UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

Version 01

December 16th 2024 Time: 2 Hours

READ ALL THE INSTRUCTIONS CAREFULLY

WRITE YOUR **NAME**, **STUDENT I.D. NUMBER** AND **VERSION NUMBER 1** ON ***BOTH*** **YOUR MULTIPLE CHOICE ANSWER SHEET** AND **WRITTEN ANSWER SHEET**.

The exam consists of **Parts 1 - 8**, each of which should be attempted. Some Parts provide you with a choice of questions, *e.g*. answer any 5 out of 6. 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** are to be answered on the multiple choice answer sheet, and **Parts 6 - 8** are to be answered **IN THE APPROPRIATE BOX ON THE WRITTEN ANSWER SHEET PROVIDED**.

Parts 1 - 5 consist of a series of multiple choice questions numbered **1 - 34** to be answered on the multiple choice answer sheet. Indicate your answer by completely blackening out the appropriate space, A, B, C, D or E on the answer sheet for that specific question. Use a soft pencil only, ***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 and spectroscopic data tables and 2 pages of scrap paper for rough work are included with this examination paper.

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

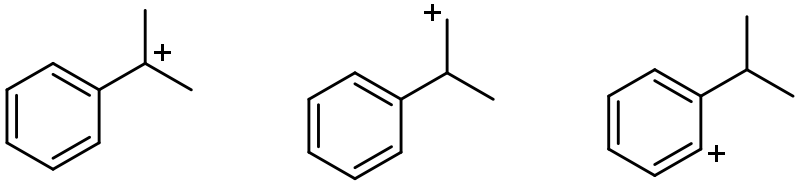
ANSWER ANY SEVEN (7) OF QUESTIONS 1 TO 8 (2 points each).

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.

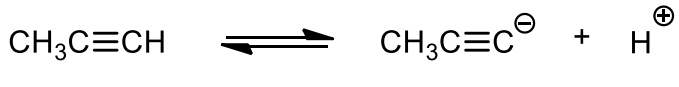
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

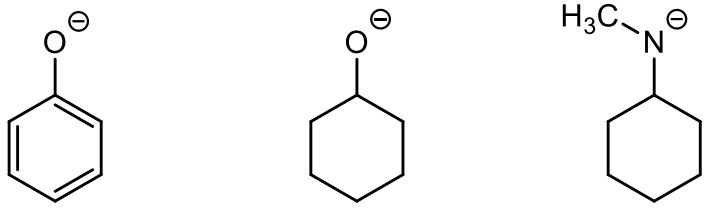
1. The relative stability of the following carbocations :



i **ii** **iii**

2. The relative amount of the conjugate base of propyne formed by the reaction of 1 mole equivalent of each of the following:





i **ii** **iii**

3. The relative nucleophilicity of the following in a polar aprotic solvent:

CH_3CH_2ONa CH_3CH_2SNa $CH_3CH_2NH_2$

i **ii** **iii**

4. The relative rate of reaction when each of the following was heated with H_2SO_4:

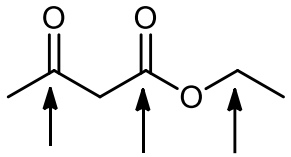
i. 1-phenylethan-1-ol **ii**. phenol **iii**. 2-phenylethan-1-ol

Cont'd -->

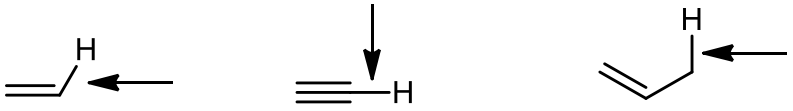
Use the following code to indicate your answers.

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

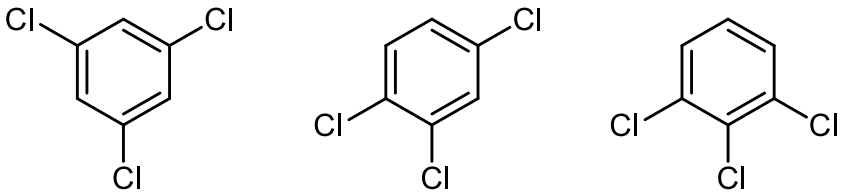
5. The relative ^{13}C-NMR chemical shifts for the carbon atoms indicated by arrows in the following structure:



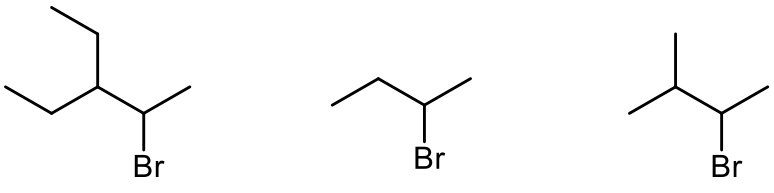
6. The relative IR spectra frequencies of the stretching vibrations of the C-H bonds indicated by arrows in the following structures:



7. The number of types of aromatic carbon in each of the following:



8. The relative yield of the anti-Zaitsev product formed when sodium ethoxide is heated with each of the following:



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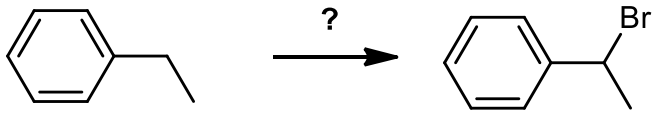
15% PART 2: MOLECULAR PROPERTIES

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. In the following reaction, what is the most appropriate reagent and condition:



A. Br_2 / heat is required because the reaction is a radical bromination

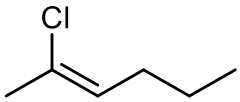
B. NaBr / uv is required because the reaction is a radical bromination

C. NaBr is required because the reaction is an S_N2.

D. HBr is required because the reaction is an S_N1.

E. PBr_3 / Et_3N is required because the reaction is an S_N1.

10. Which of the following statements about the Cahn-Ingold-Prelog priority rules applies for assigning stereochemistry for the molecule shown?



