Supplementary Information

Experimental Section

The ^{11}B NMR data (160 MHz) were obtained on a Bruker AM-500 spectrometer and referenced to external $BF_3 \times Et_2O$. Mass spectra were obtained on Mariner Biospectrometry Workstation by PerSeptive Biosystems. ESI-mass spectra were recorded by operating in negative-ion mode.

$Cs_2[closo\text{-}B_{12}(OH)_{12}]$ synthesis: *Cautiously, 10 ml of H_2SO_4 (fuming, 20% SO_3 in H_2SO_4) was added to a mixture of 0.50 g (1.2 mmol) $Cs_2[closo\text{-}B_{12}H_{12}]$ and 20 mg (0.04 mmol, 4 mol%) of $[Pt(bpym)]Cl_2$. The suspension was heated at 185 °C for 18 h, leading to a clear solution, which was cooled and then poured on ice. The resulting solution was diluted with 25 ml of water and heated at reflux for 4 days. A colorless precipitate was seen after 1 day of hydrolysis. The precipitated solid was collected by filtration and recrystallized from water to yield 192 mg (42% yield) of $(H_3O)_2[closo\text{-}B_{12}(OH)_{12}]$. This hydronium ion salt was then suspended in water, and aqueous Cs_2CO_3 solution was added until the solution was neutral. The resulting solution was concentrated by evaporation until crystals of $Cs_2[closo\text{-}B_{12}(OH)_{12}]$ appeared. Finally the solid crystals $Cs_2[closo\text{-}B_{12}(OH)_{12}]$ were separated and recrystallized twice from water.*

The scale-up of catalytic hydroxylation - synthesis of $(H_3O)_2[closo\text{-}B_{12}(OH)_{12}]$: *Cautiously, 30 ml of H_2SO_4 (fuming, 20% SO_3 in H_2SO_4) was added to a mixture of 2.0 g (4.9 mmol) of $Cs_2[closo\text{-}B_{12}H_{12}]$ and 88 mg (0.50 mmol, 10 mol%) of $[PdCl_2]$. The suspension was heated at 195 °C for 72 h, leading to a clear solution. The progress of the reaction was monitored by ^{11}B NMR. The reaction solution was poured on ice. The solution was diluted with 70 ml of water and heated at reflux for 3 days. The precipitated solid was collected by filtration and recrystallized from water to yield 880 mg (48 % yield) of $(H_3O)_2[closo\text{-}B_{12}(OH)_{12}]$. ^{11}B NMR (H_2O): -18.7 ppm.*

