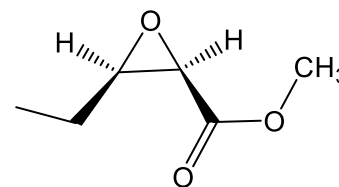


Chemistry 328N

Spring 2018

Dr. Willson

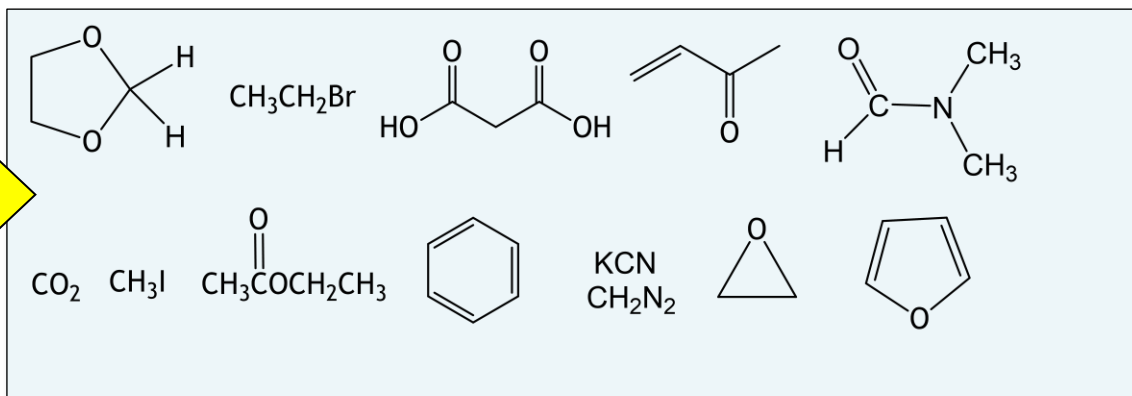
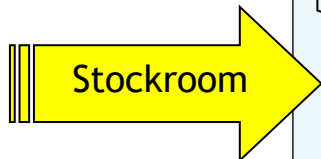


Final Exam

This evening you will take two tests, one in chemistry and one in integrity. I want you to get A's on both of these tests but if you are to fail one, let it be the one on organic chemistry. GW

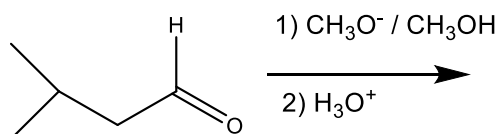
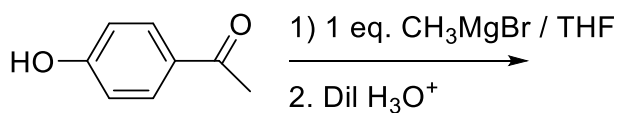
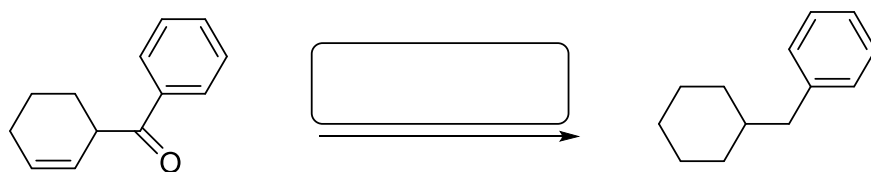
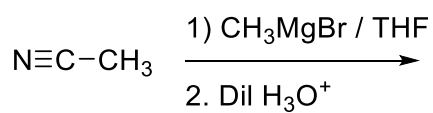
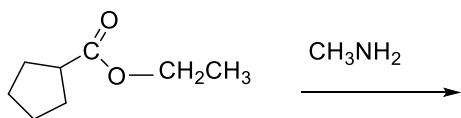
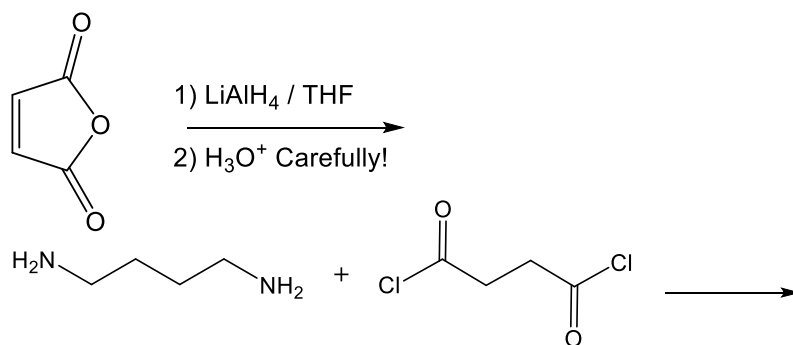
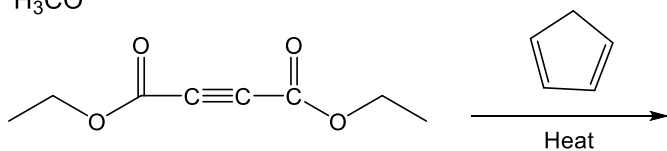
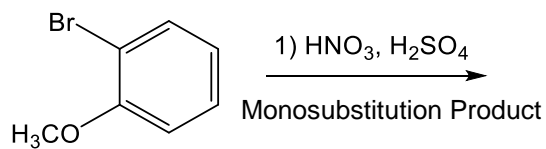
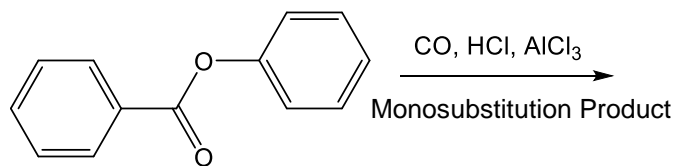
Name (Print as it appears on the Class Roster) _____

