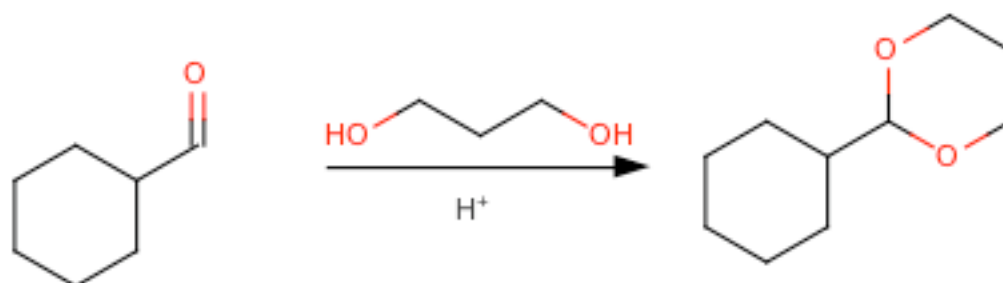


1. (5 pts. each, 20 pts. total.) Draw the *major* product of each of the following reactions, including the stereochemistry, if appropriate. Assume aqueous workup in each case, so your product should be neutral and should not contain any metals. **Do not draw mechanisms!**

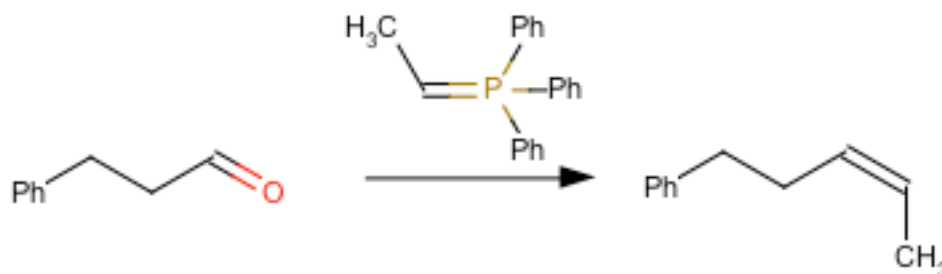
(a)



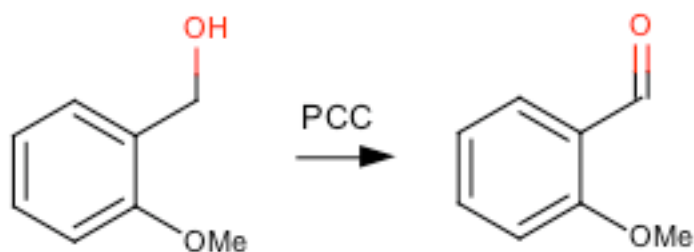
(b) Count your C atoms carefully on this one.



(c)



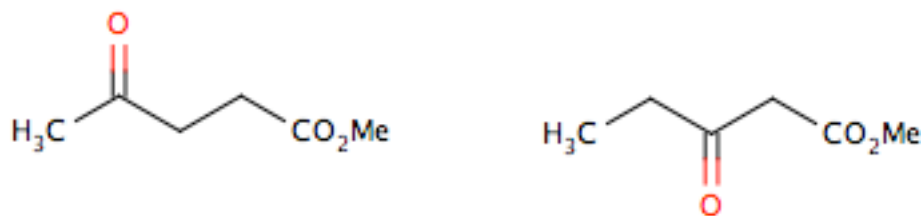
(d)



2. (5 pts. each, 25 pts. total.) Your summer job is to clean up an organic chemistry laboratory after a flood has partially destroyed the labels on many of the bottles. In each problem below, **choose a method** for distinguishing the two possibilities by MS, IR, ^1H NMR, or ^{13}C NMR, and precisely **describe one feature** of the spectrum (or the absence of a feature) that will allow you to identify the sample unambiguously.

