UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

Version

01

December 18th, 2021 Time: 2 Hours

READ THE INSTRUCTIONS CAREFULLY

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

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

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

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

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

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

14% PART 1: RELATIVE PROPERTIES

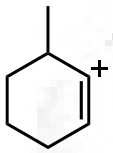
ANSWER ANY SEVEN (7) OF QUESTIONS 1 TO 8.

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

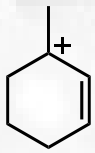
Use the following code to indicate your answers.

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

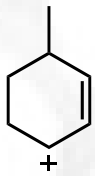
1. The relative stability of the following carbocations :



i

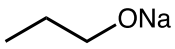


ii

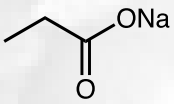


iii

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



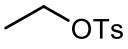
i



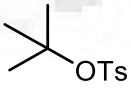
ii

iii

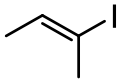
3. The relative rate of reaction when each of the following was treated with potassium bromide in acetone:



i



ii



iii

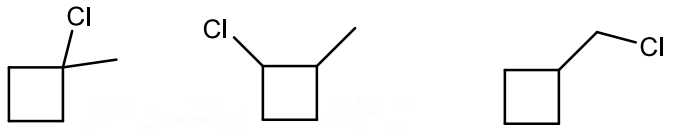
4. The relative rate of elimination when each of the following was heated with H_2SO_4:

i. butan-2-ol ii. 2-methylpropan-2-ol iii. isobutyl bromide

Use the following code to indicate your answers.

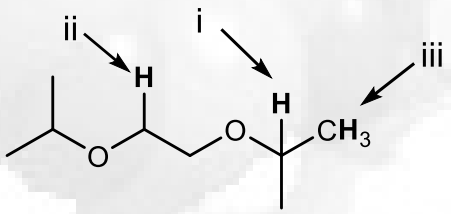
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

5. The relative yield of the following monochlorinated products formed when methylcyclobutane is reacted with chlorine under UV irradiation :



i **ii** **iii**

6. The observed number of lines in the ^{1}H-NMR spectrum for in each of the following protons:



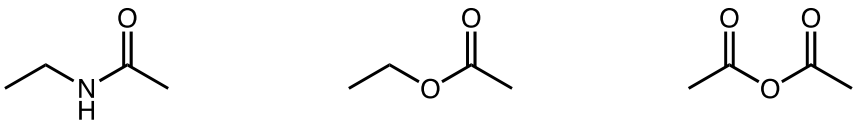
7. The relative amount of following alkenes formed when 2-chloro-2-methylpentane is heated with sodium hydroxide:

i 2-methylpent-2-ene

ii 2-methylpent-1-ene

iii (E)-3-methylpent-2-ene

8. The carbonyl stretching frequency in the infrared spectrum of each of the following structures:



i ii iii

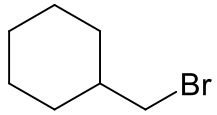
12% **PART 2: MOLECULAR PROPERTIES**

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

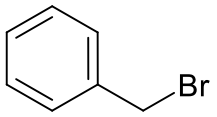
In questions 9–14 choose the single option that provides the best answer.

9. Which of the following is more reactive towards reaction with aq. $AgNO_3$?

I

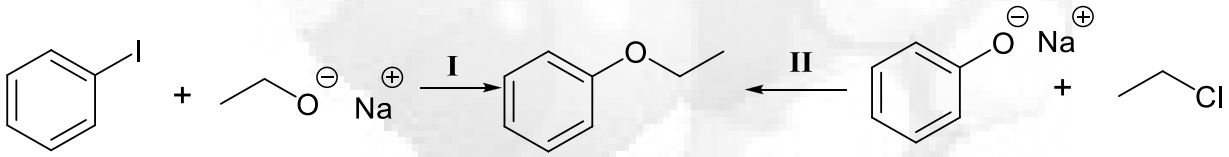


II



A. **I** because it forms a less stable primary carbocation
B. **II** because it forms a resonance stabilized carbocation
C. **I** because it is less sterically hindered
D. **II** because it is less sterically hindered
E. **I** and **II** have about equal reactivity because they are both primary.

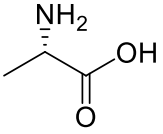
10. In the two methods (**I** and **II**) shown below, which is preferred to synthesize ethoxybenzene and why ?



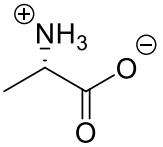
A. **I** because iodide is a better leaving group
B. **I** because ethoxide is a stronger nucleophile than phenoxide
C. Both are equally effective
D. **II** because a better electrophile is used
E. **II** because the phenoxide is a more stable anion

11. Which of the following structures corresponds to the major species present in solution when alanine is dissolved in water ?

I

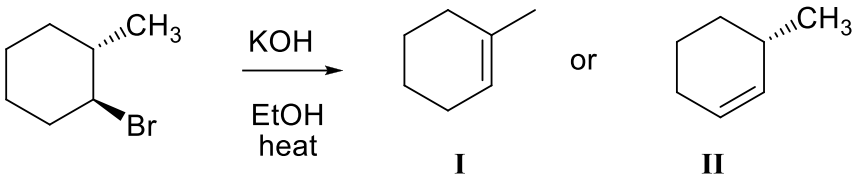


II



A. **I** because it has no formal charges
B. **II** because O is more electronegative than N
C. **I** because it is more stable
D. **II** due to an acid / base reaction
E. **II** due to a nucleophilic substitution.