A. The molecule is *E* because the two alkyl groups on the alkene are *trans*.

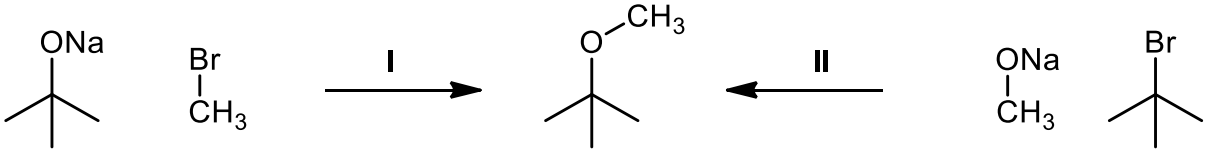
B. The molecule is *Z* because the two alkyl groups on the alkene are *cis.*

C. E/Z does not apply because there is a halogen attached to the alkene.

D. The molecule is *E* because the priority groups on the alkene are opposite.

E. The molecule is *Z* because the priority groups on the alkene are together.

11. Which synthetic strategy is the more efficient way to form tert-butyl methyl ether?



A. **I** because tert-butoxide is a stronger base than methoxide.

B. **II** because tert-butyl bromide forms a stable tertiary cation.

C. **I** because there is less competition with elimination.

D. **II** because the reaction is an SN1

E. **I** and **II** are equally efficient ways to form tert-butyl methyl ether

Cont'd -->

12. In the ^{1}H-NMR spectra, which **one** of the following choices best explains the relative **chemical shifts** of the **H atoms shown** ?

I **II**

A. **I** is higher than **II**, due to inductive effects at the sp hybridised C in the C-**H** bond.

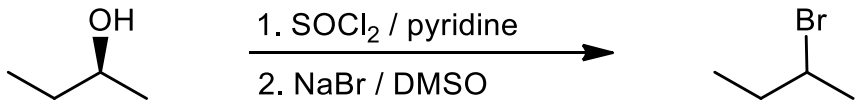
B. **II** is higher than **I**, due to inductive effects at the sp hybridised C in the C-**H** bond

C. **II** is higher than **I**, as the hydrogen in **II** is inside the deshielding cone

D. **I** is higher than **II**, because of the extra resonance of the two pi bonds

E. There is minimal difference in chemical shift because both **H** are attached to C atoms

13. For the reaction sequence shown below, where the stereochemistry of the product is not shown, the **product stereochemistry should be:**



A. Racemic due to the formation of a carbocation in step one

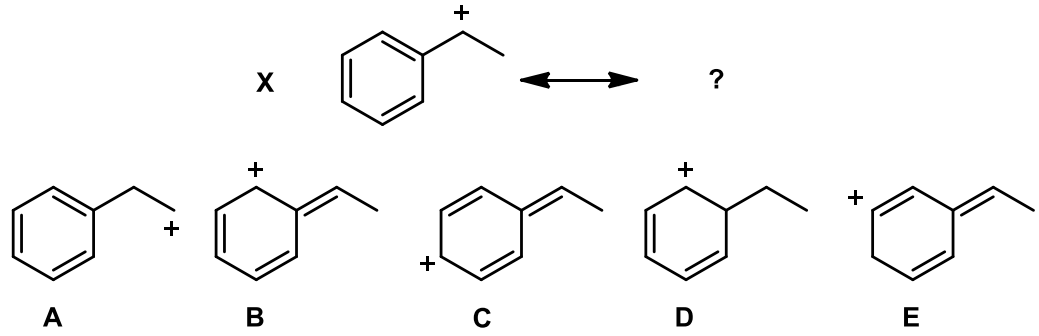
B. Racemic due to the formation of a carbocation in step tw.

C. Inverted due to the first step being an SN2 reaction

D. Preserved due to inversions happening in both of the reactions

E. Inverted due to the second step being an SN2 reaction

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



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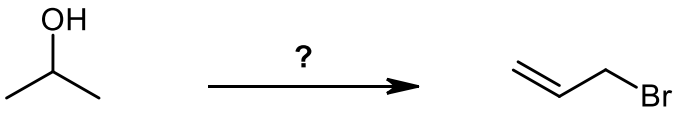
10% **PART 3: REACTIONS**

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 to BEST complete the reaction schemes.

15.



A 1. KOBu-t / HOBu-t, heat
2. NBS /heat

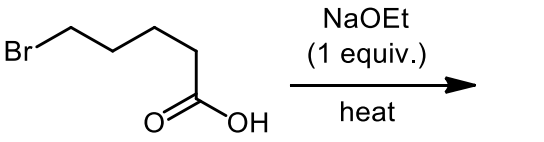
B 1. HBr
2. NaOEt / EtOH, heat

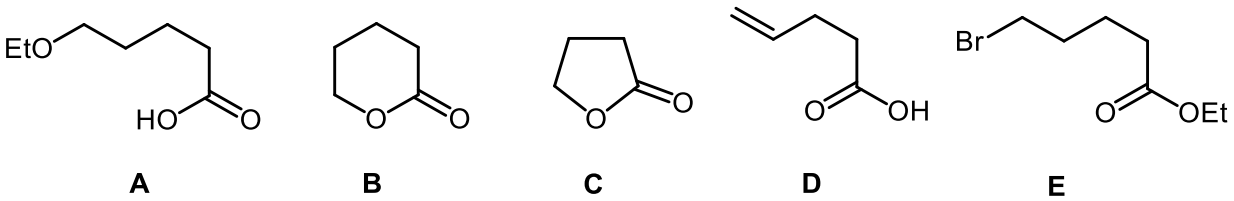
C 1. NaOEt / EtOH, cold
2. NBS / heat

D 1. H_2SO_4 / heat
2. NBS /heat

E 1. HBr
2. KOBu-t / HOBu-t, heat

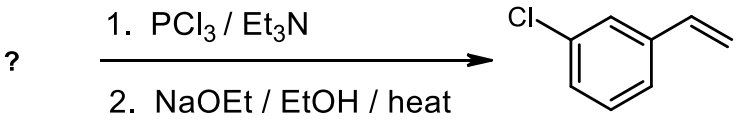
16.

