Chemistry 30B DCF
Final Review Problems

In this final set of problems, I have tried to include things that will help you on the final exam. These problems have all been adapted from the sophomore organic chemistry course at MIT (though a friend @ Berkeley). I have included sections of problem sets and exams. This being said, the numbering is completely out of order (and doesn't make since). Also, there are some problems crossed out, as they were not covered in our class.

Finally, regarding ANSWER KEYS, I have not yet decided as to whether or not I will provide an answer key online. Please do NOT e-mail me asking about it. If I am going to post a key, it will be done only within a few days of the exam. As you will, or already have seen there is a plethora of office hours available between the last day of class and the final, we are all willing to go over these problems with you.

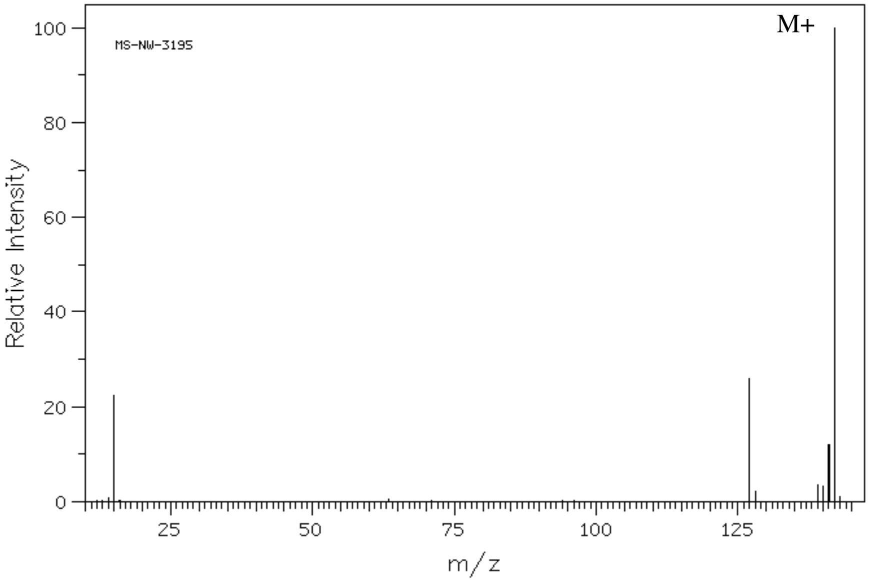
Note for Doug's Section:
During the Week X discussion section, I would like to cover question (1) on page 2 of 10 (it's buried somewhere in there toward the end with the first three questions asking about pKas). Also work on question (2) on page 4 of 10. Again, not really 4 of 10, but that's what it says on the bottom of the page.

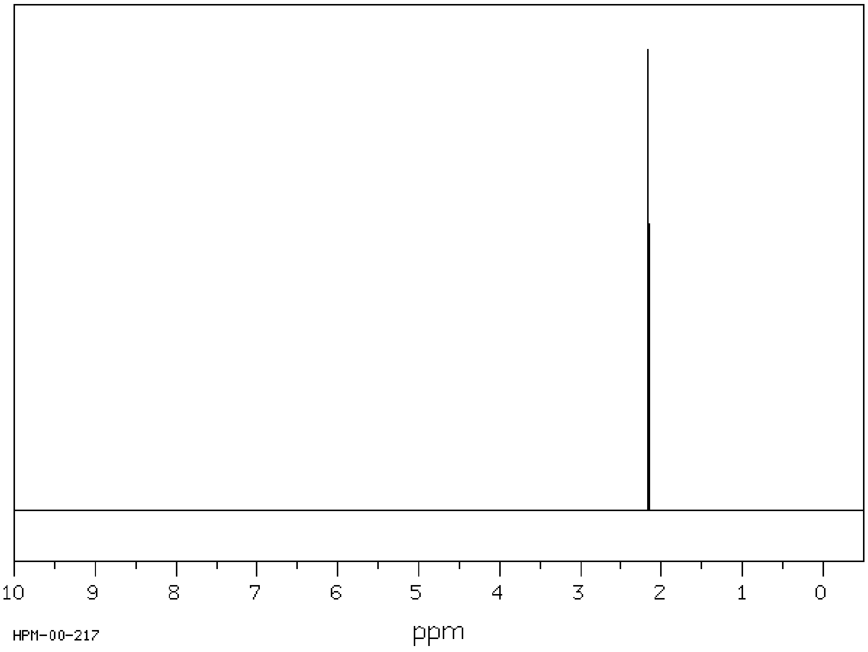
GOOD LUCK ON THE FINAL!

Problem Set 2 5.13 Due February 21, 2003 1PM

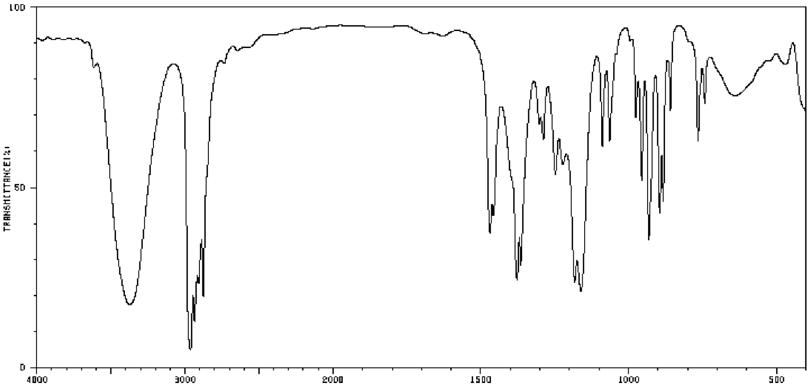
1. Compound **A** is reacted in anhydrous diethylether with Mg to give an intermediate that when reacted with compound **B** produces **C** after aqueous workup. What are **A**, **B**, and **C**. Explain how you arrived at your answer.

MS and ^{1}H- NMR of **A**

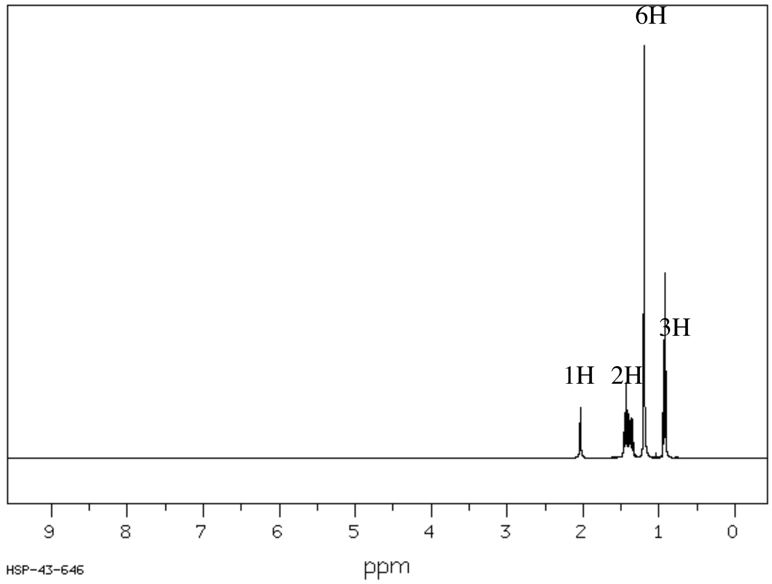


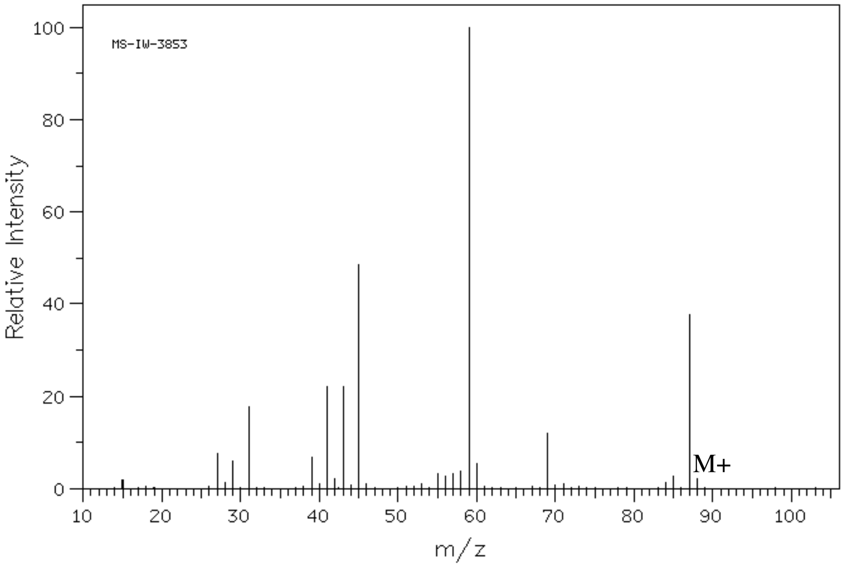


IR, ^{1}H-NMR, MS of **C** (Signal at 2.1 ppm disappears upon D_2O treatment)



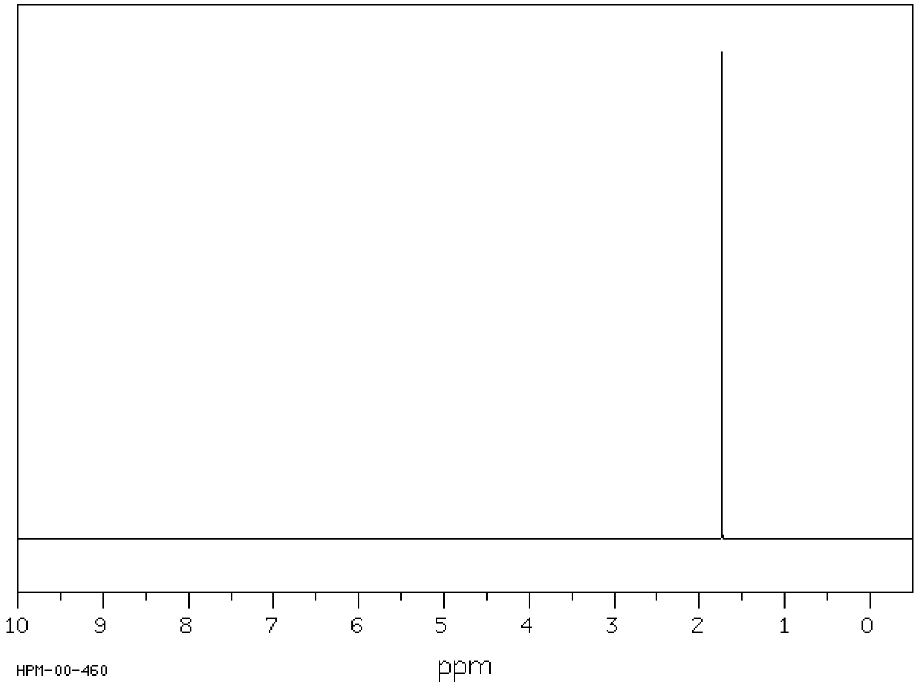
3616	79	1469	41	1183	22	896	41
3373	16	1378	23	1162	20	884	44
2963	4	1365	26	1089	58	859	68
2936	12	1303	64	1064	60	766	60
2907	22	1289	60	976	66	743	70
2875	18	1248	52	956	50	641	72
1469	36	1223	63	931	34	636	72

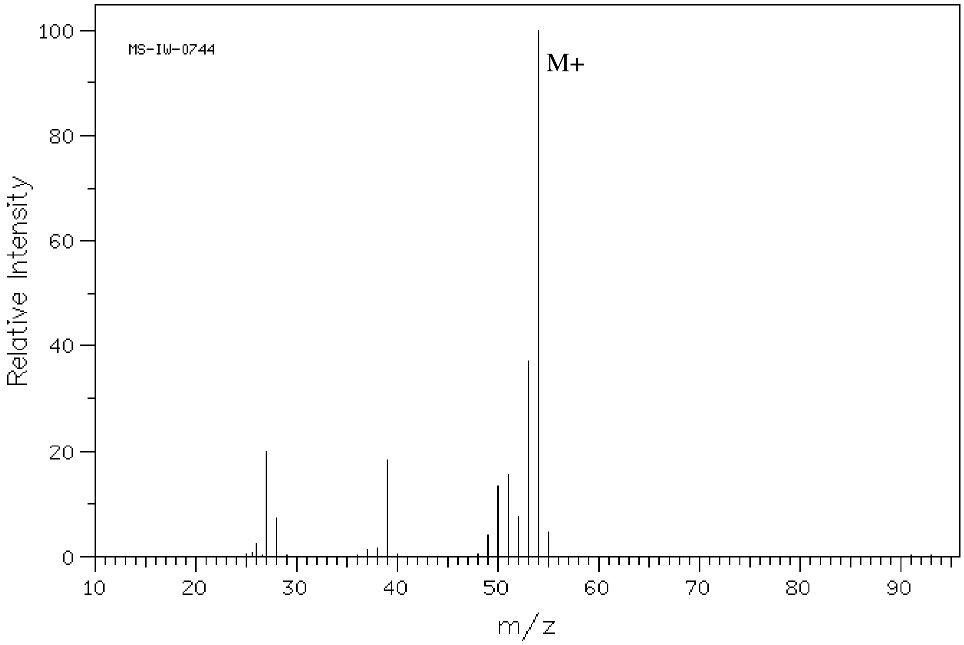




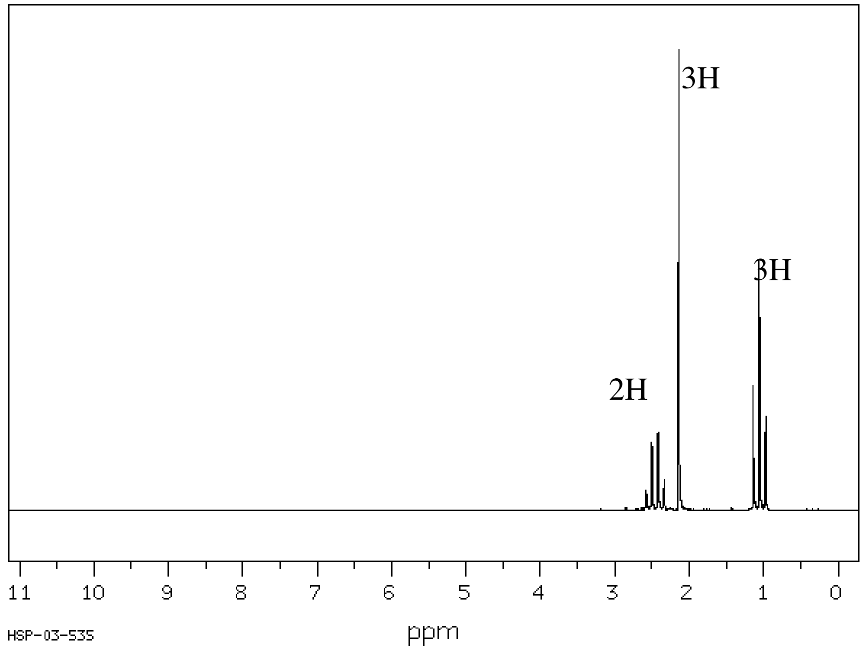
2. Compound **A** when treated with H_2SO_4 (small amount of H_2O) gives compound **B**. Provide the structures of **A** and **B**. Explain how you arrived at your answer.

