

NAME \_\_\_\_\_

ID # \_\_\_\_\_

## INTERPRETATION OF ORGANIC SPECTRA (4361/8361)

9:05 – 9:55 am, December 12, 2011

### Exam 4

This exam is open book and open note. You are permitted to use any written materials you have brought as aids on this exam. You may also use a simple calculator. Other than this, please do not use any other electronic devices (cell phones, computers, recording devices, etc.) during the exam.

You may use pen or pencil. However, re-grades will be considered only for exams completed in pen.

Please write your answers in the boxes/spaces provided. If your answer is not in the appropriate space (say, for example, it's on the back of the page), draw us an arrow and/or note telling us where to look.

Feel free to remove the corner staple if this helps you analyze the spectra; you will have the opportunity to re-staple your exam at the end. You will be given 50 minutes total to finish the test. This exam contains two main problems, which are split into parts. Many of these parts can be answered independently. *Do not get stuck* on one part and then assume that you will be unable to answer the rest of the question—move on. In addition, partial credit will be given for incorrect but still plausible answers, so *guess* on problems you cannot answer perfectly.

At the end of the 50 minute exam period you will be asked to return your exam to the proctor. Please do not take any part of the exam packet with you when you are done; everything will be returned to you after the exams are graded. This packet should contain 12 pages, including this one. Please check to make sure that your packet contains 12 pages before beginning your exam.

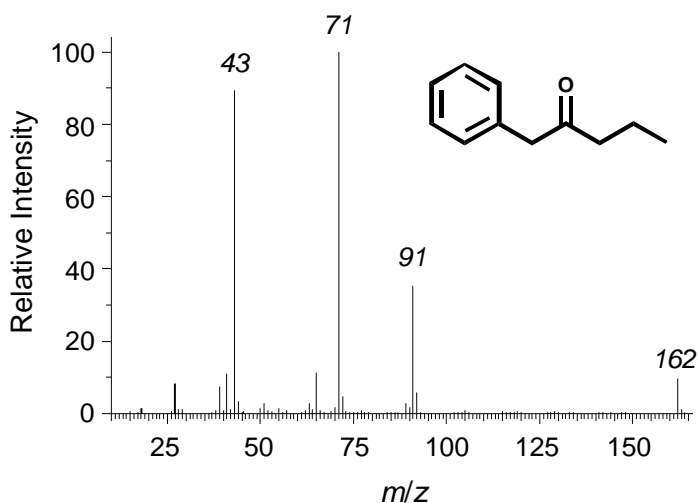
NAME \_\_\_\_\_

Scoring: 1. \_\_\_\_\_ / 6                      6. \_\_\_\_\_ / 32  
2. \_\_\_\_\_ / 21                      7. \_\_\_\_\_ / 10  
3. \_\_\_\_\_ / 4                      8. \_\_\_\_\_ / 8  
4. \_\_\_\_\_ / 7                      9. \_\_\_\_\_ / 4  
5. \_\_\_\_\_ / 8

**Total Score:** \_\_\_\_\_ / 100

The electron-ionization mass spectrum (EI-MS) of 1-phenyl-2-pentanone is shown at right. Problems 1-4 refer to these spectra.

1. A peak corresponding to the parent ion (with  $m = 162$ ) is visible in the mass spectrum. In the boxes below, illustrate the two most prevalent parent ion structures. In each structure, make sure you indicate the precise location of ionization in the molecule.



*one parent ion structure*

*another parent ion structure*

2. In the boxes below, draw mechanisms (using “electron pushing”) that explain the fragmentation of the parent ion into fragment ions with  $m/z = 91$ , 71, and 43. Use either of the parent ion structures on the previous page as your starting material.