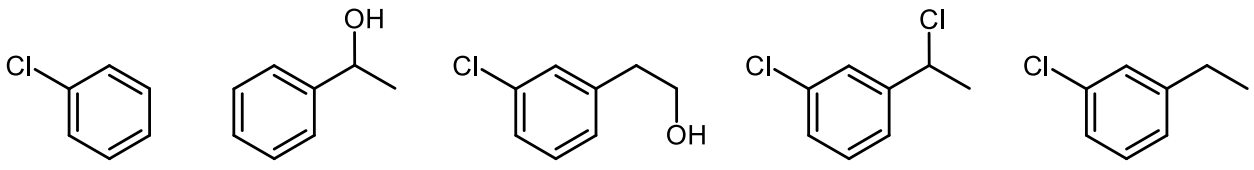




A **B** **C** **D** **E**

17.





A **B** **C** **D** **E**

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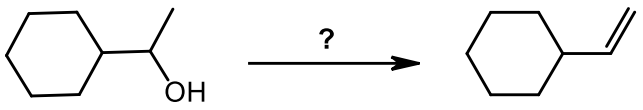
18.



A 1. HBr
2. KOBu-t / t- BuOH / heat

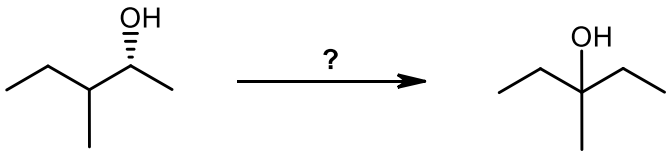
B KOBu-t / t-BuOH / heat

C 1. PBr_3 / NEt_3
2. KOBu-t / HOBu-t / heat

D 1. $SOCl_2$ / NEt_3
2. KOH / EtOH / heat

E Conc. H_2SO_4 / heat

19.



A 1. Br_2 / UV
2. H_2O / $AgNO_3$

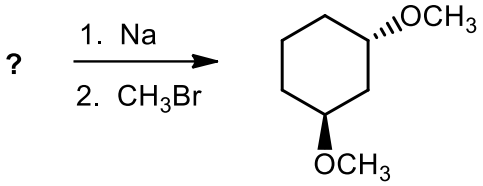
B H_2O / H_2SO_4

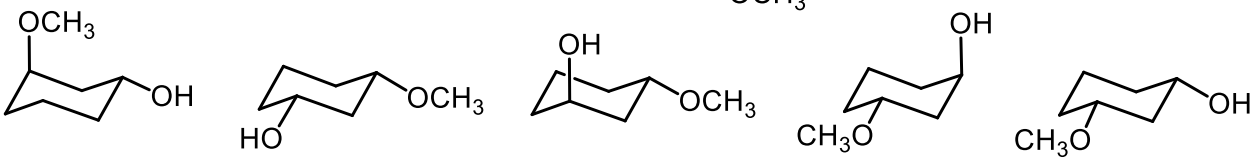
C 1. Na
2. H_2O

D 1. PBr_3 / Et_3N
2. NaOH, cold

E 1. p-TsCl / Pyridine
2. NaOH, heat

20.





A **B** **C** **D** **E**

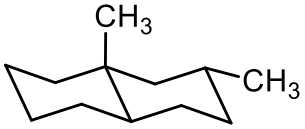
Cont'd -->

14% PART 4: CONFORMATIONAL ANALYSIS

ANSWER ANY SEVEN (7) OF THE QUESTIONS 21 TO 28 (2 points each).

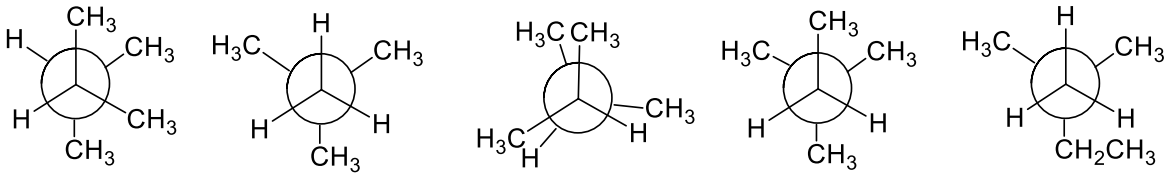
For each of the questions 21-28 select the answer(s) from those provided. In some cases more than one answer may be correct in which case all correct answers should be selected for full marks.

21. How many equatorial hydrogens are there in the structure shown ?



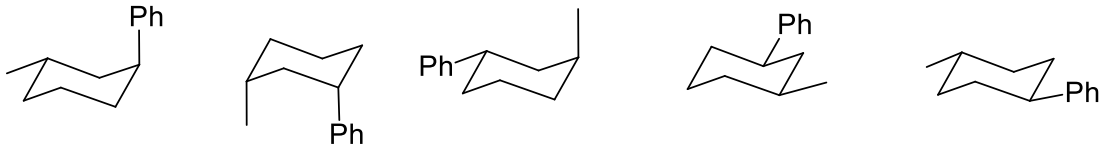
A 5 **B** 6 **C** 7 **D** 8 **E** 9 **AB** 10

22. Which of the Newman projections shown is a conformation of 2,2-dimethylbutane? (select **all that apply**)



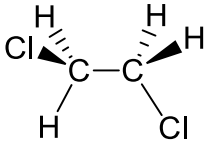
A **B** **C** **D** **E**

23. Which of the following structures represents the lowest energy conformations of *trans*-1-methyl-3-phenylcyclohexane ?



A **B** **C** **D** **E**

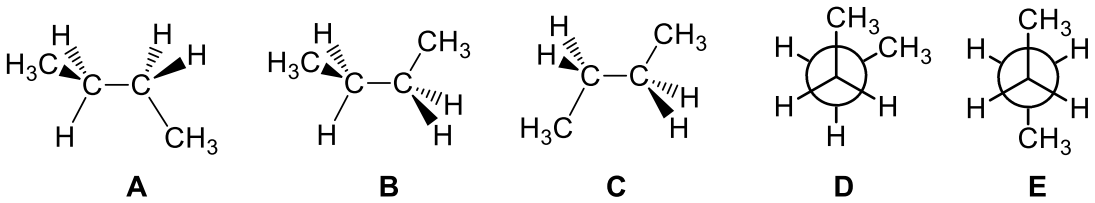
24. What is the **torsional angle** between the **two C-Cl bonds** in the conformation of 1,2-dichloroethane shown below?



A 0° **B** 60° **C** 90° **D** 109.5° **E** 120° **AB** 180°

Cont'd -->

25. Which of the following molecules has the **least strain** in the conformation shown ? (**select all that apply)**



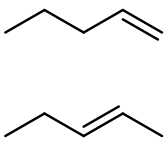
26. Which of the following structures have two equally stable chair conformations ? (**select all that apply)**

A *cis*-1,2-dimethylcyclohexane **B** *trans*-1,2-dimethylcyclohexane

C *cis*-1,3-dimethylcyclohexane **D** *trans*-1,3-dimethylcyclohexane

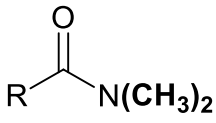
E methylcyclohexane

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



A configurational isomers
B conformational isomers
C enantiomers
D diastereomers
E regioisomers
AC stereoisomers

28. What is the **bond** angle of the **C-N-C bonds between the two methyl groups** in the most stable conformation of the structure shown below ?



A 0° **D** 109.5°
B 60° **E** 120°
C 90° **AB** 180°

Cont'd -->

12% PART 5: SPECTROSCOPY

ANSWER ALL SIX (6) OF QUESTIONS 29 TO 34 (2 points each).

For each of questions 29-34 select the compound from the list provided that corresponds BEST with the spectroscopic data provided. The following common abbreviations have been used s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet *etc*. .

29. **^{1}H NMR** : δ/ppm 1.1 (t, 3H), 2.1 (s, 3H), 2.5 (q, 2H)
^{13}C-NMR: δ/ppm 8, 29, 37, 209
IR : 1718 cm^{-1}

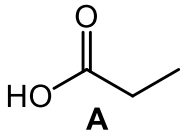
30. **^{1}H NMR** : δ/ppm 1.0 (t, 3H), 2.4 (q, 2H)
^{13}C-NMR: δ/ppm 12, 46
IR : 2974 cm^{-1}

31. **^{1}H NMR** : δ/ppm 0.7 (t, 3H), 0.8 (s, 3H), 1.2 (q, 2H)
^{13}C-NMR: δ/ppm 8, 26, 33, 34
IR : 2964 cm^{-1}

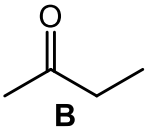
32. **^{1}H NMR** : δ/ppm 1.2 (t, 3H), 2.9 (q, 2H)
^{13}C-NMR: δ/ppm 10, 41, 175
IR : 1792 cm^{-1}

33. **^{1}H NMR** : δ/ppm 1.1 (t, 3H), 2.4 (q, 2H), 11.7 (s, 1H, D_2O exchange)
^{13}C-NMR: δ/ppm 9, 27, 181
IR : 3600-3000 cm^{-1} (very broad), 1716 cm^{-1}.

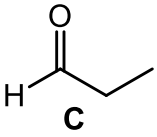
34. **^{1}H-NMR**: δ/ppm 1.2 (t, 3H), 2.6 (s, 1H, D_2O exchange), 3.7 (q, 2H)
^{13}C-NMR: δ/ppm 18, 58
IR : 3400-3200 cm^{-1} (broad)



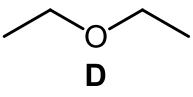
A



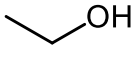
B



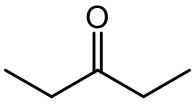
C



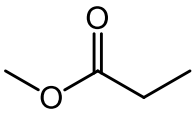
D



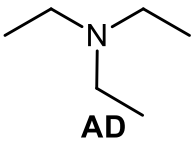
E



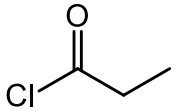
AB



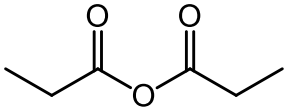
AC



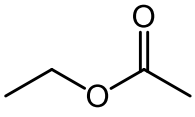
AD



AE



BC



BD


BE

Cont'd -->

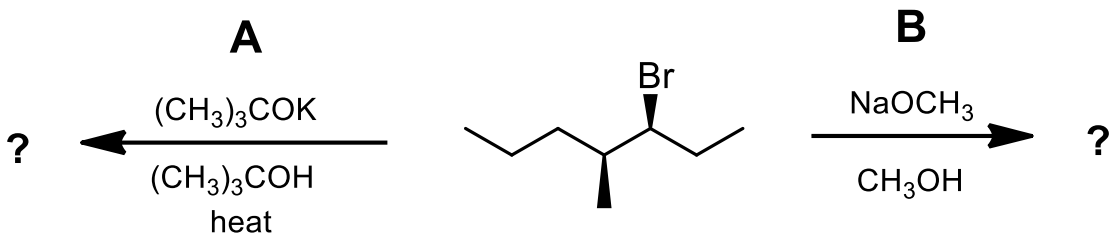
12% **PART 6: MECHANISMS**

WRITE YOUR ANSWER IN THE APPROPRIATE BOX ON THE WRITTEN ANSWER SHEET PROVIDED.

ANSWER TWO (2) QUESTIONS, ONE FROM EACH OF PART 6.1 and 6.2.

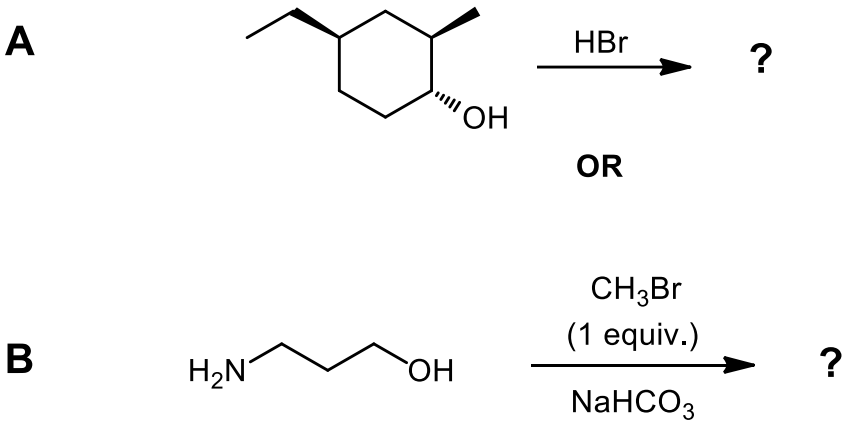
Draw curly arrow mechanisms to explain the following reactions / observations. No other reagents are required.

6.1. Draw the curly arrow mechanism for **one** of the following reactions:



AND

6.2. Predict the product and provide the curly arrow mechanism for **one** of the following reactions:



Cont'd -->

10% **PART 7: SYNTHESIS**

WRITE YOUR ANSWER IN THE APPROPRIATE BOX ON THE WRITTEN ANSWER SHEET PROVIDED

DESIGN AN EFFICIENT SYNTHESES OF ONE of the following target molecules from the indicated starting material.

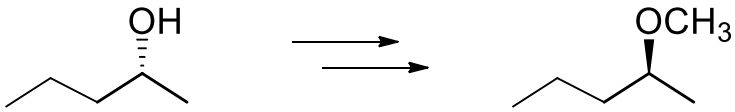
In addition, you are allowed to use **any hydrocarbon with three or fewer carbon atoms**, any solvents or inorganic reagents, and any organic reagents that do not contribute carbon atoms to the carbon skeleton in the product.

More than one step will be required for each synthesis.

SHOW YOUR ANSWER AS A STEPWISE REACTION SCHEME SHOWING THE REAGENT REQUIRED AND PRODUCT OF EACH STEP.

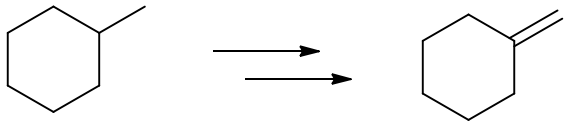
DO NOT SHOW MECHANISMS (i.e. curly arrows are NOT required)

A



OR

B



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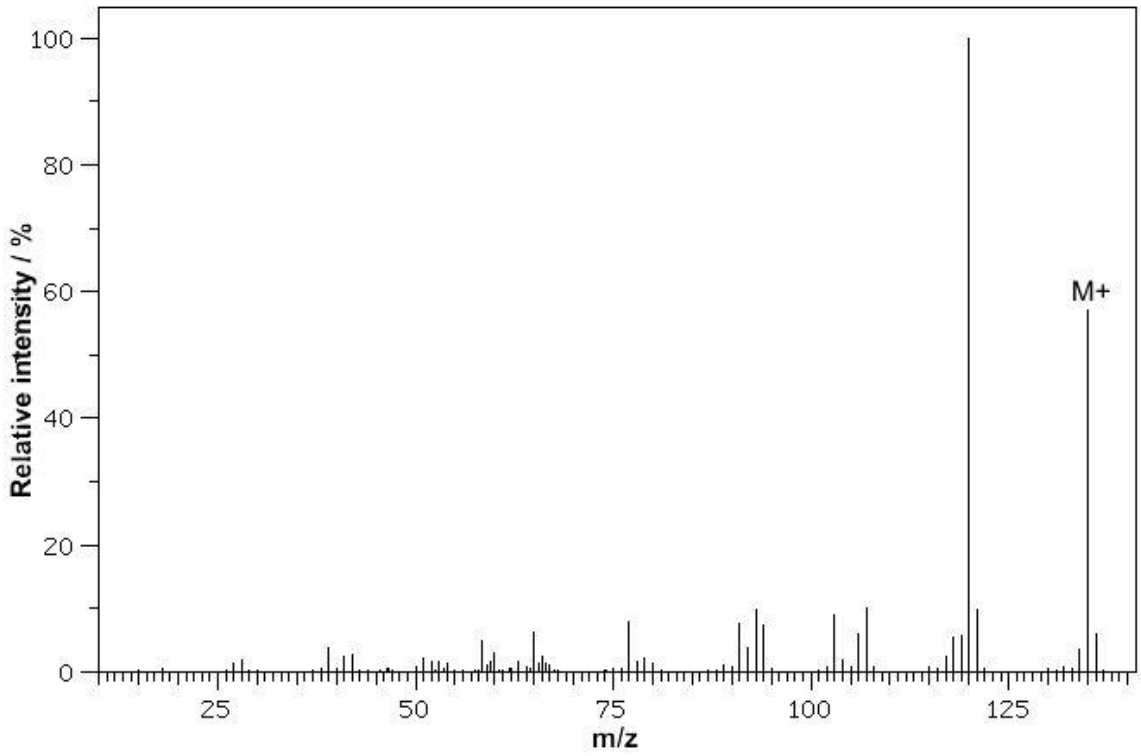
13% PART 8: SPECTROSCOPY

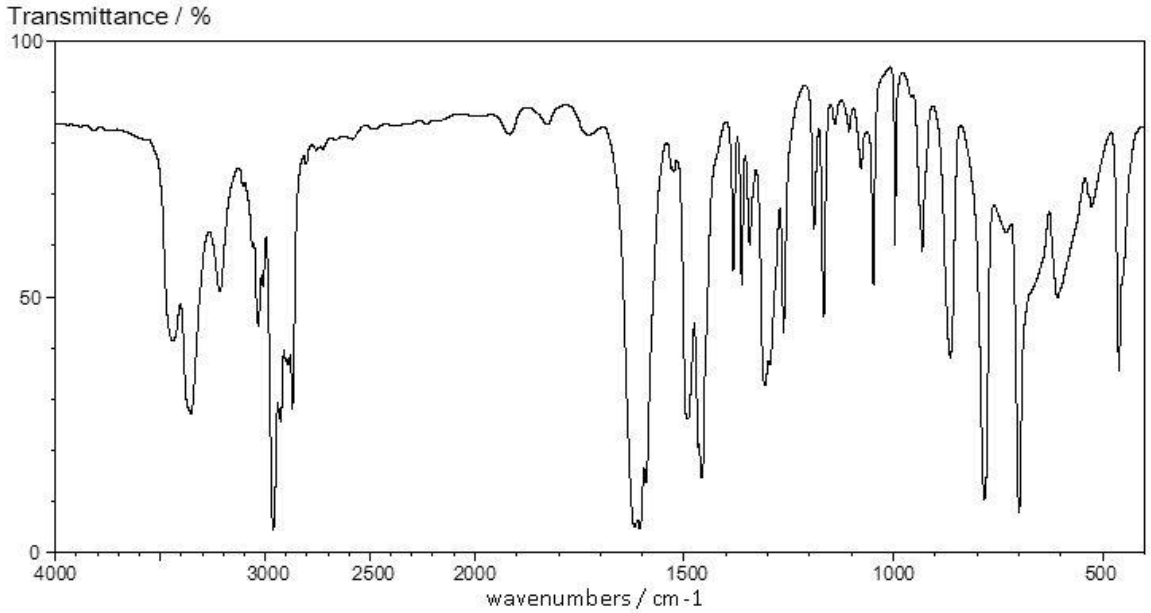
WRITE YOUR ANSWER IN THE APPROPRIATE BOX ON THE WRITTEN ANSWER SHEET PROVIDED Show your workings as PARTIAL marks will be given.

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

Mass Spectrum:



IR Spectrum:



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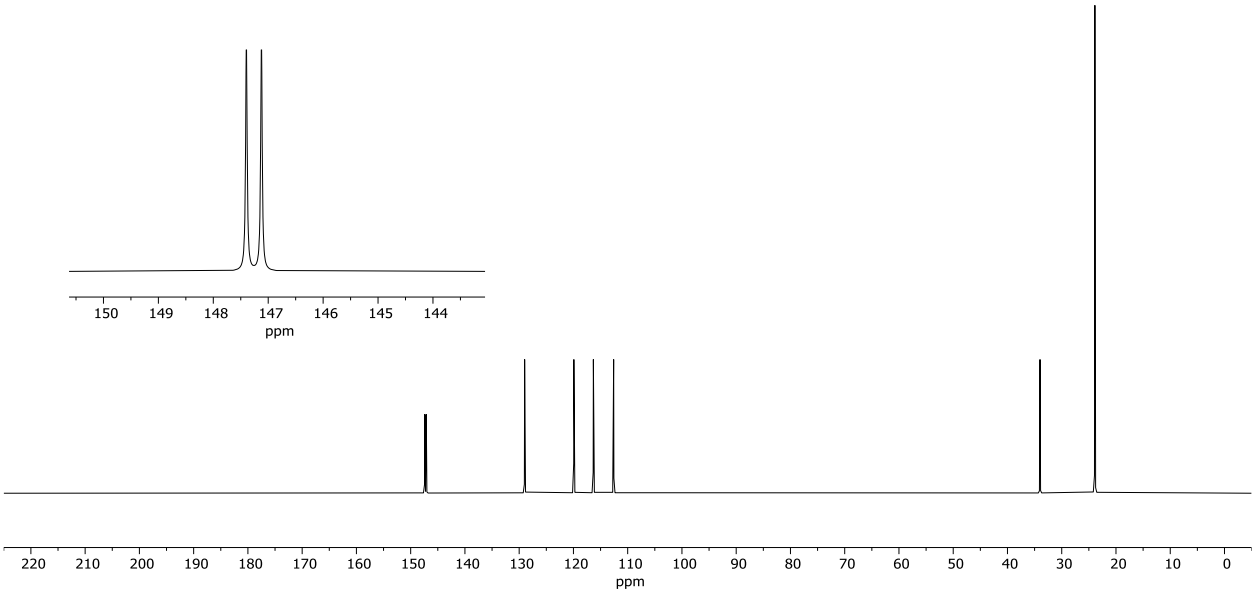
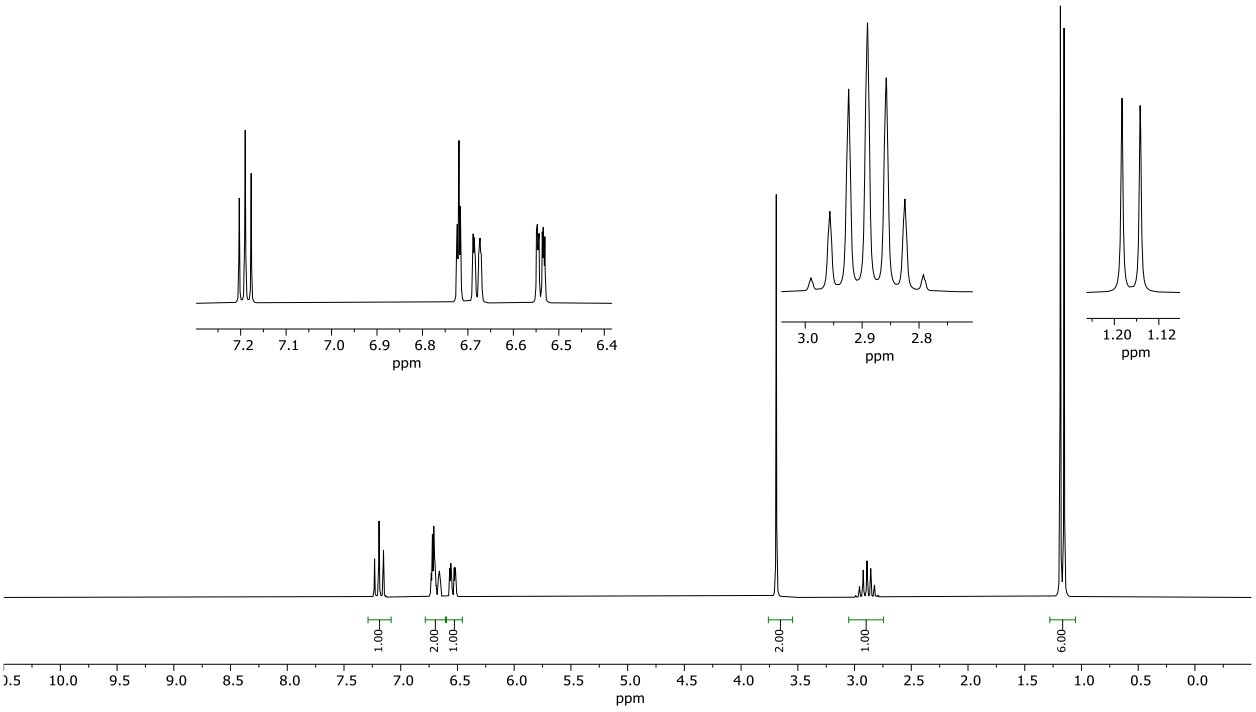
^{13}C-NMR:



^{1}H-NMR:



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

IRH /CCL 2024

Cont'd -->

SCRAP PAPER

Remember **ALL** final answers need to be entered in appropriate box on the answer sheet

