

CHM 2120 B
Final Exam
December 16, 2015

Professor: Julian Chan

Time: 3 hours

First name: _____ Last name: _____

Student number: _____ Seat number: _____

Notes:

This is a closed-book exam.

The last 3 pages contain a pK_a table, a table of IR stretching frequencies, a table of 1H NMR chemical shifts, and a periodic table.

Calculators are not permitted. Molecular models are permitted, but they cannot be shared.

Total number of pages: 14

Approximate number of marks: 134 (the marks are given as a guide and are subject to change)

Cellular phones, unauthorized electronic devices or course notes (unless an open-book exam) are not allowed during this exam. Phones and devices must be turned off and put away in your bag. Do not keep them in your possession, such as in your pockets. If caught with such a device or document, the following may occur: you will be asked to leave immediately the exam and academic fraud allegations will be filed which may result in you obtaining a 0 (zero) for the exam.

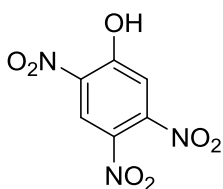
By signing below, you acknowledge that you have ensured that you are complying with the above statement.

Signature: _____

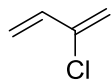
1. a) Draw the structure of *p*-toluenesulfonic acid (1 point)

b) Draw the structure of methyl trifluoromethanesulfonate (1 point)

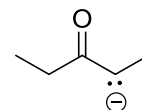
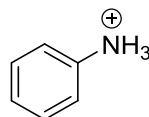
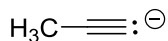
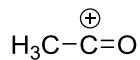
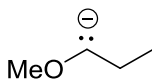
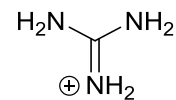
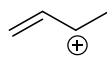
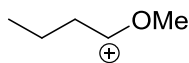
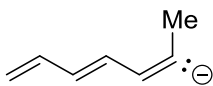
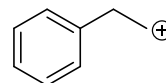
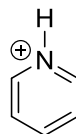
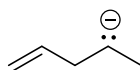
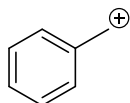
c) Name the following compound. (1 point)



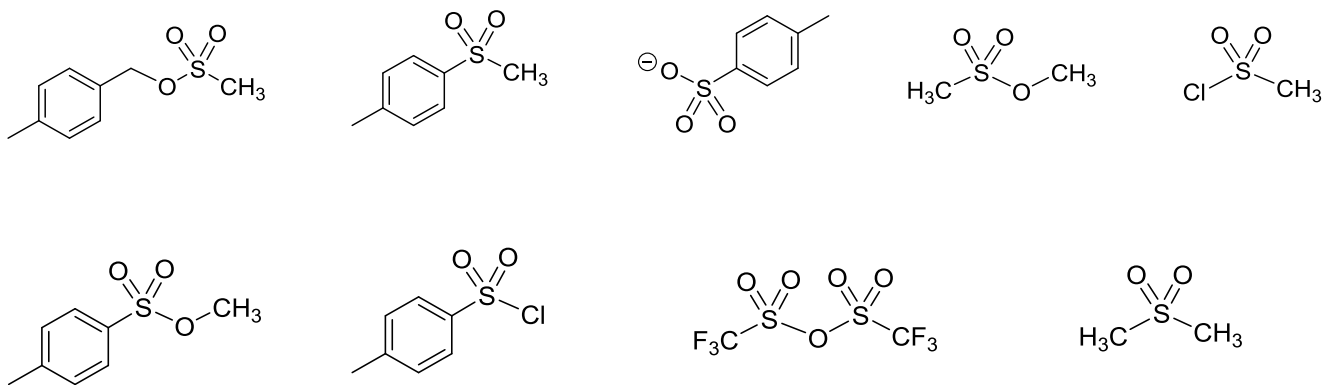
d) Name the following compound. (1 point)



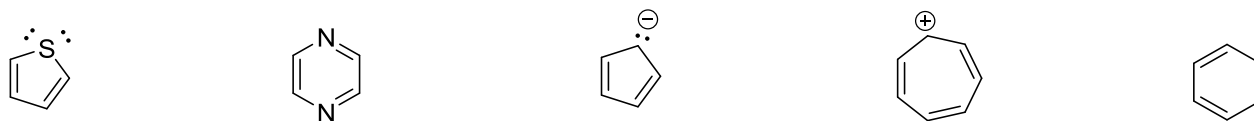
2. For each anion/cation, indicate if the charge can be delocalized and stabilized by resonance. If it can, write “Yes” below the structure; if not, write “No” below the structure. (14 points)



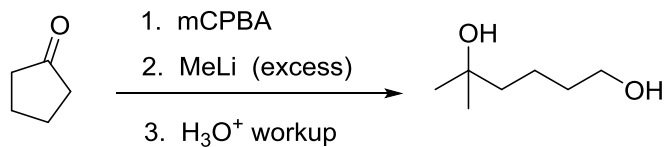
3. For each structure, circle the leaving group (LG). The LG can be part of the structure or the entire structure. If the structure is not a LG or does not contain a LG, write “**No LG**” below it. **(9 points)**



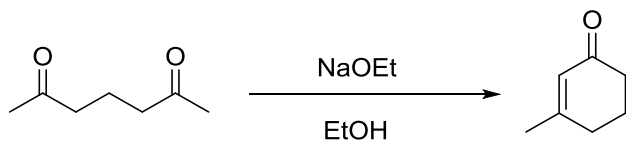
4. Indicate whether each of the following is: aromatic, anti-aromatic, or non-aromatic. **(5 points)**



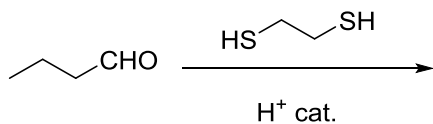
5. Give a mechanism for every step in the following reaction sequence: **(9 points)**



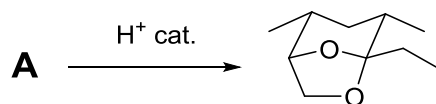
6. Provide a mechanism for the following reaction: (5 points)



7. Provide a mechanism and product for the following reaction: (7 points)

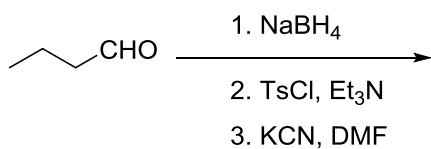


8. Draw the structure of Compound A: (2 points)

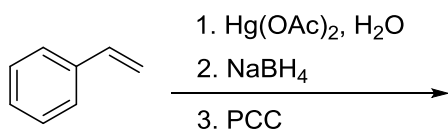


9. Give the missing reagents or the major product of the following reactions: (10 points – 2 each)

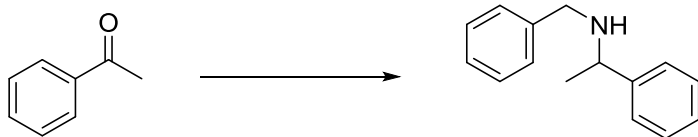
a.



b.



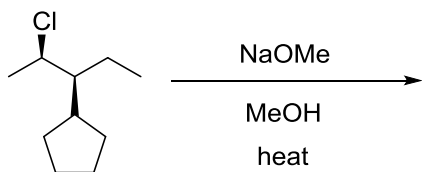
c.



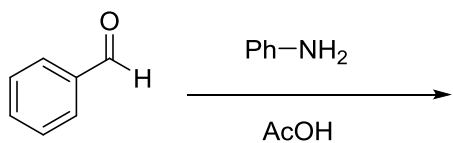
d.



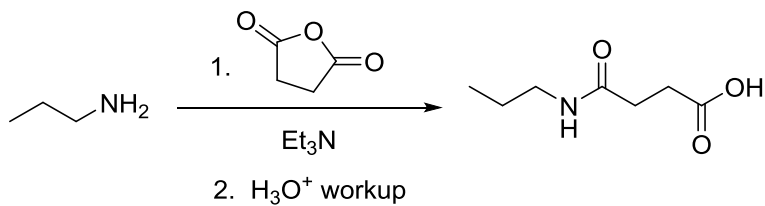
e.



10. Provide a mechanism and product for the following reaction: **(6 points)**

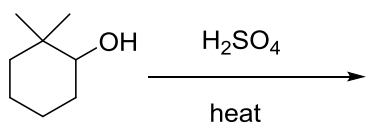


11. Provide a mechanism for the following reaction: **(4 points)**

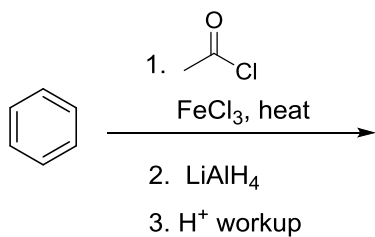


12. Give the missing reagents or the major product of the following reactions: (10 points – 2 each)

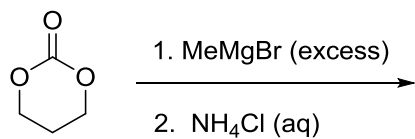
a.



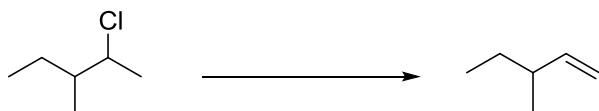
b.



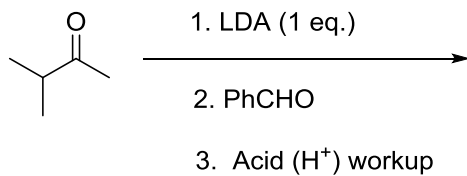
c.



d.



e.

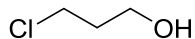


13. How many unique proton signals would be expected in the ^1H NMR spectrum of the following molecules? (3 points)

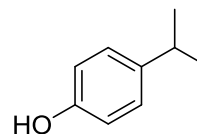
a.



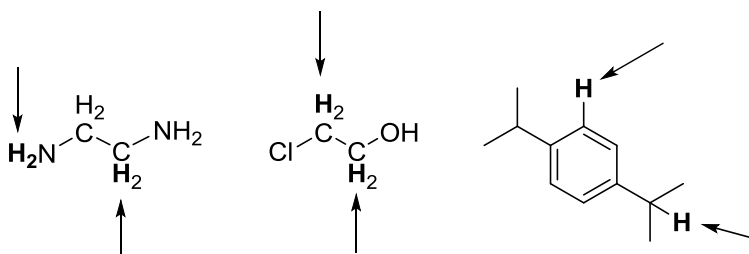
b.



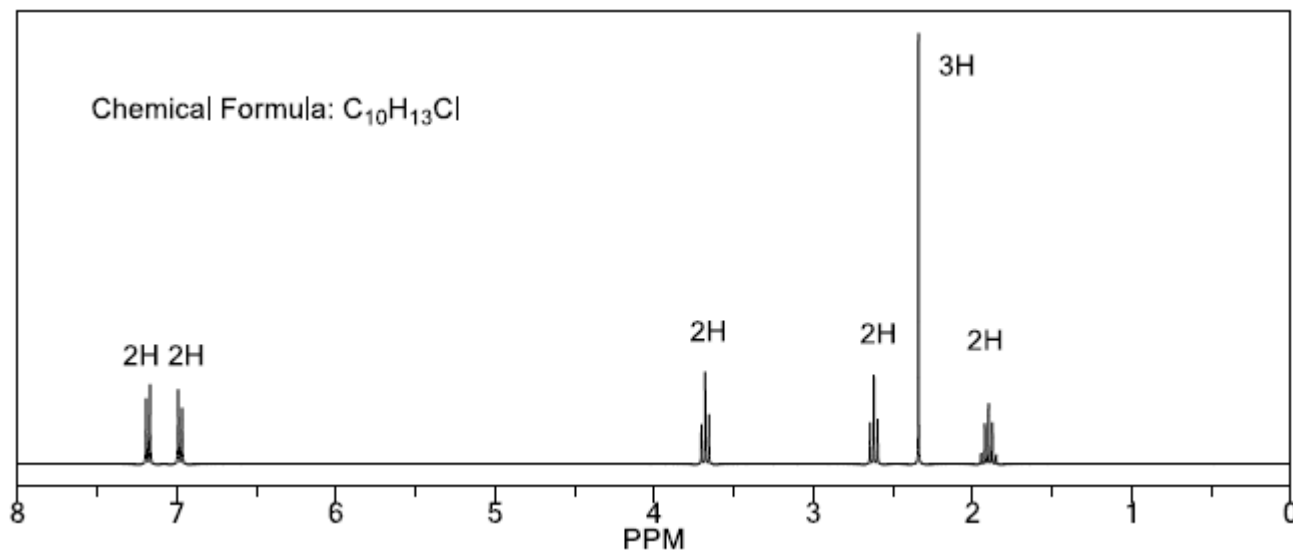
c.



14. Indicate **s**, **d**, **t**, **q**, or **m** (i.e. singlet, doublet, triplet, quartet, multiplet) expected on the ^1H NMR spectrum for the protons below: (6 points)



15. A compound $\text{C}_{10}\text{H}_{13}\text{Cl}$ has the following ^1H NMR spectrum. Write down the pertinent comments / ideas about each NMR signal and provide the structure of the unknown.



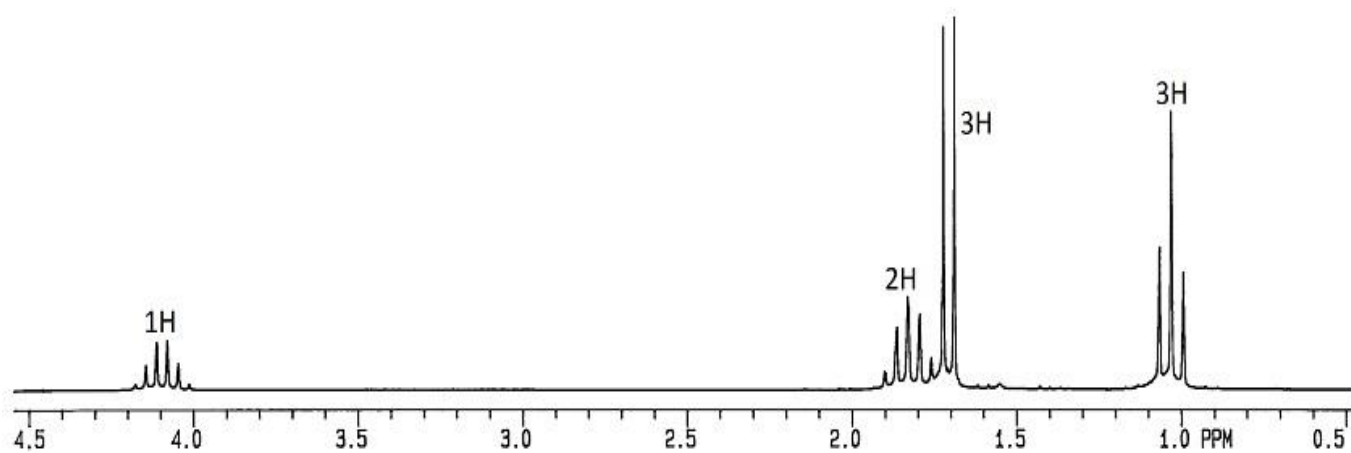
Calculate the degree of unsaturation (2 points):

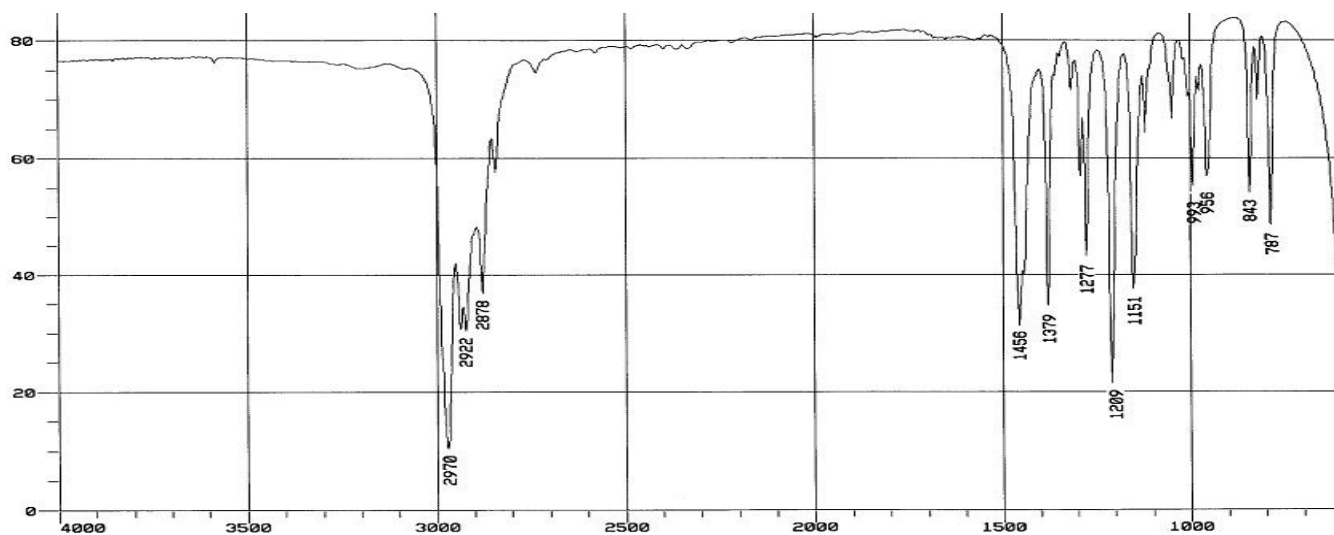
Signal	δ	Integration	Multiplicity	Comments / ideas
A	7.2	2H	d	
B	7.0	2H	d	
C	3.7	2H	t	
D	2.6	2H	t	
E	2.4	3H	s	
F	1.9	2H	m	

(11 points)

Structure of unknown:
(2 points)

16. A compound has the formula C_4H_9Br . Its 1H NMR and IR spectra are shown below:





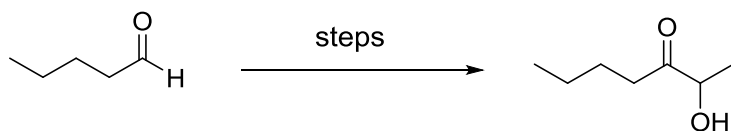
- a. Calculate the degree of unsaturation for the compound. **(2 points)**
- b. Identify the key absorbance(s) in the IR spectrum. Write the functional group or bond next to the relevant peak on the spectrum above. **(1 point)**
- c. Write down the pertinent comments / ideas about each NMR signal. **(5 points)**

Signal	δ	Integration	Multiplicity	Comments / ideas
A	4.1	1H	m	
B	1.8	2H	m	
C	1.7	3H	d	
D	1.0	3H	t	

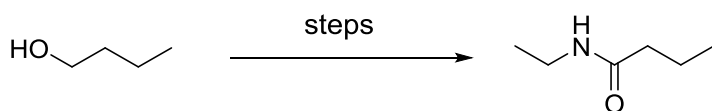
- d. Using the info above (formula, IR, NMR), draw the structure of the unknown. **(2 points)**

17. Propose a synthesis of the following compounds. Show all required reagents/solvents and intermediates. Retrosynthesis and mechanisms need not be shown. **(15 points – 5 each)**

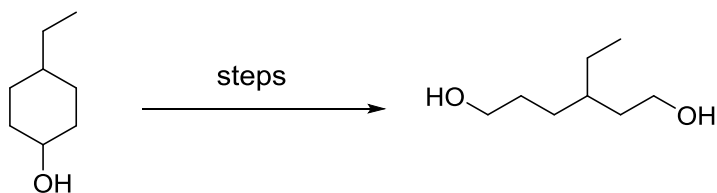
a.



b.

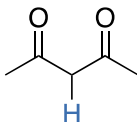
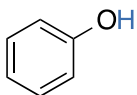
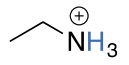
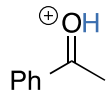

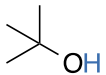
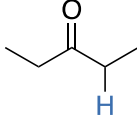
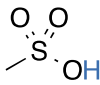

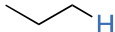
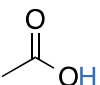


c.



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End of exam
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pK_a Table

Acid	pK _a value (H ₂ O solvent)	Acid	pK _a value (H ₂ O solvent)
HI	-10		9
HBr	-9		9.9
HCl	-8		10.6
	-6.2	H ₂ O	15.7
	-3.8		17
H ₂ SO ₄	-3		20
	-2.6	H-C≡C-H	24
CH ₃ OH ₂ ⁺	-2.2	H ₂	36
H ₃ O ⁺	-1.7	NH ₃	38
HNO ₃	-1.3		50
HF	3.17		51
	4.76		

IR Key Absorptions (cm⁻¹):

C-H alkyl	C-H	2850-2960	m, sharp
C-H sp ²	C-H	just >3000	m, sharp
Alcohol	RO-H	3200-3650	s, broad
Carboxylic acid	RC(=O)O-H	2500-3300	s, broad
Amine	R ₂ N-H	3300-3500	s, broad
*Carbonyl	R₂C=O	1650-1780	s, sharp
Nitrile	RC≡N	2220-2260	v, sharp
Alkynyl	C≡C-H	≈ 3300	m, sharp
Alkynyl	C≡C	2100-2260	v, sharp

Proton NMR chemical shifts

RCH _n	0.7 - 1.7		2.2 - 2.9		4.5 - 7.0
	1.6 - 2.6		2.0 - 3.0		6.5 - 8.0
	2.1-2.5		2.0 - 4.0		9.0 - 10.0
	2.1 - 3.0		2.7 - 4.1		11.0 - 12.0
	2.3 - 2.7		3.1 - 4.1		
	1.7 - 2.7		4.2 - 4.8		
			3.0 - 5.0		
			4.1 - 4.3		