**$m/z = 91$**

**$m/z = 71$**

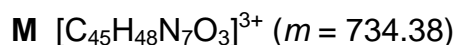
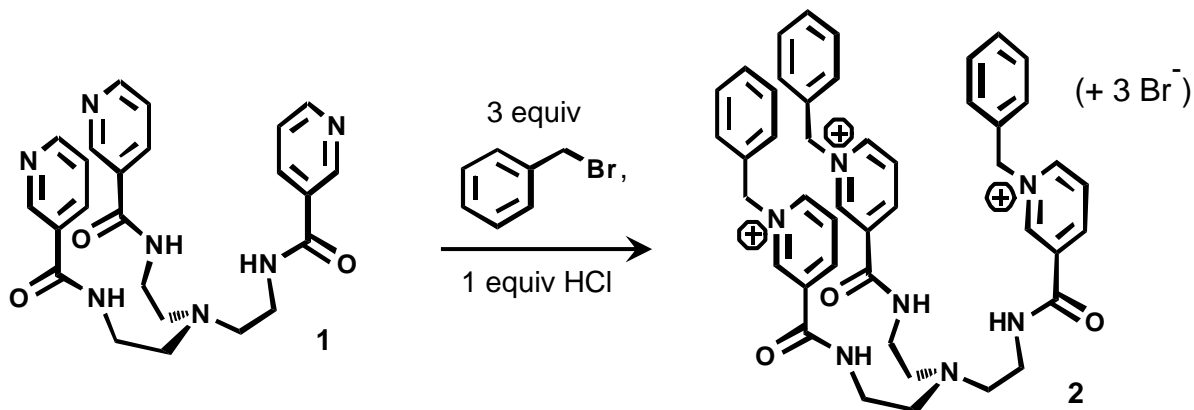
**$m/z = 43$**

3. Though you can't really see it in the EI-MS spectrum, there is a small peak at  $m/z = 163$ . Relative to the peak at  $m/z = 162$ , how intense would you expect the peak at  $m/z = 163$  to be?

%

4. The parent peak in the EI-MS is much smaller than the fragment peaks. How might the EI-MS experiment be conducted differently to reduce fragmentation, and increase the relative intensity of the parent peak? (Do *not* propose an alternate ionization method; keep this an EI-MS experiment.)

As part of an effort to synthesize organometallic ligands that react via both electron and hydride transfer, Deanna Miller (Lu group) attempted to triply benzylate the tripyridine starting material **1** to generate the tricationic ligand **2**.



Deanna analyzed her crude reaction mixture by positive-mode electrospray ionization quadrupole mass spectrometry (ESI-MS). The mass spectrum, including close-ups, are shown at the end of this exam. Problems 5-9 refer to these spectra.

5. Deanna expected to see peaks corresponding either to the trication product or, because the central amine nitrogen is basic, the protonated version of this product. What would  $m/z$  be for these two species? Answer to within 0.1 Da.

$m/z$  (**M**) =

$m/z$  (**M** +  $\text{H}^+$ ) =

6. Deanna didn't observe peaks at either of these  $m/z$  values in her measured mass spectrum. The peak patterns she observed in the close-ups also didn't make sense for the ions she predicted. She still suspected that peaks in the spectrum might correspond to the expected product somehow, or they might come from incompletely benzylated side products.

In the boxes on the next page, draw the chemical structures of the four highest- $m/z$  ions observed by Deanna. For each ion, also indicate the molecular (ion) formula and charge state.

