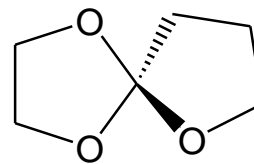


Chemistry 318N

Spring 2012
Dr. Willson

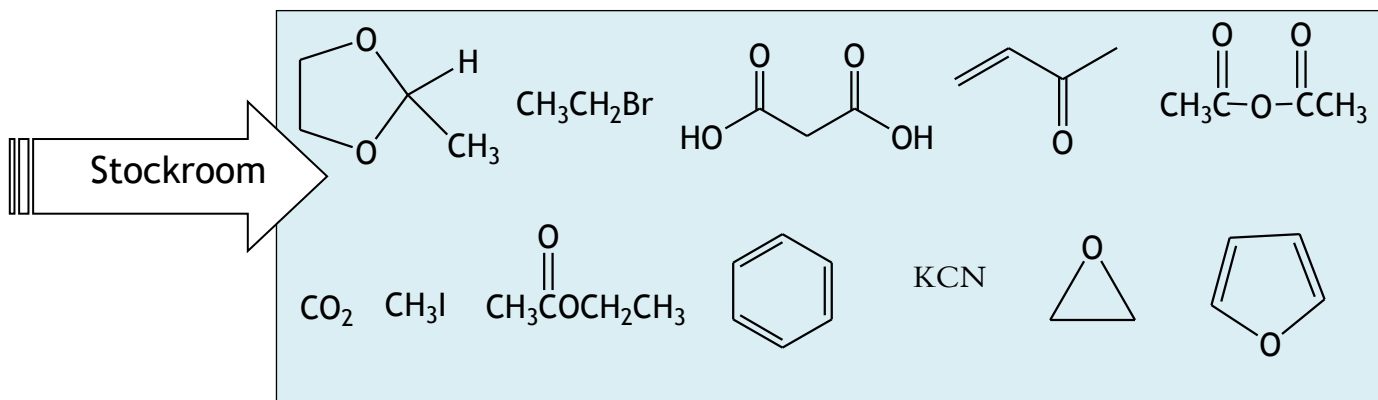


Final Exam

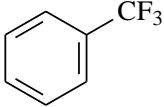
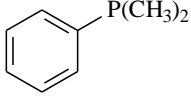
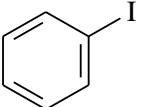
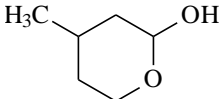
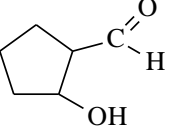
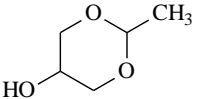
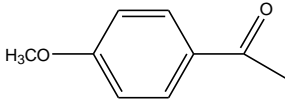
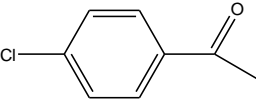
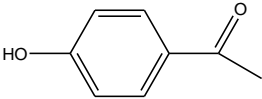
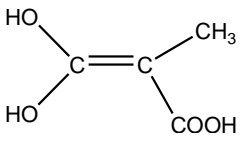
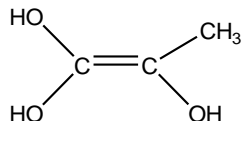
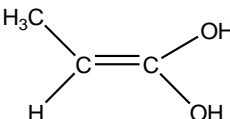
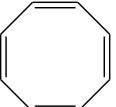
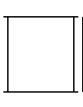
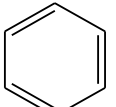
This afternoon you will take two tests, one in chemistry and one in integrity. I want you to get A's on both of these tests but if you are to fail one, let it be the one on organic chemistry. GW

