

UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
FINAL EXAMINATION
CHEMISTRY 351

Version
1

December 13th 2016

Time: 3 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 1** ON THE **COMPUTER ANSWER SHEET**

The examination consists of Parts **1 - 9**, each of which should be attempted. Note that some Parts provide you with a choice of questions, *i.e.* answer 4 out of 5. These will be graded in numerical order until the required number have been completed, **regardless** of whether they are right or wrong.

Parts 1 - 5 will be computer graded, and **Parts 6 - 9** are to be answered in the answer booklet provided. **Parts 1 - 5** consist of a series of multiple choice questions numbered 1 - 40, which are to be answered on your computer answer sheet. Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet (this must be completed within the 3hrs). Use a pencil only **not ink** to completely fill the circle(s). 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 and tables of spectroscopic data are provided at the end of the examination paper. **No other resources are allowed.**

Molecular models and calculators are permitted, **but NOT programmable calculators.**

Absolutely no other electronic devices are allowed.

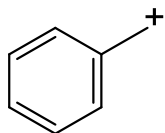
15% PART 1: RELATIVE PROPERTIES**ANSWER ANY TEN (10) OF QUESTIONS 1 TO 12.****Arrange the items in questions 1-12 in DECREASING ORDER (i.e. greatest, most etc. first) with respect to the indicated property.**

Use the following code to indicate your answers.

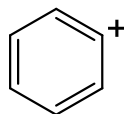
A. i > ii > iii
B. i > iii > ii
C. ii > i > iii

D. ii > iii > i
E. iii > i > ii
AB. iii > ii > i

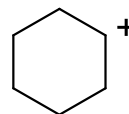
1. The relative stability of the following carbocations:



i



ii

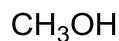


iii

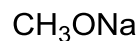
2. The relative basicity of each of the following:



i

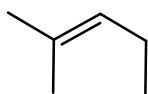


ii

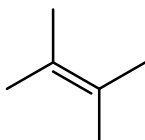


iii

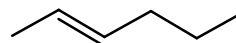
3. The heats of formation of each of the following (least negative to most negative):



i

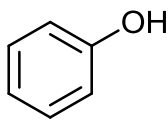


ii

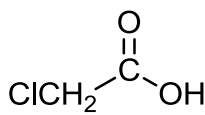


iii

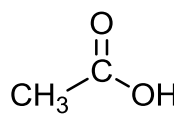
4. The relative acidity of each of the following:



i



ii



iii

Use the following code to indicate your answers.

A. i > ii > iii

B. i > iii > ii

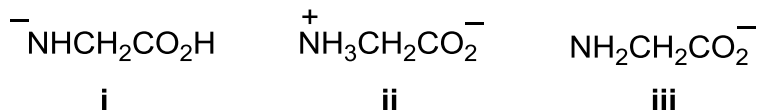
C. ii > i > iii

D. ii > iii > i

E. iii > i > ii

AB. iii > ii > i

5. The relative amounts of each of the following species of glycine (also known as 2-aminoethanoic acid) present in an aqueous solution of pH = 9 :



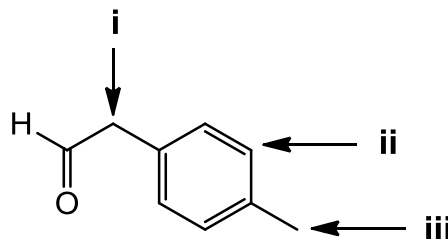
6. The relative rate of reaction of each of the following with HBr :

i. sec-butanol

ii. isobutanol

iii. tert-butanol

7. The $^1\text{H-NMR}$ chemical shifts for the groups indicated by arrows in the following structure:



8. The relative leaving group ability of the following:

Cl^-

HO^-

H_2O

i

ii

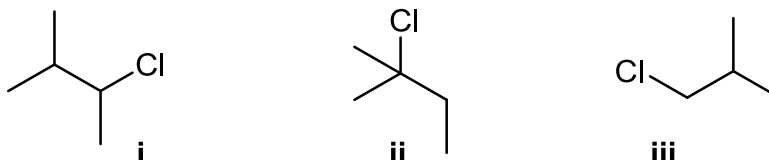
iii

Use the following code to indicate your answers.

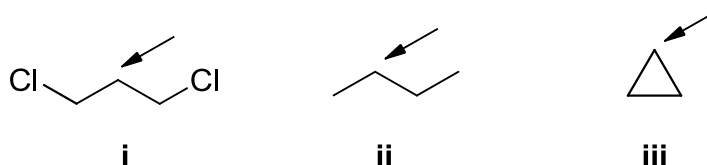
A. i > ii > iii
B. i > iii > ii
C. ii > i > iii

D. ii > iii > i
E. iii > i > ii
AB. iii > ii > i

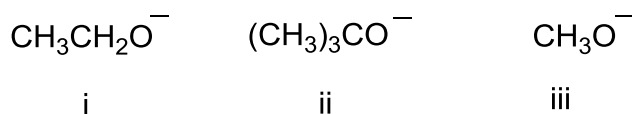
9. The relative yields of each of the following from the reaction of 2-methylbutane with chlorine / uv light:



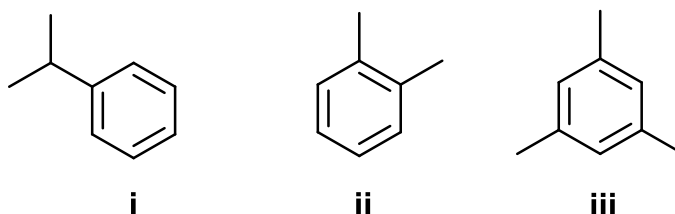
10. The number of lines in the H-NMR signals for the H atoms at the positions indicated in each of the following :



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



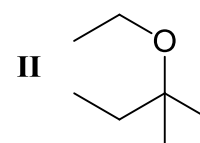
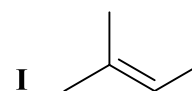
12. The number of types of carbon in each of the following:



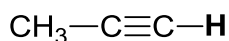
12% **PART 2: MOLECULAR PROPERTIES****ANSWER ALL SIX (6) OF THE QUESTIONS 13 TO 18.**In questions 13-17 choose the single option that provides the best answer.

13. Which of the following is the major product of the reaction of 2-bromo-2-methylbutane with NaOEt / EtOH at room temperature?

- A. **I** because EtOH is a strong base
 B. **II** because NaOEt is a strong nucleophile
 C. **I** because NaOEt is a strong base
 D. **II** because substitution is favoured at low temperatures
 E. **I and II** are formed in equivalent amounts as NaOEt is both a strong base and a strong nucleophile

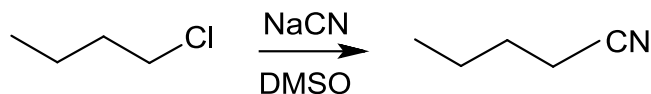


14. Which of the following best explains the H-NMR chemical shift of the alkyne **H** ?



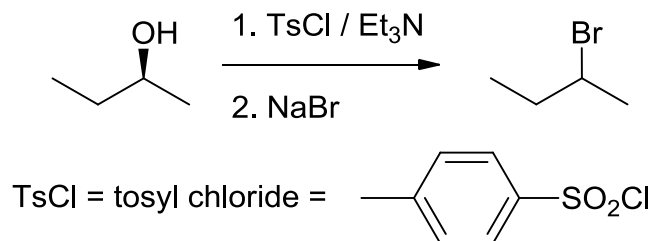
- A. Resonance of the pi bonds
 B. Alkyl are weak electron donors due to inductive effects and hyperconjugation
 C. The high electron density associated with the triple bond
 D. It falls in the shielding cone of the magnetic field due to the pi system
 E. It falls in the deshielding area of the magnetic field due to the pi system

15. In the reaction shown below, the rate of reaction is markedly increased when catalytic amounts of NaI are added to the reaction mixture. This is because:



- A. DMSO is a polar aprotic solvent
 B. NaI is a stronger nucleophile than NaCN
 C. NaI is a weaker nucleophile than NaCN
 D. NaI in DMSO favours SN2 reactions that are faster than SN1 reactions
 E. NaI reacts with the alkyl chloride to introduce a better leaving group

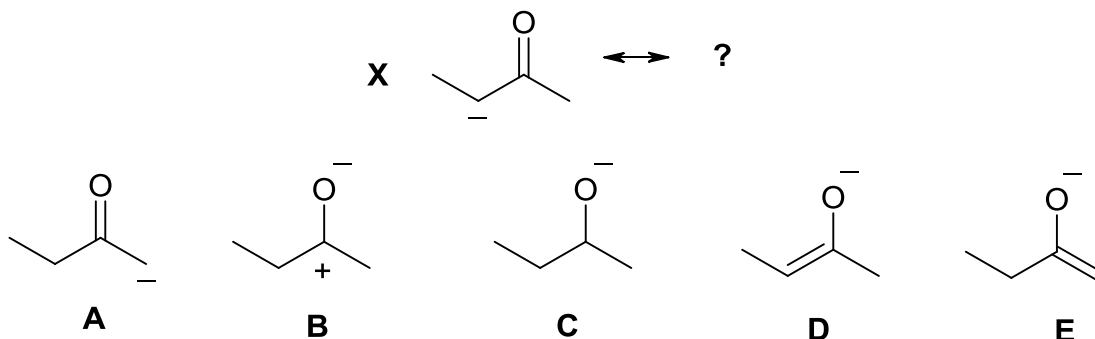
16. In the following reaction, where the stereochemistry of the product is not shown, the **product stereochemistry should be:**



- A. Racemic because the reaction proceeds via SN1 and takes place with inversion
 B. Inverted because the overall reaction is an SN2 and takes place with inversion.
 C. Racemic because the reaction occurs via a planar carbocation intermediate.
 D. Retained because there are two SN2 inversions (*i.e.* a double inversion)
 E. Irrelevant because the product does not have a chirality center
17. Which of the following has a higher IR stretching frequency and why ?



- A. I because the sp C-H bond is longer
 B. I because the sp C-H bond is stronger
 C. I because the triple bond is stronger
 D. II because the sp^2 C-H bond is longer
 E. II because the sp^2 C-H bond is stronger
18. Which of the following is/are resonance structures of the structure **X** (**select all that apply**) ?

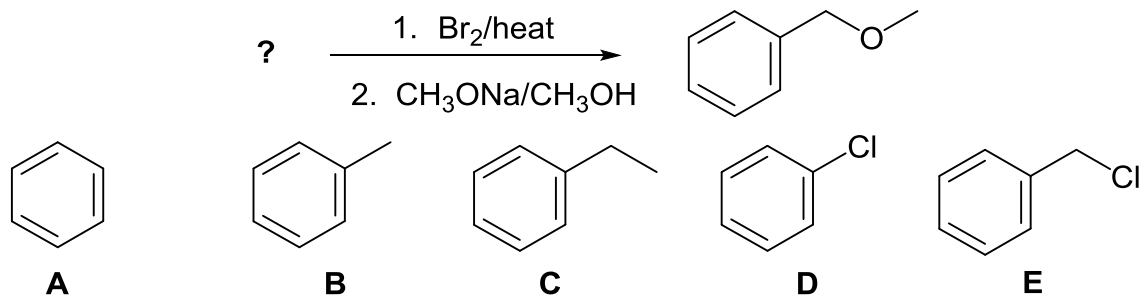


14% **PART 3: REACTIONS**

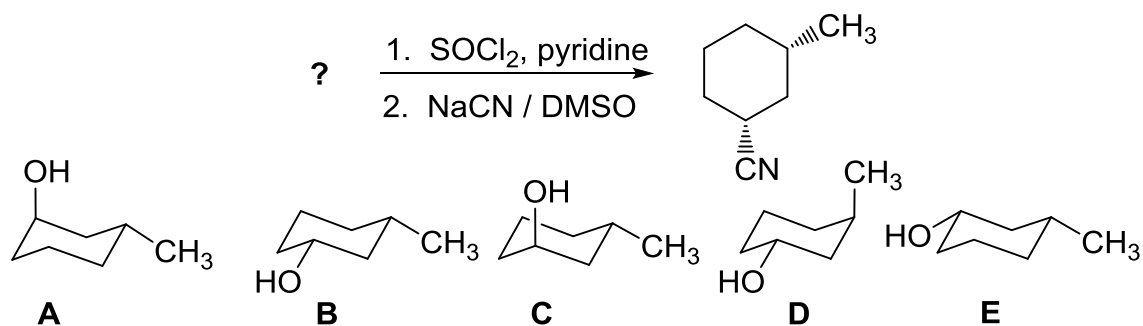
ANSWER ANY SEVEN (7) OF QUESTIONS 19 TO 26.

For each of questions 19-26 select the **MISSING** component (the best starting material, the major product or the best reagents) required in order to **BEST** complete each of the reaction schemes.

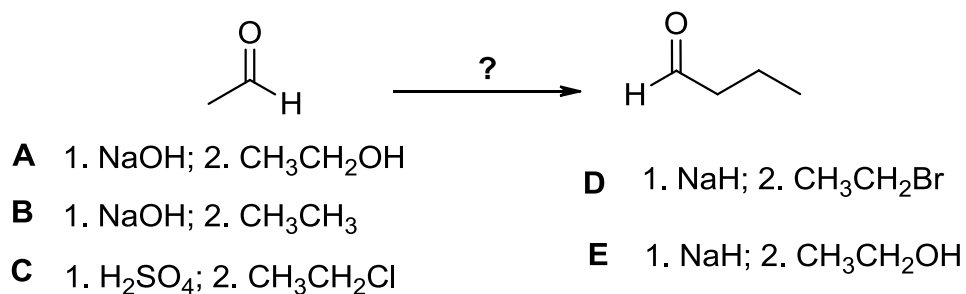
19.



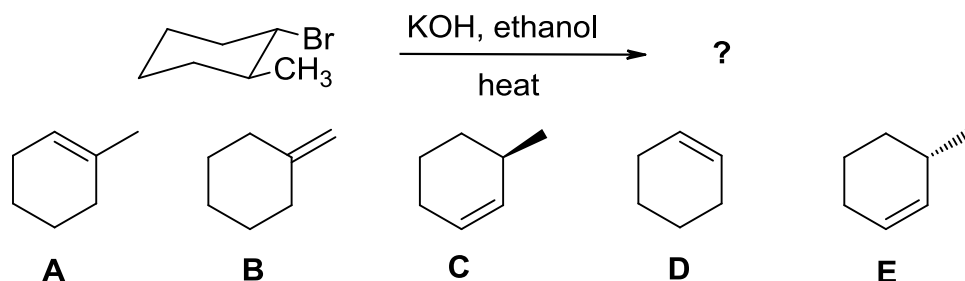
20.



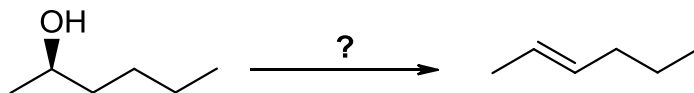
21.



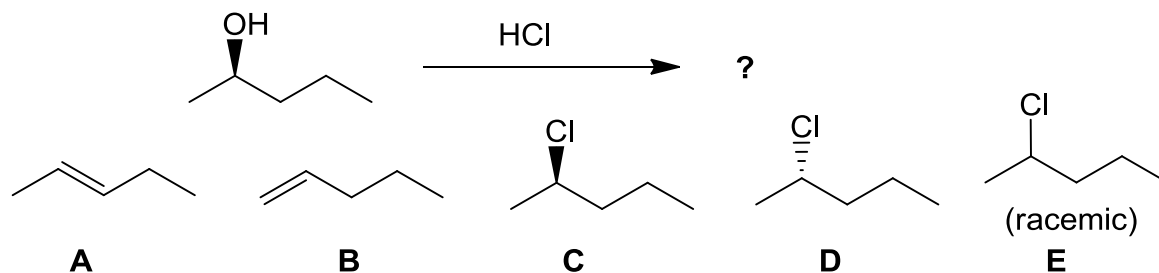
22.



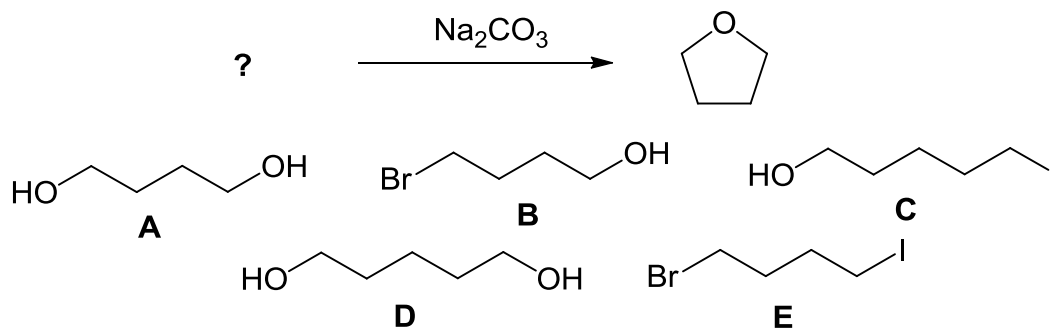
23.

**A** conc. H_2SO_4 / heat**B** HBr / heat**C** NaOH / heat**D** 1. H_2O / H_2SO_4
2. NaOH / heat**E** 1. PBr_3 / $\text{N}(\text{CH}_2\text{CH}_3)_3$
2. KO^tBu / heat

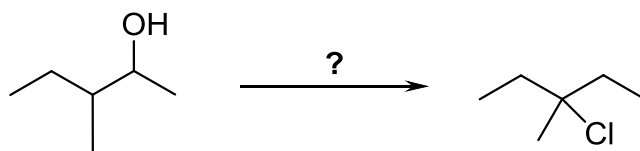
24.



25.



26.

**A** conc. HCl **B** Cl_2 **C** NaCl / DMSO **D** tosyl chloride / Et_3N **E** SOCl_2 / Et_3N

9% **PART 4: CONFORMATIONAL ANALYSIS**

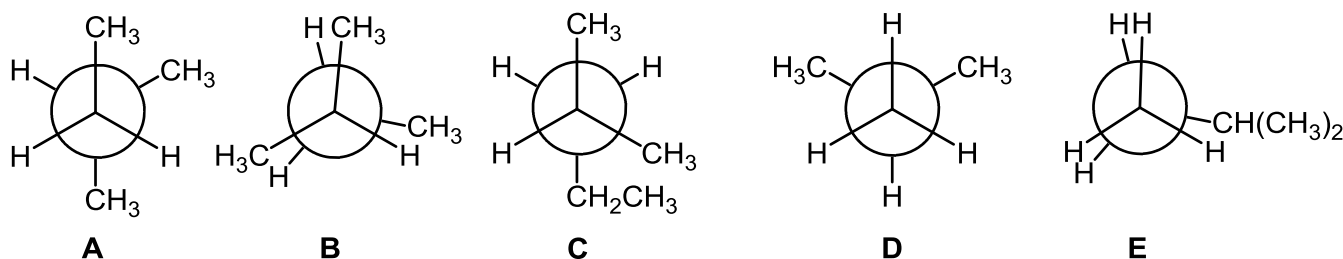
ANSWER ANY SIX (6) OF THE QUESTIONS 27 TO 34.