$m/z = 892.14$

*chemical structure*

*chemical formula*

*charge*

$m/z = 722.18$

*chemical structure*

*chemical formula*

*charge*

$m/z = 552.23$

*chemical structure*

*chemical formula*

*charge*

$m/z = 407.62$

*chemical structure*

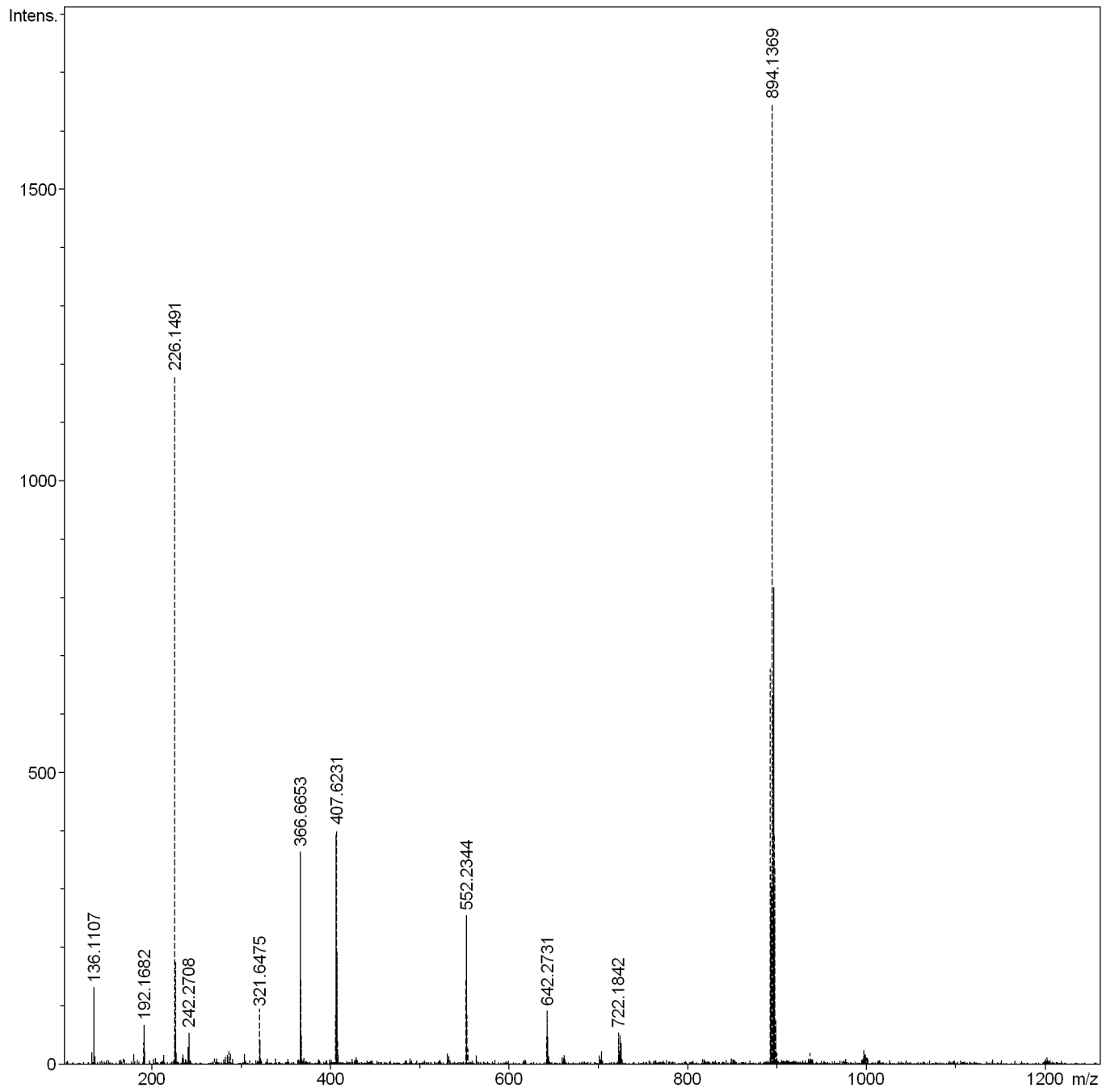
*chemical formula*

*charge*

7. What might Deanna have done to observe the original  $M^{3+}$  peak she was looking for? Name and describe an experiment she could have performed to verify the presence of the  $M^{3+}$  ion in her product mixture.

