Name_____

PID_____

CHEMISTRY 252

Exam 1 – 100 pts.

Section 703 – Grand Rapids

27 July 2006

- Make sure you have all 12 exam pages
- You will have 90 minutes to complete the 5 questions
- Please sign your name at the bottom of this page.
- Try to make your answers as **clear** as possible. You don't need to be an artist, but if an answer is ambiguous it may be marked incorrect.
- Keep all answers inside the designated boxes.
- Read the directions, and don't be distracted by the large molecules.
- **Good luck!**

By signing this test, I certify that this is my own work and that my work is in accordance with MSU's policy on academic honesty, as stated in the Academic Freedom Report.

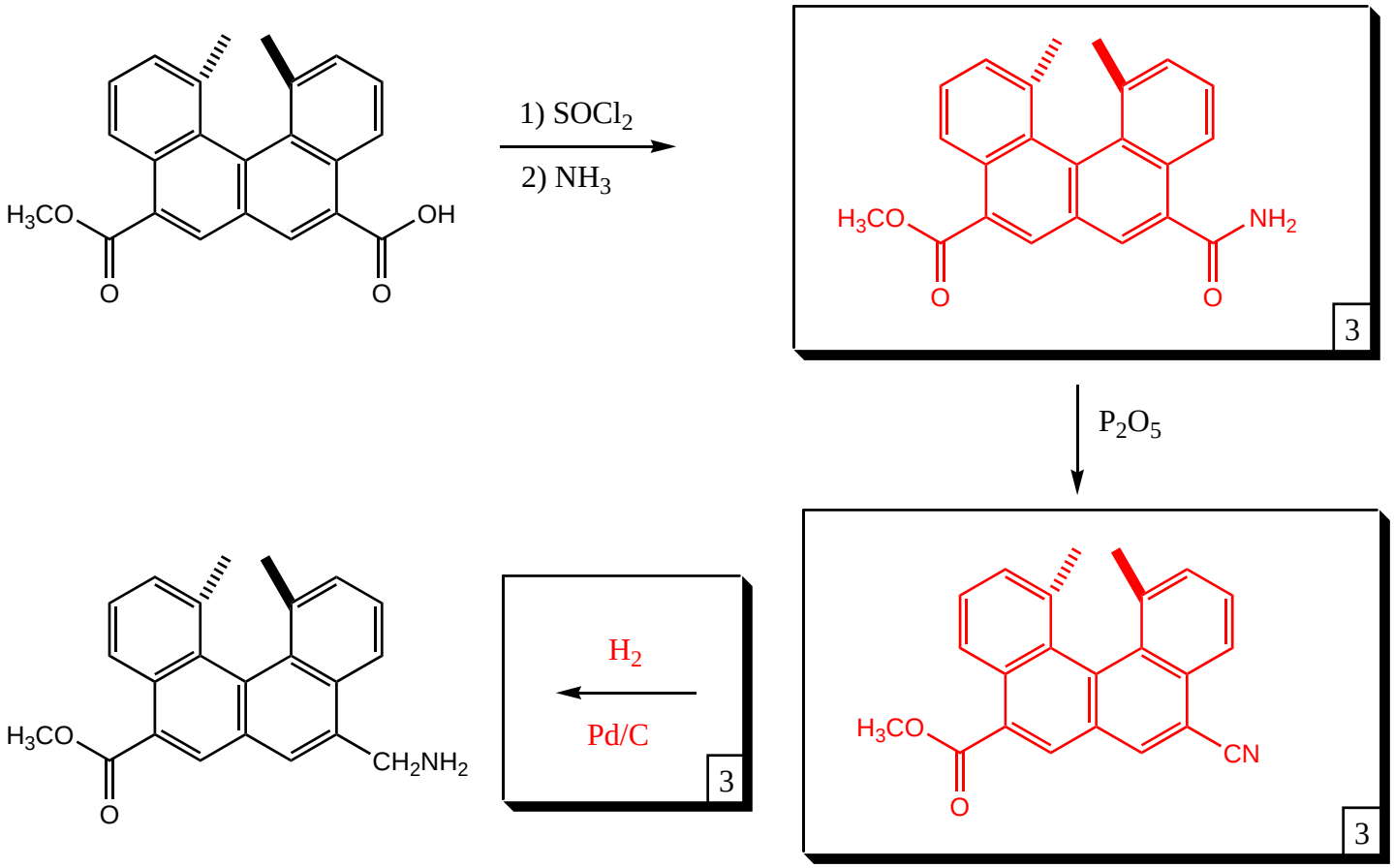
X_____

I		24
II		22
III		20
IV		10
V		24
Total		100

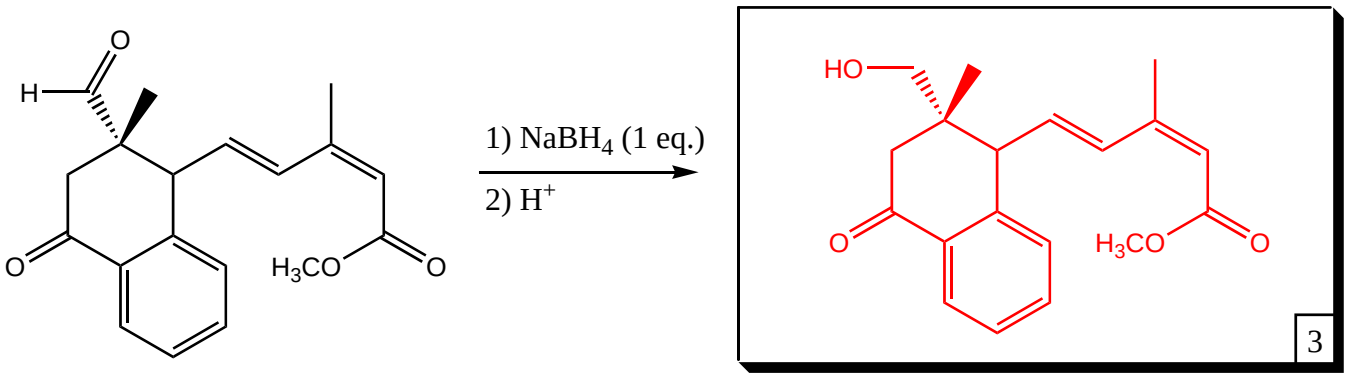
I. (24 pts.)

Complete the following reactions.

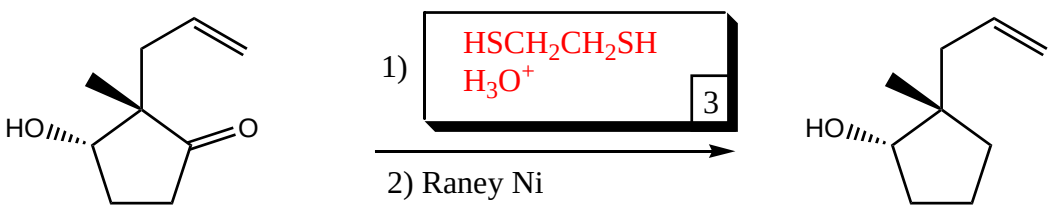
a) Synthesis of DNA-like folding molecules (*Bull. Chem. Soc. Jpn.* **2006**, *79*(2), 317-332).



b) Synthesis of abscisic acid analogues to regulate aspects of plant growth and development (*Org. Biomol. Chem.* **2006**, *4*, 1400-1412).

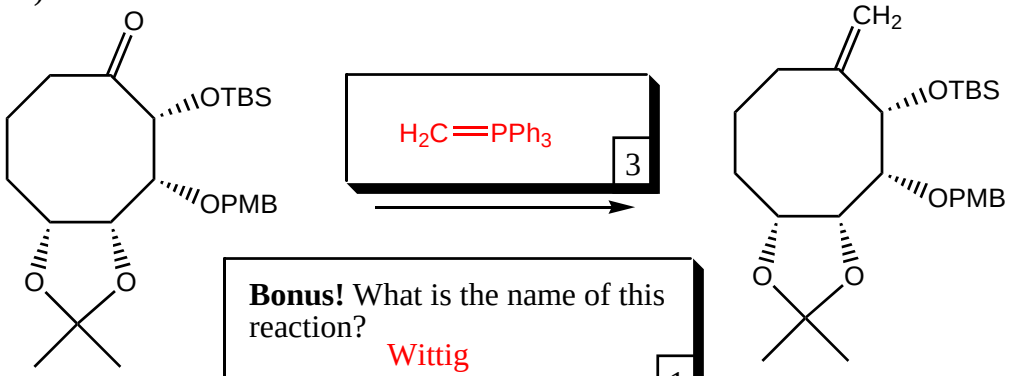


c) New techniques for synthesis of clavirolides, possible anti-cancer pharmaceuticals (*Tetrahedron Lett.* **2005**, *46*, 8431-8434).



I. continued

d) Synthetic route to new glycosidase inhibitors (anti-viral and anti-cancer) (*J. Org. Chem.* **2006**, *71*(12), 4353-4363).

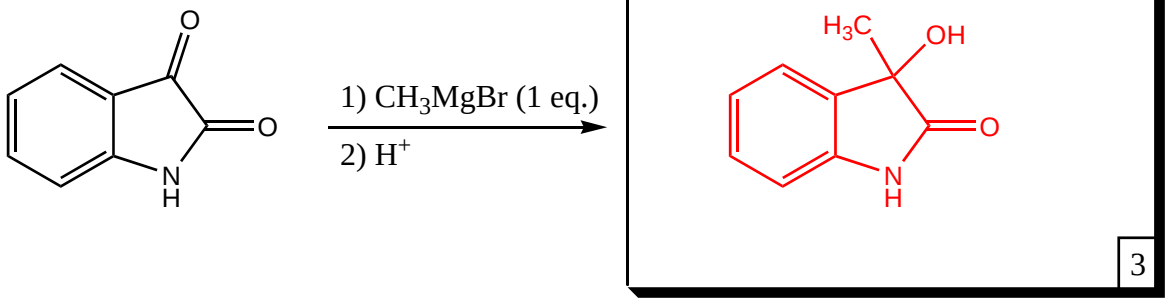


Bonus! What is the name of this reaction?

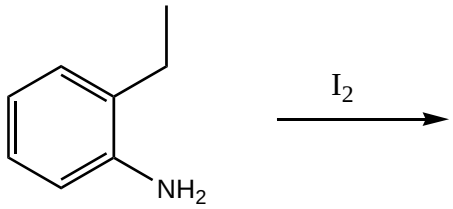
Wittig

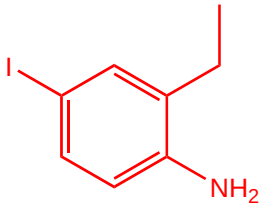
1

e) Synthesis of HIV-1 protease inhibitors for antiretroviral AIDS therapy (*Bioorg. Med. Chem. Lett.* **2006**, *16*, 1869-1873).



f) Synthesis of some potential organic semiconductors (*J. Org. Chem.* **2005**, *70*, 3396-3424).





This product shows the following ^{1}H-NMR peaks:
8.26 ppm (doublet, 1H)
8.14 ppm (doublet, 1H)
8.07 ppm (singlet, 1H)
2.95 ppm (quartet, 2H)
1.34 ppm (triplet, 3H)

Hint: the aromatic hydrogens show only *ortho*-coupling (not *meta*- or *para*-).

3

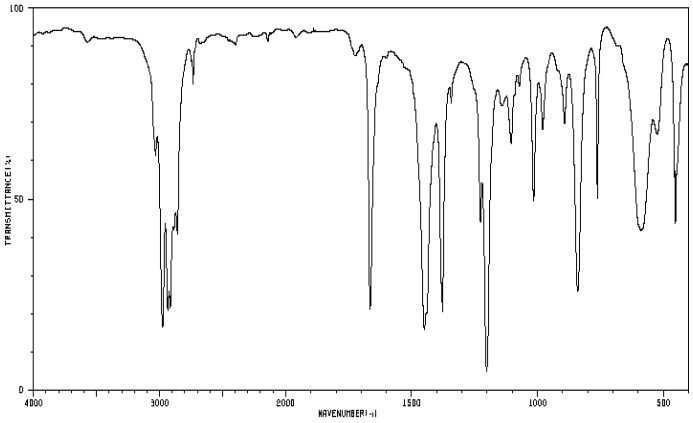
II. (22 pts.)

a) The following spectra were taken of molecule C_5H_9X, where X is a halogen.

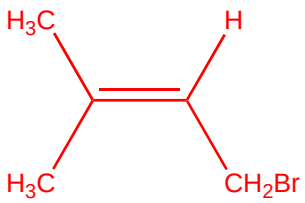
Which halogen is X?

Bromine

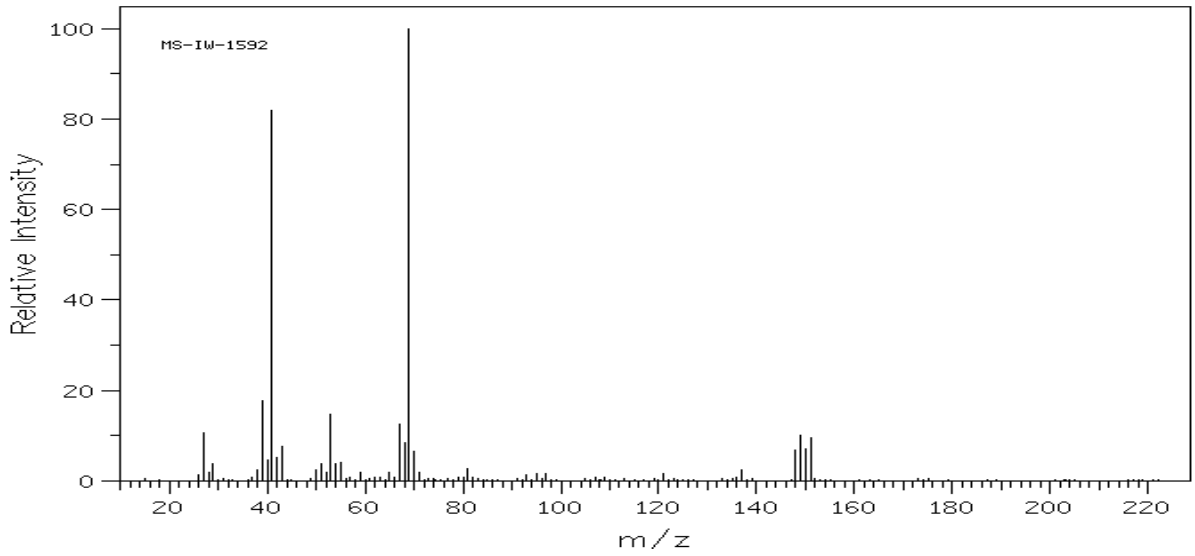
2

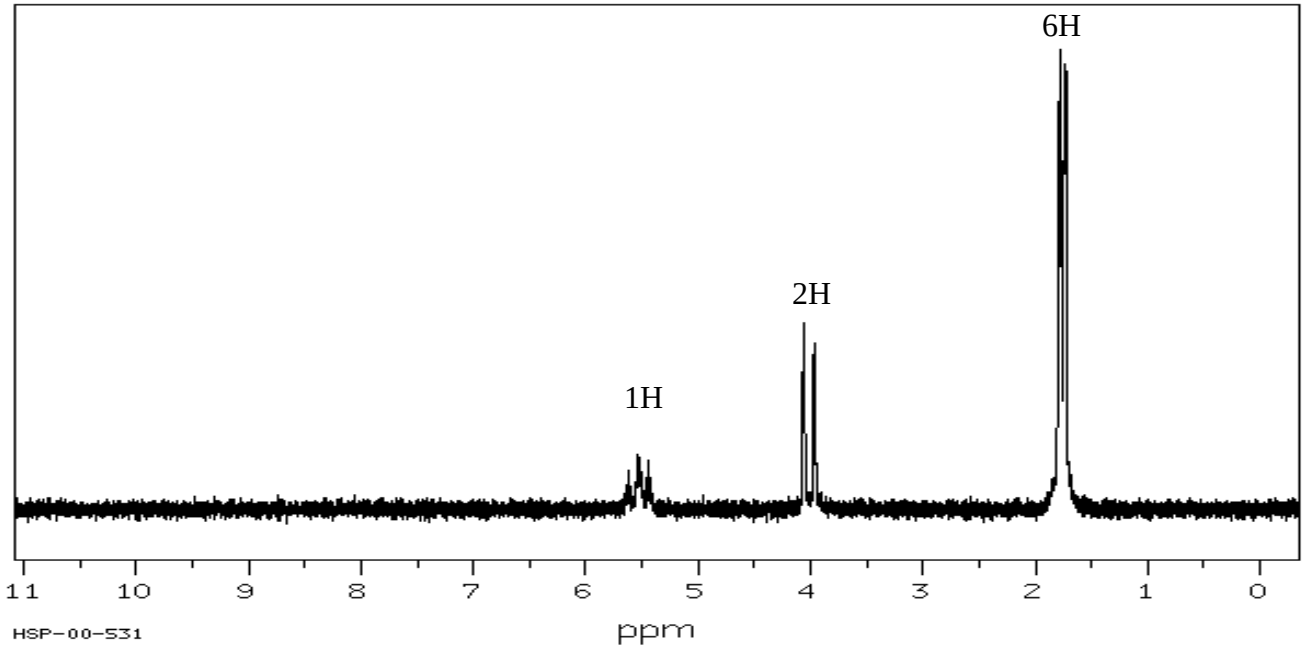


Structure of molecule C_5H_9X:

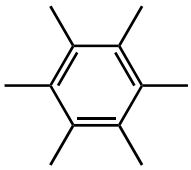


5

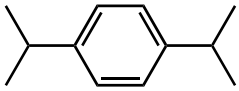




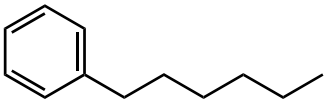
b) Use ^{1}H-NMR to differentiate among the following $C_{12}H_{18}$ isomers.



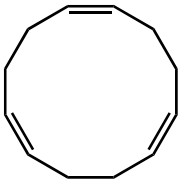
A



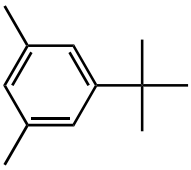
B



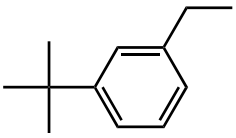
C



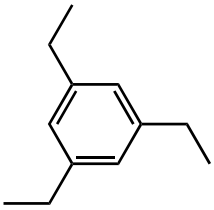
D



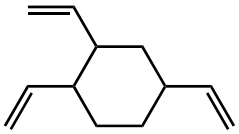
E



F



G

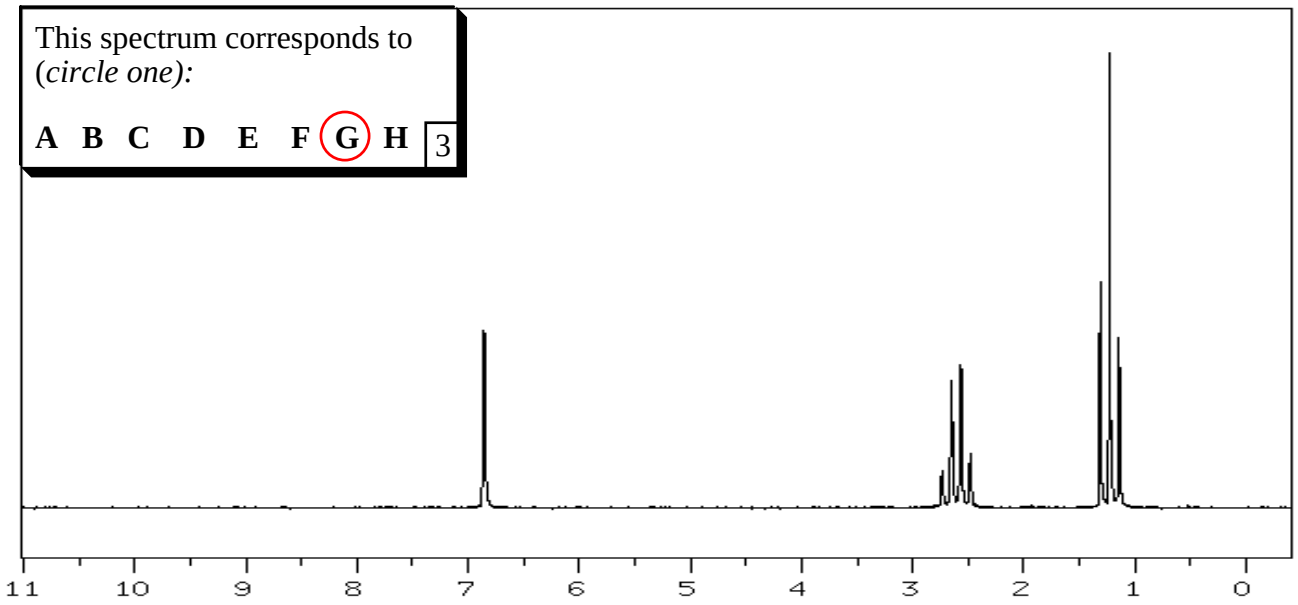


H

i)

This spectrum corresponds to (*circle one):*

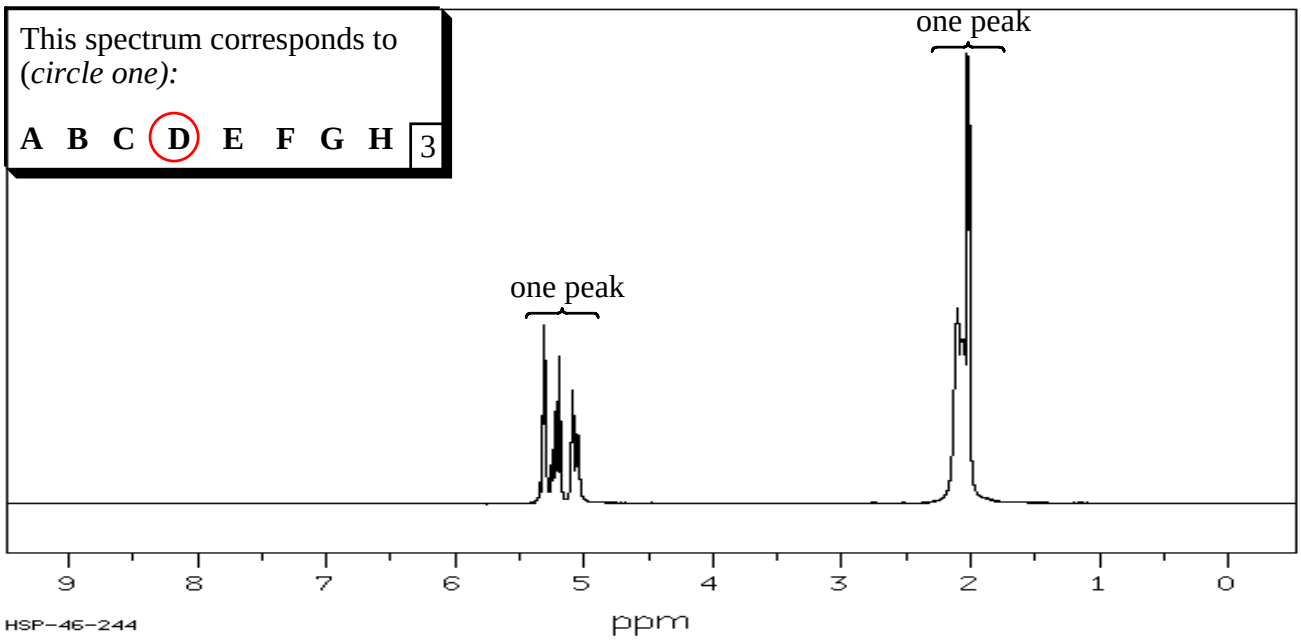
A B C D E F (G) H 3



ii)

This spectrum corresponds to (*circle one):*

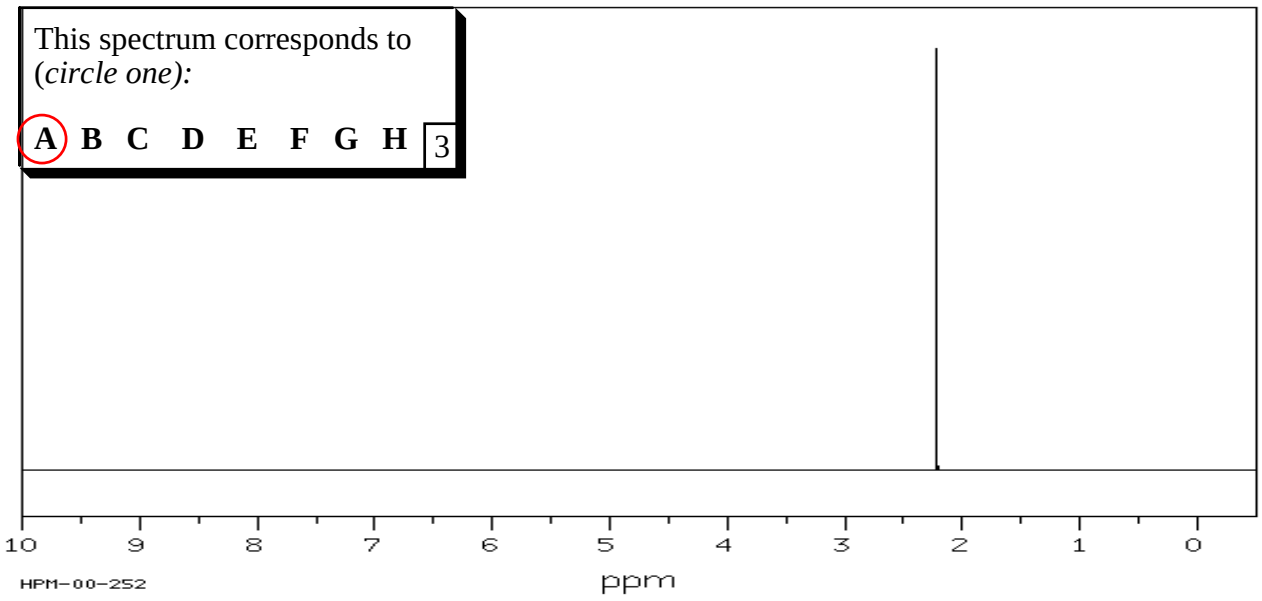
A B C (D) E F G H 3



iii)

This spectrum corresponds to (*circle one):*

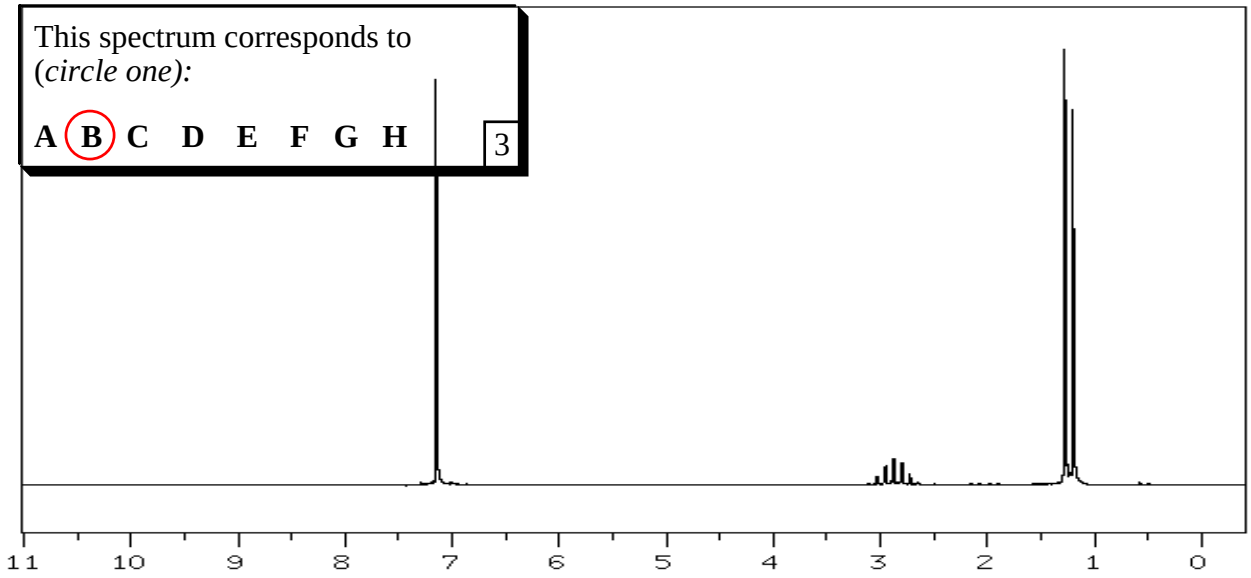
(A) **B** **C** **D** **E** **F** **G** **H** 3



iv)

This spectrum corresponds to (*circle one):*

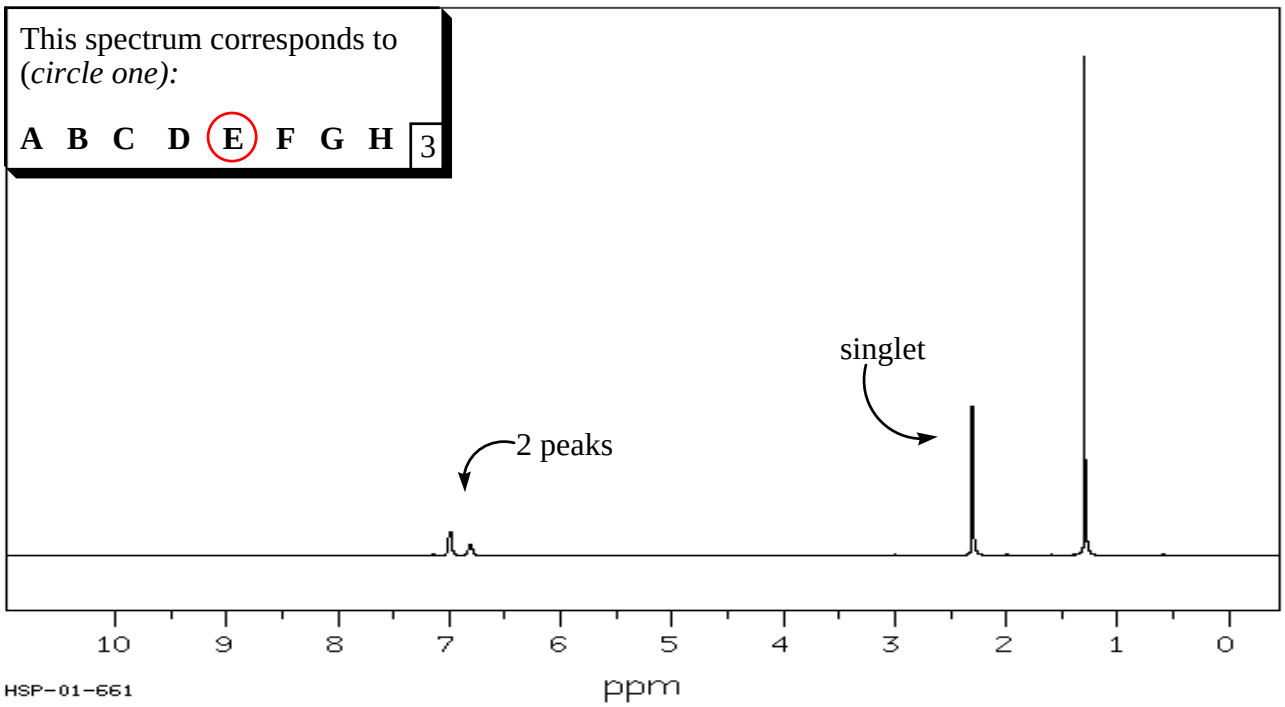
A **(B)** **C** **D** **E** **F** **G** **H** 3