Common Error Alert: Your response should tell me what you see in the *spectrum* of the compound. Don't write, "The ^1H NMR spectrum of compound 1 will show the CH_3 at δ 2.5–4.5, but the spectrum of compound 2 will not." A spectrum does not show a CH_3 . It shows resonances, absorbances, or peaks. A good response would be, "The ^1H NMR spectrum of compound 1 will show a resonance integrating to 3 H at δ 2.5–4.5, but the spectrum of compound 2 will not."

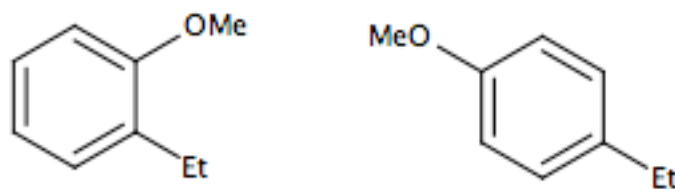
(a) Bottle 1 contains one of the following:



Method for distinguishing: ^1H NMR is best

Difference: Compound on left would show a singlet of 3 H and two triplets of 2 H; compound on right would show a singlet of 2H, a triplet of 3H, and a quartet of 2H.

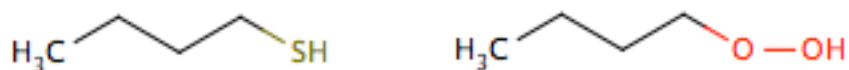
(b) Bottle 2 contains one of the following:



Method for distinguishing: ^1H or ^{13}C NMR

Difference: ^1H NMR: Compound on left would show four aromatic resonances; compound on right would show only two. ^{13}C NMR: Compound on left would show six aromatic resonances; compound on right would show only four.

(c) Bottle 3 contains one of the following:



Method for distinguishing: ^1H NMR or IR

Difference: ^1H NMR: Compound on right would show a resonance much further downfield (4 ppm?) than compound on left (2.5 ppm?). IR: Compound on right would show an absorbance at 3500 cm^{-1} ; compound on left would show an absorbance elsewhere.

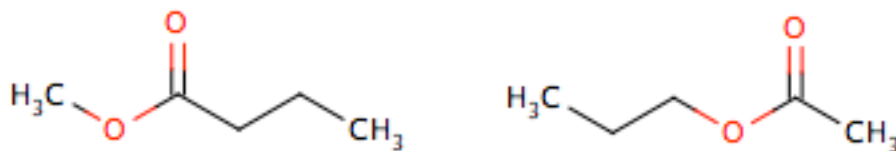
(d) Bottle 4 contains one of the following:



Method for distinguishing: MS, ^1H NMR

Difference: Compound on left would show a molecular ion at 128 amu; compound on right would show one at 130 amu. ^1H NMR: Compound on left would show only two resonances; compound on right would show three.

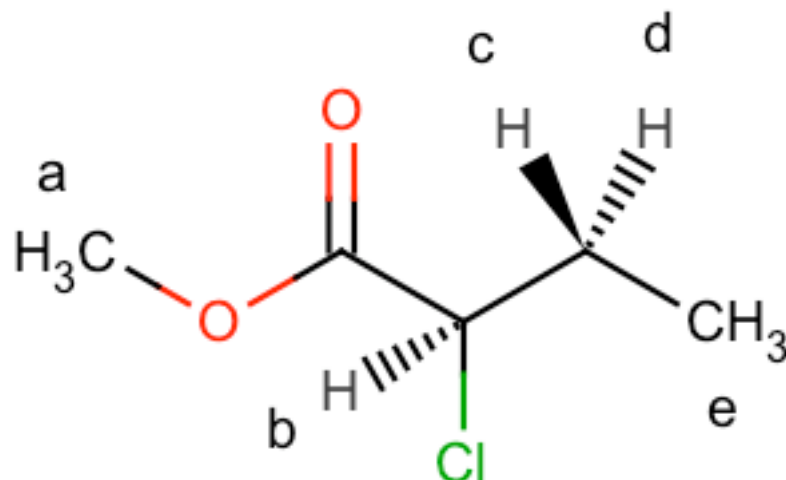
(e) Bottle 5 contains one of the following:



Method for distinguishing: ^1H NMR, ^{13}C NMR

Difference: ^1H NMR: Compound on left would have a singlet about 4.0 ppm; compound on right would have a singlet about 2.1 ppm. ^{13}C NMR: In compound on right, resonance about 60 ppm would be a quartet in the ^1H -coupled spectrum; in compound on left, it would be a triplet.