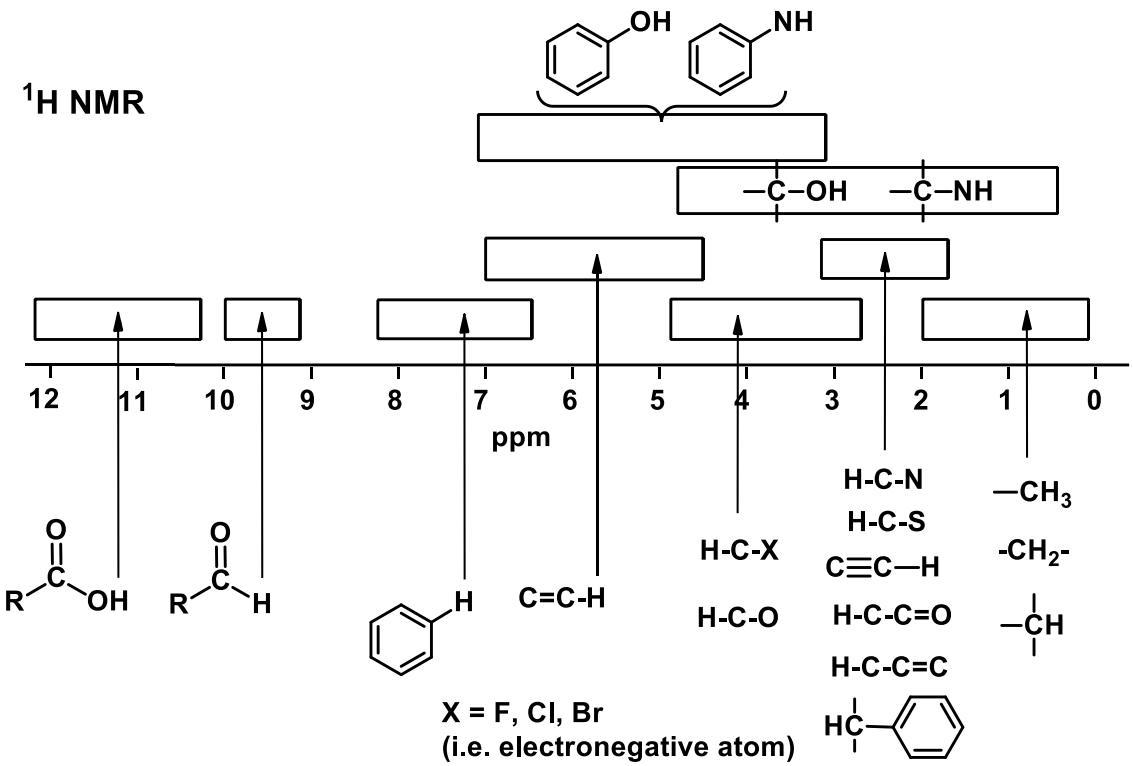
Cont'd -->

SCRAP PAPER

Remember **ALL** final answers need to be entered in appropriate box on the answer sheet

Cont'd -->

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—Ph	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
Ph—H	6.5-8
R—C(=O)—H	9-10
R—C(=O)—OH	9-12

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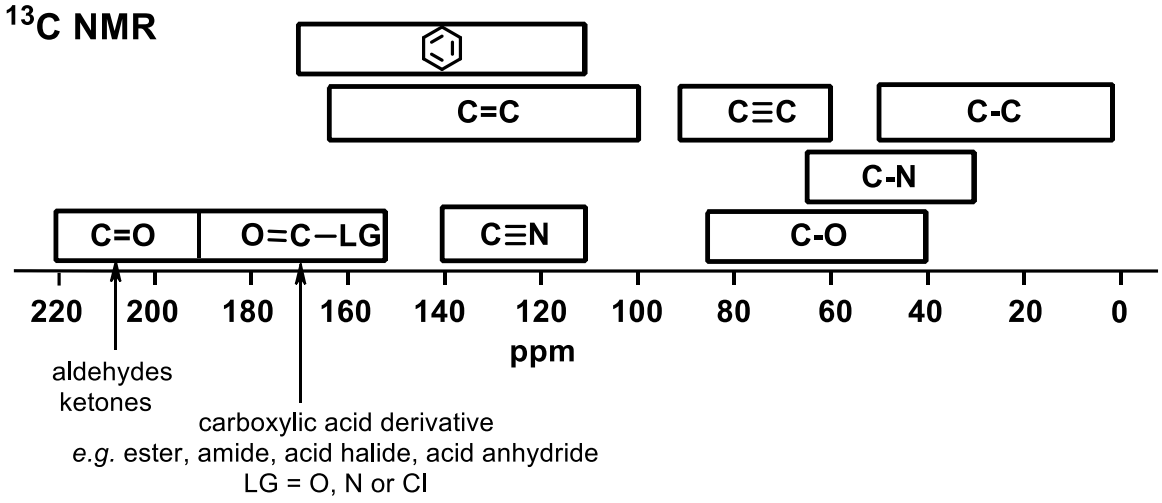
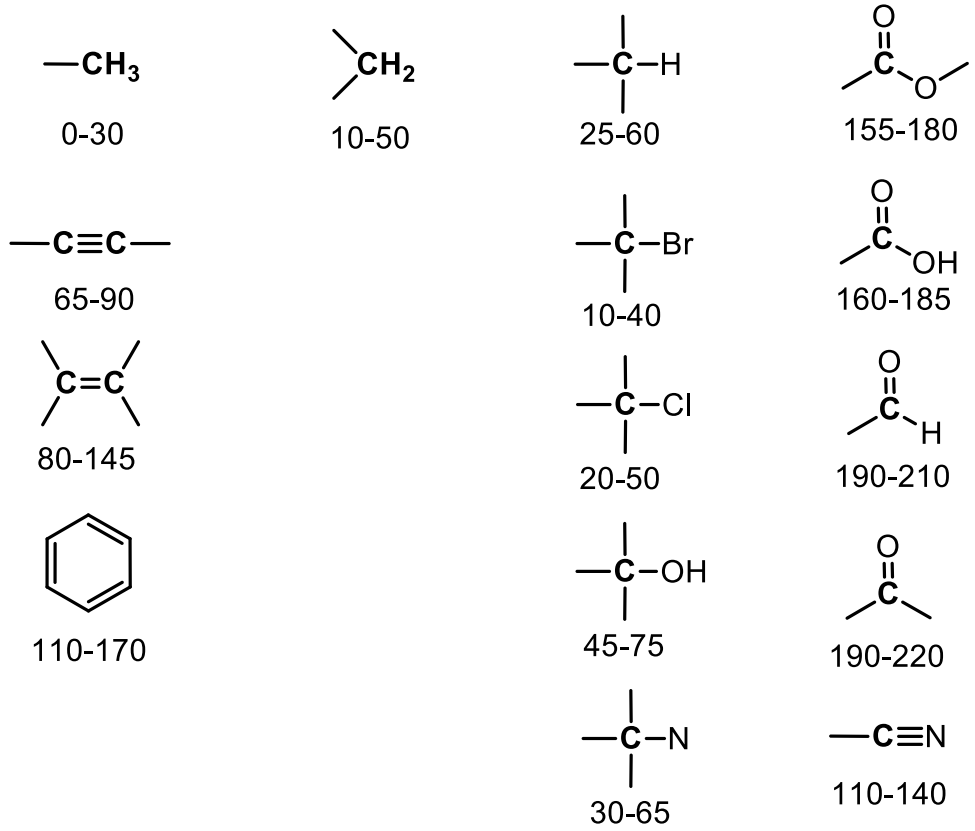


^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



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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

Cont'd -->

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)