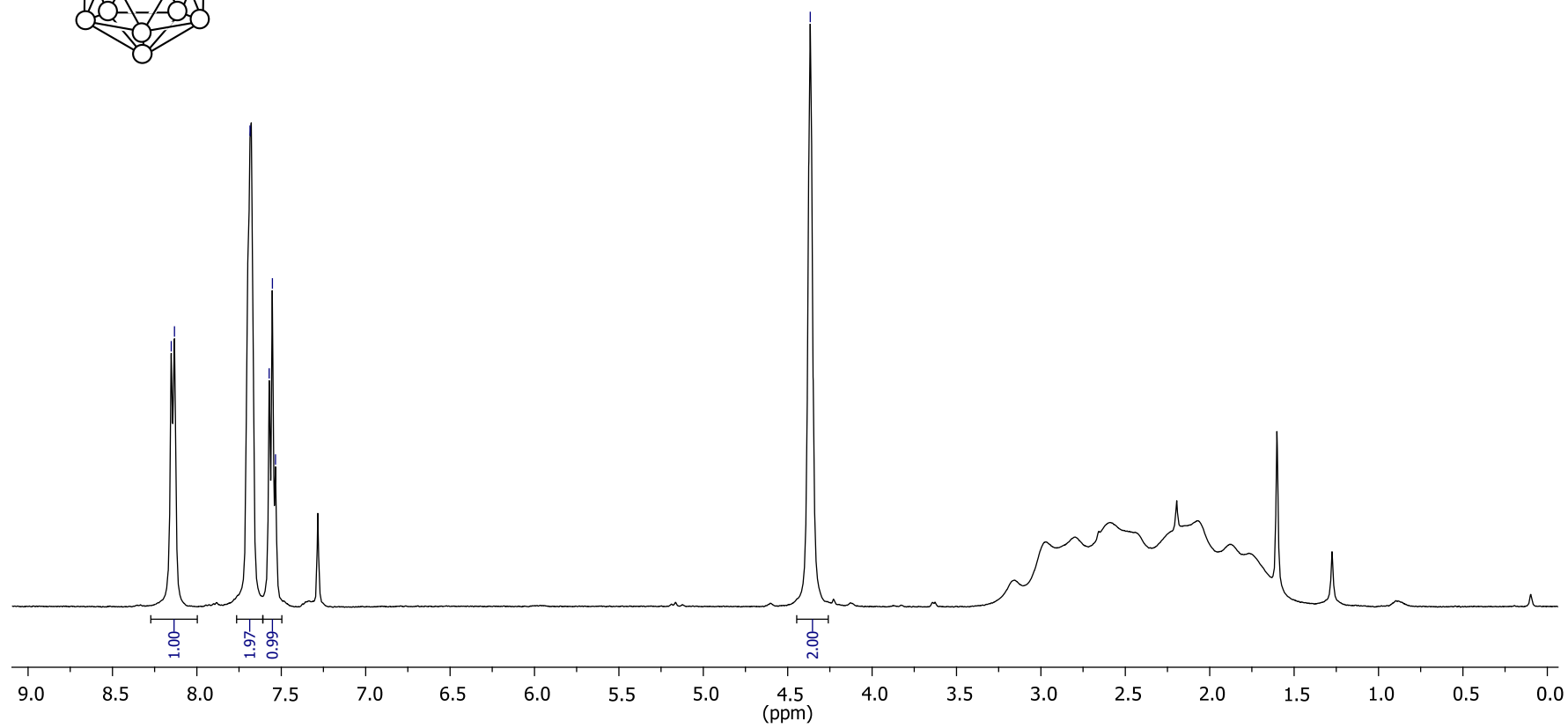
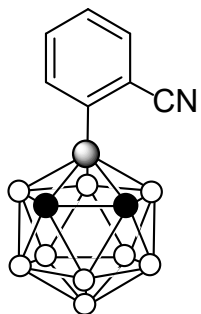




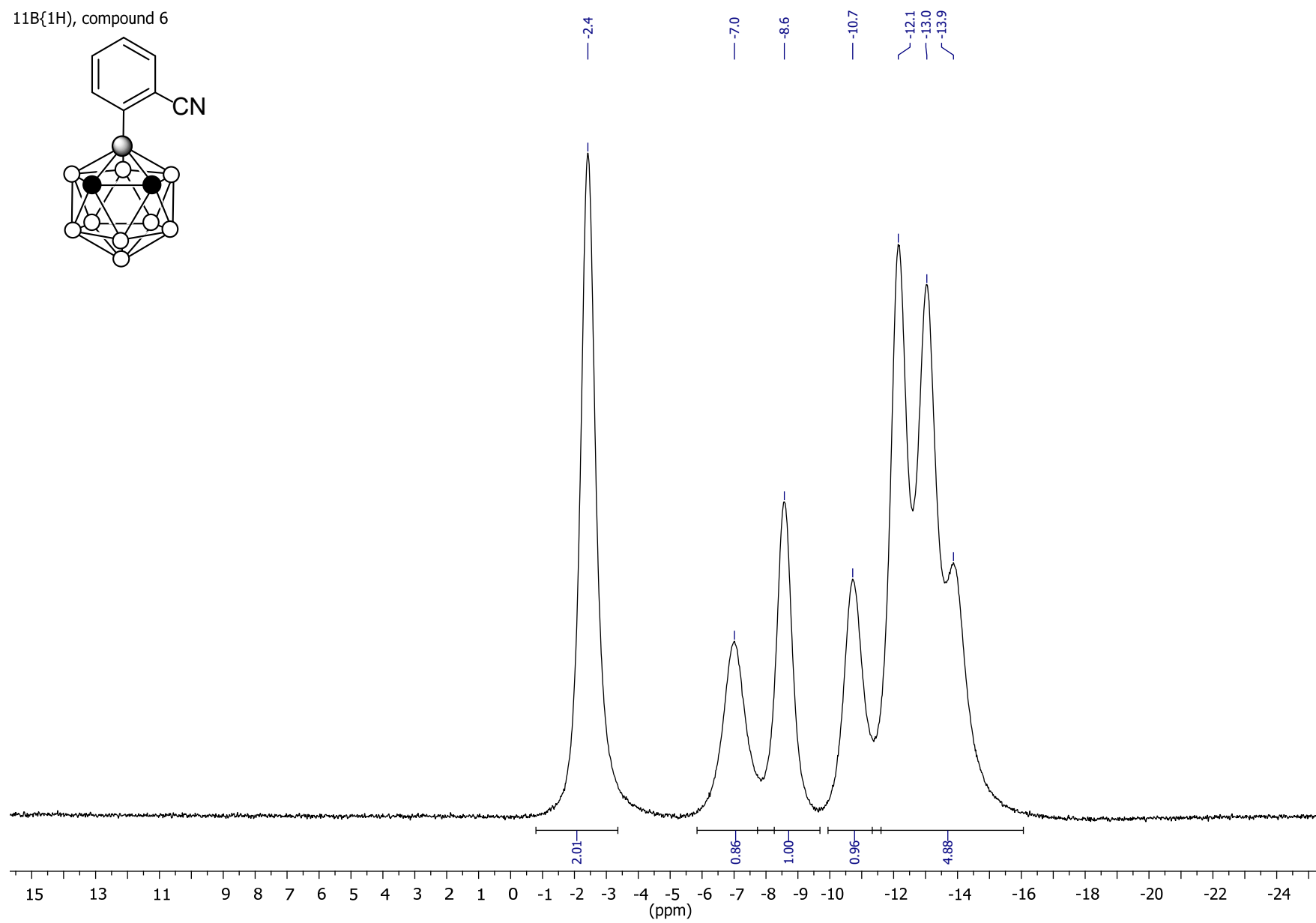
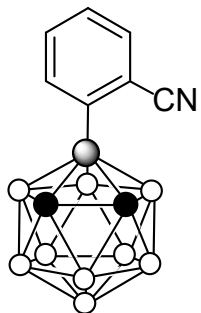




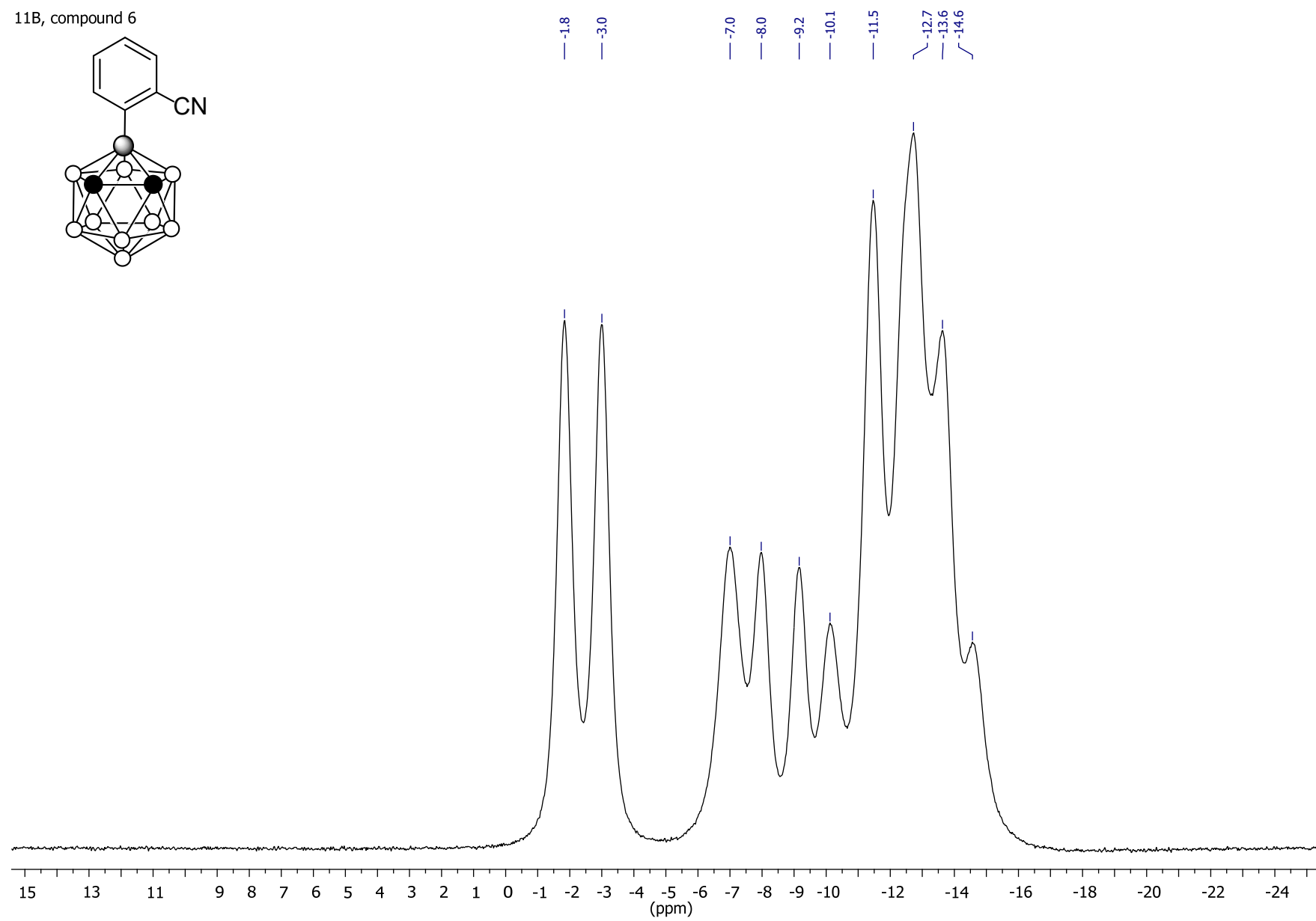
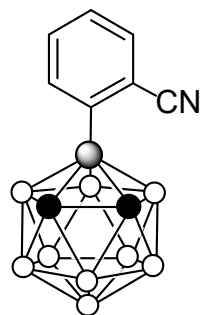
¹H, compound 6
8.15
8.13
7.69
7.57
7.55
7.53
4.37



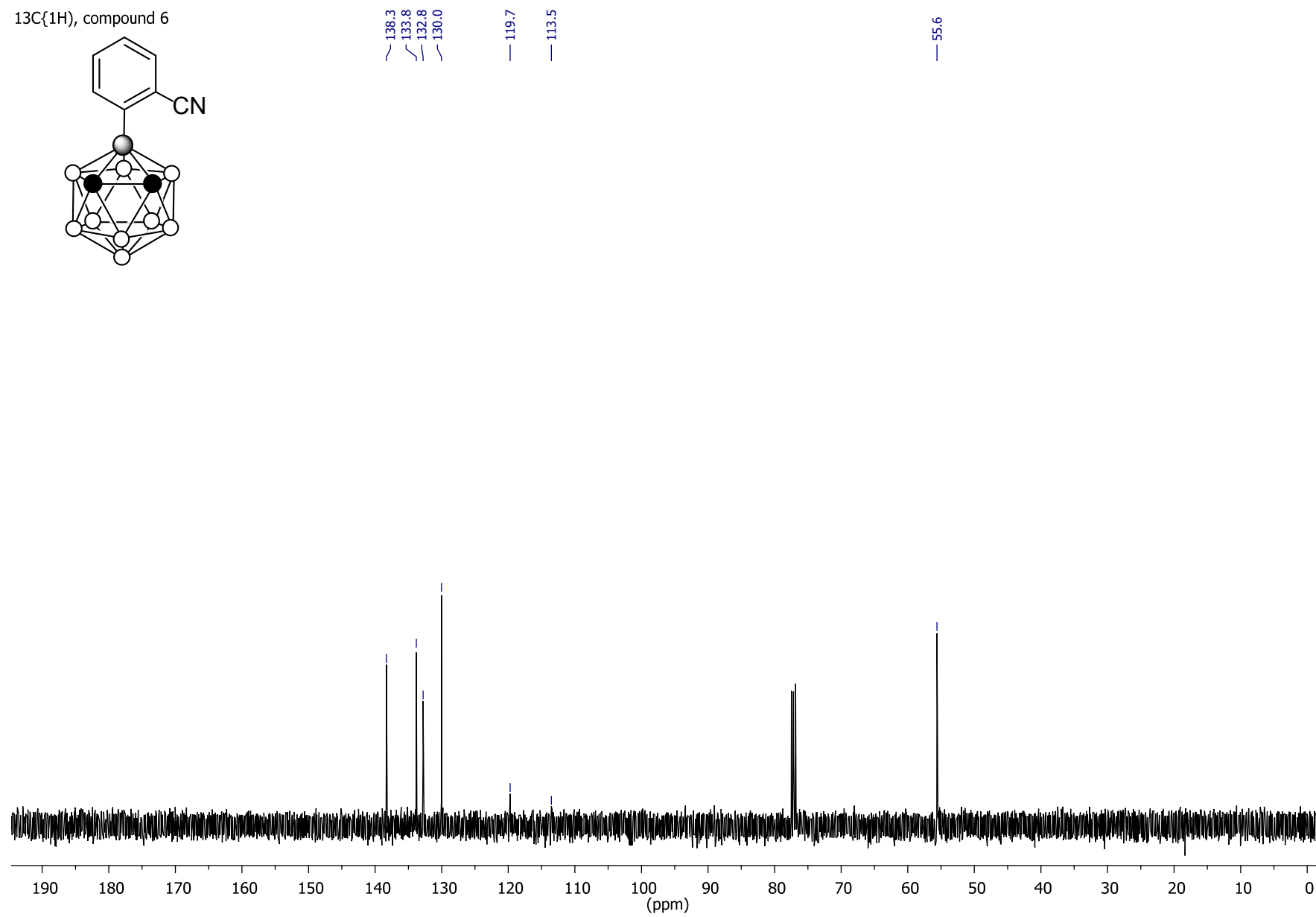
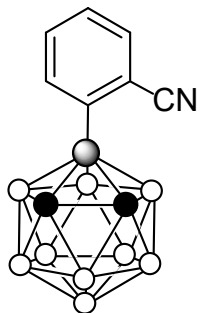
$^{11}\text{B}\{^1\text{H}\}$, compound 6

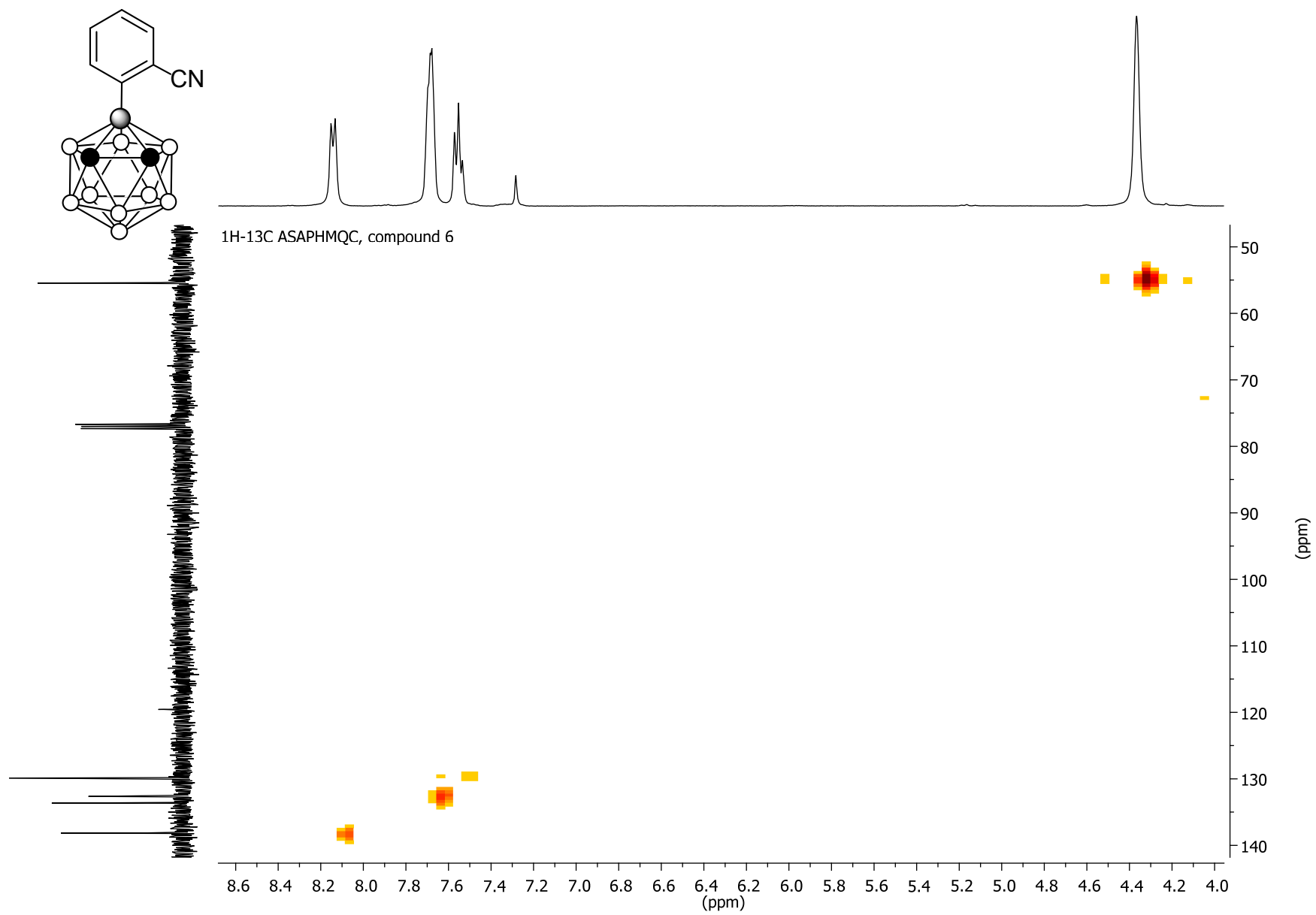


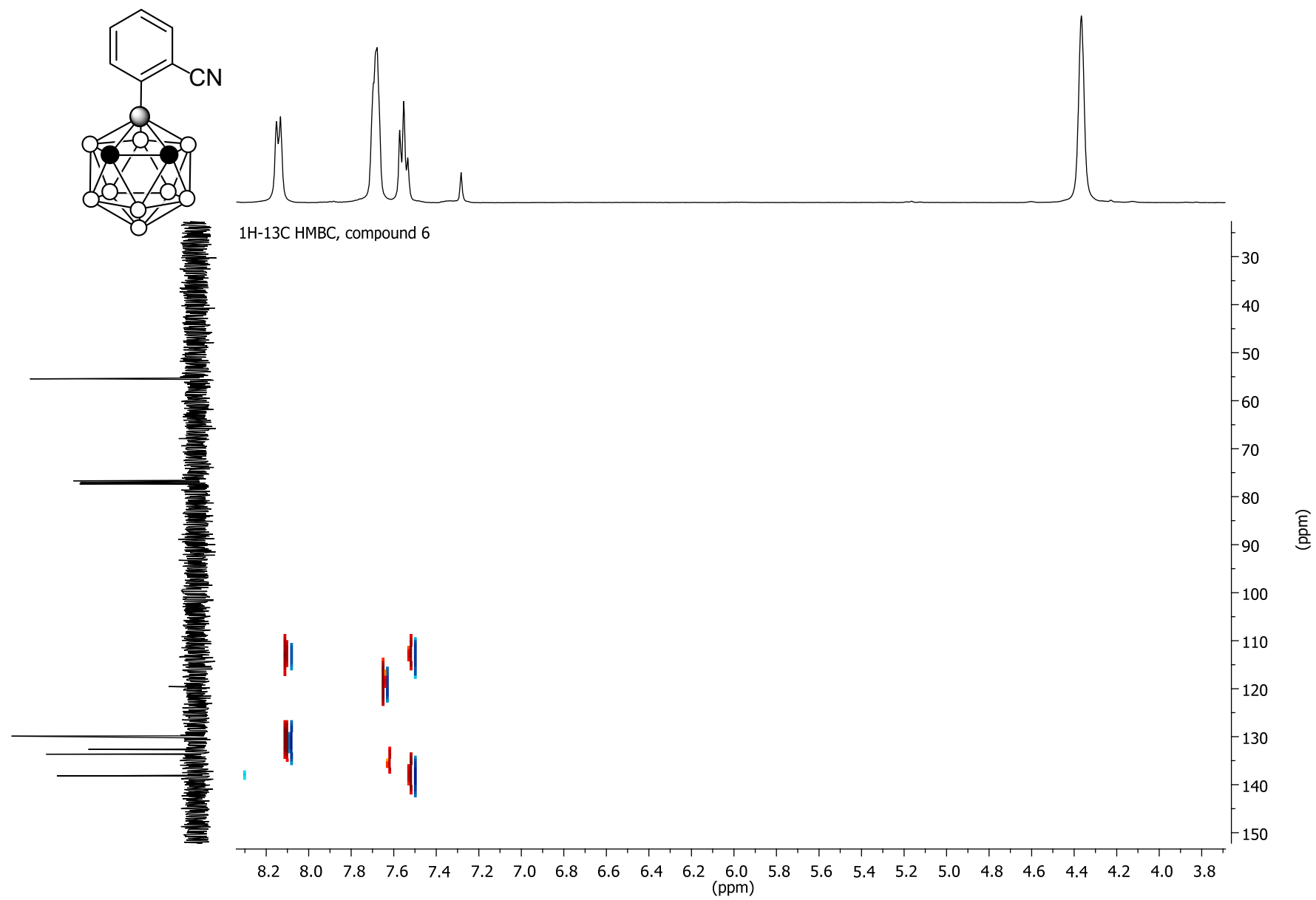
¹¹B, compound 6

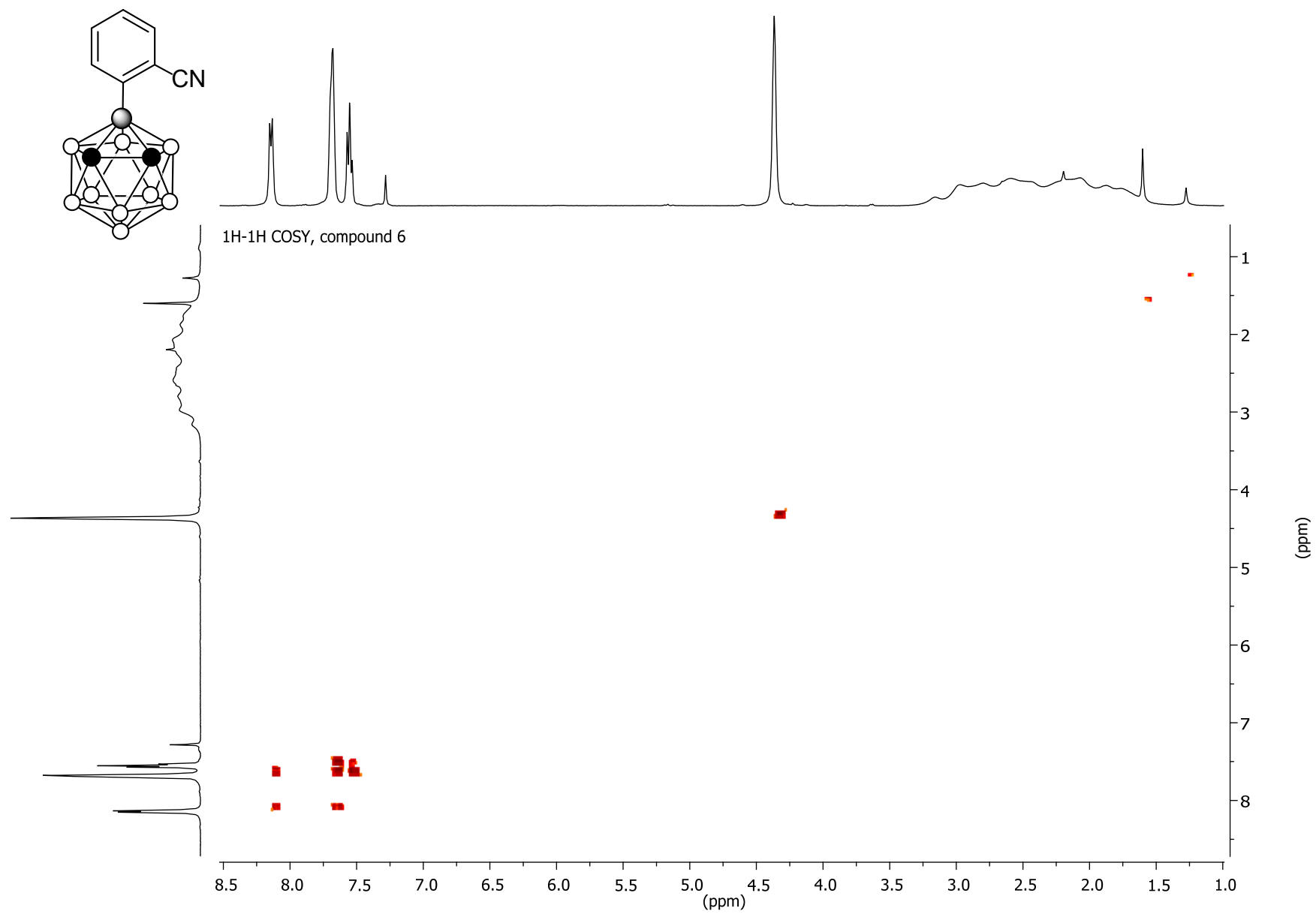


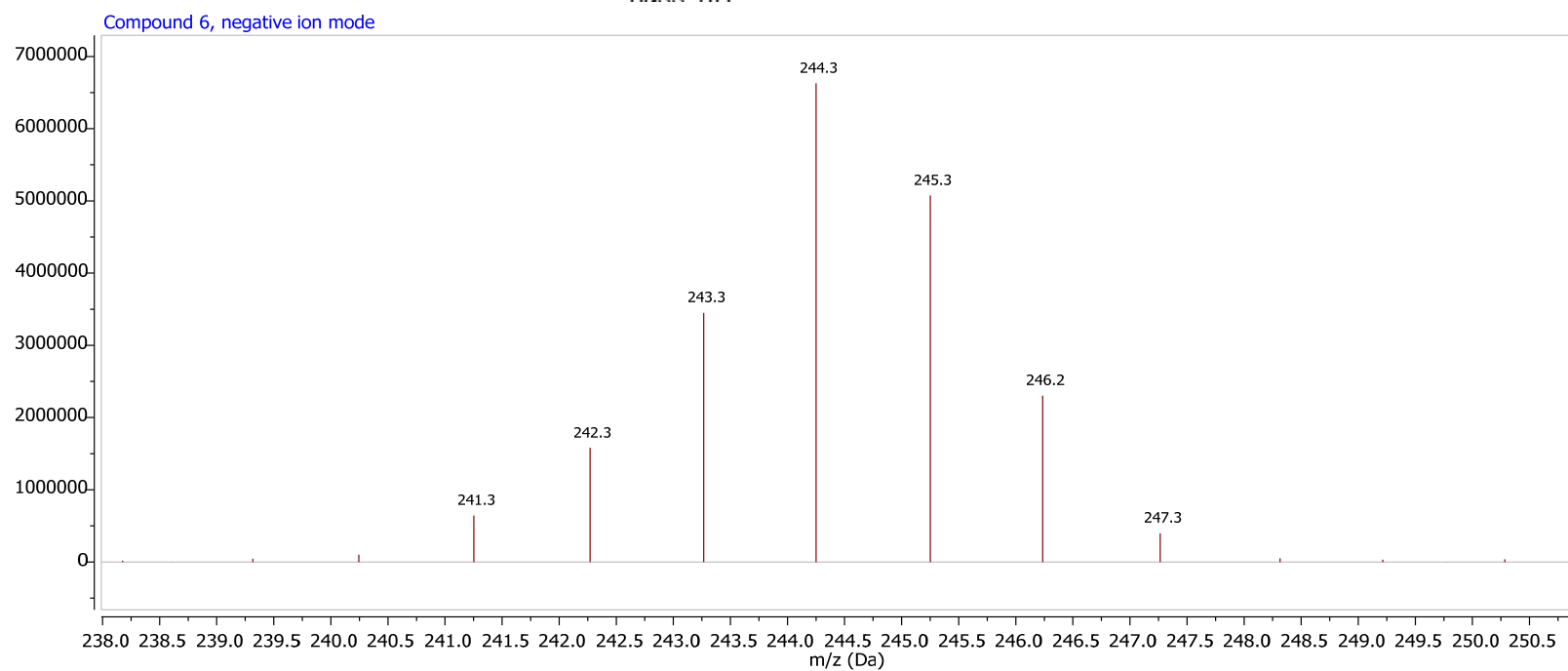
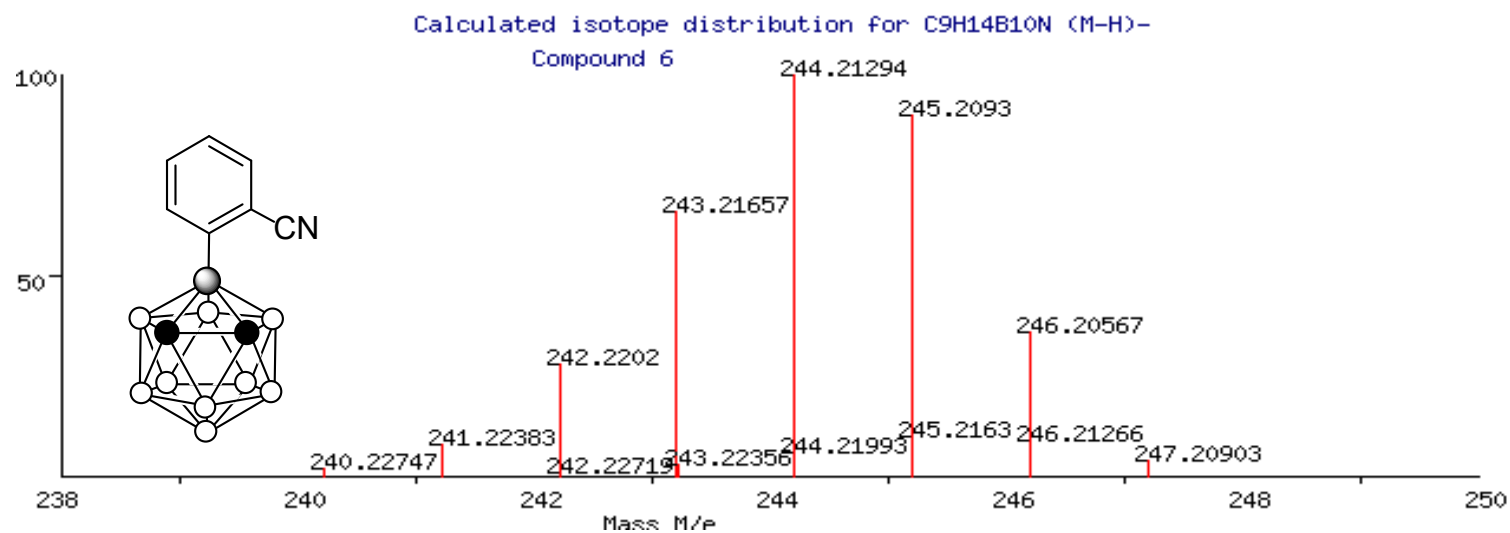
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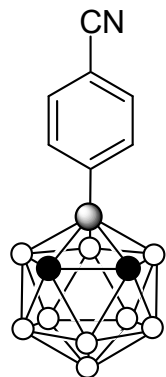






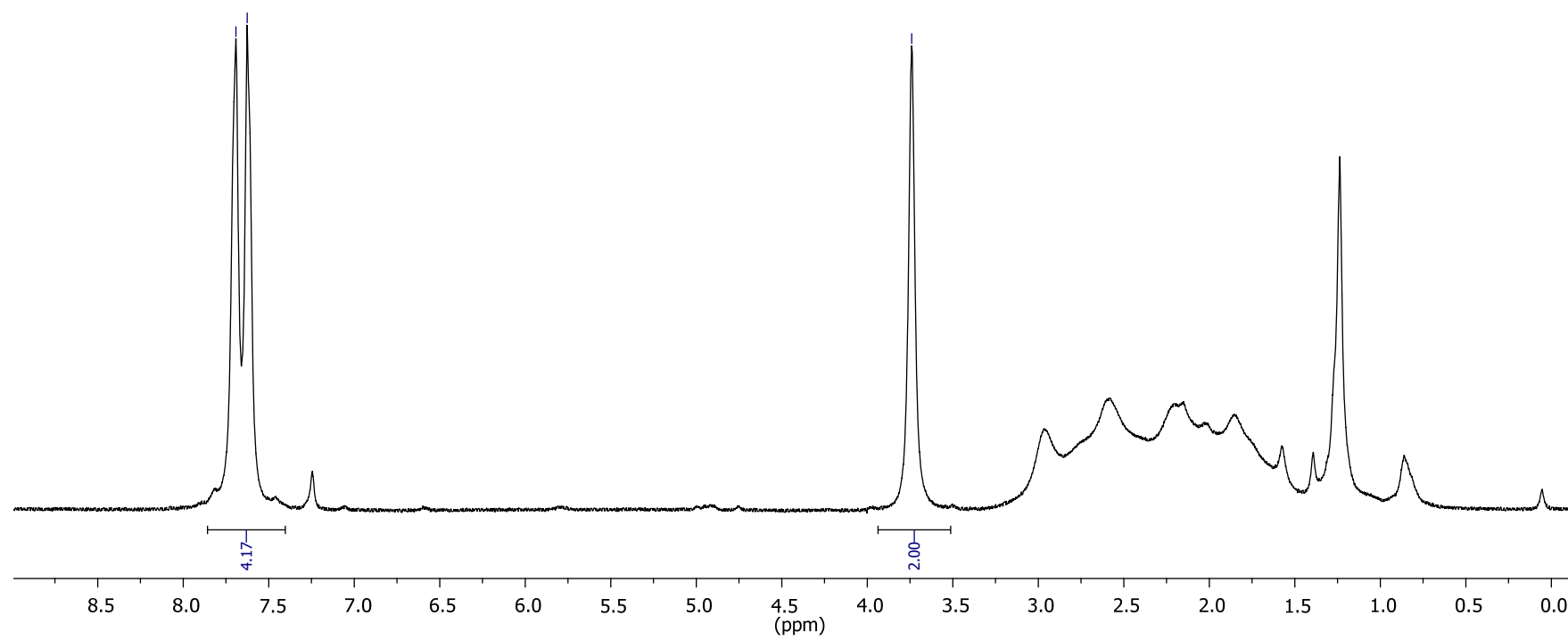


¹H, compound 7

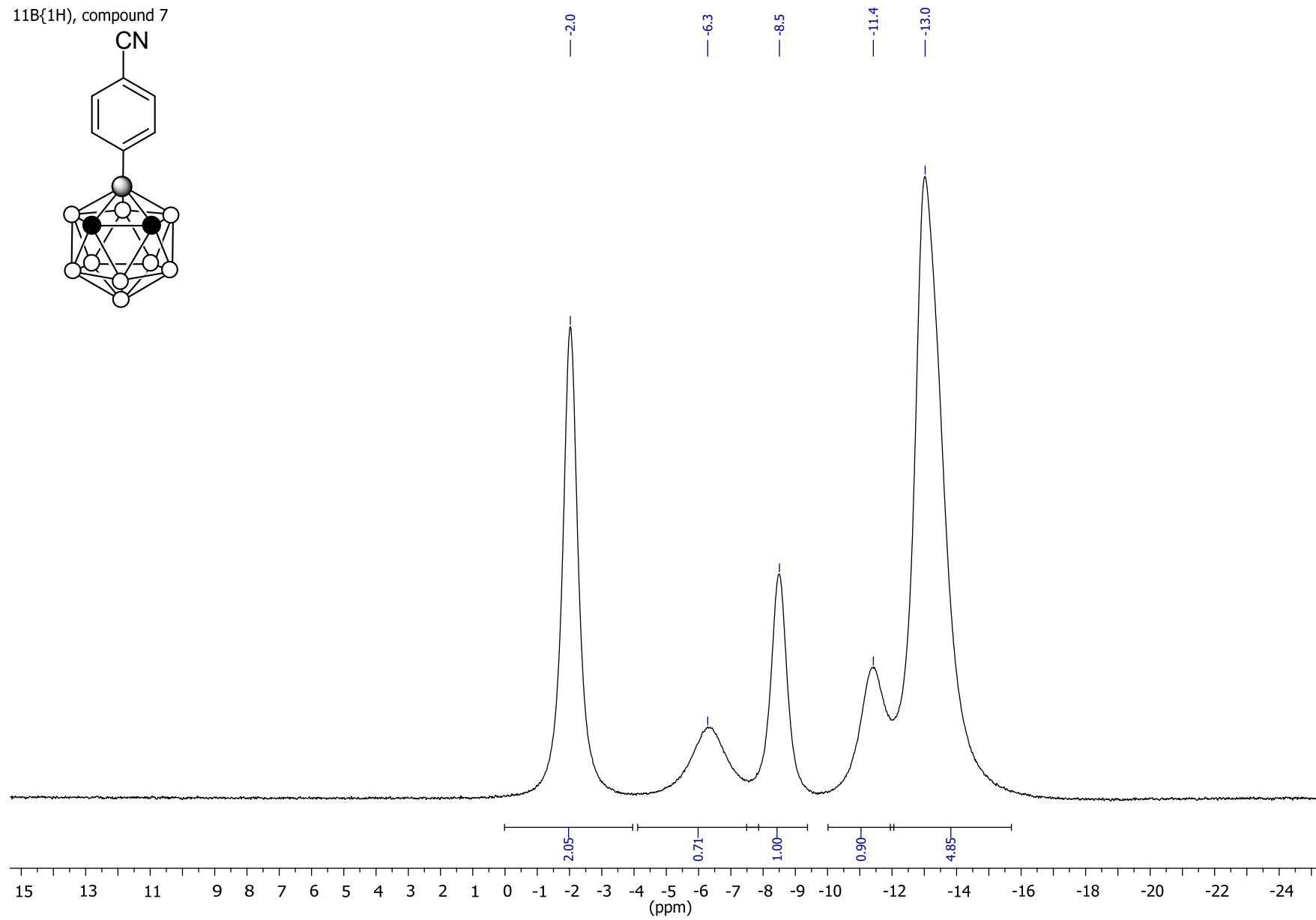
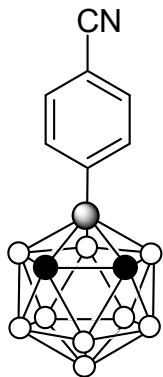


7.69
7.63

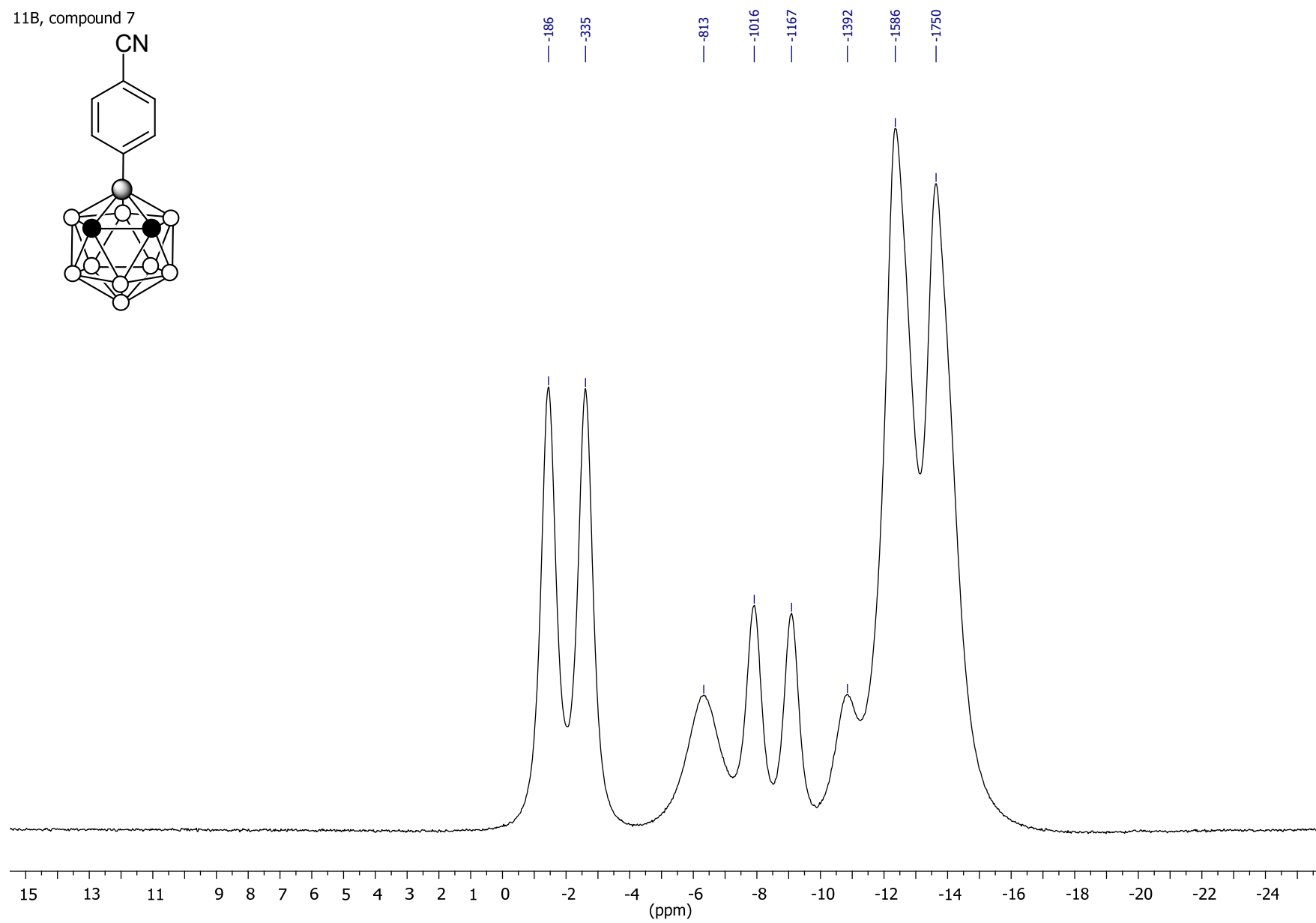
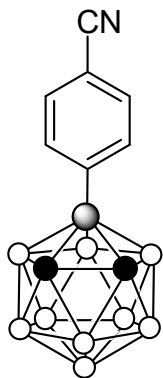
3.74



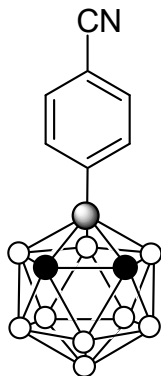
$^{11}\text{B}\{^1\text{H}\}$, compound 7



11B, compound 7



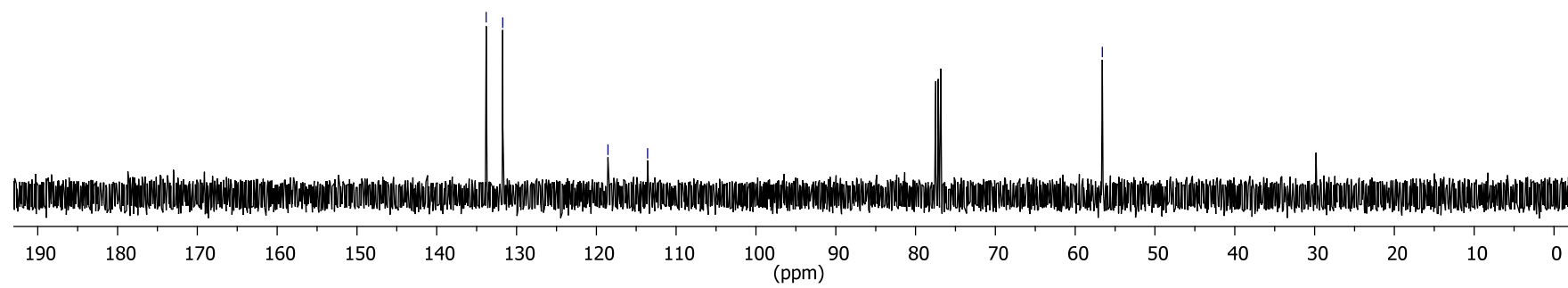
$^{13}\text{C}\{^1\text{H}\}$, compound 7

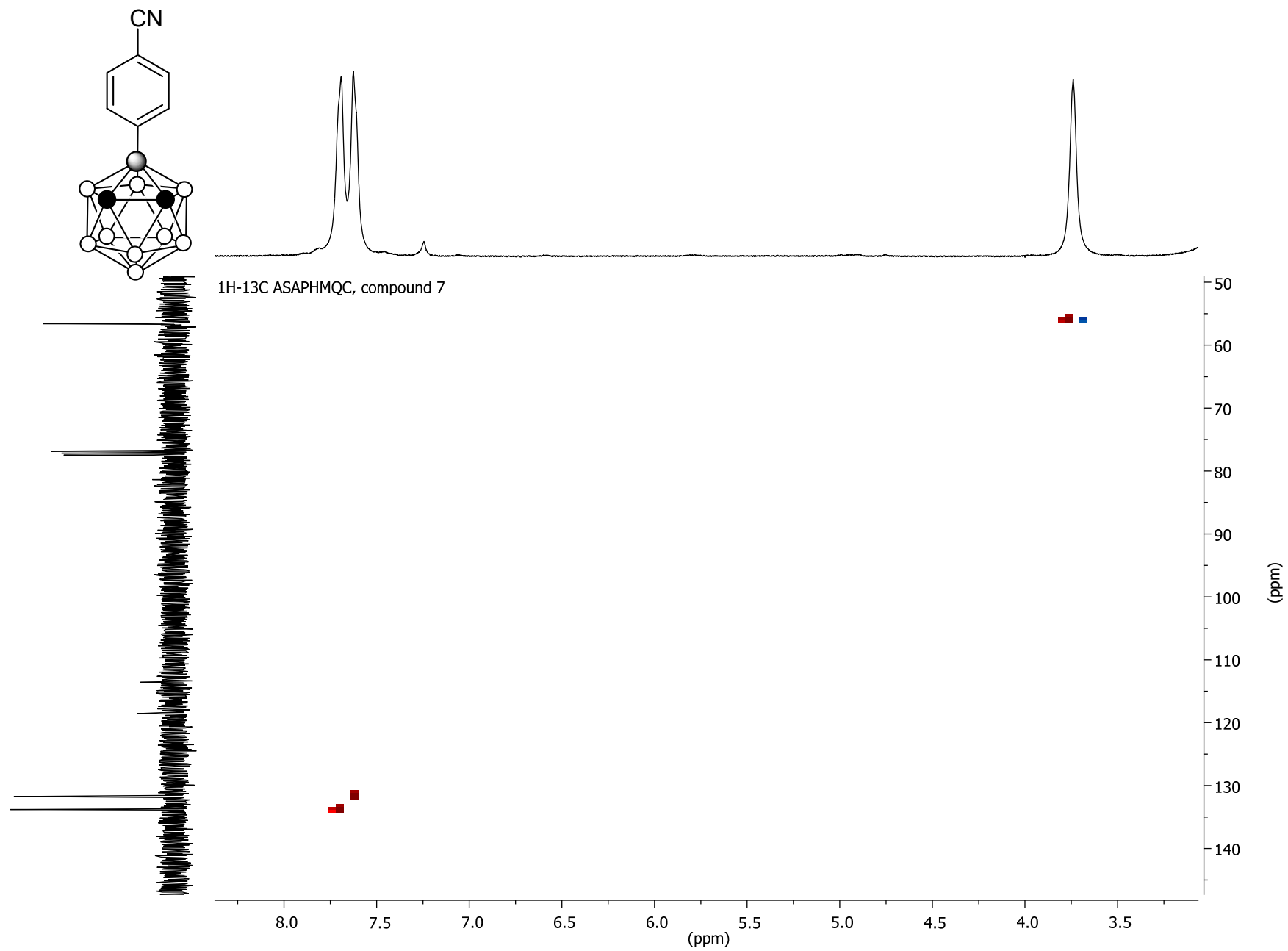


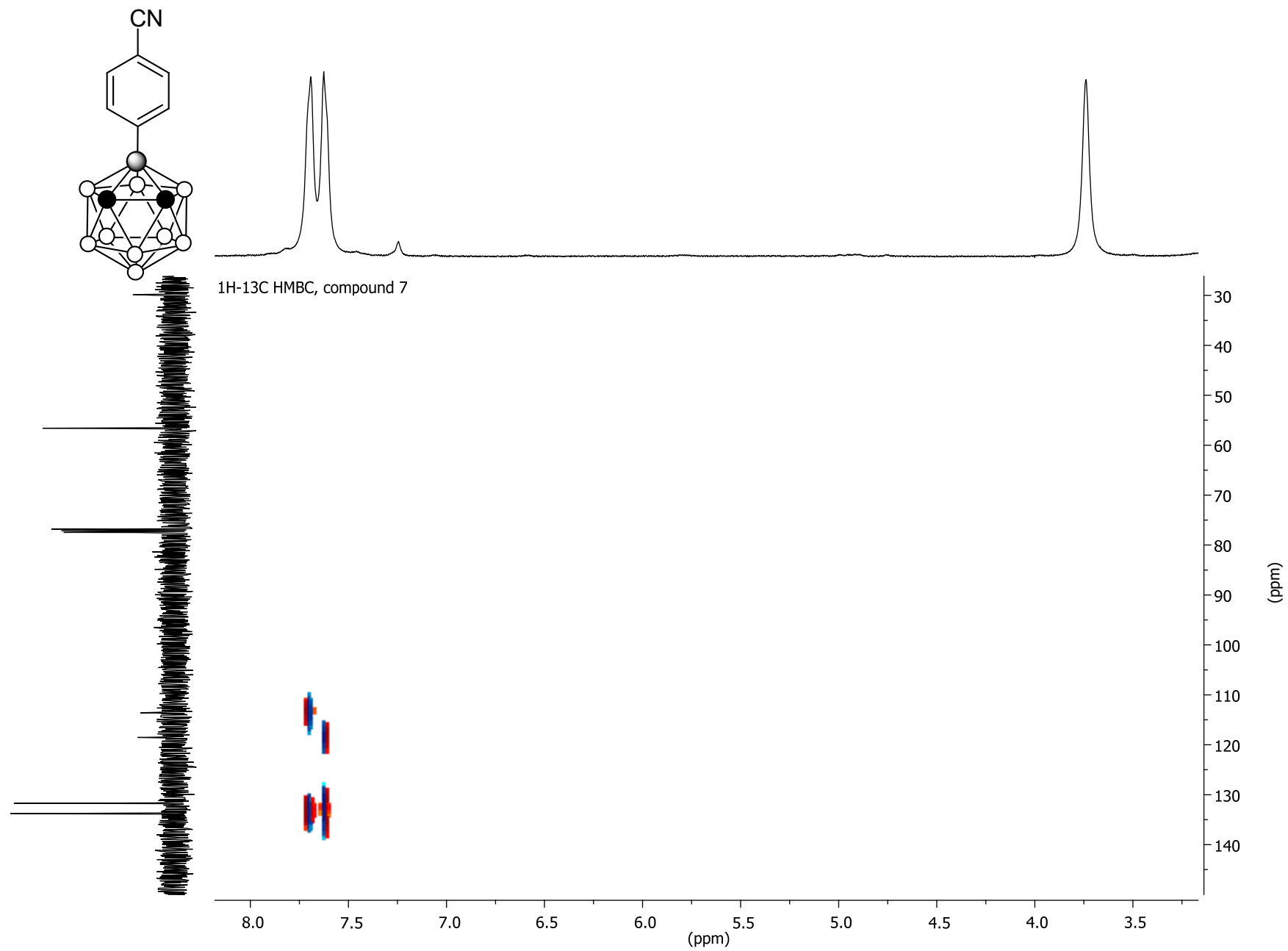
— 133.8
— 131.7

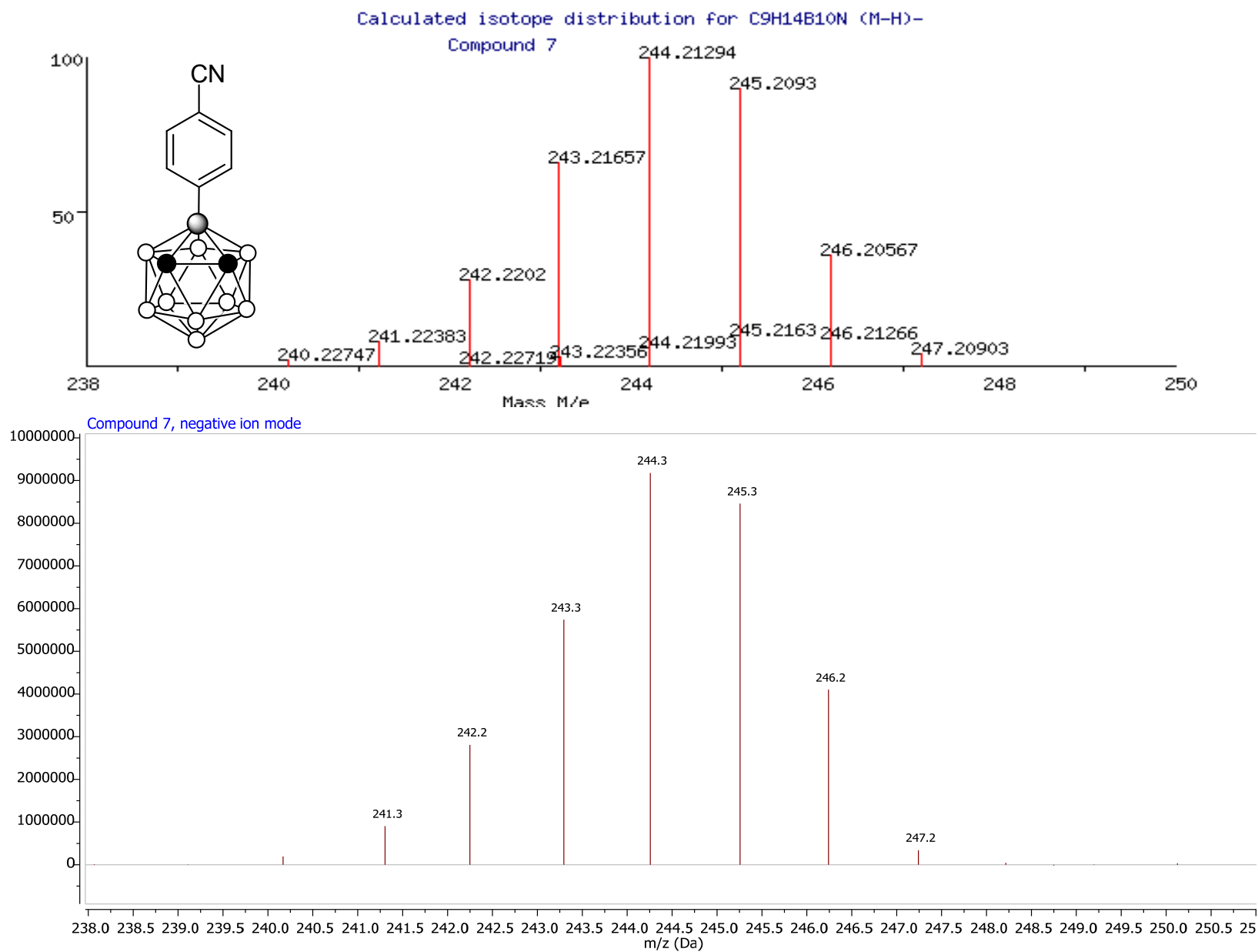
— 118.5
— 113.6

— 56.6

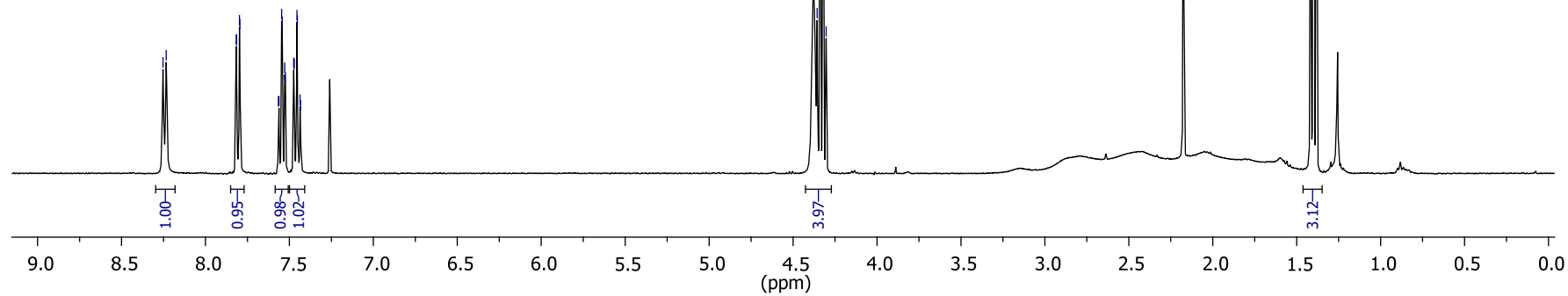
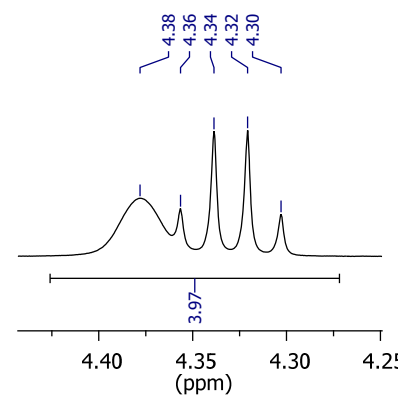
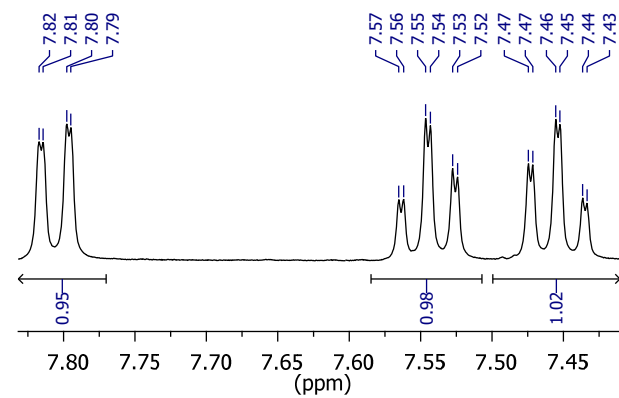
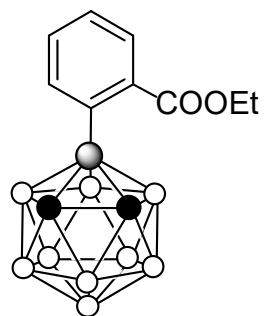
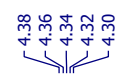




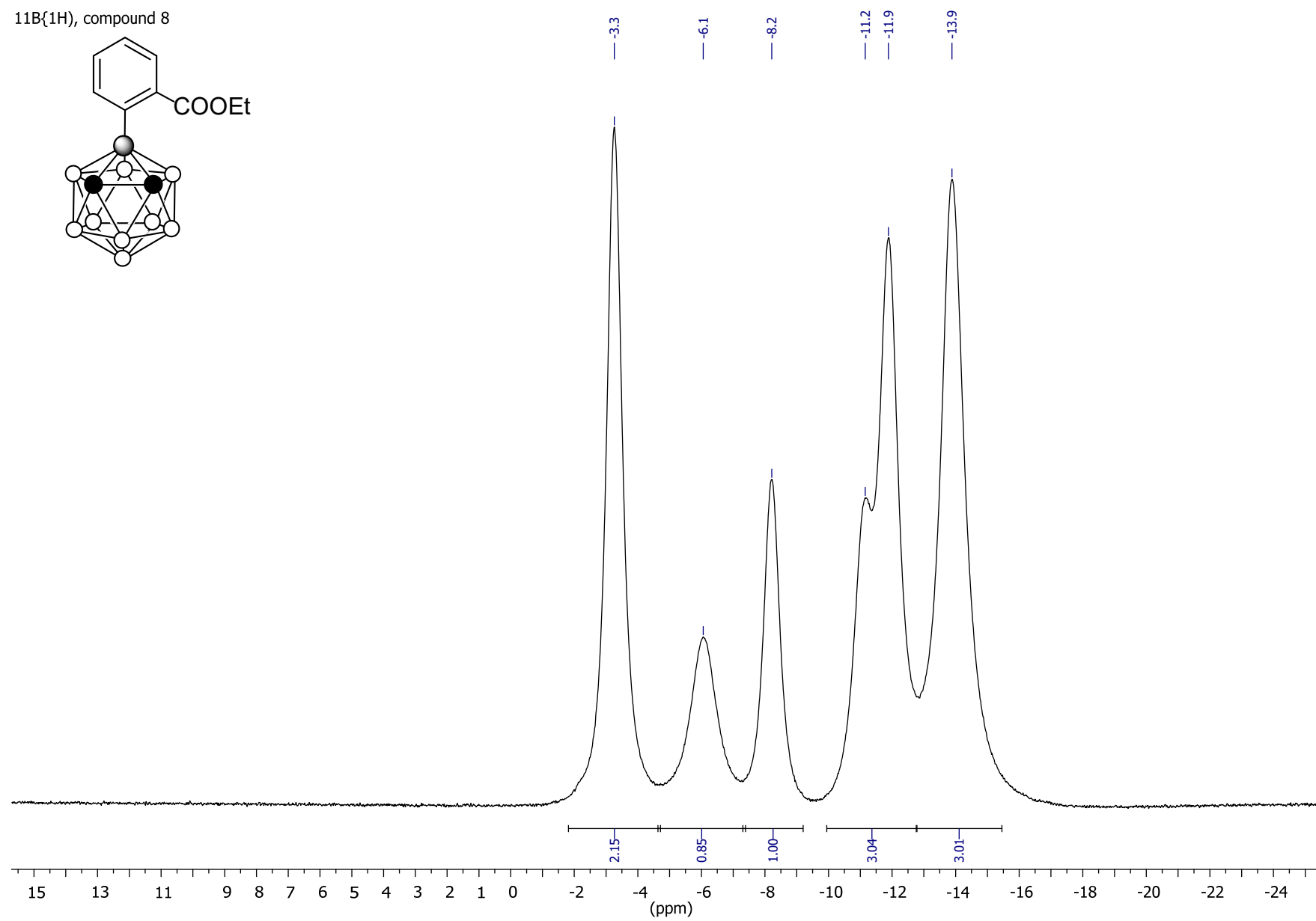
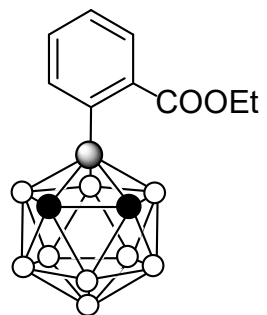




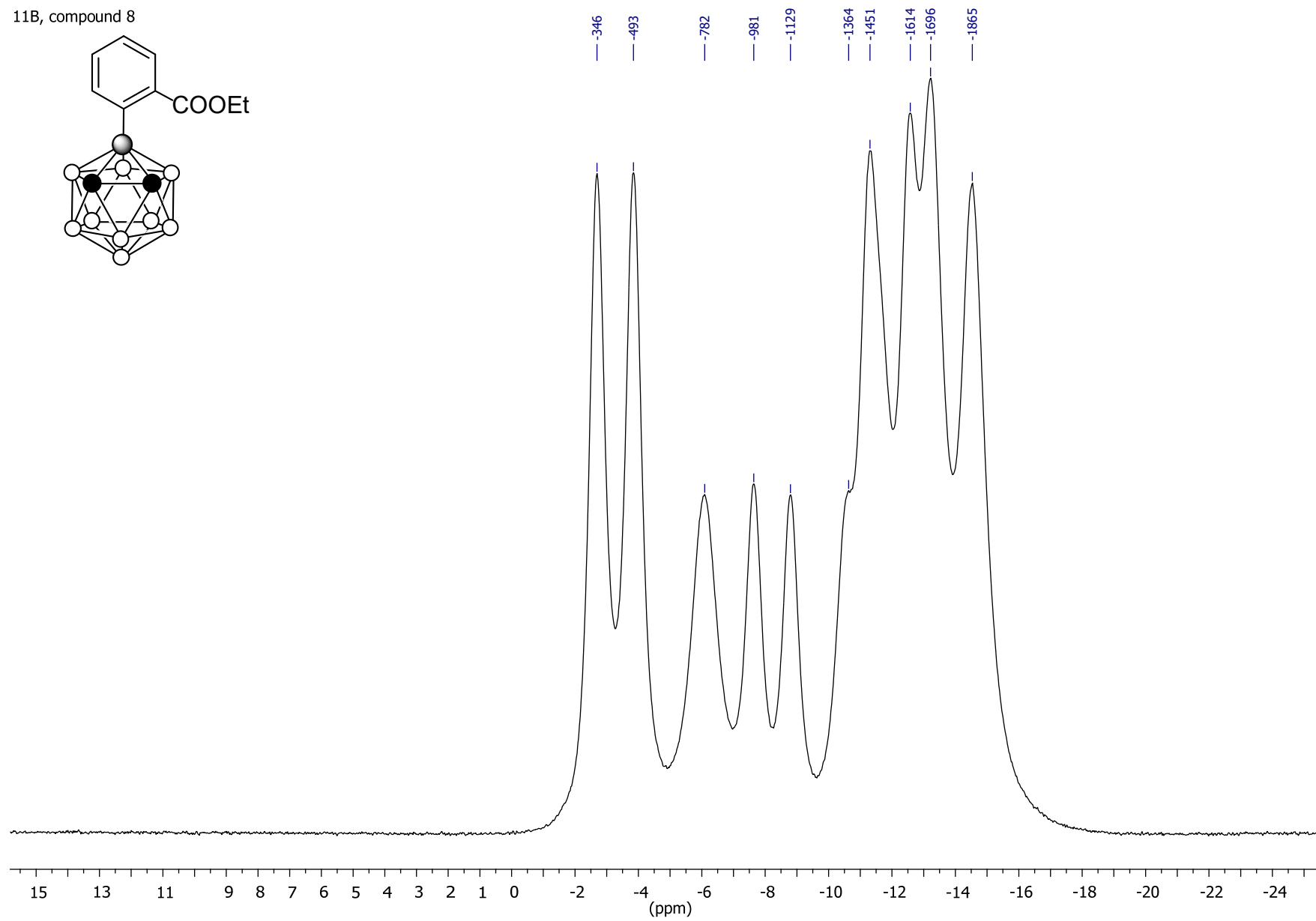
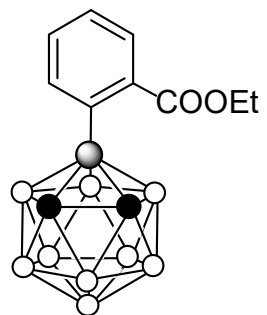
¹H, compound 8