Signature _____



Has lowest field ^1H - nmr resonance			
Described by the Carothers equation	Chain growth polymerisation	Step growth polymerization	Ring opening Polymerization
Undergoes electrophilic substitution			
C-H Absorbs at the lowest frequency in the infrared			
Acids with weak conjugate bases have...	High pKa	Low Ka	Low pKa
Syndiotactic			
Reacts fastest with NaCN in CH_3CN			
Has the largest number of peaks in ^{13}C nmr			
T_g	Gas generation temperature	Glass transition Temperature	Gyroid temperature
Product of a Michael Addition			

2. (10 pts) Provide the missing reactants, reagents or products.



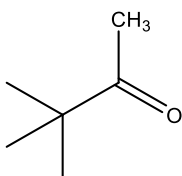
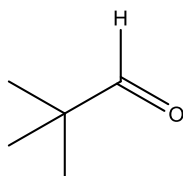
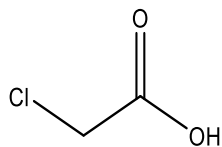
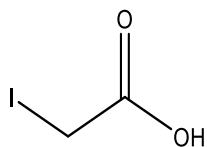
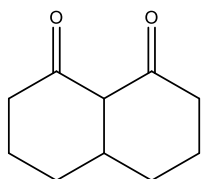
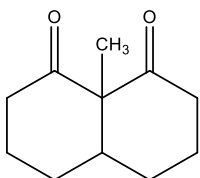
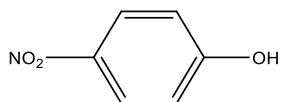
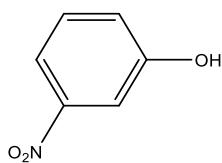
CH328N Final Exam Spring 2018

Name_____

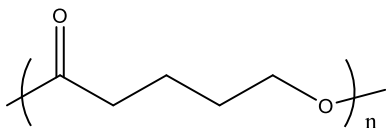
3. (10 pts) Indicate T for true, F for false or X for no answer for each question. Correct answers earn 1 point, the X response earns 0 points and incorrect answers earn -1 (negative one) point. The maximum score you can earn for this question is 10 points and the minimum score is 0 points.

