CHM 2120A
Midterm #2
November 5, 2014

ANSWERS

First Name: _____ Last Name: _____

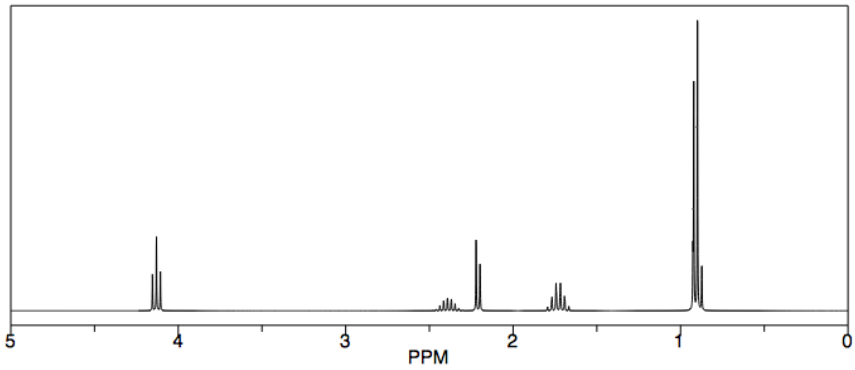
Student Number: _____ Seat number: _____

Approximate total number of marks: ~~76~~ 74

The marks are given as a guide and are subject to change.
You can write in pen or in pencil.
The use of molecular models is permitted but they cannot be shared.
The use of calculators or other electronic devices is not permitted.
The final page has a pK_a table, ^1H chemical shift table, and IR table; it can be detached.

1a	2a	3b	4b	5b	6b	7b	8		1b	2b	3a	4a	5a	6a	7a	0
1 H																2 He
3 Li	4 Be										5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg										13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Ha	106 106												

1. Determine the structure of the following unknown, which has molecular formula of $C_8H_{16}O_2$. The ^1H NMR spectrum is below. Only the three labeled areas at the bottom will be marked. **(10 points)**



Signal	δ (ppm)	Integration	Multiplicity	Ideas (not marked)
A	4.13	2H	t	CH_2
B	2.39	1H	m	CH
C	2.21	2H	d	CH_2
D	1.73	2H	m	CH_2
E	0.91	6H	d	2 x CH_3
F	0.89	3H	t	CH_3

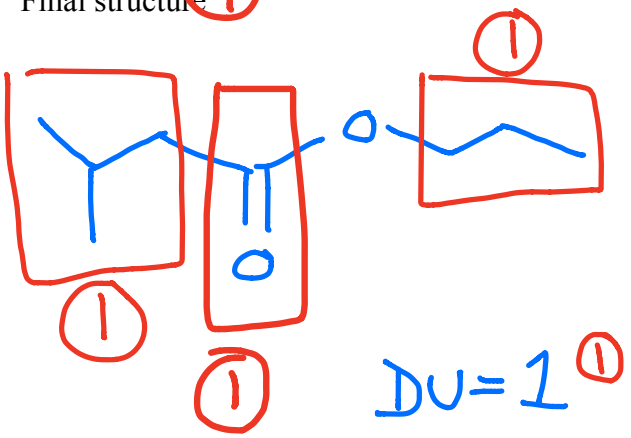
7 Cs vs C_8

Fragments that you are certain of (all atoms should be accounted for):

CH_2 CH_2 CH_2 C O

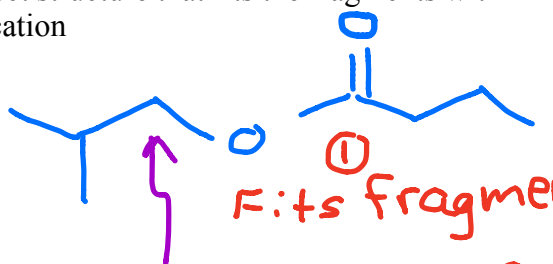
CH 2 x CH_3 CH_3 -O- (2)

Final structure (1)



DU = 1 (1)

Incorrect structure that fits the fragments with justification



Fits fragments

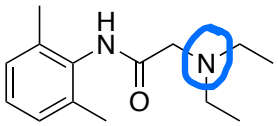
would be a d @ 4.1 ppm (1)

Is a d @ 2.2 ppm (1)