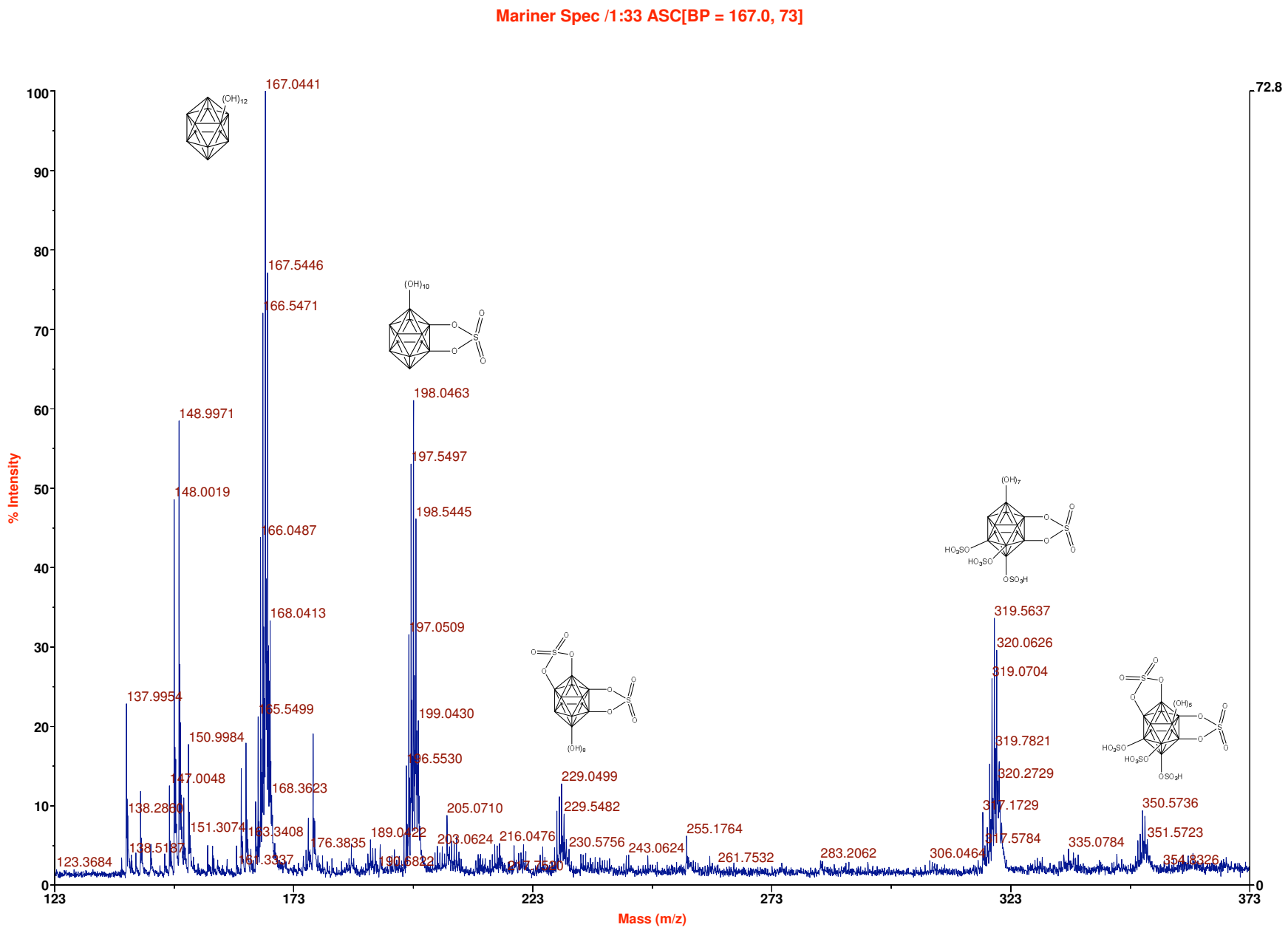


Figure 1. ESI-MS negative ion mass spectrum of $Cs_2[closo\text{-}B_{12}(OSO_3H)_{12}]$ mixture