1. ____ Changing the strength of the magnet in an nmr spectrometer results in a change in the chemical shift of peaks measured in Hz.
2. ____ Ring opening polymerization can be living.
3. ____ In UV-Vis spectroscopy transmission is expressed in percent.
4. ____ Chlorobenzene undergoes electrophilic aromatic substitution faster than nitrobenzene
5. ____ For the same magnetic field strength, the difference in energy between the spin states of ^{13}C is larger than that in ^1H .
6. ____ Soap is a fatty acid ester
7. ____ The three Nobel Prize Winners in Polymers are Flory, Staudinger and Grubbs
8. ____ The iodoform test is a qualitative method for identifying aldehydes
9. ____ Grignard Reagents react faster with carboxylic acids than with ketones.
10. ____ The empirical formula for dimethyl pimelate is $\text{C}_9\text{H}_{16}\text{O}_4$

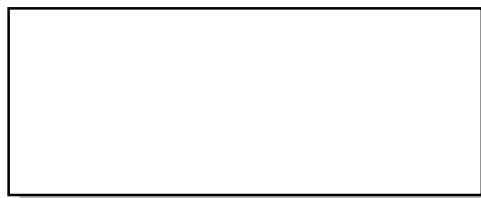
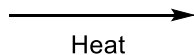
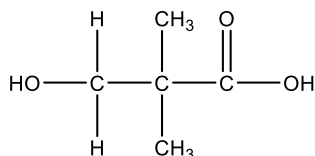
4. (5 pts) Circle the strongest acid in each pair and explain your choice in one sentence.



5. (2 pts) An ancient sample of one of Carothers' earliest experiments with polyesters was discovered in a drawer in Wilmington, Delaware. The sample is remarkable in the sense that it only contains two chain lengths. It seems to be a blend. A 0.5 kilogram sample consists of 400g of DP 10 and 100 grams of DP 20. The structure of this historic polymer is provided below. Please calculate the weight average molecular weight of the sample. Calculators are not needed but show your work.



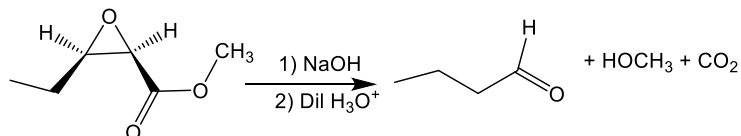
6. (3 Pts) An interesting monomer sample was also recovered from Carother's lab. The label of the bottle had his famous equation $[DP = 1/(1-P)]$ written on it in his own hand. The structure of this interesting A-B monomer is shown below. It undergoes step growth polymerization upon heating. We polymerized a sample of this monomer to 90% conversion. What is the structure of the polymer? What degree of polymerization do you predict? What is the predicted M_n of the sample? You do not need a calculator to work this problem but show your work.



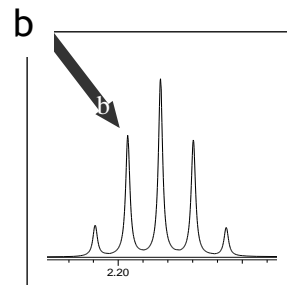
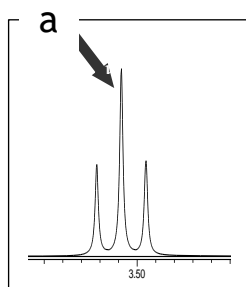
DP =

M_n =

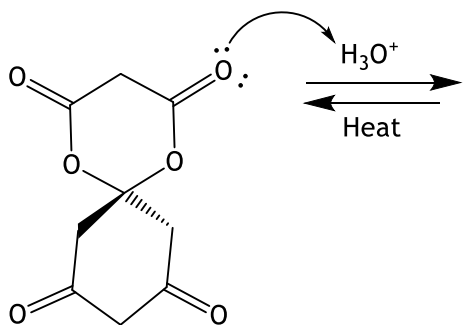
7. (5 pts) When the epoxy ester shown below is treated with aqueous sodium hydroxide and the resulting solution is then neutralized with dilute acid, the product is a high yield of butanal. Using the curved arrow convention, please show a reasonable mechanism for the formation of this product. Hint: Don't panic,,,just calmly apply what we have studied and Remember keto-enol tautomerism.



8. (5 Pts) The proton nmr spectrum of 1,3-dichloropropane shows a triplet and a pentet as shown below. Please calculate there relative areas (a/b) of the peaks marked explicitly in the multiplets. Show your work.



9. (20 pts) Predict the products that you would isolate upon treatment of the compound below with hot aqueous acid. Use the curved arrow convention to show the mechanism that leads to these products. **Please be neat !**



.....
Predicted Products.

