EXAMINATION 1
Chemistry 3B

Name: Key _____ SID #: _____

Print first name before second!
Use capital letters!

GSI (if you are taking Chem 3BL): _____

Peter Vollhardt
October 2, 2008

Please provide the following information if applicable.

Making up an I Grade _____
(If you are, please indicate the semester during which you took previous Chem 3B:

_____ _____
Semester Instructor

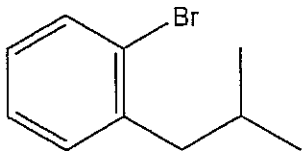
Please write the answer you wish to be graded in the spaces provided. ***Do scratch work on the back of the pages***. This test should have **20** numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **Read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy structures or phrases. It is better to be pedantic in accuracy now than sorry later!** ***Good Luck***!

DO NOT WRITE IN THIS SPACE

I.	_____	(30)
II.	_____	(30)
III.	_____	(50)
IV.	_____	(60)
V.	_____	(30)
VI.	_____	(30)
VII.	_____	(20)
Total:	_____	(250)

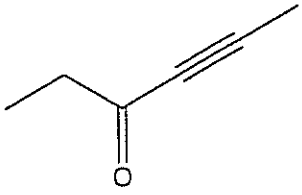
I. [30 Points] Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary (*cis*, *trans*, *R*, or *S*).

a.



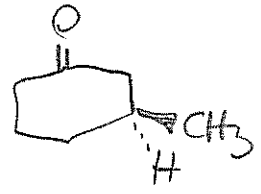
1-Bromo-2-(2-methylpropyl)-benzene

b.

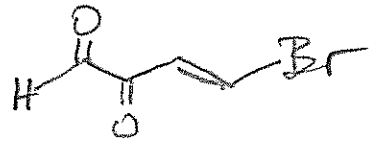


4-Hexyn-3-one

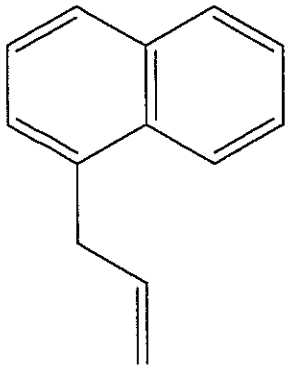
c. (*S*)-3-Methylcyclohexanone



d. *trans*-4-Bromo-2-oxo-3-butenal

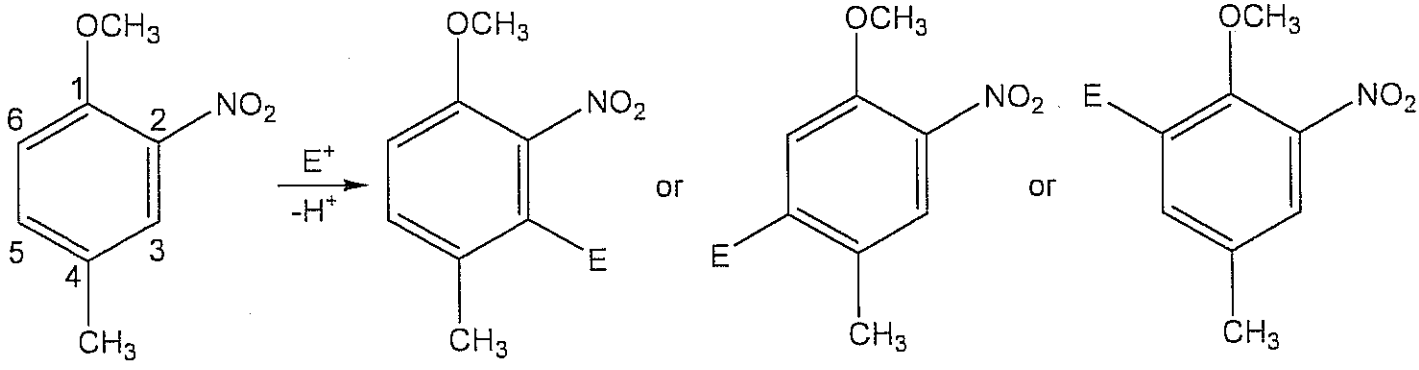


e.



1-(2-Propenyl)naphthalene

II. [30 Points] Compound **A** undergoes preferential electrophilic attack by E^+ to give only one of the three products shown.

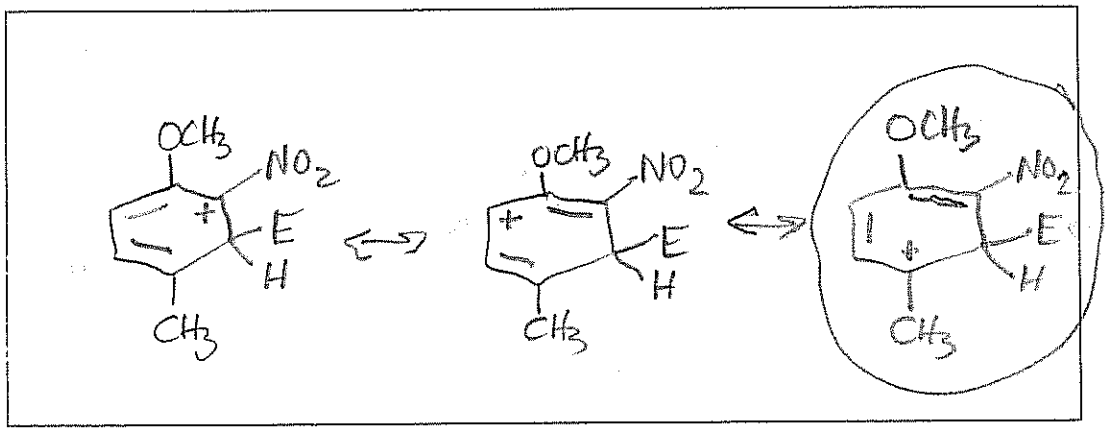


A

a. Which one? Mark the box below your choice with an X.

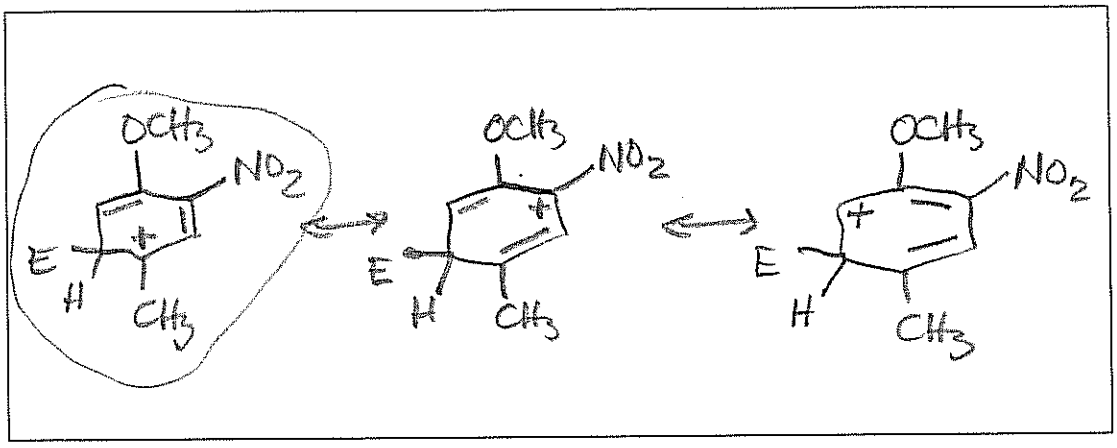
b. Write the resonance forms of the intermediate formed on attack of E^+ on **A** at:

C-3:



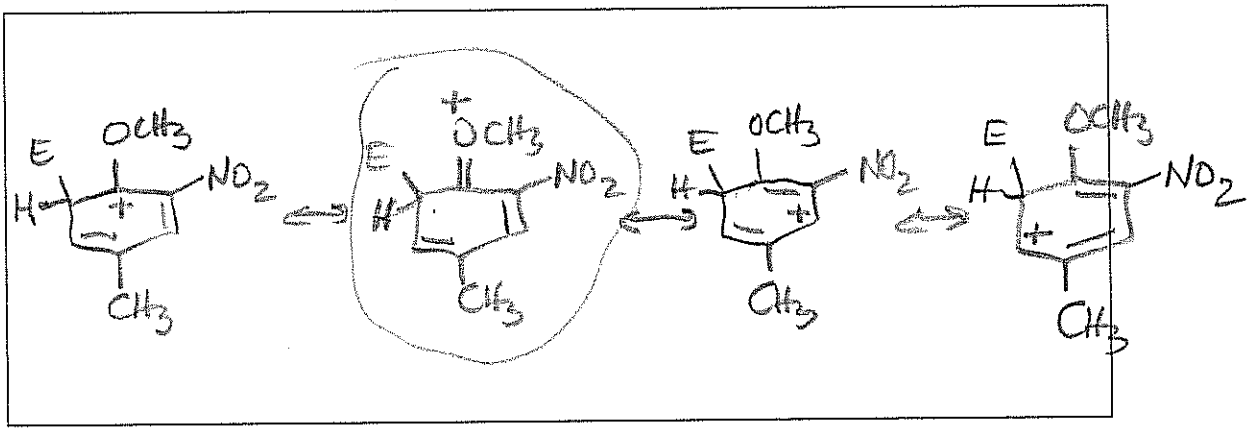
Three ~~Four~~ resonance forms

C-5:



Three resonance forms

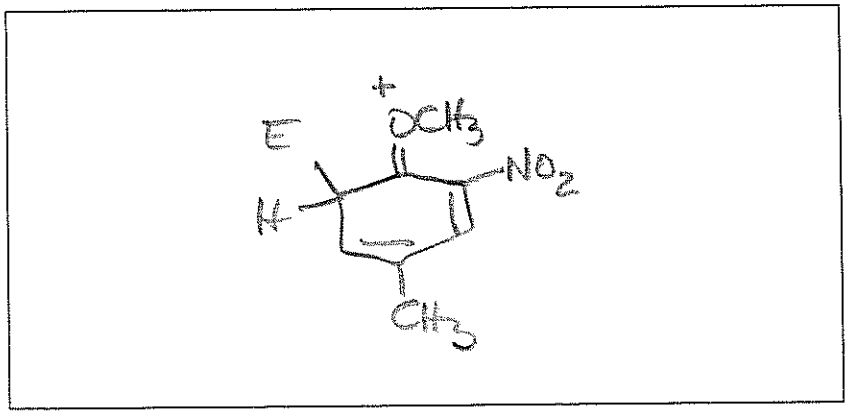
C-6:



Four ~~Three~~ resonance forms

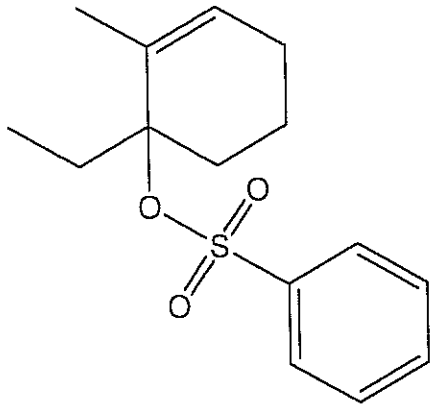
c. Circle (in your answers above) the **most strongly** contributing resonance forms of the attack at C-3, C-5, and C-6.

d. Considering all of the above **most strongly** contributing resonance forms, which one is the best overall? Redraw it in the box below.

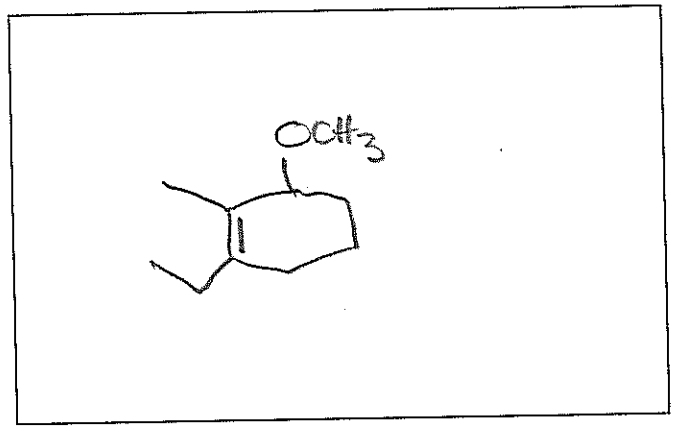


III. [50 Points] Add the missing components (starting materials, reagents, or products) of the following reactions in the boxes provided. Show stereochemistry when appropriate. Aqueous work-up (when required) is assumed to be part of a step. It is not part of any answer.

a.

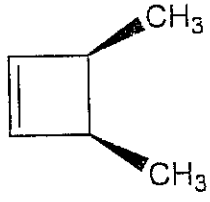


CH_3OH
(solvent)

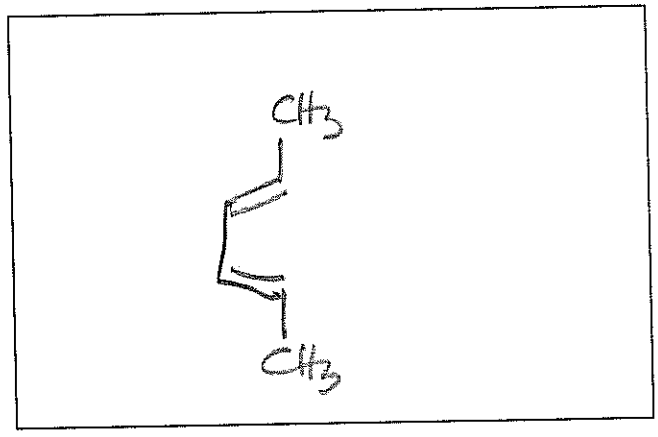


Thermodynamic product

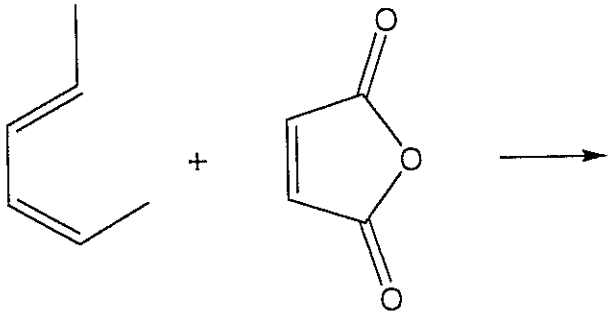
b.



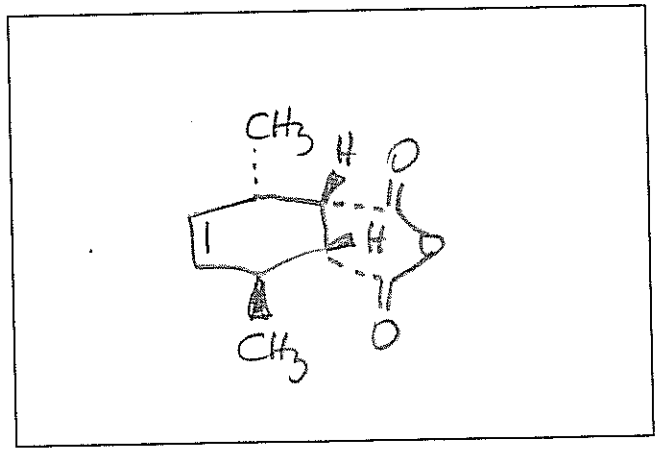
$h\nu$



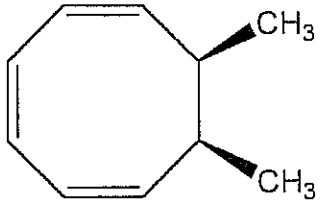
c.



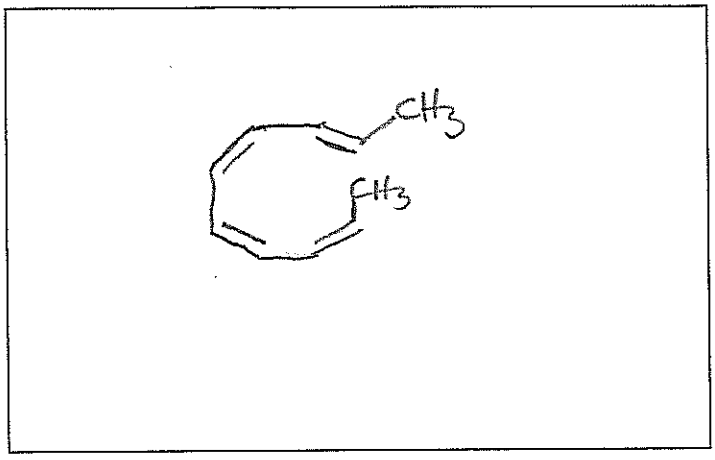
+



d.

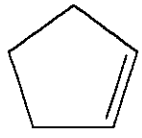


$\xrightarrow{\Delta}$

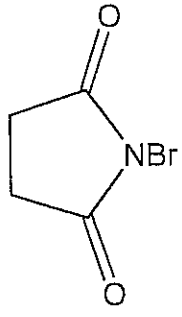


Product of ring opening

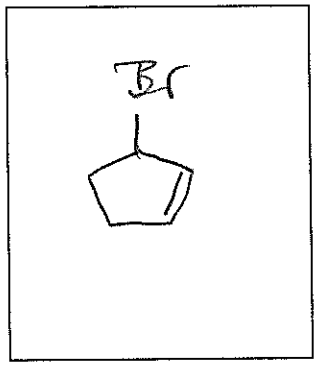
e.



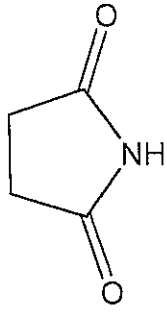
+



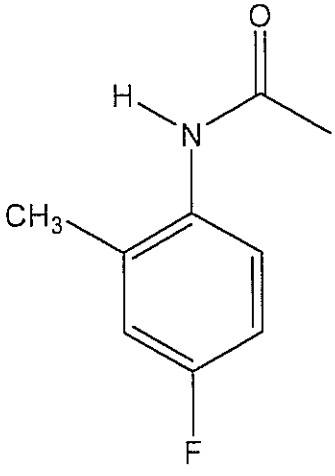
$\xrightarrow{h\upsilon}$



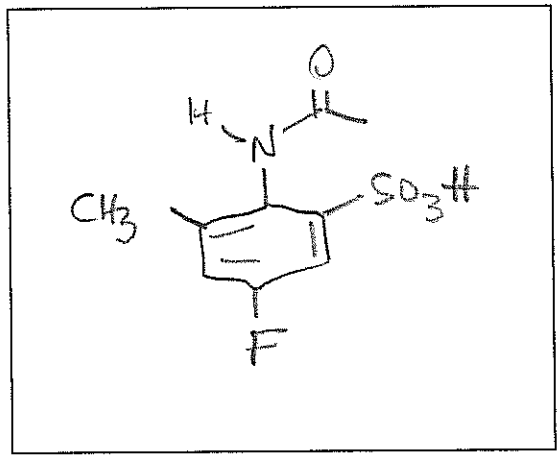
+



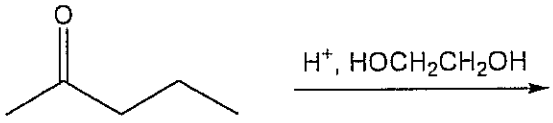
f.

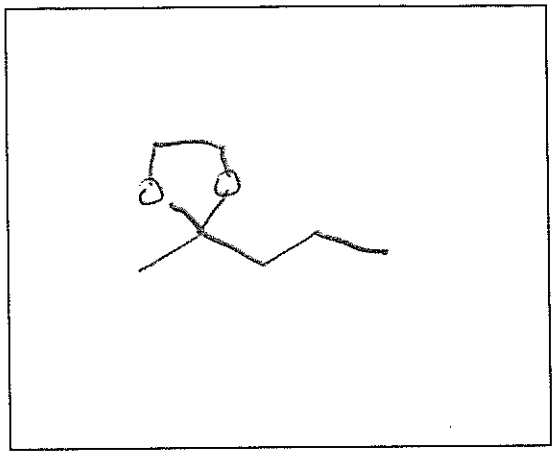


$\xrightarrow{SO_3,\ H_2SO_4}$

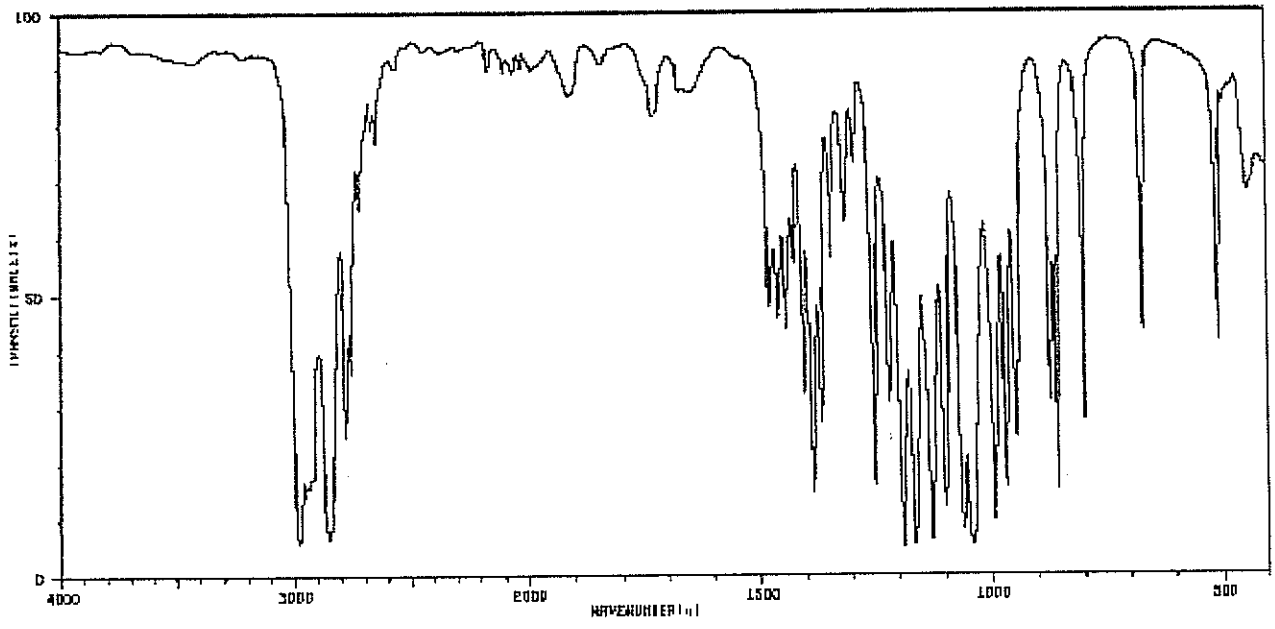


g.

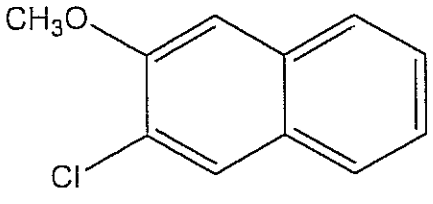




IR spectrum of product:

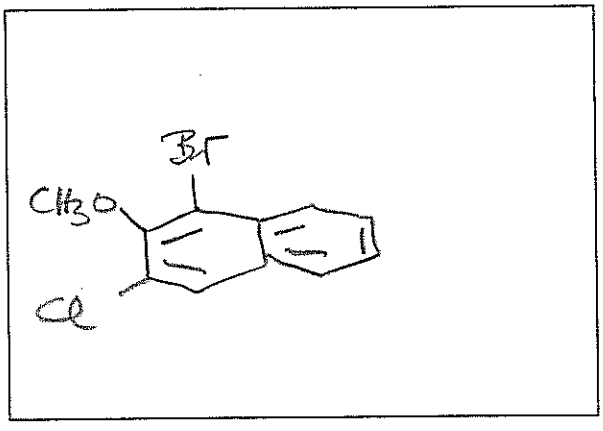


h.