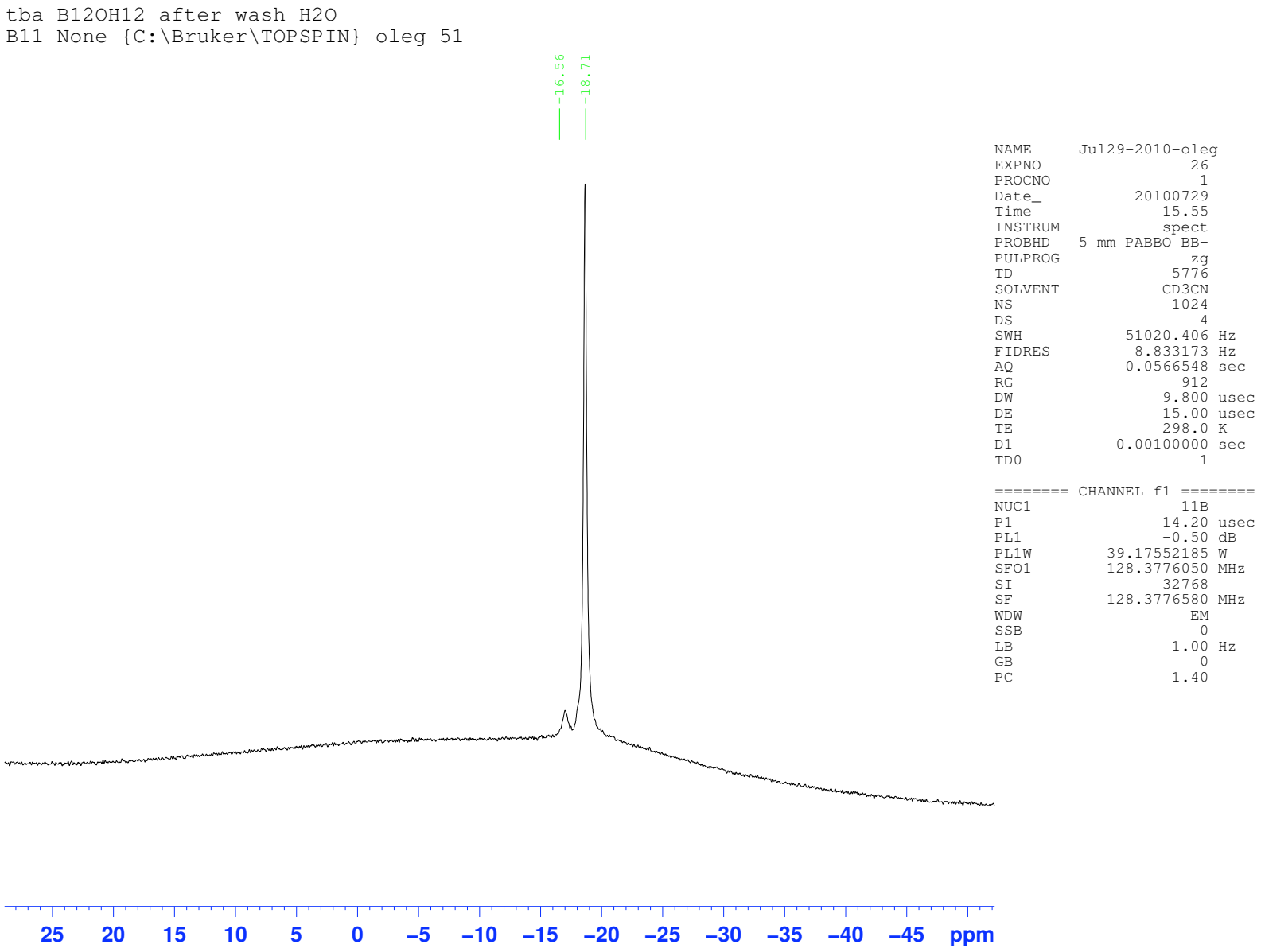
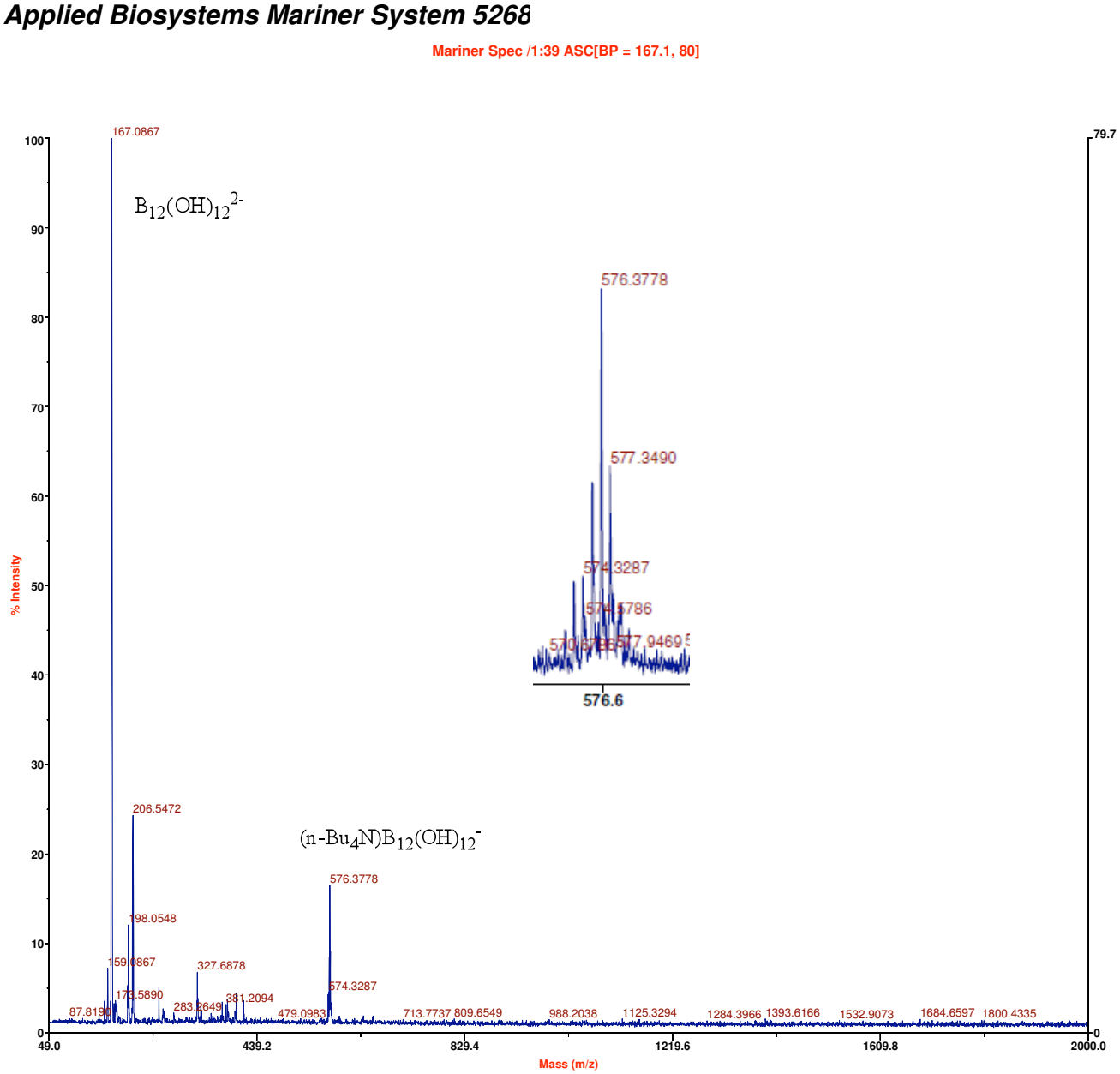