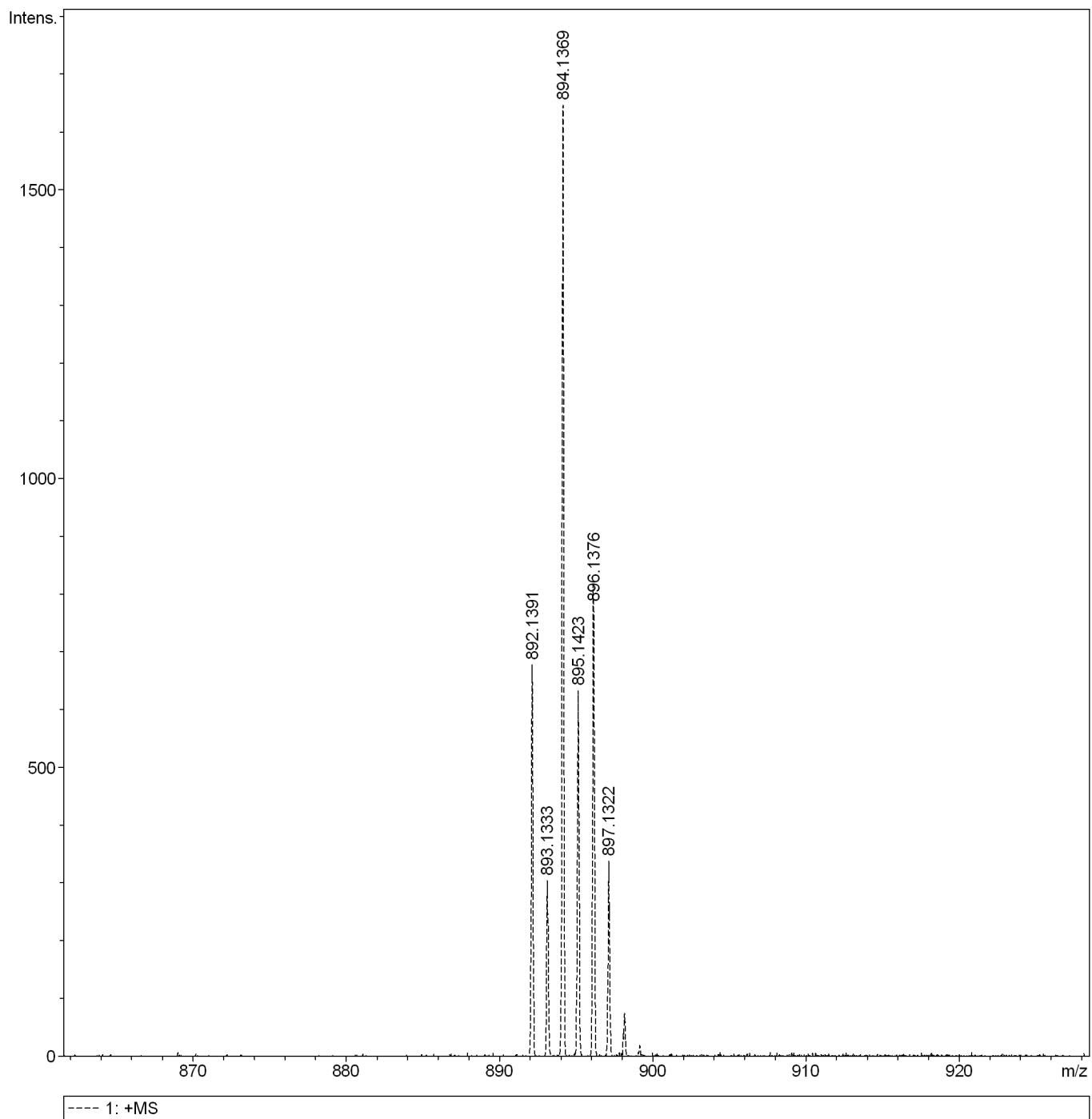
8. To achieve high mass resolution, mass selection modules are sometimes connected in series, so that a specific ion mass selected in a first module can be further refined in a second one. Reflectron time-of-flight modules offer extremely high mass resolution, but they are not directly compatible with quadropole selection. In ten words or less, why not?