Justification

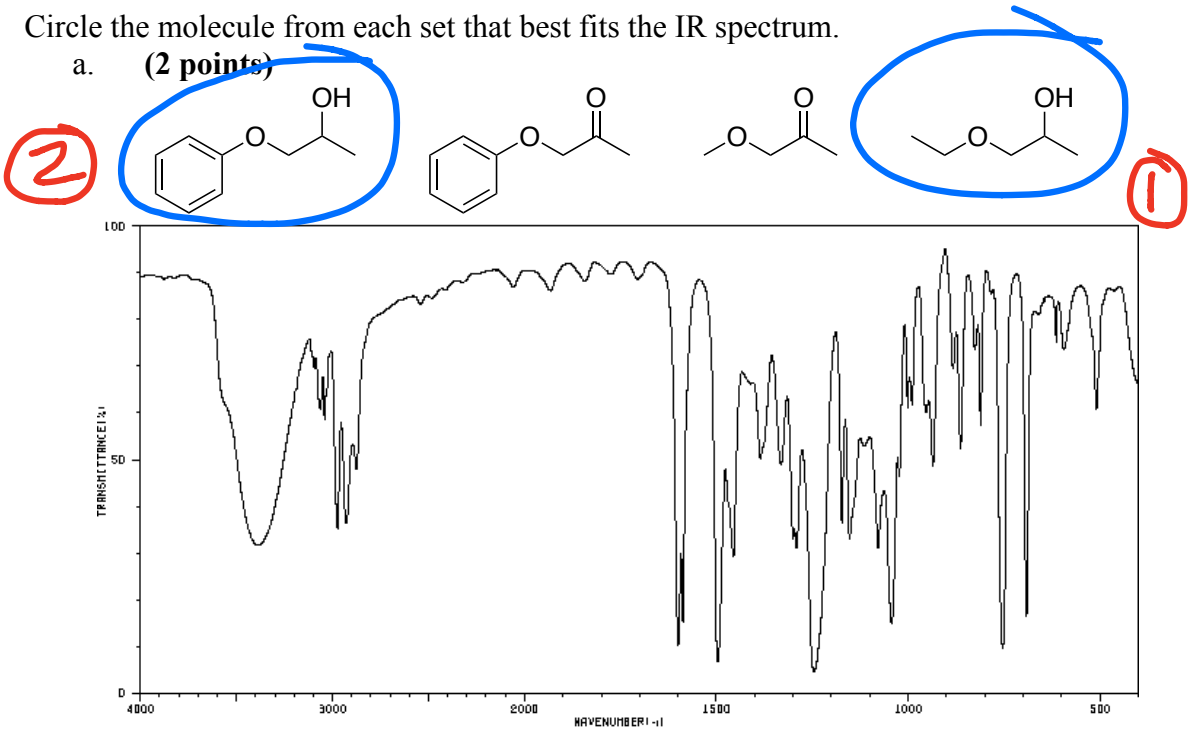
Extra space — Not marked

2. Circle the most basic atom in the Lidocaine, shown below **(1 point)**

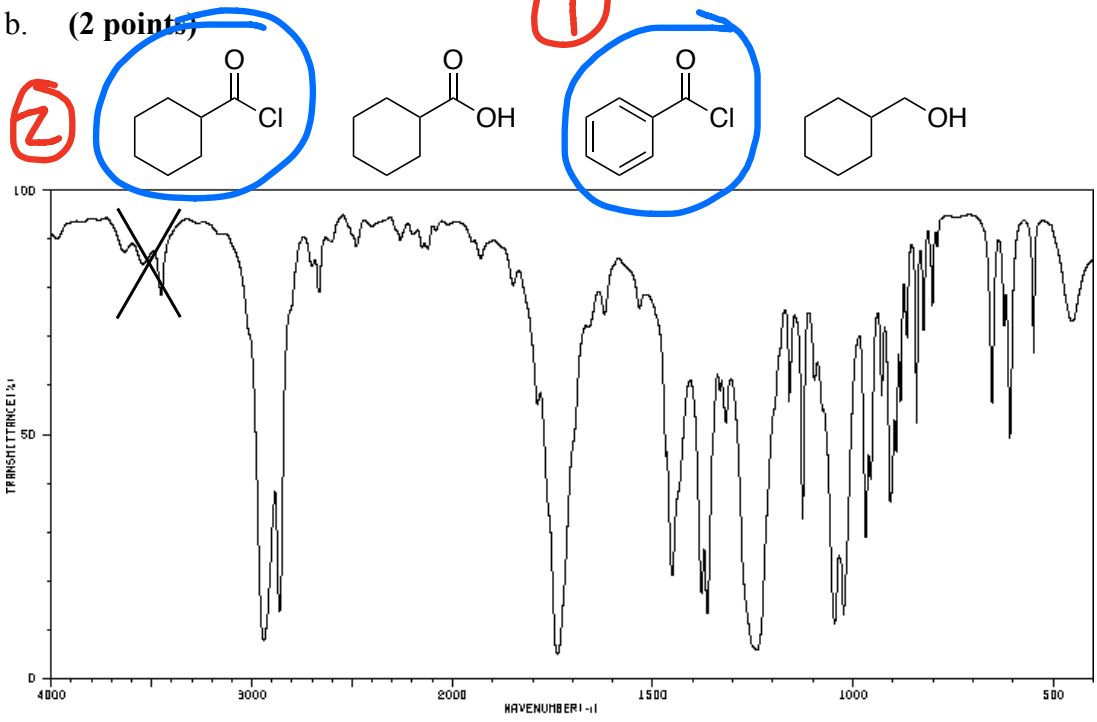


3. Circle the molecule from each set that best fits the IR spectrum.

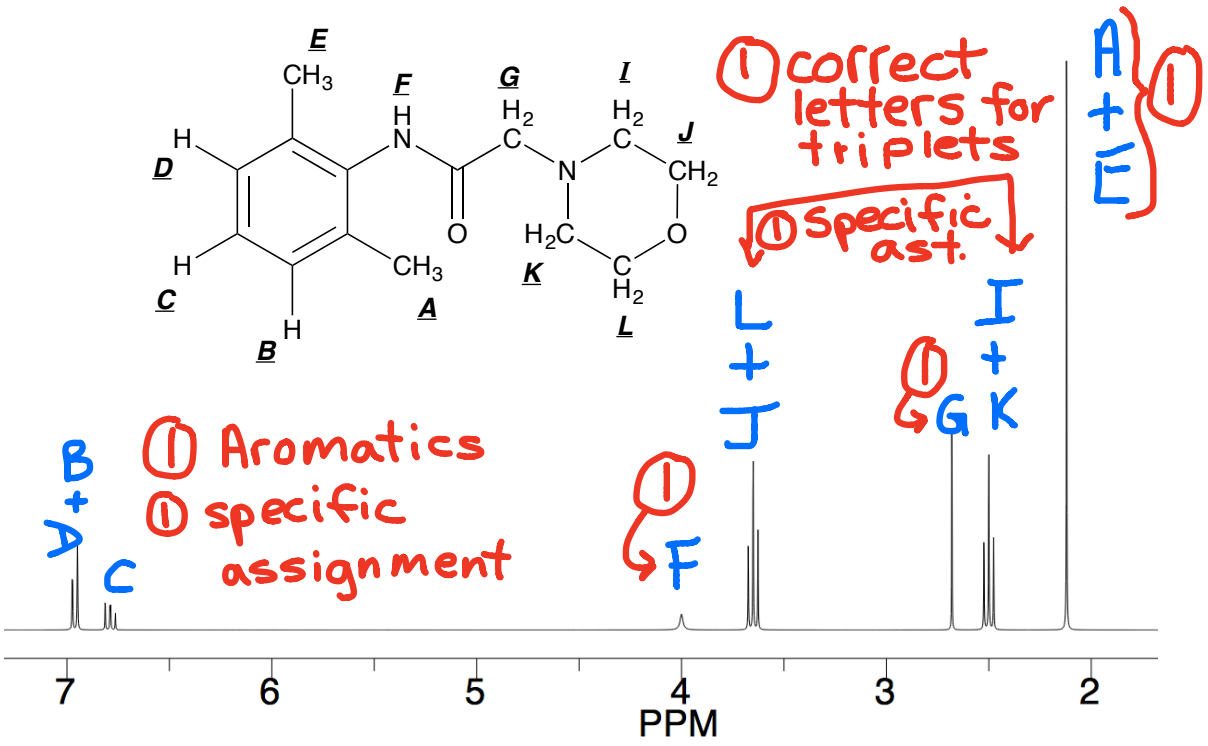
a. **(2 points)**



b. **(2 points)**



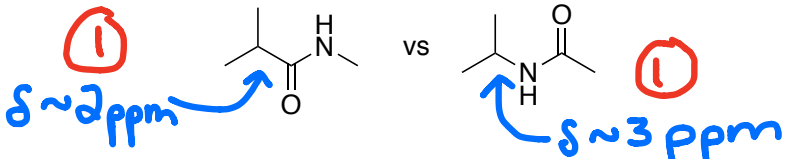
4. Assign all the signals in the 1H NMR spectrum below by writing the corresponding letter of each proton over the signal: **(9 points)**



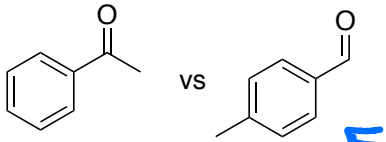
5. Specify one ^{1}H NMR method you could use to differentiate between each of the following pairs of compounds.