For each of the questions 27-34 select the answer(s) from those provided. In some cases more than one answer may be correct in which case all correct answers should be selected for full marks.

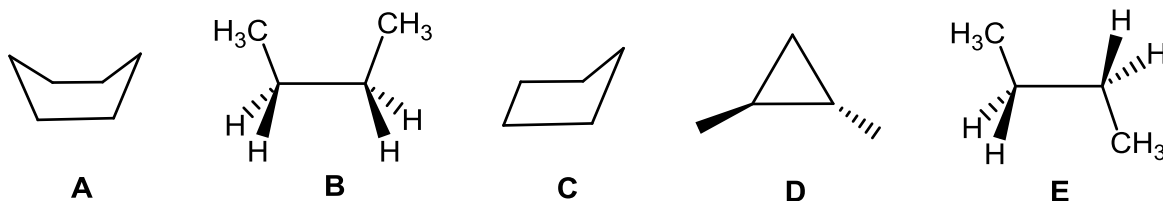
27. How many equatorial hydrogens are there in the most stable conformation of cis-1,3-dimethylcyclohexane.

- A 12 B 10 C 6 D 5 E 4 AB 3

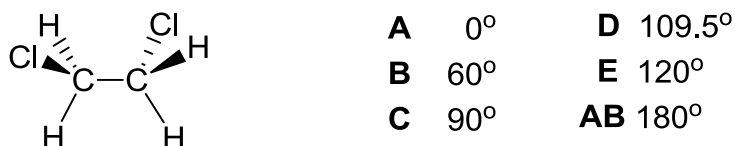
28. Which of the following Newman projections are **not** 2-methylbutane (select **all that apply**)



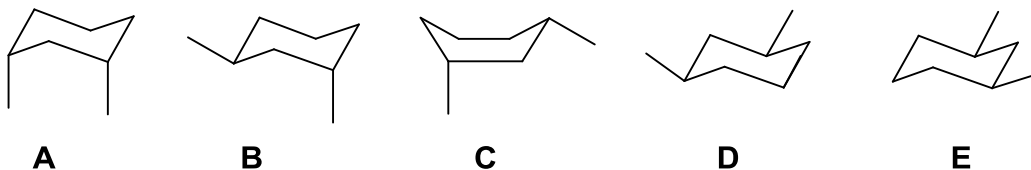
29. Among the molecular conformers listed below, which one has the **lowest** torsional strain as shown?



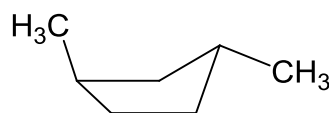
30. What is the **torsional** angle between the two chlorine groups in the conformation of 1,2-dichloroethane shown below ?



31. Which of the following structures represents the lowest energy conformations of trans-1,3-dimethylcyclohexane ?

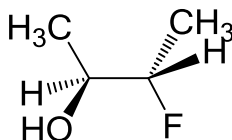
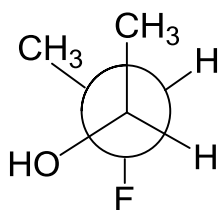


32. Which of the following terms **best** describes the relative position of the two methyl groups in the conformation of the molecule shown below?



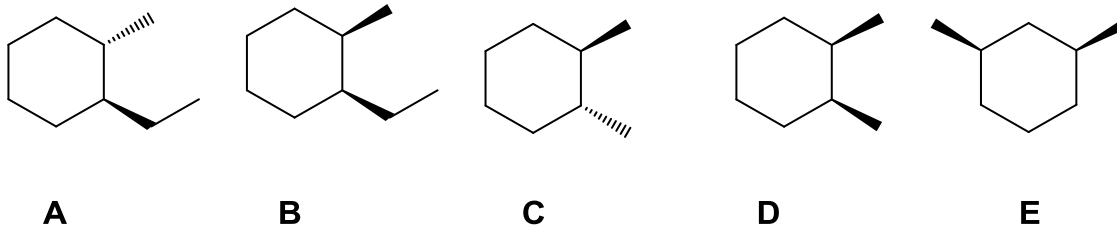
- A** eclipsed
B staggered
C anti
D cis
E trans
AB gauche

33. 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 diastereomers
AB meso
AC not isomers

34. Which of the following disubstituted cyclohexanes has chair conformers with the same energy (**select all that apply**) ?



12% PART 5: SPECTROSCOPY**ANSWER ALL SIX (6) OF QUESTIONS 35 TO 40.**

For each of questions 35-40 select the compound from the list provided that corresponds **BEST** with the spectroscopic data provided. .

35. $^1\text{H NMR}$: δ/ppm 1.1 (d, 6H), 2.7 (m, 1H), 9.7 (d, 1H)
 $^{13}\text{C NMR}$: δ/ppm 16.2, 41.2, 204.1
 IR : 1715 cm^{-1}

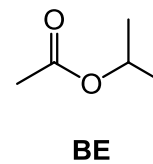
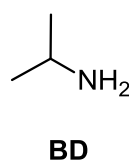
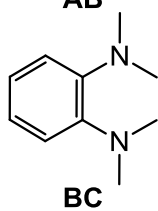
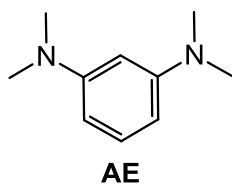
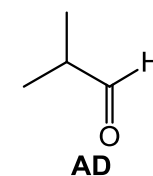
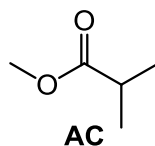
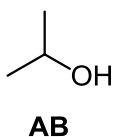
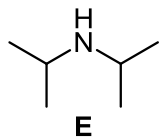
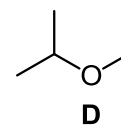
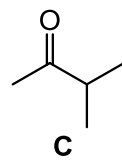
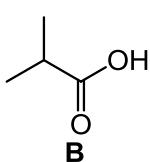
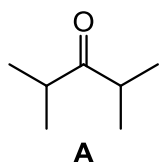
36. $^1\text{H NMR}$: δ/ppm , 1.1 (d, 6H), 3.5 (sept, 1H), 3.2 (s, 3H)
 $^{13}\text{C NMR}$: δ/ppm 22.0, 56.5, 80.3
 IR : 1210 cm^{-1}

