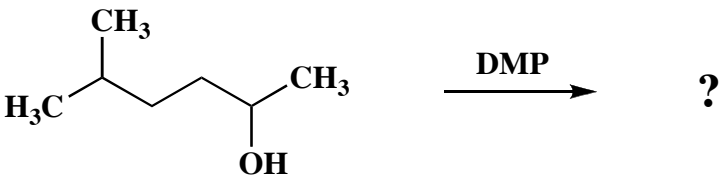
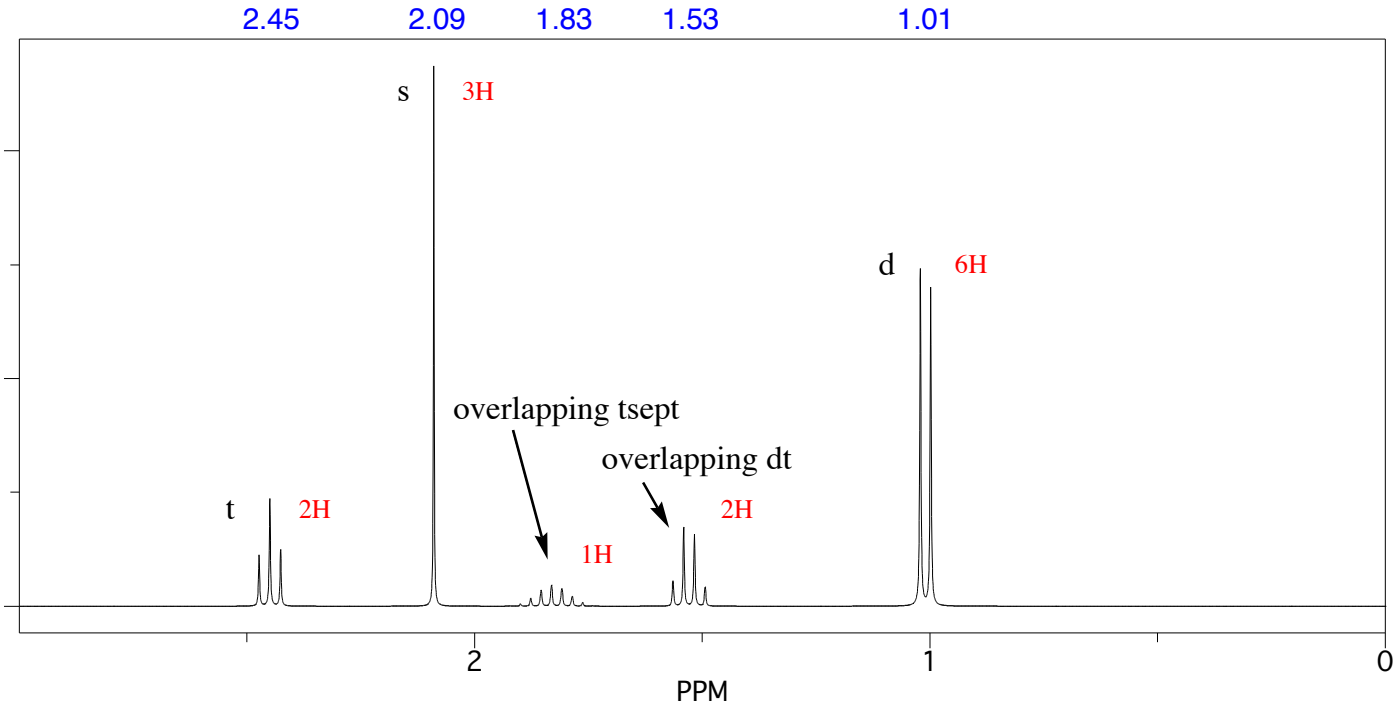
Chemistry 333 Discussion **Name:** _____

Problem Set 15

1. Draw the structure of the major organic product that is formed from the following reaction. Draw this structure in the box at the bottom of the next page. Then use letters to label all the sets of chemically equivalent protons in this structure. The ^{1}H NMR spectrum of the product is shown below. The labels next to each of the individual resonances signify the integrals and multiplicities observed in the spectrum (s = singlet, d = doublet, t = triplet, dt = doublet of triplets, tsept = triplet of septets). Use this spectroscopic data to make clear assignments of all the resonances and determine the identity of the product.

   See http://www.csun.edu/~hcchm007/333hnmr.pdf for a ^{1}H NMR correlation table.





^{1}H NMR assignments:

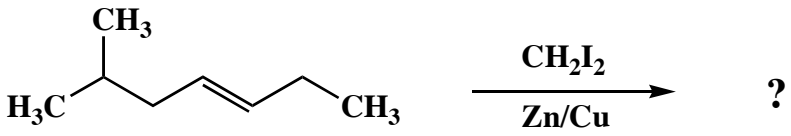
chemical shift (ppm)	assignment	explanation of multiplicity
2.45		
2.09		
1.83		
1.53		
1.01		

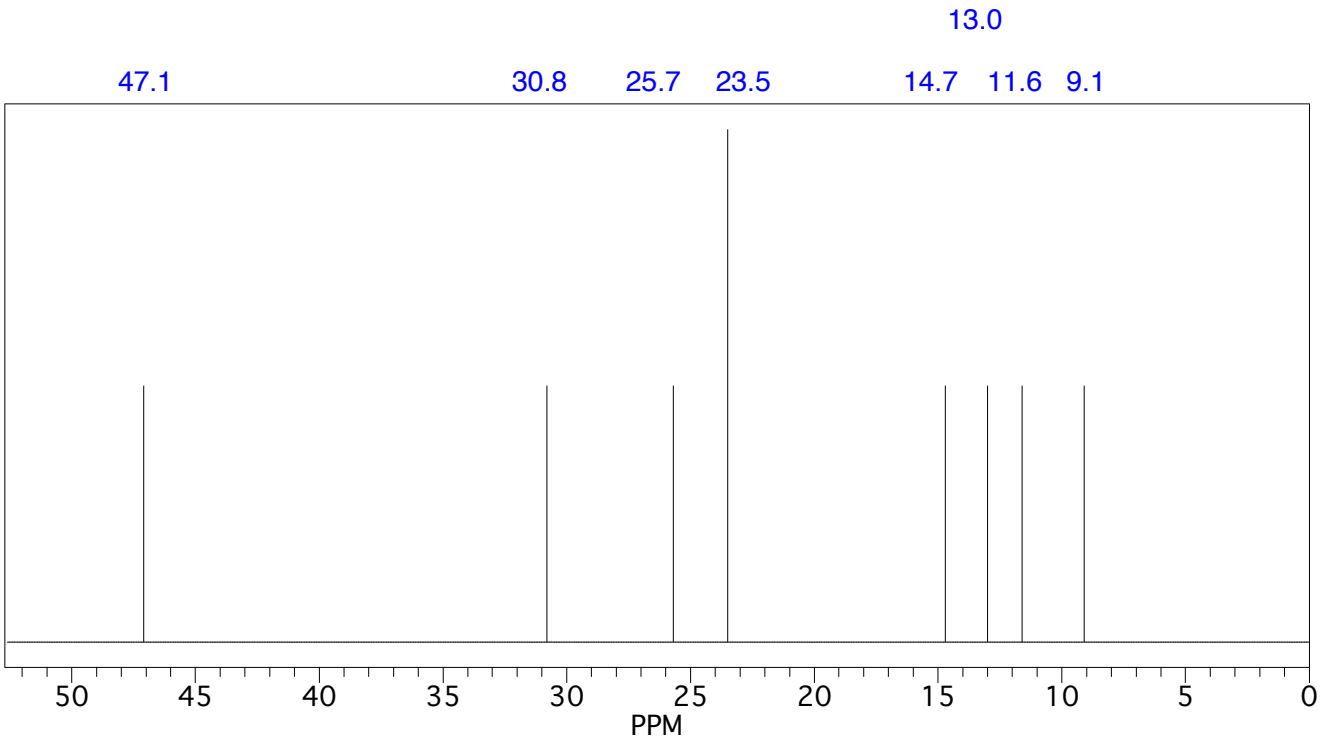
structure:

2. Draw the structure of the major organic product that is formed from the following reaction. Draw this structure in the box at the bottom of the next page. Then use letters to label all the sets of chemically equivalent carbons in this structure. The broadband proton-decoupled ^{13}C NMR spectrum of the product is shown below. DEPT 90 and DEPT 135 data are included in the table on the following page. Use this spectroscopic data to make clear assignments of all the resonances and determine the identity of the product.

Next, use the curved-arrow notation to draw the mechanism by which the product is formed. Show all lone pairs, nonzero formal charges, countercharges, and reversibility or irreversibility. Analyze this mechanism to predict whether or not the product is optically active. Then suggest a diastereomer that theoretically could have been formed. Finally, refer to the mechanism to explain in detail why the reaction forms the observed product with complete diastereoselectivity.

See http://www.csun.edu/~hcchm007/333cnmr.pdf for a ^{13}C NMR correlation table.





^{13}C NMR assignments:

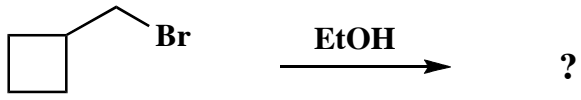
chemical shift (ppm)	assignment	DEPT 90	DEPT 135	DEPT explanation
47.1		absent	down	
30.8		absent	down	
25.7		present	up	
23.5		absent	up	
14.7		present	up	
13.0		absent	down	
11.6		absent	up	
9.1		present	up	

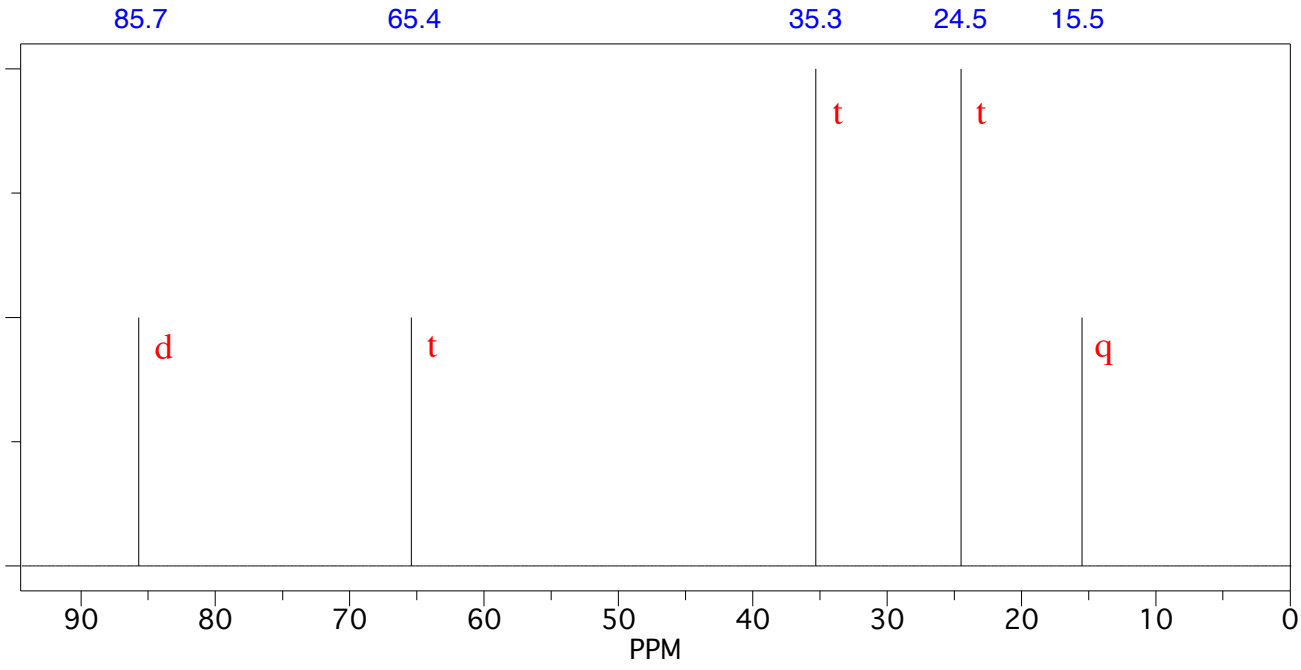
structure:

3. Draw the structure of the major organic product that is formed from the following reaction. Draw this structure in the box at the bottom of the next page. Then use letters to label all the sets of chemically equivalent carbons in this structure. The broadband proton-decoupled ^{13}C NMR spectrum of the product is shown below. The labels next to each of the individual resonances signify the multiplicities that are observed in the corresponding off-resonance proton-decoupled ^{13}C NMR spectrum (d = doublet, t = triplet, q = quartet). Use this spectroscopic data to make clear assignments of all the resonances and determine the identity of the product.

Next, use the curved-arrow notation to draw the mechanism by which the product is formed. Show all intermediates, lone pairs, nonzero formal charges, countercharges, and reversibility or irreversibility. Draw additional mechanisms to suggest two alternative structural isomers that theoretically could have been formed. Finally, explain in detail why the reaction forms the observed structural isomer selectively.

See http://www.csun.edu/~hcchm007/333cnmr.pdf for a ^{13}C NMR correlation table.





^{13}C NMR assignments:

chemical shift (ppm)	assignment	explanation of multiplicity
85.7		
65.4		
35.3		
24.5		
15.5		

structure: