UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

Version

01

December 10th, 2022 Time: 2 Hours

READ THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR **NAME**, **STUDENT I.D. NUMBER** ON ***BOTH*** **YOUR ANSWER BOOKLET** AND **COMPUTER ANSWER SHEET**.

ENTER **VERSION NUMBER 01** ON THE **COMPUTER ANSWER SHEET**

The examination consists of Parts 1 - 8, each of which should be attempted. Note that some parts provide you with a choice of questions, *e.g*. answer 6 out of 7. These will be graded in numerical order until the required number have been graded, regardless of whether they are right or wrong. Parts 1 - 5 will be computer graded, and only Parts 6, 7, and 8 are to be answered in the blue booklet provided.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 34 which are to be answered on your computer answer sheet (no extra time is provided for "bubbling" in the score sheet). Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a ***pencil only*** and ***not ink***. In some cases it is required that you indicate ***multiple*** items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out ***both*** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased ***cleanly***.

A periodic table with atomic numbers and atomic weights, infrared data tables, and $^{1}H/^{13}C$ NMR spectroscopy tables are located on the last four pages.

Molecular models are permitted during the exam; calculators are also permitted, ***but NOT programmable calculators***. **Absolutely no other electronic devices are allowed.**

14% PART 1: RELATIVE PROPERTIES

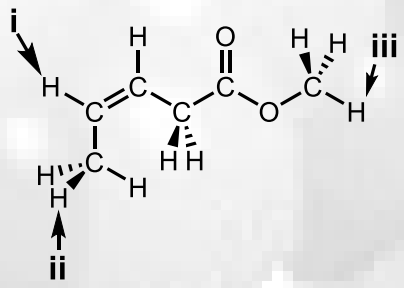
ANSWER ANY SEVEN (7) OF QUESTIONS 1 TO 8.

Arrange the items in questions 1-8 in DECREASING ORDER (i.e. greatest, most etc. first) with respect to the indicated property.

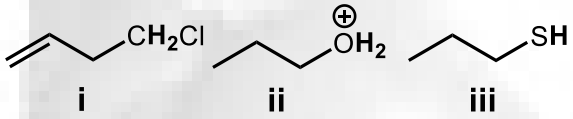
Use the following code to indicate your answers.

A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

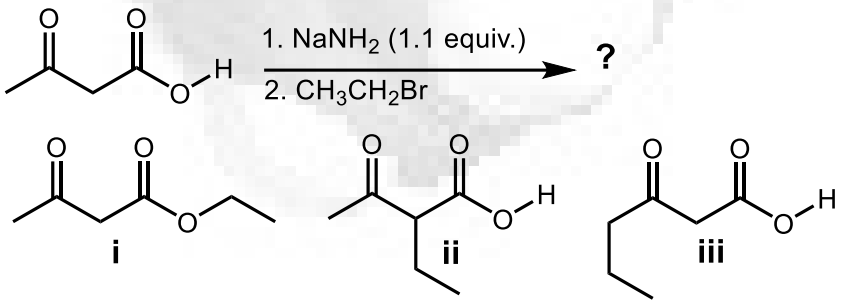
1. The ^{1}H NMR chemical shifts for the labelled atoms in the following structures:



2. The relative acidity of the hydrogens indicated in **bold**:



3. The relative amount of each product in the following reaction:



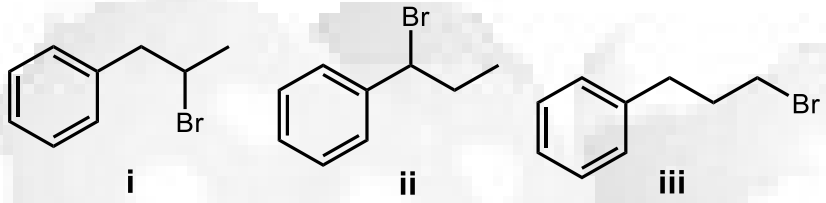
4. The relative rate of elimination when each of the following reacted with a base:

i. 1-bromohexane ii. 2-methylpentan-2-ol iii. 3-bromohexane

Use the following code to indicate your answers.

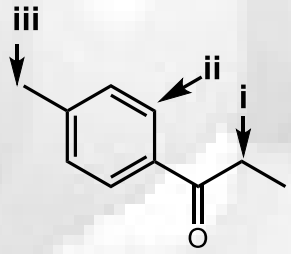
A.	**i** > **ii** > **iii**	**D**.	**ii** > **iii** > **i**
B.	**i** > **iii** > **ii**	**E**.	**iii** > **i** > **ii**
C.	**ii** > **i** > **iii**	**AB**.	**iii** > **ii** > **i**

5. The relative yield of the following monobrominated products formed when 1-phenylpropane is reacted with bromine under UV irradiation:



i **ii** **iii**

6. The number of lines observed in the ^{1}H-NMR spectrum for the hydrogens at each of the indicated positions:



7. The relative amount of the conjugate base of 3-pentanone formed by the reaction with 1 mole equivalent of each of the following:

CH_3OH **i** $NaN(i\text{-}Pr)_2$ **ii** NaOH **iii**

8. The relative yield of the anti-Zaitsev product from the reaction of 2-chloropentane with each of the following:

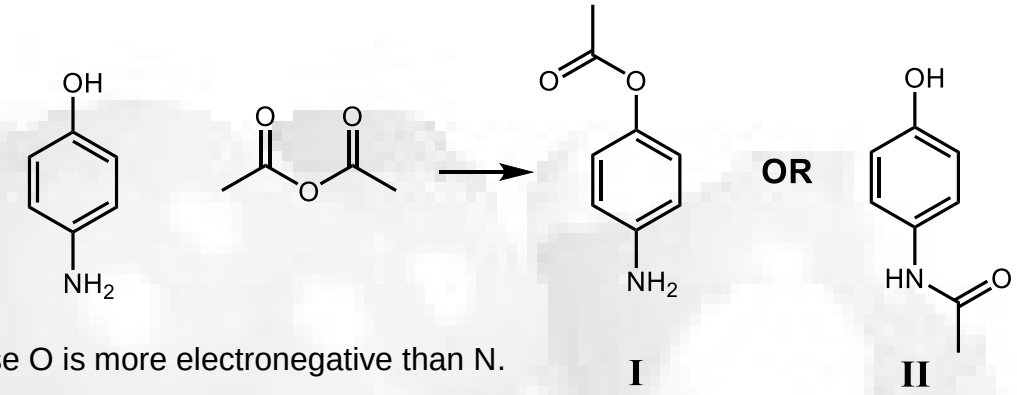
$(CH_3)_2CHOK$ **i** $(CH_3)_3CONa$ **ii** CH_3CH_2OLi **iii**

15% **PART 2: MOLECULAR PROPERTIES**

ANSWER ALL SIX (6) OF THE QUESTIONS 9 TO 14 (2.5 points each)

In questions 9-13 choose the single option that provides the best answer

9. Looking at the following reaction which is the major product and why?



A. **I** because O is more electronegative than N.

B. **II** because N is more nucleophilic than O.

C. **I** because O has more lone pairs than N.

D. **II** because O is involved with resonance within the ring, where N is not.

E. Both compounds will form in equal amounts.

10. Which of the alcohols (**I** and **II**) shown below, would undergo nucleophilic substitution with HBr the fastest and why?

A. Both are equally effective.

B. **I** because it is more acidic.

C. **I** because it proceeds via a resonance stabilized carbocation.

D. **II** because it is less sterically hindered in the SN2 reaction.

E. **II** because it proceeds via a resonance stabilized carbocation.

11. Which of the following ranks highest in the Cahn-Ingold-Prelog priority rules?

A. They have equal priority because both attach at C atoms

B. **II** because Br has a higher priority than F

C. **I** because F has a higher priority than C

D. **II** because overall it weighs more

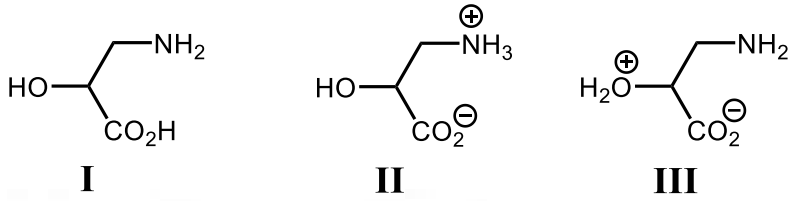
E. **I** because F has a higher priority than H

I —CH_2F

OR

II —$(CH_2)_2Br$

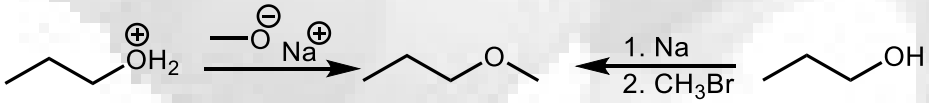
12. Which of the following structures corresponds to the major species present in an aqueous solution at pH = 7.



I **II** **III**

A. **I** because it has no formal charges.
B. **II** because the pKa of the alkylammonium cation is greater than 7.
C. All present in approximately equal amounts.
D. **III** due to an acid / base reaction occurring between close species.
E. **II** due to a hydride shift.

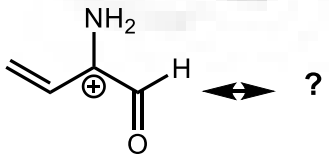
13. Which of the following is the preferred reaction pathway?

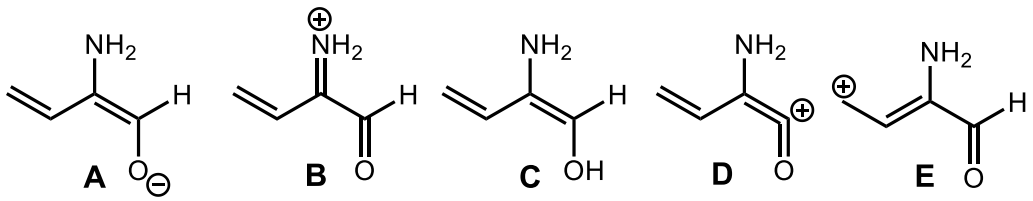


I **II**

A. **I** because the nucleophile needs to be the smaller group
B. **II** because the nucleophile needs to be the bigger group
C. **II** because only with these conditions will a substitution reaction occur
D. **I** because H_2O is a better leaving group than HO^-.
E. **I** because the methoxide is a better nucleophile than 1-propanol.

14. Which of the following is/are resonance structures of the structure shown below? (**select all that apply**)



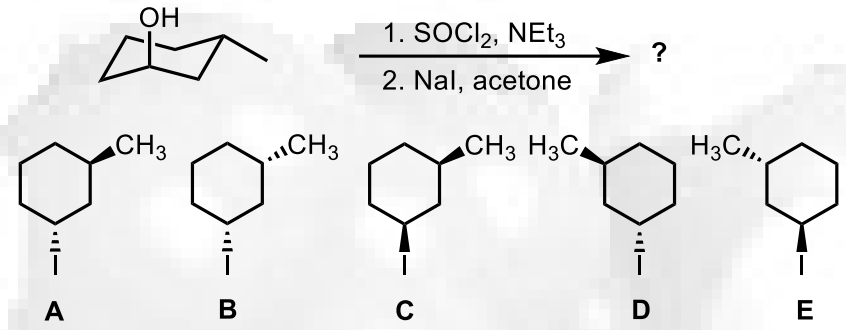


10% **PART 3: REACTIONS**

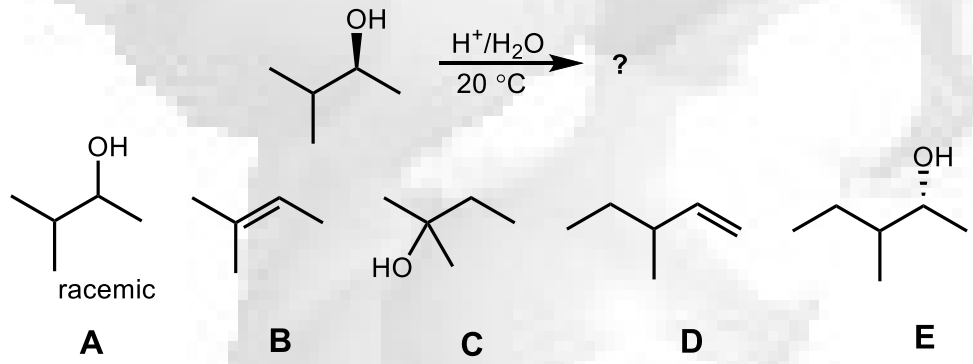
ANSWER ANY FIVE (5) of questions 15-20 (2 marks per question)

For each of questions 15-20, selecting the MISSING component (the best starting material, the major product, or the best reagents) required in order to BEST complete the reaction schemes.

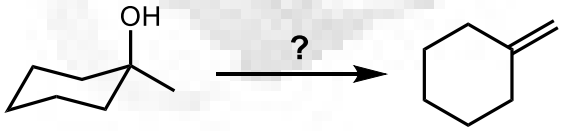
15.



16.

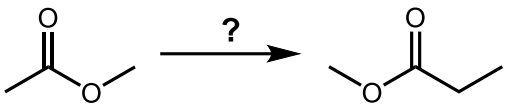


17.



A 1. PBr_3, NEt_3 2. KOH/heat **B** H_2SO_4 / heat **C** 1. Br_2, uv-light 2. NaH / heat **D** 1. TsCl, NEt_3 2. KO*t*-Bu / heat **E** HBr

18.



A 1. $NaNH_2$
2. CH_3OH

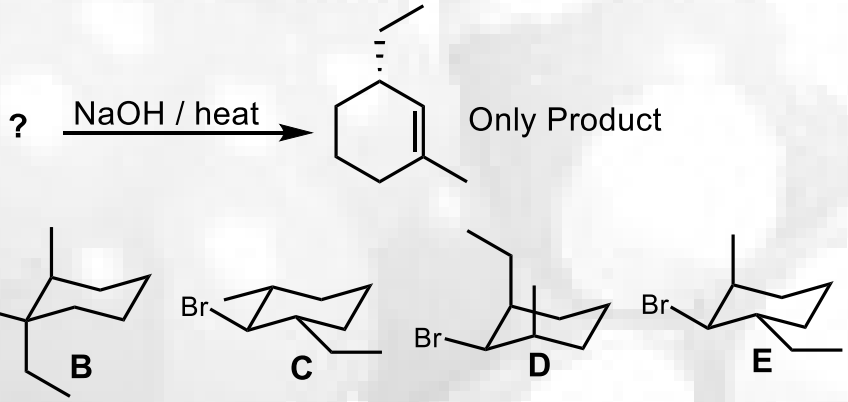
B 1. H_2SO_4 / heat
2. CH_3Br

C 1. Br_2, uv-light
2. CH_4

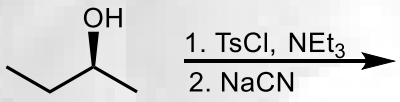
D 1. HBr / heat
2. CH_4

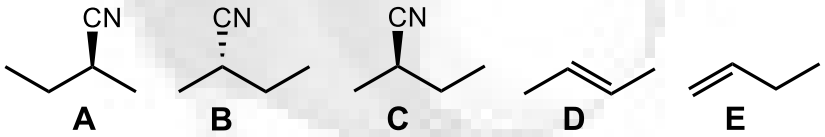
E 1. NaH
2. CH_3Br

19.



20.



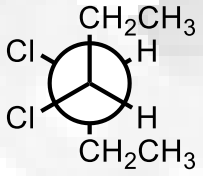


11% **PART 4: CONFORMATIONAL ANALYSIS**

ANSWER ANY SEVEN (7) of questions 21-28

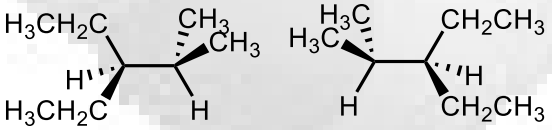
For 21 – 22 choose the best option.

21. Which term **BEST** describes the relative positions of the two chloro groups in the 3,4-dichlorohexane shown below?



A Staggered
B Eclipsed
C Anti
D Gauche
E Syn

22. Which of the following terms best describes the relationship between the two molecules shown below?



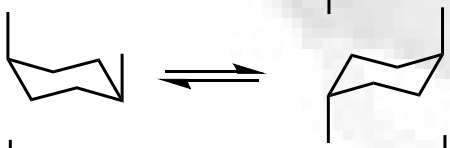
A constitutional isomers
B identical
C conformational isomers
D enantiomers
E not isomers

For 23 – 25 choose all that apply.

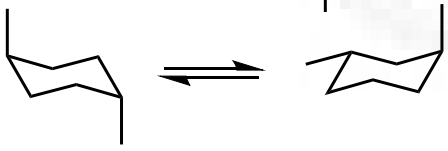
23. Which of the following shows a ring flip?

A

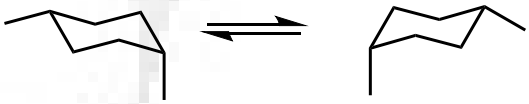
B



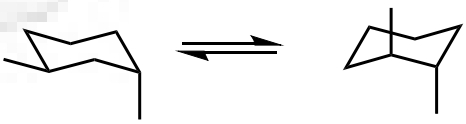
C



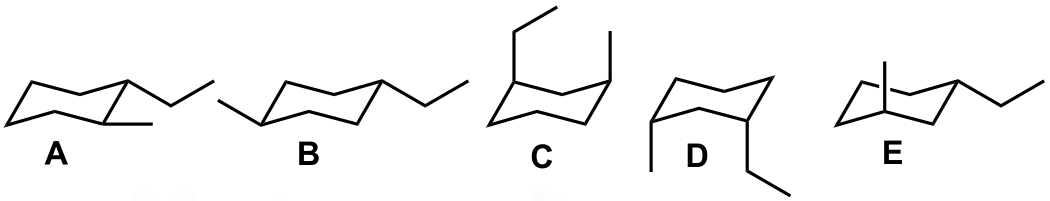
D



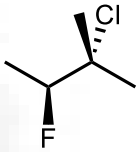
E

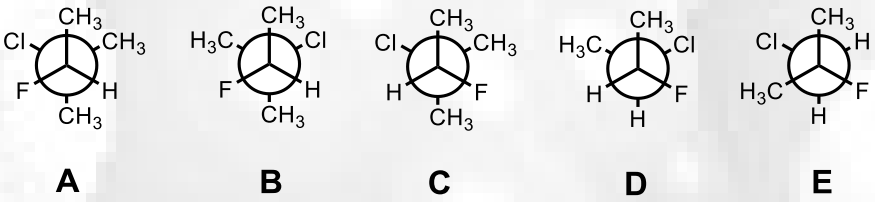


24. Which of the following structures represent the lowest energy conformation of *trans*-1-ethyl-3-methylcyclohexane?

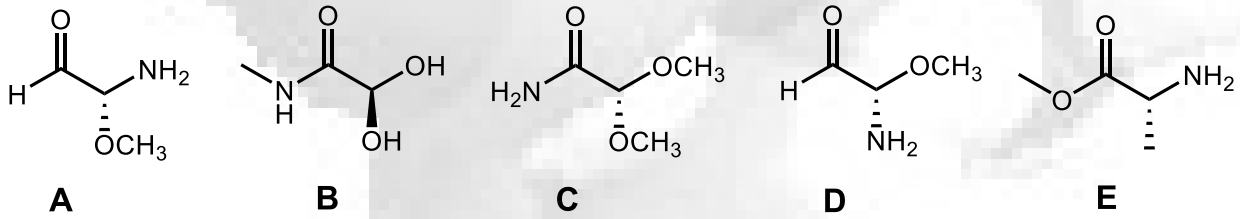


25. Which of the following Newman projections represents the structure to the right?



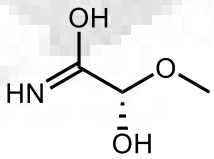


Use the following list of structures to answer questions 26 and 28.