12. In the reaction shown below, which alkene **I** or **II** is the major product and why ?



I **II**

A. **I** because KOH is a non-bulky base which favors Zaitsev product.

B. **I** because the anti arrangement controls the outcome of the E2 reaction

C. **I** because a more stable tertiary carbocation is formed via a 1,2-hydride shift

D. **II** because the anti arrangement controls the outcome of the E2 reaction

E. **II** because EtOH is a polar protic solvent.

13. Which of the following structures is more nucleophilic and why ?

I **II**

A. **I** because the negatively charged C has higher electron density.

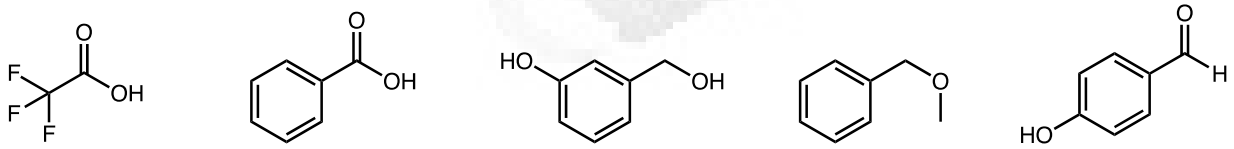
B. **II** because the carbanion is more stable

C. **II** because of the inductive effect of oxygen

D. **I** because the negative charge is delocalized

E. They have equal nucleophilicity because the negative charges are on a carbon

14. Which of the following would be soluble in NaOH solution but not in aqueous $NaHCO_3$ (**select all that apply**) ?



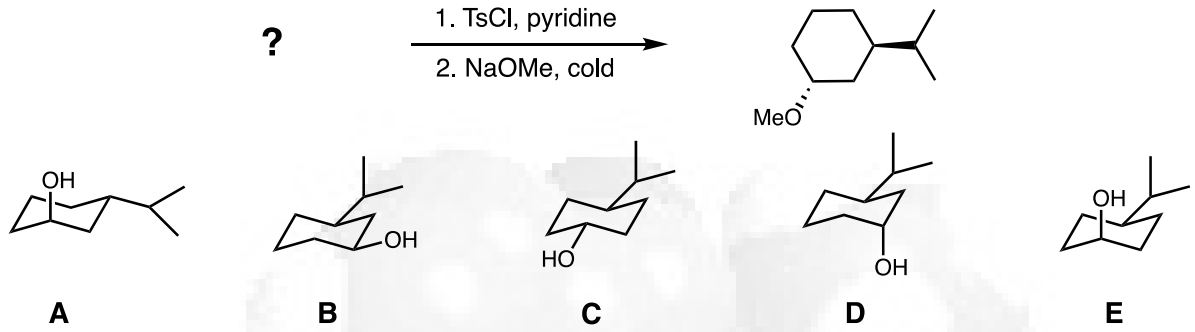
A **B** **C** **D** **E**

12% **PART 3: REACTIONS**

ANSWER ANY SIX (6) of questions 15-21 (2 marks per question)

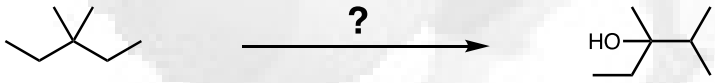
For each of questions 15-21, selecting the MISSING component (the best starting material, the major product, or the best reagents) required in order to BEST complete the reaction schemes.

15.



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

16.



A 1. Cl_2 / uv
2. NaOH / heat

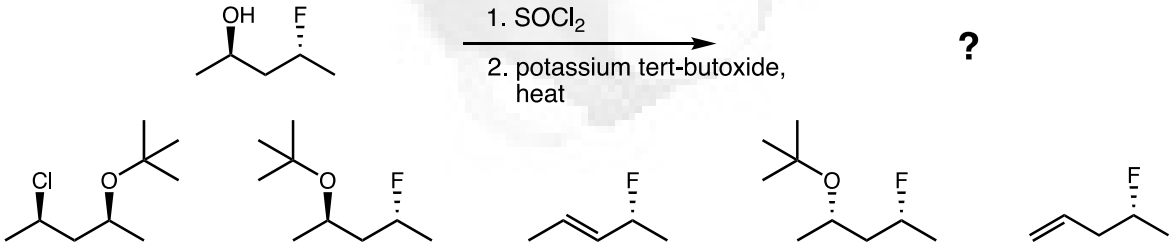
B 1. Cl_2 / uv
2. NaOH / cold

C 1. TsCl / pyridine
2. NaOH / cold

D 1. Br_2 / uv
2. NaOH / heat

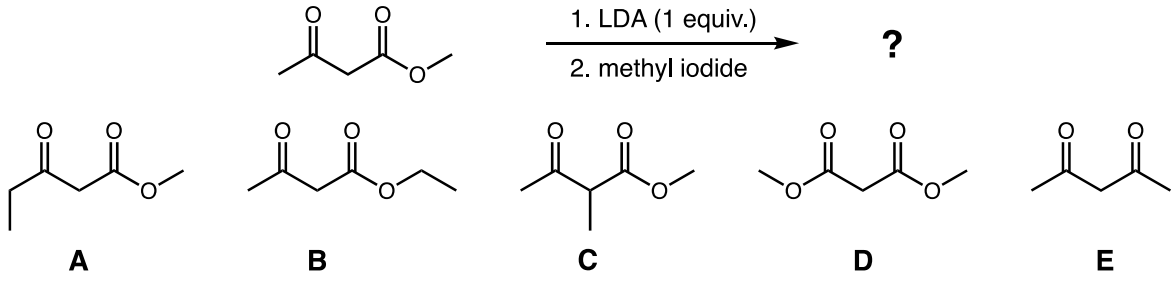
E 1. Br_2 / uv
2. aq. $AgNO_3$

17.