37. $^1\text{H NMR}$: δ/ppm 1.2 (d, 6H), 2.7 (sept, 1H), 3.7 (s, 3H).
 $^{13}\text{C NMR}$: δ/ppm 19.1, 33.7, 52.2, 173.0
 IR : $1100, 1740\text{ cm}^{-1}$

38. $^1\text{H NMR}$: δ/ppm 3.1 (s, 6H), 6.4-6.6, (m, 2H)
 $^{13}\text{C NMR}$: δ/ppm 46.1, 111.4, 119.1, 135.6
 IR : $1609, 1502\text{ cm}^{-1}$

39. $^1\text{H NMR}$: δ/ppm 1.1 (d, 12H), 2.0 (broad, 1H, D_2O exchange), 3.0 (sept, 2H).
 $^{13}\text{C NMR}$: δ/ppm 24.0, 49.6
 IR : 3415 cm^{-1}

40. $^1\text{H NMR}$: δ/ppm 1.3 (d, 6H), 2.2 (s, 3H), 4.93 (sept, 1H)
 $^{13}\text{C NMR}$: δ/ppm 21.0, 21.6, 69.2, 170.2
 IR : 1735 cm^{-1}

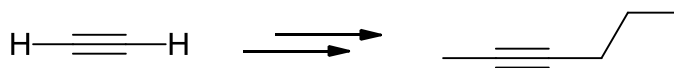


8% PART 6: SYNTHESIS

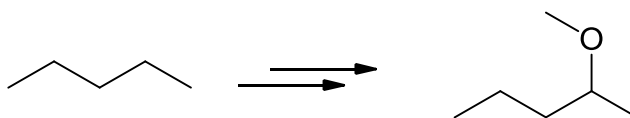
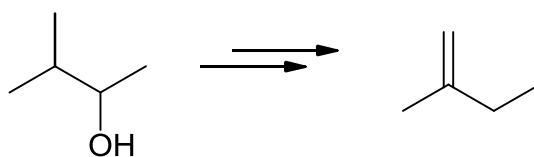
DESIGN TWO(2) EFFICIENT SYNTHESSES, ONE from PART A and ONE from PART B of the following target molecules from the indicated starting material. In addition, you are allowed to use **any hydrocarbon with three or fewer carbon atoms**, any solvents or inorganic reagents, and any organic reagents that do 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.

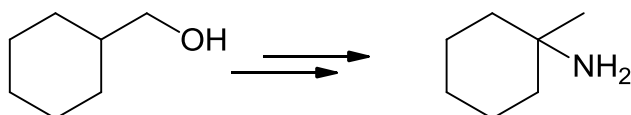
DO NOT SHOW MECHANISMS.

PART A

OR

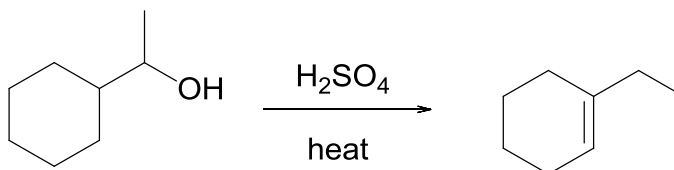
**PART B**

OR



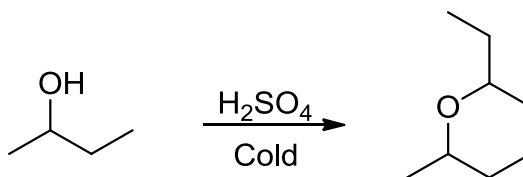
10% PART 7: MECHANISMS**WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED****ANSWER TWO (2) QUESTIONS, ONE from PART A and ONE from PART B.****NO REAGENTS OTHER THAN THOSE ALREADY SHOWN ARE REQUIRED.****(5%) PART A: Use a curly arrow mechanism to explain ONE of the following reactions:**

i.

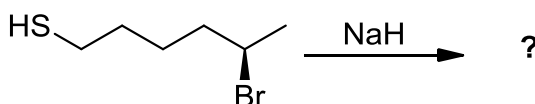


OR

ii.

**(5%) PART B: Use a curly arrow mechanism to explain ONE of the following reactions:**

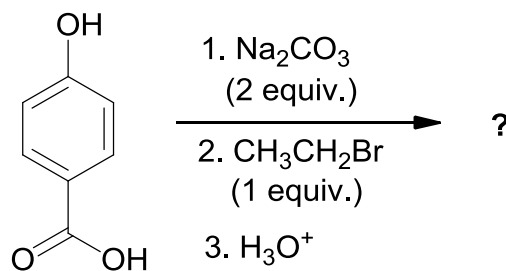
i. Predict the major product of the following reaction by showing the mechanism.



OR

ii. Predict the major product of the following reaction by showing the mechanism.

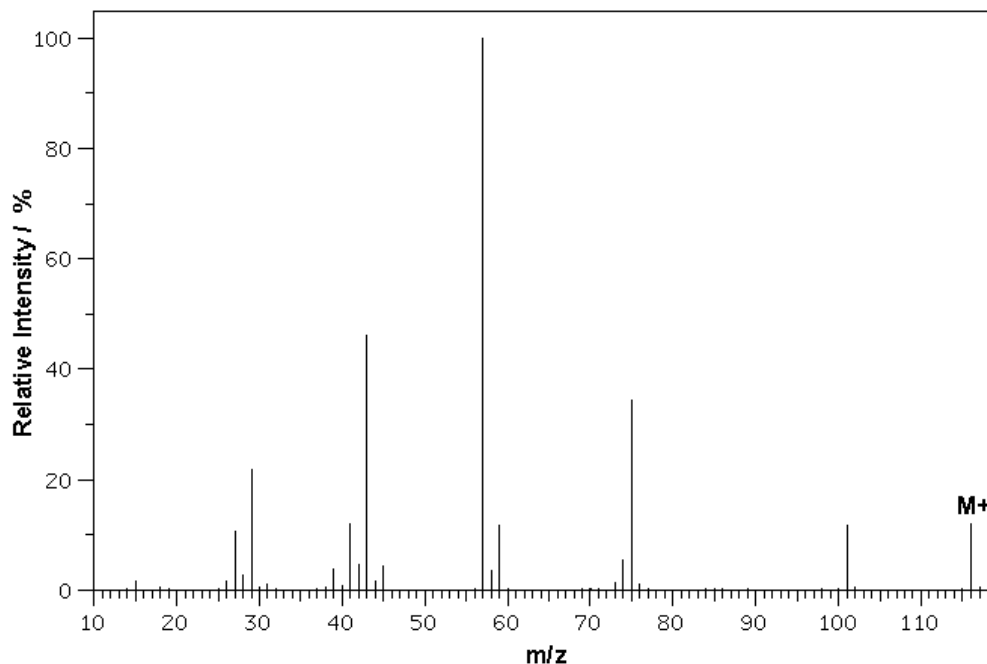
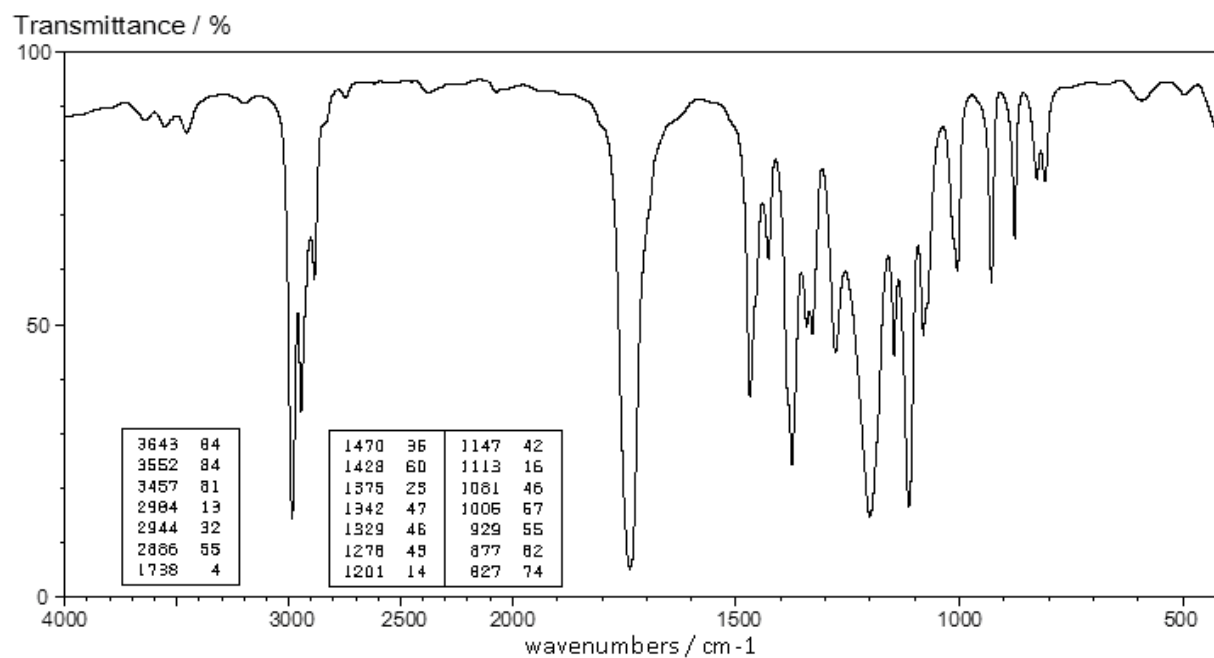
Provide a detailed justification of your choice.



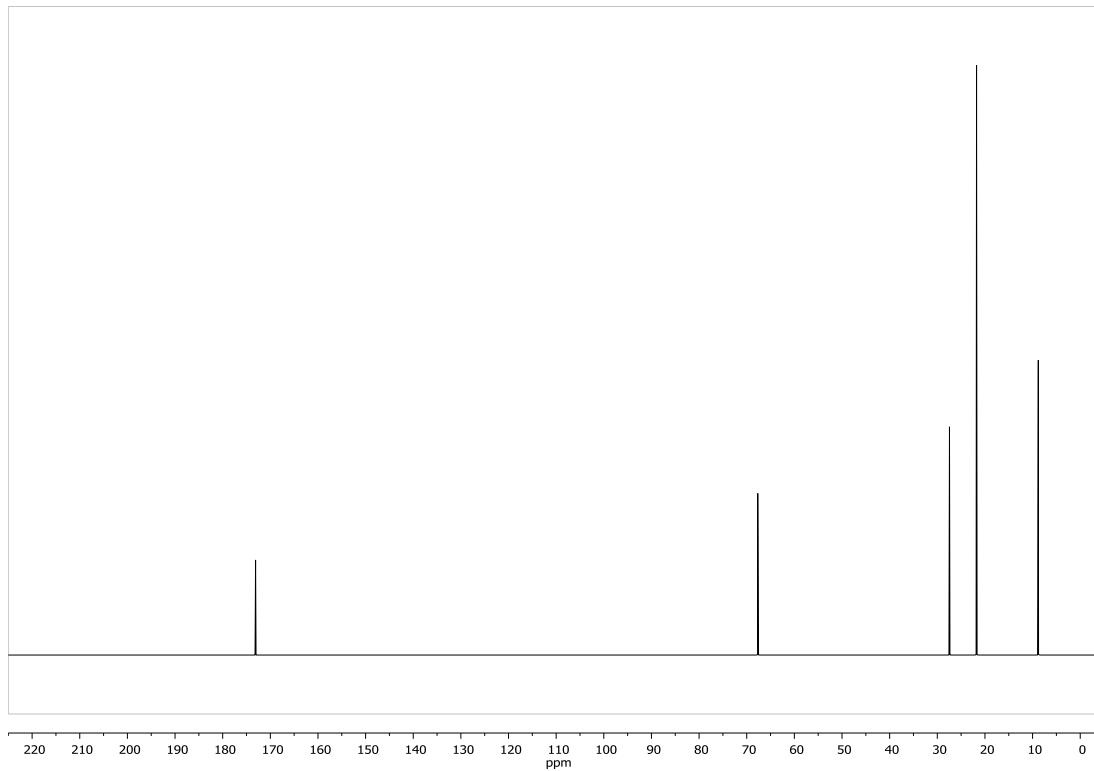
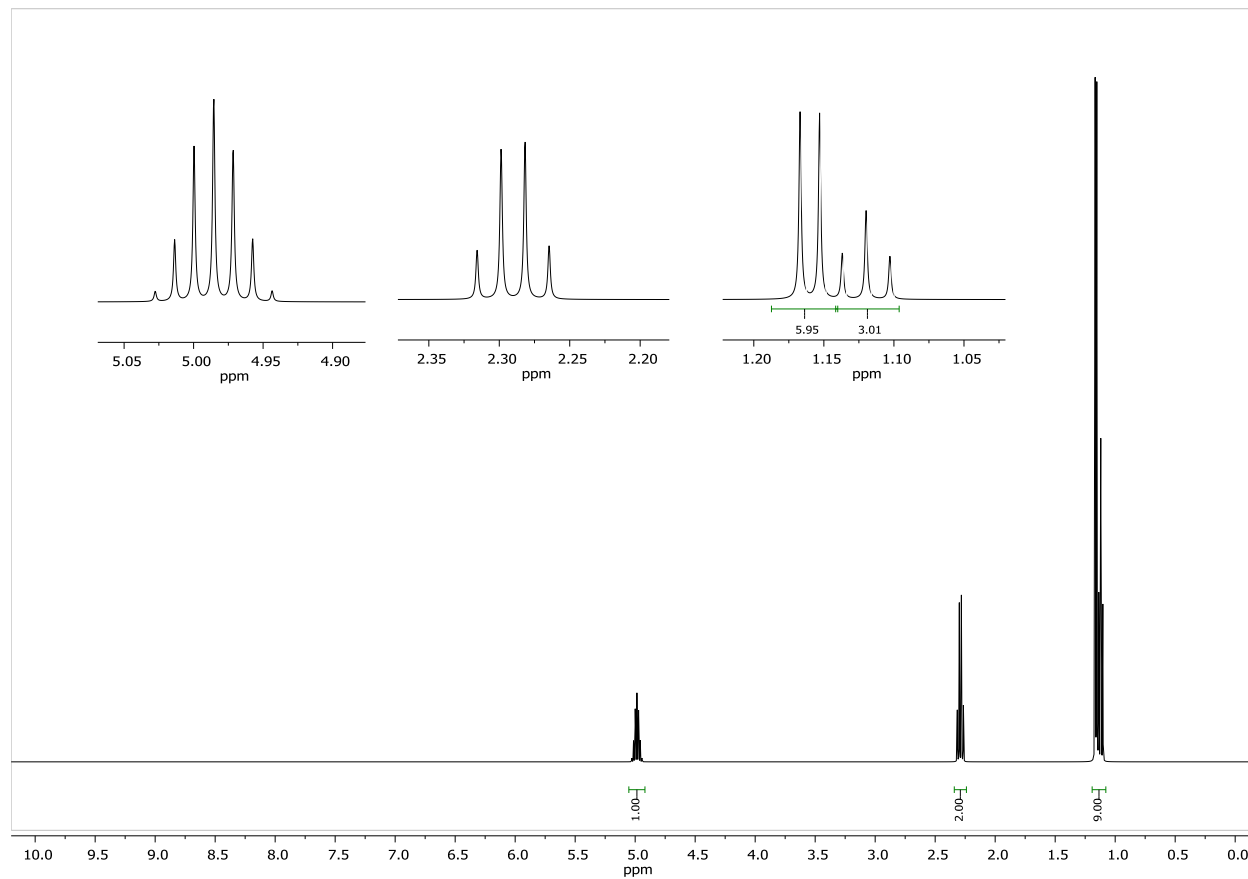
10% PART 8: SPECTROSCOPY

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED. Show your workings as PARTIAL marks will be given.

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

Mass Spectrum:**IR Spectrum:**

Cont'd -->

^{13}C -NMR: **^1H -NMR:**

Cont'd -->

10% PART 9: STRUCTURE DETERMINATION**WRITE YOUR ANSWERS IN THE ANSWER BOOKLET PROVIDED**

Compound **A** ($C_6H_{14}O$; IR: 3500 cm^{-1} , broad) is a single enantiomer with R configuration at the stereocenters.

When **A** was reacted with PBr_3 in the presence of pyridine, chiral compound **B** was obtained.

In contrast, when **A** was reacted with HBr, **C** was obtained as the major product. **C** was found to be a single achiral compound. **B** and **C** were found to be constitutional isomers.

When **C** was heated in the presence of KOH in EtOH, a mixture of stereoisomers was obtained with **D** (C_6H_{12} , IR: 1600 cm^{-1}) being the major product.

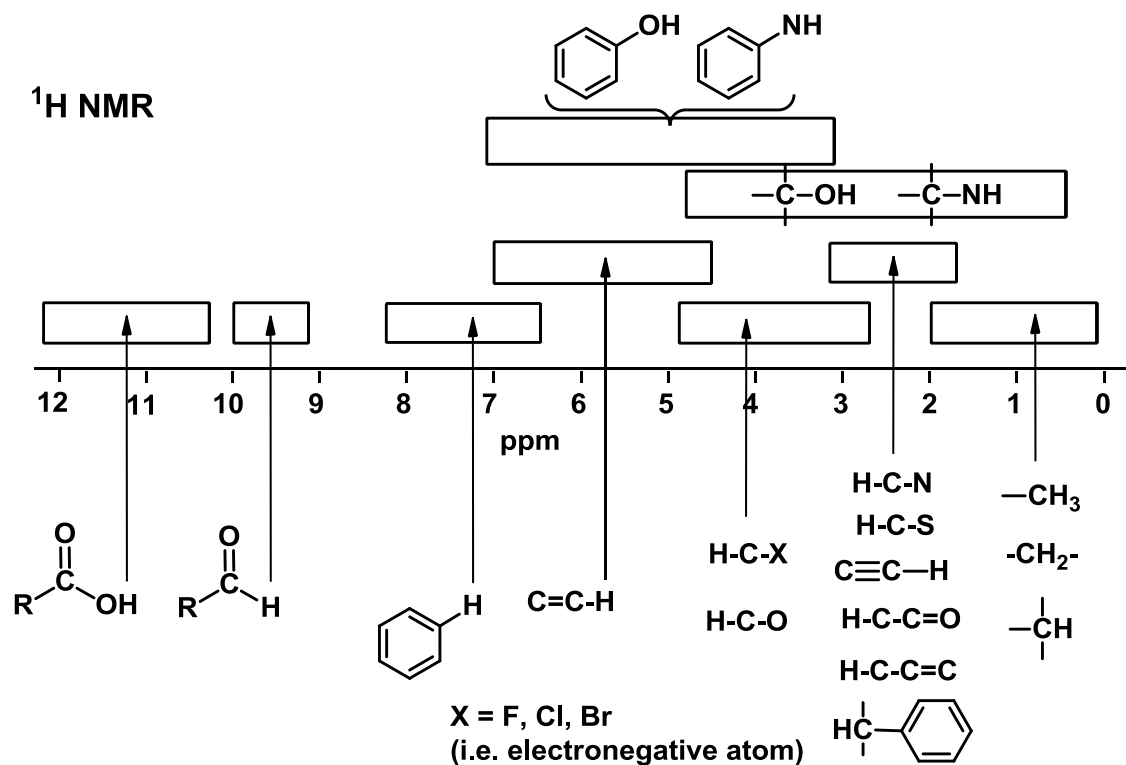
Reaction of **C** with hot KOtBu in tBuOH gave **E**, an isomer of **D**.

The ^{13}C NMR of **E** showed only 4 peaks (153, 106.29 and 12 ppm) and the H-NMR gave δ /ppm: 4.69 (1H, s), 2.03 (2H, q) and 1.04 (3H, t).

Reaction of **C** with H_2O in the presence of Na_2CO_3 gave an achiral compound, **F**, that was found to be an isomer of **A**. Reaction of **F** with HBr or PBr_3 / Et_3N gave **C**.

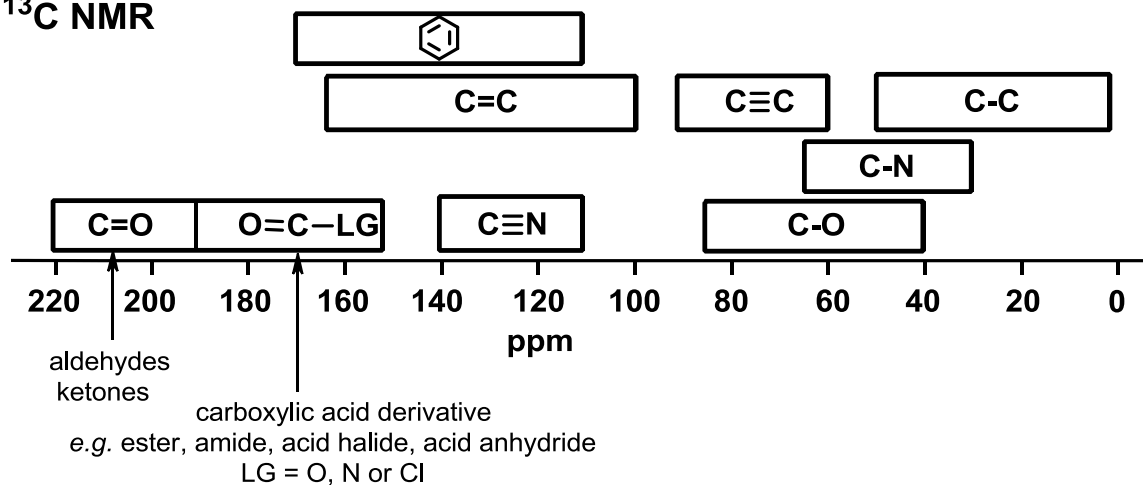
- **Identify A-F (only structures are needed)**
- **What is the IUPAC name of D ?**
- **Draw a wedge-hash 3D structure of B and assign the configuration at the chirality center(s).**

****** THE END ******

SPECTROSCOPIC TABLES **^1H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm**

	R = methyl	methylene	methyne	other
$\text{R}-\text{C}-$	$-\text{CH}_3$ 0.9	$-\text{CH}_2-$ 1.4	$-\text{CH}$ 1.5	$\text{sp}^3\text{C}-\text{OH}$ 1-5 $\text{sp}^3\text{C}-\text{NH}$ 1-3
$\text{R}-\text{C}=\text{C}$	1.6	2.3	2.6	$\text{C}\equiv\text{CH}$ 2.5
$\text{R}-\text{C}(=\text{O})$	2.1	2.4	2.5	$\text{C}=\text{C}-\text{H}$ 4.5-6.5
$\text{R}-\text{N}$	2.2	2.5	2.9	$\text{H}-\text{C}_6\text{H}_5$ 6.5-8
$\text{R}-\text{C}_6\text{H}_5$	2.3	2.7	3.0	$\text{R}-\text{C}(=\text{O})-\text{H}$ 9-10
$\text{R}-\text{Br}$	2.7	3.3	4.1	$\text{R}-\text{C}(=\text{O})-\text{OH}$ 9-12
$\text{R}-\text{Cl}$	3.1	3.4	4.1	
$\text{R}-\text{O}-$	3.3	3.4	3.7	

Cont'd -->

^{13}C NMR **^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm**

—CH_3 0-30	>CH_2 10-50	—C—H 25-60	—C—O— 155-180
$\text{—C}\equiv\text{C—}$ 65-90	>C=C< 80-145	—C—Br 10-25	—C—OH 160-185
 110-170	—C—Cl 15-30	—C—OH 45-75	—C—H 190-210
	—C—N 30-65	—C— 190-220	$\text{—C}\equiv\text{N}$ 110-140

INFRA-RED GROUP ABSORPTION FREQUENCIES

		<u>TYPE OF VIBRATION</u>	<u>FREQUENCY (cm⁻¹)</u>	<u>WAVELENGTH (μ)</u>	<u>INTENSITY (1)</u>	
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	
			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		ca. 3500	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											18						
1A											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
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)

Actinides **