Notes: → other answers are possible
→ a comparison must be made

a. **(2 points)**

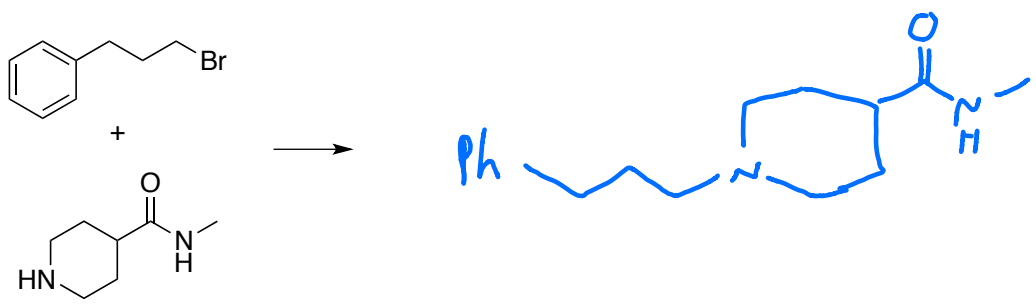


b. **(2 points)**

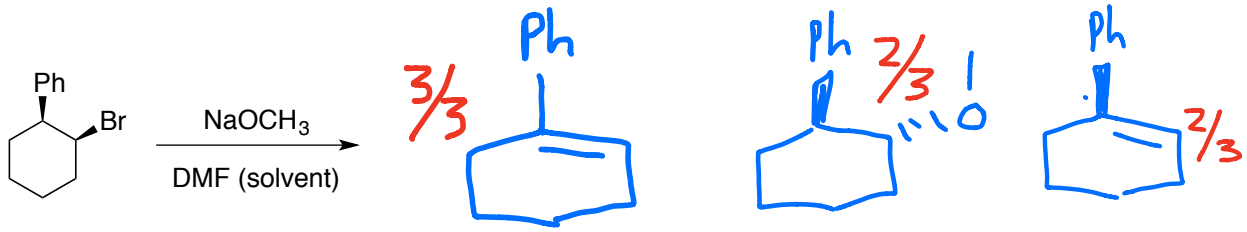


6. Draw the major organic product(s) OR the required reagents for each of the following reactions. **(3 points each: 9 points)**

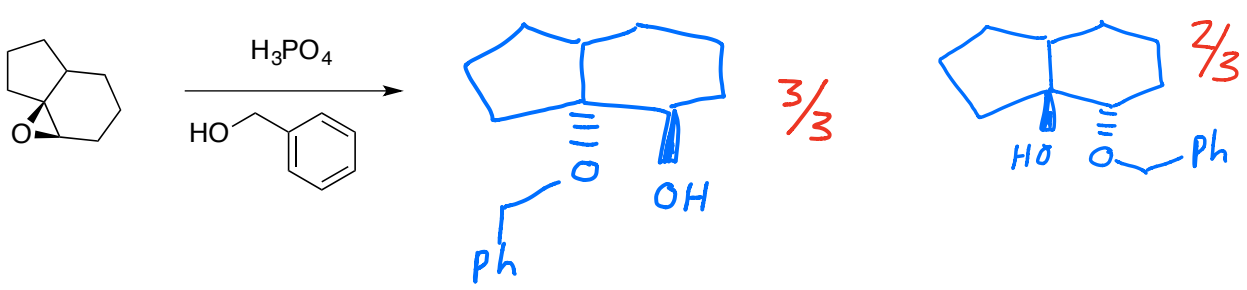
a.



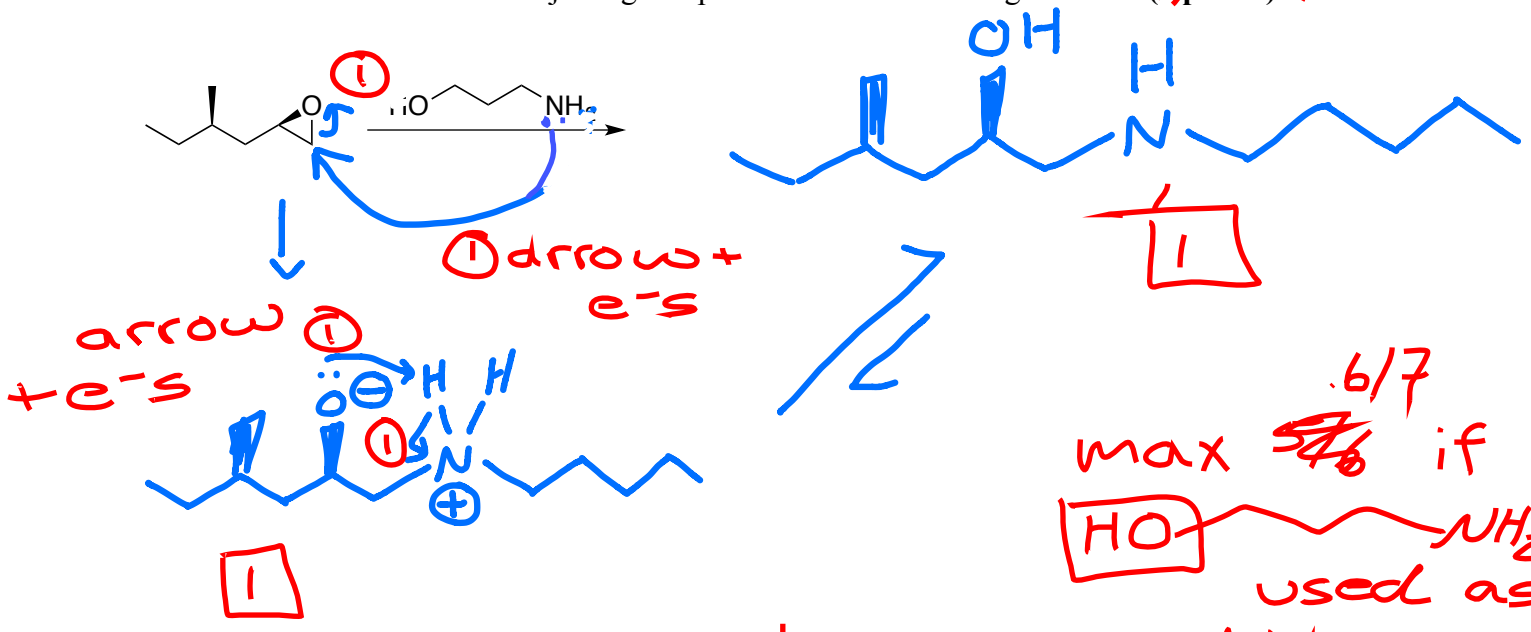
b.



