UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

Version

1

December 9th, 2014 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. A periodic table with atomic numbers and atomic weights, and spectroscopic tables are appended to this examination paper.

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***.

Molecular models are permitted during the exam; calculators are also permitted, ***but NOT programmable calculators***.

Absolutely no other electronic devices are allowed

15% PART 1: RELATIVE PROPERTIES

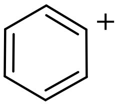
ANSWER ANY TEN (10) OF QUESTIONS 1 TO 12.

Arrange the items in questions 1-12 in DECREASING ORDER (i.e. greatest, most etc. first) with respect to the indicated property.

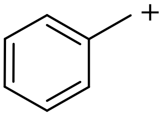
Use the following code to indicate your answers.

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

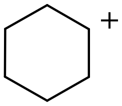
1. The relative stability of the following carbocations:



i



ii



iii

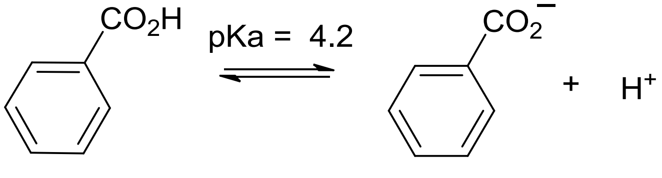
2. The relative nucleophilicity of the following in a polar, protic solvent:

$CH_3CH_2NH_2$ **i** $CH_3CH_2CH_3$ **ii** CH_3CH_2OH **iii**

3. The relative leaving group ability of the **bold group** in each of the following:

R—**Br** **i** R—**OH** **ii** R—**I** **iii**

4. The relative amount of the conjugate base of benzoic acid formed by the reaction of 1 mole equivalent with each of the following:



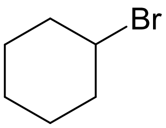
CH_3NH_2 **i** CH_3O^- **ii** CH_3CH_3 **iii**

Cont'd -->

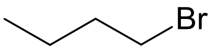
Use the following code to indicate your answers.

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

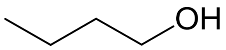
5. The relative rate of reaction of each of the following when treated with NaI / acetone:



i



ii

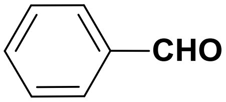


iii

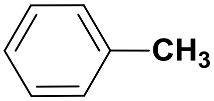
6. The relative rate of reaction of each of the following with HBr:

i. butan-2-ol **ii**. butan-1-ol **iii**. 2-methylpropan-2-ol

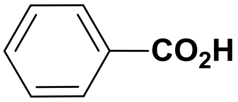
7. The ^{1}H-NMR chemical shifts for the groups shown in **bold** in each of the following structures:



i



ii



iii

8. The relative acidity of the most acidic H in each of the following:

CH_3CH_2OH **i**

CH_3Br **ii**

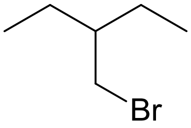
CH_3CH_2SH **iii**

Cont'd -->

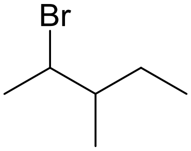
Use the following code to indicate your answers.

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

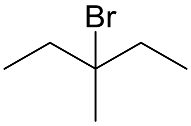
9. The relative amount of the following products formed by the reaction 3-methylpentane with Br_2 / uv light:



i

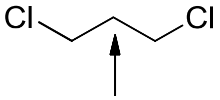


ii

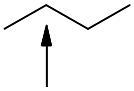


iii

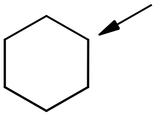
10. The number of lines in the H-NMR signals for the H atoms at the positions indicated in each of the following :



i



ii

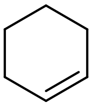


iii

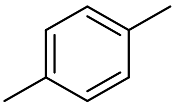
11. The relative yield of the Zaitsev product from the reaction of 2-bromooctane with each of the following:

$NaOH$ **i**
$NaOCH_3$ **ii**
$NaOC(CH_3)_3$ **iii**

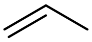
12. The number of types of hydrogen in each of the following:



i



ii



iii

Cont'd -->

12% PART 2: MOLECULAR PROPERTIES

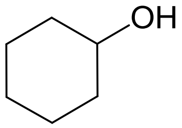
ANSWER ALL SIX (6) OF THE QUESTIONS 13 TO 18.

In questions 13-17 choose the single option that provides the best answer.

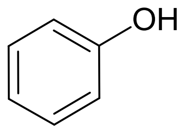
13. Which of the following is more reactive towards reaction with NaOH ?

- **A.** **I** because it forms a less stable primary carbocation
- **B.** **II** because it forms a resonance stabilized carbocation
- **C.** **I** because it can undergo an elimination reaction
- **D.** **II** because it forms a resonance stabilized anion
- **E.** **I** and **II** have about equal reactivity

I



II



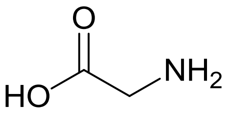
14. Which of the following ranks highest in the Cahn-Ingold-Prelog priority rules for assigning E/Z or R/S stereochemistry ?

$—(CH_2)_5CH_3$ $—C(CH_3)_3$

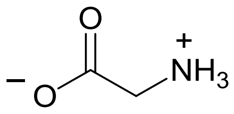
I **II**

- **A.** **I** because it has a 6 carbon chain
- **B.** **I** because it has a mass of 85 compared to **II** = 57
- **C.** **II** because there are 3 C attached to the first C
- **D.** **II** because 3 methyl groups out rank the 1 methyl group in **I**
- **E.** They have equal priority because both attach at C atoms

15. Which of the following structures corresponds to the major species present in solution when 2-aminoethanoic acid dissolved in water ?