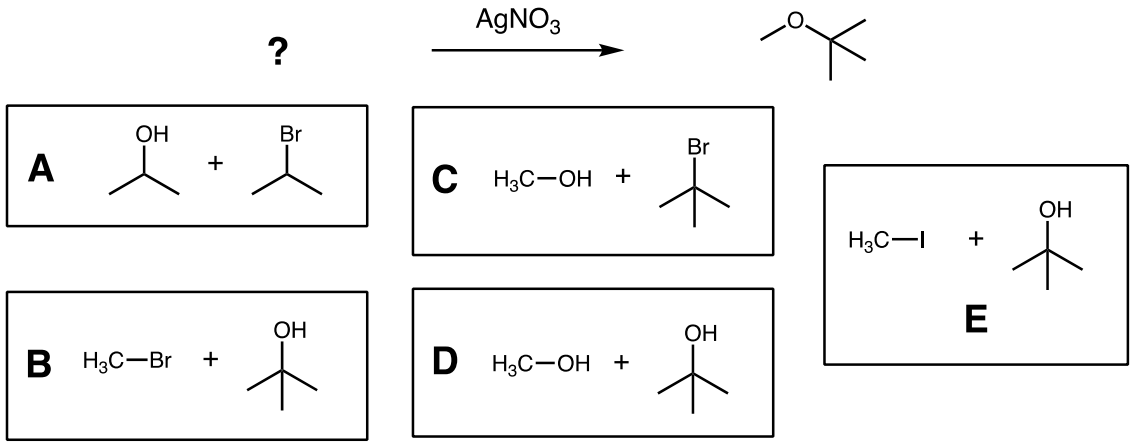
A **B** **C** **D** **E**

18.

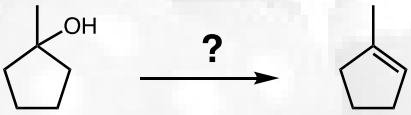


A **B** **C** **D** **E**

19.



20.



A 1. H_2SO_4 / heat

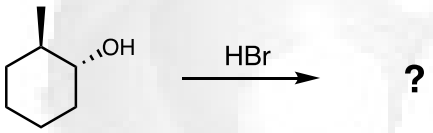
B 1. $SOCl_2$ / NEt_3
2. NaO^tBu / heat

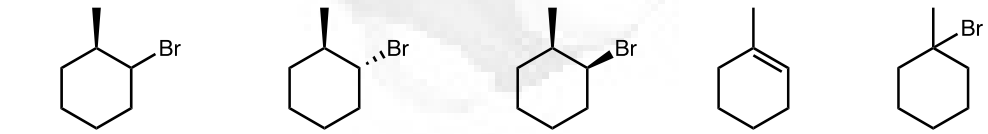
C 1. TsCl / pyridine
2. NaO^tBu / heat

D 1. Br_2 / uv
2. NaOH / heat

E 1. HBr
2. $NaSCH_3$

21.





(mixture of stereoisomers)

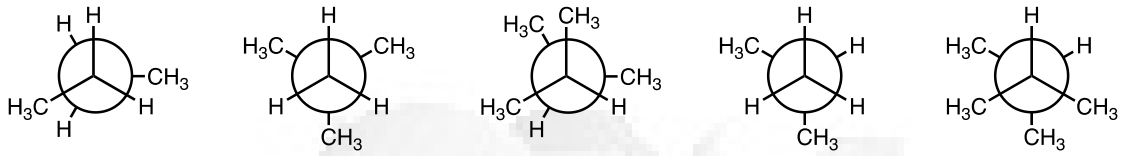
A **B** **C** **D** **E**

9% PART 4: CONFORMATIONAL ANALYSIS

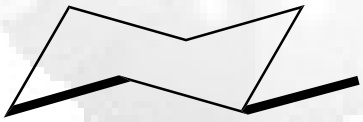
ANSWER ANY SIX (6) of questions 22-28 (1.5 marks per question)

For each of questions 22-27, selecting 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.

22. Which of the following Newman projections represent 2,3-dimethylbutane?

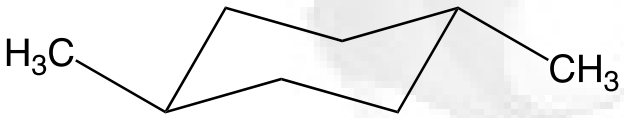


23. Which number describes the **torsional angle** between the bonds highlighted in **bold**?



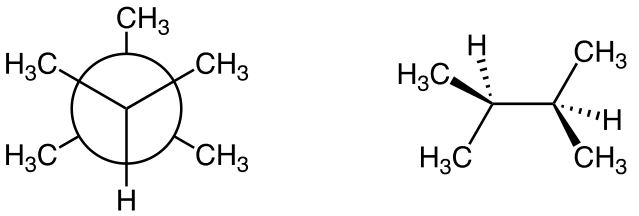
A 0°
B 60°
C 90°
D 109.5°
E 120°
AB 180°

24.Which term(s) describe the relative positions of the two methyl groups in the cyclohexane shown below?