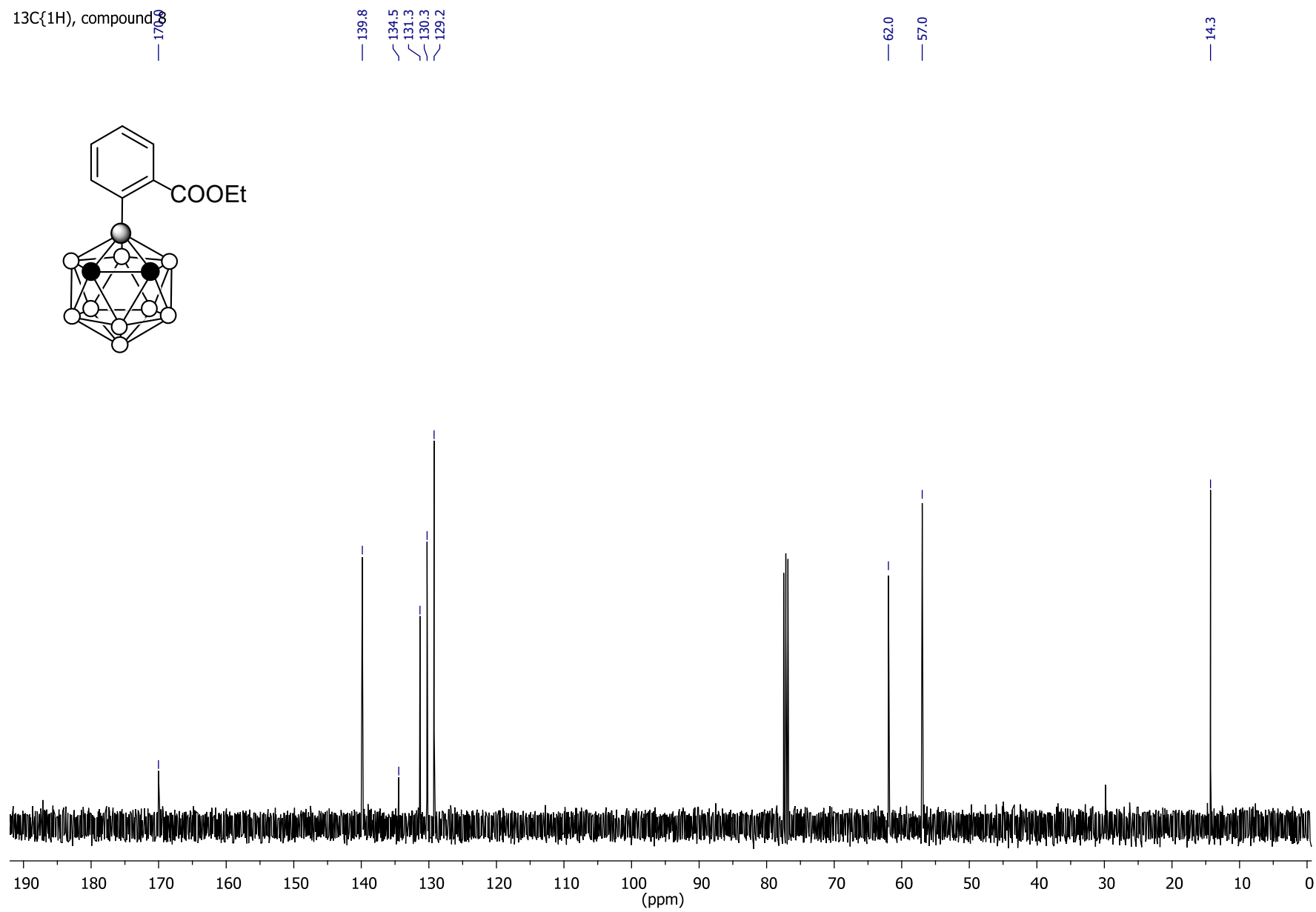
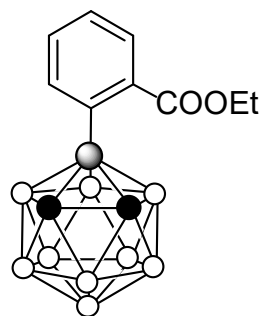
$^{11}\text{B}\{^1\text{H}\}$, compound 8