I

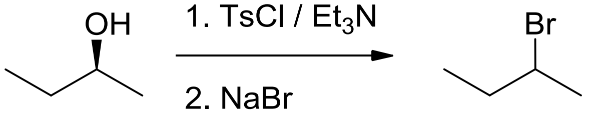


II

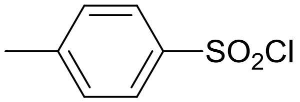
- **A.** **I** because it has no formal charges
- **B.** **II** because O is more electronegative than N
- **C.** **I** because there are no incomplete octets
- **D.** **II** due to an acid / base reaction
- **E.** Both exist in approximately equal amounts

Cont'd -->

16. In the following reaction, the stereochemistry of the product (actual stereochemistry not shown). The product stereochemistry should be:



TsCl = tosyl chloride =



A. Racemic because the reaction proceeds via SN1 and takes place with inversion

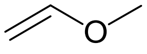
B. Inverted because the overall reaction is an SN2 and takes place with inversion.

C. Racemic because the reaction occurs via a carbocation intermediate.

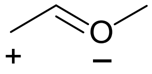
D. Retained because there are two SN2 inversions (*i.e.* double inversion) reaction

E. Irrelevant because the product does not have a chirality center

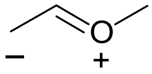
17. Which of the following resonance structures is NOT a significant contributor to the resonance hybrid ?



I



II



III

A. **I** because it has an atom with an incomplete valence shell

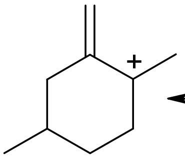
B. **II** because it has an atom with an incomplete valence shell

C. **II** because an atom exceeds the octet

D. **III** because it has an atom with an incomplete valence shell

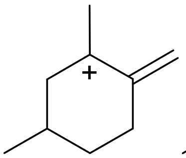
E. **III** because the charge separation is not in accord with electronegativity

18. Which of the following is/are resonance structures of the structure **X** (**select all that apply**) ?

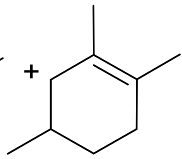


X

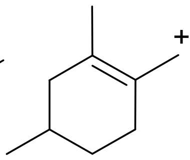
$\longleftrightarrow$ **?**



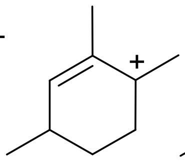
A



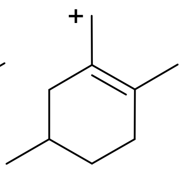
B



C



D



E

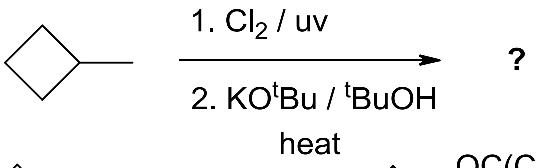
Cont'd -->

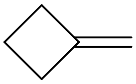
14% PART 3: REACTIONS

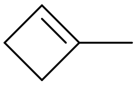
ANSWER ANY SEVEN (7) OF QUESTIONS 19 TO 26.

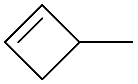
For each of questions 19-26 select the MISSING component (the best starting material, the major product or the best reagents) required in order to BEST complete each of the reaction schemes.

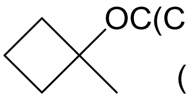
19.



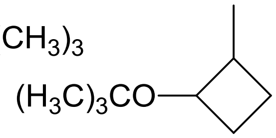

A


B


C

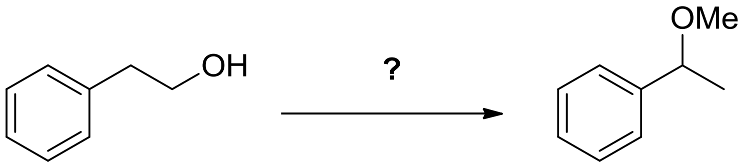


D



E

20.



A 1. TsCl / pyridine; 2. NaOMe / cold MeOH

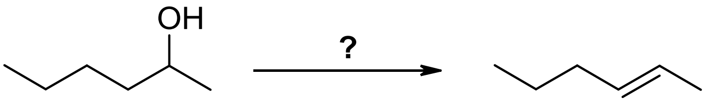
B 1. PBr_3 / pyridine; 2. NaOMe / cold MeOH

C 1. H_2SO_4 / heat; 2. Br_2; 3. MeOH

D CH_3OH, H_2SO_4

E 1. PBr_3 / pyridine; 2. MeI

21.



A HCl

B NaOH / heat

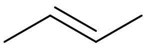
C KOtBu / heat

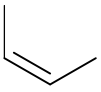
D 1. $SOCl_2$ / $N(CH_2CH_3)_3$
2. KOH / heat

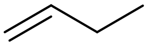
E 1. $SOCl_2$ / $N(CH_2CH_3)_3$
2. KOtBu / heat

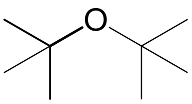
22.

butan-2-ol $\xrightarrow[\text{cold}]{H_2SO_4}$?

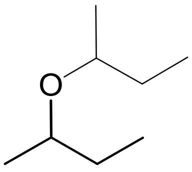

A


B


C



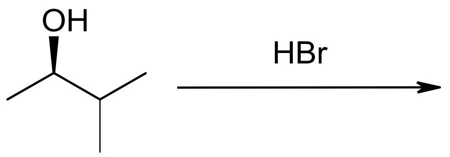
D



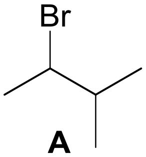
E

Cont'd -->

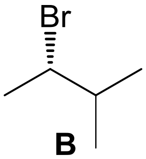
23.