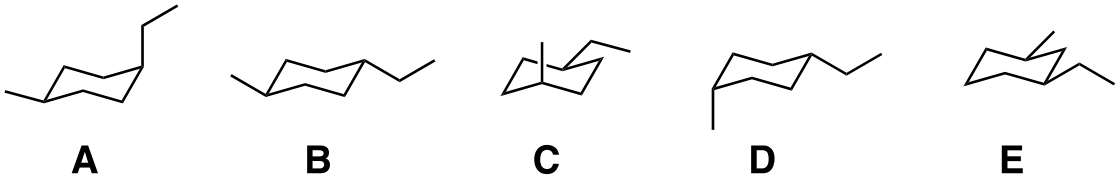
A eclipsed
B staggered
C cis
D trans
E equitorial
AB axial

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



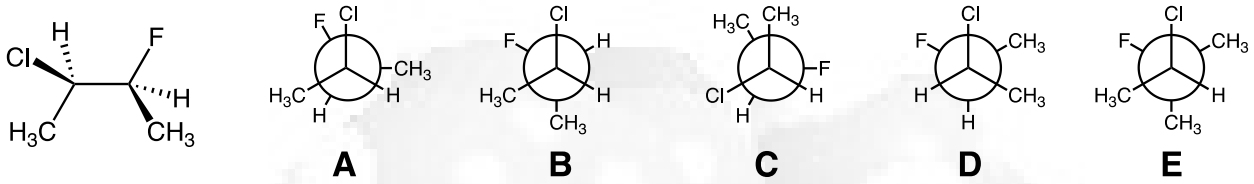
A constitutional isomers
B identical
C conformational isomers
D enantiomers
E diastereomers
AB not isomers

26. Which of the following structures represent the lowest energy conformation of *cis*-1-ethyl-4-methylcyclohexane?



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

27. Which of the following Newman projections show the same conformational isomer as the wedge/hash line drawing?



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

28. Which of the following conformers shown below has the lowest **torsional** strain?

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

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. The following common abbreviations have been used s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. NB: 'pentet' and 'quintet' are synonyms.

29. **^{1}H-NMR** : δ/ppm 1.0 (t, 3H), 1.6 (sextet, 2H), 2.0 (s, 3H), 4.1 (t, 2H).
^{13}C-NMR: δ/ppm 10.4, 20.9, 22.1, 66.1, 171
IR = 1745 cm^{-1}

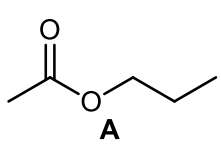
30. **^{1}H-NMR**: δ/ppm 2.3 (s, 3H), 7.0-7.1 (m, 2H)
^{13}C-NMR: δ/ppm 21, 126, 128, 130, 138
IR: 1614, 1592 cm^{-1}

31. **^{1}H-NMR**: δ/ppm 1.0 (t, 3H), 2.4 (q, 2H)
^{13}C-NMR: δ/ppm 7.9, 35.5, 212
IR: 1720 cm^{-1}

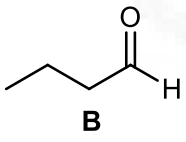
32. **^{1}H-NMR**: δ/ppm 1.2 (t, 3H), 2.6 (q, 2H), 7.0-7.1 (m, 5H)
^{13}C-NMR: δ/ppm 16, 29, 126, 127, 128, 144
IR: 1496, 1453 cm^{-1}

33. **^{1}H-NMR**: δ/ppm 0.9 (t, 3H), 1.6 (sextet, 2H), 2.1 (s, 3H), 2.4 (t, 2H)
^{13}C-NMR: δ/ppm 14, 17, 30, 45, 209
IR: 1717 cm^{-1}

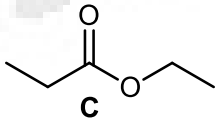
34. **^{1}H-NMR**: δ/ppm 1.7 (pentet, 1H), 1.9 (pentet, 2H), 2.3 (t, 2H)
^{13}C-NMR: δ/ppm 25, 27, 42, 212
IR: 1715 cm^{-1}



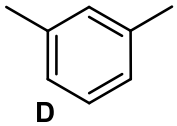
A

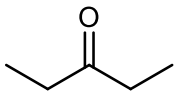


B

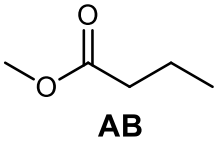


C

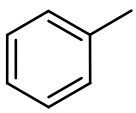

D

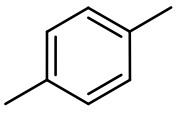


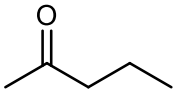
E



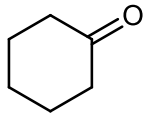
AB


AC

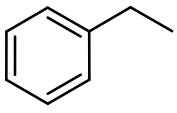

AD

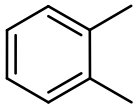


AE



BC


BD

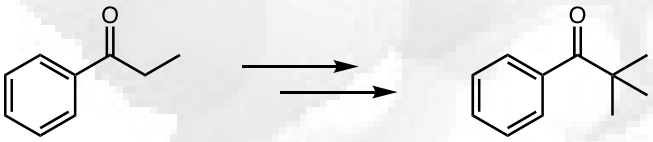

BE

13% **PART 6: SYNTHESIS**

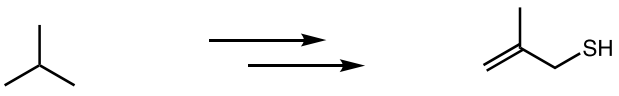
DESIGN EFFICIENT SYNTHESES OF ONE of the following two target molecules from the indicated starting material. In addition, you are allowed to use any hydrocarbon with three or fewer carbon atoms, any solvents or inorganic reagents, and any organic reagents that do not contribute carbon atoms to the carbon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

WRITE YOUR ANSWERS IN THE EXAM BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.



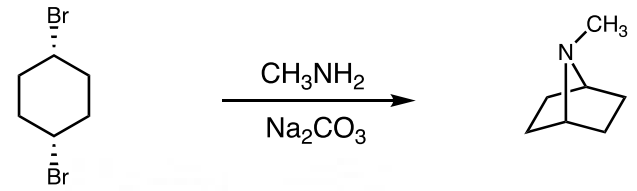
OR



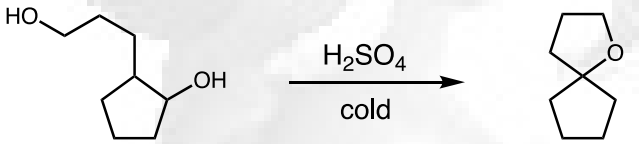
14% **PART 7: MECHANISMS**

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

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



OR



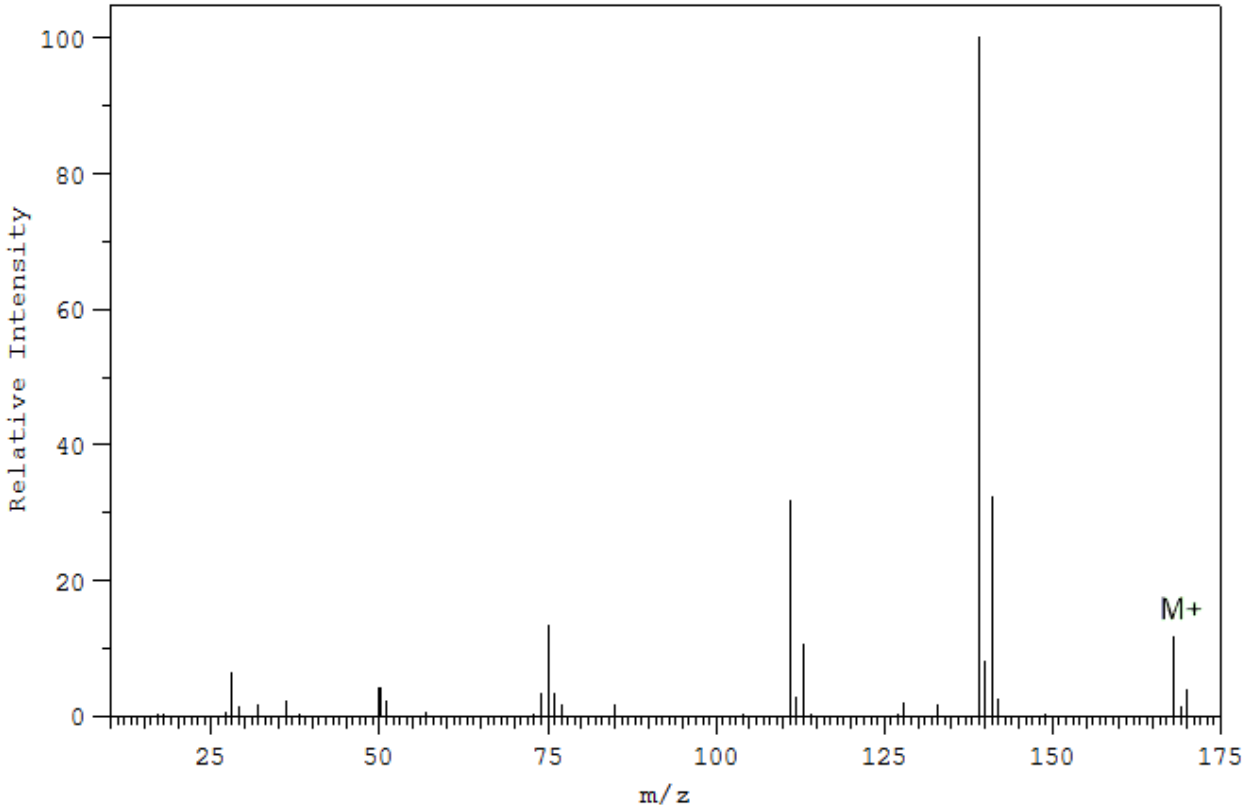
14% **PART 8: SPECTROSCOPY**

WRITE YOUR ANSWERS IN THE BLUE ANSWER BOOKLET PROVIDED.

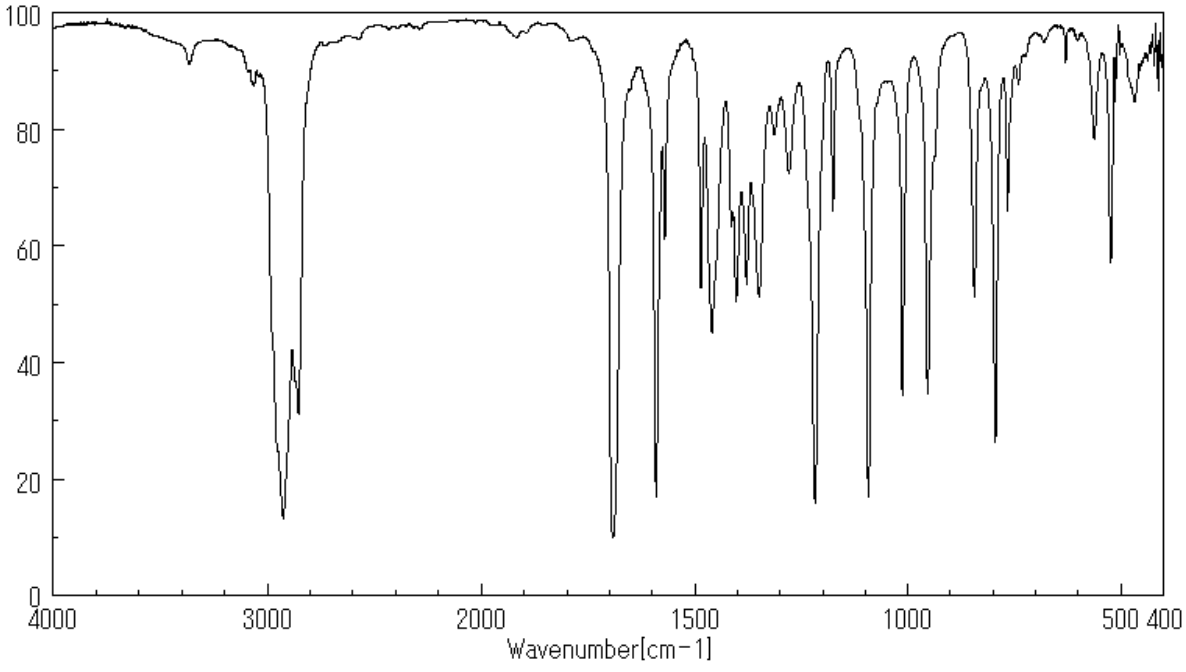
Show your working as PARTIAL marks may be given.