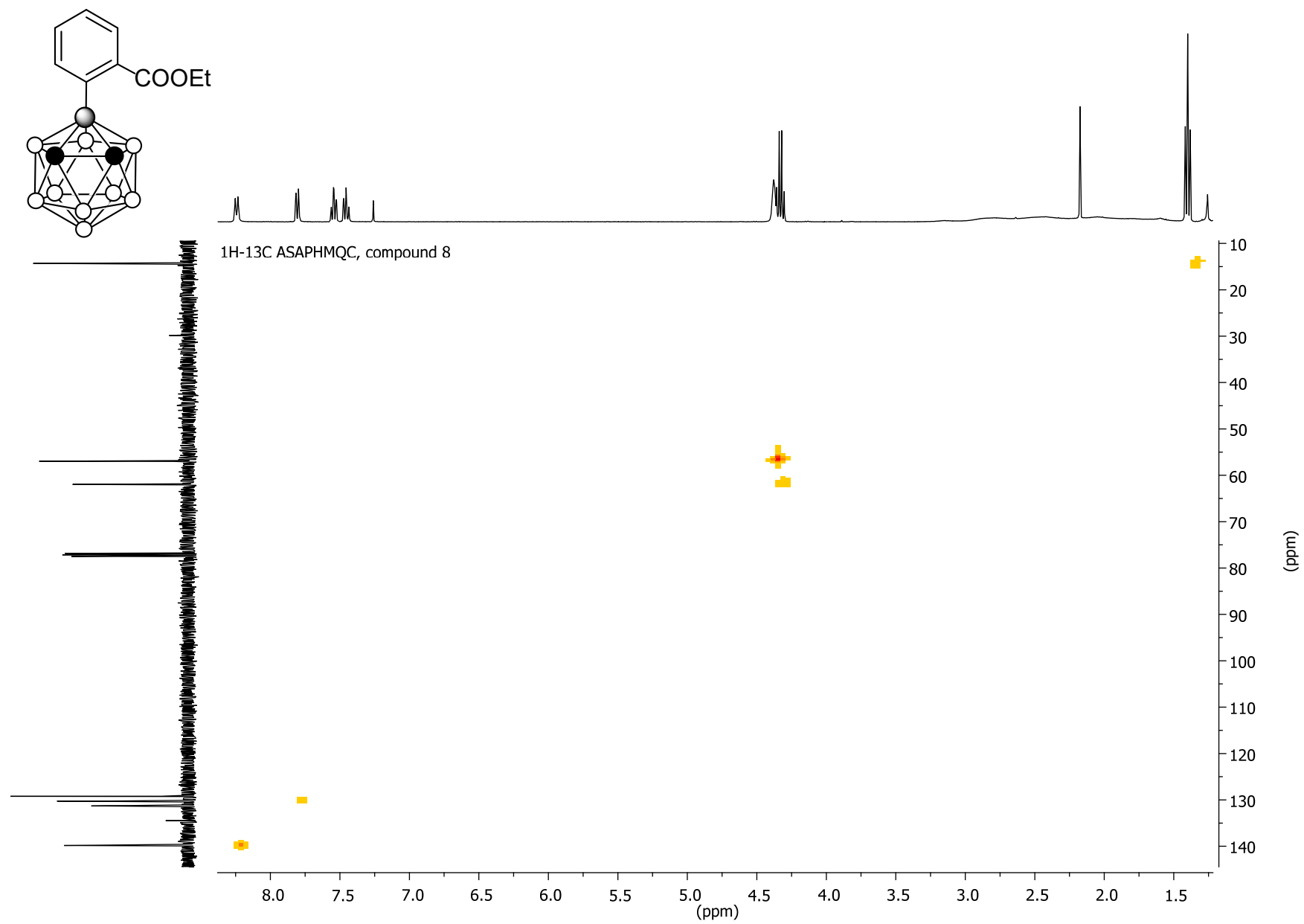


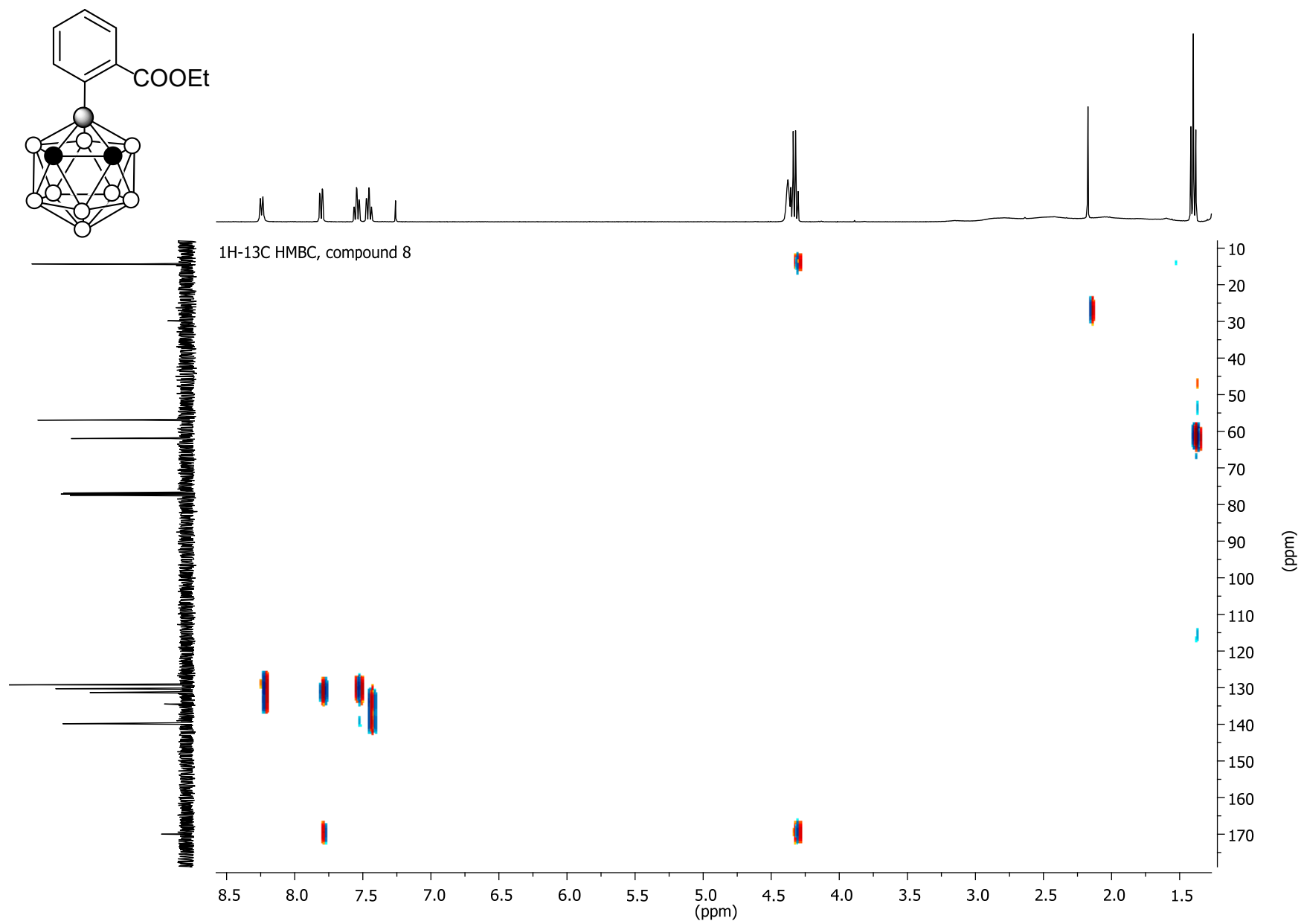
¹¹B, compound 8

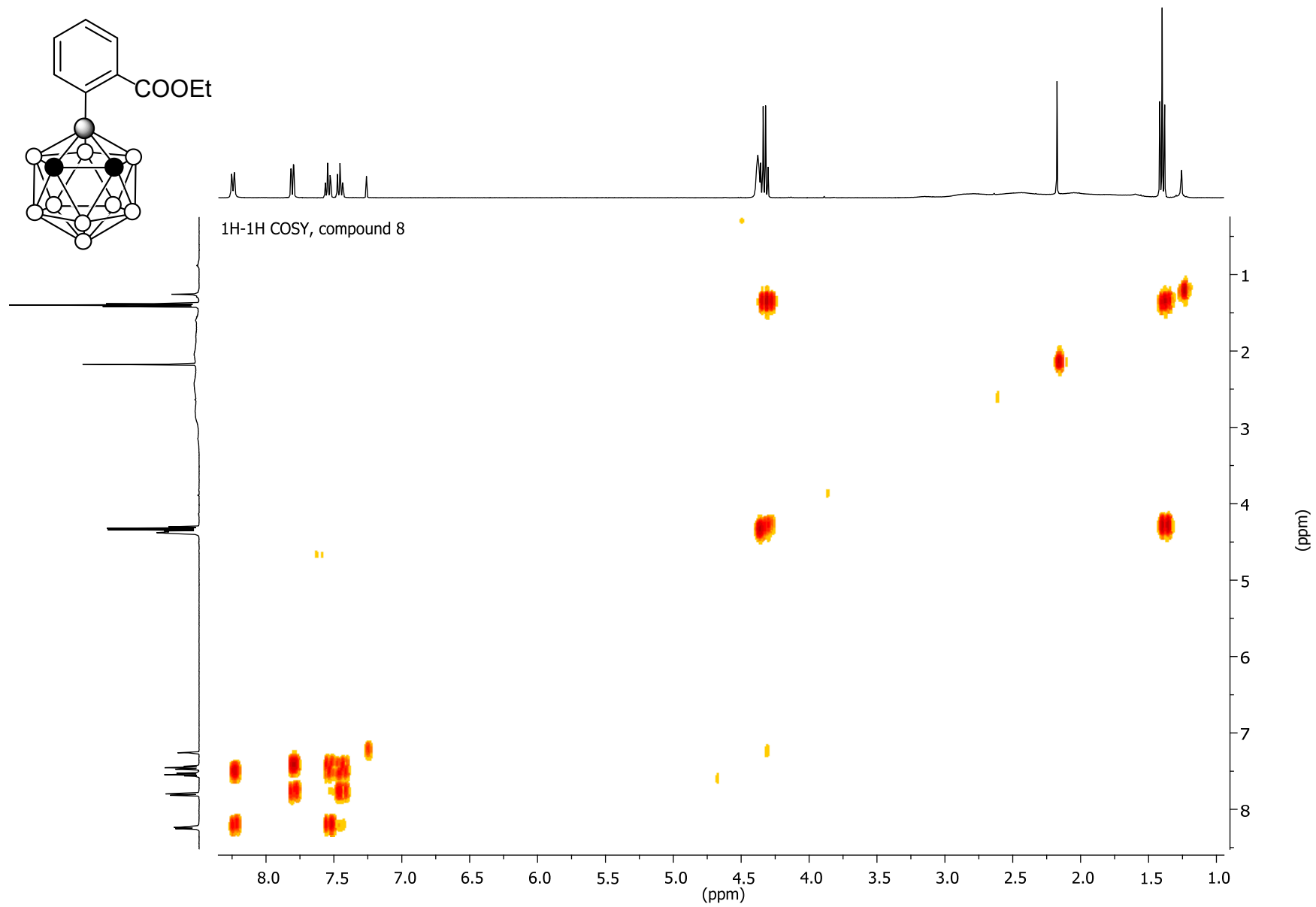


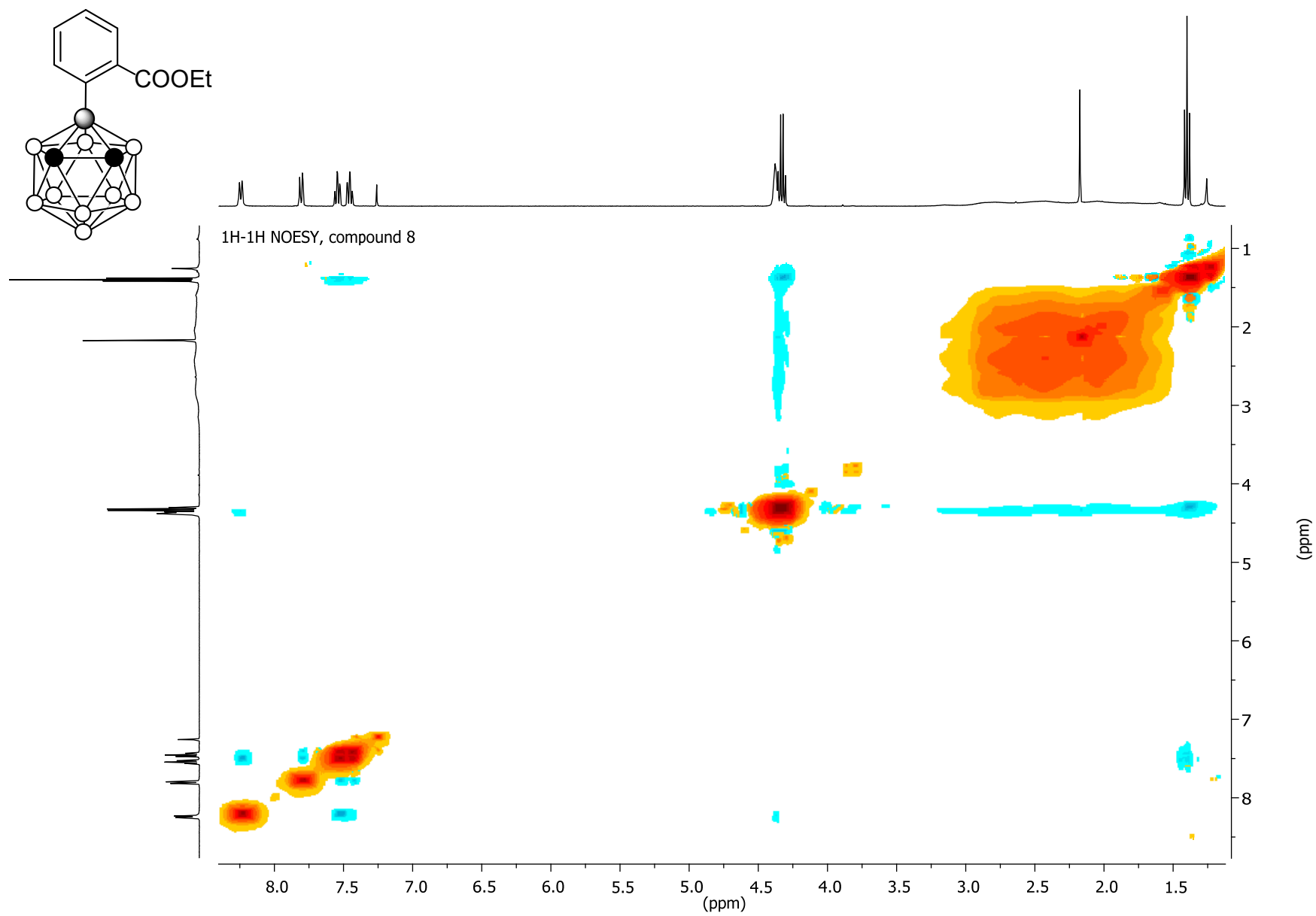
$^{13}\text{C}\{^1\text{H}\}$, compound

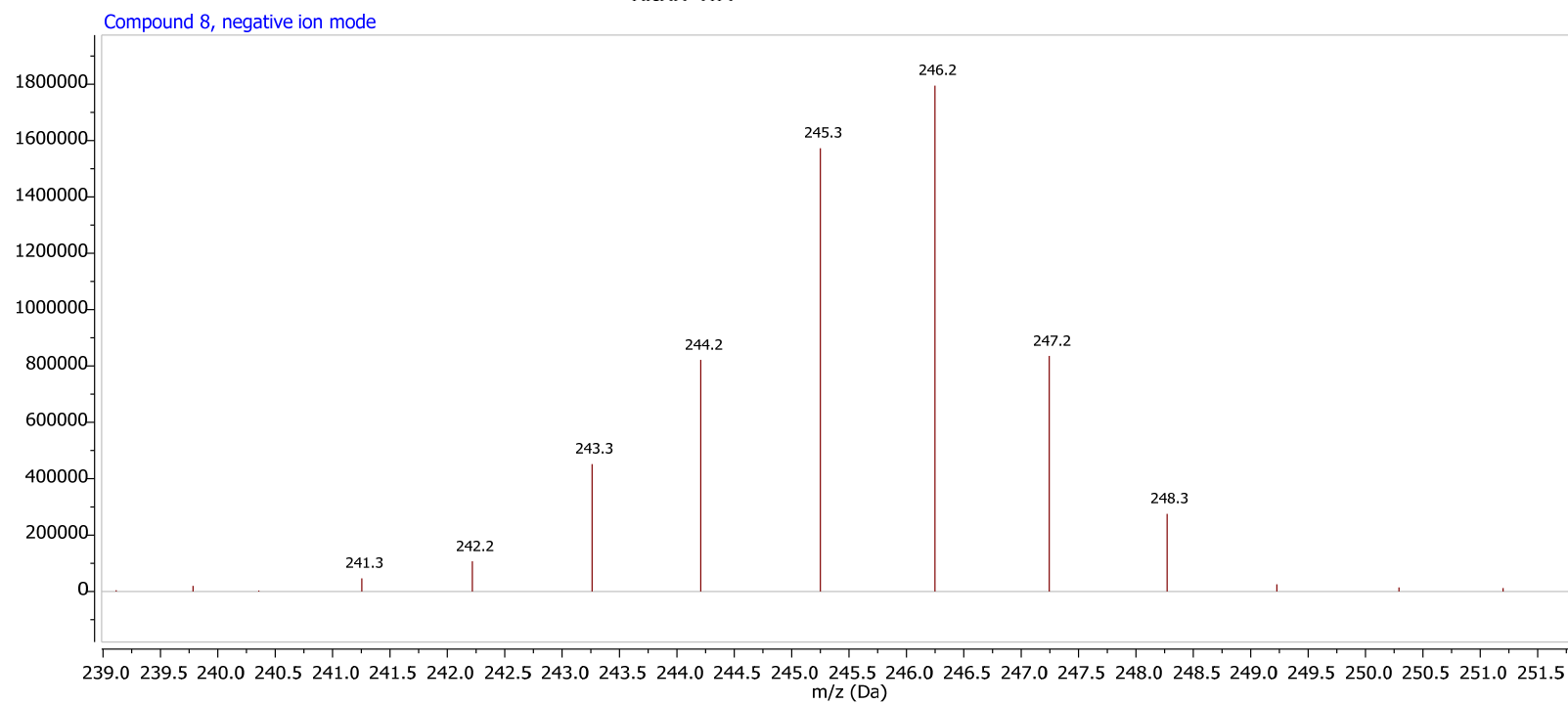
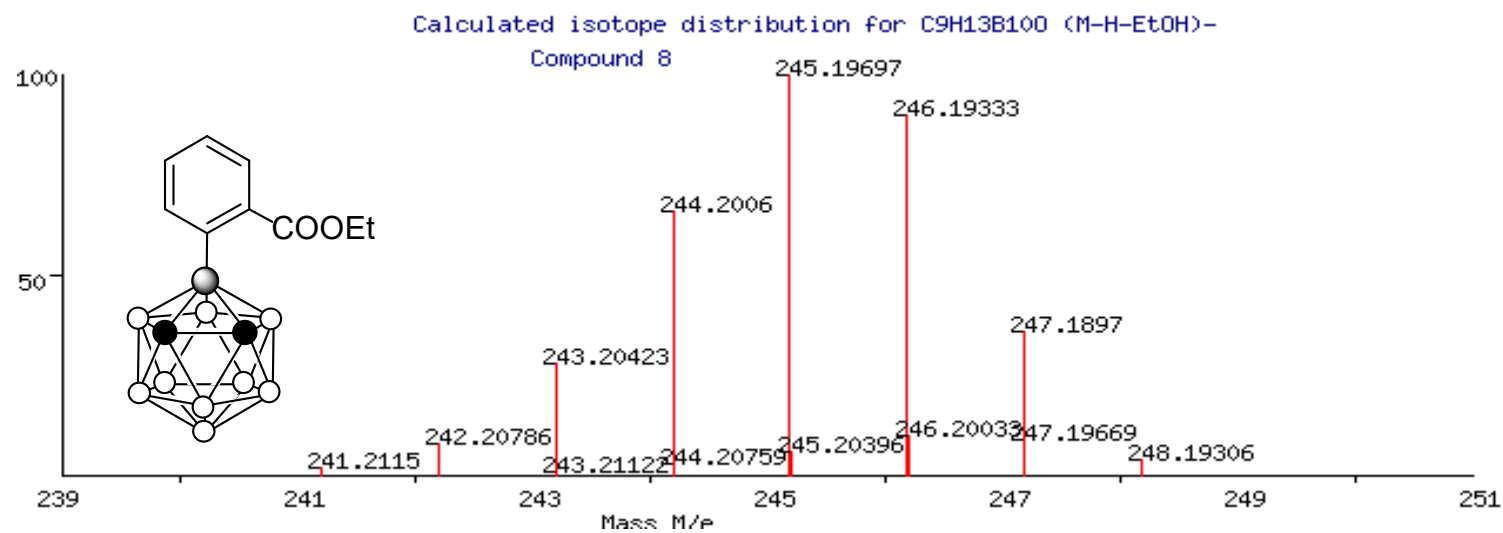




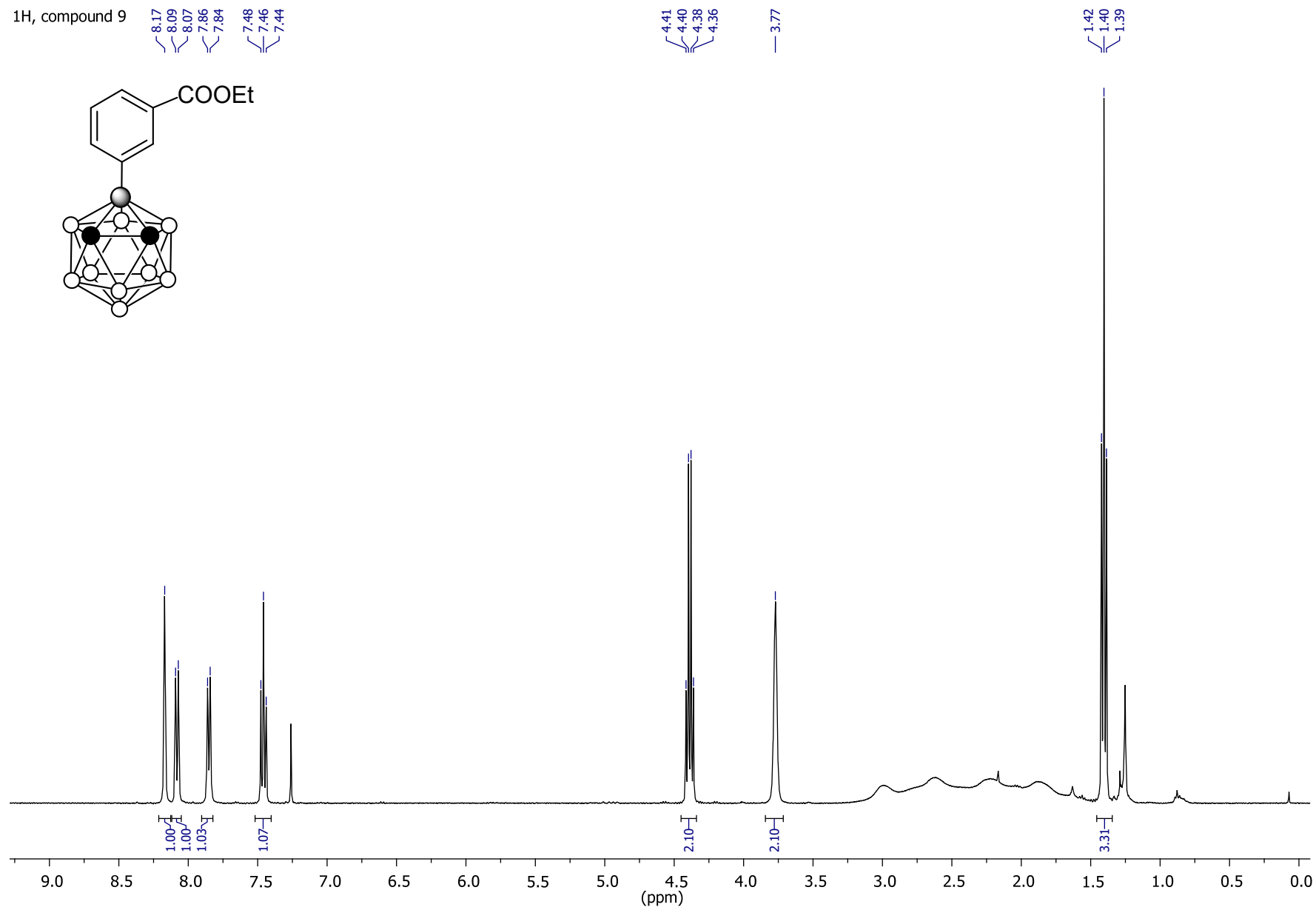
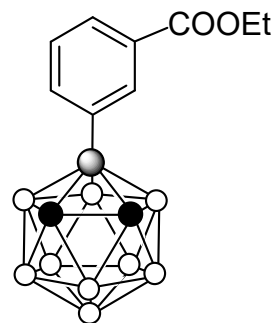




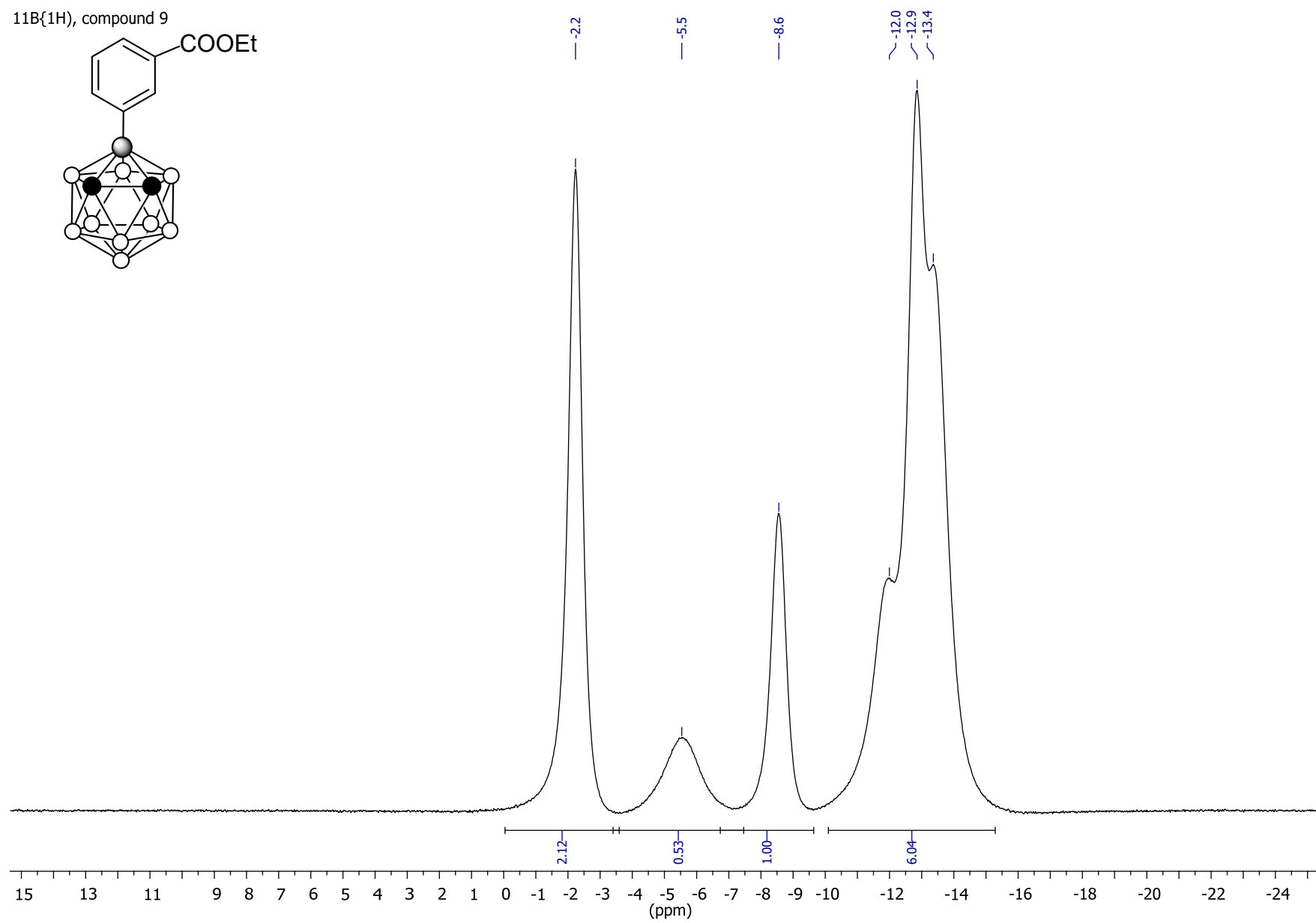
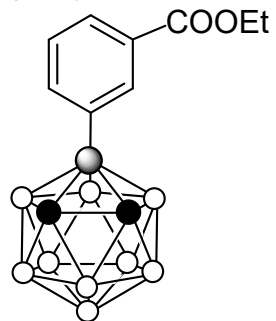




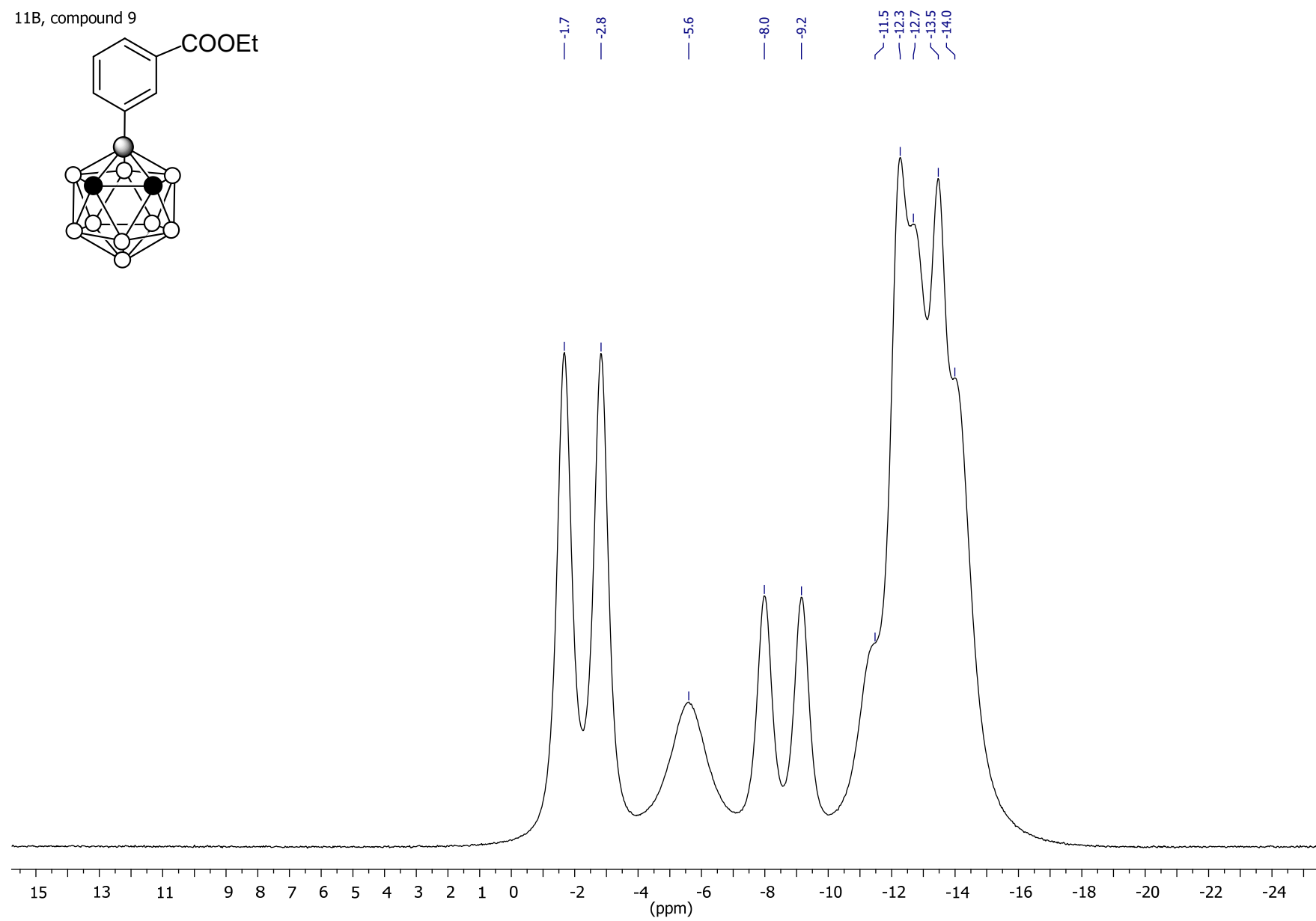
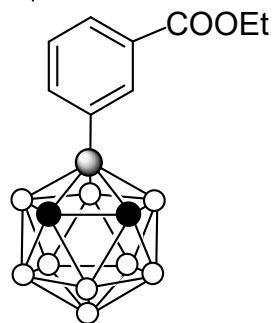
¹H, compound 9



