NAME _____

ID # _____

INTERPRETATION OF ORGANIC SPECTRA (4361/8361)

9:05 – 9:55 am, November 14, 2012

Exam 3

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 one problem, which is 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 10 pages, including this one. Please check to make sure that your packet contains 10 pages before beginning your exam.

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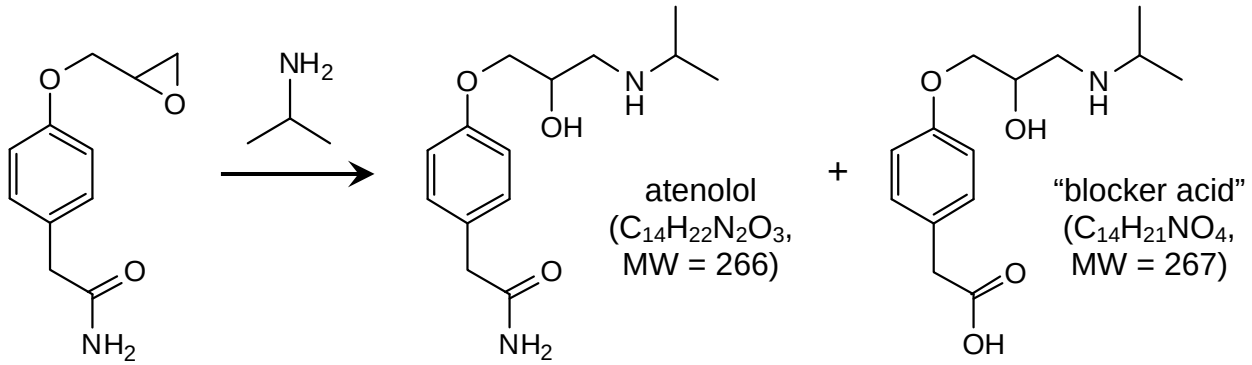
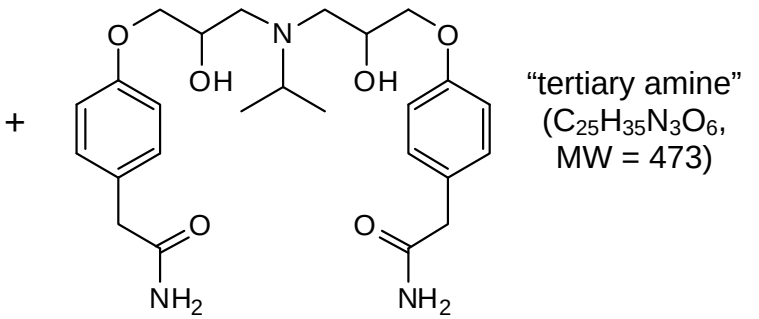
NAME _____

Scoring:		
	1. _____ / 6	6. _____ / 10
	2. _____ / 4	7. _____ / 12
	3. _____ / 5	8. _____ / 24
	4. _____ / 9	9. _____ / 6
	5. _____ / 16	10. _____ / 8

Total Score: _____ / 100

Atenolol, a “beta blocker”, is commonly prescribed to treat high blood pressure. The final step of AstraZeneca’s synthesis of atenolol, shown below, also generates a couple of side products (which AstraZeneca scientists call the “blocker acid” and “tertiary amine”), as shown below. You reproduce AstraZeneca’s synthesis, and isolate one of the products. The primary goal of this exam is to determine which of the three products you isolated.





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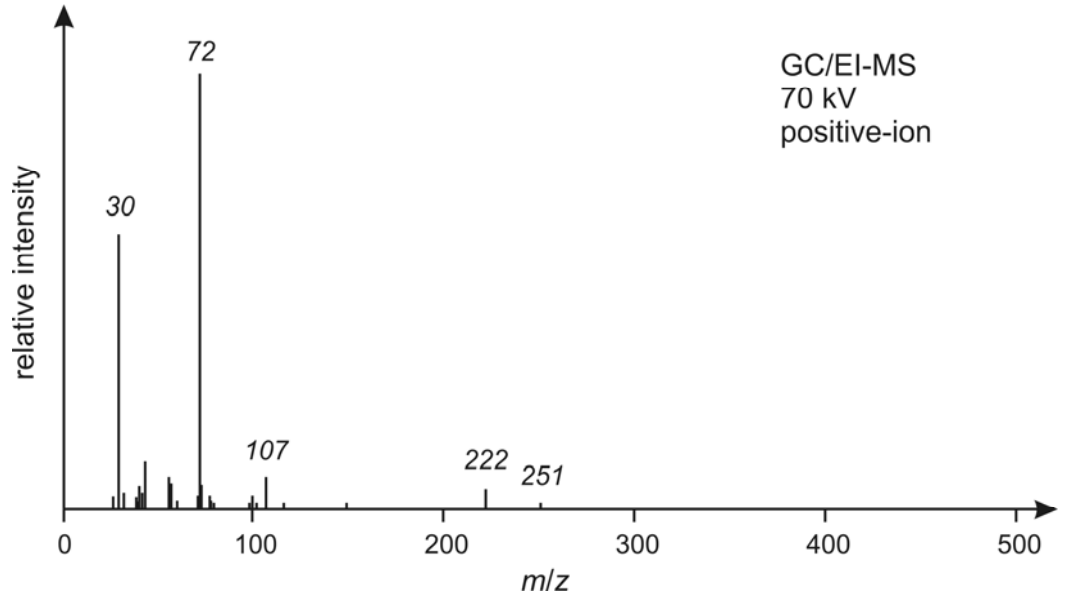
1. You first inject your purified molecule into a gas chromatography-coupled mass spectrometer (GC-MS), using electron ionization (EI) and positive-ion detection. You observe just one total-ion peak, and from that peak you collect the EI mass spectrum shown below:



Clearly, none of the peaks in this spectrum correspond to the expected parent masses shown on the previous page. If you wanted to use the same instrument, ionization and detection modes, how might you change the experiment to make a parent peak appear? *(Please be brief; I think you can answer this in ten words or less.)*

2. Instead, you choose to run your sample on a different instrument—an electrospray ionization, quadropole mass spectrometer (ESI-MS) set to generate and detect positive ions. You dissolve your sample in acetonitrile (CH_3CN) with a small amount (0.1%) of acetic acid, inject this solution directly into the instrument, and collect the spectrum shown on the next page. Based on this mass spectrum (and on the rest of the exam), is your molecule

atenolol , **"blocker acid"** , *or* **"tertiary amine"** ? *(Circle one.)*

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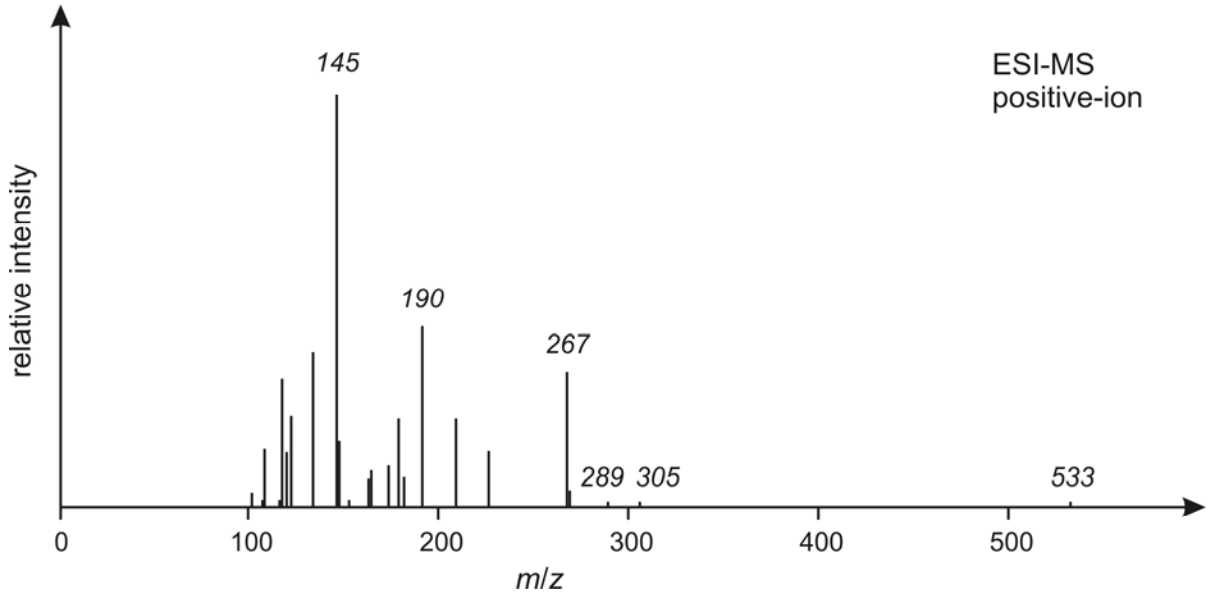