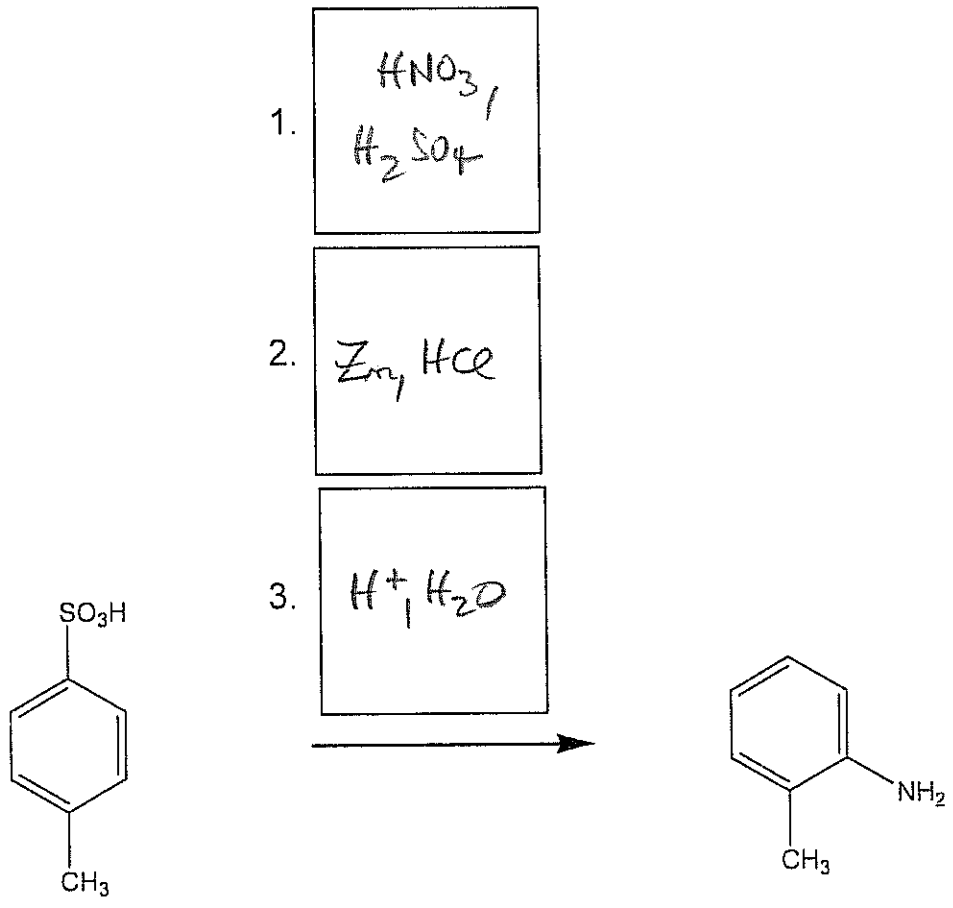


Br_2, $FeBr_3$

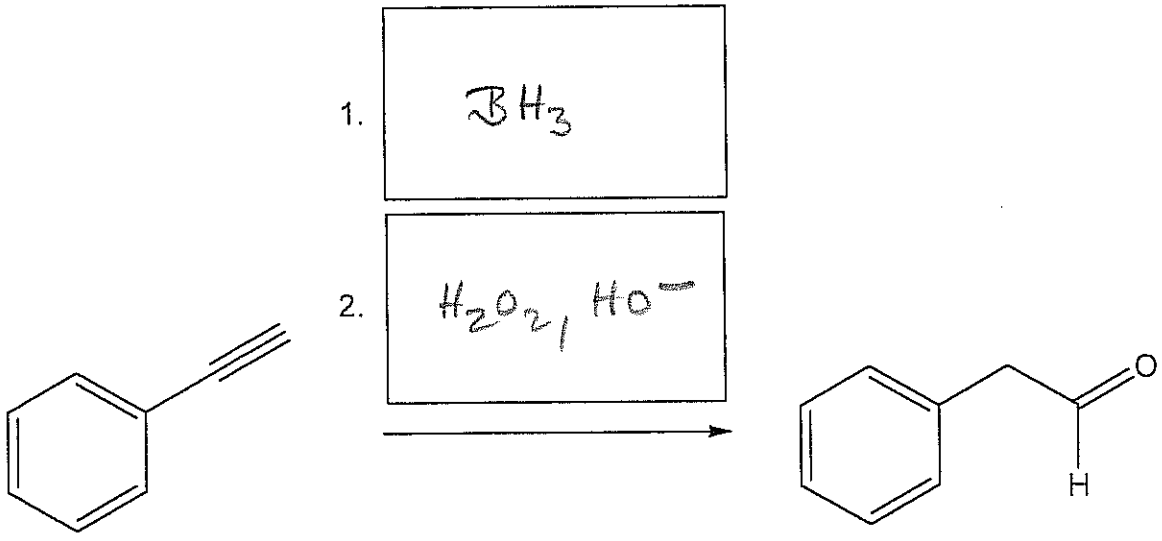
Monobromination



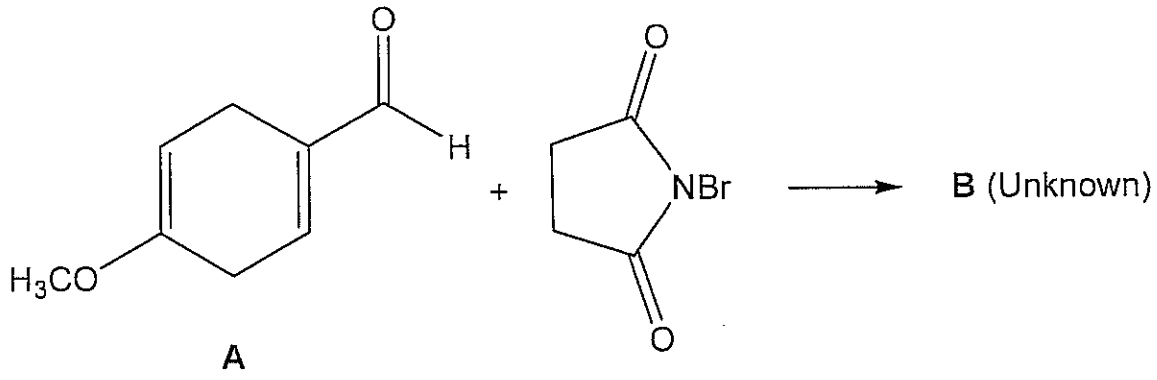
i.



j.

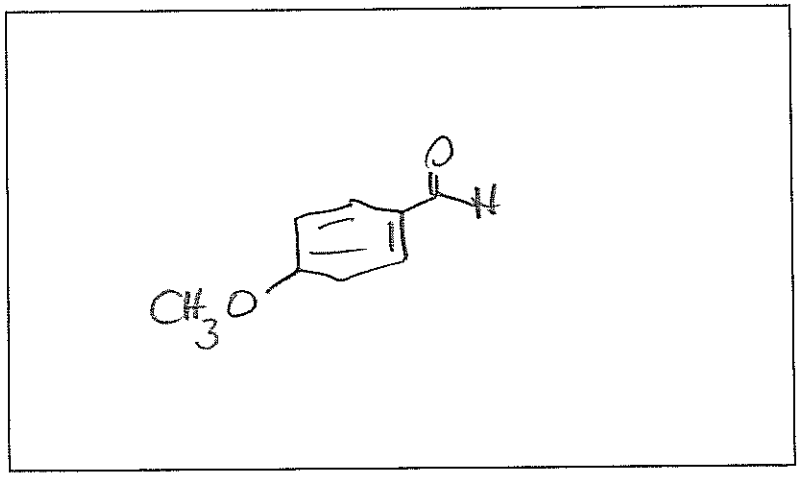


IV. [60 Points] An attempt to effect allylic bromination of **A** generated the unknown **B**. The complete spectral data for this product are shown below in the sequence:
1. ^{1}H NMR, 2. ^{13}C NMR, 3. Mass, 4. IR, 5. UV.