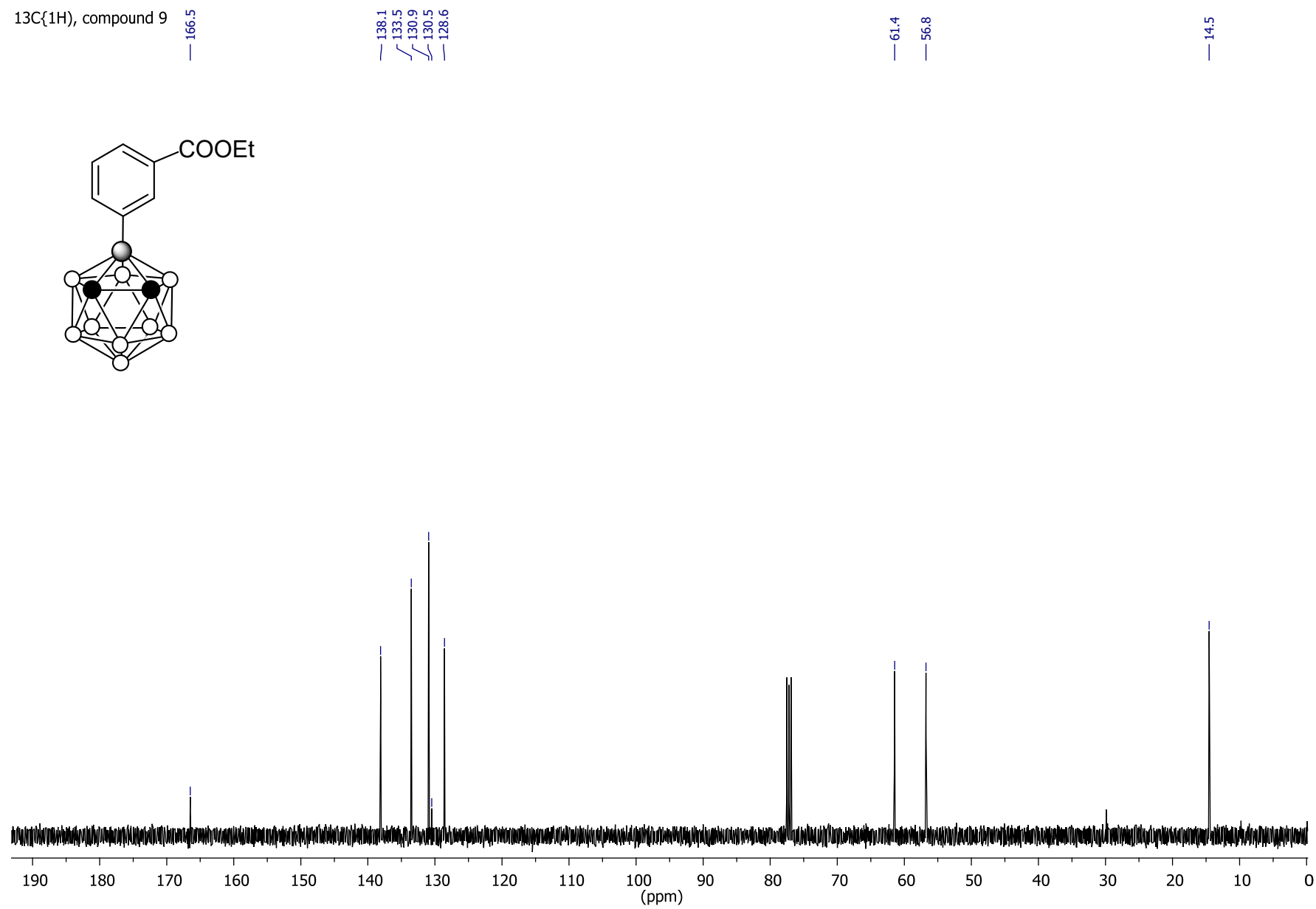
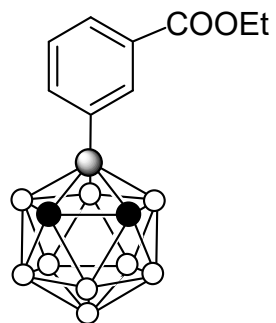
$^{11}\text{B}\{^1\text{H}\}$, compound 9

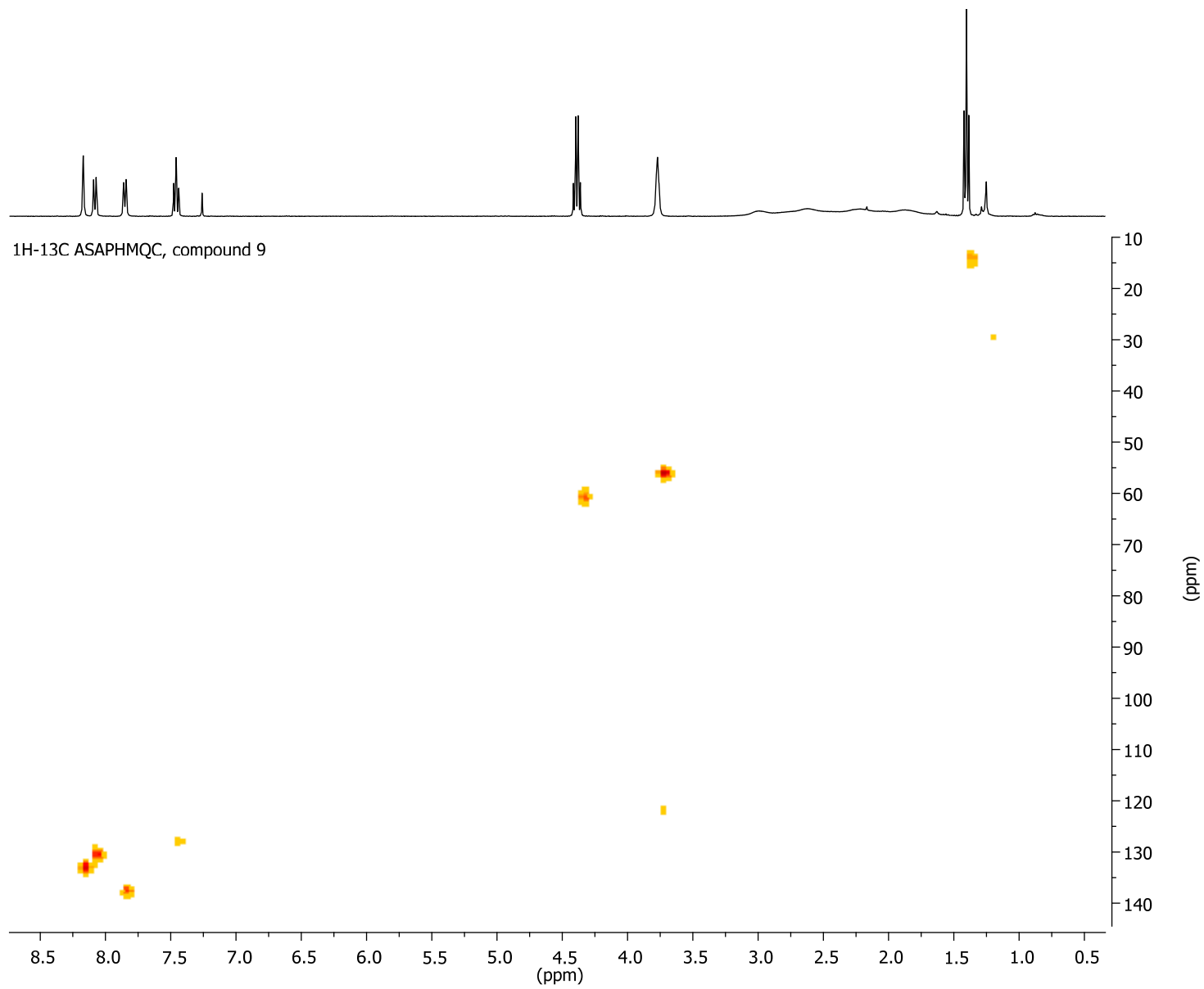
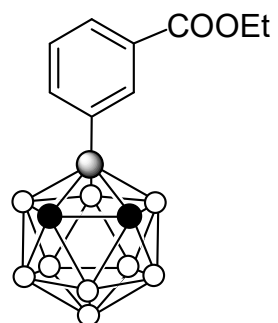


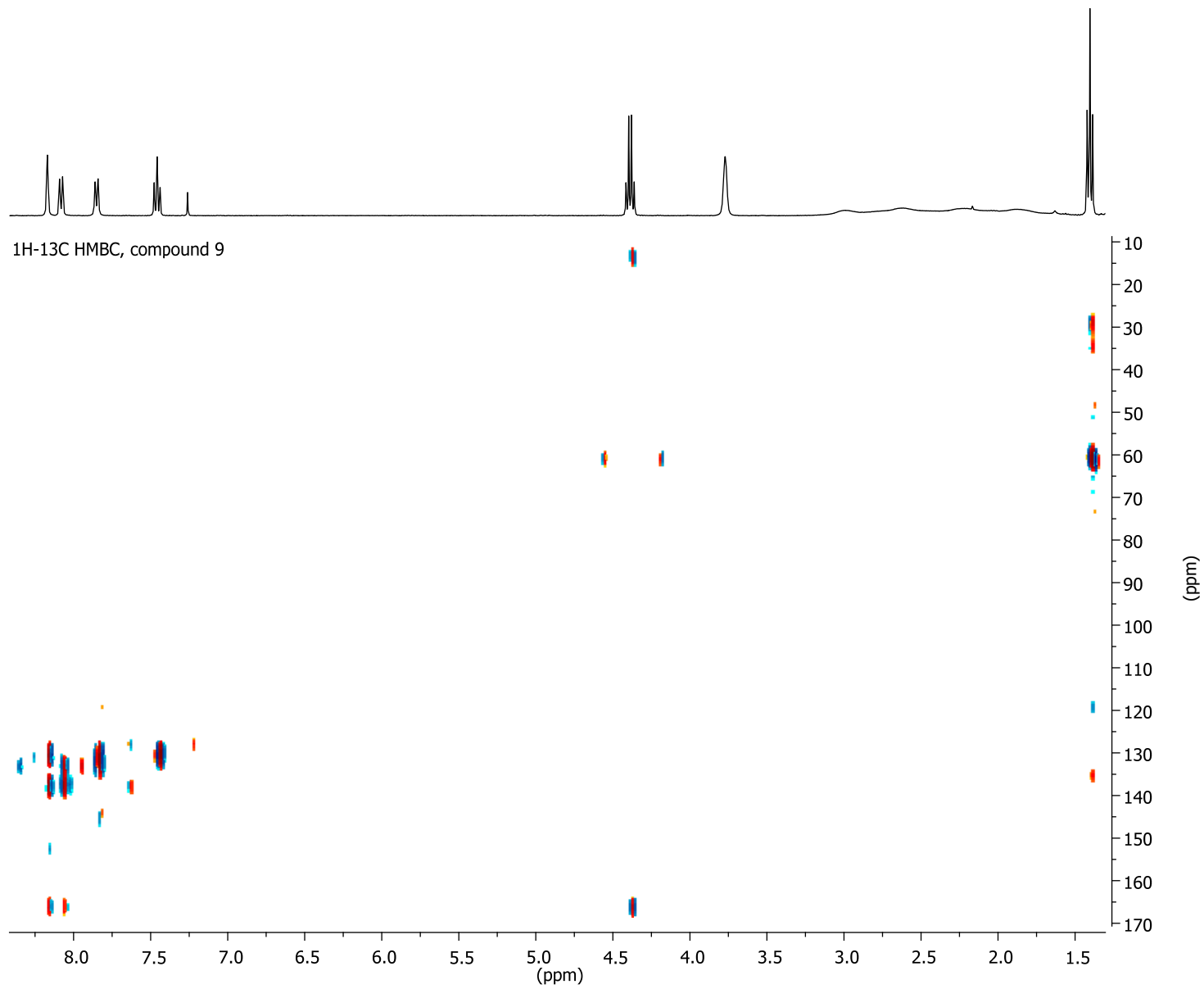
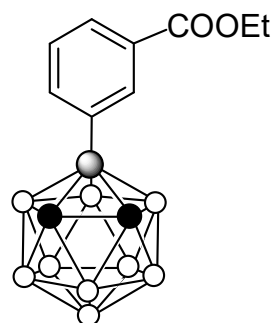
11B, compound 9

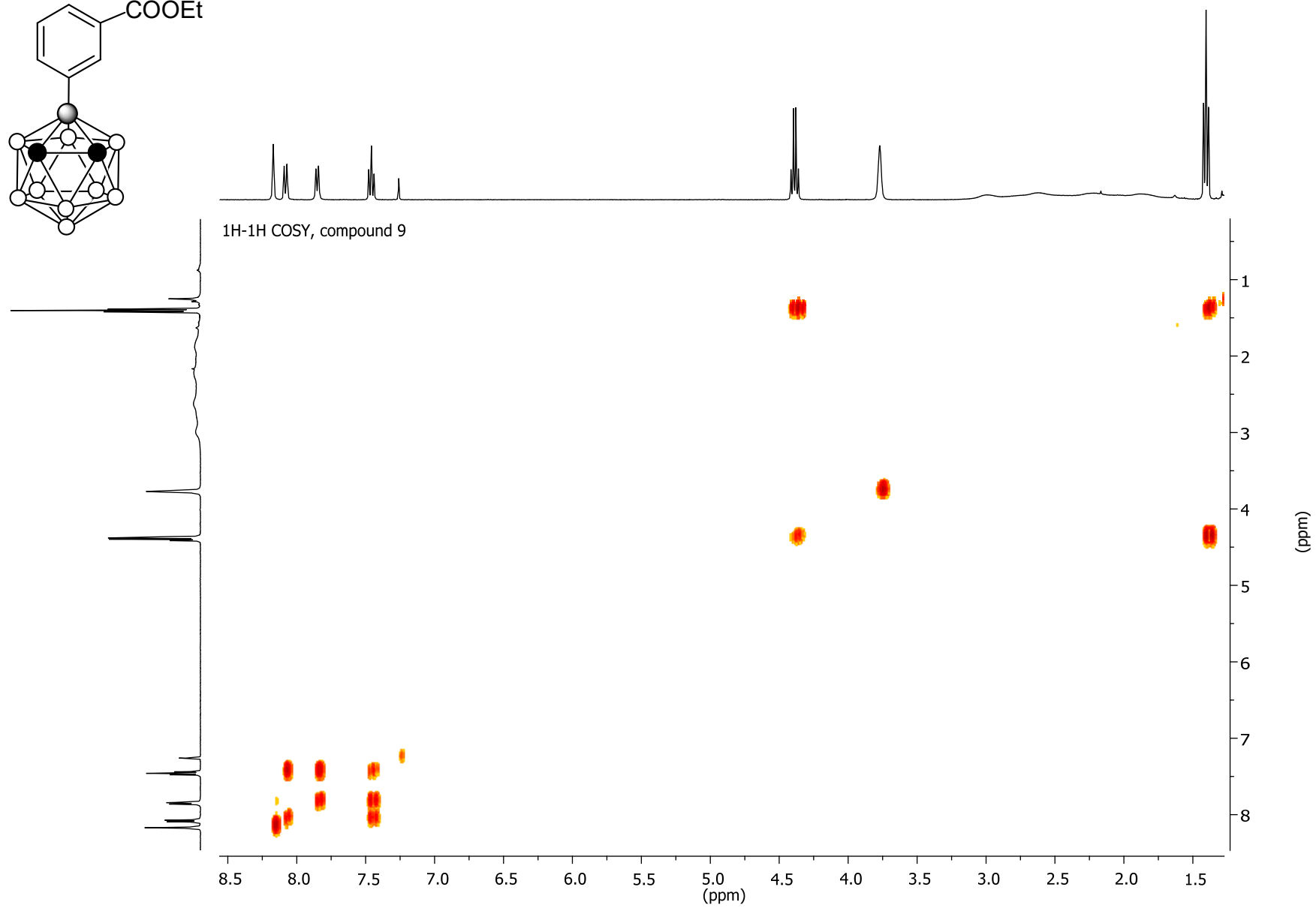
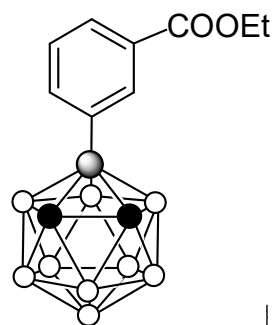


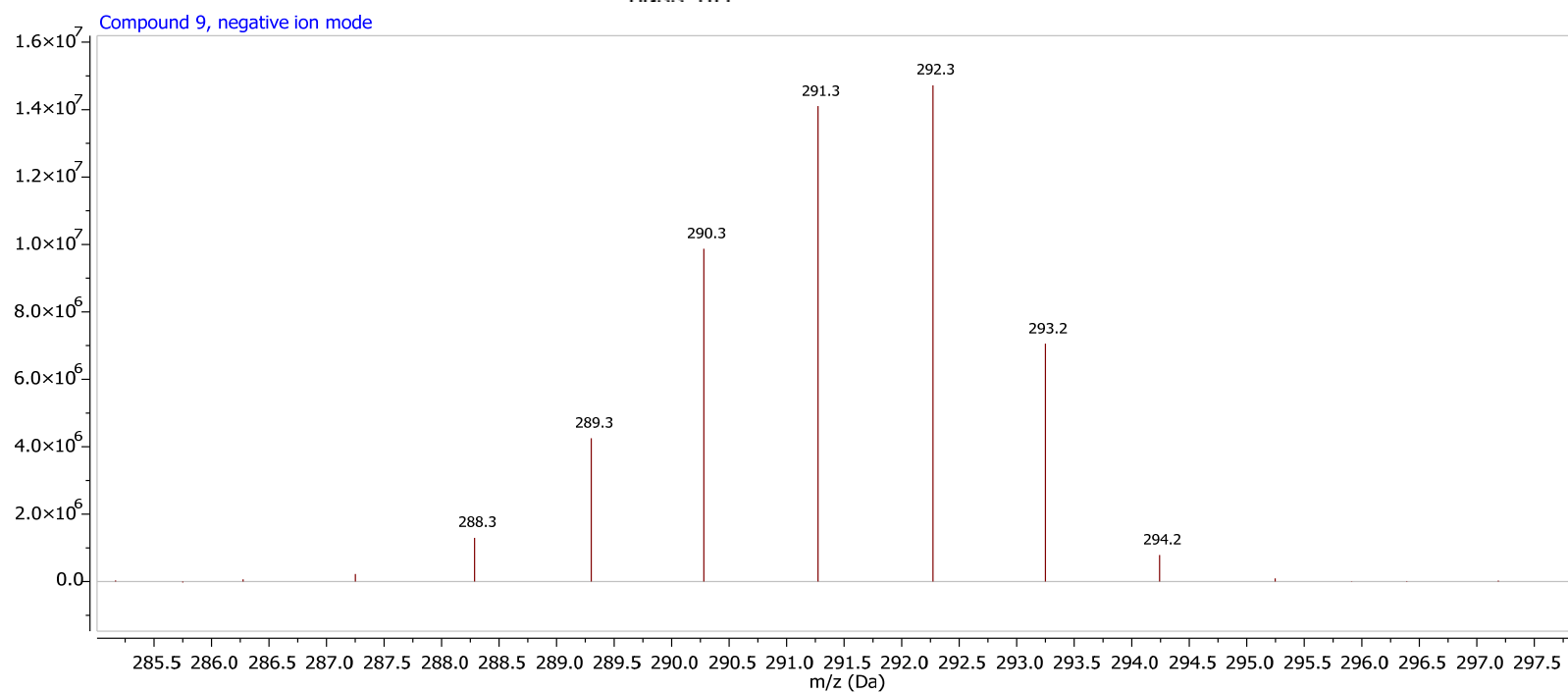
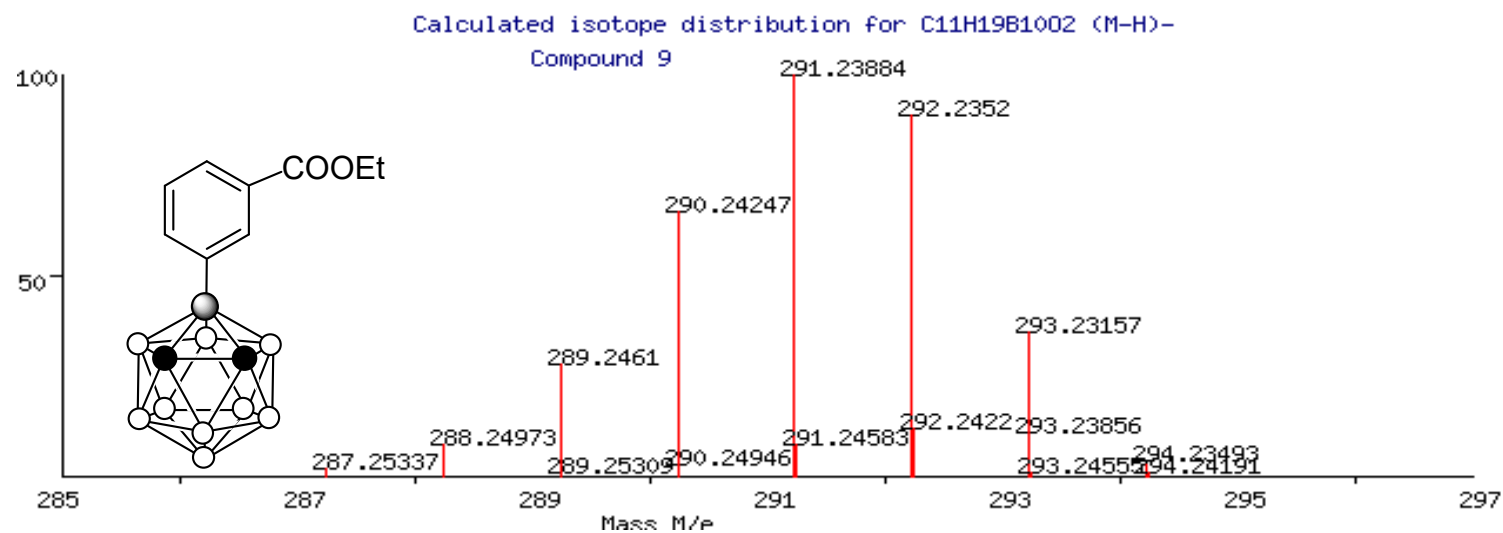
$^{13}\text{C}\{^1\text{H}\}$, compound 9











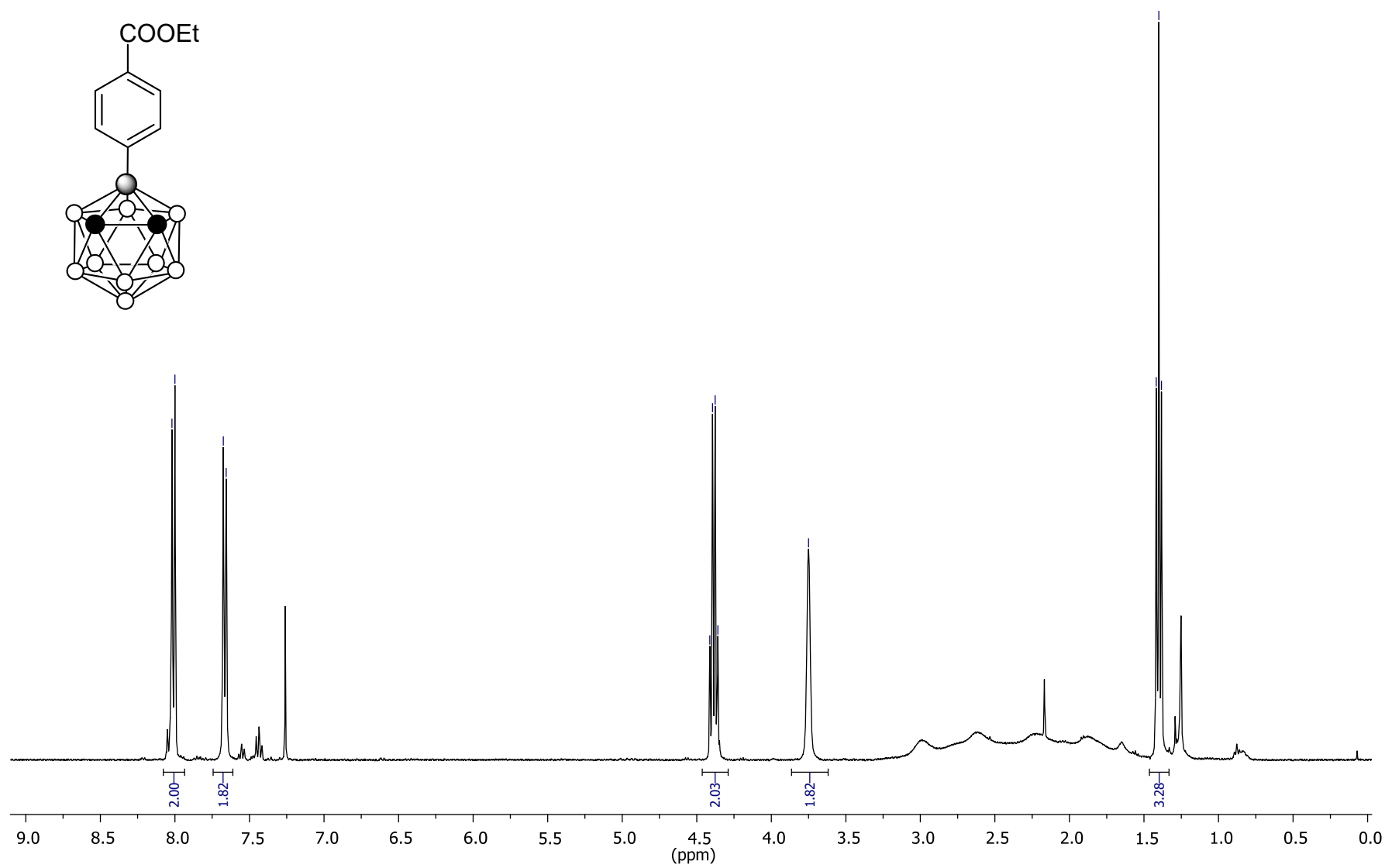
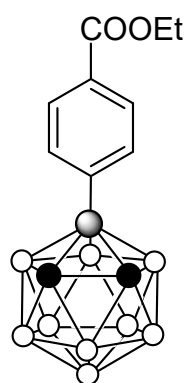
¹H, compound 10

8.02
8.00
7.68
7.66

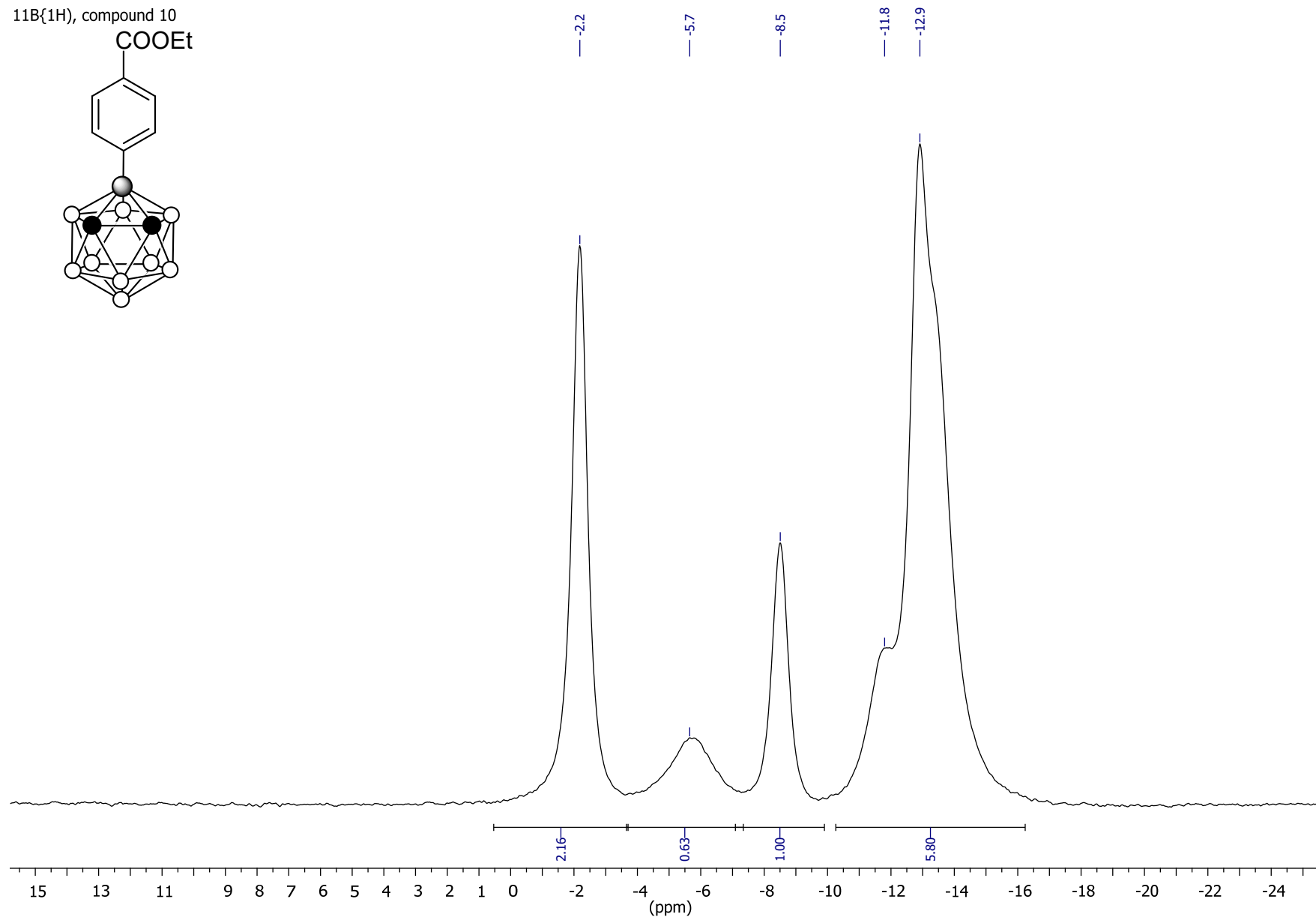
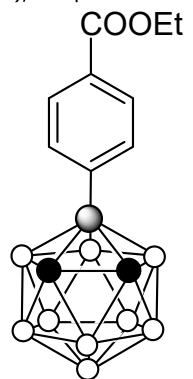
4.41
4.39
4.38
4.36

3.75

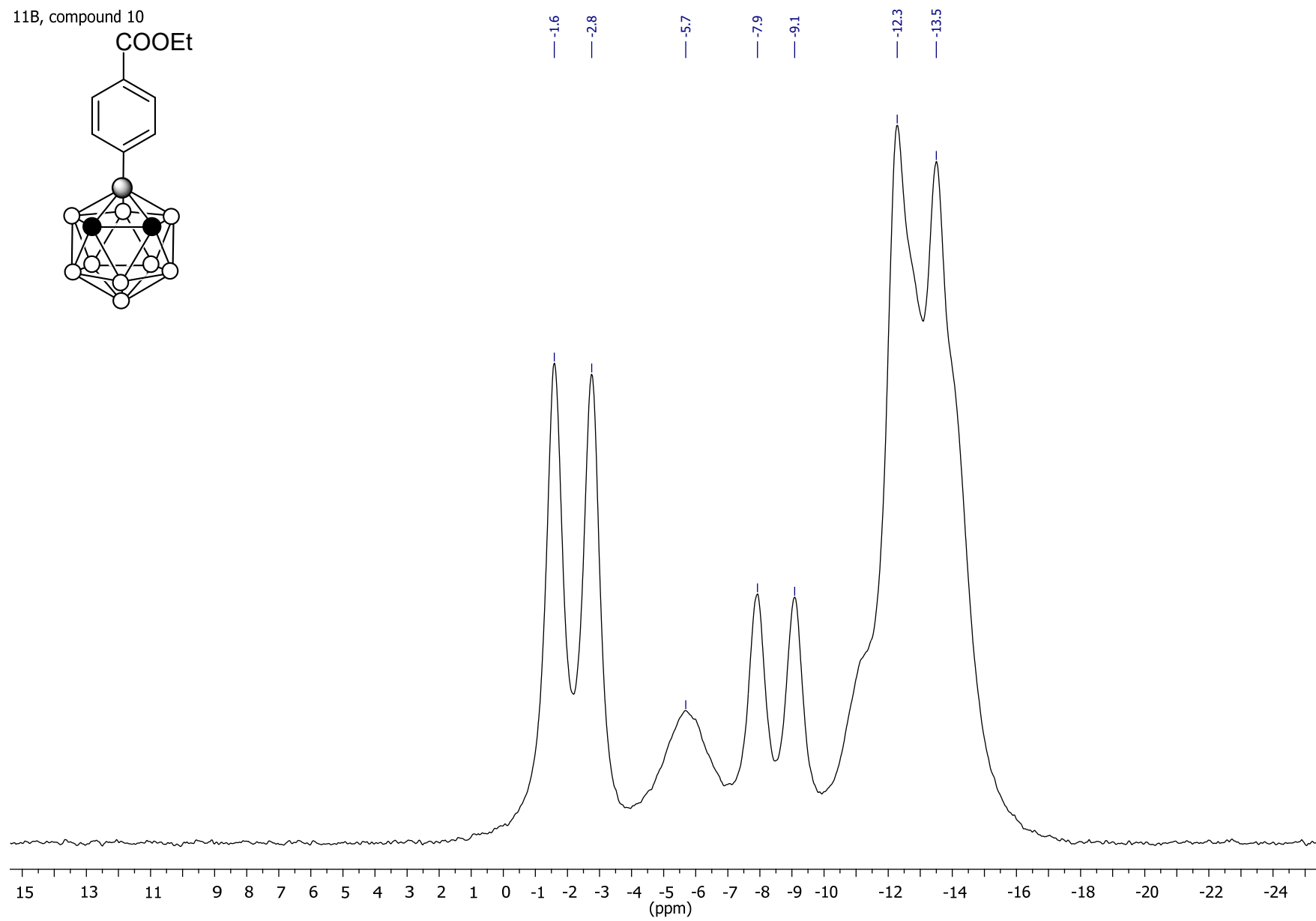
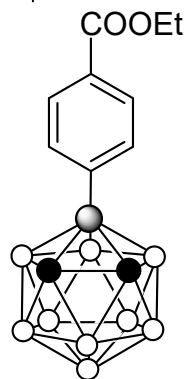
1.42
1.40
1.38



$^{11}\text{B}\{^1\text{H}\}$, compound 10



11B, compound 10



$^{13}\text{C}\{^1\text{H}\}$, compound 10