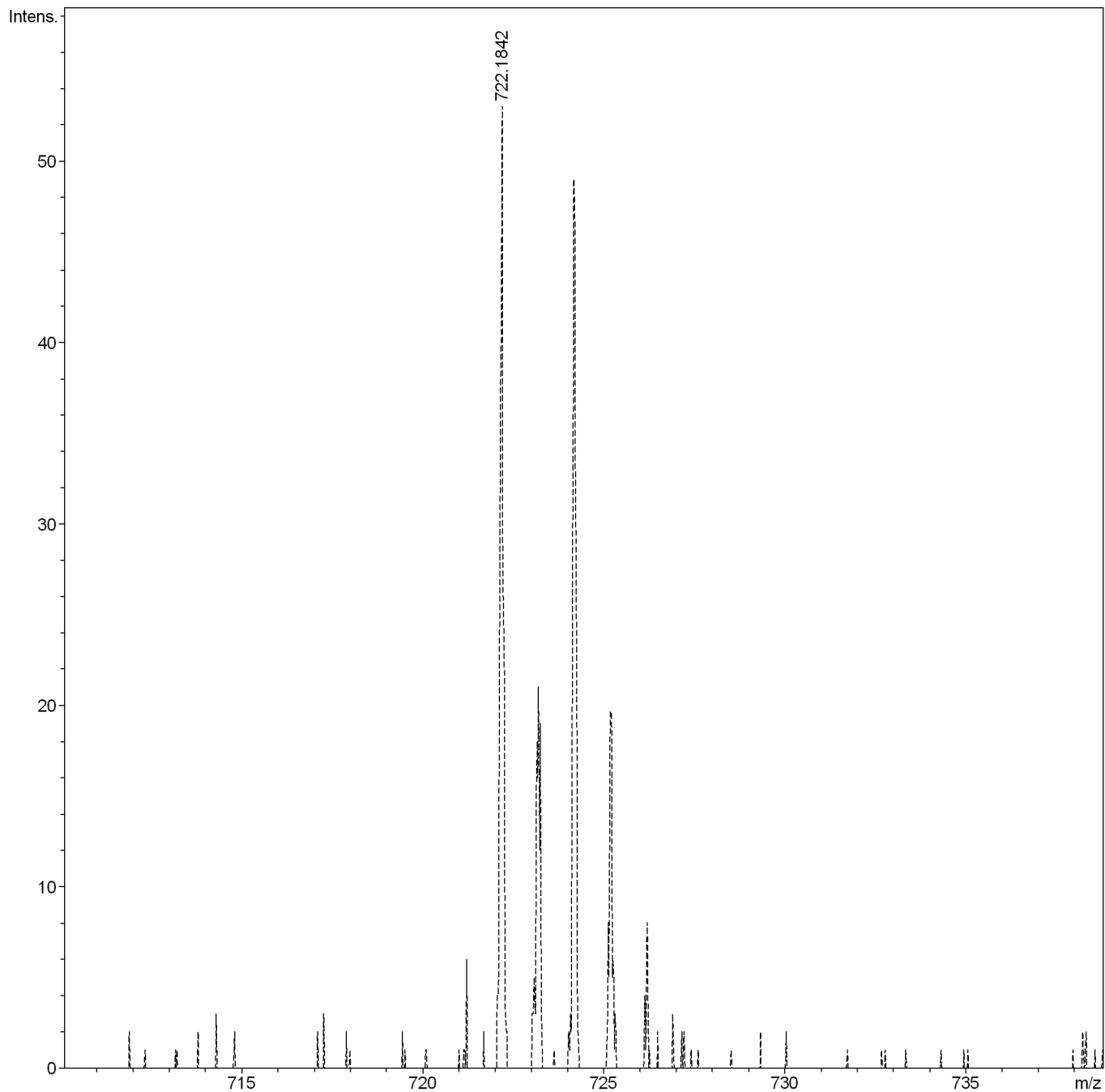
9. What initial ion selection method would be compatible with subsequent reflectron time-of-flight resolution?