10. (15pts) We now know that when Starman left Florida for Mars in his Tesla he was carrying with him a small vial of a strange organic substance. We must determine the structure of this material so that we can assess the impact it may have on contamination of the universe. The material is a white solid with a faint odor of mint and an empirical formula $C_9H_{10}O$. Mass spectrometry shows a strong molecular ion at 268 Daltons.

Ji Yeon ran an IR of this interesting material and it shows strong, sharp bands at 1704 and 1104 cm^{-1} . There are also sharp medium bands at 1696 and 2130 cm^{-1} . The spectrum displays the usual aliphatic C-H bands below 3000 cm^{-1} but also has medium strength bands at 3073 and 2745 cm^{-1} that Ji Yeon tells us are "a bit unusual". The ^{13}C and 1H nmr spectra of the material were measured by Paul and Jai Hyun and they have provided these below. Paul ran the DEPT experiment and he reports that it has a profound effect on the ^{13}C spectrum. It results in disappearance of all of the absorbances marked with a ● and the inversion of the peak marked with a ∩. The rest of the spectrum remains unchanged. Please *neatly* list the information that you can glean from each of these data then write the structure of the unknown and show which protons on your structure correspond to the resonances that are labeled with letters in the 1H nmr spectrum.

Mass Spectrum and empirical formula:

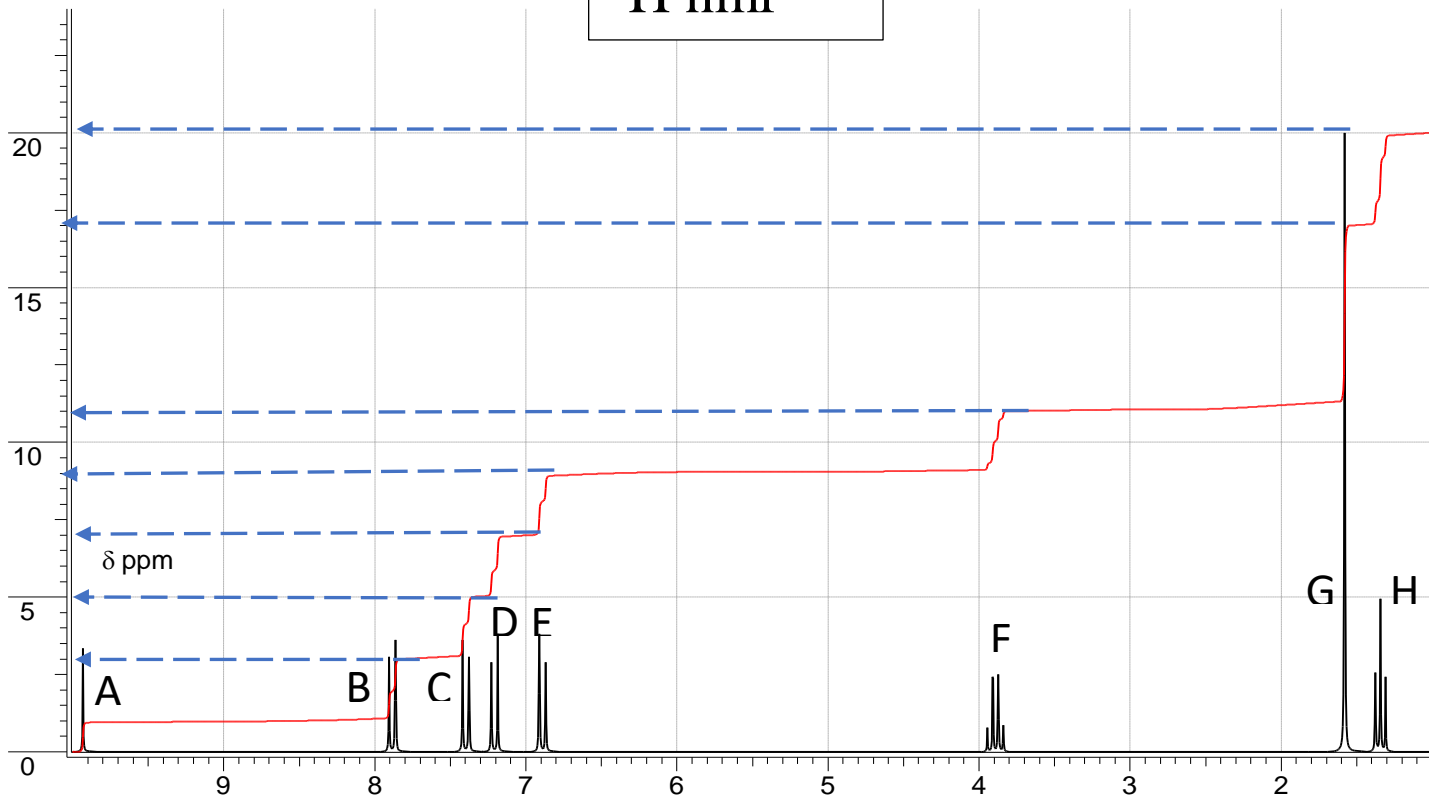
Hydrogen Deficiency Index:

Infrared Spectrum:

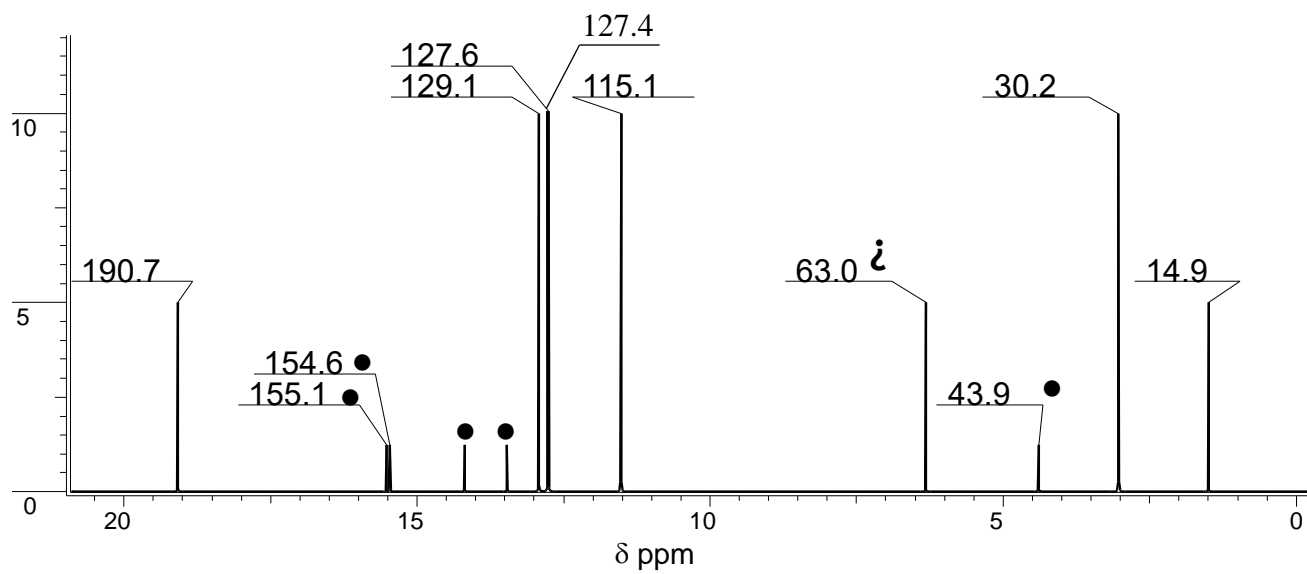
1H -nmr

^{13}C -nmr and DEPT experiment:

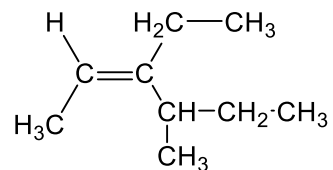
¹H nmr



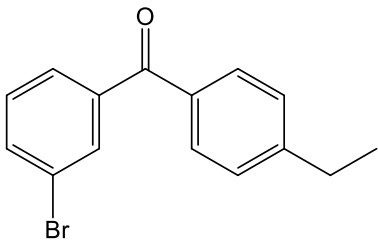
¹³C nmr



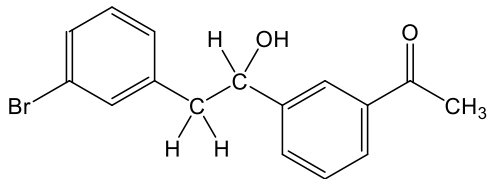
11. (5 pts) Using only the substances in your stock room (on cover page) as sources of carbon, show a synthetic path to the compound below. You may use any other substances you choose for the synthesis, but all of the carbon in the products must come from the stock room. I encourage you to look for the signatures of reactions we have studied and to work backwards. Be neat!



12. (5 pts) Using only the substances in your stock room (on cover page) as sources of carbon, show a synthetic path to the compound below. You may use any other substances you choose for the synthesis, but all of the carbon in the products must come from the stock room. I encourage you to look for the signatures of reactions we have studied and to work backwards. Be neat!



13. (5 pts) Using only the substances in your stock room (on cover page) as sources of carbon, show a synthetic path to the compound below. You may use any other substances you choose for the synthesis, but all of the carbon in the products must come from the stock room. I encourage you to look for the signatures of reactions we have studied and to work backwards. Be neat!



Intentionally Bank



CHEMISTRY 328N

Table of IR Absorptions

<i>Functional Group</i>	<i>Characteristic Absorption(s) (cm⁻¹)</i>	<i>Notes</i> <i>s=sharp, m = medium, v = variable</i>
Alkyl C-H Stretch H-C=O stretch	2950 - 2850 (m or s) 2830 - 2695 (m)	Alkane C-H bonds are fairly ubiquitous and therefore usually less useful in determining structure.
Alkenyl C-H Stretch Alkenyl C=C Stretch	3100 - 3010 (m) 1680 - 1620 (v)	Absorption peaks above 3000 cm ⁻¹ are frequently diagnostic of unsaturation
Alkynyl C-H Stretch Alkynyl C≡C Stretch	~3300 (s) 2260 - 2100 (v)	
Aromatic C-H Stretch Aromatic C-H Bending Aromatic C=C Bending	~3030 (v) 860 - 680 (s) 1700 - 1500 (m,m)	
Alcohol O-H Stretch	3550 - 3200 (broad, s)	Very strong broad peak
Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)	
Amine N-H Stretch	3500 - 3300 (m)	Primary amines produce two N-H stretch absorptions, secondary amides only one, and tertiary none.
Nitrile C≡N Stretch	2260 - 2220 (m)	Medium sharp band
Aldehyde C=O (Aromatic) Aldehyde C=O (aliphatic) Ketone C=O Stretch Ester C=O Stretch Carboxylic Acid C=O	1710 - 1685 (s) 1740 - 1720 (s) 1750 - 1680 (s) 1750 - 1735 (s) 1780 - 1710 (s)	The carbonyl stretching absorption is one of the strongest IR absorptions, and is very useful in structure determination as one can determine both the number of carbonyl groups (assuming peaks do not overlap) but also an estimation of which types.
C-O-C Stretch	1050 - 1250 (s)	Generally a strong peak in esters and ethers

All figures are for the typical case only -- signal positions and intensities may vary depending on the particular bond environment.



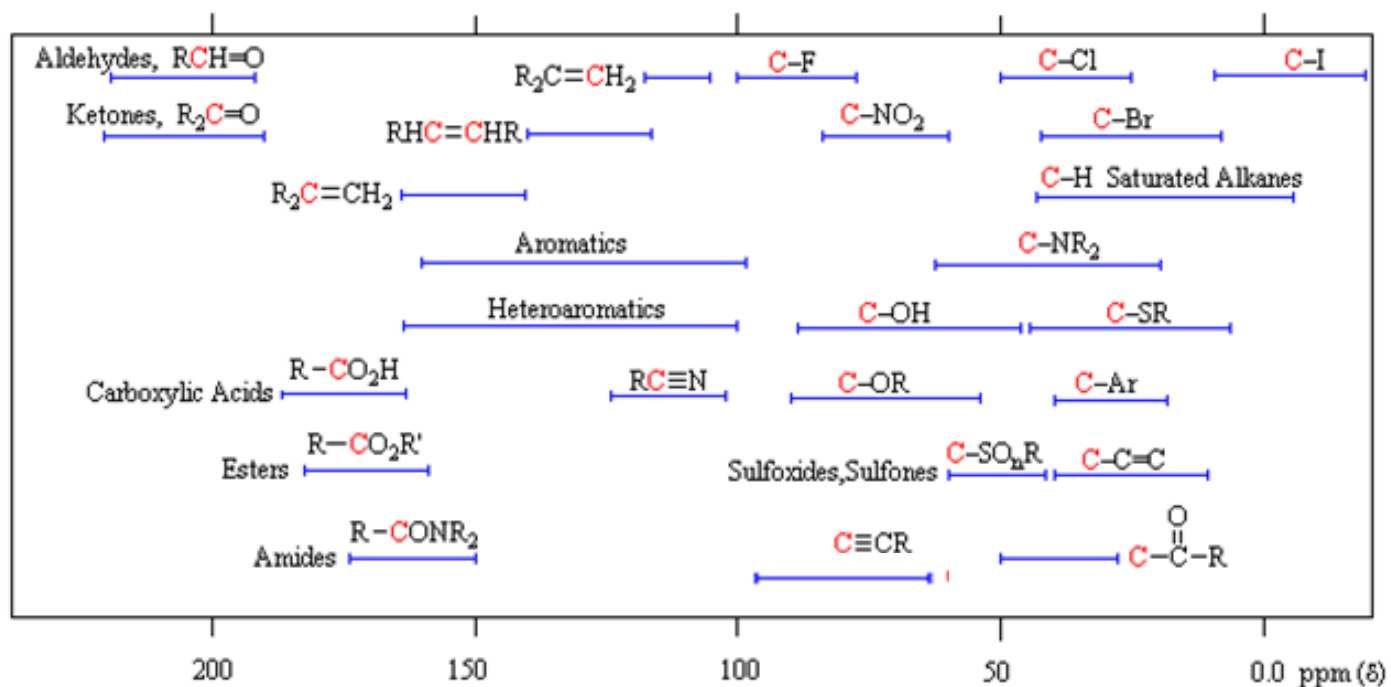
CHEMISTRY 328N

CHARACTERISTIC PROTON CHEMICAL SHIFTS		
Type of Proton	Structure	Chemical Shift, ppm
Cyclopropane	C_3H_6	0.2
Primary	$R-CH_3$	0.9
Secondary	R_2-CH_2	1.3
Tertiary	R_3-C-H	1.5
Vinylic	$C=C-H$	4.6-5.9
Acetylenic	$C\equiv C-H$	2-3
Aromatic	$Ar-H$	6-8.5
Benzylic	$Ar-C-H$	2.2-3
Allylic	$C=C-CH_3$	1.7
Fluorides	$H-C-F$	4-4.5
Chlorides	$H-C-Cl$	3-4
Bromides	$H-C-Br$	2.5-4
Iodides	$H-C-I$	2-4
Alkyl Amines	$H-C-NR$	2.5-3.5
Ethers	$H-C-OR$	3.3-4
Esters	$RCOO-C-H$	3.7-4.8
Esters	$H-C-COOR$	2-2.9
Acids	$H-C-COOH$	2-2.6
Carbonyl Compounds	$H-C-C=O$	2-2.7
Aldehydic	$R-(H-)C=O$	9-10
Hydroxylic	$R-C-OH$	1-5.5
Phenolic	$Ar-OH$	4-12
Enolic	$C=C-OH$	15-17
Carboxylic	$RCOOH$	10.5-12
Amino	RNH_2	1-5

Exact masses of common elements and isotopes

isotope	mass	natural abundance
^1H	1.00782	99.985
^2H	2.01410	0.015
^{12}C	12.0000	98.892
^{13}C	13.00335	1.108 (1.11%)
^{14}N	14.00307	99.634
^{15}N	15.00010	0.366 (0.38%)
^{16}O	15.99491	99.763
^{17}O	16.99913	0.037 (0.04%)
^{18}O	17.99916	0.200 (0.20%)
^{19}F	18.99840	100.000

Approximate ^{13}C Chemical Shifts



b