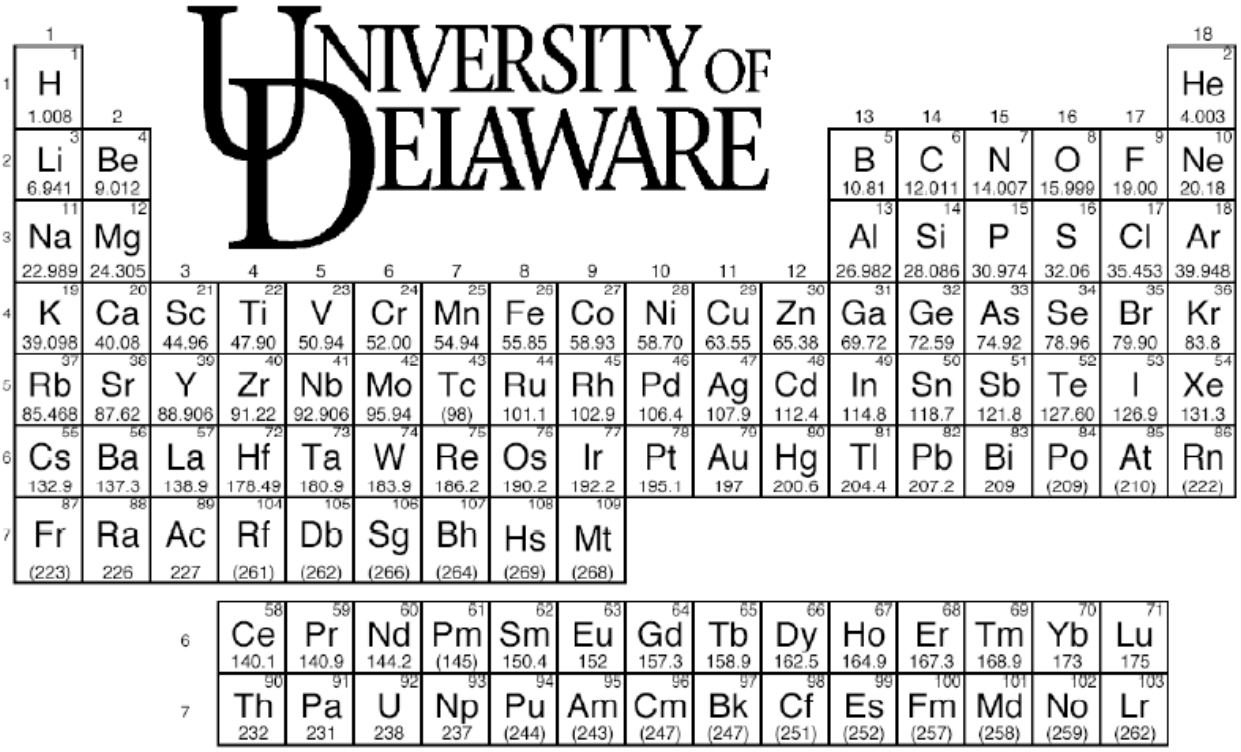
Name:_____

(Print your name clearly!)

Sametz: CHEM 322 2009

Organic Chemistry Final

All answers should be written CLEARLY in the space provided. (If it's not clear, it's wrong).



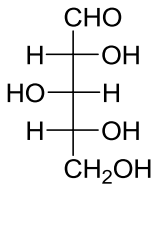
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1.008																	He 4.003
2	Li 6.941	Be 9.012											B 10.81	C 12.011	N 14.007	O 15.999	F 19.00	Ne 20.18
3	Na 22.989	Mg 24.305											Al 26.982	Si 28.086	P 30.974	S 32.06	Cl 35.453	Ar 39.948
4	K 39.098	Ca 40.08	Sc 44.96	Ti 47.90	V 50.94	Cr 52.00	Mn 54.94	Fe 55.85	Co 58.93	Ni 58.70	Cu 63.55	Zn 65.38	Ga 69.72	Ge 72.59	As 74.92	Se 78.96	Br 79.90	Kr 83.8
5	Rb 85.468	Sr 87.62	Y 88.906	Zr 91.22	Nb 92.906	Mo 95.94	Tc (98)	Ru 101.1	Rh 102.9	Pd 106.4	Ag 107.9	Cd 112.4	In 114.8	Sn 118.7	Sb 121.8	Te 127.60	I 126.9	Xe 131.3
6	Cs 132.9	Ba 137.3	La 138.9	Hf 178.49	Ta 180.9	W 183.9	Re 186.2	Os 190.2	Ir 192.2	Pt 195.1	Au 197	Hg 200.6	Tl 204.4	Pb 207.2	Bi 209	Po (209)	At (210)	Rn (222)
7	Fr (223)	Ra 226	Ac 227	Rf (261)	Db (262)	Sg (266)	Bh (264)	Hs (269)	Mt (268)									

6	Ce 140.1	Pr 140.9	Nd 144.2	Pm (145)	Sm 150.4	Eu 152	Gd 157.3	Tb 158.9	Dy 162.5	Ho 164.9	Er 167.3	Tm 168.9	Yb 173	Lu 175
7	Th 232	Pa 231	U 238	Np 237	Pu (244)	Am (243)	Cm (247)	Bk (247)	Cf (251)	Es (252)	Fm (257)	Md (258)	No (259)	Lr (262)

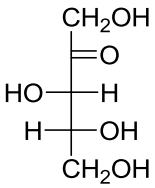
You may raise your hand to ask a question if you are unsure what a question is asking of you.