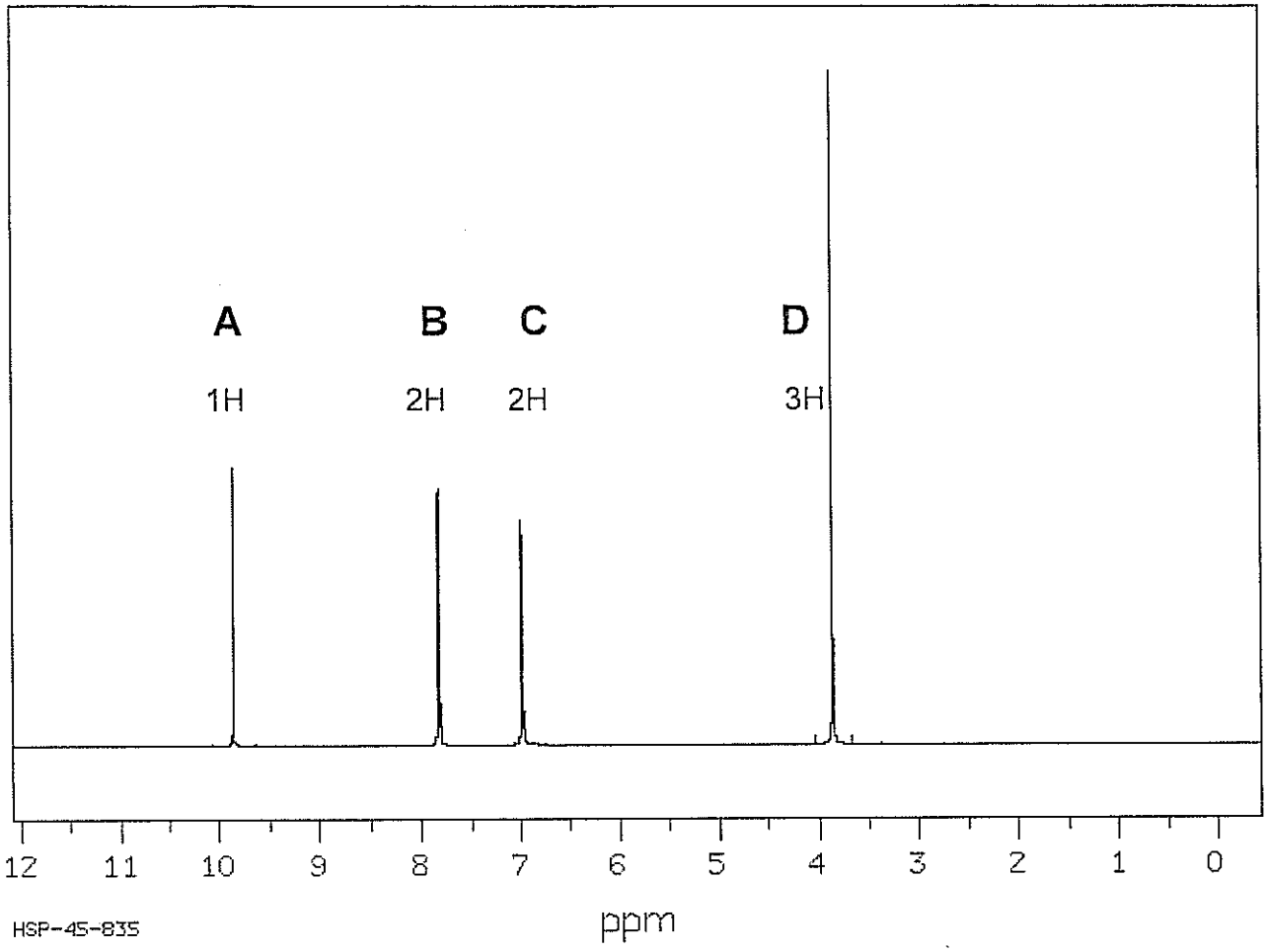


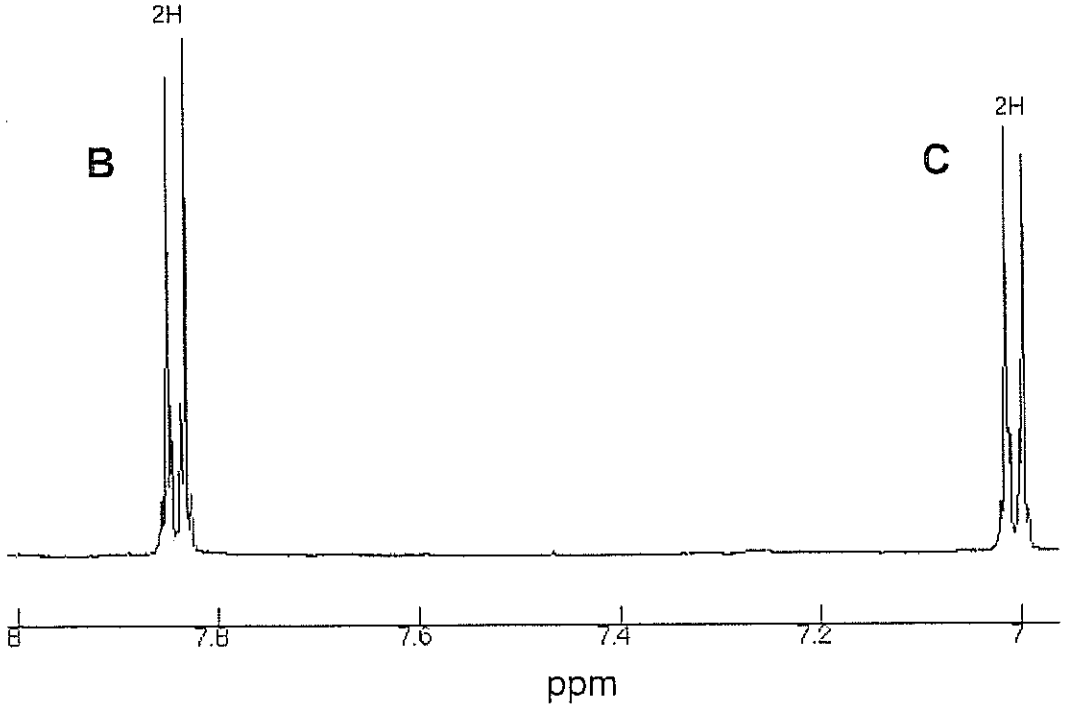
A

a. After consideration of the spectral data, write the structure of the product in the box below.

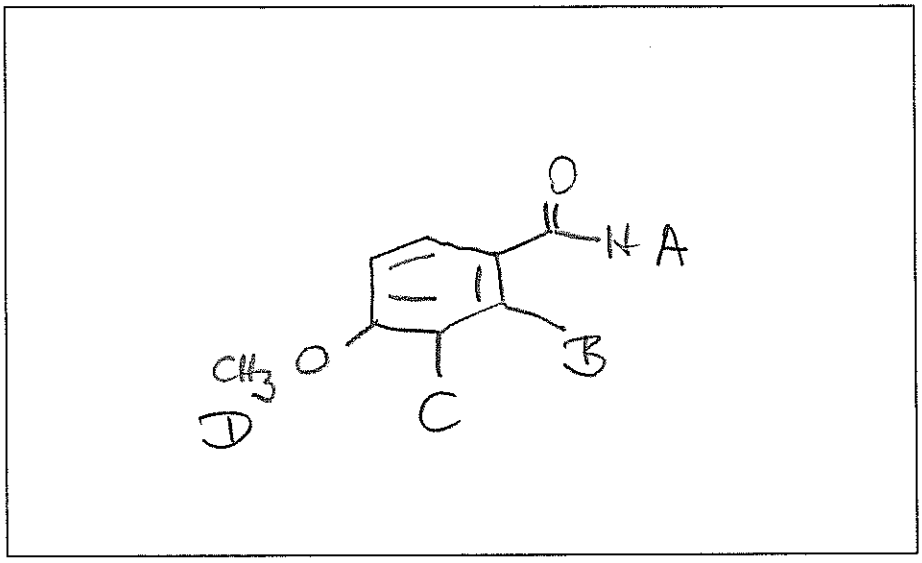


1. ^{1}H NMR Spectrum (for expanded section, see bottom spectrum).