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

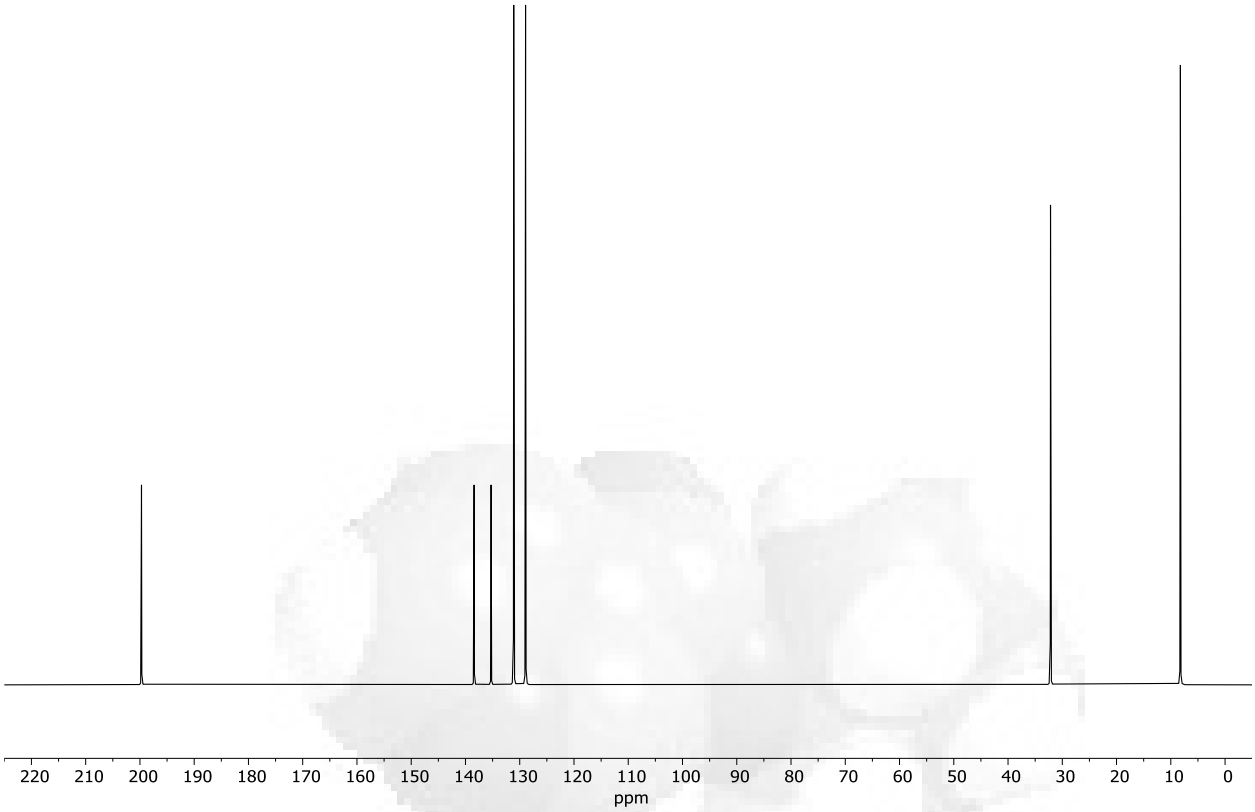
Mass Spectrum:



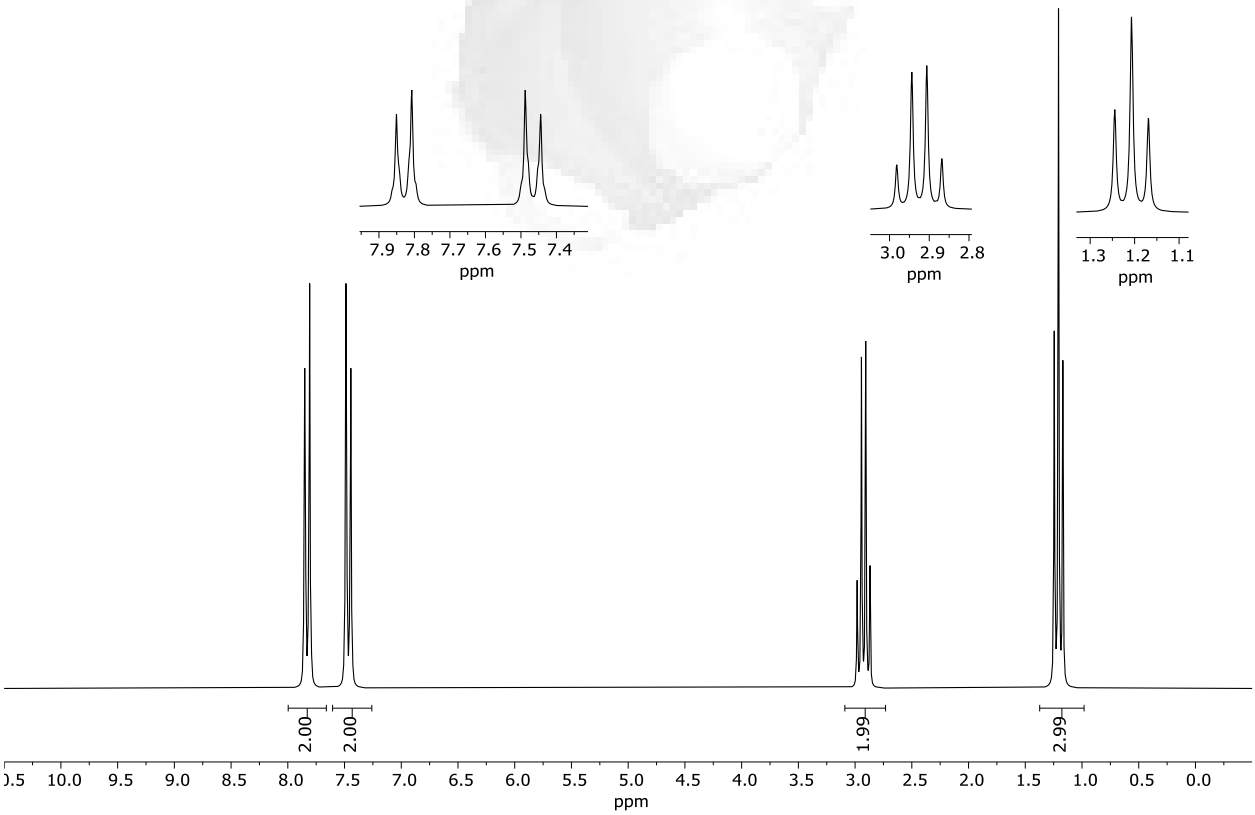
IR Spectrum:



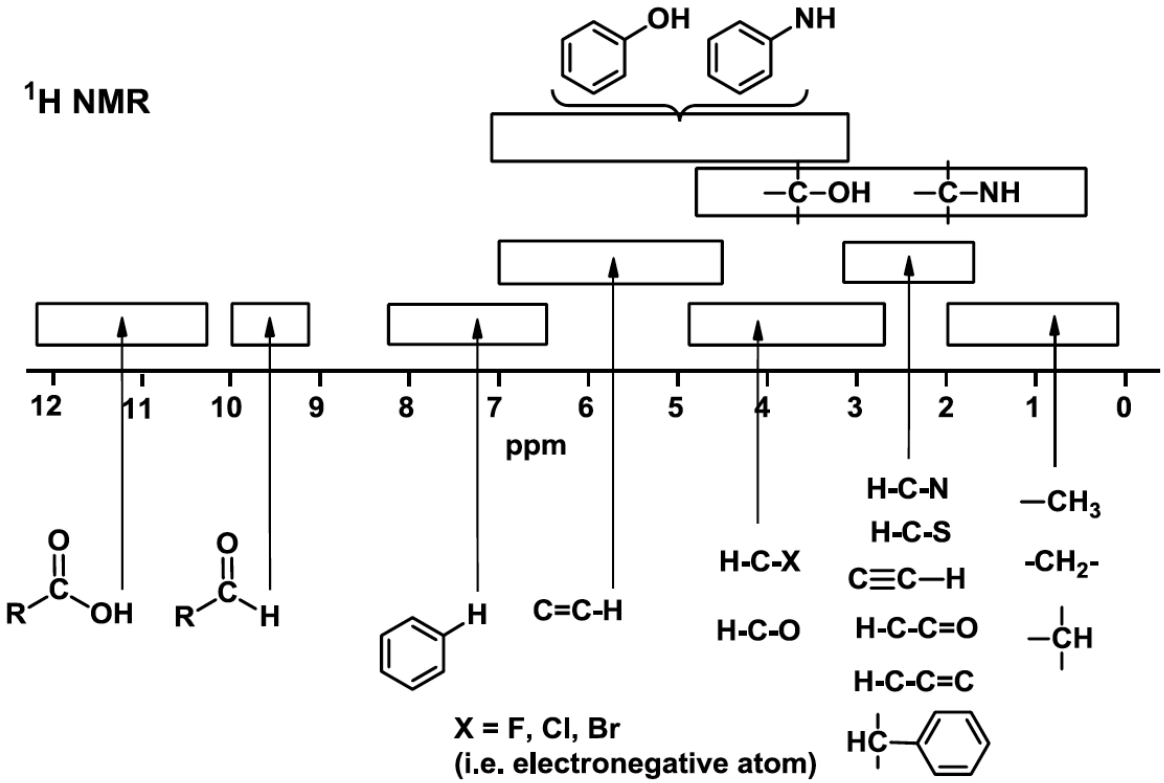
^{13}C-NMR:



^{1}H-NMR:



SPECTROSCOPIC TABLES

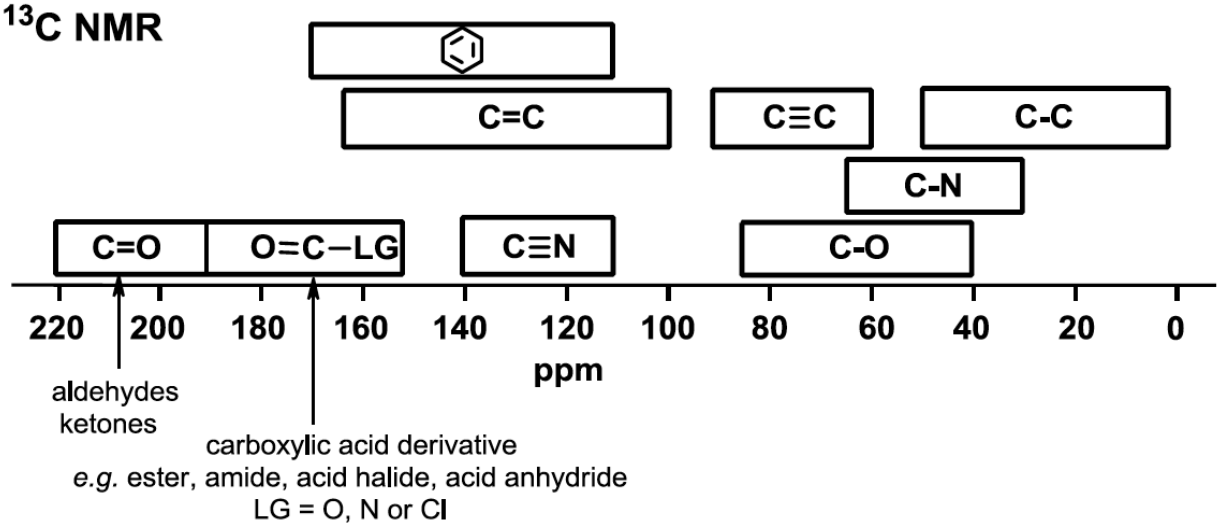


^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

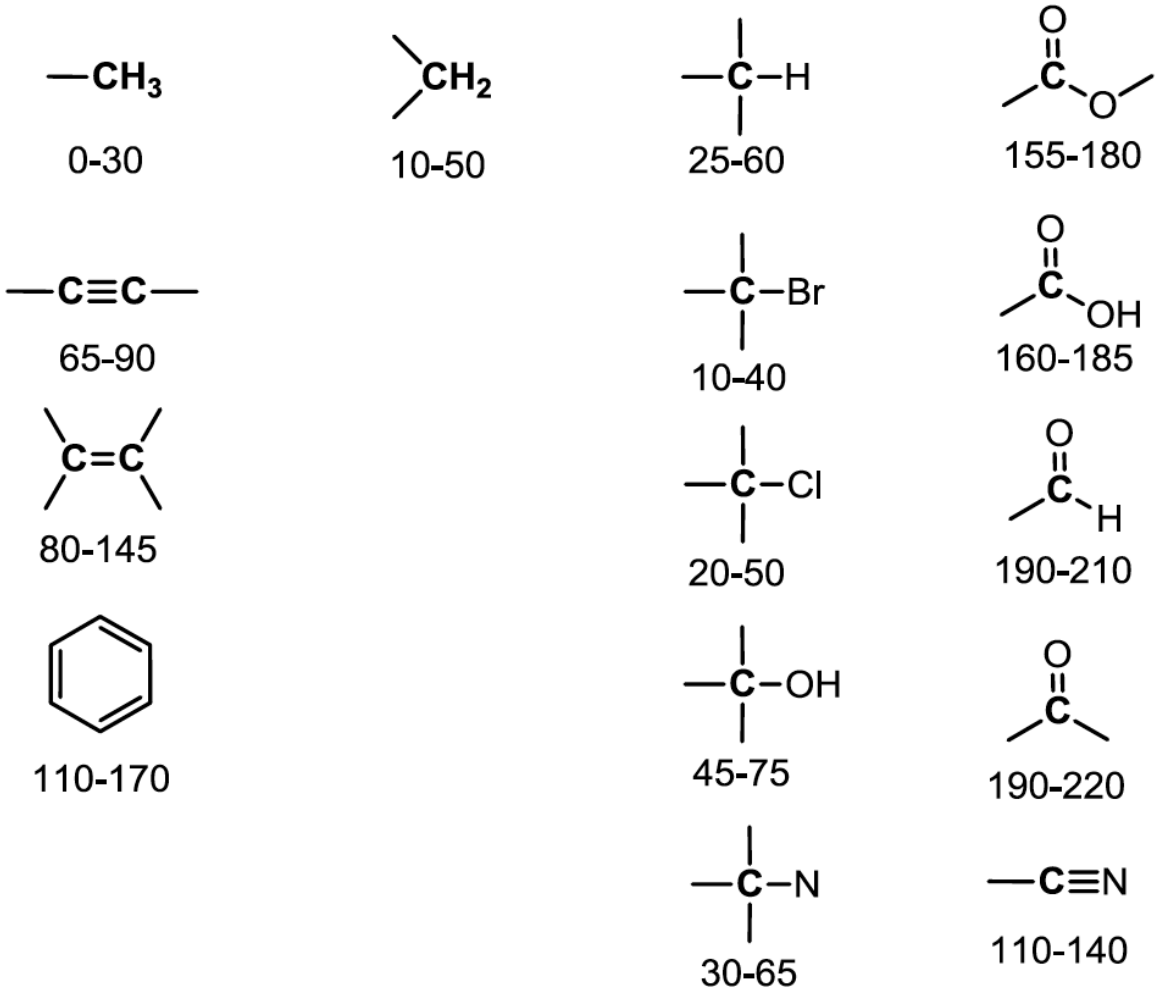
R =	methyl	methylene	methyne
	$-CH_3$	$-CH_2-$	$-\overset{\vert}{C}H$
R–C—	0.9	1.4	1.5
R, R, C=C	1.6	2.3	2.6
R–C(=O)—	2.1	2.4	2.5
R–N	2.2	2.5	2.9
R–Ar	2.3	2.7	3.0
R–Br	2.7	3.3	4.1
R–Cl	3.1	3.4	4.1
R–O—	3.3	3.4	3.7

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

^{13}C NMR



^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



INFRA-RED GROUP ABSORPTION FREQUENCIES

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

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

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

PERIODIC TABLE

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