3. What is the molecular structure of the *m*/*z* = 267 ion? Do not use any functional group abbreviations in your structure—draw the ion as you would any other organic molecule.

structure of *m*/*z* = 267 ion

4. The peaks at *m*/*z* = 289, 305 and 533 correspond to ions that are structurally related to the parent molecule. Using the letter "**M**" to abbreviate the neutral molecule you circled in problem #2, what are the molecular formulae of these three ions? (Make sure to indicate charge in each formula.)

m/*z* = 289

m/*z* = 305

m/*z* = 533

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5. Acetonitrile is a great solvent for ESI-MS, but dimethyl sulfoxide (DMSO), another solvent with similar polarity, is not. Why not? Explain your answer in terms of the mechanism of electrospray ionization.

6. Continuous-source quadropole instruments are capable of mass resolution within ~0.1 amu for small organic molecules. What if you wanted to analyze your acetonitrile solution at higher mass resolution than this? What type of ion-source and mass-selection technologies could you use?

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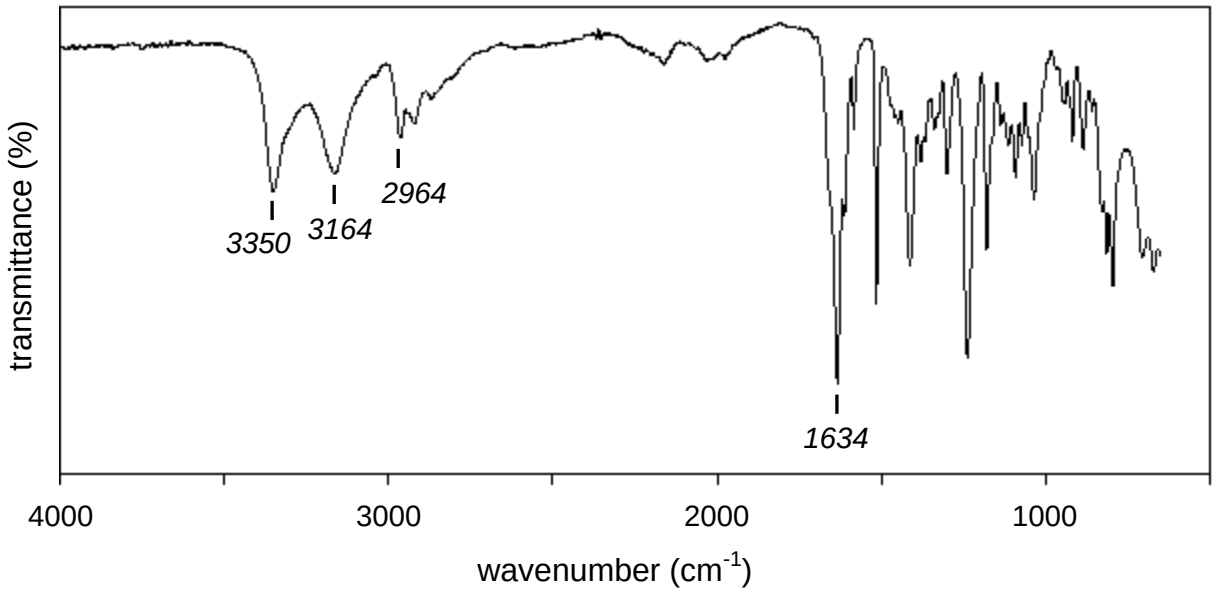
7. The infrared (IR) spectrum of your molecule is shown below.



Which functional groups or bonds are responsible for the four labeled peaks?

ν (cm^{-1})	functional group	ν (cm^{-1})	functional group
3350		2964	
3164		1634	

8. A ^{1}H NMR of the isolated molecule, and close-ups, are attached to the end of this exam. All of the potential molecule structures have similar architectures and arrangements of protons, so ^{1}H chemical shifts can't be used to distinguish them. On the next page, on the left, I have listed either individual chemical shift values or chemical shift ranges for each peak that appears in the ^{1}H NMR (and that does not correspond to H_2O or solvent). In the diagram on the right, fill in each empty box with one of these chemical shifts or shift ranges.