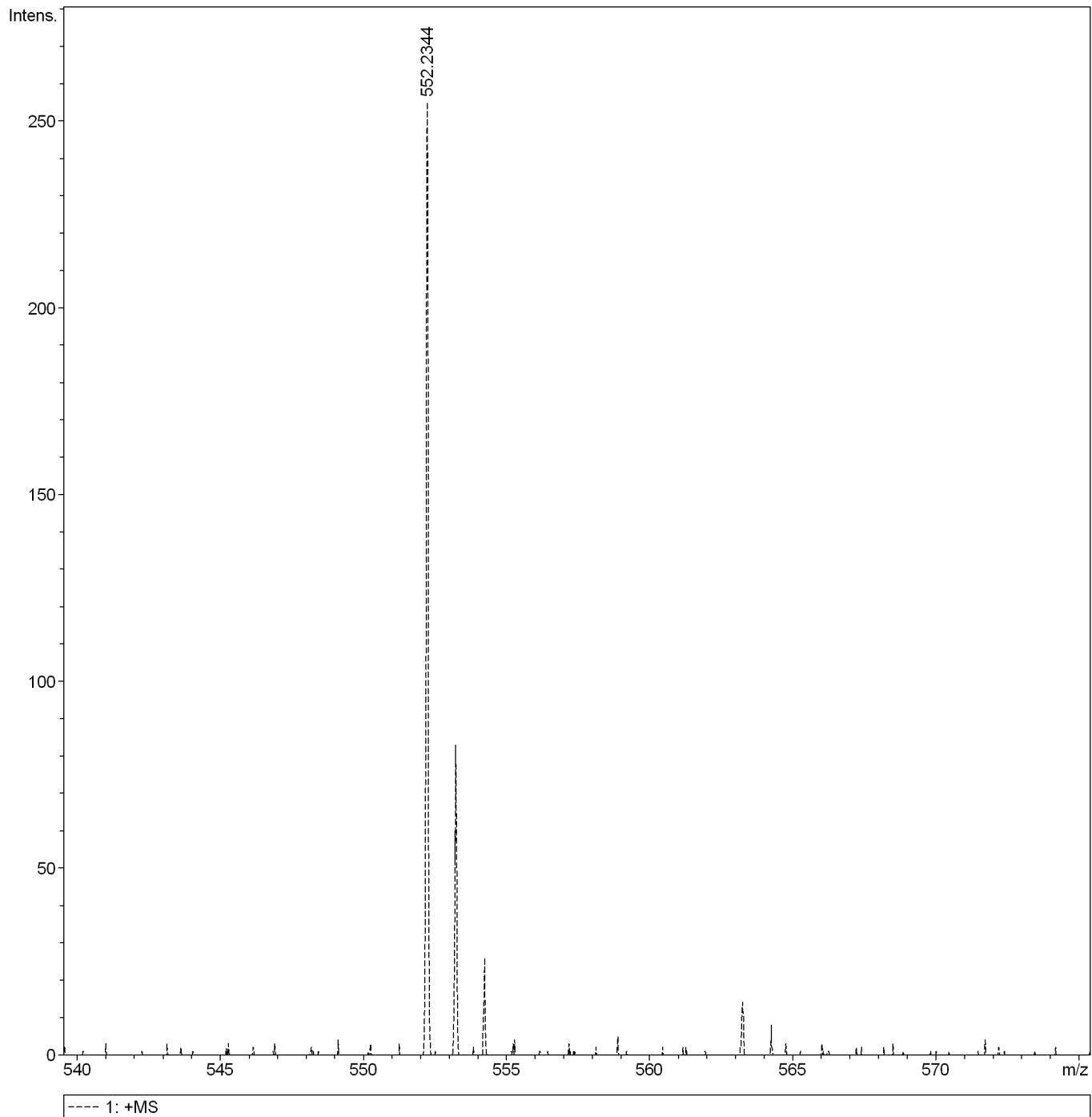
--- 1: +MS