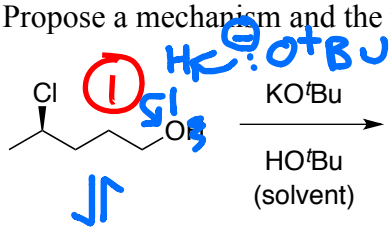
c.



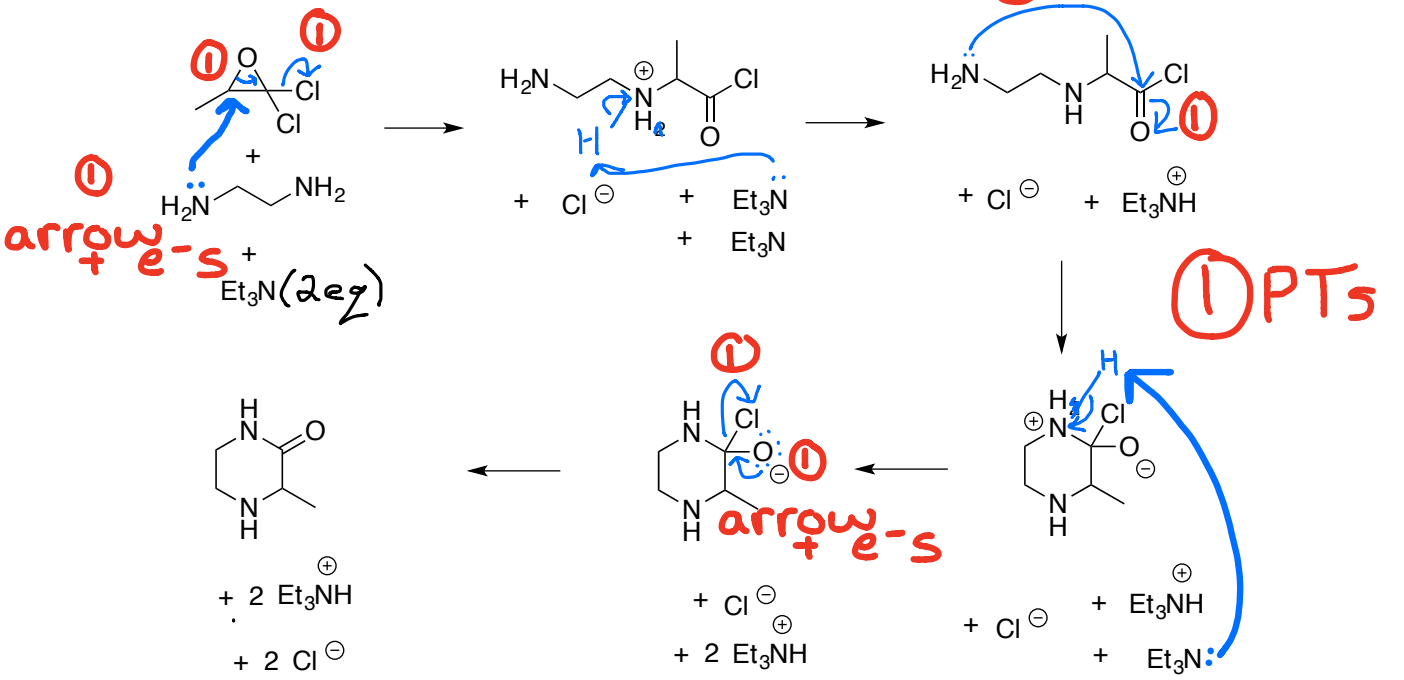
7. Give the mechanism and major organic product for the following reaction. **(5 points)** 7



8. Propose a mechanism and the major organic product for the following reaction. **(6 points)**



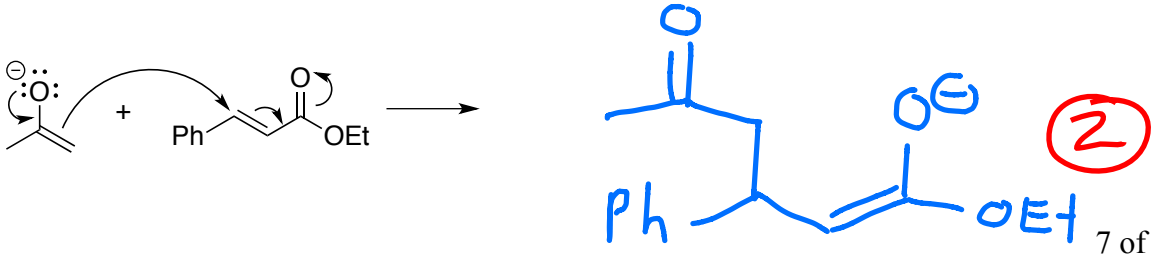
9. Add curved arrows to show the movement of electrons in each of the reaction steps below. Add lone electrons and draw carbons explicitly as needed. **(8 points)**



10. Draw the product of each of the reaction steps below. **(4 points)**

a.

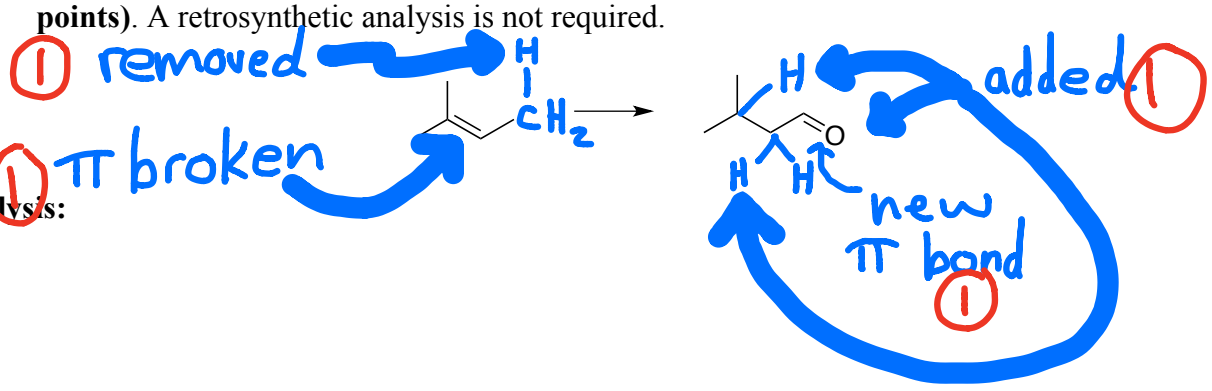
b.



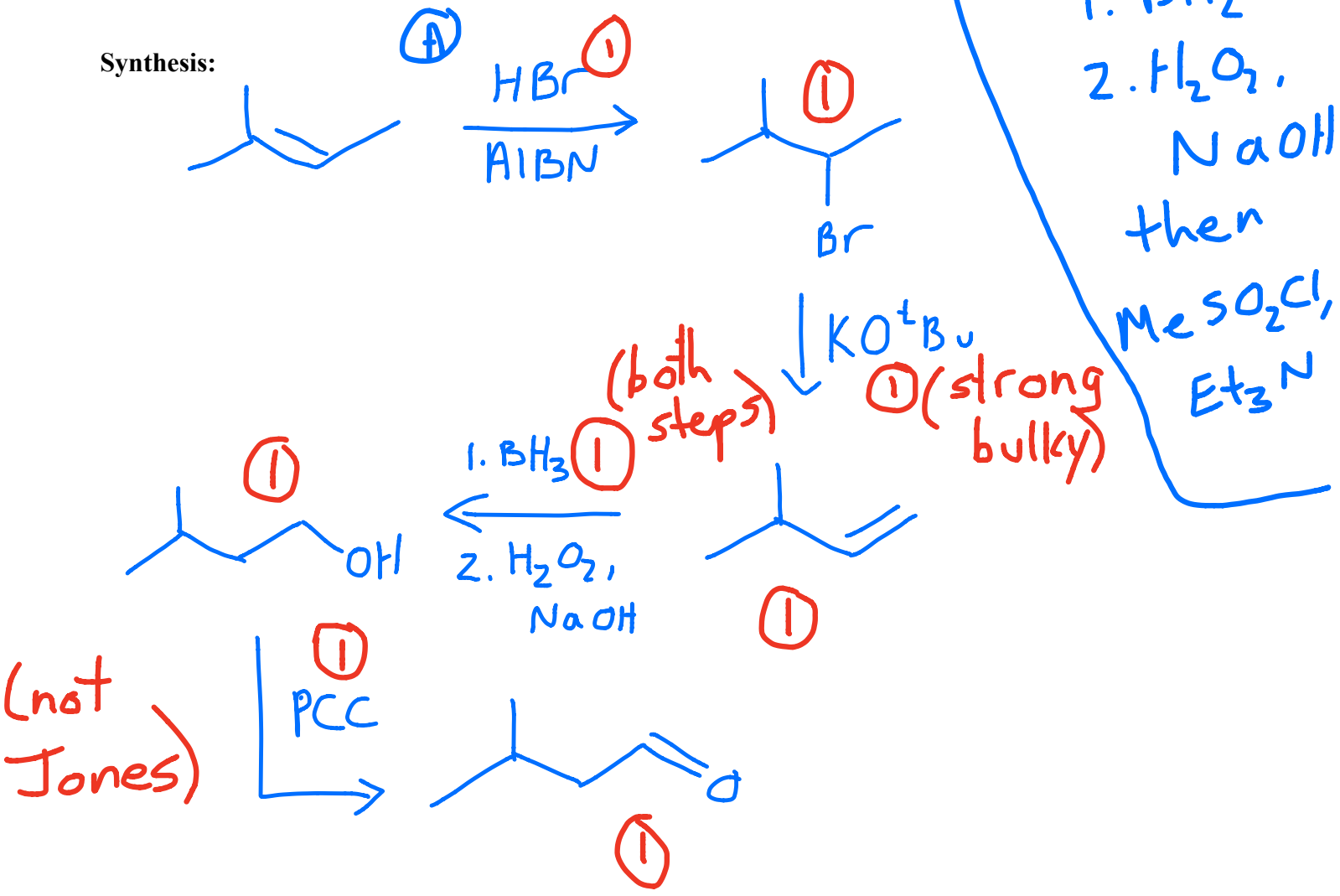
BONUS QUESTION

11. Propose a synthesis of the following molecule starting from the alkene provided **(8 points)**. Include an analysis (bonds broken, bonds formed, stereochemistry, and regiochemistry, as applicable) **(4 points)**. A retrosynthetic analysis is not required.

Analysis:



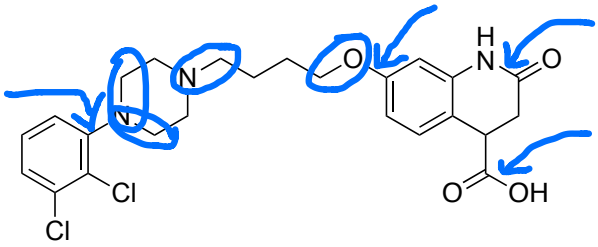
Synthesis:



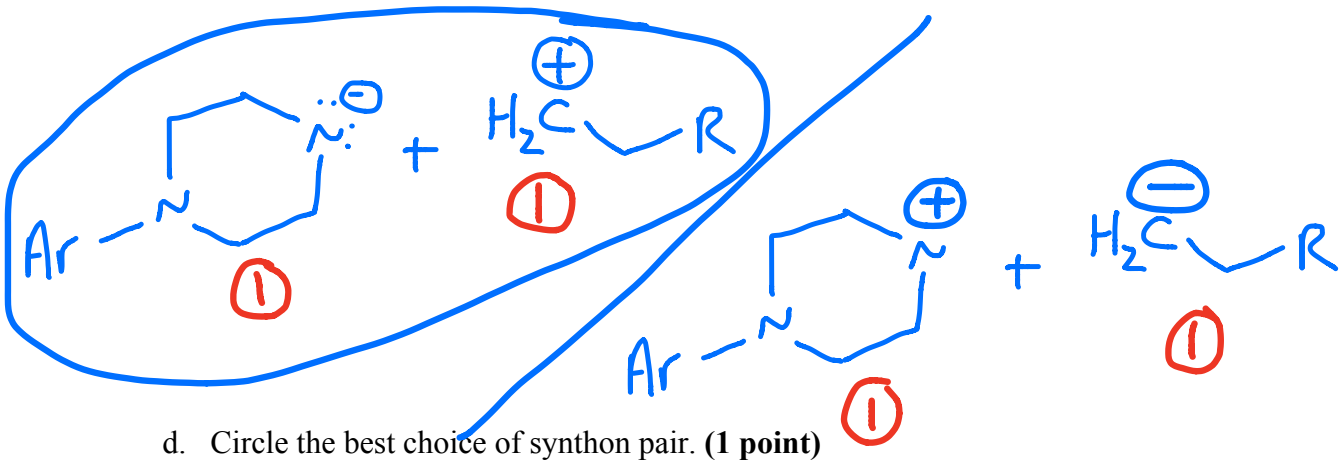
12. Consider the analog of Abilify, an antipsychotic drug, below.

a. Point (with an arrow) to one bond that could NOT be made by an S_N2 reaction. **(1 point)**

b. **Circle** one bond that **could** be made by an S_N2 reaction. **(1 point)**



c. Draw the two synthon pairs for making the bond in part b. You can use R groups. **(4 points)**



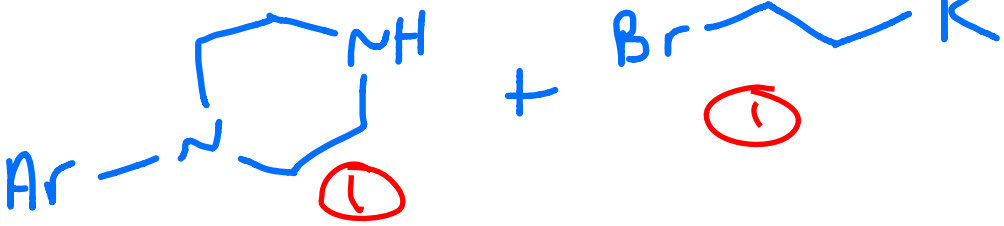
d. Circle the best choice of synthon pair. **(1 point)**

e. Justify your answer in part d. **(2 points)**

Electronegative N can more readily bear a ⊖ or δ− than a ⊕ or δ+ (as in the 2nd pair)

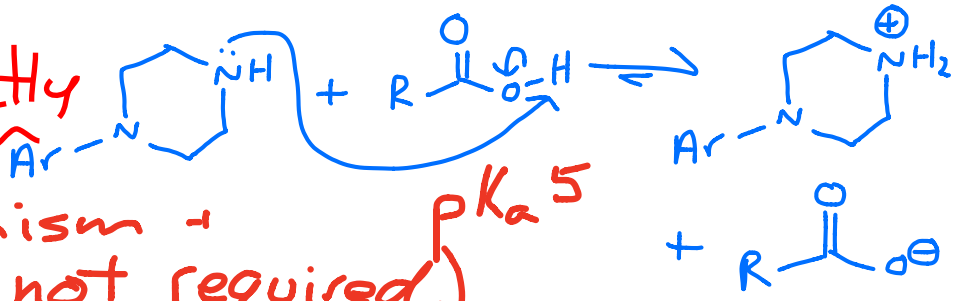
compare

f. Draw the actual reagents you would use. **(2 points)**



g. Identify (using an equation or short explanation) one potential side reaction that might occur if you performed the reaction as shown. **(2 points)**

1 A-B
1 correctly drawn

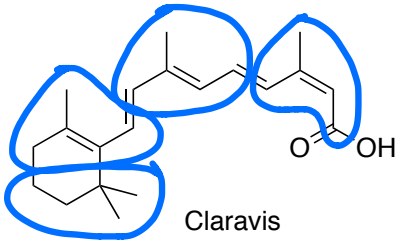


pKa 10

pKa 5

(mechanism + pKas not required)

BONUS!!!
Consider the structure of Claravis, an antiacne medication, shown below.



Claravis

2/2 : all
1/2 : 1 - 3 errors
0 : none

a. Circle the isoprene units in the molecule. **(2 points)**

b. How many signals are expected in its ^{1}H NMR spectrum? **(1 point)** 15

c. What is Claravis' pK_a? **(1 point)** ~5

TABLE 3.1 Relative Strength of Selected Acids and Their Conjugate Bases

	Acid	Approximate pK_a	Conjugate Base	
Strongest acid	$HSbF_6$	<-12	SbF_6^-	Weakest base
	HI	-10	I^-	
	H_2SO_4	-9	HSO_4^-	
	HBr	-9	Br^-	
	HCl	-7	Cl^-	
	$C_6H_5SO_3H$	-6.5	$C_6H_5SO_3^-$	
	$(CH_3)_2\overset{+}{O}H$	-3.8	$(CH_3)_2O$	
	$(CH_3)_2\overset{+}{C}{=}OH$	-2.9	$(CH_3)_2C{=}O$	
	$CH_3\overset{+}{O}H_2$	-2.5	CH_3OH	
	H_3O^+	-1.74	H_2O	
	HNO_3	-1.4	NO_3^-	
	CF_3CO_2H	0.18	$CF_3CO_2^-$	
	HF	3.2	F^-	
	$C_6H_5CO_2H$	4.21	$C_6H_5CO_2^-$	
	$C_6H_5NH_3^+$	4.63	$C_6H_5NH_2$	
	CH_3CO_2H	4.75	$CH_3CO_2^-$	
	H_2CO_3	6.35	HCO_3^-	
	$CH_3COCH_2COCH_3$	9.0	$CH_3COHCOCH_3$	
	NH_4^+	9.2	NH_3	
	C_6H_5OH	9.9	$C_6H_5O^-$	
	HCO_3^-	10.2	CO_3^{2-}	
	$CH_3NH_3^+$	10.6	CH_3NH_2	
	H_2O	15.7	OH^-	
	CH_3CH_2OH	16	$CH_3CH_2O^-$	
	$(CH_3)_3COH$	18	$(CH_3)_3CO^-$	
	CH_3COCH_3	19.2	$^-CH_2COCH_3$	
	$HC{\equiv}CH$	25	$HC{\equiv}C^-$	
	H_2	35	H^-	
	NH_3	38	NH_2^-	
	$CH_2{=}CH_2$	44	$CH_2{=}CH^-$	
Weakest acid	CH_3CH_3	50	$CH_3CH_2^-$	Strongest base

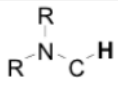
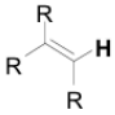
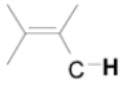
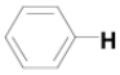
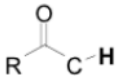
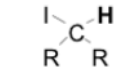
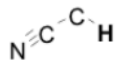
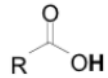
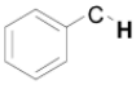
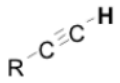
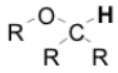
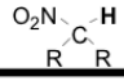
Increasing acid strength

Increasing base strength

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	R2**N-H**	3300-3500	s, broad
*Carbonyl	R2**C=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

Typical proton NMR chemical shifts

	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	OH, NH: variable	
			3.0 - 5.0		
			4.1 - 4.3		