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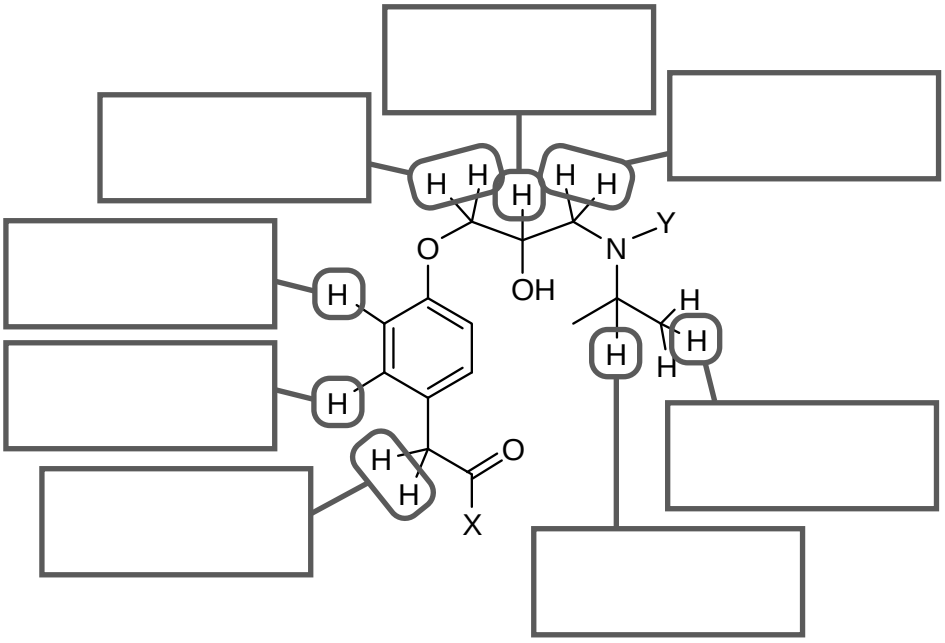
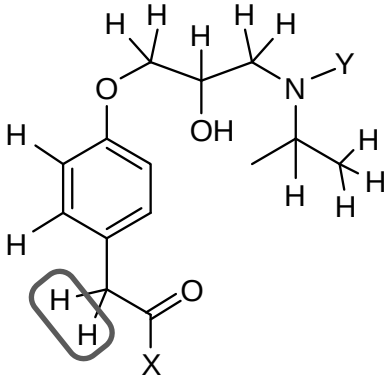
δ values observed in ^{1}H NMR (in ppm):

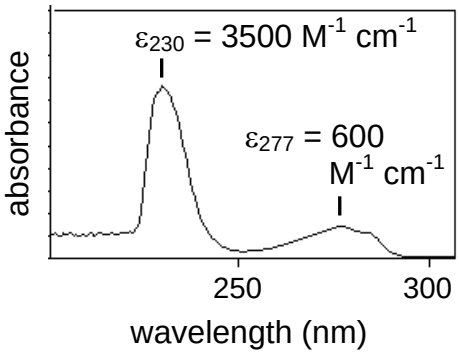
7.37
7.14
6.84
6.82
4.95
3.95-3.75
3.27
2.75-2.45
1.48
0.96

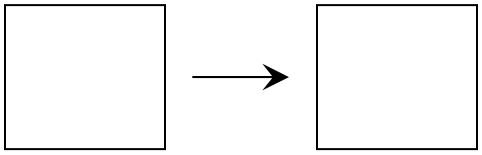


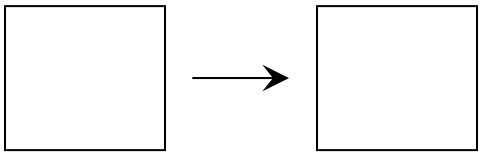
9. The protons circled on the structure on the right don't show coupling to any other protons in the molecule, so their connectivity can't be verified by ^{1}H-^{1}H coupling. But an HMBC experiment might prove that the circled protons were adjacent to the benzene ring. Using double-headed arrows, show **two** distinct correlations that you would expect to see by HMBC that would prove this connectivity.



10. The UV-vis spectrum of your molecule, collected in methanol solution, is shown at right. What type of electronic transitions are responsible for the absorbance peaks at λ = 230 and 277 nm? In each case, electrons are excited from what gound-state orbital, to what excited-state orbital?



λ = 230 nm 

λ = 277 nm 

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