Part I Multiple Choice and Short Answer(28 points)

1. (Multiple choice, 4 points) Which of the following is an aldopentose?



a



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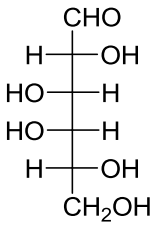

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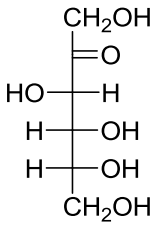

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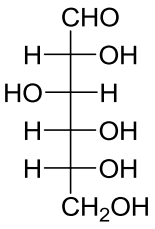
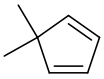
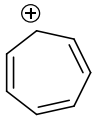
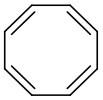


e

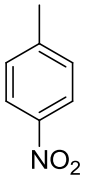
2. (8 points) Indicate for each of the following species whether they are aromatic, antiaromatic, or neither:

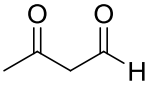


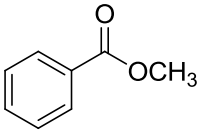




3. (6 points) Give IUPAC names for the following molecules:







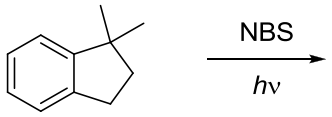
4a) (6 points) We have seen several examples of reactions that give one major product under kinetic conditions and another major product under thermodynamic conditions. Give an example of one such reaction. Indicate which product is favored kinetically, which is favored thermodynamically, and give appropriate conditions for the formation of each.

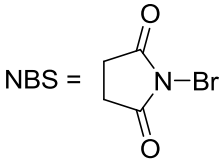
b) (4 points) We have seen several reactions where an otherwise reversible reaction is driven to completion by an (essentially) irreversible step. Give an example of one such reaction, and show the step in the mechanism that is (essentially) irreversible.

Part III: Reactions and Synthesis

5. (68 points) Give the major organic product(s) for **17** of the following **24** reactions: **YOU CAN SKIP 7 problems by checking the "SKIP" box.**

a. ❑SKIP this one





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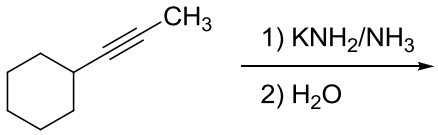

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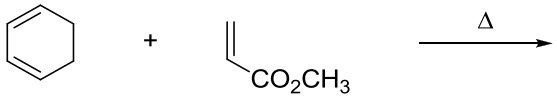

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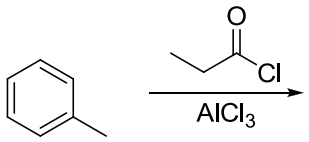

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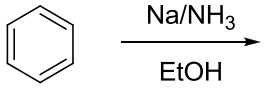

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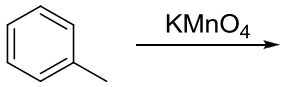

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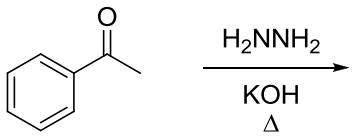

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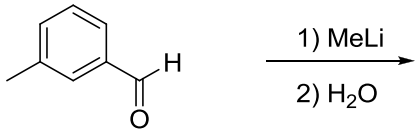

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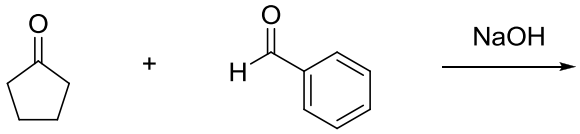

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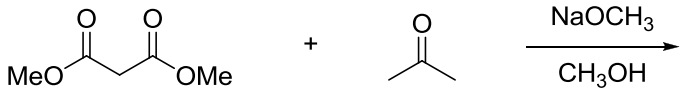

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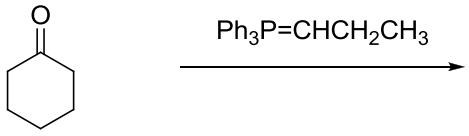

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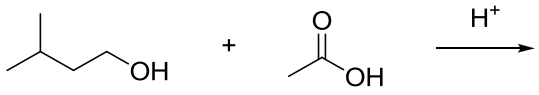
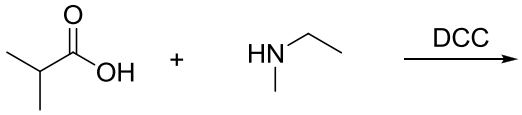

OH
+
O
OH
H+

m. ❑SKIP this one



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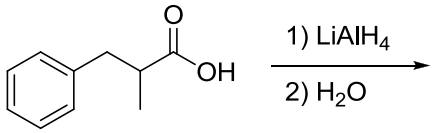

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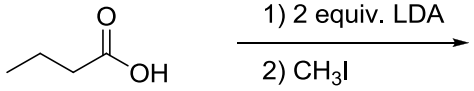

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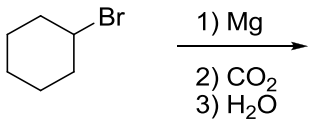

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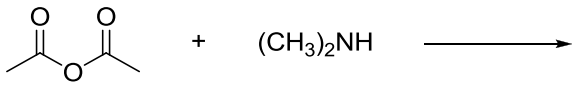

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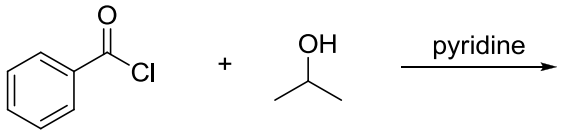

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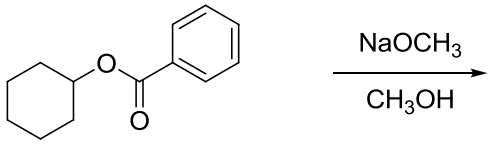

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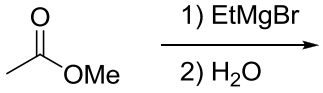

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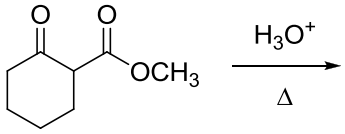

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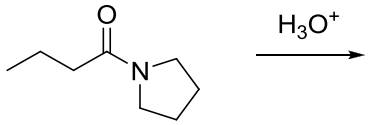

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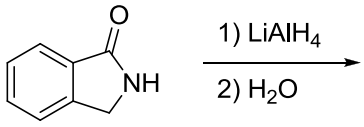

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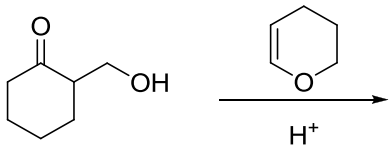
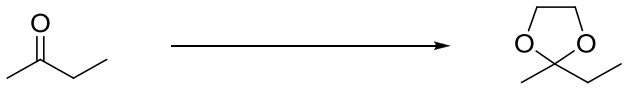


6. (15 points) Provide reagents to effect the following transformations. **DO 5 OUT OF 7 PARTS. (YOU CAN SKIP 2 parts of Problem 8 by checking the "Skip" box).**

a. ❑SKIP this one



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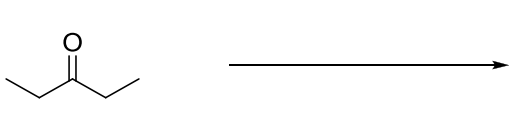

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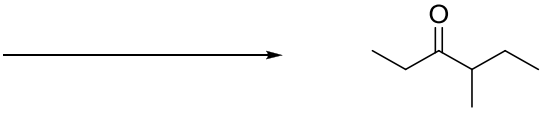

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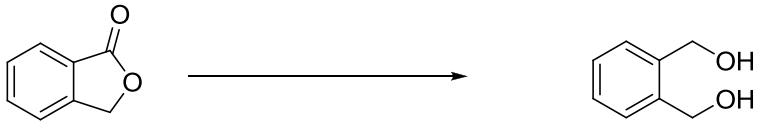

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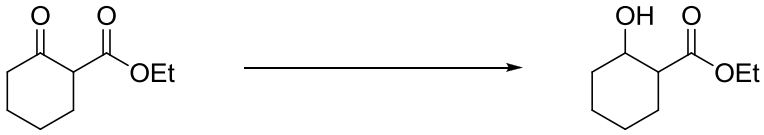

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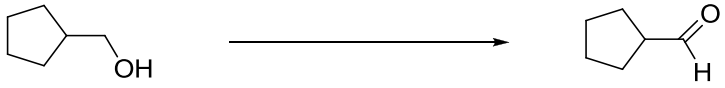
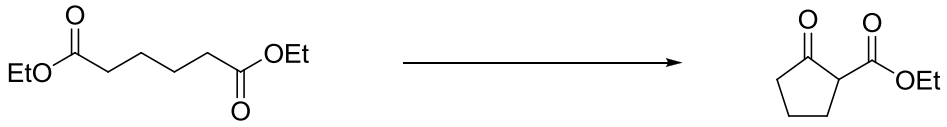
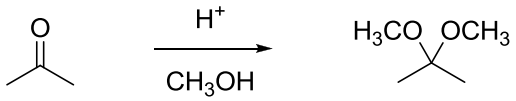


g. ❑SKIP this one

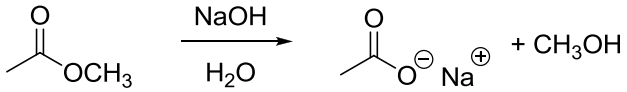


7. (10 points) Give detailed mechanisms for **2** of the following **4** reactions.

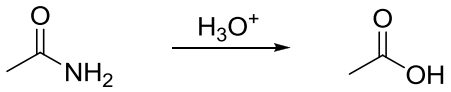
a)



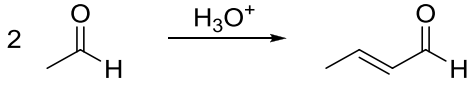
b)



c)

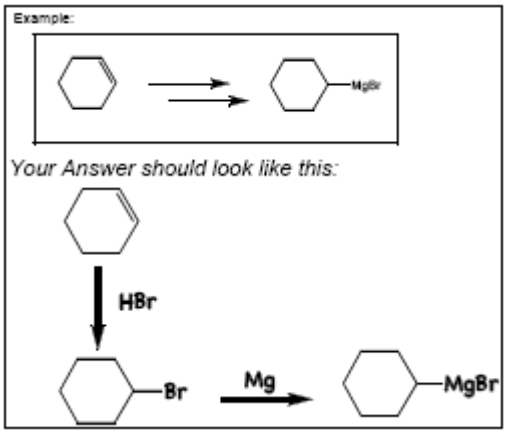


d)

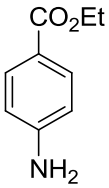


Multistep Synthesis (9 points)

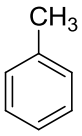
8. Choose **TWO** of the two following four synthesis problems. Show how you can synthesize the product on the left from the indicated starting material on the right. You can show a retrosynthesis for partial credit, but full credit requires writing out a sequence of forward reactions (see box at right for an example).



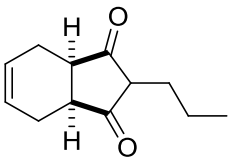
a)



from



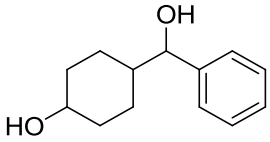
b)



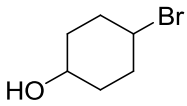
from

and any reagents with 5 or fewer carbons

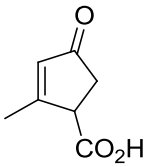
c)



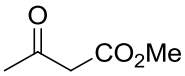
from



d)



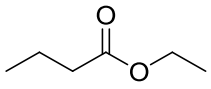
from



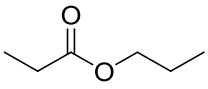
(hint: alkylation followed by aldol)

Part IV: NMR Spectroscopy

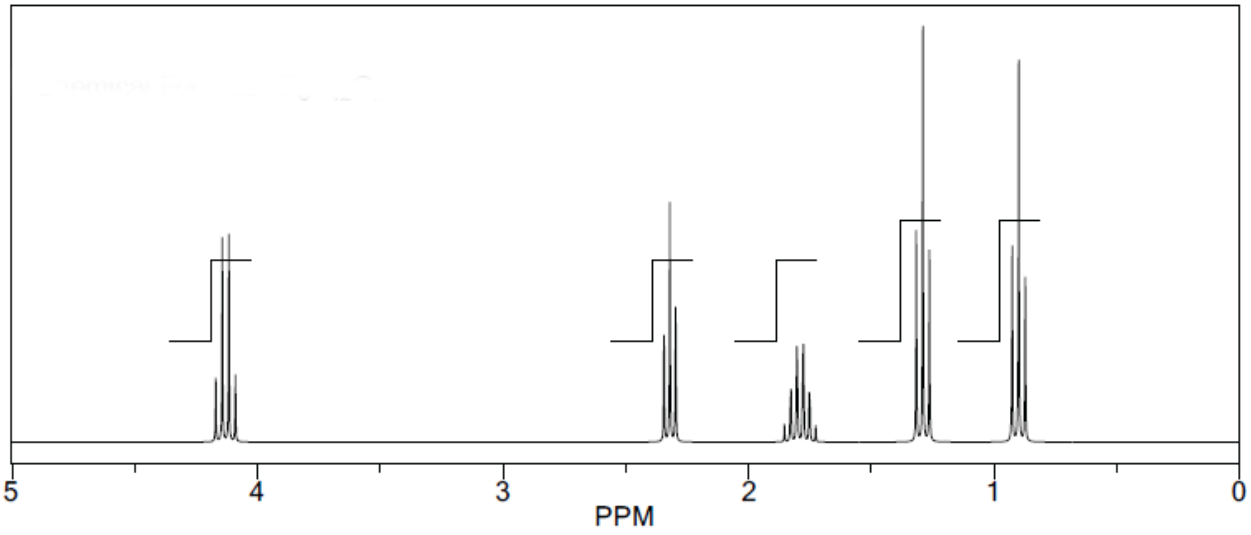
9. (8 points) The spectra for ethyl butyrate and propyl propionate are shown below. Determine which spectrum belongs to which compound. To obtain credit, you must explain how you determined which is which. It's not necessary to analyze every signal in order to reach your conclusion.