Figure 2a. ^{11}B NMR of (n-$Bu_4N)_2$[*closo*-$B_{12}(OH)_{12}$] with sulfate ester impurity.



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Curtain Gas	ON
Nebulizer Gas	ON
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Calibration Constant B	72.904961
TDC Deadtime	10
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Spray Tip Potential	4509.96
SCIEX Heater	300.05
--> API Interface Settings <--	
Nozzle Potential	80.08
Skimmer 1 Potential	9.20
Quadrupole DC Potential	5.91
Deflection Voltage	-0.20
Einzel Lens Potential	-23.61
Quadrupole RF Voltage	999.76
Quadrupole Temperature	140.01
Nozzle Temperature	190.00
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Pull Pulse Potential	213.11
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Acceleration Potential	3999.94
Reflector Potential	1549.99
Detector Voltage	1850.99
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Ion Count Threshold	0.00
First Mass	50.00
Last Mass	2000.00
Accumulate Spectra	OFF
Standby at End of Acquisition	OFF
--> Centroid Spectra Settings <--	
Centroid Spectra	OFF
--> System Settings <--	
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Syringe Pump Mode	Manual
Syringe Pump Rate	50.00
Syringe Diameter	3.26
Min Analyzer Mass	50.00
Max Analyzer Mass	4000.00

Acquired: Jul 23 14:15:00 2010
Mariner Mass Spectrum
C:\Mariner\Data\2010\July\23 Fri\Bond-87001.dat

Printed: 14:17, July 23, 2010

Figure 2b. ESI-MS negative ion mass spectrum of $(n\text{-}Bu_4N)_2$[*closo*-$B_{12}(OH)_{12}$] with sulfate ester impurity

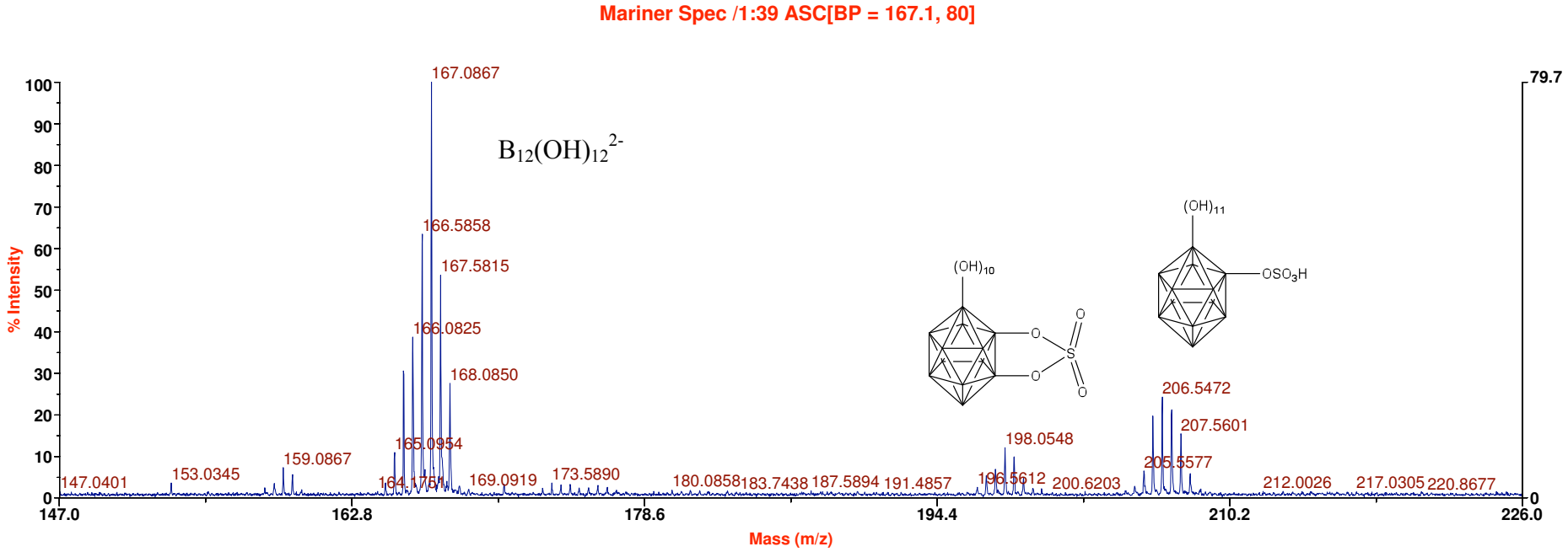

Figure 2c. Expansion of ESI-MS negative ion mass spectrum of $(n\text{-}Bu_4N)_2[\textit{closo}\text{-}B_{12}(OH)_{12}]$ with sulfate ester impurity.

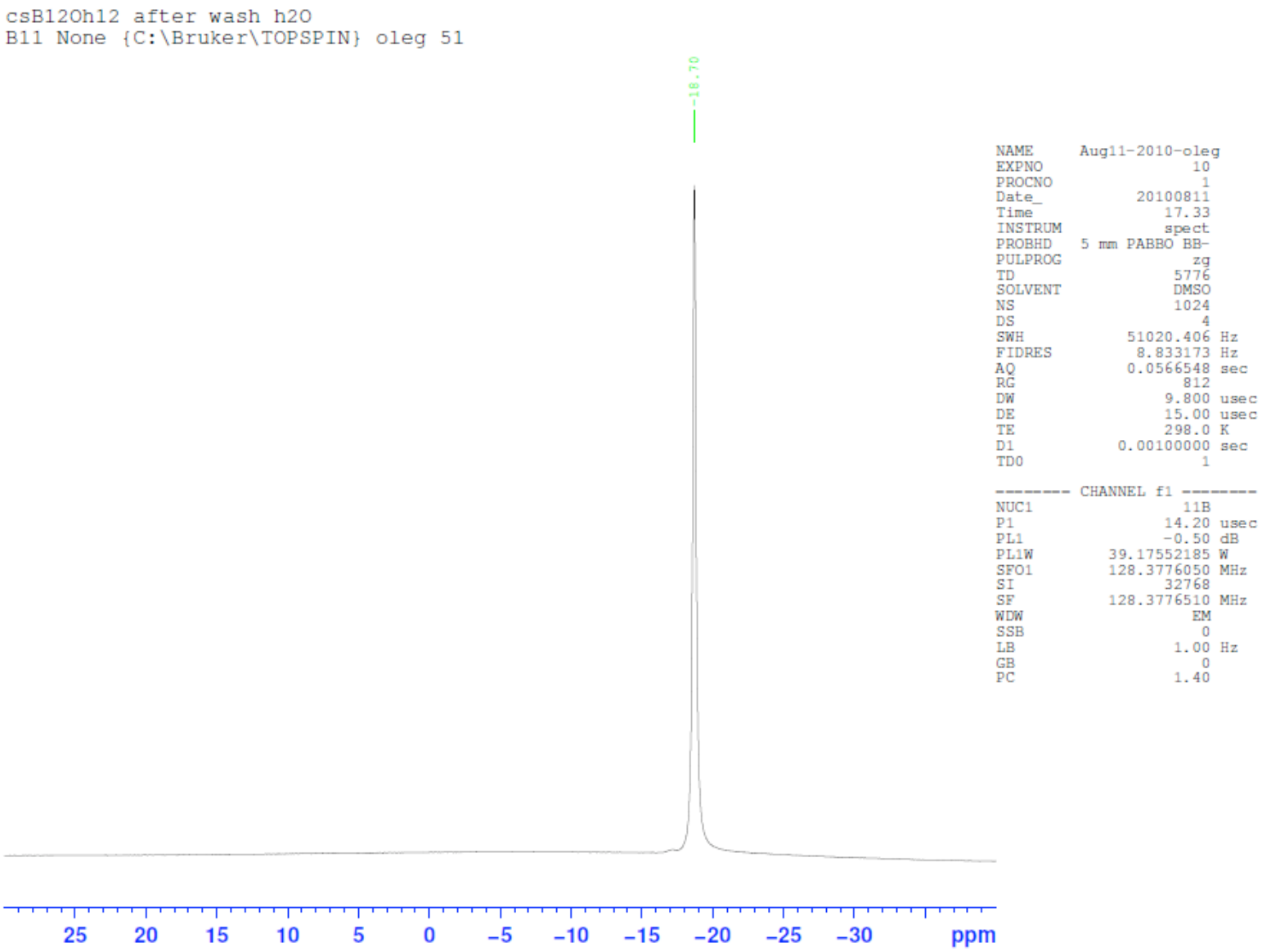

Figure 3a. ^{11}B NMR of pure $Cs_2[closo\text{-}B_{12}(OH)_{12}]$

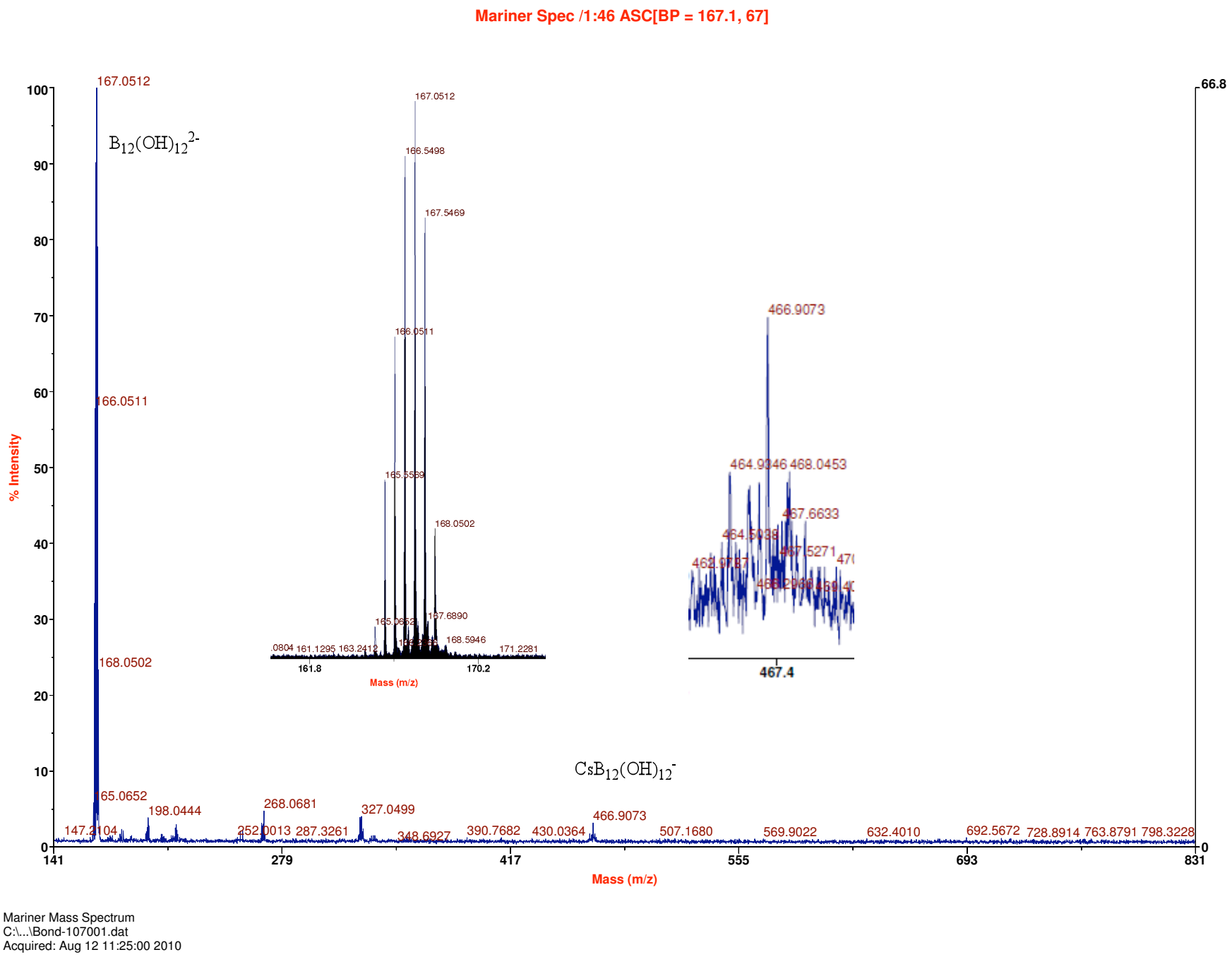

Figure 3b. ESI-MS negative ion mass spectrum of pure Cs_2[*closo*-$B_{12}(OH)_{12}$]