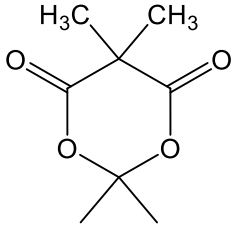
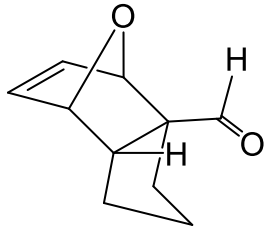


Chemistry 328N

Spring 2016



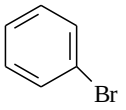
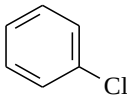
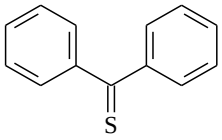
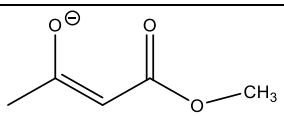
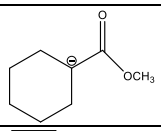
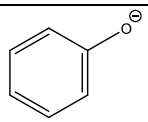
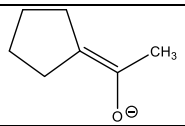
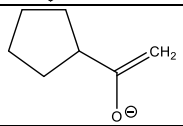
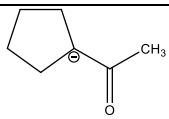
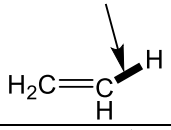
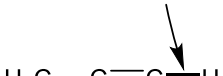
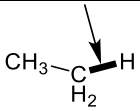
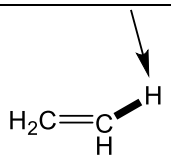
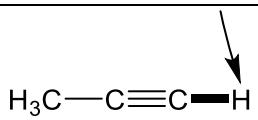
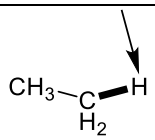
Please note:

This morning your integrity will be sorely tested!!! This room is an excellent facility for lectures, but unfortunately, it is VERY poorly designed for giving exams to a class the size of ours. It is important for the good of all of us for you to **KEEP YOUR PAPER COVERED THIS MORNING**. I fully understand that this is a bother but please do your very best to cover your work as you complete the test and keep your eyes on your paper.

Thank you,

CH 328N final exam 2016 Name_____

1. (10pts) Circle the one best answer.

The unsaturation number of $C_8H_{14}ClN$	3	2	1
Lowest energy radiation	1000 cm^{-1}	365 nm	300 megaHertz
Has the largest M+2 peak			
Carbon in this compound has oxidation state -2	$H_2C{=}O$	CH_3-OH	CH_4
Conjugate base of the strongest acid			
Kinetic anion			
Units of Absorbance	cm/(liter mole)	No units	percent
Has lowest frequency IR absorbance			
Resonance occurs at highest δ			
Units of extinction coefficient	$\frac{Moles\ cm}{liter}$	$\frac{liters}{mole\ cm}$	$\frac{liters\ cm}{mole}$

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) _____Good leaving groups are the conjugate bases of strong acids.

b) _____Grignard reagents react with nitriles to yield ketones

c) _____Saponification of fat is a nucleophilic acyl substitution reaction

d) _____All molecules have antibonding orbitals

e) _____The Diels-Alder reaction creates six membered rings.

f) _____The unsaturation number cannot be odd

g) _____$LiAlH_4$ and $NaBH_4$ react violently with water.

h) _____ on IR spectra, higher wavenumber is higher energy

i) _____Strong acids make solutions with low pH.

j) _____ Lactones are cyclic ketones

k) _____1,4-dichlorobenzene has only 2 signals in its ^{13}C-nmr spectrum.

l) _____The carbon-carbon bonds in benzene are longer than those in ethane.

m) _____Amides hydrolyze faster than esters in aqueous base.

n) _____Aromatic compounds have 2n+4 electrons in p orbitals

o) _____Living polymerizations have smaller Đ than step growth polymerizations

p) _____Ring current in benzene increases the shielding of the hydrogens.

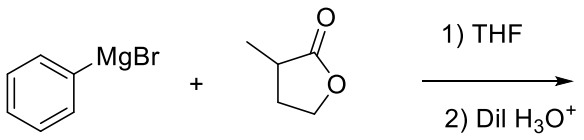
q) _____In the same spectrometer, ^{13}C resonates at a higher frequency than ^{1}H

r) ____ Benzene has unfilled nonbonding orbitals

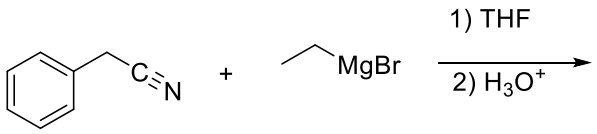
s) _____HF absorbs at a higher frequency in the infrared than HCl

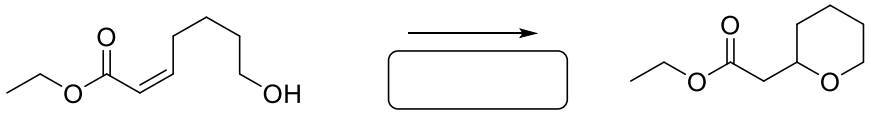
t) ____ Ortho para directing substituents increase the rate of EAS

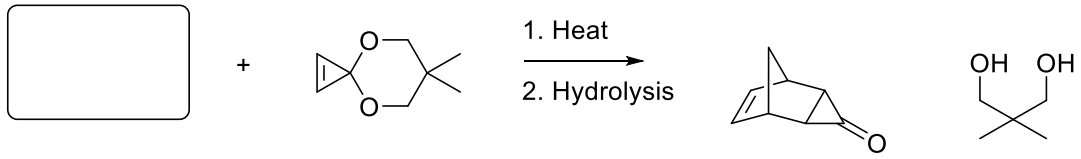
2. (5 pts) Complete the reactions below by supplying missing reagents, reactants or products.

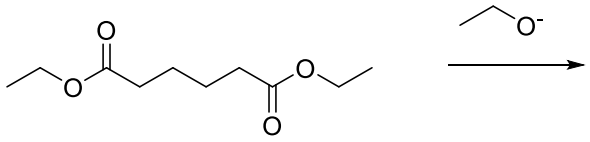


Excess

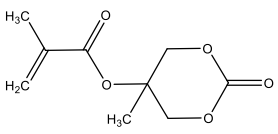




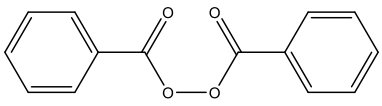




3. (5pts) We have discovered an additive that enables living free radical polymerization of the monomer shown below. I am sorry, but the structure of the additive is confidential so I am not allowed to show it to you, but if I add the appropriate amount of the secret substance that insures living type kinetics to a polymerization flask together with 10 millimoles of benzoyl peroxide (shown below) and 1.2 kilograms of the monomer and I run the reaction until 50% of the monomer has reacted, what degree of polymerization do you predict. Show your work. Calculators are not required to work this problem.

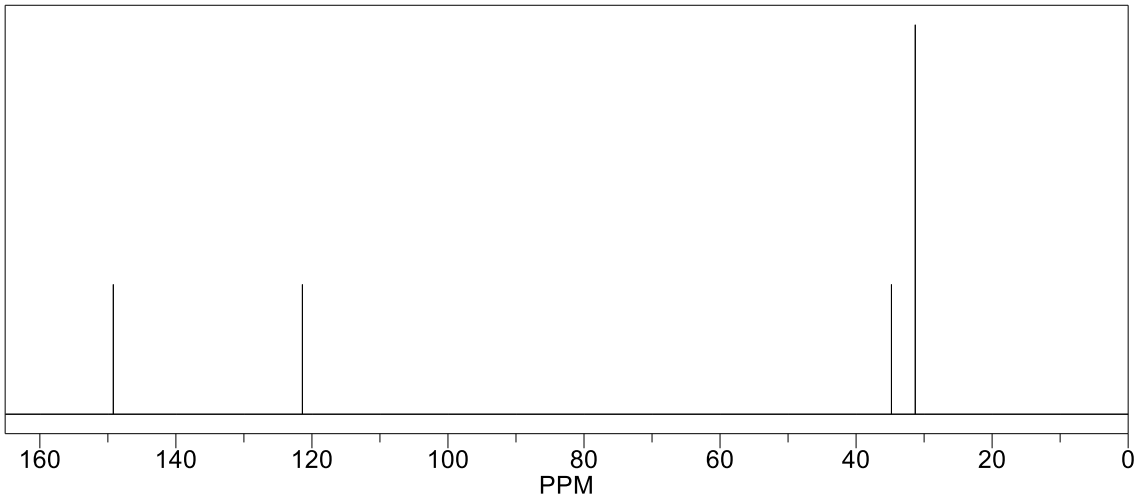


Monomer



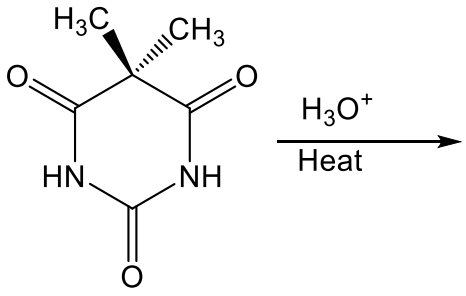
Benzoyl peroxide

4. (10 pts) An interesting hydrocarbon with an empirical formula of C_3H_5 and a molecular weight of 246 was isolated from the product stream of an experimental cracking tower. The substance has only two singlets in the proton nmr at 1.31 and 7.65 δ. The integral ratios of these peaks are 9:1 respectively. The ^{13}C-nmr is shown below. The peaks at 149 and 35 ppm disappear in the DEPT experiment while the other two peaks remain unchanged. Show what you learn from each of the pieces of information supplied. Show some work!! Because of the nature of the exam room, no credit can be given for simply drawing the correct structure. Write the structure of this hydrocarbon in the small box below. The box is purposely small to limit transmission of your answer to those with exceptional visual acuity.
Hint…don't forget to calculate the unsaturation number aka HDI!!



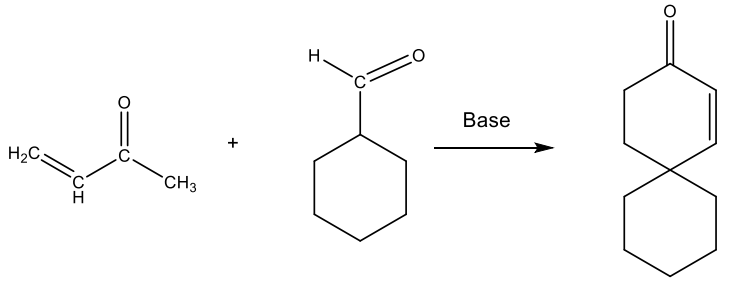
Small box

5. (15 pts) The structure below is a barbiturate, one member of a large and famous family of addictive pharmaceuticals that have a profound effect on cognition in humans. Please show the products that would result from treatment of this barbituate with hot aqueous acid. Use the curved arrow convention to show the mechanism that leads to these products.

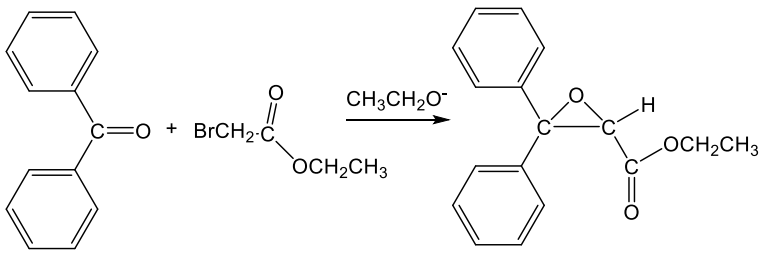


Predicted Products.

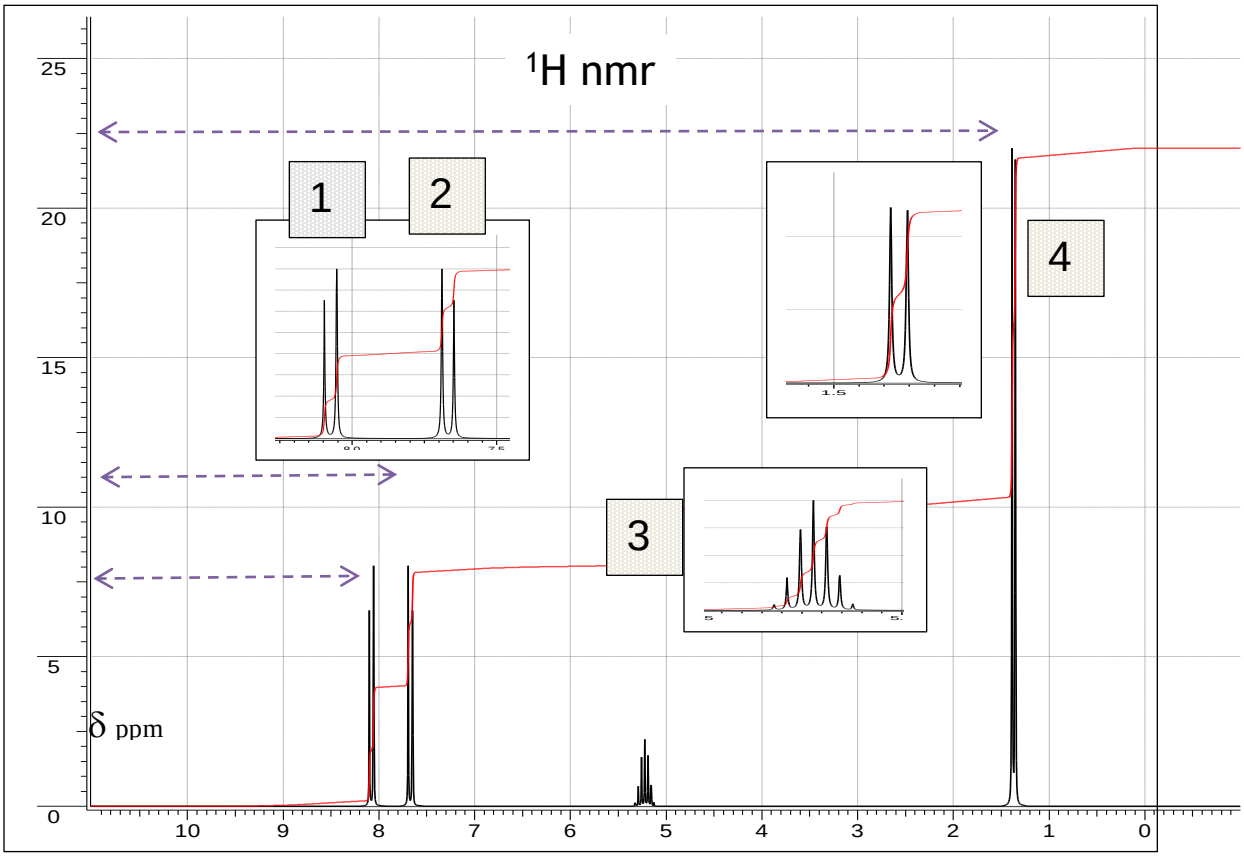
6. (5 pts) Upon treatment with base, cyclohexanecarboxaldehyde reacts with methyl vinyl ketone to produce the interesting spiro compound shown. Please use the curved arrow convention to propose a mechanism for this reaction.



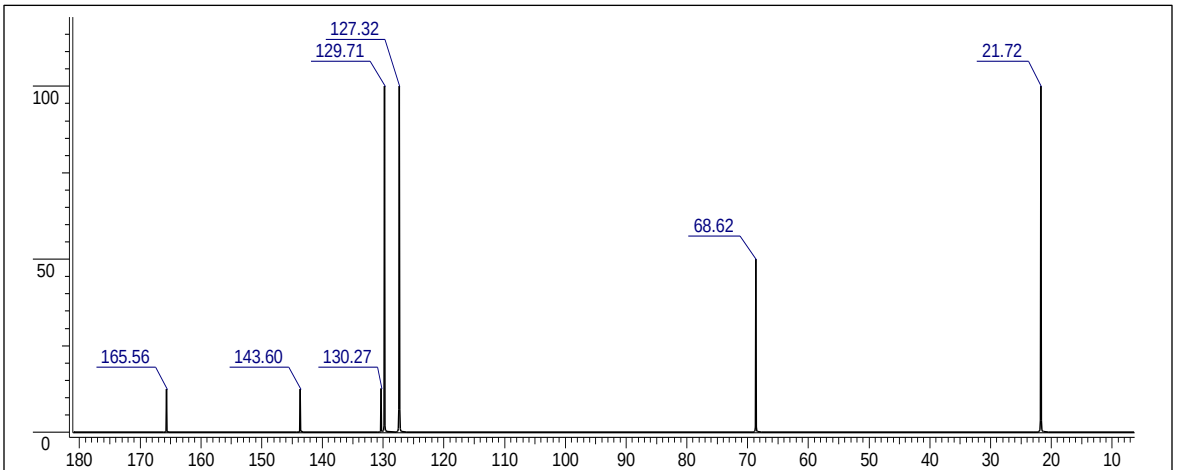
7. (5 pts) Upon treatment with base at zero degrees centigrade, diphenyl ketone reacts with ethyl bromoacetate to give an excellent yield of the oxirane product shown. Please use the curved arrow convention to propose a mechanism for this reaction.



8. (15 pts) The crew that was sent to clean up the abandoned Uber offices reports that they found an unlabeled bottle of a low viscosity liquid that was left behind. The liquid smells a bit like cilantro. The infra-red spectrum of the material is provided below as are the ^{1}H and ^{13}C nmr spectra. The mass spectrum shows a strong molecular ion at M/Z=326. Combustion analysis shows that the empirical formula is $C_{10}H_{11}O_2$. Please list and tabulate what you can deduce from the data then write the structure of this abandoned liquid. The ^{1}H-NMR show resonances for 4 different chemical shifts. Starting with the lowest field resonance, they are numbered 1 through 4 below. Please use these numbers to assign the resonances to specific protons in your proposed structure.
.

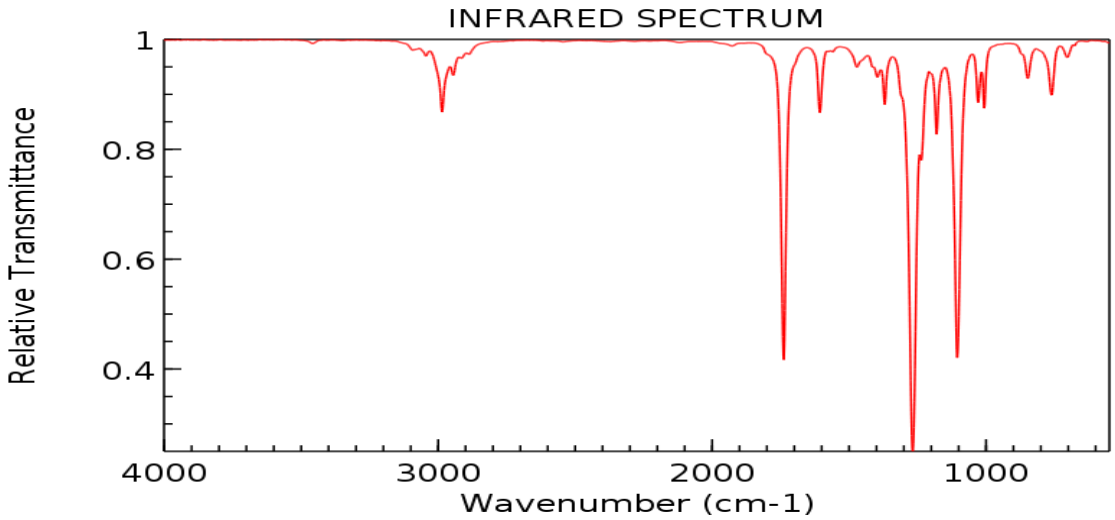


^{13}C nmr



δ

In the DEPT Spectrum the resonances at 165, 143 and 130 disappear but the remainder of the spectrum remains unchanged.



Please list the structural features that you can glean from analysis of each of these data.

Mass Spectrum and combustion analysis

Infrared spectrum:

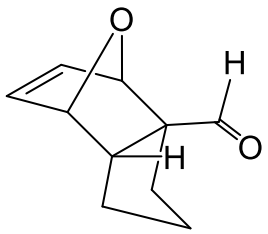
^{1}H-nmr:

CH 328N final exam 2016 Name_____

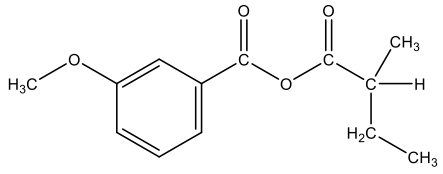
^{13}C-NMR:

Structure and assignment of resonances
Please keep your work covered.

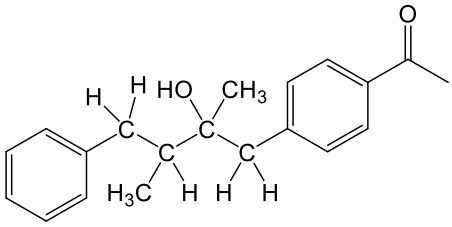
9. (10 pts) Please provide a synthetic pathway to the substance below. You may use any reagents or compounds you choose, but all of the carbon in your final product must come from the stock room, an inventory of which is on the cover page of the exam. Please be neat!!

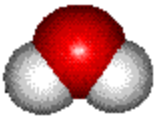


10. (10 pts) Please provide a synthetic pathway to the substance below. You may use any reagents or compounds you choose, but all of the carbon in your final product must come from the stock room, an inventory of which is on the cover page of the exam. Please be neat!!



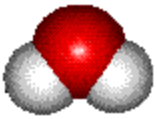
11. (10 pts) Please provide a synthetic pathway to the substance below. You may use any reagents or compounds you choose, but all of the carbon in your final product must come from the stock room, an inventory of which is on the cover page of the exam. Please be neat!!





CHEMISTRY 328N

CHARACTERISTIC PROTON CHEMICAL SHIFTS		
Type of Proton	**Structure**	**Chemical Shift, ppm**
Cyclopropane	C_3H_6	0.2
Primary	R-C**H**$_3$	0.9
Secondary	R_2-C**H**$_2$	1.3
Tertiary	R_3-C-**H**	1.5
Vinylic	C=C-**H**	4.6-5.9
Acetylenic	C≡C-**H**	2-3
Aromatic	Ar-**H**	6-8.5
Benzylic	Ar-C-**H**	2.2-3
Allylic	C=C-C**H**$_3$	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
Benzylic	**H**-C-Ar	2.6-3.2
Ethers	**H**-C-OR	3.3-4
Esters	RCOO-C-**H**	3.7-5.2
Esters	**H**-C-COOR	2-2.9
Acids	**H**-C-COOH	2-2.6
Carbonyl Compounds	**H**-C-C=O	2-2.7
Hydroxylic	R-C-O**H**	1-5.5
Phenolic	Ar-O**H**	4-12
Enolic	C=C-O**H**	15-17
Carboxylic	RCOO**H**	10.5-12
Amino	RN**H**$_2$	1-5
Aromatics	Ar-**H**	6.5 – 8.5
Aldehydic	R-(H-)C=O	9-10



CHEMISTRY 328N

CHARACTERISTIC INFRARED GROUP FREQUENCIES

wavenumber, cm–1	*bond*	*functional group*
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C(triple bond)C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2260–2210 (v)	C(triple bond)N stretch	nitriles
2260–2100 (w)	–C(triple bond)C– stretch	alkynes
1760–1665 (s	C=O stretch	carbonyls (general)
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1710-1720 (s)	C=O stretch	ketones, saturated aliphatic
1680–1640 (m)	–C=C– stretch	alkenes
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
900–675 (s)	C–H "out of Plane"	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp