UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

Version

01

December 16th, 2023 Time: 2 Hours

READ THE INSTRUCTIONS CAREFULLY

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

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

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

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

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

14% PART 1: RELATIVE PROPERTIES

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

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

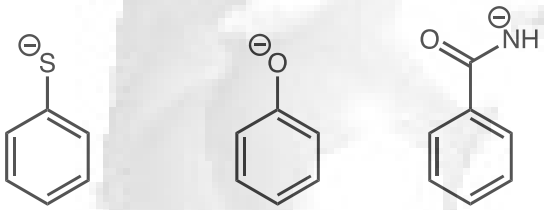
Use the following code to indicate your answers.

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

1. The relative priority of the following groups when assigning stereochemistry according to the Cahn-Ingold-Prelog ranking system (*highest priority to lowest priority):*

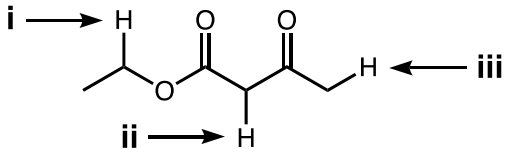
i **ii** **iii**

2. The relative basicity of the following (*most basic to least basic*):



i **ii** **iii**

3. The relative acidity of the following (*most acidic to least acidic*):



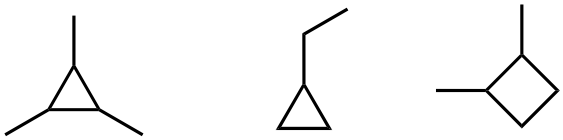
4. The relative rate of nucleophilic substitution reaction when each of the following is reacted with water (*fastest rate to slowest rate*):

i. 3-bromo-3-methylbut-1-ene **ii**. 2-bromo-3-methylbut-2-ene **iii**. 1-bromobutane

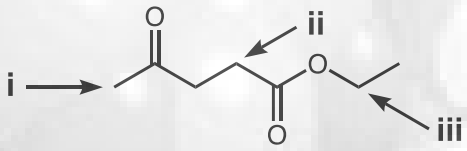
Use the following code to indicate your answers.

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

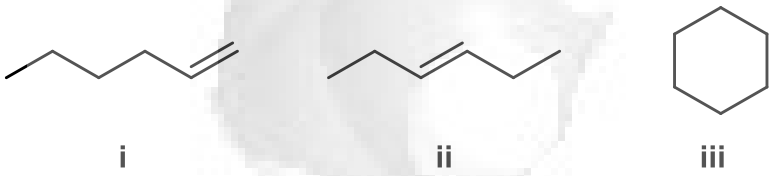
5. The number of types of carbon in each of the following (*most types to least types*):



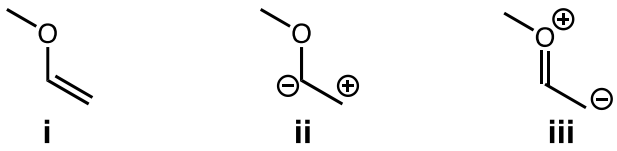
6. The number of lines observed in the ^{1}H-NMR spectrum for the hydrogens attached to each of the indicated positions (*most lines to least lines*):



7. The relative stability of the following hydrocarbons (*most stable to least stable*):



8. The relative contribution of each of the following resonance structures:
(*best resonance structure to worst resonance structure*):

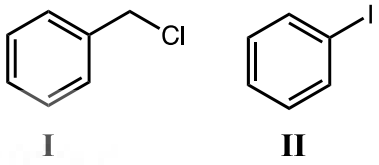


15% PART 2: MOLECULAR PROPERTIES

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. Which of the following is the better electrophile for a nucleophilic substitution and why?



I II

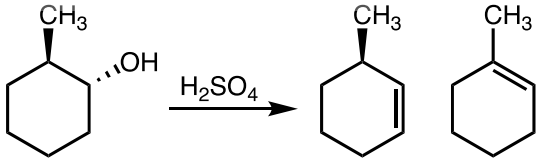
A. **I** because it has a better leaving group.
B. **II** because it reacts by SN1 at a very high rate.
C. **II** because C-I bonds are weaker than C-Cl.
D. **I** because it can react by both SN1 and SN2.
E. **II** because it has a better leaving group.

10. Which of the molecules (**III** and **IV**) shown below, would undergo a reaction with 1-bromopropane and Na_2CO_3 at the fastest rate?

III **IV**

A. **III** because it is less sterically hindered.
B. **IV** because it is more sterically hindered.
C. **IV** because it contains the most acidic proton.
D. **III** because it contains the most acidic proton.
E. **IV** because it can form a more stable carbocation.

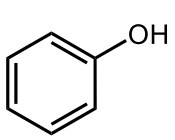
11. Which of the following is the major product:



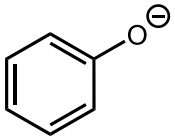
V **VI**

A. **V** because there is no axial hydrogen to give the Zaitsev product
B. **VI** because HSO_4^- is a small/non-hindered base.
C. **VI** because the reaction is E2 elimination.
D. **V** because the reaction is E1 elimination.
E. **VI** because the alkene is trisubstituted.

12. When phenol is dissolved in diethyl ether solvent, and then mixed with an aqueous sodium bicarbonate solution, the two solutions separate to form a biphasic solution. Which is the major species present in this mixture, and what solvent layer is it in?



VII



VIII

A. **VII** which is in the ether layer because it is neutral.

B. **VII** which is in the aqueous layer because it is polar.

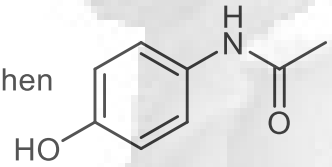
C. Both are present in approximately equal amounts in organic and aqueous layers.

D. **VIII** which is in the ether layer because it is now aprotic.

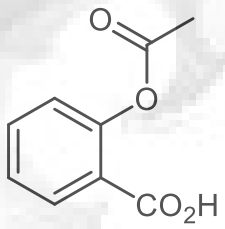
E. **VIII** which is in the aqueous layer because it is charged.

13. Which of the following would have the highest Rf value in normal phase TLC? (*i.e.* similar conditions to the TLC experiment in the CHEM 351 laboratory).

acetaminophen



IX



aspirin

X

A. **IX** because it is less polar.

B. **IX** because it is more polar.

C. **X** because it is less polar.

D. **X** because it is more polar.

E. **X** because it has a higher molecular weight.

14. If you did an extraction of a compound where the KD (ether : water) = 3, what % of the compound would be extracted from a 25 mL aqueous solution with 25 mL of ether ?

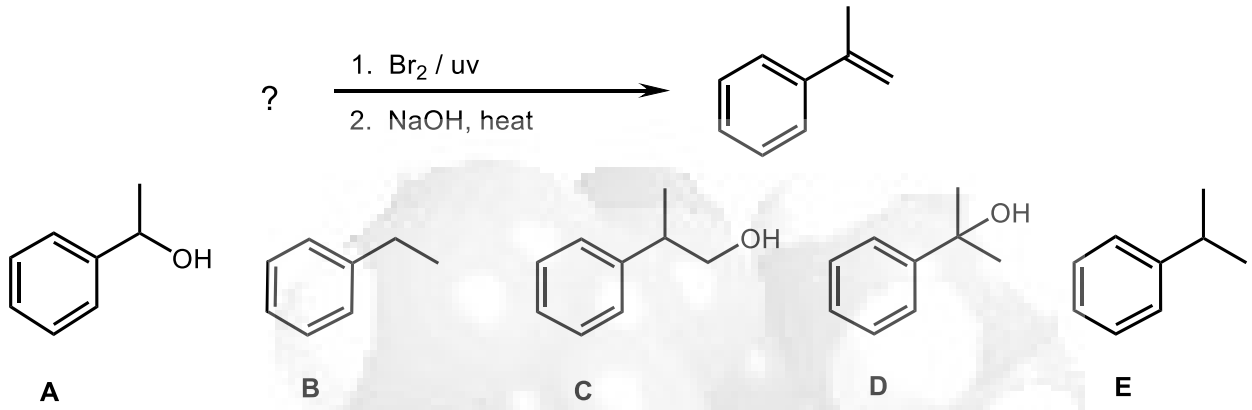
A 25 **B** 33 **C** 50 **D** 67 **E** 75

10% **PART 3: REACTIONS**

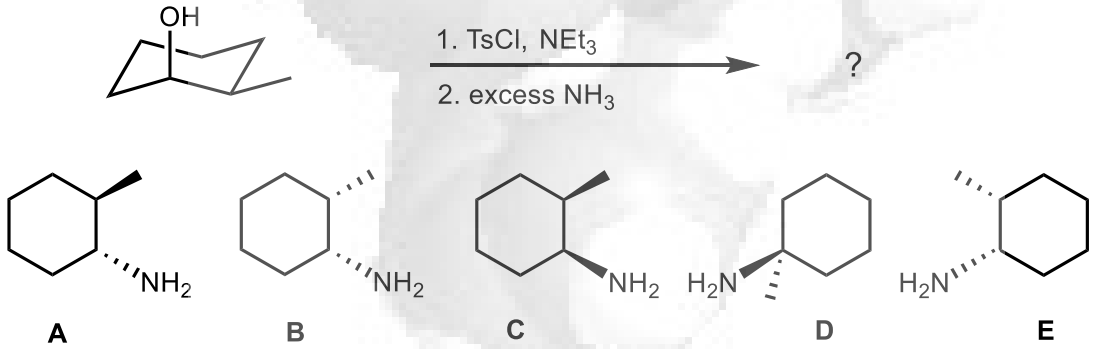
ANSWER ANY FIVE (5) of questions 15-20 (2 marks per question)

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

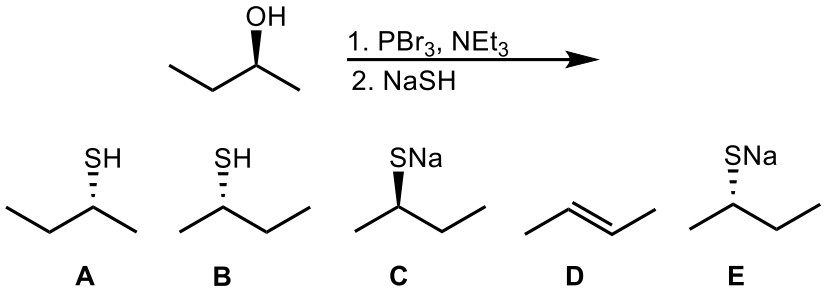
15.



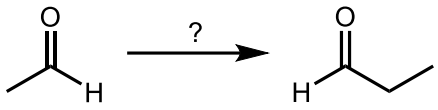
16.



17.



18.



A 1. NaH
2. CH_3OH

B 1. H_2SO_4 / heat
2. CH_3Br

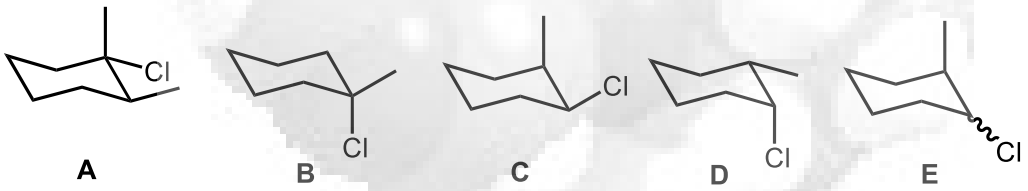
C 1. Br_2, uv-light
2. CH_4

D 1. NaH
2. CH_3Br

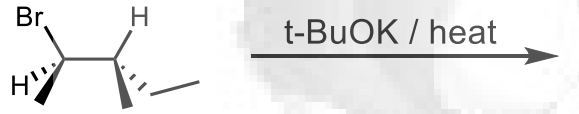
E 1. HBr / heat
2. CH_4

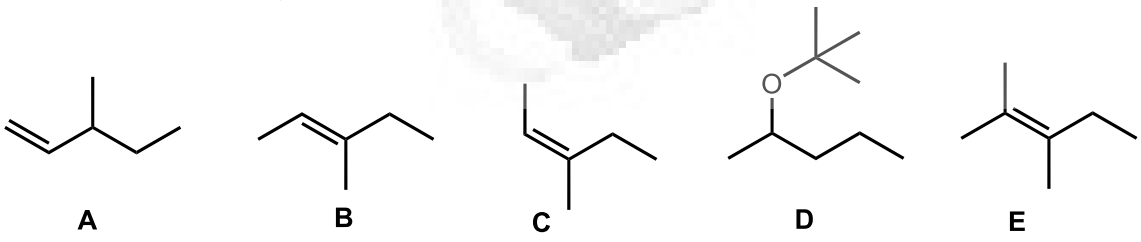
19.

Option **E** has a mix of stereoisomers



20.



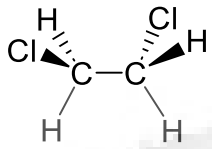


9% PART 4: CONFORMATIONAL ANALYSIS

ANSWER ANY SIX (6) of questions 21-28 (1.5 marks per question)

In some cases, more than one answer may be correct in which case all correct answers should be selected for full marks.

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

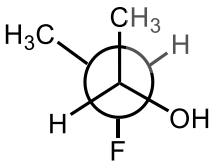


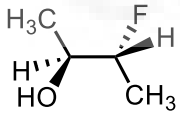
A 0° **D** 109.5°
B 60° **E** 120°
C 90° **AB** 180°

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

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

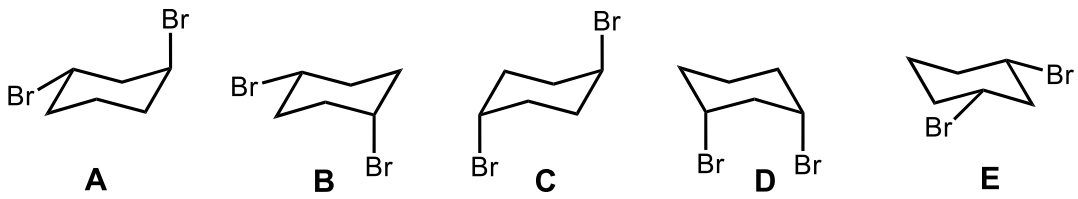
23. Which of the following terms **best** describes the relationship between the two molecules shown below?





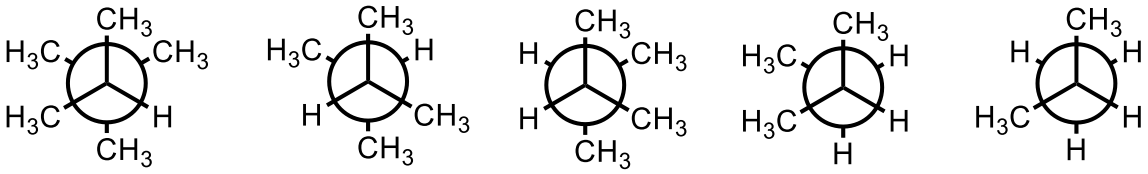
A constitutional isomers
B identical
C conformational isomers
D enantiomers
E diastereomers
AB not isomers

24. Which of the following structures represents the most stable conformation that can be adopted by trans-1,3-dibromocyclohexane?



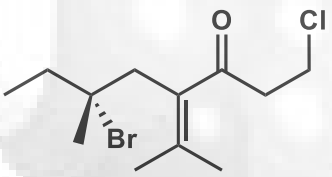
A **B** **C** **D** **E**

25. Which of the following Newman projections represents a conformer(s) of the hydrocarbon 2,3-dimethylbutane? **Select all that apply.**



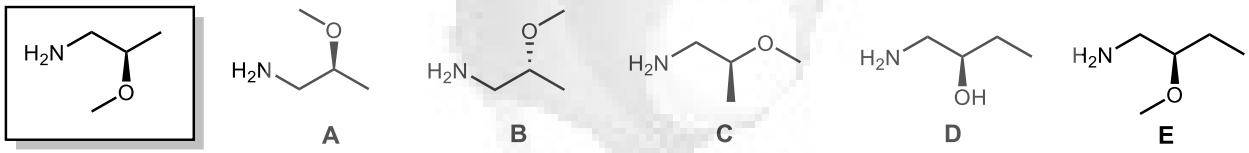
A **B** **C** **D** **E**

26. Which of the following terms describes the configuration(s) of the stereocenter(s) in the molecular shown below? (Choose all that apply of **A. – D.** or choose **E**. if none apply).



A R
B S
C E
D Z
E None apply

Use the following structure in the box and use it to compare it to structures A.-E. to answer questions 27. and 28.



27. Which of the following A-E is not an isomer of the molecule in the box? **Select all that apply.**

28. Which of A-E would be an enantiomer of the molecule in the box? **Select all that apply.**

12% **PART 5: SPECTROSCOPY**

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

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

29. **^{1}H NMR** : δ/ppm 3.8 (singlet, 3H), 6.9 (singlet, 1H).
^{13}C NMR : δ/ppm 165, 133, 52 **IR** / cm^{-1} 1735

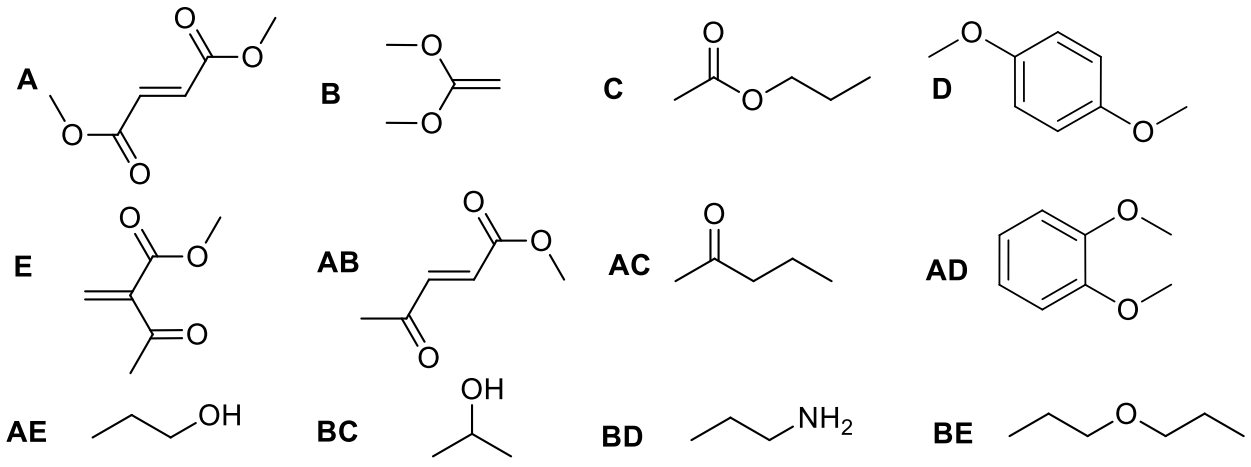
30. **^{1}H NMR** : δ/ppm 1.0 (triplet, 3H), 1.6 (sextet, 2H), 2.0 (singlet, 3H), 4.1 (triplet, 2H).
^{13}C NMR : δ/ppm 171, 66, 22, 20, 10 **IR** / cm^{-1} 1745

31. **^{1}H NMR** : δ/ppm 1.0 (triplet, 3H), 1.5 (sextet, 2H), 3.4 (triplet, 2H).
^{13}C NMR : δ/ppm 73, 23, 11 **IR** / cm^{-1} 1120

32. **^{1}H NMR** : δ/ppm 2.3 (singlet, 3H), 3.8 (singlet, 3H), 6.9 (doublet, *J*=16 Hz, 1H), 7.3 (doublet, *J* = 16 Hz, 1H).
^{13}C NMR : δ/ppm 198, 166, 140, 131, 52, 28 **IR** / cm^{-1} 1725, 1675, 1645

33. **^{1}H NMR** : δ/ppm 0.9 (triplet, 3H) 1.6 (sextet, 2H), 2.3 (broad singlet, exchangeable, 1H), 3.6 (triplet, 2H)
^{13}C NMR : δ/ppm 64, 26, 10 **IR** / cm^{-1} ~ 3400 (broad)

34. **^{1}H NMR** : δ/ppm 0.92 (triplet, 3H) 1.24 (broad singlet, exchangeable, 2H) 1.45 (sextet, 2H), 2.65 (triplet, 2H)
^{13}C NMR : δ/ppm 44, 27, 11 **IR** / cm^{-1} ~ 3370, 3291



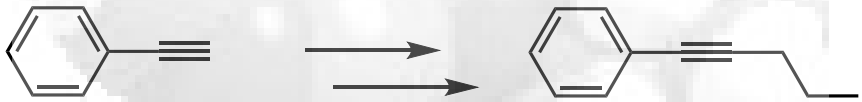
10% **PART 6: SYNTHESIS**

DESIGN EFFICIENT SYNTHESES OF ONE of the following target molecules from the indicated starting material. In addition, you are allowed to use butane or 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 CHOICE IN THE CHOICE BOX AND THEN COMPLETE YOUR ANSWER IN THE CORRESPONDING BOX IN THE EXAM BOOKLET PROVIDED.

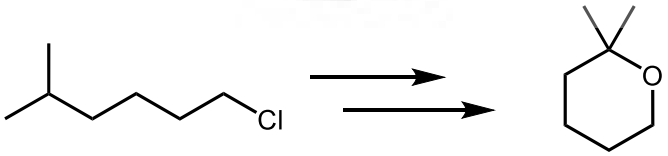
DO NOT SHOW MECHANISMS.

A



OR

B

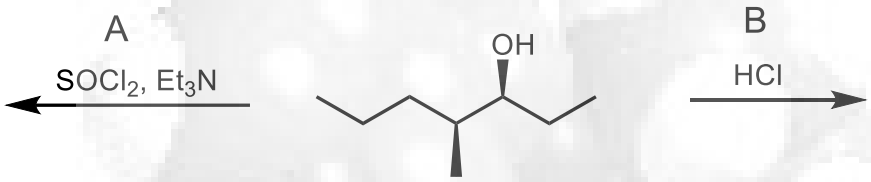


15% **PART 7: MECHANISMS**

WRITE YOUR CHOICE IN THE CHOICE BOX AND THEN COMPLETE YOUR ANSWER IN THE CORRESPONDING BOX IN THE EXAM BOOKLET PROVIDED.
USE A 'CURLY ARROW' MECHANISM TO EXPLAIN ONE of the reactions in BOTH Part I and Part II of this section. NO OTHER REAGENTS ARE REQUIRED BEYOND WHAT IS SHOWN

