A New Release of NIST Mass Interpreter for High Mass Accuracy Spectra

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Introduction

For over 10 years, MS Interpreter has been a freely available software tool for quickly examining the possible origin of mass spectral peaks in low resolution mass spectra. After input of a structure and a spectrum, it assigns peaks to plausible molecular substructures based on a set of rules for estimation of fragmentation energetics and chemical structure (connection table) analysis. This work describes changes made to both the user interface and fragmentation logic to accommodate high resolution spectra originating from positive or negative singly charged ions.

Application of MS Interpreter

MS Interpreter can work in Low Resolution and High Resolution mode. The Low Resolution mode was the only one available in the previous release of the program.

The new MS Interpreter high resolution mode enables the use of ppm-level tolerances to assign identities of fragments.

Fig.1 shows the high-resolution mass spectrum of Corydaline. There are two types of peaks in mass spectrum view, black for peaks assigned to known fragmentation products and white for undetermined ones.

Black peaks are associated with possible fragmentation paths, the underlying origin of which is shown in red in the structure. Besides, there are small ticks on the top of the Mass Spectrum view, consistent to m/z of the theoretical predicted peaks. The tick color depends on the predicted ion type. For example, the highest peak with 192.1016 corresponds to the theoretical one 192.1024 with 5 ppm precision.

If no chemical structure for a peak it is white. In this case one can apply the Formula Calculator.

The assignment of peaks determination uses a set of rules based on bond strengths in the precursor ion. These rules account for various structural factors including bond strengths, protonation, and permit unspecified losses of stable molecules such as CO, NO, SO, OH, water and ammonia.

If several/two peaks overlap, a black arrow is displayed on the top of the overlapped peak group/pair. Black color of a peak indicates that it can be assigned to a fragment, while white color of the peak means that there is no association available. Relative contributions to the black/white regions correspond to relative abundances of these two peak types.

Fig.2 shows two large peaks. The first peak 176.0703 has a black upper region and white lower region. This indicates the larger underlying peak is assigned to a fragment, and a smaller peak is not. The opposite holds for the second peak at 177.0781.

Double click on overlapping peak results in m/z zooming to show both peaks. Figure.3 shows the zoomed plot. It shows that original peak consists of two peaks. Moreover, the neighbor peak is also composed of two peaks.

When peak 176.0703 is clicked it is sent to the Formula Calculator, which shows possible chemical formulas. The precision of determination is 40 ppm.

The Fragmentor cannot assign the peak 177.0781 to a structure fragment. The Formula Calculator gives a chemical formula of C10H11NO2.

Figure.1
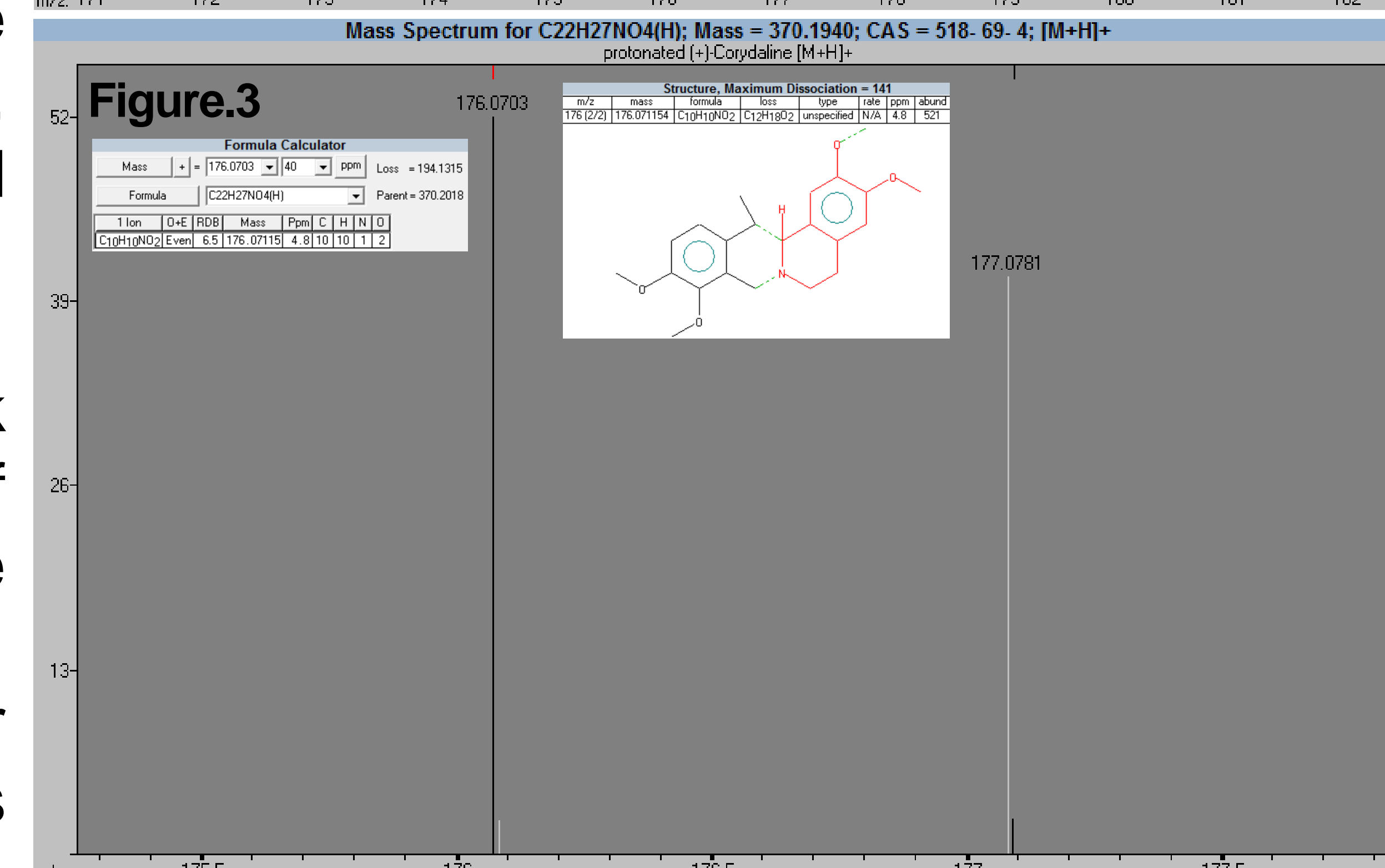