3. (20 pts. total) Draw in all of the H atoms in the following compound.

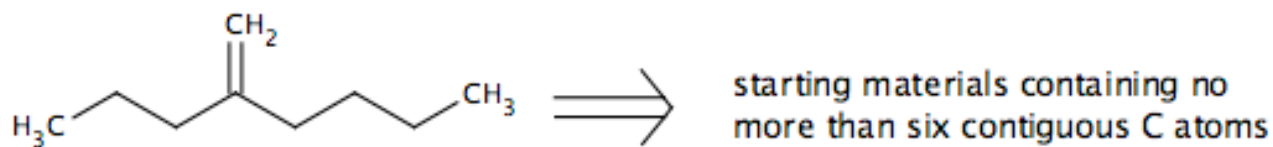


(a) (5 pts.) Label equivalent H atoms with the same letter and inequivalent H atoms with different letters, as we did in class.

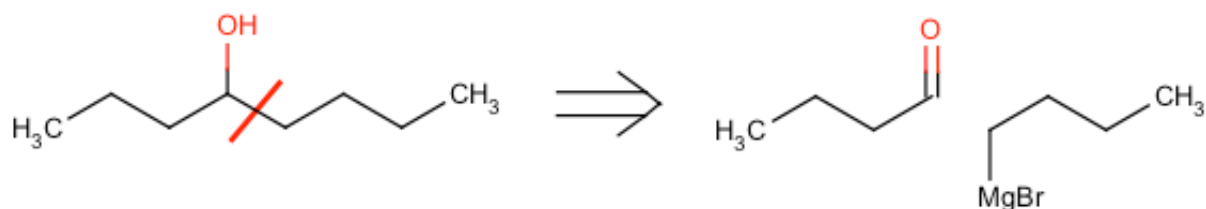
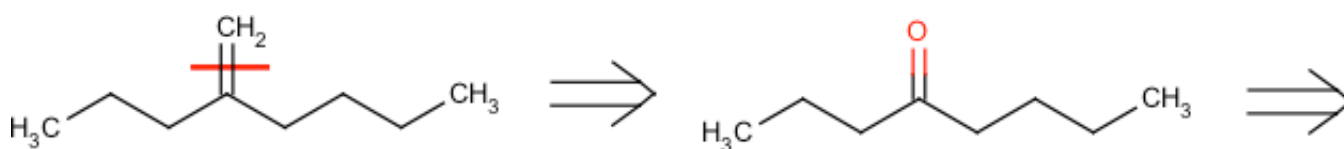
(b) (15 pts.) Predict the ^1H NMR spectrum of the compound, indicating the *approximate* chemical shift, integration, and multiplicity for each resonance that you expect to see. You can find a table of ^1H NMR chemical shifts at the front of this exam.

Type of H	δ (in ppm)	Integration	Multiplicity
a	3.8	3	s
b	3.5	1	dd
c	1.2	1	ddq
d	1.3	1	ddq
e	0.9	3	dd

4. (15 pts. total.) Design a synthesis of the following compound from the given starting materials. The synthesis will require more than one step. Show each intermediate compound and all reagents you will need for each step. (Don't panic if you can't remember the reagents for a particular step; partial credit will be given.) There may be more than one correct answer. **Do not show mechanisms. You are strongly advised to do a retrosynthetic analysis before drawing the synthetic sequence in the forward direction.**



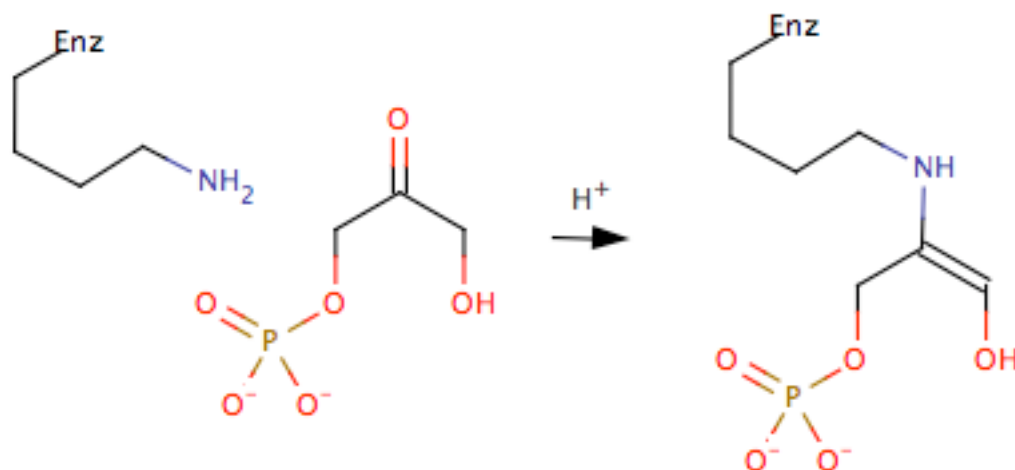
Retro:



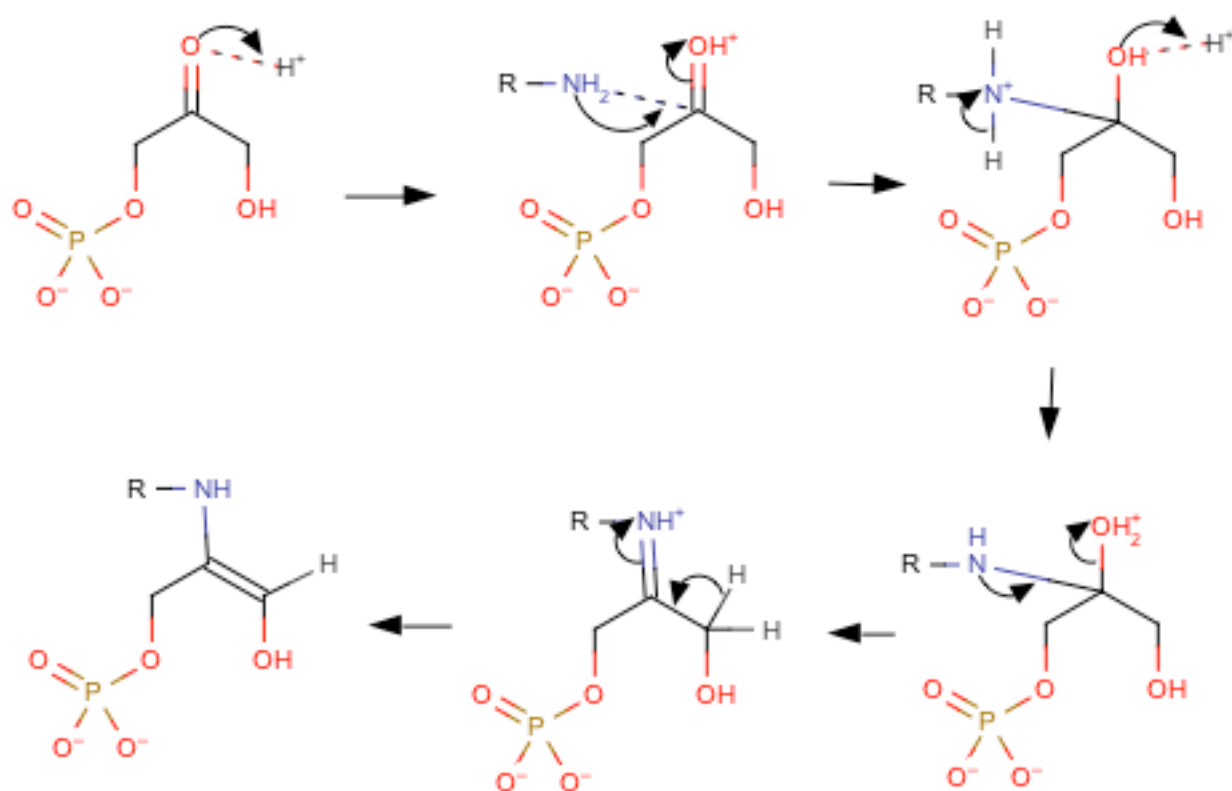
Forward:

Use PCC to oxidize the alcohol to the ketone. Use $\text{Ph}_3\text{P}=\text{CH}_2$ to make the alkene.

5. (15 pts.) An enzyme called aldolase converts two three-carbon sugars, dihydroxyacetone phosphate (DHP, shown below) and glyceraldehyde-3-phosphate (not shown), into the six-carbon sugar fructose-1,6-diphosphate (not shown). The first step in this C–C bond-forming reaction is to convert DHP into an enamine. The enzyme uses the $(\text{CH}_2)_4\text{NH}_2$ side chain of a lysine residue and an H^+ in the enzyme's bonding pocket to convert the ketone into an enamine.

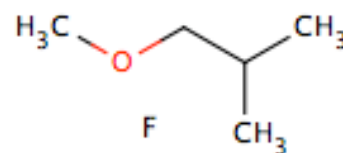
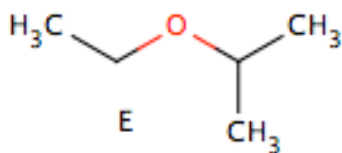
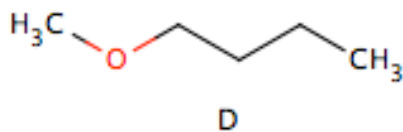
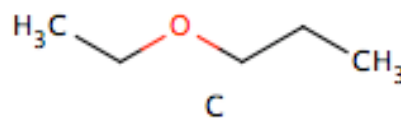
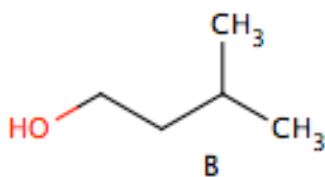
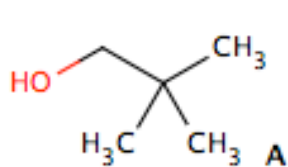
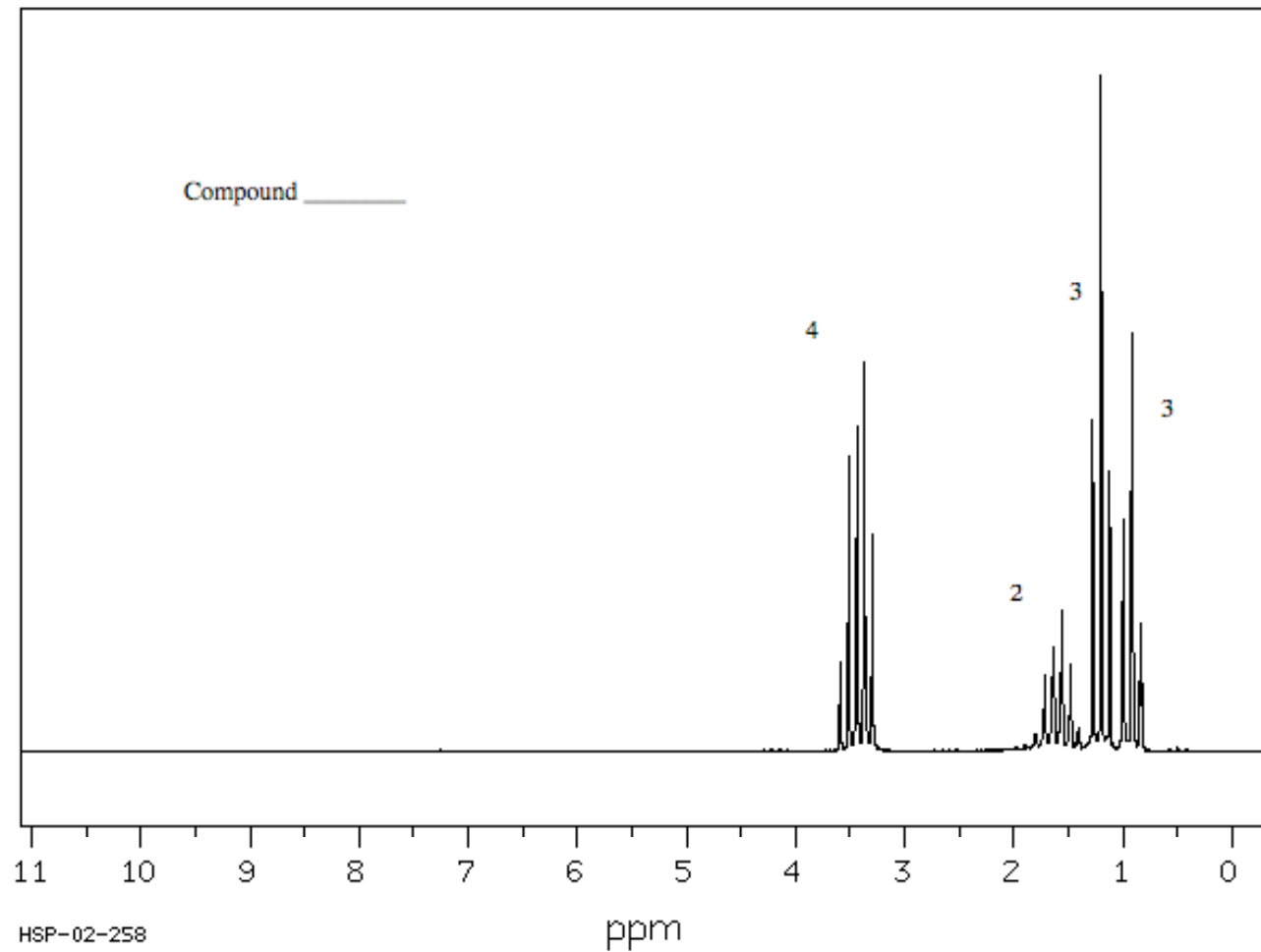


Draw a reasonable mechanism for this reaction. Use the conventional curved arrows to show the movement of electrons in each step. **You are strongly advised to obey Grossman's rule.**