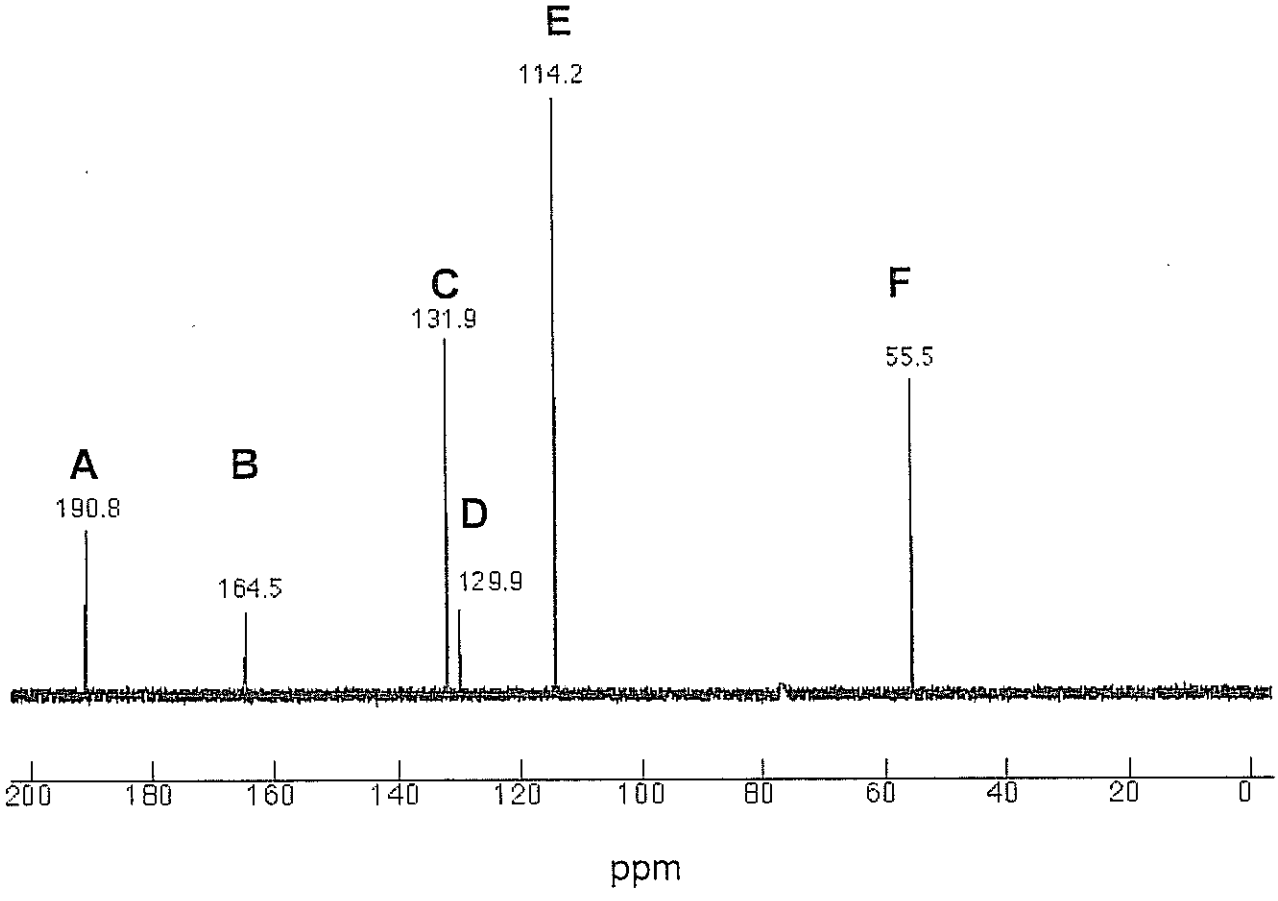




b. Draw again your suggestion for the unknown in the box and label the hydrogens A, B, C and D giving rise to the corresponding signals in the ^{1}H NMR spectrum on p. 10. Consider resonance in your assignments of B and C.

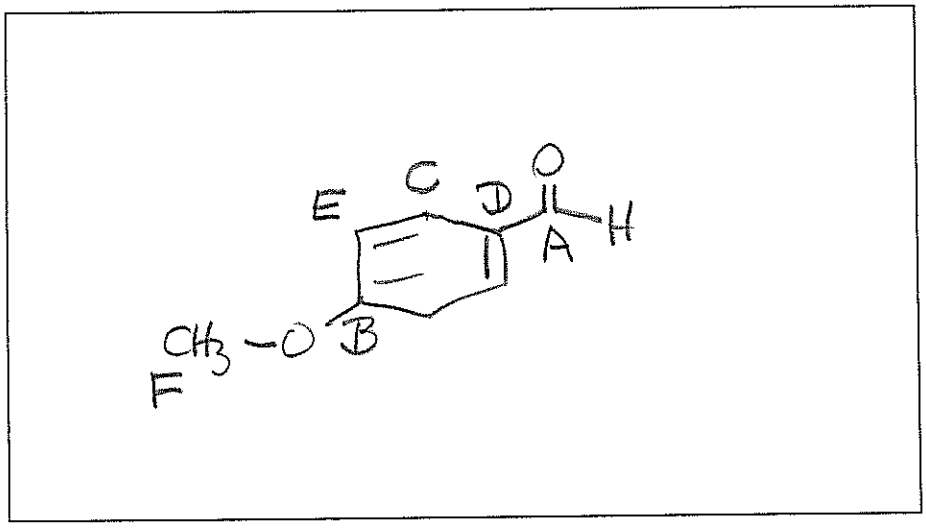


2. ^{13}C NMR Spectrum (these are six single lines).

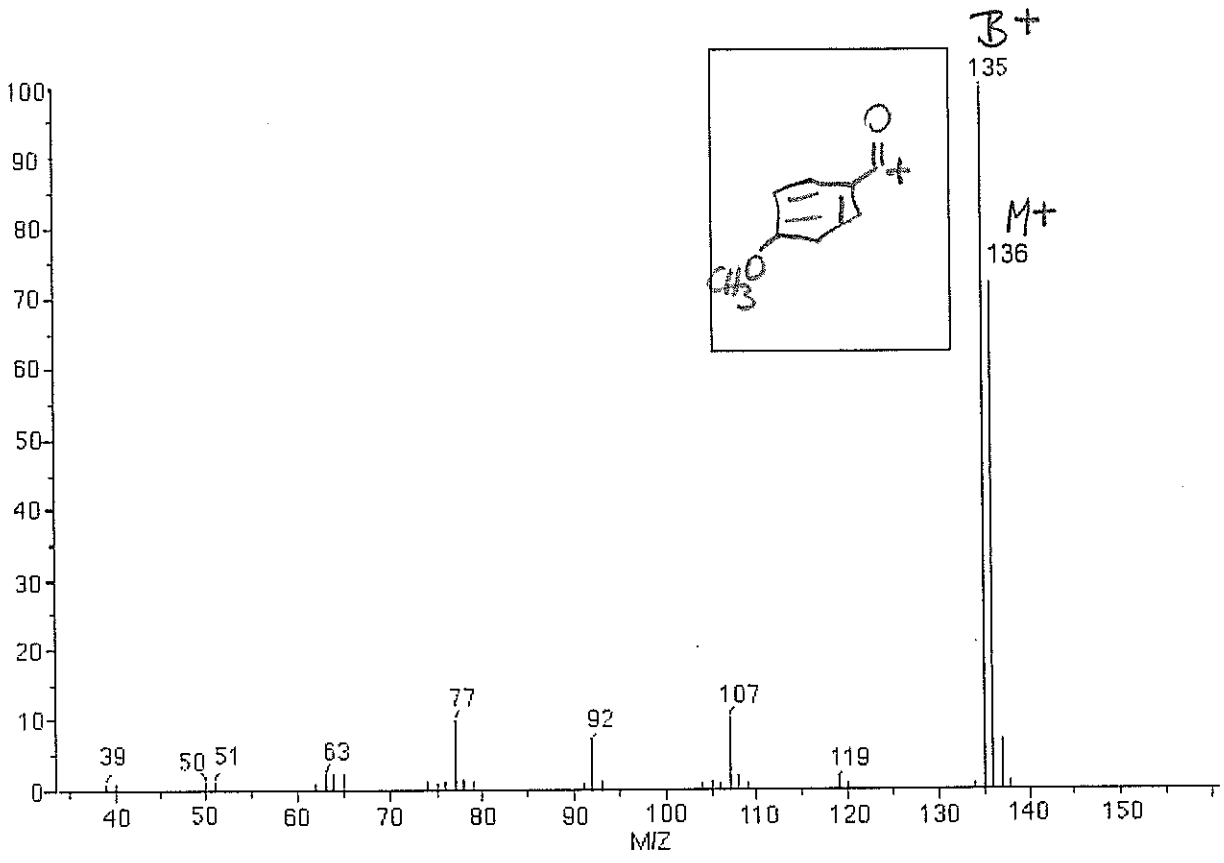


DEPT spectra (don't worry if you don't remember what that is) shows that the carbons giving rise to signals A, C, and E are attached to one hydrogen each. Signal F is due to a carbon with 3 attached hydrogens. Signals B and D are associated with carbons without any bound hydrogens.

Draw again your suggestion for the unknown in the box below and label the types of carbon atoms A–F giving rise to the corresponding signals in the ^{13}C NMR spectrum on p. 11. For the assignments of B versus D and C versus E, consider the effect of electronegativity of the attached atom and the effect of resonance, respectively.



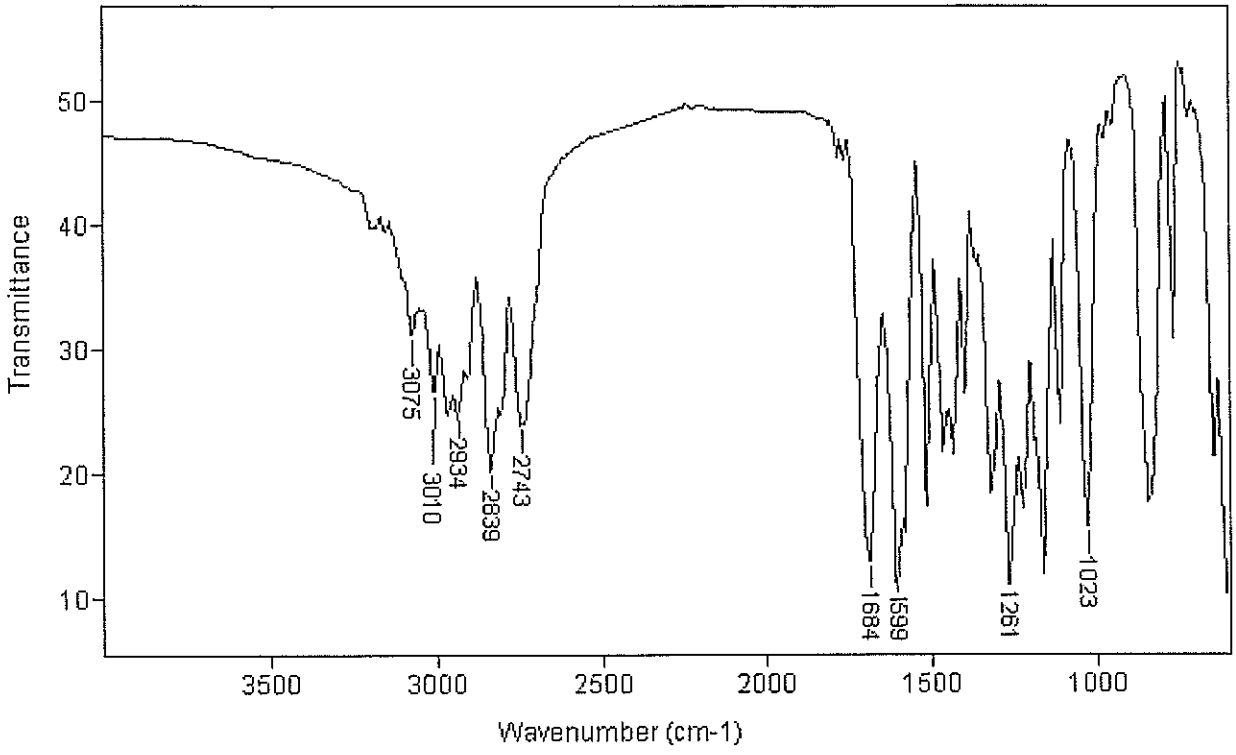
3. Mass spectrum
   Atomic weights of all the elements in the reaction on p. 9: H 1; C 12; N 14; O 16, Br 79 and 81 (1:1 isotope ratio). **Caution:** Not all of these elements are incorporated in the product.



a. Clearly mark on the spectrum the molecular ion as "M^{+}" and the base peak as "B^{+}".

b. In the box above the fragment ion *m/z* = 135, indicate the structure of this fragment.

4. IR Spectrum



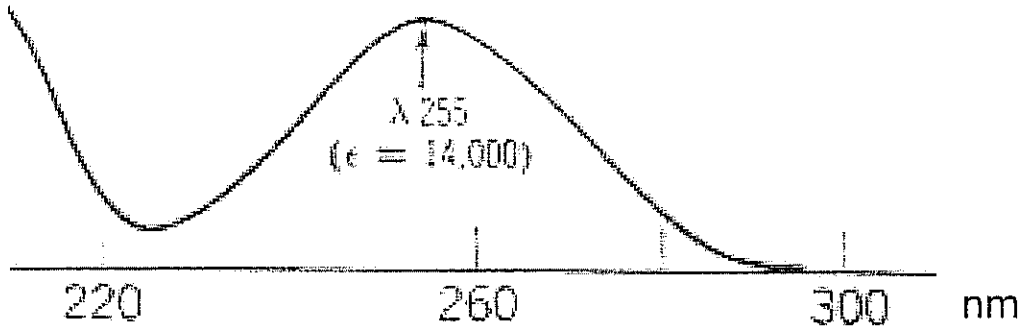
Confirm the presence or absence (circle one) of the following bonds. Enter an approximate expected stretching frequency in the box.

$\tilde{\nu}$ (C_{sp^2}–H) is: (present) absent at [3075 cm^{-1}]

$\tilde{\nu}$ (C_{sp^3}–H) is: (present) absent at [<3000 cm^{-1}]

$\tilde{\nu}$ (C=O) is: (present) absent at [1684 cm^{-1}]

5. UV spectrum



Place an X mark into the box next to the most accurate statement.

☐ The spectrum depicts a nonconjugated compound.

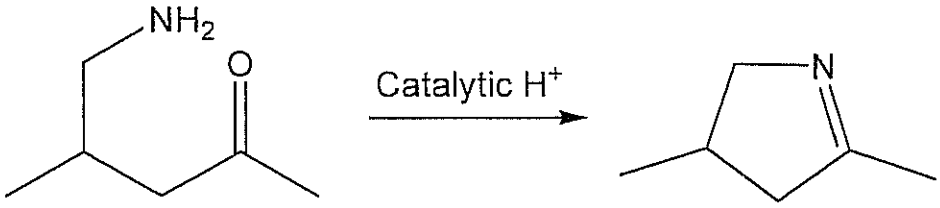
☐ The spectrum is that of a colored compound.

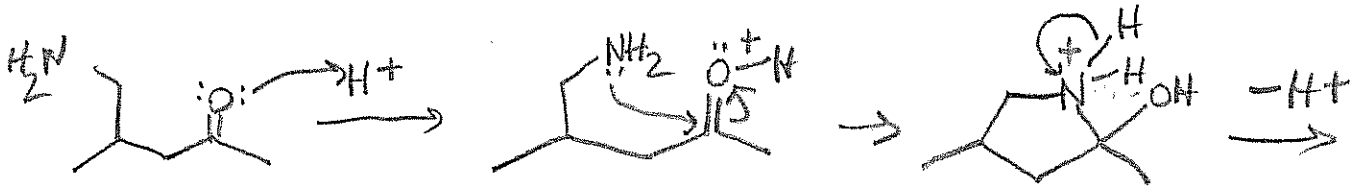
☒ The unknown is aromatic.

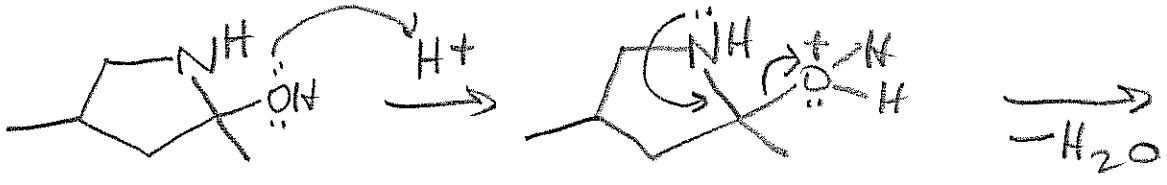
☐ The λ_{max} is at 300 nm.

V. [30 Points] Write detailed stepwise mechanisms for the following transformations. Use only structures and "arrow-pushing" techniques. Note: These are not synthetic problems. Do not add any reagents! What you see is what you have! Work from left to right in the following spaces. There is much more space than you will need.

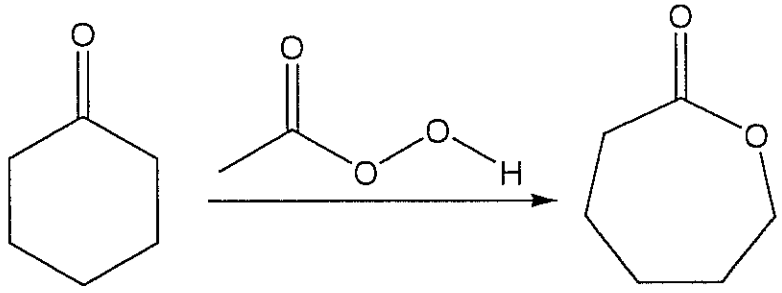
a.



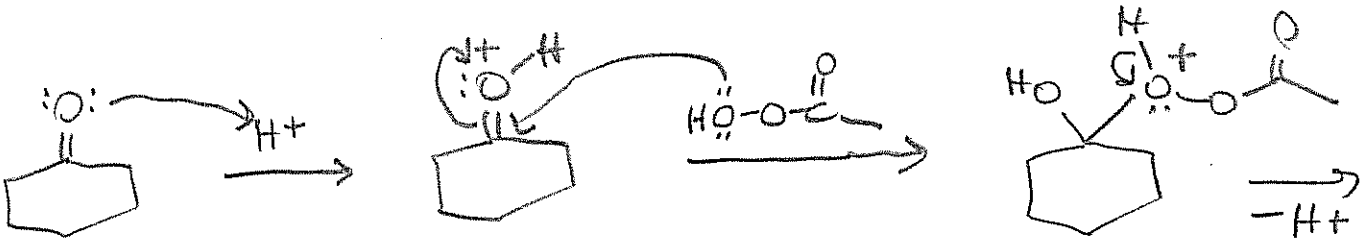


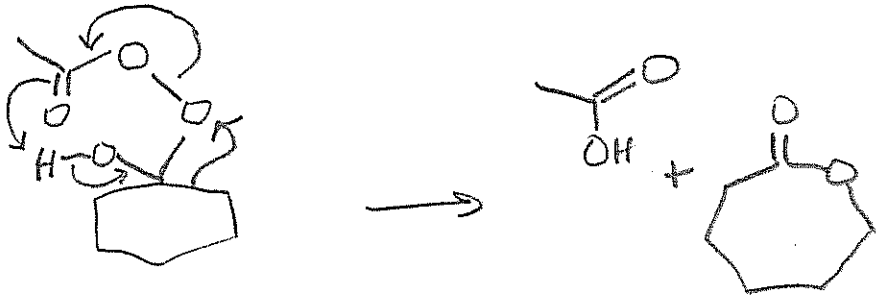


b.



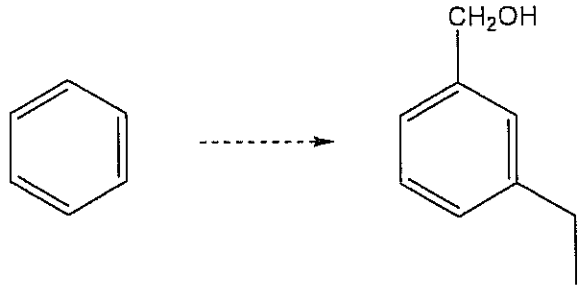
Work from left to right in the following spaces. There is much more space than you will need.



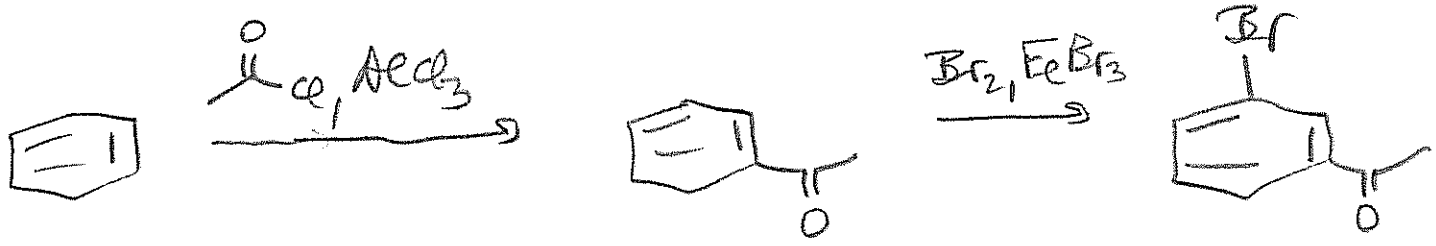


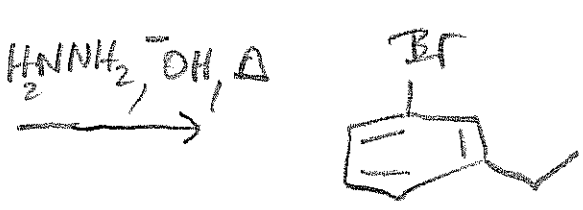
VI. [30 Points] Provide a reasonable synthetic route from starting material to product.
Note: Several steps are required, and there may be more than one solution to the problem.
Do not write mechanisms! Write out each step separately, including reagents and products.

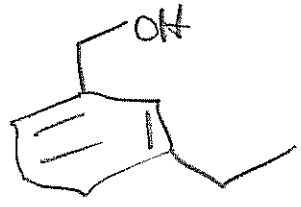
a.



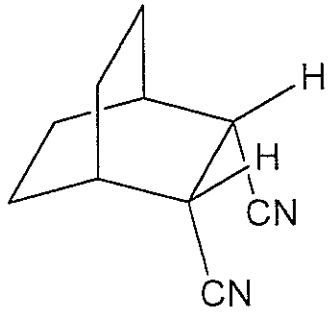
Caution: You cannot introduce the $-CH_2OH$ group directly. **Hint:** To do so, think alcohol synthesis.
Work from left to right in the following spaces. There is much more space than you will need.





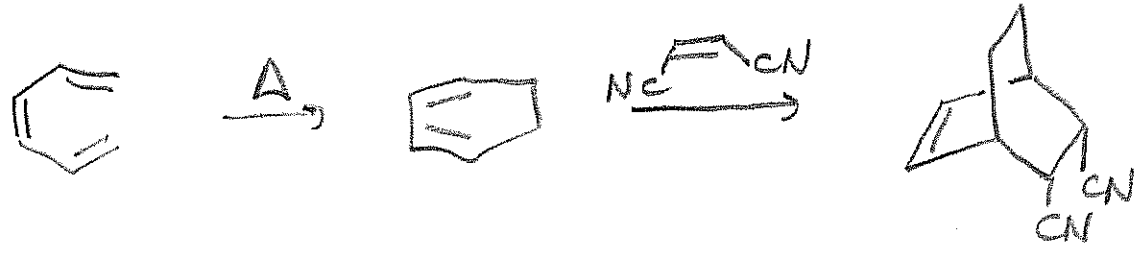


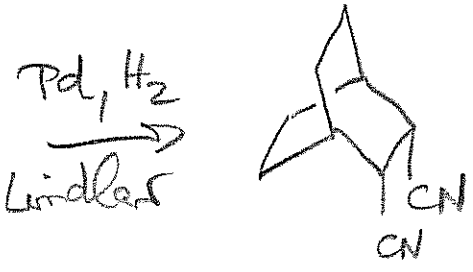
b. Synthesize compound **A** from any **acyclic** materials containing six carbons or less.
Hint: Think Diels-Alder reaction. **Caution:** Work backwards. What compound must precede **A** for a retro-Diels-Alder step?



A

Work from left to right in the following spaces. There is much more space than you will need.





VII. [20 Points] Place an X mark in the box next to the most accurate statement.

a. The electron withdrawing power of benzene substituents **1–4** decreases and their electron donating power increases in the order

$-CH_3$	$-OCH_3$	$-F$	$-NO_2$
1	**2**	**3**	**4**

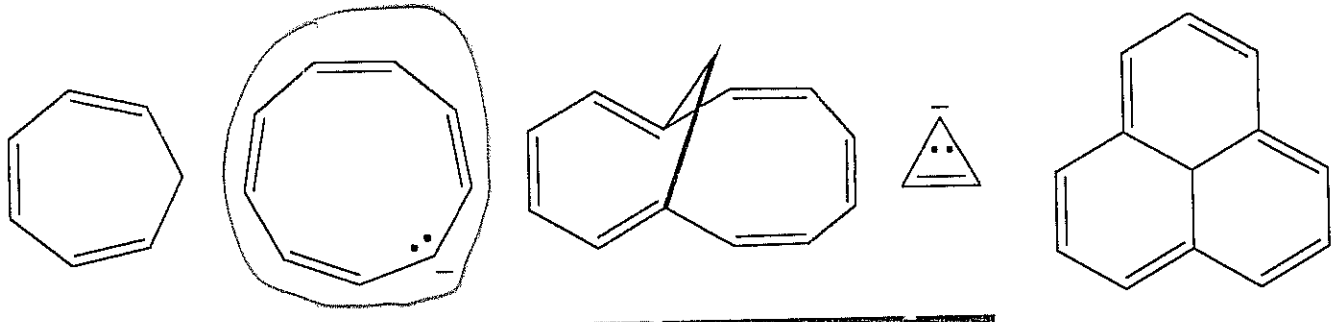
☐ **1, 2, 3, 4**

☒ **4, 3, 1, 2**

☐ **4, 2, 3, 1**

☐ **4, 1, 2, 3**

b. Circle the compounds which are aromatic



♫ The End ♫