Part I: (choose either A or B)

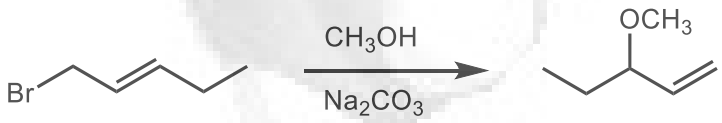
Show a curly arrow mechanism for either route A or route B conditions and what the product would be for that mechanism:



AND

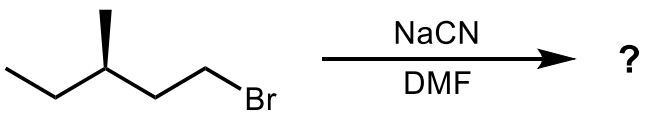
Part II: (choose either C or D)

C. Show the arrow pushing for the following reaction:



OR

D. Draw the mechanism and product for the following reaction and remember to include the specific stereochemistry of the product in your answer.



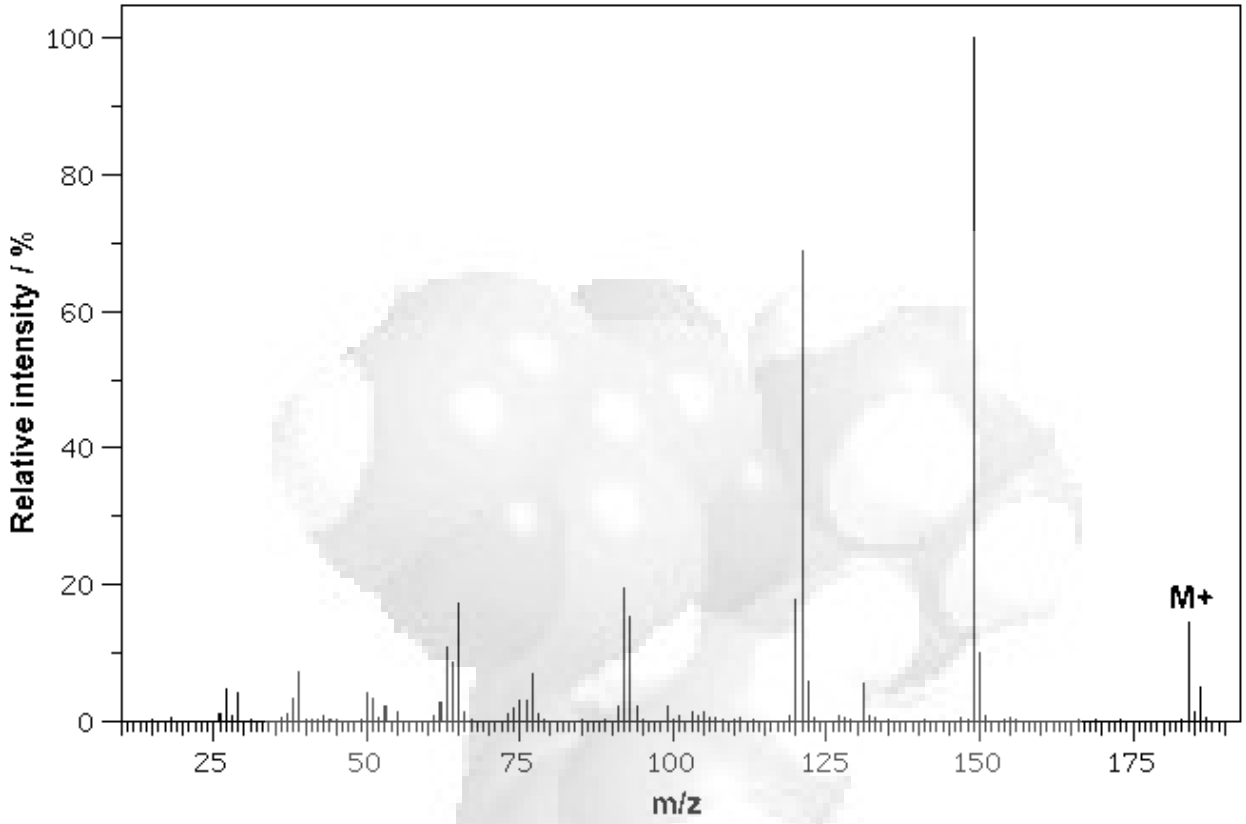
15% **PART 8: SPECTROSCOPY**

WRITE YOUR ANSWERS IN THE BLUE ANSWER BOOKLET PROVIDED.

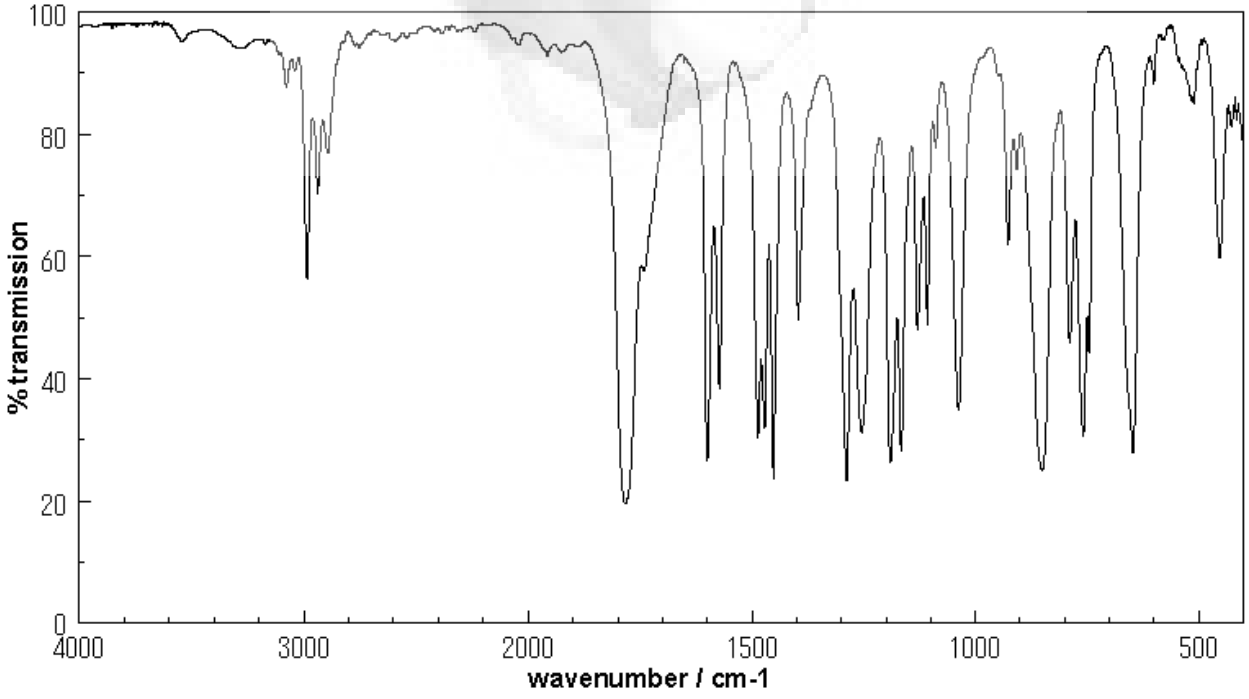
Show your working as PARTIAL marks may be given.

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

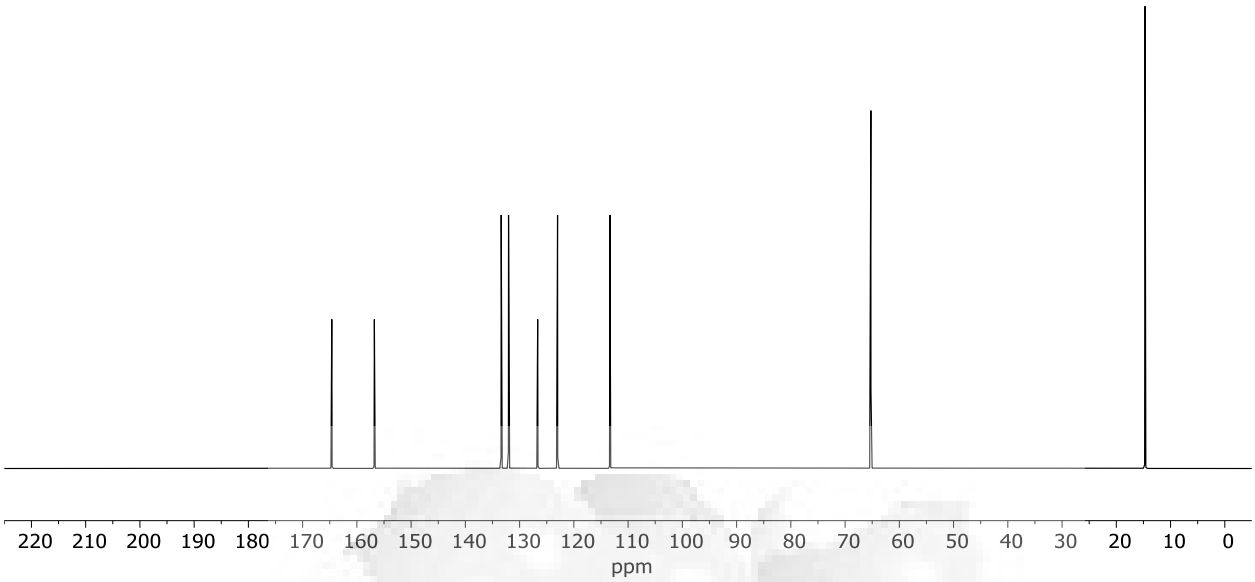
Mass Spectrum:



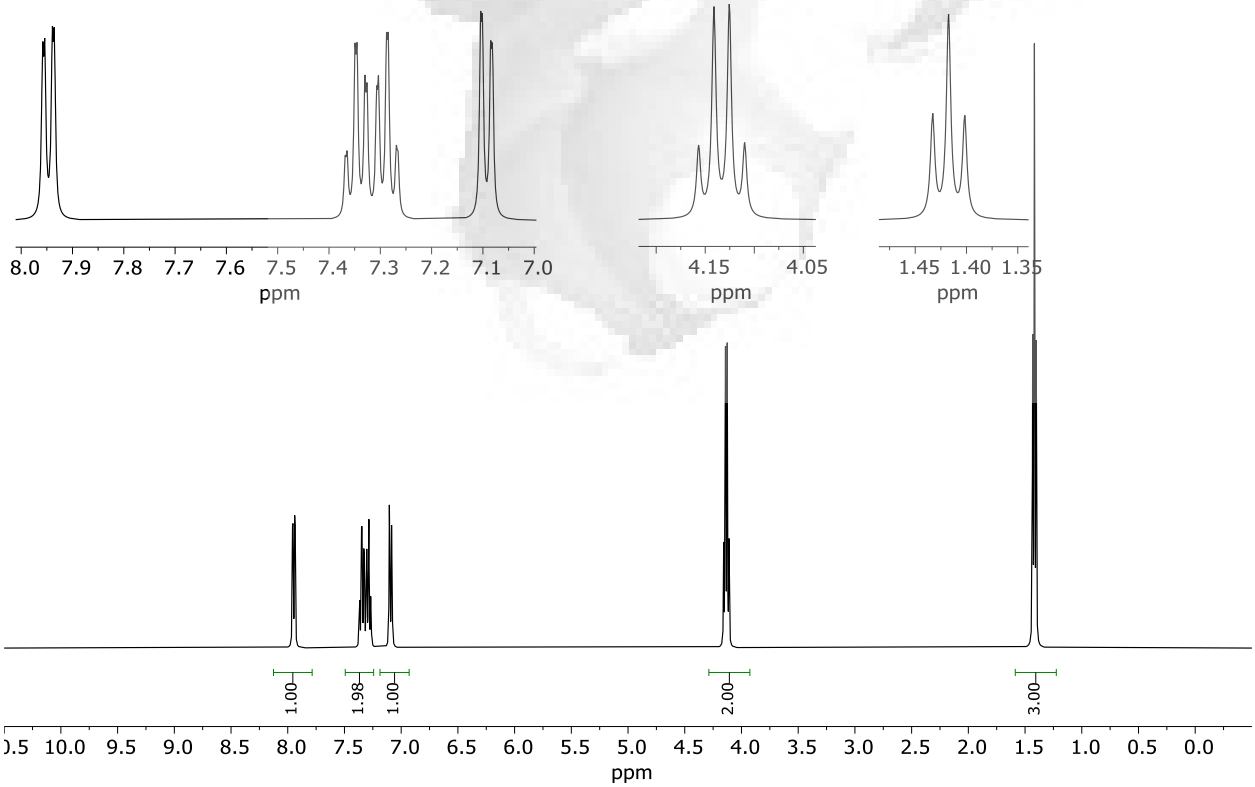
IR Spectrum:



^{13}C-NMR:



^{1}H-NMR:



SCRAP PAPER

Remember that ALL final answers need to be in your answer booklet within the boxes provided, NOT on the scrap paper.

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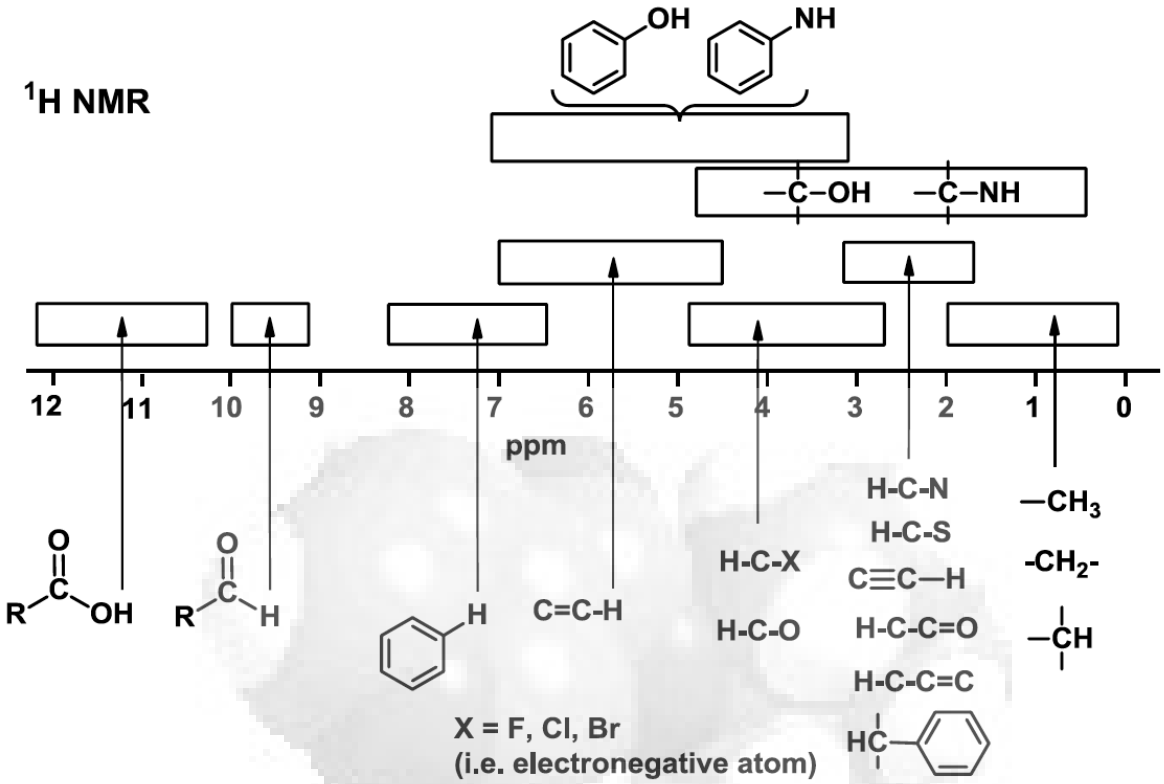
SPECTROSCOPIC TABLES

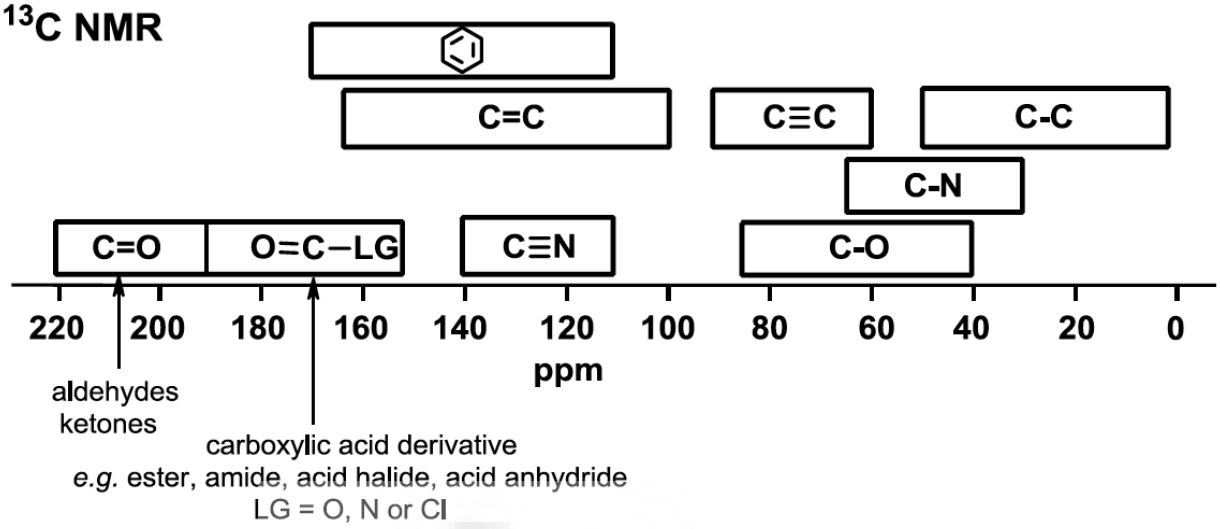


^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

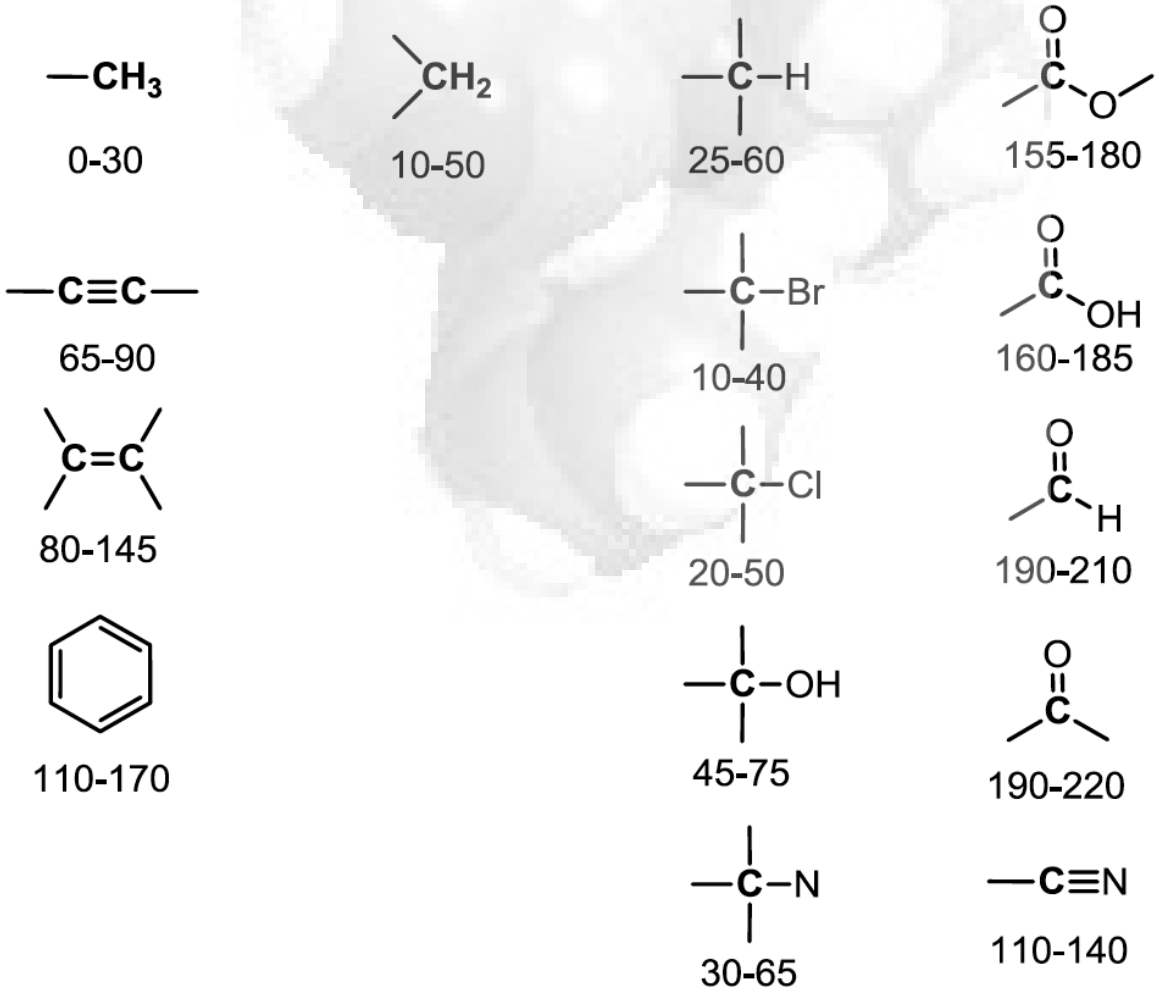
R =	methyl $-CH_3$	methylene $-CH_2-$	methyne $-CH$
R–C—	0.9	1.4	1.5
R–C=C	1.6	2.3	2.6
R–C(=O)–	2.1	2.4	2.5
R–N	2.2	2.5	2.9
R–Ar	2.3	2.7	3.0
R–Br	2.7	3.3	4.1
R–Cl	3.1	3.4	4.1
R–O—	3.3	3.4	3.7

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

^{13}C NMR



^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



INFRA-RED GROUP ABSORPTION FREQUENCIES

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

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

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

PERIODIC TABLE

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

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

IRH, ERS, JVH 2023