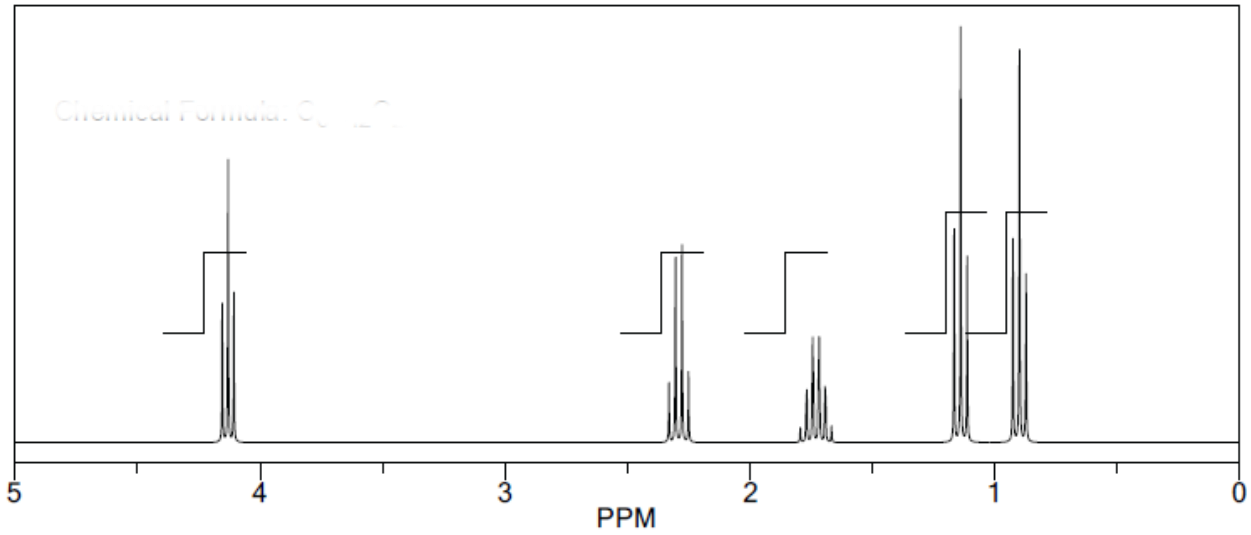


ethyl butyrate



propyl propionate

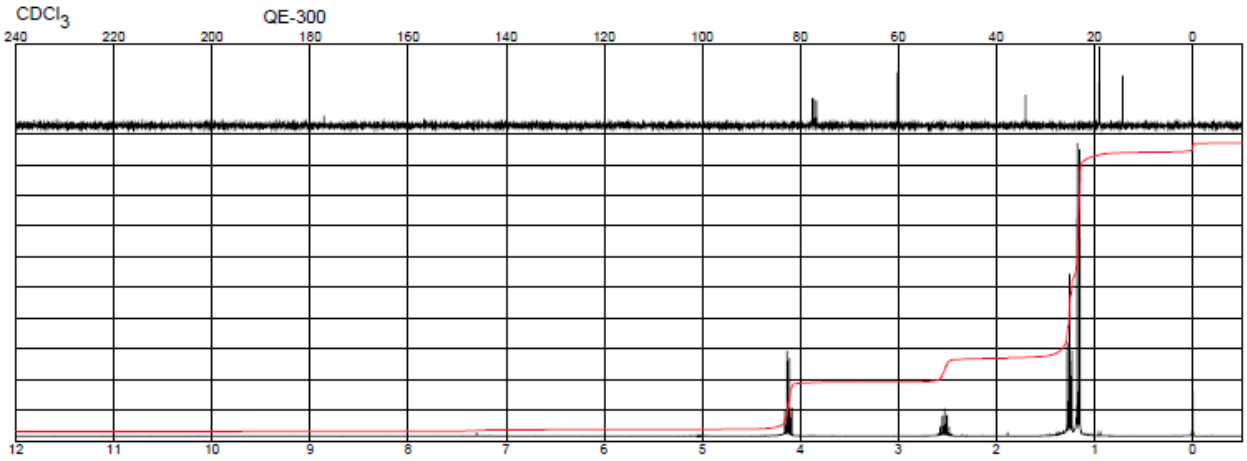


