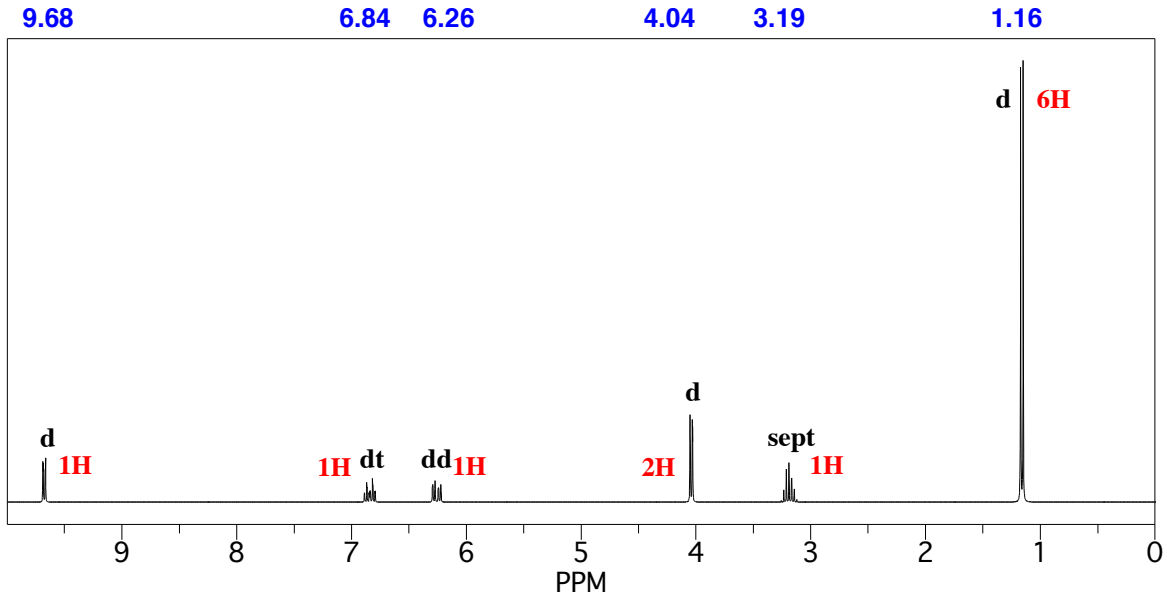
Chemistry 334R

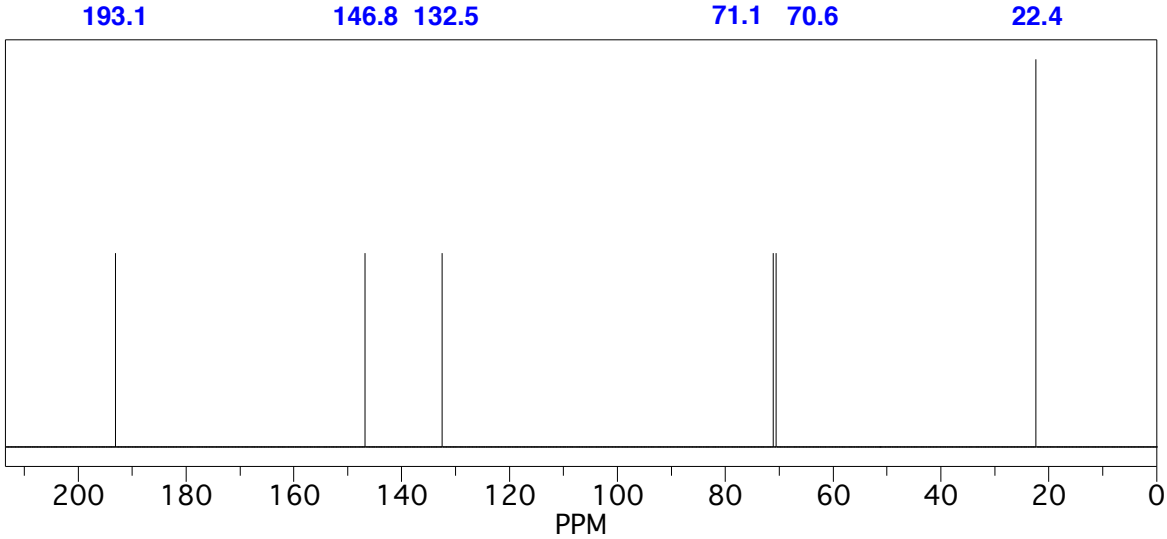
Problem Set 1

1. The ^{1}H and broadband proton-decoupled ^{13}C NMR spectra of compound A ($C_7H_{12}O_2$) are shown below. The labels next to each of the resonances in the ^{1}H NMR spectrum signify the integrals and multiplicities observed (d = doublet, dd = doublet of doublets, dt = doublet of triplets, sept = septet.) DEPT 90 and DEPT 135 data are included in the table on the following page. Use this spectroscopic evidence to determine the identity of the compound. Make clear assignments of all resonances to explain your reasoning.

^{1}H:



broadband proton-decoupled ^{13}C:



3. (continued)

^{1}H NMR assignments:

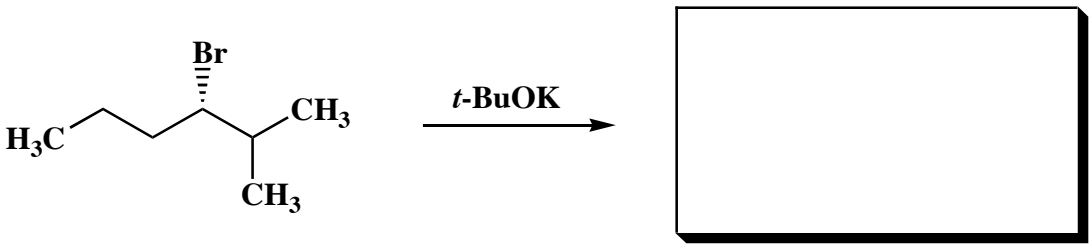
chemical shift (ppm)	assignment	explanation of multiplicity
9.68		
6.84		
6.26		
4.04		
3.19		
1.16		

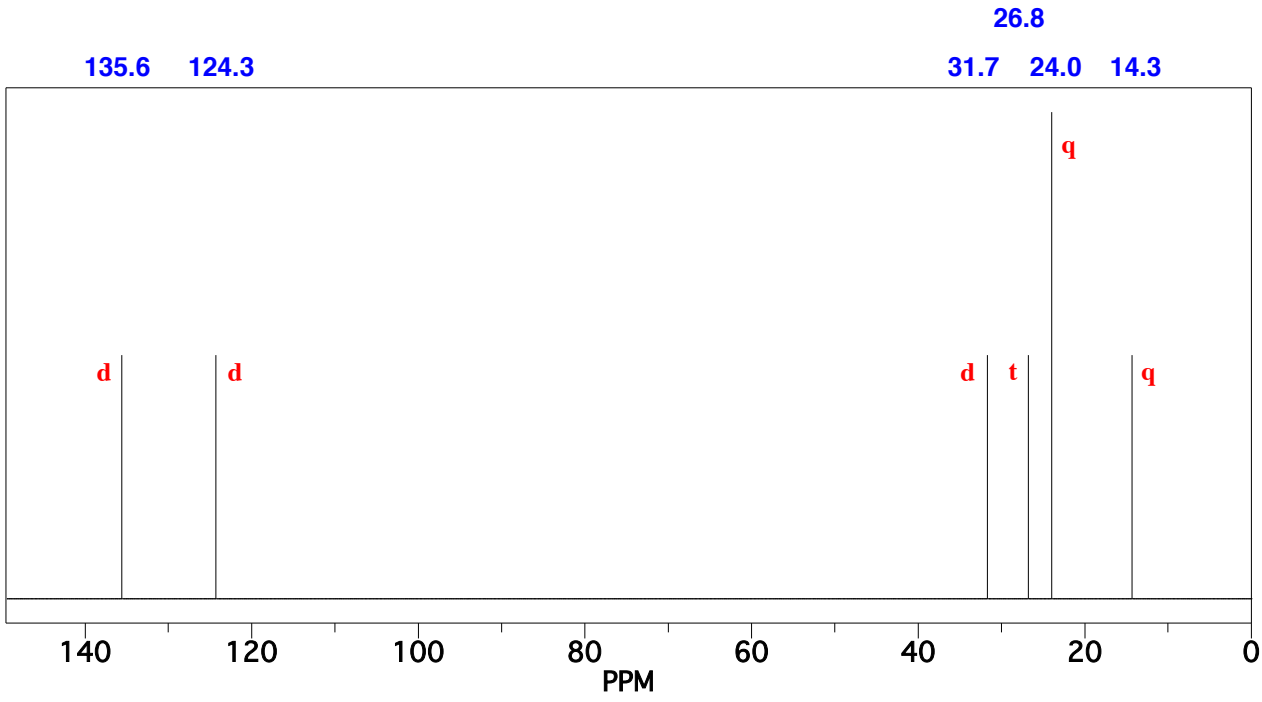
^{13}C NMR assignments:

chemical shift (ppm)	assignment	DEPT 90	DEPT 135	DEPT explanation
193.1		present	up	
146.8		present	up	
132.5		present	up	
71.1		absent	down	
70.6		present	up	
22.4		absent	up	

2. Draw the major organic product that is formed from the following reaction. The broadband proton-decoupled ^{13}C NMR spectrum of the product is shown below. The labels next to each of the resonances signify the multiplicities observed in the corresponding off-resonance proton-decoupled ^{13}C NMR spectrum (d = doublet, t = triplet, q = quartet). Use this spectroscopic evidence to determine the identity of the compound. Make clear assignments of all resonances to explain your reasoning.

   Draw all the possible alternative products that are mechanistically reasonable. Describe how the spectroscopic data rules out each of these compounds as the actual product.



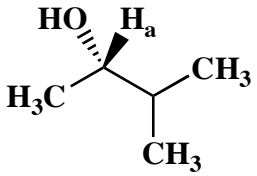


^{13}C NMR assignments:

chemical shift (ppm)	assignment	explanation of multiplicity
135.6		
124.3		
31.7		
26.8		
24.0		
14.3		

3. Label all the sets of chemically equivalent protons for both of the following two compounds. Then draw annotated tree diagrams for protons H_a and H_f. Specify, but do not quantify all the appropriate coupling constants in each tree diagram.

A.



B.