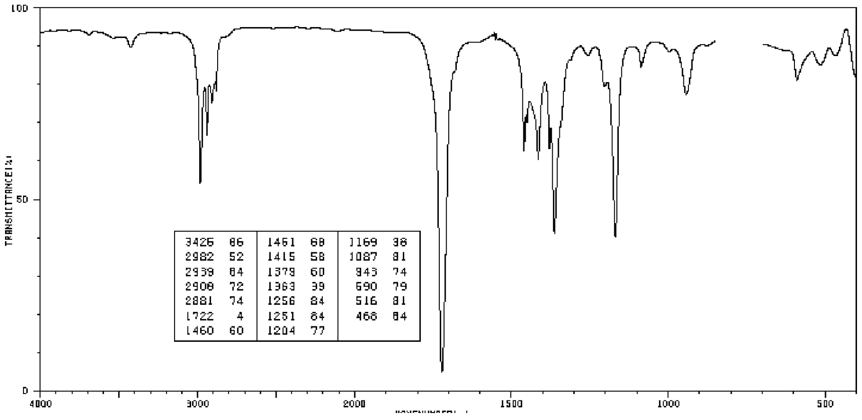
^{1}H-NMR and MS of **A**



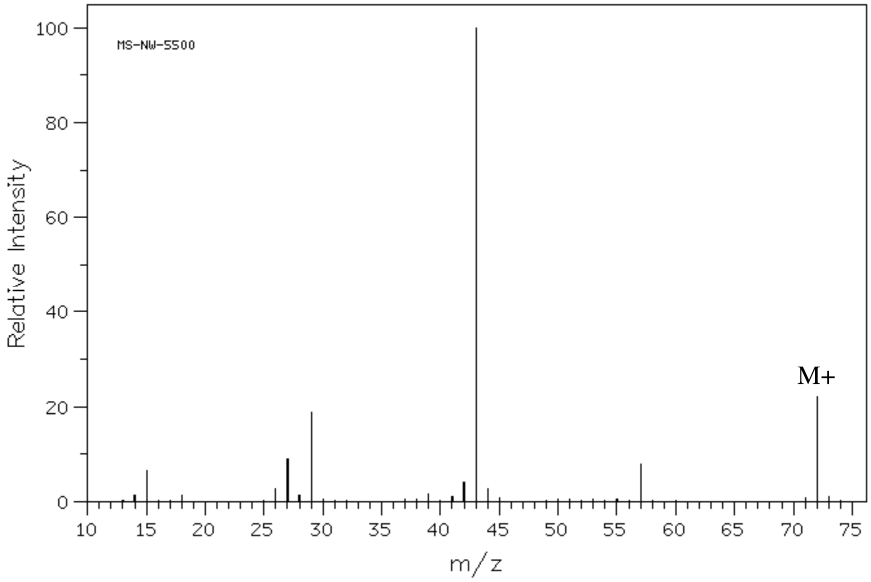


^{1}H-NMR, IR and MS of **B**



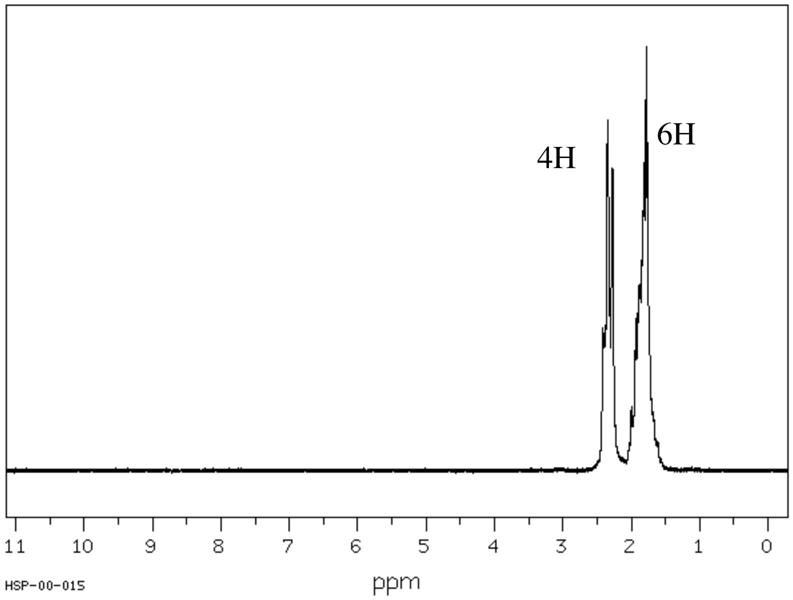


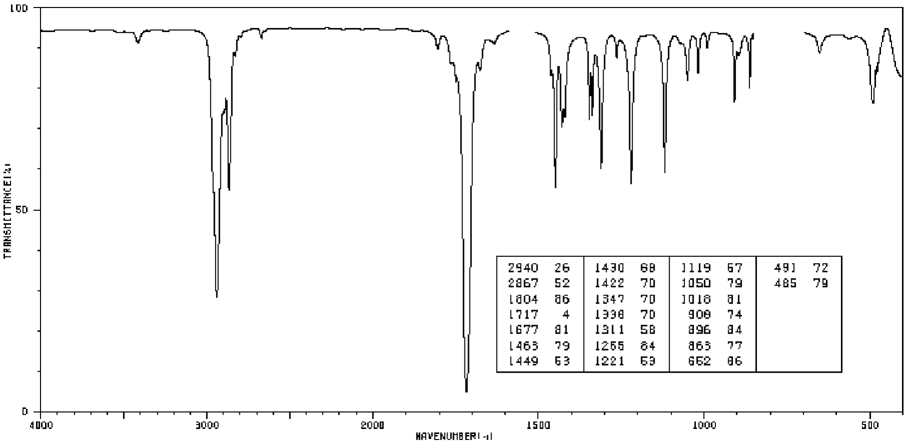
3426	86	1461	68	1169	38
2982	52	1415	58	1087	81
2939	84	1379	60	943	74
2908	72	1363	39	690	79
2881	74	1256	84	516	81
1722	4	1251	84	468	84
1460	60	1204	77		



3. Compound **A** (F.W.=94.9, ^{1}H-NMR singlet at 2.68ppm) is reacted with Triphenylphosphine to give compound **B**. Compound **B** is reacted with n-butyl lithium to give an intermediate that when reacted with compound **C** gives compound **D**. What are the compounds **A**, **B**, **C**, and **D**. Explain how you arrived at your answer.

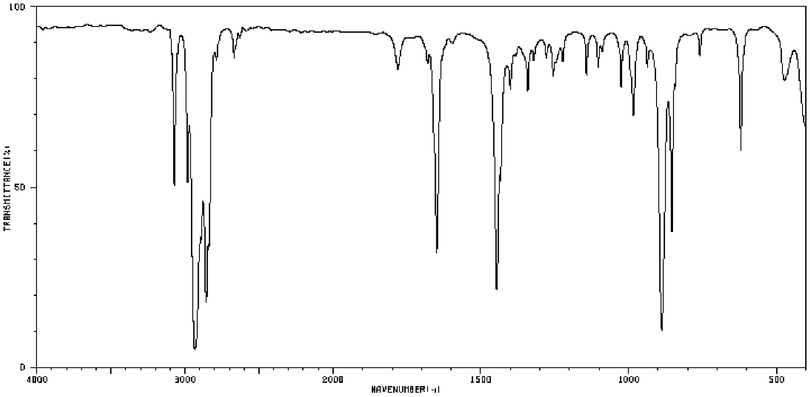
^{1}H-NMR and IR of Compound **C** (F.W.= 98.1)



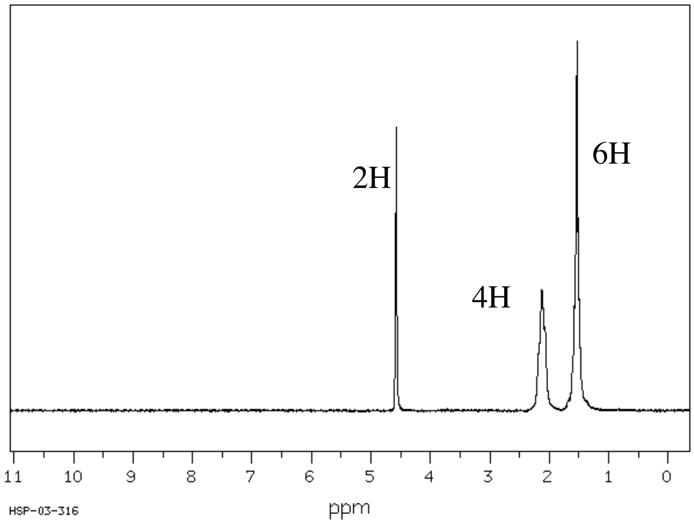


2940	26	1430	68	1119	67	491	72
2867	52	1422	70	1050	79	485	79
1804	86	1347	70	1018	81		
1717	4	1338	70	908	74		
1677	81	1311	58	896	84		
1463	79	1265	64	863	77		
1449	63	1221	63	662	86		

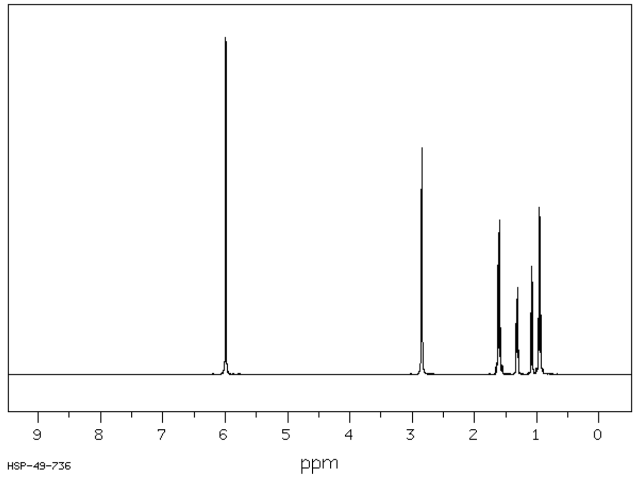
^{1}H-NMR and IRof **D** (F.W.= 96.2)

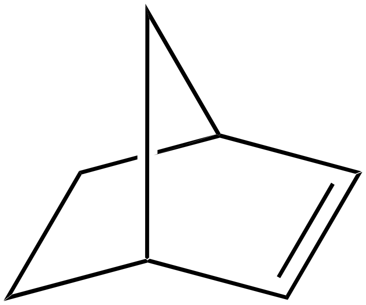


3089	84	2789	81	1434	60	1223	81	888	9
3071	49	2669	81	1400	74	1143	79	854	36
3052	84	1781	79	1341	74	1103	79	759	64
2981	49	1680	81	1322	81	1090	84	621	68
2933	4	1649	30	1279	81	1025	74	472	77
2856	17	1598	86	1256	77	984	68		
2839	31	1446	20	1247	81	937	79		



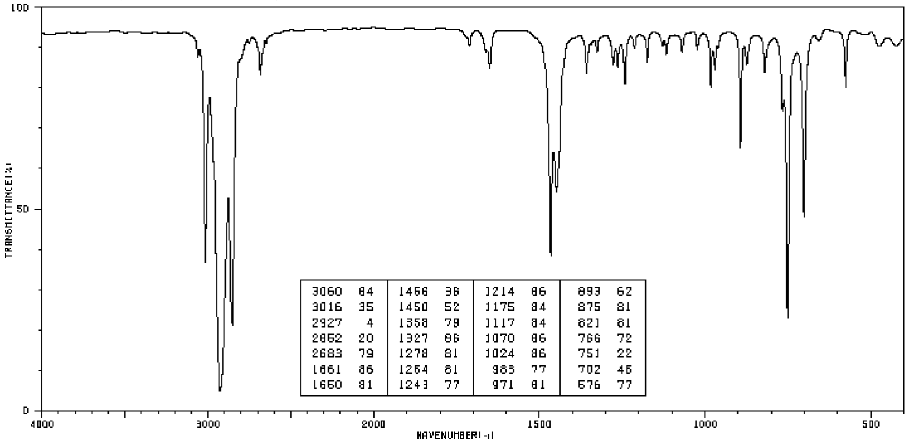
4. The following ^{1}H-NMR spectrum is of norbornylene. How many types of protons are present and label protons on the chemical structure as being the same or different. Make an educated guess as to which protons correspond to which signals. Explain your answer.





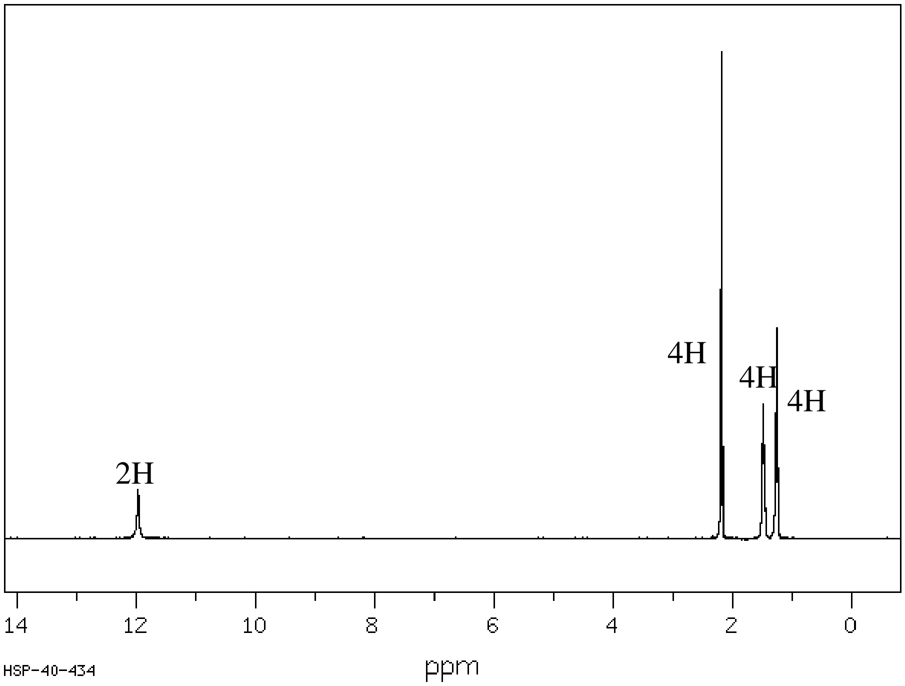
5. Compound **A** is treated with warm concentrated $KMnO_4$ to give compound **B**. Provide the structures of **A** and **B**. Explain how you arrived at your answer.

IR of **A** (F.W.=110.2)

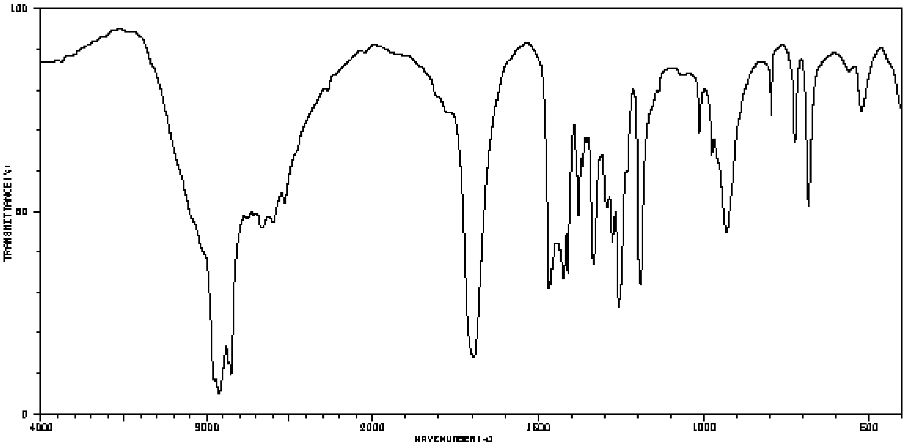


3060	84	1466	36	1214	86	893	62
3016	35	1450	52	1175	84	875	81
2927	4	1358	79	1117	84	821	81
2862	20	1327	86	1070	86	766	72
2683	79	1278	81	1024	86	751	22
1661	86	1264	81	985	77	702	46
1660	81	1243	77	971	81	676	77

^{1}H-NMR of **B** (F.W.= 174.2)

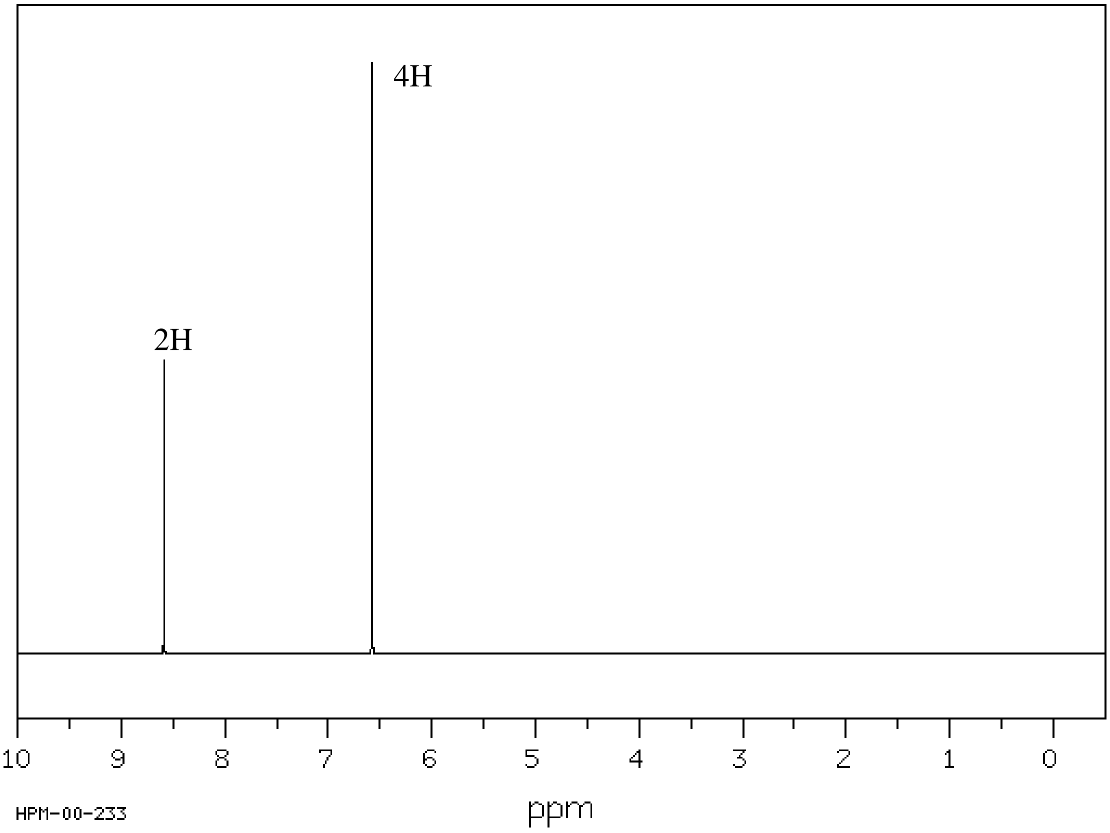


IR of **B**

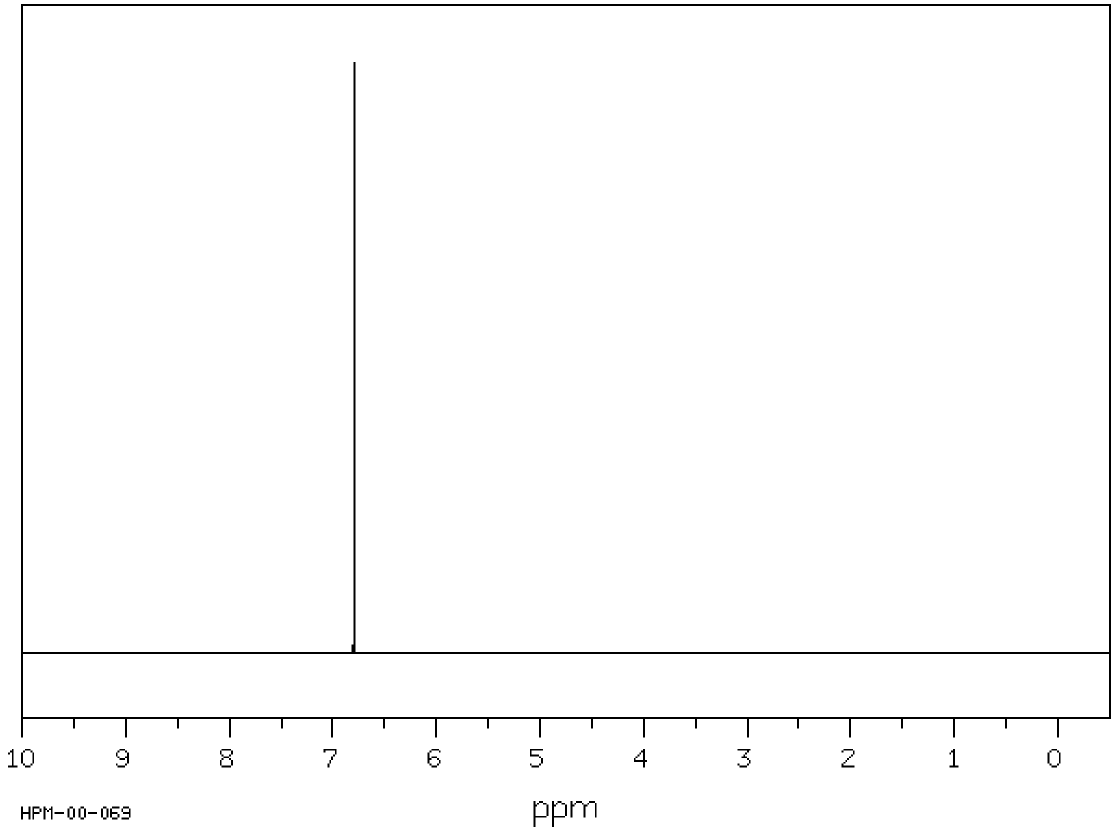


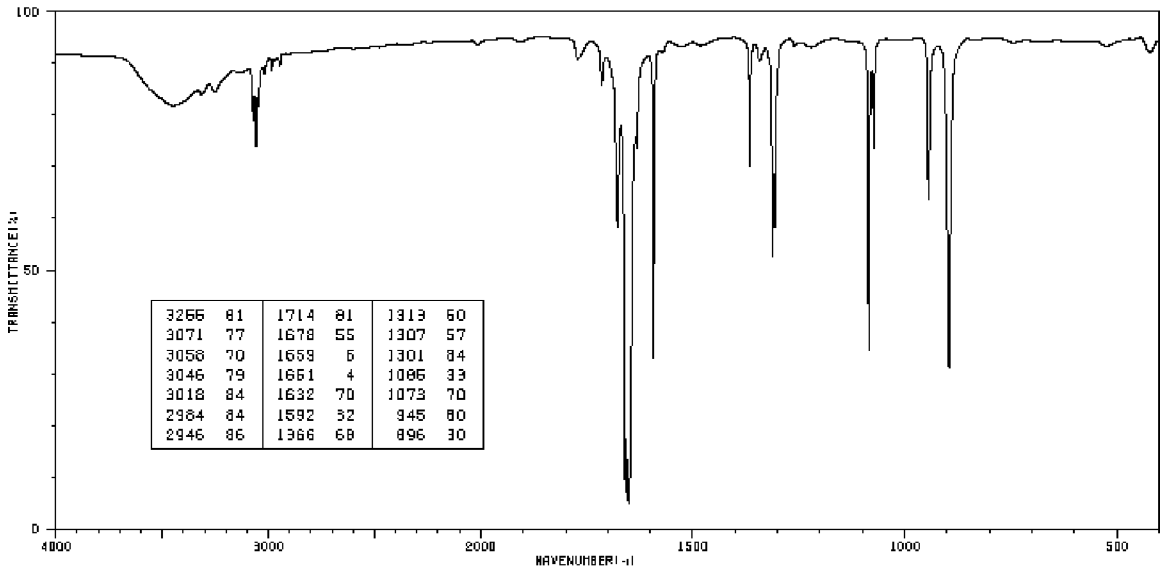
6. Aromatic compound **A** (F.W.= 110.1) is oxidized by $FeCl_3$ to give **B** (F.W. 108.1). Provide the structures of **A** and **B**. Explain how you arrived at your answer.

NMR of **A** (the signal at 8.6 ppm disappears with D_2O treatment).



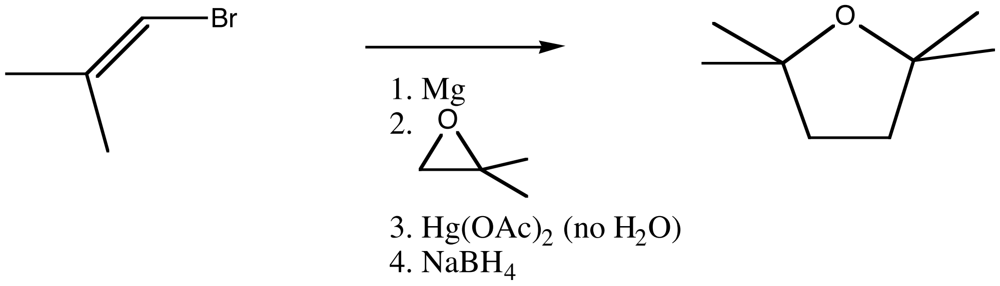
^{1}H-NMR and IR of **B**





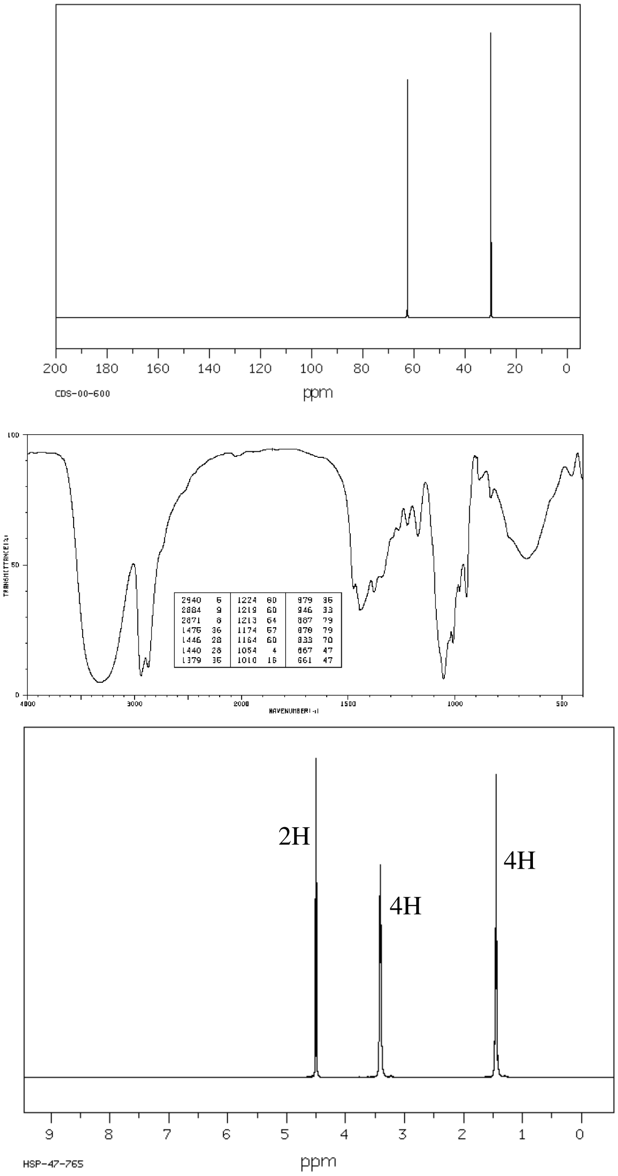
3266	81	1714	81	1313	60
3071	77	1678	55	1307	57
3058	70	1659	6	1301	84
3046	79	1651	4	1086	33
3018	84	1632	70	1073	70
2984	84	1592	32	945	80
2946	86	1366	68	896	30

3. Show all of the intermediates and the mechanism for each step in the following transformation.



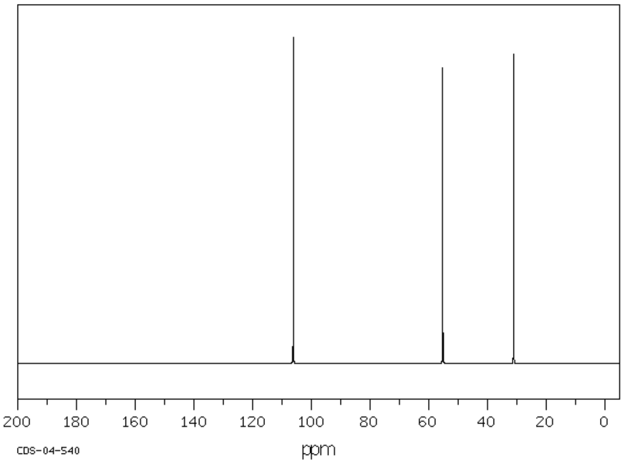
4. Compound A (F.W. = 90.1) is oxidized by pyridinium chlorochromate (PCC) in CH_2Cl_2 to give compound B (F.W. = 86) which is then treated sequentially with CH_3ONa, and CH_3I to give compound C (F.W. = 132.2) with the spectra shown and a proton NMR of 4.5 (2H, t); 3.5 (6H, s), 1.35 (4H, m). Propose structures for A, B, and C and detail the reactions. Explain your structural assignment.

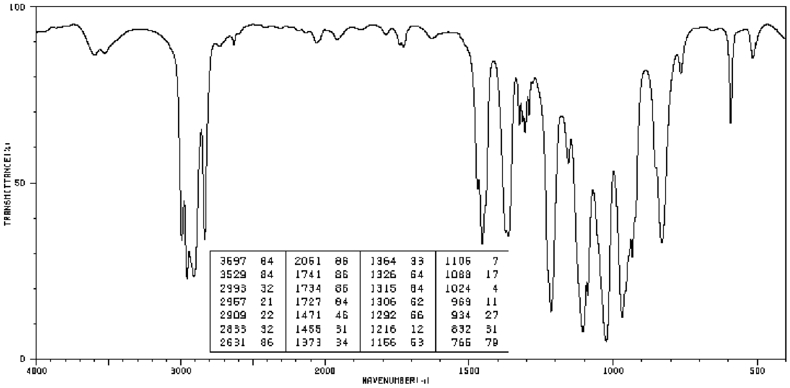
IR, ^{13}C-NMR (decoupled), ^{1}H-NMR of Compound A.



2940	5	1224	60	979	36
2884	9	1219	60	946	33
2871	8	1213	64	887	79
1475	36	1174	57	878	79
1446	28	1164	60	833	70
1440	28	1054	4	667	47
1379	36	1010	16	661	47

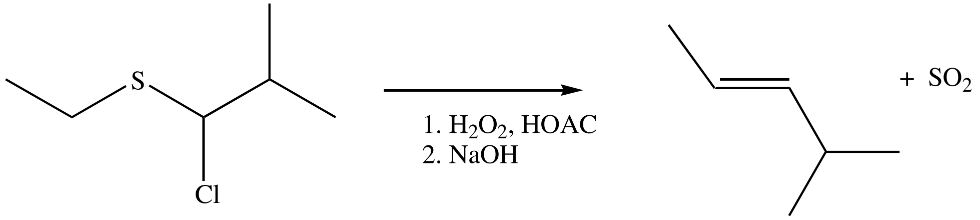
4. cont.
IR, ^{13}C-NMR (decoupled) of Compound C



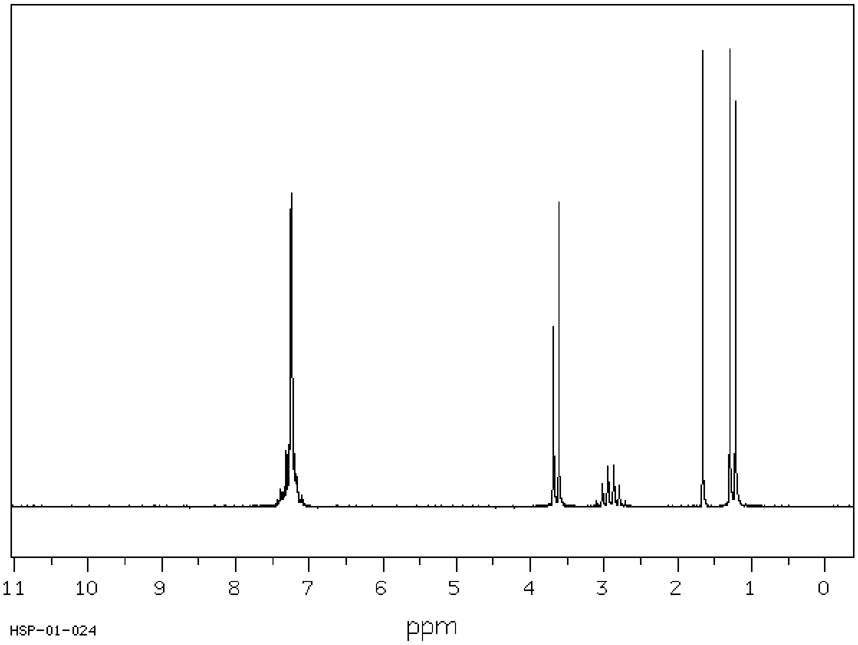


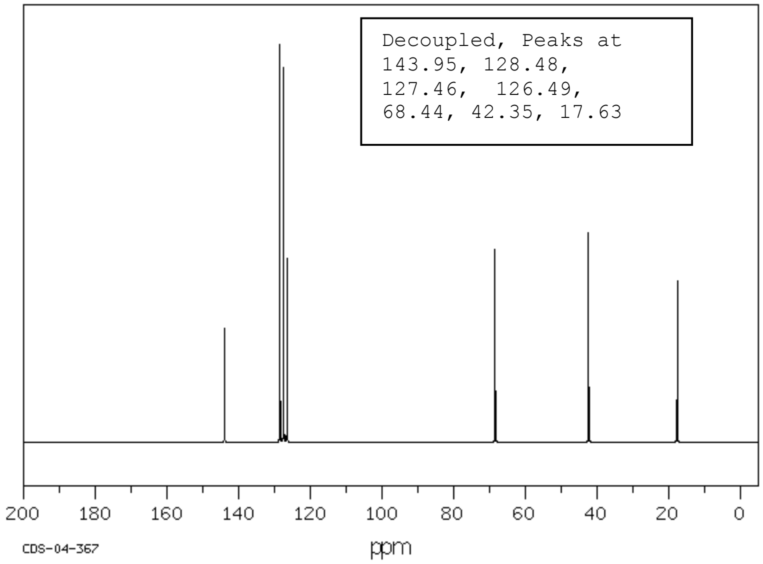
3697	84	2061	86	1364	33	1106	7
3529	84	1741	86	1326	64	1088	17
2993	32	1734	86	1315	84	1024	4
2967	21	1727	84	1306	62	969	11
2909	22	1471	46	1292	66	934	27
2833	32	1455	31	1216	12	832	31
2631	86	1373	34	1166	63	766	79

5. Give a detailed mechanism for the following reaction.



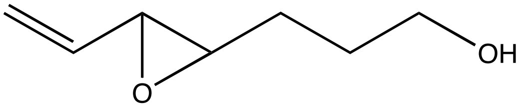
6. The following spectra are from a compound that is produced by the product of the acid catalyzed reaction with benzene and the epoxide formed from propene. Propose a structure, provide a detailed reaction mechanism, and assign the NMR signals to the best of your ability.




Decoupled, Peaks at 143.95, 128.48, 127.46, 126.49, 68.44, 42.35, 17.63

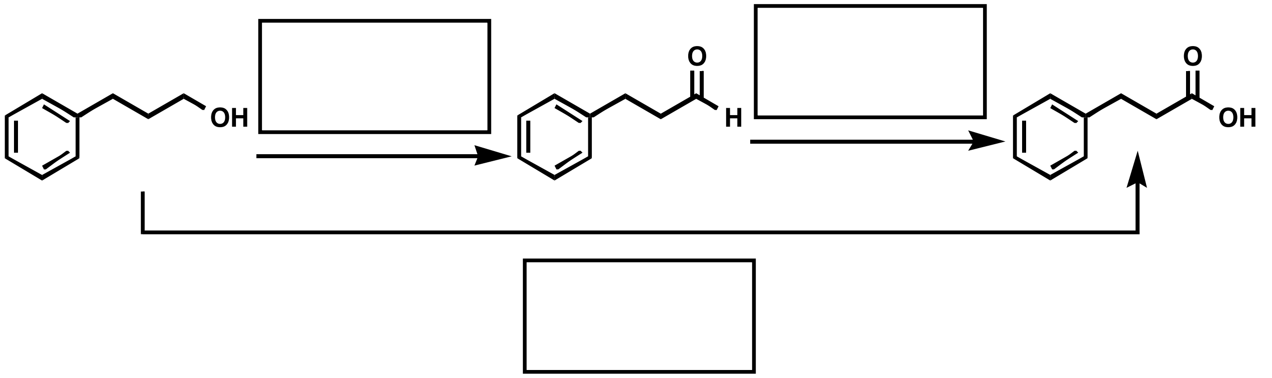
cts

2. Consider the TsOH and LDA initiated reactions of this epoxide under anhydrous conditions. Give the potential products and detailed mechanisms for both and show detailed stereochemistry with all absolute assignments (i.e. R or S).



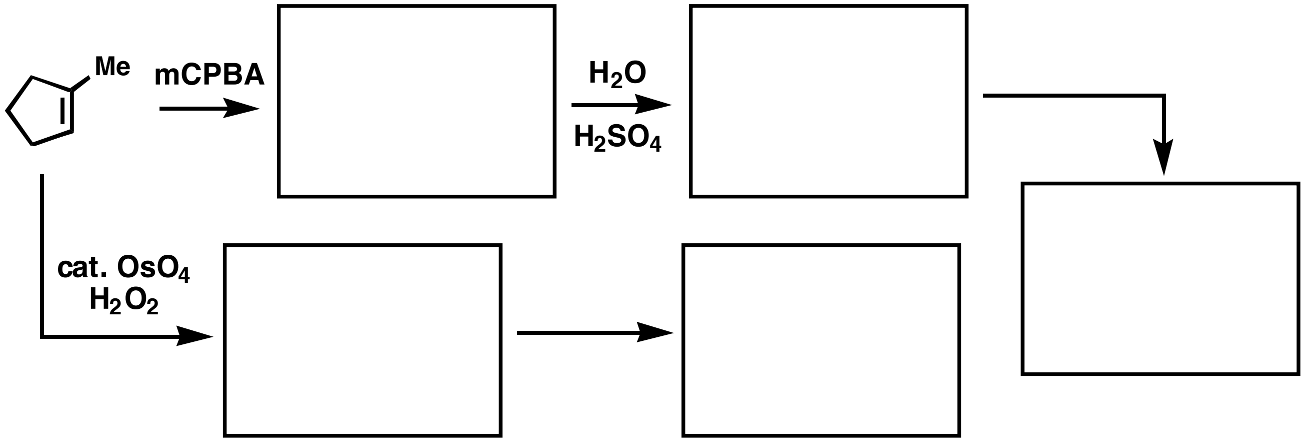
1. **(12 points, 1 point per box)** In the boxes below, write the **product** of the reaction indicated or the **reagent or reagents (e.g. not "Jones Reagent")** required for the transformations shown. Where relevant, **clearly** indicate **stereochemistry**. If no reaction occurs, write **"no reaction"** in the box.

a.

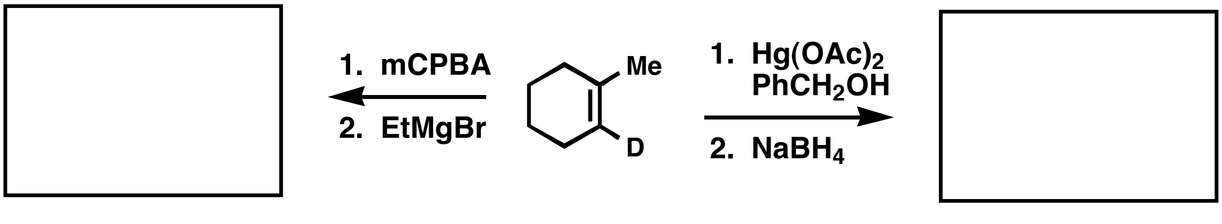


b.

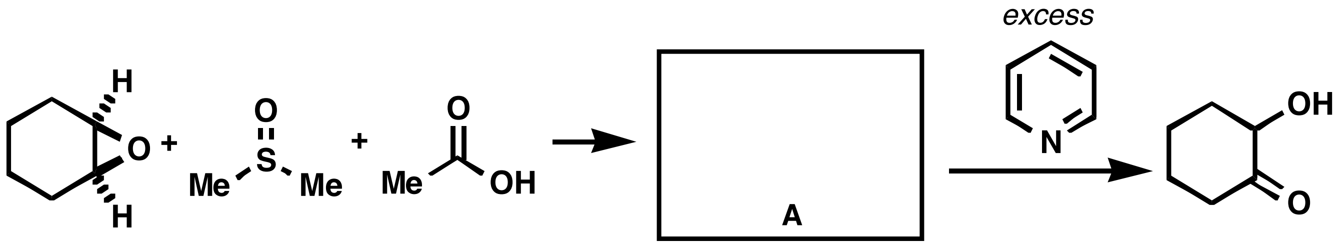
c.



d.