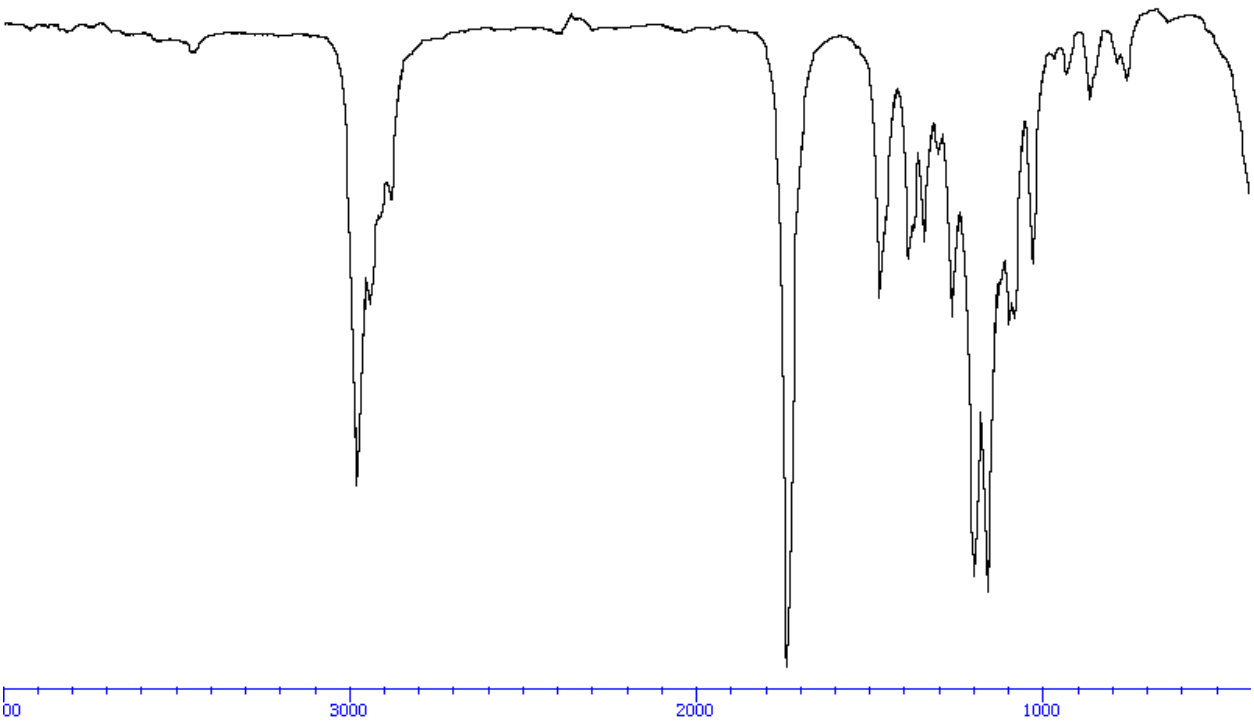


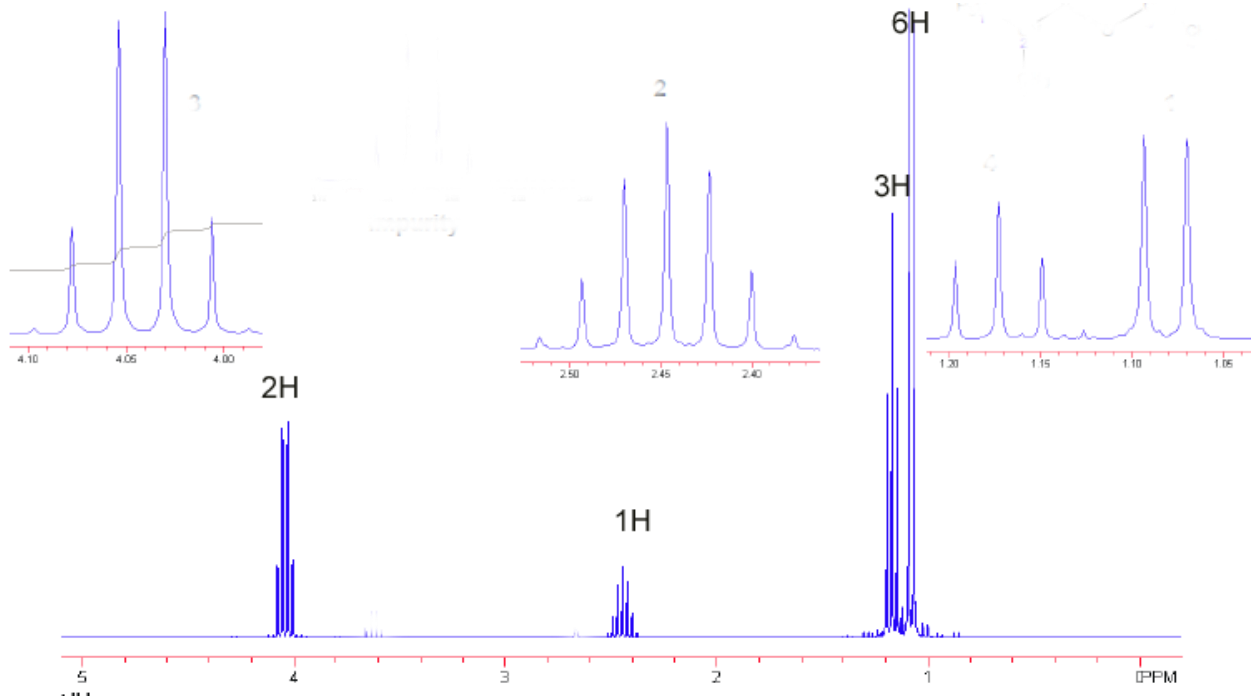
10. Spectroscopic Analysis of an Unknown Compound (10 points)

The ^{1}H (bottom) and ^{13}C (top) NMR spectra for a compound with the formula $C_6H_{12}O_2$ is shown below. An expansion of the ^{1}H NMR, and an IR spectrum, are shown on the following page. The numbers on the NMR expansion indicate the integrations for each signal.

Identify the structure of the compound. Use the ^{1}H NMR data to construct a table (chemical shift, integration, multiplicity, assignment) to identify structural fragments, then arrive at the structure. **You are being graded on your analysis**. Any use of the degrees of unsaturation, IR, or ^{13}C NMR data will be considered for extra credit



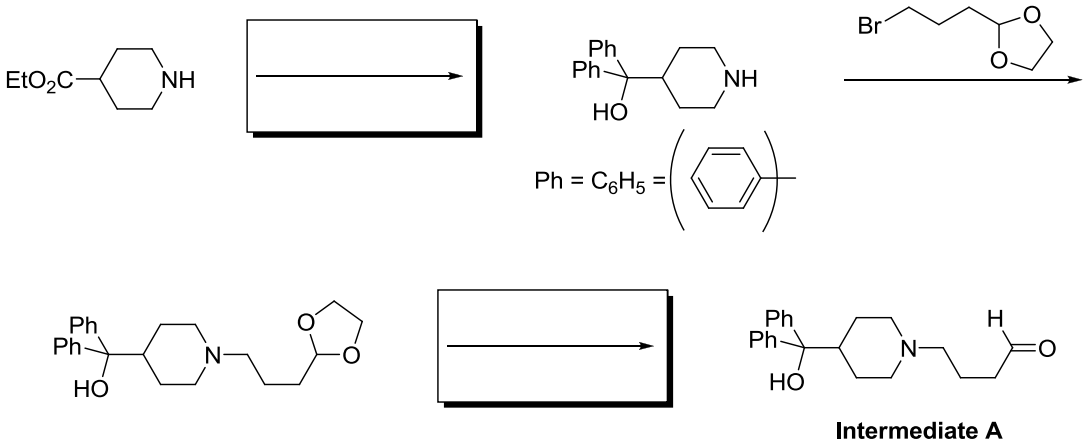

00
3000
2000
1000


6H
3H
2H
1H
5
4
3
2
1
PPM

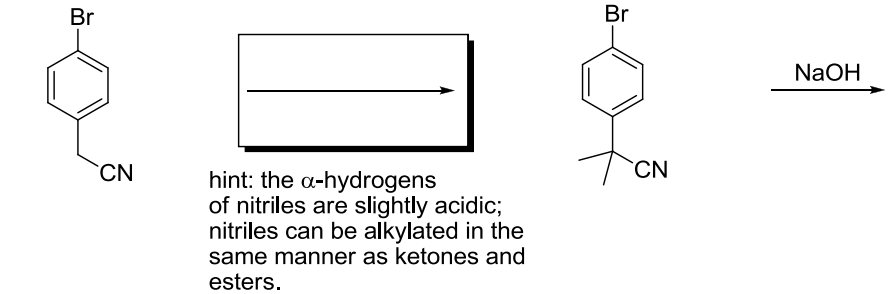
Extra Credit! (20 points): Chemical Synthesis of Fexofenadine (Allegra®).

This exam was written while I suffered from seasonal allergies. Answer as many of the following questions as you can for extra credit.

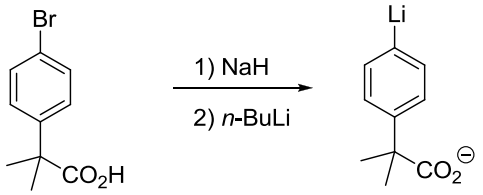
11. (9 points) For the following synthesis of fexofenadine, provide the missing reagents:



Intermediate A

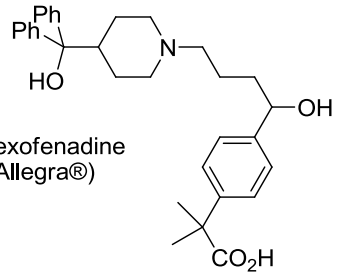


hint: the α-hydrogens of nitriles are slightly acidic; nitriles can be alkylated in the same manner as ketones and esters.



Intermediate B

Intermediate A + **Intermediate B** →

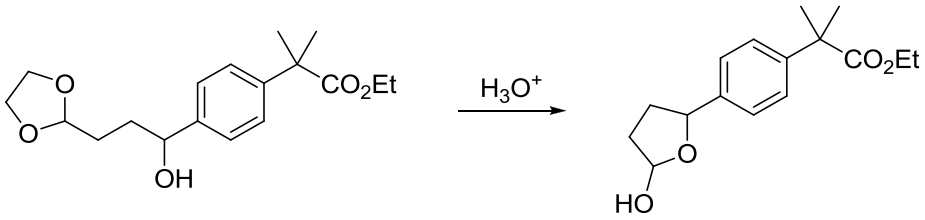


fexofenadine (Allegra®)

12. (3 points) Based on what you've learned so far, the organolithium **Intermediate B** looks unstable. Can you show a possible side reaction where it reacts with itself?

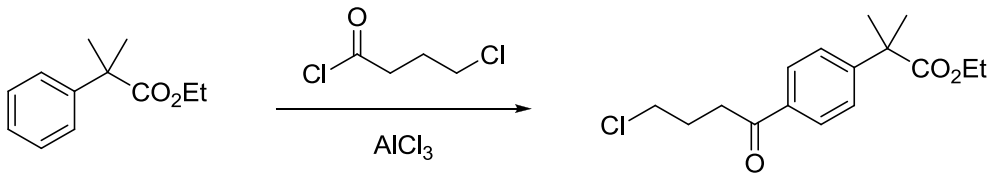
13. (2 points) Fexofenadine looks like it would be acid sensitive. Point out a part of the molecule that looks suspiciously sensitive to acid and explain why.

14. (4 points) An alternative synthesis involved the following reaction:



Explain how this transformation occurred.

15. (2 points) Another synthesis involved the following reaction:



This is another reaction that looks potentially messy. Can you forsee possible complications in this reaction?

TABLE 15.5 Some ^{13}C Chemical Shifts

Type of Carbon	Chemical Shift (δ)[a]	Type of Carbon	Chemical Shift (δ)[a]
Alkanes		Alcohols, ethers	
Methyl	0–30	C–O	50–90
Methylene	15–55	Amines	
Methine	25–55	C–N	40–60
Quaternary	30–40	Halogens	
Alkenes		C–F	70–80
C=C	80–145	C–Cl	25–50
Alkynes		C–Br	10–40
C≡C	70–90	C–I	−20–10
Aromatics	110–170	Carbonyls, C=O	
Benzene	128.7	$R_2C=O$	190–220
		RXC=O (X = O or N)	150–180

[a]The chemical shift δ is in parts per million (ppm) from TMS.

TABLE 15.4 Chemical Shifts of Various Hydrogens[a,b]

Hydrogen	δ (ppm)
CH_3	0.8–1.0
CH_2	1.2–1.5
CH	1.4–1.7
C=C–CH (allylic hydrogens)	1.8–2.3
O=C–CH	2.0–2.5
Ph–CH (benzylic hydrogens)	2.3–2.8
≡C–H	2.5
R_2N–CH	2.0–3.0
I–CH	2.8–3.3
Br–CH	2.8–3.5
Cl–CH	3.1–3.8
F–CH	4.1–4.7
O–CH	3.1–3.8
$=CH_2$ (terminal alkene)	5.0
C=CH (internal alkene)	4.5–5.5
Ph–H (aromatic hydrogens)	7.0–7.5
O=CH (aldehyde hydrogens)	9.0–10.0
RCOOH	10–13

[a]These values are approximate. There will surely be examples that lie outside the ranges indicated. Use them as guidelines, not "etched in stone" inviolable numbers.

[b]Watch out for loose talk. For example, "aromatic hydrogen" means a hydrogen attached to a benzene ring.

Some Useful IR Stretching Frequencies

Bond	Frequency (cm^{-1})	Intensity
O-H (alcohol)	3650-3200	Strong, broad
O-H (carboxylic acid)	3300-2500	Strong, **very** broad
N-H	3500-3300	Medium, broad
C-H	3300-2700	Medium
C≡N	2260-2220	Medium
C≡C	2260-2100	Medium to weak
C=O	1780-1650	Strong
C-O	1250-1050	strong

Cyanohydrins

Kinetic enolate

Td enolate

Reagents: Sandmeyer seres; cro3/pyr vs. h2cro4

Michael

SOCL2Saponification

Claisen

Aae/me;

O alkylation

Crossed claisen