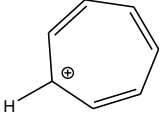
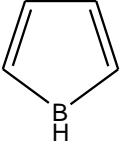
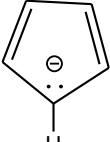
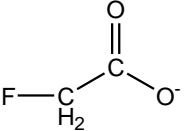
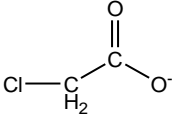
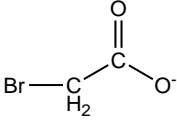
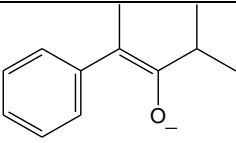
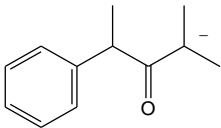
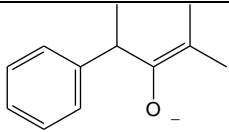
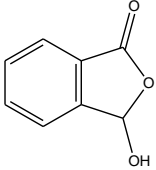
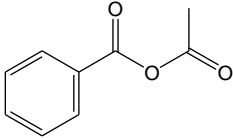
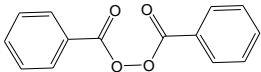
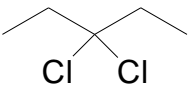
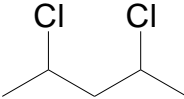
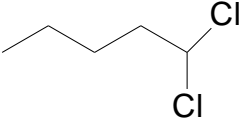
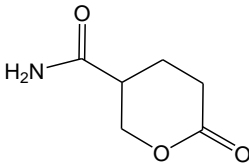
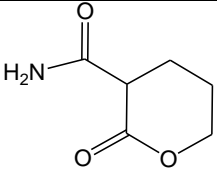
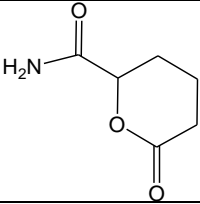
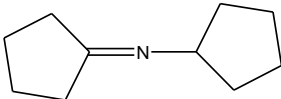
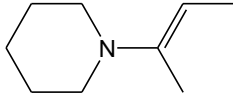
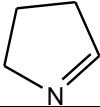
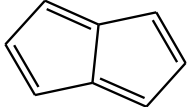
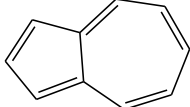
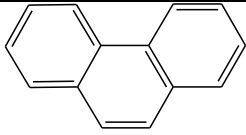
Name (Print as it appears on the Class Roster) _____

Signature _____



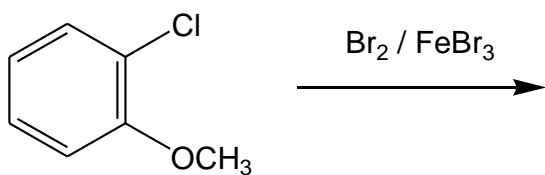
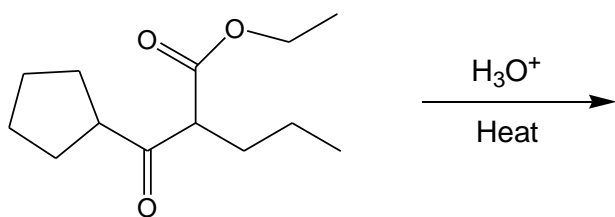
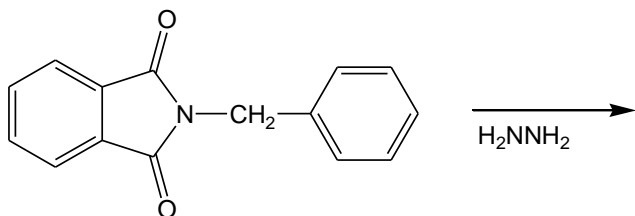
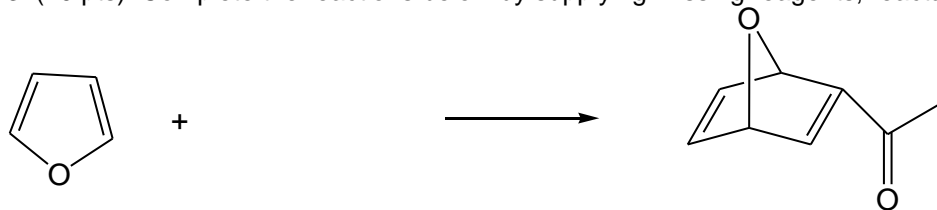
1. (10 Pts) Circle the best answer for each question below.

Substitutes meta			
An acetal			
Not used to shift the equilibrium to favor product in acetal synthesis	Dean Stark Trap	H ₂ SO ₄	<i>Excess Alcohol</i>
Strong acids have	Small pKa	Small Ka	High pH
A Phosphonium Salt	(CH ₃) ₃ P ⁺ -CH ⁻ -CH ₃	(CH ₃) ₃ P ⁺ -O ⁻	(CH ₃) ₄ P ⁺ Cl ⁻
Takes primary alcohols to acids	<i>Tollen's reagent</i>	Jones reagent	<i>Wittig reagent</i>
Reacts fastest with MgBrCH ₃ in THF			
Intermediate in decarboxylation of CH ₃ CH(COOH) ₂			
Has no non-bonding molecular orbitals			
False statement	All meta directors are deactivators	All deactivators are meta directors	All activators direct ortho and para

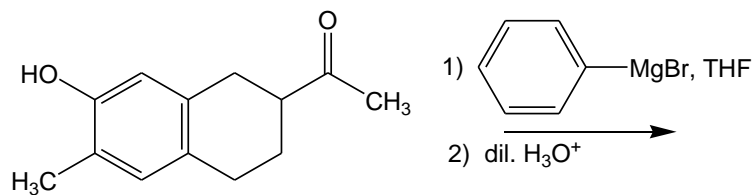
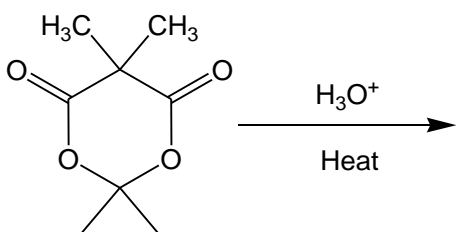
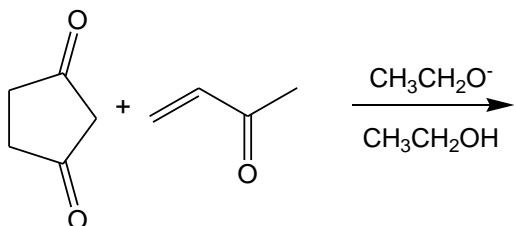
Has the smallest number of p orbital electrons			
Conjugate base of the weakest acid			
Not an equilibrium reaction	Acid hydrolysis of hemiacetal	<i>Acid hydrolysis of lactone</i>	<i>Acid hydrolysis of Nitrile</i>
"Thermodynamic" Anion			
An anhydride			
Has the lowest field resonance in ^1H -nmr			
Decarboxylates upon hydrolysis in hot acid			
An enamine			
Has the longest carbon - carbon bond			
Did not win a Nobel Prize in Chemistry	Wallace Carothers	Paul Flory	Hermann Staudinger

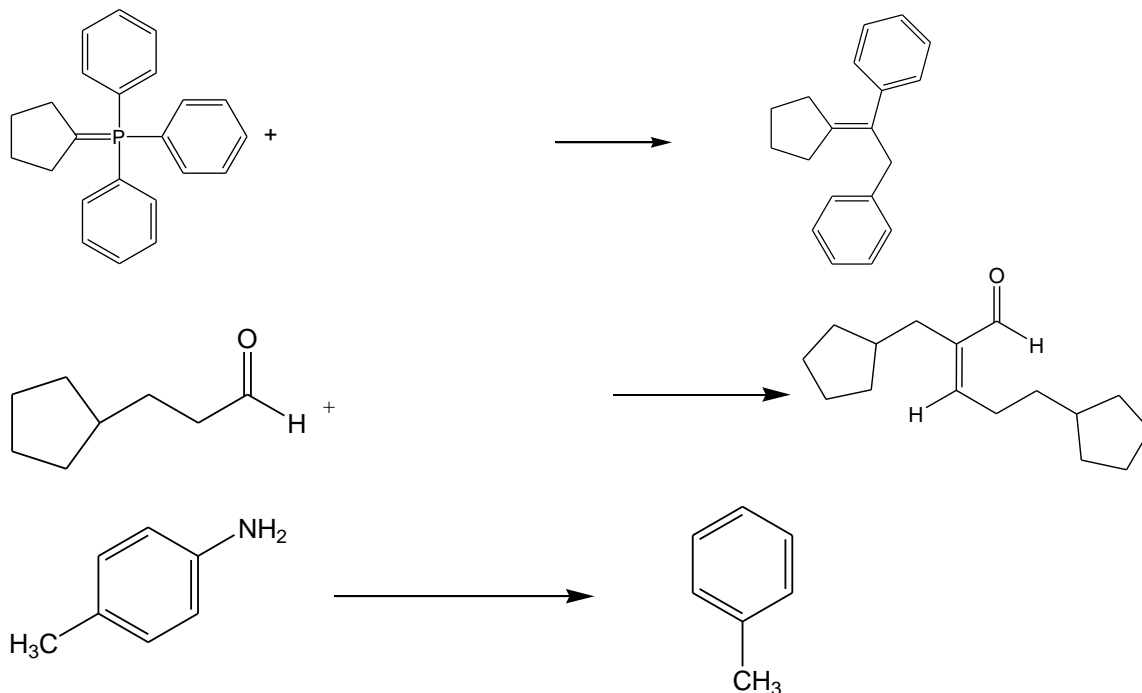
2. (10 pts) Please put a T in front of each true statement and an F in front of each false statement. Put an X in front of questions that you do not want to be graded. Your score will be the number of correct answers minus the number of wrong answers or zero, whichever is the largest. Please read the statements very carefully!
- a) ____ The right-hand end of the scale on a typical NMR spectrum is up field.
 - b) ____ Frequency increases from left to right on the typical infrared spectrum
 - c) ____ The Diels-Alder Reaction creates six membered rings.
 - d) ____ Nitrile Carbons resonate at higher field than carbonyls in ^{13}C nmr.
 - e) ____ In mass spectra, the M+2 peak is always smaller than the M+1 peak.
 - f) ____ The carbon in formic acid is more highly oxidized than that in formaldehyde.
 - g) ____ The signature of the Claisen condensation is α,α -unsaturated esters.
 - h) ____ 1,4-dimethylbenzene has 3 signals in its ^{13}C -nmr spectrum.
 - i) ____ The carbon-carbon bonds in benzene are longer than those in ethene.
 - j) ____ Good leaving groups are the conjugate bases of strong acids.
 - k) ____ The higher the pKa of an acid, the higher the pH of its 0.1 molar solution.
 - l) ____ Nitriles undergo acid catalyzed hydrolysis to give ketones and ammonia.
 - m) ____ Amides hydrolyze faster than esters in aqueous base.
 - n) ____ Anhydrides can be made from acid chlorides by nucleophilic acyl substitution
 - o) ____ The *empirical* formula for dimethyl pimelate is $\text{C}_8\text{H}_{14}\text{O}_4$.
 - p) ____ Primary alcohols can be oxidized to aldehydes by PCP
 - q) ____ Nylon is a polyamide.
 - r) ____ The Mn of a polymer is always greater than or equal to Mw.
 - s) ____ Hydrogenolysis of benzyl alcohol gives toluene.
 - t) ____ Living polymerizations produce polymers with low polydispersity.

3. (10 pts) Complete the reactions below by supplying missing reagents, reactants or products.



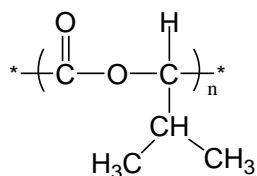
Monosubstitution product





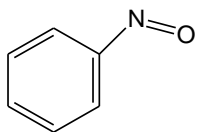
4. (10 pts) We have purchased a sample of a new polyester that has unusual properties. The structure of the polymer is shown below. We analyzed the sample and learned that it was a mixture, as all synthetic polymers are. The sample is comprised of 200 grams of material with degree of polymerization 10, 200 grams of degree of polymerization 20 and 600 grams of degree of polymerization 30. Please calculate the weight average and number average molecular weight of the sample and its polydispersity. Disregard any end groups. Show your work. You do not need a calculator to do this problem!

Mw = _____ Mn = _____ Dispersity = _____



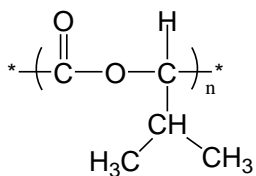
polyester

5. (5 pts) Do you predict that nitrosobenzene will produce ortho and para isomers or meta isomers when subjected to electrophilic aromatic substitution? Please support your answer with resonance theory arguments.



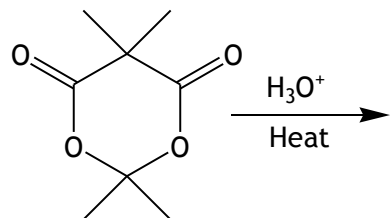
Nitrosobenzene

6. (3 Pts) We have received a sample of the polyester listed below. This sample has a polydispersity of 1.5. The weight average molecular weight of the sample is 300,000 Daltons. What is the degree of polymerization?



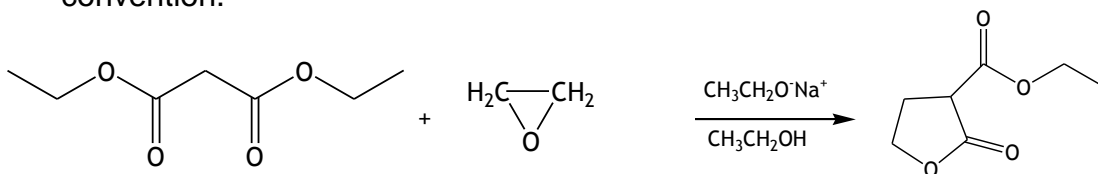
polyester

7. (15 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.



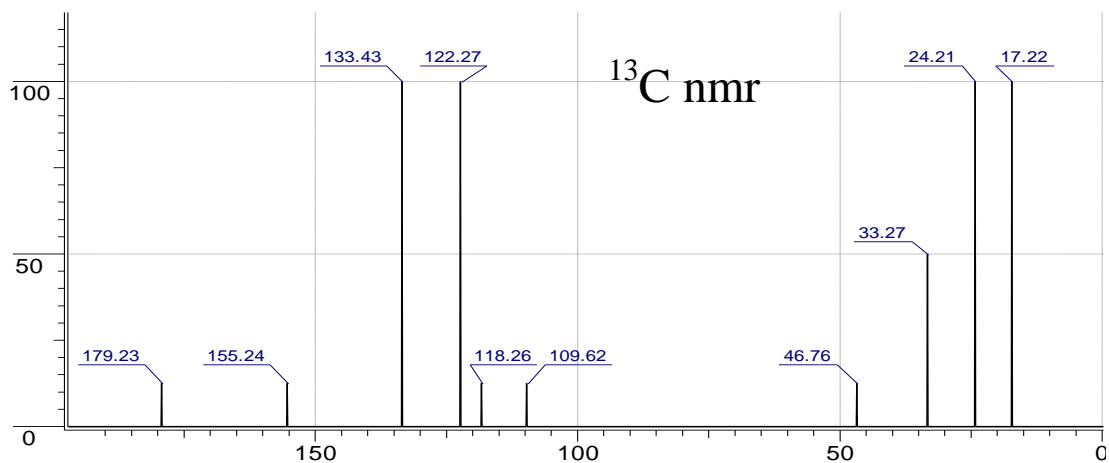
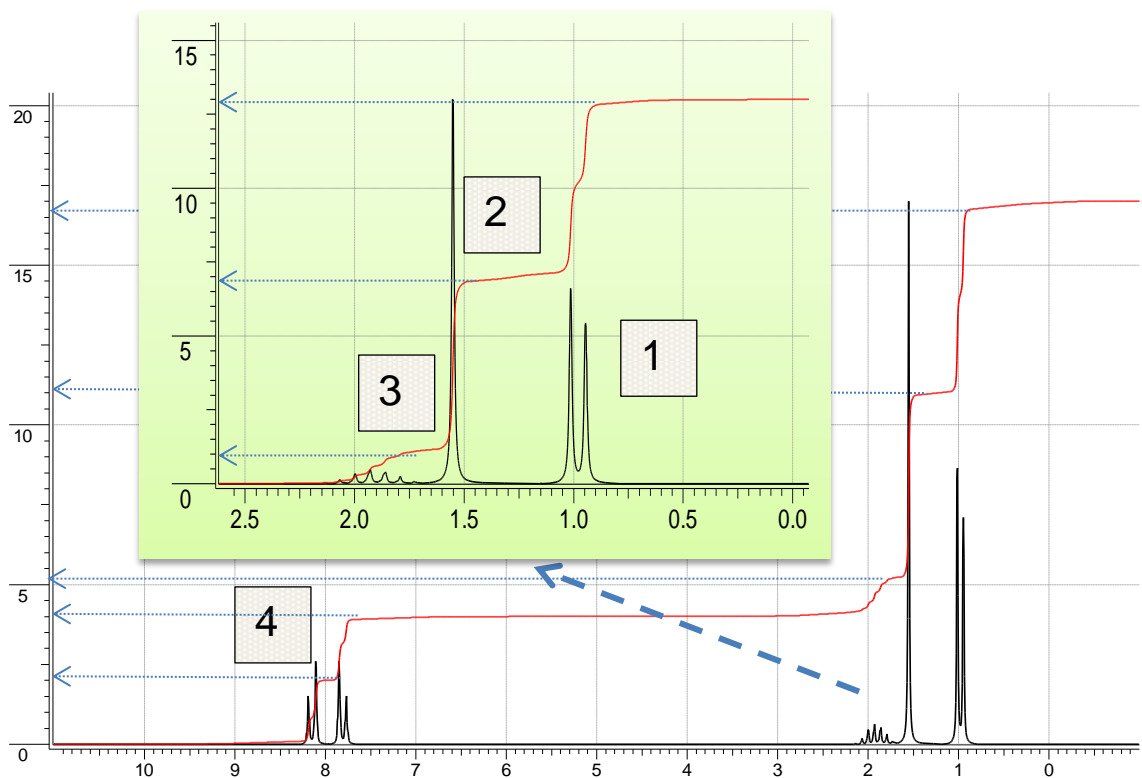
Predicted Products.

8. (3 pts) The reaction shown below takes place in good yield. Please propose a reasonable mechanism for the reaction. Show the step-by-step sequence of transformations and the corresponding movement of electrons using the curved arrow convention.



- 9 (4 pts) Dangerous Dan is struggling in his organic lab class. He was given an unknown to solve and has been working on it for 3 hours. He has used a number of very sophisticated analytical techniques and now knows that his unknown is either cyclohexane or cyclopentanone ($\text{C}_5\text{H}_8\text{O}$). The bell is about to ring so he quickly runs a high resolution mass spectrum and discovers that $M^+ = 84.059$. What is his unknown? Please show your work.

10. (15 pts) An incredibly toxic substance with 14 carbon atoms was isolated from the purple sea slug. This stuff even kills water bears! The infrared spectrum of the material shows strong peaks at 720, 1118, 1692, and 2900 cm^{-1} and there are medium intensity peaks at 2232 and 3027 cm^{-1} . The substance has a strong molecular ion at $M/Z=231$. The ^1H and ^{13}C nmr spectra are reproduced below. On the following page please list and tabulate what you can deduce from the IR, mass spectrum, ^{13}C -NMR, and ^1H -NMR; then write the structure of the unknown. The ^1H -NMR shows resonances for several different chemical shifts. The peaks are numbered 1 through 4 below. Please use these numbers to assign the resonances to specific protons in your proposed structure.



Problem 10 continued.

Infrared spectrum:

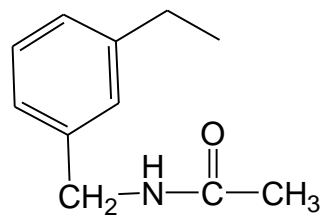
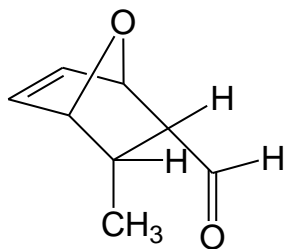
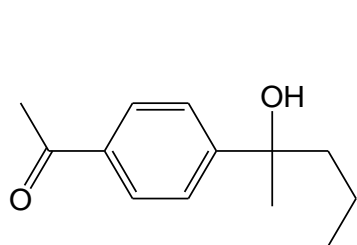
^1H -nmr:

^{13}C -NMR:

Mass Spectrum:

Structure and assignment _____

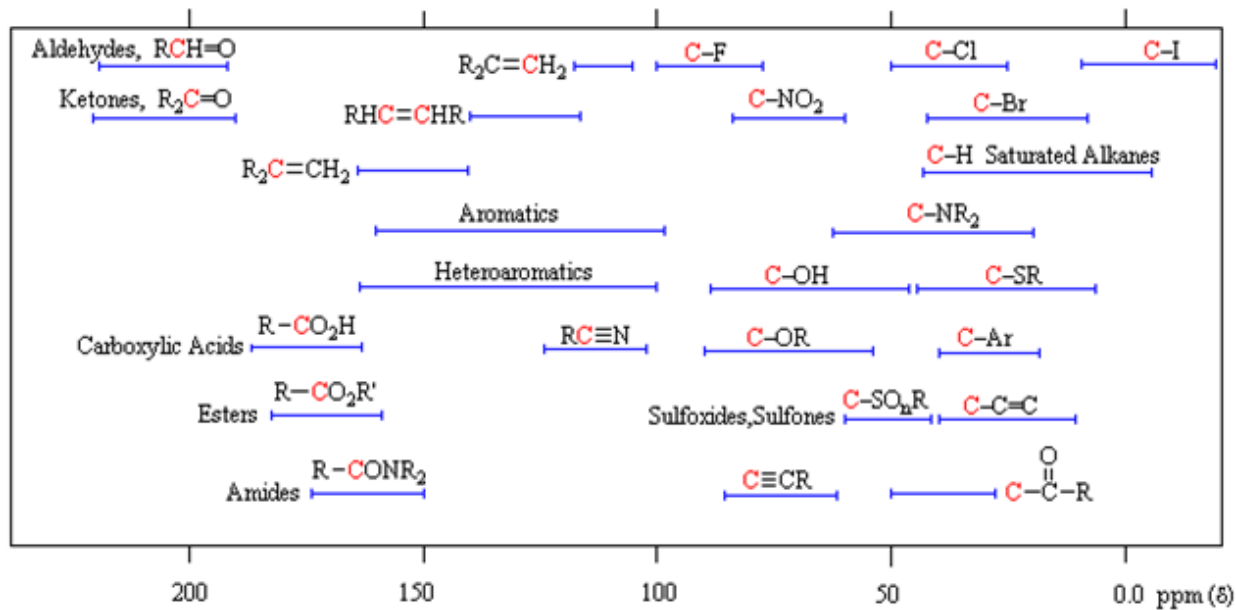
11. (15 pts) Please provide a synthetic pathway to the substances below. You may use any reagents or compounds you choose, but all of the carbon in your final product must come from the stock room, an inventory of which is on the cover page of the exam. Please be neat!!

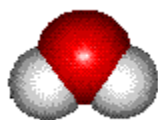


Exact masses of common elements and isotopes

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





CHEMISTRY 318N

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
Alcohols	$H-C-OH$	3.4-4
Ethers	$H-C-OR$	3.3-4
Esters	$RCOO-C-H$	3.7-4.8
Esters	$H-C-COOR$	2-2.2
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

Table of IR Absorptions	<i>Characteristic Absorption(s) (cm⁻¹)</i>	<i>Notes</i>
<i>Functional Group</i>		
Alkyl C-H Stretch	2950 - 2850 (m or s)	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
Ketone C=O Stretch Ester C=O Stretch Carboxylic Acid C=O Stretch Amide C=O Stretch	1750 - 1680 (s) 1750 - 1735 (s) 1780 - 1710 (s) 1690 - 1630 (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.
Ester C-O Stretch	1050 - 1250 (s)	Generally a strong peak in esters

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