2. (20 points) In the reaction shown below, an epoxide is converted to a hydroxyketone in two steps. Write the structure of the epoxide-derived product of the first reaction (compound **A**) in the box below. In the space below the reaction, **clearly** write an arrow-pushing mechanism for **both steps** (i.e. starting materials –> compound **A** –> products). Clearly draw all **intermediates** and **reaction by-products** in your mechanism.



3. (**36 points, 6 points each**) As part of a Ph.D. thesis, an MIT graduate student performed a reaction in the lab in which a foul-smelling organic molecule (compound **A**) was treated with **NaOH** and **CH_3I**, giving compound **B**, which had a slightly less offensive odor. Some of the spectral data for compound **B** are listed below. If applicable, **clearly** indicate the **geometry of all alkenes** (e.g. cis or trans). (MW of S = 32.06)

EA: **C, 67.69%; H, 6.49%; S, 25.82%**

MS: **$M^+ = 124$**

^{1}H NMR (ppm) **7.18 (2H, dd, *J* = 2, 8), 7.16 (2H, dd, *J* = 7, 8), 7.02 (1H, dd, *J* = 2, 7), 2.47 (3H, s)**

a. What is the molecular formula of compound **B**?

b. What is the "index of hydrogen deficiency" of compound **B**? (Hint: Treat sulfur as you would oxygen in such a calculation)

c. How many chemically nonequivalent **carbon** atoms does compound **B** have?

d. How many chemically nonequivalent **hydrogen** atoms does compound **B** have?

e. Draw the structure of compound **B**.

f. Draw the structure of compound **A** (the foul-smelling starting material).

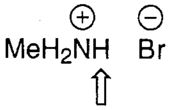
4. **(32 points)** In the box below, draw the structure of the unknown compound having **MF $C_{13}H_{16}O$** and the ^1H NMR data below. If applicable, **clearly** indicate the **geometry of all alkenes** (e.g. cis or trans).

^1H NMR (ppm) **7.54 (1H, d, J = 16), 7.30 (2H, dd, J = 2, 8), 7.21 (2H, dd, J = 7, 8), 7.14 (1H, dd, J = 2, 7), 6.67 (1H, d, J = 16), 1.21 (9H, s)**

Your proposed structure:

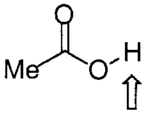
(1) (2 points each, 30 points total) Please provide the requested answer/data/reagents. If no reaction is expected, write "NR". Note: *n*-Bu = *n*-Butyl = -$CH_2CH_2CH_2CH_3$.

(a) pK$_a$ of:

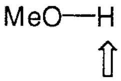


$\overset{\oplus}{MeH_2NH}\ \overset{\ominus}{Br}$

(b) pK$_a$ of:

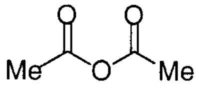


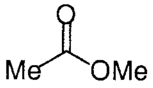
(c) pK$_a$ of:



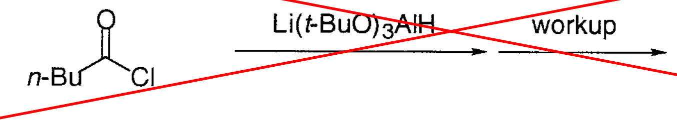
$MeO—H$

(d) Circle the compound that will react faster with Me_2NH:

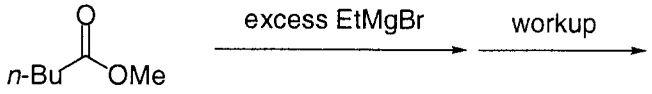




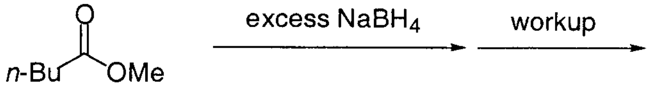
(e)



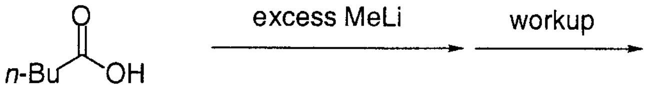
(f)



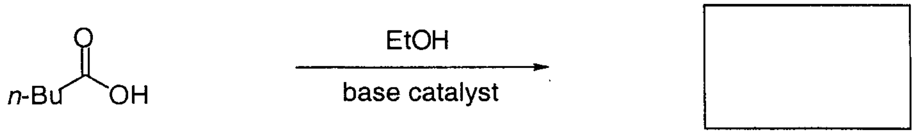
(g)



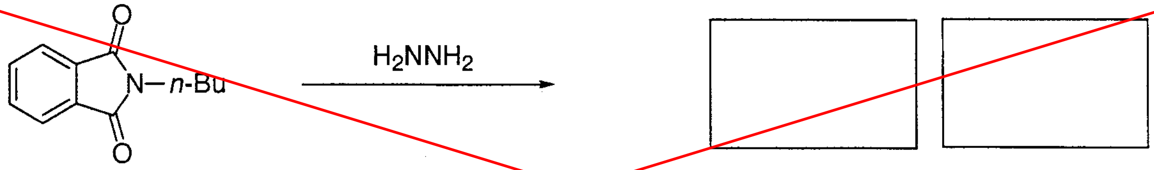
(h)



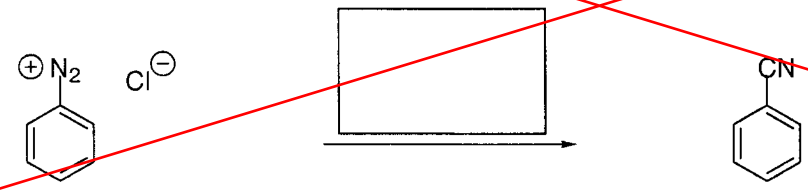
(i)



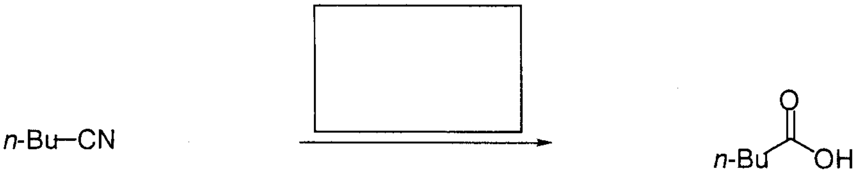
(j)



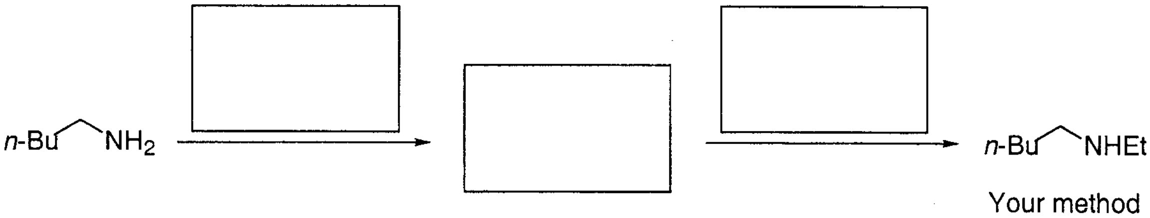
(k)



(l)

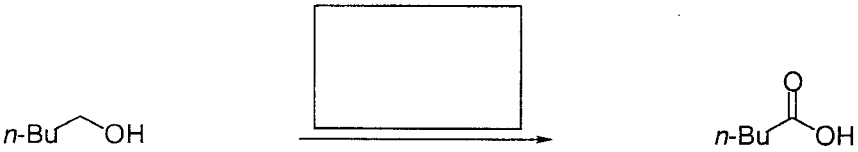


(m)

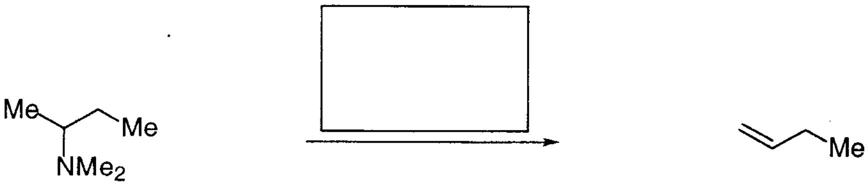


Your method should cleanly generate the secondary amine.

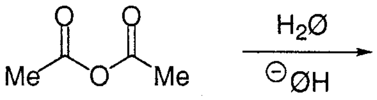
(n)



(o)



(2) (9 points) Consider the experiment outlined below:



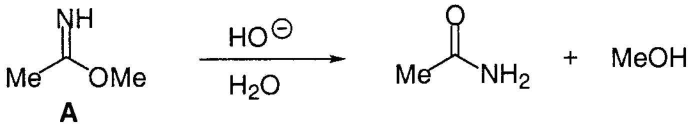
stop the reaction at 50% conversion
and examine the recovered anhydride
for incorporation of Ø

Ø = isotopically labeled oxygen

In analogy with the discussion in class regarding the labeling studies of acid chloride, amides, etc., carefully explain what level ("high" or "low") of Ø incorporation you expect to observe in the recovered anhydride. Your explanation should include the mechanism for this hydrolysis reaction.

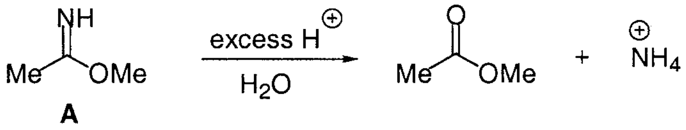
(3) (18 points total) Methyl acetimidate (**A**) is hydrolyzed in aqueous sodium hydroxide to (initially) give mainly acetamide and methanol (eq 1). In aqueous acid, **A** hydrolyzes to (initially) give primarily methyl acetate and the ammonium ion (eq 2).

(a) (7 points) Write a detailed mechanism for the illustrated process. Please show all arrow pushing.



(1)

(b) (7 points) Write a detailed mechanism for the illustrated process. Please show all arrow pushing.

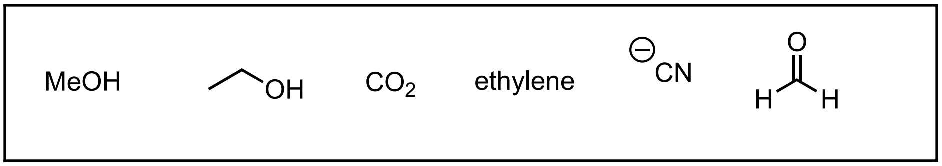


(2)

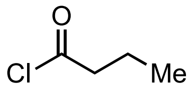
(c) (4 points) Briefly explain why the two reactions provide different products.

Synthesize the indicated compounds from the allowed starting materials shown below. All of the carbons of the target compounds should be derived from the allowed starting materials.

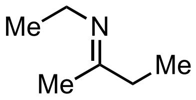
Allowed starting materials



(a)

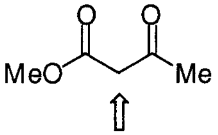


(b)



(10) (2 points each, 42 points total) Please provide the requested answer/data/reagents. If no reaction is expected, write "NR".

(a) pK$_a$ of:



~~(b) pK$_a$ of:~~ ~~$MeH_2\overset{\oplus}{N}H \quad \overset{\ominus}{Br}$~~

⇧

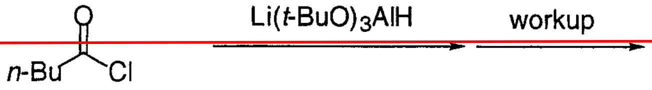
(c) pK$_a$ of: MeO—H

⇧

~~(d) Inversion barrier of NMe$_3$, in kcal/mol (circle one): 5 20 50 100~~

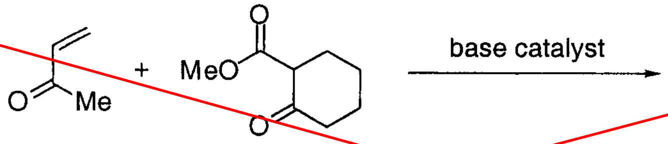
(e) The most stable radical (circle one): $Me{-}\dot{C}H_2$ $Me{-}\dot{N}H$ $Me{-}\dot{O}$

~~(f)~~

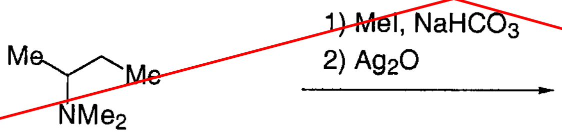


(g) $n\text{-}Bu{-}CN \xrightarrow{LiAlH_4} \xrightarrow{workup}$

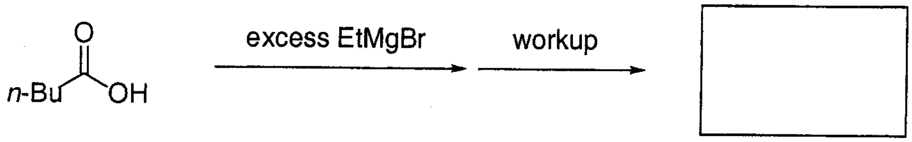
~~(h)~~



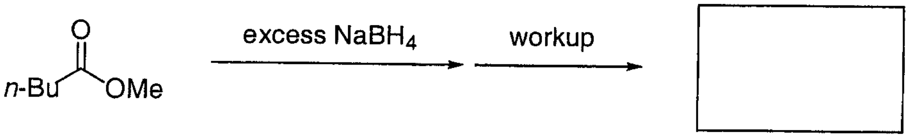
~~(i)~~



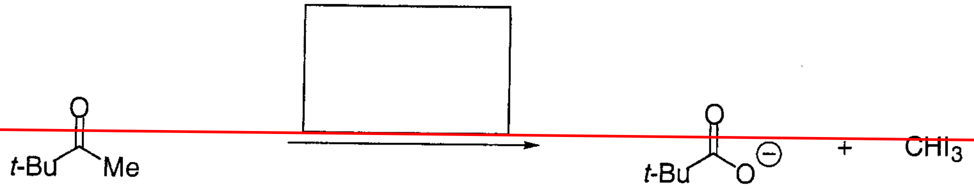
(j)


O
n-Bu
OH
excess EtMgBr
workup

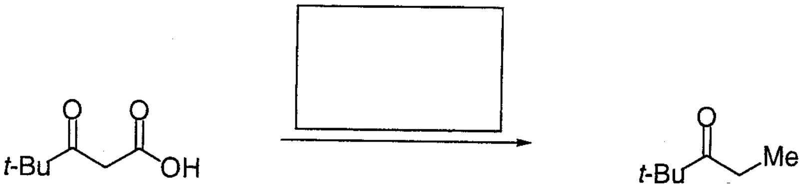
(k)


O
n-Bu
OMe
excess NaBH4
workup

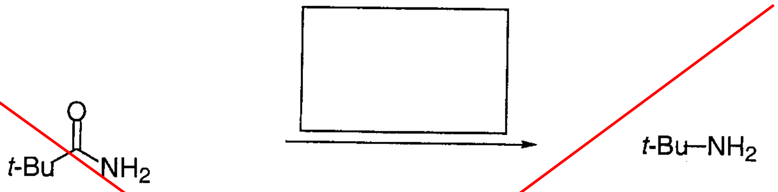
~~(l)~~


O
t-Bu
Me
O
t-Bu
O⊖
+
CHI3

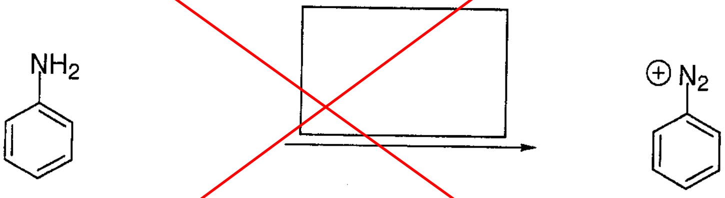
(m)


O
O
t-Bu
OH
O
t-Bu
Me

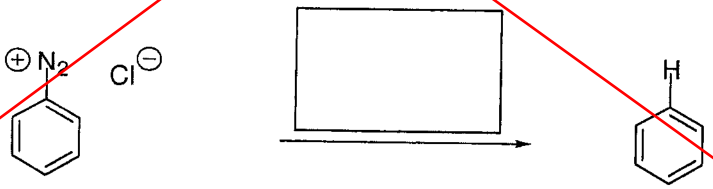
~~(n)~~


O
t-Bu
NH2
t-Bu–NH2

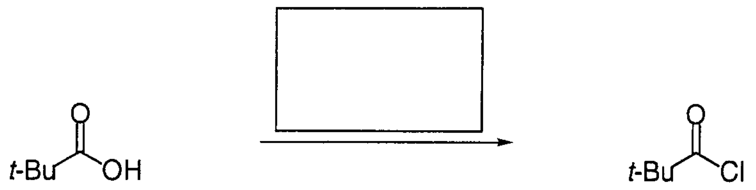
~~(o)~~


NH2
⊕ N2

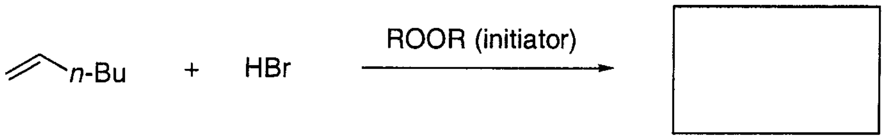
~~(p)~~


⊕ N2
Cl⊖
H

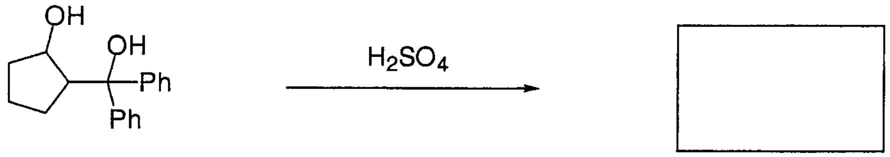
(q)



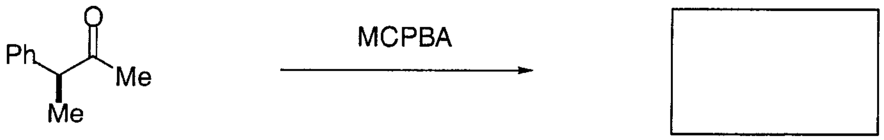
(r)



(s)



(t)



(u) $n\text{-Bu—Br} \quad + \quad \text{HSnBu}_3 \xrightarrow{\text{AIBN (initiator)}} \boxed{}$

(11) (12 points) Provide the best mechanism. Please show all arrow pushing.