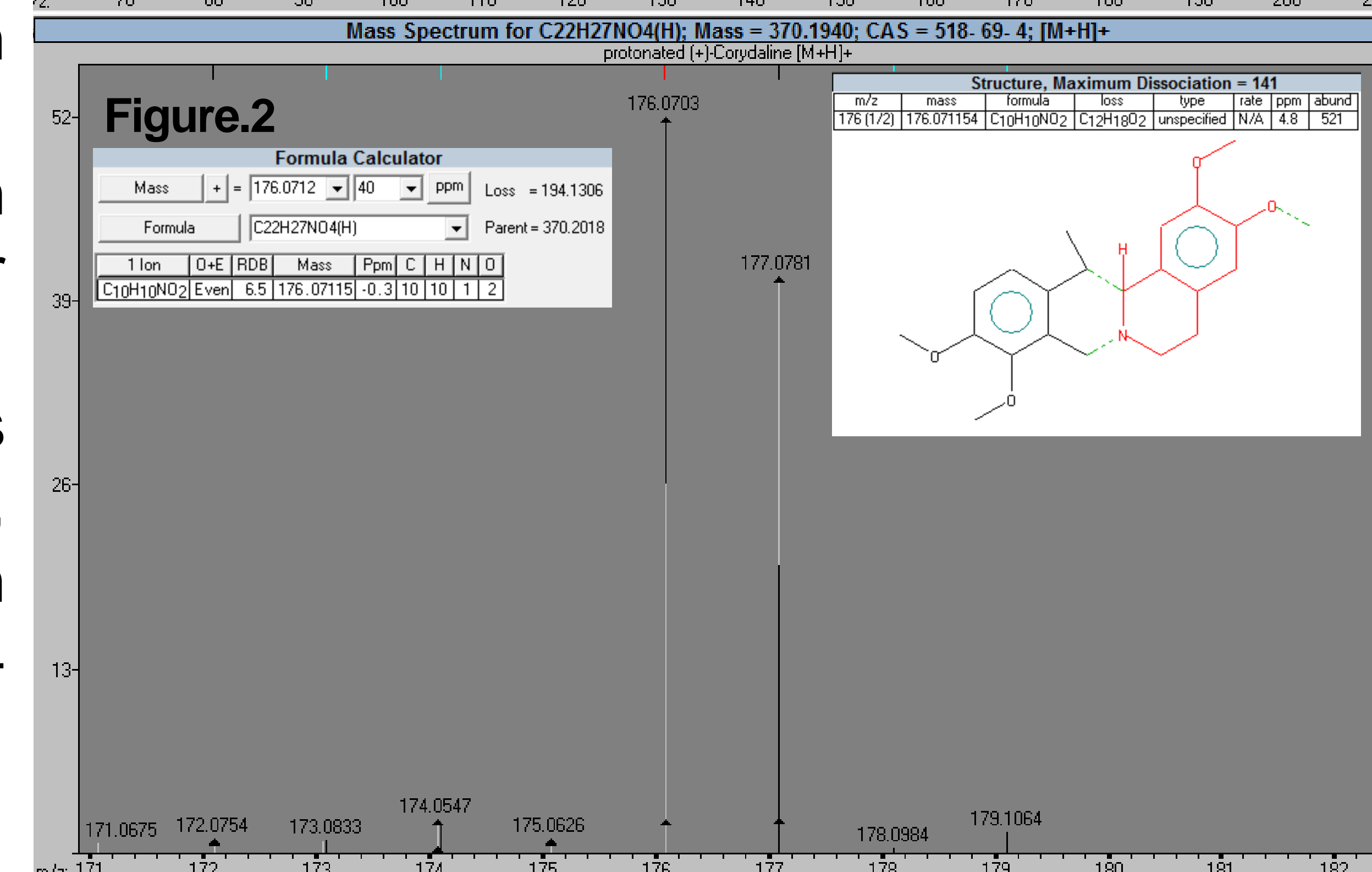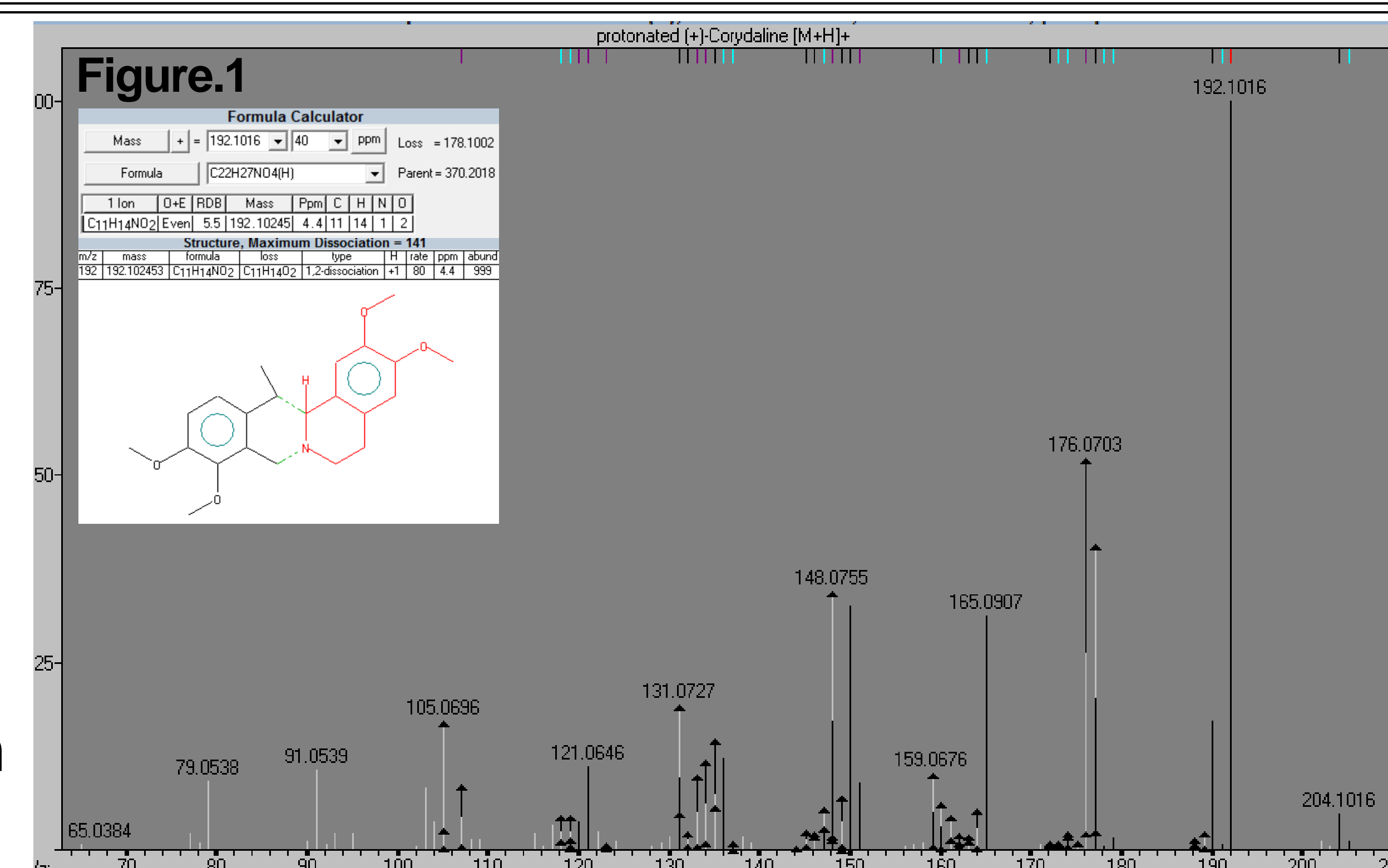
Figure.2

Figure.3

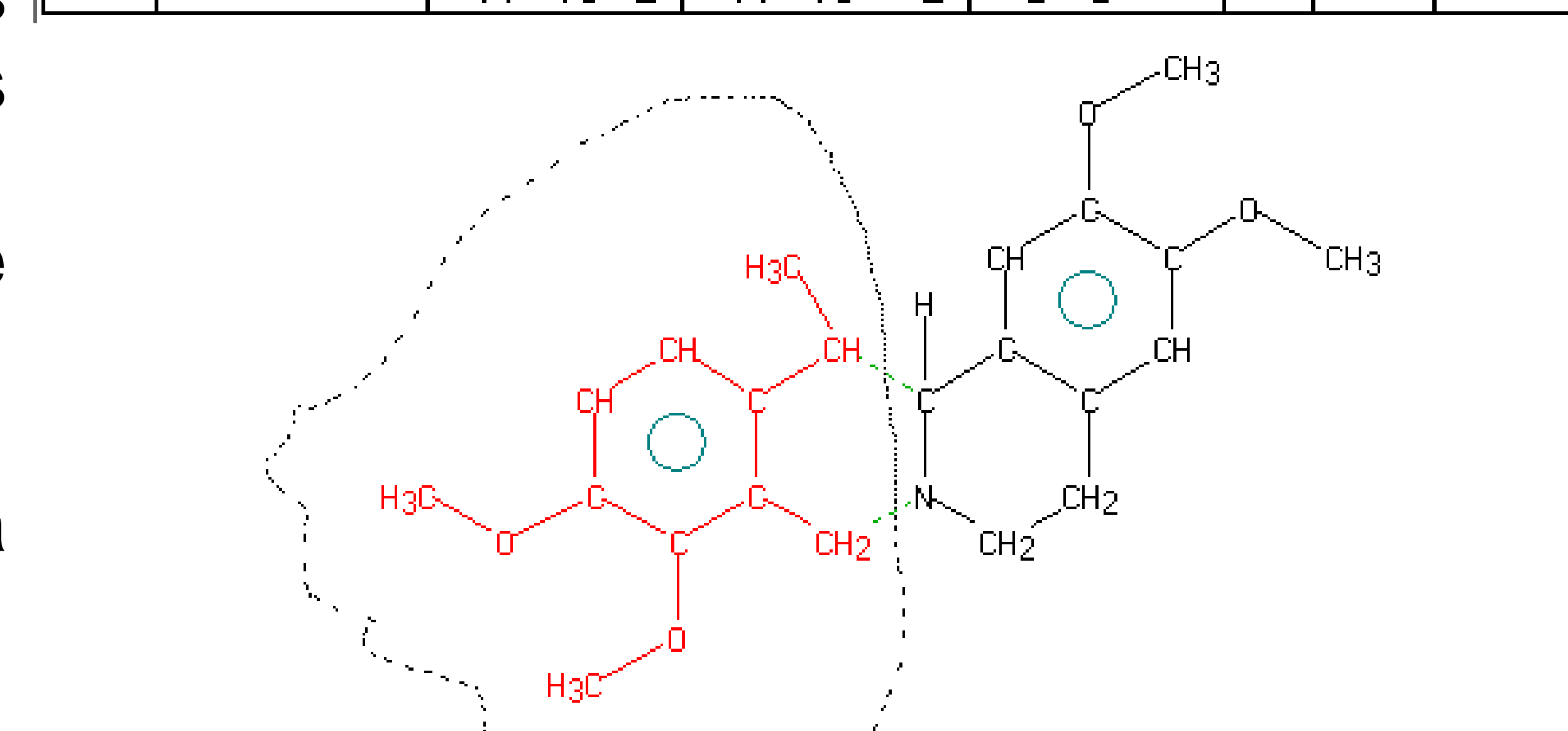| m/z	mass	formula	loss	type	H	ppm	abund
179	179.107204	C₁₁H₁₅O₂	C₁₁H₁₃NO₂	Highlighted	+1	4.5	14

Structure, Maximum Dissociation = 141

Figure.4

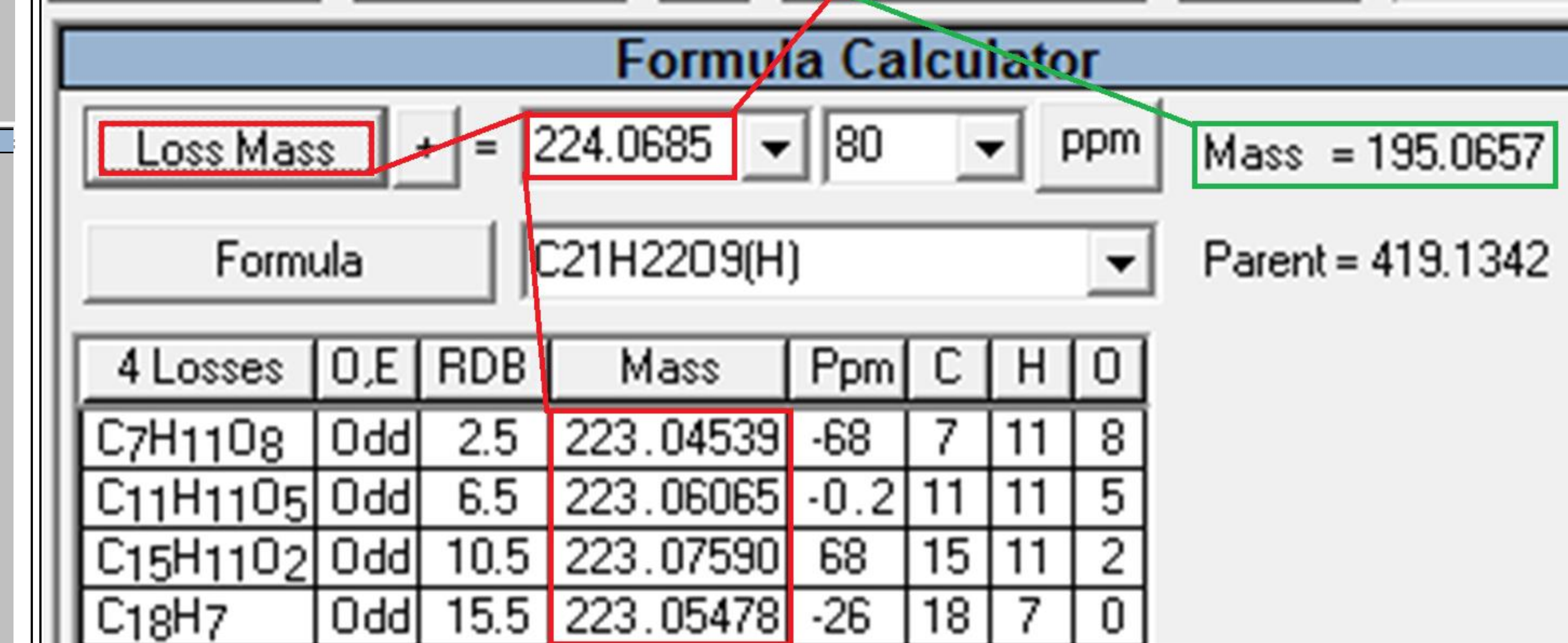**Figure.5** Formula Calculator displays formulas of ions or neutral losses corresponding to a given mass
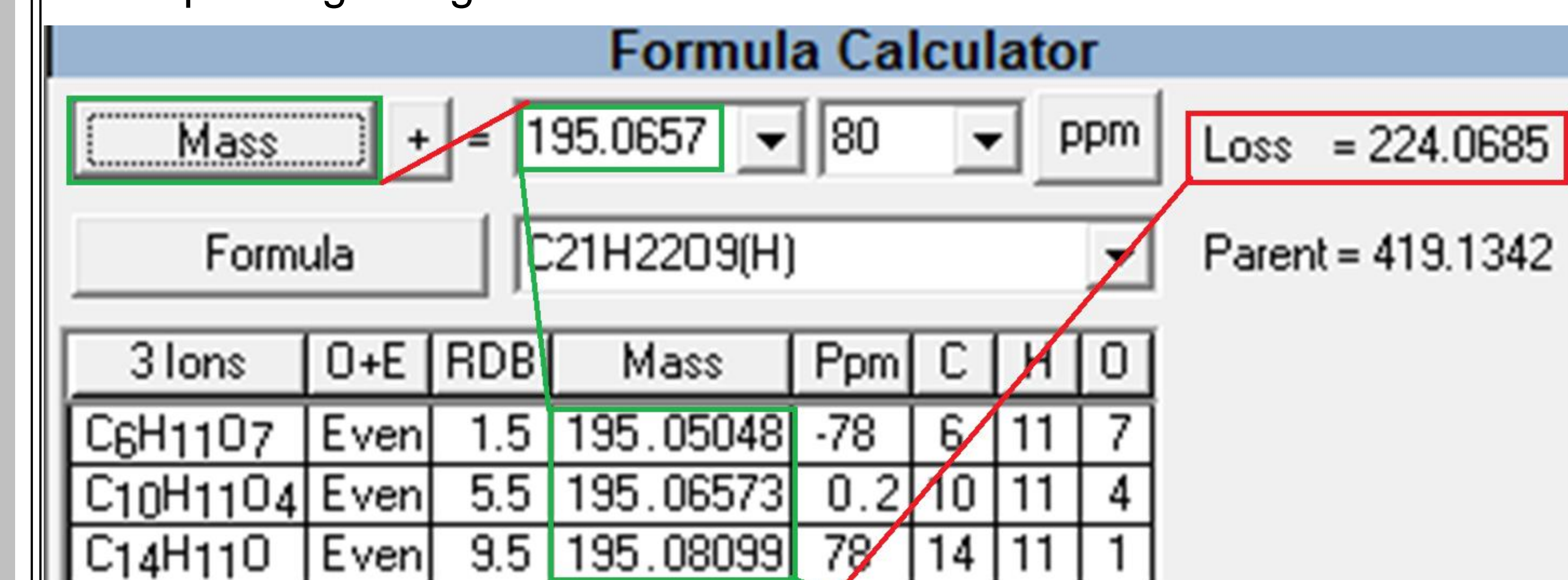

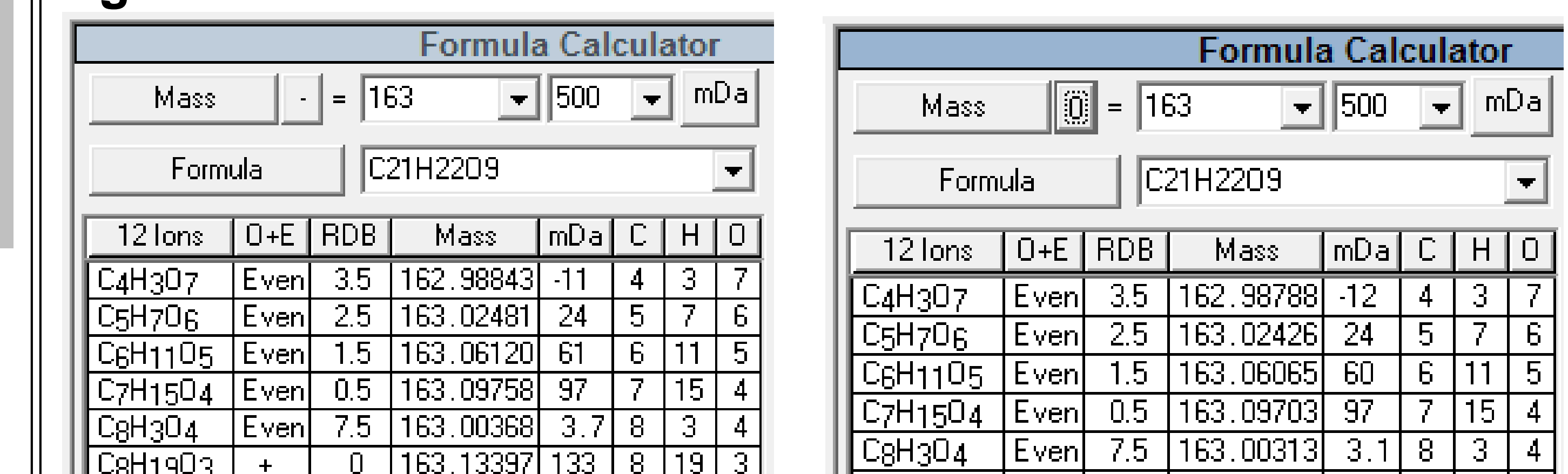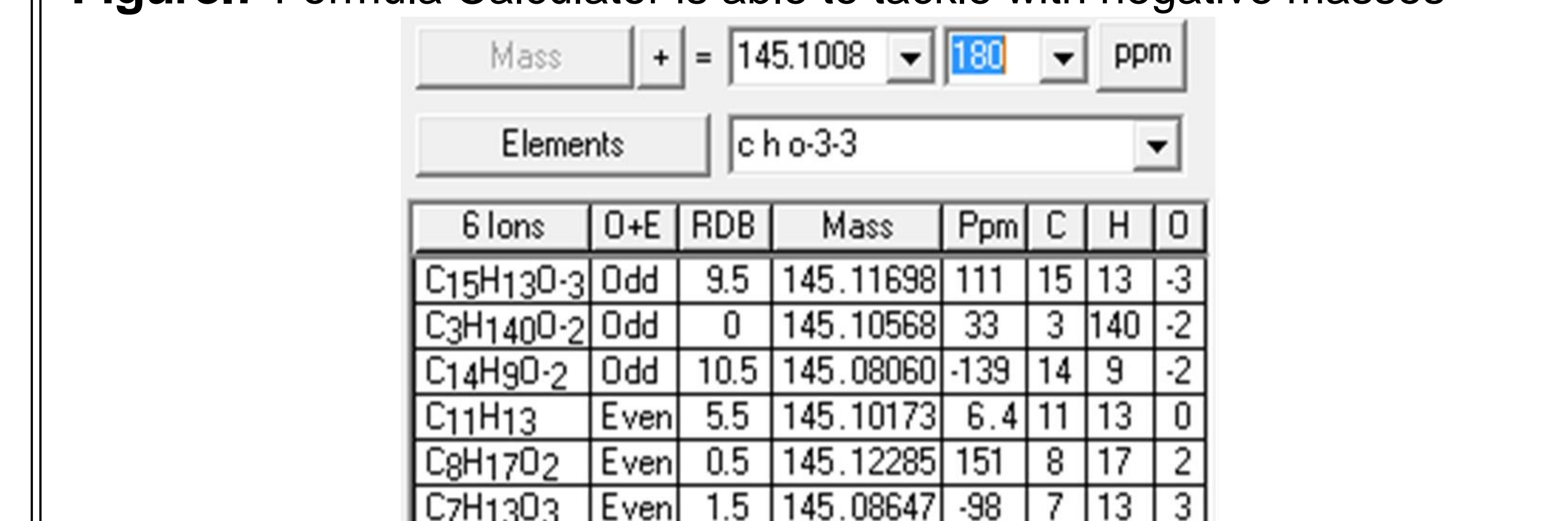**Figure.6** Formula Calculator set takes into account the electron mass

Figure.7 Formula Calculator is able to tackle with negative masses

Formula Calculator displays either a chemical formula of the parent molecule or an elemental composition. Here is a low mass accuracy (500mDa = ½ Da). All formulas shown in the table are a subset of the elements in the formula box, which is the formula of the molecule undergoing fragmentation. Odd/Even electrons, rings+double bonds, exact mass as an array of elements are also shown in sortable columns. The mass of the precursor (parent), which is that of the formula entered are also shown. By default, 500mDa is assumed for low resolution spectra (quadrupole and ion trap, typically). The box next to the Mass is the charge of the species being ionized (+, 0, -). Mass is corrected for traditional gc/ms (electron ionization) spectra. Pressing the Mass button allows Losses to be entered (with the precursor mass being fixed). Pressing the formula button will allow elements to be specified. Elements ranges may be specified using minimum negative and maximum numbers, separated by a dash ('-').