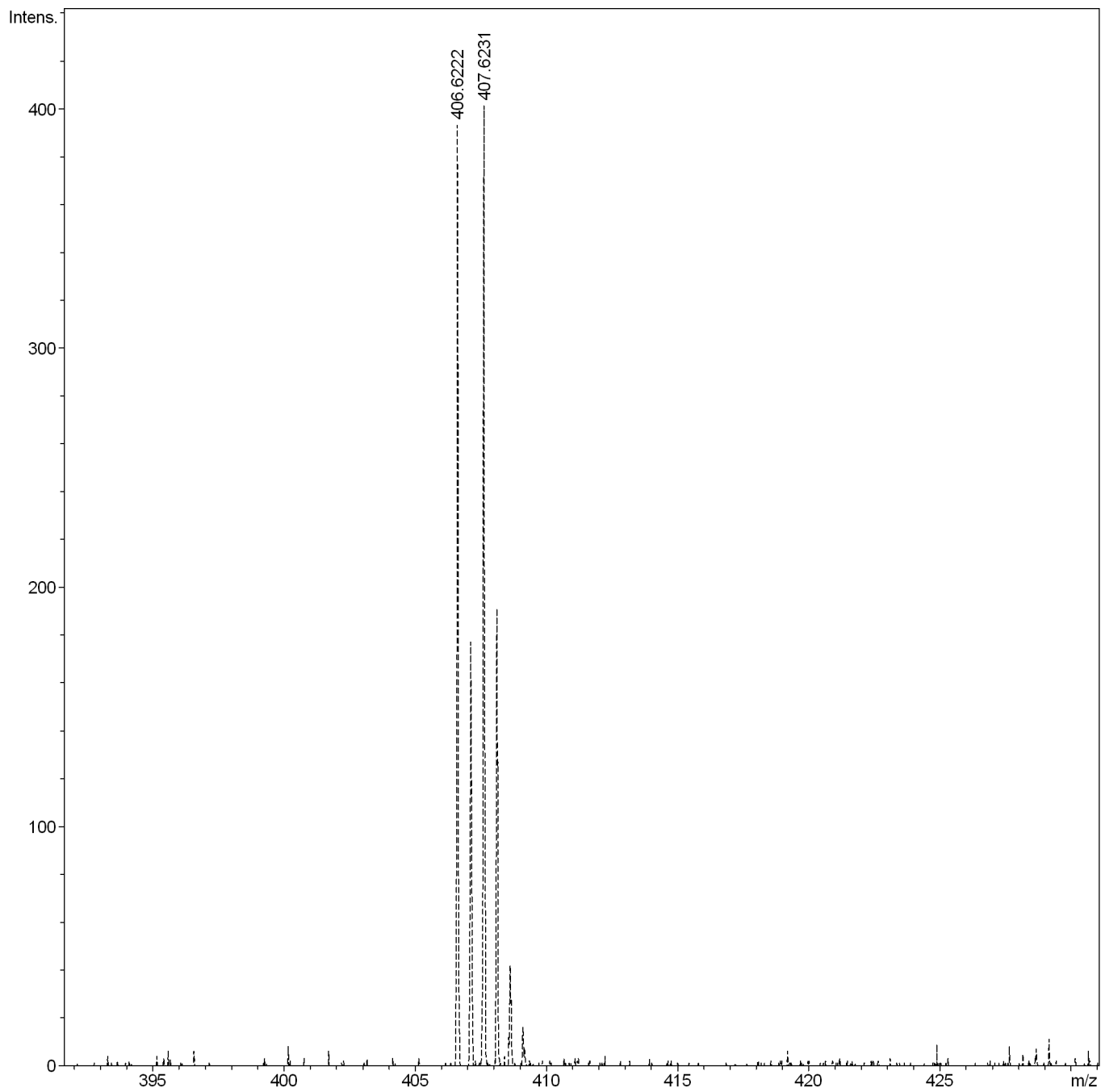






---- 1: +MS





---- 1: +MS