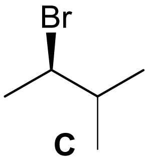
racemic



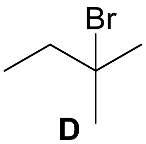
A



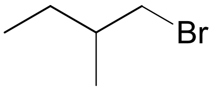
B



C

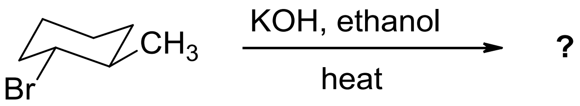


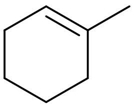
D



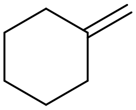
E

24.

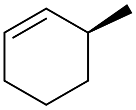




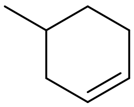
A



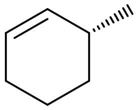
B



C

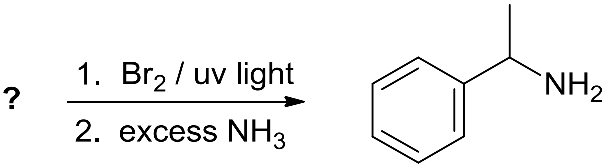


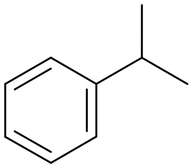
D



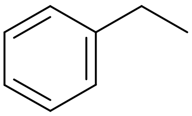
E

25.

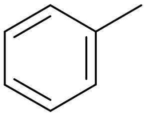




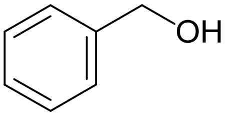
A



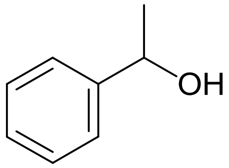
B



C

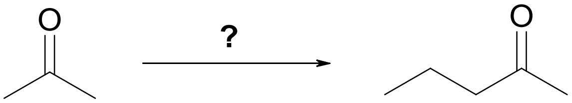


D



E

26.



A 1. Na / ether; 2. ethanol

B 1. $NaNH_2$; 2. ethyl bromide

C 1. $NaNH_2$; 2. methyl bromide

D 1. Cl_2 / uv; 2. methanol

E 1. Cl_2 / uv; 2. ethyl bromide

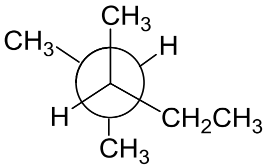
Cont'd -->

9% PART 4: CONFORMATIONAL ANALYSIS

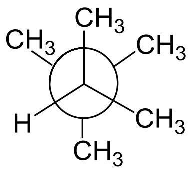
ANSWER ANY SIX (6) OF THE QUESTIONS 27 TO 34.

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.

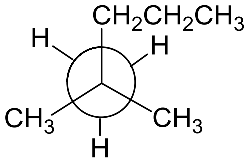
27. Which of the Newman projections shown represent conformations of 2,2-dimethylpentane ? (select **all that apply**)



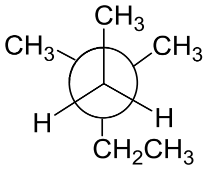
A



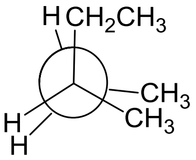
B



C

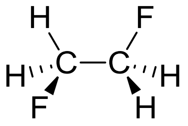


D



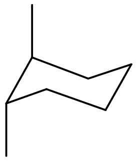
E

28. What is the **torsional** angle between the two fluorine groups in the conformation of 1,2-difluoroethane shown below ?

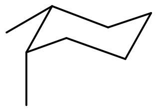


A 0^{o}
B 60^{o}
C 90^{o}
D 109.5^{o}
E 120^{o}
AB 180^{o}

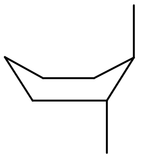
29. Which of the following structures represent conformations that can be adopted by *cis*-1,2-dimethylcyclohexane ? (select **all that apply)**



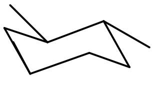
A



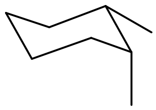
B



C

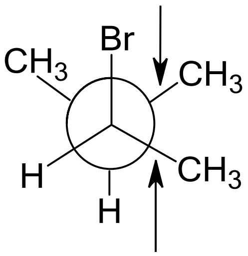


D



E

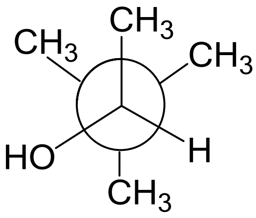
30. Which of the following terms **best** describes the relative position of the two indicated bonds in the conformation of the molecule shown below?

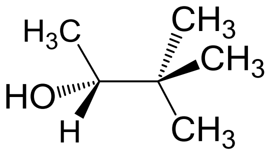


A eclipsed
B staggered
C anti
D syn
E gauche
AB trans
AC cis

Cont'd -->

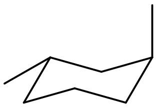
31. Which of the following terms **best** describes the relationship between the two molecules shown below ?



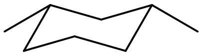


A constitutional isomers
B identical
C conformational isomers
D enantiomers
E diastereomers
AB meso
AC not isomers

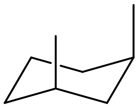
32. Which of the following conformations has the lowest energy ?



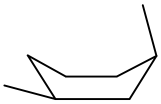
A



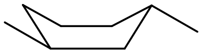
B



C



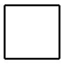
D



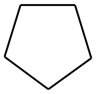
E

33. In their most stable conformations, which of the following molecules would have the least torsional strain?

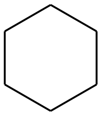
A



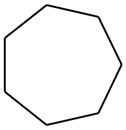
B



C

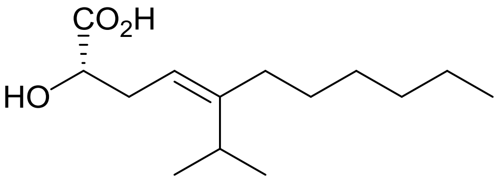


D



E

34. Which of the following terms describes the configurations of the stereocenters in the molecule shown below ?



A. R, E
B. R, Z
C. S, E
D. S, Z

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}H NMR** : δ 3.7 ppm (singlet, 3 H), 7.0 ppm (singlet, 1 H).
    IR = 1735 cm^{-1}

36. **^{1}H NMR** : δ 1.0 ppm (triplet, 3 H), 1.6 ppm (sextet, 2 H), 2.0 ppm (singlet, 3 H), 4.1 ppm (triplet, 2 H).
    IR = 1745 cm^{-1}

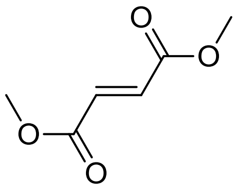
37. **^{1}H NMR** : δ1.0 ppm (triplet, 3 H), 1.5 ppm (sextet, 2 H), 3.4 ppm (triplet, 2 H).

38. **^{1}H NMR** : δ 2.3 ppm (singlet, 3 H), 3.8 ppm (singlet, 3 H), 6.9 ppm (doublet, *J*=16 Hz, 1 H), 7.3 ppm (doublet, *J* = 16 Hz, 1 H).
    IR = 1725, 1675 and 1645 cm^{-1}

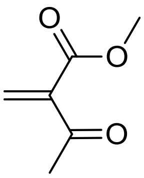
39. **^{1}H NMR** : δ 0.9 ppm (triplet, 3H) 1.6 ppm (sextet, 2 H), 2.3ppm (broad singlet, exchangeable, 1H), 3.6 ppm (triplet, 2H)
    IR = ~ 3400 cm^{-1} (broad)

40. **^{1}H NMR** : δ 0.92 ppm (triplet, 3H) 1.24ppm (broad singlet, exchangeable, 2H) 1.45 ppm (sextet, 2 H), 2.65 ppm (triplet, 2H)
    IR = ~ 3370, 3291 cm^{-1}

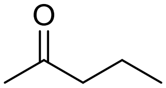
A



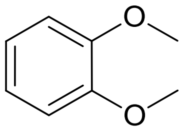
B



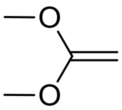
C



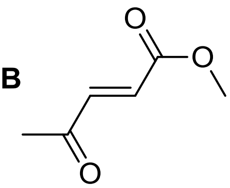
D



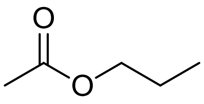
E



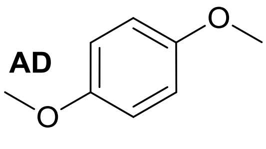
AB



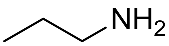
AC



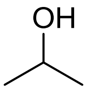
AD



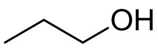
AE



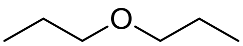
BC



BD



BE



Cont'd -->

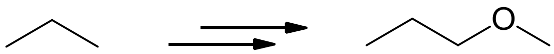
8% PART 6: SYNTHESIS

DESIGN EFFICIENT SYNTHESES OF ANY TWO (2) 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.

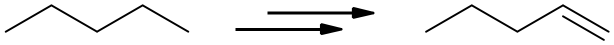
WRITE YOUR ANSWERS IN THE EXAM BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.

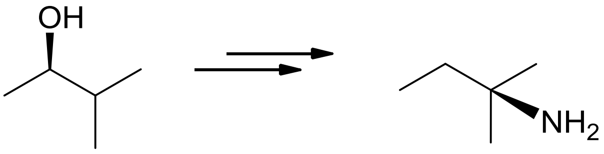
A.



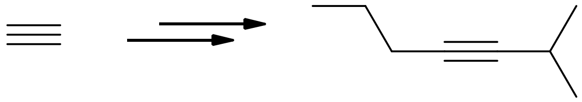
B.



C.



D.



Cont'd -->

10% PART 7: MECHANISMS

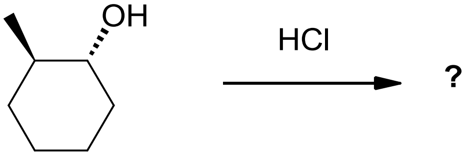
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

ANSWER TWO (2) QUESTIONS, ONE from **PART A** and **ONE** from **PART B.**

NO REAGENTS OTHER THAN THOSE ALREADY SHOWN ARE REQUIRED.

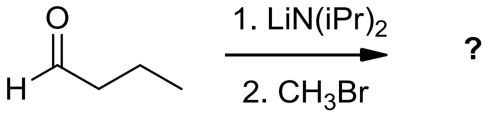
(5%) PART A: Use a curly arrow mechanism to explain ONE of the following reactions:

i. Predict the major product of this reaction by showing the mechanism. Briefly justify your choice.



OR

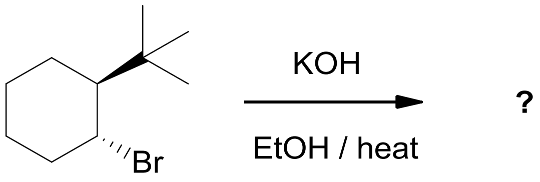
ii. Predict the major product of this reaction by showing the mechanism. Briefly justify your choice.



iPr = isopropyl

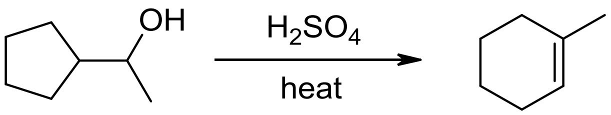
(5%) PART B: Use a curly arrow mechanism to explain ONE of the following reactions:

i. Predict the major product of this reaction by showing the mechanism. Briefly justify your choice.



OR

ii. Draw the reaction mechanism for the reaction of the alcohol shown to give 1-methylcyclohexene: Briefly explain why this is the major product.

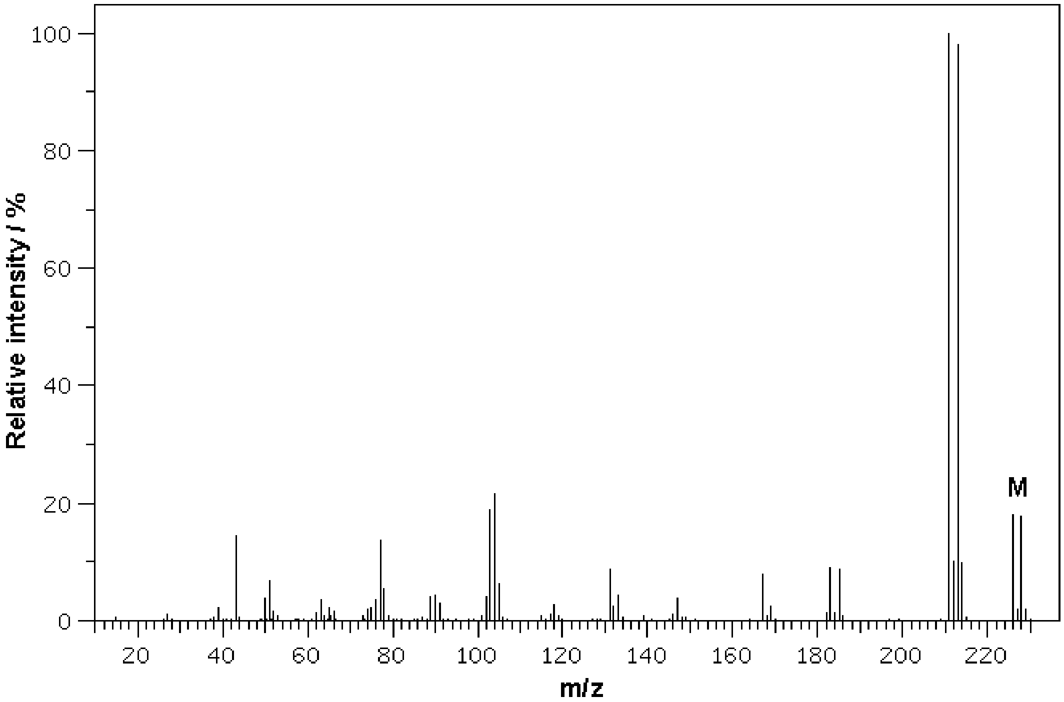


10% PART 8: SPECTROSCOPY

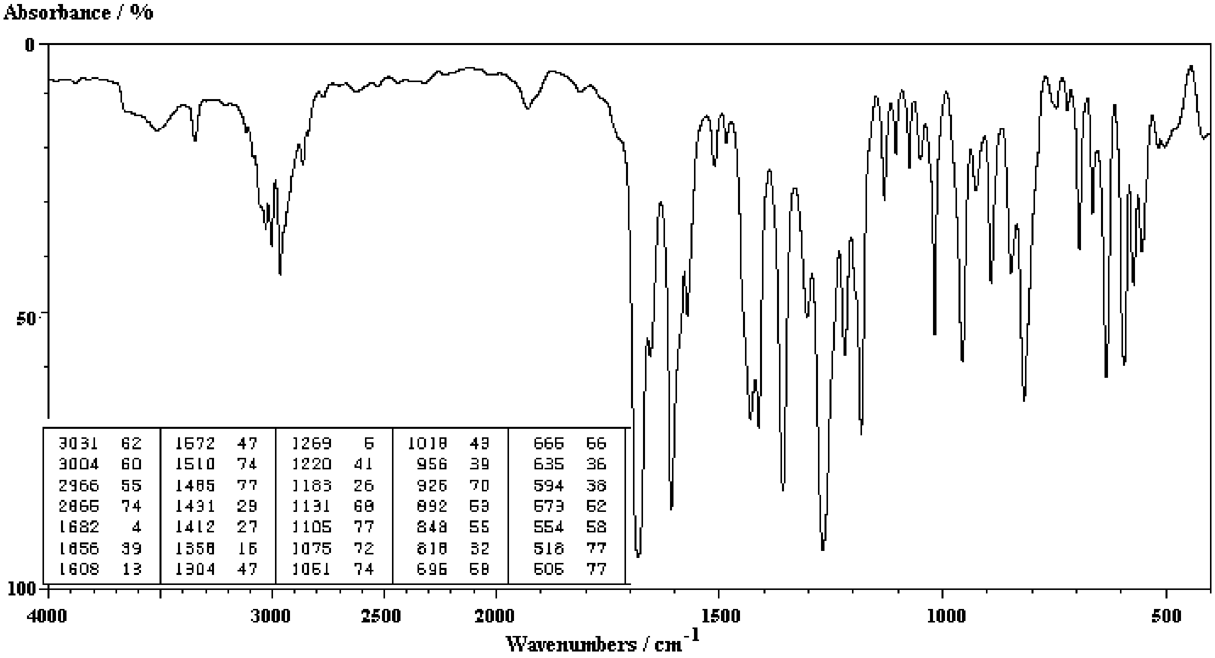
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED. Show your workings as PARTIAL marks will be given.

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

Mass Spectrum:



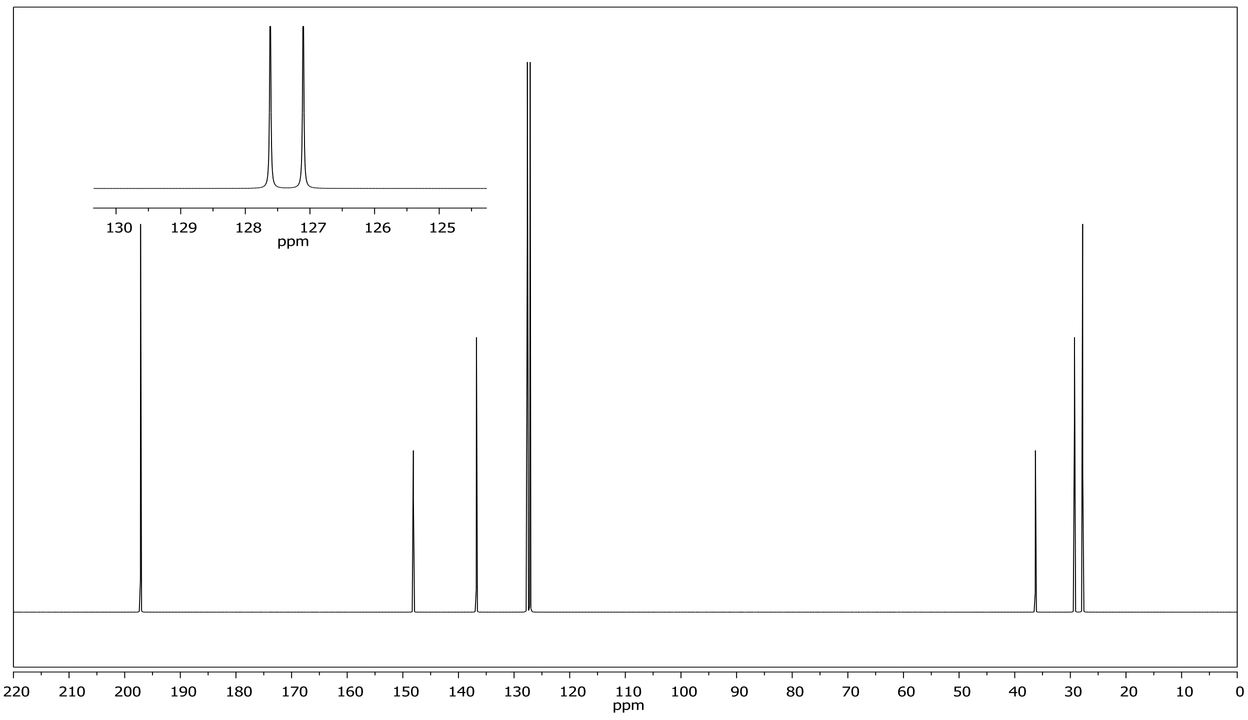
IR Spectrum:



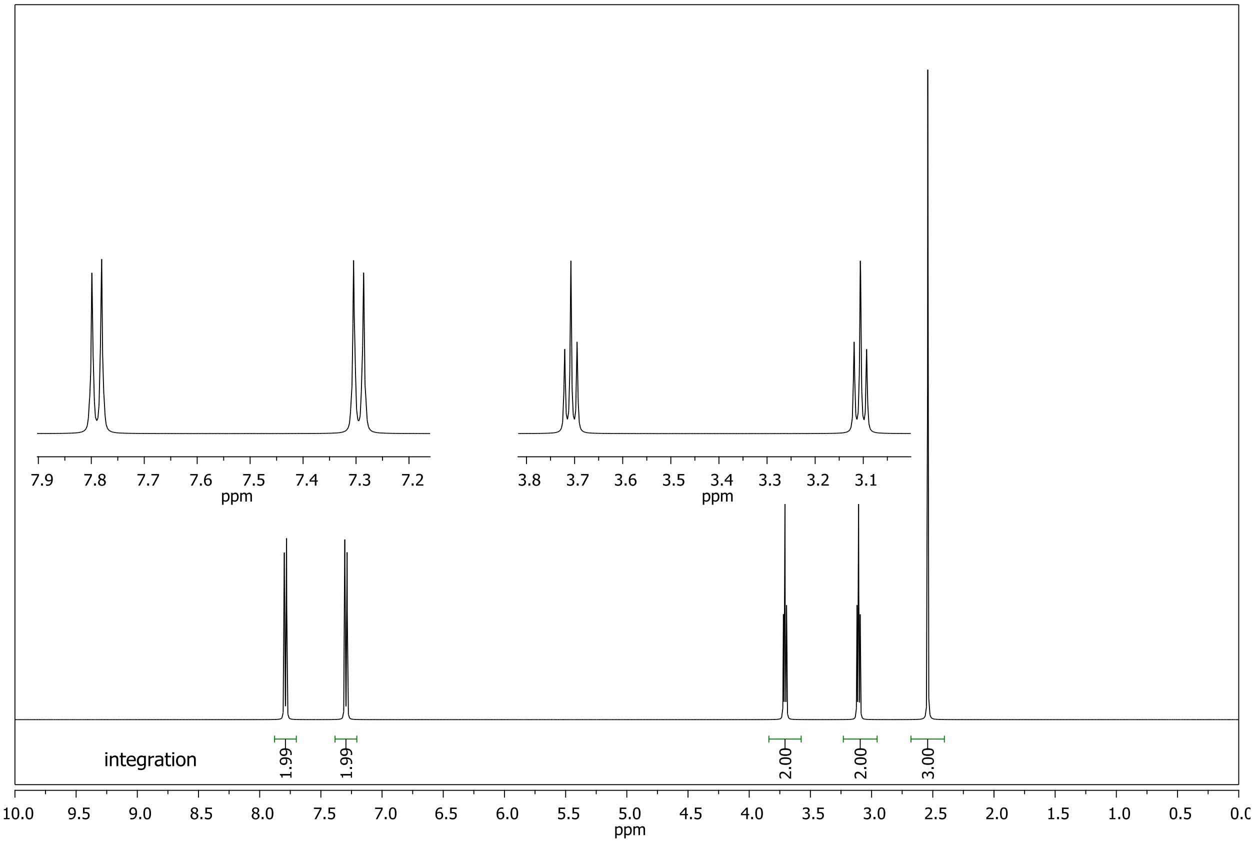
3031	62	1672	47	1269	6	1018	43	666	66
3004	60	1510	74	1220	41	956	39	635	36
2966	55	1485	77	1183	26	926	70	594	38
2866	74	1431	29	1131	68	892	63	673	62
1682	4	1412	27	1105	77	848	55	554	58
1856	39	1358	16	1075	72	818	32	518	77
1608	13	1304	47	1061	74	696	68	606	77

Cont'd -->

^{13}C-NMR:



^{1}H-NMR:



Cont'd -->

10% PART 9: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

An alkyl bromide **A**, $C_5H_{11}Br$, was reacted with aqueous sodium hydroxide solution to give **B** $C_5H_{12}O$ (IR : 3500cm^{-1}, broad) as the major product.

When **B** was reacted with PBr_3 / Et_3N, **A** was obtained. In contrast, reaction of **B** with HBr gave **C** a constitutional isomer of **A**. When **C** was heated with KOtBu / t-butanol, the major product was **D**, C_5H_{10} (IR : 1650cm^{-1}). When **C** was reacted with aqueous sodium hydroxide solution it was found to give 2-methylbutan-2-ol as the major product.

When **B** was heated with conc. H_2SO_4, the major product was **E**, a constitutional isomer of **D**. It was later found that **E** could also be prepared directly from **A** by reacting it with hot conc. KOH in ethanol.

In contrast to **C**, the reaction of **A** with KOtBu / t-butanol / heat gave **F**, which was a constitutional isomer of both **D** and **E**.

In a normal ^{13}C NMR spectroscopic analysis of the compounds, **A**, **B**, **C** and **F** each had 4 peaks, while **D** and **E** each had 5 peaks.

Of the compounds **A-F**, only **A** and **B** were chiral.

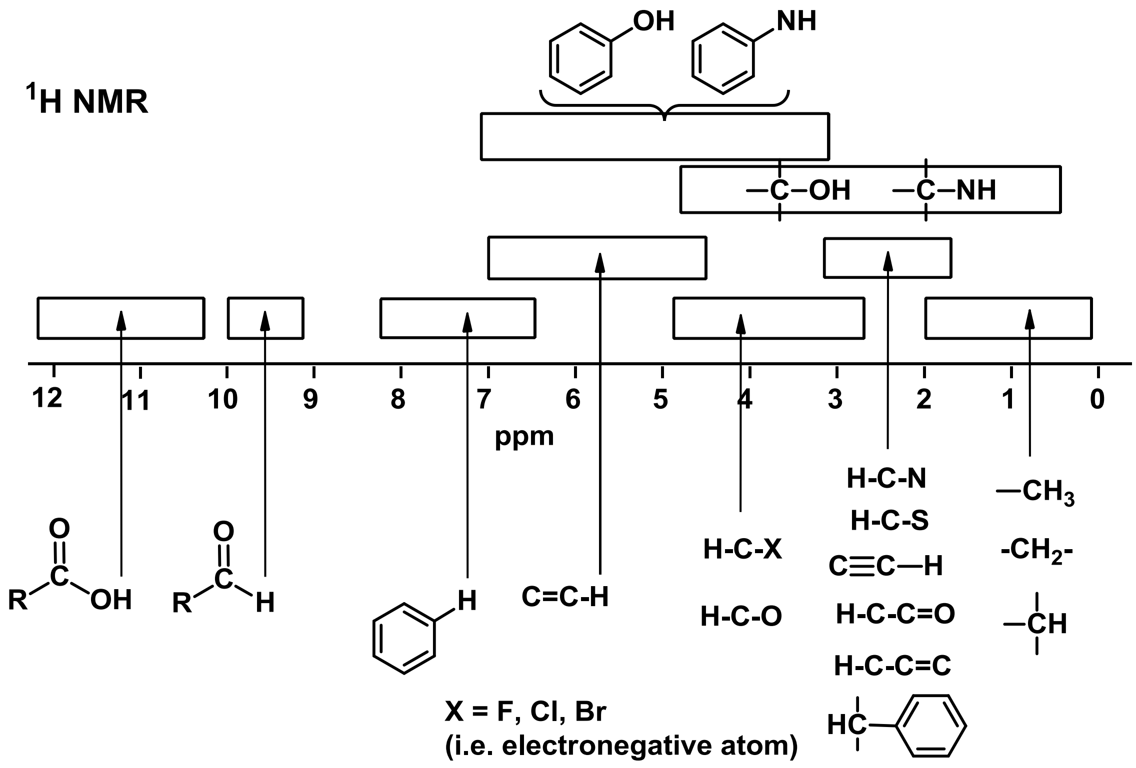
- **Identify A-F (only structures are needed)**
- **Give the complete name of one enantiomer of A**

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

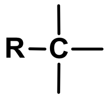
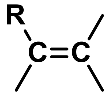
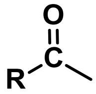
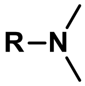
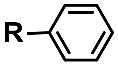
Cont'd -->

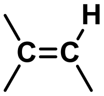
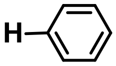
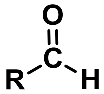
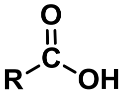
SPECTROSCOPIC TABLES

^{1}H NMR



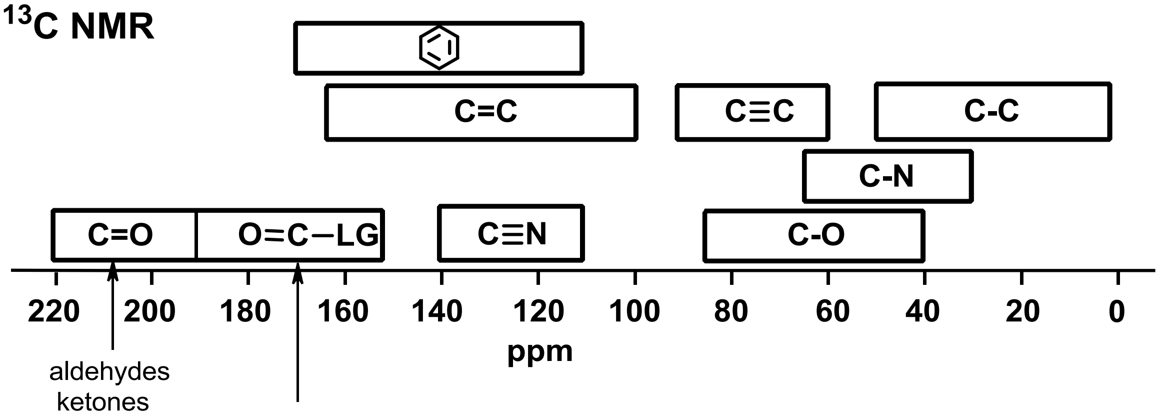
^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

R =	methyl	methylene	methyne
	$-CH_3$	$-CH_2-$	$-CH$
	0.9	1.4	1.5
	1.6	2.3	2.6
	2.1	2.4	2.5
	2.2	2.5	2.9
	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
	4.5-6.5
	6.5-8
	9-10
	9-12

Cont'd -->

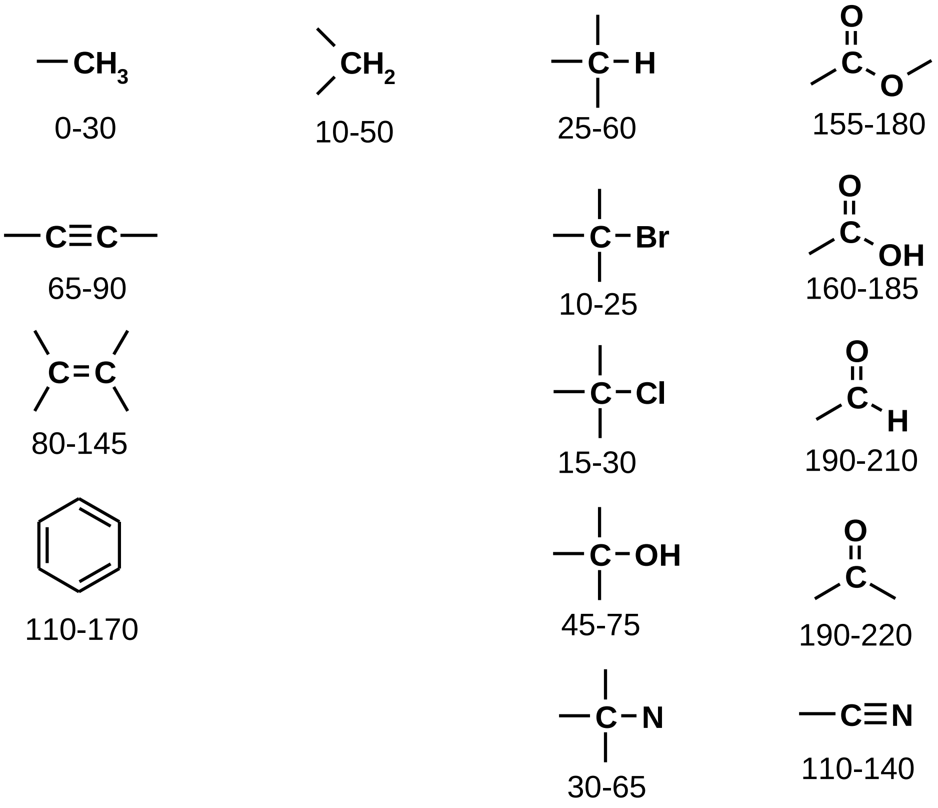
^{13}C NMR



aldehydes
ketones

carboxylic acid derivative
e.g. ester, amide, acid halide, acid anhydride
LG = O, N or Cl

^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



Cont'd -->

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		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

Cont'd -->

PERIODIC TABLE

1 1A	2 2A	3	4	5	6	7	8	9	10	11	12	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** 1.008																	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											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)