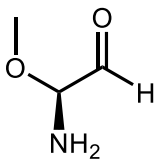


26. Which of the above contain a chirality center? (Choose all that apply)

27. Which of the above would be a constitutional isomer of the following molecule (choose all that apply):



28. Which of the above would be considered a conformational isomer of the following molecule (choose all that apply):



12% **PART 5: SPECTROSCOPY**

ANSWER ALL SIX (6) OF QUESTIONS 29 TO 34.

For each of questions 29-34 select the compound from the list provided that corresponds BEST with the spectroscopic data provided.

29. **^{1}H NMR:** δ/ppm 6.65 ppm (singlet, 1H), 13.0 (broad singlet, exchangeable 1H)
^{13}C NMR: δ/ppm 137, 177
IR: 3400-2876 (Broad), 1695, 1278 cm^{-1}

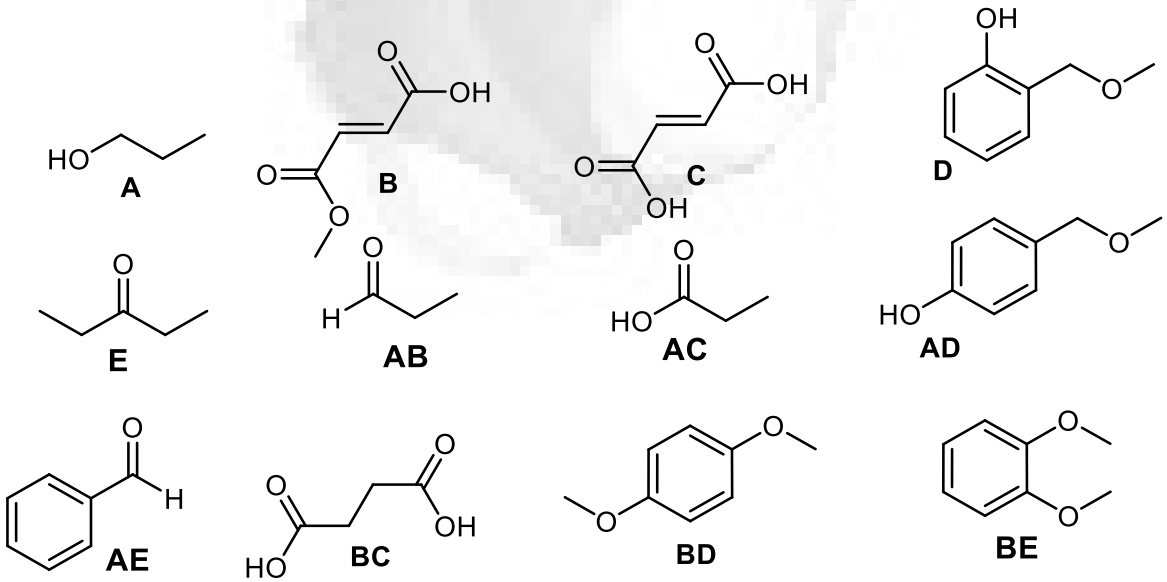
30. **^{1}H NMR:** δ/ppm 3.9 ppm (singlet, 3H), 6.9 (multiplet, 2H)
^{13}C NMR: δ/ppm 56, 112, 121, 149
IR: 3065, 2909, 1607,1254 cm^{-1}

31. **^{1}H NMR:** δ/ppm 2.4 (singlet, 2H), 12.2 (singlet, 1H)
^{13}C NMR: δ/ppm 29, 173
IR: 3200 (broad), 1693, 1206 cm^{-1}

32. **^{1}H NMR:** δ/ppm 1.1 (triplet, 3H), 2.4 (quartet, 2H)
^{13}C NMR: δ/ppm 8, 36, 212
IR: 2981, 1720 cm^{-1}

33. **^{1}H NMR:** δ/ppm 1.1 (triplet, 3H), 2.5 (quartet, 2H), 9.8 (singlet, 1H)
^{13}C NMR: δ/ppm 6, 37, 203
IR: 2980, 2900, 2828, 2724, 1733 cm^{-1}

34. **^{1}H-NMR**: δ/ppm 3.4 (singlet, 3H), 4.4 (singlet, 2H), 6.0 (broad singlet, exchangeable, 1H), 6.7 (doublet, 2H), 7.2 (doublet, 2H).
^{13}C-NMR: δ/ppm 58, 75, 115, 129, 130, 156
IR: 3289 (Broad), 1517, 1080 cm^{-1}

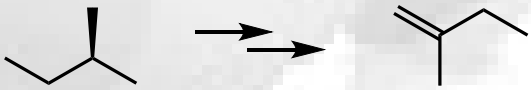


10% **PART 6: SYNTHESIS**

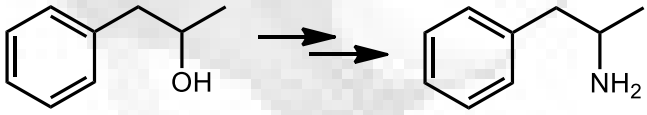
DESIGN EFFICIENT SYNTHESES OF ONE of the following two target molecules from the indicated starting material. In addition, you are allowed to use any hydrocarbon with three or fewer carbon atoms, any solvents or inorganic reagents, and any organic reagents that do not contribute carbon atoms to the carbon skeleton in the product. More than one step will be required for each synthesis. Clearly show the required reagents and the product of each step.

WRITE YOUR ANSWERS IN THE EXAM BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.



OR

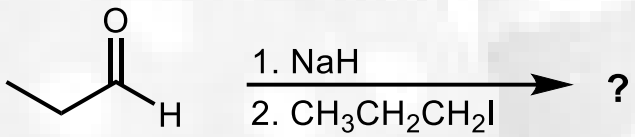


14% **PART 7: MECHANISMS**

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

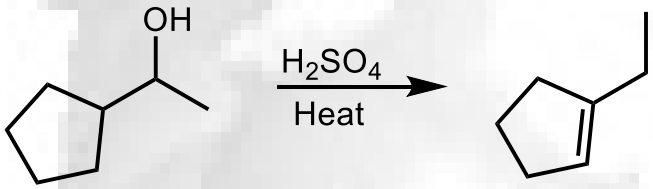
USE A 'CURLY ARROW' MECHANISM TO EXPLAIN TWO OF THE FOLLOWING THREE REACTIONS. NO OTHER REAGENTS ARE REQUIRED BEYOND WHAT IS SHOWN

Use curly arrow mechanism to explain the following reaction and predict the product:



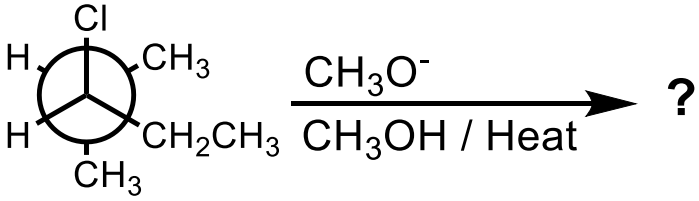
AND / OR

Show the arrow pushing for the following reaction:



AND / OR

Draw all three elimination products for the following reaction. Identify the major product and draw the reaction mechanism to explain your answer.



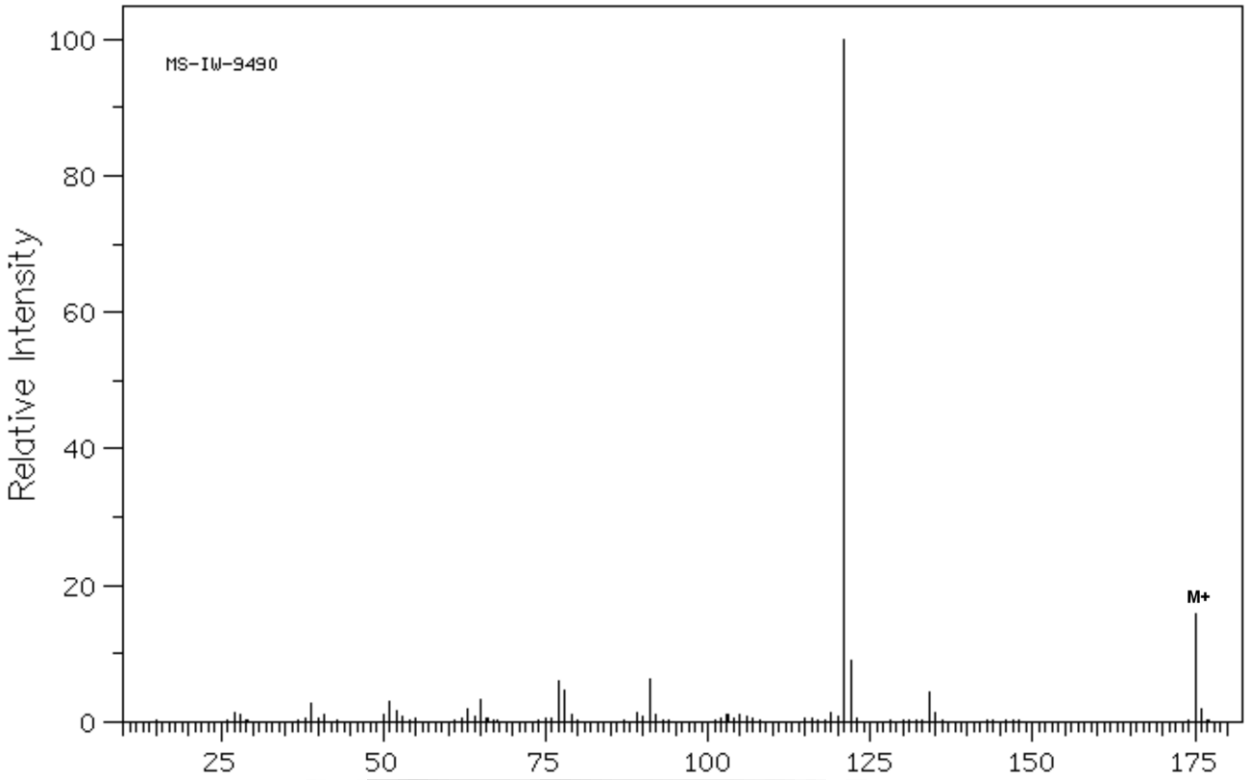
14% **PART 8: SPECTROSCOPY**

WRITE YOUR ANSWERS IN THE BLUE ANSWER BOOKLET PROVIDED.

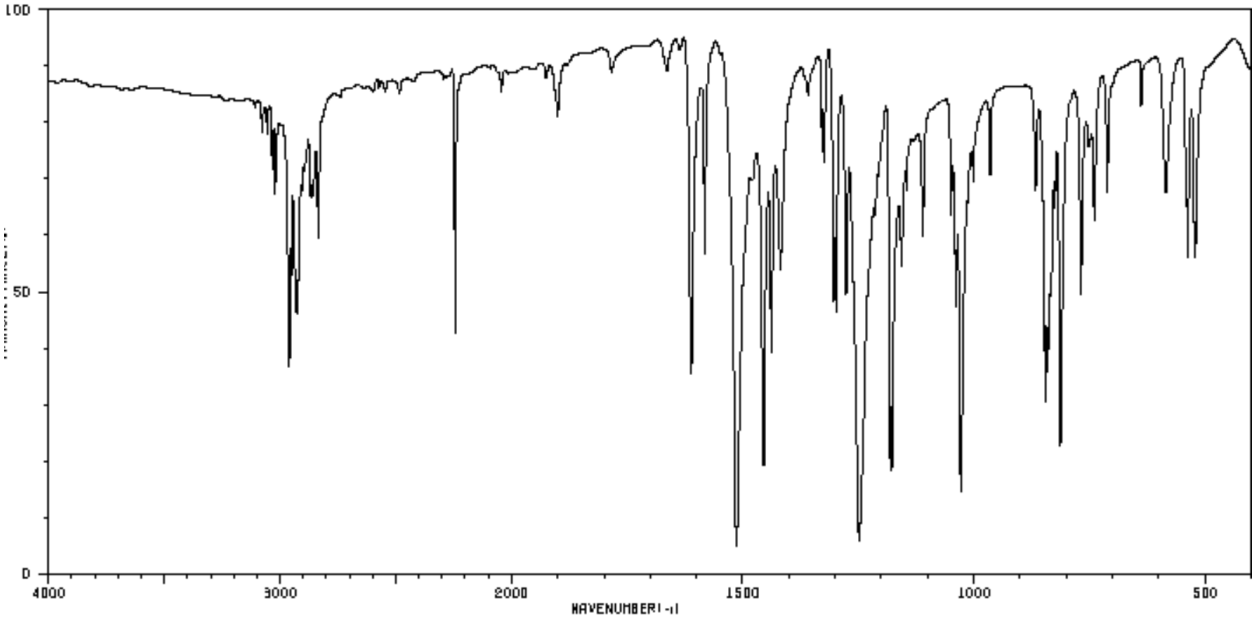
Show your working as PARTIAL marks may be given.

From the spectral data provided below, identify the structure of the "unknown" molecule.

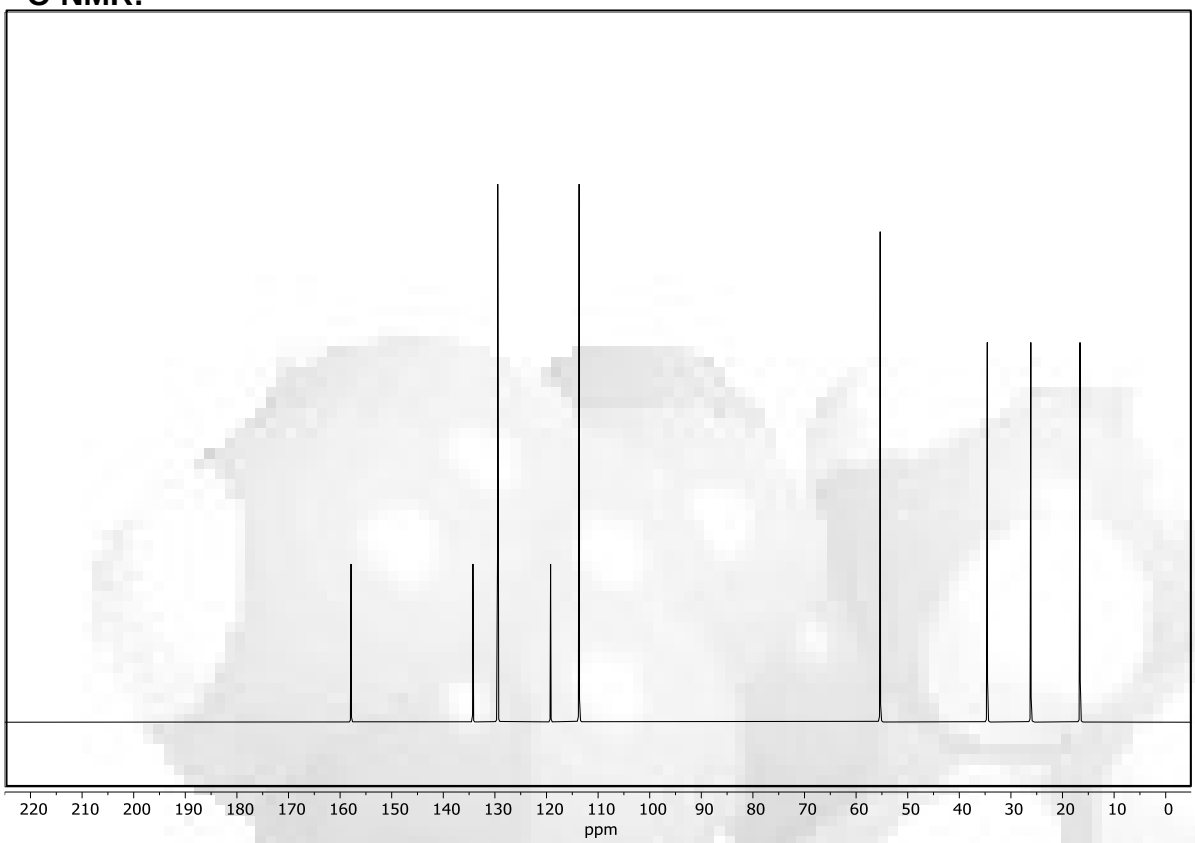
Mass Spectrum:



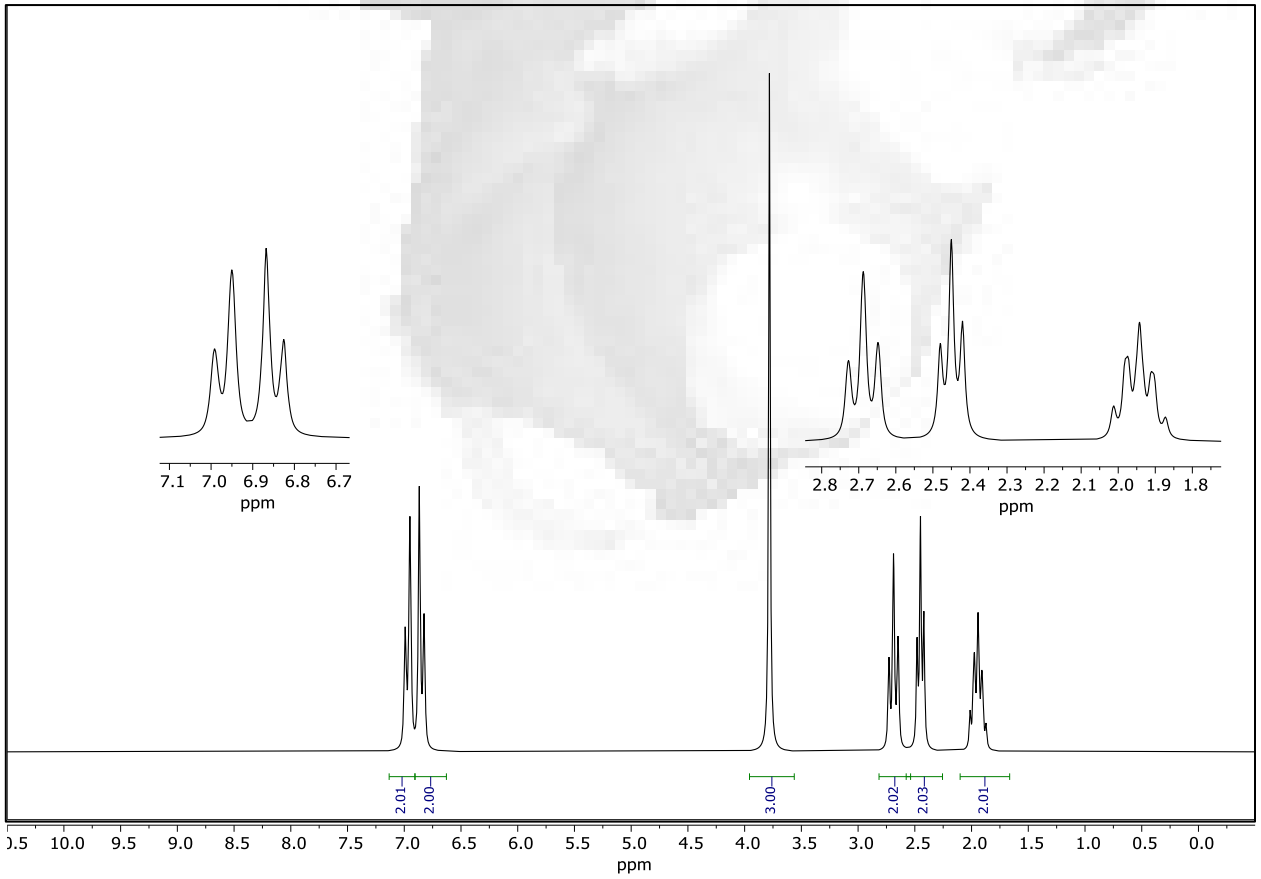
IR Spectrum:



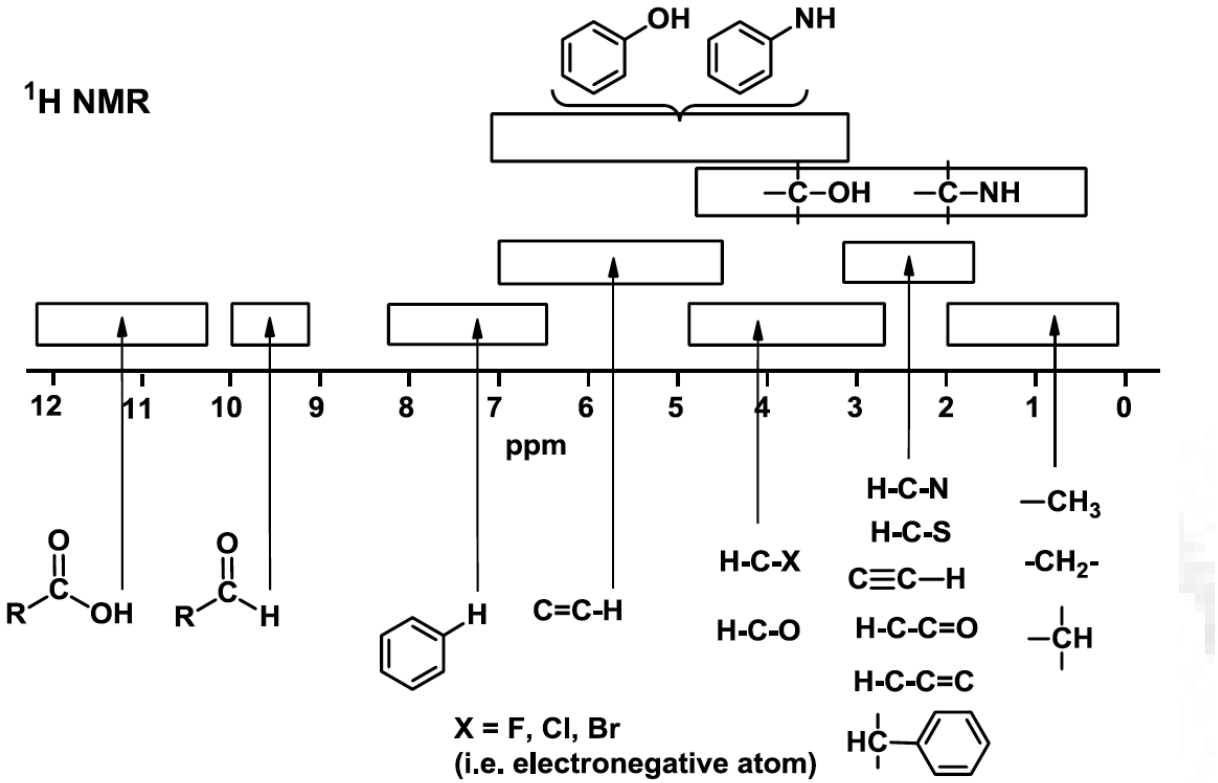
^{13}C-NMR:



^{1}H-NMR:



SPECTROSCOPIC TABLES

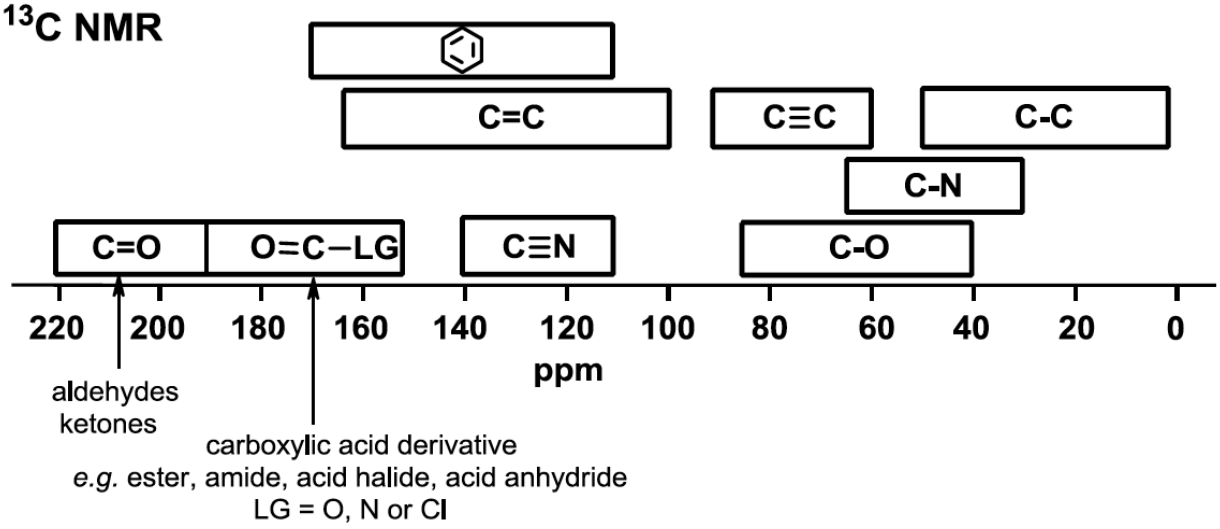


^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

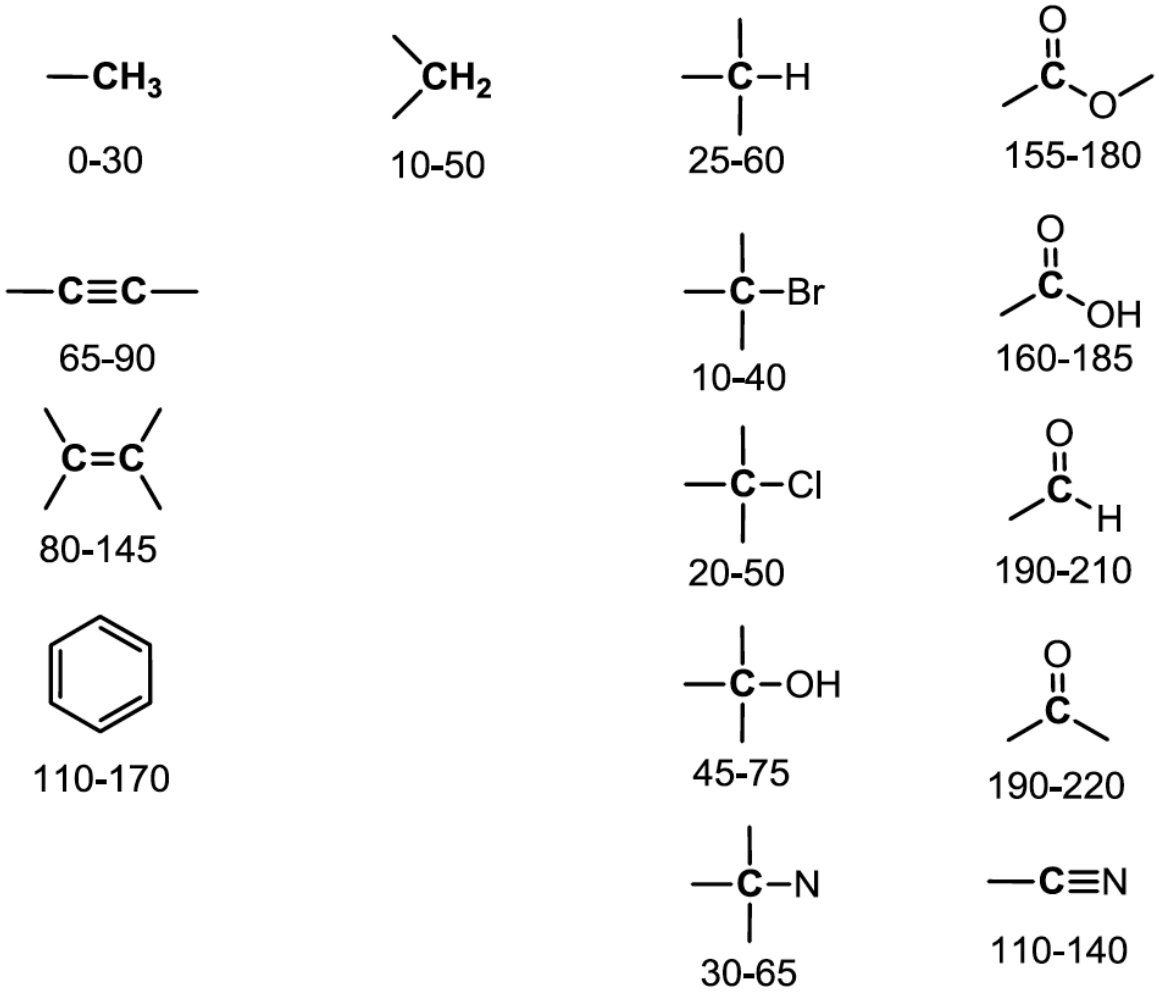
R =	methyl $-CH_3$	methylene $-CH_2-$	methyne $-CH$
R–C—	0.9	1.4	1.5
R–C=C	1.6	2.3	2.6
R–C(=O)–	2.1	2.4	2.5
R–N	2.2	2.5	2.9
R–Ar	2.3	2.7	3.0
R–Br	2.7	3.3	4.1
R–Cl	3.1	3.4	4.1
R–O—	3.3	3.4	3.7

other	
sp^3C-OH	1-5
sp^3C-NH	1-3
C≡CH	2.5
C=C(H)–	4.5-6.5
H–Ar	6.5-8
R–C(=O)–H	9-10
R–C(=O)–OH	9-12

^{13}C NMR



^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



INFRA-RED GROUP ABSORPTION FREQUENCIES

		TYPE OF VIBRATION	FREQUENCY (cm^{-1})	WAVELENGTH (μ)	INTENSITY (1)
C–H	Alkanes	(stretch)	3000-2850	3.33-3.51	s
$-CH_3$		(bend)	1450 and 1375	6.90 and 7.27	m
$-CH_2-$		(bend)	1465	6.83	m
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne	(stretch)	ca. 3300	ca.3.03	s
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C–C	Alkane	not usually useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic acid		1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
	Acyl chloride		1800	5.55	s
C–O	Alcohols, Ethers, Esters,				
	Carboxylic acids		1300-1000	7.69-10.0	s
O–H	Alcohols, Phenols				
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acids (2)		3300-2500	3.03-4.00	m
N–H	Primary and secondary amines		3500-3100	ca. 2.86	m
C≡N	Nitriles		2260-2240	4.42-4.46	m
N=O	Nitro ($R-NO_2$)		1600-1500	6.25-6.67	s
			1400-1300	7.14-7.69	s
C–X	Fluoride		1400-1000	7.14-10.0	s
	Chloride		800-600	12.5-16.7	s
	Bromide, Iodide		<600	>16.7	s

(1) s = strong, m = medium and w = weak

(2) note that the -OH absorption of solid carboxylic acids which run as a nujol mull can be difficult to see as they maybe very broad

PERIODIC TABLE

1 1A																	18 8A
1 **H** 1.008	**2** 2A											**13** 3A	**14** 4A	**15** 5A	**16** 6A	**17** 7A	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57* **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0	89** **Ac** (227)	104 **Rf** (261)	105 **Ha** (262)	106 **Sg** (263)	107 **Ns** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Uun** (269)	111 **Uuu** (272)							

Lanthanides *	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
Actinides **	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.0	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)