v)

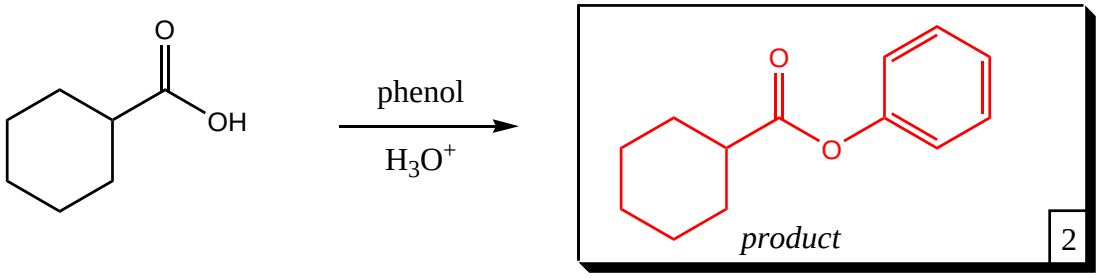
This spectrum corresponds to (*circle one):*

A **B** **C** **D** **(E)** **F** **G** **H** 3

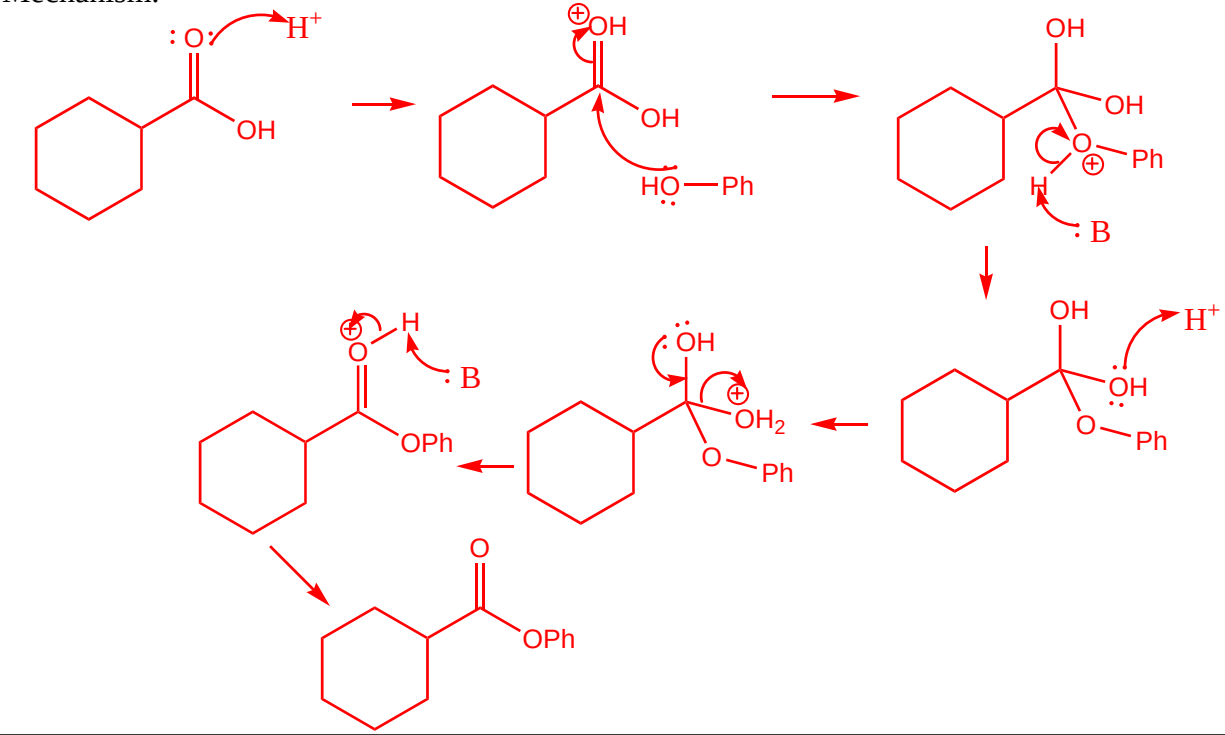


III. (20 pts.)
Provide mechanisms and/or products for the following reactions:

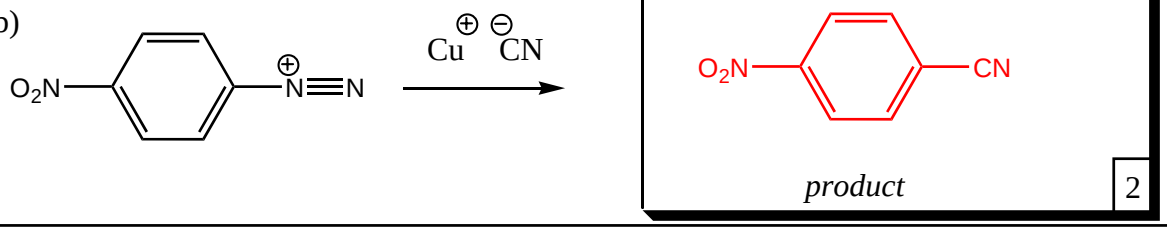
a)



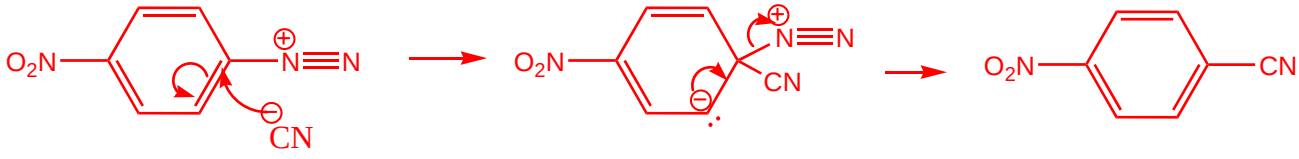
Mechanism:



b)

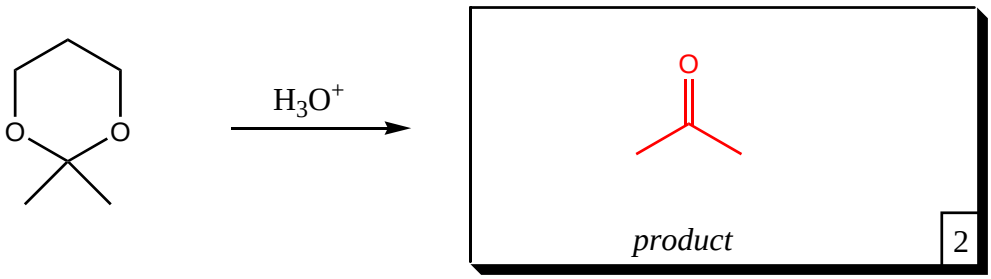


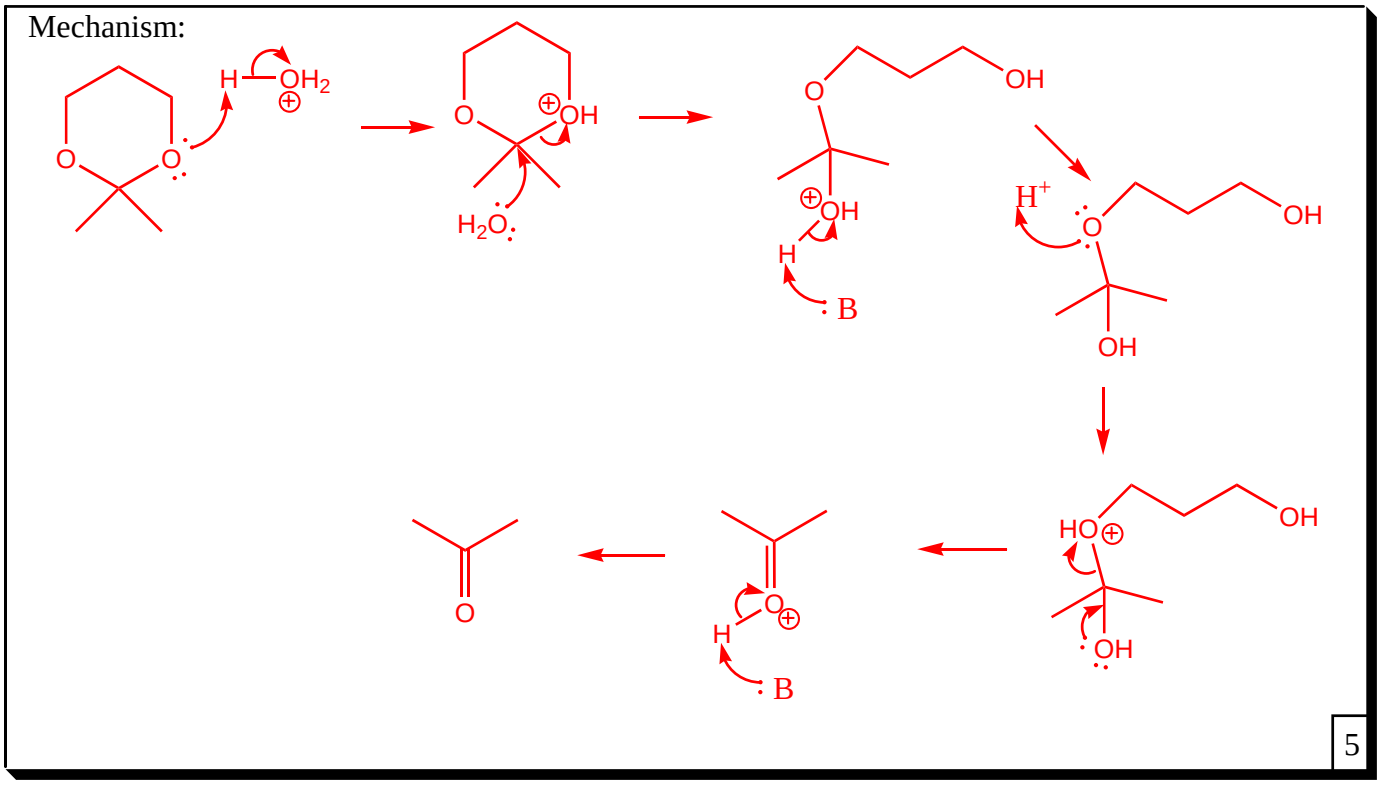
Mechanism:



III. (continued)

c)



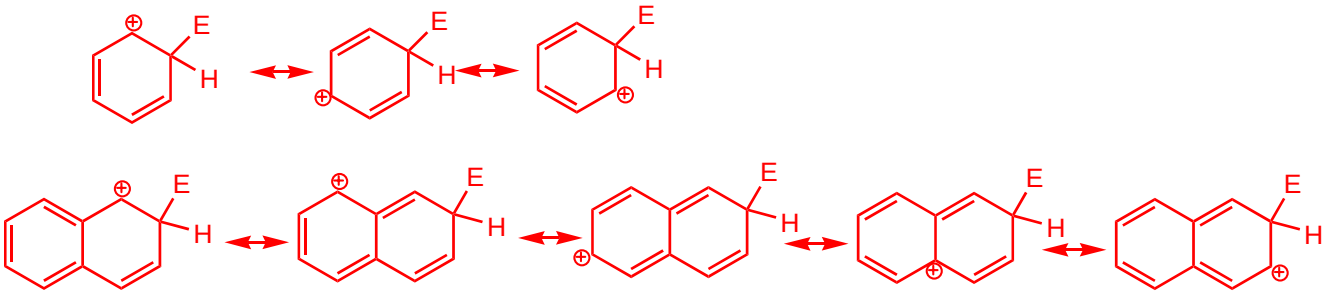


d) If you have extra time and are bored, draw me a nice picture in this extra space. I'll be especially impressed if it includes an animal in the *Mustelidae* family. I suppose you could also use the space for scrap paper to help with your exam, but what fun is that? (no points)

IV. (10 pts.)

a) Using words and resonance structures, explain why naphthalene is more reactive toward electrophilic substitution than benzene.

Consider the carbocation intermediate for each compound undergoing electrophilic substitution, where E is some electrophile:

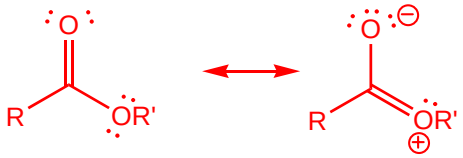


The additional resonance forms of the naphthalene intermediate show that its carbocation is more stable than the benzene cation. Therefore, naphthalene should be more reactive toward electrophilic substitution. Also, the additional 4 π electons in naphthalene make it more nucleophilic than benzene.

5

b) Using words and structures, explain why ketones are more reactive than esters.

Esters show resonance in the following way:

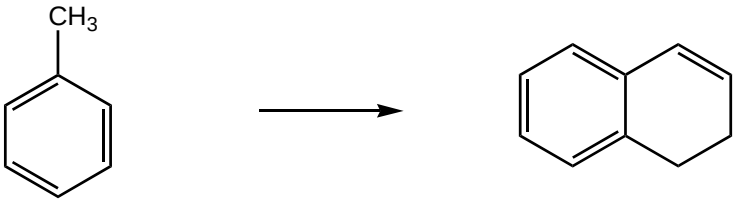


Because of the electron-donating ability of the ester oxygen, the carbonyl carbon is not as electrophilic as in a ketone, where no such resonance is possible. Therefore, the more electrophilic ketone will more readily react with a nucleophile.

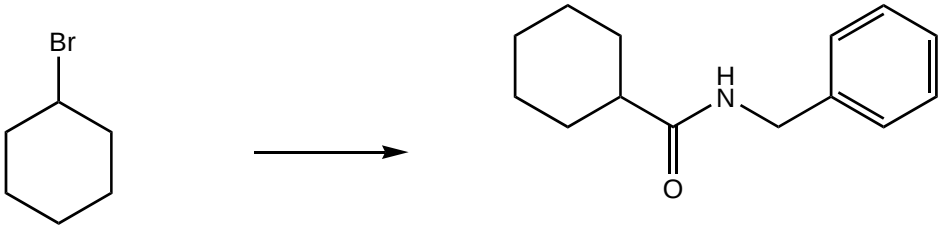
5

V. Synthesis (24 pts.)
Pick **three** of the following transformations and devise a synthesis for each. You do not get extra credit for completing more than 3 syntheses.

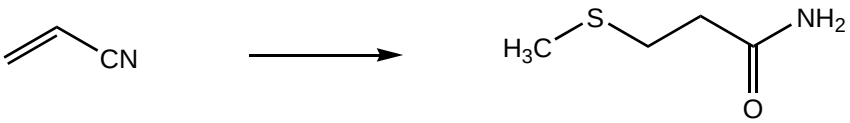
A



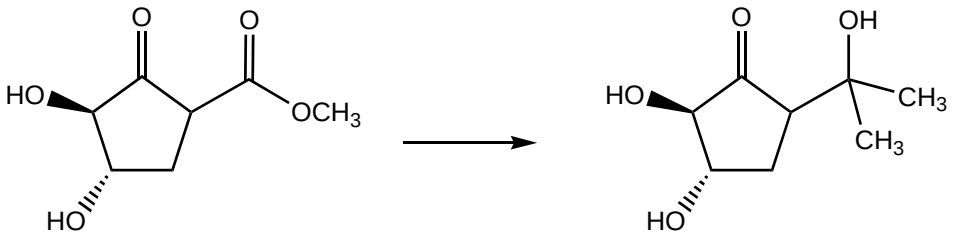
B



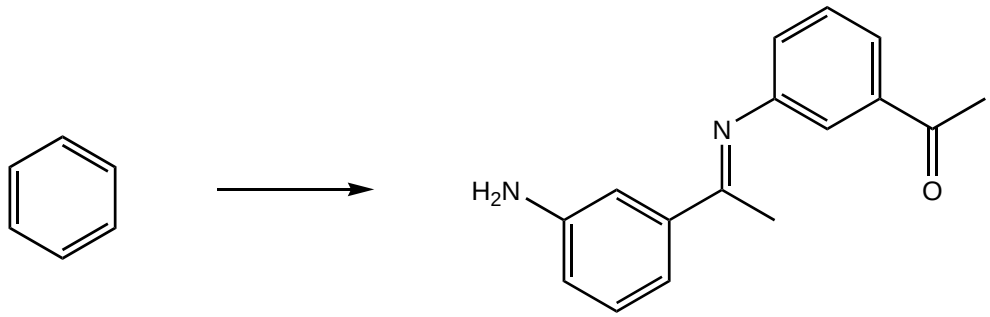
C



D

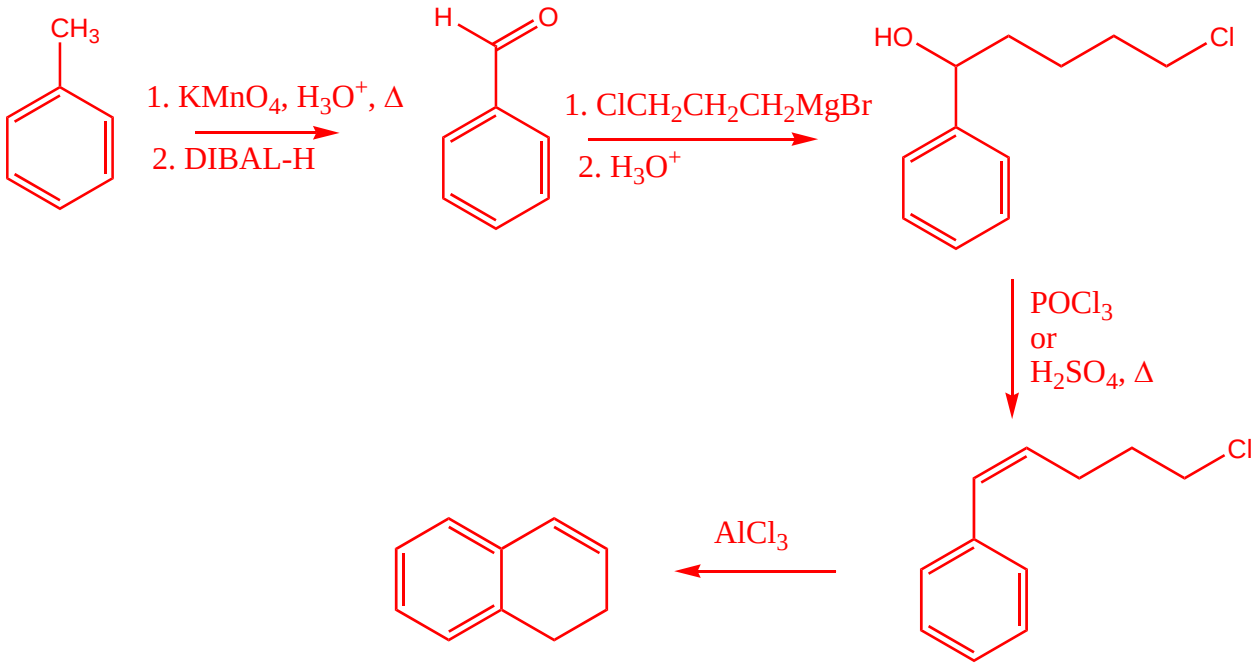


E



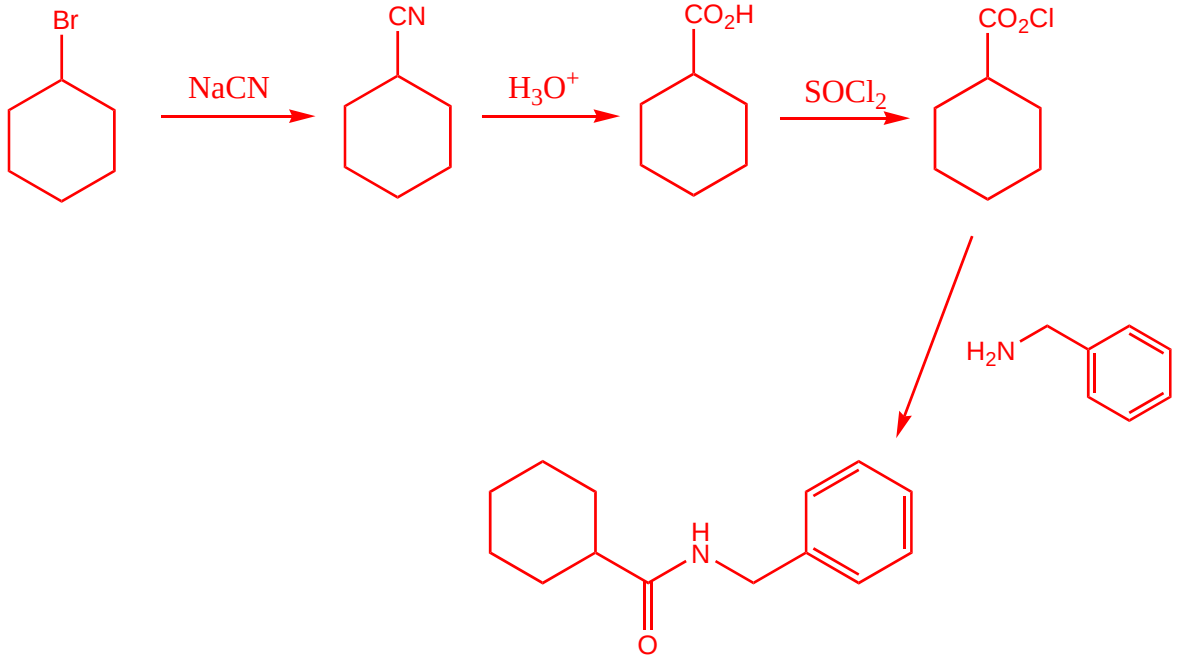
V. (continued)

Synthesis 1. (circle your choice) **(A)** **B** **C** **D** **E**



8

Synthesis 2. (circle your choice) **A** **(B)** **C** **D** **E**



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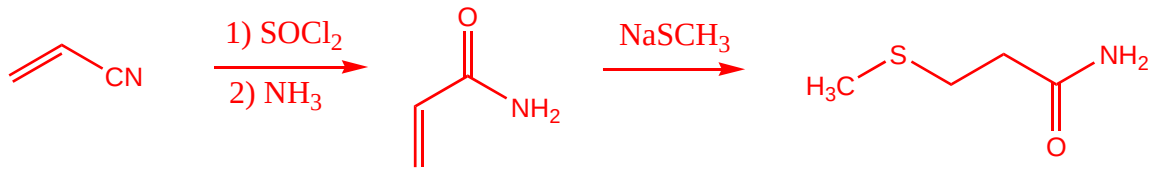
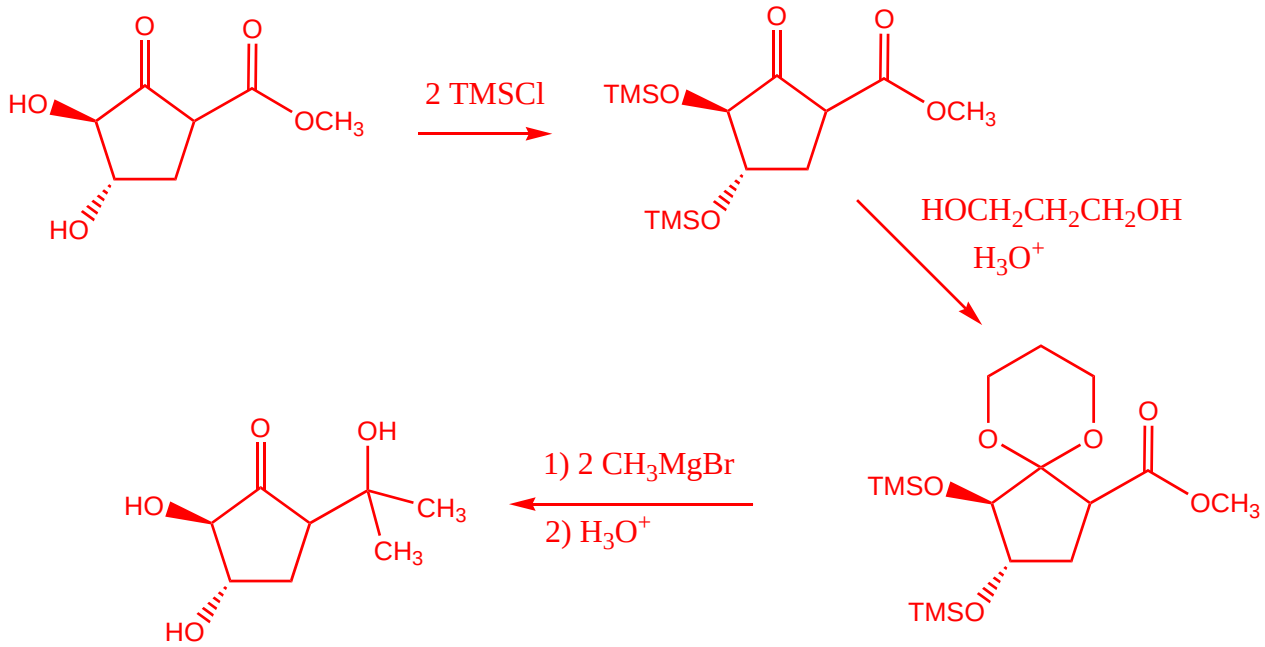
V. (continued)

Synthesis 1. (circle your choice) **A** **B** **(C)** **D** **E**



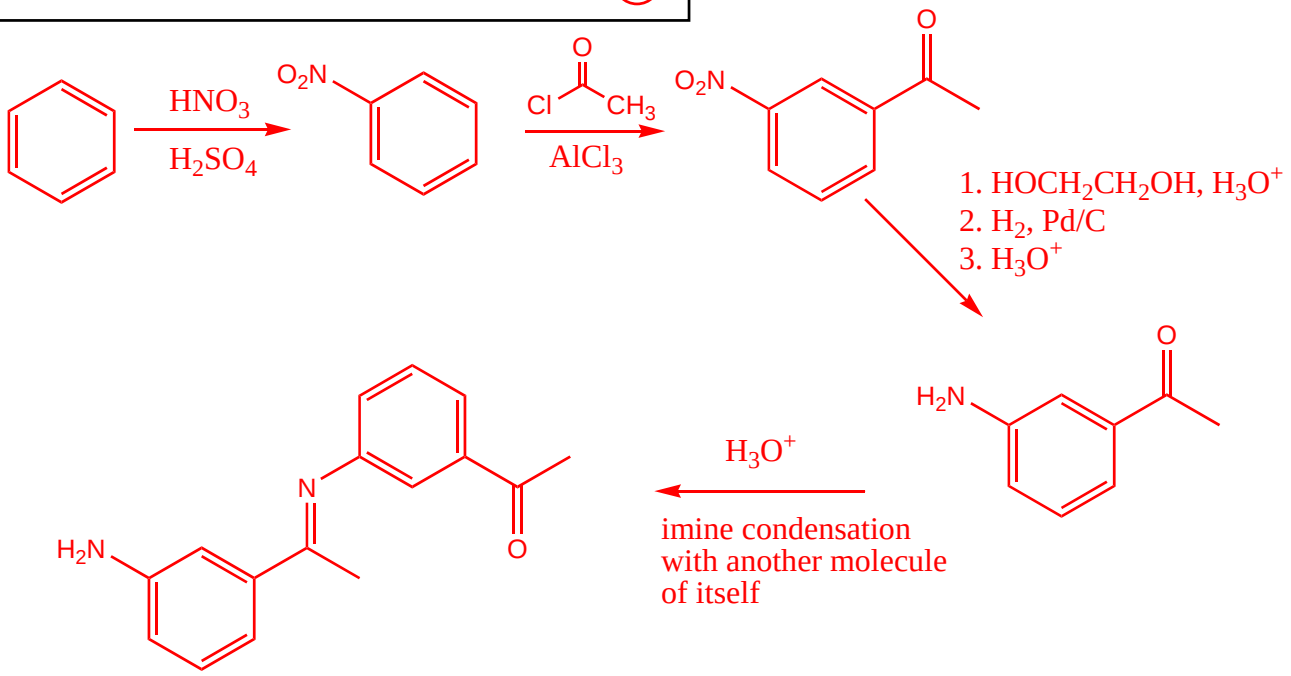
8

Synthesis 2. (circle your choice) **A** **B** **C** **(D)** **E**



8

Synthesis 3. (circle your choice) **A B C D (E)**

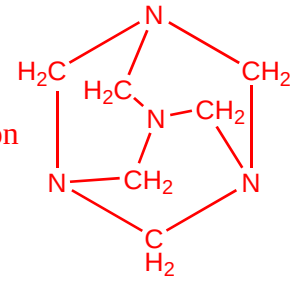


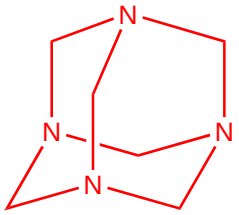
8

Bonus!

1. Molecule $C_6H_{12}N_4$ has only one peak in its ^{1}H-NMR spectrum (4.72 ppm, singlet) and only one peak in its ^{13}C-NMR spectrum (74.84 ppm). What is its structure?

2-D representation





structure of $C_6H_{12}N_4$

2

2. Which Wu-Tang member recorded the song "Street Chemistry" on his 2001 album, *Bulletproof Wallets*?

Ghostface Killah

1