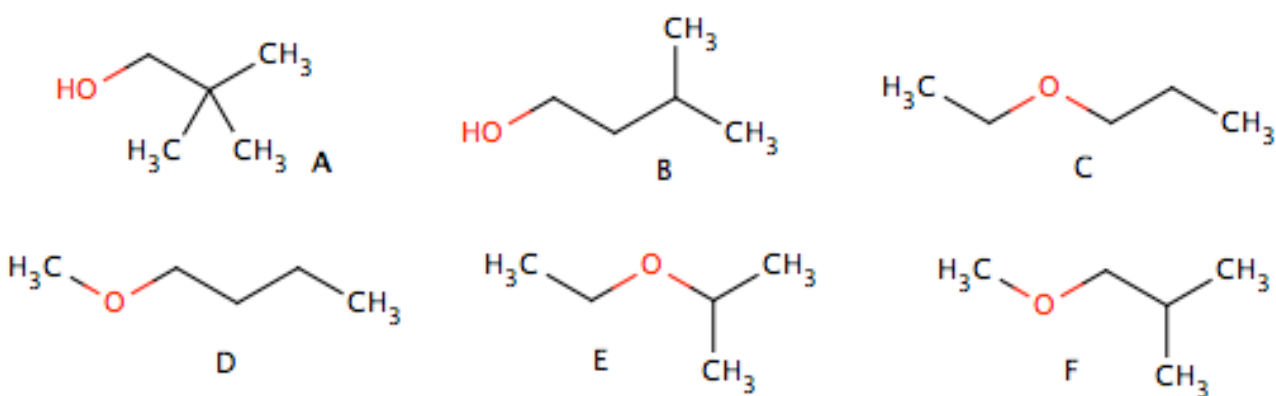
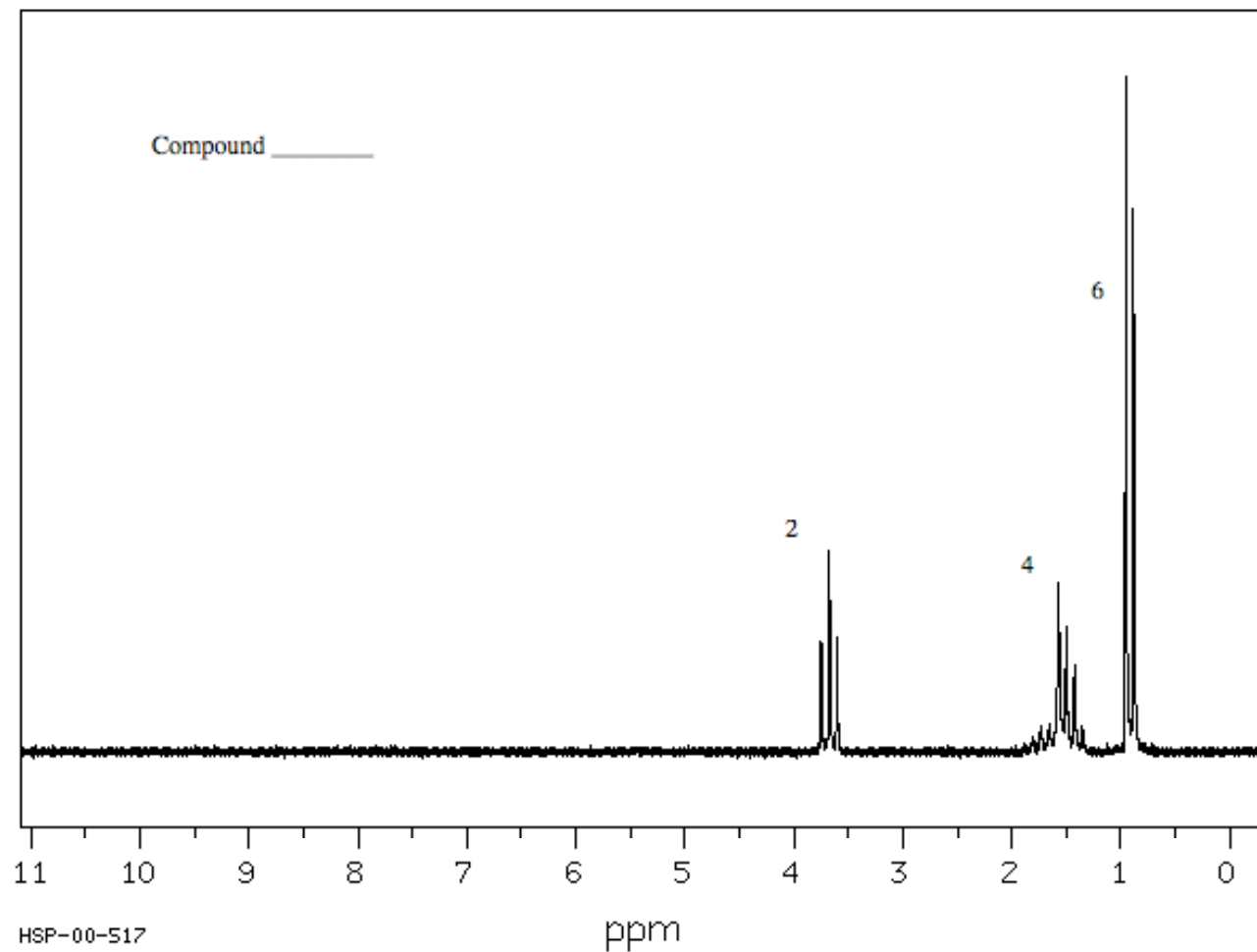


6. (5 pts. each, 10 pts. total) Indicate which of the compounds below each ^1H NMR spectrum gives rise to the spectrum. The integrations are given by the numbers next to each resonance.

(a) Compound C is the only one that shows four H atoms on the C atoms attached to the O.



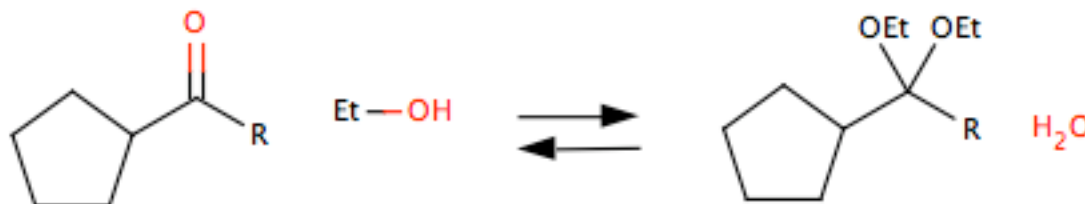
(b) The upfield doublet of 6 H indicates an isopropyl group, so must be B, E, or F. Of these, only B would have only two H atoms in the downfield region of the spectrum.



(This is the same set of compounds as in (a).)

7. (5 pts. each, 15 pts. total) Explain each of the following observations in one or two coherent, grammatically correct English sentences free of misspellings. Feel free to draw pictures to illustrate your explanations.

(a) The equilibrium constant of the reaction below is *smaller* when $R = \text{CH}_3$ than when $R = \text{H}$.

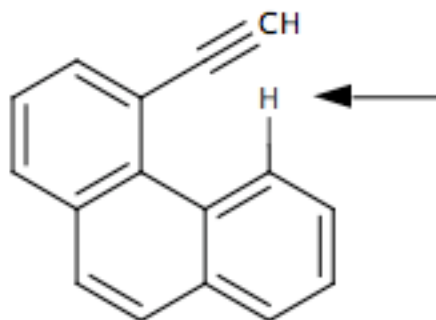


Ketones are lower in energy than aldehydes because the $\overset{+}{\text{C}}-\bar{\text{O}}$ resonance structure is more stabilized the more substituted the $\overset{+}{\text{C}}$, whereas the acetals derived from ketones and aldehydes are about the same energy.

(b) The reaction shown in part(a) works well in either direction under acidic conditions, but not under basic conditions.

The formation of the acetal requires a substitution of RO for HO in the hemiacetal intermediate. Under basic conditions, the substitution would have to proceed by the $\text{S}_{\text{N}}2$ mechanism, but this reaction is very slow for two reasons: the C atom is heavily substituted, and OH is a horrid leaving group under basic conditions. Under acidic conditions, the substitution can occur by the $\text{S}_{\text{N}}1$ mechanism. The intermediate carbocation is highly stabilized, and the HO can be protonated to give a much better leaving group.

(c) In the compound below, the indicated H atom appears considerably further *downfield* than the corresponding H atom in the compound that does not have the $C\equiv C$ triple bond.



The torus of electrons of the triple bond creates a magnetic field that enhances the applied magnetic field outside of it, deshielding the H atom shown.

END OF EXAM