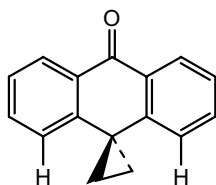
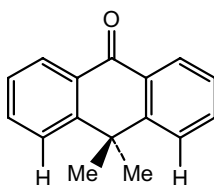


1. Explain why $\delta_b > \delta_a$ by 0.51 ppm for the indicated hydrogens.



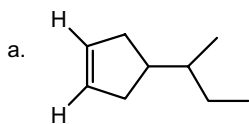
a



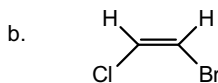
b

The region above and below the cyclopropane ring is shielding. The aromatic ring H's of "a" lie within this shielding cone, moving their signal upfield to a lower chemical shift.

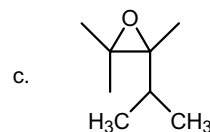
2. Label the indicated protons of the systems below as homotopic, enantiotopic, or diastereotopic. Don't worry about the protons not labelled explicitly.



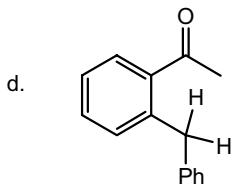
diastereotopic because of asymmetric center



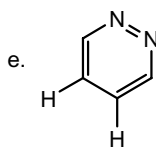
diastereotopic



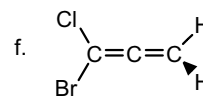
diastereotopic methyls because of asymmetric center



enantiotopic because the Z replacement structures are enantiomers

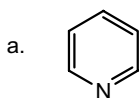


homotopic

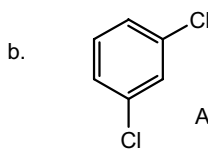


enantiotopic- the H's are reflected in a symmetry plane

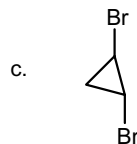
3. Write the spin notation (eg A_2X_2) for the C-H's (not the OH's or the NH's) of the following spin systems.



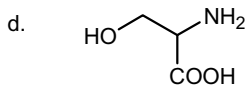
$AA'BB'C$ or better $AA'XX'Y$ because the 2-protons are much more downfield than the others



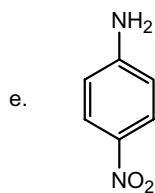
AB_2X or AB_2C



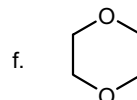
$AA'XX'$



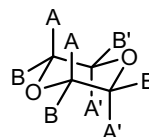
ABX



$AA'XX'$



assume frozen chair conformation



$AA'BB'$ twice

4. Calculate (or look up) the chemical shift of the underlined protons in the structures below. State which table in Silverstein and Webster (S&W) you used.

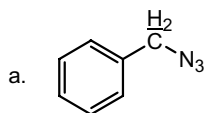


Table B.1	
start	0.23
Ph	1.83
N ₃	<u>1.97</u>
	4.03

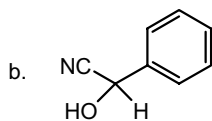
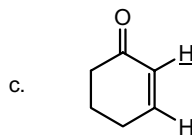
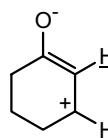


Table B.2a	
start	2.50
Ph	0.99
CN	0.66
OH	<u>1.14</u>
	5.29

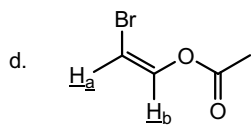


Use resonance structures to show why the chemical shift of these H's differs.

Table D.2 alpha -5.93, beta- 6.88



This resonance structure shows + charge on the beta carbon, which moves it downfield from the alpha one. Both are downfield of most alkenes due to the EWG carbonyl.



Appendix D

H _a		H _b	
start	5.25	start	5.25
gem Br	1.04	trans Br	0.55
trans OAc	<u>-0.67</u>	gem OAc	<u>2.09</u>
	5.62		7.89

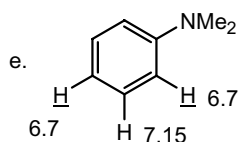


Chart D.1

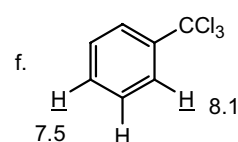
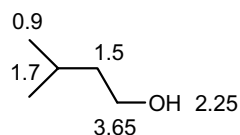


Chart D.1

5. An unknown compound has an exact mass of 88.0888 and it exhibits the ¹H NMR spectrum shown below. Calculate its formula, number of double bond equivalents (DBE) and then deduce its structure. The signal at 2.25 ppm disappeared on shaking the sample with D₂O.

88.0888 corresponds to C₅H₁₂O, which has no DBE

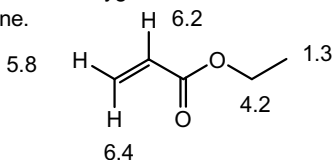
The structure is



The 2.25 ppm signal is exchangeable so it is the OH peak.

6. A compound of exact mass 100.0526 exhibits the ¹H NMR spectrum shown below. Calculate the number of DBE's and deduce its complete structure.

From the mass spec. tables, the formula is C₅H₈O₂, which has two DBE. The NMR shows an obvious ethyl ester, which accounts for both oxygens and one DBE. From the downfield shift of the remaining signals, the other DBE must be an alkene.



7. An unknown compound analyzes for C 51.60% and H 5.41%. Mass spectral analysis shows that it contains a single sulfur atom while UV spectroscopy shows that the sulfur is part of a five membered ring. Deduce its structure from the ^1H NMR spectrum on page 3. Note that shaking the sample with D_2O causes the 9 ppm peak to disappear.

$$\frac{51.6}{12.01} = 4.296 \quad \frac{5.41}{1.008} = 5.367 \quad \text{Also one sulfur.}$$

NMR shows 10 hydrogens. Since we know the % H, we can calculate the molecular weight as 186.

$$\frac{10 \times 1.008}{\text{MW}} = 0.0541 \quad \text{Knowing the MW and the \% C, we can get the number of carbons as 8.}$$

$$\frac{186 \times 0.5160}{12.01} = 7.99$$

$\text{C}_8\text{H}_{10}\text{S}$ has MW 138

$186 - 138 = 48$ so we have three oxygens

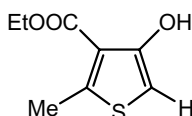
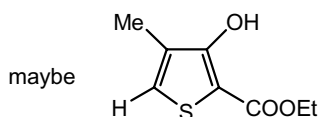
Formula is
 $\text{C}_8\text{H}_{10}\text{SO}_3$
4 DBE



is given so that takes care of one DBE and the sulfur

Ethyl ester is again obvious at 1.5 and 4.3 ppm. The COOEt group takes care of two oxygens and one DBE.

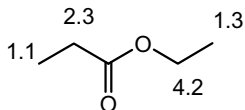
We have an exchangeable H at 9 ppm, which must be OH, accounting for the final oxygen.



is the actual structure. The usual δ of thiophene is 7.1 and 7.3 ppm (Table D.5, p. 210) so the OH must push the ring H upfield.

8. An unknown compound $\text{C}_5\text{H}_{10}\text{O}_2$ exhibits the ^1H NMR spectrum shown below. Deduce its structure.

The NMR shows two ethyl groups, one being an ethyl ester. $\text{C}_5\text{H}_{10}\text{O}_2$ corresponds to one DBE so the ester carbonyl is the only DBE.



9. In chlorocyclopropane $J_{ac} = 7 \text{ Hz}$ and $J_{bc} = 11 \text{ Hz}$. Draw a careful splitting diagram showing the position and intensity of the lines of proton c. You need not show the patterns for the other protons.

